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A convenient and efficient copper-catalyzed synthesis of unsymmetrical and symmetrical diaryl chalcogenides from arylboronic acids in ethanol at room temperature

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ABSTRACT

A simple and convenient approach for the synthesis of unsymmetrical diaryl chalcogenides (Te, Se, and S) has been developed by copper-catalyzed cross-coupling reaction of organoboronic acid with diaryl dichalcogenide in ethanol using $NaBH_4$ in air or oxygen. The present methodology is highly practical for the synthesis of unsymmetrical diaryl tellurides with various functionalities such as $-NO_2$, $-F$, $-Br$, and $-COOH$ that have been obtained in good to excellent yields. Methodology is also effective for the synthesis of unsymmetrical diaryl selenides and sulfides. Moreover, symmetrical diaryl selenides have also been obtained from arylboronic acids using elemental selenium powder under optimized reaction conditions. The use of $NaBH_4$ is the key for the development of milder reaction conditions, which enable the construction of unsymmetrical diaryl chalcogenides from boronic acid substrates in ethanol at room temperature.

1. Introduction

Synthesis of unsymmetrical organochalcogenides (chalcogens S, Se, and Te) is an attractive area of research due to their usage as convenient intermediates and reagents in organic synthesis.[1,2] Apart from synthetic applications, organochalcogen structural motifs display important properties like fluorescence, biological activities and have applications in material sciences.[3] A number of methods are available in the literature for the synthesis of unsymmetrical chalcogenides making use of transition metal catalysts. Various metals including palladium, nickel, iron, rhodium, indium, and copper have been utilized to catalyze the reaction of aryl halides with thiol/seleno dichalcogenide.[4–6] Particular interest is the transition metal catalyzed synthesis of unsymmetrical diaryl tellurides. Although, the transition metal catalyzed synthesis of carbon–sulfur and carbon–selenium is very well established, however, catalytic methods for the synthesis of unsymmetrical diaryl tellurides are rare. Synthesis of diorgano tellurides is difficult attributed to weak tellurium–carbon bond, metallic character, and oxidizing nature of tellurium. Because of labile carbon–tellurium bond and metallic nature, synthesis of organotellurides is often sluggish and leads to undesired reaction mixture. Moreover, a stoichiometric amount of copper metal is used in the synthesis of symmetrical diaryl tellurides from diaryl ditellurides at ambient temperature.[7] Diaryl ditellurides are the precursors for the synthesis of unsymmetrical diaryl telluride; therefore, it is desirable to use low catalyst loading and low temperature to avoid undesired formation of symmetrical diaryl telluride. Similarly, organotellurium compounds often tend to convert into telluroxides under oxidative reaction conditions.[8d]

Organoboronic acids are widely used as coupling partners in various coupling reactions due to their commercial availability, stability, and compatibility with a variety of functional groups.[9] The first reaction of organoboronic acids with diaryl tellurides, selenides, and sulfides has been discovered by Wang and Taniguchi using CuI as a catalyst in DMSO at 100 °C.[10a,b] Subsequently various groups have synthesized unsymmetrical diaryl sulfides and selenides; however, not tellurides, using organoboronic acid and dichalcogenide/thiol with improved reaction conditions.[10] But all the developed methodologies associated with some disadvantages like limited substrate scope, high reaction temperature, expensive catalyst, toxic solvent, and longer reaction time.[10c,e,f]

Recently, a transition metal free synthesis of unsymmetrical diaryl chalcogenide from arene and dichalcogenides (S, Se, Te) has been studied by our group under oxidative condition using a persulfate oxidant in trifluoroacetic acid.[8d] However, methodology showed compatibility only with electron-rich arenes and also oxidation of tellurides into telluroxides were observed. Moreover, we have also developed potassium *tert*-butoxide mediated synthesis of

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unsymmetrical chalcogenides (S, Se) from dichalcogenides with bromo arenes in DMSO. This methodology is only used in the synthesis of sulfides and selenides and failed to provide unsymmetrical diaryl tellurides under similar conditions.[8e] As a part of our ongoing research devoted to the synthesis of unsymmetrical organochalcogenides using new benign and practical methods,[8] herein we wish to report a convenient and highly efficient copper-catalyzed cross-coupling of organoboronic acid with diaryl dichalcogenide in ethanol as a solvent at room temperature.

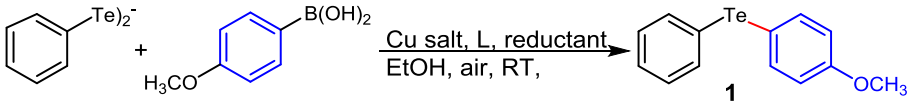
2. Results and discussion

For the optimization of reaction conditions, 4-methoxyphenylboronic acid and diphenyl ditelluride were chosen as the substrates and varied various parameters such as catalyst loading, solvent, and reductant. Among several catalysts screened (Table 1), CuI and $CuSO_4 \cdot 5H_2O$ were found to be most efficient for the carbon–tellurium bond formation. Due to low-cost and ready availability of $CuSO_4 \cdot 5H_2O$, we selected copper sulfate pentahydrate for rest of the reaction optimizations. Various bidentate ligands like 1,10-phenanthroline, 2,2′-bipyridyl, tetramethylethylenediamine (TMEDA), and dimethylethylenediamine (DMEDA) were employed for the reaction. Out of these 1,10-phenanthroline was found to be the most suitable ligand for the maximum outcome in the C–Te bond formation reaction. Both copper sulfate pentahydrate and 1,10-phenanthroline are indispensable in the reaction as the absence of either one failed to provide any diaryl telluride **1**.

provided practical yield of diaryl telluride **1**. The excess of $NaBH_4$ has the negative effect on yield of the product **1** as reaction gave 30% of biaryl side product 4,4′-dimethoxy-1,1′-biphenyl with 62% of product **1**, when 4 equiv of $NaBH_4$ was used (Table 1 entry 15). On the other hand, 1 equiv of $NaBH_4$ gave no side product, however, reaction completed in long time (Table 1 entry 15). $NaBH_4$ of 2.5 equiv noticed to be optimum for maximum yield of the unsymmetrical diaryl telluride **1**. Both air and oxygen were effective as an oxidant for the completion of reaction. The presence of oxidant is crucial in the reaction mixture as only trace amount of diaryl telluride **1** is formed in the absence of air. Next, triethylborane was used as an additive instead of $NaBH_4$ in the carbon–tellurium bond forming reaction. Reaction proceeded smoothly, however, required longer time (30 h) for the completion of the reaction (Table 1 entry 16). Sodium hydride was also screened in the reaction and yielded 59% of desired product **1** (Table 1 entry 17).

In order to evaluate the scope and limitation of this protocol, we explored the generality of our methodology with substituted arylboronic acid substrates (Table 2). In general both electron-poor and electron-rich substrates afforded good to excellent yields of the corresponding unsymmetrical diaryl tellurides (**1**–**15**). Several functional groups such as –COMe, –CN, $-CH_3$, –OMe, –COOH, $-NO_2$, –F, –Cl, and –Br showed compatibility with the developed protocol. Also heteroaryl substrate 3-pyridineboronic acid and 2-methoxy-5-(phenyltellanyl)pyridine gave corresponding tellurides **18** and **20** in 71% and 67% yields (Table 2, entries 17 and 20). Other aromatic boronic acids such as 1-naphthaleneboronic and 2-

Table 1
Optimization of reaction conditions[a]



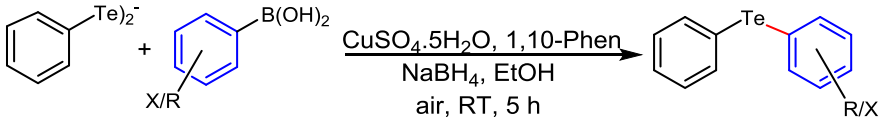
Entry	Copper salt (mol %)[b]	Ligand (L)	Reductant[c]	Time (h)	Yield[d] (%)
1	Cu_2O	1,10-Phen	$NaBH_4$	5	55
2	$Cu(OAc)_2.H_2O$	1,10-Phen	$NaBH_4$	5	51
3	Cu-Powder	1,10-Phen	$NaBH_4$	6	23
4	*CuI*	*1,10-Phen*	*$NaBH_4$*	*5*	*92*
5[e]	CuI	1,10-Phen	$NaBH_4$	8	Trace
6	$CuSO_4$	1,10-Phen	$NaBH_4$	5	81
7	*$CuSO_4 \cdot 5H_2O$*	*1,10-Phen*	*$NaBH_4$*	*5*	*90*
8	$CuSO_4 \cdot 5H_2O$	Bipyridyl	Cs_2CO_3	5	49
9	$CuSO_4 \cdot 5H_2O$	TMEDA	KO^tBu	5	39
10	$CuSO_4 \cdot 5H_2O$	DMEDA	$NaBH_4$	5	34
11	$CuSO_4 \cdot 5H_2O$	1,10-Phen	Na_2CO_3	5	62
12	$CuSO_4 \cdot 5H_2O$	1,10-Phen	—	24	Nil
13	$CuSO_4 \cdot 5H_2O$	—	$NaBH_4$	24	10
14	—	1,10-Phen	$NaBH_4$	24	Nil
15	$CuSO_4 \cdot 5H_2O$	1,10-Phen	$NaBH_4$	—	85,[f] 62[g]
16	$CuSO_4 \cdot 5H_2O$	1,10-Phen	$B(C_2H_5)_3$[h]	30	60
17	$CuSO_4 \cdot 5H_2O$	1,10-Phen	NaH	8	59

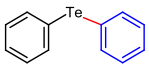
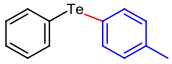
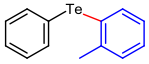
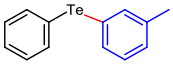
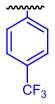
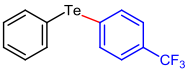
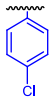
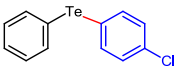
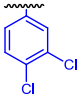
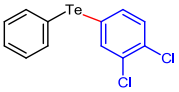
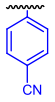
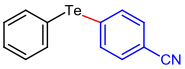
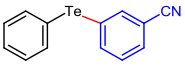
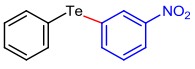
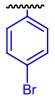
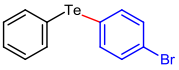
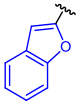
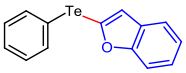
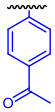
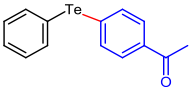
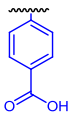
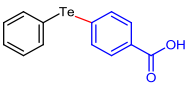
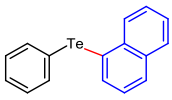
[a] Reaction was carried out at 0.5 mmol scale using 0.5 mmol of diphenyl ditelluride and 1.2 mmol of 4-methoxyphenylboronic acid in 3 mL of ethanol at room temperature.
[b] Catalyst of 5 mol %used.
[c] Reductant of 2–2.5 equiv used.
[d] Isolated yield based on diphenyl ditelluride.
[e] Reaction carried out in DMSO as solvent.
[f] Reaction mixture stirred for 14 h using 1 equiv $NaBH_4$.
[g] Reaction was carried out with 4 equiv of $NaBH_4$ for 3 h.
[h] Solution of 1 M $B(C_2H_5)_3$ in THF was used.

We have also screened various reductants in the optimization of reaction conditions. Additives such as Mg, Al, and Zn failed to improve the outcome of the reaction. Similarly, KO^tBu and Cs_2CO_3 bases were noticed to be ineffective (desired telluride **1** obtained in 39% and 49%, respectively) under our reaction conditions. Sodium carbonate provided 62% yield of telluride **1**. The use of $NaBH_4$

naphathaleneboronic acids furnished the corresponding naphthyl tellurides **16** and **17** in 82 and 91% yields, respectively (Table 2, entries 15 and 16). Next, we attempted the reaction of alkyl isopropyl boronic acid with diphenyl ditelluride under optimized condition. Unfortunately reaction did not afford the isopropyl phenyl telluride.

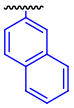
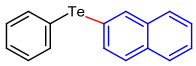
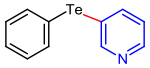
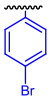
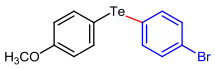
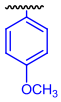
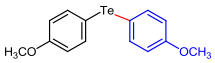
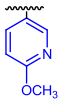
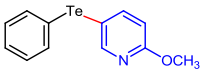
Table 2
$CuSO_4 \cdot 5H_2O$ catalyzed coupling of diaryl ditelluride with organoboronic acid



Entry	Boronic acid	Telluride		Yield (%)
1			**2**	98
2			**3**	93
3			**4**	90
4			**5**	91
5			**6**	81
6			**7**	89
7			**8**	85
8			**9**	88
9			**10**	87
10			**11**	79
11			**12**	82
12			**13**	91
13			**14**	82
14			**15**	40 (68)[a]
15			**16**	82

(*continued on next page*)

Table 2 (*continued*)

Entry	Boronic acid	Telluride		Yield (%)
16			**17**	91
17			**18**	71
18[b]			**19**	88
19[b]			**20**	85
20			**21**	67

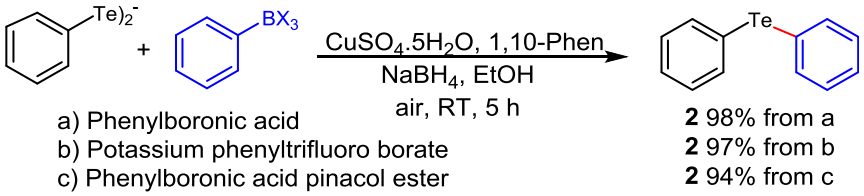
[a] CuI used as catalyst.
[b] 1,2-Bis(4-methoxyphenyl)ditellane was used.

We have also studied different arylboronic substrates with ditelluride to see the compatibility of various arylboronic substrates (Scheme 1). Indeed, diphenyl ditelluride coupled with potassium phenyltrifluoroborate and phenylboronic acid pinacol ester under optimized reaction conditions and provided comparable yields of diphenyl telluride (97% and 94% vs 98%). After exploiting various arylboronic substrates, we attempted to study 4-methoxyiodoanisole as a substrate under optimized reaction conditions. Unfortunately, reaction failed to give unsymmetrical diaryl telluride under optimized reaction conditions and presumably due to poor reactivity of aryl iodide.

To further demonstrate the practicability of the given procedure, we tested the synthesis of symmetrical diaryl selenides with selenium powder and organoboronic acids. The symmetrical diaryl selenides **22** and **55**–**58** were produced in good yields as mentioned in Table 5.

3. Mechanism

A plausible mechanism with two paths I and II is depicted in Scheme 2. Diaryl dichalcogenide reduced by $NaBH_4$ leading sodium chalcogenolate, which involve in both the paths I and II. In path I,

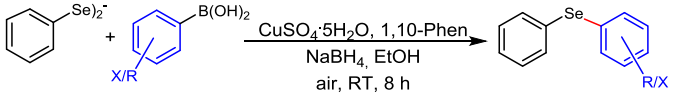


Scheme 1. Coupling with different boronic acids.

Then, we next turned our attention to explore the same protocol for the synthesis of diaryl selenides and sulfides using various organoboronic acids and diaryldiselenide/disulfides (Tables 3 and 4). As expected, unsymmetrical monoselenides **22**–**42** were obtained in good yields, which were not affected by the nature or steric hindrance of substituted groups near to reaction center in the organoboronic acid.

The reaction of organoboronic acids with diaryldisulfides furnished low yield of corresponding product compared to diselenides and ditellurides. *ortho*-Aminosubstituted disulfide has shown good compatibility with the arylboronic acids under optimization reaction conditions (entries 1–7, Table 4). In a separate experiment we found that the rate of the reaction in the order of Te>Se>S when reaction between 4-methoxyphenylboronic acid and diphenyldiselenide/telluride/sulfide was carried out. This is probably due to the stronger S–S bond present in diaryl disulfide or could be due to poor nucleophilic nature of arylthiolate (Ars^-).[10f]

Table 3
$CuSO_4 \cdot 5H_2O$ catalyzed coupling of diphenyldiselenide with organoboronic acids



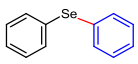
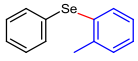
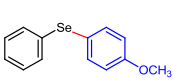
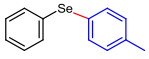
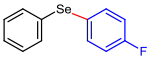
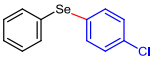
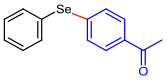
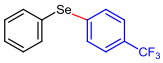
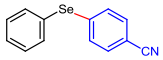
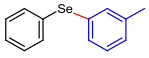
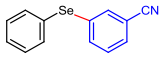
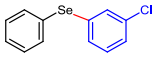
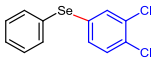
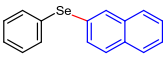
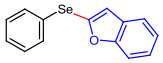
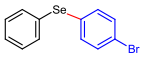
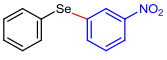
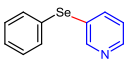
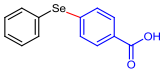
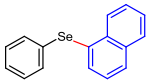
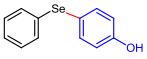
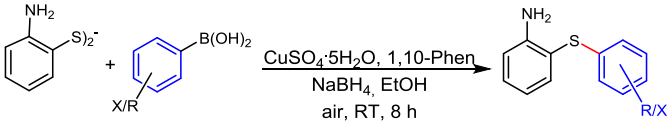
Entry	Boronic acid	Selenide		Yield (%)
1			**22**	96
2			**23**	89
3			**24**	92

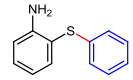
Table 3 (*continued*)

Entry	Boronic acid	Selenide		Yield (%)
4			**25**	94
5			**26**	82
6			**27**	89
7			**28**	68
8			**29**	89
9			**30**	87
10			**31**	93
11			**32**	82
12			**33**	88
13			**34**	79
14			**35**	76
15			**36**	92
16			**37**	86
17			**38**	79
18			**39**	63
19			**40**	46 (69)[a]
20			**41**	82
21			**42**	61

[a] CuI used as catalyst.

Table 4
$CuSO_4 \cdot 5H_2O$ catalyzed coupling of 2,2′-disulfanediyldianiline with arylboronic acid



Entry	Substrate	Arylsulfide		Yield (%)
1			**43**	82
2			**44**	71
3			**45**	73
4			**46**	86
5			**47**	80
6			**48**	79
7			**49**	71
8			**50**	77
9[a]			**51**	68

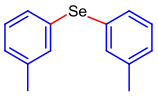
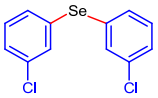
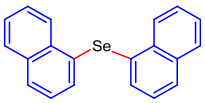
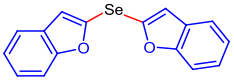
[a] 1,2-Bis(4-methoxyphenyl)disulfane was used.

Table 5
Synthesis of symmetrical diaryl selenides

Entry	Diarylselenide		Yield (%)
1		**22**	93
2		**52**	82
3		**53**	61
4		**54**	72

(*continued on next page*)

Table 5 (*continued*)

Entry	Diarylselenide		Yield (%)
5		**55**	83
6		**56**	69
7		**57**	76
8		**58**	59

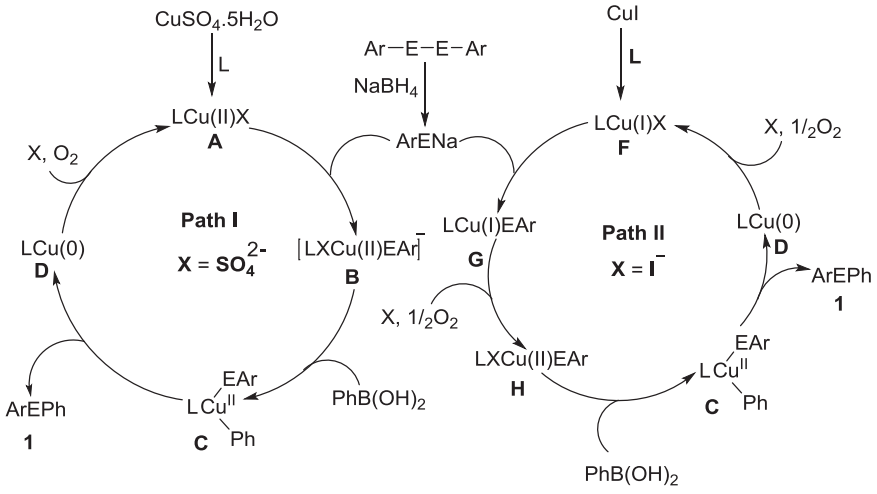
4. Conclusions

In summary, we have developed a convenient and highly efficient copper-catalyzed cross-coupling reaction of organoboronic acid with diaryl dichalcogenide in ethanol at room temperature. A wide variety of organoboronic acids with different substituted groups afforded the desired unsymmetrical diaryl chalcogenides in good to excellent yields. Also synthesis of symmetrical diaryl selenides has been achieved under optimized reaction conditions from selenium powder and arylboronic acids. Currently, we are exploring the synthesis of key synthetic precursors diaryl dichalcogenides from boronic acid substrates.

5. Experimental section

5.1. General method for the synthesis of unsymmetrical chalcogenides

In a 10 mL capacity round bottom flask diphenylditelluride (202 mg, 0.5 mmol) and sodium borohydride (48 mg, 1.25 mmol)



Scheme 2. Proposed reaction mechanism.

chalcogenolate ion may undergo ligation with the Cu(II) catalyst **A** and forms copper–chalcogenolate intermediate **B**, which may react with phenylboronic acid via trans-metalation to produce intermediate **C**. Reductive elimination could give desired telluride **1** and Cu(0). Copper(II) may be regenerated back through oxidation by air or oxygen and thus complete the catalytic cycle.[10k] In path II, chalcogenolate ion can undergo ligation with the Cu(I) catalyst **F** and forms copper–chalcogenolate intermediate **G**, which may undergo oxidation from Cu(I) to Cu(II) in the presence of oxygen forming intermediate **H**. Subsequently, trans-metalation of the aryl group from boronic acid to the intermediate **H** could give **C**. Reductive elimination of **C** may be led to the formation of the desired telluride **1** and copper(0) **D**. Finally, Cu(0) oxidizes to Cu(I) in the presence of oxygen.[10a,b]

It is worth noticing the involvement of boron in the reaction. Triethylborane assists the formation of carbon–tellurium bond (vide supra, Table 1 entry 16). On the other hand, sodium hydride, which does not have a boron atom is not an efficient promoter for the carbon–tellurium bond formation. It seems that sodium borohydride not only act as a reductant but also act as Lewis acid by interacting with the tellurium center. This interaction between boron and tellurium may facilitate reductive elimination and hence facile formation of diaryl telluride **1**.

were added in ethanol (3 mL). Reaction mixture was stirred at room temperature for 10 min under nitrogen atmosphere. Then, $CuSO_4 \cdot 5H_2O$ (0.025 mmol, 7 mg), 1,10-phenanthroline (0.025 mmol, 6 mg), and (4-methoxyphenyl) boronic acid (183 mg, 1.2 mmol) were added sequentially. Reaction mixture was stirred in air for 5 h. Progress of reaction was monitored by TLC. Then, reaction mixture was poured in water (25 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layer was dried over (Na_2SO_4), evaporated under reduced pressure at 40 °C. Crude mixture was purified by column chromatography (hexane/EtOAc, 9.5:0.5) to provide the pure (4-mhethoxyphenyl)(phenyl)tellane **1** as a white solid; yield: 282 mg (90%). Similar procedure was followed for the synthesis of tellurides **2**–**21**, selenides **22**–**42**, sulfides **43**–**51** listed in Tables 2–4. Synthesized compounds were characterized by ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR and mass spectrometry and spectroscopic data appended below.

*5.1.1. 4-Methoxyphenyl)(phenyl)tellane (**1**).*[10h] R_f=0.4 (1:9, ethyl acetate/hexane); white solid; yield 0.29 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J=8.6 Hz, 2H), 7.58 (m, 2H), 7.20 (m, 3H), 6.80 (d, J=8.6 Hz, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 141.2, 136.5, 129.4, 127.3, 116.0, 115.6, 103.3, 55.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 664.9.

*5.1.2. Diphenyltellane (**2**).*[10c] R_f=0.6 (hexane); liquid; yield 0.28 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J=6.8 Hz, 4H), 7.30 (t, J=6.8 Hz, 2H), 7.22 (t, J=6.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 129.5, 127.9, 114.4; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 689.8.

*5.1.3. Phenyl(p-tolyl)tellane (**3**).*[14] R_f=0.6 (hexane); liquid; yield 0.27 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J=7.9, 1.3 Hz, 4H), 7.30–7.28 (m, 1H), 7.26–7.22 (m, 2H), 7.10 (d, J=7.6 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.1, 137.3, 130.5, 129.5, 127.6, 115.3, 110.3, 21.3; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 674.8.

*5.1.4. Phenyl(o-tolyl)tellane (**4**).*[10c] R_f=0.6 (hexane); liquid; yield 0.90 g (90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J=8.2, 1.3 Hz, 2H), 7.55 (d, J=7.6 Hz, 1H), 7.39–7.35 (m, 1H), 7.31–7.24 (m, 4H), 7.02 (t, J=7.2 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 138.7, 137.5, 129.7, 129.4, 128.2, 128.1, 126.8, 126.1, 119.3, 114.1; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 591.3.

*5.1.5. Phenyl(m-tolyl)tellane (**5**).*[10c] R_f=0.6 (hexane); liquid; yield 0.27 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m,2H), 7.57 (s, 1H), 7.50 (m, 1H), 7.29–7.25 (m, 1H), 7.20 (t, J=7.4 Hz, 2H), 7.11–7.09 (m, 2H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 128.8, 137.8, 135.2, 129.5, 129.3, 128.8, 127.7, 114.8, 114.4, 21.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 685.2.

*5.1.6. Phenyl(4-(trifluoromethyl)phenyl)tellane (**6**).*[6b] R_f=0.6 (hexane); liquid; yield 0.28 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.65 (d, J=8.2 Hz, 2H), 7.41–7.35 (m, 3H), 7.29–7.25 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.0, 136.4, 129.9, 128.7, 125.9 (q), 122.8, 121.0, 113.3, ^{125}Te NMR (126 MHz, $CDCl_3$) δ 709.3.

*5.1.7. (4-Chlorophenyl)(phenyl)tellane (**7**).*[10c] R_f=0.7 (hexane); liquid; yield 0.28 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J=8.2, 1.3 Hz, 2H), 7.63 (d, J=8.2 Hz, 2H), 7.36–7.24 (m, 1H), 7.27 (d, J=7.8 Hz, 2H), 7.22–7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 138.2, 134.4, 129.8, 129.7, 128.1, 114.4, 112.4; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 694.5.

*5.1.8. (3,4-Dichlorophenyl)(phenyl)tellane (**8**).* R_f=0.6 (hexane); liquid; yield 0.30 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H), 7.69 (d, J=1.6 Hz, 1H), 7.41 (dd, J=8.3, 1.6 Hz, 1H), 7.34 (m, 1H), 7.28–7.21 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 136.5, 133.3, 132.3, 131.2, 129.8, 128.6, 113.8, 113.7; ^{125}Te NMR (126 M Hz, $CDCl_3$) δ 720.7; HRMS (APCI) m/z 352.9134, calcd for $C_{12}H_8Cl_2Te$+H: 352.9143.

*5.1.9. 4-(Phenyltellanyl)benzonitrile (**9**).*[10l] R_f=0.3 (1:9, ethyl acetate/hexane); yellow solid; yield 0.27 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (m, 2H), 7.54 (d, J=8.0 Hz, 2H), 7.42–7.36 (m, 3H), 7.30 (t, J=7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 135.7, 132.2, 130.1, 129.2, 124.3, 118.7, 112.8, 110.6; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 725.6.

*5.1.10. 3-(Phenyltellanyl)benzonitrile (**10**).*[14] R_f=0.3 (1:9, ethyl acetate/hexane); yellow solid at 0 °C; yield 0.27 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.76 (m, 4H), 7.49 (d, J=7.5 Hz, 1H), 7.39–7.34 (m, 1H), 7.29–7.22 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.5, 139.4, 130.9, 130.0, 129.6, 128.9, 118.2, 116.8, 113.6, 113.1; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 727.4.

*5.1.11. (3-Nitrophenyl)(phenyl)tellane (**11**).*[12] R_f=0.4 (1:9, ethyl acetate/hexane); yellow liquid; yield 0.25 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.06–8.04 (m, 1H), 7.84 (dt, J=7.6, 1.1 Hz, 1H), 7.81–7.79 (m, 2H), 7.37 (t, J=7.4, 1H), 7.33–7.26 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.3, 139.5, 131.0, 130.0, 129.9, 129.0, 122.4, 116.9, 113.1; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 735.8.

*5.1.12. (4-Bromophenyl)(phenyl)tellane (**12**).*[10h] R_f=0.6 (hexane); liquid; yield 0.29 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.68 (m, 2H), 7.50 (d, J=8.3 Hz, 2H), 7.32–7.28 (m, 3H), 7.24–7.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.3, 132.6, 129.7, 128.2, 122.5, 114.3, 113.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 695.4.

*5.1.13. 2-(Phenyltellanyl)benzofuran (**13**).* R_f=0.3 (1:9 ethyl acetate/hexane); white solid; yield 0.29 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J=8.2, 1.3 Hz, 2H), 7.59 (d, J=8.2 Hz, 1H), 7.55 (d, J=8.2 Hz, 1H), 7.33–7.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 137.2, 129.7, 128.9, 128.2, 127.0, 124.8, 122.8, 122.4, 120.5, 114.1, 111.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 557.8; HRMS (APCI) m/z 323.9787, calcd for $C_{14}H_{10}OTe$+H: 323.9793.

*5.1.14. 1-(4-(Phenyltellanyl)phenyl)ethanone (**14**).*[10l] R_f=0.4 (1:9, ethyl acetate/hexane); yellow solid; yield 0.27 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.4 Hz, 2H), 7.59 (d, J=8.4 Hz, 2H), 7.36 (t, J=7.6 Hz, 1H), 7.2–7.24 (m, 2H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 139.6, 136.0, 135.9, 129.9, 128.8, 128.7, 123.6, 113.3, 26.5; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 703.9; HRMS (APCI) m/z 326.9994, calcd for $C_{13}H_{12}OTe$+H: 327.0024.

*5.1.15. 4-(Phenyltellanyl)benzoic acid (**15**).*[10h] R_f=0.3 (2:8, ethyl acetate/hexane); white solid; yield 0.13 g (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.80 (m, 4H), 7.59 (d, J=8.5 Hz, 2H), 7.38 (t, J=7.2 Hz, 1H), 7.28 (t, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 139.7, 135.6, 130.6, 129.9, 128.8, 128.0, 125.2, 113.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 707.8.

*5.1.16. Naphthalen-1-yl(phenyl)tellane (**16**).*[6b] R_f=0.5 (hexane); liquid; yield 0.22 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19–8.08 (m, 1H), 7.91 (dd, J=7.1, 0.9 Hz, 1H), 7.76–7.71 (m, 2H), 7.54–7.52 (m, 2H), 7.45–7.39 (m, 2H), 7.22–7.14 (m, 2H), 7.08 (t, J=7.1 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 137.6, 137.5, 135.9, 133.7, 131.7, 129.5, 128.8, 127.7, 127.0, 126.6, 126.3, 117.8, 114.8; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 570.8.

*5.1.17. Naphthalen-2-yl(phenyl)tellane (**17**).*[10] R_f=0.4 (hexane); yellow solid; yield 0.30 g (91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.79 (m, 1H), 7.74–7.71 (m, 4H), 7.66 (d, J=8.4 Hz, 1H), 7,49–7.46 (m, 2H), 7.30–7.26 (m, 1H), 7.22 (t, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 137.8, 134.8, 134.3, 132.6, 129.6, 128.7, 128.9, 127.8, 127.4, 126.4, 126.3, 114.8, 112.0; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 691.9.

*5.1.18. 3-(Phenyltellanyl)pyridine (**18**).*[5g] R_f=0.4 (1:9, ethyl acetate/hexane); semisolid; yield 0.20 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 8.42 (dd, J=4.7, 1.2 Hz, 1H), 7.88 (td, J=7.7, 1.7 Hz, 1H), 7.65 (d, J=8.2 Hz, 2H), 7.25 (t, J=7.4 Hz, 1H), 7.19–7.14 (m, 2H), 7.09–7.06 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 148.6, 144.9, 138.5, 129.7, 128.4, 124.7, 113.3, 112.5; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 652.5.

*5.1.19. (4-Bromophenyl)(4-methoxyphenyl)tellane (**19**).*[19] R_f=0.5 (1:9, ethyl acetate/hexane); light yellow solid; yield 0.34 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J=8.6 Hz, 2H), 7.37 (d, J=8.6 Hz, 2H), 7.26 (d, J=8.5 Hz, 2H), 6.79 (d, J=8.5 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 141.4, 137.8, 132.4, 121.8, 115.7, 114.5, 102.9, 55.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 671.0.

*5.1.20. Bis(4-methoxyphenyl)tellane (**20**).*[2f] R_f=0.4 (1:9, ethyl acetate/hexane); white solid; yield 0.34 g (85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J=8.6 Hz, 4H), 6.75 (d, J=8.6 Hz, 4H), 3.76 (s, 6H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 139.7, 115.4, 104.3, 55.2; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 649.8.

*5.1.21. 2-Methoxy-5-(phenyltellanyl)pyridine (**21**).* R_f=0.5 (1:9, ethyl acetate/hexane); solid; yield 0.21 g (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J=1.7 Hz, 1H), 7.92 (dd, J=8.5, 2.1 Hz, 1H), 7.58–7.56 (m, 2H), 7.21 (d, J=7.0 Hz, 1H), 7.16 (t, J=7.4 Hz, 2H), 6.64 (d, J=8.5 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 156.6, 149.2, 136.8, 129.5, 127.7, 114.9, 112.6, 101.4, 53.5; ^{125}Te NMR (126 MHz, $CDCl_3$) δ 614.2.

*5.1.22. Diphenylselane (**22**).*[5g] R_f=0.6 (hexane); liquid; yield 0.22 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.45 (m, 4H), 7.27 7.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 131.1, 129.3, 127.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 416.3; GC/MS (EI): t_R=6.66 min, m/z=234.

*5.1.23. Phenyl(o-tolyl)selane (**23**).*[5g] R_f=0.6 (hexane); liquid; yield 0.22 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.39 (m, 2H), 7.34 (d, J=7.9 Hz, 1H), 7.29–7.18 (m, 5H), 7.06 (td, J=7.9, 1.9 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 133.7, 132.8, 131.7, 130.8, 130.3, 129.4, 127.8, 127.2, 126.7, 22.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 375.4.

*5.1.24. 4-Methoxyphenyl(phenyl)selane (**24**).*[10m] R_f=0.4 (1:9, ethyl acetate/hexane); liquid; yield 0.24 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.49 (m, 2H), 7.34–7.31 (m, 2H), 7.23–7.17 (m, 3H), 6.84 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 136.5, 133.2, 130.9, 129.2, 126.5, 120.0, 115.1, 55.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 400.7; HRMS (APCI) m/z 264.0068, calcd for $C_{13}H_{12}OSe$: 264.0048.

*5.1.25. Phenyl(p-tolyl)selane (**25**).*[10m] R_f=0.5 (hexane); liquid; yield 0.23 g (94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.44 (m, 4H), 7.25 (m, 3H), 7.13 (d, J=7.9 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 134.0, 132.2, 132.1, 130.3, 129.3, 126.9, 126.8, 21.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 408.1; HRMS (APCI) m/z 248.0115, calcd for $C_{13}H_{12}Se$: 248.0099.

*5.1.26. (4-Fluorophenyl)(phenyl)selane (**26**).*[10m] R_f=0.7 (hexane); liquid yield 0.21 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2H), 7.42–7.40 (m, 2H), 7.29–7.25 (m, 3H), 6.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 161.3, 135.8 (d), 132.2, 131.7, 129.3, 127.2, 125.3, 125.2, 116.7, 116.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 410.1; HRMS (APCI) m/z 251.9843, calcd for $C_{12}H_9FSe$: 251.9848.

*5.1.27. 4-Chlorophenyl(phenyl)selane (**27**).*[10m] R_f=0.6 (hexane); liquid; yield 0.24 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (m, 2H), 7.41–7.39 (m, 2H), 7.31 (m, 3H), 7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.9, 133.6, 133.3, 130.8, 129.7, 129.6, 127.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 415.0.

*5.1.28. 1-(4-(Phenylselanyl)phenyl)ethanone (**28**).*[10l] R_f=0.3 (1:9, ethyl acetate/hexane); white solid; yield 0.19 g (68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J=8.5 Hz. 2H), 7.57 (m, 2H), 7.33 (m, 5H), 2.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 140.3, 135.2, 135.1, 130.3, 129.7, 128.9, 128.6, 128.5, 29.7 (grease), 26.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 428.2; HRMS (APCI) m/z 277.0142, calcd for $C_{14}H_{12}OSe$+H: 277.0127.

*5.1.29. Phenyl(4-(trifluoromethyl)phenyl)selane (**29**).*[10m] R_f=0.6 (hexane); liquid; yield 0.27 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.57 (m, 2H), 7.45 (m, 4H), 7.38–7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 134.9, 131.0, 129.8, 128.7, 128.5, 125.9 (q), 125.5, 122.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ426.2; HRMS (APCI) m/z 301.9819, calcd for $C_{13}H_9F_3Se$: 301.9816.

*5.1.30. 4-(Phenylselanyl)benzonitrile(**30**).*[10m] R_f=0.4 (1:9, ethyl acetate/hexane); liquid; yield 0.22 g (87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.43–7.37 (m, 5H), 7.31 (d, J=8.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 135.6, 132.4, 130.3, 130.0, 129.2, 127.5, 118.8, 109.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 438.1; HRMS (APCI) m/z 259.9988, calcd for $C_{13}H_9NSe$+H: 259.9973.

*5.1.31. Phenyl(m-tolyl)selane (**31**).*[10m] R_f=0.6 (hexane); liquid; yield 0.23 g (93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.50 (m, 2H), 7.39 (s, 1H), 7.30–7.28 (m, 4H), 7.21 (t, J=7.5 Hz, 1H), 7.12 (d, J=7.6 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 133.9, 132.8, 131.5, 130.7, 130.3, 129.4, 129.2, 128.4, 127.3, 21.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 414.3; HRMS (APCI) m/z 248.0096, calcd for $C_{13}H_{12}Se$: 248.0099.

*5.1.32. 3-(Phenylselanyl)benzonitrile(**32**).*[10m] R_f=0.3 (1:9, ethyl acetate/hexane); liquid; yield 0.21 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 4H), 7.46 (dt, J=7.7, 1.3 Hz, 1H), 7.36–7.27 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 134.8, 134.4, 134.2, 130.2, 129.9, 129.7, 128.8, 128.5, 118.3, 113.4; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 429.8; HRMS (APCI) m/z 259.9964, calcd for $C_{13}H_9NSe$+H: 259.9973.

*5.1.33. 3-Chlorophenyl(phenyl)selane (**33**).*[10m] R_f=0.6 (hexane); liquid; yield 0.23 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.52 (m, 2H), 7.42 (m, 1H), 7.33–7.29 (m, 4H), 7.23–7.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0, 134.9, 133.6, 131.8, 130.3, 130.2, 129.8, 129.6, 128.1, 127.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 426.9.

*5.1.34. (3,4-Dichlorophenyl)(phenyl)selane (**34**).* R_f=0.6 (hexane); liquid; yield 0.24 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 3H), 7.33–7.28 (m, 4H), 7.21 (d, J=7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 133.4, 133.2, 131.6, 131.4, 131.3, 130.9, 129.7, 129.5, 128.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 425.2; HRMS (APCI) m/z 302.9189, calcd for $C_{12}H_8Cl_2Se$+H: 302.9236.

*5.1.35. Naphthalen-2-yl(phenyl)selane (**35**).*[10m] R_f=0.4 (hexane); white solid; yield 0.21 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.80 (m, 1H), 7.73 (d, J=8.3 Hz, 2H), 7.54–7.45 (m, 5H), 7.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 132.9, 132.5, 132.1, 131.3, 130.5, 129.4, 128.8, 128.5, 127.8, 127.4, 127.3, 126.5, 126.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 417.5; HRMS (APCI) m/z 285.0194, calcd for $C_{16}H_{12}Se$+H: 285.0177.

*5.1.36. 2-(Phenylselanyl)benzofuran (**36**).*[10m] R_f=0.5 (1:9, ethyl acetate/hexane); yellow solid; yield 0.25 g (92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J=7.6 Hz, 1H), 7.50–7.47 (m, 3H), 7.30–7.21 (m, 5H), 7.04 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 143.6, 131.7, 129.9, 129.5, 128.6, 127.6, 124.9, 123.0, 120.7, 115.9, 111.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 333.5; HRMS (APCI) m/z 273.9915, calcd for $C_{14}H_{10}OSe$: 273.9892.

*5.1.37. (4-Bromophenyl)(phenyl)selane (**37**).*[10h] R_f=0.6 (hexane); liquid; yield 0.27 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.38–7.36 (m, 2H), 7.31–7.28 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.3, 133.4, 132.4, 130.5, 130.4, 129.5, 127.8, 121.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 415.3.

*5.1.38. (3-Nitrophenyl)(phenyl)selane (**38**).*[10h] R_f=0.3 (hexane); liquid; yield 0.22 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.03–8.01 (m, 1H), 7.63–7.56 (m, 3H), 7.39–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 137.0, 134.8, 129.9, 129.8, 128.8, 128.5, 125.8, 123.5, 121.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 434.

*5.1.39. 3-(Phenylselanyl)pyridine (**39**).*[5d] R_f=0.3 (9:1, hexane/ethyl acetate); liquid; yield 0.15 g (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.46 (d, J=3.7 Hz, 1H), 7.71 (dt, J=8.0, 1.7 Hz, 1H), 7.48–7.46 (m, 2H), 7.28–7.26 (m, 3H), 7.18–7.15 (m, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 152.6, 148.1, 140.2, 133.5, 129.6, 129.5, 128.9, 128.0, 124.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 387.6.

*5.1.40. 3-(Phenylselanyl)benzoic acid (**40**).*[13] R_f=0.4 (8:2, hexane/ethyl acetate); white solid; yield; 0.13 g (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J*=8.3 Hz, 2H), 7.60–7.58 (m, 2H), 7.38–7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 141.4, 137.9, 135.3, 131.6, 130.7, 130.0, 129.8, 128.7, 128.3, 127.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 430.7.

*5.1.41. Naphthalen-1-yl(phenyl)selane (**41**).*[10h] R_f=0.5 (hexane); liquid; yield 0.23 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36–8.34 (m, 1H), 7.86–7.84 (m, 2H), 7.78 (dd, *J*=7.1, 0.8 Hz, 1H), 7.54–7.49 (m, 2H), 7.40–7.35 (m, 3H), 7.20 (t, *J*=3.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 134.1, 133.9, 131.8, 131.7, 129.4, 129.3, 129.2, 128.6, 127.7, 127.0, 126.8, 126.4, 126.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 354.2.

*5.1.42. 4-(Phenylselanyl)phenol (**42**).*[10m] R_f=0.4 (1:9, ethyl acetate/hexane); white solid; yield 0.15 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J*=8.6 Hz, 2H), 7.34–7.31 (m, 2H), 7.23–7.17 (m, 3H), 6.78 (d, *J*=8.6 Hz, 2H), 5.15 (br s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 136.7, 133.1, 131.0, 129.2, 126.5, 120.1, 116.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 401.1.

*5.1.43. 2-(Phenylthio)aniline (**43**).*[16] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); greenish liquid; yield 0.16 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J*=7.6, 1.3 Hz, 1H), 7.21 (t, *J*=7.6 Hz, 3H), 7.12–7.07 (m, 3H), 6.81–6.74 (m, 2H). 4.12 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.4, 136.7, 131.1, 129.0, 126.6, 125.5, 119.0, 115.6, 114.8.

*5.1.44. 2-((4-Fluorophenyl)thio)aniline (**44**).*[16] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); greenish liquid; yield 0.15 g (71%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J*=7.7, 1.4 Hz, 1H), 7.21 (m, 1H), 7.09–7.05 (m, 2H), 9.92 (t, *J*=8.7 Hz, 2H), 6.78–6.72 (m, 2H), 3.94 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 160.0, 148.6, 137.1, 131.7 (d), 131.1, 128.7 (d), 118.8, 116.2, 116.0, 115.4, 115.0.

*5.1.45. 2-((4-Bromophenyl)thio)aniline (**45**).*[16] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); greenish liquid; yield 0.20 g (73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J*=7.7, 1.4 Hz, 1H), 7.30 (d, *J*=8.7 Hz, 2H), 7.25–7.21 (m, 1H), 6.93 (d, *J*=8.7 Hz, 2H), 6.82–6.74 (m, 2H), 3.97 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 137.4, 136.1, 132.0, 131.4, 128.1, 119.2, 119.1, 115.7, 114.2.

*5.1.46. 2-(p-Tolylthio)aniline (**46**).*[16] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); liquid; yield 0.18 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J*=7.7, 1.4 Hz, 1H), 7.21 (dt, *J*=7.3, 1.4 Hz, 1H), 7.05–7.00 (m, 4H), 6.79–6.73 (m, 2H), 3.94 (br s, 2H). 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 137.0, 135.5, 133.0, 130.8, 129.8, 127.2, 118.9, 115.6, 115.5.

*5.1.47. 2-(o-Tolylthio)aniline (**47**).*[16] R_f=0.50 (9.5:0.5 hexane/ethyl acetate); solid; yield 0.17 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J*=7.7, 1.3 Hz, 1H), 7.25 (m, 1H), 7.17 (m, 1H), 7.05 (m, 2H), 6.78 (m, 3H), 4.08 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 137.3, 135.7, 135.4, 130.9, 130.2, 126.6, 125.6, 125.3, 119.0, 115.4, 114.2, 20.0.

*5.1.48. 2-(Naphthalen-2-ylthio)aniline (**48**).*[17] R_f=0.50 (9.5:0.5 hexane/ethyl acetate); liquid; yield 0.20 g (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J*=7.7 Hz, 1H), 7.68 (d, *J*=8.6 Hz, 1H), 7.62 (d, *J*=7.7 Hz, 1H), 7.49–7.48 (m, 2H), 7.42–7.35 (m, 2H), 7.27–7.22 (m, 2H), 6.84 (d, *J*=7.9 Hz, 1H), 6.80 (t, *J*=7.5 Hz, 1H), 3.58 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 137.3, 134.1, 133.8, 131.6, 131.1, 128.7, 127.7, 127.0, 126.5, 125.5, 125.3, 124.7, 119.3, 115.9, 115.2.

*5.1.49. 2-((4-(Trifluoromethyl)phenyl)thio)aniline (**49**).*[18] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); greenish solid; yield 0.19 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (m, 3H), 7.28 (dt, *J*=8.3, 1.4 Hz, 1H), 7.11 (d, *J*=8.3 Hz, 2H), 6.82–6.77 (m, 2H), 4.26 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 142.3, 137.8, 131.9, 127.5 (q), 125.7 (m), 122.8, 119.0, 115.5, 112.4.

*5.1.50. 2-((3-Chlorophenyl)thio)aniline (**50**).*[18] R_f=0.60 (9.5:0.5 hexane/ethyl acetate); yellow liquid; yield 0.18 g (77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J*=7.7, 1.4 Hz, 1H), 7.27–7.23 (m, 1H), 7.12 (t, *J*=7.6 Hz, 1H), 7.07–7.02 (m, 2H), 6.93 (dt, *J*=7.8, 1.2 Hz, 1H), 6.82–6.75 (m, 2H), 4.02 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 139.1, 137.6, 134.9, 131.6, 129.9, 125.9, 125.5, 124.4, 119.1, 115.7, 113.4.

*5.1.51. (4-Bromophenyl)(4-methoxyphenyl)sulfane (**51**).*[10h] R_f=0.4 (9.5:0.5 hexane/ethyl acetate); white solid; yield 0.19 g (66%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J*=8.9 Hz, 2H), 7.31 (d, *J*=8.5 Hz, 2H), 6.99 (d, *J*=8.5 Hz, 2H), 6.89 (d, *J*=8.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.1, 138.2, 135.6, 131.9, 129.4, 123.5, 119.4, 115.2, 55.4.

5.2. General method for the synthesis of symmetrical diaryl selenides

In a 10 mL capacity round bottom flask Se-powder (80 mg, 1.0 mmol) and sodium borohydride (38 mg, 1.0 mmol) were added in ethanol (3 mL). Reaction mixture was stirred at room temperature for 1 h under nitrogen atmosphere. Then, $CuSO_4 \cdot 5H_2O$ (0.1 mmol, 25 mg), 1,10-phenanthroline (0.1 mmol, 18 mg), and phenylboronic acid (121 mg, 1.0 mmol) were added sequentially. Reaction mixture was stirred under oxygen balloon for 10 h. Progress of reaction was monitored by TLC. Then, reaction mixture was poured into water (25 mL) and extracted with ethyl acetate (3×20 mL). Combined organic layer was dried over (Na_2SO_4), evaporated under reduced pressure at 40 °C. Crude mixture was purified by column chromatography (hexane) to provide diphenylselenide **22**, as a yellow liquid; yield: 217 mg (93%). Similar procedure was followed for the synthesis of compounds listed in Table 5. All the products are characterized by ^{1}H, ^{13}C, and ^{77}Se NMR. The spectroscopic data presented below.

*5.2.1. Di-p-tolylselane (**52**).*[11] R_f=0.6 (hexane); liquid; yield 0.21 g (82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J*=8.1 Hz, 4H), 7.07 (d, *J*=8.1 Hz, 4H), 2.31 (s, 6H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 133.0, 130.1, 127.8, 21.1. ^{77}Se NMR (76 MHz, $CDCl_3$) δ 399.8; HRMS (APCI) *m*/*z* 262.0267, calcd for $C_{14}H_{14}Se$: 262.0256.

*5.2.2. Bis(4-(trifluoromethyl)phenyl)selane (**53**).*[11] R_f=0.6 (hexane); liquid; yield 0.22 g (61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.1, 130.2, 126.3 (q), 125.2; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 431.7.

*5.2.3. 4,4′-Selenodibenzonitrile (**54**).*[15] R_f=0.3 (1:9, ethyl acetate/hexane); white solid; yield 0.20 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (q, *J*=8.7 Hz, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 133.2, 132.9, 118.2, 111.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 451.1; HRMS (APCI) *m*/*z* 284.9936, calcd for $C_{14}H_8N_2Se$+H: 284.9926.

*5.2.4. Di-m-tolylselane (**55**).*[11] R_f=0.5 (hexane); liquid; yield 0.22 g (83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 2H), 7.25 (d, *J*=7.7 Hz, 2H), 7.15 (t, *J*=7.7 Hz, 2H), 7.06 (d, *J*=7.7 Hz, 2H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.6, 130.9, 130.0, 129.1, 128.1, 21.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 412.6.

*5.2.5. Bis(3-chlorophenyl)selane (**56**).*[15] R_f=0.5 (hexane); liquid; yield 0.21 g (69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J*=1.7 Hz, 2H), 7.37 (t, *J*=1.3 Hz, 1H), 7.36 (t, *J*=1.3 Hz, 1H), 7.31–7.28 (m, 2H),

7.26–7.22 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 132.7, 132.0, 131.1, 130.5, 130.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 435.7; HRMS (APCI) m/z 301.9161, calcd for $C_{12}H_8Cl_2Se$: 301.9158.

*5.2.6. Di(naphthalen-1-yl)selane (**57**).*[11] R_f=0.4 (hexane); yellow solid; yield 0.25 g (76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38–8.35 (m, 2H), 7.88–7.86 (m, 2H), 7.80 (d, J=8.0 Hz, 2H), 7.55–7.50 (m, 6H), 7.28 (t, J=7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.7, 132.2, 129.9, 128.7, 128.5, 127.1, 126.9, 126.4, 126.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 305.1.

*5.2.7. Di(benzofuran-2-yl)selane (**58**).* R_f=0.4 (1:9, ethyl acetate/hexane); white sold; yield 0.18 g (59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J=7.4 Hz, 2H), 7.46 (d, J=7.4 Hz, 2H), 7.26 (m, 2H), 7.20 (m, 2H), 7.05 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 141.3, 128.4, 125.0, 123.1, 120.8, 115.2, 111.3; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 266.9; HRMS (APCI) m/z 314.9910, calcd for $C_{16}H_{10}O_2Se$+H: 314.9924.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.01.030.

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