Three-Component Aminoselenation of Arynes

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1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 25 °C Corresponds to the room temperature (rt) of the lab when the experiments were carried out. Dry CH₃CN was purchased from commercial sources and was stored under argon over 4 Å molecular sieves. CsF was dried by heating at 110 °C for 12 h and left to cool under argon. The 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **2a** and the other symmetric and unsymmetrical aryne precursors were synthesized following literature procedure.¹

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light or KMnO₄ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-CH₂Cl₂ solvent system.

All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker Ultrashield spectrometer or Jeol ECZ spectrometer in CDCl₃ as solvent. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: $\delta_H = 7.26$ ppm, $\delta_C = 77.16$ ppm). Infrared (FT-IR) spectra were recorded on a Perkin Elmer Spectrum BX spectrophotometer, v-max in cm⁻¹. HRMS (ESI) data were recorded on a Waters Xevo G2-XS Q-TOF instrument.

¹ (a) Sato, Y.; Tamura, T.; Kinbara, A.; Morib, M *Adv. Synth. Catal.* **2007**, *349*, 647. (b) Peña, D.; Cobas, A.; Pérez, D.; Guitián, E. *Synthesis*, **2002**, 1454.

2. General Procedure for the Synthesis of Aniline Derivatives²

The tertiary amines derivatives 2a, 2f, 2p and 7a were purchased from commercial sources and used as received without further purification. Substrates 2b-e, 2g-o and 7c were prepared using modified procedure (2c as an example below).²



To a suspension of NaH (1.1 g, 60% dispersion in mineral oil, 28 mmol) in DMF (15 mL) at 0 °C was added an *p*-toluidine (1.0 g, 9.0 mmol) followed by the subsequent addition of methyl iodide (28.0 mmol) under argon, and the reaction mixture was stirred for 12 h at 25 °C. The reaction was quenched with water, and organic materials were extracted with EtOAc three times. The combined extracts were washed with brine and dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (eluent: EtOAc: petroleum ether = 5:95) to afford the tertiary amine derivative **2c** (0.830 g, 66%).

3. General Procedure for the Synthesis of Diselenides³



To a stirred solution of Se metal (2.0 mmol) and aryl iodide (1.0 mmol) in dry DMSO (2.0 mL) was added CuO nanoparticles (10.0 mol %) followed by KOH (2.0 equiv) under argon atmosphere at 90 °C. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was allowed to cool to room temperature and it was then quenched with water and extracted with EtOAc. The combined organic layers were dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure, and the residue was

² Lv, Y.; Zheng, Y.; Li, Y.; Xiong, T.; Zhang, J.; Liu, Q.; Zhang, Q. Chem. Commun. 2013, 49, 8866.

³ Singh, D.; Deobald, A. M.; Camargo, L. R. S.; Tabarelli, G.; Rodrigues, O. E. D.; Braga, A. L. *Org. Lett.* **2010**, *12*, 3288.

purified by flash chromatography on a silica gel column chromatography (Pet Ether) to give the pure diselenides.

$\begin{array}{c} & \underset{la}{\overset{\text{Me}_{2}\text{N}}{\overset{\text{+}}{2a}}} \\ & \underset{solvent, temp}{1a} \\ & \underset{3a}{\overset{\text{F}^{-} \text{ source}}{\overset{\text{solvent, temp}}{time}}} \\ & \underset{4a}{\overset{\text{Me}}{\overset{\text{+}}{3a}}} \\ & \underset{3a}{\overset{\text{He}_{2}\text{N}}{\overset{\text{+}}{3a}}} \\ & \underset{3a}{\overset{3a}} \\ & \underset{3a}{\overset{3a}} \\ & \underset{3a}{\overset{3a}} \\ & \underset{3a}{\overset{3a}} \overset{3a}{\overset{3a}} \\ & \underset{3a}{\overset{3a}} \overset{3a}{\overset{3a}} \\ & \underset{3a}{\overset{3a}} \overset{3a}{\overset{3a}} \overset{3a}{\overset{3a}}{\overset{3a}} \overset{3a}{\overset{3a}} \overset{3a}{\overset{3a}} \overset{3a}{\overset{3a}} \overset{3a}{\overset{3a}$

4. General Procedure for the Optimization of Reaction Conditions

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the fluoride source (0.60 mmol) inside the glove-box. Phenylselenyl bromide **3a** (0.25 mmol) was added and the mixture was dissolved in 1.0 mL of THF outside the glove-box under argon and to this stirring solution was added *N*,*N*-dimethyl aniline **2a** (0.030 g, 32 μ L, 0.25 mmol) and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.090 g, 73 μ L, 0.30 mmol) at 25 °C. Then the reaction mixture was allowed to react at indicated temperature and time. After indicated time over, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel to afford the corresponding 2-selanyl aniline derivatives **4**.

entry	F source	solvent	Temp	Time	Yield of 4a	Yield of 5
			(°C)	(h)	(%) ^b	(%) ^b
1	KF/18-crown-6	THF	25	12	55	18
2°	KF/18-crown-6	THF	25	12	36	20
3 ^d	KF/18-crown-6	THF	25	12	50	24
4	KF/18-crown-6	DME	25	12	48	16
5	CsF	CH ₃ CN	25	12	<5	<5
6	TBAF	THF	25	12	<5	<5
7	TBAT	toluene	25	12	<5	<5
8	KF/18-crown-6	THF	-10 - 25	12	27	29
9	KF/18-crown-6	THF	60	12	16	38
10 ^e	KF/18-crown-6	THF	25	12	51	<5
11 ^f	KF/18-crown-6	THF	25	12	72	<5
13 ^g	KF/18-crown-6	THF	25	24	72	<5

Table S1: Optimization of the Reaction Conditions^a

^a Standard conditions: **1a** (0.30 mmol), **2a** (0.25 mmol), **3a** (0.25 mmol), fluoride source (2.4 equiv), solvent (1.0 mL), 25 °C and 12 h. ^b Yield of isolated product(s) is given. ^c PhSeCl (0.25 mmol) was used instead of PhSeBr. ^d PhSeSPh (0.375 mmol) was used instead of PhSeBr and 0.5 mmol of **1a**, fluoride source (4.0 equiv) was used, ^c1.5 eqiv. of **2a** was used. ^f2.0 equiv of **1a**, 1.5 equiv of **2a**, fluoride source (4.0 equiv) was used. ^gReaction was stirred for 24 h

5. General Procedure for the Aminoselenation of Arynes



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 18crown-6 (0.528 g, 2.0 mmol), KF (0.116 g, 2.0 mmol) inside the glove-box. Electrophilic selenium source **3** (0.75 mmol) was added and the mixture was dissolved in 2.0 mL of THF outside the glove box under argon and kept stirring for five minutes. To this stirring mixture was added 0.5 mmol of the *N*,*N*-dimethyl aniline derivatives **2** and aryne precursor **1** (1.0 mmol). Then the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel to afford the corresponding 2-selanyl aniline derivatives **4** in moderate to good yield.

Procedure for the 1.0 mmol scale



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 18crown-6 (1.056 g, 4.0 mmol), KF (0.232 g, 4.0 mmol) inside the glove-box. Phenylselenyl

bromide 3a (0.354 g, 1.5 mmol) was added and the mixture was dissolved in 4.0 mL of THF outside the glove-box under argon and kept stirring for five minutes. To this stirring mixture was aniline added *N*,*N*-dimethyl **2**a (0.121 g, 127 μL, 1.0 mmol) and 2-(trimethylsilyl)phenyltrifluoromethanesulfonate 1a (0.597 g, 486 µL, 2.0 mmol). Then the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography (Pet.ether/DCM = 95/05) on silica gel to afforded N-methyl-N-phenyl-2-(phenylselanyl)aniline 4a as a white solid (0.240 g, 71% yield).

6. Procedure for the Preparation of *N*-methyl-*N*-phenyl-2-(phenylthio)aniline⁴



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 18-crown-6 (0.264 g, 1.0 mmol), KF (0.058 g, 1.0 mmol) inside the glove-box. 2- (phenylthio)isoindoline-1,3-dione **8** (0.096 g, 0.375 mmol) was added and the mixture was dissolved in 1.0 mL of THF outside the glove-box under argon and kept stirring for five minutes. To this stirring mixture was added *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) and 2- (trimethylsilyl)phenyltrifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol). Then the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel to afford the *N*-methyl-*N*-phenyl-2-(phenylthio)aniline **9a** in 40% yield along with *N*-arylated product **5a** in 23% yield.

⁴ Gaykar, R. N.; Bhattacharjee, S.; Biju, A. T. Org. Lett. 2019, 21, 737.

7. Mechanistic Experiments

Experiments to show the role of nucleophile in the dealkylation step



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the 18-crown-6 (0.528 g, 2.0 mmol), KF (0.116 g, 2.0 mmol) inside the glove-box. Electrophilic selenium source **3a** or **6a** (0.75 mmol) was added and the mixture was dissolved in 2.0 mL of THF outside the glove-box under argon and kept stirring for five minutes. To this stirring mixture was added 1-phenylpyrrolidine **7d**⁵ (0.074g, 0.5 mmol) and aryne precursor **1a** (0.298 g, 243 μ L, 1.0 mmol). Then the reaction mixture was allowed to react at 25 °C for 12 h. After 12 h, the reaction was stopped, the solvent was evaporated and the crude residue pre-adsorbed on silica gel and purified by flash column chromatography on silica gel to afforded the corresponding 2-selanyl aniline derivatives **13** and **14** in 35% and 34% yield respectively.

This experiment indicates the role of nucleophile (X = Br or SePh) in the dealkylation step in the three-component reaction.

8. X-ray Data of 4f and 13

Single crystal of **4f** (recrystallized from Pet. ether at 25 °C) was mounted and the diffraction data was collected at 296 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka

⁵ Cano, R.; Ramón, D. J.; Yus, M. J. Org. Chem. 2011, 76, 654.

radiation (71.073 pm). The structure was solved by direct methods using the ShelXS⁶ and refined with ShelXS⁶. Empirical absorption corrections were applied with SADABS.⁷ All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Identification code	4f
CCDC Number	1953258
Empirical formula	C ₁₉ H ₁₆ BrNSe
Formula weight	417.20
Temperature/K	296.15
Crystal system	monoclinic
Space group	P21/n
a/Å	14.2571(4)
b/Å	6.2778(2)
c/Å	19.5208(5)
α_{\circ}	90.00
β/°	98.404(2)
γ°	90.00
Volume/Å ³	1728.41(9)
Z	4
pcalcmg/mm ³	1.603
μ/mm^{-1}	4.480
F(000)	824.0
Radiation	$MoK\alpha(\lambda = 0.71073)$
Crystal size/mm ³	$0.273 \times 0.251 \times 0.238$
2Θ range for data collection	3.32 to 55.2°
Index ranges	$-18 \le h \le 18, -8 \le k \le 8, -25 \le l \le 25$
Reflections collected	28032
Independent reflections	3991[R(int) = 0.0613]
Data/restraints/parameters	3991/0/200
Goodness-of-fit on F ²	1.012
Final R indexes	$[I \ge 2\sigma(I)] R_1 = 0.0398, wR_2 = 0.0752$
Final R indexes [all data]	$R_1 = 0.0847, wR_2 = 0.0868$
Largest diff. peak/hole / e Å ⁻³	0.59/-0.78

Table S2 Crystal data and structure refinement for 4f

⁶ SHELXS, G.M. Sheldrick, Acta Cryst. 2008, A64, 112.

⁷ Sheldrick, G. M. SADABS, University of Göttingen, Göttingen, Germany, **1999**.



Figure S1. Crystal Structure of 4f (Thermal ellipsoids are shown with 50% probability)

X-ray data of 13

Single crystal of **13** (recrystallized from DCM/Pet Ether at 25 °C) was mounted and the diffraction data was collected at 298 K on a Bruker SMART APEX CCD diffractometer using SMART/SAINT software. Intensity data were collected using graphite-monochromatized Mo-Ka radiation (71.073 pm). The structure was solved by direct methods using the ShelXS⁶ and refined with ShelXS. Empirical absorption corrections were applied with SADABS.⁷ All Non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in geometric positions. Structure was drawn using Olex-2 and ORTEP-3. The crystallographic refinement parameters are given below:

Table S3 Crystal data and structure refinement for

Identification code	13
CCDC no	1961216
Empirical formula	C ₂₂ H ₂₂ BrNSe
Formula weight	459.289
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	8.6022(8)
b/Å	10.7583(10)
c/Å	11.7185(11)
α/°	73.280(4)
β/°	74.058(4)
$\gamma/^{\circ}$	82.430(4)
Volume/Å ³	997.06(16)
Ζ	2

 $\begin{array}{l} \rho_{calc}mg/mm^{3} \\ \mu/mm^{-1} \\ F(000) \\ Crystal size/mm^{3} \\ 2\Theta range for data collection \\ Index ranges \\ Reflections collected \\ Independent reflections \\ Data/restraints/parameters \\ Goodness-of-fit on \\ Final R indexes \\ Final R indexes [all data] \\ Largest diff. peak/hole / e Å^{-3} \end{array}$

 $\begin{array}{c} 1.530\\ 3.891\\ 460.0\\ 0.6\times 0.5\times 0.4\\ 3.748\ to\ 49.998\\ -10\leq h\leq 10,\ -12\leq k\leq 12,\ -13\leq l\leq 13\\ 24565\\ 3510\ [Rint=0.0383,\ Rsigma=0.0236]\\ 3510/1/226\\ 1.033\\ R1=0.0898,\ wR2=0.2104\\ R1=0.1097,\ wR2=0.2210\\ 1.88/-2.14\end{array}$



Figure S2. Crystal Structure of 13

9. Synthesis and Characterization of 2-Selanyl Aniline Derivatives

N-Methyl-*N*-phenyl-2-(phenylselanyl)aniline (4a)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and *N*,*N*-dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction

mixture using silica gel afforded *N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline **4a** as a white solid (0.121 g, 72% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.44; ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.65 (m, 2H), 7.42-7.35 (m, 3H), 7.26-7.21 (m, 3H), 7.16 (dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.11-7.07 (m, 1H), 7.04 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 6.81 (t, J = 7.3 Hz, 1H), 6.68 (d, J = 8.0 Hz, 2H),3.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 146.9, 136.6, 136.3, 130.3, 129.7, 129.1, 128.6, 128.5, 128.4, 127.7, 127.6, 118.1, 114.0, 39.2. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₈NSe: 340.0599, found: 340.0606. FTIR (cm⁻¹) 3057, 2922, 1601, 1497, 1336, 1022.

N-(4-Methoxyphenyl)-*N*-methyl-2-(phenylselanyl)aniline (4b)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 4-methoxy-*N*,*N*-dimethylaniline **2b** (0.076 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0

mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 85/15) of the crude reaction mixture using silica gel afforded *N*-(4-methoxyphenyl)-*N*-methyl-2-(phenylselanyl)aniline **4b** as a white solid (0.135 g,73% yield).

*R*_f (Pet. ether /DCM = 90/10): 0.24; ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.64(m, 2H), 7.42-7.34(m, 3H), 7.21-7.17 (m, 1H), 7.11(dd, J_1 = 7.8 Hz, J_2 = 1.4 Hz, 1H), 7.06-7.02 (m, 1H), 6.98 (dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 1H), 6.84-6.80 (m, 2H), 6.69-6.65 (m, 2H), 3.78 (s, 3H), 3.21 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 152.8, 147.8, 143.8, 136.7, 135.9, 130.0, 129.6, 128.6, 128.5, 127.6, 127.5, 127.0, 116.2, 114.6, 55.8, 40.0. HRMS (ESI) calculated [M+H] ⁺ for

C₂₀H₂₀NOSe: 370.0705, found: 370.0690. **FTIR (cm⁻¹)** 3053, 2950, 1576, 1508, 1469, 1241, 1037.

N-Methyl-2-(phenylselanyl)-*N*-(*p*-tolyl)aniline (4c)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*,4-trimethylaniline **2c** (0.034 g, 0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed

by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-2-(phenylselanyl)-*N*-(p-tolyl)aniline **4c** as a pale yellow oil (0.060 g, 68% yield).

R_f (Pet. ether /DCM = 95/05): 0.49; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 2H), 7.43-7.35 (m, 3H), 7.23-7.19 (m, 1H), 7.14 (dd, J_I = 7.9 Hz, J_2 = 1.3 Hz, 1H), 7.09-7.04 (m, 3H), 7.01 (dd, J_I = 7.9 Hz, J_2 = 1.3 Hz, 1H), 6.61 (d, J = 8.5 Hz, 2H), 3.25 (s, 3H), 2.30 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 147.1, 136.6, 136.3, 130.1, 129.64, 129.62, 128.6, 128.5, 128.2, 127.6, 127.4, 127.3, 114.4, 39.5, 20.5. HRMS (ESI) calculated [M+H] ⁺ for C₂₀H₂₀NSe: 354.0755, found: 354.0765. FTIR (cm⁻¹) 3449, 3058, 1614, 1574, 1512, 1470, 1021.

N-(4-Ethylphenyl)-N-methyl-2-(phenylselanyl)aniline (4d)



Following the general procedure, treatment of 2 (trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 4-ethyl-*N*,*N*-dimethylaniline **2d** (0.075 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h

followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-(4-ethylphenyl)-*N*-methyl-2-(phenylselanyl)aniline **4d** as a pale yellow oil (0.135 g,74% yield).

R_f (Pet. ether /DCM = 95/05): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.69 (m, 2H), 7.45-7.38(m, 3H), 7.26-7.22 (m, 1H), 7.18(dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.13-7.08(m, 3H), 7.04 (dd, J_1 = 7.9 Hz, J_2 = 1.4 Hz, 1H), 6.69-6.66 (m, 2H), 3.28 (s, 3H), 2.64 (q, J = 7.7 Hz, 2H), 1.27

(t, J = 7.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.3, 136.6, 136.3, 133.9, 130.1, 129.6, 129.1, 128.8, 128.6, 128.4, 128.3, 127.5, 127.3, 114.3, 39.4, 28.0, 15.9. HRMS (ESI) calculated [M+H] ⁺ for C₂₁H₂₂NSe: 368.0912, found: 368.0915. FTIR (cm⁻¹) 3450, 2961, 2866, 1613, 1512, 1333.

N-(4-Iodophenyl)-*N*-methyl-2-(phenylselanyl)aniline (4e)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 4-iodo-*N*,*N*-dimethylaniline **2e** (0.124 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at25 °C for 12 h followed by

flash column chromatography (Pet.ether/DCM = 97/03) of the crude reaction mixture using silica gel afforded *N*-(4-iodophenyl)-*N*-methyl-2-(phenylselanyl)aniline **4e** as a pale yellow oil (0.147 g,63% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.60; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.62 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.41-7.36 (m, 3H), 7.25-7.21 (m, 1H), 7.14-7.09 (m, 2H), 7.04 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.2 Hz, 1H), 6.42 (d, *J* = 8.8 Hz, 2H), 3.23 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.6, 146.0, 137.6, 136.4, 136.1, 130.6, 129.7, 128.7, 128.5, 128.1, 127.9, 127.8, 116.0, 79.4, 39.1. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₇INSe: 465.9565, found: 465.9568. FTIR (cm⁻¹) 3057, 2871, 1576, 1489, 1340, 1115.

N-(4-Bromophenyl)-*N*-methyl-2-(phenylselanyl)aniline (4f)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and 4-bromo-*N*,*N*-dimethylaniline **2f** (0.050 g, 0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h

followed by flash column chromatography (Pet.ether/DCM = 97/03) of the crude reaction mixture using silica gel afforded *N*-(4-bromophenyl)-*N*-methyl-2-(phenylselanyl)aniline **4f** as a white solid (0.064 g,62% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.60; ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.65 (m, 2H), 7.43-7.37(m, 3H), 7.34-7.23 (m, 3H), 7.16-7.11(m, 2H), 7.07-7.04 (m, 1H), 6.56-6.52 (m, 2H), 3.25 (s, 3H).¹³C NMR (100 MHz, CDCl₃) δ 148.1, 146.1, 136.5, 136.2, 131.7, 130.4, 129.7, 128.8, 128.5, 128.0, 127.9, 127.8, 115.4, 110.1, 39.2. HRMS (ESI) calculated [M+H] ⁺ for C_{19H17}BrNSe: 417.9704, found:417.9704. FTIR (cm⁻¹) 3415, 2922, 1573, 1489, 1337, 1115.

N-(4-Chlorophenyl)-N-methyl-2-(phenylselanyl)aniline (4g)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 4-chloro-*N*,*N*-dimethylaniline **2g** (0.078 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the

crude reaction mixture using silica gel afforded N-(4-chlorophenyl)-N-methyl-2-(phenylselanyl)aniline **4g** as a white solid (0.119 g, 64% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.60; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 2H), 7.46-7.36 (m, 3H), 7.28-7.24 (m, 1H), 7.21-7.10 (m, 4H), 7.06 (dd, J_1 = 7.9 Hz, J_2 = 1.5 Hz, 1H), 6.61-6.58 (m, 2H), 3.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.7, 146.2, 136.5, 136.2, 130.4, 129.7, 128.9, 128.7, 128.5, 128.0, 127.9, 127.8, 122.9, 115.0, 39.3. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₇ClNSe: 374.0209, found: 374.0211. FTIR (cm⁻¹) 3056, 2873, 1597, 1492, 1338, 1111.

N-(4-Fluorophenyl)-*N*-methyl-2-(phenylselanyl)aniline (4h)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 4-fluoro-*N*,*N*-dimethylaniline **2h** (0.070 g,0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed

by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-(4-fluorophenyl)-*N*-methyl-2-(phenylselanyl)aniline **4h** as a light yellow solid (0.126 g,70% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.60; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.63 (m, 2H), 7.42-7.34 (m, 3H), 7.23-7.19 (m, 1H), 7.13-7.05 (m, 2H), 7.01 (dd, J_I = 7.9 Hz, J_2 = 1.5 Hz, 1H), 6.95-6.89 (m, 2H), 6.63-6.57 (m, 2H), 3.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 156.9 (d, J = 236.4 Hz), 147.2, 145.8 (d, J = 1.4 Hz), 136.6, 136.1, 130.4, 129.7, 128.7, 128.3, 128.2, 127.6 (d, J = 20.5 Hz), 116.0, 115.3 (d, J = 3.5 Hz), 115.3, 39.8. HRMS (ESI) calculated [M+H] ⁺for C₁₉H₁₇FNSe: 358.0505, found: 358.0515. FTIR (cm⁻¹) 3054, 2870, 1507, 1470, 1335, 1225, 1023.

N-Methyl-2-(phenylselanyl)-N-(4-(trifluoromethyl)phenyl)aniline (4i)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethyl-4-(trifluoromethyl)aniline **2i** (0.047 g, 0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0

mL) at 65 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-2-(phenylselanyl)-*N*-(4-(trifluoromethyl)phenyl)aniline **4i** as a pale yellow oil (0.028 g, 28% yield).

R^f (Pet. ether /DCM = 95/05): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.58 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.39-7.32 (m, 3H), 7.25-7.23 (m, 1H), 7.15-7.11 (m, 2H), 7.08-7.06 (m, 1H), 6.60 (d, *J* = 8.6 Hz, 2H), 3.27 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.2, 145.5, 136.4, 136.1, 131.0, 129.8, 128.9, 128.8, 128.3, 128.1, 127.9, 136.4 (q, *J* = 3.5 Hz), 125.2 (q, *J* = 270.0 Hz), 119.3 (q, *J* = 33.0 Hz), 112.7, 39.0. HRMS (ESI) calculated [M+H]⁺ for C₂₀H₁₇F₃NSe: 408.0473. found: 408.0479. FTIR (cm⁻¹) 3058, 2924, 2363, 1616, 1472, 1326, 1111.

N-Methyl-2-(phenylselanyl)-N-(m-tolyl)aniline (4j)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and *N*,*N*,3-trimethylaniline **2j** (0.068 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed

by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using

silica gel afforded *N*-methyl-2-(phenylselanyl)-*N*-(*m*-tolyl)aniline **4j** as a white solid (0.101 g, 57% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.70 (m, 2H), 7.47-7.39 (m, 3H), 7.28-7.24 (m, 1H), 7.21-7.11 (m, 3H), 7.07 (dd, J_I = 7.9 Hz, J_2 = 1.3 Hz, 1H), 6.69 (d, J = 7.9 Hz, 1H), 6.56 (s, 1H), 6.54-6.52 (m, 1H), 3.30 (s, 3H), 2.36 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.2, 147.0, 138.7, 136.5, 136.3, 130.3, 129.6, 128.9, 128.6, 128.5, 128.4, 127.6, 127.5, 119.1, 114.7, 111.4, 39.3, 22.0. HRMS (ESI) calculated [M+H] ⁺ for C₂₀H₂₀NSe: 354.0755, found: 354.0760. FTIR (cm⁻¹) 3052, 2917, 1604, 1573, 1463, 1339, 1027.

N-(3-Chlorophenyl)-*N*-methyl-2-(phenylselanyl)aniline (4k)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 3-chloro-*N*,*N*-dimethylaniline **2k** (0.078 g,0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h

followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-(3-chlorophenyl)-*N*-methyl-2-(phenylselanyl)aniline **4k** as a light yellow oil (0.092 g, 49% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.61 (m, 2H), 7.39-7.32 (m, 3H), 7.25-7.21 (m, 1H), 7.13-7.08 (m, 3H), 7.04-7.02 (m, 1H), 6.65-6.73 (m, 1H), 6.61 (t, *J* = 2.1 Hz, 1H), 6.47 (dd, *J*₁ = 8.4 Hz, *J*₂ = 2.3 Hz, 1H), 3.23 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 150.2, 146.0, 136.4, 136.1, 135.0, 134.1, 133.1, 130.8, 130.0, 129.7, 128.7, 128.0, 127.9, 117.8, 113.5, 112.0, 39.2. HRMS (ESI) calculated [M+H] ⁺for C₁₉H₁₇ClNSe: 374.0209, found: 374.0209. FTIR (cm⁻¹) 3057, 2922, 2363, 1596, 1481, 1341.

N-(3-Bromophenyl)-*N*-methyl-2-(phenylselanyl)aniline (41)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and3-bromo-*N*,*N*-dimethylaniline **2l** (0.100 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded N-(3-bromophenyl)-N-methyl-2-(phenylselanyl)aniline 41 as a sticky liquid (0.104 g, 50% yield).

 $R_{\rm f}$ (Pet. ether /DCM = 95/05): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.64-7.62 (m, 2H), 7.40-7.33 (m, 3H), 7.25-7.21 (m, 1H), 7.13-7.09 (m, 2H), 7.06-7.02 (m, 2H), 6.90-6.88 (m, 1H), 6.78 (t, J =2.0 Hz, 1H), 6.51 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.3$ Hz, 1H), 3.23 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 150.3, 145.9, 136.4, 136.1, 130.8, 130.3, 129.7, 128.73, 128.70, 128.1, 128.04, 127.96, 123.3, 120.7, 116.3, 112.5, 39.2. **HRMS (ESI)** calculated [M+H] ⁺for C₁₉H₁₇BrNSe: 417.9704, found: 417.9704. FTIR (cm⁻¹) 3057, 2922, 2363, 1593, 1479, 1340, 1075.

N-Methyl-2-(phenylselanyl)-*N*-(3-(trifluoromethyl)phenyl)aniline (4m)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1a (0.298 g, 243 µL, 1.0 mmol) and N.Ndimethyl-3-(trifluoromethyl)aniline 2m (0.095 g,0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the

crude reaction mixture using silica gel afforded N-Methyl-2-(phenylselanyl)-N-(3-(trifluoromethyl)phenyl)aniline **4m** as a pale yellow oil (0.106 g, 52% yield).

 $R_{\rm f}$ (Pet. ether /DCM = 95/05): 0.56; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 7.1 Hz, 2H), 7.43-7.36 (m, 3H), 7.31-7.26 (m, 2H), 7.18-7.11 (m, 3H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.90 (s, 1H), 6.75 (d, J = 8.3 Hz, 1H), 3.31(s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 145.9, 136.4, 136.0, 131.4 (q, J= 31.7 Hz), 131.0, 129.7, 129.4, 128.7, 128.6, 128.2, 128.1, 124.6 (q, J = 273.6 Hz), 116.9, 114.3 (q, J = 3.8 Hz), 109.6 (q, J = 3.8 Hz), 39.2. **HRMS (ESI)** calculated [M+H]⁺ for C₂₀H₁₇F₃NSe: 408.0473, found: 408.0479. FTIR (cm⁻¹) 3060, 2922, 1612, 1480, 1354, 1166, 1122, 1073.

N,2-Dimethyl-*N*-(2-(phenylselanyl)phenyl)aniline (4n)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1a (0.298 g, 243 µL, 1.0 mmol) and N,N,2trimethylaniline 2n (0.068 g,0.5 mmol) with Phenylselenyl bromide 3a (0.177

g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*,2-dimethyl-*N*-(2-(phenylselanyl)phenyl)aniline **4n** as a light yellow oil (0.054 g, 31% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.47;¹H NMR (400 MHz, CDCl₃) δ 7.63-7.61 (m, 2H), 7.40-7.32 (m, 3H), 7.2-7.14 (m, 2H), 7.10-7.05 (m, 2H), 7.02-6.99 (m, 1H), 6.94-6.92 (m, 1H), 6.89-6.84 (m, 2H), 3.22 (s, 3H), 2.10 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.4, 136.3, 132.7, 131.8, 131.6, 130.6, 129.5, 129.2, 128.3, 126.8, 126.5, 124.5, 123.5, 123.0, 120.7, 41.6, 19.1. HRMS (ESI) calculated [M+H]⁺ for C₂₀H₂₀NSe: 354.0755, found: 354.0760. FTIR (cm⁻¹) 2363, 1636, 1572, 1467, 1278, 1023.

3,4-Difluoro-*N*-methyl-*N*-(2-(phenylselanyl)phenyl)aniline (40)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 3,4-difluoro-*N*,*N*-dimethylaniline **2o** (0.079 g,0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for

12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded 3,4-difluoro-*N*-methyl-*N*-(2-(phenylselanyl)phenyl)aniline **40** as a pale yellow oil (0.109 g, 58% yield).

R^f (Pet. ether /DCM = 95/05): 0.55; ¹H NMR (400 MHz, CDCl₃) δ 7.68 (d, *J* = 7.6 Hz, 2H), 7.46-7.39 (m, 3H), 7.30-7.26 (m, 1H), 7.18-7.09 (m, 3H), 7.03 (q, *J* = 9.4 Hz, 1H), 6.49-6.44 (m, 1H), 7.35-7.32 (m, 1H), 3.26 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7 (dd, *J*₁ = 244.4 Hz, *J*₂ = 13.4 Hz), 146.3, 146.1, 143.5 (dd, *J*₁ = 237.6 Hz, *J*₂ = 13.0 Hz), 136.4, 136.0, 130.7, 129.7, 128.8, 128.5, 128.0, 127.9, 117.2 (d, *J*₁ = 17.7 Hz), 108.9 (dd, *J*₁ = 5.1 Hz, *J*₂ = 2.9 Hz), 102.8 (d, *J*₁ = 21.4 Hz), 39.5. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₆F₂NSe: 376.0411, found: 376.0419. FTIR (cm⁻¹) 3057, 2921, 1600, 1515, 1474, 1269.

N-Methyl-*N*-(2-(phenylselanyl)phenyl)naphthalen-1-amine (4p)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and *N*,*N*-dimethylnaphthalen-1-amine **2p** (0.086 g, 82 μ L0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography

(Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-*N*-(2-(phenylselanyl)phenyl)naphthalen-1-amine **4p** as a sticky liquid (0.126 g, 65% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.44; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 7.4 Hz,1H), 7.86 (d, *J* = 8.5 Hz, 1H), 7.88-7.63 (m, 3H), 7.49-7.36 (m, 6H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.12-7.04 (m, 2H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 3.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.4, 147.6, 136.2, 135.2, 131.5, 131.0, 129.6, 129.3, 129.2, 128.4, 128.3, 127.1, 125.9, 125.7, 125.6, 125.0, 124.9, 124.1, 123.4, 117.8, 42.8. HRMS (ESI) calculated [M+H] ⁺ for C₂₃H₁₉NSe: 390.0755, found: 390.0760. FTIR (cm⁻¹) 3052, 2854, 1572, 1466, 1394, 1294, 1022.

Ethyl (E)-3-(4-(methyl(2-(phenylselanyl)phenyl)amino)phenyl)acrylate (4q)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyltrifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and ethyl (*E*)-3-(4-(dimethylamino)phenyl) acrylate **2q** (0.055 g,0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol)

and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 65 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 80/20) of the crude reaction mixture using silica gel afforded ethyl (*E*)-3-(4-(methyl(2-(phenylselanyl)phenyl)amino)phenyl)acrylate **4q** as a pale yellow oil (0.055 g, 50% yield).

*R*_f (Pet. ether /DCM = 80/20): 0.30; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.59 (m, 3H), 7.39-7.32 (m, 5H), 7.26-7.22 (m, 1H), 7.15-7.10 (m, 2H), 7.07-7.05 (m, 1H), 6.57 (d, J = 8.7 Hz, 2H), 6.23 (d, J = 15.9 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.28 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 167.9, 150.6, 145.6, 145.1, 136.4, 136.0, 130.9, 129.7, 129.6, 128.83, 128.76, 128.2, 128.02, 128.00, 124.0, 113.5, 113.4, 60.3, 39.1, 14.5. HRMS (ESI) calculated

 $[M+H]^+$ for C₂₄H₂₄NO₂Se: 438.0967, found: 438.0970. **FTIR (cm⁻¹)** 3060, 2922, 2329, 1702, 1624, 1171, 1038.

N-Methyl-*N*-phenyl-2-(*p*-tolylselanyl)aniline (4r)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-di-*p*-tolyldiselane **6b** (0.128 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction

me mash column enfonatography (ret.ener/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-*N*-phenyl-2-(*p*-tolylselanyl)aniline **4r** as a pale yellow solid (0.049 g, 56% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.45; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.24-7.17 (m, 5H), 7.13-7.11 (m, 1H), 7.08-7.04 (m, 1H), 6.98-6.93 (m, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.66 (d, *J*= 8.3 Hz, 2H), 3.25 (s, 3H), 2.39 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 146.6, 138.9, 136.93, 136.88, 130.6, 129.8, 129.1, 128.5, 127.5, 127.4, 124.3, 118.0, 114.0, 39.2, 21.4. HRMS (ESI) calculated [M+H] ⁺ for C₂₀H₂₀NSe: 354.0755, found: 354.0760. FTIR (cm⁻¹) 3058, 2920, 1642, 1601, 1497, 1337.

2-((4-Bromophenyl)selanyl)-*N*-methyl-*N*-phenylaniline (4s)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-bis(4-bromophenyl)diselane **6c** (0.176 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded 2-((4-

bromophenyl)selanyl)-*N*-methyl-*N*-phenylaniline **4s** as a light yellow solid (0.058g, 56% yield). *R*_f(Pet. ether /DCM = 95/05): 0.50; ¹**H NMR (400 MHz, CDCl**₃) δ 7.50-7.45 (m, 4H), 7.26-7.20 (m, 3H), 7.17-7.15 (m, 1H), 7.12-7.08 (m, 1H), 7.03-7.01 (m, 1H), 6.80 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J*= 7.9 Hz, 2H), 3.24 (s, 3H). ¹³**C NMR (100 MHz, CDCl**₃) δ 149.1, 147.0, 138.0, 135.7, 132.8, 130.4, 129.1, 128.7, 128.0, 127.7, 127.4, 123.2, 118.2, 114.1, 39.3. **HRMS (ESI)** calculated [M+H] ⁺for C₁₉H₁₇BrNSe: 417.9704, found: 417.9713. **FTIR (cm⁻¹)** 3056, 2921, 1600, 1497, 1465, 1006.

2-((4-Chlorophenyl)selanyl)-*N*-methyl-*N*-phenylaniline (4t)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-bis(4-chlorophenyl) diselane **6d** (0.143 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the

crude reaction mixture using silica gel afforded 2-((4-chlorophenyl)selanyl)-*N*-methyl-*N*-phenylaniline **4t** as a light yellow solid (0.059 g, 63% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.54 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.20 (m, 3H), 7.17-7.15 (m, 1H), 7.12-7.08 (m, 1H), 7.01 (dd, J_I = 7.9 Hz, J_2 = 1.5 Hz, 1H), 6.83-6.79 (m, 1H), 6.66-6.64 (m, 2H), 3.25 (s, 3H).¹³C NMR (100 MHz, CDCl₃) δ 149.1, 147.0, 137.8, 135.8, 135.1, 130.3, 129.9, 129.1, 128.7, 128.0, 127.7, 126.7, 118.2, 114.1, 39.3. HRMS (ESI) calculated [M+H] ⁺for C₁₉H₁₇ClNSe: 374.0209, found: 374.0211. FTIR (cm⁻¹) 3057, 2363, 1600, 1498, 1338, 1087.

2-((4-Fluorophenyl)selanyl)-N-methyl-N-phenylaniline (4u)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-bis(4-fluorophenyl)diselane **6e** (0.131 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05)

of the crude reaction mixture using silica gel afforded 2-((4-fluorophenyl)selanyl)-*N*-methyl-*N*-phenylaniline **4u** as a yellow solid (0.063 g,71% yield).

 R_{f} (Pet. ether /DCM = 95/05): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.63 (m, 2H), 7.29-7.23 (m, 3H), 7.18 (dd, J_{1} = 7.8 Hz, J_{2} = 1.5 Hz, 1H), 7.14-7.08 (m, 3H), 6.98 (d, J= 7.8 Hz, J_{2} = 1.5

Hz, 1H), 6.84 (t, J = 7.3 Hz, 1H), 6.71-6.68 (m, 2H), 3.29 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4 (d, J = 248.6 Hz), 149.1, 146.7, 138.9 (d, J = 8.0 Hz), 137.4 (d, J = 8.1 Hz), 136.4, 129.8, 129.1, 128.6, 127.7 (d, J = 9.4 Hz), 122.8 (d, J = 3.4 Hz), 118.2, 116.9 (d, J = 21.4 Hz), 114.1, 39.2. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₇FNSe: 358.0505, found: 358.0512. FTIR (cm⁻¹) 3060, 2363, 1641, 1582, 1489, 1226.

2-((3-Chlorophenyl)selanyl)-N-methyl-N-phenylaniline (4v)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-bis(3-chlorophenyl)diselane **6f** (0.143 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05)

of the crude reaction mixture using silica gel afforded 2-((3-chlorophenyl)selanyl)-N-methyl-N-phenylaniline **4v** as a white solid (0.035 g, 38% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.57 (m, 1H), 7.49-7.47 (m, 1H), 7.35-7.32 (m, 1H), 7.28-7.09 (m, 6H), 7.06-7.04 (m, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 2H), 3.23 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 147.1, 135.7, 135.3, 135.0, 134.1, 130.8, 130.6, 130.2, 129.0, 128.68, 128.67, 128.2, 127.7, 118.2, 114.0, 39.3. HRMS (ESI) calculated [M+H] ⁺for C₁₉H₁₇ClNSe: 374.0209, found: 374.0214. FTIR (cm⁻¹) 3057, 2921, 1600, 1567, 1497, 1461, 1027.

2-((2-Chlorophenyl)selanyl)-*N*-methyl-*N*-phenylaniline (4w)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 1,2-bis(2-chlorophenyl)diselane **6g** (0.143 g, 0.375 mmol) in the presence of KF (0.058g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at

25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded 2-((2-chlorophenyl)selanyl)-*N*-methyl-*N*-phenylaniline **4w** as a pale yellow oil (0.046 g, 49% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.51; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 1H), 7.47 (dd, J_1 = 8.0 Hz, J_2 = 1.1 Hz, 1H), 7.30-7.25 (m, 2H), 7.24-7.17 (m, 4H), 7.16-7.09 (m, 2H), 6.79 (t, J = 7.3 Hz, 1H), 6.67-6.65 (m, 2H), 3.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.2, 148.1, 138.5, 136.9, 133.9, 132.1, 130.1, 129.7, 129.1, 128.9, 128.7, 127.7, 127.5, 118.2, 114.1, 39.4. HRMS (ESI) calculated [M+H] ⁺for C₁₉H₁₇ClNSe: 374.0209, found: 374.0210. FTIR (cm⁻¹) 3057, 2922, 1598, 1496, 1445, 1022.

N,4,5-Trimethyl-*N*-phenyl-2-(phenylselanyl)aniline (4x)



Following the general procedure, treatment of 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1b** (0.326 g, 1.0 mmol) and *N*,*N*-dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0

mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*,4,5-trimethyl-*N*-phenyl-2-(phenylselanyl)aniline **4x** as a white solid (0.124 g, 68% yield).

R^f (Pet. ether /DCM = 95/05): 0.45; ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.59(m, 2H), 7.36-7.31(m, 3H), 7.24-7.20 (m, 2H), 6.97 (s, 1H), 6.91 (s, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.9 Hz, 2H),3.22 (s, 3H), 2.20 (s, 3H), 2.16 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 149.4, 145.1, 136.9, 136.3, 135.6, 132.4, 131.6, 129.7, 129.4, 129.0, 128.1, 117.6, 113.7, 39.3, 19.5, 19.4. HRMS (ESI) calculated [M+H] ⁺for C₂₁H₂₂NSe: 368.0912, found: 368.0919. FTIR (cm⁻¹) 3059, 2919, 2363, 1597, 1495, 1380, 1328, 1025.

N-Methyl-*N*-phenyl-6-(phenylselanyl)-2,3-dihydro-1*H*-inden-5-amine (4y)



Following the general procedure, treatment of 6-(trimethylsilyl)-2,3dihydro-1*H*-inden-5-yl trifluoromethanesulfonate **1c** (0.338 g, 1.0 mmol) and *N*,*N*-dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at25 °C for 12 h followed by flash column chromatography

(Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded N-methyl-N-

phenyl-6-(phenylselanyl)-2,3-dihydro-1H-inden-5-amine 4y as a white solid (0.150 g, 79%) yield).

 $R_{\rm f}$ (Pet. ether /DCM = 95/05): 0.40; ¹H NMR (400 MHz, CDCl₃) δ 7.68-7.65 (m, 2H), 7.42-7.35 (m, 3H), 7.28-7.23 (m, 2H), 7.06 (s, 1H), 6.97 (s, 1H), 6.81 (tt, $J_1 = 7.4$ Hz, $J_2 = 1.0$ Hz, 1H), 6.71-6.68 (m. 2H), 3.26 (s, 3H), 2.88-2.80 (m, 4H), 2.09 (p, J = 7.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 145.3, 144.7, 144.1, 136.0, 132.9, 129.5, 129.2, 129.0, 128.2, 126.5, 124.4, 117.6, 113.8, 39.3, 32.7, 32.6, 25.8. **HRMS (ESI)**calculated [M+H] ⁺ for C₂₂H₂₂NSe: 380.0912, found: 380.0915. FTIR (cm⁻¹) 3588, 3062, 3951, 2843, 1598, 1499.

4,5-Difluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (4z)



Following the general procedure, treatment of 4,5-difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate 1d (0.334 g,1.0 mmol) and N,N-dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide 3a (0.177 g, 0.75 mmol)in the presence of KF (0.116g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL)

at25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the mixture using silica gel afforded4,5-difluoro-N-methyl-N-phenyl-2crude reaction (phenylselanyl)aniline 4z as a pale yellow oil (0.102 g, 55% yield).

 $R_{\rm f}$ (Pet. ether /DCM = 95/05): 0.55; ¹H NMR (400 MHz, CDCl₃) δ 7.65-7.63(m, 2H), 7.46-7.38(m, 3H), 7.28-7.24 (m, 2H), 6.99 (dd, $J_1 = 10.7$ Hz, $J_2 = 7.4$ Hz, 1H), 6.86 (t, J = 7.3 Hz, 1H), 6.76 (dd, $J_1 = 10.5$ Hz, $J_2 = 8.6$ Hz, 1H), 6.70-6.67 (m, 2H), 3.23 (s, 3H). ¹³C NMR (100 MHz, **CDCl**₃) δ 149.7 (dd, $J_1 = 254.1$ Hz, $J_2 = 16.6$ Hz), 149.4 (dd, $J_1 = 242.9$ Hz, $J_2 = 7.0$ Hz), 148.7, 142.6 (dd, $J_1 = 6.1$ Hz, $J_2 = 3.7$ Hz), 136.7, 132.3 (dd, $J_1 = 4.5$ Hz, $J_2 = 3.5$ Hz), 130.0, 129.3, 129.2, 127.5, 118.9, 118.0 (d, J = 19.7 Hz), 117.1 (dd, $J_1 = 16.3$ Hz, $J_2 = 1.2$ Hz), 114.4, 39.3. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₆F₂NSe: 376.0411, found: 376.0417. FTIR (cm⁻ ¹) 3061, 2877, 1597, 1488, 1392, 1286, 1170.

N-Methyl-*N*-phenyl-1-(phenylselanyl)naphthalen-2-amine (4aa)



Following the general procedure, treatment of 3-(trimethylsilyl) naphthalen-2-yl trifluoromethanesulfonate 1e (0.174 g, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-*N*-phenyl-1-(phenylselanyl)naphthalen-2-amine **4aa** as a yellow oil (0.047 g, 48% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.3; ¹H NMR (400 MHz, CDCl₃) δ 8.47-8.45(m, 1H), 7.96 (d, *J* = 8.6 Hz, 1H), 7.88-7.86 (m, 1H), 7.52-7.46 (m, 2H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.17-7.06 (m, 7H), 7.73 (t, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 7.9 Hz, 2H), 3.24 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.2, 149.2, 136.4, 133.4, 132.9, 132.0, 130.1, 129.4, 129.1, 129.0, 128.5, 127.5, 127.4, 126.2, 126.0, 117.5, 113.6, 39.9. HRMS (ESI) calculated [M+H] ⁺ for C₂₃H₂₀NSe: 390.0755, found: 390.0764. FTIR (cm⁻¹) 3056, 2923, 2364, 1589, 1497, 1362, 1131, 1023.

N-Methyl-N-phenyl-1-(phenylselanyl)-5,6,7,8-tetrahydronaphthalen-2-amine (4ab)



Following the general procedure, treatment of 1-(trimethylsilyl)-5,6,7,8tetrahydronaphthalen-2-yl trifluoromethanesulfonate **1f** (0.352 g, 1.0 mmol) and *N*,*N*-dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL)

at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-methyl-*N*-phenyl-1-(phenylselanyl)-5,6,7,8-tetrahydronaphthalen-2-amine **4ab** as a pale yellow oil (0.134 g, 68% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.4; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (d, *J* = 8.1 Hz, 1H), 7.18-7.10(m, 8H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.50(d, *J* = 8.1 Hz, 2H), 3.13 (s, 3H), 2.84 (d, *J* = 6.7 Hz, 4H), 1.76 (t, *J* = 2.8 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 149.7, 149.3, 143.5, 137.2, 133.4, 132.5, 132.0, 129.8, 129.1, 128.9, 126.7, 125.8, 116.7, 112.9, 39.7, 31.1, 30.2, 23.6, 22.8. HRMS (ESI) calculated [M+H] ⁺ for C₂₃H₂₄NSe: 394.1068, found: 394.1075. FTIR (cm⁻¹) 3059, 2934, 2861, 1602, 1501, 1347.

N,4-dimethyl-*N*-phenyl-2-(phenylselanyl)aniline (4ac) and *N*,5-dimethyl-*N*-phenyl-2-(phenylselanyl)aniline (4ac')



Following the general procedure, treatment of 4 methyl-2-(trimethylsilyl)phenyl trifluoro methanesulfonate **1g** (0.156 g, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 0.032 μ L,0.25 mmol) with Phenylselenyl bromide **3a** (0.088 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0

mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*,4-dimethyl-*N*-phenyl-2-(phenylselanyl)aniline (**4ac**) and *N*,5-dimethyl-*N*-phenyl-2-(phenylselanyl)aniline (**4ac**') as a mixture of regioisomers in 1.4:1 ratio as a pale yellow oil (0.065 g,74% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.49; ¹H NMR (400 MHz, CDCl₃) of Major isomer; δ 7.69-7.64 (m, 2H), 7.45-7.35 (m, 3H), 7.28-7.24 (m, 2H), 7.09-7.00 (m, 2H), 6.96-6.94 (m, 1H), 6.85-6.80 (m, 1H), 6.71-6.68 (m. 2H), 3.27 (s, 3H), 2.32 (s, 3H). ¹H NMR (400 MHz, CDCl₃) of Minor isomer; δ 7.69-7.64 (m, 2H), 7.45-7.35 (m, 3H), 7.28-7.24 (m, 2H), 7.09-7.00 (m, 2H), 6.89 (s, 1H), 6.85-6.80 (m, 1H), 6.71-6.68 (m. 2H), 3.27 (s, 3H), 2.26 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) of Major isomer δ 149.2, 147.1, 138.1, 135.9, 131.9, 131.0, 129.5, 129.2, 129.1, 129.0, 128.5, 128.3, 117.9, 113.9, 39.3, 20.9. ¹³C NMR (125 MHz, CDCl₃) of Major isomer δ 149.1, 144.5, 137.5, 136.3, 135.7, 130.9, 129.6, 129.0, 128.7, 128.4, 128.5, 128.3, 117.8, 113.8, 39.2, 21.2. HRMS (ESI)calculated [M+H] ⁺ for C₂₀H₂₀NSe: 354.0755, found:354.0757. FTIR (cm⁻¹) 3058, 2919, 1599, 1495, 1335, 1032.

4-Chloro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (4ad) and 5-Chloro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline(4ad')



Following the general procedure, treatment of 4chloro-2-(trimethylsilyl)phenyl trifluoro methanesulfonate **1h** (0.333 g, 1.0 mmol) N,Ndimethylaniline **2a** (0.061 g, 63 µL, 0.5 mmol) and with Phenylselenyl bromide **3a** (0.177 g, 0.75mmol)

in the presence of KF (0.116g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded 4-chloro-*N*-methyl-*N*-phenyl-2-

(phenylselanyl)aniline (4ad) and 5-chloro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (4ad') as as a mixture of regioisomers in 1.7:1 ratio (0.118 g, 68% yield, pale yellow oil, regioisomer ratio determined by ¹H-NMR analysis of crude reaction mixture).

*R*_f (Pet. ether /DCM = 95/05): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.71-7.66(m, 3H), 7.50-7.38(m, 4H), 7.31-7.27 (m, 3H), 6.75-6.72(m, 3H), 3.27 (s, 3H).Representative peaks of other isomer 1H NMR (400 MHz, CDCl₃) δ 3.28 (s). ¹³C NMR (100 MHz, CDCl₃) δ 148.8, 145.2, 138.6, 136.8, 133.1, 131.4, 129.9, 129.4, 129.14, 129.10, 128.8, 127.6, 118.5, 114.2, 39.2. Representative peaks of other isomer ¹³C NMR (125 MHz, CDCl₃) δ 148.6, 147.9, 136.4, 132.8, 132.7, 129.8, 129.3, 129.2, 128.5, 128.0, 127.5, 127.3, 118.8, 114.6, 39.2. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₇ClNSe: 374.0209, found: 374.0210. FTIR (cm⁻¹) 3061, 2950, 2871, 1601, 1499, 1332.

4-Fluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline(4ae) and 5-fluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (4ae')



Following the general procedure, treatment of 5 fluoro-2-(trimethylsilyl)phenyl trifluoro methanesulfonate **1i** (0.316 g, 1.0 mmol) and *N*,*N*dimethylaniline **2a** (0.061 g, 63 μ L, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6

(0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded 4-fluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (**4ae**) and 5-fluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (**4ae**) as a mixture of regioisomers in 2.3:1 ratio as a sticky liquid (0.100 g, 56% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.70-7.68 (m, 2H), 7.49-7.40 (m, 3H), 7.28-7.24 (m, 2H), 7.11-7.07 (m, 1H), 6.87-6.82 (m, 2H), 6.72-6.68 (m, 2H), 6.64 (dd, J_1 = 9.0 Hz, J_2 = 2.9 Hz, 1H), 3.25 (s, 3H). Representative peaks of other isomer ¹H NMR (400 MHz, CDCl₃) δ 3.26 (s). ¹³C NMR (125 MHz, CDCl₃) δ 161.7 (d, J = 248.1 Hz), 149.1, 142.4 (d, J = 2.9 Hz), 139.3 (d, J = 7.6 Hz), 137.0, 132.3 (d, J = 8.9 Hz), 129.9, 129.2, 129.1, 127.3, 118.3, 116.1 (d, J = 24.9 Hz), 114.7 (d, J = 21.4 Hz), 113.9, 39.2. Representative peaks of other isomer ¹³C NMR (125 MHz, CDCl₃) δ 162.7 (d, J = 247.7 Hz), 148.8, 148.6 (d, J = 8.4

Hz), 135.9, 129.7, 129.6, 129.1, 128.9, 128.5, 118.8, 115.4 (d, J = 21.0 Hz), 114.2 (d, J = 23.0 Hz), 114.6, 39.4. **HRMS (ESI)** calculated [M+H]⁺ for C₁₉H₁₇FNSe: 358.0505, found: 358.0508. **FTIR (cm⁻¹)** 3061, 2871, 1596, 1477, 1252, 1194.

N,*N*-Dimethyl-2-(phenylselanyl)aniline (4af)



Following the general procedure, treatment of 2- (trimethylsilyl)phenyltrifluoromethanesulfonate 1a (0.298 g, 243 μL, 1.0 mmol) and *N*,*N*-dimethyl-1-phenylmethanamine 7a (0.068 g, 75 μL, 0.5 mmol) with Phenylselenyl bromide 3a (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL)

at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*,*N*-dimethyl-2-(phenylselanyl)aniline **4af** as a white solid (0.064 g, 46% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.31; ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.67 (m, 2H), 7.43-7.36 (m, 3H), 7.18-7.14 (m, 2H), 6.91-6.84 (m, 2H), 2.80 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 151.9, 136.7, 132.3, 129.6, 129.3, 128.8, 128.5, 126.6, 125.0, 120.2, 45.1. HRMS (ESI) calculated [M+H] ⁺for C₁₄H₁₆NSe: 278.0442, found: 278.0446. FTIR (cm⁻¹) 3049, 2828, 2784, 2363, 1573, 1470, 1438, 941.

1-(2-(Phenylselanyl)phenyl)-1,2,3,4-tetrahydroquinoline (4ag)



Following the general procedure, treatment of 2-(trimethylsilyl) phenyltrifluoromethanesulfonate **1a** (0.298 g, 243μ L, 1.0 mmol) and 1methyl-1,2,3,4-tetrahydroquinoline **7c** (0.074 g,0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05)

of the crude reaction mixture using silica gel afforded 1-(2-(phenylselanyl)phenyl)-1,2,3,4tetrahydroquinoline **4ag** as a colorless oil (0.081 g,44% yield).

*R*f (Pet. ether /DCM = 95/05): 0.40; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.63(m, 2H), 7.39-7.36(m, 3H), 7.23-7.21 (m, 2H), 7.09-7.03(m, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.20 (d, *J* = 8.1 Hz, 1H), 3.61-3.50 (m, 2H), 2.91 (s, 2H), 2.18-2.13

(m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 145.8, 145.1, 136.8, 136.7, 120.0, 129.7, 129.5, 128.9, 128.7, 128.3, 127.7, 127.6, 126.8, 122.7, 117.7, 114.2, 50.8, 28.0, 22.7. HRMS (ESI) calculated [M+H] ⁺ for C₂₁H₂₀NSe: 366.0755, found: 366.0760. FTIR (cm⁻¹) 3450, 3060, 2924, 1573, 1495, 1304.

N-Methyl-N-phenyl-2-(phenylthio)aniline (9a)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.149 g, 121 μ L, 0.5 mmol) and *N*,*N*-dimethylaniline **2a** (0.030 g, 32 μ L, 0.25 mmol) with 2-(phenylthio)isoindoline-1,3-dione **8** (0.096 g, 0.375 mmol) in the presence of KF (0.058 g, 1.0 mmol) and 18-crown-6 (0.264 g, 1.0 mmol) in THF (1.0 mL)

at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded*N*-methyl-*N*-phenyl-2-(phenylthio)aniline **9a** as a white solid (0.029 g, 40% yield).

*R*_f (Pet. ether /CH₂Cl₂ = 95/05): 0.46; ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.44 (m, 2H), 7.39-7.31 (m, 3H), 7.24-7.19 (m, 4H), 7.14-7.11 (m, 1H), 7.03-7.01 (m, 1H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.65-6.63 (m, 2H), 3.25 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 146.0, 138.8, 134.1, 133.4, 129.5, 129.9, 128.9, 128.2, 127.3, 127.2, 117.7, 113.6, 39.1. HRMS (ESI) calculated [M+H] ⁺ for C₁₉H₁₈NS: 292.1154, found: 292.1160. FTIR (cm⁻¹) 3058, 2924, 2874, 2808, 2333, 1919, 1729, 1600, 1577, 1496, 1442, 1340, 1131, 1027, 867.

N-(4-Bromobutyl)-*N*-phenyl-2-(phenylselanyl)aniline (13)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyltrifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 1-phenylpyrrolidine **7d** (0.074 g, 0.5 mmol) with Phenylselenyl bromide **3a** (0.177 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography

(Pet.ether/DCM = 95/05) of the crude reaction mixture using silica gel afforded *N*-(4-bromobutyl)-*N*-phenyl-2-(phenylselanyl)aniline **13** as a white solid (0.080 g, 35% yield).

*R*_f(Pet. ether /DCM = 95/05): 0.48; ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.64 (m, 2H), 7.45-7.38 (m, 3H), 7.30-7.21 (m, 4H), 7.16-7.12 (m, 1H), 7.07 (dd, J_1 = 7.9 Hz, J_2 = 1.2 Hz, 1H), 6.83 (t, J = 7.3 Hz, 1H), 6.68-6.66 (m, 2H), 3.75-3.71 (m, 2H), 3.49 (t, J = 6.5 Hz, 2H), 2.09-1.92 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 144.7, 136.9, 136.5, 130.6, 129.9, 129.7, 129.2, 128.7, 128.3, 127.6, 127.5, 118.0, 114.0, 50.8, 33.5, 30.6, 26.4. HRMS (ESI) calculated [M+H] ⁺for C₂₂H₂₃BrNSe: 460.0174, found: 460.0178. FTIR (cm⁻¹) 3057, 2922, 1599, 1497, 1465, 1027.

N-Phenyl-2-(phenylselanyl)-*N*-(4-(phenylselanyl)butyl)aniline (14)



Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.298 g, 243 μ L, 1.0 mmol) and 1-phenylpyrrolidine **7d** (0.074 g,0.5 mmol) with 1,2-diphenyldiselane **6** (0.234 g, 0.75 mmol) in the presence of KF (0.116 g, 2.0 mmol) and 18-crown-6 (0.528 g, 2.0 mmol) in THF (2.0 mL) at 25 °C for 12 h followed by flash column chromatography (Pet.ether/DCM = 95/05) of the crude reaction

mixture using silica gel afforded*N*-phenyl-2-(phenylselanyl)-*N*-(4-(phenylselanyl)butyl)aniline **14** as a pale yellow oil (0.093 g, 34% yield).

*R*_f (Pet. ether /DCM = 95/05): 0.33; ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.60 (m, 2H), 7.51-7.49 (m, 2H), 7.39-7.33 (m, 3H), 7.29-7.18 (m, 6H), 7.14-7.12 (m, 1H), 7.10-7.06 (m, 1H), 7.02-7.00 (m, 1H), 6.77 (t, *J*= 7.3 Hz, 1H), 6.60 (d, *J* = 7.9 Hz, 2H), 3.65-3.61 (m, 2H), 2.98-2.92 (m, 2H),1.93-1.85 (m, 2H), 1.83-1.76 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 144.8, 137.0, 136.6, 132.9, 130.5, 130.4, 130.0, 129.7, 129.2, 128.7, 128.4, 127.6, 127.4, 126.9, 117.8, 114.0, 51.0, 28.0, 27.8. HRMS (ESI) calculated [M+H] ⁺for C₂₈H₂₈NSe₂: 538.0547, found: 538.0555. FTIR (cm⁻¹) 3056, 2922, 1599, 1572, 1496, 1022.

10.Synthesis and Characterization of 2-Selanyl aniline Derivatives

N-Methyl-*N*-phenyl-2-(phenylselanyl)aniline (4a)



N-(4-Methoxyphenyl)-*N*-methyl-2-(phenylselanyl)aniline (4b)



N-Methyl-2-(phenylselanyl)-*N*-(p-tolyl)aniline (4c)



N-(4-Ethylphenyl)-N-methyl-2-(phenylselanyl)aniline (4d)



N-(4-Iodophenyl)-N-methyl-2-(phenylselanyl)aniline (4e)



N-(4-Bromophenyl)-N-methyl-2-(phenylselanyl)aniline (4f)



N-(4-Chlorophenyl)-N-methyl-2-(phenylselanyl)aniline (4g)



N-(4-Fluorophenyl)-N-methyl-2-(phenylselanyl)aniline (4h)



N-Methyl-2-(phenylselanyl)-N-(4-(trifluoromethyl)phenyl)aniline (4i)







N-(3-Chlorophenyl)-N-methyl-2-(phenylselanyl)aniline (4k)

N-(3-Bromophenyl)-N-methyl-2-(phenylselanyl)aniline (41)





N-Methyl-2-(phenylselanyl)-N-(3-(trifluoromethyl)phenyl)aniline (4m)

N,2-Dimethyl-N-(2-(phenylselanyl)phenyl)aniline(4n)



3,4-Difluoro-N-methyl-N-(2-(phenylselanyl)phenyl)aniline (40)



N-Methyl-*N*-(2-(phenylselanyl)phenyl)naphthalen-1-amine (4p)



Ethyl (E)-3-(4-(methyl(2-(phenylselanyl)phenyl)amino)phenyl)acrylate (4q)

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N-Methyl-*N*-phenyl-2-(*p*-tolylselanyl)aniline (4r)



2-((4-Bromophenyl)selanyl)-N-methyl-N-phenylaniline (4s)



2-((4-Chlorophenyl)selanyl)-N-methyl-N-phenylaniline (4t)



2-((4-Fluorophenyl)selanyl)-N-methyl-N-phenylaniline (4u)



2-((3-Chlorophenyl)selanyl)-N-methyl-N-phenylaniline (4v)



2-((2-Chlorophenyl)selanyl)-N-methyl-N-phenylaniline (4w)



N,4,5-Trimethyl-*N*-phenyl-2-(phenylselanyl)aniline (4x)



N-Methyl-*N*-phenyl-6-(phenylselanyl)-2,3-dihydro-1*H*-inden-5-amine (4y)



4,5-Difluoro-*N*-methyl-*N*-phenyl-2-(phenylselanyl)aniline (4z)



N-Methyl-*N*-phenyl-1-(phenylselanyl)naphthalen-2-amine (4aa)



N-Methyl-*N*-phenyl-1-(phenylselanyl)-5,6,7,8-tetrahydronaphthalen-2-amine (4ab)



N,4-dimethyl-N-phenyl-2-(phenylselanyl)aniline (4ac) and



N,5-dimethyl-*N*-phenyl-2-(phenylselanyl)aniline (4ac')

4-Chloro-N-methyl-N-phenyl-2-(phenylselanyl)aniline (4ad) and



5-Chloro-N-methyl-N-phenyl-2-(phenylselanyl)aniline (4ad')

4-Fluoro-N-methyl-N-phenyl-2-(phenylselanyl)aniline (4ae) and



5-fluoro-N-methyl-N-phenyl-2-(phenylselanyl)aniline (4ae')

N,N-Dimethyl-2-(phenylselanyl)aniline (4af)



1-(2-(Phenylselanyl)phenyl)-1,2,3,4-tetrahydroquinoline (4ag)







N-(4-Bromobutyl)-*N*-phenyl-2-(phenylselanyl)aniline (13)



N-Phenyl-2-(phenylselanyl)-N-(4-(phenylselanyl)butyl)aniline (14)