

## I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Diselenides and allenes were synthesized according to literature reports.

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{19}\text{F}$  NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane ( $\delta$  0.00 ppm) for  $^1\text{H}$  and  $\text{CDCl}_3$  ( $\delta$  77.0 ppm) for  $^{13}\text{C}$ . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250 $\mu$ ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. HRMS data for substrates were collected on an Agilent 7890 GC-MS QTOF 7200 and 6540 LC/QTOF spectrometer in the mass-spec facility in the University of South Florida. For mechanistic studies using ESI-MS, the same MS instrument in Ohio University was used, and the samples were infused with a flow rate of 10  $\mu\text{L}/\text{min}$  and sprayed at a high voltage of 5 kV. The X-ray diffraction data for **3t**, **5i**, **6** was measured on Bruker D8 Venture PHOTON 100 CMOS system.

## II. General Procedures

### 2.1 Reaction Optimization

$\text{H}_2\text{C}=\text{C}(\text{CO}_2\text{Me})\text{C}\equiv\text{C}-\text{CO}_2\text{Me}$ ( <b>1a</b> )		$\text{PhX-XPh}$ ( <b>2a</b> , X = S; <b>2b</b> , X = Se)	cat. [M] DCE, 60 °C, 24 h	$\text{H}-\text{C}(\text{XPh})=\text{C}(\text{CO}_2\text{Me})-\text{C}(\text{XPh})=\text{C}(\text{H})-\text{CO}_2\text{Me}$ ( <b>3</b> )	$\text{H}-\text{C}(\text{XPh})=\text{C}(\text{CO}_2\text{Me})-\text{C}(\text{H})=\text{C}(\text{XPh})-\text{CO}_2\text{Me}$ ( <b>3'</b> )
entry	<b>2</b>	catalyst	conv. (%)	yield (%) of <b>3</b> ( <i>E/Z</i> )	yield (%) of <b>3'</b>
1	<b>2a</b>	5% IPrAuNTf <sub>2</sub>	100%	35% (8:1)	50%
2	<b>2b</b>	5% IPrAuNTf <sub>2</sub>	100%	91% (>100:1)	6%
3	<b>2b</b>	5% tBu <sub>3</sub> PAuNTf <sub>2</sub>	100%	77% (>100:1)	11%
4	<b>2b</b>	5% JohnPhosAuNTf <sub>2</sub>	100%	85% (>100:1)	12%
5	<b>2b</b>	5% RuPhosAuNTf <sub>2</sub>	100%	75% (50:1)	13%
6	<b>2b</b>	5% XPhosAuNTf <sub>2</sub>	100%	72% (40:1)	14%
7	<b>2b</b>	5% PPh <sub>3</sub> AuNTf <sub>2</sub>	60%	46%	-
8	<b>2b</b>	5% (PhO) <sub>3</sub> PAuNTf <sub>2</sub>	60%	31%	-
9	<b>2b</b>	5% IPrAuNTf <sub>2</sub> (in toluene)	100%	85% (>100:1)	7%
10	<b>2b</b>	5% IPrAuNTf <sub>2</sub> (in THF)	100%	50%	3%

11	<b>2b</b>	5% IPrAuNTf <sub>2</sub> (in CH <sub>3</sub> CN)	100%	90% (6:1)	<1%
12	<b>2b</b>	2% IPrAuNTf <sub>2</sub> (0.2 M)	100%	92% (>100:1)	5%
13	<b>2b</b>	2% IPrAuNTf <sub>2</sub> (0.5 M)	100%	85% (32:1)	7%
14	<b>2b</b>	1% IPrAuNTf <sub>2</sub> (0.5 M)	100%	85% (20:1)	8%
15	<b>2b</b>	10% HOTf	<5%	n.d.	-
16	<b>2b</b>	none	<5%	n.d.	-
17	<b>2b</b>	5% IPrAuCl	64%	32%	-
18	<b>2b</b>	5% JohnPhosAuCl	31%	25%	-
19	<b>2b</b>	5% PPh <sub>3</sub> AuCl	39%	31%	-
20	<b>2b</b>	10% PtCl <sub>2</sub>	80%	67%	-
21	<b>2b</b>	10% PtCl <sub>4</sub>	74%	54%	-
22	<b>2b</b>	10% AgOTf	29%	21%	-
23	<b>2b</b>	10% Cu(OAc) <sub>2</sub>	25%	16%	-
24	<b>2b</b>	10% Cu(CH <sub>3</sub> CN) <sub>4</sub> PF <sub>6</sub>	50%	<5%	-
25	<b>2b</b>	10% FeCl <sub>3</sub>	20%	15%	-
26	<b>2b</b>	10% Pd(OAc) <sub>2</sub>	<5%	n.d.	-
27	<b>2b</b>	10% Ga(OTf) <sub>3</sub>	40%	24%	-
28	<b>2b</b>	10% In(OTf) <sub>3</sub>	60%	54%	-
29	<b>2b</b>	10% Sc(OTf) <sub>3</sub>	32%	22%	-
30	<b>2b</b>	10% Zn(OTf) <sub>2</sub>	44%	34%	-

Reaction conditions: gold catalyst was added to a solution (1 mL) of alkyne **1a** (0.3 mmol) and disulfide **2a** or diselenide **2b** (0.2 mmol), and reaction was kept at 60 °C for 24 h. Conversion and yield were determined by <sup>1</sup>H NMR spectroscopy using dimethylsulfone as internal standard. <sup>a</sup> reaction at 40 °C.

In the case of Pt, the lower conversion and yield could due to the inferior  $\pi$ -acidity of platinum compared to gold cation. Other metal catalyst (Ag, Cu and Fe) gave very low conversion because it cannot undergo the proposed catalytic cycle based on our proposed mechanism; the observed small amount of desired products likely involved other pathways such as metal Lewis acid-assisted SePh<sup>+</sup> formation.

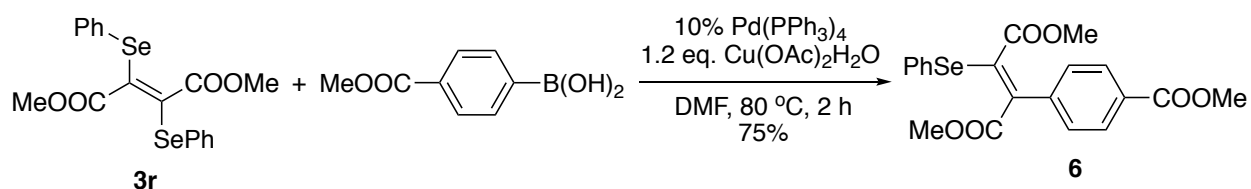
## 2.2 General Procedure for Diselenation of Alkynes

To a DCE solution (1 mL) of diselenide **2** (0.2 mmol, 1 eq) and alkyne **1** (0.3 mmol, 1.5 eq) was added IPrAuNTf<sub>2</sub> catalyst (0.004 mmol, 0.02 eq or 0.01 mmol, 0.05 eq) in one portion. The reaction was flashed with Ar and allowed to stir at 60 °C or rt for 24 h. The reaction mixture was then concentrated by rot-vap, and purified by flash chromatography (20:1 hex/EtOAc) to obtain pure product **3**.

### 2.3 General Procedure for Diselenation of Allenes

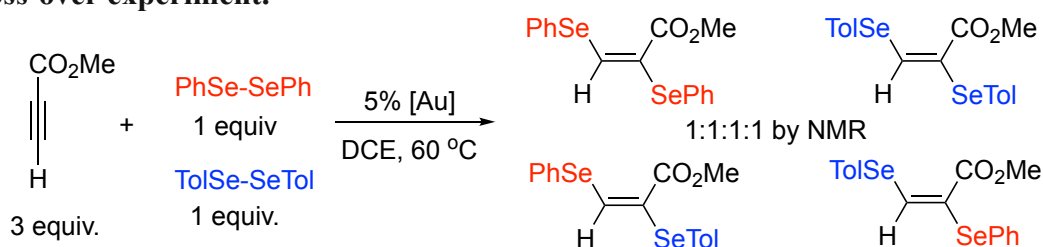
To a DCE solution (1 mL) of diselenide **2** (0.2 mmol, 1 eq) and allene **4** (0.6 mmol, 3 eq) was added IPrAuNTf<sub>2</sub> catalyst (0.004 mmol, 0.02 eq) in one portion. The reaction was flashed with Ar and allowed to stir at rt for 24 h in dark. The reaction mixture was then concentrated by rot-vap, and purified by flash chromatography (DCM:hexane = 1:10) to obtain pure product **5**.

### 2.4 Synthetic procedure for Suzuki coupling of **6**

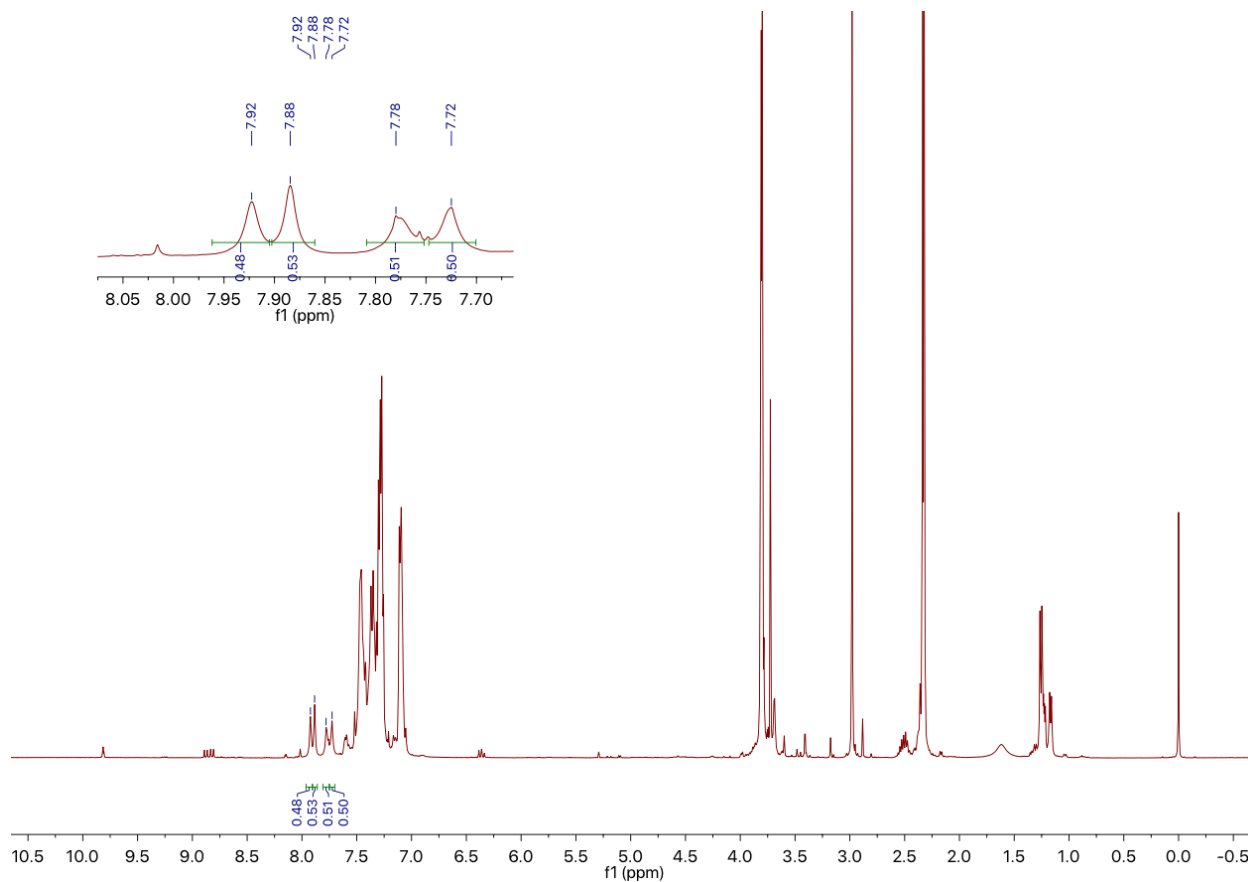


An oven-dried vial was added **3r** (273 mg, 0.6 mmol, 1 eq), boronic acid (324 mg, 1.8 mmol, 1.3 eq), Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg, 0.06 mmol, 0.1 eq) and Cu(OAc)<sub>2</sub>H<sub>2</sub>O (144 mg, 0.72 mmol, 1.2 eq) sequentially. The reaction mixture was placed under vacuum and recharged with Ar. Then DMF 3 mL was added and the reaction was flashed with Ar. After reacting for 2 h at 80 °C, the reaction was quenched with NH<sub>4</sub>Cl (sat.) 20 mL and extracted with DCM 10 mL three times. The three organic layers were combined and washed with H<sub>2</sub>O twice. The organic layer was dried with Na<sub>2</sub>SO<sub>4</sub> and concentrated under vacuum. Crude mixture was purified by flash chromatography (hexane:DCM = 10:1) to yield the desired product **6** (195 mg, 75%).

### 2.5 Cross-over experiment.

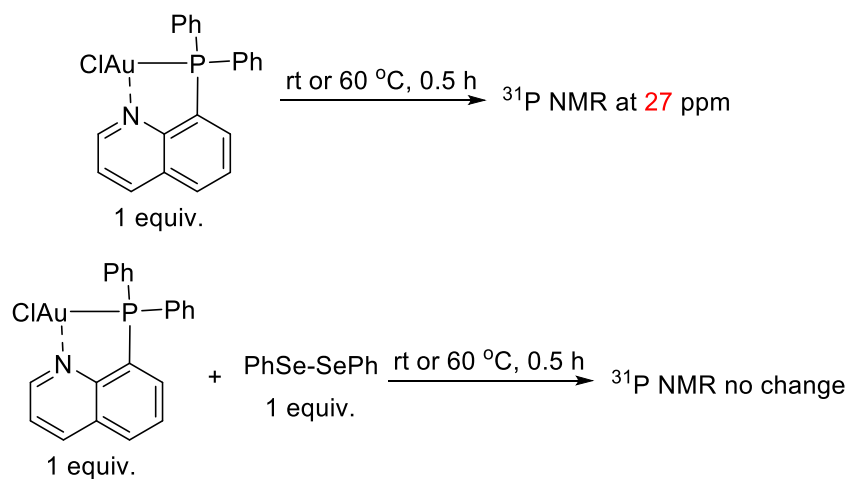


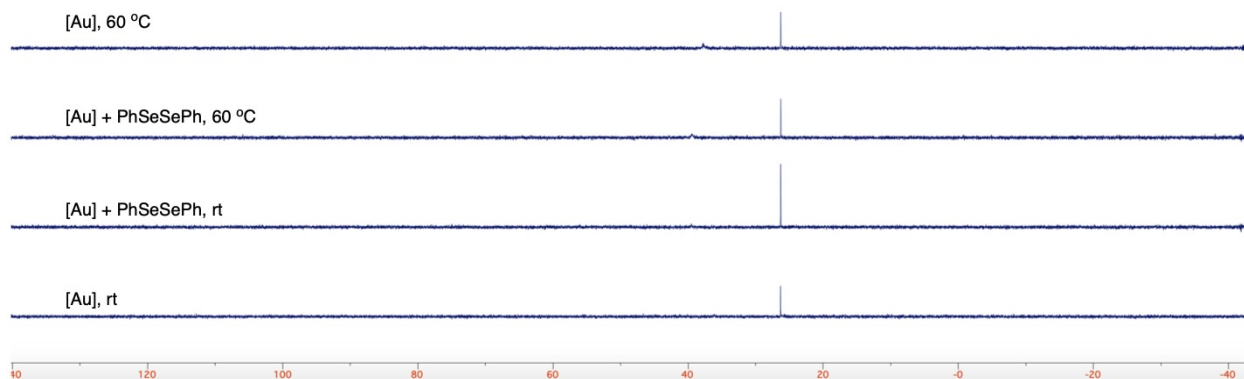
To a DCE solution (0.6 mL) of two different diselenides (0.1 mmol for each, 1 eq) and alkyne **1** (0.6 mmol, 3 eq) was added IPrAuNTf<sub>2</sub> catalyst (0.004 mmol, 0.02 eq) in one portion. The reaction was flashed with Ar and allowed to stir at 60 °C for 24 h. The ratio of four different products was determined to be around 1:1:1:1 as assigned by NMR based on the integration of the vinyl proton.



## 2.6 $^{31}\text{P}$ NMR experiment

A series of control experiments were carried out to investigate if direct oxidative addition occurred with diselenide. First, gold catalyst (5.2 mg, 0.017 mmol) in  $\text{CDCl}_3$  showed the same  $^{31}\text{P}$  NMR peak both at rt and after stirring at 60 °C for 0.5 h. Next, when treating the gold catalyst (5.2 mg, 0.017 mmol) with equal molar of diselenide (5.2 mg, 0.017 mmol) both at rt and 60 °C for 0.5 h, no change in  $^{31}\text{P}$  NMR was detected, which indicated a direct oxidative addition is unlikely for this system.





### III. ORTEP Drawing for Crystal Structures

#### X-ray Crystallography

X-ray diffraction data were measured on Bruker D8 Venture PHOTON II CPAD diffractometer equipped with a Cu K $\alpha$  INCOATEC ImuS micro-focus source ( $\lambda = 1.54178 \text{ \AA}$ ). Indexing was performed using *APEX3* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX3 [1]. Structures were solved using SHELXT [4] and refined using SHELXL-2018 [5] (full-matrix least-squares on  $F^2$ ) through OLEX2 interface program [6]. Ortep plots were done with PLATON [7]. **WCY-145**: Disordered ester group was refined with restraints. Crystal data and refinement conditions are shown in Tables 1, 2 and 3.

[1] Bruker (2019). *APEX3* Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (2019) SAINT V8.35A. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction*. University of Gottingen, Germany.

[4] XT, G.M. Sheldrick, *Acta Cryst.* (2015). A71, 3-8

[5] XL, Sheldrick, G. M. (2008). *Acta Cryst.* A64, 112-122.

[6] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). *J. Appl. Cryst.*, 42, 339-341

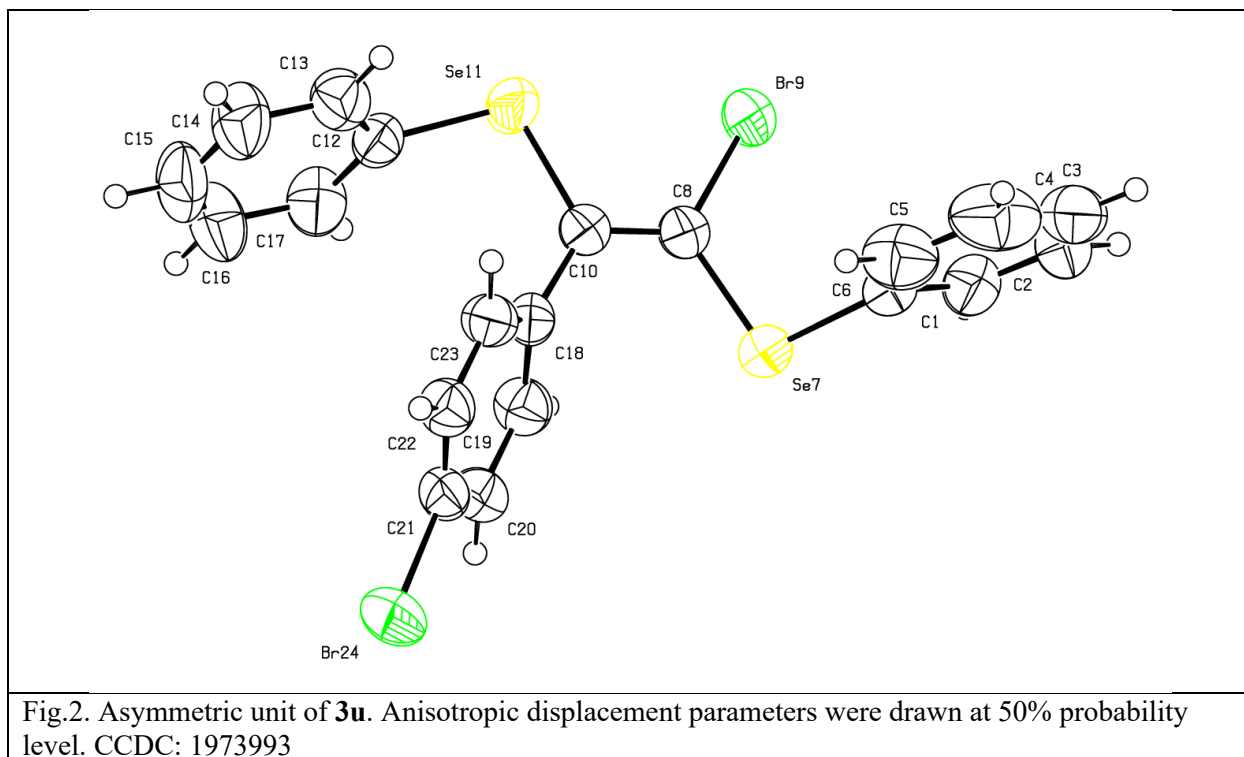
[7] A.L.Spek, *Acta Cryst.* 2009, D65, 148-155.

**Table 1 Crystal data and structure refinement for 3u.**

Identification code	3u
Empirical formula	C <sub>20</sub> H <sub>14</sub> Br <sub>2</sub> Se <sub>2</sub>
Formula weight	572.05
Temperature/K	296.65
Crystal system	triclinic
Space group	P-1

a/Å	10.3424(2)
b/Å	10.8991(2)
c/Å	11.3142(2)
$\alpha$ /°	118.4982(7)
$\beta$ /°	112.3929(7)
$\gamma$ /°	94.6421(7)
Volume/Å <sup>3</sup>	980.66(3)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.937
$\mu/\text{mm}^{-1}$	9.464
F(000)	544.0
Crystal size/mm <sup>3</sup>	0.25 × 0.08 × 0.05
Radiation	CuK $\alpha$ ( $\lambda = 1.54178$ )
2 $\Theta$ range for data collection/°	9.428 to 144.676
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	12071
Independent reflections	3701 [ $R_{\text{int}} = 0.0354$ , $R_{\text{sigma}} = 0.0341$ ]
Data/restraints/parameters	3701/0/218
Goodness-of-fit on F <sup>2</sup>	1.037
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0385$ , $wR_2 = 0.0953$
Final R indexes [all data]	$R_1 = 0.0420$ , $wR_2 = 0.0993$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.84/-0.66

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<b>Table 2 Crystal data and structure refinement for WCY-18.</b>	
Identification code	WCY-18
Empirical formula	C <sub>23</sub> H <sub>21</sub> BrSe <sub>2</sub>
Formula weight	535.23
Temperature/K	99.99
Crystal system	triclinic
Space group	P-1
a/Å	5.8168(3)
b/Å	11.2186(5)
c/Å	15.9188(7)
α/°	76.392(1)
β/°	86.334(1)
γ/°	84.372(1)
Volume/Å <sup>3</sup>	1003.88(8)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.771
μ/mm <sup>-1</sup>	6.949
F(000)	524.0
Crystal size/mm <sup>3</sup>	0.22 × 0.11 × 0.06
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.718 to 144.814
Index ranges	-7 ≤ h ≤ 6, -13 ≤ k ≤ 13, -19 ≤ l ≤ 19
Reflections collected	13581

Independent reflections	3834 [ $R_{\text{int}} = 0.0332$ , $R_{\text{sigma}} = 0.0311$ ]
Data/restraints/parameters	3834/0/237
Goodness-of-fit on $F^2$	1.121
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0265$ , $wR_2 = 0.0670$
Final R indexes [all data]	$R_1 = 0.0267$ , $wR_2 = 0.0671$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.44/-0.70

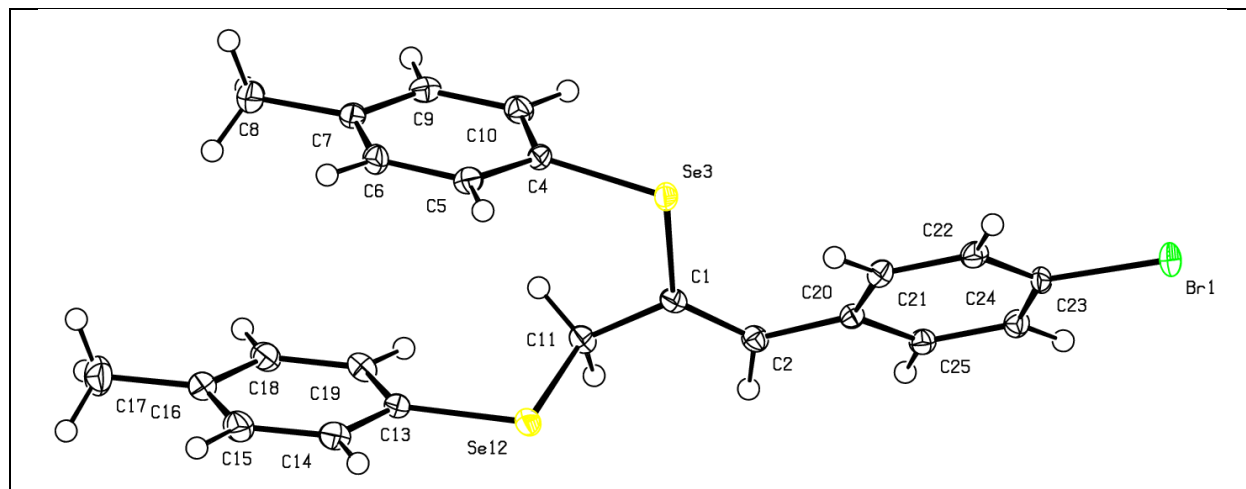


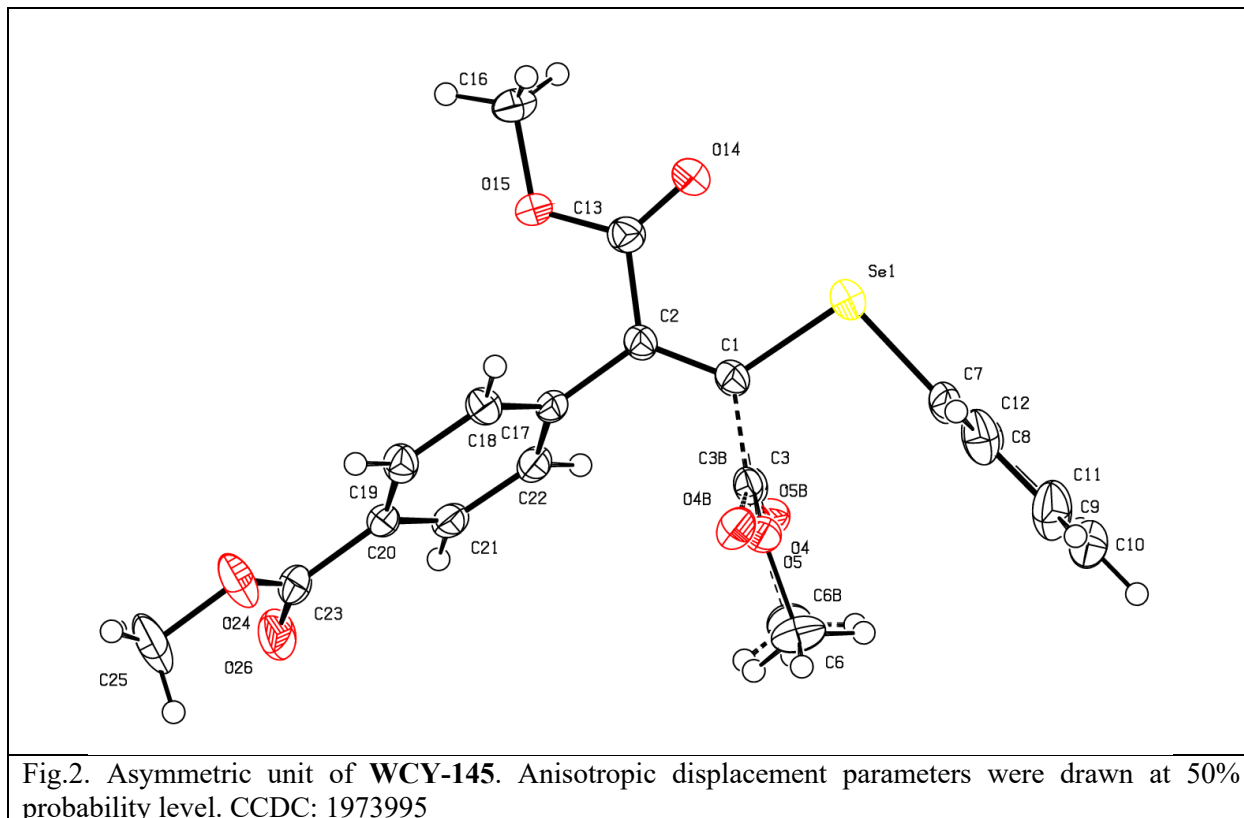
Fig.1. Asymmetric unit of **WCY-18**. Anisotropic displacement parameters were drawn at 50% probability level. CCDC: 1973994

**Table 3 Crystal data and structure refinement for WCY-145.**

Identification code	WCY-145
Empirical formula	$C_{20}H_{18}O_6Se$
Formula weight	433.30
Temperature/K	100.02
Crystal system	triclinic
Space group	P-1
$a/\text{\AA}$	7.5090(3)
$b/\text{\AA}$	7.5264(3)
$c/\text{\AA}$	17.8407(6)
$\alpha/^\circ$	79.785(1)
$\beta/^\circ$	79.205(1)
$\gamma/^\circ$	73.876(1)
Volume/ $\text{\AA}^3$	943.05(6)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.526
$\mu/\text{mm}^{-1}$	2.997
F(000)	440.0
Crystal size/ $\text{mm}^3$	$0.3 \times 0.1 \times 0.03$
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.54178$ )
$2\theta$ range for data collection/ $^\circ$	5.088 to 144.888



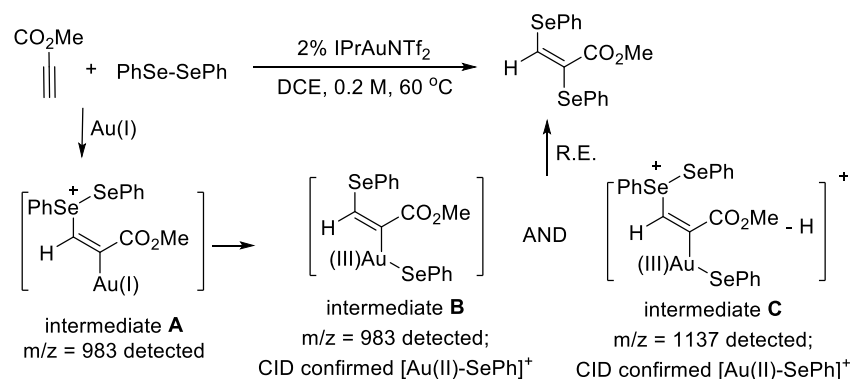
Index ranges	$-9 \leq h \leq 9, -9 \leq k \leq 9, -22 \leq l \leq 21$
Reflections collected	12230
Independent reflections	3606 [ $R_{\text{int}} = 0.0317, R_{\text{sigma}} = 0.0309$ ]
Data/restraints/parameters	3606/55/279
Goodness-of-fit on $F^2$	1.109
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0461, wR_2 = 0.1292$
Final R indexes [all data]	$R_1 = 0.0469, wR_2 = 0.1298$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.69/-0.60



#### IV. Mass Spectrometry Study

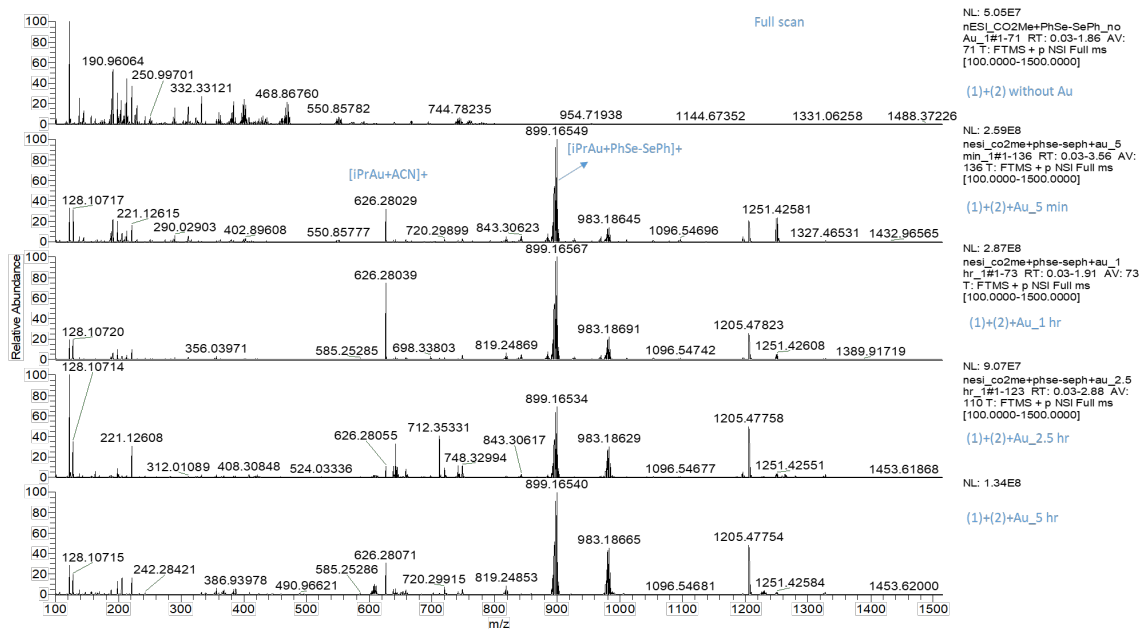
ESI-MS spectra were collected using a Thermo scientific Orbitrap Q Extractive Plus (Bremen, Germany) in the positive ion mode. Samples were infused at a flow rate of 10  $\mu\text{L}/\text{min}$  and ionized at a high voltage of +5 kV.

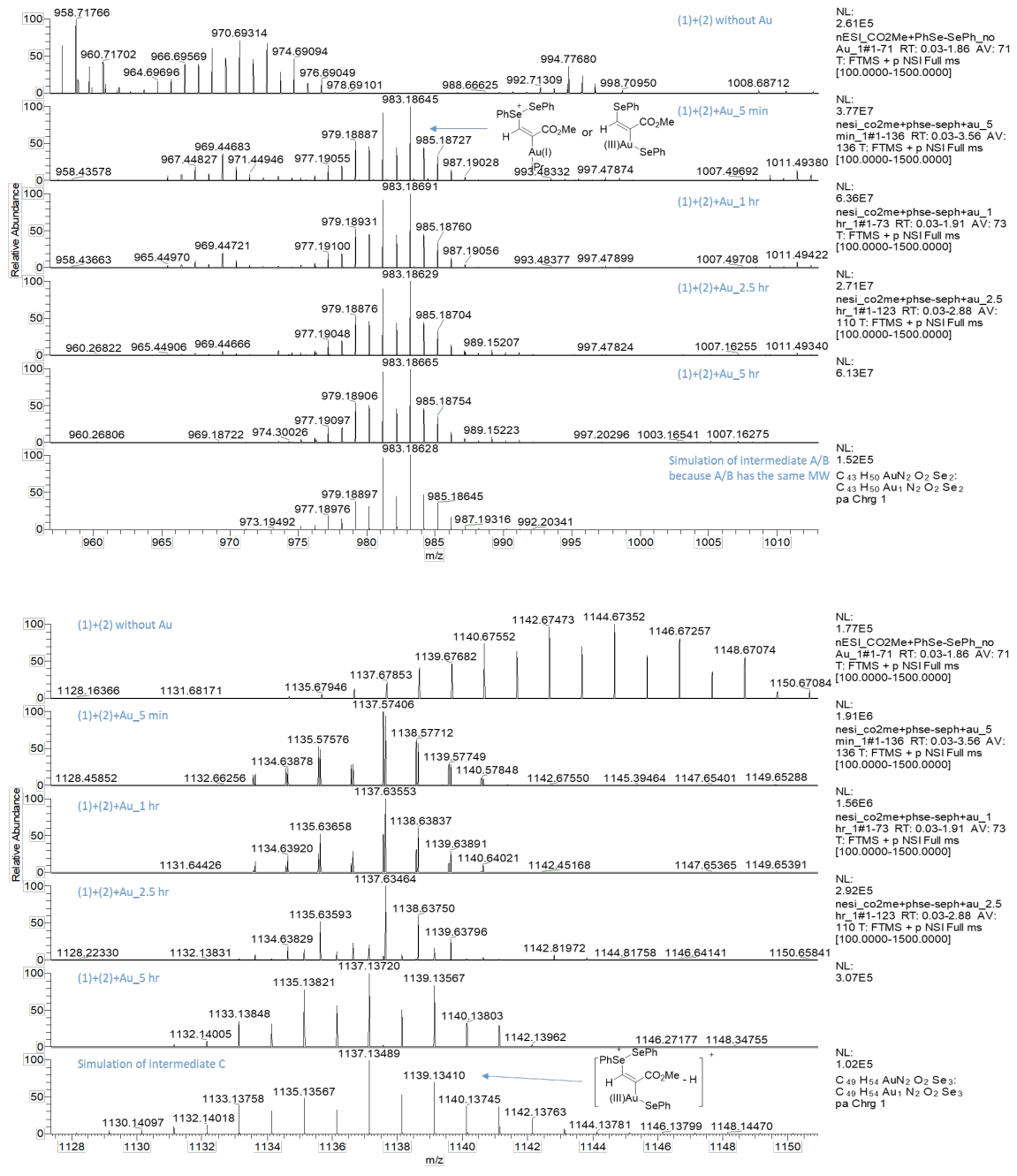
##### 4.1 ESI-MS analysis of 1c and 2a

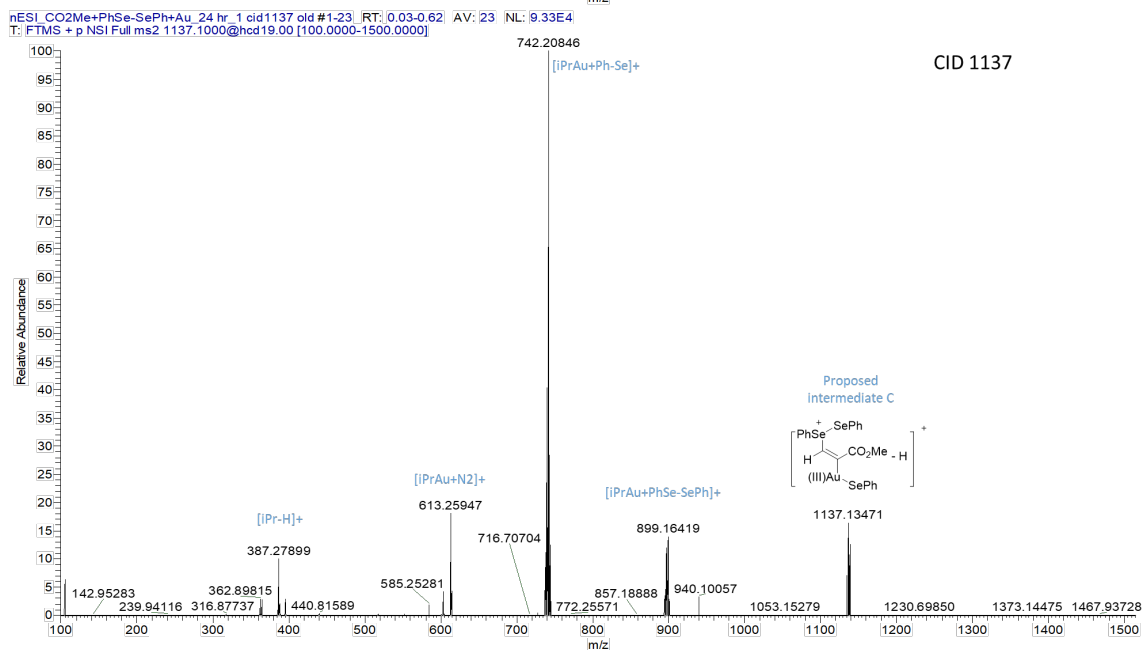
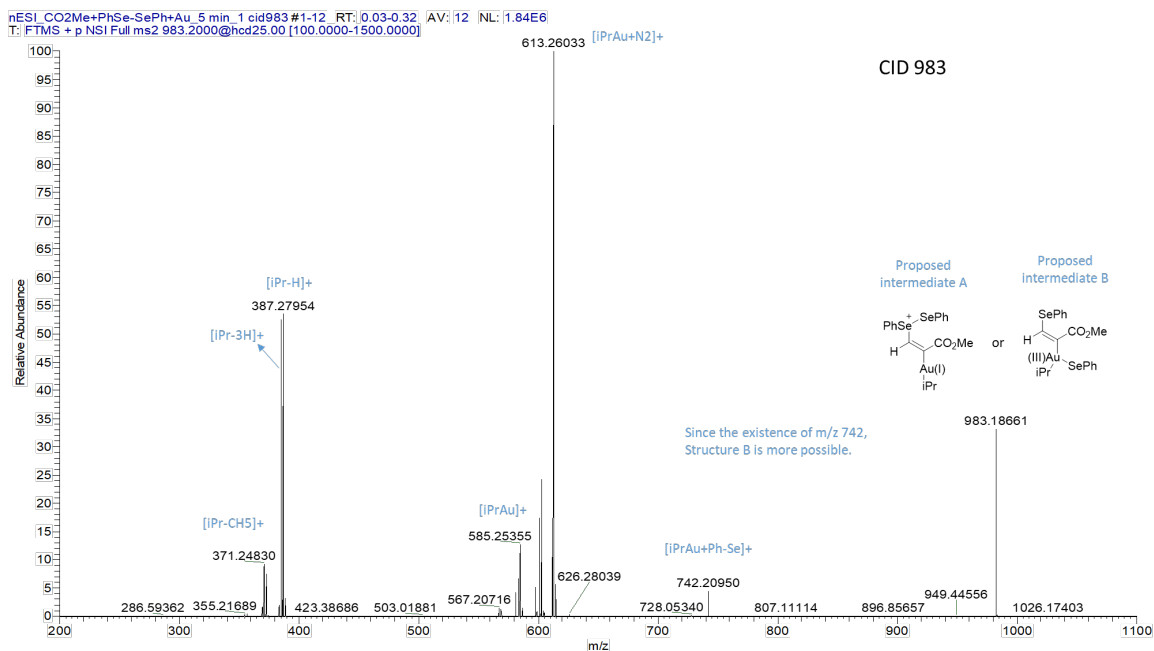


General procedure: 200  $\mu\text{M}$  IPrAuNTf<sub>2</sub> was added to 20 mM of diselenide and 30 mM methyl propiolate in 3 mL of DCE, and the reaction mixture was stirred at 60 °C for 24 h. The reaction mixture was diluted in 1:20 ratio with acetonitrile, and tested on 5 min, 1 h, 2.5 h and 5 h using ESI-MS (2  $\mu\text{L}/\text{min}$ , +2.5 kV).

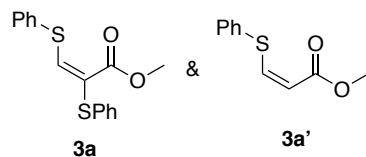
Three key intermediates were detected. Intermediate A ( $m/z = 983$ ) which represents a vinyl Au(I) complex has the same mass as a possible Au(III) intermediate B. CID experiment at 983 revealed a Au(II)-SePh fragment, which strongly supported the existence of the Au(III) intermediate B. Another intermediate C ( $m/z = 1137$ ), which had a similar formula as the Au(III) intermediate we observed in the thioallylation studies, provided a Au(II)-SePh fragment in the CID experiment too. All three intermediates existed at a noticeable concentration since 5 min. Thus, we propose a Au(I/III) redox cycle could be viable for this transformation.







## V. Compound Characterization



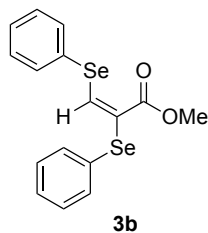
methyl (*E*)-2,3-bis(phenylthio)acrylate (**3a**)  
methyl (*Z*)-3-(phenylthio)acrylate (**3a'**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the unseparated mixture products with **3a/3a'** = 2.6:1 as colorless oil (80%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.81 (s, 1H), 7.50 – 7.41 (m, 3H), 7.38 – 7.29 (m, 4.5H), 7.28 – 7.20 (m, 4.5H), 7.18 – 7.11 (m, 1H), 5.90 (d,  $J = 10.0$  Hz, 0.4H), 3.75 (s, 1.2H), 3.73 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.69, 165.71, 156.96, 149.88, 136.34, 135.88, 135.54, 130.89, 130.82, 129.53, 129.32, 129.20, 129.11, 128.89, 128.66, 128.62, 128.42, 128.27, 128.07, 127.84, 126.16, 115.39, 112.75, 77.00, 52.39, 51.25, 29.54.

HRMS:  $m/z$  (ESI) calculated for **3a**  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{S}_2$  ( $\text{M}^+$ ): 302.0435, found: 302.0434; **3a'**  $\text{C}_{10}\text{H}_{10}\text{O}_2\text{S}$  ( $\text{M}^+$ ): 194.0402, found: 194.0399.



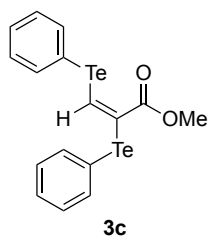
methyl (*E*)-2,3-bis(phenylselanyl)acrylate (**3b**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (94%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.90 (s, 1H), 7.50 – 7.45 (m, 4H), 7.32 – 7.25 (m, 6H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.5, 151.9, 132.9, 132.8, 132.8, 130.2, 129.4, 128.2, 127.7, 114.3, 52.8.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}^+$ ): 398.9397, found: 398.9392.



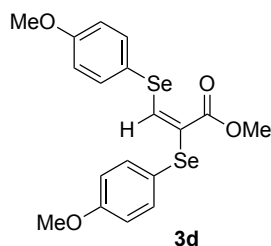
methyl (*E*)-2,3-bis(phenyltelluryl)acrylate (**3c**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (94%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.27 (s, 1H), 7.80 (d, 2H,  $J = 7.2$  Hz), 7.49 (d,  $J = 6.8$  Hz, 2H), 7.33 (t,  $J = 7.2$  Hz, 1H), 7.24 (t,  $J = 7.2$  Hz, 3H)

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  168.4, 140.2, 139.3, 136.9, 129.8, 129.1, 128.7, 127.8, 120.5, 113.9, 102.7, 53.2.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{14}\text{O}_2\text{Te}_2$  ( $\text{M}^+$ ): 493.9089, found: 493.9077.



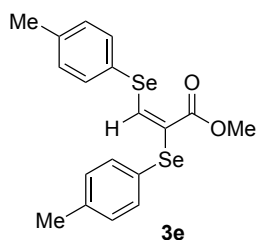
methyl (*E*)-2,3-bis((4-methoxyphenyl)selanyl)acrylate (**3d**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (92%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.56 (s, 1H), 7.45 (d,  $J = 8.8$  Hz, 2H), 7.36 (d,  $J = 8.8$  Hz, 2H), 6.82 (d,  $J = 8.8$  Hz, 2H), 6.80 (d,  $J = 8.8$  Hz, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.2, 159.8, 159.8, 149.5, 136.1, 134.6, 123.2, 119.3, 115.1, 115.0, 114.8, 55.2, 55.2, 52.6.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 480.9428, found: 480.9449.



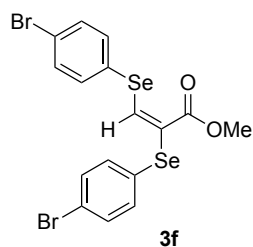
methyl (*E*)-2,3-bis(*p*-tolylselanyl)acrylate (**3e**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (88%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.78 (s, 1H), 7.37 (d,  $J = 8.0$  Hz, 2H), 7.33 (d,  $J = 8.0$  Hz, 2H), 7.10 – 7.06 (m, 4H), 3.80 (s, 3H), 2.32 (s, 3H), 2.31 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.4, 155.1, 138.2, 137.8, 133.4, 132.7, 130.2, 130.0, 129.2, 126.2, 114.5, 52.7, 21.1, 21.1.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 448.9529, found: 448.9525.



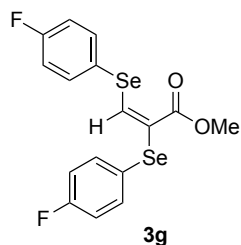
methyl (*E*)-2,3-bis((4-bromophenyl)selanyl)acrylate (**3f**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (86%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.88 (s, 1H), 7.44 (d,  $J = 8.4$  Hz, 2H), 7.40 (d,  $J = 8.4$  Hz, 2H), 7.35 (d,  $J = 8.4$  Hz, 2H), 7.31 (d,  $J = 8.4$  Hz, 2H), 3.80 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.3, 152.4, 134.5, 134.1, 132.5, 132.5, 131.4, 129.2, 122.9, 122.0, 114.3, 53.0.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{12}\text{Br}_2\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 556.7587, found: 556.7589.



methyl (*E*)-2,3-bis((4-fluorophenyl)selanyl)acrylate (**3g**)

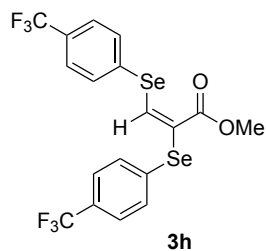
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (86%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 1H), 7.50 – 7.43 (m, 4H), 7.03 – 6.96 (m, 4H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.2, 162.9 (d,  $J = 244$  Hz), 162.7 (d,  $J = 247$  Hz), 150.8 (d,  $J = 0.9$  Hz), 135.7 (d,  $J = 8.0$  Hz), 135.2 (d,  $J = 8.0$  Hz), 127.4 (d,  $J = 3.5$  Hz), 124.2 (d,  $J = 3.5$  Hz), 116.6 (d,  $J = 21.5$  Hz), 116.5 (d,  $J = 21.5$  Hz), 114.8 (d,  $J = 0.7$  Hz), 52.8.

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -112.6, -113.1.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{13}\text{F}_2\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 434.9214, found: 434.9205.



methyl (*E*)-2,3-bis((4-(trifluoromethyl)phenyl)selanyl)acrylate (**3h**)

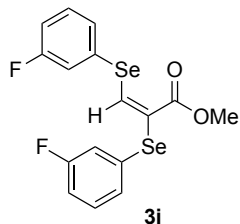
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (66%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 1H), 7.58 – 7.36 (m, 4H), 7.03 – 6.96 (m, 4H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.4, 154.3, 148.1, 137.2, 136.2, 133.1, 132.9, 131.3, 130.7 (q,  $J = 320$  Hz), 129.4 (q,  $J = 325$  Hz), 126.2 (d,  $J = 37$  Hz), 126.0 (d,  $J = 37$  Hz), 125.2 (d,  $J = 152$  Hz), 122.5 (d,  $J = 163$  Hz), 117.2, 113.8, 53.1.

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -62.8, -62.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{18}\text{H}_{12}\text{F}_6\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 534.9145, found: 534.9148.



methyl (*E*)-2,3-bis((3-fluorophenyl)selanyl)acrylate (**3i**)

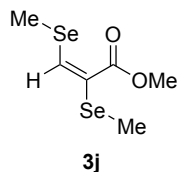
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (80%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.99 (s, 1H), 7.31 – 7.20 (m, 5H), 7.19 – 7.14 (m, 1H), 7.07 – 7.00 (m, 1H), 6.99 – 6.93 (m, 1H), 3.81 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.3, 162.8 (d,  $J = 249$  Hz), 162.8 (d,  $J = 249$  Hz), 152.9, 134.2 (d,  $J = 6.5$  Hz), 132.2 (d,  $J = 6.6$  Hz), 130.8 (d,  $J = 8.0$  Hz), 130.6 (d,  $J = 8.0$  Hz), 128.5 (d,  $J = 3.2$  Hz), 127.8 (d,  $J = 3.1$  Hz), 119.9 (d,  $J = 21.9$  Hz), 119.5 (d,  $J = 22.3$  Hz), 115.5 (d,  $J = 20.9$  Hz), 114.6 (d,  $J = 21.0$  Hz), 114.0, 53.0.

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -111.0, -111.4.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{12}\text{F}_2\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 734.9209, found: 734.9205.



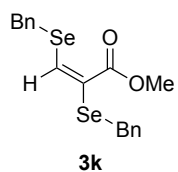
methyl (*E*)-2,3-bis(methylselanyl)acrylate (**3j**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (86%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.66 (s, 1H), 3.83 (s, 3H), 2.24 (s, 3H), 2.21 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.5, 147.1, 113.9, 52.6, 9.6, 7.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_6\text{H}_{10}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 296.8905, found: 296.8895.



methyl (*E*)-2,3-bis(benzylselanyl)acrylate (**3k**)

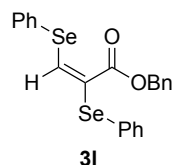
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (85%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.74 (s, 1H), 7.32 – 7.12 (m, 10H), 3.89 (s, 2H), 3.84 (s, 2H), 3.76 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  166.8, 152.1, 138.1, 138.1, 129.0, 128.8, 128.7, 128.4, 127.0, 126.8, 112.9, 52.6, 32.3, 32.0.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{18}\text{H}_{18}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 448.9520, found: 448.9525.





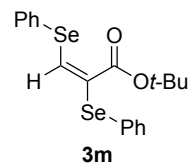
benzyl (*E*)-2,3-bis(phenylselanyl)acrylate (**3l**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (87%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.98 (s, 1H), 7.51 – 7.41 (m, 4H), 7.32 – 7.18 (m, 11H), 5.23 (s, 2H)

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  165.8, 152.6, 135.4, 132.9, 132.8, 132.8, 130.4, 129.4, 128.4, 128.3, 128.1, 127.9, 127.6, 114.5, 67.4.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{22}\text{H}_{18}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 474.9710, found: 474.9707.



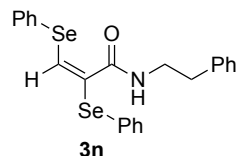
benzyl (*E*)-2,3-bis(phenylselanyl)acrylate (**3m**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (95%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.70 (s, 1H), 7.51 – 7.42 (m, 4H), 7.30 – 7.22 (m, 6H), 1.44 (s, 9H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  164.8, 147.4, 133.2, 133.2, 133.1, 132.6, 130.5, 129.2, 128.0, 127.5, 117.1, 82.7, 27.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 462.9686, found: 462.9675.



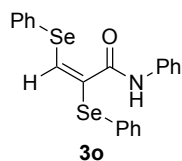
(*E*)-*N*-phenethyl-2,3-bis(phenylselanyl)acrylamide (**3n**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (82%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.31 (s, 1H), 7.66 – 7.60 (m, 2H), 7.38 – 7.32 (m, 3H), 7.28 – 7.18 (m, 8H), 7.12 (br, 1H), 7.07 – 7.01 (m, 2H), 3.54 (q,  $J$  = 6.8 Hz, 2H), 2.73 (t,  $J$  = 6.8 Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  165.6, 156.8, 138.5, 134.1, 133.2, 131.3, 129.4, 129.2, 129.1, 128.6, 128.5, 128.1, 126.8, 126.3, 113.5, 41.4, 35.5.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{23}\text{H}_{21}\text{NOSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 488.0027, found: 488.0029.



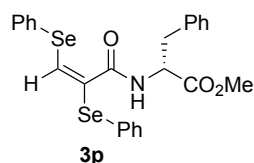
**(E)-N-phenyl-2,3-bis(phenylselanyl)acrylamide (3o)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (48%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.92 (br, 1H), 8.47 (s, 1H), 7.67 – 7.61 (m, 2H), 7.52 – 7.47 (m, 2H), 7.42 – 7.20 (m, 10H), 7.12 – 7.06 (m, 1H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  163.8, 158.6, 137.5, 134.0, 133.2, 130.9, 129.7, 129.5, 129.4, 128.9, 128.3, 127.3, 124.5, 119.8, 113.7.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{21}\text{H}_{17}\text{NOSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 459.9687, found: 459.9710.



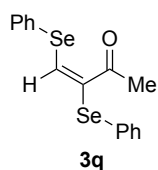
**methyl (E)-(2,3-bis(phenylselanyl)acryloyl)-D-phenylalaninate (3p)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (55%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.36 (s, 1H), 7.65 – 7.59 (m, 2H), 7.54 (broad d,  $J = 8.0$  Hz, 1H), 7.37 – 7.32 (m, 3H), 7.30 – 7.21 (m, 5H), 7.18 – 7.09 (m, 3H), 6.93 – 6.88 (m, 2H), 4.89 (dt,  $J = 8.0, 5.6$  Hz, 1H), 3.63 (s, 3H), 3.06 (t,  $J = 5.6$  Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  171.3, 165.4, 157.9, 135.5, 133.9, 133.2, 131.2, 129.7, 129.4, 129.3, 129.1, 128.5, 128.3, 127.0, 113.3, 53.9, 52.3, 37.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{25}\text{H}_{23}\text{NO}_3\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 546.0081, found: 546.0087.



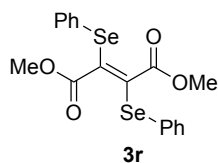
**(E)-3,4-bis(phenylselanyl)but-3-en-2-one (3q)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (85%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  8.46 (s, 1H), 7.62 – 7.57 (m, 2H), 7.37 – 7.30 (m, 5H), 7.30 – 7.19 (m, 3H), 2.42 (m, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  198.8, 159.3, 134.1, 132.9, 132.0, 129.9, 129.5, 129.4, 128.4, 126.8, 119.9, 18.8.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{16}\text{H}_{14}\text{OSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 382.9446, found: 382.9450.



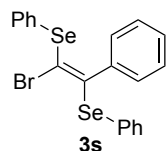
dimethyl 2,3-bis(phenylselanyl)fumarate (**3r**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (20:1 hexane/EtOAc) to yield the desired product as colorless oil (93%).

$^1\text{H NMR}$  (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.60 – 7.56 (m, 4H), 7.34 – 7.27 (m, 6H), 3.45 (s, 6H).

$^{13}\text{C NMR}$  (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  165.3, 134.9, 134.7, 129.5, 128.9, 128.6, 52.4.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 456.9452, found: 456.9455.



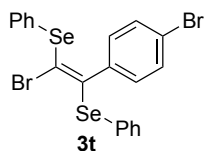
(*Z*)-(1-bromo-2-phenylethene-1,2-diyl)bis(phenylselane) (**3s**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H NMR}$  (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.47 – 7.42 (m, 2H), 7.33 – 7.23 (m, 5H), 7.13 – 7.07 (m, 1H), 7.05 – 6.97 (m, 5H), 6.96 – 6.91 (m, 2H).

$^{13}\text{C NMR}$  (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  147.0, 139.1, 136.5, 132.7, 131.6, 129.5, 129.1, 129.0, 128.4, 128.3, 127.8, 127.6, 127.5, 101.5

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{15}\text{BrSe}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 494.8761, found: 494.8748.



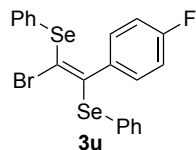
(*Z*)-(1-bromo-2-(4-bromophenyl)ethene-1,2-diyl)bis(phenylselane) (**3t**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H NMR}$  (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.45 – 7.40 (m, 2H), 7.32 – 7.28 (m, 3H), 7.27 – 7.23 (m, 2H), 7.18 – 7.12 (m, 3H), 7.07 – 7.01 (m, 2H), 6.82 – 6.77 (d,  $J = 8.4$  Hz, 2H).

$^{13}\text{C NMR}$  (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  145.5, 138.2, 136.5, 132.8, 131.3, 130.7, 130.6, 129.2, 129.2, 128.7, 128.7, 128.0, 121.8, 102.5.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{14}\text{Br}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 572.7848, found: 572.7849.



(*Z*)-(1-bromo-2-(4-fluorophenyl)ethene-1,2-diyl)bis(phenylselane) (**3u**)

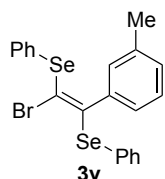
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.45 – 7.40 (m, 2H), 7.32 – 7.27 (m, 3H), 7.27 – 7.23 (m, 2H), 7.15 – 7.10 (m, 1H), 7.04 – 6.99 (m, 2H), 6.91 – 6.86 (m, 2H), 6.73 – 6.68 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  161.8 (d,  $J = 247$  Hz), 145.8, 136.6, 135.1 (d,  $J = 3.4$  Hz), 132.7, 131.4, 130.7 (d,  $J = 8.3$  Hz) 129.3, 129.2, 128.6, 128.5, 127.9, 114.6 (d,  $J = 21.7$  Hz) 102.1 (d,  $J = 1.7$  Hz).

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -113.2.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{14}\text{BrFSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 512.8666, found: 512.8667.



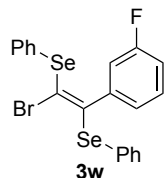
(Z)-(1-bromo-5-chloropent-1-ene-1,2-diyl)bis(phenylselene) (**3v**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.47 – 7.43 (m, 2H), 7.31 – 7.22 (m, 5H), 7.13 – 7.07 (m, 1H), 7.00 – 6.92 (m, 3H), 6.90 – 6.80 (m, 3H), 2.18 (m, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  145.9, 138.3, 136.8, 135.2, 133.1, 131.1, 129.6, 129.3, 129.1, 128.6, 128.5, 128.2, 128.0, 127.9, 125.0, 100.5, 19.6.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{21}\text{H}_{17}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 508.8917, found: 508.8909.



(Z)-(1-bromo-2-cyclopropylethene-1,2-diyl)bis(phenylselene) (**3w**)

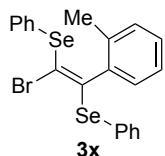
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.46 – 7.42 (m, 2H), 7.33 – 7.26 (m, 5H), 7.16 – 7.11 (m, 1H), 7.06 – 6.96 (m, 3H), 6.74 – 6.70 (m, 2H), 6.65 – 6.61 (m, 1H)

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  161.9 (d,  $J = 245$  Hz), 145.2 (d,  $J = 2.0$  Hz), 141.1 (d,  $J = 8.1$  Hz), 136.7, 133.0, 131.3, 129.3, 129.2, 129.1, 128.7, 128.6, 128.0, 124.9 (d,  $J = 3.0$  Hz), 116.1 (d,  $J = 22.1$  Hz), 114.5 (d,  $J = 20.9$  Hz).

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -131.5.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{14}\text{BrFSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 512.8666, found: 512.8675.



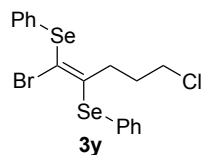
(Z)-(1-bromo-2-(*o*-tolyl)ethene-1,2-diyl)bis(phenylselene) (**3x**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.47 – 7.42 (m, 2H), 7.31 – 7.26 (m, 3H), 7.26 – 7.22 (n, 2H), 7.12 – 7.07 (m, 1H), 6.99 – 6.91 (m, 3H), 6.90 – 6.80 (m, 3H), 2.18 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  145.8, 138.3, 136.8, 135.2, 133.1, 131.1, 129.6, 129.3, 129.1, 128.6, 128.5, 128.2, 128.0, 127.9, 125.0, 100.5, 19.6.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{21}\text{H}_{17}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 508.8917, found: 508.8896.



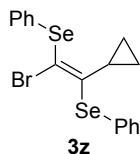
**(Z)-(1-bromo-5-chloropent-1-ene-1,2-diyl)bis(phenylselane) (3y)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.69 – 7.65 (m, 2H), 7.50 – 7.46 (m, 2H), 7.43 – 7.30 (m, 6H), 3.17 (t,  $J$  = 6.4 Hz, 2H), 2.64 – 2.58 (m, 2H), 1.81 – 1.73 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  147.7, 126.8, 131.6, 131.2, 129.4, 129.4, 129.4, 128.6, 127.6, 100.2, 43.7, 34.9, 32.0.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{17}\text{H}_{16}\text{BrClSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 494.8527, found: 494.8516.



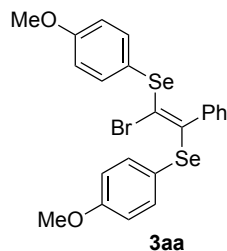
**(Z)-(1-bromo-2-cyclopropylethene-1,2-diyl)bis(phenylselane) (3z)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.55 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.35 – 7.32 (m, 3H), 7.30 – 7.26 (m, 3H), 1.85 – 1.77 (m, 1H), 0.76 – 0.68 (m, 4H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  145.5, 133.0, 131.5, 130.8, 129.2, 129.1, 127.9, 127.4, 109.0, 20.0, 10.4.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{17}\text{H}_{15}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 458.8761, found: 458.8748.



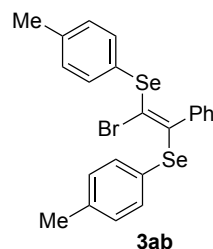
**(Z)-(1-bromo-2-phenylethene-1,2-diyl)bis((4-methoxyphenyl)selane) (3aa)**

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.40 (d,  $J$  = 8.8 Hz, 2H), 7.14 (d,  $J$  = 8.4 Hz, 2H), 7.10 – 7.04 (m, 3H), 6.95 – 6.90 (m, 2H), 6.83 (d,  $J$  = 8.8 Hz, 2H), 6.51 (d,  $J$  = 8.8 Hz, 2H), 3.80 (s, 3H), 3.68 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  159.9, 159.8, 144.6, 139.2, 138.2, 136.0, 129.0, 127.6, 127.5, 127.5, 121.5, 120.1, 114.7, 113.0, 102.8, 55.2, 55.1.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{22}\text{H}_{19}\text{BrO}_2\text{Se}_2$  ( $\text{M}+\text{Na}$ ) $^+$ : 554.8972, found: 554.8971.



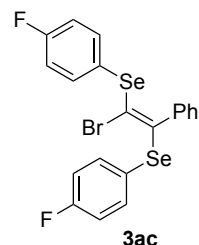
(*Z*)-(1-bromo-2-phenylethene-1,2-diyl)bis((4-fluorophenyl)selane) (**3ab**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.36 – 7.33 (m, 2H), 7.14 – 7.10 (m, 4H), 7.06 – 7.03 (m, 3H), 6.96 – 6.92 (m, 2H), 6.82 – 6.78 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  145.9, 139.2, 138.3, 138.0, 136.4, 133.3, 129.9, 129.2, 129.0, 127.8, 127.5, 125.9, 102.1, 21.2, 21.1.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{22}\text{H}_{19}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 522.9074, found 522.9057.



(*Z*)-(1-bromo-2-phenylethene-1,2-diyl)bis(*p*-tolylselane) (**3ac**)

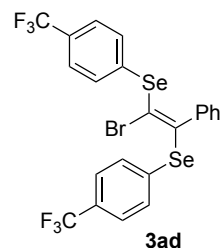
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.45 – 7.41 (m, 2H), 7.23 – 7.18 (m, 2H), 7.09 – 7.09 (m, 3H), 7.03 – 6.98 (m, 2H), 6.92 – 6.99 (m, 2H), 6.69 (t,  $J = 8.8$  Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  162.9 (d,  $J = 248$  Hz), 145.6, 138.8, 138.7 (d,  $J = 8.2$  Hz), 135.8 (d,  $J = 7.5$  Hz), 128.9, 127.8, 127.7, 125.8 (d,  $J = 2.2$  Hz), 124.3 (d,  $J = 2.2$  Hz), 116.3 (d,  $J = 21.7$  Hz), 115.6 (d,  $J = 21.5$  Hz), 102.0.

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -112.1, -112.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{13}\text{BrF}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 530.8572, found 530.8563.



(*Z*)-(1-bromo-2-phenylethene-1,2-diyl)bis((4-(trifluoromethyl)phenyl)selane) (**3ad**)

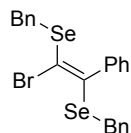
This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.54 (d,  $J = 8.4$  Hz, 2H), 7.51 (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.25 (d,  $J = 8.0$  Hz, 2H), 7.07 – 7.00 (m, 3H), 6.93 – 6.89 (m, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  148.5, 138.6, 136.5, 133.9, 131.8, 130.5 (q,  $J = 216$  Hz), 130.7 (q,  $J = 217$  Hz), 128.8, 128.2, 127.9, 126.0 (q,  $J = 24$  Hz), 125.2 (q,  $J = 24$  Hz), 124.7 (q,  $J = 267$  Hz), 122.9 (q,  $J = 267$  Hz), 100.7, 77.0

$^{19}\text{F}$  NMR (376 MHz;  $\text{CDCl}_3$ ):  $\delta$  -62.7, -63.0.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{22}\text{H}_{13}\text{BrF}_6\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 630.8508, found: 630.8507.



**3af**

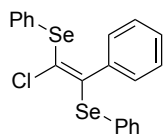
(*Z*)-(1-bromo-2-phenylethene-1,2-diyl)bis(benzylselane) (**3af**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.30 – 7.13 (m, 11H), 7.01 – 6.97 (m, 2H), 6.66 – 6.62 (m, 2H), 4.00 (s, 2H), 3.34 (s, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  146.6, 139.5, 138.0, 136.9, 129.0, 128.9, 128.5, 128.4, 128.3, 128.1, 127.8, 126.9, 101.8, 34.0, 32.9.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{22}\text{H}_{19}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 522.9074, found 522.9059.



**3ag**

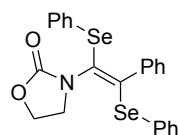
(*E*)-((1-phenyl)-2-chloroethene-1,2-diyl)bis(phenylselane) (**3ag**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.48 – 7.45 (m, 2H), 7.32 – 7.29 (m, 3H), 7.28 – 7.24 (m, 2H), 7.14 – 7.08 (m, 1H), 7.07 – 6.94 (m, 7H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  142.4, 138.3, 136.4, 133.1, 130.3, 129.3, 129.1, 128.6, 128.4, 128.2, 127.9, 127.7, 127.5, 113.4.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{14}\text{BrClSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 450.9266, found 450.9265.



**3ah**

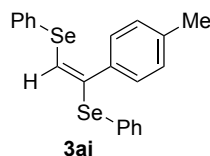
(*E*)-3-(2-phenyl-1,2-bis(phenylselanyl)vinyl)oxazolidin-2-one (**3ah**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.94 – 7.91 (m, 2H), 7.50 – 7.46 (m, 2H), 7.41 – 7.33 (m, 3H), 7.27 – 7.22 (m, 6H), 7.22 – 7.18 (m, 2H), 3.91 (t,  $J = 8.0$  Hz, 2H), 2.99 (t,  $J = 8.0$  Hz, 2H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  154.0, 143.8, 132.7, 129.9, 129.2, 129.1, 129.0, 128.6, 128.5, 127.7, 127.2, 127.1, 125.7, 107.7, 43.2, 24.3.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{23}\text{H}_{19}\text{NO}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 501.9819, found 501.9823.



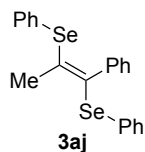
(*E*)-(1-(*p*-tolyl)ethene-1,2-diyl)bis(phenylselane) (**3ai**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.49 – 7.46 (m, 2H), 7.43 – 7.37 (m, 4H), 7.25 – 7.18 (m, 8H), 7.12 (d,  $J$  = 8.0 Hz, 2H), 2.31 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  138.23, 136.60, 132.94, 132.02, 131.30, 130.84, 130.65, 129.20, 129.15, 128.96, 128.51, 127.35, 127.32, 125.31, 21.31.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{21}\text{H}_{18}\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 430.9812, found: 430.9825.



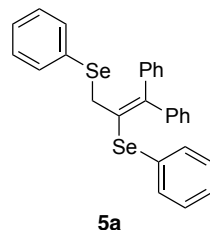
(*E*)-(1-phenylprop-1-ene-1,2-diyl)bis(phenylselane) (**3aj**)

This compound was prepared following general procedure **2.2**, and crude mixture was purified using flash chromatography (pure hexane) to yield the desired product as colorless oil (93%).

$^1\text{H}$  NMR (400 MHz;  $\text{CDCl}_3$ ):  $\delta$  7.52 – 7.48 (m, 2H), 7.32 – 7.22 (m, 5H), 7.18 – 7.07 (m, 8H), 2.30 (s, 3H).

$^{13}\text{C}$  NMR (100 MHz;  $\text{CDCl}_3$ ):  $\delta$  141.9, 135.1, 133.3, 132.4, 130.6, 129.9, 129.6, 129.3, 129.0, 128.7, 127.9, 127.7, 127.3, 127.0, 25.8.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{21}\text{H}_{18}\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 430.9812, found: 430.9815.



(3,3-diphenylprop-2-ene-1,2-diyl)bis(phenylselane) (**5a**)

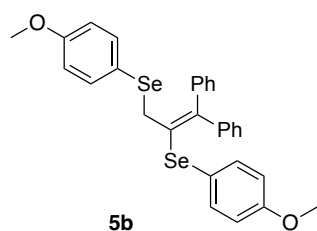
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (82%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.54 (m, 2H), 7.28 – 7.34 (m, 2H), 7.17 – 7.26 (m, 10H), 7.11 – 7.16 (m, 2H), 7.05 – 7.10 (m, 2H), 6.96 – 7.02 (m, 2H), 3.87 (s, 2H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.57, 143.01, 141.13, 134.42, 130.95, 130.11, 129.67, 129.26, 129.22, 128.96, 128.75, 128.10, 128.10, 127.84, 127.54, 127.38, 127.28, 127.13, 34.11.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{27}\text{H}_{22}\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 528.9944, found: 528.9949.





**5b**

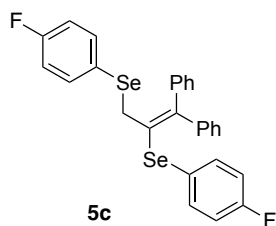
(3,3-diphenylprop-2-ene-1,2-diyl)bis(phenylselane) (**5b**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (94%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J$  = 8.7 Hz, 2H), 7.32 – 7.31 (m, 6H), 7.19 – 7.14 (m, 3H), 7.10 (dd,  $J$  = 7.9, 1.7 Hz, 2H), 6.90 (dd,  $J$  = 6.6, 2.9 Hz, 2H), 6.77 (d,  $J$  = 8.7 Hz, 2H), 6.69 (d,  $J$  = 8.7 Hz, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.70 (s, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.73, 159.57, 144.36, 143.04, 141.34, 137.27, 137.01, 131.98, 129.29, 127.95, 127.91, 127.50, 127.36, 126.84, 119.80, 119.59, 114.62, 114.42, 55.26, 33.89.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{29}\text{H}_{26}\text{O}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 567.0336, found: 527.0342.



**5c**

(3,3-diphenylprop-2-ene-1,2-diyl)bis((4-fluorophenyl)selane) (**5c**)

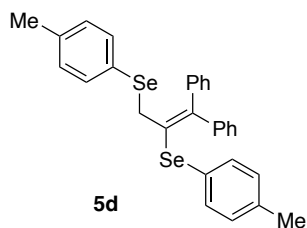
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (82%).

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (dd,  $J$  = 8.4, 5.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.17 (m, 6H), 7.04 (dd,  $J$  = 7.3, 2.2 Hz, 2H), 6.95 – 6.89 (m, 4H), 6.85 (t,  $J$  = 8.7 Hz, 2H), 3.79 (s, 2H).

$^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9 (d,  $J$  = 11 Hz), 161.5 (d,  $J$  = 16 Hz), 147.6, 142.8, 141.0, 137.0 (d,  $J$  = 37 Hz), 136.9 (d,  $J$  = 37 Hz), 131.1, 129.24, 129.17, 128.10, 127.94, 127.5, 127.2, 124.4 (d,  $J$  = 35 Hz), 123.8 (d,  $J$  = 33 Hz), 116.1 (d,  $J$  = 217 Hz), 115.9 (d,  $J$  = 216 Hz), 34.4.

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.40, -113.42, -113.43, -113.43, -113.44, -113.45, -113.46, -113.47, -113.48, -114.00, -114.01, -114.02, -114.03, -114.03, -114.04, -114.05, -114.06, -114.07.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{27}\text{H}_{20}\text{F}_2\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 542.9936, found: 542.9941.



**5d**

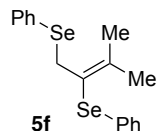
(3,3-diphenylprop-2-ene-1,2-diyl)bis(p-tolylselane) (**5d**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (91%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J$  = 8.1 Hz, 2H), 7.30 – 7.17 (m, 9H), 7.12 (dd,  $J$  = 7.9, 1.8 Hz, 2H), 7.05 (d,  $J$  = 7.8 Hz, 2H), 7.01 – 6.91 (m, 4H), 3.81 (s, 2H), 2.32 (s, 3H), 2.30 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.42, 143.07, 141.24, 137.73, 137.25, 135.00, 134.75, 131.41, 129.76, 129.48, 129.25, 128.10, 127.96, 127.83, 127.33, 126.93, 126.07, 125.93, 33.88, 21.16, 21.10.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{29}\text{H}_{26}\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 535.0438, found: 535.0443.



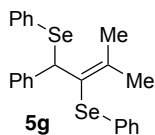
(3-methylbut-2-ene-1,2-diyl)bis(phenylselane) (**5f**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (84%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52 – 7.46 (m, 2H), 7.44 – 7.37 (m, 2H), 7.28 – 7.17 (m, 6H), 3.88 (s, 2H), 1.98 (s, 3H), 1.65 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.89, 134.55, 131.57, 131.29, 130.11, 129.05, 128.70, 127.35, 126.46, 122.06, 34.66, 25.78, 20.57.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{17}\text{H}_{18}\text{Se}_2$  ( $\text{M}$ ) $^+$ : 381.9739, found: 381.9719.



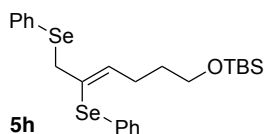
(3-methyl-1-phenylbut-2-ene-1,2-diyl)bis(phenylselane) (**5g**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (40%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.45 (m, 4H), 7.28 – 7.13 (m, 6H), 7.10 – 7.02 (m, 5H), 5.81 (s, 1H), 1.83 (s, 3H), 1.74 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.27, 140.42, 135.20, 133.08, 131.50, 130.51, 129.68, 129.16, 128.89, 128.79, 128.66, 128.62, 128.23, 128.09, 127.77, 127.06, 125.53, 54.40, 26.38, 20.99.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{23}\text{H}_{22}\text{Se}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 459.0125, found: 459.0129.



(*Z*)-((5,6-bis(phenylselanyl)hex-4-en-1-yl)oxy)(tert-butyl)dimethylsilane (**5h**)

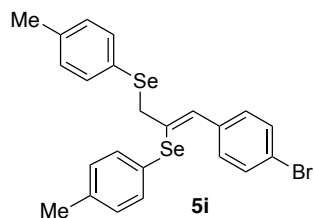
This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the unseparated mixture products with  $Z/E$  = 1.7:1 as colorless oil (96%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 – 7.51 (m, 1H), 7.50 – 7.46 (m, 1H), 7.46 – 7.40 (m, 2H), 7.31 – 7.14 (m, 6H), 5.94 (t,  $J$  = 7.5 Hz, 0.39H), 5.77 (t,  $J$  = 7.1 Hz, 0.66H), 3.77 (s, 0.82H), 3.69 (s,

1.34H), 3.51 (t,  $J = 6.4$  Hz, 2H), 2.25 (q,  $J = 7.4$  Hz, 1.28H), 1.92 (q,  $J = 7.5$  Hz, 0.85H), 1.51 – 1.40 (m, 2H), 0.88 (s, 9H), 0.02 (s, 6H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.87, 137.61, 134.55, 134.08, 132.82, 132.59, 129.06, 128.77, 127.26, 126.90, 62.42, 37.83, 32.15, 28.48, 25.91, 18.24, -5.30.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{24}\text{H}_{34}\text{OSe}_2\text{Si}$  ( $\text{M}+\text{H}$ ) $^+$ : 527.0782, found: 527.0787.



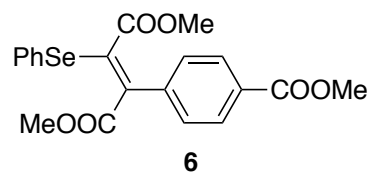
(*Z*)-3-(4-bromophenyl)prop-2-ene-1,2-diylbis(*p*-tolylselane) (**5i**)

This compound was prepared following general procedure **2.3**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the unseparated mixture products with E/Z = 2:1 as white solid (94%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 8.0$  Hz, 0.7H), 7.48 (d,  $J = 8.0$  Hz, 1.4H), 7.44 (d,  $J = 8.4$  Hz, 1.5H), 7.39 (t,  $J = 8.2$  Hz, 2.9H), 7.20 (d,  $J = 8.4$  Hz, 1.3H), 7.15 (d,  $J = 7.9$  Hz, 0.9H), 7.10 (d,  $J = 7.9$  Hz, 1.5H), 7.07-7.05 (m, 1.8H), 7.02 (t,  $J = 7.7$  Hz, 1.2H), 6.65 (s, 0.33H), 6.52 (s, 0.64H), 3.94 (s, 0.68H), 3.68 (s, 1.3H), 2.37 (s, 1.3H), 2.36 (s, 2.0H), 2.35 (s, 1.2H), 2.34 (s, 2.0H),

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.27, 138.22, 137.68, 137.61, 135.8, 135.5, 135.11, 135.10, 135.04, 134.2, 133.0, 131.9, 131.3, 131.0, 130.7, 130.4, 130.15, 129.99, 129.76, 129.74, 129.61, 125.9, 125.1, 124.1, 121.1, 120.9, 77.0, 38.0, 31.7, 21.16, 21.11

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{23}\text{H}_{21}\text{BrSe}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 536.9230, found: 536.9229.



Dimethyl 2-(4-(methoxycarbonyl)phenyl)-3-(phenylselanyl)fumarate (**6**)

This compound was prepared following general procedure **2.4**, and crude mixture was purified using flash chromatography (Hexanes/DCM = 10:1) to yield the desired product as colorless oil (75%).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 8.3$  Hz, 2H), 7.67 (d,  $J = 7.0$  Hz, 2H), 7.43 – 7.35 (m, 1H), 7.35 – 7.27 (m, 4H), 3.90 (s, 3H), 3.79 (s, 3H), 2.84 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.70, 166.51, 164.43, 150.83, 140.53, 137.50, 132.58, 129.69, 129.66, 129.13, 128.78, 128.03, 126.33, 52.72, 52.15, 51.55.

HRMS:  $m/z$  (ESI) calculated for  $\text{C}_{20}\text{H}_{18}\text{O}_6\text{Se}$  ( $\text{M}$ ) $^+$ : 434.0269, found: 434.0285.







