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Glycerol/CuI/Zn as a recyclable catalytic system for synthesis of vinyl sulfides and tellurides

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ABSTRACT

A convenient approach to the Cu-catalyzed coupling of diphenyl disulfide and diphenyl ditelluride with vinyl bromides using a recyclable catalytic system and glycerol as a green solvent is described. This protocol was efficiently used in the preparation of vinyl sulfides and vinyl tellurides with a variety of substituents in good yields and stereoselectively. The solvent/catalyst system was directly reused for four cycles without loss of activity.

Organochalcogen compounds have become intensively studied due to their biological and pharmacological activities,[1] use as efficient polydentate ligands for designing metal complexes,[2] crystalline metal chalcogenide clusters,[3] and versatile building blocks for organic synthesis.[4] Among the organochalcogenium species, vinyl chalcogenides are useful synthons in organic reactions, particularly in the synthesis of carbonyl compounds and for stereospecific synthesis of substituted alkenes.[5] In this context, vinyl sulfides and vinyl tellurides constitute very useful intermediates, because they combine the reactivity of both the organochalcogen group and the carbon–carbon double bond.[6,7]

Among various methods to synthesize selectively vinyl sulfides and tellurides is the hydrochalcogenation of alkynes using thiols or the respective chalcogenolate anion generated in situ.[6,7] Although an atom-economic procedure, the hydrochalcogenation is suitable for a restricted number of terminal and activated alkynes. Alternatively, vinyl chalcogenides can be obtained by cross-coupling of diaryl dichalcogenides with vinyl halides, however, this reaction generally requires the use of expensive noble metals and high temperature, restricting its application.[8] A wide range of metal catalysts including palladium, [8c] lanthanum,[8f] and copper-based[8g,h] have been exploited for these cross-coupling reactions. However, the use of copper catalysts remains quite rare despite the clear advantage in cost-effectiveness.

On the other hand, in view of the widespread use of solvents in nearly all of the chemical and pharmaceutical industries, it has raised a growing interest in the search for green solvents from renewable resources.[9] The peculiar physical and chemical properties of glycerol, such as high boiling point, polarity, low toxicity, biodegradability, no flammability, and ready availability from renewable feedstock, turn it a strong candidate to a safe, renewable solvent.[10] The use of glycerol as a solvent in organic synthesis has grown considerably in recent years and several successful examples have been described by us[11] and others.[12] These include Pd-catalyzed Heck and Suzuki cross-couplings, base- and acid-promoted condensations, oxidation, catalytic hydrogenation, and asymmetrical reduction.[11,12]

Recently, we have described a successful synthesis of vinyl selenides by the Cu-catalyzed cross-coupling of diaryl diselenides and vinyl bromides using CuI/Zn/glycerol as catalytic system (Scheme 1).[13] In view of our interest in the development of new and cleaner methods for the preparation of organochalcogenium compounds, we present here our results on the conversion of (*E*)- and (*Z*)-vinyl bromides to the respective (*E*)- and (*Z*)-vinyl sulfides and vinyl tellurides using the catalytic system CuI/Zn/glycerol (Scheme 1).[14]

For the reaction of diaryl diselenides with vinyl bromides using glycerol as solvent it was found that the best conditions for the coupling reaction consist of stirring a mixture of diaryl diselenide (0.3 mmol) and bromostyrene (0.6 mmol) in the presence of CuI (5 mol %), Zn dust (0.6 mmol) as additive, glycerol as solvent (1.5 mL) at 110 °C (oil bath), and under N_2 atmosphere.[13] Aiming to extend this efficient protocol to other chalcogenium species, we tested the cross-coupling reaction using (*E*)-β-bromostyrene **1a** and diphenyl disulfide **2a** as starting materials. After stirring

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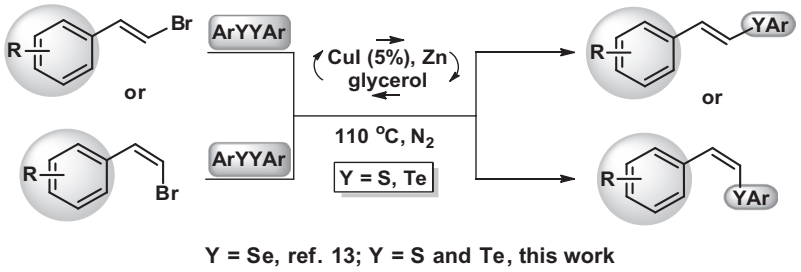


Scheme 1. General scheme of the reaction.

for 4 h at 110 °C, (*E*)-β-(phenylthio)styrene **3a** was obtained in 75% yield, a result not so good compared with the selenium analogous, which provided (*E*)-β-(phenylseleno)styrene in 95% yield. Thus, trying to improve the yield of **3a**, we screened several conditions for this cross-coupling reaction, varying the reaction time, catalyst loading, temperature, use of additive, and inert atmosphere (Table 1). No substantial increase in yield was observed in all the tested variations, even using a larger amount of catalyst or a longer reaction time (Table 1, entries 4 and 5).

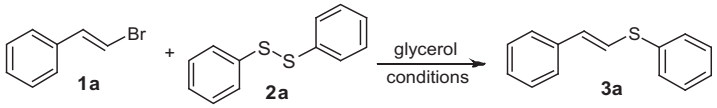
Remarkably, the formation of **3a** was not observed in the absence of CuI and when zinc was omitted from the reaction mixture, the yield was only 42% (Table 1, entries 8 and 9). We also observed that temperature and N_2 atmosphere are crucial to ensure a good yield of **3a** (Table 1, entries 7 and 10). In addition, when the reactions were performed using other copper species with or without zinc dust, poor yields of desired product **3a** were obtained (Table 1, entries 12–14).

This protocol was then extended to the cross-coupling of diaryl disulfide **2a–d** with various readily accessible (*E*)- and (*Z*)-β-bromostyrenes **1a–g** to expand the scope of the reaction (Table 2, entries 1–10). As can be seen in Table 2, a range of β-bromostyrenes were successfully used, affording the respective vinyl sulfides in good yields and with high stereoselectivity. Thus, (*E*)-4-methoxy-β-bromostyrene **1b** reacted under our conditions with diphenyl disulfide **2a** to afford exclusively (*E*)-4-methoxy-β-(phenylthio)styrene **3b** in 85% yield after 2 h (Table 2, entry 2). It was verified that the reaction works well in high level of stereoselectivity also with (*Z*)-β-bromostyrene **1f** which gave (*Z*)-β-(phenylthio)styrene **3f** in 70% yield after 6 h (Table 2, entry 6). Besides, diaryl disulfides containing electron-withdrawing or electron-donating groups at the aromatic ring also gave good yields of products **3h–j** (Table 2, entries 8–10).

In recent years, vinyl tellurides have a peculiar reactivity face to diversity of metals and are valuable synthons for the selective preparation of substituted alkenes in total organic synthesis.[15] In this sense, the development of selective and general methods to prepare vinyl tellurides with total control on the stereochemistry of the double bond is a critical challenge to synthetic organic chemists. Thus, according to our studies, the CuI/Zn/glycerol system was efficiently used for the C—Te bond formation via cross-coupling reaction of diaryl ditellurides **2e–f** with β-bromostyrenes (Table 2, entries 11–18). Similar to the reaction observed with diphenyl disulfide **2a**, styryl bromides with both, electron-donating and electron-withdrawing groups at the aromatic ring, such as methoxyl, methyl, and chloro, afforded the corresponding vinyl tellurides in good yields and selectively (Table 2, entries 12–15). When (*Z*)-β-bromostyrenes were used, a high degree of retention on the configuration of the double bond was observed (Table 2, entries 16 and 17). It was also verified that bis(4-methoxyphenyl) ditelluride **2f** easily coupled with (*E*)-β-bromostyrene **1a**, affording after 24 h exclusively (*E*)-β-(4-methoxyphenyltelluro)styrene **3r** in 75% yield (Table 2, entry 18).

Additionally, a reuse study of the CuI/Zn/glycerol system was carried out for the reaction of **1a** with **2a** to obtain **3a**. After stirring at 110 °C during 4 h, the reaction mixture was diluted and extracted with a mixture of hexane/ethyl acetate 95/5 (3 × 3.0 mL).

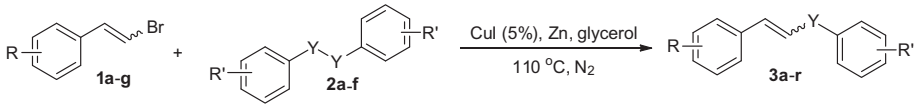
Table 1
Optimization of the synthesis of (*E*)-β-(phenylthio)styrene **3a**[a]

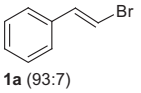
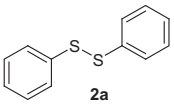
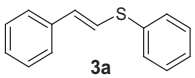
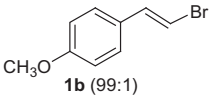
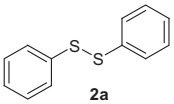
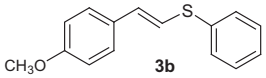
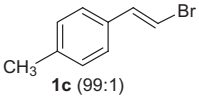
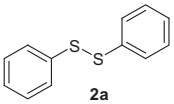
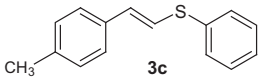
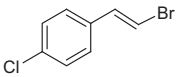
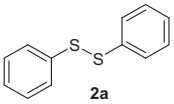
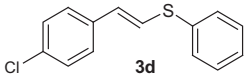
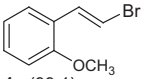
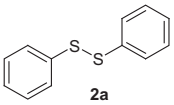
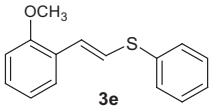
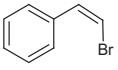
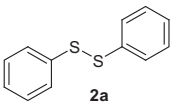
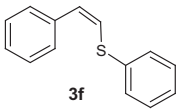
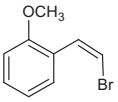
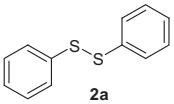
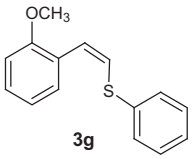
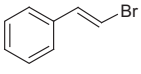
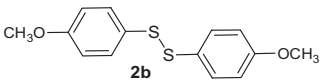
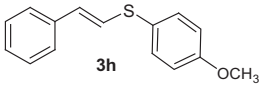
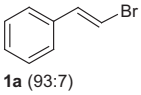
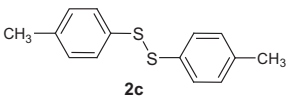
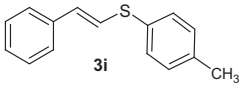
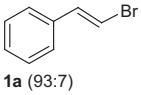
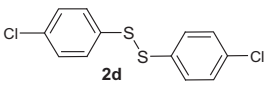
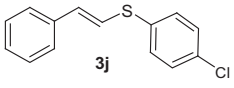
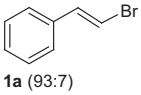
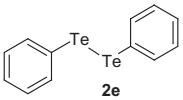
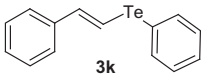
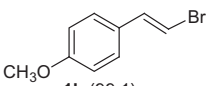
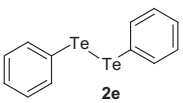
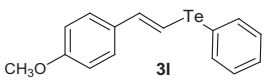
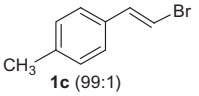
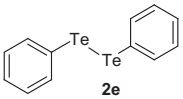
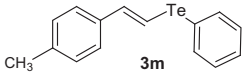


Entry	CuI (mol %)	Zinc (mmol)	Temp (°C)	Time (h)	Yield (%)
1	1	0.6	110	24	23
2	3	0.6	110	24	25
3	5	0.6	110	4	75
4	5	0.6	110	24	77
5	10	0.6	110	24	70
6	20	0.6	110	24	73
7	5	0.6	60	24	56
8	—	0.6	110	24	NR
9	5	—	110	24	42
10[b]	5	0.6	110	24	52
11	5	0.3	110	24	54
12	5[c]	0.6	110	24	25
13	5[d]	0.6	110	24	15
14	5[d]	—	110	24	6

[a] Reactions performed using (*E*)-β-bromostyrene **1a** (0.6 mmol), diphenyl disulfide **2a** (0.3 mmol), and glycerol (1.5 mL) under N_2 atmosphere.
[b] The reaction was performed in an open atmosphere.
[c] $CuCl_2$ was used as a catalyst.
[d] Copper powder was used as a catalyst.

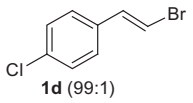
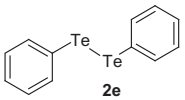
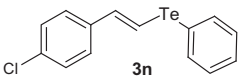
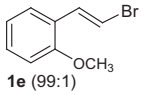
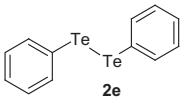
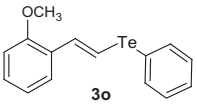
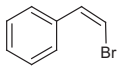
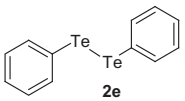
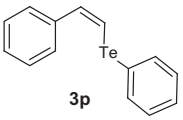
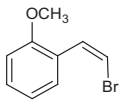
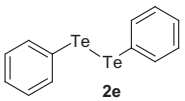
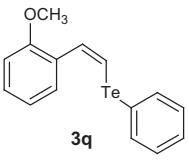
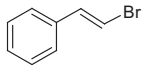
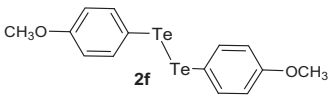
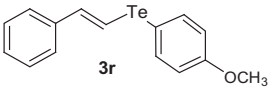
Table 2
Scope of the synthesis of vinyl sulfides **3a–j** and vinyl tellurides **3k–r**[a]



Entry	Vinyl bromide **1** (ratio *E*:*Z*)	Dichalcogenide **2**	Product **3**	Time (h)	Yield[b] (%)	Ratio[c] (*E*:*Z*)
1	 **1a** (93:7)	 **2a**	 **3a**	4	75	97:3
2	 **1b** (99:1)	 **2a**	 **3b**	2	85	100:0
3	 **1c** (99:1)	 **2a**	 **3c**	3	78	94:6
4	 **1d** (99:1)	 **2a**	 **3d**	3	70	99:1
5	 **1e** (99:1)	 **2a**	 **3e**	4	74	94:6
6	 **1f** (1:99)	 **2a**	 **3f**	6	70	0:100
7	 **1g** (36:64)	 **2a**	 **3g**	6	60	13:87
8	 **1a** (93:7)	 **2b**	 **3h**	24	62	100:0
9	 **1a** (93:7)	 **2c**	 **3i**	8	75	100:0
10	 **1a** (93:7)	 **2d**	 **3j**	24	60	85:15
11	 **1a** (93:7)	 **2e**	 **3k**	20	85	100:0
12	 **1b** (99:1)	 **2e**	 **3l**	4	89	99:1
13	 **1c** (99:1)	 **2e**	 **3m**	4	65	97:3

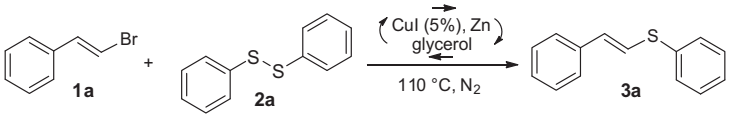
(*continued on next page*)

Table 2 (*continued*)

Entry	Vinyl bromide **1** (ratio *E*:*Z*)	Dichalcogenide **2**	Product **3**	Time (h)	Yield[b] (%)	Ratio[c] (*E*:*Z*)
14	 **1d** (99:1)	 **2e**	 **3n**	3	72	98:2
15	 **1e** (99:1)	 **2e**	 **3o**	24	75	96:4
16	 **1f** (1:99)	 **2e**	 **3p**	24	60	0:100
17	 **1g** (36:64)	 **2e**	 **3q**	24	67	24:76
18	 **1a** (93:7)	 **2f**	 **3r**	24	75	100:0

[a] Reactions performed in the presence of vinyl bromide **1a**–**g** (0.6 mmol), diaryl dichalcogenide **2a**–**f** (0.3 mmol), Zn dust (0.6 mmol), and 5 mol % of CuI in glycerol (1.5 mL).
[b] Yields are given for isolated products.
[c] Determined by GC/MS and by ^{1}H NMR of crude reaction products.

Table 3
Reuse of catalytic system CuI/Zn/glycerol

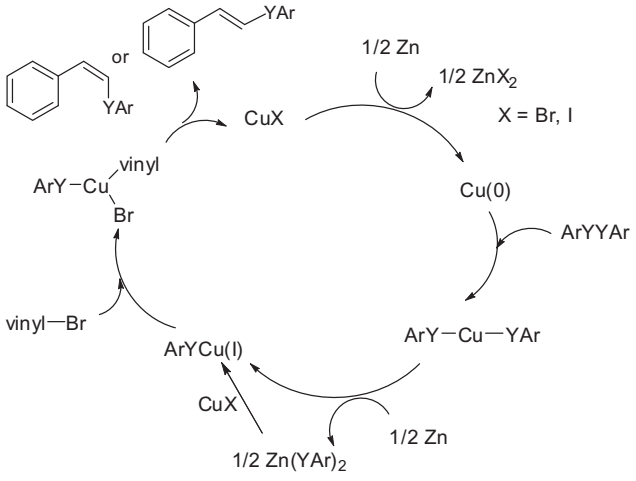


Cycle	Time	Yield of **3a**[a] (%)
1	4	75
2	4	73
3	4	72
4	4	70
5	4	64
6	24	56

[a] Yields are given for isolated products.

The upper organic phase was removed, the solvent evaporated and the product **3a** was isolated. The remaining inferior phase containing a mixture of CuI/Zn/glycerol was dried under vacuum and directly reused for further reactions, simply by adding more reagents **1a** and **2a**. (*E*)-β-(Phenylthio)styrene **3a** was obtained in 75%, 73%, 72%, and 70% yields after successive cycles showing a good level of efficiency. After four runs, the efficiency of catalytic system was reduced and the yields decreased in the fifth and sixth cycles (Table 3).[16]

We believe that a plausible mechanism of this reaction could involve the initial reduction of Cu(I) to Cu(0) by metal zinc; following, which Cu(0) undergoes an oxidative addition with diaryl dichalcogenide (ArYYAr) to form an intermediate, $(ArY)_2Cu(II)$ (Scheme 2). After reduction by Zn, this intermediate leads to ArY-Cu(I), which reacts with β-bromostyrene to give the respective β-(arylchalcogeno)styrene via a 'transitory' Cu(III) intermediate. The $Zn(YAr)_2$ formed after the reduction of $Cu(YAr)_2$ by Zn reacts with CuI to give more ArYCu(I), with both ArY moieties of ArYYAr being used in the overall reaction. A similar mechanism is believed to be involved in the Cu(0) nanoparticle-catalyzed cross couplings of vinyl bromides with diphenyl diselenide.[8d]



Scheme 2. Probable mechanism.

In conclusion, we have developed a mild and efficient method for the stereoselective synthesis of vinyl sulfides and vinyl tellurides in very good yields using a catalytic, recyclable, and eco-friendly system. The notable advantages offered by this method include stereoselectivity for *Z*- and *E*-styryl bromides, general applicability to a wide variety of substrates, and easy recovering and reusing of the catalytic system. These remarkable characteristics made this new protocol economically and eco-friendly attractive, inexpensive, and offering the possibility of performing the reaction in the absence of toxic organic solvents and heavy metals.

Acknowledgments

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14. *General procedure for the cross-coupling reaction:* The mixture of CuI (0.03 mmol, 5 mol %) and Zn dust (0.6 mmol) in glycerol (1.5 mL) was stirred under nitrogen atmosphere for 30 min at 110 °C. After that, the reaction vessel was cooled to room temperature and diaryl dichalcogenide **2** (0.3 mmol) and vinyl bromide **1** (0.6 mmol) were added. The reaction mixture was stirred at 110 °C and the reaction progress was followed by TLC. After the time indicated in Table 2, the solution was cooled to room temperature, diluted with ethyl acetate (20 mL), and washed with sat. NH_4Cl (3 × 20 mL). The organic layer was separated, dried over $MgSO_4$ and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using ethyl acetate/hexanes as eluent. Spectral data of the products prepared are listed below. *(E)-(styryl)(phenyl)sulfide* (***3a***).[8g] Yield: 0.095 g (75%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.39 (d, *J* = 7.6 Hz, 2H), 7.34–7.18 (m, 8H), 6.88 (d, *J* = 15.2 Hz, 1H), 6.69 (d, *J* = 15.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 135.1, 132.5, 131.7, 129.7, 129.3, 129.1, 128.6, 127.6, 127.5, 127.3, 126.9, 126.0, 123.3, 119.3. MS *m*/*z* (rel int.,%) 212 (100), 211 (48), 178 (40), 121 (38), 91 (19), 77 (31). *(E)-(4-methoxystyryl)(phenyl)sulfide* (***3b***).[8c] Yield: 0.123 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.43–7.37 (m, 2H), 7.33–7.13 (m, 5H), 6.87–6.78 (m, 2H), 6.69 (d, *J* = 15.4 Hz, 1H), 6.62 (d, *J* = 15.4 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 164.9, 159.3, 135.9, 132.7, 129.2, 129.0, 127.3, 126.5, 120.0, 114.1, 55.3. MS *m*/*z* (rel int.,%) 242 (70), 211 (26), 207 (36), 197 (35), 91 (31), 77 (100). *(E)-(4-methylstyryl)(phenyl)sulfide* (***3c***).[8g] Yield: 0.105 g (78%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.64–7.60 (m, 2H), 7.45–7.02 (m, 8H), 6.73 (d, *J* = 15.4 Hz, 1H), 6.64 (d, *J* = 15.4 Hz, 1H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.2, 121.8, 125.9, 126.7, 129.0, 129.4, 129.5, 132.4, 133.7, 135.6, 137.5. MS *m*/*z* (rel int.,%) 226 (61), 211 (40), 207 (24), 121 (31), 115 (62), 77 (68), 40 (100). *(E)-(4-chlorostyryl)(phenyl)sulfide* (***3d***).[8e] Yield: 0.103 g (70%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 6.51 (d, *J* = 15.6 Hz, 1H); 6.86 (d, *J* = 15.6 Hz, 1H); 7.23–7.43 (m, 9H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 124.6, 127.3, 127.2, 128.8, 129.2, 129.7, 130.2, 133.1, 134.7, 135.0. MS *m*/*z* (rel int.,%) 246 (18), 245 (6), 242 (100), 227 (20), 211 (36), 197 (51), 165 (43), 77 (32). *(E)-(2-methoxystyryl)(phenyl)sulfide* (***3e***).[17] Yield: 0.107 g (74%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.56–7.49 (m, 3H); 7.41–7.36 (m, 6H); 6.82 (d, *J* = 15.5 Hz, 1H); 6.69 (d, *J* = 15.5 Hz, 1H); 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 138.3, 138.9, 135.9, 135.5, 133.6, 133.1, 132.8, 132.5, 129.8, 129.4, 127.7, 124.1, 55.3. MS *m*/*z* (rel int.,%) 242 (16), 210 (100), 195 (19), 120 (22), 109 (12), 77 (21). *(Z)-(styryl)(phenyl)sulfide* (***3f***).[8c] Yield: 0.089 g (70%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.58–7.46 (m, 2H); 7.44–7.24 (m, 8H); 6.63 (d, *J* = 10.4 Hz, 1H); 6.53 (d, *J* = 10.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 136.5, 135.2, 125.9, 132.9, 131.7, 130.0, 129.8, 129.1, 128.6, 127.6, 123.3. MS *m*/*z* (rel int.,%) 212 (100), 211 (51), 179 (30), 121 (46), 91 (25), 77 (44). *(Z)-(2-methoxystyryl)(phenyl)sulfide* (***3g***).[18] Yield: 0.087 g (60%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.66–7.54 (m, 3H); 7.49–7.28 (m, 6H); 6.77 (d, *J* = 10.3 Hz, 1H); 6.52 (d, *J* = 10.3 Hz, 1H); 3.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 136.4, 130.4, 129.7, 129.0, 128.7, 128.2, 126.8, 125.9, 125.6, 122.6, 120.4, 117. 9, 55.4. MS *m*/*z* (rel int.,%) 242 (100), 241 (14), 211 (31), 194 (24), 118 (57), 109 (21), 77 (33). *(E)-(styryl)(4-methoxy-phenyl)sulfide* (***3h***).[8g] Yield: 0.090 g (62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.43 (d, *J* = 8.2 Hz, 2H), 7.29–7.34 (m, 4H), 6.76–6.82 (m, 3H), 6.73 (d, *J* = 15.4 Hz, 1H), 6.41 (d, *J* = 15.4 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 136.7, 133.4, 132.9, 128.9, 128.6, 128.2, 127.1, 125.6, 125.7, 114.8, 55.3. MS *m*/*z* (rel int.,%) 242 (100), 241 (22), 211 (30), 194 (16), 165 (36), 91 (19), 77 (40). *(E)-(styryl)(4-methyl-phenyl)sulfide* (***3i***).[8g] Yield: 0.102 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.44–7.49 (m, 3H), 7.34–7.07 (m, 6H), 6.78 (d, *J* = 15.5 Hz, 1H), 6.57 (d, *J* = 15.5 Hz, 1H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 137.3, 132.7, 130.6, 129.9, 128.7, 128.6, 128.3, 127.4, 125.9, 124.4, 21.0. MS *m*/*z* (rel int.,%) 226 (100), 225 (21), 211 (58), 178 (38), 91 (31), 77 (30). *(E)-(styryl)(4-chloro-phenyl)sulfide* (***3j***).[8g] Yield: 0.088 g (60%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.58–7.52 (m, 4H), 7.44–7.27 (m, 9H), 6.85 (d, *J* = 15.4 Hz, 1H), 6.76 (d, *J* = 15.4 Hz, 1H) ^{13}C NMR ($CDCl_3$,100 MHz) δ = 140.5, 140.4, 135.2, 133.8, 132.9, 132.1, 130.9, 129.2, 128.7, 127.3, 126.8, 126.4, 122.5. MS *m*/*z* (rel int.,%) 246 (100), 245 (25), 210 (27), 201 (30), 178 (64), 121 (27), 77 (54). *(E)-(styryl)(phenyl)telluride* (***3k***).[19] Yield: 0.158 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.82–7.66 (m, 2H), 7.55 (d, *J* = 16.6 Hz, 1H), 7.37–7.18 (m, 8H), 7.10 (d, *J* = 16.6 Hz, 1H. ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 143.3, 138.0, 137.8, 129.5, 129.3, 128.6, 127.8, 127.7, 126.1, 101.5. MS *m*/*z* (rel int.,%) 310 (25), 308 (24), 207 (5), 180 (100), 103 (42), 77 (17). *(E)-(4-methoxystyryl)(phenyl)telluride* (***3l***).[20] Yield: 0.181 g (89%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.80–7.68 (m, 2H); 7.49 (d, *J* = 16.4 Hz, 1H); 7.29–7.15 (m, 7H); 7.12 (d, *J* = 16.6 Hz, 1H); 3.78 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 155.2, 148.6, 139.8, 137.4, 127.8, 127.5, 126.7, 126.3, 125.8, 113.4, 55.2. MS *m*/*z* (rel int.,%) 340 (10), 307 (23), 231 (32), 205 (100), 129 (28), 108 (16), 77 (42). *(E)-(4-methylstyryl)(phenyl)telluride* (***3m***).[8e] Yield: 0.126 g (65%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 2.32 (s, 3H), 7.08–7.14 (m, 3H), 7.16–7.30 (m, 5H), 7.47 (d, *J* = 16.6 Hz, 1H), 7.67–7.70 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 21.2, 99.7, 113.7, 126.1, 127.8, 129.3, 129.5, 135.5, 137.6, 138.0, 143.8. MS *m*/*z* (rel int.,%) 324 (5), 284 (12), 207 (24), 194 (30), 154 (39), 115 (17), 77 (100). *(E)-(4-chlorostyryl)(phenyl)telluride* (***3n***).[8e] Yield: 0.148 g (72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 6.98 (d, *J* = 16.4 Hz, 1H); 7.51 (d, *J* = 16.4 Hz, 1H); 7.15–7.32 (m, 7H); 7.67–7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 102.8, 113.1, 1 27.2, 128.1, 128.7, 129.5, 133.4, 136.5, 138.1, 141.1. MS *m*/*z* (rel int.,%) 343 (9), 276 (15), 234 (14), 206 (21), 188 (37), 135 (30), 112 (100), 77 (11). *(E)-(2-methoxystyryl)(phenyl)telluride* (***3o***). Yield:

0.153 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.62–7.54 (m, 2H); 7.38–7.29 (m, 6H); 7.19 (d, *J* = 16.6 Hz, 1H); 7.12 (d, *J* = 16.6 Hz, 1H); 3.76 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 55.2, 103.4, 112.9, 113.2, 124.1, 127.9, 138.4, 138.7, 150.5, 150.9. MS *m*/*z* (rel int.,%) 342 (14), 340 (7), 234 (26), 209 (100), 207 (21), 160 (19), 116 (23), 109 (15), 77 (49). *(Z)-(styryl)(phenyl)telluride (**3p**).*[8e] Yield: 0.112 g (60%). ^{1}H NMR ($CDCl_3$, 200 MHz) δ = 7.06 (d, *J* = 10.6 Hz, 1H); 7.43 (d, *J* = 10.6 Hz, 1H); 7.13–7.37 (m, 8H); 7.70–7.75 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz) δ = 109.2, 115.3, 127.3, 127.4, 128.0, 128.4, 129.3, 136.8, 137.9, 138.8. MS *m*/*z* (rel int.,%) 310 (17), 306 (22), 231 (35), 204 (27), 173 (32), 107 (18), 77 (100). *(Z)-(2-methoxystyryl)(phenyl)telluride (**3q**).* Yield: 0.136 g (67%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.59–7.53 (m, 3H); 7.36–7.25 (m, 6H); 7.21 (d, *J* = 10.6 Hz, 1H); 7.10 (d, *J* = 10.6 Hz, 1H); 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 55.17, 104.6, 110. 29, 114.23, 126.01, 127.89, 138.91, 141.55, 150.15, 158.97. MS *m*/*z* (rel int.,%) 340 (7), 309 (21), 210 (100), 206 (11), 157 (17), 124 (33), 109 (18), 77 (21). *(E)-(styryl)(4-methoxy-phenyl)telluride (**3r**).*[19] Yield: 0.153 g (75%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 3.77 (s, 3H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 16.6 Hz, 1H), 7.24–7.29 (m, 5H), 7.48 (d, *J* = 16.6 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 55.1, 102.7, 110.2, 115.5, 126.0, 127.6, 128.5, 140.7, 140.8, 141.3, 160.0. MS *m*/*z* (rel int.,%) 340 (10), 214 (100), 199 (91), 171 (31), 128 (13), 107 (9), 77 (10).

15. For examples of vinyl tellurides as key intermediates in total organic synthesis, see: (a) Oliveira, J. M.; Zeni, G.; Malvestiti, I.; Menezes, P. H. *Tetrahedron Lett.* **2006**, *47*, 8183; (b) Alves, D.; Nogueira, C. W.; Zeni, G. *Tetrahedron Lett.* **2005**, *46*, 8761; (c) Stefani, H. A.; Costa, I. M.; Zeni, G. *Tetrahedron Lett.* **1999**, *40*, 9215; (d) Bassora, B. K.; Da Costa, C. E.; Gariani, R. A.; Comasseto, J. V.; Dos Santos, A. A. *Tetrahedron Lett.* **2007**, *48*, 1485; (e) Diego, D. G.; Cunha, R. L. O. R.; Comasseto, J. V. *Tetrahedron Lett.* **2006**, *47*, 7147; (f) Ferrarini, R. S.; Dos Santos, A. A.; Comasseto, J. V. *Tetrahedron Lett.* **2010**, *51*, 6843; (g) Oliveira, R. A.; Oliveira, J. M.; Rahmeier, L. H. S.; Comasseto, J. V.; Menezes, P. H. *Tetrahedron Lett.* **2008**, *49*, 5759.
16. *Recycle of catalytic system:* The aforementioned procedure[14] was used with (*E*)-β-bromostyrene **1a** (0.6 mmol), diphenyl disulfide **2a** (0.3 mmol), CuI (5 mol %), zinc dust (0.6 mmol), and glycerol (1.5 mL). After the reaction was complete (followed by TLC), the reaction mixture was washed with a mixture of hexane/ethyl acetate (95:5) (3× 3 mL) and the upper organic phases were separated from the glycerol one. The product was isolated according to the procedure above. The resulting glycerol phase was dried under vacuum and reused for further reactions without previous purification, simply by adding more reagents **1a** and **2a**.
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