利用自由基引发的 1,2-炔基迁移实现非活性烯烃的炔膦酰化

张 萍^{a,c} 石浩楠^b 张天舒^a 蔡佩君^{*,a} 姜 波^b 屠树江^{*,b}^(a) 中国矿业大学化工学院 江苏徐州 221116)^(b) 江苏师范大学化学与材料科学学院 江苏徐州 221116)^(c) 江苏省徐州医药高等职业学校 江苏徐州 221116)

摘要 研究了 1,4-烯炔衍生物与二芳基膦氧化物在银介导下发生的炔酰化反应. 该反应利用自由基引发的 1,2-炔基迁移策略合成了一系列 γ -酮膦氧化物, 产率适中. 该反应机理可能涉及膦中心自由基与乙烯基的加成、3-*exo-dig* 环化和 1,2-炔基迁移等连续的过程, 一步形成了 C—P、C—C 键等化学键, 实现了非活性烯烃的双官能化.

关键词 1,4-烯炔衍生物; 炔膦酰化反应; γ -酮膦氧化物; 炔基迁移; 自由基化学

Alkynylphosphonation of Unactivated Olefins via Radical-Triggered 1,2-Alkynyl Migration

Zhang, Ping^a Shi, Haonan^b Zhang, Tianshu^a Cai, Peijun^{*,a}
Jiang, Bo^b Tu, Shujiang^{*,b}^(a) School of Chemical Engineering & Technology, China University of Mining and Technology, Xuzhou, Jiangsu 221116)^(b) School of Chemistry & Materials Science, Jiangsu Normal University, Xuzhou, Jiangsu 221116)^(c) Jiangsu Provincial Xuzhou Pharmaceutical Vocational College, Xuzhou, Jiangsu 221116)

Abstract A silver-mediated alkynylphosphonation of 1,4-enynes with diarylphosphine oxides has been developed, by which a wide range of γ -ketophosphine oxides with moderate to good yields were synthesized through radical 1,2-alkynyl migration. The transformation proceeded with sequential P-centered radical addition to vinyl unit, 3-*exo-dig* cyclization and 1,2-alkynyl migration, resulting in the bond-forming events including C—P and C—C bonds to realize difunctionalization of unactivated olefins.

Keywords 1,4-enynes; alkynylphosphonation; γ -ketophosphine oxides; alkynyl migration; radical chemistry

1 Introduction

As highly important and valuable feedstocks, alkenes have been widely utilized for myriad challenging and intriguing transformations in synthetic science due to their unique reactivity profile.^[1] Specifically, radical-induced direct 1,2-difunctionalization of alkenes has emerged as a significant synthetic tool for the collection of highly functionalized molecules by incorporating two functional groups across the C=C π system.^[2] A extensive survey of literature reports revealed that the vast majority of well-developed methods generally depend on activated alkenes, due to its nascent alkyl radical needs to be stabilized by adjacent functional groups (e.g. aryl, carbonyl, heteroatom) via p- π conjugate effect (Scheme 1, path i).^[3]

However, radical induced difunctionalization of unactivated alkenes remains elusive. On the other hand, the radical functionality migration enables to reconstruct the molecular structures and assemble significant compounds which are not available through other methods.^[4] Such reaction category provides a new synthetic protocol for radical difunctionalization of unactivated alkenes.^[5] Numerous state-of-the-art works for intramolecular functionality migration strategies, such as arylation,^[6] cyanation,^[7] imidization,^[8] formylation,^[9] heteroarylation^[10] and alkenylation^[11] have been reported (Scheme 1, pathway iii). Very recently, Zhu group^[12] pioneered the intramolecular distal alkynyl migration for alkynylation of unactivated olefins (Scheme 1, path ii). However, these cases were restricted to distal 1,4- or 1,5-alkynyl migration. To

* Corresponding authors. E-mail: pjcai@cumt.edu.cn; laotu@jnsu.edu.cn

Received September 4, 2019; revised October 16, 2019; published online October 25, 2019.

Project supported by the Fundamental Research Funds for the Central Universities (No. JH180263).

中央高校基本科研专项资金基金(No. JH180263)资助项目.

achieve radical 1,2-alkynyl migration, an isopropenyl group was adopted to replace the vinyl moiety in the enyne substrates to prepare a class of new 1,4-enynes, and it found that these substrates underwent radical 3-*exo-dig* cyclization and C—C σ bond cleavage to complete their 1,2-alkynyl migration triggered by C-centered or H radical species (Scheme 1, path iii).^[13] To further investigate the generality of radical 1,2-alkynyl migration of 1,4-enynes and expand the family of α -alkynyl ketones, we attempted to utilize diarylphosphine oxides as P-centered radical precursors to trigger 1,2-alkynyl migration of 1,4-enynes to construct γ -ketophosphine oxides due to such compounds have been found to exhibit wide-spectrum biological activities and unique properties.^[14] Herein, we describe a silver-mediated alkynylphosphonation of 1,4-enynes with diarylphosphine oxides, in which a series of α -alkynyl γ -ketophosphine oxides were obtained through a sequential P-centered radical addition, 3-*exo-dig* cyclization and 1,2-alkynyl migration cascade (Scheme 1, path iv).^[15]

Scheme 1 Profiles of radical-mediated functionalization of alkenes

2 Results and discussion

Our initial investigations focused on identifying the optimized conditions by selecting the preformed 1,4-enyne **1a** and diphenylphosphine oxide **2a** as the model substrates. The reaction of **1a** with **2a** was conducted in the presence of $AgNO_3$ (2.0 equiv.) in a mixed solvent of CH_3CN and H_2O at 80 $^\circ C$, and the expected migration product **3a** was generated, albeit with a low 17% yield (Table 1, Entry 1). Subsequently, several silver salts such as $AgOAc$, Ag_2CO_3 and Ag_2O were screened, indicating that $AgOAc$ substantially suppressed the formation of **3a** (Entry 2) while the latter two could accelerate this radical transformation (Entries 3, 4) and the last one showed the

best oxidation ability, offering in 39% yield (Entry 4). The following screening of other aprotic solvents, such as 1,2-dichloroethane (DCE), methanol, *N,N*-dimethylformamide (DMF) and 1,4-dioxane revealed that all these solvents have no positive effect on the yield of **3a** as compared with CH_3CN (Entries 5~8 vs Entry 4). Adjusting the amount of Ag_2O to 1.0 equiv. was not beneficial for this transformation with observation of unconsumed starting materials (Entry 9). An increase of the amount of Ag_2O to 3.0 equiv. led to a higher yield of product **3a** (53%, Entry 10). The yield of **3a** levelled off when the loading of Ag_2O was further increased (Entry 11). Next, we attempted to change reaction temperatures to assess the effect on the efficiency of the reaction. After careful investigations, the reaction temperature was found to have remarkable influence on this radical transformation (Entries 12, 13). Elevating reaction temperature from 80 $^\circ C$ to 100 $^\circ C$ facilitated the reaction process, and an almost full consumption of the starting material was observed at 100 $^\circ C$, giving 64% yield. Further raising the temperature to 120 $^\circ C$ did not improve the conversion of **1a** into **3a** (Entry 14). Without H_2O , the lower conversion was observed (Entry 15).

Table 1 Optimization of reaction conditions^a

Entry	Ag salt (equiv.)	Solvent	<i>t</i> / $^\circ C$	Yield ^b /%
1	$AgNO_3$ (2.0)	CH_3CN/H_2O	80	17
2	$AgOAc$ (2.0)	CH_3CN/H_2O	80	6
3	Ag_2CO_3 (2.0)	CH_3CN/H_2O	80	26
4	Ag_2O (2.0)	CH_3CN/H_2O	80	39
5	Ag_2O (2.0)	DCE/ H_2O	80	Trace
6	Ag_2O (2.0)	MeOH/ H_2O	80	20
7	Ag_2O (2.0)	DMF/ H_2O	80	20
8	Ag_2O (2.0)	1,4-Dioxane/ H_2O	80	17
9	Ag_2O (1.0)	CH_3CN/H_2O	80	18
10	Ag_2O (3.0)	CH_3CN/H_2O	80	53
11	Ag_2O (4.0)	CH_3CN/H_2O	80	53
12	Ag_2O (3.0)	CH_3CN/H_2O	90	57
13	Ag_2O (3.0)	CH_3CN/H_2O	100	64
14	Ag_2O (3.0)	CH_3CN/H_2O	110	63
15	Ag_2O (3.0)	CH_3CN	100	45

^a Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), silver salt, organic solvent (3.0 mL), H_2O (0.5 mL). ^b Isolated yield based on **1a**.

With the optimized reaction conditions in hand, we then set out to study the generality of the migration reaction by examining 1,4-enynes and diarylphosphine oxide components (Table 2). 1,4-Enynes **1** with diverse substituents on the arylalkynyl moiety (R) were first investigated in combination with diphenylphosphine oxide (**2a**) under the standard conditions. Both electron-poor and electron-rich

groups at different positions were accommodated well, accessing the corresponding products **3b**~**3n** in 40%~68% yields. The different substituents including fluoro, chloro, bromo, methyl, ethyl, *tert*-butyl, and methoxy could be successfully engaged in the current migration reaction. Among them, a sterically encumbered 2-chlorophenyl and 2-methylphenyl analogues were appropriate reaction partner, enabling the radical relay alkynyl migration process to provide the corresponding products **3e** and **3h** in 52% and 50% yields, respectively. Moreover, 2-thienyl analogue **1l** was proven to be favorable for this alkynyl migration. Liner *n*-propyl group (**1n**) exhibited good compatibility, as evident by the corresponding product **3n** was offered in 40% yield. Next, the possible variation in the R¹ substituents attached by a quaternary carbon of 1,4-enynes was examined. Diverse substituents such as aryl and heteroaryl can all tolerate under the redox-neutral conditions, delivering products **3o**~**3w** in acceptable yields. All tested aryl groups, relative to tertiary alcohol moiety, with varied functionalities and substitution patterns underwent this radical alkynyl migration process, giving access to the corresponding products **3o**~**3w**. Various functional groups, such as chloro, fluoro, methyl, ethyl, *tert*-butyl, methoxy and trifluoromethyl, all worked well. Alternatively, *n*-hexyl 1,4-enyne **1x** was readily converted into product **3x** in 47% yield. Next, bis(3,5-dimethylphenyl)phosphine oxide (**2b**) was used as a P-centered radical precursor, which could participate in the P-centered radical relay approach to furnish the corresponding γ -keto-phosphine oxide **3y**, albeit with a low yield (Table 2).

To gain more insight into this reaction, radical inhibitors such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and butylhydroxytoluene (BHT) were subjected to the reaction system under the standard conditions (Scheme 3a), and the reaction process was completely suppressed without observation of product **3a**. These results indicated that this transformation may include a P-centered radical process (Scheme 2a). The removal of the methyl from the terminal olefin unit led to a complex reaction system under the standard conditions, showing that the methyl group linked to the olefin unit was crucial for this transformation (Scheme 2b).

Scheme 2 Control experiments

On the basis of the above results and previous reports,^[16] a reasonable mechanism is depicted in Scheme 3. Initially,

Table 2 Substrate scope

^a All reactions were carried out in a seal tube in the presence of **1** (0.2 mmol), **2** (0.2 mmol), CH₃CN (3.0 mL), Ag₂O (3.0 equiv.), H₂O (0.5 mL), 100 °C. Isolated yields based on **1**

diphenylphosphine oxide is oxidized by Ag(I) to form radical intermediate **A**, together with Ag(0). The addition of radical **A** to the terminal alkene unit of 1,4-enynes **1** provides radical intermediate **B**, followed by 3-*exo-dig* cyclization ("anti-Baldwin" rules) and alkynyl migration (the homolysis of C—C bond) to produce hydroxyalkyl radical **D**. Finally, a single electron oxidation of the intermediate **D** leads to the carbon cation **E**, which releases a proton to give the final products **3**.

3 Conclusions

In summary, starting from easily preformed 1,4-enynes and diarylphosphine oxides, a silver-mediated alkynyl-phosphonation of unactivated olefins have been developed for the synthesis of a wide range of γ -ketophosphine oxides through radical intramolecular 1,2-alkynyl migration of 1,4-enynes. The reaction proceeded with sequential P-

Scheme 4 Plausible reaction mechanism

centered radical addition to vinyl unit, 3-*exo-dig* cyclization and 1,2-alkynyl migration, resulting in the multiple bond-forming events including C—P and C—C bonds in a one-pot manner. Further application of this attractive radical 1,2-alkynyl migration strategy will be conducted in due course.

4 Experimental section

4.1 General information

^1H NMR (^{13}C NMR, ^{31}P NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in CDCl_3 ($\text{DMSO}-d_6$). HRMS (ESI) was determined by using a microTOF-QII HRMS/MS instrument (BRUKER).

4.1.1 General procedure for the synthesis of compounds **3a**~**3y**

In a Schlenk tube, 1,4-enynes, (0.2 mmol), diphenylphosphine oxide (0.2 mmol), Ag_2O (0.6 mmol), acetonitrile (3.0 mL), and H_2O (0.5 mL) were continuously added. Then the tube was sealed with a Teflon lined cap and stirred at 100°C for 10 h until complete consumption of starting material as monitored by thin-layer chromatography (TLC, petroleum ether/ethyl acetate, $V:V=1:1$) analysis. Then the solvent was evaporated under reduced pressure, and the crude products were purified by flash column chromatography on silica gel with petroleum ether/ EtOAc ($V:V=5:1$) as the eluent to give the desired products **3a**~**3y**.

2-[(Diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methyl-4-phenylbut-3-yn-1-one (**3a**): Yellow oil. 59.7 mg, 64% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.36~8.30 (m, 2H), 7.88~7.78 (m, 4H), 7.48~7.41 (m, 6H), 7.28 (d, $J=7.6$ Hz, 1H), 7.24~7.18 (m, 2H), 7.15~7.10 (m, 2H), 6.98 (d, $J=7.2$ Hz, 2H), 3.49~3.41 (m, 1H), 2.98~2.88 (m, 1H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.5 (d, $J_{\text{C-P}}=6.7$ Hz), 165.2 (d, $J_{\text{C-P}}=126.4$ Hz), 132.6 (d, $J_{\text{C-F}}=9.0$ Hz), 131.4, 131.3, 131.0 (d, $J_{\text{C-P}}=9.3$ Hz), 130.7 (d, $J_{\text{C-P}}=9.1$ Hz), 128.6 (d, $J_{\text{C-P}}=5.0$ Hz), 128.5 (d, $J_{\text{C-P}}=5.2$ Hz), 128.3, 127.9, 122.3, 115.0 (d, $J_{\text{C-F}}=$

21.6 Hz), 90.5 (d, $J_{\text{C-P}}=6.2$ Hz), 88.4, 44.2 (d, $J_{\text{C-P}}=3.4$ Hz), 39.0 (d, $J_{\text{C-P}}=71.8$ Hz), 28.7 (d, $J_{\text{C-P}}=6.3$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.53; IR (KBr) ν : 3056, 2927, 2197, 1685, 1598, 1437, 1232, 756, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{24}\text{FO}_2\text{PNa}$ [$\text{M} + \text{Na}$] $^+$ 489.1396, found 489.1409.

2-[(Diphenylphosphoryl)methyl]-1,4-bis(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3b**): Yellow oil. 65.9 mg, 68% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.35~8.28 (m, 2H), 7.89~7.77 (m, 4H), 7.50~7.39 (m, 6H), 7.16~7.10 (m, 2H), 6.96~6.87 (m, 4H), 3.50~3.42 (m, 1H), 2.94~2.85 (m, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.6 (d, $J_{\text{C-P}}=8.0$ Hz), 163.1, 132.5, 131.4, 131.1 (d, $J_{\text{C-P}}=9.2$ Hz), 130.7 (d, $J_{\text{C-P}}=9.1$ Hz), 128.5 (d, $J_{\text{C-P}}=11.7$ Hz), 128.2 (d, $J_{\text{C-F}}=22.3$ Hz), 127.8, 127.3, 122.6, 113.2, 91.0 (d, $J_{\text{C-P}}=6.0$ Hz), 88.1, 55.5, 43.9 (d, $J_{\text{C-P}}=3.4$ Hz), 38.6 (d, $J_{\text{C-P}}=72.2$ Hz), 28.4 (d, $J_{\text{C-P}}=5.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.83; IR (KBr) ν : 3047, 2931, 2166, 1684, 1588, 1497, 1183, 844, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{F}_2\text{O}_2\text{PNa}$ [$\text{M} + \text{Na}$] $^+$ 507.1301, found 507.1315.

2-[(Diphenylphosphoryl)methyl]-1-(3-fluorophenyl)-4-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3c**): Yellow oil. 59.1 mg, 61% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.35~8.28 (m, 2H), 7.89~7.77 (m, 4H), 7.50~7.39 (m, 6H), 7.16~7.10 (m, 2H), 6.96~6.87 (m, 4H), 3.50~3.42 (m, 1H), 2.94~2.85 (m, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.4 (d, $J_{\text{C-P}}=6.7$ Hz), 165.2 (d, $J_{\text{C-F}}=252.8$ Hz), 162.5 (d, $J_{\text{C-F}}=248.0$ Hz), 133.2 (d, $J_{\text{C-P}}=9.4$ Hz), 132.5 (d, $J_{\text{C-P}}=9.1$ Hz), 131.4 (d, $J_{\text{C-P}}=3.1$ Hz), 131.0 (d, $J_{\text{C-F}}=9.2$ Hz), 130.7 (d, $J_{\text{C-F}}=9.1$ Hz), 128.6 (d, $J_{\text{C-P}}=6.2$ Hz), 128.5 (d, $J_{\text{C-P}}=6.4$ Hz), 118.4 (d, $J_{\text{C-F}}=3.5$ Hz), 115.2 (d, $J_{\text{C-F}}=13.4$ Hz), 115.0 (d, $J_{\text{C-F}}=13.1$ Hz), 90.2 (d, $J_{\text{C-P}}=4.6$ Hz), 87.42, 44.1 (d, $J_{\text{C-P}}=3.5$ Hz), 38.9 (d, $J_{\text{C-P}}=72.0$ Hz), 28.7 (d, $J_{\text{C-P}}=6.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.53; IR (KBr) ν : 3027, 2927, 2161, 1683, 1598, 1504, 1183, 844, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{F}_2\text{O}_2\text{PNa}$ [$\text{M} + \text{Na}$] $^+$ 507.1301, found 507.1318.

4-(3-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3d**): Yellow oil. 58.1 mg, 58% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.31~8.20 (m, 2H), 7.83~7.73 (m, 4H), 7.47~7.35 (m, 6H), 7.22~7.17 (m, 1H), 7.12~7.05 (m, 3H), 6.86~6.80 (m, 1H), 6.77~6.66 (m, 1H), 3.47~3.38 (m, 1H), 2.87~2.79 (m, 1H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.3 (d, $J_{\text{C-P}}=6.9$ Hz), 166.3 (d, $J_{\text{C-F}}=253.2$ Hz), 133.8, 132.5 (d, $J_{\text{C-F}}=9.1$ Hz), 131.6 (d, $J_{\text{C-F}}=3.3$ Hz), 131.5 (d, $J_{\text{C-P}}=4.3$ Hz), 131.3, 131.0 (d, $J_{\text{C-P}}=9.4$ Hz), 130.7 (d, $J_{\text{C-P}}=9.1$ Hz), 129.4, 129.2, 128.7 (d, $J_{\text{C-P}}=4.5$ Hz), 128.6 (d, $J_{\text{C-P}}=4.8$ Hz), 124.0, 115.1 (d, $J_{\text{C-F}}=21.7$ Hz), 91.8 (d, $J_{\text{C-P}}=5.9$ Hz), 87.2, 44.2 (d, $J_{\text{C-P}}=3.7$ Hz), 38.9 (d, $J_{\text{C-P}}=72.0$ Hz), 28.8 (d, $J_{\text{C-P}}=6.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.64; IR (KBr) ν : 3057, 2928, 2167, 1686, 1598, 1504, 1189, 844, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{ClFO}_2\text{PNa}$ [$\text{M} + \text{Na}$] $^+$

523.1006, found 523.1021.

4-(2-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3e**): Yellow oil. 52.1 mg, 52% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.37~8.29 (m, 2H), 7.82~7.71 (m, 4H), 7.40~7.32 (m, 6H), 7.23 (d, $J=8.0$ Hz, 1H), 7.15~7.10 (m, 1H), 7.06~6.98 (m, 3H), 6.83~6.77 (m, 1H), 3.46~3.37 (m, 1H), 2.96~2.87 (m, 1H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 196.9 (d, $^8J_{\text{C-P}}=6.1$ Hz), 165.2 (d, $^1J_{\text{C-F}}=252.8$ Hz), 135.7, 133.5, 132.8 (d, $^6J_{\text{C-F}}=9.0$ Hz), 131.4 (d, $^{13}J_{\text{C-F}}=2.5$ Hz), 131.0 (d, $^4J_{\text{C-P}}=9.4$ Hz), 130.7 (d, $^5J_{\text{C-P}}=9.2$ Hz), 129.4, 128.9, 128.6 (d, $^{11}J_{\text{C-P}}=4.7$ Hz), 128.5 (d, $^{10}J_{\text{C-P}}=4.8$ Hz), 126.08, 122.24, 115.0 (d, $^3J_{\text{C-F}}=21.7$ Hz), 95.6 (d, $^9J_{\text{C-P}}=6.0$ Hz), 85.23, 44.4 (d, $^{12}J_{\text{C-P}}=3.5$ Hz), 39.2 (d, $^2J_{\text{C-P}}=71.3$ Hz), 28.7 (d, $^7J_{\text{C-P}}=6.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.39; IR (KBr) ν : 3056, 2928, 2264, 1683, 1597, 1485, 1190, 824, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{ClFO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 523.1006, found 523.1018.

4-(4-Bromophenyl)-2-[(diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3f**): Yellow solid; 67.6 mg, 62% yield. m.p. 101~102 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.29~8.27 (m, 2H), 7.85~7.76 (m, 4H), 7.48~7.38 (m, 6H), 7.32 (d, $J=8.0$ Hz, 2H), 7.13~7.08 (m, 2H), 6.80 (d, $J=8.4$ Hz, 2H), 3.49~3.43 (m, 1H), 2.92~2.86 (m, 1H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.2 (d, $J=6.6$ Hz), 166.5 (d, $^1J_{\text{C-F}}=252.9$ Hz), 163.92 (s), 132.8, 132.5 (d, $^4J_{\text{C-P}}=8.9$ Hz), 131.5, 131.2, 131.0 (d, $^2J_{\text{C-P}}=9.4$ Hz), 130.8 (d, $^3J_{\text{C-P}}=9.1$ Hz), 128.7 (d, $^3J_{\text{C-F}}=8$ Hz), 128.5 (d, $^7J_{\text{C-P}}=5.1$ Hz), 122.6, 121.2, 115.2 (d, $^2J_{\text{C-F}}=21.6$ Hz), 91.8 (d, $^6J_{\text{C-P}}=5.8$ Hz), 87.4, 44.2 (d, $^4J_{\text{C-F}}=3.5$ Hz), 39.21 (d, $^1J_{\text{C-P}}=71.9$ Hz), 28.7 (d, $^5J_{\text{C-P}}=6.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.21; IR (KBr) ν : 3056, 2928, 2234, 1683, 1485, 1437, 1190, 824, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{BrFO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 567.0501, found 567.0514.

2-[(Diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methyl-4-(*m*-tolyl)but-3-yn-1-one (**3g**): Yellow oil. 46.1 mg, 48% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.30~8.24 (m, 2H), 7.83~7.73 (m, 4H), 7.47~7.41 (m, 2H), 7.40~7.36 (m, 4H), 7.10~7.03 (m, 4H), 6.78~6.73 (m, 1H), 6.67 (d, $J=2.0$ Hz, 1H), 3.42~3.35 (m, 1H), 2.91~2.83 (m, 1H), 2.24 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.7 (d, $^7J_{\text{C-P}}=6.8$ Hz), 165.2 (d, $^1J_{\text{C-F}}=252.7$ Hz), 137.6, 132.6 (d, $^5J_{\text{C-F}}=9.1$ Hz), 132.0, 131.6 (d, $^{14}J_{\text{C-F}}=3.3$ Hz), 131.5, 131.4 (d, $^{13}J_{\text{C-F}}=3.4$ Hz), 131.1 (d, $^4J_{\text{C-F}}=9.3$ Hz), 130.8 (d, $^6J_{\text{C-P}}=9.1$ Hz), 129.2, 128.6 (d, $^{10}J_{\text{C-P}}=5.1$ Hz), 128.5 (d, $^{11}J_{\text{C-P}}=4.9$ Hz), 128.5, 128.4, 127.8, 122.2, 115.1 (d, $^3J_{\text{C-F}}=21.7$ Hz), 90.2 (d, $^9J_{\text{C-P}}=6.2$ Hz), 88.6, 44.2 (d, $^{12}J_{\text{C-P}}=3.6$ Hz), 39.0 (d, $^2J_{\text{C-P}}=71.9$ Hz), 28.7 (d, $^8J_{\text{C-P}}=6.4$ Hz), 21.2; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.64; IR (KBr) ν : 3056, 2924, 2216, 1684, 1505, 1437, 1192, 844, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{FO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 503.1552, found 503.1563.

2-[(Diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methyl-4-(*o*-tolyl)but-3-yn-1-one (**3h**): Yellow solid; 52.9

mg, 50% yield. m.p. 98~99 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.37~8.27 (m, 2H), 7.87~7.75 (m, 4H), 7.45~7.35 (m, 6H), 7.19~7.15 (m, 1H), 7.13~7.06 (m, 3H), 7.04~6.99 (m, 1H), 6.94~6.89 (m, 1H), 3.50~3.42 (m, 1H), 3.03~2.92 (m, 1H), 2.16 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.6 (d, $^9J_{\text{C-P}}=6.2$ Hz), 165.1 (d, $^1J_{\text{C-F}}=252.6$ Hz), 140.1, 132.6 (d, $^6J_{\text{C-F}}=9.0$ Hz), 131.9, 131.7 (d, $^{13}J_{\text{C-F}}=3.1$ Hz), 131.4 (d, $^{14}J_{\text{C-P}}=2.5$ Hz), 130.9 (d, $^4J_{\text{C-P}}=9.2$ Hz), 130.7 (d, $^5J_{\text{C-P}}=9.1$ Hz), 129.18, 128.5 (d, $^{10}J_{\text{C-P}}=4.1$ Hz), 128.4 (d, $^{11}J_{\text{C-P}}=4.1$ Hz), 128.3, 125.2, 122.1, 115.0 (d, $^3J_{\text{C-F}}=21.5$ Hz), 94.3 (d, $^7J_{\text{C-P}}=6.4$ Hz), 87.5, 44.5 (d, $^{12}J_{\text{C-P}}=4.1$ Hz), 39.5 (d, $^2J_{\text{C-P}}=71.5$ Hz), 28.8 (d, $^8J_{\text{C-P}}=6.4$ Hz), 20.5; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.29; IR (KBr) ν : 3057, 2927, 2220, 1686, 1598, 1437, 1190, 846, 696 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{FO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 503.1552, found 503.1567.

2-[(Diphenylphosphoryl)methyl]-4-(4-ethylphenyl)-1-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3i**): Yellow oil. 54.4 mg, 55% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.31~8.24 (m, 2H), 7.84~7.72 (m, 4H), 7.46~7.35 (m, 6H), 7.09~6.97 (m, 4H), 6.87~6.80 (m, 2H), 3.42~3.33 (m, 1H), 2.92~2.84 (m, 1H), 2.62~2.56 (m, 2H), 1.91 (s, 3H), 1.19 (t, $J=7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.7 (d, $^7J_{\text{C-P}}=6.8$ Hz), 165.2 (d, $^1J_{\text{C-F}}=252.6$ Hz), 144.8, 132.6 (d, $^5J_{\text{C-F}}=9.2$ Hz), 131.7 (d, $^{13}J_{\text{C-P}}=3.3$ Hz), 131.4 (d, $^{14}J_{\text{C-F}}=3.1$ Hz), 131.38, 131.1 (d, $^4J_{\text{C-P}}=9.4$ Hz), 130.8 (d, $^6J_{\text{C-P}}=9.1$ Hz), 128.6 (d, $^{10}J_{\text{C-P}}=5.1$ Hz), 128.5 (d, $^{11}J_{\text{C-P}}=5.1$ Hz), 127.52, 119.59, 115.0 (d, $^3J_{\text{C-F}}=21.5$ Hz), 89.9 (d, $^8J_{\text{C-P}}=6.4$ Hz), 88.58, 44.3 (d, $^{12}J_{\text{C-P}}=3.6$ Hz), 39.0 (d, $^2J_{\text{C-P}}=71.9$ Hz), 28.85, 28.7 (d, $^9J_{\text{C-P}}=6.3$ Hz), 15.45; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.24; IR (KBr) ν : 3052, 2915, 2210, 1685, 1598, 1422, 1187, 846, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{28}\text{FO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 517.1709, found 517.1719.

4-[4-(*tert*-Butyl)phenyl]-2-[(diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methylbut-3-yn-1-one (**3j**): Yellow oil. 53.3 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.31~8.23 (m, 2H), 7.83~7.71 (m, 4H), 7.45~7.34 (m, 6H), 7.20~7.14 (m, 2H), 7.10~7.03 (m, 2H), 6.91~6.84 (m, 2H), 3.41~3.32 (m, 1H), 2.93~2.84 (m, 1H), 1.91 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.6 (d, $^7J_{\text{C-P}}=6.8$ Hz), 165.2 (d, $^1J_{\text{C-F}}=252.9$ Hz), 151.7 (d, $^{10}J_{\text{C-P}}=6.3$ Hz), 132.6 (d, $^5J_{\text{C-F}}=9.0$ Hz), 131.7 (d, $^{14}J_{\text{C-P}}=3.3$ Hz), 131.4(3) (d, $^{15}J_{\text{C-F}}=2.9$ Hz), 131.4(8) (d, $^{16}J_{\text{C-P}}=2.9$ Hz), 131.2, 131.1 (d, $^6J_{\text{C-P}}=7.2$ Hz), 130.8 (d, $^4J_{\text{C-P}}=9.2$ Hz), 128.6 (d, $^{12}J_{\text{C-P}}=5.2$ Hz), 128.5 (d, $^{11}J_{\text{C-P}}=5.3$ Hz), 124.9, 119.4, 115.0 (d, $^3J_{\text{C-F}}=21.6$ Hz), 90.0 (d, $^8J_{\text{C-P}}=6.7$ Hz), 88.5, 44.3 (d, $^{13}J_{\text{C-P}}=3.6$ Hz), 39.1 (d, $^2J_{\text{C-P}}=71.7$ Hz), 34.8, 31.2, 28.7 (d, $^9J_{\text{C-P}}=6.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.47; IR (KBr) ν : 3059, 2920, 2226, 1680, 1489, 1448, 1175, 755, 698 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{32}\text{FO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 545.2022, found 545.2045.

2-[(Diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-4-(4-methoxyphenyl)-2-methylbut-3-yn-1-one (**3k**): Yellow oil. 44.7 mg, 45% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.34~

8.31 (m, 2H), 7.89~7.78 (m, 4H), 7.50~7.43 (m, 6H), 7.13~7.09 (m, 2H), 6.92 (d, $J=8.8$ Hz, 2H), 6.75 (d, $J=8.8$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.6, 166.4 (d, $^1J_{\text{C-F}}=252.5$), 159.6, 132.8, 132.7 (d, $^3J_{\text{C-F}}=8.9$), 131.6 (d, $^4J_{\text{C-F}}=3.1$), 131.4, 131.1 (d, $^2J_{\text{C-P}}=9.3$), 130.8 (d, $^3J_{\text{C-P}}=9.1$), 128.6 (d, $^7J_{\text{C-P}}=5.5$), 128.4 (d, $^6J_{\text{C-P}}=5.7$), 115.1 (d, $^2J_{\text{C-F}}=21.5$), 114.5, 113.5, 89.2 (d, $^5J_{\text{C-P}}=6.3$), 88.3, 55.3, 44.2 (d, $^8J_{\text{C-P}}=3.5$), 39.4 (d, $^1J_{\text{C-P}}=72.0$), 28.7 (d, $^4J_{\text{C-P}}=6.3$). ^{31}P NMR (162 MHz, CDCl_3) δ : 27.63; IR (KBr) ν : 3055, 2931, 2223, 1682, 1599, 1437, 1249, 832, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{FO}_3\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 519.1501, found 519.1515.

2-[(Diphenylphosphoryl)methyl]-1-(4-fluorophenyl)-2-methyl-4-(thiophen-2-yl)but-3-yn-1-one (**3l**): Yellow oil. 43.5 mg, 46% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.32~8.24 (m, 2H), 7.88~7.76 (m, 4H), 7.51~7.41 (m, 6H), 7.22~7.18 (m, 1H), 7.16~7.10 (m, 2H), 6.92~6.87 (m, 1H), 6.80~6.75 (m, 1H), 3.47~3.39 (m, 1H), 2.96~2.88 (m, 1H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.2 (d, $^7J_{\text{C-P}}=6.8$ Hz), 190.8, 165.2 (d, $^1J_{\text{C-F}}=253.0$ Hz), 132.6 (d, $^6J_{\text{C-P}}=9.1$ Hz), 132.0, 131.8, 131.5 (d, $^{13}J_{\text{C-F}}=2.6$ Hz), 131.5, 131.1 (d, $^4J_{\text{C-P}}=9.5$ Hz), 130.8 (d, $^5J_{\text{C-P}}=9.2$ Hz), 128.6 (d, $^{11}J_{\text{C-P}}=4.6$ Hz), 128.5 (d, $^{10}J_{\text{C-P}}=4.8$ Hz), 127.1, 126.7, 122.2, 115.1 (d, $^3J_{\text{C-F}}=21.6$ Hz), 94.3 (d, $^9J_{\text{C-F}}=6.3$ Hz), 82.0, 44.4 (d, $^{12}J_{\text{C-P}}=3.7$ Hz), 39.0 (d, $^2J_{\text{C-P}}=71.8$ Hz), 28.6 (d, $^8J_{\text{C-P}}=6.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.18; IR (KBr) ν : 3057, 2927, 2212, 1682, 1598, 1437, 1233, 844, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{22}\text{FO}_2\text{PSNa}$ [$\text{M}+\text{Na}$] $^+$ 495.0960, found 495.0976.

1-(4-Chlorophenyl)-2-((diphenylphosphoryl)methyl)-2-methyl-4-phenylbut-3-yn-1-one (**3m**): Yellow oil. 58.0 mg, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.23 (d, $J=8.4$ Hz, 1H), 7.88~7.76 (m, 1H), 7.41 (d, $J=8.0$ Hz, 1H), 7.30~7.24 (m, 1H), 7.23~7.17 (m, 1H), 6.97 (d, $J=7.2$ Hz, 1H), 3.51~3.40 (m, 1H), 2.98~2.90 (m, 1H), 1.95 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ : 198.0 (d, $^7J_{\text{C-P}}=6.2$ Hz), 138.7, 133.8, 131.47 (d, $^{11}J_{\text{C-P}}=2.2$ Hz), 131.5 (d, $^9J_{\text{C-P}}=3.3$ Hz), 131.0 (d, $^4J_{\text{C-P}}=9.3$ Hz), 130.7 (d, $^5J_{\text{C-P}}=9.1$ Hz), 128.6 (d, $^3J_{\text{C-P}}=22.8$ Hz), 128.5 (d, $^{10}J_{\text{C-P}}=3.0$ Hz), 128.4, 128.2, 128.0, 122.3, 90.4 (d, $^2J_{\text{C-P}}=42.6$ Hz), 88.4, 44.3 (d, $^8J_{\text{C-P}}=3.5$ Hz), 39.1 (d, $^1J_{\text{C-P}}=71.6$ Hz), 28.7 (d, $^6J_{\text{C-P}}=6.6$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.49; IR (KBr) ν : 3056, 2928, 2165, 1685, 1588, 1437, 1191, 754, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{24}\text{ClO}_2\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 505.1100, found 505.1124.

4-[(Diphenylphosphoryl)methyl]-4-methyl-1-phenylnona-1,5-diyn-3-one (**3n**): Yellow oil. 35.1 mg, 40% yield. ^1H NMR (400 MHz, CDCl_3) δ : 7.88~7.75 (m, 4H), 7.51~7.38 (m, 6H), 7.32~7.26 (m, 1H), 7.26~7.20 (m, 2H), 7.09~6.99 (m, 2H), 3.32~3.20 (m, 1H), 3.05~2.94 (m, 1H), 2.92~2.83 (m, 1H), 2.79~2.70 (m, 1H), 1.67 (s, 3H), 1.36~1.33 (m, 2H), 0.93 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 209.4 (d, $^5J_{\text{C-P}}=4.6$ Hz), 131.6, 131.4 (d, $^7J_{\text{C-P}}=1.5$ Hz), 131.1 (d, $^1J_{\text{C-P}}=9.4$ Hz),

131.0 (d, $^2J_{\text{C-P}}=9.1$ Hz), 128.6, 128.5 (d, $^4J_{\text{C-P}}=4.6$ Hz), 128.4, 128.2, 128.0, 127.9, 122.6, 90.0 (d, $^3J_{\text{C-P}}=5.1$ Hz), 86.9, 45.2 (d, $^6J_{\text{C-P}}=3.8$ Hz), 38.8, 31.4, 23.7, 22.6, 14.1; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.50; IR (KBr) ν : 3056, 2928, 2164, 1697, 1488, 1437, 1190, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{29}\text{H}_{27}\text{O}_2\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 461.1646, found 461.1658.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methyl-1-(*p*-tolyl)but-3-yn-1-one (**3o**): Yellow oil. 58.6 mg, 59% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.35~8.31 (m, 2H), 7.87~7.76 (m, 4H), 7.44~7.39 (m, 6H), 7.20~7.16 (m, 1H), 7.13~7.08 (m, 3H), 7.05~7.01 (m, 1H), 6.93 (d, $J=7.2$ Hz, 1H), 3.51~3.45 (m, 1H), 3.01~2.95 (m, 1H), 2.17 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8 (d, $^6J_{\text{C-P}}=7.6$ Hz), 149.6, 134.2 (d, $^2J_{\text{C-P}}=15.8$ Hz), 132.6, 132.4, 131.5 (d, $^5J_{\text{C-P}}=8.9$ Hz), 131.1 (d, $^3J_{\text{C-P}}=9.1$ Hz), 130.7 (d, $^4J_{\text{C-P}}=9.0$ Hz), 130.2, 128.7, 128.2, 127.5, 121.0, 91.8 (d, $^7J_{\text{C-P}}=5.6$ Hz), 87.1, 44.1 (d, $^9J_{\text{C-P}}=3.1$ Hz), 38.8 (d, $^1J_{\text{C-P}}=72.7$ Hz), 28.9, 28.4 (d, $^8J_{\text{C-P}}=4.9$ Hz), 15.18; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.22; IR (KBr) ν : 3055, 2966, 2126, 1682, 1605, 1437, 1183, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{ClO}_2\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 519.1257, found 519.1271.

4-(4-Chlorophenyl)-2-((diphenylphosphoryl)methyl)-2-methyl-1-(*m*-tolyl)but-3-yn-1-one (**3p**): Yellow oil. 50.7 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.12 (d, $J=8.4$ Hz, 2H), 7.85~7.72 (m, 5H), 7.47~7.34 (m, 7H), 7.20 (d, $J=8.0$ Hz, 2H), 7.14~7.10 (m, 2H), 6.85~6.82 (m, 2H), 3.42~3.36 (m, 1H), 2.84~2.78 (m, 1H), 2.39 (s, 3H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8, 143.5, 134.2, 132.7, 132.2, 131.6 (d, $^9J_{\text{C-P}}=2.9$ Hz), 131.5 (d, $^8J_{\text{C-P}}=3.1$ Hz), 131.3 (d, $^2J_{\text{C-P}}=9.4$ Hz), 130.7 (d, $^3J_{\text{C-P}}=d$, $J=9.2$ Hz), 130.1, 128.8, 128.3, 121.1, 91.8 (d, $^4J_{\text{C-P}}=6.1$ Hz), 87.2 (d, $^{10}J_{\text{C-P}}=2.1$ Hz), 44.1 (d, $^7J_{\text{C-P}}=3.6$ Hz), 38.8 (d, $^1J_{\text{C-P}}=71.9$ Hz), 28.4 (d, $^5J_{\text{C-P}}=5.9$ Hz), 21.7 (d, $^6J_{\text{C-P}}=5.4$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.92; IR (KBr) ν : 3055, 2916, 2167, 1680, 1489, 1437, 1183, 827, 692 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{ClO}_2\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 519.1257, found 519.1266.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methyl-1-(*o*-tolyl)but-3-yn-1-one (**3q**): Yellow oil. 53.7 mg, 54% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.06 (d, $J=7.6$ Hz, 1H), 7.86~7.81 (m, 4H), 7.48~7.43 (m, 6H), 7.35~7.31 (m, 1H), 7.26 (d, $J=7.6$ Hz, 1H), 7.23~7.19 (m, 1H), 7.15 (d, $J=8.4$ Hz, 2H), 6.80 (d, $J=8.0$ Hz, 2H), 3.53~3.47 (m, 1H), 2.97~2.91 (m, 1H), 2.46 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 203.2 (d, $^8J_{\text{C-P}}=5.6$ Hz), 137.3, 136.8, 134.9 (d, $^2J_{\text{C-P}}=27$ Hz), 134.1, 133.9 (d, $^3J_{\text{C-P}}=26.9$ Hz), 132.6, 131.5, 131.1 (d, $^5J_{\text{C-P}}=9.4$ Hz), 130.9 (d, $^9J_{\text{C-P}}=4.7$ Hz), 130.7, 130.2, 128.6 (d, $^4J_{\text{C-P}}=11.7$ Hz), 128.3, 128.2, 124.3, 121.0, 91.5 (d, $^7J_{\text{C-P}}=6.1$ Hz), 86.9, 45.9 (d, $^{10}J_{\text{C-P}}=3.9$ Hz), 38.7 (d, $^1J_{\text{C-P}}=71.7$ Hz), 28.3 (d, $^6J_{\text{C-P}}=7.4$ Hz), 20.4; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.44; IR (KBr) ν : 3055, 2928, 2152, 1697, 1488, 1437, 1190, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{ClO}_2\text{PNa}$ [$\text{M}+\text{Na}$] $^+$ 519.1257, found 519.1264.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-1-(4-ethylphenyl)-2-methylbut-3-yn-1-one (**3r**): Yellow oil. 52.1 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.21 (d, $J=8.4$ Hz, 2H), 7.90~7.85 (m, 2H), 7.82~7.76 (m, 2H), 7.47~7.39 (m, 6H), 7.28 (d, $J=8.4$ Hz, 2H), 7.16 (d, $J=8.4$ Hz, 2H), 6.88 (d, $J=8.4$ Hz, 2H), 3.49~3.43 (m, 1H), 2.91~2.85 (m, 1H), 2.74~2.68 (m, 2H), 2.00 (s, 3H), 1.31~1.25 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8 (d, $^7J_{\text{C-P}}=7.7$ Hz), 149.5, 135.3 (d, $^1J_{\text{C-P}}=269.9$ Hz), 134.4 (d, $^6J_{\text{C-P}}=8.3$ Hz), 134.1, 133.4, 132.6, 132.4, 131.4 (d, $^{13}J_{\text{C-P}}=2.6$ Hz), 131.384 (d, $^{12}J_{\text{C-P}}=2.7$ Hz), 131.1 (d, $^4J_{\text{C-P}}=9.3$ Hz), 130.7 (d, $^5J_{\text{C-P}}=9.1$ Hz), 130.2, 128.6 (d, $^3J_{\text{C-P}}=20.1$ Hz), 128.5 (d, $^{11}J_{\text{C-P}}=3.2$ Hz), 128.2, 127.5, 91.8 (d, $^8J_{\text{C-P}}=6$ Hz), 87.1, 44.2 (d, $^{10}J_{\text{C-P}}=3.5$ Hz), 38.8 (d, $^2J_{\text{C-P}}=72.1$ Hz), 28.9, 28.3 (d, $^9J_{\text{C-P}}=5.3$ Hz), 15.2; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.98; IR (KBr) ν : 3055, 2967, 2122, 1682, 1605, 1437, 1183, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{32}\text{H}_{28}\text{ClO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 533.1413, found 533.1409.

1-[3-(*tert*-Butyl)phenyl]-4-(4-chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methylbut-3-yn-1-one (**3s**): Yellow oil. 55.0 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.26~8.20 (m, 2H), 7.91~7.85 (m, 2H), 7.82~7.75 (m, 2H), 7.49~7.40 (m, 8H), 7.20~7.15 (m, 2H), 6.91~6.86 (m, 2H), 3.49~3.41 (m, 1H), 2.92~2.83 (m, 1H), 2.01 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8 (d, $^6J_{\text{C-P}}=6.8$ Hz), 156.3, 132.6, 131.1 (d, $^2J_{\text{C-P}}=9.2$ Hz), 130.6 (d, $^3J_{\text{C-P}}=9.0$ Hz), 129.9, 128.6 (d, $^5J_{\text{C-P}}=8.3$ Hz), 128.5 (d, $^4J_{\text{C-P}}=8.5$ Hz), 128.2, 125.0, 121.1, 91.8 (d, $^7J_{\text{C-P}}=6.1$ Hz), 87.0, 44.1 (d, $^9J_{\text{C-P}}=3.5$ Hz), 38.7 (d, $^1J_{\text{C-P}}=72.2$ Hz), 35.1, 31.1, 28.3 (d, $^8J_{\text{C-P}}=5.1$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.68; IR (KBr) ν : 3055, 2963, 2146, 1682, 1603, 1437, 1189, 828, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{34}\text{H}_{32}\text{ClO}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 561.1726, found 561.1714.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-1-(3-methoxyphenyl)-2-methylbut-3-yn-1-one (**3t**): Yellow oil. 45.1 mg, 44% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.38~8.31 (m, 2H), 7.92~7.79 (m, 4H), 7.48~7.38 (m, 6H), 7.29~7.24 (m, 1H), 7.23~7.17 (m, 2H), 7.01~6.91 (m, 4H), 3.89 (s, 3H), 3.46~3.39 (m, 1H), 2.93~2.85 (m, 1H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.6 (d, $^7J_{\text{C-P}}=6.6$ Hz), 165.1 (d, $^1J_{\text{C-P}}=252.6$ Hz), 138.4, 132.6 (d, $^6J_{\text{C-P}}=7.9$ Hz), 131.4, 131.2, 131.1 (d, $^4J_{\text{C-P}}=9.3$ Hz), 130.7 (d, $^5J_{\text{C-P}}=9.1$ Hz), 128.7, 128.6 (d, $^9J_{\text{C-P}}=5.0$ Hz), 128.5 (d, $^8J_{\text{C-P}}=5.1$ Hz), 119.3, 115.0 (d, $^3J_{\text{C-P}}=21.6$ Hz), 89.8 (d, $^1J_{\text{C-P}}=6.3$ Hz), 88.5, 44.2 (d, $^{11}J_{\text{C-P}}=3.6$ Hz), 39.0 (d, $^2J_{\text{C-P}}=71.8$ Hz), 28.7 (d, $^{10}J_{\text{C-P}}=4.2$ Hz), 21.5; ^{31}P NMR (162 MHz, CDCl_3) δ : 27.55; IR (KBr) ν : 2924, 2220, 1682, 1598, 1437, 1233, 1189, 816, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{26}\text{ClO}_3\text{PNa}$ $[\text{M}+\text{Na}]^+$ 535.1206, found 535.1215.

1,4-Bis(4-chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methylbut-3-yn-1-one (**3u**): Yellow solid; 66.2 mg, 64% yield. m.p. 111~112 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ : 8.19 (d, $J=8.4$ Hz, 2H), 7.86~7.75 (m, 4H), 7.47~7.36 (m, 8H), 7.16 (d, $J=8.4$ Hz, 2H), 6.86 (d, $J=$

8.4 Hz, 2H), 3.51~3.40 (m, 1H), 2.95~2.85 (m, 1H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 197.8 (d, $^5J_{\text{C-P}}=6.2$ Hz), 138.7, 134.9, 134.5, 134.4, 133.9, 133.7, 133.5, 132.6, 131.5 (d, $^9J_{\text{C-P}}=1.7$ Hz), 131.2, 131.0 (d, $^2J_{\text{C-P}}=9.2$ Hz), 130.7 (d, $^3J_{\text{C-P}}=9.0$ Hz), 128.6 (d, $^7J_{\text{C-P}}=3.3$ Hz), 128.5 (d, $^7J_{\text{C-P}}=3.5$ Hz), 128.2 (d, $^6J_{\text{C-P}}=3.8$ Hz), 120.8, 91.5, 91.4, 87.4, 44.2 (d, $^8J_{\text{C-P}}=3.5$ Hz), 39.0 (d, $^1J_{\text{C-P}}=71.6$ Hz), 28.7 (d, $^4J_{\text{C-P}}=6.7$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.40; IR (KBr) ν : 3056, 2928, 2156, 1685, 1589, 1437, 1191, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{30}\text{H}_{23}\text{Cl}_2\text{O}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 539.0710, found 539.0717.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methyl-1-(4-(trifluoromethyl)phenyl)but-3-yn-1-one (**3v**): Yellow oil. 74.9 mg, 68% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.31 (d, $J=8.4$ Hz, 2H), 7.86~7.76 (m, 4H), 7.72 (d, $J=8.4$ Hz, 2H), 7.50~7.40 (m, 6H), 7.19 (d, $J=8.4$ Hz, 2H), 6.85 (d, $J=8.4$ Hz, 2H), 3.54~3.46 (m, 1H), 2.99~2.90 (m, 1H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 199.1 (d, $^5J_{\text{C-P}}=5.1$ Hz), 139.1, 134.5, 132.5, 131.6 (d, $^{10}J_{\text{C-P}}=2.2$ Hz), 131.5 (d, $^{11}J_{\text{C-P}}=2.1$ Hz), 131.0, 130.8 (d, $^6J_{\text{C-P}}=4.1$ Hz), 130.7, 129.1, 128.7 (d, $^2J_{\text{C-P}}=8.9$ Hz), 128.6 (d, $^{12}J_{\text{C-P}}=2.0$ Hz), 128.3, 124.9 (d, $^8J_{\text{C-F}}=3.7$ Hz), 122.3, 120.6, 91.1 (d, $^4J_{\text{C-F}}=6.0$ Hz), 87.5, 44.5 (d, $^8J_{\text{C-P}}=3.3$ Hz), 39.2 (d, $^1J_{\text{C-P}}=71.5$ Hz), 28.8 (d, $^3J_{\text{C-P}}=7.5$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 27.41; IR (KBr) ν : 3056, 2930, 2196, 1693, 1498, 1437, 1325, 1119, 694 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{31}\text{H}_{23}\text{ClF}_3\text{O}_2\text{PNa}$ $[\text{M}+\text{Na}]^+$ 573.0974, found 573.0981.

4-(4-Chlorophenyl)-2-[(diphenylphosphoryl)methyl]-2-methyl-1-(thiophen-2-yl)but-3-yn-1-one (**3w**): Yellow oil. 44.0 mg, 45% yield. ^1H NMR (400 MHz, CDCl_3) δ : 8.28 (d, $J=3.6$ Hz, 1H), 7.90~7.78 (m, 4H), 7.66 (d, $J=4.8$ Hz, 1H), 7.51~7.43 (m, 3H), 7.40 (s, 3H), 7.20 (d, $J=8.4$ Hz, 2H), 7.15~7.11 (m, 1H), 6.96 (d, $J=8.4$ Hz, 2H), 3.43~3.35 (m, 1H), 2.91~2.81 (m, 1H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 190.7 (d, $^4J_{\text{C-P}}=8.5$ Hz), 139.9, 134.6, 134.3 (d, $^5J_{\text{C-P}}=6.4$ Hz), 132.7, 131.5 (d, $^{10}J_{\text{C-P}}=2.2$ Hz), 131.4 (d, $^9J_{\text{C-P}}=2.4$ Hz), 131.2 (d, $^3J_{\text{C-P}}=9.0$ Hz), 130.6 (d, $^2J_{\text{C-P}}=9.2$ Hz), 128.7, 128.5 (d, $^8J_{\text{C-P}}=4.5$ Hz), 128.4, 128.2, 127.8, 120.8, 91.7 (d, $^6J_{\text{C-P}}=5.2$ Hz), 87.3, 44.4 (d, $J=3.3$ Hz), 38.0 (d, $^1J_{\text{C-P}}=72.4$ Hz), 28.8 (d, $^7J_{\text{C-P}}=5.0$ Hz); ^{31}P NMR (162 MHz, CDCl_3) δ : 28.01; IR (KBr) ν : 3056, 2925, 2218, 1658, 1498, 1409, 1190, 829, 695 cm^{-1} ; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{22}\text{ClO}_2\text{PSNa}$ $[\text{M}+\text{Na}]^+$ 511.0664, found 511.0653.

3-((Diphenylphosphoryl)methyl)-3-methyl-1-phenyldec-1-yn-4-one (**3x**): Yellow oil. 54.0 mg, 47% yield. ^1H NMR (400 MHz, CDCl_3) δ : 7.83~7.71 (m, 4H), 7.42~7.39 (m, 6H), 7.23~7.17 (m, 3H), 7.03~6.96 (m, 2H), 3.25~3.18 (m, 1H), 2.97~2.91 (m, 1H), 2.86~2.80 (m, 1H), 2.74~2.68 (m, 1H), 2.22~2.17 (m, 1H), 2.02 (s, 1H), 1.74 (s, 1H), 1.63 (s, 3H), 1.29~1.26 (m, 6H), 0.88~0.85 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ : 209.4 (d, $^{13}J_{\text{C-P}}=4.7$ Hz), 134.8 (d, $^3J_{\text{C-P}}=20.2$ Hz), 133.8 (d, $^1J_{\text{C-P}}=30.2$ Hz), 131.5 (d, $^4J_{\text{C-P}}=11.5$ Hz), 131.4 (d, $^{15}J_{\text{C-P}}=3.5$ Hz), 131.1 (d, $^5J_{\text{C-P}}=9.4$ Hz), 130.9 (d, $^6J_{\text{C-P}}=9.1$ Hz), 128.6

(d, $^{10}J_{C-P}=7.5$ Hz), 128.4 (d, $^9J_{C-P}=7.6$ Hz), 128.1 (d, $^2J_{C-P}=23.2$ Hz), 122.6 (s), 90.1 (d, $^{11}J_{C-P}=5.1$ Hz), 86.8 (s), 45.2 (d, $^{14}J_{C-P}=3.8$ Hz), 38.8 (s), 38.4 (s), 37.7 (s), 31.8 (s), 28.9 (s), 28.1 (d, $^8J_{C-P}=8.9$ Hz), 24.0 (s), 22.6 (s), 14.1 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ : 27.70; IR (KBr) ν : 3055, 2922, 2361, 1717, 1437, 1187, 1118, 821, 692 cm^{-1} ; HRMS (ESI) calcd for $C_{30}H_{33}O_2PNa$ $[M+Na]^+$ 479.2116, found 479.2109.

2-([Bis(3,5-dimethylphenyl)phosphoryl)methyl]-2-methyl-1,4-diphenylbut-3-yn-1-one (**3y**): Yellow oil. 31.3 mg, 31% yield. 1H NMR (400 MHz, $CDCl_3$) δ : 8.30 (d, $J=7.6$ Hz, 2H), 7.57~7.50 (m, 2H), 7.49~7.43 (m, 3H), 7.38 (d, $J=11.6$ Hz, 2H), 7.26 (d, $J=7.6$ Hz, 1H), 7.22~7.17 (m, 2H), 7.08 (s, 1H), 6.99 (d, $J=6.8$ Hz, 3H), 3.46~3.38 (m, 1H), 2.93~2.83 (m, 1H), 2.29 (d, $J=14.8$ Hz, 12H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 198.8 (d, $^6J_{C-P}=7.8$ Hz), 138.2, 138.1 (d, $^{11}J_{C-P}=2.1$ Hz), 138.0, 135.3, 134.2 (d, $^4J_{C-P}=19.8$ Hz), 133.1 (d, $^{10}J_{C-P}=2.7$ Hz), 132.4, 131.4, 129.9, 128.7 (d, $^5J_{C-P}=9.2$ Hz), 128.2, 128.1 (d, $^{12}J_{C-P}=1.3$ Hz), 128.1, 127.8 (d, $^3J_{C-P}=20.5$ Hz), 122.6, 90.6 (d, $^1J_{C-P}=76.3$ Hz), 88.2, 44.2 (d, $^9J_{C-P}=3.4$ Hz), 38.5 (d, $^2J_{C-P}=71.3$ Hz), 29.7, 28.1 (d, $^7J_{C-P}=4.9$ Hz), 21.3 (d, $^8J_{C-P}=4.0$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ : 28.49; IR (KBr) ν : 3051, 2920, 2178, 1685, 1598, 1446, 1185, 850, 691 cm^{-1} ; HRMS (ESI) calcd for $C_{34}H_{33}O_2PNa$ $[M+Na]^+$ 527.2116, found 527.2122.

Supporting Information 1H NMR and ^{13}C NMR of all new compounds **3a**~**3x**. The Supporting Information is available free of charge via the Internet at <http://sioc-journal.cn/>.

References

- [1] (a) Sharpless, K. B.; Finn, M. G. In *Asymmetric Synthesis*, Ed.: Morrison, J. D., Academic Press, Orlando, FL, 5 (1985), 247. (b) Wei, W.; Cui, H.; Yue, H.; Yang, D. *Green Chem.* **2018**, *20*, 3197. (c) Zhang, T. S.; Xiong, Y. J.; Hao, W. J.; Zhu, X. T.; Wang, S. L.; Li, G. G.; Tu, S. J.; Jiang, B. J. *Org. Chem.* **2016**, *81*, 9350. (d) Zhang, Y.; Sigman, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 3076. (e) Martínez, C.; Muñoz, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 703. (f) Wang, Z.; Liu, Y.; Liu, H.; Bao, W.; Tan, Y.; Wang, M.; Tang, Z.; He, W. *Chin. J. Org. Chem.* **2018**, *38*, 2639 (in Chinese). (王峥, 杨柳, 刘惠兰, 谭英芝, 包文虎, 汪明, 唐子龙, 何卫民, 有机化学, **2018**, *38*, 2639.) (g) Liu, Y.; Lin, L.; Han, Y.; Zhang, X. *Chin. J. Org. Chem.* **2019**, *39*, 2705 (in Chinese). (刘颖杰, 林立青, 韩莹徽, 张鑫, 有机化学, **2019**, *39*, 2705.)
- [2] (a) Li, Y.; Studer, A. *Angew. Chem. Int. Ed.* **2012**, *51*, 8221. (b) Mizuta, S.; Verhoog, S.; Engle, K. M.; Khotavivattana, T.; O'Duill, M.; Wheelhouse, K.; Rassias, G.; Médebielle, M.; Gouverneur, V. *J. Am. Chem. Soc.* **2013**, *135*, 2505. (c) Wilger, D. J.; Gesmundo, N. J.; Nicewicz, D. A. *Chem. Sci.* **2013**, *4*, 3160. (d) Wu, X.; Chu, L.; Qing, F. L. *Angew. Chem. Int. Ed.* **2013**, *52*, 2198. (e) Oh, S. H.; Malpani, Y. R.; Ha, N.; Jung, Y. S.; Han, S. B. *Org. Lett.* **2014**, *16*, 1310. (f) Wu, C.; Xiao, H.-J.; Wang, S.-W.; Tang, M.-S.; Tang, Z.-L.; Xia, W.; Li, W.-F.; Cao, Z.; He, W.-M. *ACS Sustainable Chem. Eng.* **2019**, *7*, 9.
- (g) Lu, L.-H.; Wang, Z.; Xia, W.; Cheng, P.; Zhang, B.; Cao, Z.; He, W.-M. *Chin. Chem. Lett.* **2019**, *30*, 1237. (h) Wu, C.; Lu, L.-H.; Peng, A.-Z.; Jia, G.-K.; Peng, C.; Cao, Z.; Tang, Z.; He, W.-M.; Xu, X. *Green Chem.* **2018**, *20*, 3683.
- [3] (a) Wang, F.; Wang, D.; Wan, X.; Wu, L.; Chen, P.; Liu, G. *J. Am. Chem. Soc.* **2016**, *138*, 15547. (b) Zhang, W.; Wang, F.; McCann, S. D.; Wang, D.; Chen, P.; Stahl, S. S.; Liu, G. *Science* **2016**, *353*, 1014. (c) Wang, D.; Wu, L.; Wang, F.; Wan, X.; Chen, P.; Lin, Z.; Liu, G. *J. Am. Chem. Soc.* **2017**, *139*, 6811. (d) Fu, X.; Zhao, W. *Chin. J. Org. Chem.* **2019**, *39*, 625 (in Chinese). (付晓飞, 赵文献, 有机化学, **2019**, *39*, 625.)
- [4] (a) Chen, Z. M.; Bai, W.; Wang, S. H.; Yang, B. M.; Tu, Y. Q.; Zhang, F. M. *Angew. Chem. Int. Ed.* **2013**, *52*, 978. (b) Chen, Z. M.; Zhang, Z.; Tu, Y. Q.; Xu, M. H.; Zhang, F. M.; Li, C. C.; Wang, S. H. *Chem. Commun.* **2014**, *50*, 10805. (c) Yu, P.; Lin, J. S.; Li, L.; Zheng, S. C.; Xiong, Y. P.; Zhao, L. J.; Tan, B.; Liu, X. Y. *Angew. Chem. Int. Ed.* **2014**, *53*, 11890. (d) Li, L.; Li, Z. L.; Wang, F. L.; Guo, Z.; Cheng, Y. F.; Wang, N.; Dong, X. W.; Fang, C.; Liu, J.; Hou, C.; Tan, B.; Liu, X. Y. *Nat. Commun.* **2016**, *7*, 13852.
- [5] (a) Li, W.; Xu, W.; Xie, J.; Yu, S.; Zhu, C. *Chem. Soc. Rev.* **2018**, *47*, 654. (b) Wu, X.; Wu, S.; Zhu, C. *Tetrahedron Lett.* **2018**, *59*, 1328. (c) Wu, X.; Zhu, C. *Chin. J. Chem.* **2019**, *37*, 171. (d) Chen, Z. M.; Zhang, X. M.; Tu, Y. Q. *Chem. Soc. Rev.* **2015**, *44*, 5220.
- [6] (a) Egami, H.; Shimizu, R.; Usui, Y.; Sodeoka, M. *Chem. Commun.* **2013**, *49*, 7346. (b) Liu, X.; Xiong, F.; Huang, X.; Xu, L.; Li, P.; Wu, X. *Angew. Chem. Int. Ed.* **2013**, *52*, 6962. (c) Chu, X. Q.; Meng, H.; Zi, Y.; Xu, X. P.; Ji, S. J. *Chem. Commun.* **2014**, *50*, 9718. (d) Chu, X. Q.; Zi, Y.; Meng, H.; Xu, X. P.; Ji, S. J. *Chem. Commun.* **2014**, *50*, 7642. (e) Li, Y.; Liu, B.; Li, H. B.; Wang, Q.; Li, J. H. *Chem. Commun.* **2015**, *51*, 1024. (f) Li, L.; Gu, Q. S.; Wang, N.; Song, P.; Li, Z. L.; Li, X. H.; Wang, F. L.; Liu, X. Y. *Chem. Commun.* **2017**, *53*, 4038. (g) Zhu, Y. L.; Jiang, B.; Hao, W. J.; Qiu, J.-K.; Sun, J.; Wang, D.-C.; Wei, P.; Wang, A. F.; Li, G.; Tu, S. J. *Org. Lett.* **2015**, *17*, 6078. (h) Yang, S.; Wu, X.; Wu, S.; Zhu, C. *Org. Lett.* **2019**, *21*, 4837.
- [7] (a) Wu, Z.; Ren, R.; Zhu, C. *Angew. Chem. Int. Ed.* **2016**, *55*, 10821. (b) Ji, M.; Wu, Z.; Yu, J.; Wan, X.; Zhu, C. *Adv. Synth. Catal.* **2017**, *359*, 1959. (c) Ren, R.; Wu, Z.; Huan, L.; Zhu, C. *Adv. Synth. Catal.* **2017**, *359*, 3052. (d) Wang, N.; Li, L.; Li, Z. L.; Yang, N. Y.; Guo, Z.; Zhang, H. X.; Liu, X. Y. *Org. Lett.* **2016**, *18*, 6026.
- [8] (a) Yu, J.; Wang, D.; Xu, Y.; Wu, Z.; Zhu, C. *Adv. Synth. Catal.* **2018**, *360*, 744. (b) Chen, D.; Ji, M.; Yao, Y.; Zhu, C. *Acta Chim. Sinica* **2018**, *76*, 951. (c) Wang, N.; Wang, J.; Guo, Y. L.; Li, L.; Sun, Y.; Li, Z.; Zhang, H. X.; Guo, Z.; Li, Z. L.; Liu, X. Y. *Chem. Commun.* **2018**, *54*, 8885.
- [9] Li, Z. L.; Li, X. H.; Wang, N.; Yang, N. Y.; Liu, X. Y. *Angew. Chem. Int. Ed.* **2016**, *55*, 15100.
- [10] (a) Wu, Z.; Wang, D.; Liu, Y.; Huan, L.; Zhu, C. *J. Am. Chem. Soc.* **2017**, *139*, 1388. (b) Gu, L. J.; Gao, Y.; Ai, X. H.; Jin, C.; He, Y. H.; Li, G. P.; Yuan, M. L. *Chem. Commun.* **2017**, *53*, 12946. (c) He, Y.; Wang, Y.; Gao, J.; Zeng, L.; Li, S.; Wang, W.; Zheng, X.; Zhang, S.; Gu, L.; Li, G. *Chem. Commun.* **2018**, *54*, 7499. (d) Zhang, W.; Zou, Z.; Wang, Y.; Wang, Y.; Liang, Y.; Wu, Z.; Zheng, Y.; Pan, Y. *Angew. Chem. Int. Ed.* **2019**, *58*, 624.

- [11] (a) Tang, X.; Studer, A. *Angew. Chem. Int. Ed.* **2018**, *57*, 814.
(b) Wang, X.; Liu, J.; Yu, Z.; Guo, M.; Tang, X.; Wang, G. *Org. Lett.* **2018**, *20*, 6516.
- [12] (a) Xu, Y.; Wu, Z.; Jiang, J.; Ke, Z.; Zhu, C. *Angew. Chem. Int. Ed.* **2017**, *56*, 4545.
(b) Liu, J.; Li, W. P.; Xie, J.; Zhu, C. *J. Org. Chem. Front.* **2018**, *5*, 797.
(c) Tang, N.; Shao, X.; Wang, M.; Wu, X.; Zhu, C. *Acta Chim. Sinica* **2019**, *77*, 922 (in Chinese).
(汤娜娜, 邵鑫, 王明扬, 吴新鑫, 朱晨, 化学学报, **2019**, *77*, 922.)
- [13] (a) Zhao, Q.; Ji, X. S.; Gao, Y. Y.; Hao, W. J.; Zhang, K.-Y.; Tu, S. J.; Jiang, B. *Org. Lett.* **2018**, *20*, 3596.
(b) Zhao, Q.; Tu, S.-J.; Jiang, B. *Acta Chim. Sinica* **2019**, *77*, 927 (in Chinese).
(赵琦, 屠树江, 姜波, 化学学报, **2019**, *77*, 927.)
- [14] (a) Chakravarty, P. K.; Greenlee, W. J.; Parsons, W. H.; Patchett, A. A.; Combs, P.; Roth, A.; Busch, R. D.; Mellin, T. N. *J. Med. Chem.* **1989**, *32*, 1886.
(b) Sowa, S.; Stankevič, M.; Szmigielska, A.; Małuszyńska, H.; Koziol, A. E.; Pietrusiewicz, K. M. *J. Org. Chem.* **2015**, *80*, 1672.
(c) Li, J.; Zhang, W. W.; Wei, X. J.; Hao, W. J.; Li, G.; Tu, S. J.; Jiang, B. *Org. Lett.* **2017**, *19*, 4512.
- [15] When we prepared this manuscript, Cheng and co-workers reported the same version for the synthesis of γ -ketophosphine oxides by using 1,4-enynes and diarylphosphine oxides, see: Jin, S.; Sun, S.; Yu, J.-T.; Cheng, J. *J. Org. Chem.* **2019**, *84*, 11177.
- [16] (a) Li, Y.-M.; Sun, M.; Wang, H.-L.; Tian, Q.-P.; Yang, S.-D. *Angew. Chem. Int. Ed.* **2013**, *52*, 3972.
(b) Chen, Y. R.; Duan, W. L. *J. Am. Chem. Soc.* **2013**, *135*, 16754.
(c) Zhang, C. W.; Li, Z. D.; Zhu, L.; Yu, L. M.; Wang, Z. T.; Li, C. Z. *J. Am. Chem. Soc.* **2013**, *135*, 14082.
(d) Zhang, B. C.; Daniliuc, G.; Studer, A. *Org. Lett.* **2014**, *16*, 250.
(e) Zhu, X.-T.; Zhao, Q.; Liu, F.; Wang, A.-F.; Cai, P.-J.; Hao, W.-J.; Tu, S.-J.; Jiang, B. *Chem. Commun.* **2017**, *53*, 6828.
(f) Sun, J.; Qiu, J.-K.; Wu, Y.-N.; Hao, W.-J.; Guo, C.; Li, G.; Tu, S.-J.; Jiang, B. *Org. Lett.* **2017**, *19*, 754.
(g) Zhu, Y.-L.; Wang, D.-C.; Jiang, B.; Hao, W.-J.; Wei, P.; Wang, A.-F.; Qiu, J.-K.; Tu, S.-J. *Org. Chem. Front.* **2016**, *3*, 385.

(Li, L.; Fan, Y.)