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# The palladium-catalyzed cross-coupling reaction of 9-organothio-9-borabicyclo[3.3.1]nonanes with organic electrophiles: synthesis of unsymmetrical sulfides

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## Abstract

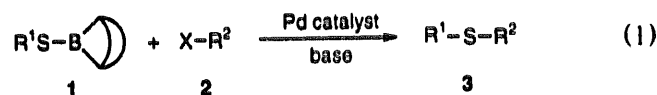
The synthesis of unsymmetrical sulfides was carried out in high yields by the palladium-catalyzed cross-coupling reaction of 9-organothio-9-borabicyclo[3.3.1]nonane (9-RS-9-BBN) with organic electrophiles, such as iodoarenes, 1-iodo-1-alkenes, allyl carbonate and propargyl carbonate. Iodoarenes and 1-iodo-1-alkenes were smoothly converted into the corresponding sulfides at 50°C in the presence of PdCl<sub>2</sub>(dppf) (3 mol%) and K<sub>3</sub>PO<sub>4</sub> (3 equiv.) in DMF. In contrast, the cross-coupling reaction of 9-RS-9-BBN with allyl or propargyl carbonates occurred in DMF without the assistance of a base. Both reactions catalyzed by Pd(dba)<sub>2</sub>-dppf regioselectively produced allyl and allenyl sulfides in excellent yields. The scope and limitations of the reactions, as well as the effects of varying the reaction conditions, are discussed.

**Keywords:** Boron; Palladium

## 1. Introduction

The transition metal-catalyzed cross-coupling reaction of sulfur nucleophiles with organic electrophiles is an attractive and straightforward method to synthesize aryl and vinyl sulfides with high regio- and stereoselectivity. A number of metal thioalkoxides, including lithium [1,2], sodium [3–8], silicon [9,10], potassium [9,11,12], and tin [13–17], have been successfully utilized, but the reaction of boron-sulfur reagents has not received much attention (for the synthetic application of (organothio)borane reagents, see Refs. [18–22]). We recently reported the palladium(0)-catalyzed thioboration [23] of terminal alkynes with 9-organothio-9-borabicyclo[3.3.1]nonane (9-RS-9-BBN) [24] (**1**) to provide [(Z)-2-organothio-1-alkenyl]boranes and their cross-coupling with organic halides to give 1-alkenyl sulfides. The reaction was carried out under mild conditions (at 50°C) with high stereoselectivity, without catalysis poisoning, and with toleration to a wide vari-

ety of functional groups (the high catalytic efficiency and chemoselectivity were achieved using the low nucleophilic sulfur atom conjugated with the boron [19,25,26]). Since **1** is readily available by the dehydrogenative condensation of 9-BBN with thiols, the results prompted us to examine other transition metal-catalyzed reactions of **1**. We found that the cross-coupling reaction of **1** with organic electrophiles (**2**) was readily catalyzed by PdCl<sub>2</sub>(dppf) under very mild conditions to afford unsymmetrical sulfides (**3**) in excellent yields (Eq. (1)).



## 2. Results and discussion

### 2.1. Reaction conditions

The reaction conditions were optimized at 50°C using **1** (R<sup>1</sup> = Ph) and iodobenzene (Table 1). The cross-

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Table 1  
Reaction conditions <sup>a</sup>

Entry	Catalyst	Base	Yield (%) <sup>b</sup>
1	PdCl <sub>2</sub> (dppf) <sup>c</sup>	K <sub>3</sub> PO <sub>4</sub>	99
2	PdCl <sub>2</sub> (dppf) <sup>c</sup>	KOH	64
3	PdCl <sub>2</sub> (dppf) <sup>c</sup>	K <sub>2</sub> CO <sub>3</sub>	8
4	Pd(dba) <sub>2</sub> /2dppf <sup>c</sup>	K <sub>3</sub> PO <sub>4</sub>	99
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	K <sub>3</sub> PO <sub>4</sub>	22
6	Pd(dba) <sub>2</sub> /2dppb <sup>d</sup>	K <sub>3</sub> PO <sub>4</sub>	12
7	Pd(dba) <sub>2</sub> /2dppp <sup>e</sup>	K <sub>3</sub> PO <sub>4</sub>	5
8	Pd(dba) <sub>2</sub> /2dppe <sup>f</sup>	K <sub>3</sub> PO <sub>4</sub>	4

<sup>a</sup> The coupling between 9-(phenylthio)-9-BBN (1.1 mmol) and iodobenzene (1.0 mmol) was conducted at 50°C for 5 h in DMF (6 ml) in the presence of catalyst (0.03 mmol) and base (3 mmol).

<sup>b</sup> GLC yields based on iodobenzene.

<sup>c</sup> 1,1'-Bis(diphenylphosphino)ferrocene.

<sup>d</sup> 1,4-Bis(diphenylphosphino)butane.

<sup>e</sup> 1,3-Bis(diphenylphosphino)propane.

<sup>f</sup> 1,2-Bis(diphenylphosphino)ethane.

coupling reaction of organoboron reagents with organic halides proceeds in the presence of a base as well as a palladium catalyst (for reviews see Refs. [27–31]). A suitable base is again essential for the present coupling reaction. The use of powdered K<sub>3</sub>PO<sub>4</sub> suspended in DMF was recognized to be most effective (entry 1) because stronger or weaker bases, such as powdered KOH or K<sub>2</sub>CO<sub>3</sub>, resulted in low yields (entries 2 and 3). As for the ligand on the palladium catalyst, 1,1'-bis(diphenylphosphino)ferrocene (dppf) [32] revealed an extremely high catalysis activity. The reaction produced **3** in quantitative yields within 5 h when using PdCl<sub>2</sub>(dppf) or Pd(dba)<sub>2</sub>/2dppf (entries 1 and 4). Although Pd(PPh<sub>3</sub>)<sub>4</sub> has been used as a catalyst for such coupling reactions of thioalkoxides [1–17], the catalysis activity was relatively low (entry 5). Other bidentate phosphine ligands, such as dppb, dppp, and dppe, were also ineffective (entries 6–8). For all these coupling reactions in the presence of K<sub>3</sub>PO<sub>4</sub>, the polar solvents accelerated the reaction rate: e.g. DMF > dioxane > toluene.

## 2.2. A relative reactivity of the representative thioalkoxides

Various metal thioalkoxides have been used for the cross-coupling with organic halides [1–17]. To examine the effect of metal ions on the reaction rate, iodobenzene was allowed to react with the representative metal thiophenoxides under neutral conditions or in the presence of 3 equiv. K<sub>3</sub>PO<sub>4</sub> (Table 2). Under neutral conditions, the trimethylstannyl thiophenoxide revealed higher reactivity than the 9-BBN or the trimethylsilyl derivative; however, the reactions of lithium and sodium thiophenoxide were very slow, presumably due to the poisoning of the catalyst by coordination of the sulfur anion to the palladium metal. In contrast, the reactivity

Table 2  
Cross-coupling of various metal thiophenoxides with iodobenzene <sup>a</sup>

Entry	PhS-m	None		K <sub>3</sub> PO <sub>4</sub> <sup>b</sup>	
		Conv. (%) <sup>c</sup>	Yield (%) <sup>d</sup>	Conv. (%) <sup>c</sup>	Yield (%) <sup>d</sup>
1	m = 9-BBN	16	13	100	99
2	m = Li	3	2		
3	m = Na	3	2		
4	m = SiMe <sub>3</sub>	18	13	81	78
5	m = SnMe <sub>3</sub>	38	37	70	70

<sup>a</sup> Reactions were conducted at 50°C for 5 h in DMF (6 ml) using a metal thiophenoxide (1.1 mmol), iodobenzene (1.0 mmol), and PdCl<sub>2</sub>(dppf) (0.03 mmol).

<sup>b</sup> The same reaction as above was carried out in the presence of K<sub>3</sub>PO<sub>4</sub> (3 mmol).

<sup>c</sup> Conversion of iodobenzene.

<sup>d</sup> GLC yields based on iodobenzene.

of the boron, silicon, and tin reagents was dramatically enhanced in the presence of K<sub>3</sub>PO<sub>4</sub> (entries 1, 4 and 5). Although the cross-coupling of stannyl thioalkoxides with organic halides has been studied under neutral conditions at high reaction temperatures (100–120°C) [13–17], the use of a base and PdCl<sub>2</sub>(dppf) may render the experimental conditions fairly mild (entry 5). The presence of a base accelerates or is often essential for other cross-coupling reactions of less reactive organometallics. For example, cesium fluoride was reported to be effective for the cross-coupling reaction of silyl thioalkoxides [9]. The bases similarly accelerated the palladium-catalyzed cross-coupling reaction of organoboron [27–31,33–35], -silicon [36,37], and -tin [38] compounds.

## 2.3. Reaction scope

A variety of (alkylthio)- or (arylthio)boron compounds can be used for the cross-coupling. A comparison of 9-(arylthio)- and 9-(alkylthio)-9-BBN derivatives, during the coupling with iodobenzene in the presence of PdCl<sub>2</sub>(dppf) and K<sub>3</sub>PO<sub>4</sub> in DMF, demonstrated that representative thioborane reagents produce **3**

Table 3  
Effect of organothio groups on the reaction rate <sup>a</sup>

Entry	1	Temperature (°C)	Yield (%) <sup>b</sup>
1	R <sup>1</sup> S = PhS	50	87
2	R <sup>1</sup> S = 4-MeC <sub>6</sub> H <sub>4</sub> S	50	98
3	R <sup>1</sup> S = 4-ClC <sub>6</sub> H <sub>4</sub> S	80	91
4	R <sup>1</sup> S = <sup>n</sup> BuS	100	82
5	R <sup>1</sup> S = <sup>i</sup> BuS	50	84
6	R <sup>1</sup> S = <sup>t</sup> BuS	50	80
7	R <sup>1</sup> S = PhCH <sub>2</sub> S	120	18

<sup>a</sup> All reactions were carried out for 5 h using **1** (1.1 mmol), iodobenzene (1.0 mmol), PdCl<sub>2</sub>(dppf) (0.03 mmol), K<sub>3</sub>PO<sub>4</sub> (3 mmol) in DMF (6 ml).

<sup>b</sup> Isolated yields based on iodobenzene.

in a range of 80–98% yields (entries 1–6 in Table 5). The reaction can readily be carried out at 50°C when using (aryltio)boranes having electron-donating groups and secondary or tertiary (alkylthio)boranes; however, (4-chlorophenylthio)borane, or sterically less hindered primary (alkylthio)boranes such as (butylthio)borane, gave satisfactory yields at higher reaction temperatures (entries 3 and 4). The coupling reaction of (benzylthio)borane was also very slow at 50°C and provided a very low yield of benzyl phenyl sulfide (18%) together with dibenzyl sulfide (7%) at 120°C (entry 7). The oxidative addition of benzyl phenyl sulfide to the palladium(0) complex may give a  $\text{PhCH}_2\text{-Pd(II)-SPh}$  species (for the oxidative addition of the carbon–sulfur bond to transition metal complexes, see Refs. [39–42]), which undergoes further reaction with (benzylthio)borane, leading to dibenzyl sulfide. Such by-product formation was also observed in the nickel(0)-catalyzed cross-coupling of thiolate anions with aryl halides [11].

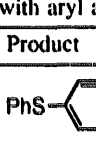








In Table 4, the representative results of the palladium-catalyzed cross-coupling reaction of **1** with **2** are summarized.

There were no large differences in the yields and the

reaction rates between aryl iodides having an electron-donating and an electron-withdrawing substituent, and both iodoarenes were completely consumed within 5 h at 50°C (entries 1–4). 2-Iodotoluene quantitatively coupled with **1** ( $\text{R}^1 = \text{tBu}$ ) at 50°C (entry 5), but the reaction of iodomesitylene with **1** ( $\text{R}^1 = \text{Ph}$ ) failed at 80°C due to steric hindrance. Although the high yields were readily achieved for the representative iodoarenes, lower yields resulted for the bromides. The reaction with 1-iodo-1-alkenes produced the corresponding alkenyl sulfides in high yields with retention of the configuration (entries 7–9).

We previously reported that the cross-coupling reaction of propargyl carbonates with organoboranes or organoboronates occurs smoothly without any assistance from bases, because the oxidative addition produces the (alkoxo)palladium(II) species able to transmetalate with boron reagents under neutral conditions [43]. Indeed, geranyl carbonate in DMF smoothly coupled with **1** ( $\text{R}^1 = \text{Ph}$ ) at 80°C in the presence of 3 mol%  $\text{Pd(dba)}_2/\text{dppf}$  to regioselectively provide a terminal coupling product in 93% yield (Eq. (2)). The oxidative addition of propargyl carbonate to the palladium(0), through an  $\text{S}_\text{N}2'$  rearrangement, led to an

Table 4  
Synthesis of sulfides via palladium-catalyzed coupling reaction of **1** with aryl and 1-alkenyl halides <sup>a</sup>

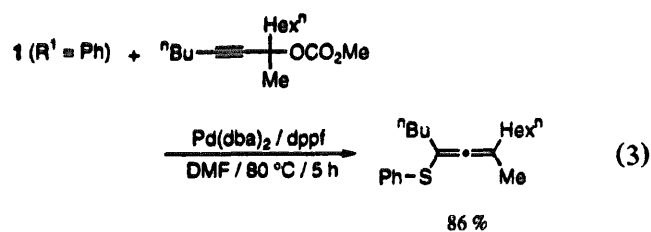
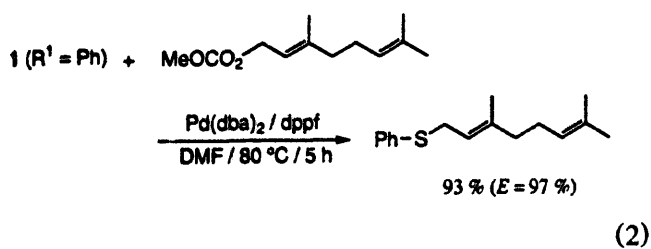
Entry	<b>1</b>	Halide	Product	Yield (%) <sup>b</sup> (isomeric purity (%) <sup>c</sup> )
1	$\text{R}^1\text{S} = \text{PhS}$	Ph		87
2	$\text{R}^1\text{S} = \text{PhS}$	4- $\text{IC}_6\text{H}_4\text{NMe}_2$		92
3	$\text{R}^1\text{S} = \text{PhS}$	4- $\text{IC}_6\text{H}_4\text{CO}_2\text{Me}$		95
4	$\text{R}^1\text{S} = \text{tBuS}$	4- $\text{IC}_6\text{H}_4\text{C}\equiv\text{N}$		99
5	$\text{R}^1\text{S} = \text{tBuS}$	2- $\text{IC}_6\text{H}_4\text{Me}$		91
6	$\text{R}^1\text{S} = \text{PhS}$	$\text{CH}_2=\underset{\text{I}}{\text{C}}-(\text{CH}_2)_5\text{CH}_3$		87
7	$\text{R}^1\text{S} = 4\text{-CH}_3\text{C}_6\text{H}_4\text{S}$	( <i>E</i> )- $\text{ICH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$		99 (99)
8	$\text{R}^1\text{S} = \text{tBuS}$	( <i>E</i> )- $\text{ICH}=\text{CHPh}$		93 (98)
9	$\text{R}^1\text{S} = \text{PhS}$	( <i>E</i> )- $\text{ICH}=\text{CH}^t\text{Bu}$		91 (99)

<sup>a</sup> All reactions were conducted in DMF (6 ml) at 50°C for 5 h using 9-(organothio)-9-BBN (1.1 mmol) and organic halide (1.0 mmol) in the presence of  $\text{PdCl}_2(\text{dppf})$  (0.03 mmol) and  $\text{K}_3\text{PO}_4$  (3 mmol).

<sup>b</sup> Isolated yields based on the halides used.

<sup>c</sup> Isomeric purity determined by GLC.

allenyl sulfide as the sole product under similar neutral conditions [43] (Eq. (3)).



## 2.4. Reaction mechanism

The reaction may proceed through a mechanism [44] similar to that of palladium-catalyzed coupling reactions of metal-sulfur compounds involving (a) the oxidative addition of organic halide to the palladium(0) complex to give  $X\text{-Pd(II)-R}^2$  (**4**), (b) the base-induced transfer of the  $R^1S$  group on boron to **4**, and (c) the reductive elimination of **3** from  $R^1S\text{-Pd(II)-R}^2$  (**5**) (Fig. 1).

Preliminary results indicate that the base activates the nucleophilic substitution reaction of **1**. For example, the reaction of **1** ( $R^1 = Ph$ ) with bromohexane at  $50^\circ\text{C}$  for 16 h in DMF produced a quantitative yield of hexyl phenyl sulfide in the presence of 3 equiv.  $K_3PO_4$ , whereas a 55% yield resulted in the absence of the base. The nucleophilicity of the thio group can be increased by coordination of the base with the boron atom, thereby

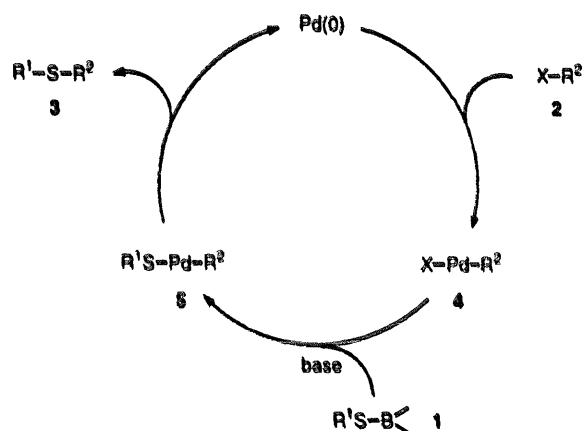


Fig. 1. Catalytic cycle for coupling.

facilitating the transfer of the thio group from boron to **4**.

Hartwig and coworker [45] have recently demonstrated that the addition of sodium thiolates to  $(\text{dppe})\text{Pd}(\text{Cl})(\text{Ar})$  provided palladium thiolate complexes,  $(\text{dppe})\text{Pd}(\text{S}^i\text{Bu})(\text{Ar})$  (**6**), which correspond to **5** and were stable at room temperature. In contrast to C-C bond-forming reactions [46-48], the reductive elimination from **6** was accelerated by electron-withdrawing substituents on the aromatic nucleus, indicating a transition state that contains some characteristic analogous to nucleophilic aromatic substitutions [49]. The electron-withdrawing groups in haloarenes, in general, accelerate the oxidative addition step and presumably also the transmetalation step; thus, the presence of these groups may accelerate the overall catalytic cycle. However, the present reaction revealed no appreciable rate difference between unsubstituted and substituted iodoarenes having 4-Me<sub>2</sub>N or 4-CO<sub>2</sub>Me (entries 1-3 in Table 4). The reaction rates were affected more strongly by the phosphine ligands on the palladium catalysts, decreasing in the order  $\text{dppf} \gg \text{dppb} > \text{dppp} > \text{dppe}$  (entries 4, 6-8 in Table 1). Although the effect of these ligands on the oxidative addition or the transmetalation step has not been fully investigated, the relative activity can be parallel to the bond angles of  $L_2\text{PdCl}_2$  ( $L_2 =$  bidentate phosphine ligands), in which the large P-Pd-P bond angle and the small Cl-Pd-Cl bond angle favor the reductive elimination from the four-coordinate palladium(II) complex **5** [50].

## 3. Experimental details

All the experiments were carried out under nitrogen atmosphere. IR spectra were taken on a Hitachi Perkin-Elmer Model 125 spectrometer. <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> by a Hitachi R-90H (90 MHz) spectrometer using Me<sub>4</sub>Si as internal 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).

### 3.1. Materials and reagents

Solvents were purified by distillation from appropriate drying reagents. The 9-organothio-9-BBN derivatives were prepared by the dehydrogenative condensation of 9-BBN with the corresponding thiols [23,24]. Lithium [2] and sodium [6] thiophenoxide were prepared by the reported procedures. (Phenylthio)trimethylsilane and -stannane were obtained by the reaction of lithium thiophenoxide with chlorotrimethylsilane and bro-

motrimethylstannane respectively [10]. Dichloro[1,1'-bis(diphenylphosphino)ferrocene]palladium(II) (PdCl<sub>2</sub>(dppf)) [50] and bis(dibenzylideneacetone)palladium(0) (Pd(dba)<sub>2</sub>) [51] were prepared using the literature procedures. 4-Iodo-*N,N*-dimethylaniline [52], 2-iodo-1-octene [53], (*E*)-1-iodo-1-hexene [54], (*E*)- $\beta$ -iodostyrene [54], and (*E*)-3,3-dimethyl-1-iodo-1-butene [54] were synthesized by the reported procedures.

### 3.2. Reaction conditions (Table 1)

The best conditions for the preparation of diphenyl sulfide were determined by the following general procedure. The palladium complex (0.03 mmol) and a base (3 mmol) were added to a flask equipped with a reflux condenser, a septum inlet, and a magnetic stirring bar. The flask was flushed with nitrogen and charged with 6 ml of solvent. Iodobenzene (204 mg, 1.0 mmol) and 9-(phenylthio)-9-BBN (1, R<sup>1</sup> = Ph) (253 mg, 1.1 mmol) were added by means of a hypodermic syringe through the septum inlet. The mixture was then stirred at 50 °C for 5 h. The product was extracted with benzene (20 ml), washed with water three times to remove DMF, and dried over magnesium sulfate. The yields based on iodobenzene were determined by GLC using hexadecane as internal standard.

### 3.3. Relative reactivity of the representative thioalkoxides (Table 2)

To a flask were added PdCl<sub>2</sub>(dppf) (22 mg, 0.03 mmol) and K<sub>3</sub>PO<sub>4</sub> (636 mg, 3 mmol), and the flask was flushed with nitrogen. DMF (6 ml), iodobenzene (204 mg, 1.0 mmol), and metal thiophenoxide (1.1 mmol) were added, and the mixture was then stirred at 50 °C for 5 h. The coupling in the absence of K<sub>3</sub>PO<sub>4</sub> was conducted under similar conditions.

### 3.4. General procedure for the coupling of 1 with aryl or 1-alkenyl iodides (Tables 3 and 4)

A flask, equipped with a magnetic stirring bar, a septum inlet, and a reflux condenser, was charged with PdCl<sub>2</sub>(dppf) (22 mg, 0.03 mmol) and K<sub>3</sub>PO<sub>4</sub> (636 mg, 3 mmol) and then flushed with nitrogen. DMF (6 ml), a halide (1.0 mmol), and 9-(organothio)-9-BBN (1.1 mmol) were successively added. After being stirred at 50 °C for 5 h, the reaction mixture was cooled to room temperature, diluted with benzene (20 ml), repeatedly washed with water to remove DMF (three times), and finally dried over magnesium sulfate. The isolation of products was carried out by chromatography over silica gel.

The following compounds were prepared by the above general procedure.

#### 3.4.1. Phenyl *p*-tolyl sulfide

*n*<sub>D</sub> 1.6173. IR (film) 3050, 2930, 1590, 1490, 1480, 1440, 1090, 1020, 810, 740, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  2.34 (s, 3H), 7.12 (d, 2H, *J* = 8.1 Hz), 7.1–7.3 (m, 5H), 7.30 (d, 2H, *J* = 9.5 Hz). MS (ITD) *m/e* 51 (22), 65 (14), 77 (8), 91 (18), 185 (19), 200 (M<sup>+</sup>, 100). Exact mass found: 200.0643; C<sub>13</sub>H<sub>12</sub>S calc.: 200.0660.

#### 3.4.2. 4-Chlorodiphenyl sulfide

*n*<sub>D</sub> 1.6344. IR (film) 3060, 1590, 1480, 1090, 1010, 820, 740, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  7.1–7.3 (m, 5H), 7.2–7.4 (m, 4H). MS (ITD) *m/e* 51 (50), 75 (16), 108 (12), 152 (6), 185 (50), 220 (M<sup>+</sup>, 100). Exact mass found: 220.0097; C<sub>12</sub>H<sub>9</sub>SCl calc.: 220.0114.

#### 3.4.3. Butyl phenyl sulfide

*n*<sub>D</sub> 1.5483. IR (film) 3060, 2960, 2870, 1590, 1480, 1440, 1090, 1020, 740, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  0.92 (t, 3H, *J* = 7.0 Hz), 1.2–1.8 (m, 4H), 2.92 (t, 2H, *J* = 7.0 Hz), 7.1–7.4 (m, 5H). MS (ITD) *m/e* 51 (2), 57 (2), 65 (5), 110 (9), 123 (6), 166 (M<sup>+</sup>, 100). Exact mass found: 166.0809; C<sub>10</sub>H<sub>14</sub>S calc.: 166.0816.

#### 3.4.4. *sec*-Butyl phenyl sulfide

*n*<sub>D</sub> 1.5393. IR (film) 3080, 2980, 2940, 1590, 1490, 1440, 1100, 1030, 740, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  1.01 (t, 3H, *J* = 7.1 Hz), 1.27 (d, 3H, *J* = 6.8 Hz), 1.4–1.8 (m, 2H), 3.0–3.4 (m, 1H), 7.1–7.5 (m, 5H). MS (ITD) *m/e* 65 (2), 109 (3), 137 (1), 166 (M<sup>+</sup>, 100). Exact mass found: 166.0801; C<sub>10</sub>H<sub>14</sub>S calc.: 166.0816.

#### 3.4.5. *tert*-Butyl phenyl sulfide

*n*<sub>D</sub> 1.5305. IR (film) 3080, 2960, 1480, 1440, 1370, 1170, 1030, 750, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  1.29 (s, 9H), 7.2–7.4 (m, 3H), 7.4–7.6 (m, 2H). MS (ITD) *m/e* 57 (35), 65 (5), 110 (34), 166 (M<sup>+</sup>, 100). Exact mass found: 166.0811; C<sub>10</sub>H<sub>14</sub>S calc.: 166.0816.

#### 3.4.6. 4-(Phenylthio)-*N,N*-dimethylaniline

M.p. 67 °C. IR (Nujol) 2930, 1600, 1510, 1460, 1380, 820, 740, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  2.97 (s, 6H), 6.69 (d, 2H, *J* = 9.0 Hz), 7.0–7.2 (m, 5H), 7.38 (d, 2H, *J* = 9.0 Hz). MS (ITD) *m/e* 51 (27), 77 (16), 109 (10), 136 (7), 152 (13), 196 (20), 229 (M<sup>+</sup>, 100). Exact mass found: 229.0923; C<sub>14</sub>H<sub>15</sub>NS calc.: 229.0926.

#### 3.4.7. Methyl 4-(phenylthio)benzoate

M.p. 79 °C. IR (Nujol) 2950, 1720, 1600, 1460, 1380, 1280, 1120, 760, 690 cm<sup>-1</sup>. <sup>1</sup>H NMR  $\delta$  3.88 (s, 3H), 7.20 (d, 2H, *J* = 8.6 Hz), 7.3–7.6 (m, 5H), 7.89 (d, 2H, *J* = 8.6 Hz). MS (ITD) *m/e* 51 (22), 69 (10), 108 (8), 137 (4), 152 (7), 184 (23), 213 (49), 244 (M<sup>+</sup>, 100). Exact mass found: 244.0541; C<sub>14</sub>H<sub>12</sub>O<sub>2</sub>S calc.: 244.0558.

### 3.4.8. 4-(*sec*-Butylthio)benzonitrile

$n_D$  1.5748. IR (film) 3070, 2980, 2940, 2240, 1600, 1490, 1460, 1090, 820  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  1.03 (t, 3H,  $J = 7.3$  Hz), 1.34 (d, 3H,  $J = 6.6$  Hz), 1.5–1.8 (m, 2H), 3.1–3.5 (m, 1H), 7.34 (d, 2H,  $J = 9.0$  Hz), 7.53 (d, 2H,  $J = 8.4$  Hz). MS (ITD)  $m/e$  50 (4), 57 (31), 63 (8), 75 (3), 90 (5), 135 (26), 162 (3), 191 ( $\text{M}^+$ , 100). Exact mass found: 191.0769;  $\text{C}_{11}\text{H}_{13}\text{NS}$  calc.: 191.0769.

### 3.4.9. *tert*-Butyl *o*-tolyl sulfide

$n_D$  1.5324. IR (film) 3070, 2970, 1480, 1360, 1170, 760  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  1.29 (s, 9H), 2.52 (s, 3H), 7.0–7.3 (m, 3H), 7.53 (d, 1H,  $J = 5.9$  Hz). MS (ITD)  $m/e$  51 (5), 57 (73), 65 (4), 77 (6), 91 (52), 124 (74), 180 ( $\text{M}^+$ , 100). Exact mass found: 180.0962;  $\text{C}_{11}\text{H}_{16}\text{S}$  calc.: 180.0973.

### 3.4.10. 2-(Phenylthio)-1-octene

$n_D$  1.5314. IR (film) 3070, 2930, 2850, 1610, 1580, 1480, 1440, 1020, 750, 690  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  0.88 (t, 3H,  $J = 5.7$  Hz), 1.1–1.8 (m, 8H), 2.23 (t, 2H,  $J = 7.1$  Hz), 4.87 (s, 1H), 5.14 (s, 1H), 7.2–7.5 (m, 5H). MS (ITD)  $m/e$  59 (33), 69 (36), 81 (22), 110 (97), 135 (78), 150 (67), 221 ( $\text{M}^+ + 1$ , 100). Exact mass found: 220.1305;  $\text{C}_{14}\text{H}_{20}\text{S}$  calc.: 220.1285.

### 3.4.11. (*E*)-1-(*p*-Tolylthio)-1-hexene

$n_D$  1.5470. IR (film) 3030, 2940, 2860, 1490, 1470, 1100, 960, 800  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  0.90 (t, 3H,  $J = 6.5$  Hz), 1.2–1.6 (m, 4H), 2.15 (q, 2H,  $J = 6.2$  Hz), 2.32 (s, 3H), 5.88 (dt, 1H,  $J = 15.0$  and 7.3 Hz), 6.13 (d, 1H,  $J = 15.2$  Hz), 7.11 (d, 2H,  $J = 5.3$  Hz), 7.22 (d, 2H,  $J = 5.9$  Hz). MS (ITD)  $m/e$  55 (23), 65 (30), 79 (21), 91 (59), 124 (74), 130 (80), 148 (24), 163 (63), 206 ( $\text{M}^+$ , 100). Exact mass found: 206.1127;  $\text{C}_{13}\text{H}_{18}\text{S}$  calc.: 206.1130.

### 3.4.12. (*E*)-1-(*sec*-Butylthio)-2-phenylethene

$n_D$  1.5843. IR (film) 3040, 2980, 2940, 1600, 1450, 940, 740, 690  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  1.02 (t, 3H,  $J = 7.3$  Hz), 1.36 (d, 3H,  $J = 6.8$  Hz), 1.5–1.8 (m, 2H), 2.8–3.2 (m, 1H), 6.54 (d, 1H,  $J = 15.4$  Hz), 6.78 (d, 1H,  $J = 15.6$  Hz), 7.0–7.4 (m, 5H). MS (ITD)  $m/e$  51 (9), 65 (7), 77 (5), 91 (34), 102 (3), 135 (78), 192 ( $\text{M}^+$ , 100). Exact mass found: 192.0987;  $\text{C}_{12}\text{H}_{16}\text{S}$  calc.: 192.0973.

### 3.4.13. (*E*)-3,3-Dimethyl-1-(phenylthio)-1-butene

$n_D$  1.5524. IR (film) 3070, 2960, 1590, 1480, 1440, 1370, 1030, 960, 740, 690  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  1.08 (s, 9H), 6.06 (s, 2H), 7.2–7.4 (m, 5H). MS (ITD)  $m/e$  55 (9), 65 (7), 83 (16), 135 (6), 177 (33), 192 ( $\text{M}^+$ , 100). Exact mass found: 192.0990;  $\text{C}_{12}\text{H}_{16}\text{S}$  calc.: 192.0972.

### 3.5. Coupling with allyl and propargyl carbonates (Eqs. (2) and (3))

A mixture of  $\text{Pd}(\text{dba})_2$  (17 mg, 0.03 mmol), dppf (17 mg, 0.03 mmol), and DMF (6 ml) was stirred at

room temperature for 30 min under nitrogen atmosphere. The carbonate (1.0 mmol) and 9-(phenylthio)-9-BBN (253 mg, 1.1 mmol) were added and the resulting solution was then stirred at 80 °C for 5 h. The product was isolated by column chromatography over silica gel.

### 3.5.1. (2*E*)-3,7-Dimethyl-1-(phenylthio)-2,6-octadiene

$n_D$  1.5527. IR (film) 3070, 2970, 2920, 1590, 1480, 1440, 1380, 730, 690  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  1.58 (s, 6H), 1.67 (s, 3H), 1.8–2.1 (m, 4H), 3.55 (d, 2H,  $J = 7.7$  Hz), 5.06 (m, 1H), 5.31 (t, 1H,  $J = 7.9$  Hz), 7.0–7.4 (m, 5H). MS (ITD)  $m/e$  53 (13), 69 (100), 81 (56), 95 (11), 109 (20), 137 (17), 231 (3), 246 ( $\text{M}^+$ , 2). Exact mass found: 246.1457;  $\text{C}_{16}\text{H}_{22}\text{S}$  calc.: 246.1443.

### 3.5.2. 7-Methyl-5-(phenylthio)-5,6-tridecadiene

$n_D$  1.5301. IR (film) 3070, 2930, 1960, 1590, 1480, 1440, 1020, 740, 690  $\text{cm}^{-1}$ .  $^1\text{H NMR}$   $\delta$  0.88 (t, 6H,  $J = 6.8$  Hz), 1.1–1.5 (m, 12H), 1.64 (s, 3H), 1.89 (t, 2H,  $J = 6.6$  Hz), 2.16 (t, 2H,  $J = 6.7$  Hz), 7.0–7.4 (m, 5H). MS (ITD)  $m/e$  55 (41), 67 (35), 81 (57), 93 (34), 109 (24), 123 (14), 193 (9), 225 (100), 302 ( $\text{M}^+$ , 22). Exact mass found: 302.2079;  $\text{C}_{20}\text{H}_{30}\text{S}$  calc.: 302.2069.

Diphenyl sulfide, benzyl phenyl sulfide, and dibenzyl sulfide were directly compared with the corresponding authentic samples.

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