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Reaction of ketone hydrazones with TeCl₄: Isolation and reactions of novel divinyl telluride

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Reaction of acetophenone hydrazones with $TeCl_4$ in the presence of DBU gave a mixture of divinyl ditellurides and divinyl tellurides, which easily reacted with Cu powder in refluxing toluene to afford divinyl tellurides in good yields. Reaction of divinyl telluride with bromine (1.2 eq) gave the corresponding tellurium dibromide rather than the addition of the double bond whereas 3 molar amount of bromine gave excess brominated and oxidized products. Reaction of divinyl tellurides with 2-(trimethylsilyl)phenyl triflate in the presence of CsF gave (*E*)-2-alkenyldiaryl tellurides in good yields.

Introduction

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Organic tellurium compounds have been the focus of intensive study and a number of literature appeared for their valuable synthetic intermediates.¹ Tellurophenes are well known for their use of organic materials due to their fluorescence activity.²

Vinyl tellurides constitute important organic tellurium compounds that is often employed in organic synthesis.³ Hydrotelluration of alkynes to give vinyl tellurides is a well-known method for the formation of 2-substituted vinyl tellurides. Preparation of simple divinyl telluride was reported by Potapov et al.,⁴ whereas 1-aryl substituted divinyl tellurides were not synthesized until our recent communication,⁵ which constitutes a convenient synthesis of 2,5diaryltellurophenes by the reaction of acetophenone hydrazones with tellurium tetrachloride in the presence of DBU, intermediates of which would be divinyl ditellurides along with small amount of divinyl tellurides. We have also reported that reaction of camphor hydrazone with TeCl₄ gave the corresponding ditelluride.⁶ During mechanistic investigation of these reactions, we have found a convenient synthesis of divinyl tellurides. Herein, we would like to show the isolation of divinyl tellurides and novel formation of tellurium dibromides by the reaction with bromine and 2alkenyldiaryl tellurides by the reaction with benzyne (Figure 1).



^{. &}lt;sup>+</sup> Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [¹H and ¹³C NMR spectra and X-ray crystallographic data]. See DOI: 10.1039/x0xx00000x







Figure 1. Previous results and this work Results and discussion

Initially, the reaction of *p*-methylacetophenone hydrazone (**1a**) with TeCl_4 was selected for screening the reaction conditions. We evaluated the influence of temperature, solvent, and molar amounts of TeCl_4 and bases. Treatment of **1a** with TeCl_4 (1 eq) and Et_3N (3 eq) in refluxing DMF resulted in the formation of 2,5-di-*p*-tolyltellurophene **2a** and bis(1-*p*-tolyl)vinyl telluride (**3a**) in 32% and 12% yields, respectively (Table 1, entry 1). Other results were shown in Table 1.

Table 1. Reaction of 1a with TeCl₄ in the presence of Base^a

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Entry	TeCl ₄	Base	(eq)	Solvent	Temp	2a ^b	3a ^{b,c}
	(eq)				(°C)	(%)	(%)
1	1.0	Et_3N	3.0	DMF	reflux	32	12
2	2.0	Et₃N	6.0	DMF	rt	5	36
3	2.0	DBU	6.0	DMF	rt	5	48
4	2.0	DBU	6.0	toluene	reflux	28	18
5	2.0	DBU	6.0	CH_2CI_2	reflux	0	52
6	2.0	DBU	6.0	CH_2CI_2	rt	0	53
7	2.0	DBU	6.0	CHCl₃	reflux	0	55
8	2.0	DBU	6.0	CHCl₃	rt	0	65
9	2.0	DBU	6.0	CHCl₃	0	0	52

a) Reactions performed in the presence of **1a** (5.0 mmol), base (3 eq or 6 eq), TeCl₄ (1 or 2 eq), and solvent at rt or reflux. b) Yields are given for isolated **2a** and **3a**. c) There is no smell problem for compound **3a** due to low volatility.

Although compound **3a** could not be obtained effectively in DMF solution at several reaction temperatures (rt to reflux) by using Et₃N or DBU as a base (Entries 1-3), we then tried the reaction in several solvents under moderate reaction temperature. When the reaction was carried out in dichloromethane solution at room temperature, a mixture of vinyl telluride (**3a**) and vinyl ditelluride (**4a**) was obtained in 4:3 ratio (60% by NMR). However, isolation of vinyl telluride **3a** was very difficult for their similar polarity. Since ditellurides are known to react with Cu powder to give the corresponding telluride⁷, we have added Cu powder to the mixture and refluxed for 3h. Vinyl telluride **3a** was isolated in 53% yield (Entry 6). When chloroform was used as a solvent, **3a** was obtained in 65% yield (Entry 8). With the optimal conditions in hand (CHCl₃, rt, 5h), we have investigated the scope and generality of this synthesis. The results were shown in Table 2.

R H ₃ C 1 + Tel	NH ₂	DBU CHCl ₃ rt +			0.1039/D0OBC)0782J 3
Entry	1	R	H ₂ C	4 Yield/%	R	
1	1a	CH ₃	3a	65		
2	1b	н	3b	62		
3	1c	Cl	3c	67		
4	1d	Br	3d	55		
5	1e	NO ₂	3e	61		
6	1f	Ph	3f	51		
7	1g	o-CH ₂	39	54		

Table 2. Reaction of acetophenone hydrazones 1 with Tecla Online

a) Reactions performed in the presence of 1 (5.0 mmol), DBU (6 eq) $TeCl_4$ (2 eq), and chloroform at rt.

Introduction of various electron-donating and electron-withdrawing groups into the *p*-positions was fully tolerated (Entries 1-6), whereas *o*-Me gave **3g** in 54% yield (Entry 7). Generally, para-substituted acetophenone hydrazones gave better yields of these products. Thus, we have developed a convenient synthesis of bis(1-aryl)vinyl tellurides **3**.

We have already reported that the reaction of camphor hydrazone with TeCl_4 afforded the corresponding divinyl ditelluride via tellurocamphor intermediate.⁶ Analogously, the reaction might proceed as follows; Hydrazones **1** reacted with TeCl_4 to afford the corresponding telluroacetophenones, which easily enolyzed to give enetellurols. Under these conditions, enetellurols oxidized to give the corresponding divinyl ditellurides **4**. Ditellurides are relatively unstable, which gradually changed to more stable divinyl tellurides **3** (Scheme 1).



Scheme 1. Formation mechanism of 3.

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Reaction of vinvl telluride with bromine

Tellurophenes and tellurides easily react with bromine to afford the corresponding tellurium dibromides, which show interesting photoelectronic properties.^{1, 2} Thus, we have tried the reaction with bromine whether the corresponding tellurium dibromide would be formed. Treatment of bis-1-(4-methylphenyl)vinyl telluride 3a with 1.2 molar amount of bromine afforded tellurium dibromide 5a. Bis-1-(4-bromophenl)vinyl telluride **3d** and bis-1-(4-nitrophenl)vinyl telluride 3e also reacted with bromine to give stable tellurium dibromide 5d and 5e, respectively (Scheme 2).



Scheme 2. Synthesis of tellurium dibromide 5

Since there is no report on the reaction with excess amount of bromine to vinyl tellurides, we then tried the reaction of tellurides 3 with excess amount of bromine whether the corresponding bromine adduct would be formed. Treatment of 3a with 3.2 molar amount of bromine afforded a mixture of (Z)-1-(1,2-dibromovinyl)-4methylbenzene and (E)-1-(1,2-dibromovinyl)-4-methylbenzene 7 (13:1) in 35% yield along with 2-bromo-p-methylphenylethanone 6a (28%). Similarly, when 3 molar amount of bromine was reacted with 3e, 1-nitro-4-(1,1,2-tribromoethyl)benzene 8 and 2-bromo-pnitrophenylethanone 6b were obtained in 65% and 5% yields, respectively (Scheme 3). The structure of tribromide 8 was determined by ¹H and ¹³C NMR along with X-ray single crystallographic analysis.8



Scheme 3. Reaction of tellurides 3 with excess amount of bromine

The reaction might proceed as follows: initially formed dibromide 5e brominated to afford bromonium ion, which further attacked by bromide and eliminated to give tribromide 8. Bromonium ion further reacted with water to give 2bromoacetophenone 6b (Scheme 4).



Thus, vinyl tellurides 3 were easily brominated to give the corresponding tellurium dibromides 5. Further bromination to double bond is relatively difficult and elimination proceeded to give 7 or 8. Difference in the reactivity between tellurides 3a and 3e would be the difference in the stability between 5a and 5e. Dibromide 5e is stable in chloroform solution at rt for 2 days, whereas 5a is easily oxidized to give p-methylacetophenone after standing at rt in chloroform for 2 days (Scheme 5).



Scheme 5. Oxidation of dibromide 5a

X-Ray crystallographic analysis

Attempts to grow single crystals of dibromides were only successful in the case of **5e**. The ORTEP view of **5e** is presented in Figure 2.⁸ In view of the steric demand of the active lone pair, the primary geometry of the tellurium atom may be describes as distorted trigonal bypyramidal. The distortion is apparent from the reduced bond angles Br(1)-Te(1)-Br(2) (171.2°) and C(1)-Te-C(1)* (111.1°) as against 180° and 120°, respectively, for idealized trigonal bipyramidal There are relatively few examples of X-ray geometry. crystallographic structures of telluride-halogen adducts, which show trigonal bypyramidal geometry around tellurium atom.⁹ This is the first example of X-ray crystallographic structure of vinyl telluridebromine adduct.



Figure 2. X-ray crystallographic analysis of Compound **5e**. (50% probability) Selcted bond lengths and bond angles Te(1)-C(1) 2.133A, Te(1)-C(1)* 2.133, Te(1)-Br(1) 2.669, Te(1)-Br(1)* 2.133, C(1)-Te(1)-C(1)* 111.1°, C(1)*-Te(1)-Br(1) 88.40°, C(1)-Te-Br(1) 86.63°. C(1)*-Te(1)-Br(1) 88.40°.

Reaction of vinyl telluride 3 with 2-trimethylsilylphenyl triflate 9a

It is well known that alkyl sulfides react with benzyne to afford the corresponding phenyl sulfides.¹⁰ Vinyl sulfides having electronwithdrawing group are known to react with benzyne followed by the addition of water to give 2-alkenylphenyl aryl sulfides in good yields.¹¹ (Figure 3) Although these methods provide a variety of functionalized aromatic sulfides, it is very difficult to synthesize functionalized aromatic tellurides.



Figure 3.

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Since divinyl tellurides 3 were obtained in one-pot operation from acetophenone hydrazones 1, we then tried the reaction of these compounds with benzyne prepared from 2-(trimethylsilyl)phenyl triflate 9. Treatment of triflate 9 (1.2 eq) with divinyl telluride 3a in the presence of CsF at 50°C for 24 h resulted in the formation of 2phenylethenylphenyl aryl telluride 10 and bis(2phenylethenyl)phenyl telluride 11a and in 5% and 8% yields, respectively. Telluride 3a was recovered in 45 % (Table 3, Entry 1). When 3 molar amount of triflate 9 was used to the reaction, compounds 10 and 11a were obtained in 12 and 35% yields along with starting 3a (20%) (Entry 2). These results clearly showed that water must be required for completion of the reaction. Treatment of 3 molar amount of triflate 9 with divinyl telluride 3a and 3 eq water in the presence of CsF at 50°C resulted in the formation of the desired trans-diaryl telluride 11a in 70% yield (Entry 3). Under these conditions, other tellurides 3 also reacted with triflate 9 to afford the

corresponding **11** in moderate yields (Entries 4-6_{iev}**8**_{Artield}**0**_n**9**)_e However, nitro derivative **3e** did not afford diaryi telluride due to row reactivity (Entry 7).

Table 3. Reaction of vinyl telluride 3 with triflate in the presenceof water



Entry	Telluri	R	9	Water	Products		Yield
	de 3		Eq.	(eq)	10	11	/%
1	3a	p-CH₃	1.2	0	10a 5	11a	8
2	3a	<i>p</i> -CH ₃	3	0	10a 12	11a	21
3	3a	p-CH₃	3	3	0	11a	70
4	3b	н	3	3	0	11b	60
5	3c	p-Cl	3	3	0	11c	60
6	3d	<i>p</i> -Br	3	3	0	11d	63
7	3e	p-NO ₂	3	3	0	11e	0
8	3f	<i>p</i> -Ph	3	3	0	11f	46
9	3g	<i>o</i> -CH₃	3	3	0	11g	51

The reaction might proceed as follows: [3+2] cycloaddition gave tellurolium ylide **a**, which reacted with water to give telluronium ion **b**. β –Hydrogen abstraction of **b** afforded the mono vinyl telluride **10a**, which further reacted with another molar of benzyne and water to give final telluride **11a** (Scheme 6). To confirm the role of water, D₂O was added to the reaction. The corresponding deuterated telluride **11a** (60% D) was obtained in 55% yield.



Scheme 6. Formation mechanism of 11 from telluride 3

Conclusions

we have successfully synthesized divinyl tellurides **3** by the reaction of acetophenone hydrazones **1** with TeCl₄.

Consequently, we completed the synthesis of divinyl tellurides via a different route from the previously reported ones. The reaction of these tellurides with bromine gave the corresponding tellurium dibromides **5**, which further reacted with additional bromine to give tribromoethylbenzene. The reaction with aryne prepared from triflate **9** afforded the corresponding insertion products **11**.

Experimental

General: All chemicals were obtained from commercial suppliers and were used without further purification. Analytical TLC was carried out on precoated plates (Merck silica gel 60, F254) and flash column chromatography was performed with silica gel (Merck, 70-230 mesh). NMR spectra (¹H at 400 MHz; ¹³C at 101 MHz) were recorded in CDCl₃ and chemical shifts are expressed in ppm relative to internal TMS for ¹H- and ¹³C-NMR. Melting points are uncorrected.

Reaction of acetophenone hydrazone with \mbox{TeCl}_4

To a solution of TeCl₄ (2.69 g, 10.0 mmol) and DBU (4.57 g, 30.0 mmol) in chloroform (30 mL) was added *p*-methylacetophenone hydrazone (0.741 g, 5.0 mmol) in chloroform (20 mL) at rt over 1 h. After being stirred for 0.5 h, the reaction mixture was filtered and poured into water which was extracted with dichloromethane (10 mL) for three times. The combined extract was dried over sodium sulfate, filtered and evaporated to give a mixture of bis(1-*p*-tolyl)vinyl ditelluride **2a** and bis(1-*p*-tolyl)vinyl telluride **3a** (0.95g, 70% by ¹H NMR). To a suspension of the mixture (0.95 g) in toluene (20 mL) was added Cu powder (0.63 g, 10 mmol) and refluxed for 12 h. After filtering the suspension, the filtrate was evaporated to give orange oil, which was chromatographed over silica gel by elution with hexane:dichloromethtane (1:1) to afford divinyl telluride **3a** (0.58 g, 1.6 mmol).

Bis-1-(*p*-tolyl)vinyl telluride **3a**: orange oil. ¹H NMR (CDCl₃) δ = 2.32 (s, 6H, CH₃), 5.79 (s, 2H, =CH), 6.30(s, 2H, =CH), 7.07 (d, 4H, *J* = 8 Hz, Ar), 7.36 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.1 (CH₃), 126.7, 127.7, 128.7 (=CH₂) ,128.9, 137.8, 139.8. HRMS (EI): Calcd for C₁₈H₁₈Te: m/z = 364.0471 (M⁺). Found: m/z = 364.0467 (M⁺)

Bis-1-(phenyl)vinyl telluride **3b**: reddish orange oil. ¹H NMR (CDCl₃) δ = 5.84 (s, 2H, =CH), 6.30 (s, 2H, =CH), 7.22-7.27 (m, 6H, Ar), 7.41-7.46 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ = 127.4, 127.7, 127.8 (=CH₂), 128.2, 128.8, 142.6. HRMS (EI): Calcd for C₁₆H₁₄Te: m/z = 336.0158 (M⁺). Found: m/z = 336.0151 (M⁺).

Bis-1-(*p*-chlorophenyl)vinyl telluride **3c**: orange oil. ¹H NMR (CDCl₃) δ = 5.83 (s, 2H, =CH), 6.23 (s, 2H, =CH), 7.19 (d, 4H, *J* = 8Hz, Ar), 7.29 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 127.4, 128.1, 128.3 (=CH₂), 129.1, 133.7z, 141.0. HRMS (EI): Calcd for C₁₆H₁₂Cl₂Te: m/z = 403.9378 (M⁺). Found: m/z = 403.9370 (M⁺)

Bis-1-(*p*-bromophenyl)vinyl telluride **3d**: orange sold, mp 154-156 °C (dec). ¹H NMR (CDCl₃) δ = 5.84 (s, 2H, =CH), 6.23 (s, 2H, =CH), 7.22 (d, 4H, *J* = 8Hz, Ar), 7.35 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 122.0, 127.5, 128.3 (=CH₂), 129.5, 131.3, 141.6. HRMS (EI): Calcd for C₁₆H₁₂Br₂Te: m/z = 493.8348 (M⁺) Found: m/z = 493.8344 (M⁺)

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Bis-1-([1,1'-biphenyl]-4-yl)vinyl telluride **3f**: orange solid, mp 147-149 °C. ¹H NMR (CDCl₃) δ = 5.90 (s, 2H, =CH), 6.36 (s, 2H, =CH), 7.33 (t, 2H, *J* = 7 Hz, Ar), 7.42 (t, 4H, *J* = 7 Hz, Ar), 7.48 (d, 4H, *J* = 8 Hz, Ar), 7.50 (d, 4H, *J* = 8 Hz, Ar), 7.56 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 126.9, 127.0, 127.4 (=CH₂), 127.6, 128.3, 128.4, 128.8, 140.6, 140.7, 141.6. Anal. Calcd for C₂₈H₂₂Te: C, 52.23; H, 3.13. Found C, 51.96; H, 3.21.

Bis-1-(*o*-tolyl)vinyl telluride **3g**: reddish orange oil. ¹H-NMR (CDCl₃) δ = 2.22 (s, 6H, CH₃), 5.94 (d, *J* = 1 Hz, 2H, = CH), 6.05 d, *J* = 1 Hz, 2H, =CH), 7.03-7.17 (m, 8H, Ar). ¹³C NMR (CDCl₃) δ = 20.3, 125.5, 127.1, 127.6, 128.9, 129.5, 133.3, 134.8, 143.7. HRMS (EI): Calcd for C₁₈H₁₈Te: m/z = 364.0471 (M⁺). Found: m/z = 364.0473 (M⁺)

Reaction of bis(1-p-nitrophenyl)vinyl telluride with bromine

To a solution of telluride **3a** (145 mg, 0.4 mmol) in dichloromethane (6 mL) was added Br₂ (4.4 ml, 0.44 mmol, 0.1 M in dichloromethane) at rt. After being stirred for 2h, the reaction mixture was evaporated to give pale yellow oily crystals, which was chromatographed over silica gel by elution with hexane:dichloromethane (1:1) to afford tellurium dibromide **5a** (198 mg, 0.38 mmol).

Bis-1-(*p*-methylphenyl)vinyltellurium dibromide **5a**: Pale yellow solid: mp 69-70 °C. ¹H NMR (CDCl₃) δ = 2.40 (s, 6H, CH₃), 6.24 (d, 2H, *J* = 3 Hz, =CH), 6.37 (d, 2H, *J* = 3 Hz, =CH), 7.23 (d, 4H, *J* = 8 Hz, Ar), 7.36 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.4 (CH₃), 128.4, 129.3, 129.4 (=CH₂), 134.0, 140.1, 147.7. Anal. Calcd for C₁₈H₁₈Br₂Te: C; 41.44; H, 3.48. Found: C, 41.36; H, 3.58.

Bis-1-(*p*-bromophenyl)vinyltellurium dibromide **5d**: yellow solid, mp 123-125°C. ¹H NMR (400 MHz, CDCl₃) δ = 6.30 (d, 2H, *J* = 3 Hz, =CH), 6.39 (d, 2H, *J* = 3 Hz, =CH), 7.32 (d, 4H, *J* = 9 Hz, Ar), 7.56 (d, 4H, *J* = 9 Hz, Ar). ¹³C NMR (CDCl₃) δ = 124.5, 130.2, 130.6, 132.0, 135.7, 146.0. Anal. Calcd for C₁₆H₁₂Br₄Te: C, 29.50; H, 1.86. Found: C, 29.86; H, 1.84.

Bis-1-(*p*-nitrophenyl)vinyltellurium dibromide **5e**: Orange solid. mp 154-156 °C. ¹H NMR (CDCl₃) δ = 6.52 (d, 2H, *J* = 3 Hz, =CH), 6.56 (d, 2H, *J* = 3 Hz, =CH), 7.62 (d, 4H, *J* = 9 Hz, Ar), 8.31 (d, 4H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 124.0, 129.8, 132.4 (=CH₂), 142.7, 144.3, 148.7. Anal. Calcd for C₁₈H₁₈Br₂N₂O₄Te: C, 32.92; H, 2.07; N, 4.80. Found: C, 32.76; H, 2.25; N, 3.52.

Reaction of bis(1-*p*-tolyl)vinyl telluride 3a with 3 molar amount of bromine

To a solution of telluride 3a (108 mg, 0.3 mmol) in dichloromethane (8 mL) was added bromine (2 ml, 1.0 mmol, 0.5 M in dichloromethane) at room temperature. After being stirred for 2 h, the solution was evaporated to give orange oil, which was chromatographed over silica gel by elution with hexane:dichloromethtane afford (1:1)to 2-bromo-pmethylphenylethanone 6a (36 mg, 0.17 mmol) and (E)- and (Z)-1,2dibromo-p-methylstyrene 7 (1:13) (58 mg, 0.21 mmol).

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2-bromo-*p*-methylphenylethanone **6a**: pale yellow oily solid, mp 46-49°C (lit.¹² mp 51-52°C). ¹H NMR (CDCl₃) δ = 2.43 (s, 3H, CH₃), 4.42 (s, 2H, CH₂), 7.28 (d, 2H, *J* = 8 Hz, Ar), 7.88 (d, 2H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.7 (CH₃), 30.8 (CH₂), 129.1, 129.5, 131.6, 144.9 (Ar), 190.9 (C=O).

(*Z*)-1,2-dibromo-*p*-methylstyrene **7**: pale orange oil.¹³ ¹H NMR (CDCl₃) δ = 2.35 (s, 3H, CH₃), 7.00 (s, 1H, =CH), 7.15 (d, 2H, *J* = 8 Hz, Ar), 7.39 (d, 2H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.2 (CH₃), 107.9 (=CH), 127.2, 129.2, 131.2, 135.7, 139.6.

Reaction of bis(1-*p*-nitrophenyl)vinyl telluride 3e with 3 molar amount of bromine

To a solution of telluride 3e (127 mg, 0.3 mmol) in dichloromethane (8 mL) was added bromine (2 ml, 1.0 mmol, 0.5 M in dichloromethane) at rt. After being stirred for 2h, the reaction mixture was evaporated to give a pale yellow oil, which was chromatographed over silica gel by elution with hexane:dichloromethane (1:1)to afford 2-bromo-pnitrophenylethanone 6b (7 mg, 0.03 mmol) and 1-nitro-4-(1,1,2tribromoethyl)benzene 8 (151 mg, 0.39 mmol).

2-bromo-*p*-nitrophenylethanone **6b**: pale orange solid: mp 97-99 °C (lit.¹⁴ mp 99-100 °C). ¹H NMR (CDCl₃) δ = 4.46 (s, 2H, CH₂), 8.16 (d, 2H, *J* = 9 Hz, Ar), 8.35 (d, 2H, *J* = 9 Hz, Ar). ¹³C NMR (CDCl₃) δ = 30.0 (CH₂), 124.0, 130.1, 138.4, 150.8 (Ar), 189.9 (C=O).

1-Nitro-4-(1,1,2-tribromoethyl)benzene **8**: colorless solid, mp 68-69 °C. ¹H NMR (CDCl₃) δ = 4.64 (s, 2H, CH₂), 7.94 (d, 2H, *J* = 9 Hz, Ar), 8.24 (d, 2H, *J* = 9 Hz, Ar). ¹³C NMR (CDCl₃) δ = 44.7 (CH₂), 61.2 (q-C), 123.5, 128.6, 147.3, 148.1 (Ar). Anal. Calcd for C₈H₆Br₃NO₂: C, 25.85; H, 1.63; N, 3.77. Found: C, 25.49; H, 1.80; N, 3.52.

Reaction of bis(1-*p*-methylphenyl)vinyl telluride with 2trimethylsilylphenyl triflate (1.2 eq) in the presence of CsF

To a suspension of vinyl telluride **3a** (72 mg, 0.20 mmol) and CsF (182 mg, 1.2 mmol) in CH₃CN (1 mL) was added a solution of 2trimethylsilylphenyl triflate **9** (135 mg, 0.44 mmol) in CH₃CN (3 mL). After being stirred for 24 h at 50 °C, the reaction mixture was poured into water and extracted with dichloromethane (6 mL x 3). The combined extract was dried over Na₂SO₄, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane:dichloromethane (3:1) to give 1-(*p*methylphenyl)vinyl-2-((*E*)-4-methylstyryl)phenyl) telluride **10a** (4.5 mg, 0.01 mmol) and bis(2-((*E*)-4-methylstyryl)phenyl) telluride **11a** (8 mg, 0.016 mmol).

1-(*p*-methylphenyl)vinyl-2-((*E*)-4-methylstyryl)phenyl) telluride **10a**: orange oil. ¹H NMR (400 MHz, CDCl₃): δ 2.31 (s, 3H, CH₃), 2.36 (s, 3H, CH₃), 5.54 (s, 1H, =C<u>H</u>H), 6.28 (s, 1H, =C<u>H</u>H), 6.92 (d, 1H, *J* = 16 Hz, =CH), 7.02-7.10 (m, 3H, Ar), 7.16 (d, 2H, *J* = 8 Hz, Ar), 7.32 (t, 1H, *J* = 8 Hz, Ar), 7.37-7.43 (m, 4H, Ar), 7.46 (d, 1H, *J* = 16 Hz, =CH), 7.66 (d, 1H, *J* = 8 Hz, Ar), 7.86 (d, 1H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 21.1(CH₃), 21.3(CH₃), 118.8, 125.0, 125.5, 126.7, 127.5, 128.2, 128.9, 129.1, 129.1, 129.4, 131.0, 121.5, 134.5, 137.8, 138.0, 139.9, 140.5, 142.3. HRMS m/z Calcd for C₂₄H₂₂Te: 440.0784 (M⁺), Found:440.0774 (M⁺).

Reaction of bis(1-*p*-methylphenyl)vinyl telluride with Z-wew Article Online trimethylsilylphenyl triflate (3 eq) and water in the presence of 823 CsF

To a suspension of vinyl telluride 3a (72 mg, 0.20 mmol), water (7.2 μ L, 0.40 mmol) and CsF (273 mg, 1.8 mmol) in CH₃CN (1 mL) was added a solution of 2-trimethylsilylphenyl triflate 9 (180 mg, 0.60 mmol) in CH₃CN (3 mL). After being stirred for 12 h at 50 °C, the reaction mixture was poured into water and extracted with dichloromethane (6 mL x 3). The combined extract was dried over Na₂SO₄, filtered, and evaporated to give a pale brown oil, which was chromatographed over silica gel by elution with hexane:dichloromethane bis(2-((E)-4-(3:1) to give methylstyryl)phenyl) telluride 11a (67 mg, 0.13 mmol).

Bis(2-((*E*)-4-methylstyryl)phenyl) telluride **11a**: orange oil. ¹H NMR (CDCl₃) δ = 2.34 (s, 6H, CH₃), 6.90 (d, 2H, *J* = 16 Hz, =CH), 7.00 (t, 2H, *J* = 8 Hz, Ar), 7.11 (d, 4H, *J* = 8 Hz, Ar), 7.27 (t, 2H, *J* = 8 Hz, Ar), 7.35 (d, 4H, *J* = 8 Hz, Ar), 7.39 (d, 2H, *J* = 16 Hz, =CH), 7.60-7.67 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ = 21.4, 119.2, 125.9, 126.8, 128.4, 128.8, 129.5, 131.0, 131.4, 134.5, 137.9, 139.5, 142.2. HRMS m/z Calcd for C₃₀H₂₆Te: 516.1097 (M+), Found: 516.1084 (M⁺).

Bis(2-((*E*)-styryl)phenyl) telluride **11b**: orange oil. ¹H NMR (CDCl₃) δ = 6.82(d, 2H, *J* = 16 Hz, =CH), 6.89 (t, 2H, *J* = 8 Hz, Ar), 7.10-7.24 (m, 8H, Ar), 7.31-7.39 (m, 6H, Ar), 7.49-7.60 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ = 119.1, 125.9, 126.8, 127.9, 128.5, 128.7, 128.8, 131.4, 131.9, 137.2, 139.5, 142.0. HRMS m/z Calcd for C₂₈H₂₂Te: 488.0784 (M⁺), Found: 488.0783 (M⁺).

Bis(2-((*E*)-4-chlorostyryl)phenyl) telluride **11c**: pale yellow oil. ¹H NMR (CDCl₃) δ = 6.85 (d, 2H, *J* = 16 Hz, =CH), 7.05 (t, 2H, *J* = 8 Hz, Ar), 7.27 (d, 4H, *J* = 8 Hz, Ar), 7.30-7.35 (m, 6H, Ar), 7.38 (d, 2H, *J* = 16 Hz, =CH), 7.62 (d, 2H, *J* = 8 Hz, Ar), 7.67 (d, 2H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 119.1, 125.9, 127.9, 128.7, 128.8, 128.9, 130.0, 132.5, 133.5, 135.6, 139.5, 141.7. HRMS m/z Calcd for C₂₈H₂₀Cl₂Te: 556.0004 (M⁺), Found: 556.0023 (M⁺).

Bis(2-((*E*)-4-bromostyryl)phenyl) telluride **11d**: pale yellow solid (MeOH then hexane). mp 70-75 °C. ¹H NMR (CDCl₃) δ = 6.83 (d, 2H, *J* = 14 Hz, =CH), 7.04 (t, 2H, *J* = 8 Hz, Ar), 7.24-7.32 (m, 6H, Ar), 7.40-7.44 (m, 6H, Ar), 7.61 (d, 2H, *J* = 8 Hz, Ar), 7.66 (d, 2H, *J* = 8 Hz, Ar). ¹³C NMR (CDCl₃) δ = 119.1, 121.6,125.9, 128.1, 128.6, 128.8, 129.9, 131.7, 132.6, 136.0, 139.4, 141.6. Anal. Calcd for C₂₈H₂₀BrTe: Calc. C, 52.23; H, 3.13. Found C, 51.96; H, 3.21.

Bis(2-((*E*)-4-phenylstyryl)phenyl) telluride **11f**: pale yellow solid (MeOH then hexane), mp 228-230 °C. ¹H NMR (CDCl₃) δ = 6.98 (d, 2H, *J* = 14 Hz, =CH), 7.03 (t, 2H, *J* = 8 Hz, Ar), 7.30-7.34 (m, 4H, Ar), 7.42 (t, 4H, *J* = 8 Hz, Ar), 7.49-7.56 (m, 14H, Ar), 7.65-7.74 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ = 119.2, 125.8, 126.9, 127.2, 127.3, 127.3, 128.5, 128.8, 128.9, 130.8, 132.1, 136.2, 139.6, 140.6, 140.6, 142.0. Anal. Calcd for C₄₀H₃₀Te · H₂O: Calc. C, 73.20; H, 4.91. Found C, 72.75; H, 5.07.

Bis(2-((*E*)-2-methylstyryl)phenyl) telluride **11g**: orange oil. ¹H NMR (CDCl₃) δ = 2.37 (s, 6H, CH₃), 7.01 (t, 2H, *J* = 8 Hz, Ar), 7.16-7.09 (m, 8H, Ar), 7.33-7.25 (m, 4H, Ar), 7.48-7.43 (m, 2H, Ar), 7.66-7.59 (m, 4H, Ar). ¹³C NMR (CDCl₃) δ = 20.0, 119.1, 125.9, 126.2, 126.3, 127.8, 128.5, 128.8, 129.4, 130.4, 133.2, 135.9, 136.2, 139.3, 142.5. HRMS m/z Calcd for C₃₀H₂₆Te (M⁺): 516.1097, Found: 516.1103 (M⁺).

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

Reaction of acetophenone hydrazones with $TeCl_4$ in the presence of DBU followed by the addition of Cu powder gave divinyl tellurides. Reaction of divinyl tellurides with bromine or benzyne afforded the corresponding tellurium dibromides or (*E*)-2-alkenyl tellurides in good yields.

