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Copper/Iron-Catalyzed Aerobic Oxyphosphorylation of Terminal Alkynes Leading to β-Ketophosphonates

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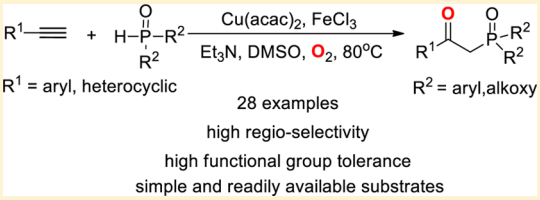
Supporting Information

ABSTRACT: A copper/iron-catalyzed oxyphosphorylation of alkynes with H-phosphonates through a radical process was developed. The present protocol provides an attractive approach to β-ketophosphonates in moderate to good yields, with the advantages of readily available substrate, high functional group tolerance and operation simplicity.

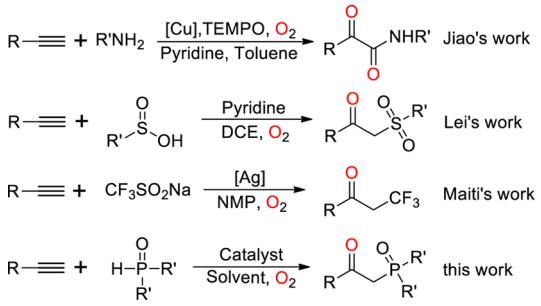


INTRODUCTION

Oxyfunctionalization of simple organic compounds with dioxygen through a radical pathway is a highly efficient and rapidly growing novel strategy for the construction of oxygen-containing compounds. Molecular oxygen, the linchpin of this strategy, is an ideal oxidant in organic synthesis because of its environmental friendliness, cleanliness, and sustainability.[1] Moreover, the activation of dioxygen finds important applications in biochemistry and enzymology.[1,2] As a result, transition metals have been used to activate dioxygen.[3] They are also well-known for initiating radical reactions under mild conditions. Merging the two roles of transition metals, that is, dioxygen activation and radical initiation, is an exciting as well as a challenging strategy for the development of new synthetically important reactions.

Over the past decade great progress has been made in synthesis of α-functionalized carbonyl compounds via transition-metal-catalyzed aerobic oxidative radical reactions of alkenes,[3a,4] but unactivated alkynes have seldom been used in this way. To the best of our knowledge, in literature only three methods, reported by Jiao,[5] Lei[6] and Maiti,[7] have been described (Scheme 1). This definitely calls for the development of more efficient catalytic methods for the synthesis of α-functionalized carbonyl compounds, keeping in mind their diverse biological properties and versatile synthetic applications in organic synthesis. Prompted by these facts and in continuation of our interest in alkyne chemistry,[8] we report herein an efficient copper/iron catalyzed aerobic oxyphosphorylation of alkynes with H-phosphonates to afford β-ketophosphonates in moderate to good yields. β-Ketophosphonates are valuable compounds in organic synthesis[9] and pharmaceutical industry.[10] A number of methods have been reported for their synthesis, but β-ketophosphonates have rarely been obtained from alkynes.[11] In 2011, Ji and co-workers reported synthesis of β-ketophosphonates via dioxygen activation-based oxidative difunctionalization of alkene.[11g] Inspired by this report, we envisaged the generation of vinylphosphonate radical from alkynes and H-phosphonate under Ji's reaction conditions. To test our hypothesis, a model reaction was performed under the conditions of Ji.

Scheme 1. Synthesis of α-Functionalized Carbonyl Compounds via Direct Aerobic Difunctionalization of Alkyne



RESULTS AND DISCUSSION

To our delight, the expected β-ketophosphonate was indeed formed and, moreover, with 19% yield based on GC analysis (Table 1, entry 1). Increasing the loading of $CuBr_2$ and $FeBr_3$ to 10 mol % and 20 mol %, respectively, leads to a considerable increase in the yield up to 30% (entry 2). A variety of transition-metal salts were examined, and some results were shown in entries 3−14. Among the salts tested, $Cu(acac)_2$ and $FeCl_3$ performed better than other catalysts. As the next optimization step we performed a solvent screening (entries 15−17). None of the other solvents was superior to DMSO. Different bases were also examined, and the results showed that Et_3N was still the best choice (entries 18−20). Moreover, elevating the reaction temperature from 55 to 80 °C led to a slightly improved yield (entry 21). Further exploration

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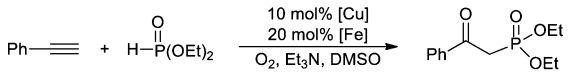
Table 1. Optimization of the Reaction Conditions[a]



1a 2a 3aa

entry	catalyst	cocatalyst	base	condition	yield (%)[b]
1[c]	$CuBr_2$	$FeBr_3$	Et_3N	DMSO, 55 °C	19
2	$CuBr_2$	$FeBr_3$	Et_3N	DMSO, 55 °C	30
3	$CuBr_2$	$FeCl_3$	Et_3N	DMSO, 55 °C	40
4	$CuBr_2$	$FeCl_2$	Et_3N	DMSO, 55 °C	9
5	$CuBr_2$	$Fe(acac)_3$	Et_3N	DMSO, 55 °C	0
6	$CuBr_2$	$ZnCl_2$	Et_3N	DMSO, 55 °C	19
7	$CuBr_2$	$AlCl_3$	Et_3N	DMSO, 55 °C	24
8	$CuBr_2$	$NiCl_2$	Et_3N	DMSO, 55 °C	34
9	CuBr	$FeCl_3$	Et_3N	DMSO, 55 °C	23
10	CuCl	$FeCl_3$	Et_3N	DMSO, 55 °C	25
11	CuI	$FeCl_3$	Et_3N	DMSO, 55 °C	20
12	$Cu(OTf)_2$	$FeCl_3$	Et_3N	DMSO, 55 °C	42
13	$Cu(TFA)_2$	$FeCl_3$	Et_3N	DMSO, 55 °C	40
14	$Cu(acac)_2$	$FeCl_3$	Et_3N	DMSO, 55 °C	52
15	$Cu(acac)_2$	$FeCl_3$	Et_3N	DMF, 55 °C	44
16	$Cu(acac)_2$	$FeCl_3$	Et_3N	DCE, 55 °C	32
17	$Cu(acac)_2$	$FeCl_3$	Et_3N	THF, 55 °C	36
18	$Cu(acac)_2$	$FeCl_3$	Et_2NH	DMSO, 55 °C	45
19	$Cu(acac)_2$	$FeCl_3$	$^iPr_2NH$	DMSO, 55 °C	48
20	$Cu(acac)_2$	$FeCl_3$	DBU	DMSO, 55 °C	43
21	$Cu(acac)_2$	$FeCl_3$	Et_3N	DMSO, 80 °C	58
22[d]	**$Cu(acac)_2$**	**$FeCl_3$**	**Et_3N**	**DMSO , 80°C**	**66 (63)**
23[e]	$Cu(acac)_2$	$FeCl_3$	Et_3N	DMSO, 80 °C	22
24	$Cu(acac)_2$	–	Et_3N	DMSO, 80 °C	0
25	–	$FeCl_3$	Et_3N	DMSO, 80 °C	trace

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1 mmol), catalyst (10 mol %), cocatalyst (20 mol %), base (0.5 mmol), solvent (1 mL), O_2 (balloon), 24 h. [b]The yield was determined by GC with biphenyl as an internal standard. [c]$CuBr_2$ (2.5 mol %), $FeBr_3$ (5 mol %). [d]**2a** (2 mmol) was used and the number in parentheses refers to the yield of isolated product. [e]Under air.

suggested that a good yield of **3aa** was obtained when the amount of H-phosphonate (**2a**) increased from 2 equiv to 4 equiv (entry 22). Unfortunately, the reaction did become sluggish under an air atmosphere (entry 23). Finally, control experiments showed that both copper salts and iron salts were necessary for this reaction (entries 24 and 25).

The scope of the transformation was then investigated under the optimized conditions. A variety of aromatic alkynes could efficiently undergo oxyphosphorylation to the desired *β*-ketophosphonates in moderate to good yields (Table 2). Electron-donating and electron-withdrawing substituents at the *m*-, *o*-, and *p*-positions on the phenyl ring of aromatic alkynes all gave moderate to good yields of their corresponding products. Oxyphosphorylation of *m*-, *o*-, and *p*-ethynyltoluenes (**3ba**–**3da**) or *m*-, *o*-, and *p*-ethynylbromobenzenes (**3ea**–**3ga**) proceeded well, and good yields were achieved, suggesting that the steric effect of substituents on aromatic rings was negligible. The intact bromo and chloro groups (**3ea**–**3ha**) are beneficial for further functionalization at a later stage using cross coupling protocols. What's more, fluorine (**3ia**) and trifluoromethyl (**3ja**) have come to be recognized as key elements in materials science, and many fluorine-containing biologically active agents are finding applications as pharmaceuticals and agrochemicals. The electron-donating substituted aromatic alkynes showed superior reaction efficiency to that of the electron-withdrawing ones. The presence of other functional groups in the phenylacetylene substrate, including *tert*-butyl, phenyl, methoxy, benzyloxy, acetoxy, ester, acetyl and nitrile groups (**3ka**–**3ra**), were tolerated under these reaction conditions. The naphthyl alkyne was also a suitable substrate for this reaction (**3sa**). Electron-rich heterocycle-containing alkynes were also suitable substrates for this transformation (**3ta**–**3va**). However, electron-poor alkynes, such as 2- and 3-ethynylpyridine, did not undergo the reaction, likely caused by the low reactivity of the C–C triple bonds. Moreover, estrone derivative (**3wa**) and amino acid derivative (**3xa**) were also successfully prepared, which highlights the good functional group tolerance and potential applications of this method. This direct oxyphosphorylation of alkynes with H-phosphonates strategy could also be extended to access the corresponding *β*-ketophosphonates (**3ab**–**3ae**) when we used other phosphonates as the substrates. Morever, diphenylphosphine oxide was suitable coupling partner (**3af**). Unfortunately, both internal (dodec-6-yne and but-1-yn-1-ylbenzene) and aliphatic terminal (dodec-1-yne) alkynes gave trace amount (<8%) of the desired products.

We also explored the reactivity of the $Cu(acac)_2/FeCl_3$-catalyzed oxyphosphorylation system for larger-scale synthesis shown in Scheme 2. The reaction with (10 mmol, 1.02 g) of phenylacetylene produced excellent yield (63%). The oxyphosphorylation proceeded smoothly even with a further increased amount of substrate (50 mmol, 5.10 g), affording *β*-ketophosphonates in 61% yield. These excellent results showed the promise of the catalytic system for larger-scale synthesis in the process of alkyne oxyphosphorylation.

In order to gain reasonable insight into the reaction mechanism, we conducted a number of experiments (Scheme 3). Initially, we studied the radical nature of the reaction using diethyl phosphonate **2a** and TEMPO under the standard conditions. As expected, the TEMPO-trapped compound **5a** was observed (Scheme 3A). The radical nature of these reactions was further confirmed by inclusion of catalytic amounts of inhibitors TEMPO; product **3aa** was formed only to the extent of 24% (Scheme 3B). Studying the role of oxygen in the reaction was also vital to unfold the intricacies of the mechanism. The reaction was considerably inhibited under nitrogen (Scheme 3C). Further investigation under an $^{18}O_2$ atmosphere proved the dioxygen activation, indicating that oxygen atoms of the *β*-ketophosphonates originated from molecular dioxygen (Scheme 3D). The results also revealed that the DMSO was not the oxidant of the oxidative coupling reaction. When diethyl (phenylethynyl)phosphonate (Scheme 3E) and (*E*)-diethyl styrylphosphonate (Scheme 3F) were used as the substrates, neither of them underwent the hydration under the standard reaction.

Based on the results described above and previous report,[7,11g,12] a mechanism for this catalytic reaction is proposed in Scheme 4. The generation of phosphonyl radical **I** and Cu^{II}-(•OOH) (hydroperoxide) species is similar to the mechanism first proposed by Ji and co-workers. The phosphonyl radical **I** attacked the alkyne **1** and delivered a reactive *α*-styrenyl radical intermediate **II** which interacted with Cu^{II}-(•OOH) species to form hydroperoxide intermediate **III**. Then, the intermediate **III** undergoes reduction by H-phosphonate **2**, producing phosphonyl radical **I**, water and enolate **IV**. Finally, the enolate **IV** isomerizes and furnishes **3**.

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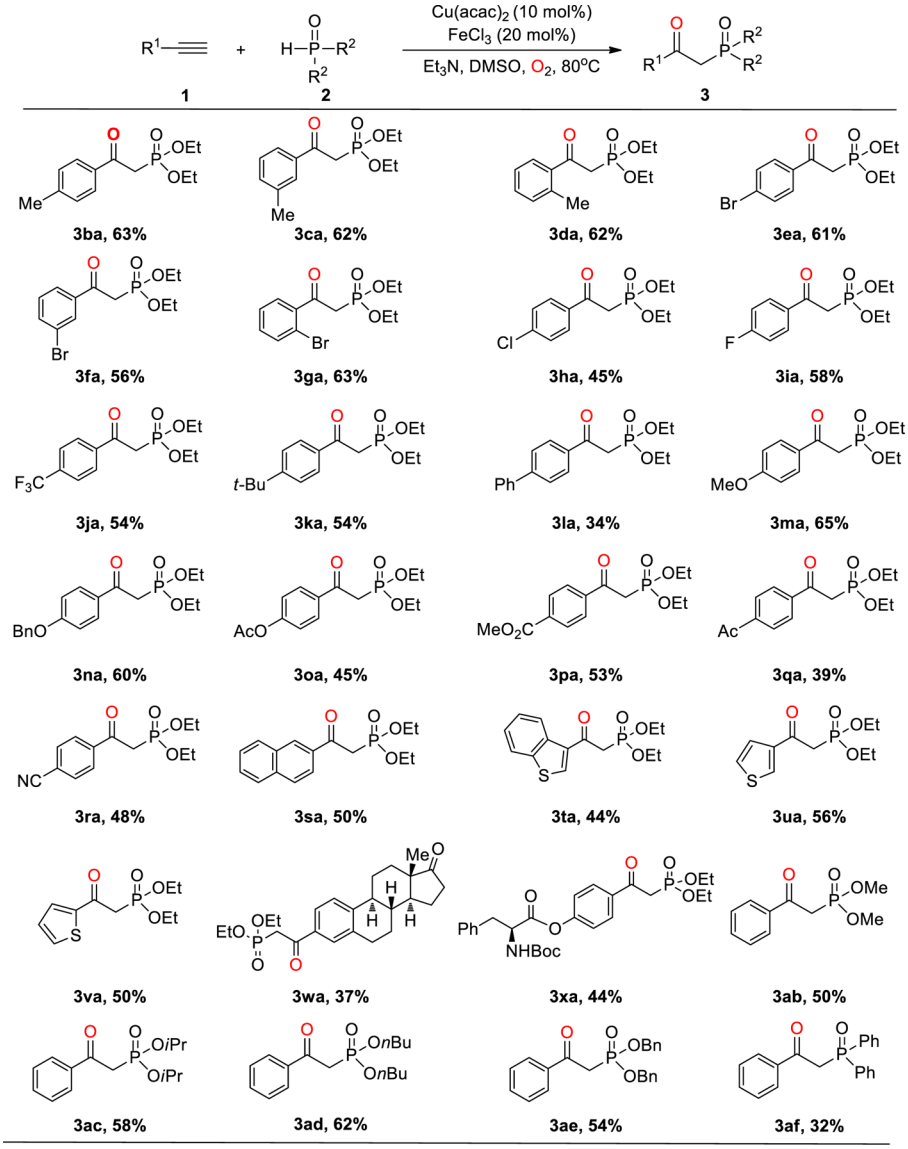
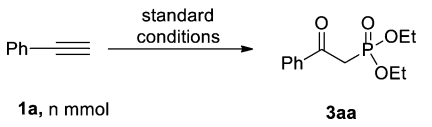
Table 2. Reaction Scope[a]



[a]Reaction conditions: **1** (0.5 mmol), **2**(2 mmol), $Cu(acac)_2$ (10 mol %), $FeCl_3$(20 mol %), Et_3N (0.5 mmol), DMSO (1 mL), O_2 (balloon), 80 °C, 24 h.

Scheme 2. Larger-Scale Synthesis of 3aa



n	*yield*
10	63%, 1.61 g
50	61%, 7.81 g

CONCLUSIONS

In conclusion, we have developed a generic approach to the synthesis of complex *β*-ketophosphonates via the direct copper/iron catalyzed oxidative coupling of alkynes and H-phosphonates. The present methodology utilizes easily available starting materials, offers operational simplicity, and enjoys a broad substrate scope as well as functionality tolerance. Preliminary mechanism revealed that O_2 not only participates as the ideal oxidant but also undergoes dioxygen activation under ambient conditions via a radical process. Further studies to clearly understand the reaction mechanism and the synthetic applications are currently underway.

EXPERIMENTAL SECTION

General Information. Commercially available reagents were of reagent grade (AR grade) and were used without further purification. Reactions were monitored by thin-layer chromatography (TLC) using silicycle precoated silica gel plates. Flash column chromatography was performed over silicycle silica gel (200−300 mesh). ^1H NMR, $^{13}C\{^1H\}$ NMR, and ^{31}P NMR spectra were recorded on 400 MHz NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with IR spectrometer and are reported in reciprocal centimeter (cm^{-1}). High-resolution mass spectra were obtained using GCT-TOF instrument with EI or ESI source.

General Procedure for the Synthesis of 3aa. Phenylacetylene (51 mg, 0.5 mmol) was added to a mixture of H-diethyl phosphonate (276 mg, 2 mmol), $Cu(acac)_2$ (13 mg, 0.05 mmol), $FeCl_3$ (16 mg, 0.1 mmol), and Et_3N (50 mg, 0.5 mmol) in DMSO (1 mL) at room temperature under O_2 (balloon). The reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction, water (5 mL) was added to the reaction mixture, and the resulting mixture was extracted with dichloromethane. The organic layer was washed with water (20 mL × 3) and brine (20 mL × 1), and the separated aqueous phase was

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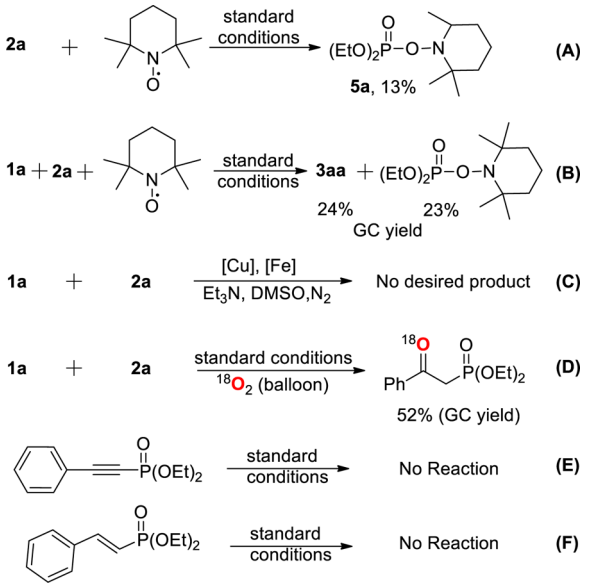
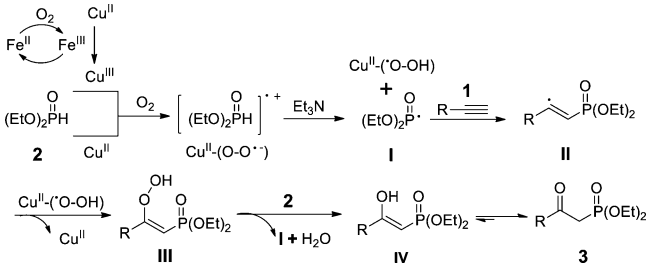
Scheme 3. Mechanistic Studies



Scheme 4. Proposed Mechanism



extracted with CH_2Cl_2 (20 mL × 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1) to afford the β-ketophosphonate **3aa** as a light-yellow oil (63%, 81 mg).

The Experimental Procedure for Larger-Scale Synthesis of 3aa. Phenylacetylene (5.1 g, 50 mmol) was added to a mixture of H-diethyl phosphonate (27.6 g, 200 mmol), $Cu(acac)_2$ (1.31 g, 5 mmol), $FeCl_3$ (1.62 g, 10 mmol), and Et_3N (5.05 g, 50 mmol) in DMSO (30 mL) at room temperature under O_2 (balloon). The reaction mixture was stirred at 80 °C for 36 h. After completion of the reaction, water (30 mL) was added to the reaction mixture, and the resulting mixture was extracted with dichloromethane. The organic layer was washed with 0.1 M HCl (50 mL × 1), water (50 mL × 3), and brine (50 mL × 1), and the separated aqueous phase was extracted with CH_2Cl_2 (50 mL × 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 2:1) to afford the β-ketophosphonate **3aa** as a light-yellow oil (61%, 7.81 g).

*Diethyl (2-Oxo-2-Phenylethyl)phosphonate (**3aa**).*[11g] Light-yellow oil; yield: 63% (81 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 4.10 (m, 4H), 3.60 (d, J_{H-P} = 22.8 Hz, 2H), 1.24 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.8 (d, J_{C-P} = 6.5 Hz), 136.4, 133.6, 128.9, 128.5, 62.5 (d, J_{C-P} = 6.6 Hz), 38.2 (d, J_{C-P} = 129.8 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0.

*Diethyl (2-Oxo-2-(p-tolyl)ethyl)phosphonate (**3ba**).*[11e] Yellow oil; yield: 63% (85 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.24 (t, J = 8.4 Hz, 2H), 4.10 (m, 4H), 3.58 (d, J_{H-P} = 22.4 Hz, 2H), 2.38 (s, 3H), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.4 (d, J_{C-P} = 6.5 Hz), 144.5, 133.9, 129.2, 129.0, 62.5 (d, J_{C-P} = 6.5 Hz), 38.2 (d, J_{C-P} = 129.0 Hz), 21.5, 16.1 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2.

*Diethyl (2-Oxo-2-(m-tolyl)ethyl)phosphonate (**3ca**).*[8l] Yellow oil; yield: 62% (83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.75 (m, 2H), 7.37−7.30 (m, 2H), 4.13−4.06 (m, 4H), 3.58 (d, J_{H-P} = 22.8 Hz, 2H), 2.37 (s, 3H), 1.24 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0 (d, J_{C-P} = 6.5 Hz), 138.3, 136.5, 134.3, 129.3, 128.3, 126.2, 62.5 (d, J_{C-P} = 6.6 Hz), 38.2 (d, J_{C-P} = 129.8 Hz), 21.1, 16.0 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1.

*Diethyl (2-Oxo-2-(o-tolyl)ethyl)phosphonate (**3da**).*[8l] Yellow oil; yield: 62% (83 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 1H), 7.31 (t, J = 7.4 Hz, 1H), 7.22−7.16 (m, 2H), 4.07−4.00 (m, 4H), 3.52 (d, J_{H-P} = 22.4 Hz, 2H), 2.44 (s, 3H), 1.18 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.9 (d, J_{C-P} = 6.6 Hz), 138.8, 137.1 (d, J = 2.2 Hz), 131.8, 131.7, 129.5, 125.6, 62.4 (d, J_{C-P} = 6.6 Hz), 40.9 (d, J_{C-P} = 129.1 Hz), 21.2, 16.1 (d, J_{C-P} =6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2.

*Diethyl (2-(4-Bromophenyl)-2-oxoethyl)phosphonate (**3ea**).*[8l] Yellow oil; yield: 61% (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.61 (m, 2H), 4.16−4.08 (m, 4H), 3.58 (d, J_{H-P} = 22.4 Hz, 2H), 1.27 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.9 (d, J_{C-P} = 6.6 Hz), 135.2, 131.9, 130.5, 129.0, 62.7 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 128.3 Hz), 16.2 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4.

*Diethyl (2-(3-Bromophenyl)-2-oxoethyl)phosphonate (**3fa**).*[8l] Yellow oil; yield: 56% (93 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.92 (d, J = 7.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 1H), 4.14−4.10 (m, 4H), 3.58 (d, J_{H-P} = 22.4 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6 (d, J_{C-P} = 6.5 Hz), 138.0, 136.4, 131.9, 130.1, 127.6, 122.8, 62.7 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 129.1 Hz), 16.1 (d, J_{C-P} = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.3.

*Diethyl (2-(2-Bromophenyl)-2-oxoethyl)phosphonate (**3ga**).* Yellow oil; yield: 63% (105 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (m, 1H), 7.53 (m, 1H), 7.39−7.35 (m, 1H), 7.32−7.28 (m, 1H), 4.13−4.06 (m, 4H), 3.68 (d, J_{H-P} = 22.4 Hz, 2H), 1.25 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0 (d, J_{C-P} = 6.6 Hz), 140.6, 133.6, 132.1, 129.7, 127.4, 118.9, 62.6 (d, J_{C-P} = 6.6 Hz), 41.8 (d, J_{C-P} = 127.6 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.0; IR (neat): 2966, 1688, 1579, 1250, 1028, 966 cm^{-1}; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{17}BrO_4P$: 335.0042, found: 335.0032.

*Diethyl (2-(4-Chlorophenyl)-2-oxoethyl)phosphonate (**3ha**).* Yellow oil; yield: 45% (65 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.15−4.08 (m, 4H), 3.58 (d, J_{H-P} = 22.8 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.6 (d, J_{C-P} = 6.5 Hz), 140.2, 134.7, 130.4, 128.9, 62.7 (d, J_{C-P} = 6.5 Hz), 38.5 (d, J_{C-P} = 129.0 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5; IR (neat): 2955, 1696, 1580, 1257, 1020, 975 cm^{-1}; HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{17}ClO_4P$: 291.0547, found: 291.0545.

*Diethyl (2-(4-Fluorophenyl)-2-oxoethyl)phosphonate (**3ia**).*[8l] Yellow oil; yield: 58% (79 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (m, 2H), 7.10 (t, J = 8.4 Hz, 2H), 4.13−4.06 (m, 4H), 3.57 (d, J_{H-P} = 22.8 Hz, 2H), 1.24 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 190.2 (d, J_{C-P} = 6.6 Hz), 165.9 (d, J_{C-F} = 254.4 Hz), 132.8, 131.7 (d, J_{C-F} = 9.5 Hz), 115.6 (d, J_{C-F} = 21.9 Hz), 62.5 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 128.4 Hz), 16.1 (d, J_{C-P} = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6.

*Diethyl (2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)phosphonate (**3ja**).*[8l] Yellow oil; yield: 54% (87 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 4.14−4.07 (m, 4H), 3.62 (d, J_{H-P} = 23.2 Hz, 2H), 1.25 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.0 (d, J_{C-P} = 6.5 Hz), 139.0, 134.2 (dd, J_{C-F} =32.8 Hz, 32.0 Hz), 129.3, 125.5 (q, J_{C-F} =3.7 Hz), 122.0, 62.7 (d, J_{C-P} =6.6 Hz), 38.8 (d, J_{C-P} = 128.3 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.0.

*Diethyl (2-(4-(tert-Butyl)phenyl)-2-oxoethyl)phosphonate (**3ka**).*[8l] Yellow oil; yield: 54% (84 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.12−4.05 (m, 4H), 3.56

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J. Org. Chem. 2015, 80, 5023−5029

(d, J_{H-P} = 22.8 Hz, 2H), 1.28 (s, 9H), 1.23 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.3 (d, J_{C-P} = 6.6 Hz), 157.3, 134.1, 128.9, 125.4, 62.4 (d, J_{C-P} = 6.6 Hz), 38.2 (d, J_{C-P} = 129.1 Hz), 34.9, 30.8 16.0 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2.

*Diethyl (2-([1,1′-Biphenyl]-4-yl)-2-oxoethyl)phosphonate (**3la**).* Light-yellow oil; yield: 34% (56 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.40 (t, J = 7.4 Hz, 1H), 4.20−4.12 (m, 4H), 3.67 (d, J_{H-P} = 22.4 Hz, 2H), 1.29 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.4 (d, J_{C-P} = 5.8 Hz), 146.3, 139.6, 135.1, 129.7, 128.9, 128.3, 127.2, 127.1, 62.7 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 129.0 Hz), 16.2 (d, J_{C-P} = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1; IR (neat): 2922, 1686, 1241, 1038, 973 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{22}O_4P$: 333.1250, found: 333.1249.

*Diethyl (2-(4-Methoxyphenyl)-2-oxoethyl)phosphonate (**3ma**).*[11e] Yellow oil; yield: 65% (93 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.15−4.08 (m, 4H), 3.86 (s, 3H), 3.57 (d, J_{H-P} = 22.8 Hz, 2H), 1.27 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.1 (d, J_{C-P} = 6.5 Hz), 163.9, 131.4, 129.5, 113.7, 62.6 (d, J_{C-P} = 6.6 Hz), 55.4, 38.1 (d, J_{C-P} = 129.1 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5.

*Diethyl (2-(4-(Benzyloxy)phenyl)-2-oxoethyl)phosphonate (**3na**).* Yellow oil; yield: 60% (108 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.8 Hz, 2H), 7.43−7.34 (m, 5H), 7.01 (d, J = 8.8 Hz, 2H), 5.13 (s, 2H), 4.17−4.09 (m, 4H), 3.58 (d, J_{H-P} = 22.8 Hz, 2H), 1.28 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.2 (d, J_{C-P} = 6.5 Hz), 163.1, 135.9, 131.5, 129.7, 128.7, 128.2, 127.4, 114.5, 70.1, 62.6 (d, J_{C-P} = 6.6 Hz), 38.1 (d, J_{C-P} = 129.1 Hz), 16.2 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.6; IR (neat): 2968, 1688, 1573, 1246, 1032, 986 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{24}O_5P$: 363.1356, found: 363.1346.

*4-(2-(Diethoxyphosphoryl)acetyl)phenyl acetate (**3oa**).* Yellow oil; yield: 45% (70 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 4.16−4.09 (m, 4H), 3.60 (d, J_{H-P} = 22.8 Hz, 2H), 2.31 (s, 3H), 1.27 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.6 (d, J_{C-P} = 6.5 Hz), 168.7, 154.7, 134.0, 130.7, 121.7, 62.7 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 129.0 Hz), 21.1, 16.1 (d, J_{C-P} = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; IR (neat): 2952, 1754, 1675, 1587, 1239, 1036, 982 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{20}O_6P$: 315.0992, found: 315.0983.

*Methyl 4-(2-(Diethoxyphosphoryl)acetyl)benzoate (**3pa**).* Colorless oil; yield: 53% (83 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 8.05 (d, J = 8.4 Hz, 2H), 4.16−4.08 (m, 4H), 3.93 (s, 3H), 3.64 (d, J_{H-P} = 22.4 Hz, 2H), 1.26 (t, J = 7.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J_{C-P} = 6.5 Hz), 166.0, 139.5, 134.2, 129.7, 128.9, 62.7 (d, J_{C-P} = 6.6 Hz), 52.5, 38.7 (d, J_{C-P} = 128.3 Hz), 16.2 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.3; IR (neat): 2958, 1724, 1685, 1574, 1243, 1042, 987 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{20}O_6P$: 315.0992, found: 315.0986.

*Diethyl (2-(4-Acetylphenyl)-2-oxoethyl)phosphonate (**3qa**).* Yellow oil; yield: 39% (58 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 4.17−4.09 (m, 4H), 3.65 (d, J_{H-P} = 23.2 Hz, 2H), 2.64 (s, 3H), 1.27 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 197.4, 191.4 (d, J_{C-P} = 6.6 Hz), 140.4, 139.5, 129.2, 128.4, 62.8 (d, J_{C-P} = 6.5 Hz), 38.8 (d, J_{C-P} = 128.3 Hz), 26.9, 16.2 (d, J_{C-P} = 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.2; IR (neat): 2969, 1692, 1680, 1587, 1251, 1038, 974 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{20}O_5P$: 299.1043, found: 299.1036.

*Diethyl (2-(4-Cyanophenyl)-2-oxoethyl)phosphonate (**3ra**).*[9f] Yellow oil; yield: 48% (67 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 4.16−4.09 (m, 4H), 3.63 (d, J_{H-P} = 23.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.7 (d, J_{C-P} = 6.5 Hz), 139.2, 132.4, 129.4, 117.7, 116.7, 62.8 (d, J_{C-P} = 6.5 Hz), 38.9 (d, J_{C-P} = 127.6 Hz), 16.1 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.6.

*Diethyl (2-(Naphthalen-2-yl)-2-oxoethyl)phosphonate (**3sa**).* Yellow oil; yield: 50% (76 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.06−8.03 (m, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 8.0 Hz, 2H), 7.62−7.53 (m, 2H), 4.18−4.11 (m, 4H), 3.76 (d, J_{H-P} = 22.8 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7 (d, J_{C-P} = 6.5 Hz), 135.7, 133.7, 132.3, 131.4, 129.7, 128.8, 128.4, 127.7, 126.8, 124.0, 62.6 (d, J_{C-P} = 6.5 Hz), 38.4 (d, J_{C-P} = 129.0 Hz), 16.2 (d, J_{C-P} = 6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2; IR (neat): 3015, 1678, 1621, 1248, 1047, 989 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{20}O_4P$: 307.1094, found: 307.1103.

*Diethyl (2-(Benzo[b]thiophen-3-yl)-2-oxoethyl)phosphonate (**3ta**).* Light-yellow oil; yield: 44% (68 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, J = 8.4 Hz, 1H), 8.55 (s, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 4.18−4.11 (m, 4H), 3.63 (d, J_{H-P} = 22.4 Hz, 2H), 1.28 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.1 (d, J_{C-P} = 6.5 Hz), 140.1, 139.6, 136.4, 134.7, 126.0, 125.6, 125.5, 122.2, 62.7 (d, J_{C-P} = 6.6 Hz), 40.7 (d, J_{C-P} = 130.3 Hz), 16.2 (d, J_{C-P} = 6.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.2; IR (neat): 3022, 1672, 1241, 1043, 981 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{18}O_4PS$: 313.0658, found: 313.0648.

*Diethyl (2-Oxo-2-(thiophen-3-yl)ethyl)phosphonate (**3ua**).*[8l] Yellow oil; yield: 56% (73 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (m, 1H), 7.50 (m, 1H), 7.24 (m, 1H), 4.10−4.03 (m, 4H), 3.46 (d, J_{H-P} = 22.8 Hz, 2H), 1.22 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 185.5 (d, J_{C-P} = 6.6 Hz), 141.7, 134.3, 127.2, 126.3, 62.6 (d, J_{C-P} = 6.6 Hz), 39.8 (d, J_{C-P} = 129.0 Hz), 16.1 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.9.

*Diethyl (2-Oxo-2-(thiophen-2-yl)ethyl)phosphonate (**3va**).* Yellow oil; yield: 50% (65 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 3.6 Hz, 1H), 7.67 (d, J = 4.8 Hz, 1H), 7.12 (t, J = 4.4 Hz, 1H), 4.15−4.08 (m, 4H), 3.52 (d, J_{H-P} = 22.4 Hz, 2H), 1.26 (t, J = 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 184.1 (d, J_{C-P} = 6.5 Hz), 143.7, 135.1, 134.1, 128.2, 62.7 (d, J_{C-P} = 6.5 Hz), 39.2 (d, J_{C-P} = 129.8 Hz), 16.1 (d, J_{C-P} = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; IR (neat): 2956, 1672, 1524, 1253, 1036, 975 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{10}H_{16}O_4PS$: 263.0501, found: 263.0498.

*Diethyl (2-((8R,9S,13S,14S)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]-phenanthren-3-yl)-2-oxoethyl)phosphonate (**3wa**).* Light-yellow oil; yield: 37% (80 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 1H), 7.74 (s, 1H), 7.39 (d, J = 8.0 Hz, 1H), 4.17−4.10 (m, 4H), 3.59 (d, J_{H-P} = 22.4 Hz, 2H), 2.98−2.94 (m, 2H), 2.50−2.42 (m, 2H), 2.36−2.33 (m, 1H), 2.18−1.97 (m, 4H), 1.64−1.49 (m, 6H), 1.29 (t, J = 6.8 Hz, 6H), 0.91 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7 (d, J_{C-P} = 6.5 Hz), 146.2, 137.0, 134.1, 129.6, 126.5, 125.6, 62.6 (d, J_{C-P} = 6.5 Hz), 50.5, 47.8, 44.7, 38.3 (d, J_{C-P} = 129.8 Hz), 37.7, 35.8, 31.5, 29.2, 26.2, 25.5, 21.5, 16.2 (d, J_{C-P} = 6.5 Hz), 13.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.3; IR (neat): 2982, 1715, 1686, 1572, 1246, 1045, 982 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{24}H_{34}O_5P$: 433.2138, found: 433.2125.

*(S)-4-(2-(Diethoxyphosphoryl)acetyl)phenyl 2-((tert-butoxycarbonyl)amino)-3-phenylpropanoate (**3xa**).* Colorless oil; yield: 44% (114 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.8 Hz, 2H), 7.36−7.29 (m, 3H), 7.23 (d, J = 6.4 Hz, 2H), 7.09 (d, J = 8.8 Hz, 2H), 5.08 (d, J = 8.0 Hz, 1H), 4.83−4.78 (m, 1H), 4.17−4.10 (m, 4H), 3.60 (d, J_{H-P} = 22.8 Hz, 2H), 3.22 (d, J = 6.0 Hz, 2H), 1.44 (s, 9H), 1.28 (t, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 190.6 (d, J_{C-P} = 6.6 Hz), 170.1, 155.1, 154.4, 135.5, 134.2, 130.7, 129.3, 128.8, 127.4, 121.5, 80.3, 62.7 (d, J_{C-P} = 6.6 Hz), 54.7, 38.5 (d, J_{C-P} = 128.3 Hz), 38.2, 28.2, 16.2 (d, J_{C-P} = 6.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7; IR (neat): 2988, 1765, 1683, 1570, 1242, 1050, 987 cm^{-1}; HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{35}NO_8P$: 520.2095, found: 520.2103.

*Dimethyl (2-Oxo-2-phenylethyl)phosphonate (**3ab**).*[11f] Yellow oil; yield: 50% (57 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 1.2 Hz, 8.4 Hz, 2H), 7.61−7.57 (m, 1H), 7.48 (t, J = 7.8 Hz, 2H), 3.77 (d, J_{H-P} = 11.2 Hz, 6H), 3.64 (d, J_{H-P} = 22.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 191.7 (d, J_{C-P} = 6.6 Hz), 136.3, 133.8, 128.9, 128.7, 53.1 (d, J_{C-P} = 6.6 Hz), 37.4 (d, J_{C-P} = 131.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9.

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J. Org. Chem. 2015, 80, 5023−5029

*Diisopropyl (2-Oxo-2-phenylethyl)phosphonate (**3ac**).*[11g] Yellow oil; yield: 58% (82 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 4.74−4.66 (m, 2H), 3.57 (d, J_{H-P} = 22.8 Hz, 2H), 1.26−1.23 (m, 12H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.0 (d, J_{C-P} = 6.5 Hz), 136.6, 133.4, 129.1, 128.4, 71.4 (d, J_{C-P} = 6.5 Hz), 39.6 (d, J_{C-P} = 129.8 Hz), 23.9 (d, J_{C-P} = 3.6 Hz), 23.7 (d, J_{C-P} = 5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.7.

*Dibutyl (2-Oxo-2-phenylethyl)phosphonate (**3ad**).*[11g] Yellow oil; yield: 62% (96 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.06−3.99 (m, 4H), 3.60 (d, J_{H-P} = 22.4 Hz, 2H), 1.59−1.52 (m, 4H), 1.33−1.24 (m, 4H), 0.84 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.8 (d, J_{C-P} = 6.6 Hz), 136.4, 133.5, 128.9, 128.5, 66.2 (d, J_{C-P} = 6.6 Hz), 38.2 (d, J_{C-P} = 128.3 Hz), 32.2 (d, J_{C-P} = 6.5 Hz), 18.5, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8.

*Dibenzyl (2-Oxo-2-phenylethyl)phosphonate (**3ae**).*[11a] Yellow oil; yield: 54% (102 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (m, 2H), 7.47 (m, 1H), 7.34 (t, J = 7.6 Hz, 2H), 7.24−7.19 (m, 10H), 5.03−4.91 (m, 4H), 3.58 (d, J_{H-P} = 22.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.5 (d, J_{C-P} = 6.6 Hz), 136.3 (d, J = 2.2 Hz), 135.7 (d, J = 5.8 Hz), 133.5, 128.9, 128.5, 128.4, 128.3, 127.9, 67.9 (d, J_{C-P} = 6.6 Hz), 38.5 (d, J_{C-P} = 130.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.2.

*2-(Diphenylphosphoryl)-1-phenylethanone (**3af**).*[11a] Yellow oil; yield: 32% (51 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2H), 7.82−7.77 (m, 4H), 7.54−7.49 (m, 3H), 7.47−7.38 (m, 6H), 4.14 (d, J_{H-P} = 15.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.7 (d, J_{C-P} = 5.8 Hz), 136.8, 133.5, 132.3, 132.1 (d, J_{C-P} = 2.1 Hz), 131.2, 131.0 (d, J_{C-P} = 10.2 Hz), 129.1, 128.6, 128.5, 128.4 (d, J_{C-P} = 4.4 Hz), 43.1 (d, J_{C-P} = 64.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.2.

The Experimental Procedure for the Synthesis of 5a. $(EtO)_2P(O)H$ (69 mg, 0.5 mmol) was added to a mixture of TEMPO (78 mg, 0.5 mmol), $Cu(acac)_2$ (13 mg, 0.05 mmol), $FeCl_3$ (16 mg, 0.1 mmol), and Et_3N (50 mg, 0.5 mmol) in DMSO (1 mL) at room temperature under O_2 (balloon). The resulting mixture was stirred at 80 °C for 6 h. Then, the reaction mixture was cooled to room temperature, filtered through silica gel, and washed with CH_2Cl_2. The resulting solution was concentrated in vacuo, and the residue was purified by flash column chromatography (Al_2O_3, neutral) to give the product **5a**.

*Diethyl (2,2,6,6-Tetramethylpiperidin-1-yl) phosphate (**5a**).* Yellow oil; yield: 13% (19 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.09−3.93 (m, 4H), 1.59−1.54 (m, 6H), 1.42 (s, 12H), 1.29 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 61.2 (d, J_{C-P} = 5.1 Hz), 55.5 (d, J_{C-P} = 3.7 Hz), 41.6 (d, J_{C-P} = 8.8 Hz), 31.3, 16.5, 16.2 (d, J_{C-P} = 7.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.0; HRMS (EI): m/z $[M]^+$ calcd for $C_{13}H_{28}NO_4P$: 293.1756, found: 293.1751.

■ ASSOCIATED CONTENT

Supporting Information

Results of mechanistic studies, ^{1}H NMR, ^{13}C{^{1}H} NMR, and ^{31}P NMR spectra of compounds **3aa**−**3af**, **5a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00408.

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Notes

The authors declare no competing financial interest.

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