Studies on Free Radical Reactions to Form Carbon–Phosphorus and Carbon–Sulfur Bonds

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Contents

Abbreviations

Ac	acetyl
AIBN	2,2'-azobis(isobutyronitrile)
aq.	aqueous
Ar	aryl
Bn	benzyl
Boc	*tert*-butoxycarbonyl
b.p.	boiling point
br	broad (spectral)
br s	broad singlet (spectral)
Bu	butyl
c	cyclo
˚C	degrees Celsius
calcd	calculated
cat.	catalytic
Chap.	chapter
cm	centimeter(s)
Co.	company
COSY	correlated spectroscopy
δ	chemical shift in perts per million
d	doublet (spectral)
d	deuterium
DEPT	distortionless enhancement by plarization transfer
dig	digonal
dppp	1,3-bis(diphenylphosphino)propane
dm	decimeter
d.r.	diastereomeric ratio
Ed(s).	editor(s)
E	*entgegen* (means "opposite")
ee	enantiomeric excess
equiv	equivalent(s)
Et	ethyl
EWG	electron-withdrawing group
g	gram(s)
GPC	gel permeation chromatography
h	hour(s)
HRMS	high-resolution mass spectrum
Hz	hertz (s^{-1})
i	iso
IR	infrared (spectral)
J	coupling constant (spectral)
m	multiplet (spectral)
M	molar (1 M = 1 mol dm^{-3})
Me	methyl
mg	milligram(s)
MHz	megahertz
min	minute(s)
mL	milliliter(s)
mm	millimeter(s)
mmol	millimole(s)
mol	mole(s)
m.p.	melting point
MS4A	molecular sieves 4A
n	normal
nm	nanometer(s)
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
o	ortho
p	para
p. (pp.)	page(s)
Ph	phenyl
ppm	parts per million (spectral)
Pr	propyl
q	quartet (spectral)
quint	quintet (spectral)
R_f	retention factor (TLC)
RI	refractive index
r.t.	room temperature (25 ± 3 ˚C)

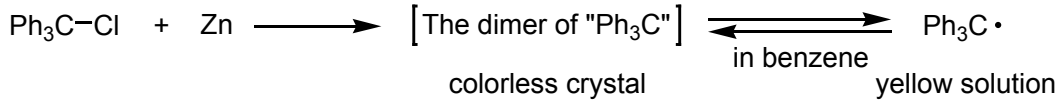
s	singlet (spectral)
S_H2	bimolecular homolytic substitution
t (*tert*)	tertiary
t	triplet (spectral)
TBS	*tert*-butyldimethylsilyl
TEMPO	2,2,6,6-tetramethylpiperidine *N*-oxyl
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TLC	thin-layer chromatography
TM	trademark
TMS	trimethylsilyl
Tf	trifluoromethanesulfonyl
Ts	*p*-toluenesulfonyl
UV	ultraviolet
vic	vicinal
Vol.	volume(s)
W	watt
wt	weight
Z	*zusammen* (means "together")

General Introduction

1. Organic Free Radicals

Today, organic free radical reactions are indispensable in organic synthesis. Organic free radicals show peculiar reactivities, and radical reactions tolerate a wider variety of functional groups than classical ionic reactions and transition-metal catalyzed reactions.[1]

The discovery of organic free radicals dates back to 1900. Moses Gomberg supposed that a colorless crystal obtained by treatment of triphenylmethyl chloride with zinc metal is the dimer of "triphenylmethyl" (Scheme 1).[2] He showed the existence of unknown organic free radicals based on the fact that the crystal turned yellow in benzene solution and reacted with molecular oxygen to afford the corresponding peroxide, although the precise structure of the dimer was confirmed after seventy years.[3]



Scheme 1.1. The first discovery of an organic free radical by Moses Gomberg

In spite of his epoch-making discovery, organic radicals had attracted little attention and development of radical chemistry was much slow at that time. About 30 years later, Paneth found out the existence of less stabilized alkyl radicals, and the lifetime of the radicals in a gas phase was also measured.[4] In 1937, Hey and Waters published a key review and attributed many known synthetic reactions to radical mechanisms.[5] In the same year, Kharasch performed the famous anti-Markovnikov addition of hydrogen bromide to alkenes in the presence of peroxide via a radical chain process.[6] In 1940s, Mayo, Walling, and Lewis developed the rules of radical polymerization and copolymerization of vinyl compounds.[7] They also established kinetic laws from the polar character of free radicals in the reaction process.[8] The character was

expressed in the concept of electrophilic and nucleophilic radicals, which is now one of the most important concepts to explain the reactivity and selectivity in free radical reactions. By 1960s, physical methods began to be used to determine the absolute rate constants of various radical reactions in solution by Ingold, Fischer, and Beckwith.[9]

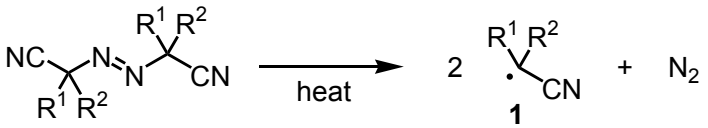
In 1970s to early 1980s, many reactions such as addition reactions of carbon-centered radicals to carbon–carbon multiple bonds including cyclization was reported by Barton, Giese, Hart, and so on as new synthetic methods.[10] In the middle of 1980s, drastic growth in organic free radical chemistry emerged.[1,11] The growth has continued up to now.

2. Generation of Organic Free Radical

Organic free radicals should be generated conveniently for organic radical reactions. Radical initiators are thus requested to have the opposite two properties: stable before use and available to produce radicals under mild conditions. Various methods to generate radicals have been investigated and some representatives are illustrated below.[12]

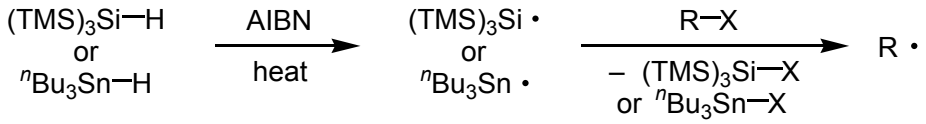
Thermolysis of azo compounds and peroxides

Organic azo compounds, which usually have nitrile moieties on azotized carbons, are among the most common radical initiators,[13] which can decompose homolytically by mild heat into cyano-stabilized alkyl radicals **1** with concomitant release of nitrogen gas (Scheme 2.1). The half-life times ($t_{1/2}$) depend on the structures of azo compounds. For example, at 80 °C (the boiling point of benzene), AIBN ($R^1 = R^2 = Me$) has $t_{1/2}$ = 90 min and V-40 (R^1, $R^2 = -(CH_2)_5-$) has $t_{1/2}$ = 30 h.[12a]



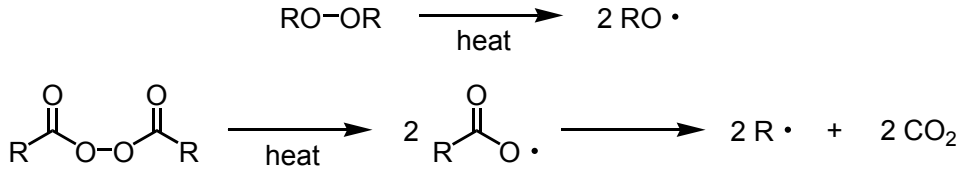
Scheme 2.1. Thermolysis of azo compounds.

The cyanated carbon-centered radical **1** can abstract hydrogen atom from tris(trimethylsilyl)silane[14] or tributylstannane[15] to generate the corresponding silyl or stannyl radical, respectively. These radicals are often used to abstract halogens of carbon–halogen bonds to create alkyl or aryl radicals (Scheme 2.2).



Scheme 2.2. Utilization of azo initiators.

Like azo compounds, peroxides are also widely used as radical initiators.[16] Thermolysis of organic peroxides proceeds to produce alkoxyl radicals. In the case of acyl peroxides, the resulting carboxyl radicals may then eliminate carbon dioxide to form alkyl or aryl radicals (Scheme 2.3). The half-life time of $(^{t}BuO)_2$ is 1 h at 150 ˚C and that of $(PhCO_2)_2$ is 1 h at 95 ˚C.[12a]



Scheme 2.3. Thermolysis of peroxides.

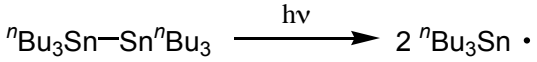
Trialkylboranes with molecular oxygen

Trialkylboranes react rapidly with molecular oxygen to furnish alkyl radicals (Scheme 2.4),[17] which were firstly utilized in organic synthesis as a radical initiator by Oshima.[18] Compared with azo compounds and peroxide that require high temperatures, trialkylboranes can give alkyl radicals even at –78 ˚C.[18c] The production of alkyl radicals at low temperatures enables highly stereoselective reactions as well as the reaction of thermally unstable substrates.

Scheme 2.4. Generation of alkyl radicals from trialkylboranes.

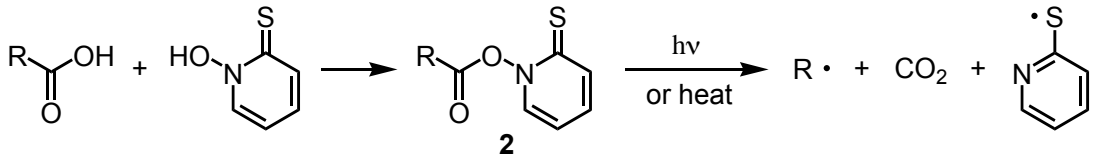
Photolysis

Relatively weak covalent bonds can be homolytically cleaved by photolysis. For instance, hexabutyldistannane decomposes into tributylstannyl radical upon irradiation (Scheme 2.5).[19]



Scheme 2.5. Photolysis of hexabutyldistannane.

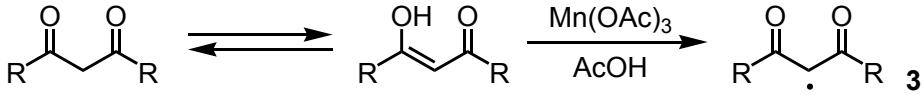
Barton developed *O*-acyl-*N*-hydroxy-2-thiopyridones **2** (so-called "Barton esters") as radical sources.[20] Alkyl radicals can be generated mildly from the thiopyridones **2** upon irradiation (Scheme 2.6). Because Barton esters are easily synthesized from carboxylic acids, this method is useful for transformation of carboxylic acids.



Scheme 2.6. *O*-Acyl-*N*-hydroxy-2-thiopyridones (Barton esters).

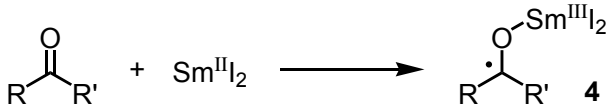
Oxidative and reductive conditions

High-valent transition metals such as manganese(III), copper(II), and cerium(IV) can oxidize electron-rich organic compounds to generate radicals. For example, *β*-dicarbonyl compounds are oxidized by manganese(III) to yield radicals **3** (Scheme 2.7).[21]



Scheme 2.7. Oxidative radical generation from β-dicarbonyl compounds.

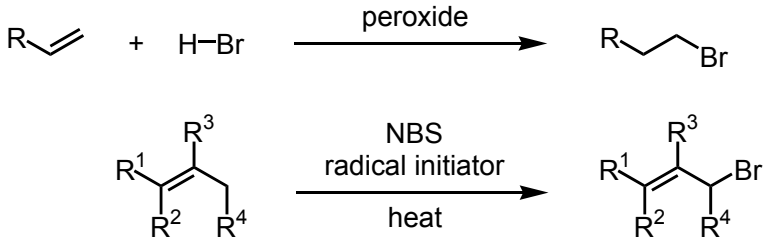
In contrast, low-valent transition metals such as samarium(II), iron(II), and titanium(III) can reduce organic compounds to form radicals. For example, ketones are reduced by samarium(II) to give ketyl radicals **4** (Scheme 2.8).[22]



Scheme 2.8. Reductive radical generation from ketones.

3. Intermolecular Radical Reactions to Form Carbon–Heteroatom Bonds

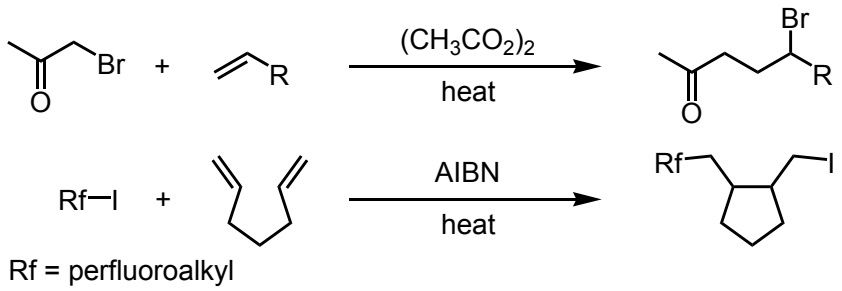
Radical reactions to form carbon–carbon bonds have been much investigated until now. In addition, formations of carbon–halogen bonds are well-known as shown in Scheme 3.1. Hydrogen bromide adds to olefins in an anti-Markovnikov manner in the presence of peroxides.[6] Upon heating in the presence of radical initiators, allylic positions are brominated by *N*-bromosuccinimide (NBS).[23]



Scheme 3.1. Representative radical reactions to form carbon–halogen bonds.

Halogen-transfer reactions are also well-documented (Scheme 3.2). α-Keto radicals generated from α-haloketones add to alkenes and the resulting radicals attack the halogens to

form carbon–halogen bonds.[24] Perfluoroalkyl iodides also react with alkenes in the presence of radical initiators.[25] In the latter example, 5-*exo* cyclization that is peculiar to radical reaction are included.



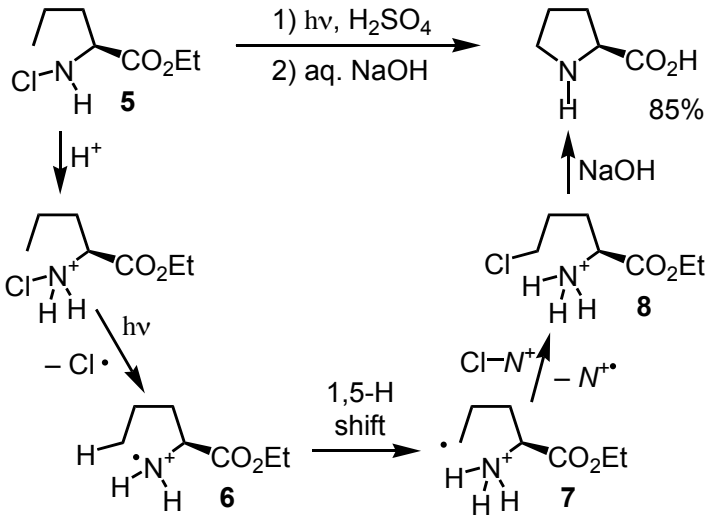
Scheme 3.2. Representative halogen-transfer reactions.

However, formations of carbon–other heteroatom bonds are yet under developing. Further, most of them are limited to intramolecular reactions.[26] Now many chemists are exploring new reactions to make carbon–heteroatom bonds at will efficiently.

To form carbon–heteroatom bonds, there are roughly two methods. One is the reaction of heteroatom-centered radicals with carbon atoms. The other is the reaction of carbon-centered radicals with heteroatoms.

3.1. Reaction of Heteroatom-centered Radicals with Carbon Atoms

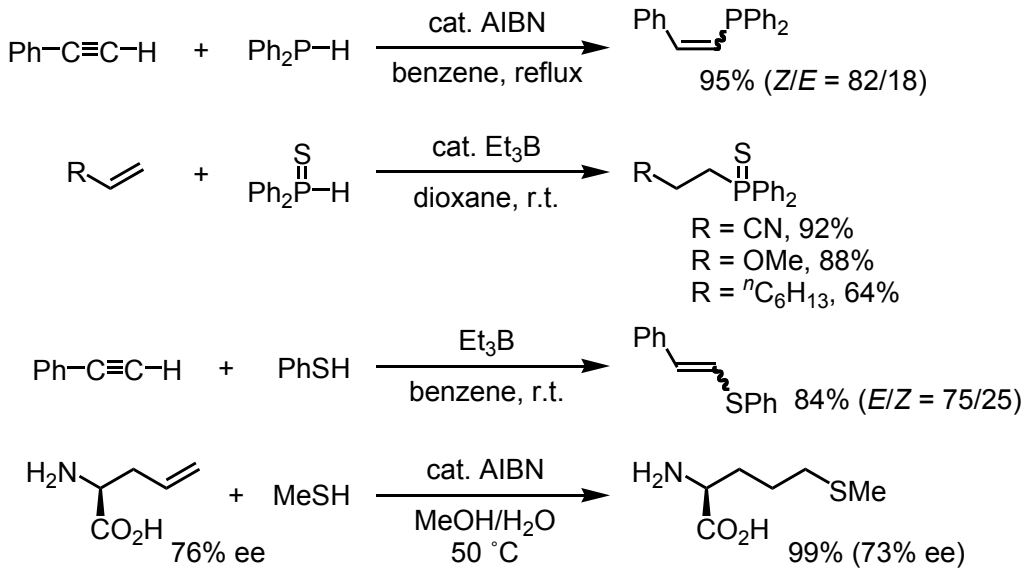
Hofmann reported a cyclization reaction of *N*-chloroamines in 1881.[27] Now the reaction is called a "Hofmann–Löffler–Freytag reaction" and is regarded as the oldest generation of nitrogen-centered radicals and their utilization.[28] Irradiation or heating *N*-chloroamine **5** in the presence of a strong acid generates cation radical **6**. Then 1,5-hydrogen shift occurs to furnish radical **7**. Radical **7** abstracts chlorine from **5** to give cation **8**. Treatment of **8** with a base affords the cyclized product, proline. However, the formation of the carbon–nitrogen bond occurs in the second step clearly in an ionic manner (Scheme 3.3).[29]



Scheme 3.3. An example of Hofmann–Löffler–Freytag reaction.

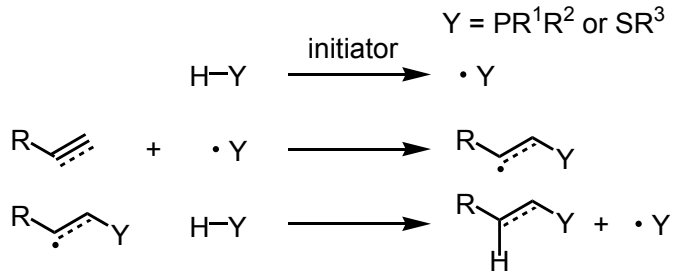
Heteroatom-centered radicals act as electron-deficient radicals based on the high electronegativity of heteroatoms. Thus they have electrophilic characters and generally react with electron-rich carbon–carbon multiple bonds efficiently.

Additions of hydrogen–heteroatom bonds to carbon–carbon multiple bonds are among the most simple methods to install heteroatoms into organic compounds. Among them, additions of hydrophosphines and thiols to carbon–carbon multiple bonds had been already reported in the middle of 1960s.[30] Now the reactions are regarded as quite efficient methods to introduce phosphorus and sulfur atoms to organic molecules (Scheme 3.4).[31]



Scheme 3.4. Examples of radical additions of hydrophosphines and thiols.

The reactions proceed as follows. First, radicals from radical initiators abstract hydrogen atoms of hydrophosphines or thiols to generate phosphinyl or thiyl radicals. The heteroatom-centered radicals then add to the carbon–carbon multiple bonds. Lastly, the resulting alkyl or alkenyl radicals abstract hydrogen atoms from hydrophosphines or thiols to afford the products. At the same time, phosphinyl or thiyl radicals are regenerated to complete the radical chains (Scheme 3.5).

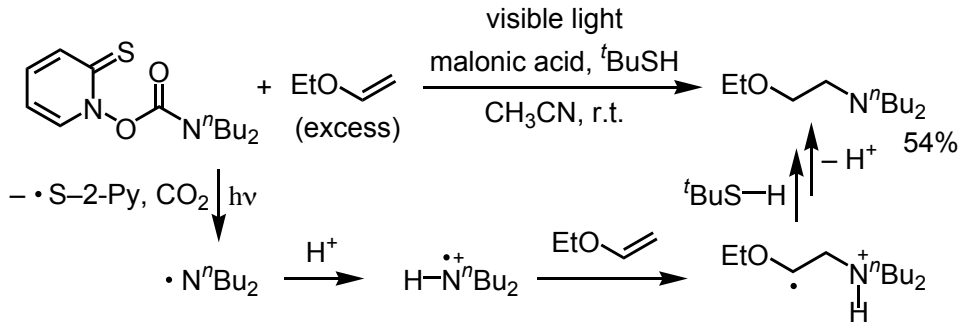


Scheme 3.5. Processes of radical hydrophosphination and hydrothiolation.

On the contrary, abstraction of hydrogen atoms on amines and alcohols by carbon-centered radical is generally difficult. The reverse reaction, hydrogen abstraction by aminyl or oxyl

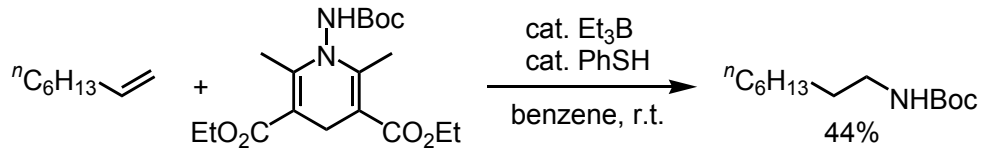
radicals, is known to be fast. The Hofmann–Löffler–Freytag reaction is a good example.[28] Indeed, no hydrooxygenation and hydroamination of alkenes or alkynes via radical processes were reported until some years ago except one example.

The only known radical hydroamination, disclosed by Newcomb, was performed under acidic conditions with an electron-rich vinyl ether in the presence of a thiol as a hydrogen donor (Scheme 3.6).[32] The presence of the acid is indispensable. Neutral aminyl radicals are too reactive toward hydrogen-abstraction and less electrophilic than cationic aminium radicals, and thus they cannot react cleanly even with electron-rich vinyl ethers.



Scheme 3.6. Radical hydroamination under acidic conditions.

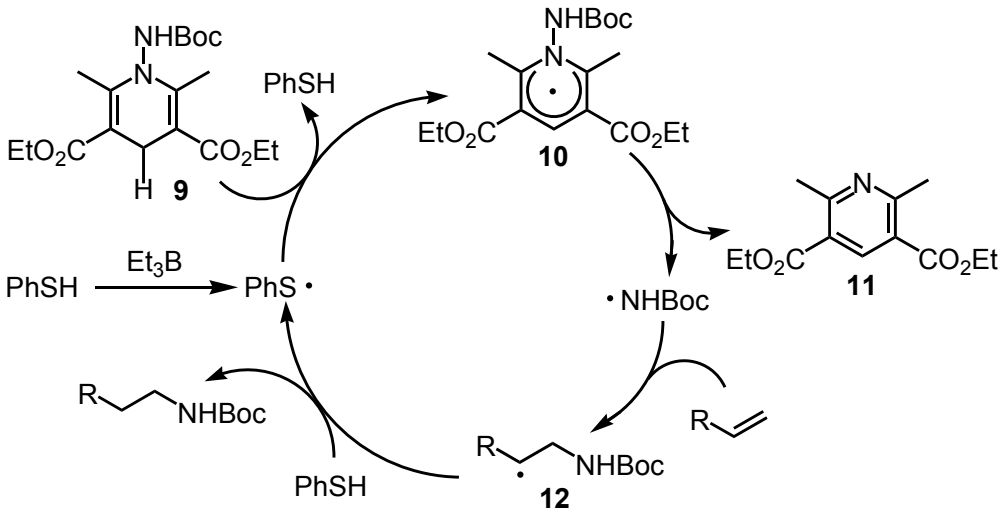
Recently, Studer achieved hydroamination of various alkenes under neutral conditions with an *N*-amidated dihydropyridine derivative (Scheme 3.7).[33] Even inactivated alkenes such as 1-octene and cyclohexene undergo the radical hydroamination under mild conditions.



Scheme 3.7. Radical hydroamination with an *N*-aminated dihydropyridine.

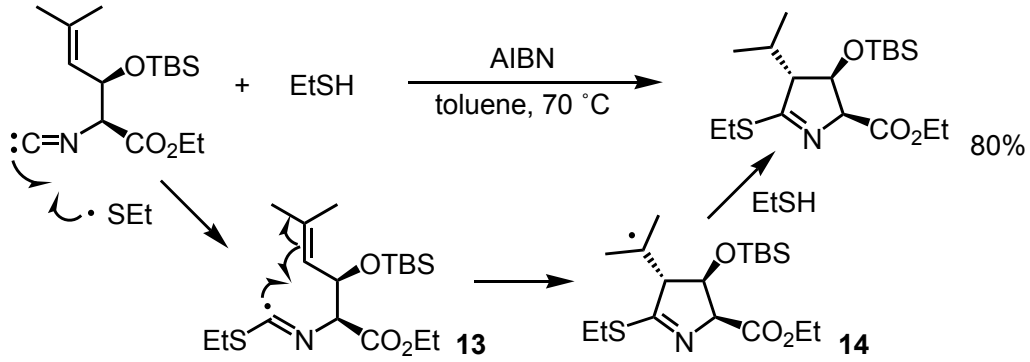
The success of very difficult radical hydroamination depends on smooth hydrogen-transfer

and efficient generation of the nitrogen-centered radical. The main driving force is the release of a stable pyridine ring. Initially, the thiyl radical from benzenethiol and triethylborane abstracts hydrogen of the dihydropyridine **9** to generate a delocalized radical **10**. The radical **10** liberates a pyridine derivative **11** to simultaneously form an amidyl radical, which adds to alkenes to furnish the corresponding alkyl radicals **12**. Finally, hydrogen-transfer from benzenethiol to the radicals affords the hydroamination products and regenerates the thiyl radical (Scheme 3.8).



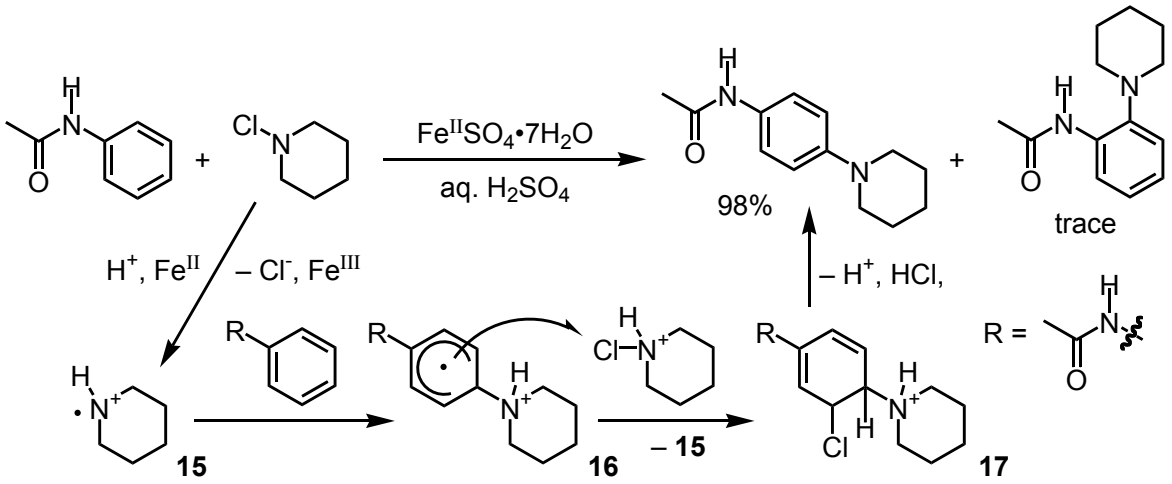
Scheme 3.8. Mechanism of Studer's radical hydroamination.

Isonitriles are good radical acceptors. Accordingly, they can react with heteroatom-centered radicals. For example, Bachi described the reaction of isonitriles with thiols (Scheme 3.9).[34] Ethylsulfanyl radical generated from ethanethiol and AIBN reacts with the carbon atom of the isonitrile moiety. The resulting imidoyl radical **13** undergoes cyclization to yield **14** having a thiolated pyrroline ring. Like this reaction, by utilizing sequential radical processes, complicated heteroatom-substituted compounds can be synthesized in one portion.



Scheme 3.9. Sequential radical reactions involving isonitrile.

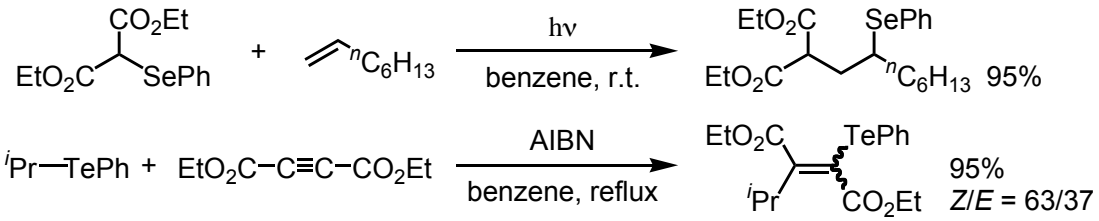
Minisci demonstrated direct amination of aromatic compounds in a strongly acidic medium (Scheme 3.10).[35] First, reductive generation of protonated aminyl radical **15** (an aminium radical) occurs by an iron(II) complex. The aminium radical **15** is still so electron-deficient that it is attacked by an electron rich aromatic compound to give **16**. Then the radical **16** abstracts chlorine atom from the protonated chloroamine to furnish **17**. The deprotonation and dehydrochlorination from **17** provide the aminated product.



Scheme 3.10. Homolytic aromatic aminations with *N*-chloroamines.

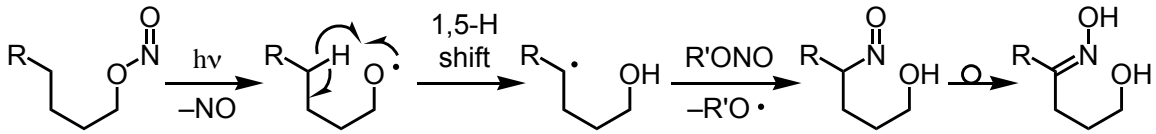
3.2. Reaction of Carbon-centered Radicals with Heteroatoms

Similar to halogenated compounds, organoselenium and organotellurium compounds undergo group-transfer reactions with alkenes and alkynes (Scheme 3.11).[36] On the other hand, heteroatoms such as oxygen, nitrogen, and sulfur are less reactive toward alkyl radicals. Thus the atom-transfer reactions are difficult. To realize reactions of such heteroatoms with carbon-centered radicals, various devices are needed.



Scheme 3.11. Group-transfer reactions of organic selenium and tellurium compounds.

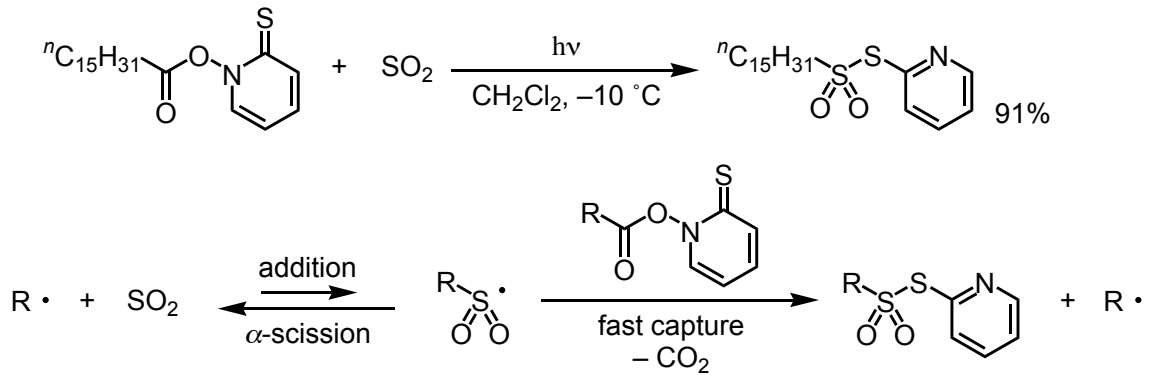
In 1960, Barton found that nitrite esters act as a radical acceptor to form a carbon–nitrogen bond.[37] Photolysis of nitrite esters gives alkoxyl radicals with releasing nitrogen oxide. Intramolecular hydrogen shift followed by NO-transfer results in the formation of oximes (Scheme 3.12).



Scheme 3.12. Intermolecular radical reactions for carbon–nitrogen bond formation.

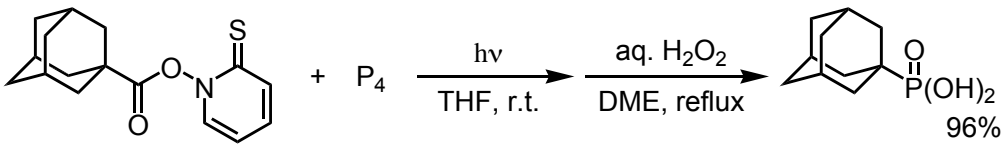
Barton esters are useful to form carbon–heteroatom bonds. For example, Barton showed sulfonylation of alkyl radicals by trapping sulfur dioxide (Scheme 3.13).[38] Sulfur dioxide acts as an alkyl radical acceptor. However, an inevitable reversible α-scission is generally very fast and it makes the formation of carbon–sulfur bonds difficult. Barton overcame the problem by using

Barton esters. The capture of sulfonyl radicals by Barton esters is fast enough to afford the products. The resulting thiolated sulfones are applicable to further transformation into unsymmetrical sulfones and sulfonamides.



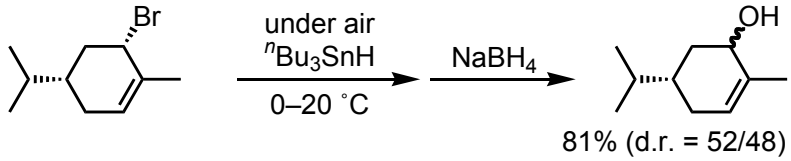
Scheme 3.13. Radical sulfonylation of Barton esters.

Barton esters were also used to generate carbon–phosphorus bonds. Irradiation of Barton esters in the presence of elemental white phosphorus (P_4) followed by oxidation afforded phosphinic acids (Scheme 3.14).[39] Elemental phosphorus acted as a radical acceptor to form carbon–phosphorus bonds.



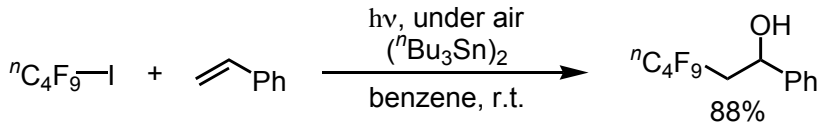
Scheme 3.14. Synthesis of phosphinic acids via a radical process.

In 1991, Nakamura discovered first radical-based procedure to convert organic halides to alcohols.[40] Molecular oxygen was used to achieve the reaction. Treatment of alkyl halides with tributylstannane under air at low temperature followed by reduction afforded the corresponding alcohols (Scheme 3.15). Namely, intermediary alkyl radicals are trapped by molecular oxygen with high efficiency.



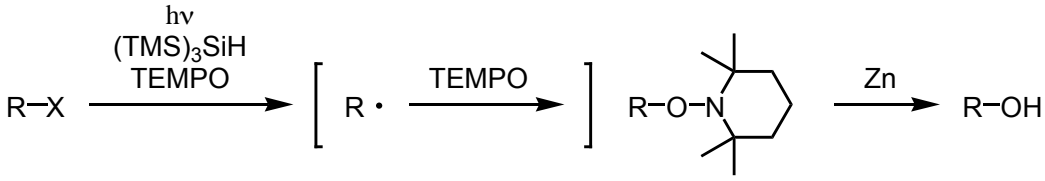
Scheme 3.15. Radical hydroxylation of organic halides with molecular oxygen.

Oxygenative addition of organic radicals to alkenes is possible. Yoshida described reactions of perfluoroalkyl iodides with styrene derivatives under air in the presence of hexabutyldistannane to afford the oxygenative adducts (Scheme 3.16).[41] Hexabutyldistannane also acts as a reducing agent for the intermediary peroxides.



Scheme 3.16. Oxygenative additions of perfluoroalkyl iodides to alkenes.

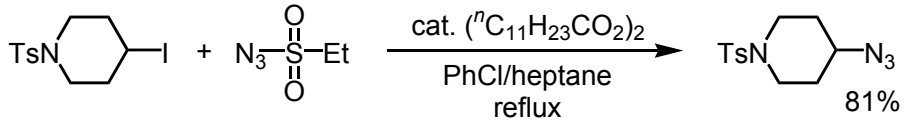
Intermediary radicals can be trapped also by TEMPO to form carbon–oxygen bonds. The resulting hydroxylamines are easily converted to alcohols by the action of reducing agents (Scheme 3.17).[42]



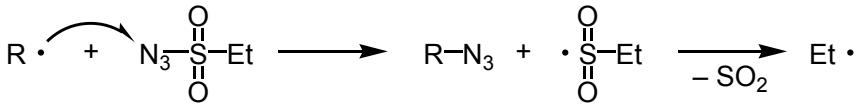
Scheme 3.17. Radical hydroxylation of organic halides with TEMPO.

Efficient and practical transformation of carbon–halogen bonds to carbon–nitrogen bonds in a radical manner was described in 2000.[43] Renaud reported azidation of organic iodides with sulfonyl azides in the presence of a radical initiator (Scheme 3.18). Sulfonyl azides can act as radical acceptors. His success was derived from the use of the ethyl-substituted sulfonyl azide.

As shown in Scheme 3.19, the eliminated ethylsulfonyl radical decomposes into sulfur dioxide and an ethyl radical. The ethyl radical can abstract an iodine atom from organic iodide, and thus the azidation proceeds in a radical chain process.

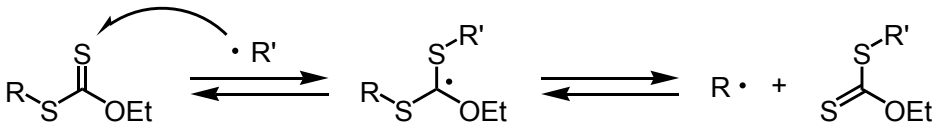


Scheme 3.18. Radical azidation of organic iodides.



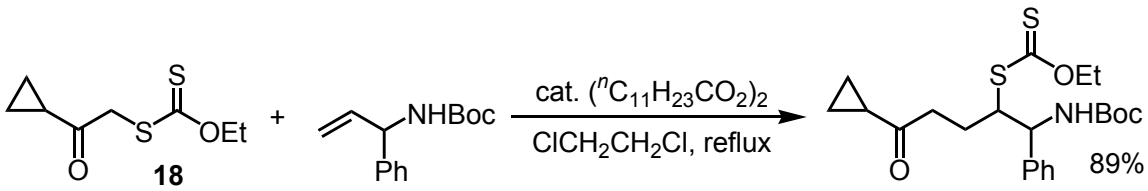
Scheme 3.19. Azide-transfer reactions.

Zard has been utilized the unique properties of dithiocarbonates for organic synthesis.[44] *S*-Alkyl dithiocarbonates are good radical acceptor to form carbon–sulfur bonds. When a dithiocarbonate is attacked by an alkyl radical, dithiocarbonate-transfer occurs and a new alkyl radical is generated (Scheme 3.20).



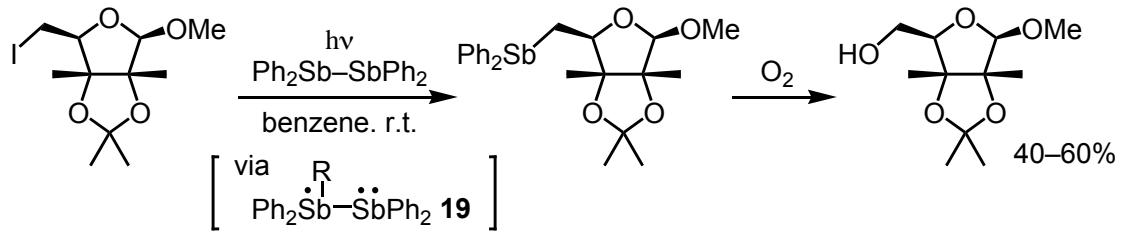
Scheme 3.20. Dithiocarbonate-transfer reactions.

For example, treatment of dithiocarbonate **18** with an electron-rich alkene in the presence of a radical initiator results in a dithiocarbonate-transfer reaction (Scheme 3.21).[45] The advantage of this reaction is that the products are also dithiocarbonates. Accordingly, further transformations are possible.



Scheme 3.21. An example of radical reactions of dithiocarbonates with alkenes.

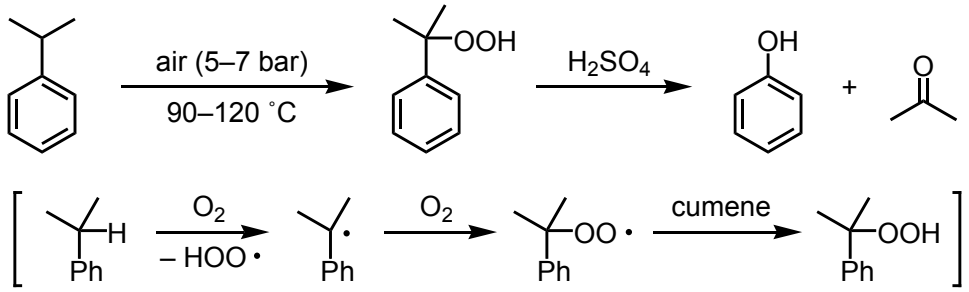
Antimony atoms are also introduced to organic molecules. Barrett described an S_H2 reaction of alkyl radicals on antimony atoms of tetraphenyldistibine under irradiation (Scheme 3.22).[46] The S_H2 reaction would proceed via intermediate **19**. The resulting antimony compounds are readily oxidized under air to the corresponding alcohols in moderate yields.



Scheme 3.22. Radical stibination of alkyl iodides with tetraphenyldistibine.

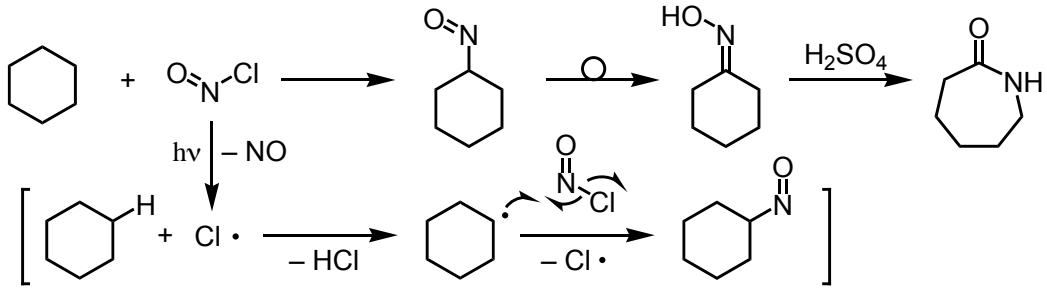
Transformation of carbon–hydrogen bonds to carbon–heteroatom bonds has been reported. Especially in industry, it is important to make carbon–heteroatom bonds from carbon–hydrogen bonds to reduce wastes in view of green chemistry. For activation of carbon–hydrogen bonds, radical reactions are often employed.

For example, phenol is now manufactured in a radical manner. Autoxidation of the α-position of cumene (isopropylbenzene) to the hydroperoxide followed by treatment with an acid gives phenol and acetone (Scheme 3.23).[47] Some of other industrially important compounds such as propylene oxide and adipic acid are synthesized through radical carbon–oxygen bond formations by autoxidation.



Scheme 3.23. Industrial synthesis of phenol (a cumene process).

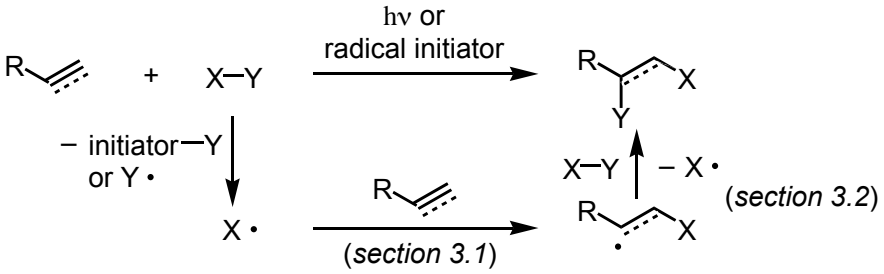
ε-Caprolactam, which is a raw material of 6-nylon, is synthesized from cyclohexane and nitrosyl chloride through a radical process in industry.[48] Chloranyl radical derived from nitrosyl chloride abstracts one hydrogen atom of cyclohexane. The resulting cyclohexyl radical attacks the nitrogen atom of nitrosyl chloride to furnish nitrosocyclohexane, which is soon tautomerized to the corresponding cyclohexanone oxime. Finally, treatment of the oximes with an acid affords the desired lactams (Scheme 3.24).



Scheme 3.24. Industrial synthesis of ε-caprolactam (a Toray process).

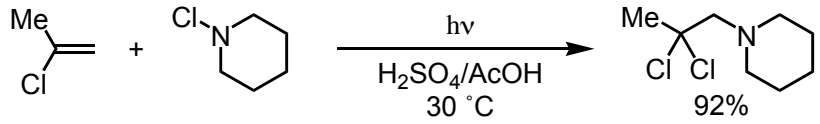
3.3. Radical Addition of Two Heteroatoms to Carbon–Carbon Multiple Bonds

Radical addition of heteroatom–heteroatom bonds to carbon–carbon multiple bonds is the most powerful method to install two heteroatoms to organic molecule simultaneously. One heteroatom is introduced by the process mentioned in section 3.1. The other carbon–heteroatom bond is formed through the manner refered in section 3.2 or an atom-transfer (a group-transfer) reaction (Scheme 3.25).



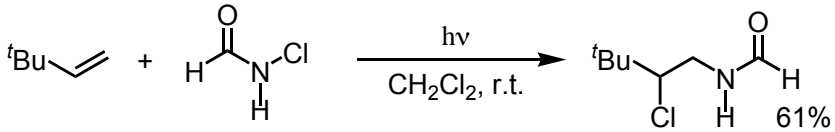
Scheme 3.25. Radical additions of heteroatom–heteroatom bonds to alkenes and alkynes

In 1967, Neale described addition reactions of chloroamines to alkenes under strongly acidic conditions (Scheme 3.26).[49] Normal aminyl radicals are so reactive that they abstract various positions of hydrogens very fast and thus cannot react with alkenes. On the contrary, aminium radicals are less reactive toward abstracting hydrogen atoms to have enough time to react with alkenes.



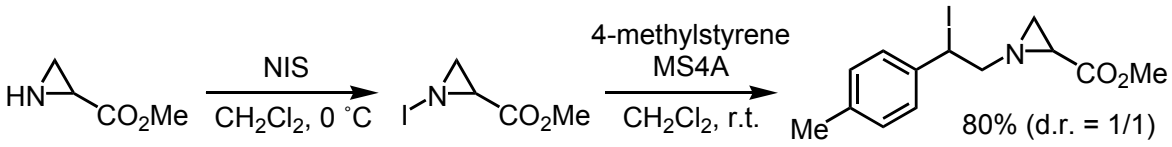
Scheme 3.26. Radical chloroamination of alkenes under acidic conditions.

Aside from aminium radicals, some amidyl radicals were found to add to alkenes. Goosen reported that *N*-chloroformamide reacted with relatively electron-rich alkenes under irradiation, although the reaction of *N*-alkylated analogues resulted in poor yields (Scheme 3.27).[50] In addition, *N*-alkyl-*N*-*p*-toluenesulfonylamidyl radicals were also shown to react with electron-rich alkenes by other researchers.[51]



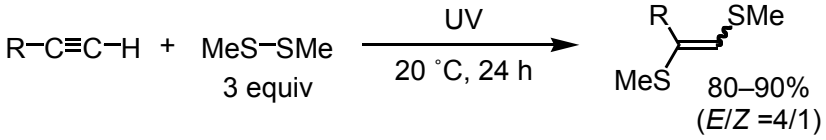
Scheme 3.27. Radical chloroamidation of alkenes.

Recently, Yudin discovered bromo- and iodoamination of styrene derivatives using *N*-haloaziridine (Scheme 3.28).[52] The nitrogen–halogen bonds of the haloaziridines, generated from aziridines and *N*-halosuccinimide prior to the reaction, are homolytically cleaved to yield aziridin-*N*-yl radicals. The nitrogen-centered radicals can react with styrenes to afford the halogenated alkyl aziridines.



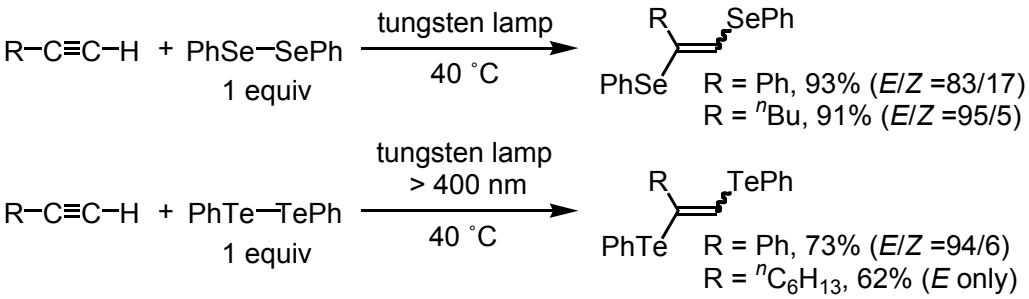
Scheme 3.28. Radical haloaziridination of styrenes.

In 1967, the same year of Neale's report of chloroamination, Heiba carried out the addition of dimethyl disulfide to terminal acetylenes under irradiation of UV light.[53] The initiation step is homolytic cleavage caused by photolysis. In most cases, the reaction proceeded in good yields and *trans* adducts were major products (Scheme 3.29).



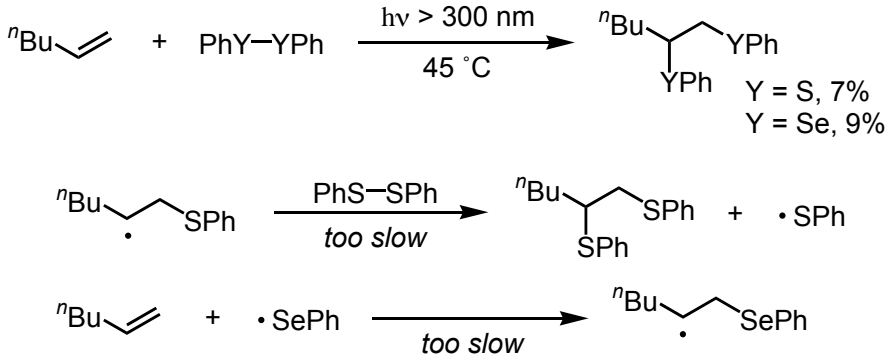
Scheme 3.29. Radical disulfidation of alkynes.

Ogawa performed diselenidation and ditelluridation of alkynes under irradiation.[54] The conditions without solvents were needed to achieve efficient addition of diselenides and ditellurides (Scheme 3.30). Because the light with wavelength of 300–400 nm promotes decomposition of the products in ditelluridation, addition of ditellurides were performed under irradiation of the light with > 400 nm.

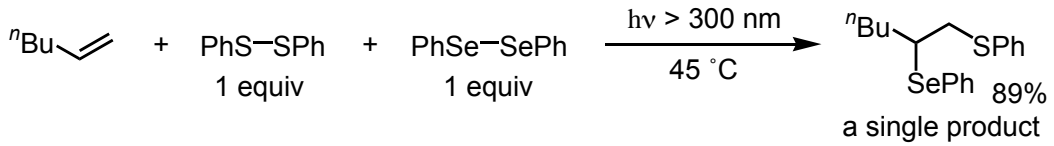


Scheme 3.30. Radical diselenidation and ditelluridation of alkynes.

However, disulfidation and diselenidation of alkenes under irradiation were reported to result in miserable yields (Scheme 3.31).[55] The thiyl radical from diphenyl disulfide can add to terminal alkenes rapidly. However, the resulted carbon-centered radical cannot react with the disulfide efficiently. In the reaction with diselenides, the addition rate of selenyl radical to alkenes is too slow though the reaction of alkyl radicals with diselenides can sufficiently occur. Application of the combined system of disulfides and diselenides to the dichalcogenation facilitated the desired dichalcogenation to afford a single product with sulfur atom on the terminal carbon and selenium atom on the internal carbon (Scheme 3.32).[55–57] The reactivities of both attacking heteroatom-centered radicals and attacked heteroatoms play crucial roles in simultaneous incorporation of two heteroatoms to carbon–carbon multiple bonds.



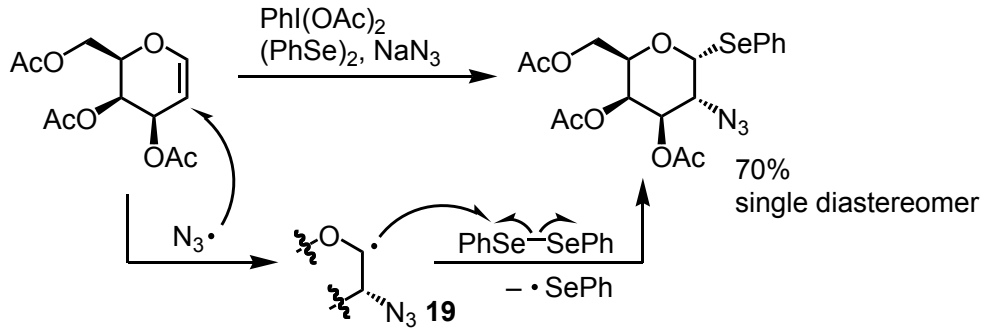
Scheme 3.31. Failure of radical disulfidation and diselenidation of alkenes.



Scheme 3.32. Radical thioselenidation of alkenes.

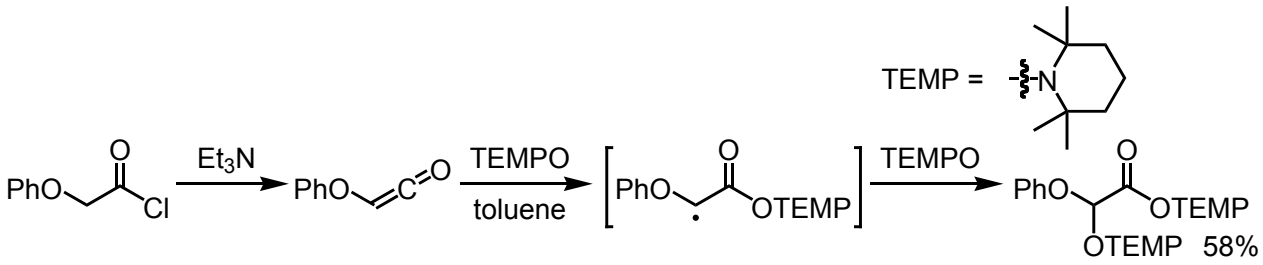
Some peculiar reactions to introduce two heteroatoms to alkenes have been reported. Santoyo-González reported a stereoselective azidoselenidation of glycals with iodobenzene diacetate, sodium azide, and diphenyl diselenide (Scheme 3.33).[58] The azidyl radical, oxidatively generated from the hypervalent iodine reagent and sodium azide, adds to the glycal

and then the resulting radical **19** is trapped by the diselenide. The stereoselectivity is explained by steric hindrance. The radical azidoselenidation proceeds with the regioselectivity opposite to the ionic azidoselenidation of the same glycal.



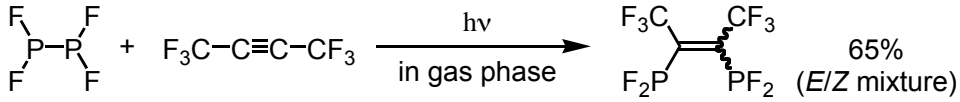
Scheme 3.33. Radical azidoselenidation of glycals.

Tidwell disclosed dioxygenation of ketenes.[59] Reaction of ketenes generated from acid chlorides and triethylamine with TEMPO gave dioxygenated products (Scheme 3.34). Initially, TEMPO adds to carbon–carbon double bonds of ketenes. The resulting carbon-centered radicals are then trapped by TEMPO to complete dioxygenation.



Scheme 3.34. Radical dioxygenation of ketenes with TEMPO.

Morse reported that radical diphosphination of alkynes with tetrafluorodiphosphine proceeded in a gas phase to yield diphosphinated compounds, though only tetrafluorodiphosphine was employed as diphosphines and the scope of alkynes was also limited (Scheme 3.35).[60]



Scheme 3.35. Diphosphination of fluorinated alkynes with tetrafluorodiphosphine.

As illustrated above, various heteroatom can be introduced to organic molecules by appropriate selections of reagents and conditions.

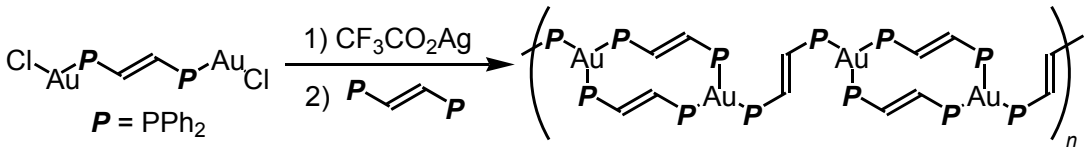
4. Overview of This Thesis

Organophosphorus[61a,61b] and organosulfur[61c,61d] compounds are utilized for general purposes in organic chemistry. However, there are few radical methods to form carbon–phosphorus bonds and most of them are hydrophosphination of alkenes and alkynes. As for carbon–sulfur bond formations through radical intermediates, though many reactions have been reported, it is still valuable to explore new reactions. The author has been much interested in the formation of carbon–phosphorus and carbon–sulfur bonds via radical processes and established some intermolecular reactions to introduce phosphorus and sulfur atoms to organic molecules.

In chapters 1–3, syntheses of organic phosphorus compounds via radical processes are described including both reactions of phosphorus-centered radicals with carbon–carbon multiple bonds and carbon-centered radical with phosphorus atoms. Especially in chapter 3, simultaneous introduction of both phosphorus and sulfur atoms to organic molecules is shown. In chapters 4 and 5, formation of carbon–sulfur bonds via radical processes are demonstrated in different ways. One proceeds via activation of carbon–hydrogen bonds and the other via addition of thiyl radicals. Overview of this thesis is outlined below.

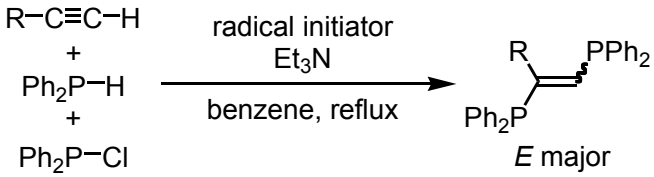
4.1. Synthesis of (*E*)-1,2-Diphosphinoethene Derivatives from Alkynes by Radical Addition of Tetraorganodiphosphine Generated In Situ (Chapter 1)

(*E*)-1,2-bis(diphenylphosphino)ethene has recently received much attention in the field of self-assembly (Scheme 4.1).[62] In addition, antitumor activity of diphosphinoethene derivatives was reported.[63] However, a limited number of methods for the synthesis of such a unique diphosphinoethene skeleton are known and these syntheses are always performed under severe conditions.[64] Thus, a general method to prepare (*E*)-1,2-bis(diphenylphosphino)ethene derivatives with functional groups are desired to induce further assembly and bioactivity.



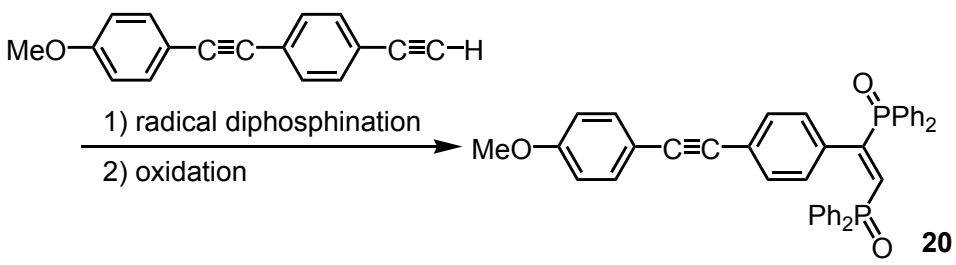
Scheme 4.1. A polymeric complex linked with *trans*-1,2-bis(diphenylphosphino)ethene

In Chapter 1, the author describes a facile synthesis of 1,2-diphosphinoethene derivatives bearing various functional groups, starting from terminal alkynes and tetraorganodiphosphines generated in situ under radical conditions (Scheme 4.2). The *E*/*Z* ratios are generally 90/10 to 95/5. The reaction conditions are so mild that many functional groups that are not tolerated in the conventional highly basic phosphination conditions to install diphenylphosphino groups can survive.



Scheme 4.2. Radical diphosphination of terminal alkynes.

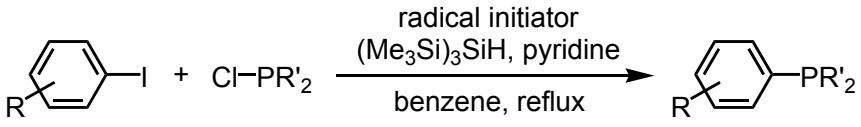
Phosphine oxide moieties are strongly electron-withdrawing groups. Thus the moieties can give organic molecules unique electronic properties. For example, the radical diphosphination followed by oxidation affords a new type of a fluorescent molecule **20** that has two phosphine oxide moieties (Scheme 4.3).



Scheme 4.3. Synthesis of a new type of a fluorescent molecule.

4.2. Radical Phosphination of Organic Halides and Alkyl Imidazole-1-carbothioates (Chapter 2)

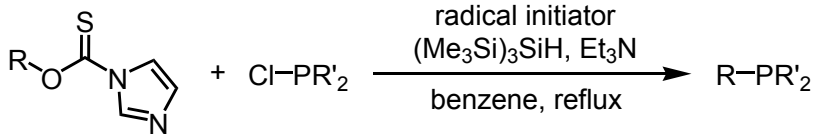
Regioselective phosphination of organic compounds is a quite important subject in organic and heteroatom chemistry. Replacement of carbon–halogen bonds to carbon–phosphorus bonds is a straightforward method to achieve the purpose. Although such reactions were performed in ionic manners or with transition metal catalysts,[65] there are no reports of reactions through a radical process. In Chapter 2, the author discloses the radical phosphination of aryl iodides with tetraorganodiphosphines generated in situ to furnish aryl-substituted phosphines (Scheme 4.4).



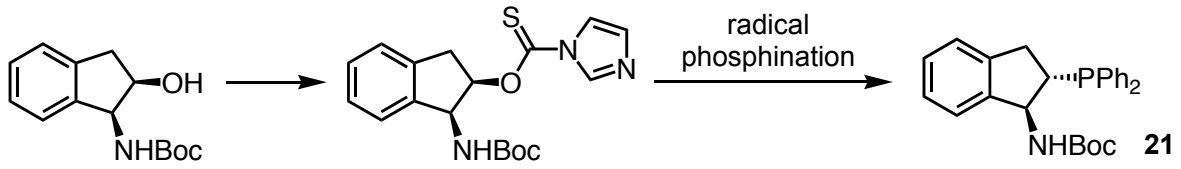
Scheme 4.4. Radical phosphination of aryl halides.

The reactions of alkyl bromides and iodides under the same conditions result in lower yields. Fortunately, alkyl imidazole-1-carbothioates[66] undergo radical phosphination to afford alkyl-

substituted phosphines (Scheme 4.5). As an application of the phosphination reaction, an optically active amino phosphine precursor **21** can be synthesized from the corresponding chiral amino alcohol (Scheme 4.6).



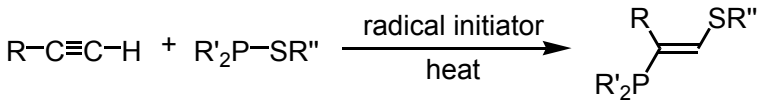
Scheme 4.5. Radical synthesis of alkyl-substituted phosphines.



Scheme 4.6. Preparation of an optically active amino phosphine precursor.

4.3. Regio- and Stereoselective Synthesis of 1-Aryl-1-thio-2-thiophosphinylethene Derivatives via a Radical Process (Chapter 3)

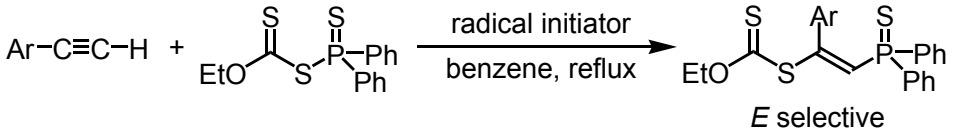
Oshima recently reported a radical thiophosphination of alkynes with thiophosphines (Scheme 4.7).[67] In the thiophosphination, sulfur atom is introduced to the terminal carbon and phosphorus atom is to the internal carbon.



Scheme 4.7. Previous radical thiophosphination of alkynes with thiophosphines.

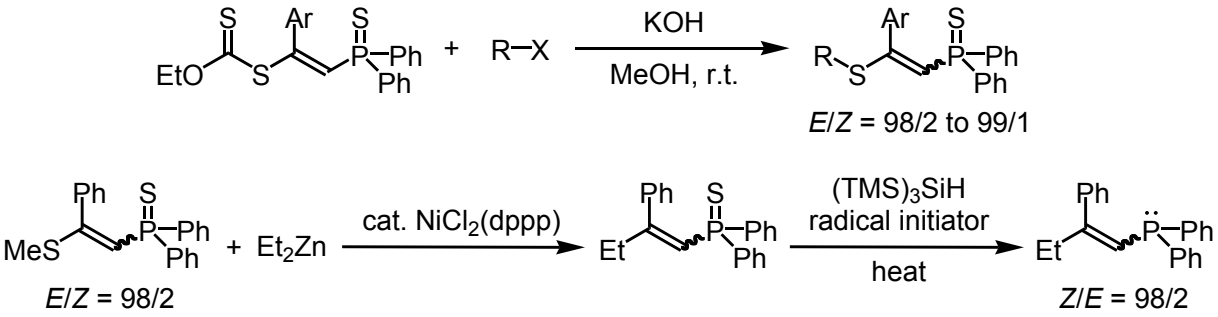
The author thought that thiophosphination with the reverse regioselectivity to the previous reaction is scientifically and structurally interesting. In Chapter 3, he shows the radical addition of a thiophosphinylated dithiocarbonate to alkynes (Scheme 4.8). The products have

phosphorus atoms on the terminal carbons and sulfur atoms on the internal carbons.



Scheme 4.8. Synthesis of 1-aryl-1-thio-2-thiophosphinylethenes via a radical process.

Transformation of the products is also performed. The thiophosphinylated vinyl dithiocarbonates are converted to the corresponding sulfides with retention of configuration. There is no stereoselective synthesis of this type of compounds. Further transformation of the sulfide can furnish a vinylphosphine derivative (Scheme 4.9).



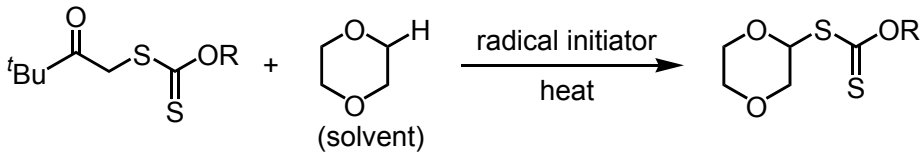
Scheme 4.9. Transformation of the resulting thiophosphinylated dithiocarbonates.

4.4. *O*-Alkyl *S*-3,3-Dimethyl-2-oxobutyl Dithiocarbonates as Versatile Sulfur-Transfer Agents in Radical C(sp^3)–H Functionalization (Chapter 4)

Regioselective functionalizations of unreactive carbon–hydrogen bonds have attracted much attention. Among them, functionalizations of carbon(sp^3)–hydrogen bonds are more challenging than those of carbon(sp^2)–hydrogen and carbon(sp)–hydrogen bonds because of the lack of a neighboring π system. To accomplish the challenging carbon(sp^3)–hydrogen functionalization, radical systems are much suitable, taking advantage of homolytic hydrogen abstraction at

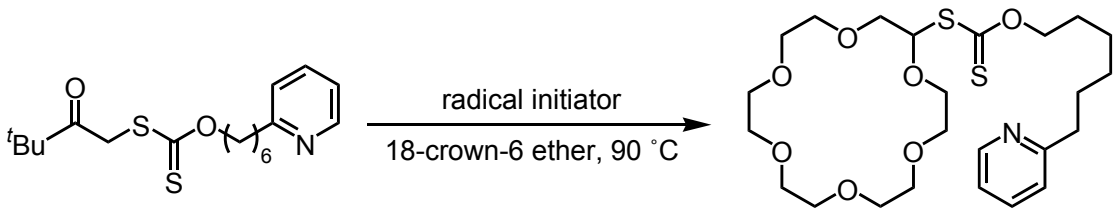
carbon(sp^3) atom.[68]

In Chapter 4, the author demonstrates radical carbon–hydrogen functionalization of ethereal solvents and cycloalkanes to form carbon–sulfur bonds with new reagents including dithiocarbonate moieties (Scheme 4.10). Resulting dithiocarbonates can be useful for the synthesis of monothioacetals, thiols, and sulfides.



Scheme 4.10. Radical C–S bond formations from C–H bonds of solvents.

Crown ethers having coordinating moieties at the side chain are called "lariat ethers",[69] which own stronger ability to capture cations than the parent crown ethers. However, the syntheses of "lariat ethers" are limited because direct functionalization of crown ethers is difficult. The radical method can functionalize carbon–hydrogen bonds of crown ethers to give "lariat ethers" directly (Scheme 4.11).

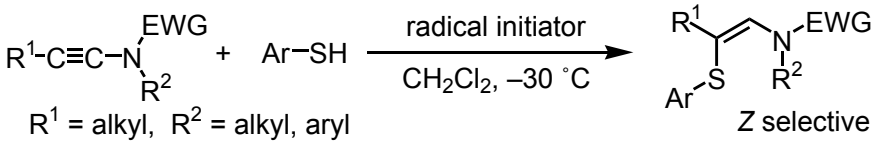


Scheme 4.11. Direct synthesis of a "lariat ether".

4.5. Regio- and Stereoselective Radical Additions of Thiols to Ynamides (Chapter 5)

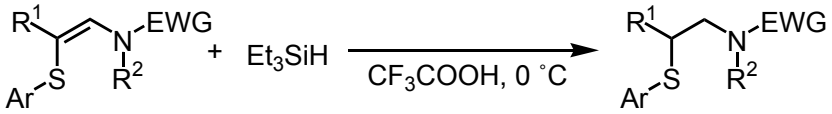
Addition of thiols to unsaturated bonds is one of the most common methods to introduce sulfur atoms to organic molecules. There are many reports of radical addition of thiols to alkenes and alkynes. Although radical additions of thiols to terminal alkynes are well-documented, additions to internal alkynes, especially to heteroatom-substituted ones are limited.

The author has focused *N*-alkynylamides (ynamides)[70] as heteroatom-substituted internal alkynes. Molecules that have both nitrogen and sulfur atoms are structurally and biologically interesting. In Chapter 5, he reports regio- and stereoselective hydrothiolation of ynamides by radical addition of arenethiols, which provides (*Z*)-1-amino-2-thio-1-alkene derivatives exclusively (Scheme 4.12).



Scheme 4.12. Radical hydrothiolation of *N*-alkynylamides (ynamides).

On the other hand, internal enamides (*N*-alkenylamides) do not undergo the radical addition of thiols to furnish 1-amino-2-thio-1-alkane derivatives. However, the alkene moieties of the resulting thiolated enamides can be reduced to form the compounds by the action of triethylsilane in a protic solvent (Scheme 4.13).



Scheme 4.13. Hydrogenation of the alkene moieties of the resulting enamides.

References and Notes

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Instrumental and Materials

^{1}H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in $CDCl_3$ with tetramethylsilane as an internal standard. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian MERCURY 300 spectrometer and were obtained in $CDCl_3$ with 85% H_3PO_4 solution as an external standard. Chemical shifts (δ) are in parts per million relative to tetramethylsilane at 0.0 ppm for ^{1}H, relative to $CDCl_3$ at 77.0 ppm for ^{13}C, and relative to H_3PO_4 at 0.0 ppm for ^{31}P. DEPT, H–H COSY, H–C COSY and NOE analyses allowed the assignments of the signals of each compounds. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL MStation 700 spectrometer. Melting points were determined on Yanaco micro melting point apparatus. Specific rotations were determined on a HORIBA SEPA-200 polarimeter. X-ray data were taken on a Bruker Smart APEX X-Ray diffractometer equipped with a large area CCD detector.[1] The structures were solved with the program system SHELXS-97 and refined with SHELXL-97 package from Bruker.[2] Microwave-assisted reactions were performed with a focused microwave unit (Biotage Initiator™). TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography. GPC was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 10 mL/min, RI detector). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF and Et_2O were purchased from Kanto Chemical Co., stored under argon, and used as they are. Benzene was dried over slices of sodium. Neat triethylborane was available from Aldrich and was diluted with degassed dry hexane to prepare a 1.0 M solution,

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1 G. M. Sheldrick, SHELXS 97 program for the solution of crystal structures. University of Göttingen, Germany, 1997.

2 G. M. Sheldrick, SHELXL 97 program for the refinement of crystal structures. University of Göttingen, Germany, 1997.

which was stored under argon. Radical initiators AIBN and V-40 were obtained from Wako Pure Chemical and DLP was from Nacalai Tesque, respectively. Chlorodicyclohexylphosphine and chlorodi(*tert*-butyl)phosphine were gifts from Hokko Chemical Industry Co., Ltd. Chlorodiphenylphosphine and tris(trimethylsilyl)silane were purchased from TCI and stored under argon.

Chapter 1

Synthesis of (*E*)-1,2-Diphosphinoethene Derivatives from Alkynes by Radical Addition of Tetraorganodiphosphine Generated In Situ

A tetraorganodiphosphine, generated in situ from a diorganophosphine and a chlorodiorganophosphine in the presence of triethylamine, adds to terminal alkynes via a radical process to afford (*E*)-diphosphinoethene derivatives in excellent yields.

Introduction

Organophosphorus compounds are an extremely important family of heteroatom-containing molecules that serve as synthetic reagents, ligands for transition metals, biologically active substances, advanced materials, and building blocks of supramolecular architectures, and thus play vital roles in organic chemistry.

Among them, (*E*)-1,2-bis(diphenylphosphino)ethene has recently attracted increasing attention in the field of self-assembly.[1] Construction of hierarchical structures for use as new functional materials[2] calls for derivatives of (*E*)-1,2-bis(diphenylphosphino)ethene that have functional groups to induce further assembly. However, there are a limited number of methods for the synthesis of such peculiar diphosphinoethene skeletons and these syntheses are always carried out under harsh and/or strongly basic conditions.[3] Highly efficient and mild reactions affording (*E*)-1,2-bis(diphenylphosphino)ethene derivatives are therefore required.

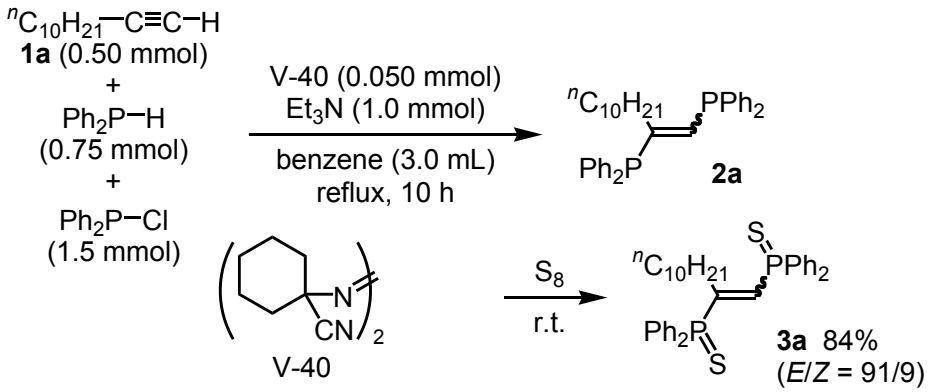
In Chapter 1, the author reports a general, facile, and reliable synthesis of (*E*)-diphosphinoethene derivatives starting from alkynes and tetraorganodiphosphines.

Results and Discussion

Radical addition of a tetraorganodiphosphine across a C–C triple bond seems to be a straightforward strategy for the synthesis of 1,2-diphosphinoethenes derivatives.[4,5] However, tetraorganodiphosphines are so sensitive to oxygen that their preparation, purification, and handling are quite difficult and must be carried out under a strictly inert atmosphere.[6] The inherent instability of diphosphines in the presence of oxygen poses a serious problem in their synthetic use. The present diphosphination reaction employs a tetraorganodiphosphine that is cleanly generated in situ prior to the reaction. The high efficiency of this method will allow the 1,2-diphosphinoethenes synthesized to be applicable in organic materials science.

A mixture of 1-dodecyne (**1a**), diphenylphosphine, chlorodiphenylphosphine, triethylamine,

and 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40)[7] was heated in boiling benzene for 10 h (Scheme 1). After elemental sulfur was added, the product was obtained as a 91:9 mixture of *E* and *Z* isomers of phosphine sulfide **3a** in 84% yield. These two stereoisomers were separable from each other by thorough chromatographic purification on silica gel.



Scheme 1. Radical diphosphination of 1-dodecyne.

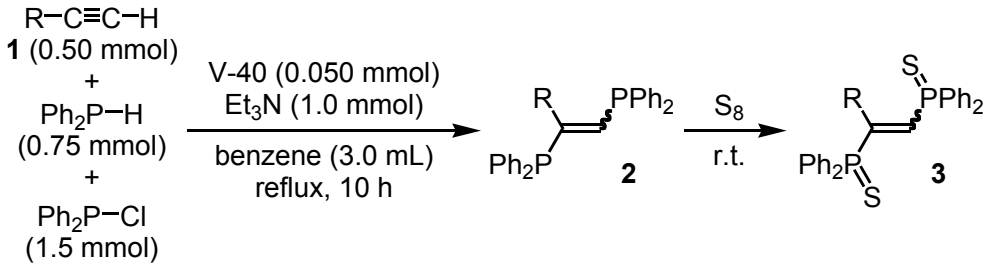
The presence of an excess of chlorodiphenylphosphine is essential for the success of the reaction. The use of a smaller amount (1.0 mmol) of chlorodiphenylphosphine gave (1-dodecenyl)diphenylphosphine sulfide (**4**, 9%, *E*/*Z* = 18/82) along with **3a** (78%, *E*/*Z* = 90/10). Complete conversion of diphenylphosphine to tetraphenyldiphosphine is important to avoid contamination by monoadduct **4**.

Tetraphenyldiphosphine is commercially available. However, the reaction of **1a** (0.50 mmol) with the purchased tetraphenyldiphosphine[8] (1.5 mmol) in the presence of V-40 (0.10 mmol) yielded both **3a** (60%, *E*/*Z* = 88/12) and **4** (27%, *E*/*Z* = 37/63). It is worth noting that addition of chlorodiphenylphosphine (1.5 mmol) to the reaction mixture suppressed the generation of **4**, and generated **3a** (87%, *E*/*Z* = 89/11) selectively.

A variety of terminal alkynes undergo this radical diphosphination reaction (Table 1). Aryl-substituted acetylenes react with tetraphenyldiphosphine prepared in situ to yield 1-aryl-1,2-bis(diphenylthiophosphinyl)ethenes in excellent yields with high stereoselectivity (entries 1–5).

The *E* configuration of the major isomer of **3c** was determined by X-ray crystallographic analysis (see the Characterization Data). Purification of **2b** under argon allowed the author to isolate this compound in 78% yield (*E*/*Z* = 92/8). Ester (entries 3 and 7), iodo (entry 4), keto (entry 5), and thioester (entry 8) moieties remained unchanged under the reaction conditions. These groups are not tolerated in the conventional incorporation of a diphenylphosphino group which requires the use of a highly nucleophilic and basic metal diphenylphosphide.[3] Gratifyingly, an carbon(sp^3)–halogen bond was also stable during the reaction, although **1j** is prone to form the corresponding Wittig salt (entry 9).

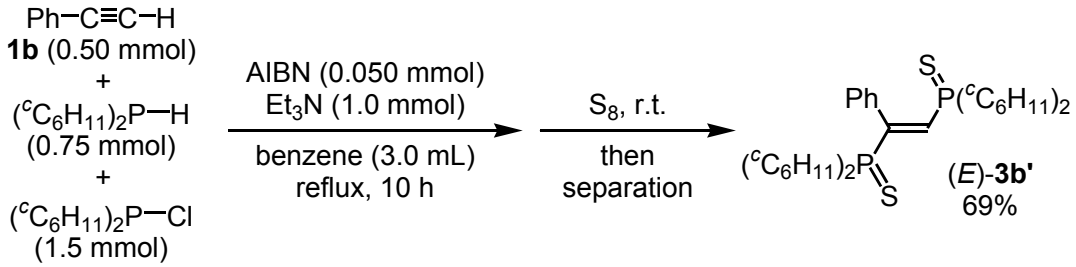
Table 1. Radical diphosphination of terminal alkynes.



entry	R	product	yield /%[a]	*E*/*Z*
1	Ph (**1b**)	**3b**	87 (96)[b]	93/7
2	*p*-MeO–C_6H_4 (**1c**)	**3c**	89	94/6
3	*p*-MeO_2C–C_6H_4 (**1d**)	**3d**	95	94/6
4	*p*-I–C_6H_4 (**1e**)	**3e**	83	94/6
5	*p*-Ac–C_6H_4 (**1f**)	**3f**	96	95/5
6	$PhCH_2O(CH_2)_3$ (**1g**)	**3g**	78	90/10
7	$EtO_2C(CH_2)_6$ (**1h**)	**3h**	86	90/10
8	$AcS(CH_2)_9$ (**1i**)	**3i**	80	90/10
9	$Cl(CH_2)_9$ (**1j**)	**3j**	86	91/9

[a] Determined by ^{31}P NMR with $(MeO)_3P{=}O$ as internal standard with a sufficient first delay period. [b] Performed on a 5.0 mmol-scale.

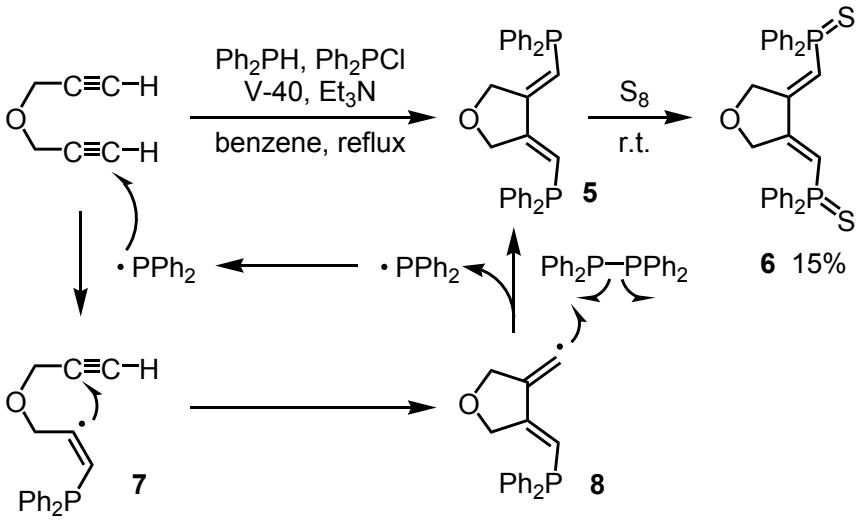
Tetracyclohexyldiphosphine, prepared in situ from dicyclohexylphosphine[7] and chlorodicyclohexylphosphine, was added to **1b** in a similar fashion to afford (*E*)-**3b'** in excellent yield after careful separation from contaminants such as (*Z*)-**3b'** (Scheme 2).



Scheme 2. Radical addition of tetracyclohexyldiphosphine to phenylacetylene.

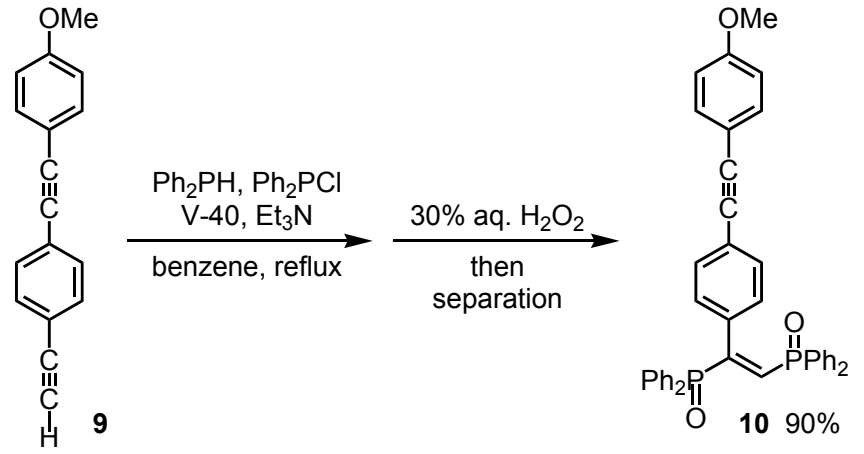
The reactions with *tert*-butylacetylene failed to yield the desired product, and internal alkynes such as diphenylacetylene and 6-dodecyne also remained intact. Under the same reaction conditions 4-pentyn-1-ol or 3-butyn-2-one gave complex mixtures containing small amounts of the desired products.

The reaction clearly proceeds via a radical pathway, as demonstrated in Scheme 3. The formation of **6** necessitates addition of a phosphorus-centered radical[9] followed by 5-*exo*-*dig* radical cyclization. Subsequent radical S_H2 substitution[10] affords the doubly phosphinated diene **6**.[11]



Scheme 3. Diphosphination of dipropargyl ether through 5-*exo* cyclization.

The high efficiency of this reaction might offer a reliable method for the synthesis of organic compounds for use in single-molecule devices, self-assembled monolayers (Table 1, entry 8), or optically intriguing organic materials. Scheme 4 illustrates the synthesis of a new fluorescent compound **10** which exhibits a couple of intense absorption bands in the UV region (λ_{max} = 302, 320 nm; $\varepsilon = 2.0 \times 10^4$ M^{-1} cm^{-1} for both) and blue fluorescence (λ_{max} = 469 nm) upon irradiation at 302 or 320 nm.



Scheme 4. Synthesis of a new fluorescent molecule through diphosphination.

Conclusion

A highly efficient and concise diphosphination reaction for terminal alkynes has been developed. The radical addition of a tetraorganodiphosphine to an alkyne affords 1,2-diphosphinoethenes in good yield with high *E* selectivity. The required tetraorganodiphosphine was readily prepared by mixing a diorganophosphine and a chlorodiorganophosphine in situ in the presence of triethylamine, which allowed the author to avoid the troublesome isolation of tetraorganodiphosphine.

The mild reaction conditions offer excellent functional-group compatibility and hence provide a powerful tool for the synthesis of important compounds by introducing two phosphorus atoms in one shot.

Experimental Section

Materials

Diphenylphosphine was purchased from TCI, distilled before use, and stored in a storage flask under argon. Dicyclohexylphosphine was obtained from Strem and stored in a glove box filled with argon. Tetraphenyldiphosphine was purchased from Aldrich or Acros and stored in a glove box filled with argon. Alkynes were commercially available or readily prepared in conventional methods.

Caution: Diphenylphosphine and dicyclohexylphosphine undergo very rapid oxidation under air. These phosphines are pyrophoric, especially when wiped with tissue under air.

General procedure for diphosphination of alkynes with tetraphenyldiphosphine (Scheme 1, Table 1).

Diphosphination of **1a** is representative. Under argon, triethylamine (0.14 mL, 1.0 mmol), chlorodiphenylphosphine (0.27 mL, 1.5 mmol), diphenylphosphine (0.13 mL, 0.75 mmol), and 1-

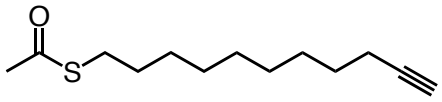
dodecyne (**1a**, 0.11 mL, 0.50 mmol) were sequentially added to a solution of V-40 (0.012 g, 0.050 mmol) in degassed benzene (3.0 mL). The resulting mixture was stirred for 10 min at ambient temperature and then for 10 h at reflux. After the mixture was cooled to room temperature, elemental sulfur (0.096 g, 3.0 mmol) was added under argon. The mixture was then stirred overnight. The solvent was removed under a reduced pressure. Water (15 mL) was added to the resulting solid. The product was extracted with EtOAc three times. The organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column purification twice (hexane/EtOAc = 2/1 for the first time, 10/1 for the second time) afforded 1,2-bis(diphenylthiophosphinyl)-1-dodecene (**3a**, 0.25 g, 0.42 mmol, 84%, *E*/*Z* = 91/9, judged by ^{31}P NMR analysis) with contamination by a trace of inseparable monoadduct **4**.

Diphosphination of phenylacetylene with tetraphenyldiphosphine to isolate 2b.

After the phosphination reaction of phenylacetylene (**1b**) as the procedure shown above, degassed water (5 mL) was added. The organic layer was collected and directly put on a silica gel column under argon. Purification under argon with hexane/EtOAc = 30/1 provided 1,2-bis(diphenylphosphino)-1-phenylethene (**2b**, 0.21 g, 0.39 mmol, 78%, *E*/*Z* = 92/8).

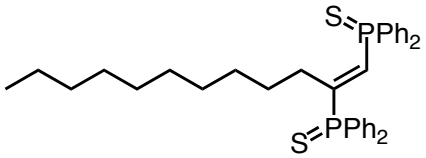
Characterization Data

***S*-10-undecynyl ethanethioate (1i)**



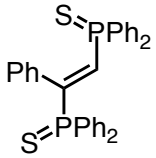
IR (neat) 3300, 2928, 2855, 2118, 1692, 1466, 1431, 1354, 1134, 1109, 955, 627 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26–1.42 (m, 10H), 1.48–1.60 (m, 4H), 1.94 (t, *J* = 2.7 Hz, 1H), 2.18 (dt, *J* = 7.1, 2.7 Hz, 2H), 2.33 (s, 3H), 2.86 (t, *J* = 7.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 18.30, 28.36, 28.61, 28.69, 28.92, 28.95, 29.04, 29.22, 29.41, 30.56, 68.04, 84.62, 195.89. Found: C, 69.02; H, 9.69%. Calcd for $C_{13}H_{22}OS$: C, 68.97; H, 9.80%.

(*E*)-1,2-bis(diphenylthiophosphinyl)-1-dodecene (3a)



IR (neat) 3055, 2924, 2853, 1437, 1310, 1101, 743, 716, 692, 631, 613, 525, 498 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76–0.83 (m, 4H), 0.83–0.91 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H), 0.91–0.98 (m, 2H), 1.05–1.12 (m, 2H), 1.12–1.23 (m, 4H), 1.23–1.30 (m, 2H), 2.65–2.76 (m, 2H), 7.24 (dd, *J* = 27.0, 20.5 Hz, 1H), 7.40–7.49 (m, 10H), 7.51–7.55 (m, 2H), 7.74–7.82 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 14.12, 22.66, 28.76, 29.23, 29.25, 29.41, 29.64, 30.77 (dd, *J* = 9.8, 7.9 Hz), 31.85, 128.70 (d, *J* = 12.4 Hz), 131.04 (d, *J* = 10.5 Hz), 131.23 (d, *J* = 82.6 Hz), 131.60 (d, *J* = 2.9 Hz), 131.91 (d, *J* = 3.4 Hz), 132.25 (d, *J* = 10.0 Hz), 133.70 (d, *J* = 84.5 Hz), 136.04 (dd, *J* = 72.0, 8.6 Hz), 156.44 (d, *J* = 59.1 Hz); ^{31}P NMR ($CDCl_3$) δ 26.14 (d, *J* = 57.0 Hz), 46.89 (d, *J* = 57.0 Hz); For (*Z*) isomer, δ 29.40 (d, *J* = 17.9 Hz), 39.68 (d, *J* = 17.9 Hz). HRMS Found: 601.2272. Calcd for $C_{36}H_{43}P_2S_2$: 601.2281 $[MH]^+$.

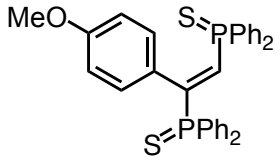
(*E*)-1,2-bis(diphenylthiophosphinyl)-1-phenylethene (3b)



IR (Nujol) 1439, 1103, 783, 743, 716, 691, 644, 633, 498 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.72–6.77 (m, 4H), 6.88–6.92 (m, 1H), 7.22–7.27 (m, 4H), 7.30–7.35 (m, 2H), 7.36–7.41 (m, 4H), 7.45–7.49 (m, 2H), 7.61–7.67 (m, 4H), 7.69–7.75 (m, 4H), 7.85 (dd, *J* = 25.0, 19.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 126.98 (d, *J* = 1.5 Hz), 127.96 (d, *J* = 1.9 Hz), 128.29 (d, *J* = 12.9 Hz), 128.40 (d, *J* = 12.5 Hz), 129.90 (d, *J* = 84.0 Hz), 130.05 (dd, *J* = 3.8, 1.4 Hz), 131.19 (d, *J* = 3.3 Hz), 131.20 (d, *J* = 11.0 Hz), 131.87 (d, *J* = 3.4 Hz), 132.18 (d, *J* = 85.4 Hz), 132.31 (dd, *J* = 8.5, 8.1 Hz), 132.60 (d, *J* = 10.1 Hz), 139.01 (dd, *J* = 72.6, 10.1 Hz), 152.69 (d, *J* = 59.3 Hz); ^{31}P NMR ($CDCl_3$) δ 28.30 (d, *J* = 50.5 Hz), 45.92 (d, *J* = 50.5 Hz); For (*Z*) isomer, δ 30.09 (d,

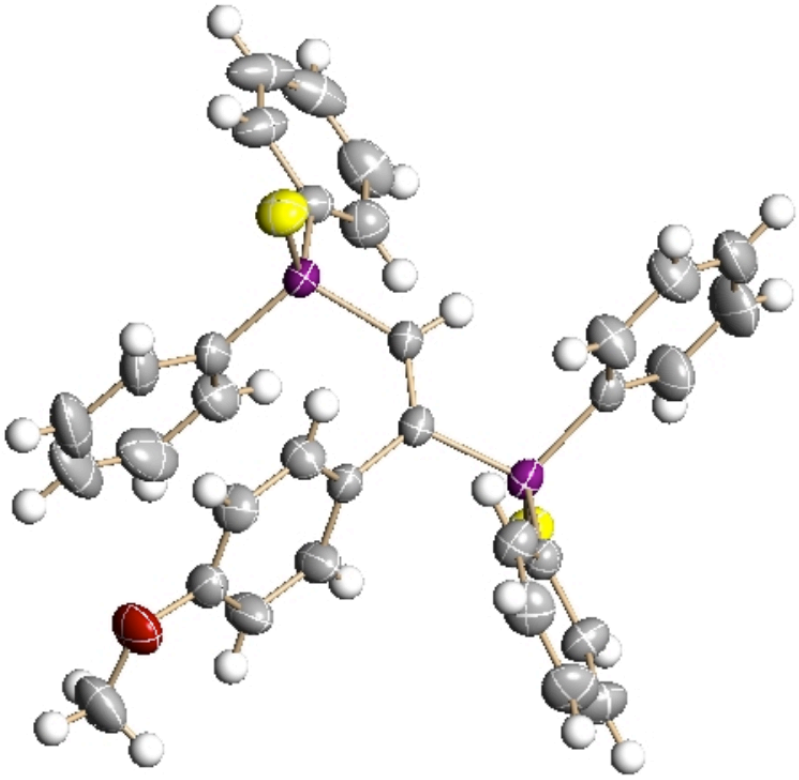
J = 13.0 Hz), 35.76 (d, *J* = 13.0 Hz). Found: C, 71.55; H, 4.81%. Calcd for $C_{32}H_{26}P_2S_2$: C, 71.62; H, 4.88%. m.p.: 163–164 ˚C.

(*E*)-1,2-bis(diphenylthiophosphinyl)-1-(4-methoxyphenyl)ethene (3c)

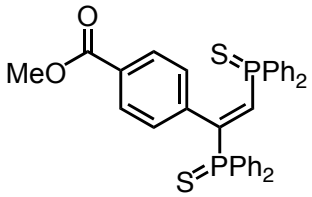


IR (Nujol) 1609, 1506, 1435, 1256, 1099, 829, 773, 741, 718, 629, 544, 515, 502, 482 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.63 (s, 3H), 6.28 (d, *J* = 8.5 Hz), 6.77 (dd, *J* = 8.5, 1.5 Hz), 7.23–7.28 (m, 4H), 7.31–7.35 (m, 2H), 7.38–7.43 (m, 4H), 7.46–7.50 (m, 2H), 7.61–7.67 (m, 4H), 7.69 (dd, *J* = 25.0, 19.5 Hz), 7.72–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.05, 112.61 (d, *J* = 1.0 Hz), 124.79 (dd, *J* = 9.1, 8.0 Hz), 128.25 (d, *J* = 12.4 Hz), 128.45 (d, *J* = 12.4 Hz), 130.20 (d, *J* = 83.5 Hz), 131.14 (d, *J* = 2.9 Hz), 131.25 (d, *J* = 11.0 Hz), 131.60 (dd, *J* = 4.3, 1.4 Hz), 131.86 (d, *J* = 3.3 Hz), 132.35 (d, *J* = 86.4 Hz), 132.66 (d, *J* = 10.0 Hz), 138.79 (dd, *J* = 73.5, 10.9 Hz), 152.48 (d, *J* = 60.6 Hz), 159.37 (d, *J* = 1.9 Hz); ^{31}P NMR ($CDCl_3$) δ 28.42 (d, *J* = 50.4 Hz), 45.55 (d, *J* = 50.4 Hz); For (*Z*) isomer, δ 29.95 (d, *J* = 13.0 Hz), 35.83 (d, *J* = 13.0 Hz). Found: C, 69.94; H, 5.09%. Calcd for $C_{33}H_{28}OP_2S_2$: C, 69.95; H, 4.98%. m.p.: 154–155 ˚C. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center (CCDC 255767, Figure S1). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: 44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk

Figure S1. Ortep diagram of **3c**



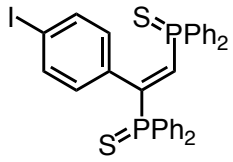
methyl 4-{(*E*)-1,2-bis(diphenylthiophosphinyl)ethenyl}benzoate (3d)



IR (Nujol) 1720, 1462, 1435, 1275, 1099, 783, 746, 716, 692, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.85 (s, 3H), 6.82 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.23–7.28 (m, 4H), 7.33–7.37 (m, 2H), 7.39–7.44 (m, 4H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.48–7.52 (m, 2H), 7.59–7.65 (m, 4H), 7.70–7.76 (m, 4H), 7.81 (dd, *J* = 25.3, 18.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 52.07, 127.99 (d, *J* = 1.4 Hz), 128.34 (d, *J* = 12.9 Hz), 128.53 (d, *J* = 12.5 Hz), 129.20 (d, *J* = 1.9 Hz), 129.37 (d, *J* = 84.4 Hz), 130.16 (dd, *J* = 3.8, 1.4 Hz), 131.17 (d, *J* = 11.0 Hz), 131.39 (d, *J* = 2.9 Hz), 131.87 (d, *J* = 85.9 Hz), 132.10 (d, *J* = 2.9 Hz), 132.53 (d, *J* = 10.5 Hz), 137.14 (dd, *J* = 8.6, 8.1 Hz), 139.54 (dd, *J* = 71.6, 9.2 Hz), 151.81 (d, *J* = 59.3 Hz), 166.45; ^{31}P NMR ($CDCl_3$) δ 28.12 (d, *J* = 48.8 Hz), 45.91 (d, *J* = 48.8

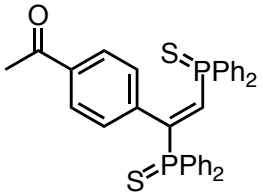
Hz); For (*Z*) isomer, δ 30.33 (d, *J* = 13.0 Hz), 35.39 (d, *J* = 13.0 Hz). Found: C, 68.45; H, 4.88%. Calcd for $C_{34}H_{28}O_2P_2S_2$: C, 68.67; H, 4.75%. m.p.: 140 ˚C.

(*E*)-1,2-bis(diphenylthiophosphinyl)-1-(4-iodophenyl)ethene (3e)



IR (Nujol) 1437, 1099, 1007, 820, 746, 716, 691, 633, 613, 571, 527, 503 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.53 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.26–7.31 (m, 4H), 7.36–7.40 (m, 2H), 7.41–7.46 (m, 4H), 7.48–7.52 (m, 2H), 7.57–7.63 (m, 4H), 7.67 (dd, *J* = 24.5, 19.0 Hz, 1H), 7.72–7.78 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 94.82 (d, *J* = 3.4 Hz), 128.37 (d, *J* = 12.4 Hz), 128.58 (d, *J* = 12.4 Hz), 129.47 (d, *J* = 84.0 Hz), 131.21 (d, *J* = 11.0 Hz), 131.32 (d, *J* = 2.9 Hz), 131.73, 131.77 (d, *J* = 85.4 Hz), 131.83 (dd, *J* = 3.9, 1.4 Hz), 132.12 (d, *J* = 2.9 Hz), 132.58 (d, *J* = 10.0 Hz), 135.99 (d, *J* = 1.4 Hz), 139.53 (dd, *J* = 72.3, 9.3 Hz), 151.21 (dd, *J* = 60.1, 0.9 Hz); ^{31}P NMR ($CDCl_3$) δ 28.38 (d, *J* = 48.8 Hz), 45.49 (d, *J* = 48.8 Hz); For (*Z*) isomer, δ 30.21 (d, *J* = 13.0 Hz), 35.54 (d, *J* = 13.0 Hz). Found: C, 58.09; H, 4.10%. Calcd for $C_{32}H_{25}P_2S_2I$: C, 58.01; H, 3.80%. m.p.: 76–77 ˚C.

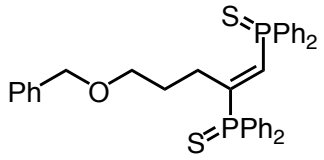
1-[4-{(*E*)-1,2-bis(diphenylthiophosphinyl)ethenyl}phenyl]ethanone (3f)



IR (Nujol) 1682, 1605, 1435, 1263, 1099, 831, 746, 716, 691, 633, 561, 494 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 3H), 6.89 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.21–7.26 (m, 4H), 7.33 (d, *J* = 8.5 Hz, 2H), 7.32–7.36 (m, 2H), 7.39–7.44 (m, 4H), 7.48–7.52 (m, 2H), 7.58–7.64 (m, 4H), 7.73 (dd, *J* = 25.0, 19.0 Hz, 1H), 7.73–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.48, 126.65 (d, *J* = 1.4 Hz), 128.31 (d, *J* = 12.5 Hz), 128.55 (d, *J* = 12.4 Hz), 129.35 (d, *J* = 84.5 Hz), 130.43 (dd, *J* = 3.8, 1.4

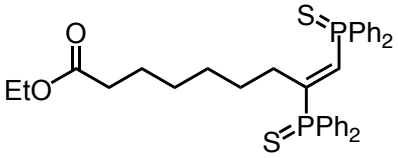
Hz), 131.15 (d, *J* = 10.9 Hz), 131.33 (d, *J* = 2.9 Hz), 131.83 (d, *J* = 85.4 Hz), 132.13 (d, *J* = 3.3 Hz), 132.52 (d, *J* = 10.5 Hz), 135.93 (d, *J* = 2.4 Hz), 137.26 (dd, *J* = 8.1, 8.1 Hz), 139.41 (dd, *J* = 71.6, 8.6 Hz), 151.62 (dd, *J* = 59.7, 1.4 Hz), 197.42; ^{31}P NMR ($CDCl_3$) δ 28.20 (d, *J* = 48.8 Hz), 45.91 (d, *J* = 48.8 Hz); For (*Z*) isomer, δ 30.31 (d, *J* = 13.0 Hz), 35.51 (d, *J* = 13.0 Hz). Found: C, 70.44; H, 4.95%. Calcd for $C_{34}H_{28}OP_2S_2$: C, 70.57; H, 4.88%. m.p. 149–150 ˚C.

benzyl (*E*)-4,5-bis(diphenylthiophosphinyl)-4-pentenyl ether (3g)



IR (Nujol) 3055, 2856, 1967, 1900, 1817, 1585, 1479, 1454, 1437, 1310, 1099, 1028, 999, 714, 692, 629, 613, 525, 496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30–1.38 (m, 2H), 2.76–2.86 (m, 2H), 3.05 (t, *J* = 6.5 Hz, 2H), 4.23 (s, 2H), 7.16–7.19 (m, 2H), 7.22–7.26 (m, 1H), 7.27–7.31 (m, 2H), 7.28 (dd, *J* = 26.5, 20.5 Hz, 1H), 7.38–7.42 (m, 4H), 7.42–7.48 (m, 6H), 7.50–7.54 (m, 2H), 7.74–7.80 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 27.41 (dd, *J* = 10.1, 8.1 Hz), 29.03, 69.51, 71.97, 127.28, 127.49, 128.15, 128.73 (d, *J* = 12.4 Hz), 128.74 (d, *J* = 12.4 Hz), 130.96 (d, *J* = 10.5 Hz), 131.02 (d, *J* = 82.6 Hz), 131.64 (d, *J* = 2.9 Hz), 131.97 (d, *J* = 2.3 Hz), 132.22 (d, *J* = 10.5 Hz), 133.55 (d, *J* = 84.5 Hz), 136.63 (dd, *J* = 72.1, 8.6 Hz), 138.51, 155.84 (d, *J* = 59.6 Hz); ^{31}P NMR ($CDCl_3$) δ 25.83 (d, *J* = 57.0 Hz), 46.78 (d, *J* = 57.0 Hz); For (*Z*) isomer, δ 29.11 (d, *J* = 16.3 Hz), 39.88 (d, *J* = 16.3 Hz). HRMS Found: 661.1948. Calcd for $C_{37}H_{43}OP_2S_3$: 661.1951 $[MH]^+$.

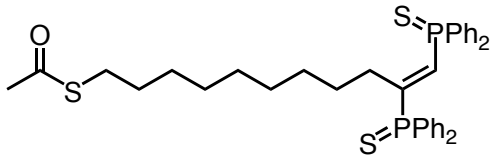
ethyl (*E*)-8,9-bis(diphenylthiophosphinyl)-8-nonenoate (3h)



IR (Nujol) 1732, 1437, 1182, 1099, 750, 714, 698, 629, 613, 525, 502 cm^{-1}; ^{1}H NMR ($CDCl_3$)

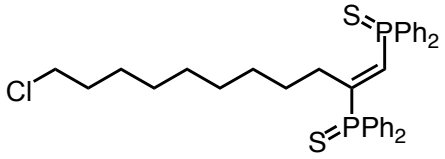
δ 0.78–0.94 (m, 6H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.32 (tt, *J* = 7.4, 7.4 Hz, 2H), 2.12 (t, *J* = 7.4 Hz, 2H), 2.66–2.76 (m, 2H), 4.10 (q, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 27.0, 20.0 Hz, 1H), 7.40–7.49 (m, 10H), 7.50–7.55 (m, 2H), 7.74–7.81 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 14.18, 24.51, 28.16, 29.13 (2C), 30.52 (dd, *J* = 9.7, 7.9 Hz), 34.08, 60.02, 128.64 (d, *J* = 12.4 Hz), 130.93 (d, *J* = 10.9 Hz), 131.06 (d, *J* = 82.5 Hz), 131.57 (d, *J* = 2.9 Hz), 131.89 (d, *J* = 2.9 Hz), 132.14 (d, *J* = 10.0 Hz), 133.56 (d, *J* = 84.4 Hz), 136.04 (dd, *J* = 72.0, 8.6 Hz), 156.17 (d, *J* = 59.8 Hz), 173.66; ^{31}P NMR ($CDCl_3$) δ 25.98 (d, *J* = 57.0 Hz), 46.88 (d, *J* = 57.0 Hz); For (*Z*) isomer, δ 29.31 (d, *J* = 16.3 Hz), 39.68 (d, *J* = 16.3 Hz). Found: C, 68.14; H, 6.26%. Calcd for $C_{35}H_{38}O_2P_2S_2$: C, 68.16; H, 6.21%. m.p.: 88–89 °C

***S*-(*E*)-10,11-bis(diphenylthiophosphinyl)-10-undecenyl ethanethioate (3i)**:



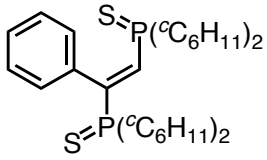
IR (neat) 3055, 2928, 2853, 1693, 1682, 1435, 1354, 1310, 1134, 1101, 999, 957, 750, 716, 629, 525, 496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76–0.85 (m, 4H), 0.86–0.92 (m, 2H), 0.92–0.99 (m, 2H), 1.07–1.14 (m, 2H), 1.21–1.28 (m, 2H), 1.50 (dt, *J* = 7.5, 7.5Hz, 2H), 2.32 (s, 3H), 2.66–2.75 (m, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 7.23 (dd, *J* = 27.0, 20.5 Hz, 1H), 7.40–7.49 (m, 10H), 7.50–7.55 (m, 2H), 7.74–7.82 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 28.56, 28.64, 28.82, 28.95, 29.07, 29.30, 29.36, 29.49, 30.60, 30.66 (dd, *J* = 9.5, 8.0 Hz), 128.65 (d, *J* = 12.5 Hz), 130.96 (d, *J* = 11.0 Hz), 131.14 (d, *J* = 82.5 Hz), 131.56 (d, *J* = 2.9 Hz), 131.88 (d, *J* = 2.8 Hz), 132.18 (d, *J* = 10.5 Hz), 133.63 (d, *J* = 84.5 Hz), 135.97 (dd, *J* = 72.6, 8.6 Hz), 156.36 (d, *J* = 59.3 Hz), 196.08; ^{31}P NMR ($CDCl_3$) δ 26.10 (d, *J* = 57.0 Hz), 46.88 (d, *J* = 57.0 Hz); For (*Z*) isomer, δ 29.33 (d, *J* = 16.3 Hz), 39.63 (d, *J* = 16.3 Hz). HRMS Found: 661.1948. Calcd for $C_{37}H_{43}OP_2S_3$: 661.1951 $[MH]^+$.

(*E*)-11-chloro-1,2-bis(diphenylthiophosphinyl)-1-undecene (3j)



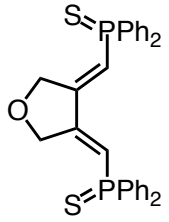
IR (Nujol) 1437, 1312, 1215, 1099, 762, 710, 629, 613, 525, 507, 494 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.78–0.86 (m, 4H), 0.86–0.94 (m, 2H), 0.94–1.02 (m, 2H), 1.09–1.16 (m, 2H), 1.28–1.35 (m, 2H), 1.67–1.74 (m, 2H), 2.66–2.76 (m, 2H), 3.51 (t, *J* = 7.0 Hz, 2H), 7.21 (dd, *J* = 27.0, 20.5 Hz, 1H), 7.40–7.50 (m, 10H), 7.50–7.55 (m, 2H), 7.74–7.82 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 26.72, 28.54, 28.60, 28.93, 29.33, 29.49, 30.66 (dd, *J* = 9.5, 8.1 Hz), 32.52, 45.18, 128.67 (d, *J* = 12.4 Hz), 130.98 (d, *J* = 10.5 Hz), 131.12 (d, *J* = 83.0 Hz), 131.58 (d, *J* = 2.8 Hz), 131.90 (d, *J* = 2.9 Hz), 132.21 (d, *J* = 10.5 Hz), 133.37 (d, *J* = 84.5 Hz), 135.95 (dd, *J* = 72.3, 8.8 Hz), 156.42 (d, *J* = 59.1 Hz); ^{31}P NMR ($CDCl_3$) δ 26.11 (d, *J* = 57.0 Hz), 46.92 (d, *J* = 57.0 Hz); For (*Z*) isomer, δ 29.36 (d, *J* = 16.3 Hz), 39.66 (d, *J* = 16.3 Hz). HRMS Found: 621.1733. Calcd for $C_{35}H_{40}ClP_2S_2$: 621.1735 $[MH]^+$. m.p.: 87–89 °C.

(*E*)-1,2-bis(dicyclohexylthiophosphinyl)-1-phenylethene (3b')



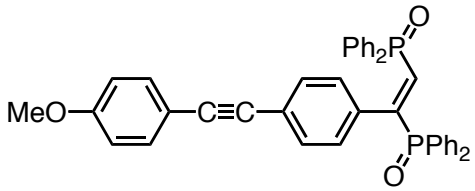
IR (Nujol) 1450, 1178, 1003, 918, 887, 853, 820, 783, 764, 706, 625, 602, 527 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12–1.38 (m, 16H), 1.41–1.53 (m, 4H), 1.63–1.94 (m, 22H), 2.00–2.09 (m, 2H), 7.12–7.17 (m, 2H), 7.35–7.41 (m, 3H), 7.49 (dd, *J* = 26.0, 20.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.63 (d, *J* = 0.9 Hz), 25.71 (d, *J* = 2.0 Hz), 25.79 (d, *J* = 1.5 Hz), 26.29–26.60 (multiplet), 36.45 (d, *J* = 47.8 Hz), 38.82 (d, *J* = 51.6 Hz), 127.91 (d, *J* = 1.4 Hz), 128.57 (d, *J* = 2.0 Hz), 129.06 (dd, *J* = 3.4, 1.5 Hz), 134.04 (dd, *J* = 8.4, 6.4 Hz), 138.45 (dd, *J* = 54.6, 8.8 Hz), 151.94 (dd, *J* = 42.9, 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 49.43 (d, *J* = 40.7 Hz), 65.95 (d, *J* = 40.7 Hz). Found: C, 68.51; H, 9.00%. Calcd for $C_{32}H_{50}P_2S_2$: C, 68.53; H, 8.99%. m.p.: 201–202 °C.

3,4-bis{(*Z*)-diphenylthiophosphinylmethylene}-1-oxacyclopentane (6)



IR (Nujol) 1435, 1099, 1078, 934, 791, 773, 743, 712, 692, 629, 611, 511 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.38 (t, *J* = 2.3 Hz, 4H), 6.70 (dd, *J* = 17.0, 0.5 Hz, 2H), 7.46–7.55 (m, 12H), 7.83–7.89 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 69.48 (d, *J* = 6.3 Hz), 114.49 (dd, *J* = 85.3, 2.6 Hz), 128.91 (d, *J* = 12.9 Hz), 131.50 (d, *J* = 11.5 Hz), 131.9–132.1 (multiplet), 132.58 (d, *J* = 85.9 Hz), 154.94 (d, *J* = 15.8, 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 29.51. Found: C, 68.37; H, 4.93%. Calcd for $C_{30}H_{26}OP_2S_2$: C, 68.16; H, 4.96%. m.p.: 187–188 °C.

4-[4-{(*E*)-1,2-bis(diphenylphosphinyl)ethenyl}phenylethynyl]anisole (10)



IR (Nujol) 1599, 1514, 1437, 1286, 1250, 1180, 1117, 1028, 833, 748, 721, 694, 563, 529, 515 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.81 (s, 3H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 6.5 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.29–7.35 (m, 4H), 7.38–7.45 (m, 8H), 7.50–7.66 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 55.25, 87.69, 90.35, 113.95, 115.02, 123.68 (d, *J* = 1.4 Hz), 128.39 (d, *J* = 12.4 Hz), 128.50 (d, *J* = 12.4 Hz), 129.29 (d, *J* = 102.1 Hz), 129.83 (d, *J* = 4.4 Hz), 130.35, 130.75 (d, *J* = 9.5 Hz), 131.61 (d, *J* = 1.9 Hz), 132.19 (d, *J* = 9.5 Hz), 132.40 (d, *J* = 2.4 Hz), 133.02, 133.10 (dd, *J* = 7.9, 7.9 Hz), 139.21 (dd, *J* = 87.3, 6.1 Hz), 156.06 (d, *J* = 78.8 Hz), 159.66; ^{31}P NMR ($CDCl_3$) δ 16.23 (d, *J* = 46 Hz), 25.45 (d, *J* = 46 Hz). HRMS Found: 635.1912. Calcd for $C_{41}H_{33}O_3P_2$: 635.1905 $[MH]^+$. m.p.: 195–196 °C. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Center (CCDC 255768, Figure S2). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12

Union Road, Cambridge CB2 1EZ, UK. Fax: 44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk

Figure S2. Ortep diagram of **10**.

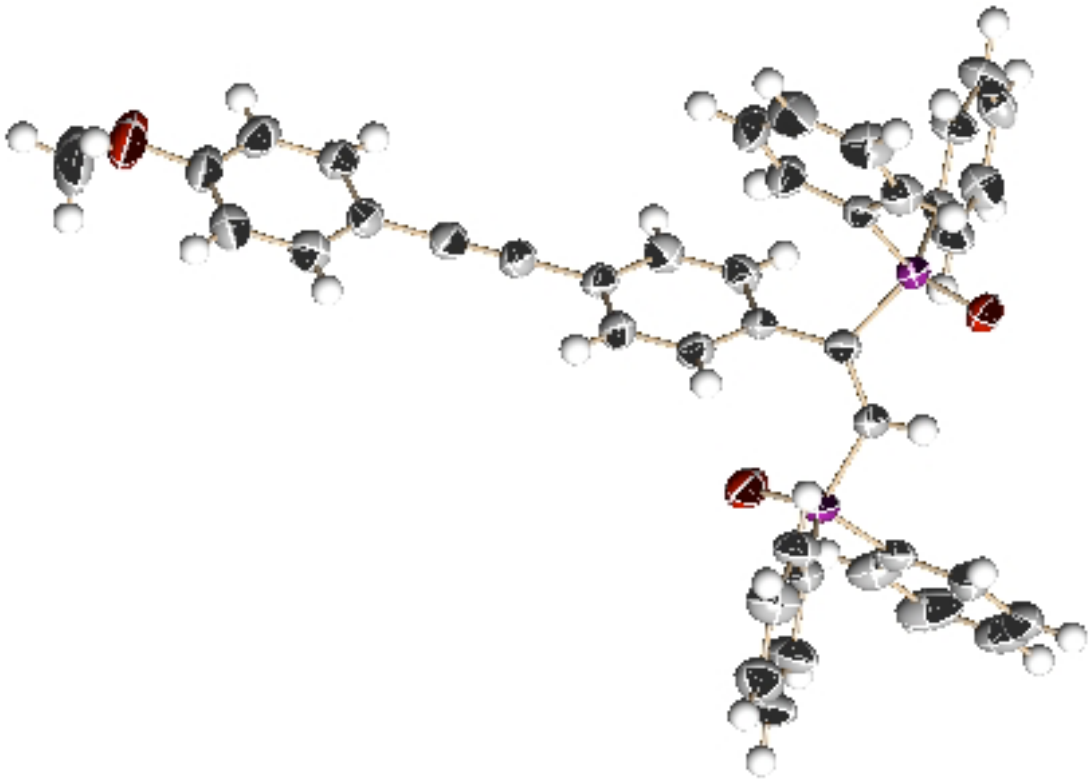


Figure S3. UV–Visible absorption spectrum of **10**

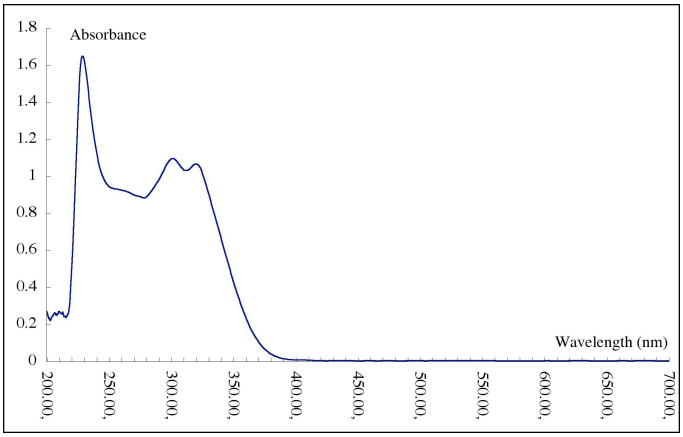
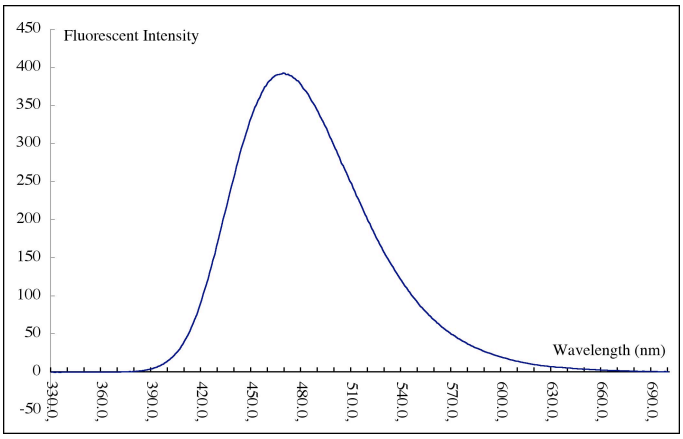


Figure S4. Fluorescent spectrum of **10**



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1. (a) M.-C. Brandys, R. J. Puddephatt, *J. Am. Chem. Soc.* **2001**, *123*, 4839–4840; (b) M.-C. Brandys, R. J. Puddephatt, *J. Am. Chem. Soc.* **2002**, *124*, 3946–3950; (c) W. J. Hunks, J. Lapierre, H. A. Jenkins, R. J. Puddephatt, *J. Chem. Soc. Dalton Trans.* **2002**, 2885–2889; (d) E. Lozano, M. Nieuwenhuyzen, S. L. James, *Chem. Eur. J.* **2001**, *7*, 2644–2651; (e) A. S. DelNegro, S. M. Woessner, B. P. Sullivan, D. M. Dattelbaum, J. R. Schoonover, *Inorg. Chem.* **2001**, *40*, 5056–5057.
2. J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, *J. Mater. Chem.* **2003**, *13*, 2661–2670.
3. (a) S. Hietkamp, O. Stelzer, *Inorg. Chem.* **1984**, *23*, 258–260; (b) A. M. Aguiar, D. Daigle, *J. Am. Chem. Soc.* **1964**, *86*, 2299–2300; (c) R. B. King, P. N. Kapoor, *J. Am. Chem. Soc.* **1971**, *93*, 4158–4166; (d) W. Hewertson, H. R.Watson, *J. Chem. Soc.* **1962**, 1490–1494; (e) K. K. Chow, W. Levason, C. A. McAuliffe, *J. Chem. Soc. Dalton Trans.* **1976**, 1429–1432.
4. A couple of reports underscore the difficulty of achieving this strategy—the attempted reactions suffered from very low yields and lack of generality. See: (a) J. G. Morse, J. J. Mielcarek, *J. Fluorine Chem.* **1988**, *40*, 41–49; (b) V. A. Tzschach, S. Baensch, *J. Prakt. Chem.* **1971**, *313*, 254–258.
5. Dichalcogenides underwent similar radical-addition reactions to alkynes. For disulfides,

see: (a) E. I. Heiba, R. M. Dessau, *J. Org. Chem.* **1967**, *32*, 3837–3840. For diselenides, see: (b) T. G. Back, M. V. Krishna, *J. Org. Chem.* **1988**, *53*, 2533–2536; (c) A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, N. Sonoda, *J. Org. Chem.* **1991**, *56*, 5721–5723; (d) A. Ogawa, N. Takami, M. Sekiguchi, H. Yokoyama, H. Kuniyasu, I. Ryu, N. Sonoda, *Chem. Lett.* **1991**, 2241–2242. For ditellurides, see: (e) A. Ogawa, K. Yokoyama, H. Yokoyama, R. Obayashi, N. Kambe, N. Sonoda, *J. Chem. Soc. Chem. Commun.* **1991**, 1748–1750; (f) A. Ogawa, K. Yokoyama, R. Obayashi, L.-B. Han, N. Kambe, N. Sonoda, *Tetrahedron* **1993**, *49*, 1177–1188. For a review of radical addition of dichalcogenides across C–C triple bonds, see: (g) A. Ogawa, *J. Synth. Org. Chem. Jpn.* **1995**, 53, 869–880.

6. (a) W. Kuchen, H. Buchwald, *Chem. Ber.* **1958**, *91*, 2871–2877; (b) E. J. Spanier, F. E. Caropreso, *J. Am. Chem. Soc.* **1970**, *92*, 3348–3351; (c) A. H. Cowley, *Chem. Rev.* **1965**, 65, 617–634.
7. Use of AIBN decreased the yield slightly by 10%.
8. Obtained from Aldrich. Diphosphine from Acros Co. led to a similar result. Note that ^{1}H NMR analysis of the purchased $Ph_2P–PPh_2$ revealed no detectable amount of $HPPh_2$ in the commercial material.
9. (a) C. M. Jessop, A. F. Parsons, A. Routledge, D. Irvine, *Tetrahedron Lett.* **2003**, *44*, 479–483, and references cited therein; (b) H. Yorimitsu, H. Shinokubo, K. Oshima, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 225–235; (c) T. N. Mitchell, K. Heesche, *J. Organomet. Chem.* **1991**, *409*, 163–170.
10. R. Okazaki, Y. Hirabayashi, K. Tamura, N. Inamoto, *J. Chem. Soc. Perkin Trans. 1* **1976**, 1034–1036. See also reference 9c.
11. Along with **6**, the crude mixture contained several by-products, which could not be exactly identified. 2,3-Bis(diphenylthiophosphinyl)-2-propenyl propargyl ether seemed to be the main by-product.

Chapter 2

Radical Phosphination of Organic Halides and Alkyl Imidazole-1-carbothioates

Aryl iodides and alkyl imidazole-1-carbothioates are converted to the corresponding aryl- or alkyldiorganophosphines via radical processes with a tetraorganodiphosphine generated in situ from a chlorodiorganophosphine. The reaction conditions are mild enough to synthesize phosphines bearing various functional groups.

Introduction

As mentioned in Chapter 1, organophosphines are extremely important in organic chemistry. Accordingly, development of unprecedented phosphination reactions has invaluable impacts.

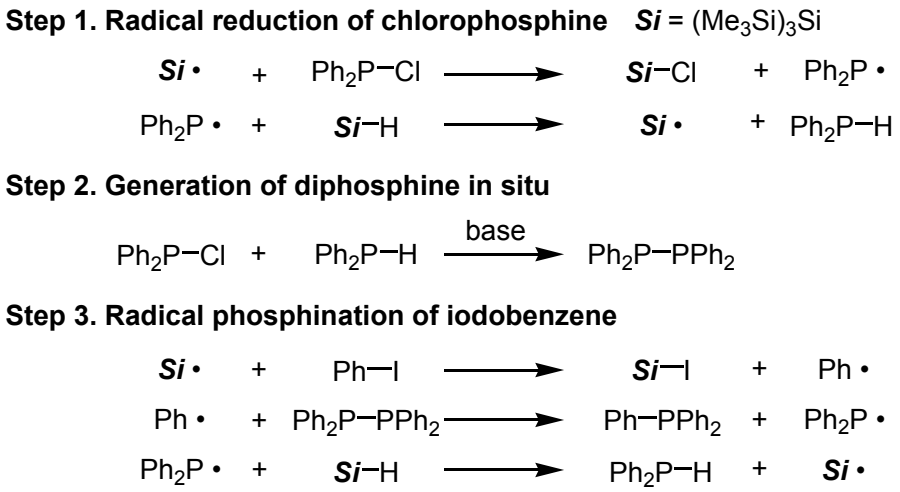
In Chapter 2, the author reports a novel phosphination reaction, taking full advantage of a chemoselective radical-based strategy.[1–4] Conventional ionic phosphination reactions often require highly basic conditions.[5] The new radical phosphination reaction can employ readily available aryl halides and alkyl imidazole-1-carbothioates as the precursors, hence offering a powerful tool for the synthesis of functionalized organophosphines.[6]

Results and Discussion

The procedure of the radical phosphination is quite simple. The transformation of iodobenzene (**1a**) to triphenylphosphine (**2a**) is representative (Table 1, entry 1). A mixture of **1a** (0.50 mmol), chlorodiphenylphosphine (2.5 mmol), tris(trimethylsilyl)silane (TTMSS, 1.5 mmol),[7] pyridine (3.0 mmol), and 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40, 0.10 mmol) was heated in boiling benzene (3.0 mL) for 20 h. Since organophosphines such as **2a** are more or less sensitive to oxygen, the phosphinated product was handled as triphenylphosphine sulfide (**3a**) to clarify the efficiency of the reaction.[8,9]

The author's working hypothesis about the reaction mechanism is outlined in Scheme 1. Initially, radical reduction of chlorodiphenylphosphine with TTMSS takes place to produce diphenylphosphine (Step 1).[10] The diphenylphosphine formed in situ reacts with remaining chlorodiphenylphosphine to afford tetraphenyldiphosphine in the presence of pyridine (Step 2). The diphosphine is responsible for the radical phosphination reaction (Step 3). Tris(trimethylsilyl)silyl radical abstracts iodine from iodobenzene to furnish phenyl radical. The S_H2 reaction of the phenyl radical with diphosphine[11] gives triphenylphosphine and diphenylphosphinyl radical.[12,13] The phosphine-centered radical abstracts the hydrogen of

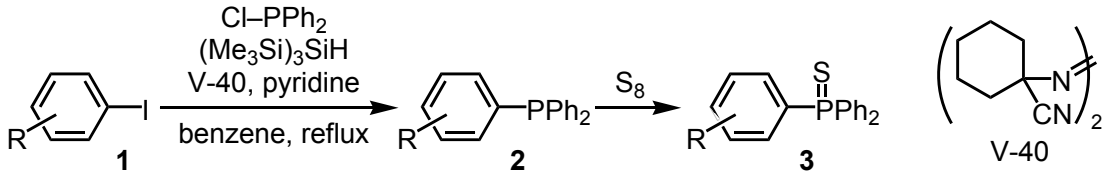
TTMSS to regenerate the corresponding silyl radical. The diphenylphosphine generated at the final step participates again in Step 2. The in situ reduction of chlorodiphenylphosphine and the in situ formation of tetraphenyldiphosphine allow the author to avoid handling air-sensitive tetraphenyldiphosphine and pyrophoric diphenylphosphine.[3]



Scheme 1. The working hypothesis of radical phosphination of iodobenzene.

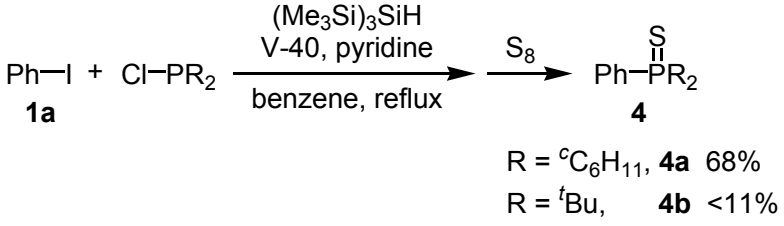
A wide range of aryl iodides **1** was subjected to the phosphination reaction (Table 1). Sterically demanding mesityl iodide (**1d**) was also phosphinated in good yield (entry 4). Functional groups such as ester (entry 10), bromo (entry 11), cyano (entry 12), and keto (entry 13) moieties were compatible under the reaction conditions. The radical conditions allowed for efficient phosphination of 4-iodophenyl triflate (**1n**) and allyl 4-iodobenzoate (**1o**), the transition metal-catalyzed phosphination of which may suffer.[14] Radical phosphination with chlorodicyclohexylphosphine was also successful, whereas a similar reaction with chlorodi(*tert*-butyl)phosphine resulted in very poor yield (Scheme 2).

Table 1. Radical phosphination of aryl iodides.



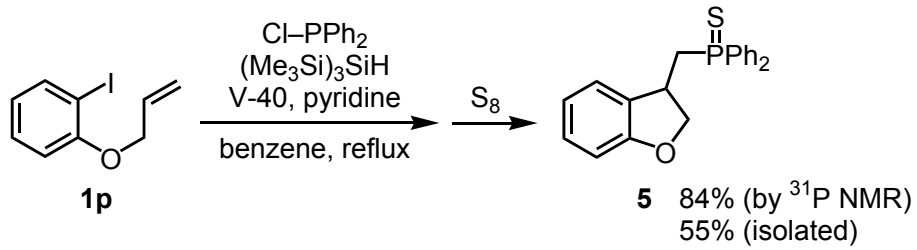
entry	R	product	yield /%[a]
1	H (**1a**)	**3a**	88 (58)
2	2-Me (**1b**)	**3b**	78 (52)
3	4-^{n}Bu (**1c**)	**3c**	81
4	2,4,6-Me_3 (**1d**)	**3d**	63
5	2-MeO (**1e**)	**3e**	65 (44)
6	3-MeO (**1f**)	**3f**	73
7	4-MeO (**1g**)	**3g**	75 (46)
8	4-CF_3 (**1h**)	**3h**	78
9	4-Cl (**1i**)	**3i**	77 (56)
10	3-EtOC(=O) (**1j**)	**3j**	82 (47)
11	4-Br (**1k**)	**3k**	66 (47)
12	4-N≡C (**1l**)	**3k**	69 (43)
13	4-CH_3C(=O) (**1m**)	**3m**	47
14	4-TfO (**1n**)	**3n**	68 (57)
15	4-[CH_2=$CHCH_2$OC(=O)] (**1o**)	**3o**	78

[a] Determined by ^{31}P NMR with $(MeO)_3P$=O as internal standard with a sufficient first delay period. Isolated yields are in parentheses.



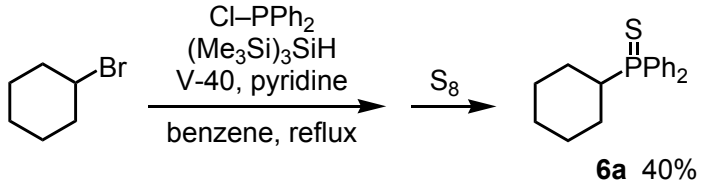
Scheme 2. Dialkylphosphination of iodobenzene.

Treatment of the allyl ether of *o*-iodophenol (**1p**) led to a sequential radical cyclization/phosphination reaction, furnishing **5** in high yield (Scheme 3). The cyclization reaction is highly suggestive of a radical mechanism.



Scheme 3. Radical phosphination through 5-*exo* cyclization.

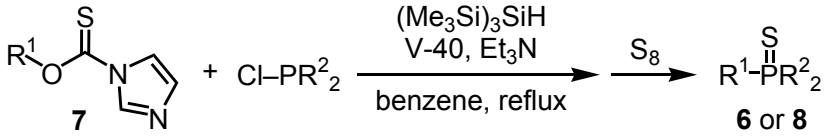
Radical phosphination of bromocyclohexane under the same reaction conditions led to an unsatisfactory yield of cyclohexyldiphenylphosphine sulfide (**6a**) (Scheme 4).

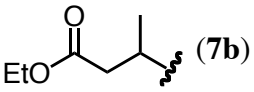
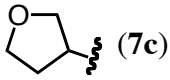


Scheme 4. Radical phosphination of bromocyclohexane.

After extensive screening of reaction conditions, the author found that imidazole-1-carbothioates[15] are the best precursors for the radical phosphination to synthesize alkylphosphines (Table 2).[9] Phosphination of secondary alkyl groups was generally excellent. Hexyl imidazole-1-carbothioate (**7d**) was also phosphinated albeit the yield was moderate (entry 5).

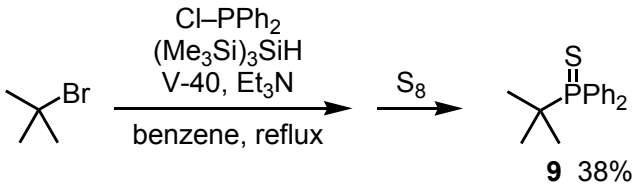
Table 2. Radical phosphination of alkyl imidazole-1-carbothioates.[a]



entry	R^1	R^2	product	yield /%[b]
1	$^cC_6H_{11}$ (**7a**)	Ph	**6a**	87
2	$^cC_6H_{11}$ (**7a**)	$^cC_6H_{11}$	**8**	68
3	 (**7b**)	Ph	**6b**	89 (67)[c]
4	 (**7c**)	Ph	**6c**	87 (76)[c]
5	$^nC_6H_{13}$ (**7d**)	Ph	**6d**	63

[a] A mixture of **7** (0.50 mmol), chlorodiphenylphosphine (1.75 mmol), TTMSS (0.75 mmol), triethylamine (1.5 mmol) and V-40 (0.60 mmol) was heated in boiling benzene (3.0 mL) for 18 h. [b] The yields were determined by ^{31}P NMR. [c] Isolated yields.

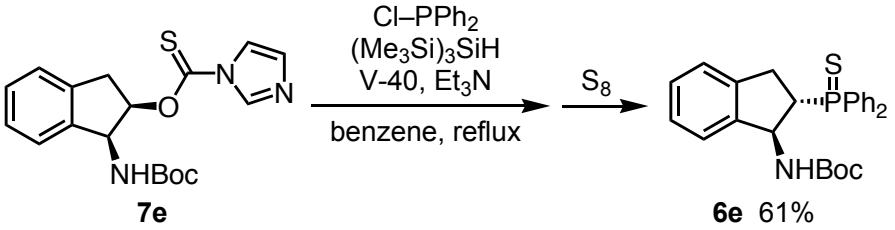
Synthesis of *tert*-butyl imidazole-1-carbothioate resulted in failure. Instead, attempted phosphination of *tert*-butyl bromide afforded **9** in 38% yield (Scheme 5).



Scheme 5. Radical phosphination of *tert*-butyl bromide.

Treatment of carbothioate **7e**, derived from an optically pure amino alcohol, under the phosphination conditions provided *trans*-aminophosphine derivative **6e** exclusively (Scheme 6). Tetraphenyldiphosphine would approach the radical derived from **7e** from the opposite side of the

bulky carbamate moiety. Phosphine sulfides such as **6e** could be useful intermediates in the preparation of chiral aminophosphine ligands.



Scheme 6. Synthesis of a stereocontrolled aminophosphine derivative.

Conclusion

The author has devised a radical phosphination reaction of aryl iodides and alkyl imidazole-1-carbothioate. The mild reaction conditions allow labile functional groups to survive during the reaction. The advantage of the radical-based phosphination culminated in the proof-of-principle stereoselective synthesis of a chiral organophosphine.

Experimental Section

Materials

Triethylamine and pyridine were dried over KOH. All the organic halides were commercially available or readily prepared by conventional methods. Alkyl imidazole-1-carbothioates were synthesized from the corresponding alcohols and 1,1'-thiocarbonyldiimidazole (*vide infra*).

General procedure for phosphination of aryl iodides (Table 1).

Under argon, pyridine (0.24 mL, 3.0 mmol), chlorodiphenylphosphine (0.45 mL, 2.5 mmol), tris(trimethylsilyl)silane (0.46 mL, 1.5 mmol), and aryl iodide (0.50 mmol) were added to a

solution of V-40 (0.024 g, 0.10 mmol) in benzene (3.0 mL). The mixture was stirred for 20 h at reflux. The resulting mixture was then cooled to room temperature. Sulfur crystal (0.16 g, 5.0 mmol) was added and stirred for 1 h at ambient temperature. Water (15 mL) was added to the resulting mixture. The product was extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. ^{31}P NMR analysis of the crude oil with $(MeO)_3P=O$ as an internal standard showed the yield of the corresponding phosphine sulfide. Silica gel column chromatography followed by GPC purification afforded the corresponding phosphine sulfide (*vide infra*).

Preparation of alkyl imidazole-1-carbothioates.

Preparation of **7c** is representative. Under argon, 1,1'-thiocarbonyldiimidazole (1.1 g, 6.0 mmol) and 3-oxacyclopentanol (0.35 g, 4.0 mmol) were added to THF (15 mL). The mixture was stirred for 3 days at ambient temperature. The solution was dried over Na_2SO_4, filtered, concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 2/1) afforded the desired 3-oxacyclopentyl imidazole-1-carbothioate (**7c**, 0.55 g, 2.8 mmol) in 70% yield.

General procedure for phosphination of alkyl imidazole-1-carbothioates (Table 2).

Phosphination of **7c** is representative (Table 2, entry 4). Under argon, triethylamine (0.21 mL, 1.5 mmol), chlorodiphenylphosphine (0.31 mL, 1.75 mmol), tris(trimethylsilyl)silane (0.23 mL, 0.75 mmol), and 3-oxacyclopentyl imidazole-1-carbothioate (**7c**, 0.099 g, 0.50 mmol) were added to a solution of V-40 (0.15 g, 0.60 mmol) in benzene (3.0 mL). The mixture was stirred for 18 h at reflux. The resulting mixture was then cooled down to room temperature. Sulfur crystal (0.13 g, 4.0 mmol) was added and stirred for 1 h at ambient temperature. Water (15 mL) was added to the resulting mixture. The product was extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. ^{31}P NMR analysis of the crude oil showed an 87% yield of diphenyl-(3-oxacyclopentyl)phosphine sulfide (**6c**). Silica gel column chromatography (hexane/EtOAc =

2/1) afforded **6c** as a white solid in 76% yield (0.11 g, 0.38 mmol).

Procedure for purification of phosphinated products.

Use of an excess of chlorodiorganophosphine is needed, which rendered the purification of the desired products difficult. As shown in Figure S1, most of the desired products (except for **6c** and **6e**) were contaminated by other phosphine residues such as tetraphenyldiphosphine disulfide. It was impossible to isolate the desired products only by using conventional silica gel column in reasonably pure forms. The author thus purified the products in the following manner. A crude reaction mixture was roughly purified on silica gel to obtain the phosphinated product with 30–60% purity. The impure product was then subjected to GPC. The separation with GPC took 3–70 h and 6–50 cycles.

Instead of sulfidation with crystal sulfur, oxidation with aqueous hydrogen peroxide yielded the corresponding phosphine oxides. The phosphine oxides are generally easy to isolate, although reduction of the oxides to trivalent phosphines requires rather harsh reaction conditions. Attempted purification of the product after addition of borane to the reaction mixture resulted in failure.

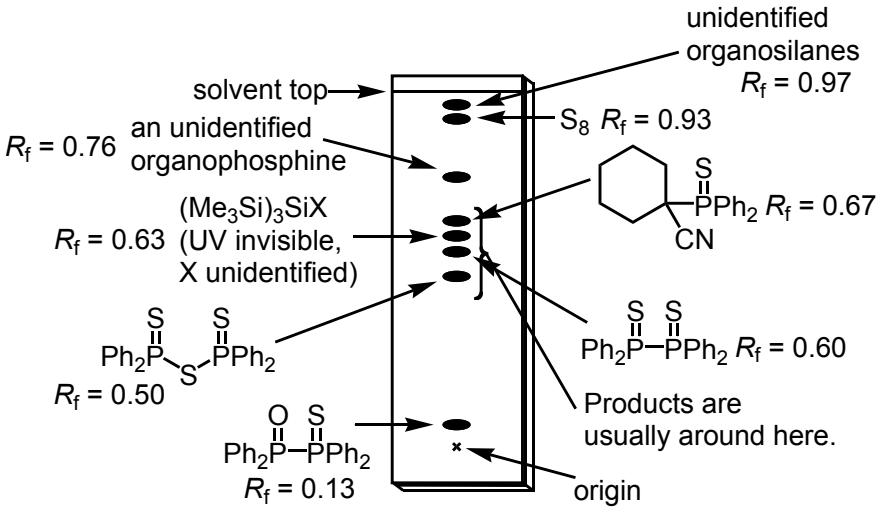
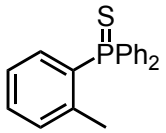


Figure S1. TLC analysis of the crude product. Hexane/EtOAc = 3/1, Merck silica gel $60F_{254}$, visualized under UV irradiation.

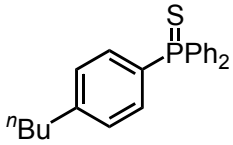
Characterization Data

(2-methylphenyl)diphenylphosphine sulfide (3b)



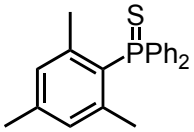
IR (Nujol) 1435, 1097, 756, 716, 692, 637, 525, 511 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.94 (ddd, *J* = 14.8, 7.8, 1.0 Hz, 1H), 7.09–7.14 (m, 1H), 7.25–7.29 (m, 1H), 7.37–7.41 (m, 1H), 7.45–7.50 (m, 4H), 7.51–7.56 (m, 2H), 7.79–7.85 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 22.09 (d, *J* = 5.6 Hz), 125.49 (d, *J* = 12.4 Hz), 128.55 (d, *J* = 12.4 Hz), 131.45 (d, *J* = 84.9 Hz), 131.50 (d, *J* = 2.9 Hz), 131.66 (d, *J* = 2.9 Hz), 132.24 (d, *J* = 10.5 Hz), 132.32 (d, *J* = 84.0 Hz), 132.54 (d, *J* = 10.5 Hz), 132.77 (d, *J* = 11.9 Hz), 142.52 (d, *J* = 9.5 Hz); ^{31}P NMR ($CDCl_3$) δ 40.17. Found: C, 73.70; H, 5.60%. Calcd for $C_{19}H_{17}PS$: C, 74.00; H, 5.56%.

(4-butylphenyl)diphenylphosphine sulfide (3c)



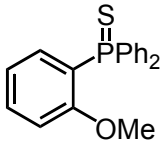
IR (neat) 2957, 2930, 1599, 1437, 1103, 748, 716, 692, 627, 511 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.35 (tq, *J* = 7.4, 7.4 Hz, 2H), 1.60 (tt, *J* = 8.0, 7.4 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 7.25 (dd, *J* = 8.5, 2.5 Hz, 2H), 7.42–7.46 (m, 4H), 7.48–7.52 (m, 2H), 7.59–7.64 (m, 2H), 7.69–7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.86, 22.28, 33.20, 35.51 (d, *J* = 1.4 Hz), 128.42 (d, *J* = 12.4 Hz), 128.61 (d, *J* = 12.9 Hz), 129.51 (d, *J* = 86.9 Hz), 131.40 (d, *J* = 2.9 Hz), 132.19 (d, *J* = 10.5 Hz), 132.24 (d, *J* = 11.0 Hz), 133.11 (d, *J* = 85.0 Hz), 146.97 (d, *J* = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 41.02. HRMS Found: 351.1333. Calcd for $C_{22}H_{24}PS$: 351.1336 $[MH]^+$.

(2,4,6-trimethylphenyl)diphenylphosphine sulfide (3d)



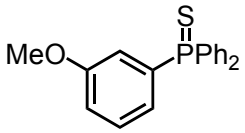
IR (Nujol) 1605, 1437, 1092, 862, 760, 721, 704, 665, 604, 517, 426 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.93 (s, 6H), 2.29 (s, 3H), 6.85 (d, *J* = 4.0 Hz, 2H), 7.37–7.44 (m, 6H), 7.94–8.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 20.93 (d, *J* = 1.0 Hz), 23.96 (d, *J* = 6.3 Hz), 127.63 (d, *J* = 88.4 Hz), 128.51 (d, *J* = 12.4 Hz), 130.79 (d, *J* = 2.9 Hz), 131.10 (d, *J* = 10.5 Hz), 131.31 (d, *J* = 11.5 Hz), 136.19 (d, *J* = 81.6 Hz), 141.06 (d, *J* = 2.9 Hz), 142.43 (d, *J* = 10.0 Hz); ^{31}P NMR ($CDCl_3$) δ 34.32. Found: C, 74.87; H, 6.31%. Calcd for $C_{21}H_{21}PS$: C, 74.97; H, 6.29%.

(2-methoxyphenyl)diphenylphosphine sulfide (3e)



IR (Nujol) 1587, 1474, 1433, 1275, 1097, 1011, 760, 710, 694, 633, 511, 496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50 (s, 3H), 6.90 (dd, *J* = 8.3, 5.3 Hz, 1H), 7.09 (dddd, *J* = 7.7, 7.6, 2.0, 1.0 Hz, 1H), 7.38–7.43 (m, 4H), 7.44–7.48 (m, 2H), 7.51–7.55 (m, 1H), 7.74–7.80 (m, 4H), 7.94 (ddd, *J* = 16.3, 7.7, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 55.19, 111.70 (d, *J* = 5.6 Hz), 120.70 (d, *J* = 84.0 Hz), 121.03 (d, *J* = 12.4 Hz), 128.05 (d, *J* = 12.9 Hz), 130.94 (d, *J* = 2.9 Hz), 131.77 (d, *J* = 11.0 Hz), 133.44 (d, *J* = 88.4 Hz), 134.20 (d, *J* = 2.4 Hz), 135.71 (d, *J* = 10.0 Hz), 160.34 (d, *J* = 1.9 Hz); ^{31}P NMR ($CDCl_3$) δ 39.23. Found: C, 70.09; H, 5.33%. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28%.

(3-methoxyphenyl)diphenylphosphine sulfide (3f)

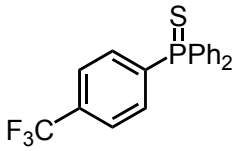


IR (Nujol) 1593, 1572, 1464, 1288, 1240, 1107, 1042, 714, 691, 638, 509 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.78 (s, 3H), 7.01–7.05 (m, 1H), 7.15–7.21 (m, 1H), 7.31–7.38 (m, 2H), 7.41–7.46 (m, 4H), 7.48–7.52 (m, 2H), 7.69–7.75 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.34, 117.29 (d, *J* = 12.4 Hz), 117.49 (d, *J* = 2.9 Hz), 124.38 (d, *J* = 10.5 Hz), 128.43 (d, *J* = 12.4 Hz), 129.51 (d, *J* = 14.8 Hz), 131.52 (d, *J* = 2.9 Hz), 132.15 (d, *J* = 10.5 Hz), 132.70 (d, *J* = 84.5 Hz), 134.14 (d, *J* = 84.0 Hz), 159.47 (d, *J* = 15.8 Hz); ^{31}P NMR ($CDCl_3$) δ 41.69. Found: C, 70.06; H, 5.33%. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28%.

(4-methoxyphenyl)diphenylphosphine sulfide (3g)

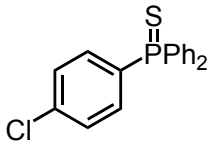
IR (Nujol) 1593, 1259, 1105, 1026, 714, 675, 519 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 3H), 6.93–6.97 (m, 2H), 7.41–7.46 (m, 4H), 7.47–7.51 (m, 2H), 7.62–7.68 (m, 2H), 7.68–7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 55.35, 114.00 (d, *J* = 13.4 Hz), 123.47 (d, *J* = 90.8 Hz), 128.40 (d, *J* = 12.4 Hz), 131.37 (d, *J* = 3.4 Hz), 132.08 (d, *J* = 10.5 Hz), 133.33 (d, *J* = 85.0 Hz), 134.08 (d, *J* = 12.5 Hz), 162.18 (d, *J* = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 40.53. Found: C, 70.34; H, 5.47%. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28%.

(4-trifluoromethylphenyl)diphenylphosphine sulfide (3h)



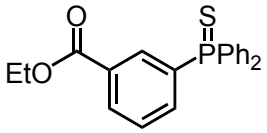
IR (neat) 3057, 1437, 1396, 1325, 1130, 1105, 1063, 1016, 708, 648, 532 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.45–7.50 (m, 4H), 7.52–7.57 (m, 2H), 7.68–7.71 (m, 2H), 7.70–7.75 (m, 4H), 7.83–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 123.48 (qd, J = 271.4, 1.1 Hz), 125.27 (dq, J = 12.4, 3.8 Hz), 128.67 (d, J = 12.9 Hz), 131.88 (d, J = 85.5 Hz), 131.89 (d, J = 2.9 Hz), 132.13 (d, J = 11.0 Hz), 132.61 (d, J = 11.0 Hz), 133.18 (qd, J = 32.7, 3.1 Hz), 137.76 (d, J = 82.1 Hz); ^{31}P NMR ($CDCl_3$) δ 40.83. Found: C, 62.90; H, 4.09%. Calcd for $C_{19}H_{14}F_3PS$: C, 62.98; H, 3.89%.

(4-chlorophenyl)diphenylphosphine sulfide (3i)



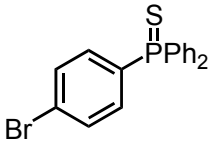
IR (Nujol) 1435, 1099, 1084, 824, 745, 719, 692, 650, 554, 515, 492 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.40–7.44 (m, 2H), 7.43–7.48 (m, 4H), 7.50–7.55 (m, 2H), 7.63–7.69 (m, 2H), 7.67–7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 128.59 (d, J = 12.9 Hz), 128.76 (d, J = 13.4 Hz), 131.56 (d, J = 85.4 Hz), 131.72 (d, J = 2.9 Hz), 132.12 (d, J = 11.0 Hz), 132.41 (d, J = 85.4 Hz), 133.60 (d, J = 11.5 Hz), 138.20 (d, J = 3.9 Hz); ^{31}P NMR ($CDCl_3$) δ 40.71. Found: C, 65.91; H, 4.33%. Calcd for $C_{18}H_{14}ClPS$: C, 65.75; H, 4.29%.

ethyl 3-(diphenylthiophosphinyl)benzoate (3j)



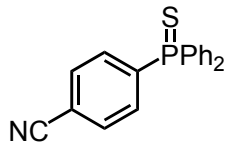
IR (neat) 3055, 2980, 1720, 1437, 1265, 1128, 1101, 750, 718, 692, 640, 517 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, *J* = 7.0 Hz, 3H), 4.35 (q, *J* = 7.0 Hz, 2H), 7.44–7.49 (m, 4H), 7.51–7.56 (m, 3H), 7.69–7.75 (m, 4H), 7.95 (dddd, *J* = 12.8, 7.6, 1.7, 1.2 Hz, 1H), 8.18 (dddd, *J* = 7.8, 1.7, 1.7, 1.4 Hz, 1H), 8.36 (dddd, *J* = 13.4, 1.7, 1.7, 0.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.20, 61.37, 128.63 (d, *J* = 12.4 Hz), 128.66 (d, *J* = 12.4 Hz), 130.83 (d, *J* = 12.5 Hz), 131.76 (d, *J* = 2.9 Hz), 132.19 (d, *J* = 11.0 Hz), 132.32 (d, *J* = 85.5 Hz), 132.47 (d, *J* = 2.9 Hz), 133.06 (d, *J* = 11.5 Hz), 133.87 (d, *J* = 84.0 Hz), 136.32 (d, *J* = 11.0 Hz), 165.59 (d, *J* = 0.9 Hz); ^{31}P NMR ($CDCl_3$) δ 41.04. HRMS Found: 367.0929. Calcd for $C_{21}H_{20}O_2PS$: 367.0923 $[MH]^+$.

(4-bromophenyl)diphenylphosphine sulfide (3k)



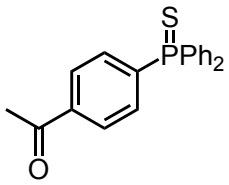
IR (Nujol) 1435, 1385, 1099, 1069, 1011, 820, 735, 718, 692, 646, 534, 511 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.42–7.47 (m, 4H), 7.51–7.55 (m, 2H), 7.55–7.61 (m, 4H), 7.67–7.73 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 126.80 (d, *J* = 3.4 Hz), 128.62 (d, *J* = 12.5 Hz), 131.71 (d, *J* = 12.9 Hz), 131.74 (d, *J* = 2.9 Hz), 132.12 (d, *J* = 87.9 Hz), 132.12 (d, *J* = 10.5 Hz), 132.35 (d, *J* = 85.4 Hz), 133.74 (d, *J* = 11.5 Hz); ^{31}P NMR ($CDCl_3$) δ 40.88. Found: C, 57.98; H, 3.95%. Calcd for $C_{18}H_{14}BrPS$: C, 57.92; H, 3.78%.

4-(diphenylthiophosphinyl)benzonitrile (3l)



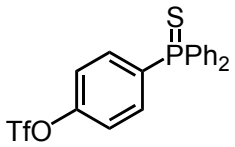
IR (neat) 3055, 2232, 1437, 1389, 1101, 750, 718, 692, 658, 577, 556, 502 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.46–7.51 (m, 4H), 7.54–7.59 (m, 2H), 7.67–7.74 (m, 4H), 7.70–7.74 (m, 2H), 7.80–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 115.13 (d, *J* = 2.8 Hz), 117.82 (d, *J* = 1.4 Hz), 128.77 (d, *J* = 12.5 Hz), 131.48 (d, *J* = 86.0 Hz), 131.92 (d, *J* = 12.4 Hz), 132.07 (d, *J* = 2.9 Hz), 132.14 (d, *J* = 10.5 Hz), 132.66 (d, *J* = 10.5 Hz), 139.13 (d, *J* = 80.6 Hz); ^{31}P NMR ($CDCl_3$) δ 40.98. HRMS Found: 320.0663. Calcd for $C_{19}H_{15}NPS$: 320.0663 $[MH]^+$.

1-{4-(diphenylthiophosphinyl)phenyl}ethanone (3m)



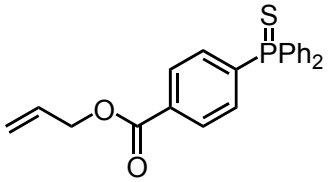
IR (Nujol) 3055, 1690, 1595, 1437, 1393, 1263, 1103, 716, 692, 655, 610, 511 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.62 (s, 3H), 7.44–7.49 (m, 4H), 7.52–7.56 (m, 2H), 7.69–7.75 (m, 4H), 7.79–7.85 (m, 2H), 7.97–8.01 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.83, 128.04 (d, *J* = 12.5 Hz), 128.66 (d, *J* = 12.4 Hz), 131.84 (d, *J* = 2.9 Hz), 132.12 (d, *J* = 85.4 Hz), 132.19 (d, *J* = 11.0 Hz), 132.52 (d, *J* = 10.5 Hz), 138.32 (d, *J* = 81.6 Hz), 139.07 (d, *J* = 2.9 Hz), 197.43 (d, *J* = 0.9 Hz); ^{31}P NMR ($CDCl_3$) δ 40.90. Found: C, 71.17; H, 5.37%. Calcd for $C_{20}H_{17}OPS$: C, 71.41; H, 5.09%.

4-(diphenylthiophosphinyl)phenyl trifluoromethanesulfonate (3n)



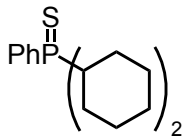
IR (neat) 3057, 1585, 1486, 1440–1420 (br), 1251, 1230–1200 (br), 1139, 1103, 1016, 885 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.33–7.37 (m, 2H), 7.46–7.51 (m, 4H), 7.53–7.58 (m, 2H), 7.68–7.74 (m, 4H), 7.80–7.86 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 118.61 (q, *J* = 319.1 Hz), 121.45 (d, *J* = 12.9 Hz), 128.74 (d, *J* = 12.5 Hz), 131.90 (d, *J* = 85.5 Hz), 131.97 (d, *J* = 3.4 Hz), 132.14 (d, *J* = 10.5 Hz), 134.29 (d, *J* = 83.5 Hz), 134.49 (d, *J* = 11.9 Hz), 151.52 (d, *J* = 3.3 Hz); ^{31}P NMR ($CDCl_3$) δ 40.41. Found: C, 51.49; H, 2.94%. Calcd for $C_{19}H_{14}O_3F_3PS_2$: C, 51.58; H, 3.19%.

allyl (4-diphenylthiophosphinyl)benzoate (3o)



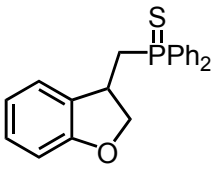
IR (neat) 3056, 1722, 1436, 1394, 1271, 1102, 1094, 718, 692, 650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.82–4.86 (m, 2H), 5.30 (doublet of multiplet, *J* = 17.2 Hz, 1H), 5.41 (doublet of multiplet, *J* = 10.9 Hz, 1H), 6.02 (ddt, *J* = 17.2, 10.9, 10.5 Hz, 1H), 7.44–7.49 (m, 4H), 7.51–7.56 (m, 2H), 7.68–7.75 (m, 4H), 7.78–7.84 (m, 2H), 8.10–8.14 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 65.91, 118.60, 128.63 (d, *J* = 12.4 Hz), 129.43 (d, *J* = 13.0 Hz), 131.76, 131.81 (d, *J* = 2.9 Hz), 132.11 (d, *J* = 86.0 Hz), 132.17 (d, *J* = 11.0 Hz), 132.25 (d, *J* = 10.0 Hz), 132.76 (d, *J* = 2.9 Hz), 138.23 (d, *J* = 82.0 Hz), 165.31 (d, *J* = 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 41.00. HRMS Found: 379.0928. Calcd for $C_{22}H_{20}O_2PS$: 379.0922 $[MH]^+$.

dicyclohexylphenylphosphine sulfide (4a)



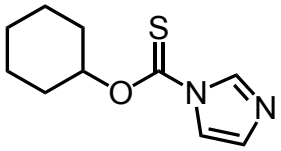
IR (Nujol) 1452, 1435, 760, 745, 694, 625, 540 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08–1.18 (m, 2H), 1.20–1.41 (m, 8H), 1.57–1.64 (m, 2H), 1.64–1.71 (m, 2H), 1.72–1.79 (m, 2H), 1.81–1.88 (m, 2H), 2.04–2.11 (m, 2H), 2.18–2.27 (m, 2H), 7.45–7.54 (m, 3H), 7.81–7.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 25.25 (d, *J* = 2.4 Hz), 25.71 (d, *J* = 1.4 Hz), 25.95 (d, *J* = 3.4 Hz), 26.33 (d, *J* = 13.9 Hz), 26.38 (d, *J* = 13.4 Hz), 36.96 (d, *J* = 50.0 Hz), 128.06 (d, *J* = 67.3 Hz), 128.18 (d, *J* = 10.5 Hz), 131.23 (d, *J* = 2.8 Hz), 132.19 (d, *J* = 8.6 Hz); ^{31}P NMR ($CDCl_3$) δ 56.78. Found: C, 70.34; H, 8.89%. Calcd for $C_{18}H_{27}PS$: C, 70.55; H, 8.88%.

[{3-(2,3-dihydrobenzofuryl)}methyl]diphenylphosphine sulfide (5)



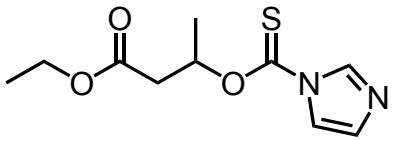
IR (neat) 3053, 2928, 2895, 1597, 1481, 1437, 1232, 1103, 750, 692, 625, 507 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.82 (ddd, *J* = 14.6, 10.4, 9.5 Hz, 1H), 2.98 (ddd, *J* = 14.6, 11.9, 2.9 Hz, 1H), 3.93–4.02 (m, 1H), 4.08 (dd, *J* = 9.3, 6.8 Hz, 1H), 4.46 (dd, *J* = 9.3, 9.3 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.83 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.07–7.14 (m, 2H), 7.45–7.56 (m, 6H), 7.83–7.92 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 36.86 (d, *J* = 1.5 Hz), 38.38 (d, *J* = 53.9 Hz), 76.72 (d, *J* = 1.9 Hz), 109.72, 120.59, 123.88, 128.68, 128.78 (d, *J* = 12.0 Hz), 128.83 (d, *J* = 11.9 Hz), 129.99 (d, *J* = 2.4 Hz), 131.06 (d, *J* = 10.0 Hz), 131.08 (d, *J* = 10.5 Hz), 131.75 (d, *J* = 2.9 Hz), 131.79 (d, *J* = 2.9 Hz), 132.44 (d, *J* = 80.6 Hz), 132.74 (d, *J* = 79.3 Hz), 159.49; ^{31}P NMR ($CDCl_3$) δ 37.85. Found: C, 72.05; H, 5.37%. Calcd for $C_{21}H_{19}OPS$: C, 71.98; H, 5.47%.

***O*-cyclohexyl 1*H*-imidazole-1-carbothioate (7a)**



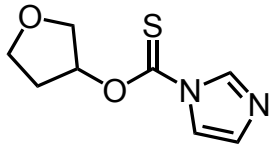
IR (neat) 3123, 2938, 2860, 1529, 1464, 1387, 1284, 1230, 1094, 1003, 972, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35–1.44 (m, 1H), 1.44–1.55 (m, 2H), 1.55–1.65 (m, 1H), 1.65–1.75 (m, 2H), 1.75–1.82 (m, 2H), 2.00–2.09 (m, 2H), 5.47–5.55 (m, 1H), 7.03 (s, 1H), 7.64 (s, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 23.35, 25.00, 30.55, 82.44, 117.74, 130.48, 136.65, 183.25. Found: C, 56.83; H, 6.80%. Calcd for $C_{10}H_{14}N_2OS$: C, 57.11; H, 6.71%.

***O*-(3-ethoxy-1-methyl-3-oxopropyl) 1*H*-imidazole-1-carbothioate (7b)**



IR (neat) 3130, 2983, 1739, 1733, 1467, 1387, 1286, 1232, 1101, 1032, 969, 656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, *J* = 7.0 Hz, 3H), 1.54 (d, *J* = 6.5 Hz, 3H), 2.75 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.92 (dd, *J* = 16.0, 7.5 Hz, 1H), 4.11–4.20 (m, 2H), 5.93–6.00 (m, 1H), 7.02–7.04 (m, 1H), 7.61–7.63 (m, 1H), 8.31–8.33 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.04, 18.90, 40.15, 60.97, 76.95, 117.82, 130.64, 136.65, 169.34, 182.94. Found: C, 49.68; H, 5.92%. Calcd for $C_{10}H_{14}N_2O_3S$: C, 49.57; H, 5.82%.

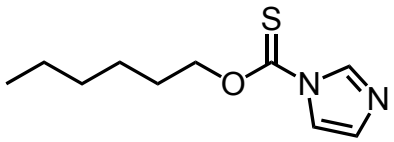
***O*-(3-oxacyclopentyl) 1*H*-imidazole-1-carbothioate (7c)**



IR (neat) 3125, 2867, 1532, 1464, 1387, 1286, 1231, 1115, 1077, 970, 746, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.25–2.32 (m, 1H), 2.39 (dtd, *J* = 14.3, 8.2, 6.2 Hz, 1H), 3.94 (td, *J* = 8.5, 4.5

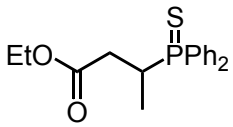
Hz, 1H), 4.00–4.07 (m, 2H), 4.09–4.14 (m, 1H), 5.93–5.97 (m, 1H), 7.04–7.05 (m, 1H), 7.62–7.64 (m, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 32.53, 67.07, 72.50, 84.11, 117.71, 130.75, 136.69, 183.24. Found: C, 48.47; H, 5.11%. Calcd for $C_8H_{10}N_2O_2S$: C, 48.47; H, 5.08%.

_O_-hexyl 1_H_-imidazole-1-carbothioate (7d)



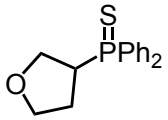
IR (neat) 3123, 2956, 2931, 1530, 1464, 1387, 1329, 1286, 1232, 1095, 990, 744, 657 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87–0.96 (m, 3H), 1.30–1.40 (m, 4H), 1.42–1.50 (m, 2H), 1.84–1.91 (m, 2H), 4.66 (t, J = 6.8 Hz, 2H), 7.03–7.05 (m, 1H), 7.63–7.65 (m, 1H), 8.34–8.36 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 22.43, 25.51, 27.91, 31.24, 73.87, 117.76, 130.63, 136.64, 184.28. Found: C, 56.96; H, 7.57%. Calcd for $C_{10}H_{16}N_2OS$: C, 56.57; H, 7.60%.

ethyl 3-(diphenylthiophosphinyl)butanoate (6b)



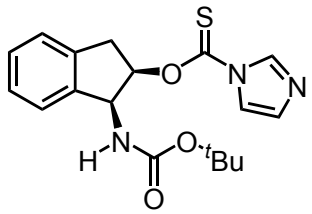
IR (neat) 3055, 2979, 1733, 1436, 1224, 1156, 1100, 1028, 752, 712, 694, 610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (dd, J = 18.8, 6.8 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 2.46–2.55 (m, 2H), 3.31–3.40 (m, 1H), 4.06 (dq, J = 10.6, 7.1 Hz, 1H), 4.11 (dq, J = 10.6, 7.1 Hz, 1H), 7.44–7.52 (m, 6H), 7.93–8.00 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.30, 14.10, 29.98 (d, J = 57.8 Hz), 35.03 (d, J = 2.4 Hz), 60.83, 128.68 (d, J = 11.9 Hz), 128.69 (d, J = 12.0 Hz), 130.86 (d, J = 77.9 Hz), 131.04 (d, J = 77.3 Hz), 131.35 (d, J = 9.6 Hz), 131.53 (d, J = 2.9 Hz), 131.58 (d, J = 2.9 Hz), 171.95 (d, J = 20.1 Hz); ^{31}P NMR ($CDCl_3$) δ 50.02. HRMS Found: 333.1078. Calcd for $C_{18}H_{22}O_2PS$: 333.1078 $[MH]^+$.

diphenyl-(3-oxacyclopentyl)phosphine sulfide (6c)



IR (Nujol) 1436, 1105, 1095, 914, 713, 693, 625, 614, 504 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.97–2.07 (m, 1H), 2.31–2.43 (m, 1H), 3.77–3.46 (m, 1H), 3.84–3.92 (m, 2H), 3.92–4.01 (m, 2H), 7.44–7.53 (m, 6H), 7.82–7.89 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 27.76, 38.73 (d, *J* = 59.1 Hz), 69.38 (d, *J* = 4.8 Hz), 68.88 (d, *J* = 8.6 Hz), 128.68 (d, *J* = 11.9 Hz), 128.70 (d, *J* = 11.9 Hz), 131.05 (d, *J* = 10.1 Hz), 131.09 (d, *J* = 10.0 Hz), 131.57 (d, *J* = 3.4 Hz), 131.66 (d, *J* = 2.9 Hz), 132.32 (d, *J* = 79.8 Hz), 132.57 (d, *J* = 80.8 Hz); ^{31}P NMR ($CDCl_3$) δ 45.30. Found: C, 66.72; H, 5.86%. Calcd for $C_{16}H_{17}OPS$: C, 66.65; H, 5.94%.

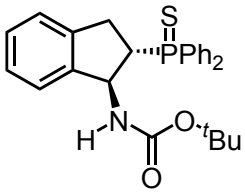
***O*-{(1*S*,2*R*)-1-(1,1-dimethylethoxycarbonyl)amino-2-indanyl} 1*H*-imidazole-1-carbothioate (7e)** (86:14 mixture of two rotamers)



IR (Nujol) 3342, 1681, 1525, 1389, 1293, 1244, 1232, 1109, 1019 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9H), 3.25 (dd, *J* = 17.1, 2.2 Hz, 1H), 3.41 (dd, *J* = 17.1, 5.3 Hz, 1H), 4.86–5.00 (br, 0.14 × 1H), 5.05–5.18 (br, 0.86 × 1H), 5.28–5.39 (br, 0.14 × 1H), 5.50 (dd, *J* = 8.5, 5.3 Hz, 0.86 × 1H), 6.25 (ddd, *J* = 5.3, 5.3, 2.2 Hz, 1H), 6.94 (s, 1H), 7.25–7.40 (m, 4H), 7.51 (s, 1H), 8.16 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 28.24, 36.57, 57.28, 80.30, 84.31, 117.96, 124.00, 125.09, 127.63, 128.81, 130.65, 136.53, 138.57, 139.57, 155.42, 183.14. Found: C, 60.14; H, 5.94%. Calcd for $C_{18}H_{21}N_3O_3S$: C, 60.15; H, 5.89%.

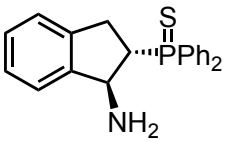
***tert*-butyl (1*S*, 2*S*)-2-(diphenylthiophosphinyl)-1-indanecarbamate (6e)**

(75:25 mixture of 2 rotamers)



IR (Nujol) 3338 (br), 1684, 1456, 1437, 1168, 1100, 744, 711, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (s, 0.25 × 9H), 1.30 (s, 0.75 × 9H), 2.86–3.02 (br, 0.25 × 1H), 2.96–3.07 (m, 0.75 × 1H), 3.28-3.40 (m, 1H), 3.60–3.72 (br, 0.25 × 1H), 3.88–3.98 (m, 0.75 × 1H), 4.30–4.42 (br, 0.25 × 1H), 4.59 (d, *J* = 8.0 Hz, 0.75 × 1H), 5.52–5.68 (m, 1H), 7.08–7.13 (m, 1H), 7.13–7.22 (m, 3H), 7.42–7.54 (m, 6H), 7.90–8.04 (br, 2H), 7.99–8.06 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.23, 32.52, 44.80 (d, *J* = 58.8 Hz), 57.01, 79.23, 123.33, 124.36, 127.06, 127.94, 128.46 (d, *J* = 12.0 Hz), 128.68 (d, *J* = 11.9 Hz), 131.23 (d, *J* = 9.5 Hz), 131.41, 131.50 (d, *J* = 2.9 Hz), 131.66 (d, *J* = 10.0 Hz), 132.37 (d, *J* = 80.1 Hz), 139.43 (d, *J* = 10.0 Hz), 142.56 (d, *J* = 10.9 Hz), 154.20; ^{31}P NMR ($CDCl_3$) δ 46.74 (br s, 0.75 × 1P), 47.19 (br s, 0.25 × 1P). HRMS Found: 450.1657. Calcd for $C_{26}H_{29}NO_2PS$: 450.1657 $[MH]^+$. The inseparable mixture of the rotamers of **6e** was subjected to deprotection of the Boc group to yield the corresponding amine **10** quantitatively.

(1*S*, 2*S*)-2-diphenylthiophosphinyl-1-indaneamine (10)



IR (neat) 3377 (br), 3052, 1589, 1480, 1436, 749, 638 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–1.65 (br, 2H), 3.04–3.11 (m, 1H), 3.28–3.39 (m, 2H), 4.94 (dd, *J* = 15.8, 7.3 Hz, 1H), 7.11–7.15 (m, 1H), 7.17–7.24 (m, 2H), 7.26–7.30 (m, 1H), 7.48–7.56 (m, 6H), 7.94–8.00 (m, 2H), 8.01–8.07 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 33.09 (d, *J* = 1.0 Hz), 50.52 (d, *J* = 57.3 Hz), 58.28 (d, *J* = 1.9 Hz), 123.72, 124.23, 127.07, 127.83, 128.72 (d, *J* = 11.4 Hz), 128.74 (d, *J* = 11.9 Hz), 131.49 (d, *J* = 10.1 Hz), 131.64 (d, *J* = 2.9 Hz), 131.69 (d, *J* = 10.0 Hz), 131.93 (d, *J* = 76.9 Hz), 132.17 (d, *J* =

77.8 Hz), 139.91 (d, J = 10.0 Hz), 144.99 (d, J = 11.4 Hz); ^{31}P NMR ($CDCl_3$) δ 46.51. HRMS Found: 350.1136. Calcd for $C_{21}H_{21}NPS$: 350.1132 $[MH]^+$.

References and Notes

1. Use of phosphorus-centered radicals in organic synthesis was summarized. See: D. Leca, L. Fensterbank, E. Lacôte, M. Malacria, *Chem. Soc. Rev.* **2005**, 34, 858–865.
2. Addition reactions of phosphorus-centered radicals to carbon–carbon multiple bonds are the general radical-based approach to organophosphines. See: F. W. Stacey, J. F. Harris Jr. *Org. React.* **1963**, *13*, 150–376. For recent advances, see reference 1.
3. A. Sato, H. Yorimitsu, K. Oshima, *Angew. Chem. Int. Ed.* **2005**, *44*, 1694–1696.
4. The synthesis of phosphonic acids by the reaction of white phosphorus with carbon-centered radicals was reported: (a) D. H. R. Barton, J. Zhu, *J. Am. Chem. Soc.* **1993**, *115*, 2071–2072; (b) D. H. R. Barton, R. A. Vonder Embse, *Tetrahedron* **1998**, *54*, 12475–12496.
5. (a) *Methoden der Organischen Chemie (Houben-Weyl)* (Ed.: G. Elsner), Georg Thieme Verlag, Stuttgart, **1982**, Vol. E1; (b) T. Kawashima in *The Fourth Series of Experimental Chemistry* (Ed.: K. Akiba), Maruzen, Tokyo, **1992**, Vol. 24, Chap. 6.1.
6. Oshima has developed phosphination reactions directed toward the synthesis of functionalized organophosphines: (a) K. Hirano, H. Yorimitsu, K. Oshima, *Org. Lett.* **2004**, *6*, 4873–4875; (b) H. Ohmiya, H. Yorimitsu, K. Oshima, *Angew. Chem. Int. Ed.* **2005**, *44*, 2368–2370. See also reference 3.
7. C. Chatgilialoglu, D. Griller, M. Lesage, *J. Org. Chem.* **1988**, *53*, 3641–3642. Tributylstannane did not serve well in the phosphination reaction. The stannane reacted rapidly only with chlorodiphenylphosphine to consume the stannane.
8. Mild reduction of phosphine sulfides to trivalent phosphines through a radical process is known. See: R. Romeo, L. A. Wozniak, C. Chatgilialoglu, *Tetrahedron Lett.* **2000**, *41*, 9899–9902.

9. See Experimental Section for the procedure to purify products **3** and **6**. The purification necessitated sequential silica gel column purification and GPC.
10. Separately, the author confirmed that the reduction of chlorodiphenylphosphine with TTMSS took place in the presence of V-40. In the absence of V-40, the reduction did not proceed.
11. R. Okazaki, Y. Hirabayashi, K. Tamura, N. Inamoto, *J. Chem. Soc. Perkin Trans. 1* **1976**, 1034–1036.
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14. (a) I. P. Beletskaya, A. V. Cheprakov, *Coord. Chem. Rev.* **2004**, *248*, 2337–2364; (b) M. Murata, S. L. Buchwald, *Tetrahedron* **2004**, *60*, 7397–7403.
15. (a) D. H. R. Barton, S. W. McCombie, *J. Chem. Soc. Perkin Trans. 1* **1975**, 1574–1585; (b) J. R. Rasmussen, C. J. Slinger, R. J. Kordish, D. D. Newman-Evans, *J. Org. Chem.* **1981**, *46*, 4843–4846.

Chapter 3

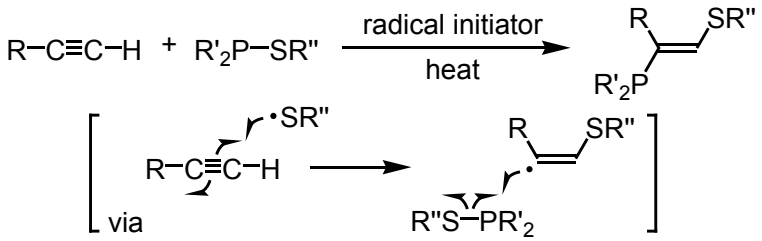
Regio- and Stereoselective Synthesis of 1-Aryl-1-thio-2-thiophosphinylethene Derivatives via a Radical Process

Radical addition of an *S*-thiophosphinyl dithiocarbonate to terminal aromatic alkynes affords (*E*)-1-aryl-1-thio-2-thiophosphinylethene derivatives regio- and stereoselectively in high yields. The transformations of the products are also described.

Introduction

Radical additions of heteroatom-heteroatom bonds to alkenes and alkynes are fundamental methods to introduce two heteroatoms to organic molecules in one operation. Among them, dicharcogenations of carbon–carbon multiple bonds have been widely investigated.[1] However, in spite of the increasing utilities of organophosphorus compounds in organic chemistry,[2] examples of radical additions of phosphorus–heteroatom bonds are limited.[3,4] As one of the limited examples, the author has described the radical diphoshination of alkynes in chapter 1.[4a]

Oshima recently reported a radical thiophosphination of alkynes with thiophosphines (Scheme 1).[4b] The reaction proceeds through the addition of sulfur-centered radical to the terminal carbon of alkyne followed by the efficient reaction of the resulting vinyl radical with the phosphino group of thiophosphine.



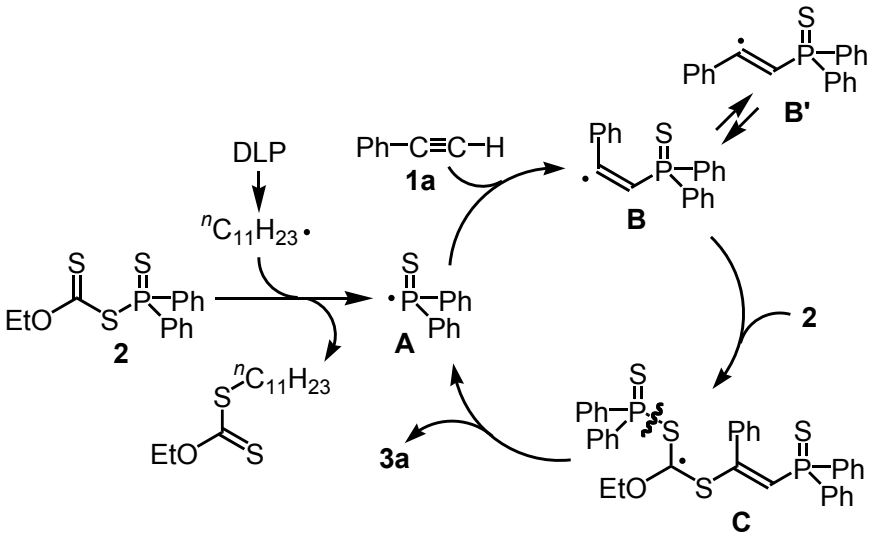
Scheme 1. Oshima's radical thiophosphination of alkynes with thiophosphines.

The author examined radical addition reactions to introduce both phosphorus and sulfur atoms to alkynes with the regioselectivity opposite to the previous reaction.[4b] In Chapter 3, he reports the synthesis of (*E*)-1-aryl-1-thio-2-thiophosphinylethene derivatives via a radical process using a thiophosphinylated dithiocarbonate.[5] Stereoselective syntheses of (*E*)-1-aryl-1-thio-2-thiophosphinylethenes are scarcely reported.[6]

Results and Discussion

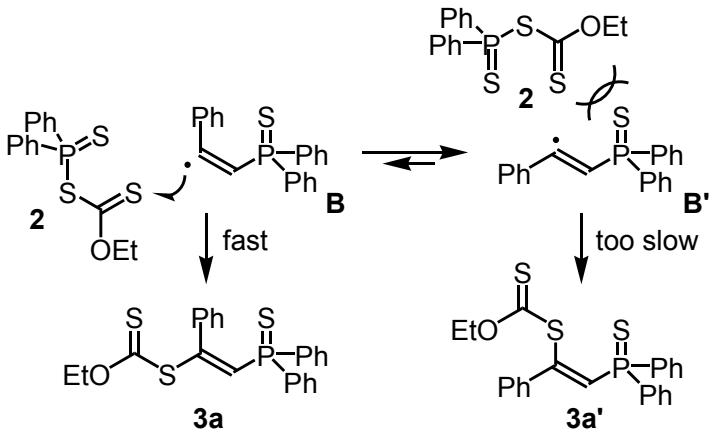
A mixture of phenylacetylene (**1a**), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**), and a catalytic amount of dilauroyl peroxide (DLP) was heated in benzene at reflux temperature for 4 h (Table 1, entry 1). NMR analysis of the crude mixture indicated the formation of the corresponding adduct, *S*-2-diphenylthiophosphinyl-1-phenylethenyl *O*-ethyl dithiocarbonate (91%) with no isomers. Silica gel column chromatography followed by GPC afforded **3a** in 76% yield. The author confirmed by X-ray analysis that the *E* isomer was exclusively formed.

This reaction would proceed as follows (Scheme 2). Initially, an undecyl radical, thermally generated from DLP, would attack the sulfur atom of the thiocarbonyl moiety of **2** to generate diphenylthiophosphinoyl radical (**A**) with the formation of *O*-ethyl *S*-undecyl dithiocarbonate.[5] The phosphorus-centered radical **A** would react with the triple bond of **1a** to furnish vinyl radical **B**.[7] An equilibrium would exist between the radicals **B** and **B'**. However, only radical **B** would react with **2** to furnish radical **C** (*vide infra*). Finally, fragmentation of radical **C** would produce **3a** and regenerate the phosphorus-centered radical **A** to complete the radical chain.



Scheme 2. Plausible reaction mechanism.

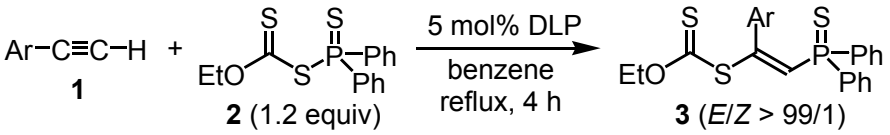
The *E* selectivity of the reaction can be explained as outlined in Scheme 3. Vinyl radical **B'** would reside in larger population than radical **B** in the equilibrium because radical **B** has a favorable *E* configuration. However, the diphenylthiophosphinyl moiety and reagent **2** are so large that the steric repulsion between **B'** and **2** would prevent the reaction. Hence, only **B** can react with **2** to form the product **3a** exclusively.



Scheme 3. A plausible explanation of the stereoselectivity.

A variety of aryl-substituted terminal alkynes underwent the radical addition reaction with complete regio- and stereoselectivity (Table 1). The *E* configurations of **3** were deduced from comparing the ^{1}H NMR spectra of **3b**–**3k** with the spectrum of **3a**. Both electron-rich and electron-deficient aryl-substituted acetylenes reacted with **2** to afford **3** in high yields. The addition of **2** to sterically hindered alkynes like **1c** and **1d** proceeded smoothly (entries 3 and 4). Functional groups such as alkoxy (entry 5), keto (entry 6), cyano (entry 7), ester (entry 8), formyl (entry 9), and bromo (entry 10) moieties remained unchanged under the reaction conditions. It is worth noting that a hydroxy group did not affect the reactivity (entry 11). However, attempts to perform addition reactions of **2** across 1-dodecyne, trimethylsilylacetylene, methyl propiolate, and 1-phenylpropyne resulted in failure, suffering from low conversion.

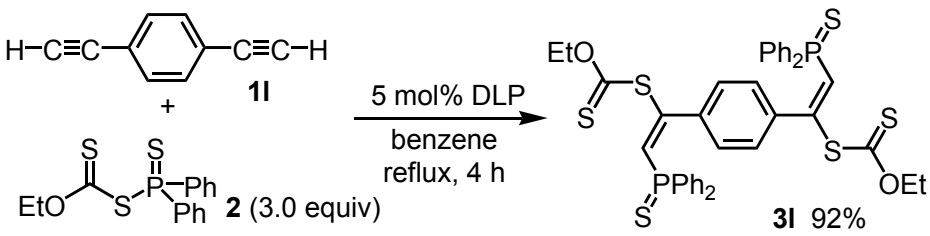
Table 1. Radical addition of **2** to various aryl-substituted terminal alkynes.



entry	Ar	product	isolated yield /%
1	Ph (**1a**)	**3a**	76[a] (91)[c]
2	4-Me–C_6H_4 (**1b**)	**3b**	71[b] (89)[c]
3	2,4,6-Me_3–C_6H_2 (**1c**)	**3c**	83[a]
4	1-naphthyl (**1d**)	**3d**	73
5	4-MeO–C_6H_4 (**1e**)	**3e**	88
6	4-Ac–C_6H_4 (**1f**)	**3f**	92
7	4-NC–C_6H_4 (**1g**)	**3g**	85
8	4-MeO_2C–C_6H_4 (**1h**)	**3h**	79
9	4-OHC–C_6H_4 (**1i**)	**3i**	88
10	4-Br–C_6H_4 (**1j**)	**3j**	87[b]
11	4-$HOCH_2$–C_6H_4 (**1k**)	**3k**	88

[a] Yields after purification by GPC. [b] Yields after recrystallization.
[c] Yields in parentheses were determined by ^{31}P NMR.

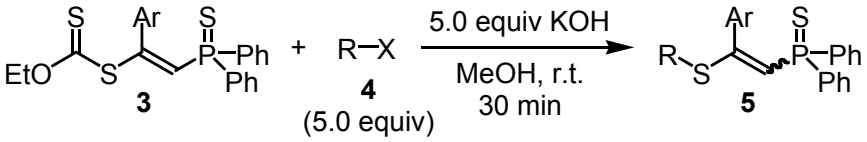
The reaction of thiophosphinyl dithiocarbonate **2** with *p*-diethynylbenzene (**1l**) efficiently afforded *p*-bis{(*E*)-1-thio-2-thiophosphinylethenyl}benzene **3l**. The double addition proceeded with perfect regio- and stereoselectivity in a very high yield (Scheme 4).



Scheme 4. Double addition of **2** to diacetylene **1l**.

The author next attempted to carry out stereospecific transformations of product **3**. It was found that hydrolysis of the dithiocarbonate moieties of **3** followed by *S*-alkylation proceeded[8] in the presence of excess potassium hydroxide and reactive alkyl halides **4** to provide the thiophosphinylated vinyl sulfides **5** in excellent yields with retention of configuration (Table 2).

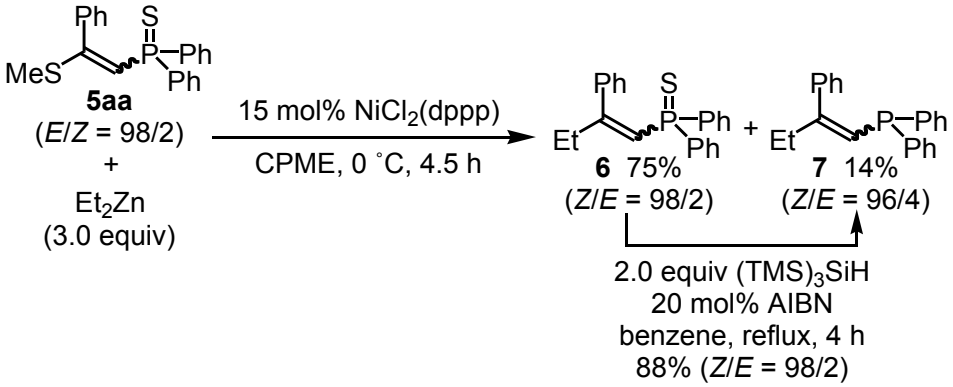
Table 2. Hydrolysis of **3** followed by alkylation with **4**.



entry	**3**	R–X (**4**)	product	isolated yield /%	[*E*/*Z*]
1	**3a**	Me–I (**4a**)	**5aa**	98	98/2
2	**3a**	allyl–Br (**4b**)	**5ab**	98	98/2
3	**3a**	Bn–Br (**4c**)	**5ac**	88	99/1
4	**3b**	Me–I (**4a**)[a]	**5ba**	93	98/2

[a] 3.2 equiv of KOH and **4a** were used.

Finally, cross-coupling reactions of vinyl sulfide **5aa** with organometallic reagents were examined.[9] Coupling reactions with Grignard reagents resulted in failure. However, treatment of **5aa** with diethylzinc in the presence of a catalytic amount of $NiCl_2$(dppp) in cyclopentyl methyl ether (CPME) at 0 ˚C afforded the ethylated compound **6** effectively (Scheme 5). This cross-coupling reaction proceeded without loss of stereochemistry, albeit partial desulfidation at the thiophosphinyl moiety was observed. The phosphine sulfide **6** could be converted to **7** by the action of tris(trimethylsilyl)silane via a radical pathway.[10] The overall reaction can be regarded as a *trans*-carbophosphination of the starting alkyne to prepare a *β*-disubstituted alkenylphosphine stereoselectively.[11]



Scheme 5. Cross-coupling reaction of **5aa** and desulfidation of **6**.

Conclusion

The author has developed an intermolecular addition of *S*-thiophosphinyl dithiocarbonate to arylacetylenes to produce (*E*)-1-aryl-1-thio-2-thiophosphinylethene derivatives which are difficult to be prepared. Taking advantage of mild radical conditions, the reactions proceed without loss of various functional groups. A stereocontrolled, multisubstituted alkenyl phosphine can be synthesized by further transformation of the product.

In light of the importance of organophosphorus and organosulfur compounds, the products or their derivatives can be useful for diverse purposes such as a new type of ligands, building blocks for organic synthesis, and components of supramolecular structures.

Experimental Section

Materials

Diphenylthiophosphinyl chloride was purchased from Wako Pure Chemicals. $NiCl_2$(dppp) was available from TCI. Neat diethylzinc was purchased from Aldrich and was diluted with degassed dry hexane to prepare a 1.0 M solution, which was stored under argon. Alkynes were commercially available or readily prepared in conventional methods. *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**) was synthesized from potassium *O*-ethyl dithiocarbonate and

diphenylthiophosphinyl chloride (*vide infra*).

Preparation of *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (2).

Under argon, diphenylthiophosphinyl chloride (3.08 mL, 15.0 mmol) was added to a suspension of potassium *O*-ethyl dithiocarbonate (2.64 g, 16.5 mmol) in THF (20.0 mL) at ambient temperature. After 4 h, a diluted NaCl solution was poured into the suspension and the mixture was extracted twice with hexane/EtOAc = 2/1. The organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 20/1 to 10/1) afforded *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**) as a yellow solid in 84% yield (4.25 g, 12.6 mmol).

General procedure for addition of thiophosphinyl dithiocarbonate 2 to alkynes 1 (Table 1).

Under argon, a mixture of alkyne **1** (0.50 mmol), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**, 0.20 g, 0.60 mmol), and DLP (0.010 g, 0.025 mmol) was heated in boiling benzene (2.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Silica gel column chromatography (hexane/EtOAc) followed by GPC or recrystallization (if needed) afforded a 1-aryl-1-thio-2-thiophosphinylethene derivative **3** as a white or yellow solid ($E/Z > 99/1$). The *E* configuration of **3a** was assigned by X-ray analysis.

Double addition of thiophosphinyl dithiocarbonate 2 to 1l (Scheme 4).

Under argon, a mixture of *p*-diethynylbenzene (**1l**, 0.063 g, 0.50 mmol), *S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (**2**, 0.51 g, 1.5 mmol), and DLP (0.010 g, 0.025 mmol) was heated in boiling benzene (3.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Filtration with EtOAc followed by short column chromatography on silica gel ($CHCl_3$) afforded 1,4-bis{(*E*)-2-diphenylthiophosphinyl-1-(ethoxythiocarbonylsulfanyl)ethenyl}benzene (**3l**) as a pale yellow solid in 92% yield (0.37 g, 0.46 mmol).

General procedure for transformation of dithiocarbonates 3 to sulfides 5 (Table 2).

Transformation of **3a** to **5aa** is representative (Table 2, entry 1). Under argon, ground potassium hydroxide (0.056 g, 1.0 mmol) was added to a suspension of dithiocarbonate **3a** (0.088 g, 0.20 mmol) and iodomethane (**4a**, 0.062 mL, 1.0 mmol) in methanol (3.0 mL) at ambient temperature. After stirred for 30 min, the mixture was quenched with a diluted NaCl/NH_4Cl solution and extracted three times with hexane/EtOAc = 1/1. The organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 10/1) afforded {2-diphenylthiophosphinyl-1-(methylthio)ethenyl}benzene (**5aa**) as a white solid in 98% yield (0.072 g, 0.20 mmol, *E*/*Z* = 98/2).

Cross-coupling reaction of 5aa with diethylzinc (Scheme 5).

Under argon, diethylzinc (1.0 M hexane solution, 0.60 mL, 0.60 mmol) was added to a suspension of (*E*)-{2-diphenylthiophosphinyl-1-(methylthio)ethenyl}benzene (**5aa**, 0.073 g, 0.20 mmol) and $NiCl_2$(dppp) (0.016 g, 0.030 mmol) in CPME (3.0 mL) at 0 ˚C. The reaction was monitored by TLC. After 4.5 h, the mixture was quenched with diluted NaCl solution and extracted three times with EtOAc, dried over Na_2SO_4, filtered through a pad of florisil®, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 20/1 to 10/1) afforded 1-diphenylthiophosphinyl-2-phenyl-1-butene (**6**) as a white solid in 75% yield (0.052 g, 0.15 mmol, *Z*/*E* = 98/2) and 1-diphenylphosphino-2-phenyl-1-butene (**7**) in 14% yield (8.7 mg, 0.027 mmol, *Z*/*E* = 96/4).

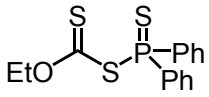
Desulfidation of vinylphosphine sulfide 6 (Scheme 5).

Under argon, a mixture of vinylphosphine sulfide **6** (0.035 g, 0.10 mmol), tris(trimethylsilyl)silane (0.062 mL, 0.20 mmol), and AIBN (3.2 mg, 0.020 mmol) was heated in boiling benzene (2.0 mL) for 4 h. After cooled to room temperature, the solvent was removed in vacuo. Silica gel column chromatography (hexane/EtOAc = 50/1 to 20/1) afforded 1-diphenylphosphino-2-phenyl-1-butene (**7**) as a colorless oil in 88% yield (0.028 g, 0.088 mmol,

Z/*E* = 98/2).

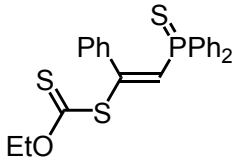
Characterization Data

***S*-diphenylthiophosphinyl *O*-ethyl dithiocarbonate (2)**



IR (neat) 1436, 1366, 1254, 1096, 1033, 722, 689, 653 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.00 (t, *J* = 7.0 Hz, 3H), 4.40 (q, *J* = 7.0 Hz, 2H), 7.47–7.52 (m, 4H), 7.53–7.58 (m, 2H), 7.95–8.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.65, 71.12, 128.67 (d, *J* = 13.4 Hz), 131.62 (d, *J* = 11.4 Hz), 132.23 (d, *J* = 2.9 Hz), 132.67 (d, *J* = 84.5 Hz), 204.27 (d, *J* = 4.4 Hz); ^{31}P NMR ($CDCl_3$) δ 59.46. Found: C, 53.36; H, 4.43%. Calcd for $C_{15}H_{15}OPS_3$: C, 53.23; H, 4.47%. m.p.: 58–59 ˚C.

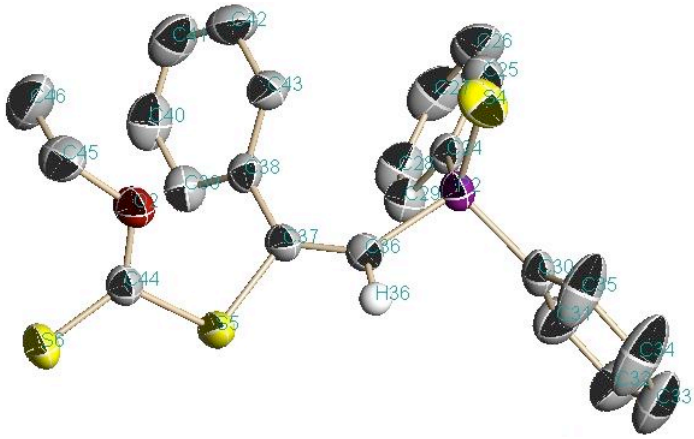
(*E*)-*S*-1-phenyl-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3a)



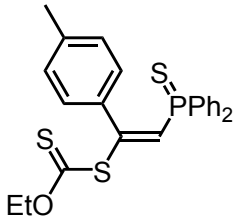
IR (Nujol) 1438, 1240, 1103, 1041 715, 693, 635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.07 (t, *J* = 7.0 Hz, 3H), 4.42 (q, *J* = 7.0 Hz, 2H), 6.96–7.01 (m, 2H), 7.02 (d, *J* = 15.5 Hz, 1H), 7.01–7.05 (m, 1H), 7.25–7.30 (m, 4H), 7.31–7.36 (m, 2H), 7.48–7.52 (m, 2H), 7.75–7.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.14, 70.53, 127.42, 128.27 (d, *J* = 12.9 Hz), 129.28, 129.65, 130.13 (d, *J* = 73.1 Hz), 131.27 (d, *J* = 3.4 Hz), 131.30 (d, *J* = 10.5 Hz), 132.03 (d, *J* = 86.0 Hz), 136.44 (d, *J* = 4.8 Hz), 149.15, 209.24 (d, *J* = 1.5 Hz); ^{31}P NMR ($CDCl_3$) δ 28.97. Found: C, 62.74; H, 5.04%. Calcd for $C_{23}H_{21}OPS_3$: C, 62.70; H, 4.80%. m.p.: 106–107 ˚C. The *E* configuration was determined by X-ray analysis. Crystallographic data for the structure has been deposited with the Cambridge Crystallographic Data Centre (CCDC 710609, Figure S1). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road,

Cambridge CB2, 1EZ, UK. Fax: 44-1223-336033 or E-mail: deposit@ccdc.cam.ac.uk

Figure S1. Ortep diagram of **3a**

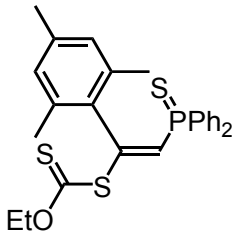


(*E*)-*S*-1-(4-methylphenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3b)



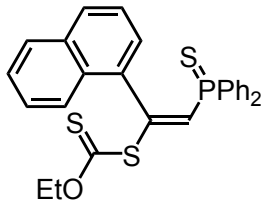
IR (Nujol) 1559, 1506, 1438, 1244, 1102, 1043, 827, 715, 631 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (t, *J* = 7.0 Hz, 3H), 2.16 (s, 3H), 4.43 (q, *J* = 7.0 Hz, 2H), 6.75–6.79 (m, 2H), 6.97 (d, *J* = 16.0 Hz, 1H), 7.25–7.30 (m, 4H), 7.32–7.38 (m, 4H), 7.75–7.82 (m, 4H) ^{13}C NMR ($CDCl_3$) δ 13.20, 21.19, 70.50, 128.03, 128.22 (d, *J* = 12.9 Hz), 129.55 (d, *J* = 74.0 Hz), 129.63, 131.11 (d, *J* = 2.9 Hz), 131.35 (d, *J* = 11.0 Hz), 132.22 (d, *J* = 85.9 Hz), 133.61 (d, *J* = 4.9 Hz), 139.49, 149.27, 209.53; ^{31}P NMR ($CDCl_3$) δ 29.11. Found: C, 63.27; H, 5.07%. Calcd for $C_{24}H_{23}OPS_3$: C, 63.41; H, 5.10%. m.p.: 123–124 ˚C.

(*E*)-*S*-1-mesityl-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3c)



IR (Nujol) 1436, 1245, 1104, 1031, 852, 712, 691, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.35 (t, *J* = 7.0 Hz, 3H), 2.13 (s, 3H), 2.16 (s, 6H), 4.68 (q, *J* = 7.0 Hz, 2H), 6.46 (d, *J* = 0.5 Hz, 2H), 7.24 (d, *J* = 15.5 Hz, 1H), 7.26–7.31 (m, 4H), 7.36–7.41 (m, 2H), 7.65–7.71 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.54, 20.27, 20.92, 70.48, 125.14 (d, *J* = 78.3 Hz), 128.05, 128.06 (d, *J* =12.9 Hz), 129.97 (d, *J* = 6.3 Hz), 131.04 (d, *J* = 2.9 Hz), 131.40 (d, *J* = 11.0 Hz), 132.41 (d, *J* = 86.4 Hz), 136.33, 138.72, 148.99 (d, *J* = 2.9 Hz), 208.48; ^{31}P NMR ($CDCl_3$) δ 29.83. Found: C, 64.65; H, 5.64%. Calcd for $C_{26}H_{27}OPS_3$: C, 64.70; H, 5.64%. m.p.: 93–94 ˚C.

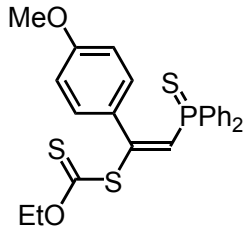
(*E*)-*S*-1-(1-naphthyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3d)



IR (Nujol) 1559, 1507, 1436, 1231, 1049, 1036, 798, 714, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.20 (dd, *J* = 7.0, 7.0 Hz, 3H), 4.48 (dq, *J* = 11.0, 7.0 Hz, 1H), 4.53 (dq, *J* = 11.0, 7.0 Hz, 1H), 6.75–6.80 (m, 2H), 6.85–6.90 (m, 1H), 7.20 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.26–7.32 (m, 2H), 7.32–7.40 (m, 3H), 7.37 (d, *J* = 16.5 Hz, 1H), 7.41–7.47 (m, 2H), 7.50–7.54 (m, 1H), 7.54–7.58 (m, 1H), 7.67 (dd, *J* = 7.0, 1.0 Hz, 1H) , 7.73–7.80 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 13.36, 70.56, 124.26, 125.40, 125.84, 126.11, 127.15 (d, *J* = 12.9 Hz), 128.08, 128.24 (d, *J* = 12.5 Hz), 129.30 (d, *J* = 1.4 Hz), 129.38 (d, *J* = 85.4 Hz), 129.89, 129.93 (d, *J* = 1.0 Hz), 130.21 (d, *J* = 2.9 Hz), 130.99 (d, *J* = 11.0 Hz), 131.10 (d, *J* = 10.0 Hz), 131.27 (d, *J* = 2.9 Hz), 132.53 (d, *J* = 5.8 Hz), 132.96, 133.07 (d, *J* = 86.9 Hz), 133.48 (d, *J* = 75.0 Hz), 147.43 (d, *J* = 1.5 Hz), 208.82 (d, *J* =

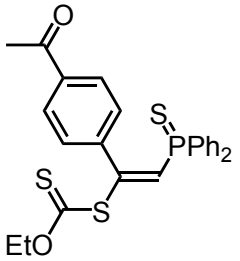
1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 29.31. Found: C, 66.25; H, 4.82%. Calcd for $C_{27}H_{23}OPS_3$: C, 66.10; H, 4.73% m.p.: 115–116 °C.

(*E*)-*S*-1-(4-methoxyphenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3e)



IR (Nujol) 1609, 1504, 1437, 1253, 1241, 1041, 834, 747, 712, 629 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, *J* = 7.0 Hz, 3H), 3.68 (s, 3H), 4.44 (q, *J* = 7.0 Hz, 2H), 6.48–6.52 (m, 2H), 6.91 (d, *J* = 16.0 Hz, 1H), 7.26–7.32 (m, 4H), 7.32–7.37 (m, 2H), 7.45–7.49 (m, 2H), 7.77–7.84 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.28, 55.23, 70.49, 112.81, 128.26 (d, *J* = 12.9 Hz), 128.72 (d, *J* = 74.0 Hz), 129.01 (d, *J* = 4.8 Hz), 131.21 (d, *J* = 3.3 Hz), 131.35 (d, *J* = 10.5 Hz), 131.39, 132.22 (d, *J* = 85.5 Hz), 148.88, 160.41, 209.71; ^{31}P NMR ($CDCl_3$) δ 29.09. Found: C, 61.25; H, 4.98%. Calcd for $C_{24}H_{23}O_2PS_3$: C, 61.25; H, 4.93%. m.p.: 105–106 °C.

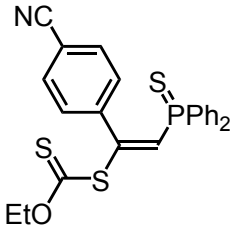
(*E*)-*S*-1-(4-acetylphenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3f)



IR (Nujol) 1681, 1436, 1247, 1099, 1037, 819, 708, 627 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, *J* = 7.0 Hz, 3H), 2.49 (s, 3H), 4.43 (q, *J* = 7.0 Hz, 2H), 7.13 (d, *J* = 15.5 Hz, 1H), 7.26–7.31 (m, 4H), 7.32–7.37 (m, 2H), 7.54–7.60 (m, 4H), 7.75–7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.25, 26.62, 70.70, 127.28, 128.38 (d, *J* = 12.9 Hz), 129.94, 131.33 (d, *J* = 11.0 Hz), 131.45 (d, *J* = 2.9 Hz), 131.81 (d, *J* = 86.9 Hz), 132.67 (d, *J* = 71.6 Hz), 137.01, 141.05 (d, *J* = 4.8 Hz), 147.53, 197.26, 208.53; ^{31}P NMR ($CDCl_3$) δ 28.73. Found: C, 62.35; H, 4.77%. Calcd for $C_{25}H_{23}O_2PS_3$:

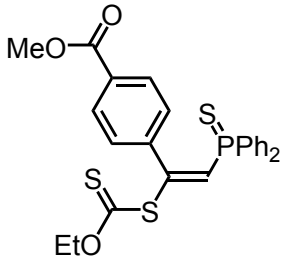
C, 62.22; H, 4.80%. m.p.: 102–103 ˚C.

(*E*)-*S*-1-(4-cyanophenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3g)



IR (Nujol) 2233, 1436, 1248, 1105, 1028, 901, 841, 716, 694, 636 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.14 (t, *J* = 7.0 Hz, 3H), 4.44 (q, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 15.0 Hz, 1H), 7.26–7.30 (m, 2H), 7.30–7.35 (m, 4H), 7.37–7.42 (m, 2H), 7.58–7.62 (m, 2H), 7.74–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.26, 70.82, 112.43, 118.16, 128.48 (d, *J* = 12.9 Hz), 130.30, 131.03, 131.28 (d, *J* = 10.9 Hz), 131.48 (d, *J* = 86.0 Hz), 131.67 (d, *J* = 2.8 Hz), 134.08 (d, *J* = 70.6 Hz), 141.09 (d, *J* = 4.8 Hz), 146.31, 208.10 (d, *J* = 1.5 Hz); ^{31}P NMR ($CDCl_3$) δ 28.41. Found: C, 61.97; H, 4.14%. Calcd for $C_{24}H_{20}NOPS_3$: C, 61.91; H, 4.33%. m.p.: 132–133 ˚C.

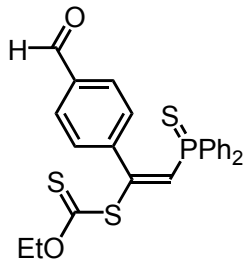
(*E*)-*S*-1-(4-methoxycarbonylphenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3h).



IR (Nujol) 1722, 1717, 1436, 1283, 1244, 1111, 1036, 707, 629 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.0 Hz, 3H), 3.88 (s, 3H), 4.41 (q, *J* = 7.0 Hz, 2H), 7.12 (d, *J* = 15.5 Hz, 1H), 7.26–7.32 (m, 4H), 7.33–7.38 (m, 2H), 7.52–7.56 (m, 2H), 7.63–7.67 (m, 2H), 7.74–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.22, 52.17, 70.67, 128.38 (d, *J* = 12.9 Hz), 128.57, 129.69, 130.30, 131.31 (d, *J* = 10.5 Hz), 131.47 (d, *J* = 2.9 Hz), 131.80 (d, *J* = 84.5 Hz), 132.31 (d, *J* = 71.6 Hz), 140.94 (d, *J* = 5.3 Hz), 147.77, 166.27, 208.49; ^{31}P NMR ($CDCl_3$) δ 28.65. Found: C, 60.16;

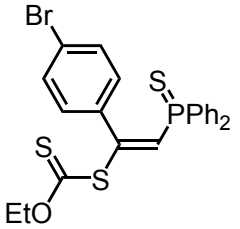
H, 4.75%. Calcd for $C_{25}H_{23}O_3PS_3$: C, 60.22; H, 4.65%. m.p.: 132–133 ˚C.

(*E*)-*S*-1-(4-formylphenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3i)



IR (Nujol) 1699, 1684, 1558, 1439, 1243, 1100, 1041, 825, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.11 (t, *J* = 7.0 Hz, 3H), 4.43 (q, *J* = 7.0 Hz, 2H), 7.17 (d, *J* = 15.5 Hz, 1H), 7.26–7.32 (m, 4H), 7.33–7.38 (m, 2H), 7.49–7.52 (m, 2H), 7.64–7.67 (m, 2H), 7.75–7.81 (m, 4H), 9.85 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.23, 70.74, 128.42 (d, *J* = 12.9 Hz), 128.60, 130.35 (d, *J* = 1.0 Hz), 131.31 (d, *J* = 10.5 Hz), 131.54 (d, *J* = 3.3 Hz), 131.69 (d, *J* = 86.0 Hz), 133.20 (d, *J* = 71.1 Hz), 136.11, 142.44 (d, *J* = 4.8 Hz), 147.23, 191.39 (d, *J* = 1.4 Hz), 208.34 (d, *J* = 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 28.61. Found: C, 61.35; H, 4.62%. Calcd for $C_{24}H_{21}O_2PS_3$: C, 61.52; H, 4.52%. m.p.: 110–111 ˚C.

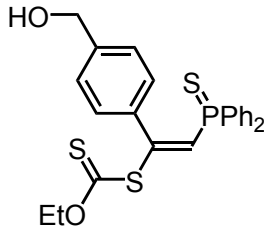
(*E*)-*S*-1-(4-bromophenyl)-2-(diphenylthiophosphinyl)ethenyl *O*-ethyl dithiocarbonate (3j)



IR (Nujol) 1480, 1436, 1264, 1248, 1107, 1030, 819, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (t, *J* = 7.0 Hz, 3H), 4.44 (q, *J* = 7.0 Hz, 2H), 7.06 (d, *J* = 15.5 Hz, 1H), 7.07–7.12 (m, 2H), 7.28–7.36 (m, 6H), 7.36–7.41 (m, 2H), 7.74–7.81 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.24, 70.67, 123.61, 128.36 (d, *J* = 12.4 Hz), 130.50, 131.18, 131.34 (d, *J* = 10.5 Hz), 131.41 (d, *J* = 2.9 Hz), 131.59 (d, *J* = 74.0 Hz), 131.75 (d, *J* = 87.4 Hz), 135.44 (d, *J* = 4.8 Hz), 147.60, 208.72; ^{31}P NMR ($CDCl_3$) δ 28.76. Found: C, 53.04; H, 3.74%. Calcd for $C_{23}H_{20}BrOPS_3$: C, 53.18; H, 3.88%.

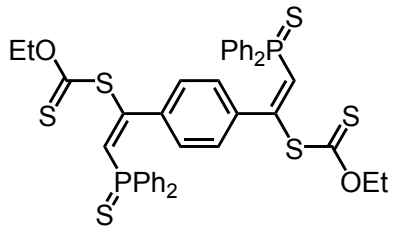
m.p.: 118–119 ˚C.

(*E*)-*S*-1-(4-hydroxymethylphenyl)-2-diphenylthiophosphinylethenyl *O*-ethyl dithiocarbonate (3k)



IR (Nujol) 3600–3300 (br), 1654, 1506, 1436, 1242, 1041, 826, 710, 692, 626 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 (t, *J* = 7.0 Hz, 3H), 1.50 (br s, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 4.51 (s, 2H), 6.96–7.00 (m, 2H), 7.03 (d, *J* = 16.0 Hz, 1H), 7.26–7.31 (m, 4H), 7.32–7.37 (m, 2H), 7.46–7.51 (m, 2H), 7.75–7.82 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.24, 64.70, 70.56, 125.73, 128.28 (d, *J* = 12.4 Hz), 129.94 (d, *J* = 1.0 Hz), 130.62 (d, *J* = 73.0 Hz), 131.21 (d, *J* = 3.4 Hz), 131.33 (d, *J* = 10.5 Hz), 132.14 (d, *J* = 85.9 Hz), 135.78 (d, *J* = 4.8 Hz), 142.05, 148.73, 209.20 (d, *J* =1.4 Hz); ^{31}P NMR ($CDCl_3$) δ 28.97. Found: C, 61.05; H, 4.90%. Calcd for $C_{24}H_{23}O_2PS_3$: C, 61.25; H, 4.93%. m.p.: 111–112 ˚C.

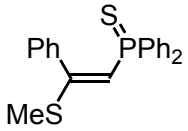
***p*-bis{(*E*)-1-ethoxythiocarbonylsulfanyl-2-(diphenylthiophosphinyl)ethenyl}benzene (3l)**



IR (Nujol) 1577, 1559, 1436, 1246, 1098, 1041, 846, 752, 715, 632 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.39 (t, *J* = 7.0 Hz, 6H), 4.62 (q, *J* = 7.0 Hz, 4H), 7.06 (s, 4H), 7.10 (d, *J* = 15.5 Hz, 2H), 7.24–7.29 (m, 8H), 7.31–7.36 (m, 4H), 7.71–7.78 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 13.70, 70.96, 128.34 (d, *J* = 12.9 Hz), 128.77, 131.29 (d, *J* = 10.5 Hz), 131.54 (d, *J* = 3.4 Hz), 131.86 (d, *J* = 85.9 Hz), 134.41 (d, *J* = 71.6 Hz), 136.99 (d, *J* = 4.8 Hz), 146.75, 209.85 (d, *J* = 1.9 Hz); ^{31}P

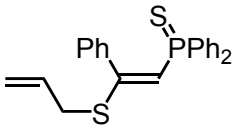
NMR ($CDCl_3$) δ 28.41. Found: C, 59.56; H, 4.47%. Calcd for $C_{40}H_{36}O_2P_2S_6$: C, 59.83; H, 4.52%. m.p.: 158–159 ˚C.

(*E*)-{1-methylthio-2-(diphenylthiophosphinyl)ethenyl}benzene (5aa)



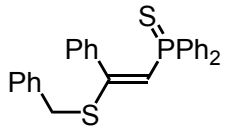
IR (Nujol) 1684, 1653, 1558, 1540, 1507, 1437, 1095, 715, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (s, 3H), 6.05 (d, *J* = 15.0 Hz, 1H), 6.97–7.01 (m, 2H), 7.03–7.08 (m, 1H), 7.24–7.29 (m, 6H), 7.29–7.34 (m, 2H), 7.73–7.80 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.40 (d, *J* = 1.5 Hz), 112.09 (d, *J* = 88.3 Hz), 127.59, 128.08 (d, *J* = 12.4 Hz), 128.91, 128.99 (d, *J* = 1.0 Hz), 130.78 (d, *J* = 2.9 Hz), 131.31 (d, *J* = 10.5 Hz), 133.72 (d, *J* = 85.9 Hz), 135.95 (d, *J* = 6.3 Hz), 159.89 (d, *J* = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 28.83. Found: C, 68.55; H, 5.25%. Calcd for $C_{21}H_{19}PS_2$: C, 68.82; H, 5.23%. m.p.: 106–107 ˚C. The *E* configuration of the major isomer was determined by NOE experiments.

(*E*)-{1-allylthio-2-(diphenylthiophosphinyl)ethenyl}benzene (5ab)



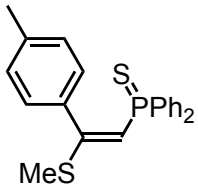
IR (Nujol) 1558, 1539, 1507, 1437, 1096, 906, 719, 632 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.43 (ddd, *J* = 6.5, 1.0, 1.0 Hz, 2H), 5.19–5.26 (m, 2H), 5.87 (ddt, *J* = 17.0, 10.0, 6.5 Hz, 1H), 6.25 (d, *J* = 15.5 Hz, 1H), 6.97–7.03 (m, 2H), 7.03–7.08 (m, 1H), 7.23–7.35 (m, 8H), 7.71–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 35.97, 114.35 (d, *J* = 86.0 Hz), 119.04, 127.59, 128.06 (d, *J* = 12.5 Hz), 128.97, 129.23 (d, *J* = 0.9 Hz), 130.80 (d, *J* = 2.9 Hz), 131.31 (d, *J* = 10.5 Hz), 131.76, 133.65 (d, *J* = 85.9 Hz), 135.70 (d, *J* = 6.3 Hz), 157.91 (d, *J* = 2.4 Hz); ^{31}P NMR ($CDCl_3$) δ 28.77. Found: C, 70.37; H, 5.37%. Calcd for $C_{23}H_{21}PS_2$: C, 70.38; H, 5.39%. m.p.: 81–82 ˚C.

(*E*)-{1-benzylthio-2-(diphenylthiophosphinyl)ethenyl}benzene (5ac)



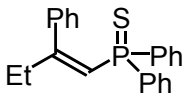
IR (Nujol) 1653, 1558, 1540, 1507, 1437, 1097, 906, 772, 719 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.05 (s, 2H), 6.17 (d, *J* = 15.0 Hz, 1H), 6.97–7.02 (m, 2H), 7.03–7.08 (m, 1H), 7.18–7.23 (m, 4H), 7.26–7.31 (m, 4H), 7.31–7.40 (m, 5H), 7.54–7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 35.57, 114.31 (d, *J* = 86.0 Hz), 127.60 (two signals overlapped), 128.03 (d, *J* = 12.4 Hz), 128.71, 128.82, 128.98, 129.23 (d, *J* = 0.9 Hz), 130.71 (d, *J* = 2.8 Hz), 131.21 (d, *J* = 11.0 Hz), 133.63 (d, *J* = 85.9 Hz), 135.18, 135.64 (d, *J* = 6.3 Hz), 157.86 (d, *J* = 2.4 Hz); ^{31}P NMR ($CDCl_3$) δ 28.55. Found: C, 72.97; H, 5.54%. Calcd for $C_{27}H_{23}PS_2$: C, 73.27; H, 5.24%. m.p.: 153–154 °C.

4-{(*E*)-1-methylthio-2-(diphenylthiophosphinyl)ethenyl}toluene (5ba)



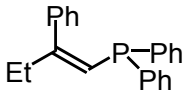
IR (Nujol) 1558, 1503, 1437, 1098, 914, 825, 752, 709, 629 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.17 (s, 3H), 2.36 (s, 3H), 6.01 (d, *J* = 15.5 Hz, 1H), 6.75–6.79 (m, 2H), 7.12–7.16 (m, 2H), 7.23–7.28 (m, 4H), 7.29–7.34 (m, 2H), 7.73–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 16.40 (d, *J* = 1.5 Hz), 21.14, 111.77 (d, *J* = 88.3 Hz), 127.99 (d, *J* = 12.4 Hz), 128.22, 128.89 (d, *J* = 1.0 Hz), 130.63 (d, *J* = 2.9 Hz), 131.34 (d, *J* = 10.5 Hz), 133.11 (d, *J* = 6.6 Hz), 133.81 (d, *J* = 86.0 Hz), 138.88, 160.03 (d, *J* = 2.9 Hz); ^{31}P NMR ($CDCl_3$) δ 29.03. Found: C, 69.37; H, 5.56%. Calcd for $C_{22}H_{21}PS_2$: C, 69.44; H, 5.56%. m.p.: 106–107 °C.

(*Z*)-1-diphenylthiophosphinyl-2-phenylbutene (6)



IR (Nujol) 1559, 1436, 1098, 725, 712, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.10 (t, *J* = 7.5 Hz, 3H), 2.57 (qdd, *J* = 7.5, 1.5, 0.5 Hz, 2H), 6.35 (d, *J* = 19.0, 1.5 Hz, 1H), 6.94–7.02 (m, 3H), 7.12–7.16 (m, 2H), 7.22–7.27 (m, 4H), 7.28–7.33 (m, 2H), 7.71–7.77 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 12.35, 35.14 (d, *J* = 15.8 Hz), 118.82 (d, *J* = 86.8 Hz), 127.47, 127.67, 128.01 (d, *J* = 12.4 Hz), 128.02 (d, *J* = 1.5 Hz), 130.66 (d, *J* = 2.8 Hz), 131.26 (d, *J* = 10.5 Hz), 133.48 (d, *J* = 85.4 Hz), 138.57 (d, *J* = 6.8 Hz), 162.87; ^{31}P NMR ($CDCl_3$) δ 28.44. Found: C, 75.96; H, 6.09%. Calcd for $C_{22}H_{21}PS$: C, 75.83; H, 6.08%. m.p.: 79–80 ˚C. The *Z* configuration of the major isomer was determined by NOE experiments.

(*Z*)-1-diphenylphosphino-2-phenylbutene (7)



IR (neat) 2966, 1585, 1478, 1433, 1095, 1026, 837, 742, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.09 (t, *J* = 7.5 Hz, 3H), 2.60 (qdd, *J* = 7.5, 1.5, 0.5 Hz, 2H), 6.25 (d, *J* = 3.5, 1.5 Hz, 1H), 7.17–7.20 (m, 2H), 7.26–7.33 (m, 9H), 7.36–7.41 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 13.00, 33.98 (d, *J* = 6.3 Hz), 123.41 (d, *J* = 7.6 Hz), 127.56, 127.80, 128.11, 128.21 (d, *J* = 3.8 Hz), 128.32 (d, *J* = 6.3 Hz), 132.56 (d, *J* = 18.1 Hz), 140.38 (d, *J* = 10.1 Hz), 141.11 (d, *J* = 7.6 Hz), 160.86 (d, *J* = 24.9 Hz); ^{31}P NMR ($CDCl_3$) δ –28.20. HRMS Found: 316.1382. Calcd for $C_{22}H_{21}P$: 316.1381 $[M]^{+}$. The *Z* configuration of the major isomer was determined by NOE experiments.

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Chapter 4

O-Alkyl *S*-3,3-Dimethyl-2-oxobutyl Dithiocarbonates as Versatile Sulfur-Transfer Agents in Radical C(sp^3)–H Functionalization

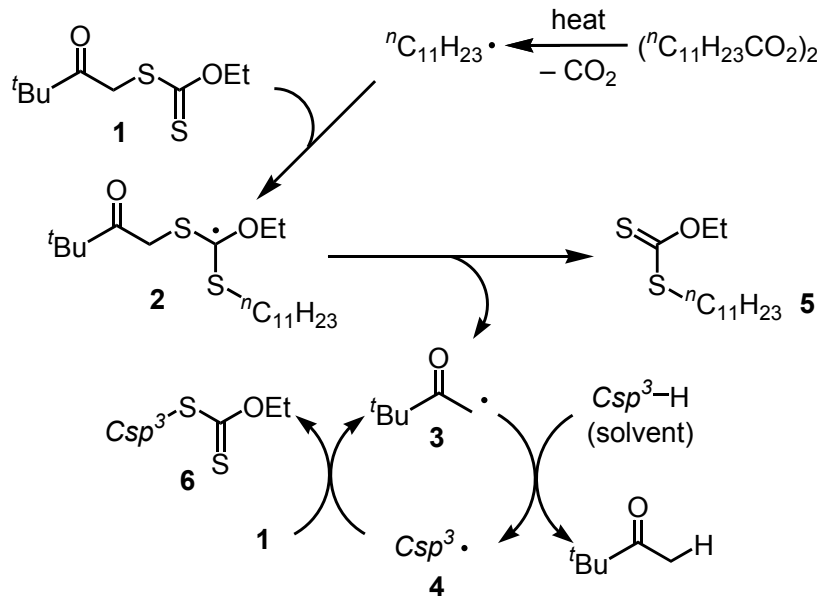
Boiling of the title compounds in ethereal solvents or cycloalkanes in the presence of a radical initiator leads to radical C(sp^3)–H functionalization, by which a sulfur atom is introduced into the ethereal solvents at the oxygenated carbon atom or into the cycloalkanes. The reaction is useful for the synthesis of monothioacetals, thiols, and sulfides from simple starting materials.

Introduction

Selective and efficient functionalizations of unreactive C–H bonds have been actively investigated.[1] Among them, functionalizations of C(sp^3)–H bonds are more difficult than those of C(sp^2)–H and C(sp)–H bonds because of the lack of a proximal π system. To realize the difficult C(sp^3)–H functionalization, radical processes are quite useful as they take advantage of homolytic hydrogen abstraction.[2] Although the formation of C–C[3] and C–O[4] bonds by intermolecular radical C–H functionalization is well-documented, examples to create carbon–other heteroatoms bonds such as C–N[5] and C–halogen[6] bonds are limited. Especially, there are few reports on C–S bond formation.[7–9] In Chapter 4, the author discloses new reagents for efficient C–S bond formation by radical C–H functionalization.

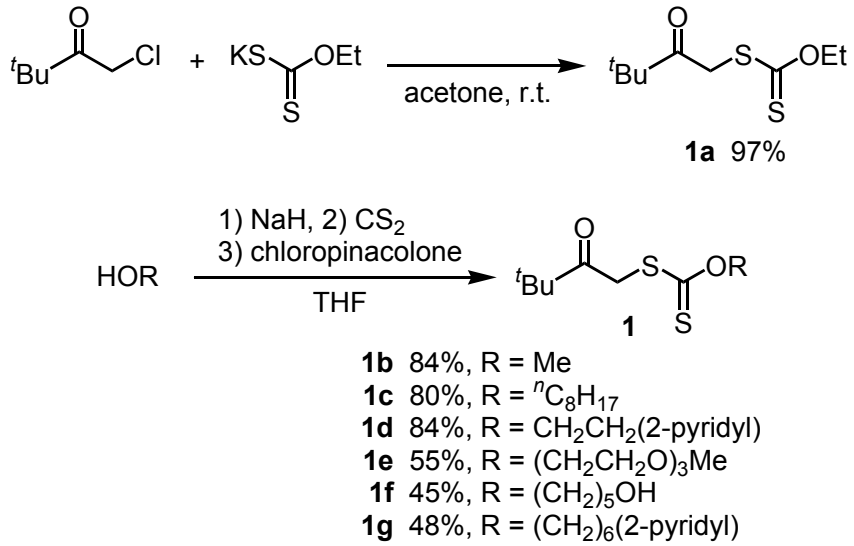
Results and Discussion

The new reagents **1** were designed based on the radical chemistry of dithiocarbonate (Scheme 1).[8,10] An undecyl radical, thermally generated from dilauroyl peroxide (DLP), would attack the sulfur atom of the thiocarbonyl group in **1** to generate the radical **2**. Liberation of the 3,3-dimethyl-2-oxobutyl radical **3** would then take place with concomitant formation of **5**. The electron-deficient radical **3** would be reactive enough to abstract hydrogen homolytically from a molecule of solvent such as ethers and cycloalkanes. The electron-rich radical **4** would react with **1** to complete the conversion of the initial C(sp^3)–H bond into a C(sp^3)–S bond and to regenerate **3**.



Scheme 1. The working hypothesis for C–S bond formation by radical C–H functionalization.

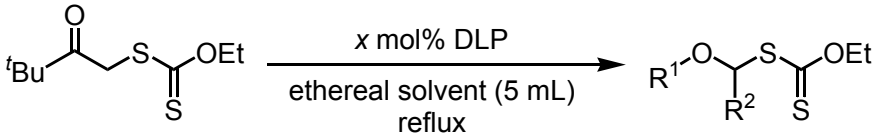
The preparation of **1** was facile. The reaction of chloropinacolone with potassium *O*-ethyl dithiocarbonate in acetone afforded **1a** quantitatively. Other dithiocarbonates **1b**–**1g** were prepared in moderate to good yields from the corresponding alcohols, carbon disulfide, and chloropinacolone in a one-pot manner (Scheme 2).



Scheme 2. Preparation of sulfur-transfer agents.

Dithiocarbonate **1a** was heated in boiling dioxane in the presence of a catalytic amount of DLP for 30 min to provide **6a** in 90% yield (Table 1, entry 1). The reaction of tetrahydropyran was less efficient and required a larger amount of the initiator as well as a longer reaction time (entry 2). The lower reactivity of tetrahydropyran could be due to the slower hydrogen-abstraction step[11] as well as its relatively low boiling point (88 ˚C). THF and acyclic dipropyl ether underwent the sulfur-transfer reaction smoothly (Table 1, entries 3 and 4). The regioselectivity in the reaction of 1,2-dimethoxyethane was moderate: a separable mixture of **6e** and **6f** in the ratio 71:29 was produced in high combined yield (entry 5). Sulfur transfer to diethyl ether was difficult due to its low boiling point (entry 7). This difficulty could be overcome by performing the reaction in a sealed vial with microwave heating at 100 ˚C (entry 8). Microwave heating in a sealed vial was also applicable to the carbon–deuterium bond activation of THF-d_8, wherein a considerable kinetic isotope effect was observed (entries 9 and 10). The conversion of THF-d_8 is useful for the synthesis of deuterated tetrahydrofuran derivatives such as γ-butyrolactone-d_6.[12]

Table 1. C–S bond formation by using sulfur-transfer agents **1a** through radical C–H functionalization of ethereal solvents.



1a (0.20 mmol) **6**

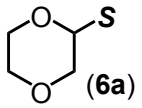
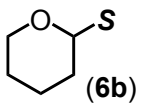
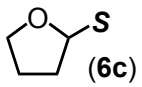
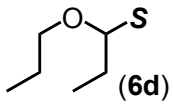
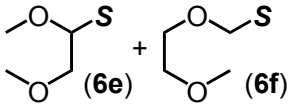
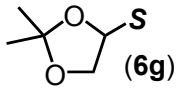
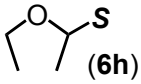
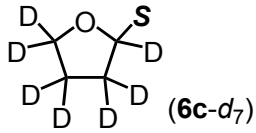
entry	solvent	*x*	b.p. /°C	time /min	product	yield /%[a]
1	1,4-dioxane	10	101	30	 (**6a**)	90
2	tetrahydropyran	20	88	100	 (**6b**)	76
3	THF	10	66	120	 (**6c**)	90

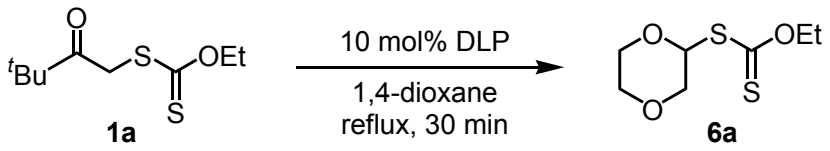
Table 1. (continued)

entry	solvent	*x*	b.p. /°C	time /min	product	yield /%[a]
4	dipropyl ether	15	88	120	 (**6d**)	69
5	1,2-dimethoxyethane	10	84	100	 (**6e**) + (**6f**)	93 (71/29)[b]
6	2,2-dimethyl-1,3-dioxolane	10	92	120	 (**6g**)	77
7	diethyl ether	20[c]	34	180	 (**6h**)	2
8	diethyl ether	10	100[d]	60	**6h**	69
9	THF-d_8	10	66	120	 (**6c**-d_7)	15
10	THF-d_8	15	120[d]	60	**6c**-d_7	79

[a] Isolated yield based on **1a**. [b] The ratio of **6e** to **6f**. [c] Triethylborane was used instead of DLP. [d] Microwave heating in a sealed vial. ***S*** = SC(S)OEt.

The above reaction should be performed under highly diluted conditions (Table 2). Although reaction with a concentration of 0.040 M provided a 90% yield of **6a** (entry 1), reaction with a concentration of 0.10 M resulted in a slight decrease in yield (entry 2). A much higher concentration, 1.0 M, led to unsatisfactory yield with the recovery of a large amount of **1a** (entry 3). The use of benzene as a cosolvent to minimize the amount of dioxane resulted in failure (entry 4). The reaction can be performed on a large scale to provide **6a** in excellent yield with 90% recovery of dioxane by simple evaporation (entry 5).

Table 2. Effect of concentration and scale on the reaction in dioxane.

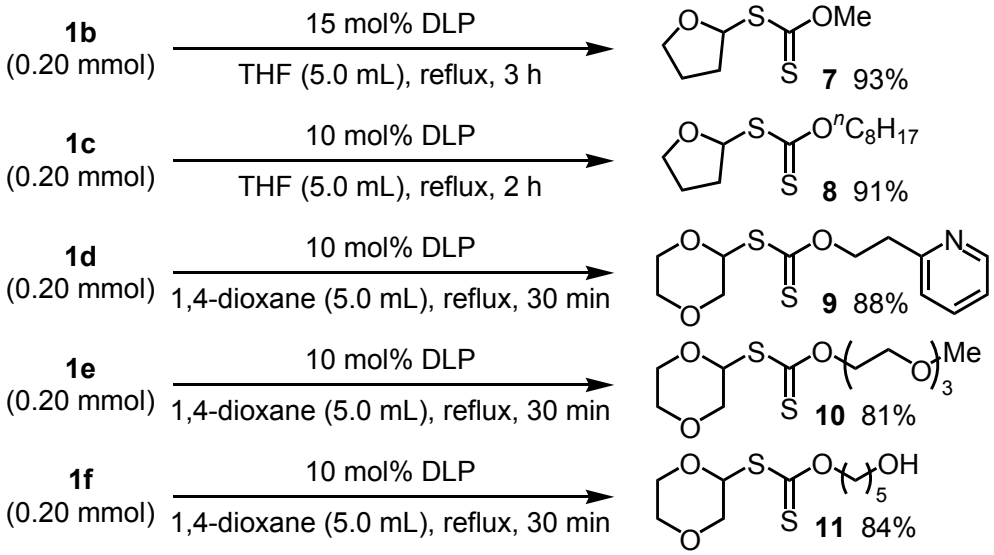


entry	**1a** /mmol	dioxane /mL	[**1a**] /M	yield /%	recovered **1a** /%
1	0.20	5.0	0.040	90	0
2	2.0	20	0.10	83	3
3	1.0	1.0	1.0	19	70
4	0.20	0.40	0.037[a]	6	90
5	20	500[b]	0.040	88	0

[a] Benzene (5.0 mL) was used as a cosolvent.

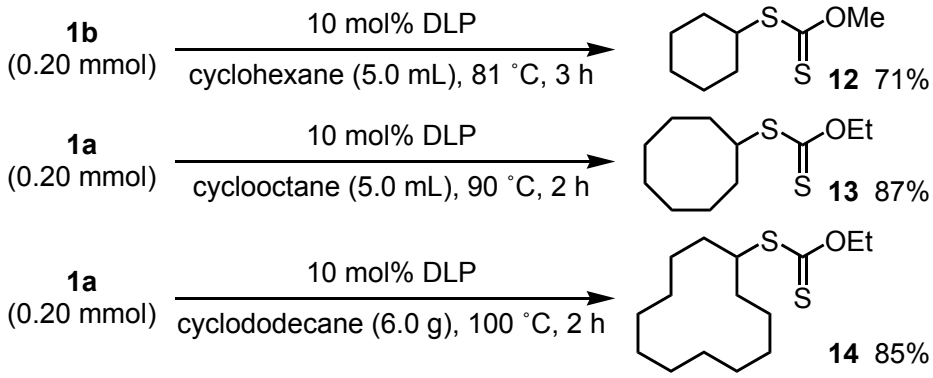
[b] Dioxane (450 mL, 90%) was recovered.

Apart from **1a**, dithiocarbonates **1b**–**1f** also affected sulfur transfer to ethereal solvents (Scheme 3). Owing to the high chemoselectivity of the radical reaction, the basic pyridyl group of **1d** and the hydroxy group of **1f** did not influence the efficiency of the reaction.



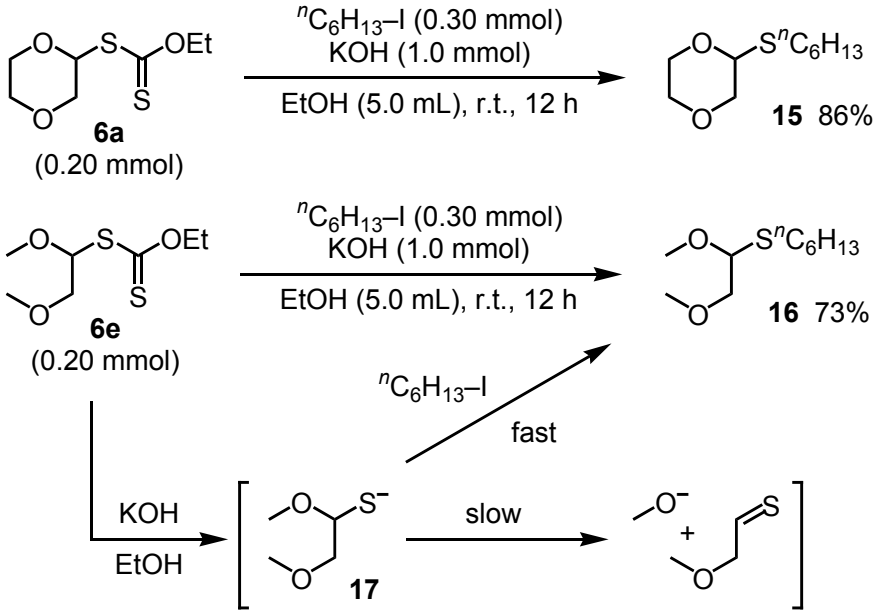
Scheme 3. Reactions with other sulfur-transfer agents.

The sulfur-transfer reaction from **1** to cycloalkanes provides a mild and efficient way for the synthesis of cycloalkanethiol derivatives (Scheme 4). Although a large excess of cycloalkane was necessary, it can be recovered. For instance, when cyclododecane was used, it was recovered in 98% yield. The reaction of other alkanes such as hexane and methylcyclohexane proceeded, albeit with little regioselectivity.



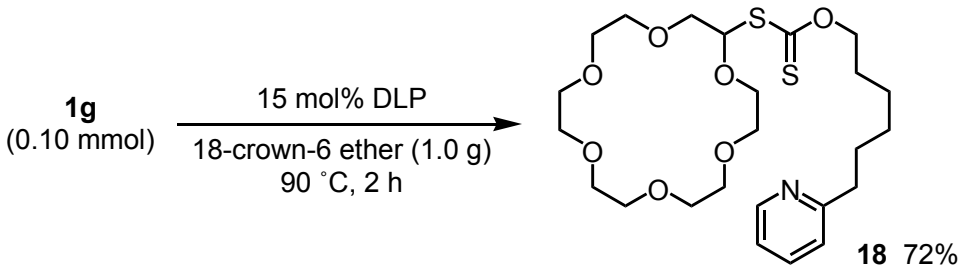
Scheme 4. C–H functionalization of cycloalkanes.

The transformations of dithiocarbonates **6a** and **6e** were examined (Scheme 5). These compounds were converted into hexylthioacetals **15** and **16**, respectively, by the action of potassium hydroxide and 1-iodohexane[13] in ethanol. Notably, the possible fragmentation of intermediate **17** was slow enough to allow it to react with 1-iodohexane.



Scheme 5. Transformations of products **6**.

The present method was applied to the functionalization of 18-crown-6 ether (Scheme 6). Owing to the involatile and highly polar nature of the crown ether, the isolation of **18** required size-exclusion chromatography. Although the expensive crown ether was used as a solvent, 92% of it was recovered during the purification procedure. The product **18** is a new "lariat ether"[14] that would interact more strongly with cations than the parent crown ether. By taking advantage of the variability of the *O*-alkyl group, this procedure offers a new method for the synthesis of crown ethers with a functionalized side arm.



Scheme 6. Functionalization of 18-crown-6 ether.

Conclusion

The author has developed an efficient sulfur-transfer agent. The reagent enables direct functionalization of carbon(sp^3)–hydrogen bonds of ethereal solvents and cycloalkanes to produce monothioacetals, thiols, and sulfides.

Experimental Section

General

Unless otherwise noted, all reactions were carried out with conventional glassware. Microwave-assisted reactions were performed with a focused microwave unit (Biotage Initiator™). The maximum irradiation power is 400 W. Each reaction was run in a 5-mL glass pressure vial, which is a commercially available and special vial for the Biotage Initiator™. It took 2–3 min to reach the indicated temperatures. After that, controlled microwave irradiation started and was continued for 60 min to keep the reaction temperature constant.

Materials

Ethereal solvents (except THF and diethyl ether) and 18-crown-6 ether were purchased from Wako Pure Chemicals just prior to use and were used as received. Cycloalkanes were obtained from TCI.

Preparation of *O*-ethyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (1a) (Scheme 2).

Under argon, potassium *O*-ethyl dithiocarbonate (0.96 g, 6.0 mmol) was added to a solution of 1-chloro-3,3-dimethyl-2-butanone (chloropinacolone, 0.66 mL, 5.0 mmol) in acetone (15 mL). The mixture was stirred for 1 h at ambient temperature. The mixture was poured into water (20 mL) and extracted with hexane/EtOAc = 5/1 three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column

chromatography (hexane/EtOAc = 5/1) afforded *O*-ethyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (**1a**) as a pale yellow oil in 97% yield (1.1 g, 4.9 mmol).

Preparation of *O*-alkyl dithiocarbonates 1b–1g (Scheme 2).

Preparation of *O*-methyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (**1b**) is representative. Under argon, methanol (0.33 mL, 8.0 mmol) was added to a suspension of sodium hydride (60 wt% in oil, 0.24 g, 6.0 mmol) in THF (10 mL). The mixture was stirred for 40 min at ambient temperature. Then carbon disulfide (0.48 mL, 8.0 mmol) in THF (5 mL) was added to the mixture at 0 ˚C and the mixture was soon warmed up to room temperature. After 2 h, 1-chloro-3,3-dimethyl-2-butanone (0.66 mL, 5.0 mmol) was added to the mixture at 0 ˚C and the mixture was soon warmed up to room temperature. After an additional 3 h, the mixture was poured into water (20 mL). The product was extracted with hexane/EtOAc = 5/1 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 20/1 to 10/1) afforded *O*-methyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (**1b**) as a yellow oil in 84% yield (0.87 g, 4.2 mmol).

General procedure for transformation of C–H bonds of solvents to C–S bonds (Table 1, Schemes 3 and 4).

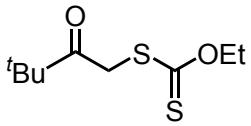
Synthesis of *O*-ethyl *S*-2-oxacyclopentyl dithiocarbonate (**6c**) is representative (Table 1, entry 3). Under argon, a solution of *O*-ethyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (**1a**, 0.044 g, 0.20 mmol) and DLP (8.0 mg, 0.020 mmol) in THF (5.0 mL) was stirred for 2 h at reflux. The mixture was cooled to room temperature, then diluted with acetone, dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 20/1 to 10/1) afforded *O*-ethyl *S*-2-oxacyclopentyl dithiocarbonate (**6c**) as a yellow oil in 90% yield (0.034 g, 0.18 mmol).

Transformation of dithiocarbonates to sulfides (Scheme 5).

Synthesis of 2-hexylthio-1,4-dioxane (**15**) is representative. Under argon, ground potassium hydroxide (0.056 g, 1.0 mmol) was added to a solution of *O*-ethyl *S*-2,5-dioxacyclohexyl dithiocarbonate (**6a**, 0.042 g, 0.020 mmol) and 1-iodohexane (0.044 mL, 0.030 mL) in ethanol (5.0 mL). The mixture was stirred for 12 h at ambient temperature. The mixture was poured into water (10 mL). The product was extracted with hexane/EtOAc = 10/1 three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 10/1) afforded 2-hexylthio-1,4-dioxane (**15**) as a colorless oil in 86% yield (0.036 g, 0.018 mmol).

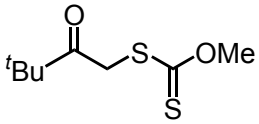
Characterization Data

***O*-ethyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (1a)**



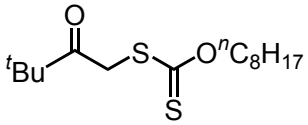
IR (neat) 2969, 1716, 1477, 1366, 1223, 1114, 1047, 1001 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.41 (t, *J* = 7.0 Hz, 3H), 4.28 (s, 2H), 4.63 (q, *J* = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.76, 26.67, 42.58, 44.36, 70.48, 207.34, 213.85. Found: C, 49.15; H, 7.11%. Calcd for $C_9H_{16}O_2S_2$: C, 49.06; H, 7.32%.

***O*-methyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (1b)**



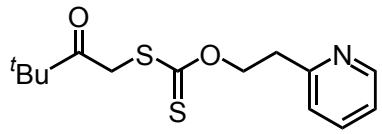
IR (neat) 2969, 1717, 1477, 1437, 1367, 1226, 1157, 1071, 1053, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 4.17 (s, 3H), 4.29 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 26.64, 42.87, 44.36, 60.52, 207.30, 214.68. Found: C, 46.63; H, 6.67%. Calcd for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84%.

_S_-3,3-dimethyl-2-oxobutyl _O_-octyl dithiocarbonate (1c)



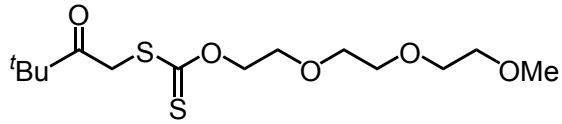
IR (neat) 2959, 2921, 2854, 1717, 1467, 1347, 1248, 1232, 1087, 1046 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.25 (s, 9H), 1.22–1.36 (m, 8H), 1.36–1.43 (m, 2H), 1.75–1.82 (m, 2H), 4.28 (s, 2H), 4.56 (t, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.60, 25.83, 26.67, 28.19, 29.11, 29.14, 31.73, 42.61, 44.37, 74.76, 207.38, 213.99. Found: C, 59.22; H, 9.34%. Calcd for $C_{15}H_{28}O_2S_2$: C, 59.16; H, 9.27%.

_S_-3,3-dimethyl-2-oxobutyl _O_-2-(2-pyridyl)ethyl dithiocarbonate (1d)



IR (neat) 2968, 1716, 1592, 1476, 1437, 1367, 1228, 1214, 1072, 1051, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.22 (s, 9H), 3.27 (t, J = 7.0 Hz, 2H), 4.24 (s, 2H), 4.97 (t, J = 7.0 Hz, 2H), 7.17 (ddd, J = 7.5, 5.0, 1.0 Hz, 1H), 7.22 (ddd, J = 7.5, 1.0, 1.0 Hz, 1H), 7.63 (ddd, J = 7.5, 7.5, 2.0 Hz, 1H), 8.55 (ddd, J = 5.0, 2.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 26.56, 36.77, 42.57, 44.27, 72.99, 121.75, 123.49, 136.46, 149.48, 157.29, 207.30, 213.54. Found: C, 56.79; H, 6.42%. Calcd for $C_{14}H_{19}NO_2S_2$: C, 56.53; H, 6.44%.

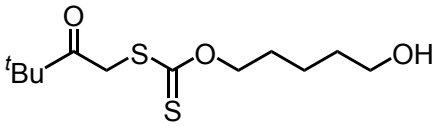
_S_-3,3-dimethyl-2-oxobutyl _O_-3,6,9-trioxadecyl dithiocarbonate (1e)



IR (neat) 2968, 2875, 1717, 1478, 1366, 1221, 1109, 1053, 1000 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 3.39 (s, 3H), 3.55–3.58 (m, 2H), 3.65–3.71 (m, 6H), 3.82–3.86 (m, 2H), 4.29 (s, 2H), 4.69–4.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 26.60, 42.73, 44.30, 58.97, 68.36, 70.53, 70.54, 70.68, 71.86, 73.13, 207.22, 213.92. Found: C, 49.42; H, 7.76%. Calcd for $C_{14}H_{26}O_5S_2$: C, 49.68;

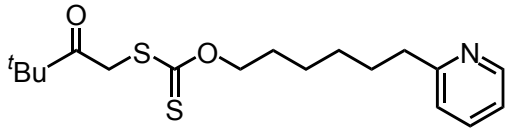
H, 7.74%.

***O*-5-hydroxypentyl *S*-3,3-dimethyl-2-oxobutyl dithiocarbonate (1f)**



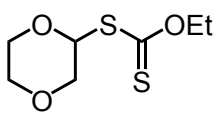
IR (neat) 3368 (br), 2938, 2869, 1714, 1477, 1367, 1229, 1048, 1001 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.46–1.53 (m, 2H), 1.55–1.66 (m, 3H), 1.80–1.87 (m, 2H), 3.67 (t, *J* = 6.5 Hz, 2H), 4.28 (s, 2H), 4.59 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 22.15, 26.64, 27.96, 32.16, 42.61, 44.34, 62.53, 74.40, 207.43, 213.96. Found: C, 51.94; H, 8.13%. Calcd for $C_{12}H_{22}O_3S_2$: C, 51.77; H, 7.96%.

***S*-3,3-dimethyl-2-oxobutyl *O*-6-(2-pyridyl)hexyl dithiocarbonate (1g)**



IR (neat) 2934, 2858, 1717, 1590, 1475, 1434, 1366, 1227, 1049, 999, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 9H), 1.37–1.49 (m, 4H), 1.70–1.83 (m, 4H), 2.79 (t, *J* = 7.5 Hz, 2H), 4.28 (s, 2H), 4.55 (t, *J* = 7.0 Hz, 2H), 7.10 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.14 (ddd, *J* = 7.5, 1.0, 1.0 Hz, 1H), 7.59 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 8.53 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.69, 26.67, 28.09, 28.86, 29.62, 38.25, 42.65, 44.37, 74.61, 120.91, 122.69, 136.24, 149.24, 162.17, 207.38, 214.02. Found: C, 61.27; H, 7.93%. Calcd for $C_{18}H_{27}NO_2S_2$: C, 61.15; H, 7.70%.

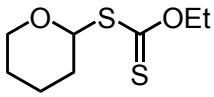
***O*-ethyl *S*-2,5-dioxacyclohexyl dithiocarbonate (6a)**



IR (neat) 2967, 2920, 2855, 1447, 1220, 1111, 1045, 893, 869 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44

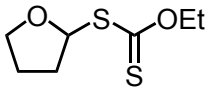
(t, *J* = 7.5 Hz, 3H), 3.70–3.81 (m, 3H), 3.88 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.04 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.07–4.13 (m, 1H), 4.63–4.73 (m, 2H), 5.92 (dd, *J* = 3.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.70, 63.55, 66.65, 69.71, 70.29, 84.22, 211.73. Found: C, 40.59; H, 5.67%. Calcd for $C_7H_{12}O_3S_2$: C, 40.36; H, 5.81%.

***O*-ethyl *S*-2-oxacyclohexyl dithiocarbonate (6b)**



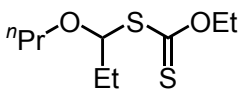
IR (neat) 2941, 2859, 1441, 1218, 1105, 1057, 1038, 1010, 882, 714 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (t, *J* = 7.0 Hz, 3H), 1.58–1.70 (m, 2H), 1.70–1.77 (m, 2H), 1.84–1.91 (m, 1H), 2.02–2.10 (m, 1H), 3.70–3.76 (m, 1H), 3.93–3.99 (m, 1H), 4.61-4.72 (m, 2H), 5.89 (dd, *J* = 5.5, 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.73, 21.56, 25.31, 30.70, 65.55, 69.90, 86.11, 212.43. Found: C, 46.81; H, 6.89%. Calcd for $C_8H_{14}O_2S_2$: C, 46.57; H, 6.84%.

***O*-ethyl *S*-2-oxacyclopentyl dithiocarbonate (6c)**



IR (neat) 2980, 2871, 1458, 1364, 1292, 1219, 1112, 1042, 933 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (t, *J* = 7.5 Hz, 3H), 1.90–2.13 (m, 3H), 2.37–2.46 (m, 1H), 3.90–4.02 (m, 2H), 4.61–4.73 (m, 2H), 6.17 (dd, *J* = 7.5, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.73, 24.62, 31.74, 68.41, 69.64, 88.34, 213.22. Found: C, 43.99; H, 6.31%. Calcd for $C_7H_{12}O_2S_2$: C, 43.72; H, 6.29%.

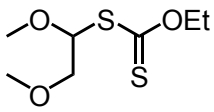
***O*-ethyl *S*-1-propoxypropyl dithiocarbonate (6d)**



IR (neat) 2965, 2936, 2877, 1462, 1208, 1108, 1053, 1011, 916 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.56–1.64 (m, 2H),

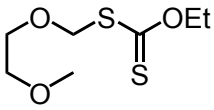
1.92–2.04 (m, 2H), 3.45 (dt, *J* = 9.5, 6.5 Hz, 1H), 3.69 (dt, *J* = 9.5, 6.5 Hz, 1H), 4.61–4.70 (m, 2H), 5.49 (dd, *J* = 6.5, 5.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 10.19, 10.58, 13.75, 22.61, 29.84, 69.57, 71.15, 93.84, 214.58. Found: C, 48.89; H, 7.95%. Calcd for $C_9H_{18}O_2S_2$: C, 48.61; H, 8.16%.

_O_-ethyl _S_-1,2-dimethoxyethyl dithiocarbonate (6e)



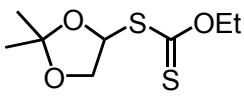
IR (neat) 2988, 2931, 2829, 1457, 1448, 1215, 1111, 1048 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (t, *J* = 7.5 Hz, 3H), 3.45 (s, 3H), 3.52 (s, 3H), 3.70–3.77 (m, 2H), 4.62–4.72 (m, 2H), 5.66 (dd, *J* = 6.5, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.71, 57.46, 59.42, 69.98, 74.48, 91.84, 213.26. Found: C, 40.26; H, 6.51%. Calcd for $C_7H_{14}O_3S_2$: C, 39.98; H, 6.71%.

_O_-ethyl _S_-2,5-dioxahexyl dithiocarbonate (6f)



IR (neat) 2982, 2924, 1454, 1366, 1308, 1221, 1101, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (t, *J* = 7.0 Hz, 3H), 3.38 (s, 3H), 3.54–3.57 (m, 2H), 3.71–3.74 (m, 2H), 4.68 (q, *J* = 7.0 Hz, 2H), 5.40 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.72, 59.03, 68.93, 70.22, 71.42, 76.75 (overlapped with the signal of $CDCl_3$), 213.06. Found: C, 40.15; H, 6.70%. Calcd for $C_7H_{14}O_3S_2$: C, 39.98; H, 6.71%.

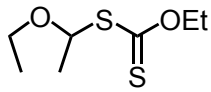
_O_-ethyl _S_-3,3-dimethyl-2,4-dioxacyclopentyl dithiocarbonate (6g)



IR (neat) 2988, 2937, 1453, 1383, 1373, 1222, 1147, 1114, 1066, 1044, 952, 837 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (d, *J* =1.0 Hz, 3H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.48 (d, *J* = 1.0 Hz, 3H), 4.21

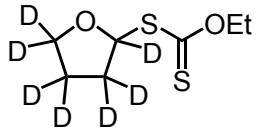
(dd, *J* = 9.5, 3.0 Hz, 1H), 4.43 (dd, *J* = 9.5, 5.5 Hz, 1H), 4.64 (dq, *J* = 10.5, 7.0 Hz, 1H), 4.67 (dq, *J* = 10.5, 7.0 Hz, 1H), 6.15 (dd, *J* = 5.5, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.73, 25.57, 26.26, 69.73, 70.44, 84.77, 111.97, 212.57. Found: C, 43.10; H, 6.59%. Calcd for $C_8H_{14}O_3S_2$: C, 43.22; H, 6.34%.

_S_-1-ethoxyethyl _O_-ethyl dithiocarbonate (6h)



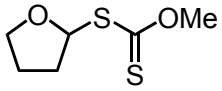
IR (neat) 2978, 2930, 1444, 1374, 1252, 1212, 1107, 1052 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, *J* = 7.0 Hz, 3H), 1.43 (t, *J* = 7.0 Hz, 3H), 1.69 (d, *J* =6.5 Hz, 3H), 3.57 (dq, *J* = 9.5, 7.0 Hz, 1H), 3.77 (dq, *J* = 9.5, 7.0 Hz, 1H), 4.61–4.70 (m, 2H), 5.63 (q, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.74, 14.90, 22.91, 64.92, 69.56, 88.16, 214.12. Found: C, 43.16; H, 7.06%. Calcd for $C_7H_{14}O_2S_2$: C, 43.27; H, 7.26%.

_S_-1,3,3,4,4,5,5-heptadeutero-2-oxacyclopentyl _O_-ethyl dithiocarbonate (6c-_d_$_7$)



IR (neat) 2982, 2239, 1221, 1114, 1062, 1044, 1004, 972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (t, *J* = 7.0 Hz, 3H), 4.65 (dq, *J* = 11.0, 7.0 Hz, 1H), 4.69 (dq, *J* = 11.0, 7.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.71, 23.56 (quint, *J* = 20.3 Hz), 30.87 (quint, *J* = 20.3 Hz), 67.62 (quint, *J* = 22.3 Hz), 69.59, 87.96 (t, *J* = 26.8 Hz), 213.20. Found: C, 41.99; H+D, 9.54%. Calcd for $C_7H_5D_7O_2S_2$: C, 42.18; H+D, 9.60%.

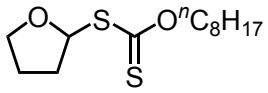
_O_-methyl _S_-2-oxacyclopentyl dithiocarbonate (7)



IR (neat) 2980, 2943, 2879, 1436, 1223, 1153, 1049, 924 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.91–2.12

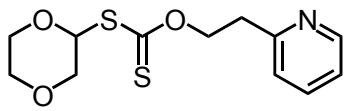
(m, 3H), 2.37–2.46 (m, 1H), 3.91–4.03 (m, 2H), 4.20 (s, 3H), 6.17 (dd, *J* = 7.5, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 24.60, 31.71, 59.85, 68.44, 88.49, 213.97. Found: C, 40.65; H, 5.54%. Calcd for $C_6H_{10}O_2S_2$: C, 40.42; H, 5.65%.

***O*-octyl *S*-2-oxacyclopentyl dithiocarbonate (8)**



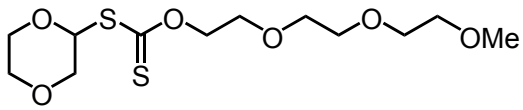
IR (neat) 2925, 2855, 1460, 1224, 1043, 934 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.22–1.37 (m, 8H), 1.37–1.45 (m, 2H), 1.77–1.84 (m, 2H), 1.90–2.12 (m, 3H), 2.36–2.46 (m, 1H), 3.90–4.02 (m, 2H), 4.54–4.64 (m, 2H), 6.16 (dd, *J* = 7.5, 3.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.61, 24.61, 25.84, 28.14, 29.11, 29.13, 31.73, 31.77, 68.40, 73.91, 88.26, 213.35. Found: C, 56.68; H, 8.50%. Calcd for $C_{13}H_{24}O_2S_2$: C, 56.48; H, 8.75%.

***S*-2,5-dioxacyclohexyl *O*-2-(2-pyridyl)ethyl dithiocarbonate (9)**



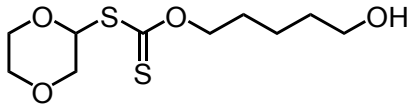
IR (neat) 2967, 2855, 1592, 1475, 1438, 1229, 1214, 1126, 1056, 893, 869 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.30 (t, *J* = 7.0 Hz, 2H), 3.66–3.77 (m, 3H), 3.83 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.98 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.03–4.09 (m, 1H), 5.00 (t, *J* = 7.0 Hz, 2H), 5.83 (dd, *J* = 3.5, 3.0 Hz, 1H), 7.17 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.23 (ddd, *J* = 7.5, 1.0, 1.0 Hz, 1H), 7.63 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 8.56 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 36.81, 63.64, 66.63, 69.65, 72.91, 84.08, 121.82, 123.53, 136.48, 149.59, 157.35, 211.50. Found: C, 50.76; H, 5.36%. Calcd for $C_{12}H_{15}NO_3S_2$: C, 50.50; H, 5.30%.

_S_-2,5-dioxacyclohexyl _O_-3,6,9-trioxadecyl dithiocarbonate (10)



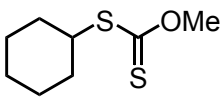
IR (neat) 2873, 1450, 1240, 1221, 1126, 1109, 1057, 894, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.39 (s, 3H), 3.55–3.58 (m, 2H), 3.64–3.69 (m, 4H), 3.69–3.74 (m, 3H), 3.75–3.80 (m, 2H), 3.85–3.91 (m, 3H), 4.04 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.07–4.13 (m, 1H), 4.70–4.79 (m, 2H), 5.92 (dd, *J* = 3.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 59.05, 63.58, 66.68, 68.40, 69.75, 70.61, 70.64, 70.77, 71.93, 72.97, 84.45, 211.96. Found: C, 44.27; H, 6.82%. Calcd for $C_{12}H_{22}O_6S_2$: C, 44.15; H, 6.79%.

_O_-5-hydroxypentyl _S_-2,5-dioxacyclohexyl dithiocarbonate (11)



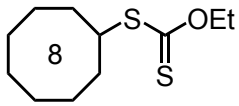
IR (neat) 3398 (br), 2938, 2861, 1457, 1232, 1126, 1049, 893, 868 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.44 (br, 1H), 1.47–1.55 (m, 2H), 1.59–1.68 (m, 2H), 1.82–1.90 (m, 2H), 3.67 (t, *J* = 6.0 Hz, 2H), 3.69–3.80 (m, 3H), 3.88 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.03 (dd, *J* = 12.0, 3.0 Hz, 1H), 4.08–4.15 (m, 1H), 4.63 (t, *J* = 6.5 Hz, 2H), 5.91 (dd, *J* = 3.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.16, 27.89, 32.13, 62.54, 63.54, 66.66, 69.65, 74.15, 84.10, 211.73. Found: C, 45.12; H, 6.66%. Calcd for $C_{10}H_{18}O_4S_2$: C, 45.09; H, 6.81%.

_S_-cyclohexyl _O_-methyl dithiocarbonate (12)



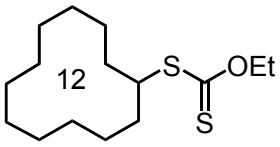
IR (neat) 2933, 2854, 1448, 1435, 1218, 1151, 1078, 1067, 998 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23–1.35 (m, 1H), 1.38–1.53 (m, 4H), 1.58–1.66 (m, 1H), 1.71–1.80 (m, 2H), 2.02–2.11 (m, 2H), 3.63–3.70 (m, 1H), 4.16 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 25.51, 25.92, 32.25, 49.07, 59.67, 215.41. Found: C, 50.49; H, 7.16%. Calcd for $C_8H_{14}OS_2$: C, 50.49; H, 7.41%.

_S_-cyclooctyl _O_-ethyl dithiocarbonate (13)



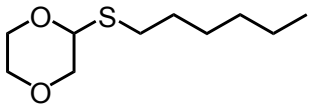
IR (neat) 2922, 2851, 1473, 1445, 1210, 1144, 1111, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (t, J = 7.0 Hz, 3H), 1.49–1.66 (m, 8H), 1.67–1.82 (m, 4H), 2.01–2.09 (m, 2H), 3.87 (tt, J = 9.5, 4.0 Hz, 1H), 4.64 (q, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.81, 25.41, 25.98, 26.87, 31.94, 49.97, 69.42, 214.87. Found: C, 57.00; H, 8.64%. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67%.

_S_-cyclododecyl _O_-ethyl dithiocarbonate (14)



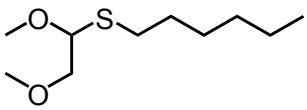
IR (neat) 2935, 2862, 2851, 1469, 1445, 1211, 1111, 1055 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28–1.54 (m, 18H), 1.43 (t, J = 7.0 Hz, 3H), 1.59–1.67 (m, 2H), 1.74–1.82 (m, 2H), 3.80–3.86 (m, 1H), 4.64 (q, J = 7.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.82, 22.57, 23.28, 23.59 (two signals overlapped), 23.66, 29.87, 47.07, 69.54, 215.15. Found: C, 62.68; H, 10.01%. Calcd for $C_{15}H_{28}OS_2$: C, 62.45; H, 9.78%.

2-hexylthio-1,4-dioxane (15)



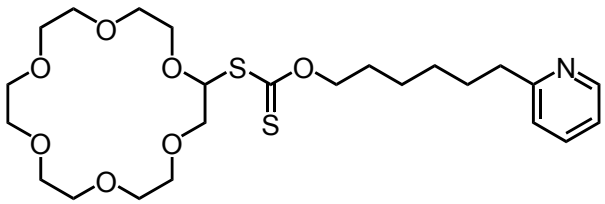
IR (neat) 2958, 2927, 2855, 1456, 1260, 1126, 1119, 1085, 1070, 908, 870 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.24–1.35 (m, 4H), 1.35–1.44 (m, 2H), 1.56–1.68 (m, 2H), 2.60–2.73 (m, 2H), 3.58 (dd, J = 12.0, 7.0 Hz, 1H), 3.63–3.74 (m, 3H), 3.90 (dd, J = 12.0, 3.0 Hz, 1H), 4.06–4.11 (m, 1H), 4.80 (dd, J = 7.0, 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.52, 28.51, 30.06, 30.47, 31.36, 64.47, 66.38, 69.86, 80.43. Found: C, 58.98; H, 9.60%. Calcd for $C_{10}H_{20}O_2S$: C, 58.78; H, 9.87%.

3-hexylthio-2,5-dioxahexane (16)



IR (neat) 2927, 2857, 1467, 1188, 1133, 1101, 926, 763 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.22–1.34 (m, 4H), 1.34–1.42 (m, 2H), 1.53–1.63 (m, 2H), 2.56 (t, *J* = 7.5 Hz, 2H), 3.41 (s, 3H), 3.46 (s, 3H), 3.60 (dd, *J* = 10.5, 4.5 Hz, 1H), 3.65 (dd, *J* = 10.5, 8.0 Hz, 1H), 4.53 (dd, *J* = 8.0, 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 22.52, 28.24, 28.64, 30.35, 31.37, 55.69, 59.08, 75.17, 85.46. Found: C, 58.27; H, 10.50%. Calcd for $C_{10}H_{22}O_2S$: C, 58.21; H, 10.75%.

***S*-2,5,8,11,14,17-hexaoxacyclooctadecyl *O*-6-(2-pyridyl)hexyl dithiocarbonate (18)**



IR (neat) 2929, 2860, 1590, 1569, 1473, 1436, 1352, 1225, 1119, 1048 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37–1.49 (m, 4H), 1.70–1.86 (m, 4H), 2.79 (t, *J* = 8.0 Hz, 2H), 3.63–3.94 (m, 22H), 4.56 (t, *J* = 7.0 Hz, 2H), 5.79 (dd, *J* = 7.5, 3.5 Hz, 1H), 7.10 (ddd, *J* = 7.5, 5.0, 1.0 Hz, 1H), 7.14 (ddd, *J* = 7.5, 1.0, 1.0 Hz, 1H), 7.59 (ddd, *J* = 7.5, 7.5, 2.0 Hz, 1H), 8.52 (ddd, *J* = 5.0, 2.0, 1.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 25.71, 28.05, 28.87, 29.63, 38.24, 69.50, 69.85, 70.60, 70.63, 70.64, 70.73, 70.80, 70.82, 70.87, 71.12, 73.18, 74.03, 90.88, 120.93, 122.70, 136.26, 149.23, 162.14, 213.38. Found: C, 55.39; H, 7.82%. Calcd for $C_{24}H_{39}NO_7S_2$: C, 55.68; H, 7.59%.

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Chapter 5

Regio- and Stereoselective Radical Additions of Thiols to Ynamides

Regioselective and stereoselective radical additions of arenethiols to various ynamides have been developed. Mixing ynamides and arenethiols in the presence of a catalytic amount of triethylborane affords the corresponding adducts, (*Z*)-1-amino-2-thio-1-alkenes, in excellent yields with high selectivities. The products can be reduced by means of trifluoroacetic acid and triethylsilane to yield 1-amino-2-thioalkanes.

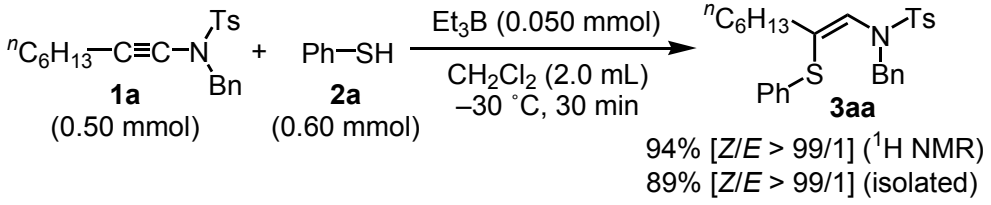
Introduction

Because of the high importance of organosulfur compounds, development of new reactions to introduce sulfur atoms to organic molecules is indispensable.[1] Radical addition of thiols to unsaturated bonds is one of the most basic and concise methods to achieve the purpose.[2,3] Although radical additions of thiols to terminal alkynes are well-known, examples of additions to internal alkynes are limited.[2c,4] Furthermore, additions to heteroatom-substituted internal alkynes have scarcely been reported.[5]

The author has focused on *N*-alkynylamides (ynamides),[6] as heteroatom-substituted internal alkynes in the radical addition reaction. In Chapter 5, he reports radical hydrothiolation of ynamides,[7,8] which yields synthetically useful (*Z*)-1-amino-2-thio-1-alkene derivatives[9] regio- and stereoselectively.[10]

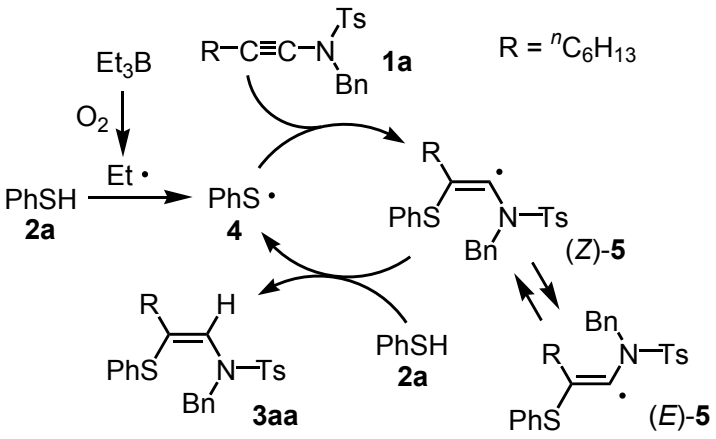
Results and Discussion

Under air, a catalytic amount of triethylborane[11] was added to a solution of *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide[12] (**1a**) and benzenethiol (**2a**, 1.2 equiv) in dichloromethane at –30 ˚C. After the mixture was stirred for 30 min at the same temperature, the mixture was concentrated. NMR analysis of the crude mixture indicated the formation of *N*-benzyl-*N*-(2-phenylthio-1-octenyl)-*p*-toluenesulfonamide (**3aa**, 94%, *Z*/*E* > 99/1). The author confirmed by NOE experiments that the *Z* isomer was exclusively formed. Silica gel column chromatography afforded **3aa** in 89% yield (Scheme 1).[13]



Scheme 1. Triethylborane-initiated hydrothiolation of ynamide **1a**.

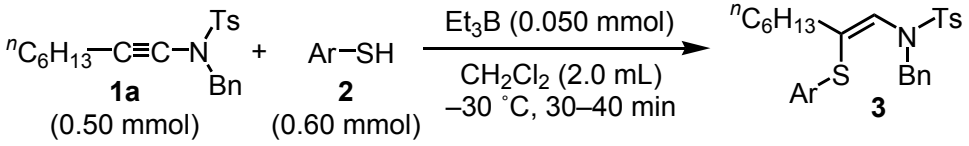
This reaction would proceed as follows (Scheme 2). Initially, an ethyl radical, generated from triethylborane with molecular oxygen in air, abstracts hydrogen atom from benzenethiol (**2a**) to form thiyl radical **4**. The electron-deficient radical[13] **4** immediately reacts with ynamide **1a**, an electron-rich alkyne, to furnish vinyl radical **5**. The carbon–sulfur bond formation occurs regioselectively at the 2-position of ynamide **1a**, where the higher electron density resides. The *Z* isomer of vinyl radical **5** selectively abstracts hydrogen atom from benzenethiol. The diastereoselectivity can be explained by steric effect.[14] Product **3aa** is thus formed, and thiyl radical **4** is regenerated to complete the radical chain.



Scheme 2. Plausible reaction mechanism.

Electron-deficient arenethiol participated smoothly in this radical reaction (Table 1, entries 2 and 3). On the other hand, additions of electron-rich arenethiols were not efficient (entries 4–6). These poor yields would be due to the low reactivity of the electrophilic thiyl radicals that are stabilized by electron-donating aryl groups. Addition of a catalytic amount of TEMPO to the reaction system or in the absence of Et_3B almost prevented the reaction (entries 7 and 8). These results strongly support that the reaction would proceed via the radical chain mechanism.

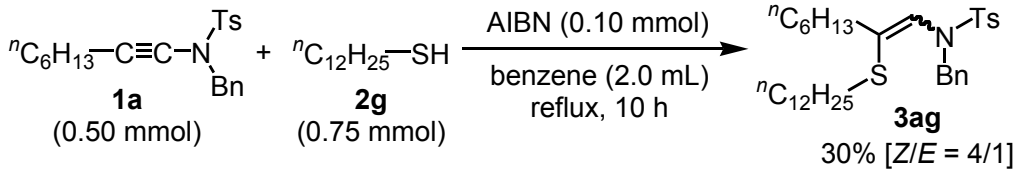
Table 1. Radical hydrothiolation of **1a** with arenethiols.



entry	Ar	product	isolated yield /% [*Z*/*E*]
1	Ph (**2a**)	**3aa**	89 [> 99/1]
2	*p*-Br–C_6H_4 (**2b**)	**3ab**	88 [> 99/1]
3	C_6F_5 (**2c**)	**3ac**	93 [> 99/1]
4	*o*-Me–C_6H_4 (**2d**)	**3ad**	31[d] [N.D.[e]]
5	*p*-Me–C_6H_4 (**2e**)	**3ae**	23[d] [N.D.[e]]
6[a]	*p*-MeO–C_6H_4 (**2f**)	**3af**	35 [> 99/1]
7[b]	Ph (**2a**)	**3aa**	6[d] [59/41]
8[c]	Ph (**2a**)	**3aa**	<2[d] [N.D.[e]]

[a] Performed at room temperature. [b] With TEMPO (0.10 mmol).
[c] Without Et_3B. [d] NMR yield. [e] Not determined.

The addition of dodecanethiol (**2g**) to ynamide **1a** did not proceed at –30 °C. The reaction in boiling benzene with AIBN instead of Et_3B proceeded, although the yield and stereoselectivity were unsatisfactory (Scheme 3).

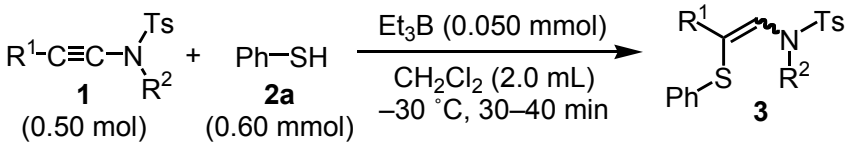


Scheme 3. Radical hydrothiolation of **1a** with dodecanethiol.

A wide range of ynamides was subjected to the radical addition of benzenethiol (**2a**) (Table 2). Ynamides bearing an acid-sensitive THP ether moiety and a base-sensitive ester moiety

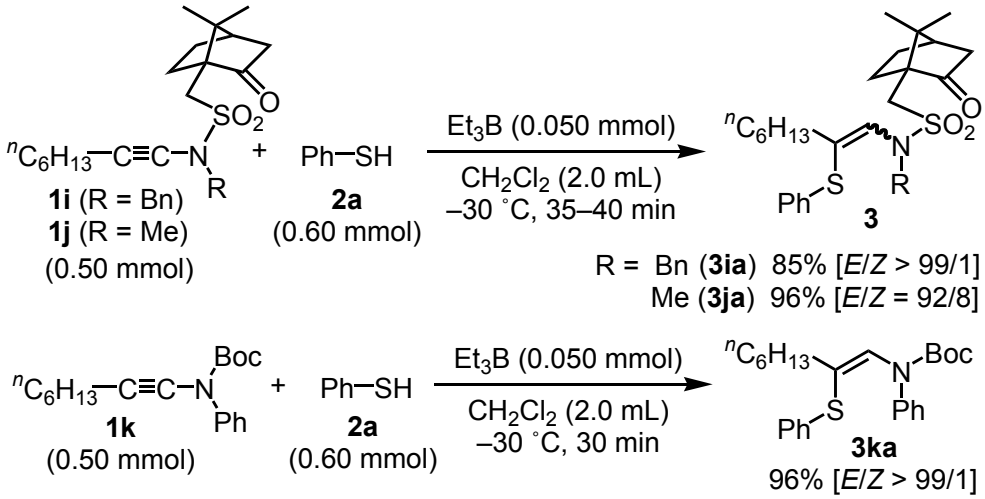
underwent the addition reactions without loss of the functional groups (entries 2 and 3). Benzenethiol added to ynamide **1d** substituted by a secondary alkyl group in lower yield with slightly lower selectivity (entry 4). Ynamide **1e** having a tertiary alkyl group resisted the addition reaction (entry 5).[15] Replacement of the benzyl group of **1a** by a methyl group slightly decreased the regioselectivity of the reaction (entry 1 vs. entry 6). The allyl group of **1g** remained unchanged under the reaction conditions (entry 7). *N*-Phenyl ynamide **1h** was less reactive than the *N*-benzyl analogue **1a** (entry 8). Not only *p*-toluenesulfonamides **1a**–**1h** but also camphorsulfonamides **1i** and **1j** and Boc-protected ynamide **1k** underwent the radical addition smoothly (Scheme 4).

Table 2. Radical hydrothiolation of *p*-toluenesulfonyl-substituted ynamides with benzenethiol.



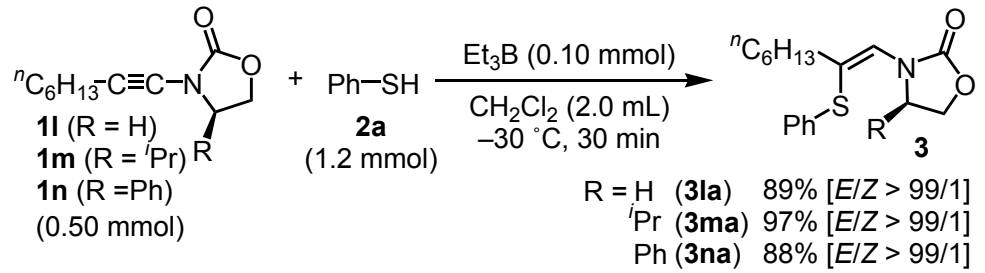
entry	R^1	R^2	**1**	product	isolated yield /% [*E*/*Z*]
1	$^n C_6H_{13}$	Bn	**1a**	**3aa**	89 [> 99/1]
2	$THPOCH_2$	Bn	**1b**	**3ba**	90 [> 99/1]
3	$EtO_2C(CH_2)_4$	Bn	**1c**	**3ca**	97 [> 99/1]
4	$^c C_6H_{11}$	Bn	**1d**	**3da**	73 [97/3]
5	^{t}Bu	Bn	**1e**	**3ea**	15[a] [N.D.[b]]
6	$^n C_6H_{13}$	Me	**1f**	**3fa**	97 [96/4]
7	$^n C_6H_{13}$	allyl	**1g**	**3ga**	84 [> 99/1]
8	$^n C_6H_{13}$	Ph	**1h**	**3ha**	60 [> 99/1]

[a] NMR yield. [b] Not determined.



Scheme 4. Radical hydrothiolation of various ynamides with benzenethiol.

The addition reactions to *N*-(1-alkynyl)oxazolidinones led to the exclusive formation of the corresponding *Z* adducts in excellent yields (Scheme 5). In these cases, 2.4 equiv of benzenethiol and a larger amount of triethylborane were needed.

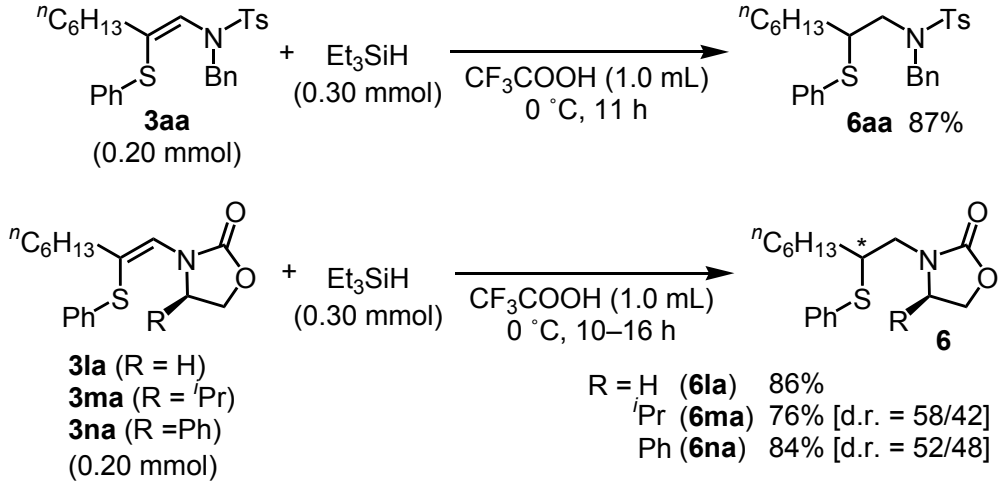


Scheme 5. Radical hydrothiolation of *N*-(1-alkynyl)oxazolidinones with benzenethiol.

Hydrogenation of the double bonds of adducts **3** could provide interesting structures having a phenylthiolated chiral center. The author hence examined to reduce alkenylamides **3**. Many attempts to reduce the double of **3aa** in the presence of various transition metal complexes under hydrogen atmosphere resulted in failure, suffering from no conversions.

On the other hand, treatment of **3aa** with triethylsilane in trifluoroacetic acid reduced the alkene moiety[16] to afford desired *N*-(2-phenylthioalkyl)amides **6aa** in good yield (Scheme 6).

Unfortunately, attempted diastereoselective reduction of chiral *N*-(1-alkenyl)oxazolidinones **3ma** and **3na** resulted in failure to form 1:1 mixtures of diastereomers. However, the diastereomers were separable from each other by flash column chromatography on silica gel.



Scheme 6. Reduction of the double bonds of adducts **3**.

Conclusion

The author has developed a concise method to synthesize (*Z*)-1-amino-2-thio-1-alkene derivatives in high yields with excellent regio- and stereoselectivity. The products can be hydrogenated by the action of triethylsilane in trifluoroacetic acid. Since reduced products **6** have asymmetric carbons, they can be useful as chiral building blocks[17] and chiral bidentate *N*,*S*-ligands of transition metal catalysts.[18]

Experimental Section

Materials

Dichloromethane was dried with MS4A. Triethylsilane was obtained from TCI. Trifluoroacetic acid was purchased from Wako Pure Chemicals. Thiols were commercially

available or readily prepared in conventional methods. *N*-Alkynylamides (ynamides) were synthesized from the corresponding bromoalkynes and amides (*vide infra*).[12]

Preparation of 1-bromo-1-alkynes.

Preparation of 1-bromo-1-octyne is representative. Under argon, *N*-bromosuccinimide (NBS, 2.85 g, 16.0 mmol) was added to a suspension of 1-octyne (2.21 mL, 15.0 mmol) and silver nitrate (0.127 g, 0.750 mmol) in acetone (10.0 mL) at ambient temperature. After 2 h, the mixture was diluted with hexane (15.0 mL), filtered, and concentrated in vacuo. Short column chromatography on silica gel (hexane) afforded 1-bromo-1-octyne as a colorless oil in 99% yield (2.81 g, 14.9 mmol). Since bromoalkynes are more or less unstable under air at room temperature, bromoalkynes must be stored in a refrigerator under inert atmosphere.

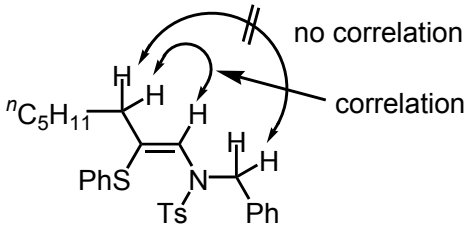
Preparation of *N*-alkynylamides (ynamides).

Preparation of *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (**1a**) is representative. Under argon, copper sulfate pentahydrate (0.12 g, 0.50 mmol), 1,10-phenanthroline (0.18 g, 1.0 mmol), and potassium carbonate (1.4 g, 10 mmol) were added to a solution of 1-bromo-1-octyne (1.1 g, 5.9 mmol) and *N*-benzyl-*p*-toluenesulfonamide (1.3 g, 5.0 mmol) in toluene (6.0 mL). The resulting mixture was heated at 80 ˚C for 11 h. The mixture was then cooled down to room temperature, filtered through a pad of florisil® with EtOAc, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 10/1) afforded *N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (**1a**) as a pale yellow oil in 78% yield (1.4 g, 3.9 mmol). Since ynamides are more or less unstable under air at room temperature, ynamides must be stored in a refrigerator under inert atmosphere.

General procedure for additions of thiols to ynamides (Tables 1 and 2, Schemes 4 and 5).

Addition of benzenethiol (**2a**) to ynamide **1a** is representative (Table 1, entry 1). Under air, triethylborane (1.0 M hexane solution, 0.050 mL, 0.050 mmol) was added to a solution of

ynamide **1a** (0.18 g, 0.50 mmol) and benzenethiol (**2a**, 0.062 mL, 0.60 mmol) in dichloromethane (2.0 mL) at –30 ˚C. The solution was stirred for 30 min at the same temperature and concentrated in vacuo. ^{1}H NMR analysis of the crude mixture indicated a 94% yield of the adduct with > 99/1 *Z*/*E* ratio. Silica gel column chromatography (hexane/EtOAc = 10/1 to 5/1) afforded *N*-benzyl-*N*-[(*Z*)-2-phenylthio-1-octenyl]-*p*-toluenesulfonamide (**3aa)** as a white solid in 89% yield (0.21 g, 0.45 mmol). The *Z* configuration was assigned by NOE analysis (See the following Figure).

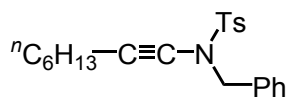


General procedure for hydrogenations of the double bonds of enamides (Scheme 6).

Hydrogenation of the double bond of **3aa** is representative. Under argon, triethylsilane (0.048 mL, 0.30 mmol) was added to a solution of **3aa** (0.096 g, 0.20 mmol) in trifluoroacetic acid (1.0 mL, 14 mmol) at 0 ˚C. The solution was stirred for 11 h at the same temperature. Then the reaction was quenched with a saturated $NaHCO_3$ solution and extracted twice with EtOAc. The organic extracts were dried over Na_2SO_4, filtered, and concentrated in vacuo. Silica gel column chromatography (hexane/EtOAc = 20/1) afforded *N*-benzyl-*N*-[2-(phenylthio)-octyl]-*p*-toluenesulfonamide (**6aa**) as a colorless oil in 87% yield (0.084 g, 0.17 mmol).

Characterization Data

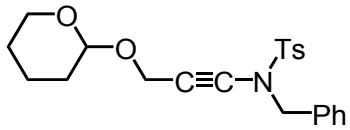
***N*-benzyl-*N*-(1-octynyl)-*p*-toluenesulfonamide (1a)**



IR (Nujol) 2925, 2855, 2255, 1597, 1454, 1169, 1093, 1056, 812, 655 cm^{-1}; ^{1}H NMR ($CDCl_3$)

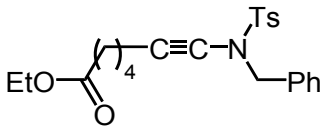
δ 0.86 (t, *J* = 7.5 Hz, 3H), 1.14–1.29 (m, 6H), 1.32–1.39 (m, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 4.44 (s, 2H), 7.26–7.31 (m, 7H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.03, 18.35, 21.58, 22.52, 28.26, 28.70, 31.29, 55.54, 70.89, 73.32, 127.68, 128.05, 128.35, 128.68, 129.51, 134.78, 134.83, 144.20. Found: C, 71.64; H, 7.37%. Calcd for $C_{22}H_{27}NO_2S$: C, 71.51; H, 7.37%.

_N_-benzyl-_N_-[3-(2-oxacyclohexyloxy)-1-propynyl]-_p_-toluenesulfonamide (1b)



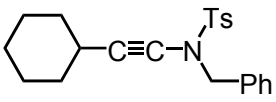
IR (Nujol) 2923, 2243, 1596, 1365, 1172, 1015 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45–1.67 (m, 5H), 1.72–1.83 (m, 1H), 2.44 (s, 3H), 3.41–3.47 (m, 1H), 3.77 (ddd, *J* = 11.5, 8.5, 3.0 Hz, 1H), 4.30 (s, 2H), 4.48 (d, *J* = 14.0 Hz, 1H), 4.53 (d, *J* = 14.0 Hz, 1H), 4.58 (dd, *J* = 4.0, 4.0 Hz, 1H), 7.26–7.33 (m, 7H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.20, 21.61, 25.33, 30.24, 54.17, 55.41, 62.10, 67.91, 79.34, 96.15, 127.68, 128.20, 128.45, 128.64, 129.64, 134.50, 134.72, 144.54. Found: C, 65.92; H, 6.25%. Calcd for $C_{22}H_{25}NO_4S$: C, 66.14; H, 6.31%.

_N_-benzyl-_N_-(6-ethoxycarbonyl-1-hexynyl)-_p_-toluenesulfonamide (1c)



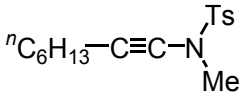
IR (neat) 2935, 2255, 1733, 1597, 1456, 1366, 1170, 1092, 1027, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, *J* = 7.0 Hz, 3H), 1.36–1.44 (m, 2H), 1.50–1.58 (m, 2H), 2.19 (t, *J* = 7.0 Hz, 2H), 2.21 (t, *J* = 7.5 Hz, 2H), 2.45 (s, 3H), 4.12 (q, *J* = 7.0 Hz, 2H), 4.44 (s, 2H), 7.25–7.34 (m, 7H), 7.73–7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.25, 18.09, 21.63, 23.83, 28.10, 33.71, 55.47, 60.24, 70.20, 73.61, 127.66, 128.10, 128.39, 128.73, 129.60, 134.65, 134.73, 144.33, 173.40. Found: C, 66.76; H, 6.57%. Calcd for $C_{23}H_{27}NO_4S$: C, 66.80; H, 6.58%.

_N_-benzyl-_N_-(2-cyclohexylethynyl)-_p_-toluenesulfonamide (1d)



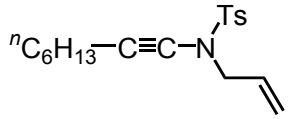
IR (neat) 2929, 2854, 2249, 2043, 1598, 1497, 1449, 1367, 1170, 1091 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.17–1.34 (m, 5H), 1.37–1.47 (m, 1H), 1.49–1.58 (m, 2H), 1.60–1.67 (m, 2H), 2.34–2.42 (m, 1H), 2.45 (s, 3H), 4.44 (s, 2H), 7.27–7.32 (m, 7H), 7.73–7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.63, 24.46, 25.82, 28.60, 32.57, 55.57, 73.63, 74.79, 127.74, 128.06, 128.32, 128.84, 129.47, 134.60, 134.76, 144.21. Found: C, 71.73; H, 6.87%. Calcd for $C_{22}H_{25}NO_2S$: C, 71.90; H, 6.86%.

_N_-methyl-_N_-(1-octynyl)-_p_-toluenesulfonamide (1f)



IR (neat) 2931, 2858, 2255, 1597, 1456, 1366, 1173, 676 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 1.22–1.37 (m, 6H), 1.43–1.50 (m, 2H), 2.23 (t, J = 7.0 Hz, 2H), 2.46 (s, 3H), 3.01 (s, 3H), 7.33–7.37 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.31, 21.59, 22.53, 28.41, 28.81, 31.30, 39.35, 68.62, 74.78, 127.79, 129.57, 133.13, 144.39. Found: C, 65.67; H, 7.72%. Calcd for $C_{16}H_{23}NO_2S$: C, 65.49; H, 7.90%.

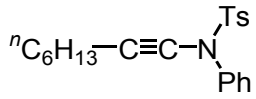
_N_-allyl-_N_-(1-octynyl)-_p_-toluenesulfonamide (1g)



IR (neat) 2930, 2858, 2253, 1597, 1367, 1171, 1091, 814, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 7.0 Hz, 3H), 1.20–1.36 (m, 6H), 1.41–1.49 (m, 2H), 2.24 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 3.92 (ddd, J = 6.5, 1.5, 1.0 Hz, 2H), 5.18 (ddt, J = 10.0, 1.0, 1.0 Hz, 1H), 5.22 (ddt, J = 17.0, 1.5, 1.0 Hz, 1H), 5.73 (ddt, J = 17.0, 10.0, 6.5 Hz, 1H), 7.31–7.35 (m, 2H), 7.77–7.81 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.40, 21.63, 22.57, 28.38, 28.85, 31.31, 54.27, 70.48, 72.95, 119.59,

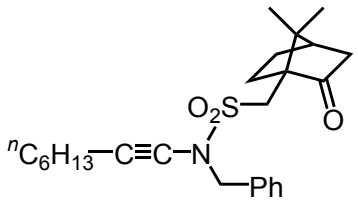
127.74, 129.56, 131.20, 134.73, 144.30. Found: C, 67.96; H, 8.04%. Calcd for $C_{18}H_{25}NO_2S$: C, 67.67; H, 7.89%.

_N_-(1-octynyl)-_N_-phenyl-_p_-toluenesulfonamide (1h)



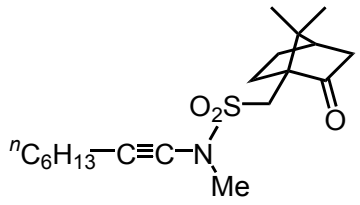
IR (neat) 2930, 2255, 1596, 1489, 1373, 1177, 1091, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 1.22–1.39 (m, 6H), 1.46–1.53 (m, 2H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 7.23–7.34 (m, 7H), 7.53–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.45, 21.66, 22.57, 28.47, 28.77, 31.31, 70.38, 73.79, 126.08, 127.84, 128.23, 128.87, 129.28, 132.92, 139.36, 144.57. Found: C, 70.81; H, 7.08%. Calcd for $C_{21}H_{25}NO_2S$: C, 70.95; H, 7.09%.

_N_-benzyl-_N_-(1-octynyl)-10-camphorsulfonamide (1i)



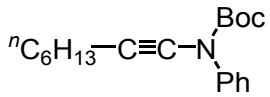
IR (neat) 2956, 2931, 2858, 2254, 2044, 1747, 1456, 1363, 1165, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.82 (s, 3H), 0.87 (t, *J* = 7.0 Hz, 3H), 1.11 (s, 3H), 1.19–1.35 (m, 6H), 1.38–1.49 (m, 3H), 1.68 (ddd, *J* = 14.0, 9.5, 5.0 Hz, 1H), 1.93 (d, *J* = 18.5 Hz, 1H), 2.00–2.12 (m, 2H), 2.25 (t, *J* = 7.0 Hz, 2H), 2.37 (ddd, *J* = 18.5, 4.0, 4.0 Hz, 1H), 2.48 (ddd, *J* = 14.5, 11.5, 4.0 Hz, 1H), 2.87 (d, *J* = 15.0 Hz, 1H), 3.55 (d, *J* = 15.0 Hz, 1H), 4.56 (d, *J* = 14.0 Hz, 1H), 4.63 (d, *J* = 14.0 Hz, 1H), 7.31–7.40 (m, 3H), 7.42–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.48, 19.64, 20.00, 22.54, 25.24, 26.92, 28.42, 28.81, 31.32, 42.52, 42.80, 47.85, 47.97, 55.68, 58.37, 71.36, 73.15, 128.37, 128.60, 128.96, 135.14, 214.39. Found: C, 70.03; H, 8.38%. Calcd for $C_{25}H_{35}NO_3S$: C, 69.89; H, 8.21%.

_N_-methyl-_N_-(1-octynyl)-10-camphorsulfonamide (1j)



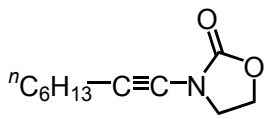
IR (neat) 2932, 2256, 1748, 1456, 1363, 1153, 1053 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.0 Hz, 3H), 0.91 (s, 3H), 1.15 (s, 3H), 1.23–1.54 (m, 9H), 1.70 (ddd, J = 14.0, 9.5, 4.5 Hz, 1H), 1.95 (d, J = 18.5 Hz, 1H), 2.02–2.14 (m, 2H), 2.28 (t, J = 7.0 Hz, 2H), 2.37–2.44 (m, 1H), 2.45–2.53 (m, 1H), 3.10 (d, J = 14.5 Hz, 1H), 3.20 (s, 3H), 3.63 (d, J = 14.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.04, 18.40, 19.72, 20.00, 22.53, 25.10, 26.89, 28.49, 28.88, 31.31, 39.26, 42.52, 42.80, 45.91, 47.92, 58.20, 69.15, 74.40, 214.68. Found: C, 64.49; H, 8.84%. Calcd for $C_{19}H_{31}NO_3S$: C, 64.55; H, 8.84%..

***tert*-butyl _N_-(1-octynyl)-_N_-phenylcarbamate (1k)**



IR (neat) 2932, 2270, 1733, 1597, 1494, 1369, 1302, 1291, 1254, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J = 7.5 Hz, 3H), 1.24–1.35 (m, 4H), 1.37–1.45 (m, 2H), 1.52 (s, 9H), 1.48–1.57 (m, 2H), 2.32 (t, J = 7.0 Hz, 2H), 7.19–7.23 (m, 1H), 7.32–7.38 (m, 2H), 7.44–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 18.50, 22.57, 28.00, 28.56, 28.90, 31.36, 69.33, 74.31, 82.87, 124.51, 126.16, 128.58, 140.24, 153.59. Found: C, 75.94; H, 9.26%. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.03%.

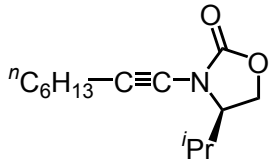
3-(1-octynyl)oxazolidin-2-one (1l)



IR (neat) 2929, 2858, 2272, 1767, 1416, 1206, 1116, 1036, 751 cm^{-1}; ^1H NMR ($CDCl_3$) δ

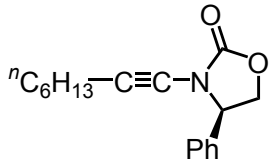
0.89 (t, *J* = 7.5 Hz, 3H), 1.23–1.34 (m, 4H), 1.34–1.42 (m, 2H), 1.49–1.56 (m, 2H), 2.30 (t, *J* = 7.0 Hz, 2H), 3.85–3.90 (m, 2H), 4.39–4.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 18.39, 22.52, 28.52, 28.73, 31.30, 47.01, 62.73, 69.93, 71.27, 156.63. Found: C, 67.82; H, 8.92%. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.78%.

(*R*)-4-isopropyl-3-(1-octynyl)oxazolidin-2-one (1m)



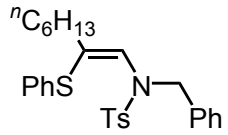
IR (neat) 2932, 2859, 2266, 1778, 1771, 1414, 1201, 1117, 1050 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.5 Hz, 3H), 0.98 (d, *J* = 7.0 Hz, 3H), 1.23–1.43 (m, 6H), 1.49–1.57 (m, 2H), 2.21 (qqd, *J* = 7.0, 6.5, 4.0 Hz, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 3.91 (ddd, *J* = 9.0, 6.0, 4.0 Hz, 1H), 4.12 (dd, *J* = 9.0, 6.0 Hz, 1H), 4.34 (dd, *J* = 9.0, 9.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.98, 17.21, 18.45, 22.52, 28.48, 28.73, 28.92, 31.26, 61.75, 64.44, 69.26, 72.30, 156.73. $[\alpha]^{25}_D$ –26 (*c* 0.82, cyclohexane). Found: C, 70.97; H, 9.82%. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77%.

(*R*)-4-phenyl-3-(1-octynyl)oxazolidin-2-one (1n)



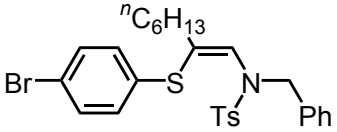
IR (neat) 2931, 2858, 2268, 1771, 1407, 1187, 1106, 1039, 751, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.0 Hz, 3H), 1.10–1.30 (m, 6H), 1.30–1.38 (m, 2H), 2.16 (t, *J* = 7.0 Hz, 2H), 4.22 (dd, *J* = 9.0, 7.0 Hz, 1H), 4.71 (dd, *J* = 9.0, 8.5 Hz, 1H), 5.00 (dd, *J* = 8.5, 7.0 Hz, 1H), 7.32–7.36 (m, 2H), 7.38–7.47 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.26, 22.46, 28.14, 28.48, 31.20, 62.11, 68.97, 70.55, 72.90, 126.85, 129.17, 129.30, 136.37, 156.31. $[\alpha]^{25}_D$ –159 (*c* 0.82, cyclohexane). Found: C, 74.95; H, 7.95%. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80%.

_N_-benzyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-_p_-toluenesulfonamide (3aa)



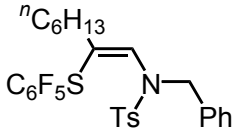
IR (Nujol) 2925, 1456, 1351, 1339, 1161, 1089, 1024, 741, 661 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, J = 7.5 Hz, 3H), 1.02–1.15 (m, 4H), 1.16–1.35 (m, 4H), 1.89 (t, J = 7.0 Hz, 2H), 2.45 (s, 3H), 4.46 (s, 2H), 5.64 (s, 1H), 6.90–6.94 (m, 2H), 7.13–7.21 (m, 3H), 7.26–7.35 (m, 5H), 7.36–7.41 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 21.57, 22.50, 28.09, 28.25, 31.40, 33.36, 54.15, 124.26, 127.14, 127.62, 127.67, 128.32, 128.58, 128.77, 129.60, 132.31, 133.10, 135.63, 135.83, 142.86, 143.59. Found: C, 70.00; H, 6.94%. Calcd for $C_{28}H_{33}NO_2S_2$: C, 70.11; H, 6.93%.

_N_-benzyl-_N_-[(_Z_)-2-(4-bromophenyl)thio-1-octenyl]-_p_-toluenesulfonamide (3ab)



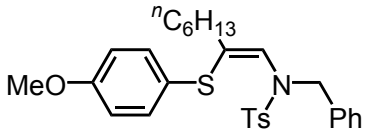
IR (Nujol) 2924, 1471, 1352, 1340, 1162, 1087, 1008, 813, 740, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.05–1.17 (m, 4H), 1.18–1.27 (m, 2H), 1.27–1.34 (m, 2H), 1.89 (t, J = 7.0 Hz, 2H), 2.46 (s, 3H), 4.41 (s, 2H), 5.63 (s, 1H), 6.69–6.73 (m, 2H), 7.23–7.30 (m, 5H), 7.31–7.38 (m, 4H), 7.73–7.77 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 21.58, 22.51, 28.09, 28.24, 31.42, 33.40, 54.22, 121.22, 125.27, 127.64, 127.72, 128.37, 128.85, 129.68, 131.68, 132.66, 133.49, 135.48, 135.65, 142.26, 143.73. Found: C, 60.14; H, 5.71%. Calcd for $C_{28}H_{32}BrNO_2S_2$: C, 60.21; H, 5.77%.

***N*-benzyl-*N*-[(*Z*)-2-(pentafluorophenyl)thio-1-octenyl]-*p*-toluenesulfonamide (3ac)**



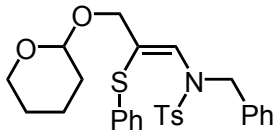
IR (Nujol) 2923, 1514, 1484, 1340, 1162, 1094, 979, 856, 739, 659 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.5 Hz, 3H), 1.07–1.18 (m, 4H), 1.19–1.34 (m, 4H), 1.85 (td, *J* = 7.0, 1.0 Hz, 2H), 2.46 (s, 3H), 4.47 (s, 2H), 5.64 (t, *J* = 1.0 Hz, 1H), 7.24–7.31 (m, 3H), 7.31–7.36 (m, 4H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.95, 21.53, 22.41, 27.96, 28.11, 31.32, 33.72, 54.12, 106.73 (td, *J* = 20.5, 3.8 Hz), 124.45, 127.63, 127.75, 128.33, 128.62, 129.69, 135.35, 135.38, 137.52 (ddddd, *J* = 253.5, 16.0, 13.5, 5.0, 2.0 Hz), 139.84, 141.63 (dtt, *J* = 255.3, 27.1, 9.5 Hz), 143.92, 147.33 (ddddd, *J* = 247.3, 10.5, 4.0, 4.0, 4.0 Hz). Found: C, 59.16; H, 4.89%. Calcd for $C_{28}H_{28}F_5NO_2S_2$: C, 59.04; H, 4.95%.

***N*-benzyl-*N*-[(*Z*)-2-(4-methoxyphenyl)thio-1-octenyl]-*p*-toluenesulfonamide (3af)**



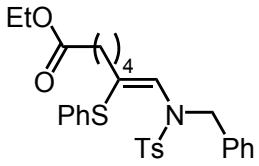
IR (Nujol) 2924, 1593, 1492, 1455, 1351, 1339, 1246, 1161, 1039, 739 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.5 Hz, 3H), 1.02–1.14 (m, 4H), 1.17–1.32 (m, 4H), 1.81 (t, *J* = 7.0 Hz, 2H), 2.45 (s, 3H), 3.77 (s, 3H), 4.44 (s, 2H), 5.49 (s, 1H), 6.69–6.73 (m, 2H), 6.88–6.92 (m, 2H), 7.28–7.35 (m, 5H), 7.39–7.42 (m, 2H), 7.76–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.06, 21.56, 22.50, 28.12, 28.16, 31.42, 33.03, 54.21, 55.25, 114.18, 122.13, 123.13, 127.59, 127.69, 128.26, 128.85, 129.56, 134.96, 135.60, 135.89, 143.51, 144.69, 159.41. Found: C, 68.47; H, 6.94%. Calcd for $C_{29}H_{35}NO_3S_2$: C, 68.33; H, 6.92%.

***N*-benzyl-*N*-[(*Z*)-3-(2-oxacyclohexyloxy)-2-phenylthio-1-propenyl]-*p*-toluenesulfonamide (3ba)**



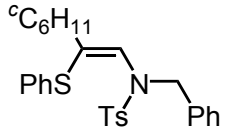
IR (Nujol) 2923, 1348, 1163, 1033, 743, 699, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39–1.61 (m, 5H), 1.67–1.78 (m, 1H), 2.45 (s, 3H), 3.29–3.35 (m, 1H), 3.62 (ddd, *J* = 11.0, 9.0, 3.0 Hz, 1H), 3.83 (dd, *J* = 14.0, 1.0 Hz, 1H), 3.97 (dd, *J* = 14.0, 1.5 Hz, 1H), 4.30 (dd, *J* = 6.5, 6.0 Hz, 1H), 4.58 (d, *J* = 14.5 Hz, 1H), 4.68 (d, *J* = 14.5 Hz, 1H), 6.29 (dd, *J* = 1.5, 1.0 Hz, 1H), 6.92–6.96 (m, 2H), 7.10–7.18 (m, 3H), 7.24–7.30 (m, 3H), 7.30–7.36 (m, 4H), 7.74–7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 19.17, 21.57, 25.31, 30.29, 53.11, 61.94, 66.80, 96.89, 127.11, 127.57 (two signals overlapped), 127.66, 128.34, 128.45, 128.68, 129.69, 131.49, 132.20, 132.90, 135.73, 135.86, 143.79. Found: C, 65.78; H, 5.95%. Calcd for $C_{28}H_{31}NO_4S_2$: C, 65.98; H, 6.13%.

***N*-benzyl-*N*-[(*Z*)-6-ethoxycarbonyl-2-phenylthio-1-hexenyl]-*p*-toluenesulfonamide (3ca)**



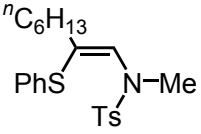
IR (Nujol) 2924, 1726, 1341, 1160, 737, 659 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, *J* = 7.0 Hz, 3H), 1.31–1.45 (m, 4H), 1.91 (t, *J* = 7.0 Hz, 2H), 2.15 (t, *J* = 7.5 Hz, 2H), 2.46 (s, 3H), 4.10 (q, *J* = 7.0 Hz, 2H), 4.44 (s, 2H), 5.62 (s, 1H), 6.89–6.93 (m, 2H), 7.13–7.21 (m, 3H), 7.26–7.31 (m, 3H), 7.33–7.41 (m, 4H), 7.76–7.80 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.23, 21.58, 23.70, 27.67, 30.93, 32.99, 33.92, 54.18, 60.19, 124.62, 127.25, 127.66, 128.34, 128.64, 128.79, 129.69, 132.29, 132.91, 135.41, 135.70, 142.49, 143.67, 173.45. HRMS Found: 523.1851. Calcd for $C_{29}H_{33}NO_4S_2$: 523.1851 $[M]^+$.

_N_-benzyl-_N_-[(_Z_)-2-cyclohexyl-2-(phenylthio)ethenyl]-_p_-toluenesulfonamide (3da)



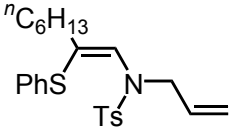
IR (Nujol) 2923, 1456, 1352, 1162, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88–1.12 (m, 5H), 1.50–1.57 (m, 1H), 1.58–1.65 (m, 2H), 1.68–1.75 (m, 3H), 2.45 (s, 3H), 4.49 (s, 2H), 5.73 (d, J = 0.5 Hz, 1H), 6.81–6.86 (m, 2H), 7.10–7.18 (m, 3H), 7.25–7.29 (m, 3H), 7.30–7.35 (m, 4H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.58, 26.04, 26.41, 33.30, 42.54, 53.94, 124.67, 126.65, 127.59, 127.68, 128.27, 128.58, 128.93, 129.58, 131.22, 134.29, 135.58, 135.77, 143.57, 146.10. Found: C, 70.46; H, 6.51%. Calcd for $C_{28}H_{31}NO_2S_2$: C, 70.40; H, 6.54%.

_N_-methyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-_p_-toluenesulfonamide (3fa)



IR (neat) 2929, 1598, 1476, 1440, 1353, 1166, 1090, 745, 666 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J = 7.5 Hz, 3H), 1.13–1.30 (m, 6H), 1.36–1.44 (m, 2H), 2.05 (td, J = 7.5, 1.0 Hz, 2H), 2.44 (s, 3H), 3.06 (s, 3H), 6.16 (t, J = 1.0 Hz, 1H), 7.20–7.28 (m, 5H), 7.30–7.34 (m, 2H), 7.70–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 21.55, 22.52, 28.27, 28.35, 31.45, 34.24, 37.02, 127.02, 127.54, 127.55, 128.85, 129.61, 131.43, 133.35, 134.21, 134.81, 143.63. Found: C, 65.48; H, 7.25%. Calcd for $C_{22}H_{29}NO_2S_2$: C, 65.47; H, 7.24%.

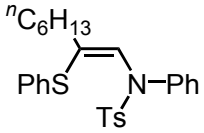
_N_-allyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-_p_-toluenesulfonamide (3ga)



IR (neat) 2928, 2856, 1598, 1440, 1354, 1164, 1091, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (t, J

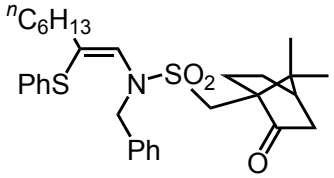
= 7.5 Hz, 3H), 1.11–1.19 (m, 4H), 1.20–1.28 (m, 2H), 1.33–1.42 (m, 2H), 2.03 (td, *J* = 7.5, 1.0 Hz, 2H), 2.43 (s, 3H), 4.00 (ddd, *J* = 6.5, 1.5, 1.5 Hz, 2H), 5.16 (ddt, *J* = 10.0, 1.5, 1.5 Hz, 1H), 5.23 (ddt, *J* = 17.5, 1.5, 1.5 Hz, 1H), 5.80 (t, *J* = 1.0 Hz, 1H), 5.83 (ddt, *J* = 17.5, 10.5, 6.5 Hz, 1H), 7.21–7.28 (m, 5H), 7.28–7.32 (m, 2H), 7.72–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 21.55, 22.53, 28.19, 28.29, 31.43, 33.52, 52.99, 118.50, 124.30, 127.29, 127.64, 128.79, 129.53, 132.26, 132.97, 132.99, 135.83, 141.28, 143.52. Found: C, 67.22; H, 7.29%. Calcd for $C_{24}H_{31}NO_2S_2$: C, 67.09; H, 7.27%.

_N_-phenyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-_p_-toluenesulfonamide (3ha)



IR (neat) 2928, 2028, 1595, 1490, 1360, 1168, 1092, 693, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.83 (t, *J* = 7.5 Hz, 3H), 1.07–1.25 (m, 6H), 1.31–1.39 (m, 2H), 2.04 (td, *J* = 7.5, 1.0 Hz, 2H), 2.42 (s, 3H), 6.53 (t, *J* = 1.0 Hz, 1H), 7.12–7.17 (m, 4H), 7.18–7.30 (m, 8H), 7.53–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.00, 21.58, 22.49, 28.22, 28.24, 31.37, 33.76, 126.06, 127.06, 127.22, 127.80, 127.82, 128.69, 128.73, 129.42, 132.25, 132.75, 135.02, 135.70, 140.97, 143.80. Found: C, 69.49; H, 6.55%. Calcd for $C_{27}H_{31}NO_2S_2$: C, 69.64; H, 6.71%.

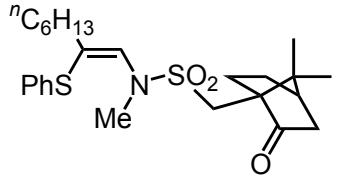
_N_-benzyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-10-camphorsulfonamide (3ia)



IR (Nujol) 2923, 1751, 1441, 1338, 1147, 1049, 698, 665 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 0.85 (s, 3H), 1.01–1.22 (m, 6H), 1.15 (s, 3H), 1.28–1.36 (m, 2H), 1.43 (ddd, *J* = 12.5, 9.5, 4.0 Hz, 1H), 1.68 (ddd, *J* = 14.0, 9.5, 4.5 Hz, 1H), 1.94 (d, *J* = 18.0 Hz, 1H), 1.99 (t, *J* = 7.5 Hz, 2H), 2.01–2.12 (m, 2H), 2.39 (ddd, *J* = 18.0, 4.0, 3.5 Hz, 1H), 2.54–2.62 (m, 1H), 2.97

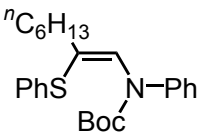
(d, *J* = 14.5 Hz, 1H), 3.57 (d, *J* = 14.5 Hz, 1H), 4.75 (s, 2H), 6.04 (s, 1H), 7.12–7.17 (m, 2H), 7.20–7.25 (m, 3H), 7.26–7.35 (m, 3H), 7.41–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 19.72, 20.08, 22.43, 25.18, 26.93, 28.05, 28.27, 31.37, 33.54, 42.59, 42.82, 47.86, 48.54, 53.61, 58.52, 124.67, 127.37, 127.68, 128.41, 128.73, 128.84, 132.25, 132.71, 136.27, 140.32, 215.15. Found: C, 68.92; H, 7.50%. Calcd for $C_{31}H_{41}NO_3S_2$: C, 68.98; H, 7.66%.

_N_-methyl-_N_-[(_Z_)-2-phenylthio-1-octenyl]-10-camphorsulfonamide (3ja)



IR (neat) 2956, 2930, 1747, 1349, 1147, 745 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.84 (t, *J* = 7.0 Hz, 3H), 0.86 (s, 3H), 1.13 (s, 3H), 1.16–1.28 (m, 6H), 1.39–1.48 (m, 3H), 1.67 (ddd, *J* = 14.0, 9.0, 4.5 Hz, 1H), 1.93 (d, *J* = 18.0 Hz, 1H), 2.01–2.12 (m, 2H), 2.12 (td, *J* = 7.5, 1.0 Hz, 2H), 2.38 (ddd, *J* = 18.0, 4.0, 4.0 Hz, 1H), 2.53 (ddd, *J* = 15.0, 12.0, 4.0 Hz, 1H), 2.89 (d, *J* = 14.5 Hz, 1H), 3.23 (s, 3H), 3.50 (d, *J* = 14.5 Hz, 1H), 6.44 (t, *J* = 1.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.28–7.32 (m, 2H), 7.34–7.37 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.02, 19.75, 20.05, 22.48, 25.07, 26.92, 28.29, 28.41, 31.43, 34.39, 36.83, 42.57, 42.80, 47.25, 47.86, 58.32, 127.09, 128.07, 129.02, 131.21, 132.67, 133.33, 214.92. Found: C, 64.44; H, 8.01%. Calcd for $C_{25}H_{37}NO_3S_2$: C, 64.76; H, 8.04%.

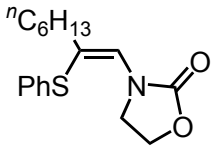
***tert*-butyl *N*-phenyl-*N*-[(*Z*)-2-phenylthio-1-octenyl]carbamate (3ka)**



IR (neat) 2930, 2856, 1714, 1596, 1496, 1367, 1300, 1160, 691 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (t, *J* = 7.0 Hz, 3H), 1.16–1.30 (m, 6H), 1.43–1.52 (m, 2H), 1.49 (s, 9H), 2.12 (t, *J* = 7.5 Hz, 2H), 6.60 (br s, 1H), 7.12–7.25 (m, 8H), 7.26–7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.05, 22.52,

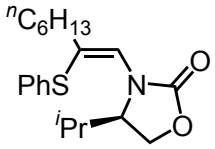
28.21, 28.38, 28.43, 31.50, 34.20, 81.38, 125.45, 126.13, 126.63, 128.31, 128.64 (two signals overlapped), 129.02, 131.15, 133.93, 141.55, 153.32. Found: C, 72.98; H, 8.09%. Calcd for $C_{25}H_{33}NO_2S$: C, 72.95; H, 8.08%.

3-[(*Z*)-2-phenylthio-1-octenyl]oxazolidin-2-one (3la)



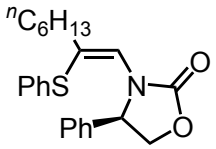
IR (neat) 2929, 1761, 1641, 1478, 1398, 1225, 1061, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, *J* = 7.0 Hz, 3H), 1.17–1.31 (m, 6H), 1.46–1.55 (m, 2H), 2.20 (td, *J* = 7.5, 1.0 Hz, 2H), 4.23–4.28 (m, 2H), 4.30–4.35 (m, 2H), 7.02 (t, *J* = 1.0 Hz, 1H), 7.15–7.20 (m, 1H), 7.21–7.25 (m, 2H), 7.26–7.31 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.53, 28.50, 28.66, 31.57, 36.87, 44.82, 62.90, 114.49, 125.83, 127.61, 129.02, 129.12, 135.78, 156.91. Found: C, 66.83; H, 7.64%. Calcd for $C_{17}H_{23}NO_2S$: C, 66.85; H, 7.59%.

(*R*)-4-isopropyl-3-[(*Z*)-2-phenylthio-1-octenyl]oxazolidin-2-one (3ma)



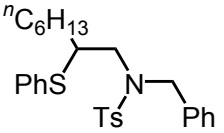
IR (neat) 2929, 1761, 1637, 1477, 1392, 1303, 1211, 1054, 742, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.83 (d, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H), 0.87 (d, *J* = 7.0 Hz, 3H), 1.17–1.31 (m, 6H), 1.46–1.55 (m, 2H), 2.12–2.27 (m, 3H), 4.07 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.14 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.67 (ddd, *J* = 9.0, 3.0, 3.0 Hz, 1H), 6.72 (s, 1H), 7.18–7.22 (m, 1H), 7.24–7.31 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.08, 17.52, 22.53, 27.69, 28.41, 28.65, 31.48, 36.26, 59.26, 63.20, 120.93, 125.09, 126.38, 128.89, 129.07, 134.05, 156.77. $[\alpha]^{25}_D$ –113 (*c* 0.82, cyclohexane). Found: C, 69.29; H, 8.48%. Calcd for $C_{20}H_{29}NO_2S$: C, 69.12; H, 8.41%.

(*R*)-4-phenyl-3-[(*Z*)-2-phenylthio-1-octenyl]oxazolidin-2-one (3na)



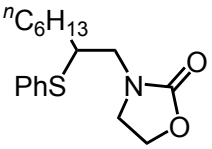
IR (neat) 2929, 1761, 1639, 1394, 1207, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.81 (t, *J* = 7.5 Hz, 3H), 0.96–1.22 (m, 6H), 1.31–1.38 (m, 2H), 1.95–2.10 (m, 2H), 4.16 (dd, *J* = 8.5, 4.0 Hz, 1H), 4.56 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.83 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.66 (s, 1H), 6.91–6.95 (m, 2H), 7.12–7.19 (m, 3H), 7.20–7.24 (m, 2H), 7.29–7.35 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.45, 28.04, 28.31, 31.44, 35.34, 59.22, 70.48, 122.48, 124.83, 126.35, 126.42, 128.55, 128.79, 129.05, 129.45, 133.76, 138.89, 156.94. $[\alpha]^{25}_D$ –33 (*c* 0.80, cyclohexane). HRMS Found: 381.1766. Calcd for $C_{23}H_{27}NO_2S$: 381.1762 $[M]^+$.

***N*-benzyl-*N*-[2-(phenylthio)octyl]-*p*-toluenesulfonamide (6aa)**



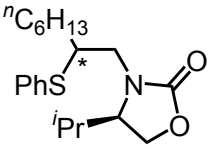
IR (neat) 2926, 2855, 1599, 1456, 1439, 1342, 1162, 1092, 737, 654 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.5 Hz, 3H), 1.02–1.31 (m, 8H), 1.34–1.46 (m, 1H), 1.65–1.75 (m, 1H), 2.42 (s, 3H), 2.95–3.05 (m, 2H), 3.26–3.34 (m, 1H), 4.05 (d, *J* = 14.5 Hz, 1H), 4.31 (d, *J* = 14.5 Hz, 1H), 7.17–7.32 (m, 12H), 7.57–7.61 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.07, 21.49, 22.58, 26.62, 28.94, 30.82, 31.64, 47.40, 53.96, 54.26, 126.75, 127.30, 127.96, 128.58, 128.62, 128.83, 129.69, 131.62, 134.66, 135.82, 136.21, 143.37. Found: C, 70.03 H, 7.38%. Calcd for $C_{28}H_{35}NO_2S_2$: C, 69.81; H, 7.32%.

3-[2-(phenylthio)octyl]oxazolidin-2-one (6la)



IR (neat) 2928, 2856, 1750, 1482, 1438, 1425, 1264, 1043, 748, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.22–1.37 (m, 6H), 1.44–1.69 (m, 4H), 3.32–3.48 (m, 3H), 3.51–3.63 (m, 2H), 4.09–4.19 (m, 2H), 7.22–7.26 (m, 1H), 7.28–7.34 (m, 2H), 7.41–7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 22.55, 26.78, 29.08, 31.61, 32.25, 45.94, 47.61, 49.42, 61.76, 127.05, 129.02, 131.67, 134.59, 158.63. Found: C, 66.29 H, 8.24%. Calcd for $C_{17}H_{25}NO_2S$: C, 66.41; H, 8.20%.

(4*R*)-4-isopropyl-3-[2-(phenylthio)octyl]oxazolidin-2-one (6ma)



< one diastereomer with R_f = 0.47 (hexane/EtOAc = 3/1) >

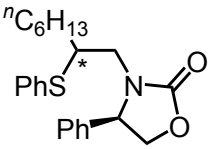
IR (neat) 2929, 1750, 1439, 1423, 1240, 1051, 745, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (d, *J* = 7.0 Hz, 3H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.22–1.34 (m, 6H), 1.42–1.68 (m, 4H), 1.89 (qqd, *J* = 7.0, 7.0, 4.0 Hz, 1H), 2.98 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.44–3.51 (m, 1H), 3.74 (dd, *J* = 14.5, 7.5 Hz, 1H), 3.78 (ddd, *J* = 8.5, 4.5, 4.0 Hz, 1H), 3.86 (dd, *J* = 9.0, 8.5 Hz, 1H), 3.96 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.21–7.25 (m, 1H), 7.27–7.32 (m, 2H), 7.38–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 14.22, 17.54, 22.53, 26.60, 27.43, 29.07, 31.60, 32.60, 46.87, 47.16, 59.97, 62.78, 126.89, 129.01, 131.11, 134.94, 158.20. $[\alpha]^{25}_D$ –7.5 (*c* 1.5, cyclohexane). Found: C, 68.71 H, 8.73%. Calcd for $C_{20}H_{31}NO_2S$: C, 68.73; H, 8.94%.

< the other diastereomer with R_f = 0.43 (hexane/EtOAc = 3/1) >

IR (neat) 2929, 1750, 1438, 1421, 1240, 1052, 747, 693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (d, *J* =

7.0 Hz, 3H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.23–1.38 (m, 6H), 1.45–1.72 (m, 4H), 1.93 (qqd, *J* = 7.0, 7.0, 3.5 Hz, 1H), 3.11 (dd, *J* = 14.5, 5.5 Hz, 1H), 3.31–3.38 (m, 1H), 3.65 (ddd, *J* = 8.5, 5.5, 3.5 Hz, 1H), 3.74 (dd, *J* = 14.5, 7.5 Hz, 1H), 3.97 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.00 (dd, *J* = 9.0, 5.5 Hz, 1H), 7.22–7.26 (m, 1H), 7.27–7.33 (m, 2H), 7.44–7.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.04, 14.15, 17.61, 22.55, 26.99, 27.33, 29.12, 31.63, 32.16, 46.04, 47.31, 59.74, 62.55, 127.05, 129.01, 131.81, 134.57, 158.52. $[\alpha]^{25}_{D}$ –16 (*c* 1.0, cyclohexane). Found: C, 68.54 H, 8.74%. Calcd for $C_{20}H_{31}NO_2S$: C, 68.73; H, 8.94%.

(4*R*)-4-phenyl-3-[2-(phenylthio)octyl]oxazolidin-2-one (6na)



< one diastereomer with R_f = 0.46 (hexane/EtOAc = 3/1) >

IR (neat) 2928, 1756, 1458, 1439, 1411, 1232, 1168, 1088, 1039, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.19–1.32 (m, 6H), 1.36–1.48 (m, 2H), 1.50–1.62 (m, 2H), 2.81 (dd, *J* = 14.5, 8.0 Hz, 1H), 3.40–3.47 (m, 1H), 3.64 (dd, *J* = 14.5, 7.0 Hz, 1H), 4.06 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.35 (dd, *J* = 9.0, 8.5 Hz, 1H), 4.89 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.15–7.26 (m, 7H), 7.35–7.41 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.53, 26.54, 29.04, 31.58, 32.40, 46.59, 47.08, 60.71, 69.89, 126.56, 127.06, 128.95, 129.09, 129.33, 130.44, 134.98, 137.85, 158.26. $[\alpha]^{25}_{D}$ –28 (*c* 0.63, $CHCl_3$). HRMS Found: 383.1919. Calcd for $C_{23}H_{29}NO_2S$: 383.1919 $[M]^+$.

< the other diastereomer with R_f = 0.42 (hexane/EtOAc = 3/1) >

IR (neat) 2928, 1756, 1459, 1438, 1414, 1214, 1168, 1089, 1039, 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.0 Hz, 3H), 1.15–1.37 (m, 7H), 1.41–1.53 (m, 2H), 1.56–1.65 (m, 1H), 3.01–3.08 (m, 2H), 3.51–3.59 (m, 1H), 4.09 (dd, *J* = 9.0, 6.5 Hz, 1H), 4.41 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.62 (dd, *J* = 9.0, 6.5 Hz, 1H), 7.18–7.32 (m, 7H), 7.36–7.41 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 14.02, 22.53, 26.73, 28.94, 31.59, 31.92, 46.96, 47.10, 60.66, 69.83, 126.95, 127.05, 128.97, 129.21,

129.31, 131.69, 134.58, 137.79, 158.80. $[\alpha]^{25}_{D}$ –47 (*c* 0.81, $CHCl_3$). HRMS Found: 383.1918. Calcd for $C_{23}H_{29}NO_2S$: 383.1919 $[M]^+$.

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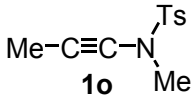
14. In reference 4b, Montevecci insisted that primary alkyl groups were bulkier than a phenylthio group. So the author assumes that the vinyl radical **5** would exist almost only in a (*Z*)-form to prevent the steric repulsion with the bulky amide moiety. Montevecci also insisted that a methyl group was smaller than a phenylthio group. Indeed, in the reaction of *N*-methyl-*N*-(1-propynyl)-*p*-toluenesulfonamide (**1o**) with benzenethiol, the reverse diastereoselectivity was observed.



1o

15. The addition reaction of phenyl-substituted ynamide PhC≡CN(Bn)Ts led to a mixture of stereo- and regioisomers.
16. Alkenes and ketones can be reduced under these conditions. See: D. N. Kursaniov, Z. N. Parnes, G. L. Bassova, N. M. Loim, V. I. Zdanovich, *Tetrahedron* **1967**, *23*, 2235–2242.
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Publication List

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

Chapter 1 Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
Angew. Chem. Int. Ed. **2005**, *44*, 1694–1696.

Chapter 2 Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
J. Am. Chem. Soc. **2006**, *128*, 4240–4241.

Chapter 3 Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
Tetrahedron **2009**, *65*, 1553–1558.

Chapter 4 Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
Chem. Asian J. **2007**, *2*, 1568–1573.

Chapter 5 Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
Synlett **2009**, 28–31.

2. Other publications not included in this thesis.

(1) Hydrosilylation of Alkynes with a Cationic Rhodium Species Formed in an Anionic Micellar System
Akinori Sato, Hidenori Kinoshita, Hiroshi Shinokubo, and Koichiro Oshima
Org. Lett. **2004**, *6*, 2217–2220.

(2) A New Approach to 4-Aryl-1,3-butanediols by Cobalt-Catalyzed Sequential Radical Cyclization–Arylation Reaction of Silicon-Tethered 6-Iodo-1-hexene Derivatives
Hidenori Someya, Azusa Kondoh, Akinori Sato, Hirohisa Ohmiya, Hideki Yorimitsu, and Koichiro Oshima
Synlett **2006**, 3061–3064.

(3) Efficient Aerobic Oxidation of Phosphines, Phosphites, and Sulfides by Using Trialkylborane
Kosuke Motoshima, Akinori Sato, Hideki Yorimitsu, and Koichiro Oshima
Bull. Chem. Soc. Jpn. **2007**, *80*, 2229–2231.

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