Fluorinations of α-Seleno Carboxylic Acid Derivatives with Hypervalent (Difluoroiodo)toluene

Maria A. Arrica[a] and Thomas Wirth*[a]

Dedicated to Dedicated to Professor Yasuyuki Kita on the occasion of his 60th birthday

Keywords: Fluorination / Hypervalent iodine / Selenides

A very efficient synthesis of (difluoroiodo)toluene avoiding the use of elemental chlorine and elemental fluorine is described. We have fluorinated a series of α-acceptor substituted selenides using (difluoroiodo)toluene. The reactions are usually very clean and under the reaction conditions no further oxidized products are observed.

Introduction

The fluorination of organic molecules has been of increasing interest to organic and medicinal chemists for the past 50 years.[1] The substitution of a hydrogen atom with an isosteric fluorine atom allows chemists to probe reactivities and to synthesize compounds with important physical and biological properties of high value. The fluorinated products do not present appreciable steric differences towards the corresponding hydrogen compounds, but at the same time their electronic structures change, sometimes in a dramatic way. The elevated stability of the carbon–fluorine bond compared with the carbon–hydrogen bond implies that these substrates can be employed in studies of metabolic transformations and in many cases they have been used as enzymatic inhibitors exploiting biomimetic effects. Therefore, the judicious placement of fluorine atoms on pharmaceutical target molecules allows a change of various properties. Additionally, positron emission tomography (PET) uses the isotope fluorine-18 as a nuclide probe for medicine and methods for a clean incorporation into organic molecules are therefore highly sought after.

The unique and useful characteristics of fluorine-containing compounds, although sometimes unpredictable, are united with numerous applications in a variety of areas. Therefore different approaches to their synthesis have been developed. The most straightforward method is a substitution reaction whereby a fluoride ion from HF, from fluoride salts or from (diethylamino)sulfur trifluoride (DAST) is displacing a leaving group. A disadvantage of these methods is that the fluoride anion can react as a base instead as a nucleophile. But also electrophilic fluorinations have become useful methods for the introduction of fluorine atoms and are based on reagents with the fluorine atom bound to a powerful leaving group. Reagents such as molecular fluorine itself (F_2), acetyl hypofluorites, and several reagents with a nitrogen–fluorine bond belong to this category, the most important of them being Selectfluor,[2] from which stereoselective fluorinations have been developed.[3]

The use of iodine(III) compounds as reagents in organic synthesis is valuable and rich.[4] Numerous transformations with these reagents have been developed and include oxidations, additions, cyclizations, and rearrangements. It should come as no surprise, given the breadth of reactivity of these compounds, that fluorinating reagents would be among them. (Difluoroiodo)toluene has, for example, become a very useful reagent in the transfer of fluorine to several organic substrates.[5,6] The use of (difluoroiodo)toluene avoids harmful reagents such as molecular fluorine, toxic fluoride salts or DAST. Double bonds, α-positions of carbonyl compounds, or triple bonds are among the functionalities, which react with (difluoroiodo)toluene, allowing the synthesis of important fluorinated compounds.

Results and Discussion

The reactivity of sulfur-containing substrates towards (difluoroiodo)toluene was demonstrated already by Motherwell et al.[5] α-Fluoro sulfides have been obtained as main reaction products through a Fluoro-Pummerer reaction. By this procedure the fluoride is incorporated into the sulfur-containing molecule allowing for the synthesis of monofluorides and difluorides. Depending on reaction conditions, fluoro-sulfoxides can be formed as well. Very little attention has been paid to the analogous organoselenium

[a] Department of Chemistry, Cardiff University
P. O. Box 912, Cardiff CF10 3TB, United Kingdom
Fax: (internat.) +44-2920-876968
E-mail: wirth@cf.ac.uk

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compounds. As we have already done research in hypervalent iodine chemistry and in organoselenium chemistry, we were particularly interested in the reactivity of organoselenium compounds towards (difluoroiodo)toluene. Sulfur and selenium have similar chemical reactivity, but differ in size and electronegativity, and thus, in nucleophilicity. Sulfur seems to exhibit a particular affinity to the iodine atom in (difluoroiodo)toluene. We were interested in determining if that affinity is similar in reactions with analogous selenium-containing compounds which would play an important role in the reactivity of selenium substrates toward (difluoroiodo)toluene. It is well known that fluorosulfides are useful synthetic intermediates.[7] The synthesis of fluoroselenides will lead also to potential building blocks and allow for the synthesis of fluoroalkenes under milder conditions (lower temperatures) than the corresponding sulfides.[8] Fluoroselenides bearing acceptor substituents can also be synthesized by other reactions like deprotonation and reaction with an electrophilic fluorinating agent.[8a,8c] The selenenyl substituent as an easily removable group can be used in subsequent synthetic steps.

Synthesis of (Difluoroiodo)toluene

Hypervalent iodine(III) difluorides have been synthesized first in 1901 by Stille[9] and several methods for their preparation are known.[10] The methods commonly used for the synthesis of (difluoroiodo)toluene are those developed by Carpenter[11] and Pollak-Zupan[12] using chlorine and mercury oxide or xenon difluoride, respectively. We have developed an alternative synthesis avoiding the use of these hazardous reagents which involves three steps, perborate oxidation, basic hydrolysis and reaction with aqueous HF as shown in Scheme 1.

The oxidation of iodotoluene (**1**) with perborate proceeds smoothly.[13] The diacetoxy derivative **2** is hydrolysed by treatment with aqueous sodium hydroxide to iodosyltoluene (**3**), which is then fluorinated using 40 % aqueous hydrogen fluoride to give (difluoroiodo)toluene (**4**) in good overall yield. Attempts to accomplish a direct ligand exchange of (diacetoxyiodo)toluene using a nucleophilic source (as LiF, NaF, etc) of fluorine failed. It is worth mentioning that acidic fluorination of (diacetoxyiodo)toluene with aqueous HF produced (difluoroiodo)toluene (**4**) along with some side products and therefore in lower overall yields.

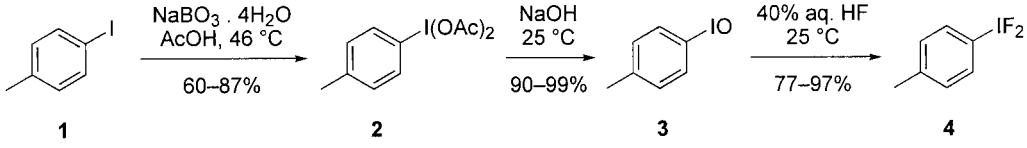
During our studies, an alternative synthesis was published which involved the preparation of (dichloroiodo)toluene.[14] In the synthesis described above we avoid the synthesis of the dichloride, which is notoriously unstable as well as light and heat-sensitive. On the other hand, (diacetoxyiodo)toluene (**2**) is a stable crystalline compound which can be stored for long periods of time. The overall yield of **4** reported by Hara and co-workers is around 80 % starting from the (dichloroiodo)toluene. In our procedure, (difluoroiodo)toluene (**4**) can be obtained in overall yield of up to 97 % starting from (diacetoxyiodo)toluene (**2**).

Preparation of Organoselenium Substrates

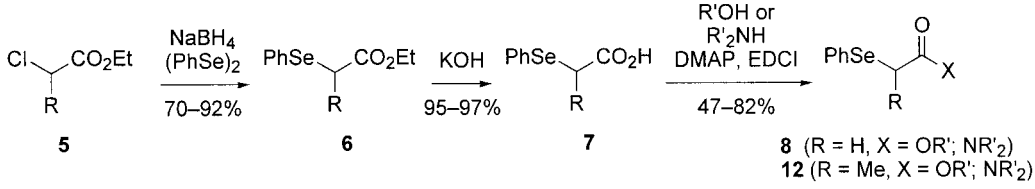
Organoselenium substrates were easily prepared by α-selenenylation of commercially available α-chloro esters **5** using $(PhSe)_2/NaBH_4$ as shown in Scheme 4. Subsequent hydrolysis to the corresponding carboxylic acid **7** and reaction with the appropriate alcohol or amine after activation with DMAP and EDCI gave a range of organoselenium substrates **8** for the investigation of fluorinations with (difluoroiodo)toluene (Scheme 2).

Fluorinations with (Difluoroiodo)toluene

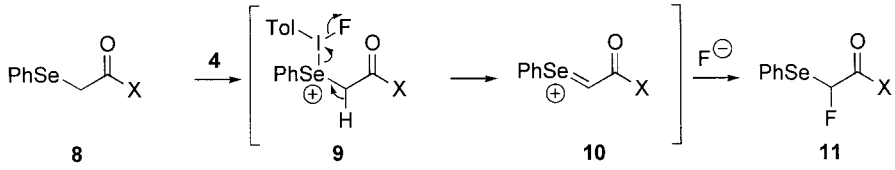
The reaction of selenide **8a** with (difluoroiodo)toluene (**4**) is believed to proceed in a similar way as the corresponding sulfides via a Seleno-Pummerer reaction. An interaction of the hypervalent iodine with the selenium atom leads to a ligand exchange on the iodine with loss of a fluoride and generate the cationic selenium intermediate **9** as shown in Scheme 3. Elimination to **10** and subsequent fluorination leads to the monofluorinated selanyl ester **11a**. An alternative reaction path is the displacement of the selanyl group by a nucleophile after activation by the hypervalent



Scheme 1. Synthesis of (difluoroiodo)toluene (**4**)



Scheme 2. Synthesis of α-selanylesters and α-selanylamides **8**



Scheme 3. Fluoro-Pummerer reaction of substrates **8** with (difluoroiodo)toluene (**4**)

iodine compound. The carbon–selenium bond is much weaker than the carbon–sulfur bond. Additionally, the PhSe–ITol(F)$^+$ group exhibits hypernucleofugicity. These characteristics could lead to the substitution of the phenylselanyl group either by a fluoride or by another nucleophile, especially because activation of selenides by electrophiles is a known mechanism.[15] Such reaction products have, however, not been identified in the reactions described here, but these reaction pathways might result in the formation of volatile side-products.

Before embarking on the reaction of different substrates **8**, we initially followed the reaction of some selected substrates and analysed their behaviour under different reaction conditions. Various temperatures (0 °C → 25 °C, 40 °C) and different ratios of (difluoroiodo)toluene:substrate were investigated.

Reactions employing a 1:1 molar ratio of **4**:**8** (either at 0 °C or at 40 °C) showed, after a reaction time of 16 hours, still significant amounts of starting material. For shorter reaction times (4 h), again with a 1:1 ratio of reagent:substrate at 0 °C, the starting material was found to be the major component of the reaction mixture. Increasing the temperature and the reaction time until 16 hours and using an excess (2 equivalents) of (difluoroiodo)toluene, increases the yield of the monofluorinated product. Several solvents differing in polarity and boiling points were also investigated. An increase in reaction temperature affected positively the ratio between the monofluorinated product and the starting material, but even working at 100 °C (e.g. toluene), a complete conversion was not observed with a 1:1 ratio of reagent to substrate.

The formation of the mono-fluorinated selenides **11** is clearly visible by the ^{1}H NMR signal and integration of the α-protons. The α-protons of **8a** appears at δ = 3.51 ppm, while the α-proton of **11a** appears at δ = 6.34 ppm as a doublet with a typical coupling constant $^1J_{HF}$ = 51.7 Hz. The absence of difluorinated products can be seen by the ^{19}F NMR of the crude reaction mixture, which shows only a doublet due to the fluorine-hydrogen coupling. This is obviously different to the corresponding sulfides, where the incorporation of two fluorine atoms was observed.[5] The monofluorinated selenides are more difficult to deprotonate than the sulfur analogues and do not undergo a second seleno-Pummerer reaction.

The mixtures of α-fluoro α-phenylselanyl esters **11**, and their starting materials **8** are almost impossible to separate by flash chromatography. They displayed identical behaviour in all solvent systems investigated. Even the use of fluorinated solvents or MPLC failed to separate the mixtures. Separation of these mixtures could only be achieved with HPLC. Unlike the fluorinated esters, the corresponding fluorinated amides were easily separated from their starting materials by column chromatography.

In Table 1 the yields of the monofluoro esters **11** using an excess of (difluoroiodo)toluene (2 equivalents) are reported. The results illustrate the formation of monofluorinated acyclic compounds with yields ranging from 20 to 65 %. A typical aqueous work-up with extraction with an organic solvent resulted in a significant loss of material. The presence of hydrofluoric acid in the reaction might result in the hydrolysis of the ester. No loss of compound was observed by work-up just by evaporation of the solvent. Additionally, decomposition of the product was detected in some cases during chromatography, while in other substrates the presence of monofluorinated phenylselanyl acetic acid was noticed.

Table 1. Fluorination of esters **8** with (difluoroiodo)toluene (**4**)

Entry	Substrate	X	Yield
1	**8a**	OEt	**11a**: 62 %
2	**8b**	OPh	**11b**: 46 %
3	**8c**	$OCH_2CH{=}CH_2$	**11c**: 41 %
4	**8d**	$OCH_2CH{=}C(CH_3)_2$	**11d**: 65 %
5	**8e**	(*E*)-$OCH_2CH{=}CHPh$	**11e**: 45 %
6	**8f**	$OCH_2CH_2C(CH_3) = CH_2$	**11f**: 20 %
7	**8g**	$OCH_2C{\equiv}CH$	**11g**: 34 %
8	**8h**	OCH_2CH_2OH	**11h**: 38 %

The reactivity of α-seleno esters did not change even when more than 2 equivalents of (difluoroiodo)toluene were used. The same was observed for the corresponding amides, these results are summarized in Table 2.

Table 2. Fluorination of amides **8** with (difluoroiodo)toluene **4**

Entry	Substrate	X	Yield
1	**8i**	$NHCH_3$	**11i**: 31 %
2	**8j**	$N(CH_3)_2$	**11j**: 42 %
3	**8k**	NHPh	**11k**: 31 %
4	**8l**	$N(CH_3)Ph$	**11l**: 40 %
5	**8m**	$NHCH_2Ph$	**11m**: 53 %

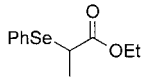
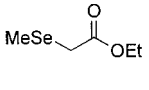
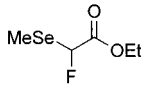
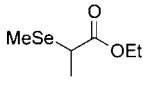
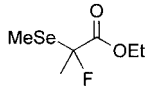
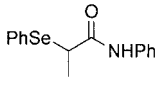
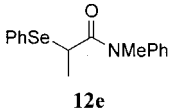
Even with large excess of (difluoroiodo)toluene, we have never observed any difluorinated products and it seems that a second fluorination reaction does not take place at all. This is probably due to the presence of the α-fluorine atom, which decreases the nucleophilicity of the selenium atom towards a second electrophilic attack by the iodine atom of (difluoroiodo)toluene.

We thought that the hypernucleofugicity of the PhSe–ITol(F)$^+$ moiety could lead to the formation of fluoroesters or, in the presence of an internal nucleophile as in substrate

8h, the formation of lactone products. In all substrates there was, however, no evidence for the formation of fluorinated products with loss of selenium. Additionally, reaction of esters containing a multiple bond showed no reaction with the hypervalent iodine compound and no evidence of lactone formation. Obviously groups such as double bonds, triple bonds or hydroxyl groups are not nucleophilic enough to carry out an attack on the activated selenium moiety.

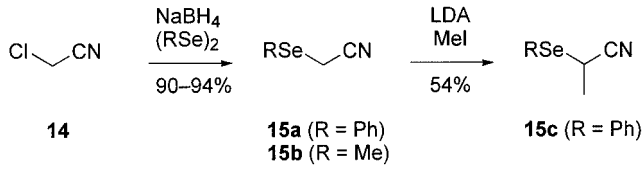
The construction of quaternary carbon atoms using (difluoroiodo)toluene was also investigated (Table 3). Reaction of ethyl α-phenylselanylpropionate (**12a**) failed to generate any fluorinated products and starting material was recovered. To investigate the steric and electronic contribution of the phenylselanyl moiety on the fluorination reaction, α-methylselanyl derivatives **12b** and **12c** were also synthesized. Higher reactivity of these substrates was expected with (difluoroiodo)toluene due to the greater localised positive charge of the selenium cation and due to the presence of the methyl group as a less sterically demanding moiety. The experimental results support this hypothesis. In contrast to **12a**, which did not react with (difluoroiodo)toluene, the corresponding (methylselanyl)propanoate **12c** was fluorinated to generate product **13c** with a quaternary carbon atom, although the conversion was not complete and unreacted starting material contaminated the product. The corresponding amide derivatives **12d** and **12e** did not react at all shown in Table 3 (Entries 4 and 5).

Table 3. Fluorination of α-methylated substrates **12** with (difluoroiodo)toluene (**4**)

Entry	Ester/Amide	Product	Yield
1	 **12a**	---	---
2	 **12b**	 **13b**	25%[a] (+**12b**, 25%)
3	 **12c**	 **13c**	28%[a] (+**12c**, 37%)
4	 **12d**	---	---
5	 **12e**	---	---

[a] Product is very volatile and an accurate determination of the isolated yield is difficult.

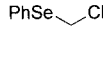
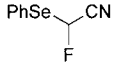
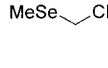
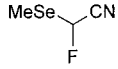
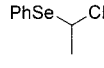
In order to compare the reactivities of acceptor-substituted α-seleno derivatives, we synthesized the corresponding α-selenonitriles as shown in Scheme 4.



Scheme 4. Synthesis of α-selenonitriles

Reaction of nitriles **15** with (difluoroiodo)toluene under the reaction conditions described above led to the formation of the α-fluoro-substituted compounds. As with esters and amides **8** and **12**, only the unsubstituted α-phenylselanylacetonitrile (**15a**) could be fluorinated, the α-methylated compound **15c** was unreactive. The low yields observed in the fluorination of nitrile **15b** are probably due to the high volatility of the fluorinated product. The results are summarized in Table 4.

Table 4. Fluorination of nitriles with (difluoroiodo)toluene (**4**)

Entry	Nitrile	Product	Yield
1	 **15a**	 **16a**	50%
2	 **15b**	 **16b**	26%
3	 **15c**	---	

Conclusion

We have developed a very efficient synthesis of (difluoroiodo)toluene avoiding the use of elemental chlorine and elemental fluorine. A series of α-acceptor-substituted selenides have been fluorinated using (difluoroiodo)toluene. Although the yields are only moderate, the reactions are usually very clean and, under the reaction conditions used, no further oxidized products are observed.

Experimental Section

General Remarks: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-400 MHz. $CDCl_3$ was used as solvent and as internal reference (δ = 7.26/77.0) in all the spectra; coupling constants J are given in Hertz. IR spectra were obtained with a Perkin–Elmer 1600 series FTIR as a liquid film.

^{19}F NMR spectra were recorded on a Jeol ECLIPSE+300 FT NMR (282.8 MHz) using BF_3 •2EtOH as external reference. ^{77}Se NMR spectra were recorded on the same instrument using diphenyl diselenide as external reference.

Mass spectroscopy analyses were performed either by atmospheric pressure chemical ionisation (APCI) over fisons VG platform II or by GC-MS over adb5 column. In this latter case (GC-MS), the following temperature conditions were used: from 70 to 200 °C for

36 minutes, from 200 to 250 °C for 4 minutes and 250 °C for 5 minutes; in this case electronical ionization (EI) were used as an ionization method. Accurate high resolution mass spectroscopic data were recorded by National Mass Spectrometry Service Centre at University of Swansea. All reagents were purchased as ACS grade and used without any further purification. CH_2Cl_2 was distilled immediately prior the use from CaH_2.

(Diacetoxyiodo)toluene (2): (Diacetoxyiodo)toluene was prepared according to the procedure described by McKillop.[13]

4-Iodosotoluene (3): (Diacetoxyiodo)toluene (**2**) (3 g, 9 mmol) was stirred in 5 M NaOH (10 mL) for 2 h at room temperature. The yellow solid was collected by suction and washed with water (500 mL) and then with $CHCl_3$ (100 mL). The collect solid was dried by suction and immediately used in the next reaction.

(Difluoroiodo)toluene (4): In a round-bottomed flask made of Teflon, a slurry of iodosyltoluene (**3**) (2 g, 8.6 mmol) in CH_2Cl_2 (30 mL) was prepared. Hydrofluoric acid 40 % was added (16 × 9 mmol) and the reaction mixture was allowed to stir for 30 min. The mixture was extracted with CH_2Cl_2 (2 × 10 mL). The combined extracts were washed several times with small portions of water, dried with molecular sieves, and the solvent was removed at atmospheric pressure through nitrogen flow to obtain a pale yellow solid, which was used without further purification. Yield was up to 97 % (2.14 g, 8.35 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.49 (s, 3 H), 7.40 (d, J = 8.5 Hz, 2 H, Ar), 7.84 (d, J = 8.5 Hz, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.2, 120.8, 130.2, 132.1, 142.3. ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –177.33 (ref.[16]: δ = –147.30; ref.[10d]: δ = –174.3 ppm).

General Procedure for the Synthesis of Ethyl α-Phenylselanyl Esters 6: To a solution of diphenyl diselenide (1.252 g, 4 mmol) in EtOH (30 mL), $NaBH_4$ (454 mg, 12 mmol) was added portionwise at 0 °C. When the solution becomes clear, a solution of ethyl 2-chloroester **5** (10 mmol) in EtOH was added. The mixture was stirred at 0 °C for 1 h and allowed to warm to room temperature. Water and diethyl ether were added. The organic layer was separated, washed with water, dried with brine and $MgSO_4$, filtered, and concentrated.

Ethyl 2-(Phenylselanyl)acetate (6, R = H) (= 8a): [17] Obtained in 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (t, J = 7.0 Hz, 3 H), 3.51 (s, 2 H), 4.13 (q, J = 7.0 Hz, 2 H), 7.26 (m, 3 H), 7.57–7.61 (m, 2 H). ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 333.25.

Ethyl 2-(Phenylselanyl)propanoate (6, R = Me) (= 12a): [17] Obtained with 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.17 (t, J = 7.1 Hz, 3 H), 1.54 (d, J = 7.0 Hz, 2 H), 3.77 (q, J = 7.0 Hz, 1 H), 4.09 (q, J = 7.1 Hz, 2 H), 7.27–7.36 (m, 3 H), 7.57–7.63 (m, 2 H).

Phenylselanylacetic Acid (7, R = H): [18] To a solution of ethyl 2-phenylselanylacetate (**6**, R = H) (410 mg, 1.69 mmol) in EtOH (10 mL) was added a solution of 30 % aq. KOH (10 mL). The mixture was stirred until completion. Water and diethyl ether were added. The basic layer was acidified with conc. HCl and extracted with diethyl ether. The combined organic layers were washed with water, dried with $MgSO_4$ and the solvent was evaporated. The product was obtained in 95 % yield as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.52 (s, 2 H), 7.28 (m, 3 H), 7.58–7.64 (m, 2 H).

2-(Phenylselanyl)propionic Acid (7, R = Me): Obtained in 97 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (d, J = 7.2 Hz, 3 H), 3.77 (q, J = 7.2 Hz, 1 H), 7.30–7.40 (m, 3 H, Ar), 7.65 (d, J = 7.8, J = 1.6 Hz, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.4, 36.9, 127.4, 128.8, 129.1, 135.8, 135.8, 179.8. IR (nujol): $\tilde{\nu}$ = 2923, 2852, 1687, 1450, 1377, 1329, 1298, 1243, 1162, 1078, 737, 667 cm^{-1}; MS (EI): m/z (%) = 230 (32), 185 (16), 157 (73), 105 (54), 77 (100), 51 (65), 45 (94). HRMS for [M + NH_4] $C_9H_{10}O_2Se$+NH_4^+: calcd. 248.0184, found 248.0184.

Esterification of 2-(Phenylselanyl)acetic Acid: To a solution of phenylselanylacetic acid (1.5 g, 7 mmol) in CH_2Cl_2 (40 mL) was added the alcohol (10 mmol), DMPA (0.98 g, 8 mmol) and EDCI (1.50 g, 8 mmol). The mixture was stirred at room temperature overnight. The organic solution was washed with 1 M NaOH to eliminate any traces of acid, dried and concentrated. The crude oil was then purified by flash chromatography (petroleum ether: EtOAc (9:1) when not specified).

Phenyl 2-(Phenylselanyl)acetate (8b): Obtained in 75 % yield as a pale yellow solid. M.p. 44–46 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.63 (s, 2 H), 6.89–6.95 (m, 2 H), 7.12–7.33 (m, 6 H), 7.57–7.63 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.4, 121.3, 125.9, 128.2, 128.7, 129.3, 129.4, 133.9, 150.6, 169.5. IR (nujol): $\tilde{\nu}$ = 2922, 1738, 1590, 1458, 1377, 1246, 1195, 1163, 1096, 934, 735, 688 cm^{-1}. MS (APCI): m/z (%) = 292 (13), 198 (36), 170 (100), 123 (8), 83 (12), 71 (50). HRMS for [M + NH_4^+] $C_{14}H_{12}O_2Se$+NH_4^+: calcd. 310.0341, found 310.0343.

Allyl 2-(Phenylselanyl)acetate (8c): Obtained in 72 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.56 (s, 2 H), 4.59 (d, J = 5.5 Hz, 2 H), 5.24 (dd, $^3J_{cis}$ = 10.5, ^2J = 2.4 Hz, 1 H), 5.31 (dd, $^3J_{trans}$ = 17.0, ^2J = 1.0 Hz, 1 H), 5.85 (m, 1 H), 7.30 (m, 3 H), 7.58–7.63 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.4, 65.8, 118.4, 127.9, 129.1, 129.1, 131.6, 133.4, 170.5. IR: $\tilde{\nu}$ = 3057, 2935, 1730, 1648, 1578, 1478, 1438, 1410, 1261, 1107, 989, 931, 690 cm^{-1}. MS (APCI): m/z (%) = 256 (58), 196 (30), 170 (40), 122 (25), 83 (41), 70 (100). HRMS for [M + NH_4] $C_{11}H_{12}O_2Se$+NH_4: calcd. 274.0341, found 274.0339.

3-Methyl-2-butenyl 2-(Phenylselanyl)acetate (8d): Obtained in 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3 H), 1.70 (s, 3 H), 3.45 (s, 2 H), 4.50 (d, J = 7.2 Hz, 2 H), 5.20 (m, 1 H), 7.20 (m, 3 H), 7.50 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9, 25.7, 27.5, 27.9, 62.3, 118.1, 127.7, 129.1, 133.3, 139.5, 170.8. IR (film): $\tilde{\nu}$ = 3005, 2969, 1726, 1578, 1478, 1438, 1260, 1105, 962, 736, 690 cm^{-1}. MS (APCI): m/z (%) = 285 (9), 216 (17), 198 (16), 170 (9), 69 (100). HRMS for [M + H] $C_{13}H_{16}O_2Se$+H: calcd. 285.0388, found 285.0388.

Cinnamyl 2-(Phenylselanyl)acetate (8e): Obtained in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.49 (s, 2 H), 4.65 (d, J = 6.5 Hz, 2 H), 6.10 (dt, J = 15.8, J = 6.5 Hz, 1 H), 6.50 (d, J = 15.9 Hz, 1 H), 7.18–7.31 (m, 8 H), 7.51 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.5, 65.8, 122.6, 126.6, 127.9, 128.1, 128.6, 128.9, 129.2, 133.6, 134.4, 136.1, 170.7. IR (film): $\tilde{\nu}$ = 3056, 2956, 1729, 1573, 1473, 1443, 1257, 1106, 966, 740, 690 cm^{-1}. MS (EI): m/z (%) = 332 (8), 171 (12), 131 (12), 117 (100), 91 (29), 77 (12), 51 (16). HRMS for $C_{17}H_{16}O_2Se$: calcd. 332.0310, found 332.0315.

3-Methyl-3-butenyl 2-(Phenylselanyl)acetate (8f): Obtained in 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 (s, 3 H), 2.19 (t, J = 6.8 Hz, 2 H), 3.40 (s, 2 H), 4.10 (t, J = 6.9 Hz, 2 H), 4.62 (s, 1 H), 4.71 (s, 1 H), 7.2 (m, 3 H), 7.5 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.4, 27.4, 36.3, 63.4, 112.3, 127.7, 129.1, 129.2, 133.3, 141.2, 170.8. IR: $\tilde{\nu}$ = 735, 891, 1106, 1262, 1473, 1579, 1649, 1724, 2955, 3066 cm^{-1}. MS (APCI): m/z (%) = 284 (45), 216 (12), 145 (38), 122 (18), 108 (18), 82 (30), 71 (100). HRMS for [M + NH_4]:$C_{13}H_{16}O_2Se$+NH_4: calcd. 302.0654, found 302.0655.

Propargyl 2-(Phenylselanyl)acetate (8g): Obtained in 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 1 H), 3.46 (s, 2 H), 4.55 (s, 2 H), 7.20 (m, 2 H), 7.53 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$):

δ = 26.9, 52.5, 75.1, 127.9, 128.6, 129.0, 133.5, 169.9. IR: $\tilde{\nu}$ = 3287, 3056, 2935, 2122, 1734, 1573, 1473, 1438, 1247, 1096, 1021, 996, 730, 695 cm^{-1}. MS (APCI): *m*/*z* (%) = 255 (17), 199 (31), 171 (42), 145 (18), 123 (26), 105 (29), 83 (25), 71 (100). HRMS for [M + NH_4] $C_{11}H_{14}O_2Se+NH_4$: calcd. 272.0184, found 272.0180.

2-Hydroxyethyl 2-(Phenylselanyl)acetate (8h): Obtained in 47 % yield as pale yellow liquid after purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.31. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.59 (s, broad, 1 H, OH), 3.48 (s, 2 H, CH_2Se), 3.65 (t, *J* = 4.0 Hz, 2 H, CH_2OH), 4.11 (t, *J* = 4.0 Hz, 2 H, CH_2O), 7.25 (m, 3 H, Ph), 7.54 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.3, 61.0, 66.8, 128.1, 129.0, 129.3, 133.6, 171.1. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 340.9. IR: $\tilde{\nu}$ = 3385 (br), 3030, 2957, 1725, 1578, 1478, 1438, 1410, 1264, 1110, 1074, 1022, 960, 886, 739, 690 cm^{-1}. GC (DB5) retention time: 23.27 min. MS (EI): *m*/*z* (%) = 260 (100), 243 (10), 216 (20), 171 (45), 157 (35), 91 (90), 77 (43), 51 (50). HRMS for $C_{10}H_{12}O_3Se$: calcd. 259.9946, found 259.9944.

2-(2-Phenylselanylacetoxy)ethyl 2-(Phenylselanyl)acetate: Obtained as side product of the reaction to 2-hydroxyethyl phenylselanylacetate as a pale yellow liquid in 10 % yield. Purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.40 (s, 4 H, CH_2Se), 4.10 (s, 4 H, CH_2O), 7.25 (m, 6 H), 7.45 (m, 4 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.1, 62.7, 127.9, 129.0, 129.2, 133.4, 170.6. IR: $\tilde{\nu}$ = 3030, 2959, 1731, 1578, 1477, 1437, 1248, 1102, 1022, 972, 911, 735, 689 cm^{-1}; MS (APCI): *m*/*z* (%) = 457 (8), 243 (100). HRMS for $C_{18}H_{18}O_4Se_2$: calcd. 457.9530, found 457.9523.

Amides from 2-(Phenylselanyl)acetic Acid and 2-(Phenylselanyl)propionic Acid: To a solution of phenylselanyl acetic acid or 2-(phenylselanyl)propionic acid (7 mmol) in CH_2Cl_2 (40 mL) was added the amine (10 mmol), DMPA (0.98 g, 8 mmol), and EDCI (1.50 g, 8 mmol). The mixture was stirred at room temperature overnight. The organic solution was washed with 1 M NaOH to eliminate any traces of acid, with 1 M HCl to eliminate any unreacted bases, dried, and concentrated. The crude reaction mixture was then purified by flash chromatography or crystallisation.

***N*-Methyl-2-(phenylselanyl)acetamide (8i):** Obtained in 66 % yield as pale yellow solid after purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.4; m.p.: 27–30 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (d, *J* = 4.9 Hz, 3 H, CH_3NH), 3.52 (s, 2 H, CH_2Se), 6.40 (s broad, 1 H, CH_3NH), 7.21 (m, 3 H, Ph), 7.40 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.8, 30.2, 127.6, 129.1, 129.4, 131.9, 169.0. IR: $\tilde{\nu}$ = 3347, 3066, 2935, 1644, 1584, 1478, 1408, 1307, 1162, 1021, 740 cm^{-1}. GC (DB5) retention time: 13.03 min. MS (EI): *m*/*z* (%) = 229 (100), 224 (10), 107 (53), 91 (10), 77 (5). HRMS for $C_9H_{11}NOSe$: calcd. 229.0000, found 229.0004.

***N*,*N*-Dimethyl-2-(phenylselanyl)acetamide (8j):** Obtained in 80 % yield as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.81 (s, 3 H, CH_3N), 2.82 (s, 3 H, CH_3N), 4.61 (s, 2 H, CH_2Se), 7.21 (m, 3 H, Ph), 7.52 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.2, 35.6, 37.9, 127.9, 129.2, 131.3, 133.2, 169.3. IR: $\tilde{\nu}$ = 3066, 2925, 1639, 1579, 1473, 1433, 1388, 1262, 735 cm^{-1}; Gc (DB5) retention time: 23.27 minutes [70/200 (5m); 200/250 (13m); 250 (5m)]; MS (EI): *m*/*z* (%) = 243 (100), 121 (24), 72 (55), 58 (40). HRMS for [M + H$^+$] $C_{10}H_{13}NOSe+H^+$: calcd. 244.0235, found 244.0236.

***N*-Phenyl-2-(phenylselanyl)acetamide (8k):** [19] Obtained in 64 % yield as pale yellow solid after purification by flash chromatography with petroleum ether/EtOAc (8:2). R_f = 0.2; m.p.: 73–75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, 2 H, CH_2Se), 6.90–7.50 (m, 10 H, Ph), 8.02 (1 H, s broad, PhN*H*). The spectroscopic data are in agreement with those in literature.[9]

***N*-Methyl-*N*-phenyl-2-(phenylselanyl)acetamide (8l):** Obtained in 45 % yield as pale yellow solid after purification by flash chromatography with petroleum ether/EtOAc (7:3). R_f = 0.4; m.p.: 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.22 (s, 3 H, CH_3N), 3.40 (s, 2 H, CH_2Se), 7.02 (d, 2 H, Ph), 7.14 (m, 3 H, Ph), 7.20–7.30 (m, 3 H, Ph), 7.38 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7, 37.8, 127.3, 127.5, 128.0, 129.0, 129.7, 129.8, 133.3, 143.6, 169.9. IR (nujol): $\tilde{\nu}$ = 2923, 1644, 1594, 1568, 1462, 1376, 1113, 722, 738, 694 cm^{-1}. GC (DB5) retention time: 30.26 min. MS (EI): *m*/*z* (%) = 305 (54), 107 (100). HRMS for [M + H$^+$] $C_{15}H_{15}NOSe+H^+$: calcd. 306.0392, found 306.0392.

***N*-Benzyl-2-(phenylselanyl)acetamide (8m):** Obtained in 83 % yield as white solid after purification by flash chromatography with petroleum ether/EtOAc (7:3). R_f = 0.2; m.p.: 70–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.54 (s, 2 H, CH_2Se), 4.43 (d, *J* = 5.8 Hz, 2 H, CH_2NH), 6.65 (s broad, 1 H, CH_2NH), 7.03–7.40 (m, 10 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.2, 44.0, 127.5, 127.6, 127.7, 128.7, 128.8, 129.5, 132.2, 137.7, 168.3. IR (nujol): $\tilde{\nu}$ = 2921, 2852, 1639, 1461, 1377, 1262, 743 cm^{-1}. GC (DB5) retention time: 32.02 min. MS (EI): *m*/*z* (%) = 306 (30), 224 (10), 148 (100), 107 (25), 91 (24), 77 (8), 65 (8), 51 (8). HRMS for $C_{15}H_{15}NOSe$: calcd. 305.0313, found 305.0316.

General Procedure to Synthesize α-Fluoroselenides: To a solution of (difluoroiodo)toluene **4** (51 mg, 0.2 mmol) in CH_2Cl_2 (2 mL) in a Teflon round-bottomed flask was added at 40 °C the chosen substrate (0.1 mmol) in CH_2Cl_2 (1 mL). The mixture was stirred overnight at 40 °C. The solvent was evaporated and the crude residue was purified by column chromatography.

Ethyl 2-Fluoro-2-(phenylselanyl)acetate (11a): Obtained in 62 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.09 (t, *J* = 7.0 Hz, 3 H, CH_3), 4.01 (q, *J* = 7.0 Hz, 2 H, CH_2), 6.34 (d, J_{HF} = 51.7 Hz, 1 H, C*H*F), 7.30 (m, 3 H, Ph), 7.63 (dd, *J* = 7.9, *J* = 1.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 62.1, 88.9 (d, $^1J_{CF}$ = 244 Hz, *C*FHSeC=O), 125.6, 129.3, 129.4, 135.9, 166.5 (d, $^3J_{CF}$ = 26.8 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.50 (d, J_{HF} = 55.64 Hz, 1 F, C*FH*SeC=O). ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 510.0. IR (nujol): $\tilde{\nu}$ = 2975, 1744, 1579, 1473, 1433, 1363, 1327, 1267, 1227, 1157, 1051, 1016, 855, 735, 695 cm^{-1}. MS (EI): *m*/*z* (%) = 262 (37), 188(12), 156 (34), 109 (100), 77 (45), 51 (30). HRMS for [M + NH_4^+] $C_{10}H_{11}O_2SeF+NH_4^+$: calcd. 280.0247, found 280.0247.

Phenyl 2-Fluoro-2-(phenylselanyl)acetate (11b): Obtained in 46 % yield as red solid after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.26; m.p.: 72–76 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.54 (d, $^2J_{HF}$ = 51.2 Hz, 1 H, *CHF*), 6.78 (d, *J* = 8.5 Hz, 2 H, Ar), 7.10–7.40 (m, 6 H, Ar), 7.66 (d, *J* = 7 z, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.3 (d, $^1J_{CF}$ = 283 Hz, *C*FHSeC=O), 120.9, 125.1, 126.3, 129.5, 129.6, 136.2, 136.2, 149.8, 165.0 (d, $^3J_{CF}$ = 28.2 Hz, CFHSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.8 (d, J_{HF} = 52.19 Hz, 1 F, C*FH*SeC=O). IR (KBr): $\tilde{\nu}$ = 3045, 2955, 1739, 1649, 1579, 1493, 1438, 1237, 1026, 931, 840, 735, 685 cm^{-1}. MS (EI): *m*/*z* (%) = 310 (42), 156 (25), 109 (48), 77 (91), 65 (59), 51 (46), 39 (100). HRMS for [M + NH_4^+] $C_{14}H_{11}O_2SeF+NH_4^+$: calcd. 328.0247, found 328.0252.

Allyl 2-Fluoro-2-(phenylselanyl)acetate (11c): Obtained in 41 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.45 (qt, ^2J = 1.3, ^3J = 11.3 Hz, 1 H), 4.47 (qt, ^2J =

1.3, ^{3}J = 11.3 Hz, 1 H), 5.17 (dq, ^{2}J = 1.3, $^{3}J_{cis}$ = 10, ^{4}J = 1.0 Hz, 1 H), 5.23 (dq, ^{2}J = 1.4, $^{3}J_{trans}$ = 17, ^{4}J = 1.4 Hz, 1 H), 5.71 (m, 1 H), 6.34 (d, $^{3}J_{HF}$ = 51.2 Hz, 1 H, *CH*F), 7.25–7.40 (m, 3 H, Ph), 7.57 (dd, *J* = 8.5, *J* = 1.5 Hz, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.4, 88.9 (d, $^{1}J_{CF}$ = 242 Hz, *C*FHSeC=O), 119.4, 125.5, 129.3, 129.4, 130.9, 135.9, 165.8 (d, $^{3}J_{CF}$ = 26.3 Hz, CFHSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.59 (d, J_{HF} = 55.17 Hz, 1 F, C*FH*SeC=O). IR (film): ṽ = 3059, 2950, 1754, 1648, 1578, 1477, 1439, 1272, 1226, 1156, 1049, 740, 691 cm^{-1}. GC (DB5) retention time: 18.36 min. MS (EI): *m*/*z* (%) = 274 (19), 189 (12), 157 (19), 109 (100), 77 (25). HRMS for [M + NH_4^+] $C_{11}H_{11}O_2SeF+NH_4^+$: calcd. 292.0247, found 292.0250.

3-Methylbut-2-enyl 2-(Fluorophenylselanyl)acetate (11d): Obtained in 65 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 3 H, C*H*$_3$), 1.67 (s, 3 H, C*H*$_3$), 4.46 (m, 2 H), 5.14 (m, 1 H), 6.35 (d, *J* = 53.2 Hz, 1 H, C*HF*), 7.25–7.40 (m, 3 H, Ph), 7.58 (d, *J* = 7.6 Hz, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 25.8, 62.8, 88.9 (d, $^{1}J_{CF}$ = 243 Hz, *CF*HSeC=O), 117.4, 125.6, 129.3, 129.4, 135.9, 140.4, 166.5 (d, $^{3}J_{CF}$ = 27.2 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.26 (d, J_{HF} = 58.94 Hz, 1 F, C*FH*SeC=O), IR (liquid film): ṽ = 2915, 1744, 1645, 1599, 1579, 1438, 1262, 1222, 1152, 1041, 740 cm^{-1}. MS (EI): *m*/*z* (%) = 302 (4), 234 (10), 157 (11), 109 (25), 77 (27), 69 (100), 41 (72). HRMS for [M + NH_4^+] $C_{13}H_{15}O_2SeF+NH_4^+$: calcd. 320.0560, found 320.0563.

Cinnamyl 2-Fluoro-2-(phenylselanyl)acetate (11e): Obtained in 45 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.60 (dd, *J* = 6.5, *J* = 1 Hz, 1 H), 4.63 (dd, *J* = 7, *J* = 1 Hz, 1 H), 6.04 (dt, *J* = 16, *J* = 7.1 Hz, 1 H), 6.35 (d, *J* = 52.3 Hz, 1 H, C*HF*), 6.54 (d, *J* = 16 Hz, 1 H), 7.20–7.30 (m, 8 H, Ar), 7.57 (dd, *J* = 8.5, *J* = 1.5 Hz, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 66.5, 88.7 (d, $^{1}J_{CF}$ = 242 Hz, *CF*HSeC=O), 121.7, 126.7, 128.3, 128.6, 128.7, 129.2, 129.4, 135.4, 135.8, 136.1, 166.3 (d, $^{3}J_{CF}$ = 25.3 Hz, CFHSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.59 (1 F, d, J_{HF} = 51.51 Hz, C*FH*SeC=O). IR (liquid film): ṽ = 3030, 1753, 1653, 1438, 1263, 1225, 1156, 966, 740 cm^{-1}. MS (EI): *m*/*z* (%) = 350 (3), 157 (22), 117 (100), 109 (65), 91 (53), 77 (63), 51 (41). HRMS for [M $^{+}$] $C_{17}H_{15}O_2SeF^+$: calcd. 350.0216, found 350.0224.

3-Methylbut-3-enyl 2-Fluoro-2-(phenylselanyl)acetate (11f): Obtained in 20 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.6. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.65 (s, 3 H), 2.18 (t, *J* = 6.9 Hz, 2 H), 4.09 (dt, *J* = 6.9, *J* = 2.2 Hz, 2 H), 4.64 (s, 1 H), 4.74 (s, 1 H), 6.33 (d, *J* = 51.8 Hz, 1 H, C*HF*), 7.23–7.38 (m, 3 H, Ar), 7.59 (dd, *J* = 8.0, *J* = 1.2 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 36.3, 64.2, 88.9 (d, $^{1}J_{CF}$ = 244 Hz, *CF*HSeC=O), 112.7, 125.7, 129.3, 129.4, 135.9, 140.9, 166.5 (d, $^{3}J_{CF}$ = 27.3 Hz, CFHSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –166.48 (d, J_{HF} = 51.48 Hz, 1 F, C*FH*SeC=O). IR (liquid film): ṽ = 3075, 2966, 1753, 1651, 1578, 1477, 1439, 1377, 1329, 1269, 1229, 1158, 1051, 895, 740, 690 cm^{-1}. MS (EI): *m*/*z* (%) = 302 (8), 234 (26), 157 (28), 109 (53), 77 (61), 51 (44), 41 (100).

Propargyl 2-Fluoro-2-(phenylselanyl)acetate (11g): Obtained in 34 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (t, *J* = 2.6 Hz, 1 H), 4.53 (dd, *J* = 23.7, *J* = 2.5 Hz, 1 H), 4.58 (dd, *J* = 23.7, *J* = 2.5 Hz, 1 H), 6.35 (d, *J* = 51.7 Hz, 1 H, C*HF*), 7.20–7.40 (m, 3 H, Ph), 7.59 (dd, *J* = 8.5, *J* = 1.5 Hz, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.1, 75.9, 76.3, 88.4 (d, $^{1}J_{CF}$ = 243 Hz, *CF*HSeC=O), 125.2, 129.4, 129.6, 136.1, 165.8 (d, $^{3}J_{CF}$ = 28.9 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –167.40 (d, J_{HF} = 55.19 Hz, 1 F, C*FH*SeC=O), IR (film): ṽ = 3293, 3056, 2935, 2360, 1760, 1476, 1438, 1220, 1153, 1050, 740 cm^{-1}. GC (DB5) retention time: 18.56 minutes [70–200 (26m)/200–250 (4m)/250 (5m)], MS (EI): *m*/*z* (%) = 272 (30), 189 (13), 157 (23), 109 (100), 77 (35), 51 (27). HRMS for [M + NH_4^+] $C_{11}H_9O_2SeF+NH_4^+$: calcd. 290.0090, found 290.0089.

2-Hydroxyethyl 2-Fluoro-2-(phenylselanyl)acetate (11h): Obtained in 38 % yield as pale yellow oil after purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (s broad, 1 H, OH), 3.62 (m, 2 H), 4.08 (m, 2 H), 6.37 (d, J_{HF} = 51.0 Hz, 1 H, C*FH*SeC=O), 7.20–7.30 (m, 3 H, Ar), 7.59 (dd, *J* = 7.0, *J* = 1.0 Hz, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 60.6, 67.4, 88.5 (d, $^{1}J_{CF}$ = 244 Hz, *CF*HSeC=O), 125.3, 129.4, 129.6, 136.1, 167.7 (d, $^{3}J_{CF}$ = 27.2 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –167.975 (d, J_{HF} = 55.2 Hz, 1 F, C*FH*SeC=O). ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 512.5. IR (film): ṽ = 3427 (br), 3056, 2945, 1744, 1579, 1473, 1433, 1373, 1327, 1277, 1232, 1162, 1051, 740, 685 cm^{-1}. MS (EI): *m*/*z* (%) = 296 (100), 140 (73), 135 (69), 122 (54), 77 (47). HRMS for [M + NH_4^+] $C_{10}H_{11}FO_3Se+NH_4^+$: calcd. 296.0196, found 296.0199.

***N*-Methyl-2-fluoro-2-(phenylselanyl)acetamide (11i):** Obtained in 31 % yield as brown solid after purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.4; m.p.: 60–64 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.59 (d, *J* = 4.9 Hz, 3 H, *CH*$_3$NH), 5.89 (s broad, 1 H, N*H*), 6.39 (d, J_{HF} = 52.3 Hz, 1 H, C*FH*SeC=O), 7.20–7.40 (m, 3 H, Ph), 7.59 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.9, 92.9 (d, $^{1}J_{CF}$ = 245.9 Hz, *C*FHSeC=O), 125.4, 129.2, 129.4, 136.3, 167.0 (d, $^{3}J_{CF}$ = 22.4 Hz, CFHSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –163.5 (d, J_{HF} = 55.2 Hz, 1 F, C*FH*SeC=O). IR: ṽ = 3447, 2925, 2855, 1664, 1458, 1376, 1263, 743 cm^{-1}. GC (DB5) retention time: 12.06 min. MS (EI): *m*/*z* (%) = 247 (100), 157 (25), 109 (81), 77 (33), 58 (58), 42 (19). HRMS for [M + H$^+$] $C_9H_{10}NOFSe+H^+$: calcd. 246.9906, found 246.9904.

***N*,*N*-Dimethyl-2-fluoro-2-(phenylselanyl)acetamide (11j):** Obtained in 42 % yield as yellow oil after purification by flash chromatography with petroleum ether/EtOAc (1:1). R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.88 (s, 3 H, CH_3), 2.98 (s, 3 H, CH_3), 6.51 (d, J_{HF} = 54.5 Hz, 1 H, C*FH*SeC=O), 7.20–7.30 (m, 3 H, Ph), 7.60 (m, 2 H, Ph), ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.2, 37.1, 92.9 (d, $^{1}J_{CF}$ = 241 Hz, *CF*HSeC=O), 127.3, 129.1, 129.4, 135.1, 165.8 (d, $^{3}J_{CF}$ = 21.4 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –160.8 (d, J_{HF} = 58.9 Hz, 1 F, C*FH*SeC=O). IR: ṽ = 3057, 2936, 1657, 1576, 1479, 1399, 1262, 1130, 1027, 741, 678 cm^{-1}. GC (DB5) retention time: 13.17 min. MS (EI): *m*/*z* (%) = 261 (75), 214 (22), 104 (23), 72 (100), 42 (11). HRMS for [M + H$^+$] $C_{10}H_{12}NOFSe+H^+$: calcd. 261.0063, found 261.0059.

2-Fluoro-*N*-phenyl-2-(phenylselanyl)acetamide (11k): Obtained in 31 % yield as brown-red solid after purification by flash chromatography with petroleum ether/EtOAc (7:3). R_f = 0.7; m.p.: 99–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.47 (d, J_{HF} = 51.7 Hz, 1 H, C*FH*SeC=O), 7.06 (m, 1 H, Ar), 7.20–7.30 (m, 7 H, Ar), 7.42 (s broad, 1 H, N*H*), 7.60 (dd, *J* = 1.6, *J* = 7.0 Hz, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 92.6 (d, $^{1}J_{CF}$ = 248 Hz, *CF*HSeC=O), 120.1, 124.8, 125.2, 128.9, 129.3, 129.6, 136.1, 136.5, 164.0 (d, $^{3}J_{CF}$ = 21.4 Hz, C*F*HSe*C*=*O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –162.2 (d, J_{HF} = 55.8 Hz, 1 F, C*FH*SeC=O). IR: ṽ = 3200, 1664, 1599, 1523, 1006, 730 cm^{-1}. GC (DB5) retention time: 29.18 min. MS (EI): *m*/*z* (%) = 309 (100), 208 (10), 132 (20), 109 (50), 93 (16),

77 (10). HRMS for [M + H$^+$] $C_{14}H_{12}NOFSe+H^+$: calcd. 310.0141, found 310.0146.

2-Fluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)acetamide (11l): Obtained in 40 % yield as brown solid after purification by flash chromatography with petroleum ether/EtOAc (7:3). R_f = 0.6; m.p.: 75–77 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.24 (s, 3 H, CH_3N), 6.11 (d, J = 54.1 Hz, 1 H, *CHF*Se), 7.03–7.42 (m, 10 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.9, 92.1 (d, $^1J_{CF}$ = 245 Hz, *CF*HSeC=O), 127.4, 127.5, 128.6, 128.7, 128.9, 129.9, 134.7, 141.8, 165.6 (d, $^3J_{CF}$ = 21.5 Hz, C*F*HSe*C=O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –162.9 (d, J_{HF} = 55.8 Hz, 1 F, C*FH*SeC=O). IR: $\tilde{\nu}$ = 3206, 3056, 2985, 1664, 1594, 1493, 1413, 1267, 725 cm^{-1}. GC (DB5) retention time: 20.10 min. MS (EI): *m*/*z* (%) = 323 (94), 146 (93), 134 (100), 109 (84), 77 (32), 51 (21). HRMS for [M + H$^+$] $C_{15}H_{14}NOFSe+H^+$: calcd. 324.0297, found 324.0300.

***N*-Benzyl-2-fluoro-2-(phenylselanyl)acetamide (11m):** Obtained in 53 % yield as brown solid after purification by flash chromatography with petroleum ether/EtOAc (7:3). R_f = 0.5; m.p: 57–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.19 (dd, J = 14.5, J = 6.5 Hz, 1 H, PhCH_2 NH), 4.20 (dd, J = 14.5, J = 6.5 Hz, 1 H, PhCH_2 NH), 6.08 (s broad, 1 H, N*H*), 6.37 (d, J_{HF} = 51.7 Hz, 1 H, C*FH*SeC=O), 6.92 (m, 2 H, Ph), 7.20–7.40 (m, 6 H, Ph), 7.59 (dd, J = 1, J = 8 Hz, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5, 92.6 (d, $^1J_{CF}$ = 245 Hz, *C*FHSeC=O), 125.1, 127.7, 127.8, 128.7, 129.3, 129.4, 136.5, 136.8, 166.4 (d, $^3J_{CF}$ = 22.3 Hz, CFHSe*C=O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –163.7 (d, J_{HF} = 55.8 Hz, 1 F, C*FH*SeC=O). IR: $\tilde{\nu}$ = 3337, 1664, 1518, 1453, 1378, 1262, 735 cm^{-1}. GC (DB5) retention time: 30.51 min. MS (EI): *m*/*z* (%) = 309 (100), 288 (10), 208 (10), 132 (20), 109 (50), 104 (31), 93 (17), 63 (11). HRMS for $C_{15}H_{14}NOFSe^+$: calcd. 323.0219, found 323.0216.

Synthesis of α-Methylselanyl Esters: To a solution of dimethyl diselenide (600 mg, 3 mmol) in EtOH (24 mL), $NaBH_4$ (363 mg, 10 mmol) was added at 0 °C. When the solution becomes clear, a solution of ethyl 2-chloroester (8 mmol) in EtOH was added. The mixture was stirred at 0 °C for 1 h and allowed to warm up to room temperature. Water and diethyl ether were added. The organic layer was separated, washed with water, dried with brine and $MgSO_4$, filtered and concentrated.

Ethyl 2-(Methylselanyl)acetate (12b): Obtained in 98 % yield as colourless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.30 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 2.19 (s, 3 H, CH_3Se), 3.15 (s, 2 H, CH_2Se), 4.19 (q, J = 7.1 Hz, 2 H, CH_3CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.9, 14.1, 23.7, 61.2, 171.5. ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 135.9. IR (liquid film): $\tilde{\nu}$ = 2927, 2853, 1727, 1458, 1419, 1365, 1263, 1109, 1031, 935, 737, 668 cm^{-1}. MS (EI): *m*/*z* (%) = 182 (57), 109 (100), 88 (71). HRMS for $C_5H_{10}O_2Se$: calcd. 181.9841, found 181.9842.

Ethyl 2-(Methylselanyl)propanoate (12c): Obtained as colourless liquid in 92 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.22 (t, J = 7.0 Hz, 3 H, CH_3 CH_2), 1.46 (d, J = 7.0 Hz, 3 H, CH_3 *CH*), 2.05 (s, 3 H, CH_3 Se), 3.36 (q, J = 7.0 Hz, 1 H, C*H*Se), 4.12 (q, J = 7.0 Hz, 2 H, CH_3 CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.9, 14.2, 17.0, 32.1, 60.9, 173.7. IR (liquid film): $\tilde{\nu}$ = 2985, 1722, 1450, 1368, 1326, 1257, 1208, 1147 cm^{-1}. GC (DB5) retention time: 5.45 min. MS (EI): *m*/*z* (%) = 196 (80), 123 (100), 102 (51), 74 (11), 55 (22), 41 (70). HRMS for $C_6H_{12}O_2Se$: calcd. 195.9997, found 195.9994.

***N*-Phenyl-2-(phenylselanyl)propionamide (12d):** Obtained in 79 % yield as white solid after crystallisation from CH_2Cl_2 and petroleum ether. m.p.: 121–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.58 (d, J = 7.1 Hz, 3 H, CH_3 CH), 3.76 (q, J = 7.1 Hz, 1 H, CH_3C*H*), 7.02 (m, 1 H, Ph), 7.20–7.30 (m, 7 H, Ph), 7.52 (d, J = 7.1, 2 H, Ph), 7.63 (s broad, 1 H, N*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.0, 41.4, 119.7, 124.4, 127.8, 128.7, 128.9, 129.5, 135.2, 137.6, 170.5. IR (nujol): $\tilde{\nu}$ = 3437, 1639, 1458, 1378, 720 cm^{-1}. GC (DB5) retention time: 30.31 min (50–250/250 10m). MS (EI): *m*/*z* (%) = 305 (67), 212 (30), 185 (20), 169 (24), 157 (27), 120 (70), 105 (81), 93 (100), 77 (71), 65 (46), 51 (39). HRMS for [M + H$^+$] $C_{15}H_{15}NOSe+H^+$: calcd. 306.0392, found 306.0392.

***N*-Methyl-*N*-phenyl-2-(phenylselanyl)propionamide (12e):** Obtained in 82 % yield as white solid after purification by flash chromatography with petroleum ether/EtOAc (6:4). R_f = 0.75; m.p.: 64–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.46 (d, J = 6.5 Hz, 3 H, CH_3 CH), 3.18 (s, CH_3N), 3.66 (q, J = 6.6 Hz, 1 H, CH_3C*H*), 7.01 (d, J = 6 Hz, 2 H, Ph), 7.10–7.30 (m, 8 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.9, 37.3, 37.7, 127.2, 127.9, 128.2, 128.3, 128.8, 129.7, 135.6, 143.5, 172.8. IR (nujol): $\tilde{\nu}$ = 2925, 1644, 1589, 1458, 1378, 1112, 625 cm^{-1}. GC (DB5) retention time: 29.54 min (50–250/250 10m). MS (EI): *m*/*z* (%) = 319 (59), 162 (54), 134 (46), 107 (100), 77 (55), 65 (100), 51 (25). HRMS for [M + H$^+$] $C_{16}H_{17}NOSe+H^+$: calcd. 320.0548, found 320.0549.

Ethyl 2-Fluoro-2-(methylselanyl)acetate (13b): Obtained in 25 % yield as yellow oil after purification by preparative TLC with petroleum ether/EtOAc (9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 2.14 (s, 3 H, CH_3Se), 4.24 (m, J = 7.1, J = 2.9 Hz, 2 H, CH_3 CH_2), 6.15 (d, J_{HF} = 47.69 Hz, 1 H, C*HF*Se). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.3, 14.1, 62.1, 84.4 (d, $^1J_{CF}$ = 239 Hz, *CF*HSeC=O), 167.1 (d, $^3J_{CF}$ = 28.1 Hz, C*F*HSe*C=O*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –173.82 (d, J_{HF} = 51.5 Hz, 1 F, C*FH*SeC=O). ^{77}Se NMR (57.3 MHz, $CDCl_3$): δ = 291.9. IR: $\tilde{\nu}$ = 2983, 1747, 1446, 1370, 1329, 1268, 1234, 1161, 1049, 912, 733 cm^{-1}. MS (EI): *m*/*z* (%) = 200 (62), 127 (93), 106 (100), 78 (36). HRMS for $C_5H_9O_2FSe$: calcd. 199.9746, found 199.9748.

Ethyl 2-Fluoromethylselanylpropanoate (13c): Obtained in about 40 % yield which could not be purified from starting material. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20 (t, J = 7.1 Hz, 3 H), 1.90 (d, J = 19.2 Hz, 3 H, CH_3C*F*), 2.10 (s, 3 H, CH_3 Se), 4.20 (dq, J = 2, J = 7.1 Hz, 2 H). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = –137.44 (q, J_{HF} = 18.5 Hz, 1 F, C*FH*SeC=O).

Procedure for the Synthesis of 15a and 15b: To a solution of diphenyl diselenide (1.252 g, 4 mmol) or dimethyl diselenide in EtOH (30 mL), $NaBH_4$ (454 mg, 12 mmol) was added portionwise at 0 °C. When the solution becomes clear, a solution of chloroacetonitrile **14** (754 mg, 10 mmol) in EtOH was added. The mixture was stirred at 0 °C for 1 h and then allowed to warm up to room temperature. Water and diethyl ether were added. The organic layer was separated, washed with water, dried with brine and $MgSO_4$, filtered and concentrated.

(Phenylselanyl)acetonitrile (15a): [20] Obtained in 90–94 % yield as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.30 (s, 2 H, CH_2), 7.30 (m, 3 H, Ph), 7.60 (m, 2 H, Ph). The spectroscopic data are in agreement with those in literature.

(Methylselanyl)acetonitrile (15b): Obtained in 67 % yield as pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 3.20 (s, 2 H, CH_2Se). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 6.1, 30.9, 117.1. IR: 2985, 2928, 2245, 1421, 1401, 1281, 1189, 923 cm^{-1}. GC (DB5) retention time: 3.14 min. MS (EI): *m*/*z* (%) = 135 (70), 84 (100), 45 (70). HRMS for [M + H$^+$] $C_3H_5NSe+H^+$: calcd. 134.9582, found 134.9585.

2-(Phenylselanyl)propionitrile (15c): [21] A solution of **15a** (5 mmol, 974 mg) in THF (10 mL) was added at –78 °C under inert and an-

hydrous atmosphere to a solution freshly prepared LDA (0.5 M). This mixture was stirred for about 30 minutes and methyl iodide (6 mmol, 851 mg) was added. The resulting solution was kept at –78 °C for 1 h and warmed up to room temperature slowly. The solution was poured into sat. aq. NH_4Cl and extracted three times with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by flash chromatography (petroleum ether/EtOAc (9:1)) and the product obtained in 54 % yield as pale yellow liquid. R_f = 0.4. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, J = 7.0 Hz, 3 H, *CH*$_3$ CH), 3.70 (q, J = 7.0 Hz, CH_3 *CH*, 1 H), 7.30 (m, 3 H, Ph), 7.6 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.2, 19.5, 120.8, 125.8, 129.5, 129.7, 136.5. IR: $\tilde{\nu}$ = 3045, 2985, 2925, 2222, 1579, 1478, 1438, 1338, 1302, 1162, 1086, 1016, 976, 730, 700 cm^{-1}. MS (EI): *m*/*z* (%) = 210 (38), 157 (100), 116 (18), 77 (88), 51 (72). HRMS for [M + NH_4^+] $C_9H_9NSe+NH_4^+$: calcd. 229.0238, found 229.0241.

2-Methyl-2-(phenylselanyl)propionitrile[22] was obtained as side product during the synthesis of **15c** in 28 % yield. Purified by flash chromatography with petroleum ether/EtOAc (9:1). R_f = 0.5. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 6 H, *CH*$_3$ C*CH*$_3$), 7.30 (m, 3 H, Ph), 7.70 (m, 2 H, Ph). The spectroscopic data are in agreement with those in literature.

2-Fluoro-2-(phenylselanyl)acetonitrile (16a): [23] Obtained in 50 % yield after purification by flash chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40 (d, J_{HF} = 50.2 Hz, 1 H, *CHF*), 7.40 (m, 3 H, Ph), 7.60 (m, 2 H, Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 76.3 (d, J_{CF} = 253.6 Hz, *C*H*F*), 113.8 (d, J_{CF} = 36.1 Hz, *C*H*F*), 124.6, 129.8, 130.5, 136.4. ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = 164.42 (d, J_{HF} = 52.2 MHz, 1 F). IR: $\tilde{\nu}$ = 3056, 2955, 2353, 1573, 1478, 1438, 1302, 1011, 926, 740, 680, 660 cm^{-1}. MS (EI): *m*/*z* (%) = 215 (80), 157 (100), 116 (17), 77 (78), 51 (43). HRMS for [M$^+$] $C_8H_6NFSe^+$: calcd. 214.9644, found 214.9645.

2-Fluoro-2-(methylselanyl)acetonitrile (16b): Obtained in 26 % yield as pale yellow liquid by preparative TLC. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, *CH*$_3$ Se); 6.32 (d, J_{HF} = 49.8 Hz, 1 H, *CHF*). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.4, 72.8 (d, J_{CF} = 235.2 Hz, *C*H*F*), 113.9 (d, J_{CF} = 39.8 Hz, *C*H*F*). ^{19}F NMR (282.8 MHz, $CDCl_3$): δ = 168.61 (d, J_{HF} = 52 Hz, 1 F). IR: $\tilde{\nu}$ = 2984, 2359, 1374, 1248, 1045, 908 cm^{-1}. MS (EI): *m*/*z* (%) = 153 (61), 95 (100), 58 (19).

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