JOC The Journal of Organic Chemistry

Article

Manganese(III) Acetate-Promoted Cross-Coupling Reaction of Benzothiazole/Thiazole Derivatives with Organophosphorus Compounds under Ball-Milling Conditions

Liang Li, Jun-Jie Wang, and Guan-Wu Wang

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.6b00786 • Publication Date (Web): 01 Jun 2016

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society.
1155 Sixteenth Street N.W., Washington, DC 20036

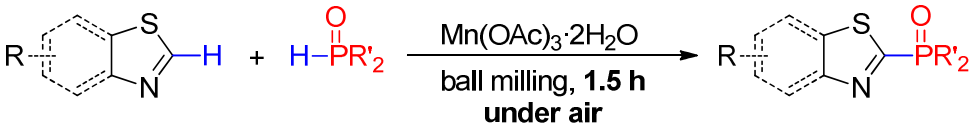
Manganese(III) Acetate-Promoted Cross-Coupling Reaction of Benzothiazole/Thiazole Derivatives with Organophosphorus Compounds under Ball-Milling Conditions

Liang Li, Jun-Jie Wang, and Guan-Wu Wang*

CAS Key Laboratory of Soft Matter Chemistry, iChEM (Collaborative Innovation Center of Chemistry for Energy Materials), Hefei National Laboratory for Physical Sciences at Microscale, and Department of Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Fax: (+86)551-360-7864; E-mail: gwang@ustc.edu.cn

ABSTRACT



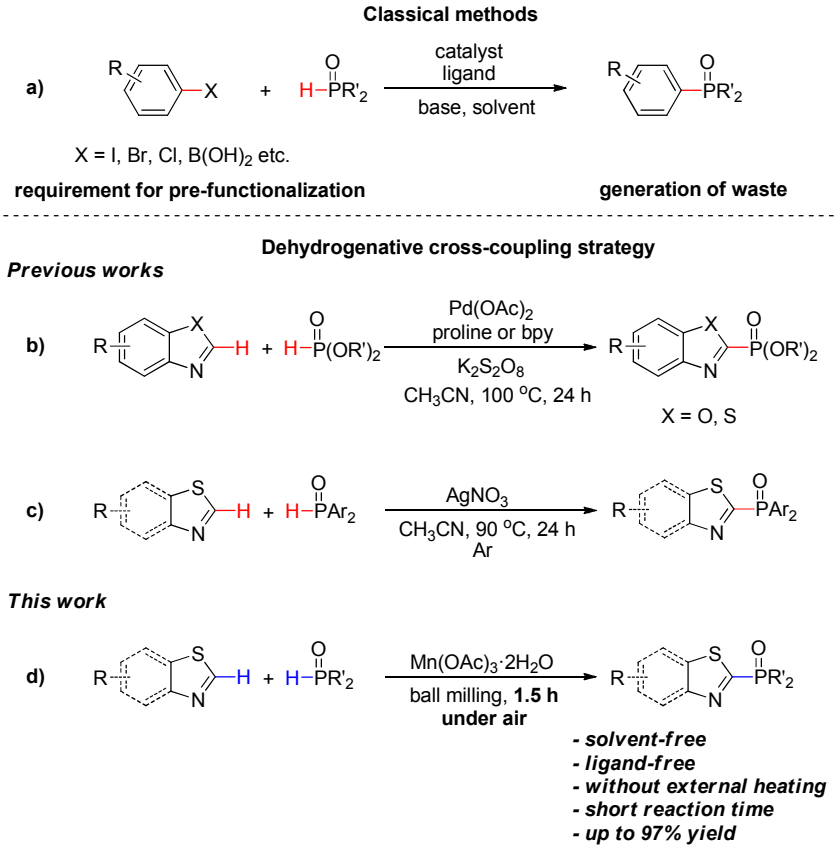
The first solvent-free manganese(III) acetate-promoted reaction of benzothiazole/thiazole derivatives with organophosphorus compounds including phosphine oxides, phosphinate ester, and phosphonate diester has been efficiently developed under ball-milling conditions, providing a highly efficient and green protocol to structurally diverse C2-phosphonylated benzothiazole/thiazole derivatives with remarkable functional group tolerance and excellent yields.

INTRODUCTION

Aromatic organophosphorus compounds, an important class of chemical building blocks, have been widely applied in medicinal chemistry,[1] phosphine-containing ligands[2] and materials science.[3] Since the pioneering work of the Hirao group in 1981,[4] the transition-metal-catalyzed coupling reactions have become practical methods to construct C(sp^2)−P bonds (Scheme 1a).[5] However, these coupling reactions were limited to functionalized (hetero)arenes (e.g., halogenated and boron-containing reagents) and would generate a large quantity of wastes, thus leading to low atom and step economy. In order to avoid the pre-functionalization of reactants, the dehydrogenative cross-coupling reaction of (hetero)arenes with organophosphorus compounds containing P(O)−H moiety under oxidative conditions would become an efficient and promising strategy for the formation of C(sp^2)−P bonds.[6] In 2006, Ishii and co-workers reported an elegant radical phosphonylation of arenes with dialkyl phosphites to afford dialkyl arylphosphonates by using a $Mn(OAc)_2/Co(OAc)_2/O_2$ redox couple.[7a] Later, Zou and co-workers developed a similar $Mn(OAc)_3$-promoted radical phosphonylation of (hetero)aromatic compounds.[7b,7c] Subsequently, the Montchamp group reported a general intermolecular C(sp^2)−H to C(sp^2)−P transformation for (hetero)arenes with phosphinate esters, phosphonate diesters and diphenylphosphine oxide using the $Mn(OAc)_2/MnO_2$ system.[7d] Notably, these radical methods required aliphatic acids as solvents, which could not be applied to acid-sensitive substrates. In 2012,

the first palladium-catalyzed direct phosphonylation of benzothiazoles and benzoxazoles with dialkyl phosphites was discovered by the Li group (Scheme 1b), which required proline or 2,2′-bipyridine as a ligand and $K_2S_2O_8$ as the oxidant to achieve the optimal results.[8] Meanwhile, the Huang group disclosed a silver-catalyzed dehydrogenative cross-coupling reaction of dialkyl phosphites with substituted furans, thiophenes, thiazoles, pyrroles and pyridines in the presence of $K_2S_2O_8$.[9] Chen *et al*. recently realized the direct C2-phosphonylation of benzothiazoles by the reaction with dialkyl phosphites in the presence of di-*tert*-butyl peroxide.[10] Very recently, Zhang, et al revealed a silver

Scheme 1. Comparison of Previous Works with This Work



nitrate-mediated phosphonylation of benzothiazoles and thiazoles with diarylphosphine oxides without additional oxidants (Scheme 1c).[11] It was believed that this process involved nucleophilic addition of the diarylphosphine oxide to the thiazole ring, which was activated through the coordination of the nitrogen atom with the Ag(I) salt rather than a phosphoryl radical path. Unfortunately, this reaction system had disadvantage of poor functional group tolerance, especially for para-halogen atom substituents on the phenyl ring of diarylphosphine oxides. In addition, the reaction conditions also had some drawbacks including the need for inert atmosphere, high temperature, long reaction time, and the involvement of toxic solvent.

On the other hand, environmental concerns have given rise to increasing attention due to the requirement of sustainable development in recent years. More and more chemists are dedicated to the development of more environmentally friendly and efficient organic reactions. To overcome the aforementioned problems, an attractive alternative is to carry out the reactions under solvent-free conditions. Solvent-free reactions, which avoid the use of toxic organic solvents, shorten the reaction time, simplify the separation procedure, and supply high-yielding organic products, have been drawing increasing attention in the field of organic synthesis. One of the protocols applied to solvent-free reactions is the ball-milling technique.[12] In light of our previous studies in this field,[13,14] herein we report a solvent-free and highly efficient $Mn(OAc)_3$-promoted cross-coupling

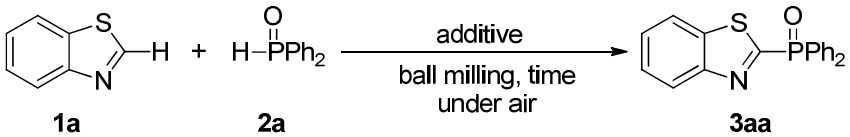
reaction of benzothiazole or thiazole derivatives with organophosphorus compounds under ball-milling conditions. To the best of our knowledge, this is the first example of $C(sp^2)$–P bond construction under ball-milling conditions.

RESULTS AND DISCUSSION

At the outset of our study, we chose benzothiazole (**1a**) and diphenylphosphine oxide (**2a**) as the model substrates to screen the optimal reaction conditions. It was encouraging to find that the solvent-free reaction of **1a** (0.3 mmol) with **2a** (2 equiv) for 2 h afforded the desired 2-diphenylphosphinyl benzothiazole (**3aa**) in 33% yield in the presence of $Mn(OAc)_3•2H_2O$ (1 equiv) under ball-milling conditions (Table 1, entry 1). Then, the effect of the additive loadings on the product yield was investigated. Increasing the amount of $Mn(OAc)_3•2H_2O$ to 2 equiv improved the product yield to 67% (Table 1, entry 2). To our delight, when 3 equiv of $Mn(OAc)_3•2H_2O$ was used, the yield of **3aa** was increased to 91% (Table 1, entry 3). The influence of the amount of **2a** on the product yield was also examined. Further increasing the amount of **2a** to 3 equiv led to a lower yield of 78% (Table 1, entry 4). Meanwhile, decreasing the amount of **2a** to 1 equiv, the yield of **3aa** sharply dropped to 54% (Table 1, entry 5). To our surprise, keeping the **1a**:**2a**:$Mn(OAc)_3•2H_2O$ ratio as 1:2:3 and shortening the reaction time to 1.5 h, no decrease of the product yield was observed (Table 1, entry 3 vs entry 6), while continuing to shorten the reaction time to 1 h would reduce the product yield to 76% (Table 1, entry 7). The efforts to replace

$Mn(OAc)_3•2H_2O$ with $AgNO_3$, AgOAc, $Cu(OAc)_2•2H_2O$, $CuCl_2•2H_2O$ or $FeCl_3•6H_2O$ (Table 1, entries 8-12) failed to provide the desired product, while the use of $Ce(NH_4)_2(NO_3)_6$ (CAN) afforded **3aa** in only 9% yield (Table 1, entry 13). A reason that the silver salt was effective in solution, but not under solvent-free ball-milling conditions remains unclear now. In addition, we also carried out the reaction in solution phase. Acetonitrile and acetic acid are known to be the most widely used solvents in $Mn(OAc)_3$-promoted reactions.[7b,7c,15] When the reaction was performed in acetonitrile at 90 ^oC for 24 h, the yield of **3aa** was 19% (Table 1, entry 14). While the reaction was performed in acetic acid, a lower yield (6%) was obtained (Table 1, entry 15). Neither of the results turned out to be efficient compared with the present solvent-free mechanical milling procedure, demonstrating the advantages of the solvent-free mechanochemical reaction over the liquid-phase reaction. Thus, this reaction was most efficient when the molar ratio of **1a**:**2a**:$Mn(OAc)_3•2H_2O$ was 1:2:3 under the solvent-free and mechanical milling conditions for 1.5 h.

Table 1. Optimization of the $Mn(OAc)_3$-Promoted Reaction of Benzothiazole (1a) with Diphenylphosphine Oxide (2a) under Ball-Milling Conditions[a]



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

entry	additive	molar ratio[b]	yield (%)
1	$Mn(OAc)_3•2H_2O$	1:2:1	33

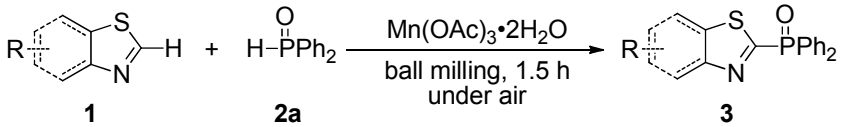
2	$Mn(OAc)_3•2H_2O$	1:2:2	67
3	$Mn(OAc)_3•2H_2O$	1:2:3	**91**
4	$Mn(OAc)_3•2H_2O$	1:3:3	78
5	$Mn(OAc)_3•2H_2O$	1:1:3	54
6[c]	**$Mn(OAc)_3•2H_2O$**	1:2:3	**91**
7[d]	$Mn(OAc)_3•2H_2O$	1:2:3	76
8	$AgNO_3$	1:2:3	0
9	AgOAc	1:2:3	0
10	$Cu(OAc)_2•2H_2O$	1:2:3	0
11	$CuCl_2•2H_2O$	1:2:3	0
12	$FeCl_3•6H_2O$	1:2:3	0
13	CAN	1:2:3	9
14[e]	$Mn(OAc)_3•2H_2O$	1:2:3	19
15[f]	$Mn(OAc)_3•2H_2O$	1:2:3	6

[a] All reactions were carried out in Spex SamplePrep 5100 Mixer Mill for 2 h unless otherwise stated. [b] Molar ratio refers to **1a**:**2a**:additive. [c] The reaction time was 1.5 h. [d] The reaction time was 1 h. [e] The reaction was performed in acetonitrile (2 mL) at 90 ^oC for 24 h. [f] The reaction was performed in acetic acid (2 mL) at 90 ^oC for 24 h.

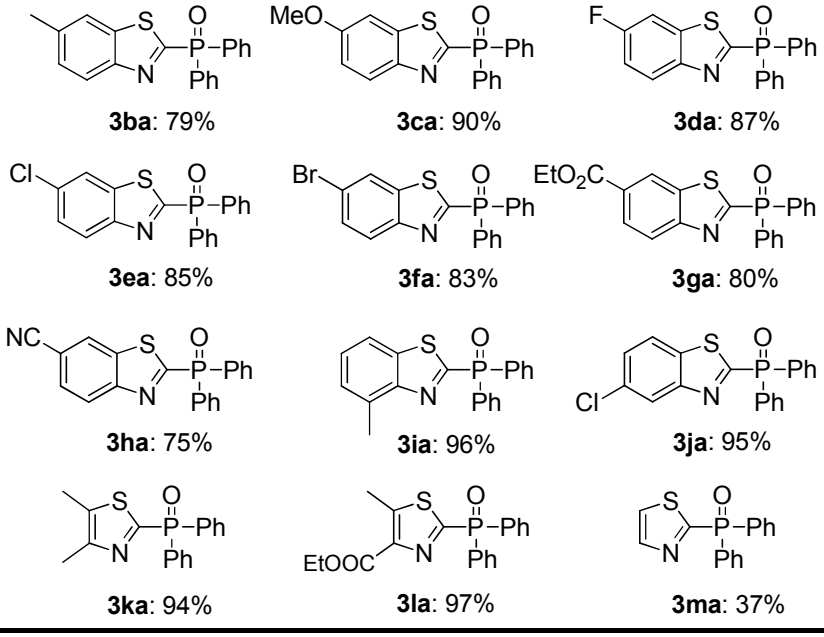
With the optimized reaction conditions in hand (Table 1, entry 6), we next turned our attention to explore various benzothiazole and thiazole derivatives **1** in this reaction. As is apparent from Table 2, the benzothiazoles bearing either an electron-donating or electron-withdrawing substituent at the 6-position of the aromatic moiety (**1b**–**h**) underwent coupling efficiently, generating the corresponding

adducts (**3ba**–**ha**) in good to excellent yields of 75-90% (Table 1). It is worthy pointing out that a wide range of functional groups, such as chloro (**1e**), bromo (**1f**), ester (**1g**), and cyano (**1h**), were adopted well under the reaction conditions. These functional groups could be transformed easily and offered versatile synthetic handle for further elaboration. In addition, the reactivity was increased when the substituents were on other positions of the phenyl ring. 4-Methyl and 5-chloro-substituted benzothiazoles (**1i** and **1j**) reacted smoothly with **2a** to afford comparable high yields of 96% and 95%, respectively. Interestingly, 4,5-dimethylthiazole (**1k**) and ethyl 4-methyl thiazole-5-carboxylate (**1l**) also proved to be excellent substrates to afford products **3ka** and **3la** in high yields of 94% and 97%, respectively. However, when the simplest thiazole (**1m**) was treated with diphenylphosphine oxide, the desired product **3ma** was isolated in a poor yield of 37% due to the formation of byproducts.[11] Benzoxazole and 1-methylbenzimidazole were also utilized to replace benzothiazole under the same conditions. Disappointedly, no desired phosphonylated products were observed.

Table 2. $Mn(OAc)_3$-Promoted Cross-Coupling Reaction of Benzothiazole/Thiazole Derivatives (1b–m) with Diphenylphosphine Oxide (2a) under Ball-Milling Conditions[a]



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

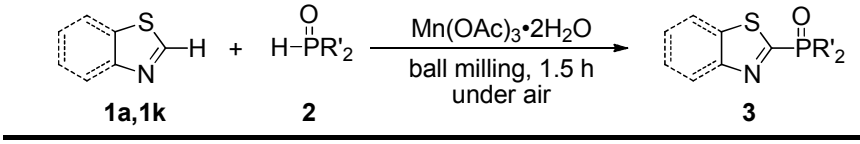


[a] Unless otherwise specified, the reaction mixture of **1** (0.3 mmol), **2a** (0.6 mmol) and additive (0.9 mmol) was milled for 1.5 h.

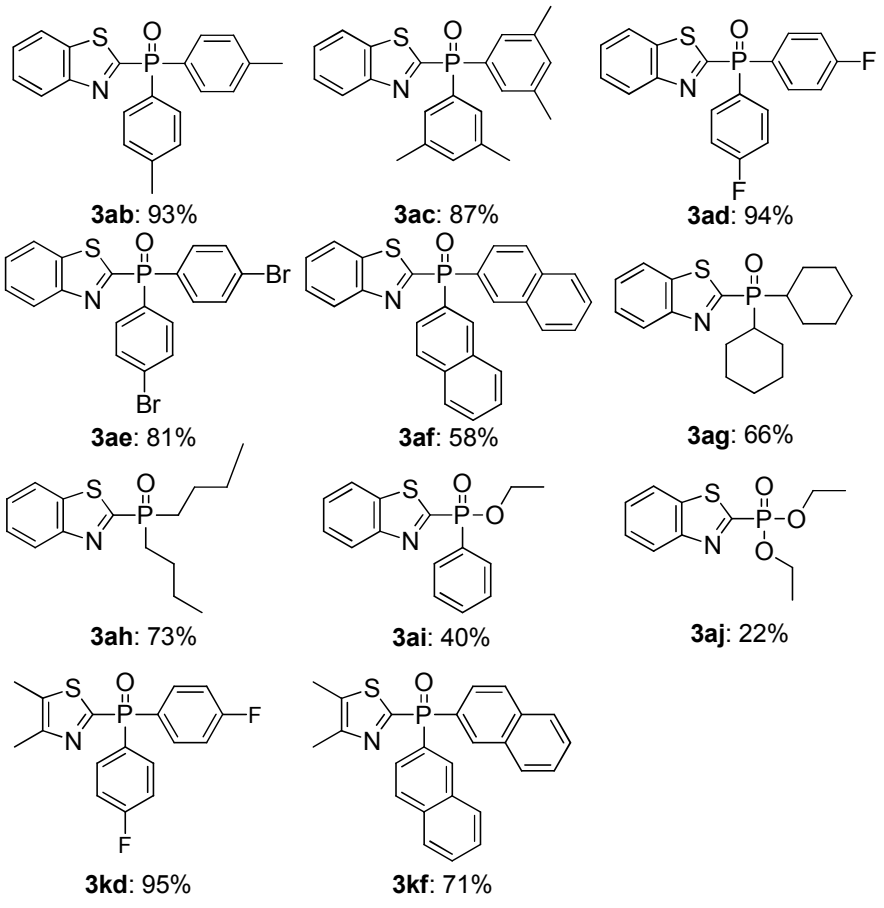
Various diarylphosphine oxides were explored as well to examine their substrate scope, and the results are illustrated in Table 3. Satisfactorily, substrates bearing methyl groups at the para-position or meta-position of the phenyl ring (**2b** and **2c**) reacted with benzothiazole (**1a**) to give the desired products **3ab** and **3ac** in 93% and 87% yields, respectively (Table 3). Gratifyingly, substrates containing halogen atoms including fluoro (**2d**) and bromo (**2e**), which had poor reactivity under Zhang's conditions,[11] performed well under our reaction conditions, and the corresponding products **3ad** and **3ae** were isolated in 94% and 81% yields, respectively. When di(naphthalen-2-yl)phosphine oxide (**2f**) was introduced as the

reactant, the desired product **3af** was obtained in moderate yield (58%). In addition, we have also examined the reactions of dialkylphosphine oxides with **1a**. To our delight, when dicyclohexylphosphine oxide (**2g**) and dibutylphosphine oxide (**2h**) were chosen as the coupling partners, both of them were successfully transformed into the desired phosphonylated products **3ag** and **3ah** in comparable yields (66% and 73%). Furthermore, other organophosphorus compounds could also be employed. Ethyl phenylphosphinate (**2i**) could react with **1a** under the standard conditions to afford the desired product **3ai** in 40% yield. It is worth mentioning that diethyl phosphonate (**2j**) exhibited less reactivity under the standard conditions, with only 22% yield of **3aj** perhaps due to the unstable nature caused by more oxygen atoms connected to the phosphoryl radical intermediate. Treatment of 4,5-dimethylthiazole **1k** with di(4-fluorophenyl)phosphine oxide (**2d**) and di(naphthalen-2-yl)phosphine oxide (**2f**) gave the corresponding phosphonylated products **3kd** and **3kf** in 95% and 71% yields, respectively.

Table 3. $Mn(OAc)_3$-Promoted Cross-Coupling Reaction of Benzothiazole (1a)/4,5-Dimethylthiazole (1k) with Organophosphorus Compounds (2b–j) under Ball-Milling Conditions[a]

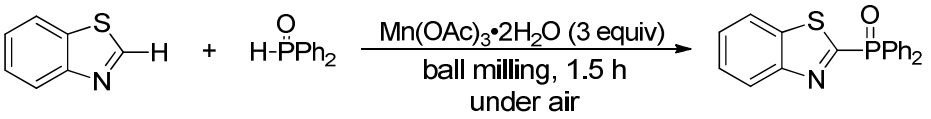


1a,1k **2** **3**



To demonstrate the practical application of the present protocol, a gram-scale experiment was carried out for the reaction of benzothiazole (**1a**, 0.81 g) with diphenylphosphine oxide (**2a**, 2.43 g) under the optimal reaction conditions (Scheme 2). The coupling product **3aa** was obtained in 95% yield (1.90 g), which showed that the present method could be easily adopted for the large-scale preparation.

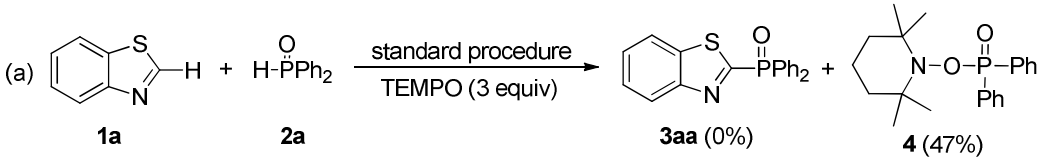
Scheme 2. Gram-Scale Synthesis of 3aa

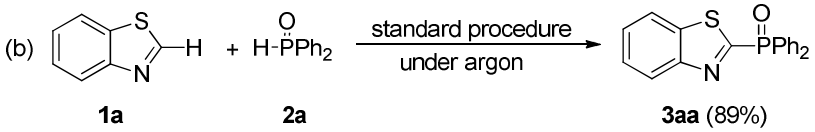


1a (0.81 g) **2a** (2.43 g) **3aa** (1.90 g, 95%)

To understand the reaction mechanism, control experiments were carried out, as shown in Scheme 3. The radical scavenging experiment was investigated by adding 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) to the reaction mixture of **1a** and **2a** under the standard conditions. It was found that 3 equiv of TEMPO suppressed the reaction completely, and the TEMPO−P(O)Ph_2 adduct (**4**) was isolated in 47% yield. This result indicates that the reaction may take place through a radical pathway, which might be different from Zhang's work.[11] In addition, the reaction of **1a** with **2a** under argon atmosphere gave product **3aa** in 89% yield (Scheme 3b), which was pretty close to that (91%) in the presence of air, suggesting that air had little effect on the reaction and that the Mn(III) species was likely the only oxidant.

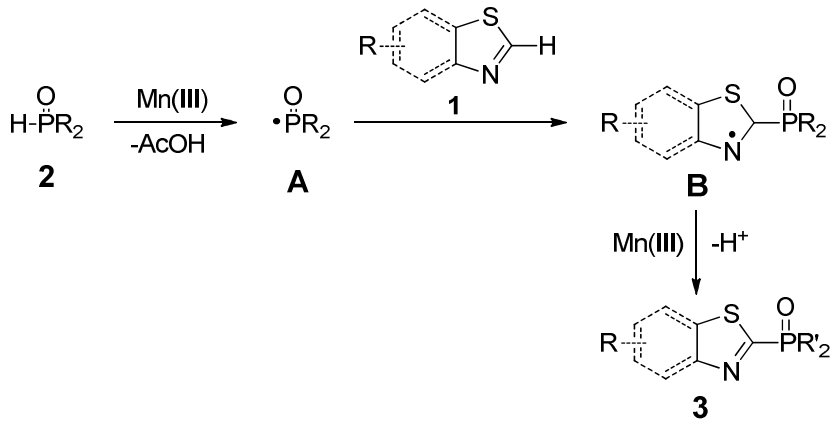
Scheme 3. Control Experiments





On the basis of the above results and the previous literature,[7] a plausible mechanism is depicted in Scheme 4. We believe that in this work, the first step involves the reaction of $Mn(OAc)_3•2H_2O$ with organophosphorus compounds **2** to afford the phosphoryl radical **A**. Then, **A** attacks the thiazole ring at the C2-position of **1** to give the radical intermediate **B**. Subsequently, the final phosphonylation products **3** are obtained via oxidation by a Mn(III) species to regain the aromaticity of the thiazole ring. Although only 1 equiv of **2** and 2 equiv of $Mn(OAc)_3$ are required for the formation of **3**, a molar ratio of **1**:**2**:$Mn(OAc)_3$ as 1:2:3 was used to achieve the highest product yield.

Scheme 3. Proposed Reaction Pathway for the Formation of Products 3



CONCLUSION

In summary, we have developed the first example of direct phosphonylation of benzothiazole and thiazole derivatives with organophosphorus compounds including phosphine oxides, phosphinate ester, and phosphonate diester promoted by $Mn(OAc)_3•2H_2O$ using a ball-milling technique. This process provides a highly

efficient and environmentally friendly solvent-free synthesis method for the construction of diverse C2-phosphonylated benzothiazole and thiazole derivatives with remarkable functional group tolerance and up to 97% yield. Further usage of a ball-milling technique to construct $C(sp^2)$−P bonds are ongoing in our laboratory.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of 3 under Ball-Milling Conditions. A mixture of benzothiazole/thiazole derivatives (**1**, 0.3 mmol), organophosphorus compounds (**2**, 0.6 mmol) along with $Mn(OAc)_3•2H_2O$ (0.9 mmol) was added to a stainless-steel jar (5 mL) containing two stainless-steel balls (6 mm). The vessel was milled in a Spex SamplePrep 5100 Mixer Mill at room temperature (~25 ^oC) for 1.5 h. After the reaction was complete, the reaction mixture was slightly sticky solid, and the temperature of the reaction mixture was raised to about 50 ^oC. The same reaction was repeated again. Then, the combined reaction mixtures were dissolved in ethyl acetate. The solution was filtered and then evaporated in vacuo to remove the solvent. Finally, the residue was purified by silica gel column chromatography using a petroleum ether/ethyl acetate mixture [from 5:1 to 1:1 (v/v)] as the eluent to give products **3**.

The new products (**3ga**, **3ha**, **3la**, **3ag**, **3kd**) were characterized by ^1H NMR, ^{13}C NMR, ^{31}P NMR and ESI-MS spectra. Other products are known compounds, and characterized by ^1H NMR and ^{13}C NMR spectra, which were consistent with those described in the literature.[10,11]

Benzo[d]thiazol-2-yldiphenylphosphine Oxide (3aa).[11] White solid, 91% yield (91.1 mg). Mp: 162–164 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 8.05–7.92 (m, 5H), 7.61–7.45 (m, 8H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 166.8 (d, J = 127.1 Hz), 155.4 (d, J = 21.7 Hz), 136.8 (s), 132.7 (d, J = 2.8 Hz), 132.0 (d, J = 10.3 Hz), 131.0 (d, J = 109.1 Hz), 128.7 (d, J = 12.9 Hz), 126.73 (s), 126.68 (s), 124.8 (s), 122.1 (s).

(6-Methylbenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3ba).[11] White solid, 79% yield (82.9 mg). Mp: 153–154 °C. ^{1}H NMR (400MHz, $CDCl_3$) δ 8.06 (d, J = 8.6 Hz, 1H), 8.01–7.91 (m, 4H), 7.79 (s, 1H), 7.60–7.53 (m, 2H), 7.52–7.45 (m, 4H), 7.35 (d, J = 8.6 Hz, 1H), 2.50 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 165.4 (d, J = 128.3 Hz), 153.7 (d, J = 21.8 Hz), 137.2 (s), 132.6 (d, J = 2.8 Hz), 132.0 (d, J = 10.2 Hz), 131.3 (d, J = 108.7 Hz), 128.7 (d, J = 12.8 Hz), 128.6 (s), 124.3 (s), 121.7 (s), 21.7 (s).

(6-Methoxybenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3ca).[11] Yellow solid, 90% yield (98.9 mg). Mp: 151–152 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 9.1 Hz, 1H), 8.00–7.90 (m, 4H), 7.59–7.53 (m, 2H), 7.52–7.45 (m, 4 H), 7.40 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 9.1, 2.5 Hz, 1H), 3.87 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 129.8 Hz), 158.8 (s), 150.1 (d, J = 21.9 Hz), 138.6 (s), 132.5 (d, J = 2.7 Hz), 131.8 (d, J = 10.3 Hz), 131.2 (d, J = 109.6 Hz), 128.6 (d, J = 12.7 Hz), 125.2 (s), 117.1 (s), 103.4 (s), 55.8 (s).

(6-Fluorobenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3da).[11] White solid, 87% yield (92.6 mg). Mp: 181–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, J =

9.0, 4.6 Hz, 1H), 8.01-7.91 (m, 4H), 7.68 (dd, *J* = 7.8, 2.2 Hz, 1H), 7.62–7.55 (m, 2H), 7.54–7.46 (m, 4H), 7.29 (td, *J* = 8.8, 2.4 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 166.9 (dd, *J* = 126.3, 3.5 Hz), 161.4 (d, *J* = 249.1 Hz), 152.2 (d, *J* = 22.3 Hz), 138.1 (d, *J* = 11.5 Hz), 132.8 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.3 Hz), 130.9 (d, *J* = 109.1 Hz), 128.8 (d, *J* = 12.9 Hz), 126.0 (d, *J* = 9.7 Hz), 116.0 (d, *J* = 25.3 Hz), 108.1 (d, *J* = 26.6 Hz).

(6-Chlorobenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3ea).[10] Light yellow solid, 85% yield (94.5 mg). Mp: 121–122 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 1H), 8.01–7.91 (m, 5H), 7.62–7.55 (m, 2H), 7.55-7.46 (m, 5H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 167.8 (d, *J* = 124.9 Hz), 154.0 (d, *J* = 21.6 Hz), 138.1 (s), 133.0 (s), 132.8 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.3 Hz), 130.8 (d, *J* = 108.7 Hz), 128.8 (d, *J* = 13.0 Hz), 127.8 (s), 125.5 (s), 121.7 (s).

(6-Bromobenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3fa).[11] Yellow solid, 83% yield (103.1 mg). Mp: 128–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 1.5 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 1H), 8.00–7.92 (m, 4H), 7.63 (dd, *J* = 8.8, 1.5 Hz, 1H), 7.61–7.55 (m, 2H), 7.54–7.46 (m, 4H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 167.8 (d, *J* = 124.8 Hz), 154.2 (d, *J* = 21.5 Hz), 138.5 (s), 132.9 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 10.4 Hz), 130.7 (d, *J* = 109.3 Hz), 130.4 (s), 128.8 (d, *J* = 13.0 Hz), 125.8 (s), 124.7 (s), 120.9 (s).

Ethyl 2-(Diphenylphosphoryl)benzo[d]thiazole-6-carboxylate (3ga). Yellow solid, 80% yield (97.9 mg). Mp: 171–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.22 (s, 2H), 8.03–7.93 (m, 4H), 7.63–7.56 (m, 2H), 7.55–7.48 (m, 4H), 4.43 (q,

J = 7.2 Hz, 2H), 1.43 (t, J = 7.2 Hz, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 170.9 (d, J = 123.4 Hz), 165.9 (s), 157.9 (d, J = 21.2 Hz), 136.7 (s), 132.9 (d, J = 2.7 Hz), 132.0 (d, J = 10.3 Hz), 130.6 (d, J = 109.1 Hz), 128.8 (d, J = 13.0 Hz), 128.7 (s), 127.7 (s), 124.5 (s), 124.4 (s), 61.6 (s), 14.4 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.92 (s); HRMS (+ESI) calcd for $C_{22}H_{19}NO_3SP$ $[M + H]^+$: 408.0818; found: 408.0813.

2-(Diphenylphosphoryl)benzo[d]thiazole-6-carbonitrile (3ha). Pale yellow solid, 75% yield (81.4 mg). Mp: 175–176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 1.3 Hz, 1H), 8.27 (d, J = 8.7 Hz, 1H), 8.02–7.93 (m, 4H), 7.79 (dd, J = 8.7, 1.3 Hz, 1H), 7.64–7.58 (m, 2H), 7.57–7.49 (m, 4H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 172.6 (d, J = 120.4 Hz), 157.3 (d, J = 20.8 Hz), 137.2 (s), 133.1 (d, J = 2.8 Hz), 132.0 (d, J = 10.4 Hz), 130.2 (d, J = 109.5 Hz), 129.6 (s), 128.9 (d, J = 13.1 Hz), 127.4 (s), 125.7 (s), 118.3 (s), 110.3 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.98 (s); HR-MS (+ESI) calcd for $C_{20}H_{14}N_2OSP$ $[M + 1]^+$: 361.0559; found: 361.0558.

(4-Methylbenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3ia).[10] White solid, 96% yield (100.3 mg). Mp: 203–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.96 (m, 4H), 7.81 (d, J = 7.6 Hz, 1H), 7.59–7.53 (m, 2H), 7.52–7.45 (m, 4H), 7.40–7.30 (m, 2H), 2.78 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 165.0 (d, J = 129.1 Hz), 155.0 (d, J = 21.2 Hz), 136.7 (s), 134.9 (s), 132.5 (d, J = 2.7 Hz), 131.9 (d, J = 10.1 Hz), 131.4 (d, J = 108.5 Hz), 128.6 (d, J = 12.9 Hz), 127.0 (s), 126.7 (s), 119.4 (s), 18.4 (s).

(5-Chlorobenzo[d]thiazol-2-yl)diphenylphosphine Oxide (3ja).[11] Pale brown solid, 95% yield (105.3 mg). Mp: 152–153 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d,

J = 1.6 Hz, 1H), 8.00–7.93 (m, 4H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.61–7.55 (m, 2H), 7.54–7.48 (m, 4H), 7.46 (dd, *J* = 8.8, 1.6 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 169.3 (d, *J* = 124.3 Hz), 156.2 (d, *J* = 21.4 Hz), 135.1 (s), 132.9 (s), 132.8 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 10.3 Hz), 130.7 (d, *J* = 109.2 Hz), 128.8 (d, *J* = 12.9 Hz), 127.3 (s), 124.4 (s), 122.9 (s).

(4,5-Dimethylthiazol-2-yl)diphenylphosphine Oxide (3ka).[11] White solid, 94% yield (88.5 mg). Mp: 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.84 (m, 4H), 7.57–7.51 (m, 2H), 7.50–7.42 (m, 4H), 2.42 (s, 3H), 2.41 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 158.9 (d, *J* = 137.0 Hz), 153.5 (d, *J* = 19.9 Hz), 133.7 (s), 132.3 (d, *J* = 2.8 Hz), 132.0 (d, *J* = 109.1 Hz), 131.9 (d, *J* = 10.2 Hz), 128.6 (d, *J* = 12.7 Hz), 15.1 (s), 11.7 (s).

Ethyl 2-(Diphenylphosphoryl)-5-methylthiazole-4-carboxylate (3la). White solid, 97% yield (108.1 mg). Mp: 133–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.77 (m, 4H), 7.52–7.44 (m, 2H), 7.44–7.35 (m, 4H), 4.25 (q, *J* = 6.9 Hz, 2H), 2.71 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 166.6 (d, *J* = 125.9 Hz), 162.0 (d, *J* = 19.0 Hz), 160.7 (s), 131.7 (d, *J* = 2.8 Hz), 130.9 (d, *J* = 10.2 Hz), 129.8 (d, *J* = 109.4 Hz), 127.7 (d, *J* = 12.8 Hz), 126.5 (s), 60.7 (s), 16.6 (s), 13.3 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.64 (s); HR-MS (+ESI) calcd for $C_{19}H_{19}NO_3SP$ $[M + H]^+$: 372.0823; found: 372.0826.

Diphenyl(thiazol-2-yl)phosphine Oxide (3ma).[11] Beige solid, 37% yield (31.8 mg). Mp: 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 1.6 Hz, 1H), 7.95–7.85 (m, 4H), 7.74 (s, 1H), 7.60–7.53 (m, 2H), 7.53–7.44 (m, 4H);

$^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$) δ 165.3 (d, J = 131.9 Hz), 146.6 (d, J = 21.3 Hz), 132.6 (d, J = 2.8 Hz), 131.9 (d, J = 10.3 Hz), 131.5 (d, J = 109.5 Hz), 128.7 (d, J = 12.7 Hz), 125.0 (s).

Benzo[d]thiazol-2-yldi-p-tolylphosphine Oxide (3ab).[11] Yellow liquid, 93% yield (101.1 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 7.6 Hz, 1H), 7.89–7.77 (m, 4H), 7.53 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.33–7.26 (m, 4H), 2.39 (s, 6H); $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$) δ 167.5 (d, J = 126.3 Hz), 155.4 (d, J = 21.4 Hz), 143.3 (d, J = 2.6 Hz), 136.9 (s), 132.1 (d, J = 10.5 Hz), 129.5 (d, J = 13.2 Hz), 127.9 (d, J = 111.6 Hz), 126.7 (s), 126.6 (s), 124.8 (s), 122.1 (s), 21.8 (s).

Benzo[d]thiazol-2-ylbis(3,5-dimethylphenyl)phosphine Oxide (3ac).[11] Yellow solid, 87% yield (101.7 mg). Mp: 167–168 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.59–7.52 (m, 5H), 7.48 (t, J = 7.4 Hz, 1H), 7.18 (s, 2H), 2.33 (s, 12H); $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$) δ 167.5 (d, J = 124.9 Hz), 155.4 (d, J = 21.3 Hz), 138.4 (d, J = 13.4 Hz), 136.9 (s), 134.5 (d, J = 2.8 Hz), 130.7 (d, J = 107.8 Hz), 129.4 (d, J = 10.3 Hz), 126.5 (s), 126.4 (s), 124.8 (s), 122.1 (s), 21.3 (s).

Benzo[d]thiazol-2-ylbis(4-fluorophenyl)phosphine Oxide (3ad).[11] Light yellow solid, 94% yield (104.9 mg). Mp: 115–117 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 8.02–7.93 (m, 4H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.20 (td, J = 8.6, 2.3 Hz, 4H); $^{13}C\{1H\}$NMR (100 MHz, $CDCl_3$) δ 166.2 (d, J = 130.1 Hz), 165.6 (dd, J = 255.1, 3.5 Hz), 155.3 (d, J =

21.8 Hz), 136.7 (s), 134.5 (dd, *J* = 11.7, 9.2 Hz), 126.9 (s), 126.8 (dd, *J* = 112.9, 3.2 Hz), 124.8 (s), 122.2 (s), 116.3 (dd, *J* = 21.7, 14.1 Hz).

Benzo[d]thiazol-2-ylbis(4-bromophenyl)phosphine Oxide (3ae).[11] Beige solid, 81% yield (119.0 mg). Mp: 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.87–7.78 (m, 4H), 7.69–7.62 (m, 4H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 165.6 (d, *J* = 130.7 Hz), 155.4 (d, *J* = 22.0 Hz), 136.8 (s), 133.4 (d, *J* = 11.1 Hz), 132.2 (d, *J* = 13.3 Hz), 129.7 (d, *J* = 110.5 Hz), 128.4 (d, *J* = 3.6 Hz), 127.1 (s), 124.9 (s), 122.3 (s).

Benzo[d]thiazol-2-yldi(naphthalen-2-yl)phosphine Oxide (3af).[11] Light red solid, 58% yield (76.2 mg). Mp: 202–204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.57 (s, 1H), 8.22 (d, *J* = 8.0, 1H), 8.06–7.83 (m, 9H), 7.63–7.46 (m, 6H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 166.9 (d, *J* = 127.6 Hz), 155.5 (d, *J* = 21.6 Hz), 136.9 (s), 135.2 (d, *J* = 2.3 Hz), 134.3 (d, *J* = 9.9 Hz), 132.5 (d, *J* = 14.3 Hz), 129.2 (s), 128.71 (s), 128.70 (d, *J* = 12.5 Hz), 128.1 (d, *J* = 109.6 Hz), 128.0 (s), 127.2 (s), 126.8 (d, *J* = 3.8 Hz), 126.7 (s), 126.5 (s), 124.9 (s), 122.2 (s).

Benzo[d]thiazol-2-yldicyclohexylphosphine Oxide (3ag). Beige solid, 66% yield (68.5 mg). Mp: 161–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 2.40–2.23 (m, 2H), 2.20–2.09 (m, 2H), 1.90–1.53 (m, 10H), 1.46–1.14 (m, 8H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 167.0 (d, *J* = 99.0 Hz), 155.3 (d, *J* = 18.5 Hz), 136.9 (s), 126.5 (s), 126.3 (s), 124.4 (s), 122.2 (s), 36.3 (d, *J* = 67.0 Hz), 26.4 (d, *J* = 5.4 Hz), 26.2 (d, *J* = 5.6 Hz), 25.8 (d, *J* = 0.9 Hz), 25.2 (d, *J* = 3.2 Hz), 24.7 (d, *J* =

3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.03 (s); HR-MS (+ESI) calcd for $C_{19}H_{27}NOSP$ $[M + H]^+$: 348.1546; found: 348.1545.

Benzo[d]thiazol-2-yldibutylphosphine Oxide (3ah).[11] White solid, 73% yield (64.7 mg). Mp: 86–87 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 2.23–2.11 (m, 4H), 1.80–1.66 (m, 2H), 1.59–1.46 (m, 2H), 1.46–1.36 (m, 4H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 167.7 (d, J = 108.8 Hz), 155.1 (d, J = 20.1 Hz), 137.0 (s), 126.8 (s), 126.5 (s), 124.4 (s), 122.4 (s), 29.9 (d, J = 69.5 Hz), 24.1 (d, J = 15.2 Hz), 23.5 (d, J = 4.8 Hz), 13.7 (s).

Ethyl Benzo[d]thiazol-2-yl(phenyl)phosphinate (3ai).[11] Yellow liquid, 40% yield (36.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 1H), 8.10–8.02 (m, 2H), 8.00 (d, J = 8.0 Hz, 1H), 7.62–7.47 (m, 5H), 4.40–4.22 (m, 2H), 1.45 (t, J = 7.0 Hz, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 164.2 (d, J = 167.1 Hz), 155.1 (d, J = 24.0 Hz), 136.9 (s), 133.3 (d, J = 2.7 Hz), 132.3 (d, J = 10.4 Hz), 129.2 (d, J = 149.1 Hz), 128.8 (d, J = 14.2 Hz), 127.0 (s), 126.9 (s), 125.0 (s), 122.1 (s), 63.0 (d, J = 6.2 Hz), 16.6 (d, J = 6.4 Hz).

Diethyl Benzo[d]thiazol-2-ylphosphonate (3aj).[11] Yellow liquid, 22% yield (18.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.0 Hz, 1H), 7.59 (t, J = 7.0 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 4.42–4.26 (m, 4H), 1.40 (t, J = 7.0 Hz, 6H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 160.1 (d, J = 238.6 Hz), 154.7 (d, J = 28.5 Hz), 136.5 (s), 127.2 (s), 127.0 (s), 125.1 (s), 122.1 (s), 64.3 (d, J = 5.8 Hz), 16.4 (d, J = 6.4 Hz).

(4,5-Dimethylthiazol-2-yl)bis(4-fluorophenyl)phosphine Oxide (3kd). Light yellow solid, 95% yield (99.8 mg). Mp: 129–130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.84 (m, 4H), 7.16 (td, J = 8.7, 2.1 Hz, 4H), 2.44 (s, 3H), 2.42 (s, 3H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 165.4 (dd, J = 254.3, 3.3 Hz), 158.4 (d, J = 140.1 Hz), 153.7 (d, J = 20.3 Hz), 134.4 (dd, J = 11.7, 9.0 Hz), 134.1 (s), 127.9 (dd, J = 112.9, 3.2 Hz), 116.1 (dd, J = 21.6, 13.9 Hz), 15.1 (s), 11.7 (s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.09 (s); HR-MS (+ESI) calcd for $C_{17}H_{15}NOF_2SP$ $[M + H]^+$: 350.0580; found: 350.0576.

(4,5-Dimethylthiazol-2-yl)di(naphthalen-2-yl)phosphine Oxide (3kf).[11] Pale yellow solid, 71% yield (88.2 mg). Mp: 136–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.50 (s, 1H), 7.95–7.88 (m, 6H), 7.86 (d, J = 8.0 Hz, 2H), 7.61–7.50 (m, 4H), 2.43 (s, 6H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 158.9 (d, J = 137.6 Hz), 153.6 (d, J = 20.0 Hz), 135.0 (d, J = 2.2 Hz), 134.0 (d, J = 9.6 Hz), 133.9 (s), 132.5 (d, J = 14.0 Hz), 129.1 (s), 129.0 (d, J = 109.4 Hz), 128.5 (s), 128.4 (d, J = 12.5 Hz), 127.9 (s), 127.0 (s), 126.6 (d, J = 11.1 Hz), 15.1 (s), 11.7 (s).

Typical Procedure for the Synthesis of 3aa in Acetonitrile or Acetic acid. Benzothiazole (**1a**, 40.6 mg, 0.3 mmol), diphenylphosphine oxide (**2a**, 121.3 mg, 0.6 mmol), $Mn(OAc)_3$•$2H_2O$ (241.3 mg, 0.9 mmol), and acetonitrile or acetic acid (2 mL) were sequentially added at room temperature. The reaction mixture was heated with stirring at 90 °C for 24 h. The reaction solution was concentrated in vacuo, and then 20 mL of saturated sodium bicarbonate solution was added, and the resultant solution was extracted with ethyl acetate (3 × 15 mL). The combined organic layer was dried

over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography using a petroleum ether/ethyl acetate mixture [from 5:1 to 1:1 (v/v)] as the eluent to give product **3aa**.

Typical Procedure for the Gram-Scale Synthesis of 3aa under Ball-Milling Conditions. By following the general procedure for the synthesis of compound **3**, the reaction of **1a** (0.81 g, 6 mmol), **2a** (2.43 g, 12 mmol) with $Mn(OAc)_3•2H_2O$ (4.83 g, 18 mmol) under ball-milling conditions for 1.5 h produced **3aa** (1.90 g, 95%).

Scavenging Experiment with TEMPO under Ball-Milling Conditions. By following the general procedure for the synthesis of compound **3**, the reaction of **1a** (40.6 mg, 0.3 mmol), **2a** (121.3 mg, 0.6 mmol) with $Mn(OAc)_3•2H_2O$ (241.3 mg, 0.9 mmol) in the presence of TEMPO (140.6 mg, 0.9 mmol) under ball-milling conditions for 1.5 h produced **4** (101.5 mg, 47%).

2,2,6,6-Tetramethylpiperidin-1-yl diphenylphosphinate (4).[16] Light yellow solid, 47% yield (101.5 mg). Mp: 110–112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.82 (m, 4H), 7.50–7.39 (m, 6H), 1.36–0.80 (m, 18H); ^{13}C{1H}NMR (100 MHz, $CDCl_3$) δ 134.0 (d, J = 135.3 Hz), 131.8 (d, J = 9.4 Hz), 131.7 (d, J = 2.5 Hz), 128.4 (d, J = 13.0 Hz), 61.7 (d, J = 2.5 Hz), 40.3 (s), 17.0(s); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.58 (s).

ACKNOWLEDGMENTS

We are grateful for financial support from the National Natural Science Foundation of China (21372211).

Supporting Information

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

NMR Spectra of Compounds **3aa-ma**, **3ab-aj**, **3kd**, **3kf**, **4** (PDF)

REFERENCES

(1) For selected examples, see: (a) Sawa, M.; Kiyoi, T.; Kurokawa, K.; Kumihara, H.; Yamamoto, M.; Miyasaka, T.; Ito, Y.; Hirayama, R.; Inoue, T.; Kirii, Y.; Nishiwaki, E.; Ohmoto, H.; Maeda, Y.; Ishibushi, E.; Inoue, Y.; Yoshino, K.; Kondo, H. *J. Med. Chem*. **2002**, *45*, 919. (b) Bialy, L.; Waldmann, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 3814. (c) "Phosphoindoles as HIV inhibitors": Storer, R.; Dousson, C.; Alexandre, F. R.; Roland, A. WO PCT Int. Appl. 054182. **2006**. (d) Alexandre, F. R.; Amador, A.; Bot, S.; Caillet, C.; Convard, T.; Jakubik, J.; Musiu, C.; Poddesu, B.; Vargiu, L.; Liuzzi, M.; Roland, A.; Seifer, M.; Standring, D.; Storer, R.; Dousson, C. B. *J. Med. Chem.* **2011**, *54*, 392. (e) Chen, X.; Kopecky, D. J.; Mihalic, J.; Jeffries, S.; Min, X.; Heath, J.; Deignan, J.; Lai, S.; Fu, Z.; Guimaraes, C.; Shen, S.; Li, S.; Johnstone, S.; Thibault, S.; Xu, H.; Cardozo, M.; Shen, W.; Walker, N.; Kayser, F.; Wang , Z. *J. Med. Chem.* **2012**, *55*, 3837.

2 For selected examples, see: (a) Tang, W.; Zhang, X. *Chem. Rev*. **2003**, *103*, 3029. (b) Kolio, D. T. *Chemistry and Application of H-Phosphonates*. Elsevier Science. **2006**. (c) Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed*. **2008**, *47*, 6338. (d) Kollr, L. *Chem. Rev.* **2010**, *110*, 4257. (e) Hu, D.-F.; Weng, C.-M.; Hong,

F.-E. *Organometallics*. **2011**, *30*, 1139. (f) Jana, R.; Pathak, T. P.; Sigman, M. S. *Chem. Rev.* **2011**, *111*, 1417. (g) Huang, Z.; Liu, Z.; Zhou, J. *J. Am. Chem. Soc*. **2011**, *133*, 15882.

3 For selected examples, see: (a) Baumgartner, T.; Reau, R. *Chem. Rev.* **2006**, *106*, 4681. (b) Chou, H. H.; Cheng, C. H. *Adv. Mater.* **2010**, *22*, 2468. (c) Cho, Y. J.; Lee, J. Y. *Chem.–Eur. J.* **2011**, *17*, 11415. (d) Jeon, S. O.; Lee, J. Y. *J. Mater. Chem.* **2012**, *22*, 7239. (e) Chen, B.; Ding, J.; Wang, L.; Jing, X.; Wang, F. *J. Mater. Chem.* **2012**, *22*, 23680.

4 Hirao, T.; Masunaga, T.; Yamada, N.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 909.

5 For selected examples, see: (a) Schwan, A. L. *Chem. Soc. Rev.* **2004**, *33*, 218. (b) Tappe, F. M. J.; Trepohl, V. T.; Oestreich, M. *Synthesis*. **2010**, *18*, 3037. (c) Zhuang, R.; Xu, J.; Cai, Z.; Tang, G.; Fang, M.; Zhao, Y. *Org. Lett.* **2011**, *13*, 2110. (d) Demmer, C. S.; Larsen, N. K.; Bunch, L. *Chem. Rev.* **2011**, *111*, 7981. (e) Zhang, H.-Y.; Sun, M.; Ma, Y.-N.; Tian, Q.-P.; Yang, S.-D. *Org. Biomol. Chem.* **2012**, *10*, 9627. (f) Zhao, Y.-L.; Wu, G.-J.; Li, Y.; Gao, L.-X.; Han, F.-S. *Chem.–Eur. J.* **2012**, *18*, 9622.

6 Budnikova, Y. H.; Sinyashin, O. G. *Russ. Chem. Rev.* **2015**, *84*, 917.

7 (a) Kagayama, T.; Nakano, A.; Sakaguchi, S.; Ishii, Y. *Org. Lett.* **2006**, *8*, 407. (b) Mu, X.-J.; Zou, J.-P.; Qian, Q.-F.; Zhang, W.; *Org. Lett.* **2006**, *8*, 5291. (c) Xu, W.; Zou, J.-P.; Zhang, W. *Tetrahedron Lett*. **2010**, *51*, 2639. (d) Berger, O.; Montchamp, J.-L. *Chem.–Eur. J.* **2014**, *20*, 12385.

8 Hou, C.; Ren, Y.; Lang, R.; Hu, X.; Xia, C.; Li, F. *Chem. Commun.* **2012**, 48, 5181.

9 Xiang, C.-B.; Bian, Y.-J.; Mao, X.-R.; Huang, Z.-Z. *J. Org. Chem.* **2012**, *77*, 7706.

10 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.

11 Zhang, H.-J.; Lin, W.-D.; Wu, Z.-J.; Ruan, W.-Q.; Wen, T.-B. *Chem. Commun*. **2015**, *51*, 3450.

12 For selected reviews, see: (a) Rodríguez, B.; Bruckmann, A.; Rantanen, T.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 2213. (b) Stolle, A.; Szuppa, T.; Leonhardt, S. E. S.; Ondruschka, B. *Chem. Soc. Rev.* **2011**, *40*, 2317. (c) James, S. L.; Adams, C. J.; Bolm, C.; Braga, D.; Collier, P.; Friščić, T.; Grepioni, F.; Harris, K. D. M.; Hyett, G.; Jones, W.; Krebs, A.; Mack, J.; Maini, L.; Orpen, A. G.; Parkin, I. P.; Shearouse, W. C.; Steed, J. W.; Waddell, D. C. *Chem. Soc. Rev.* **2012**, *41*, 413. (d) Wang, G.-W. *Chem. Soc. Rev.* **2013**, *42*, 7668. (e) Zhu, S.-E.; Li, F.; Wang, G.-W. *Chem. Soc. Rev.* **2013**, *42*, 7535.

13 For selected examples, see: (a) Wang, G.-W.; Komatsu, K.; Murata, Y.; Shiro, M. Nature. **1997**, *387*, 583. (b) Su, Y.-T.; Wang, G.-W. *Org. Lett.* **2013**, *15*, 3408.

14 For recent examples, see: (a) Wang, G.-W.; Gao, J. *Green Chem.* **2012**, *14*, 1125. (b) Liu, Z.; Fan, G.-P.; Wang, G.-W. *Chem. Commun.* **2012**, 48, 11665. (c) Fan, G.-P.; Liu, Z.; Wang, G.-W. *Green Chem.* **2013**, *15*, 1659.

15 For selected examples, see: (a) Li, P.; Zhao, J.; Xia, C.; Li, F. *Org. Lett.* **2014**, *16*, 5992. (b) Gao, Y.; Li, X.; Xu, J.; Wu, Y.; Chen, W.; Tang, G.; Zhao, Y. *Chem. Commun.* **2015**, *51*, 1605. (c) Liu, X.; Chen, X.; Mohr, J. T. *Chem.–Eur. J.* **2016**, *22*, 2274.

16 Li, Y.-W.; Qiu, G.; Ding, Q.; Wu, J. *Tetrahedron* **2014**, *70*, 4652.