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# Synthesis of 2,3-Disubstituted Benzo[*b*]selenophenes via Electrophilic Cyclization

**Tanay Kesharwani**, **Shilpa A. Worlikar**, and **Richard C. Larock***
*Department of Chemistry, Iowa State University, Ames, Iowa 50011*

## Abstract

2,3-Disubstituted benzo[*b*]selenophenes have been prepared by the electrophilic cyclization of various 1-(1-alkynyl)-2-(methylseleno)arenes by $Br_2$, NBS, $I_2$, ICl, PhSeCl, PhSeBr and Hg $(OAc)_2$. This method tolerates a wide variety of functional groups, including alcohol, ester, nitrile, nitro and silyl groups, and proceeds under exceptionally mild reaction conditions.

## Introduction

The electrophilic cyclization of alkynes having a nucleophile in close proximity to the triple bond has proven to be an efficient way of constructing a wide array of carbocycles and heterocycles.[1] Recently our group and others have successfully utilized this approach to synthesize benzo[*b*]thiophenes,[2] benzofurans,[3] furans,[4] thiophenes,[5] indoles,[3c,6] isoquinolines,[7] quinolines,[8] isocoumarins,[9] and polycyclic aromatic hydrocarbons.[10] Similar cyclizations have also been reported using transition metal catalysts.[11] However, some of these transition metal approaches are either incompatible with functionality or lack regioselectivity. Chalcogens, like sulfur, selenium and tellurium, have seldom been employed in such transition metal-catalyzed cyclizations due to their strong affinity for transition metals.

Benzo[*b*]selenophenes have received little attention as potential drugs, although their potent biological activity and synthetic utility have been discussed in the literature.[12] Recently Otsubo and co-workers have shown that high performance organic field effect transistors can be developed from benzodiselenophenes.[13] Their studies suggest that the replacement of sulfur atoms with selenium can enhance the optoelectronic properties of thiophene-containing molecules. Thus, we were encouraged to examine the synthesis of selenium analogs of benzo [*b*]thiophenes using acetylene cyclization chemistry.

Earlier syntheses of benzo[*b*]selenophenes have generally required harsh reaction conditions and suffer from poor reaction yields and intolerance of many functional groups.[14] Among the known protocols for the synthesis of 3-halobenzo[*b*]selenophenes,[15] the reaction of 1-aryl-1-alkynes with $SeBr_4$ or $SeCl_4$ is reported to give good yields.[16] Although iodides are more useful than bromides or chlorides for subsequent transition metal-catalyzed cross coupling reactions, no general method is known for the synthesis of 3-iodobenzo[*b*]selenophenes. Herein, we report a general, high yielding synthesis of 3-iodobenzo[*b*]selenophenes via iodocyclization, which also gives good yields with several other electrophiles.

larock@iastate.edu.

## Results and Discussion

The expeditious synthesis of benzo[*b*]selenophenes have been achieved by a two step approach involving the Sonogashira coupling of 2-iodoselenoanisoles with terminal alkynes, followed by electrophilic cyclization using various electrophiles (Scheme 1). The required starting compounds **1** and **2** have been prepared by a two step approach developed by Christiaens and co-worker[17] in 35% and 49% overall yields respectively (Scheme 2).

Various substituted selenium-containing alkynes have been prepared using standard Sonogashira coupling conditions[18] in order to study the scope and generality of our methodology (Table 1). Although selenium compounds **1** and **2** react slowly with terminal alkynes under standard Sonogashira reaction conditions, the required coupling products are obtained in good to excellent yields after 24–48 h. The slow reaction may be attributed to the strong coordination between selenium and palladium in the key arylpalladium intermediate. Terminal alkynes bearing simple alkyl groups have afforded the expected internal alkynes in high yields (Table 1, entries 1 and 2). The reactions of alkylalkynes bearing cyano, ester and hydroxyl groups also proceed in excellent yields (entries 3–5). Alkynes bearing a triethylsilyl group (entry 6) and a vinylic group (entry 7) furnished the desired products in 79% and 96% yields respectively. The reaction of phenylacetylene was low yielding due to homocoupling of this alkyne (entry 8). Substituted aryl groups on the alkyne were also successfully employed in the coupling reaction (entries 9 and 10). Diyne **13** was prepared from coupling of **1** and 1,4-diethynylbenzene. However, the reaction proceeded rather slowly and afforded only a 47% yield (entry 11). The reaction of **2** and 3-cyclohexyl-1-propyne also proceeded smoothly to furnish the desired product **14** in an excellent yield (entry 12).

We have found that the electrophilic cyclization of 1-(1-decynyl)-2-(methylseleno)benzene (**3)** with $I_2$ in $CH_2Cl_2$ as the solvent at room temperature affords a near quantitative yield of the desired 2,3-disubstituted benzo[*b*]selenophene **15** after only 30 min reaction time (Scheme 3).

The yield of this reaction is not much affected when different solvents are employed (Table 2). THF, $Et_2O$, $CH_3CN$ and hexanes gave **15** in greater than 90% yields, while the reaction proceeded more slowly and gave a lower yield in MeOH (entry 4). The mild reaction conditions, ease of product isolation and high yields encouraged us to broaden the scope of our methodology by using different 1-(1-alkynyl)-2-(methylseleno)arenes (Table 3).

The yield of benzo[*b*]selenophenes was excellent whether the substituent on the alkyne was alkyl, aryl or vinylic (Table 3; entries 1, 3 and 5). In some of our earlier work on the iodocyclization of functionally-substituted alkynes ICl proved to be a better electrophile than $I_2$ for some substrates. In our current methodology, ICl gave somewhat lower yields compared to $I_2$ (see entries 2, 4 and 6). The higher yields with $I_2$ as the electrophile may be attributed to the higher nucleophilicity of an iodide ion than a chloride ion, which facilitates removal of the methyl group present in the cationic intermediate presumably generated during cyclization (see the later discussion of mechanism). Alternatively, the weaker electrophile $I_2$ may simply be less likely to react directly with the selenium moiety.

Iodocyclization also readily tolerates functionally-substituted alkyl groups (entries 7–9) with little effect on the reaction yield. The sterically hindered triethylsilylalkyne **8** also reacted rapidly to give benzo[*b*]selenophene **21** in a 91% yield (entry 10). The iodocyclization of **14** proceeded slowly when compared to that of compound **4** (entries 11 and 12); this observation can be attributed to the presence of an ester group *para* to the selenium, which reduces the electron density on selenium. No such effect is observed when varying the nature of the substituents on the remote aryl group. The presence of an electron-withdrawing nitro group or an electron-donating methoxy group did not make much of a difference and the reaction

proceeded with ease giving the desired products in greater than 90% yields (entries 13 and 14). The iodocyclization of **13** resulted in the formation of the dicyclized product in a good yield of 88% (entry 15).

Electrophilic cyclization using other electrophiles, such as $Br_2$, NBS, PhSeBr, PhSeCl, $Hg(OAc)_2$ and *p*-$O_2NC_6H_4SCl$, has also been examined in order to extend the scope of our methodology (Table 4). The cyclization of alkyne **10** using PhSeBr resulted in a slightly higher yield of the desired product when compared to PhSeCl (entries 1 and 2). PhSeBr was then employed for the cyclization of alkynes bearing alkyl and vinylic groups (entries 6 and 9) and the yields were 84% and 87% respectively. With $Hg(OAc)_2$ as the electrophile, the reaction was quenched with an aqueous NaCl solution and the chloromercurio derivative **29** was isolated in 92% yield (entry 5). When *p*-$O_2NC_6H_4SCl$ was used as an electrophile on alkyne **10**, the corresponding cyclized product was not observed even after 2 d.

The cyclization of alkynes using $Br_2$ and NBS as electrophiles gave some interesting results. The use of NBS resulted in formation of the desired product in lower yields (entries 4, 8 and 10), contrary to our analogous efforts earlier in preparing benzo[*b*]thiophenes.[2b] Unlike the reactions using NBS, cyclizations employing $Br_2$ were slower and also resulted in lower yields in comparison with our earlier benzo[*b*]thiophene methodology[2b] (entries 3 and 7). When the bromocyclization of **10** was monitored by TLC, the disappearance of starting compound was observed soon after the addition of $Br_2$, but formation of the product was not observed. However, after 20 min, the product spot appeared and its intensity increased over a period of 2–3 h. A similar observation was made during the bromocyclization of **3**, indicating once again a possible intermediate.

In an attempt to clarify these results, the cyclization of alkyne **10** by $Br_2$ was carried out in $CDCl_3$ as the solvent and the reaction was monitored by $^1H$ NMR spectroscopy. A small peak **D** was observed at δ 2.5 soon after the addition of $Br_2$. This peak corresponds to MeBr, the by-product of this overall process (Figure 1). Two more peaks were observed at approximately δ 4.0, which may correspond to a methyl group on an electron-deficient selenium. From the above $^1H$ NMR studies, a possible stepwise mechanism can be derived for bromocyclization by $Br_2$. In the first step, the electrophile coordinates with the triple bond, followed by nucleophilic attack by selenium to generate a cationic intermediate **34** (Scheme 4). The peak **B** (Figure 1) can be attributed to the methyl protons in **34**, while peak **C** corresponds to the methyl group in dibromo compound **35**. The formation of dibromo compounds of type **35** on addition of bromine to selenides has been reported earlier.[19] The cationic intermediate **34** can then undergo a facile removal of the methyl group via $S_N2$ displacement by the counter ion bromide generated *in situ* during the cyclization (Scheme 4). Selenonium salts analogous to intermediate **34** are known in the literature and have been used for the alkylation of relative acidic carbon nucleophiles.[20]

To support this mechanistic hypothesis, we attempted to isolate intermediate **34**. The bromocyclization of **10** was performed in nonpolar hexanes at 0 °C, which resulted in the formation of a yellow precipitate soon after the addition of $Br_2$. The precipitate was filtered, washed with cold hexanes, and isolated in 53% yield (Scheme 5). This precipitate was then dissolved in $CDCl_3$ and monitored by $^1H$ NMR spectroscopy, which showed decomposition of this material, assumed to be intermediate **34** (Figure 2). Peak **C** slowly disappeared over a period of 6 h, which indicated the decay of intermediate **34**. The height of peak **D** increased over this same time period, supporting the formation of methyl bromide. A noticeable change in the aromatic region was also observed, which matched the aromatic peaks of compound **28**. Reactions with $I_2$ as an electrophile proceed much faster, and similar experiments to trap the cationic intermediate failed even at a lower temperature.

Our iodobenzo[*b*]selenophene products can be further functionalized by palladium-catalyzed coupling reactions. 2-(1-Octynyl)-3-phenylbenzo[*b*]selenophene (**36**) has been successfully obtained in a 90% isolated yield by the Suzuki cross-coupling of **15** with phenylboronic acid (Scheme 6). In a similar manner, the Sonogashira coupling of **16** with phenylacetylene gave alkyne **37** in 65% yield.

## Conclusions

2,3-Disubstituted benzo[*b*]selenophenes have been obtained in good yields from simple starting materials by the electrophilic cyclization of 2-(1-alkynyl)selenoanisoles by $Br_2$, NBS, $I_2$, ICl, PhSeCl, PhSeBr and $Hg(OAc)_2$. This method tolerates many functional groups, including nitrile, hydroxyl, silyl, nitro, methoxy and ester groups. An iodine moiety can be readily introduced into the heterocycle in a position not easily obtained previously. Subsequent functionalization of the resulting heterocycles by palladium-catalyzed coupling reactions leads to a number of interesting substituted benzo[*b*]selenophenes. With respect to subsequent transition metal-catalyzed reactions, 3-iodobenzo[*b*]selenophenes are expected to be more effective than the corresponding bromo and chloro derivatives and that augurs well for this new approach to benzo[*b*]selenophenes. A cationic intermediate in the cyclization with $Br_2$ has been isolated and studied, providing evidence for a stepwise cyclization process.

## Experimental Section

### General procedure for the palladium/copper-catalyzed formation of 1-(1-alkynyl)-2-(methylseleno)arenas

To a solution of $Et_3N$ (10 mL), 2.0 mmol of *o*-iodo(methylseleno)benzene and $PdCl_2(PPh_3)_2$ (2 mol %) (stirring for 5 min beforehand), CuI (1 mol %) was added and the flask was sealed and flushed with Ar. 3.0 Mmol of terminal acetylene dissolved in 2 mL of $Et_3N$ was then added dropwise and the reaction mixture was allowed to stir at room temperature for the desired time. After the reaction was over, the resulting solution was filtered, washed with satd aq NaCl and extracted with diethyl ether (3 × 15 mL). The combined ether fractions were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product. The crude product was purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

### (1-Decynyl)-2-(methylseleno)benzene (3)

The product was obtained as a yellow oil: $^1$H NMR ($CDCl_3$) δ 0.88 (t, *J* = 6.9 Hz, 3H), 1.28–1.30 (m, 8H), 1.43–1.51 (m, 2H), 1.60–1.69 (m, 2H), 2.31 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 7.05–7.11 (m, 1H), 7.16–7.21 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$) δ 6.0, 14.3, 19.8, 22.9, 28.9, 29.1, 29.3, 29.4, 32.0, 79.2, 96.9, 124.4, 125.1, 127.0, 128.3, 132.3, 136.2; IR (neat, $cm^{-1}$) 3058, 2926, 2227, 1432; HRMS calcd for $C_{17}H_{24}Se$ 308.10432, found 308.10500.

### General procedure for the iodocyclizations

To a solution of 0.25 mmol of the alkyne and 3 mL of $CH_2Cl_2$, 1.1 equiv of $I_2$ or ICl dissolved in 2 mL of $CH_2Cl_2$ was added gradually. The reaction mixture was allowed to stir at room temperature for the desired time. The excess $I_2$ or ICl was removed by washing with satd aq $Na_2S_2O_3$. The mixture was then extracted by diethyl ether (3 × 10 mL). The combined ether layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

### 3-Iodo-2-octylbenzo[*b*]selenophene (15)

The product was obtained as a yellow oil: $^1$H NMR ($CDCl_3$) δ 0.91 (t, *J* = 6.9 Hz, 3H), 1.31–1.48 (m, 10H), 1.71–1.79 (m, 2H), 3.02 (t, *J* = 7.8 Hz, 2H), 7.24–7.29 (m, 1H), 7.39–7.45 (m, 1H), 7.77–7.83 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ 14.4, 22.9, 29.4, 29.5, 29.6, 31.6, 32.1, 36.1, 83.4, 125.3, 125.5, 125.7, 127.8, 139.1, 143.2, 148.2; IR (neat, $cm^{-1}$) 3056, 2953, 2923, 1432; HRMS calcd for $C_{16}H_{21}ISe$ 419.98532, found 419.98620.

### General procedure for the bromocyclizations

To a solution of 0.25 mmol of the alkyne and 3 mL of $CH_2Cl_2$, 1.1 equiv of $Br_2$ or 2.2 equiv of NBS dissolved in 2 mL of $CH_2Cl_2$ was added gradually. The reaction mixture was allowed to stir at room temperature for the desired time. The excess $Br_2$ or NBS was removed by washing with satd aq $Na_2S_2O_3$. The mixture was then extracted by diethyl ether (3 × 10 mL). The combined ether layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product, which was purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

### 3-Bromo-2-octylbenzo[*b*]selenophene (31)

The product was obtained as a pale yellow oil: $^1$H NMR ($CDCl_3$) δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.27–1.46 (m, 10H), 1.68–1.78 (m, 2H), 2.99 (t, *J* = 7.7 Hz, 2H), 7.25–7.31 (m, 1H), 7.39–7.45 (m, 1H), 7.80 (d, *J* = 8.1 Hz, 2H); $^{13}$C NMR ($CDCl_3$) δ 14.3, 22.9, 29.3, 29.4, 29.6, 31.4, 32.1, 32.5, 125.1, 125.2, 125.4, 125.6, 138.0, 140.5, 144.5; IR (neat, $cm^{-1}$) 3059, 2954, 2925; HRMS calcd for $C_{16}H_{21}BrSe$ 371.99918, found 371.99990.

### General procedure for the PhSeCl and PhSeBr cyclizations

To a solution of 0.25 mmol of the alkyne and $CH_2Cl_2$ (3 mL), 0.375 mmol of PhSeBr or PhSeCl dissolved in 2 mL of $CH_2Cl_2$ was added dropwise. The mixture was allowed to stir at room temperature for the desired time. The reaction mixture was washed with 20 mL of water and extracted with diethyl ether (3 × 10 mL). The combined ether layers were dried over anhydrous $Na_2SO_4$ and concentrated under vacuum to yield the crude product, which was further purified by flash chromatography on silica gel using ethyl acetate/hexanes as the eluent.

### 2-Octyl-3-(phenylseleno)benzo[*b*]selenophene (30)

The product was obtained as a yellow oil: $^1$H NMR ($CDCl_3$) δ 0.86 (t, *J* = 6.5 Hz, 3H), 1.23–1.37 (m, 10H), 1.69 (quintet, *J* = 7.3 Hz, 2H), 3.21 (t, *J* = 7.4 Hz, 2H), 7.08–7.14 (m, 5H), 7.21–7.34 (m, 2H), 7.83–7.89 (m, 2H); $^{13}$C NMR ($CDCl_3$) δ 14.4, 22.9, 29.4, 29.6, 32.1, 32.7, 33.7, 118.8, 124.9, 125.3, 125.5, 126.0, 126.6, 129.0, 129.4,132.9, 139.9, 143.7, 157.8; IR (neat, $cm^{-1}$) 3058, 2925, 1577; HRMS calcd for $C_{22}H_{26}Se_2$ 448.03937, found 448.04010.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## Acknowledgements

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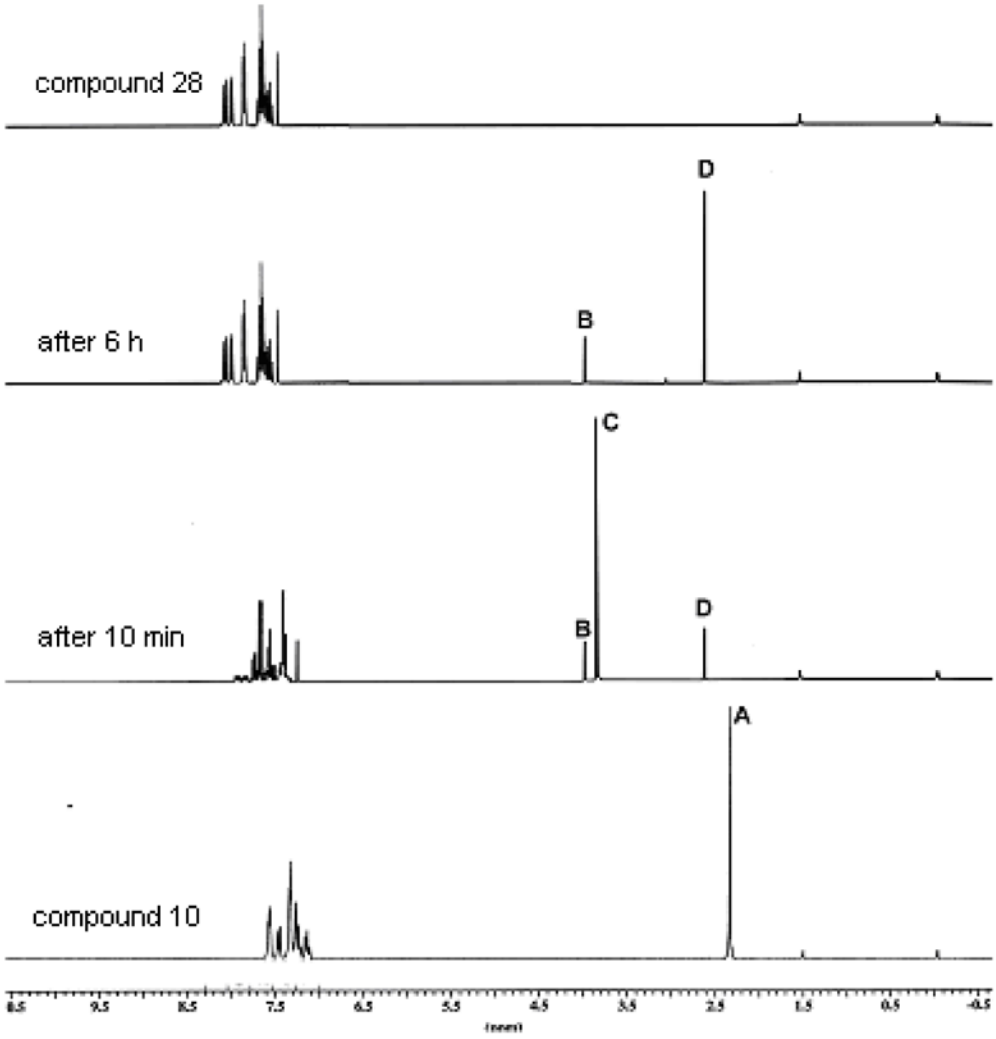



**Figure 1.**
$^{1}H$ NMR spectra from the reaction of alkyne **10** in $CDCl_3$ before and after the addition of $Br_2$.

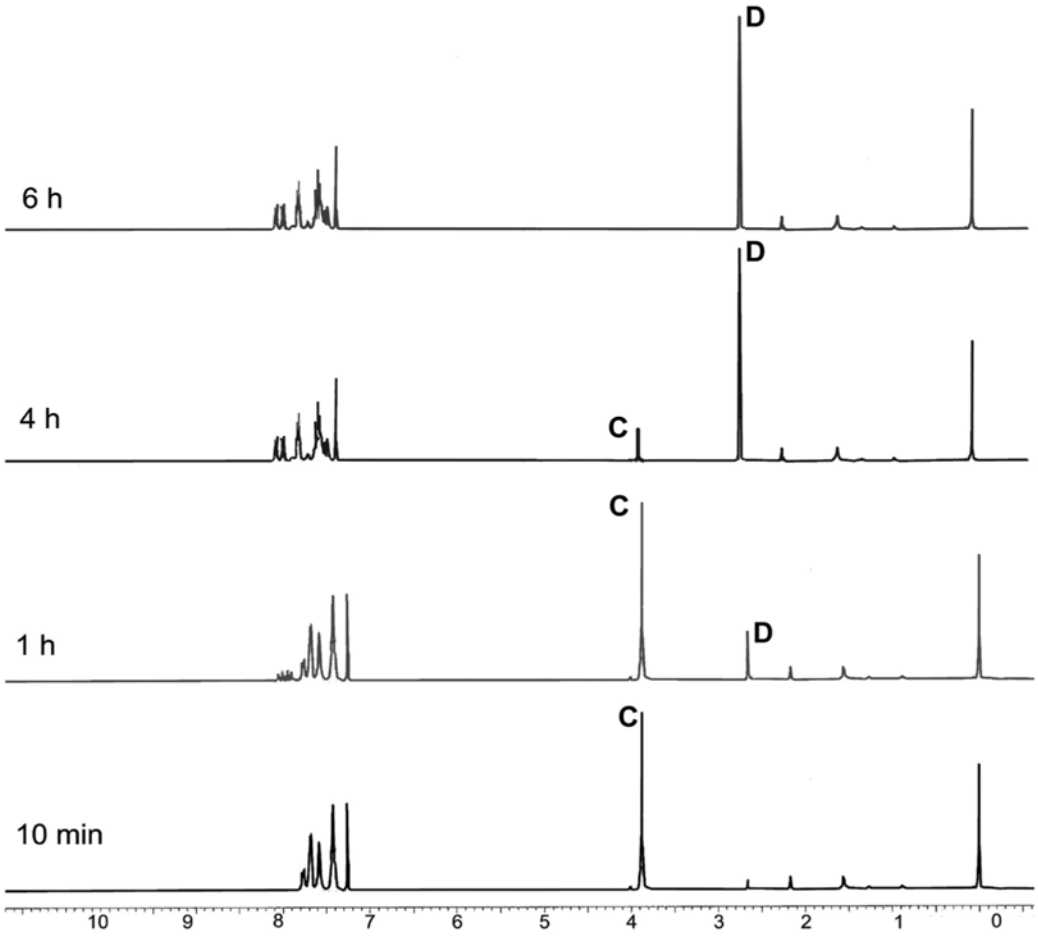
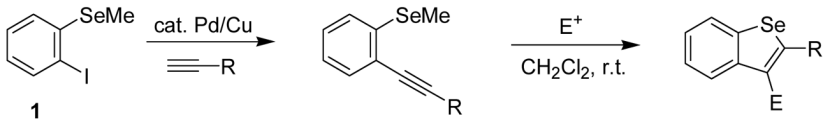
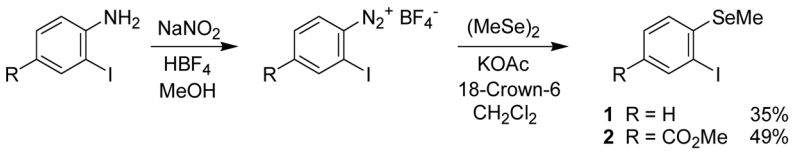


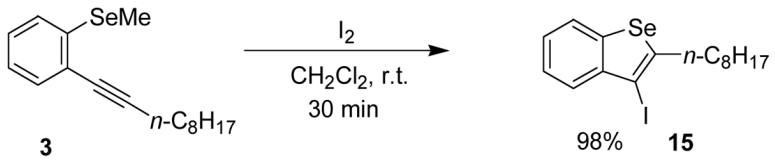

**Figure 2.**
$^{1}$H NMR spectra following the decomposition of **34** into **28** and MeBr




**Scheme 1.**

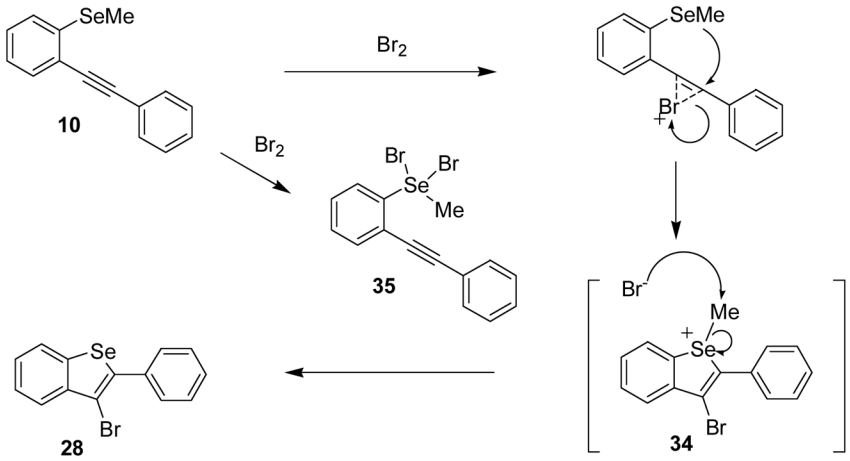



**Scheme 2.**

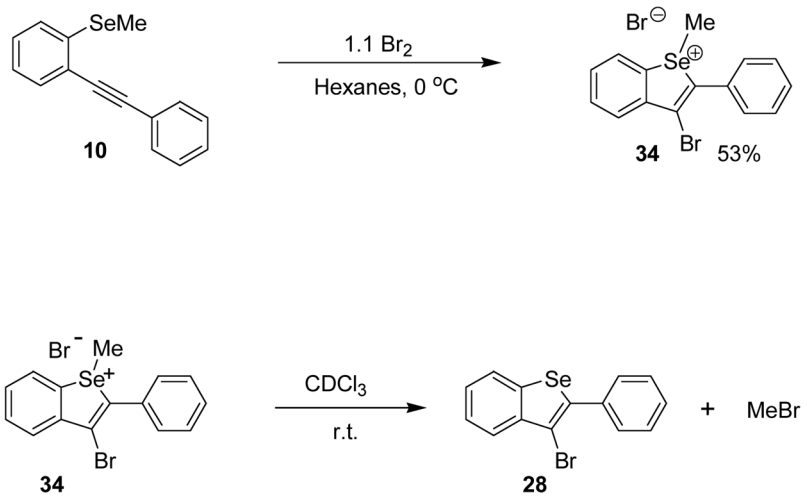



3 98% 15

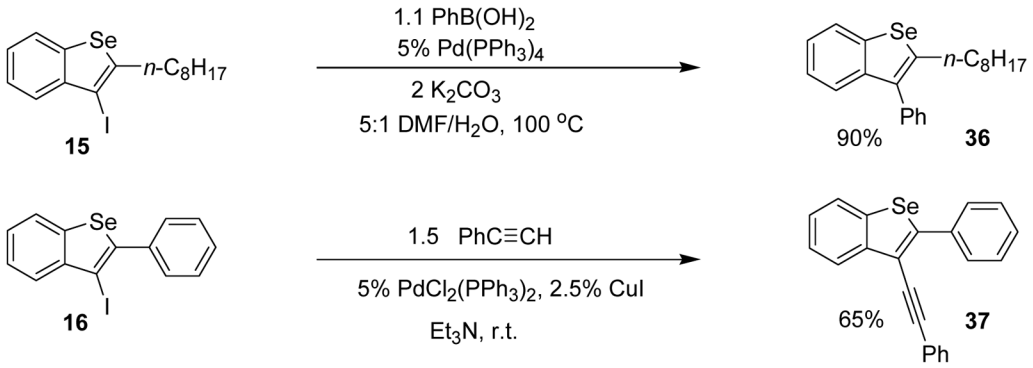
**Scheme 3.**




**Scheme 4.**



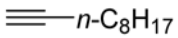
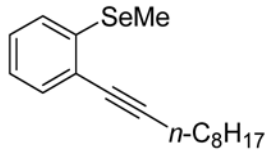
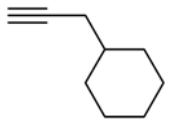
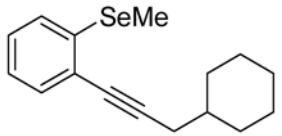
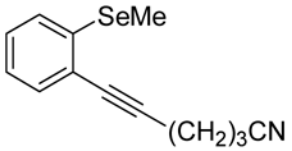
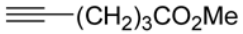
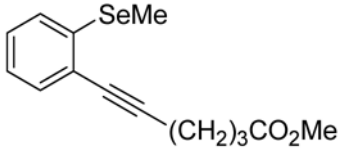
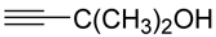
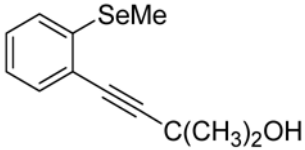
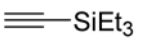
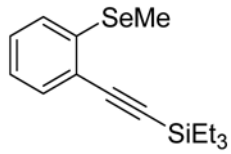
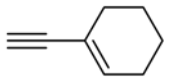
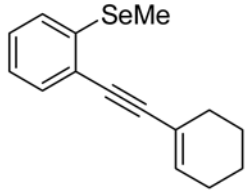

**Scheme 5.**

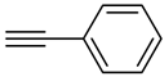
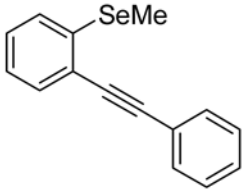
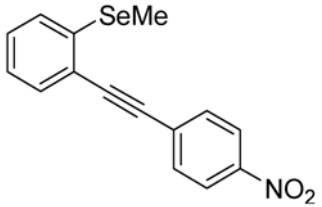
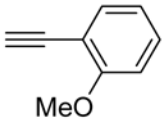
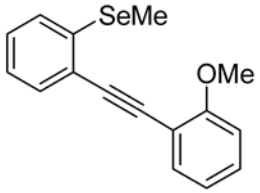
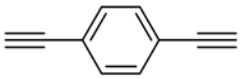
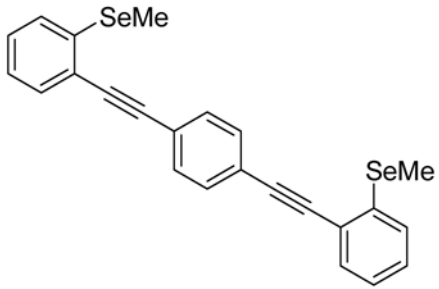
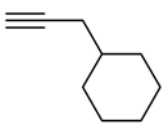
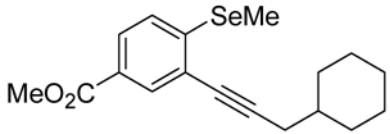



**Scheme 6.**

**Table 1**

Sonogshira coupling of 1-iodo-2-(methylseleno)arenes and terminal acetylenes.[a]

| entry | substrate | alkyne | time (h) | product | % | isolated yield |
|---|---|---|---|---|---|---|
| 1 | **1** |  | 24 |  | **3** | 82 |
| 2 | **1** |  | 24 |  | **4** | 88 |
| 3 | **1** |  | 24 |  | **5** | 86 |
| 4 | **1** |  | 48 |  | **6** | 90 |
| 5 | **1** |  | 24 |  | **7** | 95 |
| 6 | **1** |  | 24 |  | **8** | 79 |
| 7 | **1** |  | 24 |  | **9** | 96 |

| entry | substrate | alkyne | time (h) | product | % | isolated yield |
|---|---|---|---|---|---|---|
| 8 | **1** |  | 24 |  | **10** | 68 |
| 9 | **1** |  | 48 |  | **11** | 85[b] |
| 10 | **1** |  | 24 |  | **12** | 95 |
| 11 | **1** |  | 48 |  | **13** | 47[c] |
| 12 | **2** |  | 48 |  | **14** | 92 |

[a]Unless otherwise stated, all reactions were carried out on a 2.0 mmol scale in 12 mL of $Et_3N$ using 1.0 equiv of the 1-iodo-2-(methylseleno)arene, 1.5 equiv of alkyne, 2 mol % of $PdCl_2(PPh_3)_2$ and 1 mol % of CuI at room temperature for the desired time.

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[b] This reaction was carried out in a 1:1 mixture of DMF and $Et_3N$ as the solvent for 48 h.

[c] This reaction was performed using 2.2 equiv of 1-iodo-2-(methylseleno)benzene and 1.0 equiv of alkyne.

**Table 2**

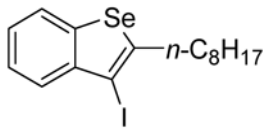
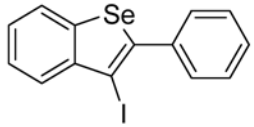
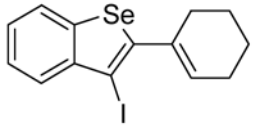
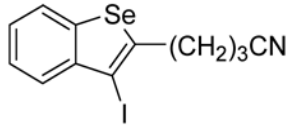
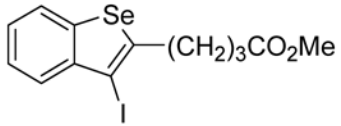
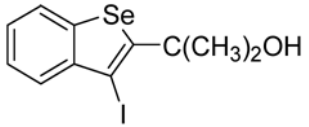
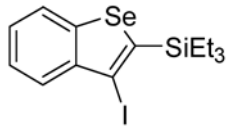
Effect of the solvent in the reaction of 1-(1-decynyl)-2-(methylseleno)benzene (**3**) with $I_2$.[a]

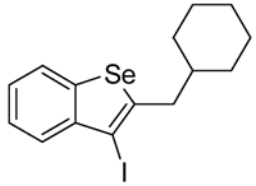
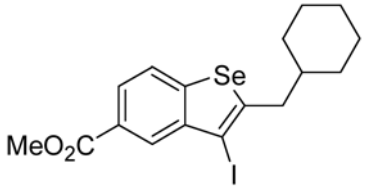
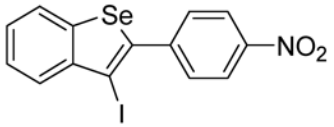
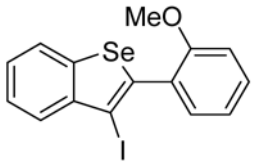
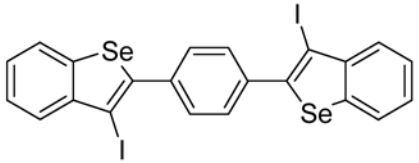
| entry | solvent | $I_2$ equiv | time (min) | % yield |
|---|---|---|---|---|
| 1 | $CH_2Cl_2$ | 1.1 | 30 | 98 |
| 2 | $CH_2Cl_2$ | 2.0 | 30 | 97 |
| 3 | $Et_2O$ | 1.1 | 30 | 91 |
| 4 | MeOH | 1.1 | 60 | 82 |
| 5 | THF | 1.1 | 30 | 92 |
| 6 | $CH_3CN$ | 1.1 | 30 | 95 |
| 7 | Hexanes | 1.1 | 30 | 90 |

[a] All reactions were carried out on a 0.25 mmol scale in 5 mL of solvent using 1.0 equiv of 1-(1-decynyl)-2-(methylseleno)benzene (**3**) and the indicated amount of $I_2$ at room temperature.

**Table 3**

Iodocyclization of various 1-(alkynyl)-2-(methylseleno)arenes.[a]

| entry | alkyne | electrophile | time (min) | product | | % isolated yield |
|---|---|---|---|---|---|---|
| 1 | **3** | $I_2$ | 30 |  | **15** | 98 |
| 2 | **3** | ICl | 60 | | **15** | 78 |
| 3 | **10** | $I_2$ | 30 |  | **16** | 90 |
| 4 | **10** | ICl | 60 | | **16** | 79 |
| 5 | **9** | $I_2$ | 30 |  | **17** | 92 |
| 6 | **9** | ICl | 60 | | **17** | 76 |
| 7 | **5** | $I_2$ | 60 |  | **18** | 87 |
| 8 | **6** | $I_2$ | 60 |  | **19** | 83 |
| 9 | **7** | $I_2$ | 30 |  | **20** | 93 |
| 10 | **8** | $I_2$ | 30 |  | **21** | 91 |

| entry | alkyne | electrophile | time (min) | product | | % isolated yield |
|---|---|---|---|---|---|---|
| 11 | **4** | $I_2$ | 30 |  | **22** | 91 |
| 12 | **14** | $I_2$ | 60 |  | **23** | 82 |
| 13 | **11** | $I_2$ | 30 |  | **24** | 94 |
| 14 | **12** | $I_2$ | 30 |  | **25** | 91 |
| 15 | **13** | $I_2$ | 30 |  | **26** | 88[b] |

[a] Unless otherwise stated, all reactions were carried out on a 0.25 mmol scale in 5 mL of solvent using 1.0 equiv of 1-(1-alkynyl-2-(methylseleno)benzene and 1.1 equiv of $I_2$ or ICl at room temperature.

[b] This reaction was carried out on a 0.25 mmol scale in 5 mL of solvent using 1.0 equiv of 1-(1-alkynyl)-2-(methylseleno)benzene and 2.2 equiv of $I_2$.

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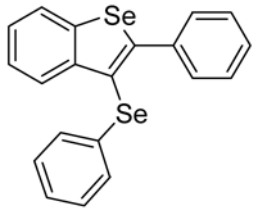
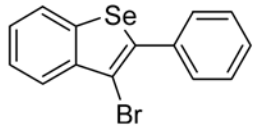
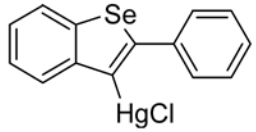
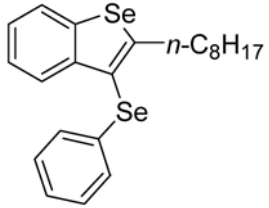
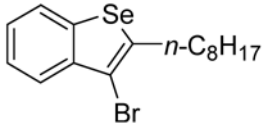
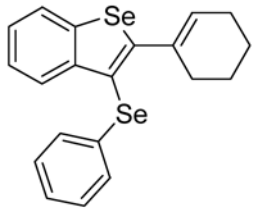
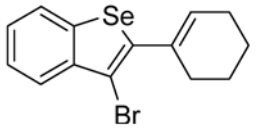
**Table 4**

Other electrophilic cyclizations of 1-(1-alkynyl)-2-(methylseleno)arenes.[a]

| entry | alkyne | Electrophile (equiv) | Time (h) | product | | % isolated yield |
|---|---|---|---|---|---|---|
| 1 | **10** | PhSeCl (1.5) | 2 |  | **27** | 92 |
| 2 | **10** | PhSeBr (1.5) | 2 | | **27** | 95 |
| 3 | **10** | $Br_2$ (1.1) | 12 |  | **28** | 75 |
| 4 | **10** | NBS (2.2) | 12 | | **28** | 46 |
| 5 | **10** | $Hg(OAc)_2$ (1.1) | 1 |  | **29** | 92[b] |
| 6 | **3** | PhSeBr (1.5) | 2 |  | **30** | 84 |
| 7 | **3** | $Br_2$ (1.1) | 12 |  | **31** | 78 |
| 8 | **3** | NBS (2.2) | 48 | | **31** | 43 |
| 9 | **9** | PhSeBr (1.5) | 2 |  | **32** | 87 |

| entry | alkyne | Electrophile (equiv) | Time (h) | product | % isolated yield |
|---|---|---|---|---|---|
| 10 | **9** | NBS (2.2) | 48 |  **33** | 48 |



[a]Unless otherwise stated, reactions were carried out on a 0.25 mmol scale in 5 mL of $CH_2Cl_2$ by using 1.0 equiv of 1-(1-alkynyl)-2-(methylseleno)benzene and 1.1 equiv of $I_2$ or ICl at room temperature.

[b]This reaction was carried out on a 0.25 mmol scale in 5 mL of AcOH using 1.0 equiv of alkyne and 1.1 equiv of $Hg(OAc)_2$ at room temperature and quenched with satd aq NaCl solution.