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Iron-Catalyzed Ligand-Free Carbon-Selenium (or Tellurium) Coupling of Arylboronic Acids with Diselenides and Ditellurides

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Abstract: Carbon-selenium and carbon-tellurium cross-couplings of arylboronic acids with diselenides and ditellurides have been catalyzed by iron(0), iron(II) chloride or iron(III) chloride without any ligand and additive in the air. The method yields the corresponding unsymmetrical diorgano monoselenides and monotellurides in good to excellent yields, displays a broad substrate scope, and is simple, convenient, effective, economical and environmentally friendly.

Keywords: arylboronic acids; C–Se (Te) cross-coupling; diselenides; ditellurides; iron

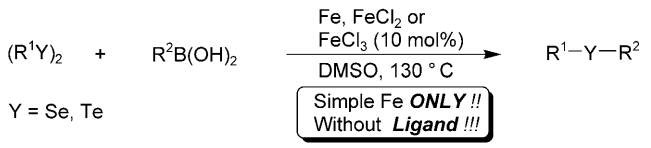
Introduction

Organic chalcogens, especially selenium and tellurium as structural motifs, are commonly found in a variety of molecules of interest to biological, pharmaceutical[1] and material sciences.[2] To synthesize these compounds, various procedures have been explored so far.[3] The commonly used method to introduce a selenium or tellurium moiety into organic molecules is the reaction of a metal selenolate or tellurolate with appropriate electrophiles, such as organic halides, acyl chlorides, epoxides, and α,β-enones.[4] However, it is more difficult to synthesize the unsymmetrical diorgano monoselenides and monotellurides through the reaction of selenide and telluride anions with aryl halides because of the lower reactivity of C(sp^2)–X bonds.

Transition metal-catalyzed aryl carbon-chalcogen bond formation is one of the important methods for the preparation of unsymmetrical organochalcogenides.[5] For the preparation of aryl chalcogenides, C–S and C–Se coupling reactions of aryl halides with thiols and selenols have been successfully carried out in the presence of palladium,[6] nickel,[7] or copper as catalyst[8] under basic reaction conditions. On the other hand, dichalcogenides are used as substrates in the synthesis of diorgano monoselenides and monotellurides since they are stable compounds in air and are easy to handle. However, the method is limited to alkyl halides.[9,10] Meanwhile, in the metal-catalyzed chalcogenylation of aryl halides with dichalcogenide used as reactant, an efficient reductant is necessary for the generation of the corresponding anion[11] or metal-monochalcogenide complex.[12]

Organoboronic acids are widely used as reagents in organic synthesis because they are commercially available, stable, generally non-toxic, and compatible with a variety of functional groups. Recently, a copper-catalyzed C–Se (Te) coupling reaction of arylboronic acids with diselenides and ditelluride has been demonstrated by our group.[13] After that, the synthesis of unsymmetrical monochalcogenides, including sulfides, selenides, and tellurides from dichalcogenides with organoboronic acids in the presence of CuI and the ligand 2,2′-dipyridyl was described.[14]

Over the past few years, iron salts as effective, alternative and promising transition metal catalysts have received much more attention because of their lower cost, ready availability and environmentally benign properties. Since the pioneering research work of Tamura and Kochi,[15] iron-catalyzed oxidation,[16] hydrogenation,[17] hydrosilylation,[18] rearrangement,[19] Michael addition,[20] and C–C bond forming reactions have been intensively investigated.[21–23] Most recently, the iron-catalyzed *S*-arylation of thiols (C–S bond formation),[24] *N*-arylation of nitrogen nucleophiles (C–N bond formation),[25] and *O*-arylation of phenols (C–O bond formation)[26] with aryl halides have been developed. Because of the interest for both the academic as well as the industrial community, it is desirable to expand the application scope of iron catalysts in organic transformations due to their unique and significant advantages. As part of our ongoing efforts devoted to the synthesis of unsymmetrical organochalcoge-



Scheme 1.

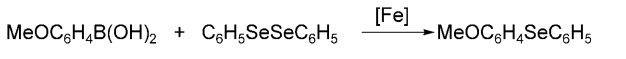
nides, herein we wish to report the first genuinely and highly efficient ligand-free iron-catalyzed preparation of unsymmetrical diorgano monoselenides and monotellurides from arylboronic acids with diselenides and ditellurides through the direct C–Se and C–Te cross-coupling reactions (Scheme 1).

Results and Discussion

For initial optimization of the reaction conditions, diphenyl diselenide and *p*-methoxyphenylboronic acid were chosen as model substrates. As shown in Table 1, we screened a wide range of iron sources as catalyst in DMSO at 130 °C and found that the cross-coupling reaction proceeded smoothly and generated the desired product *p*-methoxypheny phenyl selenide in 91% yield, representing one of the best results when 10 mol% of $FeCl_3$ was used as catalyst without any ligand and additive in an air atmosphere (Table 1, entry 1). Other iron sources, such as $FeCl_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, and $Fe(SO_4)_2{\cdot}7H_2O$ were inferior and generated *p*-methoxyphenyl phenyl selenide in 88, 43, and 25% yields, respectively (Table 1, entries 2–4). To our delight, 94 and 97% yields of the desired products were obtained respectively when 10 mol% of $FeCl_2$ and Fe(0) powder were used as catalyst for the model reaction (Table 1, entries 5 and 6). However, when $Fe_2(SO_4)_3$, $Fe(acac)_3$, Fe_2O_3 or $Fe(OH)_3$ was used as catalyst, no trace of the desired product was isolated and the starting materials were recovered (Table 1, entries 7–10). Microwave irradiation (MWI) conditions could significantly shorten the reaction time from 20 h to 0.5 h, but the yield of the desired product was reduced from 91% to 69% (Table 1, entry 1).

Next, different solvents were examined for the model reaction using 10 mol% of Fe(0) powder as catalyst at 130 °C, and the results are summarized in Table 2. Noteworthy is that the choice of DMSO as the solvent was crucial, and 97% yield of the desired product was provided (Table 2, entry 1). Indeed, when another solvent, such as DMA, toluene, xylene, benzene, CH_3OH, C_2H_5OH, or CH_3CN was used instead of DMSO, the desired coupling products were obtained in lower yields (Table 2, entries 2–8). Unfortunately, no desired product was isolated when the reaction was carried out in *N,N*-dimethylformamide (DMF), or 1,4-dioxane (Table 2, entries 9 and 10).

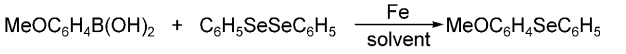
Table 1. Effect of iron source on the C–Se cross-coupling reaction.[a]



Entry	Iron Source	Yield[b] [%]
1	$FeCl_3$	91; 69[c]
2	$FeCl_3{\cdot}6H_2O$	88
3	$Fe(NO_3)_3{\cdot}9H_2O$	43
4	$Fe(SO_4)_2{\cdot}7H_2O$	25
5	$FeCl_2$	94
6	Fe powder	97
7	$Fe_2(SO_4)_3$	0
8	$Fe(acac)_3$	0
9	Fe_2O_3	0
10	$Fe(OH)_3$	0

[a] *Reaction conditions:* *p*-methoxyphenylboronic acids (1.1 equiv.), diphenyl diselenide (0.5 equiv.), Fe source (0.1 equiv.), DMSO (1.0 mL mmol^{-1}), 130 °C, 20 h.
[b] Isolated yields.
[c] A commercially available Sale WP 650, 650-watt microwave oven was utilized at 2450 MHz at 100% power for 0.5 h.

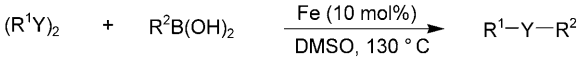
Table 2. Effect of solvent and ligand on the C–Se cross-coupling reaction.[a]



Entry	Solvent/Temp. [°C]	Ligand	Yield[b] [%]
1	DMSO/130	none	97
2	DMA/130	none	61
3	Toluene/130	none	56
4	Xylene/130	none	21
5	Benzene/80	none	19
6	CH_3OH/68	none	42
7	C_2H_5OH/78	none	53
8	CH_3CN/82	none	36
9	DMF/130	none	0
10	Dioxane/100	none	0
11	DMSO/130	DMEDA	87
12	DMSO/130	Phen	90
13	DMSO/130	$(C_6H_5)_3P$	91
14[c]	DMSO/130	DPPF	97
15[d]	DMSO/130	none	72
16[e]	DMSO/130	none	98

[a] *Reaction conditions:* *p*-methoxyphenylboronic acids (1.1 equiv.), diphenyl diselenide (0.5 equiv.), Fe powder (0.1 equiv.), ligand (0.1 equiv., if necessary), solvent (1.0 mL mmol^{-1}) at the temperature indicated in Table 2, 20 h. DPPF = 1,1′-bis(diphenylphosphino)ferrocene, Phen = 1,10-phenanthroline, DMEDA = *N,N*′-dimethylethylenediamine.
[b] Isolated yields.
[c] For 8 h.
[d] In the presence of Fe (0.05 equiv.).
[e] In the presence of Fe (0.20 equiv.).

Table 3. Fe-catalyzed direct C–Se and C–Te cross-coupling reactions.[a]

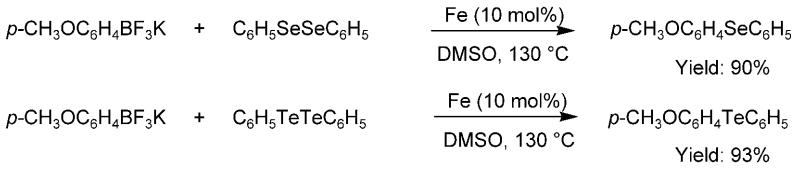


Entry	$(R^1Y)_2$	$R^2B(OH)_2$	R^1YR^2	Yield[b] [%]
1	$(C_6H_5Se)_2$	4-$MeOC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_5$	97
2	$(C_6H_5Se)_2$	2-$MeOC_6H_4B(OH)_2$	2-$MeOC_6H_4SeC_6H_5$	90
3	$(C_6H_5Se)_2$	3-$MeOC_6H_4B(OH)_2$	3-$MeOC_6H_4SeC_6H_5$	79
4	$(C_6H_5Se)_2$	2,4-$(MeO)_2C_6H_3B(OH)_2$	2,4-$(MeO)_2C_6H_3SeC_6H_5$	96
5	$(C_6H_5Se)_2$	2,6-$(MeO)_2C_6H_3B(OH)_2$	2,6-$(MeO)_2C_6H_3SeC_6H_5$	78
6	$(C_6H_5Se)_2$	4-$MeSC_6H_4B(OH)_2$	4-$MeSC_6H_4SeC_6H_5$	95
7	$(C_6H_5Se)_2$	4-$MeO_2CC_6H_4B(OH)_2$	4-$MeO_2CC_6H_4SeC_6H_5$	96
8	$(C_6H_5Se)_2$	2-$OHCC_6H_4B(OH)_2$	2-$OHCC_6H_4SeC_6H_5$	66
9	(4-$MeOC_6H_4Se)_2$	$C_6H_5B(OH)_2$	4-$MeOC_6H_4SeC_6H_5$	88
10	(4-$MeOC_6H_4Se)_2$	4-$ClC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(4-Cl)	78
11	(4-$MeOC_6H_4Se)_2$	4-$BrC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(4-Br)	62
12	(4-$MeOC_6H_4Se)_2$	4-$FC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(4-F)	91
13	(4-$MeOC_6H_4Se)_2$	4-$MeC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(4-Me)	90
14	(4-$MeOC_6H_4Se)_2$	3-$MeC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(3-Me)	80
15	(4-$MeOC_6H_4Se)_2$	2-$MeC_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(2-Me)	86
16	(4-$MeOC_6H_4Se)_2$	4-*t*-$C_4H_9C_6H_4B(OH)_2$	4-$MeOC_6H_4SeC_6H_4$(4-*t*-C_4H_9)	97
17	(4-$MeOC_6H_4Se)_2$	*n*-$C_4H_9B(OH)_2$	4-$MeOC_6H_4SeCH_2(CH_2)_2CH_3$	0
18	(*n*-$C_4H_9Se)_2$	4-$MeOC_6H_4B(OH)_2$	*n*-$C_4H_9SeC_6H_4$(4-MeO)	62
19	$(C_6H_5CH_2Se)_2$	4-$MeOC_6H_4B(OH)_2$	4-$MeOC_6H_4SeCH_2C_6H_5$	77
20	$(C_6H_5Te)_2$	4-$MeOC_6H_4B(OH)_2$	4-$MeOC_6H_4TeC_6H_5$	98
21	$(C_6H_5Te)_2$	3-$MeOC_6H_4B(OH)_2$	3-$MeOC_6H_4TeC_6H_5$	90
22	$(C_6H_5Te)_2$	2-$MeOC_6H_4B(OH)_2$	2-$MeOC_6H_4TeC_6H_5$	94
23	$(C_6H_5Te)_2$	4-$MeO_2CC_6H_4B(OH)_2$	4-$MeO_2CC_6H_4TeC_6H_5$	88
24	(4-$MeOC_6H_4Te)_2$	$C_6H_5B(OH)_2$	4-$MeOC_6H_4TeC_6H_5$	86

[a] *Reaction conditions:* arylboronic acids (1.1 mmol), dichalcogenide (0.5 mmol), Fe (0.1 mmol), DMSO (1.0 mL), 130 °C, 20 h.
[b] Isolated yield.

Meanwhile, we also investigated the influence of the ligand on the model reaction. The result showed that the yield of desired cross-coupling product was slightly decreased when DMEDA, Phen, or Ph_3P as ligand was added to the reaction system (Table 2, entries 11–13). When DPPF (10 mol%) as ligand was added to the reaction, C–Se coupling of the model substrates was smoothly accomplished within 8 h and afforded the desired monoselenide in 97% yield (Table 2, entry 14). With respect to the catalyst loading, 10 mol% of Fe was found to be optimal. When only 5 mol% of Fe was used, the desired product was isolated in 72% yield (Table 2, entry 15), and no significant improvement was observed with 20 mol% of Fe (Table 2, entry 16). During the course of our further optimization of the reaction conditions, the reaction was generally completed within 20 h at 130 °C in DMSO by using 10 mol% of Fe without an additional P ligand DPPF in consideration of environmental friendliness and low cost.

On the basis of the previously optimized reaction conditions, the scope of this transformation in the direct cross-coupling reaction of a variety of dichalcogenides with differently substituted arylboronic acids was evaluated. The results are listed in Table 3. At the beginning of the experiments to probe the substrate scope for the boronic acids, when diphenyl diselenide or di(*p*-methoxyphenyl) diselenide was taken as dichalcogenide partner, a variety of electron-rich, electron-neutral, and electron-deficient arylboronic acids underwent the C–Se cross-coupling reactions smoothly to generate the corresponding diaryl monoselenides in good to excellent yields (Table 3, entries 1–16). Furthermore, sterically demanding *ortho* substituents did not hamper the cross-coupling reaction and the corresponding unsymmetrical diaryl monoselenides were obtained in good yields (Table 3, entries 2, 4, 5, 8 and 15). A more remarkable observation was that the extremely sterically hindered 2,6-dimethoxyphenylboronic acid reacted with diphenyl diselenide under these reaction conditions to generate the desired product in 78% isolated yield (Table 3, entry 5). What's more, the tolerance of potentially reactive functional groups, such as carbonyl and ester groups, to the described protocol is remarkable (Table 3, entries 7 and 8). However, no desired product was isolated when an alkylboronic acid, such as *n*-$C_4H_9B(OH)_2$ was used as substrate (Table 3,



Scheme 2.

entry 17). Fortunately, dialkyl diselenides, such as *n*-$C_4H_9SeSeC_4H_9$-*n*, and dibenzyl diselenide $C_6H_5CH_2SeSeCH_2C_6H_5$, also reacted with *p*-methoxyphenylboronic acid to form the corresponding products in 62 and 77% yields, respectively (Table 3, entries 18 and 19).

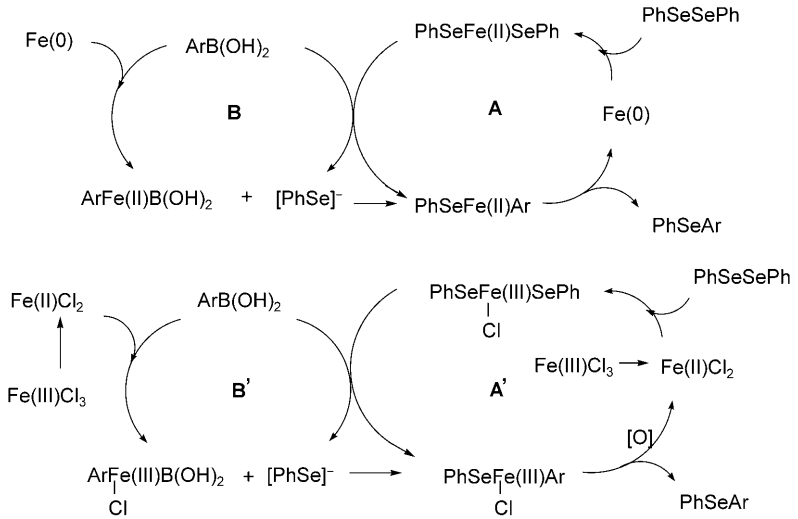
As an alternative to organoboronic acids and esters, organotrifluoroborate salts have emerged as a new class of air-stable boron derivatives, facile to prepare in high yields and purities, easy to handle, and feasible to utilize in a number of useful synthetic processes.[27] When the reactions of potassium *p*-methoxyphenyltrifluoroborate with diphenyl diselenide and diphenyl diselenide were performed under the present reaction conditions, as expected, 90% and 93% yields of the desired products were isolated (Scheme 2).

Then, we explored the cross-coupling reaction using other dichalcogenides, such as ditellurides and disulfides. The cross-coupling of diphenyl ditelluride or di(*p*-methoxyphenyl) ditelluride with a number of substituted arylboronic acids under the present reaction conditions also occurred with C–Te bond formation smoothly to afford the desired diaryl monotellurides in good yields, which were not affected by the nature or steric hindrance of substituted groups on the benzene ring in the arylboronic acids (Table 2, entries 20–24). However, all attempts to use diaryl disulfides as chalcogen source for direct C–S coupling with arylboronic acids met with failure, probably due to the stronger S–S bond, and starting materials were recovered unconsumed.

To investigate the reaction mechanism, a reaction of $(C_6H_5Se)_2$ and 4-$MeOC_6H_4B(OH)_2$ was examined initially in the absence of oxygen. When the $FeCl_2$- or $FeCl_3$-catalyzed the reaction was carried out, only a trace amount of desired cross-coupling product was isolated. When Fe(0) powder was used as catalyst, a 94% yield of desired product was obtained.

Also, an iron-promoted reaction of $(C_6H_5Se)_2$ and *n*-$C_6H_{13}Br$ was examined. When the reaction was carried out in the presence of catalytic amount of $FeCl_2$, $FeCl_3$, or Fe(0) (10 mol%), no desired product was isolated in the absence of oxygen or in the presence of oxygen. As expected, a 90% yield of *n*-$C_6H_{13}SeC_6H_5$ was obtained under an inert atmosphere when 1.2 equiv. of Fe(0) were used, indicating formation of the $[C_6H_5Se]^-$ anion.

A possible mechanism for the Fe(0)-catalyzed reaction is shown in Scheme 3. In cycle **A**, after PhSeFe(II)SePh was formed from $(PhSe)_2$ and Fe(0) *via* an oxidative addition, $ArB(OH)_2$ reacted with PhSeFe(II)SePh *via* transmetallation to form PhSeFe(II)Ar, which produced the coupling product PhSeAr and regenerated Fe(0). In cycle **B**, after the reaction of $ArB(OH)_2$ and Fe(0), $ArFe(II)B(OH)_2$ was produced, which reacted with "$[PhSe]^-$", another



Scheme 3. Possible mechanism for the reaction.

half of $(PhSe)_2$ to form PhSeFe(II)Ar, indicating the molar ratio of $(PhSe)_2$ and $ArB(OH)_2$ (1:2).

From these results we observed that $FeCl_3$ and $FeCl_2$ have a comparable catalytic activity in the reaction. For the $FeCl_3$-catalyzed reaction, the precatalyst Fe(III) would presumably be first reduced to Fe(II). Similarly, in cycle **A′**, after PhSeFe(III)(Cl)SePh was obtained from $(PhSe)_2$ and Fe(II) *via* an oxidation addition, $ArB(OH)_2$ reacted with PhSeFe(III)(Cl)SePh *via* a transmetallation to form PhSeFe(III)(Cl)Ar, which generated PhSeAr as product *via* a reductive elimination and regenerated Fe(II) in the presence of oxygen.

Conclusions

In summary, we have successfully developed novel, economical, environmentally friendly, and practical iron-catalyzed ligand-free direct C–Se and C–Te cross-couplings of arylboronic acids with diselenides and ditellurides. The reactions were carried out in the presence of catalytic amounts of iron in DMSO without any ligand and additive. This method provides the desired unsymmetrical diorgano monoselenides and monotellurides in good to excellent yields in most cases. Overall, the novel iron-catalyzed protocol reported here constitutes a promising carbon-chalcogen bond-forming process of potential industrial significance because of its operational simplicity and environmental and economic advantages, it also expands the application scope of iron catalysts as a versatile tool in organic synthesis. Studies on its increased efficiency and enlargement of the substrate scope and further investigations on the application of this kind of catalyst in asymmetric catalysis are in progress.

Experimental Section

General Remarks

All reactions were carried out under an air atmosphere. All reagents were purchased from commercial suppliers and used after further purification. Products were purified by flash chromatography on 230–400 mesh silica gel, SiO_2. All ^1H NMR, ^{13}C NMR spectra were measured on a Bruker Avance NMR spectrometer (400 MHz or 100 MHz, respectively) with $CDCl_3$ as solvent and recorded in ppm relative to tetramethylsilane as internal standard. High resolution mass spectroscopy data of the products were collected on a Waters Micromass GCT instrument.

General Procedure for Iron-Catalyzed Preparation of Monochalcogenides from Dichalcogenides with Arylboronic Acids without Any Ligand and Additive

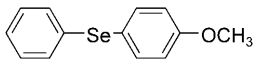
A 10-mL reaction tube was charged with dichalcogenide (0.5 mmol), arylboronic acid (1.1 mmol), Fe(0) powder (0.1 mmol), and DMSO (1.0 mL). The reaction vessel was placed in an oil bath at 130 °C. After the reaction had been carried out at this temperature for 20 h, it was cooled to room temperature, diluted with H_2O and extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: petroleum ether) to give the desired cross-coupling product.

General Procedure for Iron-Catalyzed Preparation of Monochalcogenides from Dichalcogenides with Arylboronic Acids in the Presence of DPPF

A 10-mL reaction tube was charged with dichalcogenide (0.5 mmol), arylboronic acid (1.1 mmol), Fe(0) powder (0.1 mmol), DPPF (0.1 mmol) and DMSO (1.0 mL). The reaction vessel was placed in an oil bath at 130 °C. After the reaction had been carried out at this temperature for 8 h, it was cooled to room temperature, diluted with H_2O and extracted twice with Et_2O. The organic layers were combined, dried over Na_2SO_4, and concentrated to yield the crude product, which was further purified by flash chromatography on silica gel (eluant: petroleum ether) to give the desired cross-coupling product.

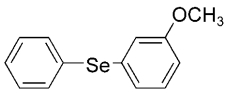
Spectral data of the monochalcogenides prepared are listed below.

4-Methoxyphenyl Phenyl Selenide[14]



^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (d, $J = 8.8$ Hz, 2H), 7.33–7.31 (m, 2H), 7.21–7.16 (m, 3H), 6.84 (d, $J = 8.4$ Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.7$, 136.5, 133.2, 130.9, 129.1, 126.4, 119.9, 115.1, 55.2.

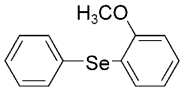
3-Methoxyphenyl Phenyl Selenide[28]



^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$–7.48 (m, 2H), 7.26–7.25 (m, 3H), 7.18–7.14 (m, 1H), 7.03–7.00 (m,

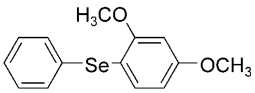
2H), 6.78 (d, $J=8.0$ Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.9$, 133.2, 132.2, 130.7, 130.0, 129.3, 127.4, 124.9, 117.9, 113.0, 55.2

2-Methoxyphenyl Phenyl Selenide[14]



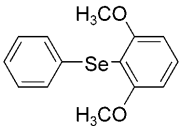
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.58$–7.56 (m, 2H), 7.33–7.30 (m, 3H), 7.20–7.15 (m, 1H), 6.94 (q, $J=1.6$, 6.0 Hz, 1H), 6.84 (q, $J=1.2$, 7.2 Hz, 1H), 6.80–6.76 (m, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=156.6$, 135.5, 130.8, 129.5, 128.3, 128.1, 127.7, 121.9, 121.6, 110.4, 55.9.

2,4-Dimethoxyphenyl Phenyl Selenide[29]



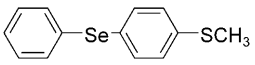
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.42$–7.39 (m, 2H), 7.25–7.22 (m, 4H), 6.50 (d, $J=2.4$ Hz, 1H), 6.43 (q, $J=2.4$, 6.0 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.3$, 159.2, 135.3, 132.4, 129.1, 126.8, 110.3, 105.7, 99.0, 56.0, 55.5.

2,6-Dimethoxyphenyl Phenyl Selenide[13]



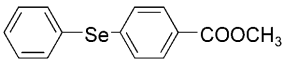
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.41$–7.38 (m, 2H), 7.24–7.19 (m, 4H), 6.49 (d, $J=2.4$ Hz, 1H), 6.41 (q, $J=2.4$, 6.0 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=161.2$, 159.1, 135.2, 132.3, 131.0, 129.1, 126.8, 110.2, 105.6, 98.9, 55.9, 55.4.

4-Methylthiophenyl Phenyl Selenide



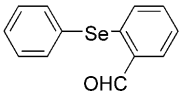
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.39$ (d, $J=8.4$ Hz, 4H), 7.23–7.21 (m, 3H), 7.12 (d, $J=8.4$ Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=138.4$, 134.0, 132.2, 131.6, 129.2, 127.1, 127.0, 126.6, 15.5; HR-MS (ESI): $m/z=276.9858$ ([M]$^+$), calcd. for $C_{13}H_{12}S^{77}Se$: 276.9859.

4-Methoxycarbonylphenyl Phenyl Selenide[14]



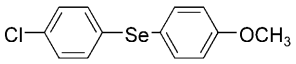
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.86$ (d, $J=8.4$ Hz, 2H), 7.58 (q, $J=2.0$, 6.0 Hz, 2H), 7.37–7.34 (m, 5H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=166.8$, 139.7, 135.0, 1302.3, 130.2, 129.7, 128.7, 128.5, 128.2, 52.1.

2-Formylphenyl Phenyl Delenide[30]



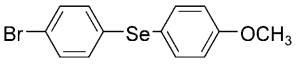
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=10.1$ (s, 1H), 7.78–7.76 (m, 1H), 7.61–7.59 (m, 2H), 7.41–7.34 (m, 3H), 7.27–7.20 (m, 2H), 6.98 (d, $J=7.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=192.6$, 139.6, 136.8, 135.1, 133.9, 133.7, 129.9, 129.1, 128.1, 125.5.

4-Chlorophenyl 4′-Methoxyphenyl Selenide



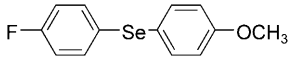
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.45$ (d, $J=8.8$ Hz, 2H), 7.19 (d, $J=8.8$ Hz, 2H), 7.12 (d, $J=8.8$ Hz, 2H), 6.82 (d, $J=8.8$ Hz, 2H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.0$, 136.7, 132.5, 132.1, 131.6, 129.3, 119.5, 115.3, 55.3; HR-MS (ESI): $m/z=$ 297.9670 ([M]$^+$), calcd. for $C_{13}H_{11}ClO^{80}Se$: 297.9664; $m/z=295.9667$, calcd. for $C_{13}H_{11}ClO^{78}Se$: 295.9671.

4-Bromophenyl 4′-Methoxyphenyl Selenide



^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.49$ (d, $J=8.8$ Hz, 2H), 7.31 (d, $J=8.4$ Hz, 2H), 7.15 (d, $J=8.4$ Hz, 2H), 6.86 (d, $J=8.4$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.0$, 136.7, 132.5, 132.1, 131.6, 129.3, 119.5, 115.3, 55.3; HR-MS (ESI): $m/z=$ 341.9157 ([M]$^+$), calcd. for $C_{13}H_{11}BrO^{80}Se$: 341.9158.

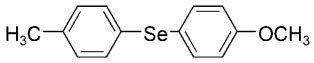
4-Flurophenyl 4′-Methoxyphenyl Selenide[31]



^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.45$ (d, $J=8.8$ Hz, 2H), 7.34 (q, $J=5.4$, 4.8 Hz, 2H), 6.91 (t, $J=8.8$ Hz,

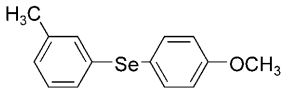
2H), 6.83 (d, $J=8.8$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=163.2$, 160.8, 159.7, 135.8, 133.5, 133.4, 127.2, 120.5, 116.3, 116.1, 115.1, 55.2.

4-Methylphenyl 4′-Methoxyphenyl Selenide



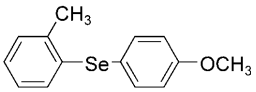
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.45$ (d, $J=8.8$ Hz, 2H), 7.27 (q, $J=8.0$ Hz, 2H), 7.03 (t, $J=8.0$ Hz, 2H), 6.81 (d, $J=8.8$ Hz, 2H), 3.77 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.5$, 136.7, 135.8, 131.8, 130.0, 129.0, 120.9, 115.1, 55.3, 21.1: HR-MS (ESI): $m/z=278.0211$ ($[M]^+$), calcd. for $C_{14}H_{14}O^{80}Se$: 278.0210; $m/z=276.0223$, calcd. for $C_{14}H_{14}O^{78}Se$: 276.0218.

3-Methylphenyl 4′-Methoxyphenyl Selenide



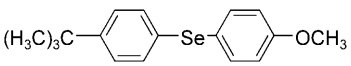
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.47$ (d, $J=8.4$ Hz, 2H), 7.16 (s, 1H), 7.11–7.04 (m, 2H), 6.96 (d, $J=7.2$ Hz, 1H), 6.81 (d, $J=8.8$ Hz, 2H), 3.75 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.6$, 138.8, 136.3, 132.7, 131.6, 128.9, 128.1, 127.3, 120.1, 115.0, 55.2, 21.2; HR-MS (ESI): $m/z=280.0215$ ($[M]^+$), calcd. for $C_{14}H_{14}O^{82}Se$: 280.0212.

4-Methoxyphenyl 2′-Methylphenyl Selenide



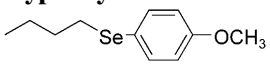
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.45$ (d, $J=8.8$ Hz, 2H), 7.15–7.13 (m, 1H), 7.11–7.06 (m, 2H), 7.00–6.96 (m, 1H), 6.85 (d, $J=9.2$ Hz, 2H), 3.79 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.8$, 138.0, 136.6, 134.0, 130.8, 130.0, 126.6, 119.3, 115.3, 55.3, 21.9; HR-MS (ESI): $m/z=276.0219$ ($[M]^+$), calcd. for $C_{14}H_{14}O^{78}Se$: 276.0218.

4-*tert*-Butylphenyl 4′-Methoxyphenyl Selenide



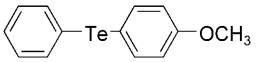
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.48$ (d, $J=8.8$ Hz, 2H), 7.26 (q, $J=8.8$, 10.0 Hz, 4H), 6.83 (d, $J=8.8$ Hz, 2H), 3.78 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.6$, 149.7, 136.1, 131.0, 129.2, 126.2, 120.4, 115.0, 55.2, 34.4, 31.2; HR-MS (ESI): $m/z=320.0677$ ($[M]^+$), calcd. for $C_{17}H_{20}O^{80}Se$: 320.0679; $m/z=318.0680$, calcd. for $C_{17}H_{20}O^{78}Se$: 318.0687.

***n*-Butyl 4-Methoxyphenyl Selenide[13]**



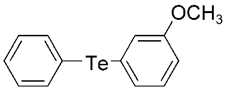
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.48$ (d, $J=8.8$ Hz, 2H), 6.83 (d, $J=8.8$ Hz, 2H), 3.80 (s, 3H), 2.83 (t, $J=7.6$ Hz, 2H), 1.67–1.63 (m, 2H), 1.44–1.39 (m, 2H), 0.91 (t, $J=7.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.1$, 135.5, 120.2, 114.7, 55.3, 32.3, 28.8, 22.9, 13.6.

4-Methoxyphenyl Phenyl Telluride[14]



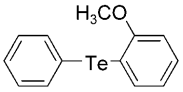
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.72$ (d, $J=8.8$ Hz, 2H), 7.55 (q, $J=2.8$, 4.0 Hz, 2H), 7.20–7.13 (m, 3H), 6.78 (d, $J=8.8$ Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=160.0$, 141.2, 136.4, 129.4, 127.3, 115.9, 115.6, 103.2, 55.2.

3-Methoxyphenyl Phenyl Telluride



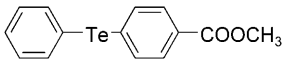
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.71$ (d, $J=9.2$ Hz, 2H), 7.31–7.20 (m, 5H), 7.12 (t, $J=7.6$ Hz, 1H), 6.81 (d, $J=8.4$ Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=159.9$, 138.2, 130.2, 130.1, 129.5, 128.0, 123.0, 113.8, 55.2; HR-MS (ESI): $m/z=313.9957$ ($[M]^+$), calcd. for $C_{13}H_{12}O^{130}Te$: 313.9950.

2-Methoxyphenyl Phenyl Telluride[14]



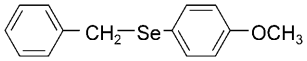
^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.88$ (d, $J=8.0$ Hz, 2H), 7.40–7.37 (m, 1H), 7.30–7.26 (m, 2H), 7.18–7.14 (m, 1H), 6.93 (d, $J=7.6$ Hz, 1H), 6.77 (d, $J=8.0$ Hz, 1H), 6.72 (t, $J=7.6$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=157.9$, 141.1, 133.4, 129.5, 128.6, 128.0, 122.3, 111.9, 109.5, 107.6, 55.8.

4-Methoxycarbonylphenyl Phenyl Telluride[14]



^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81$–7.78 (m, 4H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 6.8$ Hz, 1H), 7.26 (t, $J = 7.2$ Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.9$, 139.5, 135.9, 130.1, 129.8, 129.0, 128.7, 123.4, 113.4, 52.2.

Benzyl 4-Methoxyphenyl Selenide[32]



^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.28$ (d, $J = 8.4$ Hz, 2H), 7.16–7.09 (m, 3H), 7.04 (d, $J = 6.8$ Hz, 2H), 6.69 (d, $J = 8.8$ Hz, 2H), 3.92 (s, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.5$, 139.1, 136.5, 128.8, 128.3, 126.6, 120.0, 114.6, 55.2, 33.1.

Acknowledgements

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