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ARTICLE

DMSO/Iodine-Catalyzed Oxidative C–Se/C–S Bond Formation: A Regioselective Synthesis of Unsymmetrical Chalcogenides with Nitrogen- or Oxygen-containing Arenes

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A convenient metal-free and solvent-free iodine-catalyzed regioselective greener protocol to access different types of unsymmetrical chalcogenides with nitrogen- or oxygen-containing arenes, through oxidative C–Se/C–S formation *via* direct C(sp^2)–H bond activation was developed. The products were obtained in good to excellent yields using [O or N]-containing arenes, half equiv. of various odorless diorganyl dichalcogenides (S/Se), iodine (20 mol%) as the catalyst and 3 equiv. of DMSO as the oxidant, applying MW irradiation for 10 min.

Introduction

In recent years, reactions under metal-free and solvent-free conditions have been widely used in the functionalization of the C-H bond,[1,2] which is considered an important contribution to the development and progress of green chemistry.[3] Additionally, the use of microwave (MW) irradiation may open new horizons in the field of modern sustainable organic synthesis,[4] since it significantly reduces the reaction time and saves energy.[5]

The biological and medicinal properties of organochalcogenides (S, Se) are becoming increasingly appreciated,[6] mainly the antioxidant, antitumor, anti-inflammatory and antiviral activity.[7] Moreover, researchers in the area of modern organic synthesis[8,9] and catalysis[10] have been motivated by the potential applications of chalcogen compounds in this field.[6,9] Unsymmetrical organochalcogenides with nitrogen-or oxygen-containing arenes and their derivatives are a very important class of molecules, with different applications in biological sciences. [6,9,11] Aryl-sulfides containing these moieties are considered to be an important core structure in many important drugs.[6] However, studies on their counterpart in selenium compounds are limited.

In relation to preparing this class of compounds, particularly unsymmetrical diaryl chalcogenides containing OH and NH_2 functionalities,[12] few research articles are available on the oxidative C–Se/C–S bond formation through C(sp^2)–H bond activation of arenes.[12a-i] However, some of them suffer from limitations such as the use of non-greener solvents, pre-functionalized coupling partners, transition metal catalysts, stoichiometric or greater amounts of reagents, long reaction times, harsh reaction conditions with non-regioselective protocols and oxygen-free techniques.

Recently, the I_2/DMSO oxidative system has been successfully applied in different types of greener organic reactions.[13]

Considering the significance of unsymmetrical diorganyl chalcogenides, it would be advantageous and highly desirable to develop a regioselective, ligand-free and metal-free protocol in a solvent-free system for their preparation. In addition, this new protocol should operate with a shorter reaction time and be applicable to a broad range of selenylating and sulfenylating species.[14] To the best of our knowledge, no studies in which this attractive strategy was applied to the synthesis of diorganyl chalcogenides using arenes and diorganyl dichalcogenides have been reported.

As part of our wider research program aimed at designing and developing eco-friendly processes,[15,16] as well as the use of iodine/DMSO as a mild oxidizing agent, herein we report, for the first time, C–Se/C-S coupling by C(sp^2)–H bond activation, under MW irradiation (Scheme 1). A less extensive study using aryl thiols as sulfenylating agent, under conventional heating to produce diaryl sulfides appeared in press during the preparation of this manuscript.[17] Our new regioselective, broader, scalable and metal-free approach worked effectively using a stoichiometric amount of arenes or heteroarenes with diorganyl dichalcogenides as an odorless source of chalcogens.

Scheme 1

Results and discussion

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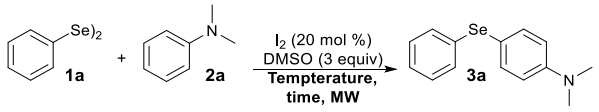
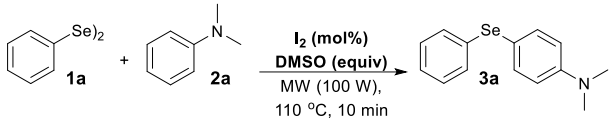
Table 1 Optimization of microwave parameters [a]



Entry	MW [W]	T [°C]	t [min]	Yield [%][b]
1	100	110	3	47
2	100	110	5	69
3	100	110	10	95
4	100	110	15	96
5	100	80	10	53
6	100	120	10	96
7	80	110	10	79
8	120	110	10	91
9 [c]	-	110	8h	65

[a] Reaction conditions: **1a** (0.125 mmol), **2a** (0.25 equiv.), I_2 (20 mol%), DMSO (3 equiv.) under MW irradiation. [b] Isolated yield. [c] Conventional heating in sealed tube .

Table 2 Optimization of reaction conditions [a]



Entry	I_2 [mol%]	Oxidant [equiv.]	Yield [%][b]
1	-	DMSO (3)	NR
2	5	DMSO (3)	45
3	10	DMSO (3)	87
4	20	DMSO (3)	95
5	30	DMSO (3)	96
6	20	-	32
7	20	DMSO (2)	75
8 [c]	20	DMSO	93
9	20	DTBP (3)	45
10	20	H_2O_2	81

[a] Reaction conditions: **1a** (0.125 mmol), **2a** (0.25 equiv.) in the presence of catalyst (20 mol%) and oxidant (3 equiv.) for 10 min at 110°C with 100 W of MW irradiation. [b] Isolated yields. [c] Reaction performed using 250μl DMSO

The initial screening and optimization of the reaction conditions were conducted with diphenyl diselenide **1a** and *N,N*-dimethylaniline **2a** as standard substrates, using a stoichiometric amount of oxidant and I_2 as a catalyst under microwave irradiation (Tables 1 and 2).

Firstly, the influence of the reaction time and microwave parameters on the performance of the direct C(sp^2)–H bond selenylation of **2a** was investigated (Tables 1). Initially, the reaction time was varied (entries 1-4). Carrying out the reaction for 3 min afforded the desired product **3a** in only 47% yield (entry 1). An increase in the reaction time to 10 min resulted in a significant improvement and product **3a** was accessed in 95% yield (entry 3). However, no considerable alteration in the yield was noted on applying a 15-min reaction time (96%, entry 4). The influence of temperature on the reaction behavior was then screened (entries 5–8) and the ideal conditions were observed at 110 °C. We observed that by decreasing the temperature a lower yield of 3a was obtained (entry 5) and a higher temperature did not show any significant influence (entry 6). We further investigated the reaction by investigating the effect of applying MW irradiation. The best result was obtained using 100 W (entries 7 and 8 *vs* 3). In order to evaluate the influence of the heating source, the reaction was also performed in a conventional oil bath heating system (entry 9). However, 8 h of heating were required to obtain 3a in 65 % yield, highlighting the superiority of the MW method.

In the subsequent step, the influence of the catalyst loading and the stoichiometric quantity of oxidant on the reaction system was explored (Table 2). No product was observed in the absence of catalyst, I_2 (entry 1). By using 5 mol% of I_2 **3a** was obtained in 45% yield (entry 2). Increasing the catalyst loading to 10 mol% led to an improvement in the yield (87%, entry 3), which was further increased significantly to 95% when 20 mol% of I_2 was used (entry 4). Further increase in the catalyst loading was not effective, giving **3a** in 96% yield (entry 5).

The influence of oxidant on the selenylation of **2a** was then evaluated (entries 6-10). By decreasing the amount of DMSO from 3 to 2 eq., the yield of **3a** was reduced from 95 to 75% (entry 4 *vs* 7), while in its absence the yield dramatically decreased to 32% (entry 6). Using DMSO as solvent did not showed any further positive influence on the yield on **3a** (entry 8 vs 4). The use of other oxidants i.e. H_2O_2 and DTBP instead of DMSO resulted in a less efficient transformation in 81 and 45% yields, respectively (entry 9-10).

With the optimized conditions in hand, the applicability of other arenes, e.g. anilines, anisoles etc., and various diorganyl diselenides were screened (Tables 3 and 4). We first explored the scope of the reaction with respect to the different arenes **2a-u** while keeping diphenyl diselenide **1a** constant, resulting in the coupled product **3a-x** in good to excellent yields (Table 3). In general, *N,N*-disubstituted anilines afforded the selenated product selectively at the *para* position of the anilines **3a-d** in excellent yields.

Furthermore, to our delight, when the reaction was carried out with a *secondary*-amine (*N*-ethyl aniline) and a *primary*-amine (aniline) only the coupled products **3e** and **3f** were observed at the *para* position, in 83% and 80% yields, respectively. In view of these results, *ortho*- and *para*-substituted aryl amines **2g-l** were reacted with **1a** under standard conditions. *Ortho*-substituted anilines resulted in selenylation at the *para*-position, providing **3g-h** in good yields. Interestingly, an electron-withdrawing group at the *ortho*-position afforded better yields (entry **3g** *vs* **3h**). When the *para* position of the aniline was blocked by using 4-substituted anilines **2i-l**, the coupling took place at the *ortho*-position forming **3i-l** in 83-72% yields. The slight decrease in the yield of **3j-l** as compare to **3g-i** is most likely due to the steric effect. Similarly, on using 3,4-(methylenedioxy)aniline **2m**, the coupling took place at C6 instead of the C2 position, which is most probably due to the steric effect and the selenated product **3m** was obtained in 82% yield.

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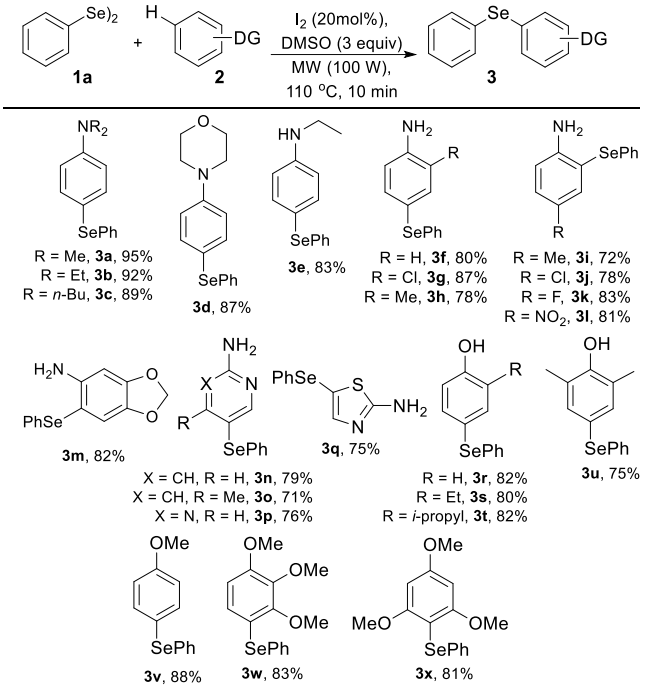
Table 3 Scope and generality of the reaction using arenes **2**[a,b]



[a] Reaction conditions: **1** (0.125 mmol), **2** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation. [b] Isolated yields.

Promising results from anilines **2a-m** motivated us to further extend this new protocol to different heteroaromatic amines **2n-p**. It is noteworthy that the compounds **2n-p** are well tolerated in this transformation and furnished exclusively the *para* selenated product **3n-p**, related to the amine, in 79-71% yields. Similarly, in the case of 2-aminothiazole **2q**, an electrophilic attachment took place at the C5 position resulting in **3q** in 75% yield. We further tested this method with the phenol and methoxy-arenes **2r-x** under the optimized conditions used for anilines. Encouragingly, the reactions proceeded cleanly and furnished the corresponding aryl selenides **3r-x** in 75-88% yields.

To extend the scope in terms of the substrate, the effects of other diorganyl diselenides **1b-k** were also investigated (Table 4). Interestingly, our protocol worked well for several diselenides containing both electron-donating and electron-withdrawing groups as well as bulky groups, verifying the sensitivity and tolerance to the electronic effects and steric effects of several different substituents. We observed that the desired products, **3y-z** and **3aa-ah**, were obtained in good to excellent yields. The results revealed that electron-withdrawing groups at the phenyl ring of **1** gave fairly good yields (**3y, 3z** *vs* **3aa, ab**). We also noted a weaker influence on the yields because of the steric hindrance of *ortho*-substituted aryl substrates as compared to the corresponding *para* derivatives (**3ac** *vs* **3y** and **3ad** *vs* **3z**). In addition, we found that C-2 heteroaryl diselenide gave the desired selenide **3ag** with 82% yield. Interestingly, in the case of dibutyl diselenide, the reaction produced the corresponding product **3ah** in 78% yield

Table 4 Scope and generality of the reaction using diorganyl diselenides **1**[a,b]

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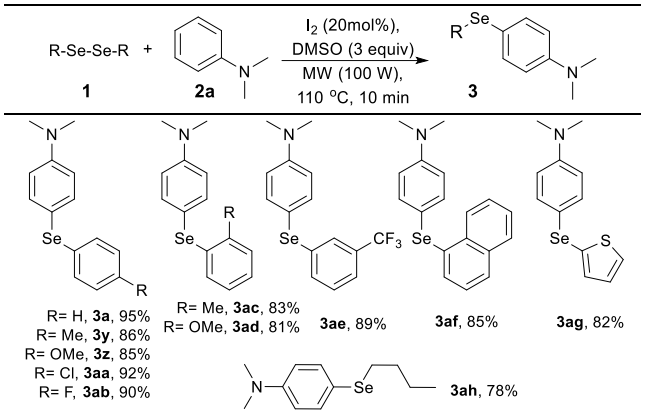
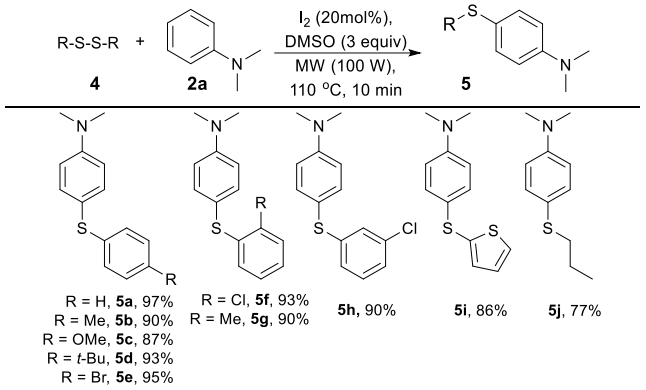


[a] Reaction conditions: **1** (0.125 mmol), **2** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation. [b] Isolated yields.

Table 5 Scope and generality of the reaction using diorganyl disulfides **4**[a,b]



[a] Reaction conditions: **4** (0.125 mmol), **2** (0.25 mmol) in the presence of I_2 (20 mol%) and DMSO (3 equiv.) for 10 min at 110°C with 100 watts of MW irradiation. [b] Isolated yields.

(Table 4). This result is important since the alkyl group does not usually furnish the product in C(sp^2)-H bond activation.

The success in the iodine-catalyzed C-Se bond formation, through C(sp^2)–H bond activation, prompted us to expand this methodology to diorganyl disulfides **4a-j** as a way to access unsymmetrical sulfides. The desired products **5a-j** were obtained in 77% to 97% yields (Table 5). It was observed that the methodology used to prepared diorganyl disulfides **4** presented similar electronic and steric effects as that used to obtain diorganyl diselenides **1**. Furthermore, diorganyl disulfides **4** afforded the coupling products in comparatively better yields compared to diorganyl diselenides **1**.

To check the versatility of this protocol, we have observed that our methodology also worked efficiently by using thiophenol **6** as another sulfenylating agent and *N,N*-dimethylaniline **2a**, affording the desired product in very good yield, in a short reaction time using MW irradiation (Scheme 2).

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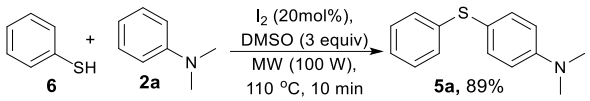
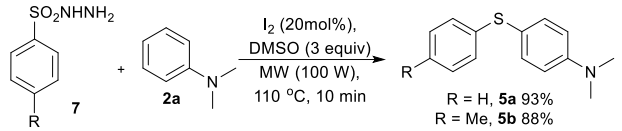


Scheme 2

In order to further explore the scope of this new methodology we extended our study to sulfonyl hydrazides **7** (Scheme 3), applying the optimal reaction conditions (Table 1, entry 3). Interestingly, the reaction of different arylsulfonyl hydrazides **7** with *N,N*-dimethylaniline **2a** proceeded smoothly and afforded the corresponding coupled products **5a** and **5b** in 93% and 88% isolated yields, respectively (Scheme 3). This demonstrates that our protocol is versatile, being applicable to various kinds of organochalcogen sources.



Scheme 3

In order to demonstrate the potential of this protocol, a series of reactions was carried out on different scales (Figure 1; up to 10 mmol). For this, *N,N*-dimethylaniline **2a**, diselenide **1a** and disulfide **5a** were selected as the reagents to be tested under optimized conditions, affording **3a** and **5a** with no major decrease in yield. Thus, this procedure could be used as a robust method for the synthesis of aryl chalcogenides on a larger scale.

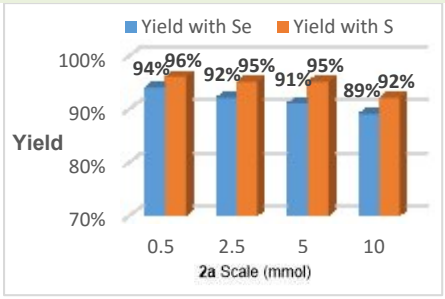
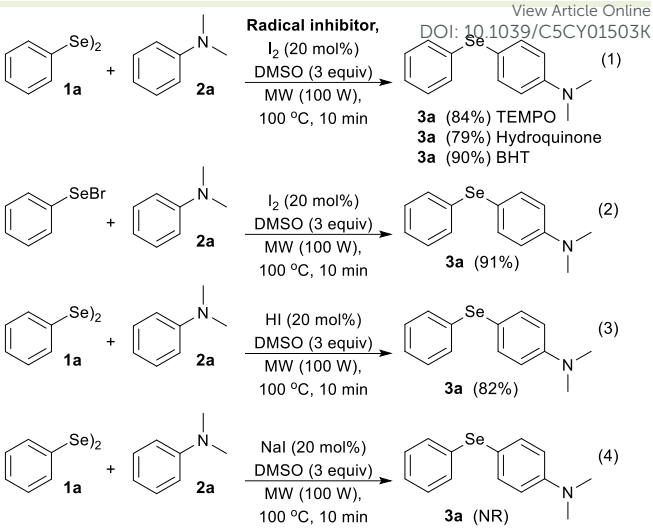


Fig. 1 Results for the reaction on different scales.

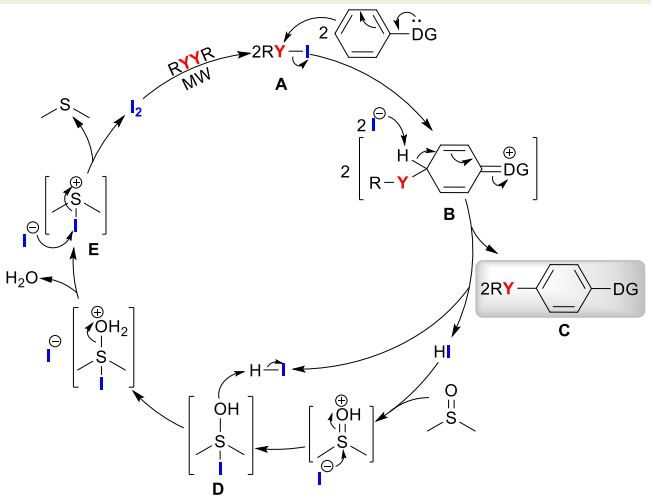
Bearing in mind that the coupling reaction of diorganyl chalcogenides and arenes under metal-free conditions is not well understood, some control experiments were performed in order to explain the mechanism (Scheme 4). Radical inhibitors, e.g. TEMPO, hydroquinone, BHT, did not hamper the reaction and the coupled product **3a** was obtained in 84, 79 and 90 % isolated yield, respectively [Eq. 1]. These experiments excluded any possibility of a radical pathway, which also indicates that the PhY radical species is not involved during the course of the reaction. Compound **3a** was obtained in 91% yield when **2a** was treated with one equiv. of PhSeBr instead of diphenyl diselenide **1a** [Eq. 2], indicating that the reaction proceeds through a phenylselenium cation species. Based on our previous experience,[16a] using a catalytic amount of HI instead of iodine [Eq. 3], the reaction afforded **3a** with 82% yield, showing that HI



Scheme 4 Investigation of the mechanism

is probably one of the intermediates of this transformation. It was observed that on using NaI instead of HI the reaction did not occur [Eq 4], demonstrating the importance of the presence of HI.

Based on the above results and on previous reports,[10b,13,18] a plausible mechanism for the direct C(sp^2)-H bond chalcogenation of arenes under metal-free conditions is illustrated in Scheme 5. Initially, the electrophilic chalcogen species **A** in the form an intermediate RYI (Y = Se, S) would be formed by the reaction of diorganyl dichalcogenide RYYR with the catalyst (I_2). Subsequently, the electron-rich arenes would attack the reactive RYI intermediates **A** at the *para*-position, to form the species **B**. This species would undergo proton elimination and would furnish the expected chalcogenides **C** with the simultaneous formation of HI. In the next step, the by-product HI would react with DMSO affording a protonated sulfur species **D**, which would be quickly converted to the iodine-dimethyl sulfide adduct **E** with the elimination of water.[19] Lastly, the cycle would be completed by the transformation of the species **E** to dimethyl sulfide (DMS)[20] with the regeneration of the catalyst (I_2).



Scheme 5. Proposed mechanism for the reaction.

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An important feature of this process is that the concentration of iodide in the reaction medium is low, since it is continuously consumed by the mild oxidant, DMSO, avoiding the nucleophilic competition.

Conclusions

In summary, we have developed a regioselective, rapid and greener iodine-catalyzed method for the synthesis of diorganyl chalcogenides through oxidative C–Se/C–S formation *via* direct C(sp^2)-H bond cleavage from using [O or N]-containing arenes. This regioselective procedure afforded the desired products in good to excellent yields under metal and solvent-free conditions, without the exclusion of air and moisture, applying microwave irradiations for 10 min.

The important features of this protocol are: (1) metal-free and solvent-free; (2) open to the air; (3) mild conditions; (4) short reaction time and under microwave irradiation; (5) regioselective; (6) applicable to different sources of organochalcogenides. Additionally, by this protocol, we were able to access biologically important Se/S containing heteroarenes, such as, pyrimidines, pyridines, thiazole.

Experimental

Materials and methods

Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained at 200 MHz on a Bruker AC-200 NMR spectrometer or at 400 MHz on a Varian AS-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained either at 50 MHz on a Bruker AC-200 NMR spectrometer or at 100 MHz on a Varian AS-400 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abbreviations to denote the multiplicity of a particular signal are: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet) and m (multiplet). Selenium-77 nuclear magnetic resonance spectra (^{77}Se NMR) at 38.14 MHz on a Bruker AC-200 NMR spectrometer. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to diphenyl diselenide as the external reference (463.15 ppm). High resolution mass spectra were recorded on a Bruker micrOTOF-Q II ESI mass spectrometer equipped with an automatic syringe pump for sample injection. Infrared spectra were recorded on a Bruker Optics Alpha benchtop FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}). The melting points were determined in a Microquimica MQRPF-301 digital model equipment with heating plate. Column chromatography was performed using Silica Gel (230-400 mesh). Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor and acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material.

Unless otherwise stated, all reactions were carried out in open atmosphere; all reagents and solvents were obtained from commercial sources and used without any further purification. All reactions were performed in 10-ml reaction vessels (Borosilicate glass) with cap and septum (Silicon) in a commercially available Microwave monomode CEM reactor with IR monitoring and a non-invasive pressure transducer. Reagents and solvents were handled using standard syringe techniques. The yields are based on isolated compounds after purification.

General procedure for the iodine-catalyzed synthesis of unsymmetrical diorganyl chalcogenides

A mixture of appropriate arene **2** (0.25 mmol), diorganyl dichalcogenide (0.125 mmol), iodine (20 mol %, 12 mg), and 3 equiv. of DMSO (0.75 mmol, 59 mg) were charged in a microwave glass tube, which was sealed and placed in a CEM Discover microwave apparatus. A maximum irradiation power of 100 W and a temperature of 110 ºC were applied for 10 min. When the reaction was finished, the homogenous reaction mixture was dissolved in ethyl acetate (10 mL), and washed with 2 x 5 mL of an aqueous solution of 10% $Na_2S_2O_4$. The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The crude product was purified by flash chromatography on silica gel using hexane or a mixture of hexane/ ethyl acetate (99:1) as the eluent.

N,N-dimethyl-4-(phenylselanyl)aniline (3a)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 94% (65 mg); yellow solid; mp 36–38°C (lit.[12b] 35–38 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 (d, J = 9.0 Hz, 2H), 7.33–7.08 (m, 5H), 6.67 (d, J = 9.0 Hz, 2H), 2.97 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.6, 137.2, 134.7, 129.9, 129.1, 125.9, 113.8, 113.3, 40.4.^{77}Se NMR (38.14 MHz, $CDCl_3$): δ 391.4.

N,N-diethyl-4-(phenylselanyl)aniline (3b)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and *N,N*-diethylaniline **2b** (0.25 mmol, 37mg) were used under standard conditions; Yield: 92% (70 mg); brown oil;[12b] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 (d, J = 9.0 Hz, 2H), 7.30–7.25 (m, 2H), 7.21–7.09 (m, 3H), 6.60 (d, J = 9.0 Hz, 2H), 3.34 (q, J = 7.1 Hz, 4H), 1.15 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.0, 137.5, 134.9, 129.7, 129.0, 125.7, 112.5, 112.2, 44.4, 12.6.

N,N-dibutyl-4-(phenylselanyl)aniline (3c)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and *N,N*-dibutylaniline **2c** (0.25 mmol, 37mg) were used under standard conditions; Yield: 89% (80 mg); brown oil;[12a] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.43 (d, J = 9.0 Hz, 2H), 7.31–7.25 (m, 2H), 7.23–7.11

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(m, 3H), 6.57 (d, *J* = 9.0 Hz, 2H), 3.34–3.16 (m, 4H), 1.67–1.46 (m, 4H), 1.44–1.26 (m, 4H), 0.95 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.4, 137.5, 134.9, 129.8, 129.0, 125.8, 112.5, 112.0, 50.8, 29.4, 20.4, 14.1.

4-(4-(phenylselanyl)phenyl)morpholine (3d)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-phenylmorpholine **2d** (0.25 mmol, 41mg) were used under standard conditions; Yield: 87% (69 mg); white solid; mp 69-71°C (lit.[12b] 69–71 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 (d, *J* = 7.5 Hz, 2H), 7.39–7.27 (m, 2H), 7.27–7.04 (m, 3H), 6.83 (d, *J* = 7.5 Hz, 2H), 3.92–3.73 (m, 4H), 3.26–3.03 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 151.2, 136.4, 133.6, 130.7, 129.2, 126.4, 118.6, 116.3, 66.9, 48.8. ^{77}Se NMR ($CDCl_3$,MHz): δ 397.7.

***N*-ethyl-4-(phenylselanyl)aniline (3e)**

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and *N*-ethylaniline **2e** (0.25 mmol, 30mg) were used under standard conditions; Yield: 83% (57 mg); brown oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 8.7 Hz, 2H), 7.36–7.23 (m, 2H), 7.23–7.11 (m, 3H), 6.56 (d, *J* = 8.7 Hz, 2H), 3.78 (s, 1H), 3.17 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 148.8, 137.4, 134.7, 129.9, 129.1, 125.9, 114.6, 113.7, 38.4, 14.9; IR (KBr); 3406, 3054, 2925, 2669, 1594, 1502, 1321, 1180, 1021, 814, 734; HRMS *m/z* Calcd. for $C_{14}H_{16}NSe$ $[M+H]^+$ 278.04427; found: 278.04429.

4-(phenylselanyl)aniline (3f)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and aniline **2f** (0.25 mmol, 23mg) were used under standard conditions; Yield: 80% (50 mg); yellow solid; mp 86-89°C (lit.[12a] 87–91 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 8.5 Hz, 2H), 7.31–7.25 (m, 2H), 7.27–7.08 (m, 3H), 6.60 (d, *J* = 8.5 Hz, 2H), 3.72(s, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.9, 137.1, 134.1, 130.2, 129.1, 126.1, 116.4, 116.1.

2-chloro-4-(phenylselanyl)aniline (3g)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 2-chloroaniline **2g** (0.25 mmol, 32 mg) were used under standard conditions; Yield: 87% (62 mg); brown solid; mp 52-55°C (lit.[12a] 51–54 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 2.4 Hz, 1H), 7.31–7.06 (m, 6H), 6.70 (d, *J* = 8.6 Hz, 1H), 4.27 (s, 2H); ^{13}C NMR (50 MHz, CDCl3) δ = 143.2, 136.1, 135.1, 133.2, 130.8, 129.2, 126.6, 119.6, 117.1, 116.5.

2-methyl-4-(phenylselanyl)aniline (3h)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 2-methylaniline **2h** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 78% (51 mg); brown soild; mp 55-57°C (lit.[12a] 56–59 °C); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.36–7.24 (m, 4H), 7.24–7.11 (m, 3H), 6.62 (d, *J* = 8.0 Hz, 1H), 3.71 (bs, 2H), 2.14 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 145.2, 138.1, 135.0, 134.4, 130.1, 129.1, 126.0, 123.5, 116.3, 115.8, 17.3.

4-methyl-2-(phenylselanyl)aniline (3i)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-methylaniline **2i** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 72% (47 mg); brown oil;[12a] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.39 (s, 1H), 7.27–7.09 (m, 5H), 7.09–6.95 (m, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 4.10 (bs, 2H), 2.22 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 146.2, 138.7, 131.9, 131.8, 129.4, 129.3, 128.2, 126.1, 115.1, 112.7, 20.2.

4-chloro-2-(phenylselanyl)aniline (3j)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-chloroaniline **2j** (0.25 mmol, 32 mg) were used under standard conditions; Yield: 78% (55 mg); brown solid; mp 58-60°C (lit.[12a] 57–60 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.54 (d, *J* = 2.4 Hz, 1H), 7.33–7.06 (m, 6H), 6.70 (d, *J* = 8.6 Hz, 1H), 4.26 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 147.1, 137.3, 130.9, 130.8, 129.9, 129.5, 126.8, 122.6, 115.9, 114.1

4-fluoro-2-(phenylselanyl)aniline (3k)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-fluoroaniline **2k** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 83% (55 mg); yellow solid; mp 56–58 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.31–7.19 (m, 6H), 7.03–6.86 (m, 1H), 6.75–6.68 (m, 1H), 4.09 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 155.4 (d, J_{c-f} = 239.4 Hz),, 144.7 (d, J_{c-f} = 2.2 Hz), 130.9, 130.2, 129.5, 126.8, 123.69 (d, J_{c-f} = 22.3 Hz), 117.71 (d, J_{c-f} = 22.4 Hz), 115.74 (d, J_{c-f} = 7.4 Hz), 113.85 (d, J J_{c-f} = 7.1 Hz); IR (KBr) 3456, 3358, 3053, 1608, 1596, 1487, 1194, 1022, 877, 802, 740; HRMS *m/z* Calcd. for $C_{12}H_{11}FNSe$ $[M+H]^+$ 268.00355; found 268.00344.

4-nitro-2-(phenylselanyl)aniline (3l)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-nitroaniline **2l** (0.25 mmol, 35 mg) were used under standard conditions; Yield: 81% (60 mg); yellow solid; mp 104–106 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.54 (d, *J* = 2.6 Hz, 1H), 8.10 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.36–7.15 (m, 5H), 6.75 (d, *J* = 9.0 Hz, 1H), 5.07 (bs, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.9, 138.8, 135.0, 130.2, 129.9, 129.7, 127.4, 127.3, 113.3, 112.0; IR (KBr) 3449, 3434, 3339, 1612, 1575, 1475, 1332, 1118, 1019, 907, 817, 740; HRMS *m/z* Calcd. for $C_{12}H_{11}N_2O_2Se$ $[M+H]^+$ 294.99806; found 294.99810.

6-(phenylselanyl)benzo[*d*][1,3]dioxol-5-amine (3m)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and benzo[*d*][1,3]dioxol-5-amine **2m** (0.25 mmol, 34 mg) were used under standard conditions; Yield: 82% (59 mg); brown solid; mp 68–70°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.26–7.15 (m, 5H), 7.04 (s, 1H), 6.40 (s, 1H), 5.89 (s, 2H), 4.13 (s, 2H). ^{13}C NMR (50MHz, $CDCl_3$) δ 150.4, 144.7, 140.5, 132.4, 129.3, 129.0, 126.2, 117.1, 102.5, 101.1, 97.0; IR (KBr) 3454, 3354, 3049, 2897, 1629, 1589, 1502, 1470, 1257, 1219, 1194, 1033, 934, 826; HRMS *m/z* Calcd. for $C_{13}H_{11}NO_2Se$ $[M]^+$ 292.9950; found 292.9955.

5-(phenylselanyl)pyridin-2-amine (3n)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and pyridin-2-amine **2n** (0.25 mmol, 24 mg) were used under standard conditions; Yield: 79% (49 mg); yellow solid; mp 110-114°C

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(lit.[12a] 111–114 °C) ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.95 (d, J = 1.8 Hz, 1H), 8.48–8.29 (m, 1H), 8.08–7.99 (m, 2H), 7.99–7.89 (m, 3H), 7.25 (d, J = 8.6 Hz, 1H), 5.27 (bs, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 157.9, 152.7, 145.6, 132.7, 130.7, 129.3, 126.8, 113.8, 110.2.

4-methyl-5-(phenylselanyl)pyridin-2-amine (3o)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 4-methylpyridin-2-amine **2o** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 71% (47 mg); yellow soild; mp 85–87 °C;^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 7.25–7.13 (m, 5H), 6.45 (s, 1H), 4.59 (bs, 2H), 2.27 (s, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 159.4, 155.8, 153.3, 132.9, 129.5, 129.3, 126.2, 115.3, 109.9, 22.5; IR (KBr) 3467, 3293, 3135, 3057, 1640, 1592, 1477, 1437, 1412, 1021, 730, 668; HRMS *m/z* Calcd. for $C_{12}H_{13}N_2Se$ $[M+H]^+$ 265.0239; found 265.0240.

5-(phenylselanyl)pyrimidin-2-amine (3p)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and pyrimidin-2-amine **2p** (0.25 mmol, 24 mg) were used under standard conditions; Yield: 76% (48 mg); white solid; mp: 146–148 °C; ^{1}H NMR (200 MHz, DMSO-d6) δ = 8.41 (s, 2H), 7.62–7.18 (m, 5H), 7.08 (s, 2H); ^{13}C NMR (50 MHz, DMSO-d6) δ = 164.1, 162.9, 132.6, 129.5, 129.4, 126.5, 109.3; IR (KBr); 3306, 3174, 3069, 1659, 1574, 1543, 1490, 1213, 1066, 1020, 936, 796, 689; HRMS *m/z* Calcd. for $C_{10}H_{10}N_3Se$ $[M+H]^+$ 252.0035; found 252.0038.

5-(phenylselanyl)thiazol-2-amine (3q)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and thiazol-2-amine **2q** (0.25 mmol, 25 mg) were used under standard conditions; Yield: 75% (48 mg); brown solid; mp 120–122°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40–7.35 (m, 1H), 7.32–7.21 (m, 5H), 5.47 (bs, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 173.3, 148.2, 133.0, 129.5, 129.3, 126.8, 106.1; IR (KBr) 3378, 3272, 3163, 3087, 1625, 1513, 1483, 1067, 1052, 726, 516; HRMS *m/z* Calcd. for $C_9H_9N_2SSe$ $[M+H]^+$ 256.9646; found 256.9645.

4-(phenylselanyl)phenol (3r)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and phenol **2r** (0.25 mmol, 25 mg) were used under standard conditions; Yield: 82% (51 mg); brown oil;[12e] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (d, J = 8.6 Hz, 2H), 7.39–7.29 (m, 2H), 7.28–7.15 (m, 3H), 6.78 (d, J = 8.6 Hz, 2H), 5.12 (bs, 2H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 155.9, 136.8, 133.1, 131.1, 129.3, 126.6, 120.3, 116.7.

2-ethyl-4-(phenylselanyl)phenol (3s)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 2-ethylphenol **2s** (0.25 mmol, 31 mg) were used under standard conditions; Yield: 80% (55 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.53 – 7.09 (m, 7H), 6.71 (d, J = 8.2 Hz, 1H), 4.98 (s, 1H), 2.61 (q, J = 7.6 Hz, 2H), 1.21 (t, J = 7.6 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = = 153.8, 136.4, 134.2, 133.5, 131.5, 130.9, 129.2, 126.5, 120.0, 116.4, 22.9, 13.9; IR (KBr) 3417, 2965, 2929, 1578, 1491, 1264, 1119, 1021, 891, 735; HRMS *m/z* Calcd. for $C_{14}H_{14}OSe$ $[M]^+$ 278.0205; found 278.0206.

2-isopropyl-4-(phenylselanyl)phenol (3t)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) 2-isopropylphenol **2t** (0.25 mmol, 34 mg) were used under standard conditions; Yield: 82% (60 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48 – 7.14 (m, 7H), 6.69 (d, J = 8.2 Hz, 1H), 4.89 (s, 1H), 3.25–3.11 (m, 1H), 1.23 (d, J = 6.9 Hz, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.2, 136.0, 133.9, 133.8, 133.5, 130.6, 129.2, 126.4, 119.9, 116.6, 27.2, 22.5; IR (KBr) 3441, 3070, 3056, 2961,1636, 1577, 1405, 1177, 1079, 813, 734; HRMS *m/z* Calcd. for $C_{15}H_{16}OSe$ $[M]^+$ 292.0361; found 292.0362.

2,6-dimethyl-4-(phenylselanyl)phenol (3u)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) 2,6-dimethylphenol**3u** (0.25 mmol, 52 mg) were used under standard conditions; Yield: 75% (57 mg); yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.35–7.17 (m, 7H), 4.74 (s, 1H), 2.21 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 152.7, 135.7, 133.6, 130.8, 129.2, 126.4, 124.5, 119.1,15.8; IR (KBr) 3474, 3068, 3055, 2919, 2851, 1578, 1475, 1437, 1192, 1021, 869, 734; HRMS *m/z* Calcd. for $C_{14}H_{14}OSe$ $[M]^+$ 278.0205; found 278.0203.

(4-methoxyphenyl)(phenyl)selane (3v)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and anisole **2v** (0.25 mmol, 27 mg) were used under standard conditions; Yield: 88% (58 mg); yellow oil;[12e] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51 (d, J = 8.8 Hz, 2H), 7.38–7.29 (m, 2H), 7.27–7.16 (m, 3H), 6.85 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 159.9, 136.6, 133.3, 131.0, 129.2, 126.5, 120.0, 115.2, 55.4.

phenyl(2,3,4-trimethoxyphenyl)selane (3w)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 1,2,3-trimethoxybenzene **2w** (0.25 mmol, 42 mg) were used under standard conditions; Yield: 83% (67 mg); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51–7.46 (m, 2H), 7.28–7.25 (m, 3H), 6.87 (d, J = 8.7 Hz, 1H), 6.57 (d, J = 8.7 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 153.7, 152.5, 142.6, 133.5, 130.4, 129.3, 127.5, 127.4, 117.3, 108.5, 61.0, 60.9, 56.1; IR (KBr) 3069, 3055, 2996, 2835, 1577, 1478, 1456, 1292, 1092, 1012, 917, 847, 739; HRMS *m/z* Calcd. for $C_{15}H_{16}O_3Se$ $[M]^+$ 324.0260; found 324.0262.

phenyl(2,4,6-trimethoxyphenyl)selane (3x)

Diphenyl diselenide **1a** (0.125 mmol, 39 mg) and 1,3,5-trimethoxybenzene **2x** (0.25 mmol, 42 mg) were used as substrates; Yield: 81% (66 mg); yellow oil;[12g] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.31–7.01 (m, 5H), 6.21 (s, 2H), 3.86 (s, 3H), 3.78 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 163.0, 162.0, 133.6, 128.9, 128.7, 125.3, 97.2, 91.3, 56.4, 55.5.

***N,N*-dimethyl-4-(*p*-tolylselanyl)aniline (3y)**

Bis(4-methylphenyl) diselenide **1b** (0.125 mmol, 43 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 86% (63 mg); yellow solid; mp 67–69°C ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45 (d, J = 9.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 7.00 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 9.0 Hz, 2H),

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2.95 (s, 6H), 2.27 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$): δ = 150.4, 136.6, 135.9, 130.6, 130.4, 129.9, 114.7, 113.3, 40.4, 21.1; IR (KBr) 3068, 3016, 2915, 2884, 2810, 1597, 1504, 1442, 1224, 1064, 1014, 807, 799; HRMS m/z Calcd. for $C_{15}H_{18}NSe$ $[M+H]^+$ 292.0599; found 292.0597.

4-((4-methoxyphenyl)selanyl)-*N,N*-dimethylaniline(3z)

Bis(4-methoxyphenyl) diselenide **1c** (0.125 mmol, 47 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 85% (65 mg); yellow solid; mp 98-102°C; ^{1}H NMR (200MHz, $CDCl_3$) δ = 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 158.8, 150.3, 135.7, 133.3, 123.7, 116.0, 114.9, 113.3, 55.4, 40.5; IR (KBr) 3087, 3058, 2940, 2810, 1591, 1504, 1359, 1238, 1031, 808, 593; HRMS m/z Calcd. for $C_{15}H_{17}NOSe$ $[M+H]^+$ 308.0540; found 308.0550.

4-((4-chlorophenyl)selanyl)-*N,N*-dimethylaniline (3aa)

Bis(4-chlorophenyl) diselenide **1d** (0.125 mmol, 48 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 92% (72 mg); white solid; mp 111-114°C (lit.[12a] 111–116 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 9.0 Hz, 2H), 7.28–7.05 (m, 5H), 6.66 (d, *J* = 9.0 Hz, 2H), 2.97 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.7, 137.2, 133.1, 131.9, 131.1, 129.1, 113.4, 113.3, 40.3.

4-((4-fluorophenyl)selanyl)-*N,N*-dimethylaniline (3ab)

Bis(4-fluorophenyl) diselenide **1e** (0.125 mmol, 44 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 90% (66 mg); yellow solid; mp 47-50°C (lit.[12b] 49–52 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ= 7.44 (d, *J* = 8.8 Hz, 2H), 7.30–7.23 (m, 2H), 6.88 (t, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 2.95 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 161.84 (d, $J_{c\text{-}f}$ = 245.2 Hz), 150.6, 136.7, 132.31 (d, $J_{c\text{-}f}$ = 7.7 Hz), 128.78 (d, $J_{c\text{-}f}$ = 3.3 Hz), 116.19 (d, $J_{c\text{-}f}$ = 21.6 Hz), 114.4, 113.3, 40.3.

***N,N*-dimethyl-4-(*o*-tolylselanyl)aniline (3ac)**

Bis(2-methylphenyl) diselenide **1f** (0.125 mmol, 43 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 83% (60 mg); yellow oil; [12b] ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 8.6 Hz, 2H), 7.29–6.90 (m, 5H), 6.69 (d, *J* = 8.6 Hz, 2H), 2.98 (s, 6H), 2.38 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.6, 137.4, 137.0, 135.4, 129.9, 129.4, 126.5, 125.9, 113.4, 113.0, 40.4, 21.7.

4-((2-methoxyphenyl)selanyl)-*N,N*-dimethylaniline (3ad)

Bis(2-methoxyphenyl) diselenide **1g** (0.125 mmol, 47 mg)and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 81% (62 mg); yellow solid; [12b] mp 85-88°C (lit. 85–90 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.51 (d, *J* = 8.3 Hz, 2H), 7.19–7.05 (m, 1H), 6.89–6.51 (m, 5H), 3.89 (s, 3H), 2.98 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 155.7, 150.8, 138.5, 128.5, 126.4, 124.7, 121.6, 113.3, 111.2, 110.0, 55.8, 40.3.

***N,N*-dimethyl-4-((3-(trifluoromethyl)phenyl)selanyl)aniline (3ae)**

Bis(3-(trifluoromethyl)phenyl) diselenide **1h** (0.125 mmol, 56 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 89% (77 mg); brown solid; mp 47-50°C (lit.[12a] 48–52 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.48–7.43 (m, 1H), 7.40 (d, *J* = 9.0 Hz, 2H), 7.32–7.24 (m, 2H), 7.23–7.07 (m, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 2.90 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.7, 137.5, 136.3, 132.7, 131.3 (q, $J_{c\text{-}f}$ = 32.2 Hz), 129.3, 126.0 (q, $J_{c\text{-}f}$ = 3.9 Hz), 123.8 (q, $J_{c\text{-}f}$ = 272.8 Hz), 122.6 (q, $J_{c\text{-}f}$ = 3.8 Hz), 113.5, 112.8, 40.4.

***N,N*-dimethyl-4-(naphthalen-1-ylselanyl)aniline (3af)**

Binaphthyl diselenide **1i** (0.125 mmol, 52 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 85% (69 mg); yellow soild; mp 122-124°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.7 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.57–7.40 (m, 4H), 7.39–7.18 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.5, 136.8, 134.0, 133.5, 132.9, 129.0, 128.5, 127.0, 126.5, 126.4, 126.2, 126.1, 113.7, 113.4, 40.4; IR (KBr) 3044, 2901, 2812, 1595, 1557, 1372, 1194, 1081, 807, 768; HRMS *m/z* Calcd. for $C_{18}H_{17}NSe$ $[M]^+$ 327.0521; found: 327.0521.

***N,N*-dimethyl-4-(thiophen-2-ylselanyl)aniline (3ag)**

Di(thiophen-2-yl) diselenide **1j** (0.125 mmol, 41 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 82% (58 mg); yellow soild; mp 50-53°C;^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 9.0 Hz, 2H), 7.32 (dd, *J* = 5.3, 1.2 Hz, 1H), 7.20 (dd, *J* = 3.5, 1.2 Hz, 1H), 6.94 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 2.93 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ = 150.1, 134.3, 133.9, 130.1, 127.8, 127.0, 117.0, 113.0, 40.3; IR (KBr) 3439, 3287, 3093, 2810, 1661, 1591, 1502, 1437, 1233, 1066, 846, 730; HRMS *m/z* Calcd. for $C_{12}H_{14}NSSe$ $[M+H]^+$ 284.0006; found 284.0009.

4-(butylselanyl)-*N,N*-dimethylaniline (3ah)

Dibutyl diselenide **1k** (0.125 mmol, 34 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 78% (50 mg); colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 2.93 (s, 6H), 2.87–2.64 (m, 2H), 1.79–1.55 (m, 2H), 1.48–1.30 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.0, 135.9, 115.0, 113.1, 40.5, 32.5, 29.1, 22.9, 13.7; IR (KBr) 3029, 2971, 2924, 2800, 1595, 1505, 1444, 1352, 1062, 945, 760; HRMS m/z Calcd. for $C_{12}H_{20}NSe$ $[M+H]^+$ 258.07558; found 258.07536.

***N,N*-dimethyl-4-(phenylthio)aniline (5a)**

Diphenyl disulfide **4a** (0.125 mmol, 27 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 97% (56 mg); yellow solid; mp 67-69°C (lit.[17] 68–69 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.39 (d, *J* = 7.5 Hz, 2H), 7.25–7.01 (m, 5H), 6.70 (d, *J* = 7.5 Hz, 2H), 2.98 (s,

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6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.7, 140.3, 136.2, 128.8, 127.0, 125.1, 117.6, 113.1, 40.5.

N,N-dimethyl-4-(*p*-tolylthio)aniline (5b)

Bis(4-methylphenyl) disulfide **4b** (0.125 mmol, 31 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 90% (55 mg); yellow solid; mp 49-51°C (lit.[17] 51–52 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 8.8 Hz, 2H), 7.20–6.99 (m, 5H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.01 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.3, 136.2, 135.4, 135.1, 129.6, 127.9, 118.9, 113.1, 40.4, 21.0.

4-((4-methoxyphenyl)thio)-*N,N*-dimethylaniline (5c)

Bis(4-methoxyphenyl) disulfide **4c** (0.125 mmol, 35 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 87% (56 mg); yellow solid; mp 91–93 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 9.0 Hz, 2H), 7.18 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 3.74 (s, 3H), 2.93 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 158.4, 150.2, 134.3, 130.9, 129.6, 120.6, 114.6, 113.1, 55.4, 40.4; IR (KBr) 3091, 3060, 2942, 2836, 1880, 1872, 1592, 1506, 1358, 1236, 1031, 827; HRMS *m/z* Calcd. for $C_{15}H_{18}NOS$ $[M+H]^+$ 260.1104; found 260.1102.

4-((4-(*tert*-butyl)phenyl)thio)-*N,N*-dimethylaniline (5d)

Bis(4-(*tert*-butyl)phenyl) disulfide **4d** (0.125 mmol, 41 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 93% (53 mg); yellow solid; mp 86–88 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 2.98 (s, 6H), 1.27 (s, 9H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.5, 148.3, 136.5, 135.8, 127.1, 125.8, 118.3, 113.0, 40.4, 34.4, 31.3; IR (KBr) 3075, 2956, 2901, 2802, 1592, 1551, 1395, 1357, 1192, 1061, 1008, 812; HRMS *m/z* Calcd. for $C_{18}H_{23}NS$ $[M+H]^+$ 286.16240; found 286.16236.

4-((4-bromophenyl)thio)-*N,N*-dimethylaniline (5e)

Bis(4-bromophenyl) disulfide **4e** (0.125 mmol, 47 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 95% (73 mg); yellow solid; mp 126–128 °C(lit.[17] 127–128 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.35 (d, *J* = 9.0 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 9.0 Hz, 2H), 2.96 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.8, 139.9, 136.3, 131.7, 128.3, 118.5, 116.5, 113.0, 40.3.

4-((2-chlorophenyl)thio)-*N,N*-dimethylaniline (5f)

Bis(4-chlorophenyl) disulfide **4f** (0.125 mmol, 36 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 93% (61 mg); white solid; mp 119–121°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.40 (d, *J* = 8.9 Hz, 2H), 7.35–7.22 (m, 1H), 7.08–6.95 (m, 2H), 6.74 (d, *J* = 8.9 Hz, 2H), 6.71–6.60 (m, 1H), 3.01 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 151.2, 140.3, 137.3, 130.2, 129.3, 127.0, 126.8, 125.4, 115.0, 113.2, 40.3; IR (KBr) 3054, 2987, 2900, 2810, 1592, 1509, 1441, 1366, 1193, 1028, 945, 814, 746; HRMS *m/z* Calcd. for $C_{14}H_{15}ClNS$ $[M+H]^+$ 264.06082; found 264.06091.

N,N-dimethyl-4-(*o*-tolylthio)aniline (5g)

Bis(4-methylphenyl) disulfide **4g** (0.125 mmol, 31 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield 90% (55 mg); white solid; mp 112–114 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.33 (d, *J* = 8.9 Hz, 2H), 7.14–7.10 (m, 1H), 7.03–6.98 (m, 2H), 6.85–6.80 (m, 1H), 6.70 (d, *J* = 8.9 Hz, 2H), 2.97 (s, 6H); 2.38 (s, 3H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.6, 139.2, 135.9, 135.5, 130.0, 127.0, 126.4, 125.1, 117.3, 113.2, 40.4, 20.2; IR (KBr) 3084, 3056, 2925, 2813, 1597, 1509, 1440, 1194, 1057, 946, 809, 797; HRMS *m/z* Calcd. for $C_{15}H_{18}NS$ $[M+H]^+$ 244.11545; found 244.11547

4-((3-chlorophenyl)thio)-*N,N*-dimethylaniline (5h)

Bis(3-chlorophenyl) disulfide **4h** (0.125 mmol, 36 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions;Yield: 90% (59 mg); white solid; mp 58–60 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.38 (d, *J* = 9.0 Hz, 2H), 7.20–6.89 (m, 4H), 6.70 (d, *J* = 9.0 Hz, 2H), 2.99 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 151.0, 143.0, 136.6, 134.8, 129.7, 126.1, 125.0, 124.5, 115.9, 113.1, 40.3; IR (KBr) 3396, 3043, 2889, 2811, 1592, 1574, 1505, 1358, 1193, 1097, 943, 884, 770; HRMS *m/z* Calcd. for $C_{14}H_{15}ClNS$ $[M+H]^+$ 264.06082; found 264.06069.

***N,N*-dimethyl-4-(thiophen-3-ylthio)aniline (5i)**

Di(thiophen-2-yl) disulfide **4i** (0.125 mmol, 29 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 86% (50 mg); yellow solid; mp 50–52 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 7.33–7.25 (m, 3H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.95–6.91 (m, 1H), 6.62 (d, *J* = 8.7 Hz, 2H), 2.91 (s, 6H); ^{13}C NMR (50MHz, $CDCl_3$) δ = 150.2, 136.8, 132.6, 132.0, 128.8, 127.5, 122.2, 112.9, 40.9; IR (KBr) 3400, 3097, 3082, 2884, 2810, 1599, 1507, 1362, 1190, 1062, 843, 713; HRMS *m/z* Calcd. for $C_{12}H_{14}NS_2$ $[M+H]^+$ 236.05622; found 236.05625.

***N,N*-dimethyl-4-(propylthio)aniline (5j)**

Dibutyl disulfide **4j** (0.125 mmol, 22mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions; Yield: 77% (38 mg); colorless oil; 1H NMR (200 MHz, CDCl3) δ = 7.32 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 2.94 (m, 6H), 2.83–2.64 (m, 2H), 1.73–1.43 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); 13C NMR (50MHz, CDCl3) δ = 149.9, 134.0, 121.3, 113.0, 40.6, 38.8, 22.9, 13.4; IR (KBr) 3444, 2959, 2929, 2870, 1596, 1504, 1443, 1352, 1061, 946, 812; HRMS m/z Calcd. for C11H18NS [M+H]+ 196.10081 found 196.10089.

Procedure for the iodine-catalyzed reactions of thiophenol with *N,N*-dimethylaniline 2a

A mixture of *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg), and thiophenol **6** (0.25 mmol, 28mg) were used under standard conditions. Yield: **5a** 89% (51 mg).

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General Procedure for the iodine-catalyzed reactions of arylsulfonyl hydrazides with *N,N*-dimethylaniline 2a

A mixture of phenylsulfonyl hydrazide **7a** (0.25 mmol, 43 mg) or *p*-tolylsulfonyl hydrazide **7b** (0.25 mmol, 47 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions. Yield: **5a**, 93% (53 mg) and **5b**, 88% (54 mg).

Control Experiments for the Study of Mechanism

Radical trapping study

A mixture of diphenyl diselenide **1a** (0.125 mmol, 39 mg), *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) and appropriate radical inhibitor (0.25 mmol) i.e. TEMPO (39 mg), hydroquinone (28 mg), BHT (55 mg), were used under standard conditions. Yield of **3a**: 84% (58 mg) in case of TEMPO, 79% (55 mg) in case of hydroquinone, 90% (62mg) in case of BHT.

Reaction between phenylselenium bromide and *N,N*-dimethylaniline 2a

A mixture of phenylselenium bromide (0.25 mmol, 59 mg) and *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg) were used under standard conditions. Yield of **3a**: 91% (63 mg).

Reaction catalyzed by HI and NaI

A mixture of diphenyl diselenide **1a** (0.125 mmol, 39 mg), *N,N*-dimethylaniline **2a** (0.25 mmol, 30 mg), 3 equiv. of DMSO (0.75 mmol, 59 mg) and 20 mol% of catalyst i.e. HI (6 mg) or NaI (8 mg), were used under standard conditions. Yield of **3a**: 82% (57mg) in case of HI; no product was observed in case of NaI.

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20 A controlled experiment has been performed under the reaction condition of Table 1 (entry 9) with some modifications in order to capture the formed DMS. By using cannula needle, it was possible to collect the formed gas directly in the NMR tube (placed in ice cold water) containing $CDCl_3$. The captured DMS was analyzed using ^1H NMR and ^{13}C NMR (S48 of supporting information).

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