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Nickel-catalyzed coupling of $R_2P(O)Me$ (R = aryl or alkoxy) with (hetero)arylmethyl alcohols†

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α-Alkylation of methyldiarylphosphine oxides with (hetero)arylmethyl alcohols was performed under nickel catalysis. Various arylmethyl and heteroarylmethyl alcohols can be used in this transformation. A series of methyldiarylphosphine oxides were alkylated with 30–90% yields. Functional groups on the aromatic rings of methyldiarylphosphine oxides or arylmethyl alcohols including OMe, NMe_2, SMe, CF_3, Cl, and F groups can be tolerated. The conditions are also suitable for the α-alkylation reaction of dialkyl methylphosphonates.

Introduction

Reactions of C–C bond formation are important transformations in organic synthesis. Among the reactions, transition-metal-catalyzed cross-coupling of organometallic reagents with electrophiles has attracted great attention. The electrophiles employed in the reactions are often organic halides or alcohol derivatives such as carboxylates, carbonates, and sulfonates.[1] Direct use of alcohols was relatively rare due to the poor leaving ability of the OH group. However, direct use of alcohols as coupling partners is more step- and atom-economical because organic halides and alcohol derivatives were mainly prepared from alcohols. In recent years, transition-metal-catalyzed α-alkylation reactions using alcohols with hydrogen borrowing methodologies have achieved significant advances.[2] Nucleophilic substrates included acetones,[3] nitriles,[4] amides,[5] alcohols[6] and other compounds containing active hydrogens.[7] The catalysts employed for the above transformations were mainly Ir, Ru, Rh, Os and Pd complexes.[2] The use of non-precious metal catalysts such as Fe, Mn, and Ni was relatively rare.[3e–h,7b–d,8]

Organophosphorus compounds have found wide applications in many fields such as organic synthesis, coordination chemistry, medicinal chemistry and photoelectric materials.[9] A series of methodologies have been developed to prepare various phosphorus-containing compounds. Traditional methods including radical methods, anionic methods and the Arbuzov reaction are well known.[10] Transition-metal-catalyzed methods to construct C–P bonds *via* cleavage of C–halide,[11] C–O,[12] C–N,[13] C–S,[14] C–CN[15] and C–H[16] bonds have also achieved great success. However, the reported methods are not flawless. It is still desirable to develop new methodologies to overcome the drawbacks of the reported methods and extend the range of reaction materials. As mentioned above, alcohols are widely available and green starting materials. Synthesizing organophosphorus compounds *via* reaction of alcohols with appropriate phosphorus substrates is attractive. Herein we report α-alkylation of methyldiarylphosphine oxides or dialkyl methylphosphonates with alcohols under catalysis with nickel complexes.

Results and discussion

Methyldiphenylphosphine oxide **1a** and benzyl alcohol **2a** were employed as model substrates to screen catalysts and reaction conditions. We chose non-precious metals including copper, cobalt, and nickel for testing (Table 1). $CuCl_2$ was found to be able to catalyze the reaction in the presence of *t*-BuOK in toluene at 130 °C. $Co(acac)_2$ was inactive under the same conditions. $Ni(COD)_2$ led to a better result than $CuCl_2$ (entries 1–3). Hence we further tested nickel compounds. Ni(II) compounds including $Ni(dppe)Cl_2$, $Ni(DME)Cl_2$ and $Ni(glyme)Cl_2$ exhibited lower activity than $Ni(COD)_2$ (entries 4–6). Subsequently, we examined the base effect using $Ni(COD)_2$ as the catalyst. *t*-BuOLi, *t*-BuONa, NaOH, Cs_2CO_3, and K_2CO_3 were respectively tested and these bases were demonstrated to be less effective than *t*-BuOK (entries 7–11). The solvent also markedly affected the reaction results. MeCN, 1,4-dioxane, THF and cyclopentyl methyl ether (CPME) were examined and CPME was demonstrated to be optimal (entries 12–15). Next, we tried to improve the catalysis of $Ni(COD)_2$ by adding

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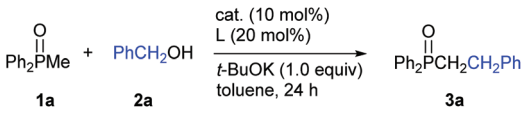
Table 1 Optimization of reaction conditions[a]



1a 2a 3a

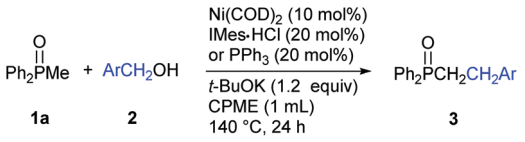
Entry	Cat.	*L* (mol%)	Solvent	Base	*T* (°C)	Yield[b] (%)
1	$CuCl_2$	—	Toluene	*t*-BuOK	130	40
2	$Co(acac)_2$	—	Toluene	*t*-BuOK	130	Trace
3	$Ni(COD)_2$	—	Toluene	*t*-BuOK	130	54
4	$Ni(dppe)Cl_2$	—	Toluene	*t*-BuONa	130	8
5	$Ni(DME)Cl_2$	—	Toluene	*t*-BuONa	130	10
6	$Ni(glyme)Cl_2$	—	Toluene	*t*-BuONa	130	20
7	$Ni(COD)_2$	—	Toluene	*t*-BuOLi	130	8
8	$Ni(COD)_2$	—	Toluene	*t*-BuONa	130	48
9	$Ni(COD)_2$	—	Toluene	NaOH	130	46
10	$Ni(COD)_2$	—	Toluene	Cs_2CO_3	130	—
11	$Ni(COD)_2$	—	Toluene	K_2CO_3	130	—
12	$Ni(COD)_2$	—	CH_3CN	*t*-BuOK	130	—
13	$Ni(COD)_2$	—	1,4-Dioxane	*t*-BuOK	130	Trace
14	$Ni(COD)_2$	—	THF	*t*-BuOK	130	35
15	$Ni(COD)_2$	—	CPME	*t*-BuOK	130	60
16	$Ni(COD)_2$	PPh_3 (20)	CPME	*t*-BuOK	130	78
17	$Ni(COD)_2$	PCy_3 (20)	CPME	*t*-BuOK	130	57
18	$Ni(COD)_2$	DPEPhos (10)	CPME	*t*-BuOK	130	42
19	$Ni(COD)_2$	Dppp (10)	CPME	*t*-BuOK	130	31
20	$Ni(COD)_2$	Dppe (10)	CPME	*t*-BuOK	130	52
21	$Ni(COD)_2$	Dppb (10)	CPME	*t*-BuOK	130	71
22	$Ni(COD)_2$	Dppb (10)	CPME	*t*-BuOK	140	80
23	$Ni(COD)_2$	Dppb (10)	CPME	*t*-BuOK	120	65
24	$Ni(COD)_2$	PPh_3 (20)	CPME	*t*-BuOK	140	83
25[c]	$Ni(COD)_2$	Dppb (10)	CPME	*t*-BuOK	140	68
26[d]	$Ni(COD)_2$	IPr·HCl (20)	CPME	*t*-BuOK	140	65
27[d]	$Ni(COD)_2$	SMes·HCl (20)	CPME	*t*-BuOK	140	68
28[d]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	85
29[d,e]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	61
30[d,f]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	65
31[d,g]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	73
32[d,h]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	53
33[d,i]	$Ni(COD)_2$	IMes·HCl (20)	CPME	*t*-BuOK	140	34
34[d]	—	IMes·HCl (20)	CPME	*t*-BuOK	140	—

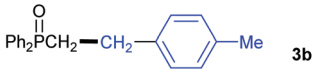
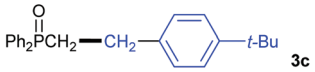
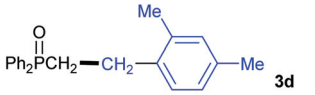
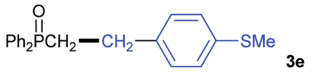
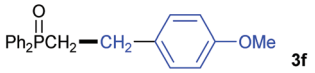
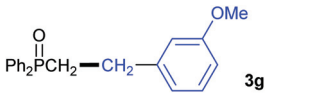
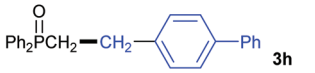
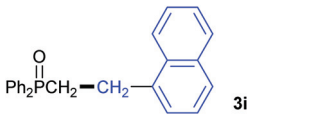
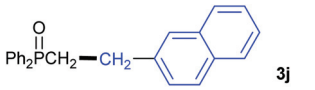
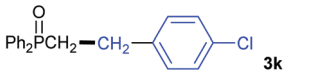
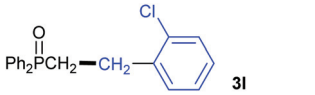
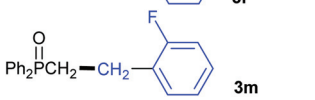
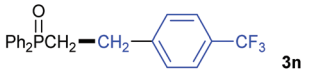
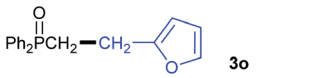
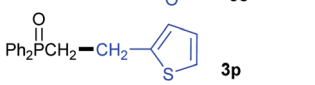
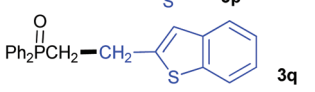
[a] Unless otherwise noted, all reactions were performed using the following reaction conditions: methyl diphenylphosphine oxide (0.25 mmol), benzyl alcohol (0.625 mmol), base (0.25 mmol), solvent (1 cm^3), and catalyst (10 mol%), 24 h. [b] Isolated yield. [c] Reaction time was 18 h. [d] 0.3 mmol of *t*-BuOK was used. [e] 5 mol% of $Ni(COD)_2$ and 10 mol% of IMes·HCl were used. [f] 0.25 mmol of benzyl alcohol was used. [g] 0.5 mmol of benzyl alcohol was used. [h] 0.175 mmol of *t*-BuOK was employed. [i] 0.075 mmol of *t*-BuOK was employed.

ligands. Phosphine ligands including PPh_3, PCy_3, DPEPhos, dppp, dppe and dppb were used and both dppb and PPh_3 led to better results than the other phosphine ligands (entries 16–21). When the reaction temperature was raised to 140 °C, the $Ni(COD)_2$/dppb and $Ni(COD)_2$/PPh_3-catalyzed reaction gave a little higher product yields than the corresponding reactions performed at 130 °C. When the reaction was run at 120 °C, the product yield markedly decreased (entries 22–24). Reducing the reaction time also led to a decrease of product yield (entry 25). Thereafter, we found that N-heterocyclic carbene ligands including IPr, SMes, and IMes were also effective at improving the catalysis of $Ni(COD)_2$. The combination of $Ni(COD)_2$ (10 mol%) and IMes (20 mol%) resulted in the highest product yield (entries 26–28). Decreasing the loading of the catalyst led to a decrease of product yield (entry 29). We also tried to decrease the dosage of benzyl alcohol and *t*-BuOK employed in the reaction. In each case the product yield decreased (entries 30–33). In addition, in the absence of $Ni(COD)_2$ the reaction cannot occur (entry 34).

$Ni(COD)_2$-dppb, $Ni(COD)_2$-PPh_3 and $Ni(COD)_2$-IMes systems showed good catalytic properties under the optimized conditions of temperature, time and solvent (entries 22, 24 and 28, Table 1). We chose a $Ni(COD)_2$–IMes combination as the catalyst to examine substrate scope. (Hetero)arylmethyl alcohols were first evaluated using methyldiphenylphosphine oxide **1a** as the coupling partner (Table 2). Alkyl-substituted arylmethyl alcohols including *p*-tolylmethanol, (4-(*tert*-butyl)-phenyl)methanol, and (2,4-dimethylphenyl)methanol reacted smoothly with **1a**, affording the corresponding products in 70%, 65% and 79% yields, respectively (entries 1–3). The steric hindrance of (2,4-dimethylphenyl)methanol did not affect the reaction. Conversely, its reaction with **1a** gave the highest product yield (79%). The reaction of (4-(methylthio)phenyl) methanol with **1a** gave comparable product yield to that of

Table 2 Scope of reaction substrates[a]



Entry	Product	Yield[b] (%)
1	 3b	70
2	 3c	65
3	 3d	79
4	 3e	73
5	 3f	80
6	 3g	82
7	 3h	88
8	 3i	90
9	 3j	87
10[c]	 3k	53
11[c]	 3l	54
12[c]	 3m	30
13[c]	 3n	45
14	 3o	53
15	 3p	54
16	 3q	49

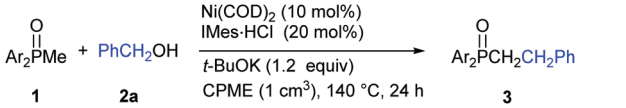
[a] Unless otherwise noted, the reactions were carried out using 0.25 mmol of **1a** and 0.625 mmol of arylmethyl alcohols according to the conditions indicated by the above equation. [b] Isolated yield. [c] 20 mol% of PPh_3 and 0.25 mmol of *t*-BuOK were employed.

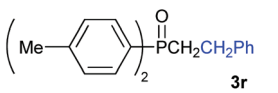
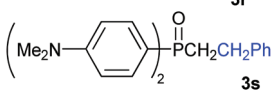
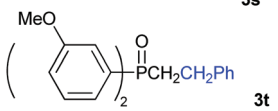
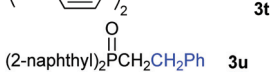
p-tolylmethanol (entry 4). Both (4-methoxyphenyl)methanol and (3-methoxyphenyl)methanol exhibited similar reactivity, and they were more reactive than (4-(methylthio)phenyl)methanol (entries 5 and 6). Arylmethyl alcohols with conjugated or extended aromatic systems showed higher reactivity than arylmethyl alcohols with alkyl or alkoxy substituents on the aromatic rings (entries 7–9). Arylmethyl alcohols with electron-withdrawing groups such as Cl, F, and CF_3 on the aromatic rings showed lower reactivity (entries 10–13). We also noted that the combination of $Ni(COD)_2$ and PPh_3 showed better catalytic activity than the combination of $Ni(COD)_2$ and IMes in these cases. The reaction of heteroarylmethanols including furan-2-ylmethanol, thiophen-2-ylmethanol and benzo[*b*]thiophen-2-ylmethanol with **1a** gave the desired products in modest yields (entries 14–16). The reaction of pyridin-2-ylmethanol with **1a** under the same conditions resulted in an unidentified product. In addition, common aliphatic alcohols such as butanol and cyclohexanol cannot be used to replace benzyl alcohols in this transformation.

Next, we examined the reaction of several diarylmethyl-phosphine oxides with benzyl alcohol (Table 3). Diarylmethylphosphine oxides with Me, NMe_2 and OMe groups on the aromatic rings reacted smoothly with benzyl alcohol under the standard conditions, giving the corresponding products in 63–66% yields (entries 1–3). Methyldi(naphthalen-2-yl)phosphine oxide exhibited higher reactivity. Its reaction with benzyl alcohol afforded the coupling product in 82% yield (entry 4).

Dialkyl methylphosphonates such as dimethyl-methylphosphonate and diethyl methylphosphonate can also react with arylmethyl alcohols (Table 4). However, they showed lower reactivity than the diarylmethylphosphine oxides. The reaction of dimethyl methylphosphonate and diethyl methyl-phosphonate with benzyl alcohol resulted in the coupling pro-

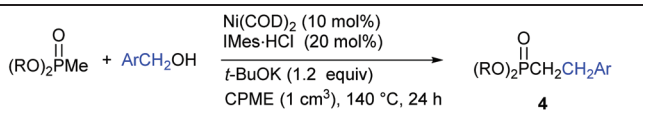
Table 3 Reaction of diarylmethylphosphine oxides with benzyl alcohol[a]



Entry	Product	Yield[b] (%)
1	 3r	63
2	 3s	63
3	 3t	66
4	 3u	82

[a] The reactions were carried out using 0.25 mmol of **1** and 0.625 mmol of benzyl alcohol according to the conditions indicated by the above equation. [b] Isolated yield.

Table 4 Reaction of dialkyl methylphosphonates with arylmethyl alcohols[a]



Entry	Product	Yield[b] (%)
1	$(MeO)_2P(O)CH_2CH_2Ph$ **4a**	43
2	$(EtO)_2P(O)CH_2CH_2Ph$ **4b**	45
3	$(EtO)_2P(O)CH_2CH_2$–C$_6$H$_4$–Me **4c**	48
4	$(EtO)_2P(O)CH_2CH_2$–C$_6$H$_4$–OMe **4d**	50
5	$(EtO)_2P(O)CH_2CH_2$–C$_6$H$_4$–F **4e**	37

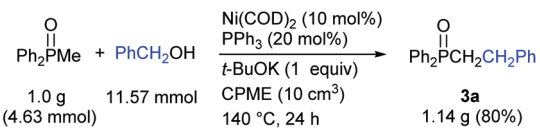
[a] The reactions were carried out using 0.25 mmol of **1** and 0.625 mmol of benzyl alcohol according to the conditions indicated by the above equation. [b] Isolated yield.

ducts in 43% and 45% yields, respectively (entries 1 and 2). The reaction of other arylmethyl alcohols gave similar results (entries 3–5).

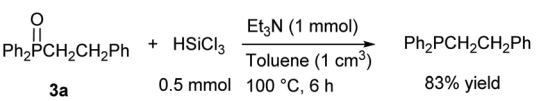
To evaluate the synthetic applicability of this method, a gram scale reaction between methyldiphenylphosphine oxide and benzyl alcohol was carried out (Scheme 1). The coupling product **3a** was isolated in 80% yield. This result well demonstrated the synthetic value of this reaction.

The compounds obtained by this approach can be further converted to other important phosphorus-containing compounds such as phosphines. For example, **3a** was reduced with $HSiCl_3$ in the presence of Et_3N to afford $Ph_2PCH_2CH_2Ph$ in 83% yield (Scheme 2).[17]

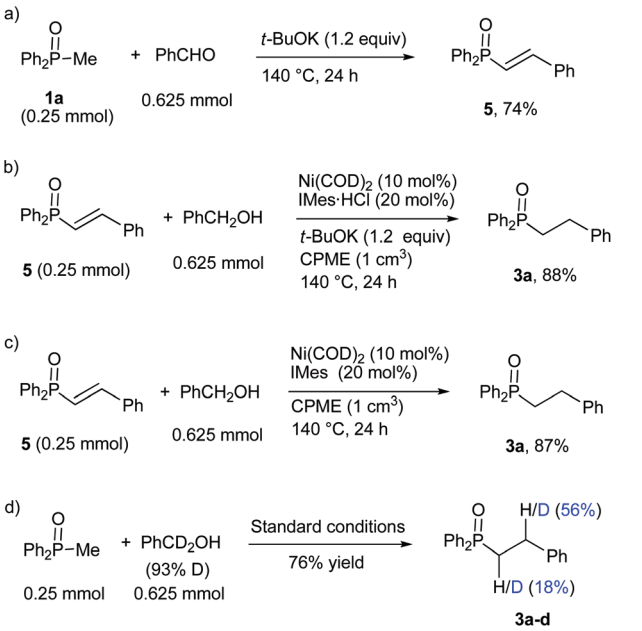
To gain insight into the reaction mechanism, several control experiments were carried out. Condensation of diphenyl(methyl)phosphine oxide with PhCHO in the presence of *t*-BuOK gave diphenyl(styryl)phosphine oxide (**5**) in 74% yield (Scheme 3a). This reaction did not require the presence of a



Scheme 1 Gram scale reaction of $Ph_2P(O)CH_3$ with $PhCH_2OH$.

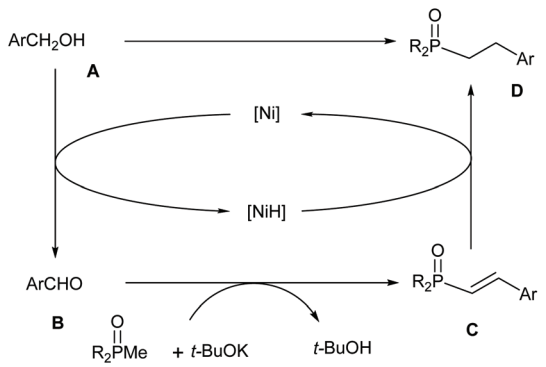


Scheme 2 Reduction of $Ph_2P(O)CH_2CH_2Ph$ with $HSiCl_3$.



Scheme 3 Mechanistic studies.

nickel catalyst. The reaction of **5** with $PhCH_2OH$ under the standard conditions afforded the coupling product **3a** in 88% NMR yield (Scheme 3b). In the absence of *t*-BuOK the reaction of **5** with $PhCH_2OH$ gave the same result as that shown in Scheme 3b (Scheme 3c). These experimental facts imply that a nickel hydride complex was *in situ* formed.[2] We observed the formation of PhCHO *via* the reaction of $L_2Ni(0)$ with $PhCH_2OH$, but the Ni–H species was not detected by the ^1H NMR spectral study. This is ascribed to the instability of the Ni–H species.[18] In addition, the reaction of **1a** with $PhCD_2OH$ (93% D) under the standard conditions afforded **3a–d** in 76% yield along with 18–56% deuterium incorporation (Scheme 3d). This study also suggests that the hydride source is derived from alcohol for the reduction step and the transfer-hydrogenation step is reversible. Based on the above experimental results and literature reports[8d,19] we propose a reaction pathway as shown in Scheme 4. Thus, the reaction of the Ni



Scheme 4 Proposed reaction mechanism.

complex with arylmethyl alcohol generates aryl aldehyde **B** and a Ni–H intermediate. Condensation of the aryl aldehyde with diaryl(methyl)phosphine oxide in the presence of *t*-BuOK produces diaryl(alkenyl)phosphine oxide **C**. The reaction of **C** with the Ni–H species affords the final coupling product **D** and regenerates the active Ni catalyst.

Conclusions

In summary, we developed a method to perform catalytic coupling of methyldiarylphosphine oxides or dialkyl methylphosphonates with (hetero)arylmethyl alcohols. The reaction proceeded under nickel catalysis, gave the products in moderate to high yields and was suited for a broad scope of substrates. Functional groups on the aromatic rings of methyldiarylphosphine oxides or arylmethyl alcohols such as OMe, NMe_2, SMe, CF_3, Cl, and F groups can be tolerated. This reaction provides an efficient and green protocol to synthesize complex phosphorus-containing molecules from simple phosphorus compounds. The reaction is believed to proceed *via* a hydrogen-borrowing process.

Experimental

All reactions were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. Di-*p*-tolylphosphine oxide, bis(4-(dimethylamino)phenyl)phosphine oxide, bis(3-methoxyphenyl)phosphine oxide, and di(naphthalen-2-yl)phosphine oxide were prepared according to the reported procedure.[20] $Ni(COD)_2$ was purchased from Alfa Aesar and used as received. The phosphine ligands and the NHC precursors were purchased from Energy Chemical and used as received. CPME (extra dry) was purchased from Energy Chemical and degassed prior to use. Other chemicals were obtained from commercial vendors. Toluene and tetrahydrofuran were purified using JC Meyer Phoenix Solvent Systems. 1,4-Dioxane was distilled under nitrogen over sodium and degassed prior to use. MeCN was dried over 4 Å molecular sieves, then fractionally distilled, and stored under a nitrogen atmosphere. NMR spectra were recorded on a Bruker AV400 or Bruker AV500 spectrometer at 25 °C. The chemical shifts of the ^{1}H NMR spectra were referenced to TMS; the chemical shifts of the ^{13}C NMR spectra were referenced to internal solvent resonances. The chemical shifts of ^{31}P NMR spectra were referenced to external phosphoric acid, and the chemical shifts of ^{19}F NMR spectra were referenced to external trifluoroacetic acid. High-resolution mass spectra (HRMS) were acquired on a Thermo Fisher LTQ Orbitrap XL mass spectrometer.

Preparation of methyldiarylphosphine oxides[21]

To a stirred solution of diarylphosphine oxides (3 mmol) in DMSO (10 cm^3) was added a 50% aqueous solution of KOH (4 mmol) at 20 °C. To the mixture MeI (4 mmol) was added dropwise at 20 °C with stirring. The resulting mixture was heated at 60 °C for 1 h, then cooled to room temperature, diluted with water (25 cm^3), and extracted with EtOAc (10 cm^3 × 3). The combined extract was dried with sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the corresponding product.

Methyldi-*p*-tolylphosphine oxide. White solid (0.73 g, 100%), mp 136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, J = 11.8, 8.1 Hz, 4H), 7.26 (dd, J = 8.2, 2.2 Hz, 4H), 2.37 (s, 6H), 1.97 (d, J = 13.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.00 (d, J = 2.8 Hz), 130.95 (d, J = 103.9 Hz), 130.43 (d, J = 10.1 Hz), 129.25 (d, J = 12.3 Hz), 21.46, 16.66 (d, J = 74.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 29.97. HRMS (APCI): m/z 245.1088 $[M + H]^+$, calcd for $C_{15}H_{18}OP$ 245.1090.

Bis(4-(dimethylamino)phenyl)(methyl)phosphine oxide. White solid (0.81 g, 90%), mp 68–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 11.3, 8.9 Hz, 4H), 6.70 (d, J = 8.6 Hz, 4H), 2.99 (d, J = 1.6 Hz, 12H), 1.90 (d, J = 13.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.18, 131.95 (d, J = 11.1 Hz), 119.88 (d, J = 112.3 Hz), 111.38 (d, J = 12.6 Hz), 40.08, 17.26 (d, J = 74.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.59. HRMS (APCI): m/z 303.1622 $[M + H]^+$, calcd for $C_{17}H_{24}ON_2P$ 303.1621.

Bis(3-methoxyphenyl)(methyl)phosphine oxide. Colorless oil (0.74 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.34 (m, 2H), 7.34–7.32 (m, 1H), 7.31–7.29 (m, 1H), 7.24 (dd, J = 11.6, 7.5 Hz, 2H), 7.04 (dd, J = 8.3, 2.6 Hz, 2H), 3.81 (s, 6H), 2.01 (d, J = 13.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 159.63 (d, J = 14.7 Hz), 135.21 (d, J = 100.9 Hz), 129.87 (d, J = 14.2 Hz), 122.46 (d, J = 10.1 Hz), 117.80 (d, J = 2.6 Hz), 115.50 (d, J = 10.3 Hz), 55.40, 16.55 (d, J = 73.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.48. HRMS (APCI): m/z 277.0988 $[M + H]^+$, calcd for $C_{15}H_{18}O_3P$ 277.0988.

Methyldi(naphthalen-2-yl)phosphine oxide. White solid (0.87 g, 92%), mp 178 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 13.6 Hz, 2H), 7.93–7.85 (m, 4H), 7.85–7.80 (m, 2H), 7.72–7.64 (m, 2H), 7.58–7.48 (m, 4H), 2.18 (d, J = 13.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.59 (d, J = 2.4 Hz), 132.49 (d, J = 13.0 Hz), 132.30 (d, J = 9.1 Hz), 131.07 (d, J = 102.0 Hz), 128.83, 128.61 (d, J = 11.8 Hz), 128.14, 127.82, 127.01, 125.51 (d, J = 10.9 Hz), 16.51 (d, J = 74.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.22. HRMS (APCI): m/z 317.1089 $[M + H]^+$, calcd for $C_{21}H_{18}OP$ 317.1090.

Reaction of methyldiarylphosphine oxides with arylmethyl alcohols

General procedure A. Methyldiarylphosphine oxide (0.25 mmol), $Ni(COD)_2$ (6.9 mg, 0.025 mmol), IMes·HCl (17 mg, 0.05 mmol), *t*-BuOK (34 mg, 0.3 mmol), arylmethyl alcohol (0.625 mmol) and CPME (1 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h and then cooled to room temperature. The resulting mixture was concentrated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give the corresponding cross-coupling product.

General procedure B. Methyldiarylphosphine oxide (0.25 mmol), $Ni(COD)_2$ (6.9 mg, 0.025 mmol), PPh_3 (13 mg,

0.05 mmol), *t*-BuOK (28 mg, 0.25 mmol), arylmethyl alcohol (0.625 mmol) and CPME (1 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h and then cooled to room temperature. The resulting mixture was concentrated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give the corresponding cross-coupling product.

Phenethyldiphenylphosphine oxide (3a).[15b] White solid (65 mg, 85%), mp 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.72 (m, 4H), 7.56–7.44 (m, 6H), 7.29–7.22 (m, 2H), 7.21–7.13 (m, 3H), 2.99–2.88 (m, 2H), 2.64–2.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.23 (d, J = 15.4 Hz), 132.82 (d, J = 98.7 Hz), 131.89 (d, J = 2.7 Hz), 130.84 (d, J = 9.4 Hz), 128.86, 128.71 (d, J = 6.2 Hz), 128.12, 126.40, 31.95 (d, J = 70.1 Hz), 27.60 (d, J = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.57.

(4-Methylphenethyl)diphenylphosphine oxide (3b).[22] White solid (56 mg, 70%), mp 124–125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (m, 4H), 7.57–7.43 (m, 6H), 7.06 (s, 4H), 2.95–2.84 (m, 2H), 2.62–2.51 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.15 (d, J = 15.6 Hz), 135.92, 132.82 (d, J = 98.3 Hz), 131.86 (d, J = 2.7 Hz), 130.84 (d, J = 9.3 Hz), 129.33, 128.78 (d, J = 11.6 Hz), 127.98, 32.06 (d, J = 69.7 Hz), 27.15 (d, J = 3.1 Hz), 21.06. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.71.

(4-(*tert*-Butyl)phenethyl)diphenylphosphine oxide (3c).[22] White solid (58.8 mg, 65%), mp 114–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.72 (m, 4H), 7.56–7.42 (m, 6H), 7.28 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 2.98–2.85 (m, 2H), 2.65–2.52 (m, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.30, 138.19 (d, J = 15.4 Hz), 132.91 (d, J = 98.2 Hz), 131.89 (d, J = 2.6 Hz), 130.88 (d, J = 9.3 Hz), 128.81 (d, J = 11.7 Hz), 127.83, 125.60, 34.49, 31.94 (d, J = 70.0 Hz), 31.47, 27.07 (d, J = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.79.

(2,4-Dimethylphenethyl)diphenylphosphine oxide (3d). Yellow solid (65.9 mg, 79%), mp 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.73 (m, 4H), 7.56–7.43 (m, 6H), 7.00 (d, J = 7.5 Hz, 1H), 6.95–6.89 (m, 2H), 2.91–2.81 (m, 2H), 2.55–2.44 (m, 2H), 2.26 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.39 (d, J = 15.2 Hz), 136.12, 135.65, 132.86 (d, J = 98.1 Hz), 131.91 (d, J = 2.7 Hz), 131.28, 130.85 (d, J = 9.3 Hz), 128.80 (d, J = 11.6 Hz), 128.39, 126.96, 30.75 (d, J = 69.6 Hz), 24.58 (d, J = 3.0 Hz), 20.97, 19.15. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.70. HRMS (EI): m/z 334.1468 $[M]^+$, calcd for $C_{22}H_{23}OP$ 334.1481.

(4-(Methylthio)phenethyl)diphenylphosphine oxide (3e). Yellow solid (64.2 mg, 73%), mp 150–151 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.72 (m, 4H), 7.57–7.43 (m, 6H), 7.16 (d, J = 8.3 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 2.94–2.84 (m, 2H), 2.61–2.50 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.26 (d, J = 15.3 Hz), 136.21, 132.80 (d, J = 98.7 Hz), 131.94 (d, J = 2.7 Hz), 130.87 (d, J = 9.4 Hz), 128.90, 128.75 (d, J = 7.0 Hz), 127.29, 31.96 (d, J = 69.6 Hz), 27.14 (d, J = 3.0 Hz), 16.30. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.67. HRMS (ESI): m/z 375.0931 $[M + Na]^+$, calcd for $C_{21}H_{21}SOPNa$ 375.0943.

(4-Methoxyphenethyl)diphenylphosphine oxide (3f).[15b] White solid (67.2 mg, 80%), mp 87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81–7.71 (m, 4H), 7.56–7.43 (m, 6H), 7.08 (d, J = 8.6 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 3.76 (s, 3H), 2.93–2.82 (m, 2H), 2.61–2.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.18, 133.20, 132.86 (d, J = 98.5 Hz), 131.89 (d, J = 2.7 Hz), 130.87 (d, J = 9.4 Hz), 129.11, 128.81 (d, J = 11.7 Hz), 114.09, 55.38, 32.21 (d, J = 69.8 Hz), 26.76 (d, J = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.75.

(3-Methoxyphenethyl)diphenylphosphine oxide (3g). Yellow solid (68.9 mg, 82%), mp 125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.72 (m, 4H), 7.56–7.42 (m, 6H), 7.18 (t, J = 7.9 Hz, 1H), 6.79–6.68 (m, 3H), 3.76 (s, 3H), 2.96–2.85 (m, 2H), 2.65–2.53 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.78, 142.81 (d, J = 15.4 Hz), 132.71 (d, J = 98.4 Hz), 131.89 (d, J = 2.7 Hz), 130.80 (d, J = 9.4 Hz), 129.67, 128.78 (d, J = 11.7 Hz), 120.41, 113.88, 111.67, 55.22, 31.85 (d, J = 69.9 Hz), 27.63 (d, J = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.63. HRMS (EI): m/z 336.1261 $[M]^+$, calcd for $C_{21}H_{21}O_2P$ 336.1274.

(2-([1,1′-Biphenyl]-4-yl)ethyl)diphenylphosphine oxide (3h).[15b] Yellow solid (84 mg, 88%), mp 171–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.73 (m, 4H), 7.57–7.44 (m, 10H), 7.41 (t, J = 7.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.23 (d, J = 8.1 Hz, 2H), 3.04–2.93 (m, 2H), 2.67–2.56 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.88, 140.28 (d, J = 15.1 Hz), 139.38, 132.80 (d, J = 98.4 Hz), 131.89 (d, J = 2.7 Hz), 130.84 (d, J = 9.3 Hz), 128.86, 128.81, 128.66 (d, J = 16.0 Hz), 127.38, 127.23, 127.04, 31.92 (d, J = 69.8 Hz), 27.27 (d, J = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.54.

(2-(Naphthalen-1-yl)ethyl)diphenylphosphine oxide (3i).[22] Yellow solid (80.1 mg, 90%), mp 119–121 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.76 (m, 6H), 7.69 (d, J = 8.0 Hz, 1H), 7.56–7.42 (m, 8H), 7.34 (t, J = 7.5 Hz, 1H), 7.29 (d, J = 6.4 Hz, 1H), 3.44–3.33 (m, 2H), 2.74–2.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.31 (d, J = 14.8 Hz), 133.95, 132.81 (d, J = 98.6 Hz), 131.94 (d, J = 2.7 Hz), 131.32, 130.86 (d, J = 9.4 Hz), 128.95, 128.79 (d, J = 11.7 Hz), 127.28, 126.21, 125.87, 125.73, 125.65, 123.35, 31.23 (d, J = 69.7 Hz), 24.83 (d, J = 2.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.66.

(2-(Naphthalen-2-yl)ethyl)diphenylphosphine oxide (3j).[15b] White solid (77.4 mg, 87%), mp 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.70 (m, 7H), 7.59 (s, 1H), 7.38–7.55 (m, 8H), 7.29 (dd, J = 8.4, 1.7 Hz, 1H), 3.15–3.05 (m, 2H), 2.72–2.62 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.64 (d, J = 15.3 Hz), 133.60, 132.77 (d, J = 98.8 Hz), 132.17, 131.93 (d, J = 2.7 Hz), 130.87 (d, J = 9.3 Hz), 128.83 (d, J = 11.7 Hz), 128.36, 127.69, 127.50, 126.76, 126.23 (d, J = 5.9 Hz), 125.55, 31.82 (d, J = 70.1 Hz), 27.79 (d, J = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.68.

(4-Chlorophenethyl)diphenylphosphine oxide (3k).[22] White solid (46.8 mg, 55%), mp 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.72 (m, 4H), 7.57–7.45 (m, 6H), 7.21 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 2.96–2.86 (m, 2H), 2.60–2.50 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.59 (d, J = 15.0 Hz), 132.59 (d, J = 99.1 Hz), 132.14, 131.99 (d, J = 2.7 Hz), 130.81 (d, J = 9.4 Hz), 129.55, 128.85 (d, J = 11.7 Hz), 128.74, 31.81 (d, J = 70.1 Hz), 27.04 (d, J = 3.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 31.27.

(2-Chlorophenethyl)diphenylphosphine oxide (3l). Yellow oil (40.8 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.74 (m

4H), 7.57–7.43 (m, 6H), 7.33–7.28 (m, 1H), 7.25–7.19 (m, 1H), 7.18–7.09 (m, 2H), 3.09–2.99 (m, 2H), 2.65–2.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.80 (d, J = 15.1 Hz), 133.75, 132.71 (d, J = 98.9 Hz), 131.95 (d, J = 2.7 Hz), 130.89 (d, J = 9.4 Hz), 130.58, 129.66, 128.79 (d, J = 11.7 Hz), 128.07, 127.25, 30.04 (d, J = 69.7 Hz), 26.24 (d, J = 2.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.74. HRMS (EI): m/z 339.0694 $[M]^+$, calcd for $C_{20}H_{18}OP^{35}Cl$ 340.0700.

(2-Fluorophenethyl)diphenylphosphine oxide (3m). Yellow solid (24.3 mg, 30%), mp 94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.73 (m, 4H), 7.56–7.43 (m, 6H), 7.21–7.12 (m, 2H), 7.05–6.94 (m, 2H), 3.03–2.91 (m, 2H), 2.65–2.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.18 (d, J = 246.1 Hz), 132.70 (d, J = 99.1 Hz), 131.95 (d, J = 2.7 Hz), 130.88 (d, J = 9.3 Hz), 130.57 (d, J = 4.8 Hz), 128.84 (d, J = 11.7 Hz), 128.34 (d, J = 8.1 Hz), 128.08, 124.35 (d, J = 3.5 Hz), 115.41 (d, J = 21.7 Hz), 30.39 (d, J = 70.3 Hz), 21.97 (t, J = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ −118.46. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.84. HRMS (EI): m/z 324.1069 $[M]^+$, calcd for $C_{20}H_{18}FOP$ 324.1074.

Diphenyl(4-(trifluoromethyl)phenethyl)phosphine oxide (3n).[22] White solid (42.1 mg, 45%), mp 99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.72 (m, 4H), 7.57–7.44 (m, 8H), 7.27 (d, J = 8.0 Hz, 2H), 3.05–2.96 (m, 2H), 2.63–2.54 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 145.27 (d, J = 14.3 Hz), 132.62 (d, J = 98.9 Hz), 132.08 (d, J = 2.8 Hz), 130.87 (d, J = 9.3 Hz), 128.92 (d, J = 11.7 Hz), 128.86 (q, J = 32.4 Hz), 128.63, 125.63 (q, J = 3.8 Hz), 124.29 (q, J = 272.0 Hz), 31.66 (d, J = 70.1 Hz), 27.61 (d, J = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.07. ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.46.

(2-(Furan-2-yl)ethyl)diphenylphosphine oxide (3o). Yellow solid (39.2 mg, 53%), mp 67–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80–7.71 (m, 4H), 7.56–7.43 (m, 6H), 7.26 (d, J = 1.1 Hz, 1H), 6.25–6.20 (m, 1H), 5.98 (d, J = 2.9 Hz, 1H), 3.01–2.91 (m, 2H), 2.68–2.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.21 (d, J = 17.0 Hz), 141.41, 132.55 (d, J = 99.0 Hz), 131.98 (d, J = 2.7 Hz), 130.87 (d, J = 9.4 Hz), 128.85 (d, J = 11.7 Hz), 110.38, 105.58, 28.51 (d, J = 71.4 Hz), 20.51 (d, J = 2.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.50. HRMS (EI): m/z 296.0952 $[M]^+$, calcd for $C_{18}H_{17}O_2P$ 296.0961.

Diphenyl(2-(thiophen-2-yl)ethyl)phosphine oxide (3p).[22] Yellow solid (42.2 mg, 54%), mp 127–128 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–7.72 (m, 4H), 7.58–7.44 (m, 6H), 7.11 (d, J = 4.8 Hz, 1H), 6.88 (dd, J = 5.0, 3.6 Hz, 1H), 6.79 (dd, J = 3.0 Hz, 1H), 3.20–3.10 (m, 2H), 2.72–2.62 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.96 (d, J = 17.5 Hz), 132.52 (d, J = 99.0 Hz), 132.07 (d, J = 2.6 Hz), 130.90 (d, J = 9.3 Hz), 128.91 (d, J = 11.8 Hz), 127.02, 124.66, 123.72, 32.29 (d, J = 69.8 Hz), 22.23 (d, J = 2.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 31.21.

2-(2-Diphenylphosphorylethyl)benzothiophene (3q). Yellow solid (44.0 mg, 49%), mp 122–123 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84–7.70 (m, 5H), 7.62 (d, J = 7.7 Hz, 1H), 7.56–7.44 (m, 6H), 7.33–7.21 (m, 2H), 7.00 (s, 1H), 3.29–3.17 (m, 2H), 2.79–2.66 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.82 (d, J = 17.0 Hz), 140.01, 139.41, 132.52 (d, J = 98.7 Hz), 132.09 (d, J = 2.4 Hz), 130.89 (d, J = 9.4 Hz), 128.90 (d, J = 11.7 Hz), 124.37, 123.91, 123.04, 122.24, 121.22, 31.72 (d, J = 70.1 Hz), 23.18 (d, J = 1.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.98. HRMS (ESI): m/z 385.0789 $[M + Na]^+$, calcd for $C_{22}H_{19}OPSNa$ 385.0786.

Phenethyldi-*p*-tolylphosphine oxide (3r).[15b] White solid (52.6 mg, 63%), mp 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 7.32–7.23 (m, 6H), 7.21–7.14 (m, 3H), 2.96–2.86 (m, 2H), 2.59–2.49 (m, 2H), 2.39 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.32 (d, J = 2.7 Hz), 141.54 (d, J = 15.7 Hz), 130.93 (d, J = 9.7 Hz), 129.79 (d, J = 101.2 Hz), 129.57 (d, J = 12.1 Hz), 128.72, 128.19, 126.39, 32.20 (d, J = 70.1 Hz), 27.75 (d, J = 3.1 Hz), 21.71. ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.90.

Bis(4-(dimethylamino)phenyl)(phenethyl)phosphine oxide (3s).[23] White solid (61.7 mg, 63%), mp 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.52 (m, 4H), 7.28–7.22 (m, 2H), 7.20–7.14 (m, 3H), 6.71 (dd, J = 8.9, 2.0 Hz, 4H), 2.99 (s, 12H), 2.95–2.86 (m, 2H), 2.52–2.42 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.28, 142.11 (d, J = 15.8 Hz), 132.31 (d, J = 10.6 Hz), 128.58, 128.19, 126.12, 118.21 (d, J = 109.5 Hz), 111.53 (d, J = 12.3 Hz), 40.12, 32.63 (d, J = 71.1 Hz), 28.05 (d, J = 2.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.46.

Bis(3-methoxyphenyl)(phenethyl)phosphine oxide (3t). Colorless oil (60.4 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.33 (m, 4H), 7.31–7.23 (m, 4H), 7.18 (t, J = 7.4 Hz, 3H), 7.05 (dd, J = 8.2, 2.5 Hz, 2H), 3.83 (s, 6H), 2.99–2.90 (m, 2H), 2.61–2.51 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.78 (d, J = 14.3 Hz), 141.20 (d, J = 15.5 Hz), 134.10 (d, J = 97.6 Hz), 130.01 (d, J = 13.8 Hz), 128.67, 128.12, 126.40, 122.71 (d, J = 9.6 Hz), 118.02, 115.81 (d, J = 9.9 Hz), 55.52, 32.01 (d, J = 70.0 Hz), 27.64 (d, J = 2.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.88. HRMS (ESI): m/z 389.1265 $[M + Na]^+$, calcd for $C_{22}H_{23}O_3PNa$ 389.1277.

Di(naphthalen-2-yl)(phenethyl)phosphine oxide (3u).[15b] Yellow solid (83.2 mg, 82%), mp 182 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (d, J = 13.2 Hz, 2H), 7.96–7.88 (m, 4H), 7.85 (d, J = 7.7 Hz, 2H), 7.72 (t, J = 8.8 Hz, 2H), 7.61–7.49 (m, 4H), 7.25 (t, J = 7.4 Hz, 2H), 7.21–7.14 (m, 3H), 3.07–2.95 (m, 2H), 2.84–2.72 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.34 (d, J = 15.4 Hz), 134.80 (d, J = 2.2 Hz), 133.02 (d, J = 8.4 Hz), 132.75 (d, J = 12.7 Hz), 129.98 (d, J = 98.7 Hz), 129.03, 128.79 (d, J = 11.6 Hz), 128.77, 128.33, 128.24, 127.98, 127.17, 126.49, 125.70 (d, J = 10.6 Hz), 31.92 (d, J = 70.2 Hz), 27.79 (d, J = 3.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 31.86.

Dimethyl phenethylphosphonate (4a).[24] Colorless oil (19.8 mg, 37%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.27 (m, 2H), 7.24–7.17 (m, 3H), 3.73 (d, J = 10.8 Hz, 6H), 2.98–2.85 (m, 2H), 2.15–2.01 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.92 (d, J = 17.4 Hz), 128.73, 128.15, 126.54, 52.48 (d, J = 6.6 Hz), 28.58 (d, J = 4.5 Hz), 26.75 (d, J = 139.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 33.41.

Diethyl phenethylphosphonate (4b).[24] Colorless oil (28.8 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32–7.26 (m, 2H), 7.25–7.16 (m, 3H), 4.18–4.03 (m, 4H), 2.99–2.85 (m, 2H), 2.13–1.98 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.98 (d, J = 17.4 Hz), 128.59, 128.06, 126.36, 61.62 (d, J = 6.5 Hz), 28.61 (d, J = 4.4 Hz), 27.61 (d, J = 139.4 Hz), 16.49 (d, J = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.80.

Diethyl (4-methylphenethyl)phosphonate (4c).[25] Colorless oil (31 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (s, 4H), 4.18–4.02 (m, 4H), 2.93–2.82 (m, 2H), 2.32 (s, 3H), 2.10–1.98 (m, 2H), 1.33 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.02 (d, J = 18.1 Hz), 135.95, 129.33, 128.00, 61.66 (d, J = 6.5 Hz), 28.51 28.23 (d, J = 4.4 Hz), 27.13, 21.11, 16.58 (d, J = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.97.

Diethyl (4-methoxyphenethyl)phosphonate (4d).[25] Colorless oil (34 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.17–4.02 (m, 4H), 3.79 (s, 3H), 2.92–2.80 (m, 2H), 2.09–1.96 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 158.23, 133.17 (d, J = 17.8 Hz), 129.09, 114.06, 61.65 (d, J = 6.5 Hz), 55.39, 28.68, 27.82 (d, J = 4.5 Hz), 27.30, 16.58 (d, J = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.91.

Diethyl (4-fluorophenethyl)phosphonate (4e). Colorless oil (24 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.12 (m, 2H), 7.02–6.94 (m, 2H), 4.17–4.02 (m, 4H), 2.95–2.84 (m, 2H), 2.10–1.97 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.51 (d, J = 244.2 Hz), 136.63 (dd, J = 17.4, 3.2 Hz), 129.54 (d, J = 7.9 Hz), 115.36 (d, J = 21.2 Hz), 61.66 (d, J = 6.5 Hz), 28.45, 27.89 (d, J = 4.4 Hz), 27.07, 16.51 (d, J = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.50. ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.90. HRMS (EI): m/z 260.0973 $[M]^+$, calcd for $C_{12}H_{18}O_3FP$ 260.0972.

Gram scale reaction of $Ph_2P(O)CH_3$ with $PhCH_2OH$

Methyldiphenylphosphine oxide (1.0 g, 4.63 mmol), $Ni(COD)_2$ (127.79 mg, 0.463 mmol), PPh_3 (240.76 mg, 0.926 mmol), t-BuOK (518.56 mg, 4.63 mmol), benzyl alcohol (1.2 cm^3, 11.58 mmol) and CPME (10 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h and then cooled to room temperature. The resulting mixture was concentrated to dryness under reduced pressure and the residue was purified by column chromatography on silica gel to give **3a** (1.14 g, 80%).

Reduction of $Ph_2P(O)CH_2CH_2Ph$ (3a) with $HSiCl_3$[17]

A Schlenk tube was charged with **3a** (0.05 mmol), $HSiCl_3$ (0.5 mmol), Et_3N (1.0 mmol) and toluene (2.0 cm^3) under a nitrogen atmosphere. The solution was stirred at 100 °C for 6 h until compound **3a** was completely consumed as indicated by TLC. Then, NaOH (1.0 mol L^{-1}) was added. The resulting mixture was extracted with EtOAc (3 × 10 cm^3). The organic phases were washed with brine, dried with anhydrous Na_2SO_4 and condensed under reduced pressure. The residue was purified by flash column chromatography to produce $Ph_2PCH_2CH_2Ph$[26] as a colorless oil (12 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.39 (m, 4H), 7.38–7.29 (m, 6H), 7.28–7.21 (m, 2H), 7.20–7.12 (m, 3H), 2.77–2.65 (m, 2H), 2.42–2.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.73 (d, J = 13.4 Hz), 138.56 (d, J = 12.7 Hz), 132.87 (d, J = 18.4 Hz), 128.76, 128.63, 128.56, 128.27, 126.14, 32.29 (d, J = 17.8 Hz), 30.32 (d, J = 12.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ −15.87.

Mechanistic experiments

Reaction of $Ph_2P(O)Me$ with PhCHO. Methyldiphenylphosphine oxide (54 mg, 0.25 mmol), t-BuOK (34 mg, 0.30 mmol), benzaldehyde (67 mg, 0.625 mmol) and CPME (1 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h and then concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel to give diphenyl (styryl)phosphine oxide (**5**)[27] in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82–7.72 (m, 4H), 7.59–7.51 (m, 5H), 7.51–7.46 (m, 4H), 7.41–7.35 (m, 3H), 6.84 (dd, J = 17.9, 14.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 147.88 (d, J = 3.0 Hz), 135.23 (d, J = 14.4 Hz), 132.88 (d, J = 85.3 Hz), 132.08 (d, J = 2.2 Hz), 131.56 (d, J = 8.1 Hz), 130.28, 130.14, 129.00, 128.79 (d, J = 9.8 Hz), 128.39, 127.94, 119.13 (d, J = 84.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): δ 25.11.

Reaction of $Ph_2P(O)CH{=}CHPh$ with $PhCH_2OH$ under the standard conditions. $Ph_2P(O)CH{=}CHPh$ (76 mg, 0.25 mmol), $Ni(COD)_2$ (6.9 mg, 0.025 mmol), IMes·HCl (17 mg, 0.05 mmol), t-BuOK (34 mg, 0.30 mmol), benzyl alcohol (68 mg, 0.625 mmol), and CPME (1 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel to give phenethyldiphenyl phosphine oxide (**3a**) in 88% yield.

Reaction of $Ph_2P(O)CH{=}CHPh$ with $PhCH_2OH$ in the absence of t-BuOK. IMes·HCl (17 mg, 0.05 mmol), t-BuOK (5.6 mg, 0.05 mmol) and CPME (1 cm^3) were successively charged into a Schlenk tube. After the mixture was stirred at room temperature for 30 min, $Ni(COD)_2$ (6.9 mg, 0.025 mmol) was added. The resulting mixture was stirred for an additional 30 min. $Ph_2P(O)CH{=}CHPh$ (76 mg, 0.25 mmol) and benzyl alcohol (68 mg, 0.625 mmol) were added into the Schlenk tube. The mixture was stirred at 140 °C for 24 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel to give phenethyldiphenyl phosphine oxide (**3a**) in 87% yield.

Reaction of $PhCH_2OH$ with $Ni(COD)_2$-IMes. IMes·HCl (682 mg, 2 mmol), t-BuOK (224 mg, 2 mmol) and CPME (3 cm^3) were successively charged into a Schlenk tube. After the mixture was stirred at room temperature for 30 min, Ni $(COD)_2$ (275 mg, 1 mmol) was added. The resulting mixture was stirred for 30 min and the color of the solution changed to dark red. Then $PhCH_2OH$ (108 mg, 1 mmol) was added and the mixture was further stirred at room temperature for 30 min. A small amount of the extract was taken out for GC-MS analysis. The remaining mixture was filtered under a N_2 atmosphere. The solvent was removed from the filtrate *in vacuo*. The residue was dissolved in C_6D_6 to record its ^{1}H NMR spectrum. No Ni–H signals were observed (until −45 ppm).

Reaction of $Ph_2P(O)Me$ with $PhCD_2OH$

Preparation of $PhCD_2OH$.[28] To a stirred suspension of $NaBD_4$ (0.55 g, 13 mmol) in dry THF (15 cm^3) was added dropwise a THF solution (20 cm^3) of benzoyl chloride (3 g, 21 mmol) at 0 °C. The resulting mixture was refluxed for 2 h, then cooled to 0 °C, and quenched by dropwise addition of

THF/H_2O (5 cm^3, 1 : 1 v/v). The mixture was acidified with 1 M aqueous HCl (100 cm^3) and extracted with Et_2O (3 × 20 cm^3). The combined organic layer was dried over anhydrous Na_2SO_4, and purified by column chromatography on silica gel to give $PhCD_2OH$ in 62% yield (93% D). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.24 (m, 5H), 4.62–4.56 (m, 0.14H), 3.02 (b, 1H).

Reaction of $Ph_2P(O)Me$ with $PhCD_2OH$. Methyldiphenylphosphine oxide (54 mg, 0.25 mmol), $Ni(COD)_2$ (6.9 mg, 0.025 mmol), IMes·HCl (17 mg, 0.05 mmol), *t*-BuOK (34 mg, 0.30 mmol), $PhCD_2OH$ (69 mg, 0.625 mmol), and CPME (1 cm^3) were successively charged into a Schlenk tube. The mixture was stirred at 140 °C for 24 h, cooled to room temperature, and concentrated to dryness under reduced pressure. The residue was purified by column chromatography on silica gel to give the product in 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83–7.72 (m, 4H), 7.57–7.43 (m, 6H), 7.26 (t, J = 7.2 Hz, 2H), 7.21–7.13 (m, 3H), 2.99–2.85 (m, 0.89H), 2.64–2.51 (m, 1.64H).

Conflicts of interest

There are no conflicts to declare.

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