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Substituent-Controlled Chemoselective Cleavage of C=C or C_{sp^2}–C(CO) Bond in α,β-Unsaturated Carbonyl Compounds with H-Phosphonates Leading to β-Ketophosphonates

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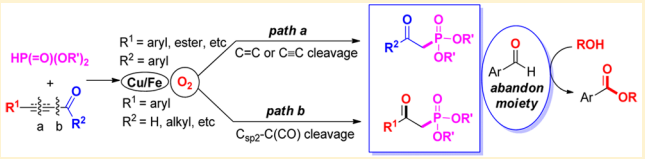
Supporting Information

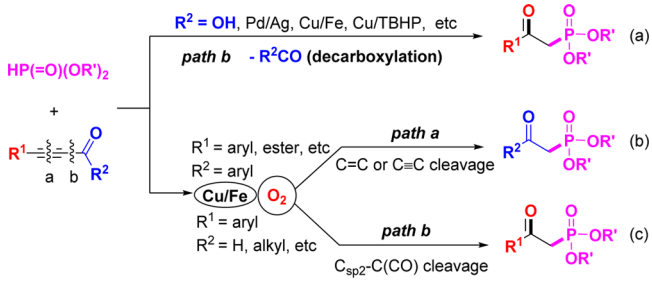
ABSTRACT: An unprecedented substituent-controlled chemoselective cleavage of C=C double bond or C(sp^2)–C(CO) bond along with aerobic phosphorylation of α,β-unsaturated carbonyl compounds with H-phosphonates through a radical process has been disclosed. The current strategy provides an access to β-ketophosphonates under mild conditions with a wide substrate scope.



INTRODUCTION

Transition-metal-catalyzed selective cleavage of carbon–carbon bond is a formidable challenging subject in the art of organic synthesis owing to the ubiquity of carbon–carbon bonds in organic molecules, and it has attracted great attentions in recent years.[1] Many noble transition metals have been employed in carbon–carbon cleavage reactions.[2] In recent times, great effort has been devoted to the development of new catalytic systems based on less expensive, nontoxic, earth-abundant, environmentally benign, and user-friendly metals, such as Cu and Fe. Therefore, many methods have been developed with Cu/Fe cocatalytic systems in the past decade due to their superior combined bimetallic catalytic reactivities.[3] Among carbon–carbon cleavage reactions, chemoselective cleavage of one carbon–carbon bond over the others is one of the most appealing yet highly challenging themes in target-oriented reconstruction of organic molecules.[4] In most of cases, the chemoselective cleavage of C–C bonds was realized by utilizing different ligands[5] or even by changing transition-metal species.[2] α,β-Unsaturated compounds are very important building blocks in organic synthesis. There are two types of functional moieties existing in them: carbon–carbon unsaturated bonds (C=C or C≡C bonds) and carbonyl groups. As a special C–C cleavage reaction, decarboxylations (cleavage of C(sp^2)–C(CO) bond) of α,β-unsaturated acids have been widely explored.[6] Very recently, several elegant methods converting cinnamic or acetylenic acids into β-ketophosphonates or β-ketophosphine oxides via carbon–carbon bond cleavage (decarboxylation) have been reported (Scheme 1a).[6a−d] In 2014, Liu and his coworkers reported copper-catalyzed oxidative cyclization of 1,5-enynes through C(sp^2)–C(CO) bond cleavage.[7] To our knowledge, cleavage of carbon–carbon unsaturated bonds instead of C–C(CO) single bonds in α,β-unsaturated compounds has yet to be reported, especially the chemoselective cleavage of carbon–carbon unsaturated bonds or C(sp^2)–C(CO) single bonds of α,β-unsaturated compounds could be realized by changing substituents, which is in sharp contrast to conventional strategies by utilizing different ligands or by changing transition metals catalysts. As our ongoing interest in carbon–carbon activation chemistry,[8] we report herein an unprecendent Cu/Fe cocatalyzed substituent-controlled chemoselective cleavage of carbon–carbon unsaturated bond or C(sp^2)–C(CO) single bond of α,β-unsaturated carbonyl compounds with H-phosphonate under mild condition (Scheme 1b,c) .

Scheme 1. Transition-Metal-Catalyzed Carbon–Carbon Bond Cleavage Leading to β-Ketophosphonates



RESULTS AND DISCUSSION

We commenced our study with chalcone (**1a**) and H-diethyl phosphonate (**2a**) as model substrates, using 5 mol % $Cu(acac)_2$ together with 10 mol % $FeCl_3$ at 90 °C under O_2 atmosphere. To our delight, the desired product β-ketophosphonate was formed in 49% yield in the presence of Et_3N in DMSO within 24 h (Table 1, entries 1). Subsequently, when we replaced the catalyst with other copper salts, $Cu(OTf)_2$ or $Cu(OAc)_2$ gave lower yields of 41% or 48%, respectively (Table

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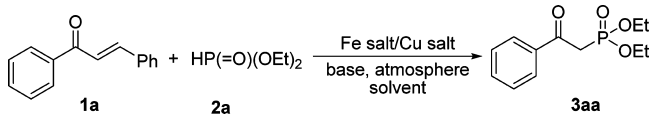
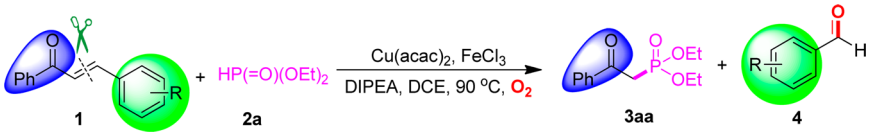
Table 1. Optimization of the Reaction Parameters[a]

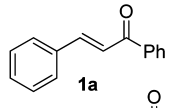
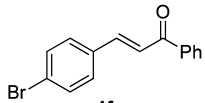
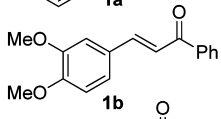
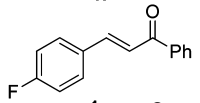
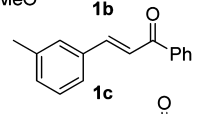
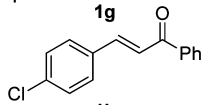
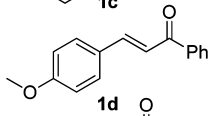
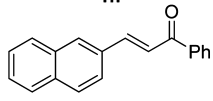
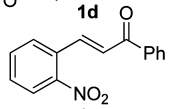


entry	Fe (10 mol %)	Cu (5 mol %)	base (1 equiv)	temp (°C)	solvent	yield[b] (%)
1	$FeCl_3$	$Cu(acac)_2$	Et_3N	90	DMSO	49
2	$FeCl_3$	$Cu(OTf)_2$	Et_3N	90	DMSO	41
3	$FeCl_3$	$Cu(OAc)_2$	Et_3N	90	DMSO	48
4	$FeSO_4{\cdot}7H_2O$	$Cu(acac)_2$	Et_3N	90	DMSO	N.D.
5	$FeCl_2$	$Cu(acac)_2$	Et_3N	90	DMSO	40
6	$Fe(acac)_2$	$Cu(acac)_2$	Et_3N	90	DMSO	trace
7	$Fe_2(SO_4)_3$	$Cu(acac)_2$	Et_3N	90	DMSO	N.D.
8	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DMSO	55
9	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DMF	48
10	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	CH_3CN	66
11	**$FeCl_3$**	**$Cu(acac)_2$**	**DIPEA**	**90**	**DCE**	**(70)**[g]
12	$FeCl_3$	$Cu(acac)_2$	DIPEA	80	DCE	63[g]
13	$FeCl_3$	$Cu(acac)_2$	DIPEA	100	DCE	60
14[c]	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DCE	53
15[d]	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DCE	55
16[e]	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DCE	52
17[f]	$FeCl_3$	$Cu(acac)_2$	DIPEA	90	DCE	N.D
18	–	$Cu(acac)_2$	DIPEA	90	DCE	N.D.
19	$FeCl_3$	–	DIPEA	90	DCE	N.D.
20	$FeCl_3$	$Cu(acac)_2$	–	90	DCE	N.D.

[a]Reaction conditions: chalcone (**1**) (0.5 mmol), H-diethyl phosphonate (**2**) (2.5 equiv), Cu salt (5 mol %), and Fe salt (10 mol %) in solvent (0.5 M), base (1 equiv), O_2 atmosphere, 24 h. [b]GC yield. [c]With 5 mol % $FeCl_3$ [d]With 2 equiv of **2a**. [e]Under air. [f]Under N_2. [g]Isolated yield in parentheses.

Table 2. Substrate Scopes of Various Chalcones by Changing the Substituents on the Aromatic Ring Adjacent to C═C Double Bond[a]



Entry	Substrate **1**	yield of **3aa**	Entry	Substrate **1**	yield of **3aa**
1	 **1a**	70%	6	 **1f**	67%
2	 **1b**	65%[b]	7	 **1g**	77%
3	 **1c**	64%	8	 **1h**	68%
4	 **1d**	69%	9	 **1i**	65%
5	 **1e**	35%			

[a]Reaction conditions: **1** (0.5 mmol), H-diethyl phosphonate **2a** (2.5 equiv), $Cu(acac)_2$ (5 mol %), $FeCl_3$ (10 mol %) and DIPEA (0.5 mmol) in DCE (1 mL), O_2 atmosphere, 90 °C, 24 h. [b]With 28 h.

1, entries 2−3). Among various iron salts tested, $FeCl_3$ showed the optimal efficiency (entries 4−7). When the base was changed from Et_3N to DIPEA, the yield of product was increased to 55%. Solvent was also important for this transformation (entries 8−11): When the reaction was performed in DCE, the yield was increased to 70%. The model reaction failed to give better results even with increasing or decreasing the temperature (entries 12−13). Moreover,

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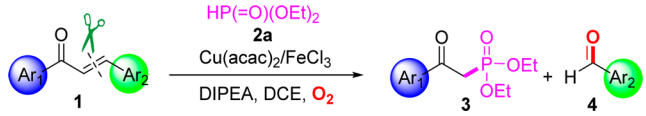
reducing the amount of $FeCl_3$ or H-diethyl phosphonate (**2a**), the yield of product was significantly decreased correspondingly. Ultimately, the use of 5 mol % $Cu(acac)_2$ together with 10 mol % $FeCl_3$ and 2.5 equiv of H-phosphonate in DCE at 90 °C was identified as the optimal reaction protocol (Table 1, entry 11). Control experiments suggested that molecular dioxygen, base, $Cu(acac)_2$, and $FeCl_3$ were all indispensable to this reaction (Table 1, entries 16−20).

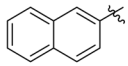
Since there are two possibilities to lead to the desired products by either cleavage of C(CO)−C(sp^2) bond or scission of C═C bond in chalcones, several reactions were conducted under the optimized conditions in order to figure out which way was involved in the transformation. As shown in Table 2, when the substituents on the aromatic ring adjacent to C═C bond on chalcones changed, the same product **3aa** was obtained, which clearly demonstrated that C═C double bonds were scissored in chalcones in this process with the carbonyl part incorporated into the final products, which was in sharp contrast to our previous report[6b,c] and Liu's work[7] where C(CO)−C(sp^2) single bonds were cleaved in *α,β*-unsaturated compounds. To our delight, both electron-donating (**1b**-**1d**) and electron-withdrawing (**1e**) substituented chalcones were both well tolerated in this transformation, affording the desired product **3aa** in moderate to good yields. (*E*)-3-(2-nitrophenyl)-1-phenylprop-2-en-1-one (**1e**) decreased the yield of **3aa**, presumably due to steric hindrance of *ortho*-substitution. Halo-substituted, such as fluoro (**1g**), chloro (**1h**), and bromo (**1f**) chalcones were also compatible substrates, and the product **3aa** was obtained in 77%, 68%, and 67%, respectively. Polyphenylene chalcone, for instance, (*E*)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (**1i**), was also a good candidate for this transformation and gave *β*-ketophosphonate **3aa** in 65% yield.

Subsequently, the substrate scopes of chalcones by changing the aromatic ring adjacent to carbonyl were also studied to obtain diversified *β*-ketophosphonates, as summarized in Table 3. To our satisfaction, versatile *β*-ketophosphonates were obtained in moderate to excellent yields. Once again, the results suggested that cleavage of C═C bond in chalcones occurred in this transformation since the substituent groups of the products were in accordance with the kinds on the aromatic ring adjacent to carbonyl groups of chalcones and corresponding benzaldehydes were detected by GC-MS as well. Although benzaldehydes could generate in this transformation, no phosphoaldol product was detected in this reaction.

To evaluate the generality of this aerobic oxyphosphorylation reaction, other varieties of *α,β*-unsaturated carbonyl systems were further employed under the standard conditions as well (Table 4). In addition to chalcones, alkynones (**5a**−**5c**) were also good substrates for this transformation. In this case, carbonyl parts were once again incorporated into the desired product by cleavage of C≡C bond in the above cases. Compound **5d** was to some extent inert in this transformation partially due to the inferior free radical stabilization capacity of ester to aryl groups. Gratifyingly, multiconjugated *α,β*-unsaturated carbonyl compounds such as **5e**, **5f** and **5g** were compatible for this transformation and lead to the desired product **3ae** in moderate to excellent yields. Yet in **5g**, the cleavage of C(sp^2)−C(CO) bond occurred instead of a C═C bond as previous cases demonstrated. Intriguingly while surprisingly, *α,β*-unsaturated ketones (**5h** and **5i**) and cinnamaldehyde (**5j**) demonstrated to be suitable candidates in this reaction as well to render product **3aa.** Obviously, in these cases (**5h**−**5j**) the C═C or C≡C bond part was

Table 3. Substrate Scopes of Various Chalcones Changing the Aromatic Ring Adjacent to Carbonyl Groups[a]



entry	Ar_1	Ar_2	product	yield
1	4-$MeOC_6H_4$	Ph	**3ba**	63%
2	4-FC_6H_4	Ph	**3ca**	67%
3	4-ClC_6H_4	Ph	**3da**	61%
4	4-MeC_6H_4	Ph	**3ea**	70%
5		Ph	**3fa**	60%
6		Ph	**3ga**	56%
7	4-MeC_6H_4		**3ea**	68%
8	4-MeC_6H_4	4-FC_6H_4	**3ea**	81%
9	4-$MeOC_6H_4$	4-$MeOC_6H_4$	**3ba**	73%
10	4-FC_6H_4	4-FC_6H_4	**3ca**	58%

[a]Reaction conditions: **1** (0.5 mmol), **2** (1.25 mmol), $Cu(acac)_2$ (5 mol %), $FeCl_3$ (10 mol %), DIPEA (0.5 mmol), DCE (1 mL) in a sealed tube under O_2 atmosphere at 90 °C for 24 h.

incorporated into the final product by cleavage of C(sp^2)−C(CO) bond, which once again in sharp constrast to chalcone cases. Additionally, phenylallylic alcohol (**5k**) was also suitable for this reaction albeit with a low yield of **3ae** (35% yield), most likely the alcohol was oxidized into either aldehyde or carboxylic acid first, thus making the further transformation feasible. Therefore, this reaction reveals a clear substituent-controlled C−C bond cleavage protocol: If the *α,β*-unsaturated systems are chalcones, the C═C bonds are cleaved with the carbonyl part incorporated into the final products; if the *α,β*-unsaturated systems are aromatic conjugated ketones or aldehydes, the C(sp^2)−C(CO) bonds are cleaved with the C═C part or C≡C incorporated into the desired products.

In regard to the H-phosphonates, various H-phosphonates were also investigated to test the compatibility of this transformation. As shown in Table 5, the reaction was amenable to different H-phosphonates. Phosphonates **2b**, **2c**, **2f**, and **2g** were all suitable donors in this oxidative transformation in addition to diethyl phosphonate (**2a**), generating corresponding *β*-ketophosphonates **3ab**, **3ac**, **3af**, and **3ag** in moderate to good yields. However, diphenylphosphine oxide (**2d**) and ethyl phenylphosphinate (**2e**) produced the desired product **3ad** and **3ae** in only 36% and 57%, respectively, which might demonstrate that phosphonates were more suitable donors than phosphine oxide or phosphinate in this transformation.

Since 1 equiv of aldehydes was eliminated as byproduct, we wondered whether the byproducts could be converted into useful compounds by addition of other nucleophiles. To verify our hypothesis, alcohols were selected as the nucleophiles. To our delight, alcohols did capture the abandoned moiety of chalcones and various benzoates were obtained as one of products as shown in Table 6, albeit the yields of benzoates were relatively low. Interestingly, the yields of *β*-ketophosph-

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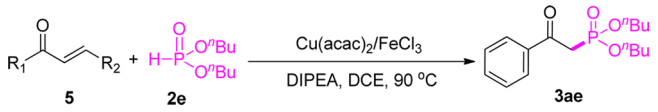
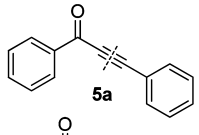
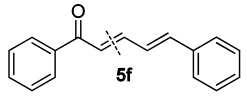
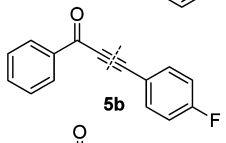
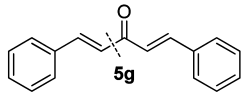
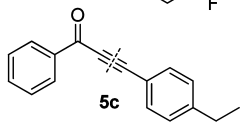
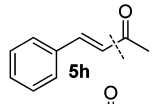
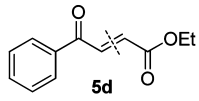
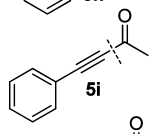
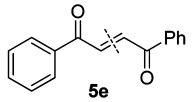
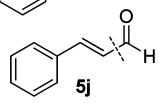
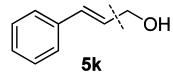
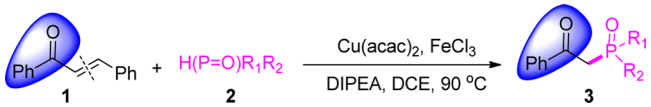
Table 4. α,β-Unsaturated Compound Scope[a]

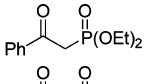
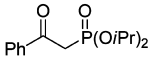
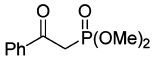
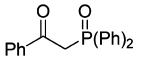
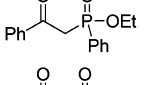
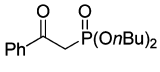
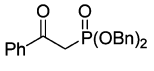


Entry	Substrate **5**	**3ae**	Entry	Substrate **5**	**3ae**
1	 **5a**	64%	6	 **5f**	47%[b]
2	 **5b**	67%	7	 **5g**	85%[b]
3	 **5c**	65%	8	 **5h**	62%
4	 **5d**	36%	9	 **5i**	53%[c]
5	 **5e**	43%[b]	10	 **5j**	67%
			11	 **5k**	35%

[a]Reaction conditions: **5** (0.5 mmol), **2e** (1.3 mmol), $Cu(acac)_2$ (5 mol %), $FeCl_3$ (10 mol %), DIPEA (0.5 mmol), DCE (1 mL) in a sealed tube under O_2 atmosphere at 90 °C for 24 h. [b]**2e** (1.5 mmol) [c]Reaction was performed in 0.3 mmol of **5** with 3 equiv of **2**.

Table 5. H-Phosphonates Scope[a]

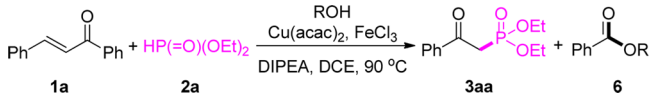


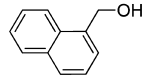
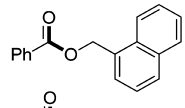
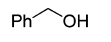
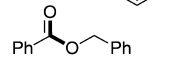
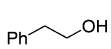
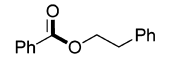
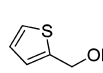
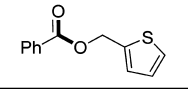
Entry	**2**	Product	**3**	Yield
1	 **2a**		**3aa**	70%
2	 **2b**		**3ab**	68%
3	 **2c**		**3ac**	72%[b]
4	 **2d**		**3ad**	36%
5	 **2e**		**3ae**	57%
6	 **2f**		**3af**	74%
7	 **2g**		**3ag**	54%

[a]Reaction conditions: **1** (0.5 mmol), **2** (2.5 equiv), $Cu(acac)_2$ (5 mol %), $FeCl_3$ (10 mol %) and DIPEA (0.5 mmol) in DCE (0.5 M), O_2 atmosphere, 90 °C, 24 h. [b]3 equiv of **2**, 28 h.

onates were significantly increased by the addition of alcohols, suggesting that extra nucleophiles could markedly promote the chemoselective cleavage of chalcones in this aerobic phosphorylation reaction.

Table 6. Utilization Two Moieties of Chalcones[a]



Entry	substrate of alcohol	yield of **3aa**	producut and yield of **6**
1		78%	 **6a** (30%)
2		85%	 **6b** (41%)
3		82%	 **6c** (37%)
4		86%	 **6d** (43%)

[a]Reaction conditions: ROH (2 equiv), **1a** (0.5 mmol), **2a** (2.5 equiv), $Cu(acac)_2$ (5 mol %), $FeCl_3$ (10 mol %), DIPEA (0.5 mmol), DCE (1 mL) in a sealed tube under O_2 at 90 °C for 24 h.

Not surprisingly, two kinds of benzyl benzoates were obtained when adscititious alcohols reacted with the unsymmetric chalcones under standard conditions with **2a** (eq 1). The result along with all above results appealed us to understand the possible mechanism of this chemoselective cleavage reaction. First, chalcone **1a** was performed under the standard conditions in absence of diethyl phosphonate (**2a**) (eq 2), and it still stayed intact, indicating that chalcones were inert in this copper/iron cocatalyzed system. Subsequently, 2,6-di*tert*-butyl-4-methylphenol (BHT) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were employed as radical probe to

DOI: 10.1021/acs.joc.5b02887
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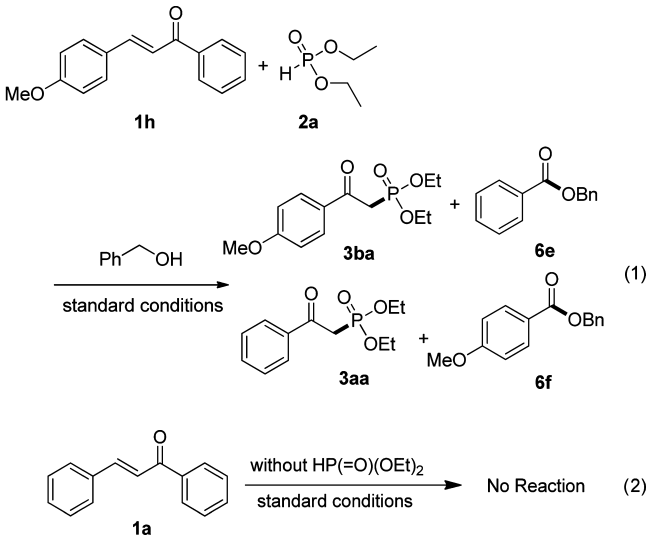
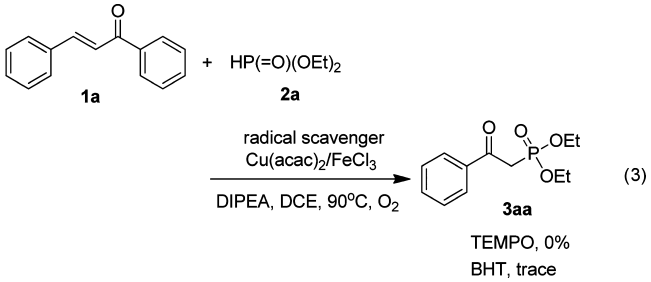
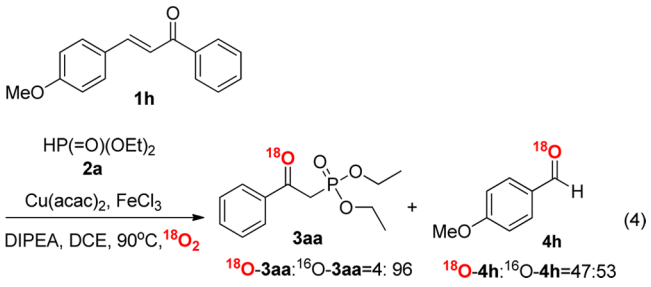


react with chalcones and H-phosphonate under the standard conditions (eq 3), which turned out the reactions were totally inhibited by TEMPO and BHT, suggesting that a radical process might be involved in the transformation.



To elucidate the origination of the carbonyl oxygen atom of β-ketophosphonates, an isotope-labeling experiment was investigated. Substrates **1h** and **2a** were performed with $^{18}O_2$ under the standard conditions, only 4% of ^{18}O-labeled product **3aa** was detected (eq 4). Meanwhile, 47% of ^{18}O-labeled 4-



methoxybenzaldehyde (**4h**) was detected by GC-MS as well. The ^{18}O-labeled experiment indicated that the oxygen in the carbonyl group of β-ketophosphonates should be originated from chalcone rather than the molecular dioxygen. The low level of ^{18}O in 4-methoxybenzaldehyde in eq 4 was probably due to the water scrambling.[9]

Based on results described above and previous reports,[6b,c,10] a tentative mechanism for this tandem oxyphosphorylation is illustrated in Scheme 2: In the presence of iron(III), a single electron transfers from an iron(III) species to HP(=O) $(OR)_2$ with molecular oxygen, leading to dialkyl phosphonate cation radical **I**. With the help of a base, the H^+ from the dialkyl phosphonate cation radical **I** was grabbed to release the P-radical **II**. Subsequently, the Cu(III)-(•O-OH) hydroperoxide species was formed in the presence of base under O_2 atmosphere. Since the α-position of chalcone has a higher electron density than the β-position, it induces this P-radical **II** attacking at the α-position of chalcone **1** to generate a more stable benzyl radical,[11] which further reacted with Cu(III)-(•O-OH) species under dioxygen atmosphere to form hydroperoxide species **III**. The oxygen−oxygen bond of hydroperoxide species **III** is weak and broken by H-phosphonate along with a retro-aldol process[12] leaving of an aldehyde **4** and intermediate **IV**, which further generated the desired product **3**. The hydroperoxide species **III** was converted to 1,3-dicarbonyl compound **V** as a byproduct as well with the help of base and H-phosphonate. If an external nucleophile existed, then there were two retro-claisen pathways[13] for subsequent nucleophilic addition of compound **V** in which path **a** gave the desired product **3** and path **b** generated product **3′**, which explained the results in eq 1. When Ar^2 is equal to Ar^1, the two pathways will give the same results.

CONCLUSIONS

In summary, a substituents-controlled aerobic oxidative chemoselective C−C bond cleavage of α,β-unsaturated carbonyl compounds with H-phosphonates under a dual metal catalysts has been disclosed, and various α,β-unsaturated carbonyl compounds can be transformed to valuable β-ketophosphonatess in moderate to good yields via a retro-HWE process. Isotope-labeling experiments suggested that the oxygen in the carbonyl of β-ketophosphonates should originate from chalcones rather than molecular oxygen. Further mechanism studies revealed that a retro-aldo process released the products and aldehydes, and if alcohols existed as an external nucleophile, the abandoned moiety of chalcones could be captured by alcohols to give various benzoates via the retro-Claisen process. Research along the future application is ongoing in our laboratory.

EXPERIMENTAL SECTION

General Information. All reagents and solvents were purchased from commercial suppliers and used without further purification. Unless otherwise stated, all experiments were conducted in a sealed tube under O_2 atmosphere. Reactions were monitored by thin-layer chromatography (TLC) or GC-MS analysis. The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 500 M spectrometer (500 MHz ^1H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^1H NMR, δ = 77.00 for ^{13}C NMR) as an internal reference. ^{31}P NMR spectra were recorded at 200 MHz, and chemical shifts were reported in ppm relative to external 85% phosphoric acid (d = 0.0 ppm).

General Procedure for Starting Materials. To a solution of the acetophenone derivative (5 mmol) and the corresponding benzaldehyde (5 mmol) in EtOH (25 mL), NaOH (400 mg, 10 mmol) was added when corresponding acetophenone and benzaldehyde were absolutely dissolved, then 1 mL water was added to the mixture. The resulting mixture was stirred overnight at room temperature. The resulting solution was extracted with EtOAc (3 × 30 mL), the combined organic layers were dried over Na_2SO_4, and the solvents were removed in vacuo. The corresponding chalcone was obtained after crystallization from 75% EtOH or by column chromatography (petroleum ether:AcOEt (30:1, v/v)). Alkynones were synthesized following the method of the previous procedure.[14] Other α,β-

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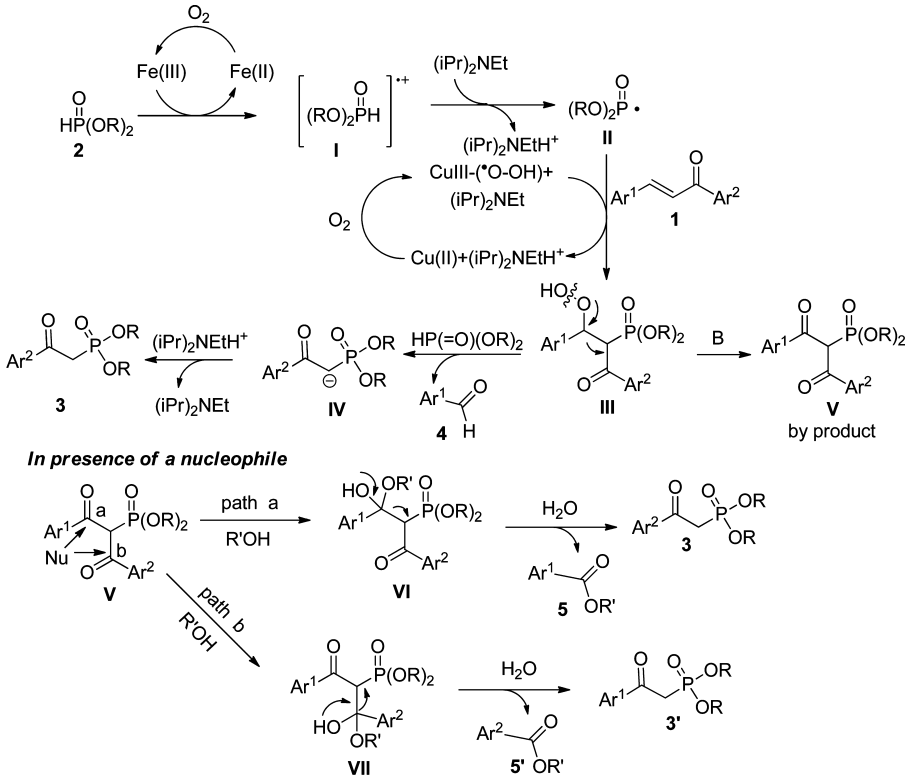
Scheme 2. Plausible Reaction Mechanism for Oxyphosphorylation of Chalcone



unsaturated carbonyl compounds were purchased from commercial companies.

General Procedure for the Synthesis of β-Ketophosphonates. To a solution of $Cu(acac)_2$ (6.5 mg, 0.025 mmol, 5 mol %), anhydrous $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol %), chalcone **1** (0.5 mmol, 1 equiv), and H-phosphonates **2** (1.25 mmol, 2.5 equiv) in DCE (1 mL), DIPEA (64.6 mg, 0.5 mmol, 0.083 mL, 1 equiv) was added at room temperature. Then the mixture was stirred at 90 °C for 24 h. Upon completion of the reaction, the solvent was removed under reduced pressure. The crude product was purified by column chromatography using petroleum ether:AcOEt (2:1, v/v) as the eluent to afford compound **3**.

General Procedure for the Utilization of Two Sections of Chalcones. To a solution of $Cu(acac)_2$ (6.5 mg, 0.025 mmol, 5 mol %), anhydrous $FeCl_3$ (8.1 mg, 0.05 mmol, 10 mol %), chalcone **1** (0.5 mmol, 1 equiv), H-phosphonates **2** (1.25 mmol, 2.5 equiv), and alcohol **5** (1 mmol, 2 equiv) in DCE (1 mL), DIPEA (64.6 mg, 0.5 mmol, 0.083 mL, 1 equiv) was added at room temperature. Then the mixture was stirred at 90 °C for 24 h. Upon completion of the reaction, ethyl acetate (20 mL) was added to the resulting solution and then washed with saturated $NaHSO_3$ aqueous solution and saturated brine three times. The combined water layers were extracted with ethyl acetate (15 mL × 2). The combined organic layers were dried over anhydrous Na_2SO_4. Then the solvent was removed under reduced pressure. The crude product was purified by column chromatography using petroleum ether:AcOEt (150:1, v/v) as the eluent to afford benzoates and using petroleum ether:AcOEt (2:1, v/v) as the eluent to afford β-Ketophosphonates.

*Diethyl (2-Oxo-2-phenylethyl)phosphonate (**3aa**).*[6a−d,10,15,16] Yellow oil (90 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.01(d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.16−4.10 (m, 2H), 3.63 (d, J_{P-H} = 22.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 191.9 (d, J_{P-C} = 6.5 Hz), 136.5, 133.6, 129.0, 128.6, 62.6 (d, J_{P-C} = 6.3 Hz), 38.5 (d, J_{P-C} = 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 19.9.

*Diethyl (2-(4-Methoxyphenyl)-2-oxoethyl) Phosphonate (**3ba**).*[6b−d,10b,16] Yellow oil (91 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.98 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.17−4.06 (m, 2H), 3.86 (s, 3H), 3.56 (d, J_{P-H} = 22.7 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 190.3 (d, J_{P-C} = 6.3 Hz), 164.0, 131.5, 129.6, 113.7, 62.6 (d, J_{P-C} = 7.5 Hz), 55.5, 38.7 (d, J_{P-C} = 128.8 Hz), 16.3 (d, J_{P-C} = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 20.4.

*(2-(4-Fluorophenyl)-2-oxoethyl) Phosphonate (**3ca**).*[6b−d,10b,15,16] Yellow oil (92 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.06−8.03 (m, 2H), 7.14 (t, *J* = 8.6 Hz, 2H), 4.17−4.09 (m, 4H), 3.59 (d, J_{P-H} = 22.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 190.3 (d, J_{P-C} = 6.6 Hz), 167.1 (d, J_{F-C} = 254.5 Hz), 132.9, 131.8 (d, J_{F-C} = 8.8 Hz), 115.8 (d, J_{F-C} = 22.5 Hz), 62.7 (d, J_{P-C} = 6.3 Hz), 39.1 (d, J_{P-C} = 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 19.6.

*Diethyl (2-(4-Chlorophenyl)-2-oxoethyl) Phosphonate (**3da**).*[6b−d,10b,16] Yellow oil (89 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.95 (d, *J* = 8.7 Hz, 2H), 7.44 (d, *J* = 8.7 Hz, 2H), 4.17−4.08 (m, 4H), 3.59 (d, J_{P-H} = 22.8 Hz, 2H), 1.28 (t, *J* = 7.1, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 190.7 (d, J_{P-C} = 6.3 Hz), 140.3, 134.8, 130.5, 128.9, 62.7 (d, J_{P-C} = 6.5 Hz), 38.6 (d, J_{P-C} = 128.8 Hz), 16.2 (d, J_{P-C} = 6.3 Hz).^{31}P NMR (200 MHz, $CDCl_3$) δ = 19.5.

*Diethyl (2-Oxo-2-(m-tolyl)ethyl) Phosphonate (**3ea**).*[6b−d,10b,15,16] Yellow oil (95 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.90 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H) 4.15−4.09 (m, 4H), 3.60 (d, J_{P-H} = 22.7 Hz, 2H), 2.40 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 191.4, 144.6, 134.1, 129.3, 129.2, 62.6 (d, J_{P-C} = 6.3 Hz), 38.9 (d, J_{P-C} = 130.0 Hz), 21.6, 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 20.2.

*Diethyl (2-Oxo-2-(thiophen-2-yl)ethyl) Phosphonate (**3fa**).*[6b,c,10b] Yellowish-brown oil (78 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.80 (d, *J* = 3.8 Hz, 1H), 7.68 (d, *J* = 4.9 Hz, 1H), 7.12−7.13 (m, 1H), 4.15−4.09 (m, 4H), 3.53 (d, J_{P-H} = 22.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$NMR (125 MHz, $CDCl_3$) δ = 184.1 (d, J_{P-C} = 6.3 Hz), 143.8, 135.0, 134.1, 128.3, 62.7 (d, J_{P-C} = 6.3 Hz), 39.3 (d, J_{P-C} = 130.0 Hz), 16.2 (d, J_{P-C} = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 19.4.

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*Diethyl (2-(Naphthalen-2-yl)-2-oxoethyl) Phosphonate (**3ga**).*[6c,10b] Yellow oil (86 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.56 (s, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.98 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 8.5 Hz 2H), 7.62 (t, 3.9 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 4.19−4.11 (m, 4H), 3.76 (d, J_{P-H} = 22.7 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 191.8 (d, J = 6.5 Hz), 135.8, 133.8, 132.4, 131.4, 129.8, 128.9, 128.5, 127.7, 126.9, 124.1, 62.7 (d, J = 6.3 Hz), 39.1 (d, J = 128.8 Hz), 16.2 (d, J = 6.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 20.1.

*Diisopropyl (2-Oxo-2-phenylethyl) Phosphonate (**3ab**).*[6b,c,10,15] Light-yellow oil (91 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.01 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.75−4.67 (m, 2H), 3.58 (d, J_{P-H} = 22.9 Hz, 2H), 1.27 (dd, J = 4.0 Hz, 4.0 Hz, 12H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 192.1 (d, J_{P-C} = 6.8 Hz), 136.7, 133.5, 129.1, 128.5, 71.5 (d, J_{P-C} = 6.3 Hz), 39.7 (d, J_{P-C} = 130.0 Hz), 23.8 (dd, J_{P-C} = 3.8 Hz, 5.0 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 17.7.

*Dimethyl (2-Oxo-2-phenylethyl)phosphonate (**3ac**).*[6b,c,10b] Colorless oil (82 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 8.01 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 3.80 (d, J = 11.2 Hz, 6H), 3.67 (d, J_{P-H} = 23.0 Hz, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 191.7 (d, J_{P-C} = 6.5 Hz), 136.3, 133.8, 128.9, 128.7, 53.2 (d, J_{P-C} = 6.3 Hz), 37.9 (d, J_{P-C} = 131.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 22.8.

*2-(Diphenylphosphoryl)-1-phenylethanone (**3ad**).*[6a−d,10b,15] Yellow oil (58 mg, 36%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.98 (dd, J = 8.4, 1.2 Hz, 2H), 7.82−7.78 (m, 4H), 7.55−7.49 (m, 3H), 7.54−7.39 (m, 6H), 4.14 (d, J_{P-H} = 15.4 Hz, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 192.8 (d, J_{P-C} = 5.7 Hz), 136.9, 133.6, 132.3, 132.1 (d, J_{P-C} = 2.5 Hz), 131.1 (d, J_{P-C} = 9.8 Hz), 129.2, 128.6 (d, J_{P-C} = 11.2 Hz), 128.5, 43.3 (d, J_{P-C} = 57.5 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 27.0.

*Ethyl (2-Oxo-2-phenylethyl) (Phenyl) Phosphinate (**3ae**).*[6a−c,10,15] Yellow oil (94 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.94 (d, J = 7.2 Hz, 2H), 7.80−7.75 (m, 2H), 7.55−7.51 (m, 2H), 7.46−7.40 (m, 4H), 4.15−4.07 (m, 1H), 3.97−3.89 (m, 1H), 3.80 (dd, J_{P-H} = 18.7, 5.6 Hz, 2H), 1.24 (t, J = 7.0 Hz, 3H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 192.1 (d, J_{P-C} = 5.5 Hz), 136.7, 133.5, 132.7 (d, J_{P-C} = 2.9 Hz), 131.8 (d, J_{P-C} = 10.3 Hz), 130.5 129.5, 128.6 (d, J_{P-C} = 13.3 Hz), 128.5, 61.4 (d, J_{P-C} = 6.3 Hz), 43.0 (d, J_{P-C} = 85.8 Hz), 16.2 (d, J_{P-C} = 6.5 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 34.4.

*Dibutyl (2-Oxo-2-phenylethyl) Phosphonate (**3af**).*[6b,c,10] Yellow oil (104 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.99 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.08−4.01 (m, 4H), 3.62 (d, J_{P-H} = 22.8 Hz, 1H), 1.58 (dt, J = 14.5, 6.6 Hz, 4H), 1.31 (dt, J = 15.1, 7.5 Hz, 4H), 0.87 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 191.9 (d, J_{P-C} = 6.5 Hz), 136.5, 133.6, 129.0, 128.5, 66.3 (d, J_{P-C} = 6.5 Hz), 38.3 (d, J_{P-C} = 130.0 Hz), 32.3 (d, J_{P-C} = 6.3 Hz), 18.6, 13.5. ^{31}P NMR (200 MHz, $CDCl_3$) δ = 19.9.

*Dibenzyl (2-Oxo-2-phenylethyl) Phosphonate (**3ag**).*[6b,c,10] Yellow oil (78 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ = 7.95 (d, J = 7.9 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.32−7.26 (m, 10H), 5.04 (ddd, J_{P-H} = 19.9, 11.7, 8.6 Hz, 4H), 3.68 (d, J = 22.6 Hz, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 191.6 (d, J_{P-C} = 6.7 Hz), 136.4 (d, J = 2.5 Hz), 135.8 (d, J = 6.3 Hz), 133.6, 129.0, 128.6, 128.5, 128.4, 128.0, 68.0 (d, J_{P-C} = 6.3 Hz), 39.2 (d, J_{P-C} = 131.3 Hz). ^{31}P NMR (200 MHz, $CDCl_3$) δ = 21.2.

*Naphthalen-1-ylmethyl Benzoate (**6a**).*[17] Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, J = 7.4 Hz, 2H), 7.61 (m, 7H), 7.47 (d, J = 7.7 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 5.44 (s, 2H).^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ 134.0, 133.0, 131.1, 129.8, 128.9, 127.7, 126.7, 126.1, 125.3, 123.6, 44.5.

*Benzyl Benzoate (**6b**).* Colorless oil.[18] ^{1}H NMR (500 MHz, CDCl3) δ= 8.10 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.34−7.47 (m, 7H), 5.38 (s, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 166.4, 136.1, 133.0, 130.1, 129.7, 128.6, 128.3, 128.2, 128.1, 66.7.

*Phenethyl Benzoate (**6c**).* Colorless oil.[19] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.05 (d, J = 7.1 Hz, 2H), 7.60−7.56 (m, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.37−7.31 (m, 4H), 7.29−7.27 (m, 1H), 4.57 (t, J = 7.0 Hz, 2H), 3.11 (t, J = 7.0 Hz, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 166.5, 137.9, 132.9, 130.3, 129.5, 128.9, 128.5, 128.3, 126.6, 65.5, 35.2.

*Thiophen-2-ylmethyl Benzoate (**6d**).* Colorless oil.[20] ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (d, J = 5.0 Hz, 1H), 7.18 (d, J = 3.4 Hz, 1H), 7.02 (d, J = 5.0 Hz, 1H), 5.52 (s, 2H). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) δ = 166.2, 138.0, 133.1, 129.9, 129.7, 128.3, 128.1, 126.8, 61.0.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02887.

^{1}H NMR, ^{13}C{1H} NMR and ^{31}P NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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