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Acyclic Selenoiminium Salts: Isolation, First Structural Characterization, and Reactions

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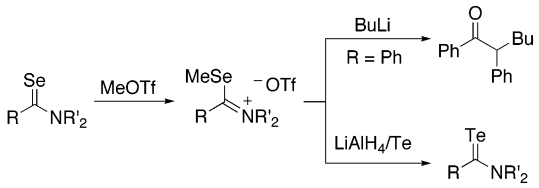
ABSTRACT



A variety of selenoiminium salts were obtained by reacting the corresponding selenoamides with methyl triflate at room temperature for 30 s. All of the salts were stable under air. The structures of the selenoiminium salts were determined by X-ray molecular analysis. An aromatic selenoiminium salt reacted with BuLi (3 equiv) to give two types of ketones. In a reaction with $LiAlH_4$/Te, the selenoiminium salts were converted to telluroamides.

Thioiminium salts, in which a sulfenyl group is attached to the carbon atom of an iminium salt, have been extensively studied.[1] In contrast, despite the fact that the first selenium isologues of thioiminium salts, i.e., selenoiminium salts, were synthesized in 1966,[2] the structure and reactivity of these salts have not yet been reported, although reactions of cyclic selenoiminium salts in which the selenium atom is located in a five- or six-membered ring have been described.[3] Recently, increasing attention has been paid to the synthesis, structure, and reactivity of selenocarbonyl compounds.[4] We previously studied the synthesis[5] and reactions[6] of selenium isologues of amides, i.e., selenoamides. For example, alky-

(1) For example, see: (a) Shiosaki, K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 2, p 865. (b) Mukaiyama, T.; Yamaguchi, T.; Nohira, H. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 2107. (c) Mukaiyama, T.; Yamaguchi, T. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2005. (d) Yamaguchi, T.; Inomata, K.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 673. (e) Mathew, S. I.; Stansfield, F. *J. Chem. Soc., Perkin Trans. 1* **1974**, 540. (f) Okecha, S. A.; Stansfield, F. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1811. (g) Shiosaki, K.; Fels, G.; Rapoport, H. *J. Org. Chem.* **1981**, *46*, 3230. (h) Sundberg, R. J.; Walters, C. P.; Bloom, J. D. *J. Org. Chem.* **1981**, *46*, 3730. (i) Singh, P.; Barata, M. S.; Singh, H. *J. Chem. Res., Synop.* **1985**, 204. (j) Takahata, H.; Yamabe, K.; Yamazaki, T. *Synthesis* **1986**, 1063. (k) Sauve, G.; Mansour, T. S.; Lachance, P.; Belleau, B. *Tetrahedron Lett.* **1988**, *29*, 2295. (l) Sauve, G.; Le Berre, N.; Zacharie, B. *Tetrahedron Lett.* **1988**, *29*, 2299. (m) Heathcock, C. H.; Davidsen, S. K.; Mills, S. G.; Sanner, M. A. *J. Org. Chem.* **1992**, *57*, 2531. (n) Devine, P. N.; Meyers, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 2633. (o) Marchand, P.; Fargeau-Bellassoued, M.-C.; Bellec, C.; Lhommet, G. *Synthesis* **1994**, 1118. (p) Mook, R. A., Jr.; Lackey, K.; Bennett, C. *Tetrahedron Lett.* **1995**, *36*, 3969. (q) Munchhof, M. J.; Meyers, A. I. *J. Am. Chem. Soc.* **1995**, *117*, 5399. (r) Smith, D. C.; Fuchs, P. L. *J. Org. Chem.* **1995**, *60*, 2692. (s) Sosnicki, J. G.; Liebscher, J. *Synlett* **1996**, 1117. (t) May, P. J.; Bradley, M.; Harrowven, D. C.; Pallin, D. *Tetrahedron Lett.* **2000**, *40*, 1627.

(2) Jensen and Nielsen reported the synthesis of selenoiminium salts by reacting selenoacetamide, selenobenzamide, selenoformamide, and selenoureas with methyl iodide: Jensen, K. A.; Nielsen, P. H. *Acta Chem. Scand.* **1966**, *20*, 597.

(3) For example, see: Quast, H.; Ivanova, S.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Liebigs Ann.* **1996**, 1541.

(4) (a) Wu, R.; Hernández, G.; Dunlap, R. B.; Odom, J. D.; Martinez, R. A.; Silks, L. A. *Trends Org. Chem.* **1998**, *7*, 105. (b) Litvinov, V. P. *Russ. Chem. Rev.* **1999**, *68*, 737. (c) Murai, T.; Kato, S. In *Topics in Current Chemistry*; Wirth, T., Ed.; Springer-Verlag: Berlin, 2000; Vol. 208, p 177. (d) Boyle, P. D.; Godfrey, S. M. *Coord. Chem. Rev.* **2001**, *223*, 265.

(5) (a) Murai, T.; Ezaka, T.; Niwa, N.; Kanda, T.; Kato, S. *Synlett* **1996**, 865. (b) Murai, T.; Ezaka, T.; Kanda, T.; Kato, S. *J. Chem. Soc., Chem. Commun.* **1996**, 1809. (c) Murai, T. Ezaka, T.; Ichimiya, T.; Kato, S. *Synlett* **1997**, 775. (d) Murai, T.; Mori, T.; Kato, S. *Synlett* **1998**, 619. (e) Murai, T.; Niwa, N.; Ezaka, T.; Kato, S. *J. Org. Chem.* **1998**, *63*, 374. (f) Murai, T.; Ezaka, T.; Kato, S. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1193. (g) Murai, T.; Suzuki, A.; Ezaka, T.; Kato, S. *Org. Lett.* **2000**, *2*, 311. (h) Murai, T.; Suzuki, A.; Kato, S. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2711. (i) Murai, T.; Aso, H.; Kato, S. *Org. Lett.* **2002**, *4*, 1407. (j) Murai, T.; Ishizuka, M.; Suzuki, A.; Kato, S. *Tetrahedron Lett.* **2003**, *44*, 1343.

(6) (a) Murai, T.; Ezaka, T.; Kato, S. *Tetrahedron Lett.* **1998**, *39*, 4329. (b) Murai, T.; Mutoh, Y.; Kato, S. *Org. Lett.* **2001**, *3*, 1993.

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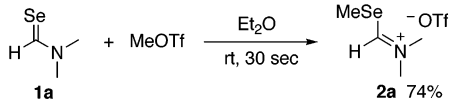
nylation of selenoamides mediated by methyl trifluoromethanesulfonate (methyl triflate) produced α,β-unsaturated ketones.[6b] In this reaction, selenoiminium salts have been postulated to be putative intermediates. Since a wide range of selenoamides are now readily available,[5,7] we expected that some of them could be converted to stable selenoiminium salts. We describe here the isolation, structure, and reactions of acyclic selenoiminium salts.

Initially, selenoformamide **1a**[7f] was reacted with methyl triflate as a methylating reagent (Scheme 1). Methyl triflate

Scheme 1



(1 equiv) was added to an Et_2O solution of selenoformamide **1a** at room temperature. The homogeneous yellow solution changed to a yellow suspension. After the suspension was stirred for 30 s, a white-yellow solid was deposited. The solid was filtered through a glass filter (G4) and washed with Et_2O to give selenoiminium salt **2a** as a pale yellow solid in 74% yield.

The methylation of a variety of selenoamides **1** leading to selenoiminium salts **2** was then carried out (Scheme 2).

Scheme 2

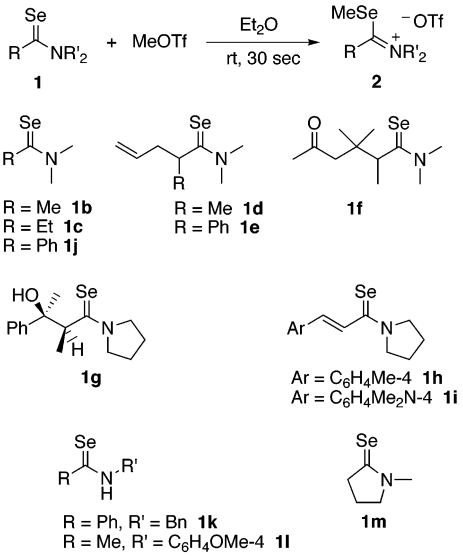
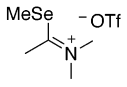
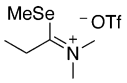
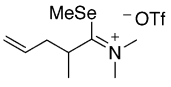
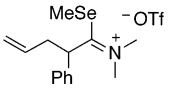
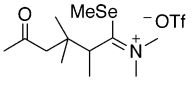
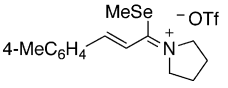
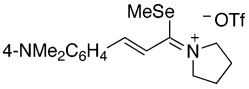
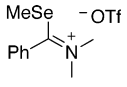
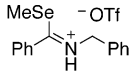
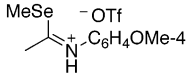
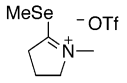


Table 1. Synthesis of Selenoiminium Salts **2**[a]

entry	selenoamide **1**	selenoiminium salt **2** yield[b]
1	**1b**	 **2b** 99% (70 : 30)
2	**1c**	 **2c** 80% (77 : 23)
3	**1d**	 **2d** 93%
4	**1e**	 **2e** 99%
5	**1f**	 **2f** 97%
6[c]	**1h**	 **2h** 91%
7[c]	**1i**	 **2i** 95%
8	**1j**	 **2j** 95%
9	**1k**	 **2k** 99%
10	**1l**	 **2l** 92%
11	**1m**	 **2m** 68%

[a] Reaction was carried out as follows, unless otherwise noted. Selenoamide **1** was treated with methyl triflate (1 equiv) in Et_2O at room temperature for 30 s. [b] Isolated yield. [c] CH_2Cl_2 was used as a solvent.

The results are summarized in Table 1.[8] The reaction of simple aliphatic selenoamides **1b**−**e**[5a,f] with methyl triflate was complete within 30 s to form the corresponding selenoiminium salts **2b**−**e** in yields of 80−99% (entries 1−4). Stereoisomers with respect to a C−Se single bond were observed for **2b** and **2c**, whereas no isomers were formed in the cases of **2d** and **2e**. The methylation of δ-oxo selenoamide **1f**[5g] took place selectively at the selenium atom of the selenocarbonyl group, and the carbonyl group of **1f** remained in the product **2f** (entry 5). On the other hand, the

(7) For example, see: (a) Cohen, V. I. *J. Org. Chem.* **1977**, *42*, 2645. (b) Blau, H.; Grobe, J.; Le Van, D.; Krebs, B.; Läge, M. *Chem. Ber.* **1997**, *130*, 913. (c) Ishihara, H.; Koketsu, M.; Fukuta, Y.; Nada, F. *J. Am. Chem. Soc.* **2001**, *123*, 8408. (d) Koketsu, M.; Kanoh, M.; Itoh, E.; Ishihara, H. *J. Org. Chem.* **2001**, *66*, 4099. (e) Bhattacharyya, P.; Woollins, J. D. *Tetrahedron Lett.* **2001**, *42*, 5949. (f) Koketsu, M.; Okayama, Y.; Aoki, H.; Ishihara, H. *Heteroatom Chem.* **2002**, *13*, 195.

reaction of β-hydroxy selenoamide **1g**[5j] gave a complex mixture. Methylation was applied to α,β-unsaturated selenoamides **1h**[5c] and **1i**[5c] and aromatic selenoamide **1j**,[7f] and the corresponding selenoiminium salts **2h**−**j** were isolated in yields of greater than 90% (entries 6−8). Notably, the highly nucleophilic dimethylamino group was inert toward methyl triflate in the reaction of selenoamide **1i** (entry 7). Secondary selenoamides **1k**[7a] and **1l**[5a] reacted with methyl triflate to give selenoiminium salts **2k** and **2l** selectively as (*Z*)-isomers with respect to a C═N double bond in high yields (entries 9 and 10).[9] The characteristic signals due to N−H protons of **2k** and **2l** were observed at δ 12.6 and 13.0, respectively, which were shifted to lower fields by about 3.0 ppm compared to the corresponding signals of the starting selenoamides **1k** and **1l**. Finally, selenolactam **1m**[7f] was converted to the corresponding salt **2m** in 68% yield (entry 11). All of the salts **2** isolated were stable and could be stored even under air at room temperature.

To elucidate the structural features of selenoiminium salts **2** in the solid state, X-ray molecular structure analysis of aromatic salt **2j** was carried out. An ORTEP drawing of **2j** is shown in Figure 1.[10] The methyl group of the methylselenenyl (MeSe) group is located at the cis position to the phenyl group with respect to a C−Se single bond. There is no apparent intramolecular interaction between the selenoiminium cation and the trifluoromethanesulfonate anion. The length of the Se1−C1 bond in **2j** is 1.885(4) Å, which is shorter than a typical C−Se single bond (1.96 Å). The torsion angle Se1−C1−N1−C9 in **2j** is 177.7(3)°, and these four atoms are located in the same plane. In contrast, the torsion angle Se1−C1−C3−C8 in **2j** is 83.0(5)°, and the benzene ring is deviated from the plane that includes the C−Se single bond. These results suggest that there is no conjugation between the benzene ring and the iminium group. Spectroscopic properties of selected selenoamides **1** and selenoiminium salts **2** are shown in Table 2, along with those of *N*-benzyl imine **3**.[5i] In the ^{13}C NMR spectra, the signals of the carbon atom of the iminium group of **2** were shifted upfield by about 6−11 ppm compared to those of the carbon atom of the selenocarbonyl group of selenoamides **1**. The signals of the selenium atoms of **2** were shifted upfield by about 180−250 ppm compared to those of the corresponding selenoamides **1** in the ^{77}Se NMR spectra but were still at a lower field than those of imine **3**. Furthermore, the coupling constants between the carbon and selenium atoms of **2** (166 ± 8 Hz) were greater than those of the imine **3** and smaller than those of the selenoamides **1**. These NMR spectra and X-ray analysis findings suggest that the C−Se bond of salts **2** has a partial double-bond character.

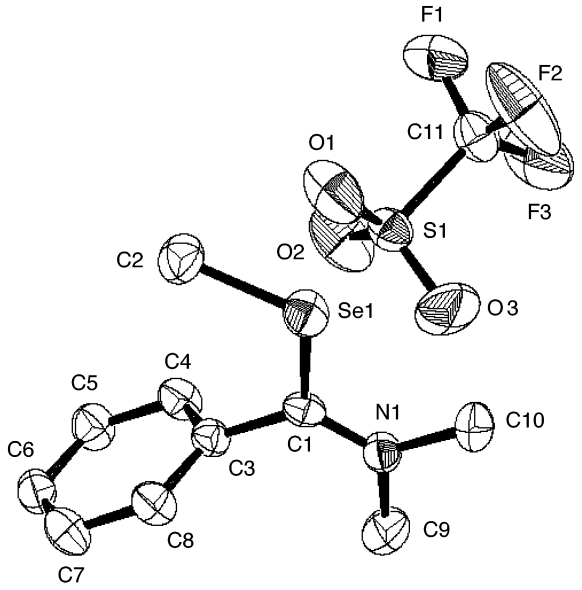


Figure 1. ORTEP drawing of selenoiminium salts **2j**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Se1−C1, 1.885(4); Se1−C2, 1.928(4); Se1−C1, 1.280(5); N1−C10, 1.461(5); C1−C3, 1.483(6). Selected torsion angles (deg): Se1−C1−N1−C9, 177.7(3); Se1−C1−N1−C8, 83.0(5); N1−C1−Se1−C2, 166.8(4); C3−C1−N1−C9, 1.7(6).

Table 2. Typical Spectroscopic Data of Selected Selenoamides Salts **1**, Selenoiminium Salts **2**, and *N*-Benzyl Imine **3**[a]

compound	^{13}C NMR[a] [ppm]	$^{1}J_{C\text{-}Se}$[b] [Hz]	^{77}Se NMR[a] [ppm]
1a	190.7	213.0	553.5
1b	202.9	204.8	622.7
1e	210.4	213.5	601.0
1h	193.0	204.5	530.8
1j	205.2	207.7	726.2
1k	204.0	210.1	618.6
2a	187.0	161.9	367.8
2b	195.5	164.3	433.4
2e	199.0	174.0	421.6
2h	185.1	158.9	390.2
2j	195.6	164.3	449.9
2k	198.1	167.7	382.9
EtSe, Ph, N, Ph **3**	162.8	138.5	354.8

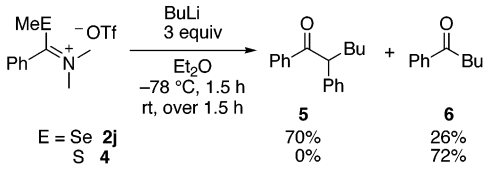
[a] $CDCl_3$ was used as a solvent. [b] Coupling constants were determined by ^{13}C NMR.

(8) **Typical Experimental Procedure.** To an Et_2O (20 mL) solution of *N*,*N*-dimethyl selenobenzamide **1j** (2.895 g, 13.6 mmol) was added methyl triflate (1.56 mL, 13.6 mmol) at room temperature. After stirring at this temperature for 30 s, the mixture was concentrated in vacuo. The residue was washed with Et_2O and hexane to give selenoiminium salt **2j** (4.854 g, 95%) as a white solid: mp 79.5−82.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.06 (s, 3H, $SeCH_3$), 3.49 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 7.44−7.46 (m, 2H, Ar), 7.59−7.66 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.2 ($SeCH_3$), 47.1, 48.4 (CH_3), 120.8 (q, $^1J_{C-F}$ = 320.6 Hz, CF_3), 126.0, 130.1, 131.7, 132.2 (Ar), 195.6 (CSe, $^1J_{C-SeMe}$ = 164.3 Hz); ^{19}F NMR ($CDCl_3$) δ −78.8; ^{77}Se NMR ($CDCl_3$) δ 449.9; MS (FAB+) *m*/*z* 228 (M^+ − OTf). Anal. Calcd for $C_{11}H_{14}F_3NO_3SSe$: C, 35.11; H, 3.75. Found: C, 35.40; H, 3.77.

(9) Stereochemistry was determined by phase-sensitive NOESY spectroscopy.

(10) Crystal data of selenoiminium salt **2j**: $C_{11}H_{14}F_3NO_3SSe$, FW = 376.28, monoclinic, space group $P2_1/c$ (No. 14), a = 6.172(3) Å, b = 8.825(2) Å, c = 26.162(2) Å, β = 95.81(1)°, V = 1417.6(6) Å^3, Z = 4, D_{calcd} = 1.693 g/cm^3, μ(Mo Kα) = 27.23 cm^{-1}, T = 193 K, F(000) = 752 R = 0.097, R_w = 0.126, R_1 = 0.047, 3395 reflections ($I > -10.00\sigma(I)$), GOF = 1.08.

Scheme 3

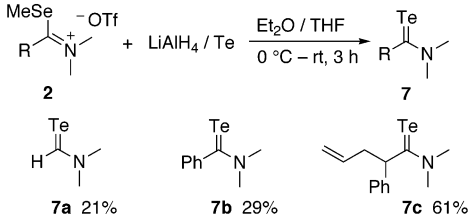


To examine the reactivity of the isolated selenoiminium salts **2**, aromatic selenoiminium salt **2j** was treated with BuLi (3 equiv) in Et_2O (Scheme 3). As a result, ketones **5**[11] and **6** were isolated in respective yields of 70 and 26%.

Interestingly, a similar reaction of thioiminium salt **4** selectively gave ketone **6**. In the formation of ketone **6**, BuLi may initially attack the carbon atom of the C═N double bond of **2j** and **4**, whereas the initial step leading to ketone **5** may involve attack by BuLi to the selenium atom of the C−Se single bond of the salt **2j**.[12] The critical difference in the reaction pathway between salts **2j** and **4** may be due to the difference in energy between the σ^*C−Se and σ^*C−S orbitals.

A further test of the reactivity of selenoiminium salts **2** showed that they could be used as key starting materials for heavier isologues of selenoamides, i.e., telluroamides. Salts **2a** and **2j** were converted to the known telluroamides **7a**[13d] and **7b**,[13a] respectively, by reaction with a reagent prepared from lithium aluminum hydride and elemental tellurium (Scheme 4). This new synthetic procedure enabled isolation of the first aliphatic telluroamide **7c** in good yield.[14,15]

Scheme 4



In summary, we successfully isolated a variety of acyclic selenoiminium salts. X-ray molecular structure analysis and ^{13}C NMR spectra of these selenoiminium salts suggested that the electrons on the selenium atom of the salts are somewhat delocalized with respect to the iminium group. In the reaction of an aromatic selenoiminium salt with BuLi, a product in which two molecules of the salt were coupled was obtained along with elimination of the MeSe group, which is in marked contrast to the reaction of the aromatic thioiminium salt. A new procedure for the synthesis of telluroamides via these selenoiminium salts is also shown. Further studies on the properties and reactions of these salts and their sulfur analogues are currently in progress.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

Supporting Information Available: Experimental procedures and spectroscopic and analytical data for **2** and **5**−**7** and tables of crystallographic data, including atomic positional and thermal parameters for **2j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Katritzky, A. R.; Qi, M. *J. Org. Chem.* **1997**, *62*, 4116.

(12) These pathways were suggested by the fact that butyl methyl selenide (BuSeMe) and dimethyl diselenide (MeSeSeMe) were detected as byproducts.

(13) Synthesis and isolation of tellurobenzamide and telluroformamides have been reported: (a) Lerstrup, K. A.; Henriksen, L. *J. Chem. Soc., Chem. Commun.* **1979**, 1102. (b) Segi, M.; Kojima, A.; Nakajama, T.; Suga, S. *Synlett* **1991**, 105. (c) Li, G. M.; Zingaro, R. A.; Segi, M.; Reibenspies, J. H.; Nakajima, T. *Organometallics* **1997**, *16*, 756. (d) Li, G. M.; Zingaro, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 647.

(14) Attempts to isolate aliphatic telluroamides have been reported to give decomposed products: Laishev, V. Z.; Petrov, M. L.; Petrov, A. A. *Zh. Org. Khim.* **1981**, *17*, 2064.

(15) **Experimental Procedure.** To an Et_2O suspension (10 mL) of selenoiminium salt **2e** (0.266, 1 mmol) was added a THF solution (30 mL) of the reagent prepared from tellurium (0.153 g, 1.2 mmol) and $LiAlH_4$ (0.046 g, 1.2 mmol) at 0 °C, and this 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, CH_2Cl_2) to give telluroamide **7c** (0.191 g, 61%) as a reddish-orange solid: ^1H NMR (CD_2Cl_2) δ 2.84 (dt, J = 7.6, 14.0 Hz, 1H, CH_2═CHCH_2), 3.13−3.22 (m, 1H, 4H, CH_2═CHCH_2, NCH_3), 3.69 (s, 3H, NCH_3), 3.90 (t, J = 7.2 Hz, 1H, PhCH), 4.97 (dt, J = 2.5, 10.4 Hz, 1H, CH_2═CHCH_2), 5.06 (dq, J = 1.6, 17.3 Hz, 1H, CH_2═CHCH_2), 5.77 (ddt, J = 6.4, 10.4, 17.2 Hz, 1H, CH_2═CHCH_2), 7.23−7.32 (m, 3H, Ar), 7.51−7.53 (m, 2H, Ar); ^{13}C NMR (CD_2Cl_2) δ 42.8 (NCH_3), 47.8 (CH_2═CHCH_2), 58.1 (NCH_3), 60.7 (PhCH), 116.9 (CH_2═CHCH_2), 127.4, 128.7, 129.1 (Ar), 136.4 (CH_2═CHCH_2), 138.9 (Ar), 206.0 (C═Te); ^{125}Te NMR (CD_2Cl_2) δ 620.4; MS (EI) m/z 317 (M^+, ^{130}Te); HRMS calcd for $C_{13}H_{17}NTe$ 317.0423, found 317.0420.