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$Zn(OTf)_2$-Catalyzed Phosphinylation of Propargylic Alcohols: an Access to γ-Ketophosphine Oxides

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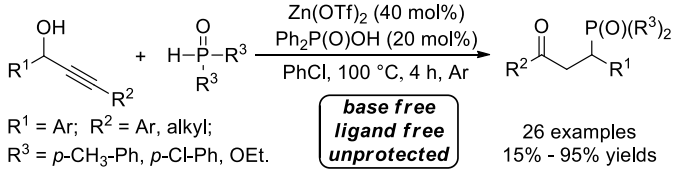
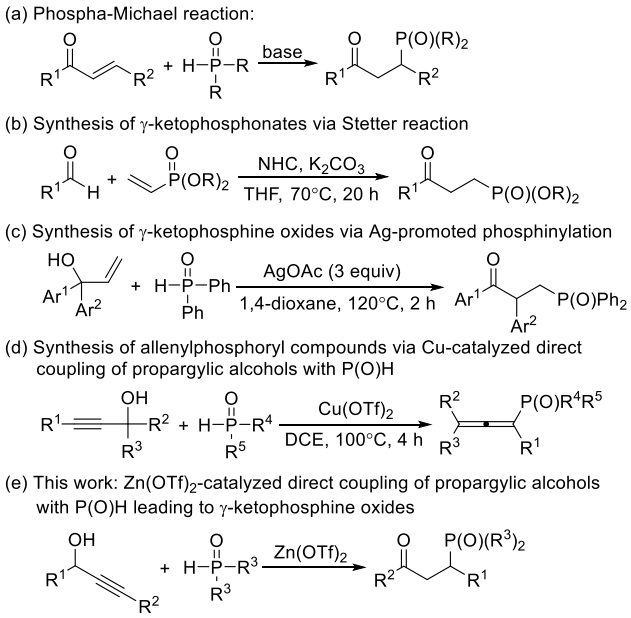


ABSTRACT: The first facile and efficient $Zn(OTf)_2$-catalyzed direct coupling of unprotected propargylic alcohols with arylphosphine oxides has been developed, affording a general, one-step approach to access structurally diverse γ-ketophosphine oxides via sequential Meyer-Schuster rearrangement/phospha-Michael reaction along with new C(sp^3)-P and C=O bonds formation, operational simplicity and complete atom-economy under ligand- and base-free conditions.

Organophosphorus compounds have aroused the continuing strong interest for synthetic chemists over the past few decades due to their great importance and wide applications in medicinal chemistry,[1] organic synthesis,[2] ligand chemistry[3] and materials science.[4] Among them, γ-ketophosphonates and γ-ketophosphine oxides have received considerable attention because of their unusual structural features and their association with wide-ranging biological activities and unique properties.[5] They are an important class of γ-keto-containing, versatile reagents in organic chemistry.[6] Moreover, some γ-ketophosphine oxides themselves are endowed with intriguing biological properties.[7] However, the methods for the synthesis of these motifs, especially for γ-ketophosphine oxides, are relatively scarce. Among all the methods developed, the most commonly used and traditional protocol is via the conjugate addition of phosphorus nucleophiles to α, β-unsaturated ketones, namely the phospha-Michael reaction (Scheme 1a),[8] but their general use suffers the limited substrate scope as well as the need for bases and complex metal salts as catalysts to sufficiently activate the poor P-nuclephiles. To overcome these drawbacks, untill recently, the N-hetero-cyclic carbene (NHC) catalyzed Stetter reaction of aromatic aldehydes with vinylphosphonates has been developed to afford γ-ketophosphonates (Scheme 1b)[9] and the Ag-promoted radical phosphinylation of α,α-diaryl allylic alcohols with arylphosphine oxides has been revealed for the preparation of γ-ketophosphine oxides (Scheme 1c).[10] Despite their usefulness, these methods also suffered from commercially unavailable catalysts, the need for additional inorganic bases or the use of a large amount of noble Ag salts, thus increasing the cost and limiting their applications. Therefore, developing convenient, economic and efficient

methods to synthesize the above-mentioned motifs for biological screening from readily available starting substrates is still desirable.

Scheme 1. Some Procedures to γ-Ketophosphonates, γ-Ketophosphine Oxides and Allenylphosphoryl Compounds

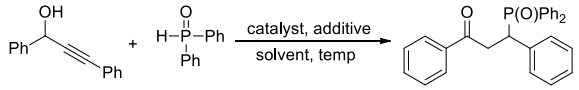


In recent years, transition-metal-catalyzed direct coupling of unprotected propargylic alcohols for selective C-C and C-heteroatom bond formation[11] has emerged as a fascinating and powerful synthetic strategy for the preparation of a wide range of valuable molecular frames in modern organic synthesis chemistry because propargylic alcohols as substrates are easily commercially available and structurally diverse building blocks and this procedure has a remarkable potential for step economy and atom economy. Recently, our group has disclosed the first copper-catalyzed direct coupling of unprotected propargylic alcohols with P(O)H compounds leading to allenylphosphoryl compounds (Scheme 1d).[12] Inspired on this protocol, a more synthetically valuable approach to γ-ketophosphine oxides would involve intermolecular direct coupling of unprotected propargylic alcohols with arylphosphine oxides since it exhibits complete atom-economy (Scheme 1e). However, to the best of our knowledge, there is no precedent for the synthesis of γ-ketophosphine oxides via direct coupling of propargylic alcohols with arylphosphine oxides. In connection with our endeavors to develop new procedures to organic phosphorus compounds,[12,13] herein, we revealed the first example of a single-step and selective preparation of diverse γ-ketophosphine oxide frameworks through a facile and efficient $Zn(OTf)_2$-catalyzed direct phosphinylation of unprotected propargylic alcohols under ligand-free and base-free conditions along with the formation of new $C(sp^3)$-P and C=O bonds, high regioselectivity and complete atom-economy.

Our initial experiment began with the coupling reaction of 1,3-diphenylprop-2-yn-1-ol **1a** with diphenylphosphine oxide **2a** as the model reaction to optimize the reaction conditions. Gratifyingly, only in the presence of 30 mol% of $Zn(OTf)_2$ as catalyst in chlorobenzene at 80 ℃ for 4 h under argon, the reaction occurred and afforded the desired β-phosphinylated carbonyl product **3a** in 29% yield (Table 1, entry 1). Encouraged by this promising result, the effect of temperature was evaluated. To our delight, raising the temperature to 100 ℃ dramatically enhanced the product yield up to 66% (Table 1, entry 2). Yet, further enhancing the reaction temperature to 120 ℃ resulted in the yield reduction (Table 1, entry 3). Subsequently, the loading of **2a** was explored, and higher loading (1.5 equivalents) could improve the yield to 69%, while

using 2 equivalents of **2a** led to a slightly lowered yield (Table 1, entries 4 and 5). To advance the process further, a subsequent survey on the role of various catalysts for the aforementioned coupling revealed $Zn(OTf)_2$ as the most favored catalyst to push the reaction forward and other catalysts like $ZnCl_2$, $Pd(OAc)_2$, $FeCl_3$, $Ni(acac)_2$ and TfOH were less effective (Table 1, entries 4 and 6-10). No targeted product **3a** was observed without $Zn(OTf)_2$ (Table 1, entry 11). Next, changing chlorobenzene to other commonly used solvents such as dioxane, toluene and DMF just led to lower yields (Table 1, entries 12-14). Additionally, using 40 mol% of $Zn(OTf)_2$ could increase the product yield up to 77% (Table 1, entry 15). Finally, various additives including TfOH, AcOH and $Ph_2P(O)OH$ were also investigated and it was found that 20 mol% of $Ph_2P(O)OH$ could remarkably improve the yield up to 95% (Table 1, entries 16-18). These results clearly indicated that the catalyst $Zn(OTf)_2$ and the additive $Ph_2P(O)OH$ were crucial for high yield.

Table 1. Optimization of Reaction Conditions[a]



1a **2a** **3a**

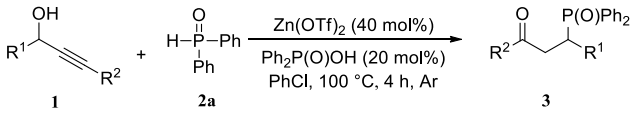
Entry	Catalyst	**2a** (mmol)	Temp (°C)	Solvent	Additive	Yield (%)
1	$Zn(OTf)_2$	0.36	80	PhCl	-	29
2	$Zn(OTf)_2$	0.36	100	PhCl	-	66
3	$Zn(OTf)_2$	0.36	120	PhCl	-	46
4	$Zn(OTf)_2$	0.45	100	PhCl	-	69
5	$Zn(OTf)_2$	0.6	100	PhCl	-	64
6	$ZnCl_2$	0.45	100	PhCl	-	37
7	$Pd(OAc)_2$	0.45	100	PhCl	-	52
8	$FeCl_3$	0.45	100	PhCl	-	trace
9	$Ni(acac)_2$	0.45	100	PhCl	-	trace
10	TfOH	0.45	100	PhCl	-	26
11	-	0.45	100	PhCl	-	0
12	$Zn(OTf)_2$	0.45	100	dioxane	-	43
13	$Zn(OTf)_2$	0.45	100	toluene	-	49
14	$Zn(OTf)_2$	0.45	100	DMF	-	30
15[b]	$Zn(OTf)_2$	0.45	100	PhCl	-	77
16[b]	$Zn(OTf)_2$	0.45	100	PhCl	TfOH	38
17[b]	$Zn(OTf)_2$	0.45	100	PhCl	AcOH	34
18[b]	**$Zn(OTf)_2$**	**0.45**	**100**	**PhCl**	$Ph_2P(O)OH$	**95**

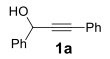
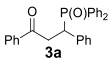
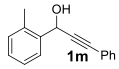
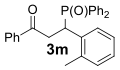
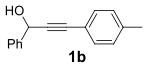
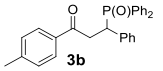
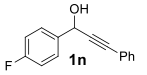
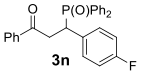
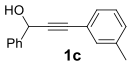
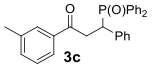
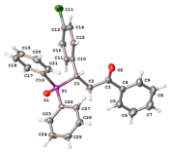
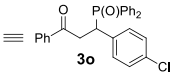
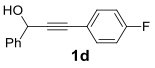
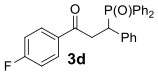
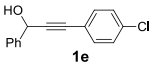
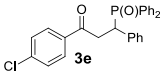
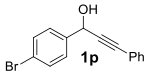
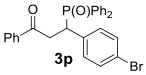
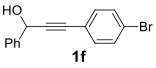
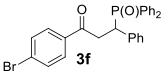
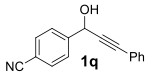
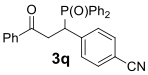
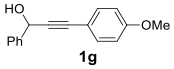
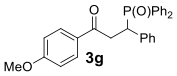
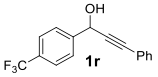
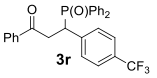
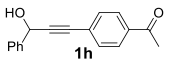
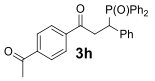
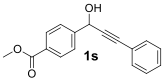
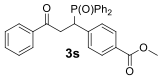
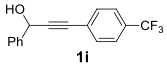
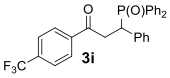
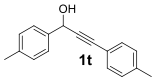
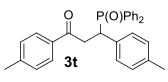
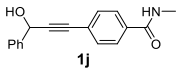
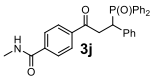
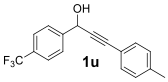
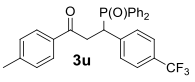
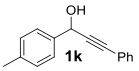
[a]Reaction conditions: **1a** (0.3 mmol), **2a**, catalyst (30 mol%), additive (20 mol%) and solvent (2 mL) at the indicated temperature for 4 h under argon. [b]Catalyst (40 mol%).

Having established the optimal conditions shown in footnote *a*, Table 2, the substrate scope of the coupling of various substituted propargylic alcohols with diphenylphosphine oxide **2a** was surveyed. As demonstrated in Table 2, a wide range of 1,3-diphenylprop-2-yn-1-ols bearing electron-donating groups and electron-withdrawing groups on the aromatic ring were all efficiently coupled under these reaction conditions to generate the desired β-phosphinylated carbonyl ketone derivatives in moderate to excellent yields, indicating that this method is an efficient protocol for the preparation of various valuable γ-ketophosphine oxides. Thus, a variety of functionalities, such as methyl, fluoro, chloro, bromo, phenyl,

methoxyl, carbonyl, trifluoromethyl, amide, cyano and ester groups, were all well tolerated for this method. Importantly, the propargylic alcohol moiety represented a higher chemoselectivity over the chlorine and bromine atoms as reaction sites under the present reaction conditions, giving the desired products (**3d-3f**) in 53-73% yields. Thus, the chemoselectivity may be further applied for the synthesis of more complex molecules through stepwise coupling of propargylic alcohols and halides. Interestingly, the substrate **1h**

Table 2. Reaction Scope of Propargylic Alcohols with 2a[a]



Entry	1	3	Yield (%)	Entry	1	3	Yield (%)
1	 1a	 3a	95	13	 1m	 3m	67
2	 1b	 3b	70	14	 1n	 3n	66
3	 1c	 3c	61	15		 3o	69
4	 1d	 3d	63				
5	 1e	 3e	53	16	 1p	 3p	67
6	 1f	 3f	73	17	 1q	 3q	41
7	 1g	 3g	86	18	 1r	 3r	88
8	 1h	 3h	84	19	 1s	 3s	60
9	 1i	 3i	69	20	 1t	 3t	54
10	 1j	 3j	48	21	 1u	 3u	32
11	 1k	3k	80	22	1v	3v	64
12	1l	3l	59	23	1w	3w	59

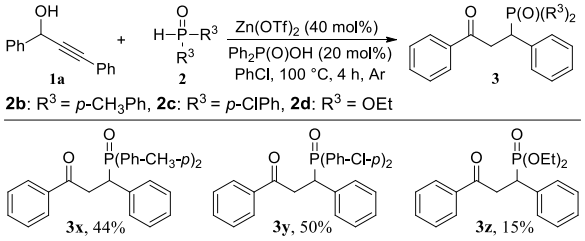
[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), $Zn(OTf)_2$ (40 mol%), $Ph_2P(O)OH$ (20 mol%), PhCl (2 mL) at 100 °C for 4 h under argon.

containing a carbonyl unit without needing any protection could also be compatible for this reaction, affording the desired product **3h** in a high yield of 84%. It's worth noting that the para-methyl substituted substrate **1k**, meta-methyl substituted substrate **1l** and sterically demanding ortho-methyl substituted counterpart **1m** afforded the corresponding products **3k**, **3l** and **3m** in 80%, 59% and 67% yields, respectively, illustrating that electronic effects and steric hindrance are evident in this transformation.

Moreover, both **1j** bearing an amide unit and **1s** having an ester group as substrates, which are prone to hydrolysis, could lead to the desired products **3j** and **3s** in moderate yields without the observation of hydrolysis. Some disubstituted 1,3-diphenylprop-2-yn-1-ols like **1t** and **1u** could also react with **2a** to provide the relative product **3t** and **3u**. The alkyl-substituted substrates (**1v** and **1w**) could all undergo the coupling to give the desired products **3v** and **3w** in good yields. However, no targeted products were detected using purely aliphatic propargylic alcohols such as dodec-5-yn-4-ol and 1-cyclopropylhex-1-yn-3-ol as substrates. In addition, primary propargylic alcohol 3-phenylprop-2-yn-1-ol and teriary propargylic alcohol 1,1,3-triphenylprop-2-yn-1-ol as substrates did not afford the targeted products. Fortunately, the product **3o** was recrystallized from CH_2Cl_2/hexane as colourless crystals and the molecular structure of **3o** as a mixture of enantiomers was confirmed by X-ray crystallography.[14] The result clearly demonstrated the phosphoryl moiety was preferentially installed at C1-position of propargylic alcohols in this coupling reaction.

To further extend the scope of this reaction, the coupling of various P(O)H substrates with **1a** was also investigated (Scheme 2). In regard to the H-phosphine oxides, apart from **2a**, di-*p*-tolylphosphine oxide (**2b**) and bis(4-chlorophenyl)phosphine oxide (**2c**) were all suitable candidates for this transformation, and also underwent the coupling to afford the corresponding products **3x** and **3y** in moderate yields (Scheme 2). However, H-phosphonates such as diethyl phosphonate (**2d**) only provided **3z** in a lower yield of 15% in the present catalyst system.

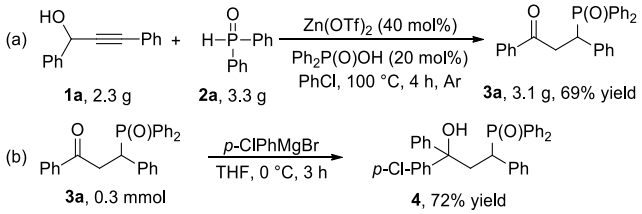
Scheme 2. The coupling of 1a with P(O)H compounds[a]



[a]Reaction conditions: **1a** (0.3 mmol), **2** (0.45 mmol), $Zn(OTf)_2$ (40 mol%), $Ph_2P(O)OH$ (20 mol%), PhCl (2 mL) at 100 °C for 4 h under argon.

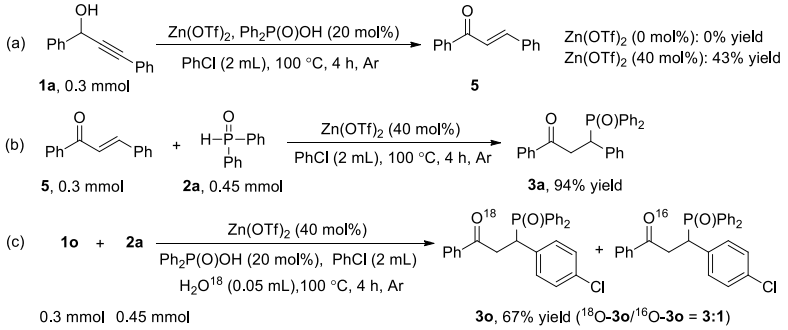
To demonstrate the synthetic application of the present method, a gram-scale experiment was conducted by employing **1a** (11 mmol, 2.3 g) with **2a** under the optimal reaction conditions and afforded the desired product **3a** in a good yield of 69% (**3a**, 3.1 g) (Scheme 3a), indicating this reaction could be effectively scaled up with high efficiency. Moreover, as expected, **3a** could react with the aryl Grignard reagent 4-ClPhMgBr to produce the corresponding γ-hydroxyl phosphine oxide **4**, which was an important class of intermediates in organic synthesis (Scheme 3b).[15]

Scheme 3. Application Studies



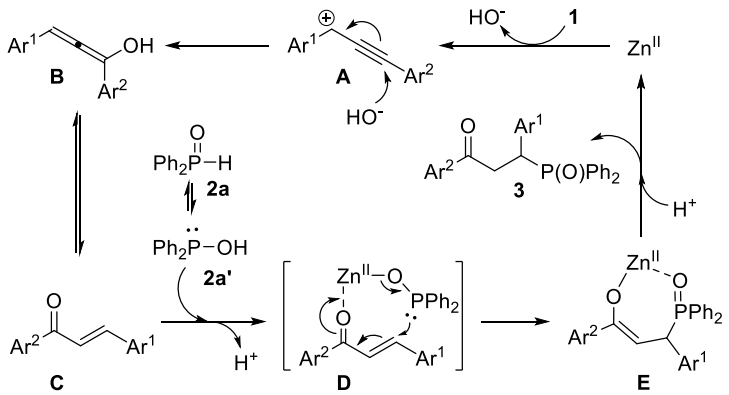
To gain insight into the reaction mechanism, several control experiments were performed (Scheme 4). Without $Zn(OTf)_2$, only in the presence of 20 mol% $Ph_2P(O)OH$, no reaction occurred, yet, the expected enone **5** was observed using 40 mol% $Zn(OTf)_2$ (Scheme 4a). Subsequent treatment of enone **5** with **2a** could afford the desired product **3a** in an excellent yield of 94% under the catalysis of 40 mol% $Zn(OTf)_2$ without $Ph_2P(O)OH$ (Scheme 4b), showing enone **5** should be the key intermediate for this reaction. Additionally, the coupling reaction of **1o** with **2a** in the presence of 0.05 mL H_2O^{18} was also detected, and gave the desired product **3o** in 67% yield with a ratio of ^{18}O-**3o** : ^{16}O-**3o** of 3:1 determined by the ESI-MS analysis (Scheme 4c), disclosing that the elimination of OH group took place and the oxygen atom on carbonyl was from the water of reaction system in the reaction process. These results also revealed that the reaction might undergo Meyer-Schuster rearrangement and phospha-Michael reaction.

Scheme 4. Control Experiments



Based on these experiment results and previous reports,[8a-e,16] a plausible mechanism was proposed (Scheme 5). Initially, the elimination of $^{-}$OH easily took place with the assistant of $Zn(OTf)_2$ and $Ph_2P(O)OH$ to generate the propargylic carbocation intermediate **A**.[12,16c] Next, $^{-}$OH attacked C3-position of **A** to form the intermediate **B**, followed by enol-keto tautomerism of **B** to provide the key enone intermediate **C**. Then, the intermolecular phospha-Michael addition of the phosphorous nucleophile **2a** (in the form of the trivalent phosphine oxide **2a**') to **C** via a seven-membered-ring transition state **D** led to the intermediate **E**.[16b] Finally, the protonolysis of **E** gave the desired product **3** along with the regeneration of Zn(II) cation as a catalytically active species. However, the details of the mechanism are not clear at present.

Scheme 5. Proposed Reaction Mechanism



In summary, we have developed the first facile and efficient $Zn(OTf)_2$-catalyzed direct phosphinylation of

various unprotected propargylic alcohols, furnishing a novel and rapid route to structurally diverse γ-ketophosphine oxides along with concurrent new C-P and C=O bonds formation. Mechanistic studies revealed that this reaction involved the Meyer-Schuster rearrangement followed by the phospha-Michael reaction. Importantly, the present reaction is performed without the need of a ligand and a base, and various useful γ-ketophosphine oxide moieties could be conveniently obtained in a simple one-step process. In addition, the use of inexpensive $Zn(OTf)_2$ as catalyst and easily accessible propargylic alcohols, operational simplicity, excellent regioselectivity, complete atom-economy and moderate to excellent yields, mean that this reaction will find broad applications in the construction of valuable γ-ketophosphine oxide frameworks in synthetic chemistry and pharmaceutical research.

Experimental Section

General Information

All reactions were performed under dry argon. Solvents were purified by standard methods unless otherwise noted. Commercially available reagents were used without further purification. ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were recorded on a 500 MHz spectrometer with TMS as internal standard (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C{^{1}H} NMR: $CDCl_3$ at 77.16 ppm). ^{31}P{^{1}H} NMR spectra were recorded on the same instrument with 85% H_3PO_4 as external standard. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration. New compounds were further characterized by HRMS and IR. High-resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. The products were purified by column chromatography on silica gel 300-400 mesh.

General Procedure for the Synthesis of γ-Ketophosphine Oxides

In an oven dried Schlenk tube, propargylic alcohol **1** (0.30 mmol), P(O)H **2** (0.45 mmol), $Ph_2P(O)OH$ (0.06 mmol, 13 mg) and $Zn(OTf)_2$ (0.12 mmol, 44 mg) were mixed in PhCl (2 mL) and stirred at 100 ℃ for 4 h under argon. The resulting mixture was directly purified by silica gel chromatography using a mixture of petroleum ether and ethyl acetate as eluent (petroleum ether/ethyl acetate = 2:1-1:3).

*3-(Diphenylphosphoryl)-1,3-diphenylpropan-1-one **3a***. 95% yield, 117 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01-7.97 (m, 2H), 7.85-7.83 (m, 2H), 7.54-7.45 (m, 6H), 7.39-7.32 (m, 5H), 7.27-7.23 (m, 2H), 7.16-7.13 (m, 2H), 7.11-7.08 (m, 1H), 4.48 (ddd, *J* = 9.9, 2.4, 2.4 Hz, 1H), 4.02 (ddd, *J* = 18.1, 10.4, 4.4 Hz, 1H), 3.40 (ddd, *J* = 18.1, 11.3, 2.4 Hz, 1H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 196.9 (d, J_{C-P} = 12.7 Hz), 136.6, 136.1 (d, J_{C-P} = 5.4 Hz), 133.5, 132.2 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 99.9 Hz), 131.7 (d, J_{C-P} = 94.5 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 8.2 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.1 (d, J_{C-P} = 5.4 Hz), 129.1 (d, J_{C-P} = 11.8 Hz), 128.7, 128.5 (d, J_{C-P} = 1.8 Hz), 128.3, 128.2 (d, J_{C-P} = 12.7 Hz), 127.3 (d, J_{C-P} = 2.7 Hz), 41.3 (d, J_{C-P} = 69.0 Hz), 39.2; ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz): δ 34.3; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{23}O_2PNa^+$ 433.1328; found 433.1328. Known compound.[17a]

*3-(Diphenylphosphoryl)-3-phenyl-1-(p-tolyl)propan-1-one **3b***. 70% yield, 89 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00-7.96 (m, 2H), 7.75-7.73 (m, 2H), 7.52-7.44 (m, 5H), 7.38-7.31 (m, 3H), 7.25-7.22 (m, 2H), 7.17-7.12 (m, 4H), 7.10-7.07 (m, 1H), 4.47 (ddd, *J* = 9.7, 2.3, 2.3 Hz, 1H), 3.99 (ddd, *J* = 18.0, 10.4, 4.4 Hz, 1H), 3.35 (ddd, *J* = 18.0, 11.3, 2.4 Hz, 1H), 2.34 (s, 3H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 196.5 (d, J_{C-P} = 12.7 Hz), 144.4, 136.2 (d, J_{C-P} = 5.5 Hz), 134.2, 132.2 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 98.1 Hz), 131.7 (d, J_{C-P} = 94.5 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 8.2 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.0 (d, J_{C-P} = 5.4 Hz), 129.4, 129.1 (d, J_{C-P} = 11.8 Hz), 128.5 (d, J_{C-P} = 1.8 Hz), 128.4, 128.2 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} =

2.7 Hz), 41.3 (d, J_{C-P} = 69.0 Hz), 39.0, 21.8; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}O_2PNa^+$ 447.1484; found 447.1483.

3-(Diphenylphosphoryl)-3-phenyl-1-(m-tolyl)propan-1-one ***3c***. 61% yield, 78 mg; white solid; mp 231.2-232.7 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.01-7.97 (m, 2H), 7.66-7.63 (m, 2H), 7.54-7.50 (m, 3H), 7.47-7.43 (m, 2H), 7.39-7.37 (m, 2H), 7.35-7.30 (m, 2H), 7.27-7.22 (m, 3H), 7.16-7.13 (m, 2H), 7.10-7.07 (m, 1H), 4.47 (ddd, *J* = 9.8, 2.3, 2.3 Hz, 1H), 4.02 (ddd, *J* = 18.2, 10.4, 4.3 Hz, 1H), 3.37 (ddd, *J* = 18.0, 11.1, 2.3 Hz, 1H), 2.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 197.0 (d, J_{C-P} = 13.6 Hz), 138.6, 136.6, 136.2 (d, J_{C-P} = 5.4 Hz), 134.3, 132.2 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 100.8 Hz), 131.7 (d, J_{C-P} = 94.5 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 8.2 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.1 (d, J_{C-P} = 5.4 Hz), 129.2 (d, J_{C-P} = 11.8 Hz), 128.9, 128.6, 128.5 (d, J_{C-P} = 2.7 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} = 2.7 Hz), 125.5, 41.2 (d, J_{C-P} = 69.0 Hz), 39.3, 21.4; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.5; IR (film) υ_{max}: 3055, 2920, 2850, 1681, 1180, 1118 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}O_2PNa^+$ 447.1484; found 447.1491.

3-(Diphenylphosphoryl)-1-(4-fluorophenyl)-3-phenylpropan-1-one ***3d***. 63% yield, 81 mg; white solid; mp 232.3-233.9 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.87-7.84 (m, 2H), 7.53-7.43 (m, 5H), 7.37-7.32 (m, 3H), 7.26-7.22 (m, 2H), 7.16-7.08 (m, 3H), 7.04-7.01 (m, 2H), 4.44 (ddd, *J* = 9.8, 2.4, 2.4 Hz, 1H), 3.97 (ddd, *J* = 17.9, 10.3, 4.6 Hz, 1H), 3.36 (ddd, *J* = 18.1, 11.1, 2.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 195.4 (d, J_{C-P} = 13.4 Hz), 166.0 (d, J_{C-F} = 255.4 Hz), 136.0 (d, J_{C-P} = 5.5 Hz), 133.0 (d, J_{C-P} = 2.6 Hz), 132.3 (d, J_{C-P} = 2.5 Hz), 131.7 (d, J_{C-P} = 100.8 Hz), 131.7 (d, J_{C-P} = 2.6 Hz), 131.6 (d, J_{C-P} = 94.5 Hz), 131.5 (d, J_{C-F} = 8.3 Hz), 131.2 (d, J_{C-P} = 8.8 Hz), 131.0 (d, J_{C-P} = 9.3 Hz), 130.0 (d, J_{C-P} = 5.5 Hz), 129.2 (d, J_{C-P} = 11.1 Hz), 128.5 (d, J_{C-F} = 1.8 Hz), 128.3 (d, J_{C-P} = 11.7 Hz), 127.3 (d, J_{C-P} = 2.6 Hz), 115.9 (d, J_{C-F} = 21.8 Hz), 41.3 (d, J_{C-P} = 68.9 Hz), 39.1; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.3; IR (film) υ_{max}: 3055, 2918, 1687, 1177, 1118 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{22}FO_2PH^+$ 429.1414; found 429.1420.

1-(4-Chlorophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one ***3e***. 53% yield, 71 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.77-7.75 (m, 2H), 7.55-7.49 (m, 3H), 7.47-7.43 (m, 2H), 7.36-7.32 (m, 5H), 7.26-7.22 (m, 2H), 7.15-7.08 (m, 3H), 4.44 (ddd, *J* = 9.9, 2.6, 2.6 Hz, 1H), 3.95 (ddd, *J* = 18.0, 10.3, 4.8 Hz, 1H), 3.36 (ddd, *J* = 18.0, 11.1, 2.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 195.9 (d, J_{C-P} = 13.6 Hz), 140.1, 136.0 (d, J_{C-P} = 5.4 Hz), 135.0, 132.3 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 100.8 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 94.5 Hz), 131.5 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.0 (d, J_{C-P} = 6.4 Hz), 129.7, 129.2 (d, J_{C-P} = 10.9 Hz), 129.1, 128.5 (d, J_{C-P} = 1.8 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 127.3 (d, J_{C-P} = 2.7 Hz), 41.4 (d, J_{C-P} = 69.0 Hz), 39.1; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.2; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}ClO_2PNa^+$ 467.0938; found 467.0938. Known compound.[17b]

1-(4-Bromophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one ***3f***. 73% yield, 107 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.69-7.67 (m, 2H), 7.54-7.49 (m, 5H), 7.47-7.43 (m, 2H), 7.36-7.32 (m, 3H), 7.26-7.22 (m, 2H), 7.16-7.13 (m, 2H), 7.11-7.08 (m, 1H), 4.43 (ddd, *J* = 10.0, 2.6, 2.6 Hz, 1H), 3.94 (ddd, *J* = 18.1, 10.3, 4.8 Hz, 1H), 3.35 (ddd, *J* = 18.0, 11.1, 2.6 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.9 (d, J_{C-P} = 13.6 Hz), 136.6, 136.1 (d, J_{C-P} = 6.4 Hz), 133.5, 132.2 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 99.9 Hz), 131.6 (d, J_{C-P} = 95.4 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 8.2 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 130.0 (d, J_{C-P} = 5.4 Hz), 129.1 (d, J_{C-P} = 10.9 Hz), 128.7, 128.5 (d, J_{C-P} = 1.8 Hz), 128.3, 128.3 (d, J_{C-P} = 12.9 Hz), 127.3 (d, J_{C-P} = 2.7 Hz), 41.3 (d, J_{C-P} = 69.0 Hz), 39.2; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}BrO_2PNa^+$ 511.0433; found 511.0425.

3-(Diphenylphosphoryl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one ***3g***. 86% yield, 114 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.83-7.81 (m, 2H), 7.71-7.67 (m, 1H), 7.48-7.43 (m, 4H), 7.37-7.36 (m, 2H), 7.33-7.30 (m, 1H), 7.24-7.20 (m, 2H), 7.14-7.11 (m, 2H), 7.09-7.06 (m, 1H), 6.82 (d, *J* = 9.1 Hz, 2H), 4.47 (ddd, *J* = 10.0, 2.4, 2.4 Hz, 1H), 3.97 (ddd, *J* = 17.9, 10.4, 4.4 Hz, 1H), 3.80 (s, 3H), 3.31

(ddd, *J* = 17.9, 11.3, 2.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 195.3 (d, J_{C-P} = 13.6 Hz), 163.8, 136.2 (d, J_{C-P} = 5.4 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 99.9 Hz), 131.6 (d, J_{C-P} = 94.5 Hz), 131.5 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 8.2 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.6, 130.0 (d, J_{C-P} = 5.4 Hz), 129.7, 129.1 (d, J_{C-P} = 11.8 Hz), 128.4 (d, J_{C-P} = 2.7 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} = 2.7 Hz), 113.8, 55.6, 41.3 (d, J_{C-P} = 69.0 Hz), 38.7; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.6; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}O_3PNa^+$ 463.1434; found 463.1431. Known compound.[17c]

1-(4-Acetylphenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one ***3h***. 84% yield, 114 mg; white solid; mp 208.5-209.0 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.95-7.88 (m, 4H), 7.52-7.50 (m, 2H), 7.47-7.43 (m, 2H), 7.36-7.32 (m, 4H), 7.25-7.21 (m, 2H), 7.14-7.07 (m, 3H), 4.44 (ddd, *J* = 9.8, 2.4, 2.4 Hz, 1H), 4.02 (ddd, *J* = 18.1, 10.3, 4.9 Hz, 1H), 3.41 (ddd, *J* = 18.1, 11.0, 2.4 Hz, 1H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 197.5, 196.6 (d, J_{C-P} = 12.7 Hz), 140.4, 139.6, 135.8 (d, J_{C-P} = 5.4 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.5 (d, J_{C-P} = 100.8 Hz), 131.4 (d, J_{C-P} = 9.1 Hz), 131.3 (d, J_{C-P} = 93.8 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 130.9 (d, J_{C-P} = 11.5 Hz), 129.9 (d, J_{C-P} = 5.4 Hz), 129.1 (d, J_{C-P} = 10.9 Hz), 128.5 (d, J_{C-P} = 1.8 Hz), 128.5 (d, J_{C-P} = 9.1 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 127.3 (d, J_{C-P} = 2.7 Hz), 41.3 (d, J_{C-P} = 69.0 Hz), 39.5, 27.0; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.3; IR (film) υ_{max}: 3357, 3059, 2920, 1686, 1177, 1033 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{25}O_3PNa^+$ 475.1434; found 475.1433.

3-(Diphenylphosphoryl)-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one ***3i***. 69% yield, 99 mg; white solid; mp 235.1-236.0 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.00-7.96 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 9.0 Hz, 2H), 7.55-7.44 (m, 5H), 7.37-7.32 (m, 3H), 7.26-7.22 (m, 2H), 7.15 (t, *J* = 7.0 Hz, 2H), 7.11-7.08 (m, 1H), 4.44 (ddd, *J* = 9.9, 2.6, 2.6 Hz, 1H), 4.00 (ddd, *J* = 18.1, 10.2, 4.9 Hz, 1H), 3.43 (ddd, *J* = 18.1, 11.0, 2.9 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.2 (d, J_{C-P} = 13.6 Hz), 139.2, 135.9 (d, J_{C-P} = 5.4 Hz), 134.7 (dd, J_{C-F} = 65.2 Hz, J_{C-P} = 32.5Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 100.8 Hz), 131.5 (d, J_{C-P} = 95.4 Hz), 131.5 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 129.9 (d, J_{C-P} = 6.4 Hz), 129.2 (d, J_{C-P} = 10.9 Hz), 128.6, 128.6 (d, J_{C-P} = 1.8 Hz), 128.3 (d, J_{C-P} = 11.8 Hz), 127.4 (d, J_{C-P} = 2.7 Hz), 125.8 (dd, J_{C-F} = 8.1 Hz, J_{C-P} = 3.6 Hz), 123.6 (d, J_{C-F} = 273.4 Hz), 41.4 (d, J_{C-P} = 69.0 Hz), 39.5; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.4; IR (film) υ_{max}: 3056, 2920, 1692, 1177, 1130 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}F_3O_2PH^+$ 479.1382; found 479.1389.

4-(3-(Diphenylphosphoryl)-3-phenylpropanoyl)-N-methylbenzamide ***3j***. 60% yield, 84 mg; pale yellow solid; mp 122.3-124.6 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.86-7.82 (m, 2H), 7.70-7.69 (d, *J* = 8.3 Hz, 2H), 7.59-7.57 (d, *J* = 7.8 Hz, 2H), 7.38-7.33 (m, 6H), 7.23-7.20 (m, 2H), 7.19 (s, 1H), 7.09-7.06 (m, 2H), 6.97-6.92 (m, 3H),4.36 (ddd, *J* = 9.7, 7.0, 3.0 Hz, 1H), 3.80 (ddd, *J* = 16.7, 9.8, 4.7 Hz, 1H), 3.25 (ddd, *J* = 18.8, 11.6, 2.6 Hz, 1H), 2.82 (d, *J* = 4.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.4 (d, J_{C-P} = 12.7 Hz), 167.4, 138.8, 138.2, 135.7 (d, J_{C-P} = 5.4 Hz), 132.4, 131.8, 131.3 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 100.8 Hz), 131.1 (d, J_{C-P} = 94.5 Hz), 131.1 (d, J_{C-P} = 9.1 Hz), 129.9 (d, J_{C-P} = 5.4 Hz), 129.2 (d, J_{C-P} = 10.9 Hz), 128.5, 128.3 (d, J_{C-P} = 11.8 Hz), 128.2, 127.6, 127.3 (d, J_{C-P} = 1.8 Hz), 41.2 (d, J_{C-P} = 69.0 Hz), 39.1; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.9; IR (film) υ_{max}: 3296, 3059, 2927, 1659, 1183, 1117 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{26}NO_3PNa^+$ 490.1543; found 490.1544.

3-(Diphenylphosphoryl)-1-phenyl-3-(p-tolyl)propan-1-one ***3k***. 80% yield, 102 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93-7.89 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.45-7.40 (m, 6H), 7.31-7.26 (m, 3H), 7.21-7.17 (m, 4H), 6.88 (d, *J* = 7.8 Hz, 2H), 4.41 (ddd, *J* = 9.8, 2.2, 2.2 Hz, 1H), 3.93 (ddd, *J* = 18.0, 10.4, 4.4 Hz, 1H), 3.30 (ddd, *J* = 18.1, 11.2, 2.3 Hz, 1H), 2.13 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.9 (d, J_{C-P} = 13.6 Hz), 136.8 (d, J_{C-P} = 2.7 Hz), 136.6, 133.5, 132.8 (d, J_{C-P} = 5.5 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 98.6 Hz), 131.8 (d, J_{C-P} = 95.4 Hz), 131.6 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 129.8 (d, J_{C-P} = 5.5 Hz), 129.2 (d, J_{C-P} = 1.8 Hz), 129.1 (d, J_{C-P} = 11.8 Hz), 128.7, 128.3, 128.2 (d, J_{C-P} =

11.8 Hz), 40.7 (d, $J_{C\text{-}P}$ = 69.0 Hz), 39.2, 21.2; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.4; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}O_2PNa^+$ 447.1484; found 447.1475. Known compound.[17c]

3-(Diphenylphosphoryl)-1-phenyl-3-(m-tolyl)propan-1-one ***3l***. 59% yield, 75 mg; white solid; mp 219.2-220.5 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.85-7.83 (m, 2H), 7.51-7.44 (m, 6H), 7.38-7.32 (m, 3H), 7.26-7.23 (m, 2H), 7.17-7.14 (m, 2H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 4.44 (ddd, *J* = 9.8, 2.4, 2.4 Hz, 1H), 4.02 (ddd, *J* = 18.1, 10.3, 4.5 Hz, 1H), 3.39 (ddd, *J* = 18.1, 11.4, 2.4 Hz, 1H), 2.18 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.9 (d, $J_{C\text{-}P}$ = 13.6 Hz), 137.9 (d, $J_{C\text{-}P}$ = 1.8 Hz), 136.6 (d, $J_{C\text{-}P}$ = 0.9 Hz), 135.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 133.5, 132.2 (d, $J_{C\text{-}P}$ = 1.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 100.8 Hz), 131.6 (d, $J_{C\text{-}P}$ = 94.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 8.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.7 (d, $J_{C\text{-}P}$ = 6.4 Hz), 129.1 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.7, 128.28, 128.27, 128.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.0 (d, $J_{C\text{-}P}$ = 2.7 Hz), 127.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 41.1 (d, $J_{C\text{-}P}$ = 69.0 Hz), 39.0, 21.5; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.5; IR (film) υ_{max}: 3055, 2921, 1687, 1180, 1117 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{25}O_2PH^+$ 425.1665; found 425.1667.

3-(Diphenylphosphoryl)-1-phenyl-3-(o-tolyl)propan-1-one ***3m***. 67% yield, 85 mg; white solid; mp 180.1-182.5 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.02-7.98 (m, 2H), 7.84-7.82 (m, 2H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 3H), 7.49-7.46 (m, 1H), 7.37-7.31 (m, 3H), 7.24-7.15 (m, 5H), 7.06-7.03 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 4.67 (ddd, *J* = 9.9, 2.4, 2.4 Hz, 1H), 4.07 (ddd, *J* = 18.3, 10.3, 4.5 Hz, 1H), 3.40 (ddd, *J* = 18.3, 11.2, 2.4 Hz, 1H), 2.06 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 197.1 (d, $J_{C\text{-}P}$ = 13.6 Hz), 137.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 136.5, 134.5 (d, $J_{C\text{-}P}$ = 5.4 Hz), 133.5, 132.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.0 (d, $J_{C\text{-}P}$ = 100.8 Hz), 131.9 (d, $J_{C\text{-}P}$ = 8.2 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.1 Hz), 130.7 (d, $J_{C\text{-}P}$ = 94.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 129.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 129.0 (d, $J_{C\text{-}P}$ = 2.6 Hz), 128.7, 128.3, 128.0 (d, $J_{C\text{-}P}$ = 11.8 Hz), 127.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 126.4 (d, $J_{C\text{-}P}$ = 2.7 Hz), 40.0, 36.3 (d, $J_{C\text{-}P}$ = 69.9 Hz), 19.8; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 35.0; IR (film) υ_{max}: 3057, 2953, 1686, 1198, 1117 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}O_2PNa^+$ 447.1484; found 447.1488.

3-(Diphenylphosphoryl)-3-(4-fluorophenyl)-1-phenylpropan-1-one ***3n***. 66% yield, 85 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.83-7.82 (m, 2H), 7.53-7.45 (m, 6H), 7.39-7.34 (m, 5H), 7.28-7.25 (m, 2H), 6.85-6.82 (m, 2H), 4.45 (ddd, *J* = 9.8, 2.5, 2.5 Hz, 1H), 3.97 (ddd, *J* = 18.1, 10.5, 4.3 Hz, 1H), 3.35 (ddd, *J* = 18.1, 10.8, 2.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.8 (d, $J_{C\text{-}P}$ = 13.6 Hz), 162.0 (dd, $J_{C\text{-}F}$ = 245.2 Hz, $J_{C\text{-}P}$ = 2.2 Hz), 136.5, 133.7, 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.9 (dd, $J_{C\text{-}P}$ = 5.4 Hz, $J_{C\text{-}F}$ = 3.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 100.8 Hz), 131.6 (dd, $J_{C\text{-}F}$ = 8.2 Hz, $J_{C\text{-}P}$ = 5.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.1 Hz), 131.4 (d, $J_{C\text{-}P}$ = 95.4 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.1 Hz), 129.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.8, 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.3, 115.4 (dd, $J_{C\text{-}F}$ = 21.8 Hz, $J_{C\text{-}P}$ = 1.5 Hz), 40.5 (d, $J_{C\text{-}P}$ = 69.0 Hz), 39.3; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}FO_2PNa^+$ 451.1234; found 451.1234.

3-(4-Chlorophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one ***3o***. 69% yield, 92 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95 (t, *J* = 9.2 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.50-7.46 (m, 6H), 7.37-7.31 (m, 5H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.43 (ddd, *J* = 8.3, 2.5, 2.5 Hz, 1H), 3.95 (ddd, *J* = 18.1, 10.7, 4.3 Hz, 1H), 3.34 (ddd, *J* = 18.1, 10.8, 2.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.6 (d, $J_{C\text{-}P}$ = 13.6 Hz), 136.4, 134.8 (d, $J_{C\text{-}P}$ = 5.4 Hz), 133.7, 133.2 (d, $J_{C\text{-}P}$ = 2.7 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 100.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 11.8 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.2 Hz), 131.3 (d, $J_{C\text{-}P}$ = 95.4 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.1 Hz), 129.2 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.8, 128.6, 128.4 (d, $J_{C\text{-}P}$ = 11.8 Hz), 128.3, 40.6 (d, $J_{C\text{-}P}$ = 69.0 Hz), 39.1; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.0; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}ClO_2PNa^+$ 467.0938; found 467.0941.

3-(4-Bromophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one ***3p***. 67% yield, 98 mg; white solid; ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 7.91-7.87 (m, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.44-7.40 (m, 6H), 7.29 (d, *J* = 7.4 Hz, 3H), 7.22-7.17 (m, 6H), 4.36 (ddd, *J* = 9.9, 2.3, 2.3 Hz, 1H), 3.89 (ddd, *J* = 18.2, 10.6, 4.3 Hz, 1H), 3.28 (ddd, *J* = 18.2, 10.8, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.6 (d, J_{C-P} = 13.6 Hz), 136.3, 135.3 (d, J_{C-P} = 5.4 Hz), 133.7, 132.3 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 2.7 Hz), 131.6 (d, J_{C-P} = 9.1 Hz), 131.6, 131.4 (d, J_{C-P} = 101.7 Hz), 131.3 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 93.6 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 129.2 (d, J_{C-P} = 10.9 Hz), 128.8, 128.5 (d, J_{C-P} = 11.8 Hz), 128.2, 121.4 (d, J_{C-P} = 2.7 Hz), 40.7 (d, J_{C-P} = 69.0 Hz), 39.0; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.9; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{27}H_{22}BrO_2PNa^+$ 511.0433; found 511.0424. Known compound.[17c]

4-(1-(Diphenylphosphoryl)-3-oxo-3-phenylpropyl)benzonitrile ***3q***. 41% yield, 54 mg; white solid; mp 216.9-218.0 ℃; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.95 (m, 2H), 7.83-7.82 (m, 2H), 7.56-7.45 (m, 8H), 7.43-7.36 (m, 5H), 7.30-7.26 (m, 2H), 4.49 (ddd, *J* = 10.2, 2.2, 2.2 Hz, 1H), 4.00 (ddd, *J* = 18.3, 10.6, 4.3 Hz, 1H), 3.41 (ddd, *J* = 18.3, 10.7, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.3 (d, J_{C-P} = 12.7 Hz), 142.2 (d, J_{C-P} = 5.4 Hz), 136.2, 133.9, 132.6 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 1.8 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 9.1 Hz), 131.2 (d, J_{C-P} = 100.8 Hz), 130.9 (d, J_{C-P} = 9.1 Hz), 130.8 (d, J_{C-P} = 96.3 Hz), 130.7 (d, J_{C-P} = 5.4 Hz), 129.4 (d, J_{C-P} = 10.9 Hz), 128.9, 128.6 (d, J_{C-P} = 11.8 Hz), 128.3, 118.9, 111.1 (d, J_{C-P} = 2.6 Hz), 41.7 (d, J_{C-P} = 67.2 Hz), 39.0; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.4; IR (film) υ_{max}: 3056, 2917, 1681, 1188, 1116 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{28}H_{22}NO_2PNa^+$ 458.1280; found 458.1285.

3-(Diphenylphosphoryl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one ***3r***. 88% yield, 126 mg; white solid; mp 258.3-260.0 ℃; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00-7.96 (m, 2H), 7.84-7.82 (m, 2H), 7.54-7.46 (m, 8H), 7.40-7.34 (m, 5H), 7.28-7.25 (m, 2H), 4.54 (ddd, *J* = 9.6, 2.2, 2.2 Hz, 1H), 4.01 (ddd, *J* = 18.3, 10.5, 4.3 Hz, 1H), 3.41 (ddd, *J* = 18.3, 11.0, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.4 (d, J_{C-P} = 12.7 Hz), 140.6 (d, J_{C-P} = 5.5 Hz), 136.3, 133.8, 133.5 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 131.4 (d, J_{C-P} = 8.2 Hz), 131.4 (d, J_{C-P} = 100.8 Hz), 131.1 (d, J_{C-P} = 95.4 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 130.3 (d, J_{C-P} = 5.5 Hz), 129.5 (d, J_{C-P} = 2.7 Hz), 129.3 (d, J_{C-P} = 10.9 Hz), 128.8, 128.5 (d, J_{C-P} = 11.8 Hz), 128.3, 125.4 (dd, J_{C-F} = 3.6 Hz, J_{C-P} = 1.9 Hz), 124.2 (dd, J_{C-F} = 274.3 Hz, J_{C-P} = 0.9 Hz), 41.3 (d, J_{C-P} = 68.1 Hz), 39.1; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.7; IR (film) υ_{max}: 3054, 2918, 1682, 1176, 1117 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{22}F_3O_2PH^+$ 479.1382; found 479.1388.

Methyl 4-(1-(diphenylphosphoryl)-3-oxo-3-phenylpropyl)benzoate ***3s***. 48% yield, 67 mg; white solid; mp 238.5-239.6 ℃; ^1H NMR ($CDCl_3$, 500 MHz): δ 8.00-7.97 (m, 2H), 7.84-7.81 (m, 4H), 7.73-7.69 (m, 1H), 7.54-7.46 (m, 7H), 7.39-7.33 (m, 3H), 7.27-7.24 (m, 2H), 4.53 (ddd, *J* = 9.8, 6.9, 2.3 Hz, 1H), 4.04 (ddd, *J* = 15.0, 10.5, 4.5 Hz, 1H), 3.83 (s, 3H), 3.41 (ddd, *J* = 18.2, 11.2, 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.5 (d, J_{C-P} = 12.7 Hz), 167.0, 141.7 (d, J_{C-P} = 5.4 Hz), 136.4, 133.7, 132.8 (d, J_{C-P} = 2.7 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 131.9 (d, J_{C-P} = 1.8 Hz), 131.4 (d, J_{C-P} = 8.2 Hz), 131.2 (d, J_{C-P} = 100.8 Hz), 131.2 (d, J_{C-P} = 95.6 Hz), 131.0 (d, J_{C-P} = 9.1 Hz), 130.0 (d, J_{C-P} = 5.4 Hz), 129.7 (d, J_{C-P} = 1.8 Hz), 129.2 (d, J_{C-P} = 11.5 Hz), 128.8, 128.4 (d, J_{C-P} = 11.8 Hz), 128.3, 52.2, 41.6 (d, J_{C-P} = 68.1 Hz), 39.0; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.9; IR (film) υ_{max}: 3057, 2922, 1684, 1435, 1185, 1111 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{25}O_4PNa^+$ 491.1383; found 491.1384.

3-(Diphenylphosphoryl)-1,3-di-p-tolylpropan-1-one ***3t***. 54% yield, 71 mg; white solid; mp 244.2-245.8 ℃; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.98-7.94 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.50-7.47 (m, 5H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.26-7.23 (m, 4H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 4.45 (ddd, *J* = 9.8, 2.2, 2.2 Hz, 1H), 3.95 (ddd, *J* = 17.9, 10.4, 4.4 Hz, 1H), 3.32 (ddd, *J* = 17.9, 11.2, 2.3 Hz, 1H), 2.33 (s, 3H), 2.18 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.5 (d, J_{C-P} = 13.6 Hz), 144.3, 136.7 (d, J_{C-P} = 2.7 Hz), 134.2, 133.0 (d, J_{C-P} = 6.4 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 132.0 (d, J_{C-P} = 99.9 Hz), 131.9 (d, J_{C-P} = 98.1 Hz), 131.5, 131.5 (d, J_{C-P} = 12.7 Hz), 131.2 (d, J_{C-P} = 9.1 Hz), 129.8 (d, J_{C-P} = 5.4 Hz), 129.4, 129.2 (d, J_{C-P} = 1.8 Hz), 129.0 (d, J_{C-P} =

11.8 Hz), 128.4, 128.2 (d, J_{C-P} = 11.8 Hz), 40.8 (d, J_{C-P} = 69.0 Hz), 39.0, 21.7, 21.2; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.4; IR (film) υ_{max}: 3054, 2919, 1680, 1181, 1116 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{27}O_2PH^+$ 439.1821; found 439.1825.

3-(Diphenylphosphoryl)-1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)propan-1-one ***3u***. 32% yield, 47 mg; white solid; mp 263.4-264.1 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93-7.89 (m, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.46-7.38 (m, 7H), 7.32-7.27 (m, 3H), 7.20-7.17 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 4.45 (ddd, *J* = 10.4, 2.3, 2.3 Hz, 1H), 3.91 (ddd, *J* = 17.8, 10.4, 3.8 Hz, 1H), 3.30 (ddd, *J* = 18.1, 11.0, 2.1 Hz, 1H), 2.27 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 194.8 (d, J_{C-P} = 12.7 Hz), 143.5, 139.5 (dd, J_{C-F} = 5.5 Hz, J_{C-P} = 1.9 Hz), 132.7, 131.2 (d, J_{C-F} = 2.7 Hz), 130.7, 130.3 (d, J_{C-P} = 97.2 Hz), 130.2 (d, J_{C-P} = 8.2 Hz), 130.0 (d, J_{C-P} = 96.3 Hz), 129.8 (d, J_{C-P} = 9.1 Hz), 129.1 (d, J_{C-P} = 5.5 Hz), 128.3, 128.0 (d, J_{C-P} = 11.8 Hz), 127.3, 127.2, 124.1 (d, J_{C-P} = 1.8 Hz), 124.1 (d, J_{C-P} = 1.8 Hz), 120.9 (d, J_{C-F} = 272.5 Hz), 40.1 (d, J_{C-P} = 68.1 Hz), 37.7, 20.6; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.7; IR (film) υ_{max}: 3460, 2921, 1677, 1327, 1074 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{24}F_3O_2PH^+$ 493.1539; found 493.1542.

1-(Diphenylphosphoryl)-1-phenylheptan-3-one ***3v***. 64% yield, 75 mg; white solid; mp 188.8-190.0 ℃; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.89-7.85 (m, 2H), 7.50-7.43 (m, 3H), 7. 38-7.35 (m, 2H), 7.26-7.20 (m, 3H), 7.17-7.14 (m, 2H), 7.10-7.03 (m, 3H), 4.17 (ddd, *J* = 17.6, 10.2, 2.6 Hz, 1H), 3.22 (ddd, *J* = 17.6, 9.9, 5.4 Hz, 1H), 3.82 (ddd, *J* = 17.6, 11.2, 1.9 Hz, 1H), 2.14-2.03 (m, 2H), 1.28-1.21 (m, 2H), 0.99 (tq, *J* = 7.2, 7.2 Hz, 2H), 0.67 (d, *J* = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 208.1 (d, J_{C-P} = 12.7 Hz), 136.1 (d, J_{C-P} = 5.4 Hz), 131.2 (d, J_{C-P} = 19.0 Hz), 132.1 (d, J_{C-P} = 1.8 Hz), 131.6, 131.5 (d, J_{C-P} = 5.4 Hz), 131.4 (d, J_{C-P} = 13.6 Hz), 131.1 (d, J_{C-P} = 8.2 Hz), 128.7 (d, J_{C-P} = 100.3 Hz), 128.6 (d, J_{C-P} = 100.8 Hz), 128.5 (d, J_{C-P} = 1.8 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} = 1.8 Hz), 43.1 (d, J_{C-P} = 80.0 Hz), 41.5, 41.0, 25.7, 22.2, 13.8; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.5; IR (film) υ_{max}: 3460, 2927, 1713, 1179, 1094 cm^{-1}; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{27}O_2PH^+$: 391.1821; found 391.1825.

1-(Diphenylphosphoryl)-4,4-dimethyl-1-phenylpentan-3-one ***3w***. 59% yield, 69 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90-7.86 (m, 2H), 7.48-7.44 (m, 3H), 7.38-7.34 (m, 2H), 7.25-7.22 (m, 3H), 7.16-7.13 (m, 2H), 7.09-7.02 (m, 3H), 4.20 (ddd, *J* = 14.2, 8.1, 2.4 Hz, 1H), 3.40 (ddd, *J* = 14.7, 10.2, 4.6 Hz, 1H), 2.77 (ddd, *J* = 17.6, 11.5, 2.0 Hz, 1H), 0.80 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 212.7 (d, J_{C-P} = 11.8 Hz), 136.3 (d, J_{C-P} = 5.5 Hz), 132.1 (d, J_{C-P} = 100.2 Hz), 132.1 (d, J_{C-P} = 2.7 Hz), 131.8 (d, J_{C-P} = 94.5 Hz), 131.5 (d, J_{C-P} =4.5 Hz), 131.5, 131.1 (d, J_{C-P} = 8.2 Hz), 130.0 (d, J_{C-P} = 5.4 Hz), 129.0 (d, J_{C-P} = 11.8 Hz), 128.4 (d, J_{C-P} = 1.8 Hz), 128.2 (d, J_{C-P} = 11.8 Hz), 127.2 (d, J_{C-P} = 2.7 Hz), 44.2, 41.3 (d, J_{C-P} = 69.0 Hz), 37.7, 25.9; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.1; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}O_2PNa^+$: 413.1641; found 413.1642.

3-(Bis(4-methylphenyl)phosphinyl)-1,3-diphenylpropan-1-one ***3x***. 44% yield, 58 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79-7.75 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.33-7.24 (m, 6H), 7.24-7.22 (m, 2H), 7.08 (t, *J* = 7.4 Hz, 2H), 7.04-7.01 (m, 1H), 6.98-6.96 (m, 2H), 4.35 (ddd, *J* = 9.9, 2.3, 2.3 Hz, 1H), 3.92 (ddd, *J* = 18.1, 10.4, 4.3 Hz, 1H), 3.31 (ddd, *J* = 18.0, 11.2, 2.3 Hz, 1H), 2.30 (s, 3H), 2.18 (s, 3H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.0 (d, J_{C-P} = 13.6 Hz), 141.5 (d, J_{C-P} = 2.7 Hz), 140.9 (d, J_{C-P} = 2.7 Hz), 135.7, 135.5 (d, J_{C-P} = 5.5 Hz), 132.4, 130.5 (d, J_{C-P} = 9.1 Hz), 130.2 (d, J_{C-P} = 9.1 Hz), 129.1 (d, J_{C-P} = 5.4 Hz), 129.8 (d, J_{C-P} = 11.8 Hz), 128.0 (d, J_{C-P} = 11.8 Hz), 127.9 (d, J_{C-P} = 102.6 Hz), 127.7, 127.6 (d, J_{C-P} = 97.2 Hz), 127.4 (d, J_{C-P} = 1.8 Hz), 127.2, 126.1 (d, J_{C-P} = 1.8 Hz), 40.4 (d, J_{C-P} = 69.0 Hz), 39.4, 20.7, 20.6; $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz): δ 34.5; HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}O_2PNa^+$: 461.1641; found 461.1641. Known compound.[8f]

3-(Bis(4-chlorophenyl)phosphoryl)-1,3-diphenylpropan-1-one ***3y***. 50% yield, 72 mg; white solid; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81-7.77 (m, 2H), 7.74-7.72 (m, 2H), 7.42-7.38 (m, 3H), 7.30-7.26 (m, 6H), 7.17-7.13

(m, 2H), 7.08 (t, J = 7.0 Hz, 2H), 7.05-7.02 (m, 1H), 4.35 (ddd, J = 9.6, 2.5, 2.5 Hz, 1H), 3.87 (ddd, J = 14.9, 9.7, 5.0 Hz, 1H), 3.29 (ddd, J = 18.1, 12.1, 2.6 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.5 (d, J_{C-P} = 12.7 Hz), 139.2 (d, J_{C-P} = 2.7 Hz), 138.4 (d, J_{C-P} = 3.6 Hz), 136.4, 135.7 (d, J_{C-P} = 5.4 Hz), 133.7, 132.9 (d, J_{C-P} = 10.0 Hz), 132.5 (d, J_{C-P} = 10.0 Hz), 130.1 (d, J_{C-P} = 101.7 Hz), 130.0 (d, J_{C-P} = 6.4 Hz), 129.8 (d, J_{C-P} = 95.4 Hz), 129.6 (d, J_{C-P} = 11.8 Hz), 128.8 (d, J_{C-P} = 1.8 Hz), 128.8, 128.7 (d, J_{C-P} = 3.6 Hz), 128.7, 128.3, 127.6 (d, J_{C-P} = 2.7 Hz), 41.2 (d, J_{C-P} = 70.8 Hz), 39.1; $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 33.3; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{21}Cl_2O_2PH^+$: 479.0729; found 479.0728. Known compound.[17c]

Diethyl (3-oxo-1,3-diphenylpropyl)phosphonate ***3z***. 15% yield, 16 mg; colorless oil; ^1H NMR ($CDCl_3$, 500 MHz): δ 7.86 (J = 8.9 Hz, 2H), 7.48-7.45 (m, 1H), 7.37-7.34 (m, 4H), 7.21 (t, J = 7.5 Hz, 2H), 7.13 (t, J = 7.0 Hz, 1H), 4.03-3.96 (m, 2H), 3.93-3.80 (m, 2H), 3.70-3.56 (m, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 196.5 (d, J_{C-P} = 15.4 Hz), 136.8, 136.2 (d, J_{C-P} = 7.3 Hz), 133.4, 129.4 (d, J_{C-P} = 6.4 Hz), 128.8, 128.6 (d, J_{C-P} = 2.7 Hz), 128.2, 127.4 (d, J_{C-P} = 2.7 Hz), 63.1 (d, J_{C-P} = 6.4 Hz), 62.1 (d, J_{C-P} = 7.3 Hz), 39.3, 39.2 (d, J_{C-P} = 139.9 Hz), 16.5 (d, J_{C-P} = 6.4 Hz), 16.3 (d, J_{C-P} = 6.4 Hz); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 28.6; HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{23}O_4PH^+$: 347.1407; found 347.1404. Known compound.[17d]

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Supporting Information Available: Copies of compound NMR spectra and crystallographic data (CIF file) of **3n** are available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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