ORGANOMETALLICS

Article

Cite This: *Organometallics* XXXX, XXX, XXX−XXX

pubs.acs.org/Organometallics

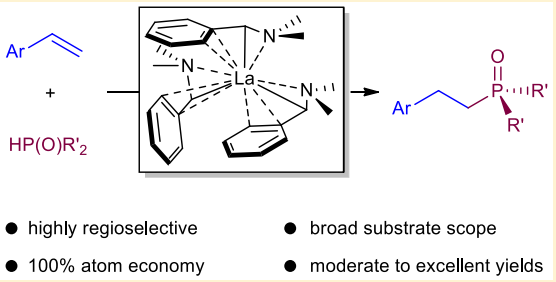
Lanthanum-Catalyzed Regioselective Anti-Markovnikov Hydrophosphinylation of Styrenes

Yesmin Akter Rina and Joseph A. R. Schmidt*

Department of Chemistry & Biochemistry, School of Green Chemistry and Engineering, College of Natural Sciences and Mathematics, The University of Toledo, 2801 West Bancroft Street MS 602, Toledo, Ohio 43606-3390, United States

Supporting Information

ABSTRACT: A useful and convenient method for sp^3 C−P(O) bond formation via direct regioselective hydrophosphinylation of simple and readily available alkenes using a lanthanum-based *N,N*-dimethylbenzylamine complex ($La(DMBA)_3$) as a precatalyst is demonstrated. The reaction proceeds with perfect atom economy for a wide range of styrenes with secondary phosphine oxides, giving moderate to excellent yields.



INTRODUCTION

Due to the wide practical applications of organophosphorus compounds[1] containing a phosphoryl group (P═O; phosphonates, phosphinates, and phosphine oxides) in medicinal chemistry,[2] agrochemistry,[3] biological chemistry,[4] materials chemistry,[5] organic synthesis,[6] pharmaceuticals,[7] and organometallic catalysis,[8] an efficient and atom-economical construction of C−P(O) building blocks has engendered significant research interest. Moreover, organophosphorus compounds have also been utilized as chelating agents,[9] as inhibitors, and most commonly as ligands for metal stabilization in metal-catalyzed reactions.[10] Despite these tremendous applications of organophosphoryl compounds in both laboratory and industry, general and efficient methods for their preparation still represent significant challenges.[11] Traditionally, the famous Michaelis−Arbuzov reaction has been used for their preparation, although it requires toxic alkyl halide precursors and harsh conditions (high temperature >150 °C) and suffers from low atom efficiency, low functional group tolerance, and the environmental problems associated with toxic waste products.[12]

As a means to address the drawbacks of the traditional synthetic method and to fulfill modern demands for more efficient production of phosphoryl compounds, various efforts have been undertaken.[13] Recently, Han demonstrated several elegant approaches for the preparation of C−P(O) building blocks, including an alcohol-based Michaelis−Arbuzov reaction,[14] the Ni-catalyzed phosphorylation of sp^3 C−CN species with secondary phosphine oxides,[15] and the reductive addition of P(O)H to terminal alkynes.[16] An attractive alternative approach involving hydrophosphinylation[17] (addition of the H−P bond of a secondary phosphine oxide across an unsaturated C−C bond)[18] represents a powerful potential strategy. In the past two decades, several groups have demonstrated the transition-metal-catalyzed (Pd,[13c,19] Rh,[20] and Ni[21]) hydrophosphinylation of alkynes (Scheme 1). Very recently, Dong reported Pd-catalyzed hydrophosphinylation of 1,3-dienes, affording chiral allylic phosphine oxide compounds.[22]

Despite these advancements, the regioselective hydrophosphinylation of alkenes for the formation of C−P(O) bonds still represents an area of high significance. In 2009, Ogawa first reported photoinduced hydrophosphinylation of aliphatic alkenes with diphenylphosphine oxide.[23] Kobayashi later disclosed a photocatalytic hydrophosphinylation of unactivated aliphatic alkenes with secondary phosphine oxides.[24] Recently, Liu reported a silver-initiated free-radical intermolecular hydrophosphinylation of unactivated alkenes in which styrenes and their derivatives were not compatible.[25] To the best of our knowledge, direct hydrophosphinylation of aryl alkenes affording the regiospecific anti-Markovnikov addition product (*β*-arylphosphine oxide) mediated by the rare-earth metal lanthanum (La) has not yet been realized.

RESULTS AND DISCUSSION

In connection with our ongoing interest in the production of new C−P and C−P(O) bonds using rare-earth-metal catalysts, we have recently demonstrated La(III)-catalyzed hydrophosphination of heterocumulenes,[26] double hydrophosphinylation of nitriles,[27] and hydrophosphination and hydrophosphinylation of alkynes.[28] Inspired by these advancements and to fill the need for hydrophosphinylation of alkenes, accessing the C−P(O) linkage, herein we disclose the direct hydrophosphinylation of styrenes, affording only the anti-Markovnikov addition product using a La(III) catalyst ($La(DMBA)_3$) in an efficient, attractive, and atom-economical

Received: August 12, 2019

DOI: 10.1021/acs.organomet.9b00549
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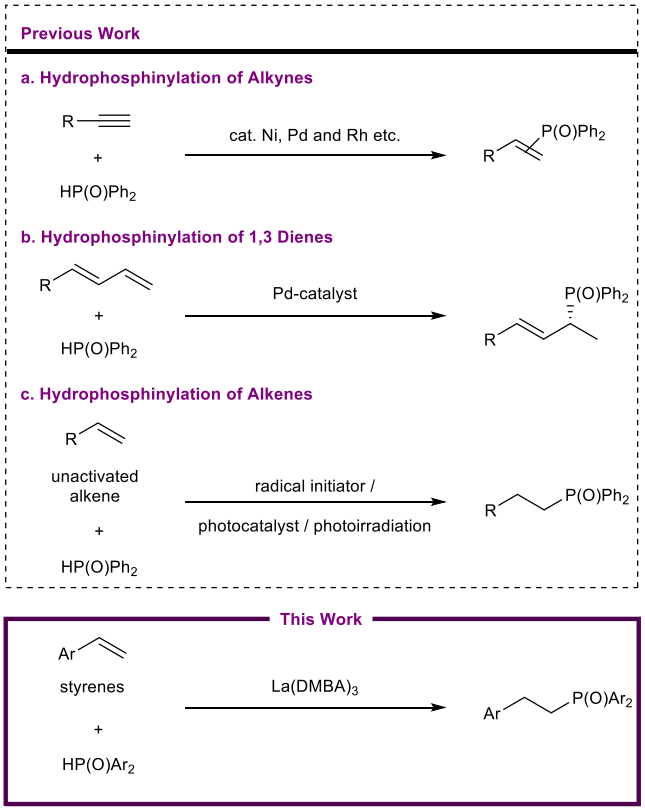
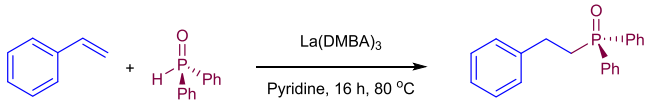
Scheme 1. Hydrophosphinylation of Unsaturated C−C Bonds



manner (Scheme 1). As part of our reaction design, we decided to use styrenes and secondary phosphine oxides as our precursors since both are commercially available, are used as chemical feedstocks, and are easy to synthesize. In addition, secondary phosphine oxides are air and moisture stable, easy to handle, and easy to synthesize and are readily reduced to the corresponding phosphine.[29]

On the basis of our previous work with La-based catalysts, we felt that $La(DMBA)_3$ would serve as a good precatalyst for styrene hydrophosphinylation. To validate this hypothesis, an initial screening reaction utilized styrene **1a** and diphenylphosphine oxide **2a** as test substrates with $La(DMBA)_3$ (5 mol %) in pyridine at room temperature. Gratifyingly, the reaction furnished the desired product **3a**, albeit in merely 6% yield (Table 1, entry 1). Encouraged by the production of **3a**, but disappointed in the overall yield, we increased the temperature from room temperature to 60 and 80 °C, resulting in increasing yields of the product from 6% to 60% and 82%, respectively (Table 1, entries 2 and 3). After that, a careful screening of different catalyst loadings revealed that 5 mol % of $La(DMBA)_3$ was optimal for the reaction and confirmed that, in the absence of precatalyst, no product was observed (Table 1, entries 3−6). Furthermore, an increase in the amount of $HP(O)Ph_2$ from 1.0 to 1.3 equiv increased the yield of the desired product to 97% (Table 1, **entry 7**). Alternatively, increasing the amount of alkene from 1.0 to 1.5 equiv had a less dramatic effect (Table 1, entry 8). On the basis of these optimization studies, we found that a combination of styrene (0.50 mmol), $HP(O)Ph_2$ (0.65 mmol), and 5 mol % of $La(DMBA)_3$ in pyridine at 80 °C provided the optimal conditions for this catalysis.

Table 1. Optimization of $La(DMBA)_3$-Catalyzed Hydrophosphinylation of Styrene[a]



1a 2a 3a

entry	styrene (equiv)	$HP(O)Ph_2$ (equiv)	$La(DMBA)_3$ (mol %)	temp (°C)	yield (%)
1	1.0	1.0	5	25	6
2	1.0	1.0	5	60	60
3	1.0	1.0	5	80	82
4	1.0	1.0	0	80	0
5	1.0	1.0	2.5	80	63
6	1.0	1.0	10	80	79
7	**1.0**	**1.3**	**5**	**80**	**97**
8	1.5	1.0	5	80	86

[a]Optimized catalysis conditions: alkene **1a** (0.5 mmol), diphenylphosphine oxide **2a** (0.65 mmol), $La(DMBA)_3$ (5 mol %, 0.025 mmol, 13.55 mg), pyridine (1 mL), 16 h, 80 °C. Yields were calculated on the basis of the crude NMR spectra using 1,3-benzodioxole as an internal standard.

With the optimized catalysis conditions in hand, we first explored the scope of alkene substrates amenable to this reaction (Table 2). It was found that a wide range of styrenes were well-suited to the reaction conditions. Electron-deficient aromatic alkenes bearing cross-coupling-ready functional groups such as halogens generated the desired products **3g−k** in good to excellent yields. Moreover, styrenes bearing the electron-withdrawing bromo group at the para, meta, or ortho position reacted with diphenylphosphine oxide under the standard reaction conditions to provide the corresponding products **3i−k** in excellent yields, irrespective of the substitution position. Also, the medicinally relevant highly fluorinated moiety 2,3,4,5,6-pentafluorostyrene worked well in the catalysis, providing the desired product **3l** in moderate yield. Additional experiments showed that *p*-nitrostyrene was also tolerant to the reaction conditions, resulting in the formation of the desired product **3f** with reasonable yield. Aromatic alkenes bearing electron-donating substituents such as Me or *t*-Bu at the para position afforded the corresponding products **3b,c** in moderate yields, although a slightly higher catalyst loading (7.5 mol %) was required. 3-Methoxystyrene underwent hydrophosphinylation, providing an excellent yield of the desired product **3d** under the standard reaction conditions, whereas the reaction of 4-methoxystyrene proceeded quite slowly but gave a reasonable yield of 56% of the corresponding product **3e** after several days. Finally, to our delight, heteroaromatics such as pyridine, benzodioxole, furan, and thiophene were tolerated, furnishing the desired products **3m−q** in moderate to excellent yields. Unfortunately, the reaction was not without limits and aliphatic alkenes proved to be unreactive, while *α*-methylstyrene and *β*-methylstyrene gave only negligible yields of the desired products even at high temperature (110 °C) and elongated reaction times.

Next, we turned our attention to investigation of the functional group tolerance in the secondary phosphine oxide component of these reactions, as shown in Table 3. We observed that diaryl phosphine oxides bearing electron-donating substituents such as −Me, −OMe, and $-^tBu$ in the para position led to the predicted products **3s−u** in excellent yields. Furthermore, a disubstituted diaryl phosphine oxide was

DOI: 10.1021/acs.organomet.9b00549
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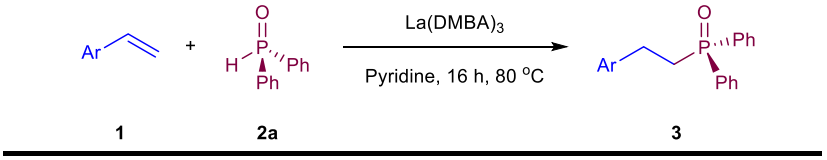
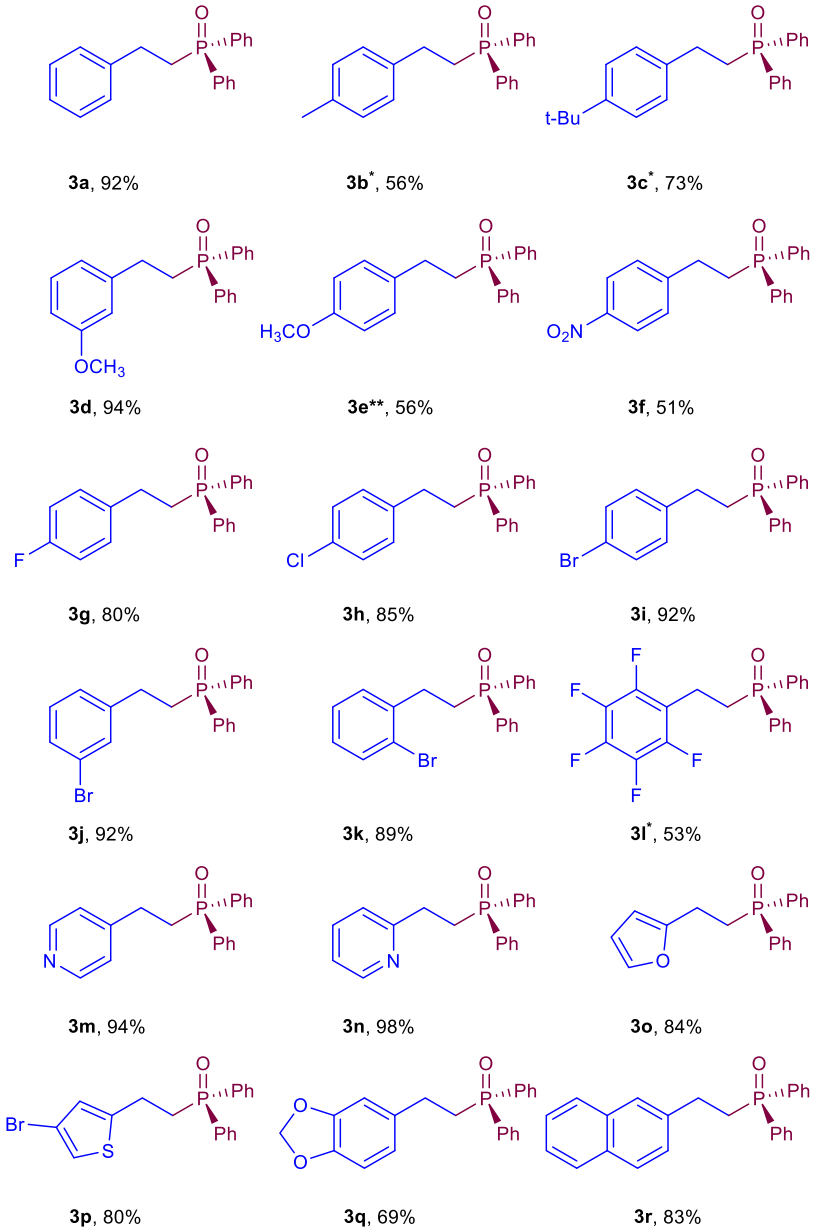
Table 2. Hydrophosphinylation of Styrenes[a]





[a]Reaction conditions: alkene **1** (0.5 mmol), diphenylphosphine oxide **2a** (0.65 mmol), $La(DMBA)_3$ (5 mol %, 0.025 mmol, 13.55 mg), pyridine (1 mL), 16 h, 80 °C unless otherwise specified. Legend for alternative reaction conditions: (*) alkene **1** (0.5 mmol), diphenylphosphine oxide **2a** (0.725 mmol), $La(DMBA)_3$ (7.5 mol %, 0.0375 mmol, 20.32 mg), pyridine (1 mL), 16 h, 80 °C; (**) alkene **1** (0.5 mmol), diphenylphosphine oxide **2a** (0.65 mmol), $La(DMBA)_3$ (5 mol %, 0.025 mmol, 13.55 mg), pyridine (1 mL), 3 days, 80 °C. Isolated yields are reported.

also tolerated by the standard catalytic conditions to give the desired product **3v** in high yield. Additionally, a bulky naphthyl- substituted secondary phosphine oxide underwent the transformation, leading to the predicted product **3w** in high yield. In contrast, diaryl phosphine oxides bearing electron-withdrawing substituents at the para position were not suitable for this catalysis. For example, bis(4-chlorophenyl)phosphine oxide gave only trace amounts of desired product and bis(4-(trifluoromethyl)phenyl)phosphine oxide did not produce any product. Also, di-*tert*-butyl phosphine oxide did not undergo the reaction.

In order to demonstrate the practical applicability of this catalytic system, we scaled up the reaction (Scheme 2). A gram-scale reaction of styrene (1.04 g, 10 mmol) with diphenylphosphine oxide (2.63 g, 13 mmol) using $La(DMBA)_3$ (0.271 g, 0.500 mmol) in 10 mL of pyridine at 80 °C provided 1.9 g of the desired product *β*-arylphosphine oxide in 62% isolated yield after 16 h.

DOI: 10.1021/acs.organomet.9b00549
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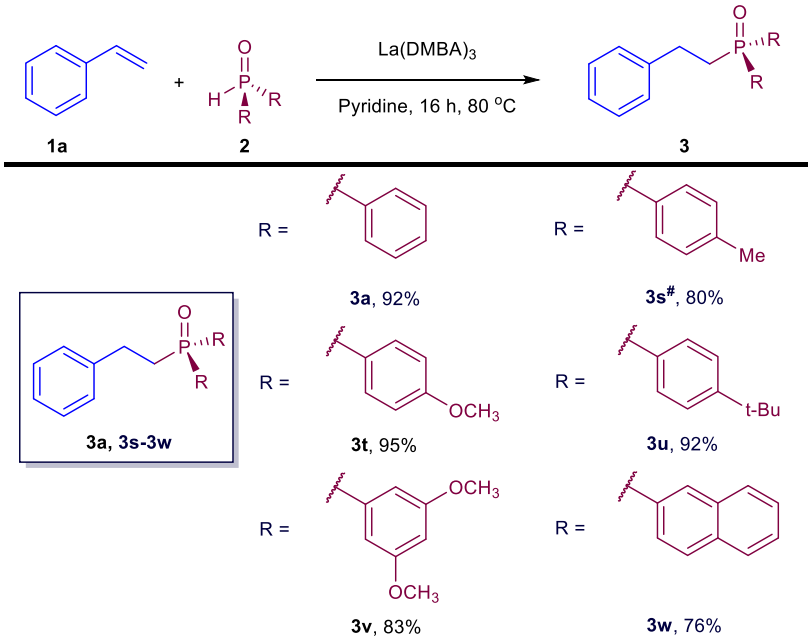
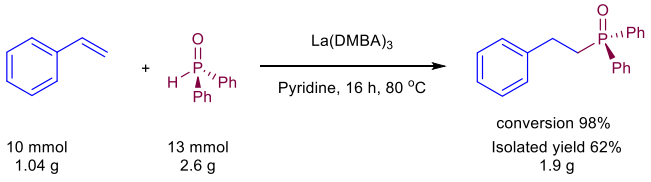
Table 3. Hydrophosphinylation of Styrene with Various Phosphine Oxides[a]



[a]Reaction conditions: alkene **1a** (0.5 mmol), diarylphosphine oxide **2** (0.65 mmol), La(DMBA)$_3$ (5 mol %, 0.025 mmol, 13.55 mg), pyridine (1 mL), 16 h, 80 °C. Legend for alternative reaction conditions: (#) alkene **1a** (0.25 mmol), diarylphosphine oxide **2** (0.4 mmol), La(DMBA)$_3$ (5 mol %, 0.0125 mmol, 6.775 mg), pyridine (0.75 mL), 16 h, 80 °C. Isolated yields are reported.

Scheme 2. Scale-Up Experiment

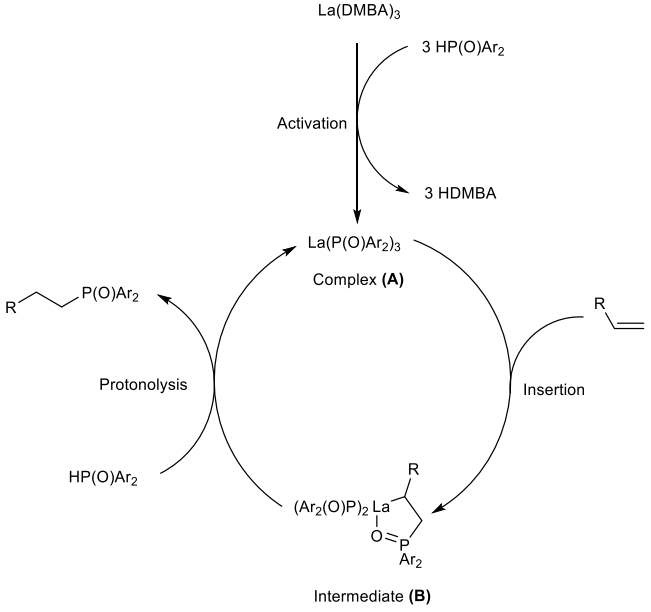


On the basis of literature precedents and our own observations,[26−28] we hypothesize that this reaction takes place utilizing the catalytic cycle depicted in Scheme 3. The precatalyst La(DMBA)$_3$ is first activated by reaction with 3 equiv of HP(O)Ar$_2$, generating the active catalyst La(P(O)-Ar$_2$)$_3$ (complex (**A**)) via protonolysis. Complex (**A**) then undergoes insertion of the styrene to produce intermediate (**B**) via a [3 + 2] transition state similar to that observed with terminal alkynes.[28] Finally, protonolysis of intermediate (**B**) by a secondary phosphine oxide furnishes the desired product and regenerates the active catalyst (**A**).

CONCLUSIONS

In conclusion, we have developed a regiospecific hydrophosphinylation of styrenes with secondary phosphine oxides using the rare-earth-metal catalyst lanthanum tris(*N*,*N*-dimethylbenzylamine) (La(DMBA)$_3$). These results provide a straightforward and efficient approach to access *β*-arylphosphine oxides in an atom-economical manner with reduced waste and reduced energy consumption. This transformation exhibits good functional group tolerance and broad substrate scope for many combinations of styrenes and secondary phosphine oxides under mild conditions.

Scheme 3. Plausible Catalytic Cycle for Hydrophosphinylation of Alkenes Using La(DMBA)$_3$ Precatalyst



EXPERIMENTAL SECTION

General Information. Lanthanum tris(*N*,*N*-dimethylbenzylamine) (La(DMBA)$_3$) was synthesized according to the procedure previously published by our laboratory.[30] Diphenylphosphine oxide was purchased from AK Scientific, dried under vacuum, transferred into the glovebox, and used without further purification. Secondary phosphine oxide substrates for products **3s−w** were prepared according to reported methods.[31] Styrene substrates were purchased from Oakwood, Alfa, Aldrich, Acros, or AK Scientific. Styrene substrates for products **3d,e,j,o−q** were synthesized according to

DOI: 10.1021/acs.organomet.9b00549
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literature reports.[32] All styrene substrates were dried over calcium hydride, filtered, freeze−pump−thawed three times, and stored in a nitrogen-filled glovebox. Pyridine was purchased from Acros, dried over sodium metal, distilled under nitrogen, freeze−pump−thawed three times, and stored in a nitrogen-filled glovebox.

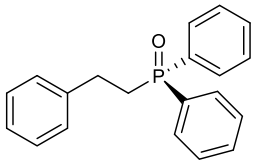
Characterization. All ^{1}H NMR spectra were collected on either a Varian Inova 600 MHz or a Bruker 600 MHz instrument and were internally referenced to residual proton solvent signals for $CDCl_3$ at δ 7.26 ppm. $^{13}C\{^{1}H\}$ NMR spectra were recorded on either a Varian Inova 600 (151 MHz) or a Bruker 600 (151 MHz) instrument and were also internally referenced at 77.00 ppm to deuterated chloroform. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration, and coupling constant (Hz). All $^{31}P\{^{1}H\}$ NMR spectra were obtained from either a Varian Inova 600 (243 MHz) or a Varian VXRS 400 (162 MHz) instrument and were externally referenced to 0.00 ppm with 85% H_3PO_4 in D_2O. $^{19}F\{^{1}H\}$ NMR spectra were recorded on a Varian VXRS 400 (376 MHz) and were externally referenced to $CFCl_3$ at 0.00 ppm. Infrared spectra were collected on a PerkinElmer FT-IR spectrophotometer and are reported in terms of wavenumber of absorption (cm^{-1}). High-resolution mass spectra were obtained on a Waters Synapt High Definition Mass Spectrometer (HDMS) by electrospray ionization at the University of Toledo. Melting points were determined in capillary tubes using a capillary melting point apparatus.

General Procedure for the Catalytic Hydrophosphinylation of Styrenes. In the glovebox, an oven-dried 20 mL vial was charged with α-La(DMBA)$_3$ (13.6 mg, 0.0250 mmol), diphenylphosphine oxide (131 mg, 0.650 mmol), and pyridine (1 mL). Then the styrene (0.5 mmol) was added to that mixture, and the vial was taken out of the glovebox. The vial was placed in an 80 °C oil bath, where the mixture was stirred for 16 h. Then, the pyridine was removed under reduced pressure to afford crude β-arylphosphine oxide. Each was then purified by either method A or method B.

Purification Method A. The crude reaction product was extracted with dichloromethane (5 mL) and filtered through a Celite pad in a small pipet. The solvent was removed under reduced pressure, and the residue was triturated with hexane, causing a precipitate to form. The precipitate was then washed with cold diethyl ether and recrystallized from dichloromethane to afford the pure β-arylphosphine oxide. Compounds **3a,d,g−k,o−w** were purified using this method.

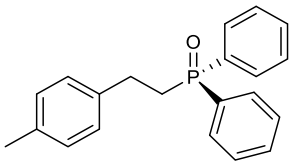
Purification Method B. The crude reaction product was extracted with dichloromethane (5 mL) and filtered through a Celite pad in a small pipet. The residue was then purified by flash chromatography on silica using ethyl acetate/hexane (3/7 to 10/0) as eluent. Compounds **3b,c,e,f,l−n** were purified using this method.

Characterization of Products. *Phenethyldiphenylphosphine Oxide (**3a**).*



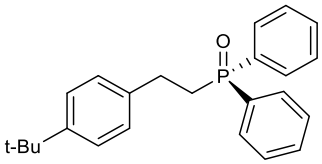
White solid (141 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.78 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.56−7.45 (m, 6H), 7.29−7.23 (m, 2H), 7.21−7.13 (m, 3H), 2.97−2.90 (m, 2H), 2.63−2.55 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 141.1 (d, J_{P-C} = 15.6 Hz), 132.7 (d, J_{P-C} = 98.0 Hz), 131.7 (d, J_{P-C} = 2.4 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.7, 128.6 (d, J_{P-C} = 11.5 Hz), 128.0, 126.3, 31.8 (d, J_{P-C} = 69.7 Hz), 27.5 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.7. This compound is known in the literature.[14−16,33]

*(4-Methylphenethyl)diphenylphosphine Oxide (**3b**).*



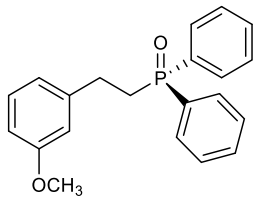
White solid (90 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.55−7.43 (m, 6H), 7.09−7.03 (m, 4H), 2.92−2.84 (m, 2H), 2.60−2.52 (m, 2H), 2.29 (s, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 138.0 (d, J_{P-C} = 16.2 Hz), 135.8, 132.7 (d, J_{P-C} = 98.6 Hz), 131.7 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 129.2, 128.6 (d, J_{P-C} = 11.4 Hz), 127.8, 32.0 (d, J_{P-C} = 69.7 Hz), 27.0 (d, J_{P-C} = 3.5 Hz), 20.9. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.7. This compound is known in the literature.[16,33]

*(4-(tert-Butyl)phenethyl)diphenylphosphine Oxide (**3c**).*



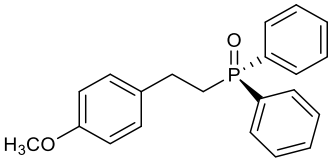
White solid (133 mg, 73%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.54−7.44 (m, 6H), 7.28 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 7.10 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 2.96−2.87 (m, 2H), 2.63−2.54 (m, 2H), 1.29 (s, 9H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 149.1, 138.0 (d, J_{P-C} = 15.6 Hz), 132.7 (d, J_{P-C} = 98.6 Hz), 131.7 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.6 (d, J_{P-C} = 11.5 Hz), 127.7, 125.4, 34.3, 31.8 (d, J_{P-C} = 69.8 Hz), 31.3, 26.9 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.7. This compound is known in the literature.[16]

*(3-Methoxyphenethyl)diphenylphosphine Oxide (**3d**).*



White solid (158 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.55−7.43 (m, 6H), 7.17 (t, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 6.77−6.68 (m, 3H), 3.75 (s, 3H), 2.94−2.85 (m, 2H), 2.62−2.53 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 159.6, 142.7 (d, J_{P-C} = 15.4 Hz), 132.6 (d, J_{P-C} = 98.6 Hz), 131.7 (d, J_{P-C} = 2.9 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 129.5, 128.6 (d, J_{P-C} = 11.5 Hz), 120.3, 113.7, 111.5, 55.1, 31.7 (d, J_{P-C} = 70.4 Hz), 27.5 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.6. IR (cm^{-1}): 3045.12 (w), 2948.70 (w), 1585.55 (m), 1486.84 (m), 1435.49 (s), 1252.89 (m), 1179.86 (s), 1152.63 (s), 1119.50 (s), 1039.99 (s), 993.46 (m), 936.97 (m), 897.07 (m), 804.42 (m), 773.85 (s), 731.45 (s), 694.20 (s), 563.55 (s), 508.35 (s). Mp: 132−133 °C. HRMS (ESI): m/z calcd for $C_{21}H_{22}O_2P$ [(M + H)$^+$] 337.1357, found 337.1358.

*(4-Methoxyphenethyl)diphenylphosphine Oxide (**3e**).*



White solid (94 mg, 56%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 8.4 Hz, 4H), 7.54−7.42 (m, 6H), 7.06 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 6.78 (d, $^{3}J_{H-H}$ = 8.4 Hz, 2H), 3.74 (s, 3H), 2.91−2.82 (m, 2H), 2.59−2.49 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 158.0, 133.0 (d, J_{P-C} = 15.6 Hz), 132.6 (d, J_{P-C} = 98.6 Hz), 131.7 (d, J_{P-C} = 2.9 Hz), 130.6 (d, J_{P-C} = 9.2 Hz), 128.9, 128.6 (d, J_{P-C} = 11.5 Hz), 114.0, 55.1, 32.0 (d, J_{P-C} = 69.7 Hz), 26.5 (d,

DOI: 10.1021/acs.organomet.9b00549
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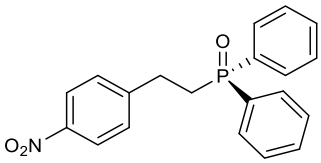
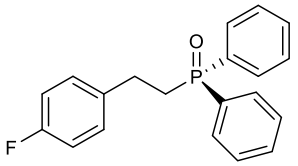
J_{P-C} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.8. This compound is known in the literature.[15,16,33]

*(4-Nitrophenethyl)diphenylphosphine Oxide (**3f**).*



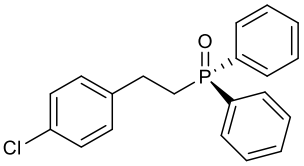
Yellow-white solid (90 mg, 51%). ^1H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.75 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.56−7.51 (m, 2H), 7.50−7.45 (m, 4H), 7.31 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 3.08−3.01 (m, 2H), 2.62−2.55 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 148.7 (d, J_{P-C} = 13.7 Hz), 146.5, 132.2 (d, J_{P-C} = 99.7 Hz), 132.0 (d, J_{P-C} = 2.4 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 129.0, 128.8 (d, J_{P-C} = 11.5 Hz), 123.8, 31.2 (d, J_{P-C} = 70.2 Hz), 27.5 (d, J_{P-C} = 3.5 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.0. IR (cm^{-1}): 3055.50 (w), 2901.68 (w), 1595.34 (m), 1511.39 (s), 1435.37 (m), 1346.67 (s), 1191.97 (s), 1119.58 (s), 1102.75 (s), 850.00 (m), 808.92 (m), 750.11 (s), 740.31 (s), 717.57 (s), 693.10 (s), 640.62 (s), 536.37 (s), 509.45 (s), 473.05 (s). Mp: 133−135 °C. HRMS (ESI): m/z calcd for $C_{20}H_{19}NO_3P$ $[(M + H)^+]$ 352.1103, found 352.1111.

*(4-Fluorophenethyl)diphenylphosphine Oxide (**3g**).*



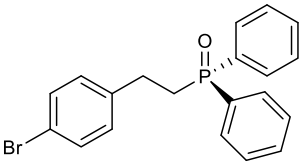
White solid (130 mg, 80%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (dd, $^3J_{H-P}$ = 10.8 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.55−7.44 (m, 6H), 7.10 (dd, $^3J_{H-H}$ = 7.8 Hz, $^3J_{H-F}$= 6.0 Hz, 2H), 6.95−6.88 (m, 2H), 2.94−2.86 (m, 2H), 2.59−2.51 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 161.4 (d, J_{F-C} = 244.5 Hz), 136.7 (dd, J_{F-C} = 3.5 Hz, J_{P-C} = 14.9 Hz), 132.6 (d, J_{P-C} = 98.6 Hz), 131.8 (d, J_{P-C} = 2.4 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 129.4 (d, J_{F-C} = 8.0 Hz), 128.7 (d, J_{P-C} = 11.5 Hz), 115.3 (d, J_{F-C} = 21.3 Hz), 31.9 (d, J_{P-C} = 69.8 Hz), 26.7 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.4. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −117.0. This compound is known in the literature.[15,16,33]

*(4-Chlorophenethyl)diphenylphosphine Oxide (**3h**).*



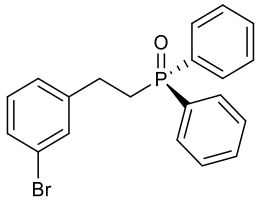
White solid (145 mg, 85%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (dd, $^3J_{H-P}$ = 10.8 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.55−7.50 (m, 2H), 7.49−7.44 (m, 4H), 7.20 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 7.07 (d, $^3J_{H-H}$ = 7.8 Hz, 2H), 2.94−2.85 (m, 2H), 2.58−2.49 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 139.4 (d, J_{P-C} = 14.9 Hz), 132.5 (d, J_{P-C} = 98.6 Hz), 131.9, 131.8 (d, J_{P-C} = 2.3 Hz), 130.6 (d, J_{P-C} = 9.2 Hz), 129.4, 128.6 (d, J_{P-C} = 11.5 Hz), 128.5, 31.6 (d, J_{P-C} = 69.8 Hz), 26.9 (d, J_{P-C} = 3.0 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.4. This compound is known in the literature.[16,33]

*(4-Bromophenethyl)diphenylphosphine Oxide (**3i**).*



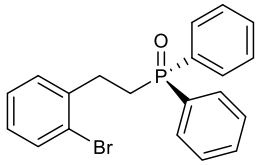
Yellow-white solid (170 mg, 92%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.74 (dd, $^3J_{H-P}$ = 10.8 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.55−7.50 (m, 2H), 7.49−7.44 (m, 4H), 7.34 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.02 (d, $^3J_{H-H}$ = 8.4 Hz, 2H), 2.92−2.84 (m, 2H), 2.58−2.49 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 140.0 (d, J_{P-C} = 15.6 Hz), 132.5 (d, J_{P-C} = 98.0 Hz), 131.8 (d, J_{P-C} = 2.3 Hz), 131.5, 130.7 (d, J_{P-C} = 9.2 Hz), 129.8, 128.7 (d, J_{P-C} = 11.5 Hz), 120.0, 31.6 (d, J_{P-C} = 70.3 Hz), 27.0 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.4. This compound is known in the literature.[16]

*(3-Bromophenethyl)diphenylphosphine Oxide (**3j**).*



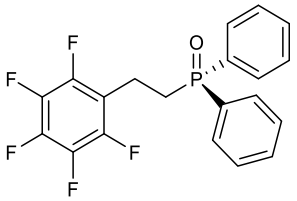
White solid (170 mg, 92%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.76 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.56−7.51 (m, 2H), 7.51−7.45 (m, 4H), 7.32−7.28 (m, 2H), 7.14−7.07 (m, 2H), 2.94−2.87 (m, 2H), 2.59−2.52 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 143.4 (d, J_{P-C} = 15.1 Hz), 132.5 (d, J_{P-C} = 98.6 Hz), 131.9 (d, J_{P-C} = 2.3 Hz), 131.1, 130.7 (d, J_{P-C} = 9.2 Hz), 130.1, 129.4, 128.7 (d, J_{P-C} = 11.5 Hz), 126.8, 122.5, 31.6 (d, J_{P-C} = 70.3 Hz), 27.2 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.3. This compound is known in the literature.[33]

*(2-Bromophenethyl)diphenylphosphine Oxide (**3k**).*



White solid (165 mg, 89%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.79 (dd, $^3J_{H-P}$ = 11.4 Hz, $^3J_{H-H}$ = 7.8 Hz, 4H), 7.54−7.44 (m, 7H), 7.24−7.16 (m, 2H), 7.04 (t, $^3J_{H-H}$ = 7.2 Hz, 1H), 3.08−2.98 (m, 2H), 2.64−2.53 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 140.4 (d, J_{P-C} = 15.6 Hz), 132.8, 132.5 (d, J_{P-C} = 97.4 Hz), 131.7 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 9.4 Hz), 130.4, 128.6 (d, J_{P-C} = 11.6 Hz), 128.1, 127.7, 123.9, 30.0 (d, J_{P-C} = 69.2 Hz), 28.5 (d, J_{P-C} = 2.3 Hz). $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 31.6. IR (cm^{-1}): 3056.06 (w), 1470.76 (w), 1436.59 (m), 1177.96 (s), 1118.58 (m), 1099.37 (m), 996.44 (w), 775.44 (m), 740.86 (s), 712.51 (s), 692.24 (s), 656.87 (m), 589.82 (s), 532.41 (s), 517.83 (s), 504.33 (s), 495.20 (s). Mp: 82−83 °C. HRMS (ESI): m/z calcd for $C_{20}H_{19}BrOP$ $[(M + H)^+]$ 385.0357, found 385.0371.

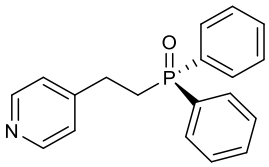
*(2,3,4,5,6-Pentafluorophenethyl)diphenylphosphine Oxide (**3l**).*



White solid (105 mg, 53%). ^1H NMR (600 MHz, $CDCl_3$): δ 7.79−7.72 (m, 4H), 7.56−7.51 (m, 2H), 7.50−7.45 (m, 4H), 3.06−3.00 (m, 2H), 2.58−2.51 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 144.9 (dm, J_{F-C} = 247.2 Hz), 139.9 (dm, J_{F-C} = 252.2 Hz), 137.4 (dm, J_{F-C} = 252.2 Hz), 132.1 (d, J_{P-C} = 100.1 Hz), 132.0 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 8.8 Hz), 128.8 (d, J_{P-C} = 11.0 Hz), 113.7 (m), 29.1 (d, J_{P-C} = 70.5 Hz), 15.1. $^{31}P\{^1H\}$ NMR (243 MHz, $CDCl_3$): δ 30.5. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$): δ −143.5 (dd, J = 22.8 Hz, 8.3 Hz), −157.0 (t, J = 20.5 Hz), −162.5 - −162.6 (m). IR (cm^{-1}): 2951.29 (w), 1520.65 (m), 1500.51 (s), 1436.30 (m), 1260.25 (m), 1182.69 (s), 1115.78 (s), 994.71 (s), 955.52 (s), 915.11 (s), 797.06 (s), 752.01 (s), 741.64 (s), 720.21 (s), 692.77 (s), 527.99 (s), 507.64 (s). Mp: 136−138 °C. HRMS (ESI): m/z calcd for $C_{20}H_{15}F_5OP$ $[(M + H)^+]$ 397.0781, found 397.0793.

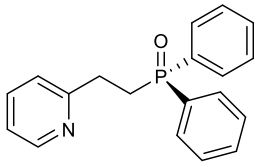
DOI: 10.1021/acs.organomet.9b00549
Organometallics XXXX, XXX, XXX−XXX

*Diphenyl(2-(pyridin-4-yl)ethyl)phosphine Oxide (**3m**).*



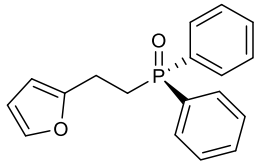
White solid (144 mg, 94%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46 (d, $^{3}J_{H-H}$ = 5.4 Hz, 2H), 7.76 (dd, $^{3}J_{H-P}$ = 11.4 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.58−7.45 (m, 6H), 7.09 (d, $^{3}J_{H-H}$ = 5.4 Hz, 2H), 2.96−2.89 (m, 2H), 2.60−2.53 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 149.9, 149.9 (d, J_{P-C} = 14.9 Hz), 132.2 (d, J_{P-C} = 99.7 Hz), 132.0 (d, J_{P-C} = 2.9 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.8 (d, J_{P-C} = 11.5 Hz), 123.4, 30.6 (d, J_{P-C} = 70.2 Hz), 26.9 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.3. IR (cm^{-1}): 3054.42 (w), 2930.29 (w), 1600.65 (m), 1560.01 (w), 1436.92 (m), 1171.16 (s), 1118.51 (s), 1100.47 (m), 992.73 (m), 942.70 (m), 806.81 (s), 774.75 (s), 744.42 (s), 733.57 (s), 715.57 (s), 692.23 (s), 586.93 (s), 536.94 (s), 508.13 (s), 490.62 (s). Mp: 114−116 °C. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{19}NOP$ [(M + H)$^{+}$] 308.1204, found 308.1207.

*Diphenyl(2-(pyridin-2-yl)ethyl)phosphine Oxide (**3n**).*



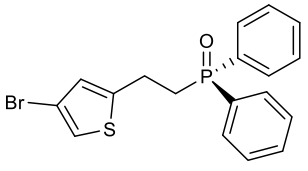
White solid (150 mg, 98%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48 (d, $^{3}J_{H-H}$ = 4.8 Hz, 1H), 7.77 (dd, $^{3}J_{H-P}$ = 11.4 Hz, $^{3}J_{H-H}$ = 7.2 Hz, 4H), 7.56−7.39 (m, 7H), 7.11 (d, $^{3}J_{H-H}$ = 7.8 Hz, 1H), 7.07 (dd, $^{3}J_{H-H}$ = 7.2 Hz, $^{3}J_{H-H}$ = 4.8 Hz, 1H), 3.14−3.06 (m, 2H), 2.82−2.73 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 160.0 (d, J_{P-C} = 14.9 Hz), 149.1, 136.3, 132.6 (d, J_{P-C} = 98.6 Hz), 131.6 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.5 (d, J_{P-C} = 11.5 Hz), 123.0, 121.3, 29.6 (d, J_{P-C} = 2.9 Hz), 29.0 (d, J_{P-C} = 71.4 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 32.4. This compound is known in the literature.[16,33]

*(2-(Furan-2-yl)ethyl)diphenylphosphine Oxide (**3o**).*



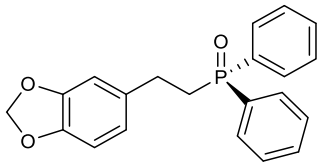
White solid (125 mg, 84%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79−7.70 (m, 4H), 7.55−7.43 (m, 6H), 7.24 (dd, $^{3}J_{H-H}$ = 1.8 Hz, $^{4}J_{H-H}$ = 0.6 Hz, 1H), 6.21 (dd, $^{3}J_{H-H}$ = 3.0 Hz, $^{3}J_{H-H}$ = 1.8 Hz, 1H), 5.97 (dd, $^{3}J_{H-H}$ = 3.0 Hz, $^{4}J_{H-H}$ = 0.6 Hz, 1H), 3.00−2.90 (m, 2H), 2.67−2.55 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 154.0 (d, J_{P-C} = 16.8 Hz), 141.2, 132.3 (d, J_{P-C} = 98.6 Hz), 131.8 (d, J_{P-C} = 2.4 Hz), 130.6 (d, J_{P-C} = 9.2 Hz), 128.6 (d, J_{P-C} = 11.6 Hz), 110.2, 105.4, 28.3 (d, J_{P-C} = 70.8 Hz), 20.3 (d, J_{P-C} = 2.4 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.5. IR (cm^{-1}): 3441.01 (w), 3050.67 (w), 2907.33 (w), 1436.48 (s), 1167.90 (s), 1142.74 (s), 1118.04 (s), 1069.42 (m), 1046.01 (m), 994.79 (m), 910.10 (s), 818.58 (m), 790.80 (m), 763.63 (s), 733.21 (s), 721.89 (s), 694.96 (s), 598.41 (m), 556.99 (s), 524.74 (s), 510.92 (s), 480.95 (s). Mp: 74−76 °C. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{18}O_2P$ [(M + H)$^{+}$] 297.1044, found 297.1044.

*(2-(4-Bromothiophen-2-yl)ethyl)diphenylphosphine Oxide (**3p**).*



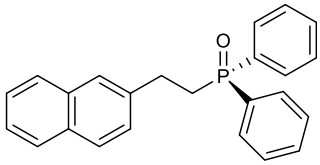
White solid (156 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.74 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 7.8 Hz, 4H), 7.59−7.43 (m, 6H), 6.98 (s, 1H), 6.68 (s, 1H), 3.17−3.04 (m, 2H), 2.67−2.55 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 145.1 (d, J_{P-C} = 17.2 Hz), 132.2 (d, J_{P-C} = 98.5 Hz), 132.0 (d, J_{P-C} = 2.4 Hz), 130.7 (d, J_{P-C} = 9.4 Hz), 128.8 (d, J_{P-C} = 11.5 Hz), 127.3, 120.8, 109.1, 31.7 (d, J_{P-C} = 69.8 Hz), 22.2 (d, J_{P-C} = 2.3 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 30.8. IR (cm^{-1}): 3116.00 (w), 3069.57 (w), 3055.03 (w), 2926.04 (w), 1526.38 (w), 1436.24 (s), 1200.88 (m), 1176.68 (s), 1158.65 (s), 1120.60 (s), 1096.08 (m), 1070.36 (m), 993.73 (m), 936.13 (m), 834.73 (m), 818.34 (m), 786.42 (m), 739.17 (s), 716.90 (s), 692.35 (s), 607.90 (s), 528.98 (s), 514.68 (s), 498.86 (s). Mp: 88−90 °C. HRMS (ESI): *m*/*z* calcd for $C_{18}H_{17}BrOPS$ [(M + H)$^{+}$] 390.9922, found 390.9929.

*(2-(Benzo[d][1,3]dioxol-5-yl)ethyl)diphenylphosphine Oxide (**3q**).*



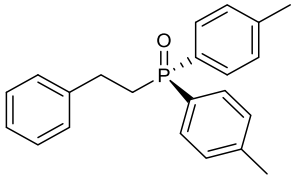
White solid (120 mg, 69%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 8.4 Hz, 4H), 7.54−7.44 (m, 6H), 6.69−6.57 (m, 3H), 5.89 (s, 2H), 2.90−2.79 (m, 2H), 2.58−2.48 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 147.6, 145.9, 134.9 (d, J_{P-C} = 15.0 Hz), 132.7 (d, J_{P-C} = 98.6 Hz), 131.7 (d, J_{P-C} = 2.4 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.7 (d, J_{P-C} = 11.5 Hz), 120.8, 108.5, 108.3, 100.8, 32.1 (d, J_{P-C} = 69.2 Hz), 27.3 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.5. IR (cm^{-1}): 3051.54 (w), 2892.92 (w), 1608.69 (w), 1503.32 (m), 1489.78 (m), 1436.84 (m), 1247.99 (m), 1176.46 (s), 1132.31 (m), 1119.11 (m), 1038.60 (m), 934.03 (m), 785.26 (m), 746.24 (m), 716.04 (m), 693.16 (s), 547.42 (s), 513.56 (s), 494.38 (s). Mp: 136−138 °C. HRMS (ESI): *m*/*z* calcd for $C_{21}H_{20}O_3P$ [(M + H)$^{+}$] 351.1150, found 351.1152.

*(2-(Naphthalen-2-yl)ethyl)diphenylphosphine Oxide (**3r**).*



White solid (148 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84−7.72 (m, 7H), 7.59 (s, 1H), 7.54−7.39 (m, 8H), 7.30 (d, $^{3}J_{H-H}$ = 8.4 Hz, 1H), 3.16−3.07 (m, 2H), 2.71−2.64 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 138.5 (d, J_{P-C} = 14.9 Hz), 133.4, 132.7 (d, J_{P-C} = 98.5 Hz), 132.0, 131.7 (d, J_{P-C} = 2.3 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 128.6 (d, J_{P-C} = 11.5 Hz), 128.2, 127.5, 127.3, 126.6, 126.1, 126.0, 125.4, 31.7 (d, J_{P-C} = 69.8 Hz), 27.6 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.7. This compound is known in the literature.[15]

*Phenethyldi-p-tolylphosphine Oxide (**3s**).*



White solid (67 mg, 80%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.62 (dd, $^{3}J_{H-P}$ = 11.4 Hz, $^{3}J_{H-H}$ = 8.4 Hz, 4H), 7.29−7.21 (m, 6H), 7.18−7.11 (m, 3H), 2.93−2.84 (m, 2H), 2.55−2.48 (m, 2H), 2.37 (s, 6H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 142.2 (d, J_{P-C} = 2.4 Hz), 141.3 (d, J_{P-C} = 15.6 Hz), 130.7 (d, J_{P-C} = 9.7 Hz), 129.4 (d, J_{P-C} = 100.9 Hz), 129.4 (d, J_{P-C} = 12.2 Hz), 128.5, 128.0, 126.2, 31.9 (d, J_{P-C} = 70.4 Hz), 27.5 (d, J_{P-C} = 2.9 Hz), 21.5. $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 32.3. This compound is known in the literature.[15,16,33]

DOI: 10.1021/acs.organomet.9b00549
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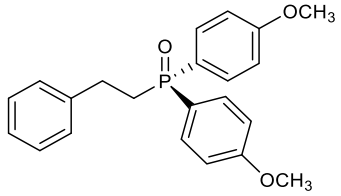
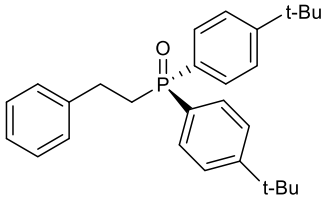
*Bis(4-methoxyphenyl)(phenethyl)phosphine Oxide (**3t**).*



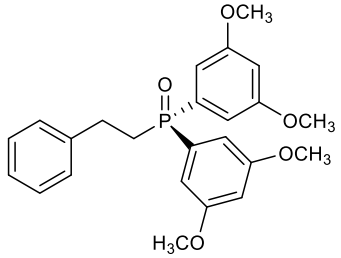
White solid (173 mg, 95%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.67 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 8.4 Hz, 4H), 7.28−7.24 (m, 2H), 7.20−7.12 (m, 3H), 6.97 (d, $^{3}J_{H-H}$ = 7.2 Hz, 4H), 3.84 (s, 6H), 2.96−2.85 (m, 2H), 2.57−2.47 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 162.1 (d, J_{P-C} = 2.3 Hz), 141.2 (d, J_{P-C} = 15.7 Hz), 132.5 (d, J_{P-C} = 11.0 Hz), 128.4, 127.9, 126.1, 123.8 (d, J_{P-C} = 105.5 Hz), 114.3, 114.2, 114.1 (d, J_{P-C} = 12.7 Hz), 55.2, 32.1 (d, J_{P-C} = 70.8 Hz), 27.5 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.7. IR (cm^{-1}): 3010.66 (w), 2935.24 (w), 2832.88 (w), 1594.22 (s), 1569.76 (m), 1499.78 (s), 1462.54 (m), 1293.89 (m), 1254.31 (s), 1169.56 (s), 1116.38 (s), 1101.76 (s), 1021.19 (s), 932.28 (m), 817.69 (s), 799.09 (s), 770.32 (m), 742.79 (s), 696.80 (s), 654.35 (m), 575.89 (s), 526.03 (s), 500.11 (s). Mp: 95−98 °C. HRMS (ESI): m/z calcd for $C_{22}H_{24}O_3P$ $[(M + H)^+]$ 367.1463, found 367.1468.

*Bis(4-tert-butylphenyl)(phenethyl)phosphine Oxide (**3u**).*



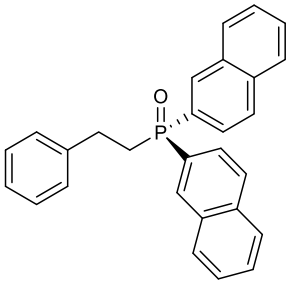
White solid (193 mg, 92%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.70 (dd, $^{3}J_{H-P}$ = 10.8 Hz, $^{3}J_{H-H}$ = 8.4 Hz, 4H), 7.52−7.44 (m, 4H), 7.28−7.22 (m, 2H), 7.20−7.13 (m, 3H), 3.02−2.87 (m, 2H), 2.63−2.49 (m, 2H), 1.32 (s, 18H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 155.0 (d, J_{P-C} = 2.7 Hz), 141.3 (d, J_{P-C} = 15.6 Hz), 130.7 (d, J_{P-C} = 9.2 Hz), 129.6 (d, J_{P-C} = 99.7 Hz), 128.4, 128.0, 126.1, 125.6 (d, J_{P-C} = 12.1 Hz), 34.9, 32.0 (d, J_{P-C} = 70.2 Hz), 31.0, 27.5 (d, J_{P-C} = 3.3 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 31.5. IR (cm^{-1}): 3026.99 (w), 2961.45 (w), 2866.62 (w), 1599.95 (w), 1496.31 (w), 1392.52 (w), 1362.06 (w), 1267.99 (w), 1178.90 (s), 1112.17 (m), 1092.71 (m), 835.42 (m), 773.78 (m), 757.18 (m), 724.41 (m), 697.16 (m), 611.71 (s), 591.12 (m), 562.83 (m), 555.24 (m), 507.10 (m), 488.92 (m), 472.85 (m). Mp: 227−230 °C. HRMS (ESI): m/z calcd for $C_{28}H_{36}OP$ $[(M + H)^+]$ 419.2504, found 419.2512.

*Bis(3,5-dimethoxyphenyl)(phenethyl)phosphine Oxide (**3v**).*



White solid (176 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28−7.23 (m, 2H), 7.21−7.14 (m, 3H), 6.84 (dd, $^{3}J_{H-P}$ = 13.2 Hz, $^{4}J_{H-H}$ = 2.4 Hz, 4H), 6.57 (s, 2H), 3.80 (s, 12 H), 3.01−2.89 (m, 2H), 2.59−2.47 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 160.9 (d, J_{P-C} = 17.4 Hz), 141.1 (d, J_{P-C} = 15.7 Hz), 134.6 (d, J_{P-C} = 98.0 Hz), 128.5, 128.0, 126.3, 108.2 (d, J_{P-C} = 11.0 Hz), 103.8 (d, J_{P-C} = 1.8 Hz), 55.5, 31.8 (d, J_{P-C} = 70.4 Hz), 27.5 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 32.8. IR (cm^{-1}): 2992.58 (w), 2934.20 (w), 2833.51 (w), 1582.23 (s), 1450.68 (m), 1417.61 (s), 1336.50 (m), 1284.55 (s), 1204.50 (s), 1172.88 (s), 1152.42 (s), 1059.98 (s), 987.45 (m), 841.78 (s), 756.43 (m), 741.34 (s), 693.87 (s), 605.33 (s), 578.26 (m), 510.09 (m), 469.06 (s). Mp: 105−107 °C. HRMS (ESI): m/z calcd for $C_{24}H_{28}O_5P$ $[(M + H)^+]$ 427.1674, found 427.1680.

*Bis(naphthalen-2-yl)(phenethyl)phosphine Oxide (**3w**).*



White solid (155 mg, 76%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.48 (d, $^{3}J_{H-P}$ = 13.2 Hz, 2H), 7.96−7.88 (m, 4H), 7.85 (d, $^{3}J_{H-H}$ = 7.8 Hz, 2H), 7.73 (t, $^{3}J_{H-H}$ = 9.0 Hz, 2H), 7.58−7.51 (m, 4H), 7.28−7.22 (m, 2H), 7.21−7.13 (m, 3H), 3.11−2.92 (m, 2H), 2.85−2.69 (m, 2H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$): δ 141.1 (d, J_{P-C} = 15.0 Hz), 134.6 (d, J_{P-C} = 2.3 Hz), 132.8 (d, J_{P-C} = 8.0 Hz), 132.5 (d, J_{P-C} = 12.7 Hz), 130.2 (d, J_{P-C} = 98.6 Hz), 128.8, 128.7 (d, J_{P-C} = 11.6 Hz), 128.6, 128.1, 128.0, 127.8, 127.0, 126.3, 125.5 (d, J_{P-C} = 10.4 Hz), 31.7 (d, J_{P-C} = 70.4 Hz), 27.6 (d, J_{P-C} = 2.9 Hz). $^{31}P\{^{1}H\}$ NMR (243 MHz, $CDCl_3$): δ 32.0. This compound is known in the literature.[15,33]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.9b00549.

NMR spectra for all hydrophosphinylation products (**3a**−**w**) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*J.A.R.S.: e-mail, Joseph.Schmidt@utoledo.edu; tel, 419-530-1512; fax, 419-530-4033.

ORCID

Joseph A. R. Schmidt: 0000-0003-3019-0055

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Acknowledgement is made to the Donors of the American Chemical Society Petroleum Research Fund for support of this research.

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DOI: 10.1021/acs.organomet.9b00549
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