JOC The Journal of Organic Chemistry

Note

pubs.acs.org/joc

Direct Radical Acetoxyphosphorylation of Styrenes Mediated by Manganese(III)

Shao-Fang Zhou,[†] Da-Peng Li,[†] Kui Liu,[†] Jian-Ping Zou,*[,†,‡] and Olayinka Taiwo Asekun[§]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry and Chemical Engineering, Soochow University, 199 Renai Street, Suzhou, Jiangsu 215123, China

[‡]Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

[§]Department of Chemistry, University of Lagos, Akoka, Yaba 101017, Nigeria

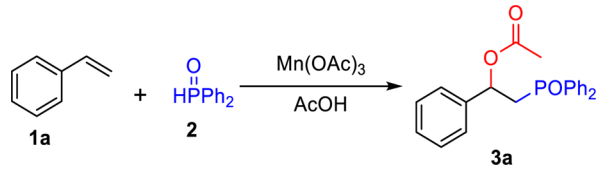
Supporting Information

ABSTRACT: Direct radical acetoxyphosphorylation of styrenes mediated by $Mn(OAc)_3$ with diphenylphosphine oxide and dialkyl phosphites was described, and a new type of difunctionalization of alkenes was achieved.

Direct difunctionalization of alkenes is one of the most powerful transformations known in the field of chemical synthesis,[1] so it has gained increasing considerable attention, in which phosphorus-related difunctionalization of alkenes is still a challenge, although this strategy can easily transform alkenes to β-keto, β-amino, and β-hydroxyphosphonates.[2] Recently, many C−P bond formation reports have been published;[3] however, phosphorus-related difunctionalization of alkenes is limited.[4] The Ji group reported the Cu/Fe cocatalyzed oxyphosphorylation of alkenes with dioxygen and H-phosphonates;[4a] the Li group described the first example of fluorophosphonylation catalyzed by $AgNO_3$.[4b] $Mn(OAc)_3$ is a useful reagent for C−C, C−P, and other bond formations.[5] Our laboratory developed a novel $Mn(OAc)_3$-mediated monofunctionalization of the α-sp^2 C−H bond of α,β-unsaturated arylketones.[6] Herein, we report a new type of direct difunctionalization of alkenes mediated by $Mn(OAc)_3$ with diphenylphosphine oxide and dialkyl phosphites.

In our previous paper,[6] we disclosed a reaction of β-phenylethylene styrene and diphenylphosphine oxide that afforded a tetrahydronaphthalene as the major product through benzyl radical cyclization intramolecularly, accompanied by one acetoxyphosphorylation byproduct formed. To let the byproduct become as major one, reaction conditions were improved, but the result remained unchanged. It might be attributed to the presence of a β-phenyl moiety in styrene to facilitate the radical cyclization. To confirm this hypothesis, the reaction of styrene and $HP(O)Ph_2/Mn(OAc)_3$ was tried at 50 °C for 20 min. To our delight, a major product was isolated, which was characterized to be 2-(diphenylphosphoryl)-1-phenylethyl acetate (**3a**), an acetoxyphosphorylation product, by ^1H NMR, ^{13}C NMR, and HRMS spectral analyses (Table 1). Afterward, the optimal reaction conditions were screened and we found that the reaction carried out in AcOH at 50 °C for 0.5 h with ratio of styrene/$HP(O)Ph_2/Mn(OAc)_3$ (1:1.5:2) gave the best result (Table 1, entry 5).

Table 1. Optimization of the Reaction Conditions



1a 2 3a

entry	1a:2:$Mn(OAc)_3$	temp/°C	time/min	yield/%[a]
1	1:2:2	30	60	56
2	1:2:2	50	30	70
3	1:2:2	70	20	36
4	1:2:2	90	10	20
5	1:1.5:2	50	30	70
6	1:1.5:1.5	50	30	50

[a]Isolated yield.

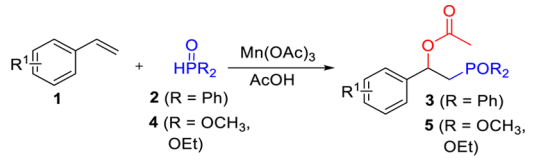
Subsequently, the above optimal reaction conditions were applied for the different styrenes. We found that styrenes bearing electron-donating groups like Me and OMe on the phenyl ring produced the expected 2-(diphenylphosphoryl)-1-arylethyl acetates in 65% and 73% yields (Table 2, **3b**−**c**). On the other hand, styrenes bearing halogens like F, Cl, and Br on the phenyl ring formed the products in slightly lower yields (50−60%) (Table 2, **3d**−**g**). It is noteworthy that styrenes bearing electron-withdrawing groups such as CF_3 gave the low yield of acetoxyphosphorylation product (Table 2, **3h**), whereas CN and NO_2 derivatives did not afford the expected products (Table 2, **3i**−**j**).

Thereafter, dimethyl phosphites (**4**) were employed for the reaction under similar conditions to **2**, except the reaction temperature has to be raised to 70 °C and the reaction time was prolonged to 60 min due to the lower reactivity of **4** than **2**. The results showed that the styrenes bearing electron-donating

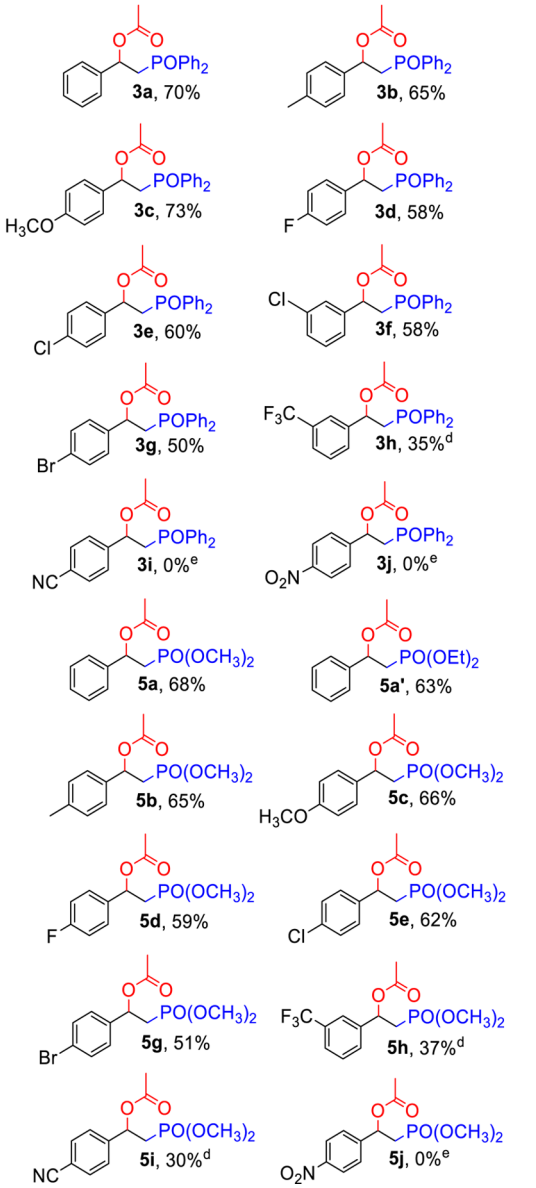
Received: October 12, 2014
Published: December 9, 2014

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220

Table 2. Reactions of Alkenes 1 and Diphenylphosphine Oxide 2 and Dialkyl Phosphites 4[a,b,c,d,e]



Products **3**, **5** and yield[c]



[a]Reaction conditions: styrene (1.0 mmol), $HP(0)Ph_2$ (1.5 mmol), $Mn(OAc)_3$ (2.0 mmol) in HOAc (10 mL), 50 °C, 30 min. [b]Reaction conditions: styrene (1.0 mmol), $HP(0)(OR)_2$ (1.5 mmol), $Mn(OAc)_3$ (2.0 mmol) in HOAc (10 mL), 70 °C, 60 min. [c]Isolated yield. [d]Mixture of acetoxyphosphorylation and oxyphosphorylation cannot be separated from each other. [e]Only oxyphosphorylation product was isolated.

groups like Me and OMe and halogens such as F, Cl, and Br on the phenyl ring all formed acetoxyphosphorylation products in moderate yields (up to 68%, Table 2, **5a**–**g**). In contrast, electron-withdrawing groups like CF_3 and CN afforded the expected products (**5h** and **5i**) in low yields, and the NO_2 derivative did not give the expected product (Table 2, **5h**–**j**).

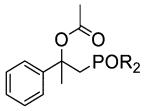
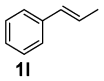
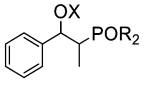
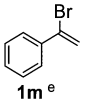
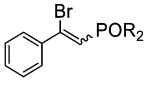
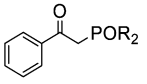
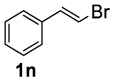
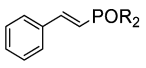
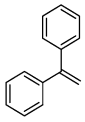
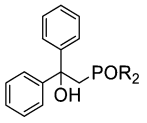
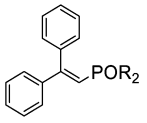
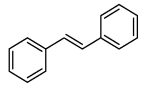
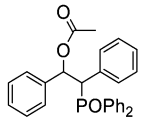
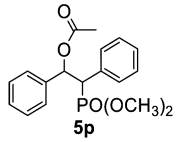
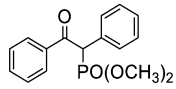
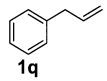
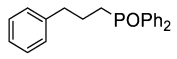
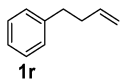
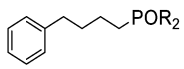
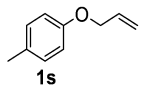
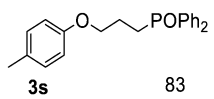
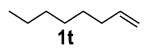
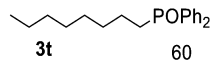
To know the effect of α- or β-substituents of styrene on the reaction, CH_3, Br, and Ph substituted styrenes were used for the reaction. First, the reactions of α-methylstyrene (**1k**) with **2** and **4** were explored, and we found that they all afforded the acetoxyphosphorylation products **3k** and **5k** both in 67% yield, respectively (Table 3, entry 1). It revealed that the α-methyl of styrene has no impact on the reaction. In contrast, the reactions of β-methylstyrene (**1l**) with **2** and **4** afforded the mixture of acetoxyphosphorylation products (**3l**, **5l**) and hydroxyphosphorylation products (**3l′**, **5l′**) (Table 3, entry 2). The further experiments showed that the acetoxyl groups of **3l** and **5l** were not able to leave and transform to hydroxy groups under the reaction conditions. Second, the reaction of α-bromostyrene (**1m**) with **2** was carried out; two products, viz. 1-(diphenylphosphoryl)-2-bromo-2-phenyl-ethylene (**3m**) and 2-(diphenylphosphoryl)-1-phenylethanone (**3m′**) were isolated in 30% and 50% yields, respectively (Table 3, entry 3). Instead, the reaction of **1m** with **4** gave the dimethyl (2-bromo-2-phenylvinyl)phosphonate (**5m**) and dimethyl (2-oxo-2-phenylethyl)phosphonate (**5m′**) in 21% and 50% yields, respectively (Table 3, entry 3). Furthermore, the reactions of β-bromostyrene (**1n**) with **2** and **4** were performed; they all gave the addition–elimination products **3n** and **5n** through the phosphorus-centered radical addition to the terminal C=C double bond, followed elimination of Br• radical to form alkenylphosphorylation products (Table 3, entry 4). Third, the reaction of α-phenylstyrene (**1o**) with **2** was performed, and hydroxyphosphorylation product **3o** in 71% yield was obtained (Table 3, entry 5). However, using **4** instead of **2** afforded dimethyl (2,2-diphenylvinyl) phosphonate (**5o′**) in 78% yield, which was derived from dimethyl (2-hydroxy-2,2-diphenylethyl)phosphonate (**5o**) by loss of H_2O (Table 3, entry 5). Compared to α-phenylstyrene (**1o**), the reaction of β-phenylstyrene (**1p**) with **2** afforded a sole acetoxyphosphorylation product **3p** in 50% yield, while the reaction of **1p** with **4** gave the mixture of acetoxy- and oxyphosphorylation (**5p** and **5p′**) through a similar way to **5l** and **5l′** (Table 3, entries 2, 6). Based on the results described above, using α- or β-substituted (CH_3, Br, and Ph) styrenes as substrates, diverse products were obtained, and the structure of products depended on both the kind of substituents and their location. Finally, nonconjugated terminal alkenes (**1q**–**1t**) were conducted for the reaction, and the exclusive hydrophosphorylation products were obtained with up to 92% yield (Table 3, entries 7–10).

The above acetoxyphosphorylation reaction proceeded through a radical pathway; viz. phosphorus-centered radical selectively adds to the terminal C=C double bond of **1** to yield a carbon radical intermediate. It is oxidized by $Mn(OAc)_3$ to form a carbocation, followed by combinating with HOAc and deprotonation, to afford products **3** or **5**. The carbocation intermediate is captured by adding tetrabutylammonium bromide (**TBAB**) to the reaction of **1a** and **2** to form 1-(diphenylphosphoryl)-2-bromophenylethane (**3a′**).

In conclusion, a new type of difunctionalization of alkenes was developed from the reaction of diphenylphosphine oxide and dialkyl phosphites with alkenes in the presence of $Mn(OAc)_3$ through a tandem radical process. The reactions proceeded under mild conditions in air to afford acetoxyphosphorylation products in moderate to good yields. This methodology has the advantages of being straightforward, no need of additives and other oxidants, short reaction time,

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214–1220

Table 3. Reactions of α- and β-Substituted Styrenes 1 with Diphenylphosphine Oxide 2 and Dimethyl Phosphite 4[a,b,c,d,e,f]

Entry	Olefin	Product and Yield/%[c]
1	 **1k**	 **3k** (R = Ph) 67 **5k** (R = OCH_3) 67
2	 **1l**	 I, X = Ac; **I'**, X = H **3l** and **3l'** (R = Ph) 80[d] **5l** and **5l'** (R = OCH_3) 75[d]
3	 **1m**[e]	 **3m** (R = Ph) 30 **5m** (R = OCH_3) 21  **3m'** (R = Ph) 50 **5m'** (R = OCH_3) 50
4	 **1n**	 **3n** (R = Ph) 65 **5n** (R = OCH_3) 61
5	 **1o**	 **3o** (R = Ph) 71 **5o** (R = OCH_3) 0  **3o'** (R = Ph) 0 **5o'** (R = OCH_3) 78
6	 **1p**	 **3p** 50  **5p** and  **5p'** 60[f] (**5p** + **5p'**)
7	 **1q**	 **3q** 87
8	 **1r**	 **3r** (R = Ph) 92 **5r** (R = OCH_3) 75
9	 **1s**	 **3s** 83
10	 **1t**	 **3t** 60

[a]Reactions of diphenylphosphine oxide (**2**) and dimethyl phosphite (**4**) were performed at 50 and 70 °C, respectively. [b]Reaction conditions: olefin (1.0 mmol), $HP(0)R_2$ (1.5 mmol), $Mn(OAc)_3$ (2.0 mmol) in HOAc (10 mL), 30 min. [c]Isolated yield. [d]Mixture of acetoxy- and hydroxyphosphorylation; they cannot be separated from each other. [e]Reaction conditions: olefin (1.0 mmol), $HP(0)R_2$ (2 mmol), $Mn(OAc)_3$ (3.0 mmol) in HOAc (10 mL), 30 min. [f]Mixture of acetoxy- and oxyphosphorylation; they cannot be separated from each other.

simple manipulations, and the acetoxyphosphorylation products can be easily transformed into a variety of useful functionalized compounds.

EXPERIMENTAL SECTION

General Methods. ^1H NMR (400 or 300 MHz) and ^{13}C NMR (150, 100, or 75 MHz) spectra were determined with $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as internal standard or 85% H_3PO_4 as external standard for ^{31}P NMR (162 MHz). Chemical shifts were reported in ppm from internal TMS (δ); all coupling constants (J values) were reported in hertz (Hz). High-resolution mass spectra were recorded on a TOF machine (ESI). Column chromatography was performed with 300−400 mesh silica gel using flash column techniques. All of the reagents were used directly as obtained commercially unless otherwise noted. All alkenes were purified by flash column chromatography (Al_2O_3) before use.

Preparation of 2-(Diphenylphosphoryl)-1-arylethyl Acetates 3. *Typical Procedure for the Preparation of 2-(Diphenylphosphoryl)-1-phenylethyl Acetate (**3a**).* To a solution of acetic acid (10 mL), styrene (1.0 mmol), and diphenylphosphine oxide (1.5 mmol) was added $Mn(OAc)_3$ (2.0 mmol) in 10 min at 50 °C; about 30 min later, the reaction was completed. The mixture was cooled to room temperature, and the solvent was removed under vacuum. To the residue was added water (20 mL), and the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc/CH_2Cl_2 (8:1:1)) to give pure 2-(diphenylphosphoryl)-1-phenylethyl acetate (**3a**).

*2-(Diphenylphosphoryl)-1-phenylethyl Acetate (**3a**).* White solid; mp 150−151 °C, 70% yield (254.9 mg). ^1H NMR (400 MHz, $CDCl_3$): δ 7.79−7.85 (m, 2H), 7.65−7.71 (m, 2H), 7.45−7.54 (m, 4H), 7.37−7.43 (m, 2H), 7.27−7.36 (m, 3H), 7.19−7.25 (m, 2H),

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220

6.24 (td, J = 3.6, 9.0 Hz, 1H), 3.01−3.13 (m, 1H), 2.65−2.76 (m, 1H), 1.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 140.4 (d, J = 10.0 Hz), 133.1 (d, J = 99.8 Hz), 131.7 (d, J = 3.0 Hz), 131.6 (d, J = 2.8 Hz), 130.9 (d, J = 10.0 Hz), 130.6 (d, J = 10.0 Hz), 128.7, 128.6, 128.5, 128.4 (d, J = 20.9 Hz), 126.2, 70.2 (d, J = 3.0 Hz), 37.5 (d, J = 68.6 Hz), 20.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.0. HRMS (ESI-TOF) m/z: (M + H)$^+$ Calcd for $C_{22}H_{22}O_3P$ 365.1307, found 365.1305.

*(2-Bromo-2-phenylethyl)diphenylphosphine Oxide (**3a′**).* This compound was obtained from the $Mn(OAc)_3$-mediated reaction of styrene and diphenylphosphine oxide in HOAc in the presence of tetrabutylammonium bromide (**TBAB**) for mechanism investigation. White solid; mp 153−154 °C, 30% yield (115.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 7.74−7.82 (m, 2H), 7.43−7.58 (m, 5H), 7.24−7.39 (m, 5H), 7.08−7.15 (m, 3H), 5.55−5.65 (m, 1H), 3.36−3.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9 (d, J = 3.7 Hz), 132.1, 131.5, 130.8, 130.7 (d, J = 1.7 Hz), 130.6, 128.8 (d, J = 11.7 Hz), 128.6, 128.5, 128.4 (d, J = 12, 2 Hz), 127.4, 46.4, 41.6 (d, J = 64.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. HRMS (ESI-TOF) m/z: (M + H)$^+$ Calcd for $C_{20}H_{19}BrOP$ 385.0357, found 385.0387.

*2-(Diphenylphosphoryl)-1-(p-tolyl)ethyl Acetate (**3b**).* White solid; mp 174−175 °C, 65% yield (245.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.87 (m, 2H), 7.64−7.74 (m, 2H), 7.46−7.55 (m, 4H), 7.37−7.44 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 6.23 (td, J = 3.8, 9.1 Hz, 1H), 3.03−3.15 (m, 1H), 2.65−2.75 (m, 1H), 2.29 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 138.1, 137.5 (d, J = 9.6 Hz), 133.6 (d, J = 3.6 Hz), 132.6 (d, J = 3.5 Hz), 131.7 (d, J = 2.5 Hz), 131.0 (d, J = 9.4 Hz), 130.6 (d, J = 9.4 Hz), 129.3, 128.6 (d, J = 5.7 Hz), 128.5 (d, J = 5.8 Hz), 126.3, 70.2 (d, J = 2.9 Hz), 37.4 (d, J = 68.4 Hz), 21.1, 20.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.5. HRMS (ESI-TOF) m/z: (M + Na)$^+$ Calcd for $C_{23}H_{23}NaO_3P$ 401.1283, found 401.1279.

*2-(Diphenylphosphoryl)-1-(4-methoxyphenyl)ethyl Acetate (**3c**).* White solid; mp 165−166 °C, 73% yield (287.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.85 (m, 2H), 7.63−7.72 (m, 2H), 7.35−7.53 (m, 6H), 7.20−7.25 (m, 2H), 6.76−6.84 (m, 2H), 6.16−6.28 (m, 1H), 3.74 (d, J = 4.4 Hz, 3H), 3.01−3.17 (m, 1H), 2.64−2.78 (m, 1H), 1.64 (d, J = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 159.5, 133.6, 132.6, 132.4, 132.3, 131.6 (d, J = 2.6 Hz), 130.9 (d, J = 9.4 Hz), 130.6 (d, J = 9.2 Hz), 128.6 (d, J = 3.7 Hz), 128.5 (d, J = 3.7 Hz), 127.8, 113.9, 70.2 (d, J = 2.6 Hz), 55.2, 37.2 (d, J = 69.0 Hz), 20.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.0. HRMS (ESI-TOF) m/z: (M − OAc)$^+$ Calcd for $C_{21}H_{20}O_2P$ 335.1201, found 335.1239.

*2-(Diphenylphosphoryl)-1-(4-fluorophenyl)ethyl Acetate (**3d**).* White solid; mp 134−135 °C, 61% yield (233.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79−7.84 (m, 2H), 7.62−7.71 (m, 2H), 7.46−7.58 (m, 5H), 7.37−7.45 (m, 2H), 7.28−7.33 (m, 1H), 6.90−7.00 (m, 2H), 6.18−6.28 (m, 1H), 3.01−3.14 (m, 1H), 2.63−2.78 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 162.4 (d, J = 245.5 Hz), 132.3 (d, J = 2.1 Hz), 132.2 (d, J = 9.6 Hz), 131.8 (d, J = 2.2 Hz), 131.1 (d, J = 9.6 Hz), 130.9 (d, J = 9.3 Hz), 130.6 (d, J = 9.3 Hz), 128.69 (d, J = 12.1 Hz), 128.68 (d, J = 2.3 Hz), 128.5 (d, J = 2.3 Hz), 128.3 (d, J = 8.3 Hz), 115.5 (d, J = 21.5 Hz), 69.8, 37.4 (d, J = 68.9 Hz), 20.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.8. HRMS (ESI-TOF) m/z: (M + Na)$^+$ Calcd for $C_{22}H_{20}FNaO_3P$ 405.1032, found 405.1047.

*1-(4-Chlorophenyl)-2-(diphenylphosphoryl)ethyl Acetate (**3e**).* White solid; mp 166−167 °C, 60% yield (238.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.83 (m, 2H), 7.62−7.68 (m, 2H), 7.47−7.60 (m, 4H), 7.37−7.45 (m, 2H), 7.20−7.25 (m, 4H), 6.22 (td, J = 4.8, 8.4 Hz, 1H), 3.00−3.10 (m, 1H), 2.65−2.74 (m, 1H), 1.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 138.7 (d, J = 9.0 Hz), 134.1, 131.8 (d, J = 2.0 Hz), 130.9 (d, J = 10.0 Hz), 130.6 (d, J = 9.0 Hz), 128.8, 128.7 (d, J = 3.0 Hz), 128.6 (d, J = 4.0 Hz), 127.9, 69.8 (d, J = 4.0 Hz), 37.3 (d, J = 68.0 Hz), 20.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.9. HRMS (ESI-TOF) m/z: (M + H)$^+$ Calcd for $C_{22}H_{21}ClO_3P$ 399.0917, found 399.0933.

*1-(3-Chlorophenyl)-2-(diphenylphosphoryl)ethyl Acetate (**3f**).* White solid; mp 172−173 °C, 58% yield (230.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.84 (m, 2H), 7.62−7.70 (m, 2H), 7.45−7.59 (m, 5H), 7.37−7.44 (m, 2H), 7.17−7.23 (m, 3H), 6.20 (td, J = 4.4, 8.8 Hz, 1H), 2.98−3.09 (m, 1H), 2.64−2.74 (m, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 142.3 (d, J = 9.2 Hz), 134.5, 131.9 (d, J = 2.6 Hz), 131.8 (d, J = 2.7 Hz), 130.9 (d, J = 9.4 Hz), 130.6 (d, J = 9.4 Hz), 129.9, 128.7 (d, J = 3.8 Hz), 128.6 (d, J = 3.9 Hz), 128.5, 126.4, 124.7, 69.7 (d, J = 2.5 Hz), 37.6 (d, J = 68.5 Hz), 20.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.4. HRMS (ESI-TOF) m/z: (M + H)$^+$ Calcd for $C_{22}H_{21}ClO_3P$ 399.0917, found 399.0922.

*1-(4-Bromophenyl)-2-(diphenylphosphoryl)ethyl Acetate (**3g**).* White solid; mp 130−131 °C, 60% yield (265.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78−7.85 (m, 2H), 7.62−7.70 (m, 2H), 7.42−7.58 (m, 6H), 7.38 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 6.13−6.24 (m, 1H), 2.96−3.14 (m, 1H), 2.63−2.79 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.2, 139.2 (d, J = 8.8 Hz), 131.7, 130.9 (d, J = 9.4 Hz), 130.6 (d, J = 9.3 Hz), 128.7 (d, J = 3.5 Hz), 128.6 (d, J = 3.7 Hz), 128.2, 122.3, 69.9, 37.2 (d, J = 68.5 Hz), 20.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.1. HRMS (ESI-TOF) m/z: (M + Na)$^+$ Calcd for $C_{22}H_{20}BrNaO_3P$ 465.0231, found 465.0252.

*Mixture of 2-(Diphenylphosphoryl)-1-(3-(trifluoromethyl)phenyl)-ethyl Acetate (**3h**) and 2-(Diphenylphosphoryl)-1-(3-(trifluoromethyl)phenyl)ethanone (**3h′**).* White solid; 35% (**3h**) and 28% (**3h′**) yield (259.9 mg), respectively, **3h**:**3h′** = 1:0.8, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, J = 7.9 Hz, 1H), 8.19 (s, 1H), 7.70−7.88 (m, 6H), 7.45−7.60 (m, 9H), 7.32−7.40 (m, 2H), 4.16 (d, J = 15.3 Hz, 2H), 2.95−3.06 (m, 1H), 2.52−2.62 (m, 1H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.7 (d, J = 5.6 Hz), 141.9 (d, J = 14.5 Hz), 137.4, 132.8, 132.4 (d, J = 2.8 Hz), 132.2, 131.9 (d, J = 2.6 Hz), 131.7, 131.1, 131.0, 130.8 (d, J = 9.3 Hz), 129.9 (d, J = 3.6 Hz), 129.3, 129.1, 128.8 (d, J = 12.0 Hz), 125.8 (d, J = 3.8 Hz), 124.8 (d, J = 3.8 Hz), 123.3 (d, J = 3.9 Hz), 43.9 (d, J = 55.9 Hz), 29.7, 27.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.7, 31.2. HRMS (ESI-TOF) of **3h** m/z: (M + H)$^+$ Calcd for $C_{23}H_{21}F_3O_3P$ 433.1180, found 433.1193; HRMS (ESI-TOF) of **3h′** m/z: (M + H)$^+$ Calcd for $C_{21}H_{17}F_3O_2P$ 389.0918, found 389.0927.

*4-(2-(Diphenylphosphoryl)acetyl)benzonitrile (**3i′**).* White solid; mp 169−170 °C, 48% yield (165.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, J = 8.2 Hz, 2H), 7.79 (dd, J = 7.5, 12.0 Hz, 4H), 7.72 (d, J = 8.2 Hz, 2H), 7.53−7.58 (m, 2H), 7.45−7.51 (m, 4H), 4.15 (d, J = 15.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.8 (d, J = 5.8 Hz), 139.8, 132.4 (d, J = 2.7 Hz), 132.3, 131.0 (d, J = 9.8 Hz), 129.8, 128.8 (d, J = 12.4 Hz), 117.9, 116.7, 44.0 (d, J = 55.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 26.5. HRMS (ESI-TOF) m/z: (M + H)$^+$ Calcd for $C_{21}H_{17}NO_2P$ 346.0997, found 346.1002.

*2-(Diphenylphosphoryl)-1-(4-nitrophenyl)ethanone (**3j′**).* Yellow solid; mp 163−164 °C,[7] 30% yield (109.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.9 Hz, 2H), 8.20 (d, J = 8.9 Hz, 2H), 7.76−7.83 (m, 4H), 7.54−7.59 (m, 2H), 7.46−7.53 (m, 4H), 4.17 (d, J = 15.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6 (d, J = 5.8 Hz), 150.5, 141.2, 132.5 (d, J = 2.9 Hz), 131.9, 131.0 (d, J = 9.8 Hz), 130.4, 128.8 (d, J = 12.4 Hz), 123.7, 44.3 (d, J = 54.8 Hz).

*1-(Diphenylphosphoryl)-2-phenylpropan-2-yl Acetate (**3k**).* White solid; mp 137−138 °C, 67% yield (253.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.86 (m, 2H), 7.61−7.70 (m, 2H), 7.33−7.53 (m, 7H), 7.12−7.30 (m, 4H), 3.33−3.43 (m, 1H), 2.90−3.02 (m, 1H), 2.17 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.1, 144.8 (d, J = 7.5 Hz), 134.2 (d, J = 48.5 Hz), 133.2 (d, J = 49.3 Hz), 131.1 (d, J = 5.8 Hz), 130.7 (d, J = 9.2 Hz), 130.1 (d, J = 8.9 Hz), 128.3, 128.2 (d, J = 5.1 Hz), 128.1, 127.0, 123.8, 81.8 (d, J = 4.0 Hz), 37.5 (d, J = 68.3 Hz), 26.5, 21.3; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.4. HRMS (ESI-TOF) m/z: (M + Na)$^+$ Calcd for $C_{23}H_{23}NaO_3P$ 401.1283, found 401.1286.

*Mixture of 2-(Diphenylphosphoryl)-1-phenylpropyl Acetate (**3l**) and (1-Hydroxy-1-phenylpropan-2-yl) Diphenylphosphine Oxide (**3l′**).* White solid; 40% (**3l**) and 40% (**3l′**) yield (285.8 mg), respectively, **3l**:**3l′** = 1:1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81−7.86 (m, 2H), 7.71−7.80 (m, 4H), 7.42−7.54 (m, 6H), 7.26−7.37 (m, 6H), 7.15−7.24 (m, 7H), 7.04−7.13 (m, 5H), 6.24 (d, J = 21.0 Hz, 1H), 4.60 (d, J = 30.0 Hz, 1H), 2.95−3.01 (m, 1H), 2.74−2.80 (m, 1H), 1.95 (s, 3H), 1.20 (dd, J = 7.2, 15.6 Hz, 1H), 1.05 (dd, J = 7.2, 16.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220

169.3, 139.4 (d, J = 12.2 Hz), 139.2 (d, J = 3.9 Hz), 135.0 (d, J = 95.3 Hz), 132.2 (d, J = 8.3 Hz), 131.7 (d, J = 2.4 Hz), 131.6 (d, J = 2.4 Hz), 131.2 (d, J = 8.6 Hz), 131.0 (d, J = 8.7 Hz), 130.8, 130.6 (d, J = 8.9 Hz), 128.7 (d, J = 11.3 Hz), 128.6 (d, J = 11.3 Hz), 128.4, 128.1 (d, J = 11.0 Hz), 127.9, 127.7, 127.5 (d, J = 11.3 Hz), 126.7, 125.7, 71.9 (d, J = 1.7 Hz), 53.5 (d, J = 2.9 Hz), 39.9 (d, J = 68.7 Hz), 37.1 (d, J = 72.9 Hz), 20.8, 16.7, 7.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.1, 37.5. HRMS (ESI-TOF) of **3l** m/z: $(M + H)^+$ Calcd for $C_{23}H_{24}O_3P$ 379.1463, found 379.1482; HRMS (ESI-TOF) of **3l′** m/z: $(M + Na)^+$ Calcd for $C_{21}H_{21}O_2PNa$ 359.1177, found 359.1150.

*(2-Bromo-2-phenylvinyl)diphenylphosphine Oxide (**3m**).* Colorless liquid, 30% yield (114.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77−7.88 (m, 4H), 7.62−7.67 (m, 2H), 7.45−7.55 (m, 7H), 7.35−7.40 (m, 2H), 7.14 (d, J = 16.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.1, 139.3 (d, J = 11.9 Hz), 131.9, 131.2 (d, J = 9.5 Hz), 130.7, 128.8, 128.7, 128.5, 127.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.1. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{20}H_{17}BrOP$ 383.0200, found 383.0207.

*2-(Diphenylphosphoryl)-1-phenylethanone (**3m′**).* White solid; mp 160−161 °C,[8] 50% yield (160.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96−8.02 (m, 2H), 7.77−7.85 (m, 4H), 7.50−7.55 (m, 3H), 7.39−7.49 (m, 6H), 4.14 (d, J = 15.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.8 (d, J = 5.2 Hz), 136.9, 133.6, 132.6, 132.2, 131.1 (d, J = 9.8 Hz), 129.2, 128.7, 128.5, 43.2 (d, J = 57.8 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{20}H_{18}O_2P$ 321.1044, found 321.1047.

*(E)-Diphenyl(styryl)phosphine Oxide (**3n**).* White solid; mp 169−170 °C,[9] 65% yield (197.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 7.4, 11.9 Hz, 4H), 7.45−7.60 (m, 9H), 7.35−7.42 (m, 3H), 6.87 (dd, J = 17.4, 22.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6 (d, J = 3.6 Hz), 135.2 (d, J = 17.9 Hz), 133.0 (d, J = 105.2 Hz), 131.9 (d, J = 2.7 Hz), 131.4 (d, J = 10.0 Hz), 130.1, 128.9, 128.7 (d, J = 12.1 Hz), 127.8, 119.2 (d, J = 103.9 Hz).

*(2-Hydroxy-2,2-diphenylethyl)diphenylphosphine Oxide (**3o**).* White solid; mp 183−184 °C,[10] 71% yield (282.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.53 (m, 4H), 7.40−7.45 (m, 2H), 7.30−7.38 (m, 8H), 7.02−7.13 (m, 6H), 4.50 (s, 1 H), 3.40 (d, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1 (d, J = 7.3 Hz), 133.4, 132.4, 131.6 (d, J = 2.6 Hz), 130.4 (d, J = 9.6 Hz), 128.5 (d, J = 7.9 Hz), 127.9, 126.9, 125.9, 77.7 (d, J = 4.8 Hz), 41.2 (d, J = 69.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.4.

*2-(Diphenylphosphoryl)-1,2-diphenylethyl Acetate (**3p**).* White solid; mp 248−249 °C, 50% yield (220.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): 7.71−7.83 (m, 2H), 7.55−7.65 (m, 1H), 7.40−7.53 (m, 5H), 7.10−7.25 (m, 7H), 6.97−7.07 (m, 5H), 6.52−6.62 (m, 1H), 3.80−3.90 (m, 1H), 1.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.3, 138.7 (d, J = 7.0 Hz), 131.4 (d, J = 2.8 Hz), 131.2 (d, J = 6.0 Hz), 131.1, 131.0, 130.9, 130.8, 128.5 (d, J = 12.0 Hz), 128.2 (d, J = 1.6 Hz), 128.04, 128.0, 127.9, 127.8, 127.3 (d, J = 1.8 Hz), 127.1, 126.8, 73.4, 53.4 (d, J = 66.0 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.0. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{28}H_{26}O_3P$ 441.1620, found 441.1631.

*Diphenyl (3-Phenylpropyl)phosphine Oxide (**3q**).* White solid; mp 116−117 °C,[11] 87% yield (278.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63−7.73 (m, 4H), 7.40−7.56 (m, 7H), 7.06−7.28 (m, 4H), 2.68−2.78 (m, 2H), 2.18−2.40 (m, 2H), 1.90−2.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 132.8 (d, J = 97.4 Hz), 131.7, 130.7 (d, J = 11.7 Hz), 128.7, 128.5 (d, J = 2.9 Hz), 128.4, 126.1, 36.6 (d, J = 14.7 Hz), 28.9 (d, J = 71.5 Hz), 23.0. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{21}H_{22}OP$ 321.1408, found 321.1415.

*Diphenyl(4-phenylbutyl)phosphine Oxide (**3r**).* White solid; mp 150−151 °C,[12] 92% yield (307.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66−7.75 (m, 4H), 7.38−7.55 (m, 6H), 7.08−7.25 (m, 5H), 2.52−2.62 (m, 2H), 2.20−2.31 (m, 2H), 1.63−1.75 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.9, 133.0 (d, J = 96.9 Hz), 131.7, 130.8 (d, J = 8.8 Hz), 128.7, 128.5, 128.3, 125.8, 36.4, 32.7 (d, J = 14.2 Hz), 29.6 (d, J = 71.3 Hz), 21.2. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{22}H_{24}OP$ 335.1565, found 335.1575.

*Diphenyl(3-(p-tolyloxy)propyl)phosphine Oxide (**3s**).* White solid; mp 113−114 °C,[12] 83% yield (290.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.80 (m, 4H), 7.43−7.54 (m, 6H), 7.04 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 3.93−4.00 (m, 2H), 2.42−2.52 (m, 2H), 2.27 (s, 3H), 2.05−2.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 132.8 (d, J = 97.6 Hz), 131.8, 130.8 (d, J = 9.1 Hz), 129.9, 129.8, 128.7 (d, J = 11.3 Hz), 114.3, 67.6 (d, J = 14.2 Hz), 26.5 (d, J = 72.4 Hz), 21.8 (d, J = 2.0 Hz), 20.5. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{22}H_{24}O_2P$ 351.1514, found 351.1513.

*Octyldiphenylphosphine Oxide (**3t**).* White solid; mp 57−58 °C;[12] 60% yield (188.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68−7.80 (m, 4H), 7.42−7.53 (m, 6H), 2.10−2.32 (m, 2H), 1.53−1.65 (m, 2H), 1.32−1.42 (m, 2H), 1.18−1.30 (m, 8H), 0.80−0.88 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.3 (d, J = 97.4 Hz), 131.6, 130.6 (d, J = 8.1 Hz), 128.5 (d, J = 11.3 Hz), 31.6, 30.8 (d, J = 14.2 Hz), 29.5 (d, J = 71.8 Hz), 28.9, 22.4, 21.2 (d, J = 2.6 Hz), 21.1, 14.0.

Preparation of 2-(Dialkoxyphosphoryl)-1-arylethyl Acetate 5. *Typical Procedure for the Preparation of 2-(Dimethoxyphosphoryl)-1-phenylethyl Acetate (**5a**).* To a solution of acetic acid (10 mL), styrene (1.0 mmol), and dimethyl phosphite (1.5 mmol) was added $Mn(OAc)_3$ (2.0 mmol) in 30 min at 70 °C; about 60 min later, the reaction was completed. The mixture was cooled to room temperature, and the solvent was removed under vacuum. To the residue was added water (20 mL), and the mixture was extracted with ethyl acetate (10 mL × 3). The combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield the crude product, which was purified by column chromatography (silica gel, petroleum ether/EtOAc/CH_2Cl_2 (8:1:1)) to give pure 2-(dimethoxyphosphoryl)-1-phenylethyl acetate (**5a**).

*2-(Dimethoxyphosphoryl)-1-phenylethyl Acetate (**5a**).* Colorless liquid; 68% yield (195.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.42 (m, 5H), 6.02−6.11 (m, 1H), 3.63 (d, J = 10.8 Hz, 6H), 2.42−2.55 (m, 1H), 2.21−2.32 (m, 1H), 2.05 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.5, 139.7 (d, J = 10.5 Hz), 128.5, 128.4, 126.4, 70.5, 52.4 (d, J = 6.5 Hz), 52.2 (d, J = 6.5 Hz), 32.3 (d, J = 139.7 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.1. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{12}H_{17}NaO_5P$ 295.0711, found 295.0706.

*2-(Diethoxyphosphoryl)-1-phenylethyl Acetate (**5a′**).* Colorless liquid; 63% yield (189.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.42 (m, 5H), 6.05−6.15 (m, 1H), 3.94−4.10 (m, 4H), 2.45−2.58 (m, 1H), 2.22−2.35 (m, 1H), 2.07 (s, 3H), 1.21−1.30 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 139.9 (d, J = 10.3 Hz), 128.6, 128.4, 126.6, 70.8 (d, J = 1.5 Hz), 61.8 (d, J = 6.4 Hz), 61.6 (d, J = 6.4 Hz), 33.3 (d, J = 139.5 Hz), 21.1, 16.3 (d, J = 4.8 Hz), 16.2 (d, J = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.3. HRMS (ESI-TOF) m/z: $(M - OAc)^+$ Calcd for $C_{12}H_{18}O_3P$ 241.0994, found 241.0997.

*2-(Dimethoxyphosphoryl)-1-(p-tolyl)ethyl Acetate (**5b**).* Colorless liquid; 65% yield (183.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 6.05 (td, J = 5.7, 8.7 Hz, 1H), 3.66 (d, J = 1.6 Hz, 3H), 3.64 (d, J = 1.6 Hz, 3H), 2.46−2.57 (m, 1H), 2.33 (s, 3H), 2.20−2.30 (m, 1H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 138.3, 136.8 (d, J = 10.7 Hz), 129.3, 126.5, 70.5 (d, J = 1.7 Hz), 52.5 (d, J = 6.5 Hz), 52.3 (d, J = 6.5 Hz), 32.4 (d, J = 139.3 Hz), 21.1 (d, J = 3.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.3. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{13}H_{19}NaO_5P$ 309.0868, found 309.0877.

*2-(Dimethoxyphosphoryl)-1-(4-methoxyphenyl)ethyl Acetate (**5c**).* Colorless liquid; 66% yield (119.4 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.98−6.04 (m, 1H), 3.76 (s, 3H), 3.63 (d, J = 6.0 Hz, 3H), 3.61 (d, J = 6.0 Hz, 3H), 2.46−2.54 (m, 1H), 2.22−2.30 (m, 1H), 2.02 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.6, 159.6, 131.0 (d, J = 10.2 Hz), 128.0, 113.9, 70.3, 52.4 (d, J = 6.5 Hz), 52.2 (d, J = 6.5 Hz), 32.3 (d, J = 139.2 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.3. HRMS (ESI-TOF) m/z: $(M - OAc)^+$ Calcd for $C_{11}H_{16}O_4P$ 243.0786, found 243.0810.

*2-(Dimethoxyphosphoryl)-1-(4-fluorophenyl)ethyl Acetate (**5d**).* Colorless liquid; 59% yield (171.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.38 (m, 2H), 6.96−7.06 (m, 2H), 5.98−6.08 (m, 1H), 3.64 (d, J = 4.8 Hz, 3H), 3.62 (d, J = 4.8 Hz, 3H), 2.48 (ddd, J = 8.0, 15.5, 17.6 Hz, 1H), 2.25 (ddd, J = 6.1, 15.4, 18.9 Hz, 1H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 162.6 (d, J = 245.8 Hz), 135.6 (dd,

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220

J = 3.3, 10.0 Hz), 128.5 (d, J = 8.3 Hz), 115.6, 115.4, 70.0, 52.5 (d, J = 6.4 Hz), 52.3 (d, J = 6.4 Hz), 32.4 (d, J = 139.7 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.8. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{12}H_{16}FNaO_5P$ 313.0617, found 313.0633.

*2-(Dimethoxyphosphoryl)-1-(4-chlorophenyl)ethyl Acetate (**5e**).* Colorless liquid; 62% yield (189.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.4 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.99−6.08 (m, 1H), 3.67 (d, J = 6.0 Hz, 3H), 3.65 (d, J = 6.0 Hz, 3H), 2.43−2.51 (m, 1H), 2.20−2.32 (m, 1H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 138.2 (d, J = 10.2 Hz), 134.3, 130.0 (d, J = 139.3 Hz), 128.4 (d, J = 85.2 Hz), 70.0, 52.5 (d, J = 7.4 Hz), 52.4 (d, J = 7.4 Hz), 33.1 (d, J = 14.0 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.7. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{12}H_{17}ClO_5P$ 307.0502, found 307.0512.

*2-(Dimethoxyphosphoryl)-1-(4-bromophenyl)ethyl Acetate (**5g**).* Colorless liquid; 51% yield (180.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 6.00−6.08 (m, 1H), 3.71 (d, J = 2.6 Hz, 3H), 3.68 (d, J = 2.6 Hz, 3H), 2.46−2.58 (m, 1H), 2.23−2.34 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 138.7 (d, J = 10.3 Hz), 131.8 (d, J = 6.3 Hz), 128.3, 122.5, 70.1, 52.6 (d, J = 6.4 Hz), 52.4 (d, J = 6.4 Hz), 32.3 (d, J = 140.0 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 27.7. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{12}H_{16}BrNaO_5P$ 372.9816, found 372.9827.

*Mixture of 2-(Dimethoxyphosphoryl)-1-(3-(trifluoromethyl)-phenyl)ethyl Acetate (**5h**) and Dimethyl (2-Oxo-2-(3-(trifluoro-methyl)phenyl)ethyl)phosphonate (**5h′**).* Colorless liquid; 37% (**5h**) and 37% (**5h′**) yield (245.5 mg), respectively, **5h**:**5h′** = 1:1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16−8.28 (m, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.32−7.70 (m, 6H), 7.40 (dd, J = 8.0, 18.4 Hz, 1H), 6.05−6.15 (m, 1H), 3.75−3.80 (m, 2H), 3.31−3.68 (m, 6H), 2.44−2.56 (m, 1H), 2.22−2.33 (m, 1H), 2.08 (d, J = 2.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.5 (d, J = 6.7 Hz), 169.5, 140.8 (d, J = 10.2 Hz), 136.7 (d, J = 2.1 Hz), 132.2, 131.0 (d, J = 32.4 Hz), 130.1 (d, J = 14.6 Hz), 129.4, 129.2, 125.8 (d, J = 3.8 Hz), 125.7 (d, J = 3.8 Hz), 125.3 (d, J = 3.7 Hz), 123.3 (d, J = 3.7 Hz), 122.5, 70.0, 52.5 (d, J = 6.5 Hz), 52.4 (d, J = 6.5 Hz), 38.4, 37.8 (d, J = 130.0 Hz), 37.1, 32.4 (d, J = 140.0 Hz), 21.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.9, 27.4. HRMS (ESI-TOF) of **5h** m/z: $(M\text{-}OAc)^+$ Calcd for $C_{10}H_{13}F_3O_3P$ 281.0554, found 281.0561; HRMS (ESI-TOF) of **5h′** m/z: $(M + H)^+$ Calcd for $C_{11}H_{13}F_3O_4P$ 297.0504, found 297.0511.

*Mixture of 2-(Dimethoxyphosphoryl)-1-(4-cyanophenyl)ethyl Acetate (**5i**) and Dimethyl (2-(4-Cyanophenyl)-2-oxoethyl)phosphonate (**5i′**).* Colorless liquid; 30% (**5i**) and 30% (**5i′**) yield (165.0 mg), respectively, **5i**:**5i′** = 1:1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 8.3 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.66 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 8.2 Hz, 2H), 6.02−6.11 (m, 1H), 3.79 (d, J = 11.3 Hz, 6H), 3.67 (d, J = 1.6 Hz, 3H), 3.65 (d, J = 1.6 Hz, 3H), 3.63 (d, J = 57.0 Hz, 2H), 2.42−2.53 (m, 1H), 2.20−2.32 (m, 1H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.6 (d, J = 6.6 Hz), 169.4, 144.8 (d, J = 10.0 Hz), 139.2, 132.5 (d, J = 5.2 Hz), 130.9, 129.4, 128.9 (d, J = 10.0 Hz), 127.3, 118.1 (d, J = 63.2 Hz), 117.0, 112.4, 70.0, 53.3 (d, J = 6.6 Hz), 52.6 (d, J = 6.5 Hz), 52.5 (d, J = 6.5 Hz), 38.0 (d, J = 129.4 Hz), 32.3 (d, J = 140.4 Hz), 20.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.5, 27.1. HRMS (ESI-TOF) of **5i** m/z: $(M + Na)^+$ Calcd for $C_{13}H_{16}NO_5PNa$ 320.0664, found 320.0681; HRMS (ESI-TOF) of **5i′** m/z: $(M + Na)^+$ Calcd for $C_{11}H_{12}NO_4PNa$ 276.0402, found 276.0409.

*Dimethyl (2-(4-Nitrophenyl)-2-oxoethyl)phosphonate (**5j′**).* Yellow oil; 45% yield (122.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.8 Hz, 2H), 8.18 (d, J = 8.8 Hz, 2H), 3.80 (d, J = 11.3 Hz, 6H), 3.68 (d, J = 57.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.4 (d, J = 6.6 Hz), 150.6, 140.6, 130.1, 123.9, 53.4 (d, J = 6.6 Hz), 38.2 (d, J = 129.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.3. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{10}H_{12}NNaO_6P$ 296.0300, found 296.0318.

*1-(Dimethoxyphosphoryl)-2-phenylpropan-2-yl Acetate (**5k**).* Colorless liquid; 67% yield (191.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.39 (m, 4H), 7.23−7.30 (m, 1H), 3.76 (s, 3H), 3.61 (d, J = 11.2 Hz, 3H), 3.54 (d, J = 11.2 Hz, 3H), 2.90−3.00 (m, 1H), 2.64−2.75 (m, 1H), 2.02 (s, 3H), 1.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.8, 144.7 (d, J = 9.2 Hz), 128.4, 127.3, 124.2, 80.2 (d, J = 2.7 Hz), 52.3 (d, J = 6.5 Hz), 52.1 (d, J = 6.5 Hz), 35.4 (d, J = 64.4 Hz), 27.8, 22.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ 28.1. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{13}H_{19}NaO_5P$ 309.0868, found 309.0878.

*Mixture of 2-(Dimethoxyphosphoryl)-1-phenylpropyl Acetate (**5l**) and Dimethyl (1-Hydroxy-1-phenylpropan-2-yl)phosphonate (**5l′**).* Colorless liquid; 50% (**5l**) and 25% (**5l′**) yield (204 mg), respectively, **5l**:**5l′** = 2:1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.39 (m, 9 H), 7.26−7.30 (m, 6H), 6.21 (dd, J = 4.5, 8.3 Hz, 2H), 5.91 (t, J = 9.0 Hz, 1H), 3.76 (d, J = 3.0 Hz, 3H), 3.74 (d, J = 3.0 Hz, 3H), 3.67 (d, J = 10.7 Hz, 12H), 2.53 (ddd, J = 7.4, 9.2, 17.9 Hz, 1H), 2.29−2.40 (m, 2H), 2.13 (s, 6H), 2.07 (s, 3H), 1.21 (dd, J = 7.3, 17.8, 6H), 0.99 (dd, J = 7.4, 17.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 (d, J = 9.4 Hz), 138.8 (d, J = 11.4 Hz), 138.0 (d, J = 11.8 Hz), 128.4 (d, J = 2.7 Hz), 128.3, 127.9, 127.4, 126.2, 74.9 (d, J = 2.8 Hz), 73.1, 52.7 (d, J = 7.0 Hz), 52.6 (d, J = 7.0 Hz), 52.5 (d, J = 6.7 Hz), 52.4 (d, J = 6.7 Hz), 37.4 (d, J = 140.0 Hz), 36.2 (d, J = 140.0 Hz), 21.0 (d, J = 18.3 Hz), 11.2 (d, J = 5.5 Hz), 8.5 (d, J = 3.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 32.0, 32.1. HRMS (ESI-TOF) of **5l** m/z: $(M - OAc)^+$ Calcd for $C_{11}H_{16}O_3P$ 227.0837, found 227.0833; HRMS (ESI-TOF) of **5l′** m/z: $(M + Na)^+$ Calcd for $C_{11}H_{17}O_4P$ Na 267.0762, found 267.0763.

*Dimethyl (2-Bromo-2-phenylvinyl)phosphonate (**5m**).* Colorless liquid; 21% yield (60.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60−7.65 (m, 2H), 7.37−7.44 (m, 3H), 6.65 (d, J = 9.7 Hz, 1H), 3.85 (d, J = 11.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 138.9 (d, J = 17.7 Hz), 130.7, 128.6, 127.8, 117.0 (d, J = 196.0 Hz), 52.8 (d, J = 5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.0. HRMS (ESI-TOF) m/z: $(M + Na)^+$ Calcd for $C_{10}H_{12}BrNaO_3P$ 312.9605, found 312.9606.

*Dimethyl (2-Oxo-2-phenylethyl)phosphonate (**5m′**).*[13] Colorless liquid; 50% yield (114.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97−8.02 (m, 2H), 7.56−7.62 (m, 1H), 7.45−7.52 (m, 2H), 3.77 (d, J = 11.2 Hz, 6H), 3.64 (d, J = 22.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7 (d, J = 6.5 Hz), 136.3 (d, J = 2.5 Hz), 133.8, 128.9, 128.7, 53.2 (d, J = 6.5 Hz), 37.4 (d, J = 131.0 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{10}H_{14}O_4P$ 229.0630, found 229.0635.

*(E)-Dimethyl Styrylphosphonate (**5n**).*[14] Colorless liquid; 61% yield (129.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54−7.62 (m, 1H), 7.49−7.53 (m, 2H), 7.38−7.43 (m, 3H), 6.24 (dd, J = 17.6, 17.8 Hz, 1H), 3.79 (d, J = 11.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.7 (d, J = 6.7 Hz), 134.6 (d, J = 23.3 Hz), 130.4, 128.9, 127.8, 112.3 (d, J = 191.3 Hz), 52.5 (d, J = 5.6 Hz).

*Dimethyl (2,2-Diphenylvinyl)phosphonate (**5o′**).*[15] Colorless liquid; 78% yield (224.7 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.42 (m, 10H), 6.18 (d, J = 15.6 Hz, 1H), 3.49 (d, J = 11.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.8 (d, J = 6.4 Hz), 141.1 (d, J = 23.8 Hz), 138.7 (d, J = 7.6 Hz), 129.5, 128.7, 128.2 (d, J = 15.2 Hz), 127.9, 127.0, 125.7, 113.5 (d, J = 193.3 Hz), 52.3 (d, J = 6.5 Hz), 52.1 (d, J = 6.0 Hz). HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{16}H_{18}O_3P$ 289.0994, found 289.1003.

*Mixture of 2-(Dimethoxyphosphoryl)-1,2-diphenylethyl Acetate (**5p**) and Dimethyl (2-Oxo-1,2-diphenylethyl) Phosphonate (**5p′**).* Colorless liquid; 48% (**5p**) and 12% (**5p′**) yield (200.0 mg), respectively, **5p**:**5p′** = 4:1, analyzed by ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38−7.43 (m, 2H), 7.26−7.35 (m, 8 H), 6.52 (dd, J = 6.2, 7.5 Hz, 1H), 3.85 (dd, J = 0.5, 11.3 Hz, 1H), 3.56 (dd, J = 7.6, 23.1 Hz, 1H), 3.43 (d, J = 10.9 Hz, 3H), 3.31 (d, J = 10.6 Hz, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6 (d, J = 4.0 Hz), 169.4, 138.5 (d, J = 6.5 Hz), 134.3 (d, J = 8.8 Hz), 133.3, 133.0, 132.9 (d, J = 2.9 Hz), 132.8 (d, J = 5.5 Hz), 130.2 (d, J = 6.9 Hz), 128.3 (d, J = 1.8 Hz), 128.2, 128.1, 127.6 (d, J = 2.5 Hz), 127.2, 74.0 (d, J = 3.9 Hz), 53.4 (d, J = 6.9 Hz), 53.0 (d, J = 5.9 Hz), 52.4 (d, J = 7.3 Hz), 51.9, 50.5, 20.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.9, 26.0. HRMS (ESI-TOF) of **5p** m/z: $(M + Na)^+$ Calcd for $C_{18}H_{21}O_5PNa$ 371.1025, found 371.1035.

*Dimethyl (4-Phenylbutyl)phosphonate (**5r**).* Colorless liquid; 75% yield (181.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27−7.32 (m, 2H), 7.15−7.23 (m, 3H), 3.74 (d, J = 10.8 Hz, 6H), 2.64 (t, J = 7.6 Hz, 2H), 1.64−1.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 128.4,

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220

128.3, 125.8, 52.4 (d, J = 6.6 Hz), 35.4 (d, J = 1.0 Hz), 32.2 (d, J = 16.0 Hz), 24.4 (d, J = 140.0 Hz), 21.9 (d, J = 5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 34.9. HRMS (ESI-TOF) m/z: $(M + H)^+$ Calcd for $C_{12}H_{20}O_3P$ 243.1150, found 243.1164.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H, ^{13}C, and ^{31}P NMR spectra for compounds **3** and **5**, and mechanism discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jpzou@suda.edu.cn (J.-P.Z.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.-P.Z. is thankful for the grant support by the National Natural Science Foundation of China (Nos. 20772088, 21172163) and the Priority Academic Program Development of Jiangsu Higher Education Institutions for financial support.

■ REFERENCES

(1) For selected reviews, see: (a) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (b) Bataille, C. J. R.; Donohoe, T. J. *Chem. Soc. Rev.* **2011**, *40*, 114.

(2) (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Yan, B.; Spilling, C. D. *J. Org. Chem.* **2008**, *73*, 5385. (c) Perumal, S. K.; Adediran, S. A.; Pratt, R. F. *Bioorg. Med. Chem.* **2008**, *16*, 6987. (d) Cotton, F. A.; Schunn, R. A. *J. Am. Chem. Soc.* **1963**, *85*, 2394. (e) Ryglowski, A.; Kafarski, P. *Tetrahedron* **1996**, *52*, 10685. (f) Kitamura, M.; Tokunaga, M.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2931. (g) Woodyer, R. D.; Li, G.; Zhao, H.; van der Donk, W. A. *Chem. Commun.* **2007**, 359. (h) Cui, P.; Tomsig, J. L.; McCalmont, W. F.; Lee, S.; Becker, C. J.; Lynch, K. R.; Macdonald, T. L. *Bioorg. Med. Chem. Lett.* **2007**, *17*, 1634. (i) Munos, J. W.; Moon, S. J.; Mansoorabadi, S. O.; Chang, W.; Hong, L.; Yan, F.; Liu, A.; Liu, H. W. *Biochemistry* **2008**, *47*, 8726.

(3) Selected recent P-centered radical reviews: (a) Hideki, Y. *Beilstein J. Org. Chem.* **2013**, *9*, 1269. (b) Van der Jeught, S.; Stevens, C. V. *Chem. Rev.* **2009**, *109*, 2672. (c) Coudray, L.; Montchamp, J. L. *Eur. J. Org. Chem.* **2008**, 3601. (d) Arbuzova, S. N.; Gusarova, N. K.; Trofimov, B. A. *ARKIVOC* **2006**, 12. (e) Laca, D.; Fensterbank, L.; Lacote, E.; Malacria, M. *Chem. Soc. Rev.* **2005**, *34*, 858. (f) Marque, S.; Tordo, P. *Top. Curr. Chem.* **2005**, *250*, 43. (g) Delacroix, O.; Gaumont, A. C. *Curr. Org. Chem.* **2005**, *9*, 1851. Selected recent P-centered radical papers: (h) Ma, W.; Ackermann, L. *Synthesis* **2014**, *46*, 2297. (i) Zhang, F.; Wang, L.; Zhang, C.; Zhao, Y. *Chem. Commun.* **2014**, *50*, 2046. (j) Zhang, B.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2014**, *16*, 250. (k) Mi, X.; Wang, C.; Huang, M.; Zhang, J.; Wu, Y.; Wu, Y. *Org. Lett.* **2014**, *16*, 3356. (l) Chu, X.-Q.; Zi, Y.; Meng, H.; Xu, X.-P.; Ji, S.-J. *Chem. Commun.* **2014**, *50*, 7642. (m) Chen, X.-L.; Li, X.; Qu, L.-B.; Tang, Y.-C.; Mai, W.-P.; Wei, D.-H.; Bi, W.-Z.; Duan, L.-K.; Sun, K.; Chen, J.-Y.; Ke, D.-D.; Zhao, Y.-F. *J. Org. Chem.* **2014**, *79*, 8407. (n) Li, Y.; Qiu, G.; Ding, Q.; Wu, J. *Tetrahedron* **2014**, *70*, 4652. (o) Yoo, W.-J.; Kobayashi, S. *Green Chem.* **2014**, *16*, 2438. (p) Kong, W.; Merino, E.; Nevado, C. *Angew. Chem., Int. Ed.* **2014**, *53*, 5078. (q) Chen, S.-Y.; Zeng, R.-S.; Zou, J.-P.; Asekun, O. T. *J. Org. Chem.* **2014**, *79*, 1449. (r) Chen, Y.-R.; Duan, W.-L. *J. Am. Chem. Soc.* **2013**, *135*, 16754. (s) Biresaw, G.; Bantchev, G. B. *J. Am. Oil Chem. Soc.* **2013**, *90*, 891. (t) Hernandez-Guerra, D.; Rodriguez, M. S.; Suarez, E. *Org. Lett.* **2013**, *15*, 250.

(4) (a) Wei, W.; Ji, J.-X. *Angew. Chem., Int. Ed.* **2011**, *50*, 9097. (b) Zhang, C.-W.; Li, Z.-D.; Zhu, L.; Yu, L.- M.; Wang, Z.-T.; Li, C.-Z. *J. Am. Chem. Soc.* **2013**, *135*, 14082.

(5) Selected recent $Mn(OAc)_3$-mediated reaction reviews: (a) Mondal, M.; Bora, U. *RSC Adv.* **2013**, *3*, 18716. (b) Yan, G.; Yang, M.; Wu, X. *Org. Biomol. Chem.* **2013**, *11*, 7999. (c) Pan, X.-Q.; Zou, J.-P.; Zhang, W. *Mol. Diversity* **2009**, *13*, 421. (d) Snider, B. B. *Tetrahedron* **2009**, *65*, 10738. (e) Demir, A. S.; Emrullahoglu, M. *Curr. Org. Synth.* **2007**, *4*, 321. (f) Linker, T. *J. Organomet. Chem.* **2002**, *661*, 159. (g) Parsons, A. F. *C. R. Acad. Sci. Paris, Chim./Chem.* **2001**, *4*, 391. (h) Snider, B. B. *Chem. Rev.* **1996**, *96*, 339. Selected recent $Mn(OAc)_3$-mediated reaction papers: (i) Li, Y.; Qiu, G.; Ding, Q.; Wu, J. *Tetrahedron* **2014**, *70*, 4652. (j) Alagoez, O.; Yilmaz, M.; Pekel, A. T.; Graiff, C.; Maggi, R. *RSC Adv.* **2014**, *4*, 14644. (k) Li, D.-P.; Pan, X.-Q.; An, L.-T.; Zou, J.-P.; Zhang, W. *J. Org. Chem.* **2014**, *79*, 1850. (l) He, S.; Yang, W.; Zhu, L.; Du, G.; Lee, C.-S. *Org. Lett.* **2014**, *16*, 496. (m) Cao, X.-H.; Pan, X.-Q.; Zhou, P.-J.; Zou, J.-P.; Asekun, O. T. *Chem. Commun.* **2014**, *50*, 3359. (n) Bouhlel, A.; Curti, C.; Tabele, C.; Vanelle, P. *Molecules* **2013**, *18*, 4293. (o) Chuang, C.-P.; Tsai, A.-I.; Tsai, M.-Y. *Tetrahedron* **2013**, *69*, 3293. (p) Sun, W.-B.; Ji, Y.-F.; Pan, X.-Q.; Zhou, S.-F.; Zou, J.-P.; Zhang, W.; Asekun, O. T. *Synthesis* **2013**, *45*, 1529.

(6) Pan, X.-Q.; Wang, L.; Zou, J.-P.; Zhang, W. *Chem. Commun.* **2011**, *47*, 7875.

(7) Steenis, V.; Hein, J.; Gen, V. D. *Eur. J. Org. Chem.* **2001**, *5*, 897.

(8) González-Nogal, A. M.; Cuadrado, P.; Sarmentero, M. A. *Eur. J. Org. Chem.* **2009**, 850.

(9) Kawaguchi, S.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Tetrahedron Lett.* **2009**, *506*, 624.

(10) Christiane, S. R. *Synthesis* **1988**, *1*, 64.

(11) Vedejs, E. *J. Org. Chem.* **1981**, *46*, 5253.

(12) Takaki, K.; Takeda, M.; Koshoji, G.; Shishido, T.; Takehira, K. *Tetrahedron Lett.* **2001**, *42*, 6357.

(13) Maloney, K. M.; Chung, J. Y. L. *J. Org. Chem.* **2009**, *74*, 7574.

(14) Koh, Y. J.; Oh, D. Y. *Synth. Commun.* **1995**, *25*, 2587.

(15) Kawashima, T. *Tetrahedron Lett.* **1983**, *24*, 739.

DOI: 10.1021/jo5023298
J. Org. Chem. 2015, 80, 1214−1220