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Cobalt(II)-Catalyzed Bisfunctionalization of Alkenes with Diarylphosphine Oxide and Peroxide

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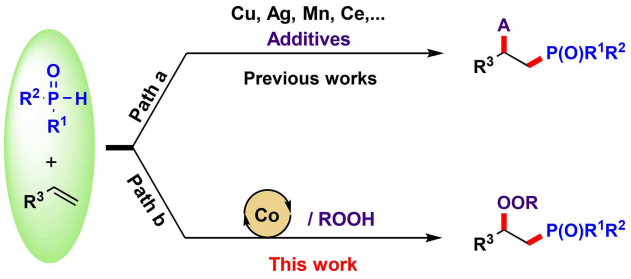
Abstract: The low-cost cobalt(II) catalyst has been used for the first time to achieve P(O)-radical-mediated bisfunctionalization of alkenes with diarylphosphine oxide and peroxides. This simple process is performed under mild conditions to afford a wide variety of phosphonation-peroxidation products in a one-pot manner. Computational studies are carried out to provide a theoretical support for the P(O)-radical-involved bisfunctionalization of alkenes.

Keywords: cobalt-catalyzed; phosphonation; difunctionalization; peroxidation; radicals

Introduction

Organophosphorus compounds have attracted significant attention from chemists due to their remarkable biological,[1] chemical[2] and physical[3] properties. This range of properties makes them applicable to diverse fields, ranging from pharmaceutical chemistry to the material sciences.[4] Consequently, considerable effort has been directed towards exploring practical and efficient methods for the formation of C–P bonds. In the past decade, P-radical initiated bisfunctionalization of alkenes has emerged as one of the most powerful strategies to install a P(O) moiety along with another functional group in a single step.[5] Among these, the metal mediated transformations dominate this field (Scheme 1, Path a), with Mn,[6] Ag[7] and Cu[8] being the most commonly used metals. Recently, our group has also developed a Ce(IV)-initiated bisfunctionalization of alkenes.[9] Despite the high efficiency of these systems in most transformations, the problems associated with the limited metal scope and the use of excess metal salts hinder the development of this area. Therefore, exploiting more efficient reaction systems is highly desirable and presents a challenge.

At the same time, peroxide-containing skeletons are found in a wide variety of natural products and pharmaceutical compounds.[10] Furthermore, peroxides are often key intermediates and building blocks in synthetic chemistry.[11] Since Li's group pioneered a new method of Fe-catalyzed acylation-peroxidation in 2011,[12] the bisfunctionalization of alkenes has evolved as an attractive strategy for the synthesis of peroxides.[13,14] Last year, the same group developed a Cu-catalyzed phosphorylation-peroxidation reaction of alkenes.[8g] However, in this work, the $P(O)(Ar)_2$ radical could not be generated. As diaryl phosphorus is the basic framework of most P-ligands, the simultaneous generation of diarylphosphoryl and peroxide moieties in the same molecule may provide easy access to P-ligands. Considering this, as well as our continued interest in the development of new strategies and reaction systems for C–P bond formation,[9,15] herein, we introduce the first example of a Co(II)-catalyzed



Scheme 1. P(O)-radical-mediated difunctionalizations.

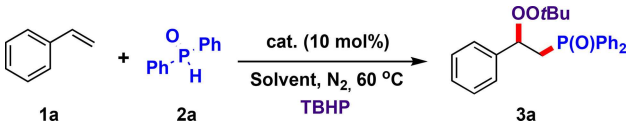
alkene phosphonation-peroxidation transformation (Scheme 1, Path b). To the best of our knowledge, Co (II)-catalyzed P(O)-radical-mediated bisfunctionalization has not been reported, and hence this presents an alternative approach in organophosphorus chemistry.

Results and Discussion

We began our investigation with styrene (**1a**) and diphenylphosphine oxide (**2a**) as model substrates in the presence of 10 mol% $Co(OAc)_2 \cdot 4H_2O$ and 4.0 equiv. of TBHP in MeCN (2.0 mL) at 60 °C under a nitrogen atmosphere (Table 1, entry 1). To our delight, the phosphonation-peroxidation product (**3a**) was obtained in 59% yield. Encouraged by this result, various parameters were screened to optimize the reaction conditions. Firstly, when we reversed the ratio of **1a** to **2a**, the yield was improved to 68% (Table 1, entry 2). Pleasingly, by increasing the amount of **1a**, the yield increased to 81%. There were no subsequent improvements upon increasing the equivalents of **1a** further (Table 1, entries 3–5). In the screening of experimental conditions, a bisperoxide by-product was detected. The formation of this by-product consumed the amount of styrene, which lead to the use of excessive styrene. Following this, the effect of altering reaction temperature was examined. Changes from the standard conditions resulted in a lower yield (Table 1, entries 6–7). Solvent screening showed that MeCN is the optimum solvent for the reaction (Table 1, entries 8–10). Next, different catalysts were tested. However, none performed as well as $Co(OAc)_2 \cdot 4H_2O$ (Table 1, entries 11–15). Altering the amount of TBHP resulted in a lower yield (Table 1, entries 16–17). Moreover, when the catalyst loading was reduced to 5 mol%, the yield dropped sharply (Table 1, entry 18). When the catalyst loading was increased (Table 1, entry 19), the yield did not increase beyond the previous best results (Table 1, entry 4).It should be noted that when TBHP (5.0–6.0 mol/L in decane) was employed, only a small amount of **3a** was obtained (entry 20). Likewise, when the reaction was performed in air, desired product **3a** was obtained in just 29% yield (Table 1, entry 21). Finally, control experiments indicated that the phosphonation-peroxidation reaction did not occur in the absence of either Co(II)catalyst or TBHP (entries 22–23). More detailed reaction conditions screenings are listed in the SI. After the screening, the optimal reaction conditions were established as listed in Table 1, entry 4: 3.0 equiv. of **1a** and 1.0 equiv. of **2a** with 10 mol% of $Co(OAc)_2 \cdot 4H_2O$ and 4.0 equiv. of TBHP (70% in water) in the presence of 2.0 mL of MeCN at 60 °C under a nitrogen atmosphere.

With the optimized reaction conditions in hand, the generality of this new protocol was explored and the results are listed in Table 2. A variety of substituted styrenes were investigated (**1b–1u**). Both electron-rich (**1b–1h**) and electron-poor (**1i–1m**) substituents on the *para*-position of aryl ring were well tolerated, and the corresponding products **3b–3m**, containing alkyl (**3a–3e**), alkoxy (**3f**), ester (**3g**), aryl (**3h**), halogens (**3i–3k**), cyano (**3l**) and trifluoromethyl (**3m**) groups, were afforded in moderate to good yields. Additionally, both *ortho*- and *meta*- substituted styrenes are well-tolerated in this reaction (**3n–3s**). The results indicate that steric hindrance has an obvious influence on the yield. Despite this, multi-substituted styrenes still participated in the reaction smoothly, to afford prod-

Table 1. Selected reaction condition optimizations. [a]

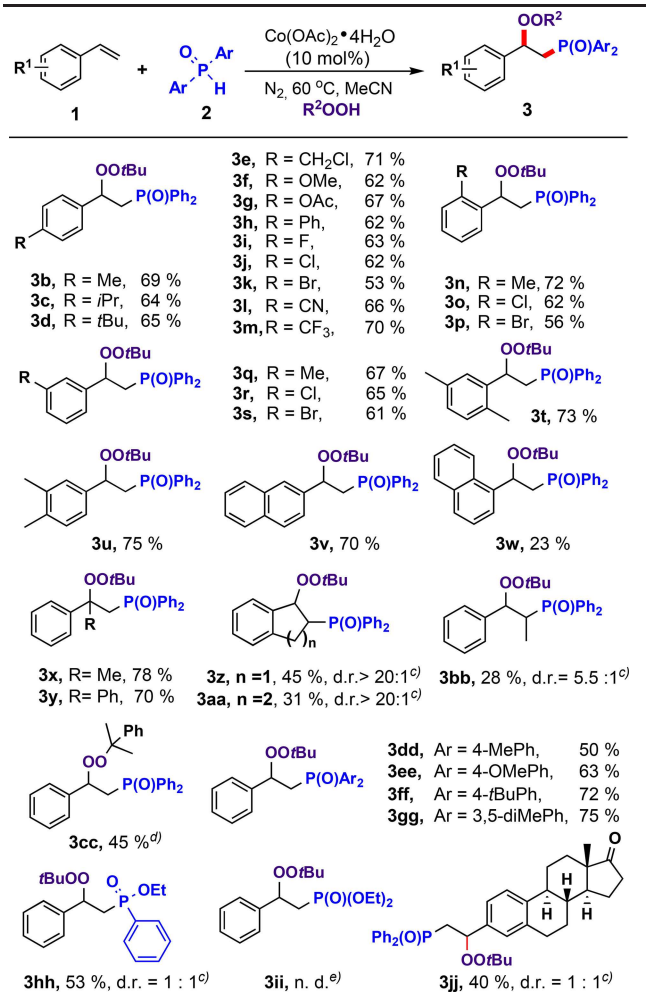


1a 2a 3a

Entry	catalyst (10 mol%)	1a/2a	Solvent	Yield (%)[b]
1	$Co(OAc)_2 \cdot 4H_2O$	1.0:2.0	MeCN	59
2	$Co(OAc)_2 \cdot 4H_2O$	2.0:1.0	MeCN	68
3	$Co(OAc)_2 \cdot 4H_2O$	1.5:1.0	MeCN	62
4	**$Co(OAc)_2 \cdot 4H_2O$**	**3.0:1.0**	**MeCN**	**81**
5	$Co(OAc)_2 \cdot 4H_2O$	3.5:1.0	MeCN	78
6[c]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	64
7[d]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	70
8	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	DCM	40
9	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	THF	13
10	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	DMSO	trace
11	AgOAc	3.0:1.0	MeCN	17
12	$Cu(OAc)_2$	3.0:1.0	MeCN	n.d.[e]
13	$Mn(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	24
14	$CoCl_2 \cdot 6H_2O$	3.0:1.0	MeCN	35
15	$Co(acac)_2$	3.0:1.0	MeCN	36
16[f]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	63
17[g]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	80
18[h]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	37
19[i]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	78
20[j]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	20
21[k]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	29
22	–	3.0:1.0	MeCN	n.d.
23[l]	$Co(OAc)_2 \cdot 4H_2O$	3.0:1.0	MeCN	n.d.

[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.2 mmol), catalyst (10 mol%), TBHP (70% in water, 4 eq.), solvent (2.0 mL), N_2, stirred at 60 °C for 11 h.
[b] Isolated yield.
[c] Performed at 50 °C.
[d] Performed at 70 °C.
[e] n. d. = not detected.
[f] TBHP 3 eq.
[g] TBHP 5 eq.
[h] cat 5 mol%.
[i] cat 15 mol%.
[j] TBHP (5.0–6.0 mol/L in decane) was used.
[k] Performed in air.
[l] Without TBHP.

Table 2. Substrate scope. [a], [b]



[a] Unless specifically noted otherwise, reaction conditions: **1** (0.6 mmol), **2** (0.2 mmol), $Co(OAc)_2 \cdot 4H_2O$ (10 mol%), TBHP (70% in water, 0.8 mmol), MeCN (2.0 mL), N_2, stirred at 60 °C for 11 h.

[b] Isolated yield.

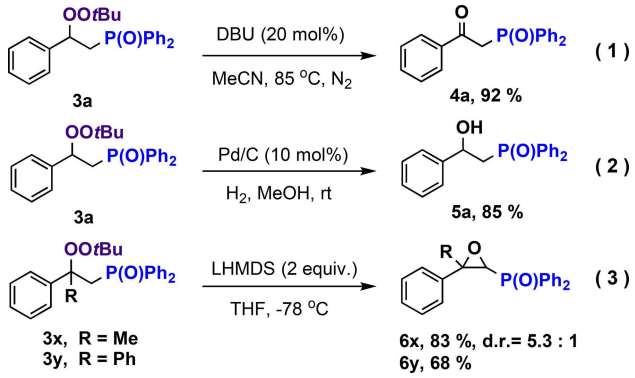
[c] Diastereomeric ratio determined by ^{31}P NMR.

[d] Cumyl hydroperoxide (contains ca. 20% aromatic hydrocarbon, 0.8 mmol).

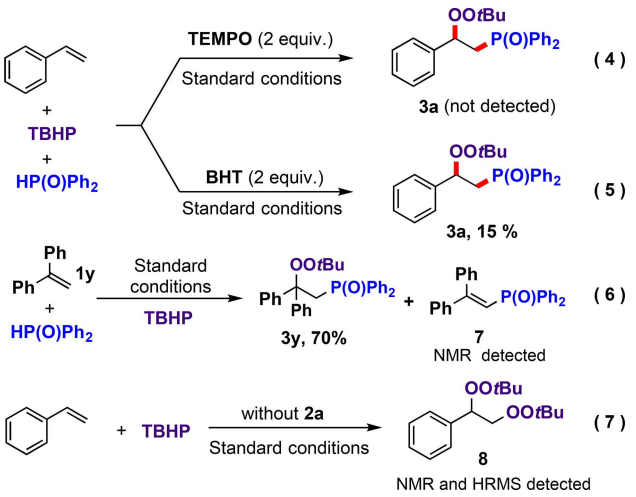
[e] n. d. = not detected.

ucts (**3 t**–**3 u**) in good yields. When extended aromatic systems were employed as substrates, the corresponding products were obtained (**3 v**–**3 w**), although the yield of 1-vinylnaphthalene is much lower than that of 2-vinylnaphthalene, potentially due to the effect of steric hindrance. To our delight, the reaction of *α*-substituted styrenes proceeded well, to give **3 x** and **3 y** in 78% and 70% yield, respectively. Cyclic alkenes were also tolerated in this reaction, with products obtained in excellent diastereomeric ratio (**3 z**–**3 aa**). In contrast, the use of *β*-methylstyrene resulted in a low yield of **3 bb**, perhaps as a result of increased steric hindrance. In addition, when TBHP was replaced by cumyl hydroperoxide, the phosphonation-peroxidation process was still achieved (**3 cc**). It is noteworthy that alternative P(O)–H reagents, such as other diarylphosphine oxides and ethyl phenylphosphinate, were amenable to this reaction, with products **3 dd**–**3 hh** in moderate to good yields. Nevertheless, this process was not applicable to phosphites, the expected phosphorylation-peroxidation product **3 ii** was not detected under standard conditions. It is suggested that our Co(II)/TBHP initiating system could not generate the $P(O)(OR)_2$ radical, and this supposition is supported by the theoretical bond dissociation energies (BDE) of the P–H bonds and the stability of P-radicals.[16] Moreover, when we use dimethylphosphine oxide as the P-source, no products were detected. This may be due to the instability of dialkylphosphine oxide radical. It should be noted that alkylalkenes were unsuitable for use in this reaction, and hydrophosphination-products were detected instead of the desired phosphonation-peroxidation products. Other alkenes, which are conjugated with heteroatom, including phenyl(vinyl)sulfane, 4-vinylpyridine, α,β-unsaturated carbonyl compounds (methyl acrylate and methyl methacrylate) have also been investigated, however, no phosphonation-peroxidation product was detected. We also investigated a few alkynes, including ethynylbenzene and some substituted ethynylbenzene, an inseparable mixture was obtained. No phosphonation-peroxidation products were detected from the NMR of the crude products mixture. Finally, to showcase the potential of this method in modification of natural products, the derivative of estrone (**1 jj**) was chosen as a substrate, with **3 jj** was obtained in a moderate yield.

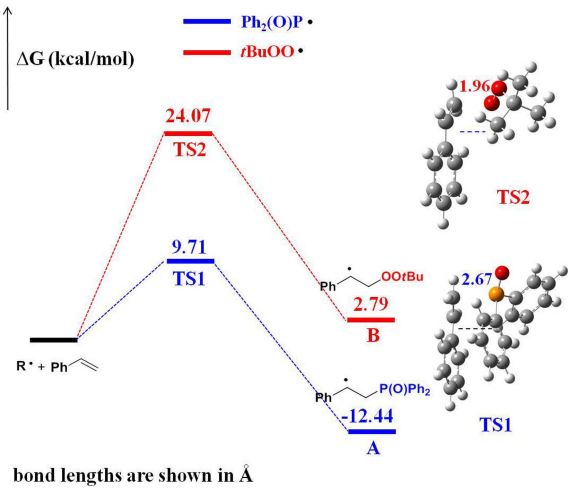
To demonstrate the utility of this reaction in organic synthesis, several transformations of the peroxide group on the substrates were performed (Scheme 2). When 20 mol% DBU was used as a catalytic base, *β*-ketophosphonate **4 a** was formed smoothly in an excellent yield through a Kornblum-DeLaMare rearrangement (Scheme 2, eq 1). Moreover, in the presence of palladium on carbon in methanol under a H_2



Scheme 2. Transformations of the peroxide group.



Scheme 3. Control experiments.



Scheme 4. Computational studies.

atmosphere, the peroxide group was transformed to a hydroxyl group, yielding *β*-hydroxyphosphonate **5a** in 85% yield (Scheme 2, eq 2). Furthermore, the *α,β*-epoxy phosphorus unit is widely found in natural products and commonly used as a precursor for the synthesis of various functionalized phosphorus compounds, including chiral phosphorus ligands.[17] Pleasingly, the epoxide products **6x** or **6y** could be readily obtained by treating **3x** or **3y** with 2 equivalents of LHMDS in THF (Scheme 2, eq 3).

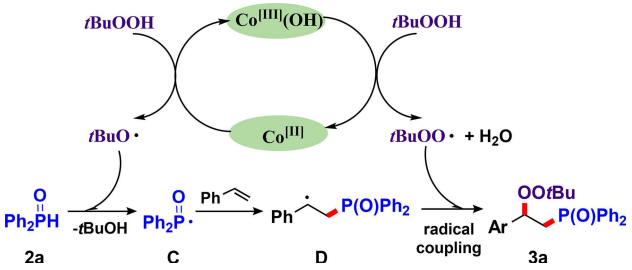
In order to shed light on the reaction mechanism, several control experiments were conducted (Scheme 3). As shown, the phosphonation-peroxidation reaction was completely suppressed by the addition of 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) (Scheme 3, eq 4). When another radical inhibitor, 2,6-di-*tert*-butyl-*p*-cresol (BHT), was present in the reaction mixture, only a small amount **3a** was isolated (Scheme 3, eq 5). Furthermore, when 1, 1-diphenylethylene (**1y**) was employed as a substrate, we observed the generation of alkenyl diphenylphosphine oxide **7** in addition to the desired product **3y** (Scheme 3, eq 6). The above results indicate a radical pathway is likely to be operative in this reaction. In addition, when the reaction was carried out in the absence of **2a**, product **8** was detected (Scheme 3, eq 7). It suggested that a peroxyl radical was generated in the presence of Co(II) from TBHP and could attack the double bond of styrene.

To provide an explanation for the presence of $Ph_2(O)P^{\bullet}$ radical adduct and the chemoselectivity of this reaction, computational studies were carried out (Scheme 4). The results indicate that the attack of $Ph_2(O)P^{\bullet}$ to styrene has the lowest energy barrier (9.71 kcal/mol), and the formed radical adduct **A** is exothermic by 12.44 kcal/mol. Therefore, $Ph_2(O)P^{\bullet}$ is more likely to undergo electrophilic addition with styrene. These results could also provide theoretical support for other P(O)-radical-involved bisfunctionalizations of alkenes.[5]

Based on the above experimental results and previous reports,[5,14] we have devised a plausible mechanistic pathway, and this is as illustrated in Scheme 5. The generation of *tert*-butyloxy and *tert*-butylperoxy radicals is likely to be facilitated by a Co(II)/Co(III) cycle. Subsequently, phosphorus radical **C** is then generated from diphenylphosphine oxide (**2a**) by hydrogen atom abstraction by the *tert*-butyloxy radical. Following this, **C** undergoes addition to the double bond, leading to a carbon-radical **D**. Finally, according to the persistent radical effect (PRE),[18] the transient carbon-radical **D** undergoes a radical-radical cross-coupling with a persistent *tert*-butylperoxy radical to afford the product (**3a**).

Conclusion

In summary, we have developed the first example of cobalt(II)-catalyzed bisfunctionalization of styrenes with aryl phosphorus reagents and peroxides. The reaction proceeds efficiently under mild conditions to



Scheme 5. Plausible mechanistic pathway.

provide a convenient approach to various phosphonation-peroxidation compounds in a one-pot manner. A P(O)-radical-mediated pathway is proposed following the computational and preliminary mechanistic studies. Further investigations into the mechanism and the potential applications of this methodology are ongoing in our laboratory.

Experimental Section

General methods: ^{1}H and ^{13}C NMR spectra were recorded on a 500 M Bruker AVANCE NEO spectrometer in $CDCl_3$ with TMS as internal standard. ^{31}P NMR and ^{19}F NMR spectra were recorded on the same instrument. High resolution mass spectroscopic (HRMS) and mass spectra were measured using Thermo Scientific DS II mass spectrometer and Bruker micro TOF-Q mass spectrometer. Melting points were measured on a WRS-1C digital melting point apparatus and are uncorrected. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was carried out on silica gel (particle size 200–400 mesh ASTM). All the computational calculations are carried out with the GAUSSIAN 09 program.[19] The optimized geometries and harmonic frequencies of the stable structures and transition states are calculated using the M06-2X method[20] with 6-31+G (d,p) basis set. To consider the solvent effects, the polarizable continuum method (PCM) model[21] with CH_3CN as the solvent is employed.

Typical Procedure for the Synthesis of Compounds 3: To a Schlenk tube were added **2a** (0.2 mmol), Cobalt (II) acetate tetrahydrate (10 mol%) and charged with nitrogen for three times. Then, TBHP (70% in water, 4.0 eq.), anhydrous MeCN (2.0 mL) and styrene **1a** (0.6 mmol) were added *via* syringe. The mixture was allowed to stir at 60 °C in an oil bath overnight. At the completion of the reaction, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to afford the product (2-(tert-butylperoxy)-2-phenylethyl)diphenylphosphine oxide **3a**.

Characterization of the Products

(2-(*tert*-butylperoxy)-2-phenylethyl) diphenylphosphine oxide (3a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3a** (81% yield, 63.8 mg) as white solid, m. p. = 139–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.57–7.53 (m, 2H), 7.52–7.45 (m, 3H), 7.39–7.36 (m, 1H), 7.32–7.26 (m, 4H), 7.24–7.17 (m, 3H), 5.45 (dd, J_1 = 7.3 Hz, J_2 = 13.7 Hz, 1H), 3.16–3.09 (m, 1H), 2.68–2.61 (m, 1H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.2 (d, $J_{C\text{-}P}$ = 6.9 Hz), 134.0 (d, $J_{C\text{-}P}$ = 21.0 Hz), 133.2 (d, $J_{C\text{-}P}$ = 21.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.2, 128.0, 127.0, 80.5, 80.1, 35.9 (d, $J_{C\text{-}P}$ = 69.0 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.26. HRMS calc. for $C_{24}H_{28}O_3P$ $(M+H)^+$: 395.1771, found 395.1771.

(2-(*tert*-butylperoxy)-2-(*p*-tolyl)ethyl) diphenylphosphine oxide (3b): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3b** (69% yield, 56.3 mg) as white solid, m. p. = 145–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.82 (m, 2H), 7.56–7.45 (m, 5H), 7.39–7.36 (m, 1H), 7.31–7.26 (m, 2H), 7.19–7.18 (m, 2H), 7.02–7.01 (m, 2H), 5.40 (dd, J_1 = 6.9 Hz, J_2 = 13.9 Hz, 1H), 3.18–3.12 (m, 1H), 2.68–2.61 (m, 1H), 2.27 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 137.0 (d, $J_{C\text{-}P}$ = 6.5 Hz), 133.9 (d, $J_{C\text{-}P}$ = 19.1 Hz), 133.1 (d, $J_{C\text{-}P}$ = 19.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.9, 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.0, 80.5, 80.1, 35.8 (d, $J_{C\text{-}P}$ = 69.1 Hz), 26.2, 21.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.50. HRMS calc. for $C_{25}H_{30}O_3P$ $(M+H)^+$: 409.1927, found 409.1934.

(2-(*tert*-butylperoxy)-2-(4-isopropylphenyl)ethyl) diphenylphosphine oxide (3c): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3c** (64% yield, 55.8 mg) as white solid, m. p. = 142–144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.79 (m, 2H), 7.53–7.45 (m, 5H), 7.35–7.33 (m, 1H), 7.29–7.25 (m, 2H), 7.21–7.19 (m, 2H), 7.05–7.03 (m, 2H), 5.42 (dd, J_1 = 6.9 Hz, J_2 = 13.8 Hz, 1H), 3.22–3.15 (m, 1H), 2.84–2.79 (m, 1H), 2.70–2.64 (m, 1H), 1.19 (d, J = 6.9 Hz, 6H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 137.0 (d, $J_{C\text{-}P}$ = 6.2 Hz), 133.9 (d, $J_{C\text{-}P}$ = 29.2 Hz), 133.1 (d, $J_{C\text{-}P}$ = 29.1 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.1, 126.2, 80.6, 80.3, 35.7 (d, $J_{C\text{-}P}$ = 69.3 Hz), 33.8, 26.2, 23.9, 23.8. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.68. HRMS calc. for $C_{27}H_{34}O_3P$ $(M+H)^+$: 437.2240, found 437.2230.

(2-(4-(tert-butyl)phenyl)-2-(*tert*-butylperoxy)ethyl) diphenylphosphine oxide (3d): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3d** (65% yield, 58.5 mg) as white solid, m. p. = 161–163 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.79 (m, 2H), 7.53–7.44 (m, 5H), 7.35–7.32 (m, 1H), 7.27–7.24 (m, 2H), 7.22–7.18 (m, 4H), 5.44 (dd, J_1 = 6.9 Hz, J_2 = 13.7 Hz, 1H), 3.22–3.16 (m, 1H), 2.71–2.64 (m, 1H), 1.26 (s, 9H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.7, 136.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 134.0 (d, $J_{C\text{-}P}$ = 38.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 38.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.7 Hz), 126.7, 125.1, 80.6, 80.2, 35.6 (d, $J_{C\text{-}P}$ = 69.0 Hz), 34.4, 31.2, 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.42. HRMS calc. for $C_{28}H_{36}O_3P$ $(M+H)^+$: 451.2397, found 451.2401.

(2-(*tert*-butylperoxy)-2-(4-(chloromethyl)phenyl)ethyl) diphenylphosphine oxide (3e): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3e** (71% yield, 62.7 mg) as white solid, m. p. = 151–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2H), 7.54–7.46 (m, 5H), 7.39–7.36 (m, 1H), 7.31–7.27 (m, 4H), 7.23–7.22 (m, 2H), 5.45 (dd, J_1 = 6.9 Hz, J_2 = 14.0 Hz, 1H), 4.51 (s, 2H), 3.14–3.08(m,

1H), 2.66–2.59 (m, 1H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4 (d, J_{C-P} = 6.4 Hz), 137.0, 133.7 (d, J_{C-P} = 10.5 Hz), 132.9 (d, J_{C-P} = 10.3 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.4 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 9.6 Hz), 130.3 (d, J_{C-P} = 9.3 Hz), 128.5, 128.4 (d, J_{C-P} = 1.6 Hz), 128.3 (d, J_{C-P} = 11.6 Hz), 127.3, 80.7, 79.8, 45.9, 35.8 (d, J_{C-P} = 69.1 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.19. HRMS calc. for $C_{25}H_{29}ClO_3P$ $(M+H)^+$: 443.1537, found 443.1542.

(2-(*tert*-butylperoxy)-2-(4-methoxyphenyl)ethyl) diphenylphosphine oxide (3f): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3f** (62% yield, 52.6 mg) as white solid, m. p. = 139–140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.55–7.45 (m, 5H), 7.38–7.36 (m, 1H), 7.31–7.27 (m, 2H), 7.19–7.18 (m, 2H), 7.20 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 8.6 Hz, 2H), 5.38 (dd, J_1 = 6.9 Hz, J_2 = 13.8 Hz, 1H), 3.74 (s, 3H), 3.23–3.17 (m, 1H), 2.69–2.63 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 133.8, 133.0, 131.7 (d, J_{C-P} = 6.0 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 2.6 Hz), 130.8 (d, J_{C-P} = 9.5 Hz), 130.4 (d, J_{C-P} = 9.3 Hz), 128.5, 128.4, 128.2 (d, J_{C-P} = 11.8 Hz), 113.5, 80.5, 79.9, 55.1, 35.5 (d, J_{C-P} = 69.3 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.69. HRMS calc. for $C_{25}H_{30}O_4P$ $(M+H)^+$: 425.1876, found 425.1869.

4-(1-(*tert*-butylperoxy)-2-(diphenylphosphoryl)ethyl) phenyl acetate (3g): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3g** (67% yield, 60.6 mg) as white solid, m. p. = 167–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.57–7.46 (m, 5H), 7.41–7.31 (m, 5H), 6.95 (d, J = 8.6 Hz, 2H), 5.46 (dd, J_1 = 7.2 Hz, J_2 = 13.8 Hz, 1H), 3.13–3.07 (m, 1H), 2.66–2.59 (m, 1H), 2.27 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.2, 150.2, 137.8 (d, J_{C-P} = 7.1 Hz), 133.7 (d, J_{C-P} = 10.9 Hz), 132.9 (d, J_{C-P} = 11.5 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 9.3 Hz), 130.3 (d, J_{C-P} = 9.6 Hz), 128.4 (d, J_{C-P} = 7.7 Hz), 128.3 (d, J_{C-P} = 7.5 Hz), 128.0, 121.2, 80.6, 79.5, 35.9 (d, J_{C-P} = 69.1 Hz), 26.1, 21.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.26. HRMS calc. for $C_{26}H_{30}O_5P$ $(M+H)^+$: 453.1825, found 453.1832.

(2-([1,1′-biphenyl]-4-yl)-2-(*tert*-butylperoxy)ethyl) diphenylphosphine oxide (3h): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3h** (62% yield, 58.3 mg) as white solid, m. p. = 180–182 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.55–7.45 (m, 7H), 7.43–7.40 (m, 4H), 7.37–7.32 (m, 4H), 7.28–7.24 (m, 2H), 5.50 (dd, J_1 = 6.9 Hz, J_2 = 13.9 Hz, 1H), 3.23–3.16 (m, 1H), 2.73–2.66 (m, 1H), 1.07 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.9, 140.8, 138.9 (d, J_{C-P} = 6.2 Hz), 133.8 (d, J_{C-P} = 24.0 Hz), 133.0 (d, J_{C-P} = 23.6 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.1 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 9.5 Hz), 130.4 (d, J_{C-P} = 9.4 Hz), 128.6, 128.5 (d, J_{C-P} = 11.8 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 127.5, 127.2, 127.0, 126.9, 80.7, 80.1, 35.8 (d, J_{C-P} = 68.9 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.19. HRMS calc. for $C_{30}H_{32}O_3P$ $(M+H)^+$: 471.2084, found 471.2093.

(2-(*tert*-butylperoxy)-2-(4-fluorophenyl)ethyl) diphenylphosphine oxide (3i): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3i** (63% yield, 51.9 mg) as white solid, m. p. = 146–147 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.55–7.45 (m, 5H), 7.41–7.38 (m, 1H), 7.32–7.25 (m, 4H), 6.90–6.86 (m, 2H), 5.42 (dd, J_1 = 6.9 Hz, J_2 = 14.0 Hz, 1H), 3.17–3.11 (m, 1H), 2.66–2.59 (m, 1H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.4 (d, J_{C-F} = 244.7 Hz), 135.7 (dd, J_1 = 3.3 Hz, J_2 = 6.2 Hz), 133.7 (d, J_{C-P} = 7.2 Hz), 132.9 (d, J_{C-P} = 7.0 Hz), 131.6 (d, J_{C-P} = 2.6 Hz), 131.3 (d, J_{C-P} = 2.6 Hz), 130.7 (d, J_{C-P} = 9.5 Hz), 130.3 (d, J_{C-P} = 9.2 Hz), 128.9 (d, J_{C-P} = 8.2 Hz), 128.5 (d, J_{C-P} = 11.9 Hz), 128.3 (d, J_{C-P} = 11.7 Hz), 115.0 (d, J_{C-F} = 21.6 Hz), 80.6, 79.6, 35.7 (d, J_{C-P} = 69.2 Hz), 26.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −114.17. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.17. HRMS calc. for $C_{24}H_{27}FO_3P$ $(M+H)^+$: 413.1676, found 413.1682.

(2-(*tert*-butylperoxy)-2-(4-chlorophenyl)ethyl) diphenylphosphine oxide (3j): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3j** (62% yield, 53.1 mg) as white solid, m. p. = 148–150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.55–7.46 (m, 5H), 7.43–7.40 (m, 1H), 7.33–7.30 (m, 2H), 7.24–7.22 (m, 2H), 7.17–7.15 (m, 2H), 5.42 (dd, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 3.14–3.07 (m, 1H), 2.63–2.57 (m, 1H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6 (d, J_{C-P} = 6.3 Hz), 133.8, 133.7 (d, J_{C-P} = 8.7 Hz), 132.9 (d, J_{C-P} = 8.1 Hz), 131.7 (d, J_{C-P} = 2.5 Hz), 131.3 (d, J_{C-P} = 2.5 Hz), 130.8 (d, J_{C-P} = 9.3 Hz), 130.4 (d, J_{C-P} = 9.4 Hz), 128.5 (d, J_{C-P} = 11.9 Hz), 128.5, 128.4, 128.3, 80.7, 79.6, 35.8 (d, J_{C-P} = 69.1 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.06. HRMS calc. for $C_{24}H_{27}ClO_3P$ $(M+H)^+$: 429.1381, found 429.1387.

(2-(4-bromophenyl)-2-(*tert*-butylperoxy)ethyl) diphenylphosphine oxide (3k): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3k** (53% yield, 50.0 mg) as white solid, m. p. = 157–158 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.54–7.46 (m, 5H), 7.43–7.40 (m, 1H), 7.33–7.27 (m, 4H), 7.18–7.16 (m, 2H), 5.40 (dd, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 3.13–3.06 (m, 1H), 2.62–2.56 (m, 1H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.1 (d, J_{C-P} = 6.3 Hz), 133.6 (d, J_{C-P} = 13.3 Hz), 132.8 (d, J_{C-P} = 12.7 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.3, 131.2, 130.7 (d, J_{C-P} = 9.2 Hz), 130.3 (d, J_{C-P} = 9.3 Hz), 128.8, 128.5 (d, J_{C-P} = 11.8 Hz), 128.4 (d, J_{C-P} = 11.8 Hz), 122.0, 80.7, 79.6, 35.8 (d, J_{C-P} = 69.3 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.05. HRMS calc. for $C_{24}H_{27}BrO_3P$ $(M+H)^+$: 473.0876, found 473.0884.

4-(1-(*tert*-butylperoxy)-2-(diphenylphosphoryl)ethyl) benzonitrile (3l): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3l** (66% yield, 55.3 mg) as white solid, m. p. = 156–157 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2H), 7.56–7.48 (m, 7H), 7.45–7.41 (m, 3H), 7.35–7.31 (m, 2H), 5.49 (dd, J_1 = 7.1 Hz, J_2 = 14.2 Hz, 1H), 3.07–3.01 (m, 1H), 2.61–2.55 (m, 1H), 1.01 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8 (d, J_{C-P} = 6.4 Hz), 133.3 (d, J_{C-P} = 8.4 Hz), 132.5 (d, J_{C-P} = 9.1 Hz), 131.9, 131.8 (d, J_{C-P} = 2.6 Hz), 131.5 (d, J_{C-P} = 2.6 Hz), 130.6 (d, J_{C-P} = 9.5 Hz), 130.2 (d, J_{C-P} = 9.3 Hz), 128.5 (d, J_{C-P} = 11.9 Hz), 128.4 (d, J_{C-P} = 11.8 Hz), 127.6, 118.6, 111.6, 80.9, 79.3, 35.7 (d, J_{C-P} = 68.9 Hz), 26.0. ^{31}P NMR (203 MHz, $CDCl_3$): δ 26.75. HRMS calc. for $C_{25}H_{27}NO_3P$ $(M+H)^+$: 420.1723, found 420.1714.

(2-(*tert*-butylperoxy)-2-(4-(trifluoromethyl)phenyl) ethyl) diphenylphosphine oxide (3 m): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 m** (70% yield, 64.7 mg) as white solid, m. p. = 144–146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.53–7.36 (m, 10H), 7.30–7.27 (m, 2H), 5.51 (dd, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 3.12–3.06 (m, 1H), 2.64–2.57 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 133.6 (d, $J_{C\text{-}P}$ = 33.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 33.4 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.1 (d, $J_{C\text{-}F}$ = 32.2 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.5, 128.4, 127.4, 125.2 (q, $J_{C\text{-}F}$ = 3.5 Hz), 80.9, 79.7, 35.9 (d, $J_{C\text{-}P}$ = 69.1 Hz), 26.2. ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.64.^{31}P NMR (203 MHz, $CDCl_3$): δ 26.86. HRMS calc. for $C_{25}H_{27}F_3O_3P$ $(M+H)^+$: 463.1644, found 463.1630.

(2-(*tert*-butylperoxy)-2-(*o*-tolyl)ethyl) diphenylphosphine oxide (3 n): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 n** (72% yield, 58.8 mg) as white solid, m. p. = 117–118 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.55–7.45 (m, 5H), 7.37–7.26 (m, 4H), 7.08–6.99 (m, 3H), 5.73 (dd, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 3.19–3.13 (m, 1H), 2.69–2.62 (m, 1H), 2.35 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1 (d, $J_{C\text{-}P}$ = 6.3 Hz), 135.7, 133.9 (d, $J_{C\text{-}P}$ = 24.8 Hz), 133.2 (d, $J_{C\text{-}P}$ = 24.2 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.3, 130.2 (d, $J_{C\text{-}P}$ = 9.4 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.7 Hz), 127.8, 126.7, 125.8, 80.4, 76.5, 35.2 (d, $J_{C\text{-}P}$ = 69.2 Hz), 26.2, 19.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.31. HRMS calc. for $C_{25}H_{30}O_3P$ $(M+H)^+$: 409.1927, found 409.1933.

(2-(*tert*-butylperoxy)-2-(2-chlorophenyl)ethyl) diphenylphosphine oxide (3 o): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 o** (62% yield, 53.1 mg) as white solid, m. p. = 114–116 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87–7.83 (m, 2H), 7.70–7.66 (m, 2H), 7.53–7.41 (m, 5H), 7.39–7.35 (m, 2H), 7.27–7.21 (m, 3H), 5.88–5.83 (m, 1H), 2.93–2.87 (m, 1H), 2.79–2.72 (m, 1H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3 (d, $J_{C\text{-}P}$ = 9.1 Hz), 133.9 (d, $J_{C\text{-}P}$ = 15.5 Hz), 133.1 (d, $J_{C\text{-}P}$ = 16.2 Hz), 132.4, 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.5, 128.8, 128.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 128.3, 126.8, 80.8, 76.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 34.9 (d, $J_{C\text{-}P}$ = 68.6 Hz), 26.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 26.84. HRMS calc. for $C_{24}H_{27}ClO_3P$ $(M+H)^+$: 429.1381, found 429.1387.

(2-(2-bromophenyl)-2-(*tert*-butylperoxy)ethyl) diphenylphosphine oxide (3 p): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 p** (56% yield, 52.9 mg) as white solid, m. p. = 131–133 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.83 (m, 2H), 7.72–7.68 (m, 2H), 7.54–7.42 (m, 6H), 7.39–7.36 (m, 2H), 7.29–7.26 (m, 1H), 7.10–7.06 (m, 1H), 5.84–5.79 (m, 1H), 2.87–2.72 (m, 2H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 133.9 (d, $J_{C\text{-}P}$ = 23.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 24.6 Hz), 132.7, 131.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 129.1, 128.4, 128.3, 127.4, 122.2, 80.8, 79.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 35.1 (d, $J_{C\text{-}P}$ = 68.4 Hz), 26.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 26.13. HRMS calc. for $C_{24}H_{27}BrO_3P$ $(M+H)^+$: 473.0876, found 473.0885.

(2-(*tert*-butylperoxy)-2-(m-tolyl)ethyl) diphenylphosphine oxide (3 q): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 q** (67% yield, 54.7 mg) as white solid, m. p. = 134–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2H), 7.56–7.45 (m, 5H), 7.38–7.35 (m, 1H), 7.31–7.26 (m, 2H), 7.12–7.11 (m, 2H), 7.06 (s, 1H), 6.98 (d, J = 5.8 Hz, 1H), 5.41 (dd, J_1 = 7.0 Hz, J_2 = 13.9 Hz, 1H), 3.17–3.11 (m, 1H), 2.68–2.61 (m, 1H), 2.24 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9 (d, $J_{C\text{-}P}$ = 6.4 Hz), 137.7, 133.9 (d, $J_{C\text{-}P}$ = 3.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 3.5 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.8, 128.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.2, 128.1 (d, $J_{C\text{-}P}$ = 4.6 Hz), 127.7, 124.1, 80.6, 80.3, 35.8 (d, $J_{C\text{-}P}$ = 69.0 Hz), 26.2, 21.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.58. HRMS calc. for $C_{25}H_{30}O_3P$ $(M+H)^+$: 409.1927, found 409.1917.

(2-(*tert*-butylperoxy)-2-(3-chlorophenyl)ethyl) diphenylphosphine oxide (3 r): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 r** (65% yield, 55.6 mg) as white solid, m. p. = 127–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2H), 7.57–7.46 (m, 5H), 7.41–7.37 (m, 1H), 7.34–7.30 (m, 2H), 7.27 (s, 1H), 7.21–7.19 (m, 1H), 7.15–7.13 (m, 2H), 5.42 (dd, J_1 = 7.2 Hz, J_2 = 13.9 Hz, 1H), 3.10–3.03 (m, 1H), 2.62–2.56 (m, 1H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 134.0, 133.6 (d, $J_{C\text{-}P}$ = 11.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 11.2 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.5 Hz), 129.5, 128.5 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.1, 127.0, 125.2, 80.7, 79.5, 35.8 (d, $J_{C\text{-}P}$ = 68.8 Hz), 26.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 26.99. HRMS calc. for $C_{24}H_{27}ClO_3P$ $(M+H)^+$: 429.1381, found 429.1384.

(2-(3-bromophenyl)-2-(*tert*-butylperoxy)ethyl) diphenylphosphine oxide (3 s): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 s** (61% yield, 57.6 mg) as white solid, m. p. = 128–129 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.80 (m, 2H), 7.57–7.46 (m, 5H), 7.42–7.37 (m, 2H), 7.34–7.24 (m, 4H), 7.07 (t, J = 7.8 Hz, 1H), 5.41 (dd, J_1 = 7.1 Hz, J_2 = 13.9 Hz, 1H), 3.10–3.03 (m, 1H), 2.62–2.55 (m, 1H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.6 (d, $J_{C\text{-}P}$ = 6.8 Hz), 133.6 (d, $J_{C\text{-}P}$ = 19.3 Hz), 132.8 (d, $J_{C\text{-}P}$ = 18.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.0, 130.7 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.9, 129.8, 128.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 125.7, 122.3, 80.7, 79.4, 35.8 (d, $J_{C\text{-}P}$ = 68.8 Hz), 26.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 26.98. HRMS calc. for $C_{24}H_{27}BrO_3P$ $(M+H)^+$: 473.0876, found 473.0885.

(2-(*tert*-butylperoxy)-2-(2,5-dimethylphenyl)ethyl) diphenylphosphine oxide (3 t): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 t** (73% yield, 61.6 mg) as white solid, m. p. = 141–143 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.81 (m, 2H), 7.52–7.44 (m, 5H),

7.35–7.32 (m, 1H), 7.28–7.24 (m, 2H), 7.05 (s, 1H), 6.90–6.84 (m, 2H), 5.70 (dd, J_1 = 6.9 Hz, J_2 = 13.8 Hz, 1H), 3.23–3.17 (m, 1H), 2.70–2.63 (m, 1H), 2.32 (s, 3H), 2.18 (s, 3H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.3 (d, $J_{C\text{-}P}$ = 5.8 Hz), 135.0, 134.0 (d, $J_{C\text{-}P}$ = 48.1 Hz), 133.2 (d, $J_{C\text{-}P}$ = 47.7 Hz), 132.7, 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.2, 130.1, 128.6, 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.5, 80.4, 76.7, 35.1 (d, $J_{C\text{-}P}$ = 69.3 Hz), 26.2, 20.9, 18.8. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.36. HRMS calc. for $C_{26}H_{32}O_3P$ $(M+H)^+$: 423.2084, found 423.2088.

(2-(*tert*-butylperoxy)-2-(3,4-dimethylphenyl)ethyl) diphenylphosphine oxide (3u): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3u** (75% yield, 63.3 mg) as white solid, m. p. = 109–110 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.80 (m, 2H), 7.53–7.44 (m, 5H), 7.37–7.34 (m, 1H), 7.28–7.25 (m, 2H), 7.05–6.96 (m, 3H), 5.38 (dd, J_1 = 6.9 Hz, J_2 = 13.8 Hz, 1H), 3.21–3.14 (m, 1H), 2.68–2.62 (m, 1H), 2.15 (s, 3H), 2.13 (s, 3H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1 (d, $J_{C\text{-}P}$ = 6.1 Hz), 136.4, 136.1, 133.8 (d, $J_{C\text{-}P}$ = 15.1 Hz), 133.0 (d, $J_{C\text{-}P}$ = 14.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.4, 128.4 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.3, 128.1 (d, $J_{C\text{-}P}$ = 11.8 Hz), 124.5, 80.6, 80.3, 35.8 (d, $J_{C\text{-}P}$ = 69.3 Hz), 26.2, 19.6, 19.4. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.77. HRMS calc. for $C_{26}H_{32}O_3P$ $(M+H)^+$: 423.2084, found 423.2074.

(2-(*tert*-butylperoxy)-2-(naphthalen-2-yl)ethyl) diphenylphosphine oxide (3v): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3v** (70% yield, 62.2 mg) as white solid, m. p. = 172–173 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.82 (m, 2H), 7.74–7.68 (m, 4H), 7.51–7.44 (m, 6H), 7.43–7.40 (m, 2H), 7.21–7.18 (m, 1H), 7.16–7.12 (m, 2H), 5.62 (dd, J_1 = 7.0 Hz, J_2 = 14.0 Hz, 1H), 3.23–3.17 (m, 1H), 2.74–2.68 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5 (d, $J_{C\text{-}P}$ = 6.7 Hz), 133.7 (d, $J_{C\text{-}P}$ = 35.5 Hz), 133.1, 132.9, 132.8 (d, $J_{C\text{-}P}$ = 34.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.2 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2, 128.1, 128.0, 127.9, 127.4, 126.5, 125.8 (d, $J_{C\text{-}P}$ = 3.3 Hz), 124.4, 80.6, 80.3, 35.9 (d, $J_{C\text{-}P}$ = 69.0 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.52. HRMS calc. for $C_{28}H_{30}O_3P$ $(M+H)^+$: 445.1927, found 445.1933.

(2-(*tert*-butylperoxy)-2-(naphthalen-1-yl)ethyl) diphenylphosphine oxide (3w): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3w** (23% yield, 20.4 mg) as white solid, m. p. = 134–136 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87–7.82 (m, 2H), 7.75–7.69 (m, 4H), 7.52–7.42 (m, 8H), 7.23–7.19 (m, 1H), 7.17–7.13 (m, 2H), 5.62 (dd, J_1 = 7.0 Hz, J_2 = 13.9 Hz, 1H), 3.23–3.17 (m, 1H), 2.74–2.68 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.5 (d, $J_{C\text{-}P}$ = 6.5 Hz), 133.8 (d, $J_{C\text{-}P}$ = 35.0 Hz), 133.2, 133.0 (d, $J_{C\text{-}P}$ = 35.0 Hz), 132.9, 131.6 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.2 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.2, 128.1, 128.0, 127.9, 127.5, 126.6, 125.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 124.4, 80.,7, 80.4, 36.0 (d, $J_{C\text{-}P}$ = 69.1 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.47. HRMS calc. for $C_{28}H_{30}O_3P$ $(M+H)^+$: 445.1927, found 445.1921.

(2-(*tert*-butylperoxy)-2-phenylpropyl) diphenylphosphine oxide (3x): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3x** (78% yield, 63.6 mg) as white solid, m. p. = 150–152 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.78 (m, 2H), 7.46–7.29 (m, 8H), 7.23–7.20 (m, 2H), 7.16–7.08 (m, 3H), 3.08–3.03 (m, 1H), 2.80–2.75 (m, 1H), 2.05 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.2 (d, $J_{C\text{-}P}$ = 5.6 Hz), 134.7 (d, $J_{C\text{-}P}$ = 100.1 Hz), 133.8 (d, $J_{C\text{-}P}$ = 99.4 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.2 (d, $J_{C\text{-}P}$ = 9.2 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.6 Hz), 127.8, 127.1, 125.8, 125.2, 82.9 (d, $J_{C\text{-}P}$ = 1.9 Hz),, 79.2, 41.7 (d, $J_{C\text{-}P}$ = 68.1 Hz), 26.4, 23.6. ^{31}P NMR (203 MHz, $CDCl_3$): δ 25.79. HRMS calc. for $C_{25}H_{30}O_3P$ $(M+H)^+$: 409.1927, found 409.1918.

(2-(*tert*-butylperoxy)-2,2-diphenylethyl) diphenylphosphine oxide (3y): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3y** (70% yield, 65.8 mg) as white solid, m. p. = 164–165 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63–7.60 (m, 4H), 7.39–7.29 (m, 10H), 7.17–7.13 (m, 6H), 3.64 (d, J = 11.7 Hz, 2H), 0.96 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.9 (d, $J_{C\text{-}P}$ = 4.7 Hz), 134.7 (d, $J_{C\text{-}P}$ = 99.9 Hz), 130.8 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.0 Hz), 128.2, 128.0 (d, $J_{C\text{-}P}$ = 11.7 Hz), 127.2, 127.1, 86.1 (d, $J_{C\text{-}P}$ = 3.5 Hz), 79.7, 39.4 (d, $J_{C\text{-}P}$ = 70.4 Hz), 26.4. ^{31}P NMR (203 MHz, $CDCl_3$): δ 24.68. HRMS calc. for $C_{30}H_{32}O_3P$ $(M+H)^+$: 471.2084, found 471.2075.

(1-(*tert*-butylperoxy)-2,3-dihydro-1H-inden-2-yl) diphenylphosphine oxide (3z): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3z** (45% yield, 36.5 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90–7.84 (m, 4H), 7.52–7.41 (m, 7H), 7.26–7.23 (m, 1H), 7.19–7.14 (m, 2H), 5.77 (dd, J_1 = 2.3 Hz, J_2 = 12.1 Hz, 1H), 3.64–3.60 (m, 1H), 3.42–3.34 (m, 1H), 3.28–3.20 (m, 1H), 1.06 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1 (d, $J_{C\text{-}P}$ = 3.3 Hz), 138.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 133.2, 132.3 (d, $J_{C\text{-}P}$ = 11.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.5, 130.9 (d, $J_{C\text{-}P}$ = 9.0 Hz), 129.4, 128.7 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 126.6 (d, $J_{C\text{-}P}$ = 49.7 Hz), 124.6, 87.3 (d, $J_{C\text{-}P}$ = 2.8 Hz), 80.5, 40.9 (d, $J_{C\text{-}P}$ = 70.8 Hz), 31.5, 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.73. HRMS calc. for $C_{25}H_{28}O_3P$ $(M+H)^+$: 407.1771, found 407.1764.

(1-(*tert*-butylperoxy)-1,2,3,4-tetrahydronaphthalen-2-yl) diphenylphosphine oxide (3aa): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3aa** (31% yield, 26.0 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.92–7.83 (m, 4H), 7.52–7.40 (m, 6H), 7.27–7.25 (m, 1H), 7.21–7.18 (m, 1H), 7.14–7.11 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 5.22 (d, J = 7.9 Hz, 1H), 3.67–3.63 (m, 1H), 3.17–3.11 (m, 1H), 2.72–2.67 (m, 1H), 2.34–2.21 (m, 1H), 2.04–1.94 (m, 1H), 1.19 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.0, 132.9 (d, $J_{C\text{-}P}$ = 39.2 Hz), 132.1 (d, $J_{C\text{-}P}$ = 38.1 Hz), 131.5, 131.4, 131.3, 130.9, 130.8, 130.7, 128.7, 128.6, 128.5, 128.3 (d, $J_{C\text{-}P}$ = 11.2 Hz), 125.8, 80.7, 78.3 (d, $J_{C\text{-}P}$ = 5.5 Hz), 34.9 (d, $J_{C\text{-}P}$ = 69.4 Hz),

26.8 (d, $J_{C\text{-}P}$ = 3.9 Hz), 26.5, 18.7 (d, $J_{C\text{-}P}$ = 2.2 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 32.26. HRMS calc. for $C_{26}H_{30}O_3P$ $(M+H)^+$: 421.1927, found 421.1920.

(1-(*tert*-butylperoxy)-1-phenylpropan-2-yl) diphenylphosphine oxide (3 bb): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 bb** (28% yield, 22.8 mg) as white solid. d.r. = 5.5:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.80 (m, 2H), 7.73–7.69 (m, 2H), 7.48–7.40 (m, 4H), 7.38–7.33 (m, 2H), 7.27–7.25 (m, 2H), 7.23–7.18 (m, 2H), 7.16–7.13 (m, 1H), 5.37 (dd, J_1 = 4.5 Hz, J_2 = 8.8 Hz, 1H), 2.76–2.69 (m, 1H), 1.21 (dd, J_1 = 7.4 Hz, J_2 = 16.3 Hz, 3H), 1.14 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.4 (d, $J_{C\text{-}P}$ = 8.8 Hz), 132.6(d, $J_{C\text{-}P}$ = 95.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.4 Hz), 130.9 (d, $J_{C\text{-}P}$ = 8.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.2 Hz), 128.1, 127.8, 127.4, 126.9, 125.6, 82.0, 80.5, 40.6 (d, $J_{C\text{-}P}$ = 68.9 Hz), 26.5, 8.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 32.72. HRMS calc. for $C_{25}H_{30}O_3P$ $(M+H)^+$: 409.1927, found 409.1929.

diphenyl(2-phenyl-2-((2-phenylpropan-2-yl)peroxy) ethyl) phosphine oxide (3 cc): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 cc** (45% yield, 41.0 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73–7.69 (m, 2H), 7.53–7.45 (m, 3H), 7.40–7.35 (m, 3H), 7.30–7.19 (m, 12H), 5.47 (dd, J_1 = 7.0 Hz, J_2 = 14.2 Hz, 1H), 3.05–2.99 (m, 1H), 2.63–2.56 (m, 1H), 1.39 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.2, 140.1 (d, $J_{C\text{-}P}$ = 6.6 Hz), 133.8 (d, $J_{C\text{-}P}$ = 35.7 Hz), 133.0 (d, $J_{C\text{-}P}$ = 36.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 24.5 Hz), 128.3, 128.1, 128.0, 127.8, 127.0, 126.8, 125.5, 83.2, 80.0, 35.8 (d, $J_{C\text{-}P}$ = 69.2 Hz), 27.0, 25.9. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.53. HRMS calc. for $C_{29}H_{30}O_3P$ $(M+H)^+$: 457.1927, found 457.1921.

(2-(*tert*-butylperoxy)-2-phenylethyl)di-*p*-tolylphosphine oxide (3 dd): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 dd** (50% yield, 42.2 mg) as white solid, m. p. = 154–156 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.73–7.69 (m, 2H), 7.45–7.41 (m, 2H), 7.31–7.26 (m, 4H), 7.24–7.19 (m, 3H), 7.11–7.09 (m, 2H), 5.41 (dd, J_1 = 7.3 Hz, J_2 = 13.8 Hz, 1H), 3.10–3.04 (m, 1H), 2.64–2.57 (m, 1H), 2.38 (s, 3H), 2.31 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 140.4 (d, $J_{C\text{-}P}$ = 7.0 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 27.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.0 (d, $J_{C\text{-}P}$ = 27.7 Hz), 129.1 (d, $J_{C\text{-}P}$ = 13.5 Hz), 129.0, 128.1, 127.8, 127.0, 80.5, 80.3, 36.1 (d, $J_{C\text{-}P}$ = 69.0 Hz), 26.2, 21.5, 21.4. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.74. HRMS calc. for $C_{26}H_{32}O_3P$ $(M+H)^+$: 423.2084, found 423.2076.

(2-(*tert*-butylperoxy)-2-phenylethyl)bis(4-methoxyphenyl) phosphine oxide (3 ee): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 ee** (63% yield, 57.2 mg) as white solid, m. p. = 152–154 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.71 (m, 2H), 7.47–7.43 (m, 2H), 7.30–7.18 (m, 5H), 6.98–6.96 (m, 2H), 6.81–6.79 (m, 2H), 5.39 (dd, J_1 = 7.0 Hz, J_2 = 14.1 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.09–3.03 (m, 1H), 2.62–2.55 (m, 1H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1 (d, $J_{C\text{-}P}$ = 2.6 Hz), 161.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 140.3 (d, $J_{C\text{-}P}$ = 6.6 Hz), 132.7 (d, $J_{C\text{-}P}$ = 10.8 Hz), 132.2 (d, $J_{C\text{-}P}$ = 10.8 Hz), 128.1, 127.9, 127.0, 125.4 (d, $J_{C\text{-}P}$ = 20.6 Hz), 124.5 (d, $J_{C\text{-}P}$ = 20.8 Hz), 113.9 (d, $J_{C\text{-}P}$ = 12.9 Hz), 113.8 (d, $J_{C\text{-}P}$ = 12.8 Hz), 80.5, 80.3, 55.3, 55.2, 36.2 (d, $J_{C\text{-}P}$ = 69.7 Hz), 26.2. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.66. HRMS calc. for $C_{26}H_{32}O_5P$ $(M+H)^+$: 455.1982, found 455.1971.

bis(4-(*tert*-butyl)phenyl)(2-(*tert*-butylperoxy)-2-phenylethyl) phosphine oxide (3 ff): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 ff** (72% yield, 72.8 mg) as white solid, m. p. = 177–178 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.76 (m, 2H), 7.50–7.46 (m, 4H), 7.31–7.26 (m, 4H), 7.21–7.14 (m, 3H), 5.45 (dd, J_1 = 7.2 Hz, J_2 = 13.8 Hz, 1H), 3.10–3.04 (m, 1H), 2.64–2.57 (m, 1H), 1.31 (s, 9H), 1.26 (s, 9H), 0.99 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 154.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 140.4 (d, $J_{C\text{-}P}$ = 6.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.4 Hz), 130.6, 130.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 16.3 Hz), 128.1, 127.8, 127.0, 125.4 (d, $J_{C\text{-}P}$ = 11.9 Hz), 125.2 (d, $J_{C\text{-}P}$ = 11.9 Hz), 80.5, 80.2, 36.3 (d, $J_{C\text{-}P}$ = 69.2 Hz), 34.9, 34.7, 31.0, 30.9, 26.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.11. HRMS calc. for $C_{32}H_{44}O_3P$ $(M+H)^+$: 507.3023, found 507.3017.

(2-(*tert*-butylperoxy)-2-phenylethyl)bis(3,5-dimethylphenyl) phosphine oxide (3 gg): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 gg** (75% yield, 67.5 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, J = 12.0 Hz, 2H), 7.31–7.29 (m, 2H), 7.23–7.17 (m, 3H), 7.13 (m, d, J = 12.4 Hz, 2H), 6.98 (s, 1H), 5.40 (dd, J_1 = 6.8 Hz, J_2 = 14.1 Hz, 1H), 3.11–3.05 (m, 1H), 2.65–2.58 (m, 1H), 2.34 (s, 6H), 2.23 (s, 6H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.3 (d, $J_{C\text{-}P}$ = 6.1 Hz), 138.0 (d, $J_{C\text{-}P}$ = 12.2 Hz), 137.9, 137.8, 133.6 (d, $J_{C\text{-}P}$ = 6.1 Hz), 133.2 (d, $J_{C\text{-}P}$ = 2.8 Hz), 132.9 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 128.3 (d, $J_{C\text{-}P}$ = 9.2 Hz), 128.0, 127.9, 127.0, 80.5, 80.3, 35.8 (d, $J_{C\text{-}P}$ = 68.6 Hz), 26.1, 21.2, 21.1. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.98. HRMS calc. for $C_{28}H_{36}O_3P$ $(M+H)^+$: 451.2397, found 451.2388.

ethyl (2-(*tert*-butylperoxy)-2-phenylethyl) (3,5-dimethylphenyl)phosphinate (3 gg): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3 gg** (53% yield, 38.4 mg) as colorless oil. d.r. = 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78–7.74 (m, 2H), 7.58–7.51 (m, 3H), 7.47–7.41 (m, 3H), 7.36–7.28 (m, 7H), 7.22–7.16 (m, 5H), 5.28 (dd, J_1 = 7.2 Hz, J_2 = 14.4 Hz, 1H), 5.23 (dd, J_1 = 7.6 Hz, J_2 = 13.8 Hz, 1H), 4.03–3.95 (m, 1H), 3.93–3.87 (m, 1H), 3.85–3.77 (m, 1H), 3.75–3.69 (m, 1H), 2.89–2.82 (m, 1H), 2.77–2.70 (m, 1H), 2.44–2.32 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H), 1.19 (s, 9H), 1.12 (t, J = 7.1 Hz, 3H), 1.03 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.1 (d, $J_{C\text{-}P}$ = 7.7 Hz), 139.2 (d, $J_{C\text{-}P}$ = 5.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.5 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.0 Hz), 131.3, 130.6 (d, $J_{C\text{-}P}$ = 70.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3, 128.2, 128.2, 128.1, 128.1, 128.0, 127.3 (d, $J_{C\text{-}P}$ = 11.9 Hz), 80.6 (d, $J_{C\text{-}P}$ = 1.7 Hz), 80.4 (d, $J_{C\text{-}P}$ = 1.6 Hz), 60.5 (d, $J_{C\text{-}P}$ = 5.9 Hz), 60.3 (d, $J_{C\text{-}P}$ = 6.3 Hz), 35.8 (d, $J_{C\text{-}P}$ = 2.3 Hz), 35.0 (d, $J_{C\text{-}P}$ = 1.5 Hz), 26.3, 26.2, 16.3 (d, $J_{C\text{-}P}$ =

6.8 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.6 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 39.77, 39.55. HRMS calc. for $C_{20}H_{28}O_4P$ $(M+H)^+$: 363.1720, found 363.1725.

3-(1-(*tert*-butylperoxy)-2-(diphenylphosphoryl)ethyl)-13-methyl-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[*a*]phenanthren-17(14*H*)-one (3jj): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **3jj** (40% yield, 45.6 mg) as colorless oil. d.r. = 1:1. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.79 (m, 2H), 7.52–7.45 (m, 5H), 7.36–7.33 (m, 1H), 7.29–7.25 (m, 2H), 7.13–7.09 (m, 2H), 6.95 (s, 1H), 5.39 (d, J_1 = 6.5 Hz, J_2 = 13.1 Hz, 1H), 3.23–3.16 (m, 1H), 2.78–2.75 (m, 2H), 2.70–2.62 (m, 1H), 2.53–2.48 (m, 1H), 2.38–2.35 (m, 1H), 2.21–2.11 (m, 2H), 2.09–2.03 (m, 1H), 1.98–1.94 (m, 2H), 1.64–1.60 (m, 1H), 1.54–1.42 (m, 3H), 1.38–1.26 (m, 2H), 1.08 (m, 9H), 0.91 (d, J = 3.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 220.9, 139.5 (d, $J_{C\text{-}P}$ = 1.7 Hz), 136.9 (dd, J_1 = 5.5 Hz, J_2 = 13.3 Hz), 136.1 (d, $J_{C\text{-}P}$ = 1.7 Hz), 133.9 (dd, J_1 = 3.6 Hz, J_2 = 27.6 Hz), 133.1 (dd, J_1 = 3.5 Hz, J_2 = 27.3 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 2.4 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.4 (dd, J_1 = 2.2 Hz, J_2 = 9.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 127.8 (d, $J_{C\text{-}P}$ = 21.9 Hz), 125.3, 124.5 (d, $J_{C\text{-}P}$ = 13.5 Hz), 80.7, 80.3 (d, $J_{C\text{-}P}$ = 14.3 Hz), 50.4 (d, $J_{C\text{-}P}$ = 1.5 Hz), 47.9, 44.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 37.9 (d, $J_{C\text{-}P}$ = 3.6 Hz), 35.8, 35.7 (dd, J_1 = 8.5 Hz, J_2 = 69.2 Hz), 31.5, 29.2 (d, $J_{C\text{-}P}$ = 6.1 Hz), 26.4, 26.2, 25.5 (d, $J_{C\text{-}P}$ = 1.5 Hz), 21.5, 13.8. ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.69, 27.63. HRMS calc. for $C_{36}H_{44}O_4P$ $(M+H)^+$: 571.2972, found 571.2966.

2-(diphenylphosphoryl)-1-phenylethanone (4a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **4a** (92% yield, 58.9 mg) as white solid, m. p. = 138–140 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.96 (m, 2H), 7.82–7.78 (m, 4H), 7.53–7.49 (m, 3H), 7.46–7.38 (m, 6H), 4.16 (d, J = 15.4 Hz, 2H), 2.80–2.73 (m, 1H), 2.61–2.56 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.7 (d, $J_{C\text{-}P}$ = 5.8 Hz), 136.8, 133.5, 132.1 (d, $J_{C\text{-}P}$ = 2.3 Hz), 131.3, 131.0 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.1, 128.6, 128.4 (d, $J_{C\text{-}P}$ = 7.8 Hz), 43.0 (d, $J_{C\text{-}P}$ = 57.8 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 27.46. HRMS calc. for $C_{20}H_18O_2P$ $(M+H)^+$: 321.1039, found 321.1031.

(2-hydroxy-2-phenylethyl)diphenylphosphine oxide (5a): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 1:1 as an eluent) to afford the product **5a** (85% yield, 54.7 mg) as white solid, m. p. = 139–141 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.77 (m, 2H), 7.71–7.67 (m, 2H), 7.58–7.49 (m, 4H), 7.45–7.42 (m, 2H), 7.34–7.20 (m, 5H), 5.18–5.14 (m, 1H), 5.08 (s, 1H), 2.80–2.73 (m, 1H), 2.61–2.56 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.8 (d, $J_{C\text{-}P}$ = 13.4 Hz), 133.0 (d, $J_{C\text{-}P}$ = 99.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.2, 130.9 (d, $J_{C\text{-}P}$ = 9.3 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.9 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.4, 127.5, 125.4, 69.1 (d, $J_{C\text{-}P}$ = 4.3 Hz), 39.1 (d, $J_{C\text{-}P}$ = 68.0 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 33.75. HRMS calc. for $C_{20}H_{20}O_2P$ $(M+H)^+$: 323.1195, found 323.1197.

(3-methyl-3-phenyloxiran-2-yl)diphenylphosphine oxide (6x): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **6x** (Isomer 1) (70% yield, 46.8 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86–7.77 (m, 4H), 7.60–7.49 (m, 6H), 7.38–7.26 (m, 5H), 3.33 (d, J = 33.4 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.4, 132.4 (d, $J_{C\text{-}P}$ = 2.6 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 40.1 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.3, 130.9 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.9 Hz), 128.5, 127.9, 124.9, 63.7 (d, $J_{C\text{-}P}$ = 1.8 Hz), 62.5 (d, $J_{C\text{-}P}$ = 95.6 Hz), 18.3. ^{31}P NMR (203 MHz, $CDCl_3$): δ 22.73. HRMS calc. for $C_{21}H_{20}O_2P$ $(M+H)^+$: 335.1195, found 335.1199.

(3,3-diphenyloxiran-2-yl)diphenylphosphine oxide (6y): The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2:1 as an eluent) to afford the product **6y** (68% yield, 53.9 mg) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08–8.03 (m, 2H), 7.72–7.63 (m, 3H), 7.56–7.49 (m, 4H), 7.46–7.39 (m, 6H), 7.29–7.17 (m, 5H), 4.17 (d, J = 25.6 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 134.2, 133.4 (d, $J_{C\text{-}P}$ = 101.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.1 Hz), 129.0, 128.7 (d, $J_{C\text{-}P}$ = 11.6 Hz), 128.4, 128.2, 127.8, 127.7, 127.6, 127.5, 126.3, 67.3 (d, $J_{C\text{-}P}$ = 1.5 Hz), 63.1 (d, $J_{C\text{-}P}$ = 98.7 Hz). ^{31}P NMR (203 MHz, $CDCl_3$): δ 23.38. HRMS calc. for $C_{26}H_{22}O_2P$ $(M+H)^+$: 397.1352, found 397.1358.

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References

[1] a) H. W. He, *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 266–279; b) G. La Regina, A. Coluccia, R. Silvestri, *Antiviral Chem. Chemother.* **2010**, *20*, 213–237; c) W. Feng, X. Y. Teo, W. N. P. Ramanujulu, M. D. Liang, D. Huang, P. K. Moore, L. W. Deng, B. W. Dymock, *J. Med. Chem.* **2015**, *58*, 6456–6480.

[2] a) L. Mater, *Phosphorus Sulfur Relat. Elem.* **1983**, *14*, 295–322; b) W. J. Tang, X. M. Zhang, *Chem. Rev.* **2003**, *103*, 3029–3069; c) J. H. Xie, Q. L. Zhou, *Acc. Chem. Res.* **2008**, *41*, 581–593; d) M. M. Pereira, M. J. Calvete, R. M. Carrilho, A. R. Abreu, *Chem. Soc. Rev.* **2013**, *42*, 6990–7027.

[3] a) S. Monge, G. David, *Phosphorus-Based Polymers from Synthesis to Applications*; The Royal Society of Chemistry: Cambridge; **2014**; b) R. S. Ullah, L. Wang, H. Yu, N. M. Abbasi, M. Akram, M. Saleem, M. Haroon, R. U. Khan, *RSC Adv.* **2017**, *7*, 23363–23391.

[4] a) T. Baumgartner, R. Reau, *Chem. Rev.* **2006**, *106*, 4681–4727; b) M. N. Birkholz, Z. Freixa, P. W. N. M. van Leeuwen, *Chem. Soc. Rev.* **2009**, *38*, 1099–1118; c) L. Kollar, G. Keglevich, *Chem. Rev.* **2010**, *110*, 4257–4302; d) C. S. Demmer, N. Krogsgaard Larsen, L. Bunch, *Chem. Rev.* **2011**, *111*, 7981–8006; e) C. Queffelec, M. Petit, P. Janvier, D. A. Knight, B. Bujoli, *Chem.*

Rev. **2012**, *112*, 3777–3807; f) L. Duan, H. Yang, Y. Shi, Y. Hou, Y. Zhu, Z. Gui, Y. Hu, *Ind. Eng. Chem. Res.* **2016**, *55*, 10218–10225; g) L. Lu, X. Qian, Z. Zeng, S. Yang, G. Shao, H. Wang, J. Jin, X. Xu, *J. Appl. Polym. Sci.* **2017**, *134*, 45105–45113.

[5] Selected reviews on P-radical involved reactions: a) D. Leca, L. Fensterbank, E. Lacote, M. Malacria, *Chem. Soc. Rev.* **2005**, *34*, 858–865; b) I. Wauters, W. Debrouwer, C. V. Stevens, *Beilstein J. Org. Chem.* **2014**, *10*, 1064–1096; c) X. L. Chen, X. Li, L. B. Qu, Y. C. Tang, W. P. Mai, D. H. Wei, W. Z. Bi, L. K. Duan, K. Sun, J. Y. Chen, D. D. Ke, Y. F. Zhao, *J. Org. Chem.* **2014**, *79*, 8407–8416; d) S. Furukawa, S. Haga, J. Kobayashi, T. Kawashima, *Org. Lett.* **2014**, *16*, 3228–3231; e) V. Rodriguez-Ruiz, R. Carlino, S. Bezzenine-Lafollée, R. Gil, D. Prim, E. Schulz, J. Hannedouche, *Dalton Trans.* **2015**, *44*, 12029–12059; f) X. Q. Pan, J. P. Zou, W. B. Yi, W. Zhang, *Tetrahedron* **2015**, *71*, 7481–7529; g) M. Gao, Y. Li, L. Xie, R. Chauvin, X. Cui, *Chem. Commun.* **2016**, *52*, 2846–2849; h) H. Yi, D. Yang, Y. Luo, C. W. Pao, J. F. Lee, A. Lei, *Organometallics* **2016**, *35*, 1426–1429; i) V. Quint, L. Noël Duchesneau, E. Lagadic, F. Morlet-Savary, J. Lalevée, A. C. Gaumont, S. Lakhdar, *Synthesis* **2017**, *49*, 3444–3452; j) T. Taniguchi, *Synthesis* **2017**, *49*, 3511–3534; k) G. C. Fang, X. F. Cong, G. Zanoni, Q. Liu, X. H. Bi, *Adv. Synth. Catal.* **2017**, *359*, 1422–1502; l) Y. Z. Gao, G. Tang, Y. F. Zhao, *Phosphorus Sulfur Silicon Relat. Elem.* **2017**, *192*, 589–596; m) Y. Z. Gao, G. Tang, Y. F. Zhao, *Chin. J. Org. Chem.* **2018**, *38*, 62–74; n) D. Chen, Z. Wu, Y. Yao, C. Zhu, *Org. Chem. Front.* **2018**, *5*, 2370–2374.

[6] Selected papers on Mn-involved difunctionalizations: a) Y. Gao, J. Wu, J. Xu, P. Zhang, G. Tang, Y. Zhao, *RSC Adv.* **2014**, *4*, 51776–51779; b) S. F. Zhou, D. P. Li, K. Liu, J. P. Zou, O. T. Asekun, *J. Org. Chem.* **2015**, *80*, 1214–1220; c) V. Richard, H. C. Fisher, J. L. Montchamp, *Tetrahedron Lett.* **2015**, *56*, 3197–3199; d) Y. Gao, X. Li, J. Xu, Y. Wu, W. Chen, G. Tang, Y. Zhao, *Chem. Commun.* **2015**, *51*, 1605–1607; e) J. Xu, X. Li, Y. Gao, L. Zhang, W. Chen, H. Fang, G. Tang, Y. Zhao, *Chem. Commun.* **2015**, *51*, 11240–11243; f) G. Y. Zhang, C. K. Li, D. P. Li, R. S. Zeng, A. Shoberu, J. P. Zou, *Tetrahedron* **2016**, *72*, 2972–2978; g) P. Z. Zhang, L. Zhang, J. A. Li, A. Shoberu, J. P. Zou, W. Zhang, *Org. Lett.* **2017**, *19*, 5537–5540.

[7] Selected papers on Ag-involved difunctionalizations: a) Y. M. Li, M. Sun, H. L. Wang, Q. P. Tian, S. D. Yang, *Angew. Chem. Int. Ed.* **2013**, *52*, 3972–3976; *Angew. Chem.* **2013**, *125*, 4064–4068; b) C. W. Zhang, Z. D. Li, L. Zhu, L. M. Yu, Z. T. Wang, C. Z. Li, *J. Am. Chem. Soc.* **2013**, *135*, 14082–14085; c) W. Kong, E. Merino, C. Nevado, *Angew. Chem. Int. Ed.* **2014**, *53*, 5078–5082; *Angew. Chem.* **2014**, *126*, 5178–5182; d) X. Mi, C. Y. Wang, M. M. Huang, Y. S. Wu, Y. J. Wu, *Org. Biomol. Chem.* **2014**, *12*, 8394–8397; e) J. Zhao, P. Li, X. Li, C. Xia, F. Li, *Chem. Commun.* **2016**, *52*, 3661–3664; f) H. Zhang, Z. Gu, Z. Li, C. Pan, W. Li, H. Hu, C. Zhu, *J. Org. Chem.* **2016**, *81*, 2122–2127; g) J. Zheng, Y. Zhang, D. Wang, S. Cui, *Org. Lett.* **2016**, *18*, 1768–1771.

[8] Selected papers on Cu-involved difunctionalizations: a) W. Wei, J. X. Ji, *Angew. Chem. Int. Ed.* **2011**, *50*, 9097–9099; *Angew. Chem.* **2011**, *123*, 9263–9265; b) V. Gutierrez, E. Mascaró, F. Alonso, Y. Moglie, G. Radivoy, *RSC Adv.* **2015**, *5*, 65739–65744; c) H. Y. Zhang, L. L. Mao, B. Yang, S. D. Yang, *Chem. Commun.* **2015**, *51*, 4101–4104; d) J. A. Li, P. Z. Zhang, K. Liu, A. Shoberu, J. P. Zou, W. Zhang, *Org. Lett.* **2017**, *19*, 4704–4706; e) D. Yi, Q. Fu, S. Y. Chen, M. Gao, L. Yang, Z. J. Zhang, W. Liang, Q. Zhang, J. X. Ji, W. Wei, *Tetrahedron Lett.* **2017**, *58*, 2058–2061; f) Z. K. Tao, C. K. Li, P. Z. Zhang, A. Shoberu, J. P. Zou, W. Zhang, *J. Org. Chem.* **2018**, *83*, 2418–2424; g) Y. Chen, Y. Chen, S. Lu, Z. Li, *Org. Chem. Front.* **2018**, *5*, 972–976.

[9] B. Yang, S. M. Hou, S. Y. Ding, X. N. Zhao, Y. Gao, X. Wang, S. D. Yang, *Adv. Synth. Catal.* **2018**, *360*, 4470–4474.

[10] a) A.-M. Rydén, O. Kayser, Chemistry, Biosynthesis and Biological Activity of Artemisinin and Related Natural Peroxides. In *Bioactive Heterocycles III*; M. T. H., Ed. Khan, Springer: Berlin, Heidelberg, **2007**; pp 1–31; b) H. Yin, L. Xu, N. A. Porter, *Chem. Rev.* **2011**, *111*, 5944–5972; c) G. H. Posner, P. M. O′Neill, *Acc. Chem. Res.* **2004**, *37*, 397–404; d) V. M. Dembitsky, *Eur. J. Med. Chem.* **2008**, *43*, 223–251.

[11] a) Z. Rappoport, *The Chemistry of Peroxides*; Wiley, Chichester, U. K., **2006**; Vol. 2; b) W. Adam, *Peroxide Chemistry*, Wiley-VCH, Weinheim, Germany, **2000**; c) A. Russo, A. Lattanzi, *Adv. Synth. Catal.* **2008**, *350*, 1991–1995; d) L. Lv, B. Shen, Z. Li, *Angew. Chem. Int. Ed.* **2014**, *53*, 4164–4167; *Angew. Chem.* **2014**, *126*, 4248–4251; e) J. Li, D. Z. Wang, *Org. Lett.* **2015**, *17*, 5260–5263; f) W. T. Wei, X. H. Yang, H. B. Li, J. H. Li, *Adv. Synth. Catal.* **2015**, *357*, 59–63; g) J. Dhineshkumar, P. Samaddar, K. R. Prabhu, *Chem. Commun.* **2016**, *52*, 11084–11087.

[12] W. Liu, Y. Li, K. Liu, Z. Li, *J. Am. Chem. Soc.* **2011**, *133*, 10756–10759.

[13] A recent review: H. Gandhi, K. O'Reilly, M. K. Gupta, C. Horgan, E. M. O'Leary, T. P. O'Sullivan, *RSC Adv.* **2017**, *7*, 19506–19556.

[14] Recent papers: a) B. Schweitzer-Chaput, J. Demaerel, H. Engler, M. Klussmann, *Angew. Chem. Int. Ed.* **2014**, *53*, 8737–8740; *Angew. Chem.* **2014**, *126*, 8882–8885; b) L. Hu, X. Lu, L. Deng, *J. Am. Chem. Soc.* **2015**, *137*, 8400–8403; c) J. K. Cheng, T. P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 42–45; d) E. Shi, J. Liu, C. Liu, Y. Shao, H. Wang, Y. Lv, M. Ji, X. Bao, X. Wan, *J. Org. Chem.* **2016**, *81*, 5878–5885; e) L. Zhao, Y. Wang, Z. Ma, Y. Wang, *Inorg. Chem.* **2017**, *56*, 8166–8174; f) J. K. Cheng, L. Shen, L. H. Wu, X. H. Hu, T. P. Loh, *Chem. Commun.* **2017**, *53*, 12830–12833; g) S. Lu, L. Qi, Z. Li, *Asian J. Org. Chem.* **2017**, *6*, 313–321; h) H. Y. Zhang, C. Ge, J. Zhao, Y. Zhang, *Org. Lett.*, **2017**, *19*, 5260–5263; i) H. Wang, C. Chen, W. Liu, Z. Zhu, *Beilstein J. Org. Chem.* **2017**, *13*, 2023–2027; j) Y. Lan, X. H. Chang, P. Fan, C. C.

Shan, Z. B. Liu, T. P. Loh, Y. H. Xu, *ACS Catal.* **2017**, *7*, 7120–7125; k) Y. Yao, Z. Wang, B. Wang, *Org. Chem. Front.* **2018**, *5*, 2501–2504; l) C. Chen, H. Tan, B. Liu, C. Yue, W. Liu, *Org. Chem. Front.* **2018**, *5*, 3143–3147; m) X. Gao, H. Yang, C. Cheng, Q. Jia, F. Gao, H. Chen, Q. Cai, C. Wang, *Green Chem.* **2018**, *20*, 2225–2230; n) Y. Chen, Y. Ma, L. Li, H. Jiang, Z. Li, *Org. Lett.* **2019**, *21*, 1480–1483; o) C. S. Wu, R. Li, Q. Q. Wang, L. Yang, *Green Chem.* **2019**, *21*, 269–274.

[15] a) B. Yang, T. T. Yang, X. A. Li, J. J. Wang, S. D. Yang, *Org. Lett.* **2013**, *15*, 5024–5027; b) B. Yang, Q. P. Tian, S. D. Yang, *Chin. J. Org. Chem.* **2014**, *34*, 717–721; c) B. Yang, H. Y. Zhang, S. D. Yang, *Org. Biomol. Chem.* **2015**, *13*, 3561–3565; d) J. Shen, R. X. Yu. Y. Luo, L. X. Zhu, Y. Zhang, X. Wang, B. Xiao, J. B. Cheng, B. Yang, G. Z. Li, *Eur. J. Org. Chem.* **2019**, 2065–2070.

[16] C. M. Jessop, A. F. Parsons, A. Routledge, D. J. Irvine, *Eur. J. Org. Chem.* **2006**, 1547–1554.

[17] a) B. Iorga, F. Eymery, P. Savignac, *Synthesis* **1999**, *2*, 207–224; b) Y. Kobayashi, A. D. William, Y. Tokoro, *J. Org. Chem.* **2001**, *66*, 7903–7906; c) K. Hara, S. Y. Park, N. Yamagiwa, S. Matsunaga, M. Shibasaki, *Chem. Asian J.* **2008**, *3*, 1500–1504; d) D. R. Boyd, N. D. Sharma, M. Kaik, M. Bell, M. V. Berberian, P. B. A. M. Intyre, B. Kelly, C. Hardacre, P. J. Stevenson, C. C. R. Allen, *Adv. Synth. Catal.* **2011**, *353*, 2455–2465.

[18] D. Leifert, A. Studer, *Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201903726.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, revision C.01; Gaussian, Inc.: Wallingford, CT.

[20] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215–241.

[21] a) S. Miertus, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117–129; b) J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999–3094.

FULL PAPER

Cobalt(II)-Catalyzed Bisfunctionalization of Alkenes with Diarylphosphine Oxide and Peroxide

Adv. Synth. Catal. **2019**, *361*, 1 – 13

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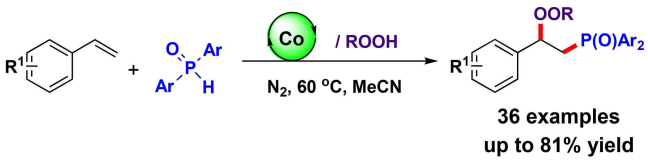

- *first example of cobalt catalysis*
- *broad substrate scope*
- *atom-economic synthesis*
- *mild reaction conditions*