# Palladium-catalyzed successive C-H bond arylations and annulations toward the pi-extension of selenophene-containing aromatic skeletons

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# Palladium-Catalyzed Successive C–H Bond Arylations and Annulations toward the π-Extension of Selenophene-Containing Aromatic Skeletons

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A modular approach for the synthesis of planar π-extended selenium containing molecules from selenophene has been developed. Different combinations of Pd-catalyzed desulfitative C–H bond arylations with (2-bromo)arylsulfonyl chlorides and Pd-catalyzed intra- or/and inter-molecular C–H bond arylations with aryl bromides allowed to extend the selenophene-containing aromatic skeleton at the [b]-, [c]- or [b:d]-junctions to give phenanthro[b]selenophenes, phenanthro[c]selenophenes or diphenanthro[b:d]selenophenes

## Introduction

Planar π-extended organic molecules are considered the next generation of charge carrier trasnporting materials for opto-electronic devices.[1] Several analogues containing an heteroaromatic unit such as thiophene, or pyrrole have been synthetized and have found number of applications as electronic components for the preparation of devices.[2] Despite the recent interest of selenophenes as building blocks for the preparation of optoelectronic organic materials,[3] only scarce examples of planar π-extended molecules containing Se atoms have been prepared.[4] In 2016, Zeni *et al* prepared two phenanthroselenophenes in three steps *via* two electrophilic cyclizations as the key steps.[5] Other methods involved the use of elemental selenium and multi-steps-synthesis, which often prevent the access to well-decorated π-extended selenophene derivatives bearing sensitive functional groups.[6]

Nowadays C–H bond functionalization has emerged as a suitable alternative to other cross-coupling reactions owing its steps and atom economy and its broad functional group tolerance.[7] Interestingly, a more direct strategy enabling C–H bond functionalization coupled with annulation reaction allowed to prepare planar π-extended organic molecules[8] including sulfur-,[9] nitrogen-,[10] or oxygen- analogues.[11] However, to our knowledge, a protocol enabling successive C–H bond arylations for the preparation of selenium-containing π-extended organic molecules was not reported yet.[12] Indeed, only a few reports focused on the reactivity of selenophenes *via* transition metal-catalyzed C–H bond functionalizations. In 2011, Mori, Koumura *et al.* reported the first examples of Pd-catalyzed α-arylations of selenophenes using aryl iodides for the preparation of new dyes incorporated in photovoltaic cells.[13] Later, Schneider and co-workers succeeded to generalize α-arylation of selenophenes with other aryl halides (bromides and iodides).[14] The arylation of heteroarenes at *β*-position is still more challenging.[15] There are four main strategies to control the regioselectivity toward the C3 or C4 arylations of thiophenes: i) using a directing group,[16] ii) using a specific catalytic system,[17] iii) using C2,C5-disubstituted thiophenes[18] or iv) using specific arylating sources (*e.g.*, ArB(OH)$_2$,[19] ArSiMe$_3$,[20] ArSO$_2$Cl[21]). In 2017, our group achieved the first Pd-catalyzed β-arylation of selenophenes using ArSO$_2$Cl.[22] We also demonstrated that well-decorated tetraarylated selenophenes could be obtained in good yields *via* successive C–H bond

arylations. Besides the switch of regioselectivity, Pd-catalyzed C–H bond arylations with ArSO$_2$Cl allowed orthogonal transformations owing their chemoselectivity with halogenated substrates.[23] As a continuation of our research program dealing with the synthesis of heteroaromatic analogues of planar π-extended organic molecules,[24] we became interested in the phenanthroselenophene series.
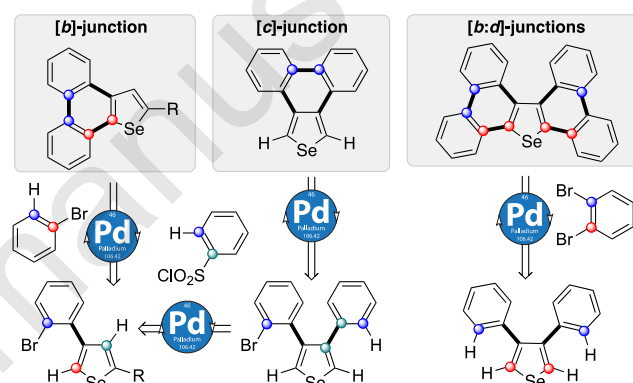


**Figure 1.** Unified Strategy for the Preparation of Phenanthroselenophenes

Our retrosynthetic analysis is outlined in Figure 2. Firstly, we planned to build phenanthro[b]selenophenes in two-operations *via* Pd-catalyzed desulfitative β-arylation with 2-bromobenzenesulfonyl chlorides, followed by Pd-catalyzed α-arylation coupled with annulation; while phenanthro[c]selenophenes will be obtained *via* three consecutive C–H bond arylations, namely Pd-catalyzed desulfitative C3-arylation with 2-bromobenzenesulfonyl chlorides of selenophene followed by a second desulfitative C4-arylation and intramolecular C–H bond arylation. Finally, diphenanthro[b:d]selenophenes will be synthetized from 3,4-diarylselenophenes and 1,2-dibromobenzene *via* Pd-catalyzed double Pd-catalyzed α-arylation coupled with annulation.

## Results

Using our previous reaction conditions for the β C–H bond arylation of selenophenes,[22] we firstly prepared the 4-(2-bromophenyl)selenophene intermediates **1**-**7** from 2-arylselenophene derivatives and diversely substituted 2-bromobenzenesulfonyl chlorides (Scheme 1). This unique regioselectivity might be due to Pd$^{II}$/Pd$^{IV}$ catalytic cycle rather

than $Pd^0/Pd^{II}$ owing the fast oxidative addition of $ArSO_2Cl$ to $Pd^{II}$.[25] Notably, 2-arylated selenophenes were prepared from selenophene *via* C–H bond arylation with aryl bromides using slightly modified literature procedures (see SI).[14] In the presence of 10 mol% $Pd(OAc)_2$ and 6 equivalents of base ($Li_2CO_3$) in 1,4-dioxane, selenophenes substituted at C2-position by 4-chlorophenyl, 4-pyridyl, 4-tolyl or 1-naphtyl groups reacted with 2-bromobenzenesulfonyl chloride to afford the C2,C4-diarylated selenophenes **1-4** in moderate to good yields, without C–Br bond cleavage. The reactions tolerated substituents on the 2-bromobenzenesulfonyl chloride, such as 4-trifluoromethyl-, 4-fluoro-, or 3-trifluoromethyl and their coupling with 2-(4-chlorophenyl)selenophene afforded the 2,4-diarylselenophenes **5-7** in 55-70% yields. Compounds **8** and **9** were prepared *via* our reported procedure.[22]
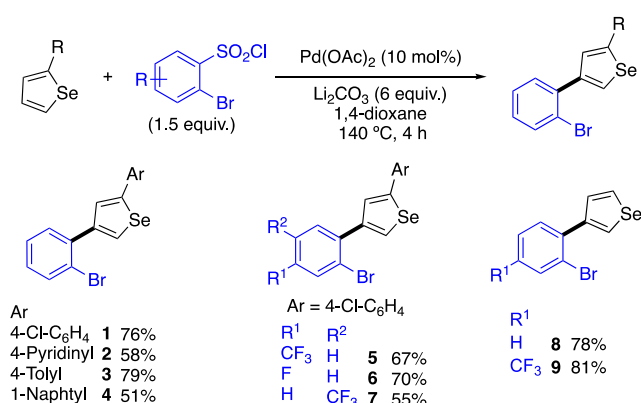


**Scheme 1.** Pd-Catalyzed Direct C4 Arylations of 2-Arylselenophenes Using 2-Bromobenzenesulfonyl Chlorides

Then, with the selenophene derivatives **1-7** bearing a 2-bromophenyl unit at C4 position in hand, we turned our attention to the second step, namely Pd-catalyzed tandem C5-arylation with aryl bromides followed by annulation reaction to generate the phenanthroselenophenes in a one-pot two steps process (Scheme 2). Firstly, the reactivity of a set of aryl bromides was evaluated with 4-(2-bromophenyl)-2-(4-chlorophenyl)selenophene (**1**) using a diphosphine-palladium catalyst [$PdCl(C_3H_5)(dppb)$] in the presence of KOPiv in DMA at 150 ºC. Reactions with electron-poor aryl bromides (e.g., 4-bromobenzonitrile, 4-bromobenzotrifluoride, 4-bromopropiophenone) with which the oxidative addition of the C–Br bond to Pd(0) is faster than the C–Br of the C4-phenyl unit of selenophene **1**, gave C5-arylation followed by annulation reaction to afford the desired phenanthroselenophenes **10-12** in good yields. Notably, the C–Cl bond was untouched during this tandem reaction. From a *meta*-substituted aryl bromide, the product **13** was isolated in moderate yield as a single regioisomer because the intramolecular C–H bond arylation (annulation) occurred at the less hindered position. *ortho*-Substituted aryl bromides yielded **14** and **15**. Notably, with 2-bromobenzonitrile, the phenanthroselenophene **14** was obtained in a two-pots procedure. In the first instance, only the C5-arylated selenophene intermediate **14i** was obtained due to

the formation of non-active black palladium species. However, when this isolated intermediate was subjected to the same reaction conditions, namely $PdCl(C_3H_5)(dppb)$ in the presence of KOPiv in DMA, we were pleased to find that cyclization reaction occurred to deliver the phenanthroselenophene **14**. The use of larger amount of $PdCl(C_3H_5)(dppb)$ affords the desired product **14** in one-pot, albeit in a lower yield. Next, we found that the nature of C2-aryl group on the selenophene exhibits a minor effect on the reactivity, as 4-tolyl, 1-naphtyl or 4-pyridyl C2-substituted selenophenes **2-4** nicely reacted with 4-bromobenzonitrile to give the phenanthroselenophenes **16-18** in good yields. Interestingly, the reaction was not limited to aryl bromides, and heteroaryl bromides could also be employed. The π-extended aromatic **19** containing both selenophene and thiophene units with a 2,2'-link was obtained in 45% yield from **1** and 2-acetyl-5-bromothiophene. Then, the influence of an additional substituent on the 4-aryl group of 4-(2-bromoaryl)-2-(4-chlorophenyl)selenophenes was investigated. 4-Arylselenophene derivatives **5** or **6** bearing trifluoromethyl or fluoro substituents at the *meta* position of the C–Br bond, nicely reacted with 4-bromobenzonitrile to afford the phenanthroselenophenes **20** and **21** in 57% and 48% yield, respectively. This tandem C5-arylation-annulation was also successful with the selenophene derivative **7** bearing a trifluoromethyl at the *para*-position of the C–Br bond, yielding the target product **22** in one step. However, it should be noted that reactions with electron-rich aryl bromides afforded complexes mixtures without the formation of the desired planar π-extended compounds.
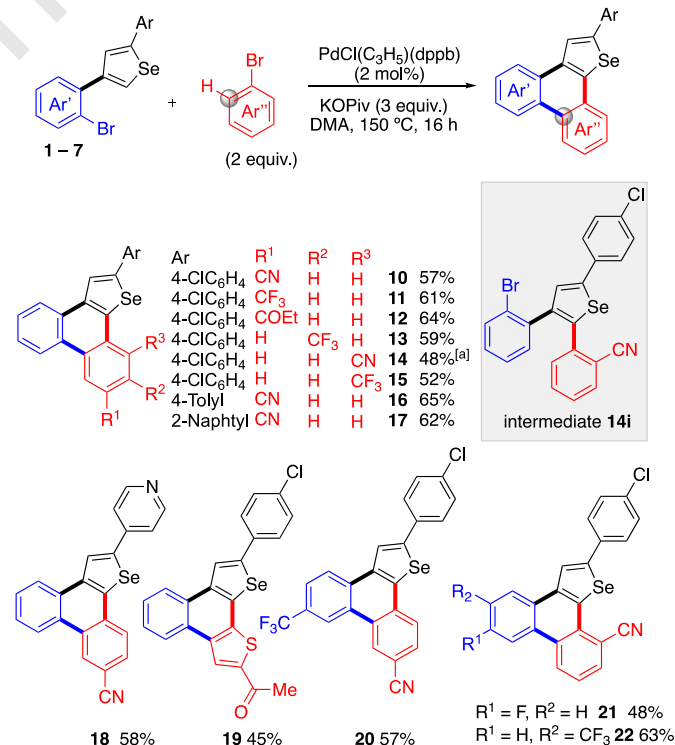


[a] Overall yield over two steps, intermediate **14i** was isolated and reacted with $PdCl(C_3H_5)(dppb)$ (2 mol%), KOPiv (2 equiv.) in DMA at 150 ºC, 16 h

**Scheme 2.** Pd-Catalyzed Tandem C5-Arylation – Annulation of 4-(2-Bromophenyl)selenophene Derivatives **1**–**7** with Aryl Bromides for the Synthesis of Phenanthro[*b*]selenophenes

Interestingly we found that using the same catalyst [PdCl(C₃H₅)(dppb)] in the presence of a larger amount of KOPiv (4 equiv.) in DMA at 150 ºC, 3-(2-bromophenyl)selenophene (**8**) was diarylated at C2 and C5 positions with aryl bromides and that intramolecular C–H bond arylation also occurred affording a one-pot protocol for the preparation of phenanthroselenophenes *via* a three-fold C–H bond arylation (Scheme 3). From aryl bromides p*ara*-substituted by chloro, cyano, or propionyl groups, the seleno π-extended compounds **23**-**25** were obtained in a two-steps procedure after isolation of the non-cyclized 2,5-diaryl-4-(2-bromophenyl)selenophene intermediates **23i**-**25i**. In contrast, aryl bromides p*ara*-substituted by fluoro or trifluoromethyl groups underwent Pd-catalyzed three-fold direct arylations to afford the desired phenanthroselenophenes **26** and **27** in one-pot. Moreover, the use of 4-fluoro-1-iodobenzene instead of 1-bromo-4-fluorobenzene gives a lower yield in the desired phenanthroselenophene **26**. Reactions with 1-bromo-4-*tert*-butylbenzene or 4-iodotoluene did not resulted in the formation of the corresponding phenanthro[*b*]selenophenes. 2-Bromobenzonitrile and 2-bromobenzotrifluoride were efficiently coupled with **8** to afford the fused selenophenes **28** and **29** in 51% and 53% yield, respectively. The structure of **29** was secured by X-Ray analysis.[26] To prepare a π-extended aromatics containing both selenophene and pyridine units, an excess amount of base was required to neutralize the HCl salt of 4-bromopyridine, but the C2,C5-diarylation reaction followed by annulation reaction proceeded in one-pot affording **30** in 56% yield.
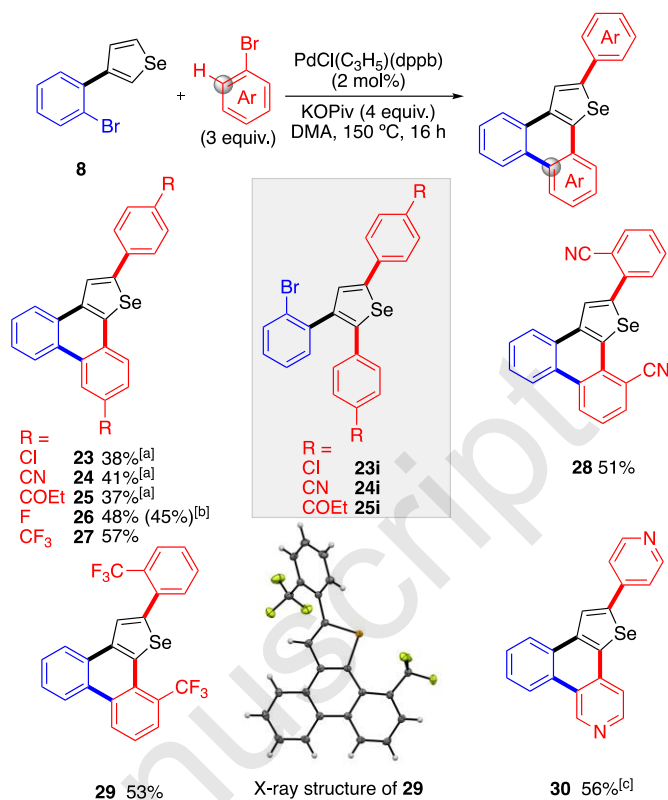


[a] Overall yield over two steps, intermediates **23i**-**25i** were isolated and reacted with PdCl(C₃H₅)(dppb) (2 mol%), KOPiv (2 equiv.) in DMA at 150 ºC, 16 h. [b] Using ArI instead of ArBr. [c] 7 Equiv. of KOPiv.

**Scheme 3.** Pd-Catalyzed One-Pot Three-Fold Direct Arylations of 3-(2-Bromophenyl)selenophene **8** with Aryl Bromides for the Synthesis of Phenanthro[*b*]selenophenes

Then, from a mixture of 3-(2-bromophenyl)selenophene (8) and 4-CN-, 4-NO2- or 4-MeO-benzenesulfonyl chlorides the 3,4-diarylated selenophenes 31–33 were obtained in moderate yields (Scheme 4). The introduction of a second aryl group at C4 position of 9 and 3-phenylselenophene was also achieved to give 34 and 35 in 32% and 49% yield, respectively. The second C4-arylation was more sluggish than the C3-arylation, but could be conducted using the same catalytic system provided that the reaction time was extended to 40 h. Similarly, using this extended reaction time, the one-pot 3,4-diarylation of selenophene has been performed with 4-(trifluoromethyl)benzenesulfonyl chloride, benzenesulfonyl chloride or 4-chlorobenzenesulfonyl chloride to give the symmetrical 3,4-diarylated selenophenes 36 and 37 in low yields.
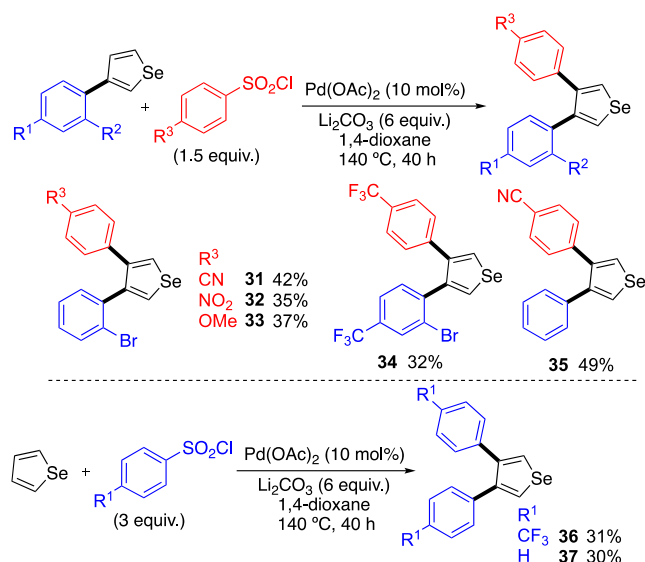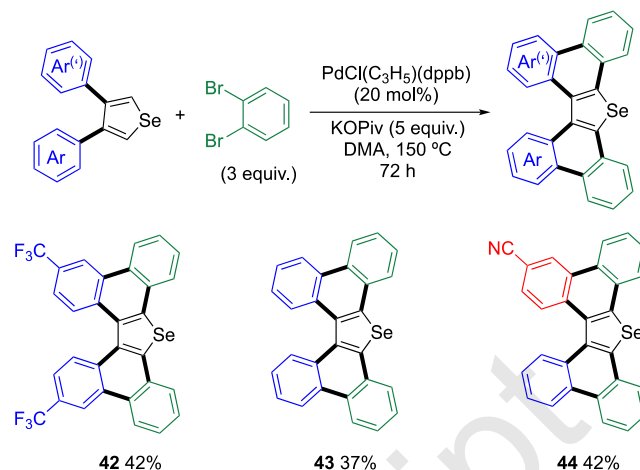
**Scheme 4.** Pd-Catalyzed Direct C4 Arylations of 3-Arylselenophenes (top) or C3,C4-diarylation of Selenophene (bottom)

Having synthetized 3,4-diarylselenophenes, in which one of the aryl groups is a 2-bromoaryl, we investigated the Pd-catalyzed intramolecular C–H bond arylation to access to phenanthro[*c*]selenophene structures (Scheme 5). The treatment of **31**–**35** by annulative conditions, namely 2 mol% of PdCl(C₃H₅)(dppb) in the presence of KOPiv (4 equiv.) in DMA at 150 ºC led to the phenanthro[*c*]selenophene derivatives **38**–**41** in good yields *via* a 6-membered ring formation. The reaction tolerated different functional group on the aryl unit such as CN, NO₂, OMe and CF₃.
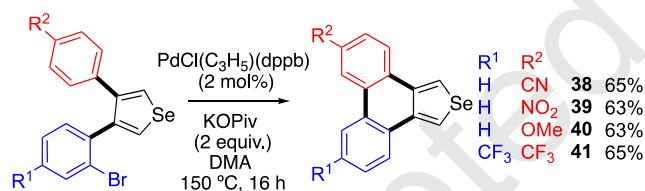


**Scheme 5.** Pd-Catalyzed Intramolecular C–H Bond Arylation of 3-(2-Bromoaryl)-4-arylselenophenes for the Synthesis of Phenanthro[*c*]selenophene Derivatives

Later, we were pleased to find that diphenanthro[*b*:*d*]selenophenes could be synthetized in a one-pot operation from 3,4-diarylselenophenes and 3 equivalents of 1,2-dibromobenzene *via* double Pd-catalyzed α-arylation coupled with C–H annulation. The symmetrical diphenanthro[*b*:*d*]selenophenes **42** and **43** were isolated in moderate yields from **36** and **3**7 using 20 mol% of PdCl(C₃H₅)(dppb) in the presence of KOPiv (5 equiv.) in DMA at 150 ºC. Interestingly, from unsymmetrical C3,C4-diarylselenophene **35**, prepared from selenophene via two successive desulfitative C–H bond arylations, the diphenanthro[*b*:*d*]selenophene **44** was isolated in 42% yield.



**Scheme 6.** Pd-Catalyzed One-Pot Four-Fold Direct Arylations of 3,4-Diarylselenophenes with 1,2-Dibromobenzene for the Synthesis of Diphenanthro[*b*:*d*]selenophenes

Finally, we explored the preparation of phenanthro[*b*]selenophenes from 2,4-diarylselenophenes (Scheme 7). From 2-(4-chlorophenyl)selenophene, Pd-catalyzed desulfitative arylation using benzenesulfonyl chloride afforded the 2,4-diarylselenophene **45** in 63% yield. Then, in the presence of 1,2-dibromobenzene, C5-H bond arylation followed by annulation reaction gives the desired phenanthro[*b*]selenophene **46** in 65% yield using 20 mol% of PdCl(C₃H₅)(dppb) associated with KOPiv (5 equiv.) in DMA at 150 ºC.
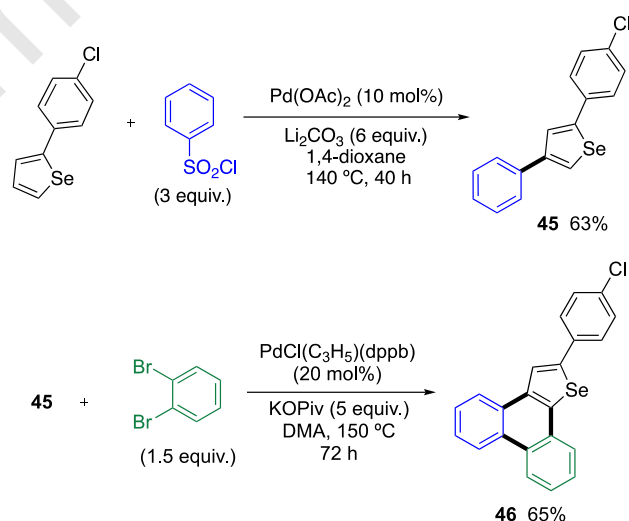


**Scheme 7.** Synthesis of a Phenanthro[*b*]selenophene *via* Pd-Catalyzed C4 Desulfitative arylation followed by One-Pot Two-Fold Direct Arylation of a 2,4-Diarylselenophene with 1,2-Dibromobenzene

## Conclusions

In summary, we have achieved the synthesis of a wide diversity of well-decorated π-extended aromatics containing selenium atom from selenophene using the combination of three to six C–H bond arylations. The key step was the introduction of (2-bromo)aryl group(s) at β-position of selenophenes using Pd-catalyzed desulfitative arylation with (2-bromo)arylsulfonyl

chorides. Then, Pd-catalyzed one-pot tandem C–H direct arylations of selenophene rings at α-position with aryl bromides followed by annulation reactions afforded phenanthro[b]selenophenes. In contrast, using a second Pd-catalyzed desulfitative arylation at β'-position of selenophenenes followed by a cyclization reaction, phenanthro[c]selenophenes were obtained. Rapid construction to exotic scaffolds such as diphenanthro[b:d]selenophenes has also been achieved by double Pd-catalyzed α-arylation − annulation reaction.

## Conclusions

The conclusions section should come in this section at the end of the article, before the acknowledgements.

## Conflicts of interest

There are no conflicts to declare

## Acknowledgements

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