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Selenium dioxide Promoted Dinitrogen Extrusion/Direct Selenation of Arylhydrazines and Anilines

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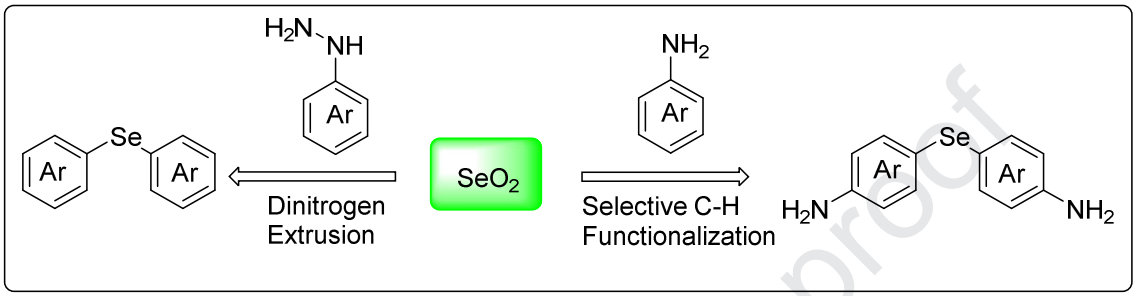
Economical

Broad scope



Metal free

Gram Scale

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Selenium dioxide Promoted Dinitrogen Extrusion/Direct Selenation of Arylhydrazines and Anilines.

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ABSTRACT

A novel, efficient, economical strategy for the coupling and direct selenation of arylhydrazines to selenides using SeO_2 has been developed. Our method employs SeO_2 as the selenium source with hydrazines as coupling reactants to generate selenides via dinitrogen extrusion. This reagent also helped to generate ArSesubstitued aniline derivatives via C- H functionalization reaction in good yields. The application of this method in gram scale was also carried out.

1. Introduction

Organoselenides, in particular the diaryl selenidesembracing carbon-selenium-carbon connectivity engendered a prominent position in material, biological, pharmaceutical science and are often found active as medicinal hits displaying a broad range of bioactivities.[1]For example,the diaryl selenide **A** could be used as human breast cancercell growth inhibitor, **B** is useful as a thioredoxin reductase (TR) and glutathione reductase (GR) inhibitorand **C** can serve as an antitumor agent (Figure 1). Moreover, the 2-substituted 1-naphthol **D** is a potent 5-lipoxygenase inhibitorwhile as the carboxylic acid **E** is a retinoic acid receptor (RAR) agonist which is ~10 times more powerful than its sulphur analogue. On the other hand, 4-substituted quinoline **F** possesses antioxidant properties (Figure 1).[1g]Besides this, they have also shown significant applications as catalysts and are useful intermediates in organic reactions.[2] As a result, a number of methods have been esta-

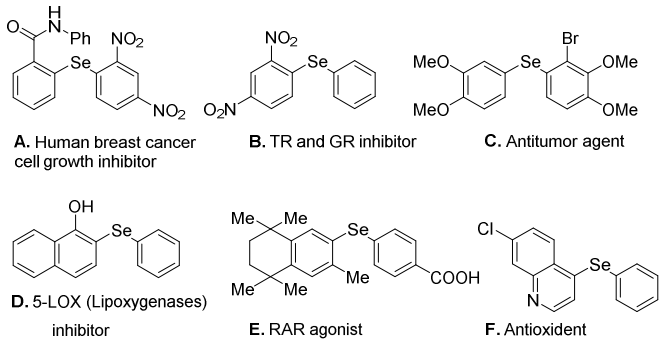
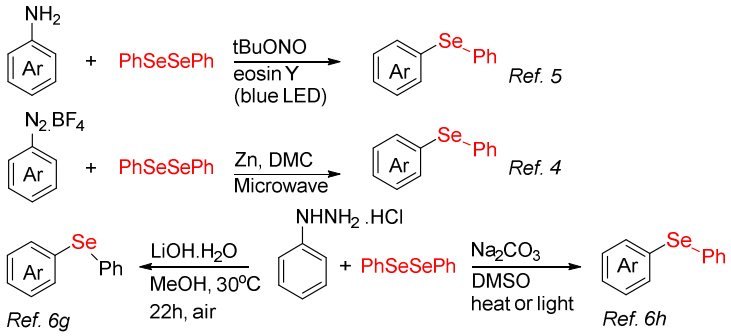


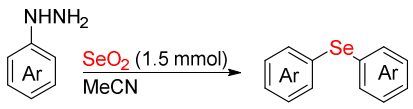
Figure 1. Selected biologically active organoselenium compounds.

Previous work:



This work:

a) SeO_2 promoted dinitrogen extrusion reaction



b) *Application:* Amine directed metal free coupling with SeO_2

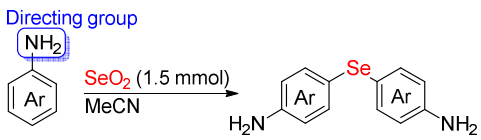


Figure 2. Summary of this work

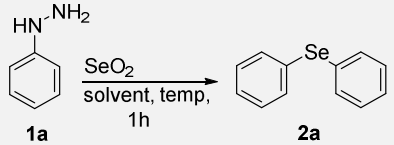
blished in the past towards the development of novel synthetic protocols for organoselenides.[3] Among the diverse customary approaches, synthesis of organoselenides using aryldiazonium salts have attracted much attention as a significant source of aryl radicals

and have been employed successfully for variety of aryl substitution reactions.[4-5]Although, the visible light photocatalyzed C−Se bond formation involving diazonium ion appeared useful, these conversions were carried out using diselenides as an expensive and foul smelling reagents in the presence ofdifferent additives for in-situ generation of diazonium. In this regard, we envisage the possibility of presenting selenium dioxide promoted dinitrogen extrusion assisted selenation reaction with different hydrazines (Figure 2). These types of reactions besides being the surrogate of diazocompouds, can also overcome the limitations of using expensive reactantsor additives. Compared to previously reported routes,[6] our methods are probably more suitable for larger scale syntheses since the selenium dioxide is cheap, stable, odorless, readily available and convenient to handle. Further, weextended the application to anilines as coupling reactants and successfully generated different ArSesubstitued aniline derivatives viaC-H functionalization. Previously, success in the area of C-H activation has been accomplished using directing groups in the presence of copper, palladium, ruthenium or rhodium catalysts withdiselenides/selenylchlorides.[7] Thereby, as an advantage, we also presented a metal free methodin which bulky directing groups and expensive selenium reagents with low atom/step-economyis avoided. In general, both aspects of reactivities highlight the strength of selenium dioxide to promote the coupling and direct selenation of both aryl- hydrazines and anilines. All the reactions were performedwithout any external additives or co-oxidants. The most imperative feature of the synthesis can be the ease of SeO_2 to promote dinitrogen extrusion in hydrazines and C-H activation in anilines.In addition, these strategies were successfully applied for the gram scale synthesis of different selenides.

2. Results and discussion

We initiated our investigation by evaluating the selenation reaction of phenylhydrazine**1a** (1 mmol) with SeO_2 (0.5 mmol) in MeCN in which the desired product **2a** was obtained in 39% yield (Table 1, entry 1). The temperature of the reaction and concentration of SeO_2 appeared to play an important role, therefore, different optimization reactions were performed as summarized in Table 1 (entry 2-11). Good yields of the desired product **2a** was observed when 1.5 mmol of SeO_2 was treated with phenylhydrazine**1a** (1 mmol) at 60°C in MeCN(entry 5).

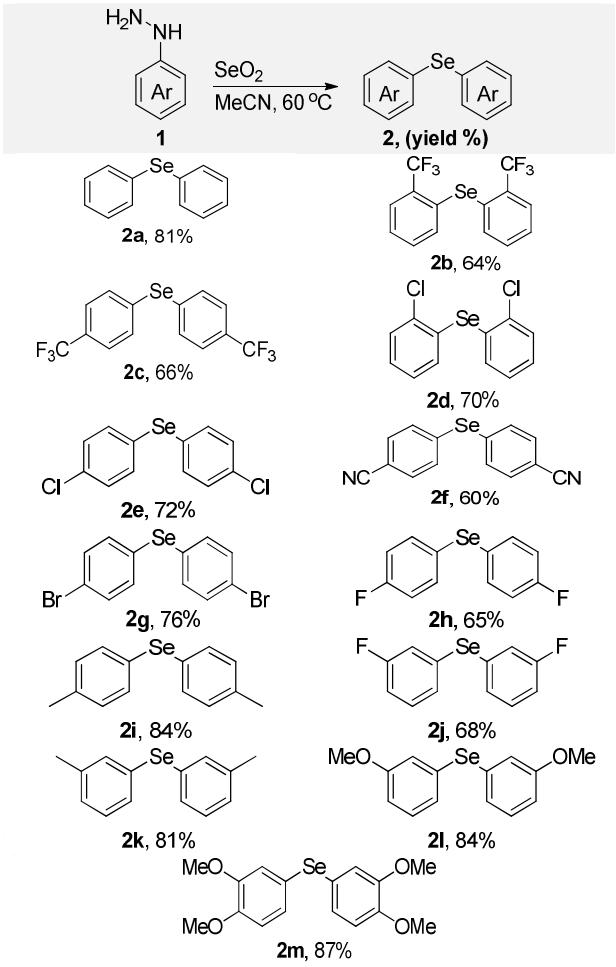
Table 1. Optimization of the reaction conditions.[a]



1a **2a**

entry	SeO_2 (mmol)	temp (°C)	solvent	yield[b](%)
1	0.5	rt	MeCN	39
2	1.0	rt	MeCN	44
3	1.5	rt	MeCN	57
4	1.5	45	MeCN	69
5	**1.5**	**60**	**MeCN**	**81**
6	1.5	60	DCM	72
7	1.5	60	Toluene	62
8	1.5	60	MeOH	69
9	1.5	60	DMSO	71
10	1.5	80	DMSO	71
11	1.5	100	DMSO	71

[a]Phenylhydrazine**1a** (1 mmol), SeO_2 (1.5 mmol) in MeCN at 60°C for 1h.[b]Isolated yields.



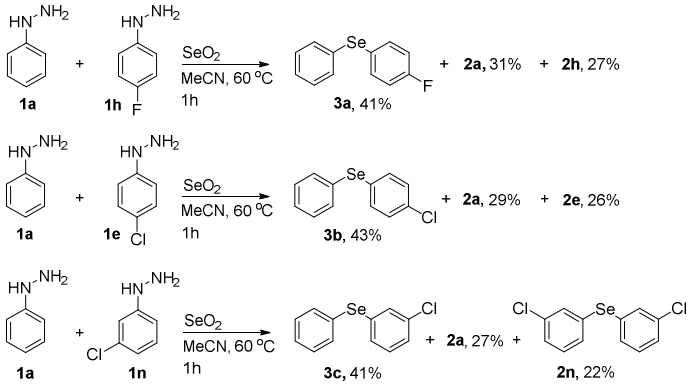
Reaction conditions: Phenylhydrazines**1**(1 mmol), and SeO_2 (1.5 mmol) in 5 mL of MeCNat 60°C for 1h.

Scheme1.Scope of dinitrogen extrusion assisted selenationreaction.

The same reaction when tried with different solvents generated the desired product in lower yields (entries 6-11). Increased temperature in DMSO does not improve much yield of the desired product (entries 10-11).

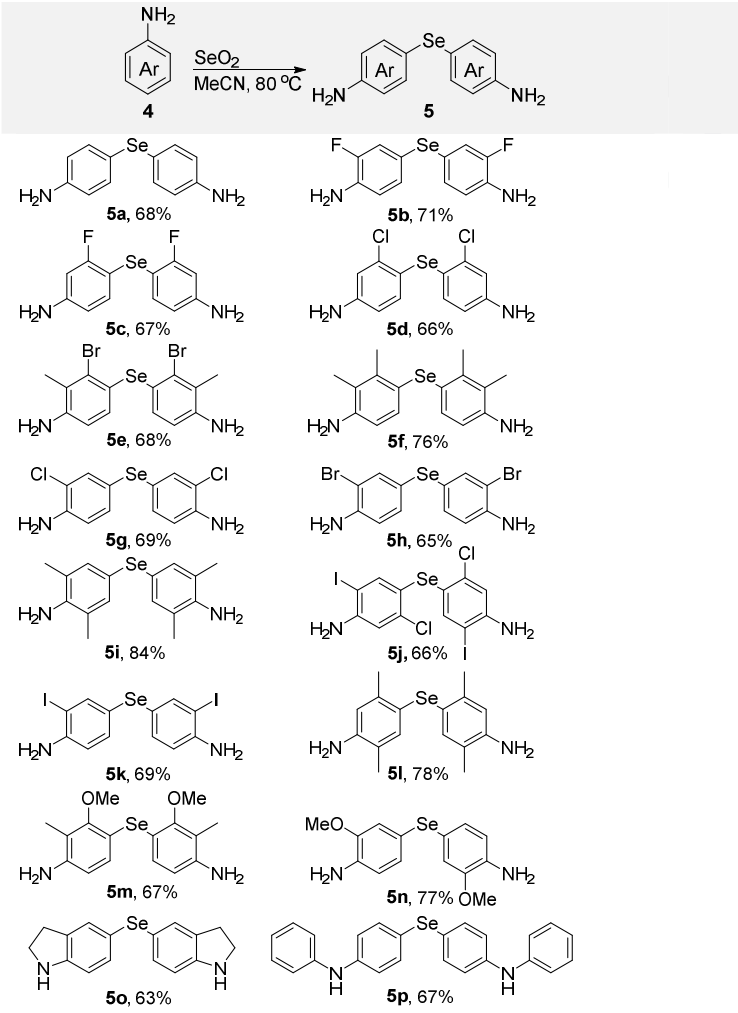
Having identified optimized reaction conditions, various reactions with divergent substrates and substituents were tested (Scheme 1). The scope of SeO_2 promoted dinitrogen extrusion reactions with different hydrazines**1** were demonstrated as listed in Scheme 1. Yields were generally good for all the substrates being tested. However, it was observed that the electronic environment of phenyl ring in hydrazines affected the yields of products to some extent. On the basis of our results, we observed that the substrates bearing electron withdrawing groups like -CF_3, -CN, -F (**2b**, **2c**, **2f**and **2j**) afforded slightly lower yields in comparison to unsubstituted substrates (**2a**) and those containing electron donatinggroups like-Cl, -Br, -CH_3 and OMe(**2d, 2e, 2g**, **2i, 2k, 2l** and **2m**).This observation can be attributed to more migratory aptitude of aromatic rings that bear electron donating groups in intermediate **C** (Scheme 6) as compared to electron withdrawing groups. The hetero-coupling efficiency was also demonstrated by reaction of different hydrazines as depicted in Scheme 2.Interestingly, in all experiments the cross coupledproducts (**3a**-**3c**) were isolated in good yields in comparison to the self coupled products. The hetero-coupling reactions presented in Scheme 2clearly highlights the merit of current reactions to generate unsymmetrical products in predominant yields. These reactions also show the benefit of using SeO_2 as selenating reagent.

Next, we extended the application of our concept by treating anilines **4** (1 mmol) with SeO_2 (1.5 mmol) in MeCN at 80°C (for detailed



Scheme 2. Dinitrogen extrusion assisted hetero-couplingselenation

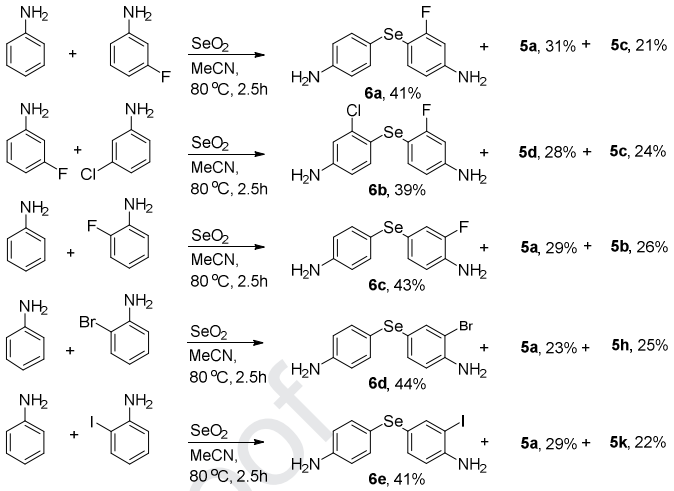
optimization see Supporting information). To our surprise we got *para-para* Se inserted dianiline in major and *ortho-para* in minor concentration. Different substituted anilines were tested and it was found that substitution does not affect much on the yields of the desired products (Scheme 3). However, the reactions with anilines having electron donating group(s) at *meta* positionincrease the ortho product slightly than unsubstituted and electron withdrawing groups at *meta* position. With hydrogen atom at para position like aniline, 2-F, 3-F, 3-Cl, 3-Br-2-Me, 2,3-diMe, 2,6-diMe, 2,5-diMe, 2-Cl, 2I, 2-Cl-5-I,2-OMe,2-Me-3-OMethe para coupledselenatedproduct was predominantlyobtained.



Reaction conditions[a]: Anilines **4** (1 mmol), and SeO_2 (1.5 mmol) in 5 mL of MeCN at 80°C for 3h.

Scheme 3. Scope of amine directed selenationreaction.[a]

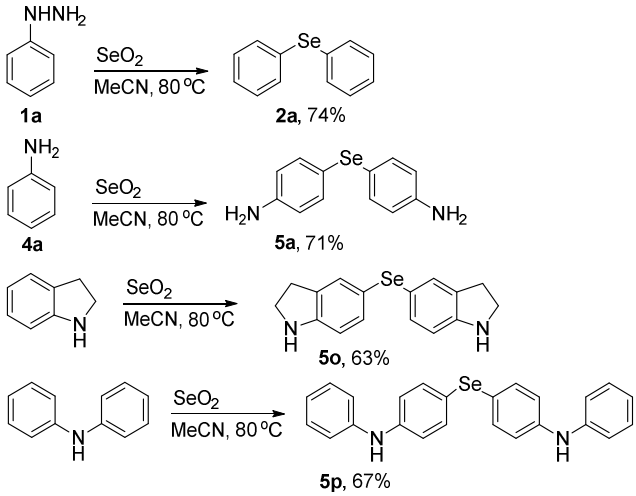
5a-**5n** in good yields, due to strong ortho, para nature of aniline. However, as expected in all these reactions, we didn't isolated any *ortho-ortho* coupled products due to steric and electronic reasons. In addition, our reactionworked well withindoline



Scheme 4. Amine directed hetero-couplingselenation

and diphenylamine (**5o**and**5p**). In continuation, many differentreactions were performed with different anilines **4** as per the optimizedconditionsand cross coupled products**6a**-**6e**were obtainedin appreciable yields (Scheme 4). However, in all the cases, self coupled products were also isolated in minor quantities.

Further, these strategies were successfully applied for the gram scale synthesis of different selenides **2a**, **5a**, **5o** and **5p** in good yields (Scheme 5).



Scheme 5. Gram scale synthesis of selenides.

Most likely, these reactions occur by the interaction of the SeO_2 in two different pathways as outlined in Scheme 6. In the preceding reaction with hydrazines, we presume that the reaction of hydrazines withSeO_2initially generates intermediate **A** that undergoes dehydration to form **B.**Addition of second mole of hydrazine to **B**again undergoes dehydration to form intermediate **C**. Intermediate **C**on 1,3-sigmatropic rearrangement followed by dinitrogen extrusion leads to the generation of **2**.Further, in case of anilines,SeO_2 first undergoes a disproportionation processto afforddianilinetriselenides as per theWilshire'sassumption.[8]However;there exist possibilities ofthree different triselinides out of which the *para-para* isformed in major quantity followed by *ortho-para*triselenation.Sincewe failed to isolate

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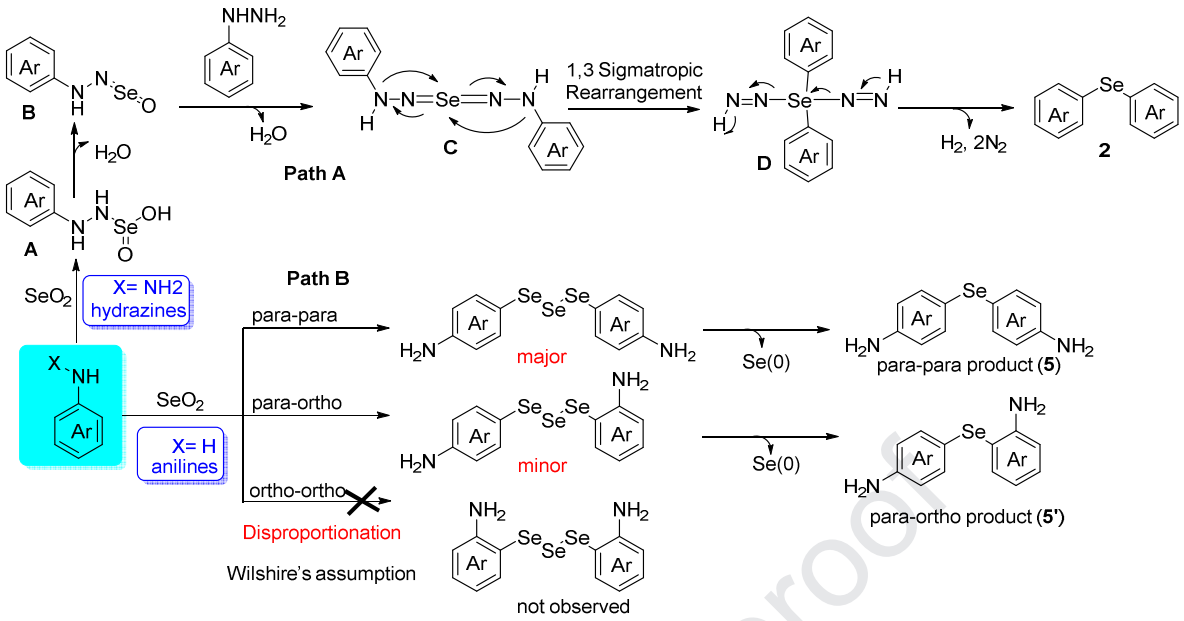
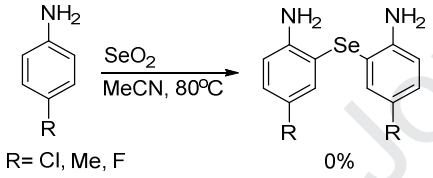


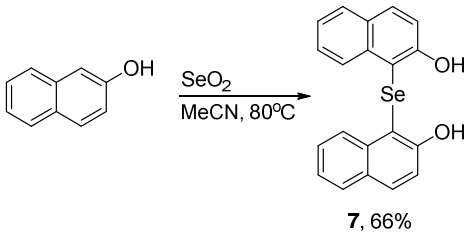
Scheme 6. Possible Reaction Pathway

the *ortho-ortho* coupled product,therefore, the thirdcoupling possibility is ignored. However, the *para-para*and *ortho-para* intermediates later on decompose to liberate metallicSe(0) leaving behind dianiline selenides **5**.[9] In case of different anilinestested (Scheme 4),we failed to isolate the *ortho-ortho* coupled product and thereby few reactionswereconducted with *para* substituted anilines.As expected, all thesereactions failed to produce the selenated products (Scheme 7).



Scheme 7. Control Experiment.

Since, *β*-napthol is a good C-nucleophile, we premeditated to accomplish selenation reaction under optimized conditions for the synthesis of **7** in good yield (Scheme 8).



Scheme 8.Selenation of β-Napthol.

3. Conclusion

To conclude, an efficient, economical, metal free coupling and direct selenation methods for the conversion of hydrazines/anilines to selenides were developed. These procedures avoid handlingand isolationof expensive reagents and protecting groups. Both the methodologies tolerate a broad range of functionalities. This protocol can also be employed for the synthesis of hetero-coupling reactions. In addition, the methodologywas successfully applied for the gram scale synthesis of selinides and selenation of β-Napthol. Furthermore, applications across different C-nucleophiles are in progress.

4. Experimental Section.

1. General information

All chemicals were obtained from Sigma-Aldrich, Alfa Aesar and S. D. Fine chemicals and used as received.The progress of the reactions was monitored by thin-layer chromatography (TLC) on precoated silica-gel plates using Merck Silica Gel 60 F254, Cat. No. 1.05554.0007 and visualized by short-wave ultraviolet light as well as by treatment with I_2. Column chromatography was performed by hand using silica-gel (100–200 mesh, Silicycle).^{1}H and ^{13}C NMR spectra were recorded on Brucker-Avance DPX FT-NMR 500 and 400 MHz instruments. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent (CDCl3: 7.26 ppm). Carbon nuclear magnetic resonance spectra (^{13}C NMR solvent $CDCl_3$:77.0ppm) were recorded at 125 MHz or 100 MHz: chemical data for carbons are reported in parts per million (ppm, δ scale) down field from tetramethylsilane and are referenced to the carbon resonance of the solvent. ESI-MS and HRMS spectra were recorded on Agilent 1100 LC-Q-TOF and HRMS-6540-UHD machines respectively.

General procedure for the synthesis of 2a-2m:Phenylhydrazine (1 mmol), selenium dioxide (1.5mmol) was taken in 5mL of acetonitrile and stirred at 60°C for 1h. Desired product was observed on TLC after 1 h. However, after column purification on silica gel (100-200 #) using hexane as an eluent afforded the corresponding product 2a-2m in good yield (60-87 %).

General procedure for the synthesis of 3a-3c: Phenylhydrazine (1mmol) substituted phenylhydrazine (1 mmol) and selenium dioxide (1.5 mmol) were taken in 5mL of acetonitrile and stirred at 60 °C for 1h. Desired product was observed on TLC after 1 h. However, after column purification on silica gel (100-200 #) using hexane as an eluent afforded the corresponding product 3a-3c in good yield (47-52%).

General procedure for the synthesis of 5a-5p: A reaction vessel was charged with aniline (1 mmol), selenium dioxide (1.5 mmol) in 5 mL of acetonitrile solvent. The reaction mixture was stirred at 80 °C for 2.5 h. After completion of the reaction, confirmed by thin layer

chromatography, the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (7:3) as an eluent. It afforded the corresponding product 5a-5p in good yields (62-86 %).

General procedure for the synthesis of 6a-6e: A reaction vessel was charged with aniline (1 mmol), substituted aniline (1mmol) and selenium dioxide (1.5 mmol) in 5 mL of acetonitrile solvent. The reaction mixture was stirred at 80 ^{o}C for 2.5h. After completion of the reaction, confirmed by thin layer chromatography, the solvent was removed under reduced pressure. The crude mixture was purified by column chromatography on silica gel (100-200#) using hexane and ethyl acetate (7:3) as an eluent. It afforded the corresponding product 6a-6e in good yields (43-51 %).

5. Spectral Data

2a.Diphenylselane

Yellow liquid (174.75 mg, 81% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dd, J = 6.1, 2.6 Hz, 4H), 7.43 – 7.39 (m, 4H). ^{13}C NMR (100 MHz, CDCl3) δ 133.23, 131.44, 129.61, 127.58.HRMS(TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{11}Se$ 235.0020 found 235.0016. IR ($CHCl_3$ cm^{-1}) *v*; 3070, 3056, 3016, 2997, 2922, 2850, 1650, 1575.

2b.Bis(2-(trifluoromethyl)phenyl)selane

Yellow solid (134.18 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 4H), 7.43 – 7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.62 (q), 132.52 (s), 131.83 (d, *J* = 24.0 Hz), 130.05 (s), 127.78 (s), 126.94 (m, *J* = 5.0 Hz), 123.73 (d, *J* = 218.0 HzHRMS (TOF) m/z [M + H]$^{+}$ Calcd for $C_{14}H_9F_6Se$ 370.9768 found 370.9772. IR ($CHCl_3$ cm^{-1}) *v*; 3200, 2952, 2918,2846,1695, 1659, 1642,1612, 1554, 1257, 1217.

2c.Bis(4-(trifluoromethyl)phenyl)selane

Yellow solid (138.37 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.47 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.15 (q), 133.07 (s), 129.98 (m, *J* = 26.0 Hz), 126.33 (d, *J* = 3.4 Hz), 123.92 (d, *J* = 217.0 Hz).HRMS(TOF) m/z [M + H]$^{+}$Calcd for $C_{14}H_9F_6Se$ 370.9768 found 370.9770. IR($CHCl_3$ cm^{-1}) *v*; 2956, 2923, 2849,1695, 1658,1652, 1641, 1261, 1216.

2d.Bis(2-chlorophenyl)selane

Yellow solid (148.38 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 2H), 7.29 – 7.23 (m, 4H), 7.19 – 7.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.46, 134.22, 130.35, 129.89, 129.12, 127.63.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9Cl_2Se$ 302.9241 found 302.9237. IR ($CHCl_3$ cm^{-1}) *v*; 2922, 2851, 2822, 1695, 1642, 1612, 1516, 893, 801.

2e.Bis(4-chlorophenyl)selane

Yellow solid (152.61 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.60, 132.60, 132.35, 129.43.HRMS(TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9Cl_2Se$ 302.9241 found 302.9249. IR ($CHCl_3$ cm^{-1}) *v*; 2918, 2955, 2847, 1620, 1554, 1533,1516, 893, 866.

2f.4,4'-Selenodibenzonitrile

Yellow solid (127.66 mg, 60% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.61 – 7.51 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.28, 132.99, 132.75, 130.63, 118.25.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{14}H_9N_2Se$ 284.9925 found 284.9930. IR ($CHCl_3$ cm^{-1}) *v*; 3080, 3030, 2958, 2852, 2227, 1696, 1653, 1584, 1553, 1481.

2g.Bis(4-bromophenyl)selane

Yellow solid (159.80 mg, 76% yield); ^{l}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.20 (m, 8H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.60, 132.60, 132.35, 129.43.HRMS(TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9Br_2Se$ 390.8231 found 390.8235. IR ($CHCl_3$ cm^{-1}) *v*; 3070, 2919, 2959, 2847, 1684, 1534, 1516, 1512, 727, 707.

2h.Bis(4-fluorophenyl)selane

Yellow solid (138.76 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.50 (m, 2H), 7.48 – 7.44 (m, 2H), 7.04 – 6.97 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.01 (d, *J* = 48.0 Hz), 161.55 (d, *J* = 47.6 Hz), 134.92 (dd, *J* = 15.2, 8.0 Hz), 116.49 (t, *J* = 21.0 Hz).HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9F_2Se$ 270.9832 found 270.9840. IR ($CHCl_3$ cm^{-1}) *v*;2995, 2961, 2934, 2875, 1695, 1684, 1653, 1616, 1261, 1218.

,2i.Di-p-tolylselane

Yellow solid (180.39 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.3 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 4H), 2.32 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.03, 132.35, 130.10, 129.94, 29.73.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{14}H_{15}Se$ 263.0333 found 263.0336. IR ($CHCl_3$ cm^{-1}) *v*; 2919, 2951, 2849, 1623, 1613, 1595, 1568.

2j.Dis(3-fluorophenyl)selane

Yellow solid (145.49 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.9 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.31 – 7.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.75 (s), 161.76 (s), 131.24 (s), 129.93 (d, *J* = 5.0 Hz), 121.66 (d, *J* = 15.0 Hz), 119.97 (d, *J* = 16 Hz).HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9F_2Se$ 270.9832 found 270.9830. IR ($CHCl_3$ cm^{-1}) *v*;3065, 2961, 2923, 2849, 1700, 1611, 1580, 1523, 1262, 1197.

2k.Di-m-tolylselane

Yellow solid (173.28 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 4H), 7.36 (d, *J* = 5.7 Hz, 4H), 2.42 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.39, 135.26, 131.92, 131.84, 127.89, 21.2.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{14}H_{15}Se$ 263.0333 found 263.0337. IR ($CHCl_3$ cm^{-1}) *v*; 2919, 2951, 2849, 1623, 1613, 1595, 1568, 270, 261.

2l.Bis(3-methoxyphenyl)selane

Yellow solid (178.95 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 4.9 Hz, 4H), 7.34 (d, *J* = 2.1 Hz, 2H), 7.10 – 7.04 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.14, 129.19, 127.02, 119.48, 116.94, 54.89.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{14}H_{15}O_2Se$ 295.0232found 295.0233. IR ($CHCl_3$ cm^{-1}) *v*; 3070, 3056, 3016, 2997, 2922, 2850, 1650, 1575, 1095, 1055.

2m.Bis(3,4-dimethoxyphenyl)selane

Yellow solid (183.32 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.35 (s, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 6H), 3.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.67, 148.47, 128.92, 116.84, 110.55, 55.87, 55.82.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{16}H_{19}O_4Se$ 355.0443 found 355.0449. IR ($CHCl_3$ cm^{-1}) *v*; 3030, 3016, 3005, 2997, 2930, 2850, 1650, 1520, 1095, 1055. 1025.

3a. (4-Fluorophenyl)(phenyl)selane

Yellow solid (95.66 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 6.5, 3.0 Hz, 3H), 7.45 – 7.41 (m, 1H), 7.31 – 7.27 (m, 4H), 7.03 – 6.98 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.76 (d, *J* = 6.0Hz), 134.99 (d, *J* = 7.8 Hz), 132.97 (s), 132.22 (s), 131.15 (s), 129.38 (s), 127.31 (d, *J* = 13.0 Hz), 116.71 (d, *J* = 2.1 Hz).HRMS (TOF) m/z [M + H]$^{+}$Calcd for$C_{12}H_{10}FSe$ 252.9926 found 252.9930. IR ($CHCl_3$ cm^{-1}) *v*; 3146, 3058, 3016, 2998, 2959, 2923, 2852, 1635, 1581, 1485, 1476, 1437, 1291, 1180, 1261.

3b. (4-Chlorophenyl)(phenyl)selane

Yellow solid (106.70 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20 – 7.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.79, 134.96, 133.01, 132.22, 131.15, 129.40, 127.33, 116.64.HRMS(TOF) m/z [M + H]$^{+}$Calcd for$C_{12}H_{10}ClSe$ 268.9631 found 268.9637. IR ($CHCl_3$ cm^{-1}) *v*; 3063, 2952, 2919, 2849, 1662, 1652, 1640,1635, 1623, 1616, 771, 733.

3c. (3-Chlorophenyl)(phenyl)selane

Yellow solid (101.74mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.24 – 7.21 (m, 2H), 7.20 – 7.15 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.79, 134.96, 133.01, 132.22, 131.15, 129.40, 127.33, 116.64. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{10}ClSe$ 268.9631 found 268.9637. IR ($CHCl_3$ cm^{-1})

v; 3063, 2952, 2919, 2849, 1662, 1652, 1640, 1635, 1623, 1616, 771, 733.

5a. 4,4'-Selenodianiline.

Black solid (193.77 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H), 6.63 – 6.58 (m, 4H), 3.49 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.75, 135.10, 119.34, 116.04. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{13}N_2Se$ 265.0238 found 265.0247.IR ($CHCl_3$ cm^{-1}) *v* ; 3451, 3339, 3021, 2970, 2955, 2928, 1684, 1675, 1669, 1623, 1550, 1533

5b. 4, 4'-Selenobis (2-fluoroaniline)

Black solid (192.93 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.00 (m, 2H), 6.81 – 6.61 (m, 4H), 3.65 (s, 4H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.78 (d, *J* = 240 .3 Hz), 148.73 (d, *J* = 10.7 Hz), 136.57 (d, *J* = 7.7 Hz), 111.67 (d, *J* = 2.0 Hz), 104.12 (d, *J* = 23.4 Hz), 102.24 (d, *J* = 27.3 Hz). HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{11}F_2N_2Se$ 301.0056 found 301.0051.IR ($CHCl_3$ cm^{-1}) *v*; 3355, 2918, 2847, 1695, 1659, 1642, 1554, 1534, 1516, 1489, 1279, 1175.

5c.4,4'-Selenobis(3-fluoroaniline)

Black solid (181.68 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d *J* = 8.0 Hz, 2H), 6.30 (m, *J* = 10.6, 9.2, 2.2 Hz, 4H), 3.70 (s, 4H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.78 (d, *J* = 240 .3 Hz), 148.73 (d, *J* = 10.7 Hz), 136.57 (d, *J* = 7.7 Hz), 111.67 (d, *J* = 2.0 Hz), 104.12 (d, *J* = 23.4 Hz), 102.24 (d, *J* = 27.3 Hz). HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{11}F_2N_2Se$ 301.0056 found 301.0054.IR ($CHCl_3$ cm^{-1}) *v*; 3373, 2922, 2847, 1622, 1603, 1487, 1466, 1318, 1236

5d. 4,4'-Selenobis(3-chloroaniline)

Black solid (173.02 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 2.4 Hz, 2H), 6.49 (dd, *J* = 8.4, 2.5 Hz, 2H), 3.76 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.35, 137.45, 135.27, 117.96, 115.96, 114.29. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{11}Cl_2N_2Se$ 332.9465 found 332.9469.IR ($CHCl_3$ cm^{-1}) *v*; 3469, 3375, 3192, 3048, 3019, 2957, 2924, 2852, 1613, 1583, 1481, 845, 755.

5e. 4,4'-Selenobis(3-bromo-2-methylaniline)

Black solid (164.67 mg, 68% yield); ^{1}H NMR (400 MHz, MeOD) δ 6.72 (d, *J* = 8.3 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 3.21 (s, 4H), 2.21 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 150.08, 135.42, 133.60, 127.04, 125.57, 118.63, 21.22. HRMS (TOF) m/z [M +H]$^{+}$Calcd for $C_{14}H_{15}Br_2N_2Se$ 448.8767 found 448.8774.IR ($CHCl_3$ cm^{-1}) *v*; 3375, 2922, 2851, 1695, 1659, 1621, 1555, 1486, 1461, 1379, 769, 669.

5f. 4,4'-Selenobis(2,3-dimethylaniline)

Black solid (201.67 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.2 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 2H), 3.62 (s, 4H), 2.47 – 2.38 (s, 6H), 2.19 – 2.12 (s, 6H)..^{13}C NMR (100 MHz, $CDCl_3$) δ 144.12, 138.62, 131.53, 121.84, 121.35, 113.91, 19.43, 13.79.HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{16}H_{21}N_2Se$ 321.0864 found 321.0867.IR ($CHCl_3$ cm^{-1}) *v*; 3373, 3229, 2960, 2921, 2859, 1653, 1617, 1576, 1505, 1464, 1415.

5g. 4,4'-Selenobis(2-chloroaniline

Black solid (180.24 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, *J* = 1.6 Hz, 2H), 7.11 (dd, *J* = 8.2, 1.7 Hz, 2H), 6.58 (d, *J* = 8.3 Hz, 2H), 3.94 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.62, 134.15, 133.09, 119.62, 119.35, 116.48. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_{11}Cl_2N_2Se$ 332.9465 found 332.9468.IR ($CHCl_3$ cm^{-1}) *v*; 3461, 3371, 3219, 3054, 2971, 2925, 1620, 1588, 1556, 1470, 1412, 812, 757.

5h. 4,4'-Selenobis(2-bromoaniline)

Black solid (159.13 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (s, *J* = 0.9 Hz, 2H), 7.22 (dd, *J* = 8.3, 0.9 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 4.11 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.80, 137.30, 133.81, 119.74, 116.41, 109.58. HRMS (TOF) m/z [M +H]$^{+}$Calcd for $C_{12}H_{11}Br_2N_2Se$ 420.8449 found 420.8446.IR($CHCl_3$ cm^{-1}) *v*; 3465, 3374, 3187, 3014, 3045, 2958, 2922, 2851, 1613, 1579, 1552, 1477, 756, 682

5i. 4,4'-Selenobis(2,6-dimethylaniline)

Black solid (222.87 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (s, 4H), 3.58 (s, 4H), 2.16 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.36, 133.34, 122.64, 118.91, 17.55. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{16}H_{21}N_2Se$ 321.0864 found 321.0859.IR ($CHCl_3$ cm^{-1}) *v*;3451, 3359, 3021, 2970, 2928, 2855, 1684, 1675, 1669, 1653, 1623, 1533, 1472.

5j. 4,4'-Selenobis(5-chloro-2-iodoaniline)

Black solid (152.40 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 2H), 6.86 (s, 2H), 4.40 – 4.01 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.03, 143.86, 138.18, 119.43, 114.98, 82.35. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{12}H_9Cl_2I_2N_2Se$ 584.7392 found 584.7382.IR($CHCl_3$ cm^{-1}) *v*; 3365, 2920, 2847, 1695, 1659, 1642, 1612, 1565, 1554, 1533, 1453, 839, 770, 665, 502.

5k. 4,4'-Selenobis(2-iodoaniline)

Black solid (151.50 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, *J* = 1.6 Hz, 2H), 7.20 – 7.09 (m, 2H), 6.57 (d, *J* = 8.3 Hz, 2H), 4.19 – 3.35 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.28, 142.58, 134.76, 120.20, 115.09, 84.21. HRMS (TOF) m/z [M +H]$^{+}$Calcd for $C_{12}H_{11}I_2N_2Se$ 516.0029 found 516.0033.IR($CHCl_3$ cm^{-1}) *v*; 3362, 2955, 2923, 2851, 1695, 1665, 1659, 1642, 1573, 1554, 1539, 1471, 666, 523.

5l. 4,4'-Selenobis(2,5-dimethylaniline)

Brown black solid (206.97 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 2H), 6.50 (s, 2H), 3.44 (s, 4H), 2.22 (s, 6H), 1.98 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.05, 138.61, 135.54, 120.96, 119.65, 116.82, 21.97, 16.80. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{16}H_{21}N_2Se$ 321.0864 found 321.0860.IR ($CHCl_3$ cm^{-1}) *v*; 3372, 30006, 2956, 2858, 1621, 1565, 1489, 1457, 1395, 1371, 1291.

5m. 4,4'-Selenobis(3-methoxy-2-methylaniline)

Brown black solid (172.63 mg, 67% yield); ^{1}HNMR (400 MHz, $CDCl_3$) δ 6.64 (dd, *J* = 27.5, 10.0 Hz, 4H), 4.80 (s, 4H), 4.01 (s, 3H), 2.49 (s, 3H), 1.90 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.48, 139.05, 132.12, 119.75, 110.56, 60.43, 29.57, 12.98, 8.43. HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{16}H_{21}N_2Se$ 353.0763 found 353.0761. IR ($CHCl_3$ cm^{-1}) *v*; 3372, 30006, 2956, 2858, 1621, 1565, 1489, 1457, 1395, 1371, 1291.

5n. 4,4'-Selenobis(2-methoxyaniline)

Brown black solid (203.45 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.02 (m, 1H), 6.97 (d, *J* = 6.5 Hz, 3H), 6.64 (dd, *J* = 12.2, 8.1 Hz, 2H), 3.92 (s, 4H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.40, 146.89, 137.15, 135.60, 128.26, 127.69, 126.28, 119.22, 117.05, 115.57, 115.39, 114.60, 55.27.HRMS(TOF) m/z [M + H]$^{+}$ Calcd for $C_{16}H_{21}N_2Se$ 325.0450 found 325.0447. IR ($CHCl_3$ cm^{-1}) *v*; 3372, 30006, 2956, 2858, 1621, 1565, 1489, 1457, 1395, 1371, 1291

5o. 5-Di(indolin-5-yl)selane

Black solid 167.72 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 3H), 7.11 (d, *J* = 8.0 Hz, 3H), 6.46 (d, *J* = 8.0 Hz, 2H), 3.47 (t, *J* = 8.4 Hz, 4H), 2.91 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.87, 132.50, 131.09, 129.59, 120.05, 110.21, 47.24, 29.97. HRMS (TOF) m/z [M + H]$^{+}$Calcd for$C_{16}H_{17}N_2Se$ 317.0551 found 317.055IR ($CHCl_3$ cm^{-1}) *v*; 3379, 2923, 2849, 1695, 1659, 1642, 1599, 1485, 1469, 1454, 1434, 1416, 1317, 1277.

5p. 4,4'-Selenobis(N-phenylaniline)

Black solid (165.27 mg, 67% yield); ^{1}H NMR (400 MHz, CDCl3) δ 7.41 (d, J = 8.6 Hz, 4H), 7.29 (dd, J = 13.0, 5.3 Hz, 4H), 7.09 (d, J = 7.8 Hz, 4H), 6.98 (t, J = 7.0 Hz, 6H), 5.73 (s, 2H).^{13}C NMR (100 MHz, CDCl3) δ 142.75 , 142.45 , 134.45 , 129.45 , 121.97 , 121.57 , 118.38 , 118.17 .HRMS (TOF) m/z [M + H]$^{+}$Calcd for $C_{24}H_{21}N_2Se$ 417.0864 found 417.0874.IR ($CHCl_3$ cm^{-1}) v; 3393, 3052, 3025, 2960, 2921, 1585, 1503, 1486, 1441, 1390.

6a. 4,4'-Aminophenyl)selanyl)-3-fluoroaniline

Black solid (124.76 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 23.2, 7.8 Hz, 2H), 6.61 (d, *J* = 7.8 Hz,

1H), 6.45 – 6.32 (m, 2H), 3.73 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.73 (s), 145.52 (s), 139.12 (s), 136.98 (s), 132.82 (d, *J* = 56.4 Hz), 130.42 (s), 129.98 (s), 118.82 (s), 116.26 (s), 115.03 (d, *J* = 5.0 Hz), 105.73 (d, *J* = 21.9 Hz), 101.49 (d, *J* = 28.0Hz).HRMS (TOF) m/z [M + H]$^+$Calcd for $C_{12}H_{12}FN_2Se$ 283.0144 found 283.0143.IR ($CHCl_3$ cm^{-1}) *v*; 3360, 3213, 2955, 2921, 2850, 1695, 1680, 1658, 1612, 1554, 1516, 1443, 1433, 1281, 1165.

6b.44' -Amino-2-chlorophenyl)selanyl)-3-fluoroaniline

Black solid (111.02 mg, 39% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.42 (s, 1H), 6.92 (d, *J* = 16.0, 8.0 Hz, 1H), 6.41 – 6.22 (m, 4H), 3.93 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.83 – 163.62 (m), 163.35 – 163.26 (m), 161.83 – 161.77 (m), 161.41 – 161.34 (m), 136.58 (d, *J* = 3.0 Hz), 135.92 (d, *J* = 3.0 Hz), 135.31 (s), 134.57 (s), 115.96 (s), 111.66 (s), 104.23 – 103.99 (m), 102.24 (d, *J* = 22.0 Hz). HRMS (TOF) m/z [M + H]$^+$Calcd for $C_{12}H_{11}ClFN_2Se$ 316.9755 found 316.9761.IR ($CHCl_3$ cm^{-1}) *v*; 3373, 3219, 2955, 2921, 2851, 1695, 1687, 1622, 1602, 1487, 1469, 1437, 1314, 1235, 1044, 958, 840.

6c. 4-4'-Aminophenyl)selanyl)-2-fluoroaniline

Black solid (130.8561 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.16 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 2H), 4.35 (s, 2H), 3.69 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 147.77 (s), 145.77 (s), 136.98 (s), 133.18 (s), 130.02 (s), 118.82 (s), 118.29 – 115.19 (d), 116.17 (s), 114.99 (s).HRMS (TOF) m/z [M + H]$^+$Calcd for $C_{12}H_{12}FN_2Se$ 283.0144 found 283.0140. IR ($CHCl_3$ cm^{-1}) *v*; 3360, 3213, 2955, 2921, 2850, 1695, 1680, 1658, 1612, 1554, 1516, 1443, 1433, 1281, 1165.

6d. 44'-Aminophenyl)selanyl)-2-bromoaniline

Black solid (161.80 mg, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 16.0, 8.3 Hz, 2H), 7.11 (dt, *J* = 21.8, 8.0 Hz, 1H), 6.54 (d, *J* = 8.1 Hz, 2H), 6.37 – 6.27 (m, 2H), 3.72 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.69, 145.75, 137.01, 136.44, 135.15, 133.06, 129.98, 118.69, 116.26, 114.88 HRMS (TOF) m/z [M + H]$^+$Calcd for $C_{12}H_{12}FN_2Se$ 342.9344 found 342.9347. IR ($CHCl_3$ cm^{-1}) *v*; 3360, 3213, 2955, 2921, 2850, 1695, 1680, 1658, 1612, 1554, 1516, 1443, 1433, 1281, 1165.

6e.44'-Amino-2-fluorophenyl)selanyl)-2-iodoaniline

Black solid (150.70 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 6.53 – 6.33 (m, 4H), 4.32 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.83 – 163.62 (m), 163.35 – 163.26 (m), 161.83 – 161.77 (m), 161.41 – 161.34 (m), 136.58 (d, *J* = 3.0 Hz), 135.92 (d, *J* = 3.0 Hz), 135.31 (s), 134.57 (s), 115.96 (s), 111.66 (s), 104.23 – 103.99 (m), 102.24 (d, *J* = 22.0 Hz).HRMS (TOF) m/z [M + H]$^+$Calcd for $C_{12}H_{12}FN_2Se$ 408.9111 found 408.9110 IR ($CHCl_3$ cm^{-1}) *v*; 3360, 3213, 2955, 2921, 2850, 1695, 1680, 1658, 1612, 1554, 1516, 1443, 1433, 1281, 1165

7. 1,1'-Selenobis(naphthalen-2-ol)

Brown solid (167.29mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.90 (d, *J* = 6.9 Hz, 2H), 7.36 (dd, *J* = 25.9, 6.7 Hz, 6H), 7.17 (d, *J* = 6.8 Hz, 2H), 5.08 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.78, 134.43, 129.17, 128.94, 127.71, 125.82, 124.42, 122.33, 117.89, 114.63. HRMS (TOF) m/z [M - H]$^+$Calcd for $C_{20}H_{13}O_2Se$ 365.0086 found 365.0077.IR($CHCl_3$ cm^{-1}) *v*; 3487, 3058, 3013, 2956; 2923, 2853, 1695, 1658, 1642, 1619, 1596, 1554, 1515, 1462, 1433, 1383.

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The present work highlights the following important findings:

1. A novel, efficient, economical strategy for the direct selenation of arylamines and hydrazines to selenides using SeO_2 was successfully developed.
2. Our reaction revealed a good functional group tolerance and proceeded well with variation in the electronic nature of Anilines and Phenylhydrazines.
3. This reagent is compatible with hydrazines and helps to promotes unusual dinitrogen extrusion assisted selenation reaction in good yields**.**
4. The application of our work is the gram scale synthesis and extension to *β*-napthol.
5. Mechanistically, first SeO_2 undergoes a disproportionation process to afford dianilinetriselenides as per Wilshire's assumption. However, there exist three different possibilities of trisilinides out of which the *para-para* is formed in maximum quantity followed by *para-ortho* triselenation.
6. Application of this approach towards Selenation of *β*-Napthol
7. Further studies related to the application of this system against different C-nucleophiles is in progress