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Ruthenium-Catalyzed *ortho*-Alkenylation of Phenylphosphine Oxides through Regio- and Stereoselective Alkyne Insertion into C−H Bonds

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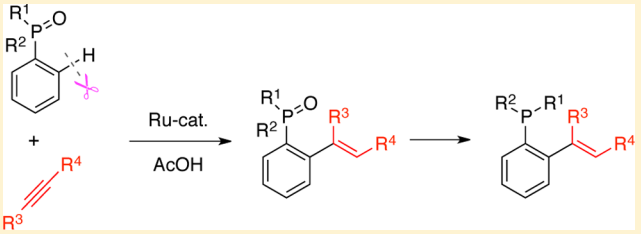
Supporting Information

ABSTRACT: Direct *ortho*-substitution took place efficiently upon treatment of tri-, di-, and monoarylphosphine oxides with internal alkynes in the presence of a ruthenium catalyst to produce (*o*-alkenylphenyl)phosphine oxides regio- and stereoselectively. Chemoselective reduction of a product gave the corresponding (*o*-alkenylphenyl)phosphine, which may be useful as a ligand for transition metals.

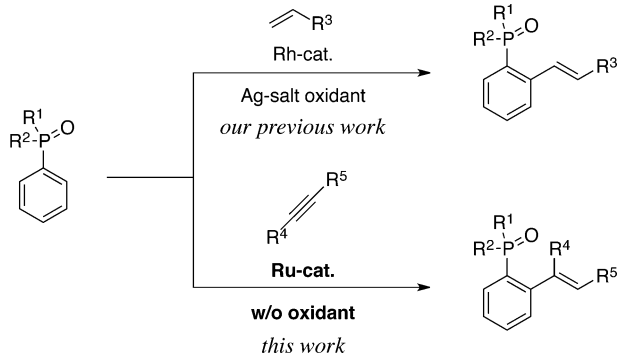


INTRODUCTION

Well-designed arylphosphine oxides ($Ar_nR_{3-n}P{=}O$) have attracted considerable attention in organic materials field due to their wide bandgaps and application as host materials in phosphorescent organic light-emitting diodes.[1] They have also been utilized as potential antitumor agents[2] as well as organocatalysts.[3] Furthermore, needless to say, phosphine oxides have been recognized as important intermediates in the preparation of the corresponding phosphine ligands.[4] Therefore, simple methods for their precious synthesis and modification have been continuously needed to be developed in these wide fields.

Meanwhile, the transition-metal-catalyzed *ortho* C−H bond functionalization of aromatic substrates possessing a directing group has been significantly developed in recent years as atom- and step-economical tools in precise organic synthesis.[5] As directing groups, carbonyl, hydroxy, imino, amide, and pyridyl groups have been widely employed to realize regioselective substitution on arenes. Recently, the palladium-,[5h,m,r,s,w,x] rhodium-,[5c,f,g,i,o,q] and ruthenium-catalyzed[5a,b] *ortho*-alkenylation of aromatic substrates possessing such common directing groups has been explosively developed. Against the recent trend, we have explored new directing groups and found that the P═O function of phenylphosphine oxides can exhibit an effective function to allow the *ortho*-alkenylation upon treatment of them with alkenes in the presence of a silver salt as oxidant under rhodium catalysis (Scheme 1).[6] This is a rare example of *ortho*-fuctionalization with the aid of P═O groups,[7] whose coordination abilities toward a transition-metal center have been presumed to be relatively weak. During our further studies on the utilization of this uncommon directing group, we succeeded in finding that a wide range of tri-, di-, and monoarylphosphine oxides efficiently undergo *ortho*-alkenylation through insertion of alkynes under ruthenium catalysis. Such a ruthenium-catalyzed reaction is attractive because of its lower catalyst cost relative to Rh.[8] Furthermore, the present reaction appears to be more environmentally benign because no oxidant such as stoichiometric silver or copper salts is needed. Under the ruthenium catalysis, a similar *ortho*-alkylation could also be achieved by using an alkene in place of alkynes.[9] The results obtained with respect to these reactions are described herein.

Scheme 1. Catalytic *ortho*-Alkenylation of Phenylphosphine Oxides



RESULTS AND DISCUSSION

In an initial attempt, triphenylphosphine oxide (**1a**) (0.5 mmol) was treated with diphenylacetylene (**2a**) (0.25 mmol) in the presence of $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), and 1-$AdCO_2H$ (Ad = adamantyl) (1 mmol) in dioxane at 100 °C for 3 h. As a result, *ortho*-alkenylated product **3aa** was obtained in 74% yield (Table 1, entry 1). In this case, formation of multiply alkenylated products was also detected. To our delight, **3aa** was obtained quantitatively by using an excess amount of **1a** (entry 2). It was confirmed that the

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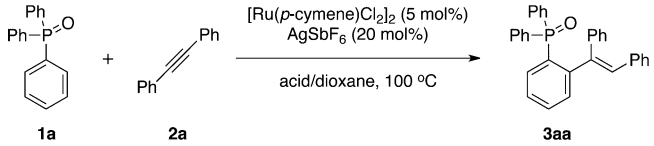
Table 1. Reaction of Triphenylphosphine Oxide (1a) with Diphenylacetylene (2a)[a]



1a 2a 3aa

entry	acid	yield of 3aa (%)[b]
1[c]	1-AdCO$_2$H	74
2	1-AdCO$_2$H	>99 (82)
3[d]	1-AdCO$_2$H	0
4[e]	1-AdCO$_2$H	0
5	AcOH	97 (86)
6	PivOH	>99
7	2,6-Me$_2$C$_6$H$_3$CO$_2$H	95

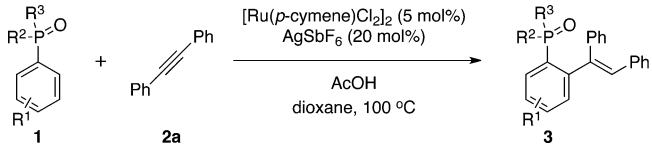
[a]Reaction conditions: **1a** (1.25 mmol), **2a** (0.25 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (0.013 mmol), AgSbF$_6$ (0.05 mmol), acid (1 mmol) in dioxane (3 mL) under N$_2$ at 100 °C for 3 h. [b]GC yield based on the amount of **2a** used. Value in parentheses indicates yield after purification. [c]With **1a** (0.5 mmol). [d]Without [Ru(*p*-cymene)Cl$_2$]$_2$. [e]Without AgSbF$_6$.

reaction did not proceed at all without [Ru(*p*-cymene)Cl$_2$]$_2$ (entry 3) or AgSbF$_6$ (entry 4). Other acids such as AcOH, PivOH, and 2,6-dimethylbenzoic acid were found to be comparably effective as 1-AdCO$_2$H (entries 5–7). Therefore, we decided to use the cheapest acid, AcOH, in further experiments.

The reactions of various arylphosphine oxides **1b–n** with **2a** were next examined under conditions using AcOH. A series of tris(*p*-substituted phenyl)phosphine oxides **1b–f** underwent alkenylation to produce **3ba–3fa** in good yields (Table 2, entries 1–5). Although the reaction of **1f** was relatively sluggish, the corresponding product **3fa** was obtained in 80% yield by extending the reaction time to 24 h under refluxing conditions (entry 5). While tris(*m*-tolyl)phosphine oxide (**1g**) underwent the reaction smoothly, the reaction of *m*-chlorinated substrate **1h** required 18 h to be completed (entries 6 and 7). Even sterically hindered tris(*o*-tolyl)phosphine oxide (**1i**) coupled with **2a** efficiently to produce **3ia** in 77% yield (entry 8). Similarly to triarylphosphine oxides, alkyl(diphenyl)-phosphine oxides **1j,k** and dialkyl(phenyl)phosphine oxides **1l,m** also underwent *ortho*-alkenylation (entries 9–12). Note that the oxide of CyJohnPhos (**1n**) could be employed as the substrate to produce **3na** in an excellent yield (entry 13). Only in the last case, the product was formed as an *E*/*Z* mixture.

The reactions of various internal alkynes **2b–j** with **1a** were also examined. Bis(*p*-substituted phenyl)acetylenes underwent the coupling with **1a** to give **3ab–3ae** in 90–98% yields (Table 3, entries 1–4). The reaction of di(2-thienyl)acetylene (**2f**) took place under similar conditions, albeit with low efficiency (entry 5). It would be possible that some interaction between the thienyl moiety and Ru retarded the reaction. Unsymmetrical alkyl(phenyl)acetylenes **2g–i** and phenyl-(trimethylsilyl)acetylene (**2j**) could also be used as alkenyl sources to afford **3ag–3aj** stereo- and regioselectively (entries 6–9). Other isomers were not detected at all. The reaction of **2j** proceeded involving desilylation to form **3aj** as a single major product (entry 9). In contrast to internal alkynes, the reactions with terminal alkynes were found to be inefficient. Under similar conditions, the reaction of **1a** with (triisopropylsilyl)-acetylene gave only a trace amount of alkenylated product. In

Table 2. Reaction of Arylphosphine Oxides 1 with 2a[a]



1 2a 3

entry	1	time (h)	product, % yield[b]
1	**1b**: R = Me	3	**3ba**: R = Me, 85
2	**1c**: R = OMe	3	**3ca**: R = OMe, 92
3	**1d**: R = Cl	3	**3da**: R = Cl, 85
4	**1e**: R = F	3	**3ea**: R = F, 83
5[c]	**1f**: R = CF$_3$	24	**3fa**: R = CF$_3$, 80
6	**1g**: R = Me	3	**3ga**: R = Me, 88
7	**1h**: R = Cl	18	**3ha**: R = Cl, 78
8	**1i**	10	**3ia**, 77
9	**1j**: R = Me	18	**3ja**: R = Me, 74
10	**1k**: R = Cy	18	**3ka**: R = Cy, 91
11	**1l**: R = Cy	18	**3la**: R = Cy, 82
12	**1m**: R = *t*-Bu	40	**3ma**: R = *t*-Bu, 44
13	**1n**	36	**3na**, 98[d]

[a]Reaction conditions: **1** (1.25 mmol), **2a** (0.25 mmol), [Ru(*p*-cymene)Cl$_2$]$_2$ (0.013 mmol), AgSbF$_6$ (0.05 mmol), AcOH (1 mmol) in dioxane (3 mL) at 100 °C under N$_2$. [b]Isolated yield. [c]In refluxing dioxane (bath temperature: 120 °C). [d]*E*/*Z* = 84:16.

the case using phenylacetylene, any coupling products could not be detected at all. In both cases, significant amounts of substrates remained unconsumed.

Chemoselective reduction methods from phosphine oxides to the corresponding phosphines have been established.[10] As a

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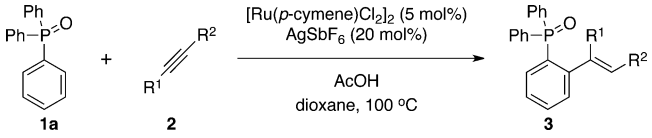
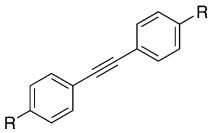
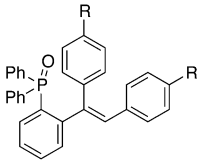
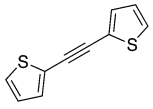
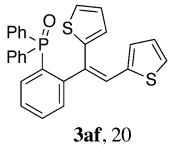
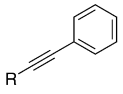
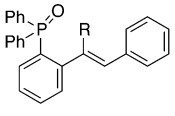
Table 3. Reaction of 1a with Alkynes 2[a]

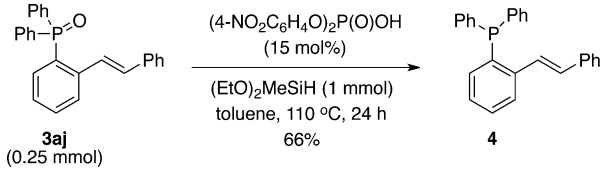


entry	2	time (h)	product, % yield[b]
			
1	**2b**: R = Me	3	**3ab**: R = Me, 91
2	**2c**: R = *t*-Bu	3	**3ac**: R = *t*-Bu, 90
3	**2d**: R = Cl	3	**3ad**: R = Cl, 92
4	**2e**: R = CF_3	5	**3ae**: R = CF_3, 98
			
5	**2f**	6	**3af**, 20
			
6	**2g**: R = Me	3	**3ag**: R = Me, 81
7	**2h**: R = Bu	3	**3ah**: R = Bu, 86
8	**2i**: R = *cyclo*-Pr	3	**3ai**: R = *cyclo*-Pr, 58
9	**2j**: R = TMS	18	**3aj**: R = H, 50

[a]Reaction conditions: **1a** (1.25 mmol), **2** (0.25 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (0.013 mmol), $AgSbF_6$ (0.05 mmol), AcOH (1 mmol) in dioxane (3 mL) at 100 °C under N_2. [b]Isolated yield.

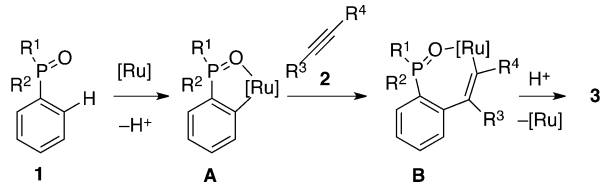
preliminary attempt, we examined the reduction of one of our alkenylated product **3aj** by the Beller's procedure using (4-$NO_2C_6H_4O)_2P(O)OH/(EtO)_2MeSiH$.[10a] As a result, we succeeded in obtaining diphenyl(*o*-styrylphenyl)phosphine (**4**), as shown in Scheme 2. It is well-known that (*o*-substituted phenyl)phosphines are useful as ligands for transition-metals.[11] The reduction of more sterically hindered **3aa** also proceeded to some extent under similar conditions. However, considerable contamination of an isomer of product was observed by GC–MS.

Scheme 2. Reduction of 3aj



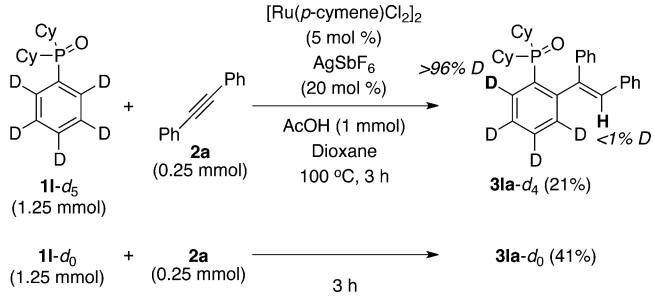
The *ortho*-alkenylation of **1** seems to proceed via *ortho*-metalation, alkyne insertion, and protonolysis, as shown in Scheme 3. The added acid may promote the last step.[12] The *ortho*-metalation on parent triphenylphosphine itself has been reported to produce a four-membered ruthenacycle.[13] Unfortunately, its treatment with **2a** under our standard conditions did not give any *ortho*-alkenylated product at all.

Scheme 3. Possible Pathway for the *ortho*-Alkenylation



For providing further mechanistic information, the reaction of deuterated dicyclohexyl(phenyl)phosphine oxide (**1l**-d_5) with **2a** was conducted under standard conditions (Scheme 4). In the early stage (3 h), deuterium incorporation at the alkenyl position of the product was not detected at all by ^1H NMR. This result appears to exclude the possibility of a reaction route involving initial oxidative addition of an *ortho* C–H bond, which should result in deuterium incorporation at the position. During the reaction, no significant D–H exchange at the *ortho*-positions of recovered **1l**-d_5 as well as at the 6-position of product **3la**-d_4 was observed. More informative is that the reaction rate of **1l**-d_5 was considerably lower than that of **1l**-d_0. Thus, the kinetic isotope effect was determined to be 2.1. These observations suggest that the *ortho* C–H bond cleavage step to form intermediate **A** is likely irreversible and involved as the rate-determining step.

Scheme 4. Parallel Reactions of 1l-d_5 and 1l-d_0 with 2a

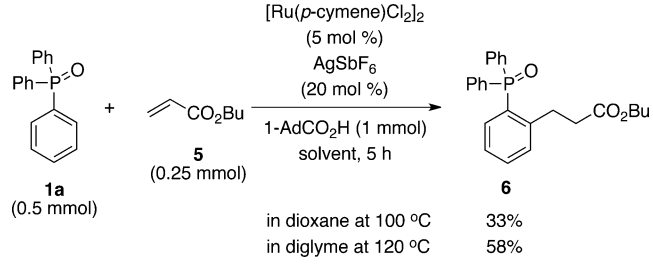


Under similar conditions, *ortho*-alkylation of phosphine oxide **1a** using butyl acrylate (**5**) in place of alkynes was finally examined. Treatment of **1a** (0.5 mmol) with **5** (0.25 mmol) in the presence of [Ru(*p*-cymene)Cl_2]$_2$ (5 mol %), $AgSbF_6$ (20 mol %), and 1-$AdCO_2H$ (1 mmol) in dioxane at 100 °C for 5 h gave alkylated product **6** in 33% yield (Scheme 5). At 120 °C in diglyme, the yield of **6** was improved to 58%.

CONCLUSIONS

We have demonstrated that various arylphosphine oxides undergo *ortho*-alkenylation on treatment with alkynes under ruthenium catalysis through P=O group-directed C–H bond

Scheme 5. *ortho*-Alkylation of 1a with Butyl Acrylate (6)



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cleavage. The relevant alkylation with an acrylate ester has also been achieved. Work is underway toward further utilization of related phosphorus-containing groups.

EXPERIMENTAL SECTION

General. H and ^{13}C NMR spectra were recorded at 400 or 600 and 100 or 150 MHz, respectively, for $CDCl_3$ solutions. HRMS data were obtained by EI using a double focusing mass spectrometer, unless noted. GC analysis was carried out using a silicon OV-17 column (i.d. 2.6 mm × 1.5 m). GC−MS analysis was carried out using a CBP-1 capillary column (i.d. 0.25 mm × 25 m). The structures of all products listed below were unambiguously determined by ^1H, ^{13}C, and ^{31}P NMR with the aid of NOE, COSY, HSQC, and HMBC experiments.

Phosphine oxides **1b−n** and dicyclohexyl(d_5-phenyl)phosphine oxide (**1l**-d_5) were prepared as noted below. Diarylacetylenes **2b−f**[14] and 1-cyclopropyl-2-phenylacetylene (**2i**)[15] were prepared according to published procedures. Phosphine oxides **4a−c** were prepared as noted below. Other reagents were commercially available.

Preparation of Phosphine Oxides 1. Synthesis of **1b** is representative. To a solution of tris(*p*-tolyl)phosphine (5 mmol, 1.52 g) in THF (5 mL) was dropped slowly H_2O_2 (30% aqueous solution, 3 equiv), and the mixture was stirred at room temperature. The exothermic reaction terminated within a few minutes. After the consumption of phosphine was checked by TLC, the reaction mixture was quenched by saturated $NaHCO_3$ (10 mL) and saturated $Na_2S_2O_3$ (20 mL) and additionally stirred for a few minutes. Then, the reaction mixture was extracted by ethyl acetate (20 mL, three times) and dried over Na_2SO_4. Volatiles were removed in vacuo to afford tris(*p*-tolyl)phosphine oxide (**1b**) quantitatively without further purification.

General Procedure for the Reaction of Phosphine Oxides 1 with Alkynes 2. To a 20 mL two-necked flask with a reflux condenser, a balloon filled with N_2, and a rubber septum were added phosphine oxide **1** (1.25 mmol), alkyne **2** (0.25 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.013 mmol, 7.7 mg), $AgSbF_6$ (0.05 mmol, 17 mg), AcOH (1 mmol, 60 mg), 1-methylnaphthalene (ca. 40 mg) as internal standard, and dioxane (3 mL). Then, the resulting mixture was stirred under nitrogen at 100 °C for 3−40 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with water (100 mL, three times) and dried over Na_2SO_4. After evaporation of the solvents under vacuum, product **3** was isolated by column chromatography on silica gel using hexane/ethyl acetate (1:1, v/v) as eluent.

Procedure for Reduction of Phosphine Oxide 3aj.[10a] To a 20 mL two-necked flask with a reflux condenser, a balloon filled with N_2, and a rubber septum were added phosphine oxide **3aj** (0.25 mmol, 95 mg), bis(4-nitrophenyl)phosphate (0.038 mmol, 13 mg), diethoxymethylsilane (1 mmol, 134 mg), 1-methylnaphthalene (ca. 30 mg) as internal standard, and toluene (2 mL). After the solution stirred under nitrogen at 110 °C for 24 h, the reaction mixture was cooled to 0 °C, and 3 N methanolic KOH (5 mL) was added slowly. Then, the reaction mixture was stirred at room temperature for 3 h. The reaction mixture was extracted with ethyl acetate (100 mL). The organic layer was washed with 1 N HCl (5 mL) and saturated $NaHCO_3$ (5 mL), and dried over Na_2SO_4. Concentration in vacuo followed by column chromatography on silica gel using hexane/ethyl acetate (20:1, v/v) as eluent gave phosphine **4** (60 mg, 0.16 mmol) in 66% yield.

Procedure for Reaction of Deuterated Substrate 1l-d_5. To a 20 mL two-necked flask were added dicyclohexyl(d_5-phenyl)-phosphine oxide (**1l**-d_5) (1.25 mmol), diphenylacetylene (**2a**) (0.25 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (0.0125 mmol), $AgSbF_6$ (0.05 mmol), AcOH (1 mmol), 1-methylnaphthalene (ca. 30 mg) as internal standard, and dioxane (3 mL). The resulting mixture was stirred under N_2 at 100 °C for 5 h. After cooling, the reaction mixture was extracted with ethyl acetate (100 mL), washed with water (100 mL, three times), and dried over Na_2SO_4. Produced **3la**-d_4 and recovered **1l**-d_5 were isolated by column chromatography on silica gel using ethyl acetate as eluant. Recovered **1l**-d_5 (305 mg, 1.03 mmol); ^1H NMR (400 MHz, $CDCl_3$) δ 1.09−1.35 (m, 10H), 1.60−1.82 (m, 8H), 1.99−2.06 (m, 4H), 7.67 (d, J = 9.7 Hz, 0.06H). Produced **3la**-d_4 (30 mg, 25%); ^1H NMR (400 MHz, $CDCl_3$) δ 0.93−1.35 (m, 10H), 1.55−1.84 (m, 12H), 6.57 (s, 1H), 7.15−7.26 (m, 10H), 8.06 (d, J = 11.4 Hz, 0.04H).

(*E*)-[2-(1,2-Diphenylethenyl)phenyl]diphenylphosphine Oxide (3aa). Mp 68−69 °C (colorless powder), 98 mg (86%); ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, J = 6.0 Hz, 2H), 6.83 (s, 1H), 6.99−7.25 (m, 10H), 7.32−7.44 (m, 8H), 7.73 (dd, J = 7.3, 11.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.3 (d, J = 12.4 Hz), 126.6, 127.1, 127.5, 127.8, 128.2 (d, J = 12.5 Hz), 129.7, 130.6, 131.2 (d, J = 2.9 Hz), 131.3 (d, J = 2.8 Hz), 131.6 (d, J = 9.5 Hz), 131.9 (d, J = 102.5 Hz), 132.0 (d, J = 9.6 Hz), 133.9 (d, J = 104.5 Hz), 134.1, 134.6 (d, J = 12.5 Hz), 136.8, 140.1 (d, J = 3.9 Hz), 140.2, 149.6 (d, J = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.97; HRMS m/z calcd for $C_{32}H_{25}OP$ (M^+) 456.1643, found 456.1646.

(*E*)-[2-(1,2-Diphenylethenyl)-4-methylphenyl]bis(4-methylphenyl)phosphine Oxide (3ba). Mp 160−161 °C (colorless powder), 105 mg (85%); ^1H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 2.32 (s, 6H), 6.72−6.75 (m, 3H), 6.97−7.04 (m, 5H), 7.07−7.14 (m, 9H), 7.28 (dd, J = 7.8, 13.7 Hz, 1H), 7.59 (dd, J = 8.2, 11.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.4, 126.5, 126.9, 127.1 (d, J = 13.4 Hz), 127.4, 127.8, 128.9 (d, J = 12.5 Hz), 129.2 (d, J = 104.5 Hz), 129.6, 130.5, 131.1 (d, J = 107.5 Hz), 131.6 (d, J = 9.6 Hz), 132.5 (d, J = 9.5 Hz), 133.7, 134.7 (d, J = 12.4 Hz), 137.0, 140.1 (d, J = 3.8 Hz), 140.3, 141.3 (d, J = 2.9 Hz), 141.5 (d, J = 2.9 Hz), 149.3 (d, J = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.83; HRMS m/z calcd for $C_{35}H_{31}OP$ (M^+) 498.2113, found 498.2112.

(*E*)-[2-(1,2-Diphenylethenyl)-4-methoxyphenyl]bis(4-methoxyphenyl)phosphine Oxide (3ca). Mp 153−154 °C (colorless powder), 126 mg (92%); ^1H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.77 (s, 6H), 6.68−6.69 (m, 1H), 6.73−6.79 (m, 4H), 6.84 (dd, J = 2.3, 8.7 Hz, 4H), 6.99−7.13 (m, 8H), 7.32 (dd, J = 8.5, 13.5 Hz, 1H), 7.61 (d, J = 8.7, 11.2 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.16, 55.20, 111.5 (d, J = 13.4 Hz), 113.7 (d, J = 13.4 Hz), 117.6 (d, J = 10.5 Hz), 124.3 (d, J = 108.3 Hz), 125.9 (d, J = 111.2 Hz), 126.6, 127.1, 127.4, 127.8, 129.7, 130.5, 133.3 (d, J = 10.5 Hz), 133.7, 136.5 (d, J = 14.3 Hz), 136.9, 139.8 (d, J = 3.8 Hz), 140.1, 151.3 (d, J = 8.6 Hz), 161.5 (d, J = 2.8 Hz), 161.7 (d, J = 2.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.12; HRMS m/z calcd for $C_{35}H_{31}O_4P$ (M^+) 546.1960, found 546.1954.

(*E*)-[4-Chloro-2-(1,2-diphenylethenyl)phenyl]bis(4-chlorophenyl)phosphine Oxide (3da). Mp 73−74 °C (colorless powder), 119 mg (85%); ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 6.76−6.78 (m, 2H), 7.03−7.29 (m, 11H), 7.33 (dd, J = 2.3, 8.3 Hz, 4H), 7.59 (dd, J = 8.3, 11.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.8 (d, J = 13.4 Hz), 127.2, 127.6, 127.7, 128.1, 128.8 (d, J = 12.5 Hz), 129.53, 129.54 (d, J = 105.4 Hz), 130.4, 131.6 (d, J = 106.4 Hz), 132.2 (d, J = 10.5 Hz), 132.8 (d, J = 10.6 Hz), 134.7, 135.6 (d, J = 14.4 Hz), 136.1, 138.2 (d, J = 4.8 Hz), 138.3 (d, J = 3.8 Hz), 138.7 (d, J = 3.8 Hz), 139.0, 151.3 (d, J = 8.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.21; HRMS m/z calcd for $C_{32}H_{22}Cl_3OP$ (M^+) 558.0474, found 558.0477.

(*E*)-[2-(1,2-Diphenylethenyl)-4-fluorophenyl]bis(4-fluorophenyl)phosphine Oxide (3ea). Mp 67−68 °C (colorless powder), 106 mg (83%); ^1H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, J = 6.8 Hz, 2H), 6.81 (s, 1H), 6.88−7.17 (m, 14H), 7.34 (ddd, J = 5.9, 8.6, 14.5 Hz, 1H), 7.68 (ddd, J = 5.9, 7.7, 11.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.8 (dd, J = 13.4, 21.0 Hz), 115.8 (dd, J = 13.4, 21.0 Hz), 119.3 (dd, J = 10.5, 21.0 Hz), 127.2, 127.5 (dd, J = 3.8, 106.8 Hz), 127.6, 127.7, 128.1, 129.5 (dd, J = 3.8, 108.7 Hz), 129.6, 130.4, 133.9 (dd, J = 8.6, 10.5 Hz), 134.6, 136.2, 136.9 (dd, J = 8.6, 14.3 Hz), 138.9 (dd, J = 1.9, 3.8 Hz), 139.3, 152.8 (dd, J = 8.6, 8.6 Hz), 164.4 (dd, J = 2.9, 254.6 Hz), 164.7 (dd, J = 2.9, 253.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.88; HRMS m/z calcd for $C_{32}H_{22}F_3OP$ (M^+) 510.1360, found 510.1358.

(*E*)-[2-(1,2-Diphenylethenyl)-4-(trifluoromethyl)phenyl]bis-[4-(trifluoromethyl)phenyl]phosphine Oxide (3fa). Mp 70−71 °C (pale yellow powder), 131 mg (80%); ^1H NMR (400 MHz, $CDCl_3$) δ 6.71−6.74 (m, 3H), 7.03−7.19 (m, 8H), 7.43−7.58 (m, 3H), 7.63 (dd, J = 2.3, 8.3 Hz, 4H), 7.82 (dd, J = 8.3, 11.5 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.2 (q, J = 273.1 Hz), 123.4 (q, J = 273.1 Hz), 123.5 (dq, J = 2.9, 13.4 Hz), 125.5 (dq, J = 2.8, 11.5 Hz),

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127.6, 127.8, 128.1, 128.3, 129.1 (dq, J = 2.9, 10.6 Hz), 129.5, 130.4, 131.9 (d, J = 9.6 Hz), 133.8 (dq, J = 2.9, 32.6 Hz), 133.9 (dq, J = 2.9, 33.6 Hz), 134.9 (d, J = 13.4 Hz), 135.3 (d, J = 102.5 Hz), 135.4, 136.8 (d, J = 101.6 Hz), 137.3 (d, J = 1.9 Hz), 138.6, 138.8 (d, J = 2.8 Hz), 150.8 (d, J = 7.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.45; HRMS m/z calcd for $C_{35}H_{22}F_9OP$ (M^+) 660.1265, found 660.1259.

(*E*)-[2-(1,2-Diphenylethenyl)-5-methylphenyl]bis(3-methylphenyl)phosphine Oxide (3ga). Mp 203−204 °C (colorless powder), 110 mg (88%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 6H), 2.25 (s, 3H), 6.68 (dd, J = 2.2, 7.3 Hz, 2H), 6.91 (s, 1H), 6.99−7.14 (m, 9H), 7.18−7.27 (m, 6H), 7.49 (dd, J = 7.3, 11.8 Hz, 2H), 7.63 (d, J = 11.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.3, 126.5, 127.1, 127.4, 127.8, 128.0 (d, J = 12.4 Hz), 128.5 (d, J = 9.5 Hz), 129.8, 130.6, 131.8 (d, J = 2.9 Hz), 131.9 (d, J = 9.5 Hz), 132.0 (d, J = 2.8 Hz), 132.1 (d, J = 102.0 Hz), 132.3 (d, J = 8.5 Hz), 133.9 (d, J = 103.0 Hz), 134.1, 135.2 (d, J = 12.4 Hz), 136.2 (d, J = 12.4 Hz), 136.9, 138.1 (d, J = 11.4 Hz), 139.7 (d, J = 3.8 Hz), 140.6, 146.6 (d, J = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.81; HRMS m/z calcd for $C_{35}H_{31}OP$ (M^+) 498.2113, found 498.2115.

(*E*)-[5-Chloro-2-(1,2-diphenylethenyl)phenyl]bis(3-chlorophenyl)phosphine Oxide (3ha). Mp 73−74 °C (colorless powder), 109 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (dd, J = 1.8, 7.7 Hz, 2H), 6.89 (s, 1H), 7.03−7.17 (m, 9H), 7.28−7.34 (m, 3H), 7.40−7.44 (m, 3H), 7.57 (dd, J = 7.7, 11.3 Hz, 2H), 7.69 (d, J = 12.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.2, 127.69, 127.74, 128.1, 129.5 (d, J = 9.5 Hz), 129.6, 130.0 (d, J = 12.4 Hz), 130.5, 131.2 (d, J = 9.6 Hz), 131.97 (d, J = 2.8 Hz), 132.01 (d, J = 3.9 Hz), 132.8 (d, J = 102.0 Hz), 133.0 (d, J = 16.2 Hz), 133.9 (d, J = 8.6 Hz), 134.0 (d, J = 12.4 Hz), 134.90 (d, J = 103.0 Hz), 134.92, 135.1 (d, J = 15.3 Hz), 136.1, 138.7 (d, J = 3.8 Hz), 139.4, 148.1 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.02; HRMS m/z calcd for $C_{32}H_{22}Cl_3OP$ (M^+) 558.0474, found 558.0471.

(*E*)-[2-(1,2-Diphenylethenyl)-6-methylphenyl]bis(2-methylphenyl)phosphine Oxide (3ia). Mp 91−92 °C (pale yellow powder), 96 mg (77%); ^{1}H NMR (600 MHz, DMSO-d_6, 100 °C) δ 1.83 (s, 3H), 2.37 (s, 6H), 6.08 (s, 1H), 6.79 (dd, J = 1.5, 7.3 Hz, 2H), 6.98−7.02 (m, 3H), 7.07−7.14 (m, 6H), 7.17−7.21 (m, 3H), 7.25 (dd, J = 4.1, 7.6 Hz, 2H), 7.32 (d, J = 6.2 Hz, 2H), 7.40 (tt, J = 1.5, 7.3 Hz, 2H), 7.43 (dt, J = 1.5, 7.9 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6, 100 °C) δ 20.3 (d, J = 4.0 Hz), 22.9 (d, J = 3.9 Hz), 124.9 (d, J = 12.9 Hz), 125.7, 126.2, 126.8, 126.9, 128.2, 129.2 (d, J = 9.9 Hz), 129.3, 129.7 (d, J = 102.9 Hz), 130.0 (d, J = 9.9 Hz), 130.07, 130.11 (d, J = 3.0 Hz), 130.8 (d, J = 2.9 Hz), 131.1 (d, J = 9.9 Hz), 131.2 (d, J = 102.9 Hz), 131.4 (d, J = 12.9 Hz), 136.9, 140.0, 140.9 (d, J = 9.9 Hz), 141.9, 142.9 (d, J = 4.0 Hz), 150.5 (d, J = 6.9 Hz); ^{31}P NMR (243 MHz, DMSO-d_6) δ 34.64; HRMS m/z calcd for $C_{35}H_{31}OP$ (M^+) 498.2113, found 498.2108.

(*E*)-[2-(1,2-Diphenylethenyl)phenyl](methyl)(phenyl)-phosphine Oxide (3ja). Mp 149−150 °C (brown powder), 73 mg (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (d, J = 12.8 Hz, 3H), 6.57 (s, 1H), 6.89−6.91 (m, 2H), 6.96 (dd, J = 1.8, 8.2 Hz, 2H), 7.09−7.19 (m, 7H), 7.32 (dt, J = 2.8, 7.3 Hz, 2H), 7.38−7.45 (m, 3H), 7.54−7.59 (m, 2H), 7.96−8.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5 (d, J = 74.8 Hz), 126.9 (d, J = 11.5 Hz), 127.1, 127.5, 127.9, 128.1, 128.3 (d, J = 11.5 Hz), 129.6, 130.3, 130.5 (d, J = 10.5 Hz), 131.1 (d, J = 1.9 Hz), 131.3 (d, J = 1.9 Hz), 131.9 (d, J = 9.6 Hz), 132.6 (d, J = 90.1 Hz), 133.0 (d, J = 10.5 Hz), 135.6 (d, J = 102.5 Hz), 136.4, 139.9, 140.00, 140.04, 148.2 (d, J = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.54; HRMS m/z calcd for $C_{27}H_{23}OP$ (M^+) 394.1487, found 394.1487.

(*E*)-Cyclohexyl[2-(1,2-diphenylethenyl)phenyl](phenyl)-phosphine Oxide (3ka). Mp 71−72 °C (colorless powder), 105 mg (91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13−1.23 (m, 3H), 1.53−1.81 (m, 7H), 2.25−2.26 (m, 1H), 6.21 (s, 1H), 6.92−6.94 (m, 4H), 7.06−7.15 (m, 7H), 7.26−7.30 (m, 2H), 7.37−7.46 (m, 3H), 7.51−7.56 (m, 2H), 8.06−8.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0 (d, J = 2.9 Hz), 25.4 (d, J = 2.9 Hz), 25.8, 26.3 (d, J = 13.4 Hz), 26.4 (d, J = 14.3 Hz), 36.9 (d, J = 73.5 Hz), 126.7 (d, J = 10.5 Hz), 126.9, 127.2, 127.8, 127.9, 128.1 (d, J = 11.5 Hz), 129.6, 130.4, 130.8 (d, J = 2.8 Hz), 130.9 (d, J = 1.9 Hz), 131.09 (d, J = 90.6 Hz), 131.14 (d, J = 8.5 Hz), 131.9, 132.2 (d, J = 9.5 Hz), 132.9 (d, J = 8.6 Hz), 133.6 (d, J = 94.4 Hz), 136.7, 139.8, 141.0 (d, J = 2.9 Hz), 148.7 (d, J = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.99; HRMS m/z calcd for $C_{32}H_{31}OP$ (M^+) 462.2113, found 462.2111.

(*E*)-Dicyclohexyl[2-(1,2-diphenylethenyl)phenyl]phosphine Oxide (3la). Mp 32−33 °C (brown powder), 96 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93−1.36 (m, 10H), 1.55−1.84 (m, 12H), 6.57 (s, 1H), 7.15−7.25 (m, 10H), 7.37 (ddd, J = 1.4, 4.1, 7.3 Hz, 1H), 7.46 (tt, J = 1.4, 7.8 Hz, 1H), 7.51 (tt, J = 1.4, 7.3 Hz, 1H), 8.06 (ddd, J = 1.4, 7.8, 11.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6 (d, J = 1.9 Hz), 26.1 (d, J = 3.8 Hz), 26.2 (d, J = 3.8 Hz), 26.3 (d, J = 12.5 Hz), 26.4 (d, J = 12.5 Hz), 37.4 (d, J = 65.1 Hz), 127.1, 127.2 (d, J = 9.6 Hz), 127.8, 128.2, 128.29, 128.33, 130.4, 130.5 (d, J = 78.6 Hz), 130.6 (d, J = 2.9 Hz), 130.8, 132.7 (d, J = 9.6 Hz), 134.6 (d, J = 6.7 Hz), 136.9, 139.0, 142.8 (d, J = 2.9 Hz), 145.5 (d, J = 8.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.28; HRMS m/z calcd for $C_{32}H_{37}OP$ (M^+) 468.2582, found 468.2590.

(*E*)-Di-*tert*-butyl[2-(1,2-diphenylethenyl)phenyl]phosphine Oxide (3ma). Mp 129−130 °C (brown powder), 46 mg (44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 13.1 Hz, 18H), 6.43 (s, 1H), 7.06−7.16 (m, 8H), 7.30−7.37 (m, 3H), 7.49−7.60 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 37.2 (d, J = 59.1 Hz), 125.2 (d, J = 11.4 Hz), 126.2, 126.3, 127.0, 127.8, 127.9, 129.0 (d, J = 76.3 Hz), 129.2, 130.2 (d, J = 2.9 Hz), 130.7, 131.6 (d, J = 11.4 Hz), 133.4 (d, J = 8.6 Hz), 137.8, 140.3, 143.2 (d, J = 2.9 Hz), 150.5 (d, J = 3.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 53.48; HRMS m/z calcd for $C_{28}H_{33}OP$ (M^+) 416.2269, found 416.2266.

(*E*)-Dicyclohexyl[3-(1,2-diphenylethenyl)-[1,1′-biphenyl]-2-yl]phosphine Oxide (3na). (*E*:*Z* = 84:16) 133 mg (98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74−1.62 (m, 22H), 6.47 (s, 0.84H, *E*), 6.74 (s, 0.16H, *Z*), 7.06−7.19 (m, 7H), 7.22−7.30 (m, 4H), 7.34−7.47 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$, 40 °C) δ 25.7 (d, J = 1.9 Hz), 26.5 (d, J = 2.9 Hz), 26.6 (d, J = 3.8 Hz), 26.7 (d, J = 13.4 Hz, overlapped), 39.8 (d, J = 66.2 Hz), 126.2, 126.6, 127.4, 127.5 (d, J = 3.8 Hz), 127.7, 127.8, 129.1, 129.3 (d, J = 2.8 Hz), 129.5, 129.7 (d, J = 74.7 Hz), 129.8, 130.9 (d, J = 9.6 Hz), 131.2, 132.5 (d, J = 8.6 Hz), 137.8, 138.0, 140.7, 143.3 (d, J = 2.9 Hz), 144.6 (d, J = 2.9 Hz), 145.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.86 (*Z*), 51.40 (*E*); HRMS m/z calcd for $C_{38}H_{41}OP$ (M^+) 544.2895, found 544.2897.

(*E*)-{2-[1,2-Bis(4-methylphenyl)ethenyl]phenyl}-diphenylphosphine Oxide (3ab). Mp 68−69 °C (colorless powder), 110 mg, 91%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.23 (s, 3H), 2.26 (s, 3H), 6.63 (d, J = 7.8 Hz, 2H), 6.80 (s, 1H), 6.83 (d, J = 7.8 Hz, 2H), 6.89−6.94 (m, 4H), 7.14−7.17 (m, 1H), 7.19−7.23 (m, 1H), 7.31−7.44 (m, 8H), 7.69−7.75 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2 (overlapped), 126.2 (d, J = 13.4 Hz), 128.18 (d, J = 11.5 Hz), 128.19, 128.6, 129.6, 130.4, 131.1 (d, J = 1.9 Hz), 131.2 (d, J = 2.9 Hz), 131.6 (d, J = 9.6 Hz), 131.8 (d, J = 101.6 Hz), 132.0 (d, J = 9.5 Hz), 133.8, 133.99 (d, J = 103.5 Hz), 134.04, 134.7 (d, J = 12.5 Hz), 136.3, 136.7, 137.5, 139.2 (d, J = 3.8 Hz), 150.0 (d, J = 7.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.83; HRMS m/z calcd for $C_{34}H_{29}OP$ (M^+) 484.1956, found 484.1960.

(*E*)-[2-{1,2-Bis[4-(*tert*-butyl)phenyl] ethenyl}phenyl]-diphenylphosphine Oxide (3ac). Mp 69−70 °C (colorless powder), 128 mg (90%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 9H), 1.28 (s, 9H), 6.69 (d, J = 8.3 Hz, 2H), 6.75 (s, 1H), 6.99 (d, J = 8.7 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 8.7 Hz, 2H), 7.17−7.23 (m, 2H), 7.32 (dt, J = 2.8, 7.8 Hz, 4H), 7.37−7.42 (m, 4H), 7.68−7.73 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.2, 31.3, 34.4 (overlapped), 124.4, 124.7, 126.1 (d, J = 12.5 Hz), 128.1 (d, J = 11.5 Hz), 129.3, 129.8, 131.1 (d, J = 1.9 Hz), 131.2 (d, J = 2.9 Hz), 131.6 (d, J = 103.5 Hz), 131.7 (d, J = 8.7 Hz), 132.0 (d, J = 8.6 Hz), 133.86, 133.92, 134.0 (d, J = 103.5 Hz), 134.6 (d, J = 12.4 Hz), 137.2, 138.9 (d, J = 3.8 Hz), 149.6, 149.8, 150.1 (d, J = 7.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.93; HRMS m/z calcd for $C_{40}H_{41}OP$ (M^+) 568.2895, found 568.2898.

(*E*)-{2-[1,2-Bis(4-chlorophenyl)ethenyl]phenyl}-diphenylphosphine Oxide (3ad). Mp 74−75 °C (colorless powder), 121 mg (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (s, 1H), 6.70 (d, J = 8.2 Hz, 2H), 7.01−7.07 (m, 6H), 7.17 (dd, J = 4.1,

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7.3 Hz, 1H), 7.23−7.38 (m, 6H), 7.41−7.47 (m, 3H), 7.64−7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.7 (d, J = 12.4 Hz), 127.9, 128.2, 128.3 (d, J = 11.5 Hz), 130.9, 131.4 (d, J = 2.9 Hz), 131.5 (d, J = 1.9 Hz), 131.6 (d, J = 9.6 Hz), 132.0 (d, J = 8.6 Hz), 132.1, 132.52, 132.54 (d, J = 2.9 Hz), 132.6 (d, J = 108.3 Hz), 133.2, 133.7 (d, J = 104.5 Hz), 134.6 (d, J = 12.4 Hz), 135.1, 138.2, 140.0 (d, J = 3.8 Hz), 148.8 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.31; HRMS m/z calcd for $C_{32}H_{23}Cl_2OP$ (M^+) 524.0864, found 524.0859.

(*E*)-[2-{1,2-Bis[4-(trifluoromethyl)phenyl]ethenyl}phenyl]-diphenylphosphine Oxide (3ae). Mp 79−80 °C (colorless powder), 146 mg (98%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (s, 1H), 6.91 (d, J = 8.3 Hz, 2H), 7.19−7.39 (m, 13H), 7.44−7.48 (m, 3H), 7.62−7.67 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.1 (q, J = 272.2 Hz), 124.2 (q, J = 272.2 Hz), 124.8 (q, J = 3.8 Hz), 124.9 (q, J = 3.8 Hz), 127.0 (d, J = 12.4 Hz), 128.4 (d, J = 11.5 Hz), 128.8 (q, J = 32.6 Hz), 129.3 (q, J = 32.6 Hz), 129.7, 131.0, 131.58 (d, J = 9.6 Hz), 131.62 (d, J = 2.8 Hz), 131.7 (d, J = 2.9 Hz), 132.0 (d, J = 8.6 Hz), 132.1 (d, J = 101.6 Hz), 132.8, 133.5 (d, J = 104.5 Hz), 134.5 (d, J = 12.5 Hz), 140.1 (d, J = 1.9 Hz), 141.5 (d, J = 3.8 Hz), 143.0, 148.1 (d, J = 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.36; HRMS m/z calcd for $C_{34}H_{23}F_6OP$ (M^+) 592.1391, found 592.1395.

(*Z*)-{2-[1,2-Di(2-thienyl)ethenyl]phenyl}diphenylphosphine Oxide (3af). Mp 188−189 °C (pale yellow powder), 24 mg (20%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (dd, J = 3.7, 5.0 Hz, 1H), 6.88 (dd, J = 0.9, 3.7 Hz, 1H), 6.92−6.95 (m, 2H), 7.05 (d, J = 5.0 Hz, 1H), 7.21−7.25 (m, 1H), 7.31−7.47 (m, 11H), 7.71−7.77 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.0, 126.6 (d, J = 12.5 Hz), 126.8 (d, J = 13.4 Hz), 127.2, 128.3 (d, J = 12.4 Hz), 129.4, 130.0 (d, J = 3.9 Hz), 130.8, 130.9, 131.26, 131.27 (d, J = 102.6 Hz), 131.36 (d, J = 13.4 Hz), 131.44 (d, J = 3.9 Hz), 131.48 (d, J = 3.8 Hz), 131.51, 133.5 (d, J = 104.5 Hz), 134.9 (d, J = 13.4 Hz), 139.7, 140.5, 148.0 (d, J = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.36; HRMS m/z calcd for $C_{28}H_{21}OPS_2$ (M^+) 468.0771, found 468.0775.

(*E*)-Diphenyl[2-(1-phenylprop-1-en-2-yl)phenyl]phosphine Oxide (3ag). Oil, 80 mg (81%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (d, J = 1.4 Hz, 3H), 6.38 (s, 1H), 6.99 (d, J = 7.3 Hz, 2H), 7.15 (t, J = 7.3 Hz, 1H), 7.22−7.53 (m, 12H), 7.69−7.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 126.0 (d, J = 13.4 Hz), 126.3, 127.7, 128.2 (d, J = 12.4 Hz), 129.0, 129.7 (d, J = 9.6 Hz), 131.1 (d, J = 104.5 Hz), 131.2 (d, J = 1.9 Hz), 131.69 (d, J = 8.7 Hz), 131.72 (d, J = 2.9 Hz), 132.7, 133.7 (d, J = 104.5 Hz), 134.1 (d, J = 12.5 Hz), 136.8 (d, J = 3.8 Hz), 137.3, 151.3 (d, J = 8.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.77; HRMS m/z calcd for $C_{27}H_{23}OP$ (M^+) 394.1487, found 394.1485.

(*E*)-Diphenyl[2-(1-phenylhex-1-en-2-yl)phenyl]phosphine Oxide (3ah). Mp 104−105 °C (pale yellow powder), 94 mg (86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (t, J = 6.9 Hz, 3H), 1.13−1.30 (m, 4H), 2.51 (t, J = 7.3 Hz, 2H), 6.02 (s, 1H), 6.93 (d, J = 7.3 Hz, 2H), 7.13−7.34 (m, 6H), 7.37−7.41 (m, 4H), 7.45−7.53 (m, 3H), 7.69 (dd, J = 7.3, 11.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 22.8, 30.5, 32.8, 126.0 (d, J = 12.4 Hz), 126.2, 127.7, 128.2 (d, J = 11.5 Hz), 128.7, 130.6 (d, J = 103.5 Hz), 131.0 (d, J = 9.5 Hz), 131.27, 131.34 (d, J = 2.8 Hz), 131.4 (d, J = 2.9 Hz), 131.9 (d, J = 8.6 Hz), 133.8 (d, J = 103.5 Hz), 134.0 (d, J = 12.5 Hz), 137.4, 143.2 (d, J = 3.8 Hz), 149.9 (d, J = 7.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.42; HRMS m/z calcd for $C_{30}H_{29}OP$ (M^+) 436.1956, found 436.1954.

(*E*)-[2-(1-Cyclopropyl-2-phenylethenyl)phenyl]-diphenylphosphine Oxide (3ai). Mp 26−27 °C (pale yellow powder), 61 mg, (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.26 (dt, J = 5.8, 5.8 Hz, 2H), 0.55 (dt, J = 5.8, 5.8 Hz, 2H), 1.69 (m, 1H), 6.13 (s, 1H), 7.14−7.19 (m, 2H), 7.22−7.29 (m, 5H), 7.33−7.49 (m, 8H), 7.65−7.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.6, 14.7, 126.2 (d, J = 12.4 Hz), 126.3, 127.6, 128.1 (d, J = 12.4 Hz), 129.3, 130.8 (d, J = 9.5 Hz), 131.1 (d, J = 1.9 Hz), 131.29 (d, J = 2.8 Hz), 131.34 (d, J = 104.0 Hz), 132.0 (d, J = 9.6 Hz), 132.5, 133.8 (d, J = 105.0 Hz), 133.0 (d, J = 12.4 Hz), 137.1, 141.4 (d, J = 3.8 Hz), 147.2 (d, J = 8.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.04; HRMS m/z calcd for $C_{29}H_{25}OP$ (M^+) 420.1643, found 420.1640.

(*E*)-Diphenyl[2-(2-phenylethenyl)phenyl]phosphine Oxide (3aj).[16] Mp 169−170 °C (colorless powder), 57 mg (50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 16.0 Hz, 1H), 7.17−7.24 (m, 7H), 7.42−7.54 (m, 7H), 7.68−7.73 (m, 4H), 7.80−7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.6 (d, J = 12.5 Hz), 126.7, 126.8, 127.2 (d, J = 6.8 Hz), 127.8, 128.4, 128.5 (d, J = 12.5 Hz), 130.1 (d, J = 101.6 Hz), 131.3, 131.8 (d, J = 2.9 Hz), 131.9 (d, J = 9.6 Hz), 132.2 (d, J = 2.9 Hz), 132.9 (d, J = 103.5 Hz), 133.7 (d, J = 12.5 Hz), 137.0, 142.3 (d, J = 6.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.73; HRMS m/z calcd for $C_{26}H_{21}OP$ (M^+) 380.1330, found 380.1328.

(*E*)-Diphenyl[2-(2-phenylethenyl)phenyl]phosphine (4).[16] Mp 58−59 °C (pale yellow powder), 60 mg (66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (ddd, J = 0.9, 4.5, 7.7 Hz, 1H), 6.96 (d, J = 16.3 Hz, 1H), 7.14−7.37 (m, 17H), 7.71 (dd, J = 4.0, 7.7 Hz, 1H), 7.78 (dd, J = 4.0, 15.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.4 (d, J = 3.8 Hz), 126.7, 127.2, 127.5 (d, J = 17.2 Hz), 127.6, 128.5 (d, J = 2.9 Hz), 128.7 (d, J = 16.2 Hz), 129.0, 130.4 (d, J = 2.9 Hz), 133.5, 133.9, 134.1, 135.7 (d, J = 13.3 Hz), 136.4 (d, J = 9.5 Hz), 137.4, 141.9 (d, J = 21.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ −13.41; HRMS m/z calcd for $C_{26}H_{21}P$ (M^+) 364.1381, found 364.1378.

Butyl 3-[2-(Diphenylphosphoryl)phenyl]propanoate (6). Oil, 59 mg (58%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.3 Hz, 3H), 1.26−1.35 (m, 2H), 1.50−1.57 (m, 2H), 2.52 (t, J = 7.7 Hz, 2H), 3.19 (t, J = 7.7 Hz, 2H), 4.00 (t, J = 6.7 Hz, 2H), 7.07 (ddd, J = 1.2, 7.7, 13.9 Hz, 1H), 7.16 (ddt, J = 1.2, 2.6, 7.7 Hz, 1H), 7.36 (ddd, J = 0.7, 4.2, 7.7 Hz, 1H), 7.44−7.49 (m, 5H), 7.55 (dtt, J = 1.4, 1.4, 6.6 Hz, 2H), 7.65 (ddt, J = 1.4, 6.9, 11.9 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 19.0, 29.7 (d, J = 5.1 Hz), 30.6, 35.6, 64.1, 125.7 (d, J = 12.4 Hz), 128.5 (d, J = 12.5 Hz), 130.97 (d, J = 10.3 Hz), 131.00 (d, J = 102.0 Hz), 131.8 (d, J = 2.9 Hz), 131.9 (d, J = 9.5 Hz), 132.2 (d, J = 3.0 Hz), 133.0 (d, J = 103.4 Hz), 133.6 (d, J = 12.5 Hz), 146.1 (d, J = 8.0 Hz), 172.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.20; HRMS m/z calcd for $C_{25}H_{28}O_3P$ ($M+H^+$) 407.1776, found 407.1770.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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