Cerium(III)-Mediated Efficient and Stereoselective Hydrochalcogenation of Terminal Alkynes

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Abstract: Vinylic chalcogenides were synthesized stereospecifically by hydrochalcogenation of propargylic amines or alcohols mediated by cerium(III) chloride. The products were obtained in good yields and with high regio- and stereoselectivities.

Key words: cerium chloride, vinylic chalcogenides, hydrochalcogenation, selenium, tellurium

Cerium chloride has recently emerged as a very useful, cheap, nontoxic, and water-tolerant Lewis acid catalyst that imparts high regio- and chemoselectivity in various chemical transformations. It can be used in several forms, such as the heptahydrate,[1] the anhydrous form,[2] or in combination with sodium iodide.[3] These forms can also be used on solid supports that modify the reactivity of the cerium salt.[4] Organocerium compounds are also extensively used in organic synthesis.[5]

The recent and remarkable developments in the use of organochalcogenide compounds as synthetic reagents and intermediates are the subject of many review articles[6] and books.[7] Among the organochalcogenide compounds, vinylic chalcogenides play an important role in organic synthesis because of their unusual reactivity.[8]

The transition metal-catalyzed addition of organochalcogenide compounds to alkynes has recently attracted a considerable amount of interest, and palladium-[9] and nickel-catalyzed[10] thiolation and selenation reactions of alkynes have been described. Most of these methods give the desired compounds as mixtures of regio- and stereoisomers. Noncatalytic addition reactions have also been described, but these also show low regioselectivity.[11] The use of expensive indium reagents has been recently described for the hydrochalcogenation of aminoalkynes[12] or alkynols[13] to give the corresponding Markovnikov products. Mixtures of Markovnikov and anti-Markovnikov products have also been obtained by hydroselanylation of alkynes by using sodium borohydride and ionic liquids.[14]

Many applications of vinylic chalcogenides have recently been described. Among a number of useful applications of vinyl selenides and vinyl sulfides are nickel-[15,16] or palladium-catalyzed[17]cross-coupling reactions with Grignard reagents. In the case of vinylic tellurides, palladium-catalyzed homocoupling[18] and cross-coupling reactions,[19] and nickel(II)-catalyzed cross-coupling reactions with alkynes[20a] or metal acetylides[20b] are useful transformations. Transmetalation reactions are particularly important in the chemistry of vinylic tellurides; treatment of these compounds with lithium[21], lithium/cerium,[21a] lithium/zinc,[22] zinc,[23] sodium,[24] calcium,[25] or Grignard reagents,[26] followed by the capture of the vinyl metals with electrophiles, occurs with retention of the geometry of the carbon–carbon bond. In addition, vinylcuprates can be prepared by transmetalation of vinyl tellurides.[27–29] The direct substitution of tellurium moieties by alkyl or alkynyl groups has also been described.[21d,30–32] The vinyl organometallic compounds obtained in this way can react with carbonyl compounds,[33] α,β-unsaturated systems,[34] or epoxides.[28]

To the best of our knowledge, however, there is no protocol that describes the preparation of vinylic chalcogenides promoted by cerium chloride. In the light of the above comments, it was of interest to design a simple, efficient, and versatile method for the stereoselective synthesis of vinylic chalcogenides, with the aim of using them in the construction of olefins with defined stereochemistry, thereby giving ready access to vinylic metal species.

We describe preparations of functionalized vinylic selenides and tellurides by cerium chloride catalyzed hydrochalcogenation of propargylic alcohols and amines. The first reactions were performed by using diphenyl diselenide (1 mmol) and sodium borohydride (2 equiv) as a reducing agent in methanol as the solvent. Propargylic alcohol (1 mmol) and cerium(III) chloride heptahydrate (1 mmol) were added, and the mixture was refluxed for 4 hours. The corresponding vinylic selenide was obtained in low yield (~10%) and with low regioselectivity. Increasing the amount of sodium borohydride to four equivalents did not improve the results. Next, we cleaved diphenyl diselenide with sodium borohydride in a separate flask and transferred this mixture to a solution of the alkyne and cerium trichloride heptahydrate in methanol at 0 °C. Finally, the mixture was then heated at the reflux temperature. The corresponding vinylic selenide was isolated in very high yield (96%), but again with low regioselectivity, the selenides **2a** and **3a** being isolated in a 45:55 ratio (Scheme 1).

With the aim of improving the regioselectivity of the reaction, we changed the solvent from methanol to isopropanol. The reaction once more occurred in high yield, but with a higher preference for isomer **3a** (**2a**/**3a** 37:63). In a

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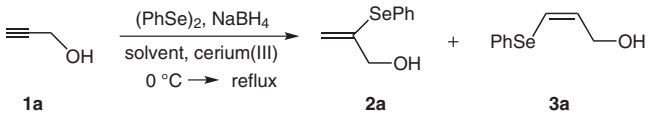


Scheme 1

Table 1 Effects of the Solvent and the Temperature on the Selectivity of the Reaction

Entry	Solvent[a]	Temp (°C)[b]	Ratio **2a/3a**[c]
1	*i*-PrOH	0	>98:2
2	MeOH	0	40:60
3	*s*-BuOH	0	70:30
4	*i*-PrOH	−20	>98:2
5	*i*-PrOH	r.t.	96:4
6	*i*-PrOH	40	90:10
7	*i*-PrOH	reflux	87:13

[a] Reaction performed with **1a** (1 mmol), $(PhSe)_2$ (1 mmol), $NaBH_4$ (3 mmol), and dry $CeCl_3$ (1 mmol).[2c,]
[b] Initial temperature of the reaction mixture.
[c] Ratio determined by ^1H NMR.

search for better regioselectivity, we replaced cerium(III) chloride heptahydrate with the anhydrous salt. In this case, a very high regioselectivity was observed (**2a/3a** >98:2; Table 1, entry 1). However, a drastic change in the ratio of the products occurred, as the geminal isomer **2a** became the main product in this case. On the basis of this result, we decided to reevaluate the use of isopropanol as a solvent, since this change in regioselectivity could have been a result of using anhydrous cerium chloride. As can be seen in Table 1, the high selectivity was indeed a result of using a combination of anhydrous cerium chloride and isopropanol, because, under the same conditions, methanol or *sec*-butanol gave mixtures of products (Table 1, entries 2 and 3). We then investigated the effects of temperature on the reaction. Changing the initial temperature to 0 °C or –20 °C had a dramatic effect on the selectivity (Table 1, entries 5–7).

After evaluating the effects of the solvent, the temperature, and the form of the cerium salt, we turned our attention to the effect of the amount of cerium(III) chloride on the reaction. The results, presented in Table 2, show that for propargyl alcohol **1a**, very high selectivity can only be achieved by the use of a stoichiometric amount of anhydrous cerium(III) chloride, because smaller amounts reduced the regioselectivity (Table 2, entries 2–5). Note the result shown in entry 6, which shows that a mixture of the three possible isomers was formed in the absence of cerium(III) chloride (Table 2, entry 6). We also observed that the use of equivalent amounts of diphenyl dichalcogenides (i.e., 0.5 equiv) and alkyne reduced the yield from nearly quantitative to 83%. Because diphenyl diselenide as a reagent is readily recovered by column chromatography at the end of reaction, we used this reagent in excess during our subsequent studies.

Table 2 Synthesis of Vinylic Chalcogenides by Hydrochalcogenation Catalyzed by Anhydrous Cerium(III) Chloride

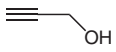
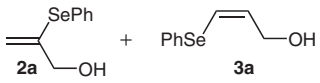
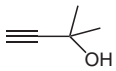
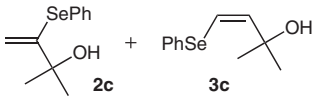
Entry	Alkyne	$CeCl_3$ (equiv)	Product	Time (h)	Yield (%)[a]	Ratio **2/3**[b]
1	 **1a**	1.0[c]	 **2a** + **3a**	3.0	95	37:63
2	**1a**	1.0	**2a + 3a**	3.0	98	>98:2
3	**1a**	0.5	**2a + 3a**	3.0	97	48:52
4	**1a**	0.1	**2a + 3a**	3.0	97	25:75
5	**1a**	0.05	**2a + 3a**	3.0	98	20:80
6	**1a**	–	**2a + 3a + *E***	3.0	95	50:20:30[d]
7	**1a**	1.0	 **2b** + **3b**	3.0	95	>98:2
8	**1a**	0.05	**2b + 3b**	3.0	95	21:79
9	 **1b**	1.0	 **2c** + **3c**	4.5	98	4:96
10	**1b**	0.05	**2c + 3c**	4.5	98	4:96

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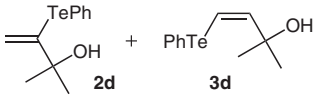
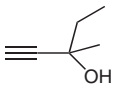
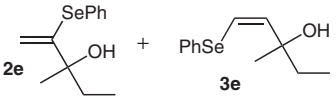
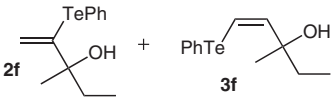
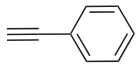
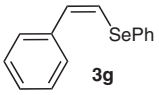
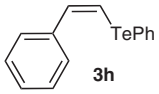
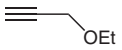
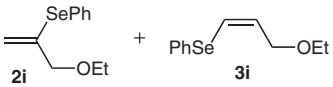
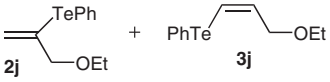
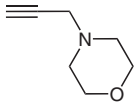
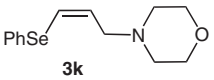
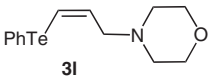
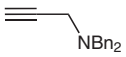
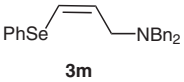
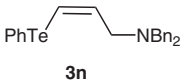
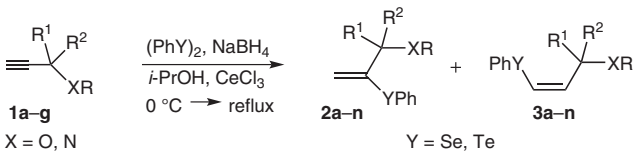
Table 2 Synthesis of Vinylic Chalcogenides by Hydrochalcogenation Catalyzed by Anhydrous Cerium(III) Chloride (continued)

Entry	Alkyne	$CeCl_3$ (equiv)	Product	Time (h)	Yield (%)[a]	Ratio **2/3**[b]
11	**1b**	0.05	 **2d** + **3d**	4.5	94	4:96
12	 **1c**	0.05	 **2e** + **3e**	4.5	97	7:93
13	**1c**	0.05	 **2f** + **3f**	4.5	94	6:94
14	 **1d**	0.05	 **3g**	6.0	79	>2:98 [e]
15	**1d**	0.05	 **3h**	6.0	78	>2:98 [e]
16	 **1e**	1.0	 **2i** + **3i**	4.5	96	3:97
17	**1e**	0.05	**2i + 3i**	4.5	96	3:97
18	**1e**	0.05	 **2j** + **3j**	4.5	94	7:93
19	 **1f**	0.05	 **3k**	4.5	92	>2:98[e]
20	**1f**	0,05	 **3l**	4.5	90	>2:98[e]
21	 **1g**	0,05	 **3m**	24	73	>2:98[e]
22	**1g**	0,05	 **3n**	24	69	>2:98[e]

[a] Isolated yield.
[b] Determined by ^1H NMR.
[c] $CeCl_3 \cdot 7H_2O$ (in all other examples, dry $CeCl_3$ was used).[2c]
[d] **2/3/*E***.
[e] Geminal isomer **2** was undetectable by ^1H NMR.

Having identified the optimal conditions, we next extended the reaction to some related compounds to determine the scope and limitations of our method. As can be seen in Table 2, completely different behavior was observed with propargyl alcohol **1b** or ether **1e**, and the corresponding (*Z*)-vinylic selenides were isolated with a high selectivity, irrespective of the amount of cerium(III) chloride that was used (1 equiv or 0.05 equiv) or of variations in the solvent and temperature.

The reaction was also extended to the other functionalized alkynes **1a**–**g**, which showed a similar general behavior (Scheme 2).



Scheme 2

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Under the conditions studied, propargyl amines could also be used as substrates to give the corresponding vinylic selenides. We also examined the corresponding reactions of phenyl acetylene and hex-1-yne. In the case of phenylacetylene, the (*Z*)-vinylic selenide was obtained in good yield and high regioselectivity (Table 2, entry 14), whereas the hex-1-yne gave the vinylic selenide as a mixture of isomers in very low yield, even after 12 hours of heating.

The method was also applied to the corresponding tellurium derivatives, with very similar results to those obtained with the selenium analogues in terms of the yield and stereoselectivity of the reaction (Table 2).

In the hydrotelluration reactions, which gave (*Z*)-vinylic tellurides exclusively, the tellurolate anion and the vinylic hydrogen are known to add to the alkyne in a *trans*-fashion and the vinylic hydrogen comes from the hydroxyl group of ethanol.[11,13b,35] We used these results to confirm the source of the vinylic hydrogen to our reaction. When the reaction in was performed in tetrahydrofuran[36] (an aprotic solvent), the vinylic products **2a** and **3a** (>98:2) were obtained in a yield of less than 83%. In addition, when the reaction was repeated with propargyl ether **1e**, which lacks an acidic proton in the hydroxyl group, in tetrahydrofuran as the solvent, the vinylic products were not obtained. These results, unlike those from previous work,[11,13b,35] strongly suggest that the cerium(III)-mediated addition of dichalcogenides across the triple bond follows an anti-pathway, with effective participation by the hydroxy group from the propargyl alcohol as the source of the vinylic hydrogen.

In conclusion, we have developed a convenient method for the preparation of functionalized vinylic selenides and tellurides from the corresponding alkynes by means of a cerium chloride mediated reaction. This is the first report describing the association between organochalcogen group and cerium chloride, suggesting that a cerium–selenium or cerium–tellurium complex may be involved in the control of the regio- and stereoselectivity of a hydrochalcogenation reaction of alkynes. The products formed were markedly dependent on the substitution pattern of the alkyne, but very high regio- and stereoselectivities were observed. We believe that this approach to vinylic chalcogenides should prove quite useful in synthesis, particularly as there are many ways of transforming the resulting chalcogen functionalities into a number of interesting substituted olefins with defined stereochemistries.

Column chromatography was performed on Merck silica gel (230–400 mesh). IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer of samples prepared as KBr pellets. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were recorded on a Bruker DPX 200 spectrometer of samples dissolved in $CDCl_3$. Mass spectra were recorded on a Hewlett Packard EM/CG HP-5988A spectrometer. All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use.

Vinyl Chalcogenides 2 and 3: General Procedure

$NaBH_4$ (0.152 g, 4 mmol) was added to a soln of diphenyl dichalcogenide (1 mmol) in *i*-PrOH (3 mL) under argon, and the mixture was stirred until colorless. A second two-necked flask equipped with a reflux condenser was charged the alkyne (1 mmol), *i*-PrOH (2 mL), and dry $CeCl_3$ (0.012 g, 5 mol% or 0.246 g, 1 mmol; see Table 2) under argon, and the contents of the first flask were added at 0 °C. The mixture was then refluxed for the time indicated in Table 2, and then cooled to r.t. H_2O (15 mL) was added and the mixture was extracted with EtOAc (3 × 10 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (EtOAc–hexanes, 5:95).

2-(Phenylselanyl)prop-2-en-1-ol (2a)[13a]

IR (KBr): 3356, 3057, 2922, 2858, 1615, 1577, 1476, 1438, 1037, 738, 690, 473 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 2 H), 7.28–7.24 (m, 3 H), 5.84 (t, *J* = 1.47 Hz, 1 H), 5.39 (t, *J* = 1.10 Hz, 1 H), 4.14 (s, 2 H), 2.46 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.37, 133.83, 129.24, 128.12, 127.72, 118.19, 66.25.

MS (EI): *m/z* (%) = 214 (49) [M$^+$], 183 (38), 158 (31), 91 (49), 78 (100), 51 (36).

2-(Phenyltellanyl)prop-2-en-1-ol (2b)[37]

IR (KBr): 3356, 3057, 2922, 2858, 1615, 1577, 1476, 1438, 1037, 738, 690, 473 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.82–7.76 (m, 2 H), 7.33–7.20 (m, 3 H), 6.25 (t, *J* = 1.76 Hz, 1 H), 5.57 (t, *J* = 1.42 Hz, 1 H), 4.21 (s, 2 H), 2.46 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.96, 129.86, 129.33, 127.94, 123.31, 112.06, 69.19.

MS (EI): *m/z* (%) = 264 (42) [M$^+$], 207 (14), 117 (22), 77 (100), 57 (20), 51 (52).

(2*Z*)-3-(Phenylselanyl)prop-2-en-1-ol (3a)[13a]

IR (KBr): 3355, 3056, 2921, 2860, 1609, 1577, 1476, 1438, 1072, 736, 690, 464 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54–7.43 (m, 2 H), 7.27–7.22 (m, 3 H), 6.61 (dt, *J* = 9.15 and 1.24 Hz, 1 H), 6.22 (dt, *J* = 9.15 and 6.05 Hz, 1 H), 4.28 (dd, *J* = 6.05 and 1.24 Hz, 2 H), 2.37 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 134.54, 132.52, 131.81, 129.14, 127.07, 122.83, 61.26.

MS (EI): *m/z* (%) = 214 (46) [M$^+$], 158 (89), 115 (24), 78 (100), 57 (35), 51 (37).

(2*Z*)-3-(Phenyltellanyl)prop-2-en-1-ol (3b)[37]

IR (KBr): 3359, 3051, 2920, 2853, 1610, 1582, 1472, 1434, 1035, 735, 692, 470 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.74–7.69 (m, 2 H), 7.29–7.25 (m, 3 H), 6.92 (dt, *J* = 9.60 and 1.40 Hz, 1 H), 6.53 (dt, *J* = 9.60 and 5.0 Hz, 1 H), 4.24–4.22 (m, 2 H), 2.50 (br s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.99, 137.38, 136.53, 129.13, 127.50, 107.40, 64.07.

MS (EI): *m/z* (%) = 264 (46) [M$^+$], 207 (38), 117 (24), 77 (100), 57 (36), 51 (38).

(3*Z*)-2-Methyl-4-(phenylselanyl)but-3-en-2-ol (3c)[38]

IR (KBr): 3385, 3057, 2972, 2928, 1604, 1578, 1476, 1438, 1143, 739, 691, 470 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.57–7.51 (m, 2 H), 7.28–7.24 (m, 3 H), 6.43 (d, *J* = 10.0 Hz, 1 H), 6.00 (d, *J* = 10.0 Hz, 1 H), 2.15 (br s, 1 H), 1.41 (s, 6 H).

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^{13}C NMR (50 MHz, $CDCl_3$): δ = 136.78, 132.82, 132.63, 128.99, 127.09, 120.59, 72.77, 29.48.

MS (EI): *m/z* (%) = 242 (39) [M$^+$], 227 (45), 158 (15), 147 (100), 128 (44), 85 (63), 77 (75), 65 (35), 51 (46).

(3*Z*)-2-Methyl-4-(phenyltellanyl)but-3-en-2-ol (3d)[38]
IR (KBr): 3423, 3064, 2970, 2865, 1600, 1574, 1474, 1460, 1063, 732, 692, 458 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 2 H), 7.29–7.17 (m, 3 H), 6.68 (d, *J* = 9.85 Hz, 1 H), 6.43 (d, *J* = 9.85 Hz, 1 H), 2.26 (br s, 1 H), 1.36 (s, 6 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 141.28, 140.37, 137.75, 129.02, 127.42, 104.45, 73.31, 29.14.

MS (EI): *m/z* (%) = 292 (46) [M$^+$], 207 (21), 197 (42), 147 (42), 129 (41), 85 (41), 77 (100), 67 (54), 51 (52).

(1*Z*)-3-Methyl-1-(phenylselanyl)pent-1-en-3-ol (3e)[14]
IR (KBr): 3443, 3057, 2968, 2927, 1606, 1578, 1477, 1458, 1142, 737, 691, 472 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.54–7.51 (m, 2 H), 7.29–7.25 (m, 3 H), 6.48 (d, *J* = 10.14 Hz, 1 H), 5.93 (d, *J* = 10.14 Hz, 1 H), 2.09 (br s, 1 H), 1.66 (q, *J* = 7.50 Hz, 2 H), 1.35 (s, 3 H), 0.96 (t, *J* = 7.50, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 135.49, 132.95, 132.39, 128.97, 127.03, 121.21, 75.34, 35.00, 27.16, 8.21.

MS (EI): *m/z* (%) = 256 (43) [M$^+$], 227 (100), 157 (65), 147 (88), 129 (60), 77 (82), 51 (39).

(1*Z*)-3-Methyl-1-(phenyltellanyl)pent-1-en-3-ol (3f)[38]
IR (KBr): 3442, 3064, 2967, 2925, 1596, 1574, 1474, 1457, 1063, 732, 692, 458 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.79–7.74 (m, 2 H), 7.27–7.20 (m, 3 H), 6.72 (d, *J* = 10.04 Hz, 1 H), 6.37 (d, *J* = 10.04 Hz, 1 H), 2.04 (br s, 1 H), 1.63 (q, *J* = 7.50, 2 H), 1.31 (s, 3 H), 0.95 (t, *J* = 7.50, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 140.50, 139.97, 137.60, 128.90, 127.27, 105.15, 75.51, 34.70, 26.79, 7.99.

MS (EI): *m/z* (%) = 306 (24) [M$^+$], 277 (13), 207 (20), 199 (41), 129 (60), 77 (100), 51 (44).

[(*Z*)-2-(Phenylselanyl)vinyl]benzene (3g)
Mp 43.5–45 °C (Lit.[39] 44–45 °C).

IR (KBr): 3050, 3020, 1740, 1690, 1610, 1500, 1480, 1430, 1075, 730, 640 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.59–7.54 (m, 2 H), 7.40–7.36 (m, 4 H), 7.20–7.35 (m, 4 H), 6.97 (d, *J* = 10.40 Hz, 1 H), 6.77 (d, *J* = 10.40 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.1, 132.6, 131.5, 130.0, 129.2, 128.3, 128.2, 127.5, 127.2, 123.8.

MS (EI): *m/z* (%) = 260 (5) [M$^+$], 258 (6), 179 (52), 158 (22), 103 (26), 91 (51), 77 (100), 51 (45).

[(*Z*)-2-(Phenyltellanyl)vinyl]benzene (3h)
Mp 40–42.5 °C (Lit.[40] 40–42 °C).

IR (KBr): 3050, 3015, 1767, 1597, 1489, 1426, 1016, 769, 656 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.81–7.75 (m, 2 H), 7.48 (d, *J* = 10.6 Hz, 1 H), 7.44–7.20 (m, 8 H), 7.09 (d, *J* = 10.6 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.8, 137.9, 136.8, 129.3, 128.4, 128.0, 127.4, 127.3, 115.3, 109.15.

MS (EI): *m/z* (%) = 309 (8) [M$^+$ – 1], 207 (17), 181 (42), 165 (39), 103 (28), 91 (54), 77 (100), 51 (49).

{[(1*Z*)-3-Ethoxyprop-1-en-1-yl]selanyl}benzene (3i)
IR (KBr): 3057, 2974, 2866, 1608, 1578, 1477, 1438, 1102, 737, 690, 467 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.52–7.47 (m, 2 H), 7.31–7.26 (m, 3 H), 6.66 (dt, *J* = 9.41 and 1.22 Hz, 1 H), 6.18 (dt, *J* = 9.41 and 5.87 Hz, 1 H), 4.12 (dd, *J* = 5.87 and 1.22 Hz, 2 H), 3.54 (q, *J* = 7.09 Hz, 2 H), 1.25 (t, *J* = 7.09 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.98, 131.99, 130.94, 129.15, 127.09, 123.91, 68.77, 65.81, 15.17.

MS (EI): *m/z* (%) = 242 (17) [M$^+$], 198 (35), 158 (33), 117 (26), 77 (56), 57 (100).

Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.78; H, 5.85. Found: C, 54.63; H, 5.81.

{[(1*Z*)-3-ethoxyprop-1-en-1-yl]tellanyl}benzene (3j)
IR (KBr): 3064, 2973, 2866, 1574, 1474, 1433, 1104, 732, 692, 633, 456 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77–7.71 (m, 2 H), 7.29–7.20 (m, 3 H), 6.97 (dt, *J* = 10.00 and 1.47 Hz, 1 H), 6.51 (dt, *J* = 10.00 and 4.56 Hz, 1 H), 4.04 (dd, *J* = 4.56 and 1.47 Hz, 2 H), 3.52 (q, *J* = 7.06 Hz, 2 H), 1.27 (t, *J* = 7.06 Hz, 3 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.83, 137.53, 133.69, 129.13, 127.51, 108.71, 70.94, 66.11, 15.28.

MS (EI): *m/z* (%) = 292 (17) [M$^+$], 207 (7), 115 (18), 85 (54), 77 (41), 57 (100), 51 (16).

HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{11}H_{14}OTe$: 292.0107; found: 292.0121.

4-[(2*Z*)-3-(Phenylselanyl)prop-2-en-1-yl]morpholine (3k)[41]
IR (KBr): 3060, 2957, 2853, 2806, 1578, 1477, 1451, 1116, 1021, 738, 691, 467 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 2 H), 7.29–7.26 (m, 3 H), 6.68 (dt, *J* = 9.26 and 1.18 Hz, 1 H), 6.09 (dt, *J* = 9.26 and 6.32 Hz, 1 H), 3.74 (t, *J* = 4.70 Hz, 4 H), 3.09 (dd, *J* = 6.32 and 1.18 Hz, 2 H), 2.59–2.49 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 132.01, 131.42, 129.15, 128.48, 127.08, 125.37, 66.86, 58.40, 53.35.

MS (EI): *m/z* (%) = 283 (17) [M$^+$], 202 (25), 157 (4), 126 (100), 95 (20), 77 (19), 56 (39), 42 (37).

4-[(2*Z*)-3-(Phenyltellanyl)prop-2-en-1-yl]morpholine (3l)
IR (KBr): 3062, 2854, 2814, 1594, 1574, 1451, 1432, 1116, 1032, 733, 694, 456 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73–7.71 (m, 2 H), 7.25–7.20 (m, 3 H), 7.08 (dt, *J* = 9.40 and 1.50 Hz, 1 H), 6.47 (dt, *J* = 9.40 and 4.39 Hz, 0.98 H), 3.79 (t, *J* = 4.70 Hz, 4 H), 2.96 (dd, *J* = 4.39 and 1,50 Hz, 2 H), 2.52–2.46 (m, 4 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 137.18, 130.74, 128.95, 127.17, 120.98, 112.72, 66.93, 59.67, 53.14.

MS (EI): *m/z* (%) = 333 (11) [M$^+$], 207 (3), 126 (100), 117 (50), 100 (65), 77 (52), 56 (53).

HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{13}H_{17}NOTe$: 334.0445; found: 334.0448.

(2*Z*)-*N*,*N*-Dibenzyl-3-(phenylselanyl)prop-2-en-1-amine (3m)
IR (KBr): 3060, 3027, 2920, 2795, 1598, 1574, 1453, 1120, 1072, 737, 697, 464 cm^{-1}.

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^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.47–7.17 (m, 15 H), 6.60 (dt, *J* = 9.05 and 1.22 Hz, 1 H), 6.18 (dt, *J* = 9.05 and 6.24 Hz, 1 H), 3.59 (s, 4 H), 3.15 (dd, *J* = 6.24 and 1.22 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 139.23, 131.89, 131.37, 131.32, 129.14, 128.92, 128.15, 126.95, 126.86, 123.70, 58.03, 53.60.

MS (EI): *m/z* (%) = 393 (2) [M$^+$], 312 (11), 236 (35), 157 (4), 144 (42), 115 (30), 91 (100), 77 (13), 65 (35), 51 (15).

HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{23}H_{23}NSe$: 394.1068; found: 394.1068.

(2*Z*)-*N*,*N*-Dibenzyl-3-(phenyltellanyl)prop-2-en-1-amine (3n)
IR (KBr): 3061, 3026, 2922, 2797, 2709, 1596, 1574, 1295, 1119, 1069, 1028, 732, 697, 454 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.71–7.66 (m, 2 H), 7.38–7.19 (m, 13 H), 7.03 (dt, *J* = 9.41 and 1.12 Hz, 1 H), 6.53 (dt, *J* = 9.41 and 5.59 Hz, 1 H), 3.58 (s, 4 H), 3.04 (dd, *J* = 5.59 and 1.12 Hz, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 138.34, 137.36, 135.58, 129.42, 129.21, 128.13, 127.46, 126.97, 116.24, 110.94, 68.76, 57.45.

MS (EI): *m/z* (%) = 443 (4) [M$^+$], 236 (31), 207 (2), 144 (56), 115 (30), 91 (100), 77(31), 65 (35), 51 (25).

HRMS (ESI): *m/z* [M]$^+$ calcd for $C_{23}H_{23}NTe$: 444.0965; found: 444.0965.

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