Palladium(0)-Catalyzed Thioboration of Terminal Alkynes with 9-(Alkylthio)-9-borabicyclo[3.3.1]nonane Derivatives: Stereoselective Synthesis of Vinyl Sulfides *via* the Thioboration–Cross-Coupling Sequence

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Abstract: The addition of 9-(alkylthio)-9-borabicyclo[3.3.1]nonanes (9-(RS)-9-BBN) **1** to terminal alkynes was catalyzed by $Pd(PPh_3)_4$ (3 mol %) to produce 9-[(*Z*)-2-(alkylthio)-1-alkenyl]-9-BBN derivatives **2** in high yields. The reactions were highly regio- and stereoselective, and their conditions were sufficiently mild that a variety of functionalized alkenylboranes **2** with defined stereochemistry were readily synthesized. The boranes **2** exhibited exceptionally high reactivity on protonolysis with methanol to produce the Markovnikov adducts of thiols to 1-alkynes, 2-(alkylthio)-1-alkenes **3**. The synthetic utility of the present reaction was demonstrated by the regio- and stereoselective one-pot synthesis of alkenyl sulfides **7** *via* the palladium-catalyzed thioboration–cross-coupling sequence.

The addition of the X–B compounds (X = H, halogen, and heteroatoms) to an alkyne is an attractive method to produce the synthetically valuable 1-alkenylboron reagents with defined regio- and stereochemistry. 1-Alkenylboron compounds are readily accessible by hydroboration[1] of alkynes and are widely used for syntheses of unsaturated organic compounds. Recently, we have shown that the haloboration[2] of alkynes with 9-halo-9-BBN or other haloborane reagents provides an efficient method for the synthesis of variously substituted 1-alkenylboron compounds which are not accessible by the conventional hydroboration techniques. Although similar addition of the boron–heteroatom bonds to alkynes is an attractive route to the functionalized 1-alkenylboron compounds, this reaction usually does not take place due to the high boron–heteroatom bond energy and the low Lewis acidities of borons conjugated to heteroatoms.

Recently, transition metal complexes have emerged as efficient catalysts for the addition of metal reagents, including magnesium,[3] aluminum,[3d,f,4] silicon,[3d,e,4d,5] zinc,[3d,f,4d,6] germanium,[7] and tin[3f,4e,f,5j–l,6,7d,8] compounds, to alkenes and alkynes. Although the corresponding reactions of boron compounds are not yet well developed, the catalytic hydroboration[9] of alkenes and alkynes with catecholborane or polyhedral boranes has been extensively studied. The mechanism is fundamentally different from the uncatalyzed hydroboration process and was postulated to proceed through the migratory insertion of alkenes or alkynes into the transition metal–hydride complexes. The copper(I)- or cobalt-

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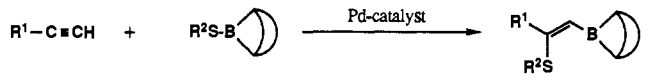
(II)-catalyzed addition of the Si–B (silylboration)[10] and the Sn–B compounds (stannylboration)[10,11] to alkynes was also reported.

Herein, we wish to report the novel palladium(0)-catalyzed addition reaction of the 9-(alkylthio)-9-BBN derivatives **1** to terminal alkynes to produce (β-(alkylthio)vinyl)boranes **2** (eq 1). (Alkylthio)boranes are readily prepared by the reaction of



1 **2** (1)

boranes or haloboranes with thiols[12] and are known as versatile reagents to introduce thio groups into organic molecules.[13-15] The present study provides the first example[16] of the addition of such thioboranes to unactivated alkynes, which is useful for further synthetic applications, e.g., as coupling partners for the boron cross-coupling reaction, as is demonstrated in the present study.

Results and Discussion

Reaction Conditions for Thioboration. When a solution of 1-octyne and **1** (R^2 = Ph) (1 equiv) in THF was heated at 50 °C for 3 h in the presence of $Pd(PPh_3)_4$ (3 mol %), the addition of the B–S bond to octyne was observed to proceed regio- and stereoselectively (eq 1). The ^1H NMR spectra of the reaction mixture exhibited four singlets at 6.55, 5.76, 5.14, and 4.87 ppm in a ratio of 15:1:2:2. The former two signals were tentatively assigned to the vinylic protons of **2** and its (*E*)-isomer, and the latter two signals, to the vinylic protons of 2-(phenylthio)-1-octene. An addition of 2 equiv of methanol immediately enhanced the signals at 5.14 and 4.87 ppm while the other two singlets disappeared, indicating a very fast protodeboronation of **2** (eq 2). The formation of (*Z*)-**2** predominated, as was established by the presence of NOE (6.8%) between the vinylic proton at 6.55 and allylic protons at 2.24 ppm.

3 (2)

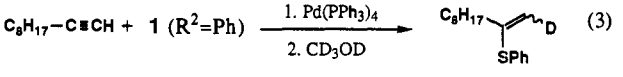
A series of reactions between 1-octyne and **1** (R^2 = Ph) (1.1 equiv) were carried out under various conditions to optimize the reaction yields. The yields of 2-(phenylthio)-1-octene shown in Table I were analyzed by GLC after treatment with methanol. It was shown that $Pd(PPh_3)_4$ was the best catalyst and the reaction efficiently proceeded in THF solvent (entries 2–6). The presence of 1 equiv of styrene, which was expected to avoid catalyst deactivation by trapping free thiophenol generated in the reaction mixture, was found to further improve the yield to 81% (entry 8). $RhCl(PPh_3)_3$ also exhibited some catalytic activity, but $PdCl_2(PPh_3)_2$, CuI, and $CoCl(PPh_3)_3$ were ineffective.

Table I. Reaction Conditions for Thioboration (Eq 1)[a]

entry	catalyst	solvent	additive	time/h	temp/°C	yield/%[b]
1	none	THF	none	3	50	0
2	$Pd(PPh_3)_4$	benzene	none	3	50	47
3	$Pd(PPh_3)_4$	dioxane	none	3	50	58
4	$Pd(PPh_3)_4$	THF	none	3	50	72
5	$Pd(PPh_3)_4$	THF	none	16	50	72
6	$Pd(PPh_3)_4$	THF	none	3	65	70
7	$Pd(PPh_3)_4$	THF	styrene[c]	3	50	76
8	$Pd(PPh_3)_4$	THF	styrene[c]	24	50	81
9	$PdCl_2(PPh_3)_2$	THF	none	3	50	0
10	$RhCl(PPh_3)_3$	THF	none	3	50	15
11	CuI	THF	none	3	50	0
12	$CoCl(PPh_3)_3$	THF	none	3	50	0

[a] All reactions were carried out by using 9-(phenylthio)-9-BBN (1.1 mmol), 1-octyne (1.0 mmol), catalyst (0.03 mmol), and solvent (4 mL). The reaction mixture was treated with methanol (1 mL) before GC analysis. [b] GC yields of 2-(phenylthio)-1-octene. [c] Styrene (1.0 mmol) was used.

In order to determine the stereochemistry and the selectivity of the thioboration reaction, the boron adduct **2** obtained from 1-decyne with **1** (R^2 = Ph) was directly subjected to deuteriolysis (eq 3). The treatment of the reaction mixture with CD_3OD after



4 (3)

time	additive	**4**
24 h	none	78 % (D= 8 % ; Z= 50 %)
3 h	none	82 % (D= 92 % ; Z= 52 %)
3 h	NaOH	73 % (D= 93 % ; Z= 82 %)

3 h at 50 °C provided monodeuterated **4** in 82% yield with 92% deuterium incorporation, whereas only 8% deuterium incorporation resulted in deuteriolysis after standing for 24 h. The stereochemistry of **4** was also somewhat troublesome. The treatment of the reaction mixture with CD_3OD gave a 1:1 mixture of (*E*)- and (*Z*)-isomers, presumably as a result of the radical isomerization[17] induced by free thiophenol. This stereoselectivity was improved to a *Z*:*E* = 82:18 ratio when the deuteriolysis at low temperature was followed by trapping of thiophenol with aqueous NaOH, but complete control of the stereochemistry during protonolysis was unsuccessful. Thioboration of 1-deuterio-1-decyne with **1** (R^2 = Ph) followed by protonolysis with methanol also produced a mixture of stereoisomers (*Z*:*E* = 22:78).

Although the formation of (*Z*)-**2** predominating through syn addition was suggested by ^1H NMR and deuteriolysis experiments, these analyses may not reflect the real selectivities of the present reaction because adduct **2** is highly susceptible to C–B bond breaking or isomerization. However, the achieved stereoselectivity of over 99% in the cross-coupling reaction with aryl or 1-alkenyl halides obviously reveals that the reaction is highly regio- and stereoselective, as is discussed in a later section.

Thioboration of Representative Alkynes. A comparison of the representative (alkylthio)- and (arylthio)boranes **1** during the reaction with 1-octyne at 50 °C in the presence of $Pd(PPh_3)_4$ (3 mol %) (procedure A) or $Pd(PPh_3)_4$ (3 mol %) and styrene (1 equiv) (procedure B) indicated that higher yields could be easily achieved in the presence of styrene (Table II). There were no large differences in the yields and selectivities of adducts between (alkylthio)- and (arylthio)boranes, except for the sterically very hindered *tert*-butylthio derivative (entry 5). For this addition, diphenyl(2,4,6-trimethoxyphenyl)phosphine was found to work more effectively than triphenylphosphine as a ligand for the

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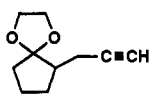
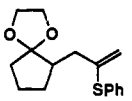
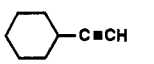
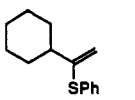
Table II. Palladium-Catalyzed Thioboration Reaction of 1-Octyne with 9-(Alkylthio)-9-BBN Derivatives[a]

entry	1, R^2S =	yield/%[b] A[c]	B[d]
1	PhS	65	76
2	$PhCH_2S$		73
3	^{n}BuS	65	75
4	^{s}BuS	58	71
5	^{t}BuS	2 (60)[e]	3

[a] All reactions were carried out at 50 °C for 24 h by using 9-(RS)-9-BBN (1.1 mmol), 1-octyne (1.0 mmol), and THF (4 mL) under two reaction conditions. [b] Isolated yields based on 1-octyne. [c] Procedure A: $Pd(PPh_3)_4$ (3 mol %). [d] Procedure B: $Pd(PPh_3)_4$ (3 mol %) and styrene (1 mmol). [e] Pd complex generated from $Pd(dba)_2$ (0.03 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.12 mmol) was used as a catalyst.

Table III. Palladium-Catalyzed Thioboration of Representative 1-Alkynes with 9-(Phenylthio)-9-BBN[a]

entry	1-alkyne	product	yield/%[b]
1	$C_8H_{17}-C\equiv CH$	C_8H_{17}, SPh	80
2	$CH_2=CH(CH_2)_5-C\equiv CH$	$CH_2=CH(CH_2)_5$, SPh	86
3	$Cl(CH_2)_3-C\equiv CH$	$Cl(CH_2)_3$, SPh	83
4			67
5	$THPOCH_2-C\equiv CH$	$THPOCH_2$, SPh	70
6	$MeO_2C(CH_2)_4-C\equiv CH$	$MeO_2C(CH_2)_4$, SPh	81
7	$NC(CH_2)_3-C\equiv CH$	$NC(CH_2)_3$, SPh	81
8	$CH_3CO(CH_2)_4-C\equiv CH$	$CH_3CO(CH_2)_4$, SPh	69
9			8 (65)[c]

[a] All reactions were conducted in THF (4 mL) at 50 °C for 24 h by using 9-(phenylthio)-9-BBN (1.1 mmol) and 1-alkyne (1 mmol) in the presence of $Pd(PPh_3)_4$ (0.03 mmol) and styrene (1 mmol). The thioboration products were isolated as vinylic sulfides after protonolysis with methanol (1 mL). [b] Isolated yields based on 1-alkynes. [c] A mixture of $Pd(dba)_2$ and diphenyl(2,4,6-trimethoxyphenyl)phosphine (4 equiv) was used as a catalyst.

palladium catalyst, presumably due to acceleration of the rate of oxidative addition of **1** to the palladium(0) complex by ready formation of a coordinatively unsaturated palladium species[18] (entry 5).

In Table III, the results of thioboration of a variety of terminal alkynes with **1** (R^2 = Ph) in the presence of $Pd(PPh_3)_4$ and styrene (1 equiv) are summarized. The reaction is specific for terminal alkynes; thus the double bonds remained intact during this reaction (entry 2). Although the thioboron compounds are known to undergo thioacetalization[15] of carbonyls, exchange[13] of acetals to thioacetals, or ether cleavage,[13] the present conditions were sufficiently mild to permit the syntheses of a variety of alkenyl sulfides possessing such functionalities (entries 3–8). The reaction is rather sensitive to the steric hindrance of alkynes; for example, the addition to cyclohexylethyne resulted in only 8% adduct formation (entry 9). Although this addition was again achieved in a 65% yield by using the diphenyl(2,4,6-trimethoxyphenyl)-phosphine ligand, all attempts to achieve quantitative yields for internal alkynes and phenylethyne were unsuccessful.

It is well established that free radical addition of thiols to terminal alkynes produces anti-Markovnikov adducts,[19] while the present Pd-catalyzed thioboration always provides the Markovnikov adducts **3** regioselectively.

Mechanism of Thioboration. The principal features of the present palladium-catalyzed thioboration reaction, which are of importance for mechanistic consideration, are as follows. (a) The reaction is catalyzed by palladium(0) catalysts but not by palladium(II) complexes. (b) The addition proceeds regioselectively in favor of terminal boron adducts and produces the (*Z*)-alkenylboranes through syn addition of the B–S bonds to alkynes. These regio- and stereochemical facts are in good agreement with the related transition metal-catalyzed addition reactions,[3-8] notably the addition of thiols to alkynes in which the selectivities are controlled at the point of insertion of alkynes into the ArS–$Pd^{II}X$ bond.[20] (c) The reversibility of the palladium-catalyzed thioboration reaction was demonstrated by a crossover experiment (eq 4). The reaction of **1** (R^2 = Ph) with 1-octyne

2 ($R^1=C_6H_{13}$, R^2=Ph) $\xrightarrow[\text{2. } CH_3OH]{\text{1. 1-hexyne (5 equivs)/Pd(PPh}_3)_4\text{/ 50°C}}$

	1-octyne + **3** ($R^1=C_6H_{13}$) +	**3** ($R^1=C_4H_9$)	(4)
3 h	31 %	62 %	29 %
37 h	53 %	36 %	38 %

(1 equiv) at 50 °C in the presence of $Pd(PPh_3)_4$ (3 mol %) and styrene (1 equiv) was conducted for 3 h. This solution was then treated with 5 equiv of 1-hexyne for additional hours at 50 °C. Heating for 3 h produced 2-(phenylthio)-1-hexene (29%), 2-(phenylthio)-1-octene (62%), and 1-octyne (31%) by treatment with methanol. After 37 h, the yields of 2-(phenylthio)-1-hexene and 1-octyne were improved to 38% and 53%, respectively, and 2-(phenylthio)-1-octene was reversely reduced to 36%. Thus, the results are consistent with an equilibrium between adduct **2** and its components. The reversibility can be explained by β-elimination of thioborane from **2** through the uncatalyzed process, or it can be induced by the oxidative addition of the B–C bond to the Pd(0) complexes (**2** to **6**) which was reported in dimerization,[21] carbonylation,[22] and Heck's reaction[23] of aryl- or 1-alkenylboron compounds.

Like other related reactions catalyzed by transition metals,[3-8] especially the catalytic hydroboration[9] and the addition of thiols or disulfides to alkynes,[20] the present thioboration reaction may involve an oxidative addition of the B–S bond to the palladium(0) complex, the insertion of an alkyne, and the reductive elimination of sulfides, as outlined in Figure 1. Although we postulate that the oxidative addition of thioborane to the Pd(0) complex produces **5**, we have no direct evidence that such a species exists. Attempts to detect an intermediate by ^{11}B and ^{31}P NMR were unsuccessful, presumably due to a strong thermodynamic preference for the formation of a B–S bond rather than the

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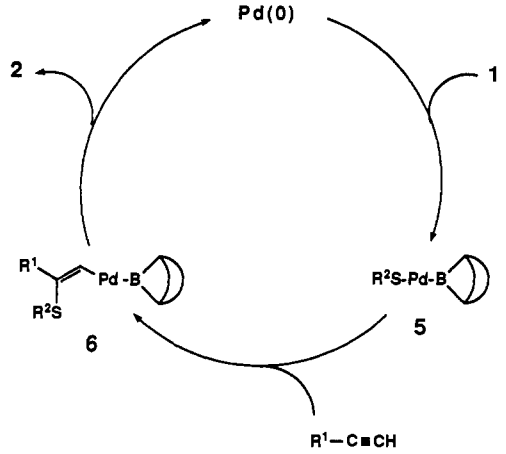
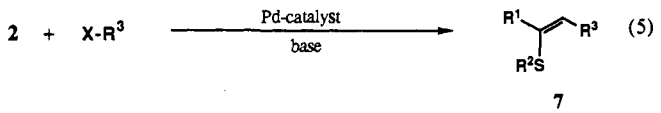


Figure 1.

oxidative adduct **5** in the presence of a phosphine ligand.[24] However, the high selectivities observed in the current study imply, although the equilibrium concentration of an oxidative adduct is low, that the addition may proceed through this activated intermediate. The following two steps, the insertion of alkynes into the RS–$Pd^{II}BX_2$ bond (**5** to **6**) and the reductive elimination of alkenylboron compounds from the vinyl–Pd(II)–BX_2 complexes (**6** to **2**), are known[9,20] to proceed regio- and stereoselectively.

Cross-Coupling Reaction of 2 with Organic Halides. Previously, we reported the palladium-catalyzed boron cross-coupling reaction[25] of 1-alkenyl-, aryl-, and alkylboron compounds with organic halides. The reaction of (*E*)- and (*Z*)-1-alkenylboron derivatives took place readily in the presence of base and palladium catalyst, thus allowing the preparation of isomerically pure alkenes or dienes in high yields.[26] The usefulness of the present study was demonstrated in the one-pot synthesis of vinylic sulfides by sequential thioboration and cross-coupling reactions, both of which were catalyzed by a common palladium(0) catalyst (eq 5).



(5)

The (β-(alkylthio)alkenyl)boranes **2** obtained by the thioboration of 1-hexyne (1.5 equiv) with **1** (1.5 equiv) were directly subjected to the next cross-coupling with iodobenzene (1 equiv) under various reaction conditions (Table IV). The cross-coupling proceeded smoothly in THF at 50 °C in the presence of aqueous NaOH (3 equiv) and $Pd(PPh_3)_4$ (3 mol %) (entry 3). When there are functionalities sensitive to bases on either alkynes or organic halides, the use of K_3PO_4 suspended in DMF can be superior to aqueous NaOH (entry 2). Although the adducts **2** exhibited exceptionally high reactivity on protonolysis with methanol,[27] they were sufficiently stable to these bases under conditions for cross-coupling. The preparations of **2** from a 50% excess of **1** and alkynes were sufficient to consume the halide partners. When the amounts of **2** were less than the amounts of organic halides, the products were contaminated by several byproducts such as R^2SR^3 and R^1CCR^3. These conditions worked equally well for the representative phenylthio or alkylthio derivatives of 9-BBN (entries 5–8).

Table IV. Reaction Conditions for Cross-Coupling of **2** with Iodobenzene[a]

entry	**1**, R^2 =	base	solvent	yield/%[b] (isomeric purity/%)
1	PhS	K_3PO_4	dioxane	37
2	PhS	K_3PO_4	DMF	95 (99)
3	PhS	NaOH	THF–H_2O (8:1)	89 (99)
4	PhS	NaOH	benzene–H_2O (6:1)	87
5	$PhCH_2S$	NaOH	THF–H_2O (8:1)	89 (98)
6	^{n}BuS	NaOH	THF–H_2O (8:1)	86 (99)
7	^{s}BuS	NaOH	THF–H_2O (8:1)	85 (96)[c]
8	^{t}Bu	NaOH	THF–H_2O (8:1)	81 (99)[c]

[a] The preparation of **2** by thioboration of 1-hexyne (1.5 mmol) with **1** (1.5 mmol) in THF at 50 °C for 3 h in the presence of $Pd(PPh_3)_4$ (0.045 mmol) and styrene (1.5 mmol) was followed by the next coupling reaction with iodobenzene (1 mmol) at 50 °C for 16 h. [b] Isolated yields based on iodobenzene. [c] The catalyst prepared from $Pd(dba)_2$ (0.045 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.18 mmol) was used in place of $Pd(PPh_3)_4$.

The regio- and stereochemical integrities of the boron intermediates were completely maintained during the cross-coupling reaction. For example, the ^1H NMR spectrum of **7** ($R^1 = C_4H_9$; R^2,R^3 = Ph) showed two vinylic protons at 6.80 and 6.62 ppm in a 99:1 ratio. The former signal was readily assigned to the (*Z*)-isomer by NOE (6.1%) with allylic protons. Hydrolysis[28] of this sulfide by $HgCl_2$ in aqueous acetonitrile afforded 1-phenyl-2-hexanone as the sole product.

Representative results of the synthesis of alkenyl sulfides *via* the thioboration–coupling sequence are summarized in Table V. Thioboration of alkynes with **1** (R^2 = Ph) at 50 °C for 3 h in the presence of $Pd(PPh_3)_4$ (3 mol %) and styrene (1.5 equiv) was followed by cross-coupling with organic halides at 50 °C in the presence of aqueous NaOH (Procedure A) or in DMF by using K_3PO_4 as a base (Procedure B). From these results, it was shown that this coupling was applicable to representative organic halides, including aryl, 1-alkynyl, 1-alkenyl, allylic, and benzylic halides (entries 1–10). Between procedures A and B, there are no large differences in the yields or the selectivities. However, the superiority of the potassium phosphate base for the synthesis of functionalized sulfides was demonstrated in entries 11–14.

1-Alkenyl sulfides are valuable precursors for the preparation of carbonyl compounds by mercury(II)-promoted hydrolysis,[28] the synthesis of 1-alkenyl sulfoxides[29] as the dienophiles of cycloaddition or the acceptors for Michael addition, and the synthesis of stereodefined alkenes by the cross-coupling reaction[30] with Grignard reagents. However, the reported method using the reaction of carbonyl compounds with (1-(methylthio)alkyl)-phosphonate[31] or ((alkylthio)methyl)trimethylsilane[32] unfortunately leads to a mixture of (*E*)- and (*Z*)-isomers. The palladium-catalyzed substitution of 1-alkenyl halides with metal thioalkoxides[33] and the cross-coupling reaction of 2-(phenylthio)-1-bromo-1-alkene with alkyl- or 1-alkenylboron compounds[34] are known to stereoselectively provide such sulfides.

We recently reported that the catalytic hydroboration of 1-(alkylthio)-1-alkynes with catecholborane selectively produced

(24) The attempt to synthesize the $(PhS)M(BR_2)(PPh_3)_2$ (M = Pt, Pd) complexes by the reaction of $HM(SPh)(PPh_3)_2$ with 9-BBN resulted in the formation of 9-(PhS)-9-BBN with evolution of hydrogen (unpublished results).

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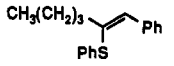
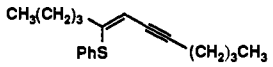
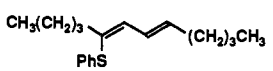
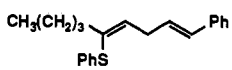
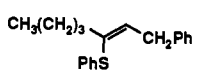
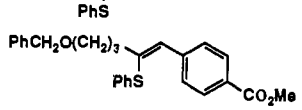
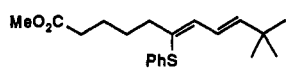
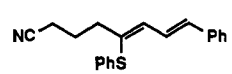
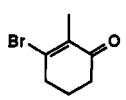
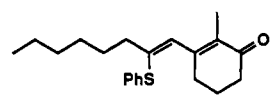
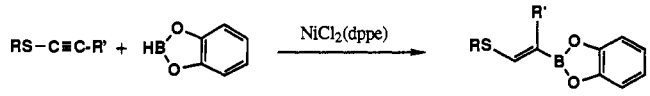
Table V. Synthesis of Functionalized Vinyl Sulfides *via* the Palladium-Catalyzed Thioboration–Coupling Sequence[a]

entry	1-alkyne	halide	product	yield/% (isomeric purity/%)[b] A[c]	B[d]
1	C_4H_9—C≡CH	PhI		89 (99)	95 (99)
2	C_4H_9—C≡CH	PhBr		52	35
3	C_4H_9—C≡CH	I—C≡C$(CH_2)_3CH_3$		66	62
4	C_4H_9—C≡CH	Br—C≡C$(CH_2)_3CH_3$		70 (99)	61
5	C_4H_9—C≡CH	(*E*)-ICH=CH$(CH_2)_3CH_3$		77 (94)	71
6	C_4H_9—C≡CH	(*E*)-BrCH=CH$(CH_2)_3CH_3$		77	83
7	C_4H_9—C≡CH	(*E*)-$BrCH_2$CH=CHPh		52	11
8	C_4H_9—C≡CH	(*E*)-$ClCH_2$CH=CHPh		69 (99)	34
9	C_4H_9—C≡CH	$BrCH_2Ph$		81 (99)	42
10	C_4H_9—C≡CH	$ClCH_2Ph$		86	74
11	$PhCH_2O(CH_2)_3$—C≡CH	*p*-$IC_6H_4CO_2Me$			83 (95)
12	$MeO_2C(CH_2)_4$—C≡CH	(*E*)-ICH=CHBu^t			65 (99)
13	$NC(CH_2)_3$—C≡CH	(*E*)-ICH=CHPh			69 (95)
14	C_6H_{13}—C≡CH				67 (98)

[a] Thioboration of alkyne (1.5 mmol) was carried out at 50 °C for 2–3 h by using 9-(PhS)-9-BBN (1.5 mmol), $Pd(PPh_3)_4$ (0.045 mmol), and styrene (1.5 mmol) followed by cross-coupling with organic halides (1 mmol) under two reaction conditions. [b] Isolated yields based on halides used and isomeric purity were determined by ^1H NMR. [c] Procedure A: NaOH (3 mmol) in THF–H_2O. [d] Procedure B: K_3PO_4 (3 mmol) in THF–DMF.

(β-(alkylthio)vinyl)boronates **8** in high yields (eq 6).[35] The ready



(6)

availability of such boron reagents (**2** and **8**) by catalytic thioboration or hydroboration may now offer a more flexible and reliable route to such stereodefined alkenyl sulfides in combinations with numerous reactions reported in organoboron chemistry.

Experimental Section

All the experiments were carried out under a nitrogen atmosphere. THF was purified by distillation from benzophenone ketyl under nitrogen. 9-Borabicyclo[3.3.1]nonane (9-BBN) in THF (0.5 M) was purchased from Aldrich Chemical Co. IR spectra were taken with a Hitachi Perkin-Elmer Model 125 spectrometer. ^1H NMR spectra were recorded in $CDCl_3$ solutions by a Hitachi R-90H (90 MHz) or JEOL EX-400 (400 MHz) using Me_4Si as an internal standard. ^{11}B and ^{31}P NMR spectra were recorded with a Bruker MSL-400 (128 or 162 MHz) using $BF_3 \cdot OEt_2$ or H_3PO_4 as an external standard. Mass spectra were obtained with a Finnigan ITD 800 for the GC-MS analyses and a JEOL JMS-DX303 for the high-resolution analyses. GC analyses were performed using a Hitachi 263 equipped with a stainless steel column (OV-17 on Uniport B, 2 m).

9-(Alkylthio)-9-BBN. To an oven-dried flask equipped with a distillation apparatus and an oil bubbler were added 9-BBN (0.5 M solution in THF, 30 mmol) and then thiophenol (30 mmol) under nitrogen. Hydrogen began to evolve within a few minutes. The resulting mixture was stirred at 50 °C for 16 h. Evaporation of solvent and distillation under reduced pressure afforded 6.56 g (95%) of 9-(phenylthio)-9-BBN, bp 101 °C/0.15 mmHg. Other derivatives were prepared similarly: 9-(benzylthio)-9-BBN (86%; bp 119 °C/0.15 mmHg), 9-(butylthio)-9-BBN (89%; bp 78 °C/0.15 mmHg), 9-(*sec*-butylthio)-9-BBN (42%; bp 69 °C/0.15 mmHg), 9-(*tert*-butylthio)-9-BBN (10%; bp 66 °C/0.15 mmHg).

Catalysts and Ligands. Tetrakis(triphenylphosphine)palladium(0), dichlorobis(triphenylphosphine)palladium(II), and chlorotris(triphenylphosphine)rhodium(I) are commercial products. Chlorotris(triphenylphosphine)cobalt(I),[36] bis(dibenzylideneacetone)palladium(0),[37] and diphenyl(2,4,6-trimethoxyphenyl)phosphine[38] were prepared by known procedures.

Alkynes. 5-Chloro-1-pentyne, 5-cyano-1-pentyne, cyclohexylethyne, phenylethyne, and 3-hexyne are commercial products. 1-Nonen-8-yne,[39] propargyl alcohol THP ether,[40] and 5-(benzyloxy)-1-pentyne[41] were prepared by reported procedures. 2-(2-Propynyl)cyclopentanone ethylene acetal, methyl 6-heptynoate, and 7-octyn-2-one were synthesized by using the acetoacetic ester synthesis[42] or the malonic ester synthesis.[43] 1-Deuterio-1-decyne (D = 99%) was obtained from the corresponding lithium acetylide and deuterium oxide.[44]

Halides. (*E*)-1-Iodo-1-hexene,[44] (*E*)-1-bromo-1-hexene,[44] 1-iodo-1-hexyne,[45] 1-bromo-1-hexyne,[45] (*E*)-3,3-dimethyl-1-iodo-1-butene,[44] (*E*)-β-iodostyrene,[44] and 3-bromo-2-methyl-2-cyclohexenone[46] were prepared by literature procedures.

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9-[(*Z*)-2-(Phenylthio)-1-octenyl]-9-BBN (2). A mixture of 1-octyne (2.0 mmol), 9-(phenylthio)-9-BBN (2.0 mmol), and $Pd(PPh_3)_4$ (0.06 mmol) was stirred for 3 h at 50 °C. After evaporation in vacuo (10^{-1} mmHg), the residue was dissolved in hexane (5 mL). Filtration through a Celite pad removed the catalyst, and concentration of the filtrate in vacuo gave a viscous oil: ^{1}H NMR δ 0.85 (t, 3 H, J = 7.1 Hz), 1.2–1.4 (m, 6 H), 1.5–1.6 (m, 2 H), 1.8–2.0 (m, 14 H), 2.24 (t, 2 H, J = 7.6 Hz), 6.55 (s, 1 H), 7.2–7.4 (m, 5 H). Irradiation of the vinyl proton at 6.55 ppm resulted in a 6.8% enhancement of the allylic methylene signals at 2.24 ppm.

(*Z*)-1-Deuterio-2-(phenylthio)-1-decene. A mixture of 1-decyne (1.0 mmol) and 9-(phenylthio)-9-BBN (1.1 mmol) was stirred at 50 °C for 3 h in the presence of $Pd(PPh_3)_4$ (0.03 mmol) and styrene (1 mmol). The reaction mixture was treated with CD_3OD (1 mL) (99.8 atom % D) for 30 min at −78 °C and then at room temperature for 1 h. Aqueous 3 M NaOH (4 mL) was added, and the mixture was stirred for an additional 30 min. Chromatography over silica gel with hexane gave 2-(phenylthio)-1-decene (73%, D = 93%, *Z*:*E* = 82:18): n_D 1.5203; IR (film) 3060, 2940, 2860, 1590, 1480, 1440, 745, 690 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.2–1.4 (m, 10 H), 1.5–1.6 (m, 2 H), 2.22 (t, 2 H, J = 7.6 Hz), 4.87 (s, 0.18 H), 5.13 (s, 0.82 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 55 (49), 83 (34), 110 (29), 135 (100), 151 (52), 249 (M$^+$, 42); exact mass calcd for $C_{16}H_{23}DS$ 249.1662, found 249.1681.

(*E*)-1-Deuterio-2-(phenylthio)-1-decene. Thioboration of 1-deuterio-1-decyne (D = 99%) followed by protonolysis with methanol (1 mL) was carried out by a procedure similar to that described above (81%, D = 99%, *Z*:*E* = 22:78): n_D 1.5210; IR (film) 3070, 2940, 2860, 1590, 1480, 1440, 750, 690 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.2–1.4 (m, 10 H), 1.5–1.6 (m, 2 H), 2.22 (t, 2 H, J = 7.6 Hz), 4.86 (s, 0.78 H), 5.13 (s, 0.22 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 55 (48), 83 (33), 110 (40), 135 (100), 151 (72), 249 (M$^+$, 13); exact mass calcd for $C_{16}H_{23}DS$ 249.1662, found 249.1675.

General Procedures for Thioboration of Alkynes. Procedure A. A dry 25-mL flask equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser was flushed with nitrogen. The flask was charged with $Pd(PPh_3)_4$ (35 mg, 0.03 mmol), THF (4 mL), 9-(alkylthio)-9-BBN **1** (1.1 mmol), and 1-alkyne (1.0 mmol). After being stirred for 24 h at 50 °C, the reaction mixture was treated with methanol (1 mL) for 1 h at room temperature. The product was extracted with benzene, and the extract was washed with water and dried over anhydrous magnesium sulfate. Isolation by chromatography over silica gel gave the desired compound.

Procedure B. This method is the same as procedure A, except that the reaction of **1** with alkynes was carried out in the presence of styrene (1 mmol) and $Pd(PPh_3)_4$ (3 mol %).

The following compounds were prepared by the above procedures.

2-(Phenylthio)-1-octene: n_D 1.5328; IR (film) 3080, 2940, 2860, 1615, 1590, 1480, 1440, 750, 690 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.2–1.4 (m, 6 H), 1.5–1.6 (m, 2 H), 2.23 (t, 2 H, J = 7.6 Hz), 4.86 (s, 1 H), 5.14 (s, 1 H), 7.2–7.4 (m, 3 H), 7.44 (d, 2 H, J = 6.8 Hz); MS (EI) *m*/*e* 41 (47), 59 (50), 69 (53), 110 (51), 135 (71), 150 (100), 220 (M$^+$, 24); exact mass calcd for $C_{14}H_{20}S$ 220.1286, found 220.1305.

2-(Butylthio)-1-octene: n_D 1.4710; IR (film) 3100, 2930, 2860, 1600, 1465, 840 cm^{-1}; ^{1}H NMR δ 0.93 (t, 6 H, J = 5.2 Hz), 1.2–1.8 (m, 12 H), 2.21 (t, 2 H, J = 7.5 Hz), 2.69 (t, 2 H, J = 7.0 Hz), 4.68 (s, 1 H), 5.00 (s, 1 H); MS (ITD) *m*/*e* 41 (100), 59 (48), 69 (59), 87 (63), 110 (31), 143 (55), 200 (M$^+$, 11); exact mass calcd for $C_{12}H_{24}S$ 200.1599, found 200.1606.

2-(*sec*-Butylthio)-1-octene: n_D 1.4713; IR (film) 3100, 2930, 2860, 1610, 1460, 1380, 840 cm^{-1}; ^{1}H NMR δ 0.89 (t, 3 H, J = 6.6 Hz), 0.99 (t, 3 H, J = 7.0 Hz), 1.29 (d, 3 H, J = 6.6 Hz), 1.2–1.8 (m, 10 H), 2.20 (t, 2 H, J = 6.8 Hz), 2.9–3.1 (m, 1 H), 4.79 (s, 1 H), 5.07 (s, 1 H); MS (ITD) *m*/*e* 41 (100), 59 (35), 69 (42), 74 (55), 87 (54), 110 (18), 143 (36), 201 (M$^+$ + 1, 3); exact mass calcd for $C_{12}H_{24}S$ 200.1599, found 200.1574.

2-(*tert*-Butylthio)-1-octene. The palladium catalyst generated from $Pd(dba)_2$ (0.03 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.12 mmol) in THF for 30 min at room temperature was used directly: n_D 1.4668; IR (film) 3100, 2955, 2860, 1610, 1460, 1370, 1160, 920 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 5.7 Hz), 1.2–1.8 (m, 8 H), 1.37 (s, 9 H), 2.26 (t, 2 H, J = 6.9 Hz), 5.28 (s, 1 H), 5.41 (s, 1 H); MS (ITD) *m*/*e* 41 (100), 57 (86), 74 (39), 111 (47), 143 (11), 200 (M$^+$, 6); exact mass calcd for $C_{12}H_{24}S$ 200.1599, found 200.1588.

2-(Benzylthio)-1-octene: n_D 1.5320; IR (film) 3030, 2930, 2850, 1600, 1490, 1450, 840, 710, 690 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 5.8 Hz), 1.2–1.8 (m, 8 H), 2.23 (t, 2 H, J = 7.0 Hz), 3.92 (s, 2 H), 4.76 (s, 1 H), 5.02 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 93 (95), 112 (39), 133 (20), 145 (100), 202 (33), 234 (M$^+$, 30); exact mass calcd for $C_{15}H_{22}S$ 234.1442, found 234.1436.

2-(Phenylthio)-1-decene: n_D 1.5421; IR (film) 3070, 2940, 2860, 1615, 1590, 1480, 1440, 750, 690 cm^{-1}; ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.2–1.3 (m, 10 H), 1.5–1.6 (m, 2 H), 2.22 (t, 2 H, J = 7.1 Hz), 4.86 (s, 1 H), 5.14 (s, 1 H), 7.2–7.4 (m, 3 H), 7.43 (d, 2 H, J = 7.8 Hz) (irradiation of the vinyl proton at 5.14 ppm resulted in a 1.4% enhancement of the allylic methylene signal at 2.22 ppm); MS (ITD) *m*/*e* 55 (60), 69 (28), 83 (53), 110 (32), 135 (100), 150 (57), 248 (M$^+$, 15); exact mass calcd for $C_{16}H_{24}S$ 248.1598, found 248.1578.

2-(Phenylthio)-1,8-nonadiene: n_D 1.5368; IR (film) 3080, 2930, 2860, 1645, 1610, 1585, 1480, 1440, 910, 750, 690 cm^{-1}; ^{1}H NMR δ 1.2–1.8 (m, 6 H), 1.9–2.2 (m, 2 H), 2.23 (t, 2 H, J = 7.1 Hz), 4.87 (s, 1 H), 4.93 (d, 1 H, J = 10.3 Hz), 4.97 (d, 1 H, J = 16.9 Hz), 5.14 (s, 1 H), 5.81 (ddt, 1 H, J = 17.1, 9.9, and 7.3 Hz), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 39 (100), 59 (41), 81 (90), 110 (26), 122 (34), 135 (59), 155 (30), 232 (M$^+$, 5); exact mass calcd for $C_{15}H_{20}S$ 232.1286, found 232.1302.

5-Chloro-2-(phenylthio)-1-pentene: n_D 1.5685; IR (film) 3080, 2960, 2860, 1615, 1590, 1480, 1440, 745, 690 cm^{-1}; ^{1}H NMR δ 1.9–2.2 (m, 2 H), 2.41 (t, 2 H, J = 6.9 Hz), 3.54 (t, 2 H, J = 6.4 Hz), 4.95 (s, 1 H), 5.21 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 59 (24), 109 (16), 135 (57), 150 (60), 212 (M$^+$, 100); exact mass calcd for $C_{11}H_{13}ClS$ 212.0427, found 212.0399.

2-(2-(Phenylthio)-2-propenyl)cyclopentanone ethylene acetal: n_D 1.5516; IR (film) 3070, 2950, 2880, 1615, 1590, 1480, 1440, 1150, 1030, 750, 690 cm^{-1}; ^{1}H NMR δ 1.2–2.6 (m, 9 H), 3.7–3.9 (m, 4 H), 4.87 (s, 1 H), 5.16 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 39 (46), 55 (47), 73 (27), 99 (100), 167 (68), 276 (M$^+$, 3); exact mass calcd for $C_{16}H_{20}O_2S$ 276.1185, found 276.1189.

Methyl 6-(phenylthio)-6-heptenoate: n_D 1.5402; IR (film) 3060, 2950, 2870, 1740, 1615, 1590, 1440, 1170, 750, 690 cm^{-1}; ^{1}H NMR δ 1.5–1.8 (m, 4 H), 2.1–2.5 (m, 4 H), 3.67 (s, 3 H), 4.90 (s, 1 H), 5.15 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 59 (67), 81 (63), 109 (55), 141 (100), 150 (51), 250 (M$^+$, 39); exact mass calcd for $C_{14}H_{18}O_2S$ 250.1028, found 250.1003.

5-(Phenylthio)-5-hexenenitrile: n_D 1.5545; IR (film) 3060, 2950, 2870, 2250, 1615, 1590, 1480, 1440, 750, 690 cm^{-1}; ^{1}H NMR δ 1.7–2.1 (m, 2 H), 2.34 (t, 2 H, J = 5.9 Hz), 2.40 (t, 2 H, J = 5.3 Hz), 4.99 (s, 1 H), 5.22 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 65 (45), 109 (35), 135 (88), 175 (100), 186 (47), 203 (M$^+$, 90); exact mass calcd for $C_{12}H_{13}NS$ 203.0769, found 203.0767.

7-(Phenylthio)-7-octen-2-one: n_D 1.5414; IR (film) 3060, 2950, 2870, 1720, 1615, 1590, 1480, 1440, 1360, 1170, 750, 690 cm^{-1}; ^{1}H NMR δ 1.4–1.7 (m, 4 H), 2.12 (s, 3 H), 2.2–2.6 (m, 4 H), 4.89 (s, 1 H), 5.15 (s, 1 H), 7.2–7.5 (m, 5 H); MS (ITD) *m*/*e* 51 (26), 65 (24), 99 (92), 125 (45), 135 (31), 176 (100), 234 (M$^+$, 44); exact mass calcd for $C_{14}H_{18}OS$ 234.1078, found 234.1069.

2-(Phenylthio)-2-propenol tetrahydropyranyl ether: n_D 1.5523; IR (film) 3060, 2950, 2870, 1615, 1585, 1480, 1440, 1200, 1120, 1065, 1030, 905, 870, 750, 690 cm^{-1}; ^{1}H NMR δ 1.4–2.0 (m, 6 H), 3.3–4.4 (m, 4 H), 4.63 (br s, 1 H), 5.18 (s, 1 H), 5.55 (s, 1 H), 7.1–7.5 (m, 5 H); MS (EI) *m*/*e* 41 (24), 59 (20), 85 (59), 135 (46), 150 (100), 250 (M$^+$, 2); exact mass calcd for $C_{14}H_{18}O_2S$ 250.1028, found 250.1003.

1-Cyclohexyl-1-(phenylthio)ethene. A mixture of $Pd(dba)_2$ (0.03 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.12 mmol) was used as a catalyst: n_D 1.5662; IR (film) 3090, 2950, 2860, 1615, 1595, 1480, 1450, 750, 690 cm^{-1}; ^{1}H NMR δ 1.0–1.5 (m, 6 H), 1.5–1.9 (m, 2 H), 1.9–2.2 (m, 3 H), 4.78 (s, 1 H), 5.16 (s, 1 H), 7.1–7.5 (m, 5 H); MS (ITD) *m*/*e* 40 (88), 67 (100), 109 (55), 141 (99), 218 (M$^+$, 77); exact mass calcd for $C_{14}H_{18}S$ 218.1130, found 218.1107.

Crossover Experiment. A mixture of 1-octyne (1.0 mmol), 9-(phenylthio)-9-BBN (1.0 mmol), $Pd(PPh_3)_4$ (0.03 mmol), and styrene (1 mmol) in THF (4 mL) was stirred for 3 h at 50 °C. 1-Hexyne (5.0 mmol) was then added at the same temperature. At suitable time intervals, portions of the solution were sampled with a syringe (ca. 0.5 mL) and subjected to protonolysis with methanol (0.1 mL). GC analyses at the following intervals revealed the formation of these compounds: after 3 h, 2-(phenylthio)-1-hexene (29%), 2-(phenylthio)-1-octene (62%), and 1-octyne (31%); after 37 h, 2-(phenylthio)-1-hexene (38%), 2-(phenylthio)-1-octene (36%), and 1-octyne (53%).

General Procedure for Cross-Coupling of 2 with Organic Halides. A dry 25-mL flask equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser was charged with $Pd(PPh_3)_4$ (0.045 mmol), THF (2 mL), styrene (1.5 mmol), 9-(alkylthio)-9-BBN (1.5 mmol), and

1-alkyne (1.5 mmol) under nitrogen. The mixture was stirred at 50 °C for 2–3 h to give a solution of 9-[(*Z*)-2-(alkylthio)-1-alkenyl]-9-BBN **2**.

Procedure A. To the above solution were added additional THF (6 mL), organic halide (1.0 mmol), and aqueous 3M NaOH (1 mL, 3 mmol), and the resulting mixture was then stirred at 50 °C for 16 h. The product was extracted with benzene, and the extract was washed with water and dried over $MgSO_4$. The isolation of products was carried out by chromatography over silica gel.

Procedure B. To the above solution of **2** were added DMF (6 mL), organic halide (1.0 mmol), and powdered K_3PO_4 (3 mmol). After 16 h of stirring at 50 °C, the product was isolated by the method described in procedure A.

(*Z*)-1-Phenyl-2-(phenylthio)-1-hexene: n_D 1.6102; IR (film) 3050, 2950, 2850, 1585, 1475, 1435, 740, 685 cm^{-1}; ^1H NMR δ 0.85 (t, 3 H, J = 7.3 Hz), 1.2–1.3 (m, 2 H), 1.5–1.6 (m, 2 H), 2.28 (t, 2 H, J = 7.6 Hz), 6.80 (s, 1 H), 7.2–7.4 (m, 8 H), 7.55 (d, 2 H, J = 7.3 Hz) (irradiation of the vinyl proton at 6.80 ppm enhanced (6.1%) the allylic methylene signal at 2.28 ppm); MS (ITD) m/e 40 (100), 65 (32), 91 (58), 115 (74), 135 (64), 226 (29), 268 (M^+, 59); exact mass calcd for $C_{18}H_{20}S$ 268.1286, found 268.1302.

(*Z*)-2-(Butylthio)-1-phenyl-1-hexene: n_D 1.5496; IR (film) 3060, 2960, 2870, 1600, 1490, 1460, 745, 690 cm^{-1}; ^1H NMR δ 0.87 (t, 3 H, J = 7.3 Hz), 0.96 (t, 3 H, J = 7.3 Hz), 1.30–1.45 (m, 4 H), 1.5–1.6 (m, 2 H), 1.60–1.65 (m, 2 H), 2.41 (t, 2 H, J = 7.1 Hz), 2.66 (t, 2 H, J = 7.6 Hz), 6.53 (s, 1 H), 7.19 (t, 1 H, J = 7.3 Hz), 7.32 (t, 2 H, J = 7.6 Hz), 7.52 (d, 2 H, J = 7.3 Hz); MS (ITD) m/e 59 (7), 101 (11), 115 (24), 135 (14), 150 (5), 191 (9), 249 (M^+ + 1, 100); exact mass calcd for $C_{16}H_{24}S$ 248.1599, found 248.1594.

(*Z*)-2-(*sec*-Butylthio)-1-phenyl-1-hexene. The palladium complex prepared from $Pd(dba)_2$ (0.045 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.18 mmol) was used in place of $Pd(PPh_3)_4$: n_D 1.5503; IR (film) 3060, 2960, 2880, 1605, 1500, 1445, 1380, 750, 690 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7.6 Hz), 0.95 (t, 3 H, J = 7.3 Hz), 1.19 (d, 3 H, J = 6.4 Hz), 1.3–1.7 (m, 6 H), 2.40 (t, 2 H, J = 7.6 Hz), 2.95–3.05 (m, 1 H), 6.59 (s, 1 H), 7.19 (t, 1 H, J = 7.3 Hz), 7.31 (t, 2 H, J = 7.6 Hz), 7.55 (d, 2 H, J = 7.3 Hz); MS (ITD) m/e 57 (29), 101 (34), 117 (94), 135 (43), 150 (26), 191 (21), 248 (M^+, 100); exact mass calcd for $C_{16}H_{24}S$ 248.1600, found 248.1607.

(*Z*)-2-(*tert*-Butylthio)-1-phenyl-1-hexene. The palladium catalyst obtained from $Pd(dba)_2$ (0.045 mmol) and diphenyl(2,4,6-trimethoxyphenyl)phosphine (0.18 mmol) was used in place of $Pd(PPh_3)_4$: n_D 1.5415; IR (film) 3060, 2960, 2850, 1605, 1495, 1455, 1360, 1160, 750, 690 cm^{-1}; ^1H NMR δ 0.94 (t, 3 H, J = 7.3 Hz), 1.27 (s, 9 H), 1.3–1.4 (m, 2 H), 1.60–1.65 (m, 2 H), 2.46 (t, 2 H, J = 7.6 Hz), 6.85 (s, 1 H), 7.20 (t, 1 H, J = 7.3 Hz), 7.29 (t, 2 H, J = 7.6 Hz), 7.68 (d, 2 H, J = 7.3 Hz); MS (ITD) m/e 57 (37), 101 (14), 117 (51), 135 (8), 193 (15), 248 (M^+, 100); exact mass calcd for $C_{16}H_{24}S$ 248.1599, found 248.1626.

(*Z*)-2-(Benzylthio)-1-phenyl-1-hexene: n_D 1.5955; IR (film) 3060, 2960, 2880, 1610, 1500, 1460, 755, 695 cm^{-1}; ^1H NMR δ 0.93 (t, 3 H, J = 7.3 Hz), 1.3–1.4 (m, 2 H), 1.55–1.65 (m, 2 H), 2.39 (t, 2 H, J = 7.6 Hz), 3.88 (s, 2 H), 6.54 (s, 1 H), 7.19 (t, 1 H, J = 7.3 Hz), 7.25 (s, 5 H), 7.30 (t, 2 H, J = 7.6 Hz), 7.47 (d, 2 H, J = 7.3 Hz); MS (ITD) m/e 65 (29), 91 (100), 135 (70), 191 (26), 282 (M^+, 21); exact mass calcd for $C_{19}H_{22}S$ 282.1442, found 282.1420.

(5*Z*,7*E*)-5-(Phenylthio)-5,7-dodecadiene: n_D 1.5580; IR (film) 3060, 2920, 2850, 1645, 1585, 1475, 1435, 970, 735, 685 cm^{-1}; ^1H NMR δ 0.83 (t, 3 H, J = 7.3 Hz), 0.89 (t, 3 H, J = 6.8 Hz), 1.2–1.5 (m, 8 H), 2.11 (dt, 2 H, J = 7.3 and 6.8 Hz), 2.19 (t, 2 H, J = 7.6 Hz), 5.81 (dt, 1 H, J = 15.1 and 7.3 Hz), 6.42 (d, 1 H, J = 10.3 Hz), 6.65 (dd, 1 H, J = 15.1 and 10.3 Hz), 7.2–7.4 (m, 5 H); MS (ITD) m/e 57 (25), 67 (19), 79 (27), 109 (18), 123 (11), 141 (15), 197 (63), 274 (M^+, 100); exact mass calcd for $C_{18}H_{26}S$ 274.1756, found 274.1743.

(*Z*)-5-(Phenylthio)-5-dodecen-7-yne: n_D 1.5591; IR (film) 3050, 2920, 2860, 2200, 1580, 1475, 1435, 740, 685 cm^{-1}; ^1H NMR δ 0.77 (t, 3 H, J = 7.3 Hz), 0.91 (t, 3 H, J = 7.3 Hz), 1.1–1.2 (m, 2 H), 1.35–1.55 (m, 6 H), 2.12 (t, 2 H, J = 7.6 Hz), 2.36 (dt, 2 H, J = 6.8 and 2.0 Hz), 5.65 (s, 1 H), 7.2–7.3 (m, 3 H), 7.40–7.45 (m, 2 H); MS (ITD) m/e 40 (100), 51 (27), 79 (28), 91 (28), 153 (42), 272 (M^+, 23); exact mass calcd for $C_{18}H_{24}S$ 272.1599, found 272.1588.

(1*E*,4*Z*)-1-Phenyl-5-(phenylthio)-1,4-nonadiene: n_D 1.5990; IR (film) 3045, 2950, 2880, 1590, 1480, 1440, 970, 740, 690 cm^{-1}; ^1H NMR δ 0.85 (t, 3 H, J = 7.3 Hz), 1.2–1.4 (m, 2 H), 1.4–1.6 (m, 2 H), 2.20 (t, 2 H, J = 7.6 Hz), 3.26 (t, 2 H, J = 6.8 Hz), 5.96 (t, 1 H, J = 7.1 Hz), 6.19 (dt, 1 H, J = 15.6 and 6.6 Hz), 6.40 (d, 1 H, J = 16.1 Hz), 7.2–7.4 (m, 10 H); MS (ITD) m/e 91 (100), 115 (33), 129 (23), 143 (45), 199 (19), 308 (M^+, 40); exact mass calcd for $C_{21}H_{24}S$ 308.1599, found 308.1597.

(*Z*)-1-Phenyl-3-(phenylthio)-2-heptene: n_D 1.5838; IR (film) 3055, 2940, 2880, 1590, 1480, 1440, 740, 695 cm^{-1}; ^1H NMR δ 0.83 (t, 3 H, J = 7.3 Hz), 1.2–1.3 (m, 2 H), 1.45–1.50 (m, 2 H), 2.19 (t, 2 H, J = 7.6 Hz), 3.71 (d, 2 H, J = 7.3 Hz), 6.04 (t, 1 H, J = 7.3 Hz), 7.2–7.4 (m, 10 H); MS (EI) m/e 41 (26), 65 (22), 91 (100), 117 (85), 129 (37), 173 (25), 240 (17), 282 (M^+, 42); exact mass calcd for $C_{19}H_{22}S$ 282.1443, found 282.1422.

Methyl 4-[(*Z*)-5-(benzyloxy)-2-(phenylthio)-1-pentenyl]benzoate: n_D 1.6089; IR (film) 3030, 2950, 2850, 1720, 1605, 1430, 1270, 1100, 740, 690 cm^{-1}; ^1H NMR δ 1.8–1.9 (m, 2 H), 2.41 (t, 2 H, J = 7.3 Hz), 3.43 (t, 2 H, J = 6.3 Hz), 3.90 (s, 3 H), 4.44 (s, 2 H), 6.77 (s, 1 H), 7.2–7.4 (m, 10 H), 7.59 (d, 2 H, J = 8.3 Hz), 7.99 (d, 2 H, J = 8.3 Hz); MS (EI) m/e 59 (19), 91 (100), 115 (24), 135 (40), 235 (19), 284 (59), 309 (18), 418 (M^+, 17); exact mass calcd for $C_{26}H_{26}O_3S$ 418.1603, found 418.1586.

Methyl (6*Z*,8*E*)-10,10-dimethyl-6-(phenylthio)-6,8-undecadienoate: n_D 1.5483; IR (film) 3070, 2970, 2880, 1750, 1645, 1590, 1485, 1440, 1200, 985, 740, 690 cm^{-1}; ^1H NMR δ 1.03 (s, 9 H), 1.4–1.6 (m, 4 H), 2.20 (t, 2 H, J = 6.8 Hz), 2.25 (t, 2 H, J = 7.1 Hz), 3.64 (s, 3 H), 5.84 (d, 1 H, J = 15.1 Hz), 6.40 (d, 1 H, J = 10.3 Hz), 6.56 (dd, 1 H, J = 15.6 and 10.3 Hz), 7.1–7.4 (m, 5 H); MS (ITD) m/e 55 (50), 91 (57), 133 (45), 167 (37), 199 (23), 332 (M^+, 100); exact mass calcd for $C_{20}H_{28}O_2S$ 332.1810, found 332.1800.

(5*Z*,7*E*)-8-Phenyl-5-(phenylthio)-5,7-octadienenitrile: mp 72 °C; IR (Nujol) 3060, 2950, 2870, 2250, 1590, 1480, 1440, 975, 750, 690 cm^{-1}; ^1H NMR δ 1.8–2.0 (m, 2 H), 2.29 (t, 2 H, J = 7.1 Hz), 2.42 (t, 2 H, J = 7.1 Hz), 6.66 (d, 1 H, J = 10.8 Hz), 6.70 (d, 1 H, J = 15.6 Hz), 7.2–7.5 (m, 11 H); MS (EI) m/e 91 (24), 115 (31), 128 (20), 141 (41), 154 (25), 196 (23), 228 (61), 305 (M^+, 100); exact mass calcd for $C_{20}H_{19}NS$ 305.1239, found 305.1255.

2-Methyl-3-[(*Z*)-2-(phenylthio)-1-octenyl]-2-cyclohexenone: n_D 1.5655; IR (film) 3050, 2930, 2860, 1670, 1590, 1440, 1350, 740, 690 cm^{-1}; ^1H NMR δ 0.86 (t, 3 H, J = 6.8 Hz), 1.2–1.3 (m, 6 H), 1.45–1.60 (m, 2 H), 1.78 (s, 3 H), 1.85–1.95 (m, 2 H), 2.22 (t, 2 H, J = 7.3 Hz), 2.35–2.45 (m, 2 H), 2.55 (t, 2 H, J = 6.1 Hz), 6.38 (s, 1 H), 7.2–7.3 (m, 5 H); MS (EI) m/e 41 (88), 55 (57), 77 (58), 91 (98), 195 (57), 223 (57), 251 (100), 328 (M^+, 40); exact mass calcd for $C_{21}H_{28}OS$ 328.1861, found 328.1838.

1-Phenyl-2-hexanone. A mixture of $HgCl_2$ (2.7 g, 10 mmol) and (*Z*)-1-phenyl-2-(phenylthio)-1-hexene (268 mg, 1.0 mmol) in acetonitrile–water (3:1, 16 mL) was stirred at reflux temperature for 12 h under nitrogen. The product was extracted with hexane, and the extract was washed with water and dried over $MgSO_4$. Evaporation of solvent gave the crude ketone in a 98% yield: IR (film) 3060, 2960, 2880, 1715, 1500, 1455, 740, 700 cm^{-1}; ^1H NMR δ 0.86 (t, 3 H, J = 6.8 Hz), 1.1–1.8 (m, 4 H), 2.44 (t, 2 H, J = 7.0 Hz), 3.67 (s, 2 H), 7.1–7.5 (m, 5 H); MS (ITD) m/e 41 (95), 57 (100), 65 (34), 85 (75), 91 (63), 176 (M^+, 10).