Alkyne-Based, Highly Stereo- and Regioselective Synthesis of Stereodefined Functionalized Vinyl Tellurides

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(*Z*)-*β*-Aryltellurovinylphosphonates and (*Z*)-*β*-aryltellurovinyl sulfones were synthesized via the highly stereoselective *anti*-hydrotelluration of 1-alkynylphosphonates and 1-alkynyl sulfones. The configurations of these compounds were characterized via ^{1}H NMR spectra or NOESY experiments and by X-ray diffraction analysis; (*E*)-*β*-aryltellurovinyl sulfones were obtained with the reaction of sodium aryltellurate with (*E*)-2-iodovinyl sulfones to confirm the stereochemistry of the above *anti*-hydrotelluration. When the tandem reaction of alkynes with diaryl ditellurides and sodium arylsulfinates was carried out in AcOH/H_2O (4/1), the corresponding (*E*)-*β*-aryltellurovinyl sulfones were obtained in *one step* in good yields. This reaction is highly regio- and stereoselective and proceeds by using arylsulfinate as the sulfonyl radical precursor and diaryl ditellurides as free radical acceptors. (*E*)-1-Iodo-2-aryltelluroalkenes can be obtained by the *anti*-addition of ArTeI with terminal alkynes in THF. The stereochemistry of compound **17b** was also determined by X-ray diffraction analysis.

Introduction

Stereoselective synthesis of substituted alkenes has drawn a lot of attention in organic synthesis. Stereo- and regioselecitve addition of organic reagents to alkynes is one of the most efficient routes to stereodefined alkenes (Figure 1).

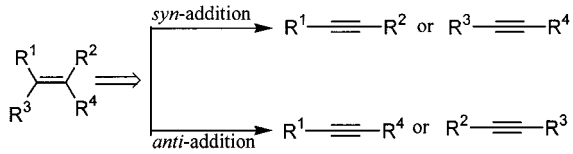

Figure 1.

Vinyl tellurides are important synthetic intermediates because of their ready transformation to other organic compounds with retention of configuration,[1] e.g., transmetalations to form their corresponding vinyllithium,[2] copper,[3] zinc,[4] magnesium,[5] calcium,[5] and sodium reagents[5] and their subsequent cross-coupling reaction to form stereodefined substituted alkenes.[6] Recently the synthesis of metal- or heteroatom-substituted vinyl tellurides has received intensive attention because of their application in carbon−carbon or carbon-heteroatom bond formation reactions affording polyfunctionalized olefines. Although the preparation of α-heteroatom-substituted vinyl tellurides **1** and **2** have been extensively studied,[1b,e,7] there are only a few reports on the synthesis of **3**- and

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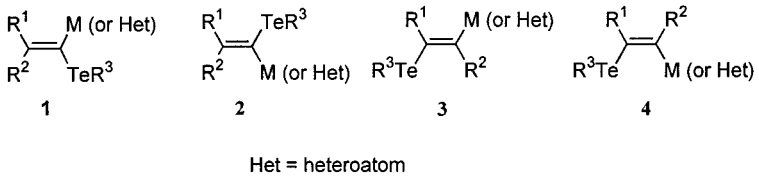
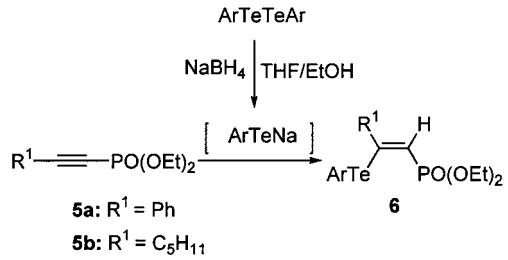


Figure 2.

Scheme 1



4-type of highly β-functionalized vinylic tellurides[2f,8,9] (Figure 2).

As a part of our ongoing study aimed at the synthesis and application of bifunctionalized vinyl tellurides,[7h,9a−c] we report herein the stereo- and regioselective synthesis of vinyltellurides containing sulfonyl, phosphonyl, and iodo groups via the stereo- and regiodefined addition of organic tellurides with alkynes.

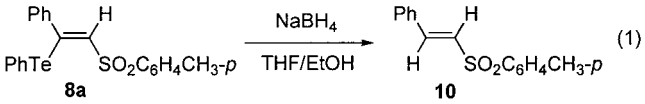
Results and Discussion

Highly Stereo- and Regioselective *Anti*-Hydrotelluration of 1-Alkynylphosphonates and 1-Alkynyl Sulfones. Hydrotelluration of acetylenes is a widely used method for the synthesis of vinyl tellurides. In the case of addition to acetylenes bearing electron-withdrawing groups such as acetylenic aldehydes, ketones, carboxylic acids, and esters, β-carbonylvinyl tellurides with *Z*-configuration can be obtained.[10] As our work was initiated, there was no report on the hydrotelluration of 1-alkynyl sulfones and 1-alkynylphosphonates. First, we investigated the reaction of 1-alkynylphosphonate **5a** (R^1 = Ph) with PhTeNa (prepared by the reduction of ditelluride with $NaBH_4$) in THF/EtOH (1/1) at room temperature (monitored by TLC). This reaction afforded *anti*-hydrotelluration product, i.e., *Z*-2-phenyltellurovinylphosphonate **6c**, stereo- and regioselectively as determined by the ^{1}H NMR spectrum of the crude product. Other substrates gave the same results (Scheme 1 and Table 1).

The structures of these compounds were affirmatively characterized via ^{1}H NMR spectra or NOESY experiments (*Z*-**6a** and *Z*-**6e**) and by X-ray diffraction analysis of compound **6a** to be in *Z*-configuration. In all cases, the attack of sodium tellurate on alkynes occurred at the β-position exclusively.

When the reaction of 1-alkynyl sulfones with ArTeNa was carried out at room temperature for 20 min, the *Z*-2-aryltelluro-1-alkenyl sulfones (**8**) were obtained in good yields (Scheme 2 and Table 1). No isomeric compounds were obtained as determined by the ^{1}H NMR spectra of the crude products. The *Z*-configurations of these compounds were characterized via the coupling constant of vinyl protons (J = 8.69 Hz) of compound **9a** and the NOE experiments for compounds **8b** and **9b**. The correlations between the vinyl hydrogen and aryl proton in **8b** or the vinyl hydrogen and allylic hydrogen in **9b** indicated that the vinyl hydrogen is situated close to those groups (*cis* relation) (Figure 3).

However, when the reaction mixture was stirred for a longer time (overnight), **8a** was easily converted to (*E*)-2-phenylvinyl sulfone **10** in 76% yield via reductive detelluration (eq 1).



To further confirm the stereochemistry of the hydrotelluration of 1-alkynyl sulfones **7**, we developed a way to reach *E*-2-aryltelluryl-1-alkenyl sulfones by the reaction of *E*-2-iodo-1-alkenyl sulfones with sodium aryltellurates in THF/EtOH at 0 °C. In all cases studied, only the *E*-isomers (Scheme 3 and Table 2), which were characterized by IR, MS, and ^{1}H and ^{13}C NMR spectroscopy and comparison with the corresponding *Z*-isomers, were obtained.

On the other hand, for compound *E*-**13f**, there was no NOE correlation between the vinyl proton (6.73 ppm) and the allylic hydrogen (3.55−3.58 ppm). NOE correlation between the vinyl proton and aryl proton of the aryltellurium group was observed. This indicated that vinyl proton situated close to aryltellurium group (*trans* relation) (compare with compound *Z*-**9b**) (Figure 3).

***Anti*-Tellurosulfonation of 1-Alkynes.** It was reported that arylselenovinyl sulfones can be prepared conveniently from the selenosulfonation of alkynes with $PhSeSO_2Ar$.[11] We have developed here the stereo- and regioselective synthesis of *E*-2-aryltelluryl-1-alkenyl sulfones **12** by the tellurosulfonation reaction of alkynes with ArTeTeAr and sodium arylsulfinates in $AcOH/H_2O$ at 80 °C. The results of the reaction of alkynes (1.1 mmol) with diaryl ditellurides (0.5 mmol) and $ArSO_2Na$ (5 mmol) in $AcOH/H_2O$ at 80 °C are shown in Table 3. With R = aryl, the reaction finished within 5 h, while with R = alkyl, the reaction was slower and finished within 24 h (Scheme 4). The reaction of trimethylsilylacetylene with PhTeTePh and sodium arylsulfinate in $AcOH/H_2O$ for 48

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Table 1. Synthesis of *Z*-2-aryltelluro-1-alkenylphosphonates 6a−f, *Z*-2-aryltelluro-1-alkenyl sulfones 8a,b, or Dibromides 9a,b

entries	R^1	E	Ar	reaction conditon	product: yield (%)
1	C_6H_5	$PO(OEt)_2$	4-CH_3-C_6H_4	rt, overnight	*Z*-**6a**: 59[a]
2	C_6H_5	$PO(OEt)_2$	4-Cl-C_6H_4	rt, overnight	*Z*-**6b**: 63[a]
3	C_6H_5	$PO(OEt)_2$	C_6H_5	rt, overnight	*Z*-**6c**: 61[a]
4	C_6H_5	$PO(OEt)_2$	4-F-C_6H_4	rt, overnight	*Z*-**6d**: 67[a]
5	C_5H_{11}	$PO(OEt)_2$	4-CH_3-C_6H_4	rt, overnight	*Z*-**6e**: 57[a]
6	C_5H_{11}	$PO(OEt)_2$	4-F-C_6H_4	rt, overnight	*Z*-**6f**: 59[a]
7	Ph	4-CH_3-$C_6H_4SO_2$	Ph	rt, 20 min	*Z*-**8a**: 74[b]
8	Ph	4-CH_3-$C_6H_4SO_2$	4-F-C_6H_4	rt, 20 min	*Z*-**8b**: 75[b]
9	H	4-CH_3-$C_6H_4SO_2$	Ph	rt, 20 min	*Z*-**9a**: 82[c]
10	C_6H_{13}	4-CH_3-$C_6H_4SO_2$	Ph	rt, 20 min	*Z*-**9b**: 71[c]

[a] Isolated by preparative TLC eluted with AcOEt/hexanes = 1/5. [b] Isolated by chromatography eluted with AcOEt/hexanes = 1/10. [c] Isolated by recrystallization with $HCCl_3/CH_3OH$.

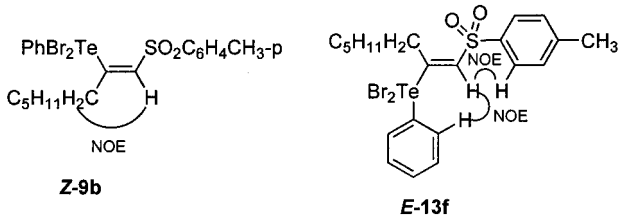
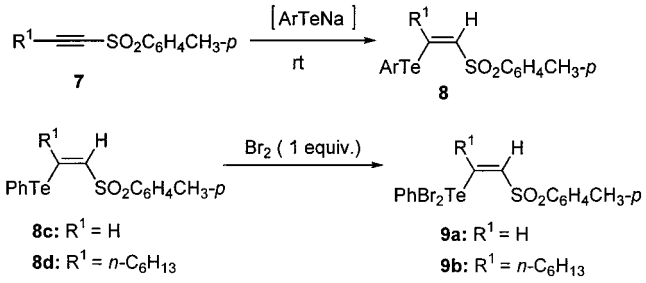
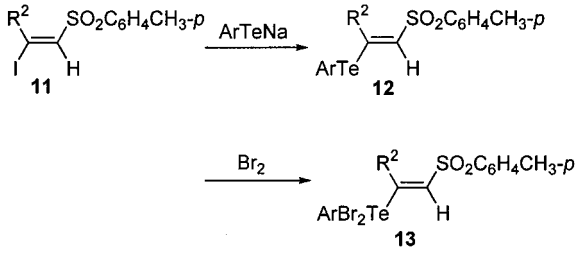


Figure 3.

Scheme 2



Scheme 3



h produced the desilylated *E*-2-phenyltelluro-1-alkenyl sulfone (**12k**) (J = 15.82 Hz)[12] in 26% yield after a workup with aqueous sodium bicarbonate followed by chromatography on silica gel (see Scheme 5 and entry **26**, Table 3). The *Z*-isomer was not obtained. The configurations of other compounds were determined by ^{1}H NMR, IR, and MS spectroscopy and comparison with the products which were obtained by the reaction of *E*-2-iodo-1-alkenyl sulfones with sodium aryltellurates. No significant amounts of stereoisomers of the above products could be isolated.

Recent reports have shown sulfonyl radical can be generated from sodium arylsulfinate in aqueous acetic acid.[13] A plausible mechanism for the formation of *E*-2-aryltelluro-1-alkenyl sulfones **12** is the regiospecific addition of a sulfonyl radical to the alkyne to form the 2-sulfonylvinyl radical intermediates **14** and **15**,[11a] further reaction of **14** with diaryl ditelluride produces products **12** highly stereoselectively probably due to the bigger steric interaction of SO_2Ar^1 in **15** with the approaching ArTeTeAr (Scheme 6). [14]

***Anti*-Addition of ArTeI with 1-Alkynes.** Recent reports by our group and others have shown that the

Table 2. Stereoselective Synthesis of *E*-2-Aryltelluro-1-alkenyl Sulfone 12g and Dibromides 13a−f (method A)

entry	R	Ar	product:[a] yield (%)
11	C_4H_9	C_6H_5	*E*-**13a:** 72[c]
12	C_4H_9	4-FC_6H_4	*E*-**13b**: 71[c]
13	C_5H_{11}	C_6H_5	*E*-**13c**: 64[c]
14	C_5H_{11}	4-FC_6H_4	*E*-**13d**: 63[c]
15	C_6H_{13}	C_6H_5	*E*-**13e**: 57[c]
16	C_6H_{13}	4-FC_6H_4	*E*-**13f**: 62[c]
17	C_6H_5	C_6H_5	*E*-**12g:** 63[b]

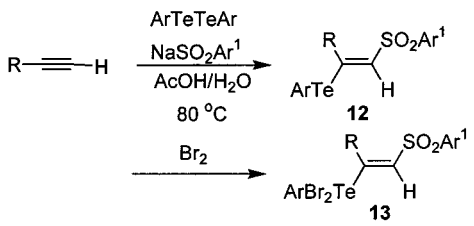
[a] Reaction conditions: 0 °C, 20 min. [b] Isolated yields by chromatography on silica gel eluted with AcOEt/hexanes = 1/10. [c] The yield of dibromotelluryl compounds by recrystallization from $HCCl_3/CH_3OH$.

Table 3. Synthesis of *E*-2-aryltelluro-1-alkenyl sulfones 12g, 12h, and 12k or Dibromides 13 from Tellurosulfonation of 1-Alkynes (method B)

entry	R	Ar	Ar′	reaction time (h)	product: yield[a](%)
18	C_4H_9	C_6H_5	4-CH_3-C_6H_4	24	*E*-**13a**: 55
19	C_5H_{11}	C_6H_5	4-CH_3-C_6H_4	24	*E*-**13c**: 70
20	C_5H_{11}	4-F-C_6H_4	4-CH_3-C_6H_4	24	*E*-**13d**: 53
21	C_6H_{13}	C_6H_5	4-CH_3-C_6H_4	24	*E*-**13e**: 68
22	C_6H_5	C_6H_5	4-CH_3-C_6H_4	5	*E*-**12g**: 74
23	C_6H_5	C_6H_5	4-Cl-C_6H_4	2	*E*-**12h**: 85
24	C_4H_9	C_6H_5	C_6H_5	24	*E*-**13i**: 51
25	C_6H_{13}	C_6H_5	C_6H_5	24	*E*-**13j**: 61
26	Me_{3Si}	C_6H_5	4-CH_3-C_6H_4	48	*E*-**12k**: 26[b]

[a] Isolated yield based on ArTeTeAr. [b] The yield of desilylated product.

Scheme 4



(12) Desilylation reaction of a vinylsilane with a similar structure in HOAc was known; see: Ohnuma, T.; Heta, N.; Fujiwara, H.; Ban, Y. *J. Org. Chem.* **1982**, *47*, 4713.

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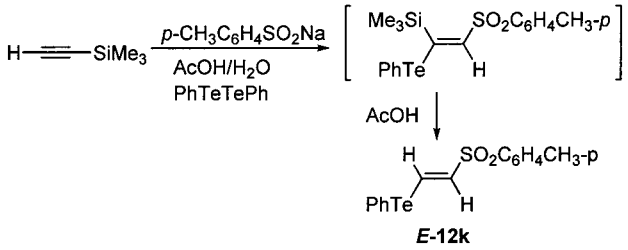
Scheme 5



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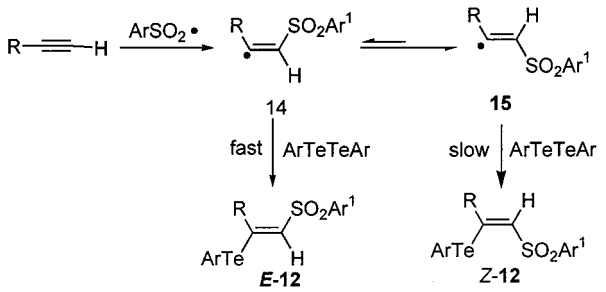

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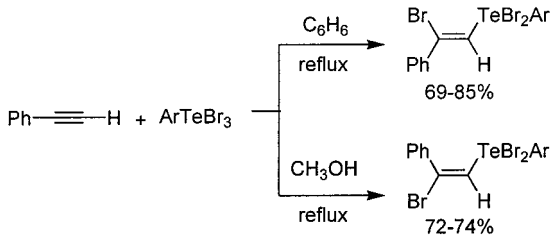
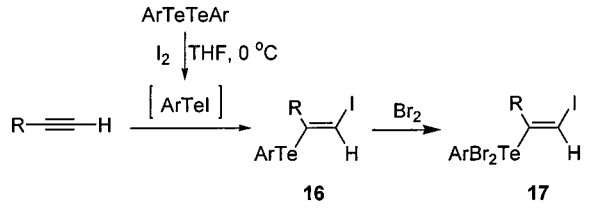


Scheme 8



addition reaction of alkynes with $ArTeX_3$ (X = Cl, Br) occurred stereo- and regioselectively. We have found the reaction of aryltellurim tribromides with alkynes gave *E*- or *Z*-2-bromovinyl aryl tellurium dibromides, depending on the solvents used.[9a] Further studies involve their application to the synthesis of polysubstituted alkenes (Scheme 7).[9a,b]

It was also been reported that aryltelluryl iodides can react as good electrophilic reagents with alkenes[15] or alkynylboronates.[16] All these promoted us to examine the reaction of aryltelluryl iodides with alkynes. It was found that aryltelluryl iodides reacted stereo- and regioselectively with alkynes in THF to afford *E*-1-iodo-2-aryltelluro-1-alkenes **16**, which can react with Br_2 to give the more stable dibromotellurides **17** with the retention of the configuration (Scheme 8 and Table 4). The structure of product **17b** was clearly established by an X-ray diffraction analysis. Reaction of aryltelluryl iodides with alkynes in benzene and CH_2Cl_2 was not clean.

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Table 4. Synthesis of (2-Iodo-1-alkyl)vinyl Aryl Tellurium Dibromides 17a−f

entry	Ar	R	product:[a,b] (yield%)
27	C_6H_5	C_4H_9	*E*-**17a**: 45
28	4-Cl-C_6H_4	C_4H_9	*E*-**17b**: 53
29	C_6H_5	C_5H_{11}	*E*-**17c**: 48
30	4-Cl-C_6H_4	C_5H_{11}	*E*-**17d**: 51
31	C_6H_5	C_6H_{13}	*E*-**17e**: 37
32	4-Cl-C_6H_4	C_6H_{13}	*E*-**17f**: 43

[a] Reaction conditions: the reaction was carried out using ArTeTeAr (0.5 mmol), I_2 (0.55 mmol), and alkyne (1 mmol) in THF at room temperature for 24 h. [b] Isolated yields by recrystallization from $HCCl_3/CH_3OH$.

Conclusion

Anti-hydrotelluration of 1-alkynyl sulfones or 1-alkynylphosphonates afforded *Z*-2-aryltelluro-1-alkenyl sulfone or phosphonates exclusively; *E*-2-Aryltelluro-1-alkenyl sulfones were obtained by the reaction of aryltellurol with *E*-2-iodo-1-alkenyl sulfones. When the reaction of alkynes with diaryl ditelluride and sodium arylsulfinate was carried in $AcOH/H_2O$ (4:1), the corresponding *E*-2-aryltelluro-1-alkenyl sulfones were obtained in good yields stereo- and regioselectively. ArTeI reacted with alkynes in THF to afford *E*-1-iodo-2-aryltelluroalkenes stereo- and regioselectively. Since vinyl sulfones,[17] vinylphosphonates,[18] and vinyl iodides[19] are important intermediates in organic synthesis, we envisaged that these three classes of compounds are intermediates of synthetic importance with the combination of the well-known chemical reactivity of the carbon−tellurium bonds.

Experimental Section

General. ^1H NMR spectra were recorded on a 400 or 500 MHz spectrometer and all ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using $CDCl_3$ as the solvent. Diaryl ditellurides,[10a] 1-alkynyl sulfones,[20] 1-alkynylphosphonates,[21] and *E*-2-iodovinylsulfonates[22] were prepared by the methods reported in the literature.

***Anti*-Hydrotelluration of 1-Alkynylphosphonates with ArTeNa.** To a solution of diaryl ditelluride (0.5 mmol) in (1/1) (V/V) THF/EtOH (5 mL) under N_2 was added sodium borohydride (1.2 mmol) in EtOH dropwise until the characteristic dark-red color of the ditelluride faded. Then 1-alkynylphosphonate (1 mmol) in THF (2 mL) was added, and the resulting solution was stirred overnight at room temperature, quenched with saturated aqueous NH_4Cl, and extracted with CH_2Cl_2. The organic phase was dried over sodium sulfate and concentrated under vacuum. The residue was purified by preparative TLC on silica gel (eluent: AcOEt:hexanes = 1:5) to give compounds **6a**−**f**.

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(*Z*)-1-(Diethoxyphosphonyl)-2-(4-methylphenyltelluryl)-2-phenylethene (6a): yield 0.27 g (59%); mp 95−96 °C; ν (KBr)/cm^{-1}: 3060, 2985, 2810, 1650, 1560, 1490, 1450, 1400, 1235, 840, 700, 610 cm^{-1}; δ_H (400 MHz) 7.28−7.30 (d, J = 7.9, 2H), 6.98 (m, 5H), 6.40−6.72 (d, J = 17.3, 1H), 4.16−4.23 (m, 4H), 2.19 (s, 3H), 1.37−1.41 (m, 6H); ^{13}C NMR δ 153.72 (d, $^2J_{P-C}$ = 7.7 Hz), 142.94 (d, $^3J_{P-C}$ = 24.6 Hz), 140.58, 137.83, 129.43, 127.74 (d, $^4J_{P-C}$ = 1 Hz), 127.53, 127.37, 119.97 (d, $^1J_{P-C}$ = 189.9 Hz), 114.01, 62.21 (d, $^2J_{P-C}$ = 5 Hz), 21.26, 16.56 (d, $^3J_{P-C}$ = 6.1 Hz); MS (EI) *m*/*z*: 460 (M$^+$, 38.22), 369 (5.45), 239 (42.74), 195 (68.29), 183 (36.13), 167 (100), 109 (46.26), 91 (49.99); (Found: C, 49.66; H, 4.98. Calcd for $C_{19}H_{23}O_3PTe$: C, 49.83; H 5.06%).

(*Z*)-1-(Diethoxyphosphonyl)-2-(4-chlorophenyltelluryl)-2-phenylethene (6b): yield 0.30 g (63%); mp 54−55 °C; ν (KBr)/cm^{-1} 3070, 2987, 1570, 1500, 1450, 1400, 1225, 1013, 835, 690, 610 cm^{-1}; δ_H (400 MHz) 6.83−7.43 (m, 9H), 6.23−6.53 (d, J = 17.1, 1H), 4.02−4.41 (m, 4H), 1.21−1.43 (m, 6H); ^{13}C NMR δ 153.46 (d, $^2J_{P-C}$=7.6 Hz), 142.54 (d, $^3J_{P-C}$ =24.5 Hz), 141.83, 128.72, 127.84, 127.69 (d, $^4J_{P-C}$ = 1.3 Hz), 127.54, 120.02 (d, $^1J_{PC}$ = 189.2 Hz), 115.99, 62.31 (d, $^2J_{P-C}$ = 5.2 Hz), 16.54 (d, $^3J_{P-C}$ = 6.2 Hz); MS (EI) *m*/*z*: 480 (M$^+$, 20.83), 367 (6.48), 239 (47.61), 195 (78.72), 167 (100), 109 (47.61), 81 (33.63); (Found: C, 45.07; H, 4.13. Calcd for $C_{18}H_{20}ClO_3PTe$: C, 45.19; H 4.21%).

(*Z*)-1-(Diethoxyphosphonyl)-2-(phenyltelluryl)-2-phenylethene (6c): yield 0.27 g (61%); mp 29−30 °C; ν (KBr)/cm^{-1}: 3100, 2985, 1560, 1480, 1450, 1400, 1230, 1020, 830, 690, 610 cm^{-1}; δ_H (400 MHz) 7.40−7.42 (m, 2H), 6.89−7.08 (m, 8H), 6.38−6.42 (d, J = 17.1, 1H), 4.16−4.23 (m, 4H), 1.38−1.41 (m, 6H); ^{13}C NMR δ 153.56 (d, $^2J_{P-C}$ = 7.7 Hz), 142.63 (d, $^3J_{P-C}$ = 24.5 Hz), 140.42, 128.38, 127.68, 127.62 (d, $^4J_{P-C}$ = 1.1 Hz), 127.50, 127.28, 119.83 (d, $^1J_{P-C}$ = 189.7 Hz), 117.91, 62.13 (d, $^2J_{P-C}$ = 5.1 Hz), 16.46 (d, $^3J_{PC}$ = 6.3 Hz); MS (EI) *m*/*z*: 446 (M$^+$, 40.94), 369 (12.24), 239 (44.68), 195 (69.72), 167 (100), 109 (43.34), 77 (35.94); (Found: C, 48.77; H, 4.73. Calcd for $C_{18}H_{21}O_3PTe$: C, 48.70; H 4.77%).

(*Z*)-1-(Diethoxyphosphonyl)-2-(4-fluorophenyltelluryl)-2-phenylethene (6d): yield 0.31 g (67%); mp 39−40 °C; ν (KBr)/cm^{-1}: 3080, 2987, 1580, 1480, 1230, 1030, 830, 695, 600; δ_H (400 MHz) 7.35−7.38 (m 2H), 6.92−7.0 (m, 5H), 6.58−6.62 (m, 2H), 6.37−6.41 (d, J = 17.2, 1H), 4.17−4.21 (m, 4H), 1.38−1.41 (m, 6H); ^{13}C NMR δ 162.74 (d, $^1J_{F-C}$ = 247 Hz), 153.69 (d, $^2J_{P-C}$ = 7.5 Hz), 142.73 (d, $^3J_{F-C}$ = 7.6 Hz), 142.52 (d, $^3J_{P-C}$ = 24.6 Hz), 127.63, 127.57 (d, $^4J_{P-C}$ = 1.3 Hz), 127.41, 119.77 (d, $^1J_{P-C}$ = 189.4 Hz), 115.81 (d, $^2J_{F-C}$ = 20.6 Hz), 112.49 (d, $^4J_{F-C}$ = 3.8 Hz), 62.23 (d, $^2J_{P-C}$ = 5.3 Hz), 16.49 (d, $^3J_{P-C}$ = 6 Hz); MS (EI) *m*/*z*: 464 (M$^+$, 37.78), 369 (10.57), 239 (47.43), 195 (75.99), 183 (36.03), 167 (100), 109 (46.73) 91 (49.99); (Found: C, 46.56; H, 4.43. Calcd for $C_{18}H_{20}FO_3PTe$: C, 46.80; H 4.36%).

(*Z*)-1-(Diethoxyphosphonato)-2-(4-methylphenyltelluryl)-1-heptene (6e): yield 0.26 g (57%); oil; ν (film)/cm^{-1} 3030, 2950, 1570, 1500, 1465, 1400, 1235, 1040, 960, 800; δ_H (400 MHz) 7.78−7.80 (m, 2H), 7.05−7.07 (m, 2H), 6.21−6.26 (d, J = 16.74, 1H), 4.08−4.13 (m, 4H), 2.36 (s, 3H), 2.17−2.20 (t, J = 7.84, 2H), 1.31−1.36 (m, 8H), 1.08−1.10 (m, 2H), 0.96−0.98 (m, 2H), 0.74−0.78 (t, J = 7.19, 3H); MS (EI) *m*/*z*: 454 (M$^+$, 28.33), 363 (9.65), 233 (100), 221(8.29), 205 (33.50), 177 (50.13), 95 (87.94); (Found: C, 47.57; H, 6.43. Calcd for $C_{18}H_{29}PO_3Te$: C, 47.83; H 6.47%).

(*Z*)-1-(Diethoxyphosphonyl)-2-(4-fluorophenyltelluryl)-1-heptene (6f): yield 0.26 g (59%); Oil; ν (film)/cm^{-1} 3030, 2950, 1570, 1500,1400, 1230, 1050, 960, 825; δ_H (400 MHz) 7.87−7.91 (m, 2H), 6.93−6.98 (m, 3H), 6.24−6.28 (d, J = 16.51, 1H), 4.08−4.14 (m, 4H), 2.16−2.19 (t, J = 7.08, 2H), 0.1.31−1.37 (m, 8H), 1.09−1.12 (m, 2H), 0.98−1.00 (m, 2H), 0.76−0.80 (t, J = 7.19, 3H); ^{13}C NMR δ 163.47 (d, $^1J_{F-C}$ = 248 Hz), 155.31 (d, $^2J_{P-C}$ = 6.1 Hz), 144.18 (d, $^3J_{F-C}$ = 7.8 Hz), 116.60 (d, $^2J_{F-C}$ = 20.5 Hz), 115.85 (d, $^1J_{P-C}$ = 192.4 Hz), 110.34 (d, $^4J_{F-C}$ = 3.7 Hz), 61.94 (d, $^2J_{P-C}$ = 5 Hz), 42.43 (d, $^1J_{P-C}$ = 23 Hz), 30.83, 29.62 (d, $^4J_{P-C}$ = 1.2 Hz), 22.25, 16.45 (d, $^3J_{P-C}$ = 6.3 Hz), 13.90; MS (EI) *m*/*z*: 458 (M$^+$, 27.82), 363 (17.09), 233 (75.13), 177 (44.59), 95 (100); (Found: C, 44.60; H, 5.71. Calcd for $C_{17}H_{26}FO_3PTe$: C, 44.78; H 5.75%).

***Anti*-Hydrotelluration of 1-Alkynyl Sulfones with ArTe-Na.** To a solution of diaryl ditelluride (0.25 mmol) dissolved in (1/1) (V/V) THF/ethanol (2.5 mL) under N_2 was added a solution of sodium borohydride (0.6 mmol) in EtOH dropwise until the characteristic dark-red color of the ditelluride faded, and then 1-alkynyl sulfone (0.5 mmol) in THF was added. The resulting solution was stirred at room temperature for 20 min, quenched with saturated aqueous NH_4Cl, and extracted with AcOEt. The organic phase was dried over sodium sulfate. Crude products (entries **7** and **8**) were concentrated under vacuum, and the residues were purified by preparative TLC on silica gel (AcOEt/hexanes = 1/10) to give compounds **8a**,**b**. Crude products (entries **9** and **10**) were treated with 1 equiv of Br_2 in AcOEt and concentrated under vacuum. The residues were purified by recrystallization with $CH_3OH/HCCl_3$ to give products (*Z*)-**9a** and (*Z*)-**9b**.

(*Z*)-1-(4-Methylphenylsulfonyl)-2-(phenyltelluryl)-2-phenylethene (8a): yield 0.172 g (74%); mp 142−143 °C; ν (KBr)/cm^{-1} 2940, 1601, 1529, 1434, 1320, 1083, 810, 655; δ_H (500 MHz): 7.95−7.97 (d, J = 8.2, 2H), 7.37−7.39 (m, 4H), 7.08−7.11 (m, 1H), 6.85−6.95 (m, 8H), 2.47 (s, 3H); ^{13}C NMR δ 147.94, 144.74, 140.80, 139.75, 138.09, 130.10, 130.03, 128.64, 128.26, 128.03, 127.87, 127.49, 127.43, 117.19, 21.78; MS (EI) *m*/*z*: 464 (M$^+$, 16.96), 207 (16.15), 193 (43.96), 155 (45.62), 139 (26.50), 91(100), 77 (53.45), 65 (19.11); (Found: C, 54.29; H, 3.86. Calcd for $C_{21}H_{18}O_2STe$: C, 54.59; H, 3.93%).

(*Z*)-1-(4-Methylphenylsulfonyl)-2-(4-fluorophenyltelluryl)-2-phenylethene (8b): yield 0.180 g (75%); mp 144−145 °C; ν(KBr)/cm^{-1}: 2940, 1576, 1486, 1394, 11314, 1234, 1142, 1018, 810, 655; δ_H (500 MHz): 7.94−7.95 (d, J = 8.2, 2H), 7.32−7.39 (m, 4H), 6.95−6.98 (m, 3H), 6.91 (s, 1H), 6.81−6.83 (m, 2H), 6.58−6.62 (t, J = 8.75, 2H), 2.47 (s, 3H); MS (EI) *m*/*z*: 482 (M$^+$, 14.55), 225 (11.45), 193 (45.25), 155 (46.98), 139 (22.38), 91(100); (Found: C, 52.34; H, 3.50. Calcd for $C_{21}H_{17}FO_2STe$: C, 52.55; H 3.57%).

(*Z*)-2-(4-Methylphenylsulfonyl)vinylphenyltellurium dibromides (9a): yield 0.224 g (82%); mp161−162 °C; ν (KBr)/cm^{-1}: 3002, 1594, 1436, 1295, 1257, 1140, 1078, 710; δ_H (400 MHz): 8.26−8.28 (m, 3H), 8.06−8.08 (d, J = 8.32, 2H), 7.54−7.56 (m, 3H), 7.43−7.45 (d, J = 8.20, 2H), 6.95−6.97 (d, J = 8.69, 1H), 2.49 (s, 3H); δ ^{13}C NMR 146.69, 134.64, 134.49, 134.14, 133.37, 131.81, 131.53, 130.48, 130.12, 129.13; MS (EI) *m*/*z*: 467 (M$^+$ − Br, 2.68), 388 (M$^+$ − 2Br, 56.85), 298 (17.69), 232 (24.60), 207 (43.64), 168 (29.80), 139 (41.76), 102 (35.29), 91 (65.35), 77 (100); (Found: C, 32.73; H, 2.52. Calcd for $C_{15}H_{14}Br_2O_2STe$: C, 33.01; H 2.59%).

(*Z*)-2-(4-Methylphenylsulfonyl)-1-hexylvinyl phenyl tellurium dibromide (9b): yield 0.224 g (71%); mp 127−128 °C; δ_H (400 MHz): 8.64−8.66 (d, J = 7.23, 2H), 8.07−8.10 (d, J = 8.29, 2H), 7.55−7.61 (m, 3H), 7.41−7.43 (d, J = 8.21, 2H), 6.44 (s, 1H), 2.54−2.58 (m, 2H), 2.48 (s, 3H), 1.40−1.43 (m, 2H), 1.07−1.16 (m, 6H), 0.75−0.79 (t, J = 6.88, 3H); δ ^{13}CNMR 153.31, 146.05, 137.45, 135.40, 131.99, 130.30, 130.10, 128.29, 126.96, 124.35, 35.91, 31.25, 28.54, 28.15, 22.32, 21.87, 13.95; MS (EI) *m*/*z*: 551 (M$^+$ − Br, 2.02), 472 (M$^+$ − 2Br, 31.47), 207 (36.55), 109(100), 91(71.51), 77 (56.99); (Found: C, 39.80; H, 4.06. Calcd for $C_{21}H_{26}Br_2O_2STe$: C, 40.04; H, 4.16%).

Reaction of (*E*)-2-Iodo-1-alkenyl Sulfones with ArTe-Na. To a solution of diaryl ditelluride (0.25 mmol) dissolved in (1/1) (v/v) THF/ethanol (2.5 mL) under N_2 was added sodium borohydride (0.6 mmol) in EtOH dropwise until the characteristic dark-red color of the ditelluride faded, and then (*E*)-2-iodo-1-alkenyl sulfone (0.5 mmol) in THF was added at 0 °C. The resulting solution was stirred at room temperature for 20 min, quenched with saturated aqueous NH_4Cl, and extracted with AcOEt. The organic phase was dried over sodium sulfate. Crude products **12a**−**f** (entries **11**−**16**) were treated with 1 equiv of Br_2 in AcOEt and concentrated under vacuum. The residues were purified via recrystallization with $CH_3OH/HCCl_3$ to give (*E*)-**13a**−**f**. The crude product (entry **17**) was concentrated under vacuum, and the residue was purified by preparative TLC on silica gel (AcOEt:*n*-hexane = 1:10) to give compound (*E*)-**12g**.

(*E*)-2-(4-Methylphenylsulfonyl)-1-butylvinyl phenyl tellurium dibromide (13a): yield 0.217 g (72%); mp 149−150

°C; ν (KBr)/cm^{-1}: 2926, 1595, 1438, 1319, 1142, 1082, 736; δ_H (500 MHz): 8.16−8.18 (m, 2H), 7.71−7.73 (d, J = 8.26, 2H), 7.57−7.59 (m, 1H), 7.47−7.50 (m, 2H), 7.36−7.37 (d, J = 8.0, 2H), 6.77 (s, 1H), 3.56−3.59 (t, J = 7.87, 2H), 2.46 (s, 3H), 1.61−1.65 (m, 2H), 1.45−1.48 (m, 2H), 0.94−0.97 (t, J = 7.37, 3H); δ ^{13}C NMR 157.85, 145.49, 139.91, 137.10, 135.72, 132.46, 130.58, 130.20, 128.79, 127.60, 32.06, 31.38, 22.53, 21.79, 13.78; MS (EI) *m*/*z*: 523 (M^+ − Br, 3.89), 444 (M^+ − 2Br, 49.31), 237 (28.62), 207 (54.21), 139 (41.63), 91 (84.77), 81 (100); (Found: C, 37.77; H, 3.60; Calcd for $C_{19}H_{22}SO_2Br_2Te$: C, 37.92; H 3.68%).

(*E*)-2-(4-Methylphenylsulfonyl)-1-butylvinyl 4-fluorophenyl tellurium dibromide (13b): yield 0.22 g (71%); mp 170−171 °C; ν (KBr)/cm^{-1}: 2930, 1577, 1486, 1390, 1313, 1234, 1142, 1081, 811, 777; δ_H (500 MHz): 8.19−8.21 (m, 2H), 7.71−7.73 (d, J = 11.35, 2H), 7.37−7.38 (d, J = 7.73, 2H), 7.16−7.20 (m, 2H), 6.72 (s, 1H), 3.56−3.59 (t, J = 7.52, 2H), 2.47 (s, 3H), 1.58−1.66 (m, 2H), 1.44−1.48 (m, 2H), 0.94−0.97 (t, J = 7.14, 3H); δ ^{13}C NMR 164.88 (d, $^1J_{F-C}$ = 255.3 Hz), 158.07, 145.59, 139.81, 138.33 (d, $^3J_{F-C}$ = 8.8 Hz), 136.94, 130.22, 127.58, 122.81 (d, $^4J_{F-C}$ = 3.1 Hz), 117.98 (d, $^2J_{F-C}$ = 22 Hz), 32.02, 31.29, 22.51, 21.78, 13.75; MS (EI) *m*/*z*: 541 (M^+ − Br, 8.88), 462 (M^+ − 2Br, 48.20), 225 (39.20), 155 (49.04), 139 (45.74), 95 (43,66), 91 (100), 81 (70.99); (Found: C, 36.70; H, 3.35. Calcd for $C_{19}H_{21}Br_2FO_2STe$: C, 36.82; H, 3.41%).

(*E*)-2-(4-Methylphenylsulfonyl)-1-pentylvinyl phenyl tellurium dibromide (13c): yield 0.193 g (64%); mp 97−98 °C; ν (KBr)/cm^{-1}: 2926, 1595, 1438, 1319, 1143, 1081, 811, 736; δ_H (500 MHz): 8.17−8.19 (m, 2H), 7.71−7.73 (d, J = 8.27, 2H), 7.58−7.59 (m, 1H), 7.47−7.50 (m, 2H), 7.35−7.37 (d, J = 8.17, 2H), 6.78 (s, 1H), 3.55−3.58 (t, J = 7.74, 2H), 2.46 (s, 3H), 1.63−1.66 (m, 2H), 1.34−1.41 (m, 4H), 0.88−0.92 (t, J = 6.94, 3H); δ ^{13}C NMR 157.86, 145.41, 139.93, 137.04, 135.67, 132.37, 130.49, 130.12, 128.79, 127.51, 31.51, 31.28, 29.64, 22.22, 21.73, 13.86; MS (EI) *m*/*z*: 523 (M^+ − Br, 3.89), 444 (M^+ − 2Br, 49.31), 237 (28.62), 207 (54.21), 139 (41.63), 91 (84.77), 81 (100); (Found: C, 38.81; H, 3.88. Calcd for $C_{20}H_{24}Br_2O_2$-STe: C, 39.00; H,3.93%).

(*E*)-2-(4-Methylphenylsulfonyl)-1-pentylvinyl 4-fluorophenyl tellurium dibromide (13d): yield 0.199 g (63%); mp 158−159 °C; ν (KBr)/cm^{-1}: 2930, 1578, 1486, 1393, 1313, 1234, 1141, 1081, 811, 653; δ_H (500 MHz): 8.19−8.22 (m, 2H), 7.72−7.73 (d, J = 8.02, 2H), 7.57−7.59 (d, J = 8.02, 1H), 7.37−7.38 (m, 2H), 7.17−7.20 (m, 2H), 6.73 (s, 1H), 3.55−3.58 (t, J = 7.67, 2H), 2.47 (s, 3H), 1.63−1.66 (m, 2H), 1.34−1.40 (m, 4H), 0.89−0.92 (t, J = 6.62, 3H); δ ^{13}C NMR 164.92 (d, $^1J_{F-C}$ = 255.1 Hz), 158.13, 145.57, 139.93, 138.32 (d, $^3J_{F-C}$ = 8.8 Hz), 137.05, 130.21, 127.61, 122.84, 117.98 (d, $^2J_{F-C}$ = 22.1), 31.49, 31.33, 29.69, 22.26, 21.75, 13.85; MS (EI) *m*/*z*: 553 (M^+ − Br, 1.14), 476 (M^+ − 2Br, 17.72), 225 (27.04), 157 (31.10), 95(100), 91 (59.61); (Found: C, 37,77; H, 3.60. Calcd for $C_{20}H_{23}Br_2FO_2$-STe: C, 37.90; H, 3.66%).

(*E*)-2-(4-Methylphenylsulfonyl)-1-hexylvinyl 4-fluorophenyl tellurium dibromide (13e): yield 0.185 g (57%); mp 118−120 °C; ν (KBr)/cm^{-1}: 2926, 2854, 1578, 1486, 1394, 1314, 1234, 1141, 1081, 811, 654; δ_H (500 MHz): 8.19−8.22 (m, 2H), 7.71−7.73 (m, 2H), 7.36−7.38 (m, 2H), 7.17−7.20 (m, 2H), 6.73 (s, 1H), 3.55−3.58 (m, 2H), 2.47 (s, 3H), 1.61−1.65 (m, 2H), 1.38−1.40 (m, 2H), 1.28−1.30 (m, 4H), 0.89−0.91 (m, 3H); δ ^{13}C NMR 164.89 (d, $^1J_{F-C}$= 255.3 Hz), 158.21, 145.57, 139.93, 138.34 (d, $^3J_{F-C}$= 8.7 Hz), 137.02, 130.21, 127.60, 122.85 (d, $^4J_{F-C}$=3.2 Hz), 117.98 (d, $^2J_{F-C}$= 22.1 Hz), 31.55, 31.34, 29.99, 28.93, 22.46, 21.77, 14.05; MS (EI) *m*/*z*: 569 (M^+ − Br, 2.60), 490 (M^+ − 2Br, 41.09), 265 (16.94), 225 (40.52), 155 (45.73), 139 (38.03), 109 (100), 91 (74.35); (Found: C, 38.73; H, 3.81. Calcd for $C_{21}H_{25}Br_2FO_2STe$: C, 38.93; H3.89%).

(*E*)-2-(4-Methylphenylsulfonyl)-1-hexylvinyl phenyl tellurium dibromide (13f): yield 0.195 g (62%); mp96−97 °C; ν (KBr)/cm^{-1}: 2924, 1595, 1437, 1319, 1143, 1081, 811, 736, 644, 539; δ_H (500 MHz): 8.17−8.19 (m, 2H), 7.72−7.73 (m, 2H), 7.57−7.59 (m, 1H), 7.48−7.50 (m, 2H), 7.35−7.37 (m, 2H), 6.78 (s, 1H), 3.55−3.58 (m, 2H), 2.46 (s, 3H), 1.62−1.65 (m, 2H), 1.38−1.40 (m, 2H), 1.28−1.31 (m, 4H), 0.89−0.91 (m, 3H); δ ^{13}C NMR 157.91, 145.40, 139.95, 137.08, 135.67, 132.38, 130.50, 130.12, 128.78, 127.52, 31.57, 31.30, 29.95, 28.88, 22.41, 21.72, 14.02; MS (EI) *m*/*z*: 551 (M^+ − Br, 2.22), 472 (M^+ − 2Br, 33.05), 265 (16.65), 207 (36.55), 157 (36.77), 109 (100), 91 (71.51), 77 (56.99); (Found: C, 39.88; H, 4.11. Calcd for $C_{21}H_{26}Br_2O_2STe$: C, 40.04; H, 4.16%).

(*E*)-1-(4-Methylphenylsulfonyl)-2-phenyltelluryl-2-phenylethene (12g): yield 0.146 g (63%); mp 129−130 °C; ν (KBr)/cm^{-1}: 3046, 1576, 1435, 1322, 1140, 1083, 769; δ_H (500 MHz): 7.77−7.79 (m, 2H), 7.42 (m, 1H), 7.30−7.32 (m, 4H), 7.26−7.20 (m, 3H), 7.09−7.12 (m, 4H), 6.39 (s, 1H), 2.36 (s, 1H); δ ^{13}C NMR 144.90, 143.66, 140.83, 138.68, 137.26, 132.30, 130.29, 129.92, 129.34, 128.66, 127.83, 127.57, 127.41, 114.84, 21.59; MS (EI) *m*/*z*: 462 (M^+, 16.36), 309 (7.44), 207 (24.14), 155 (52.24), 105 (24.68), 91 (100), 77 (66.71); (Found: C, 54.12; H, 3.87. Calcd for $C_{21}H_{18}O_2STe$: C, 54.59; H, 3.93%).

***Anti*-Tellurosulfonates of 1-Alkynes.** A solution of alkyne (1.1 mmol), sodium arylsulfinate (5 mmol), and diorgano ditelluride (0.5 mmol) in 5 mL of 80% aqueous acetic acid was heated at 80 °C for the time indicated in Table 3. The reaction mixture was diluted with 20 mL of AcOEt, washed with saturated aqueous sodium bicarbonate, dried over Na_2SO_4, and concentrated in a vacuum. Crude products (entreis **22**, **23**, and **26**) were concentrated under vacuum, and the residues were purified by preparative TLC on silica gel (AcOEt:hexanes = 1:10) to give compounds **12g**, **12h**, and **12k**. Crude products (entries **18**−**21**, and **24** and **25**) were treated with 1 equiv of Br_2 in AcOEt and concentrated under vacuum. The residues were purified by recrystallization with $CH_3OH/HCCl_3$.

(*E*)-1-(4-Chlorophenylsulfonyl)-2-phenyltelluryl-2-phenylethene (12h): yield 0.412 g (85%); mp154−155 °C; ν (KBr)/cm^{-1}: 3020, 1576, 1326, 1142, 1083, 776, 605, 540; δ_H (500 MHz): 7.80−7.82 (m, 2H), 7.43−7.45 (m, 1H), 7.31−7.35 (m, 4H), 7.20−7.24 (m, 3H), 7.08−7.10 (m, 2H), 6.38 (s, 1H); δ ^{13}C NMR 146.57, 140.94, 140.17, 139.46, 137.13, 131.91, 130.45, 130.13, 129.09, 128.98, 128.93, 128.02, 127.45, 114.81; MS (EI) *m*/*z*: 484 (M^+, 25.01), 309 (11.57), 277 (7.24), 213 (43.59), 205 (32.02), 175 (36.40), 111 (59.97), 77 (100); (Found: C, 49.69; H,3.08. Calcd for $C_{20}H_{15}ClO_2STe$: C, 49.79; H, 3.13%).

(*E*)-2-(Phenylsulfonyl)-1-butylvinyl phenyl tellurium dibromide (13i): yield 0.300 g (51%); mp 135−136 °C; ν (KBr)/cm^{-1}: 3057, 2930, 1436, 1390, 1147, 1081, 735, 659; δ_H (500 MHz): 8.19−8.21 (m, 2H), 7.87−7.88 (m, 2H), 7.69−7.72 (m, 1H), 7.59−7.62 (m, 3H), 7.49−7.52 (m, 2H), 6.79 (s, 1H), 3.60−3.63 (m, 2H), 1.64−1.68 (m, 2H), 1.46−1.50 (m, 2H), 0.96−0.99 (m, 3H); δ ^{13}C NMR 158.33, 139.93, 139.51, 135.66, 134.22, 132.43, 130.52, 129.53, 128.87, 127.45, 31.99, 31.39, 22.46, 13.73; MS (EI) *m*/*z*: 509 (M^+ − Br, 2.98), 430 (M^+ − 2Br, 28.58), 223 (19.10), 207 (38.51), 143 (30.67), 77 (100); (Found: C, 36.66; H, 3.32; Calcd for $C_{18}H_{20}Br_2O_2STe$: C, 36.78; H, 3.43%).

(*E*)-2-(Phenylsulfonyl)-1-hexylvinyl phenyl tellurium dibromide (13j): yield 0.376 g (61%); mp 96−98 °C; ν (KBr)/cm^{-1}: 3032, 2925, 1446, 1326, 1147, 1081, 792, 635; δ_H (500 MHz): 8.17−8.18 (m, 2H), 7.84−7.86 (m, 2H), 7.66−7.69 (m, 1H), 7.56−7.59 (m, 3H), 7.47−7.50 (m, 2H), 6.78 (s, 1H), 3.56−3.59 (m, 2H), 1.62−1.68 (m, 2H), 1.38−1.42 (m, 2H), 1.29−1.31 (m, 4H) 0.89−0.91 (m, 3H); δ ^{13}C NMR 158.52, 140.17, 139.70, 135.71, 134.27, 132.52, 130.65, 129.60, 128.75, 127.58, 31.70, 31.39, 30.07, 28.99, 22.49, 14.07; MS (EI) *m*/*z*: 537 (M^+ − Br, 2.32), 458 (M^+ − 2Br, 35.20), 207 (39.46), 143 (40.32), 109 (97.88), 77 (100); (Found: C, 38.85; H, 3.84. Calcd for $C_{20}H_{24}Br_2O_2STe$: C, 39.00; H, 3.93%).

(*E*)-1-(4-Methylphenylsulfonyl)-2-(phenyltelluryl)-ethene (12k): yield 0.1 g (26%); Mp 124−126 °C; δ_H (400 MHz): 8.57−8.61 (d, J = 15.83, 1H), 7.76−7.78 (m, 2H), 7.69−7.72 (m, 2H), 741−7.43 (m, 1H), 730−7.33 (m, 4H), 6.41−6.45 (d, J = 15.82, 1H), 2.42 (s, 3H); δ ^{13}C NMR 144.32, 140.09, 137.48, 134.77, 130.29, 130.01, 129.72, 127.76, 126.15, 110.83, 21.69; MS (EI) *m*/*z*: 388 (M^+, 50.83), 207 (40.66), 91 (65.35), 77 (100); (Found: C, 46.42; H, 3.56; Calcd for $C_{15}H_{14}O_2STe$: C, 46.68; H, 3.66%).

***Anti*-Addition of ArTeI with 1-Alkynes.** A mixture of 1 mmol of ArTeI (prepared by the reaction of a diaryldiditelluride (0.5 mmol) with I_2 (0.55 mmol) in THF at 0 °C) and 1 mmol of an alkyne was stirred at room temperature for 12 h followed

by the treatment with saturated $Na_2S_2O_3$. After stirring for 30 min, the mixture was extracted with hexanes, dried over $CaCl_2$, and concentrated in a vacuum. The residues were purified by preparative TLC on silica gel eluted with hexanes to give compounds **16**, which reacted with Br_2 (1 equiv) to afford (*E*)-**17a**−**f**.

(*E*)-(2-Iodo-1-butyl)vinyl phenyl tellurium dibromide (17a): yield 0.258 g (45%); mp 146−147 °C; ν (film)/cm^{-1}: 3067, 2928, 1636, 1438, 1253, 1112, 994, 730, 680; δ_H (400 MHz) 8.29−8.32 (m, 2H), 7.54−7.61 (m, 3H), 7.37 (s, 1H), 3.10−3.14 (t, J 7.92, 2H), 1.72−1.77 (m, 2H), 1.48−1.54 (m, 2H), 0.98−1.01 (t, J = 7.3, 3H); δ ^{13}C NMR 144.52, 135.74, 132.19, 130.51, 130.39, 129.40, 95.52, 38.00, 30.72, 22.28, 13.90; MS (EI) *m*/*z*: 495 (M$^+$ − 79, 4.32), 416 (17.03), 334 (10.95), 207 (53.19), 77 (100). (Found: C, 24.96; H, 2.55. Calcd for $C_{12}H_{15}Br_2ITe$: C, 25.13; H 2.64%).

(*E*)-(2-Iodo-1-butyl)vinyl 4-chlorophenyl tellurium dibromide (17b): yield 0.322 g (53%); mp. 123−124 °C; ν (film)/cm^{-1} : 3065, 2955, 1636, 1559, 1471, 1385, 1094, 1088, 1003, 807, 702; δ_H (400 MHz) 8.25−8.27 (m, 2H), 7.52−7.54 (m, 2H), 7.35 (s, 1H), 3.09−3.13 (t, J = 7.98, 2H), 1.71−1.75 (m, 2H), 1.48−1.54 (m, 2H), 0.98−1.01 (t, J = 7.3, 3H); δ ^{13}C NMR 144.58, 139.12, 137.06, 130.59, 127.04, 95.68, 37.87, 30.68, 22.23, 13.89; MS (EI) *m*/*z*: 529 (M$^+$ − 79, 4.69), 450 (26.66), 368 (17.00), 241 (87.09), 81 (100). (Found: C, 23.83; H, 2.28. Calcd for $C_{12}H_{14}Br_2ClITe$: C, 23.71; H 2.32%).

(*E*)-(2-Iodo-1-pentyl)vinyl phenyl tellurium dibromide (17c): yield 0.282 g (48%); mp 93−94 °C; ν (film)/cm^{-1}: 3054, 2930, 2984, 1636, 1584, 1437, 1116, 994, 729, 679; δ_H (400 MHz) 8.30−8.32 (m, 2H), 7.54−7.61 (m, 3H), 7.37 (s, 1H), 3.09−3.13 (t, J = 7.86, 2H), 1.75−1.78 (m, 2H), 1.39−1.49 (m, 4H), 0.92−0.96 (t, J = 7.0, 3H); δ ^{13}C NMR 144.47, 135.73, 132.15, 130.46, 129.37, 95.63, 38.16, 31.10, 28.03, 22.40, 14.00; MS (EI) *m*/*z*: 509 (M$^+$ − 79, 7.36), 430 (16.44), 334 (4.85), 207 (38.17), 95 (100). (Found: C, 26.88; H, 2.92. Calcd for $C_{13}H_{17}Br_2ITe$: C, 26.57; H 2.92%).

(*E*)−(2-Iodo-1-pentyl)vinyl 4-chlorophenyl tellurium dibromide (17d): yield 0.317 g (51%); mp 104−105 °C; ν (film)/cm^{-1} 3054, 2931, 2869, 1560, 1472, 1385, 1179, 1093, 1004, 806, 721, 655; δ_H (400 MHz) 8.25−8.27 (m, 2H), 7.52−7.54 (m, 2H), 7.36 (s, 1H), 3.09−3.12 (t, J = 7.63, 2H), 1.73−1.77 (m, 2H), 1.39−1.48 (m, 4H), 0.92−0.96 (t, J = 7.16, 3H); δ ^{13}C NMR 144.62, 139.16, 137.05, 130.62, 127.08, 95.66, 38.08, 31.10, 28.33, 22.41, 13.97; MS (EI) *m*/*z*: 543 (M$^+$ − 79, 11.90), 464 (31.12), 241(40.27), 95 (100); (Found: C, 25.17; H, 2.55. Calcd for $C_{13}H_{16}Br_2ClITe$: C, 25.10; H 2.59%).

(*E*)-(2-Iodo-1-hexyl)vinyl phenyl tellurium dibromide (17e): yield 0.222 g (37%); mp 72−73 °C; ν (film)/cm^{-1} : 3056, 2925, 2850, 1582, 1437, 994, 728, 678; δ_H (400 MHz) 8.30−8.32 (m, 2H), 7.54−7.61 (m, 3H), 7.37 (s, 1H), 3.09−3.13 (t, J = 7.78, 2H), 1.74−1.78 (m, 2H), 1.46−1.50 (m, 2H), 1.34−1.36 (m, 4H), 0.90−0.93 (t, J = 6.72, 3H); δ ^{13}C NMR 144.53, 135.73, 132.19, 130.51, 129.43, 95.53, 38.25, 31.51, 28.73, 28.64, 22.57, 14.12, MS (EI) *m*/*z*: 523 (M$^+$ − 79, 2.36), 442 (12.09), 334 (7.27), 207 (40.43),109 (100); (Found: C, 27.85; H, 3.14. Calcd for $C_{14}H_{19}Br_2ITe$: C, 27.95; H 3.18%).

(*E*)-(2-Iodo-1-hexyl)vinyl 4-chlorophenyl tellurium dibromide (17f): yield 0.273 g (43%); mp. 80−81 °C; ν (film)/cm^{-1} : 3057, 2925, 2950, 1571, 1560, 1472, 1385, 1091, 1002, 804, 720; δ_H (400 MHz) 8.25−8.27 (m, 2H), 7.52−7.54 (m, 2H), 7.36 (s, 1H), 3.09−3.12 (t, J = 7.54, 2H), 1.72−1.76 (m, 2H), 1.46−1.49 (m, 2H), 1.33−1.37 (m, 4H), 0.90−0.93 (t, J = 6.89, 3H); δ ^{13}C NMR 144.65, 139.21, 137.05, 130.65, 127.08, 95.58, 38.15, 31.49, 28.71, 28.64, 22.56, 14.12; MS (EI) *m*/*z*: 557 (M$^+$ − 79, 4.83), 478 (22.96), 241 (55.30), 109 (100); (Found: C, 26.41; H, 2.81. Calcd for $C_{14}H_{18}Br_2ClITe$: C, 26.44; H 2.85%).

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Supporting Information Available: ^{1}H NMR spectra of **6a**−**f, 8a**,**b**, **9a**,**b**, **12g**, **12h**, **12k**, **13a**−**f**, **13i**, **13j**, and **17a**−**f**; ^{13}C NMR spectra of **6a**−**d, 6f**, **8a**, **9a**,**b**, **12g**, **12h**, **12k**, **13a**−**f**, **13i**−**j**, and **17a**−**f**; ^{1}H−^{1}H NOESY spectra of **6c**, **6e**, **8b**, **9b**, and **13f**, and ORTEP figures of **6a** and **17b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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