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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/jo302480j • Publication Date (Web): 17 Jan 2013

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Transition Metal Free Synthesis of Unsymmetrical Diaryl Chalcogenides from Arenes and Diaryl Dichalcogenides

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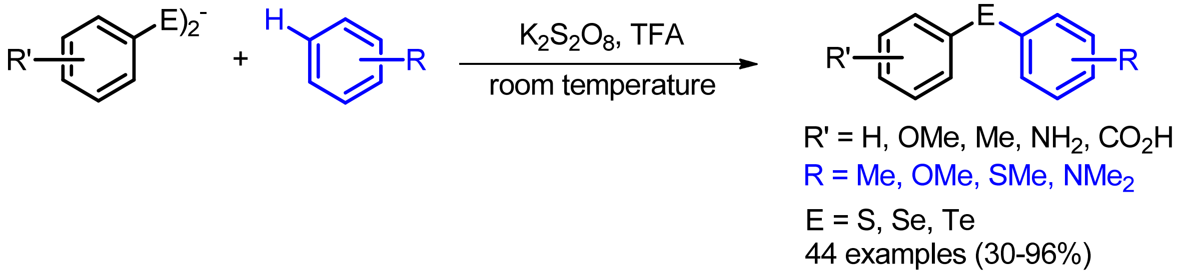
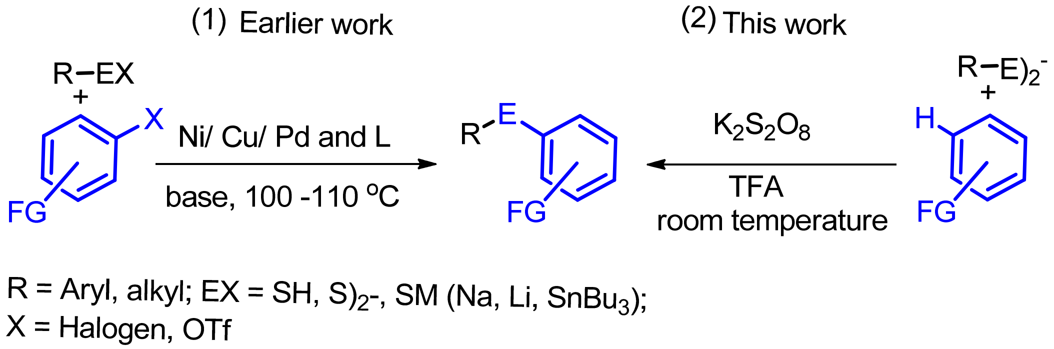


Abstract: A transition metal free synthetic method has been developed for the synthesis of unsymmetrical diaryl chalcogenides (S, Se, and Te) from diaryl dichalcogenides and arenes under oxidative conditions by using potassium persulfate at room temperature. Variously substituted arenes such as anisole, thioanisole, diphenyl ether, phenol, naphthol, di- and trimethoxy benzenes, xylene, mesitylene, *N*,*N*-dimethylaniline, bromine substituted arenes, naphthalene and diaryl dichalcogenides underwent carbon-chalcogen bond forming reaction to give unsymmetrical diaryl chalcogenides in trifluoroacetic acid. To understand the mechanistic part of the reaction, a detailed *in-situ* characterization of the intermediates has been carried out by ^{77}Se NMR spectroscopy by using diphenyl diselenide as the substrate. ^{77}Se NMR study suggests that electrophilic species ArE^+ is generated by the reaction of diaryl dichalcogenide with persulfate in trifluoroacetic acid. The electrophilic attack of arylchalcogenium ion on the arene may be responsible for the formation of the aryl-chalcogen bond.

Introduction

The formation of the aryl C-E (S/Se/Te) bond is one of the fundamental reactions in organic synthesis, and represents a key step for the construction of a broad range of organic molecules, which are of paramount importance in drugs, functional materials, and metal complexes.[1-3] The carbon-chalcogen coupling reactions were mainly achieved in two pathways: a) transtion metal catalyzed coupling of aryl halides with aryl chalcogenide precursors (Scheme 1);[4-7] b) conventional methods in which aryllithiums/ aryl Grignard reagents were coupled with aryl dichalcogenide precursors.[8] The synthesis of diaryl chalcogenides from arenes has been rarely described in the literature.[9,10] Recently, copper-catalyzed synthesis of diaryl chalcogenides from arenes and diaryl disulfides has been reported using oxygen as an oxidant.[9i] However, only trimethoxy benzene was found to be an efficient substrate for C-S coupling and the reaction required high temperature. Beller *et al*. have reported a Pd-catalyzed synthesis of diaryl sulfides through C-H activation of arenes.[9j] Nonetheless, arylsulfonyl cyanide (ArSCN) was required as an arylsulfur substrate in this methodology. The corresponding selenium and tellurium analogues of arylsulfonyl cyanides are not easily available.

Scheme 1. Synthesis of Diorganochalcogenides



In view of the above mentioned facts, a method which avoids transition metal catalyst, aryl chalcogenyl halides (ArEX), longer reaction time, and high temperature would be highly desirable for the synthesis of diaryl chalcogenides.

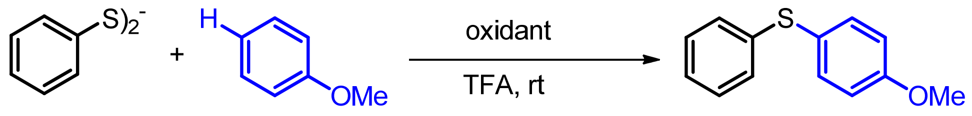
The synthesis of unsymmetrical diaryl selenides by the coupling of phenylselenenyl sulfate ($PhSeOSO_3^-$) with arenes under refluxing conditions without using any transition metal catalyst has been reported in 1996 by Engman *et al*.[10b] However, synthesis of diaryl sulfide and telluride has not been described. Similarly, other methods have also been reported which are limited to the synthesis of diaryl selenides.[10a,d-f]

We envisioned utilizing diaryl dichalcogenide and arene substrates in the Pd-catalyzed oxidative coupling reaction.[11] Diaryl dichalcogenides are readily available substrates and have been used in many transition metal catalyzed coupling reactions.[5l,6a,7a,d-f,9i] Surprisingly, the reaction also proceeded in the absence of a palladium catalyst, and the presence of potassium persulfate is sufficient for the formation of aryl-sulfur bond. Indeed, slightly better yield of diaryl sulfide **1** was obtained in the absence of palladium catalyst (85% with and 89% without $Pd(OAc)_2$). In continuation of our work on the synthesis of organochalcogenides and coupling reactions,[12] herein, we present a transition metal free methodology for the synthesis of unsymmetrical diaryl chalcogenides from arenes and diaryl dichalcogenide substrates at room temperature. By using this alternative chemical reaction, a series of diaryl chalcogenides, particularly electron rich diaryl chalcogenides can be synthesized from diaryl dichalcogenide precursors and arenes in the presence of potassium persulfate without using any transition metal catalyst.

Results and Discussion

Optimization of reaction conditions was carried out in the presence of various oxidants with diphenyl disulfide and anisole in trifluoroacetic acid TFA (Table 1).

Table 1. Optimization of Reaction Conditions[a]



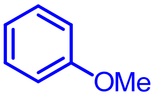
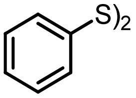
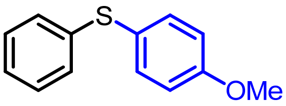
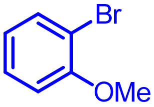
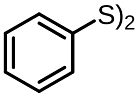
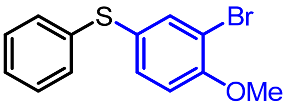
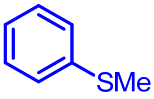
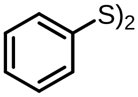
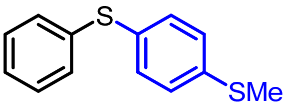
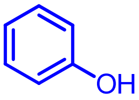
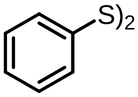
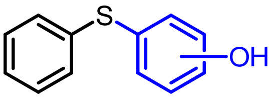
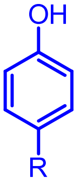
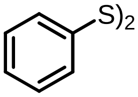
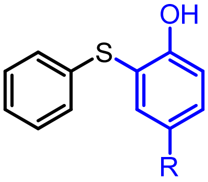
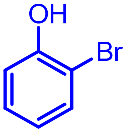
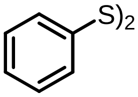
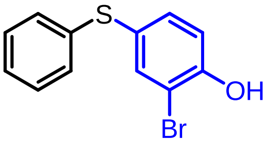
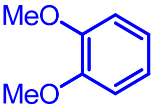
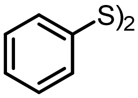
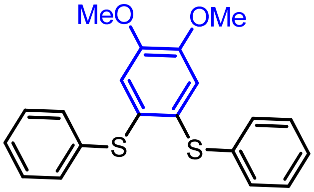
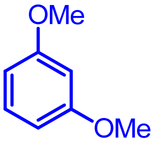
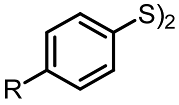
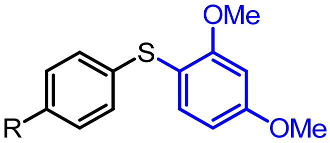
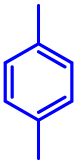
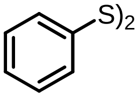
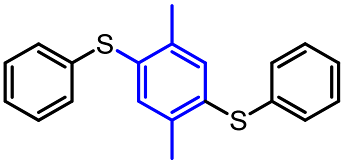
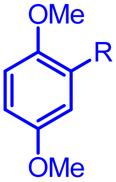
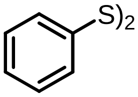
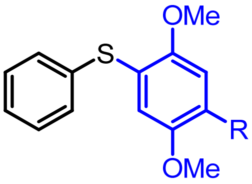
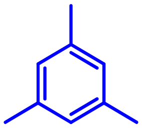
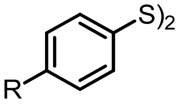
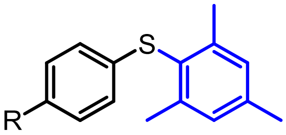
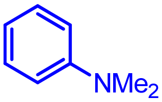
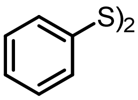
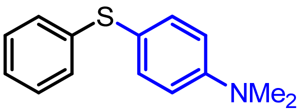
Entry	Oxidant	Isolated Yield (%)	Entry	Oxidant	Isolated Yield (%)
1	H_2O_2	-[b]	9[e]	$K_2S_2O_8$	85
2	^{t}BuOOH	20	10[f]	$K_2S_2O_8$	80
3	mCPBA	52	**11[d]**	**$(NH_4)_2S_2O_8$**	**89**
4	AgOAc	-[b]	12[d]	$Na_2S_2O_8$	74
5	Ag_2SO_4	-[b]	13[d]	Oxone	45
6	$Cu(OAc)_2$	40	14[d]	Py-SO_3	5
7[c]	$K_2S_2O_8$	70	15[g]	-	-[b]
8[d]	**$K_2S_2O_8$**	**89**	16[h]	$K_2S_2O_8$	-[b]

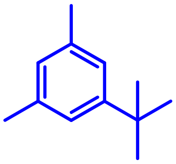
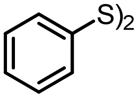
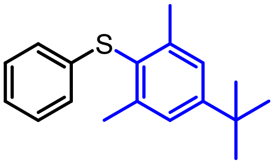
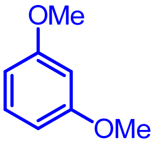
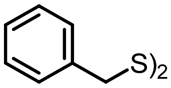
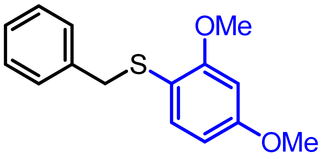
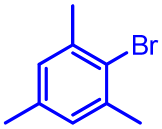
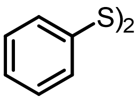
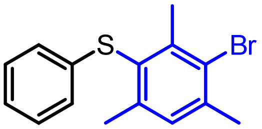
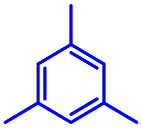
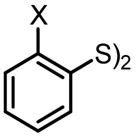
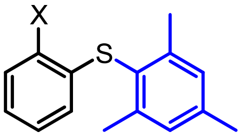
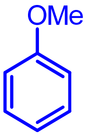
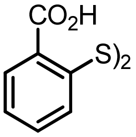
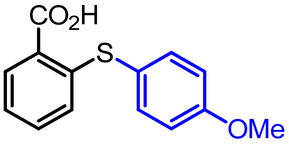
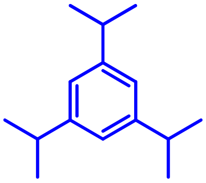
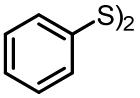
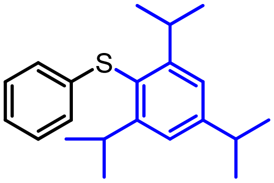
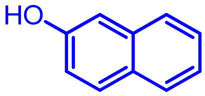
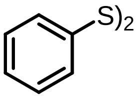
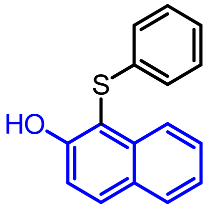
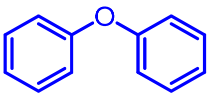
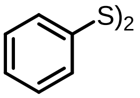
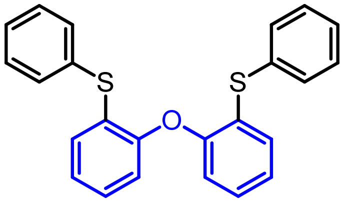
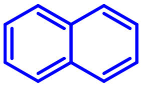
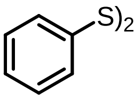
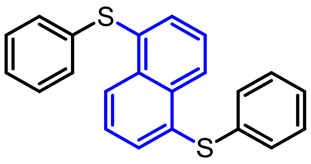
[a] Reaction was carried out at 1 mmol scale using 5 equiv of anisole, 1 equiv of diphenyl disulfide and 2 equiv of oxidant in 5 equiv of TFA, otherwise noticed. [b] Product was not observed by TLC. [c,d,e,f] 1, 2, 3, and 4 equiv of $K_2S_2O_8$ were used respectively. [g] Reaction was carried out in the absence of $K_2S_2O_8$. [h] Instead of TFA, DMF and DMSO were used.

Oxidants such as *tert*-butyl hydroperoxide and *meta*-chloroperbenzoic acid were found to be less effective and gave **1** in 20% and 52% yields, respectively and hydrogen peroxide was ineffective (entries 1-3, Table 1). Silver acetate and silver sulfate were found to be inactive for C-S bond formation despite the complete conversion of diaryl disulfide. The use of potassium persulfate ($K_2S_2O_8$) provided a better yield (70-89%) in TFA. We have also screened other sulfur containing oxidants such as oxone, sodium persulfate, ammonium persulfate and pyridine sulfur trioxide complex. Out of these, the persulfate oxidants resulted in good yields of diaryl sulfide **1** (entries 11-14, Table 1). It was observed that the five equivalents of TFA are optimum to achieve high yield of diaryl sulfide **1**. Furthermore, presence of TFA seems to be crucial as the reaction failed to yield the corresponding diaryl sulfide in the absence of TFA (entry 16, Table 1).

After screening various solvents and oxidants, we decided to use $K_2S_2O_8$ as an oxidant and TFA as a solvent to study the scope of this reaction. Under these conditions, a series of arenes were utilized for the synthesis of diaryl sulfides (**1-28**) and the results are presented in Table 2.

Table 2. Synthesis of Diaryl Sulfides

Entry	Arene	ArSSAr	Product	Yield (%)[a]
1				**1** (89)
2				**2** (45)
3				**3** (73)
4				**4a** *ortho* OH (28) **4b** *para* OH (64)
5 6				**5** R= Me (85) **6** R= ^{t}Bu (74)
7				**7**[b] (52)
8				**8** (75)
9 10 11				**9** R = H (92) **10** R = OMe (96) **11** R = Me (94)
12				**12** (55)
13 14				**13** R = H (86) **14** R = OMe (92)
15 16 17				**15** R = H (94) **16** R = Me (75) **17** R = OMe (78)
18				**18** (trace) (30)[c,d]

19				**19** (72)
20				**20** (68)
21				**21** (76)
22 23				**22** X = CO$_2$H (12) (55)[c] **23** X = NH$_2$ (7) (48)[c]
24				**24** (10) (54)[c]
25				**25** (74)
26				**26** (62)
27				**27** (72)
28				**28** (76)

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[a] Isolated yield. [b] Structure of **7** was established by 1D-NOE NMR. [c] Reaction was carried out at 80 °C. [d] Formation of 4,4'-methylenebis(N,N-dimethylaniline) (50%) was noticed. Structures of diaryl sulfides were established by ^{13}C DEPT-135 NMR and by comparing with the reported NMR data.

Arenes with electron donating functional groups such as methoxy, dimethoxy, trimethoxy, methyl thio and alkyl substituents underwent C-S bond formation readily and produced a moderate to good yield of respective diaryl sulfides. Most of the arenes gave monosubstituted arylsulfides, however, 1,2-dimethoxybenzene, para xylene, phenyl ether, and naphthalene underwent double C-S bond formation and produced corresponding bisaryl sulfides exclusively (entries 8, 12, 27 and 28, Table 2). The synthesis of monosubstituted arylsulfides in the above arenes was not successful despite varying the reaction conditions. Arenes with OH functionality such as phenol, substituted phenols, and naphthol also underwent C-S coupling reaction (entries 4-7, 26, Table 2). Synthesis of chalcogen substituted phenolic compounds is difficult due to presence of acidic OH proton. Here, a series of phenolic compounds were exploited in arylthiolation reaction and the desired phenolic sulfides **4a**, **4b**, **5-7** and **26** were obtained in a one pot reaction.

After studying the hydroxyl substituted arenes, we turned our attention to amino substituted arenes. It was observed that aniline was unreactive under optimized reaction conditions. *N*,*N*,-Dimethylaniline underwent coupling reaction sluggishly under heating and yielded the respective diaryl sulfide in poor yield (entry 18, Table 2). Additionally, formation of the C-C coupled product, 4,4'-methylenebis(*N*,*N*-dimethylaniline) was noticed. Arenes with a bromine substituent also underwent C-S bond formation to give the desired diaryl sulfides **2**, **7**, and **21**. Next, substituted diaryl disulfides were explored in the coupling reaction for the synthesis of substituted diaryl sulfides (entries 10, 11, 16, 17 and 22-24, Table 2). To our delight, the diaryl disulfides having substituents such as Me, OMe, CO_2H, and NH_2 reacted with arene smoothly and yielded desired sulfides in moderate to excellent yield. The structure of 2-(mesitylthio)benzoic acid **22** was also established by single crystal X-ray diffraction (Figure 1).[13]

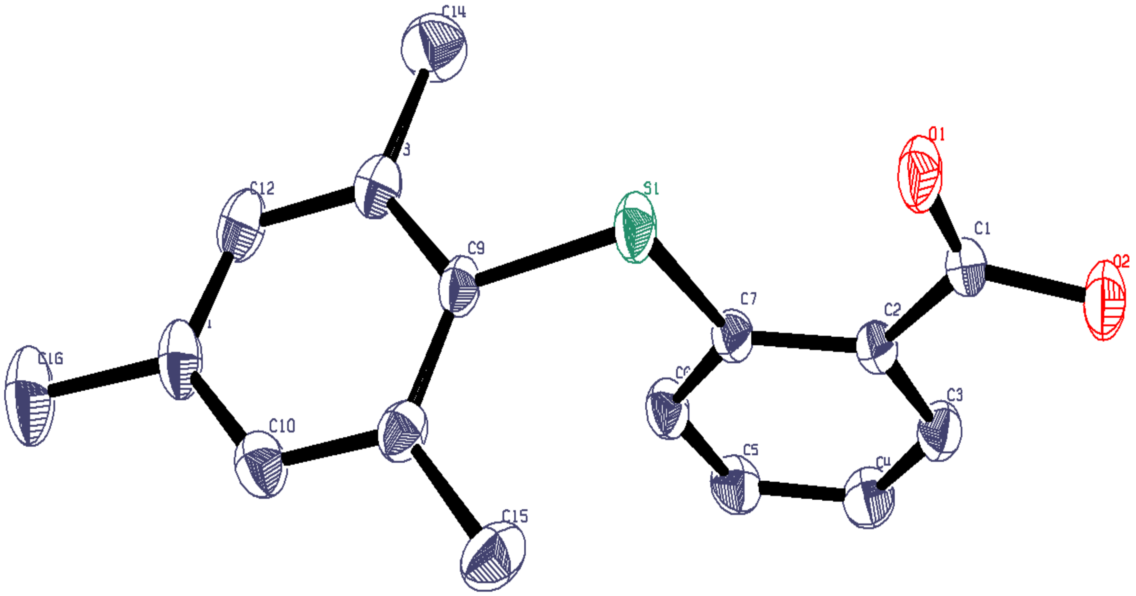
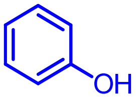
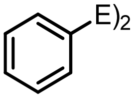
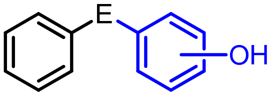
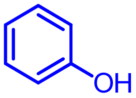
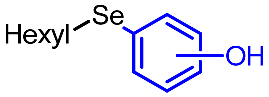
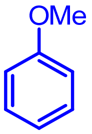
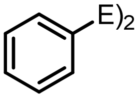
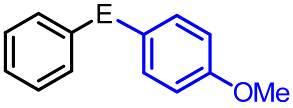
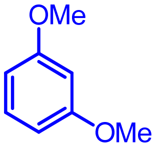
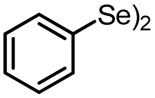
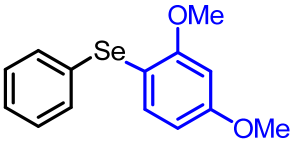
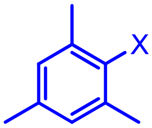
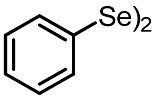
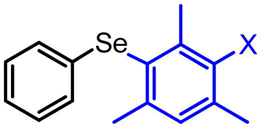
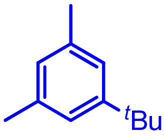
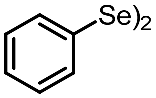
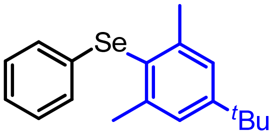
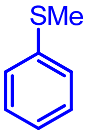
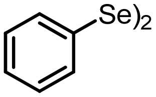
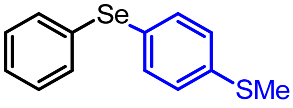
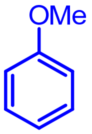
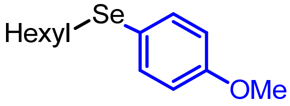
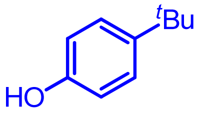
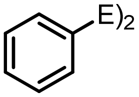
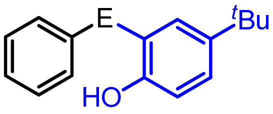
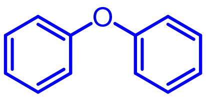
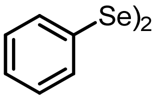
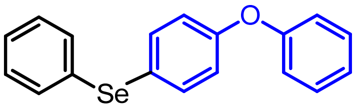
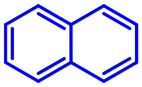
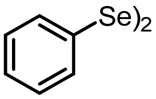
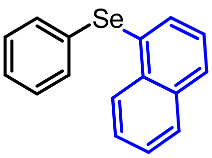


Figure 1. X-Ray Structure of **22**. Structure shows strong intramolecular S…O interaction. Intramolecular S(1)…O(1) distance (2.747Å) is significantly shorter than the sum of their van der Waals radii (S + O: 3.30 Å).

Similar to substituted aryl disulfides, benzyl disulfide was also exploited for the synthesis of benzyl aryl sulfide **20** under optimized reaction conditions.

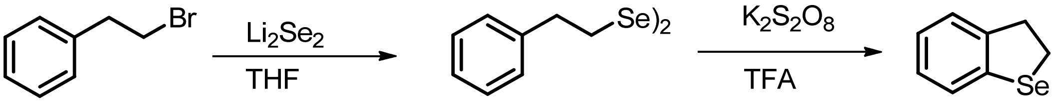
Table 3. Synthesis of Diaryl Selenides/ Tellurides

Entry	Arene	(ArE)$_2$-	Product	Isolated Yield
1				**29a** *ortho* E = Se (36)[a] **29b** *para* E = Se (49)[a]
2				**30** *para* E = Te (64)
3		Hexyl—Se)$_2$		**31a** *ortho* (38)[a] **31b** *para* (47)[a]
4				**32** E = Se (92)
5				**33** E = Te (60)
6				**34** (93)
7				**35** X = H (95)
8				**36** X = Br (62)
9				**37** (94)
10				**38** (55)
11		Hexyl—Se)$_2$		**39** (57)
12				**40** E = Se (94)
13				**41** E = Te (71)
14				**42** (82)
15				**43** (67)

[a] Both products are isolated.

Next, synthesis of diaryl selenides and tellurides was studied under optimized reaction conditions (Table 3). Electrophilic selenation in arenes such as phenol, anisole, *N*,*N*-dimethyl aniline, and thiophene under refluxing conditions has been reported by using phenylselenenyl sulfate.[10b,c] To see the compatibility of diaryl diselenide in our reaction conditions, various arenes were explored. As expected, diaryl and dialkyl diselenides were reacted with arenes in a similar fashion as diaryl disulfides and a series of diaryl selenides (**29**, **31**, **32**, **34-40**, **42**, and **43**) were obtained in moderate to excellent (55-95%) yields. Similarly, synthesis of diaryl tellurides **30**, **33**, and **41** was achieved. However, oxidation of diaryl tellurides (Ar_2Te) into corresponding telluroxides ($Ar_2Te=O$), presumably due to oxidative reaction conditions, was observed during the progress of the reaction. Diaryl telluroxides were readily converted back into diaryl telluride by reducing the reaction mixture with sodium sulfite. Tellurium substituted phenols have attracted considerable interest in biology attributed to their promising antioxidant function.[14] The introduction of aryltellurium in phenol is challenging. By using this methodology, tellurium substituted phenolic antioxidants **30** and **41** were obtained in 64 and 71% yield, respectively in a one pot.

Scheme 2. Synthesis of Selenophene



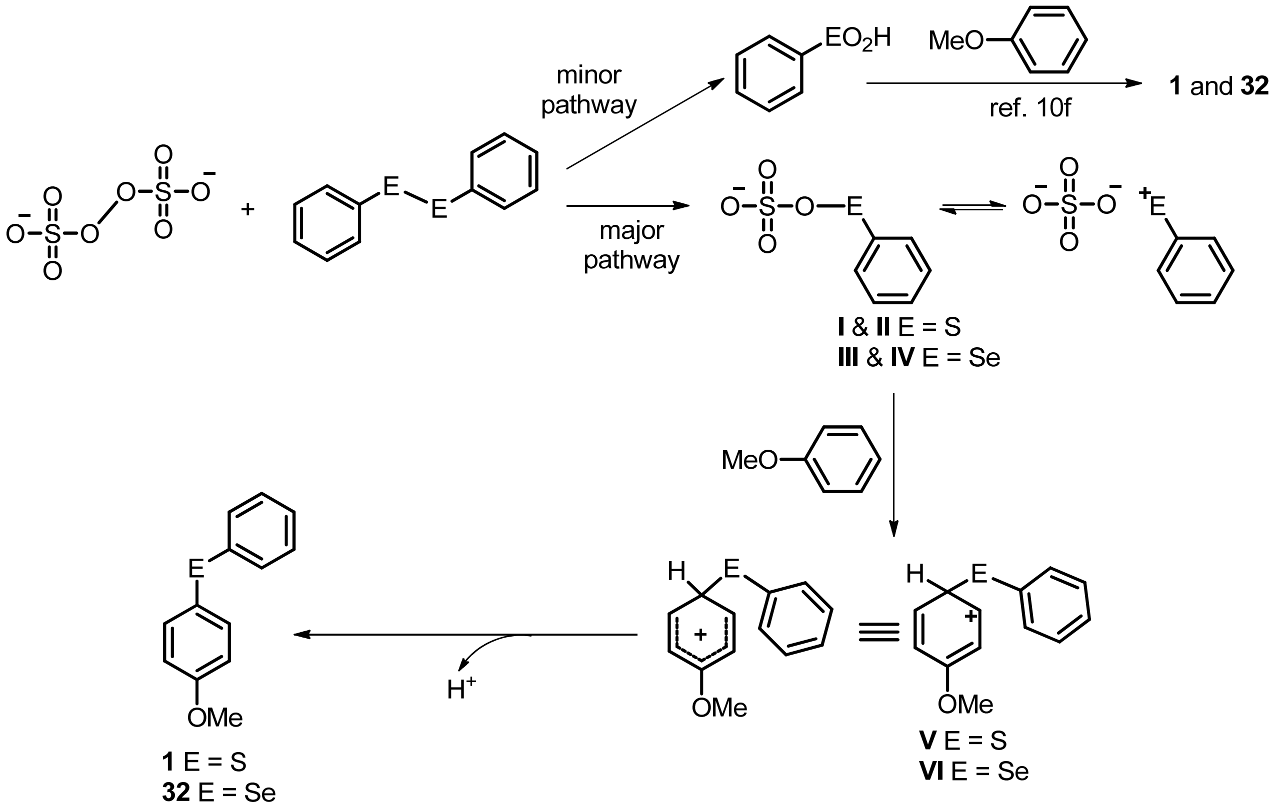
44 (40%)

The carbon-selenium coupling was also applied for the synthesis of selenophene **44** (Scheme 2). Reported synthetic protocols involve 2-iodo-phenethyl-2-bromide substrate and $^{n}Bu_3SnH$,[15] or sodium benzylselenolate ($BenzSe^+Na^-$) and butyl ditelluride reagents[16,2c] for the synthesis of selenophene analogues. Here, synthesis of selenophene **44** was achieved in one pot from readily accessible diphenethyl diselenide.

It is worth comparing the reactivity of diphenyl disulfide, diselenide and ditelluride in the persulfate mediated carbon-chalcogen bond forming reaction. In a few examples, diphenyl disulfide produced dithiolated products when reacted with arenes (entries 8, 12, 27, and 28, Table 2), whereas diselenide and ditelluride selectively yielded monoselenated and tellurated compounds, respectively, under similar reaction conditions (Table 3). Diaryl sulfides and selenides were not oxidized into respective sulfoxides and selenoxides under oxidative reaction conditions. On the other hand, diaryl tellurides were completely converted into respective telluroxides. Therefore, it is necessary to carry out reductive workup of the reaction mixture in the case of diaryl telluride synthesis.

Mechanistic Study

Scheme 3. Proposed Mechanism for C-E Bond Formation



Possible reaction pathways for potassium persulfate mediated synthesis of unsymmetrical diaryl chalcogenides are depicted in Scheme 3. It seems that potassium persulfate at first reacts with phenyl dichalcogenide and forms phenylchalcogenium ion intermediates **I** and **II**. Electrophilic addition of phenylchalcogenium ion with the electron rich arene generates the arenium ion intermediate **V**, which may give the product diaryl sulfide **1** by release of the proton (major pathway, Scheme 3). The presence of potassium persulfate and TFA seems to be crucial for the formation of diarylchalcogenide in the reaction mixture, as the reaction failed to provide sulfide **1** in the absence of both reagents. In another minor pathway (A, Scheme 3), diaryl chalcogenide could also be formed *via* generation of benzenechalcogeninic acid ($PhEO_2H$) from diphenyl dichalcogenide and potassium persulfate. Electrophilic substitution of benzeneseleninic acid into arenes would give diaryl chalcogenides.[10f] Since diaryl sulfide **1** was also formed in the presence of ^{t}BuOOH and mCPBA (entries 2-3, Table 1), and trace amount of benzeneseleninic anhydride was detected in mass spectrometry, therefore, it can be concluded that the formation of diarylchalcogenides may also be possible *via* arylchalcogeninic acid intermediate.

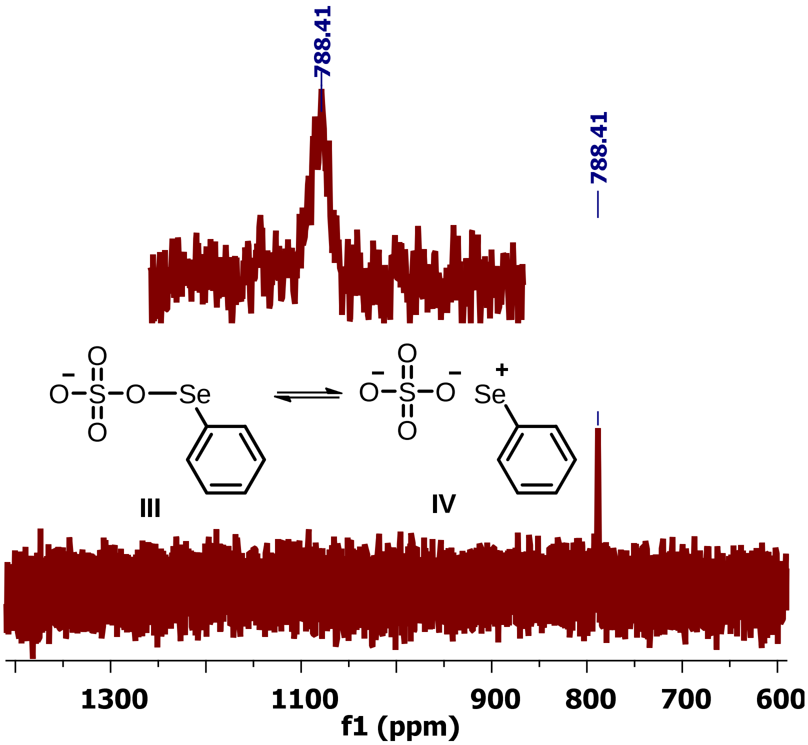
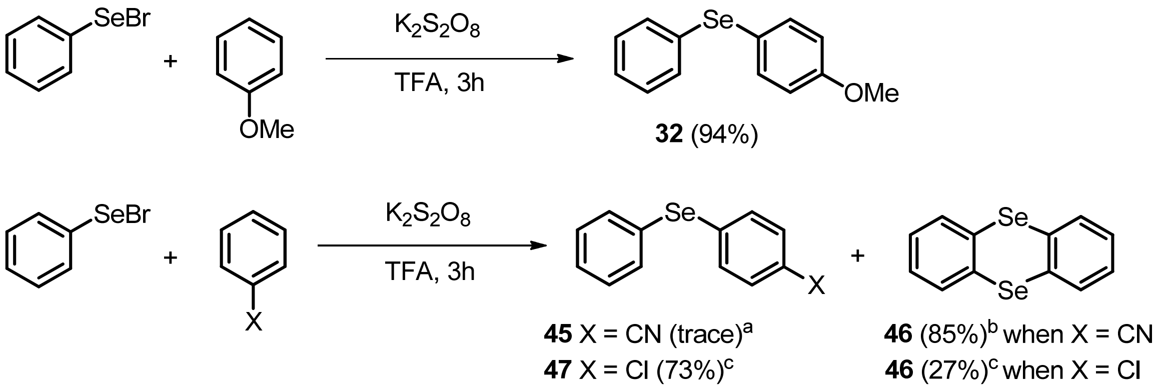


Figure 2. ^{77}Se NMR ($CDCl_3$) Spectra of the Proposed Intermediate

Mechanism of this reaction was also studied by ^{77}Se NMR spectroscopy by taking diphenyl diselenide as a substrate. Electronic nature of ^{77}Se nucleus in the organoselenium compounds can be very well correlated with its NMR chemical shift due to its high sensitivity in NMR. Moreover, based on ^{77}Se NMR study, it is possible to propose the structure of the intermediate involved in the reaction by comparing the ^{77}Se NMR chemical shift value with the related organoselenium compounds. Equimolar reaction mixture of diphenyl diselenide and potassium persulfate in TFA gave a signal at 788.4 ppm attributed to intermediate **III**. The intermediate **III** has been proposed by Tiecco *et al*. and also the electrophilic nature of selenium in the intermediate **III** is well illustrated in a series of electrophilic phenylselenation reactions with alkenes.[17] Nonetheless, characterization and electrophilic nature of intermediate **III** have not been studied by ^{77}Se NMR. ^{77}Se NMR chemical shift of proposed intermediate **III** was signficantly downfield shifted by 327 ppm as compared to the diphenyl diselenide (δ 461 ppm) and upfield shifted by 80 ppm as compared to phenylselenenyl bromide, PhSeBr (δ 869 ppm) and the related organoselenenyl bromides (δ 800±50 ppm).[18] Downfield ^{77}Se NMR chemical shift value clearly indicates a significant positive charge on the selenium nucleus which makes it a better electrophile for the selenation reaction. Reaction mixture of diphenyl diselenide and potassium persulfate in solvent DMSO-d_6 or $CDCl_3$ in the absence of TFA yielded no change in the ^{77}Se NMR chemical shift of diphenyl diselenide. Similarly, ^{77}Se NMR chemical shift remains unchanged in the absence of potassium persulfate, which suggests that the presence of TFA and potassium persulfate are crucial for the generation of $PhSe^+$ from diphenyl diselenide.

To see experimentally whether diaryl dichalcogenide serves as an electrophile in the reaction, phenylselenenyl bromide (PhSeBr) was used as a selenium source which could serve as a better electrophile (Scheme 4). Indeed, anisole reacted much faster with phenylselenenyl bromide and gave quantitative yield (94%) of diaryl selenide in 3 h.

Scheme 4. Synthesis of Diaryl Selenide using Phenylselenenyl Bromide



[a] Observed in the ES-MS spectra.[b] Isolated yield.[c] Relative ration of **46** and **47** was observed by GC-study.

We also studied the reaction of electron poor benzonitrile and chlorobenzene with phenylselenenyl bromide in TFA. Benzonitrile reacted sluggishly with phenylselenenyl bromide and expected selenide **45** was not isolated, but its presence was detected by ES-MS. However, the formation of selenanthrene **46** was observed quantitatively in the reaction. Chlorobenzene smoothly reacted with phenylselenenyl bromide and produced *para*-chlorophenyl phenyl selenide **47** in 73% yield along with the cyclized selenanthrene **46** in 27% yield, which was monitored by GC-MS study.

Summary

In conclusion, we have presented a transition metal free method for the synthesis of unsymmetrical diaryl sulfides from arenes and readily available diaryl disulfide substrates. Unsymmetrical diaryl sulfides having various functional groups have been synthesized using potassium persulfate in TFA at room temperature. Also, this methodology was successfully extended to the synthesis of diaryl selenides and tellurides. ^{77}Se NMR study of the reaction reveals that reaction proceeds by the generation of arylchalcogenium ion, which adds to arene leading to the carbon-chalcogen bond formation. This simple transition metal free methodology could be useful for the synthesis of substituted diaryl and arylalkyl chalcogenides from arenes using readily available reagent potassium persulfate.

Experimental Section

All NMR experiments were carried out on 400 MHz spectrometer in DMSO-d_6 or $CDCl_3$ and NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 (±0.06) ppm for ^{13}C, respectively) or DMSO-d_6 (2.50 ppm for ^{1}H and 39.50 ppm for ^{13}C, respectively). The ^{77}Se and ^{125}Te NMR spectra were obtained at 76.31 and 126.24 MHz, respectively, in $CDCl_3$ using diphenyl diselenide and diphenyl ditelluride as external standards. Chemical shifts are reported relative to dimethyl selenide (^{77}Se) and dimethyl telluride (^{125}Te) (0 ppm) by assuming that the resonance of the standards are at 461 and 421 ppm, respectively. High resolution mass spectra (HRMS) are reported for ions of ^{80}Se. Mass analysis is performed on quadruple-time of a flight (Q-TOF) mass spectrometer equipped with an ESI (+ve) or atmospheric pressure chemical ionization (APCI) source. Phenyl disulfide, 2,2'-dithiodibenzoic acid, and phenyl diselenide were used as received from Aldrich. Substituted aryl disulfides like benzyl disulfide, 4-methylphenyl disulfide, 4-methoxyphenyl disulfide, and 2-aminophenyl disulfide were prepared by the oxidation of respective thiols by using *tert*-butyl hydroperoxide in the presence of a catalytic amount of *N,N*-dimethylbenzylamine ditelluride. Silica gel (100-200 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates. Reaction mixture was stirred at room temperature.

General procedure for the synthesis of diaryl chalcogenides.

A single neck round bottom flask (5 ml) containing TFA (0.4 mL, 4.5 mmol) is charged with anisole (495 mg, 4.5 mmol), diphenyl disulfide (200 mg, 0.9 mmol), and potassium persulfate (495 mg, 1.8 mmol). The resulted reaction mixture was stirred for 16 h at room temperature. For the synthesis of compounds **18**, and **22-24**, reaction mixture was heated at 80 °C. The progress of the reaction was monitored by TLC. Reaction mixture was stirred for 8h (**3**, **6-8**, **12**, **13**, **15-17**, **19**, **22**, **24**, **27**, **36**, and **42**), 12h (**5**, **25**, **26**, **28**, **43**, and **44**), 16h (**1**, **2**, **4**, **9-11**, **14**, **18**, **20**, **21**, **23**, **29**, **30-35**, and **37-41**). After completion of the reaction, water (100 mL) was added to the brownish solid and stirred for 30 minutes. Reaction mixture was extracted with ethyl acetate (15 mL x 3), dried over Na_2SO_4, concentrated on rotary evaporator. Crude product was purified by column chromatography using silica gel as stationary phase and hexane as eluent to obtain diaryl sulfide **1** as colorless liquid. Yield 0.35 g, (89%). Compounds with COOH and NH_2 functional groups **22-24**, are obtained by carrying aqueous $NaHCO_3$ work-up and for tellurides **30**, **33**, and **41**, aqueous $NaHSO_3$ work-up is carried out.

(4-Methoxyphenyl)(phenyl)sulfane (1). Light yellow oil.[7a,19] Yield: 0.35 g (89%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.25 (m, 5H), 6.96 (d, *J* = 8.5 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 138.7, 135.4, 131.0, 129.0, 128.3, 125.8, 124.4, 115.1, 55.4. HRMS-ES$^+$ *m*/*z*: 216.0628 (calculated for $C_{13}H_{12}OS$: 216.0609).

(3-Bromo-4-methoxyphenyl)(phenyl)sulfane (2). White solid. Yield: 0.12 g (45%); mp 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.1 Hz, 1H), 7.65-7.61 (m, 2H), 7.59 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.52-7.46 (m, 3H), 6.96 (d, *J* = 8.5 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.2, 145.4, 138.1, 131.2, 130.0, 129.4, 125.9, 124.6, 112.9, 112.2, 56.5. HRMS-APCI$^+$ *m*/*z*: 293.9698 (calculated for $C_{13}H_{11}BrOS$: 293.9708).

Methyl(4-(phenylthio)phenyl)sulfane (3). Colorless oil.[20] Yield: 0.15 g (73%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.31 (m, 6H), 7.28-7.22 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 136.6, 132.4, 130.2, 129.2, 127.2, 126.8, 15.8. HRMS-ES$^+$ *m*/*z*: 232.0369 (calculated for $C_{13}H_{12}S_2$: 232.0375).

2-(Phenylthio)phenol (4a). Light brown oil.[21] Yield: 0.10 g (28%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.44-7.39 (m, 1H), 7.30-7.23 (m, 2H), 7.22 - 7.15 (m, 1H), 7.14 - 7.08 (m, 3H), 7.02 - 6.96 (m, 1H), 6.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 136.9, 135.9, 132.3, 129.2, 126.9, 126.2, 121.3, 116.3, 115.6. HRMS-ES$^+$ *m*/*z*: 201.0399 (calculated for $C_{12}H_{10}OS$ - H^+: 201.0369).

4-(Phenylthio)phenol (4b). Light brown oil.[7e,20] Yield: 0.18 g (64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.37 (dt, *J* = 8.5, 2.1 Hz, 2H), 7.30-7.24 (m, 2H), 7.22-7.15 (m, 3H), 6.88 - 6.84 (dt, *J* = 8.5, 2.0

Hz, 2H), 5.84 - 4.50 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 138.5, 135.6, 129.0, 128.3, 125.9, 124.5, 116.5. GCMS-ES$^+$ *m*/*z*: 202.0 (calculated for $C_{12}H_{10}OS$ - H^+: 202.0).

4-Methyl-2-(phenylthio)phenol (5). Light yellow oil.[22] Yield: 0.17 g (85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 1.5Hz, 1H), 7.18-7.12 (m, 2H), 7.11-7.03 (m, 2H), 7.03-6.98 (m, 2H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.27 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 136.9, 136.1, 133.0, 130.6, 129.2, 126.8, 126.0, 115.8, 115.3, 20.3. GCMS-ES$^+$ *m*/*z*: 216.0 (calculated for $C_{12}H_{12}OS$: 216.0).

4-(tert-Butyl)-2-(phenylthio)phenol (6). Light yellow solid.[21] Yield: 0.175 g (74%); mp 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.5 Hz, 1H), 7.48 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.32-7.26 (m, 2H), 7.22-7.17 (m, 1H), 7.16-7.11 (m, 2H), 7.08 (d, *J* = 8.6 Hz, 1H), 6.41(s, 1H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 144.3, 136.2, 133.6, 129.6, 129.2, 126.6, 126.0, 115.3, 115.1, 34.3, 31.5. HRMS-ES$^+$*m*/*z*: 259.1163 (calculated for $C_{16}H_{18}OS$ + H^+: 259.1151).

2-Bromo-6-(phenylthio)phenol (7). Brown oil. Yield: 0.13 g (52%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, J = 8.5, 2.1 Hz, 1H), 7.32-7.20 (m, 5H), 7.03 (d, *J* = 8.5 Hz, 1H), 5.76 (bs, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 137.2, 136.4, 134.3, 129.2, 129.2, 126.7, 126.5, 116.9, 110.7. HRMS-APCI$^+$ *m*/*z*: 280.9622 (calculated for $C_{12}H_{19}BrOS$ + H^+: 280.9630).

(4,5-Dimethoxy-1,2-phenylene)bis(phenylsulfane) (8). White solid.[23] Yield: 0.12 g (75%); mp 94-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 10H), 6.87 (s, 2H), 3.76 (s, 6). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 136.4, 129.9, 129.2, 129.1, 126.7, 116.1, 56.0. HRMS-ES$^+$*m*/*z*: 354.0738 (calculated for $C_{20}H_{17}O_2S_2$ + H^+: 354.0743).

(2,4-Dimethoxyphenyl)(phenyl)sulfane (9). Light yellow solid.[9i] Yield: 0.21 g (92%); mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.4Hz, 1H), 7.29-7.22 (m, 2H), 7.22-7.13 (m, 3H), 6.59-6.52 (m, 2H), 3.85 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 160.5, 137.9, 136.8, 128.8, 127.7, 125.5, 112.2, 105.5, 99.4, 56.0, 55.5. HRMS-ES$^+$ *m*/*z*: 269.0603 (calculated for $C_{14}H_{14}O_2S$ + Na^+: 269.0607).

2,4-(Dimethoxyphenyl)(4-methoxyphenyl)sulfane (10). Light yellow oil. Yield: 0.19 g (96%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* =8.0Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 12 Hz, 2H), 6.51 (d, *J* = 2.0 Hz, 1H), 6.45 (dd, *J* =8.0, 2.0 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7, 158.9, 158.8, 133.4, 132.7, 126.3, 115.8, 114.7, 105.2, 99.1, 55.9, 55.5, 55.3. HRMS-ES$^+$ *m*/*z*: 299.0709 (calculated for $C_{15}H_{16}O_3S$ + Na^+: 299.0712).

2,4-(Dimethoxyphenyl)(4-methylphenyl)sulfane (11). White solid.[9j] Yield: 0.3 g (94%); mp 71-73 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* =8.3Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.46 (dd, *J* =8.5, 2.5 Hz, 1H), 3.80 (d, *J* = 2.8 Hz, 6H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 159.9, 135.8, 135.5, 133.5, 129.7, 129.0, 113.6, 105.4, 99.2, 56.0, 21.0. GCMS-ES$^+$*m*/*z*: 260.1 (calculated for $C_{15}H_{16}O_2S$: 260.1).

(2,5-Dimethyl-1,4-phenylene)bis-(phenylsulfane) (12). White solid.[24] Yield: 0.16 g (55%); mp 55-57 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.35- 7.24 (m, 10H), 7.20 (s, 2H), 2.31 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 135.7, 134.4, 133.5, 129.9, 129.2, 126.6, 20.0. HRMS-ES$^+$*m*/*z*: 322.0854 (calculated for $C_{20}H_{18}S_2$: 322.0844).

(2,5-Dimethoxyphenyl)(phenyl)sulfane (13). White solid.[25] Yield: 0.2 g (86%); mp 61-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ7.45 (d, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30 (m, 2H), 6.88 (s, 1H), 6.75 (s, 1H), 3.86 (s, 3H), 3.59 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$)δ 151.3, 151.2, 134.4, 131.6, 129.2, 127.2, 126.8, 123.9, 115.2, 114.6. HRMS-APCI$^+$*m*/*z*: 246.0713 (calculated for $C_{14}H_{14}O_2S$: 246.0709).

Phenyl(2,3,5-trimethoxyphenyl)sulfane (14). White solid.[9i] Yield: 0.23 g (92%); mp 56-58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.07 (m, 2H), 7.05-6.97 (m, 3H), 6.83 (s, 1H), 6.47 (s, 1H), 3.80 (s, 3H), 3.69 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 150.8, 143.5, 137.3, 128.8, 127.6, 125.5, 118.9, 110.7, 98.0, 57.0, 56.5, 56.2. HRMS-ES$^+$ *m*/*z*: 299.0709 (calculated for $C_{15}H_{16}O_3S + Na^+$: 299.0712).

Mesityl(phenyl)sulfane (15). Colorless oil.[5o] Yield: 0.2 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 8.14 Hz, 2H), 7.13-7.08 (m,3H), 7.00 (d, *J* = 6.8 Hz, 2H), 2.46 (s, 3H), 2.39 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 139.3, 138.5, 129.4, 127.0, 125.5, 124.5, 21.76, 21.18. HRMS-APCI$^+$*m*/*z*: 229.1022 (calculated for $C_{15}H_{16}S + H^+$: 229.1045).

Mesityl(p-tolyl)sulfane (16). White solid.[9j] Yield: 0.22 g (75%); mp 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.07 (d, *J* = 6.0Hz, 4H), 6.98-6.87 (m, 2H), 2.49-2.31 (m, 12H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 139.1, 134.8, 134.3, 129.7, 129.4, 127.5, 125.8, 21.8, 21.2, 20.9. GCMS-ES$^+$ *m*/*z*: 242.1 (calculated for $C_{16}H_{18}S$: 242.1).

Mesityl(4-methoxyphenyl)sulfane (17). Colorless oil.[26] Yield: 145 mg (78%); ^{1}H NMR (400 MHz, $CDCl_3$)δ 7.09 (s, 2H), 7.03 (d, *J* = 8.8Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H), 2.52 (s, 6H), 2.41 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$)δ 157.5, 143.4, 140.0, 129.4, 128.5, 127.8, 114.7, 114.4, 55.3, 21.9, 21.2. GCMS-ES$^+$ *m*/*z*: 258.1 (calculated for $C_{15}H_{16}OS$: 258.1).

Synthesis of N,N-dimethyl-4-(phenylthio)aniline (18) and 4,4'-Methylenebis(N,N-dimethylaniline).

Phenyl disulfide 200 mg, (0.9mmol) was added into the flask containing TFA (0.5 mL), potassium persulfate 495 mg (1.83 mmol) and *N,N*-dimethylaniline 556 mg (4.58 mmol). The resulting reaction mixture was stirred for 24 h at 80 °C. After this, reaction mixture was poured into saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate (50 mL x 3), dried over Na_2SO_4, concentrated under *vacuo*. Column chromatography using hexane: ethyl acetate (9:1) gave two fractions; (i) *N,N*-dimethyl-4-(phenylthio)aniline **(18)**. Light green oil.[19] Yield: 60 mg (30%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.25-7.20 (m, 2H), 7.16-7.08 (m, 3H), 6.75 (d, *J* = 8.0 Hz, 2H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$)δ 150.9, 140.3, 136.1, 128.7, 126.9, 125.0, 117.5, 113.0, 40.3. HRMS-ES$^+$ *m*/*z*:

230.0999 (calculated for $C_{14}H_{15}NS + H^+$: 230.0998). (ii) 4,4’-Methylenebis(N,N-dimethylaniline). Yellow solid.[27] Yield: 116 mg (50%); mp 77-79 ºC. ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.0 Hz, 4H), 6.59 (d, *J* = 8.0 Hz, 4H), 3.70 (s, 2H), 2.79 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 130.4, 129.4, 113.1, 41.0, 39.9. HRMS-ES$^+$*m*/*z*: 255.1846 (calculated for $C_{17}H_{22}N_2 + H^+$: 255.1856).

(4-(*tert*-Butyl)-2,6-dimethylphenyl)(phenyl)sulfane (19). White solid. Yield: 0.18 g (72%); mp 63-65 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.19 (m, 4H), 7.11-7.04 (m, 1H), 6.99-6.95 (m, 2H), 2.46 (s, 6H), 1.31 (s, 9H); Other isomer: 2.36 (s, 6H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 143.3, 138.4, 128.9, 127.0, (d, 125.6, 125.6), 124.5, 123.2, 34.5, 31.4, 31.3, 22.1, 21.6. HRMS-APCI$^+$*m*/*z*: 271.1518 (calculated for $C_{18}H_{22}S + H^+$: 271.1515).

Benzyl(2,4-dimethoxyphenyl)sulfane (20). Light yellow oil. Yield: 0.21 g (68%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.17 (m, 6H), 6.48 (d, *J* = 2.6 Hz, 1H), 6.39 (dd, *J* = 8.5, 2.5 Hz, 1H), 4.00 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.1, 138.4, 135.2, 128.9, 128.3, 126.8, 114.1, 104.7, 99.0, 55.8, 55.4, 39.0. HRMS-ES$^+$*m*/*z*: 261.0938 (calculated for $C_{15}H_{16}O_2S + H^+$: 261.0944).

(3-Bromo-2,4,6-trimethylphenyl)(phenyl)sulfane (21). White solid. Yield: 0.21 g (76%); mp 45-47 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29-7.19 (m, 2H), 7.18-7.08 (m, 2H), 7.00-6.92 (d, *J* = 7.6 Hz, 2H), 2.69(s, 3H), 2.48 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.35, 142.57, 139.83, 137.84, 130.40, 129.3, 129.0, 125.9, 125.7, 124.9, 24.4, 23.1, 21.9. GCMS-ES$^+$ *m*/*z*: 306.0 (calculated for $C_{15}H_{15}BrS$: 306.0). HRMS-APCI$^+$ *m*/*z*: 307.0133 (calculated for $C_{15}H_{15}BrS + H^+$: 307.0151).

2-(Mesitylthio)benzoic acid (22). Light yellow solid. Yield: 0.1 g (55%); mp 308-310 °C. ^1H NMR (400 MHz, DMSO-*d*$_6$) δ 13.14 (bs, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.18-7.08 (m, 3H), 6.41(d, *J* =8.2 Hz, 1H), 2.30 (s, 3H), 2.26 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 167.9, 143.6, 141.9, 139.9, 133.0, 131.8, 130.0, 127.5, 127.3, 124.8, 124.5, 21.5, 21.2. HRMS-ES$^+$*m*/*z*: 295.0775 (calculated for $C_{16}H_{16}O_2S$ + Na: 295.0763).

2-(Mesitylthio)aniline (23). Dark green solid.[28] Yield: 0.19 g (48%); mp 67-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.95 (m, 3H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 4.4 Hz, 2H), 3.70-2.60 (bs, 1H), 2.40 (s, 6H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 143.1, 138.8, 129.4, 127.9, 127.5, 126.3, 121.6, 119.8, 115.5, 21.7, 21.1. GCMS-ES$^+$*m/z*: 243.1 (calculated for $C_{15}H_{17}NS$: 243.1).

2-((4-Methoxyphenyl)thio)benzoic acid (24). Light yellow semisolid.[29] Yield: 135 mg (54%); ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.14 (bs, 1H), 7.92 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.37-7.31 (m, 1H), 7.17(t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 160.8, 143.9, 137.9, 132.8, 131.4, 127.2, 126.4, 124.6, 122.5, 116.2, 55.8. HRMS-ES$^+$ *m/z*: 261.0585 (calculated for $C_{14}H_{12}O_3S + H^+$: 261.0580).

Phenyl(2,4,6-triisopropylphenyl)sulfane (25). Light yellow oil. Yield: 0.21 g (74%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 4H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.8Hz, 2H), 3.76 (septet, *J* = 6.8 Hz, 2H), 2.99 (septet, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.6Hz, 6H), 1.20 (d, *J* = 6.8Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 150.8, 140.3, 128.7, 125.4, 124.9, 124,3, 122.3, 34.4, 31.7, 24.3, 24.0. HRMS-APCI$^+$*m/z*: 313.1969 (calculated for $C_{21}H_{28}S + H^+$: 313.1984).

1-(Phenylthio)naphthalen-2-ol (26). White solid.[30] Yield: 0.14 g (62%); mp 63-65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.2Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.2Hz, 1H), 7.53 (t, *J* = 8.2 Hz, 1H), 7.40, (q, *J* = 8.2Hz, 2H), 7.20 (d, J= 11Hz, 3H), 7.15 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.2Hz. 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 135.5, 135.4, 132.9, 129.5, 129.2, 128.6, 128.0, 126.4, 125.9, 124.7, 123.9, 116.9, 108.1. HRMS-ES$^+$ *m/z*: 251.0544 (calculated for $C_{16}H_{12}OS - H^+$: 251.0525).

(Oxybis(3,1-phenylene))bis(phenylsulfane) (27). Colorless oil. Yield: 0.19 g (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 1H), 7.25-7.23 (m, 2H), 7.22-7.20 (m, 1H), 7.20-7.19 (m, 1H), 7.16-7.11 (m, 5H), 7.08-7.03 (m, 1H), 7.02-6.97 (m, 1H), 6.93-6.89 (m, 3H), 6.85-6.81 (m, 3H). ^{13}C NMR (100

MHz, $CDCl_3$)δ157.5, 156.7, 137.4, 134.3, 130.0, 129.6, 129.2, 128.3, 126.5, 123.9, 119.4. HRMS-ES$^+$*m*/*z*: 387.0869 (calculated for $C_{24}H_{18}OS_2 + H^+$: 387.0872).

2,7-Bis(phenylthio)naphthalene (28). White solid.[31] Yield: 0.24 g (76%); mp 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54-8.49 (m, 2H), 7.64-7.59 (m, 2H), 7.51 (s, 2H), 7.37-7.25 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 133.6, 133.1, 130.8, 130.3, 129.4, 127.4, 126.9, 126.1. ES-MS$^+$ *m*/*z*: 345.2 (calculated for $C_{22}H_{16}S_2 + H^+$: 345.2). GCMS-ES$^+$ *m*/*z*: 344.1 (calculated for $C_{22}H_{16}S_2$: 344.1).

2-(Phenylselanyl)phenol (29a). Brown oil.[32] Yield: 60 mg (36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 1H), 7.4 (t, *J* = 7.5 Hz, 1H), 7.22-7.30 (m, 5H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.47 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 138.0, 132.3, 130.8, 129.7, 129.5, 126.8, 121.3, 115.2, 114.8. HRMS-ES$^+$*m*/*z*: 248.9816 (calculated for $C_{12}H_{10}O\ ^{80}Se - H^+$: 248.9813). ^{77}Se NMR 247.4 ppm.

4-(Phenylselanyl)phenol (29b). Brown color semisolid.[7e] Yield: 78 mg (49%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.39 (m, 2H), 7.23-7.30 (m,3H), 6.82 (d, *J* = 7.8 Hz, 2H), 5.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 136.7, 133.0, 131.1, 129.3, 126.6, 120.3, 116.7. HRMS-ES$^+$*m*/*z*: 249.9894 (calculated for $C_{12}H_{10}O\ ^{80}Se$: 249.9892). ^{77}Se NMR δ 399.4.

4-(Phenyltellanyl)phenol (30). Brown color semisolid.[7e] Yield: 0.14 g (64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (bs, 1H), 7.62 (d, *J* = *8.0* Hz, 2H), 7.49 (d, *J* = *8.0* Hz, 2H), 7.21 (d, *J* = *8.0* Hz, 3H), 6.72 (d, *J* = *8.0* Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ.158.6, 141.0, 135.9, 129.9, 127.5, 117.7, 116.9, 101.1. ES-MS$^+$*m*/*z*: 299.9 (calculated for $C_{12}H_{10}O^{129}Te$: 299.9). ^{125}Te NMR δ 750.0.

2-(Hexylselanyl)phenol (31a). Yellow color oil. Yield: 60 mg (38%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7,1.6 Hz, 1H), 7.32-7.26 (m, 1H), 7.03 (dd, *J* = 8.1,1.2 Hz, 1H), 6.85 (dt, *J* = 7.4,1.3 Hz, 1H), 6.63(s, 1H), 2.73 (t, *J* = 7.5 Hz, 2H), 1.69-1.58 (m, 2H), 1.43-1.35 (m, 2H), 1.34-1.21 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 137.5, 131.3, 120.8, 115.5, 114.3, 31.2, 30.3, 29.9, 29.3, 22.5, 14.0. HRMS-ES$^+$ *m*/*z*: 259.0572 (calculated for $C_{12}H_{18}O^{80}Se + H^+$: 259.0596). ^{77}Se NMR δ 126.0.

4-(Hexylselanyl)phenol (31b). Brown oil. Yield: 74 mg (47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.41 (m, 2H), 6.79-6.75 (m, 2H), 5.45-4.65 (bs, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 1.71-1.62 (m, 2H), 1.43-1.36 (m, 2H), 1.31-1.27 (m, 4H), 0.92-0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 135.7, 120.4, 116.2, 31.3, 30.2, 29.7, 29.4, 29.2, 22.5, 14.0. HRMS-ES$^+$ *m*/*z*: 257.0448 (calculated for $C_{12}H_{18}O^{80}Se - H^+$: 257.0439). ^{77}Se NMR δ 281.8.

(4-Methoxyphenyl)(phenyl)selane (32). Colorless oil.[7a] Yield: 0.31 g (92%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.45 (m, 2H), 7.29 (m, 1H), 6.95 (d, *J* = 7.8 Hz, 2H), 3.87 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 136.6, 133.4, 131.0, 129.2, 126.5, 120.1, 115.2, 55.3. HRMS-ES$^+$ *m*/*z*: 264.0035 (calculated for $C_{13}H_{12}O\ ^{80}Se$: 264.0048). ^{77}Se NMR δ 399.2.

(4-Methoxyphenyl)(phenyl)tellane (33). White solid.[7f] Yield: 0.18 g (60%); mp 49-51 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = *8.0* Hz, 2H), 7.53 (td, *J* = *8.0* 2.0 Hz, 2H), 7.23 (m, 3H), 6.89 (d, *J* = *8.0* Hz, 3H), 3.76 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ. 160.2, 141.4, 136.4, 130.0, 127.8, 116.6, 116.3, 103.5, 55.5. GCMS-ES$^+$ *m*/*z*: 313.9 (calculated for $C_{13}H_{12}O^{129}Te$: 313.9). ^{125}Te NMR δ 657.6.

(2,4-Dimethoxyphenyl)(phenyl)selane (34). Light yellow oil.[33] Yield: 0.17 g (93%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.28 (m, 4H), 6.56 (s, 1H), 6.47 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 159.3, 135.3, 132.4, 131.2, 129.2, 126.9, 110.3, 105.7, 99.1, 56.0, 55.5. HRMS-ES$^+$ *m*/*z*: 294.0166 (calculated for $C_{14}H_{14}O_2\ ^{80}Se$: 294.0154). ^{77}Se NMR δ 333.7.

Mesityl(phenyl)selane (35). Colorless oil.[34] Yield: 0.33 g (95%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.26 (m, 5H), 7.09 (s, 2H), 2.54 (s, 6H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 139.1, 133.6, 129.2, 128.9, 128.5, 126.9, 125.4, 24.4, 21.2. HRMS-ES$^+$ *m*/*z*: 276.0407 (calculated for $C_{15}H_{16}\ ^{80}Se$: 276.0412). ^{77}Se NMR δ 289.0.

(3-Bromo-2,4,6-trimethylphenyl)(phenyl)selane (36). Light yellow oil. Yield: 0.14 g (62%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.20 (m, 1H), 7.17-7.18 (m, 1H), 7.14-7.17 (m, 1H), 7.12-7.14 (m, 1H), 7.08-7.11 (m, 2H), 2.74 (s, 3H), 2.45 (d, *J* = 2.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 142.4, 139.6, 133.1, 130.0, 129.5, 129.2, 128.6, 125.7, 125.2, 25.9, 24.4, 24.3. GCMS-ES$^+$*m*/*z*: 353.9 (calculated for $C_{15}H_{15}Br^{80}Se$: 353.9). HRMS-APCI$^+$*m*/*z*: 353.9509 (calculated for $C_{15}H_{15}Br^{80}Se$: 353.9514). ^{77}Se NMR δ 331.8.

(4-(tert-Butyl)-2,6-dimethylphenyl)(phenyl)selane (37). White solid. Yield: 0.28 g (94%); mp 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.27 (m, 7H), 2.55 (s, 6H), 1.4 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 143.3, 133.5, 129.1, 128.6, 126.9, 125.4, 125.2, 34.5, 31.3, 24.7. GCMS-ES$^+$*m*/*z*: 318.1 (calculated for $C_{18}H_{22}$ ^{80}Se: 318.08). HRMS-APCI$^+$*m*/*z*: 318.0862 (calculated for $C_{18}H_{22}$ ^{80}Se: 318.0882). ^{77}Se NMR δ 291.1.

Methyl(4-(phenylselanyl)phenyl)sulfane (38). Light yellow oil.[33] Yield: 0.1 g (55%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.60(m,2H), 7.27-7.43(m,4H), 7.10-7.27(m,3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 134.2, 132.4, 132.4, 129.4, 129.2, 127.3, 127.2, 15.8. HRMS-ES$^+$*m*/*z*: 279.9834 (calculated for $C_{13}H_{12}S^{80}Se$: 279.9819). ^{77}Se NMR δ 410.4.

Hexyl(4-methoxyphenyl)selane (39). Light yellow oil. Yield: 0.14 g (57%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.46 (m, 2H), 6.86-6.82 (m, 2H), 3.82(s, 3H), 2.84 (t, *J* = 7.5 Hz, 2H), 1.72-1.62 (m, 2H), 1.45-1.36 (m, 2H), 1.35-1.24 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 135.5, 120.3, 114.7, 55.3, 31.3, 30.2, 29.4, 29.2, 22.6, 14.0. HRMS-ES$^+$*m*/*z*: 272.0661 (calculated for $C_{13}H_{20}O^{80}Se$: 272.0674). ^{77}Se NMR δ 279.2.

4-(tert-Butyl)-2-(phenylselanyl)phenol (40). White color semisolid. Yield: 0.18 g (94%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.22-7.29 (m, 5H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.29 (s, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz,$CDCl_3$) δ 154.5, 144.3, 134.6, 131.1, 129.5, 129.4, 126.7, 114.5, 113.9, 34.2, 31.5. HRMS-ES$^+$ *m*/*z*: 305.0430 (calculated for $C_{16}H_{18}O^{80}Se–H^+$: 305.0440). ^{77}Se NMR 252.3.

4-(*tert*-Butyl)-2-(phenyltellanyl)phenol (41). Brown color semisolid. Yield: 0.18 g (71%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.80 (d, *J = 8.0* Hz, 2H), 7.44 (d, *J = 8.0* Hz, 1H), 7.35 (d, *J = 8.0* Hz, 2H), 7.06 (d, *J = 8.0* Hz, 1H), 6.82 (s, 1H), 6.72 (d, *J = 8.0* Hz, 1H), 1.04 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ. 154.7, 143.1, 140.6, 130.5, 130.2, 130.0, 125.5, 113.8, 112.8, 104.7, 34.1, 31.6. HRMS-APCI$^+$*m*/*z*: 355.0345 (calculated for $C_{16}H_{18}O^{129}Te – H^+$: 355.0337). ^{125}Te NMR δ 565.0.

(3-Phenoxyphenyl)(phenyl)selane (42). Colorless oil. Yield: 115 mg (82%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2H), 7.49-7.44 (m, 2H), 7.42-7.36 (m, 2H), 7.33-7.26 (m,3H), 7.17 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H). ^{13}C NMR (100 MHz,$CDCl_3$) δ 157.5, 156.6, 135.7, 132.2, 132.0, 129.9, 129.3, 127.0, 123.8, 123.6, 119.5, 119.3. HRMS-APCI$^+$*m*/*z*: 326.0203 (calculated for $C_{18}H_{14}O^{80}Se$: 326.0205). ^{77}Se NMR δ 404.6.

Naphthalen-1-yl(phenyl)selane (43). Light yellow oil.[7a] Yield: 0.19 g (67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.62 (m, 3H), 7.44-7.39 (m, 3H), 7.27-7.24 (m, 3H), 7.11-7.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.1, 134.2, 133.9, 131.7, 129.5, 129.4, 129.3, 129.2, 128.6, 127.7, 127.0, 126.8, 126.4, 126.1. ESMS-ES$^+$*m*/*z*: 301.0 (calculated for $C_{16}H_{12}{}^{80}Se$ + OH: 301.0); GCMS-ES$^+$*m*/*z*: 284.0 (calculated for $C_{16}H_{12}{}^{80}Se$: 284.0). ^{77}Se NMR δ 352.4. This compound **43** showed impurities in NMR (please see Figures S150-S152).

2,3-Dihydrobenzo[b]selenophene (44). A single neck round bottom flask (5 ml) containing TFA (0.6 mL) is charged with diphenylethyl selenide (184 mg, 0.5 mmol), and potassium persulfate (270 mg, 1.0 mmol). The resultant reaction mixture was stirred for 12 h at room temperature. After completion of the reaction, reaction mixture is poured into saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate (50 mL x 3), dried over Na_2SO_4, concentrated under *vacuo*. Column chromatography using hexane gave 2,3-dihydrobenzo[b]selenophene (**44**). Yellow oil.[15] Yield: 80 mg (40%); ^{1}H NMR (400

MHz, $CDCl_3$) δ 7.33-7.31(m, 1H), 7.17-7.15 (m, 1H), 7.09-7.03 (m, 2H), 3.37 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.0, 127.3, 125.7, 124.8, 124.7, 38.7, 26.6. HRMS-ES$^+$*m*/*z*: 183.9751 (calculated for $C_8H_8{}^{80}Se$: 183.9786).

Synthesis of (4-Methoxyphenyl)(phenyl)selane (32) using PhSeBr. Phenylselenenyl bromide 236 mg, (1.0 mmol) was added into the flask containing TFA (0.5 mL), potassium persulfate 270 mg (1.0 mmol) and anisole 540 mg (5.0 mmol). The resulting reaction mixture was stirred for 3 h. Then, reaction mixture was poured into saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate (50 mL x 3), dried over Na_2SO_4, concentrated under *vacuo*. Column chromatography using hexane gave mixture of (4-Methoxyphenyl)(phenyl)selane **32.** Colorless oil.[7f] Yield: 0.25 g (94%);

Selenanthrene (46) and (4-Chlorophenyl)(phenyl)selane (47). Phenylselenenyl bromide 236 mg, (1.0 mmol) was added into the flask containing TFA (0.5 mL), potassium persulfate 270 mg (1.0 mmol) and chlorobenzene 563 mg (5.0 mmol). The resulting reaction mixture was stirred for 3 h. The reaction mixture was poured into saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate (50 mL x 3), dried over Na_2SO_4, concentrated under *vacuo*. Column chromatography using hexane gave mixture of (4-chlorophenyl)(phenyl)selane **47** and selenanthrene **46.** GC-MS study shows 73% of **47** and 27% of **46** in the mixture. Analytical data of **47** and **46**; Yellow solid.[35] Yield: 0.41 g; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m), 7.40-7.35 (m), 7.30-7.27 (m), 7.25-7.22 (m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.4, 133.4, 132.6, 132.3, 129.7, 129.5, 122.4. GC-MS for **47**: retention time = 9.1 min, *m*/*z*: 267.9 (calculated for $C_{12}H_9Cl^{80}Se$: 267.9); GC-MS for **46**: retention time = 9.8 min, m/z: 311.8 (calculated for $C_{12}H_8{}^{80}Se_2$: 311.8). ^{77}Se NMR δ 473.6, 412.6.

Synthesis of Selenanthrene (46). Phenylselenenyl bromide 236 mg, (1.0 mmol) was added into the flask containing TFA (0.5 mL), potassium persulfate 270 mg (1.0 mmol) and benzonitrile 515 mg (5.0 mmol). The resulting reaction mixture was stirred for 3 h, poured into saturated aqueous $NaHCO_3$ solution, extracted with ethyl acetate (50 mL x 3), dried over Na_2SO_4, and concentrated under *vacuo*.

Column chromatography using hexane gave mixture of Selenanthrene **46.** Yellow solid.[36] Yield: 0.13 g (84%); mp 104-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 4H), 7.39-7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.4, 132.3, 129.5, 122.4. GCMS-ES$^+$ *m*/*z*: 311.8 (calculated for $C_{12}H_8{}^{80}Se_2$: 311.8). ^{77}Se NMR δ 473.7.

Synthesis and *in-situ* Characterization of Reaction Intermediates by ^{77}Se NMR. In a single necked flask (5 mL) containing TFA (0.3 mL), diphenyl diselenide (50 mg, 0.16 mmol) and potassium persulfate (43 mg, 0.16 mmol) were added and the resulted reaction mixture was stirred at room temperature for 12 h. After this, 0.1 mL of the reaction mixture was transferred to NMR tube containing 0.6 mL of $CDCl_3$. ^{77}Se NMR was recorded for 12 h and 2000 scans were made in -200 to 600 ppm range and 600 to 1400 ppm range. A peak at 788 ppm presumably due to intermediate **III** was observed. To understand the effect of TFA on chemical shift, ^{77}Se NMR experiment was also carried out on diphenyl diselenide in TFA using $CDCl_3$ without adding potassium persulfate. A peak at 460 ppm was observed which corresponds to diphenyl diselenide (461 ppm).

Acknowledgment. We are thankful to Department of Science and Technology (DST), New Delhi, India, Department of Atomic Energy (DAE-BRNS) Mumbai, Defence Research and Development Organization (DRDO) New Delhi and IISER Bhopal for financial support. CDP and SJB are grateful to CSIR-UGC New Delhi and IISER Bhopal, respectively, for fellowship. Authors acknowledge Dr. D. Chopra, IISER Bhopal for proof reading of the manuscript.

Supporting Information. ^{1}H, ^{13}C, ^{13}C DEPT-135 and ^{77}Se/ ^{125}Te NMR of diaryl chalcogenides (**1-47**), and selected NMR spectra for intermediate **III**, crystal structure data and CIF file for **22** (CCDC No. 897377). This material is available free of charge via the Internet at http://pubs.acs.org.

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