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PAPER
Jason B. Benedict *et al.*
The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks

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Journal Name

ARTICLE

Synthesis of Symmetrical and Unsymmetrical Tellurides via Silver Catalysis

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Bruna Goldani,[a] Manoela do Sacramento,[a] Eder J. Lenardão,[a] Ricardo F. Schumacher,[a]
Thiago Barcellos[b]* and Diego Alves[a]*

We describe here a simple and efficient methodology for the cross-coupling reaction of diaryl ditellurides with aryl boronic acids catalyzed by $AgNO_3$. The general applicability and wide substrate scope make this an interesting method for the synthesis of a series of symmetrical and unsymmetrical diaryl tellurides. This silver-catalyzed protocol tolerates a variety of diaryl ditellurides as well as aryl boronic acids by using only 10 mol% of $AgNO_3$ to provide the desired products in high yields. The reaction mechanism was proposed after high resolution mass spectrometry analysis and the active $(PhTe)_2Ag^{III}$ intermediate could be detected.

Introduction

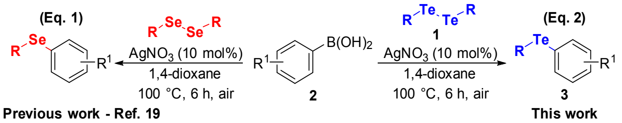
The synthesis of symmetrical and unsymmetrical chalcogenides is a field of great interest, since they are widely used as synthetic intermediates in a series of organic reactions,[1] as ligands for coordination chemistry,[2] besides presenting many biological properties.[3] In recent years, studies on the chemistry of organotellurium compounds have been growing and several methodologies for their synthesis have been developed.[4] Diaryl tellurides are a class of organochalcogen compounds largely explored due its synthetic importance, mainly with regard to the formation of new carbon-carbon bonds.[5]

In this context, recent advances related to the preparation of diaryl tellurides have been described. These protocols include the reaction of diaryl ditellurides with arylboronic acids under copper,[6] indium,[7] iron,[8] and iodine[9] catalysis, with potassium aryltrifluoroborate salts under copper catalysis,[10] with electron-rich arenes in the presence of $K_2S_2O_8$/TFA media,[11] or with aryl halides under copper catalysis.[12] Alternatively, Zhang described the use of elemental tellurium, aryl iodides, and KOH at 110 °C in DMSO to prepare symmetrical diaryl tellurides.[13]

On the other hand, silver-catalyzed reactions emerged as an important synthetic tool for a variety of organic transformations.[14] A range of traditional reactions, including cyclizations[15] and C-H bond activation[16] could be performed using salts of this metal as a catalyst. Concerning the synthesis of selenium or tellurium compounds, silver salts were used as a catalyst for the direct selenylation of terminal alkynes[17] or electron rich arenes.[18] However, to the best of our knowledge, the use of silver catalyst in the synthesis of organotellurium compounds have not been reported before.

Recently, our research group has developed the synthesis of diaryl selenides from diaryl diselenides and arylboronic acids using $AgNO_3$ as a catalyst.[19] The methodology is tolerant to the presence of electron-donor and electron-withdrawing groups at the substrates and the desired products were obtained in good to excellent yields (Eq. 1, Scheme 1). Considering the described protocols to access diorganyl selenides from arylboronic acids and diorganyl diselenides, which use indium, iron, and copper catalysts,[20] the Ag-catalyzed reaction can be considered an efficient and attractive alternative, since $AgNO_3$ is not expensive and is easily handled.

Thus, in order to extend this methodology for the synthesis of tellurium analogues, we present here our results on the silver-catalyzed cross coupling reaction of diaryl ditellurides with aryl boronic acids ((Eq. 2, Scheme 1).



Scheme 1 Silver-catalyzed cross coupling reactions of diaryl dichalcogenides with aryl boronic acids.

Results and discussion

In our previous work (Eq. 1, Scheme 1), after some optimization experiments (time, temperature, solvents and

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[b] Laboratory of Biotechnology of Natural and Synthetic Products, University of Caxias do Sul, Caxias do Sul, RS, Brazil.
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Electronic Supplementary Information (ESI) available: General experimental procedures, characterization details, and ^1H and ^{13}C NMR spectra of compounds. See DOI: 10.1039/x0xx00000x

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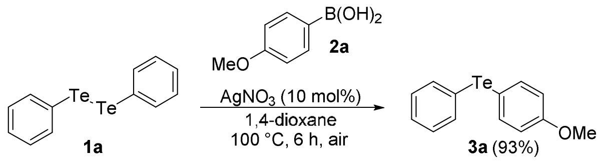
silver species), we found that the best condition was reacting diaryl diselenides and aryl boronic acids at 100 °C in 1,4-dioxane under air during 6 h using 10 mol% of $AgNO_3$ as catalyst. Thus, we applied the same reaction conditions, just changing diphenyl diselenide to diphenyl ditelluride **1a** (Scheme 2) and gratifyingly, the corresponding diaryl telluride **3a** was obtained in an excellent yield.

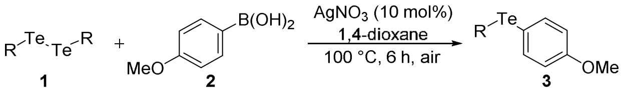


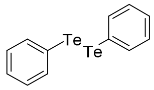
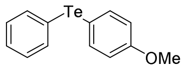
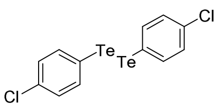
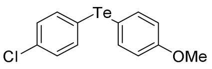
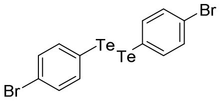
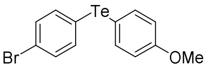
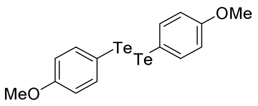
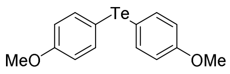
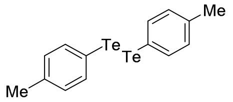
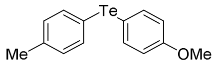
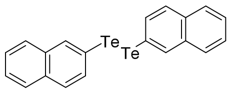
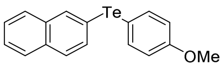
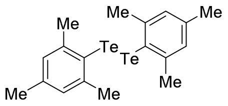
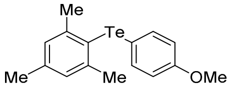
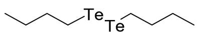
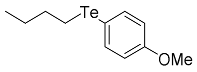
Scheme 2 Silver catalysed synthesis of telluride **3a**.

With this result in hands, we extend these reaction conditions to various substituted diaryl ditellurides **1a-g** and dibutyl ditelluride **1h**, as well as aryl boronic acids **2a-n** to evaluate the substrate scope. Analyzing the results shown in Table 1, it can be seen that this protocol effectively promoted the reaction in almost all cases.

Firstly, we reacted 4-methoxy-phenyl boronic acid **2a** with a range of diaryl ditellurides **1a-g** and our results reveal that the reactions are not sensitive to the electronic effect in the aromatic ring in the diaryl ditelluride (Table 1, entries 1-7). We also observed that steric effects in the diaryl ditelluride had little influence, with the reaction of substrate **2a** with dimesityl ditelluride **1g** furnishing the product **3g** in 74% yield (Table 1, entry 7). A good result was obtained when we used di(2-naphthyl) ditelluride **1f**, yielding the desired product **3f** in 72% yield (Table 1, entry 6). In addition, 4-methoxy-phenyl boronic acid **2a** reacted with dibutyl ditelluride **1h** under the optimized conditions to produce the corresponding telluride **3h** in 64% yield (Table 1, entry 8).

Table 1 Substrate scope for the $AgNO_3$-catalyzed synthesis of diorganyl tellurides.[a]



Entry	Ditelluride **1**	Product **3** (Yield)
1	 **1a**	 **3a** (93%)
2	 **1b**	 **3b** (89%)
3	 **1c**	 **3c** (78%)
4	 **1d**	 **3d** (89%)
5	 **1e**	 **3e** (93%)
6	 **1f**	 **3f** (72%)
7	 **1g**	 **3g** (74%)
8	 **1h**	 **3h** (64%)

[a] The reactions were performed using diorganyl ditelluride **1a-h** (0.2 mmol), 4-methoxy-phenyl boronic acid **2a** (0.4 mmol), $AgNO_3$ (10 mol%) and 1,4-dioxane (0.8 mL), at 100 °C under air for 6 h.

Besides, the reactivity of diphenyl ditelluride **1a** with different functionalized arylboronic acids **2b-m** was verified (Table 2). Phenyl boronic acid **2b** was treated with diphenyl ditelluride **1a** to afford the desired product **3i** in 92% yield (Table 2, entry 1). Also, reactions were performed with arylboronic acids containing substituents such as OMe, Me, Cl, Br, CF_3 and acetyl, and the desired diaryl tellurides **3j-s** were obtained in moderated to excellent yields (Table 2, entries 2-11). These results revealed that the conducted reactions were sensitive to electronic effects, since aryl boronic acids containing electron-donor groups (EDG), 4-OCH_3 (**2a**) or 4-CH_3 (**2c**), gave better yields than those containing electron-withdrawing groups (EWG), 4-Br (**2d**) or 4-Cl (**2e**) (Table 1, entry 1 and Table 2, entries 2-4). A similar behavior was observed for the *o*-substituted aryl boronic acids **2f-i**, with lower yields being obtained for diaryl tellurides containing EWG groups (**3o-p**), even after 24 h of reaction (Table 2, entries 5-6 *vs.* entries 7-8).

Moderated yields were obtained for diaryl tellurides **3q-s**, derived from 3-substituted aryl boronic acids **2j-l** (Table 2, Entries 9-11). 2-Naphthyl boronic acid **2m** and 3-thienylboronic acid **2n** were efficiently reacted with diphenyl ditelluride **1a** giving the respective products **3t**

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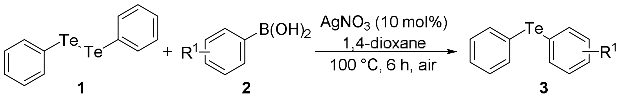
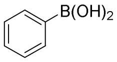
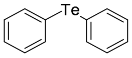
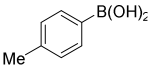
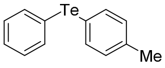
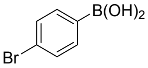
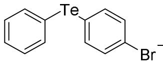
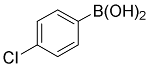
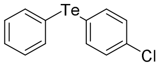
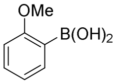
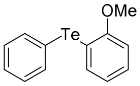
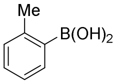
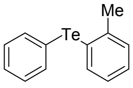
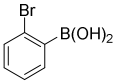
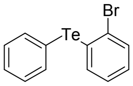
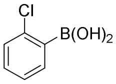
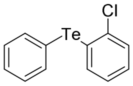
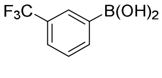
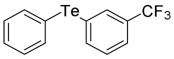
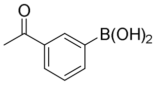
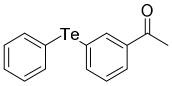
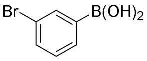
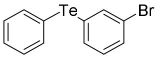
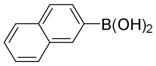
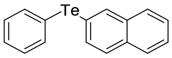
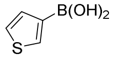
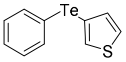
and **3u** in 80% and 87% yields, respectively (Table 2, entries 12-13).

Table 2. Substrate scope for the $AgNO_3$-catalyzed synthesis of diorganyl tellurides.[a]



Entry	Boronic Acid **2**	Product **3** (Yield)[b]
1	 **2b**	 **3i** (92%)
2	 **2c**	 **3j** (99%)
3	 **2d**	 **3k** (62%)
4	 **2e**	 **3l** (82%)
5	 **2f**	 **3m** (74%)
6	 **2g**	 **3n** (70%)
7	 **2h**	 **3o** (28%)[b]
8	 **2i**	 **3p** (28%)[b]
9	 **2j**	 **3q** (66%)
10	 **2k**	 **3r** (52%)
11	 **2l**	 **3s** (62%)
12	 **2m**	 **3t** (80%)
13	 **2n**	 **3u** (87%)

[a] The reactions were performed using diphenyl ditelluride **1a** (0.2 mmol), aryl boronic acids **2a-n** (0.4 mmol), $AgNO_3$ (10 mol%) and 1,4-dioxane (0.8 mL), at 100 °C under air for 6 h. [b] Reaction time of 24 h.

To understand the reaction mechanism involved in the developed catalytic reaction an investigation was performed through high resolution mass spectrometry using electrospray ionization (ESI) and atmosphere-pressure chemical ionization (APCI) as sources for soft ionization conditions, in both positive and negative modes.

The first proposed intermediate **A** (Figure 1) was detected by reaction of the diorganyl ditelluride (Ph_2Te_2) with $AgNO_3$ in 1,4-dioxane, at 100 °C and in the absence of the boronic acid. The cationized silver-tellurium complex **A** with *m/z* 518.7929 was observed after 1 minute of reaction in the ESI(+). In addition to the molecular ion, water $[M+H_2O]^+$ (m/z 536.8046) and acetonitrile $[M+CH_3CN]^+$ (m/z 559.8179) adducts ions were also recorded (see SI, Figure S1).

An important feature of HRMS analysis for mechanism investigation is the isotope pattern. The complex **A** shows a unique isotope pattern due to eight stable tellurium isotopes plus two stable silver isotopes. As showed in Figure S2 (see SI), the observed isotope pattern agrees with the calculated mass, including exactly two tellurium atoms and one silver atom. Aliquots taken within 15, 30 and 45 minutes of reaction presents the same mass spectra shown in Figure S1 suggesting the stability of the initially formed ion in the reaction conditions. The ion corresponding to the intermediate **A** was not detected in ESI(-) or APCI(+) analysis. The ion *m/z* 518.7925 (ESI+) was subjected to MS^2 fragmentation showing the silver containing ions of *m/z* 313.8504 $[M-C_6H_5Te]^+$, *m/z* 331.8610 $[M-C_6H_5Te+H_2O]+$ and *m/z* 106.9051 which correspond to the silver ion (Ag^+) (see SI, Figure S3).

The formation of intermediate **A** involves two-electrons redox chemistry, which is not commonly described for

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silver-catalytic cycles. Although some reports suggest the presence Ag(III) intermediates,[16f,21] there is a lack of spectroscopy data available that evidence the Ag(III) intermediates. Font and coworks[22] reported a crystallographic and spectroscopic studies, including NMR and HRMS analysis, providing direct characterization of an aryl-Ag(III) intermediate as catalytically active species in coupling catalysis. In addition, the researches demonstrate via cyclic voltammetry data and DFT calculations that Ag(I)/Ag(III) redox process occurs through a one-step, two-electrons process.

On the other hand, tellurium compounds are highly redox-active,[23] Although experimental data regarding the electrochemistry of organic ditellurides (and diselenides) in organic aprotic solvents are scarce,[24] it is well established that diorganyl selenides and tellurides undergoes oxidative insertion towards RSe-SeR or RTe-TeR bonds by transition metals.[20]

The HRMS ESI(+) or ESI(-) analysis of the mixture of the boronic acid and $AgNO_3$ in 1,4-dioxane, at 100 °C and in the absence of diphenyl ditelluride did not show any ion containing boron and silver. Only the boronic acid adducts were detected. Interestingly the silver(I) nitrate shows poor or no solubility under these conditions.

In the experiment carried out with the 4-methoxyphenylboronic acid it was possible to detect the ion with *m/z* 420.9001. The isotope pattern analysis suggests the structure of the proposed intermediate **C**, which would be formed by the reaction of the intermediate **B** with a second equivalent of boronic acid. The ion having *m/z* 438.9092, which correspond to the adduct of intermediate **C** and water $[M+H_2O]^+$ shows as high-intense peak. The *m/z* matching the intermediate **C** appears with very low intensity. Nevertheless, the MS^2 fragmentation of the either ions lead to a series product ions that were important to confirm the structural identity of the intermediate **C**, including the expected *m/z* for the silver ion (see SI, Figure S4). The isotope distribution for the ion with *m/z* 438 (see SI, Figure S5) is also an indication which confirms the proposed intermediate **C**. The reductive elimination of intermediate **C** forms the second equivalent of the desired product.

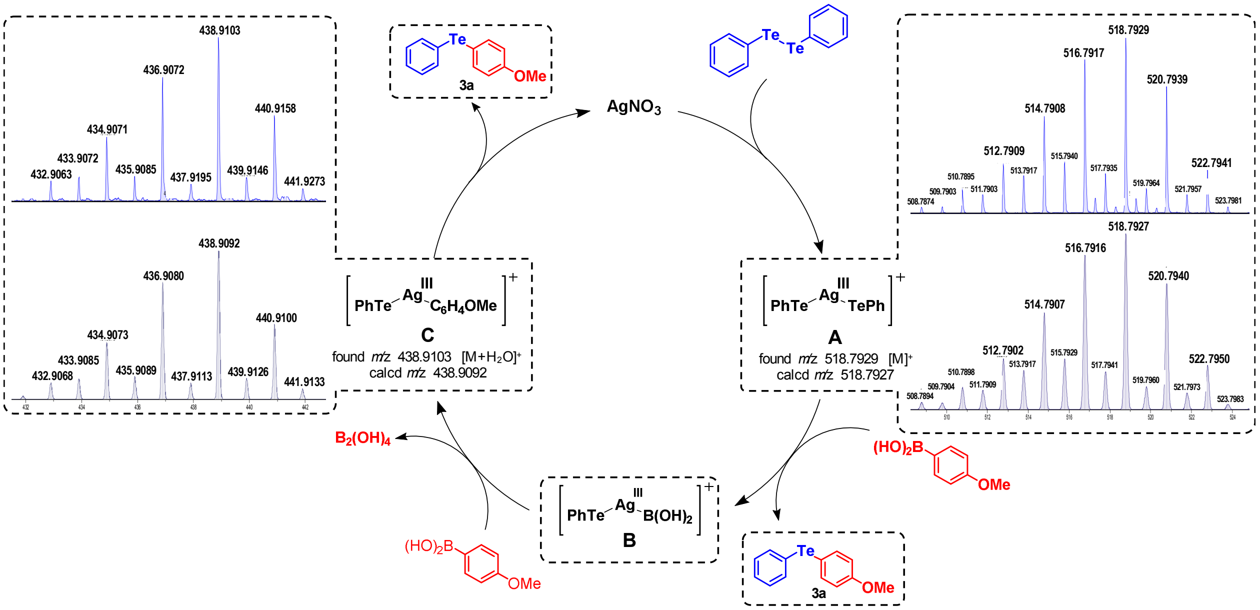

Figure 1 Proposed Mechanism.

Based in the HRMS data and in previously proposed mechanisms for silver-catalyzed reactions,[16] we proposed the catalytic cycle shown in Figure 1, for the reaction between **1a** and **2a**. We believe that, at first, the reaction of $AgNO_3$ with diphenyl ditelluride **1a** leads to the Ag(III) intermediate **A**. After that, aryl boronic acid **2** attacks intermediate **A** to form the corresponding product **3a** and intermediate $(PhTe)[B(OH)_2]Ag^{III}$ **B**, which reacts with other equivalent of aryl boronic acid **2a**, leading to intermediate **C** and tetrahydroxydiboron **D**. Finally, intermediate **C** undergoes a reductive elimination to form the desired product **3a** regenerating the Ag(I) catalyst in the catalytic cycle. The proposed mechanism indicates that this Ag(I)-catalyzed C–Te coupling reaction is able to use both groups of diphenyl ditelluride **1a** (Figure 1). Even though the expected ion of the proposed intermediate **B** was not detected in ESI(+) or ESI(-) modes, it is suggested to be a key intermediated between species **A** and **C**, since no symmetrical diphenyl telluride **3i** was detected, either by NMR or HRMS analyses.

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Conclusions

In conclusion, we developed an efficient method for the synthesis of symmetrical and unsymmetrical tellurides by the $AgNO_3$-catalyzed cross-coupling reaction of diorganyl ditellurides with commercial available aryl boronic acids. The described methodology tolerates a range of substituents both in the aryl boronic acids and in the diorganyl ditellurides, providing moderated to excellent yields of the desired products. The active $(PhTe)_2Ag^{III}$ intermediate could be detected by high resolution mass spectrometry experiments and a reaction mechanism was proposed.

Experimental

General Information: The reactions were monitored by TLC carried out on Merck silica gel (60 F_{254}) by using UV light as visualizing agent and 5% vanillin in 10% H_2SO_4 and heat as developing agents. Baker silica gel (particle size 0.040-0.063 mm) was used for flash chromatography. Proton and carbon-13 nuclear magnetic resonance spectra (^{1}H NMR) were acquired using a Bruker Fourier 300 spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR). All NMR spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the internal reference in the ^{1}H NMR spectra or referenced to the solvent peak in the ^{13}C NMR spectra. Coupling constants (*J*) are reported in Hertz. Abbreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), dd (doublet of doublet), dt (doublet of triplet), t (triplet), q (quartet), quint (quintet), sex (sextet) and m (multiplet). Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP2010 mass spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics micrOTOF-Q II instrument.

General Procedure for Silver(I)-Catalyzed Synthesis of Diaryl Tellurides 3a-u: To a 5 mL Schlenk tube equipped with a small magnetic stirring bar were added the appropriate diorganoyl ditelluride **1a-h** (0.2 mmol), the appropriate aryl boronic acid **2a-n** (0.4 mmol), $AgNO_3$ (0.04 mmol, 10 mol%) and 1,4-dioxane (0.8 mL). The resulting mixture was stirred at 100 °C for 6 h. After that, the reaction mixture was cooled to room temperature, and was quenched using water (5 mL). The mixture was then extracted using ethyl acetate (10 mL) and washed with water (3 x 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ethyl acetate as eluent. Spectral data for the products prepared are listed below.

Phenyl(4-methoxyphenyl)telluride[10] (3a): Yield: 0.117 g (93%); Yellow solid; mp 57-59 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (dt, *J* = 8.8, 2.8 Hz, 2H), 7.61 - 7.50 (m, 2H), 7.27 - 7.08 (m, 3H), 6.78 (dd, *J* = 8.8, 2.8 Hz, 2H), 3.77 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.9, 141.15, 136.3, 129.3, 127.2, 115.9, 115.5, 103.1, 55.1. MS *m/z* (relative intensity): 314 (M^+, 24), 312 (22), 184 (100), 169 (62), 141 (37), 115 (18), 92 (11), 77 (44), 51 (26).

4-Chlorophenyl(4-methoxyphenyl)telluride (3b): Yield: 0.124 g (89%); Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.1, 141.3, 137.5, 133.6, 129.4, 115.6, 113.6, 102.9, 55.1. MS *m/z* (relative intensity): 348 (M^+, 31), 346 (28), 218 (100), 203 (45), 175 (20), 75 (11), 63 (12). HRMS calculated for $C_{13}H_{11}ClOTe$ $[M]^+$: 347.9561, Found: 347.9545.

4-bromophenyl(4-methoxyphenyl)telluride (3c): Yield: 0.122 g (78%); Yellow solid; mp 42-43°C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.1, 141.4, 139.7, 137.7, 132.3, 121.7, 115.6, 102.8, 55.1. MS *m/z* (relative intensity): 392 (M^+, 36), 388 (12), 264 (99), 262 (100), 249 (47), 247 (49), 237 (18), 221 (25), 140 (18), 92 (19), 77 (26), 63 (42), 50 (40). HRMS calculated for $C_{13}H_{11}BrOTe$ $[M]^+$: 391.9056, Found: 391.9045.

Bis(4-methoxyphenyl)telluride[10] (3d): Yield: 0.122 g (89%); Yellow solid; mp 46-48 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.61 (d, *J* = 8.8 Hz, 4H), 6.74 (d, *J* = 8.9 Hz, 4H), 3.74 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.1, 139.6, 115.3, 104.2, 55.0. MS *m/z* (relative intensity): 344 (M^+, 28), 340 (17), 214 (100), 199 (94), 171 (30), 128 (15), 107 (7), 77 (10), 63 (17).

4-Methylphenyl(4-methoxyphenyl)telluride[10] (3e): Yield: 0.122 g (93%); Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.68 (d, *J* = 8.8 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.7, 140.5, 137.3, 137.1, 130.2, 115.3, 111.3, 103.5. MS *m/z* (relative intensity): 328 (M^+, 32), 296 (52), 237 (46), 198 (100), 183 (63), 155 (29), 91 (19), 65 (21).

Naphthalen-2-yl(4-methoxyphenyl)telluride (3f): Yield: 0.105 g (72%); Yellow solid; mp 80-83; °C ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.07 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 3H), 7.71 - 7.59 (m, 1H), 7.59 (s, 2H), 7.48 - 7.34 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.9, 141.0, 135.8, 134.2, 133.4, 132.3, 128.4, 127.7, 127.2, 126.2, 126.0, 115.5, 113.3, 103.3, 55.1. MS *m/z* (relative intensity): 364 (M^+, 21), 234 (100), 219 (61), 191 (30), 127 (35), 77 (19), 63 (13). HRMS calculated for $C_{17}H_{14}OTe$ $[M]^+$: 364.0107, Found: 364.0118.

Mesityl(4-methoxyphenyl)telluride[10] (3g): Yield: 0.105 g (74%); Yellow solid; mp 31-32 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.35 (dt, *J* = 8.8, 2.9 Hz, 2H), 6.96 (s, 2H), 6.69 (dt, *J* = 8.8, 2.9 Hz, 2H), 3.73 (s, 3H), 2.53 (s, 6H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.0, 145.1, 139.0, 137.2, 127.5, 118.8, 115.3, 104.6, 55.1, 29.7, 29.4, 21.0. MS *m/z* (relative intensity): 356 (M^+, 100), 354 (92), 248 (52), 244 (30), 237 (12), 226 (81), 214 (17), 211 (46), 199 (15), 195 (19), 119 (58), 115 (22), 103 (18), 91 (52), 77 (40), 63 (22), 51 (15), 41 (24).

Butyl(4-methoxyphenyl)telluride (3h): Yield: 0.075 g (64%); Yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.67 (dt, *J* = 8.8, 2.9 Hz, 2H), 6.75 (dt, *J* = 8.8, 2.9 Hz, 2H), 3.79 (s, 3H), 2.82 (t, *J* = 7.3 Hz, 2H), 1.73 (quint, *J* = 7.3 Hz, 2H), 1.37 (sex, *J* = 7.3 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.5, 140.8, 115.0, 100.5, 55.1, 33.8, 24.9, 13.4, 8.7. MS *m/z* (relative intensity): 294 (M^+, 23), 290 (13), 237 (15), 222 (7), 108 (100), 92 (7), 63

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(12), 57 (14), 41 (25). HRMS calculated for $C_{11}H_{16}OTe$ $[M]^+$: 294.0263, Found: 294.0263.

Diphenyl telluride[10] (3i): Yield: 0.104 g (92%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.76 - 7.63 (m, 4H), 7.34 - 7.14 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.9, 129.5, 127.8, 114.6. MS *m/z* (relative intensity): 284 (M^+, 23), 280 (15), 206 (10), 154 (100), 77 (85), 51 (49). HRMS calculated for $C_{12}H_{10}Te$ $[M]^+$: 283.9845, Found: 283.9842.

Phenyl(4-methylphenyl)telluride[10] (3j): Yield: 0.118 g (99%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.73 - 7.52 (m, 3H), 7.29 - 7.09 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.7, 138.0, 137.2, 130.4, 129.3, 127.4, 115.2, 110.2, 21.2. MS *m/z* (relative intensity): 298 (M^+, 27), 168 (100), 153 (21), 91 (51), 77 (35), 65 (32), 51 (29).

Phenyl(4-bromophenyl)telluride (3k): Yield: 0.090 g (62%); Yellow solid; mp 59-61 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.70 - 7.67 (m, 2H), 7.52 - 7.48 (m, 2H), 7.34 - 7.27 (m, 3H), 7.25 - 7.19 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.3, 138.2, 132.6, 129.6, 128.1, 122.5, 114.2, 113.2. MS *m/z* (relative intensity): 362 (M^+, 21), 232 (79), 207 (11), 152 (37), 77 (100), 51 (69). HRMS calculated for $C_{12}H_9BrTe$ $[M]^+$: 361.8950, Found: 361.8941.

Phenyl(4-chlorophenyl)telluride (3l): Yield: 0.104 g (82%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.73 - 7.63 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.35 - 7.09 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.1, 138.1, 134.2, 129.7, 129.6, 128.1, 114.4, 112.3. MS *m/z* (relative intensity): 318 (M^+, 44), 316 (37), 188 (100), 153 (18), 111 (12), 77 (57), 51 (55). HRMS calculated for $C_{12}H_9ClTe$ $[M]^+$: 317.9455, Found: 317.9453.

Phenyl(2-methoxyphenyl)telluride (3m): Yield: 0.093 g (74%); Yellow solid; mp 50-53 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.88 (d, *J* = 6.7 Hz, 2H), 7.42 - 7.34 (m, 1H), 7.33 - 7.21 (m, 2H), 7.22 - 7.09 (m, 1H), 6.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.81 - 6.65 (m, 2H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.9, 141.1, 133.3, 129.5, 128.5, 128.00, 122.3, 111.9, 109.5, 107.6, 55.7. MS *m/z* (relative intensity): 314 (M^+, 17), 184 (48), 169 (36), 141 (26), 107 (23), 92 (10), 77 (100), 51 (43). HRMS calculated for $C_{13}H_{13}O_2Te$ $[M + OH]^+$: 330.9978, Found: 330.9985.

Phenyl(2-methylphenyl)telluride (3n): Yield: 0.083 g (70%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.74 - 7.64 (m, 2H), 7.48 - 7.44 (m, 1H), 7.34 - 7.24 (m, 1H), 7.27 - 7.15 (m, 4H), 2.40 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.8, 138.6, 137.3, 129.6, 129.3, 128.0, 128.0, 126.7, 119.2, 113.9, 26.0. MS *m/z* (relative intensity): 298 (M^+, 41), 296 (38), 167 (92), 153 (43), 91 (100), 77 (53), 65 (67), 51 (58). HRMS calculated for $C_{13}H_{12}Te$ $[M]^+$: 298.0001, Found: 297.9999.

Phenyl(2-bromophenyl)telluride (3o): Yield: 0.041 g (28%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.96 - 7.91 (m, 2H), 7.49 - 7.31 (m, 4H), 7.05 - 6.95 (m, 2H), 6.89 - 6.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.2, 134.3, 132.0, 130.0, 129.2, 128.0, 127.8, 126.9, 123.9, 114.6. MS *m/z* (relative intensity): 362 (M^+, 12), 234 (18), 207 (13), 152 (33), 77 (100), 51 (85), 44 (43), 40 (51). HRMS calculated for $C_{12}H_9BrTe$ $[M]^+$: 361.8950, Found: 361.8940.

Phenyl(2-chlorophenyl)telluride (3p): Yield: 0.036 g (28%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.94 - 7.91 (m, 2H), 7.48 - 7.43 (m, 1H), 7.37 - 7.29 (m, 3H), 7.14 - 7.08 (m, 1H), 6.96 - 6.93 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 141.3, 136.4, 134.2, 130.0, 129.2, 128.7, 128.0, 127.4, 120.5, 113.2. MS *m/z* (relative intensity): 318 (M^+, 27), 316 (23), 188 (100), 152 (30), 111 (10), 77 (99), 51 (77). HRMS calculated for $C_{12}H_9ClTe$ $[M]^+$: 317.9455, Found: 317.9432.

Phenyl(3-trifluoromethylphenyl)telluride[25] (3q): Yield: 0.093 g (66%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.89 (s, 1H), 7.82 - 7.70 (m, 3H), 7.40 - 7.17 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 140.4, 138.8, 133.6 (q, $J_{C\text{–}F}$ = 3 Hz), 131.4 (q, $J_{C\text{–}F}$ = 32 Hz), 129.8, 125.5, 128.5, 124.4 (q, $J_{C\text{–}F}$ = 3 Hz), 123.6 (q, $J_{C\text{–}F}$ = 272 Hz), 115.8, 113.7. MS *m/z* (relative intensity): 352 (M^+, 15), 222 (88), 203 (10), 153 (16), 145 (17), 126 (20), 95 (11), 77 (100), 51 (72), 40 (16).

Phenyl(naphthalen-2-yl)telluride (3r): Yield: 0.107 g (80%); Yellow solid; mp 39-42 °C; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.23 (s, 1H), 7.82 - 7.76 (m, 1H), 7.74 - 7.63 (m, 5H), 7.49 - 7.42 (m, 2H), 7.32 - 7.16 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 137.8, 134.7, 134.3, 132.6, 129.5 (2C), 128.6, 127.8, 127.7, 127.4, 126.4, 126.3, 114.8, 111.9.MS *m/z* (relative intensity): 334 (M^+, 12), 204 (100), 127 (59), 101 (10), 77 (48), 51 (33). HRMS calculated for $C_{16}H_{12}Te$ $[M]^+$: 334.0001, Found: 333.9999.

Phenyl(3-acetylphenyl)telluride (3s): Yield: 0.068 g (52%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 8.40 - 8.05 (m, 2H), 7.89 - 7.77 (m, 2H), 7.77 - 7.69 (m, 2H), 7.35 - 7.17 (m, 2H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 197.5, 141.8, 138.5, 137.8, 137.1, 129.6, 129.5, 128.2, 127.5, 115.5, 114.0, 26.6. MS *m/z* (relative intensity): 326 (M^+, 14), 207 (13), 181 (56), 153 (31), 77 (96), 51 (60, 43 (100), 40 (13). HRMS calculated for $C_{14}H_{12}OTe$ $[M]^+$: 325.9950, Found: 325.9948.

Phenyl(3-bromophenyl)telluride (3t): Yield: 0.090 g (62%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.83 - 7.66 (m, 3H), 7.53 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.43 - 7.16 (m, 4H), 7.03 (t, *J* = 7.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 139.4, 138.6, 135.7, 130.7, 130.7, 129.7, 128.3, 123.3, 116.7, 113.9. MS *m/z* (relative intensity): 362 (M^+, 16), 234 (52), 152 (33), 77 (100), 51 (63). HRMS calculated for $C_{12}H_9BrTe$ $[M]^+$: 361.8950, Found: 361.8932.

Phenyl(3-thienyl)telluride[8a] (3u): Yield: 0.101 g (87%); Yellow oil; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.47 - 7.44 (m, 3H), 7.14 - 7.05 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 136.7, 136.3, 134.4, 129.3, 127.4, 127.1, 115.2, 103.8. MS *m/z* (relative intensity): 290 (M^+, 28), 288 (27), 160 (100), 128 (13), 115 (17), 77 (47), 51 (30).

Conflicts of interest

There are no conflicts to declare.

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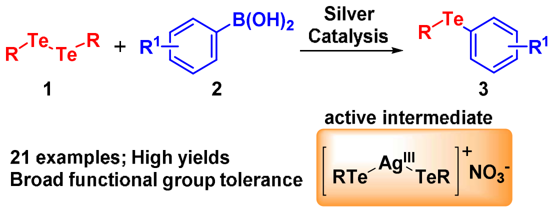

The cross-coupling reaction of diaryl ditellurides with aryl boronic acids is described using $AgNO_3$ as a catalyst.