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Studies on 1-Alkynylphosphines and Their Derivatives as Key Starting Materials in Creating New Phosphines

Azusa Kondoh

2010
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<td>AIBN</td>
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R^2  larger group
R^3  smaller group
rt  room temperature (25 ± 3 °C)
s  singlet (spectral)
sept  septet (spectral)
t  triplet (spectral)
t (terr)  tertiary
temp.  temperature
THF  tetrahydrofuran
TLC  thin-layer chromatography
Tf  trifluoromethanesulfonyl
tfa  trifluoroacetate
TMEDA  N,N,N',N'-tetramethylethylenediamine
TMS  trimethylsilyl
Ts  p-toluenesulfonyl
TTMSS  tris(trimethylsilyl)silane
vide infra  see below
vide supra  see above
Vol(s).  volume(s)
General Introduction

1. Introduction

Organophosphines play invaluable roles in organic synthesis, especially as ligands for transition metal catalysts. A variety of phosphine ligands have been designed and used in many reactions including cross-coupling reactions\(^1\) and asymmetric transformations\(^2\). Creation of new organophosphines and development of novel approaches to organophosphines are thus quite important.

There are some general methods for the synthesis of phosphines. One of the most general methods is a reaction of an organometallic reagent such as an organolithium reagent or a Grignard reagent with a halophosphine or any phosphines with a good leaving group (Scheme 1).

**Scheme 1.**

\[
\text{R}^1\text{-M} + \text{L-PR}_2^2 \rightarrow \text{R}^1\text{-PR}_2^2
\]

\[
M = \text{Li, MgX}
\]

\[
L = \text{leaving group}
\]

Another method is a reaction of a metal phosphide with an organic electrophile. Metal phosphides can be prepared by metalation of hydrophosphines by strong bases such as butyllithium or alkali metals. Halophosphines can be also metalated by using lithium metal. These nucleophilic reagents react with common electrophiles such as organohalides, tosylates, aldehydes, ketones, epoxides, and activated alkenes (Scheme 2). Phosphide reagents also react with activated arenes to afford mixed arylphosphines (Scheme 3).
The other important method for the synthesis of phosphines utilizes transition metal catalysts. A transition-metal-catalyzed approach often enables the incorporation of sensitive functional groups into the target phosphine. One example is shown in Scheme 4. The synthesis of chiral BINAP was achieved using nickel-catalyzed cross-coupling of 2,2'-naphthol-derived ditriflate with diphenylphosphine. Not only nickel complexes but also palladium and copper complexes can catalyze the cross-coupling of aryl halides or aryl triflates with secondary phosphines to provide tertiary arylphosphines.

Besides the cross-coupling reaction, transition metal catalysts are also utilized for hydrophosphinination of unsaturated substrates. The reaction of P–H bonds with unsaturated substrates often proceeds without a metal catalyst. In addition, acid- or base-catalyzed as well as radical reactions have been developed. However, transition-metal-catalyzed transformation,
often offers improvements in rate, selectivity, and stereocontrol. For instance, Oshima and co-workers reported cobalt-catalyzed syn-hydrophosphination of alkynes to provide (E)-alkenylphosphines, which is complementary to anti-selective radical hydrophosphination reactions (Scheme 5).6

**Scheme 5.**

\[ R^L \cdot C \equiv C \cdot R^S + H_2PPh_2 \xrightarrow{\text{20 mol\% } n-\text{BuLi}, \text{10 mol\% } \text{Co(acac)}_2, \text{dioxane, reflux}} S \xrightarrow{R^L \cdot R^S \cdot PPh_2} \]

1-Alkynylphosphines and Their Derivatives

1-Alkynylphosphines are an attractive and useful class of phosphines7 in the field of coordination chemistry because of their versatile behavior, which results from their ability to react at the phosphine and the alkyne functions. 1-Alkynylphosphines can coordinate to metal centers via phosphorus atom and/or alkyne moiety, thus favoring the formation of a rich variety of homo- or heteropolynuclear species.8 They also have an aptitude to act as sources of phosphido and alkylnyl fragments via metal-mediated P–C bond cleavage.9 The studies on a broad range of 1-alkynylphosphine–metal complexes have revealed other interesting abilities of these phosphines. For instance, the 1-alkynylphosphines in bis(1-alkynylphosphine)platinum undergo dimerization on the platinum, reacting at the two alkyne moieties to yield a bidentate phosphine–platinum complex.10 The triple bonds of 1-alkynylphosphines are reactive enough to undergo insertion into some M–H and M–C bonds to form new transition metal complexes.11 In addition, 1-alkynylphosphines serve as useful ligands in some transition-metal-catalyzed reactions.12
Meanwhile, 1-alkynylphosphines and their derivatives, such as phosphine oxides and phosphine sulfides, can be identified as useful building blocks in constructing other phosphines. For example, nucleophilic additions to a carbon–carbon triple bond lead to the formation of functionalized alkenylphosphines. Cycloadditions with other unsaturated bonds lead to the construction of cyclic structures having phosphorus pendants. The following are preparation of 1-alkynylphosphines and their derivatives, and representative reactions in which 1-alkynylphosphines and their derivatives are used as key starting materials.

1.1. Preparation of 1-Alkynylphosphines and Their Derivatives

Synthesis of 1-alkynylphosphines is usually accomplished by nucleophilic substitution reactions of halophosphines with acetylides of sodium,\textsuperscript{13a} lithium,\textsuperscript{13a} magnesium,\textsuperscript{13b} or titanium.\textsuperscript{13c}

An alternative approach to 1-alkynylphosphines is transition-metal-catalyzed coupling reactions of terminal alkynes with chlorophosphines.\textsuperscript{14,15} Treatment of terminal alkynes with chlorophosphines in the presence of a nickel catalyst affords 1-alkynylphosphines in good yields (Scheme 6).\textsuperscript{14} Besides the nickel complex, palladium\textsuperscript{14} and copper complexes\textsuperscript{15} also catalyze the coupling of terminal alkynes with chlorophosphines.

\textbf{Scheme 6.}

\[
\text{R}^1\text{C}≡\text{C–H} + \text{ClPR}_2^2 \xrightarrow{\text{3 mol}\% \text{ Ni(acac)}_2 \text{ Et}_3\text{N}} \text{toluene, 80 °C or rt} \rightarrow \text{R}^1\text{C}≡\text{C–PR}_2^2 \quad 94–99\%
\]

\(\text{R}^1 = \text{Ph, 4-Me-C}_6\text{H}_4, \text{n-Pr, Am, t-Bu} \)
\(\text{R}^2 = \text{Ph, i-Pr, n-Bu} \)

1-Alkynylphosphine oxides can be usually synthesized by the oxidation of the corresponding 1-alkynylphosphines. 1-Alkynylphosphine sulfides can be obtained by treatment of the corresponding 1-alkynylphosphines with crystalline sulfur.
1.2. Nucleophilic Addition to 1-Alkynylphosphines and Their Derivatives

1.2.1. Addition of Heteroatom Nucleophiles

Addition reactions of nucleophiles to 1-alkynylphosphine derivatives are straightforward methods for the synthesis of 1-alkenylphosphine derivatives. The addition mainly occurs at the 2-position of the substrates. In the case of the addition of heteroatom nucleophiles such as hydrophosphines, thiols, and amines, the products are 1-alkenylphosphine derivatives containing a heteroatom substituent at the 2-position.

*Hydrophosphination and Hydrophosphinylation*

Ethynylidiphenylphosphine and bis(diphenylphosphino)ethyne undergo syn-hydrophosphination in the presence of strong bases such as phenyllithium and potassium tert-butoxide. Upon complexation with stoichiometric amounts of platinum, palladium, or nickel, 1-alkynylphosphines participate in anti-hydrophosphination.

Taran and co-workers reported α-addition of diphenylphosphine oxide to 1-alkynylphosphine oxides catalyzed by tributylphosphine (Scheme 7). This reaction can provide a new route to P–C–P backbones.

*Scheme 7.*

![Scheme 7](image)

*Hydrothiolation*

Under basic conditions, addition of thiols to 1-alkynylphosphine oxides and sulfides proceeds
smoothly to afford 1-phosphinyl-2-thio-1-alkenes and 2-thio-1-thiophosphinyl-1-alkenes, respectively.\textsuperscript{19} The addition proceeds regioselectively, while the stereoselectivity is low.

**Hydroamination**

In the presence or absence of strong bases such as butyllithium, nucleophilic addition of primary or secondary amines to 1-alkynyldiphenylphosphine oxides proceeds to provide 2-amino-1-phosphinyl-1-alkenes as a mixture of \( E/Z \) isomers.\textsuperscript{20} Exceptionally, the addition to ethynyldiphenylphosphine oxide affords the \( E \) isomer exclusively.

Leung and co-workers reported hydroamination of 1-alkynylphosphines with aniline in the presence of an organopalladium template to give bidentate iminophosphines (Scheme 8).\textsuperscript{21} The reaction started with regiospecific coordination of 1-alkynylphosphine onto the palladium complex to form the monomeric chloro complex 1. After removal of the chloro ligand in 1 by means of silver perchlorate, the hydroamination of the resulting cationic palladium complex with aniline proceeded to form the iminophosphine complex 2. The naphthylamine ligand on the template complex 2 could be removed chemoselectively by treatment with concentrated HCl to furnish dichloro complex 3. The liberation of the iminophosphine ligand 4 from 3 was achieved by treatment of 3 with potassium cyanide. Iminophosphines are important ligands as potential catalyst supporters.\textsuperscript{22}

**Scheme 8.**

![Scheme 8](image-url)
Addition of Other Nucleophiles

Michael addition of alcohols to 1-alkynylphosphine oxides is described in the literature.\textsuperscript{23} In addition, anti-Markovnikov addition of methanol and ethanol to ethynylphosphine–gold complex was observed under basic conditions (Scheme 9).\textsuperscript{24,25}

\textbf{Scheme 9.}

Hydrotelluration of 1-alkynylphosphine oxides afforded 2-telluro-1-alkenylphosphine oxides.\textsuperscript{26} The adducts were subjected to cross-coupling with terminal alkynes under palladium catalysis to yield (Z)-2-alkynyl-1-alkenylphosphine oxides (Scheme 10).

\textbf{Scheme 10.}

Michael addition of silylcopper reagents to 1-alkynylphosphine oxides was reported by Huang and Xu.\textsuperscript{27} This reaction proceeded in a syn fashion, and the resulting (Z)-alkenyl copper intermediate could be trapped with a variety of electrophiles to afford 2-silyl-substituted alkenylphosphine oxides (Scheme 11).
1.2.2. Carbometalation

Carbometalation of 1-alkynylphosphine derivatives is an efficient method for the synthesis of polysubstituted alkenylphosphine derivatives. In 1976, Meijer and co-workers reported the addition of alkylcopper reagents to ethynylidiphenylphosphine and diphenyl(1-propynyl)phosphine. Recently, Oshima, Yorimitsu and co-workers reported their detailed examination of carbocupration of 1-alkynylphosphines. Addition of magnesium dialkylcuprate to 1-alkynylphosphines proceeded in a syn fashion to form alkenylcopper intermediate. Trapping of the intermediate with electrophiles such as allyl bromide and benzoyl chloride afforded tetrastubstituted alkenes in good yields (Scheme 12).

This reaction was applicable to the synthesis of gem-diphosphinoalkene derivatives, which were difficult to synthesize despite the interesting structure, by trapping the intermediate with chlorodiphenylphosphine (Scheme 13). Interestingly, TMEDA or 1,2-bis(diphenylphosphino)-ethane proved to be essential as an additive for the trapping. Without the additive, only trace amounts of gem-diphosphinoalkenes were formed, and the protonated products were mainly obtained after aqueous work up.
1-Alkynylphosphine oxides and 1-alkynylphosphine sulfides also undergo carbocupration. Huang and Wu reported syn-carbocupration of 1-alkynylphosphine oxides. Not only dialkylcuprate but also diphenylcuprate reacted with 1-alkynylphosphine oxides to form alkenylcopper intermediate. The trapping of the intermediate with electrophiles afforded a variety of alkenylphosphine oxides in good yields (Scheme 14).

1.3. Cycloaddition Reactions of 1-Alkynylphosphines and Their Derivatives

1.3.1. [4+2] Cycloaddition Reactions

Cycloaddition reactions of 1-alkynylphosphine derivatives lead to cyclic compounds containing a phosphorus substituent. This concept has been applied to the synthesis of new phosphines which are difficult to synthesize by other methods.

The Diels-Alder reaction is promising for this purpose. Carter and co-workers reported the synthesis of tri- and tetra-ortho-substituted phosphorus-containing biaryls using a Diels-Alder approach (Scheme 15). Diels-Alder reaction of 1-alkynylphosphine oxide 5 with Brassard
diene proceeded regioselectively. Aromatization followed by benzylation of the hydroxy group of 6 furnished biarylphosphine oxide 7. Further transformation of 7 led to tetra-ortho-substituted biaryl 8. The utility of the newly synthesized biarylphosphine 8 was shown in Suzuki-Miyaura cross-coupling reaction.

**Scheme 15.**

BIPHEP-type ligands are also accessible by the Diels-Alder approach. Doherty, Smyth and co-workers developed a stepwise regioselective double Diels-Alder cycloaddition-elimination sequence protocol (Scheme 16). First, the reaction of 1,4-bis(diphenylphosphinyl)-1,3-butadiyne with 1-methoxy-1,3-cyclohexadiene proceeded regioselectively to form isolable monoadduct 9 with extrusion of ethylene. The second Diels-Alder reaction of 9 with 1-methoxy-1,3-butadiene followed by elimination of methanol furnished dissymmetric biaryl diphosphine dioxide 10. Finally, the reduction of the phosphinyl groups of 10 by treating with trichlorosilane and tributylamine afforded biaryl diphosphine 11. This stepwise cycloaddition-elimination sequence approach complements other approaches to dissymmetric atropos biaryl diphosphines.
Doherty, Knight, Smyth and co-workers synthesized biaryl-like mono- and diphosphines via Diels-Alder reaction of 1-alkynylphosphine oxides with anthracene (Scheme 17).\textsuperscript{35} These phosphines proved to serve as efficient ligands for palladium-catalyzed C–N and C–C bond formation reactions.

1,3,2-diazaphosphinines are versatile precursors of 1,2-azaphosphinines and polyfunctional
phosphinines. They behave as diazaphosphacyclohexatrienes and participate in [4+2] cycloaddition with alkynes followed by cycloreversion to afford 1,2-azaphosphinines with extrusion of nitriles. 1,2-azaphosphinines can be converted to phosphinines by a similar process. The reaction of 1-alkynylphosphines with 1,3,2-diazaphosphinine afforded phosphinine which had two phosphino groups at the 2- and 6-positions (Scheme 18). 1-Alkynylphosphine oxides and sulfides also undergo similar [4+2] cycloaddition/elimination sequence with azaphosphinines to afford phosphinines having a phosphinyl or thiophosphinyl moiety.

\[ \ce{Ph-C≡C-PPPh2} \]

1.3.2. [2+2+2] Cycloaddition Reactions

Transition-metal-catalyzed [2+2+2] cycloaddition reactions of alkynes have received much attention due to their utility for the synthesis of substituted benzenes. Recently, this methodology has been applied for the synthesis of new arylphosphines.

A practical method for the synthesis of axially chiral biaryl monophosphine oxides was developed by Tanaka and co-workers. Enantioselective [2+2+2] cycloaddition of 2-naphthol-derived 1-alkynylphosphine oxides with 1,6-diynes in the presence of a cationic rhodium/H\_8-BINAP catalyst furnished axially chiral phosphine oxides in high yield with high enantioselectivity (Scheme 19).
The synthesis of axially chiral biarylphosphine oxides was also accomplished under cobalt catalysis.\textsuperscript{40,41} Heller and co-workers reported that enantioselective [2+2+2] cycloaddition of 1-alkynylphosphine oxides with acetylene proceeded in the presence of chiral cobalt catalyst to yield axially chiral biarylphosphine oxides (Scheme 20). Subsequent reduction of the product afforded the corresponding phosphines. The utility of the newly synthesized phosphine was demonstrated in palladium-catalyzed asymmetric hydrosilylation of alkenes.

The application of the [2+2+2] cycloaddition approach to the synthesis of biaryl diphosphines was reported by Doherty and co-workers.\textsuperscript{42,43} They reported that the double [2+2+2] cycloaddition of 1,4-bis(diphenylphosphinyl)-1,3-butadiyne with tethered diynes proceeded in the presence of a cationic rhodium/BINAP catalyst to furnish biaryl diphosphine dioxides in high yields (Scheme 21). Enantiopure platinum complexes of biaryl diphosphines 13, which were obtained by the reduction of 12 followed by optical resolution using enantiopure BINOL as a resolving agent, were highly efficient catalysts for asymmetric carbonyl-ene reactions and Diels-Alder reactions. They also reported the highly enantioselective synthesis of axially chiral
biaryl diphosphine dioxide via stepwise double [2+2+2] cycloadditions.\textsuperscript{42b}

**Scheme 21.**

\[
\begin{align*}
\text{C} &= \text{C} - \text{H} \\
\text{C} &= \text{C} - \text{H} \\
\text{P(O)Ph}_2 + &\quad \text{P(O)Ph}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{TsN, O, C(C_2\text{Me}_2)_2, CH}_2, \text{CH}_2\text{CH}_2
\end{align*}
\]

\[\text{X} = \text{TsN, O, C(C_2\text{Me}_2)_2, CH}_2, \text{CH}_2\text{CH}_2\]

The other application of the [2+2+2] cycloaddition approach is the construction of P-stereogenic center. Tanaka and co-workers reported enantioselective synthesis of P-stereogenic 1-alkynylphosphine oxides by rhodium-catalyzed [2+2+2] cycloaddition of symmetrical dialkynylphosphine oxides with 1,6-diynes (Scheme 22).\textsuperscript{44}

**Scheme 22.**

\[
\begin{align*}
\text{C} &= \text{C} - \text{Me} \\
\text{C} &= \text{C} - \text{Me} \\
\text{P(O)Ph}_2 + &\quad \text{P(O)Ph}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{TsN, 4-BrC}_6\text{H}_4\text{SO}_2\text{N, O, CH}_2
\end{align*}
\]

\[\text{X} = \text{TsN, 4-BrC}_6\text{H}_4\text{SO}_2\text{N, O, CH}_2\]

**1.4. Miscellaneous Reactions**

*Nickel-Mediated Reactions*

Bennett and co-workers reported the regiospecific synthesis of 2,3-bis(diphosphino)naphthalenes by double insertion of 1-alkynylphosphines into nickel(0)–benzyne complexes.\textsuperscript{45} Nickel(0)–benzyne complex reacted with two equivalents of 1-alkynyldiphenylphosphines to form a mixture of nickel complexes 14 and 15. Treatment of the mixture with bromine afforded dibromonickel complex 16. Reaction of 16 with sodium...
cyanide in dimethyl sulfoxide liberated pure 2,3-bis(diphenylphosphino)naphthalene 17 (Scheme 23).

Scheme 23.

Zirconium-Mediated Reactions

Zirconocene–benzyne complexes also react with 1-alkynylphosphines. Majoral and co-workers reported that treatment of 1-alkynylphosphine with zirconocene complex led to the formation of phosphinozirconaindene arising from regioselective insertion of carbon–carbon triple bond of 1-alkynylphosphine into a zirconium–carbon bond of the transient zirconocene–benzyne complex. The reactions of phosphinozirconaindenes with dichlorophosphines afforded 2-phosphinophosphole derivatives (Scheme 24).
Xi, Takahashi and Zhang developed zirconocene-mediated reactions of 1-alkynylphosphines with ethylene or simple alkynes.\(^{48}\) Treatment of 1-alkynylphosphines with zirconocene ethylene complex generated in situ led to the formation of \(\alpha\)-phosphinozirconacyclopentenes. Protonation or iodination of this intermediate furnished 1-alkenylphosphine derivatives in good yields (Scheme 25). The reactions of \(\alpha\)-phosphinozirconacyclopentenes with alkynes afforded \(\alpha\)-phosphinozirconacyclopentadienes.\(^{49}\) Protonation or iodination furnished 1,3-alkadienylphosphine derivatives (Scheme 26).

**Scheme 24.**

![Reaction Scheme](image)

**Scheme 25.**

![Reaction Scheme](image)
**Cobalt-Mediated Reactions**

Hong and co-workers investigated the reaction of cobalt complex 18 with 1-alkynylphosphines. The reaction provided cobalt-containing diphosphine 19, which was employed as a ligand in Suzuki-Miyaura cross-coupling reaction (Scheme 27).

**Scheme 26.**

**Scheme 27.**

2. **Overview of This Thesis**

The author focused on 1-alkynylphosphines and 1-alkynylphosphine sulfides as precursors of new phosphines, and developed several methods for the synthesis of various phosphines starting from 1-alkynylphosphines and 1-alkynylphosphine sulfides. In Chapters 1–3, addition reactions of heteroatom nucleophiles such as diphenylphosphine, thiols, and amides to 1-alkynylphosphine derivatives are disclosed. In Chapters 4 and 5, conceptually novel approaches to bulky
arylphosphines and heteroarylphosphines are described. In Chapter 6, an intriguing transformation of 1-alkynylphosphines to (E)-1-alkenyphosphine oxides is disclosed. The methods described in this thesis not only provide a variety of new phosphines that are otherwise difficult to synthesize but also offer creative and reliable approaches to phosphines. Considering the importance of phosphines in organic synthesis, especially as ligands, this study would contribute to the advancement in various fields of chemistry.

2.1. Copper-Catalyzed anti-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (Z)-1,2-Diphosphino-1-alkenes (Chapter 1)

Hydrophosphination of unsaturated substrates, that is addition of trivalent hydrophosphines across multiple bonds, represents a straightforward method for the synthesis of organophosphines.\textsuperscript{51} In Chapter 1, the author describes copper-catalyzed anti-hydrophosphination reaction of 1-alkynylphosphines with diphenylphosphine. Treatment of 1-alkynylphosphines with diphenylphosphine in the presence of catalytic amounts of copper iodide and cesium carbonate in DMF afforded (Z)-1,2-diphosphino-1-alkenes in good yields with perfect regio- and stereoselectivity (Scheme 28). The diphosphines obtained are not only structurally intriguing entities but also potentially useful ligands for transition metals. Despite their potential, the efficient synthesis of (Z)-1,2-diphosphino-1-alkenes has been scarcely reported so far.\textsuperscript{16,17}

The reaction is highly chemoselective and can be performed even in an aqueous medium. The adducts, diphosphine disulfides, could be easily reduced to the parent trivalent diphosphines

\begin{center}
\textbf{Scheme 28.}
\end{center}
under radical desulfidation conditions. Enantioselective hydrogenation of diphosphate disulfide 20 followed by desulfidation afforded new chiral bidentate phosphine 21 (Scheme 29). The sequential phosphination/hydrogenation protocol offers an alternative to the conventional approach to chiral bidentate diphosphines.

\[ \text{Scheme 29.} \]

2.2. Palladium-Catalyzed anti-Hydrothiolation of 1-Alkynylphosphines

Addition of thiols to alkynes (hydrothiolation) is an important reaction for synthesizing 1-alkenylsulfides. In Chapter 2, the author shows palladium-catalyzed anti-hydrothiolation of 1-alkynylphosphines. Treatment of 1-alkynylphosphines with thiols in the presence of a catalytic amount of palladium acetate in ethanol resulted in regio- and stereoselective anti-hydrothiolation (Scheme 30). In general, transition-metal-catalyzed hydrothiolation proceeds in a syn fashion. In contrast, the present reaction represents a rare example of highly selective anti-hydrothiolation. The products, (Z)-1-phosphino-2-thio-1-alkenes, are a new class of heteroatom-containing compounds and can potentially serve as useful ligands of transition-metal complexes.

\[ \text{Scheme 30.} \]

R\(^1\)-C=CHR\(^2\) + R\(^3\)SH + 5 mol% Pd(OAc)\(_2\) ethanol

R\(^1\) = alkyl, aryl, H
R\(^2\) = Ph, c-C\(_8\)H\(_{11}\)
R\(^3\) = alkyl, aryl

60–93%
2.3. Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides Catalyzed by Cesium Base

In Chapter 3, the author shows cesium-catalyzed addition of amides or imides to 1-alkynylphosphine sulfides, directed toward the construction of vicinal N,P-frameworks (Scheme 31).

Scheme 31.

\[ \begin{align*}
R^1\text{C}≡\text{C}−\text{PPh}_2 + \text{R}^2\text{R}^3\text{NH} & \xrightarrow{10 \text{ mol}\% \text{Cs}_2\text{CO}_3} \text{DMSO, 90 °C or rt} \xrightarrow{\text{E/Z}} \\
\text{S} & \text{N} & \text{Ph} & \text{H} & \text{Ts} & \text{Bn} & \text{Ph} & \text{S} & \text{PPh}_2 & \text{O} & \text{N} & \text{H} & \text{Ts} & \text{S} & \text{PPh}_2 & \text{N} & \text{H} & \text{Ts} & \text{S} & \text{PPh}_2 & \text{N} & \text{H} & \text{Ts} & \text{S} & \text{PPh}_2 & \text{N} & \text{H}
\end{align*}\]

\[ \begin{align*}
84\% \text{ E/Z} = 96/4 \\
\text{After recrystallization} & \\
71\% \text{ E/Z} = 100/0 \\
93\% \text{ E/Z} = 100/0 \\
92\% \text{ E/Z} = 100/0
\end{align*}\]

This addition proceeded mainly in a *syn* fashion, and recrystallization of the products allowed for the isolation of the major *E* isomers. The amidation was applicable to intramolecular cyclizations.

The adducts underwent enantioselective hydrogenation catalyzed by a cationic iridium complex (Scheme 32). The sequential hydroamidation/hydrogenation protocol offers a new approach to chiral N,P-ligands that will potentially serve as ligands in asymmetric reactions. The phosphine sulfides synthesized by hydroamidation/hydrogenation could be easily reduced to the corresponding trivalent phosphines under radical desulfidation conditions.
2.4. Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition
Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

In the past decade, bulky triorganophosphines have attracted increasing attention as excellent ligands for transition metal catalysts in preparing biologically intriguing compounds as well as functional organic materials.\textsuperscript{1c,54} Synthesis of such ligands is hence quite important. In Chapter 4, the author describes rhodium-catalyzed formal [2+2+2] cycloaddition reactions of 1-alkynylphosphine sulfides with tethered diynes, which offer a conceptually new approach to bulky phosphines. Treatment of a variety of 1-alkynylphosphine sulfides with tethered diynes in the presence of a cationic rhodium catalyst and BINAP afforded arylphosphine sulfides in good yields (Scheme 33).
The newly formed benzene rings have one or two substituents next to the thiophosphinyl group, which provide sterically congested environment around the phosphorus. The product, phosphine sulfides, could be easily converted to the corresponding bulky phosphines under radical desulfidation conditions. Dicyclohexyl(2,6-diphenylaryl)phosphine, which was synthesized by this method, proved to serve as an efficient ligand in palladium-catalyzed amination of aryl chloride with morpholine.

2.5. New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines

In Chapter 5, the author focuses on the conceptually new approach to 2-indolylphosphines by using 1-alkynylphosphine sulfides as starting materials. Treatment of 1-alkynylphosphine sulfides with N-alkyl-2-iodoanilines in the presence of (acetylacetonato)palladium and potassium carbonate afforded 2-indolylphosphine sulfides in good yields (Scheme 34).

The newly formed indole rings naturally have a substituent derived from 1-alkynylphosphine sulfides next to the thiophosphinyl group, which creates sterically hindered environment around the phosphorus. The products could be easily reduced to the corresponding trivalent phosphines under radical desulfidation conditions.
2.6. Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (E)-1-Alkenylphosphine Oxides

In Chapter 6, a formal hydration reaction of 1-alkynylphosphines is described. Treatment of 1-alkynylphosphines with a rhodium catalyst in 1,4-dioxane/H$_2$O provided (E)-1-alkenylphosphine oxides (Scheme 35).

Scheme 35.

The reaction proceeds as follows. First, oxidative addition of 1-alkynylphosphine to rhodium followed by hydrolysis yields the corresponding terminal alkyne and diphenylphosphine oxide. Next, rhodium-catalyzed hydrophosphinylation of the terminal alkyne, which is generated in the first step, with diphenylphosphine oxide proceeds to afford (E)-1-alkenylphosphine oxide.
References and Notes


Copper-Catalyzed *anti*-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (Z)-1,2-Diphosphino-1-alkenes

Hydrophosphination of 1-alkynylphosphines with diphenylphosphine proceeds in an *anti* fashion under copper catalysis, providing an easy and efficient access to a variety of (Z)-1,2-diphosphino-1-alkenes and their sulfides. Radical reduction of the diphosphine disulfides with tris(trimethylsilyl)silane yields the parent trivalent diphosphines without suffering from the isomerization of the olefinic geometry. Enantioselective hydrogenation of (Z)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene followed by desulfidation leads to a new chiral bidentate phosphine ligand.
Introduction

Organophosphines have been gaining in importance as ligands for transition metal catalysts, as clearly demonstrated in cross-coupling reactions\(^1\) and asymmetric transformations.\(^2\) Creation of new organophosphines and, naturally, of new phosphination reactions can thus have great impact on various fields of chemical science.

Metal-catalyzed hydrophosphination reactions of C–C multiple bonds represent a straightforward method for the synthesis of organophosphines.\(^3\) In particular, catalytic hydrophosphinations of phosphorus-substituted unsaturated C–C bonds seem to be quite useful since the reactions provide bidentate diphosphines. In spite of their potential utility, the hydrophosphinations providing bidentate phosphines are rather limited. Although the hydrophosphinations of vinylphosphines proceed smoothly in the presence of a base to afford useful 1,2-diphosphinoethanes, the hydrophosphinations require the native vinyl group, i.e., \((\text{CH}_2\equiv\text{CH})_n\text{PR}_3\_n.\)\(^4,5\)

In this chapter, the author focuses on 1-alkynylphosphines as the substrates. The precedent hydrophosphinations of 1-alkynylphosphines highlight the difficulty in achieving the transformation. Ethynyldiphenylphosphine and bis(diphenylphosphino)ethyne undergo \textit{syn}-hydrophosphination in the presence of strong bases such as phenyllithium.\(^4b,6\) Upon complexation with platinum, palladium or nickel, 1-alkynylphosphines of some generality participate in \textit{anti}-hydrophosphination.\(^7\) The use of stoichiometric amounts of expensive transition metals is a definite and significant drawback. Here the author describes that hydrophosphinations of various 1-alkynylphosphines with diphenylphosphine proceed in an \textit{anti} fashion under copper catalysis with perfect stereo- and regioselectivity. The diphosphines obtained, \((Z)\)-1,2-diphosphino-1-alkenes, are not only structurally intriguing entities but also potentially useful bidentate ligands for transition metals. Furthermore, the carbon–carbon double bonds of the diphosphines can enjoy further functionalizations. Despite their latent rich chemistry, efficient and general methods for the synthesis of \((Z)\)-1,2-diphosphino-1-alkenes have scarcely been reported so far.\(^8,9\)
Results and Discussion

Preparation of 1-Alkynylphosphines. Starting alkynes 1 were prepared by nucleophilic substitution reactions of chlorophosphines with 1-lithio-1-alkynes (Scheme 1, method A) or nickel-catalyzed coupling reactions of chlorodiphenylphosphine and terminal alkynes in the presence of triethylamine (method B).10 Whereas method A was high-yielding, method B was suitable for the synthesis of 1 having labile functional groups. The nickel-catalyzed reactions of aliphatic alkynes did not go to completion (1g, 1h). Alkynylphosphine 1i, having a hydroxy group, was available in three steps, i.e., preparation of diphenyl(trimethylsilyl)ethynylphosphine by method A, protodesilylation, and nucleophilic addition of diphenylphosphinoethynyllithium to benzaldehyde. Diphosphine 1j was prepared by the dilithiation of 4,4’-diethynylbiphenyl followed by the reaction with chlorodiphenylphosphine (method A’). Aliphatic phosphine 1k was prepared in fashions similar to method A by using chlorodicyclopentylphosphine (method A’’).

Scheme 1.

Method A

\[
\text{R=CH}_2\text{=CH} \rightarrow \text{R=CH}_2\text{=C-PPh}_2
\]

1) n-BuLi, 2) CIPPh\(_2\)

\(1a (R = n-C_6H_{13}): 85\%, \ 1b (R = i-Pr): 82\%
\)

\(1c (R = t-Bu): 81\%, \ 1d (R = Ph): 88\%
\)

\(1f (R = 3\text{-pyridyl}): 74\%
\)

Method B

\[
\text{R=CH}_2\text{=CH} \rightarrow \text{R=CH}_2\text{=C-PPh}_2
\]

3 mol% Ni(acac)\(_2\)

CIPPh\(_2\), Et\(_3\)N

\(1e (R = 4\text{-Ac-C}_6\text{H}_4): 70\%
\)

\(1g (R = \text{EtO}_2\text{C(CH}_2)_3): 32\% (68\% \text{recovery})
\)

\(1h (R = \text{AcS(CH}_2)_3): 30\% (40\% \text{recovery})
\)

Method A

\[
\text{Me}_3\text{SiC=CH}_2 \rightarrow \text{Me}_3\text{SiC=CH}_2\text{=C-PPh}_2
\]

1) n-BuLi, 2) CIPPh\(_2\)

\(1i \ 95\%
\)
Hydrophosphination Reactions of 1-Alkynylphosphines. Treatment of 1-octynyldiphenylphosphine (1a) with diphenylphosphine in the presence of catalytic amounts of copper(I) iodide and cesium carbonate in N,N-dimethylformamide (DMF) at 25 °C yielded (Z)-1,2-bis(diphenylphosphino)-1-octene (2a) exclusively (Table 1, entry 1). Handling of 2a under air for purification led to gradual oxidation. To evaluate the efficiency of the reaction accurately, the author isolated the product as phosphine sulfide 3a after treatment with crystalline sulfur. Isolation of the parent phosphine 2a and its analogues is discussed in the following section. The yield of 3a based on $^{31}$P NMR was 99%, and the isolated yield was 88%. The formation of the Z isomer was determined by the coupling constant of $J(^{31}P-^{31}P)$ of 3a (16 Hz), whereas (E)-1,2-bis(diphenylthiophosphinyl)-1-alkenes and 1,1-bis(diphenylthiophosphinyl)-1-alkenes exhibit ca. 50 and 30 Hz of $J(^{31}P-^{31}P)$, respectively.  

Aprotic polar solvents are the choice of solvents. The reactions in dimethyl sulfoxide, THF, and ether afforded 3a in 94%, 62%, and 0% NMR yields, respectively, under the otherwise same reaction conditions. Surprisingly, the reaction in aqueous DMF (1:1) also provided 3a in 82% yield.

Copper(I) iodide is the best among transition metal catalysts the author tested. Copper(I)
chloride was as effective as CuI (98% yield). Other copper salts such as CuCN, CuBr, CuBr·Me₂S, and CuCl₂ also effected the hydrophosphination albeit the yields were lower (10%, 57%, 87%, and 84%, respectively). Neither metallic copper, CuO, nor Cu₂O are inactive. Silver(I) iodide (5 mol% in DMSO) also served to afford 3a in 88% yield. None of gold(I) chloride, nickel(II) chloride, or cobalt(II) chloride exhibited any catalytic activity. The use of 5 mol% of palladium(II) chloride or platinum(II) chloride yielded 3a in 5% yield, which invokes the formation of a stable and catalytically inactive palladium or platinum complex in the reaction mixture.⁷ It is worth noting that a diphenylphosphide anion has been regarded as an untransferable dummy ligand in cuprate chemistry.¹²

The use of Cs₂CO₃ is crucial. Potassium carbonate, sodium carbonate, and triethylamine promoted the hydrophosphination reaction much less effectively (18%, 3%, and 2% yields, respectively). Neutral CsCl did not induce the reaction. Instead of the CuI/Cs₂CO₃/DMF system, a CuI (10 mol%)/n-BuLi (20 mol%)/THF system was effective yet led to slower conversion (4 h, 49%; 8 h, 76%; 20 h, 86%). Without copper salts, Cs₂CO₃ by itself could not promote the reaction. Although butyllithium alone could effect the hydrophosphination in THF at ambient temperature, the reaction afforded a mixture of the Z and E isomers in 27% and 70% yields, respectively.

A wide range of 1-alkynylphosphines 1 were subjected to the phosphination reaction (Table 1). Sterically demanding 1-alkynylphosphines including 1b and 1c underwent the hydrophosphination smoothly, although higher catalyst loadings were required to complete the reaction (Table 1, entries 2 and 4). An elevated temperature also facilitated the reaction of 1c (Table 1, entry 3). A variety of functional groups such as keto and hydroxy groups were compatible under the reaction conditions (Table 1, entries 6–10), whereas known hydrophosphination reactions of alkynes were generally unsatisfactory with regard to the functional group compatibility.¹³ Pyridine-containing 2f or 3f (Table 1, entry 7) and sulfur-containing 2h or 3h (Table 1, entry 9) can be useful for constructing supramolecular architectures.
The reaction was efficient enough to provide tetraphosphine sulfide 3j in excellent yield (eq 1). Although hydrophosphination across 1k having a dicyclohexylphosphino group at 25 °C led to complete recovery of 1k, the anticipated 3k could be prepared at 90 °C (eq 2). Attempts to perform the addition of dicyclohexylphosphine to 1a or 1d resulted in failure.
Reaction Mechanism. The mechanism of the phosphination reaction is not clear. Radical inhibitors such as 2,2,6,6-tetramethylpiperidine-N-oxyl had little influence on the reaction, which is suggestive of an ionic reaction process. With several experiments, the author is tempted to propose the mechanism outlined in Scheme 2. Deprotonation by Cs$_2$CO$_3$ with the aid of copper iodide would provide copper phosphide$^{14}$ (step A). As mentioned above, highly basic Cs$_2$CO$_3$ is thus essential to abstract the hydrogen of the CuI·HPPh$_2$ complex.$^{15}$ The phosphide would then attack 1-alkynylphosphine to form 7 (steps B and D). The alkynylphosphine probably coordinates to copper to be activated in the form of 5$^{16}$ (step C)$^{17}$. The activation by copper is indispensable, due to the experimental fact that both 1-octynylphosphine sulfide and oxide resisted the hydrophosphination reaction under the otherwise same reaction conditions. Unlike the insertion of an alkyne to a transition metal–phosphorus bond which proceeds in a $\text{syn}$ manner, nucleophilic addition to alkyne usually proceeds in an $\text{anti}$ manner. The latter is the case for the present reaction (step D). Immediate formation of chelating diphosphine skeleton 7 controls the complete stereoselectivity. During the reaction, no $E$ isomer was detected, which suggests that it is improbable that initially formed ($E$)-diphosphine isomerizes into its $Z$ form in the reaction flask. Protonation of the vinylcopper 7 by HPPh$_2$ affords the product and regenerates the copper
phosphide (step E).

**Isolation of Trivalent Phosphines 2.** The diphosphines 2 could be handled under air, although gradual oxidation occurred. The isolations of trivalent phosphines 2 are summarized in Table 2. The oxidation led to lower yields of 2, compared to the yields of sulfides 3 (Table 2 vs Table 1). When the hydrophosphination reaction of 1c was conducted on a 0.5 mmol scale, 2c was obtained in 99% NMR yield and 69% isolated yield (Table 2, entry 1). Without special care to avoid oxidation, other phosphines, 2a, 2d–2f, and 2i, were isolated in good yields (Table 2, entries 2–6).

The catalytic hydrophosphination reaction was reliable enough to permit a gram-scale synthesis (Table 2, entry 7). The reaction of 1.0 g of 1c (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol) provided 1.5 g of 2c (3.3 mmol) in 87% isolated yield after purification on silica gel under ambient atmosphere. The lower isolated yield in the smaller-scale synthesis (Table 2, entry 1) would originate from the formation of a larger proportion of phosphine oxide of 2c.
Table 2. Isolation of 1,2-Bis(diphenylphosphino)-1-alkenes\textsuperscript{a}

\begin{center}
\begin{tabular}{llcc}
\hline
entry & R & Cul /mol\% & Cs\textsubscript{2}CO\textsubscript{3} /mol\% & yield of 2 /\% \textsuperscript{b} \\
\hline
1\textsuperscript{c} & t-Bu (c) & 2 & 10 & 69 (99) \\
2 & n-C\textsubscript{6}H\textsubscript{13} (a) & 1 & 10 & 71 \\
3 & Ph (d) & 1 & 10 & 70 \\
4 & 4-Ac-C\textsubscript{6}H\textsubscript{4} (e) & 10 & 20 & 60 \\
5 & 3-pyridyl (f) & 2 & 10 & 65 \\
6 & PhCH(OH) (i) & 10 & 20 & 51 \\
7\textsuperscript{c,d} & t-Bu (c) & 10 & 20 & 87 \\
\hline
\end{tabular}
\end{center}

\textsuperscript{a}Hydrophosphinilation conditions: 1 (0.50 mmol), Ph\textsubscript{2}PH (0.52 mmol), DMF (3.0 mL), 25 °C, 4 h. \textsuperscript{b}Isolated yields. NMR yield is in parenthesis. \textsuperscript{c}The reaction was performed at 90 °C. \textsuperscript{d}The reaction was performed with 1.0 g of 1\textit{c} (3.8 mmol) and 0.71 g of diphenylphosphine (3.8 mmol).

Radical Reduction of 3 to 2. The author surveyed an efficient method for the reduction of phosphine sulfides 3 to the parent phosphines 2. Radical desulfidation with tris(trimethylsilyl)silane (TTMSS) proved to be a reliable procedure (Table 3). Although the original report employed 1–3 equimolar amounts of TTMSS,\textsuperscript{18} he found that a substoichiometric amount of TTMSS to P=S bond is sufficient. A plausible radical chain mechanism is depicted in Scheme 3. The first equimolar amount of 3 would undergo desulfidation in the reported manner\textsuperscript{18} (steps F and G). The silicon-centered radical 10, which is to be generated by a 1,2-Si shift\textsuperscript{19} (step H), would be reactive enough to reduce a P=S moiety. [Bis(trimethylsilylthio)trimethylsilyl]silyl radical (13), formed through the second 1,2-shift (step K), seemed unreactive, based on the fact that a smaller amount of TTMSS for the reduction of 3 led to unsatisfactory conversion of 3. The radical 13 would abstract the hydrogen of TTMSS (step L) to form tris(trimethylsilyl)silyl radical, which completes the radical chain. Purification
on silica gel was quite easy, simply removing less polar silicon residues through a short-path column.

Table 3. Radical Reduction of 3 to 2 by TTMSS

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>isolated yield of 2 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>t-Bu (c)</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>n-C₆H₁₃ (a)</td>
<td>87 (97)ᵇ</td>
</tr>
<tr>
<td>3</td>
<td>Ph (d)</td>
<td>78 (94)ᵇ</td>
</tr>
<tr>
<td>4</td>
<td>4-Ac-C₆H₄ (e)</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>3-pyridyl (f)</td>
<td>44</td>
</tr>
<tr>
<td>6ᶜ</td>
<td>3-pyridyl (f)</td>
<td>58</td>
</tr>
</tbody>
</table>

ᵃ Conditions: 3 (0.25 mmol), TTMSS (0.30 mmol), AIBN (0.025 mmol), benzene (3.0 mL), reflux, 4 h. ᵇ NMR yields are in parentheses. ᶜ The reaction was performed with TTMSS (0.60 mmol) for 12 h.

Scheme 3. Mechanism for Desulfidation of 3 with a Substoichiometric Amount of TTMSS
Complexation of NiCl₂ with 2c. The Z stereochemistry of 2 was also confirmed by X-ray crystallographic analysis of [NiCl₂(2c)] (Figure 1). Due to the bulky tert-butyl group, the atoms, P1, P2, Cl1, and Cl2, coordinating to the nickel are not in one plane (Figure 1b).

**Figure 1.** ORTEP Drawing of [NiCl₂(2c)]. (a) Top View. (b) Side View.

Enantioselective Hydrogenation Leading to Chiral Bidentate Phospine Ligand. Compounds 2 and 3 have carbon–carbon double bonds, which can enjoy further transformations. In light of the importance of chiral bidentate ligands in transition-metal-catalyzed asymmetric synthesis, the author examined enantioselective hydrogenation of 3c to obtain a new chiral ligand. Enantioselective hydrogenation of 3c under the catalysis of [RuCl₂(PPh₃)₃]/(R)-(+)-BINAP provided a tert-butyl-substituted chiral diphosphine disulfide 15 in 91% isolated yield with 83% ee (Scheme 4). Recrystallization of the product yielded an enantiomerically pure form of 15 in the supernatant, whereas the crystals were a mixture of the enantiomers. The desulfidation of 15 with a large excess of Cp₂Zr(H)Cl²¹,²² afforded enantiomerically pure bidentate phosphine 16. The typical Sₘ₂ phosphination reactions of ditosylates of chiral diols²³ may suffer in the synthesis of phosphines with a sterically congested chiral center. The sequential phosphination/hydrogenation protocol offers an alternative to the conventional approach.
Conclusion

The author has devised a highly efficient method for the synthesis of (Z)-1,2-diphosphino-1-alkenes. The method will create a variety of functionalized bidentate phosphines, which can be applicable to various fields of chemical science. As exemplified by the synthesis of a new chiral bidentate ligand 16, the (Z)-1,2-diphosphino-1-alkene derivatives can be precursors of new phosphorus compounds.
Experimental Section

Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl$_3$ or C$_6$D$_6$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and relative to CDCl$_3$ at 77.0 ppm for $^{13}$C or benzene at 7.15 ppm for $^1$H and at 128.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl$_3$ or C$_6$D$_6$ with 85% H$_3$PO$_4$ solution as an external standard. NMR yields were determined by fine $^{31}$P NMR spectra with (MeO)$_3$P=O as an internal standard. The first delay of $^{31}$P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University. Sep-Pak® cartridges (silica, long body) for the purification of 16 were purchased from Waters and were used after conditioned with 10 mL of hexane/ethyl acetate (5:1) prior to use.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Diphenylphosphine was purchased from TCI, distilled, and stored under argon. For the preparation of 1, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was a gift from Hokko Chemical Industry Co., Ltd. Starting 1-alkynylphosphines 1 were prepared by the reactions of lithium acetylides with chlorophosphines or by nickel-catalyzed reactions of alkynes with chlorodiphenylphosphine. In general, 1-alkynylphosphines are stable under air. DMF was distilled from calcium hydride and stored under argon. Copper(I) iodide and cesium carbonate were purchased from Wako Pure Chemicals. Tris(triphenylphosphine)ruthenium(II) dichloride was purchased from TCI. Unless otherwise noted, reactions were carried out under argon atmosphere.
Preparation of 1-Alkynylphosphines 1a–1d, 1f, 1j, and 1k (Method A)

Preparation of 1a is representative. Under an atmosphere of argon, a solution of 1-octyne (1.2 g, 11 mmol) in THF (15 mL) was placed in a 50-mL reaction flask. Butyllithium (6.6 mL, 1.6 M in hexane, 11 mmol) was added to the flask at 0 °C. The resulting mixture was stirred for 30 min at the same temperature. Chlorodiphenylphosphine (2.2 g, 10 mmol) was then added at 0 °C. After the addition, the reaction mixture was stirred for 1 h at ambient temperature. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Concentration followed by silica gel column purification provided 2.5 g of 1a (8.5 mmol, 85%) as a yellow oil. It is worth noting that 1-alkynylphosphines are so stable under air that no observable oxidation occurred during the conventional handling. The alkynylphosphines could be stored at least for 6 months in a capped vial.

Preparation of 1-Alkynylphosphines 1e, 1g, and 1h (Method B)

Preparation of 1e is representative. Nickel acetylacetonate (39 mg, 0.15 mmol) was placed in a 50-mL reaction flask under argon. Toluene (10 mL), p-ethynylacetophenone (0.79 g, 5.5 mmol), chlorodiphenylphosphine (1.1 g, 5.0 mmol), and triethylamine (1.5 g, 15 mmol) were sequentially added. The mixture was heated at 80 °C for 4 h. After being cooled to room temperature, the mixture was filtered and the filtrate was concentrated. The crude oil obtained was chromatographed on silica gel to yield 1e in 70% yield (1.1 g, 3.5 mmol).

Preparation of 1i

Crude diphenyl(trimethylsilylthynyl)phosphine was prepared from trimethylsilylacetylene (0.99 mL, 7.0 mmol) by method A. The crude product was dissolved in methanol (10 mL). Potassium carbonate (2.0 g, 14 mmol) was then added. The whole mixture was stirred for 1 h. The product was extracted with a hexane/ethyl acetate mixture. Concentration followed by purification on silica gel provided 1.3 g of ethynyldiphenylphosphine (6.0 mmol, 86%). A part of the ethynylphosphine (0.44 g, 2.1 mmol) was dissolved in 4.0 mL of THF under argon. At 0
°C, butyllithium (1.3 mL, 1.6 M in hexane, 2.0 mmol) was added dropwise. The mixture was stirred for 30 min. After benzaldehyde (0.20 g, 1.9 mmol) was charged, the mixture was stirred for an additional 1 h at 25 °C. The reaction was quenched with 10 mL of water. Extraction, concentration, and purification furnished 1i in 95% yield (0.57 g, 1.8 mmol).

**Typical Procedure for Copper-Catalyzed anti-Hydrophosphination of 1-Alkynylphosphines with Diphenylphosphine to Obtain 1,2-Bis(diphenylthiophosphinyl)-1-alkene 3 (Table 1)**

Copper(I) iodide (1 mg, 0.005 mmol) and cesium carbonate (16 mg, 0.050 mmol) were placed in a 20-mL reaction flask under argon. DMF (3.0 mL), 1a (0.15 g, 0.50 mmol), and diphenylphosphine (0.11 g, 0.60 mmol) were sequentially added. The resulting mixture was stirred for 4 h at 25 °C. Elemental sulfur (64 mg, 2.0 mmol) was then added and the mixture was stirred for 1 h. Water (10 mL) was added and the product was extracted with ethyl acetate (10 mL x 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded (Z)-1,2-bis(diphenylthiophosphinyl)-1-octene (3a, 0.24 g, 0.44 mmol, 88%) as a white solid.

**Hydrophosphination to Isolate 1,2-Bis(diphenylphosphino)-1-alkene (Table 2, Entries 1–6)**

Isolation of 2c is representative. Copper(I) iodide (1.9 mg, 0.010 mmol) and cesium carbonate (0.016 g, 0.050 mmol) were placed in a 20-mL reaction flask under an atmosphere of argon. DMF (3.0 mL), 1c (0.13 g, 0.50 mmol), and diphenylphosphine (0.097 g, 0.52 mmol) were sequentially added. The mixture was heated at 90 °C for 4 h. After being cooled to room temperature, the mixture was passed through a pad of florisil. The filtrate obtained was evaporated to leave solid. Purification on silica gel provided 2c (0.16 g, 0.35 mmol) in 69% yield as a white solid. During the process, no deaerated solvents were employed.

**Gram-Scale Hydrophosphination to Isolate 2c (Table 2, Entry 7)**

The procedure is similar to the smaller-scale reaction. Copper(I) iodide (0.014 g, 0.075
mmol), cesium carbonate (0.12 g, 0.38 mmol), 1c (1.0 g, 3.8 mmol), and diphenylphosphate (0.71 g, 3.8 mmol) were mixed in DMF (7.5 mL). The whole mixture was heated at 90 °C for 4 h. Filtration through a pad of florisil, concentration, and purification afforded 1.5 g of 2c (3.3 mmol) in 87% yield.

**Representative Procedure for TTMSS-Mediated Radical Reduction of 3 to 2 (Table 3)**

In a 20-mL reaction flask, 3c (0.13 g, 0.25 mmol) and AIBN (4.1 mg, 0.025 mmol) were placed under argon. Benzene (3.0 mL) and TTMSS (0.075 g, 0.30 mmol) were added, and the resulting mixture was boiled for 4 h. After cooling, evaporation followed by purification on silica gel furnished 0.10 g of 2c (0.22 mmol) in 89% yield.

**Preparation of [NiCl₂(2c)] for X-ray Crystallographic Analysis**

Nickel(II) chloride (52 mg, 0.40 mmol) was placed in a 20-mL reaction flask under argon. Ethanol (2.0 mL) was charged to dissolve the nickel salt. Diphosphine 2c (0.20 g, 0.44 mmol) in ethanol (20 mL) was added. Immediately, orange precipitate appeared. The precipitate was washed with ether, and dried in vacuo. The complex weighed 0.093 g (0.16 mmol, 40%, unoptimized). X-ray quality crystals were grown from acetonitrile. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center (CCDC 601317).

**Ruthenium-Catalyzed Enantioselective Hydrogenation of (Z)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)-1-buthene**

Tris(triphenylphosphate)ruthenium(II) dichloride (9.6 mg, 0.010 mmol) and (R)-(+-)2,2'-bis(diphenylphosphino)-1,1'-biphenyl ((R)-BINAP, 12 mg, 0.020 mmol) were placed in a 20-mL reaction flask under hydrogen. Ethanol (0.50 mL) and benzene (0.50 mL) were added at 25 °C. After the mixture was stirred for 10 min, (Z)-3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene (3c, 65 mg, 0.13 mmol) was added.
The resulting mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was extracted with ethyl acetate (10 mL × 3). The organic layer was dried over sodium sulfate and evaporated in vacuo. Purification of the crude solid by gel permeation chromatography provided 3,3-dimethyl-1,2-bis(diphenylthiophosphinyl)butane (15, 59 mg, 0.11 mmol) in 91% yield and with 83% ee. Recrystallization from ethanol/benzene yielded crystals. The crystals were a mixture of the enantiomers. Concentration of the supernatant provided an optically pure form of 15 (37 mg, 0.071 mmol, 57%, >99% ee). HPLC conditions: CHIRALCEL AD-H, hexane/2-propanol = 90:10, 1.3 mL/min, retention time = 4.0 min for the major enantiomer; retention time = 5.7 min for the minor enantiomer.

**Desulfidation of 15 for Synthesis of New Bidentate Ligand 16**

Zirconocene chloride hydride (0.19 g, 0.75 mmol) and 15 (0.052 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. After 1,4-dioxane (3.0 mL) was added, the mixture was stirred for 12 h at reflux. The reaction mixture was directly subjected to evaporation. A mixture of hexane and ethyl acetate (5:1, 10 mL, degassed) was added to dissolve 16. The supernatant was passed through a silica, long-body Sep-Pak cartridge. The filtrate was concentrated to afford 0.045 g of pure 16 (0.10 mmol, 100%). The absolute configuration of 16 was assigned as R by comparing the specific rotations of 16 and of analogous chiral diphosphines.  

**Characterization Data**

Phosphines 1a, 1c, 1d, and 1k showed the same spectroscopic data in the literature.

**Diene (3-Methyl-1-butynyl)diphenylphosphine (1b)**

IR (neat) 2970, 2930, 2870, 2175, 1683, 1585, 1479, 1436, 1363, 1313, 1267, 1095, 1026, 999, 830, 740, 694, 592 cm⁻¹; \(^1H\) NMR (CDCl\textsubscript{3}) \(δ\) 1.33 (d, \(J = 6.5\) Hz, 6H),
2.85 (dsept, J = 1.5, 6.5 Hz, 1H), 7.32–7.43 (m, 6H), 7.64–7.72 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 21.95, 22.73, 74.69, 115.66 (d, J = 3.8 Hz), 128.35, 128.54 (d, J = 32.0 Hz), 132.22 (d, J = 21.0 Hz), 137.02 (d, J = 7.1 Hz); $^{31}$P NMR (CDCl$_3$) δ –35.13. HRMS (EI$^+$) (m/z) Observed: 252.1069 (Δ = +0.3 ppm). Calcd for C$_{17}$H$_{17}$P [M$^+$]: 252.1068.

(4-Acetylphenylethynyl)diphenylphosphine (1e)

IR (neat) 3054, 1684, 1600, 1557, 1479, 1435, 1402, 1304, 1265, 1178, 1095, 999, 846, 694, 598 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 2.61 (s, 3H), 7.35–7.41 (m, 6H), 7.63 (d, J = 8.5 Hz, 2H), 7.65–7.70 (m, 4H), 7.93 (d, J = 8.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$) δ 26.63, 89.91 (d, J = 10.0 Hz), 106.58 (d, J = 3.3 Hz), 127.41 (d, J = 1.1 Hz), 128.20, 128.69 (d, J = 7.6 Hz), 129.19, 131.79 (d, J = 1.5 Hz), 132.62 (d, J = 21.0 Hz), 135.59 (d, J = 5.8 Hz), 136.53, 197.20; $^{31}$P NMR (CDCl$_3$) δ –34.75. Found: C, 80.46; H, 5.38%. Calcd for C$_{22}$H$_{17}$OP: C, 80.48; H, 5.22%. m.p.: 77.0–78.0 °C.

Diphenyl(3-pyridinylethynyl)phosphine (1f)

IR (neat) 3053, 2164, 1584, 1560, 1475, 1435, 1406, 1307, 1185, 1023, 804, 741, 659 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) δ 6.42 (dd, J = 5.0, 8.0 Hz, 1H), 6.98–7.17 (m, 7H), 7.67–7.75 (m, 4H), 8.27 (d, J = 5.0 Hz, 1H), 8.76 (s, 1H); $^{13}$C NMR (C$_6$D$_6$) δ 90.53 (d, J = 11.9 Hz), 104.93 (d, J = 3.4 Hz), 119.91 (d, J = 1.5 Hz), 122.77, 129.01 (d, J = 7.6 Hz), 129.39, 133.05 (d, J = 21.0 Hz), 136.33 (d, J = 7.1 Hz), 138.15 (d, J = 1.4 Hz), 149.37, 152.81 (d, J = 1.9 Hz); $^{31}$P NMR (C$_6$D$_6$) δ –34.52. Found: C, 79.33; H, 4.97%. Calcd for C$_{19}$H$_{14}$NP: C, 79.43; H, 4.91%.

Ethyl 9-diphenylphosphino-8-nonynoate (1g)

IR (neat) 3054, 2936, 2858, 2179, 1733, 1436, 1373, 1181, 1091, 1026, 740, 695 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 1.26 (t, J = 7.0 Hz, 3H), 1.36 (dd, J = 8.0, 8.0 Hz, 2H), 1.47 (dd, J = 8.0, 8.0 Hz, 2H), 1.58–1.68 (m, 4H), 2.30 (t, J = 7.5 Hz,
2H), 2.45 (dd, \( J = 7.0, 1.5 \) Hz, 2H), 4.13 (q, \( J = 7.0 \) Hz, 2H), 7.29–7.37 (m, 6H), 7.57–7.63 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 14.22, 20.26, 24.78, 28.26 (d, \( J = 1.0 \) Hz), 28.44, 28.53, 34.22, 60.16, 75.84, 110.22 (d, \( J = 3.9 \) Hz), 128.42 (d, \( J = 7.1 \) Hz), 128.75, 132.33 (d, \( J = 20.5 \) Hz), 136.94 (d, \( J = 6.6 \) Hz), 173.72; \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) –34.51.  Found: C, 75.12; H, 7.52%.  Calcd for C\(_{23}\)H\(_{27}\)O\(_2\)P: C, 75.39; H, 7.43%.

\( S - 11\)-Diphenylphosphino-10-undecynyl ethanethioate (1h)

IR (neat) 2928, 2855, 2179, 1733, 1694, 1435, 1353, 1097, 1027, 740, 697 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 1.24–1.48 (m, 10H), 1.56 (dd, \( J = 7.5, 7.5 \) Hz, 2H), 1.62 (dd, \( J = 7.5, 7.0 \) Hz, 2H), 2.32 (s, 3H), 2.44 (dd, \( J = 7.0, 1.5 \) Hz, 2H), 2.86 (t, \( J = 7.5 \) Hz, 2H), 7.29–7.37 (m, 6H), 7.58–7.64 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 20.31, 28.45 (d, \( J = 1.1 \) Hz), 28.73, 28.78, 28.94, 28.99, 29.08, 29.28, 29.43, 30.61, 75.66, 110.46 (d, \( J = 3.9 \) Hz), 128.41 (d, \( J = 7.1 \) Hz), 128.72, 132.32 (d, \( J = 20.5 \) Hz), 136.99 (d, \( J = 6.8 \) Hz), 196.04; \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) –34.48.  Found: C, 72.90; H, 7.90%.  Calcd for C\(_{25}\)H\(_{31}\)OPS: C, 73.14; H, 7.61%.

1-Phenyl-3-diphenylphosphino-2-propyn-1-ol (1i)

IR (neat) 3265, 3055, 2857, 1585, 1456, 1436, 1185, 1043, 1027, 986, 916, 741, 695, 511 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \( \delta \) 2.01 (s, 1H), 5.31 (d, 1H), 6.96–7.10 (m, 9H), 7.45 (d, \( J = 8.0 \) Hz, 2H), 7.64–7.71 (m, 4H); \(^{13}\)C NMR (C\(_6\)D\(_6\)) \( \delta \) 65.27, 83.64 (d, \( J = 11.5 \) Hz), 109.30, 126.95, 128.29, 128.66, 128.90 (d, \( J = 7.6 \) Hz), 129.24, 133.00 (d, \( J = 21.0 \) Hz), 136.59 (d, \( J = 6.6 \) Hz), 140.97; \(^{31}\)P NMR (C\(_6\)D\(_6\)) \( \delta \) –35.40.  Found: C, 79.43; H, 5.54%.  Calcd for C\(_{21}\)H\(_{17}\)OP: C, 79.73; H, 5.42%.

4,4’-Bis(2-diphenylphosphinoethynyl)biphenyl (1j)

IR (nujol) 2924, 2855, 2389, 2161, 1729, 1652, 1456, 1436, 1367, 1026, 843, 821, 739 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \)
7.34–7.42 (m, 12H), 7.56–7.65 (m, 8H), 7.66–7.72 (m, 8H); $^{13}$C NMR (CDCl$_3$) δ 86.99 (d, $J = 6.6$ Hz), 107.42 (d, $J = 3.8$ Hz), 122.12 (d, $J = 1.6$ Hz), 126.89, 128.64 (d, $J = 7.6$ Hz), 129.07, 132.35 (d, $J = 1.4$ Hz), 132.60 (d, $J = 21.0$ Hz), 136.14 (d, $J = 6.1$ Hz), 140.50; $^{31}$P NMR (CDCl$_3$) δ −34.72. HRMS (EI$^+$) (m/z) Observed: 570.1666 (Δ= 0.0 ppm). Calcd for C$_{40}$H$_{28}$P$_2$ [M$^+$]: 570.1666. m.p.: 123.5–125.0 °C.

(Z)-1,2-Bis(diphenylphosphino)-1-octene (2a)

IR (neat) 3052, 3000, 2926, 2855, 1951, 1884, 1585, 1480, 1436, 1378, 1093, 839, 741, 694 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.20–1.30 (m, 8H), 2.08–2.15 (m, 2H), 7.00 (d, $J = 33.5$ Hz, 1H), 7.24–7.40 (m, 20H); $^{13}$C NMR (CDCl$_3$) δ 13.94, 22.42, 28.81, 28.83, 31.40, 36.86, 128.10, 128.13 (d, $J = 7.1$ Hz), 128.18, 128.24 (d, $J = 6.6$ Hz), 132.78 (d, $J = 18.6$ Hz), 133.33 (d, $J = 19.0$ Hz), 136.40 (dd, $J = 5.3$, 12.9 Hz), 139.57 (dd, $J = 4.3$, 12.8 Hz), 141.37 (dd, $J = 7.6$, 35.8 Hz), 156.12 (dd, $J = 18.6$, 25.8 Hz); $^{31}$P NMR (CDCl$_3$) δ −27.48 (d, $J = 161.1$ Hz), −9.67 (d, $J = 161.1$ Hz). Found: C, 80.11; H, 7.10%. Calcd for C$_{32}$H$_{34}$P$_2$: C, 79.98; H, 7.13%.

(Z)-3,3-Dimethyl-1,2-bis(diphenylphosphino)-1-butene (2c)

IR (nujol) 2924, 2854, 1700, 1559, 1456, 1432, 1377, 1356, 1230, 1028, 846, 736, 692 cm$^{-1}$; $^1$H NMR (CD$_6$D$_6$) δ 1.26 (s, 9H), 6.94–7.07 (m, 12H), 7.20–7.27 (m, 4H), 7.31 (dd, $J = 16.0$, 3.5 Hz, 1H), 7.62–7.68 (m, 4H); $^{13}$C NMR (CD$_6$D$_6$) δ 30.30 (d, $J = 9.5$ Hz), 41.32 (dd, $J = 27.4$, 6.9 Hz), 127.95, 128.32 (d, $J = 6.3$ Hz), 128.34, 128.44 (d, $J = 5.8$ Hz), 133.02 (d, $J = 19.0$ Hz), 133.44 (dd, $J = 18.9$, 3.5 Hz), 137.18 (dd, $J = 14.1$, 4.1 Hz), 139.55 (dd, $J = 14.1$, 1.2 Hz), 140.82 (d, $J = 14.8$ Hz), 165.39 (dd, $J = 29.1$, 22.9 Hz); $^{31}$P NMR (CD$_6$D$_6$) δ −32.26 (d, $J = 29.3$ Hz), −12.35 (d, $J = 29.3$ Hz). Found: C, 79.39; H, 6.65%. Calcd for C$_{30}$H$_{30}$P$_2$: C, 79.63; H, 6.68%. m.p.: 85.5–87.0 °C.
(Z)-1-Phenyl-1,2-bis(diphenylphosphino)ethene (2d)

\[
\text{Ph} \quad \text{Ph}_2P \quad \text{H} \quad \text{Ph}_2P \quad \text{H} \quad \text{Ph} \\
\]

IR (neat) 3052, 3000, 2925, 2855, 1951, 1884, 1811, 1584, 1480, 1307, 1093, 1069, 1026, 999, 738, 694 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 6.86–6.90 (m, 2H), 6.96–7.05 (m, 3H), 7.10–7.20 (m, 6H), 7.21–7.30 (m, 11H), 7.35–7.41 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 126.87, 127.38, 127.82, 128.01 (d, \(J = 6.6\) Hz), 128.10, 128.34, 128.37 (d, \(J = 6.6\) Hz), 132.97 (d, \(J = 19.0\) Hz), 133.24 (d, \(J = 19.1\) Hz), 133.80 (dd, \(J = 5.1, 12.0\) Hz), 139.04 (dd, \(J = 4.9, 10.5\) Hz), 142.35 (dd, \(J = 2.4, 8.1\) Hz), 146.03 (dd, \(J = 11.5, 37.8\) Hz), 155.71 (dd, \(J = 23.4, 27.1\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) –27.19 (d, \(J = 144.8\) Hz), –6.24 (d, \(J = 144.8\) Hz). Found: C, 81.19; H, 5.72%. Calcd for C\(_{32}\)H\(_{26}\)P\(_2\): C, 81.34; H, 5.55%.

(Z)-2-(4-Acetylphenyl)-1,2-bis(diphenylphosphino)ethene (2e)

\[
\begin{align*}
\text{IR (nujol)} & \quad 2925, 2855, 2723, 1738, 1673, 1598, 1456, 1377, 1265, 1160, 740, 693 \\
\quad \text{cm}^{-1}; \quad \text{H NMR (CDCl}_3) & \quad \delta\) 2.48 (s, 3H), 6.97 (d, \(J = 8.5\) Hz, 2H), 7.12–7.26 (m, 10H), 7.27–7.36 (m, 7H), 7.37–7.44 (m, 4H), 7.61 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 26.52, 127.54, 127.99, 128.17 (d, \(J = 6.8\) Hz), 128.41 (d, \(J = 7.6\) Hz), 128.49, 128.51, 132.98 (d, \(J = 16.3\) Hz), 133.13 (d, \(J = 16.8\) Hz), 135.20 (dd, \(J = 5.3, 12.9\) Hz), 135.27, 138.67 (dd, \(J = 4.8, 10.5\) Hz), 147.23 (dd, \(J = 3.3, 8.5\) Hz), 147.69 (dd, \(J = 13.4, 38.1\) Hz), 154.57 (dd, \(J = 24.8, 27.8\) Hz), 197.62; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) –26.54 (d, \(J = 141.5\) Hz), –6.54 (d, \(J = 141.5\) Hz). Found: C, 79.09; H, 5.53%. Calcd for C\(_{34}\)H\(_{28}\)OP\(_2\): C, 79.37; H, 5.48%. m.p.: 160.0–162.5° C.
\end{align*}
\]

(Z)-2-(3-Pyridyl)-1,2-bis(diphenylphosphino)ethene (2f)

\[
\text{IR (nujol)} 3051, 2925, 2855, 1959, 1882, 1814, 1584, 1568, 1471, 1436, 1407, 1377, 1184, 1094, 1025, 739 \text{ cm}^{-1}; \quad \text{H NMR (CDCl}_3) & \quad \delta\) 6.86 (dd, \(J = 5.0, 8.0\) Hz, 1H), 7.05 (d, \(J = 8.0\) Hz, 1H), 7.12–7.25 (m, 10H), 7.26–7.36 (m, 7H), 7.37–7.46 (m, 4H), 8.22 (s, 1H), 8.26 (d, \(J = 5.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 121.99, 128.21 (d, \(J = 6.3\) Hz), 128.40 (2C), 128.47 (d, \(J = 4.9\) Hz), 132.91 (d, \(J = 19.1\) Hz), 133.06 (d, \(J = 19.1\) Hz), 134.67,
135.00 (dd, \( J = 5.3, 13.0 \) Hz), 138.03 (dd, \( J = 3.4, 6.1 \) Hz), 138.47 (dd, \( J = 4.8, 10.5 \) Hz), 147.86, 148.22 (dd, \( J = 13.4, 37.3 \) Hz), 148.26, 151.98 (dd, \( J = 24.9, 28.6 \) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) –26.51 (d, \( J = 140.0 \) Hz), –6.75 (d, \( J = 140.0 \) Hz). Found: C, 78.51; H, 5.46%. Calcd for C\(_{31}\)H\(_{28}\)NP\(_2\): C, 78.64; H, 5.32%. m.p.: 111.0–112.5°C.

(Z)-1-Phenyl-2,3-bis(diphenylphosphino)-2-propen-1-ol (2i)

IR (nujol) 3446, 3047, 2953, 2923, 2854, 1652, 1569, 1456, 1436, 1377, 1306, 1177, 1070, 989, 913, 857 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 1.71 (s, 1H), 5.23 (s, 1H), 6.89–6.94 (m, 2H), 7.05–7.19 (m, 8H), 7.20–7.33 (m, 13H), 7.34–7.53 (m, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 76.12 (dd, \( J = 1.8, 7.8 \) Hz), 127.03, 127.61, 128.03, 128.12 (d, \( J = 6.6 \) Hz), 128.23, 128.28, 128.32 (d, \( J = 6.3 \) Hz), 128.37 (d, \( J = 7.6 \) Hz), 128.43, 128.46 (d, \( J = 7.3 \) Hz), 128.56, 132.52 (d, \( J = 18.6 \) Hz), 133.28 (d, \( J = 19.0 \) Hz), 133.39 (d, \( J = 19.0 \) Hz), 134.27 (d, \( J = 20.5 \) Hz), 135.03 (dd, \( J = 7.5, 13.0 \) Hz), 135.56 (dd, \( J = 2.6, 10.5 \) Hz), 138.31 (dd, \( J = 3.9, 10.5 \) Hz), 139.38 (dd, \( J = 4.6, 10.5 \) Hz), 141.28, 142.22 (dd, \( J = 10.0, 32.4 \) Hz), 155.57 (dd, \( J = 22.4, 25.8 \) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) –29.55 (d, \( J = 143.2 \) Hz), –13.18 (d, \( J = 143.2 \) Hz). Found: C, 78.74; H, 5.58%. Calcd for C\(_{31}\)H\(_{28}\)OP\(_2\): C, 78.88; H, 5.62%. m.p.: 106.0–109.0°C.

(Z)-1,2-Bis(diphenylthiophosphinyl)-1-octene (3a)

IR (nujol) 2923, 2854, 2392, 1456, 1436, 1377, 1313, 1101, 1030, 818, 747, 707, 686 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \( \delta \) 0.81 (t, \( J = 7.5 \) Hz, 3H), 1.07–1.22 (m, 6H), 1.54 (tt, \( J = 8.0, 8.0 \) Hz, 2H), 2.38 (dt, \( J = 12.0, 8.0 \) Hz, 2H), 6.94 (dd, \( J = 41.5, 13.0 \) Hz, 1H), 7.22–7.40 (m, 12H), 7.65–7.80 (m, 8H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 13.97, 22.44, 28.74, 30.63 (d, \( J = 3.8 \) Hz), 31.30, 39.69 (dd, \( J = 14.9, 12.9 \) Hz), 128.20 (d, \( J = 12.9 \) Hz), 128.35 (d, \( J = 12.9 \) Hz), 130.99 (d, \( J = 2.9 \) Hz), 131.18 (d, \( J = 10.5 \) Hz), 131.25 (d, \( J = 83.0 \) Hz), 131.28 (d, \( J = 2.9 \) Hz), 132.33 (d, \( J = 10.9 \) Hz), 133.59 (d, \( J = 86.4 \) Hz), 134.66 (dd, \( J = 81.5, 7.6 \) Hz), 152.21 (dd, \( J = 67.9, 3.3 \) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) 29.28 (d, \( J = 16.3 \) Hz), 39.58 (d, \( J = 16.3 \) Hz). Found: C, 70.48; H, 6.32%. Calcd for C\(_{32}\)H\(_{34}\)P\(_2\)S\(_2\): C, 70.56; H, 6.29%. m.p.: 119.0–120.5°C.
(Z)-3-Methyl-1,2-bis(diphenylthiophosphinyl)-1-butene (3b)

\[
\begin{align*}
\text{IR (nujol)} & \ 2924, \ 2855, \ 2391, \ 1457, \ 1436, \ 1381, \ 1101, \ 998, \ 832, \ 742 \ \text{cm}^{-1}; \\
\text{\textsuperscript{1}H NMR (CDCl\textsubscript{3})} & \ \delta \ 1.20 \ (d, \ J = 7.0 \ Hz, \ 6H), \ 2.88 \ (dsept, \ J = 3.5, \ 6.5 \ Hz, \ 1H), \ 6.98 \ (dd, \ J = 12.0, \ 45.0 \ Hz, \ 1H), \ 7.20–7.41 \ (m, \ 12H), \ 7.62–7.70 \ (m, \ 4H), \ 7.76–7.83 \ (m, \ 4H); \\
\text{\textsuperscript{13}C NMR (CDCl\textsubscript{3})} & \ \delta \ 25.40 \ (dd, \ J = 3.4, \ 0.90 \ Hz), \ 35.44 \ (dd, \ J = 13.8, \ 14.0 \ Hz), \ 128.09 \ (d, \ J = 12.9 \ Hz), \ 128.48 \ (d, \ J = 12.5 \ Hz), \ 130.72 \ (d, \ J = 83.1 \ Hz), \ 130.89 \ (d, \ J = 10.5 \ Hz), \ 130.99 \ (d, \ J = 2.9 \ Hz), \ 131.32 \ (d, \ J = 2.9 \ Hz), \ 132.59 \ (d, \ J = 10.5 \ Hz), \ 132.70 \ (dd, \ J = 7.3, \ 83.6 \ Hz), \ 133.93 \ (d, \ J = 86.9 \ Hz), \ 159.53 \ (dd, \ J = 4.3, \ 68.3 \ Hz); \\
\text{\textsuperscript{31}P NMR (CDCl\textsubscript{3})} & \ \delta \ 28.93 \ (d, \ J = 5.7 \ Hz), \ 41.58 \ (d, \ J = 5.7 \ Hz). \\
\text{Found: C, 69.11%; H, 5.56%. Calcd for C\textsubscript{29}H\textsubscript{28}P\textsubscript{2}S\textsubscript{2}: C, 69.30%; H, 5.61%. m.p.: 149.0–150.5 ºC.}
\end{align*}
\]

(Z)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)-1-butene (3c)

\[
\begin{align*}
\text{IR (nujol)} & \ 2925, \ 2855, \ 1700, \ 1653, \ 1457, \ 1437, \ 1097 \ \text{cm}^{-1}; \\
\text{\textsuperscript{1}H NMR (CDCl\textsubscript{3})} & \ \delta \ 1.34 \ (s, \ 9H), \ 7.14–7.24 \ (m, \ 5H), \ 7.27–7.40 \ (m, \ 8H), \ 7.60–7.68 \ (m, \ 4H), \ 7.70–7.77 \ (m, \ 4H); \\
\text{\textsuperscript{13}C NMR (CDCl\textsubscript{3})} & \ \delta \ 32.67 \ (d, \ J = 2.9 \ Hz), \ 42.98 \ (dd, \ J = 10.5, \ 13.4 \ Hz), \ 127.55 \ (d, \ J = 12.4 \ Hz), \ 128.31 \ (d, \ J = 13.0 \ Hz), \ 130.87 \ (d, \ J = 2.5 \ Hz), \ 130.90 \ (d, \ J = 10.5 \ Hz), \ 131.01 \ (d, \ J = 2.9 \ Hz), \ 132.71 \ (d, \ J = 11.0 \ Hz), \ 132.87 \ (d, \ J = 82.0 \ Hz), \ 134.25 \ (d, \ J = 86.9 \ Hz), \ 135.71 \ (dd, \ J = 7.3, \ 80.3 \ Hz), \ 159.52 \ (dd, \ J = 6.6, \ 61.5 \ Hz); \\
\text{\textsuperscript{31}P NMR (CDCl\textsubscript{3})} & \ \delta \ 31.37 \ (d, \ J = 19.4 \ Hz), \ 36.64 \ (d, \ J = 19.4 \ Hz). \\
\text{Found: C, 69.66%; H, 5.83%. Calcd for C\textsubscript{30}H\textsubscript{30}P\textsubscript{2}S\textsubscript{2}: C, 69.74%; H, 5.85%. m.p.: 165.0–166.0 ºC.}
\end{align*}
\]

(Z)-1-Phenyl-1,2-bis(diphenylthiophosphinyl)ethene (3d)

\[
\begin{align*}
\text{IR (nujol)} & \ 2924, \ 2855, \ 2390, \ 2349, \ 1507, \ 1457, \ 1437, \ 645 \ \text{cm}^{-1}; \\
\text{\textsuperscript{1}H NMR (CDCl\textsubscript{3})} & \ \delta \ 6.92–7.20 \ (m, \ 8H), \ 7.22–7.43 \ (m, \ 10H), \ 7.62–7.70 \ (m, \ 4H), \ 7.73–7.81 \ (m, \ 4H); \\
\text{\textsuperscript{13}C NMR (CDCl\textsubscript{3})} & \ \delta \ 127.82, \ 127.96 \ (d, \ J = 1.5 \ Hz), \ 128.07 \ (d, \ J = 12.9 \ Hz), \ 128.21 \ (d, \ J = 3.8 \ Hz), \ 128.34 \ (d, \ J = 12.9 \ Hz), \ 130.93 \ (d, \ J = 2.9 \ Hz), \ 131.15 \ (d, \ J = 3.4 \ Hz), \ 131.57 \ (d, \ J = 10.5 \ Hz), \ 131.72 \ (d, \ J = 84.9 \ Hz), \ 131.94 \ (d, \ J = 10.5 \ Hz), \ 132.63 \ (d, \ J = 86.4 \ Hz), \ 138.97
\end{align*}
\]
(dd, $J = 8.1, 74.5$ Hz), 141.87 (dd, $J = 10.0, 16.6$ Hz), 150.76 (dd, $J = 1.8, 70.0$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 30.12 (d, $J = 11.4$ Hz), 35.71 (d, $J = 11.4$ Hz). Found: C, 71.38; H, 4.72%. Calcd for C$_{32}$H$_{26}$P$_2$S$_2$: C, 71.62; H, 4.88%. m.p.: 179.5–181.0 °C.

(Z)-2-(4-Acetylphenyl)-1,2-bis(diphenylthiophosphinyl)ethene (3e)

IR (nujol) 2924, 2854, 1734, 1568, 1456, 1438, 1386, 1265, 1098, 919 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 2.49 (s, 3H), 7.06 (dd, $J = 12.0, 38.0$ Hz, 1H), 7.12–7.20 (m, 4H), 7.23–7.42 (m, 8H), 7.54 (d, $J = 7.0$ Hz, 2H), 7.63–7.80 (m, 10H); $^{13}$C NMR (CDCl$_3$) $\delta$ 26.57, 127.80, 128.20 (d, $J = 12.9$ Hz), 128.41 (d, $J = 12.9$ Hz), 128.54 (d, $J = 3.4$ Hz), 131.16 (d, $J = 85.4$ Hz), 131.18 (d, $J = 2.9$ Hz), 131.27 (d, $J = 2.8$ Hz), 131.48 (d, $J = 11.0$ Hz), 131.90 (d, $J = 10.5$ Hz), 132.28 (d, $J = 85.4$ Hz), 136.09 (d, $J = 1.5$ Hz), 139.61 (dd, $J = 7.6, 74.4$ Hz), 146.48 (dd, $J = 10.5, 16.6$ Hz), 149.66 (d, $J = 69.8$ Hz), 197.33; $^{31}$P NMR (CDCl$_3$) $\delta$ 30.28 (d, $J = 11.4$ Hz), 35.44 (d, $J = 11.4$ Hz). Found: C, 70.60; H, 4.70%. Calcd for C$_{34}$H$_{28}$OP$_2$S$_2$: C, 70.57; H, 4.88%. m.p.: 175.5–177.0 °C.

(Z)-2-(3-Pyridinyl)-1,2-bis(diphenylthiophosphinyl)ethene (3f)

IR (nujol) 2924, 2854, 2389, 1734, 1653, 1558, 1457, 1437, 687, 651, 587 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) $\delta$ 6.32 (dd, $J = 5.0, 8.0$ Hz, 1H), 6.74–6.95 (m, 12H), 7.08 (dd, $J = 11.5, 38.0$ Hz, 1H) 7.66–7.71 (m, 1H), 7.77–7.85 (m, 4H), 7.88–7.97 (m, 4H), 8.15 (d, $J = 4.0$ Hz, 1H), 8.93 (s, 1H); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 122.14, 128.42 (d, $J = 12.5$ Hz), 128.56 (d, $J = 12.8$ Hz), 131.14 (d, $J = 2.9$ Hz), 131.16 (d, $J = 2.9$ Hz), 131.82 (d, $J = 10.9$ Hz), 131.90 (d, $J = 83.0$ Hz), 132.28 (d, $J = 10.5$ Hz), 133.22 (d, $J = 86.4$ Hz), 135.06 (d, $J = 2.9$ Hz), 138.25 (dd, $J = 10.5, 16.8$ Hz), 140.38 (dd, $J = 8.1, 66.4$ Hz), 147.13 (d, $J = 71.1$ Hz), 149.30 (d, $J = 3.8$ Hz), 149.40 (d, $J = 1.4$ Hz); $^{31}$P NMR (C$_6$D$_6$) $\delta$ 30.38 (d, $J = 11.4$ Hz), 35.66 (d, $J = 11.4$ Hz). Found: C, 68.97; H, 4.78%. Calcd for C$_{31}$H$_{25}$NP$_2$S$_2$: C, 69.26; H, 4.69%. m.p.: 182.0–183.0 °C.
**Ethyl (Z)-8,9-bis(diphenylthiophosphinyl)-8-nonenoate (3g)**

![Chemical structure](image)

IR (nujol) 2924, 2855, 1734, 1700, 1653, 1457, 1437, 749 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.12–1.21 (m, 4H), 1.24 (t, \(J = 7.0\) Hz, 3H), 1.46–1.60 (m, 4H), 2.21 (t, \(J = 7.5\) Hz, 2H), 2.38 (dt, \(J = 11.5, 8.0\) Hz, 2H), 4.11 (q, \(J = 7.5\) Hz, 2H), 6.94 (dd, \(J = 13.0, 41.5\) Hz, 1H), 7.22–7.40 (m, 12H), 7.66–7.78 (m, 8H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 14.15, 24.59, 28.48, 28.61, 30.43 (d, \(J = 2.9\) Hz), 34.04, 39.52 (dd, \(J = 12.9, 14.9\) Hz), 60.06, 128.09 (d, \(J = 12.4\) Hz), 128.26 (d, \(J = 12.4\) Hz), 130.92 (d, \(J = 2.9\) Hz), 131.04 (d, \(J = 10.5\) Hz), 131.10 (d, \(J = 83.5\) Hz), 131.21 (d, \(J = 2.9\) Hz), 132.22 (d, \(J = 11.0\) Hz), 133.45 (d, \(J = 86.4\) Hz), 134.71 (dd, \(J = 7.1, 81.1\) Hz), 151.95 (dd, \(J = 2.9, 68.3\) Hz), 173.52; \(^31\)P NMR (CDCl\(_3\)) \(\delta\) 29.30 (d, \(J = 17.9\) Hz), 39.67 (d, \(J = 17.9\) Hz). Found: C, 67.96; H, 6.32%. Calcd for C\(_{35}\)H\(_{38}\)O\(_2\)P\(_2\)S\(_2\): C, 68.16; H, 6.21%. m.p.: 44.0–46.5 °C.

**S-(Z)-10,11-Bis(diphenylthiophosphinyl)-10-undecenyl ethanethioate (3h)**

![Chemical structure](image)

IR (nujol) 2924, 2854, 1686, 1588, 1462, 1438, 1378, 1100, 1027, 749, 665 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.07–1.35 (m, 10H), 1.50–1.59 (m, 4H), 2.32 (s, 3H), 2.39 (dt, \(J = 11.0, 8.0\) Hz, 2H), 2.85 (t, \(J = 7.5\) Hz, 2H), 6.93 (dd, \(J = 12.5, 42.0\) Hz, 1H), 7.21–7.42 (m, 12H), 7.65–7.82 (m, 8H); \(^13\)C NMR (CDCl\(_3\)) \(\delta\) 28.54, 28.78, 28.84, 28.86, 28.95, 29.05, 29.31, 30.50, 30.53, 39.54 (dd, \(J = 12.9, 14.9\) Hz), 128.07 (d, \(J = 12.9\) Hz), 128.22 (d, \(J = 12.4\) Hz), 130.87 (d, \(J = 2.9\) Hz), 131.03 (d, \(J = 10.5\) Hz), 131.13 (d, \(J = 83.0\) Hz), 131.17 (d, \(J = 2.9\) Hz), 132.18 (d, \(J = 10.5\) Hz), 133.46 (d, \(J = 86.4\) Hz), 134.58 (dd, \(J = 7.1, 81.1\) Hz), 152.05 (dd, \(J = 2.9, 67.8\) Hz), 195.86; \(^31\)P NMR (CDCl\(_3\)) \(\delta\) 29.38 (d, \(J = 16.3\) Hz), 39.68 (d, \(J = 16.3\) Hz). Found: C, 67.34; H, 6.62%. Calcd for C\(_{37}\)H\(_{42}\)O\(_2\)P\(_2\)S\(_3\): C, 67.24; H, 6.41%. m.p.: 61.0–63.0 °C.

**Z-(Z)-Phenyl-2,3-bis(diphenylthiophosphinyl)-2-propen-1-ol (3i)**

![Chemical structure](image)

IR (nujol) 3392, 2924, 2855, 1700, 1451, 1439, 1378, 1097, 841, 706 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.76 (s, 1H), 5.78 (dd, \(J = 3.0, 8.5\) Hz, 1H), 7.01–7.07 (m, 2H), 55
$7.17-7.45$ (m, 20H), $7.54-7.61$ (m, 2H), $7.97-8.04$ (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 75.18 (dd, $J = 14.8, 17.3$ Hz), 126.71, 127.75 (d, $J = 13.0$ Hz), 127.95, 128.41 (d, $J = 12.4$ Hz), 128.50, 128.53 (d, $J = 13.1$ Hz), 128.55 (d, $J = 12.5$ Hz), 129.33 (d, $J = 53.9$ Hz), 130.01 (d, $J = 53.0$ Hz), 130.38 (d, $J = 10.1$ Hz), 130.90 (d, $J = 3.3$ Hz), 131.06 (d, $J = 11.0$ Hz), 131.29 (d, $J = 2.9$ Hz), 131.56 (d, $J = 3.4$ Hz), 132.08 (d, $J = 2.9$ Hz), 132.30 (d, $J = 85.9$ Hz), 132.77 (d, $J = 10.9$ Hz), 133.51 (d, $J = 11.5$ Hz), 135.49 (d, $J = 88.3$ Hz), 137.77 (dd, $J = 5.8, 80.3$ Hz), 139.91 (d, $J = 6.3$ Hz), 154.89 (dd, $J = 2.5, 68.6$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 27.62 (d, $J = 16.3$ Hz), 40.41 (d, $J = 16.3$ Hz).

Found: C, 70.04; H, 4.89%. Calcd for C$_{35}$H$_{28}$O$_2$S$_2$: C, 69.95; H, 4.98%. m.p.: 207.2–208.5 °C.

(Z),(Z)-4,4’-Bis[1,2-bis(diphenylthiophosphinyl)ethenyl]biphenyl (3j)

\[
\text{IR (nujol) 2925, 2855, 1456, 1436, 1377, 1256, 1099, 999, 826, 786, 743, 707, 644, 614, 609 \text{ cm}^{-1}; } \quad \text{^1H NMR (CDCl}_3\text{) } \delta 7.05-7.50 \text{ (m, 34H), 7.64-7.84 (m, 16H); } \quad \text{^13C NMR (CDCl}_3\text{) } \delta 126.12, 128.04 (d, J = 12.5$ Hz), 128.33 (d, $J = 12.9$ Hz), 128.72 (d, $J = 3.3$ Hz), 130.96 (d, $J = 2.4$ Hz), 131.15 (d, $J = 2.4$ Hz), 131.41 (d, $J = 10.5$ Hz), 131.48 (d, $J = 84.5$ Hz), 131.94 (d, $J = 10.5$ Hz), 132.61 (d, $J = 86.4$ Hz), 138.86 (dd, $J = 8.6, 74.5$ Hz), 139.51, 141.14 (dd, $J = 10.5, 16.8$ Hz), 150.39 (d, $J = 69.8$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 30.03 (d, $J = 13.0$ Hz), 35.93 (d, $J = 13.0$ Hz). HRMS (FAB$^+$, Matrix: NBA/CHCl$_3$) (m/z) Observed: 1071.1827 ($\Delta = +0.3$ ppm). Calcd for C$_{64}$H$_{50}$P$_2$S$_4$ [MH$^+$]: 1071.1824. m.p.: 217.5–219.5 °C.

(Z)-1-Phenyl-2-dicyclohexylthiophosphinyl-1-diphenylthiophosphinylethane (3k)

\[
\begin{align*}
\text{IR (nujol) 2923, 2852, 1436, 1377, 1091, 1000, 881, 868, 796, 764, 749, 696, 622, 519 \text{ cm}^{-1}; } \quad \text{^1H NMR (CDCl}_3\text{) } \delta 1.02-1.34 \text{ (m, 6H), 1.42-1.57 (m, 4H), 1.60-1.94 \text{ (m, 10H), 2.52-2.63 \text{ (m, 2H), 6.66 \text{ (dd, J = 12.0, 40.5 Hz, 1H), 6.93-7.08 \text{ (m, 5H), 7.25-7.32 \text{ (m, 4H), 7.33-7.40 \text{ (m, 2H), 7.68-7.76 \text{ (m, 4H); } \quad ^{13}\text{C NMR (CDCl}_3\text{) } \delta 25.65 \text{ (d, J = 1.9 Hz), 26.23 \text{ (d, J = 13.8 Hz), 26.31 \text{ (d, J = 13.8 Hz), 26.66 \text{ (d, J = 1.9}}}
\end{align*}
\]
Hz), 26.98 (d, J = 3.3 Hz), 39.61 (d, J = 49.6 Hz), 127.54 (d, J = 1.5 Hz), 127.76, 127.97 (d, J = 4.6 Hz), 128.00 (d, J = 12.9 Hz), 131.20 (d, J = 2.9 Hz), 131.54 (d, J = 10.5 Hz), 133.48 (d, J = 85.9 Hz), 142.50 (dd, J = 10.5, 14.4 Hz), 142.80 (dd, J = 9.1, 54.9 Hz), 153.46 (dd, J = 3.3, 68.3 Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 36.08 (d, J = 11.3 Hz), 52.21 (d, J = 11.3 Hz). Found: C, 70.03; H, 7.03%. Calcd for C$_{32}$H$_{59}$P$_2$S$_2$: C, 70.04; H, 6.98%. m.p.: 205.0–206.5 °C.

(R)-3,3-Dimethyl-1,2-bis(diphenylthiophosphinyl)butane (15)

IR (nujol) 2925, 2854, 1617, 1464, 1432, 1377, 1309, 1097, 1025, 999, 820, 715, 697, 627, 539 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.88 (s, 9H), 2.74–2.96 (m, 2H), 4.28–4.46 (m, 1H), 7.04–7.30 (m, 8H), 7.40–7.52 (m, 6H), 7.84–7.94 (m, 2H), 8.18–8.35 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 27.77 (dd, J = 4.8, 49.6 Hz), 30.40 (dd, J = 6.3 Hz), 36.26, 42.64 (dd, J = 2.8, 50.6 Hz), 128.21 (d, J = 12.4 Hz, 2C), 128.35 (d, J = 11.9 Hz), 128.52 (d, J = 12.5 Hz), 130.13 (d, J = 10.0 Hz), 130.64 (d, J = 2.8 Hz), 130.83 (d, J = 2.9 Hz), 131.12 (d, J = 10.0 Hz), 131.16 (d, J = 3.9 Hz), 131.32 (d, J = 2.9 Hz), 131.68 (d, J = 9.6 Hz), 132.25 (d, J = 76.4 Hz), 132.27 (d, J = 9.0 Hz), 133.47 (d, J = 78.8 Hz), 134.45 (d, J = 57.8 Hz), 135.08 (d, J = 65.9 Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 45.23 (d, J = 37.4 Hz), 48.72 (d, J = 37.4 Hz). HRMS (EI$^+$) (m/z) Observed: 518.1425 (Δ = +0.9 ppm). Calcd for C$_{32}$H$_{59}$P$_2$S$_2$ [M$^+$]: 518.1421. m.p.: 208.0–209.5 °C. $[\alpha]_D^{25}$ = -30 (c 0.61, CHCl$_3$). The R configuration was deduced from the assignment of 16.

(R)-3,3-Dimethyl-1,2-bis(diphenylphosphino)butane (16)

IR (neat) 3052, 2959, 2863, 2321, 1734, 1584, 1476, 1434, 1392, 1363, 1261, 1094, 801, 740, 694 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.99 (s, 9H), 1.87–1.97 (m, 1H), 2.21–2.31 (m, 2H), 6.80–6.87 (m, 2H), 7.13–7.42 (m, 12H), 7.44–7.55 (m, 4H), 7.60–7.67 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 27.92 (d, J = 16.1 Hz), 28.76 (d, J = 12.4 Hz), 35.49 (dd, J = 6.3, 22.5 Hz), 43.72 (dd, J = 14.3, 24.3 Hz), 127.65, 127.82 (d, J = 7.6 Hz), 127.97 (d, J = 5.3 Hz), 128.27, 128.30 (d, J = 7.3 Hz), 128.32 (d, J = 7.1 Hz), 128.45, 129.11, 132.04 (d, J =
17.3 Hz), 134.00 (dd, $J = 2.9, 20.6$ Hz), 134.43 (d, $J = 20.5$ Hz), 135.73 (dd, $J = 3.4, 21.5$ Hz), 137.02 (d, $J = 18.6$ Hz), 138.00 (d, $J = 16.8$ Hz), 138.30 (d, $J = 11.9$ Hz), 139.80 (d, $J = 16.3$ Hz); $^{31}$P NMR (CDCl$_3$) δ −15.81, −4.92. \([\alpha]_D^{25} = +15 \ (c \ 0.063, \text{CHCl}_3)\). The $R$ configuration was assigned by comparing the specific rotations of 16, (R)-1,2-bis(diphenylthiophosphinyl)propane \([\alpha]_D^{25} = +186 \ (c \ 1, \text{acetone})\),$^{23c}$ and (R)-[1,2-bis(diphenylthiophosphinyl)ethyl]-cyclohexane \([\alpha]_D^{25} = +103.3 \ (c \ 1, \text{THF})\).$^{23d}$
References and Notes


Chapter 1


(9) A number of hydrophosphonylations, the additions of pentavalent hydrophosphorous compounds, aiming at the synthesis of bidentate ligands, were reported: (a) Stockland, Jr., R. A.; Taylor, R. I.; Thompson, L. E.; Patel, P. B. Org. Lett. 2005, 7, 851–853 and references cited therein. (b) Allen, Jr., A.; Ma, L.; Lin, W. Tetrahedron Lett. 2002, 43, 3707–3710. (c) Reference 4f.


(15) One singlet signal appeared at $\delta = -41.6$ ppm in the $^{31}$P NMR spectrum of
diphenylphosphine in DMF. The addition of a stoichiometric amount of CuI to the DMF solution resulted in the formation of a clear solution and in broadening the signal with unambiguous splitting. Upon further addition of a stoichiometric amount of cesium carbonate, the signal disappeared and no new discrete signals were observed. These facts indicate that the copper-phosphorus bond of the complex \([\text{CuI} \cdot \text{HPPh}_2] \) would be labile and that many sorts of copper-phosphide species might be formed upon the addition of cesium carbonate.

(16) There can be an interaction between the copper and the acetylenic part of 5.

(17) One singlet signal appeared at \(\delta = -34.7 \text{ ppm} \) in the \(^{31}\text{P} \) NMR spectrum of 1a in DMF. The addition of a stoichiometric amount of CuI to the DMF solution furnished a clear homogeneous solution, which exhibited a broad and highly splitting signal at the same chemical shift. The dissolution of CuI indicates the formation of the complex \([\text{CuI} \cdot 1a] \). The NMR experiments suggest that the complex would not be robust.


(22) The radical desulfidation of 15 with TTMSS (1.2 equiv to 15) was also successful. However, after several attempts, separation of 15 and silicon-containing residue proved to be problematic in the author’s hands. Small amounts of the corresponding monooxides of 15 were generated during careful chromatographic purification on silica gel for isolation of 15. Purification using a solid phase technique resulted in unsatisfactory separation of 15 and the silicon-containing residue. The author expects that, if the TTMSS-mediated reduction and
purification of 15 were performed in a glove box filled with inert gas, one could isolate 15 in excellent yield.


Chapter 2

Palladium-Catalyzed *anti*-Hydrothiolation of 1-Alkynylphosphines

Treatment of 1-alkynylphosphine with thiol in the presence of a catalytic amount of palladium acetate results in regio- and stereoselective *anti*-hydrothiolation, yielding the corresponding (Z)-1-phosphino-2-thio-1-alkene.
Introduction

Metal-catalyzed addition of thiols to alkynes (hydrothiolation) is an important reaction for synthesizing 1-alkenylsulfides under mild conditions.\textsuperscript{1,2} In this chapter, the author discloses that hydrothiolation of 1-alkynylphosphines proceeds smoothly under palladium catalysis. In general, transition-metal-catalyzed hydrothiolation proceeds in a syn fashion.\textsuperscript{1,2f,3} In contrast, the present reaction represents a rare example of highly selective anti-hydrothiolation.\textsuperscript{2d,g,4} The products, (Z)-1-phosphino-2-thio-1-alkenes, are a new class of heteroatom-containing compounds and can potentially serve as useful ligands of transition metal complexes.\textsuperscript{5}

Results and Discussion

Treatment of 1-octynylidiphenylphosphine (1\textsuperscript{a}) with dodecanethiol\textsuperscript{6} (2\textsuperscript{a}) in the presence of a catalytic amount of palladium acetate in ethanol for 1 h at 25 °C provided (Z)-1-diphenylphosphino-2-dodecylthio-1-octene (3\textsuperscript{aa}) in 87% isolated yield and in 90% NMR yield (Table 1, entry 1).\textsuperscript{7} Other palladium complexes such as PdCl\textsubscript{2} and Pd\textsubscript{2}(dba)\textsubscript{3} also showed catalytic activity (entries 2 and 3). Nickel chloride and platinum chloride were inferior to palladium chloride (entries 4 and 5). Copper(II) chloride was ineffective (entry 6). The effect of solvent on the reaction was not significant (entries 7–11). The reactions proceeded in nonpolar solvents such as toluene and dichloromethane (entries 8 and 9) as well as in polar DMF (entry 10). It is worth noting that the reaction in water resulted in the highest yield of 3\textsuperscript{aa} (entry 11), although the reaction was heterogeneous.\textsuperscript{8} To guarantee a wide scope of substrates, ethanol was selected as the best solvent.\textsuperscript{9}
Table 1. Hydrothiolation of 1-Octynyldiphenylphosphine (1a) with Dodecanethiol (2a)\(^a\)

\[
\begin{align*}
\text{entry} & \quad \text{catalyst} & \quad \text{solvent} & \quad \text{yield \%}^b \\
1 & \text{Pd(OAc)}_2 & \text{ethanol} & 90 (87) \\
2 & \text{PdCl}_2 & \text{ethanol} & 86 \\
3 & \text{Pd}_2(\text{dba})_3^c & \text{ethanol} & 85 \\
4 & \text{PtCl}_2 & \text{ethanol} & 78 \\
5 & \text{NiCl}_2 & \text{ethanol} & 58 \\
6 & \text{CuCl}_2 & \text{ethanol} & 17 \\
7 & \text{Pd(OAc)}_2 & \text{THF} & 86 \\
8 & \text{Pd(OAc)}_2 & 1,2\text{-dichloroethane} & 89 \\
9 & \text{Pd(OAc)}_2 & \text{toluene} & 89 \\
10 & \text{Pd(OAc)}_2 & \text{DMF} & 79 \\
11 & \text{Pd(OAc)}_2 & \text{water} & 92 \\
\end{align*}
\]

\(^a\) Conditions: 1a (0.50 mmol), 2a (0.60 mmol), solvent (3.0 mL), 25 °C, 1 h. \(^b\) Based on \(^{31}\)P NMR with a sufficient first decay period. An isolated yield is in parenthesis. 
\(^c\) 2.5 mol\% of Pd\(_2(\text{dba})_3\) was used.

A variety of 1-alkynylphosphines underwent the hydrothiolation reactions (Table 2). Sterically demanding 1-alkynylphosphines including 1b and 1c underwent the hydrothiolation smoothly (entries 1 and 2). Phenylethynylphosphine 1d as well as terminal ethynylphosphine 1e afforded the corresponding anti-adducts in good yields (entries 3 and 4). A variety of functional groups such as keto and hydroxy groups were compatible under the reaction conditions (entries 5–7). Pyridine-containing 3ia (entry 8) can be useful for constructing supramolecular architectures. The addition of 2a to bis(diphenylphosphino)ethyne (1j) took place to yield the corresponding anti-adduct 3ja in 55% yield (entry 9). Alkynyldicyclohexylphosphine 1k also underwent the hydrothiolation, although a longer reaction time was required to complete the reaction (entry 10).
The scope of thiol 2 was satisfactory (entries 11–18). Not only bulky thiol 2b but also thiols having an additional functionality such as 2e–i added to 1a under the palladium catalysis. The successful hydrothiolation with protected cysteine 2h implies that the reaction would be

---

**Table 2. Palladium-Catalyzed Hydrothiolation of 1-Alkynylphosphines 1 with Thiols 2**

![Chemical Equation Image]

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
<th>R^1</th>
<th>R^2</th>
<th>2</th>
<th>R^3</th>
<th>yield (%)^b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1b</td>
<td>t-Bu</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>93 (3ba)</td>
</tr>
<tr>
<td>2</td>
<td>1c</td>
<td>i-Pr</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>83 (3ca)</td>
</tr>
<tr>
<td>3</td>
<td>1d</td>
<td>Ph</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>81 (3da)</td>
</tr>
<tr>
<td>4</td>
<td>1e</td>
<td>H</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>78 (3ea)</td>
</tr>
<tr>
<td>5</td>
<td>1f</td>
<td>EtO(_2)C(CH(_2))(_6)</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>77 (3fa)</td>
</tr>
<tr>
<td>6</td>
<td>1g</td>
<td>4-Ac-C(_6)H(_4)</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>75 (3ga)</td>
</tr>
<tr>
<td>7</td>
<td>1h</td>
<td>PhCH(OH)</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>72 (3ha)</td>
</tr>
<tr>
<td>8</td>
<td>1i</td>
<td>3-pyridyl</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>78 (3ia)</td>
</tr>
<tr>
<td>9</td>
<td>1j</td>
<td>Ph(_2)P</td>
<td>Ph</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>55 (3ja)</td>
</tr>
<tr>
<td>10</td>
<td>1k</td>
<td>Ph</td>
<td>c-C(<em>6)H(</em>{11})</td>
<td>2a</td>
<td>n-C(<em>{12})H(</em>{25})</td>
<td>82 (3ka)</td>
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<tr>
<td>11</td>
<td>1a</td>
<td>n-C(<em>6)H(</em>{13})</td>
<td>Ph</td>
<td>2b</td>
<td>t-Bu</td>
<td>62 (3ab)</td>
</tr>
<tr>
<td>12</td>
<td>1a</td>
<td>n-C(<em>6)H(</em>{13})</td>
<td>Ph</td>
<td>2c</td>
<td>Ph</td>
<td>82 (3ac)</td>
</tr>
<tr>
<td>13</td>
<td>1a</td>
<td>n-C(<em>3)H(</em>{13})</td>
<td>Ph</td>
<td>2d</td>
<td>2-furfuryl</td>
<td>75 (3ad)</td>
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<tr>
<td>14</td>
<td>1a</td>
<td>n-C(<em>3)H(</em>{13})</td>
<td>Ph</td>
<td>2e</td>
<td>cinnamyl</td>
<td>60 (3ae)</td>
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<tr>
<td>15</td>
<td>1a</td>
<td>n-C(<em>6)H(</em>{13})</td>
<td>Ph</td>
<td>2f</td>
<td>4-Br-C(_6)H(_4)</td>
<td>80 (3af)</td>
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<tr>
<td>16</td>
<td>1a</td>
<td>n-C(<em>3)H(</em>{13})</td>
<td>Ph</td>
<td>2g</td>
<td>HO(CH(_2))(_3)</td>
<td>74 (3ag)</td>
</tr>
<tr>
<td>17</td>
<td>1a</td>
<td>n-C(<em>6)H(</em>{13})</td>
<td>Ph</td>
<td>2h</td>
<td>N-acetylCys(^f)</td>
<td>66 (3ah)</td>
</tr>
<tr>
<td>18</td>
<td>1k</td>
<td>Ph</td>
<td>c-C(<em>6)H(</em>{11})</td>
<td>2i</td>
<td>4-MeO-C(_6)H(_4)</td>
<td>70 (3ki)</td>
</tr>
</tbody>
</table>

---

^a Conditions: 1 (0.50 mmol), 2 (0.60 mmol), Pd(OAc)\(_2\) (0.025 mmol), ethanol (3.0 mL), 25 °C, 1 h. ^b Isolated yields. ^c 1,2-Dichloroethane was used as a solvent. ^d The reaction was performed with 10 mol% of Pd(OAc)\(_2\) in ethanol/1,2-dichloroethane (2 mL:1 mL) for 16 h. ^e The reaction was performed for 4 h. ^f N-Acetyl-L-cysteine was used.
applicable to modification of proteins and peptides (entry 17). The X-ray crystallographic analysis of 3ki verified the Z stereochemistry of the products.

The reaction was efficient enough to allow for multiple hydrothiolation (Scheme 1). Treatment of biphenyl-based di(alkynylphosphine) 1l with 2a in the presence of a catalytic amount of Pd(OAc)$_2$ in 1,2-dichloroethane provided the corresponding bifunctional diphosphine 3la in good yield. Di(phenylethynyl)phenylphosphine (1m) underwent hydrothiolation twice to yield 3ma. However, attempted 3-fold hydrothiolation of tri(phenylethynyl)phosphine resulted in the formation of mixtures of the corresponding mono-, di- and triadducts. 1,3-Propanedithiol (2j) reacted with 1a to afford an 81% yield of 3aj. Such products having multicoordination sites can be useful building blocks for supramolecular architecture.

Scheme 1. Multiple Hydrothiolations
**Reaction Mechanism.** Judging from the regio- and stereoselectivity of the reaction, the author is tempted to assume the reaction mechanism as follows (Scheme 2). A palladium salt initially reacts with 1 to generate a palladium(1-alkynylphosphine) complex 4. Thiol 2 attacks the carbon–carbon triple bond that is activated by the coordination to form intermediate 6. Protonolysis of 6 affords 3 and regenerates the initial palladium species. The stereochemistry of the products suggests that the reaction should not proceed via oxidative addition of the thiol to a palladium complex followed by thiopalladation or hydropalladation\(^1,3\) but via the coordination-assisted activation of the triple bond. The regioselectivity in the reaction of \(1g\) strongly supports his plausible mechanism that involves the transition state 5. Without the coordination of the phosphorus center of \(1g\) to the palladium, the regioselectivity of the reaction of \(1g\) could be opposite because of the strong electron-withdrawing nature of the acetyl group. It is also worth noting that the corresponding phosphine oxide of \(1a\) completely resisted the reaction.

**Scheme 2.** Plausible Reaction Mechanism

---

\(\text{Reaction Mechanism.}\) **Judging from the regio- and stereoselectivity of the reaction, the**
**author is tempted to assume the reaction mechanism as follows (Scheme 2). A palladium salt**
**initially reacts with 1 to generate a palladium(1-alkynylphosphine) complex 4. Thiol 2 attacks**
**the carbon–carbon triple bond that is activated by the coordination to form intermediate 6.**
**Protonolysis of 6 affords 3 and regenerates the initial palladium species. The stereochemistry of**
**the products suggests that the reaction should not proceed via oxidative addition of the thiol to a**
**palladium complex followed by thiopalladation or hydropalladation\(^1,3\) but via the**
**coordination-assisted activation of the triple bond. The regioselectivity in the reaction of \(1g\)**
**strongly supports his plausible mechanism that involves the transition state 5. Without the**
**coordination of the phosphorus center of \(1g\) to the palladium, the regioselectivity of the reaction**
**of \(1g\) could be opposite because of the strong electron-withdrawing nature of the acetyl group.**
**It is also worth noting that the corresponding phosphine oxide of \(1a\) completely resisted the**
**reaction.**

**Scheme 2.** Plausible Reaction Mechanism

---

\(\text{Scheme 2. Plausible Reaction Mechanism}\)
Conclusion

The author has found a concise method for the synthesis of an array of (Z)-1-phosphino-2-thio-1-alkenes through the hydrothiolation of 1-alkynylphosphines. The method will create a new type of heteroatom-containing molecules which find applications in various fields of chemical science.
Experimental Procedure

Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in C$_6$D$_6$ or CD$_3$OD. Chemical shifts (δ) are in parts per million relative to benzene at 7.15 ppm for $^1$H and relative to at 128.0 ppm for $^{13}$C or methanol at 3.34 ppm for $^1$H and at 49.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in C$_6$D$_6$ or CD$_3$OD with 85% H$_3$PO$_4$ solution as an external standard. NMR yields were determined by fine $^{31}$P NMR spectra with (MeO)$_3$P=O as an internal standard. The first delay of $^{31}$P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was a gift from Hokko Chemical Industry Co., Ltd. Starting 1-alkynylphosphines 1 were prepared by the reactions of lithium acetylidies with chlorophosphines or by nickel-catalyzed reactions of alkynes with chlorodiphenylphosphine described in Chapter 1. Palladium(II) acetate was obtained from TCI. All reactions were carried out under argon atmosphere.

Typical Procedure for Palladium-Catalyzed anti-Hydrothiolation of 1-Alkynylphosphines

Palladium acetate (6 mg, 0.025 mmol) was placed in a 20-mL reaction flask under argon. A solution of 1a (0.15 g, 0.50 mmol) in ethanol (3.0 mL) was added to the flask. Dodecanethiol (2a, 0.12 g, 0.60 mmol) was added, and the resulting solution was stirred for 1 h at 25 °C. The solvent was evaporated under reduced pressure, and the crude product obtained was
chromatographed on silica gel to afford 3aa (0.22 g, 0.44 mmol, 87 %).

Characterization Data

(Z)-1-Diphenylphosphino-2-dodecylthio-1-octene (3aa)

IR (neat) 3053, 2927, 2854, 2342, 1585, 1555, 1480, 1456, 1433, 1378, 1094, 1027, 739, 695 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.88 (t, \(J = 7.5\) Hz, 3H), 0.91 (t, \(J = 7.5\) Hz, 3H), 1.10–1.36 (m, 24H), 1.45 (tt, \(J = 7.0, 7.5\) Hz, 2H), 1.57 (tt, \(J = 7.0, 7.5\) Hz, 2H), 2.32 (t, \(J = 7.0\) Hz, 2H), 2.53 (t, \(J = 7.0\) Hz, 2H), 6.33 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.50–7.57 (m, 4H); \(^1\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 14.29, 14.38, 23.03, 23.10, 29.03, 29.08, 29.34 (d, \(J = 1.4\) Hz), 29.59, 29.81, 29.92, 30.05, 30.10 (2C), 30.19, 31.70 (d, \(J = 6.3\) Hz), 31.97, 32.32, 38.24 (d, \(J = 4.3\) Hz), 128.33, 128.35 (d, \(J = 14.9\) Hz), 128.68 (d, \(J = 6.6\) Hz), 133.14 (d, \(J = 19.0\) Hz), 140.63 (d, \(J = 12.4\) Hz), 153.60 (d, \(J = 24.8\) Hz); \(^{31}\)P NMR (C\(_6\)D\(_6\)) \(\delta\) –25.65. Found: C, 77.13; H, 10.10%. Calcd for C\(_{32}\)H\(_{49}\)PS: C, 77.37; H, 9.94%.

(Z)-3,3-Dimethyl-1-diphenylphosphino-2-dodecylthio-1-butene (3ba)

IR (neat) 3053, 2924, 2854, 1585, 1555, 1464, 1433, 1356, 1231, 1096, 951, 835, 739, 695 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.91 (t, \(J = 7.0\) Hz, 3H), 1.19 (s, 9H), 1.16–1.36 (m, 18H), 1.60 (tt, \(J = 7.5, 7.5\) Hz, 2H), 2.98 (dd, \(J = 1.5, 7.5\) Hz, 2H), 6.75 (s, 1H), 7.02–7.07 (m, 2H), 7.08–7.13 (m, 4H), 7.51–7.57 (m, 4H); \(^1\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 14.33, 23.08, 29.29, 29.64 (2C), 29.77, 29.92, 30.01, 30.06, 30.07, 30.12, 32.30, 38.70 (d, \(J = 12.0\) Hz), 41.30 (d, \(J = 3.8\) Hz), 128.47, 128.74 (d, \(J = 6.3\) Hz), 133.10 (d, \(J = 10.0\) Hz), 133.28 (d, \(J = 6.8\) Hz), 140.82 (d, \(J = 12.9\) Hz), 163.66 (d, \(J = 22.5\) Hz); \(^{31}\)P NMR (C\(_6\)D\(_6\)) \(\delta\) –24.06. Found: C, 76.65; H, 9.76%. Calcd for C\(_{30}\)H\(_{45}\)PS: C, 76.87; H, 9.68%.

(Z)-3-Methyl-1-diphenylphosphino-2-dodecylthio-1-butene (3ca)

IR (neat) 3053, 2959, 2925, 2854, 2364, 1540, 1479, 1458, 1433, 1380, 1094, 740, 695 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.91 (t, \(J = 7.0\) Hz, 3H), 1.10 (d, \(J = 7.0\) Hz,
6H), 1.12–1.35 (m, 18H), 1.45 (tt, $J = 7.5, 7.5$ Hz, 2H), 2.50 (sept, $J = 7.0$ Hz, 1H), 2.56 (t, $J = 7.5$ Hz, 2H), 6.43 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.50–7.57 (m, 4H); $^{13}$C NMR ($C_6D_6$) δ 14.33, 22.55, 23.08, 29.05, 29.58, 29.78, 29.90, 30.02, 30.07, 30.08, 30.13, 32.30, 32.86 (d, $J = 7.1$ Hz), 35.27 (d, $J = 4.4$ Hz), 127.27 (d, $J = 8.1$ Hz), 128.34, 128.71 (d, $J = 6.6$ Hz), 133.09 (d, $J = 19.6$ Hz), 140.78 (d, $J = 12.9$ Hz), 159.70 (d, $J = 23.9$ Hz); $^{31}$P NMR ($C_6D_6$) δ –25.61. Found: C, 76.64%; H, 9.66%. Calcd for $C_{29}H_{43}PS$: C, 76.60%; H, 9.53%.

(Z)-2-Diphenylphosphino-1-dodecylthio-1-phenylethene (3da)

IR (neat) 3053, 2924, 2854, 2333, 1585, 1540, 1480, 1433, 1305, 1232, 1094, 1027, 740, 695 cm$^{-1}$; $^1$H NMR ($C_6D_6$) δ 0.91 (t, $J = 7.0$ Hz, 3H), 0.95–1.36 (m, 20H), 2.33 (t, $J = 7.5$ Hz, 2H), 6.73 (s, 1H), 7.01–7.13 (m, 9H), 7.49–7.57 (m, 6H); $^{13}$C NMR ($C_6D_6$) δ 14.38, 23.10, 28.68, 29.43, 29.80, 29.83, 29.97, 29.99, 30.08 (2C), 32.31, 33.14 (d, $J = 4.4$ Hz), 128.40 (d, $J = 2.0$ Hz), 128.49, 128.60, 128.71, 128.78 (d, $J = 6.8$ Hz), 133.01 (d, $J = 10.5$ Hz), 133.31 (d, $J = 19.6$ Hz), 140.26 (d, $J = 4.8$ Hz), 140.41 (d, $J = 12.0$ Hz), 152.42 (d, $J = 25.8$ Hz); $^{31}$P NMR ($C_6D_6$) δ –23.27. Found: C, 78.37%; H, 8.46%. Calcd for $C_{32}H_{41}PS$: C, 78.64%; H, 8.46%.

(Z)-2-Diphenylphosphino-1-dodecylthioethene (3ea)

IR (neat) 3053, 2925, 2853, 1586, 1532, 1467, 1433, 1269, 1097, 1027, 820, 740, 695 cm$^{-1}$; $^1$H NMR ($C_6D_6$) δ 0.92 (t, $J = 7.0$ Hz, 3H), 1.06–1.42 (m, 20H), 2.33 (t, $J = 7.5$ Hz, 2H), 6.22 (d, $J = 10.5$ Hz, 1H), 6.72 (dd, $J = 10.5, 15.5$ Hz, 1H), 7.01–7.05 (m, 2H), 7.06–7.11 (m, 4H), 7.48–7.54 (m, 4H); $^{13}$C NMR ($C_6D_6$) δ 14.36, 23.10, 28.76, 29.50, 29.80, 29.87, 30.01, 30.08 (2C), 30.70, 32.31, 34.74 (d, $J = 4.8$ Hz), 124.38 (d, $J = 11.0$ Hz), 128.50, 128.73 (d, $J = 6.6$ Hz), 133.11 (d, $J = 19.1$ Hz), 139.37 (d, $J = 10.5$ Hz), 144.17 (d, $J = 27.1$ Hz); $^{31}$P NMR ($C_6D_6$) δ –25.73. Found: C, 75.90%; H, 9.33%. Calcd for $C_{20}H_{37}PS$: C, 75.68%; H, 9.04%.
Ethyl (Z)-9-diphenylphosphino-8-dodecylthio-8-nonenoate (3fa)

IR (neat) 2926, 2854, 1737, 1467, 1434, 1374, 1181, 1096, 1027, 740, 696 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.91 (t, \(J = 7.0\) Hz, 3H), 0.97 (t, \(J = 7.5\) Hz, 3H), 1.10–1.36 (m, 22H), 1.40–1.60 (m, 6H), 2.12 (t, \(J = 7.5\) Hz, 2H), 2.27 (t, \(J = 7.5\) Hz, 2H), 2.52 (t, \(J = 7.5\) Hz, 2H), 3.97 (q, \(J = 7.5\) Hz, 2H), 6.32 (s, 1H), 7.02–7.08 (m, 2H), 7.09–7.16 (m, 4H), 7.10–7.16 (m, 4H), 7.50–7.56 (m, 4H); \(^13\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 14.33, 14.36, 23.09, 25.23, 28.96, 29.03, 29.11 (d, \(J = 1.9\) Hz), 29.16, 29.59, 29.79, 29.92, 30.04, 30.08, 30.09, 30.19, 31.71 (d, \(J = 6.1\) Hz), 32.31, 34.27, 38.09 (d, \(J = 3.8\) Hz), 59.96, 128.35, 128.52 (d, \(J = 8.6\) Hz), 128.70 (d, \(J = 6.8\) Hz), 133.13 (d, \(J = 19.1\) Hz), 140.61 (d, \(J = 11.9\) Hz), 153.43 (d, \(J = 24.9\) Hz), 172.85; \(^{31}\)P NMR (C\(_6\)D\(_6\)) \(\delta\) –25.68. Found: C, 73.72%; H, 9.44%. Calcd for C\(_{35}\)H\(_{53}\)O\(_2\)P\(_2\): C, 73.90; H, 9.39%.

(Z)-1-(4-Acetylphenyl)-2-diphenylphosphino-1-dodecylthioethene (3ga)

IR (neat) 3053, 2925, 2854, 1684, 1600, 1433, 1402, 1356, 1265, 1178, 956, 853, 742, 695 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.91 (t, \(J = 7.0\) Hz, 3H), 1.01–1.36 (m, 20H), 2.10 (s, 3H), 2.92 (t, \(J = 7.5\) Hz, 2H), 6.80 (d, \(J = 1.5\) Hz, 1H), 7.03–7.09 (m, 2H), 7.10–7.15 (m, 4H), 7.46 (d, \(J = 8.5\) Hz, 2H), 7.50–7.57 (m, 4H), 7.74 (d, \(J = 8.5\) Hz, 2H); \(^13\)C NMR (C\(_6\)D\(_6\)) \(\delta\) 14.35, 23.08, 26.16, 28.70 (d, \(J = 1.0\) Hz), 29.42, 29.78, 29.82, 29.94, 29.99, 30.06 (2C), 32.29, 33.17 (d, \(J = 4.3\) Hz), 128.36 (d, \(J = 2.4\) Hz), 128.70, 128.81, 128.87 (d, \(J = 6.6\) Hz), 133.33 (d, \(J = 20.0\) Hz), 135.30 (d, \(J = 11.4\) Hz), 137.28, 139.95 (d, \(J = 11.5\) Hz), 144.12 (d, \(J = 4.8\) Hz), 150.99 (d, \(J = 26.3\) Hz), 195.80; \(^{31}\)P NMR (C\(_6\)D\(_6\)) \(\delta\) –22.25. Found: C, 77.20%; H, 8.42%. Calcd for C\(_{33}\)H\(_{35}\)OP\(_2\): C, 76.94; H, 8.17%.

(Z)-3-Diphenylphosphino-2-dodecylthio-1-phenyl-2-propen-1-ol (3ha)

IR (neat) 3388, 3055, 2925, 2854, 2333, 1585, 1454, 1435, 1378, 1187, 1068, 865, 741, 697 cm\(^{-1}\); \(^1\)H NMR (C\(_6\)D\(_6\)) \(\delta\) 0.91 (t, \(J = 7.0\) Hz, 3H), 1.00–1.37 (m, 20H), 2.16 (d, \(J = 4.5\) Hz, 1H), 2.43–2.57 (m, 2H), 5.23 (d, \(J = 4.5\) Hz, 1H),
7.00–7.16 (m, 10H), 7.40 (d, J = 7.5 Hz, 2H), 7.46–7.55 (m, 4H); \(^{13}\)C NMR (CD\(_6\)) \(\delta\) 14.36, 23.09, 28.97, 29.49, 29.79, 29.87, 29.96, 30.01, 30.08 (2C), 32.30, 33.75 (d, J = 6.8 Hz), 77.55 (d, J = 4.3 Hz), 127.17, 128.52 (2C), 128.54, 128.55, 128.75 (d, J = 6.6 Hz), 128.76 (d, J = 6.6 Hz), 132.71 (d, J = 10.0 Hz), 133.21 (d, J = 19.6 Hz), 133.24 (d, J = 19.0 Hz), 139.92 (d, J = 11.9 Hz), 140.19 (d, J = 11.5 Hz), 142.36 (d, J = 1.5 Hz), 153.65 (d, J = 24.4 Hz); \(^{31}\)P NMR (CD\(_6\)) \(\delta\) –25.54.  Found: C, 76.29; H, 8.50%.  Calcd for C\(_{33}\)H\(_{43}\)OP\(_S\): C, 76.41; H, 8.35%.

(Z)-2-Diphenylphosphino-1-dodecylthio-1-(3-pyridyl)ethene (3ia)

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\text{IR (neat) 2925, 2854, 1566, 1459, 1433, 1410, 1184, 1095, 1025, 740, 695 cm}\^-1; \quad \text{\(^1\)H NMR (CD\(_6\)) } \delta 0.91 (t, J = 7.0 Hz, 3H), 0.96–1.36 (m, 20H), 2.19 (t, J = 7.5 Hz, 2H), 6.67 (s, 1H), 6.67 (dd, J = 5.0, 8.5 Hz, 1H), 7.03–7.13 (m, 6H), 7.46 (ddd, J = 1.5, 2.5, 8.5 Hz, 1H), 7.47–7.52 (m, 4H), 8.45 (dd, J = 1.5, 5.0 Hz, 1H), 9.00 (d, J = 2.5 Hz, 1H); \quad \text{\(^{13}\)C NMR (CD\(_6\)) } \delta 14.36, 23.09, 28.59, 29.37, 29.79 (2C), 29.82, 29.97, 30.06 (2C), 32.30, 33.05 (d, J = 3.9 Hz), 123.13, 128.64, 128.84 (d, J = 6.8 Hz), 133.28 (d, J = 19.5 Hz), 134.87 (d, J = 2.4 Hz), 135.14 (d, J = 11.5 Hz), 135.51 (d, J = 4.8 Hz), 139.88 (d, J = 11.4 Hz), 148.72 (d, J = 26.6 Hz), 149.63 (d, J = 2.0 Hz), 149.90; \quad \text{\(^{31}\)P NMR (CD\(_6\)) } \delta –22.64.  \text{ Found: C, 76.02; H, 8.36%.  Calcd for C\(_{31}\)H\(_{40}\)NP\(_S\): C, 76.03; H, 8.23%}.

(Z)-1,2-Bis(diphenylphosphino)-1-dodecylthioethene (3ja)

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\text{IR (neat) 3070, 2924, 2853, 2364, 1719, 1654, 1434, 1307, 1237, 1152, 1091 cm}\^-1; \quad \text{\(^1\)H NMR (CD\(_6\)) } \delta 0.91 (t, J = 7.0 Hz, 3H), 1.07–1.35 (m, 18H), 1.56 (tt, J = 7.0, 7.5 Hz, 2H), 3.00 (dt, J = 1.0, 7.5 Hz, 2H), 6.67 (dd, J = 2.0, 4.5 Hz, 1H), 6.97–7.08 (m, 12H), 7.41–7.53 (m, 8H); \quad \text{\(^{13}\)C NMR (CD\(_6\)) } \delta 14.33, 23.08, 28.93, 29.50, 29.79, 29.86, 30.00, 30.07, 30.08, 30.39 (d, J = 2.4 Hz), 32.30, 33.86 (dd, J = 5.8, 18.1 Hz), 128.45, 128.67 (d, J = 6.3 Hz), 128.89 (d, J = 7.1 Hz), 129.34, 133.15 (d, J = 19.1 Hz), 134.45 (d, J = 20.1 Hz), 136.07 (d, J = 12.9 Hz), 140.17 (dd, J = 1.5, 12.5 Hz), 140.83 (dd, J = 3.8, 16.3 Hz), 152.11 (dd, J = 20.5, 41.0 Hz); \quad \text{\(^{31}\)P NMR (CD\(_6\)) } \delta –22.93, –4.30.  \text{ Found: C, 76.68; H, 7.74%.  Calcd for}
(Z)-2-Dicyclohexylphosphino-1-dodecylthio-1-phenylethene (3ka)

IR (neat) 2926, 2853, 1538, 1486, 1447, 1178, 1073, 1029, 1000, 907, 850, 752, 697 cm⁻¹; ¹H NMR (C₆D₆) δ 0.89 (t, J = 7.0 Hz, 3H), 1.01–1.42 (m, 30H), 1.54–2.00 (m, 12H), 2.37 (t, J = 7.5 Hz, 2H), 6.36 (d, J = 4.0 Hz, 1H), 7.04–7.17 (m, 3H), 7.62 (d, J = 7.0 Hz, 2H); ¹³C NMR (C₆D₆) δ 14.37, 23.10, 26.91, 27.56, 27.65, 28.70 (d, J = 4.8 Hz), 29.93, 30.04, 30.06, 30.09, 30.10, 31.08 (d, J = 16.8 Hz), 32.32, 33.07 (d, J = 3.9 Hz), 35.26 (d, J = 12.4 Hz), 128.35, 128.43, 128.63, 128.89 (d, J = 19.5 Hz), 141.61 (d, J = 5.3 Hz), 154.16 (d, J = 25.3 Hz); ³¹P NMR (C₆D₆) δ –19.44. Found: C, 76.86; H, 10.58%. Calcd for C₃₂H₅₃PS: C, 76.75; H, 10.67%.

4,4'-Bis((Z)-2-diphenylphosphino-1-dodecylthio-1-ethenyl)biphenyl (3la)

IR (nujol) 2923, 2854, 1685, 1583, 1457, 1377, 1304, 1268, 1092, 1026, 915, 815, 744, 698 cm⁻¹; ¹H NMR (C₆D₆) δ 0.91 (t, J = 7.0 Hz, 6H), 1.03–1.34 (m, 36H), 1.38 (tt, J = 7.0, 7.5 Hz, 4H), 2.42 (t, J = 7.0 Hz, 4H), 6.86 (d, J = 1.5 Hz, 2H), 7.04–7.09 (m, 4H), 7.10–7.07 (m, 8H), 7.46 (d, J = 8.5 Hz, 4H), 7.56–7.62 (m, 8H), 7.63 (d, J = 8.5 Hz, 4H); ¹³C NMR (C₆D₆) δ 14.36, 23.09, 28.72 (d, J = 1.0 Hz), 29.47, 29.79, 29.85, 30.01 (2C), 30.07 (2C), 32.29, 33.30 (d, J = 3.4 Hz), 127.38, 128.58, 128.84 (d, J = 6.8 Hz), 128.98 (d, J = 1.9 Hz), 133.34 (d, J = 19.5 Hz), 133.51 (d, J = 10.5 Hz), 139.44 (d, J = 4.8 Hz), 140.38 (d, J = 11.9 Hz), 140.87, 151.83 (d, J = 26.3 Hz); ³¹P NMR (C₆D₆) δ –22.85. Found: C, 78.57; H, 8.19%. Calcd for C₆₄H₇₀P₂S₂: C, 78.81; H, 8.27%. m.p.: 77.0–79.0 °C.
Di[(Z)-2-Dodecylthio-2-phenylethenyl]phenylphosphine (3ma)

IR (neat) 3054, 2924, 2854, 1486, 1466, 1434, 1074, 1028, 909, 741, 697 cm⁻¹;

¹H NMR (CDCl₃) δ 0.91 (t, J = 7.0 Hz, 6H), 1.06–1.37 (m, 36H), 1.40–1.50 (m, 4H),
2.34–2.47 (m, 4H), 6.70 (d, J = 1.0 Hz, 2H), 7.04–7.21 (m, 9H), 7.60–7.65 (m, 4H),
7.70–7.77 (m, 2H); ¹³C NMR (CDCl₃) δ 14.36, 23.10, 28.88 (d, J = 1.0 Hz), 29.55,
29.82, 29.91, 30.08, 30.12 (2C), 30.20, 32.32, 33.19 (d, J = 4.3 Hz), 128.39, 128.41 (2C),
128.65, 128.80 (d, J = 6.3 Hz), 132.93 (d, J = 19.6 Hz), 135.11 (d, J = 9.5 Hz), 140.52 (d, J = 4.8 Hz),
141.26 (d, J = 12.9 Hz), 150.41 (d, J = 26.8 Hz); ³¹P NMR (CDCl₃) δ –39.13.  Found: C, 77.54;
H, 9.49%.  Calcd for C₄₆H₆₇PS₂: C, 77.26; H, 9.44%.

(Z)-2-(1,1-Dimethylethylthio)-1-diphenylphosphino-1-octene (3ab)

IR (neat) 3053, 2927, 2855, 1585, 1458, 1433, 1364, 1158, 1095, 1027, 740, 695 cm⁻¹;
¹H NMR (CDCl₃) δ 0.87 (t, J = 7.0 Hz, 3H), 1.16–1.30 (m, 6H), 1.31 (s, 9H),
1.65 (tt, J = 7.0, 7.5 Hz, 2H), 2.41 (t, J = 7.5 Hz, 2H), 6.62 (s, 1H), 7.01–7.06 (m, 2H),
7.07–7.13 (m, 4H), 7.48–7.54 (m, 4H); ¹³C NMR (CDCl₃) δ 14.27, 23.01, 29.08, 29.52 (d, J = 2.4 Hz),
31.96, 32.23 (d, J = 1.5 Hz), 42.32 (d, J = 2.4 Hz), 46.97 (d, J = 1.9 Hz), 128.27, 128.65 (d, J =
6.3 Hz), 133.19 (d, J = 19.1 Hz), 138.14 (d, J = 7.6 Hz), 140.78 (d, J = 13.4 Hz), 152.84 (d, J =
24.8 Hz); ³¹P NMR (CDCl₃) δ –24.02.  Found: C, 75.02; H, 8.36%.  Calcd for C₂₄H₃₃PS: C, 74.96;
H, 8.65%.

(Z)-1-Diphenylphosphino-2-phenylthio-1-octene (3ac)

IR (neat) 3054, 2927, 2855, 2340, 1583, 1478, 1436, 1378, 1094, 1968, 1025, 999,
740, 695 cm⁻¹; ¹H NMR (CDCl₃) δ 0.81 (t, J = 7.0 Hz, 3H), 1.05–1.20 (m, 6H),
1.47 (tt, J = 7.0, 7.5 Hz, 2H), 2.32 (t, J = 7.5 Hz, 2H), 6.54 (s, 1H), 6.86–6.95 (m, 3H),
7.04–7.09 (m, 2H), 7.10–7.17 (m, 4H), 7.31 (d, J = 7.0 Hz, 2H), 7.54–7.60 (m, 4H); ¹³C NMR (CDCl₃) δ
14.21, 22.86, 28.78, 29.25 (d, J = 2.0 Hz), 31.77, 38.37 (d, J = 3.8 Hz), 127.40, 128.51, 128.80 (d, J =
6.8 Hz), 129.10, 131.50 (d, J = 10.0 Hz), 132.43, 133.21 (d, J = 19.1 Hz), 134.28 (d, J = 5.3
Hz), 140.35 (d, $J = 12.0$ Hz), 153.06 (d, $J = 25.4$ Hz); $^{31}$P NMR (C$_6$D$_6$) $\delta$ –23.88. Found: C, 76.93; H, 7.18%. Calcd for C$_{26}$H$_{29}$PS: C, 77.19; H, 7.23%.

NOE analysis:

(Z)-2-(2-Furlymethythio)-1-diphenylphosphino-1-octene (3ad)

IR (neat) 2928, 2855, 1557, 1436, 1242, 1151, 1010, 934, 885, 805, 739, 695 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.86 (t, $J = 7.0$ Hz, 3H), 1.10–1.27 (m, 6H), 1.47 (tt, $J = 7.0$, 7.5 Hz, 2H), 2.27 (t, $J = 7.5$ Hz, 2H), 3.65 (s, 2H), 5.99 (dd, $J = 2.0$, 3.5 Hz, 1H), 6.05 (dd, $J = 1.0$, 3.5 Hz, 1H), 6.32 (s, 1H), 7.00 (dd, $J = 1.0$, 2.0 Hz, 1H), 7.02–7.06 (m, 2H), 7.07–7.12 (m, 4H), 7.45–7.51 (m, 4H); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 14.24, 22.96, 28.56 (d, $J = 6.3$ Hz), 28.96, 29.03 (d, $J = 1.4$ Hz), 31.88, 38.28 (d, $J = 3.8$ Hz), 107.86 (d, $J = 0.9$ Hz), 110.77, 128.38, 128.70 (d, $J = 6.6$ Hz), 129.60 (d, $J = 9.0$ Hz), 133.10 (d, $J = 19.1$ Hz), 140.33 (d, $J = 12.0$ Hz), 142.00, 151.19, 152.78 (d, $J = 24.3$ Hz); $^{31}$P NMR (C$_6$D$_6$) $\delta$ –25.72. Found: C, 73.68; H, 7.13%. Calcd for C$_{25}$H$_{29}$OPS: C, 73.50; H, 7.15%.

(Z)-1-Diphenylphosphino-2-((E)-3-phenyl-2-propenylthio)-1-octene (3ae)

IR (neat) 3026, 2929, 2855, 2334, 1554, 1436, 1217, 1095, 1027, 962, 740, 695 cm$^{-1}$; $^1$H NMR (C$_6$D$_6$) $\delta$ 0.87 (t, $J = 7.0$ Hz, 3H), 1.10–1.28 (m, 6H), 1.55 (tt, $J = 7.0$, 7.5 Hz, 2H), 2.30 (t, $J = 7.5$ Hz, 2H), 3.24 (dd, $J = 1.5$, 7.5 Hz, 2H), 6.06 (dt, $J = 7.5$, 15.5 Hz, 1H), 6.30 (d, $J = 15.5$ Hz, 1H), 6.36 (s, 1H), 7.00–7.20 (m, 11H), 7.48–7.56 (m, 4H); $^{13}$C NMR (C$_6$D$_6$) $\delta$ 14.23, 22.98, 29.06, 29.13 (d, $J = 1.9$ Hz), 31.93, 34.77 (d, $J = 6.3$ Hz), 38.60 (d, $J = 4.3$ Hz), 126.05, 126.73, 127.67, 128.37, 128.70 (d, $J = 5.6$ Hz), 128.73, 129.91 (d, $J = 8.6$ Hz), 132.55, 133.13 (d, $J = 19.1$ Hz), 137.21, 140.41 (d, $J = 12.0$ Hz), 152.97 (d, $J = 24.8$ Hz); $^{31}$P NMR (C$_6$D$_6$) $\delta$ –25.54. Found: C, 78.57; H, 7.70%. Calcd for C$_{29}$H$_{33}$PS: C, 78.34; H, 7.48%.
(Z)-2-(4-Bromophenylthio)-1-diphenylphosphino-1-octene (3af)

IR (neat) 2926, 2855, 1568, 1471, 1435, 1379, 1089, 1068, 1010, 815, 740, 696 cm\(^{-1}\); \(^1^H\) NMR (C\(_6\)D\(_6\)) \(\delta\) 0.82 (t, \(J = 7.5\) Hz, 3H), 1.02–1.22 (m, 6H), 1.42 (tt, \(J = 7.0, 7.5\) Hz, 2H), 2.14 (t, \(J = 7.5\) Hz, 2H), 6.53 (s, 1H), 6.90 (d, \(J = 8.5\) Hz, 2H), 7.02 (d, \(J = 8.5\) Hz, 2H), 7.03–7.09 (m, 2H), 7.10–7.15 (m, 4H), 7.50–7.56 (m, 4H); \(^1^C\) NMR (C\(_6\)D\(_6\)) \(\delta\) 14.25, 22.87, 28.72, 29.12 (d, \(J = 2.0\) Hz), 31.77, 38.32 (d, \(J = 3.4\) Hz), 121.62, 128.63, 128.84 (d, \(J = 6.8\) Hz), 132.19, 132.62 (d, \(J = 10.9\) Hz), 133.17 (d, \(J = 19.1\) Hz), 133.41 (d, \(J = 5.8\) Hz), 133.57, 140.03 (d, \(J = 11.5\) Hz), 152.02 (d, \(J = 24.8\) Hz); \(^3^P\) NMR (C\(_6\)D\(_6\)) \(\delta\) –23.67. Found: C, 64.39; H, 5.78%. Calcd for C\(_{26}\)H\(_{28}\)Br: C, 64.60; H, 5.84%.

(Z)-1-Diphenylphosphino-2-(3-hydroxypropylthio)-1-octene (3ag)

IR (neat) 3336, 3053, 2928, 2855, 1555, 1433, 1027, 740, 696 cm\(^{-1}\); \(^1^H\) NMR (C\(_6\)D\(_6\)) \(\delta\) 0.88 (t, \(J = 7.0\) Hz, 3H), 1.15–1.30 (m, 6H), 1.48–1.63 (m, 4H), 2.29 (t, \(J = 7.5\) Hz, 2H), 2.62 (t, \(J = 7.0\) Hz, 2H), 3.43 (t, \(J = 6.0\) Hz, 2H), 6.32 (s, 1H), 7.01–7.07 (m, 2H), 7.08–7.14 (m, 4H), 7.49–7.56 (m, 4H); \(^1^C\) NMR (C\(_6\)D\(_6\)) \(\delta\) 14.28, 23.00, 28.17 (d, \(J = 5.8\) Hz), 29.01, 29.24 (d, \(J = 1.9\) Hz), 31.93, 32.66, 38.01 (d, \(J = 4.3\) Hz), 60.79, 128.42, 128.61 (d, \(J = 8.1\) Hz), 128.72 (d, \(J = 6.1\) Hz), 133.11 (d, \(J = 19.1\) Hz), 140.32 (d, \(J = 11.0\) Hz), 153.43 (d, \(J = 24.8\) Hz); \(^3^P\) NMR (C\(_6\)D\(_6\)) \(\delta\) –25.54. Found: C, 71.67; H, 8.19%. Calcd for C\(_{23}\)H\(_{35}\)OPS: C, 71.47; H, 8.08%.

(S)-N-Acetyl-(Z)-2-diphenylphosphino-1-hexylethenylthio)-1-cysteine (3ah)

IR (nujol) 3349, 2924, 2854, 2483, 2194, 1740, 1700, 1653, 1456, 1377, 1308, 1226, 1027, 817, 739, 694 cm\(^{-1}\); \(^1^H\) NMR (CD\(_3\)OD) \(\delta\) 0.77 (t, \(J = 7.0\) Hz, 3H), 1.13–1.28 (m, 6H), 1.48 (tt, \(J = 7.0, 7.5\) Hz, 2H), 1.88 (s, 3H), 2.40 (t, \(J = 7.5\) Hz, 2H), 2.88–2.96 (m, 1H), 3.14–3.22 (m, 1H), 4.36–4.46 (m, 1H), 6.15 (s, 1H), 7.10–7.22 (m, 10H); \(^1^C\) NMR (CD\(_3\)OD) \(\delta\) 14.37, 22.67, 23.60, 29.48, 29.79, 32.61, 33.57, 38.52, 53.94, 129.40, 131.15, 133.51 (d, \(J = 21.0\) Hz), 133.68 (d, \(J = 21.9\) Hz), 140.55 (d, \(J = 41.5\) Hz), 153.15
(d, J = 23.4 Hz), 173.11, 173.70; 31P NMR (CD3OD) δ –22.46. Found: C, 65.44; H, 6.85%.
Calcd for C23H32NO3PS: C, 65.62; H, 7.05%. m.p.: 49.0–51.0 °C. [α]D25 = +100 (c 0.32, methanol).

1,3-Bis((Z)-2-diphenylphosphino-1-hexylethenylthio)propane (3aj)

IR (neat) 3052, 2927, 2855, 1585, 1480, 1436, 1240, 1095, 1026, 798, 740, 695 cm\(^{-1}\); 1H NMR (CD3OD) δ 0.88 (t, J = 7.0 Hz, 6H), 1.15–1.32 (m, 12H), 1.50–1.63 (m, 6H), 2.32 (t, J = 7.5 Hz, 4H), 2.64 (t, J = 7.0 Hz, 4H), 6.32 (s, 2H), 7.02–7.07 (m, 4H), 7.08–7.14 (m, 8H), 7.23–7.54 (m, 8H); 13C NMR (CD3OD) δ 14.30, 23.02, 29.03, 29.32 (d, J = 1.4 Hz), 29.95, 29.98, 31.97, 38.08 (d, J = 4.3 Hz), 128.37, 128.71 (d, J = 6.6 Hz), 129.28 (d, J = 8.6 Hz), 133.10 (d, J = 19.1 Hz), 140.47 (d, J = 12.0 Hz), 153.10 (d, J = 24.8 Hz); 31P NMR (CD3OD) δ –25.36. Found: C, 73.93; H, 7.99%. Calcd for C43H54P2S2: C, 74.10; H, 7.81%.

(Z)-2-Dicyclohexylphosphino-1-(4-methoxyphenylthio)-1-phenylethene (3ki)

IR (nujol) 2920, 2853, 1592, 1573, 1495, 1436, 1291, 1247, 1185, 1035, 830, 754, 696 cm\(^{-1}\); 1H NMR (CD3OD) δ 1.12–1.50 (m, 10H), 1.56–2.05 (m, 12H), 3.00 (s, 3H), 6.42 (d, J = 8.5 Hz, 2H), 6.59 (d, J = 4.5 Hz, 1H), 6.90 (dd, J = 7.5, 7.5 Hz, 1H), 7.00 (dd, J = 7.5, 7.5 Hz, 2H), 7.21 (d, J = 8.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H); 13C NMR (CD3OD) δ 26.89, 27.56 (d, J = 4.3 Hz), 27.64, 29.96 (d, J = 8.5 Hz), 31.12 (d, J = 16.8 Hz), 35.35 (d, J = 12.9 Hz), 54.46, 114.60, 126.08 (d, J = 3.8 Hz), 128.19, 128.26, 128.63, 133.12, 133.86 (d, J = 20.1 Hz), 141.24 (d, J = 4.9 Hz), 153.60 (d, J = 24.9 Hz), 159.04; 31P NMR (CD3OD) δ –17.39. m.p.: 144.0–146.0 °C. CCDC No.: 635602.
Figure 1. ORTEP diagram of 3ki
References and Notes


(7) The perfect Z stereoselectivity was observed at the initial stage of the reaction.


(9) No reactions took place in the absence of the catalyst in ethanol or in water.
Chapter 3

Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides
Catalyzed by Cesium Base

Regio- and stereoselective hydroamidation of 1-alkynylphosphine sulfides proceeds in the presence of cesium carbonate to provide (E)-2-amino-1-thiophosphinyl-1-alkenes. Asymmetric hydrogenation of the adducts catalyzed by an iridium complex followed by desulfidation yields 2-amino-1-phosphinoalkanes, which offers a new approach to chiral N,P-ligands that will potentially serve as ligands in asymmetric reactions.
**Introduction**

Organophosphines play invaluable roles in organic synthesis, especially as ligands for transition metal catalysts. Development of novel approaches to organophosphines is thus quite important. The author has been focusing on 1-alkynylphosphine derivatives as precursors of new phosphines and developed addition reactions of diphenylphosphine (Chapter 1) and thiols (Chapter 2). Considering the importance of bidentate aminophosphine ligands in homogeneous transition metal catalysis,\(^1\) he investigated the addition reaction of nitrogen nucleophiles. In this chapter, the author describes cesium-catalyzed addition of amides or imides to 1-alkynylphosphine sulfides,\(^2-4\) directed toward the construction of vicinal N,P-frameworks.

**Results and Discussion**

Treatment of diphenyl(phenylethynyl)phosphine sulfide (1a) with 2 equivalents of \(N\)-benzyltosylamide (2a) in the presence of a catalytic amount of cesium carbonate (10 mol%) in DMSO for 11 h at 90 °C provided 1-(\(N\)-benzyl-\(N\)-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3aa) in 84% isolated yield with an \(E/Z\) ratio of 96/4 (Table 1, entry 1). Recrystallization of the product allowed for the isolation of the \(E\) isomer in 71% yield.\(^5\) Aprotic polar solvents, such as DMSO, DMF, and NMP, are the solvents of choice. The reactions in 1,4-dioxane (bp 100 °C), acetonitrile (bp 82 °C), and toluene (bp 111 °C) at reflux afforded the product in moderate yields. In protic solvents such as 2-propanol at reflux, a trace amount of the product was obtained. Cesium carbonate is the most effective base. The uses of potassium carbonate and sodium carbonate led to lower yields. When organic bases such as DBU and DABCO were used, no reaction occurred. The optimizations of the reaction conditions are summarized in the following section.
Various combinations of 1-alkynylphosphine sulfides and amides were examined under the optimized reaction conditions (Table 1). A variety of functional groups, such as keto, ester, methoxy, and pyridyl groups, were compatible under the reaction conditions (entries 2–5). The reaction of ethynylidiphenylphosphine sulfide (1f) also proceeded smoothly with perfect stereoselectivity (entry 6). However, the reactions of sterically demanding o-methoxyphenyl-
and tert-butyl-substituted substrates did not take place. The additions to primary and secondary alkyl-substituted 1-alkynylphosphine sulfides also proceeded, although migration of the carbon–carbon double bond occurred to afford 3ga’ and 3ha’ exclusively (entries 7 and 8). The scope of sulfonamides was investigated (entries 9–11). The addition of primary alkyl-substituted tosylamides proceeded in high yields (entries 1 and 9). However, additions of secondary alkyl-substituted tosylamide 2c and tosylamide (2d) provided the corresponding products in low yields (entries 10 and 11), and no reaction occurred when N-phenyltosylamide and N-tert-butyltosylamide were used. The reaction of N-benzyl-10-camphorsulfonylamide proceeded smoothly (eq 1).

![Reaction Scheme 1](image1.png)

Other nitrogen nucleophiles were examined. Imides were suitable nucleophiles for this addition reaction (eqs 2 and 3). Interestingly, the stereoselectivity was completely controlled when imides were used. In addition, succinimide (2f) could react with sterically hindered tert-butyl-substituted substrate, with which N-benzyltosylamide (2a) could not react, and the corresponding adduct was obtained in good yield. The addition of 2-pyrrolidinone also proceeded, albeit with lower stereoselectivity (eq 4). Acyclic amides such as N-benzylacetamide did not react at all.

![Reaction Scheme 2](image2.png)
The amidation was applicable to intramolecular cyclizations. When 1-alkynylphosphine sulfide 4a which has a tosylamido group was treated with cesium carbonate at ambient temperature, the cyclization proceeded smoothly (eq 5). In the case of eq 6, where tetramethylene-tethered 4b was used as a substrate, the migration of the C–C double bond of the product occurred.

**Enantioselective Hydrogenation of 3.** The author envisioned that the enantioselective hydrogenation of the adducts would offer a new approach to chiral bidentate N,P-ligands. However, the enantioselective hydrogenation was not trivial because the adducts are regarded as the sterically demanding and doubly heteroatom-substituted unusual alkenes. After extensive
screening of the reaction conditions, he finally found that a combination of a cationic iridium complex and ligand \( \text{7} \) catalyzed the desired reaction with high enantioselectivity (Scheme 1).

The hydrogenation of \( 3\text{aa} \) in the presence of catalytic amounts of \([\text{IrCl(cod)}]_2, \text{AgBF}_4, \) and \( \text{7} \) under 0.1 MPa of hydrogen in boiling ethanol provided \( 6\text{a} \) in excellent yield (93%) with 97% ee. The hydrogenation of \( 3\text{af} \) was less enantioselective (89% ee), yet high enough to potentially allow for improving the optical purity by recrystallization.

**Scheme 1.** Iridium-Catalyzed Enantioselective Hydrogenation

Radical Desulfidation of Phosphine Sulfides. Some of the phosphine sulfides thus synthesized were subjected to radical desulfidation conditions to provide the corresponding trivalent phosphines in high yields (Scheme 2). In particular, the optically active phosphine \( 6\text{a}–\text{S} \) would be useful as a ligand after further modifications.
Conclusion

The author has found that the cesium-catalyzed hydroamidation of 1-alkynylphosphine sulfides proceeds in good yields with high regio- and stereoselectivities. In light of the importance of organophosphorus compounds, the products and their derivatives can be useful in organic synthesis. In addition, he has demonstrated that the iridium-catalyzed enantioselective hydrogenation of the adducts afforded optically active phosphine sulfides. The protocol, the sequential hydroamidation/hydrogenation, offers an alternative to the conventional approach to chiral 2-amino-1-phosphinoalkanes.
Experimental Section
Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl$_3$. Chemical shifts ($\delta$) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and relative to CDCl$_3$ at 77.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl$_3$ with 85% H$_3$PO$_4$ solution as an external standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1-alkynylphosphine, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was obtained from Aldrich. Starting 1-alkynylphosphine sulfides were prepared quantitatively by treatment of 1-alkynylphosphines with 3 equiv of crystalline sulfur in THF or DMF with monitoring TLC. Cesium carbonate and chloro(bis-1,5-cyclooctadiene)iridium(I) dimer were purchased from Wako Pure Chemicals. Ligand 7 was available from Strem. Unless otherwise noted, reactions were carried out under argon atmosphere.

Typical Procedure for Hydroamidation of 1-Alkynylphosphine Sulfides

Synthesis of 3aa is representative. Cs$_2$CO$_3$ (0.016 g, 0.050 mmol) was placed in a 20-mL reaction flask under argon. DMSO (3 mL), 1a (0.16 g, 0.5 mmol), and 2a (0.26 g, 1.0 mmol) were sequentially added. The resulting solution was heated in an oil bath (90 °C) for 11 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was
extracted with hexane/ethyl acetate (2 : 1, 10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded 3aa (0.24 g, 0.42 mmol) in 84% yield with $E/Z = 96/4$ as a white solid. Recrystallization from hexane/ethyl acetate provided the $E$ isomer (0.21 g, 0.36 mmol) exclusively in 71% yield.

**Iridium-Catalyzed Enantioselective Hydrogenation**

$[\text{IrCl(cod)}]_2$ (5.0 mg, 0.0075 mmol), AgBF$_4$ (2.9 mg, 0.015 mmol), and ligand 7 (8.1 mg, 0.015 mmol) were placed in a 20-mL reaction flask under hydrogen. Ethanol (1.0 mL) was added and the mixture was stirred for 1 h. 3aa (0.058 g, 0.10 mmol) was added and the resulting mixture was heated at reflux for 18 h. After the reaction mixture was cooled to room temperature, filtration through a pad of florisil, concentration, and purification on silica gel yielded 6a (0.054 g, 0.093 mmol) in 93% yield with 97% ee. HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 90:10, 1.5 mL/min, retention time = 9.9 min for the major enantiomer; retention time = 8.1 min for the minor enantiomer. 6b was synthesized from 3af, in a fashion similar to the synthesis of 6a from 3aa, in 99% yield with 89% ee (0.042 g, 0.099 mmol). HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 90:10, 1.5 mL/min, retention time = 8.5 min for the major enantiomer; retention time = 10.3 min for the minor enantiomer.

**Typical Procedure for the (Me$_3$Si)$_3$SiH-Mediated Radical Desulfidation Reaction**

Synthesis of 6a–S is representative. AIBN (1.6 mg, 0.010 mmol) and 6a (0.058 g, 0.10 mmol, 97%ee) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided 6a–S (0.045 g, 0.082 mmol, 82%, 97% ee). HPLC conditions: CHIRALCEL OD-H, hexane/2-propanol = 98.5:1.5, 1.0
mL/min, retention time = 17.7 min for the major enantiomer; retention time = 15.7 min for the minor enantiomer.

**Preparation of 4**

Synthesis of 4a is representative.

![Chemical diagram](image)

Preparation of A.

In a 50-mL reaction flask, p-TsOH·H₂O (0.19 g, 1.0 mmol) was placed under argon. CH₂Cl₂ (15 mL), 4-pentyn-1-ol (0.84 g, 10 mmol), and 3,4-dihydro-2H-pyran (1.0 g, 12 mmol) were sequentially added. The resulting mixture was stirred for 8 h. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Concentration followed by silica gel column purification provided 1.5 g of A (9.1 mmol, 91%).

A to B.

Under argon, a solution of A (1.5 g, 9.1 mmol) in THF (15 mL) was placed in a 50-mL reaction flask. Butyllithium (5.8 mL, 1.6 M in hexane, 9.3 mmol) was added at 0 °C. The resulting mixture was stirred for 30 min at the same temperature. Chlorodiphenylphosphine (2.1...
g, 9.5 mmol) was then added at 0 °C. The mixture was warmed to room temperature and stirred for 1 h. After water (20 mL) was added, the product was extracted with a hexane/ethyl acetate mixture. Evaporation followed by chromatographic purification afforded B (2.8 g, 8.0 mmol, 87%).

B to C.

A solution of B (2.8 g, 8.0 mmol) in THF (15 mL) was placed in a 50-mL reaction flask under argon. Elemental sulfur (0.27 g, 8.5 mmol) was added, and resulting mixture was stirred for 4 h. Concentration and purification furnished C (2.5 g, 6.6 mmol) in 83% yield.

C to D.

In a 50-mL reaction flask, p-TsOH·H₂O (0.13 g, 0.70 mmol) and a solution of C (2.5 g, 6.6 mmol) in ethanol (10 mL) were mixed under argon. The mixture was stirred for 18 h at ambient temperature. Water (20 mL) was added and the product was extracted with ethyl acetate. Evaporation followed by purification on silica gel provided 1.4 g of D (4.8 mmol, 73%).

D to E.

Under argon, a solution of D (1.4 g, 4.8 mmol) in THF (40 mL) was placed in a 100-mL reaction flask. PPh₃ (1.26 g, 4.8 mmol) and N-Boc-tosylamide (1.3 g, 4.8 mmol) were added. Diisopropyl azodicarboxylate (0.97 g, 4.8 mmol) was added dropwise and the resulting mixture was stirred for 14 h. Water (20 mL) was added and the product was extracted with a hexane/ethyl acetate mixture. Concentration and purification on silica gel provided E (1.9 g, 3.4 mmol) in 71% yield.

E to 4a.

A solution of E (1.9 g, 3.4 mmol) in dichloromethane (15 mL) was placed in a 50-mL reaction flask under argon. Trifluoroacetic acid (1.96 g, 17.2 mmol) was added and the mixture was stirred for 18 h. A solution of saturated sodium hydrogen carbonate was added and the product was extracted with a hexane/ethyl acetate mixture. Concentration under reduced pressure followed by chromatographic purification afforded 4a (1.5 g, 3.4 mmol, 99%).
Optimization of Reaction Conditions

Table 2. Optimization of Reaction Conditions

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*a* Conditions: 1a (0.50 mmol), 2a (0.60 mmol), base (0.050 mmol), solvent (3.0 mL), 11 h. *b* Based on ³¹P NMR with a sufficient first decay period.

Characterization Data

Diphenyl(phenylethynyl)phosphine sulfide (1a)

IR (nujol) 2923, 2854, 2171, 1684, 1653, 1558, 1457, 1436, 1100, 849, 720, 688 cm⁻¹; ¹H NMR (CDCl₃) δ 7.34–7.64 (m, 11H), 7.96–8.06 (m, 4H); ¹³C NMR (CDCl₃) δ 81.96 (d, J = 151.3 Hz), 105.77 (d, J = 25.9 Hz), 120.12 (d, J = 4.3 Hz), 128.48, 128.60 (d, J = 13.9 Hz), 130.57, 130.80 (d, J = 12.4 Hz), 131.74 (d, J = 2.9 Hz), 132.37 (d, J = 2.4 Hz), 133.76 (d, J = 98.4 Hz); ³¹P NMR (CDCl₃) δ 18.39. Found: C, 75.58; H, 4.65%.
Calcd for C\textsubscript{20}H\textsubscript{15}PS: C, 75.45; H, 4.75%. m.p.: 108.0–109.5 °C.

(4-Acetylphenylethynyl)diphenylphosphine sulfide (1b)

IR (nujol) 2923, 2854, 2176, 1683, 1436, 1266, 1101, 853, 719 cm\textsuperscript{-1}; \(^1\)H NMR (CD\textsubscript{3}Cl) \(\delta 2.59\) (s, 3H), 7.44–7.54 (m, 6H), 7.65 (d, \(J = 8.5\) Hz, 2H), 7.93 (d, \(J = 8.5\) Hz, 2H), 7.94–8.02 (m, 4H); \(^{13}\)C NMR (CD\textsubscript{3}Cl) \(\delta 26.61\), 84.79 (d, \(J = 147.4\) Hz), 104.01 (d, \(J = 25.4\) Hz), 124.49 (d, \(J = 4.3\) Hz), 128.14, 128.64 (d, \(J = 13.9\) Hz), 130.73 (d, \(J = 12.0\) Hz), 131.90 (d, \(J = 2.9\) Hz), 132.49 (d, \(J = 2.4\) Hz), 133.13 (d, \(J = 98.3\) Hz), 137.82, 196.87; \(^{31}\)P NMR (CD\textsubscript{3}Cl) \(\delta 18.65\). Found: C, 73.04; H, 4.71%. Calcd for C\textsubscript{22}H\textsubscript{17}OPS: C, 73.32; H, 4.75%. m.p.: 136.0–137.0 °C.

(4-Methoxycarbonylphenylethynyl)diphenylphosphine sulfide (1c)

IR (nujol) 2924, 2854, 2178, 1718, 1456, 1436, 1377, 1280, 1102, 856, 766, 721 cm\textsuperscript{-1}; \(^1\)H NMR (CD\textsubscript{3}Cl) \(\delta 3.91\) (s, 3H), 7.45–7.55 (m, 6H), 7.64 (d, \(J = 8.5\) Hz, 2H), 7.95–8.10 (m, 4H), 8.03 (d, \(J = 8.5\) Hz, 2H); \(^{13}\)C NMR (CD\textsubscript{3}Cl) \(\delta 52.33\), 84.58 (d, \(J = 147.5\) Hz), 104.11 (d, \(J = 25.3\) Hz), 124.44 (d, \(J = 3.9\) Hz), 128.65 (d, \(J = 13.9\) Hz), 129.46, 130.76 (d, \(J = 11.9\) Hz), 131.52, 131.89 (d, \(J = 3.4\) Hz), 132.28 (d, \(J = 1.9\) Hz), 133.21 (d, \(J = 98.4\) Hz), 165.88; \(^{31}\)P NMR (CD\textsubscript{3}Cl) \(\delta 18.62\). Found: C, 69.95; H, 4.57%. Calcd for C\textsubscript{22}H\textsubscript{17}O\textsubscript{2}PS: C, 70.20; H, 4.55%. m.p.: 107.0–108.0 °C.

(4-Methoxyphenylethynyl)diphenylphosphine sulfide (1d)

IR (nujol) 2923, 2854, 2170, 1603, 1509, 1436, 1259, 1172, 1101, 1022, 828, 719 cm\textsuperscript{-1}; \(^1\)H NMR (CD\textsubscript{3}Cl) \(\delta 3.81\) (s, 3H), 6.88 (d, \(J = 8.5\) Hz, 2H), 7.43–7.52 (m, 6H), 7.53 (d, \(J = 8.5\) Hz, 2H), 7.96–8.04 (m, 4H); \(^{13}\)C NMR (CD\textsubscript{3}Cl) \(\delta 55.31\), 80.54 (d, \(J = 155.1\) Hz), 106.52 (d, \(J = 27.3\) Hz), 111.83 (d, \(J = 4.4\) Hz), 114.11, 128.51 (d, \(J = 13.9\) Hz), 130.71 (d, \(J = 11.9\) Hz), 131.61 (d, \(J = 2.9\) Hz), 133.88 (d, \(J = 97.9\) Hz), 134.11 (d, \(J = 1.9\) Hz), 161.28; \(^{31}\)P NMR (CD\textsubscript{3}Cl) \(\delta 18.22\). Found: C, 72.16; H, 5.12%. Calcd for
C_{21}H_{17}OPS: C, 72.40; H, 4.92%. m.p.: 92.0–93.5 °C.

Diphenyl(2-pyridylethynyl)phosphine sulfide (1e)

IR (nujol) 2924, 2855, 1558, 1506, 1457, 1097, 865, 782, 720 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.32 (dd, \(J = 4.0, 7.5\) Hz, 1H), 7.40–7.54 (m, 6H), 7.59 (d, \(J = 8.0\) Hz, 1H), 7.69 (dd, \(J = 7.5, 8.0\) Hz, 1H), 7.94–8.05 (m, 4H), 8.63 (d, \(J = 4.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 81.28 (d, \(J = 144.6\) Hz), 103.25 (d, \(J = 23.9\) Hz), 124.66, 128.48 (d, \(J = 1.0\) Hz), 128.63 (d, \(J = 13.8\) Hz), 130.84 (d, \(J = 12.4\) Hz), 131.89 (d, \(J = 2.9\) Hz), 132.96 (d, \(J = 98.4\) Hz), 136.29, 140.75 (d, \(J = 4.3\) Hz), 150.31; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 18.99. Found: C, 71.21; H, 4.29%. Calcd for C\(_{19}\)H\(_{14}\)NP:S: C, 71.46; H, 4.42%.

Ethynyl(diphenyl)phosphine sulfide (1f)

IR (neat) 3221, 3055, 2055, 1479, 1437, 1309, 1104, 1027, 999, 826, 714 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.45 (d, \(J = 10.0\) Hz, 1H), 7.45–7.55 (m, 6H), 7.90–7.97 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 78.16 (d, \(J = 141.8\) Hz), 94.37 (d, \(J = 23.9\) Hz), 128.69 (d, \(J = 13.9\) Hz), 130.82 (d, \(J = 12.4\) Hz), 132.03 (d, \(J = 2.9\) Hz), 132.69 (d, \(J = 97.9\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 18.78. Found: C, 69.14; H, 4.37%. Calcd for C\(_{14}\)H\(_{11}\)PS: C, 69.40; H, 4.58%.

1-Octynylidiphenylphosphine sulfide (1g)

IR (neat) 2930, 2857, 2193, 1437, 1103, 1027, 999, 747, 720, 619, 666 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.87 (t, \(J = 7.0\) Hz, 3H), 1.22–1.34 (m, 4H), 1.36–1.46 (m, 2H), 1.62 (tt, \(J = 7.5, 7.5\) Hz, 2H), 2.46 (dt, \(J = 3.5, 7.5\) Hz, 2H), 3.79–3.97 (m, 6H), 7.89–7.97 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.80, 19.87 (d, \(J = 2.9\) Hz), 3.82, 3.87 (d, \(J = 1.9\) Hz), 28.35, 30.94, 73.80 (d, \(J = 15.7\) Hz), 110.16 (d, \(J = 26.3\) Hz), 128.85 (d, \(J = 13.9\) Hz), 130.56 (d, \(J = 12.4\) Hz), 131.43 (d, \(J = 3.4\) Hz), 134.00 (d, \(J = 97.9\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 17.55. Found: C, 73.81; H, 7.18%. Calcd for C\(_{20}\)H\(_{13}\)PS: C, 73.59; H, 7.10%.
(Cyclohexylethynyl)diphenylphosphine sulfide (1h)

IR (nujol) 2929, 2855, 2185, 1559, 1439, 1311, 1098, 990, 842, 721 cm⁻¹; ¹H NMR (CDCl₃) δ 1.30–1.41 (m, 3H), 1.46–1.65 (m, 3H), 1.67–1.78 (m, 2H), 1.83–1.94 (m, 2H), 2.63–2.72 (m, 1H), 7.42–7.51 (m, 6H), 7.89–7.96 (m, 4H); ¹³C NMR (CDCl₃) δ 24.57, 25.54, 30.00 (d, J = 2.4 Hz), 31.41 (d, J = 1.5 Hz), 73.60 (d, J = 157.5 Hz), 113.63 (d, J = 25.9 Hz), 128.50 (d, J = 13.4 Hz), 130.68 (d, J = 12.0 Hz), 131.52 (d, J = 2.9 Hz), 134.24 (d, J = 97.9 Hz); ³¹P NMR (CDCl₃) δ 17.41. Found: C, 73.87; H, 6.59%. Calcd for C₂₀H₂₁PS: C, 74.04; H, 6.52%. m.p.: 104.5–105.5 °C.

(3,3-Dimethyl-1-butynyl)diphenylphosphine sulfide (1i)

IR (nujol) 2922, 2853, 2158, 1684, 1653, 1558, 1506, 1457, 1437, 1250, 1096, 752, 710 cm⁻¹; ¹H NMR (CDCl₃) δ 1.35 (s, 9H), 7.41–7.51 (m, 6H), 7.88–7.96 (m, 4H); ¹³C NMR (CDCl₃) δ 28.69 (d, J = 2.9 Hz), 29.98 (d, J = 1.9 Hz), 72.31 (d, J = 157.0 Hz), 117.02 (d, J = 24.9 Hz), 128.51 (d, J = 13.9 Hz), 130.69 (d, J = 11.9 Hz), 131.50 (d, J = 3.3 Hz), 134.43 (d, J = 97.9 Hz); ³¹P NMR (CDCl₃) δ 17.28. m.p.: 136.0–137.5 °C.

(E)-1-(N-Benzyl-N-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3aa)

IR (nujol) 2922, 2854, 1559, 1458, 1439, 1359, 1170, 1099, 956, 812, 751, 716 cm⁻¹; ¹H NMR (CDCl₃) δ 2.41 (s, 3H), 4.50 (s, 2H), 6.30 (d, J = 13.0 Hz, 1H), 6.93 (dd, J = 7.5, 7.5 Hz, 2H), 7.01–7.07 (m, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.19–7.33 (m, 11H), 7.60 (d, J = 8.0 Hz, 2H), 7.62–7.69 (m, 4H); ¹³C NMR (CDCl₃) δ 21.56, 52.33, 119.49 (d, J = 86.4 Hz), 127.65, 127.66, 127.82, 128.03 (d, J = 12.4 Hz), 128.44, 128.53, 129.74, 129.76 (d, J = 5.3 Hz), 130.12, 130.87 (d, J = 2.9 Hz), 131.29 (d, J = 10.5 Hz), 132.80 (d, J = 86.9 Hz), 133.83 (d, J = 3.4 Hz), 135.75, 136.90, 144.10, 151.43 (d, J = 8.1 Hz); ³¹P NMR (CDCl₃) δ 29.15. Found: C, 70.33; H, 5.18%. Calcd for C₂₅H₂₅NO₂PS₂: C, 70.44; H, 5.22%. m.p.: 134.0–135.0 °C.
(E)-1-(4-Acetylphenyl)-1-(N-benzyl-N-tosylamino)-2-diphenylthiophosphinylethene (3ba)

IR (nujol) 2923, 2855, 1674, 1569, 1360, 1092, 957, 849, 739 cm⁻¹; ¹H NMR (CDCl₃) δ 2.44 (s, 3H), 2.47 (s, 3H), 4.50 (s, 2H), 6.36 (d, J = 12.6 Hz, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.18–7.33 (m, 13H), 7.48 (d, J = 9.0 Hz, 2H), 7.55–7.63 (m, 4H), 7.65 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 21.61, 26.60, 26.47, 121.43 (d, J = 84.4 Hz), 127.39, 127.67, 128.01, 128.11 (d, J = 13.0 Hz), 128.48, 128.64, 129.89, 130.28, 131.05 (d, J = 2.9 Hz), 131.26 (d, J = 10.5 Hz), 132.47 (d, J = 86.9 Hz), 135.24, 136.24, 137.38, 138.72 (d, J = 3.4 Hz), 144.44, 149.86 (d, J = 7.6 Hz), 197.36; ³¹P NMR (CDCl₃) δ 28.89. Found: C, 69.71; H, 5.27%. Calcd for C₃₆H₃₂NO₃PS₂: C, 69.54; H, 5.19%. m.p.: 139.0–140.5 °C.

(E)-1-(N-Benzyl-N-tosylamino)-1-(4-methoxycarbonylphenyl)-2-diphenylthiophosphinylethene (3ca)

IR (nujol) 2923, 2854, 1719, 1653, 1559, 1507, 1437, 1345, 1274, 1158, 1048, 813, 742 cm⁻¹; ¹H NMR (CDCl₃) δ 2.44 (s, 3H), 3.87 (s, 3H), 4.48 (s, 2H), 6.38 (d, J = 12.5 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.19–7.33 (m, 13H), 7.55–7.67 (m, 8H); ¹³C NMR (CDCl₃) δ 21.60, 52.16, 52.42, 121.48 (d, J = 84.5 Hz), 127.65, 127.98, 128.12 (d, J = 12.4 Hz), 128.45, 128.62, 128.71, 129.88, 130.07, 130.75, 131.07 (d, J = 2.9 Hz), 131.26 (d, J = 10.9 Hz), 132.53 (d, J = 86.9 Hz), 135.27, 136.42, 138.45 (d, J = 3.4 Hz), 144.39, 149.99 (d, J = 7.6 Hz), 166.28; ³¹P NMR (CDCl₃) δ 28.72. Found: C, 68.08; H, 5.13%. Calcd for C₃₆H₃₂NO₄PS₂: C, 67.80; H, 5.06%. m.p.: 156.5–158.0 °C. CCDC No.: 682521.
Figure 1. ORTEP diagram of 3ca

\[(\text{E})-1-(\text{N-Benzyl-N-tosylamino})-1-(4\text{-methoxyphenyl})-2\text{-diphenylthiophosphinylethene (3da)}\]

IR (nujol) 2923, 2854, 1559, 1457, 1340, 1254, 1175, 840, 731 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.40 (s, 3H), 3.67 (s, 3H), 4.52 (s, 2H), 6.14 (d, \(J = 13.5\) Hz, 1H), 6.45 (d, \(J = 9.0\) Hz, 2H), 7.02–7.08 (m, 2H), 7.15 (d, \(J = 8.5\) Hz, 2H), 7.18–7.33 (m, 11H), 7.58 (d, \(J = 8.5\) Hz, 2H), 7.63–7.70 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 21.55, 52.39, 55.19, 113.11, 118.17 (d, \(J = 86.9\) Hz), 126.36 (d, \(J = 3.9\) Hz), 127.61, 127.79, 128.00 (d, \(J = 12.9\) Hz), 128.48, 128.52, 129.70, 130.82 (d, \(J = 2.9\) Hz), 131.34 (d, \(J = 11.0\) Hz), 131.80, 132.87 (d, \(J = 86.4\) Hz), 135.83, 136.99, 144.00, 151.30 (d, \(J = 8.6\) Hz), 160.75; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 29.40. HRMS (EI\(^{+}\)) (m/z) Observed: 609.1567 (\(\Delta = +1.0\) ppm). Calcld for C\(_{35}\)H\(_{32}\)NO\(_3\)PS\(_2\) [M\(^{+}\)]: 609.1561. m.p.: 128.0–129.5 °C.
(E)-1-(N-Benzyl-N-tosylamino)-2-diphenylthiophosphinyl-1-(2-pyridyl)ethene (3ea)

IR (nujol) 2923, 2854, 1458, 1439, 1375, 1357, 1169, 1099, 962, 718 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.42 (s, 3H), 4.59 (s, 2H), 6.20 (d, \(J = 12.0\) Hz, 1H), 6.84 (dd, \(J = 5.5, 7.5\) Hz, 1H), 7.14–7.36 (m, 14H), 7.50–7.62 (m, 5H), 7.78 (d, \(J = 8.0\) Hz, 2H), 8.07 (d, \(J = 4.0\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 21.56, 52.80, 122.08 (d, \(J = 84.0\) Hz), 123.58, 126.14, 127.89, 127.94 (d, \(J = 12.9\) Hz), 128.24, 128.53, 128.68, 129.47, 130.73 (d, \(J = 2.9\) Hz), 131.11 (d, \(J = 10.5\) Hz), 133.05 (d, \(J = 87.9\) Hz), 135.17, 135.25, 135.31, 144.00, 148.43, 148.71 (d, \(J = 6.3\) Hz), 152.10 (d, \(J = 3.4\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 31.16.  Found: C, 68.05; H, 5.26%. Calcd for C\(_{33}\)H\(_{29}\)N\(_2\)O\(_2\)PS\(_2\): C, 68.25; H, 5.03%.  m.p.: 152.0–153.5 °C.

(E)-1-(N-Benzyl-N-tosylamino)-2-diphenylthiophosphinylethene (3fa)

IR (nujol) 2923, 2854, 1598, 1456, 1437, 1353, 1168, 1089, 1048, 762, 712 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 2.44 (s, 3H), 4.72 (s, 2H), 5.18 (dd, \(J = 15.0, 15.0\) Hz, 1H), 7.25–7.36 (m, 11H), 7.38–7.47 (m, 6H), 7.68 (d, \(J = 8.5\) Hz, 2H), 7.74 (dd, \(J = 15.0, 17.5\) Hz, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 21.61, 49.87, 99.53 (d, \(J = 94.5\) Hz), 126.94, 127.20, 127.81, 128.40 (d, \(J = 12.5\) Hz), 128.95, 130.18, 131.08 (d, \(J = 11.0\) Hz), 131.20 (d, \(J = 2.9\) Hz), 134.04 (d, \(J = 86.9\) Hz), 134.39, 135.42, 142.34 (d, \(J = 18.1\) Hz), 144.78; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 34.29. Found: C, 66.87; H, 5.32%. Calcd for C\(_{28}\)H\(_{26}\)N\(_2\)O\(_2\)PS\(_2\): C, 66.78; H, 5.20%.  m.p.: 163.5–164.5 °C.

(E)-2-(N-Benzyl-N-tosylamino)-1-diphenylthiophosphinyl-2-octene (3ga’)

IR (neat) 3033, 2921, 2852, 1598, 1497, 1434, 1213, 1097, 801 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.84 (t, \(J = 7.5\) Hz, 3H), 1.03–1.25 (m, 6H), 2.01–2.08 (m, 2H), 2.34 (s, 3H), 3.93 (d, \(J = 13.0\) Hz, 2H), 3.96 (s, 2H), 4.82 (dt, \(J = 5.0, 8.0\) Hz, 1H), 7.10–7.21 (m, 7H), 7.44–7.55 (m, 8H), 8.01–8.10 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.86, 21.32, 22.29, 28.25 (d, \(J = 2.4\) Hz), 28.72 (d, \(J = 2.4\) Hz), 31.09, 37.41 (d, \(J = 51.5\) Hz), 53.78, 127.54, 127.75, 127.80, 128.54 (d, \(J = 11.9\) Hz), 128.66 (d, \(J = 10.5\) Hz), 128.76, 130.35, 131.07 (d, \(J =
Calcd for C$_{34}$H$_{38}$NO$_2$PS$_2$: C, 69.48; H, 6.52%.

1-(N-Benzyl-N-tosylamino)-1-cyclohexylidene-2-diphenylthiophosphinylethane (3ha’)

IR (nujol) 2921, 2852, 1558, 1437, 1155, 1093, 1016, 897, 742 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.63–0.73 (m, 1H), 0.76–0.86 (m, 1H), 1.16–1.36 (m, 3H), 1.37–1.50 (m, 2H), 1.54–1.64 (m, 1H), 1.97–2.06 (m, 1H), 2.19–2.29 (m, 1H), 2.44 (s, 3H), 3.50 (d, $J = 14.5$ Hz, 1H), 3.70 (dd, $J = 15.0$, 15.0 Hz, 1H), 3.92 (dd, $J = 10.5$, 15.0 Hz, 1H), 4.20 (d, $J = 14.5$ Hz, 1H), 7.17–7.24 (m, 3H), 7.27 (d, $J = 8.0$ Hz, 2H), 7.39–7.52 (m, 8H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.77–7.83 (m, 2H), 7.90–7.97 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 21.52, 25.77, 26.42 (d, $J = 2.3$ Hz), 27.34 (d, $J = 2.0$ Hz), 31.10 (d, $J = 2.4$ Hz), 32.29 (d, $J = 2.9$ Hz), 36.54 (d, $J = 49.8$ Hz), 52.28, 118.25 (d, $J = 10.0$ Hz), 127.53, 127.82, 127.96, 128.62 (d, $J = 11.9$ Hz), 128.73 (d, $J = 12.0$ Hz), 129.40, 130.32 (d, $J = 9.5$ Hz), 130.53, 131.16 (d, $J = 2.9$ Hz), 131.46 (d, $J = 10.0$ Hz), 131.55 (d, $J = 2.9$ Hz), 132.79 (d, $J = 75.9$ Hz), 135.77 (d, $J = 78.8$ Hz), 136.63, 138.01, 143.14, 152.05 (d, $J = 9.0$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 38.23. Found: C, 69.34; H, 6.17%. m.p.: 68.0–70.0 °C.

Calcd for C$_{34}$H$_{38}$NO$_2$PS$_2$: C, 69.72; H, 6.19%.

(3E)-1-(N-Butyl-N-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3ab)

IR (nujol) 2924, 2853, 1559, 1507, 1457, 1437, 1340, 1152, 786 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.74 (t, $J = 7.5$ Hz, 3H), 1.11 (qt, $J = 7.5$, 7.5 Hz, 2H), 1.40 (tt, $J = 7.5$, 7.5 Hz, 2H), 2.43 (s, 3H), 3.27 (t, $J = 7.5$ Hz, 2H), 6.47 (d, $J = 13.5$ Hz, 1H), 6.97 (dd, $J = 7.0$, 7.0 Hz, 2H), 7.04 (t, $J = 7.0$ Hz, 1H), 7.20–7.33 (m, 8H), 7.37 (d, $J = 7.0$ Hz, 2H), 7.73 (d, $J = 8.5$ Hz, 2H), 7.75–7.83 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 13.47, 19.59, 21.56, 30.74, 48.28, 119.79 (d, $J = 85.4$ Hz), 127.54, 127.79, 128.07 (d, $J = 12.9$ Hz), 129.80, 129.82, 130.02, 130.90 (d, $J = 2.9$ Hz), 131.34 (d, $J = 10.5$ Hz), 132.78 (d, $J = 86.4$ Hz), 133.73 (d, $J = 3.4$ Hz), 137.47, 143.99, 151.08 (d, $J = 8.1$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ 28.93. Found: C, 68.28; H, 5.89%.
Calcd for C_{31}H_{32}NO_{2}PS_{2}: C, 68.23; H, 5.91%. m.p.: 129.0–130.5 °C.

**(E)-1-(N-Cyclohexyl-N-tosylamino)-2-diphenylthiophosphinyl-1-phenylethene (3ac)**

![Structure of 3ac](image)

IR (nujol) 2923, 2855, 1558, 1439, 1329, 1288, 1153, 1093, 1039, 887 cm⁻¹; ¹H NMR (CDCl₃) δ 0.65–1.70 (m, 10H), 2.37 (s, 3H), 3.80–3.90 (m, 1H), 6.07 (d, J = 13.5 Hz, 1H), 6.94–7.04 (m, 3H), 7.07 (d, J = 8.0 Hz, 2H), 7.23–7.36 (m, 6H), 7.67 (d, J = 8.0 Hz, 2H), 7.73 (d, J = 7.0 Hz, 2H), 7.79–7.88 (m, 4H); ¹³C NMR (CDCl₃) δ 21.48, 24.79, 26.28, 32.74, 61.14, 124.07 (d, J = 80.1 Hz), 126.95, 127.45, 128.13 (d, J = 12.9 Hz), 129.77, 129.90, 130.34, 131.05 (d, J = 2.9 Hz), 131.45 (d, J = 10.5 Hz), 131.61 (d, J = 86.4 Hz), 137.25 (d, J = 2.5 Hz), 138.50, 143.51, 149.46 (d, J = 6.1 Hz); ³¹P NMR (CDCl₃) δ 29.08. HRMS (EI⁺) (m/z) Observed: 571.1768 (Δ = −0.1 ppm). Calcd for C_{33}H_{34}NO_{2}PS_{2} [M⁺]: 571.1769. m.p.: 190.5–192.5 °C.

**(E)-2-Diphenylthiophosphinyl-1-phenyl-1-(N-tosylamino)ethene (3ad)**

![Structure of 3ad](image)

IR (nujol) 2923, 2854, 1560, 1507, 1457, 1377, 1344, 1166, 747, 736 cm⁻¹; ¹H NMR (CDCl₃) δ 2.31 (s, 3H), 5.30 (d, J = 16.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 7.30–7.50 (m, 13H), 7.53–7.63 (m, 4H), 11.14 (s, 1H); ¹³C NMR (CDCl₃) δ 21.57, 100.31 (d, J = 85.5 Hz), 127.68, 127.87, 128.59, 128.60 (d, J = 12.9 Hz), 129.12, 130.45, 130.78 (d, J = 10.9 Hz), 131.43 (d, J = 2.9 Hz), 133.89 (d, J = 87.8 Hz), 136.11, 136.79 (d, J = 11.9 Hz), 143.52, 156.24; ³¹P NMR (CDCl₃) δ 26.00. Found: C, 66.14; H, 4.94%. Calcd for C_{27}H_{32}NO_{2}PS_{2}: C, 66.24; H, 4.94%. m.p.: 192.0–193.5 °C.

**(E)-1-[N-Benzyl-N-((1S)-(+-)10-camphorsulfonamido]-2-diphenylthiophosphinyl-1-phenylethene (3ae)**

![Structure of 3ae](image)

IR (nujol) 2923, 2853, 1749, 1790, 1437, 1348, 1260, 1154, 1097, 1048, 792 cm⁻¹; ¹H NMR (CDCl₃) δ 0.68 (s, 3H), 1.01 (s, 3H), 1.40–1.50 (m, 1H), 1.65–1.75 (m, 1H), 1.93 (d, J = 18.0 Hz, 1H), 2.00–2.10 (m, 2H), 2.30–2.40 cm⁻¹; ¹H NMR (CDCl₃) δ 0.68 (s, 3H), 1.01 (s, 3H), 1.40–1.50 (m, 1H), 1.65–1.75 (m, 1H), 1.93 (d, J = 18.0 Hz, 1H), 2.00–2.10 (m, 2H), 2.30–2.40
(E)-2-Diphenylthiophosphinyl-1-phenyl-1-succinimidoethene (3af)

IR (nujol) 2923, 2854, 1718, 1558, 1507, 1457, 1437, 1181, 757 cm⁻¹; ¹H NMR (CDCl₃) δ 2.71–2.87 (m, 4H), 6.92 (d, J = 14.0 Hz, 1H), 7.34–7.43 (m, 5H), 7.45–7.55 (m, 6H), 7.80–7.88 (m, 4H); ¹³C NMR (CDCl₃) δ 28.96, 119.88 (d, J = 80.6 Hz), 126.04, 128.71 (d, J = 12.5 Hz), 128.98, 130.68, 131.48 (d, J = 11.0 Hz), 131.71 (d, J = 2.9 Hz), 133.12 (d, J = 89.3 Hz), 135.49 (d, J = 11.5 Hz), 145.81 (d, J = 2.9 Hz), 175.98; ³¹P NMR (CDCl₃) δ 29.17. Found: C, 68.75; H, 4.90%. Calcd for C₃₇H₃₈NO₃PS₂: C, 69.05; H, 4.83%. m.p.: 199.0–200.0 °C.

(E)-2-Diphenylthiophosphinyl-1-phenyl-1-phthalimidoethene (3ag)

IR (nujol) 2924, 2854, 1740, 1558, 1506, 1456, 1374, 784 cm⁻¹; ¹H NMR (CDCl₃) δ 7.02 (d, J = 12.5 Hz, 1H), 7.29–7.48 (m, 11H), 7.66–7.77 (m, 4H), 7.83–7.91 (m, 4H); ¹³C NMR (CDCl₃) δ 122.42 (d, J = 81.1 Hz), 123.72, 126.18, 128.51 (d, J = 12.9 Hz), 128.94, 130.54, 131.34 (d, J = 2.9 Hz), 131.67 (d, J = 11.5 Hz), 131.91, 132.35 (d, J = 87.9 Hz), 134.05, 134.35, 136.02 (d, J = 12.0 Hz), 142.90 (d, J = 3.8 Hz), 166.43; ³¹P NMR (CDCl₃) δ 30.03. Found: C, 72.02; H, 4.20%. Calcd for C₃₈H₃₇NO₃PS: C, 72.24; H, 4.33%. m.p.: 172.0–174.0 °C.
2-Diphenylthiophosphinyl-1-phenyl-1-(2-oxopyrrolidino)ethene (3ah) (E/Z = 69/31)

\[
\text{\includegraphics[width=0.5\textwidth]{2-Diphenylthiophosphinyl-1-phenyl-1-(2-oxopyrrolidino)ethene.png}}
\]

IR (nujol) 2921, 2852, 1700, 1590, 1437, 1378, 1340, 1258, 1098, 887, 753 cm\(^{-1}\);

\(^1\)H NMR (CDCl\(_3\)) (For E isomer) \(\delta\) 1.78 (tt, \(J = 7.0, 8.0\) Hz, 2H), 2.13 (t, \(J = 8.0\) Hz, 2H), 3.57 (t, \(J = 7.0\) Hz, 2H), 6.64 (d, \(J = 14.0\) Hz, 1H), 7.35–7.41 (m, 5H), 7.43–7.51 (m, 6H), 7.95–8.02 (m, 4H) (For Z isomer) \(\delta\) 1.97 (tt, \(J = 7.5, 8.0\) Hz, 2H), 2.60 (t, \(J = 8.0\) Hz, 2H), 3.28 (t, \(J = 7.5\) Hz, 2H), 7.01 (dd, \(J = 7.5, 7.5\) Hz, 2H), 7.06 (d, \(J = 14.0\) Hz, 1H), 7.07 (t, \(J = 7.5\) Hz, 1H), 7.20–7.29 (m, 8H), 7.82–7.90 (m, 4H);

\(^{13}\)C NMR (CDCl\(_3\)) (For E isomer) \(\delta\) 18.32, 30.72, 49.52, 118.79 (d, \(J = 84.4\) Hz), 126.78, 128.39 (d, \(J = 12.4\) Hz), 128.85, 130.24, 131.36 (d, \(J = 3.4\) Hz), 131.49 (d, \(J = 11.0\) Hz), 132.96 (d, \(J = 87.4\) Hz), 135.79 (d, \(J = 12.9\) Hz), 149.62 (d, \(J = 2.9\) Hz), 175.26 (For Z isomer) \(\delta\) 18.12, 32.66, 49.10, 113.84 (d, \(J = 91.6\) Hz), 127.88, 128.04 (d, \(J = 12.4\) Hz), 129.23, 129.42, 130.64 (d, \(J = 2.9\) Hz), 131.30 (d, \(J = 11.0\) Hz), 133.15 (d, \(J = 4.8\) Hz), 133.54 (d, \(J = 86.5\) Hz), 149.36 (d, \(J = 8.6\) Hz), 175.28; 

\(^{31}\)P NMR (CDCl\(_3\)) (For E isomer) \(\delta\) 29.38. (For Z isomer) \(\delta\) 28.77. Found: C, 71.74; H, 5.65%. 
Calcd for C\(_{24}\)H\(_{25}\)NOPS: C, 71.44; H, 5.50\%.

\((E)-1\)-Diphenylthiophosphinyl-3,3-dimethyl-2-succinimido-1-butene (3if)

\[
\text{\includegraphics[width=0.5\textwidth]{(E)-1-Diphenylthiophosphinyl-3,3-dimethyl-2-succinimido-1-butene.png}}
\]

IR (nujol) 2925, 2855, 1700, 1539, 1521, 1456, 1363, 1186, 1098, 841, 752 cm\(^{-1}\);

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.18 (s, 9H), 2.62–2.78 (m, 4H), 6.46 (d, \(J = 15.0\) Hz, 1H), 7.40–7.52 (m, 6H), 7.71–7.79 (m, 4H);

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 28.85, 28.91, 39.91 (d, \(J = 9.6\) Hz), 118.52 (d, \(J = 80.6\) Hz), 128.59 (d, \(J = 13.0\) Hz), 131.28 (d, \(J = 10.5\) Hz), 131.46 (d, \(J = 3.4\) Hz), 133.46 (d, \(J = 88.8\) Hz), 158.14 (d, \(J = 5.6\) Hz), 176.62; 

\(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 28.41. Found: C, 66.37; H, 6.11\%. Calcd for C\(_{22}\)H\(_{23}\)NO\(_2\)PS: C, 66.48; H, 6.09\%. m.p.: 166.5–167.5 °C.

1-Diphenylthiophosphinyl-5-(N-tosylamino)-1-pentyne (4a)

\[
\text{\includegraphics[width=0.5\textwidth]{1-Diphenylthiophosphinyl-5-(N-tosylamino)-1-pentyne.png}}
\]

IR (nujol) 3200, 2923, 2854, 2197, 1558, 1457, 1439, 1330, 1159, 1072, 716 cm\(^{-1}\);

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.80 (tt, \(J = 7.0, 7.0\) Hz, 2H), 2.39 (s, 3H), 2.53
(dt, J = 4.0, 7.0 Hz, 2H), 3.04 (dt, J = 6.5, 7.0 Hz, 2H), 4.84 (t, J = 6.5 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 7.42–7.52 (m, 6H), 7.70 (d, J = 8.5 Hz, 2H), 7.87–7.94 (m, 4H); \( ^{13} \text{C} \text{NMR (CDCl}_3 \) \( \delta \) 17.22 (d, J = 3.4 Hz), 21.49, 27.69 (d, J = 1.4 Hz), 41.91, 75.03 (d, J = 154.3 Hz), 108.25 (d, J = 26.3 Hz), 126.98, 128.61 (d, J = 13.8 Hz), 129.78, 130.73 (d, J = 12.0 Hz), 131.73 (d, J = 2.9 Hz), 133.66 (d, J = 97.9 Hz), 136.65, 143.54; \( ^{31} \text{P} \text{NMR (CDCl}_3 \) \( \delta \) 17.84. Found: C, 63.41; H, 5.54%. Calcd for C\textsubscript{24}H\textsubscript{24}NO\textsubscript{2}PS\textsubscript{2}: C, 63.55; H, 5.33%. m.p.: 104.5–105.5 °C.

1-Diphenylthiophosphinyl-6-(N-tosylamino)-1-hexyne (4b)

\[
\begin{align*}
\text{Ts} & \quad \text{N} \\
\quad & \quad \text{S} \quad \text{PPb}_2 \\
\quad & \quad \text{H}
\end{align*}
\]

IR (nujol) 3240, 2924, 2855, 2200, 1456, 1437, 1375, 1326, 1163, 1097, 812, 722 cm\textsuperscript{-1}; \( ^{1} \text{H NMR (CDCl}_3 \) \( \delta \) 1.56–1.68 (m, 4H), 2.40 (s, 3H), 2.44 (dt, J = 4.0, 7.0 Hz, 2H), 2.93 (dt, J = 6.5, 6.5 Hz, 2H), 4.71 (t, J = 6.5 Hz, 1H), 7.28 (d, J = 8.0 Hz, 2H), 7.42–7.51 (m, 6H), 7.72 (d, J = 8.0 Hz, 2H), 7.86–7.93 (m, 4H); \( ^{13} \text{C} \text{NMR (CDCl}_3 \) \( \delta \) 19.49 (d, J = 3.4 Hz), 21.47, 24.42 (d, J = 1.9 Hz), 28.68, 42.39, 74.62 (d, J = 155.1 Hz), 109.29 (d, J = 26.3 Hz), 127.01, 128.58 (d, J = 13.9 Hz), 129.71, 130.70 (d, J = 12.4 Hz), 131.67 (d, J = 3.4 Hz), 133.76 (d, J = 97.9 Hz), 136.69, 143.44; \( ^{31} \text{P} \text{NMR (CDCl}_3 \) \( \delta \) 17.76. Found: C, 63.93; H, 5.81%. Calcd for C\textsubscript{26}H\textsubscript{26}NO\textsubscript{2}PS\textsubscript{2}: C, 64.22; H, 5.60%. m.p.: 112.5–114.0 °C.

2-\{(E)-2-Diphenylthiophosphinylmethyldiene\}-1-tosylpyrrolidine (5a)

\[
\begin{align*}
\text{N} & \quad \text{S} \\
\quad & \quad \text{PPb}_2 \\
\quad & \quad \text{H}
\end{align*}
\]

IR (nujol) 2924, 2854, 1606, 1436, 1345, 1270, 1202, 1154, 1065, 1004, 813 cm\textsuperscript{-1}; \( ^{1} \text{H NMR (CDCl}_3 \) \( \delta \) 1.79 (tt, J = 7.5, 7.5 Hz, 2H), 2.45 (s, 3H), 2.73 (t, J = 7.5 Hz, 2H), 3.73 (t, J = 7.5 Hz, 2H), 6.22 (d, J = 15.5 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.35–7.50 (m, 6H), 7.70 (d, J = 8.0 Hz, 2H), 7.71–7.80 (m, 4H); \( ^{13} \text{C} \text{NMR (CDCl}_3 \) \( \delta \) 21.35, 21.61, 31.37 (d, J = 5.3 Hz), 51.23, 94.17 (d, J = 98.3 Hz), 127.39, 128.44 (d, J = 12.4 Hz), 129.81, 130.89 (d, J = 11.0 Hz), 131.04 (d, J = 2.9 Hz), 134.31, 135.02 (d, J = 86.9 Hz), 144.87, 155.84 (d, J = 13.9 Hz); \( ^{31} \text{P} \text{NMR (CDCl}_3 \) \( \delta \) 30.35. Found: C, 63.29; H, 5.34%. Calcd for C\textsubscript{26}H\textsubscript{26}NO\textsubscript{2}PS\textsubscript{2}: C, 63.55; H, 5.33%. m.p.: 155.0–156.5 °C.
6-Diphenylthiophosphinylmethyl-1-tosyl-2,3,4-trihydropyridine (5b)

IR (nujol) 2923, 2854, 1456, 1438, 1338, 1170, 1151, 1093, 948, 797 cm⁻¹; ¹H NMR (CDCl₃) δ 1.05 (tt, J = 6.0, 7.5 Hz, 2H), 1.76–1.84 (m, 2H), 2.41 (s, 3H), 2.95 (t, J = 6.0 Hz, 2H), 4.02 (d, J = 13.0 Hz, 2H), 5.71–5.76 (m, 1H), 7.25 (d, J = 8.0 Hz, 2H), 7.43–7.53 (m, 6H), 7.60 (d, J = 8.0 Hz, 2H), 7.92–8.00 (m, 4H); ¹³C NMR (CDCl₃) δ 18.79, 21.55, 22.10 (d, J = 2.8 Hz), 40.23 (d, J = 48.6 Hz), 46.00, 124.14 (d, J = 9.6 Hz), 127.43, 128.03 (d, J = 10.5 Hz), 128.33 (d, J = 11.9 Hz), 129.60, 131.40 (d, J = 2.9 Hz), 131.68 (d, J = 10.0 Hz), 132.44 (d, J = 78.9 Hz), 136.27, 143.66; ³¹P NMR (CDCl₃) δ 41.65. Found: C, 64.33; H, 5.38%. Calcd for C₂₅H₂₆NO₄PS₂: C, 64.22; H, 5.66%. m.p.: 155.0–157.0 °C.

1-(N-Benzyl-N-tosylamino)-2-diphenylthiophosphinyl-1-phenylethane (6a)

IR (nujol) 2867, 1582, 1492, 1455, 1286, 1243, 1196, 1171, 1094, 1008, 824 cm⁻¹; ¹H NMR (CDCl₃) δ 2.40 (s, 3H), 2.95–3.05 (m, 1H), 3.18–3.28 (m, 1H), 3.98 (d, J = 16.0 Hz, 1H), 4.62 (d, J = 16.0 Hz, 1H), 5.54 (dt, J = 2.0, 11.5 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 8.0, 8.0 Hz, 2H), 7.00 (t, J = 8.0 Hz, 1H), 7.10–7.16 (m, 2H), 7.18–7.52 (m, 13H), 7.55 (d, J = 8.0 Hz, 2H), 7.62–7.70 (m, 2H); ¹³C NMR (CDCl₃) δ 21.47, 36.14 (d, J = 51.5 Hz), 49.33, 57.95 (d, J = 4.4 Hz), 127.40, 127.55, 127.63, 127.89, 127.93 (d, J = 11.9 Hz), 128.35, 128.43, 128.52 (d, J = 12.4 Hz), 129.28, 129.49, 130.85 (d, J = 2.9 Hz), 130.94 (d, J = 10.0 Hz), 131.03 (d, J = 10.5 Hz), 131.39 (d, J = 2.9 Hz), 131.81 (d, J = 80.1 Hz), 133.32 (d, J = 82.6 Hz), 134.69, 137.60, 137.75, 143.21; ³¹P NMR (CDCl₃) δ 36.46. HRMS (EI⁺) (m/z) Observed: 581.1625 (Δ = +2.3 ppm). Calcd for C₃₅H₃₂NO₄PS₂ [M⁺]: 581.1612. m.p.: 149.0–150.0 °C. [α]D²⁵ = −105 (c 0.0020, CHCl₃).

2-Diphenylthiophosphinyl-1-phenyl-1-succinimidoethane (6b)

IR (nujol) 2923, 2854, 1700, 1454, 1437, 1364, 1139, 1101, 743 cm⁻¹; ¹H NMR (CDCl₃) δ 2.02–2.60 (m, 4H), 2.85–2.95 (m, 1H), 4.40–4.50 (m, 1H), 5.92 (dt, J = 2.5, 13.5 Hz, 1H), 7.24–7.31 (m, 3H), 7.43–7.53 (m, 8H), 7.80–7.91 (m, 4H); ¹³C
NMR (CDCl$_3$) $\delta$ 27.73, 31.49 (d, $J = 54.4$ Hz), 49.59 (d, $J = 1.5$ Hz), 127.96, 128.24, 128.45 (d, $J = 12.4$ Hz), 128.62, 128.73 (d, $J = 12.4$ Hz), 130.99 (d, $J = 10.0$ Hz), 131.39 (d, $J = 10.5$ Hz), 131.52 (d, $J = 2.9$ Hz), 131.72 (d, $J = 2.9$ Hz), 132.02 (d, $J = 77.4$ Hz), 132.34 (d, $J = 82.1$ Hz), 139.23 (d, $J = 12.4$ Hz), 176.83; $^{31}$P NMR (CDCl$_3$) $\delta$ 36.56. HRMS (EI$^+$) ($m/z$) Observed: 419.1111 ($\Delta = +0.6$ ppm). Calcd for C$_{24}$H$_{22}$NO$_2$PS [M$^+$]: 419.1109. m.p.: 63.5–65.0 °C. $[\alpha]_D^{25} = -24$ (c 0.0050, CHCl$_3$).

$(E)$-1-(N-Benzyl-N-tosylamino)-2-diphenylphosphino-1-phenylethene (3aa–S)

IR (nujol) 2924, 2854, 1590, 1456, 1377, 1311, 1154, 1082, 874, 742 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 2.43 (s, 3H), 4.62 (s, 2H), 6.29 (d, $J = 4.0$ Hz, 1H), 7.05 (d, $J = 7.0$ Hz, 2H), 7.10 (d, $J = 7.5$ Hz, 2H), 7.12–7.19 (m, 6H), 7.21–7.35 (m, 12H), 7.58 (d, $J = 7.0$ Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$ 21.57, 52.17, 126.91 (d, $J = 12.9$ Hz), 127.64, 127.83 (merged signals), 128.32, 128.34, 128.40 (d, $J = 7.6$ Hz), 128.95, 129.27, 129.48, 129.51, 132.58 (d, $J = 18.6$ Hz), 135.55 (d, $J = 3.8$ Hz), 136.13, 136.72, 139.22 (d, $J = 10.0$ Hz), 143.54, 149.05 (d, $J = 32.5$ Hz); $^{31}$P NMR (CDCl$_3$) $\delta$ –25.53. Found: C, 74.83; H, 5.58%. Calcd for C$_{34}$H$_{30}$NO$_2$PS: C, 74.57; H, 5.52%. m.p.: 131.5–132.5 °C.

$(E)$-2-Diphenylphosphino-1-phenyl-1-succinimidoethene (3af–S)

IR (nujol) 2924, 2855, 1719, 1560, 1457, 1375, 1178, 764, 747 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 2.50–2.82 (m, 4H), 7.01 (d, $J = 1.5$ Hz, 1H), 7.30–7.39 (m, 11H), 7.46–7.53 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$ 28.50, 125.47, 128.67 (d, $J = 7.3$ Hz), 128.76, 129.05, 129.21, 129.36, 133.18 (d, $J = 19.5$ Hz), 135.56 (d, $J = 3.9$ Hz), 136.50 (d, $J = 8.6$ Hz), 141.51 (d, $J = 17.6$ Hz), 175.53; $^{31}$P NMR (CDCl$_3$) $\delta$ –22.08. Found: C, 74.51; H, 5.34%. Calcd for C$_{24}$H$_{20}$NO$_2$P: C, 74.80; H, 5.23%. m.p.: 178.5–179.5 °C.
1-(N-Benzyl-N-tosylamino)-2-diphenylphosphino-1-phenylethane (6a–S)

IR (nujol) 2823, 2854, 1598, 1377, 1337, 1157, 1091, 1046, 923, 738 cm⁻¹;

¹H NMR (CDCl₃) δ 2.42 (s, 3H), 2.56–2.68 (m, 2H), 3.92 (d, J = 16.0 Hz, 1H), 4.60 (d, J = 16.0 Hz, 1H), 4.74–4.82 (m, 1H), 6.86 (d, J = 7.5 Hz, 2H), 7.13–7.31 (m, 17H), 7.32–7.42 (m, 5H); ¹³C NMR (CDCl₃) δ 21.50, 32.34 (d, J = 15.8 Hz), 48.32, 59.05 (d, J = 21.0 Hz), 127.30, 127.32, 128.19, 128.21 (merged signals), 128.26, 128.32 (d, J = 6.3 Hz), 128.35, 128.43 (d, J = 7.1 Hz), 129.00, 129.17 (d, J = 2.4 Hz), 129.40, 132.17 (d, J = 18.6 Hz), 133.58 (d, J = 20.0 Hz), 136.35 (d, J = 2.0 Hz), 137.05 (d, J = 14.9 Hz), 137.80, 138.01, 138.17 (d, J = 12.4 Hz), 142.98; ³¹P NMR (CDCl₃) δ –24.35. HRMS (EI⁺) (m/z) Observed: 549.1888 (Δ = –0.5 ppm). Calcd for C₃₄H₃₂NO₂PS [M⁺]: 549.1891. m.p.: 43.0–45.0 °C. [α]₀²⁵ = –6.0 (c 0.0635, CHCl₃)
References and Notes


(5) The X-ray crystallographic analysis of 3ca verified the E stereochemistry of the major isomers.


(8) When (R)-BINAP was used as a ligand instead of 7, 91% ee of 6a was obtained in 82% yield. However, (R)-BINAP was less effective for the enantioselective hydrogenation of 3af to provide 6b in 99% yield with 15% ee.
Chapter 4

Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

Treatment of 1-alkynylphosphine sulfides with 1,6- or 1,7-diynes in the presence of a cationic rhodium catalyst results in a formal [2+2+2] cycloaddition reaction to afford the corresponding aromatic phosphine sulfides. The aromatic rings formed in the cycloaddition naturally bear one or two substituents at the ortho positions to the phosphorus atom, which creates a sterically hindered environment around the phosphorus atom. The following desulfidation yields bulky phosphines that will potentially serve as ligands in transition-metal-catalyzed reactions.
Introduction

In the modern organic synthesis, bulky phosphine ligands play an indispensable role in preparing biologically interesting compounds as well as organic functional materials.\(^1\) Synthesis of such bulky ligands is hence quite important. However, the methods for the synthesis are mostly limited to the reaction of a chlorophosphine with a bulky organometallic reagent\(^2\) and the transition-metal-catalyzed phosphination or phosphinylation of a bulky aryl halide.\(^3\)

In chapter 4, the author describes a conceptually different approach to bulky phosphines. Rhodium-catalyzed formal [2+2+2] cycloaddition reaction\(^4\) of 1,6-diynes and 1-alkynylphosphine sulfides\(^5\) afforded benzene rings having a thiophosphinyl moiety. When substrates are properly designed, the newly formed benzene rings naturally have one or two substituents next to the thiophosphinyl group, which provide stERICALLY congested environment around the phosphorus.\(^6,7\)

Results and Discussion

The reaction of 1,6-diyne \(1a\) with 1-octynyldiphenylphosphine sulfide (\(2a\)) proceeded smoothly in dichloromethane in the presence of a cationic rhodium catalyst and BINAP (Table 1, entry 1). Among the ligands the author screened, BINAP was the best ligand. When DPPE, DPPF, or \(\text{PPh}_3\) (2 equiv to Rh) was used, the yield was moderate. The generation of the cationic rhodium species by the action of silver tetrafluoroborate was essential. Without the silver salt, only \(1a\) participated in the cycloaddition reaction to form dimerized \(4a\) and no \(3aa\) was obtained. The cationic rhodium center would induce the strong coordination of \(2a\). Iridium catalysis, \([\text{IrCl(cod)}]_2\) with or without the silver salt, for instance, left \(2a\) untouched and provided \(4a\) instead. The use of \([\text{Cp}^*\text{RuCl(cod)}]\) only promoted the very slow dimerization of \(1a\). The reaction of trivalent 1-octynyldiphenylphosphine with \(1a\) resulted in no conversion. The highly coordinating nature of the trivalent phosphine would cause deactivation of the catalyst. The reaction of 1-octynyldiphenylphosphine oxide with \(1a\) provided 40% yield of the corresponding product along with \(4a\). The sulfide moiety seems to properly assist the reaction of a rhodacyclopentadiene intermediate with \(2a\) in the catalytic cycle.\(^8\)
Table 1. Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides\(^{a}\)

![Diagram of the reaction](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>1</th>
<th>(X)</th>
<th>(R^1)</th>
<th>2</th>
<th>(R^2)</th>
<th>3</th>
<th>yield /%(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>TsN</td>
<td>H</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3a(_a)</td>
<td>71</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>O</td>
<td>H</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3b(_a)</td>
<td>77</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>E(_2)C</td>
<td>H</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3c(_a)</td>
<td>97</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>CH(_2)</td>
<td>H</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3d(_a)</td>
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</tr>
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<td>1e</td>
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<td>H</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3e(_a)</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>1c</td>
<td>E(_2)C</td>
<td>H</td>
<td>2b</td>
<td>Ph</td>
<td>3c(_b)</td>
<td>85</td>
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<tr>
<td>7</td>
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<td>E(_2)C</td>
<td>H</td>
<td>2c</td>
<td>(i)-Pr</td>
<td>3c(_c)</td>
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<tr>
<td>8</td>
<td>1c</td>
<td>E(_2)C</td>
<td>H</td>
<td>2d</td>
<td>(t)-Bu</td>
<td>3c(_d)</td>
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<tr>
<td>9</td>
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<td>E(_2)C</td>
<td>H</td>
<td>2e</td>
<td>2-MeO-C(_6)H(_4)</td>
<td>3c(_e)</td>
<td>85</td>
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<tr>
<td>10</td>
<td>1c</td>
<td>E(_2)C</td>
<td>H</td>
<td>2f</td>
<td>Me(_2)Si</td>
<td>3c(_f)</td>
<td>80</td>
</tr>
<tr>
<td>11</td>
<td>1f</td>
<td>E(_2)C</td>
<td>Me</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3f(_a)</td>
<td>87(^d)</td>
</tr>
<tr>
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<td>1g</td>
<td>E(_2)C</td>
<td>Ph</td>
<td>2a</td>
<td>(n)-C(<em>6)H(</em>{13})</td>
<td>3g(_a)</td>
<td>90(^d)</td>
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<tr>
<td>13</td>
<td>1g</td>
<td>E(_2)C</td>
<td>Ph</td>
<td>2b</td>
<td>Ph</td>
<td>3g(_b)</td>
<td>65(^{d,e})</td>
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<tr>
<td>14</td>
<td>1h</td>
<td>E(_2)C</td>
<td>(i)-Pr</td>
<td>2c</td>
<td>(i)-Pr</td>
<td>3h(_c)</td>
<td>70(^{d,f})</td>
</tr>
<tr>
<td>15</td>
<td>1h</td>
<td>E(_2)C</td>
<td>(i)-Pr</td>
<td>2g</td>
<td>2-MeO-Np(^g)</td>
<td>3h(_g)</td>
<td>77(^{d,f})</td>
</tr>
</tbody>
</table>

\(^{a}\) Conditions: 1 (0.60 mmol), 2 (0.50 mmol), [RhCl(cod)]\(_2\) (0.0075 mmol), AgBF\(_4\) (0.015 mmol), rac-BINAP (0.015 mmol), dichloromethane (4.0 mL), 25 °C, 4 h.
\(^{b}\) Ts = 4-Me-C\(_6\)H\(_4\)-SO\(_2\), E = CO\(_2\)Me. \(^{c}\) Isolated yields. \(^{d}\) The reaction was performed in 1,2-dichloroethane at reflux. \(^{e}\) The reaction was performed for 12 h. \(^{f}\) [RhCl(cod)]\(_2\) (5 mol%), AgBF\(_4\) (10 mol%), rac-BINAP (10 mol%), 12 h. \(^{g}\) 2-Methoxy-1-naphthyl.
Various combinations of tethered diynes and 1-alkynylphosphine sulfides were examined (Table 1). Dipropargyl ether (1b) and a diyne 1c derived from dimethyl malonate reacted smoothly with 2a. The latter provided the corresponding triarylphosphine sulfide 3ca in the highest yield of 97% (entry 3). 1,7-Octadiyne (1e) was superior to 1,6-heptadiyne (1d) as a substrate.

The scope of 1-alkynylphosphine sulfides (entries 6–10) is wide enough to employ not only phenyl-substituted 2b but also bulky isopropyl- and tert-butyl-substituted 2c and 2d. The reactions of o-methoxyphenyl-substituted 2e and trimethylsilyl-substituted 2f proceeded smoothly. The reaction is so powerful that dialkynylphosphine sulfide 5a and trialkynylphenylphosphine sulfide 5b participated in multiple cycloadditions to yield the corresponding products in high yields (eqs 1 and 2).

Reactions of internal diynes (\(R^1 \neq H\)) did not proceed at all in dichloromethane at 25 °C. Instead, performing the reactions in refluxing 1,2-dichloroethane resulted in smooth conversion to afford the corresponding products in good yields (entries 11–15). The products have a 2,6-disubstituted phenyl group on the phosphorus, which creates a considerable steric effect. Interestingly, the reaction of 1h with diphenyl[(2-methoxy-1-naphthyl)ethynyl]phosphine sulfide

![chemical structure](1c (2.4 equiv) + 1c (3.6 equiv))
(2g) provided phosphine sulfide 3hg, which has a chiral axis.\textsuperscript{10} The use of monosubstituted 1, where one R\textsuperscript{1} is H and the other R\textsuperscript{1} is Ph, resulted in self-dimerization of the diyne.

1-Alkynyldicyclohexylphosphine sulfides 7 were less reactive than the corresponding diphenyl analogues 2. The reaction of terminal diyne 1c with 7a provided the desired product 8a in moderate yield with concomitant formation of 4b (eq 3). The reaction of internal diyne 1g with dicyclohexylphosphine sulfide 7b was successful to yield highly crowded 8b in high yield (eq 4).

\[
\begin{align*}
1c \text{ (1.2 equiv)} & + \quad 1.5 \text{ mol\% [RhCl(cod)]_2} & \quad 3 \text{ mol\% AgBF}_4 & \quad 3 \text{ mol\% rac-BINAP} \\
S & P(c-C_6H_{11})_2 & \quad \text{CH}_2Cl_2, 25 ^\circC, 4 \text{ h} \\
n-C_6H_{13} & 8a & 44\% (3) \\
\text{C} & \text{C} \\
\text{X} & \text{X} & \text{X} & \text{HC} & \text{C} \\
\text{Ph} & \text{H} & \text{P(c-C_6H_{11})_2} & \text{C} & \text{Me} \\
1g \text{ (1.2 equiv)} & + \quad 1.5 \text{ mol\% [RhCl(cod)]_2} & \quad 3 \text{ mol\% AgBF}_4 & \quad 3 \text{ mol\% rac-BINAP} \\
S & P(c-C_6H_{11})_2 & \quad \text{ClCH}_2\text{CH}_2\text{Cl}, \text{reflux, 12 h} \\
\text{C} & \text{C} & \text{X} & \text{X} & \text{Ph} & \text{Ph} & \text{C} & \text{Me} \\
\text{Ph} & \text{Ph} & \text{H} & \text{P(c-C_6H_{11})_2} & \text{C} & \text{Me} \\
\end{align*}
\]

Radical Desulfidation of Phosphine Sulfides. The products, phosphine sulfides, were subjected to radical desulfidation conditions\textsuperscript{11} to provide the corresponding trivalent phosphines in high yields (Scheme 1). The desulfidation reactions of these bulky phosphines were clean and high-yielding. Except for triisopropyl-substituted 3hc–S, the phosphines obtained were stable under air. The author could perform the purification of the trivalent phosphines on silica gel without any special care. The present method offers a novel access to bulky phosphate ligands.
Application of Newly Synthesized Bulky Phosphine. Application of the bulky phosphine was examined. The ligand 8b–S proved to serve as a ligand for the amination of aryl chloride with morpholine (eq 5).\textsuperscript{12}
Conclusion

The combination of the rhodium-catalyzed formal cycloaddition of diynes with 1-alkynylphosphine sulfides and subsequent desulfidation of the cycloadducts thus represents a conceptually novel access to bulky phosphines. The bulky phosphine ligands prepared by this method will find many applications in organic synthesis.
Experimental Section

Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl$_3$. Chemical shifts (δ) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and relative to CDCl$_3$ at 77.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl$_3$ with 85% H$_3$PO$_4$ solution as an external standard. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Determination of enantiomeric excess was performed with Shimadzu LCMS-2010A. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1-alkynylphosphine, chlorodiphenylphosphine was purchased from TCI. Chlorodicyclohexylphosphine was obtained from Aldrich. Starting 1-alkynylphosphine sulfides 2 were prepared by the methods described in Chapter 3.

Chloro(bis-1,5-cyclooctadiene)rhodium(I) dimer was purchased from Wako Pure Chemicals. Silver(I) tetrafluoroborate and racemic BINAP were obtained from Aldrich. Palladium(II) acetate was purchased from TCI. All reactions were carried out under argon atmosphere.

Typical Procedure for the Rhodium-Catalyzed Reaction

Synthesis of 3ca is representative. [RhCl(cod)]$_2$ (3.7 mg, 0.0075 mmol), AgBF$_4$ (2.9 mg, 0.015 mmol), and BINAP (9.3 mg, 0.015 mmol) were placed in a 20-mL reaction flask under argon. Dichloromethane (4.0 mL), 1-octynyldiphenylphosphine sulfide (2a, 0.16 g, 0.50 mmol), and 4,4-di(methoxycarbonyl)-1,6-heptadiyne (1c, 0.13 g, 0.60 mmol) were sequentially added. The resulting solution was stirred for 4 h at 25 °C. Water (10 mL) was added, and the product
was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded 3ca (0.26 g, 0.49 mmol, 97%) as a white solid.

**Typical Procedure for the (Me₃Si)₃SiH-Mediated Radical Desulfidation Reaction**

Synthesis of 3gb–S is representative. AIBN (1.6 mg, 0.010 mmol) and 3gb (0.068 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided 3gb–S (0.054 g, 0.084 mmol, 84%) as a white solid.

**Procedure for the Amination of Aryl Chloride with Morpholine (eq 5)**

Palladium acetate (2.8 mg, 0.013 mmol), 8b–S (0.017 g, 0.025 mmol), and sodium tert-butoxide were placed in a 20-mL reaction flask under argon. Toluene (3.0 mL) was added, and the mixture was stirred for 10 min. 4-Chlorotoluene and morpholine were sequentially added. The resulting mixture was heated at reflux for 12 h. After the mixture was cooled to room temperature, water (10 mL) was added. Extractive workup with ethyl acetate followed by silica gel column purification provided N-(4-methylphenyl)morpholine (0.075g, 0.42 mmol) in 83% yield.

**Characterization Data**

6,6-Di(methoxycarbonyl)-2,10-dimethyl-3,8-undecadiyne (1h)

| IR (neat) | 2970, 2873, 1744, 1436, 1326, 1293, 1210, 1181, 1062, 950, 902, 854 cm⁻¹; δ 1.09 (d, J = 7.0 Hz, 12H), 2.46 (sept, J = 7.0 Hz, 2H), 2.88 (s, 4H), 3.72 (s, 6H); δ 20.41, 22.86, 23.16, 52.71, 57.55, 73.42, 89.34, 169.65. | Found: C, 68.58; H, 8.23%. Calcd for C₁₇H₂₄O₄: C, 69.84; H, 8.27%. |

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(3-Methyl-1-butynyl)diphenylphosphine sulfide (2c)

\[ \text{IR (nujol) 2924, 2854, 1478, 1436, 1311, 978, 835, 720, 662 cm}^{-1}; \]
\[ ^1\text{H NMR (CDCl}_3) \delta 1.30 (d, J = 7.0 \text{ Hz}, 6\text{H}), 2.84 (dsept, J = 3.5, 7.0 \text{ Hz}, 1\text{H}), 7.42–7.52 (m, 6\text{H}), 7.88–7.96 (m, 4\text{H}); \]
\[ ^13\text{C NMR (CDCl}_3) \delta 21.72 (d, J = 1.9 \text{ Hz}), 72.94 (d, J = 33.5 \text{ Hz}), 114.68 (d, J = 25.3 \text{ Hz}), 128.52 (d, J = 13.9 \text{ Hz}), 130.73 (d, J = 12.4 \text{ Hz}), 131.56 (d, J = 2.9 \text{ Hz}), 134.19 (d, J = 99.3 \text{ Hz}); \]
\[ ^{31}\text{P NMR (CDCl}_3) \delta 17.40. \]

Found: C, 71.58%; H, 6.03%. Calcd for C\textsubscript{17}H\textsubscript{17}PS: C, 71.80%; H, 6.03%. m.p.: 80.5–82.0 °C.

(2-Methoxyphenylethynyl)diphenylphosphine sulfide (2e)

\[ \text{IR (nujol) 2920, 2851, 1773, 1718, 1684, 1653, 1559, 1507, 1420, 1263, 1024, 665 cm}^{-1}; \]
\[ ^1\text{H NMR (CDCl}_3) \delta 3.91 (s, 3\text{H}), 6.90–6.97 (m, 2\text{H}), 7.38–7.55 (m, 8\text{H}), 8.02–8.10 (m, 4\text{H}); \]
\[ ^13\text{C NMR (CDCl}_3) \delta 55.84, 85.47 (d, J = 155.1 \text{ Hz}), 103.04 (d, J = 27.3 \text{ Hz}), 109.63 (d, J = 4.4 \text{ Hz}), 110.80, 120.48, 128.52 (d, J = 13.4 \text{ Hz}), 130.93 (d, J = 12.4 \text{ Hz}), 131.58 (d, J = 2.9 \text{ Hz}), 132.17, 134.04 (d, J = 2.0 \text{ Hz}), 134.20 (d, J = 98.4 \text{ Hz}), 161.54; \]
\[ ^{31}\text{P NMR (CDCl}_3) \delta 18.42. \]

Found: C, 72.47%; H, 4.97%. Calcd for C\textsubscript{21}H\textsubscript{17}OPS: C, 71.80%; H, 4.92%. m.p.: 77.0–78.5 °C.

(Trimethylsilylethynyl)diphenylphosphine sulfide (2f)

\[ \text{IR (nujol) 2920, 2851, 2401, 1735, 1685, 1560, 1540, 1438, 1252, 1097, 713 cm}^{-1}; \]
\[ ^1\text{H NMR (CDCl}_3) \delta 0.28 (s, 9\text{H}), 7.43–7.53 (m, 6\text{H}), 7.88–7.96 (m, 4\text{H}); \]
\[ ^13\text{C NMR (CDCl}_3) \delta -0.77, 97.60 (d, J = 133.6 \text{ Hz}), 116.01 (d, J = 14.8 \text{ Hz}), 128.60 (d, J = 13.8 \text{ Hz}), 130.81 (d, J = 12.0 \text{ Hz}), 131.73 (d, J = 3.4 \text{ Hz}), 133.58 (d, J = 97.4 \text{ Hz}); \]
\[ ^{31}\text{P NMR (CDCl}_3) \delta 17.12. \]

Found: C, 64.75%; H, 6.25%. Calcd for C\textsubscript{17}H\textsubscript{19}PSSi: C, 64.93%; H, 6.09%. m.p.: 158.0–159.5 °C.
(2-Methoxy-1-naphthylethynyl)diphenylphosphine sulfide (2g)

IR (nujol) 2923, 2854, 2316, 1587, 1460, 1378, 1277, 1095, 812, 718, 660 cm⁻¹; ¹H NMR (CDCl₃) δ 4.01 (s, 3H), 7.22 (d, J = 9.0 Hz, 1H), 7.34–7.40 (m, 1H), 7.46–7.55 (m, 7H), 7.76 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 8.10–8.20 (m, 5H); ¹³C NMR (CDCl₃) δ 56.49, 90.56 (d, J = 155.0 Hz), 102.12 (d, J = 27.3 Hz), 102.98, 112.16, 124.51, 124.69, 128.05, 128.22, 128.51 (d, J = 13.9 Hz), 130.90 (d, J = 12.0 Hz), 131.57 (d, J = 3.3 Hz), 132.83, 134.33 (d, J = 97.9 Hz), 134.44, 161.39 (d, J = 1.9 Hz); ³¹P NMR (CDCl₃) δ 18.59. Found: C, 75.10; H, 4.72%. Calcd for C₂₅H₁₉OPS: C, 75.36; H, 4.81%. m.p.: 117.5–119.0 °C.

(6-Hexyl-N-tosyl-5-isoindolinyl)diphenylphosphine sulfide (3aa)

IR (nujol) 2923, 2854, 1597, 1459, 1437, 1378, 1350, 1166, 1099, 695, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.79 (t, J = 7.5 Hz, 3H), 0.98–1.07 (m, 4H), 1.10–1.20 (m, 2H), 1.28–1.38 (m, 2H), 2.41 (s, 3H), 2.66–2.74 (m, 2H), 4.43 s, 2H), 4.60 (s, 2H), 5.41–7.55 (m, 6H), 7.70–7.81 (m, 6H); ¹³C NMR (CDCl₃) δ 56.49, 90.56 (d, J = 155.0 Hz), 102.12 (d, J = 27.3 Hz), 102.98, 112.16, 124.51, 124.69, 128.05, 128.22, 128.51 (d, J = 13.9 Hz), 130.90 (d, J = 12.0 Hz), 131.57 (d, J = 3.3 Hz), 132.83, 134.33 (d, J = 97.9 Hz), 134.44, 161.39 (d, J = 1.9 Hz); ³¹P NMR (CDCl₃) δ 18.59. Found: C, 75.10; H, 4.72%. Calcd for C₃₃H₃₆NO₂PS: C, 69.08; H, 6.32%. m.p.: 189.0–191.0 °C.

(6-Hexyl-1,3-dihydro-5-isobenzofuranyl)diphenylphosphine sulfide (3ba)

IR (nujol) 2925, 2853, 1684, 1653, 1558, 1437, 1097, 1049, 904, 759 cm⁻¹; ¹H NMR (CDCl₃) δ 0.80 (t, J = 7.5 Hz, 3H), 1.02–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.35–1.44 (m, 2H), 2.75–2.82 (m, 2H), 4.94 (s, 2H), 5.09 (s, 2H), 6.86 (d, J = 14.5 Hz, 1H), 7.25 (d, J = 4.5 Hz, 1H), 7.43–7.55 (m, 6H), 7.78–7.86 (m, 4H); ¹³C NMR
(CDCl$_3$) δ 13.97, 22.40, 29.17, 30.88, 31.45, 34.25 (d, $J = 6.1$ Hz), 73.24, 73.28, 123.55 (d, $J = 11.4$ Hz), 125.25 (d, $J = 13.3$ Hz), 128.46 (d, $J = 12.4$ Hz), 132.24 (d, $J = 85.9$ Hz), 131.43 (d, $J = 2.9$ Hz), 132.23 (d, $J = 10.5$ Hz), 132.98 (d, $J = 83.5$ Hz), 136.36 (d, $J = 13.4$ Hz), 143.33 (d, $J = 2.9$ Hz), 147.03 (d, $J = 10.5$ Hz); $^{31}$P NMR (CDCl$_3$) δ 40.87. Found: C, 74.00; H, 6.97%. Calcd for C$_{26}$H$_{29}$O: C, 74.26%; H, 6.95%. m.p.: 117.5–119.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-5-indanyl]diphenylphosphine sulfide (3ca)

IR (nujol) 2923, 2853, 1731, 1654, 1560, 1457, 1430, 1250, 1162, 1120, 1075, 1059, 701, 665 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.00–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.30–1.41 (m, 2H), 2.67–2.73 (m, 2H), 3.44 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 6.79 (d, $J = 14.5$ Hz, 1H), 7.19 (d, $J = 4.5$ Hz, 1H), 7.42–7.54 (m, 6H), 7.76–7.84 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 14.02, 22.46, 29.27, 30.89, 31.53, 34.26 (d, $J = 5.8$ Hz), 40.30, 40.60, 53.02, 60.07, 126.83 (d, $J = 11.4$ Hz), 128.44 (d, $J = 12.0$ Hz), 128.47 (d, $J = 12.9$ Hz), 130.11 (d, $J = 85.9$ Hz), 131.36 (d, $J = 2.9$ Hz), 132.33 (d, $J = 10.5$ Hz), 133.19 (d, $J = 83.5$ Hz), 137.04 (d, $J = 13.8$ Hz), 144.20 (d, $J = 2.9$ Hz), 146.57 (d, $J = 10.0$ Hz), 171.83; $^{31}$P NMR (CDCl$_3$) δ 40.69. Found: C, 69.44; H, 6.33%. Calcd for C$_{31}$H$_{35}$O$_4$PS: C, 69.64%; H, 6.60%. m.p.: 159.0–160.5 °C.

(6-Hexyl-5-indanyl)diphenylphosphine sulfide (3da)

IR (neat) 3054, 2848, 1963, 1898, 1817, 1775, 1675, 1607, 1557, 1436, 1391, 1309, 1097, 998 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.81 (t, $J = 7.5$ Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.34–1.44 (m, 2H), 2.03 (tt, $J = 7.5, 7.5$ Hz, 2H), 2.71 (t, $J = 7.5$ Hz, 2H), 2.73 (t, $J = 7.5$ Hz, 2H), 2.90 (t, $J = 7.5$ Hz, 2H), 6.83 (d, $J = 15.0$ Hz, 1H), 7.22 (d, $J = 4.5$ Hz, 1H), 7.41–7.53 (m, 6H), 7.79–7.86 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 14.03, 22.47, 25.25, 29.30, 31.05, 31.56, 32.47, 32.90, 34.27 (d, $J = 6.1$ Hz), 127.06 (d, $J = 11.5$ Hz), 128.36 (d, $J = 12.0$ Hz), 128.62 (d, $J = 12.9$ Hz), 128.65 (d, $J = 84.5$ Hz), 131.21 (d, $J = 2.9$ Hz), 132.33 (d, $J = 10.5$ Hz), 133.58 (d, $J = 83.1$ Hz), 141.25 (d, $J = 13.4$ Hz), 145.48 (d, $J = 10.0$ Hz).
(7-Hexyl-1,2,3,4-tetrahydro-6-naphthyl)diphenylphosphine sulfide (3ea)

\[
\text{IR (neat) 3055, 2848, 2218, 1962, 1896, 1817, 1602, 1554, 1436, 1309, 1097, 1028, 912 cm}^{-1};\quad \text{\textsuperscript{1}H NMR (CDCl}_3\text{) \delta 0.81 (t, } J = 7.5 \text{ Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.33–1.42 (m, 2H), 1.68–1.80 (m, 4H), 2.52 (t, } J = 6.0 \text{ Hz, 2H), 2.64–2.68 (m, 2H), 2.75 (t, } J = 6.0 \text{ Hz, 2H), 6.69 (d, } J = 15.5 \text{ Hz, 1H), 7.04 (d, } J = 5.0 \text{ Hz, 1H), 7.41–7.53 (m, 6H), 7.78–7.87 (m, 4H); \quad \text{\textsuperscript{13}C NMR (CDCl}_3\text{) \delta 14.01, 22.46, 22.84, 22.97, 28.90, 29.25, 29.26, 30.91, 31.54, 33.85 (d, } J = 5.8 \text{ Hz), 128.02 (d, } J = 84.5 \text{ Hz), 128.31 (d, } J = 12.4 \text{ Hz), 131.19 (d, } J = 2.9 \text{ Hz), 131.67 (d, } J = 11.0 \text{ Hz), 132.28 (d, } J = 10.5 \text{ Hz), 133.47 (d, } J = 83.5 \text{ Hz), 133.77 (d, } J = 12.4 \text{ Hz), 134.17 (d, } J = 12.9 \text{ Hz), 141.27 (d, } J = 2.9 \text{ Hz), 143.84 (d, } J = 9.6 \text{ Hz); \quad \text{\textsuperscript{31}P NMR (CDCl}_3\text{) \delta 39.86. \quad \text{Found: C, 77.56; H, 7.65%. \quad \text{Calcd for C}_{28}\text{H}_{33}\text{PS: C, 77.47; H, 7.46%.}}
\]

\[\text{m.p.: 165.0–167.0} \degree\text{C.}\]

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine sulfide (3cb)

\[
\text{IR (nujol) 2923, 2853, 1738, 1436, 1282, 1243, 1199, 1098, 1069 cm}^{-1};\quad \text{\textsuperscript{1}H NMR (CDCl}_3\text{) \delta 3.58 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.92–7.03 (m, 3H), 7.06–7.14 (m, 3H), 7.25–7.40 (m, 7H), 7.69–7.77 (m, 4H); \quad \text{\textsuperscript{13}C NMR (CDCl}_3\text{) \delta 40.36, 40.54, 53.07, 60.04, 126.91, 126.96, 128.00 (d, } J = 12.5 \text{ Hz), 128.58 (d, } J = 11.0 \text{ Hz), 129.31 (d, } J = 12.9 \text{ Hz), 130.19, 130.86 (d, } J = 2.9 \text{ Hz), 130.93 (d, } J = 84.5 \text{ Hz), 132.20 (d, } J = 10.0 \text{ Hz), 132.56 (d, } J = 84.5 \text{ Hz), 138.85 (d, } J = 13.9 \text{ Hz), 140.15 (d, } J = 3.9 \text{ Hz), 143.79 (d, } J = 2.9 \text{ Hz), 145.81 (d, } J = 9.5 \text{ Hz), 171.73; \quad \text{\textsuperscript{31}P NMR (CDCl}_3\text{) \delta 40.69. \quad \text{Found: C, 70.48; H, 5.07%. \quad \text{Calcd for C}_{31}\text{H}_{27}\text{O}_{4}\text{PS: C, 70.71; H, 5.17%. \quad \text{m.p.: 165.0–167.0} \degree\text{C.}}\]
\]

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[2,2-Di(methoxycarbonyl)-6-(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3cc)

IR (nujol) 2923, 2854, 1734, 1479, 1436, 1271, 1243, 1198, 1098, 1066, 712 cm⁻¹; ¹H NMR (CDCl₃) δ 0.99 (d, J = 7.0 Hz, 6H), 3.43 (s, 2H), 3.57 (dsept, J = 1.5, 7.0 Hz, 1H), 3.61 (s, 2H), 3.74 (s, 6H), 6.67 (d, J = 14.5 Hz, 1H), 7.27 (d, J = 5.5 Hz, 1H), 7.43–7.55 (m, 6H), 7.76–7.84 (m, 4H); ¹³C NMR (CDCl₃) δ 23.66, 31.31 (d, J = 6.6 Hz), 40.31, 40.68, 53.02, 59.98, 124.20 (d, J = 11.5 Hz), 128.02 (d, J = 13.4 Hz), 128.40 (d, J = 12.0 Hz), 129.73 (d, J = 86.4 Hz), 131.39 (d, J = 2.9 Hz), 132.36 (d, J = 10.5 Hz), 133.18 (d, J = 83.5 Hz), 137.14 (d, J = 13.8 Hz), 144.50 (d, J = 2.9 Hz), 152.80 (d, J = 10.5 Hz), 171.84; ³¹P NMR (CDCl₃) δ 40.82. Found: C, 68.08; H, 5.75%. Calcd for C₂₈H₂₉O₄PS: C, 68.27; H, 5.93%. m.p.: 216.0–217.5 °C.

[2,2-Di(methoxycarbonyl)-6-(1,1-dimethylethyl)-5-indanyl]diphenylphosphine sulfide (3cd)

IR (nujol) 2924, 2854, 1743, 1734, 1456, 1436, 1259, 1198, 1156, 1098, 901, 754, 707 cm⁻¹; ¹H NMR (CDCl₃) δ 1.47 (s, 9H), 3.37 (s, 2H), 3.63 (s, 2H), 3.74 (s, 6H), 6.86 (d, J = 18.0 Hz, 1H), 7.36–7.51 (m, 6H), 7.57 (d, J = 5.5 Hz, 1H), 7.60–7.70 (m, 4H); ¹³C NMR (CDCl₃) δ 33.51, 38.74 (d, J = 2.1 Hz), 40.27, 40.83, 53.03, 59.90, 126.23 (d, J = 12.9 Hz), 128.35 (d, J = 12.5 Hz), 129.18 (d, J = 75.9 Hz), 131.02 (d, J = 2.9 Hz), 132.15 (d, J = 13.8 Hz), 132.22 (d, J = 10.0 Hz), 136.51 (d, J = 13.9 Hz), 136.37 (d, J = 85.4 Hz), 144.00 (d, J = 2.9 Hz), 155.35 (d, J = 9.0 Hz), 171.86; ³¹P NMR (CDCl₃) 50.66. Found: C, 68.55; H, 6.05%. Calcd for C₂₉H₃₁O₄PS: C, 68.76; H, 6.17%. m.p.: 165.0–166.5 °C.

[2,2-Di(methoxycarbonyl)-6-(2-methoxyphenyl)-5-indanyl]diphenylphosphine sulfide (3ce)

IR (nujol) 2922, 2853, 1734, 1684, 1653, 1559, 1507, 1457, 1437, 1276, 1198, 1095, 895 cm⁻¹; ¹H NMR (CDCl₃) δ 3.46 (s, 3H), 3.59 (s, 1H), 3.61 (s, 1H), 3.65 (s, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 6.31 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 7.5, 7.5 Hz, 1H), 6.95–7.02 (m, 1H), 7.04 (d, J = 4.5 Hz, 1H), 7.14–7.47 (m, 8H), 7.58–7.68 (m, 2H), 7.80–7.88 (m, 2H); ¹³C NMR (CDCl₃) δ 40.43, 40.56,
53.05, 53.09, 54.39, 59.99, 109.31, 119.00, 127.43 (d, \( J = 12.4 \) Hz), 127.90 (d, \( J = 12.5 \) Hz), 128.46 (d, \( J = 4.3 \) Hz), 128.99 (d, \( J = 11.9 \) Hz), 129.04, 129.49 (d, \( J = 12.9 \) Hz), 130.38 (d, \( J = 2.9 \) Hz), 130.83 (d, \( J = 2.9 \) Hz), 131.28 (d, \( J = 85.4 \) Hz), 131.67 (d, \( J = 10.5 \) Hz), 132.36, 132.47 (d, \( J = 84.5 \) Hz), 132.53 (d, \( J = 10.5 \) Hz), 133.65 (d, \( J = 84.0 \) Hz), 138.91 (d, \( J = 13.9 \) Hz), 141.78 (d, \( J = 9.6 \) Hz), 143.42 (d, \( J = 2.9 \) Hz), 155.69, 171.81, 171.91; \( ^{31} \)P NMR (CDCl\(_3\)) \( \delta \) 40.56. Found: C, 68.80; H, 5.38\%. Calcd for C\(_{32}\)H\(_{29}\)O\(_3\)PS: C, 69.05; H, 5.25\%. m.p.: 89.5–92.0 °C.

**[2,2-Di(methoxycarbonyl)-6-trimethylsilyl-5-indany]diphenylphosphine sulfide (3cf)**

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\text{IR (nujol) 2925, 2855, 1740, 1457, 1436, 1377, 1304, 1247, 1198, 1099, 848, 710 cm}^{-1}; \quad ^1\text{H NMR (CDCl}_3\text{)} \delta 0.18 (s, 9H), 3.43 (s, 2H), 3.64 (s, 2H), 3.74 (s, 6H), 6.73 (d, \( J = 15.0 \) Hz, 1H), 7.40–7.53 (m, 6H), 7.62–7.69 (m, 4H), 7.72 (d, \( J = 3.0 \) Hz, 1H); \quad ^{13}\text{C NMR (CDCl}_3\text{)} \delta 2.73, 40.59, 40.68, 53.04, 59.70, 128.37 (d, \( J = 12.4 \) Hz), 129.20 (d, \( J = 15.3 \) Hz), 131.32 (d, \( J = 2.9 \) Hz), 132.58 (d, \( J = 10.5 \) Hz), 133.84 (d, \( J = 17.1 \) Hz), 134.34 (d, \( J = 82.6 \) Hz), 137.95 (d, \( J = 87.8 \) Hz), 139.70 (d, \( J = 13.8 \) Hz), 142.33 (d, \( J = 2.9 \) Hz), 144.88 (d, \( J = 19.5 \) Hz), 171.81; \quad ^{31}\text{P NMR (CDCl}_3\text{)} \delta 44.97. \quad \text{HRMS (EI)}^+ \text{ Observed: 522.1431 (\( \Delta = -3.6 \) ppm). Calcd for C\(_{32}\)H\(_{33}\)O\(_3\)PSSi [M\(^+\): 522.1450. m.p.: 178.0–180.0 °C.}

**[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-dimethyl-5-indany]diphenylphosphine sulfide (3fa)**

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\text{IR (nujol) 2924, 2854, 1734, 1653, 1558, 1457, 1437, 1260, 1165, 749, 701, 651 cm}^{-1}; \quad ^1\text{H NMR (CDCl}_3\text{)} \delta 0.82 (t, \( J = 7.5 \) Hz, 3H), 0.93–1.01 (m, 2H), 1.04–1.12 (m, 2H), 1.16–1.30 (m, 4H), 1.80 (s, 3H), 2.16 (s, 3H), 2.34–2.41 (m, 2H), 3.45 (s, 2H), 3.61 (s, 2H), 3.77 (s, 6H), 7.31–7.41 (m, 6H), 7.84–7.93 (m, 4H); \quad ^{13}\text{C NMR (CDCl}_3\text{)} \delta 14.01, 15.97 (d, \( J = 0.9 \) Hz), 21.06 (d, \( J = 7.3 \) Hz), 25.51, 29.51, 30.53, 31.40, 33.04 (d, \( J = 7.3 \) Hz), 40.39 (d, \( J = 1.9 \) Hz), 40.80, 53.04, 58.67, 128.35 (d, \( J = 11.9 \) Hz), 129.73 (d, \( J = 88.9 \) Hz), 130.37 (d, \( J = 2.9 \) Hz), 130.69 (d, \( J = 10.5 \) Hz), 131.26 (d, \( J = 11.9 \) Hz), 135.63 (d, \( J = 11.0 \) Hz), 137.59 (d, \( J = 81.1 \) Hz), 138.24 (d, \( J = 12.9 \) Hz), 142.92 (d, \( J = 2.9 \) Hz).}
Hz), 145.76 (d, $J = 10.5$ Hz), 172.16; $^{31}$P NMR (CDCl$_3$) δ 35.01. m.p.: 59.5–61.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-diphenyl-5-indanyl]diphenylphosphine sulfide (3ga)

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\text{IR (nujol) 2924, 2854, 1741, 1724, 1456, 1437, 1377, 1267, 1201, 1091, 714, 697 cm}^{-1}; \quad \text{^1H NMR (CDCl}_3\text{) δ 0.69 (t, } J = 7.0 \text{ Hz, 3H), 0.72–0.86 (m, 4H), 0.95–1.05 (m, 2H), 2.46–2.54 (m, 2H), 3.26 (s, 2H), 3.37 (s, 2H), 3.66 (s, 6H), 6.90–7.04 (m, 5H), 7.10–7.23 (m, 6H), 7.24–7.46 (m, 5H), 7.56–7.66 (m, 4H);} \quad \text{^13C NMR (CDCl}_3\text{) δ 13.93, 22.21, 29.17, 30.89, 30.98, 34.57 (d, } J = 7.6 \text{ Hz), 40.82 (d, } J = 1.3 \text{ Hz), 41.10, 52.91, 59.09, 126.71, 127.19, 127.52, 127.72 (d, } J = 12.4 \text{ Hz), 128.50, 129.24, 129.73 (d, } J = 2.9 \text{ Hz), 130.03 (d, } J = 89.3 \text{ Hz), 130.45, 130.99 (d, } J = 10.0 \text{ Hz), 136.69 (d, } J = 83.1 \text{ Hz), 137.61 (d, } J = 11.9 \text{ Hz), 138.91 (d, } J = 4.8 \text{ Hz), 139.22 (d, } J = 10.5 \text{ Hz), 139.26, 142.69 (d, } J = 2.9 \text{ Hz), 143.01 (d, } J = 11.0 \text{ Hz), 147.43 (d, } J = 10.5 \text{ Hz), 171.90;} \quad \text{^31P NMR (CDCl}_3\text{) δ 36.66. Found: C, 75.23; H, 6.37%. Calcd for C$_{43}$H$_{43}$O$_4$PS: C, 75.19; H, 6.31%. m.p.: 122.0–124.0 °C.}

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine sulfide (3gb)

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\text{IR (nujol) 2924, 2854, 2364, 1735, 1701, 1654, 1559, 1457, 1420, 1267, 696, 668 cm}^{-1}; \quad \text{^1H NMR (CDCl}_3\text{) δ 3.34 (s, 2H), 3.43 (s, 2H), 3.66 (s, 6H), 6.57–6.74 (m, 3H), 6.80–7.30 (m, 18H), 7.54–7.68 (m, 4H);} \quad \text{^13C NMR (CDCl}_3\text{) δ 41.27, 41.63, 52.95, 59.00, 125.85, 126.09, 126.32, 126.72, 127.03, 127.28 (d, } J = 12.4 \text{ Hz), 127.57, 129.39 (2C), 131.06, 131.11 (d, } J = 85.4 \text{ Hz), 131.22 (d, } J = 10.0 \text{ Hz), 133.02, 134.79 (d, } J = 83.6 \text{ Hz), 137.40 (d, } J = 5.1 \text{ Hz), 138.52 (d, } J = 4.8 \text{ Hz), 138.86, 139.03 (d, } J = 11.0 \text{ Hz), 139.92 (d, } J = 11.3 \text{ Hz), 142.73 (d, } J = 2.9 \text{ Hz), 143.63 (d, } J = 10.5 \text{ Hz), 146.43 (d, } J = 10.5 \text{ Hz), 171.81;} \quad \text{^31P NMR (CDCl}_3\text{) δ 36.49. Found: C, 76.03; H, 5.58%. Calcd for C$_{43}$H$_{36}$O$_4$PS: C, 76.09; H, 5.20%. m.p.: 140.0–142.0 °C.}
[2,2-di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hc)

IR (neat) 2924, 2854, 1735, 1438, 1377, 1261, 1167, 1046, 665 cm⁻¹;
¹H NMR (CDCl₃) δ 0.75 (t, J = 7.0 Hz, 12H), 1.28 (d, J = 7.5 Hz, 6H), 3.44 (sept, J = 7.0 Hz, 1H), 3.47 (dsept, J = 2.0, 7.0 Hz, 1H), 3.54 (s, 2H), 3.68 (dsept, J = 2.5, 7.5 Hz, 1H), 3.69 (s, 2H), 3.76 (s, 6H), 7.26–7.36 (m, 6H), 7.82–7.93 (m, 4H);
¹³C NMR (CDCl₃) δ 20.72, 20.92, 22.37, 28.22, 34.22 (d, J = 9.1 Hz), 34.55 (d, J = 10.5 Hz), 39.28, 40.05, 52.92, 60.72, 128.06 (d, J = 11.9 Hz), 130.02 (d, J = 2.9 Hz), 130.57 (d, J = 10.0 Hz), 131.22 (d, J = 94.5 Hz), 137.91 (d, J = 12.4 Hz), 138.66 (d, J = 82.0 Hz), 141.96 (d, J = 10.5 Hz), 144.58 (d, J = 2.8 Hz), 147.07 (d, J = 11.0 Hz), 149.84 (d, J = 10.0 Hz), 171.86; ³¹P NMR (CDCl₃) δ 35.79. Found: C, 70.55; H, 7.07%. Calcd for C₃₄H₄₁O₄PS: C, 70.81; H, 7.17%.

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hg)

IR (nujol) 2923, 2854, 1457, 1263, 1172, 1071, 750 cm⁻¹;
¹H NMR (CDCl₃) δ 0.72 (d, J = 7.0 Hz, 3H), 0.75 (d, J = 7.0 Hz, 3H), 1.01 (d, J = 7.0 Hz, 3H), 1.21 (d, J = 7.0 Hz, 3H), 2.14 (qq, J = 7.0, 7.0 Hz, 1H), 3.62–3.68 (m, 2H), 3.69 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 3.80–3.87 (m, 2H), 4.12 (dqq, J = 2.5, 7.0, 7.0 Hz, 1H), 6.47 (d, J = 9.0 Hz, 1H), 6.72–6.81 (m, 2H), 6.87–6.90 (m, 3H), 7.14–7.40 (m, 7H), 7.56 (d, J = 8.0 Hz, 1H), 7.59–7.72 (m, 2H); ¹³C NMR (CDCl₃) δ 18.93, 20.42, 20.51, 20.68, 29.72, 32.46 (d, J = 8.6 Hz), 40.12, 40.39, 52.97 (2C), 54.61, 60.81, 110.93, 121.68, 121.73, 123.46, 126.18 (d, J = 10.0 Hz), 126.28 (d, J = 16.8 Hz), 127.13, 127.44 (d, J = 10.5 Hz), 128.39, 129.06 (d, J = 2.9 Hz), 129.93, 130.49, 131.10 (d, J = 10.0 Hz), 132.02, 132.10 (d, J = 86.9 Hz), 134.22, 135.95 (d, J = 84.5 Hz), 136.92 (d, J = 83.0 Hz), 137.29 (d, J = 10.0 Hz), 140.90 (d, J = 12.0 Hz), 141.36 (d, J = 10.5 Hz), 143.51, 146.31 (d, J = 11.5 Hz), 153.62, 171.88, 172.04; ³¹P NMR (CDCl₃) δ 40.13. m.p.: 247.5–249.0 °C.
Phenyl[di(phenylethynyl)]phosphine sulfide (5a)

IR (nujol) 2919, 2850, 2173, 1685, 1486, 1457, 1364, 1106, 1023, 855, 766 cm⁻¹; ¹H NMR (CDCl₃) δ 7.34–7.47 (m, 6H), 7.54–7.63 (m, 7H), 8.18–8.26 (m, 2H); ¹³C NMR (CDCl₃) δ 82.41 (d, J = 176.0 Hz), 103.79 (d, J = 33.0 Hz), 119.93 (d, J = 4.8 Hz), 128.45, 128.78 (d, J = 15.3 Hz), 130.46 (d, J = 13.4 Hz), 130.67, 132.35 (d, J = 3.4 Hz), 132.48 (d, J = 2.4 Hz), 133.15 (d, J = 114.5 Hz); ³¹P NMR (CDCl₃) δ −10.56. Found: C, 77.12; H, 4.51%. Calcd for C₂₂H₁₄PS: C, 77.17; H, 4.41%. m.p.: 122.0–124.0 °C.

Tri(phenylethynyl)phosphine sulfide (5b)

IR (nujol) 2923, 2854, 2181, 1684, 1558, 1489, 1457, 1374, 1231, 1070, 923, 852, 759 cm⁻¹; ¹H NMR (CDCl₃) δ 7.37–7.43 (m, 6H), 7.45–7.50 (m, 3H), 7.63–7.68 (m, 6H); ¹³C NMR (CDCl₃) δ 82.19 (d, J = 205.6 Hz), 102.46 (d, J = 40.6 Hz), 119.78 (d, J = 4.8 Hz), 128.53, 130.90, 132.69 (d, J = 2.4 Hz); ³¹P NMR (CDCl₃) δ −43.59. Found: C, 78.57; H, 4.35%. Calcd for C₂₄H₁₅PS: C, 78.67; H, 4.13%. m.p.: 129.5–130.5 °C.

Bis[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phenylphosphine sulfide (6a)

IR (nujol) 2924, 2853, 1734, 1559, 1507, 1457, 1420, 1240, 1157, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 3.52 (s, 2H), 3.54 (s, 2H), 3.61 (s, 4H), 3.79 (s, 6H), 3.81 (s, 6H), 6.85–6.91 (m, 4H), 6.92–7.01 (m, 6H), 7.08–7.14 (m, 2H), 7.20–7.26 (m, 2H), 7.31–7.46 (m, 5H); ¹³C NMR (CDCl₃) δ 40.28, 40.47, 53.05, 53.06, 60.00, 126.85, 126.92, 127.75 (d, J = 12.5 Hz), 128.28 (d, J = 10.9 Hz), 129.60 (d, J = 12.9 Hz), 129.79, 130.39 (d, J = 82.5 Hz), 130.49 (d, J = 2.4 Hz), 132.52 (d, J = 10.9 Hz), 134.47 (d, J = 85.4 Hz), 138.53 (d, J = 13.9 Hz), 140.95 (d, J = 3.9 Hz), 143.24 (d, J = 2.4 Hz), 144.79 (d, J = 9.5 Hz), 171.76, 171.84; ³¹P NMR (CDCl₃) δ 42.93. Found: C, 69.77; H, 5.47%. Calcd for C₄₄H₃₉O₈PS: C, 69.64; H, 5.18%. m.p.: 124.0–126.5 °C.
Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine sulfide (6b)

IR (nujol) 2923, 2853, 1734, 1653, 1457, 1420, 1240, 1151, 1051, 768, 698 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.45 (s, 6H), 3.57 (s, 6H), 3.81 (s, 18H), 6.80–7.26 (m, 21H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 40.17, 40.41, 53.02, 59.97, 126.73, 126.82, 128.17 (d, \(J = 11.0\) Hz), 129.89, 130.55 (d, \(J = 81.3\) Hz), 130.76 (d, \(J = 13.4\) Hz), 137.82 (d, \(J = 13.9\) Hz), 141.52 (d, \(J = 2.9\) Hz), 142.83 (d, \(J = 2.4\) Hz), 144.34 (d, \(J = 9.5\) Hz), 171.84; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 44.79. Found: C, 68.75; H, 5.31%. Calcd for C\(_{57}\)H\(_{51}\)O\(_{12}\)PS: C, 69.08; H, 5.19%. m.p.: 157.0–160.0 °C.

Dicyclohexyl(1-octynyl)phosphine sulfide (7a)

IR (neat) 2930, 2854, 2192, 1448, 1268, 1179, 1115, 1002, 887, 758, 648 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.84 (t, \(J = 7.0\) Hz, 3H), 1.12–2.02 (m, 30H), 2.31 (dt, \(J = 4.0, 7.0\) Hz, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 13.82, 19.60 (d, \(J = 2.9\) Hz), 22.34, 24.83, 25.62 (d, \(J = 1.5\) Hz), 26.01 (d, \(J = 15.8\) Hz), 26.13 (d, \(J = 14.8\) Hz), 26.20 (d, \(J = 3.4\) Hz), 27.55 (d, \(J = 1.9\) Hz), 28.31, 30.98, 38.49 (d, \(J = 59.3\) Hz), 71.41 (d, \(J = 126.5\) Hz), 107.63 (d, \(J = 18.6\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 41.71. Found: C, 70.71; H, 10.71%. Calcd for C\(_{20}\)H\(_{35}\)PS: C, 70.96; H, 10.42%.

Dicyclohexyl(phenylethynyl)phosphine sulfide (7b)

IR (nujol) 2921, 2852, 2177, 1734, 1685, 1489, 1443, 1117, 1048, 885, 757, 665 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 1.20–2.12 (m, 22H), 7.33–7.38 (m, 2H), 7.39–7.44 (m, 1H), 7.50–7.55 (m, 2H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 25.05, 25.73 (d, \(J = 1.5\) Hz), 26.15 (d, \(J = 14.9\) Hz), 26.29 (d, \(J = 14.3\) Hz), 26.47 (d, \(J = 3.9\) Hz), 38.82 (d, \(J = 58.8\) Hz), 80.03 (d, \(J = 120.3\) Hz), 103.94 (d, \(J = 17.6\) Hz), 120.52 (d, \(J = 3.3\) Hz), 128.43, 130.16, 132.34 (d, \(J = 2.0\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 42.96. Found: C, 72.40; H, 8.38%. Calcd for C\(_{20}\)H\(_{27}\)PS: C, 72.69; H, 8.23%. m.p.: 150.0–151.5 °C.
Dicyclohexyl[6-hexyl-2,2-di(methoxycarbonyl)-5-indany1]phosphine sulfide (8a)

IR (neat) 2918, 2852, 2214, 1733, 1559, 1436, 1258, 1200, 1162, 1072, 913, 762, 732, 615 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (t, J = 7.0 Hz, 3H), 1.10–2.05 (m, 28H), 2.20–2.30 (m, 2H), 2.70–2.80 (m, 2H), 3.59 (s, 2H), 3.61 (s, 2H), 3.74 (s, 6H), 7.10 (d, J = 4.5 Hz, 1H), 8.21 (d, J = 15.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.07, 22.61, 25.58 (d, J = 1.5 Hz), 26.50 (d, J = 11.9 Hz), 26.55 (d, J = 13.4 Hz), 26.56, 27.99 (d, J = 1.1 Hz), 29.79, 31.85, 32.13, 34.58 (d, J = 1.5 Hz), 39.45, 40.23 (d, J = 23.4 Hz), 40.47, 53.02, 60.11, 125.05, 125.57, 125.64 (d, J = 10.5 Hz), 131.79, 137.69 (d, J = 12.9 Hz), 143.53 (d, J = 2.4 Hz), 171.97; ³¹P NMR (CDCl₃) δ 63.80.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indany1]phosphine sulfide (8b)

IR (nujol) 2922, 2853, 1735, 1457, 1378, 1262, 1198, 1165, 1071, 771, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.90–1.90 (m, 22H), 3.15 (s, 2H), 3.33 (s, 2H), 3.66 (s, 6H), 6.83–6.89 (m, 2H), 7.00–7.13 (m, 8H), 7.23–7.30 (m, 2H), 7.37–7.44 (m, 3H); ¹³C NMR (CDCl₃) δ 25.51, 26.20 (d, J = 13.9 Hz), 26.52 (d, J = 13.9 Hz), 27.06, 28.13 (d, J = 2.4 Hz), 40.92 (d, J = 48.1 Hz), 41.57, 41.84, 52.93, 58.63, 125.78 (d, J = 59.3 Hz), 126.19, 126.39, 127.09, 127.19, 127.55, 127.61, 129.28, 129.68, 132.07, 139.32, 139.41 (d, J = 2.3 Hz), 139.77 (d, J = 9.6 Hz), 140.69 (d, J = 3.3 Hz), 140.91 (d, J = 10.5 Hz), 141.16 (d, J = 2.9 Hz), 143.70, 144.30, 171.91; ³¹P NMR (CDCl₃) δ 65.01. Found: C, 74.61; H, 7.15%. Calcd for C₄₃H₄₇O₄PS: C, 74.76; H, 6.86%. m.p.: 118.5–121.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-5-indany1]diphenylphosphine (3ca–S)

IR (neat) 2953, 2928, 2855, 1738, 1434, 1273, 1247, 1200, 1162, 1070, 910, 734, 698 cm⁻¹; ¹H NMR (CDCl₃) δ 0.84 (t, J = 7.5 Hz, 3H), 1.14–1.32 (m, 6H), 1.44–1.53 (m, 2H), 2.76–2.83 (m, 2H), 3.45 (s, 2H), 3.60 (s, 2H), 3.74 (s, 6H), 6.66 (d, J = 4.0 Hz, 1H), 7.09 (d, J = 4.5 Hz, 1H), 7.22–7.29 (m, 4H), 7.30–7.36 (m, 6H); ¹³C NMR (CDCl₃) δ 14.05, 22.49, 29.23, 31.46 (d, J = 2.9 Hz), 31.59, 34.42 (d, J = 21.5 Hz), 40.34,
40.55, 52.92, 59.99, 124.78 (d, J = 5.8 Hz), 128.41 (d, J = 7.1 Hz), 128.48, 129.02, 133.79 (d, J = 11.0 Hz), 133.86 (d, J = 19.6 Hz), 137.23 (d, J = 11.0 Hz), 137.56, 140.98, 146.48 (d, J = 25.8 Hz), 172.16; $^{31}$P NMR (CDCl$_3$) δ –16.30. Found: C, 73.73; H, 7.08%. Calcd for C$_{31}$H$_{35}$O$_4$P: C, 74.09; H, 7.02%.

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine (3cb−S)

IR (nujol) 2923, 2854, 1731, 1655, 1462, 1377, 1262, 1027, 665 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 3.54 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.85 (d, J = 3.5 Hz, 1H), 7.11–7.32 (m, 16H); $^{13}$C NMR (CDCl$_3$) δ 40.44, 40.53, 53.02, 59.99, 125.95 (d, J = 4.8 Hz), 127.06, 127.48, 128.32 (d, J = 6.8 Hz), 128.39, 129.47, 129.76 (d, J = 3.9 Hz), 133.89 (d, J = 19.5 Hz), 134.53 (d, J = 12.8 Hz), 137.75 (d, J = 12.5 Hz), 139.14, 140.84, 141.73 (d, J = 6.6 Hz), 147.30 (d, J = 29.0 Hz), 172.10; $^{31}$P NMR (CDCl$_3$) δ –14.84. Found: C, 75.12; H, 5.55%. Calcd for C$_{31}$H$_{27}$O$_4$P: C, 75.29; H, 5.50%. m.p.: 55.5–58.0 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine (3gb−S)

IR (nujol) 2924, 2855, 1735, 1462, 1377, 1262, 1159, 1027, 697, 665 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 3.23 (s, 2H), 3.49 (s, 2H), 3.68 (s, 6H), 6.76–7.17 (m, 25H); $^{13}$C NMR (CDCl$_3$) δ 41.27, 41.38, 52.88, 58.98, 125.93, 126.17 (d, J = 1.9 Hz), 126.55, 126.71, 127.49 (2C), 127.58 (d, J = 10.5 Hz), 128.68, 129.54, 130.65 (d, J = 2.4 Hz), 131.76 (d, J = 20.5 Hz), 132.12 (d, J = 19.6 Hz), 137.30, 137.41, 138.22 (d, J = 4.8 Hz), 139.58, 139.75 (d, J = 2.9 Hz), 140.11 (d, J = 3.4 Hz), 140.47, 140.56 (d, J = 7.6 Hz), 144.65 (d, J = 10.5 Hz), 148.15 (d, J = 25.3 Hz), 172.07; $^{31}$P NMR (CDCl$_3$) δ –8.31. Found: C, 80.08; H, 5.71%. Calcd for C$_{43}$H$_{35}$O$_4$P: C, 79.86; H, 5.45%. m.p.: 97.5–99.5 °C.
[2,2-Di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine (3hc–S)

IR (neat) 2958, 2874, 2259, 1733, 1584, 1461, 1436, 1259, 1209, 1117, 1069, 910, 742, 698 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 0.80–1.10\) (m, 12H), 1.31 (d, \(J = 7.0\) Hz, 6H), 3.50–3.62 (m, 1H), 3.59 (s, 2H), 3.68 (s, 2H), 3.70–3.85 (m, 1H), 3.76 (s, 6H), 4.00–4.20 (m, 1H), 7.20–7.25 (m, 2H), 7.28–7.34 (m, 4H), 7.36–7.43 (m, 4H); \(^13\)C NMR (CDCl\(_3\)) \(\delta 20.56, 20.80, 22.36, 28.64, 33.17\) (d, \(J = 20.0\) Hz), 33.93 (d, \(J = 21.6\) Hz), 39.55, 40.19, 52.87, 60.83, 127.08, 128.14 (d, \(J = 4.9\) Hz), 128.24 (d, \(J = 18.6\) Hz), 131.39 (d, \(J = 18.1\) Hz), 132.25 (d, \(J = 14.9\) Hz), 137.73 (d, \(J = 16.8\) Hz), 141.58, 143.40, 148.47 (d, \(J = 12.5\) Hz), 151.59 (d, \(J = 10.3\) Hz), 172.09; \(^31\)P NMR (CDCl\(_3\)) \(\delta -12.58\).

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-indanyl]diphenylphosphine (3hg–S)

IR (nujol) 2920, 2851, 1734, 1685, 1559, 1507, 1457, 1437, 1260, 1072, 1020, 804 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 0.52\) (d, \(J = 7.0\) Hz, 3H), 0.81 (d, \(J = 7.0\) Hz, 3H), 1.03 (d, \(J = 7.0\) Hz, 3H), 1.10 (d, \(J = 7.0\) Hz, 3H), 2.61 (qq, \(J = 7.0, 7.0\) Hz, 1H), 3.17 (qq, \(J = 7.0, 7.0\) Hz, 1H), 3.54 (s, 3H), 3.70 (s, 1H), 3.72 (s, 1H), 3.78 (s, 1H), 3.79 (s, 3H), 3.80 (s, 1H), 3.81 (s, 3H), 7.05–7.38 (m, 14H), 7.77 (d, \(J = 8.0\) Hz, 1H), 7.83 (d, \(J = 9.0\) Hz, 1H); \(^13\)C NMR (CDCl\(_3\)) \(\delta 19.68, 20.18, 20.87, 20.89, 31.53\) (d, \(J = 3.4\) Hz), 32.22, 39.67, 39.84, 52.93, 52.94, 55.12, 60.72, 112.08, 123.25, 125.84, 126.51 (d, \(J = 13.9\) Hz), 126.67 (d, \(J = 8.6\) Hz), 127.62 (d, \(J = 11.5\) Hz), 127.66 (d, \(J = 11.4\) Hz), 127.88, 128.39, 128.48, 131.27 (d, \(J = 19.0\) Hz), 131.77 (d, \(J = 17.6\) Hz), 134.07 (d, \(J = 12.9\) Hz), 134.15, 137.45 (d, \(J = 18.6\) Hz), 138.53 (d, \(J = 21.0\) Hz), 139.83, 140.94, 141.01, 142.11, 143.79, 144.14, 147.36 (d, \(J = 3.9\) Hz), 154.21 (d, \(J = 3.8\) Hz), 172.25 (2C); \(^31\)P NMR (CDCl\(_3\)) \(\delta -9.51\).

m.p.: 258.0–260.0 °C.
Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine (6b–S)

IR (nujol) 2924, 2854, 1731, 1655, 1377, 1239, 1158, 1049, 893, 768 cm⁻¹; ¹H NMR (CDCl₃) δ 3.56 (s, 6H), 3.61 (s, 6H), 3.78 (s, 18H), 6.66–6.72 (m, 6H), 6.79 (d, J = 2.5 Hz, 3H), 6.92 (d, J = 4.0 Hz, 3H), 7.01–7.08 (m, 6H), 7.10–7.15 (m, 3H); ¹³C NMR (CDCl₃) δ 40.47, 40.48, 52.99, 60.09, 125.43 (d, J = 4.3 Hz), 126.31, 127.01, 129.56 (d, J = 4.3 Hz), 130.21, 135.12 (d, J = 19.6 Hz), 138.75, 140.19, 141.61 (d, J = 6.8 Hz), 146.77 (d, J = 30.5 Hz), 172.18; ³¹P NMR (CDCl₃) δ -27.93. m.p.: 250.0–252.0 °C.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]phosphine (8b–S)

IR (nujol) 2923, 2853, 2363, 1735, 1654, 1560, 1453, 1365, 1261, 1046, 952, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.83–1.74 (m, 22H), 3.24 (s, 2H), 3.41 (s, 2H), 3.67 (s, 6H), 6.90–7.00 (m, 4H), 7.02–7.15 (m, 6H), 7.20–7.24 (m, 2H), 7.36–7.48 (m, 3H); ¹³C NMR (CDCl₃) δ 26.21, 26.85 (d, J = 17.6 Hz), 26.94 (d, J = 12.9 Hz), 31.59 (d, J = 11.5 Hz), 32.75 (d, J = 25.3 Hz), 35.58 (d, J = 15.3 Hz), 41.29, 41.41, 52.84, 59.00, 125.86, 125.93, 126.43, 126.82, 127.39, 127.85, 129.36, 129.56, 131.52, 132.32 (d, J = 29.1 Hz), 137.94 (d, J = 3.3 Hz), 138.56 (d, J = 3.4 Hz), 139.09, 140.06, 141.59 (2C), 144.73, 148.07, 172.17; ³¹P NMR (CDCl₃) δ 0.83. m.p.: 102.0–105.0 °C.
References and Notes


(9) The author performed the reaction of 2,6-diphenylphenyllithium with chlorodiphenylphosphine. However, the corresponding bulky phosphine, diphenyl(2,6-diphenylphenyl)phosphine, was obtained in only 22% yield, along with a significant amount of m-terphenyl.

(10) When (R)-Tol-BINAP was used as a ligand, a 55% ee of 3hg was obtained in 72% yield.


Chapter 5

New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines

Palladium-catalyzed annulation of 1-alkynylphosphine sulfides with 2-iodoanilines followed by desulfidation affords 3-substituted 2-indolylphosphines. This annulation/desulfidation sequential protocol offers a conceptually new approach to bulky heteroarylphosphines.
Introduction

In modern organic synthesis, organophosphines play indispensable roles as ligands applicable to a broad range of transition-metal-catalyzed reactions. Creation of new phosphines and development of novel approaches to phosphines are thus quite important. Recently, bulky phosphines have attracted increasing attention as useful ligands for preparation of biologically intriguing compounds as well as functional organic materials. In Chapter 4, the author disclosed a method for the synthesis of bulky arylphosphines via rhodium-catalyzed formal [2+2+2] cycloaddition reactions of tethered diynes with 1-alkynylphosphine sulfides (Scheme 1). In this reaction, the carbon–carbon triple bonds of 1-alkynylphosphine sulfides participated in the construction of benzene rings.

Scheme 1. The Author's Strategies for the Synthesis of Bulky Phosphines

[2+2+2] Cycloaddition Approach (Chapter 4)

Annulation Approach (Chapter 5)

By using 1-alkynylphosphine derivatives as key starting materials, the author has developed a new strategy aiming at the synthesis of bulky heteroarylphosphines (Scheme 1). In this chapter, the author describes palladium-catalyzed annulation of 1-alkynylphosphine sulfides with 2-iodoanilines to afford 2-indolylphosphine sulfides. The newly formed indole rings naturally have a substituent derived from 1-alkynylphosphine sulfides adjacent to the thiophosphinyl group, which creates a sterically congested environment around the phosphorus in cooperation with a substituent on the nitrogen atom. The product, phosphine sulfides, can be easily reduced to the
corresponding trivalent phosphines.

Although a variety of heteroarylphosphines,\textsuperscript{7} including indole-based phosphines,\textsuperscript{8,9} have been designed and synthesized so far, most of the syntheses involve metalation of heteroaromatic compounds followed by treating with chlorophosphines. This conventional approach requires preparation of proper heteroaromatic compounds prior to introduction of a phosphorus moiety, which sometimes necessitates a multistep synthesis. In the present reaction, incorporation of a phosphorus moiety and a substituent at the proper positions occurs at the same time as construction of a heteroaromatic ring. Hence, this protocol does not only provide new phosphines that are difficult to synthesize by other methods but also offers a conceptually new approach to heteroarylphosphines.

**Results and Discussion**

**Annulation of 1-Alkynylphosphine Sulfides.** Treatment of diphenyl(phenylethynyl)-phosphine sulfide (1\textsuperscript{a}) with 2 equivalents of \textit{N}-methyl-2-iodoaniline (2\textsuperscript{a}) in the presence of a catalytic amount of bis(acetylacetonato)palladium and 2 equivalents of potassium carbonate in DMSO at 90 °C for 11 h afforded 2-diphenylthiophosphinyl-1-methyl-3-phenylindole (3\textsuperscript{aa}) in 76% NMR yield and in 74% isolated yield as a major product (Table 1, entry 1).\textsuperscript{10} Regioisomer 4\textsuperscript{aa} was also observed as a minor product (6% NMR yield), which was easily separable from 3\textsuperscript{aa} by column chromatographic purification. Choice of palladium source was important. Other palladium(II) complexes such as Pd(OAc)\textsubscript{2} and PdCl\textsubscript{2} as well as palladium(0) complexes such as Pd\textsubscript{2}(dba)\textsubscript{3} led to lower yields. Aprotic polar solvents were suitable solvents and DMSO gave the best result. Choice of base also affected the yield. Cesium carbonate and sodium carbonate were less effective, while potassium phosphate gave a similar result to potassium carbonate. Addition of phosphine ligands such as triphenylphosphine led to lower yield. Under the reaction conditions, sulfur transfer from 1-alkynylphosphine sulfide to phosphine ligands occurred, which would deactivate the palladium catalyst.\textsuperscript{11} The result of optimization of reaction conditions is summarized in the following section (Experimental Section, Table 2).
With the optimized reaction conditions in hand, the scope of 1-alkynylphosphine sulfides was investigated (Table 1, entries 1–9). Not only phenylacetylene derivative 1a but also alkyl-substituted substrates 1b–1d underwent the annulation reactions (entries 1–4). The reactions of primary and secondary-alkyl-substituted 1b and 1c proceeded smoothly, while tert-butyl-substituted 1d provided product 3da in low yield probably due to its bulkiness. It is worth noting that none of the regioisomers 4 were detected in the reactions of 1b–1d. A variety
of functional groups, such as keto, ester, methoxy, and 2-thienyl groups, were compatible under the reaction conditions (entries 5–9).

The scope of 2-iodoaniline derivatives was examined (entries 10–15). In this reaction, an alkyl substituent on nitrogen was crucial. Primary and secondary-alkyl-substituted \(2b–2d\) underwent the reaction smoothly to yield the corresponding indoles in good yields. However, the reactions of \(N\)-acetyl-, \(N\text{-}\text{tert}-\text{butoxycarbonyl}-, \(N\)-tosyl-2-idoanilines and 2-idoaniline did not proceed at all. Chloro and bromo groups on the benzene ring of 2 were intact under the reaction conditions. The halo moieties would allow for further transformations of \(3af\) and \(3ag\).

1-Alkynylidicyclohexylphosphine sulfide also underwent the annulation reaction although the higher temperature was required (Scheme 2). This reaction was reliable enough to permit a gram-scale synthesis. The reaction of 1.2 g of 5 provided 1.1 g of 6 in 74% isolated yield after purification on silica gel followed by recrystallization.

**Scheme 2.** The Reaction of 1-Alkynylidicyclohexylphosphine Sulfide

Annulation of 1-Alkynylphosphine Oxides. Next, the author tested 1-alkynylphosphine oxides instead of 1-alkynylphosphine sulfides (Scheme 3). Interestingly, the use of 1-alkynylphosphine oxides as substrates expanded the scope of accessible 2-indolylphosphines. For instance, annulation of 1,2-bis(diphenylphosphinyl)ethyne (7b) occurred smoothly to yield diphosphine dioxide \(8ba\) in good yield, while the reaction of 1,2-bis(diphenylthiophosphinyl)ethyne did not proceed. The corresponding trivalent diphosphine would serve as a bidentate ligand. 1-Alkynyl-di-\text{tert}-butylphosphine oxide \(9\) also underwent the annulation reaction in moderate yield although the longer reaction time was
required. Furthermore, 2-iodoaniline (2h) could react with 7a to provide N-unprotected indolylphosphine oxide, which allowed for further transformations on nitrogen atom i.e. tert-butoxycarbonylation and arylation\textsuperscript{12} (Scheme 4). The corresponding trivalent phosphine of 11 would serve as a potential bidentate ligand.\textsuperscript{6c} The product 12, which has aryl groups at the 1,3-positions, would be a potential precursor of a very bulky phosphine.

**Scheme 3. The Reactions of 1-Alkynylphosphine Oxides**

\[
\begin{align*}
\text{Me} \quad \text{NH} \quad + \quad \text{O}^\text{PPh}_2 \quad \xrightarrow{10 \text{ mol\% Pd(acac)}_2, 2.0 \text{ equiv } K_2CO_3} \quad \text{DMSO, 90 °C, 11 h} \quad \text{Me} \quad \text{O}^\text{PPh}_2 \\
2a \quad (2.0 \text{ equiv}) \quad 7a \quad R = \text{Ph} \quad 8aa \quad 80 \% \text{ (isomer 20\%)} \quad 8ba \quad 57 \%
\end{align*}
\]

\[
\begin{align*}
\text{Me} \quad \text{NH} \quad + \quad \text{O}^\text{PPh}_2 \quad \xrightarrow{10 \text{ mol\% Pd(acac)}_2, 2.0 \text{ equiv } K_2CO_3} \quad \text{DMSO, 120 °C, 22 h} \quad \text{Me} \quad \text{O}^\text{PPh}_2 \\
2a \quad (2.0 \text{ equiv}) \quad 9 \quad 10 \quad 50 \%
\end{align*}
\]

\[
\begin{align*}
\text{NH}_2 \quad + \quad \text{O}^\text{PPh}_2 \quad \xrightarrow{10 \text{ mol\% Pd(acac)}_2, 2.0 \text{ equiv } K_2CO_3} \quad \text{DMSO, 120 °C, 11 h} \quad \text{NH} \quad \text{O}^\text{PPh}_2 \\
2h \quad (2.0 \text{ equiv}) \quad 7a \quad 8ah \quad 80 \%
\end{align*}
\]

**Scheme 4. Transformations of 8ah**

\[
\begin{align*}
\text{8ah} \quad \xrightarrow{1.5 \text{ equiv Boc}_2O, 1.5 \text{ equiv DMAP}} \quad \text{THF, 25 °C, 5 h} \quad \text{8ah} \quad 11 \quad \text{quant.}
\end{align*}
\]

\[
\begin{align*}
\text{8ah} \quad + \quad \text{Ph} \quad \xrightarrow{2.0 \text{ equiv } Cs_2CO_3} \quad \text{DMSO, 110 °C, 24 h} \quad \text{Ar} = 4-\text{NO}_2-C_6H_4 \quad 12 \quad 70\%
\end{align*}
\]
Radical Desulfidation of 2-Indolylphosphine Sulfides. Some of the phosphine sulfides thus synthesized were subjected to radical desulfidation conditions (Scheme 5). Treatment of 2-indolylphosphine sulfides with tris(trimethylsilyl)silane in the presence of a catalytic amount of AIBN in benzene at reflux afforded the corresponding trivalent phosphines in good yields. The desulfidation reactions of these indolylphosphine sulfides were clean and high-yielding. The phosphines synthesized through this sequential annulation/desulfidation protocol were so stable under air that column purification on silica gel was applicable without any special care.

**Scheme 5.** Radical Desulfidation of 2-Indolylphosphine Sulfides

![Reaction Scheme]

Application of Newly Synthesized 2-indolylphosphine. Finally, an application of the newly synthesized phosphine was examined. The ligand 6-S proved to serve as an efficient ligand for Suzuki-Miyaura cross-coupling reaction of electron-rich aryl chloride (Scheme 6).

**Scheme 6.** Suzuki-Miyaura Cross-Coupling of Aryl Chloride

![Reaction Scheme]
Conclusion

The author has developed a conceptually new method for the synthesis of bulky indole-based heteroarylphosphines by using 1-alkynylphosphine derivatives as key starting materials. This methodology, the sequential annulation/desulfidation, offers an efficient alternative to the conventional approach to heteroarylphosphines. The phosphines synthesized by this method will find many applications in organic synthesis.
Experimental Section

Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl$_3$. Chemical shifts ($\delta$) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and relative to CDCl$_3$ at 77.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl$_3$ with 85% H$_3$PO$_4$ solution as an external standard. NMR yields were determined by fine $^{31}$P NMR spectra with (MeO)$_3$P=O as an internal standard. The first delay of $^{31}$P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. 1-alkynylphosphine sulfides were prepared by using the method described in Chapter 3. $N$-alkyl-2-iodoanilines were prepared via alkylation of 2-iodoaniline with iodoalkanes or bromoalkanes by using the method described in the literature.$^{15}$ 4-Substituted 2-iodoanilines were synthesized via iodination of 4-substituted anilines$^{16}$ followed by alkylation.

Typical Procedure for Palladium-Catalyzed Annulation reactions

Pd(acac)$_2$ (7.6 mg, 0.025 mmol) and K$_2$CO$_3$ (0.069 g, 0.50 mmol) were placed in a 20-mL reaction flask under argon. DMSO (2.0 mL), 1a (0.080 g, 0.25 mmol), and 2a (0.12 g, 0.50 mmol) were sequentially added. The resulting mixture was stirred at 90 °C for 11 h. After the mixture was cooled to room temperature, a saturated aqueous NH$_4$Cl (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na$_2$SO$_4$ and concentrated in vacuo. Chromatographic purification on silica gel yielded 3aa.
(0.078 g, 0.18 mmol) in 74% yield as a white solid.

**Procedure for tert-Butoxycarbonylation of 8ah (Scheme 4)**

Under argon atmosphere, a mixture of 8ah (0.039 g, 0.10 mmol), Boc₂O (0.033 g, 0.15 mmol) and DMAP (0.018 g, 0.15 mmol) in THF (2.0 mL) was stirred at ambient temperature for 5 h. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over Na₂SO₄. Concentration followed by silica gel column purification afforded 11 (0.049 g, 0.10 mmol, quant.) as a white solid.

**Procedure for Arylation of 8ah (Scheme 4)**

Phosphine oxide 8ah (0.039 g, 0.10 mmol) and Cs₂CO₃ (0.065 g, 0.20 mmol) were placed in a 20-mL reaction flask under argon. DMSO (1.0 mL) and 4-fluoronitrobenzene (0.028 g, 0.20 mmol) were sequentially added. The resulting mixture was heated at 110 °C for 24 h. After the mixture was cooled to room temperature, extraction with ethyl acetate (10 mL × 3) followed by silica gel column chromatography yielded 12 (0.036 g, 0.070 mmol, 70%) as a pale yellow solid.

**Typical Procedure for (Me₃Si)₂SiH-Mediated Radical Desulfidation Reaction (Scheme 5)**

Synthesis of 3aa–S is representative. AIBN (1.6 mg, 0.010 mmol) and 3aa (0.042 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 11 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided 3aa–S (0.038 g, 0.097 mmol, 97%) as a white solid.

**Procedure for Palladium-Catalyzed Cross-Coupling Reaction (Scheme 6)**

Pd(OAc)₂ (2.2 mg, 0.010 mmol), 6–S (0.012 g, 0.030 mmol), and CsF (0.23 g, 1.5 mmol)
were placed in a 20-mL reaction flask under argon. 1,4-Dioxane (2.0 mL) was added, and the mixture was stirred at room temperature for 15 min. \( p \)-Chloroanisole (0.071 g, 0.50 mmol) and phenylboronic acid (0.091 g, 0.75 mmol) were sequentially added, and the resulting mixture was heated at reflux for 18 h. After the mixture was cooled to room temperature, water (10 mL) was added and the product was extracted with hexane/ethyl acetate (5:1, 10 mL \( \times \) 3). The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \). The crude product was purified on silica gel to provide 4-methoxybiphenyl (13) (0.88 g, 0.48 mmol, 96%) as a white solid.
**Optimization of Reaction Conditions**

**Table 2. Optimization of Reaction Conditions**

<table>
<thead>
<tr>
<th>entry</th>
<th>[Pd]</th>
<th>base (equiv)</th>
<th>solvent</th>
<th>yield (^{%} ) (^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd(_2)(dba)(_3)(^{c})</td>
<td>K(_2)CO(_3) (4.0)</td>
<td>DMF</td>
<td>17</td>
</tr>
<tr>
<td>2</td>
<td>Pd(OAc)(_2)</td>
<td>K(_2)CO(_3) (4.0)</td>
<td>DMF</td>
<td>35</td>
</tr>
<tr>
<td>3</td>
<td>Pd(tfa)(_2)</td>
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<td>DMSO</td>
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\(^a\) Conditions: \(^{1}\)a (0.25 mmol), \(^{2}\)a (0.30 mmol), Pd(acac)\(_2\) (0.025 mmol), base (0.50–1.0 mmol), solvent (2.0 mL), 90 °C, 11 h. \(^b\) Based on \(^{31}\)P NMR. \(^c\) 0.013 mmol of Pd\(_2\)(dba)\(_3\) was used. \(^d\) The reaction was performed with 0.50 mmol of \(^{2}\)a.
Characterization Data

Compounds 2a, 15 2c, 16 2d, 17 2e, 18 2f, 18 2g, 18 7a, 20 and 13 21 showed the identical spectra as reported in the literature.

Diphenyl(2-thienylethynyl)phosphine sulfide (1i)

IR (nujol) 2924, 2854, 2158, 1437, 1376, 1172, 1106, 853, 717 cm⁻¹; ¹H NMR (CDCl₃) δ 7.03 (dd, J = 5.0, 1.0 Hz, 1H), 7.43 (d, J = 5.0 Hz, 1H), 7.44–7.56 (m, 7H), 7.93–8.03 (m, 4H); ¹³C NMR (CDCl₃) δ 85.79 (d, J = 150.9 Hz), 99.04 (d, J = 27.3 Hz), 119.80 (d, J = 4.8 Hz), 127.37, 128.63 (d, J = 13.8 Hz), 130.51, 130.83 (d, J = 12.0 Hz), 131.81 (d, J = 2.9 Hz), 133.52 (d, J = 98.3 Hz), 135.61 (d, J = 1.9 Hz); ³¹P NMR (CDCl₃) δ 18.70. Found: C, 66.70; H, 3.85%. Calcd for C₁₈H₁₃PS₂: C, 66.64; H, 4.04%. m.p.: 86.5–88.0 °C.

N-Ethyl-2-iodoaniline (2b)

IR (neat) 3391, 3066, 2968, 2872, 1590, 1507, 1450, 1317, 1164, 1004, 741 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32 (t, J = 7.0 Hz, 3H), 3.20 (dq, J = 5.5, 7.0 Hz, 2H), 4.06 (br, 1H), 6.44 (dd, J = 8.0, 8.0 Hz, 1H), 6.56 (d, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.0, 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 14.63, 38.73, 85.24, 110.50, 118.37, 129.40, 138.96, 147.36; Found: C, 38.90; H, 4.06%. Calcd for C₈H₁₀NI: C, 38.89; H, 4.08%.

2-Diphenylthiophosphinyl-1-methyl-3-phenylindole (3aa)

IR (nujol) 2923, 2854, 1456, 1436, 1377, 1309, 1151, 1095, 1072, 1027, 837 cm⁻¹; ¹H NMR (CDCl₃) δ 3.77 (s, 3H), 6.92–6.96 (m, 3H), 7.06–7.10 (m, 2H), 7.11–7.15 (m, 1H), 7.17–7.23 (m, 4H), 7.26–7.32 (m, 2H), 7.36–7.40 (m, 2H), 7.46 (d, J = 8.0 Hz, 1H), 7.72–7.78 (m, 4H); ¹³C NMR (CDCl₃) δ 33.34 (d, J = 2.4 Hz), 109.60, 120.49, 121.13, 124.41 (d, J = 102.1 Hz), 124.90, 126.37, 127.49, 127.61 (d, J = 13.4 Hz), 127.71 (d, J = 12.0 Hz), 128.21 (d, J = 12.9 Hz), 130.86, 131.34 (d, J = 2.8 Hz), 131.99 (d, J = 10.9 Hz), 132.24 (d, J = 87.3 Hz), 133.30, 139.60 (d, J = 7.6 Hz); ³¹P NMR (CDCl₃) δ 27.61. Found: C,
76.68; H, 5.33%. Calcd for C_{27}H_{32}NPS: C, 76.57; H, 5.24%. m.p.: 194.0–195.0 °C. CCDC No.: 753397.

**Figure 1. ORTEP diagram of 3aa**

2-Diphenylthiophosphinyl-3-hexyl-1-methylindole (3ba)

IR (nujol) 2923, 2854, 1503, 1460, 1440, 1350, 1310, 1170, 1099, 741 cm⁻¹; ¹H NMR (CDCl₃) δ 0.84–0.92 (m, 5H), 1.08–1.15 (m, 2H), 1.19–1.32 (m, 4H), 1.88–1.93 (m, 2H), 3.71 (s, 3H), 7.11–7.16 (m, 1H), 7.28–7.35 (m, 2H), 7.46–7.52 (m, 4H), 7.54–7.60 (m, 3H), 7.89–7.96 (m, 4H); ¹³C NMR (CDCl₃) δ 14.04, 22.54, 24.62, 29.55, 31.56, 32.43, 33.14 (d, J = 1.9 Hz), 109.59 (d, J = 1.4 Hz), 119.52, 120.09, 123.54 (d, J = 103.5 Hz), 124.49, 127.00 (d, J = 13.9 Hz), 127.46 (d, J = 12.9 Hz), 128.64 (d, J = 12.4 Hz), 131.82 (d, J = 2.9 Hz), 132.32 (d, J = 11.5 Hz), 132.76 (d, J = 87.3 Hz), 139.93 (d, J = 8.1 Hz); ³¹P NMR (CDCl₃) δ 28.20. Found: C, 75.10; H, 7.14%. Calcd for C_{27}H_{30}NPS: C, 75.14; H, 7.01%. m.p.: 77.0–79.0 °C.
3-Cyclohexyl-2-diphenylthiophosphinyl-1-methylindole (3ca)

IR (nujol) 2923, 2852, 1437, 1367, 1315, 1230, 1098, 753 cm^-1; ^1H NMR (CDCl₃) δ 0.50–0.60 (m, 2H), 1.10–1.20 (m, 1H), 1.45–1.60 (m, 5H), 1.65–1.75 (m, 1H), 1.80–1.95 (m, 2H), 3.68 (s, 3H), 7.07–7.11 (m, 1H), 7.27–7.32 (m, 2H), 7.46–7.52 (m, 4H), 7.54–7.60 (m, 2H), 7.86–7.95 (m, 5H); ^13C NMR (CDCl₃) δ 25.86, 26.65, 32.29, 33.29 (d, J = 2.4 Hz), 35.44, 109.95 (d, J = 2.0 Hz), 118.99, 122.88, 123.48 (d, J = 104.0 Hz), 124.01, 125.87 (d, J = 11.9 Hz), 128.78 (d, J = 12.9 Hz), 131.32 (d, J = 13.8 Hz), 131.79 (d, J = 2.9 Hz), 132.05 (d, J = 11.0 Hz), 133.33 (d, J = 87.4 Hz), 140.68 (d, J = 8.1 Hz); ^31P NMR (CDCl₃) δ 28.44. Found: C, 75.52; H, 6.50%. Calcd for C_{27}H_{28}NP:S: C, 75.49; H, 6.57%.

m.p.: 186.5–188.0 °C.

3-tert-Butyl-2-diphenylthiophosphinyl-1-methylindole (3da)

IR (nujol) 2923, 2853, 1457, 1436, 1377, 1210, 1154, 1090, 751 cm^-1; ^1H NMR (CDCl₃) δ 1.35 (s, 9H), 3.18 (s, 3H), 7.12–7.16 (m, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.28–7.32 (m, 1H), 7.35–7.44 (m, 6H), 7.94–8.02 (m, 5H); ^13C NMR (CDCl₃) δ 32.39, 34.74, 35.37 (d, J = 2.9 Hz), 110.46 (d, J = 1.9 Hz), 119.20, 123.80 (d, J = 0.88 Hz), 124.11, 125.59 (d, J = 103.0 Hz), 127.21 (d, J = 12.9 Hz), 128.50 (d, J = 12.4 Hz), 130.87 (d, J = 11.0 Hz), 130.93 (d, J = 3.6 Hz), 137.37 (d, J = 85.4 Hz), 137.61 (d, J = 12.4 Hz), 141.81 (d, J = 8.6 Hz); ^31P NMR (CDCl₃) δ 30.25. Found: C, 74.52; H, 6.63%. Calcd for C_{25}H_{26}NP:S: C, 74.49; H, 6.49%. m.p.: 143.5–145.5 °C.

3-(4-Acetylphenyl)-2-diphenylthiophosphinyl-1-methylindole (3ea)

IR (nujol) 2924, 2854, 1736, 1682, 1607, 1457, 1437, 1356, 1265, 1245, 1096, 857 cm^-1; ^1H NMR (CDCl₃) δ 2.52 (s, 3H), 3.78 (s, 3H), 7.14–7.23 (m, 7H), 7.27–7.31 (m, 2H), 7.38–7.46 (m, 3H), 7.53 (d, J = 8.5 Hz, 2H), 7.71–7.79 (m, 4H); ^13C NMR (CDCl₃) δ 26.52, 33.40 (d, J = 1.6 Hz), 109.83, 120.72, 120.96, 125.14, 125.32 (d, J = 101.1 Hz), 126.08 (d, J = 11.9 Hz), 127.23 (d, J = 11.5 Hz), 151.
127.44, 128.33 (d, J = 12.9 Hz), 131.02, 131.40 (d, J = 3.3 Hz), 132.03 (d, J = 11.0 Hz), 132.13 (d, J = 87.4 Hz), 134.89, 138.76, 139.64 (d, J = 7.6 Hz), 197.65; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 27.46.

HRMS (EI\(^{+}\)) \((m/z)\) Observed: 465.1309 (\(\Delta = -1.5\) ppm). Calcd for C\(_{29}\)H\(_{24}\)NOPS [M\(^{+}\)]: 465.1316. m.p.: 204.0–206.0 °C.

2-Diphenylthiophosphinyl-3-(4-methoxycarbonylphenyl)-1-methylindole (3fa)

IR (nujol) 2924, 2855, 1720, 1609, 1456, 1435, 1405, 1280, 1173, 1113, 1099, 1020, 871, 832 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.78 (s, 3H), 3.91 (s, 3H), 7.12–7.17 (m, 1H), 7.14 (d, \(J = 8.5\) Hz, 2H), 7.18–7.23 (m, 4H), 7.27–7.32 (m, 2H), 7.38–7.42 (m, 3H), 7.61 (d, \(J = 8.5\) Hz, 2H), 7.71–7.78 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 33.38 (d, \(J = 2.4\) Hz), 52.03, 109.77 (d, \(J = 1.5\) Hz), 120.73, 120.88, 125.09, 125.19 (d, \(J = 101.1\) Hz), 126.19 (d, \(J = 11.9\) Hz), 127.32 (d, \(J = 11.4\) Hz), 127.79, 128.33 (d, \(J = 12.9\) Hz), 128.66, 130.80, 131.50 (d, \(J = 2.9\) Hz), 131.97 (d, \(J = 87.3\) Hz), 132.01 (d, \(J = 11.0\) Hz), 138.53, 139.58 (d, \(J = 7.8\) Hz), 166.93; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 27.51. Found: C, 72.53; H, 5.19%. Calcd for C\(_{29}\)H\(_{24}\)NOPS: C, 72.33; H, 5.02%. m.p.: 245.0–247.0 °C.

2-Diphenylthiophosphinyl-3-(4-methoxyphenyl)-1-methylindole (3ga)

IR (nujol) 2925, 2855, 1611, 1532, 1459, 1435, 1377, 1243, 1177 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 3.71 (s, 3H), 3.75 (s, 3H), 6.47 (d, \(J = 8.5\) Hz, 2H), 6.99 (d, \(J = 8.5\) Hz, 2H), 7.10–7.15 (m, 1H), 7.18–7.24 (m, 4H), 7.28–7.34 (m, 2H), 7.35–7.40 (m, 2H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.70–7.79 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 33.30 (d, \(J = 1.1\) Hz), 55.19, 109.58 (d, \(J = 1.4\) Hz), 113.17, 120.39, 121.11, 124.32 (d, \(J = 103.1\) Hz), 124.85, 125.63, 127.33 (d, \(J = 12.5\) Hz), 127.79 (d, \(J = 11.4\) Hz), 128.21 (d, \(J = 12.9\) Hz), 131.15 (d, \(J = 2.9\) Hz), 131.90, 132.02 (d, \(J = 11.0\) Hz), 132.42 (d, \(J = 88.9\) Hz), 139.65 (d, \(J = 7.6\) Hz), 158.07; \(^{31}\)P NMR (CDCl\(_3\)) \(\delta\) 27.55. Found: C, 74.10; H, 5.37%. Calcd for C\(_{28}\)H\(_{24}\)NOOPS: C, 74.15; H, 5.33%. m.p.: 207.0–209.0 °C.
2-Diphenylthiophosphinyl-3-(2-methoxyphenyl)-1-methylindole (3ha)

IR (nujol) 2925, 2854, 1489, 1436, 1367, 1320, 1253, 1097, 1044, 1025, 834 cm⁻¹; ¹H NMR (CDCl₃) δ 3.52 (s, 3H), 3.81 (s, 3H), 6.29 (d, J = 7.5 Hz, 1H), 6.70–6.75 (m, 1H), 6.91–6.97 (m, 1H), 7.06–7.16 (m, 4H), 7.20–7.30 (m, 4H), 7.32–7.38 (m, 3H), 7.58–7.64 (m, 2H), 7.84–7.90 (m, 2H); ¹³C NMR (CDCl₃) δ 33.16 (d, J = 1.4 Hz), 54.22, 109.52 (d, J = 2.1 Hz), 109.65, 119.70, 120.17, 121.14, 122.49, 122.80 (d, J = 12.5 Hz), 124.55, 124.73 (d, J = 103.5 Hz), 127.68 (d, J = 13.4 Hz), 127.79 (d, J = 13.4 Hz), 128.00 (d, J = 12.0 Hz), 128.55, 131.21 (d, J = 2.9 Hz), 131.27 (d, J = 88.4 Hz), 131.42 (d, J = 2.9 Hz), 131.87 (d, J = 10.9 Hz), 132.38 (d, J = 11.0 Hz), 132.42, 132.78 (d, J = 88.9 Hz), 139.68 (d, J = 8.0 Hz), 156.25; ³¹P NMR (CDCl₃) δ 28.81. Found: C, 73.94; H, 5.51%. Calcd for C₂₈H₂₄NOP₂S: C, 74.15; H, 5.33%. m.p.: 173.5–174.0 °C.

2-Diphenylthiophosphinyl-1-methyl-3-(2-thienyl)indole (3ia)

IR (nujol) 2925, 2855, 1450, 1436, 1377, 1347, 1310, 1239, 1177, 1149, 1095, 848 cm⁻¹; ¹H NMR (CDCl₃) δ 3.74 (s, 3H), 6.50 (dd, J = 5.5, 4.0 Hz, 1H), 6.52 (dd, J = 4.0, 1.5 Hz, 1H), 7.01 (dd, J = 5.5, 1.5 Hz, 1H), 7.15–7.19 (m, 1H), 7.24–7.29 (m, 4H), 7.32–7.39 (m, 4H), 7.62 (d, J = 8.5 Hz, 1H), 7.76–7.82 (m, 4H); ¹³C NMR (CDCl₃) δ 33.51 (d, J = 1.9 Hz), 109.65 (d, J = 1.4 Hz), 119.34 (d, J = 12.0 Hz), 120.84, 121.20, 125.07, 125.81, 126.30 (d, J = 101.6 Hz), 127.05, 128.26 (d, J = 9.5 Hz), 128.28 (d, J = 13.0 Hz), 130.11, 131.35 (d, J = 3.4 Hz), 131.80 (d, J = 11.0 Hz), 132.27 (d, J = 87.9 Hz), 133.52, 139.56 (d, J = 7.6 Hz); ³¹P NMR (CDCl₃) δ 27.81. Found: C, 69.71; H, 4.69%. Calcd for C₂₅H₂₀NOP₂S: C, 69.90; H, 4.69%. m.p.: 173.0–174.0 °C.

2-Diphenylthiophosphinyl-1-ethyl-3-phenylindole (3ab)

IR (nujol) 2922, 2855, 1468, 1437, 1376, 1330, 1151, 1099, 1070, 840 cm⁻¹; ¹H NMR (CDCl₃) δ 1.26 (t, J = 7.0 Hz, 3H), 4.41 (q, J = 7.0 Hz, 2H), 6.90–6.97 (m, 3H), 7.03–7.07 (m, 2H), 7.10–7.15 (m, 1H), 7.17–7.23 (m, 4H), 7.26–7.31 (m,
2H), 7.34–7.39 (m, 1H), 7.40–7.45 (m, 2H), 7.70–7.77 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 14.29, 41.37 (d, J = 2.9 Hz), 110.32 (d, J = 1.4 Hz), 120.39, 121.33, 123.95 (d, J = 102.6 Hz), 124.77, 126.30, 127.45, 127.50 (d, J = 12.4 Hz), 128.14 (d, J = 12.9 Hz), 128.35 (d, J = 11.9 Hz), 130.89, 131.32 (d, J = 2.9 Hz), 132.15 (d, J = 11.0 Hz), 132.45 (d, J = 87.9 Hz), 133.44, 138.54 (d, J = 7.6 Hz); $^{31}$P NMR (CDCl$_3$) δ 27.43. Found: C, 76.68; H, 5.72%. Calcd for C$_{28}$H$_{24}$NP$_2$: C, 76.86; H, 5.53%. m.p.: 165.0–166.5 °C.

2-Diphenylthiophosphinyl-1-isopropyl-3-phenylindole (3ac)

IR (nujol) 2924, 2854, 1457, 1438, 1367, 1319, 1153, 1097, 835 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 1.42 (d, J = 7.0 Hz, 6H), 5.39 (sept, J = 7.0 Hz, 1H), 6.89–6.96 (m, 3H), 6.99–7.09 (m, 3H), 7.16–7.23 (m, 4H), 7.25–7.32 (m, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.72–7.79 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 20.39, 50.56 (d, J = 3.9 Hz), 112.96 (d, J = 0.88 Hz), 119.96, 121.60, 124.17, 124.55 (d, J = 102.6 Hz), 126.29, 127.08 (d, J = 13.4 Hz), 127.43, 128.09 (d, J = 12.9 Hz), 129.55 (d, J = 12.5 Hz), 131.00, 131.31 (d, J = 2.9 Hz), 132.30 (d, J = 11.0 Hz), 132.43 (d, J = 87.8 Hz), 133.51, 136.90 (d, J = 7.1 Hz); $^{31}$P NMR (CDCl$_3$) δ 28.37. Found: C, 77.40; H, 5.69%. Calcd for C$_{29}$H$_{26}$NP$_2$: C, 77.13; H, 5.80%. m.p.: 180.0–182.0 °C.

1-Benzyl-2-diphenylthiophosphinyl-3-phenylindole (3ad)

IR (nujol) 2924, 2855, 1453, 1437, 1378, 1324, 1209, 1174, 1151, 1099, 839 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 5.68 (s, 2H), 6.95–7.00 (m, 5H), 7.08–7.17 (m, 11H), 7.18–7.26 (m, 3H), 7.45 (d, J = 8.0 Hz, 1H), 7.68–7.74 (m, 4H); $^{13}$C NMR (CDCl$_3$) δ 50.06 (d, J = 2.4 Hz), 111.25, 120.67, 121.11, 124.74 (d, J = 101.1 Hz), 124.99, 126.43, 126.52, 126.80, 127.50, 128.02 (d, J = 13.0 Hz), 128.06, 128.11 (d, J = 12.4 Hz), 128.36 (d, J = 12.0 Hz), 130.90, 131.25 (d, J = 2.9 Hz), 131.95 (d, J = 87.9 Hz), 132.08 (d, J = 10.9 Hz), 133.36, 137.09, 139.43 (d, J = 7.6 Hz); $^{31}$P NMR (CDCl$_3$) δ 27.74. Found: C, 79.27; H, 5.20%. Calcd for C$_{33}$H$_{26}$NP$_2$: C, 79.33; H, 5.25%. m.p.: 159.5–160.5 °C.
2-Diphenylthiophosphinyl-1,5-dimethyl-3-phenylindole (3ae)

IR (nujol) 2923, 2854, 1456, 1436, 1377, 1330, 1097, 1028, 880 cm\(^{-1}\); \(^1^H\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 2.39 (s, 3H), 3.75 (s, 3H), 6.92–6.97 (m, 3H), 7.05–7.09 (m, 2H), 7.16–7.24 (m, 6H), 7.25–7.31 (m, 3H), 7.70–7.78 (m, 4H); \(^1^3^C\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 21.27, 33.35, 109.35 (d, \(J = 1.4\) Hz), 120.30, 124.31 (d, \(J = 102.6\) Hz), 126.29, 126.77, 127.09 (d, \(J = 12.9\) Hz), 127.48, 127.89 (d, \(J = 11.5\) Hz), 128.18 (d, \(J = 12.9\) Hz), 129.97, 130.91, 131.28 (d, \(J = 3.4\) Hz), 132.02 (d, \(J = 11.5\) Hz), 132.39 (d, \(J = 87.8\) Hz), 133.52, 138.16 (d, \(J = 8.1\) Hz); \(^3^1^P\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 27.57. Found: C, 76.77; H, 5.70%. Calcd for C\(_{28}\)H\(_{24}\)NP\(_2\)S: C, 76.86; H, 5.53%. m.p.: 212.0–213.5 °C.

5-Chloro-2-diphenylthiophosphinyl-1-methyl-3-phenylindole (3af)

IR (nujol) 2924, 2854, 1457, 1437, 1376, 1331, 1270, 1098, 1058, 1028, 716 cm\(^{-1}\); \(^1^H\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 3.75 (s, 3H), 6.92–6.98 (m, 3H), 7.01–7.05 (m, 2H), 7.18–7.24 (m, 4H), 7.27–7.33 (m, 4H), 7.39 (d, \(J = 1.5\) Hz, 1H), 7.70–7.77 (m, 4H); \(^1^3^C\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 33.51 (d, \(J = 2.0\) Hz), 110.75 (d, \(J = 1.0\) Hz), 120.30, 125.32, 126.02 (d, \(J = 100.6\) Hz), 126.39, 126.65, 126.90 (d, \(J = 12.4\) Hz), 127.66, 128.30 (d, \(J = 12.9\) Hz), 128.69 (d, \(J = 11.5\) Hz), 130.76, 131.49 (d, \(J = 2.9\) Hz), 131.96 (d, \(J = 87.9\) Hz), 131.99 (d, \(J = 11.0\) Hz), 132.69, 137.95 (d, \(J = 7.6\) Hz); \(^3^1^P\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 27.63. Found: C, 70.57; H, 4.47%. Calcd for C\(_{27}\)H\(_{21}\)ClNP\(_2\)S: C, 70.81; H, 4.62%. m.p.: 175.5–177.0 °C.

5-Bromo-2-diphenylthiophosphinyl-1-methyl-3-phenylindole (3ag)

IR (nujol) 2924, 2854, 1479, 1436, 1377, 1270, 1100, 1071, 1028, 874 cm\(^{-1}\); \(^1^H\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 3.75 (s, 3H), 6.92–6.98 (m, 3H), 7.01–7.06 (m, 2H), 7.18–7.26 (m, 5H), 7.27–7.32 (m, 2H), 7.41–7.45 (m, 1H), 7.54 (d, \(J = 1.5\) Hz, 1H), 7.69–7.76 (m, 4H); \(^1^3^C\) NMR (CD\(_3\)Cl\(_2\)) \(\delta\) 33.48, 111.14, 113.82 (d, \(J = 1.4\) Hz), 123.43, 125.89 (d, \(J = 100.8\) Hz), 126.66, 126.80 (d, \(J = 12.4\) Hz), 127.67, 127.82, 128.30 (d, \(J = 12.9\) Hz), 129.32 (d, \(J = 11.5\) Hz), 130.76, 131.49 (d, \(J = 3.4\) Hz), 131.92 (d, \(J = 87.3\) Hz), 131.98 (d, \(J = 8.1\) Hz).
= 11.0 Hz), 132.63, 138.19 (d, \( J = 7.6 \) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) 27.59. HRMS (EI\(^+\)) (m/z) Observed: 501.0313 (\( \Delta = -0.6 \) ppm). Calcd for C\(_{27}\)H\(_{34}\)NPSBr [M\(^+\)]: 501.0316. m.p.: 198.0–200.0 °C.

2-Dicyclohexylthiophosphinyl-1-methyl-3-phenylindole (6)

\[ \text{IR (nujol)} 2923, 2853, 1448, 1374, 1320, 1206, 1004, 738 \text{ cm}^{-1}; \quad \text{}^{1}\text{H NMR (CDCl}\(_3\)) \delta 0.87–1.20 (m, 6H), 1.46–1.72 (m, 10H), 1.73–1.96 (m, 6H), 4.41 (s, 3H), 7.08 (dd, \( J = 7.5, 7.5 \) Hz, 1H), 7.18 (d, \( J = 7.5 \) Hz, 1H), 7.31–7.38 (m, 3H), 7.41 (d, \( J = 8.5 \) Hz, 1H), 7.45–7.52 (m, 3H); \(^{13}\)C NMR (CDCl\(_3\)) \( \delta \) 25.56 (d, \( J = 1.5 \) Hz), 26.06 (d, \( J = 13.9 \) Hz), 26.21 (d, \( J = 2.4 \) Hz), 26.37 (d, \( J = 14.3 \) Hz), 26.96 (d, \( J = 2.9 \) Hz), 34.47, 39.89 (d, \( J = 51.5 \) Hz), 109.70, 120.37, 120.52, 121.86 (d, \( J = 74.0 \) Hz), 124.28, 124.54 (d, \( J = 11.5 \) Hz), 127.76, 128.29, 128.40 (d, \( J = 11.0 \) Hz), 130.89, 135.38, 139.77 (d, \( J = 6.1 \) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \( \delta \) 52.51. Found: C, 74.44; H, 7.96%. Calcd for C\(_{27}\)H\(_{34}\)O\(_2\)P\(_2\): C, 74.45; H, 7.87%.

m.p.: 154.0–155.0 °C.

1,2-Bis(diphenylphosphinyl)ethyne (7b)

\[ \text{IR (nujol)} 2923, 2855, 1442, 1377, 1328, 1207, 1122, 1103, 1074, 993, 800, 748 \text{ cm}^{-1}; \quad \text{}^{1}\text{H NMR (CDCl}\(_3\)) \delta 7.44–7.51 (m, 8H), 7.54–7.60 (m, 4H), 7.76–7.80, 691 \text{ cm}^{-1}; \quad \text{}^{1}\text{H NMR (CDCl}\(_3\)) \delta 7.44–7.51 (m, 8H), 7.54–7.60 (m, 4H), 7.76–7.84 (m, 8H); \quad \text{}^{13}\text{C NMR (CDCl}\(_3\)) \delta 99.00 (dd, \( J = 136.0, 17.1 \) Hz), 128.89 (m), 130.96 (d, \( J = 121.8 \) Hz), 131.05 (m), 132.96; \quad \text{}^{31}\text{P NMR (CDCl}\(_3\)) \delta 7.30. Found: C, 73.19; H, 4.80%. Calcd for C\(_{26}\)H\(_{20}\)O\(_2\)P\(_2\): C, 73.24; H, 4.73%. m.p.: 154.0–156.0 °C.

2-Diphenylphosphinyl-1-methyl-3-phenylindole (8aa)

\[ \text{IR (nujol)} 2923, 2853, 1456, 1437, 1323, 1183, 1103, 840, 702, 691 \text{ cm}^{-1}; \quad \text{}^{1}\text{H NMR (CDCl}\(_3\)) \delta 3.93 (s, 3H), 6.89–6.70 (m, 5H), 7.09–7.14 (m, 1H), 7.19–7.25 (m, 4H), 7.32–7.43 (m, 5H), 7.47–7.54 (m, 4H); \quad \text{}^{13}\text{C NMR (CDCl}\(_3\)) \delta 32.91, 109.59, 120.32, 121.26, 125.00, 125.27 (d, \( J = 118.9 \) Hz), 126.32, 127.40, 127.96 (d, \( J = 11.5 \) Hz), 156
128.26 (d, \(J = 12.5\) Hz), 128.40 (d, \(J = 14.8\) Hz), 130.68, 131.69 (d, \(J = 2.9\) Hz), 131.83 (d, \(J = 10.0\) Hz), 132.68 (d, \(J = 108.9\) Hz), 133.38, 139.25 (d, \(J = 8.1\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta 19.06\). HRMS (EI\(^{+}\)) (\(m/z\)) Observed: 407.1438 (\(\Delta = -0.3\) ppm). Calcd for C\(_{27}\)H\(_{22}\)NOP [M\(^{+}\)]: 407.1439. m.p.: 173.5–174.5 °C.

2,3-Bis(diphenylphosphinyl)-1-methylindole (8ba)

IR (nujol) 2924, 2855, 2360, 2323, 1456, 1436, 1181, 1119, 745 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 4.21\) (s, 3H), 6.56 (d, \(J = 8.0\) Hz, 1H), 6.86 (dd, \(J = 8.0\) Hz, 1H), 7.17–7.30 (m, 13H), 7.32–7.46 (m, 5H), 7.82–7.92 (m, 4H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 34.23, 110.51, 112.76\) (dd, \(J = 119.4, 13.4\) Hz), 121.66, 121.81, 124.25, 127.63 (d, \(J = 13.4\) Hz), 128.18 (d, \(J = 12.4\) Hz), 128.95 (d, \(J = 11.0, 10.0\) Hz), 131.32 (d, \(J = 2.4\) Hz), 131.41 (d, \(J = 10.5\) Hz), 131.78 (d, \(J = 2.9\) Hz), 132.62 (d, \(J = 112.6\) Hz), 132.80 (d, \(J = 11.0\) Hz), 134.68 (d, \(J = 107.9\) Hz), 138.72 (dd, \(J = 106.4, 17.6\) Hz), 140.45 (dd, \(J = 10.6, 8.1\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta 20.41, 26.08\). HRMS (EI\(^{+}\)) (\(m/z\)) Observed: 531.1525 (\(\Delta = +1.5\) ppm). Calcd for C\(_{33}\)H\(_{27}\)NO\(_2\)P\(_2\) [M\(^{+}\)]: 531.1517. m.p.: 200.0–202.0 °C.

2-Diphenylphosphinyl-3-phenylindole (8ah)

IR (nujol) 2923, 2854, 1456, 1439, 1377, 1162, 1121, 828, 746 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta 7.06–7.17\) (m, 6H), 7.28–7.37 (m, 5H), 7.42–7.50 (m, 3H), 7.51–7.62 (m, 5H), 9.56 (s, 1H); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta 111.90, 120.68, 120.80, 124.17\) (d, \(J = 119.9\) Hz), 124.76, 126.68 (d, \(J = 12.9\) Hz), 126.82, 127.84, 128.34 (d, \(J = 12.9\) Hz), 128.63 (d, \(J = 11.5\) Hz), 130.45, 131.94 (d, \(J = 10.5\) Hz), 131.99 (d, \(J = 109.3\) Hz), 132.05 (d, \(J = 2.9\) Hz), 133.37, 137.18 (d, \(J = 10.0\) Hz); \(^{31}\)P NMR (CDCl\(_3\)) \(\delta 19.76\). Found: C, 78.99; H, 5.12%. Calcd for C\(_{26}\)H\(_{20}\)NOP: C, 79.38; H, 5.12%. m.p.: 208.0–210.0 °C.
Di-tert-butyl(phenylethynyl)phosphine oxide (9)

IR (nujol) 2923, 2854, 2181, 1490, 1363, 1155, 837, 767 cm⁻¹; ¹H NMR (CDCl₃) δ 1.39 (d, J = 15.0 Hz, 18H), 7.37 (dd, J = 7.0, 7.0 Hz, 2H), 7.43 (t, J = 7.0 Hz, 1H), 7.55 (d, J = 7.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 26.42, 36.24 (d, J = 72.0 Hz), 81.75 (d, J = 126.9 Hz), 103.00 (d, J = 18.6 Hz), 120.64 (d, J = 3.4 Hz), 128.52, 130.11, 132.30 (d, J = 1.5 Hz); ³¹P NMR (CDCl₃) δ 46.41. Found: C, 73.02; H, 8.89%. Calcd for C₁₆H₂₃OP: C, 73.26; H, 8.84%. m.p.: 124.0–126.0 °C.

2-Di-tert-butylphosphinyl-1-methyl-3-phenylindole (10)

IR (nujol) 2923, 2854, 1684, 1447, 1363, 1307, 1201, 1155, 825, 818 cm⁻¹; ¹H NMR (CDCl₃) δ 1.16 (d, J = 14.5 Hz, 18H), 4.40 (s, 3H), 6.98 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 8.0, 8.0 Hz, 1H), 7.33 (dd, J = 8.0, 8.0 Hz, 1H), 7.39–7.42 (m, 5H), 7.44 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 26.91 (d, J = 0.90 Hz), 34.01, 37.50 (d, J = 61.0 Hz), 109.68, 120.01, 120.85, 123.85 (d, J = 12.9 Hz), 123.94, 124.22 (d, J = 78.8 Hz), 127.72, 127.78, 129.86 (d, J = 10.5 Hz), 132.50, 136.06, 139.27 (d, J = 6.6 Hz); ³¹P NMR (CDCl₃) δ 60.10. HRMS (EI⁺) (m/z) Observed: 367.2068 (Δ = +0.8 ppm). Calcd for C₂₃H₃₀NOP [M⁺]: 367.2065. m.p.: 112.5–114.0 °C.

1-tert-Butoxycarbonyl-2-diphenylphosphinyl-3-phenylindole (11)

IR (nujol) 2921, 2852, 1731, 1701, 1438, 1317, 1300, 1149 cm⁻¹; ¹H NMR (CDCl₃) δ 1.32 (s, 9H), 7.00–7.30 (m, 12H), 7.41 (d, J = 7.5 Hz, 1H), 7.47 (dd, J = 7.5, 7.0 Hz, 1H), 7.50–7.63 (m, 4H), 8.19 (d, J = 8.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 27.51, 85.64, 115.25, 121.23, 123.26, 126.67 (d, J = 117.0 Hz), 127.43, 127.64, 127.91 (d, J = 12.4 Hz), 127.92, 129.51 (d, J = 11.5 Hz), 130.68 (d, J = 2.9 Hz), 130.86, 131.02 (d, J = 10.0 Hz), 132.48 (d, J = 1.5 Hz), 135.08 (d, J = 111.6 Hz), 137.69 (d, J = 12.9 Hz), 137.89 (d, J = 5.8 Hz), 149.82; ³¹P NMR (CDCl₃) δ 14.76. HRMS (EI⁺) (m/z) Observed: 493.1797 (Δ = –2.0 ppm). Calcd for C₃₁H₂₈NO₃P [M⁺]: 493.1807. m.p.: 61.0–63.0 °C.
2-Diphenylphosphinyl-1-(4-nitrophenyl)-3-phenylindole (12)

IR (nujol) 2922, 2853, 1593, 1510, 1497, 1440, 1346, 1203, 1189, 1099, 871, 855 cm⁻¹; ¹H NMR (CDCl₃) δ 7.02–7.10 (m, 7H), 7.14 (d, J = 8.5 Hz, 1H), 7.17–7.25 (m, 3H), 7.28–7.37 (m, 3H), 7.43–7.50 (m, 4H), 7.52 (d, J = 9.0 Hz, 2H), 7.66 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 110.45, 121.64, 122.01, 123.95, 126.32, 127.27, 127.68 (d, J = 10.9 Hz), 127.89, 127.95 (d, J = 115.4 Hz), 127.97 (d, J = 12.4 Hz), 129.87, 130.78, 131.27 (d, J = 2.9 Hz), 131.37 (d, J = 9.5 Hz), 132.24 (d, J = 12.9 Hz), 132.51 (d, J = 108.8 Hz), 132.69, 139.76 (d, J = 7.3 Hz), 143.77, 146.44; ³¹P NMR (CDCl₃) δ 12.70. HRMS (EI⁺) (m/z) Observed: 514.1452 (Δ = +1.1 ppm). Calcd for C₃₂H₂₃N₂O₃P [M⁺]: 514.1446. m.p.: 236.0–237.0 °C.

2-Diphenylphosphino-1-methyl-3-phenylindole (3aa–S)

IR (nujol) 2923, 2853, 1507, 1457, 1430, 1369, 1340, 1324, 1275, 1261, 1149, 738 cm⁻¹; ¹H NMR (CDCl₃) δ 3.33 (s, 3H), 7.17–7.22 (m, 1H), 7.28–7.36 (m, 9H), 7.37–7.43 (m, 6H), 7.49 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 109.46, 119.92, 120.49 (d, J = 1.9 Hz), 123.72, 126.68, 127.31 (d, J = 8.0 Hz), 127.86, 128.01, 128.57 (d, J = 5.8 Hz), 129.04 (d, J = 28.6 Hz), 131.05 (d, J = 31.0 Hz), 131.06 (d, J = 3.4 Hz), 131.69 (d, J = 17.6 Hz), 134.93 (d, J = 3.9 Hz), 135.73 (d, J = 11.4 Hz), 139.66; ³¹P NMR (CDCl₃) δ –32.15. Found: C, 82.77; H, 5.72%. Calcd for C₂₇H₂₃NP: C, 82.84; H, 5.66%. m.p.: 159.5–160.5 °C.

3-Cyclohexyl-2-diphenylphosphino-1-methylindole (3ca–S)

IR (nujol) 2922, 2851, 1583, 1505, 1479, 1447, 1373, 1320, 1189, 1136, 1091, 1016, 887 cm⁻¹; ¹H NMR (CDCl₃) δ 1.25–1.42 (m, 3H), 1.72–1.84 (m, 5H), 2.04–2.14 (m, 2H), 3.28–3.36 (m, 1H), 3.60 (s, 3H), 7.11–7.15 (m, 1H), 7.26–7.39 (m, 8H), 7.40–7.45 (m, 4H), 7.95 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 26.32, 27.13, 32.13 (d, J = 6.6 Hz), 33.56, 37.85 (d, J = 14.4 Hz), 109.66, 118.46, 121.55, 122.86, 126.19 (d, J = 7.1
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Hz, 127.65 (d, J = 19.5 Hz), 127.92, 128.53 (d, J = 5.8 Hz), 131.63 (d, J = 17.8 Hz), 134.25 (d, J = 23.4 Hz), 135.83 (d, J = 9.6 Hz), 140.15 (d, J = 1.4 Hz); 31P NMR (CDCl₃) δ –36.05. HRMS (EI⁺) (m/z) Observed: 397.1956 (Δ = –0.9 ppm). Calcd for C₂₇H₃₈NP [M⁺]: 397.1959. m.p.: 133.0–135.0 °C.

2-Diphenylphosphino-3-(2-methoxyphenyl)-1-methylindole (3ha–S)

IR (nujol) 2922, 2853, 1457, 1369, 1322, 1240, 1081, 941, 801 cm⁻¹; ¹H NMR (CDCl₃) δ 3.34 (s, 3H), 3.42 (s, 3H), 6.89 (d, J = 8.0 Hz, 1H), 6.99 (dd, J = 7.5, 7.5 Hz, 1H), 7.10–7.16 (m, 1H), 7.20–7.40 (m, 12H), 7.42–7.48 (m, 2H), 7.53 (d, J = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 32.39 (d, J = 3.4 Hz), 54.59, 109.33, 110.59, 119.58, 120.02, 120.60 (d, J = 1.4 Hz), 123.24, 124.01 (d, J = 4.4 Hz), 126.04 (d, J = 32.5 Hz), 127.78, 127.80, 127.81 (d, J = 3.6 Hz), 128.30 (d, J = 5.3 Hz), 128.32, 128.39 (d, J = 5.8 Hz), 130.25 (d, J = 26.3 Hz), 131.74 (d, J = 17.8 Hz), 131.99 (d, J = 17.1 Hz), 132.73, 135.69 (d, J = 11.0 Hz), 136.20 (d, J = 11.0 Hz), 139.70, 157.55; 31P NMR (CDCl₃) δ –29.98. HRMS (EI⁺) (m/z) Observed: 421.1600 (Δ = +1.1 ppm). Calcd for C₂₇H₃₄NP [M⁺]: 421.1596. m.p.: 63.0–65.0 °C.

2-Dicyclohexylphosphino-1-methyl-3-phenylindole (6–S)

IR (nujol) 2924, 2851, 1456, 1441, 1389, 1320, 1243, 1151, 1031, 771 cm⁻¹; ¹H NMR (CDCl₃) δ 0.96–2.06 (m, 22H), 3.98 (s, 3H), 7.10 (dd, J = 7.5, 7.5 Hz, 1H), 7.26–7.31 (m, 1H), 7.35–7.48 (m, 7H); ¹³C NMR (CDCl₃) δ 26.17, 26.85 (d, J = 13.9 Hz), 26.86 (d, J = 10.5 Hz), 30.76 (d, J = 8.6 Hz), 31.99 (d, J = 13.9 Hz), 32.65 (d, J = 22.9 Hz), 35.40 (d, J = 8.6 Hz), 109.21, 119.46, 119.68, 122.55, 126.61, 127.80, 128.42, 131.07, 131.57, 131.75, 136.11, 138.67; 31P NMR (CDCl₃) δ –21.53. HRMS (EI⁺) (m/z) Observed: 403.2426 (Δ = –0.8 ppm). Calcd for C₂₇H₃₄NP [M⁺]: 403.2429. m.p.: 89.0–91.0 °C.
References and Notes


(10) The structure of 3aa was confirmed by X-ray crystallographic analysis. See Experimental Section.

(11) A significant amount of phosphine sulfide derived from an additional phosphine ligand was observed after the reaction.


Chapter 6

Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (E)-1-Alkenylphosphine Oxides

Treatment of 1-alkynylphosphines with a rhodium catalyst in 1,4-dioxane/H_2O at reflux provides (E)-1-alkenylphosphine oxides in good yields with perfect stereoselectivity.
**Introduction**

During the course of his study on the use of 1-alkynylphosphine derivatives as key starting materials for the synthesis of new phosphines, the author found a new transformation of 1-alkynylphosphines. 1-Alkynylphosphines react with water in the presence of a rhodium catalyst to provide the corresponding \((E)\)-1-alkenylphosphine oxides\(^1\) with perfect stereoselectivity. This is an interesting formal hydration reaction of 1-alkynylphosphines from mechanistic and synthetic points of view.

**Results and Discussion**

Treatment of 1-octynyldiphenylphosphine \((1a)\) under \([\text{RhCl}(\text{cod})]\)\(_2\) catalysis in 1,4-dioxane/H\(_2\)O (10:1) at reflux provided \((E)\)-1-octenyldiphenylphosphine oxide \((2a)\) in 84\% NMR yield and 73\% isolated yield (Table 1, entry 1). Other rhodium complexes such as \([\text{Rh}(\text{OH})(\text{cod})]\)\(_2\) also showed catalytic activity (entry 2). Addition of PPh\(_3\) (2 equiv to Rh) as a ligand had no effect on the reactivity (entry 3). In contrast, when BINAP (1 equiv to Rh) or P(OEt)\(_3\) (2 equiv to Rh) was used instead of PPh\(_3\), the reaction was completely inhibited (entries 4 and 5). Rh(acac)\(_3\) and an iridium catalyst, \([\text{IrCl}(\text{cod})]\)\(_2\), were inactive (entries 6 and 7).

1,4-Dioxane/H\(_2\)O was the choice of solvent. Although the reaction proceeded in a toluene/H\(_2\)O mixed solvent, the reaction suffered from poor reproducibility (entry 8). When toluene was used, the reaction proceeded in a two-phase medium. The erratic amount of water in the nonpolar organic phase would be responsible for the poor reproducibility. When THF or acetonitrile was used instead of 1,4-dioxane, the reaction did not proceed, albeit the reaction is homogeneous (entries 9 and 10). The reaction in a 1,2-dichloroethane/H\(_2\)O biphasic medium failed, probably because of the highly hydrophobic nature of 1,2-dichloroethane (entry 11). The use of 1,4-dioxane without H\(_2\)O resulted in complete recovery of 1a (entry 12). When the amount of water was reduced to 3 equivalents to the alkynylphosphine, poor reproducibility was observed (entry 13). The amount of water in the organic phase is the key for reproducibility.
Table 1. Optimization of Reaction Conditions\textsuperscript{a}

<table>
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<th>entry</th>
<th>catalyst</th>
<th>additive</th>
<th>solvent\textsuperscript{b}</th>
<th>yield /%\textsuperscript{c}</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>84 (73)</td>
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<tr>
<td>2</td>
<td>[Rh(OH)(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>75</td>
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<tr>
<td>3</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>PPh\textsubscript{3}\textsuperscript{d}</td>
<td>1,4-dioxane</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>BINAP\textsuperscript{a}</td>
<td>1,4-dioxane</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>P(OEt)\textsubscript{3}\textsuperscript{d}</td>
<td>1,4-dioxane</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>Rh(acac)\textsubscript{3}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>[IrCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>toluene\textsuperscript{f}</td>
<td>0–84</td>
</tr>
<tr>
<td>9</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>THF</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>acetonitrile</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,2-dichloroethane\textsuperscript{f}</td>
<td>0</td>
</tr>
<tr>
<td>12\textsuperscript{g}</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>0</td>
</tr>
<tr>
<td>13\textsuperscript{h}</td>
<td>[RhCl(cod)]\textsubscript{2}</td>
<td>none</td>
<td>1,4-dioxane</td>
<td>0–84</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: 1a (0.50 mmol), [RhCl(cod)]\textsubscript{2} (0.0075 mmol), 1,4-dioxane (3.0 mL), H\textsubscript{2}O (0.30 mL), reflux, 3 h. \textsuperscript{b} The reaction is homogeneous unless otherwise noted. \textsuperscript{c} Based on \textsuperscript{31}P NMR with a sufficient first decay period. Isolated yield is in parenthesis. \textsuperscript{d} 2 equiv to Rh. \textsuperscript{a} 1 equiv to Rh. \textsuperscript{f} The reaction proceeded in a two-phase medium. \textsuperscript{g} The reaction was performed without H\textsubscript{2}O. \textsuperscript{h} The reaction was performed with H\textsubscript{2}O (3 equiv to 1a).

The scope of 1-alkynylphosphines was investigated (Table 2). Although a bulky tert-butyl group of 1d completely suppressed the reaction\textsuperscript{2} phenyl- and isopropyl-substituted alkynylphosphines 1b and 1c underwent the reaction. The reactions of methoxyphenyl-substituted 1e and 1f and p-acetlyphenyl-substituted 1g proceeded smoothly. However, neither pyridine-containing 1h, hydroxy group-containing 1i, nor 1-octynylidicyclohexylphosphine reacted.
Table 2. Synthesis of (E)-1-Alkenylphosphine Oxides

<table>
<thead>
<tr>
<th>entry</th>
<th>R</th>
<th>time /h</th>
<th>yield /%b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph (1b)</td>
<td>6</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>i-Pr (1c)</td>
<td>8</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>t-Bu (1d)</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>2-MeO-C₆H₄ (1e)</td>
<td>21</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>4-MeO-C₆H₄ (1f)</td>
<td>7</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>4-Ac-C₆H₄ (1g)</td>
<td>5</td>
<td>62</td>
</tr>
<tr>
<td>7</td>
<td>2-pyridyl (1h)</td>
<td>12</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>PhCH(OH) (1i)</td>
<td>12</td>
<td>0</td>
</tr>
</tbody>
</table>

*Conditions: 1 (0.50 mmol), [RhCl(cod)]₂ (0.0075 mmol), 1,4-dioxane (3.0 mL), H₂O (0.30 mL). b Isolated yields.*

**Reaction Mechanism.** To reveal the mechanism of this reaction, the author carried out the following two experiments. First, D₂O was used instead of H₂O. As a result, the product deuterated at the two alkenylpositions was obtained as the sole product (eq 1). From a mechanistic point of view, it is worth noting that the reaction in 1,4-dioxane/D₂O was slow (vide infra). Next, a mixture of 1f and 1j was exposed to the reaction conditions. In this case, four 1-alkenylphosphine oxides were obtained in almost equal amounts (eq 2). This result suggests that cleavage of the Cₚ–P bonds of 1-alkynylphosphines would occur.

\[
\begin{align*}
R-\text{C}≡\text{C}-\text{PPh}_2 & \quad 1.5 \text{ mol% [RhCl(cod)]}_2 \\
1 & \quad 1,4\text{-dioxane / H}_2\text{O} = 10:1, \text{ reflux} \\
\text{R} & \quad \text{yield /%b} \\
\text{entry} & \quad \text{time /h} & \quad \text{yield /%b} \\
1 & \quad \text{Ph (1b)} & \quad 6 & \quad 72 \\
2 & \quad \text{i-Pr (1c)} & \quad 8 & \quad 69 \\
3 & \quad \text{t-Bu (1d)} & \quad 8 & \quad 0 \\
4 & \quad \text{2-MeO-C}_6\text{H}_4 (1e) & \quad 21 & \quad 72 \\
5 & \quad \text{4-MeO-C}_6\text{H}_4 (1f) & \quad 7 & \quad 75 \\
6 & \quad \text{4-Ac-C}_6\text{H}_4 (1g) & \quad 5 & \quad 62 \\
7 & \quad \text{2-pyridyl (1h)} & \quad 12 & \quad 0 \\
8 & \quad \text{PhCH(OH) (1i)} & \quad 12 & \quad 0 \\
\end{align*}
\]
Based on these results, the author assumes that the reaction mechanism is as follows (Scheme 1). This reaction seems to consist of two steps. In the first step, C–P bond cleavage proceeds. Oxidative addition of 1-alkynylyphosphine to a Rh(I) complex occurs to yield 4. The oxidative addition would be reversible because no reaction took place in the absence of water (vide supra). Protonation with H₂O followed by reductive elimination provides 1-alkyne 5 and diphenylphosphine oxide. In the second step, rhodium-catalyzed hydrophosphinylation of 1-alkyne with diphenylphosphine oxide proceeds to yield 1-alkenylphosphine oxide. Oxidative addition of diphenylphosphine oxide occurs to afford 7. Hydorhodation of alkyne 5 followed by reductive elimination provides the product 2. Such a rhodium-catalyzed hydrophosphinylation reaction has been reported.³ Actually, treatment of 1-octyne with diphenylphosphine oxide under the reaction conditions provided (E)-1-octenyldiphenylphosphine oxide in high yield (eq 3). This result supports the proposed mechanism. During the reaction, accumulation of neither diphenylphosphine oxide, 1-alkyne, nor rhodium hydride 7 was observed. Therefore, oxidative addition of diphenylphosphine oxide to a Rh(I) complex is not rate-determining step, since the use of D₂O retarded the reaction (eq 1).
\[
\begin{align*}
\text{n-C}_6\text{H}_{13}\text{C}≡\text{C-H} + \text{HPPH}_2 \xrightarrow{1.5 \text{ mol\% [RhCl(cod)]}_2} \text{n-C}_6\text{H}_{13}\text{H} \equiv \text{C-PPh}_2 \text{O}^\prime \quad (3)
\end{align*}
\]

**Scheme 1. Plausible Reaction Mechanism**

**First Step**

\[
\text{R-C≡C-PPh}_2 \quad 1 \xrightarrow{\text{[Rh]}} \text{R-C≡C-[Rh]-PPh}_2 \xrightarrow{\text{H}_2\text{O}} \text{HO-[Rh]-PPh}_2 \xrightarrow{\text{[Rh]}} \text{HO-PPh}_2 \xrightarrow{\text{[Rh]}} \text{HPPh}_2 \text{O}^\prime
\]

**Second Step**

\[
\text{[Rh]} \xrightarrow{\text{HPPh}_2 \text{O}^\prime} \text{H-[Rh]-PPh}_2 \xrightarrow{\text{5}} \text{R-C≡C-H} \xrightarrow{\text{[Rh]}} \text{H-[Rh]-PPh}_2 \xrightarrow{\text{5}} \text{R-C≡C-H} \xrightarrow{\text{[Rh]}} \text{R} \equiv \text{C-PPh}_2 \text{O}^\prime \quad 2
\]

**Conclusion**

The author has found a reaction for the synthesis of (E)-1-alkenylphosphine oxides from 1-alkynylphosphines. The reaction is an interesting formal hydration reaction that involves carbon–phosphorus bond cleavage with a rhodium complex. Transition-metal-mediated carbon–phosphorus bond cleavage has been an attractive topic in organometallic chemistry.\(^\text{4,5}\) The present reaction gives new information on the reactivity of 1-alkynylphosphine under rhodium catalysis.
Experimental Section

Instrumentation and Chemicals

$^1$H NMR (500 MHz) and $^{13}$C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl$_3$. Chemical shifts ($\delta$) are in parts per million relative to chloroform at 7.26 ppm for $^1$H and relative to CDCl$_3$ at 77.0 ppm for $^{13}$C. $^{31}$P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl$_3$ with 85% H$_3$PO$_4$ solution as an external standard. NMR yields were determined by fine $^{31}$P NMR spectra with (MeO)$_3$P=O as an internal standard. The first delay of $^{31}$P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were taken on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Materials obtained from commercial suppliers were used without further purification. For the preparation of 1, chlorodiphenylphosphine was purchased from TCI. Starting 1-alkynylphosphines 1 were prepared by the methods described in Chapter 1. Chloro(bis-1,5-cyclooctadiene)rhodium(I) dimer was purchased from Wako Pure Chemicals. All reactions were carried out under argon atmosphere.

Typical Procedure for Rhodium-Catalyzed Reaction to Yield (E)-1-Alkenylphosphine Oxides

Synthesis of 2a is representative. [RhCl(cod)$_2$ (3.7 mg, 0.0075 mmol) was placed in a 20-mL reaction flask under argon. 1,4-Dioxane (3.0 mL), H$_2$O (0.30 mL), and 1-octynyl diphenylphosphine (1a, 0.15 g, 0.50 mmol) were sequentially added. The resulting solution was stirred for 3 h at reflux. After the mixture was cooled to room temperature, water (10 mL) was added, and the product was extracted with dichloromethane (10 mL x 3). The
combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded 2a (0.11 g, 0.37 mmol, 73%) as a white solid.

**Characterization Data**

Phosphines 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, and 1i and phosphine oxides 2a, 2b, 2c, and 2f showed the same spectroscopic data as those described in the literature.

**Bis(4-methylphenyl)-1-octynylphosphine (1j)**

IR (neat) 3015, 2928, 2853, 2178, 1905, 1598, 1456, 1395, 1184, 1094, 1019, 803, 624 cm⁻¹; ¹H NMR (CDCl₃) δ 0.91 (t, J = 7.0 Hz, 3H), 1.27–1.37 (m, 4H), 1.46 (dd, J = 7.5, 7.5 Hz, 2H), 1.61 (dd, J = 7.5, 7.5 Hz, 2H), 2.33 (s, 6H), 2.43 (dt, J = 1.5, 7.5 Hz, 2H), 7.13–7.17 (m, 4H), 7.47–7.53 (m, 4H); ¹³C NMR (CDCl₃) δ 14.30, 20.64, 21.53, 22.81, 28.53, 28.55, 31.29, 76.23 (d, J = 1.6 Hz), 109.94 (d, J = 3.9 Hz), 129.24 (d, J = 7.6 Hz), 132.36 (d, J = 21.0 Hz), 133.84 (d, J = 4.9 Hz), 138.68; ³¹P NMR (CDCl₃) δ –36.38. Found: C, 82.18; H, 8.62%. Calcd for C₂₂H₂₇P: C, 81.95; H, 8.44%.

**(E)-1-Diphenyl phosphinyl-2-(2-methoxyphenyl)ethene (2e)**

IR (nujol) 2923, 2853, 1598, 1484, 1461, 1247, 1181, 1004, 821, 744, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 3.82 (s, 3H), 6.90 (d, J = 8.5 Hz, 1H), 6.94 (dd, J = 18.0, 24.0 Hz, 1H), 6.95 (dd, J = 8.5, 8.5 Hz, 1H), 7.33 (dd, J = 8.5, 8.5 Hz, 1H), 7.44–7.55 (m, 7H), 7.73–7.83 (m, 5H); ¹³C NMR (CDCl₃) δ 55.41, 111.16, 119.69 (d, J = 104.1 Hz), 120.57, 124.12 (d, J = 17.1 Hz), 128.49 (d, J = 11.9 Hz), 128.76 (d, J = 1.0 Hz), 131.20, 131.43 (d, J = 10.0 Hz), 131.65 (d, J = 2.4 Hz), 133.35 (d, J = 104.5 Hz), 143.00 (d, J = 4.9 Hz), 158.08; ³¹P NMR (CDCl₃) δ 23.09. Found: C, 75.11; H, 5.62%. Calcd for C₂₁H₁₀O₂P: C, 75.44; H, 5.73%. m.p.: 150.5–152.0 °C.
4-[(E)-2-(Diphenylphosphinyl)ethenyl]acetophenone (2g)

IR (nujol) 2924, 2853, 1438, 1359, 1270, 1182, 1107, 1000, 728, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 2.59 (s, 3H), 6.97 (dd, J = 17.5, 22.0 Hz, 1H), 7.44–7.57 (m, 7H), 7.60 (d, J = 8.0 Hz, 2H), 7.70–7.79 (m, 4H), 7.95 (d, J = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 26.63, 122.45 (d, J = 101.8 Hz), 127.83, 128.66 (d, J = 11.9 Hz), 128.79, 131.29 (d, J = 10.0 Hz), 132.47 (d, J = 2.5 Hz), 132.47 (d, J = 105.9 Hz), 137.80, 139.24 (d, J = 17.6 Hz), 145.93 (d, J = 3.4 Hz), 197.26; ³¹P NMR (CDCl₃) δ 22.00. Found: C, 76.23; H, 5.54%. Calcd for C₂₂H₁₉O₂P: C, 76.29; H, 5.53%. m.p.: 176.0–177.5 °C.

(E)-1-Bis(4-methylphenyl)phosphinyl-1-octene (2j)

IR (neat) 2927, 2856, 1453, 1400, 1182, 1118, 1101, 807, 656 cm⁻¹; ¹H NMR (CDCl₃) δ 0.85 (t, J = 7.0 Hz, 3H), 1.21–1.34 (m, 6H), 1.45 (tt, J = 7.0, 7.5 Hz, 2H), 2.26 (dt, J = 6.5, 7.5 Hz, 2H), 2.36 (s, 6H), 6.17 (dd, J = 17.0, 24.0 Hz, 1H), 6.66 (ddt, J = 17.0, 19.5, 6.5 Hz, 1H), 7.21–7.26 (m, 4H), 7.51–7.59 (m, 4H); ¹³C NMR (CDCl₃) δ 13.95, 21.48 (d, J = 1.0 Hz), 22.46, 27.80 (d, J = 1.0 Hz), 28.73, 31.47, 34.40 (d, J = 16.8 Hz), 122.00 (d, J = 102.6 Hz), 129.11 (d, J = 12.5 Hz), 130.05 (d, J = 106.4 Hz), 131.24 (d, J = 10.5 Hz), 141.92 (d, J = 2.9 Hz), 152.24 (d, J = 1.4 Hz); ³¹P NMR (CDCl₃) δ 22.02. HRMS (EI⁺) (m/z) Observed: 340.1954 (Δ = −0.7 ppm). Calcd for C₂₂H₂₉OP [M⁺]: 340.1956.

(E)-2-Bis(4-methylphenyl)phosphinyl-1-(4-methoxyphenyl)ethene (2k)

IR (nujol) 2924, 2855, 1602, 1511, 1464, 1438, 1378, 1307, 1257, 1176, 1100, 1020, 823, 756 cm⁻¹; ¹H NMR (CDCl₃) δ 2.39 (s, 6H), 2.82 (s, 3H), 6.64 (dd, J = 17.5, 22.0 Hz, 1H), 6.88 (d, J = 8.5 Hz, 2H), 7.23–7.31 (m, 4H), 7.39 (dd, J = 17.5, 19.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 2H), 7.59–7.67 (m, 4H); ¹³C NMR (CDCl₃) δ 21.53 (d, J = 1.0 Hz), 55.31, 114.13, 116.78 (d, J
= 105.9 Hz), 128.06 (d, J = 18.1 Hz), 129.21 (d, J = 12.4 Hz), 129.14, 130.10 (d, J = 107.4 Hz), 131.36 (d, J = 10.5 Hz), 142.06 (d, J = 2.4 Hz), 146.51 (d, J = 3.8 Hz), 161.01; ³¹P NMR (CDCl₃) δ 23.19. HRMS (EI⁺) (m/z) Observed: 362.1433 (Δ = -0.8 ppm). Calcd for C₂₃H₂₃O₂P[M⁺]: 362.1436. m.p.: 148.0–149.5 °C.

(E)-1,2-Dideuterio-1-diphenylphosphinyl-1-octene (2a–D)

\[
\text{IR (nujol) 2923, 2854, 1593, 1546, 1438, 1180, 1120, 722, 665 cm}^{-1}; \quad \text{¹H NMR} \\
\text{(CDCl₃) δ 0.86 (t, J = 7.0 Hz, 3H), 1.20–1.36 (m, 6H), 1.46 (tt, J = 7.5, 7.5 Hz, 2H), 2.27 (dt, J = 2.0, 7.5 Hz, 2H), 7.40–7.53 (m, 6H), 7.64–7.71 (m, 4H);} \\
\text{¹³C NMR} \\
\text{(CDCl₃) δ 13.96, 22.48, 27.76, 28.74, 31.48, 34.27 (d, J = 16.3 Hz), 121.09 (dt, J = 101.3, 24.8 Hz), 128.42 (d, J = 12.0 Hz), 131.23 (d, J = 10.0 Hz), 131.58 (d, J = 2.9 Hz), 133.22 (d, J = 104.5 Hz), 152.46 (t, J = 23.4 Hz);} \\
\text{³¹P NMR (CDCl₃) δ 21.78.} \quad \text{²H NMR (CDCl₃) δ 6.20, 6.73. HRMS (EI⁺) (m/z) Observed: 314.1767 (Δ = -0.4 ppm). Calcd for C₂₀H₂₂D₂OP [M⁺]: 314.1769. m.p.: 58.0–60.0 °C.}
References and Notes


(2) The tert-butyl group would retard the oxidative addition (Scheme 1). Treatment of tert-butylacetylene with diphenylphosphine oxide under conditions similar to those in eq 3 led to smooth hydrophosphinylation.


(7) See Chapter 1.


Publication List

I. Parts of the present thesis have been published in the following journals.

General Introduction

1-Alkynylphosphines and Their Derivatives as Key Starting Materials in Creating New Phosphines
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima
Chem. Asian J. in press

Chapter 1 Copper-Catalyzed \textit{anti}-Hydrophosphination Reaction of 1-Alkynylphosphines with Diphenylphosphine Providing (Z)-1,2-Diphosphino-1-alkenes
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Chapter 2 Palladium-Catalyzed \textit{anti}-Hydrothiolation of 1-Alkynylphosphines
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Chapter 3 Regio- and Stereoselective Hydroamidation of 1-Alkynylphosphine Sulfides Catalyzed by Cesium Base
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

Chapter 4 Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima
Chapter 5  New Synthesis of 2-Indolylphosphines by Palladium-Catalyzed Annulation of 1-Alkynylphosphine Sulfides with 2-Iodoanilines
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima
To be submitted.

Chapter 6  Rhodium-Catalyzed Reaction of 1-Alkynylphosphines with Water Yielding (E)-1-Alkenylphosphine Oxides
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

II. Other Publications not included in this thesis.

(1) Stereoselective Hydrothiolation of Alkynes Catalyzed by Cesium Base: Facile Access to (Z)-1-Alkenyl Sulfides
Azusa Kondoh, Kazuaki Takami, Hideki Yorimitsu, and Koichiro Oshima

(2) Nucleophilic Aromatic Substitution Reaction of Nitroarenes with Alkyl- or Arylthio Groups in Dimethyl Sulfoxide by Means of Cesium Carbonate
Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

(3) A New Approach to 4-Aryl-1,3-butanediols by Cobalt-Catalyzed Sequential Radical Cyclization-Arylation Reaction of Silicon-Tethered 6-Iodo-1-hexene Derivatives
Hidenori Someya, Azusa Kondoh, Akinori Sato, Hirohisa Ohmiya, Hideki Yorimitsu, and Koichiro Oshima

(4) Carbocupration of 1-Alkynylphosphines Followed by Trapping with Electrophiles
Shigenari Kanemura, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

(5) Intermolecular Radical Addition of Alkylthio- and Arylthiodiphenylphosphines to Terminal Alkynes
Tatsuya Wada, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima
(6) Regio- and Stereoselective Additions of Diphenyldithiophosphinic Acid to N-(1-Alkynyl)amides and 1-Alkynyl Sulfides
Shigenari Kanemura, Azusa Kondoh, Hiroto Yasui, Hideki Yorimitsu, and Koichiro Oshima

(7) Synthesis of Bulky Arylphosphanes by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reaction and Their Use as Ligands
Takayuki Kobatake, Azusa Kondoh, Suguru Yoshida, Hideki Yorimitsu, and Koichiro Oshima

(8) Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Aryl Sulfides and Alkenyl Alkyl Sulfides with Alkyl Grignard Reagents Using (Z)-3,3-Dimethyl-1,2-bis(diphenylphosphino)-but-1-ene as Ligand
Shigenari Kanemura, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

(9) Radical Addition of Polyhaloalkanes to 2-Ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
Tatsuya Wada, Yuto Sumida, Azusa Kondoh, Hideki Yorimitsu, and Koichiro Oshima

(10) Rhodium-Catalyzed Dehydrogenative Borylation of Cyclic Alkenes
Azusa Kondoh and Timothy F. Jamison
*Chem. Commun.* in press
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Azusa Kondoh