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Organylzinc Chalcogenolate Promoted Michael-Type Addition of α,β-Unsaturated Carbonyl Compounds

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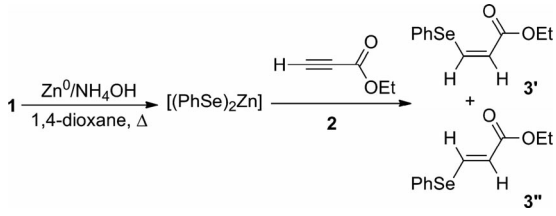
We present the chemo-, regio-, and stereoselective synthesis of vinyl chalcogenide compounds promoted by organylzinc chalcogenolates. In this protocol, reductive cleavage of diorganyl dichalcogenide bonds by the Zn/NH_4OH system led to organylzinc chalcogenolates. The reaction was performed with propiolic acids and esters and afforded β-organochalcogenacrylic acids and esters under mild basic conditions. The stereochemistry corresponded to anti-Markovnikov addition of the organyl chalcogenolate constituents across the triple bond.

Introduction

Organochalcogen compounds have emerged as important reagents and intermediates in modern organic syntheses in view of their chemo-, regio-, and stereoselectivity reactions[1] and their useful biological activities, as was recently reviewed.[2] A chalcogen can be introduced in an organic substrate as an electrophile or a nucleophile under mild experimental conditions.[3] After being introduced into a substrate, the organochalcogen group can be easily removed[4] or directly converted into different functional groups.[5]

The development of new methods for the efficient and inexpensive introduction of a chalcogen group into organic molecules with a highly reactive reagent has been explored. In the last decade, several zinc systems, such as Zn/MeCN,[6] $Zn/AlCl_3$,[7] $Zn/ZrCl_4$,[8] Zn/BMIM-BF_4 (BMIM = 1-butyl-3-methylimidazolium hexafluorophosphate),[9] Zn/CAN (CAN = ceric ammonium nitrate),[10] and $Zn/RuCl_3$,[11] have been employed to produce "in situ" zinc selenolate through reductive cleavage of the Se–Se bond. These selenolate anions can be easily introduced into organic substrates, primarily by addition to unsaturated organic compounds through hydroselenation reactions. In addition, treatment of electrophilic selenium species, such as phenylselenyl halides, with zinc dust leads to air-stable zinc selenolate compounds (PhSeZnX), which have shown nucleophilic reactivity in water suspensions.[12] However, there are few reports describing the preparation of thiolate anions by the reductive cleavage of the S–S bond or through an umpolung process on the electrophilic sulfur species.[10,13] Additionally, despite the well-known reducing properties of zinc, the preparation of zinc telurolate has remained unexplored. Realizing the importance of the development of environmentally benign protocols for the preparation of vinyl chalcogenides by applying milder and inexpensive methods, the goal of this study was the preparation β-organochalcogenacrylic acids and esters **3** through Michael-type addition of various diorganyl dichalcogenides **1** to propiolic acids and esters **2** promoted by the Zn/NH_4OH system (Scheme 1).



Scheme 1. General scheme.

Results and Discussion

Our initial studies focused on the development of an optimized set of reactions to obtain β-selenoacrylic acids and esters. For preliminary optimization of the reaction conditions, we chose ethyl propiolate, diphenyl diselenide, and zinc dust as the model system. We examined the reaction behavior by changing solvents, temperatures, molar ratios, and additives under a nitrogen atmosphere. The results of these studies are shown in Table 1.

It is very important to select the proper solvent to readily promote the insertion of zinc into the Se–Se bond. Therefore, acetonitrile or an acetonitrile/water system is commonly used;[6] however, in our case, good yields of **3aa** were obtained in these solvents but with an unsatisfactory diastereoselectivity even at reflux temperature. Other solvents including toluene and CH_2Cl_2 at room temperature or un-

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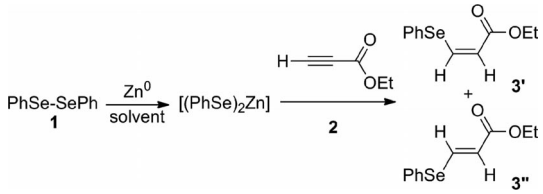
Table 1. Optimization of the reaction condition.



Entry	Solvent (2 mL)	Additive (0.2 mL)	*T* [°C]	Yield [%][a]
1	CH_3CN	H_2O	82	80
2	CH_3CN	–	82	n.r.
3	CH_2Cl_2	–	45	n.r.
4	toluene	–	110	n.r.
5	THF	–	65	32
6	THF	H_2O	65	37
7	1,4-dioxane	H_2O	65	48
8	1,4-dioxane	CH_3COOH	100	50
9	1,4-dioxane	HCl	100	60
10	1,4-dioxane	NH_4OH	100	96

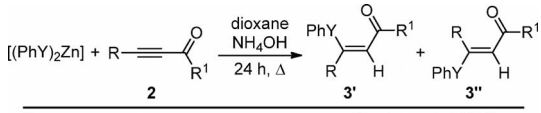
[a] Yield of pure isolated product characterized by spectroscopic methods; n.r. = no reaction.

der reflux were also ineffective, and the starting material was recovered. Next, the use of 1,4-dioxane and THF as the solvent was investigated; however, no improvement in the yield or diastereoselectivity was observed. We also evaluated the reaction by using 1,4-dioxane as the solvent in the presence of a base (NH_4OH) and a neutral (H_2O) or acid (HCl and EtOAc) medium. Through the control experiments, we found that the use of 1,4-dioxane in base medium (NH_4OH) at the boiling point of the solvent proved to be the best reaction conditions for obtaining the desired product in good yield with high diastereoselectivity.

Thus, careful analysis of the optimized reaction revealed that the best conditions for Michael addition to the α,β-unsaturated ester were the use of zinc (1 mmol) in 1,4-dioxane (2 mL) with diphenyl diselenide (0.5 mmol), ethyl propiolate (0.5 mmol), and NH_4OH (0.2 mL). The reaction mixture was heated at reflux for 24 h to afford products **3** with yields up of 96%. To demonstrate the efficiency of this reaction, we explored the generality of our method and extended the conditions to diphenyl disulfides, diphenyl and dibutyl ditellurides, as well as to various functionalized α,β-unsaturated acids and esters. The results are summarized in Table 2.

Inspection of Table 2 shows that the Michael-type additions worked well for a variety of propiolic acids and esters with high regio- and stereoselectivity. The observed *Z* stereochemistry preference is consistent with minimized steric interactions between the carbonyl oxygen atom and the chalcogen atom.[14,16] In general, terminal propiolic acids and esters gave better yields than internal acids and esters. However, the reaction performed with the use of dibutyl ditelluride did not proceed well, which resulted in considerable losses in the yields, most likely due to the instability of these products during chromatographic purification. To avoid this instability, the reaction was performed

Table 2. Michael-type addition of α,β-unsaturated carbonyl compounds promoted by organylzinc chalcogenolate.

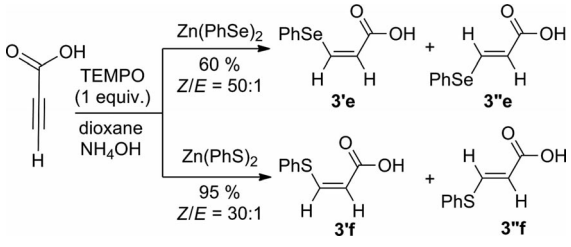


Entry	Substrate	PhY–YPh	Product, yield [%] (**3'**/**3"**)
1	**2a**	PhSeSePh**1a**	**3aa**, 96 (10:1)
2	**2a**	PhSSPh**1b**	**3ab**, 83 (10:2)
3	**2a**	BuTeTeBu**1c**	**3ac**, 51 (100:0)
4	**2a**	PhTeTePh**1d**	**3ad**, 76 (10:1)
5	**2b**	**1a**	**3ba**, 60 (10:1)
6	**2b**	**1b**	**3bb**, 95 (3:2)
7	**2b**	**1c**	**3bc**, 40 (100:0)
8	**2b**	**1d**	**3bd**, 75 (10:1)
9	**2c**	**1a**	**3ca**, 60 (100:0)
10	**2c**	**1b**	**3cb**, 60 (3:2)
11	**2c**	**1c**	**3cc**, 40 (100:0)
12	**2c**	**1d**	**3cd**, 74 (100:0)
13	**2d**	**1a**	**3da**,[a] 50 (5:2)[b]
14	**2d**	**1b**	**3db**,[a] 60 (2:1)
15	**2d**	**1c**	**3dc**,[a] 45 (10:1)[b]
16	**2d**	**1d**	**3dd**,[a] 69 (1:2)[b]

[a] Phenyl propiolic acid (1 mmol). [b] **3′**/*gen* according to ref.[16]

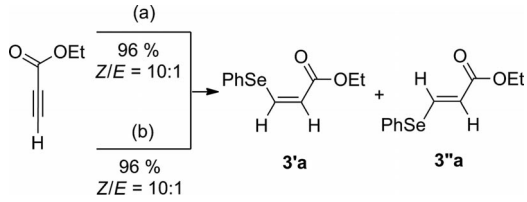
by using diphenyl ditelluride, which gave the products in acceptable yields (Table 2, entries 8, 12, and 16). This set of experiments demonstrated that stereochemical control depends on the diorganyl dichalcogenide group. The Michael addition of zinc selenolates [$(PhSe)_2Zn$] preferentially afforded (*Z*)-β-acrylic selenides in a 10:1 ratio, whereas zinc tellurolates [$(RTe)_2Zn$] exclusively afforded (*Z*)-β-acrylic acid tellurides, diastereoisomers **3ac** and **3bc**. Moreover, a significant loss in stereoselectivity was observed with the addition of zinc thiolates [$(PhS)_2Zn$] to propiolic acids, which afforded a mixture of (*Z*)- and (*E*)-β-acrylic sulfides in a 3:2 ratio (Table 2, entries 6 and 10). We also observed that internal propiolic acids with a phenyl group provided the geminal regioisomer (Table 2, entries 13, 15, and 16).

To determine how to prepare exclusively the (*Z*)-β-acrylic chalcogenide diastereoisomer, we investigated the reaction mechanism in an attempt to explain the generation of the mixture of the (*Z*)- and (*E*)-β-acrylic sulfides and selenides. Bieber and co-workers[15] described the preparation of alkyl phenyl selenides by using zinc dust in acetonitrile/water. They reported that the formation of the products could be explained by two different reaction mechanisms: a single-electron transfer (SET) reaction to produce a radical species if the reaction medium is basic and an ionic mechanism under neutral conditions. Therefore, we performed the reactions by using the radical inhibitor 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) under reaction conditions similar to those previously described to investigate a radical hydrochalcogenation mechanism. The (*Z*)-β-acrylic selenide and (*Z*)-β-acrylic thiolate diastereoisomers were obtained with significant improvement in the stereoselectivity with a comparable yield (Scheme 2). On the basis of these results, we deduced that the reaction proceeds through competing radical and ionic mechanisms.



Scheme 2. Michael addition of propiolic acid with TEMPO.

In another study, we investigated the formation of the zinc selenolate intermediate through reductive cleavage of the Se–Se bond by zinc. In this experiment, a mixture of zinc dust, diphenyl diselenide, 1,4-dioxane, and NH_4OH was stirred at reflux temperature for 2 h until the yellow solution became gray. Then, the solvent was evaporated under reduced pressure to afford a gray powdered stable intermediate. The Michael addition of ethyl propiolate promoted by this previously prepared intermediate afforded product **3** in the same yield and stereochemistry as the reaction that proceeded through a zinc selenolate prepared "in situ". We concluded that our method works as both a one-pot synthetic procedure and if the zinc selenolate was previously prepared (Scheme 3). A more detailed study of the crystal structure of the [$(PhSe)_2Zn$] intermediate by X-ray diffraction analysis is underway in our laboratory.



Scheme 3. Reagents and conditions: (a) $(PhSe)_2Zn$ (1 equiv.), ethyl propiolate (1 equiv.), 1,4-dioxane/NH_4OH. (b) Zn^0 (2 equiv.), PhSeSePh (1 equiv.), ethyl propiolate (1 equiv.), 1,4-dioxane/NH_4OH.

Conclusions

In summary, we have developed a regio- and stereoselective protocol for the Michael-type addition of several propiolic acids and esters promoted by organylzinc chalcogenolates by using either a one-pot synthesis or a previously prepared reagent to afford the corresponding (*Z*)-β-acrylic chalcogenides in moderate to excellent yields. In the presence of the TEMPO radical inhibitor, we produced (*Z*)-β-acrylic chalcogenides with high diastereoselectivity. Efforts to explore the detailed mechanism and extend the applications of the Zn/NH_4OH system as a reaction partner in other transformations are underway in our laboratory.

Experimental Section

General Remarks: All new compounds were characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopy and elemental analysis. ^1H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance III 500 (500 MHz for ^1H, 125 MHz for ^{13}C) spectrometer. All spectra were recorded in $CDCl_3$, and the chemical shifts are given in ppm with respect to tetramethylsilane as an internal standard. Near-IR spectra were obtained with a Perkin–Elmer Precisely Spectrum 400 FTIR/FTFIR spectrometer. Column chromatography was performed by using Merck silica gel (230–400 mesh). Thin-layer chromatography (TLC) was performed by using Merck silica gel GF254 (0.25 mm thickness). For visualization, TLC plates were either placed under UV light or stained with iodine vapor or acidic vanillin. Most reactions were monitored by TLC for disappearance of the starting material. Elemental analyses were performed with a Thermo scientific Flash 2000 Organic Elemental Analyzer. The IUPAC names were obtained by using ChemDraw software, version 8.0. Spectroscopic data of **3da**, **3dc**, and **3dd** are in accord with the data reported in ref.[16] Compounds **3ad**, **3bc**, **3cc**, **3dc**, and **3dd** were easily purified by column chromatography; however, they were unstable and reliable elemental analysis could not be obtained.

General Procedure for the Preparation of β-Acrylic Chalcogenides 3/3′ by a One-Pot Synthesis: In a Schlenk tube, a mixture of zinc dust (0.064 g, 1.0 mmol), diphenyl diselenide (0.157 g, 0.5 mmol),

ethyl propiolate (0.049 g, 0.5 mmol), and NH_4OH (0.2 mL) was suspended in 1,4-dioxane (2 mL). The reaction mixture was heated at reflux for 24 h under a nitrogen atmosphere. Then, the reaction was quenched with NH_4Cl (10 mL), and the mixture was extracted with EtOAc (2× 10 mL). The organic layer was then dried with Na_2SO_4. The solvent was evaporated under reduced pressure, and the crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate, 7:3) to afford ethyl 3-(phenylselanyl)-acrylate **3aa** (0.123 g, 0.5 mmol, 97%) as a colorless oil. The yields reported in Table 2 refer to the isolated products, and the *Z*/*E* ratios were determined through NMR spectroscopy.

Ethyl 3-(Phenylselanyl)acrylate (3aa): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.12 (d, *J* = 15.4 Hz, 0.1 H), 7.73 (d, *J* = 9.6 Hz, 1 H), 7.60–7.58 (m, 2 H), 7.33–7.32 (m, 3 H), 6.34 (d, *J* = 9.6 Hz, 1 H), 5.85 (d, *J* = 15.4 Hz, 0.1 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 4.13 (q, *J* = 7.2 Hz, 0.3 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 0.3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.2, 149.8, 134.8, 133.3, 132.9, 132.5, 129.7, 129.3, 128.2, 116.7, 60.5, 14.3 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 2924, 1664, 1567, 1245, 736 cm^{-1}. $C_{12}H_{12}O_2Se$ (267.19): calcd. C 51.78, H 4.74; found C 52.37, H 4.63.

Ethyl 3-(Phenylthio)acrylate (3ab): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 15.1 Hz, 0.2 H), 7.48–7.45 (m, 2 H), 7.38–7.32 (m, 3 H), 7.26 (d, *J* = 10.1 Hz, 1 H), 5.90 (d, *J* = 10.1 Hz, 1 H), 5.64 (d, *J* = 15.1 Hz, 0.2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.14 (q, *J* = 7.2 Hz, 0.4 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 0.6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 165.4, 149.8, 146.9, 136.4, 133.1, 131.3, 129.8, 129.5, 128.4, 113.6, 60.5, 14.5 ppm. IR (KBr): $\tilde{\nu}$ = 2981, 1699, 1165, 1569, 1025, 744, 691 cm^{-1}. $C_{11}H_{12}O_2S$ (208.27): calcd. C 63.43, H 5.81; found C 63.64, H 5.93.

Ethyl 3-(Butyltellanyl)acrylate (3ac): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.42 (d, *J* = 9.8 Hz, 1 H), 7.61 (d, *J* = 9.8 Hz, 0.2 H), 6.90 (d, *J* = 9.8 Hz, 1 H), 6.28 (d, *J* = 9.8 Hz, 0.2 H), 4.23 (q, *J* = 7.2 Hz, 2.5 H), 2.58 (t, *J* = 7.6 Hz, 2 H), 1.81 (quint., *J* = 7.6 Hz, 2 H), 1.41 (sext, *J* = 7.6 Hz, 2.6 H), 1.3 (t, *J* = 7.2 Hz, 4.5 H), 0.92 (t, *J* = 7.6 Hz, 4.3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.84, 136.40, 123.55, 117.28, 60.87, 34.26, 25.23, 14.58, 13.64, 9.57 ppm. IR (KBr): $\tilde{\nu}$ = 3450, 2958, 1682, 1556, 1332, 1204, 803 cm^{-1}. $C_9H_{16}O_2Te$ (283.82): calcd. C 38.09, H 5.68; found C 39.74, H 5.76.

Ethyl 3-(Phenyltellanyl)acrylate (3ad): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.54 (d, *J* = 16.5 Hz, 0.1 H), 8.46 (d, *J* = 9.3 Hz, 1 H), 7.79–7.77 (m, 2 H), 7.33–7.23 (m, 3 H), 6.95 (d, *J* = 9.3 Hz, 1 H), 6.13 (d, *J* = 16.5 Hz, 0.1 H), 4.26 (q, *J* = 7.2 Hz, 2 H), 4.14 (q, *J* = 7.2 Hz, 0.2 H), 1.31 (t, *J* = 7.2 Hz, 3 H), 1.23 (t, *J* = 7.1 Hz, 0.3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.7, 140.4, 139.6, 137.9, 129.7, 129.1, 128.0, 122.3, 119.6, 60.8,14.2 ppm.

3-(Phenylselanyl)acrylic Acid (3ba): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.26 (d, *J* = 15.6 Hz, 0.1 H), 7.85 (d, *J* = 9.6 Hz, 1 H), 7.51–7.53 (m, 2 H), 7.27 (d, *J* = 1.8 Hz, 2 H), 7.26 (d, *J* = 1.8 Hz, 1 H), 6.33 (d, *J* = 9.6 Hz, 1 H), 5.78 (d, *J* = 15.6 Hz, 0.1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.5, 153.8, 153.7, 133.6, 133.5, 132.5, 129.6, 128.6, 116.5, 116.3 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 2924, 1664, 1567, 1245, 690 cm^{-1}. $C_9H_8O_2Se$ (227.12): calcd. C 47.59, H 3.55; found C 48.80, H 3.52.

3-(Phenylthio)acrylic Acid (3bb): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92 (d, *J* = 14.9 Hz, 1 H), 7.47–7.49 (m, 5 H), 7.41 (d, *J* = 10.2 Hz, 1.6 H), 7.32–7.39 (m, 5 H), 5.93 (d, *J* = 10.2 Hz, 1.6 H), 5.63 (d, *J* = 14.9 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.6, 170.6, 152.9, 150.3, 135.8, 133.0, 131.1, 129.7, 129.4, 129.4 128.4,114.4, 112.6 ppm. IR (KBr): $\tilde{\nu}$ = 3468, 2924, 1668, 1419, 1244, 689 cm^{-1}. $C_9H_8O_2S$ (180.22): calcd. C 59.98, H 4.47; found C 60.28, H 4.32.

3-(Butyltellanyl)acrylic Acid (3bc): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.67 (d, *J* = 9.8 Hz, 1 H), 7.81 (d, *J* = 9.8 Hz, 0.2 H), 6.95 (d, *J* = 9.8 Hz, 1 H), 6.36 (d, *J* = 9.8 Hz, 0.2 H), 2.60 (t, *J* = 7.6 Hz, 2 H), 1.82 (quint., *J* = 7.6 Hz, 2 H), 1.42 (sext, *J* = 7.5 Hz, 2 H), 0.93 (t, *J* = 7.5 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.77, 140.36, 122.63, 33.92, 24.96, 13.40, 9.82 ppm. IR (KBr): $\tilde{\nu}$ = 3440, 2958, 1727, 1463, 1288, 1124, 1073, 670 cm^{-1}.

3-(Phenyltellanyl)acrylic Acid (3bd): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 16.5 Hz,0.1 H), 8.72 (d, *J* = 9.6 Hz, 1 H), 7.83–7.81 (m, 2 H), 7.38–7.35 (m, 1 H), 7.31–7.28 (m, 2 H), 7.05 (d, *J* = 9.6 Hz, 1 H), 6.15 (d, *J* = 16.5 Hz, 0.1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.3, 145.0, 138.4, 129.6, 128.6, 122.2, 119.7 ppm. IR (KBr): $\tilde{\nu}$ = 2960, 2629, 1650, 1549, 1424, 1237, 730 cm^{-1}. $C_9H_8O_2Te$ (275.76): calcd. C 39.20, H 2.92; found C 39.13, H 2.89.

3-(Phenylselanyl)but-2-enoic Acid (3ca): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.66 (m, 1 H), 7.66–7.65 (m, 1 H), 7.43–7.40 (m, 1 H), 7.37–7.34 (m, 2 H), 6.24 (q, *J* = 1.2 Hz, 1 H), 1.95 (d, *J* = 1.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.52, 162.78, 137.49, 129.27, 129.14, 127.59, 114.00, 26.67 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 2923, 1654, 1438, 1225, 694 cm^{-1}. $C_{10}H_{10}O_2Se$ (241.15): calcd. C 49.81, H 4.18; found C 51.81, H 4.29.

3-(Phenylthio)but-2-enoic Acid (3cb): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.55–7.53 (m, 1.4 H), 7.50–7.48 (m, 2.2 H), 7.45–7.36 (m, 5.4 H), 5.87 (q, *J* = 1.2 Hz,. 0.9 H), 5.20 (q, *J* = 1.1 Hz, 1.5 H), 2.43 (d, *J* = 1.1 Hz, 4.5 H), 1.84 (d, *J* = 1.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.4, 170.8, 163.8, 162.1, 136.3, 135.7, 130.6, 130.3, 130.1, 129.8, 129.3, 111.4, 109.9, 25.7, 20.7 ppm. IR (KBr): $\tilde{\nu}$ = 2922, 1673, 1597, 1442, 1233, 916, 751 cm^{-1}. $C_{10}H_{10}O_2S$ (194.25): calcd. C 61.83, H 5.19; found C 61.62, H 5.38.

3-(Butyltellanyl)but-2-enoic Acid (3cc): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.62 (q, *J* = 1.4 Hz, 0.5 H), 6.17 (q, *J* = 1.2 Hz, 1 H), 2.80 (t, *J* = 7.6 Hz, 2.4 H), 2.66 (t, *J* = 7.8 Hz, 1 H), 2.42 (d, *J* = 1.4 Hz, 1.4 H), 2.33 (d, *J* = 1.2 Hz, 2.8 H), 1.75 (quint., *J* = 7.8 Hz, 1.5 H), 1.66 (quint., *J* = 7.6 Hz, 2.3 H), 1.49–1.35 (m, 4.5 H), 0.94 (t, *J* = 7.8 Hz, 4.9 H), 0.89 (t, *J* = 7.8 Hz, 1.2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.1, 171.3, 154.1, 152.3, 120.5, 114.7, 33.6, 32.0, 25.7, 25.5, 23.9, 23.3, 13.80, 13.7, 8.4, 6.4 ppm. IR (KBr): $\tilde{\nu}$ = 3435, 2959, 1652, 1650, 1463, 1288 cm^{-1}.

3-(Phenyltellanyl)but-2-enoic Acid (3cd): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.93–7.90 (m, 2 H), 7.42 (m, 1 H), 7.30 (m, 2 H), 6.69 (q, *J* = 1.2 Hz, 1 H), 2.10 (d, *J* = 1.2 Hz, 3 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.6, 156.7, 141.8, 129.5, 129.4, 119.6, 117.0, 29.0 ppm. IR (KBr): $\tilde{\nu}$ = 2979, 2602, 1646, 1560, 1434, 1224, 737 cm^{-1}. $C_{10}H_{10}O_2Te$ (289.79): calcd. C 41.45, H 3.48; found C 42.90, H 3.45.

(*Z*)-3-Phenyl-3-(phenylselanyl)acrylic Acid and 3-Phenyl-2-(phenylselanyl)acrylic Acid (3da): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41 (s, 0.4 H), 7.75–7.77 (m, 1 H), 7.39–7.41 (m, 2 H), 7.19–7.24 (m, 3 H), 6.98–7.11 (m, 8 H), 6.38 (s, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.69, 165.41, 149.36, 139.20, 136.53, 131.42, 130.98, 130.46, 129.50, 129.31, 128.77, 128.70, 128.53, 128.45, 128.28, 127.77, 127.32, 116.47 ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2594, 2347, 1663, 1558, 1209, 737, 689 cm^{-1}. $C_{15}H_{12}O_2Se$ (303.22): calcd. C 59.42, H 3.99; found C 59.20, H 4.40.

(*Z*)-3-Phenyl-2-(phenylthio)acrylic Acid and 3-Phenyl-3-(phenylthio)acrylic Acid (3db): ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.6 (s, 1 H), 8.33 (s, 0.5 H), 7.18–7.15 (m, 4 H), 7.13–7.10 (m. 3 H), 7.07–7.03 (m, 3 H) 6.13 (s, 1 H), 5.36 (s, 0.5 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.00, 162.41, 138.14, 134.14, 132.07, 128.75, 128.60, 128.44, 127.91, 127.79, 115.22 ppm. IR (KBr): $\tilde{\nu}$ =

2601, 1664, 1561, 1412, 1312, 1211, 703 cm^{-1}. $C_{15}H_{12}O_2S$ (256.32): calcd. C 70.29, H 4.72; found C 99.71, H 4.53.

(*Z*)-2-(Butyltellanyl)-3-phenylacrylic Acid and (*Z*)-3-(Butyltellanyl)-3-phenylacrylic Acid (3dc): ^1H NMR (500 MHz, $CDCl_3$): δ = 8.25 (s, 0.1 H), 7.34–7.27 (m, 5 H), 7.24–7.18 (m, 3 H), 7.15–7.14 (m, 2 H), 6.60 (s, 1 H), 2.08 (t, J = 7.5 Hz, 2.0 H), 1.42 (quint., J = 7.5 Hz, 2.0 H), 1.12 (sext, J = 7.5 Hz. 2.0 H), 0.72 (t, J = 7.5 Hz, 3.0 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 171.39, 156.65, 142.29, 128.46, 128.33, 127.46, 122.20, 33.40, 25.22, 13.40, 10.44 ppm. IR (KBr): $\tilde{\nu}$ = 2958, 1660, 1561, 1230, 702 cm^{-1}. $C_{13}H_{16}O_2Te$ (331.87): calcd. C 47.05, H 4.86; found C 42.11, H 4.16.

(*Z*)-3-(Phenyltellanyl)-3-phenylacrylic Acid and (*Z*)-3-Phenyl-2-(phenyltellanyl)acrylic Acid (3dd): ^1H NMR (500 MHz, $CDCl_3$): δ = 10.19 (s, 1.5 H), 8.39 (s, 1 H), 7.64–7.62 (m, 2 H), 7.50–7.48 (m, 2 H), 7.43–7.41 (m, 2 H), 7.34–7.33 (m, 3 H), 7.22–7.19 (m, 1 H), 7.14–7.11 (m, 2.6 H), 7.02–7.00 (m, 2 H), 6.97–6.94 (m, 2.4 H), 6.79 (s, 0.6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.39, 160.25, 151.54, 140.99, 140.55, 138.11, 129.78, 129.35, 128.67, 128.56, 128.10, 128.07, 127.94, 127.46, 120.91, 119.10, 114.50, 111.85 ppm. IR (KBr): $\tilde{\nu}$ = 2977, 2594, 1652, 1558, 1477, 1212, 738 cm^{-1}.

General Procedure for the Preparation of β-Acrylic Chalcogenides 3/3′ Effected Under the $(PhSe)_2Zn$ Previously Prepared: In a Schlenk tube, ethyl propiolate (0.049 g, 0.5 mmol) was mixed with $(PhSe)_2Zn$ (0.189 g, 0.5 mmol) and 1,4-dioxane (2 mL), and the reaction mixture was heated at reflux for 24 h under a nitrogen atmosphere. Then, the reaction was quenched with NH_4Cl (10 mL), and the mixture was extracted with EtOAc (2× 10 mL). The organic layer was then dried with (Na_2SO_4). The solvent was evaporated under reduced pressure, and the crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate, 7:3) to afford ethyl 3-(phenylselanyl)acrylate **3aa** (0.123 g, 0.5 mmol, 97%) as a colorless oil.

General Procedure for the Preparation of (*Z*)-β-Acrylic Chalcogenides Effected Under Radical Inhibitor (TEMPO) Conditions: In a Schlenk tube, a mixture of zinc dust (0.064 g, 1.0 mmol), diphenyl diselenide (0.157 g, 0.5 mmol), propiolic acid (0.035 g, 0.5 mmol), NH_4OH (0.2 mL), and TEMPO (0.078 g, 0.5 mmol) was suspended in 1,4-dioxane (2 mL), and this reaction mixture was heated at reflux for 24 h under a nitrogen atmosphere. Then, the reaction was quenched with NH_4Cl (10 mL), and the mixture was extracted with EtOAc (2× 10 mL). The organic layer was dried with (Na_2SO_4). The solvent was evaporated under reduced pressure, and the crude mixture was purified by silica gel column chromatography (hexane/ethyl acetate, 7:3) to produce ethyl 3-(phenylselanyl)acrylate **3aa** (0.123 g, 0.5 mmol, 97%) as a colorless oil.

Procedure for the Preparation of $(PhSe)_2Zn$: In a Schlenk tube, a mixture of zinc dust (0.064 g, 1.0 mmol), diphenyl diselenide (0.157 g, 0.5 mmol), and NH_4OH (0.2 mL) was suspended in 1,4-dioxane (2 mL). This reaction mixture was heated at reflux at the boiling point of the solvent for 2 h under a nitrogen atmosphere, during which time the diphenyl diselenide was almost completely consumed. Upon completion of the reaction, the solution was filtered, and the solid product was washed with CH_2Cl_2 and dried under vacuum. The product was obtained as a gray powder stable in air.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and copies of the ^1H NMR and ^{13}C NMR spectra of β-acrylic chalcogenides **3/3′**.

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