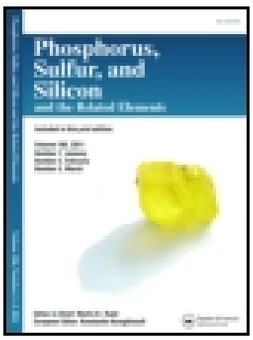

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Facile Synthesis of Bisphosphine Monoxides from Morita-Baylis-Hillman Carbonates

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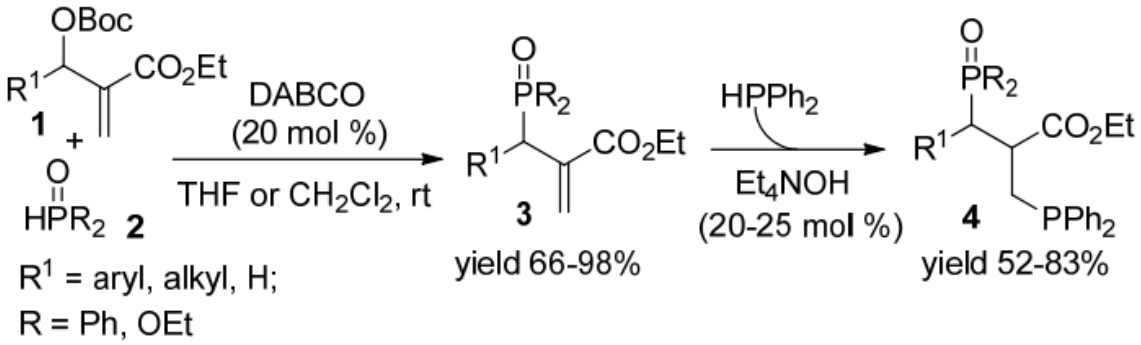
Running title: Synthesis of Bisphosphine Monoxides

Abstract A facile two-step synthesis of bisphosphine monoxides (with both the phosphine and phosphine oxide moieties within one molecule) from readily available Morita-Baylis-Hillman (MBH) carbonates was realized. Under the catalysis of DABCO, the MBH carbonates undergo allylic phosphorylation reaction with diphenylphosphine oxide or diethyl phosphonate to give monophosphine oxides bearing an activated alkene moiety; subsequent base-catalyzed hydrophosphination of the prepared monophosphine oxide with $HPPh_2$ readily affords the bisphosphine monoxides.



Key words Morita-Baylis-Hillman carbonates; bisphosphine monoxides; hydrophosphination; allylic alkylation; monophosphine oxides

INTRODUCTION

Bisphosphine monoxides (BPMOs) are an important class of compounds widely used in medicinal research[1] as well as metal catalysis[2]. Due to the presence of both the soft (phosphorus) and hard (oxygen) Lewis base centers on one molecule, BPMOs frequently function as important hemilabile ligands[2,3] enabling the coordination to various transition metals to form labile metal chelates which can easily generate reactive, coordinatively unsaturated species.[2, 4] As a result, transition metal-BPMO complexes are often capable of catalyzing various reactions under mild conditions with high selectivities, as witnessed by the valuable processes such as hydroformylation[2,5], olefin hydrocarboxylation[2], methanol carbonylation[2] and other important transformations[6]. The development of efficient synthetic methods for BPMOs has therefore attracted great efforts from chemists and a series of approaches have been accordingly established. Generally, the existing synthetic approaches for BPMOs mainly focus on the following two strategies: one involves characteristic coupling of two monophosphines with different oxidation states; the other is based on the selective mono oxidation of bidentate tertiary phosphines.[2] Although these strategies have been proved effective in preparing BPMOs with specific structures, they still suffer from limitations such as tedious manipulation, harsh conditions, low yields, and poor selectivities. Thus, the development of new facile approaches for efficient assembly of BPMOs remains highly desirable.

Recently, a class of so-called modified MBH derivatives such as halides, acetates, and *tert*-butyl carbonates, which could be easily prepared from Morita-Baylis-Hillman adducts, have emerged as versatile substrates in a number of valuable transformations.[7] For example, the MBH derivatives

were proved to be versatile C_3 and C_1 synthons in a series of phosphine-catalyzed [3 + n] (n = 2, 3, 4, 6) and [1 + 4] annulations with electrophiles, affording synthetically useful multifunctional cyclic and heterocyclic compounds.[8] In addition, the MBH derivatives were also reported to undertake allylic alkylation reactions with nucleophiles under the catalysis of phosphine or tertiary amine Lewis bases, producing functionalized products bearing an electrophilic terminal alkene subunit.[9] With these diverse reactivity patterns of MBH derivatives, recently, we demonstrated a phosphine-trigged tandem [3 + 4] annulation of MBH carbonates with 1,4-diheteroatom dinucleophiles, providing an efficient access to seven-membered 1,4-heterocycles.[10] Detailed mechanistic studies unveiled that the reaction proceeded through a phosphine-catalyzed allylic alkylation followed by a general base-promoted intramolecular Michael cyclization (Scheme 1, eq a). Inspired by this strategy, we envisioned that, the allylic carbonate could undertake an allylic alkylation with phosphine oxide nucleophile (*e.g.* diphenylphosphine oxide, diethyl phosphonate) under the catalysis of a Lewis base,[9e] forming monophosphine oxide bearing an activated alkene moiety. Subsequent hydrophosphination of the prepared monophosphine oxide with phosphine such as $HPPh_2$ would afford the bisphosphine monoxides (Scheme 1, eq b). Thus, a new facile entry for bisphosphine monoxides would be developed, which involves two C-P bond forming reactions under metal-free conditions. Recently, the metal-free or metal-catalyzed C-P bond formations have attracted extensive interest from chemists.[11] Herein, we reported the results from such an investigation in detail.

RESULTS AND DISCUSSION

Our initial efforts focused on the preparation of monophosphine oxides via allylic alkylation of MBH carbonates with phosphine oxide nucleophiles. As can be seen in Table 1, under the catalysis of DABCO (20 mol %), the allylic alkylation reaction of heteroaryl-substituted MBH carbonate **1a** and diphenylphosphine oxide **2a** uneventfully occurred in common solvents such as toluene, CH_2Cl_2 and THF (entries 1-3), with THF affording the best yield of product **3a** (entry 3). Using THF as the medium, the reactions of diphenylphosphine oxide **2a** with aryl-substituted allylic carbonate **1b**, alkyl-substituted allylic carbonate **1c**, as well as non-substituted allylic carbonate **1d** proceeded smoothly to deliver their corresponding allylic alkylation products in moderate to excellent yields (entries 4-6). Apart from diphenylphosphine oxide **2a**, diethyl phosphonate **2b** was also a viable substrate in the reaction with allylic carbonate **1a**, affording product **3e** in good yield (entry 7). So, a series of monophosphine oxides with variable substituents were conveniently prepared under very mild conditions in good yields.

Subsequently, we investigated the hydrophosphination of monophosphine oxide with $HPPh_2$ to deliver the bisphosphine monoxide. With the reaction of **3d** and $HPPh_2$ as a model, a brief survey on the reaction conditions was carried out. In view of the hydrophosphination reaction was best run in basic conditions, different bases were examined.[2,12] As depicted in Table 2, with *t*-BuOK or EtONa employed as the base in different equivalents, the hydrophosphination reaction smoothly occurred in THF, toluene, as well as ethanol, but afforded the bisphosphine monoxide **4a** in inferior yields (entries 1-6). When the reaction was conducted using 20 mol % Et_4NOH (25 wt.% in aqueous solution) as the base catalyst in CH_3CN, the yield of **4a** was improved significantly in shorter time (entry 7). Increasing the loading of Et_4NOH to 1.0 equiv led to a

disorder reaction outcome (entry 8). Thus, the optimal conditions for the hydrophosphination reaction were established.

Under the optimal conditions, all the monophosphine oxides prepared above smoothly underwent the hydrophosphination reaction with $HPPh_2$, affording their corresponding bisphosphine monoxides in moderate to good yields (Table 3, entries 1-5). The structures of monophosphine oxides **3** and bisphosphine monoxides **4** were identified by ^{1}H, ^{13}C, ^{31}P NMR, as well as HRMS-ESI measurements. Thus, an efficient synthesis of functionalized bisphosphine monoxides with a C_3 spacer was realized through a simple two-step reaction. Due to the easy variation of substituents on the starting MBH carbonates, this strategy is convenient to assemble bisphosphine monoxides with good functional diversity.

CONCLUSIONS

In summary, we have developed a facile two-step synthesis of functionalized bisphosphine monoxides from MBH carbonates. The approach involves a DABCO-catalyzed allylic phosphorylation, followed by a base-promoted intermolecular hydrophosphination. Compared with the existed entries for bisphosphine monoxides, the newly established method features such merits as readily available of the materials, mild conditions, good yields and selectivities, which make this method potentially useful for preparing bisphosphine monoxides for metal catalysis and medicinal research. Future efforts in our laboratory will be directed toward further expanding the scope and developing asymmetric versions of these transformations.

EXPERIMENTAL

Reactions involving air-sensitive compounds were performed under a N_2 atmosphere. Solvents were purified prior to use according to conventional procedures. Nuclear magnetic resonances (^1H, ^{13}C, and ^{31}P) were recorded on Bruker 400 MHz NMR spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as the internal reference (for ^1H and ^{13}C NMR) or with 85% H_3PO_4 as the external standard (for ^{31}P NMR). Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluant. MBH carbonates were prepared according to our previously reported procedures.[13]

Typical procedure for the synthesis of monophosphine oxides

To a solution of MBH carbonate **1** (0.5 mmol), nucleophile **2** (0.6 mmol) in solvent (5.0 mL) was added DABCO (12 mg, 0.1 mmol). The resulting mixture was stirred at room temperature until MBH carbonate **1** was completely consumed, as monitored by TLC. Then the solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to column chromatographic isolation on silica gel (gradient elution, petroleum ether (bp 60–90 ^oC) / ethyl acetate) to give monophosphine oxide **3**.

Ethyl 2-((diphenylphosphoryl)(furan-2-yl)methyl)acrylate (**3a**), **table 1 entry 3.** Prepared according to the typical procedure in 97% yield as an oil; ^1H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.1 Hz, 3H), 4.00 (q, *J* = 7.1 Hz, 2H), 5.38 (d, *J* = 10.7 Hz, 1H), 6.22 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.39 (t, *J* = 2.5 Hz, 1H), 6.51 - 6.53 (m, 2H), 7.23 (t, *J* = 0.84 Hz, 1H), 7.38 - 7.48 (m, 6H), 7.69 - 7.71 (m, 2H), 7.75 - 7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 39.9 (d, *J* = 67.0 Hz), 61.3, 109.7 (d, *J* = 4.4 Hz), 110.7, 128.3 (d, *J* = 11.9 Hz), 130.9, 131.1, 131.2, 131.3, 131.5, 131.6, 131.8, 132.3 (d, *J* = 20,0 Hz), 133.7 (d, *J* = 3.8 Hz), 142.1, 148.7 (d, *J* = 4.2 Hz),

165.9 (d, *J* = 5.8 Hz); ^{31}P NMR (160 MHz): δ 30.4; HRMS-ESI calcd for $C_{22}H_{22}O_4P$ $(M + H)^+$ 381.1250, found 381.1255.

Ethyl 2-((diphenylphosphoryl)(4-nitrophenyl)methyl)acrylate (**3b**), **table 1 entry 4.** Prepared according to the typical procedure in 91% yield as an oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.19 (t, *J* = 7.1 Hz, 3H), 4.05 - 4.14 (m, 2H), 5.15 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 1.5 Hz, 1H), 6.84 (d, *J* = 1.9 Hz, 1H), 7.29 - 7.32 (m, 2H), 7.38 - 7.42 (m, 1H), 7.47 - 7.55 (m, 7H), 7.88 (dd, *J* = 11.0, 7.0 Hz, 2H), 8.02 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 45.7 (d, *J* = 65.8 Hz), 61.6, 123.3, 128.4 (d, *J* = 11.8 Hz), 128.8 (d, *J* = 11.7 Hz), 130.7, 130.8, 130.9, 131.0, 131.1, 131.9, 132.0, 135.8, 142.7 (d, *J* = 4.7 Hz), 147.0, 165.9 (d, *J* = 9.4 Hz); ^{31}P NMR (160 MHz): δ 32.2; HRMS-ESI calcd for $C_{24}H_{22}NO_5PNa$ $(M + Na)^+$ 458.1128, found, 458.1122

Ethyl 3-(diphenylphosphoryl)-2-methylenehexanoate (**3c**), **table 1 entry 5.** Prepared according to the typical procedure in 66% yield as a white solid; m.p. 83~84 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (t, *J* = 7.3 Hz, 3H), 1.04 (t, *J* = 7.1 Hz, 3H), 1.12 - 1.19 (m, 1H), 1.25 - 1.33 (m, 1H), 1.64 (br s, 1H), 1.79 (br s, 1H), 3.84 - 3.92 (m, 3H), 6.13 (d, *J* = 4.4 Hz, 1H), 6.36 (d, *J* = 4.8 Hz, 1H), 7.26 - 7.32 (m, 3H), 7.40 - 7.43 (m, 3H), 7.62 (dd, *J* = 7.0, 4.0 Hz, 2H), 7.81 - 7.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 13.9, 20.4 (d, *J* = 12.7 Hz), 31.6, 37.6, 38.0 (d, *J* = 68.6 Hz), 60.9, 128.0 (d, *J* = 11.2 Hz), 128.6 (d, *J* = 11.0 Hz), 130.6 (d, *J* = 10.8 Hz), 130.9, 131.0, 131.1, 131.2, 131.5, 132.9 (d, *J* = 15.0 Hz), 135.8 (d, *J* = 5.2 Hz), 166.7 (d, *J* = 5.3 Hz); ^{31}P NMR (160 MHz): δ 32.4; HRMS-ESI calcd for $C_{21}H_{26}O_3P$ $(M + H)^+$ 357.1614, found 357.1620

Ethyl 2-((diphenylphosphoryl)methyl)acrylate (**3d**), **table 1 entry 6.** A known compound, and the characterization data are in accordance with the literature.[14] Prepared according to the typical

procedure in 98% yield as a white solid; m.p. 82~83 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.14 (t, *J* = 7.1 Hz, 3H), 3.47 (d, *J* = 14.7 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 6.00 (d, *J* = 4.3 Hz, 1H), 6.36 (d, *J* = 4.6 Hz, 1H), 7.45 - 7.51 (m, 6H), 7.74 - 7.79 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 32.0 (d, *J* = 67.8 Hz), 61.1, 128.4 (d, *J* = 11.8 Hz), 129.7 (d, *J* = 7.7 Hz), 130.6 (d, *J* = 8.4 Hz), 131.1 (d, *J* = 9.4 Hz), 131.9, 132.9, 166.1 (d, *J* = 4.4 Hz); ^{31}P NMR (160 MHz): δ 30.35.

Ethyl 2-((diethoxyphosphoryl)(furan-2-yl)methyl)acrylate (**3e**), **table 1 entry 7.** Prepared according to the typical procedure in 80% yield as an oil; ^{1}H NMR (400MHz, $CDCl_3$): δ 1.21 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 3.93 - 4.02 (m, 1H), 4.04 - 4.13 (m, 3H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.87 (d, *J* = 26.1 Hz, 1H), 6.25 (d, *J* = 4.4 Hz, 1H), 6.33 (br s, 1H), 6.41 (t, *J* = 2.9 Hz, 1H), 6.54 (d, *J* = 4.8 Hz, 1H), 7.29 (s, 1H); ^{13}C NMR (100 M, $CDCl_3$): δ 13.9, 16.0, 16.1, 38.1 (d, *J* = 142.6 Hz), 61.1, 62.5 (d, *J* = 7.2 Hz), 62.9 (d, *J* = 6.9 Hz), 108.8 (d, *J* = 5.6 Hz), 110.5, 129.2 (d, *J* = 7.3 Hz), 134.1 (d, *J* = 5.2 Hz), 142.0, 148.4 (d, *J* = 4.8 Hz), 165.7 (d, *J* = 7.8 Hz); ^{31}P NMR (160 MHz): δ 21.4; HRMS-ESI calcd for $C_{14}H_{21}O_6PNa$ $(M + Na)^+$ 339.0968, found 339.0960.

Typical procedure for the hydrophosphination reaction

Under a N_2 atmosphere, to a solution of monophosphine oxide **3** (0.5 mmol), $HPPh_2$ **2** (130 μL, 0.75 mmol) in CH_3CN (6.0 mL) was added 25 wt.% aqueous solution of Et_4NOH (58.8~73.5 mg, 0.1~0.125 mmol). The resulting mixture was stirred at room temperature until the monophosphine oxide **3** was completely consumed, as monitored by TLC. Degassed H_2O (5.0 mL) was then added and the mixture was extracted with degassed CH_2Cl_2 (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed on a rotary evaporator under reduced pressure and the residue was subjected to flash column

chromatographic isolation on silica gel (gradient elution, petroleum ether (bp 60–90 ^{o}C) / ethyl acetate) to give bisphosphine monoxide **4**.

Ethyl 3-(diphenylphosphino)-2-((diphenylphosphoryl)methyl)propanoate (**4a**), **table 3 entry 1.** Prepared according to the typical procedure in 76% yield as an oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.98 (t, *J* = 7.1 Hz, 3H), 2.39 (ddd, *J* = 20.1, 13.7, 6.3 Hz, 2H), 2.61 - 2.69 (m, 1H), 2.72 - 2.86 (m, 2H), 3.68 (q, *J* = 7.1 Hz, 2H), 7.15 - 7.21 (m, 7H), 7.27 - 7.37 (m, 9H), 7.58 - 7.62 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.5, 31.9 (d, *J* = 10.9 Hz), 32.6 (ddd, *J* = 32.5, 15.1, 8.4 Hz), 36.7 (d, *J* = 18.2 Hz) , 60.5, [128.0, 128.1, 128.2, 128.3, 128.4, 128.5, 130.3, 130.4, 130.5, 130.6, 131.4, 132.2, 132.4, 132.5, 132.6, 133.4] (the ^{13}C NMR signals of the benzene rings overlapped and could not be identified), 137.2 (d, *J* = 11.5 Hz), 173.6 (dd, *J* = 7.4, 2.9 Hz); ^{31}P NMR(160 MHz): δ 31.3, -20.4; HRMS-ESI calcd for $C_{30}H_{31}O_3P_2$ $(M + H)^+$ 501.1734, found 501.1739.

Ethyl 2-((diphenylphosphino)methyl)-3-(diphenylphosphoryl)-3-(furan-2-yl)propanoate (**4b**), **table 3 entry 2.** Prepared according to the typical procedure in 83% yield as a oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (t, *J* = 7.1 Hz, 3H), 2.16 - 2.24 (m, 1H), 2.71 (ddd, *J* = 7.3, 4.6, 2.7 Hz, 1H), 3.30 (br s, 1H), 3.80 (q, *J* = 7.1 Hz, 2H), 4.29 - 4.37 (m, 1H), 6.10 (d, *J* = 1.4 Hz, 2H), 7.11 (s, 1H), 7.17 - 7.24 (m, 5H), 7.28 - 7.33 (m, 6H), 7.37 - 7.46 (m, 5H), 7.56 - 7.63 (m, 2H), 7.77 - 7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 30.3 (d, *J* = 14.3 Hz), 43.8 (d, *J* = 19.5 Hz), 44.9 (dd, *J* = 69.1, 10.8 Hz), 60.6, 110.5 (d, *J* = 5.4 Hz), 110.6, 128.1, 128.2, 128.3, 128.4, 128.5, 128.6, 130.6, 131.0, 131.1, 131.2, 131.6 (d, *J* = 14.3 Hz), 132.5 (d, *J* = 18.8 Hz), 132.9 (d, *J* = 19.3 Hz), 133.5, 137.4 (d, *J* = 13.2 Hz), 138.0 (d, *J* = 12.0 Hz), 141.7 (d, *J* = 2.3 Hz),

147.9 (d, J = 4.8 Hz), 172.4 (d, J = 13.3 Hz); ^{31}P NMR (160 MHz): δ 30.9, -19.7; HRMS-ESI calcd for $C_{34}H_{32}O_4P_2Na$ $(M + Na)^+$ 589.1668, found 589.1664.

Ethyl 2-((diphenylphosphino)methyl)-3-(diphenylphosphoryl)-3-(4-nitrophenyl)propanoate (**4c**), **table 3 entry 3.** Prepared according to the typical procedure in 76% yield as a white solid; m.p. > 173 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, J = 7.1 Hz, 3H), 1.97 (t, J = 11.7 Hz, 1H), 2.41 - 2.45 (m, 1H), 3.46 (br s, 1H), 3.68 (q, J = 7.1 Hz, 2H), 4.18 (t, J = 7.7 Hz, 1H), 7.03 (t, J = 7.5 Hz, 2H), 7.16 - 7.24 (m, 5H), 7.27 - 7.32 (m, 5H), 7.42 - 7.54 (m, 8H), 7.91 (d, J = 8.6 Hz, 2H), 8.00 - 8.04 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 30.0 (d, J = 14.8 Hz), 45.2 (d, J = 19.0 Hz), 50.2 (dd, J = 65.9, 9.7 Hz), 60.7, 122.9, [128.2, 128.3, 128.4, 128.5, 128.6, 128.7, 128.9, 129.0, 129.1, 130.5, 130.6, 130.8, 130.9, 131.1, 131.2, 131.5, 131.9, 132.3, 132.5, 132.6, 132.8, 133.9] (the ^{13}C NMR signals of the benzene rings overlapped and could not be identified), 137.2 (d, J = 13.2 Hz), 137.7 (d, J = 11.6 Hz), 143.0 (d, J = 4.4 Hz), 146.9, 172.4 (d, J = 12.3 Hz); ^{31}P NMR (160 MHz): δ 29.5, -21.0; HRMS-ESI calcd for $C_{36}H_{34}NO_5P_2$ $(M + H)^+$ 622.1907, found 622.1908.

Ethyl 2-((diphenylphosphino)methyl)-3-(diphenylphosphoryl)hexanoate (**4d**), **table 3 entry 4.** Two separable diastereomers were afforded in 52% overall yield according to the typical procedure. The major isomer: 46% yield; an oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (t, J = 7.2 Hz, 3H), 0.83 - 0.87 (m, 1H), 1.06 - 1.10 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H), 1.51 - 1.63 (m, 2H), 2.38 - 2.45 (m, 1H), 2.49 - 2.54 (m, 1H), 2.74 - 2.83 (m, 1H), 2.94 - 2.97 (m, 1H), 3.79 - 3.87 (m, 1H), 3.90 - 3.98 (m, 1H), 7.27 - 7.29 (m, 7H), 7.35 - 7.39 (m, 5H), 7.40 - 7.46 (m, 4H), 7.76 - 7.85 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.8, 21.4 (d, J = 7.6 Hz), 28.3, 28.9 (dd, J = 13.1, 6.6 Hz), 40.2 (d, J = 9.7 Hz), 41.1 (d, J = 9.7 Hz), 41.7 (d, J = 18.8 Hz), 60.7, [128.2,

128.3, 128.4, 128.5, 128.6, 128.8, 130.6, 130.7, 130.9, 131.0, 131.2, 131.4, 132.1, 132.3, 132.4, 133.0, 133.3, 133.7] (the ^{13}C NMR signals of the benzene rings overlapped and could not be identified), 137.9 (d, J = 11.5 Hz), 173.0 (d, J = 10.4 Hz); ^{31}P NMR (160 MHz): δ 33.3, -18.5; HRMS-ESI calcd for $C_{33}H_{36}O_3P_2Na$ $(M + Na)^+$ 565.2032, found 565.2037. The minor isomer: 6% yield; an oil; ^{31}P NMR (160 MHz): δ 35.3, -14.7; HRMS-ESI calcd for $C_{33}H_{36}O_3P_2Na$ $(M + Na)^+$ 565.2032, found 565.2021.

Ethyl 3-(diethoxyphosphoryl)-2-((diphenylphosphino)methyl)-3-(furan-2-yl)propanoate (**4e**), **table 3 entry 5.** Two separable diastereomers were afforded in 66% combined yield according to the typical procedure. The major isomer: 63% yield; an oil; ^1H NMR (400 MHz, $CDCl_3$): δ 1.13 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 2.17 (td, J = 11.6, 2.8 Hz, 1H), 2.34 - 2.39 (m, 1H), 3.04 - 3.09 (m, 1H), 3.76 (d, J = 8.4 Hz, 1H), 3.80 - 3.87 (m, 1H), 3.92 - 4.06 (m, 5H), 6.29 - 6.31 (m, 1H), 6.35 (s, 1H), 7.25 - 7.27 (m, 4H), 7.32 - 7.33 (m, 3H), 7.37 (s, 1H), 7.39 - 7.44 (m, 2H), 7.47 - 7.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 16.0, 16.1, 28.9 (dd, J = 14.6, 8.8 Hz), 41.4 (dd, J = 142.7, 10.1 Hz), 42.8 (d, J = 21.0 Hz), 60.8, 62.1 (d, J = 7.1 Hz), 62.8 (d, J = 6.7 Hz), 110.2 (d, J = 6.4 Hz), 110.7, 128.2 (d, J = 5.7 Hz), 128.3 (d, J = 7.2 Hz), 128.9, 130.6 (d, J = 11.4 Hz), 132.1 (d, J = 18.4 Hz), 133.3 (d, J = 20.0 Hz), 137.1 (d, J = 13.7 Hz), 138.5 (d, J = 12.3 Hz), 142.3 (d, J = 2.5 Hz), 147.3 (d, J = 6.2 Hz), 172.8 (d, J = 8.2 Hz); ^{31}P NMR(160 MHz): δ 22.5, -19.4; HRMS-ESI calcd for $C_{26}H_{32}O_6P_2Na$ $(M + Na)^+$ 525.1566, found 525.1563. The minor isomer: 3% yield; an oil; ^1H NMR (400MHz, $CDCl_3$): δ 1.04 (t, J = 7.1 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 2.40 (td, J = 13.6, 2.4 Hz, 1H), 2.94 - 2.99 (m, 1H), 3.12 - 3.18 (m, 1H), 3.72 - 3.76 (m, 1H), 3.78 - 3.86 (m, 3H), 3.96 - 3.98 (m, 1H), 4.02 - 4.08 (m, 2H), 6.23 - 6.24 (m, 1H), 6.27 - 6.29 (m, 1H), 7.28

- 7.34 (m, 6H), 7.38 - 7.42 (m, 2H), 7.46 - 7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 16.1, 16.2, 29.6 (d, *J* = 13.9 Hz), 41.9 (d, *J* = 143.4, 10.8 Hz), 44.1 (d, *J* = 19.8 Hz) , 60.5, 62.2 (d, *J* = 6.9 Hz), 62.7 (d, *J* = 6.9 Hz), 109.0 (d, *J* = 6.6 Hz), 110.5, 128.3 (d, *J* = 6.6 Hz), 128.4 (d, *J* = 6.4 Hz), 128.8, 130.9 (d, *J* = 9.4 Hz), 132.5 (d, *J* = 18.7 Hz), 133.1 (d, *J* = 19.6 Hz), 137.4 (d, *J* = 13.4 Hz), 138.3 (d, *J* = 11.9 Hz), 141.9 (d, *J* = 2.6 Hz), 148.4 (d, *J* = 7.7 Hz), 172.4 (d, *J* = 16.6 Hz); ^{31}P NMR (160 MHz): δ 23.1, -19.9; HRMS-ESI calcd for $C_{26}H_{33}O_6P_2$ $(M + H)^+$ 503.1747, found 503.1740.

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SUPPORTING INFORMATION

Copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds **3** and **4**. This material can be found via the ‘‘Supplementary Content’’ section of this article’s webpage.

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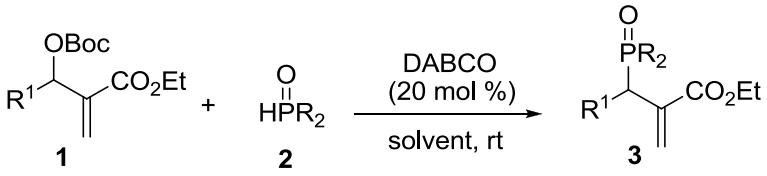
Table 1. Preparation of monophosphine oxides via allylic alkylation of MBH carbonates[a]

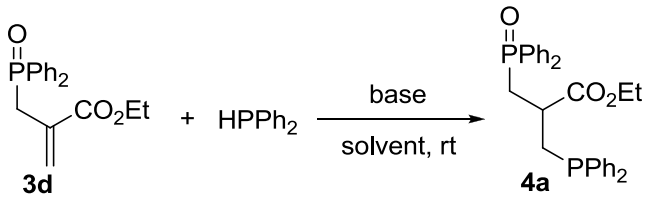


entry	R^1	R	solvent	yield (%)[b]
1	2-furyl, **1a**	Ph, **2a**	toluene	**3a**, 51
2	2-furyl, **1a**	Ph, **2a**	CH_2Cl_2	**3a**, 70
3	2-furyl, **1a**	Ph, **2a**	THF	**3a**, 97
4	4-$NO_2C_6H_5$, **1b**	Ph, **2a**	THF	**3b**, 91
5	*n*-Pr, **1c**	Ph, **2a**	THF	**3c**, 66
6	H, **1d**	Ph, **2a**	THF	**3d**, 98
7	2-furyl, **1a**	OEt, **2b**	CH_2Cl_2	**3e**, 80%

[a] General conditions: A mixture of MBH carbonate **1** (0.5 mmol), nucleophile **2** (0.6 mmol), and DABCO (12 mg, 0.1 mmol) in solvent (5.0 mL) was stirred at room temperature for 24 h.

[b] Isolated yield.

Table 2. Survey on the model hydrophosphination reaction conditions[a]



entry	base ([equiv.])[b]	solvent	time (h)	yield of **4a** (%)[c]
1	*t*-BuOK (0.2)	THF	24	39
2	*t*-BuOK (0.2)	toluene	23	37
3	*t*-BuOK (0.3)	THF	23	34
4	EtONa (0.2)	THF	24	28
5	EtONa (1.0)	THF	24	27
6	EtONa (1.0)	EtOH	17	44
7[d]	Et_4NOH (0.2)	CH_3CN	6	76
8[d]	Et_4NOH (1.0)	CH_3CN	1	disorder

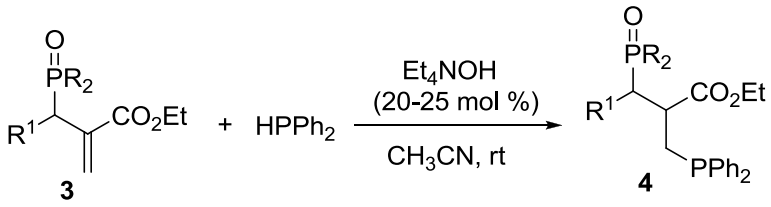
[a] General conditions: under a N_2 atmosphere, to a solution of **3d** (157 mg, 0.5 mmol) and $HPPh_2$ (130 μL, 0.75 mmol) in solvent (6.0 mL) was added the base in a specified equivalent, and the resulting mixture was stirred at room temperature for a indicated time.

[b] The equivalents were relative to **3d**.

[c] Isolated yield.

[d] Et_4NOH was used as 25 wt.% aqueous solution.

Table 3. Hydrophosphination of the monophosphine oxides[a]



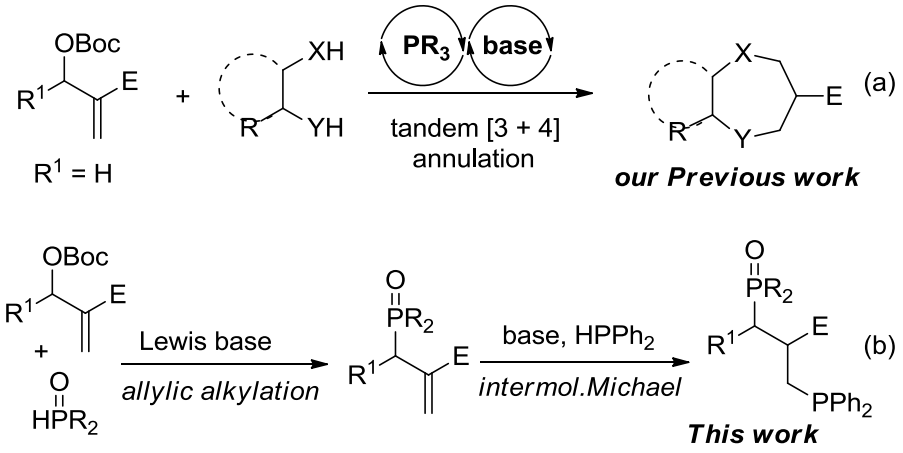
entry	R	R^1	time (h)	yield (%)[b]
1	Ph	H, **3d**	6	**4a**, 76
2	Ph	2-furyl, **3a**	2	**4b**, 83
3	Ph	4-$NO_2C_6H_5$, **3b**	7	**4c**, 76
4[c]	Ph	*n*-Pr, **3c**	2	**4d**, 52
5[d]	OEt	2-furyl, **3e**	19	**4e**, 66

[a] General conditions: under a N_2 atmosphere, to a solution of momophosphine oxide **3** (0.5 mol) and $HPPh_2$ (130 μL, 0.75 mmol) in CH_3CN (6.0 mL) was added 25 wt.% aqueous Et_4NOH (0.1~0.125 mmol), and the resulting mixture was stirred at rt for a specified time.

[b] Isolated yield.

[c] Two separable diastereomers were isolated in 46% and 6% yields, respectively.

[d] Two separable diastereomers were isolated in 63% and 3% yields, respectively.



Scheme 1. Synthesis of functionalized molecules from MBH carbonates