Supporting Information

for

Acyclic Telluroiminium Salts: Isolation and Characterization

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General Considerations. When telluroamides were prepared, all glassware was wrapped in aluminum foil because of the characteristic photosensitivity of tellurium compounds. Laboratory lights were extinguished to minimize any illumination. Methyl triflate is corrosive and potentially toxic compounds. The handling should be carried out with great care.

IR spectra were obtained on a JASCO FT / IR 410 spectrophotometer. ^1H (399.7 MHz), ^{13}C (100.4 MHz), ^{19}F (376.0 MHz), and ^{125}Te (126.0 MHz) NMR spectra were measured on a JEOL *a*-400 spectrometer. The ^1H and ^{13}C chemical shifts are reported in δ values with reference to Me_4Si and CDCl_3 as internal standards, respectively. The ^{19}F and ^{125}Te chemical shifts are expressed in δ values deshielded with respect to CF_3COOH and Me_2Te as external standards, respectively. All spectra were acquired in the proton-decoupled mode. Mass (MS) and high-resolution mass spectra (HRMS) were measured on a JEOL GC-mate II mass spectrometer (FAB) or a JEOL JMS-700 spectrometer (EI and FAB). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Anhydrous diethyl ether (Et_2O) and tetrahydrofuran (THF) were purchased from Kanto Chemical Co., Inc. Dichloromethane (CH_2Cl_2) was distilled over diphosphorus pentaoxide after refluxing for 5 h. Hexane was distilled from sodium metal. All solvents were degassed by bubbling with argon or by the freeze-pump-thaw method. Tellurium was purchased from Nacalai Tesque, Inc. and finely crushed prior to use. Methyl trifluoromethanesulfonate (methyl triflate) was purchased from Aldrich Chemical Co., Inc., and used without further purification. Telluroamides were prepared as described in the literature.^{1,2} Lithium aluminum hydride (LiAlH_4) was purchased from Nacalai Tesque, Inc. and Wako Pure Chemical Industry Co., Ltd., and used without further purification. Silica gel used in column chromatography was silica gel 60N (Spherical, Neutral, 100–210 μm) and Florisil used in column chromatography was Florisil (150–250 μm) from Kanto Chemical Co., Inc.

Telluroamides 1

***N,N*-Dimethyl 4-Methoxybenzenecarbotelluroamide (1b).**² To an Et_2O solution (15 mL) of *N,N*-dimethyl 4-methoxybenzamide (0.895 g, 5.0 mmol) was added oxalyl chloride (0.45 mL, 5.0 mmol) at 0 $^\circ\text{C}$, and the mixture was stirred at this temperature for 0.5 h. The reaction mixture was further stirred at room

temperature overnight. On the other hand, to a THF suspension (15 mL) of tellurium (0.638 g, 5.0 mmol) was added LiAlH_4 (0.19 g, 5.0 mmol) at 0 $^\circ\text{C}$, and this was stirred at the same temperature for 1 h. To the white Et_2O suspension was then cannulated the gray THF suspension at 0 $^\circ\text{C}$, and the

mixture was stirred at room temperature for 3 h. The mixture was passed through a glass filter (G4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Florisil, CH₂Cl₂) to give telluroamide **1b** (0.623 g, 43%) as a wine-red solid: mp 67.0–70.5 °C; IR (Nujol) 1626, 1601, 1571, 1531, 1504, 1438, 1393, 1296, 1247, 1175, 1129, 1110, 1082, 1026, 831, 593 cm⁻¹; ¹H NMR (CDCl₃) δ 3.07 (s, 3H, CH₃), 3.809 (s, 3H, CH₃), 3.812 (s, 3H, CH₃), 6.83 (d, *J* = 8.8 Hz, 2H, Ar), 7.29 (d, *J* = 8.8 Hz, 2H, Ar); ¹³C NMR (CDCl₃) δ 44.6, 55.3, 55.4 (CH₃), 113.2, 125.3, 144.7, 159.6 (Ar), 197.6 (C=Te, ¹*J*_{C=Te} = 553.8 Hz); ¹²⁵Te NMR (CDCl₃) δ 915.9 (s, 50 °C); δ 884.6 (brn, rt); MS (EI) 293 (M⁺, ¹³⁰Te); HRMS (EI) calcd for C₁₀H₁₃NO¹³⁰Te (M⁺) 293.0059, found: 293.0065.

***N,N*-Dimethyl 4-Dimethylaminobenzenecarbotelluroamide (1c).**² Telluroamide **1c** was prepared by utilizing the procedure described for **1b**. The title compound was obtained in 41% yield as a wine-red solid: mp 64.5–69.0 °C; IR (Nujol) 1607, 1511, 1284, 1230, 1186, 1121, 1084, 946, 903, 813, 765 cm⁻¹; ¹H NMR (CDCl₃) δ 2.89 (s, 6H, N(CH₃)₂), 3.07 (s, 3H, NCH₃), 3.72 (s, 3H, NCH₃), 6.49 (d, *J* = 8.6 Hz, 2H, Ar), 7.23 (d, *J* = 8.6 Hz, 2H, Ar); ¹³C NMR (CDCl₃) δ 40.0 (N(CH₃)₂), 44.6, 55.5 (NCH₃), 110.2, 126.3, 139.0, 150.2 (Ar), 196.9 (C=Te, *J*_{C=Te} = 545.5 Hz); ¹²⁵Te (CDCl₃) δ 849.2 (s, 50 °C); δ 818.5 (brn, rt); MS (EI) 306 (M⁺, ¹³⁰Te); HRMS (EI) calcd for C₁₁H₁₆N₂¹³⁰Te (M⁺) 306.0376, found 306.0357.

***N,N*-Dimethyl 4-Bromobenzenecarbotelluroamide (1d).**² Telluroamide **1d** was prepared by utilizing the procedure described for **1b**. The title compound was obtained in 26% yield as a wine red-solid: mp 116.5–129.0 °C; IR (Nujol) 1578, 1525, 1389, 1254, 1130, 1103, 1007, 906, 870, 817 cm⁻¹; ¹H NMR (CDCl₃) δ 2.93 (s, 3H, NCH₃), 3.73 (s, 3H, NCH₃), 7.11 (d, *J* = 8.8 Hz, 2H, Ar), 7.22 (d, *J* = 8.8 Hz, 2H, Ar); ¹³C NMR (CDCl₃) δ 44.6, 55.0 (NCH₃), 122.3, 124.5, 131.0, 150.8 (Ar), 196.4 (C=Te, *J*_{C=Te} = 559.7 Hz); ¹²⁵Te (CDCl₃) δ 978.7 (s, 50 °C); MS (EI) 341 (M⁺, ¹³⁰Te); HRMS (EI) calcd for C₉H₁₀BrN¹³⁰Te (M⁺) 340.9059, found 340.9032.

***N,N*-Di-2-propenyl Benzenecarbotelluroamide (1e).**² Telluroamide **1e** was prepared by utilizing the procedure described for **1b**. The title compound was obtained in 45% yield as a wine-red oil: IR (neat) 3079, 2985, 1701, 1638, 1494, 1477, 1410, 1257, 1202, 1156, 1028, 991, 756, 698, 657 cm⁻¹; ¹H NMR (CDCl₃) δ 3.89 (d, *J*

= 5.6 Hz, 2H, NCH₂), 4.89 (d, *J* = 6.0 Hz, 2H, NCH₂), 5.10 (d, *J* = 17.2 Hz, 1H, CH₂=CH), 5.21 (d, *J* = 10.0 Hz, 1H, CH₂=CH), 5.32 (d, *J* = 17.2 Hz, 1H, CH₂=CH), 5.35 (s, 1H, 5.83 CH₂=CH), 5.65 (ddt, *J* = 7.8, 10.1, 17.2 Hz, 1H, CH₂=CH), 6.01 (ddt, *J* = 7.8, 10.1, 17.2 Hz, 1H, CH₂=CH), 7.16–7.26 (m, 5H, Ar); ¹³C NMR (CDCl₃) δ 55.6, 64.0 (NCH₂), 120.0, 120.2 (CH₂=CH), 122.1, 127.6, 128.1 (Ar), 129.8 (CH₂=CH; The signals due to two olefinic carbon atoms were overlapped.), 152.0 (Ar), 200.2 (C=Te, ¹*J*_{C=Te} = 561.6 Hz); ¹²⁵Te NMR (CDCl₃) δ 957.3 (s, 50 °C); δ 923.2 (brm, rt); MS (EI) 315 (M⁺, ¹³⁰Te); HRMS (EI) calcd for C₁₃H₁₅N¹³⁰Te (M⁺) 315.0267, found 315.0282.

***N*-(Phenylmethyl) Benzenecarbotelluroamide (1f).**¹ To a THF suspension (15 mL) of tellurium (0.459 g, 3.6 mmol) was added LiAlH₄ (0.138 g, 3.6 mmol) at 0 °C, and this was stirred at the temperature for 1 h. Then, to an Et₂O suspension (15 mL)

of [C(Z)]-*N*-(phenylmethyl)-benzenecarboximidoseleonic acid methyl ester trifluoromethanesulfonate¹ (1.315g, 3.0 mmol) was cannulated the gray THF suspension at 0 °C, and the mixture was stirred at room temperature for 3 h. The mixture was passed through a glass filter (G4), and the solvent was removed under reduced pressure. The residue was purified by column chromatography (Florisil, CH₂Cl₂) to give telluroamide **1f** (0.777 g, 80%) as a chocolate viscous oil: IR (neat) 3026, 2917, 2849, 1607, 1524, 1493, 1443, 1384, 1341, 1027, 693 cm⁻¹; ¹H NMR (CDCl₃) δ 4.93 (br, 2H, CH₂), 7.31 (t, *J* = 7.2 Hz, 2H, Ar), 7.44–7.52 (m, 6H, Ar), 7.68 (d, *J* = 7.2 Hz, 2H, Ar), 8.94 (br, 1H, NH); ¹³C NMR (CDCl₃) δ 60.5 (CH₂), 125.9, 128.1, 128.2, 128.6, 130.4, 149.6 (Ar; The signals due to several aromatic carbon atoms were overlapped), 198.3 (C=Te, ¹*J*_{C=Te} = 567.5 Hz); ¹²⁵Te NMR (CDCl₃) δ 668.4 (s, 50 °C); δ 710.3 (brm, rt); MS (EI) 325 (M⁺, ¹³⁰Te); HRMS (EI) calcd for C₁₄H₁₃N¹³⁰Te (M⁺) 325.0110, found 325.0098.

***N*-(4-Methylphenyl)methyl 2-Phenyl-4-pentenetelluroamide (1h).**¹

Telluroamide **1h** was prepared by utilizing the procedure described for **1f**.

The title compound was obtained in 23% yield as a yellow solid: mp 98.5–101.5 (dec.); IR (KBr) 2861, 1636, 1616, 1541, 1525, 1453, 1123,

907, 802, 702 cm⁻¹; ¹H NMR (CDCl₃) δ 2.25 (s, 3H, CH₃), 2.70 (dt, *J* = 7.6, 14.6 Hz, 1H, CH₂=CHCH₂), 3.20 (dt, *J* = 6.6, 14.6 Hz, 1H, CH₂=CHCH₂), 4.16 (dd, *J* = 6.0, 8.8 Hz, 1H, PhCH), 4.57 (dd, *J* = 5.3, 16.1 Hz, 1H, CH₂Ar), 4.63 (dd, *J* = 5.3, 16.1 Hz, 1H, CH₂Ar), 4.90 (dq, *J* = 1.4, 10.2 Hz, 1H, CH₂=CHCH₂), 5.01 (dq, *J* = 1.4, 17.2 Hz, 1H, CH₂=CHCH₂), 5.66 (ddt, *J* = 6.4, 10.2, 17.2 Hz, 1H, CH₂=CHCH₂), 6.97 (d, *J* = 8.0 Hz, 2H, Ar), 7.05 (d, *J* = 8.0 Hz, 2H, Ar), 7.20–7.29 (m, 5H, Ar),

8.21 (br, 1H, NH); ^{13}C NMR (CDCl_3) δ 21.1 (CH_3), 40.2 ($\text{CH}_2=\text{CHCH}_2$), 60.1 (CH_2Ar), 69.3 (PhCH), 117.5 ($\text{CH}_2=\text{CHCH}_2$), 127.96, 127.98, 128.4, 129.1, 129.6, 131.2 (Ar), 134.9 ($\text{CH}_2=\text{CHCH}_2$), 137.5, 138.3 (Ar), 206.3 ($\text{C}=\text{Te}$, $^1J_{\text{C}=\text{Te}} = 579.6$ Hz); ^{125}Te NMR (CDCl_3) δ 589.5 (s, 50 °C); δ 561.2 (s, rt); MS (EI) 393 (M^+ , ^{130}Te); HRMS (EI) calcd for $\text{C}_{19}\text{H}_{21}\text{N}^{130}\text{Te}$ (M^+) 393.0736, found 393.0749.

Telluroiminium Salts 2

Dimethyl-*N*-(1-methyltellurenyl-1-phenylmethylidene)aminium Trifluoromethanesulfonate (2a). To a CH_2Cl_2 (5 mL) solution of telluroamide **1a** (0.339 g, 1.3 mmol) was added methyl triflate (0.150 mL, 1.3 mmol) at room temperature.

The wine-red solution rapidly changed to a greenish yellow suspension with the precipitation of a small amount of black tellurium. After stirring for 30 s at room temperature, black tellurium was filtered off, and the resulting solution was concentrated in vacuo. The residue was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give telluroiminium salt **2a** (0.508 g, 92%) as a light lemon-yellow solid: mp 53.5–56.0 °C; IR (KBr) 2963, 1604, 1445, 1409, 1262, 1225, 1154, 1031, 801, 766, 703, 638 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.77 (s, 3H, TeCH_3), 3.51 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 7.33 (d, $J = 7.6$ Hz, 2H, Ar), 7.47–7.53 (m, 1H, Ar), 7.59–7.63 (m, 2H, Ar); ^{13}C NMR (CDCl_3) δ –3.8 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 177.2$ Hz), 48.4, 50.7 (CH_3), 120.6 (q, $^1J_{\text{C}-\text{F}} = 319.9$ Hz, CF_3), 124.7, 129.6, 131.6, 135.7 (Ar), 196.5 (CTe , $^1J_{\text{C}-\text{TeMe}} = 464.6$ Hz); ^{19}F NMR (CDCl_3) δ –78.7; ^{125}Te NMR (CDCl_3) δ 682.7 (s, 50 °C); δ 676.9 (s, rt); MS (FAB+) m/z 278 ($\text{M}^+ - \text{OTf}$, ^{130}Te). Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}_3\text{STe}$: C, 31.09; H, 3.32; N, 3.30. Found: C, 31.17; H, 3.28; N, 3.13.

Dimethyl-*N*-(1-methyltellurenyl-1-(4-methoxyphenyl)methylidene)-

aminium Trifluoromethanesulfonate (2b). The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give **2b** as a olive viscous oil: IR (neat) 2927, 1603, 1509, 1460, 1412, 1256, 1225, 1158, 1030, 638 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.84

(s, 3H, TeCH_3), 3.53 (s, 3H, NCH_3), 3.78 (s, 3H, NCH_3), 3.88 (s, 3H, CH_3), 7.08 (d, $J = 8.8$ Hz, 2H, Ar), 7.31 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3) δ –3.7 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 175.8$ Hz), 48.4, 50.9, (NCH_3), 55.6 (OCH_3), 115.0 (Ar), 120.6 (q, $^1J_{\text{C}-\text{F}} = 319.9$ Hz, CF_3), 127.6, 127.8, 162.1 (Ar), 196.2 (CTe , $^1J_{\text{C}-\text{TeMe}} = 459.2$ Hz); ^{19}F NMR (CDCl_3) δ –78.8; ^{125}Te NMR (CDCl_3) δ 679.0 (s, 50 °C); δ 672.7 (s, rt); MS (FAB+) m/z 330 ($\text{M}^+ - \text{OTf}$, ^{130}Te); HRMS (FAB+) calcd for $\text{C}_{11}\text{H}_{16}\text{F}_3\text{NO}^{130}\text{Te}$ ($\text{M}^+ - \text{OTf}$) 308.0289, found 308.0298.

Dimethyl-*N*-(1-methyltellurenyl-1-(4-dimethylaminophenyl)methylidene)aminium Trifluoromethanesulfonate (2c).

The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give **2c** as an orange viscous oil: IR (neat) 2920, 1603, 1525, 1383, 1261, 1156, 1029, 637 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.93 (s, 3H, TeCH_3), 3.10 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.60 (s, 3H, NCH_3), 3.79 (s, 3H, NCH_3), 6.75 (d, $J = 8.8$ Hz, 2H, Ar), 7.27 (d, $J = 8.8$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3) δ -3.7 (TeCH_3), 40.0 ($\text{N}(\text{CH}_3)_2$), 48.3, 51.3 (NCH_3), 111.4 (Ar), 120.8 (q, $J = 319.4$ Hz, CF_3), 121.7, 129.6, 152.7 (Ar), 194.6 (CTe, $J_{\text{C-TeMe}} = 446.1$ Hz); ^{19}F NMR (CDCl_3) δ -78.8; ^{125}Te NMR (CDCl_3) δ 644.6 (s, 50 $^\circ\text{C}$); δ 636.2 (s, rt); MS (FAB+) m/z 321 ($\text{M}^+ - \text{OTf}$, ^{130}Te); HRMS (FAB+); calcd for $\text{C}_{12}\text{H}_{19}\text{N}_2^{130}\text{Te}$ ($\text{M}^+ - \text{OTf}$) 321.0605, found 321.0589.

Dimethyl-*N*-(1-methyltellurenyl-1-(4-bromophenyl)methylidene)aminium Trifluoromethanesulfonate (2d).

The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give **2d** as a pale olive solid: mp 131.5–134.0 $^\circ\text{C}$; IR (KBr) 2927, 1584, 1487, 1458, 1414, 1262, 1227, 1145, 1072, 1029, 1011, 817, 634 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.82 (s, 3H, TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 176.8$ Hz), 3.51 (s, 3H, NCH_3), 3.79 (s, 3H, NCH_3), 7.29 (d, $J = 8.6$ Hz, 2H, Ar), 7.75 (d, $J = 8.6$ Hz, 2H, Ar); ^{13}C NMR (CDCl_3) δ -3.6 (TeCH_3), 48.7, 51.0 (NCH_3), 120.7 (q, $J = 320.4$ Hz, CF_3), 126.4, 126.7, 133.0, 134.5 (Ar), 195.4 (CTe, $J_{\text{C-TeMe}} = 467.0$ Hz); ^{19}F NMR (CDCl_3) δ -78.7; ^{125}Te NMR (CDCl_3) δ 691.4 (s, 50 $^\circ\text{C}$); δ 684.7 (s, rt); MS (FAB+) m/z 356 ($\text{M}^+ - \text{OTf}$, ^{130}Te); HRMS (FAB+) calcd for $\text{C}_{10}\text{H}_{13}\text{BrN}^{130}\text{Te}$ ($\text{M}^+ - \text{OTf}$) 355.9288, found 355.9294. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{BrF}_3\text{NO}_3\text{STe}$: C, 26.22; H, 2.60; N, 2.78. Found: C, 26.21; H, 2.58; N, 2.76.

Di-2-propenyl-*N*-(1-methyltellurenyl-1-phenylmethylidene)aminium Trifluoromethanesulfonate (2e).

The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give **2e** as a bright pale yellow solid: mp 79.0–80.5 $^\circ\text{C}$; IR (KBr) 3215, 3124, 3010, 1606, 1517, 1439, 1281, 1240, 1162, 1030, 638 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.78 (s, 3H, TeCH_3), 4.38 (d, $J = 6.4$ Hz, 2H, NCH_2), 4.69 (d, $J = 6.0$ Hz, 2H, NCH_2), 5.30 (d, $J = 17.2$ Hz, 1H, $\text{CH}_2=\text{CH}$), 5.42 (d, $J = 10.0$ Hz, 1H, $\text{CH}_2=\text{CH}$), 5.55 (d, $J = 17.2$ Hz, 1H, $\text{CH}_2=\text{CH}$), 5.61 (d, $J = 10.4$ Hz, 1H, $\text{CH}_2=\text{CH}$), 5.77 (ddt, $J = 6.4, 10.4, 16.8$ Hz, 1H, $\text{CH}_2=\text{CH}$), 5.97 (ddt, $J = 6.4, 10.4, 17.2$ Hz, 1H, $\text{CH}_2=\text{CH}$), 7.30–7.34 (m, 2H, Ar), 7.52–7.55 (m, 1H, Ar), 7.60–7.64 (m, 2H, Ar); ^{13}C NMR (CDCl_3) δ -2.8 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 181.8$ Hz), 61.7, 63.7 (NCH_2), 120.7 (q, $^1J_{\text{C-F}} = 320.4$ Hz, CF_3),

123.3, 123.9 ($\text{CH}_2=\text{CH}$), 124.6, 126.2, 128.6, 129.7 (Ar), 131.9, 135.8 ($\text{CH}_2=\text{CH}$), 201.0 (CTe, $^1J_{\text{C-TeMe}}=477.8$ Hz); ^{19}F NMR (CDCl_3) δ -78.7 ; ^{125}Te NMR (CDCl_3) δ 729.2 (s, 50 °C); δ 723.0 (s, rt); MS (FAB+) m/z 330 ($\text{M}^+ - \text{OTf}$, ^{130}Te). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NO}_3\text{STe}$: C, 37.77; H, 3.80; N, 2.94. Found: C, 37.69; H, 3.64; N, 2.92.

[C(Z)]-N-(Phenylmethyl)benzenecarboximidotelluroic Acid Methyl Ester Tri-fluoromethanesulfonate (2f). The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$

(80/1) to give **2f** as a yellow solid: mp 119.0–122.0 °C; IR (KBr) 3063, 2976, 1591, 1577, 1499, 1417, 1287, 1223, 1161, 1027, 770, 743, 702, 636 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.94 (s, 3H, TeCH_3), 5.00 (s, 2H, CH_2), 7.35–7.48 (m, 7H, Ar), 7.53 (t, $J = 7.2$ Hz, 2H, Ar), 7.61 (t, $J = 7.2$ Hz, 1H, Ar), 12.7 (br, 1H, NH); ^{13}C NMR (CDCl_3) δ -4.6 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 172.6$ Hz), 58.0 (CH_2), 120.2 (q, $^1J_{\text{C-F}} = 318.0$ Hz, CF_3), 128.1, 128.7, 129.3, 129.5, 129.7, 131.9, 134.2, 135.6 (Ar), 199.2 (CTe, $^1J_{\text{C-TeMe}} = 473.9$ Hz); ^{19}F NMR (CDCl_3) δ -78.9 ; ^{125}Te NMR (CDCl_3) δ 556.0 (s, 50 °C); δ 550.1 (s, rt); MS (FAB+) 340 ($\text{M}^+ - \text{OTf}$, ^{130}Te). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{NO}_3\text{STe}$: C, 39.46; H, 3.31; N, 2.88. Found: C, 39.65; H, 3.33; N, 2.85.

Dimethyl-N-(1-methyltellurenyl-2-phenyl-4-pentenylidene) Trifluoromethanesulfonate (2g). The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to

give **2g** as a yellow oil: IR (neat) 3030, 1641, 1599, 1450, 1418, 1263, 1225, 1155, 1031, 638 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.31 (s, 3H, TeCH_3), 2.89 (dt, $J = 7.2$, 14.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2$), 3.01 (dt, $J = 7.2$, 14.8 Hz, 1H, $\text{CH}_2=\text{CHCH}_2$), 3.79 (s, 6H, NCH_3), 4.64 (t, $J = 7.2$ Hz, 1H, PhCH_2), 5.19 (d, $J = 10.6$ Hz 1H, $\text{CH}_2=\text{CH}$), 5.25 (d, $J = 10.6$ Hz 1H, $\text{CH}_2=\text{CH}$), 5.86 (ddt, $J = 7.2$, 10.6, 17.2 Hz, 1H, $\text{CH}_2=\text{CH}$) 7.30–7.33 (m, 2H Ar), 7.38–7.39 (m, 3H, Ar); ^{13}C NMR (CDCl_3) δ -5.7 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 179.9$ Hz), 35.5 ($\text{CH}_2=\text{CHCH}_2$), 47.3, 54.1 (NCH_3), 54.9 (PhCH_2), 119.6 ($\text{CH}_2=\text{CH}$), 120.7 (q, $^1J_{\text{C-F}} = 320.4$ Hz, CF_3), 128.6, 129.1, 129.2, 132.3, 134.1 (Ar, $\text{CH}_2=\text{CH}$), 198.3 (CTe, $^1J_{\text{C-TeMe}} = 483.6$ Hz); ^{19}F NMR (CDCl_3) δ -78.8 ; ^{125}Te NMR (CDCl_3) δ 584.1 (brm, 50 °C); MS (FAB+) m/z 332 ($\text{M}^+ - \text{OTf}$, ^{130}Te); HRMS (FAB+) calcd for $\text{C}_{14}\text{H}_{20}\text{N}^{130}\text{Te}$ ($\text{M}^+ - \text{OTf}$) 332.0653, found 332.0643.

(1Z)-N-[(4-Methylphenyl)methyl]-2-phenyl-4-pentenimidotelluroic Acid Methyl Ester Trifluoromethanesulfonate (2h). The crude product was washed with $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ (80/1) to give **2h** as an olive viscous oil: IR

(neat) 3191, 3086, 2925, 2873, 1642, 1578, 1517, 1453, 1281, 1237, 1168, 1029, 803, 759, 701, 637 cm^{-1} ; **Z-isomer** ^1H NMR (CDCl_3) δ 2.25 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.86 (dt, $J = 6.7, 14.7$ Hz, 1H, $\text{CH}_2=\text{CHCH}_2$), 3.00 (dt, $J = 7.8, 14.7$ Hz, 1H, $\text{CH}_2=\text{CHCH}_2$), 4.49 (t, $J = 7.8$ Hz, 1H, PhCH), 4.88 (dd, $J = 5.6, 15.4$ Hz 2H, CH_2Ar), 5.06 (d, $J = 10.4$ Hz 1H, $\text{CH}_2=\text{CHCH}_2$), 5.15 (dd, $J = 0.8, 16.8$ Hz 1H, $\text{CH}_2=\text{CHCH}_2$), 5.68 (ddt, $J = 6.7, 10.4, 16.8$ Hz, 1H, $\text{CH}_2=\text{CHCH}_2$) 7.12 (d, $J = 7.8$ Hz, 2H, Ar), 7.21 (d, $J = 7.8$ Hz, 2H, Ar), 7.25–7.27 (m, 2H, Ar), 7.30–7.38 (m, 3H, Ar), 12.4 (br, 1H, NH); ^{13}C NMR (CDCl_3) δ –7.6 (TeCH_3 , $^1J_{\text{CH}_3-\text{Te}} = 180.4$ Hz), 21.2 (CH_3), 37.4 ($\text{CH}_2=\text{CHCH}_2$), 57.4 (CH_2Ar), 57.6 (PhCH), 118.8 ($\text{CH}_2=\text{CHCH}_2$), 120.4 (q, $^1J_{\text{C-F}} = 319.5$ Hz, CF_3), 127.8, 127.8, 128.7, 128.7, 129.6, 129.9 (Ar), 132.7 ($\text{CH}_2=\text{CHCH}_2$), 135.2, 139.3 (Ar), 201.9 (CTe, $^1J_{\text{C-TeMe}} = 487.5$ Hz); ^{19}F NMR (CDCl_3) δ –78.7; ^{125}Te NMR (CDCl_3) δ 581.9 (s, rt); **E-isomer** ^1H NMR (CDCl_3) δ 11.6 (br, 1H, NH); ^{125}Te NMR (CDCl_3) δ 606.0; MS (FAB+) m/z 408 ($\text{M}^+ - \text{OTf}$, ^{130}Te); HRMS (FAB+) calcd for $\text{C}_{20}\text{H}_{24}\text{N}^{130}\text{Te}$ ($\text{M}^+ - \text{OTf}$) 408.0966, found 408.0971.

X-ray Structure Analysis of Telluroiminium Salt 2a. The measurement of telluroiminium salt **2a** was carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069$ Å). The structure was solved and refined using the teXsan[®] crystallographic software package of Molecular Structure Corporation. The X-ray quality crystal was obtained by slow diffusion of Et_2O (0.8 mL) into a CH_2Cl_2 solution (0.4 mL) of **2a** (0.020 g). The crystal was cut from the grown crystals and mounted on a glass fiber. The structure was solved by direct method using SIR92³ and expanded using DIRDIF94.⁴ Scattering factors for neutral atoms were from Cromer and Waber,⁵ and anomalous dispersion effects⁶ were used. The function minimized was $\sum w(F_o^2 - F_c^2)^2$, and the weighting scheme employed was $w = [\sigma_c^2(F_o^2) + (p(\max(F_o^2, 0) + 2F_c^2/3)^2)]^{-1}$. A full-matrix least-squares refinement was executed with non-hydrogen atoms being anisotropic. The final least square cycle included fixed hydrogen atoms at calculated positions of which each isotropic thermal parameter was set to 1.2 times of that of the connecting atom.

Figure S1. ORTEP drawing of telluroiminium salt **2a**

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{11}H_{14}F_3NO_3STe$
Formula Weight	424.89
Crystal Color, Habit	Yellow, Prism
Crystal Dimensions	0.31 X 0.26 X 0.14 mm
Crystal System	monoclinic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2θ range)	4899 (6.8 - 55.0°)
Lattice Parameters	$a = 7.431(3) \text{ \AA}$

	$b = 17.951(7) \text{ \AA}$
	$c = 11.478(4) \text{ \AA}$
	$\beta = 95.736(5)^\circ$
	$V = 1523(1) \text{ \AA}^3$
Space Group	$P2_1/n$ (#14)
Z value	4
D_{calc}	1.852 g/cm^3
F_{000}	824.00
μ (MoK α)	21.27 cm^{-1}

B. Intensity Measurements

Diffractometer	Rigaku/MSM Mercury CCD
Radiation	MoK α ($\lambda = 0.71070 \text{ \AA}$)
	graphite monochromated
Temperature	-80.0°C
Voltage, Current	40 kV, 200 mA
Collimator Size	0.5 mm
Detector Aperture	70 mm x 70 mm
Data Images	744 exposures
ϕ oscillation Range ($\chi = 0.0, \omega = 0.0$)	$-80.0 - 100.0^\circ$
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.06°
Detector Position	44.96 mm
ω oscillation Range ($\chi = 90.0, \phi = 0.0$)	$-20.0 - 28.0^\circ$
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.06°
Detector Position	44.96 mm
ω oscillation Range ($\chi = 90.0, \phi = 90.0$)	$-20.0 - 28.0^\circ$
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.06°
Detector Position	44.96 mm
ω oscillation Range ($\chi = 90.0, \phi = 180.0$)	$-20.0 - 28.0^\circ$
Exposure Rate	10.0 sec./°
Detector Swing Angle	20.06°

Detector Position	44.96 mm
ω oscillation Range ($\chi = 90.0$, $\phi = 270.0$)	-20.0 -28.0°
Exposure Rate	10.0 sec./ $^\circ$
Detector Swing Angle	20.06°
Detector Position	44.96 mm
$2\theta_{\text{max}}$	55.0°
No. of Reflections Measured	Total: 12258
	Unique: 3472 ($R_{\text{int}} = 0.030$)
Corrections	Lorentz-polarization
	Absorption
	(trans. factors: 0.4719–0.5822)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares
Function Minimized	$\Sigma w(\text{Fo}^2 - \text{Fc}^2)^2$
Least Squares Weights	$1/\sigma^2(\text{Fo}^2)$
p-factor	0.0500
Anomalous Dispersion	All non-hydrogen atoms
No. of Reflections (All, $2\theta < 54.97^\circ$)	3472
No. Variables	181
Reflection/Parameter Ratio	19.18
Residuals: R; Rw	0.052; 0.107
Residuals: R1	0.038
No. of Reflections to calc R1	3080
Goodness of Fit Indicator	1.31
Max Shift/Error in Final Cycle	0.002
Maximum peak in Final Diff. Map	$0.92 \text{ e}\text{\AA}^{-3}$
Minimum peak in Final Diff. Map	$-0.52 \text{ e}\text{\AA}^{-3}$

Table S1. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B _{eq}
Te(1)	0.68428(3)	0.31890(1)	1.07376(2)	2.754(7)
S(1)	0.6438(1)	0.13634(5)	0.78597(8)	2.69(2)
F(1)	0.6985(5)	−0.0079(1)	0.7974(3)	5.94(8)
F(2)	0.8869(6)	0.0553(2)	0.9096(3)	6.60(9)
F(3)	0.9045(4)	0.0514(2)	0.7262(3)	5.62(8)
O(1)	0.7658(5)	0.1973(2)	0.8085(4)	5.49(9)
O(2)	0.5709(4)	0.1301(2)	0.6661(3)	4.63(8)
O(3)	0.5152(5)	0.1262(2)	0.8680(3)	6.0(1)
N(1)	0.3322(4)	0.2422(2)	1.0078(2)	2.41(6)
C(1)	0.4336(4)	0.2974(2)	0.9797(3)	2.11(6)
C(2)	0.7670(6)	0.3970(3)	0.9511(4)	3.86(9)
C(3)	0.3697(4)	0.3484(2)	0.8826(3)	2.06(6)
C(4)	0.4140(5)	0.3354(2)	0.7700(3)	2.71(7)
C(5)	0.3536(6)	0.3840(2)	0.6803(3)	3.07(8)
C(6)	0.2525(5)	0.4458(2)	0.7023(3)	3.06(8)
C(7)	0.2099(6)	0.4590(2)	0.8155(4)	3.40(8)
C(8)	0.2677(5)	0.4113(2)	0.9047(3)	2.98(8)
C(9)	0.1541(5)	0.2248(2)	0.9449(4)	3.39(8)
C(10)	0.3913(6)	0.1906(2)	1.1037(4)	3.27(9)
C(11)	0.7902(5)	0.0553(2)	0.8069(3)	2.87(7)
H(1)	0.8849	0.4148	0.9769	4.7
H(2)	0.7698	0.3733	0.8769	4.7
H(3)	0.6848	0.4374	0.9437	4.7
H(4)	0.4851	0.2935	0.7540	3.3
H(5)	0.3823	0.3744	0.6029	3.7
H(6)	0.2123	0.4790	0.6408	3.7
H(7)	0.1399	0.5015	0.8313	4.1
H(8)	0.2379	0.4210	0.9818	3.6
H(9)	0.1252	0.2616	0.8864	4.1
H(10)	0.0652	0.2254	0.9990	4.1
H(11)	0.1581	0.1773	0.9100	4.1
H(12)	0.3090	0.1505	1.1045	4.0
H(13)	0.3967	0.2165	1.1766	4.0
H(14)	0.5086	0.1720	1.0932	4.0

$$B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb^*)\cos \gamma + 2U_{13}(aa*cc^*)\cos \beta + 2U_{23}(bb*cc^*)\cos \alpha)$$

Table S2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Te(1)	0.0300(2)	0.0419(2)	0.0308(2)	−0.00295(9)	−0.00616(10)	0.00604(9)
S(1)	0.0303(4)	0.0336(5)	0.0373(5)	0.0049(3)	−0.0006(3)	−0.0044(3)
F(1)	0.069(2)	0.036(1)	0.120(3)	−0.003(1)	0.001(2)	−0.003(1)
F(2)	0.114(3)	0.073(2)	0.055(2)	0.038(2)	−0.038(2)	−0.003(1)
F(3)	0.054(2)	0.081(2)	0.082(2)	0.030(2)	0.027(1)	0.011(2)
O(1)	0.057(2)	0.036(2)	0.109(3)	−0.005(2)	−0.021(2)	−0.008(2)
O(2)	0.053(2)	0.073(2)	0.046(2)	0.018(2)	−0.017(1)	0.000(2)
O(3)	0.072(3)	0.081(3)	0.082(3)	0.022(2)	0.046(2)	0.000(2)
N(1)	0.025(1)	0.036(1)	0.031(1)	0.001(1)	0.003(1)	0.002(1)
C(1)	0.024(2)	0.031(2)	0.025(2)	0.002(1)	0.001(1)	−0.003(1)
C(2)	0.037(2)	0.061(3)	0.048(2)	−0.017(2)	−0.002(2)	0.013(2)
C(3)	0.020(1)	0.031(2)	0.027(2)	−0.001(1)	−0.002(1)	−0.001(1)
C(4)	0.039(2)	0.030(2)	0.033(2)	0.009(1)	0.001(1)	0.002(1)
C(5)	0.046(2)	0.039(2)	0.031(2)	0.006(2)	0.000(2)	0.006(1)
C(6)	0.036(2)	0.037(2)	0.041(2)	−0.001(2)	−0.007(1)	0.011(2)
C(7)	0.038(2)	0.041(2)	0.049(2)	0.013(2)	−0.001(2)	0.003(2)
C(8)	0.029(2)	0.047(2)	0.037(2)	0.014(2)	0.000(1)	0.000(2)
C(9)	0.031(2)	0.046(2)	0.052(2)	−0.010(2)	0.004(2)	0.001(2)
C(10)	0.044(2)	0.040(2)	0.041(2)	0.001(2)	0.007(2)	0.011(2)
C(11)	0.041(2)	0.035(2)	0.031(2)	0.004(2)	−0.001(1)	−0.007(1)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table S3. Bond Lengths (Å)

atom	atom	distance	atom	atom	distance
Te(1)	C(1)	2.093(3)	Te(1)	C(2)	2.120(4)
S(1)	O(1)	1.428(3)	S(1)	O(2)	1.432(3)
S(1)	O(3)	1.419(3)	S(1)	C(11)	1.818(4)
F(1)	C(11)	1.321(4)	F(2)	C(11)	1.318(4)
F(3)	C(11)	1.320(4)	N(1)	C(1)	1.304(4)
N(1)	C(9)	1.477(5)	N(1)	C(10)	1.472(5)
C(1)	C(3)	1.485(5)	C(2)	H(1)	0.95
C(2)	H(2)	0.95	C(2)	H(3)	0.95
C(3)	C(4)	1.385(5)	C(3)	C(8)	1.397(5)
C(4)	C(5)	1.390(5)	C(4)	H(4)	0.95
C(5)	C(6)	1.377(5)	C(5)	H(5)	0.95
C(6)	C(7)	1.388(6)	C(6)	H(6)	0.95
C(7)	C(8)	1.370(5)	C(7)	H(7)	0.95
C(8)	H(8)	0.95	C(9)	H(9)	0.95
C(9)	H(10)	0.95	C(9)	H(11)	0.94
C(10)	H(12)	0.95	C(10)	H(13)	0.95
C(10)	H(14)	0.95			

Table S4. Bond Angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Te(1)	C(2)	94.7(1)	O(1)	S(1)	O(2)	114.0(2)
O(1)	S(1)	O(3)	115.8(3)	O(1)	S(1)	C(11)	103.2(2)
O(2)	S(1)	O(3)	114.3(2)	O(2)	S(1)	C(11)	103.2(2)
O(3)	S(1)	C(11)	104.1(2)	C(1)	N(1)	C(9)	123.5(3)
C(1)	N(1)	C(10)	121.7(3)	C(9)	N(1)	C(10)	114.7(3)
Te(1)	C(1)	N(1)	121.3(2)	Te(1)	C(1)	C(3)	118.3(2)
N(1)	C(1)	C(3)	120.3(3)	Te(1)	C(2)	H(1)	109.5
Te(1)	C(2)	H(2)	109.4	Te(1)	C(2)	H(3)	109.8
H(1)	C(2)	H(2)	109.0	H(1)	C(2)	H(3)	109.6
H(2)	C(2)	H(3)	109.4	C(1)	C(3)	C(4)	120.6(3)
C(1)	C(3)	C(8)	120.1(3)	C(4)	C(3)	C(8)	119.3(3)
C(3)	C(4)	C(5)	119.8(3)	C(3)	C(4)	H(4)	120.3
C(5)	C(4)	H(4)	120.0	C(4)	C(5)	C(6)	120.7(3)
C(4)	C(5)	H(5)	119.6	C(6)	C(5)	H(5)	119.7
C(5)	C(6)	C(7)	119.3(3)	C(5)	C(6)	H(6)	120.4
C(7)	C(6)	H(6)	120.3	C(6)	C(7)	C(8)	120.5(3)
C(6)	C(7)	H(7)	119.7	C(8)	C(7)	H(7)	119.7
C(3)	C(8)	C(7)	120.3(3)	C(3)	C(8)	H(8)	120.0
C(7)	C(8)	H(8)	119.7	N(1)	C(9)	H(9)	109.1
N(1)	C(9)	H(10)	109.0	N(1)	C(9)	H(11)	109.5
H(9)	C(9)	H(10)	109.3	H(9)	C(9)	H(11)	110.0
H(10)	C(9)	H(11)	109.9	N(1)	C(10)	H(12)	110.0
N(1)	C(10)	H(13)	109.4	N(1)	C(10)	H(14)	109.5
H(12)	C(10)	H(13)	109.4	H(12)	C(10)	H(14)	109.6
H(13)	C(10)	H(14)	108.9	S(1)	C(11)	F(1)	112.3(3)
S(1)	C(11)	F(2)	112.5(3)	S(1)	C(11)	F(3)	111.6(3)
F(1)	C(11)	F(2)	107.7(4)	F(1)	C(11)	F(3)	105.0(3)
F(2)	C(11)	F(3)	107.2(4)				

Table S5. Torsion Angles (°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
Te(1)	C(1)	N(1)	C(9)	179.7(3)	Te(1)	C(1)	N(1)	C(10)	−2.4(4)
Te(1)	C(1)	C(3)	C(4)	89.1(4)	Te(1)	C(1)	C(3)	C(8)	−89.3(4)
F(1)	C(11)	S(1)	O(1)	175.7(3)	F(1)	C(11)	S(1)	O(2)	−65.4(3)
F(1)	C(11)	S(1)	O(3)	54.3(4)	F(2)	C(11)	S(1)	O(1)	53.9(4)
F(2)	C(11)	S(1)	O(2)	172.8(3)	F(2)	C(11)	S(1)	O(3)	−67.5(4)
F(3)	C(11)	S(1)	O(1)	−66.7(3)	F(3)	C(11)	S(1)	O(2)	52.2(3)
F(3)	C(11)	S(1)	O(3)	171.9(3)	N(1)	C(1)	Te(1)	C(2)	169.1(3)
N(1)	C(1)	C(3)	C(4)	−93.3(4)	N(1)	C(1)	C(3)	C(8)	88.3(4)
C(1)	C(3)	C(4)	C(5)	−179.7(3)	C(1)	C(3)	C(8)	C(7)	179.3(4)
C(2)	Te(1)	C(1)	C(3)	−13.4(3)	C(3)	C(1)	N(1)	C(9)	2.2(5)
C(3)	C(1)	N(1)	C(10)	−179.9(3)	C(3)	C(4)	C(5)	C(6)	1.1(6)
C(3)	C(8)	C(7)	C(6)	−0.3(6)	C(4)	C(3)	C(8)	C(7)	0.9(6)
C(4)	C(5)	C(6)	C(7)	−0.5(6)	C(5)	C(4)	C(3)	C(8)	−1.3(6)
C(5)	C(6)	C(7)	C(8)	0.1(6)					

Table S6. Least Squares Planes

Plane number 1		Plane number 2	
Atoms defining plane	Distance	Atoms defining plane	Distance
Te(1)	0.0	C(3)	-0.004(2)
C(1)	0.0	C(4)	0.007(3)
N(1)	0.0	C(5)	-0.003(3)
		C(6)	-0.001(3)
		C(7)	0.001(3)
		C(8)	0.003(3)
Plane number 3		Plane number 4	
Atoms defining plane	Distance	Atoms defining plane	Distance
N(1)	0.0	C(1)	0.0
Te(1)	0.0	C(9)	0.0
C(2)	0.0	C(10)	0.0
Summary			
plane	mean deviation	σ^2	
1	0.0000	0.0	
2	0.0032	5.4	
3	0.0000	0.0	
4	0.0000	0.0	
Dihedral angles between planes (°)			
plane	plane	angle	
1	2	88.88(10)	
1	3	10.9	
1	4	2.2	
2	3	83.85(10)	
2	4	89.56(10)	
3	4	13.1	

Reaction of Telluroiminium salt **2a with Lithium Acetylide **4** (Scheme 2).** To an Et₂O solution (5 mL) of (trimethylsilyl)acetylene (0.07 mL, 0.5 mmol) was added *n*-BuLi (1.6 M solution in hexane, 0.31 mL, 0.5 mmol) at 0 °C, and the mixture was stirred at this temperature for 5 min. To this was added telluroiminium salt **2a** (0.212 g, 0.5 mmol) at 0 °C, and this was stirred for 1 h at room temperature. The resulting mixture was poured into a saturated aqueous solution of NaHCO₃ and extracted with Et₂O. The organic layer was dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (SiO₂, hexane : Et₂O = 1 : 1) to give ketone **5** (0.043 g, 72%) and telluride **6** (0.084 g, 70 %). Analytical data matched the data reported previously.

2-Dimethylamino-1,2-diphenylethanone (5**).**⁷ A slightly yellow oil: *R_f* = 0.06; ¹H NMR (CDCl₃) δ 2.30 (s, 6H, N(CH₃)₂), 4.83 (s, 1H, CH), 7.23–7.55 (m, 8H, Ar), 7.99–8.01 (m, 2H, Ar); ¹³C NMR (CDCl₃) δ 43.9 (N(CH₃)₂), 76.9 (CH), 128.3, 128.5, 128.7, 128.8, 129.5, 133.0, 135.6, 136.5 (Ar), 197.9 (C=O).

Trimethyl[(methyltelluro)ethynyl]silane (6**).**⁸ A yellow oil: *R_f* = 0.95; ¹H NMR (CDCl₃) δ 0.18 (s, 9H, SiMe₃), 2.15 (s, 3H, TeCH₃); ¹³C NMR (CDCl₃) δ -14.8 (TeCH₃), 0.12 (SiMe₃), 61.8, 120.5 (C≡C); ¹²⁵Te NMR (CDCl₃) δ 175.4.

Elucidation of the Reaction Pathway Shown in Scheme 2. Formation of **8** may be due to the dimerization of **7**.⁹ Alternatively, the reaction of generated **7** and **2a** may led to **8**. To prove the intermediacy of **7**, trapping reactions with cyclohexene, methyl cinnamate, and Cr(CO)₆ was attempted, but no adducts were obtained. Additionally, a similar reaction involving the dimerization of **7** was achieved by the reaction of **2e** with *n*-BuLi (Scheme S1), although the purification of **11** and **12** has not yet been successful.

Scheme S1

The Reaction Pathway Leading to 10. The reaction may proceed as suggested in Scheme S2. First, the nucleophilic attack of lithium acetylide **4** to the iminium carbon atom of thio- and selenoiminium salts **9** generates *S,N*- and *Se,N*-acetals **13**, followed by [1,3]-shift of MeS and MeSe groups in **13** to yield aminoallenes **14**. Finally, hydrolysis of **14** may lead to α,β -unsaturated ketones **10**.

Scheme S2

Molecular Orbital Calculation for the Model Compounds 2i, 9c, and 9d. The geometry of the model compounds **2i**, **9c**, and **9d** was optimized using the Gaussian 03 program at the B3LYP/LANL2DZ level.⁹ NPA (natural population analysis) charge distributions were calculated at the same level. The NPA charge distributions of **2i** are summarized in Table S7.

Table S7. The NPA Charge Distributions of **2i** at the B3LYP/LANL2DZ Level

Atom No	Natural Charge	Atom No	Natural Charge
C 1	0.03131	Te 11	0.80997
N 2	-0.38434	C 12	-0.69836
C 3	-0.43422	H 13	0.26699
H 4	0.25292	H 14	0.26699
H 5	0.24424	H 15	0.25315
H 6	0.24425	C 16	-0.95501
C 7	-0.41771	H 17	0.25759
H 8	0.24785	H 18	0.25759
H 9	0.24785	H 19	0.27332
H 10	0.23561	total	1.00000

2i

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