JOC Article

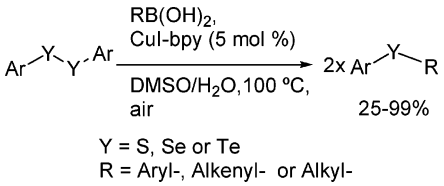
Convenient Synthesis of Unsymmetrical Organochalcogenides Using Organoboronic Acids with Dichalcogenides via Cleavage of the S−S, Se−Se, or Te−Te Bond by a Copper Catalyst

Nobukazu Taniguchi*

Department of Chemistry, Fukushima Medical University, Fukushima 960-1295, Japan

taniguti@fmu.ac.jp

Received October 15, 2006



This article describes the methodology for a copper-catalyzed preparation of numerous monochalcogenides from dichalcogenides with organoboronic acids. Unsymmetrical diorgano-monosulfides, selenides, and tellurides can be synthesized by the coupling of dichalcogenides with aryl- or alkylboronic acids using a copper catalyst in air. The present reaction can take advantage of both organochalcogenide groups on dichalcogenide.

Introduction

Organochalcogenides have found widespread utilization as convenient intermediates or reagents in organic syntheses.[1] To synthesize these compounds, various procedures have been explored so far.[2] Especially, transition metal-catalyzed aryl carbon−chalcogen bond formation is an important method for the preparation of unsymmetrical organochalcogenides and is studied by many researchers.[3]

For the preparation of aryl chalcogenides using a palladium,[4] nickel,[5] or copper catalyst,[6] a combination of aryl halide with thiol or selenol is usually employed under basic conditions. However, the synthesis using dichalcogenide has been limited to a reaction using alkyl halides;[7,8] nevertheless, dichalcogenides are easy to treat and are stable compounds in air. As a general rule, in the metal-catalyzed chalcogenylation of aryl halides using dichalcogenide, a reductant is necessary for the generation of a corresponding anion[9] or a metal−monochalcogenide complex.[10,11]

On the contrary, the transition metal-catalyzed preparation of monosulfide from disulfide and organoboronic acid under oxidative conditions has been rarely developed, despite the fact

* Corresponding author. Tel.: 81-24-547-1369. Fax: 81-24-547-1369.

(1) For selected reviews: (a) Metzner, P.; Thuillier, A. *Sulfur Reagents in Organic Synthesis*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Academic Press: San Diego, 1994. (b) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press Ltd.: New York, 1991; Vol. 6. (c) Paulmier, C. In *Selenium Reagents and Intermediates in Organic Synthesis, Organic Chemistry Series 4*; Baldwin, J. E., Ed.; Pergamon Press Ltd.: Oxford, 1986. (d) Wirth, T., Ed. *Organoselenium Chemistry; Topics in Current Chemistry 208;* Springer-Verlag: Heidelberg; 2000. (e) Petragnani, N. *Tellurium in Organic Synthesis*; Katritzky, A. R., Meth-Cohn, O., Rees, C. W., Eds.; Academic Press: San Diego, 1994. (f) Comasseto, J. V.; Barientos-Astigarraga, R. E. *Aldrichim. Acta* **2000**, *33*, 66−78.

(2) For selected reviews: (a) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press Ltd.: New York, 1991; Vol. 4. (b) Krief, A. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon Press Ltd.: New York, 1995; Vol. 11, Ch. 13. (c) Miyaura, N. In *Metal-Catalyzed Cross-Coupling Reactions*; Meijere, A., Diederich, F., Eds.; Wiley-VCH: Weinheim, 2004; Vol. 1, pp 41−123.

(3) For selected reviews: (a) Ley, S. V.; Thomas, A. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 5400−5449. (b) Kondo, T.; Mitsudo, T. *Chem. Rev.* **2000**, *100*, 3205−3220.

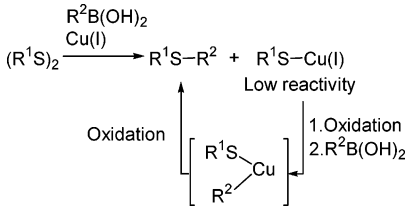
(4) For selected paper for the method using Pd catalyst: (a) Kosugi, M.; Shimizu, T.; Migita, T. *Chem. Lett.* **1978**, 13−14. (b) Migita, T.; Shimizu, T.; Asami, Y.; Shiobara, J.; Kosugi, M. *Bull Chem. Soc. Jpn.* **1980**, *53*, 1385−1389. (c) Cristau, H. J.; Chabaud, B.; Christol, C. H. *Synthesis* **1981**, 892−894. (d) Kosugi, M.; Ogata, T.; Terada, M.; Sano, H.; Migita, T. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 3657−3658. (e) Hartwig, J. F.; Barrañano, D. *J. Am. Chem. Soc.* **1995**, *117*, 2937−2938. (f) Ciattini, P. G.; Morera, E.; Ortar, G. *Tetrahedron Lett.* **1995**, *36*, 4133−4136. (g) Zheng, N.; McWilliams, J. C.; Fleitz, F. J.; Armstrong, J. D., III; Volante, R. P. *J. Org. Chem.* **1998**, *63*, 9606−9607. (h) Nishiyama, Y.; Tokunaga, K.; Sonoda, N. *Org. Lett.* **1999**, *1*, 1725−1727. (i) Itoh, T.; Mase, T. *Org. Lett.* **2004**, *6*, 4587−4590.

(5) The method using Ni catalyst: (a) Cristau, H. J.; Chabaud, B.; Chêne, A.; Christol, H. *Synthesis* **1981**, 892−894. (b) Yamamoto, T.; Sekine, Y. *Can. J. Chem.* **1984**, *62*, 1544−1547. (c) Takagi, K. *Chem. Lett.* **1985**, 1307−1308. (d) Takagi, K. *Chem. Lett*. **1987**, 2221−2224.

(6) The method using Cu catalyst: (a) Suzuki, H.; Abe, H.; Osuka, A. *Chem. Lett.* **1980**, 1363−1364. (b) Suzuki, H.; Abe, H.; Osuka, A. *Chem. Lett.* **1981**, 151−152. (c) Bowman, W. R.; Heaney, H.; Smith, P. H. G. *Tetrahedron Lett.* **1984**, *25*, 5821−5824. (d) Kwong, F. Y.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 3517−3520. (e) Gujadhur, R. K.; Venkataruman, D. *Tetrahedron Lett.* **2003**, *44*, 81−84.

10.1021/jo062131+ CCC: $37.00
Published on Web 01/17/2007

SCHEME 1. Reaction of Disulfides with Organoboronic Acids by CuX



that a reaction using a stoichiometric copper(II) salt with thiol[12] or, recently, a copper-catalyzed reaction using other dichalcogenides having high reactivity has been reported.[13] The cause is attributed to the lower activity of the generated metal−sulfide complex as an intermediate. Therefore, in the catalytic synthesis of organosulfides using organoboronic acids, a method employing thioimide as a sulfur source has been explored.[14]

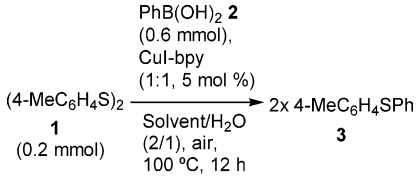
To accelerate the catalytic cycle using disulfide, after oxidation of CuSR,[1] a reaction of the obtained complex with $R^2B(OH)_2$ should produce the corresponding sulfide (Scheme 1). Consequently, the present process requires an oxidant. As a procedure to carry out the reaction, we examined conditions in air and found that unsymmetrical monosulfides could be synthesized from disulfide and organoboronic acid by a copper catalyst at 100 °C in a DMSO−H_2O solvent.[15]

In this paper, we wish to describe the synthesis of unsymmetrical monochalcogenides (sulfides, selenides, or tellurides) from dichalcogenides with organoboronic acids by a copper catalyst.

Results and Discussion

Preparation of Monosulfide from Disulfide and Phenylboronic Acid. Initially, to carry out copper-catalyzed coupling of dichalcogendie with organoboronic acid, the reaction with disulfide was investigated.

TABLE 1. Copper-Catalyzed Coupling of $(4\text{-}MeC_6H_4S)_2$ with $PhB(OH)_2$



entry	solvent	**3** (%)[a,b]	**1** (%)[a]
1[c]	$PhCH_3$	45	46
2	DMF	82	13
3	DMSO	97	0
4[c]	DMSO	76	10
5[d]	DMSO	18	79

[a] Isolated yields after silica-gel chromatography. [b] Yields of **3** are based on disulfide **1** (2 mol). [c] H_2O was not added. [d] bpy was not used.

When a mixture of $(4\text{-}MeC_6H_4S)_2$ **1** (0.2 mmol), phenylboronic acid **2** (0.6 mmol), and CuI-bpy (5 mol %) in toluene (0.3 mL) was treated at 100 °C, phenyl 4-tolyl sulfide **3** was obtained in only 45% yield (Table 1, entry 1). The reaction in DMF/H_2O could give **3** in 82% yield with the recovery of **1** in 13% yield (Table 1, entry 2). Other solvents (1,3-dimethyl-2-imidazolidinone and dioxane) also showed the same result. However, these conditions could not be used because a small amount of **1** was recovered, and the separation of **1** and **3** was very complicated.

Fortunately, the system of DMSO/H_2O (0.2 mL/0.1 mL) could afford **3** in 97% yield with complete consumption of **1** (Table 1, entry 3).[16] The absence of a bpy ligand decreased the production of **3** (Table 1, entry 5), and other ligands (TMEDA and PPh_3) did not work effectively.[17] The present system could also use other copper catalysts (CuCl, CuBr, CuOAc, $CuCl_2$, and $CuBr_2$), although the use of $Cu(OAc)_2$ decreased the yield slightly.

Application to the Copper-Catalyzed Preparation of Diorganosulfides, Selenides, or Tellurides Using Dichalcogenides with Organoboronic Acids. On the basis of the previously described experimental results, we next examined a CuI-catalyzed aryl- or alkylation of disulfide by the use of organoboronic acid in DMSO−H_2O (Table 2).

At first, various organoboronic acids (0.6 mmol) and diphenyl disulfide (0.2 mmol) were treated with CuI-bpy (5 mol %) at 100 °C in air, to afford expected sulfides **6** in good yields. The present reactions could afford **6** in good yields without the influence of the para-substituted groups. In the use of ortho-substituted arylboronic acid, the reactivity decreased owing to steric hindrance (Table 2, entries 3 and 4). Furthermore, this procedure could tolerate alkenyl- or alkylboronic acids, but the employment of alkylboronic acid required longer reaction times than the reaction of arylboronic acids (Table 2, entries 12−16).

The combination of diaryl disulfides with phenylboronic acids could also afford the corresponding products (Table 2, entries 17−24). However, the reactivity was dependent on substrates. Unfortunately, the reaction of di-*n*-butyl disulfide proceeded in low yield (Table 2, entry 25).

(7) Chalcogenations of alkyl halides or alkenyl borane with dichalcogenide are known. See: (a) Chowdhury, S.; Roy, S. *Tetrahedron Lett.* **1997**, *38*, 2149−2152. (b) Kundu, A.; Roy, S. *Organometallics* **2000**, *19*, 105−107. (c) Nishino, T.; Okada, M.; Kuroki, T.; Watanabe, T.; Nishiyama, Y.; Sonoda, N. *J. Org. Chem.* **2002**, *67*, 8696−8698. (d) Nishino, T.; Nishiyama, Y.; Sonoda, N. *Chem. Lett.* **2003**, 928−929. (e) Ranu, B. C. Mandal, T. *J. Org. Chem.* **2004**, *69*, 5793−5795. (f) Ajiki, K.; Tanaka, K. *Org. Lett.* **2005**, *7*, 4193−4195. (g) Huang, X.; Liang, C.-G. *J. Chem. Soc., Perkin Trans 1* **1999**, 2625−2626.

(8) A reaction of disulfide with RMgX or RLi can also give a corresponding monosulfide. But, this case cannot use one sulfide group on disulfide. See: Negishi, E., Ed. *Organometallics in Organic Synthesis*; Wiley: New York, 1980.

(9) Millois, C.; Diaz, P. *Org. Lett.* **2000**, *2*, 1705−1708.

(10) (a) Taniguchi, N.; Onami, T. *Synlett* **2003**, 829−832. (b) Taniguchi, N.; Onami, T. *J. Org. Chem.* **2004**, *69*, 915−920. (c) Taniguchi, N. *J. Org. Chem.* **2004**, *69*, 6904−6906. (d) Taniguchi, N. *Synlett* **2005**, 1687−1690. (e) Gómez-Betez, V.; Baldovino-Pantaleón, O.; Herrera-Álvarez, C.; Toscano, R. A.; Morales-Morales, D. *Tetrahedron Lett.* **2006**, *47*, 5059−5062. (f) Kumar, S.; Engman, L. *J. Org. Chem.* **2006**, *71*, 5400−5403. (g) Chang, D.; Bao, W. *Synlett* **2006**, 1786−1788. (h) Fukuzawa, S.-i.; Tanihara, D.; Kikuchi, S. *Synlett* **2006**, 2145−2147.

(11) Transition metals can be inserted into dichalcogenide bonds: (a) Zanella, R.; Ros, R.; Graziani, M. *Inorg. Chem.* **1973**, *12*, 2736−2738. (b) Lam, C. T.; Senoff, C. V. *Can. J. Chem.* **1973**, *51*, 3790−3794. (c) Canich, J. A. M.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R. *Inorg. Chem.* **1988**, *27*, 804−811.

(12) Herradura, P. S.; Pendola, K. A.; Guy, R. K. *Org. Lett.* **2000**, *2*, 2019−2022.

(13) Wang, L.; Wang, M.; Huang, F. *Synlett* **2005**, 2007−2010.

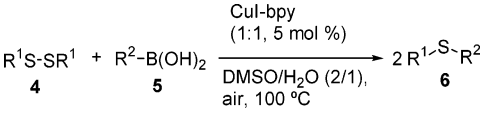
(14) Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2002**, *4*, 4309−4312.

(15) Taniguchi, N. *Synlett* **2006**, 1351−1354.

(16) In transition metal-catalyzed organic reactions using organoboronic acids, water has been added: (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457−2483. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829−2844.

(17) When TMEDA and PPh_3 as a ligand were employed, the yields were 58 and 4%, respectively.

TABLE 2. CuI-Catalyzed Coupling of Disulfides with Organoboronic Acids[a]

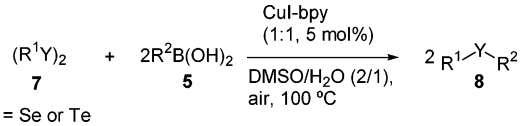


4 + **5** → 2 **6**

entry	R^1	R^2	time (h)	**6** (%)[b,c]	entry	R^1	R^2	time (h)	**6** (%)[b,c]
1	Ph	Ph	12	97	13	Ph	Me	12	93
2		2-MeC_6H_4	12	97	14		*n*-Bu	42	72
3		2-$MeOC_6H_4$	24	50	15[e]		*cyclo*-C_6H_{11}	48	94
4[e]		2-ClC_6H_4	24	76	16[e]		$PhCH_2CH_2$	48	65
5		4-MeC_6H_4	12	97	17	4-MeC_6H_4	Ph	12	97
6		4-$MeOC_6H_4$	12	98	18	4-$MeOC_6H_4$		48	74
7		4-BrC_6H_4	12	88	19	4-BrC_6H_4		12	67
8		4-ClC_6H_4	12	96	20	4-ClC_6H_4		24	66
9		4-HOC_6H_4	12	90	21	4-$O_2NC_6H_4$		12	97
10		4-$OHCC_6H_4$	12	98	22[d]	4-$H_2NC_6H_4$		24	65
11		4-$MeO_2CC_6H_4$	12	89	23	4-$HO_2CC_6H_4$		42	72
12		(*E*)−PhCH=CH	30	97	24	4-HOC_6H_4		42	25
					25[e]	*n*-Bu		24	29

[a] Reaction conditions: the mixture of **4** (0.2 mmol), **5** (0.6 mmol), and CuI-bpy (1:1, 5 mol %) in DMSO (0.2 mL) and H_2O (0.1 mL) was treated at 100 °C. [b] Isolated yields after silica-gel chromatography. [c] Yields of **6** are based on disulfide **4** (2 mol). [d] This reaction was carried out at 90 °C. [e] 10 mol %CuI-bpy was used.

TABLE 3. CuI-Catalyzed Coupling of Diselenides or Ditellurides with Organoboronic Acids[a]



7 (Y = Se or Te) + $2R^2B(OH)_2$ **5** → 2 R^1YR^2 **8**

entry	$(R^1Y)_2$	R^2	time (h)	**8** (%)[b,c]	entry	$(R^1Y)_2$	R^2	time (h)	**8** (%)[b,c]
1	$(PhSe)_2$	Ph	12	93	15	$(BnSe)_2$	Ph	24	84
2		2-MeC_6H_4	12	99	16	$(PhTe)_2$	Ph	4	87
3		2-$MeOC_6H_4$	12	96	17		2-MeC_6H_4	4	79
4		2-ClC_6H_4	12	93	18		2-$MeOC_6H_4$	12	75
5		4-MeC_6H_4	12	98	19		2-ClC_6H_4	4	95
6		4-$MeOC_6H_4$	12	93	20		4-MeC_6H_4	4	81
7		4-BrC_6H_4	12	83	21		4-$MeOC_6H_4$	12	97
8		4-ClC_6H_4	12	95	22		4-BrC_6H_4	4	90
9		4-HOC_6H_4	12	80	23		4-ClC_6H_4	4	85
10		4-$OHCC_6H_4$	12	96	24		4-HOC_6H_4	12	79
11		4-$MeO_2CC_6H_4$	12	95	25		4-$OHCC_6H_4$	12	88
12		(*E*)−PhCH=CH	12	89	26		4-$MeO_2CC_6H_4$	12	86
13		Me	12	86	27		(*E*)−PhCH=CH	4	71
14[d]		*n*-Bu	38	63	28		*n*-Bu	18	38

[a] Reaction conditions: the mixture of **7** (0.2 mmol), **5** (0.6 mmol), and CuI-bpy (1:1, 5 mol %) in DMSO (0.2 mL) and H_2O (0.1 mL) was treated at 100 °C. [b] Isolated yields after silica-gel chromatography. [c] Yields of **8** are based on dichalcogenide **7** (2 mol). [d] 10 mol % CuI was used.

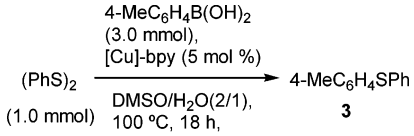
Thus, the coupling of diaryl disulfides with organoboronic acids by a copper catalyst could furnish the desired sulfides in good yields and was able to use both sulfide groups on disulfide.

Then, we explored the reaction using other dichalcogenides. According to the previously developed procedure, the copper-catalyzed coupling of diselenides or ditellurides with organoboronic acids was carried out (Table 3).

As expected, various unsymmetrical monochalcogenides **8** were obtained in good yields, and the present reaction was not affected by substrates. In the reaction using ditelluride, the monotellurides were obtained in very short time. However, the yield of butyl phenyl telluride decreased (Table 3, entry 28).

Proposed Reaction Mechanism of the Copper-Catalyzed Coupling of Disulfides with Organoboronic Acids. For the purpose of investigation of the reaction mechanism, we initially examined a reaction in the absence of oxygen. When the CuI- or $CuCl_2$-catalyzed reaction of $(PhS)_2$ with 4-$MeC_6H_4B(OH)_2$ was carried out, the corresponding sulfide **3** was obtained in only 7% production or 3% (Scheme 2).

SCHEME 2. Reaction of $(PhS)_2$ with 4-$MeC_6H_4B(OH)_2$ in the Absence of Oxygen



[Cu]	**3** (%)
CuI	7
$CuCl_2$	3

Also, the reactivity of PhSCu considered as an intermediate was examined.[18] When a reaction of PhSCu and 4-$MeC_6H_4B(OH)_2$ was performed in DMSO−H_2O, the corresponding sulfide **3** was obtained in 53% yield (Scheme 3). Moreover, the

(18) For the preparation of PhSCu: Adams, R., Reifschneider, W., Ferretti, A. *Organic Synthesis*; John Wiley & Sons: New York, 1973; Vol. V, pp 107−110.

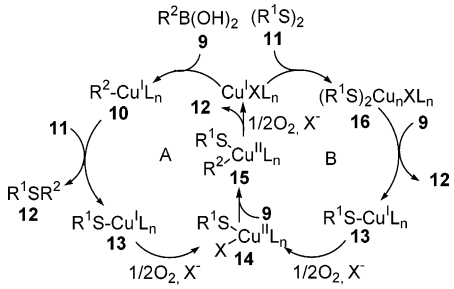
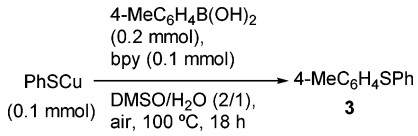


FIGURE 1. Plausible reaction mechanism.

SCHEME 3. Reaction of PhSCu with 4-MeC$_6$H$_4$B(OH)$_2$



additive	**3** (%)
none	53
n-Bu$_4$NI (0.1 mmol)	68

production was increased to 68% yield in the presence of *n*-Bu$_4$NI as the anion source of PhSCu(II) after the oxidation of PhSCu(I).[19]

Thus, the coupling of disulfide with organoboronic acid requires oxygen. This fact shows that PhSCu(I) can react with organoboronic acid through a formation of PhSCu(II)X by the oxidation of PhSCu(I) in the presence of oxygen.

From these results, a plausible reaction mechanism is considered as follows (Figure 1).[20] In cycle A, after R^{2}Cu(I) **10** is formed from R^{2}B(OH)$_2$ with CuX, both the sulfide **12** and the PhSCu(I)L$_n$ **13** produced by the reaction of **10** react with (R^{1}S)$_2$. Sequentially, (R^{1}S)(R^2)Cu(II) **15** is formed via the oxidation of R^{1}SCuL$_n$ **13**. Finally, R^{1}SR^2 **12** is produced again through the oxidation of **15**.

In cycle B, after the reaction of CuX with (R^{1}S)$_2$, the sulfide **12** and R^{1}SCu(I)L$_n$ **13** are produced from the generated copper−disulfide complex **16** with R^{2}B(OH)$_2$ **9**.[21,22]

Similarly, it seems that in the case of the CuX$_2$ catalyst, complex **13** is formed via some processes after the generation of a Cu(II)−disulfide complex by cleavage of disulfide at the first step.[23]

In addition, it is considered that the generating proportion of these two processes is different according to the kind of substrate (disulfides or organoboronic acids) or copper catalyst. In the case of other chalcogenides, the same process can apply.

Conclusion

In conclusion, we were able to synthesize various unsymmetrical organosulfides, selenides, and tellurides from dichalcogenides using organoboronic acids by a CuI-bpy catalyst in DMSO−H$_2$O. Furthermore, this procedure requires oxygen in air as oxidant to promote the reaction and can tolerate aryl- or alkylation of two chalcogenide groups on dichalcogenide.

Experimental Section

General Procedure. All reactions were carried out in air. NMR spectra were recorded on a JEOL EX-270 spectrometer (270 MHz for ^{1}H, 67.5 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR and chloroform-*d* (δ 77.0) for ^{13}C NMR. IR spectra were measured by a Spectrum One FT−IR spectrometer. Melting points were measured on a Melting Point B-540 apparatus. Elemental analysis was performed at the Instrumental Analysis Center for Chemistry, Tohoku University (Japan).

Coupling of Disulfide with Organoboronic Acid (Table 2): Entry 10. ^{1}H NMR (270 MHz, CDCl$_3$) δ 9.89 (s, 1H), 7.70 (d, J = 8.6 Hz, 2H), 7.49−7.53 (m, 2H), 7.43−7.39 (m, 3H), 7.23 (d, J = 8.6 Hz, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 191.0, 147.1, 134.2, 133.6, 131.2, 130.0, 129.7, 129.0, 127.1; IR (neat) 3058, 1697, 1591, 1561, 1475 cm^{-1}; Anal. Calcd for C$_{13}$H$_{10}$OS: C, 72.87; H, 4.70. Found: C, 72.69; H, 4.95.

Entry 11. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.88 (d, J = 8.6 Hz, 2H), 7.49−7.45 (m, 2H), 7.39−7.35 (m, 3H), 7.20 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 166.5, 144.2, 133.6, 132.3, 130.0, 129.5, 128.5, 127.5, 127.4, 51.9; IR (CHCl$_3$) 1715, 1594, 1436 cm^{-1}; Anal. Calcd for C$_{14}$H$_{12}$O$_2$S: C, 68.83; H, 4.95. Found: C, 68.66; H, 5.10.

Entry 16. ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.37−7.14 (m, 10H), 3.19−3.12 (m, 2H), 2.95−2.88 (m, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 140.2, 136.3, 129.2, 128.9, 128.5, 127.0, 126.4, 125.9, 35.6, 35.1; IR (neat) 3060, 3026, 2923, 1583, 1495, 1479 cm^{-1}; Anal. Calcd for C$_{14}$H$_{14}$S: C, 78.45; H, 6.58. Found: C, 78.71; H 6.70.

Entry 22. mp 94−95 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.30 (d, J = 8.2 Hz, 2H), 7.24−7.05 (m, 5H), 6.65 (d, J = 8.4 Hz, 2H), 3.78 (br, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 147.0, 139.6, 136.0, 128.7, 127.2, 125.2, 120.4, 115.8; IR (CHCl$_3$) 3400, 1618, 1494, 1477 cm^{-1}; Anal. Calcd for C$_{12}$H$_{11}$NS: C, 71.60; H, 5.51. Found: C, 71.30; H, 5.70.

Entry 23. mp 172−173 °C; ^{1}H NMR (270 MHz, CDCl$_3$) δ 7.95 (d, J = 8.5 Hz, 2H), 7.53−7.38 (m, 5H), 7.20 (d, J = 8.5 Hz, 2H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 171.4, 146.0, 134.0, 131.8, 130.6, 129.7, 128.9, 127.1, 126.3; IR (CHCl$_3$) 3412, 1691, 1594 cm^{-1}; Anal. Calcd for C$_{13}$H$_{10}$O$_2$S: C, 67.80; H, 4.38. Found: C, 67.54; H, 4.20.

Coupling of Diselenide with Organoboronic Acid (Table 3): Entry 4. ^{1}H NMR (CDCl$_3$) δ 7.63−7.59 (m, 2H), 7.40−7.29 (m, 4H), 7.09 (dt, J = 7.6 and 1.6 Hz, 1H), 7.01 (dt, J = 7.6 and 1.3 Hz, 1H), 6.91 (dd, J = 7.6 and 1.6 Hz, 1H); ^{13}C NMR (CDCl$_3$) δ 136.0, 135.9, 133.8, 133.4, 130.5, 129.7, 129.3, 128.8, 127.8, 127.2; IR (neat) 3057, 1950, 1573, 1476, 1437 cm^{-1}; Anal. Calcd for C$_{12}$H$_9$SeCl: C, 53.86; H, 3.39. Found: C, 53.85; H, 3.56.

Entry 10. ^{1}H NMR (270 MHz, CDCl$_3$) δ 9.90 (s, 1H), 7.67 (d, J = 8.6 Hz, 2H), 7.59−7.62 (m, 2H), 7.41−7.34 (m, 5H); ^{13}C NMR (67.5 MHz, CDCl$_3$) δ 191.2, 142.6, 135.4, 134.4, 130.1, 130.0, 129.7, 128.8, 127.8; IR (neat) 3055, 2828, 2733, 1696, 1587 cm^{-1}; Anal. Calcd for C$_{13}$H$_{10}$OSe: C, 59.78; H, 3.86. Found: C, 59.55; H, 3.96.

(19) Other salts (KI and LiI) also gave the same results (63 and 68%, respectively).

(20) (a) Evans, D. A.; Katz, J. L.; West, T. R. *Tetrahedron Lett.* **1998**, *39*, 2937−2940. (b) Collman, J. P.; Zhong, M. *Org. Lett.* **2000**, *2*, 1233−1236. (c) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651−2710.

(21) A disulfide bond can be cleaved by Cu(I)X: (a) Kadooka, M. M.; Warner, L. G.; Seff, K. *J. Am. Chem. Soc.* **1976**, *98*, 7569−7578. (b) Taniguchi, N. *J. Org. Chem.* **2006**, *71*, 7874−7876; see ref 9b,d.

(22) It is well known that a transition metal can cleave a disulfide bond: (a) Bewick, A.; Mellor, J. M.; Milano, D.; Owton, W. M. *J. Chem. Soc., Perkin Trans, 1* **1985**, 1045−1048. (b) Bach, R. D.; Rajan, S. J.; Vardhan, H. B.; Lang, T. J.; Albrecht, N. G. *J. Am. Chem. Soc.* **1981**, *103*, 7727−7734. (c) Ichimura, A.; Nosco, D. L.; Deutsch, E. *J. Am. Chem. Soc.* **1983**, *105*, 844−850.

(23) Cu(I)−sulfide complex can be prepared by a reaction of disulfide with Cu(II)−salt in air: (a) Odani, A.; Maruyama, T.; Yamaguchi, O.; Fujiwara, T.; Tomita, K.-i. *J. Chem. Soc., Chem. Commun.* **1982**, 646−647. (b) Higashi, L. S.; Lundeen, M.; Milti, E.; Seff, K. *Inorg. Chem.* **1977**, *16*, 310−313.

Entry 11. ^{1}H NMR ($CDCl_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.58−7.55 (m, 2H), 7.37−7.25 (m, 4H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 166.6, 139.5, 134.8, 130.3, 130.0, 129.6, 128.6, 128.4, 128.1, 52.0. IR (neat) 3020, 1718, 1591, 1436 cm^{-1}; Anal. Calcd for $C_{14}H_{12}O_2Se$: C, 57.74; H, 4.15. Found: C, 57.38; H, 4.21.

Coupling of Ditelluride with Organoboronic Acid (Table 3): Entry 17. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.49−7.46 (m, 1H), 7.32−7.13 (m, 5H), 6.96−6.90 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 141.8, 138.6, 137.4, 129.5, 129.3, 128.0, 127.9, 126.7, 119.1, 113.9, 26.0; IR (neat) 3052, 1949, 1575, 1473 cm^{-1}; Anal. Calcd for $C_{13}H_{12}Te$: C, 52.78; H, 4.09. Found: C, 52.58; H, 4.15.

Entry 18. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.91−7.87 (m, 2H), 7.42−7.26 (m, 3H), 7.25−7.13 (m, 1H), 6.96−6.93 (m, 1H), 6.79−6.69 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 158.0, 141.1, 133.5, 129.5, 128.5, 128.0, 122.3, 112.0, 109.6, 107.6, 55.8; IR (neat): 3062, 2937, 2833, 1572, 1469, 1431 cm^{-1}; Anal. Calcd for $C_{13}H_{12}OTe$: C, 50.07; H, 3.88. Found: C, 49.78; H, 4.02.

Entry 19. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.93−7.89 (m, 2H), 7.46−7.22 (m, 4H), 7.12−7.05 (m, 1H), 6.96−6.92 (m, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 141.1, 136.4, 134.3, 129.9, 129.1, 128.6, 128.0, 127.3, 120.5, 113.3; IR (neat) 3053, 1567, 1473, 1443 cm^{-1}; Anal. Calcd for $C_{12}H_9ClTe$: C, 45.57; H, 2.87. Found: C, 45.26; H, 3.04.

Entry 22. ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.70−7.67 (m, 2H), 7.50 (d, J = 8.2 Hz, 2H), 7.33−7.26 (m, 3H), 7.23−7.17 (m, 2H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 139.2, 138.2, 132.5, 129.6, 128.1, 122.4, 114.2, 113.1; IR (neat): 3065, 1893, 1573, 1470 cm^{-1}; Anal. Calcd for $C_{12}H_9BrTe$: C, 39.96; H, 2.51. Found: C, 39.66; H, 2.62.

Entry 25. ^{1}H NMR (270 MHz, $CDCl_3$) δ 9.89 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.62−7.61 (m, 4H), 7.59−7.25 (m, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 191.5, 139.8, 135.6, 135.1, 129.8, 128.9, 126.6, 112.9; IR (neat): 3052, 2827, 2734, 1694, 1582 cm^{-1}; Anal. Calcd for $C_{13}H_{10}OTe$: C, 50.40; H, 3.25. Found: C, 50.12; H, 3.35.

Entry 26. mp 71−72 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.81−7.76 (m, 4H), 7.59 (d, J = 8.2 Hz, 2H), 7.35−7.22 (m, 3H), 3.87 (s, 3H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 166.7, 139.3, 135.8, 130.0, 129.7, 129.0, 128.5, 123.2, 113.3, 52.0; IR ($CHCl_3$): 3019, 1719, 1587, 1435 cm^{-1}; Anal. Calcd for $C_{14}H_{12}O_2Te$: C, 49.48; H, 3.56. Found: C, 49.25; H, 3.61.

Acknowledgment. This work was supported by Meiji Seika Co. Ltd.

Supporting Information Available: Analytical data (^{1}H and ^{13}C NMR spectra) and literature citations for known compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO062131+