C–Te Cross-Coupling of Diaryl Ditellurides with Arylboronic Acids by Using Copper(I) Thiophene-2-carboxylate under Mild Conditions

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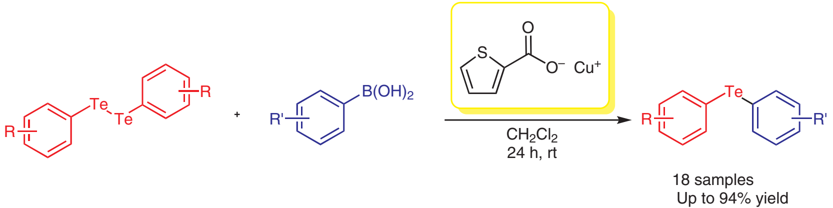

This reaction proceeds at room temperature.
No base or acid is required.
General-purpose solvents such as THF and methylene chloride can be used.
Tellurium coupling proceeds selectively.

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Abstract We describe the successful cross-coupling of diaryl ditellurides with arylboronic acids by using copper(I) thiophene-2-carboxylate (CuTC) under mild conditions. Although other studies have reported that highly polar solvents (such as DMSO) or bases are required, this reaction was completed by using CuTC and common solvents under neutral conditions at room temperature. This cross-coupling reaction was performed with diaryl ditellurides and arylboronic acids bearing various groups, affording the corresponding diaryl tellurides in good to excellent yields.

Key words C–Te coupling, copper catalysis, diaryl ditellurides, arylboronic acids, diaryl tellurides

Chalcogenide compounds have become attractive targets for synthesis because of their unique chemistry and the resulting useful biological activities.[1] Therefore, many classes of organotellurium compounds have been prepared and studied, and tellurides are certainly the most useful and promising of these compounds in view of their usefulness in organic synthesis.[2] In recent years, Oba et al.[3] synthesized symmetrical diaryl telluroxides and symmetrical diaryl tellurones by oxidizing symmetrical diaryl tellurides. In addition, the oxidation of alcohols and thiols by telluroxides or tellurones has been reported.[3b] However, only symmetric telluroxides and tellurones were used in these oxidation reactions. We were interested in performing oxidation reactions by using asymmetric diaryl telluroxides or asymmetric diaryl tellurones. Therefore, we examined efficient methods for synthesizing asymmetric diaryl tellurides.

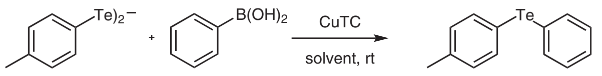
To synthesize asymmetric diaryl tellurides, we chose a readily available arylboronic acids and a conveniently synthesizable symmetrical diaryl ditellurides as substrates. Several methods for synthesizing asymmetric diaryl chalcogenides by the cross-coupling of arylboronic acids and symmetrical diaryl dichalcogenides have been reported. The first C–Te and C–Se cross-coupling reactions of boronic acids with diaryl dichalcogenides by using CuI (and a bipyridine ligand) was reported by Taniguchi.[4] His synthetic method used aqueous DMSO as the solvent and required a temperature of 100 °C. Wang and co-workers reported C–Te and C–Se coupling reactions that used $InBr_3$ or Fe ($FeCl_2$ or $FeCl_3$),[5] but these reactions required a high temperature of 130 °C. Kumar and Kumar recently succeeded in cross-coupling arylboronic acids; however, their method required $NaBH_4$ as a reducing agent.[6] A $Cu(OAc)_2$-catalyzed reaction of diaryl tellurides with aryl trifluoroborates was reported by Stefani and co-workers.[7a] More recently, a cross-coupling reaction of diaryl ditellurides and arylboronic acids by using a silver catalyst was reported by Alves and co-workers.[7b] However, these two reactions also required high temperatures. All the developed methods have various disadvantages, such as high reaction temperatures, expensive catalysts, difficult removal steps, highly polar solvents, or an acidic or basic (not neutral) additive. Additionally, few examples of cross-coupling reactions specific to tellurium compounds have been reported, as most of the reported examples involve cross-coupling reactions between selenium or tellurium and other atomic groups.

In this study, we focused on copper(I) thiophene-2-carboxylate (CuTC), which can be easily synthesized from thiophene-2-carboxylic acid and Cu_2O (commercially available). CuTC is a good reagent for Ullmann coupling reactions; however, its use in cross-coupling reactions of diaryl dichalcogenides with arylboronic acids has not been reported.

Initially, we investigated the C–Te coupling of a diaryl ditelluride with an arylboronic acid in several solvents. A mixture of di(4-tolyl) ditelluride (0.5 mmol) and phenylboronic acid (1.2 mmol) in the appropriate solvent (3 mL) was stirred at room temperature for 30 minutes, and then CuTC (1.2 mmol) was added. The reaction mixture was then stirred at room temperate before the product was purified and isolated

When chloroform ($CHCl_3$) or dichloromethane (CH_2Cl_2) was used as the solvent, the product was obtained in good yield (Table 1, entries 1 and 2). In particular, when dichloromethane was used, the yield of the product was 94%. The yield was lower when a halogen-free solvent [tetrahydrofuran (THF), ethyl acetate (EtOAc), or methanol (MeOH)] was used (entries 4, 5, and 9). In the highly polar solvents *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), the yield was further reduced (entries 7 and 8). We then tested the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) as a solvent, with the aim of recycling the reaction system; however, the coupling reaction did not proceed in this solvent. A shorter reaction time was examined in dichloromethane, the most suitable solvent for this reaction, but the yield of the reaction was poor (entry 3). Dichloromethane was therefore the most suitable solvent for the C–Te coupling reaction of bis(4-tolyl) ditelluride and phenylboronic in the presence of CuTC with a reaction time of 24 hours.

Table 1 Optimization of the Reaction Conditions[a]

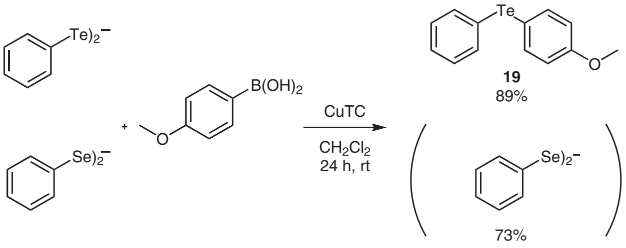


Entry	Solvent	Time (h)	Yield[b] (%)
1	$CHCl_3$	24	77
2	CH_2Cl_2	24	94
3	CH_2Cl_2	6	58
4	THF	24	40
5	EtOAc	24	25
6	NMP	24	15
7	DMF	24	13
8	DMSO	24	7
9	MeOH	24	34
10	[bmim]PF_6	24	n.r.[c]

[a] Reaction conditions: di(4-tolyl) ditelluride (0.5 mmol), $PhB(OH)_2$ (1.2 mmol), CuTC (1.2 mmol), solvent (3 mL), r.t.
[b] Isolated yield.
[c] n.r. = no reaction.

We then examined the preparation of various substituted diaryl chalcogenides by using various diaryl dichalcogenides and arylboronic acids in this reaction system. As a result, a variety of diaryl tellurides were synthesized in relatively good yields (Table 2). However, the yields decreased when diaryl ditellurides with bulky substituents, such as dimesityl ditelluride or bis(2,4,6-triisopropylphenyl) ditelluride, were used (entries 9–12). The reaction mixtures shown in entries 9 and 10 were heated, with the aim of improving the yield; however, these reactions remained ineffective. (In entry 9, the yield at r.t. was 46% and the yield upon heating was 45%; in entry 10, the yield at r.t. was 62% and the yield upon heating was 64%.) When we used (4-formylphenyl)boronic acid as a substrate, the yield decreased (entries 14–18); however, when the temperature for these reactions was changed from room temperature to reflux conditions, the yields of the reactions improved. Finally, we examined the preparation of diaryl selenides using diaryl diselenides and arylboronic acids in this reaction system; however, the intended diaryl selenides were not obtained. In other words, this reaction system is unique for the synthesis of diaryl tellurides by reacting diaryl ditellurides and boronic acids.

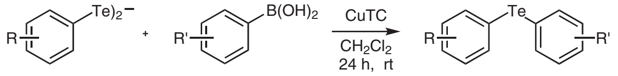
The following experiment was conducted to clarify the selectivity toward tellurium and selenium in this reaction. Diphenyl ditelluride (1 equiv), diphenyl diselenide (1 equiv), and (4-methoxyphenyl)boronic acid (1 equiv) were stirred in dichloromethane at room temperature for 30 minutes. CuTC (1 equiv) was then added and the mixture was stirred at room temperature for 24 hours. (Scheme 1). As a result, 1-methoxy-4-(phenyltelluro)benzene, the coupling product of the ditelluride and the boronic acid, was obtained in an isolated yield of 89%. Further, the unreacted selenium compound (diphenyl diselenide) was recovered in yield of 73%. This confirmed that this reaction is specific to tellurium compounds.



Scheme 1

In summary, we have reported the C–Te cross-coupling of diaryl ditellurides with arylboronic acids by using copper(I) thiophene-2-carboxylate as a catalyst.[8] The developed process is advantageous because the reaction proceeds at room temperature, a variety of organic solvents can be used, and good yields are obtained. Moreover, this reaction system is specific to the C–Te cross-coupling of diaryl ditellurides with arylboronic acids.

Table 2 C–Te Cross-Coupling of Diaryl Ditellurides with Arylboronic Acids in the Presence of CuTC [a]



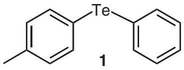
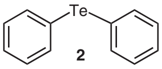
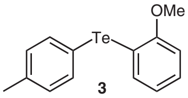
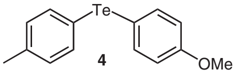
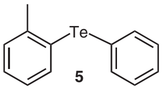
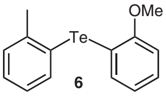
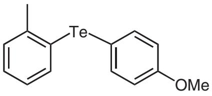
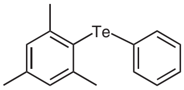
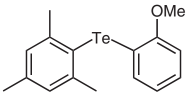
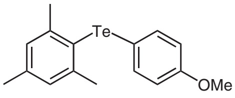
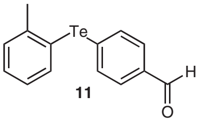
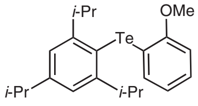
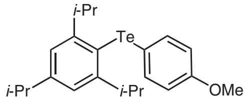
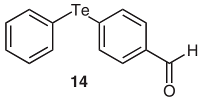
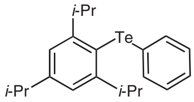
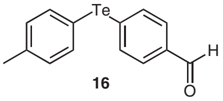
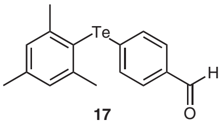
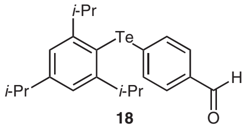
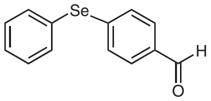
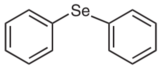
Entry	Dichalcogenide	Boronic acid	Product	Yield (%)[b]
1	$(4\text{-TolTe})_2$	$PhB(OH)_2$	 **1**	94
2	$(PhTe)_2$	$PhB(OH)_2$	 **2**	82
3	$(4\text{-TolTe})_2$	$2\text{-MeOC}_6H_4B(OH)_2$	 **3**	88
4	$(4\text{-TolTe})_2$	$4\text{-MeOC}_6H_4B(OH)_2$	 **4**	74
5	$(2\text{-TolTe})_2$	$PhB(OH)_2$	 **5**	84
6	$(2\text{-TolTe})_2$	$2\text{-MeOC}_6H_4B(OH)_2$	 **6**	86
7	$(2\text{-TolTe})_2$	$4\text{-MeOC}_6H_4B(OH)_2$		69
8	$(MesTe)_2$	$PhB(OH)_2$	 **8**	82
9	$(MesTe)_2$	$2\text{-MeOC}_6H_4B(OH)_2$	 **9**	46 (45)[c]
10	$(MesTe)_2$	$4\text{-MeOC}_6H_4B(OH)_2$	 **10**	62 (64)[c]
11	$(2,4,6\text{-}i\text{-PrC}_6H_2Te)_2$	$PhB(OH)_2$	 **11**	61

Table 2 (continued)

Entry	Dichalcogenide	Boronic acid	Product	Yield (%)[b]
12	$(2,4,6\text{-}i\text{-}PrC_6H_2Te)_2$	$2\text{-}MeOC_6H_4B(OH)_2$	 **12**	56
13	$(2,4,6\text{-}i\text{-}PrC_6H_2Te)_2$	$4\text{-}MeOC_6H_4B(OH)_2$	 **13**	88
14	$(PhTe)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 **14**	31 (69)[c]
15	$(2\text{-}TolTe)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 **15**	26 (82)[c]
16	$(4\text{-}TolTe)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 **16**	22 (75)[c]
17	$(MesTe)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 **17**	35 (57)[c]
18	$(2,4,6\text{-}i\text{-}PrC_6H_2Te)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 **18**	40 (56)[c]
19	$(PhSe)_2$	$4\text{-}HCOC_6H_4B(OH)_2$	 	n.r.[d]
20	$(PhSe)_2$	$PhB(OH)_2$	 	n.r.

[a] Reaction conditions: diaryl dichalcogenide (0.5 mmol), arylboronic acid (1.2 mmol), CuTC (1.2 mmol), CH_2Cl_2 (3 mL), r.t., 24 h.
[b] Isolated yield.
[c] Reflux conditions.
[d] n.r. = no reaction.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1610324.

References and Notes

(1) (a) Nogueira, C. W.; Zeni, G.; Rocha, J. B. *Chem. Rev.* **2004**, *104*, 6255. (b) Mugesh, G.; du Mont, W.-W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125. (c) Parnham, M. J.; Graf, E. *Prog. Drug Res.* **1991**, *36*, 9.

(2) (a) Zeni, G.; Braga, A. L.; Stefani, H. A. *Acc. Chem. Res.* **2003**, *36*, 731. (b) Zeni, G.; Lüdtke, D. S.; Panatieri, R. B.; Braga, A. L. *Chem. Rev.* **2006**, *106*, 1032. (c) Petragnani, N.; Stefani, H. A. *Tetrahedron* **2005**, *61*, 1613. (d) Comasseto, J. V.; Ling, L. W.; Petragnani, N.; Stefani, H. A. *Synthesis* **1997**, *1997*, 373.

(3) (a) Oba, M.; Nishiyama, K.; Koguchi, S.; Shimada, S.; Ando, W. *Organometallics* **2013**, *32*, 6620. (b) Oba, M.; Tanaka, K.; Nishiyama, K.; Ando, W. *J. Org. Chem.* **2011**, *76*, 4173. (c) Oba, M.; Okada, Y.; Endo, M.; Tanaka, K.; Nishiyama, K.; Shimada, S.; Ando, W. *Inorg. Chem.* **2010**, *49*, 10680. (d) Okada, Y.; Oba, M.; Arai, A.; Tanaka, K.; Nishiyama, K.; Ando, W. *Inorg. Chem.* **2010**, *49*, 383. (e) Oba, M.; Okada, Y.; Nishiyama, K.; Ando, W. *Org. Lett.* **2009**, *11*, 1879.

(4) Taniguchi, N. *J. Org. Chem.* **2007**, *72*, 1241.

(5) (a) Ren, K.; Wang, M.; Wang, L. *Org. Biomol. Chem.* **2009**, *7*, 4858. (b) Wang, M.; Ren, K.; Wang, L. *Adv. Synth. Catal.* **2009**, *351*, 1586.

(6) Kumar, A.; Kumar, S. *Tetrahedron* **2014**, *70*, 1763.

(7) (a) Alves, S.; Pena, J.; Vieira, A.; Botteselle, G.; Guadagnin, R.; Stefani, H. *J. Braz. Chem. Soc.* **2009**, *20*, 988. (b) Goldani, B.; Sacramento, M.; Lenardão, E.; Schumacher, R.; Barcellos, T.; Alves, D. *New J. Chem.* **2018**, *42*, 15603.

(8) **Diaryl Tellurides 1–10; General Procedure**
The appropriate diaryl ditelluride (0.5 mmol) and arylboronic acid (1.2 mmol) were stirred in CH$_2$Cl$_2$ (3 ml) at r.t. for 30 min. CuTC (1.2 mmol) was then added and the mixture was stirred at r.t. for 24 h. The mixture was concentrated, and the product was purified by column chromatography.
1-Phenyl-4-(phenyltelluro)benzene (1)
Yellow oil; yield: 274.5 mg (0.93 mmol; 94%); R_f = 0.35 (hexane). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.25 (s, 3 H), 6.95–7.56 (m, 9 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 21.3, 110.3, 115.3, 127.6, 129.5 (2 C), 130.5 (2 C), 137.3 (2 C), 138.1, 138.8 (2 C). HRMS (APCI): *m/z* $[M + H]^+$ calcd for C$_{13}$H$_{13}$Te: 299.0079; found: 299.02484.