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Indium-mediated cleavage of diphenyl diselenide and diphenyl disulfide: efficient one-pot synthesis of unsymmetrical diorganyl selenides, sulfides, and selenoesters

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ABSTRACT

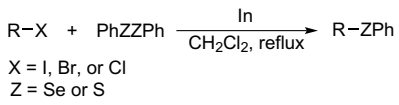
A convenient and efficient method was developed for the synthesis of alkyl phenyl selenides, sulfides, and selenoesters in one-pot reaction by using indium metal. The reaction showed the selectivity for *tert*-alkyl, benzylic, and allylic halides over primary and secondary alkyl halides. For the reaction of primary and secondary alkyl iodides and bromides, the yields of selenides were improved by the addition of a catalytic amount of iodine.

1. Introduction

Interest in organochalcogenides has increased continuously for their important role in organic synthesis and their useful biological activities. Organoselenium compounds, for instance, have been proved to play a role as important therapeutic compounds such as antiviral and anticancer agents.[1] Organochalcogenides have also emerged as crucial intermediates in the transformations of a variety of functional groups.[2]

Much effort has been devoted to accomplish the synthesis of organochalcogenides, and a number of reports on the preparation of organochalcogenides have been published.[3,4] However, many preparative methods proceeded with multi-step procedures under strongly basic or acidic reaction conditions and sometimes suffered from improper handling of unstable reagents in air and moisture. Therefore, development of new synthetic methods is required in organic synthesis for the preparation of organochalcogenides using stable reagents and one-step procedure under neutral conditions.

Over the past decade, indium metal and its salts have been chosen as the reagents for carbon–carbon bond formation, rearrangements, and a variety of useful reactions.[5] They have drawn an increasing attention for their unique properties such as low toxicity and high stability in water and air compared with other metals. As part of our effort toward developing applications of indium metal in organic synthesis,[6] we developed an indium-mediated reaction for preparing unsymmetrical organochalcogenides from alkyl halides and diphenyl diselenide (diphenyl disulfide).[7] Herein, we wish to report an account on a mild and efficient one-pot procedure for the synthesis of alkyl phenyl selenides, sulfides, and selenoesters using indium metal under neutral conditions (Scheme 1).



Scheme 1.

2. Results and discussion

We first performed the reaction of ^{t}BuCl with PhSeSePh under various reaction conditions as shown in Table 1. The reaction of

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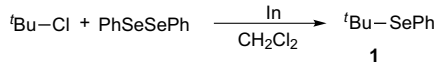
Table 1
Reaction of ^{t}BuCl with PhSeSePh in the presence of indium



Entry	^{t}BuCl (equiv)	In (equiv)	Temp	Time (h)	Yield[a] (%)
1	2.0	1.0	Reflux	1	95
2	2.0	1.0	rt	3	99
3	2.0	0	Reflux	1	0
4	2.0	0.5	Reflux	1	91
5	2.0	0.1	Reflux	1	20
6	2.0	1.0	Reflux	1	3[b]

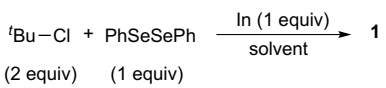
[a] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of ^{t}BuCl.
[b] $InCl_3$ was used instead of In.

diphenyl diselenide with 2.0 equiv of ^{t}BuCl in the presence of an equimolar amount of indium in CH_2Cl_2 at reflux for 1 h afforded *tert*-butyl phenyl selenide (**1**) in 95% yield, which was determined on the base of the amount of ^{t}BuCl (entry 1). When the reaction was carried out at ambient temperature, a quantitative yield of the product was obtained (entry 2), although longer reaction time was required for completion. In the absence of indium metal, however, the reaction did not proceed at all, implying that indium acts as a promoter of the reaction (entry 3). The essential amount of indium required for efficient promoting of the reaction could be reduced to 0.5 equiv affording the product in 91% yield (entry 4). With 0.1 equiv of indium (entry 5) or 1.0 equiv of $InCl_3$, the reaction was not efficient (entry 6).

Next, we investigated the solvent effects on the reaction (Table 2). The reaction of ^{t}BuCl with PhSeSePh in common organic solvents including benzene, toluene, THF, and CH_3CN at ambient temperature and boiling temperature of the solvents gave the product **1** in low to moderate yields. At room temperature, chlorinated solvents such as CH_2Cl_2 (Table 1, entry 2) and $ClCH_2CH_2Cl$ (Table 2, entry 4) were optimal. However, the yield of the product **1** decreased dramatically at the boiling temperature of $ClCH_2CH_2Cl$ (entry 4). We thought that it might be related with the thermal stability of the product **1**. In controlled experiments, it was found that the reaction in CH_2Cl_2 was completed within 3 h at room temperature and in 1 h at reflux giving quantitative yields of the product. On the other hand, when the reaction time increased to 24 h in both cases, it caused a decrease in the yield of the product to 80% and 70%, respectively. Thus, it proved that the prolonged reaction time gave a detrimental effect on the yield of the product. We also carried out the reaction in aqueous CH_2Cl_2 to afford a low yield of the product (entry 6). Notably, CH_2Cl_2 was the solvent of choice.

Under optimal reaction conditions, a variety of sterically diverse organic halides brought into the reaction with diphenyl diselenide in order to evaluate the scope and limitations of the present procedure. The results are presented in Table 3. Tertiary alkyl halides underwent a clean reaction to provide the corresponding alkyl phenyl selenides in high yields (entries 1–5). Note that the reaction of *tert*-alkyl halides with metal phenyl selenolates, which were made from the reaction of PhSeSePh with La[4m] or Zn,[4o] or from the reaction of PhSeH with CsOH,[4h] could not be achieved even under harsh reaction conditions. It is interesting to note that the reaction with bridged halides, 1-haloadamantanes, also proceeded without difficulty (entries 3–5). Various primary and secondary alkyl halides were examined. In contrast to tertiary alkyl halides, they were found to be inactive to the present indium-promoted selenation of alkyl halides (entries 6–9). Benzyl phenyl selenides were also formed from benzyl bromide and chloride (entries 10–15). With substituent groups on benzene

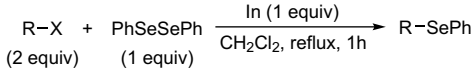
Table 2
Solvent effects on the reaction of ^{t}BuCl with PhSeSePh in the presence of indium

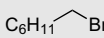
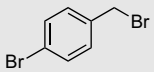
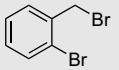
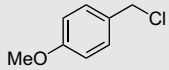
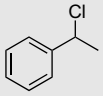
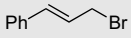
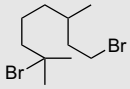


Entry	Solvent	Yield[a,c] (%)	Yield[b,c] (%)
1	Benzene	51	65
2	Toluene	38	41
3	THF	0	22
4	$ClCH_2CH_2Cl$	99	52
5	CH_3CN	50	66
6	CH_2Cl_2/H_2O (9:1, v/v)	—	42

[a] The reaction was carried out at room temperature for 3 h.
[b] The reaction was carried out in a boiling solvent for 1 h.
[c] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of ^{t}BuCl.

Table 3
Synthesis of alkyl phenyl selenides from alkyl halides



Entry	RX	RSePh	Yield[a] (%)
1	^{t}BuI	**1**[b]	99
2	^{t}BuBr	**1**[b]	95 (86)
3	1-Iodoadamantane	**2**[c]	86 (76)
4	1-Bromoadamantane	**2**[c]	84 (74)
5	1-Chloroadamantane	**2**[c]	99 (88)
6	^{i}PrI	**3**[d]	NR
7	Cyclohexyl bromide	**4**[d]	NR
8	$CH_3(CH_2)_5I$	**5**[e]	NR
9		**6**	NR
10	$PhCH_2Br$	**7**[f]	86 (70)
11		**8**[g]	98 (85)
12		**9**	99 (95)
13	$PhCH_2Cl$	**7**[f]	- (84)
14		**10**[d]	- (52)
15		**11**[d]	67 (59)
16		**12**[b]	99 (89)
17		**12**[b]	97 (73)
18		**13**[d]	40 (32)
19	PhBr	**14**[h]	NR
20	PhI	**14**[h]	NR
21		**15**[i]	85

[a] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of RX. The yields in parentheses are isolated yields.
[b] Ref. 4m.
[c] Ref. 11.
[d] Ref. 4g.
[e] Ref. 13.
[f] Ref. 4g.
[g] Ref. 12.
[h] Ref. 4a.
[i] Ref. 4f.

ring, the position of the substituent did not affect the yield of the products. Therefore, *p*- and *o*-bromobenzyl phenyl selenides (**8** and **9**) were afforded in 98% and 99% yields, respectively (entries 11 and 12). On the other hand, *p*-methoxybenzyl chloride was converted into the selenide **10** in moderate yield (entry 14). The reaction was then attempted with allyl halides, which were transformed into allyl phenyl selenide (**12**) in excellent yields (entries 16 and 17). Cinnamyl bromide was converted to cinnamyl phenyl selenide (**13**) in 32% isolated yield along with the by-product of rearrangement (entry 18). Aryl halides turned out to be inactive under the present reaction conditions (entries 19 and 20). The substitution reaction of a dibromo substrate took place selectively at the tertiary carbon center (entry 21). These findings led us to conclude that the consecutive order of reactivity of alkyl halides is *tert*-alkyl, allyl, benzyl ≫ secondary and primary alkyl halides.

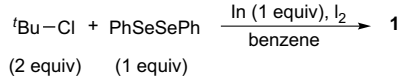
It has been reported that the reactions using metal have been promoted by the addition of iodine.[4m,8] We thought that the addition of iodine might increase the yields of the desired products under the present reaction conditions. When 1.0 equiv of PhSeSePh was allowed to react with 2.0 equiv of ^{t}BuCl in the presence of indium (1.0 equiv) in benzene at room temperature for 3 h, the product **1** was obtained in 51% yield (Table 4, entry 1). When 0.2 equiv of iodine was added, the yield improved somewhat (entry 2). However, in boiling benzene, the addition of a catalytic amount of iodine (0.2 equiv) to the reaction caused a tremendous increase in the yield of the product **1** to a quantitative yield compared with the case in which iodine was absent (entries 3 and 4).

We thought that these reaction conditions might be applicable to the preparation of primary and secondary alkyl phenyl selenides, which were obtained in very low yields without iodine (Table 3, entries 6–9). Various primary and secondary alkyl halides were allowed to react under the reaction conditions, and the results are shown in Table 5. Secondary alkyl iodides and bromides (entries 1 and 2), and primary alkyl iodides and bromides (entries 5–8) were highly effective to In/I_2 promoted selenation. It was interesting to note that sterically congested iodide, bornyl iodide, proceeded efficiently affording the corresponding alkyl phenyl selenide **16** in high yield (entry 3). In general, alkyl iodides were more reactive than alkyl bromides. In the case of secondary alkyl chlorides such as 2-chloroadamantane, the reaction did not proceed (entry 4). Furthermore, the reaction of primary alkyl chlorides did not proceed under the same reaction conditions (entries 9 and 10). Addition of iodine to the reaction enhanced the rate of reaction.

Next, we applied the method to the preparation of alkyl phenyl sulfides. Various alkyl phenyl sulfides were prepared, and the results are summarized in Table 6. Generally, the formation of sulfides took longer reaction time than the formation of selenides. The reactions with tertiary alkyl halides were completed within 3–5 h without difficulty (entries 1–5). The transformation of benzyl bromide and chloride to benzyl phenyl sulfide (**23**) could also be accomplished giving high yields (entries 6 and 7). With allyl iodide, allyl phenyl sulfide (**24**) was produced in 40% isolated yield (entry 8). Primary and secondary alkyl iodides were practically inactive under the present reaction conditions even in the presence of iodine (entries 9 and 10).

In an effort to extend the scope of our newly developed system, we carried out the reaction of a wide range of structurally diverse acid chlorides with diphenyl diselenide to produce the corresponding acyl phenyl selenides, and the results are presented in Table 7. Treatment of benzoyl chloride (2.0 equiv) with PhSeSePh (1.0 equiv) in CH_2Cl_2 in the presence of indium (1.0 equiv) at reflux for 1 h furnished benzoyl phenyl selenide (**27**) in 62% yield (entry 1). The yield of **27** was improved to 92% yield by employing 1.5 equiv of indium (entry 2). *p*-Methoxy (**28**) and *p*-bromobenzoyl (**29**) phenyl selenides were also obtained in high yields (entries 3 and 4). However, benzoic acid chlorides with nitro group at *o*- or *p*-position were not active substrates under the same reaction conditions giving low yields of the corresponding acyl phenyl selenides (**30** and **31**) even though they were allowed to react for prolonged time (entries 5 and 6). A heterocyclic acid chloride, 2-thiophenecarbonyl chloride, produced 2-thiophenecarbonyl

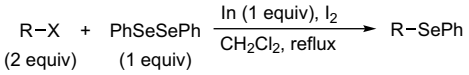
Table 4
Effects of the amount of iodine on the reaction of ^{t}BuCl with PhSeSePh



Entry	I_2 (equiv)	Temp	Time (h)	Yield[a] (%)
1	0	rt	3	51
2	0.2	rt	1	76
3	0	Reflux	1	65
4	0.2	Reflux	0.5	99

[a] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of ^{t}BuCl.

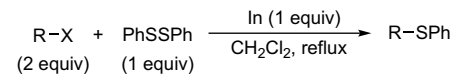
Table 5
Synthesis of primary and secondary alkyl phenyl selenides with indium in the presence of a catalytic amount of iodine



Entry	RX	I_2 (equiv)	Time (h)	RSePh	Yield[a] (%)
1	^{i}PrI	0.2	1	**3**[b]	98 (70)
2	Cyclohexyl bromide	0.5	4	**4**[b]	90 (82)
3	Bornyl iodide	0.2	2.5	**16**[b]	96 (81)
4	2-Chloroadamantane	0.5	7	**17**	NR
5	$CH_3(CH_2)_5I$	0.5	4	**5**[c]	96 (88)
6	$CH_3(CH_2)_{11}I$	0.2	3	**18**[d]	99 (78)
7	$CH_3(CH_2)_5Br$	0.5	7	**5**[c]	85 (74)
8	$CH_3(CH_2)_{11}Br$	0.2	7	**18**[d]	99 (85)
9	$PhCH_2CH_2Cl$	0.5	7	**19**	NR
10	$CH_3(CH_2)_{19}Cl$	0.5	7	**20**	NR

[a] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of RX. The yields in parentheses are isolated yields.
[b] Ref. 4g.
[c] Ref. 13.
[d] Ref. 4m.

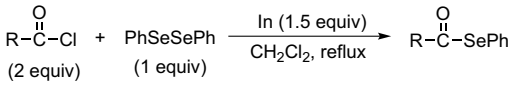
Table 6
Synthesis of alkyl phenyl sulfides from alkyl halides

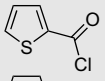
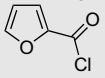
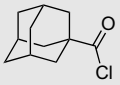


Entry	RX	RSPh	Time (h)	Yield[a] (%)
1	^{t}BuI	**21**[c]	1	99 (89)
2	^{t}BuBr	**21**[c]	3	96 (85)
3	^{t}BuCl	**21**[c]	5	80 (72)
4	1-Iodoadamantane	**22**[d]	3	80
5	1-Bromoadamantane	**22**[d]	3	65 (58)
6	$PhCH_2Br$	**23**[e]	3	88 (86)
7	$PhCH_2Cl$	**23**[e]	3	80
8	$CH_2{=}CHCH_2I$	**24**[f]	6	- (40)
9	^{i}PrI	**25**[f]	8	- (10)[b]
10	$CH_3(CH_2)_{11}I$	**26**[g]	21	- (10)[b]

[a] The reaction was analyzed by GC, and the yield was calculated on the base of the amount of RX. The yields in parentheses are isolated yields.
[b] I_2 (0.2 equiv) was added.
[c] Ref. 4m.
[d] Ref. 14.
[e] Ref. 15.
[f] Refs. 16 and 17.
[g] Ref. 4c.

Table 7
Synthesis of acyl phenyl selenides from acid chlorides

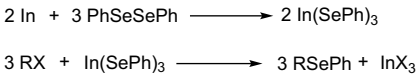


Entry	RC(O)Cl	Time (h)	RC(O)SePh	Yield[a] (%)
1	PhC(O)Cl	2	**27**[c]	62[b]
2	PhC(O)Cl	2	**27**[c]	92
3	(*p*-OMe)C_6H_4C(O)Cl	1.5	**28**[c]	80
4	(*p*-Br)C_6H_4C(O)Cl	1.5	**29**[d]	88
5	(*p*-NO_2)C_6H_4C(O)Cl	24	**30**[c]	20
6	(*m*-NO_2)C_6H_4C(O)Cl	24	**31**	10
7		1.5	**32**[c]	90
8		1.5	**33**	55
9	$CH_3(CH_2)_2C(O)Cl$	1.5	**34**[c]	80
10	$(CH_3)_2CHC(O)Cl$	2	**35**[c]	92
11	$C_6H_{11}C(O)Cl$	3	**36**[e]	62
12		2	**37**	59
13	^{t}BuC(O)Cl	1.5	**38**[c]	65

[a] The yield was calculated on the base of the amount of RC(O)Cl.
[b] In (1.0 equiv) was used.
[c] Ref. 4k.
[d] Ref. 18.
[e] Ref. 19.

phenyl selenide (**32**) in excellent yield (entry 7) under the present reaction conditions, while 2-furoyl phenyl selenide (**33**) was obtained by the reaction of 2-furoyl chloride in moderate yield (entry 8). In addition, aliphatic acid chlorides gave high yields of acyl phenyl selenides, **34** and **35** (entries 9 and 10). On the other hand, the aliphatic acid chlorides, which were sterically hindered proved to be less reactive substrates to the present method (entries 11–13).

Compared with primary alkyl halides, tertiary alkyl halides showed a higher reactivity under the present reaction conditions (Table 2). This trend in the reactivity of the substrates is in the line of radical or carbocation intermediates. We carried out some competitive experiments with mixtures of tertiary alkyl halides. A set of mixture of *tert*-butyl halides was treated with indium metal in CH_2Cl_2 at reflux for 15 min. The resulting mixtures were analyzed. The ratio of the remaining *tert*-butyl halides as Cl/I, Cl/Br, and Br/I was 6.5:1, 3.6:1, and 2.6:1, respectively. Thus, the relative reactivity of halides was found to follow the sequence of I>Br>Cl. It is consistent with the order of halides with respect to the reactivity under radical reaction conditions. To prove whether the reaction occurs via a free radical pathway, a controlled reaction of 1-iodoadamantane was performed in the presence of galvinoxyl free redical.[9] The efficiency of the reaction was the same as that of the reaction performed without the radical scavenger. In addition, no dimerization product was found in the reaction of PhSeSePh with an alkyl halide. On the basis of these results, the free radical pathway might be excluded. The reactivity of tertiary alkyl, benzylic, and allylic halides is higher than that of primary and secondary alkyl halides. In addition, the reactions of aromatic acid halides with an electron-withdrawing group were sluggish. These facts imply that in the case of alkyl halides, which can generate a stable carbocation, an electron-deficient intermediate is produced during the reaction. Thus, indium metal first reacts with an alkyl halide to generate $In(SePh)_3$,[10] which may coordinate to a substrate and produce a carbocation-like intermediate. The intermediate reacts with a nucleophilic phenyl selenide to produce alkyl phenyl selenide via S_N1 pathway. In the presence of iodine, the reactivity of the reaction depends mainly on the leaving group of substrates. The reaction with primary alkyl iodides or bromides proceeded efficiently while the reaction with primary alkyl chlorides did not take place. Indium species, $In(SePh)_3$, may react with iodine, and then it cannot coordinate with the substrate. Thus, it is possible that the nucleophilic phenyl selenide can approach from the backside of the substrate, and the reaction proceeds via S_N2 pathway. Scheme 2 illustrates the plausible mechanism for the reaction of alkyl halides with diphenyl diselenide in the presence of indium.



Scheme 2.

3. Conclusions

In summary, an efficient and practical one-pot process was developed for synthesizing alkyl phenyl selenides, sulfides, selenoesters by using indium metal. The reaction showed the selectivity for *tert*-alkyl, benzylic, and allylic halides over primary and secondary alkyl halides. In these applied reactions appending iodine, the primary and secondary alkyl phenyl selenides were obtained in high yields with the exception of primary and secondary alkyl chlorides. The trend in the reactivity of the substrates under the present reaction conditions differs from the reaction in which metal phenyl selenolates are generated by other metals or bases. The novel method has the advantages of a simple experimental procedure, mild and neutral reaction conditions, and high yields of the desired products.

4. Experimental section

4.1. General

All solvents were dried by standard methods. Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (230–400 mesh, Merck). TLC was performed on glass sheets pre-coated with silica gel (Kieselgel 60 PF_{254}, Merck). Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were performed on a Bruker 400 NMR spectrometer, which operated at 400 MHz for ^1H and 100 MHz for ^{13}C nuclei and are internally referenced to residual protio solvent signals. Chemical shifts are reported in parts per million (ppm). IR spectra were recorded on a Perkin–Elmer 16 PC FTIR spectrometer. Gas chromatography analyses were carried out on a Shimadzu gas chromatograph GC-14A instrument equipped with a flame ionization detector (FID) using nitrogen as a carrier gas. The column used for chromatography was a capillary column type HP-5 (30 m×250 mm) from Hewlett–Packard. Gas chromatography–mass spectrometry analyses were carried out on an Agilent Technologies G1530N instrument (6890N Network GC system-5973 mass selective detector, EI, 70 eV). Microanalyses were performed on a CE instrument EA1110 elemental analyzer.

4.2. General procedure for the synthesis of alkyl phenyl selenides and sulfides

A mixture of indium powder (57.4 mg, 0.5 mmol), diphenyl diselenide or diphenyl disulfide (0.5 mmol), and an organic halide

(1.0 mmol) in CH_2Cl_2 (5 mL) was stirred at reflux for 1 h under nitrogen. The mixture was then quenched with 1 M HCl and extracted with ether. The organic layer was washed with brine, dried over $MgSO_4$, and purified by column chromatography on silica gel to give the corresponding alkyl phenyl selenide.

*4.2.1. o-Bromobenzyl phenyl selenide (**9**)*

Pale yellow oil. R_f 0.25 (hexane); ^{1}H NMR ($CDCl_3$) δ 4.19 (s, 2H), 7.01–7.08 (m, 3H), 7.22–7.29 (m, 3H), 7.47–7.49 (m, 2H), 7.54 (d, 1H, J=7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 33.0, 124.4, 127.3, 127.7, 128.5, 129.0, 130.6, 133.1, 134.5, 138.3. Anal. Calcd for $C_{13}H_{11}BrSe$: C, 47.88; H, 3.40. Found: C, 47.90; H, 3.37.

4.3. General procedure for the synthesis of acyl phenyl selenides

Indium powder (86.1 mg, 0.75 mmol), diphenyl diselenide (156.1 mg, 0.5 mmol), and CH_2Cl_2 (2 mL) were placed in a two-necked flask. An acid chloride (1.0 mmol) in CH_2Cl_2 (1 mL) was added to the mixture, and the resulting mixture was stirred at reflux for 1 h under argon. The mixture was then quenched with 1 M HCl and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over $MgSO_4$. After evaporation, the residue was purified by column chromatography on silica gel to give the corresponding acyl phenyl selenide.

*4.3.1. m-Nitrobenzoyl phenyl selenide (**31**)*

Pale yellow solid. Mp 109–111 °C (hexane/EtOAc); R_f 0.23 (hexane/EtOAc, 9:1); IR (KBr) 3070, 2922, 1680, 1536, 1439, 1346, 1194, 1089, 925, 844 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.43–7.67 (m, 5H), 7.71 (t, 1H, J=8.0 Hz), 8.24 (d, 1H, J=7.7 Hz), 8.48 (d, 1H, J=8.0 Hz), 8.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 122.2, 124.9, 128.0, 129.6, 129.6, 130.2, 132.6, 136.2, 139.9, 148.5, 191.9; MS m/z (relative intensity) 307 (M^+), 207, 157, 150, 104, 92, 76, 65, 50. Anal. Calcd for $C_{13}H_9NO_3Se$: C, 51.00; H, 2.96; N, 4.57. Found: C, 51.00; H, 2.95; N, 4.50.

*4.3.2. 2-Furoyl phenyl selenide (**33**)*

Pale yellow oil. R_f 0.26 (hexane/EtOAc, 95:5); IR (neat) 3136, 3050, 1766, 1657, 1556, 1454, 1377, 1248, 1151, 1023, 945, 816 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.59 (dd, 1H, J=3.6, 1.6 Hz), 7.22 (d, 1H, J=3.5 Hz), 7.38–7.48 (m, 3H), 7.57 (d, 1H, J=3.7 Hz), 7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 112.9, 115.4, 124.8, 129.2, 129.4, 136.4, 146.8, 151.7, 180.8; MS m/z (relative intensity) 252 (M^+), 157, 154, 115, 95, 77, 67, 51. Anal. Calcd for $C_{11}H_8O_2Se$: C, 52.61; H, 3.21. Found: C, 52.64; H, 3.19.

*4.3.3. 1-Adamantanecarbonyl phenyl selenide (**37**)*

Pale yellow solid. Mp 51–53 °C (hexane/EtOAc); R_f 0.29 (hexane/EtOAc, 9:1); IR (neat) 3070, 2906, 2852, 1715, 1575, 1451, 1342, 1260, 1124, 980, 902 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 6H), 1.99 (s, 6H), 2.09 (s, 3H), 7.32–7.53 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 25.8, 27.8, 35.1, 37.6, 37.8, 129.0, 129.5, 131.0, 135.2, 185.0; MS m/z (relative intensity) 163 (M^+−PhSe), 157, 135, 107, 93, 79, 55. Anal. Calcd for $C_{17}H_{20}OSe$: C, 63.95; H, 6.31; O, 5.01; Se, 24.73. Found: C, 63.91; H, 6.28.

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