Studies on Selective Synthesis of Functionalized Phosphines Based on the Characteristic Features of Phosphorus in Radical Reactions

Studies on Selective Synthesis of Functionalized Phosphines Based on the Characteristic Features of Phosphorus in Radical Reactions

Yuki Sato

January 2019

Doctoral Thesis at Osaka Prefecture University

Preface

This thesis deals with the studies conducted during April 2016 to March 2019 under the guidance of Professor Akiya Ogawa at the Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University.

This thesis is concerned with the selective synthesis of functionalized phosphines based on the characteristic features of phosphorus in radical reactions. Two important topics of this thesis are 1) the development of the phosphorus valence-selective synthetic methods of organophosphorus compounds; 2) the regioselective addition reactions of phosphorus compounds to carbon–carbon unsaturated bonds based on the difference of reactivity between pentavalent and trivalent phosphorus radicals.

Department of Applied Chemistry

Graduate School of Engineering

Osaka Prefecture University

January 2019 ***Yuki Sato***

List of Abbreviations

Functional Groups

Me	methyl	Et	ethyl
^{n}Pr	normal propyl	^{i}Pr	*iso*-propyl
^{n}Bu	normal butyl	^{t}Bu	*tert*-butyl (tertiary butyl)
^{n}Hex	normal hexyl	^{n}Dec	normal decyl
Cy	cyclohexyl	Ph	phenyl
Ar	aryl	Ac	acetyl
Tf	trifluoromethanesulfonyl	TMS	trimethylsilyl
R_f	perfluoroalkyl group		

Organic Compounds

TMDPO	(2,4,6-trimethylbenzoyl)phosphine oxide	AIBN	2,2'-azobis(isobutyronitrile)
V-40	1,1'-azobis(cyclohexane-1-carbonitrile)	V-70	2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)
Tf_2O	trifluoromethanesulfonic anhydride	BTF	benzotrifluoride
THF	tetrahydrofuran	FC-72	perfluorocarbon, $^{n}C_6F_{14}$
dppe	1,2-bis(diphenylphosphino)ethane	BPMS	bis(phosphine) monosulfide
BPSO	bis(phosphine) monosulfide monoxide		

Technical Terms

N.D.	not detected	N.R.	no reaction
rt	room temperature	NMR	nuclear magnetic resonance
DFT	density functional theory	SOMO	singly occupied molecular orbital
HOMO	highest occupied molecular orbital	LUMO	lowest unoccupied molecular orbital
HRMS	high resolution mass spectrometry	FAB	fast atom bombardment method
EI	electron ionization method	ESI	electrospray ionization method
IR	infrared spectroscopy	ORTEP	Oak Ridge thermal-ellipsoid plot program
PTLC	preparative tin layer chromatography	HPLC	high performance liquid chromatography
GPC	gel permeation chromatography	GC-MS	gas chromatography - mass spectrometry

Contents

Chapter 1

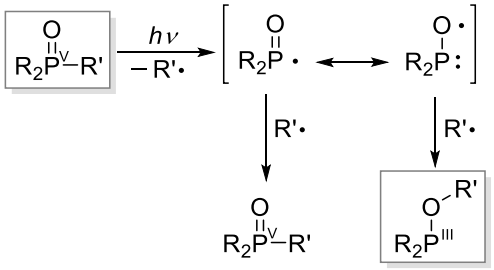
General Introduction

Organophosphorus compounds are widely used as functional materials that include physiologically active substances, pharmaceuticals, heat-resistant materials, and transition-metal catalysts.[1] Therefore, development of convenient and highly selective synthetic methods for these organophosphorus compounds is of great importance. For their synthesis, many methods based on ionic reactions[1] and transition-metal-catalyzed reactions[2] have been developed. Considering the sustainabe use of phosphorus resources and green chemistry,[3] development of eco-friendly synthetic methods are strongly desired. Radical reactions are ones of the powerful and eco-friendly tool because of its high tolerance for many functional groups. In addition, radical reactions can often proceed without any acids or bases in a variety of solvents.

In this thesis, the author focused on the difference of reactivity between pentavalent and trivalent phosphorus compounds under several radical conditions and developed several atom-economical addition reactions based on the homolytic cleavage of the phosphorus–phosphorus single bond. In addition, a synthesis method of fluorous phosphines which are useful for recycling of phosphorus resources by introducing fluorous groups is also developed. In contrast to trivalent phosphorus radical, which has a lone pair and behaves as a nucleophile, pentavalent phosphorus radical does not have a lone pair on phosphorus and shows relatively electrophilic reactivity because it charges positively. Among pentavalent phosphorus radicals, secondary phosphinyl radical ($R_2P(O)\cdot$) has an interesting electron structure which has a delocalized unpaired electron on its phosphorus and oxygen atom despite its pyramidal structure.[1] This delocalized electron structure enables the bond formation on its phosphorus and oxygen

atom. For example, $R_2P(O)\cdot$, generated from $R_2P(O)–R'$, can be recombined with the other radical ($R'\cdot$) on its phosphorus and oxygen atom to form $R_2P^{V}(O)–R'$ and $R_2P^{III}–O–R'$, respectively. In particular, the latter transformation is a powerful tool for converting an air-stable pentavalent phosphorus radical source to trivalent phosphorus compounds which are useful for ligands of transition-metal-catalyzed reactions.

Scheme 1-1. Reductive rearrangement from pentavalent phosphorus radical sources ($R_2P^{V}(O)–R'$) to trivalent phosphorus compounds ($R_2P^{III}–O–R'$) under light

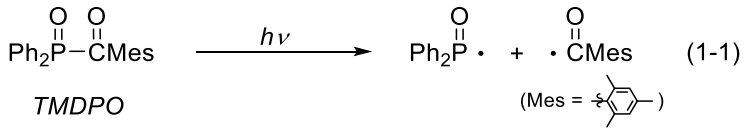


Therefore, the author investigated the characteristic features of pentavalent phosphorus radicals in detail, and several phosphorus valence-selective synthetic methods of organophosphorus compounds are developed. Furthermore, several regio-selective addition reactions of phosphorus compounds to carbon-carbon unsaturated bonds are also developed based on the difference of reactivity between pentavalent and trivalent phosphorus radicals. This thesis is consisted of seven chapters and the outlines of each chapter are described as follows.

Chapter 1 describes the background, the purpose, and the contents of this thesis.

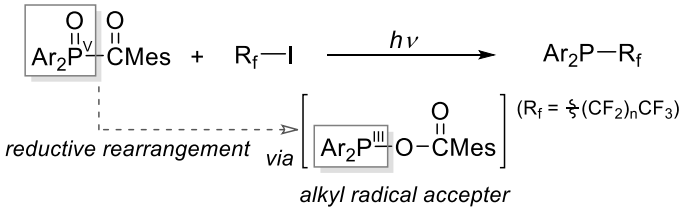
Chapters 2 and 3 describe the synthetic methods of functionalized phosphines using (2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO, Eq. 1-1)[4] which is typically used as a photoinitiator for radical polymerization.[5] TMDPO is a shelf-stable pentavalent phosphorus compound which releases a diphenylphosphinyl radical along with 2,4,6-trimethylbenzoyl radical by homolytic cleavage of its phosphorus–carbon single bond under light.[6,7] In addition, TMDPO

has a relatively long absorption maximum with high quantum yield of radical formation (λ_{max} = 380 nm, ϕ 0.5–0.7). Therefore, TMDPO is an attractive phosphorus source; however, there are only limited examples of the synthetic reaction of organophosphorus compounds using TMDPO.[8]



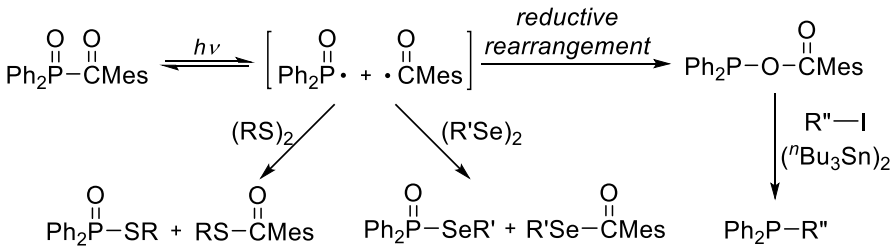
Chapter 2 describes the reductive perfluoroalkylation reaction of TMDPO (Scheme 1-2).[9] *P*-Perfluoroalkylated phosphines,[10] in which the perfluoroalkyl group is directly bonded to the trivalent phosphorus atom, can be used as a ligand for transition-metal-catalyzed reactions[10a,10b] and they have sufficient fluorous affinity for recovering the catalysts using a fluorous biphasic system.[4,] Although *P*-perfluoroalkylated phosphines are synthetically attractive, hitherto known synthetic methods of *P*-perfluoroalkylated phosphines are limited to a few methods, which require strict reaction conditions[6] and/or use of air- and moisture-sensitive trivalent phosphine species.[5, 6a,f,g,i] In contrast, the author found that the reaction between TMDPO and perfluoroalkyl iodides under light successfully afforded *P*-perfluoroalkylated phosphines in good yields. In this reaction, the reductive rearrangement of TMDPO to a trivalent phosphorus intermediate[7f,7b] enabled the electrophilic attack of perfluoroalkyl radical, generated from perfluoroalkyl iodide under light, to its trivalent phosphorus center, resulting to generate *P*-perfluoroalkylated phosphines.

Scheme 1-2. Chapter 2



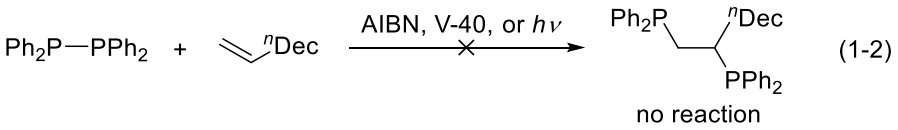
Chapter 3 describes the photoinduced coupling reaction between TMDPO and interelement compounds (Scheme 1-3).[11] Interelement compounds, having a heteroatom–heteroatom single bond, releases the corresponding heteroatom radicals via the homolytic cleavage of the heteroatom–heteroatom single bond. In order to clarify the reactivity of pentavalent phosphorus radicals to a variety of heteroatom–heteroatom single bonds, the author investigated the photoreaction between TMDPO and a variety of interelement compounds. Diphenylphosphinyl radical, generated from TMDPO under light, was efficiently captured by a variety of disulfides and diselenides to afford the corresponding thiophosphinate and selenophosphinate, respectively, in good yields. In contrast, ditelluride, disilane, distannane, digermane, and diboron did not react with the phosphinyl radical at all. The low reactivity of the phosphinyl radical to distannane enabled the reductive formation of trivalent alkylphosphine by generation of alkyl radical from alkyl iodide and distannane.

Scheme 1-3. Chapter 3

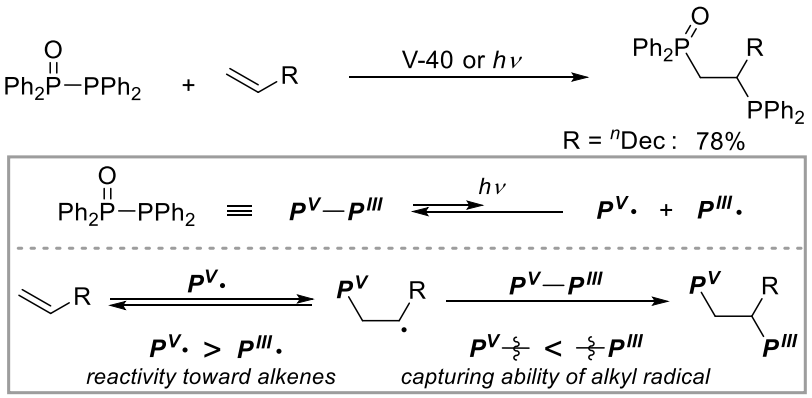


Chapters 4–6 describe the addition reaction of diphosphines and their analogues, bearing a phosphorus–phosphorus single bond, to alkenes. Radical addition reactions of diphosphines to carbon–carbon unsaturated bonds are ones of the most useful and atom-economical methods for the synthesis of *vic*-bisphosphinated ligands,[12] such as dppe (*vic*-bis(diphenylphosphino)ethane). Although several excellent reactions have been reported for the 1,2-additions of diphosphine compounds bearing phosphorus–phosphorus single bonds to alkynes,[13] there are very limited examples of the corresponding additions to alkenes, which highlights poor substrate versatility.[14]

Chapter 4 describes the 1,2-addition reaction of tetraphenyldiphosphine monoxide ($Ph_2P(O)–PPh_2$) to alkenes.[15] Tetraphenyldiphosphine ($Ph_2P–PPh_2$) does not add to alkenes efficiently under light or in the presence of radical initiator (Eq. 1-2). In contrast, its monoxide ($Ph_2P(O)–PPh_2$) can engage in a radical addition to various alkenes, affording the corresponding 1-phosphinyl-2-phosphinoalkanes in good yields with high regioselectivities (Scheme 1-4). In this reaction, the photoinduced homolytic cleavage of the $\boldsymbol{P^V–P^{III}}$ bond of the diphosphine monoxide generates two radicals, namely $\boldsymbol{P^V\bullet}$ and $\boldsymbol{P^{III}\bullet}$. The more electrophilic phosphorus radical ($\boldsymbol{P^V\bullet}$) adds to the alkene and the generated carbon radical is captured by the more electron-rich phosphorus group ($\boldsymbol{P^{III}}$) of the diphosphine monoxide, resulting to the regioselective formation of the 1,2-adduct.



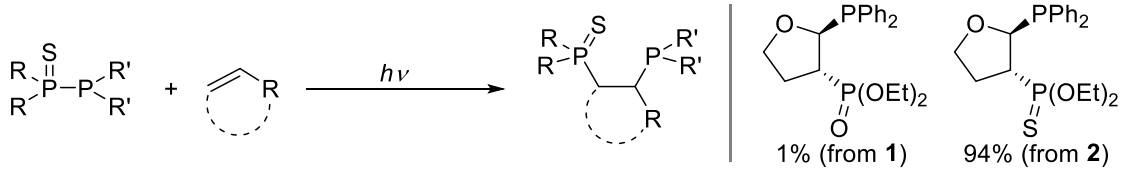
Scheme 1-4. Chapter 4



Chapter 5 describes the 1,2-addition reaction of diphosphine monosulfides ($R_2P(S)–PR'_2$) to alkenes and its promotion by sulfur atom of the thiophosphinyl group (Scheme 1-5).[16] The 1,2-addition of tetraphenyldiphosphine monoxide to alkenes[15] strongly indicated that diphosphine analogues, bearing a $P^V–P^{III}$ single bond, are not only effective for 1,2-addition reaction to alkenes but also potentially promising compounds for the selective introduction of two

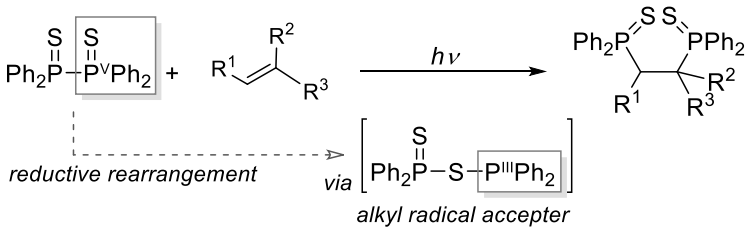
different phosphorus groups. However, some diphosphine monoxides, for example, *O,O*-diethyl(diphenylphosphino)phosphate ($(EtO)_2P(O)–PPh_2$, **1**), do not add to alkenes. In order to develop a highly reactive diphosphine analogue, comparative research of the 1,2-addition of several diphosphine monochalcogenides to an alkene was carried out, and it was found that diphosphine monosulfide indicated the remarkably higher reactivity in the addition to an alkene. Further detail investigation revealed that the sulfur atom of the thiophosphinyl group of diphosphine monosulfide largely enhanced both its absorption of light and capturing ability toward alkyl radicals. This reaction requires only equimolar amount of the diphosphine monosulfide relative to alkenes and facilitates the highly selective introductions of two different types of phosphorus groups: for an instance, $(EtO)_2P(S)–PPh_2$ (**2**) efficiently added to 2,3-dihydrofuran, regioselectively.

Scheme 1-5. Chapter 5



Chapter 6 describes the bisthiophosphinylation reaction of alkenes which is triggered by the reductive rearrangement of tetraphenyldiphosphine disulfide ($Ph_2P(S)–P(S)Ph_2$) (Scheme 1-6). Diphosphine disulfides, bearing a P(V)–P(V) single bond, are shelf-stable and can release two thiophosphinyl radicals under light via the homolytic cleavage of the P(V)–P(V) bond. Therefore, they are attractive phosphorus radical sources for *vic*-bisthiophosphinylation but examples of their addition reactions to alkenes are very limited. In this chapter, the author found that tetraphenyldiphosphine disulfide transformed to $Ph_2P(S)–SPPh_2$ under light. Furthermore, this reductive rearrangement triggered the 1,2-addition reaction of tetraphenyldiphosphine disulfide to alkenes.

Scheme 1-6. Chapter 6



Chapter 7 describes the conclusion of this thesis.

References

1. Quin, L. D., *A Guide to Organophosphorus Chemistry*. John Wiley & Sons: New York, 2000.

2. Xu, Q.; Han, L.-B. *J. Organomet. Chem.* **2011**, *696*, 130-140.

3. Withers, P. J. A.; Elser, J. J.; Hilton, J.; Ohtake, H.; Schipper, W. J.; van Dijk, K. C. *Green Chem.* **2015**, *17*, 2087-2099.

4. (a) Lechtken, P.; Buethe, I.; Hesse, A. US4324744, 1982. (b) Lechtken, P.; Buethe, I.; Jacobi, M.; Trimborn, W. US4710523, 1987.

5. (a) Decker, C.; Bendaikha, T. *J. Appl. Polym. Sci.* **1998**, *70*, 2269-2282. (b) Decker, C.; Zahouily, K.; Decker, D.; Nguyen, T.; Viet, T. *Polymer* **2001**, *42*, 7551-7560.

6. (a) Sumiyoshi, T.; Katayama, M.; Schnabel, W. *Chem. Lett.* **1985**, *14*, 1647-1650. (b) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141-146.

7. (a) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148-5153. (b) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477-6489. (c) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367-7372. (d) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495-11501. (e) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773-11777. (f) Colley, C. S.; Grills, D. C.; Besley, N. A.; Jockusch, S.; Matousek, P.; Parker, A. W.; Towrie, M.; Turro, N. J.; Gill, P. M. W.; George, M. W. *J. Am. Chem. Soc.* **2002**, *124*, 14952-14958.

8. (a) Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 1456-1463. (b) Frey, G.; Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 763-772. (c) Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 793-798. (d) Lindner, E.; Kern, H. *Chem. Ber.* **1984**, *117*, 355-365. (e) Cho, C. H.; Kim, S.; Yamane, M.; Miyauchi, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1665-1672. (f) Said, N.; Touil, S.; Akacha, A. B.; Efrit, M. L. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 2726-2733.

9. Sato, Y.; Kawaguchi, S-i.; Ogawa, A. *Chem. Commun.* **2015**, *51*, 10385-10388.

10. (a) Kawaguchi, S-i.; Minamida, Y.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 1748-1752. (b) Kawaguchi, S-i.; Minamida, Y.; Okuda, T.; Sato, Y.; Saeki, T.; Yoshimura, A.; Nomoto, A.; Ogawa, A. *Adv. Synth. Catal.* **2015**, *357*, 2509-2519. (c) Kawaguchi, S-i.; Saga, Y.; Sato, Y.; Minamida, Y.; Nomoto, A.; Ogawa, A. *Inorganics* **2017**, *5*, 5.

11. Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Synthesis* **2017**, *49*, 3558-3567.

12. Yorimitsu, H. *Beilstein J. Org. Chem.* **2013**, *9*, 1269-1277.

13. (a) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254-258. (b) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694-1696. (c) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937-5945. (d) Kawaguchi, S-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919-3922.

14. (a) Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226-2231. (b) Morse, K. W.; Morse, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 8469-8470. (c) Morse, J. G.; Morse, K. W. *Inorg. Chem.* **1975**, *14*, 565-569. (d) Drieß, M.; Haiber, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 215-219. (e) Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4801-4804. (f) Hajdók, I.; Lissner, F.; Nieger, M.; Strobel, S.; Gudat, D. *Organometallics* **2009**, *28*, 1644-1651.

15. Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 9700-9703.

    Sato, Y.; Kawaguchi, S.-i.; Nomoto, A.; Ogawa, A. *Chem. Eur. J.* **2019**, *25*, 2295-2302.

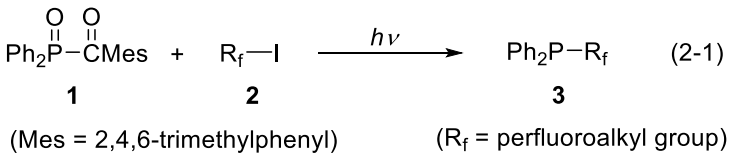
Chapter 2

Photoinduced Reductive Perfluoroalkylation of Phosphine Oxides: Synthesis of *P*-Perfluoroalkylated Phosphines Using TMDPO and Perfluoroalkyl Iodides

2-1 Introduction

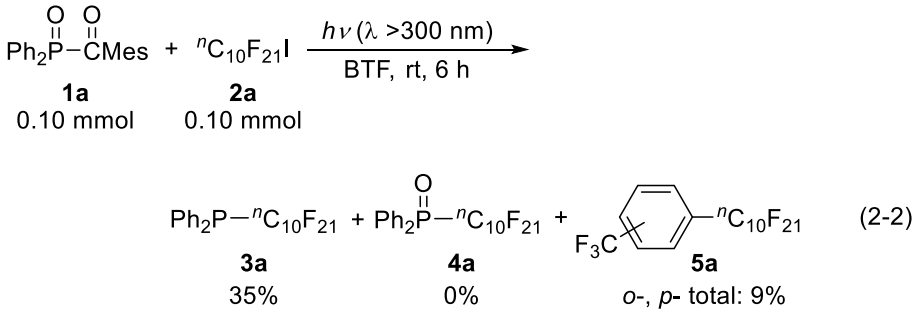
Organophosphine compounds[1] are widely used as ligands for metal catalysts and as reagents in Wittig[2] and Mitsunobu reactions.[3] However, the synthesis of organophosphines is often difficult owing to their oxophilicity. As such, phosphines are usually converted to air- and moisture-stable phosphine derivatives such as phosphine sulfides, phosphine oxides, and phosphine-borane complexes prior to modification and isolation. Alternatively, the introduction of fluorous tags onto phosphines is another way to handle phosphines without oxidation. Phosphines with fluorous moieties exhibit fluorous affinity and can be manipulated using fluorous/organic biphasic systems (FBS) without any prior organic transformations.[4] *P*-Perfluoroalkylated phosphines such as $Ph_2P^nC_{10}F_{21}$, in which a perfluoroalkyl group is directly linked to the phosphorus atom, have sufficient fluorous affinity for manipulation via FBS. *P*-Perfluoroalkylated phosphines can form a complex with palladium(II) in spite of its electron deficiency, and the formed Pd(II) complex catalyzes common coupling reactions such as Suzuki-Miyaura coupling, Sonogashira coupling, and the Heck reaction.[5] Therefore, *P*-perfluoroalkylated phosphines are attractive phosphines; however, synthetic routes toward *P*-perfluoroalkylated phosphines are limited to methods, which require strict reaction conditions,[6] such as Birch reduction conditions,[1] or trivalent phosphine species, which are unstable in the

presence of moisture and oxygen.[5, 6a,f,g,i] Therefore, synthetic methods which utilize shelf-stable phosphorus sources under mild conditions are strongly desired. During exploration of air- and moisture-stable phosphorus sources, the author focused on diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO).[7] TMDPO is commercially available and is a shelf-stable solid; it is typically used as a photoinitiator for radical polymerization,[8] as it releases phosphinoyl radicals. The author expected that perfluoroalkylation using this phosphorus-centered radical and photoinduced reaction between TMDPO and perfluoroalkyl iodide was conducted. As a result, a trivalent phosphorus compound, *P*-perfluoroalkylphosphine, was obtained in spite of the use of a pentavalent phosphorus source, i.e., TMDPO (Eq. 2-1). Such transformations accompanied with the reduction of pentavalent phosphorus compounds to trivalent phosphorus compounds are rare, with the exception of simple reductions.[9] Moreover, there are only a few examples of reactions which utilize TMDPO as a phosphorus source.[10] Therefore, it was set out to investigate the reductive perfluoroalkylation of TMDPO in detail.



2-2 Results and Discussion

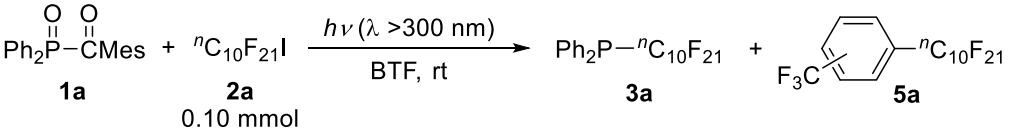
When a mixture of TMDPO (**1a**, 0.30 mmol) and $^{n}C_{10}F_{21}I$ (**2a**, 0.30 mmol) was irradiated in BTF (benzotrifluoride, 0.60 mL) with a xenon lamp (500 W) through a sealed Pyrex NMR tube for 6 h at room temperature, perfluoroalkylated phosphine oxide **4a** was not obtained at all (Eq. 2-2).[11] Surprisingly, however, *P*-(perfluorodecyl)diphenylphosphine **3a** was obtained in a moderate yield. Perfluoroalkylated arenes (**5a**) from BTF were also obtained, albeit only in a small quantity.



(2-2)

In an attempt to improve the yield of **3a**, several reaction conditions were examined (Table 2-1). Specifically, the reaction time and ratio of **1a**:**2a** were evaluated. When excessive amounts of **1a** were used, **2a** was consumed completely in 1.5 h to afford the desired **3a** in good yields (entries 4, 5). Irradiation with a tungsten lamp (450 W) also afforded **3a** in a good yield, although a prolonged reaction time was required (entry 6). Notably, BTF was used as the solvent in all cases, because the starting materials, TMDPO and $^{n}C_{10}F_{21}I$, were not sufficiently soluble in solvents such as $CHCl_3$, C_6H_6, and 1,1,1,3,3-pentafluorobutane. The reaction mixtures were extracted with an FBS (FC-72 (perfluorohexane, $^{n}C_6F_{14}$)/MeOH) to afford the pure product, **3a**.

Table 2-1. Optimization of reaction conditions[a]

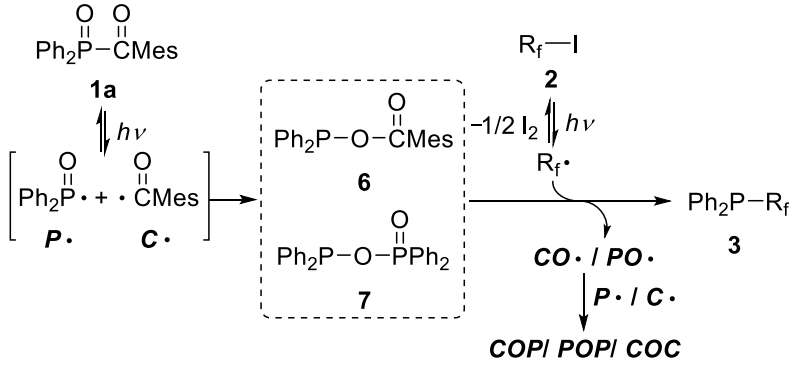


entry	**1a** : **2a**[b]	time	yield [%][c]		conversion of **2a** [%][c]
			3a	**5a**	
1[b]	1 :1	6 h	35	9	64
2[c]	1 : 1	1.5 h	34	8	65
3	3 : 1	1.5 h	67	7	96
4	4 : 1	1.5 h	77	7	100
5	5 : 1	1.5 h	78	6	100
6	4 : 1	24 h	81	2	99

[a] Reaction conditions: $^{n}C_{10}F_{21}I$ (**2a**, 0.1 mmol), BTF (0.6 mL), xenon lamp (500 W), room temperature.
[b] Molar ratios. [c] Determined by ^{19}F NMR. [d] Irradiation with tungsten lamp (450 W). BTF = benzotrifluoride.

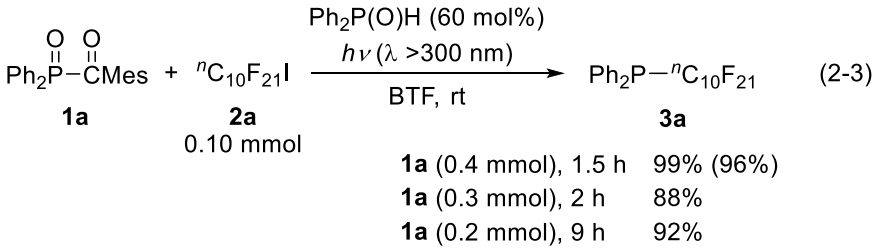
A plausible pathway of the reductive perfluoroalkylation of TMDPO is shown in Scheme 2-1, on the basis of related studies.[2] Near-UV light irradiation induces the homolytic P–C bond cleavage of **1a**, resulting in the formation of diphenylphosphinoyl radical (***P*·**) and 2,4,6-trimethylbenzoyl radical (***C*·**). These radicals recombine to give intermediate **6** and **7**. The formation of **6** from TMDPO under photoirradiation was supported by a diode laser-based, time-resolved IR study by George et al.[2d] and ^{31}P-NMR-CIDNP (chemically induced dynamic nuclear polarization) spectroscopy described by Wirtz et al.[2e] Subsequently, intermediate **6** reacts with a perfluoroalkyl radical (R_f·), which is generated from R_f–I upon near-UV irradiation,[3] to give **3** with concomitant release of MesC(O)O· (***CO*·**). The generation of **7** from TMDPO is also supported by ^{31}P-NMR-CIDNP[2e] and **7** reacts with R_f· to give **3** with concomitant release of $Ph_2P(O)O$· (***PO*·**). Furthermore, the formation of $MesC(O)OP(O)Ph_2$ (***COP***)[15] and $Ph_2P(O)OP(O)Ph_2$ (***POP***)[15] generated by the coupling of ***CO*·** and ***PO*·** with ***P*·**, respectively, was observed, which strongly supports the proposed mechanism.

Scheme 2-1. A plausible reaction pathway for the photoinduced reaction of **1a** with **2**. ***COP*** = $MesC(O)OP(O)Ph_2$, ***POP*** = $Ph_2P(O)OP(O)Ph_2$, ***COC*** = $MesC(O)OC(O)Mes$



To enhance the synthetic utility of the reaction, additives were investigated. On the basis of the proposed reaction pathway, the efficient formation of intermediate **6** or **7** would improve the yield of **3a**. The intermediate **6** cannot be influenced by any additive because it is generated

mainly in a cage[12d, e] and $Ph_2P(O)H$ cannot penetrate the cage; however, the generation of **7** can be increased by the addition of $Ph_2P(O)H$, which has a diphenylphosphinoyl unit. When $Ph_2P(O)H$ (**8a**, 60 mol%, 0.06 mmol) was added to the reaction system, the yield of **3a** was improved as expected, and the generation of **5a**, which cannot be separated using FBS, was completely suppressed (Eq. 2-3).[14] Furthermore, upon addition of $Ph_2P(O)H$, the amount of **1a** could be reduced to 2 equivalent amounts, although a prolonged reaction time was required. Notably, when $Ph_2P(O)H$ was added, the amount of $Ph_2P(O)OP(O)Ph_2$, generated through the reaction of **7** with R_f•, increased, indicating that the addition of $Ph_2P(O)H$ promoted the formation of **7**.

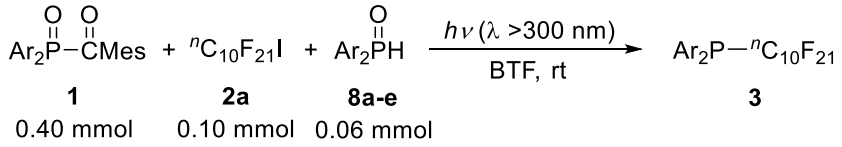


(2-3)

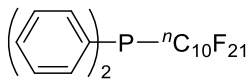
(Determined by ^{19}F NMR. Isolated yield is shown in paretheses.)

Next, the scope of viable substrates was investigated. Notably, several aryl substituted *P*-perfluoroalkylphosphines could be synthesized from TMDPO analogues (Table 2-2). TMDPO analogues **1b**, **1c**, and **1e**, bearing -^{t}Bu, -OMe, and -F groups, respectively, at the *para*-positions of the diaryl unit of phosphine oxide, reacted with **2a** to afford the corresponding *P*-perfluoroalkylphosphines **3b**, **3c**, and **3e** in good yields. TMDPO analogue **1d**, with an -OMe group at the *meta*-positions, also produced *P*-perfluoroalkylphosphine **3d** in a good yield. In addition, the reaction could be scaled up to 2 mmol, and yielded >1 g of *P*-perfluoroalkylphosphine **3a**.

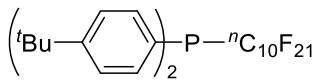
Table 2-2. Photoinduced synthesis of *P*-perfluoroalkylphosphines from several TMDPO derivatives and $^{n}C_{10}F_{21}I$ [a]



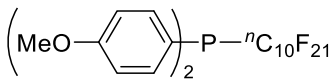
1 0.40 mmol | **2a** 0.10 mmol | **8a-e** 0.06 mmol | **3**



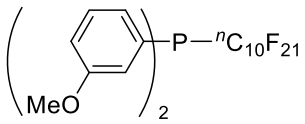
3a, 1.5 h, 96%[b]
(18 h, 1.2 g, 88%)[c]



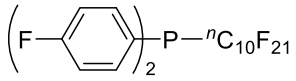
3b, 4 h, 78%[b]



3c, 3 h, 67%[b]



3d, 10 h, 74%[b]

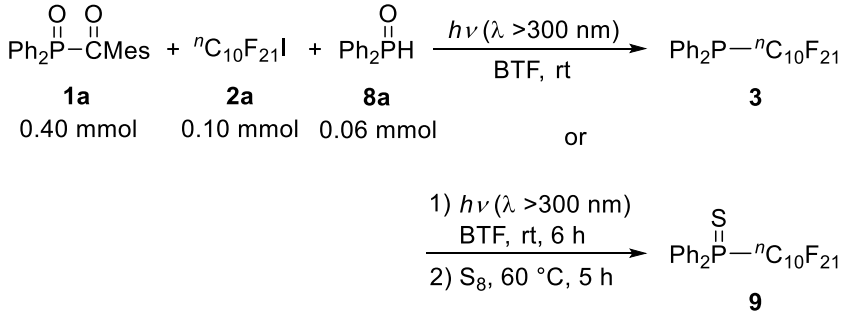


3e, 4 h, 82%[b]

[a]Reaction conditions: diaryl(2,4,6-trimethylbenzoyl)phosphine oxide (**1**: 0.4 mmol), heneicosafluorodecyl iodide (**2a**: 0.1 mmol), diarylphosphine oxide (**8**: 0.06 mmol), BTF (0.6 mL), xenon lamp (500 W), Pyrex, 20 °C. [b]Isolated yield after purification using MeOH /FC-72 biphasic system. [c]The reaction was conducted using 8 mmol of **1a**, 2 mmol of **2a**, 1.2 mmol of **8a** and BTF (12 mL) were used.

The viability of several perfluoroalkyl iodides was also evaluated (Table 2-3). Phosphines with long perfluoroalkyl chains (more than eight carbons) were purified using a MeOH/FC-72 biphasic system and were obtained in good yields (entries 1 and 2). On the other hand, phosphines bearing less than seven carbons were treated with S_8 after the reaction, and were purified by silica gel column chromatography because their fluorous character was insufficient for manipulation via FBS (entries 3 and 4). Secondary perfluoroalkyl iodides such as perfluorocyclohexyl iodide **2d** did not give the corresponding phosphine sulfide **9a** in a satisfactory yield (entry 3). Notably, 1,6-diiodoperfluorohexane **2e** gave the corresponding phosphine sulfide **9b** in an excellent yield (entry 4).

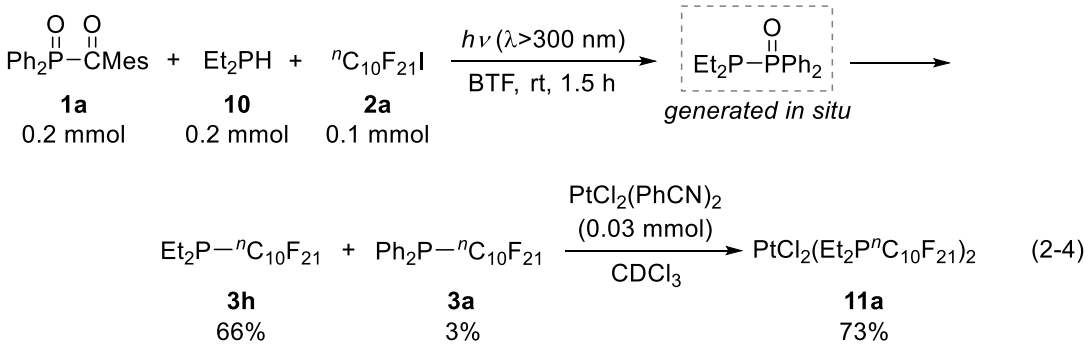
Table 2-3. Photoinduced synthesis of *P*-perfluoroalkylphosphines from TMDPO and several perfluoroalkyl iodides[a]



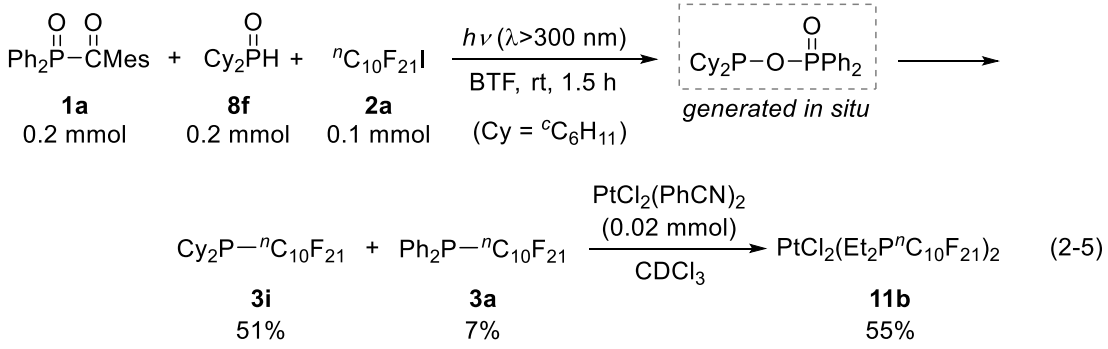
entry	R_f–I	time	product	yield [%]
1[c]	$^nC_{12}F_{25}I$ (**2b**)	6 h	Ph_2P–$^nC_{12}F_{25}$ (**3f**)	98
2[c]	$^nC_8F_{17}I$ (**2c**)	3 h	Ph_2P–$^nC_8F_{17}$ (**3g**)	82
3[d]	$^cC_6F_{11}I$ (**2d**)	3 h	$Ph_2P(S)$–$^cC_6F_{11}$ (**9a**)	(31)
4[d]	$I(CF_2)_6I$ (**2e**)	6 h	$Ph_2P(S)$–$(CF_2)_6$–$P(S)Ph_2$ (**9b**)	96

[a]Reaction conditions: TMDPO (**1a**; 0.30 mmol), perfluoroalkyl iodide (**2**; 0.10 mmol), diphenyl phosphine oxide (**8a**, 0.06 mmol), BTF (0.60 mL), xenon lamp (500 W), room temperature. [b]Isolated yield. The yield of **9a** (shown in parenthesis) was determined by ^{19}F NMR. [c]TMDPO (**1a**; 0.40 mmol) was used. Products **3f** and **3g** were isolated using a MeOH/FC-72 biphasic system. [d]After the reaction, the mixture was treated with S_8 (0.60 mmol) for 5 h. The products were isolated by silica gel column chromatography (eluent: *n*-hexane/AcOEt).

This reaction could be utilized in the synthesis of dialkyl *P*-perfluoroalkylphosphines. When 2 equivalent amounts of **1a** and Et_2PH relative to **2a** were used, Et_2P–$^nC_{10}F_{21}$ was obtained in a moderate yield along with a trace amount of **3a**, after separation using the MeOH/FC-72 biphasic system (Eq. 2-4).[16] In this reaction, Et_2P–$P(O)Ph_2$ was generated in situ and reacted with a $R_f^{\bullet}$ to give **3h**. In order to obtain a transition metal/**3h** complex, $PtCl_2(PhCN)_2$ was added to separate **3a**, diethyl *P*-perfluoroalkylphosphine **3h** was successfully complexed with platinum and **11a**, which is a promising recyclable catalyst, was isolated in 73% yield.



Moreover, dialkylphosphine oxides could also be used for the synthesis of dialkyl *P*-perfluoroalkylphosphines. When 2 equivalent amounts of **1a** and (^{c}C$_6$H$_{11}$)$_2$P(O)H (**8f**) relative to **2a** were used, (^{c}C$_6$H$_{11}$)$_2$P–^{n}C$_{10}$F$_{21}$ (**3i**) was obtained in a moderate yield (Eq. 2-5).[17] In this reaction, (^{c}C$_6$H$_{11}$)$_2$POP(O)Ph$_2$ was generated and reacted with a R$_f$· prior to intermediates **6** and **7**, derived from **1a**. The phosphine was successfully converted to a platinum complex, **11b**, in 55% yield.



2-4 Conclusion

In conclusion, a method for the rapid synthesis of *P*-perfluoroalkyl phosphines using TMDPO as a phosphorus source was developped. This reaction generates phosphorus(III) compounds from phosphorus(V) species via perfluoroalkylation. This method is viable for the synthesis of a variety of *P*-perfluoroalkylphosphines. In addition, the generated *P*-perfluoroalkylphosphines could be complexed with a transition-metal, platinum(II). Therefore, the generated *P*-perfluoroalkylphosphines can be used as ligands, and in the near future, new

reactions are expected to be developed using the produced *P*-perfluoroalkylphosphine ligand-metal complexes.

2-5 Experimental Section

General Comment

All perfluoroalkyl iodides were obtained from commercial supplies. TMDPO (**1a**) were obtained from Tokyo Chemical Industry Co., Ltd. A series of TMDPO analogues and diarylphosphine oxides were synthesized according to the literature with minor changes.[7] All solvents were distilled and degassed with argon before use. ^{1}H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz) FT NMR system or JEOL JNM-ECX400 (400 MHz) FT NMR system in $CDCl_3$ with Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on JEOL JNM-ECX400 (100 MHz) FT NMR or JEOL JNM-ECS400 (100 MHz) FT NMR in $CDCl_3$. ^{31}P NMR spectra were recorded on JEOL JNM-ECX400 (162 MHz) FT NMR or JNM-ECS400 (162 MHz) FT NMR in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. ^{19}F NMR spectra were taken on JEOL JNM-ECX400 (376 MHz) FT NMR system in $CDCl_3$ with $CFCl_3$ as an external standard. Low resolution mass spectra were obtained on SHIMADZU GCMS-QP5000. High resolution mass spectra were obtained on JEOL JMS-DX303 in the analytical section of Osaka University or Kyoto-Nara Advanced Nanotechnology Network. Melting points were not determined because oxidation of phosphines occurred during measurement of their melting points.

Experimental procedure for the synthesis of diaryl methoxyphosphine

To a three–necked flask, magnesium (20 mmol), I_2 (one shot) and dry THF (5 mL) was added under an inert atmosphere, and aryl bromide (20 mmol) was added dropwise. When the

solution was heated to ca. 50 °C, dry THF (30 mL) was added. After it was stirred for 3 h, dichloro methoxyphosphine (10 mmol) was added dropwise at 0 °C, and then stirred for 6 h at room temperature. If the reaction was not proceeded, the solution was heated to 80 °C for 12 h. When methyl dichloro methoxyphosphine was consumed, dry MeOH (5 mL) was added dropwise, and then Grignard salt was precipitated. After it was stirred for 1 h at room temperature, the mixture was filtrated using neutral alumina in glove box, and concentrated under reduced pressure to give the product.

Experimental procedure for the synthesis of TMDPO derivatives 1b–e

All operation of this reaction was conducted in a dark room. Under an inert atmosphere, to a solution of 2,4,6-trimethylbenzoyl chloride (1 equivalent against methoxy diarylphosphine) in toluene (10 mL), methyl diarylphosphine dissolved in toluene (10 mL) was added dropwise for 10 min at 0 °C, and the mixture was stirred for 3 h at room temperature. If the reaction did not proceed, the solution was heated to 80 °C for 12 h. When diaryl methoxyphosphine was consumed, dry MeOH (5 mL) was added, and then neutralized with pyridine and concentrated under reduced pressure. When AcOEt was added, pyridyl salt was precipitated, and then it was filtered out and washed with AcOEt. After concentration of the solution, the crude product was purified by recrystallization.

2,4,6-Trimethylbenzoyl bis(4-tert-butylphenyl)phosphine oxide (1b) The crude product was purified by recrystallization from benzene as white solid, whereas it couldn't separate from 4,4'-di-*tert*-butyl-1,1'-biphenyl. Then, the crude product (**1b** was 78 wt% purity) was used. white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.33 (s, 18H), 2.02 (s, 6H), 2.27 (s, 3H), 6.83 (s, 2H), 7.51 (dd, $J_{H\text{-}H}$= 8.2 Hz, $J_{H\text{-}P}$= 2.8 Hz, 4H), 7.89 (dd, $J_{H\text{-}H}$= 8.2 Hz, $J_{H\text{-}P}$= 10.5 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.7, 21.2, 31.0, 35.0, 125.1, 125.7 (d, $J_{C\text{-}P}$= 11.5 Hz), 126.4 (d, $J_{C\text{-}P}$= 95.9 Hz), 128.8, 131.8 (d, $J_{C\text{-}P}$= 8.6 Hz), 135.2 (d, $J_{C\text{-}P}$= 59.4 Hz), 140.4, 155.8, 210.7 (d, $J_{C\text{-}P}$= 75.7 Hz);

^{31}P NMR (162 MHz, $CDCl_3$): δ 15.1; **HRMS** (FAB+) Calcd for [M + H^+] $C_{30}H_{38}O_2P$: 461.2604, Found: 461.2600.

2,4,6-Trimethylbenzoyl bis(4-tert-butylphenyl)phosphine oxide (1b) The crude product was purified by recrystallization from benzene as white solid, whereas it couldn't separate from 4,4'-di-*tert*-butyl-1,1'-biphenyl. Then, the crude product (**1b** was 78 wt% purity) was used. white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.33 (s, 18H), 2.02 (s, 6H), 2.27 (s, 3H), 6.83 (s, 2H), 7.51 (dd, J_{H-H}= 8.2 Hz, J_{H-P}= 2.8 Hz, 4H), 7.89 (dd, J_{H-H}= 8.2 Hz, J_{H-P}= 10.5 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.7, 21.2, 31.0, 35.0, 125.1, 125.7 (d, J_{C-P}= 11.5 Hz), 126.4 (d, J_{C-P}= 95.9 Hz), 128.8, 131.8 (d, J_{C-P}= 8.6 Hz), 135.2 (d, J_{C-P}= 59.4 Hz), 140.4, 155.8, 210.7 (d, J_{C-P}= 75.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 15.1; **HRMS** (FAB+) Calcd for [M + H^+] $C_{30}H_{38}O_2P$: 461.2604, Found: 461.2600.

2,4,6-Trimethylbenzoyl bis(4-methoxyphenyl)phosphine oxide (1c) The crude product was purified by recrystallization from hexane /AcOEt as white solid in 17% yield. [CAS Registry Number: 127025-85-8];[18] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.03 (s, 6H), 2.26 (s, 3H), 3.85 (s, 6H), 6.80 (s, 2H), 7.00 (dd, J_{H-H}= 9.1 Hz, J_{H-P}= 2.3 Hz, 4H), 7.87 (dd, J_{H-H}= 10.4 Hz, J_{H-P}= 8.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.7, 21.2, 53.3, 114.3 (d, J_{C-P}= 12.4 Hz), 120.7 (d, J_{C-P}= 101.1 Hz), 128.8, 133.8 (d, J_{C-P}= 10.5 Hz), 134.8, 136.5 (d, J_{C-P}= 39.1 Hz), 140.3, 162.8, 220.8 (d, J_{C-P}= 74.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 15.2; **HRMS** (FAB+) Calcd for [M + H^+] $C_{24}H_{26}O_4P$: 409.1563, Found: 409.1566.

2,4,6-Trimethylbenzoyl bis(3-methoxyphenyl)phosphine oxide (1d) Acyl phosphine oxide **1d** couldn't be purified by recrystallization because it was probably liquid. Then, the crude product (**1d** was 82 wt% purity determined by ^{1}H NMR; contaminated with bis(3-methoxyphenyl)phosphinic acid (6 wt%) and 2,4,6-trimethylbenzoic acid (10 wt%)) was used for the synthesis of bis(3-methoxyphenyl)(perfluorodecyl)phosphine **3d**. white solid; **^{1}H**

NMR (400 MHz, $CDCl_3$): δ 2.04 (s, 6H), 2.25 (s, 3H), 6.80 (s, 2H), 7.21 (dd, J_{H-H}= 8.2 Hz, 2.3 Hz, 2H), 7.40 (ddd, J_{H-H}= 8.2 Hz, 7.8 Hz, J_{H-P}= 4.2 Hz, 2H), 7.48‑7.46 (m, 4H); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 14.2.

2,4,6-Trimethylbenzoyl bis(4-fluorophenyl)phosphine oxide (1e) The crude product was purified by recrystallization from benzene as white solid in 12% yield. white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.02 (s, 6H), 2.27 (s, 3H), 6.83 (s, 2H), 7.21 (ddd, J_{H-H}= 8.7 Hz, J_{H-F}= 8.7 Hz, J_{H-P}= 2.3 Hz, 4H), 7.99 (ddd, J_{H-H}= 10.5 Hz, J_{H-P}= 9.2 Hz, J_{H-F}= 5.5 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.3, 20.8, 116.0 (dd, J_{C-P}= 22.0 Hz, J_{C-F}= 12.7 Hz), 125.2 (dd, J_{C-P}= 99.4 Hz, J_{C-F}= 3.5 Hz), 128.6, 134.1 (dd, J_{C-P}= 9.3 Hz, J_{C-F}= 9.3 Hz), 134.5, 135.6 (d, J_{C-P}= 40.5 Hz), 140.9, 165.1 (d, J_{C-F}= 254.3 Hz), 219.4 (d, J_{C-P}= 74.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 11.9; **HRMS** (FAB+) Calcd for [M + H^+] $C_{22}H_{20}O_2F_2P$: 385.1163, Found: 385.1163.

Experimental procedure for the synthesis of perfluoroalkyl phosphines 3a‑g

TMDPO (dipenyl(2,4,6–trimethylbenzoyl)phosphine oxide; 0.4 mmol) or its analogue, diarylphosphine oxide (0.06 mmol) and perfluoroalkyl iodide (0.1 mmol) in degassed BTF (600 μL) were placed in a sealed Pyrex NMR tube under an inert atmosphere. The mixture was vortexed hardly until TMDPO was disssolved and then irradiated with a xenon lamp (500 W) for each reaction time at room temperature. The reaction mixture was then concentrated under reduced pressure, diluted MeOH, and extracted with FC–72 (3 x 5 mL) in a glove box. The combined fluorous phases were concentrated under reduced pressure to give the product.

Experimental procedure for the gram-scale synthesis of perfluoroalkyl phosphine 3a

TMDPO (8 mmol), diphenylphosphine oxide (1.2 mmol), and perfluoroalkyl iodide (2 mmol) in degassed BTF (12 mL) were placed in a sealed Pyrex test tube under an inert atmosphere. The mixture was vortexed hardly and irradiated with a xenon lamp (500 W) for 18 h

at room temperature. The following operation is the same as the upper experimental procedure for the synthesis of perfluoroalkyl phosphines.

Diphenyl(perfluorodecyl)phosphine (3a) [CAS Registry Number: 1424372-87-1];[5] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40–7.49 (m, 6H), 7.70 (dd, J_{H-H}= 8.2 Hz, J_{H-P}= 7.3 Hz, 4H); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 1.21–2.44 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.1 (2F), −122.7 (2F), −121.8 (2F), −121.7 (6F), −121.3 (2F), −117.5 (d, J_{F-P}= 28.9 Hz, 2F), −108.7 (dt, J_{F-P}= 57.8 Hz, J= 17.3 Hz, 2F), −80.8 (3F).

Bis(4-tert-butylphenyl)(perfluorodecyl)phosphine (3b) White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.32 (s, 18H), 7.44 (dd, J_{H-H}= 8.7 Hz, J_{H-P}= 1.4 Hz, 4H), 7.63 (dd, J_{H-H}= 8.7 Hz, J_{H-P}= 8.2 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 31.1, 34.8, 125.7 (d, J_{C-P}= 9.6 Hz), 135.0 (d, J_{C-P}= 23.0 Hz), 154.0; **^{31}P NMR** (162 MHz, $CDCl_3$): δ −0.80–−1.31 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.1 (2F), −122.7 (2F), −121.8 (2F), −121.7 (6F), −121.3 (2F), −117.6 (d, J_{F-P}= 28.9 Hz, 2F), −108.9 (dt, J_{F-P}= 51.2 Hz, J= 17.1 Hz, 2F), −80.8 (3F); **HRMS** (ESI+) Calcd for [M + O + Na^+] (oxidized during the analysis) $C_{30}H_{26}F_{21}NaOP$: 855.1278, Found: 855.1263.

Bis(4-methoxyphenyl)(perfluorodecyl)phosphine (3c) White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.83 (s, 6H), 6.95 (dd, J_{H-H}= 8.2 Hz, J_{H-P}= 0.9 Hz, 4H), 7.63 (dd, J_{H-H}= 8.7 Hz, J_{H-P}= 8.7 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.2, 114.4 (d, J_{C-P}= 9.5 Hz), 136.8 (d, J_{C-P}= 24.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −0.91–−2.06 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.0 (2F), −122.6 (2F), −121.8 (2F), −121.6 (6F), −121.3 (2F), −117.7 (d, J_{F-P}= 28.9 Hz, 2F), −109.5 (dt, J_{F-P}= 57.8 Hz, J= 11.7 Hz, 2F), −80.7 (3F); **HRMS** (ESI+) Calcd for [M + O + Na^+] (oxidized during the analysis) $C_{24}H_{14}F_{21}NaO^3P$: 803.0237, Found: 803.0213.

Bis(3-methoxyphenyl)(perfluorodecyl)phosphine (3d) White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.81 (s, 6H), 7.01 (dd, J_{H-H}= 8.2 Hz, 2.3 Hz, 2H), 7.22 (d, J_{H-P}= 8.2 Hz, 2H), 7.27 (dd, J_{H-H}= 8.2 Hz, 7.8 Hz, 2H), 7.35 (ddd, J_{H-H}= 7.7 Hz, 2.3 Hz, J_{H-P}= 8.2 Hz, 2H); **^{13}C NMR** (100

MHz, $CDCl_3$): δ 55.3, 116.4, 114.4 (d, $J_{C\text{-}P}$= 24.8 Hz), 127.4 (d, $J_{C\text{-}P}$= 21.9 Hz), 129.7 (d, $J_{C\text{-}P}$= 9.5 Hz), 159.5 (d, $J_{C\text{-}P}$= 10.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 2.34–3.65 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.1 (2F), −122.7 (2F), −121.8 (2F), −121.7 (6F), −121.3 (2F), −117.4 (d, $J_{F\text{-}P}$= 28.5 Hz, 2F), −109.5 (dt, $J_{F\text{-}P}$= 56.9 Hz, J= 11.4 Hz, 2F), −80.7 (3F); **HRMS** (FAB+) Calcd for [M + H^+] $C_{24}H_{15}F_{21}O_2P$: 765.0469, Found: 765.0462.

Bis(4-fluorophenyl)(perfluorodecyl)phosphine (3e) White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.14 (dd, $J_{H\text{-}H}$= 8.2 Hz, $J_{H\text{-}F}$= 8.2 Hz, 4H), 7.67 (ddd, $J_{H\text{-}H}$= 8.2 Hz, $J_{H\text{-}P}$= 8.2 Hz, $J_{H\text{-}F}$= 2.3 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 116.3 (dd, $J_{C\text{-}P}$= 8.6 Hz, $J_{C\text{-}F}$= 21.1 Hz), 137.3 (dd, $J_{C\text{-}P}$= 24.9 Hz, $J_{C\text{-}F}$= 8.6Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −1.66–−0.38 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.1 (2F), −122.6 (2F), −121.8 (2F), −121.7 (6F), −121.3 (2F), −117.6 (d, JF-P= 34.7 Hz, 2F), −109.3 (dt, $J_{F\text{-}P}$= 57.8 Hz, J= 11.6 Hz, 2F), −108.4 (2F), −80.3 (3F); **HRMS** (ESI+) Calcd for [M + O + Na^+] (oxidized during the analysis) $C_{22}H_8F_{23}NaOP$: 778.9838, Found: 778.9817.

Diphenyl(perfluorododecyl)phosphine (3f) [CAS Registry Number: 1424373-37-4]; [5] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40–7.50 (m, 6H), 7.63 (dd, $J_{H\text{-}H}$= 8.6 Hz, 1.8 Hz, $J_{H\text{-}P}$= 8.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 128.7 (d, $J_{C\text{-}P}$= 8.5 Hz), 130.7, 135.2 (d, $J_{C\text{-}P}$= 22.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 1.40–2.36 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.1 (2F), −122.7 (2F), −121.8 (2F), −121.7 (10F), −121.3 (2F), −117.5 (d, $J_{F\text{-}P}$= 34.2 Hz, 2F), −109.5 (dt, $J_{F\text{-}P}$= 56.9 Hz, J= 11.4 Hz, 2F), −80.7 (3F).

Diphenyl(perfluorooctyl)phosphine (3g) [CAS Registry Number: 1202071-48-4];[5] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54–7.69 (dt, $J_{H\text{-}H}$= 8.6 Hz, $J_{H\text{-}P}$= 1.4 Hz, 4H), 7.40–7.49 (m,, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 128.7 (d, $J_{C\text{-}P}$= 8.6 Hz), 130.7, 135.2 (d, $J_{C\text{-}P}$= 22.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 1.13–2.36 (m); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.0 (2F), −122.7 (2F), −121.9 (2F), −121.8 (2F), −121.3 (2F), −117.5 (dd, $J_{F\text{-}P}$= 17.1 Hz, J= 17.1 Hz, 2F),

−111.0 (dt, $J_{F\text{-}P}$= 56.9 Hz, J= 11.4 Hz, 2F), −80.6 (3F).

Experimental procedure for the synthesis of perfluoroalkyl phosphine sulfides 9a and 9b

S_8 (0.3 mmol for **9a**, 0.6 mmol for **9b**) was added under inert atmosphere after the reaction of TMDPO with perfluoroalkyl iodide, and then the mixture was stirred for 5 h at 80 °C. After the reaction mixture was concentrated, **9a** and **9b** was obtained after isolation by column chromatography on silica gel.

Diphenyl(perfluorocyclohexyl)phosphine sulfide (9a) [CAS Registry Number: 1424373-18-1];[5] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54–7.59 (dt, $J_{H\text{-}H}$= 7.7 Hz, $J_{H\text{-}P}$= 3.6 Hz, 4H), 7.59–7.65 (m, 2H), 8.07 (dd, $J_{H\text{-}H}$= 8.6 Hz, $J_{H\text{-}P}$= 14.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 128.6 (d, $J_{C\text{-}P}$= 13.4 Hz), 133.0, 133.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 40.4 (d, $J_{P\text{-}F}$= 43.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −178.4–−178.8 (m), −141.9, −141.2, −138.6 (d, $J_{F\text{-}F}$= 11.4 Hz), −137.9 (d, $J_{F\text{-}F}$= 11.4 Hz), −124.7 (d, $J_{F\text{-}F}$= 11.4 Hz), −123.9 (d, $J_{F\text{-}F}$= 11.4 Hz), −123.1 (d, $J_{F\text{-}F}$= 17.1 Hz), −122.2 (d, $J_{F\text{-}P}$= 22.8 Hz), −121.4 (d, $J_{F\text{-}F}$= 17.1 Hz), −112.4, −111.6.

1,6-Bis(diphenylthiophosphinyl)perfluorohexane (9b) [CAS Registry Number: 1424373-26-1];[5] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (dt, $J_{H\text{-}H}$=7.7 Hz, $J_{H\text{-}P}$ = 3.6 Hz, 8H), 7.58–7.62 (m, 4H), 8.02 (dd, $J_{H\text{-}H}$= 7.3 Hz, $J_{H\text{-}P}$= 13.6 Hz, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.7 (d, $J_{C\text{-}P}$= 83.9 Hz), 128.9 (d, $J_{C\text{-}P}$= 13.4 Hz), 132.9 (d, $J_{C\text{-}P}$= 10.5 Hz), 133.2 (d, $J_{C\text{-}P}$= 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 46.2 (t, $J_{P\text{-}F}$= 68.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −121.3 (4F), −115.4 (4F), −111.0 (d, $J_{F\text{-}P}$= 68.3 Hz, 4F).

Experimental procedure for the synthesis of platinum(II) complex of perfluoroalkyl phosphines 11a and 11b

The reaction mixture was then concentrated under reduced pressure, diluted MeOH, and extracted with FC–72 (3 x 5 mL) in a glove box. After the combined fluorous phases were

concentrated under reduced pressure, $PtCl_2(C_6H_5CN)_2$ (0.07 mmol for **11a**, 0.02 mmol for **11b**) was added under inert atmosphere, and the reaction mixture was stirred at room temperature for 12 h. After the reaction mixture was concentrated, **11a** and **11b** was obtained after isolation by column chromatography on silica gel.

Dichloro bis(diethyl(perfluorodecyl)phosphine)platinum(II) (11a) Light yellow solid; **mp** 106–108 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.32 (dt, $J_{H\text{-}Pt}$= 17.7 Hz, $J_{H\text{-}H}$= 8.2 Hz, 12H), 2.27–2.56 (m, 8H); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.6 (quint, $J_{P\text{-}F}$= 25.8 Hz with two satellite derived from the coupling with ^{195}Pt, $J_{P\text{-}Pt}$= 2720 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.2 (4F), −122.8 (4F), −122.0 (4F), −121.8 (12F), −121.5 (4F), −116.5 (4F), −109.1–−109.3 (m, 4F), −80.8 (6F); **HRMS** (ESI+) Calcd for [M + Na^+] $C_{28}H_{20}Cl_2F_{42}NaP_2Pt$: 1504.9288, Found: 1504.9282.

Dichloro bis(dicyclohexyl(perfluorodecyl)phosphine)platinum(II) (11b) Light yellow solid; **mp** 136–138 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.20–1.43 (m, 12H), 1.68–1.92 (m, 20H), 2.03–2.14 (m, 4H), 2.29–2.42 (m, 4H), 3.07–3.24 (m, 4H); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.9 (quint, $J_{P\text{-}F}$= 21.5 Hz with two satellite derived from the coupling with ^{195}Pt, $J_{P\text{-}Pt}$= 2700 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −126.4 (4F), −122.9 (4F), −122.1 (4F), −121.8 (12F), −121.5 (4F), −115.0 (4F), − 100.6 (m, 4F), − 81.0 (6F); **HRMS** (ESI+) Calcd for [M + Na^+] $C_{44}H_{44}Cl_2F_{42}NaP_2Pt$: 1721.1172, Found: 1721.1178.

2-6 References

1. (a) Quin, L. D. *A Guide to Organophosphorus Chemistry*. John Wiley & Sons: New York, **2000**. (b) Yorimitsu, H. *Beilstein J. Org. Chem.* **2013**, *9*, 1269-1277. (c) Xu, Q.; Zhou, Y. -B.; Zhao, C. -Q.; Yin, S. -F.; Han, L. -B. *Mini-Rev. Med. Chem.* **2013**, *12*, 824-835.

2. (a) Wittig, G.; Schöllkopf, U. *Chem. Ber.* **1954**, *87*, 1318-1330. (b) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863-927.

3. (a) Mitsunobu, O.; Yamada, M.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 935-939. (b) Mitsunobu, O.; Yamada, M. *Bull. Chem. Soc. Jpn.* **1967**, *40*, 2380-2382. (c) Dandapani, S.; Curran, D. P. *Chem. Eur. J.* **2004**, *10*, 3130-3138.

4. (a) Gládysz, J. A.; Curran, D. P.; Horváth, I. T. *Handbook of Fluorous Chemistry*. Wiley-VCH: Weinheim, Germany, **2004**. (b) Horváth, I. T.; Rábai, J. *Science* **1994**, *266*, 72-75.

5. Kawaguchi, S-i.; Minamida, Y.; Ohe, T.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 1748-1752.

6. (a) Brisdon, A. K.; Herbert, C. J. *Chem. Commun.* **2009**, 6658-6660. (b) Banger, K. K.; Brisdon, A. K.; Herbert, C. J.; Ghaba, H. A.; Tidmarsh, I. S. *J. Fluorine Chem.* **2009**, *130*, 1117-1129. (c) Mikhaylov, D. Y.; Gryaznova, T. V.; Dudkina, Y. B.; Polyancev, F. M.; Latypov, S. K.; Sinyashin, O. G.; Budnikova, Y. H. *J. Fluorine Chem.* **2013**, *153*, 178-182. (d) Lindner, E.; Kranz, H. *Chem. Ber.* **1968**, *101*, 3438-3444. (e) Murphy-Jolly, M. B.; Lewis, L. C.; Caffyn, A. J. M. *Chem. Commun.* **2005**, 4479-4480. (f) Palcic, J. D.; Kapoor, P. N.; Roddick, D. M.; Gregory Peters, R. *Dalton Trans.* **2004**, 1644-1647. (g) Gosling, K.; Holman, D. J.; Smith, J. D.; Ghose, B. N. *J. Chem. Soc. A.* **1968**, 1909-1914. (h) Vaillard, S. E.; Postigo, A.; Rossi, R. A. *Organometallics* **2004**, *23*, 3003-3007. (i) Lanteri, M. N.; Rossi, R. A.; Martín, S. E. *J. Organomet. Chem.* **2009**, *694*, 3425-3430.

7. a) Lechtken, P.; Buethe, I.; Jacobi, M.; Trimborn, W. US4710523, **1987**. b) Lechtken, P.; Buethe, I.; Hesse, A. US4324744, **1982**.

8. (a) Ikemura, K.; Kadoma, Y.; Endo, T. *Dent. Mater. J.* **2011**, *30*, 769-789. (b) Nazir, R.; Danilevicius, P.; Gray, D.; Farsari, M.; Gryko, D. T. *Macromolecules* **2013**, *46*, 7239-7244. (c) Tian, Y.; Zhang, Y.-L.; Ku, J.-F.; He, Y.; Xu, B.-B.; Chen, Q.-D.; Xia, H.; Sun, H.-B. *Lab on a Chip* **2010**, *10*, 2902-2905. (d) Griesser, T.; Wolfberger, A.; Daschiel, U.; Schmidt, V.; Fian, A.; Jerrar, A.; Teichert, C.; Kern, W. *Polym. Chem.* **2013**, *4*, 1708-1714. (e) Gonsalvi, L.; Peruzzini, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 7895-7897.

9. (a) Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X. D.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277-4280. (b) Berthod, M.; Favre-Réguillon, A.; Mohamad, J.; Mignani, G.; Docherty, G.; Lemaire, M. *Synlett* **2007**, *2007*, 1545-1548. (c) Li, Y.; Das, S.; Zhou, S.; Junge, K.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 9727-9732. (d) Fritzsche, H.; Hasserodt, U.; Korte, F. *Chem. Ber.* **1964**, *97*, 1988-1993. (e) Köster, R.; Morita, Y. *Angew. Chem.* **1965**, *77*, 589-590. (f) Masaki, M.; Fukui, K. *Chem. Lett.* **1977**, *6*, 151-152. (g) Coumbe, T.; Lawrence, N. J.; Muhammad, F. *Tetrahedron Lett.* **1994**, *35*, 625-628. (h) Marsi, K. L. *J. Org. Chem.* **1974**, *39*, 265-267. (i) Horner, L.; Hoffmann, H.; Beck, P. *Chem. Ber.* **1958**, *91*, 1583-1588. (j) Griffin, S.; Heath, L.; Wyatt, P. *Tetrahedron Lett.* **1998**, *39*, 4405-4406.

10. (a) Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 1456-1463. (b) Frey, G.; Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 763-772. (c) Cho, C. H.; Kim, S.; Yamane, M.; Miyauchi, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1665-1672. (d) Said, N.; Touil, S.; Akacha, A. B.; Efrit, M. L. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 2726-2733. (e) Lindner, E.; Kern, H. *Chem. Ber.* **1984**, *117*, 355-365. (f) Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 793-798.

11. The reaction condition was referred to our previous report, reference 5.

12. (a) Sumiyoshi, T.; Katayama, M.; Schnabel, W. *Chem. Lett.* **1985**, *14*, 1647-1650. (b) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141-146. (c) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148-5153. (d) Colley, C. S.; Grills, D. C.; Besley, N. A.; Jockusch, S.; Matousek, P.; Parker, A. W.; Towrie, M.; Turro, N. J.; Gill, P. M. W.; George, M. W. *J. Am. Chem. Soc.* **2002**, *124*, 14952-14958. (e) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477-6489.

13. (a) Habib, M. H.; Mallouk, T. E. *J. Fluorine Chem.* **1991**, *53*, 53-60. (b) Qiu, Z.-M.; Burton, D. J. *J. Org. Chem.* **1995**, *60*, 3465-3472. (c) Ogawa, A.; Imura, M.; Kamada, N.; Hirao, T. *Tetrahedron Lett.* **2001**, *42*, 2489-2492. (d) Tsuchii, K.; Imura, M.; Kamada, N.; Hirao, T.; Ogawa, A. *J. Org. Chem.* **2004**, *69*, 6658-6665. (e) Yjima, T.; Jahan, I.; Tonoi, T.; Shinmen, M.; Nishikawa, K.; Yamaguchi, K.; Sekine, I.; Nagano, H. *Tetrahedron* **2012**, *68*, 6856-6861.

14. When $Ph_2P(O)H$ (0.1 mmol) was added to the reaction system in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 10% yield, along with the desired product in 19% yield.

15. After the reaction, ***COP*** and ***POP*** were obtained in 6% and 81% yields (***COP***, δ_P = 30 ppm; ***POP***, δ_P = 29 ppm), respectively. These chemical shifts are supported from reference 12e for ***COP*** and Korth, H. G.; Lusztyk, J.; Ingold, K. U. *J. Org. Chem.* **1990**, *55*, 624-631. for ***POP***.

16. When Et_2PH (0.2 mmol) and $^{n}C_{10}F_{21}I$ (0.1 mmol) were irradiated under the same condition in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 13% yield, along with $Et_2P^{n}C_{10}F_{21}$ in 47% yield.

17. When $Cy_2P(O)H$ (0.2 mmol) and $^{n}C_{10}F_{21}I$ (0.1 mmol) were irradiated under the same condition in the absence of TMDPO, byproduct $^{n}C_{10}F_{21}H$ was obtained in 21% yield, along with $Cy_2P^{n}C_{10}F_{21}$ in 18% yield.

18. Majima, T.; Schnabel, W. *J. Photochem. Photobiol. A: Chem.* **1989**, *50*, 31-39.

Chapter 3

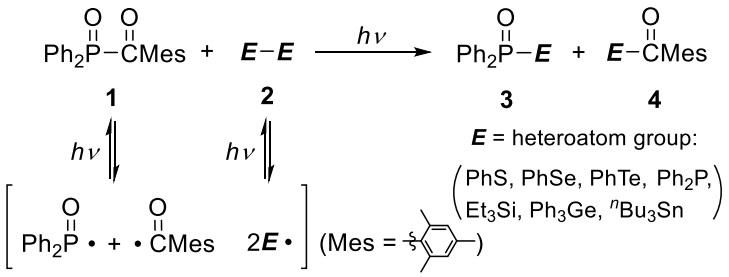
Photoinduced Coupling Reaction of Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide with Interelement Compounds: Application to the Synthesis of Thio- or Selenophosphinates

3-1 Introduction

(2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (TMDPO)[1] is potentially an attractive phosphorus source a radical initiator which affords diphenylphosphinoyl radical along with 2,4,6-trimethylbenzoyl radical by homolytic cleavage of the P–C bond upon photoirradiation.[2,3,4] TMDPO is widely used in the field of macromolecular chemistry, not only for surface processing such as coating[5] and adhesive materials[6] but also photonic crystals[7] and mechanical devices.[8,9] However, there are only very limited examples of the synthetic reaction of organophosphorus compounds using TMDPO as a phosphorus source.[10]

On the other hand, the organic heteroatom compounds having interelement linkages (***E***–***E***) are also attractive heteroatom sources. ***E***–***E*** compounds such as disulfide (S–S),[11] diselenide (Se–Se),[11] ditelluride (Te–Te),[12] diphosphine (P–P),[13] disilane (Si–Si),[14] digermane (Ge–Ge),[15] and distannane (Sn–Sn)[16] can afford the corresponding heteroatom-centered radicals by homolytic cleavage of ***E***–***E*** under photoirradiation conditions. The author thus expected that cross-coupling reaction between TMDPO and ***E***–***E*** would occur under light to afford the corresponding phosphine oxides **3** and carbonyl compounds **4** (Scheme 3-1).

Scheme 3-1. Photoinduced coupling reaction between TMDPO and ***E–E***



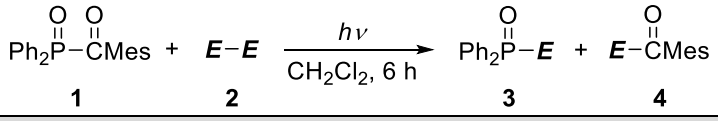
In this chapter, the photoinduced coupling reaction between TMDPO and ***E–E*** compounds was described. Moreover, on the basis of our insight into the results, the photoinduced coupling reaction of TMDPO was successfully applied to efficient synthesis of thio- and selenophosphinates.

3-2 Results and Discussion

First, the author investigated the reactions of TMDPO with different ***E–E*** compounds containing a heteroatom–heteroatom single bond of group 13–16 elements,[17] under light irradiation (Table 3-1). When a mixture of TMDPO and diphenyl disulfide **2aa** was irradiated with a xenon lamp through Pyrex, the photoinduced cross-coupling reaction between TMDPO and **2aa** successfully proceeded to afford *S*-phenyl diphenylthiophosphinate **3aa** and *S*-phenyl 2,4,6-trimethylthiobenzoate **4aa** in good yields (entry 1). The reaction did not proceed at all in the dark (entry 2). Using diphenyl diselenide **2ba** instead of **2aa** afforded *Se*-phenyl diphenylselenophosphinate **3ba** and *Se*-phenyl 2,4,6-trimethylselenobenzoate **4ba** in excellent yields (entry 3). Upon irradiation of a mixture of TMDPO and diphenyl ditelluride **2ca**, *Te*-phenyl 2,4,6-trimethyltellurobenzoate **4ca** was obtained in good yield; however, *Te*-phenyl diphenyltellurophosphinate **3ca** was not detected, most probably because of its instability under photoirradiation (entry 4).[18] In the case of tetraphenyldiphosphine **2da**, tetraphenyldiphosphine

monoxide **3da** was obtained quantitatively, and diphenyl(2,4,6-trimethylbenzoyl)phosphine **4da** was generated in only 9% yield along with the formation of a complex mixture derived from 2,4,6-trimethylbenzoyl unit (entry 5). In contrast, hexamethyldisilane **2ea**, hexaphenyldigermane **2fa**, hexabutyldistannane **2ga**, and bis(pinacolato)diboron **2ha**[19] did not afford the corresponding coupling products (entries 6-9). In these reactions, large amounts of ***E–E*** compounds remained unreacted, and many byproducts derived from the photolysis of TMDPO were generated, such as $Ph_2P(O)OP(O)Ph_2$ and $Ph_2P(O)P(O)Ph_2$.

Table 3-1. Photoinduced reactions of TMDPO with different ***E–E*** compounds[a]



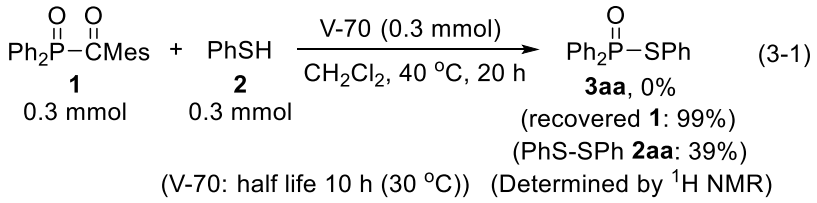
1 **2** **3** **4**

entry	***E–E***	yield [%][b]	
		3	**4**
1	PhS–SPh (**2aa**)	99% (95%)	84% (78%)
2[c]	PhS–SPh (**2aa**)	0%	0%
3	PhSe–SePh (**2ba**)	99% (92%)	95% (88%)
4	PhTe–TePh (**2ca**)	0%	86% (54%)
5	Ph_2P–PPh_2 (**2da**)	>99%	9%
6	Me_3Si–$SiMe_3$ (**2ea**)	0%	0%
7	Ph_3Ge–$GePh_3$ (**2fa**)	0%	0%
8	$^nBu_3Sn$–Sn^nBu_3 (**2ga**)	0%	0%
9	pinB–Bpin (**2ha**)	0%	0%

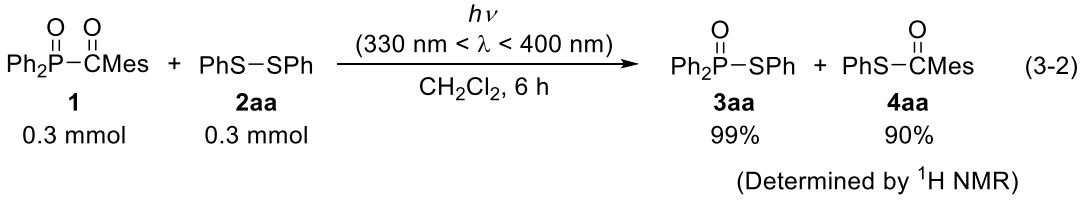
[a]Reaction conditions: TMDPO (**3**, 0.3 mmol), interelement compound (**4**, 0.3 mmol), CH_2Cl_2 (0.6 mL), xenon lamp (500 W), room temperature, 6 h. [b]Determined by ^{31}P and ^1H NMR. Isolated yields are shown in parentheses. [c]In the dark.

To gain insight into the pathway of this transformation, two experiments were performed using the photoinduced cross-coupling reaction of TMDPO with disulfide as a model. When a mixture of TMDPO and PhSH was stirred in the presence of the radical initiator V-70 (2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)) at 40 °C for 20 h, thiophosphinate **3aa** was

not obtained, and unreacted TMDPO was fully recovered (Eq. 3-1). V-70 can abstract a hydrogen atom from PhSH to generate a thiyl radical but it cannot cleave the C–P bond of TMDPO. As a result, PhS–SPh was obtained from homocoupling of PhS·.



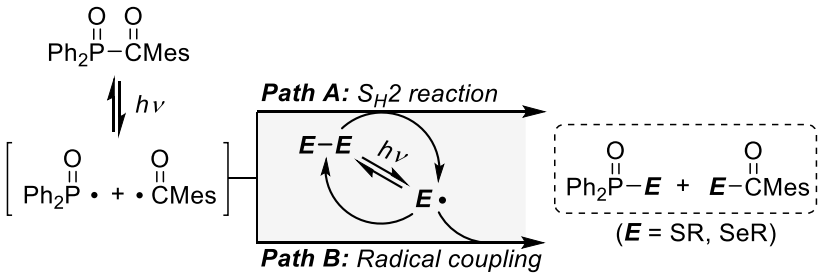
TMDPO shows an absorption maximum at λ = 380 nm,[3b] whereas PhS–SPh exhibits absorption up to about λ = 320 nm.[20] Thus, a mixture of TMDPO and PhS–SPh was irradiated with a xenon lamp through a filter (330 nm < λ < 400 nm), and thiophosphinate **3aa** and thioester **4aa** were obtained in high yields (Eq. 3-2). Clearly, under these conditions, only TMDPO can undergo homolytic cleavage to give the phosphinoyl radical, which can be captured by the disulfide.



On the basis of these results, plausible pathways for the photoinduced cross-coupling reaction of TMDPO with ***E***–***E*** compounds are illustrated in Scheme 3-2. In the case of ***E*** = PhS, the phosphinoyl radical ($Ph_2P(O)$·) formed by irradiation of TMDPO undergoes S_H2 reaction with the sulfur atom of the disulfide to give thiophosphinate **3aa** and a thiyl radical. The S_H2 reaction of the carbonyl radical (MesC(O)·) with the disulfide also proceeds efficiently to give thioester **4aa** (Path A). In another pathway, $Ph_2P(O)$· and MesC(O)· couple with the thiyl radical to afford thiophosphinate **3aa** and thioester **4aa**, respectively (Path B). Moreover, the thiyl radicals can react with each other to regenerate the disulfide. In the case of ***E*** = PhSe, the generated $Ph_2P(O)$· attacks the diselenide to give the corresponding selenophosphinate **3ba** as in the case of $(PhS)_2$.

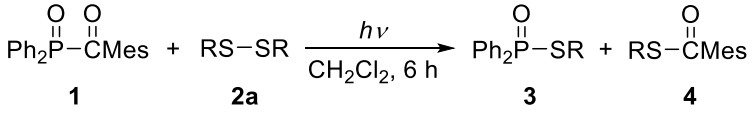
On the other hand, when diphenyl ditelluride is used, MesC(O)· can attack the ditelluride to give telluroester (Path A), but the desired $Ph_2P(O)TePh$, generated from the reaction of $Ph_2P(O)$· with the ditelluride, is quite unstable.[21] In addition, tetraphenyldiphosphine (***E*** = Ph_2P) can be attacked by $Ph_2P(O)$· efficiently to give diphosphine monoxide, whereas the reaction with MesC(O)· is not efficient. In the case of ***E*** = Et_3Si, Ph_3Ge, $^nBu_3Sn$, or (pin)B, the in situ generated $Ph_2P(O)$· and MesC(O)· do not undergo S_H2 reaction with ***E***–***E***.

Scheme 3-2. Plausible pathways for the reaction between TMDPO and ***E–E*** compounds

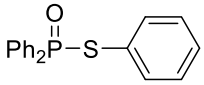
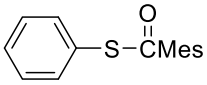
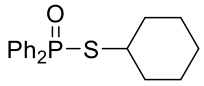
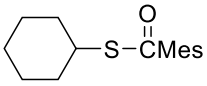
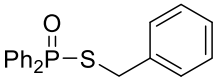
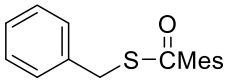
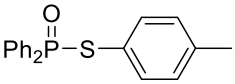
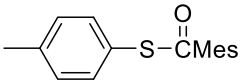
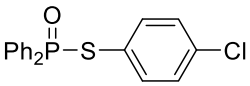
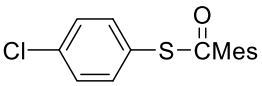
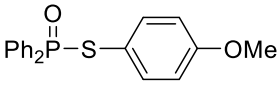
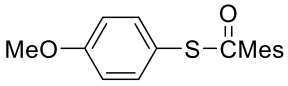
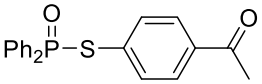
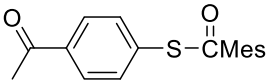
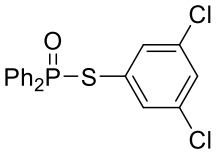
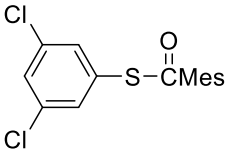


These findings show that the cross-coupling reaction between TMDPO and PhS–SPh or PhSe–SePh can be useful for the synthesis of *S*- or *Se*-substituted thio- or selenophosphinates, respectively. Thiophosphinates are important building blocks for the synthesis of biologically active molecules.[22] Thus, several synthetic methods for thiophosphinates have been reported recently,[23] and a number of synthetic routes to selenophosphinates have also been developed.[24] Nevertheless, the present reaction is considered advantageous in terms of easy operation. Next, the author investigated the scope of disulfides for the synthesis of thiophosphinates using TMDPO as a phosphorus source (Table 3-2). As mentioned above, the cross-coupling reaction between TMDPO and diphenyl disulfide **2aa** afforded *S*-phenyl diphenylthiophosphinate **3aa** and *S*-phenyl mesitylthioate **4aa** in good yields (entry 1). Aliphatic disulfides **2ab** and **2ac** also afforded the corresponding thiophosphinates in excellent yields along with moderate amounts of the corresponding thioesters (entries 2 and 3). When aromatic disulfides such as bis(4-methylphenyl) disulfide (**2ac**), bis(4-chlorophenyl) disul fide (**2ad**), bis(4-methoxyphenyl)

Table 3-2. Scope of disulfides in the photoinduced cross-coupling reaction with TMDPO[a]



1 **2a** **3** **4**

entry	yield [%][b]	
	3	**4**
1	 **3aa**, >99% (95%)	 **4aa**, 84% (78%)
2[c]	 **3ab**, 99% (87%)	 **4ab**, 43%
3	 **3ac**, 98% (91%)	 **4ac**, 40%
4	 **3ad**, >99% (93%)	 **4ad**, >99% (94%)
5	 **3ae**, 98% (87%)	 **4ae**, 72% (64%)
6	 **3af**, 99% (96%)	 **4ac**, 96% (87%)
7	 **3ag**, 0%	 **4ag**, 0%
8	 **3ah**, 98% (87%)	 **4ah**, 95% (87%)

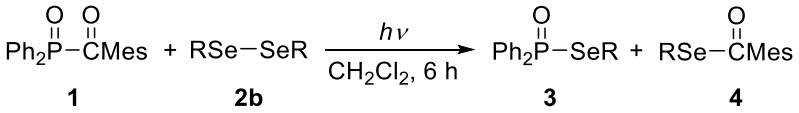
[a]Reaction conditions: TMDPO (**1**, 0.3 mmol), disulfide (**2a**, 0.3 mmol), CH_2Cl_2 (0.6 mL), xenon lamp (500 W), room temperature, 6 h. [b]Determined by ^{31}P and ^{1}H NMR. Isolated yields are shown in parentheses.

disulfide (**2ae**), bis(4-acetylphenyl) disulfide (**2af**), and bis(3,5-dichlorophenyl) disulfide (**2ah**)

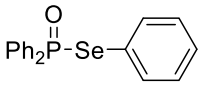
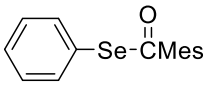
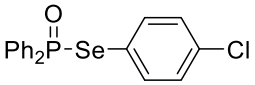
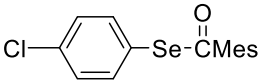
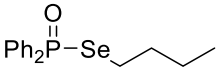
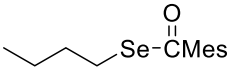
were employed, the corresponding *S*-aryl diphenylthiophosphinates (**3ac**–**3af** and **3ah**) were obtained in good yields (entries 4–6 and 8). In contrast, the reaction of bis(4-acetylphenyl) disulfide (**2ag**) did not afford the corresponding **3ag** and **4ag**, most probably due to the lower radical capturing ability of **2ag** (entry 7).

Next, the photoinduced cross-coupling reaction of TMDPO with different diselenides were conducted (Table 3-3). The reaction of TMDPO with aromatic bis(4-chlorophenyl) diselenide (**2bb**) successfully afforded the corresponding *Se*-(4-chlorophenyl) diphenylselenophosphinate (**3bb**) in good yield (entry 2). Gratifyingly, aliphatic di-*n*-butyl diselenide also efficiently reacted with TMDPO to give *Se*-*n*-butyl diphenylselenophosphinate (**3bc**) in excellent yield (entry 3).

Table 3-3. Scope of diselenides in the photoinduced cross-coupling reaction with TMDPO[a]



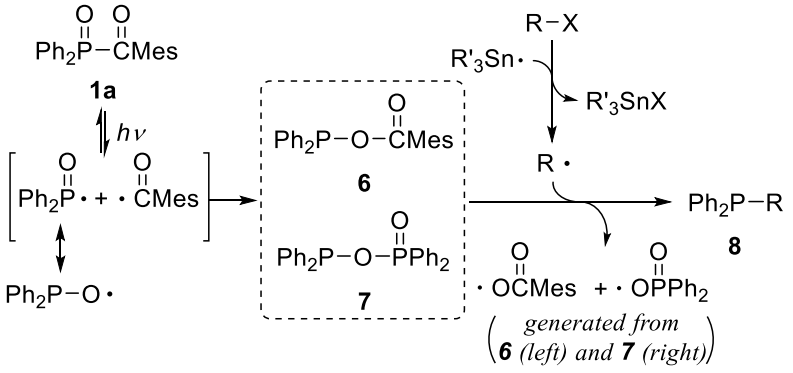
1 **2b** **3** **4**

entry	yield [%][b]	
	3	**4**
1		
	3ba, >99% (92%)	**4ba**, 95% (88%)
2[c]		
	3bb, >99% (92%)	**4bb**, 99% (94%)
3		
	3bc, >99% (91%)	**4bc**, >99% (94%)

[a]Reaction conditions: TMDPO (**1**, 0.3 mmol), diselenide (**2b**, 0.3 mmol), CH_2Cl_2 (0.6 mL), xenon lamp (500 W), room temperature, 6 h. [b]Determined by ^{31}P and ^{1}H NMR. Isolated yields are shown in parentheses.

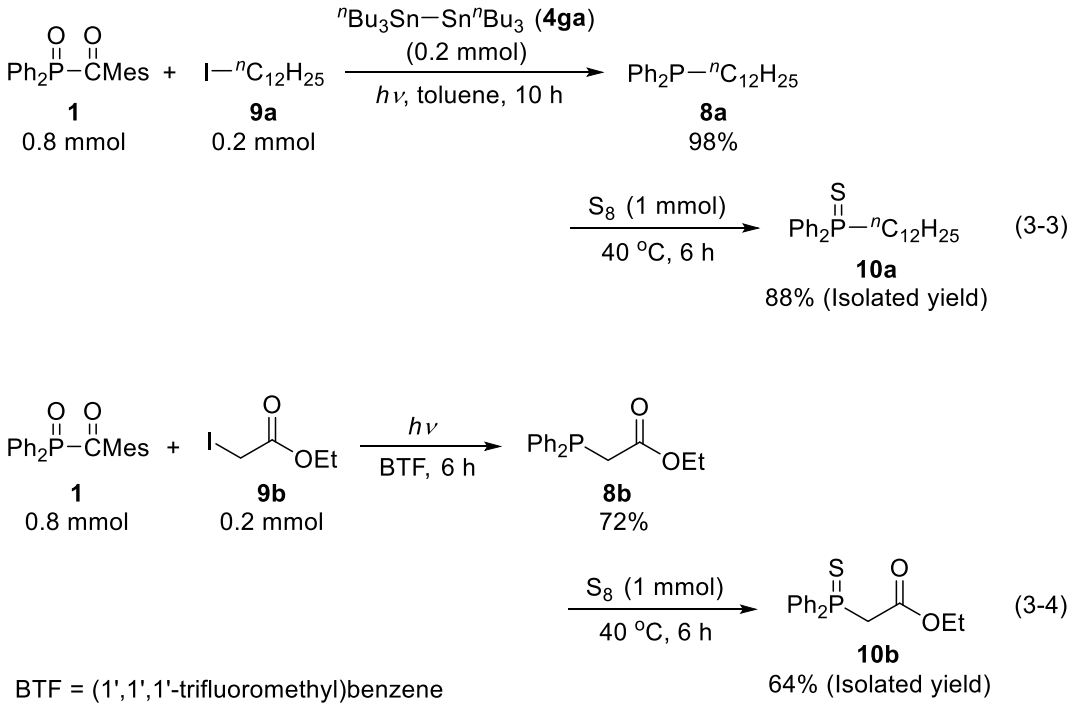
Moreover, the unsuccessful cross-coupling reaction between TMDPO and hexabutyldistannane (**2ga**) under light irradiation prompted us to investigate the possibility to use this distannane in a novel synthetic method. In particular, the author envisioned that hexabutyldistannane could be used as a radical mediator for the formation of alkyl radicals from alkyl halides in the presence of TMDPO, as summarized in Scheme 3-3. The formation of trivalent phosphorus species **6** and **7** in a solvent cage from TMDPO under photoirradiation was supported by the reports of Wirz[4b] and George.[4f] The stannyl radical formed upon photoirradiation of distannane could abstract a halogen atom from alkyl halide to form an alkyl radical. Intermediates **6** and **7** could then undergo substitution by the alkyl radical on the phosphorus atom to provide alkylphosphines **8**.

Scheme 3-3. A proposed pathway for the reductive alkylation of TMDPO with alkyl halides and distannanes



On the basis of this hypothesis, a mixture of TMDPO, hexabutyldistannane **2ga**, and 1-iodododecane **9a** in toluene was irradiated with a xenon lamp through Pyrex. The ^{31}P NMR spectrum indicated the generation of dodecylphosphine **8a** (δ = –16 ppm). Treatment of the resulting mixture with sulfur gave dodecyldiphenylphosphine sulfide **10a** in moderate yield (Eq. 3-3). Ethyl iodoacetate **9b** (Eq. 3-4) also successfully provided the corresponding alkylphosphine **8b**, but in this case the alkyl radical was formed under light irradiation without the aid of a

distannane.



3-3 Conclusion

In summary, the photoinduced coupling reactions between TMDPO and a series of ***E***–***E*** compounds have been investigated in detail, and novel synthetic methods for *S*- or *Se*-substituted thio- or selenophosphinates, respectively, and diphosphine monoxide have been successfully developed. In addition, after a thorough study of the characteristic features of the reaction of each interelement compound with TMDPO under light irradiation, a novel synthesis of alkylphosphines was successfully demonstrated. The author believes that this study of the reactivity of TMDPO under light irradiation will be useful for the development of new reactions using TMDPO as a phosphorus source.

3-4 Experimental Section

General Comment

All reactions were carried out in a sealed Pyrex NMR tube under argon atmosphere. TMDPO (**1**) was obtained from Tokyo Chemical Industry Co., Ltd. All diaryl disulfides and diphenyl diselenide were obtained from commercial suppliers. The other diaryl diselenides were synthesized according to the literature procedures.[25] Di-*n*-butyl diselenide (**2bc**) was also prepared according to the literature.[26] All solvents were distilled, dried, and degassed with argon before use.

Experimental procedure for the photoinduced reaction between TMDPO and interelement compounds 2

TMDPO (**1**, 0.3 mmol), interelement compound (**2**, 0.3 mmol), and degassed dry CH_2Cl_2 (0.6 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at room temperature. The reaction mixture was then concentrated under reduced pressure, and the product was determined by ^{1}H, ^{31}P, and appropriate multinuclear NMR analysis.

Experimental procedure for the synthesis of chalcogenophosphinates 3 and chalcogenocarboxylates 4

TMDPO (**1**, 0.3 mmol), dichalcogenide (**2**, 0.3 mmol), and degassed dry CH_2Cl_2 (0.6 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at room temperature. The reaction mixture was then concentrated under reduced pressure, and the crude mixture was purified by gel permeation chromatography to give the desired products.

S-Phenyl diphenylthiophosphinate (3aa) [CAS Registry No. 5510-78-1];[23e] white

solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.15–7.26 (m, 3H), 7.38–7.52 (m, 8H), 7.85 (ddd, $J_{H–H}$ = 12.8 Hz, 1.4 Hz, $J_{H–P}$ = 6.9 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.1 (d, $J_{C–P}$ = 4.5 Hz), 128.4 (d, $J_{C–P}$ = 13.4 Hz), 128.8, 129.0, 131.5 (d, $J_{C–P}$ = 10.5 Hz), 132.2 (d, $J_{C–P}$ = 2.9 Hz), 132.5 (d, $J_{C–P}$ = 107.4 Hz), 135.3 (d, $J_{C–P}$ = 3.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 42.0; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{16}OPS^+$: 311.0654; found: 311.0656.

S-Cyclohexyl diphenylthiophosphinate (3ab) [CAS Registry No. 157949-54-7];[23f] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.18–1.33 (m, 3H), 1.43–1.58 (m, 3H), 1.60–1.72 (m, 2H), 1.89–2.00 (m, 2H), 3.24–3.38 (m, 1H), 7.41–7.54 (m, 6H), 7.82–7.93 (m, 4H);**^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.1, 25.6, 35.4, 44.3, 128.4 (d, J_{C-P}= 13.4 Hz), 131.3 (d, J_{C-P}= 10.5 Hz), 131.9, 134.1 (d, J_{C-P}= 109.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 42.5; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{22}OPS^+$: 317.1123; found: 317.1104.

S-Benzyl diphenylthiophosphinate (3ac) [CAS Registry No. 3096-05-7];[23f] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 4.02 (d, $J_{H–H}$ = 9.2 Hz, 2H), 7.15–7.22 (m, 5H), 7.42–7.48 (m, 4H), 7.49–7.55 (m, 2H), 7.85 (ddd, $J_{H–H}$ = 13.3 Hz, 1.4 Hz, $J_{H–P}$ = 6.9 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 33.1 (d, $J_{C–P}$ = 1.9 Hz), 127.4, 128.5, 128.6 (d, $J_{C–P}$ = 13.4 Hz), 129.0, 131.5 (d, $J_{C–P}$ = 10.5 Hz), 132.2 (d, $J_{C–P}$ = 2.9 Hz), 133.0 (d, $J_{C–P}$ = 106.4 Hz), 136.8 (d, $J_{C–P}$ = 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.4; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}OPS^+$: 325.0810; found: 325.0805.

S-(4-Methylphenyl) diphenylthiophosphinate (3ad) [CAS Registry No. 5510-81-6];[27] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 7.00 (d, $J_{H–H}$ = 8.2 Hz, 2H), 7.32 (dd, $J_{H–H}$ = 8.2 Hz, $J_{H–P}$ = 1.8 Hz, 2H), 7.39–7.46 (m, 4H), 7.49 (dt, $J_{H–H}$ = 7.3 Hz, 1.8 Hz, 2H), 7.85 (ddd, $J_{H–H}$ = 12.8 Hz, 1.4 Hz, $J_{H–P}$ = 6.9 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.1, 122.2 (d, $J_{C–P}$ = 4.8 Hz), 128.4 (d, $J_{C–P}$ = 13.4 Hz), 129.9, 131.5 (d, $J_{C–P}$ = 9.6 Hz), 132.1 (d, $J_{C–P}$ = 2.9 Hz), 132.6 (d, $J_{C–P}$ = 106.4 Hz), 135.3 (d, $J_{C–P}$ = 3.8 Hz), 139.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 41.8;

HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{17}OPS^+$: 325.0810; found: 325.0830.

S-(4-Chlorophenyl) diphenylthiophosphinate (3ae) [CAS Registry No. 21081-94-7];[27] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (d, $J_{H–H}$ = 8.2 Hz, 2H), 7.34–7.54 (m, 8H), 7.78–7.89 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 124.7 (d, $J_{C–P}$ = 5.8 Hz), 128.5 (d, $J_{C–P}$ = 12.5 Hz), 129.2, 131.5 (d, $J_{C–P}$ = 10.5 Hz), 132.2 (d, $J_{C–P}$ = 107.4 Hz), 132.4 (d, $J_{C–P}$ = 2.9 Hz), 135.4, 136.4 (d, $J_{C–P}$ = 3.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 42.0; **HRMS** (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}ClOPS^+$: 345.0264; found: 345.0261.

S-(4-Methoxyphenyl) diphenylthiophosphinate (3af) [CAS Registry No. 99234-85-2];[27] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.71 (s, 3H), 6.72 (d, $J_{H–H}$ = 8.2 Hz, 2H), 7.33 (d, $J_{H–H}$ = 8.2 Hz, 2H), 7.39–7.53 (m, 6H), 7.84 (dd, $J_{H–H}$ = 11.8 Hz, $J_{H–P}$ = 7.8 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.2, 114.7, 115.9, 128.4 (d, $J_{C–P}$ = 12.4 Hz), 131.5 (d, $J_{C–P}$ = 9.5 Hz), 132.1, 136.9, 160.4 (*ipso*-carbon of diphenylphosphine oxide overlapped with the *ortho*-carbon of the thiophenyl ring); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 41.9; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}O_2PS^+$: 341.0760; found: 341.0760.

S-(3,5-Dichlorophenyl) diphenylthiophosphinate (3ah) White solid; mp 121–122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.23–7.25 (m, 1H), 7.32–7.34 (m, 2H), 7.33 (dd, $J_{H–H}$ = 1.8 Hz, 1.8 Hz, 2H), 7.52–7.45 (m, 4H), 7.56 (td, $J_{H–H}$ = 7.3 Hz, 1.4 Hz, 2H), 7.85 (ddd, $J_{H–H}$ = 12.4 Hz, 1.4 Hz, $J_{H–P}$ = 8.2 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 128.7 (d, $J_{C–P}$ = 13.4 Hz), 129.2, 129.6 (d, $J_{C–P}$ = 5.8 Hz), 131.6 (d, $J_{C–P}$ = 10.5 Hz), 131.7 (d, $J_{C–P}$ = 108.3 Hz), 132.7 (d, $J_{C–P}$ = 2.9 Hz), 133.0 (d, $J_{C–P}$ = 3.8 Hz), 135.0 (d, $J_{C–P}$ = 1.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 42.4; **IR** (KBr): 697, 724, 850, 1101, 1112, 1201, 1436, 1558, 2360, 3051 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{13}Cl_2OPS^+$: 378.9875; found: 378.9875.

Se-Phenyl diphenylselenophosphinate (3ba) [CAS Registry No. 2049-62-9];[24b] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.16 (t, $J_{H–H}$ = 7.7 Hz, 2H), 7.24 (t, $J_{H–H}$ = 7.3 Hz, 1H),

7.39–7.46 (m, 4H), 7.47–7.53 (m, 4H), 7.82 (dd, $J_{H–H}$ = 13.1 Hz, $J_{H–P}$ = 7.7 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 123.8 (d, $J_{C–P}$ = 4.5 Hz), 128.5 (d, $J_{C–P}$ = 13.4 Hz), 128.7, 129.2, 131.3 (d, $J_{C–P}$ = 10.5 Hz), 132.2 (d, $J_{C–P}$ = 2.9 Hz), 133.5 (d, $J_{C–P}$ = 97.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 40.4 (d, $J_{P–Se}$ = 382.5 Hz); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 381.3 (d, $J_{Se–P}$ = 381.5 Hz); **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{16}OPSe^+$: 359.0098; found: 359.0105.

Se-(4-Chlorophenyl) diphenylselenophosphinate (3bb) White solid; **mp** 85–86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.13 (d, $J_{H–H}$ = 8.2 Hz, 2H), 7.38–7.47 (m, 4H), 7.48–7.54 (m, 2H), 7.77–7.86 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 121.7 (d, $J_{C–P}$ = 5.8 Hz), 128.4 (d, $J_{C–P}$ = 13.4 Hz), 129.2, 131.0 (d, $J_{C–P}$ = 10.5 Hz), 132.2 (d, $J_{C–P}$ = 2.9 Hz), 132.9 (d, $J_{C–P}$ = 97.8 Hz), 135.1 (d, $J_{C–P}$ = 1.9 Hz), 137.2 (d, $J_{C–P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 40.6 (d, $J_{P–Se}$ = 377.1 Hz); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 377.8 (d, $J_{Se–P}$ = 372.7 Hz); **IR** (KBr): 723, 747, 815, 1089, 1114, 1198, 1437, 2360, 3056 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{15}ClOPSe^+$: 392.9709; found: 392.9723.

Se-n-Butyl diphenylselenophosphinate (3bc) [CAS Registry No. 882000-56-8];[24a] colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.81 (t, $J_{H–H}$= 7.3 Hz, 3H), 1.31 (sextet, $J_{H–H}$ = 7.3 Hz, 2H), 1.64 (quint, $J_{H–H}$ = 7.3 Hz, 2H), 2.83 (dt, $J_{H–H}$ = 7.3 Hz, $J_{H–P}$ = 9.5 Hz, 2H), 7.44–7.54 (m, 6H), 7.88 (dddd, $J_{H–H}$ = 13.1 Hz, 1.8 Hz, 1.4 Hz, $J_{H–P}$ = 6.8 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.3, 22.7, 25.1 (d, $J_{C–P}$ = 2.9 Hz), 32.7 (d, $J_{C–P}$ = 3.8 Hz), 128.5 (d, $J_{C–P}$ = 13.4 Hz), 131.1 (d, $J_{C–P}$ = 10.5 Hz), 132.1 (d, $J_{C–P}$ = 2.9 Hz), 134.4 (d, $J_{C–P}$ = 97.3 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 40.2 (d, $J_{P–Se}$ = 391.1 Hz); **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 215.8 (d, $J_{Se–P}$ = 393.0 Hz); **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{20}OPSe^+$: 339.0411; found: 339.0416.

S-Phenyl 2,4,6-trimethylthiobenzoate (4aa) [CAS Registry No. 50404-53-0];[28] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.38 (s, 6H), 6.86 (s, 2H), 7.39–7.48 (m, 3H), 7.49–7.54 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.1, 128.0, 128.4, 129.3, 129.5, 133.7,

134.3, 137.2, 139.5, 196.0; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{17}OS^+$: 257.0995; found: 257.1008.

S-(4-Methylphenyl) 2,4,6-trimethylthiobenzoate (4ad) White solid; **mp** 67–68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.37 (s, 6H), 2.39 (s, 3H), 6.86 (s, 2H), 7.26 (d, J_{H-H}= 7.8 Hz, 2H), 7.40 (d, J_{H-H}= 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.1, 21.3, 124.4, 128.4, 130.1, 133.7, 134.3, 137.3, 139.4, 139.8, 196.5; **IR** (KBr): 810, 842, 870, 1017, 1141, 1202, 1450, 1690, 2359, 2918 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{18}OS$: 271.1151; found: 271.1150.

S-(4-Chlorophenyl) 2,4,6-trimethylthiobenzoate (4ae) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.29 (s, 3H), 2.36 (s, 6H), 6.87 (s, 2H), 7.42 (d, J_{H-H}= 8.7 Hz, 2H), 7.45 (d, J_{H-H}= 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.1, 126.5, 128.4, 129.5, 133.7, 135.5, 135.9, 136.9, 139.7, 195.4; **IR** (NaCl): 818, 848, 869, 1014, 1094, 1206, 1476, 1681, 2920 cm^{-1}; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{15}ClOS$: 290.0532; found: 290.0532.

S-(4-Methoxyphenyl) 2,4,6-trimethylthiobenzoate (4af) White solid; **mp** 68–69 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.37 (s, 6H), 3.81 (s, 3H), 6.85 (s, 2H), 6.97 (d, $J_{H–H}$ = 8.6 Hz, 2H), 7.42 (d, $J_{H–H}$ = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.1, 55.3, 114.9, 118.6, 128.3, 133.6, 135.9, 137.2, 139.4, 160.7, 197.0; **IR** (KBr): 827, 855, 874, 1031, 1175, 1251, 1492, 1684, 2937 cm^{-1}; **HRMS** (FAB+): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{19}O_2S^+$: 287.1100; found: 287.1101.

S-(3,5-Dichlorophenyl) 2,4,6-trimethylthiobenzoate (4ah) White solid; **mp** 111–112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.36 (s, 6H), 6.88 (s, 2H), 7.41–7.44 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.1, 21.2, 128.5, 129.7, 131.1, 132.2, 133.8, 135.4, 136.5, 140.1, 194.2; **IR** (KBr): 796, 841, 862, 1143, 1203, 1404, 1558, 1693 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{17}H_{18}Cl_2OS^+$: 325.0215; found: 325.0215.

Se-Phenyl 2,4,6-trimethylselenobenzoate (4ba) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.28 (s, 3H), 2.37 (s, 6H), 6.83 (s, 2H), 7.36–7.42 (m, 3H), 7.55–7.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.0, 21.1, 127.1, 128.5, 128.9, 129.4, 132.7, 135.6, 138.9, 140.0, 200.0; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 693.9; **IR** (NaCl): 726, 740, 833, 1022, 1141, 1203, 1438, 1716, 2918 cm^{-1}; **HRMS** (FAB+): *m/z* $[M + H]^+$ calcd for $C_{16}H_{17}OSe^+$: 305.0439; found: 305.0447.

Se-(4-Chlorophenyl) 2,4,6-trimethylselenobenzoate (4bb) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.35 (s, 6H), 3.82 (s, 3H), 6.83 (s, 2H), 7.35 (d, $J_{H–H}$ = 8.7 Hz, 2H), 7.49 (d, $J_{H–H}$ = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.9, 21.1, 125.2, 128.5, 129.6, 132.6, 135.3, 136.8, 138.6, 139.7, 199.3; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 689.1; **IR** (NaCl): 812, 833, 1012, 1089, 1140. 1203, 1474, 1716, 2920 cm^{-1}; **HRMS** (FAB+): *m/z* $[M + H]^+$ calcd for $C_{16}H_{16}ClOSe^+$: 339.0049; found: 339.0035.

Se-n-Butyl 2,4,6-trimethylselenobenzoate (4bc) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, $J_{H–H}$ = 7.3 Hz, 3H), 1.44 (sextet, $J_{H–H}$ = 7.3 Hz, 2H), 1.75 (quint, $J_{H–H}$ = 7.3 Hz, 2H), 2.27 (s, 3H), 2.29 (s, 6H), 3.07 (t, $J_{H–H}$ = 7.3 Hz, 2H), 6.82 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.6, 18.9, 21.1, 23.1, 26.1, 32.6, 128.4, 132.5, 139.1, 139.9, 201.6; **^{77}Se NMR** (75 MHz, $CDCl_3$): δ 587.0; **IR** (NaCl): 843, 859, 1143. 1204, 1461, 1674, 2860, 2929, 2958 cm^{-1}; **HRMS** (FAB+): *m/z* $[M + H]^+$ calcd for $C_{14}H_{21}OSe^+$: 285.0752; found: 285.0746.

Te-Phenyl 2,4,6-trimethyltellurobenzoate (4ca) Telluroester **4ca** was decomposed by the EtOH contained in $CHCl_3$ and was obtained in 81 wt% purity (including ethyl 2,4,6-trimethylbenzoate (12 wt%) and diphenyl ditelluride **2ca** (6 wt%)). Reddish-yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.33 (s, 6H), 6.76 (s, 2H), 7.26–7.31 (m, 2H), 7.32–7.38 (m, 1H), 7.73 (dd, $J_{H–H}$ = 8.2 Hz, 1.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 18.8, 21.1, 115.4, 128.6, 129.5, 130.9, 139.4, 139.6, 140.7, 143.0, 204.1; **^{123}Te NMR** (75 MHz, $CDCl_3$): δ 1041; **IR** (NaCl): 720, 733, 812, 1017, 1136, 1198, 1434, 1696, 2917 cm^{-1}.

Experimental procedure for the synthesis of alkyldiphenylphosphine sulfide 10

TMDPO (**1**, 278.7 mg, 0.8 mmol), alkyl iodide (**9**, 0.2 mmol), 1,1,1,2,2,2-hexabutyldistannane (**2ga**, 0.2 mmol, only for Scheme 10a), and degassed dry toluene (0.6 mL) or BTF ((1',1',1'-trifluoromethyl)benzene, 0.6 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere, and the mixture was irradiated with a xenon lamp (500 W) for 6 h at room temperature. Elemental sulfur (S_8, 1 mmol) was added to the mixture under an inert atmosphere, and the resulting mixture was stirred for 6 h at 40 °C. The reaction mixture was concentrated, and **10** was isolated by gel permeation chromatography.

Dodecyldiphenylphosphine sulfide (10a) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, $J_{H–H}$ = 6.4 Hz, 3H), 1.16–1.32 (m, 16H), 1.33–1.42 (m, 2H), 1.56–1.68 (m, 2H), 2.39–2.49 (m, 2H), 7.39–7.50 (m, 6H), 7.83 (ddd, $J_{H–H}$ = 12.4 Hz, 0.9 Hz, $J_{H–P}$ = 7.3 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.0, 22.0, 22.5, 29.0, 29.16, 29.23, 29.38, 29.44 (two carbons of the alkyl chain are overlapped), 30.5 (d, $J_{C–P}$ = 16.3 Hz), 31.7, 32.4 (d, $J_{C–P}$ = 56.6 Hz), 128.4 (d, $J_{C–P}$ = 11.5 Hz), 130.9 (d, $J_{C–P}$ = 9.6 Hz), 131.2 (d, $J_{C–P}$ = 2.9 Hz), 132.9 (d, $J_{C–P}$ = 79.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.3; **IR** (NaCl): 691, 710, 755, 1104, 1437, 2853, 2925 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{35}NaPS^+$: 409.2095; found: 409.2097.

Ethyl 2-(diphenylthiophosphinyl)acetate (10b) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.10 (t, $J_{H–H}$ = 7.0 Hz, 3H), 3.65 (d, $J_{H–P}$ = 14.5 Hz, 2H), 4.02 (q, $J_{H–H}$ = 7.3 Hz, 2H), 7.44–7.56 (m, 6H), 7.88 (ddd, $J_{H–H}$ = 13.6 Hz, 1.8 Hz, $J_{H–P}$ = 6.8 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.8, 42.4 (d, $J_{C–P}$ = 47.9 Hz), 61.5, 128.5 (d, $J_{C–P}$ = 12.5 Hz), 131.3 (d, $J_{C–P}$ = 10.5 Hz), 131.8 (d, $J_{C–P}$ = 2.9 Hz), 132.0 (d, $J_{C–P}$ = 84.4 Hz), 165.7 (d, $J_{C–P}$ = 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 38.4; **IR** (NaCl): 691, 708, 1103, 1115, 1263, 1437, 1731, 2928, 2981 cm^{-1}; **HRMS** (ESI+): *m*/*z* $[M + Na]^+$ calcd for $C_{16}H_{17}NaO_2PS^+$: 327.0585; found: 327.0583.

3-5 References

1. (a) Lechtken, P.; Buethe, I.; Hesse, A. US4324744, 1982. (b) Lechtken, P.; Buethe, I.; Jacobi, M.; Trimborn, W. US4710523, 1987.

2. The absorption maximum of TMDPO is 380 nm (S_0 to S_1) and 295 nm (S_0 to S_2). The quantum yield of radical formation is φ 0.5 to 0.7.

3. (a) Sumiyoshi, T.; Katayama, M.; Schnabel, W. *Chem. Lett.* **1985**, *14*, 1647-1650. (b) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141-146. (c) Quin, L. D. *A Guide to Organophosphorus Chemistry.* John Wiley & Sons: New York, 2000.

4. (a) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148-5153. (b) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.* **1996**, *118*, 6477-6489. (c) Sluggett, G. W.; McGarry, P. F.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1996**, *118*, 7367-7372. (d) Jockusch, S.; Koptyug, I. V.; McGarry, P. F.; Sluggett, G. W.; Turro, N. J.; Watkins, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11495-11501. (e) Jockusch, S.; Turro, N. J. *J. Am. Chem. Soc.* **1998**, *120*, 11773-11777. (f) Colley, C. S.; Grills, D. C.; Besley, N. A.; Jockusch, S.; Matousek, P.; Parker, A. W.; Towrie, M.; Turro, N. J.; Gill, P. M. W.; George, M. W. *J. Am. Chem. Soc.* **2002**, *124*, 14952-14958.

5. (a) Decker, C.; Bendaikha, T. *J. Appl. Polym. Sci.* **1998**, *70*, 2269-2282. (b) Decker, C.; Zahouily, K.; Decker, D.; Nguyen, T.; Viet, T. *Polymer* **2001**, *42*, 7551-7560.

6. (a) Ikemura, K.; Ichizawa, K.; Yoshida, M.; Ito, S.; Endo, T. *Dent. Mater. J.* **2008**, *27*, 765-774. (b) Ikemura, K.; Ichizawa, K.; Jogetsu, Y.; Endo, T. *Dent. Mater. J.* **2010**, *29*, 122-131. (c) Ikemura, K.; Kadoma, Y.; Endo, T. *Dent. Mater. J.* **2011,** *30*, 769-789; (d) Miletic, V.; Santini, A. *Dent. Mater. J.* **2012**, *31*, 717-723.

7. (a) Radke, A.; Gissibl, T.; Klotzbücher, T.; Braun, P. V.; Giessen, H. *Adv. Mater.* **2011**, *23*, 3018-3021. (b) Vasilantonakis, N.; Terzaki, K.; Sakellari, I.; Purlys, V.; Gray, D.; Soukoulis, C. M.; Vamvakaki, M.; Kafesaki, M.; Farsari, M. *Adv. Mater.* **2012**, *24*, 1101-1105.

8. Tian, Y.; Zhang, Y.-L.; Ku, J.-F.; He, Y.; Xu, B.-B.; Chen, Q.-D.; Xia, H.; Sun, H.-B. *Lab on a Chip* **2010,** *10*, 2902-2905.

9. Gansel, J. K.; Thiel, M.; Rill, M. S.; Decker, M.; Bade, K.; Saile, V.; von Freymann, G.; Linden, S.; Wegener, M. *Science* **2009**, *325*, 1513-1515.

10. (a) Lindner, E.; Vordermaier, G., *Chem. Ber.* **1979**, *112*, 1456-1463. (b) Frey, G.; Lesiecki, H.; Lindner, E.; Vordermaier, G. *Chem. Ber.* **1979**, *112*, 763-772. (c) Lesiecki, H.; Lindner, E.; Vordermaier, G., *Chem. Ber.* **1979**, *112*, 793-798. (d) Lindner, E.; Kern, H. *Chem. Ber.* **1984,** *117*, 355-365. (e) Cho, C. H.; Kim, S.; Yamane, M.; Miyauchi, H.; Narasaka, K. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1665-1672. (f) Said, N.; Touil, S.; Akacha, A. B.; Efrit, M. L. *Phosphorus Sulfur Silicon Relat. Elem.* **2008**, *183*, 2726-2733. (g) Sato, Y.; Kawaguchi, S- i.; Ogawa, A. *Chem. Commun.* **2015**, *51*, 10385-10388.

11. Schmidt, U.; Müller, A.; Markau, K. *Chem. Ber.* **1964**, *97*, 405-414.

12. Ogawa, A.; Yokoyama, K.; Obayashi, R.; Han, L. B.; Kambe, N.; Sonoda, N. *Tetrahedron* **1993**, *49*, 1177-1188.

13. Troy, D.; Turpin, R.; Voigt, D., *B Soc Chim Fr I-Phys* **1979**, 241-246.

14. Craw, M. T.; Alberti, A.; Depew, M. C.; Wan, J. K. S. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3675-3676.

15. Saiful, I. S. M.; Ohba, Y.; Mochida, K.; Yamauchi, S. *Phys. Chem. Chem. Phys.* **2001**, *3*, 1011-1014.

16. Chambers, R. D. C., H. C.; Willis, C. J. , *Chem. Ind. (London)* **1960**, 76-77.

17. The ***E-E*** compounds which were most commonly used in each element were selected for the photoinduced reaction.

18. The bond-dissociation energy (BDE) of P–Te single bond (297.9 ± 10.0 $kJmol^{-1}$) is much weaker than P–S (442.0 ± 10.0 $kJmol^{-1}$) and P–Se (363.7 ± 10.0 $kJmol^{-1}$). The BDEs were referred from Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*. CRC Press: Boca Raton, 2007.

19. (a) Yoshimura, A.; Takamachi, Y.; Han, L.-B.; Ogawa, A. *Chem. Eur. J.* **2015**, *21*, 13930-13933. (b) Yoshimura, A.; Takamachi, Y.; Mihara, K.; Saeki, T.; Kawaguchi, S-i.; Han, L.-B.; Nomoto, A.; Ogawa, A. *Tetrahedron* **2015**, *21*, 13930-13933.

20. Patai, S. *The Chemistry of Organic Selenium and Tellurium compounds*. Wiley & Sons: 1987; Vol. 2, p 657.

21. At the present moment, $R^1R^2P(O)TeR^3$ species are not reported at all.

22. (a) Quin, L. D. *A Guide to Organophosphorus Chemistry*. Wiley & Sons: New York, 2000. (b) Loranger, M. W.; Beaton, S. A.; Lines, K. L.; Jakeman, D. L. *Carbohydr. Res.* **2013**, *379*, 43-50.

23. (a) Grayson, M.; Farley, C. E.; Streuli, C. A. *Tetrahedron* **1967**, *23*, 1065-1078. (b) Arisawa, M.; Ono, T.; Yamaguchi, M. *Tetrahedron Lett.* **2005**, *46*, 5669-5671. (c) Wang, J.; Huang, X.; Ni, Z.; Wang, S.; Wu, J.; Pan, Y., *Green Chem.* **2015**, *17*, 314-319. (d) Li, S.; Chen, T.; Saga, Y.; Han, L.-B., *RSC Adv.* **2015**, *5*, 71544-71546. (e) Zhang, L.; Zhang, P.; Li, X.; Xu, J.; Tang, G.; Zhao, Y. *J. Org. Chem.* **2016**, *81*, 5588-5594. (f) Renard, P.-Y.; Schwebel, H.; Vayron, P.; Josien, L.; Valleix, A.; Mioskowski, C. *Chem. Eur. J.* **2002**, *8*, 2910-2916.

24. (a) Kimura, T.; Murai, T.; Mizuhata, N. *Heteroat. Chem.* **2005**, *16*, 185-191. (b) Kawaguchi, S.-i.; Kotani, M.; Atobe, S.; Nomoto, A.; Sonoda, M.; Ogawa, A. *Organometallics* **2011**, *30*, 6766-6769. (c) Kobiki, Y.; Kawaguchi, S-i.; Ogawa, A., *Tetrahedron Lett.* **2013**, *54*, 5453-5456.

25. Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434-5447.

26. Krief, A.; Van Wemmel, T.; Redon, M.; Dumont, W.; Delmotte, C. *Angew. Chem. Int. Ed.* **1999**, *38*, 2245-2248.

27. Wang, D.; Zhao, J.; Xu, W.; Shao, C.; Shi, Z.; Li, L.; Zhang, X. *Org. Biomol. Chem.* **2017**, *15*, 545-549.

28. Imamoto, T.; Kodera, M.; Yokoyama, M. *Synthesis* **1982**, *1982*, 134-136.

Chapter 4

Highly Selective Phosphinylphosphination of Alkenes with Tetraphenyldiphosphine Monoxide

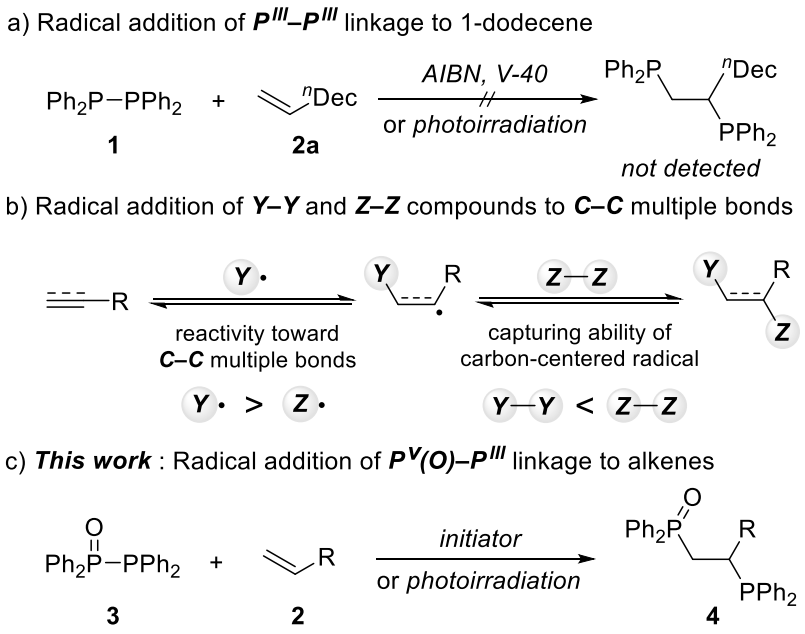
4-1 Introduction

Organophosphorus compounds play a vital role in organic synthesis, catalysis, materials chemistry, medicinal chemistry, and coordination chemistry.[1] Therefore, the development of new synthetic methods to create organophosphorus species is of great importance. For the selective introduction of phosphorus moieties onto organic molecules, the addition reaction to carbon–carbon multiple bonds is one of the most useful and atom-economical methods.[2] In particular, the 1,2-addition of phosphorus compounds bearing a P–P single bond to carbon–carbon multiple bonds is the most straightforward method for the preparation of vicinally bisphosphinated molecules,[3] which are useful bidentate ligands in transition—metal-catalyzed reactions.[4] Although several attractive examples of the addition of phosphorus compounds to alkynes have been reported,[5] to the best of the author's knowledge, the corresponding addition to alkenes has not been achieved, with the exception of the addition of specified diphosphines, such as tetramethyldiphosphine ($(Me_2P)_2$),[6] tetrachlorodiphosphine ($(Cl_2P)_2$),[7] tetrafluorodiphosphine ($(F_2P)_2$)[8], and 1,1-diaminodiphosphine,[9] to only very limited alkenes.

The author initiated the study by investigating the addition of tetraphenyldiphosphine (**1**) to 1-dodecene (**2a**) in the presence of a radical initiator (AIBN or V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)) or under photoirradiation (Scheme 4-1a). The addition reaction did not proceed at all, and **1** was recovered quantitatively. It is known that the

regioselective thioselenation of alkenes proceeds smoothly using a disulfide–diselenide mixed system,[10] although the addition to alkenes did not proceed efficiently using disulfide or diselenide species alone. In such heteroatom-mixed systems, two different heteroatom-centered radicals (***Y***•, ***Z***•) can be generated and two heteroatom-containing compounds (***Y***–***Y***, ***Z***–***Z***) with different radical capturing abilities exist. The more reactive radical attacks carbon–carbon multiple bonds and the generated carbon radical is captured by the heteroatom-containing compound with the higher capturing ability (Scheme 4-1b).

Scheme 4-1. Radical addition of diphosphine **1** and diphosphine monoxide **3** to alkenes



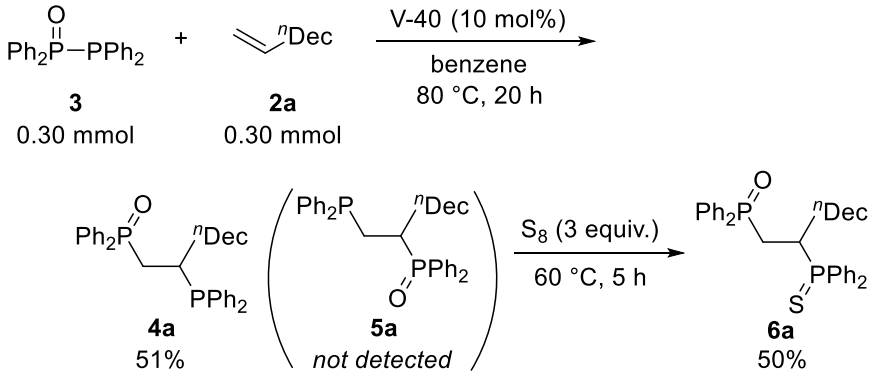
With this information in mind, the author selected tetraphenyldiphosphine monoxide **3,** bearing a $P^{V}(O)$–P^{III} single bond, as an initial phosphorus compound for the radical addition to alkenes. This is because the homolytic cleavage of the $P^{V}(O)$–P^{III} bond can afford two different phosphorus-centered radicals and **3** has pentavalent and trivalent phosphorus atoms, which might have different radical capturing abilities. When the addition reaction of **3** to alkenes was performed, the 1,2-addition of **3** to alkenes proceeded regioselectively to afford

1-phosphinyl-2-phosphinoalkanes **4** (Scheme 4-1c). Recently, organophosphines with vicinal soft (P^{III}) and hard ($P^{V}(O)$) Lewis-base centers,[11] are used as hemilabile ligands in transition-metal-catalyzed reactions.[12] Furthermore, the reduction of **4** readily affords bidentate bisphosphine ligands. Therefore, the author set out to investigate the novel phosphinylphosphination of alkenes with diphosphine monoxides.

4-2 Results and Discussion

When a mixture of tetraphenyldiphosphine monoxide (**3**, 0.3 mmol), 1-dodecene (**2a**, 0.3 mmol), and V-40 (0.03 mmol, 10 mol%) was dissolved in benzene and refluxed for 20 h, the complete consumption of **2a** and phosphinylphosphination product **4a**, which has a diphenylphosphinyl group at the terminal carbon, were confirmed by ^{1}H and ^{31}P NMR spectroscopy (Scheme 4-2). Regioisomer **5a** was not detected, and product **4a** was converted to bisphosphinoalkane 1-*P*-oxide 2-*P*-sulfide (BPOS) **6a** upon treatment with elemental sulfur.

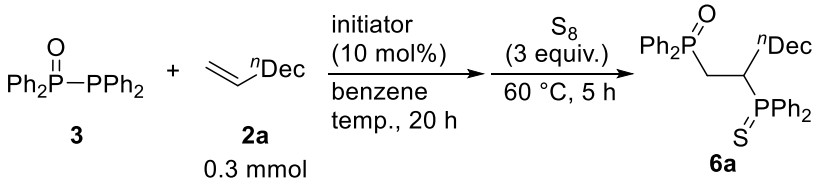
Scheme 4-2. Phosphinylphosphination of alkene **2a** with diphosphine monoxide **3**



Since a small amount of the self-polymerization product of **2a** was observed, the ratio of **3** to **2a**, initiator, and temperature were screened (Table 4-1) in order to identify the optimal conditions. When the reaction was conducted at low temperatures such as 30 °C and 60 °C, the

self-polymerization of **2a** preferentially occurred (entries 2, 3). In contrast, a high temperature (80 °C) and the use of excess **3** suppressed the polymerization effectively and thus improved the yield of **6a** (entry 4). The phosphinylphosphination did not take place without a radical initiator (entry 5). Photoirradiation with a xenon lamp (500 W) through a sealed Pyrex NMR tube afforded **6a** in a good yield, although a prolonged reaction time was required (entry 6).

Table 4-1. Optimization of the phosphinylphosphination of **2a** with **3**[a]



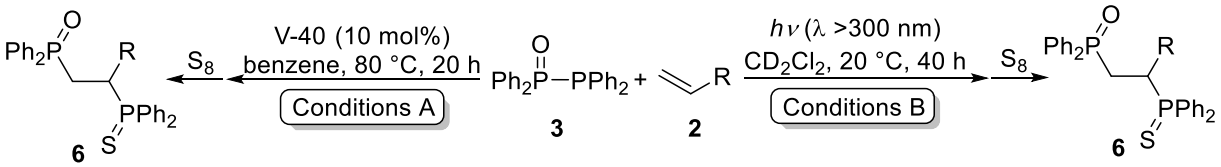
entry	**3** [mmol]	initiator	temp. [°C]	yield
1	0.30	V-40	80	50%
2[c]	0.30	AIBN	60	23%
3	0.30	V-70	30	14%
4	0.45	V-40	80	79% (72%)
5	0.45	–	80	0%
6	0.90	xenon lamp	20	78% (72%)

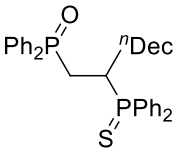
[a]Reaction conditions: **2a** (0.3 mmol), benzene (0.6 mL). [b]Determined by ^{1}H NMR. Isolated yields are shown in parentheses. [c]The substrates were dissolved in CH_2Cl_2. [d]The mixture was irradiated with a xenon lamp (500 W) through a sealed Pyrex NMR tube for 55 h at room temperature. V-40 = 1,1'-azobis(cyclohexanecarbonitrile), V-70 = 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), and AIBN = 2,2'-azobisisobutyronitrile.

The phosphinylphosphination of **3** was conducted using various alkenes with a catalytic amount of V-40 (Conditions A) or under photoirradiation (Conditions B) (Table 4-2). Vinyl ether **2b** reacted with **3** efficiently. After the mixture was treated with S_8 (1 mmol) at 60 °C for 5 h, BPOS **6b** was obtained in a good yield. Allyl ethers afforded the corresponding 1,2-adducts **6c**–**6h** in excellent yields under photoirradiation. The reaction was tolerant of various functional groups such as fluoro (**2e**), methoxy (**2f**), ester (**2g**), and nitrile (**2h**) groups. The use of allyl ester **2i** also gave the corresponding 1,2-adduct **6i** in a good yield. Cyclohexane-containing species (**2j** and **2k**) gave the corresponding BPOSs in good yields. Styrene (**2l**) did not undergo the

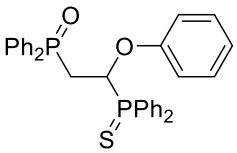
phosphinylphosphination at all, because the self-polymerization of **2l** preferentially occurred. In contrast, the reaction of allylbenzene (**2m**) proceeded to afford the desired adduct, **6m**, in a moderate yield. Furthermore, terminal alkyne **2n** also served as a viable substrate to give BPOS **6n** in a good yield, with excellent stereoselectivity.

Table 4-2. Phosphinylphosphination of several alkenes **2** with diphosphine monoxide **3**[a]

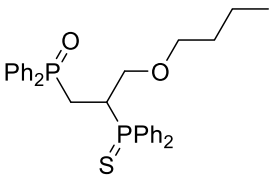




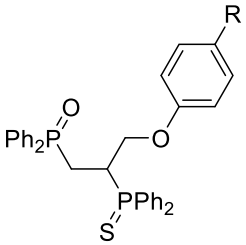
6a, 72% (**A**)
72% (**B**)[b]



6b, 70% (**A**)



6c, 83% (**B**)



R = H, **6d**, 72% (**A**)

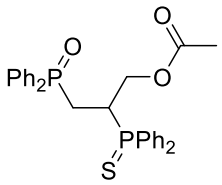
R = H, **6d**, 95% (**B**)[c]

R = F, **6e**, 90% (**B**)

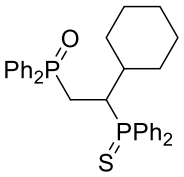
R = OMe, **6f**, 90% (**B**)

R = COOEt, **6g**, 79% (**B**)

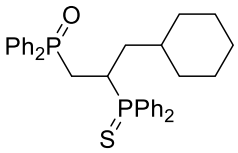
R = CN, **6h**, 80% (**B**)



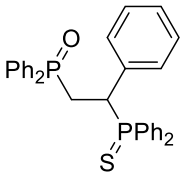
6i, 70% (**A**)



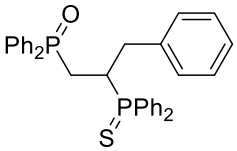
6j, 68% (**A**)



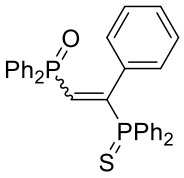
6k, 70% (**A**)



6l, 0% (**A**)



6m, 56% (**A**)

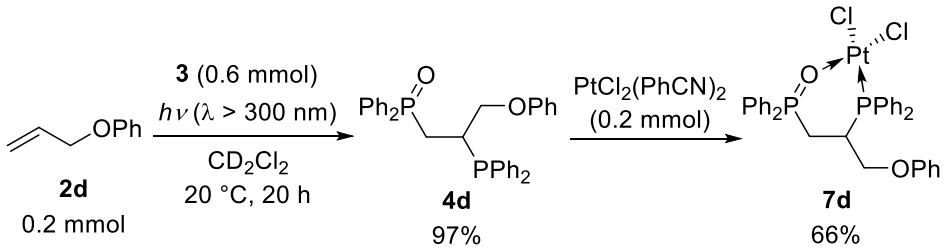


6n, 68% [*E*/*Z* = 97/3][d] (**A**)

[a]Reaction conditions **A**: 1) **3** (0.45 mmol), **2** (0.3 mmol), V-40 (0.03 mmol), benzene (0.6 mL), 80 °C, and 20 h. 2) S_8 (0.9 mmol), 60 °C, and 5 h; reaction conditions **B**: 1) **3** (0.6 mmol), **2** (0.2 mmol), CD_2Cl_2 (0.4 mL), xenon lamp (500 W), Pyrex, 20 °C, and 40 h. 2) S_8 (0.9 mmol), 60 °C, and 5 h. [b]The mixture was irradiated for 55 h. [c]The mixture was irradiated for 20 h. [d]Phenylacetylene (0.3 mmol) was added.

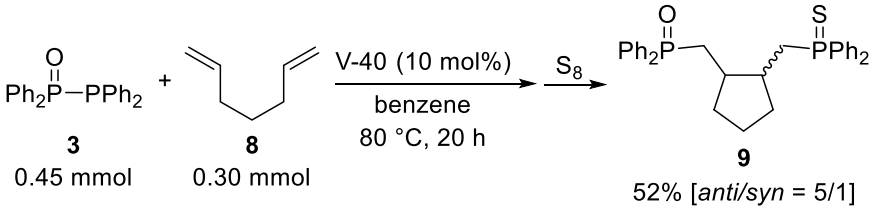
The present reaction is a novel and straightforward method to synthesize 1-phosphinyl-2-phosphinoalkanes, which can be used as ligands for transition-metal-catalyzed reactions.[12] Therefore, we set out to create a **4d**/transition metal complex using the present method (Scheme 4-3). When a mixture of diphosphine monoxide **3** (0.6 mmol) and alkene **2d** (0.2 mmol) was photoirradiated, 1-phosphinyl-2-phosphinoalkane **4d** was obtained in a high yield. Subsequently, $PtCl_2(PhCN)_2$ (0.2 mmol) was added to the resulting reaction mixture, and platinum complex **7d** was successfully isolated in 66% yield.

Scheme 4-3. The facile preparation of platinum(II)/bisphosphine monoxide complex **7d**



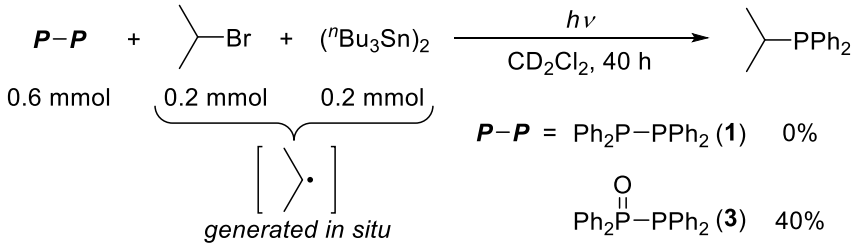
In order to shed light on the reaction pathway, diene **8** was mixed with **3** in the presence of a catalytic amount of V-40 (Scheme 4-4). As a result, cyclized product **9** (*anti*/*syn* = 5/1) was obtained and the non-cyclized 1,2-adducts were not detected at all. This result strongly indicates that the phosphinylphosphination proceeds via a radical pathway. In addition, the rate of carbon radical capture by **3** was estimated to be 5 x 10^3 $s^{-1}M^{-1}$ at most, because the rate for the 5-*exo* cyclization of 5-hexenyl radical is 4 x 10^5 s^{-1}.[13] The carbon radical capture rate of **3** is very slow, considering the rate constant for the radical attack of diphenylphosphinyl radical on isoprene (k = (1.4 ± 0.3) x 10^7 $s^{-1}M^{-1}$)[14] and phenyl vinyl ether (k = (2.6 ± 0.2) x 10^6 $s^{-1}M^{-1}$).[15] Therefore, the key step of the phosphinylphosphination is the carbon radical capture by **3**.

Scheme 4-4. Phosphinylphospnination of diene **8** with diphosphine monoxide **3**



To clarify the difference in reactivity between **1** and **3**, the author conducted the reaction between 2-bromopropane (0.2 mmol) and **1** or **3** (0.6 mmol) with hexabutylditin (0.2 mmol) under photoirradiation (Scheme 4-5). In this system, an isopropyl radical was generated in situ by the abstraction of bromine from 2-bromopropane, which was caused by the Sn–Sn bond cleavage of hexabutylditin upon near-UV irradiation. In sharp contrast to **1**, which did not react with the generated isopropyl radical, **3** caused homolytic substitution at the trivalent phosphorus atom[16] to generate isopropyl(diphenyl)phosphine in 40% yield. This result strongly indicates that the π-type alkyl radical capturing ability of **3**, such as isopropyl radicals, is much higher than that of **1**; so the phosphinylphosphination of various alkenes with **3** successfully proceeded.

Scheme 4-5. Phosphinylphospnination of diene **8** with diphosphine monoxide **3**



A plausible reaction pathway for the present reaction is illustrated in Figure 4-1a. The $P^{V}(O)$–P^{III} bond cleavage of diphosphine monoxide **3** is induced by the radical initiator or near-UV light to generate the diphenylphosphinyl ($Ph_2P(O)\cdot$) radical.[17] The generated radical reacts with alkene **2** at the terminal carbon, to generate alkyl radical **10**. Alkyl radical **10** is

captured by **3** to give 1-phosphinyl-2-phosphinoalkane **4** via an S_H2-type mechanism.

Preliminary density functional theory (DFT) calculations (B3LYP/6-31G(d)) were performed in order to explain the observed regioselectivity of the reaction. Regarding the addition of **3** to propene **2o** (R = CH_3 in Figure 4-1a), the single occupied molecular orbital (SOMO) level of **10o** (−4.85 eV) was similar to the highest occupied molecular orbital (HOMO) level of **3** (−6.30 eV), which is localized on the trivalent phosphorus atom, while the lowest occupied molecular orbital (LUMO) level of **3** was −1.34 eV (Figure 4-1b). This result indicates that the reactive cite of **3** to **10o** is at the trivalent phosphorus atom. Therefore, the radical chain reaction, involving both the radical attack of $Ph_2P(O)\cdot$ to alkenes and the radical capture of **10** by **3**, proceeds to afford 1-diphenylphosphinyl-2-phosphino alkane **4**, selectively.[18]

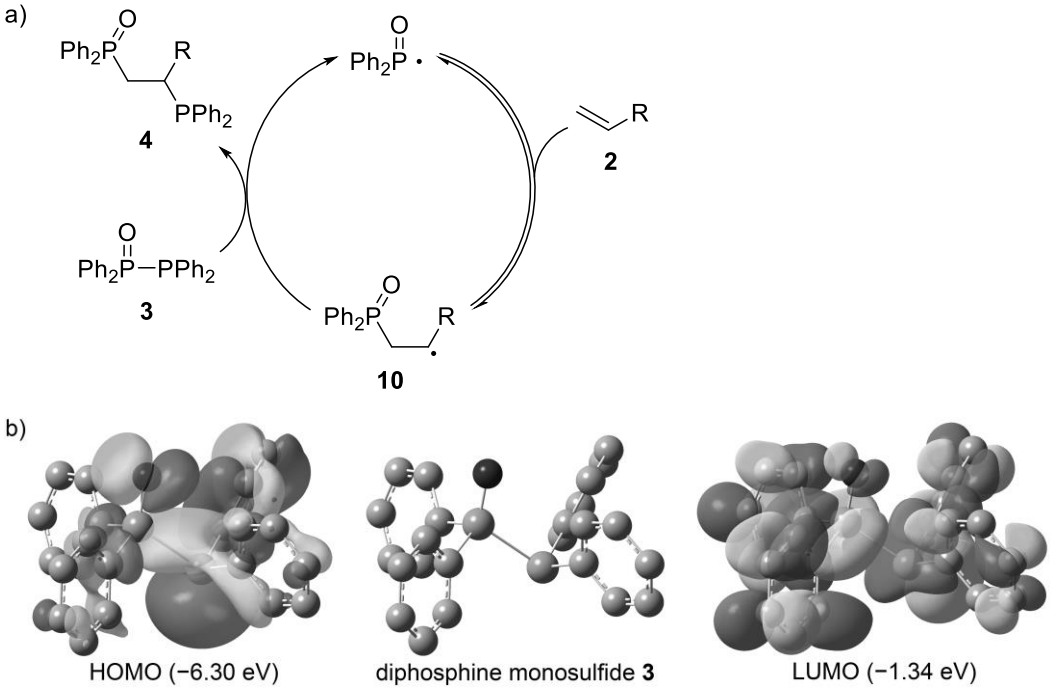


Figure 4-1. a) A plausible reaction pathway. b) Kohn-Sham molecular orbitals (HOMO and LUMO) of **3** calculated at the B3LYP/6-31G(d) level of theory

4-3 Conclusion

In summary, the author has developed a protocol for the highly regioselective addition of

tetraphenyldiphosphine monoxides to a variety of alkenes. This approach enables the regioselective introduction of diphenylphosphino and diphenylphosphinyl groups on various aliphatic alkenes and phenylacetylene. A plausible reaction pathway involving a regioselective radical capturing process was proposed. The author believes this method will facilitate significant opportunities in the synthesis of bis-phosphine monoxide ligands.

4-4 Experimental Section

General Comment

Tetraphenyldiphosphine monoxide **3** was synthesized according to the literature with minor changes.[19] A series of allyl aryl ethers **2e**–**2h** were synthesized according to the literature.[20] The other alkenes were obtained from commercial supplies. All solvents were distilled and degassed with argon before use. All theoretical calculations were performed with the Gaussian 09W Revision D.01 program package.[21] Geometry optimizations were performed with the hybrid B3LYP and UB3LYP functions in the gas-phase. The 6-31G(d) basis set was used for tetraphenyldiphosphine monoxide (**3**), 1-diphenylphosphinyl-2-propenyl radical (**10o**). The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached. The molecular orbitals were drawn by the GaussView 5.0 program.[22]

Experimental procedure for the synthesis of 3

To a 50 mL round bottom Schlenk flask, methoxydiphenylphosphine (20 mmol) and chlorodiphenylphosphine (20 mmol) dissolved in degassed benzene (10 mL) was added under an argon atmosphere, and the mixture was refluxed for 3 h. The reaction mixture was filtered and washed with benzene under an argon atmosphere to give the product in 86% yield. The purity of

the product was confirmed by ^{1}H and ^{31}P NMR.

Experimental procedure for the synthesis of 6 using radical initiator

Conditions A: to a 10 mL Schlenk test tube, tetraphenyldiphosphine monoxide (0.45 mmol), alkene (0.3 mmol), and V-40 (1,1'-azobis(cyclohexane-1-carbonitrile, 0.03 mmol) dissolved in degassed benzene (0.6 mL) were added under an argon atmosphere and the mixture was refluxed for 20 h. After the reaction, amorphous sulfur (S_8, 1 mmol) was added under inert atmosphere and then the mixture was stirred for 5 h at 60 °C. After the reaction, **6** was obtained after isolation by gel permutation chromatography.

Experimental procedure for the synthesis of 6 upon photoirradiation

Conditions B: tetraphenyldiphosphine monoxide (0.6 mmol) and alkene (0.2 mmol) in degassed dry CD_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 40 h at room temperature. After the reaction, amorphous sulfur (S_8, 1 mmol) was added under inert atmosphere and then the mixture was stirred for 5 h at 60 °C. After the reaction, **6** was obtained after isolation by gel permutation chromatography.

(2-(Diphenylthiophosphinyl)dodecyl)diphenylphosphine oxide (6a) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.67–0.76 (m, 2H), 0.77–0.84 (m, 2H), 0.84 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H), 0.92–1.02 (m, 2H), 1.04–1.32 (m, 10H), 1.38–1.51 (m, 1H), 1.66–1.83 (m, 1H), 2.44–2.64 (m, 2H), 3.35–3.49 (m, 1H), 7.31–7.51 (m, 14H), 7.76 (dd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 7.92 (dd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 8.00 (dd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.0, 22.5, 27.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 28.7, 29.07, 29.13, 29.2, 29.3, 29.5, 29.9 (d, $J_{C\text{-}P}$ = 68.1 Hz), 31.7, 32.0 (d, $J_{C\text{-}P}$ = 53.7 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and two *ortho*-carbons of

diphenylphosphinyl group are overlapped), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 77.6 Hz), 131.34 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.35 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 75.8 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 132.9 (d, $J_{C\text{-}P}$ = 97.8 Hz), 133.4 (d, $J_{C\text{-}P}$ = 99.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.6 (d, $J_{P\text{-}P}$ = 52.0 Hz), 55.2 (d, $J_{P\text{-}P}$ = 52.0 Hz); **IR** (NaCl): 534, 753, 998, 1071, 1120, 1216, 1438, 2854, 2926, 3059 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{36}H_{44}NaOP_2S$: 609.2486, Found: 609.2487.

(2-(Diphenylthiophosphinyl)-2-phenoxyethyl)diphenylphosphine oxide (6b) White solid; **mp**. 188–189 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.88–2.99 (m, 1H), 3.13–3.23 (m, 1H), 5.90 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, $J_{H\text{-}P}$ = 11.0 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 1H), 6.50 (d, $J_{H\text{-}H}$ = 7.8 Hz, 2H), 6.67 (t, $J_{H\text{-}H}$ = 7.3 Hz, 1H), 6.82–6.87 (m, 2H), 7.24 (ddd, $J_{H\text{-}H}$ = 14.7 Hz, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 2.8 Hz, 4H), 7.29–7.34 (m, 2H), 7.37–7.52 (m, 6H), 7.60 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 7.3 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.65 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.73 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 7.3 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 8.12 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 7.3 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 31.0 (dd, $J_{C\text{-}P}$ = 68.1 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 75.6 (dd, $J_{C\text{-}P}$ = 66.1 Hz, $J_{C\text{-}P}$ = 5.8 Hz), 115.9, 121.4, 127.8 (d, $J_{C\text{-}P}$ = 76.7 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6, 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 78.6 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 132.2 (d, $J_{C\text{-}P}$ = 102.6 Hz), 132.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 100.6 Hz), 157.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.4 (d, $J_{P\text{-}P}$ = 47.7 Hz), 48.0 (d, $J_{P\text{-}P}$ = 47.7 Hz); **IR** (KBr): 519, 689, 738, 807, 971, 1042, 1100, 1119, 1178, 1220, 1436, 1498, 1590, 2944, 3050 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{28}NaO_2P_2S$: 561.1183, Found: 561.1182.

(2-Butoxy-2-(diphenylthiophosphinyl)ethyl)diphenylphosphine oxide (6c) White solid; **mp.** 78–79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.71 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H), 0.91–1.04 (m, 4H), 2.46–2.54 (m, 2H), 2.84–2.96 (m, 2H), 3.55–3.65 (m, 2H), 3.66–3.78 (m, 1H), 7.35–7.53 (m, 14H), 7.72 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.87–7.96 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.7, 18.9, 26.6 (d, $J_{C\text{-}P}$ = 67.1 Hz), 31.0, 34.3 (d, $J_{C\text{-}P}$ = 52.7 Hz), 68.6, 70.5, 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.52 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.54 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz, four *meta*-carbons of diphenylthiophosphinyl group are overlapped), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.3 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.6 (d, $J_{C\text{-}P}$ = 81.5 Hz, two *ipso*-carbons of diphenylthiophosphinyl group are overlapped), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.9 (d, $J_{C\text{-}P}$ = 99.7 Hz), 133.1 (d, $J_{C\text{-}P}$ = 99.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 47.7 Hz), 53.1 (d, $J_{P\text{-}P}$ = 47.7 Hz); **IR** (NaCl): 693, 721, 752, 1102, 1118, 1184, 1437, 2869, 2960, 3059 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{31}H_{34}NaO_2P_2S$: 555.1652, Found: 555.1656.

(2-(Diphenylthiophosphinyl)-3-phenoxypropyl)diphenylphosphine oxide (6d) White solid; **mp**. 179–180 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.47–2.66 (m, 2H), 3.77–3.90 (m, 1H), 4.21 (ddd, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}P}$ = 8.2 Hz, $J_{H\text{-}H}$ = 7.7 Hz, 1H), 4.50 (ddd, $J_{H\text{-}H}$ = 12.7 Hz, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}P}$ = 4.5 Hz, 1H), 6.25 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 6.80 (t, $J_{H\text{-}H}$ = 7.3 Hz, 1H), 7.05 (dd, $J_{H\text{-}H}$ = 8.2 Hz, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.32–7.44 (m, 10H), 7.45–7.55 (m, 4H), 7.71 (ddd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}P}$ = 6.8 Hz, $J_{H\text{-}H}$ = 1.8 Hz, 2H), 7.85–7.94 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.5 (d, $J_{C\text{-}P}$ = 67.7 Hz), 33.7 (dd, $J_{C\text{-}P}$ = 53.4 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 65.4, 114.0, 120.6, 128.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and two *ortho*-carbons of diphenylphosphinyl group are overlapped), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.9, 130.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 89.7 Hz), 131.26 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.30 (d, $J_{C\text{-}P}$ = 79.2 Hz), 131.9 (two

para-carbons of diphenylphosphinyl group are overlapped), 132.5 (d, $J_{C\text{-}P}$ = 100.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 99.2 Hz), 157.2; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 47.3 Hz), 52.3 (d, $J_{P\text{-}P}$ = 47.3 Hz); **IR** (KBr): 692, 720, 750, 804, 996, 1099, 1144, 1178, 1232, 1436, 1467, 1585, 2920, 3054, 3375 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{33}H_{30}NaO_2P_2S$: 575.1339, Found: 575.1334.

(2-(Diphenylthiophosphinyl)-3-(4-fluorophenoxy)propyl)diphenylphosphine oxide (6e) White solid; **mp**. 223–224 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.44–2.64 (m, 2H), 3.74–3.87 (m, 1H), 4.18 (ddd, $J_{H\text{-}H}$ = 10.1 Hz, $J_{H\text{-}P}$ = 8.2 Hz, $J_{H\text{-}H}$ = 7.8 Hz, 1H), 4.45 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, $J_{H\text{-}H}$ = 10.1 Hz, $J_{H\text{-}P}$ = 4.1 Hz, 1H), 6.19 (dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{H\text{-}F}$ = 4.4 Hz, 2H), 6.74 (dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{H\text{-}F}$ = 8.2 Hz, 2H), 7.33–7.54 (m, 14H), 7.70 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.84–7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.6 (d, $J_{C\text{-}P}$ = 68.1 Hz), 33.8 (dd, $J_{C\text{-}P}$ = 53.7 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 66.2, 115.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.3 (d, $J_{C\text{-}F}$ = 23.0 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.5 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and two *ortho*-carbons of diphenylphosphinyl group are overlapped), 128.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 79.6 Hz), 131.36 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.44 (d, $J_{C\text{-}P}$ = 78.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz, four *meta*-carbons of diphenylphosphinyl group are overlapped), 131.9 (two *para*-carbons of diphenylphosphinyl group are overlapped), 132.5 (d, $J_{C\text{-}P}$ = 99.7 Hz), 132.8 (d, $J_{C\text{-}P}$ = 98.7 Hz), 153.4, 157.2 (d, $J_{C\text{-}P}$ = 237.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.3 (d, $J_{P\text{-}P}$ = 47.7 Hz), 52.2 (d, $J_{P\text{-}P}$ = 47.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$): δ −123.9; **IR** (KBr): 694, 725, 825, 997, 1071, 1100, 1115, 1187, 1250, 1436, 1533, 2920, 3054 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{33}H_{29}FNaO_2P_2S$: 593.1245, Found: 593.1241.

(2-(Diphenylthiophosphinyl)-3-(4-methoxyphenoxy)propyl)diphenylphosphine oxide (6f) White solid; **mp**. 169–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.46–2.64 (m, 2H), 3.70 (s, 3H), 3.76–3.88 (m, 1H), 4.16 (ddd, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}P}$ = 8.2 Hz, $J_{H\text{-}H}$ = 7.7 Hz, 1H), 4.43 (ddd, $J_{H\text{-}H}$ =

12.7 Hz, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}P}$ = 4.5 Hz, 1H), 6.19 (d, $J_{H\text{-}H}$ = 9.1 Hz, 2H), 6.61 (d, $J_{H\text{-}H}$ = 9.1 Hz, 2H), 7.32–7.55 (m, 14H), 7.72 (ddd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}P}$ = 7.3 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 2H), 7.85–7.94 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.6 (d, $J_{C\text{-}P}$ = 67.7 Hz), 33.8 (d, $J_{C\text{-}P}$ = 53.4 Hz), 55.6, 66.1, 114.1, 114.9, 128.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.68 (d, $J_{C\text{-}P}$ = 12.4 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and two *ortho*-carbons of diphenylphosphinyl group are overlapped), 128.72 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 83.0 Hz), 131.28 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.33 (d, $J_{C\text{-}P}$ = 79.2 Hz), 131.9 (two *para*-carbons of diphenylphosphinyl group are overlapped), 132.5 (d, $J_{C\text{-}P}$ = 100.1 Hz), 132.7 (d, $J_{C\text{-}P}$ = 100.1 Hz), 151.4, 153.7; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.3 (d, $J_{P\text{-}P}$ = 47.3 Hz), 52.4 (d, $J_{P\text{-}P}$ = 47.3 Hz); **IR** (KBr): 695, 722, 800, 997, 1034, 1069, 1098, 1194, 1226, 1436, 1457, 1506, 1558, 2937, 3056 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{34}H_{32}NaO_3P_2S$: 605.1445, Found: 605.1449.

Ethyl 4-(2-(diphenylthiophosphinyl)-3-(diphenylphosphinyl)propoxy)benzoate (6g) White solid; **mp**. 156–157 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1,36 (t, 3H), 2.43–2.66 (m, 2H), 3.77–3.91 (m, 1H), 4.23–4.36 (m, 1H), 4.31 (q, $J_{H\text{-}H}$ = 7.0 Hz, 2H), 4.55 (ddd, $J_{H\text{-}H}$ = 12.7 Hz, $J_{H\text{-}H}$ = 10.0 Hz, $J_{H\text{-}P}$ = 4.1 Hz, 1H), 6.25 (d, $J_{H\text{-}H}$ = 9.1 Hz, 2H), 7.33–7.55 (m, 14H), 7.71 (dd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}P}$ = 6.8 Hz, 2H), 7.83–7.93 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.3, 26.5 (d, $J_{C\text{-}P}$ = 66.8 Hz), 33.6 (dd, $J_{C\text{-}P}$ = 53.4 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 60.6, 65.8, 113.7, 122.9, 128.3 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.4 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and four *ortho*-carbons of diphenylphosphinyl group are overlapped), 130.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 80.1 Hz), 131.1 (two *para*-carbons of diphenylthiophosphinyl group and an *ipso*-carbon of benzoate moiety are overlapped), 131.3 (d, $J_{C\text{-}P}$ = 76.3 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 3.8 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 132.4 (d, $J_{C\text{-}P}$ = 100.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 103.0 Hz), 160.9, 166.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 47.3 Hz), 52.0 (d, $J_{P\text{-}P}$ = 47.3 Hz); **IR**

(NaCl): 694, 723, 755, 848, 998, 1103, 1170, 1216, 1253, 1279, 1438, 1510, 1606, 1706, 2984, 3013 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{36}H_{34}NaO_4P_2S$: 647.1551, Found: 647.1547.

4-(2-(Diphenylthiophosphinyl)-3-(diphenylphosphinyl)propoxy)benzonitrile (6h) White solid; **mp**. 157–158 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.44 (ddd, J_{H-H} = 15.4 Hz, J_{H-H} = 15.0 Hz, J_{H-P} = 11.8 Hz, 1H), 2.52–2.64 (m, 1H), 3.73–3.85 (m, 1H), 4.35 (ddd, J_{H-H} = 10.0 Hz, J_{H-P} = 8.2 Hz, J_{H-H} = 7.7 Hz, 1H), 4.65 (ddd, J_{H-H} = 13.1 Hz, J_{H-H} = 10.0 Hz, J_{H-P} = 3.6 Hz, 1H), 6.33 (d, J_{H-H} = 9.1 Hz, 2H), 7.33–7.57 (m, 16H), 7.69 (dd, J_{H-H} = 11.3 Hz, J_{H-P} = 7.3 Hz, 2H), 7.81–7.89 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.4 (d, J_{C-P} = 67.7 Hz), 33.5 (d, J_{C-P} = 54.4 Hz), 66.0, 104.0, 114.9, 119.1, 128.3 (d, J_{C-P} = 12.4 Hz), 128.8 (d, J_{C-P} = 12.4 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and four *ortho*-carbons of diphenylphosphinyl group are overlapped), 130.4 (d, J_{C-P} = 9.5 Hz), 130.5 (d, J_{C-P} = 80.1 Hz), 130.7 (d, J_{C-P} = 9.5 Hz), 131.36 (d, J_{C-P} = 79.2 Hz), 131.37 (d, J_{C-P} = 9.5 Hz), 131.5 (d, J_{C-P} = 9.5 Hz), 131.8 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.09 (d, J_{C-P} = 101.1 Hz), 132.10 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.6 (d, J_{C-P} = 97.3 Hz), 133.5, 160.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, J_{P-P} = 47.3 Hz), 51.8 (d, J_{P-P} = 47.3 Hz); **IR** (KBr): 693, 723, 834, 998, 1099, 1173, 1259, 1436, 1506, 2223, 2925, 3052 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{34}H_{29}NNaO_2P_2S$: 600.1292, Found: 600.1295.

2-(Diphenylthiophosphinyl)-3-(diphenylphosphinyl)propyl acetate (6i) White solid; **mp**. 148–149 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.41 (s, 3H), 2.45 (dddd, J_{H-H} = 16.5 Hz, J_{H-H} = 15.6 Hz, J_{H-P} = 12.4 Hz, J_{H-P} = 1.8 Hz, 1H), 2.57 (dddd, J_{H-H} = 15.6 Hz, J_{H-H} = 10.0 Hz, J_{H-P} = 8.2 Hz, J_{H-P} = 3.2 Hz, 1H), 3.79–3.91 (m, 1H), 4.35 (dd, J_{H-H} = 17.4 Hz, J_{H-P} = 6.4 Hz, 2H), 7.34–7.54 (m, 14H), 7.73 (ddd, J_{H-H} = 11.5 Hz, J_{H-P} = 6.9 Hz, J_{H-H} = 1.4 Hz, 2H), 7.90–7.97 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.0, 26.9 (d, J_{C-P} = 67.7 Hz), 32.4 (dd, J_{C-P} = 54.4 Hz, J_{C-P} = 2.9 Hz), 62.6, 128.4 (d, J_{C-P} = 11.4 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 128.7 (d, J_{C-P} = 11.4 Hz), 128.8 (d, J_{C-P} = 11.4 Hz), 130.55 (d, J_{C-P} = 80.1 Hz), 130.58 (d, J_{C-P} = 8.6 Hz), 130.7 (d, J_{C-P} = 8.6 Hz), 131.3 (d, J_{C-P} =

81.1 Hz), 131.4 (d, $J_{C\text{-}P}$ = 8.6 Hz, four *meta*-carbons of diphenylphosphinyl group are overlapped), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 132.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 102.0 Hz), 132.8 (d, $J_{C\text{-}P}$ = 100.1 Hz), 170.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.7 (d, $J_{P\text{-}P}$ = 43.0 Hz), 51.1 (d, $J_{P\text{-}P}$ = 43.0 Hz); **IR** (NaCl): 694, 723, 755, 1100, 1120, 1181, 1216, 1438, 1740, 2986, 3018 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{29}H_{28}NaO_3P_2S$: 541.1132, Found: 541.1132.

(2-Cyclohexyl-2-(diphenylthiophosphinyl)ethyl)diphenylphosphine oxide (6j) White solid; **mp**. 222–223 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.74–0.98 (m, 3H), 0.99–1.09 (m, 1H), 1.35–1.43 (m, 2H), 1.47–1.58 (m, 3H), 1.62–1.76 (m, 1H), 1.81–1.88 (m, 1H), 2.51–2.65 (m, 1H), 2.72 (dddd, $J_{H\text{-}H}$ = 16.0 Hz, $J_{H\text{-}H}$ = 13.7 Hz, $J_{H\text{-}P}$ = 9.6 Hz, $J_{H\text{-}P}$ = 4.1 Hz, 1H), 3.21–3.32 (m, 1H), 7.26–7.52 (m, 14H), 7.72 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.7 Hz, 2H), 7.88–7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.4, 25.7 (d, $J_{C\text{-}P}$ = 69.0 Hz), 26.1, 26.4, 30.2, 33.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 37.0 (dd, $J_{C\text{-}P}$ = 52.7 Hz, $J_{C\text{-}P}$ = 1.9 Hz), 37.8, 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.55 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.58 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.5 (d, $J_{C\text{-}P}$ = 8.6 Hz, four *meta*-carbons of diphenylphosphinyl group are overlapped), 131.70 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.74 (d, $J_{C\text{-}P}$ = 76.7 Hz), 132.7 (d, $J_{C\text{-}P}$ = 79.6 Hz), 133.1 (d, $J_{C\text{-}P}$ = 99.7 Hz), 133.6 (d, $J_{C\text{-}P}$ = 99.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.7 (d, $J_{P\text{-}P}$ = 51.6 Hz), 54.9 (d, $J_{P\text{-}P}$ = 51.6 Hz); **IR** (KBr): 695, 724, 995, 1116, 1180, 1256, 1436, 1558, 1653, 2851, 2925, 3052 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{34}NaOP_2S$: 551.1703, Found: 551.1701.

(3-Cyclohexyl-2-(diphenylthiophosphinyl)propyl)diphenylphosphine oxide (6k) White solid; **mp**. 200–201 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.20–0.32 (m, 1H), 0.40–0.74 (m, 4H), 0.78–0.94 (m, 1H), 1.19–1.26 (m, 1H), 1.28–1.63 (m, 6H), 2.39–2.49 (m, 1H), 2.52–2.66 (m, 1H),

3.51–3.63 (m, 1H), 7.32 (dt, J_{H-H} = 7.5 Hz, J_{H-H} = 2.7 Hz, 2H), 7.37–7.54 (m, 12H), 7.77 (ddd, J_{H-H} = 11.3 Hz, J_{H-P} = 6.8 Hz, J_{H-H} = 1.8 Hz, 2H), 7.94 (ddd, J_{H-H} = 12.2 Hz, J_{H-P} = 7.3 Hz, J_{H-H} = 1.8 Hz, 2H), 8.05 (ddd, J_{H-H} = 12.2 Hz, J_{H-P} = 7.3 Hz, J_{H-H} = 1.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.7, 25.9, 26.1, 29.1 (dd, J_{C-P} = 53.7 Hz, J_{C-P} = 2.9 Hz), 30.9 (d, J_{C-P} = 67.1 Hz), 32.6, 33.0, 35.0 (d, J_{C-P} = 7.7 Hz), 37.6, 128.3 (d, J_{C-P} = 11.5 Hz), 128.5 (d, J_{C-P} = 11.5 Hz), 128.59 (d, J_{C-P} = 11.5 Hz), 128.64 (d, J_{C-P} = 11.5 Hz), 130.3 (d, J_{C-P} = 9.6 Hz), 130.9 (d, J_{C-P} = 9.6 Hz), 131.2 (d, J_{C-P} = 77.5 Hz), 131.46 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.51 (d, J_{C-P} = 9.6 Hz), 131.6 (d, J_{C-P} = 76.7 Hz), 131.7 (two *para*-carbons of diphenylphosphinyl group are overlapped), 131.8 (d, J_{C-P} = 9.6 Hz), 133.1 (d, J_{C-P} = 97.8 Hz), 133.9 (d, J_{C-P} = 99.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.9 (d, J_{P-P} = 47.7 Hz), 56.5 (d, J_{P-P} = 47.7 Hz); **IR** (KBr): 695, 724, 889, 998, 1119, 1221, 1437, 1558, 1641, 2851, 2922, 3058 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{33}H_{36}NaOP_2S$: 565.1860, Found: 565.1851.

(2-(Diphenylthiophosphinyl)-3-phenylpropyl)diphenylphosphine oxide (6m) White solid; **mp**. 187–188 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.46 (dddd, J_{H-H} = 16.8 Hz, J_{H-H} = 15.9 Hz, J_{H-P} = 11.8 Hz, J_{H-P} = 1.8 Hz, 1H), 2.60 (dddd, J_{H-H} = 15.9 Hz, J_{H-H} = 10.4 Hz, J_{H-P} = 9.1 Hz, J_{H-P} = 4.5 Hz, 1H), 3.09–3.27 (m, 1H), 3.84–3.97 (m, 1H), 6.82–6.87 (m, 3H), 6.90–6.94 (m, 2H), 7.08 (dt, J_{H-H} = 7.7 Hz, J_{H-P} = 2.3 Hz, 2H), 7.19 (t, J_{H-H} = 7.3 Hz, 1H), 7.29–7.48 (m, 11H), 7.59–7.68 (m, 4H), 7.92 (ddd, J_{H-H} = 12.2 Hz, J_{H-P} = 8.6 Hz, J_{H-H} = 1.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 29.6 (d, J_{C-P} = 67.7 Hz), 34.1 (dd, J_{C-P} = 52.5 Hz, J_{C-P} = 2.9 Hz), 35.5, 125.8, 127.7, 127.8 (d, J_{C-P} = 11.4 Hz), 128.57 (d, J_{C-P} = 11.4 Hz, two *ortho*-carbons of diphenylthiophosphinyl group and two *ortho*-carbons of diphenylphosphinyl group are overlapped), 128.61 (d, J_{C-P} = 11.4 Hz), 129.2, 130.5 (d, J_{C-P} = 9.5 Hz, four *meta*-carbons of diphenylthiophosphinyl group are overlapped), 130.6 (d, J_{C-P} = 77.3 Hz), 130.8 (d, J_{C-P} = 2.9 Hz), 131.2 (d, J_{C-P} = 9.5 Hz), 131.32 (d, J_{C-P} = 9.5 Hz), 131.33 (d, J_{C-P} = 2.9 Hz), 131.5 (d, J_{C-P} = 77.3 Hz), 131.6 (d, J_{C-P} = 1.9 Hz), 131.7 (d, J_{C-P} = 1.9 Hz), 133.2 (d, J_{C-P} = 99.2 Hz, two *ipso*-carbons of diphenylphosphinyl group are

overlapped), 138.7 (d, $J_{C\text{-}P}$ = 4.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.2 (d, $J_{P\text{-}P}$ = 47.3 Hz), 55.1 (d, $J_{P\text{-}P}$ = 47.3 Hz); **IR** (KBr): 698, 720, 998, 1027, 1072, 1100, 1204, 1436, 1558, 2852, 2924, 3052 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{33}H_{30}NaOP_2S$: 569.1390, Found: 569.1394.

(E)-(2-(Diphenylthiophosphinyl)-2-phenylvinyl)diphenylphosphine oxide (6n) White solid; **mp**. 194–195 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.81–6.87 (m, 4H), 6.96–7.02 (m, 1H), 7.26–7.31 (m, 4H), 7.34–7.39 (m, 6H), 7.46 (dt, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}H}$ = 1.8 Hz, 2H), 7.53 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 4H), 7.71 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, $J_{H\text{-}P}$ = 6.9 Hz, $J_{H\text{-}H}$ = 1.4 Hz, 4H), 7.72 (dd, $J_{H\text{-}P}$ = 25.2 Hz, $J_{H\text{-}P}$ = 20.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 127.1, 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz, the *ortho*-carbons of diphenylthiophosphinyl group and the *ortho*-carbons of diphenylphosphinyl group are overlapped), 129.7 (d, $J_{C\text{-}P}$ = 84.4 Hz), 129.87, 129.91, 130.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.0 (d, $J_{C\text{-}P}$ = 101.6 Hz), 133.3 (t, $J_{C\text{-}P}$ = 7.7 Hz), 138.4 (dd, $J_{C\text{-}P}$ = 88.2 Hz, $J_{C\text{-}P}$ = 8.6 Hz), 156.5 (d, $J_{C\text{-}P}$ = 58.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 18.5 (d, $J_{P\text{-}P}$ = 52.0 Hz), 48.5 (d, $J_{P\text{-}P}$ = 52.0 Hz); **IR** (KBr): 648, 692, 724, 750, 786, 1099, 1185, 1312, 1436, 1558, 1683, 3031, 3053 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{26}NaOP_2S$: 543.1077, Found: 543.1078.

Experimental procedure for the synthesis of 4d/platinum(II) complex 7d

Tetraphenyldiphosphine monoxide (0.6 mmol) and allylphenylether (0.2 mmol) in degassed dry CD_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an inert atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 40 h at room temperature. The reaction mixture was then concentrated, and $PtCl_2(PhCN)_2$ (0.2 mmol) in degassed dry $CDCl_3$ was added under inert atmosphere. The reaction mixture was stirred at room temperature for 10 min. After the reaction, **7d** was obtained after isolation by column chromatography on silica gel.

Dichloro[[(2-(diphenylphosphino-κP)-3-phenoxypropyl]diphenylphosphine oxide-κO] platinum(II) (7d) Light yellow solid; **mp**. 124–125 °C (decomposition); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.42–2.59 (m, 1H), 2.80–2.95 (m, 1H), 3.82–3.93 (m, 1H), 4.06–4.18 (m, 1H), 4.58–4.69 (m, 1H), 6.24–6.31 (m, 2H), 6.78–6.84 (m, 1H), 6.98–7.05 (m, 2H), 7.20–7.31 (m, 6H), 7.32–7.41 (m, 5H), 7.43–7.49 (m, 1H), 7.57–7.71 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.3 (dd, $J_{C\text{-}P}$ = 37.2 Hz, $J_{C\text{-}P}$ = 20.0 Hz), 28.5 (dd, $J_{C\text{-}P}$ = 43.9 Hz, $J_{C\text{-}P}$ = 21.9 Hz), 66.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 114.1 (d, $J_{C\text{-}P}$ = 4.8 Hz), 120.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 127.9 (dt, $J_{C\text{-}P}$ = 46.7 Hz, $J_{C\text{-}P}$ = 4.8 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.8 (dd, $J_{C\text{-}P}$ = 28.6 Hz, $J_{C\text{-}P}$ = 2.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 130.4 (d, $J_{C\text{-}P}$ = 18.1 Hz), 130.5 (d, $J_{C\text{-}P}$ = 18.1 Hz), 130.6 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.5 (two *para*-carbons of diphenylphosphino group are overlapped), 131.7 (two *para*-carbons of diphenylphosphinyl group are overlapped), 132.8 (dd, $J_{C\text{-}P}$ = 98.2 Hz, $J_{C\text{-}P}$ = 6.7 Hz), 134.3 (dquint, $J_{C\text{-}P}$ = 47.2 Hz, J = 5.7 Hz), 157.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.6 (dd with two satellites, $J_{P\text{-}Pt}$ = 2560 Hz, $J_{P\text{-}P}$ = 39.0 Hz, $J_{P\text{-}P}$ = 17.3 Hz), 30.7 (dd, $J_{P\text{-}P}$ = 43.4 Hz, $J_{P\text{-}P}$ = 21.7 Hz); **IR** (KBr): 517, 692, 720, 745, 801, 873, 989, 1102, 1119, 1185, 1238, 1288, 1436, 1490, 1558, 1586, 1596, 2884, 2891, 2910, 2958, 3054 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{33}H_{30}Cl_2NaO_2P_2Pt$: 809.0593, Found: 809.0619.

4-5 References

1. Quin, L. D. *A Guide to Organophosphorus Chemistry.* John Wiley & Sons: New York, 2000.

2. For the addition reactions of *H*-phosphonates and phosphine oxides to carbon–carbon multiple bonds, see; (a) Xu, Q.; Han, L.-B., *J. Organomet. Chem.* **2011**, *696*, 130-140. (b) Bunlaksananusorn, T.; Knochel, P. *Tetrahedron Lett.* **2002**, *43*, 5817-5819. (c) Khemchyan, L. L.; Ivanova, J. V.; Zalesskiy, S. S.; Ananikov, V. P.; Beletskaya, I. P.; Starikova, Z. A. *Adv. Synth. Catal.* **2014,** *356*, 771-780.

3. Yorimitsu, H. *Beilstein J. Org. Chem.* **2013**, *9*, 1269-1277.

4. (a) Fruchey, E. R.; Monks, B. M.; Cook, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 13130-13133. (b) Fan, J.-H.; Wei, W.-T.; Zhou, M.-B.; Song, R.-J.; Li, J.-H. *Angew. Chem. Int. Ed.* **2014**, *53*, 6650-6654. (c) Uesugi, S.; Li, Z.; Yazaki, R.; Ohshima, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 1611-1615. (d) Arisawa, M.; Ichikawa, T.; Yamaguchi, M. *Chem. Commun.* **2015**, *51*, 8821-8824.

5. (a) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254-258. (b) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694-1696. (c) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937-5945. (d) Kawaguchi, S.-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919-3922.

6. Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226-2231.

7. Drieß, M.; Haiber, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 215-219.

8. (a) Morse, K. W.; Morse, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 8469-8470. (b) Morse, J. G.; Morse, K. W. *Inorg. Chem.* **1975**, *14*, 565-56.

9. Hajdók, I.; Lissner, F.; Nieger, M.; Strobel, S.; Gudat, D. *Organometallics* **2009**, *28*, 1644-1651.

10. (a) Ogawa, A.; Tanaka, H.; Yokoyama, H.; Obayashi, R.; Yokoyama, K.; Sonoda, N. *J. Org. Chem.* **1992**, *57*, 111-115. (b) Ogawa, A.; Obayashi, R.; Doi, M.; Sonoda, N.; Hirao, T. *J. Org. Chem.* **1998**, *63*, 4277-4281. (c) Ogawa, A.; Ogawa, I.; Obayashi, R.; Umezu, K.; Doi, M.; Hirao, T. *J. Org. Chem.* **1999**, *64*, 86-92.

11. Grushin, V. V. *Chem. Rev.* **2004**, *104*, 1629-1662.

12. (a) Côté, A.; Charette, A. B. *J. Org. Chem.* **2005**, *70*, 10864-10867. (b) Côté, A.; Lindsay, V. N. G.; Charette, A. B. *Org. Lett.* **2007**, *9*, 85-87. (c) McConville, M.; Saidi, O.; Blacker, J.; Xiao, J. *J. Org. Chem.* **2009**, *74*, 2692-2698. (d) Hamada, A.; Braunstein, P. *Organometallics* **2009**, *28*, 1688-1696. (e) Wöste, T. H.; Oestreich, M. *Chem. Eur. J.* **2011**, *17*, 11914-11918. (f) Hu, J.; Lu, Y.; Li, Y.; Zhou, J. *Chem. Commun.* **2013**, *49*, 9425-9427. (g) Hahn, C.; Cruz, L.; Villalobos, A.; Garza, L.; Adeosun, S. *Dalton Trans.* **2014**, *43*, 16300-16309. (h) Li, C.; Chen, T.; Li, B.; Xiao, G.; Tang, W. *Angew. Chem. Int. Ed.* **2015**, *54*, 3792-3796. (i) Shi, J.; Wang, T.; Huang, Y.; Zhang, X.; Wu, Y.-D.; Cai, Q. *Org. Lett.* **2015**, *17*, 840-843. (j) Borrajo-Calleja, G. M.; Bizet, V.; Mazet, C. *J. Am. Chem. Soc.* **2016**, *138*, 4014-4017. (k) Fukuzaki, Y.; Tomita, Y.; Terashima, T.; Ouchi, M.; Sawamoto, M. *Macromolecules* **2010**, *43*, 5989-5995. (l) Carrow, B. P.; Nozaki, K. *J. Am. Chem. Soc.* **2012**, *134*, 8802-8805.

13. Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073-3100.

14. Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y. *Macromolecules* **1993**, *26*, 7369-7371.

15. Kajiwara, A.; Konishi, Y.; Morishima, Y.; Schnabel, W.; Kuwata, K.; Kamachi, M. *Macromolecules* **1993**, *26*, 1656-1658.

16. (a) Sato, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 4240-4241. (b) Vaillard, S. E.; Mück-Lichtenfeld, C.; Grimme, S.; Studer, A. *Angew. Chem. Int. Ed.* **2007**, *46*, 6533-6536.

17. The diphenylphosphino radical ($Ph_2P\cdot$) is also generated by near-UV light. However, $Ph_2P(O)\cdot$ is more reactive to alkenes than $Ph_2P\cdot$ and initiates the radical chain reaction. In this reaction, the $P^{V}(O)$–P^{III} bond cleavage, induced by near-UV light, is much slower than the radical chain reaction.

18. 1,2-Bisphosphinoalkane was obtained in <1% yield.

19. Fluck, E.; Binder, H. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 307-313.

20. Yoshida, M.; Higuchi, M.; Shishido, K. *Org. Lett.* **2009**, *11*, 4752-4755.

21. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.

22. Roy, D.; Todd, K.; Millam., J. *GaussView, Version 5*, Shawnee Mission KS, 2009.

Chapter 5

Synthesis of Bis(phosphino)alkane Monosulfides by the Addition of Diphosphine Monosulfides to Alkenes under Light

5-1 Introduction

Organophosphorus compounds are frequently used as functional materials that include physiologically active substances, pharmaceuticals, and transition-metal catalysts.[1] In particular, bis-phosphinated compounds are regarded to be the most ubiquitous privileged ligand structures in transition-metal catalysis. For the syntheses of phosphine compounds, complicated purification operations under inert atmospheres are often required due to their air-sensitivities, as a consequence of their high oxophilicities. Therefore, reactions with high atom economies that selectively afford the desired bisphosphine products in high purity are essential. The 1,2-addition of a phosphorus compound to an unsaturated carbon–carbon bond is one of the most atom-economical methods[2] for the synthesis of vicinal bisphosphine ligands,[3] such as dppe (*vic*-bis(diphenylphosphino)ethane),[4] because all of the starting materials can be included in the product. Although several excellent reactions have been reported for the 1,2-additions of diphosphine compounds bearing phosphorus–phosphorus single bonds to alkynes,[5] there are very limited examples of the corresponding additions to alkenes, which highlights poor substrate versatility.[6] Recently, Hirano and Miura et al. reported bisphosphination reactions of styrenes with diphenyl(trimethylsilyl)phosphine ($Ph_2P–SiMe_3$) using metal catalysts.[7,8]

In contrast, the free-radical addition of tetraphenyldiphosphine ($(Ph_2P)_2$), bearing a

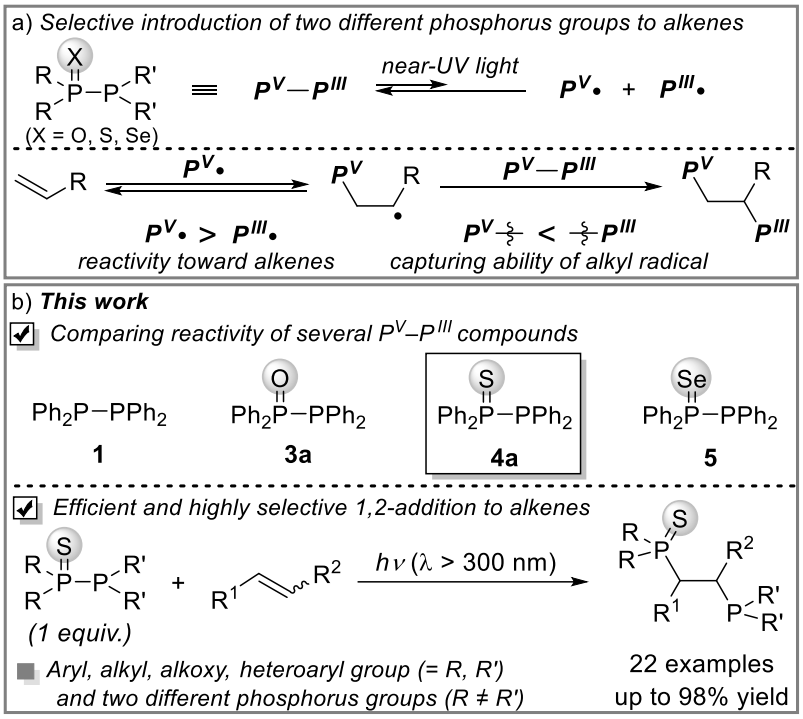
P^{III}–P^{III} single bond, to alkenes is difficult because of their low carbon-radical capturing ability. On the contrary, the author's previous report successfully overcame the low carbon-radical capturing ability of such phosphorus compounds by using tetraphenyldiphosphine monoxide ($Ph_2P(O)$–PPh_2), bearing a P^{V}–P^{III} single bond. Diphosphine monoxides have both of electronphilic (P^{V}) and nucleophilic (P^{III}) phosphorus centers and they can engage in radical additions to a variety of alkenes, regioselectively.[9] This reaction strongly indicates that diphosphine analogues, bearing a P^{V}–P^{III} single bond, are not only effective for 1,2-addition reaction to alkenes but also potentially promising compounds for the selective introduction of two different phosphorus groups. The 1,2-addition reaction proceeds in three steps (Scheme 5-1a): The photoinduced homolytic cleavage of the P^{V}–P^{III} bond of the diphosphine analogue generates two phosphorus radicals, namely $\boldsymbol{P^{V}\cdot}$ and $\boldsymbol{P^{III}\cdot}$. The more electrophilic phosphorus radical ($\boldsymbol{P^{V}\cdot}$) adds to the alkene and the generated carbon radical is captured by the more electron-rich phosphorus group ($\boldsymbol{P^{III}}$) of the diphosphine analogue. However, some diphosphine monoxides, for example, *O,O*-diethyl(diphenylphosphino)phosphate ($(EtO)_2P(O)$–PPh_2), do not add to alkenes.

In order to develop a highly reactive diphosphine analogue, the author carried out comparative research of the 1,2-addition of diphosphine monochalcogenides to alkene **2a** (Scheme 5-1b). These results showed the remarkably higher reactivity of diphosphine monosulfide **4a**, bearing a $P^{V}(S)$–P^{III} single bond,[10] to alkene **2a** than diphosphine monoxide **3a**.

Recently, organophosphines with soft Lewis-base center (P^{III}) and relatively hard one ($P^{V}(S)$) at the vicinal position, have been used as hemilabile P/S bidentate ligands in transition-metal-catalyzed reactions.[11] Furthermore, phosphine sulfides are easily reduced to afford bidentate bis(phosphine) ligands. Therefore, the 1,2-adducts of diphosphine monosulfides are themselves useful and promising ligands as well as valuable precursors to bidentate bis(phosphine) ligands. Therefore, the author focused on the high reactivities of diphosphine

monosulfides toward alkenes, and investigated this thiophosphinylphosphination process in detail.

Scheme 5-1. Selective radical additions of diphosphine analogues to alkenes

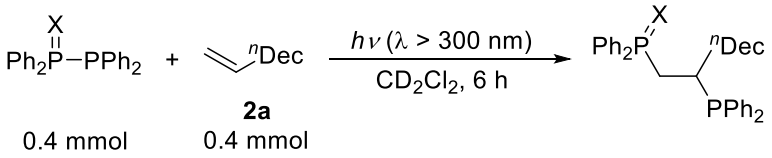


5-2 Results and Discussion

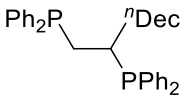
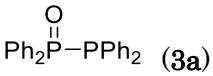
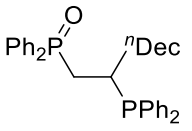
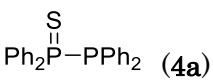
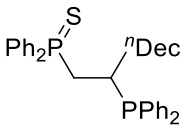
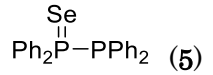
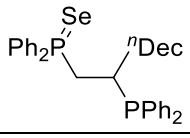
The author initiated the study by investigating the addition reactions of several diphosphine analogues, bearing a P^V–P^{III} bond, to alkene **2a** (Table 5-1). A mixture of diphosphine **1** (0.4 mmol), 1-dodecene (**2a**, 0.4 mmol), and dichloromethane (0.4 mL) was irradiated with a xenon lamp (500 W) through Pyrex for 6 h (entry 1). The reaction did not proceed at all and **1** was recovered quantitatively. The 1,2-addition of diphosphine monoxide **3a** slightly proceeded to afford the corresponding bis-adduct **7aa** in 6% yield (entry 2). In contrast to **1** and **3a**, diphosphine monosulfide **4a** gave 87% of 1-thiophosphinyl-2-phosphinoalkane **8aa** which bears diphenylthiophosphinyl and diphenylphosphino groups at its terminal and inner

carbon atoms, respectively (entry 3). No regioisomer was detected by ^{1}H or ^{31}P NMR spectroscopy. This reaction also proceeded under 400 nm LEDs light (4.5 W) to afford bis-adduct **8aa** in 74% yield (entry 4). In the absence of photoirradiation, **8aa** was not observed under the same reaction conditions (entry 5). Diphosphine monosulfide **4a** was unsuitable for conditions involving radical initiator V-40 (1,1′-azobis(cyclohexanecarbonitrile), 88 °C, $\tau_{1/2}$ = 10 h), which is often used in radical reactions of diphosphine analogues,[5b,9] because it decomposes under thermal conditions (entry 6).[12] For diphosphine monoselenide **5**, the bis-adduct **9a** was not obtained because the selenium atom transfer from **5** might immediately occurred after generation of **9a** (entry 7).[13,14]

Table 5-1. Comparative investigation of the 1,2-addition reactions of several diphosphine analogues to alkenes[a]



0.4 mmol 0.4 mmol

entry	diphosphine analogue	product	yield
1	Ph_2P-PPh_2 (**1**)	 (**6a**)	0%
2	 (**3a**)	 (**7aa**)	6%
3	 (**4a**)	 (**8aa**)	87%
4[b]			74%
5[c]			0%
6[d]			11%
7	 (**5**)	 (**9a**)	0%

Yields were determined by ^{1}H NMR spectroscopy. [a]Reaction conditions: diphosphine analogue (0.4 mmol), **2a** (0.4 mmol), CH_2Cl_2 (0.4 mL), xenon lamp (500 W), Pyrex, 20 °C, and 10 h. [b]Irradiation with a 400 nm UV-LEDs (4.5 W) for 20 h. [c]The reaction was carried out in the dark. [d]Thermal reaction conditions: **4a** (0.4 mmol), **2a** (0.4 mmol), benzene (0.6 mL), V-40 (1,1′-azobis(cyclohexanecarbonitrile), 10 mol%), 80 °C, and 20 h.

In order to compare the reactivity of **4a** with **3a** in detail, the conversions of 1-dodecene (**2a**) to their corresponding 1,2-adducts were monitored by ^{1}H NMR spectroscopy over the initial 6 h, the results of which are summarized in Figure 5-1. Over the time course of these reactions, the 1,2-addition of **4a** proceeded efficiently over the first 2 h to generate **8aa** in 70% yield, while the addition of **3a** was very slow, with only 6% of **3a** converted into its adduct **7aa** over 6 h. Over the initial 30 min, the addition of **4a** to **2a** (48% yield) proceeded approximately 70 times faster than the addition involving **3a** (0.7% yield). These results showed that only the structural difference between phosphine sulfide and phosphine oxide caused a large influence on their reaction rates.

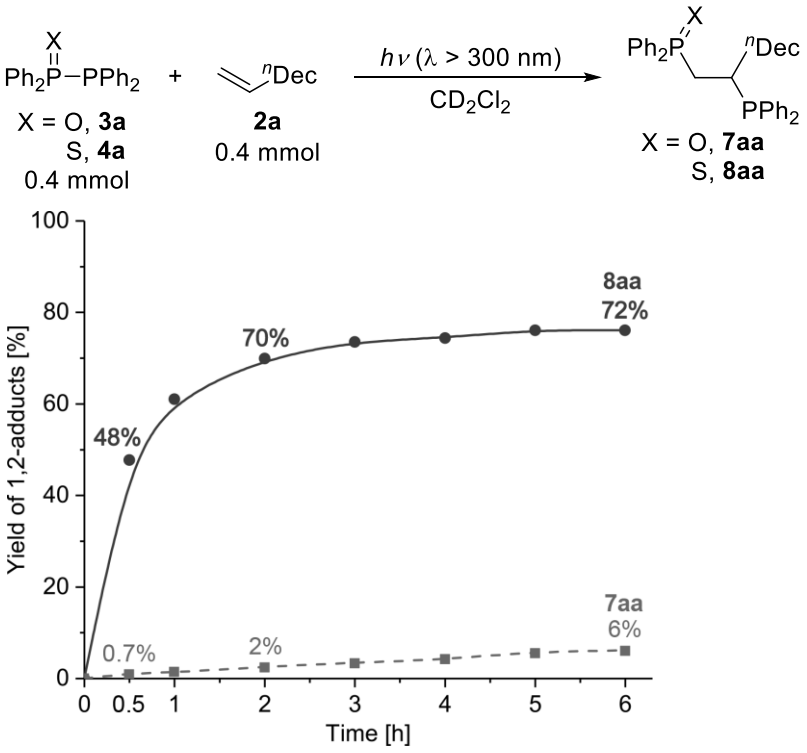


Figure 5-1. Yields during the addition reactions of diphosphine monosulfide **4a** and monoxide **3a** to alkene **2a** as functions of time, monitored by ^{1}H NMR spectroscopy

Several comparative studies were performed in order to clarify the reasons for why **4a** exhibits higher reactivity than **3a**. The UV-vis absorption spectra of **4a** and **3a**, acquired in

CH_2Cl_2, are shown in Figure 5-2. In sharp contrast to the absorption spectrum of **4a**, which exhibits a broad maximum absorption at 300 nm that extends almost to 350 nm, the absorption tail of **3a** extends only to about 320 nm. When the transmittance of light through Pyrex glass (40% transmission at 290 nm) is considered, it is clear that the absorption of light by **4a** is more efficient for its homolysis than that of **3a**. The efficient homolysis of **4a** can increase the concentration of the thiophosphinyl radical, resulting in an efficient formation of the corresponding carbon radical to afford the addition product **8**.

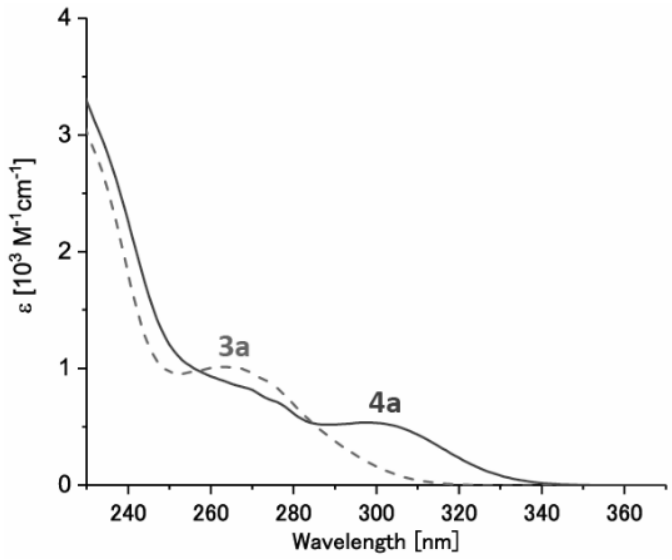


Figure 5-2. UV-vis absorption spectra of diphosphine monosulfide **4a** and monoxide **3a** in CH_2Cl_2 (7.0×10^{-5} M)

In order to understand the observed absorption properties, **4a** and **3a** were subjected to density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory (Figure 5-3). The calculated highest-occupied Kohn–Sham orbitals (HOMOs) of $\mathbf{4a_{opt}}$ and $\mathbf{3a_{opt}}$ reveal significantly different populations. Although the HOMO of $\mathbf{3a_{opt}}$ distributes to its $P^V(O)$–P^{III} moiety and its phenyl groups, the HOMO of $\mathbf{4a_{opt}}$ is mostly located to its $P^V(S)$–P^{III} moiety. We hypothesized that the localized HOMO of $\mathbf{4a_{opt}}$ contributes the higher reactivity of **4a** and decreases the influence of its substituents on phosphorus atom. Time-dependent DFT calculations

for **4a** at the CAM-B3LYP/6-311++G(2d,p) level reveal transition energies and oscillator strengths that are in good agreement with the observed values. The calculated band at λ = 287 nm (*f* 0.3546) of **4a**$_{opt}$ is assigned to the HOMO→LUMO transition (88% contribution) that mainly corresponds to the donations of the lone pairs on the sulfur and phosphorus atoms to the phosphorus–phosphorus σ* orbital.

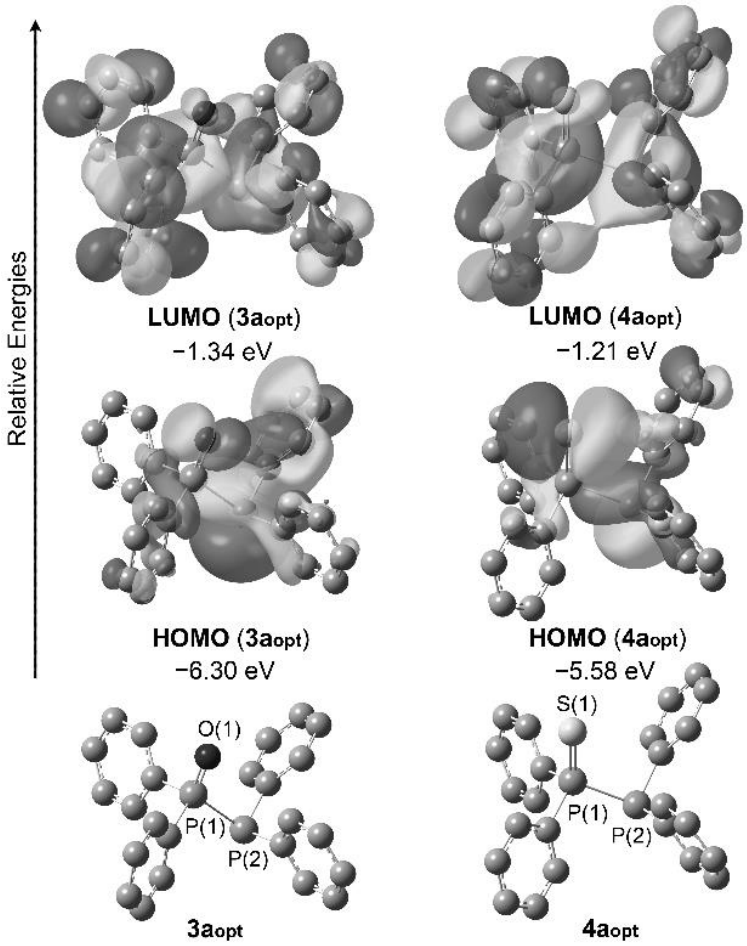
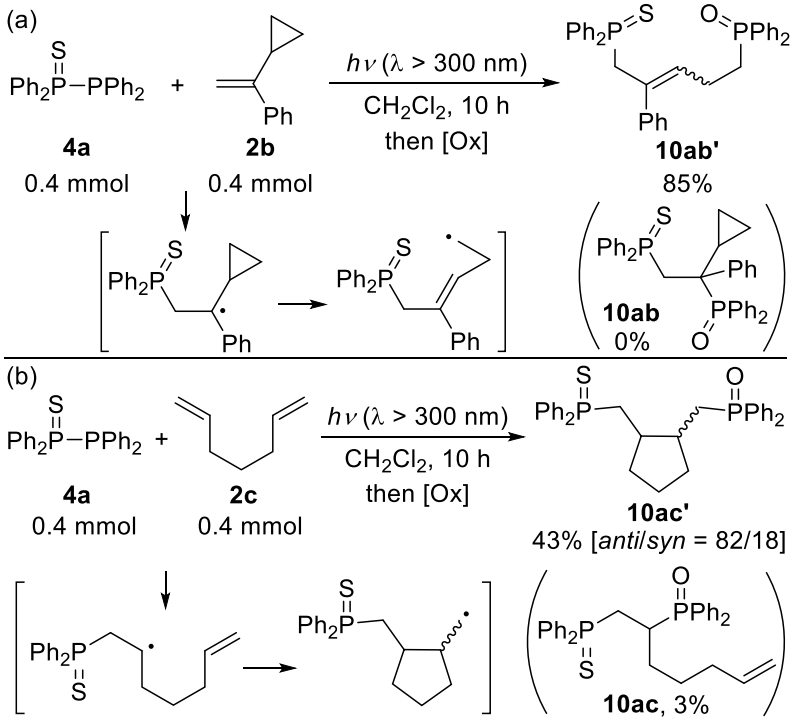


Figure 5-3. Kohn–Sham molecular orbitals (HOMOs and LUMOs) of **3a**$_{opt}$ and **4a**$_{opt}$ calculated at B3LYP/6-31G(d) level of theory

In order to shed light on the reaction pathway, vinylcyclopropane **2b** was mixed with **4a** and irradiated with a xenon lamp. As a result, the corresponding ring-opened 1,5-adduct **10ab'** was obtained in 85% yield, without the formation of the cyclopropane-ring-bearing 1,2-adduct

10ab (Scheme 5-2a). This result suggests that the cyclopropylcarbinyl radical generated underwent fast ring-opening (k = 5 x 10^7 s^{-1} at 37 °C)[15] to give the homoallylic radical, which was captured by **4a**. In addition, **4a** adds to diene **2c** to afford the cyclized product **10ac'** in 43% yield along with the uncyclized 1,2-adduct **10ac** in 3% yield (Scheme 5-2b). The rate constant for the *5-exo* cyclization of 1-methyl-5-hexenyl radical is 4.2 x 10^4 s^{-1} (25 °C);[16] hence the rate constant for carbon-radical capture by **4a** was roughly estimated to be 3.3 x 10^3 s^{-1} M^{-1} (25 °C), which is much faster than carbon-radical capture by diphosphine monoxide **3a** (k' < 5.6 x 10^2 s^{-1} M^{-1} (25 °C)).[9]

Scheme 5-2. Radical (a) ring-opening addition and (b) cycloaddition reactions using diphosphine monosulfide **4a**



A plausible reaction pathway for the present reaction is illustrated in Figure 5-4. Homolytic cleavage of the P(S)–P single bond in **4a** is reversibly induced by photoirradiation[17,[18]] to generate the diphenylthiophosphinyl radical ($Ph_2P(S)$·) and

diphenylphosphino radical (Ph_2P·). $Ph_2P(S)$· has a higher reactivity toward alkenes than Ph_2P·; consequently, $Ph_2P(S)$· selectively attacks the alkene to afford the 2-thiophosphinylated alkyl radical. The alkyl radical reacts with the phosphino group of **4a**, which has a higher carbon-radical capturing ability than the thiophosphinyl group, to regioselectively afford the 1-thiophosphinyl-2-phosphinoalkane **8a**.

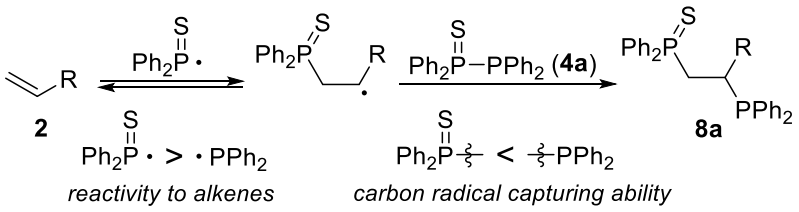


Figure 5-4. A plausible reaction pathway

The calculated spin on the diphenylphosphinyl radical (**11**$_{opt}$) is distributed largely on the phosphorus atom rather than the oxygen atom, while the spin of the diphenylthiophosphinyl radical (**12**$_{opt}$) is distributed on the sulfur atom as well as the phosphorus atom (Figure 5-5).

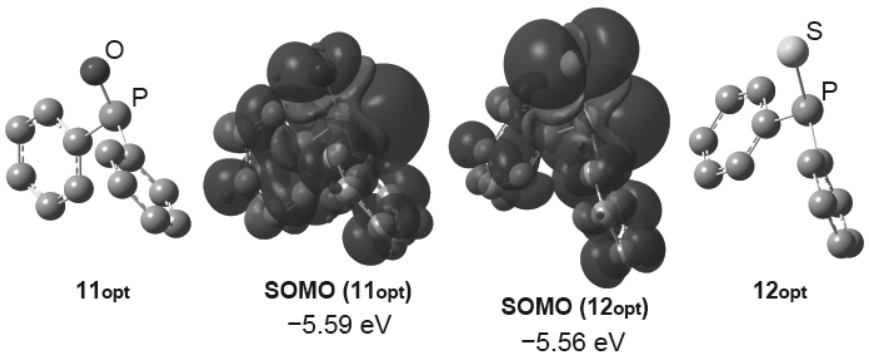


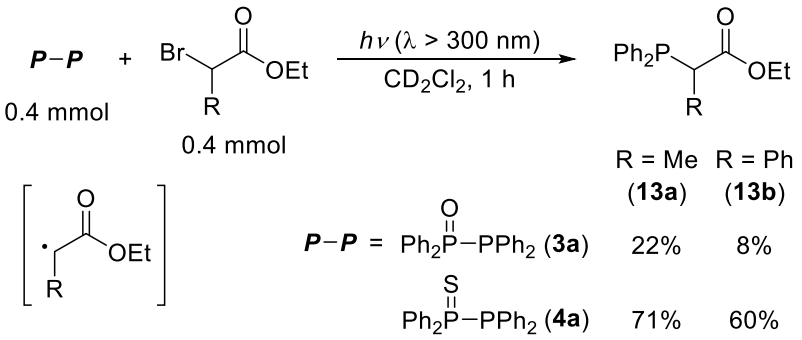
Figure 5-5. Calculated SOMOs for **11**$_{opt}$ and **12**$_{opt}$ calculated at UB3LYP/6-31G++(2d,p) level

The energy of the singly occupied molecular orbital (SOMO) of **11**$_{opt}$ (−5.59 eV) is very similar to that of **12**$_{opt}$ (−5.56 eV). Radicals with similar SOMO energies usually show similar reactivities toward alkenes; hence the carbon-radical capturing abilities of **3a** and **4a** were investigated. In the addition of **3a** to propene (R = CH_3, Figure 5-4), the SOMO of the alkyl

radical, generated by the addition of **11** to propene, was calculated to be −4.85 eV and the gap between this orbital and the HOMO of **3a** (−6.30 eV) was calculated to be 1.45 eV. In the addition of **4a** to propene, the SOMO level of the corresponding alkyl radical (−4.93 eV) was similar to the HOMO level of **4a** (−5.58 eV), resulting in a SOMO–HOMO gap of only 0.65 eV.

With this information in mind, the mixture of ethyl 2-bromopropanoate (0.4 mmol) and **3a** or **4a** (0.4 mmol) was photoirradiated (Scheme 5-3). These reactions generate secondary alkyl radicals in situ by the cleavage of the carbon–bromine bond in ethyl 2-bromopropanoate upon irradiation with near-UV light. The homolytic substitution of the generated carbon radical at the trivalent phosphorus atom of **3a** afforded ethyl 2-(diphenylphosphino)propanoate (**13a**) in 22% yield. Conversely, the homolytic substitution of **4a** proceeded more efficiently to afford the phosphinated product **13a** in 71% yield. In the reaction between ethyl 2-bromo-2-phenylacetate and **3a** or **4a** (Scheme 5-3), **4a** afforded the corresponding phosphine **13b** much more efficiently than **3a**. These results strongly indicate that the secondary-alkyl-radical-capturing ability of **4a** (involving the 2-propiolate radical) is much higher than that of **3a**; consequently, the addition of **4a** to **2a** requires only equimolar amounts to be successful.

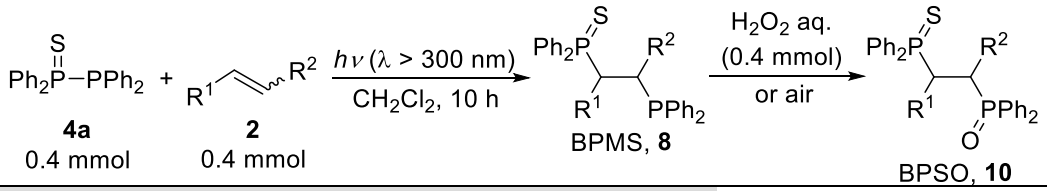
Scheme 5-3. Photoinduced homolytic substitution reaction of **3a** and **4a** with the secondary alkyl radicals generated from ethyl 2-bromopropionate and ethyl 2-bromo-2-phenylacetate



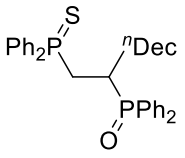
Next, the addition reactions of diphosphine monosulfide **4a** to a variety of alkenes were performed under photoirradiation conditions (Table 5-2). This thiophosphinylphosphination

reaction was effective for terminal and internal aliphatic alkenes **2a**, **2d**, and **2f**–**2l**, as well as the aromatic alkene **2e**. The formed thiophosphinylphosphination products were isolated as their oxides after oxidative workups. For example, vinylcyclohexane (**2d**) and 4-*tert*-butoxystyrene (**2e**) were transformed into the corresponding bis(phosphino)alkane monosulfide monoxides (BPSOs) **10ad** and **10ae** in yields of 64% and 45%, respectively, following oxidation. For internal alkenes, such as maleic ester **2f** and the cyclic five-membered alkenes **2g**–**2l**, the desired products **10af**–**10al** were obtained in good yields. The thiophosphinylphosphinations of 2- or 3-aryl dihydrofurans **2i**–**2l** proceeded with excellent diastereoselectivities. The regio- and stereoselectivity of this reaction was supported by X-ray crystal-structure analysis of **10ai**. In these reactions, $Ph_2P(S)\cdot$ attacks the β position relative to the furan oxygen atom because the lone pair on the oxygen atom can stabilize the formed carbon radical (Figure 5-6). The conformation of this carbon radical is determined by steric repulsion between the aryl group of **2i**–**2l** and the thiophosphinyl group, resulting in the formation of bis-adducts **8ai**–**8al** that have thiophosphinyl groups with high *anti* selectivities relative to their aryl groups. The 1,2-addition of **4a** to a terminal alkyne, namely 1-octyne (**2m**), also proceeded to give the *E*-isomer of BPSO **10am** in 66% yield with good regio- and stereoselectivity. In some cases, the corresponding bis(phosphino)alkane monosulfides (BPMSs) **8an**–**8ap** were isolated in good yields without the need for oxidation.

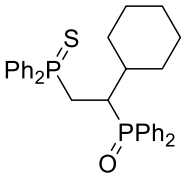
Table 5-2. Thiophosphinylphosphination of several alkenes **2** with **4a**[a]



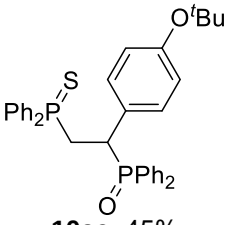
Isolated after oxidation



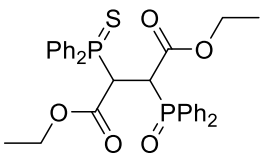
10aa, 72%[b]



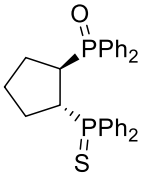
10ad, 64%



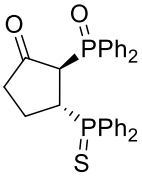
10ae, 45%



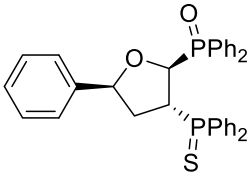
10af, 70%[b,c]



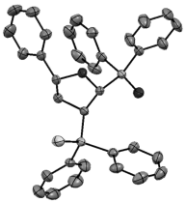
10ag, 86%



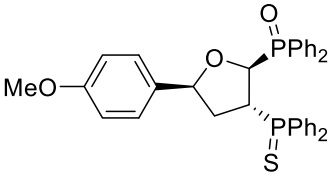
10ah, 80%



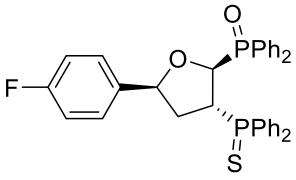
10ai, 89% [*dr* = 91/9]



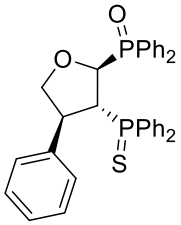
(**10ai**, *X-ray*)



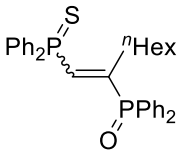
10aj, 87% [*dr* = 92/8]



10ak, 68% [*dr* = 91/9]

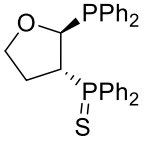


10al, 76% [*dr* = 99/1]

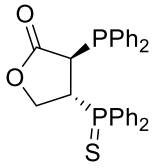


10am, 66% [*E*/*Z* = 91/9][d]

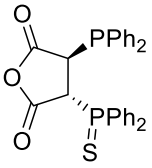
Isolated without oxidation



8an, 98%[b]
(95%: 400 nm LEDs)[e]



8ao, 84%



8ap, 95%[b]

Isolated yields of the products were noted above. [a]Reaction conditions: **4a** (0.4 mmol), **2** (0.4 mmol), CH_2Cl_2 (0.4 mL), xenon lamp (500 W), Pyrex, 20 °C, and 10 h. For the syntheses of **10aa** and **10ad**–**10am**, the resulting mixtures were exposed to air and then treated with 30 wt% aqueous hydrogen peroxide solution at 20 °C for 1 h. [b]Reaction time was 6 h. [c]Oxidized in air. [d]1-Octyne (0.4 mmol) was used instead of an alkene. [e]Irradiated with a 400 nm LEDs (4.5 W) for 16 h. The yield was determined by ^{1}H NMR spectroscopy.

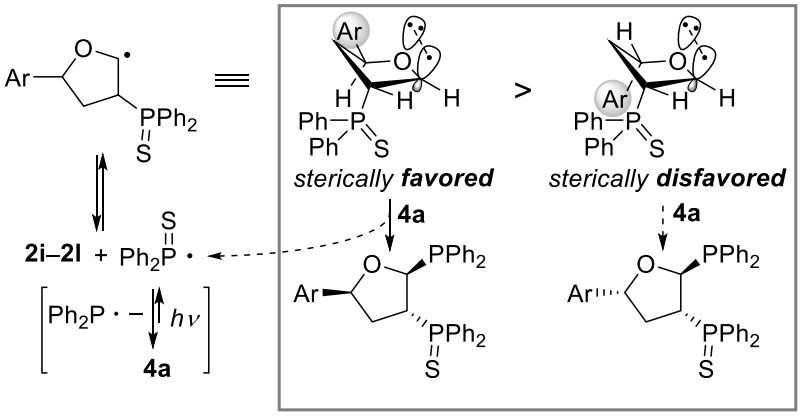


Figure 5-6. Model for diastereodiscrimination during the 1,2-addition of **4a** to alkenes **2i–2l**

This reaction can be scaled to 2.6 mmol to provide more than 1 g of product, as demonstrated by the thiophosphinylphosphination of **2n** (Figure 5-7). The addition of **4a** to dihydrofuran **2n** gave 1.2 g (96% yield) of BPMS **8an** with *anti*-selectivity after washing with *n*-hexane and without oxidation. The positions of phosphino- and thiophosphino-groups substitution were unambiguously confirmed by X-ray crystal-structure analysis.

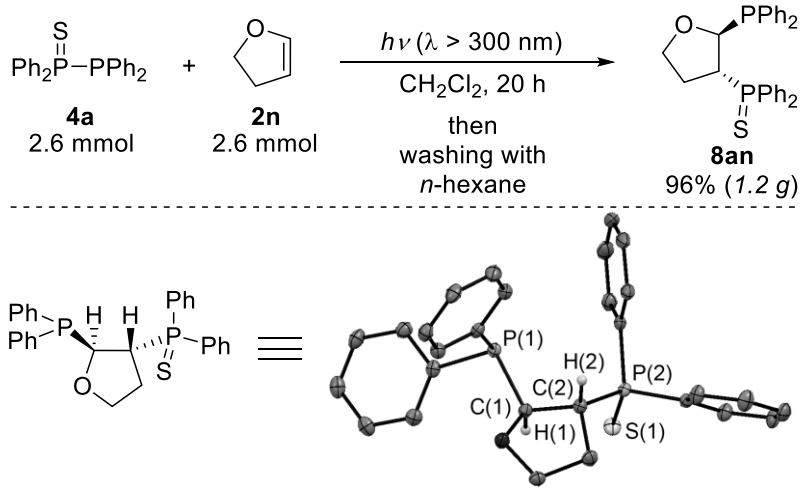
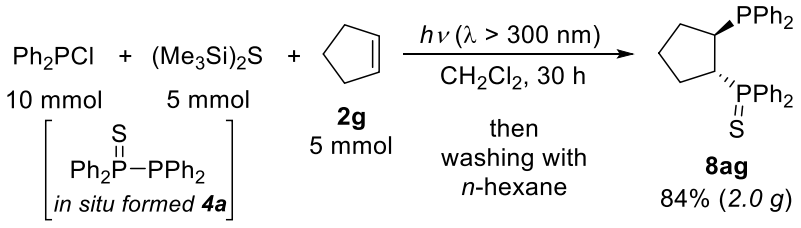


Figure 5-7. Gram-scale synthesis and the molecular structure of **8an** (50% thermal ellipsoids; hydrogen atoms (except H(1) and H(2)) have been omitted for clarity)

Diphosphine monosulfide **4a** generated from Ph_2PCl and $(Me_3Si)_2S$ in situ[10c] was also

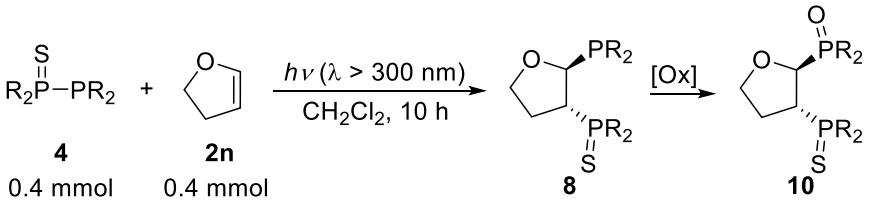
effective in this reaction, to give 2.0 g of bis-adduct **8ag** in 84% yield (Scheme 5-4).

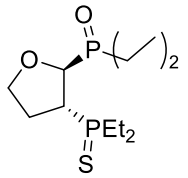
Scheme 5-4. Gram-scale synthesis of bis(phosphine) monosulfide **8ag** using in situ formed **4a**



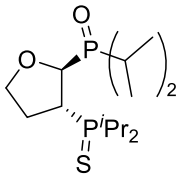
Several diphosphine monosulfides and its phosphonate analogue could be used in this 1,2-addition reaction (Table 5-3). Aliphatic diphosphine monosulfides such as tetraethyl- and tetra(isopropyl)diphosphine monosulfide (**4b** and **4c**) reacted smoothly with **2n** to give the 1,2-adducts **10bn** and **10cn** in good yields, respectively. Although the reactivities of phosphines and phosphonates are generally different, notably, the reaction of diphosphonate monosulfide **4d** also afforded the bis-adduct **8dn** in 84% yield. The bis-adduct **8dn** partially decomposed under the oxidation conditions and its BPSO **10dn** was isolated in 31% yield. Steric hindrance imposed by the phosphorus substituent is important for this reaction. Diphosphine monosulfide **4e**, with the *para*-tolyl substituent, afforded BPSO **10en** in 87% yield but the bulky *ortho*-derivative **4f** was completely unreactive toward alkene **2n**. The furyl-substituted diphosphine monosulfide **4g** also added to **2n** to give BPSO **10gn** in 89% yield.

Table 5-3. Thiophosphinylphosphinations of **2n** with several diphosphine monosulfides **4**[a]

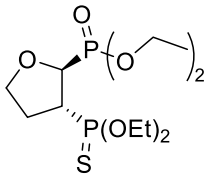




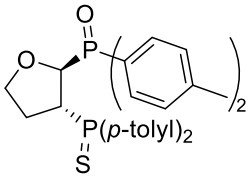
10bn, 83%



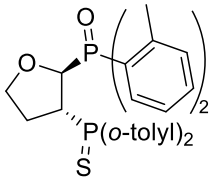
10cn, 71%



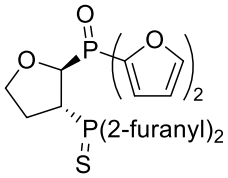
10dn, 31% (**8dn**, 84%)[b]



10en, 87%



10fn, 0%

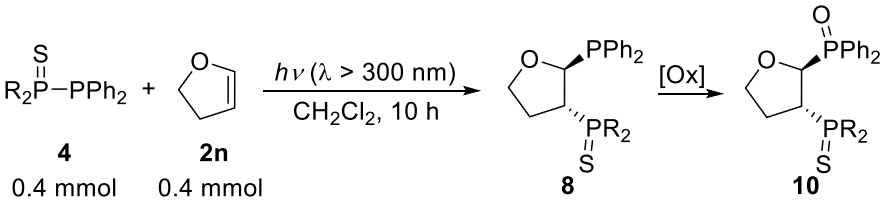


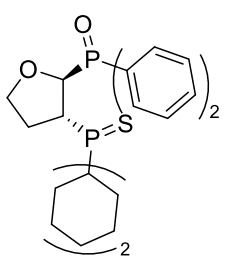
10gn, 89%

Isolated yields of the products were noted above. [a]Reaction conditions: **4** (0.4 mmol), **2n** (0.4 mmol), CH_2Cl_2 (0.4 mL), xenon lamp (500 W), Pyrex, 20 °C, and 10 h. After the reaction, the resulting mixture was exposed to air and then treated with 30 wt% aqueous hydrogen peroxide solution at 20 °C for 1 h. [b]The yield shown in parentheses was determined by ^{31}P NMR spectroscopy.

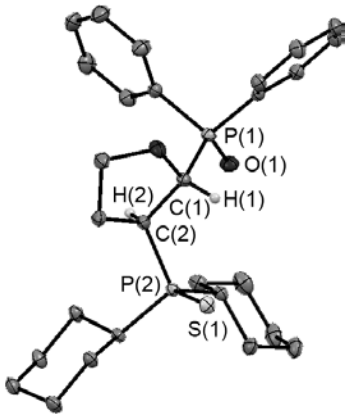
The wide scope of **4** facilitates the highly selective additions of unsymmetrically substituted diphosphine monosulfides to alkenes. Several unsymmetrical diphosphine monosulfides **4h**–**4j** were synthesized by a modification of the method reported by Burford and Weigand.[10c] The starting diphosphines can be used in the next step without strict purification, as shown in Table 5-4. The reaction of dicyclohexyl(diphenylphosphino)phosphine sulfide (**4h**) with **2n** afforded the corresponding BPSO **10hn** in good yield. The regio- and stereoselectivity of this reaction was determined by X-ray crystal-structure analysis. The regioisomer of **10hn** was not observed in this reaction. Diphosphine monosulfide **4i**, bearing isopropyl and phenyl substituents, was also available for the unsymmetrical addition. The addition of *O,O'*-diethyl(diphenylphosphino)phosphonothioate (**4j**) with **2n** also proceeded efficiently to give BPOS **10jn** in 88% yield.

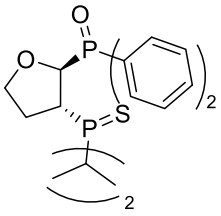
Table 5-4. The 1,2-addition of several unsymmetrical diphosphine monosulfides **4**[a]



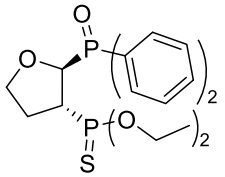


10hn, 76%[b]





10in, 84%

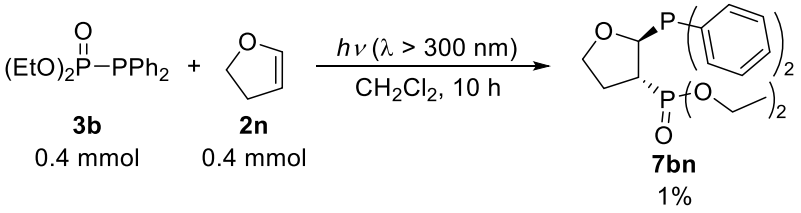


10jn, 88%

Isolated yields of the products were noted above. [a]Reaction conditions: **4** (0.4 mmol), **2n** (0.4 mmol), CH_2Cl_2 (0.4 mL), xenon lamp (500 W), Pyrex, 20 °C, and 10 h. After the reaction, the resulting mixture was treated with 30 wt% aqueous hydrogen peroxide solution at 20 °C for 3 h. [b]Alkene **2n** (0.5 mmol) was used. [c]The molecular structure of BPSO **10hn** (50% thermal ellipsoids; hydrogen atoms (except H(1) and H(2)) have been omitted for clarity).

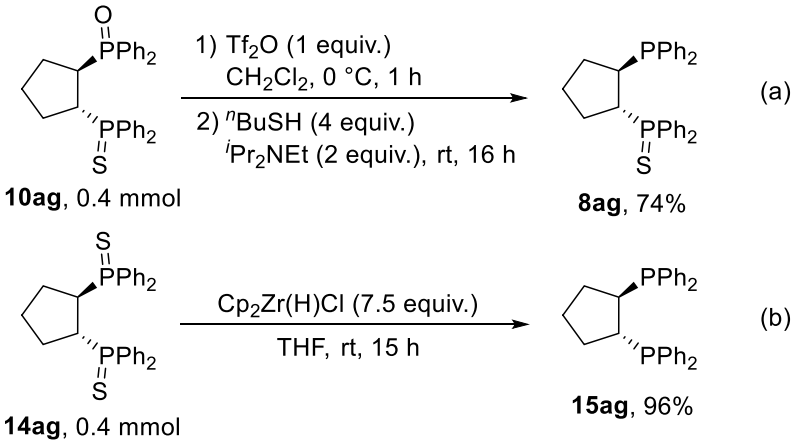
As summarized in Tables 5-3 and 5-4, diphosphine monosulfides **4** are generally tolerant toward this reaction, whereas the corresponding diphosphine monoxides, e.g., *O,O'*-diethyl(diphenylphosphino)phosphonate (**3b**), do not add to **2n** efficiently (Scheme 5-5).

Scheme 5-5. Phosphinylphosphination of **2n** with unsymmetrical diphosphine monoxide **3b**



These BPSOs were easily transformed into their corresponding BPMSs and bidentate bisphosphine ligands (Scheme 5-6). The author developed a novel phosphine-oxide-selective reduction from BPSO to BPMS by applying the bis(phosphine oxide) mono-reduction conditions.[18] Treatment of BPSO **10ag** with an equal amount of trifluoromethanesulfonic anhydride (Tf_2O), followed by addition of an excess amount of *n*-butanethiol, selectively provided BPMS **8ag** in 74% yield (Scheme 5-6a). The desulfidation of bis(phosphine sulfide) **14ag**, generated by treatment of the thiophosphinylphosphination product **8ag** with elemental sulfur, with the Schwartz reagent [$Cp_2Zr(H)Cl$] afforded bis(phosphine) **15ag** in 96% yield (Scheme 5-6b).[19]

Scheme 5-6. (a) Selective reduction of **10ag** and (b) desulfidation of **14ag**



This atom-efficient reaction enables the facile preparation of a Pd complex bearing a BPMS ligand,[11a-d, 11f,20] such as **16aj**, without the need for BPMS purification (Figure 5-8). When a mixture of diphosphine monosulfide **4a** (0.4 mmol) and alkene **2j** (0.4 mmol) was photoirradiated, BPMS **8aj** was obtained in 92% yield. Subsequently, $PdCl_2(PhCN)_2$ (0.4 mmol) was added to the resulting reaction mixture, and palladium complex **16aj** was successfully isolated in 84% yield after washing with ethyl acetate in air. The X-ray crystal structure of **16aj** is shown in Figure 5-2. The coordination geometry around the Pd center of **16aj** is square planar,

with the bis-adduct **8aj** acting as a phosphorus/sulfur bidentate ligand.

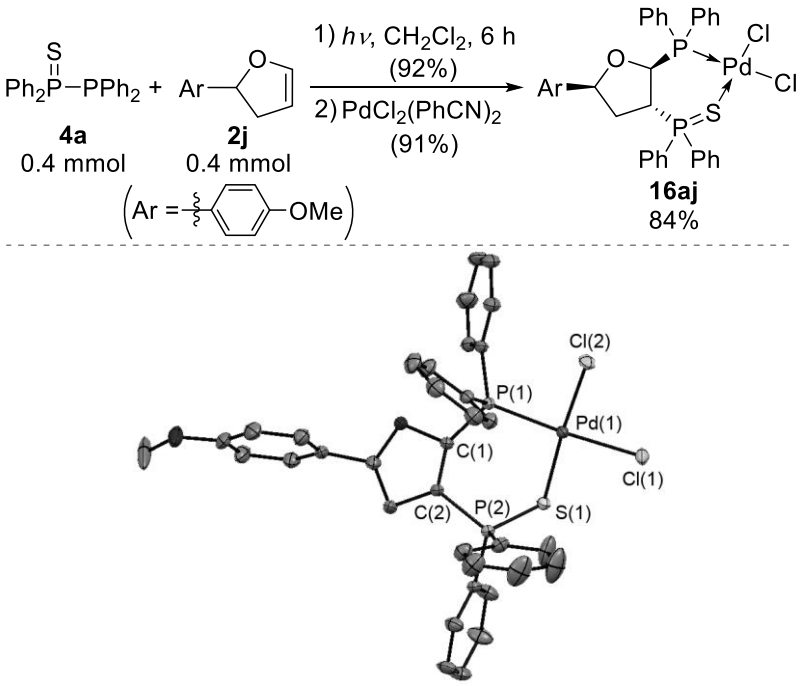


Figure 5-8. One-pot synthesis and molecular structure of Pd(II)/bis(phosphine) monosulfide complex **16aj** (50% thermal ellipsoids; hydrogen atoms have been omitted for clarity)

5-4 Conclusion

In conclusion, the author developed a simple method for the preparation of vicinally located bis(phosphine) monosulfides by investigating the addition reactions of diphosphine monosulfides to alkenes. This reaction readily affords a variety of symmetrical and unsymmetrical bis(phosphine) monosulfides with excellent regio- and diastereoselectivities without the need for a catalyst, base, or additive. Several mechanistic experiments revealed that the HOMO of diphosphine monosulfide, which, due to the sulfur atom, is higher than that of the corresponding phosphine oxide, contributes to an extended absorption-wavelength profile and improvements in its carbon-radical capturing ability. In view of the easy accessibility of diphosphine monosulfides and their high reactivities toward alkenes, the author believes this

work provides a powerful tool for the synthesis of symmetrical and unsymmetrical bis(phosphine) monosulfides as hemilabile ligands for transition-metal-catalyzed reactions.

5-5 Experimental Section

General Comment

Diphosphine **1**,[21] diphosphine monoxide **3a**,[22] a series of diphosphine monosulfides **4a–4g**,[10c] and diphosphine monoselenide **5**[10c] were synthesized according to the corresponding literatures, respectively. The other diphosphine monosulfides **4h**–**4j** were also synthesized according to the literature[10c] with minor changes. A series of dihydrofurans **2i**–**2l** were synthesized according to the literature.[23] The other alkenes and bis(trimethylsilyl) sulfide were obtained from commercial supplies. All solvents were distilled and degassed with argon before use. All theoretical calculations were performed with the Gaussian 09W Revision D.01 program package. Geometry optimizations were performed by density functional theory (DFT) and a time-dependent (TD)-DFT method, respectively, with the hybrid (U)B3LYP and CAM-B3LYP[24] functions, employing a basis set consisting of 6-31G(d) (for **3a**, **4a**, 1-diphenylphosphinylpropyl radical, and 1-diphenylthiophosphinylpropyl radical), 6-31G++(2d,p) (for **11** and **12**), and 6-311G++(2d,p)/def2tzv (for **4a** (TD-DFT)), respectively.

Experimental procedure for the synthesis of 4a

To a 50 mL round bottom Schlenk flask, diphenylphosphine chloride (40 mmol) and bis(trimethylsilyl) sulfide (20 mmol) dissolved in degassed dry CH_3CN (100 mL) was added under an argon atmosphere, and the mixture was stirred for 10 h. The reaction mixture was then concentrated under reduced pressure. The resulting white solid was washed with *n*-hexane (3 x 20 mL) to give the pure product in 92% yield (7.4 g). The purity of the product was confirmed by ^1H

and ^{31}P NMR spectroscopy.

Experimental procedure for the 1,2-addition of diphosphine 1 or its analogue 3a, 4a, and 5a to 2a (Table 5-1)

Diphosphine or its analogue (0.4 mmol) and alkene (0.4 mmol) in degassed dry CD_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 6 h at 20–25 °C. The yield of the product was determined by ^{1}H NMR spectroscopy using 1,3,5-trioxane as an internal standard.

Experimental procedure for homolytic substitution reaction of 3a and 4a with the secondary alkyl radicals (Scheme 5-3)

Tetraphenyldiphosphine monoxide **3a** or its monosulfide **4a** (0.4 mmol) and ethyl 2-bromopropanoate or ethyl 2-bromo-2-phenylacetate (0.4 mmol) dissolved in degassed dry CD_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for an hour at 20–25 °C. The yield of the phosphinated product **13a** and **13b** was calculated by ^{1}H NMR spectroscopy. In order to confirm the generation of undesirable side product, such as phosphonium bromide, the reaction between ethyl bromoacetate and **3a** or **4a** dissolved in CD_2Cl_2 was also performed. As a result, **3a** and **4a** did not react with ethyl bromoacetate and the starting materials were recovered completely.

Ethyl 2-(diphenylphosphinyl)propanoate (13a-O) After the reaction, the mixture was exposure to air for an hour and then 30 wt % aqueous hydrogen peroxide solution (0.4 mmol) was added. The product was obtained as phosphine oxide **13a-O** in 62% yield after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$). [CAS registry number: 25263-08-5];[25] white solid; **mp.** 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.91 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 1.47 (dd, $J_{H\text{-}H}$ = 15.6 Hz, 7.3 Hz, 3H), 3.59 (qd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 13.7 Hz, 1H), 3.81–3.98 (m, 2H), 7.45–7.511 (m, 4H), 7.512–7.57 (m, 2H), 7.83 (ddd, $J_{H\text{-}H}$ = 11.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.87 (ddd,

$J_{H\text{-}H}$ = 11.9 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 10.9 (d, $J_{C\text{-}P}$ = 3.8 Hz), 13.5, 42.4 (d, $J_{C\text{-}P}$ = 60.4 Hz), 61.1, 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.4 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 170.0 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.6; **IR** (NaCl): 691, 700, 714, 762, 788, 1015, 1099, 1211, 1311, 1440, 1723, 2981 cm^{-1}.

Ethyl 2-(diphenylphosphinyl)-2-phenylacetate (13b-O) After the reaction, the mixture was exposure to air for an hour and then 30 wt % aqueous hydrogen peroxide solution (0.4 mmol) was added. The product was obtained as phosphine oxide **13b-O** in 50% yield after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$). White solid; **mp.** 169–170 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.97 (t , $J_{H\text{-}H}$ = 7.0 Hz, 3H), 3.99 (q, $J_{H\text{-}H}$ = 7.0 Hz, 2H), 4.69 (d, $J_{H\text{-}P}$ = 11.5 Hz, 1H), 7.20–7.25 (m, 3H), 7.33 (td, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 3.2 Hz, 2H), 7.38–7.46 (m, 3H), 7.50 (td, $J_{H\text{-}H}$ = 7.6 Hz, $J_{H\text{-}P}$ = 3.2 Hz, 2H), 7.54–7.61 (m, 3H), 7.94 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.7, 55.5 (d, $J_{C\text{-}P}$ = 58.5 Hz), 61.6, 127.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.28, 128.34 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 4.8 Hz), 130.6 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 102.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.80 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.84, 132.1 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 167.7 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 27.8; **IR** (NaCl): 529, 697, 725, 1030, 1115, 1151, 1192, 1286, 1312, 1438, 1728, 2938, 3047 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{22}H_{22}O_3P$: 365.1306, Found: 365.1296.

Experimental procedure for the synthesis of 10aa and 10ad–10am (Table 5-2)

Tetraphenyldiphosphine monosulfide (0.4 mmol) and alkene (0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 10 h (6 h for **10aa** and **10af**) at 20–25 °C. Carefully control of the reaction temperature among 10–25 °C was required because **4a** was decomposed over 30 °C to tetraphenyldiphosphine (Ph_2P–PPh_2), tetraphenyldiphosphinothiane

sulfide ($Ph_2P(S)–S–PPh_2$), and tetraphenyldiphosphine disulfide ($Ph_2P(S)–P(S)Ph_2$). After the reaction, the mixture was exposure to air for an hour and then 30 wt % aqueous hydrogen peroxide solution (0.4 mmol) was added except for **10af**. BPSO **10** was obtained after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$).

(1-(Diphenylthiophosphinyl)dodecan-2-yl)diphenylphosphine oxide (10aa) White solid; **mp.** 121–122 °C;**^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.42–0.63 (m, 2H), 0.67–0.82 (m, 2H), 0.88 (t, J_{H-H} = 7.1 Hz, 3H), 0.92–0.99 (m, 2H), 1.03–1.12 (m, 2H), 1.13–1.32 (m, 8H), 1.38–1.56 (m, 1H), 2.49–2.63 (m, 1H), 2.98–3.11 (m, 1H), 3.38–3.51 (m, 1H), 7.29–7.35 (m, 2H), 7.36–7.51 (m, 10H), 7.57 (dd, J_{H-H} = 12.4 Hz, J_{H-P} = 7.8 Hz, 2H), 7.76–7.85 (m, 2H), 7.89–8.03 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.1, 22.6, 26.5 (d, J_{C-P} = 2.9 Hz), 27.3, 28.7, 29.16, 29.23, 29.37 (two carbons of long alkyl chain are overlapped), 29.41 (d, J_{C-P} = 51.8 Hz), 31.8, 32.0 (dd, J_{C-P} = 69.0 Hz, 1.9 Hz), 128.4 (d, J_{C-P} = 11.5 Hz, four *ortho*-carbons of diphenylthiophosphinyl group are overlapped), 128.6 (d, J_{C-P} = 11.5 Hz), 128.8 (d, J_{C-P} = 11.5 Hz), 130.3 (d, J_{C-P} = 10.5 Hz), 130.8 (d, J_{C-P} = 8.6 Hz), 131.2 (d, J_{C-P} = 8.6 Hz), 131.3 (d, J_{C-P} = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.4 (d, J_{C-P} = 10.5 Hz), 131.68 (d, J_{C-P} = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.65 (d, J_{C-P} = 93.0 Hz), 131.9 (d, J_{C-P} = 78.6 Hz), 132.3 (d, J_{C-P} = 93.9 Hz), 134.2 (d, J_{C-P} = 82.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 38.1 (d, J_{P-P} = 52.0 Hz), 43.7 (d, J_{P-P} = 56.4 Hz); **IR** (KBr): 613, 623, 694, 714, 1104, 1117, 1171, 1189, 1436, 2851, 2923, 3051 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{36}H_{44}NaOP_2S$: 609.2480, Found: 609.2480.

(1-Cyclohexyl-2-(diphenylthiophosphinyl)ethyl)diphenylphosphine oxide (10ad) White solid; **mp.** 273–274 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.37–0.48 (m, 1H), 0.50–0.74 (m, 3H), 1.05–1.17 (m, 1H), 1.24–1.50 (m, 4H), 1.54–1.67 (m, 2H), 2.62–2.67 (m, 1H), 2.96–3.07 (m, 1H), 3.54–3.65 (m, 1H), 7.20–7.26 (m, 2H), 7.30–7.355 (m, 1H), 7.358–7.54 (m, 10H), 7.87 (ddd, J_{H-H} = 11.2 Hz, 1.8 Hz, J_{H-P} = 7.6 Hz, 2H), 7.90–7.99 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.8,

26.6, 26.8, 27.6 (d, $J_{C\text{-}P}$ = 52.7 Hz), 30.7 (d, $J_{C\text{-}P}$ = 8.6 Hz), 31.6, 38.0 (dd, $J_{C\text{-}P}$ = 69.0 Hz, 1.9 Hz), 38.7, 128.46 (d, $J_{C\text{-}P}$ = 12.5 Hz, four *ortho*-carbons of diphenylphosphinyl group are overlapped), 128.53 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.2 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.4 (d, $J_{C\text{-}P}$ = 78.6 Hz), 132.9 (d, $J_{C\text{-}P}$ = 94.9 Hz), 133.7 (d, $J_{C\text{-}P}$ = 93.9 Hz), 134.6 (d, $J_{C\text{-}P}$ = 83.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 36.8 (d, $J_{P\text{-}P}$ = 47.7 Hz), 45.4 (d, $J_{P\text{-}P}$ = 47.7 Hz); **IR** (KBr): 695, 724, 1117, 1180, 1436, 2851, 2925, 3052 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{32}H_{35}OP_2S$: 529.1884, Found: 529.1880.

(1-(4-(tert-Butoxy)phenyl)-2-(diphenylthiophosphinyl)diphenylphosphine oxide (10ae) White solid; **mp.** 234–235 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1,16 (s, 9H), 2.70–2.82 (m, 1H), 3.56 (dddd, $J_{H\text{-}H}$ = 14.7 Hz, 7.3 Hz, $J_{H\text{-}P}$ = 11.5 Hz, 2.8 Hz, 1H), 4.55–4.66 (m, 1H), 6.43 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.96 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.04–7.14 (m, 4H), 7.15–7.200 (m, 1H), 7.204–7.28 (m, 3H), 7.31–7.365 (m, 2H), 7.372–7.43 (m, 1H), 7.48 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.56–7.60 (m, 3H), 7.63 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.09–8.18 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.6, 31.9 (d, $J_{C\text{-}P}$ = 53.7 Hz), 39.7 (d, $J_{C\text{-}P}$ = 65.2 Hz), 78.3, 123.6, 127.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 127.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 4.8 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.8 (d, $J_{C\text{-}P}$ = 4.8 Hz), 130.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.3 (d, $J_{C\text{-}P}$ = 97.8 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 102.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 8.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 134.5 (d, $J_{C\text{-}P}$ = 83.4 Hz), 154.0; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 36.5 (d, $J_{P\text{-}P}$ = 56.4 Hz), 44.2 (d, $J_{P\text{-}P}$ = 56.4 Hz); **IR** (KBr): 695, 723, 802, 850, 897, 1102,, 1117, 1163, 1195, 1437, 1500, 2978, 3056 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{36}H_{36}NaO_2P_2S$: 617.1804, Found: 617.1803.

Diethyl 2-(diphenylthiophosphinyl)-3-(diphenylphosphinyl)succinate (10af) BPSO **10af** was obtained as a mixture of two diastereomers (*trans*/*cis* = 93/7). White solid; **mp.** 184–185 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.58 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 0.69 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 2.96 (qd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 10.5 Hz, 1H), 3.11 (qd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 10.5 Hz, 1H), 3.30 (qd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 10.5 Hz, 1H), 3.43 (qd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 10.5 Hz, 1H), 4.78–4.89 (m, 2H), 7.28–7.34 (m, 4H), 7.35–7.41 (m, 2H) 7.52–7.65 (m, 8H), 7.74 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.04 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.21 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 6.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 12.9, 13.0, 48.2 (d, $J_{C\text{-}P}$ = 36.4 Hz), 50.2 (d, $J_{C\text{-}P}$ = 49.8 Hz), 61.2, 61.3, 127.7 (d, $J_{C\text{-}P}$ = 12.5 Hz), 127.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 13.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 13.4 Hz), 130.99 (d, $J_{C\text{-}P}$ = 82.4 Hz), 131.02 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.04 (d, $J_{C\text{-}P}$ = 84.4 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.95 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 102.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 107.4 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 167.1, 167.6; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.4 (d, $J_{P\text{-}P}$ = 39.0 Hz), 49.4 (d, $J_{P\text{-}P}$ = 43.4 Hz) [for diastereomer: δ 28.5 (d, $J_{P\text{-}P}$ = 17.3 Hz), 49.2 (d, $J_{P\text{-}P}$ = 17.3 Hz)]; **IR** (KBr): 691, 719, 752, 1029, 1099, 1196, 1246, 1280, 1437, 1730, 2984, 3052 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{32}NaO_5P_2S$: 613.1338, Found: 613.1338.

(2-(Diphenylthiophosphinyl)cyclopentyl)diphenylphosphine oxide (10ag) White solid; **mp.** 209–210 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.78–2.01 (m, 4H), 2.06–2.32 (m, 2H), 3.40–3.51 (m, 1H), 3.83–3.95 (m, 1H), 7.04–7.11 (m, 4H), 7.19–7.27 (m, 2H), 7.34–7.48 (m, 8H), 7.64–7.74 (m, 4H), 7.89 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.1, 29.7, 29.8, 37.5 (d, $J_{C\text{-}P}$ = 54.6 Hz), 38.1 (d, $J_{C\text{-}P}$ = 69.0 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.5 Hz, two *ortho*-carbons of diphenylthiophosphinyl group are overlapped with two *ortho*-carbons of diphenylphosphinyl group), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of

diphenylthiophosphinyl group are overlapped), 130.98 (d, $J_{C\text{-}P}$ = 75.7 Hz), 130.99 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 95.9 Hz), 132.4 (d, $J_{C\text{-}P}$ = 79.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 97.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 36.8 (d, $J_{P\text{-}P}$ = 34.7 Hz), 54.4 (d, $J_{P\text{-}P}$ = 34.7 Hz); **IR** (KBr): 696, 720, 1099, 1195, 1437, 2951, 3054 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{29}H_{29}OP_2S$: 487.1414, Found: 487.1408.

3-(Diphenylthiophosphinyl)-2-(diphenylphosphinyl)cyclopentan-1-one (10ah) White solid; **mp.** 192–193 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.94–2.05 (m, 1H), 2.10–2.38 (m, 2H), 2.67–2.79 (m, 1H), 3.64–3.76 (m, 1H), 4.20 (ddd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 17.7 Hz, 1.4 Hz, 1H), 7.29–7.38 (m, 4H), 7.39–7.53 (m, 8H), 7.64 (ddd, $J_{H\text{-}H}$ = 12.2 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.4 Hz, 2H), 7.70 (ddd, $J_{H\text{-}H}$ = 11.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.4 Hz, 2H), 7.85 (ddd, $J_{H\text{-}H}$ = 12.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.4 Hz, 2H), 7.92 (ddd, $J_{H\text{-}H}$ = 12.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.9 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 22.3, 36.6 (d, $J_{C\text{-}P}$ = 55.3 Hz), 37.7, 52.1 (d, $J_{C\text{-}P}$ = 51.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.70 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.74 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.8 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.1 (d, $J_{C\text{-}P}$ = 98.2 Hz), 130.3 (d, $J_{C\text{-}P}$ = 78.2 Hz), 130.7 (d, $J_{C\text{-}P}$ = 102.0 Hz), 131.0 (d, $J_{C\text{-}P}$ = 76.3 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.58 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.63 (d, $J_{C\text{-}P}$ = 9.5 Hz, two *meta*-carbons of diphenylphosphinyl group are overlapped with a *para*-carbon of diphenylthiophosphinyl group), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 211.4 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.7 (d, $J_{P\text{-}P}$ = 38.7 Hz), 52.5 (d, $J_{P\text{-}P}$ = 38.7 Hz); **IR** (NaCl): 693,, 717, 972, 997, 1099, 1118, 1195, 1391, 1437, 1477, 1740, 2919, 3049 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{29}H_{27}O_2P_2S$: 501.1207, Found: 501.1224.

(3-(Diphenylthiophosphinyl)-5-phenyltetrahydrofuran-2-yl)diphenylphosphine oxide (10ai) White solid; **mp.** 175–176 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.12–2.28 (m, 1H), 2.47 (ddd, $J_{H\text{-}H}$ = 17.9 Hz, 12.8 Hz, 5.5 Hz, 1H), 4.21–4.30 (m, 1H), 5.37 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, $J_{H\text{-}P}$ = 21.8 Hz, 3.7 Hz, 1H), 5.62 (dd, $J_{H\text{-}H}$ = 11.0 Hz, 5.5 Hz, 1H), 7.09–7.13 (m, 2H), 7.14–7.18 (m, 3H),

7.19–7.34 (m, 7H), 7.36–7.48 (m, 5H), 7.65 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.77 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.85 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.97 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 37.7, 40.6 (d, $J_{C\text{-}P}$ = 54.6 Hz), 76.8 (d, $J_{C\text{-}P}$ = 85.3 Hz), 83.8 (d, $J_{C\text{-}P}$ = 3.8 Hz), 126.4, 127.5, 128.0, 128.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 79.6 Hz), 130.4 (d, $J_{C\text{-}P}$ = 94.9 Hz), 130.7 (d, $J_{C\text{-}P}$ = 99.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.35 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 132.0 (d, $J_{C\text{-}P}$ = 80.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 140.0; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 30.3 Hz), 50.1 (d, $J_{P\text{-}P}$ = 30.3 Hz); **IR** (KBr): 549, 695, 751, 998, 1062, 1100, 1117, 1194, 1437, 2920, 3051 cm^{-1}; **HRMS** (ESI+) Calcd for [M + H^+] $C_{34}H_{31}O_2P_2S$: 565.1520, Found: 565.1534.

(3-(Diphenylthiophosphinyl)-5-(4-methoxyphenyl)tetrahydrofuran-2-yl)diphenylphosphine oxide (10aj) White solid; **mp.** 161–162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.14–2.30 (m, 1H), 2.42 (ddd, $J_{H\text{-}H}$ = 17.9 Hz, 12.6 Hz, 5.5 Hz, 1H), 3.74 (s, 3H), 4.18–4.28 (m, 1H), 5.33 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, $J_{H\text{-}P}$ = 22.2 Hz, 3.7 Hz, 1H), 5.56 (dd, $J_{H\text{-}H}$ = 11.0 Hz, 5.5 Hz, 1H), 6.72 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.07 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.20–7.297 (m, 4H), 7.313–7.37 (m, 3H), 7.38–7.50 (m, 5H), 7.64 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.77 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.84 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.96 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 37.7, 40.7 (d, $J_{C\text{-}P}$ = 54.6 Hz), 55.1, 76.7 (d, $J_{C\text{-}P}$ = 85.3 Hz), 83.7 (d, $J_{C\text{-}P}$ = 3.8 Hz), 113.4, 128.1, 128.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.4 (d, $J_{C\text{-}P}$ = 84.4 Hz), 130.5 (d, $J_{C\text{-}P}$ = 90.1 Hz), 130.9 (d, $J_{C\text{-}P}$ = 101.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are

overlapped), 132.0, 132.1 (d, $J_{C\text{-}P}$ = 80.1 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 159.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 34.7 Hz), 50.1 (d, $J_{P\text{-}P}$ = 30.3 Hz); **IR** (KBr): 698, 709, 837, 1029, 1061, 1099, 1192, 1246, 1310, 1437, 1513, 1610, 2909, 3055 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{35}H_{33}O_3P_2S$: 595.1626, Found: 595.1645.

(3-(Diphenylthiophosphinyl)-5-(4-fluorophenyl)tetrahydrofuran-2-yl)diphenylphosphine oxide (10ak) White solid; **mp.** 196–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.16–2.34 (m, 1H), 2.40–2.51 (m, 1H), 4.19–4.28 (m, 1H), 5.34 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 22.0 Hz, 3.7 Hz, 1H), 5.60 (dd, $J_{H\text{-}H}$ = 10.5 Hz, 5.5 Hz, 1H), 6.86 (dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{H\text{-}F}$ = 8.7 Hz, 2H), 7.13 (dd, $J_{H\text{-}H}$ = 8.7 Hz, $J_{H\text{-}F}$ = 5.5 Hz, 2H), 7.18–7.239 (m, 2H), 7.241–7.294 (m, 2H), 7.296–7.377 (m, 3H), 7.383–7.53 (m, 5H), 7.62 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.76 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.81 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.97 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 37.9, 40.8 (d, $J_{C\text{-}P}$ = 55.3 Hz), 76.9 (d, $J_{C\text{-}P}$ = 85.2 Hz), 83.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 114.8 (d, $J_{C\text{-}F}$ = 21.0 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.4 Hz), 130.2 (d, $J_{C\text{-}P}$ = 95.4 Hz), 130.3 (d, $J_{C\text{-}P}$ = 78.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 100.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 1.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.8 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.9 (d, $J_{C\text{-}P}$ = 77.3 Hz), 132.0 (d, $J_{C\text{-}P}$ = 8.6 Hz), 135.9 (d, $J_{C\text{-}F}$ = 2.9 Hz), 162.2 (d, $J_{C\text{-}F}$ = 246.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.4 (d, $J_{P\text{-}P}$ = 34.4 Hz), 49.9 (d, $J_{P\text{-}P}$ = 34.4 Hz); **IR** (KBr): 696, 752, 1069, 1100, 1118, 1196, 1226, 1437, 1510, 1606, 2980, 3056 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{34}H_{30}FO_2P_2S$: 583.1421, Found: 583.1411.

(3-(Diphenylthiophosphinyl)-4-phenyltetrahydrofuran-2-yl)diphenylphosphine oxide (10al) White solid; **mp.** 188–189 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.64–3.80 (m, 1H), 3.83 (dd, $J_{H\text{-}H}$ = 9.2 Hz, 8.2 Hz, 1H), 4.16 (dd, $J_{H\text{-}H}$ = 8.2 Hz, 7.8 Hz, 1H), 4.49 (dddd, $J_{H\text{-}H}$ = 7.3 Hz, 5.0 Hz,

$J_{H\text{-}P}$ = 16.0 Hz, 1.8 Hz, 1H), 5.53 (ddd, $J_{H\text{-}H}$ = 11.7 Hz, $J_{H\text{-}P}$ = 20.2 Hz, 5.0 Hz, 1H), 6.97–7.10 (m, 9H), 7.14–7.20 (m, 3H), 7.24 (dt, $J_{H\text{-}H}$ = 7.8 Hz, 1.4 Hz, 1H), 7.30 (dt, $J_{H\text{-}H}$ = 7.8 Hz, 1.4 Hz, 1H), 7.39–7.50 (m, 3H), 7.55 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.65 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.76 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.87 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 46.5 (dd, $J_{C\text{-}P}$ = 54.8 Hz, 3.8 Hz), 48.6, 77.2, 78.3 (dd, $J_{C\text{-}P}$ = 79.6 Hz, 4.8 Hz), 126.5, 127.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.1, 128.27 (d, $J_{C\text{-}P}$ = 11.5 Hz, two *ortho*-carbons of diphenylthiophosphinyl group are overlapped with two *ortho*-carbons of diphenylphosphinyl group), 128.32, 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 94.9 Hz), 130.3 (d, $J_{C\text{-}P}$ = 78.6 Hz), 130.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 130.8 (d, $J_{C\text{-}P}$ = 77.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 95.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylphosphinyl group are overlapped), 131.60 (d, $J_{C\text{-}P}$ = 8.6 Hz), 131.64 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 139.3 (d, $J_{C\text{-}P}$ = 1.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.7 (d, $J_{P\text{-}P}$ = 30.3 Hz), 53.0 (d, $J_{P\text{-}P}$ = 30.3 Hz); **IR** (KBr): 611, 639, 716, 817, 930, 1036, 1073, 1098, 1117, 1205, 1438, 1455, 1480, 2883, 3050 cm^{-1}; **HRMS** (ESI+) Calcd for [M + H^+] $C_{34}H_{31}O_2P_2S$: 565.1520, Found: 565.1512.

(E)-(1-(Diphenylthiophosphinyl)oct-1-en-2-yl)diphenylphosphine oxide (10am) The stereoselectivity of the product (*E*/*Z* = 91/9) was calculated from the integral ratio of their allyl protons (δ_H 2.56–2.67 (m, 2H, for *E*-isomer) vs δ_H 2.21–2.24 (m, 2H, for *Z*-isomer)) by ^{1}H NMR spectroscopy. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.71 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 0.76–0.85 (m, 4H), 0.87–1.03 (m, 4H), 2.56–2.67 (m, 2H), 7.20 (dd, $J_{H\text{-}P}$ = 23.6 Hz, 21.5 Hz, 1H), 7.39–7.44 (m, 4H), 7.45–7.52 (m, 6H), 7.57 (dt, $J_{H\text{-}H}$ = 7.3 Hz, 1.4 Hz, 2H), 7.71 (ddd, $J_{H\text{-}H}$ = 11.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 4H), 7.82 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.9, 22.2, 28.8, 29.3, 30.6 (dd, $J_{C\text{-}P}$ = 8.6 Hz, 8.6 Hz), 31.0, 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 101.6 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.6 (d, $J_{C\text{-}P}$ = 84.4 Hz), 136.2

(dd, $J_{C\text{-}P}$ = 72.8 Hz, 8.6 Hz), 156.8 (d, $J_{C\text{-}P}$ = 79.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.5 (d, $J_{P\text{-}P}$ = 56.4 Hz), 31.0 (d, $J_{P\text{-}P}$ = 56.4 Hz) (for *Z*-isomer: δ 26.7 (d, $J_{P\text{-}P}$ = 17.3 Hz), 35.6 (d, $J_{P\text{-}P}$ = 17.3 Hz)); **IR** (NaCl): 693, 723, 748, 1099, 1118, 1195, 1436, 1506, 1558, 1684, 2855, 2928, 2950, 3056 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{34}NaOP_2S$: 551.1698, Found: 551.1698.

Experimental procedure for the synthesis of 8an–8ap (Table 5-2)

Tetraphenyldiphosphine monosulfide (0.4 mmol) and alkene (0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 6 h (10 h for **8ao**) at 20–25 °C. After the reaction, the mixture was concentrated under reduced pressure and then the residue was washed with *n*-hexane to give the product.

(2-(Diphenylphosphino)tetrahydrofuran-3-yl)diphenylphosphine sulfide (8an) White solid; **mp.** 177–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.80–1.95 (m, 1H), 2.14–2.28 (m, 1H), 3.26–3.36 (m, 1H), 3.66 (dt, $J_{H\text{-}H}$ = 15.1 Hz, 7.3 Hz, 1H), 3.93 (dt, $J_{H\text{-}H}$ = 15.1 Hz, 7.3 Hz, 1H), 5.27 (ddd, $J_{H\text{-}H}$ = 10.5 Hz, $J_{H\text{-}P}$ = 18.3 Hz, 5.5 Hz, 1H), 7.19–7.27 (m, 3H), 7.29–7.49 (m, 11H), 7.56 (dt, $J_{H\text{-}H}$ = 7.3 Hz, 0.9 Hz, 2H), 7.82 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 0.9 Hz, $J_{H\text{-}P}$ = 7.3 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 42.6 (dd, $J_{C\text{-}P}$ = 55.1 Hz, 19.2 Hz), 69.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 78.8 (d, $J_{C\text{-}P}$ = 21.1 Hz), 128.2 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.4, 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.3, 131.2 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (dd, $J_{C\text{-}P}$ = 9.6 Hz, 1.9 Hz), 132.6 (d, $J_{C\text{-}P}$ = 79.6 Hz), 133.2 (d, $J_{C\text{-}P}$ = 19.2 Hz), 134.6 (d, $J_{C\text{-}P}$ = 14.4 Hz), 135.1 (d, $J_{C\text{-}P}$ = 19.2 Hz), 136.1 (d, $J_{C\text{-}P}$ = 11.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −2.4 (d, $J_{P\text{-}P}$ = 17.3 Hz), 49.6 (d, $J_{P\text{-}P}$ = 21.7 Hz); **IR** (KBr): 695, 751, 1039, 1100, 1432, 1478, 2887, 3050 cm^{-1}; **HRMS** (ESI+) Calcd for [M + O + Na^+] $C_{28}H_{26}NaO_2P_2S$: 511.1026, Found: 511.1029.

3-(Diphenylphosphino)-4-(diphenylthiophosphinyl)dihydrofuran-2(3H)-one (8ao) White solid; **mp.** 176–177 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.55–3.70 (m, 2H), 3.84 (ddd, $J_{H\text{-}H}$ = 23.4 Hz, 9.6 Hz, $J_{H\text{-}P}$ = 9.6 Hz, 1H), 4.28 (ddd, $J_{H\text{-}H}$ = 9.6 Hz, $J_{H\text{-}P}$ = 20.4 Hz, 2.3 Hz, 1H), 7.24–7.61 (m, 16H), 7.81 (ddd, $J_{H\text{-}H}$ = 12.6 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.83 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 39.1 (d, $J_{C\text{-}P}$ = 31.6 Hz), 40.7 (dd, $J_{C\text{-}P}$ = 54.2 Hz, 21.1 Hz), 65.1, 128.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.85 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.94 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.0, 129.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.7 (d, $J_{C\text{-}P}$ = 80.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 79.6 Hz), 130.6, 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.2 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.8 (d, $J_{C\text{-}P}$ = 19.2 Hz, two *ortho*-carbons of diphenylphosphino group are overlapped with one of its *ipso*-carbon), 134.0 (d, $J_{C\text{-}P}$ = 14.4 Hz), 134.3 (d, $J_{C\text{-}P}$ = 22.0 Hz), 173.4; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 4.9 (d, $J_{P\text{-}P}$ = 21.7 Hz), 50.2 (d, $J_{P\text{-}P}$ = 21.7 Hz); **IR** (NaCl): 691, 748, 1101, 1177, 1437, 1482, 1773, 2986, 3054 cm^{-1}; **HRMS** (ESI+) Calcd for [M + O + Na^+] $C_{28}H_{24}NaO_3P_2S$: 525.0819, Found: 525.0811.

3-(Diphenylphosphino)-4-(diphenylthiophosphinyl)dihydrofuran-2,5-dione (8ap) Reddish brown solid; **mp.** 182–183 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.97 (ddd, $J_{H\text{-}H}$ = 5.5 Hz, $J_{H\text{-}P}$ = 19.5 Hz, 2.3 Hz, 1H), 4.13–4.21 (m, 1H), 7.21–7.29 (m, 5H), 7.31–7.52 (m, 11H), 7.77 (ddd, $J_{H\text{-}H}$ = 14.0 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 7.84 (ddd, $J_{H\text{-}H}$ = 13.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 42.3 (d, $J_{C\text{-}P}$ = 35.5 Hz), 50.9 (dd, $J_{C\text{-}P}$ = 39.3 Hz, 24.0 Hz), 128.73 (d, $J_{C\text{-}P}$ = 83.0 Hz), 128.74 (d, $J_{C\text{-}P}$ = 12.8 Hz), 128.80 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.83 (d, $J_{C\text{-}P}$ = 81.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 12.8 Hz), 129.3 (d, $J_{C\text{-}P}$ = 6.7 Hz), 129.7, 131.0 (d, $J_{C\text{-}P}$ = 17.3 Hz), 131.2, 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.1 (d, $J_{C\text{-}P}$ = 14.4 Hz), 132.75 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.76 (d, $J_{C\text{-}P}$ = 19.2 Hz), 134.0 (d, $J_{C\text{-}P}$ = 22.0 Hz), 165.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 167.8; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 9.5 (d, $J_{P\text{-}P}$ = 17.3 Hz), 49.3 (d, $J_{P\text{-}P}$ = 17.3 Hz); **IR** (KBr): 691, 741, 920, 1046, 1100, 1437, 1781, 1854, 2923, 3055 cm^{-1}; **HRMS** (ESI+) Calcd for [M + O + Na^+] $C_{28}H_{22}NaO_4P_2S$: 539.0612, Found: 539.0607.

Experimental procedure for the synthesis of 8an by 400 nm LEDs (Table 5-2)

Tetraphenyldiphosphine monosulfide (**4a**, 0.4 mmol) and 2,3-dihydrofuran (**2n**, 0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a 400 nm LEDs (APATNER, SMD 5050 LED Strip Light, 4.5 W) for 16 h at 20–25 °C in a dark room. After the reaction, the mixture was concentrated under reduced pressure. The yield of **8an** was determined by ^{1}H NMR using 1,3,5-trioxane as an internal standard.

Experimental procedure for the gram-scale synthesis of 8an (Figure 5-7)

Tetraphenyldiphosphine monosulfide (2.6 mmol) and 2,3-dihydrofuran (2.6 mmol) in degassed dry CH_2Cl_2 (2.6 mL) were placed in a 10 mL sealed Pyrex test tube with a stirrer bar under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 20 h at 20–25 °C. After the reaction, the mixture was concentrated under reduced pressure and then the residue was washed with *n*-hexane to give the product.

Experimental procedure for the gram-scale synthesis of 8ag using in situ generated 4a (Scheme 5-4)

Chlorodiphenylphosphine (10 mmol) and bis(trimethylsilyl)sulfide (5 mmol) in degassed dry CH_2Cl_2 (5 mL) were placed in a 10 mL sealed Pyrex test tube under an argon atmosphere. The mixture was stirred for 10 min at room temperature, and then it was irradiated with a xenon lamp (500 W) for 30 h at 20–25 °C. After the reaction, the mixture was concentrated under reduced pressure and then the residue was washed with *n*-hexane. The precipitate was passed through a silica, long-body Sep-Pak cartridge (Waters) using *n*-hexane/toluene gradient 100/0 to 10/1. The filtrate was evaporated to give the product.

(2-(Diphenylphosphino)cyclopentyl)diphenylphosphine sulfide (8ag) White solid; **mp.** 102–103 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.50–1.64 (m, 2H), 1.73–1.81 (m, 1H), 1.89–2.04 (m, 2H), 2.26–2.42 (m, 1H), 3.08–3.19 (m, 2H), 7.02–7.18 (m, 7H), 7.20–7.27 (m, 4H), 7.30–7.37 (m, 5H), 7.52 (ddd, J_{H-H} = 12.6 Hz, 1.4 Hz, J_{H-P} = 8.0 Hz, 2H), 7.77 (ddd, J_{H-H} = 11.7 Hz, 1.8 Hz, J_{H-P} = 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.6, 28.0, 31.1 (d, J_{C-P} = 9.6 Hz), 37.1 (d, J_{C-P} = 16.3 Hz), 41.3 (dd, J_{C-P} = 53.7 Hz, 20.1 Hz), 128.31 (d, J_{C-P} = 11.5 Hz), 128.33 (d, J_{C-P} = 6.7 Hz, four *meta*-carbons of diphenylphosphino group are overlapped), 128.4 (d, J_{C-P} = 11.5 Hz), 128.5, 128.9, 130.9 (d, J_{C-P} = 2.9 Hz), 131.1 (d, J_{C-P} = 2.9 Hz), 131.4 (d, J_{C-P} = 9.6 Hz), 131.5 (d, J_{C-P} = 9.6 Hz), 131.8 (d, J_{C-P} = 79.6 Hz), 132.9 (d, J_{C-P} = 81.5 Hz), 133.4 (d, J_{C-P} = 19.2 Hz), 133.8 (d, J_{C-P} = 20.1 Hz), 136.5 (d, J_{C-P} = 15.3 Hz), 136.9 (d, J_{C-P} = 14.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −1.4 (d, J_{P-P} = 30.3 Hz), 53.5 (d, J_{P-P} = 30.3 Hz); **IR** (NaCl): 694, 754, 998, 1027, 1099, 1435, 1479, 2960, 3058 cm^{-1}; **HRMS** (ESI+) Calcd for [M + O + Na^+] $C_{29}H_{28}NaOP_2S$: 509.1234, Found: 509.1225.

Experimental procedure for the gram-scale synthesis of 10ag and 14ag (starting material of Scheme 5-6) using in situ generated 4a

After photoirradiation with a xenon lamp, 30 wt % aqueous hydrogen peroxide solution (5 mmol, for **10ag**) or an excess amount of elemental sulfur (15 mmol for **14ag**) was added and the mixture was stirred at room temperature for 3 h. The resulting solution was pathed through a cotton and the filtrate was then evaporated, followed by washing with *n*-hexane. Further purification was not required for the synthesis of **14ag**, and **10ag** was obtained after isolation by silica gel column chromatography (eluent: *n*-hexane/AcOEt/$CHCl_3$ = 10/20/1, R_f = 0.54).

(Cyclopentane-1,2-diyl)bis(diphenylphosphine sulfide) (14ag) White solid; **mp.** 245–246 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.76–1.95 (m, 4H), 2.00–2.18 (m, 2H), 3.99–4.12 (m, 2H), 6.98–7.07 (m, 4H), 7.12–7.19 (m, 2H), 7.34–7.44 (m, 6H), 7.63–7.72 (m, 4H), 7.83–7.92 (m,

4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.4 (t, $J_{C\text{-}P}$ = 3.8 Hz), 31.2, 38.9 (dd, $J_{C\text{-}P}$ = 68.1 Hz, 12.5 Hz), 128.2 (t, $J_{C\text{-}P}$ = 5.8 Hz), 128.4 (t, $J_{C\text{-}P}$ = 5.8 Hz), 131.00 (dd, $J_{C\text{-}P}$ = 87.2 Hz, 10.5 Hz), 131.02 (four *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.1 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.2 (t, $J_{C\text{-}P}$ = 4.8 Hz), 132.8 (dd, $J_{C\text{-}P}$ = 89.6 Hz, 10.5 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 54.2; **IR** (KBr): 654, 714, 998, 1025, 1101, 1437, 1480, 2901, 2961 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{29}H_{28}NaP_2S_2$: 525.1005, Found: 525.0996.

Experimental procedure for the synthesis of 10bn–10en and 10gn (Table 5-3)

Diphosphine monosulfide was synthesized according to the literature.[10c] Diphosphine monosulfide **4b**–**4d** are liquid and could not be isolated because impurities are also liquid and diphosphine monosulfides decompose at high temperature or under air. The purity was calculated by ^{31}P NMR spectroscopy and the crude mixture was directly used for the synthesis of BPSO **10**. Diphosphine monosulfide (0.4 mmol, calculated mass from the purity of diphosphine monosulfide) and 2,3-dihydrofuran (0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 10 h at 20–25 °C. After the reaction, the mixture was exposure to air for an hour and then 30 wt % aqueous hydrogen peroxide solution (0.4 mmol) was added. BPSO **10** was obtained after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$).

(3-(Diethylthiophosphinyl)tetrahydrofuran-2-yl)diethylphosphine oxide (10bn)

Tetraethyldiphosphine monosulfide (95 wt % purity, contaminated with $Et_2POSiMe_3$ (2 wt %), $Et_2P(S)–P(S)Et_2$ (1.6 wt %), and $Et_2P(O)H$ (1.2 wt %)) was used for this reaction. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.229 (dt, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 18.8 Hz, 6H), 1.232 (dt, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 16.0 Hz, 6H), 1.74–2.10 (m, 8H), 2.19–2.36 (m, 2H), 2.93–3.05 (m, 1H), 3.95–4.09 (m, 2H), 4.62 (ddd, $J_{H\text{-}H}$ = 6.0 Hz, $J_{H\text{-}P}$ = 19.2 Hz, 6.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 5.3 (d, $J_{C\text{-}P}$ = 4.8 Hz), 5.5 (d, $J_{C\text{-}P}$ = 4.8 Hz), 6.5 (d, $J_{C\text{-}P}$ = 4.8 Hz), 6.7 (d, $J_{C\text{-}P}$ = 4.8 Hz), 17.1 (d, $J_{C\text{-}P}$ =

65.2 Hz), 19.1 (d, $J_{C\text{-}P}$ = 63.3 Hz), 22.4 (d, $J_{C\text{-}P}$ = 18.7 Hz), 22.9 (d, $J_{C\text{-}P}$ = 18.7 Hz), 28.3, 38.3 (d, $J_{C\text{-}P}$ = 48.9 Hz), 70.0, 74.8 (d, $J_{C\text{-}P}$ = 78.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 54.1 (d, $J_{P\text{-}P}$ = 17.3 Hz), 61.9 (d, $J_{P\text{-}P}$ = 21.7 Hz); **IR** (NaCl): 768, 1040, 1078, 1154, 1243, 1403, 1456, 2881, 2972 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{12}H_{27}O_2P_2S$: 297.1207, Found: 297.1208.

(3-(Diisopropylthiophosphinyl)tetrahydrofuran-2-yl)diethylphosphine oxide (10cn)

Tetraisopropyldiphosphine monosulfide (82 wt % purity, contaminated with $^{i}Pr_2P\text{–}S\text{–}P^{i}Pr_2$ (10 wt %) and $^{i}Pr_2P(O)H$ (8 wt %)) was used for this reaction. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.24–1.37 (m, 24H), 2.17–2.49 (m, 6H), 3.16–3.27 (m, 1H), 3.99–4.07 (m, 1H), 4.10–4.18 (m, 1H), 4.93 (ddd, $J_{H\text{-}H}$ = 8.7 Hz, 4.3 Hz, $J_{H\text{-}P}$ = 18.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 15.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 16.29 (d, $J_{C\text{-}P}$ = 2.9 Hz), 16.34 (d, $J_{C\text{-}P}$ = 2.9 Hz), 16.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 16.9 (d, $J_{C\text{-}P}$ = 1.9 Hz), 16.98 (d, $J_{C\text{-}P}$ = 1.9 Hz), 17.03 (d, $J_{C\text{-}P}$ = 1.9 Hz), 17.2 (d, $J_{C\text{-}P}$ = 1.9 Hz), 24.8 (d, $J_{C\text{-}P}$ = 61.3 Hz), 25.6 (d, $J_{C\text{-}P}$ = 58.5 Hz), 26.6 (d, $J_{C\text{-}P}$ = 45.1 Hz), 28.6, 28.8 (d, $J_{C\text{-}P}$ = 47.0 Hz), 37.5 (d, $J_{C\text{-}P}$ = 41.2 Hz), 70.0, 75.4 (d, $J_{C\text{-}P}$ = 70.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 58.0 (d, $J_{P\text{-}P}$ = 21.7 Hz), 73.9 (d, $J_{P\text{-}P}$ = 21.7 Hz); **IR** (NaCl): 701, 884, 931, 1027, 1073, 1147, 1167, 1385, 2875, 2963 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{16}H_{35}O_2P_2S$: 353.1828, Found: 353.1824.

Diethyl (3-(diethoxythiophosphinyl)tetrahydrofuran-2-yl)phosphonate (10dn)

Tetraethoxydiphosphine monosulfide (81 wt % purity, contaminated with many unidentified impurities (19 mol %)) was used for this reaction. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.31 (t, $J_{H\text{-}H}$ = 6.9 Hz, 6H), 1.35 (td, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 1.4 Hz, 6H), 2.21–2.39 (m, 2H), 2.96–3.11 (m, 1H), 3.99–4.04 (m, 2H), 4.08–4.26 (m, 8H), 4.49 (dd, $J_{H\text{-}H}$ = 5.0 Hz, $J_{H\text{-}P}$ = 22.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.2 (d, $J_{C\text{-}P}$ = 6.7 Hz, two terminal carbons of diethylphosphoryl group are overlapped), 16.47 (d, $J_{C\text{-}P}$ = 5.8 Hz), 16.49 (d, $J_{C\text{-}P}$ = 5.8 Hz), 28.6, 44.2 (d, $J_{C\text{-}P}$ = 116.0 Hz), 62.4 (d, $J_{C\text{-}P}$ = 7.7 Hz), 63.0 (d, $J_{C\text{-}P}$ = 7.7 Hz), 63.09 (d, $J_{C\text{-}P}$ = 6.7 Hz), 63.12 (d, $J_{C\text{-}P}$ = 6.7 Hz), 69.5 (dd, $J_{C\text{-}P}$ = 5.8 Hz, 3.8 Hz), 74.1 (d, $J_{C\text{-}P}$ = 170.6 Hz); **^{31}P NMR** (162

MHz, $CDCl_3$): δ 22.3 (d, $J_{P\text{-}P}$ = 47.7 Hz), 99.0 (d, $J_{P\text{-}P}$ = 47.7 Hz); **IR** (NaCl): 772, 961, 1023, 1161, 1250, 1216, 1390, 1440, 2932, 2980 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{12}H_{27}O_6P_2S$: 361.0998, Found: 361.0991.

(3-(Bis(4-methylphenyl)thiophosphinyl)tetrahydrofuran-2-yl)bis(4-methylphenyl)phosphine oxide (10en) Tetrakis(4-methylphenyl)diphosphine monosulfide (>99 mol % purity) was used for this reaction. White solid; **mp.** 152–153 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.85–2.01 (m, 1H), 2.03–2.18 (m, 1H), 2.30 (s, 3H), 2.33 (s, 6H), 2.34 (s, 3H), 3.81–3.87 (m, 1H), 3.99–4.16 (m, 2H), 5.21 (ddd, $J_{H\text{-}H}$ = 9.6 Hz, $J_{H\text{-}P}$ = 21.1 Hz, 3.2 Hz, 1H), 7.04–7.10 (m, 4H), 7.19–7.24 (m, 4H), 7.53 (dd, $J_{H\text{-}H}$ = 11.0 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H), 7.70 (dd, $J_{H\text{-}H}$ = 11.0 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H), 7.77 (dd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H), 7.78 (dd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.2, 21.3, 21.42, 21.46, 28.7, 39.6 (d, $J_{C\text{-}P}$ = 55.6 Hz), 70.4, 77.4 (d, $J_{C\text{-}P}$ = 83.9 Hz), 127.5 (d, $J_{C\text{-}P}$ = 93.9 Hz), 127.6 (d, $J_{C\text{-}P}$ = 84.4 Hz), 127.7 (d, $J_{C\text{-}P}$ = 99.7 Hz), 128.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.01 (d, $J_{C\text{-}P}$ = 11.5 Hz, two *ortho*-carbons of bis(4-methylphenyl)phosphinyl group are overlapped with two *ortho*-carbons of bis(4-methylphenyl)thiophosphinyl group), 129.03 (d, $J_{C\text{-}P}$ = 81.5 Hz), 129.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 141.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 141.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 142.2 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.1 (d, $J_{P\text{-}P}$ = 39.0 Hz), 50.5 (d, $J_{P\text{-}P}$ = 39.0 Hz); **IR** (KBr): 660, 714, 805, 1078, 1099, 1146, 1188, 1399, 1437, 1601, 2920, 3020 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{32}H_{34}NaO_2P_2S$: 567.1652, Found: 567.1655.

(3-(Di(furan-2-yl)thiophosphinyl)tetrahydrofuran-2-yl)di(furan-2-yl)phosphine oxide (10gn) Tetra(furan-2-yl)diphosphine monosulfide (93 mol % purity, contaminated with *H*-di(furan-2-yl)phosphinate (2 mol %) and other unidentified impurities (5 mol %)) was used for this reaction. White solid; **mp.** 163–164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.13–2.36 (m, 2H), 3.91–4.05 (m, 3H), 5.16 (ddd, $J_{H\text{-}H}$ = 10.1 Hz, $J_{H\text{-}P}$ = 22.7 Hz, 3.7 Hz, 1H), 6.42–6.44 (m, 1H),

6.46–6.488 (m, 1H), 6.492–6.515 (m, 1H), 6.521–6.55 (m, 1H), 7.13–7.15 (m, 1H), 7.21–7.26 (m, 3H), 7.57–7.59 (m, 1H), 7.61–7.63 (m, 1H), 7.69–7.71 (m, 1H), 7.72–7.74 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 27.7, 40.9 (dd, $J_{C\text{-}P}$ = 62.8 Hz, 3.8 Hz), 70.3, 76.3 (d, $J_{C\text{-}P}$ = 96.8 Hz), 110.8 (d, $J_{C\text{-}P}$ = 8.6 Hz), 110.9 (d, $J_{C\text{-}P}$ = 8.6 Hz), 111.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 111.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 123.3 (d, $J_{C\text{-}P}$ = 18.2 Hz), 123.7 (d, $J_{C\text{-}P}$ = 20.1 Hz, two β-carbons of di(furan-2-yl)phosphinyl group are overlapped), 123.8 (d, $J_{C\text{-}P}$ = 18.2 Hz), 144.6 (d, $J_{C\text{-}P}$ = 139.9 Hz), 144.7 (d, $J_{C\text{-}P}$ = 126.5 Hz), 145.3 (d, $J_{C\text{-}P}$ = 118.9 Hz), 145.9 (d, $J_{C\text{-}P}$ = 110.2 Hz), 148.7 (d, $J_{C\text{-}P}$ = 7.7 Hz), 148.77 (d, $J_{C\text{-}P}$ = 7.7 Hz), 148.81 (d, $J_{C\text{-}P}$ = 7.7 Hz), 149.1 (d, $J_{C\text{-}P}$ = 7.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 10.6 (d, $J_{P\text{-}P}$ = 47.7 Hz), 21.7 (d, $J_{P\text{-}P}$ = 43.4 Hz); **IR** (KBr): 753, 882, 909, 1007, 1079, 1128, 1212, 1368, 1458, 1550, 2893, 2984, 3113 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{20}H_{18}NaO_6P_2S$: 471.0197, Found: 471.0193.

1,1,2,2-Tetra(furan-2-yl)diphosphine 1-sulfide (4g) Diphosphine monosulfide **4g** was synthesized from chlorodi(furan-2-yl)phosphine (6 mmol) and bis(trimethylsilyl)sulfide (3 mmol) and recrystallized from *n*-hexane/toluene (10/1) solution in 86% yield. It was obtained as a crude mixture (93 wt % purity), which was contaminated with di(furan-2-yl)phosphine oxide (1 wt %), tetra(furan-2-yl)diphosphine (2 wt %), and its monoxide (4 wt %). The crude product was used for the next reaction. White solid; **mp.** 85–86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.44–6.465 (m, 2H), 6.467–6.49 (m, 2H), 7.02–7.05 (m, 2H), 7.06–7.08 (m, 2H), 7.65–7.69 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 111.3 (d, $J_{C\text{-}P}$ = 8.6 Hz, two γ-carbons of di(furan-2-yl)thiophosphinyl group are overlapped with two β-carbons of di(furan-2-yl)phosphino group), 123.10 (d, $J_{C\text{-}P}$ = 19.1 Hz), 123.12 (d, $J_{C\text{-}P}$ = 19.1 Hz), 124.5 (d, $J_{C\text{-}P}$ = 20.1 Hz), 124.6 (d, $J_{C\text{-}P}$ = 20.1 Hz), 147.0 (d, $J_{C\text{-}P}$ = 121.7 Hz), 147.2 (d, $J_{C\text{-}P}$ = 126.5 Hz), 148.6 (d, $J_{C\text{-}P}$ = 5.8 Hz, two γ- and δ-carbons of di(furan-2-yl)phosphino group are overlapped with two δ-carbons of di(furan-2-yl)thiophosphinyl group); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −50.9 (d, $J_{P\text{-}P}$ = 225.4 Hz), 11.4 (d, $J_{P\text{-}P}$ = 221.1 Hz); **IR** (NaCl): 647, 690, 757, 908, 955, 1010, 1135, 1215, 1369, 1457, 1554, 3129 cm^{-1}.

Experimental procedure for the synthesis of the unsymmetrical diphosphine monosulfide 4h–4j

To a 50 mL round bottom Schlenk flask, secondary phosphine chloride R_2PCl (5 mmol) was added dropwise to a solution of bis(trimethylsilyl) sulfide (5 mmol) dissolved in degassed dry CH_3CN (100 mL) at 0 °C for 30 min under an argon atmosphere. The mixture was warmed to room temperature and it was stirred for 10 h. Diphenylphosphine chloride (5 mmol) was added dropwise to the mixture for 10 min at room temperature, and it was then stirred for 10 h. The reaction mixture was concentrated under reduced pressure to give diphosphine monosulfide **4h**–**4j** as a crude product. The purity of the product was confirmed by ^{1}H and ^{31}P NMR spectroscopy.

1,1-Dicyclohexyl-2,2-diphenyldiphosphine 1-sulfide (4h) Diphosphine monosulfide **4h** was recrystallized from *n*-hexane/toluene (10/1) solution in 87% yield. It was obtained as a crude mixture (78 wt % purity), which was contaminated with $Ph_2P(S)–PPh_2$ (22 wt %). The crude product was used for the next reaction. [CAS Registory Number: 109012-12-6];[26] white solid; **mp.** 113–114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.06–1.05 (m, 6H), 1.23–1.38 (m, 4H), 1.59–1.65 (m, 2H), 1.67–1.80 (m, 4H), 1.86–1.97 (m, 4H), 2.02–2.12 (m, 2H), 7.34–7.41 (m, 6H), 7.97–8.03 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.9 (two δ-carbons of cyclohexyl group are overlapped), 26.9 (d, $J_{C\text{-}P}$ = 12.5 Hz, two β-carbons of cyclohexyl group are overlapped), 27.0 (d, $J_{C\text{-}P}$ = 12.5 Hz, two β-carbons of cyclohexyl group are overlapped), 27.49 (d, $J_{C\text{-}P}$ = 3.8 Hz), 27.53 (d, $J_{C\text{-}P}$ = 3.8 Hz), 27.63 (d, $J_{C\text{-}P}$ = 3.8 Hz), 27.69 (d, $J_{C\text{-}P}$ = 3.8 Hz), 128.4 (d, $J_{C\text{-}P}$ = 8.6 Hz, four *meta*-carbons of phenyl group are overlapped), 130.2, two *ipso*-carbons of phenyl group could not be determined because of the overlapping with four *meta*-carbons of diphenylthiophosphinyl group of the contaminated $Ph_2P(S)–PPh_2$, 135.6 (d, $J_{C\text{-}P}$ = 23.0 Hz), 135.7 (d, $J_{C\text{-}P}$ = 23.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −32.7 (d, $J_{P\text{-}P}$ = 273.1 Hz), 62.4 (d, $J_{P\text{-}P}$ = 273.1 Hz); **IR** (KBr): 693, 742, 884, 918, 1093, 1436, 2851, 2929, 3052 cm^{-1}.

1,1-Diisopropyl-2,2-diphenyldiphosphine 1-sulfide (4i) Diphosphine monosulfide **4i** was obtained in 85% yield as a crude mixture (90 mol % purity) which was contaminated with $Ph_2P(S)–PPh_2$ (4 mol %), $Ph_2P–PPh_2$ (2 mol %), and $^{i}Pr_2P(O)H$ (2 mol %). The crude product was used for the next reaction. White solid; **mp.** 72–73 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.08 (d, J_{H-H} = 7.1 Hz, 3H), 1.12 (d, J_{H-H} = 7.1 Hz, 3H), 1.14 (d, J_{H-H} = 7.1 Hz, 3H), 1.19 (d, J_{H-H} = 7.1 Hz, 3H), 2.20–2.31 (m, 2H), 7.35–7.42 (m, 6H), 8.03–8.09 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 17.38 (d, J_{C-P} = 2.9 Hz), 17.43 (d, J_{C-P} = 2.9 Hz), 17.5 (d, J_{C-P} = 2.9 Hz), 17.6 (d, J_{C-P} = 2.9 Hz), 31.0 (d, J_{C-P} = 37.4 Hz), 31.1 (d, J_{C-P} = 37.4 Hz), 128.4 (d, J_{C-P} = 8.6 Hz, four *meta*-carbons of phenyl group are overlapped), 130.3 (two *para*-carbons of phenyl group are overlapped), 131.75 (d, J_{C-P} = 16.3 Hz), 131.79 (d, J_{C-P} = 16.3 Hz), 135.5 (d, J_{C-P} = 24.0 Hz), 135.6 (d, J_{C-P} = 24.0 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ –34.4 (d, J_{P-P} = 286.1 Hz), 68.8 (d, J_{P-P} = 277.4 Hz); **IR** (KBr): 692, 742, 1026, 1088, 1435, 1458, 1477, 2868, 2929, 2963, 3050 cm^{-1}.

O,O-Diethyl (diphenylphosphino)thiophosphonate (4j) Diphosphine monosulfide **4j** was obtained in 94% yield as a crude mixture (76 mol % purity), which was contaminated with $(EtO)_2P(S)H$ (7 mol %), $Ph_2P(S)–PPh_2$ (2 mol %), and many unidentified products (15 mol %), which may formed via Arbuzov-type reactions. The crude product was used for the next reaction. Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.18 (t, J_{H-H} = 7.1 Hz, 6H), 3.93–4.10 (m, 4H), 7.35–7.41 (m, 6H), 7.67–7.74 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.06, 16.12, 63.30 (d, J_{C-P} = 9.6 Hz), 63.32 (d, J_{C-P} = 9.6 Hz), 128.4 (d, J_{C-P} = 7.7 Hz, four *meta*-carbons of phenyl group are overlapped), 129.7 (d, J_{C-P} = 2.9 Hz, two *para*-carbons of phenyl group are overlapped), 130.85 (d, J_{C-P} = 15.3 Hz), 130.89 (d, J_{C-P} = 14.4 Hz), 134.5 (d, J_{C-P} = 20.1 Hz), 134.6 (d, J_{C-P} = 20.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −8.4 (d, J_{P-P} = 234.1 Hz), 104.9 (d, J_{P-P} = 234.1 Hz); **IR** (KBr): 656, 692, 744, 773, 948, 1016, 1159, 1387, 1436, 1480, 2899, 2933, 2980, 3054 cm^{-1}.

Experimental procedure for the synthesis of 10hn–10jn (Table 5-4)

Diphosphine monosulfide (0.4 mmol, calculated mass from the purity of diphosphine monosulfide) and 2,3-dihydrofuran (0.4 mmol for **10in** and **10jn**; 0.5 mmol for **10hn** because the crude mixture of **4h**, contaminated with 22 wt % of **4a**, was used for this reaction) in degassed dry CH_2Cl_2 (0.4 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 10 h at 20–25 °C. After the reaction, the mixture was exposure to air for an hour and then 30 wt % aqueous hydrogen peroxide solution (0.4 mmol) was added. BPSO **10** was obtained after isolation by silica gel chromatography (*n*-hexane/AcOEt/$CHCl_3$).

(3-(Dicyclohexylthiophosphinyl)tetrahydrofuran-2-yl)diphenylphosphine oxide (10hn) White solid; **mp.** 196–197 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.10–1.52 (m, 10H), 1.64–2.14 (m, 13H), 2.16–2.30 (m, 1H), 3.10–3.21 (m, 1H), 3.63–3.70 (m, 1H), 3.96–4.03 (m, 1H), 5.35 (ddd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 17.9 Hz, 4.6 Hz, 1H), 7.43–7.57 (m, 6H), 7.85 (ddd, $J_{H\text{-}H}$ = 10.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 7.97 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.70, 25.74, 26.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 26.57 (d, $J_{C\text{-}P}$ = 7.7 Hz), 26.61 (d, $J_{C\text{-}P}$ = 8.6 Hz), 26.79 (d, $J_{C\text{-}P}$ = 7.7 Hz), 26.83 (d, $J_{C\text{-}P}$ = 1.9 Hz, two γ-carbons of cyclohexyl group are overlapped), 27.0 (two γ-carbons of cyclohexyl group are overlapped), 28.5, 36.0 (dd, $J_{C\text{-}P}$ = 42.7 Hz, 2.9 Hz), 38.1 (d, $J_{C\text{-}P}$ = 45.1 Hz), 38.9 (d, $J_{C\text{-}P}$ = 45.1 Hz), 69.8, 77.2 (d, $J_{C\text{-}P}$ = 85.3 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 95.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 95.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.9 (two *para*-carbons of phenyl group are overlapped), 132.0 (d, $J_{C\text{-}P}$ = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 26.0 Hz), 67.0 (d, $J_{P\text{-}P}$ = 26.0 Hz); **IR** (KBr): 698, 721, 751, 1079, 1120, 1195, 1436, 2853, 2929 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{28}H_{38}NaO_2P_2S$: 523.1960, Found: 523.1960.

(3-(Diisopropylthiophosphinyl)tetrahydrofuran-2-yl)diphenylphosphine oxide (10in) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.20 (dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 16.5 Hz, 3H), 1.26 (dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 16.5 Hz, 6H), 1.27 (dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 16.5 Hz, 3H), 3.11–3.23 (m,

1H), 3.58–3.66 (m, 1H), 3.96–4.04 (m, 1H), 5.34 (ddd, $J_{H\text{-}H}$ = 6.9 Hz $J_{H\text{-}P}$ = 17.4 Hz, 5.0 Hz, 1H), 7.44–7.57 (m, 6H), 7.86 (ddd, $J_{H\text{-}H}$ = 10.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 7.99 (ddd, $J_{H\text{-}H}$ = 11.2 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.96 (d, $J_{C\text{-}P}$ = 1.9 Hz), 17.01 (d, $J_{C\text{-}P}$ = 1.9 Hz), 17.2 (d, $J_{C\text{-}P}$ = 1.9 Hz, two terminal carbons of isopropyl group are overlapped), 27.9 (d, $J_{C\text{-}P}$ = 46.0 Hz), 28.6, 29.0 (d, $J_{C\text{-}P}$ = 46.0 Hz), 36.2 (dd, $J_{C\text{-}P}$ = 42.7 Hz, 2.9 Hz), 69.8, 77.4 (d, $J_{C\text{-}P}$ = 84.4 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 95.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 93.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 8.6 Hz), 132.08 (d, $J_{C\text{-}P}$ = 8.6 Hz), 132.09 (two *para*-carbons of phenyl group are overlapped); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.8 (d, $J_{P\text{-}P}$ = 26.0 Hz), 73.6 (d, $J_{P\text{-}P}$ = 26.0 Hz); **IR** (NaCl): 699, 721, 752, 1074, 1119, 1189, 1437, 1457, 2874, 2965 cm^{-1}; **HRMS** (CI+) Calcd for [M + H^+] $C_{22}H_{31}O2P_2S$: 421.1520, Found: 421.1524.

O,O-Diethyl (2-diphenylphosphinyl)tetrahydrofuran-3-yl)thiophosphonate (10jn) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.19 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 1.24 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 1.93–2.11 (m, 1H), 2.18–2.32 (m, 1H), 3.08–3.21 (m, 1H), 3.88–3.94 (m, 1H), 3.95–4.10 (m, 5H), 5.13 (ddd, $J_{H\text{-}H}$ = 9.2 Hz, $J_{H\text{-}P}$ = 22.4 Hz, 4.1 Hz, 1H), 7.43–7.57 (m, 6H), 7.84–7.93 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.0 (d, $J_{C\text{-}P}$ = 6.7 Hz), 28.4, 43.2 (d, $J_{C\text{-}P}$ = 116.0 Hz), 62.9 (d, $J_{C\text{-}P}$ = 36.4 Hz, 6.7 Hz), 69.9, 77.1 (d, $J_{C\text{-}P}$ = 85.3 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 97.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 96.8 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.92 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.93 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of phenyl group are overlapped); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.4 (d, $J_{P\text{-}P}$ = 39.0 Hz), 98.8 (d, $J_{P\text{-}P}$ = 39.0 Hz); **IR** (NaCl): 698, 723, 790, 957, 1021, 1119, 1192, 1387, 1437, 2894, 2978 cm^{-1}; **HRMS** (EI+) Calcd for [M] $C_{20}H_{26}O_4P_2S$: 424.1027, Found: 424.1027.

Experimental procedure for the addition reaction of diphosphine monoxide 3b to 2n (Scheme 5-5)

Diphosphine monoxide **3b** (0.4 mmol), synthesized from triethylphosphite and

diphenylphosphine chloride,[27] and 2,3-dihydrofuran **2n** (0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mmol) were placed in a sealed Pyrex NMR tube under an argon atmosphere. The mixture was irradiated with a xenon lamp (500 W) for 10 h at room temperature, then it was concentrated under reduced pressure. The yield of the bis-adduct **7bn** was calculated by ^{1}H NMR spectroscopy.

Experimental procedure for the synthesis of 8ag from 10ag (Scheme 5-6a)

BPSO **10ag** (0.4 mmol) dissolved in CH_2Cl_2 was placed in a 10 mL sealed Pyrex test tube under an argon atmosphere. Trifluoromethanesulfonic anhydride (Tf_2O, 0.4 mmol) was added dropwise to the mixture at 0 °C for 10 min and it was stirred for an hour. An excess amount of *n*-butan-1-thiol (^{n}BuSH, 2.4 mmol) and diisopropylethylamine (^{i}Pr$_2$NEt, 0.8 mmol) was then slowly added to the mixture and then it was allowed to reach room temperature. After the mixture was stirred for 16 h, it was washed with saturated $NaHCO_3$ aqueous solution (2 x 30 mL), brine (30 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure and the residue was passed through a silica, long-body Sep-Pak cartridge (Waters) using *n*-hexane/toluene (gradient 100/0 to 10/1). The filtrate was evaporated to give the pure product in 74% yield.

Experimental procedure for the synthesis of 15ag via desulfidation of 14ag (Scheme 5-6b)

Bis(phosphine sulfide) **14ag** (0.4 mmol) and Schwartz reagent ($Cp_2Zr(H)Cl$, 3 mmol) dissolved in THF (6 mL) were placed in a 10 mL sealed Pyrex test tube under an argon atmosphere. The mixture was stirred at room temperature for 15 h, and then it was concentrated under reduced pressure. The residue was passed through a silica, long-body Sep-Pak cartridge (Waters) using *n*-hexane/toluene (10/1). The filtrate was evaporated to give the pure product in 96% yield.

1,2-Bis(diphenylphospinyl)cyclopentane (15ag) [CAS registry number: (*1R*,*2R*) 88293-04-3, (*1S*,*2S*) 88315-23-5];[28] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.61–1.75 (m, 2H), 1.87–1.97 (m, 2H), 2.20–2.40 (m, 2H), 2.72–2.87 (m, 2H), 7.14–7.22 (m, 8H), 7.26–7.36 (m, 8H), 7.43–7.49 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.2, 29.0 (t, $J_{C\text{-}P}$ = 8.3 Hz), 39.5 (dd, $J_{C\text{-}P}$ = 21.1 Hz, 19.2 Hz), 128.25 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.29 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.5, 128.6, 133.6 (d, $J_{C\text{-}P}$ = 19.2 Hz), 133.7 (d, $J_{C\text{-}P}$ = 19.2 Hz), 137.4 (d, $J_{C\text{-}P}$ = 13.4 Hz), 137.6 (d, $J_{C\text{-}P}$ = 13.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ −7.5.

Experimental procedure for the synthesis of Pd(II)/BPMS complex 16aj (Figure 5-8)

Tetraphenyldiphosphine monosulfide **4a** (0.4 mmol) and 5-(4-methoxyphenyl)-2,3-dihydrofuran **2j** (0.4 mmol) in degassed dry CH_2Cl_2 (0.4 mmol) were placed in a sealed Pyrex NMR tube under an argon atmosphere. The mixture was irradiated with a xenon lamp (500 W) for 10 h at room temperature. The reaction mixture was then concentrated, and $PdCl_2(PhCN)_2$ (0.4 mmol) in degassed dry $CDCl_3$ was added under inert atmosphere. The reaction was monitored by ^{31}P NMR spectroscopy. After BPMS **8aj** was fully converted to its palladium(II) complex, the suspension was concentrated under reduced pressure to give the pure product **16aj** in 84% yield after washing with AcOEt.

Dichloro((2-(diphenylphosphino-κP)-5-(4-methoxyphenyl)tetrahydrofuran-3-yl)diphenylphosphine sulfide-κS)palladium(II) (16aj) Light yellow solid; **mp.** 276–277 °C (decomposition); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.84–1.97 (m, 1H), 2.11–2.26 (m, 1H), 3.26–3.41 (m, 1H), 3.73 (s, 3H), 4.87 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H), 5.65 (dt, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 11.5 Hz, 1H), 6.51 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.64 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.27–7.33 (m, 2H), 7.36–7.47 (m, 3H), 7.49–7.57 (m, 3H), 7.58–7.79 (m, 7H), 7.80–7.86 (m, 1H), 8.10 (ddd, $J_{H\text{-}H}$ = 13.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 8.26 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 37.9 (d, $J_{C\text{-}P}$ = 10.5 Hz), 41.7 (dd, $J_{C\text{-}P}$ = 50.5 Hz, 4.8 Hz), 55.3, 76.0 (dd, $J_{C\text{-}P}$ = 36.2 Hz, 3.8 Hz), 84.1 (t, $J_{C\text{-}P}$ =

8.6 Hz), 113.8, 123.4 (d, $J_{C\text{-}P}$ = 58.2 Hz), 124.7 (d, $J_{C\text{-}P}$ = 79.2 Hz), 125.9 (d, $J_{C\text{-}P}$ = 58.2 Hz), 126.3 (d, $J_{C\text{-}P}$ = 85.8 Hz), 127.3, 127.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.9 (d, $J_{C\text{-}P}$ = 13.4 Hz), 130.1 (d, $J_{C\text{-}P}$ = 13.4 Hz), 131.7 (two *para*-carbons of diphenylphosphino group are overlapped), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz, two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 134.1 (dd, $J_{C\text{-}P}$ = 13.4 Hz, 1.9 Hz), 134.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 136.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 159.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 19.7, 48.1; **IR** (KBr): 690, 749, 829, 1034, 1100, 1176, 1247, 1305, 1437, 1480, 1515, 1612, 2833, 3056 cm^{-1}; **HRMS** (ESI+) Calcd for [M + Na^+] $C_{35}H_{32}Cl_2NaO_2P_2PdS$: 776.9908, Found: 776.9915.

5-6 References

1. Quin, L. D. *A Guide to Organophosphorus Chemistry.* John Wiley & Sons: New York, 2000.

2. (a) Xu, Q.; Han, L.-B. *J. Organomet. Chem.* **2011**, *696*, 130-140. (b) Bunlaksananusorn, T.; Knochel, P. *Tetrahedron Lett.* **2002**, *43*, 5817-5819. (c) Khemchyan, L. L.; Ivanova, J. V.; Zalesskiy, S. S.; Ananikov, V. P.; Beletskaya, I. P.; Starikova, Z. A. *Adv. Synth. Catal.* **2014**, *356*, 771-780.

3. (a) Hirano, K.; Miura, M. *Tetrahedron Lett.* **2017**, *58*, 4317-4322. (b) Yoshimura, A.; Saga, Y.; Sato, Y.; Ogawa, A.; Chen, T.; Han, L.-B. *Tetrahedron Lett.* **2016**, *57*, 3382-3384. (c) Guo, H.; Yoshimura, A.; Chen, T.; Saga, Y.; Han, L.-B. *Green Chem.* **2017**, *19*, 1502-1506.

4. (a) Fruchey, E. R.; Monks, B. M.; Cook, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 13130-13133. (b) Fan, J.-H.; Wei, W.-T.; Zhou, M.-B.; Song, R.-J.; Li, J.-H. *Angew. Chem. Int. Ed.* **2014**, *53*, 6650-6654. (c) Uesugi, S.; Li, Z.; Yazaki, R.; Ohshima, T. *Angew. Chem. Int. Ed.* **2014**, *53*,

1611-1615. (d) Arisawa, M.; Ichikawa, T.; Yamaguchi, M. *Chem. Commun.* **2015**, *51*, 8821-8824.

5. (a) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254-258. (b) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694-1696. (c) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937-5945. (d) Kawaguchi, S-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919-3922. (e) Burck, S.; Hajdók, I.; Nieger, M.; Bubrin, D.; Schulze, S.; Gudat, D.; Gudat, D. *Z. Naturforsch.* **2009**, *64b*, 63-72. (f) Dodds, D. L.; Floure, J.; Garland, M.; Haddow, M. F.; Leonard, T. R.; McMullin, C. L.; Orpen, A. G.; Pringle, P. G. *Dalton Trans.* **2011**, *40*, 7137-7146. (g) Förstera, D.; Hartenbach, I.; Nieger, M.; Gudat, D., *Z. Naturforsch.* **2012***, 67b,* 765-773. (h) Förster, D.; Dilger, H.; Ehret, F.; Nieger, M.; Gudat, D. *Eur. J. Inorg. Chem.* **2012**, *2012*, 3989-3994. (i) Okugawa, Y.; Hirano, K.; Miura, M. *Org. Lett.* **2017**, *19*, 2973-2976.

6. (a) Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226-2231. (b) Morse, K. W.; Morse, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 8469-8470. (c) Morse, J. G.; Morse, K. W. *Inorg. Chem.* **1975**, *14*, 565-569. (d) Drieß, M.; Haiber, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 215-219. (e) Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4801-4804. (f) Hajdók, I.; Lissner, F.; Nieger, M.; Strobel, S.; Gudat, D. *Organometallics* **2009**, *28*, 1644-1651.

7. For copper/*N*-heterocyclic carbene catalyzed reaction, see: Okugawa, Y.; Hirano, K.; Miura, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 13558. For $Ir(ppy)_3$, see: Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. *Org. Lett.* **2017**, *19*, 4802.

8. Recently, an addition reaction of diphosphine **1** to styrenes using *N*-bromosccinimide and Ir photoredox catalyst was reported. The reaction can used only arylalkenes and tetraaryldiphosphines. see: Otomura, N.; Okugawa, Y.; Hirano, K.; and Miura, M. *Synthesis*

2018, *50*, 3402-3407.

9. Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 9700-9703.

10. (a) Elder, P. J. W.; Chivers, T. *Inorg. Chem.* **2013**, *52*, 7791-7804. (b) Sues, P. E.; Lough, A. J.; Morris, R. H. *Chem. Commun.* **2014**, *50*, 4707-4710. (c) Yogendra, S.; Chitnis, S. S.; Hennersdorf, F.; Bodensteiner, M.; Fischer, R.; Burford, N.; Weigand, J. J. *Inorg. Chem.* **2016**, *55*, 1854-1860.

11. (a) Faller, J. W.; Milheiro, S. C.; Parr, J. *J. Organomet. Chem.* **2008**, *693*, 1478-1493. (b) Faller, J. W.; Wilt, J. C.; Parr, J. *Org. Lett.* **2004**, *6*, 1301-1304. (c) Faller, J. W.; Wilt, J. C. *Org. Lett.* **2005**, *7*, 633-636. (d) Faller, J. W.; Wilt, J. C. *Organometallics* **2005**, *24*, 5076-5083. (e) Deb, B.; Sarmah, P. P.; Dutta, D. K. *Eur. J. Inorg. Chem.* **2010**, *2010*, 1710-1716. (f) Milheiro, S. C.; Faller, J. W. *J. Organomet. Chem.* **2011**, *696*, 879-886.

12. Diphosphine monosulfide **4a** decomposed at 40 °C over 3 h to form $Ph_2P(S)P(S)Ph_2$ (51%) and Ph_2PPPh_2 (63%).

13. 1,2-Bis(selenophosphinyl)dodecane (41%), Ph_2PPPh_2 (44%), and $Ph_2P(Se)PPh_2$ (8%) were generated in the reaction. 1,2-Adduct **9a** was not detected by ^{1}H NMR spectroscopy.

14. Diphosphine monoselenide **5a** (0.4 mmol) was dissolved in CD_2Cl_2 (0.4 mL) and exposed to photoirradiation condition for 20 h. Most of the **5a** remained unchanged, but a small amount of **5a** was transformed into $Ph_2PSePPh_2$ (11%).

15. (a) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317-323. (b) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151-1176.

16. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925-3941.

17. Diphosphine monosulfide **4a** (0.4 mmol) was dissolved in CD_2Cl_2 (0.4 mL) and exposed to photoirradiation condition for 20 h. Most of the **4a** remained unchanged, but a small amount of **4a** decomposed to diphosphine **1** (6%), $Ph_2P(S)SPPh_2$ (5%), and $Ph_2P(S)P(S)Ph_2$ (1%). This result shows that the homolytic cleavage of the P(S)–P single bond in **4a** under photoirradiation condition is highly reversible.

18. For selective mono-reduction of bis(phosphine oxide), see: Petersson, M.-J., Loughlin, W.-J., Jenkins, I.-D. *Chem. Commun.* **2008**, *37*, 4493-4494.

19. Zablocka, M.; Delest, B.; Igau, A.; Skowronska, A.; Majoral, J.-P. *Tetrahedron Lett.* **1997**, *38*, 5997-6000.

20. For other Pd(II)/bis(phosphine) monosulfide complexes, see: (a) Qin, Y.; Selvaratnam, S.; Vittal, J. J.; Leung, P.-H. *Organometallics* **2002**, *21*, 5301-5306; (b) Pullarkat, S. A.; Tan, K.-W.; Ma, M.; Tan, G.-K.; Koh, L. L.; Vittal, J. J.; Leung, P.-H. *J. Organomet. Chem.* **2006**, *691*, 3083-3088; (c) Oberhauser, W.; Manca, G.; Ienco, A.; Strabler, C.; Prock, J.; Weninger, A.; Gutmann, R.; Brüggeller, P. *Organometallics* **2014**, *33*, 4067-4075; (d) Sui, S.; Dai, S.; Chen, C. *ACS Catal.* **2015**, *5*, 5932-5937.

21. Dörken, C. *Chem. Ber.* **1888**, *21*, 1505-1515.

22. Fluck, E.; Binder, H. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 307-313.

23. (a) Larock, R. C.; Baker, B. E. *Tetrahedron Lett.* **1988**, *29*, 905-908. (b) Jeffery, T.; David, M. *Tetrahedron Lett.* **1998**, *39*, 5751-5754.

24. Yanai, T.; Tew, D. P.; Handy, N. C. *Chem. Phys. Lett.* **2004**, *393*, 51-57.

25. Yarkevich, A.; Tsvetkov, E. *Russ. J. Gen. Chem.* **1994**, *64*, 1451-1455.

26. Gelmini, L.; Stephan, D. W. *Organometallics* **1987**, *6*, 1515-1522.

27. Tishkov, A.; Massonne, K. US20110034734, 2011.

28. Allen, D. L.; Gibson, V. C.; Green, M. L. H.; Skinner, J. F.; Bashkin, J.; Grebenik, P. D. *J. Chem. Soc., Chem. Commun.* **1983**, 895-896.

Chapter 6

Reductive Rearrangement of Tetraphenyldiphosphine Disulfide to Trigger the Bisthiophosphinylation of Alkenes and Alkynes

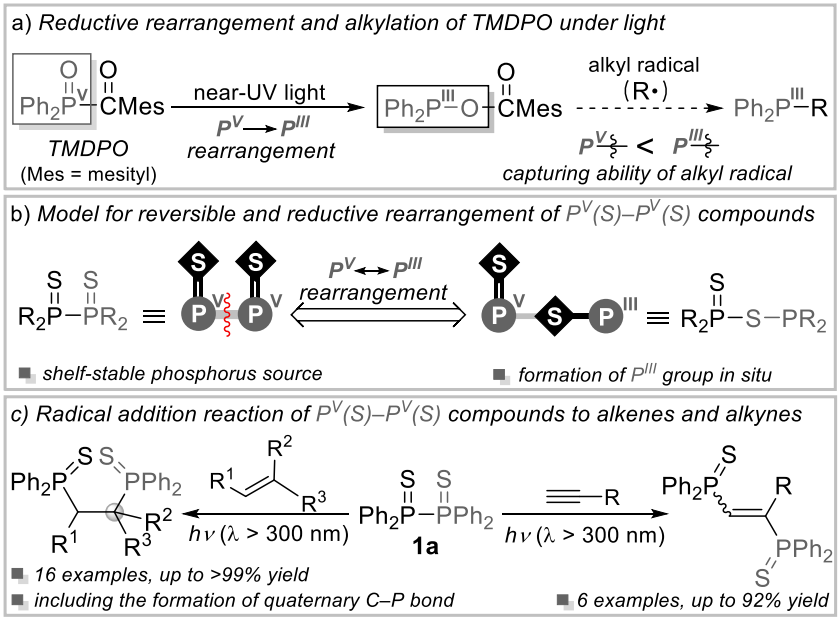
6-1 Introduction

Organophosphorus compounds are widely used as ligands for reactions catalyzed by transition metals, pharmaceuticals, and physiologically active compounds.[1] The synthesis of these compounds often requires the use of air- and moisture-sensitive sources of phosphorus. Therefore, the development of new synthetic methods involving air-stable sources of phosphorus, such as pentavalent phosphorus compounds, is of great importance. Methods that employ the reductive rearrangement of pentavalent to trivalent phosphorus compounds therefore constitute a powerful tool, because they enable pentavalent phosphorus compounds to be used efficiently. For instance, it is known that (2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO, Scheme 6-1a), bearing a P(O)–C(O) single bond,[2] is transformed into a reactive trivalent phosphorus compound (Ph_2P–OC(O)Mes) when exposed to light.[3] The author previously reported the application of this rearrangement to the synthesis of alkyl phosphines, which are trivalent phosphorus compounds.[4] In this reaction, alkyl radicals, generated in situ, efficiently react with the trivalent phosphorus atom of Ph_2P–OC(O)Mes to afford alkyl phosphines. In contrast, alkyl radicals are not captured by the pentavalent phosphorus atom of TMDPO at all because of its low radical capturing ability.

Inspired by the reductive rearrangement of TMDPO, the author next focused on the reductive rearrangement of diphosphine disulfides, bearing $P^V(S)$–$P^V(S)$ single bonds (Scheme

6-1b). The author expected a similar reductive rearrangement of several diphosphine disulfides to proceed under radical conditions to afford reactive trivalent phosphorus species in situ.

Scheme 6-1. Reductive rearrangement of TMDPO and diphosphine disulfide



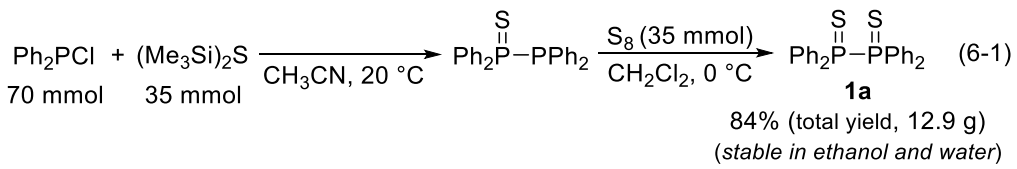
Diphosphines, bearing a P^{III}–P^{III} single bond, are important phosphorus sources for the *vic*-bisphosphination of carbon-carbon unsaturated bonds,[5,6,7] but they are difficult to handle because they are highly sensitive to air and moisture. In contrast, diphosphine disulfides[8,9] are often sufficiently shelf-stable to be stored in the presence of air for several months. Therefore, diphosphine disulfides are attractive phosphorus sources for *vic*-bisthiophosphinylation, yet limited examples of their addition reactions to alkynes and alkenes[10] have been reported. The reported addition reactions using diphosphines and their analogues, which bear a P^{V}–P^{III} single bond,[11] require a trivalent phosphorus center because the ability to capture carbon radicals is the key step in these reactions. Therefore, the author hypothesized that the reductive rearrangements of diphosphine disulfides would generate reactive trivalent phosphorus species in situ and would enable the *vic*-bisthiophosphinylation of alkenes and alkynes.

In this context, the reductive rearrangement of diphosphine disulfides and their addition

reactions to alkenes and alkynes were investigated. As a result, it was found that tetraphenyldiphosphine disulfide (**1a**) efficiently underwent reductive rearrangement to form tetraphenyldiphosphatiane monosulfide ($Ph_2P(S)–SPPh_2$) under light. This reductive rearrangement triggered the 1,2-addition of diphosphine disulfide to a variety of alkenes and alkynes to afford bisthiophosphinylated alkanes and alkenes, respectively (Scheme 6-1c). The reason why not P^{III}-adducts but P^{V}-adducts are obtained selectively is discribed in detail in the text. Furthermore, bis(thiophosphinyl)alkanes can be easily reduced to afford bidentate bis(phosphino)alkane ligands,[7b, 11b] such as dppe (*vic*-bis(diphenylphosphino)ethane).[12] Therefore, the author focused on the reductive rearrangement of diphosphine disulfides, and investigated this bisthiophosphinylation process in detail.

6-2 Results and Discussion

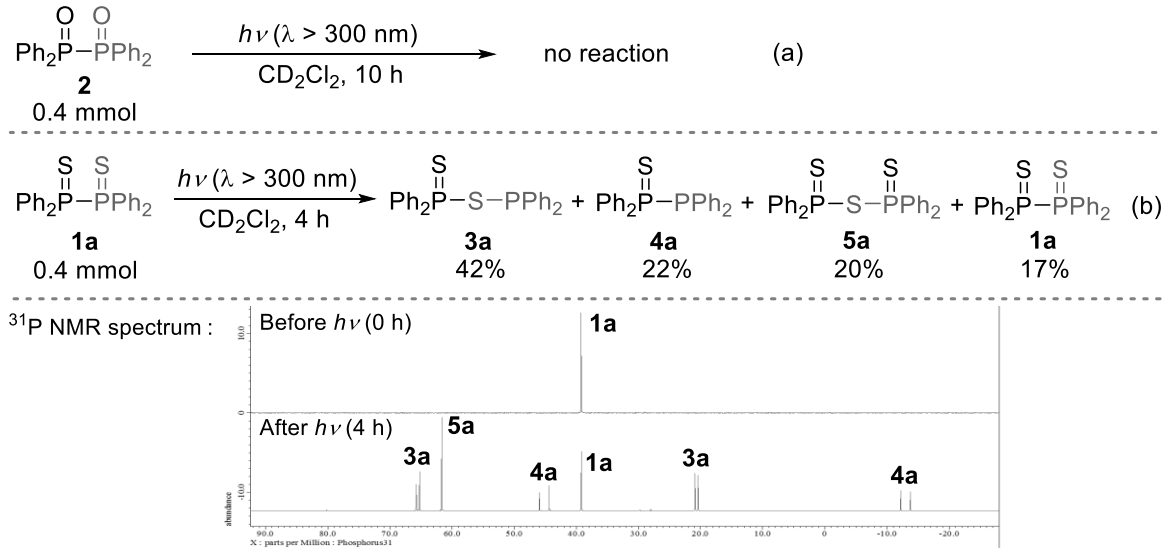
First, the synthetic method of tetraphenyldiphosphine disulfide **1a** was developed. Diphosphine disulfide **1a** is often synthesized via disulfurization of tetraphenyldiphosphine, prepared from diphenylphosphine and diphenylphosphine chloride, with a reported total yield of **1a** of 34%.[8d] The author modified the existing method to synthesize diphosphine monosulfide, reported by Burford and Weigand et al.,[13] and successfully synthesized **1a** in 84% yield (12.9 g, Eq. 6-1) via a one-pot sequence from diphenylphosphine chloride (70 mmol) and bis(trimethylsilyl) sulfide (35 mmol). Diphosphine disulfide **1a** is shelf-stable solid, which does not undergo any noticeable decomposition in ethanol and water.



Next, the rearrangement of diphosphine dioxide **2** and diphosphine disulfide **1a**, bearing

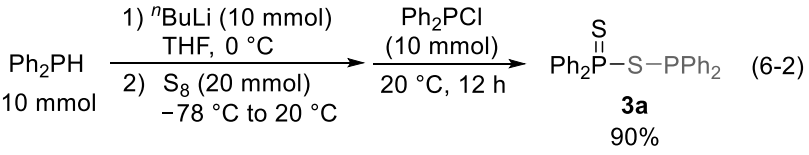
both of which have a P^V–P^V single bond, was investigated. Diphosphine dioxide **2** was irradiated with a xenon lamp (500 W) in a Pyrex NMR tube for 6 h (Scheme 6-2a), but the rearrangement of diphosphine dioxide **2** did not proceed at all. In the case of diphosphine disulfide **1a**, a pair of doublet peaks (δ_P = 20.6 ppm ($J_{P\text{-}P}$ = 78.0 Hz) and 65.4 ppm ($J_{P\text{-}P}$ = 78.0 Hz)) were observed by ^{31}P NMR spectroscopy of the mixture after irradiation (Scheme 6-2b). These peaks were assigned to diphosphathiane monosulfide **3a**, which has both pentavalent and trivalent phosphorus centers, and which was obtained in 42% yield. Additionally, diphosphine monosulfide **4a** (δ_P = −13.0 ppm ($J_{P\text{-}P}$ = 251.4 Hz) and 45.1 ppm ($J_{P\text{-}P}$ = 251.4 Hz)) and dithiophosphinoic anhydride **5a** (δ_P = 61.6 ppm) formed in yields of 22% and 20%, respectively. These results indicate that **1a** can undergo reductive rearrangement to generate trivalent phosphorus compounds **3a** accompanied with the formation of **4a** and **5a**.

Scheme 6-2. Photoinduced rearrangements of diphosphine dioxide **2** and **1a**

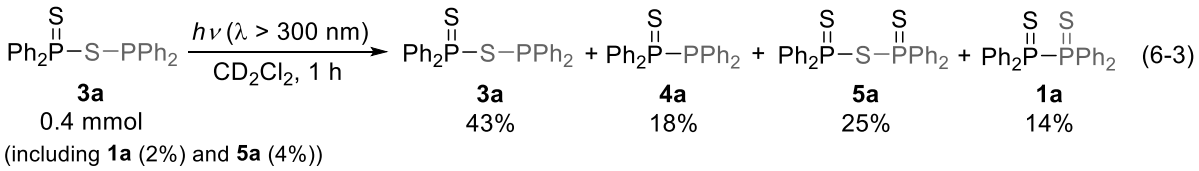


The reversibility of the rearrangement between **1a** and **3a** was confirmed by developing a novel synthetic method for **3a** (Eq. 6-2). ^{n}BuLi (1.6 M in ^{n}hexane) was added to diphenylphosphine dissolved in THF followed by slow addition of two equivalents of elemental sulfur at −78 °C. This mixture was allowed to warm to room temperature slowly.

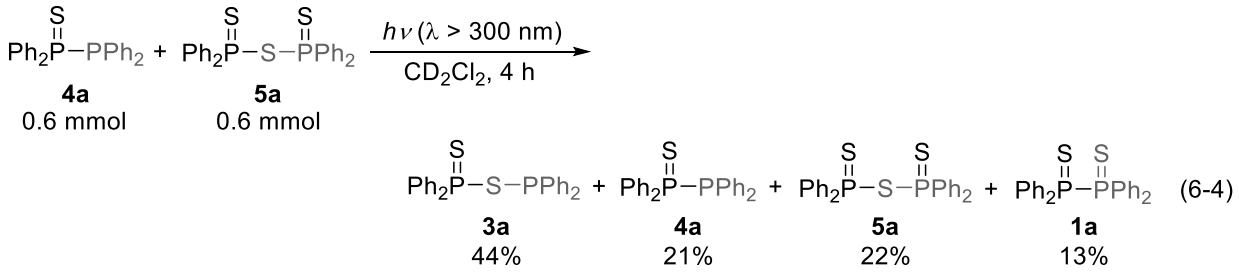
Diphenylphosphine chloride was then added to the mixture, which was stirred for 12 h to give **3a** in 90% yield as a crude mixture containing **1a** (2%) and **5a** (4%).



After exposing **3a** to irradiation by a xenon lamp for 1 h, the conversion of **3a** to **1a** (14%), **4a** (18%), and **5a** (25%) was observed by ^{31}P NMR spectroscopy (Eq. 6-3). The ratio of the phosphorus compounds generated from **3a** was similar to the result shown in Scheme 6-2b.



When the mixture containing equal amounts of **4a** and **5a** was also irradiated with a xenon lamp for 4 h, **4a** and **5a** were transformed into **1a** and **3a** (Eq. 6-4). The ratio of the phosphorus compounds generated from **4a** and **5a** was also similar to the results shown in Scheme 6-2b and Eq. 6-3.



These results revealed that **1a** and **3a**–**5a** were reversibly transformed to each other and they existed in the same molar ratio under light (Figure 6-1): Homolytic cleavage of the P(S)–P(S) single bond in **1a** is reversibly induced by photoirradiation to generate two diphenylthiophosphinyl radicals ($Ph_2P(S)\cdot$).[14] The unpaired electron of $Ph_2P(S)\cdot$ is delocalized on

its phosphorus and sulfur atoms, as shown in a single occupied molecular orbital (SOMO) of $Ph_2P(S)\cdot$ calculated at B3LYP/6-31G++(2d,p) level. Thus, $Ph_2P(S)\cdot$ partially coupled to form **3a**, bearing a P(S)–S–P structure, during the reversible homolytic cleavage of the P(S)–P(S) single bond. The transfer of a sulfur atom[15] from **1a** to **3a** also occurred to generate **4a** and **5a**, respectively.

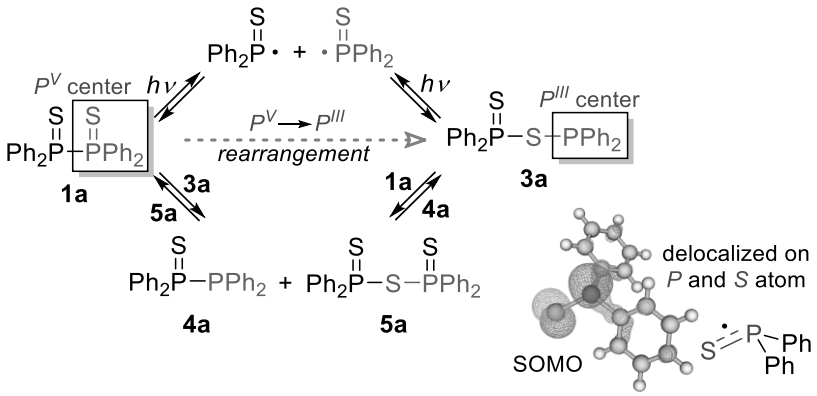
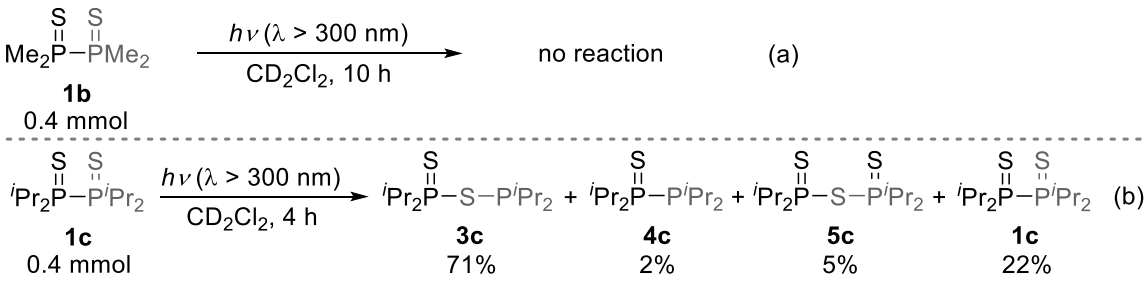


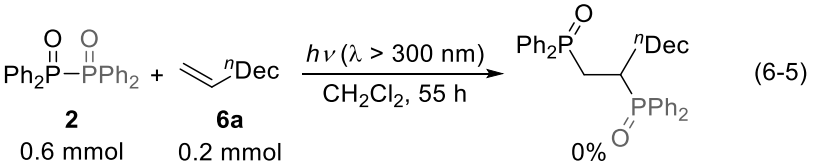
Figure 6-1. Reversible rearrangement between **1a** and **3a**–**5a**

The influence of carbon substituents of diphosphine disulfides on their rearrangement was investigated by irradiating diphosphine disulfide **1b** and **1c** with a xenon lamp (Scheme 6-3). Although diphosphine disulfide **1b** was not consumed under light at all (Scheme 6-3a), **1c** was efficiently transformed to **3c** (71%), **4c** (2%), and **5c** (5%) (Scheme 6-3b). These results indicated that the bulkiness of the carbon substituents influences the product ratio of **1** and **3**–**5** under light.

Scheme 6-3. Photoinduced rearrangements of diphosphine disulfides **1b** and **1c**



Next, the radical addition reaction of diphosphine dioxide **2** and **1a** to 1-dodecene (**6a**) was examined. The addition reaction of **2** to **6a** did not proceed at all under light (Eq. 6-5).



(6-5)

In contrast, the auhtor previously reported that diphosphine monoxide **7**, bearing a $P^{V}(O)$–P^{III} single bond, adds to **6a** and affords the corresponding 1,2-adduct in 78% yield under the same conditions as in Eq. 6-5.[11a] The addition reaction proceeds in three steps (Figure 6-2): The photoinduced homolytic cleavage of the $P^{V}(O)$–P^{III} bond of **7** generates two phosphorus radicals, namely ***P(O)*·** and ***P*·**. The more electrophilic phosphorus radical (***P(O)*·**) adds to an alkene and the generated alkyl radical is captured by the more electron-rich phosphorus group (***P***) of **7**. In this reaction, the diphenylphosphinyl group (***P(O)***) of **7** does not react with the alkyl radical because of its low capturing ability to alkyl radicals.

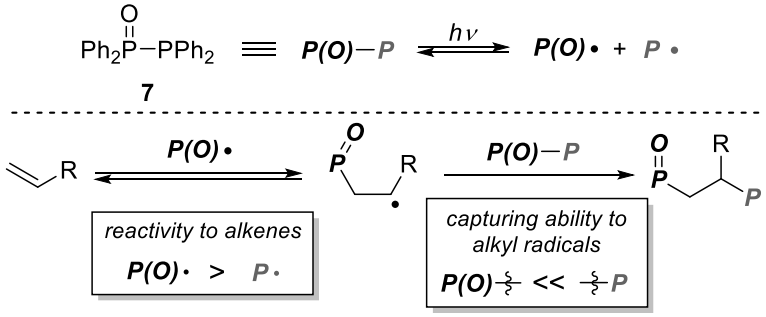


Figure 6-2. Model for radical addition of diphosphine monoxide **7** to alkenes under light

In the case of diphosphine dioxide **2** (Figure 6-3, top), photoinduced homolytic cleavage of the $P^{V}(O)$–$P^{V}(O)$ bond of **2** can be achieved but the generated alkyl radical is not captured by the diphenylphosphinyl group (***P(O)***) of **2**. In contrast, diphosphine disulfide **1a** (***P(S)*–*P(S)***) generates the trivalent phosphorus species **3a** (***P(S)*–*SP***) and **4a** (***P(S)*–*P***), which are potentially

good acceptors of alkyl radicals under exposure to UV light (Figure 6-3, bottom). Therefore, the author hypothesized that the reductive rearrangement of **1a** enables the bisthiophosphinylation of alkenes.

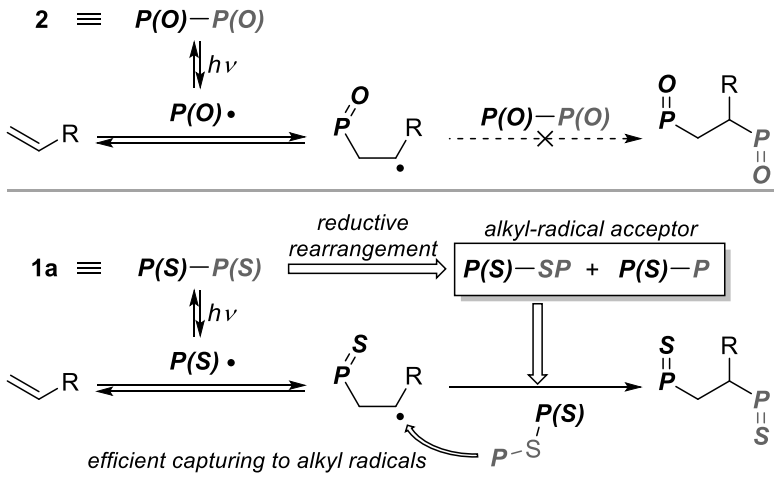
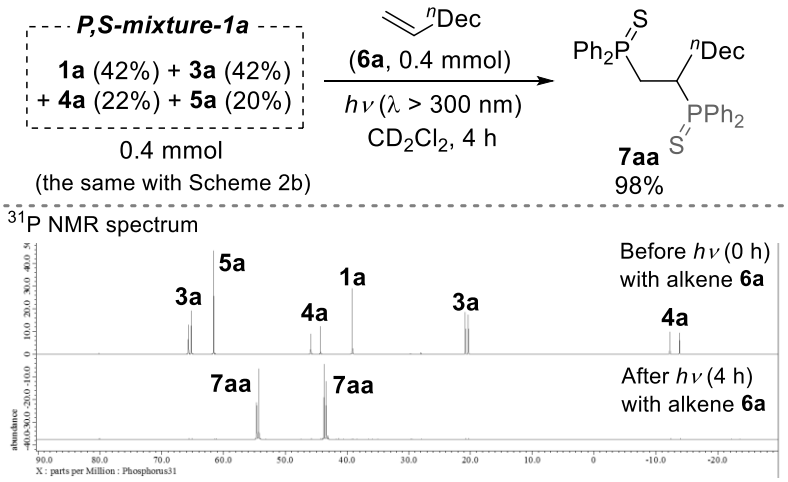


Figure 6-3. Model for radical addition of diphosphine dioxide **2** and diphosphine disulfide **1a** to alkenes under light

Based on this hypothesis, the mixture of **1a** and **3a**–**5a**, generated by exposing **1a** to light (***P,S-mixture-1a***), was used as the phosphorus source for the bisthiophosphinylation of alkene **6a** (Scheme 6-4). After ***P,S-mixture-1a*** and **6a** was irradiated by light for 4 h, interestingly, **1a** and **3a**–**5a** were almost completely consumed and 1,2-bis(thiophosphinyl)alkane **7aa** was generated in 98% yield. In general, reactions consisting of four or more substrates usually afford complex mixtures of many products. In contrast, all components (**1a** and **3a**–**5a**) of ***P,S-mixture-1a*** converged to yield only one product **7aa**, almost quantitatively.

Scheme 6-4. Bisthiophosphinylation of alkene **6a** using the mixture of **1a** and **3a**–**5a**



The bisthiophosphinylation of **6a** was investigated in detail by monitoring the conversion of **1a** and **3a**–**5a** to the 1,2-adduct **7aa** by ^{31}P NMR spectroscopy during the addition reaction, and the results are summarized in Figure 6-4. During the initial 1 h, **1a** was mainly converted to **3a**–**5a**. During the subsequent course of time, the conversion of **1a** and **3a**–**5a** and the bisthiophosphinylation of **6a** proceeded efficiently to generate the 1,2-adduct **7aa** in 98% yield. In particular, **1a** and **3a** were converted much faster than **4a** and **5a**. The addition of **4a** also occurred during the initial 1 h to 2 h but the 1,2-adduct of **4a** was converted to **7aa** after 2 h accompanied with the slow consumption of **1a** and **5a**.[16] These results indicate that **1a** and **3a** play a key role in this bisthiophosphinylation reaction and the 1,2-adduct of **4a** was sulfurized by the transfer of a sulfur atom from **1a** and **5a** to generate **7aa**.

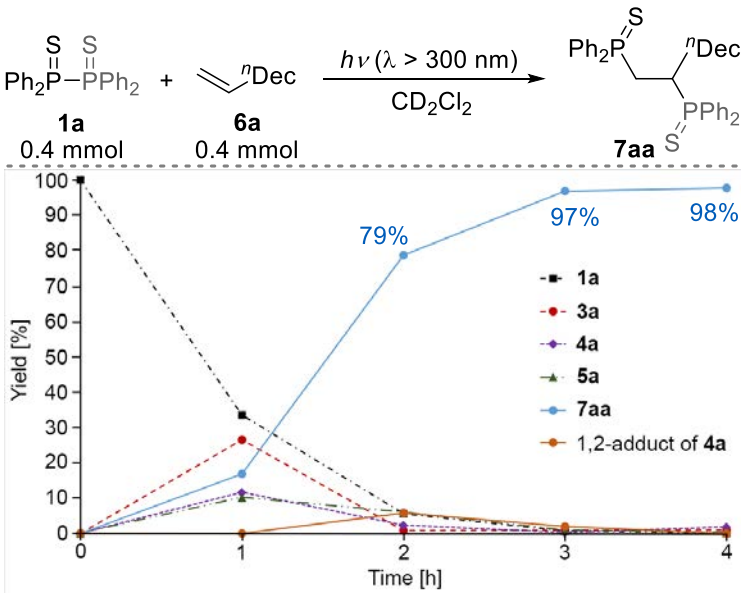


Figure 6-4. Yields during the addition reactions of diphosphine disulfide **1a** to alkene **6a** as a function of time, as monitored by ^{31}P NMR spectroscopy

The reaction progress of bisthiophosphinylation of alkene **6a** using diphosphine disulfide **1a** or ***P,S-mixture-1a*** was monitored by ^{1}H NMR spectroscopy and compared (Figure 6-5). During the initial 1 h, it was found that the bisthiophosphinylation of **6a** with ***P,S-mixture-1a*** (86% yield) proceeded approximately five times faster than the bisthiophosphinylation with **1a** (17% yield). The results summarized in Figures 6-4 and 6-5 strongly indicate that the formation of **3a**–**5a** is the induction step of the addition of **1a** and this step triggered the generation of 1,2-adduct **7aa**.

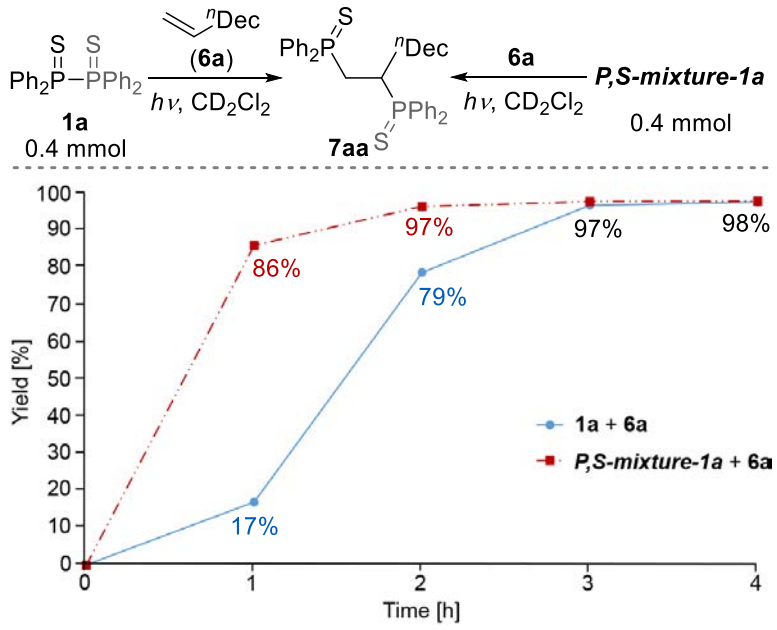
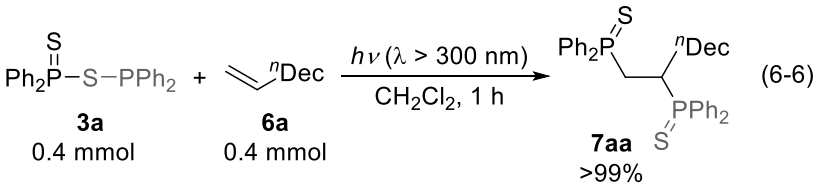


Figure 6-5. Yields during bisthiophosphinylation of alkene **6a** using diphosphine disulfide **1a** or ***P,S-mixture-1a*** as a function of time, as monitored by ^{1}H NMR spectroscopy

Notably, the addition of **3a** to **6a** efficiently proceeded to afford **7aa**, quantitatively, in an hour (Eq. 6-6). In our previous report, the addition of **4a** to **6a** while exposed to light for an hour provided the corresponding 1,2-adduct of **4a** in 62% yield.[11b] These results indicate that **3a** behaves as the main active species of the addition reaction to **6a**.



A plausible reaction pathway for the present reaction is illustrated in Figure 6-6. The bisthiophosphinylation proceeds via three steps: the $Ph_2P(S)\cdot$ attacks an alkene to afford the β-thiophosphinylated alkyl radical. The generated radical reacts with the diphenylphosphino group of **3a** and **4a** to afford the 1,2-bisthiophosphinylalkane **7a** and 1-thiophosphinyl-2-phosphinoalkane **8a**, respectively, accompanied with the release of $Ph_2P(S)\cdot$. The sulfur atom was also transferred from **1a** and **5a** to **8a** to afford **7a** accompanied by the

regeneration of **4a** and **3a**, respectively.

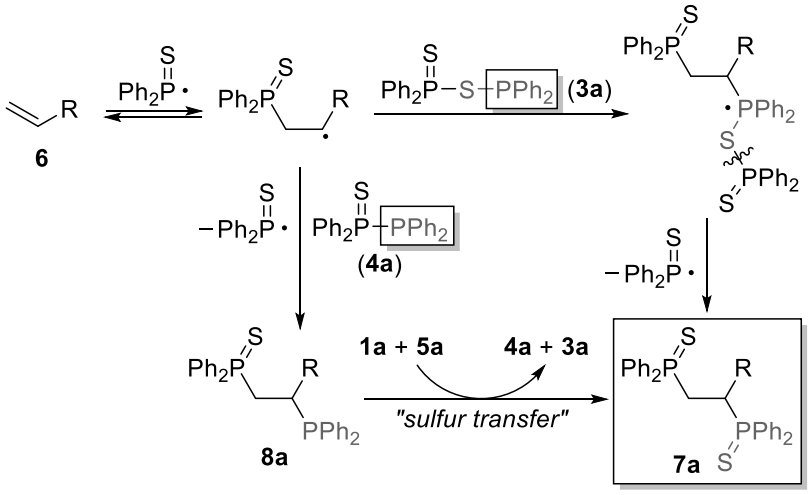
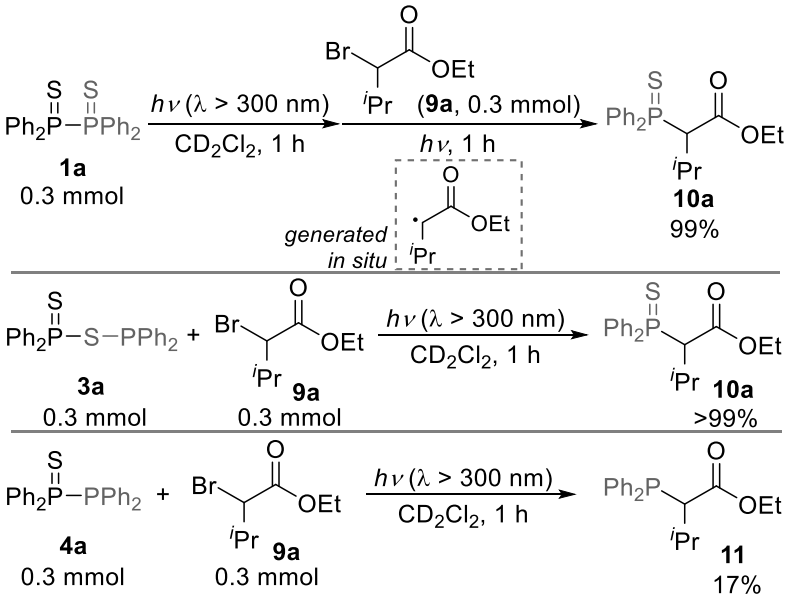


Figure 6-6. A plausible reaction pathway of bisthiophosphinylation of alkene **6** using the mixture of **1a** and **3a**–**5a**

The capturing ability of alkyl radicals on **3a** and **4a** generated from **1a** was compared by conducting several capturing experiments using the secondary alkyl radical generated from bromoacetate **9a** under light (Scheme 6-5). Diphosphine disulfide **1a** was irradiated with a xenon lamp for 1 h followed by the addition of **9a**. The mixture was irradiated for 1 h. In this reaction, **3a**–**5a** were generated from **1a** in situ by cleaving the P(S)–P(S) bond of **1a** under near-UV light in the first step, and the secondary alkyl radical was then also formed by the cleavage of the carbon–bromine bond in **9a** in the second step. The generated alkyl radical underwent homolytic substitution at the trivalent phosphorus group of **3a** and **4a** to afford alkylphosphine sulfide **10a** in 99% yield. Diphosphathiane monosulfide **3a** also reacted with **9a**, quantitatively. In contrast to **3a**, the reaction of **4a** was inefficient and alkylphosphine **11** was obtained in only 17% yield. These results indicate that the capturing ability of **3a** to secondary alkyl radicals (involving the 3-methyl-2-butanoate radicals) is higher than that of **4a**.

Scheme 6-5. Homolytic substitution of **3a** and **4a** with the secondary alkyl radical generated from bromoacetate **9a** under light



The difference between the ability of **3a** and **4a** to capture alkyl radicals can be attributed to the weakness of the phosphorus–sulfur bond and the lower steric hindrance around the trivalent phosphorus center of **3a**. The alkyl-radical-capturing of **3a** can proceed via an Arbuzov-type pathway: the alkyl radical undergoes a nucleophilic attack by the lone pair of the trivalent phosphorus atom of **3a** accompanied with homolytic cleavage of the P(S)–SP bond and formation of the P=S bond, as shown in Figure 6-7. In contrast, **4a** captures alkyl radicals via homolytic cleavage of the relatively strong P(S)–P bond. In general, the bond dissociation energy of the phosphorus–sulfur bond (442 ± 10 $kJmol^{-1}$)[17] is lower than that of the phosphorus–phosphorus bond (489 ± 10 $kJmol^{-1}$).[17] In addition, the trivalent phosphorus center of **3a** is less sterically hindered than that of **4a** because of the greater distance maintained between the bulky thiophosphinyl group and the trivalent phosphorus center of **3a** by its sulfur bridge.

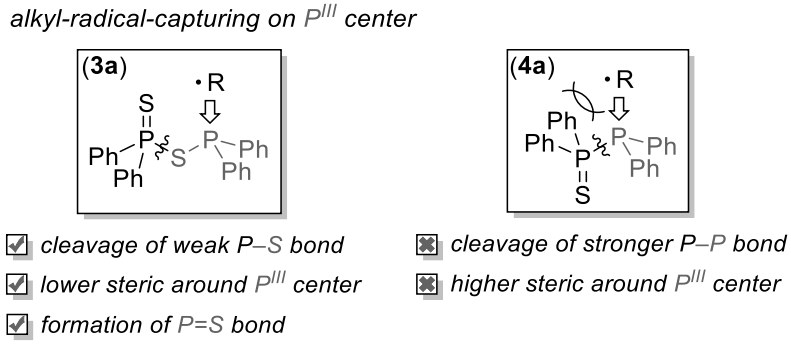
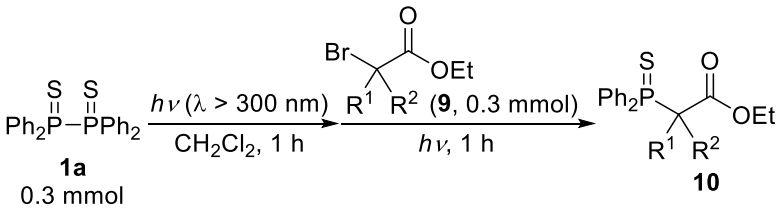


Figure 6-7. Model for the difference between the ability of **3a** and **4a** to capture alkyl radicals

Homolytic substitution reactions of **3a** and **4a**, generated from **1a**, with several bromoacetates **9** were examined to reveal the scope of their ability to capture alkyl radicals (Table 6-1). Diphosphine disulfide **1a** efficiently reacts with aliphatic secondary bromoacetates **9a** and **9b** to afford alkylphosphine sulfides **10a** and **10b**, respectively, in excellent yields. The reaction with tertiary bromoacetate **9c** provided **10c**, bearing a quaternary carbon–phosphorus bond, in 59% yield. The alkyl radical generated from **9d**, bearing a cyclobutyl group, was also captured by **3a** and **4a** efficiently, to give **10d** in 94% yield. In contrast, the benzyl radical generated from **9e** could not be captured by **3a** and **4a**. Considering the electron-withdrawing from the ester groups of the acetate radicals generated from **9**, these results indicate that aliphatic and electron-rich alkyl radicals are efficiently captured by **3a** and **4a**.

Table 6-1. Thiophosphinylation of several bromoacetates **9** with **1a**[a]

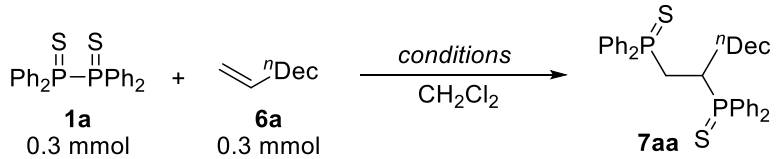


10a, 94%	**10b**, 95%	**10c**, 59%[b]	**10d**, 91%	**10e**, 6%

Isolated yields. [a]Reaction conditions: **1a** (0.3 mmol), **9** (0.3 mmol), CH_2Cl_2 (0.3 mL), 20 °C, xenon lamp (500 W), Pyrex, and 1 h. [b]Irradiation for 10 h.

Next, the ability of **1a** to undergo an addition reaction with alkenes under several radical conditions was investigated. The bisthiophosphinylation reaction of alkene **6a** proceeded efficiently even under weak irradiation and radical initiators (Table 2). Under 400 nm LED light (4.5 W), **1a** added to **6a** in 95% yield (entry 2). This reaction also proceeded under a 20 W fluorescent lamp to give the 1,2-adduct **7aa** in 51% yield (entry 3). The addition of **1a** was promoted by heating (80 °C) and the 1,2-adduct **7aa** was afforded in 95% yield under the 20 W fluorescent lamp (entry 4). Photoredox reaction conditions were also available for this reaction: under blue LED light (6.5 W), 0.5 mol% of *fac*-Ir(ppy)$_3$ catalyzed the bisthiophosphinylation of **6a** to generate 1,2-adduct **7aa** in 91% yield (entry 5). In the presence of a catalytic amount of the radical initiator V-40 (1,1'-azobis(cyclohexane-1-carbonitrile)), **1a** added to **6a**, efficiently, and 1,2-adduct **7aa** was obtained in 95% yield (entry 6). In the absence of either light or the radical initiator, **7aa** was not observed by ^{1}H NMR spectroscopy under the same reaction conditions and **1a** was recovered quantitatively (entry 7).

Table 6-2. Bisthiophosphinylation of **6a** with **1a** under several radical reaction conditions[a]



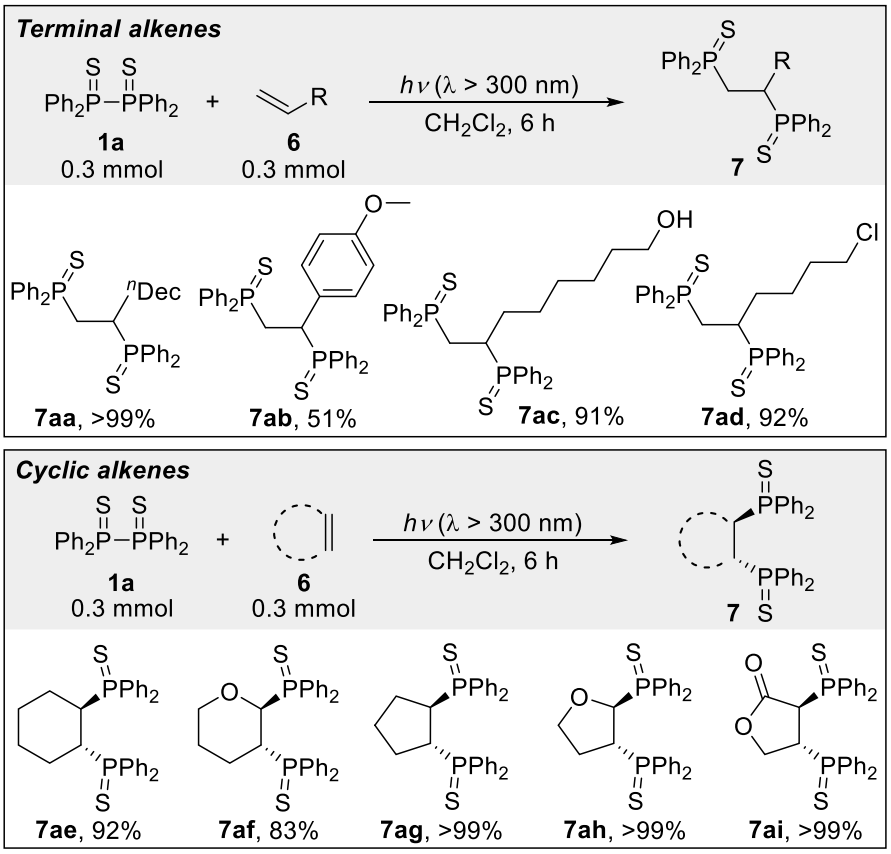
entry	conditions	yield
1	xenon lamp (λ > 300 nm, 500 W), 20 °C, 6 h	>99%
2	400 nm LEDs (4.5 W), 20 °C, 20 h	95%
3	20W fluorescent lamp, 20 °C, 20 h	51%
4	20W fluorescent lamp, 80 °C, 20 h	95%
5	blue LEDs (6.5 W), *fac*-Ir(ppy)$_3$ (0.5 mol%), 20 °C, 20 h	91%
6	dark, V-40 (10 mol%), 80 °C, 20 h	95%
7	dark, 80 °C, 20 h	0%

Yields were determined by ^{1}H NMR. [a]Reaction conditions: **1a** (0.3 mmol), **6a** (0.3 mmol), and CH_2Cl_2 (0.3 mL). [b]Benzene (0.45 mL) was used instead of CH_2Cl_2.

The addition reactions of **1a** to a variety of alkenes were performed under light. This

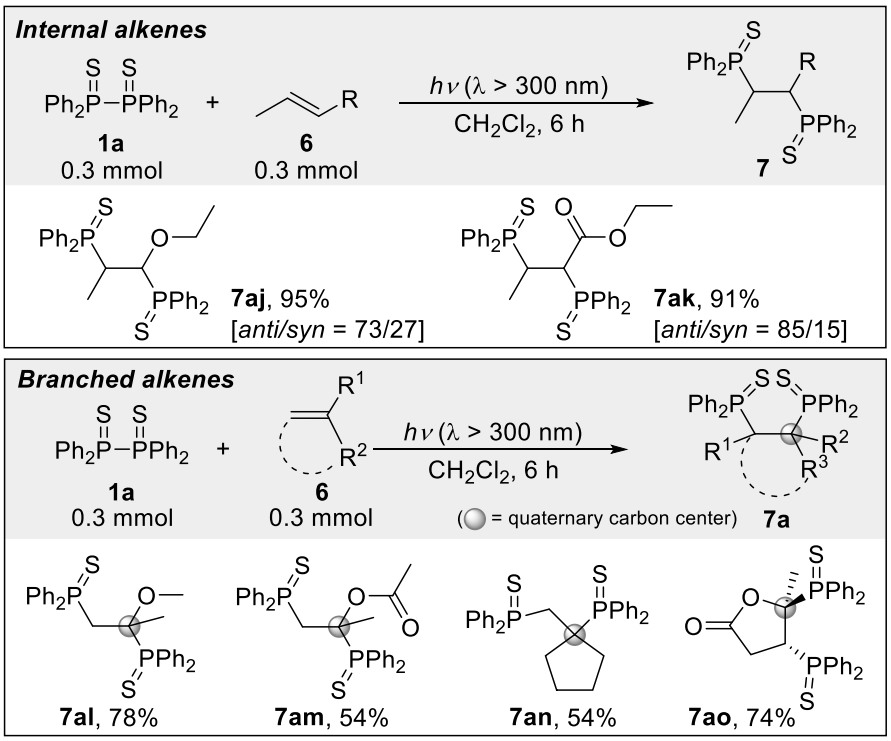
bisthiophosphinylation reaction was effective for terminal and cyclic aliphatic alkenes **6a** and **6c**–**6i** as well as the aromatic alkene **6b** (Scheme 6-6). Diphosphine disulfide **1a** was tolerated by the hydroxy- (**6c**) and chloro- (**6d**) group under light and gave the desired product **7ac** and **7ad**, respectively, in excellent yields. Diphosphines with a trivalent phosphorus center, such as tetraphenyldisphosphine, immediately decompose in the presence of alchohol, such as **6c**. In contrast, **1a** is stable in the presence of alchohols, such as ethanol and water solvent, and therefore it can efficiently add to **6c** without decomposition. 4-Methoxystyrene (**6b**) was transformed into the 1,2-adduct in 55% yield. The addition to cyclic alkenes **6c**–**6h** afforded the corresponding 1,2-adducts **7ae**–**7ai** in excellent yields with excellent diastereoselectivities. In particular, sufficiently pure 1,2-adducts **7aa** and **7ag**–**7ai** were directly obtained, quantitatively, without any need for purification.

Scheme 6-6. Bisthiophosphinylation of several terminal and cyclic alkenes **6** with **1a**.



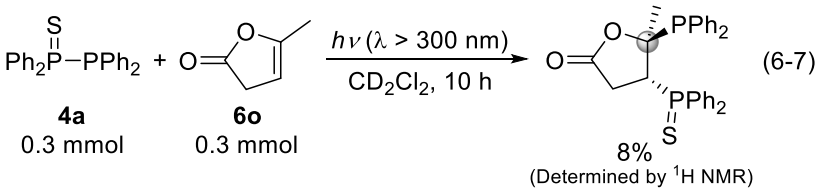
The higher capturing ability of **3a** to bulky alkyl radicals enabled efficient 1,2-additions to internal and branched alkenes. Therefore, the scope of internal and branched alkenes was also investigated (Scheme 6-7). For internal alkenes, such as vinyl ether **6j** and acrylate **6k**, the desired products **7aj** and **7ak** were generated in 95% and 91% yield, respectively, with good stereoselectivities. In general, 1,2-addition of diphosphines and their analogues, bearing a phosphorus–phosphorus single bond, to branched alkenes is difficult because of the bulkiness of their phosphorus groups. However, **1a** successfully added to α-branched alkenes **6l**–**6o** to afford the corresponding 1,2-adducts **7al**–**7ao**, bearing a quaternary carbon center, in good yields. These results demonstrate the high substrate generality of this reaction.

Scheme 6-7. Bisthiophosphinylation of several internal and branched alkenes **6** with **1a**.



As summarized in Schemes 6-6 and 6-7, this bisthiophosphinylation reaction is effective for relatively bulky alkenes, such as branched alkenes **6l**–**6o**. In the case of diphosphine monosulfide **4a**, the attempted addition to **6o** did not proceed efficiently and gave the 1,2-adduct

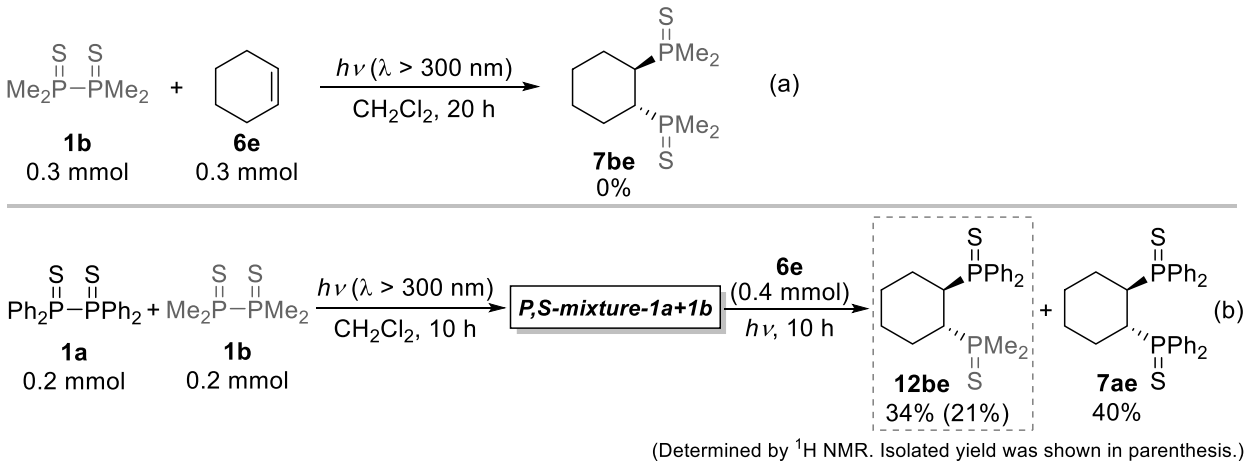
of **4a** in 8% yield (Eq. 6-7). The difference in the reactivity between **1a** and **4a** supported that **4a** does not play a key role in the addition reaction of **1a** to alkenes.



(6-7)

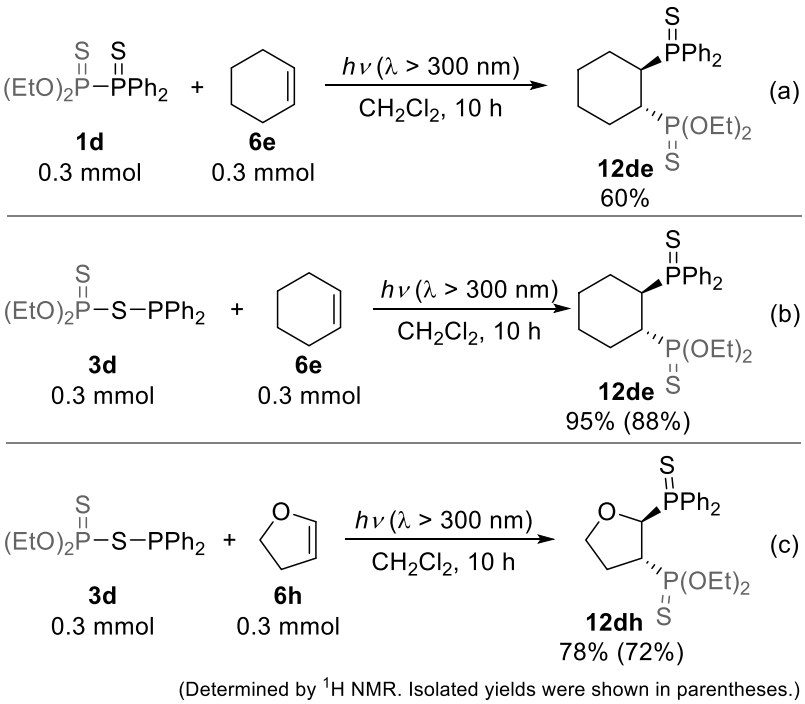
The influence of the carbon substituents of diphosphine disulfides on their addition to alkenes was investigated by irradiating a mixture of diphosphine disulfide **1b** and **6c** under light for 20 h but the addition reaction did not proceed at all (Scheme 6-8a). Diphosphine disulfide **1b** did not undergo the reductive rearrangement under light as shown in Scheme 6-3a. Thus, the author hypothesized that **1b** could be activated by other trivalent phosphorus species, such as **3a** and **4a**, followed by the generation of the unsymmetrical coupled products, such as $Me_2P(S)–P(S)Ph_2$, and they could react with alkenes. When the mixture of **1a** and **1b** was irradiated under light for 10 h (Scheme 6-8b), the conversion of **1a** and **1b** to more than 11 phosphorus species (***P,S-mixture-1a+1b***), including $Me_2P(S)–P(S)Ph_2$ (56%), $Me_2P(S)–SPPh_2$ (11%), $Me_2P(S)–PPh_2$ (2%), and $Me_2P(S)–SP(S)Ph_2$ (25%), was observed by ^{31}P NMR spectroscopy. After addition of alkene **6e** and irradiation under light for 10 h, unsymmetrical 1,2-adduct **12be** was obtained in 34% yield accompanied with the generation of **7ae** (40%) and **7be** (5%).

Scheme 6-8. Radical addition of diphosphine disulfide **1b** to alkene **6e** with/without **1a**



In the case of unsymmetrical diphosphine disulfide **1d**, 1,2-adduct **12de** was obtained in 60% yield (Scheme 6-9a). In this reaction, symmetrical 1,2-adduct **7ae** was generated in 20% yield because of the presence of the two competing phosphorus radicals, $Ph_2P(S)\cdot$ and $(EtO)_2P(S)\cdot$. In contrast, the addition of **3d** selectively afforded **12de** in 88% yield (Scheme 6-9b). Interestingly, **3d** added to alkene **6h** regioselectively, and the 1,2-adduct **12dh** was obtained in 72% yield (Scheme 6-9c). In these reactions, **1d** was efficiently converted to **3d**–**5d** (Scheme 6-9a) but the conversion of **3d** was relatively slower than **1d** (Scheme 6-9b and 6-9c). The author concluded that the slow release of the thiophosphoryl radical from **3d** and its relatively fast ability to capture carbon radicals prevented the scramble for the two phosphorus radicals $(EtO)_2P(S)\cdot$ and $Ph_2P(S)\cdot$ (Figure 6-8).

Scheme 6-9. Selectivity in bisthiophosphinylation reaction of **6e** and **6h** using unsymmetrical diphosphine disulfide **1d** and diphosphathiane monosulfide **3d**



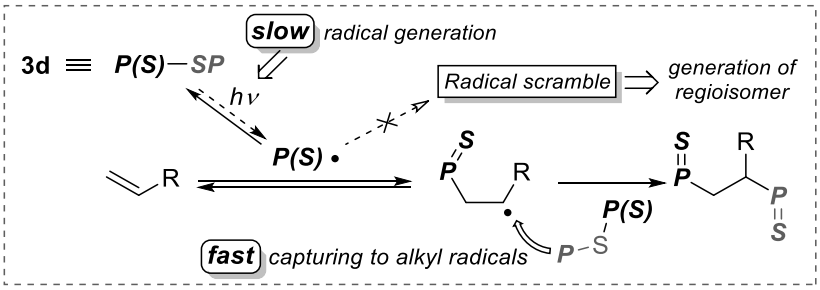
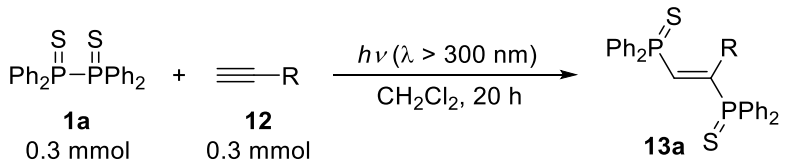


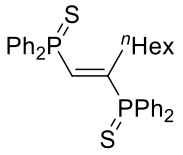
Figure 6-8. Model for regioselective 1,2-addition of diphosphathiane monosulfide **3d** to alkenes.

The bisthiophosphinylation reaction of a variety of alkynes **12** also proceeded efficiently to afford (*E*)-1,2-bisthiophosphinylated alkenes **13** with good stereoselectivities (Table 6-3). Diphosphine disulfide **1a** efficiently added to aliphatic alkynes with a long carbon chain (**12a**), cyclohexyl (**12b**), and trimethylsilyl groups (**12c**), and the desired products **13a**–**13c** were obtained in good yield with good stereoselectivities. The addition to phenylacetylene (**12d**) gave

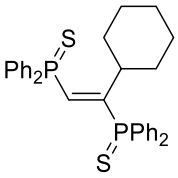
the 1,2-adduct **13ad** in 85% yield with good stereoselectivity. Both alkynes with an electron-donating group (**12e**) and electron-withdrawing group (**12f**) were available for this reaction and the corresponding 1,2-adducts **13ae** and **13af** were obtained in good yield with good stereoselectivities, respectively.

Table 6-3. Bisthiophosphinylation of several alkynes 12 with 1a[a]

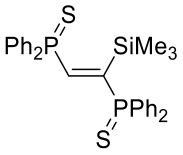




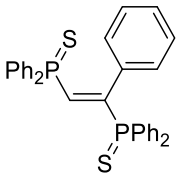
13aa, 92% (71%)
[*E*/*Z* = 82/18]



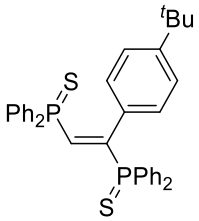
13ab, 86% (65%)
[*E*/*Z* = 80/20]



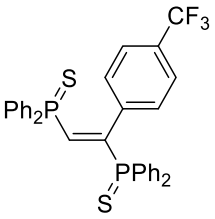
13ac, 82% (64%)
[*E*/*Z* = 82/18]



13ad, 85% (62%)
[*E*/*Z* = 75/25]



13ae, 93% (68%)
[*E*/*Z* = 76/24]



13af, 80% (54%)
[*E*/*Z* = 75/25][b]

NMR yield (Isolated yields of *E*-isomers). The NMR yields were determined by ^{31}P NMR. The *E*/*Z* ratios were determined by ^{31}P NMR of the crude mixture. [a]Reaction conditions: **1a** (0.3 mmol), **6** (0.3 mmol), CH_2Cl_2 (0.3 mL), 20 °C, xenon lamp (500 W), Pyrex, and 20 h. [b]Irradiation for 30 h.

6-4 Conclusion

In conclusion, the author developed a simple and facile synthetic method for the preparation of bis(thiophosphinyl)alkanes and bis(thiophosphinyl)alkenes. Diphosphine disulfides are promising sources of phosphorus because of their facile preparation and because they are shelf-stable solids. However, previous examples of addition reactions involving

diphosphine disulfides were limited. The results of this chapter showed that diphosphine disulfides underwent reductive rearrangement to reactive trivalent phosphorus species, such as diphosphathiane monosulfide, which has a P(S)–SP single bond, when exposed to light. In addition, this rearrangement triggered the efficient radical chain for the bisthiophosphinylation reaction of a variety of alkenes and alkynes. This reaction readily affords a variety of bis(thiophosphinyl)alkanes without the need for a catalyst, base, or additive. The author believes this work provides a powerful tool for the synthesis of bis(phosphino)alkane ligands, such as dppe, which can easily be obtained by the desulfurization of bis(thiophosphinyl)alkanes.

6-5 Experimental Section

General Comment

All alkenes, alkynes, tetramethyldiphosphine disulfide **1b**, and bromoacetates were obtained from commercial supplies. All solvents were distilled and degassed with argon before use. All calculations were performed with the Gaussian 09W Revision D.01 program package. Geometry optimizations were performed by density functional theory (DFT) with the hybrid UB3LYP functions, employing a basis set consisting of 6-31G++(2d,p) level. The geometry optimizations were performed without any symmetry constraint followed by analytical frequency calculations to confirm that a minimum had been reached.

Experimental procedure for the synthesis of 1a

To a 100 mL round bottom Schlenk flask, chlorodiphenylphosphine (70 mmol) and bis(trimethylsilyl)sulfide (35 mmol) dissolved in degassed dry CH_3CN (100 mL) was added under an argon atmosphere, and the mixture was stirred for 10 hours. The reaction mixture was then concentrated under reduced pressure. If necessary, the resulting white solid was washed with

deggased dry *n*-hexane (50 mL). The white solid was dissolved in degassed dry CH_2Cl_2 (40 mL) and elemental sulfur (35 mmol) was slowly added at 0 °C followed by sttiring at room temperature for 3 h. After evapolation of the reaction mixture, the resulting white solid was washed with deggased EtOH (100 mL) to give the pure product in 84% yield (12.9 g). The purity of the product was confirmed by ^{1}H and ^{31}P NMR spectroscopy.

Experimental procedure for the synthesis of 3a (Eq. 6-2)

To a 100 mL Shrenck flask, diphenylphosphine (10 mmol) dissolved in deggased dry THF (100 mL) was added under an argon atmosphere and *n*-butyllithium (1.6 M in *n*-hexane, 10 mmol) was added dropwise for 1 h at 0 °C. Elemental sulfur (20 mmol) was then slowly added at −78 °C and it was slowly allowed to reach room temperature. After the mixture was stirred for 3 h, chlorodiphenylphosphine (10 mmol) was added dropwise for 1 h at 0 °C and the mixture was stirred at room temperature for 12 h in a dark room. The reaction mixture was concentrated under reduced pressure to give the product in 90% yield contaminated with **1a** (2%) and **5a** (4%).

1,1,3,3-Tetraphenyldiphosphathiane 1-sulfide (3a) Diphosphathiane monosulfide **3a** was obtained in 90% purity as a mixture with **1a** (2%) and **5a** (4%). The mixture was used for the next reaction. Light yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25–7.31 (m, 5H), 7.34–7.48 (m, 11H), 7.91–8.00 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 6.7 Hz), 129.4, 131.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 131.6, 133.0 (d, $J_{C\text{-}P}$ = 21.1 Hz), 134.9 (d, $J_{C\text{-}P}$ = 85.3 Hz), 136.4 (dd, $J_{C\text{-}P}$ = 24.9 Hz, 5.8 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 21.1 (d, $J_{P\text{-}P}$ = 78.0 Hz), 65.7 (d, $J_{P\text{-}P}$ = 78.0 Hz) (for **3a**: δ 39.3, for **5a**: δ 62.0).

Experimental procedure for the synthesis of 5a

Diphosphathiane monosulfide **3a** (0.6 mmol) in degassed dry CD_2Cl_2 (0.6 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and elemental sulfur (0.6 mmol) was slowly added at 0 °C. The mixture was placed in dark room for 3 h and it was then

concentrated under reduced pressure to give the product, quantitatively. The structure and purity of the product was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy according to the literature.[18]

Experimental procedure for photoinduced reaction between 1a and 9 (Table 6-1)

Diphosphine disulfide **1a** (0.3 mmol) dissolved in degassed dry CD_2Cl_2 (0.3 mL) was placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for an hour. Bromoacetate **9a** (0.3 mmol) was then added and the mixture wa irradicated with a xenon lamp for an hour. After the reaction, the reaction mixture was concentrated under reduced pressure. The desired product **10** was obtained after isolation by silica-gel chromatography (eluent: *n*-hexane/AcOEt/$CHCl_3$).

Ethyl 2-(diphenylthiophosphinyl)-3-methylbutanoate (10a) White solid; **mp.** 98–99 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.86 (d, $J_{H\text{-}H}$ = 6.7 Hz, 3H), 0.91 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.01 (d, $J_{H\text{-}H}$ = 6.7 Hz, 3H), 2.57–2.73 (m, 1 H), 3.56 (dd, $J_{H\text{-}H}$ = 9.6 Hz, $J_{H\text{-}P}$ = 9.6 Hz, 1H), 3.62 (dq, $J_{H\text{-}H}$ = 10.8 Hz, 7.3 Hz, 1H), 3.80 (dq, $J_{H\text{-}H}$ = 10.8 Hz, 7.3 Hz, 1H), 7.39–7.52 (m, 6H), 8.02 (ddd, $J_{H\text{-}H}$ = 15.1 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 8.06 (ddd, $J_{H\text{-}H}$ = 13.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.5, 21.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 22.0 (d, $J_{C\text{-}P}$ = 4.8 Hz), 29.2, 56.6 (d, $J_{C\text{-}P}$ = 46.0 Hz), 60.9, 128.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.4 (two *para*-carbons of diphenylthiophosphinyl group are overlapped), 132.1 (d, $J_{C\text{-}P}$ = 10.1 Hz), 132.6 (d, $J_{C\text{-}P}$ = 80.5 Hz), 169.1; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.5; **IR** (KBr): 611, 693, 716, 752, 1028, 1096, 1117, 1144, 1288, 1437, 1730, 2964 cm^{-1}.

Ethyl 2-(diphenylthiophosphinyl)propanoate (10b) White solid; **mp.** 109–110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.42 (dd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 18.3 Hz, 3H), 3.82–3.97 (m, 3H), 7.42–7.54 (m, 6H), 7.92 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.03 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 11.6, 13.5, 43.4

(d, $J_{C\text{-}P}$ = 46.0 Hz), 61.2, 128.1 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.1 Hz), 131.6 (two para-carbons of diphenylthiophosphinyl group are overlapped), 132.0 (d, $J_{C\text{-}P}$ = 10.1 Hz), 169.3 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 49.0; **IR** (KBr): 646, 694, 714, 752, 787, 1017, 1099, 1157, 1213, 1311, 1438, 1731, 2981 cm^{-1}.

Ethyl 2-(diphenylthiophosphinyl)-2-methylpropanoate (10c) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.94 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.55 (s, 3H), 1.59 (s, 3H), 3.93 (q, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.42–7.478 (m, 4H), 7.482–7.54 (m, 2H), 7.99 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.4, 22.5, 48.0 (d, $J_{C\text{-}P}$ = 43.1 Hz), 61.4, 128.1 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.6 (d, $J_{C\text{-}P}$ = 78.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 173.9; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 58.0; **IR** (NaCl): 693, 717, 751, 857, 1025, 1097, 1131, 1163, 1252, 1437, 1718, 2978 cm^{-1}.

Ethyl 1-(diphenylthiophosphinyl)cyclobutene-1-carboxylate (10d) White solid; **mp.** 83–84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.83–1.97 (m, 1H), 1.98–2.12 (m, 1H), 2.56–2.68 (m, 2H), 2.93–3.09 (m, 2H), 3.84 (q, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 7.39–7.45 (m, 4H), 7.46–7.52 (m, 2H), 7.84 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.4, 17.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 28.89, 28.91, 50.9 (d, $J_{C\text{-}P}$ = 39.3 Hz), 61.4, 128.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 173.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 54.5; **IR** (KBr): 520, 693, 714, 751, 1099, 1206, 1273, 1437, 1715, 2945, 2988 cm^{-1}; **HRMS** (EI+) Calcd for [M + H^+] $C_{22}H_{22}O_3P$: 365.1306, Found: 365.1296.

Experimental procedure for the 1,2-addition reaction of 1a to 6a under several radical conditions (Table 6-2)

Conditions for Entry 2 and 3: Tetraphenyldiphosphine disulfide (**1a**, 0.3 mmol) and 1-dodecene (**6a**, 0.3 mmol) in degassed dry CH_2Cl_2 (0.3 mL) were placed in a sealed Pyrex NMR

tube under an argon atmosphere and the mixture was irradiated with a 400 nm LEDs (APATNER, SMD 5050 LED Strip Light, 4.5 W) or a Fluorescent lamp (Panasonic, FPL27EXN, 20 W) for 20 hours in a dark room. After the reaction, the mixture was concentrated under reduced pressure. The yield of **7aa** was determined by ^{1}H NMR using 1,3,5-trioxane as an internal standard.

Conditions for Entry 4: **1a** (0.3 mmol) and **6a** (0.3 mmol) in degassed dry benzene (0.45 mL) were placed in a 10 mL Pyrex Shrenck tube with a stirrer bar under an argon atmosphere and the mixture was heated at 80 °C and irradiated with a Fluorescent lamp for 20 hours in a dark room.

Conditions for Entry 5: **1a** (0.3 mmol), **6a** (0.3 mmol), and *fac*-Ir(ppy)$_3$ (0.015 mmol) in degassed dry CH_2Cl_2 (0.3 mL) were placed in a 10 mL Pyrex Shrenck tube with a stirrer bar under an argon atmosphere and the mixture was irradiated with a blue-LEDs lamp (Akiba LED Pikarikan, 5050 3chipSMD, 6.5 W) for 20 hours in a dark room.

Conditions for Entry 6: **1a** (0.3 mmol), **6a** (0.3 mmol), and V-40 (1,1'-azobis(cyclohexane-1-carbonitrile), 0.03 mmol) in degassed dry benzene (0.45 mL) were placed in a 10 mL Pyrex Shrenck tube with a stirrer bar under an argon atmosphere and the mixture was heated at 80 °C for 20 hours in a dark room.

Conditions for Entry 7: **1a** (0.3 mmol), **6a** (0.3 mmol) in degassed dry benzene (0.45 mL) were placed in a 10 mL Pyrex Shrenck tube with a stirrer bar under an argon atmosphere and the mixture was heated at 80 °C for 20 hours in a dark room.

Experimental procedure for the synthesis of 7aa–7ap (Scheme 6-6 and 6-7) and 13aa–13af (Table 6-3)

Diphosphine disulfide **1a** (0.3 mmol) and alkene **6** (0.3 mmol) or alkyne **12** (0.3 mmol) in degassed dry CH_2Cl_2 (0.3 mL) were placed in a sealed Pyrex NMR tube under an argon

atmosphere and the mixture was irradiated with a xenon lamp (500 W) for the specified times. The desired products were obtained after isolation by silica gel chromatography (eluent: *n*-hexane/AcOEt/$CHCl_3$). In the case of **7aa** and **7ag**–**7ai**, the desired products were directly obtained without further purification.

Dodecane-1,2-diylbis(diphenylphosphine sulfide) (7aa) White solid; **mp.** 90–91 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.43–0.59 (m, 3H), 0.66–0.76 (m, 2H), 0.88 (t, $J_{H\text{-}H}$ = 7.1 Hz, 3H), 0.84–1.11 (m, 6H), 1.12–1.34 (m, 6H), 1.50–1.68 (m, 1H), 2.44–2.58 (m, 1H), 2.91–3.02 (m, 1H), 3.76–3.89 (m, 1H), 7.27 (td, $J_{H\text{-}H}$ = 7.8 Hz, 3.2 Hz, 2H), 7.32–7.48 (m, 10H), 7.51 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.95 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 4H), 8.13–8.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 14.0, 22.5, 27.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 28.6, 28.8, 29.06, 29.09, 29.14, 29,3, 31.7, 32.1 (d, $J_{C\text{-}P}$ = 51.8 Hz), 32.9 (d, $J_{C\text{-}P}$ = 52.7 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 77.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.28 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.29 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.49 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.50 (d, $J_{C\text{-}P}$ = 77.2 Hz), 131.55 (d, $J_{C\text{-}P}$ = 82.4 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 134.3 (d, $J_{C\text{-}P}$ = 82.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.7 (d, $J_{P\text{-}P}$ = 56.4 Hz), 54.7 (d, $J_{P\text{-}P}$ = 56.4 Hz); **IR** (KBr): 612, 623, 694, 713, 753, 1100, 1437, 2852, 2924, 3055 cm^{-1}.

(1-(4-Methoxyphenyl)ethane-1,2-diyl)bis(diphenylphosphine sulfide) (7ab) [CAS registry number: 2020354-75-8];[7c] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.61–2.75 (m, 1H), 3.47–3.62 (m, 1H), 3.60 (s, 3H), 4.94–5.08 (m, 1H), 6.23 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 6.94 (d, $J_{H\text{-}H}$ = 8.7 Hz, 2H), 7.01–7.08 (m, 2H), 7.12–7.20 (m, 3H), 7.32–7.46 (m, 8H), 7.55–7.61 (m, 3H), 7.62–7.71 (m, 2H), 8.26–8.35 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 32.9 (d, $J_{C\text{-}P}$ = 52.7 Hz), 39.7 (d, $J_{C\text{-}P}$ = 51.8 Hz), 55.0, 112.8, 123.9, 127.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 127.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 129.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.40 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.41 (d, $J_{C\text{-}P}$ = 75.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 78.6 Hz), 131.0, 131.29 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.34 (d, $J_{C\text{-}P}$ = 9.6 Hz),

131.38 (d, $J_{C\text{-}P}$ = 74.8 Hz), 131.40, 131.9, 132.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 134.3 (d, $J_{C\text{-}P}$ = 84.4 Hz), 158.5; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.5 (d, $J_{P\text{-}P}$ = 60.7 Hz), 53.1 (d, $J_{P\text{-}P}$ = 60.7 Hz).

(8-Hydroxyoctane-1,2-diyl)bis(diphenylphosphine sulfide) (7ac) White solid; **mp.** 70–71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.45–0.64 (m, 3H), 0.74–0.84 (m, 2H), 0.93–1.15 (m, 2H), 1.16–1.25 (m, 2H), 1.49 (brs, 1H), 1.51–1.68 (m, 1H), 2.43–2.58 (m, 1H), 2.90–3.02 (m, 1H), 3.38–3.45 (m, 2H), 3.75–3.89 (m, 1H), 7.28 (td, $J_{H\text{-}H}$ = 7.8 Hz, 3.2 Hz, 2H), 7.35–7.55 (m, 12H), 7.51 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.95 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 4H), 8.15 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, 2.3 Hz, $J_{H\text{-}P}$ = 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 24.7, 27.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 28.7, 28.9, 32.1 (d, $J_{C\text{-}P}$ = 52.7 Hz), 32.2, 32.9 (d, $J_{C\text{-}P}$ = 53.7 Hz), 62.6, 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 73.8 Hz), 131.0 (d, $J_{C\text{-}P}$ = 84.4 Hz), 131.2, 131.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.52 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.55, 131.55 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 134.3 (d, $J_{C\text{-}P}$ = 82.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.7 (d, $J_{P\text{-}P}$ = 56.4 Hz), 54.7 (d, $J_{P\text{-}P}$ = 56.4 Hz); **IR** (KBr): 612, 623, 696, 712, 751, 951, 998, 1027, 1100, 1437, 2860, 2931, 3450 cm^{-1}.

(6-Chlorohexane-1,2-diyl)bis(diphenylphosphine sulfide) (7ad) White solid; **mp.** 164–165 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.57–0.71 (m, 1H), 0.94–1.21 (m, 4H), 1.52–1.71 (m, 1H), 2.44–2.59 (m, 1H), 2.89–3.02 (m, 1H), 2.97 (t, $J_{H\text{-}H}$ = 6.9 Hz, 2H), 3.74–3.89 (m, 1H), 7.26–7.33 (m, 2H), 7.35–7.56 (m, 12H), 7.90–8.02 (m, 4H), 8.10–8.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.1 (d, $J_{C\text{-}P}$ = 4.8 Hz), 28.0, 32.0 (d, $J_{C\text{-}P}$ = 51.8 Hz), 32.2, 32.8 (d, $J_{C\text{-}P}$ = 53.7 Hz), 44.0, 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.56 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.58 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.6 (d, $J_{C\text{-}P}$ = 80.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.28 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.30, 131.50 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.53 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.6, 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 134.1 (d, $J_{C\text{-}P}$ = 82.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 43.5 (d, $J_{P\text{-}P}$ =

56.4 Hz), 54.5 (d, $J_{P\text{-}P}$ = 56.4 Hz); **IR** (KBr): 612, 623, 695, 714, 752, 998, 1100, 1313, 1436, 2954, 3051 cm^{-1}.

(Cyclohexane-1,2-diyl)bis(diphenylphosphine sulfide) (7ae) White solid; ~~**mp.** 209–210 °C;~~ **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.23–1.37 (m, 2H), 1.70–1.78 (m, 2H), 1.79–1.91 (m, 2H), 2.46–2.70 (m, 2H), 3.60–3.71 (m, 2H), 7.34–7.40 (m, 2H), 7.41–7.52 (m, 6H), 7.22–7.29 (m, 4H), 7.33–7.40 (m, 2H), 7.41–7.52 (m, 6H), 7.66–7.75 (m, 4H), 7.86–7.95 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.2, 23.0, 31.9 (t, $J_{C\text{-}P}$ = 25.4 Hz), 128.47 (t, $J_{C\text{-}P}$ = 5.8 Hz), 128.53 (d, $J_{C\text{-}P}$ = 5.8 Hz), 131.1, 131.4 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.7 (d, $J_{C\text{-}P}$ = 75.7 Hz), 132.0 (t, $J_{C\text{-}P}$ = 4.8 Hz), 132.1 (d, $J_{C\text{-}P}$ = 76.7 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 51.5; **IR** (KBr): 540, 598, 696, 718, 751, 1096, 1436, 2862, 2931, 3055 cm^{-1}.

(Tetrahydro-2H-pyran-2,3-diyl)bis(diphenylphosphine sulfide) (7af) White solid; **mp.** 197–198 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.21–1.31 (m, 1H), 1.96–2.20 (m, 2H), 2.83–3.04 (m, 1H), 3.47–3.55 (m, 1H), 3.72 (td, $J_{H\text{-}H}$ = 11.7 Hz, 7.3 Hz, 1H), 3.99 (td, $J_{H\text{-}H}$ = 11.7 Hz, 2.3 Hz, 1H), 5.55–5.60 (m, 1H), 7.18 (td, $J_{H\text{-}H}$ = 7.8 Hz, 3.2 Hz, 2H), 7.22–7.33 (m, 3H), 7.37 (td, $J_{H\text{-}H}$ = 7.3 Hz, 1.8 Hz, 1H), 7.40–7.52 (m, 6H), 7.68–7.78 (m, 4H), 7.89 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 8.1 Hz, 2H), 8.05 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.3, 20.7, 32.0 (d, $J_{C\text{-}P}$ = 50.3 Hz, 9.6 Hz), 63.5, 72.0 (d, $J_{C\text{-}P}$ = 55.6 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.55 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.59 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.7 (d, $J_{C\text{-}P}$ = 77.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 75.7 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.31 (d, $J_{C\text{-}P}$ = 75.7 Hz), 131.34 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.5 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.58 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.61 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.4 (d, $J_{C\text{-}P}$ = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 44.8 (d, $J_{P\text{-}P}$ = 56.4 Hz), 50.3 (d, $J_{P\text{-}P}$ = 56.4 Hz); **IR** (KBr): 536, 606, 695, 714, 722, 1063, 1097, 1436, 1480, 2860, 2963, 3055 cm^{-1}.

(Cyclopentane-1,2-diyl)bis(diphenylphosphine sulfide) (7ag)[11b] White solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.77–1.94 (m, 4H), 2.00–2.18 (m, 2H), 4.00–4.12 (m, 2H), 6.98–7.05 (m, 4H), 7.11–7.18 (m, 2H), 7.33–7.42 (m, 6H), 7.63–7.72 (m, 4H), 7.83–7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 26.3 (t, $J_{C\text{-}P}$ = 3.8 Hz), 31.2, 38.9 (dd, $J_{C\text{-}P}$ = 67.1 Hz, 12.5 Hz), 128.1 (t, $J_{C\text{-}P}$ = 5.8 Hz), 128.3 (t, $J_{C\text{-}P}$ = 5.8 Hz), 130.9 (dd, $J_{C\text{-}P}$ = 87.2 Hz, 10.5 Hz), 131.0 (d, $J_{C\text{-}P}$ = 3.8 Hz), 131.1 (four *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.2 (t, $J_{C\text{-}P}$ = 4.8 Hz), 132.8 (dd, $J_{C\text{-}P}$ = 90.1 Hz, 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 54.1.

(Tetrahydrofuran-2,3-diyl)bis(diphenylphosphine sulfide) (7ah) White solid; **mp.** 195–196 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.86–2.14 (m, 2H), 3.84 (ddd, $J_{H\text{-}H}$ = 8.2 Hz, 7.8 Hz, 4.1 Hz, 1H), 4.16 (tdd, $J_{H\text{-}H}$ = 7.8 Hz, 7.8 Hz, $J_{H\text{-}P}$ = 1.8 Hz, 1H), 4.25–4.35 (m, 1H), 5.47 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, $J_{H\text{-}P}$ = 20.2 Hz, 2.8 Hz, 1H), 7.23–7.30 (m, 4H), 7.31–7.52 (m, 8H), 7.81 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.84–7.98 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 28.8, 40.8 (dd, $J_{C\text{-}P}$ = 54.6 Hz, 5.8 Hz), 71.2, 80.2 (d, $J_{C\text{-}P}$ = 64.2 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.2 (d, $J_{C\text{-}P}$ = 78.6 Hz), 130.4 (d, $J_{C\text{-}P}$ = 75.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 77.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.5, 131.57 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.64 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 79.6 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 46.4 (d, $J_{P\text{-}P}$ = 43.4 Hz), 50.9 (d, $J_{P\text{-}P}$ = 43.4 Hz); **IR** (KBr): 522, 596, 607, 690, 716, 746, 1102, 1436, 1484, 2891, 3044 cm^{-1}.

3,4-Bis(diphenylthiophosphinyl)dihydrofuran-2(3H)-one (7ai) White solid; **mp.** 198–199 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.13 (ddd, $J_{H\text{-}H}$ = 11.0 Hz, $J_{H\text{-}P}$ = 20.6 Hz, 1.8 Hz, 1H), 4.27–4.38 (m, 2H), 4.41 (ddd, $J_{H\text{-}H}$ = 23.4 Hz, 9.6 Hz, $J_{H\text{-}P}$ = 9.6 Hz, 1H), 7.25–7.33 (m, 4H), 7.37–7.56 (m, 8H), 7.77 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 0.9 Hz, $J_{H\text{-}F}$ = 8.2 Hz, 4H), 7.83–7.92 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 38.1 (d, $J_{C\text{-}P}$ = 54.6 Hz), 45.7 (d, $J_{C\text{-}P}$ = 40.3 Hz), 66.9, 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 80.0 Hz), 128.7 (d, $J_{C\text{-}P}$ = 12.5 Hz, two *ortho*-carbons of diphenylthiophosphinyl group are overlapped), 129.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.1 (d, $J_{C\text{-}P}$ = 84.4 Hz), 129.3 (d, $J_{C\text{-}P}$ = 83.4

Hz), 129.8 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.6 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 132.29 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.34 (d, $J_{C\text{-}P}$ = 2.9 Hz), 170.6 (d, $J_{C\text{-}P}$ = 2.9 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 48.1 (d, $J_{P\text{-}P}$ = 34.7 Hz), 50.9 (d, $J_{P\text{-}P}$ = 34.7 Hz); **IR** (KBr): 533, 589, 611, 654, 691, 717, 823, 1028, 1101, 1126, 1167, 1437, 1774, 3054 cm^{-1}.

(1-Ethoxypropane-1,2-diyl)bis(diphenylphosphine sulfide) (7aj) 1,2-Adduct **7aj** was obtained as a mixture of two diastereomers (*anti*/*syn* = 72/28). The diastereomer ratio was determined by ^{1}H NMR spectroscopy. White solid; **mp.** 117–118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.84 (t, $J_{H\text{-}H}$ = 6.9 Hz, 3H), 0.90 (dd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 19.2 Hz, 3H), 2.64 (qd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 6.9 Hz, 1H), 3.77 (qd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 6.9 Hz, 1H), 4.30–4.43 (m, 1H), 4.66 (dd, $J_{H\text{-}P}$ = 16.5 Hz, 6.4 Hz, 1H), 7.30–7.44 (m, 7H), 7.47–7.59 (m, 5H), 7.62 (dd, $J_{H\text{-}H}$ = 12.4 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 2H), 8.00 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 2.3 Hz, $J_{H\text{-}P}$ = 7.1 Hz, 2H), 8.19 (ddd, $J_{H\text{-}H}$ = 12.1 Hz, 2.3 Hz, $J_{H\text{-}P}$ = 7.0 Hz, 2H), 8.33 (dd, $J_{H\text{-}H}$ = 11.9 Hz, $J_{H\text{-}P}$ = 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 8.8, 14.7, 33.7 (dd, $J_{C\text{-}P}$ = 50.8 Hz, 9.6 Hz), 70.1 (d, $J_{C\text{-}P}$ = 4.8 Hz), 81.9 (d, $J_{C\text{-}P}$ = 65.2 Hz), 128.1 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 74.8 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.4 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.8 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 79.6 Hz), 134.0 (d, $J_{C\text{-}P}$ = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 44.5 (d, $J_{P\text{-}P}$ = 60.7 Hz), 52.2 (d, $J_{P\text{-}P}$ = 65.0 Hz) (for *syn*-adduct: 47.8 (d, $J_{P\text{-}P}$ = 43.4 Hz), 52.7 (d, $J_{P\text{-}P}$ = 43.4 Hz)); **IR** (KBr): 614, 635, 646, 692, 715, 752,1070, 1099, 1437, 2975, 3053 cm^{-1}.

Ethyl 2,3-bis(diphenylthiophosphinyl)butanoate (7ak) 1,2-Adduct **7ak** was obtained as a mixture of two diastereomers (*anti*/*syn* = 85/15). The diastereomer ratio was determined by ^{1}H NMR spectroscopy. White solid; **mp.** 177–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.38 (dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 18.8 Hz, 3H), 3.72 (q, $J_{H\text{-}H}$ = 7.3 Hz, 2H), 3.92 (qddd, $J_{H\text{-}H}$ = 7.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 21.3 Hz, 12.1 Hz, 1H), 4.26 (ddd, $J_{H\text{-}H}$ = 1.4 Hz, $J_{H\text{-}P}$ = 16.0 Hz, 14.7 Hz, 1H), 7.33–7.54 (m, 12H), 7.74 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz,, 2H), 7.86–7.94

(m, 4H), 7.97 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 10.8, 13.3, 33.4 (d, $J_{C\text{-}P}$ = 52.7 Hz), 46.3 (d, $J_{C\text{-}P}$ = 40.3 Hz), 60.9, 128.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.5 (d, $J_{C\text{-}P}$ = 79.6 Hz), 129.9 (d, $J_{C\text{-}P}$ = 76.7 Hz), 131.0 (d, $J_{C\text{-}P}$ = 79.6 Hz), 131.4 (d, $J_{C\text{-}P}$ = 83.4 Hz), 131.47 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.52 (four *para*-carbons of diphenylthiophosphinyl group are overlapped), 131.6 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 160.8; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 48.6 (d, $J_{P\text{-}P}$ = 52.0 Hz), 53.7 (d, $J_{P\text{-}P}$ = 52.0 Hz) (for *syn*-adduct: δ 45.8 (d, $J_{P\text{-}P}$ = 43.4 Hz), 56.0 (d, $J_{P\text{-}P}$ = 47.7 Hz)); **IR** (KBr): 612, 624, 693, 737, 1028, 1099, 1142, 1328, 1364, 1437, 1479, 1735, 2983, 3053 cm^{-1}.

(2-Methoxypropane-1,2-diyl)bis(diphenylphosphine sulfide) (7al) White solid; **mp.** 149–150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.97 (d, $J_{H\text{-}P}$ = 19.2 Hz, 3H), 3.02 (s, 3H), 3.15 (ddd, $J_{H\text{-}H}$ = 15.1 Hz, $J_{H\text{-}P}$ = 11.9 Hz, 11.0 Hz, 1H), 3.50 (ddd, $J_{H\text{-}H}$ = 15.1 Hz, $J_{H\text{-}P}$ = 11.9 Hz, 4.1 Hz, 1H), 7.30–7.50 (m, 11H), 7.55 (td, $J_{H\text{-}H}$ = 7.6 Hz, 1.4 Hz, 1H), 7.70 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 7.78 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H), 7.96 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.29 (ddd, $J_{H\text{-}H}$ = 11.5 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.5, 38.6 (dd, $J_{C\text{-}P}$ = 51.8 Hz, 12.5 Hz), 54.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 84.6 (dd, $J_{C\text{-}P}$ = 69.0 Hz, 5.8 Hz), 127.9 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.0 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.8 (d, $J_{C\text{-}P}$ = 72.8 Hz), 129.1 (d, $J_{C\text{-}P}$ = 72.8 Hz), 130.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 130.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 9.6 Hz); 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.0 (d, $J_{C\text{-}P}$ = 81.5 Hz), 133.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 134.3 (d, $J_{C\text{-}P}$ = 84.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 36.3 (d, $J_{P\text{-}P}$ = 43.4 Hz), 54.8 (d, $J_{P\text{-}P}$ = 47.7 Hz); **IR** (KBr): 609, 640, 693, 712, 752, 1073, 1097, 1164, 1437, 2984, 3056 cm^{-1}.

1,2-Bis(diphenylthiophosphinyl)propan-2-yl acetate (7am) White solid; **mp.** 172–173 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.74 (s, 3H), 2.08 (d, $J_{H\text{-}H}$ = 17.2 Hz, 3H), 3.56–3.79 (m, 2H), 7.33–7.52 (m, 10H), 7.57 (t, $J_{H\text{-}H}$ = 7.3 Hz, 1H), 7.69 (dd, $J_{H\text{-}H}$ = 13.1 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H), 7.85

(dd, $J_{H\text{-}H}$ = 12.7 Hz, $J_{H\text{-}P}$ = 7.7 Hz, 2H), 7.98 (ddd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H), 8.12 (dd, $J_{H\text{-}H}$ = 11.8 Hz, $J_{H\text{-}P}$ = 8.2 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 21.5 (t, $J_{C\text{-}P}$ = 3.8 Hz), 22.3, 35.7 (dd, $J_{C\text{-}P}$ = 52.5 Hz, 6.7 Hz), 87.1 (dd, $J_{C\text{-}P}$ = 61.0 Hz, 5.7 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.4 Hz), 128.59 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.62 (d, $J_{C\text{-}P}$ = 76.3 Hz), 128.8 (d, $J_{C\text{-}P}$ = 78.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 9.5 Hz), 131.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.95 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.03 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 133.3 (d, $J_{C\text{-}P}$ = 9.5 Hz), 133.56 (d, $J_{C\text{-}P}$ = 80.1 Hz), 133.60 (d, $J_{C\text{-}P}$ = 82.4 Hz), 168.3; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 35.8 (d, $J_{P\text{-}P}$ = 43.4 Hz), 57.6 (d, $J_{P\text{-}P}$ = 43.4 Hz); **IR** (KBr): 639, 694, 715, 750, 949, 1099, 1160, 1204, 1437, 1751, 3056 cm^{-1}.

((1-(Diphenylthiophosphinyl)cyclopentyl)methyl)diphenylphosphine sulfide (7an) White solid; **mp.** 174–175 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.76–0.90 (m, 2H), 1.67–1.81 (m, 2H), 2.29–2.58 (m, 4H), 3.43 (dd, $J_{H\text{-}P}$ = 11.9 Hz, 9.6 Hz, 2H), 7.38–7.52 (m, 12H), 7.82–7.93 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 27.0 (d, $J_{C\text{-}P}$ = 3.8 Hz), 34.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 37.0 (dd, $J_{C\text{-}P}$ = 52.7 Hz, 5.8 Hz), 49.3 (dd, $J_{C\text{-}P}$ = 47.4 Hz, 3.8 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.85 (d, $J_{C\text{-}P}$ = 73.8 Hz), 130.90 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 133.1 (d, $J_{C\text{-}P}$ = 8.6 Hz), 134.1 (d, $J_{C\text{-}P}$ = 79.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 37.0 (d, $J_{P\text{-}P}$ = 58.8 Hz), 65.5 (d, $J_{P\text{-}P}$ = 58.8 Hz); **IR** (KBr): 613, 694, 709, 751, 999, 1098, 1437, 2960, 3054 cm^{-1}.

(4,5-Bis(diphenylthiophosphinyl)-5-methyldihydrofuran-2(3H)-one (7ao) White solid; **mp.** 250–251 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.37 (ddd, $J_{H\text{-}H}$ = 18.8 Hz, 11.0 Hz, $J_{H\text{-}P}$ = 25.7 Hz, 1H), 1.84 (d, $J_{H\text{-}H}$ = 16.5 Hz, 3H), 2.42 (ddd, $J_{H\text{-}H}$ = 18.8 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 22.0 Hz, 1H), 4.79 (dddd, $J_{H\text{-}H}$ = 11.0 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 15.6 Hz, 5.7 Hz, 1H), 7.40–7.54 (m, 12H), 7.91 (ddd, $J_{H\text{-}H}$ = 12.4 Hz, 2.3 Hz, $J_{H\text{-}P}$ = 6.7 Hz, 2H), 8.16 (ddd, $J_{H\text{-}H}$ = 11.9 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 2H), 8.33–8.43 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.3 (t, $J_{C\text{-}P}$ = 8.6 Hz), 32.1, 38.1 (dd, $J_{C\text{-}P}$ = 53.2 Hz, 7.2 Hz), 90.2 (dd, $J_{C\text{-}P}$ = 59.9 Hz, 2.9 Hz), 127.5 (d, $J_{C\text{-}P}$ = 77.6 Hz), 128.1 (d, $J_{C\text{-}P}$ = 70.9

Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.78 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.84 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.0 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.9 (d, $J_{C\text{-}P}$ = 79.6 Hz), 131.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.82 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.82 (d, $J_{C\text{-}P}$ = 78.6 Hz), 132.1 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.9 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 172.9; **^{31}P NMR** (162 MHz, $CDCl_3$): δ 46.0 (d, $J_{P\text{-}P}$ = 34.7 Hz), 54.8 (d, $J_{P\text{-}P}$ = 34.7 Hz); **IR** (KBr): 547, 647, 694, 719, 732, 952, 1097, 1194, 1437, 1801, 3048 cm^{-1}.

(E)-Oct-1-ene-1,2-bis(diphenylphosphine sulfide) (13aa) The *E*-isomer was obtained in 93% purity contaminated with the *Z*-isomer (7%) after purification by silica-gel column chlomatography. The isomer ratio was determined by ^{1}H NMR spectroscopy. [CAS registry number: 2097457-22-0];[5e] colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.71 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 0.78–0.84 (m, 4H), 0.85–0.93 (m, 2H), 0.94–1.03 (m, 2H), 2.65–2.77 (m, 2H), 7.24 (dd, $J_{H\text{-}P}$ = 26.8 Hz, 20.4 Hz, 1H), 7.38–7.49 (m, 10H), 7.52 (td, $J_{H\text{-}H}$ = 7.3 Hz, 1.8 Hz, 2H), 7.74–7.83 (m, 8H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 13.9, 22.2, 29.2, 29.3, 30.7 (dd, $J_{C\text{-}P}$ = 9.6 Hz, 8.6 Hz), 30.9, 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz, four-*ortho* carbons of diphenylthiophosphinyl group are overlapped), 131.0 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 133.6 (d, $J_{C\text{-}P}$ = 85.3 Hz), 136.0 (dd, $J_{C\text{-}P}$ = 73.3 Hz, 8.6 Hz), 156.4 (d, $J_{C\text{-}P}$ = 59.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.7 (d, $J_{P\text{-}P}$ = 57.4 Hz), 49.6 (d, $J_{P\text{-}P}$ = 57.4 Hz) (for *Z*-isomer: 31.9 (d, $J_{P\text{-}P}$ = 17.3 Hz), 42.3 (d, $J_{P\text{-}P}$ = 17.3 Hz)).[5d]

(E)-(1-Cyclohexylethene-1,2-diyl)bis(diphenylphosphine sulfide) (13ab) [CAS registry number: 2097457-25-3];[5e] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.63–0.77 (m, 2H), 0.91–1.05 (m, 1H), 1.12–1.20 (m, 2H), 1.32–1.44 (m, 3H), 1.91–2.04 (m, 2H), 3.20–3.37 (m, 1H), 6.64 (dd, $J_{H\text{-}P}$ = 25.9 Hz, 20.2 Hz, 1H), 7.34–7.408 (m, 4H), 7.412–7.55 (m, 8H), 7.72 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 0.9 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 4H), 7.83 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 0.9 Hz, $J_{H\text{-}P}$ = 7.3 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 25.1, 26.2, 30.8, 44.9 (dd, $J_{C\text{-}P}$ = 9.6 Hz, 9.6 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz, four-ortho carbons of diphenylthiophosphinyl group are overlapped), 130.8 (d, $J_{C\text{-}P}$ =

10.5 Hz), 131.5 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 82.4 Hz), 132.2 (d, $J_{C\text{-}P}$ = 9.6 Hz), 133.7 (d, $J_{C\text{-}P}$ = 84.4 Hz), 136.6 (dd, $J_{C\text{-}P}$ = 73.3 Hz, 8.6 Hz), 159.3 (d, $J_{C\text{-}P}$ = 56.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 28.2 (d, $J_{P\text{-}P}$ = 56.4 Hz), 46.7 (d, $J_{P\text{-}P}$ = 56.4 Hz).

(E)-(1-(Trimethylsilyl)ethane-1,2-diyl)bis(diphenylphosphine sulfide) (13ac) 1,2-Adduct **13ac** was obtained in 98% purity contaminated with desilylation product (*E*)-ethene-1,2-diylbis(diphenylphosphine sulfide)[19] (2%) after purification by silica gel column chlomatography. White solid; **mp.** 152–153 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.16 (s, 9H), 7.19 (dd, $J_{H\text{-}P}$ = 42.4 Hz, 22.9 Hz, 1H), 7.35 (td, $J_{H\text{-}H}$ = 7.3 Hz, 3.2 Hz, 4H), 7.39–7.52 (m, 8H), 7.60 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 4H), 7.79 (ddd, $J_{H\text{-}H}$ = 12.8 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.5 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 3.1 (d, $J_{C\text{-}P}$ = 1.9 Hz), 128.5 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 130.8 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 80.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 10.5 Hz), 134.3 (d, $J_{C\text{-}P}$ = 84.4 Hz), 149.9 (d, $J_{C\text{-}P}$ = 74.8 Hz), 159.9 (dd, $J_{C\text{-}P}$ = 25.4 Hz, 7.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 29.9 (d, $J_{P\text{-}P}$ = 80.7 Hz), 55.2 (d, $J_{P\text{-}P}$ = 80.7 Hz); **IR** (KBr): 614, 631, 660, 692, 713, 751, 848, 880, 1098, 1437, 2982, 3056 cm^{-1}.

(E)-(1-Phenylethene-1,2-diyl)bis(diphenylphosphine sulfide) (13ad) The *E*-isomer was obtained in 97% purity contaminated with the *Z*-isomer (3%) after purification by silica gel column chlomatography. [CAS registry number: 851380-56-8];[5b] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.69–6.78 (m, 4H), 6.85–6.93 (m, 1H), 7.20–7.27 (m, 4H), 7.28–7.338 (m, 2H), 7.342–7.40 (m, 4H), 7.42–7.49 (m, 2H), 7.64 (ddd, $J_{H\text{-}H}$ = 13.7 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 4H), 7.72 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 8.0 Hz, 4H), 7.85 (dd, $J_{H\text{-}P}$ = 25.2 Hz, 19.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.9, 127.9, 128.2 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 12.0 Hz), 129.9 (d, $J_{C\text{-}P}$ = 84.4 Hz), 130.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.15 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.15 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.8 (d, $J_{C\text{-}P}$ = 1.9 Hz), 132.2 (d, $J_{C\text{-}P}$ = 88.2 Hz), 132.3 (t, $J_{C\text{-}P}$ = 8.2 Hz), 132.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 139.0 (dd, $J_{C\text{-}P}$ = 72.8 Hz, 9.6 Hz), 152.6 (d, $J_{C\text{-}P}$ = 59.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ

30.9 (d, $J_{P\text{-}P}$ = 51.5 Hz), 48.6 (d, $J_{P\text{-}P}$ = 51.5 Hz) (for *Z*-isomer: δ 32.7 (d, $J_{P\text{-}P}$ = 13.0 Hz), 38.4 (d, $J_{P\text{-}P}$ = 13.0 Hz)).[5d]

(E)-(1-(4-tert-Butyl)phenyl)ethane-1,2-diyl)bis(diphenylphosphine sulfide) (13ae) White solid; **mp.** 177–178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.12 (s, 9H), 6.71–6.74 (m, 4H), 7.17–7.23 (m, 4H), 7.24–7.30 (m, 2H), 7.32–7.38 (m, 4H), 7.41–7.47 (m, 2H), 7.63 (dd, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 13.7 Hz, 4H), 7.71 (dd, $J_{H\text{-}H}$ = 7.8 Hz, $J_{H\text{-}P}$ = 13.3 Hz, 4H), 7.80 (dd, $J_{H\text{-}P}$ = 25.2 Hz, 19.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 30.9, 34.2, 123.8, 128.1 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.2 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.3 (dd, $J_{C\text{-}P}$ = 8.6 Hz, 7.7 Hz), 129.6 (d, $J_{C\text{-}P}$ = 4.8 Hz), 130.1 (d, $J_{C\text{-}P}$ = 85.3 Hz), 131.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.9 (d, $J_{C\text{-}P}$ = 88.2 Hz), 132.4 (d, $J_{C\text{-}P}$ = 10.5 Hz), 138.7 (dd, $J_{C\text{-}P}$ = 73.8 Hz, 10.5 Hz), 150.7 (d, $J_{C\text{-}P}$ = 1.9 Hz), 152.2 (d, $J_{C\text{-}P}$ = 60.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 31.2 (d, $J_{P\text{-}P}$ = 52.0 Hz), 48.5 (d, $J_{P\text{-}P}$ = 52.0 Hz); **IR** (KBr): 616, 634, 692, 716, 749, 831, 1102, 1437, 2964, 3055 cm^{-1}.

(E)-(1-(4-Trifluoromethyl)phenyl)ehtene-1,2-diyl)bis(diphenylphosphine sulfide) (13af) [CAS registry number: 2097457-10-6];[5e] white solid; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.92 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 6.99 (d, $J_{H\text{-}H}$ = 8.2 Hz, 2H), 7.21–7.27 (m, 4H), 7.30–7.35 (m, 2H), 7.39–7.45 (m, 4H), 7.47–7.52 (m, 2H), 7.59 (ddd, $J_{H\text{-}H}$ = 13.7 Hz, 1.8 Hz, $J_{H\text{-}P}$ = 7.8 Hz, 4H), 7.70 (dd, $J_{H\text{-}P}$ = 28.7 Hz, 18.8 Hz, 1H), 7.77 (ddd, $J_{H\text{-}H}$ = 13.3 Hz, 1.4 Hz, $J_{H\text{-}P}$ = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 123.6 (q, $J_{C\text{-}F}$ = 272.2 Hz), 123.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.3 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 12.5 Hz), 129.3 (d, $J_{C\text{-}P}$ = 85.3 Hz), 129.7 (dq, $J_{C\text{-}P}$ = 1.9 Hz, $J_{C\text{-}F}$ = 31.6 Hz), 130.5 (d, $J_{C\text{-}F}$ = 2.9 Hz), 131.1 (d, $J_{C\text{-}P}$ = 10.5 Hz), 131.4 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.6 (d, $J_{C\text{-}P}$ = 85.3 Hz), 132.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.5 (d, $J_{C\text{-}P}$ = 10.5 Hz), 135.9 (dd, $J_{C\text{-}P}$ = 8.6 Hz, 7.7 Hz), 139.8 (dd, $J_{C\text{-}P}$ = 71.9 Hz, 8.6 Hz), 150.9 (d, $J_{C\text{-}P}$ = 60.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 30.8 (d, $J_{P\text{-}P}$ = 47.7 Hz), 48.7 (d, $J_{P\text{-}P}$ = 47.7 Hz).

Experimental procedure for the synthesis of 12be (Scheme 6-8)

Diphosphine disulfide **1a** (0.3 mmol) and **1b** (0.3 mmol) in degassed dry CH_2Cl_2 (0.3 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 10 h. To the resulting mixture (***P,S-mixture-1a+1b***), **6e** was added and it was irradiated with a xenon lamp for 10 h. The desired products were obtained after isolation by silica gel chromatography (eluent: *n*-hexane/AcOEt/$CHCl_3$).

The components of ***P,S-mixture-1a+1b*** was determined by ^{31}P NMR spectroscopy. In contrast to **1a**, most of **1b** was converted to $Me_2P(S)–P(S)Ph_2$ (56%), $Me_2P(S)–SPPh_2$ (11%), and $Me_2P(S)–S–P(S)Ph_2$ (25%). The 1,2-addition of these species mainly gave **12be** in 34% yield in competition with the generation of **7ae** (40%).

(2-(Dimethylthiophosphinyl)cyclohexyl)diphenylphosphine sulfide (12be) 1,2-Adduct **12be** was obtained in 98% purity contaminated with **7ae** (2%), generated from the 1,2-addition of tetraphenyldiphosphine disulfide (**1a**), after purification by silica gel column chlomatography. White solid; **mp.** 162–163 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.36 (d, J_{H-P} = 12.0 Hz, 3H), 1.43–1.51 (m, 1H), 1.59–1.72 (m, 2H), 1.77 (d, J_{H-P} = 12.4 Hz, 3H), 1.81–2.28 (m, 4H), 2.38 (ddd, J_{H-H} = 6.4 Hz, J_{H-P} = 18.3 Hz, 13.3 Hz, 1H), 2.67–2.89 (m, 1H), 3.96 (ddd, J_{H-H} = 6.4 Hz, J_{H-P} = 20.1 Hz, 10.5 Hz, 1H), 7.43–7.52 (m, 6H), 8.02–8.09 (m, 2H), 8.13–8.20 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 20.5, 21.1 (d, J_{C-P} = 14.7 Hz), 21.3, 21.6 (d, J_{C-P} = 10.5 Hz), 22.4 (d, J_{C-P} = 2.0 Hz), 22.9, 31.5 (d, J_{C-P} = 52.4 Hz), 34.8 (dd, J_{C-P} = 45.8 Hz, 1.2 Hz), 128.5 (d, J_{C-P} = 11.6 Hz), 128.6 (d, J_{C-P} = 11.6 Hz), 131.3 (d, J_{C-P} = 76.2 Hz), 131.48 (d, J_{C-P} = 3.2 Hz), 131.51 (d, J_{C-P} = 3.2 Hz), 131.6 (d, J_{C-P} = 77.6 Hz), 131.7 (d, J_{C-P} = 9.6 Hz), 132.0 (d, J_{C-P} = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 48.1 (d, J_{P-P} = 56.4 Hz), 50.4 (d, J_{P-P} = 56.4 Hz); **IR** (KBr): 526, 583, 603, 698, 726, 753, 918, 1097, 1436, 2863, 2936 cm^{-1}.

Experimental procedure for the synthesis of 3d (Scheme 6-9)

To a 100 mL Shrenck flask, the mixture of *O,O'*-diethyl dithiophosphate ($(EtO)_2P(S)SH$,

10 mmol) and triethylamine (20 mmol) dissolved in deggased dry THF (10 mL) was added dropwise to diphenylphosphine chloride (10 mmol) dissolved in degassed dry THF (50 mL) under an argon atmosphere at 0 °C for 30 min. After it was stirred for 10 h at room temperature in a dark room, the reaction mixture was concentrated under reduced pressure to give the product in 92% yield as a mixture with $Ph_2P(S)H$ (4 mol%). The mixture was used for the next reaction.

O,O'-Diethyl-S-(diphenylphosphino)dithiophosphate (3d) White solid; **mp.** 33–34 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.27 (t, $J_{H\text{-}H}$ = 7.3 Hz, 6H), 4.01–4.13 (m, 2H), 4.15–4.27 (m, 2H), 7.34–7.40 (m, 6H), 7.53–7.60 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 15.6 (d, $J_{C\text{-}P}$ = 8.6 Hz), 64.2 (d, $J_{C\text{-}P}$ = 5.7 Hz), 128.6 (d, $J_{C\text{-}P}$ = 6.7 Hz), 129.6, 132.8 (d, $J_{C\text{-}P}$ = 21.9 Hz), 136.5 (dd, $J_{C\text{-}P}$ = 25.8 Hz, 7.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 26.7 (d, $J_{P\text{-}P}$ = 53.7 Hz), 89.1 (d, $J_{P\text{-}P}$ = 53.7 Hz).

Experimental procedure for the synthesis of 12de and 12dh (Scheme 6-9)

Diphosphine disulfide **1d** (0.3 mmol) or **3d** (0.3 mmol), and alkene **6e** (0.3 mmol) or **6h** (0.3 mmol), respectively, in degassed dry CH_2Cl_2 (0.3 mL) were placed in a sealed Pyrex NMR tube under an argon atmosphere and the mixture was irradiated with a xenon lamp (500 W) for 10 h. The desired products were obtained after isolation by silica gel chromatography (eluent: *n*-hexane/AcOEt/$CHCl_3$).

(O,O-Diethyl (2-(diphenylthiophosphinyl)cyclohexyl)thiophosphonate (12de) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.22 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.27 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.36–1.44 (m, 1H), 1.54–1.63 (m, 1H), 1.65–1.88 (m, 2H), 1.95–2.16 (m, 2H), 2.25–2.48 (m, 2H), 2.53–2.77 (m, 1H), 3.72 (ddd, $J_{H\text{-}H}$ = 6.9 Hz, $J_{H\text{-}P}$ = 21.5 Hz, 11.5 Hz, 1H), 3.89–4.11 (m, 4H), 7.40–7.52 (m, 6H), 7.98–8.05 (m, 2H), 8.11–8.19 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 16.2 (d, $J_{C\text{-}P}$ = 6.7 Hz), 20.8, 21.1, 21.7 (d, $J_{C\text{-}P}$ = 3.8 Hz), 22.5, 31.6 (d, $J_{C\text{-}P}$ = 52.7 Hz), 37.9 (d, $J_{C\text{-}P}$ = 104.5 Hz), 62.5 (d, $J_{C\text{-}P}$ = 18.2 Hz), 62.6 (d, $J_{C\text{-}P}$ = 18.2 Hz), 128.3 (d, $J_{C\text{-}P}$

= 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 131.2 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.5 (d, $J_{C\text{-}P}$ = 9.6 Hz), 131.7 (d, $J_{C\text{-}P}$ = 76.9 Hz), 132.0 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.2 (d, $J_{C\text{-}P}$ = 75.4 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 50.4 (d, $J_{P\text{-}P}$ = 73.7 Hz), 103.9 (d, $J_{P\text{-}P}$ = 73.7 Hz); **IR** (NaCl): 697, 722, 753, 785, 955, 1022, 1051, 1097, 1437, 2936, 2979 cm^{-1}.

(O,O-Diethyl (2-(diphenylthiophosphinyl)tetrahydrofuran-3-yl)thiophosphonate (12dh) Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.19 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.24 (t, $J_{H\text{-}H}$ = 7.3 Hz, 3H), 1.79–1.99 (m, 1H), 2.13–2.27 (m, 1H), 3.19–3.34 (m, 1H), 3.91–4.10 (m, 6H), 5.39 (dddd, $J_{H\text{-}H}$ = 3.2 Hz, $J_{H\text{-}P}$ = 22.0 Hz, 10.7 Hz, 1H), 7.41–7.56 (m, 6H), 7.91–8.04 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 16.0 (d, $J_{C\text{-}P}$ = 6.7 Hz), 16.1 (d, $J_{C\text{-}P}$ = 6.7 Hz), 28.1, 44.4 (dd, $J_{C\text{-}P}$ = 114.9 Hz, 4.7 Hz), 62.9 (d, $J_{C\text{-}P}$ = 60.1 Hz), 63.0 (d, $J_{C\text{-}P}$ = 60.1 Hz), 70.7, 80.0 (d, $J_{C\text{-}P}$ = 66.8 Hz), 128.3 (d, $J_{C\text{-}P}$ = 11.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.5 Hz), 130.1 (d, $J_{C\text{-}P}$ = 77.3 Hz), 131.0 (d, $J_{C\text{-}P}$ = 77.3 Hz), 131.6 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.1 (d, $J_{C\text{-}P}$ = 9.6 Hz), 132.6 (d, $J_{C\text{-}P}$ = 9.6 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$): δ 46.5 (d, $J_{P\text{-}P}$ = 48.1 Hz), 98.5 (d, $J_{P\text{-}P}$ = 48.1 Hz); **IR** (NaCl): 693, 718, 752, 785, 817, 958, 1022, 1050, 1100, 1437, 2892, 2976 cm^{-1}.

6-6 References

1. Quin, L. D. *A Guide to Organophosphorus Chemistry.* John Wiley & Sons: New York, 2000.

2. (a) Lechtken, P.; Buethe, I.; Hesse, A. US4324744, 1982. (b) Lechtken, P.; Buethe, I.; Jacobi, M.; Trimborn, W. US4710523, 1987. (c) Sumiyoshi, T.; Katayama, M.; Schnabel, W. *Chem. Lett.* **1985**, *14*, 1647-1650. (d) Sumiyoshi, T.; Schnabel, W.; Henne, A.; Lechtken, P. *Polymer* **1985**, *26*, 141-146.

3. (a) Sluggett, G. W.; Turro, C.; George, M. W.; Koptyug, I. V.; Turro, N. J. *J. Am. Chem. Soc.* **1995**, *117*, 5148-5153. (b) Kolczak, U.; Rist, G.; Dietliker, K.; Wirz, J. *J. Am. Chem. Soc.*

1996, *118*, 6477-6489. (c) Colley, C. S.; Grills, D. C.; Besley, N. A.; Jockusch, S.; Matousek, P.; Parker, A. W.; Towrie, M.; Turro, N. J.; Gill, P. M. W.; George, M. W. *J. Am. Chem. Soc.* **2002**, *124*, 14952-14958.

4. (a) Sato, Y.; Kawaguchi, S-i.; Ogawa, A. *Chem. Commun.* **2015**, *51*, 10385-10388; (b) Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Synthesis* **2017**, *49*, 3558-3567.

5. For addition reactions of diphosphines to alkynes, see: (a) Tzschach, A.; Baensch, S. *J. Prakt. Chem.* **1971**, *313*, 254-258. (b) Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem. Int. Ed.* **2005**, *44*, 1694-1696. (c) Dodds, D. L.; Haddow, M. F.; Orpen, A. G.; Pringle, P. G.; Woodward, G. *Organometallics* **2006**, *25*, 5937-5945. (d) Kawaguchi, S-i.; Nagata, S.; Shirai, T.; Tsuchii, K.; Nomoto, A.; Ogawa, A. *Tetrahedron Lett.* **2006**, *47*, 3919-3922. (e) Okugawa, Y.; Hirano, K.; Miura, M. *Org. Lett.* **2017**, *19*, 2973-2976.

6. For addition reactions of diphosphines to alkenes, see: (a) Burg, A. B. *J. Am. Chem. Soc.* **1961**, *83*, 2226-2231. (b) Morse, K. W.; Morse, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 8469-8470. (c) Morse, J. G.; Morse, K. W. *Inorg. Chem.* **1975**, *14*, 565-569. (d) Drieß, M.; Haiber, G. *Z. Anorg. Allg. Chem.* **1993**, *619*, 215-219. (e) Burck, S.; Gudat, D.; Nieger, M. *Angew. Chem. Int. Ed.* **2004**, *43*, 4801-4804. (f) Hajdók, I.; Lissner, F.; Nieger, M.; Strobel, S.; Gudat, D. *Organometallics* **2009**, *28*, 1644-1651. (g) Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. *Synthesis* **2018**, *50*, 3402-3407.

7. For bisphosphination reactions of alkenes and alkynes, see: (a) Hirano, K.; Miura, M. *Tetrahedron Lett.* **2017**, *58*, 4317-4322. (b) Okugawa, Y.; Hirano, K.; Miura, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 13558-13561. (c) Otomura, N.; Okugawa, Y.; Hirano, K.; Miura, M. *Org. Lett.* **2017**, *19*, 4802-4805. (d) Yoshimura, A.; Saga, Y.; Sato, Y.; Ogawa, A.; Chen, T.; Han, L.-B. *Tetrahedron Lett.* **2016**, *57*, 3382-3384. (e) Guo, H.; Yoshimura, A.; Chen, T.; Saga, Y.; Han, L.-B. *Green Chem.* **2017**, *19*, 1502-1506.

8. For synthetic methods of diphosphine disulfides, see: (a) Mayer, L. *Chem. Ber.* **1961**, *94*, 3051-3055. (b) Patel, N. K.; Harwood, H. J. *J. Org. Chem.* **1967**, *32*, 2999-3003. (c) Hägele, G.; Tossing, G.; Kückelhaus, W.; Seega, J. *Z. Naturforsch. B* **1984**, *39*, 1574. (d) Hahn, K.; Kriha, O.; Bellin, I.; Spies, P.; Fuchs, S.; Deglmann, P.; Massonne, K.; Denecke, H.; Fleckenstein, C.; Janssens, G. US20120178842, 2012.

9. For reactions using diphosphine disulfides, see: (a) Emoto, T.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 898-901. (b) Arisawa, M.; Yamaguchi, M. *Tetrahedron Lett.* **2009**, *50*, 3639-3640. (c) Arisawa, M.; Yamada, T.; Yamaguchi, M. *Tetrahedron Lett.* **2010**, *51*, 4957-4958. (d) Arisawa, M.; Watanabe, T.; Yamaguchi, M. *Tetrahedron Lett.* **2011**, *52*, 2410-2412. (e) Arisawa, M.; Yamada, T.; Tanii, S.; Kawada, Y.; Hashimoto, H.; Yamaguchi, M. *Chem. Commun.* **2016**, *52*, 13580-13583. (f) Arisawa, M.; Tazawa, T.; Ichinose, W.; Kobayashi, H.; Yamaguchi, M. *Adv. Synth. Catal.* **2018**, *360*, 3488-3491.

10. (a) Parshall, G. W. *J. Inorg. Nucl. Chem.* **1960**, *14*, 291-292. (b) Schmutzler, R. *Inorg. Chem.* **1964**, *3*, 421-428.
    (a) Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Angew. Chem. Int. Ed.* **2016**, *55*, 9700-9703. (b) Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A. *Chem. Eur. J.* **2019**, *25*, 2295-2302.

11. (a) Fruchey, E. R.; Monks, B. M.; Cook, S. P. *J. Am. Chem. Soc.* **2014**, *136*, 13130-13133. (b) Fan, J.-H.; Wei, W.-T.; Zhou, M.-B.; Song, R.-J.; Li, J.-H. *Angew. Chem. Int. Ed.* **2014**, *53*, 6650-6654. (c) Uesugi, S.; Li, Z.; Yazaki, R.; Ohshima, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 1611-1615. (d) Arisawa, M.; Ichikawa, T.; Yamaguchi, M. *Chem. Commun.* **2015**, *51*, 8821-8824.

12. Yogendra, S.; Chitnis, S. S.; Hennersdorf, F.; Bodensteiner, M.; Fischer, R.; Burford, N.; Weigand, J. J. *Inorg. Chem.* **2016**, *55*, 1854-1860

13. (a) Karlsson, H.; Lagercrantz, C. *Acta Chem. Scand* **1970**, *24*, 3411-3413. (b) Medsker, R. E.; Sebenik, A.; Harwood, H. J. *Polym. Bull.* **2002**, *48*, 17-23.

14. Kullberg, M.; Stawinski, J. *J. Organomet. Chem.* **2005**, *690*, 2571-2576.

15. Diphosphine disulfide **1a** (0.3 mmol) and 1,2-adduct of **4a** to **6a** ((1-diphenylthiophosphinyl-2-diphenylphosphino)dodecane) dissolved in CD_2Cl_2 (0.3 mL) were exposed to photoirradiation conditions for 6 h. Most of the 1,2-adduct of **4a** was sulfurized to afford **7aa**, quantitatively.

16. Luo, Y. R. *Comprehensive Handbook of Chemical Bond Energies*. CRC Press: Boca Raton, 2007.

17. Min, S.; Ishihara, H.; Murai, T.; Kato, S. *Z. Naturforsch. B* **1989**, *44*, 153.

18. Duncan, M.; Gallagher, M. J. *Org. Magn. Reson.* **1981**, *15*, 37-42.

Chapter 7

Conclusion

In this research work, the characteristic features of pentavalent phosphorus radicals was investigated in detail, and several phosphorus valence-selective synthetic methods of fluorous phosphines and chalcogenophosphinates are developed. Furthermore, several regioselective addition reactions of diphosphine analogues to alkenes based on the difference of reactivity between pentavalent and trivalent phosphorus radicals are also developed.

Chapter 2 described a method for the rapid synthesis of *P*-perfluoroalkyl phosphines using TMDPO as a phosphorus source. This reaction generates phosphorus(III) compounds from phosphorus(V) species via perfluoroalkylation. This method is viable for the synthesis of a variety of *P*-perfluoroalkylphosphines. In addition, the generated *P*-perfluoroalkylphosphines could be complexed with a transition-metal, platinum(II). Therefore, the generated *P*-perfluoroalkylphosphines can be used as ligands, and in the near future, new reactions are expected to be developed using the produced *P*-perfluoroalkylphosphine ligand-metal complexes.

Chapter 3 mentioned the photoinduced coupling reactions between TMDPO and a series of ***E***–***E*** compounds have been investigated in detail, and novel synthetic methods for *S*- or *Se*-substituted thio- or selenophosphinates, respectively, and diphosphine monoxide have been successfully developed. In addition, after the through study of the characteristic features of the reaction of each interelement compound with TMDPO under light irradiation, a novel synthesis of alkylphosphines was successfully demonstrated.

Chapter 4 described a protocol for the highly regioselective addition of tetraphenyldiphosphine monoxides to a variety of alkenes. This approach enables the regioselective introduction of diphenylphosphino and diphenylphosphinyl groups on various

aliphatic alkenes and phenylacetylene. A plausible reaction pathway involving a regioselective radical capturing process was proposed.

Chapter 5 described a simple synthetic method for the preparation of vicinally located bis(phosphine) monosulfides by investigating the addition reactions of diphosphine monosulfides to alkenes. This reaction readily affords a variety of symmetrical and unsymmetrical bis(phosphine) monosulfides with excellent regio- and diastereoselectivities without the need for a catalyst, base, or additive. Several mechanistic experiments revealed that the HOMO of diphosphine monosulfide, which, due to the sulfur atom, is higher than that of the corresponding phosphine oxide, contributes to an extended absorption-wavelength profile and improvements in its carbon-radical capturing ability.

Chapter 6 described a simple and facile synthetic method for the preparation of bis(thiophosphinyl)alkanes and bis(thiophosphinyl)alkenes. Diphosphine disulfides are promising phosphorus sources because they are facile preparable and shelf-stable solid but the addition reactions using diphosphine disulfides were very limited. It was found that diphosphine disulfides underwent the reductive rearrangement to active trivalent phosphorus species, such as diphosphathiane monosulfide having a P(S)–SP single bond, under light. In addition, this rearrangement triggered the radical chain for bisthiophosphinylation reaction to a variety of alkenes and alkynes. This reaction readily affords a variety of bis(thiophosphinyl)alkanes without the need for a catalyst, base, or additive.

In summary, the detail investigation of the characteristic feature of pentavalent phosphorus radicals contributed to opening door to developing a novel and powerful synthetic tool: the reductive rearrangement, which can transform pentavalent phosphorus compounds to trivalent phosphorus compounds. Some pentavalent phosphorus radicals, such as secondary phosphinyl- and thiophosphinyl radicals, can be recombined with electrophilic radicals, such as benzoyl- and thiophosphinyl radicals, respectively, to form the corresponding active trivalent phosphorus species, efficiently. The generated trivalent phosphorus species have

electron-withdrawing groups, such as benzoyloxy- and dithiophosphinate groups, respectively, which also behave as good leaving groups. Therefore, the trivalent phosphorus species have enough nucleophilicity to capture a variety of transient carbon-centered radicals. Pentavalent phosphorus radicals can also strictly control the regio-selectivity in its radical addition reaction by combination with trivalent phosphorus radicals. This regio-control strategy facilitated the highly selective introduction of two different phosphorus groups to alkenes and alkynes. The author believes that these two powerful tools, “reductive rearrangement” and “strict regio-control”, provide broad chemists to come up many inspirations for developing novel reactions.

List of Publications

1. Photoinduced Reductive Perfluoroalkylation of Phosphine Oxides: Synthesis of *P*-Perfluoroalkylated Phosphines Using TMDPO and Perfluoroalkyl Iodides

   Sato, Y.; Kawaguchi, S-i.; Ogawa, A.

   Chem. Commun. **2015**, *51*, 10385–10388.

   (Chapter 2)

2. Photoinduced Coupling Reaction of Diphenyl(2,4,6-trimethylbenzoyl)phosphine Oxide with Interelement Compounds: Application to the Synthesis of Thio- or Selenophosphinates

   Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A.

   Synthesis **2017**, *49*, 3558–3567.

   (Chapter 3)

3. Highly Selective Phosphinylphosphination of Alkenes with Tetraphenyldiphosphine Monoxide

   Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A.

   Angew. Chem. Int. Ed. **2016**, *55*, 9700–9703.

   (Chapter 4)

4. Synthesis of Bis(phosphino)alkane Monosulfides by the Addition of Diphosphine Monosulfides to Alkenes under Light

   Sato, Y.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A.

   Chem. Eur. J. **2019**, *25*, 2295-2302.

   (Chapter 5)

5. Reductive Rearrangement of Tetraphenyldiphosphine Disulfide to Trigger the Bisthiophosphinylation of Alkenes and Alkynes

   Sato, Y.; Nishimura, M.; Kawaguchi, S-i.; Nomoto, A.; Ogawa, A.

   Chem. Eur. J. in press.

(Chapter 6)

Other Publications

6. *P*-Perfluoroalkylated Phosphines from Triarylphosphines and Their Application in the Cu-Free Cross-Coupling of Acid Chlorides and Terminal Alkynes

   Kawaguchi, S-i.; Minamida, Y.; Okuda, T.; Sato, Y.; Saeki, T.; Yoshimura, A.; Nomoto, A.; Ogawa, A.

   Adv. Synth. Catal. **2015**, *357*, 2509–2519.

Acknowledgement

First of all, I would like to express my sincerest gratitude and thanks to my research supervisor Professor Akiya Ogawa for his kind guidance, helpful suggestions, continuous encouragement, and invaluable assistance throughout the course of this challenging work.

I also would like to express grateful to Professor Hiroshi Ikeda and Professor Akikazu Matsumoto of Osaka Prefecture University for their helpful remarks and suggestions to this thesis.

I would also like to express my thanks to Visiting Professor Michio Ueshima and Associate Professor Akihiro Nomoto of Osaka Prefecture University, Doctor Li-Biao Han of National Institute of Advanced Industrial Science and Technology (AIST), and Assistant Professor Shin-ichi Kawaguchi of Saga University for their significant advices and stimulating discussions on this work. I would like to acknowledge the continuous encouragement and valuable discussions from Associate Professor Motohiro Sonoda of Osaka Prefecture University, Lecturer Yoshimasa Makita of Osaka Dental University, Visiting Researcher Toshiya Ozaki from Water Agency Co., Ltd., Assistant Professor Aya Yoshimura of Ehime University, and Postdoctoral Researcher Shintaro Kodama of Osaka Prefecture University. I express my acknowledgement to my co-workers of my research group: Mr. Yohsuke Kobiki, Mr. Yoshihisa Shimada, and Mr. Kentaro Nakamura. Special thanks are also given to all other members of Prof. Ogawa's research group for their assistances, daily discussions to this work.

Furthermore, I acknowledge the Research Fellowship from Japan Society for the Promotion of Science (JSPS) for Young Scientists for financial support.

Finally, I would like to express my deepest appreciation to all my family for their understanding, continuous encouragement, and supports.

January 2019 ***Yuki Sato***