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Sequential Carbon–Carbon/Carbon–Selenium Bond Formation Mediated by Iron(III) Chloride and Diorganyl Diselenides: Synthesis and Reactivity of 2-Organoselenyl-Naphthalenes

Ana M. S. Recchi,[†] Davi F. Back,[‡] and Gilson Zeni*[,†]

[†]Laboratório de Síntese, Reatividade, Avaliação Farmacológica e Toxicológica de Organocalcogênios and [‡]Laboratório de Materiais Inorgânicos, CCNE, UFSM, Santa Maria, Rio Grande do Sul 97105-900, Brazil

Supporting Information

ABSTRACT: In this paper, we report an intramolecular cyclization of benzylic-substituted propargyl alcohols promoted by iron(III) chloride and diorganyl diselenides to give 2-organoselenyl-naphthalenes via a sequential carbon–carbon/carbon–selenium bond formation. The present reaction tolerated a wide range of substituents in both propargyl alcohols and diorganyl diselenides to give the desired 2-organoselenyl-naphthalenes in good yields with high selectivity. In addition, O-acyl protected propargyl alcohol and propargyl bromide were also subjected to this protocol giving the corresponding 2-organoselenyl-naphthalenes. We found that dichalcogenide species affected the formation of cyclized products, whereas diorganyl diselenides gave high yields, moderate yields were obtained with diorganyl disulfides, and no product formation was found with diorganyl ditellurides. The key transformations could be attributed to the carbon–carbon triple bond activation of benzylic-substituted propargyl alcohols by a seleniranium ion, antiattack of the electron cloud from the aromatic ring at the activated triple bond, and cyclization via an exclusive 6-*endo*-dig process. We also found that the corresponding 2-organoselenyl-naphthalenes are suitable substrates to the selenium–lithium exchange reactions followed by trapping with aldehydes affording the corresponding secondary alcohols.

INTRODUCTION

The initial observations that selenium prevents liver necrosis in rats fed a selenium-deficient Torula yeast in the early 1950s[1] and its molecular function in mammalian cells led to demonstration that selenium is a nutritionally important trace element.[2] The detection of selenocysteine in the active center of hepatic rat glutathione peroxidase confirmed the existence of a new nucleophile, the selenolate.[3] These studies had a decisive contribution to change the view of researchers about selenium chemistry.[4] As a result, intense interest has been directed toward the development of new methods for the synthesis of organoselenium compounds, and a variety of well-established classical methods to introduce a selenium moiety in organic substrates are now available in the literature.[5] One of the ways to access organoselenium compounds is the transformation of elemental selenium into nucleophilic species by reaction with lithium and Grignard reagents or by reduction of diorganyl diselenides by alkali metals or alkali hydrides.[6] Other common approach to introduce a selenium moiety into organic molecules involves the use of selenium electrophilic species, which can be easily prepared by reaction of diorganyl diselenides with a halogen source,[7] although nowadays they are commercially available. Further important methods include the use of selenium radical species, which can be obtained by homolytic cleavage of the selenium–selenium single bond using irradiation with light near-UV region.[8] Organoselenyl radicals thus formed exhibit high reactivity toward other substrates.[9] In recent years, the concept of combining iron salts with diorganyl diselenides has emerged as a promising strategy for the synthesis of a variety of substituted organoselenium compounds from readily accessible starting materials under mild conditions.[10] Iron reagents have appeared as an attractive alternative to other transition metals because their relative stability, abundance, low toxicity, economic and ecologic advantages, and excellent tolerance toward various functional groups.[11] The iron(III)-catalyzed annulation reactions are particularly efficient strategy for the naphthalene derivatives construction.[12] The importance of naphthalenes derives from their well-known physical, chemical[13] and biological properties.[14] The previous investigation of Larock and co-workers utilized PhSeBr as electrophilic source in the cyclization reaction of alkynols **1**, aiming at introducing PhSe at 2-position of naphthalene rings.[15] However, the reaction afforded the desired product in a modest 36% yield together with the product of PhSeBr addition to alkyne **3** in 53% yield. In order to introduce an organoselenium moiety at the 2-position of naphthalene rings, in a one-step reaction, we explored if alkynols **1** can be used as starting materials to prepare 2-organoselenyl-naphthalenes **2**, instead of vinylic selenides **3**, in a cyclization reaction promoted by diorganyl diselenides and iron salts (Scheme 1). From a synthetic point of view, molecules having a C(sp)^2-Se bond have been extensively modified for selective construction of more complex structures via carbon–carbon bond formation.[16]

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Scheme 1

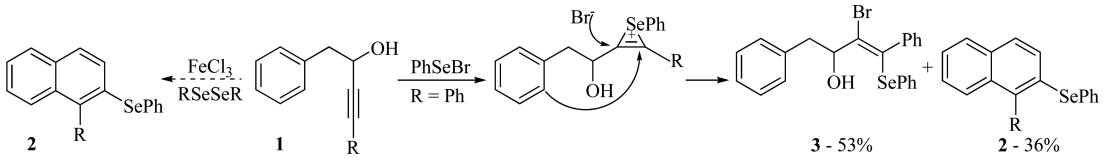
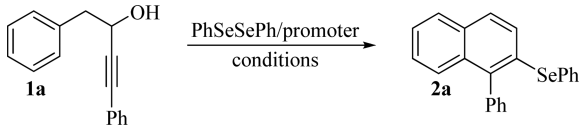


Table 1. Effect of Different Reaction Parameters on the Preparation of 2-(Phenylselanyl)-naphthalene 2a[a]



entry	PhSeSePh (equiv)	promoter (equiv)	solvent	temperature (°C)	yield (%)[b]
1	1.5	$FeCl_3$ (1.5)	CH_2Cl_2	40	71
2	1.5	BF_3OEt_2 (1.5)	CH_2Cl_2	40	37
3	1.5	$ZnCl_2$ (1.5)	CH_2Cl_2	40	N.R.
4	1.5	PTSA (1.5)	CH_2Cl_2	40	16
5	1.5	H_3PO_4 (1.5)	CH_2Cl_2	40	N.R.
6	1.5	$FeCl_3$ (1.5)	CH_2Cl_2	25	60
7	0.75	$FeCl_3$ (1.5)	CH_2Cl_2	40	55
8	0.6	$FeCl_3$ (1.5)	CH_2Cl_2	40	77
9	0.6	$FeCl_3$ (1.5)	CH_2Cl_2	40	77[c]
10	0.6	$FeCl_3$ (2.0)	CH_2Cl_2	40	67
11	0.6	$FeCl_3$ (1.5)	CH_2Cl_2	40	67
12	0.6	$FeCl_3$ (1.5)	DCE	70	63[c]
13	0.6	$FeCl_3$ (1.0)	DCE	70	59
14	0.6	$FeCl_3$ (1.0)	DCE	70	56[c]
15	0.6	$FeCl_3$ (0.5)	DCE	70	69
16	0.6	$FeCl_3$ (0.75)	DCE	70	71[c]
17	0.6	$FeCl_3$ (0.3)	CH_2Cl_2	40	11
18	0.6	$FeCl_3$ (0.3)	CH_2Cl_2	40	42[d]
19	0.6	$FeCl_3$ (0.3)	DCE	70	50
20	0.6	$FeCl_3$ (0.75)	$CHCl_3$	60	65[c]
21	0.6	$FeCl_3$ (0.75)	CH_3CN	82	64[c]
22	0.6	$FeCl_3$ 0.75	toluene	110	45[c]
23	0.6	$FeCl_3$ (0.75)	CH_3NO_2	100	27[c]
24	0.6	$FeCl_3$ 0.75	EtOH	78	16[c]
25	0.6	$FeCl_3$ (0.75)	THF	67	15[c]
26	0.6	$FeCl_3$ (0.75)	1,4-dioxane	100	10[c]
27	0.6	$FeCl_3 \cdot 6H_2O$ (0.75)	DCE	70	51[c]
28	0.6	$FeSO_4 \cdot 7H_2O$ (0.75)	DCE	70	>5[c]
29	0.6	$Fe(acac)_3$ (0.75)	DCE	70	>5[c]
30	0.6	$FeCl_2 \cdot 4H_2O$ (0.75)	DCE	70	29[c]
31	0.6	Fe_2O_3 (0.75)	DCE	70	N.R.[c]
32	0.6	$FeCl_3$ (0.75)	DCE	70	77[e]
33	0.6	$FeCl_3$ (0.75)	DCE	70	56[c,e,f]
34	0.6	–	DCE	70	N.R.

[a]The reaction was performed by addition of diphenyl diselenide to a solution of promoter in solvent (5 mL), under argon atmosphere at room temperature. After 15 min at this temperature, alkynol **1a** (0.25 mmol) was added. The resulting mixture was stirred under temperature indicated in the table for 12 h. [b]Yield of purified product. [c]The reaction was carried out under air atmosphere in an open flask. [d]The reaction was performed with K_2CO_3 (2 equiv). [e]The resulting mixture was stirred for 1 h. [f]The reaction was performed with DCE (2 mL).

RESULTS AND DISCUSSION

General Conditions. The starting alkynols **1** used for the synthesis of 2-organoselenyl-naphthalenes **2** are easily accessible from alkynylation of commercially available carbonyl compounds using lithium acetylides as the alkynylating agent. Initial investigations for the cyclization of alkynols **1** were made using diphenyl diselenide as organoselenium source and a Bronsted or a Lewis acid as promoter. Thus, the cyclization was carried out by addition of diorganyl diselenide (1.5 equiv) to a solution of the promoter (1.5 equiv) in dichloromethane (5 mL), under argon atmosphere at room temperature. After 15 min at this temperature, the alkynol **1a** (0.25 mmol) was added and the reaction was heated to reflux. Among the Lewis acid tested, that with iron(III) chloride gave the 2-phenyselenyl-naphthalene **2a** in a higher yield (Table 1, entries 1−3). Further investigations indicated that the Bronsted acids tested were ineffective in promoting the cyclization of alkynol **1a** (Table 1,

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entries 4 and 5). These results are in agreement with previously report that iron salts are the most efficient Lewis acid for selenium−selenium bond cleavage under proper conditions.[10d,17] Because the high yield obtained for the cyclization of alkynol **1a**, iron(III) chloride was shown to be the promoter of choice for additional optimization studies. Decreasing the reaction temperature to 25 °C led to the formation of **2a** in 60% yield together with the starting material (Table 1, entry 6). Next, our experimental protocol turned to the effect of diphenyl diselenide amount. The decrease in the amount of diphenyl diselenide to 0.75 gave the product in moderate yield, while the reduction to 0.6 equiv led to obtain **2a** in 77% yield (Table 1, entries 7 and 8). The use 0.6 equiv implies that both portions (2 PhSe) of diphenyl diselenide (PhSeSePh) are incorporated into the structure of the final product. This is important because the atom economy obtained results in a reduction in the quantity of waste and unwanted byproducts delivering significant environmental benefits and cost savings. We carried out many experiments using open tube instead of inert atmosphere (argon), to determine if the oxygen could be the oxidizing agent for the regeneration of diphenyl diselenide (PhSeSePh) from selenol (PhSeH). These studies revealed that the yield in the formation of **2a** was not significantly modified using air atmosphere instead of inert atmosphere (argon), owing to economic or technical reasons, an open flask was adopted for further studies (Table 1, entry 9). Additional investigations indicated that the cyclization proceeded smoothly to give the 2-phenyselenyl-naphthalene **2a** in good yield even when the loading of iron(III) chloride was reduced to 0.75 equiv (Table 1, entries 10−16). However, low yields were obtained when the reactions were performed in a catalytic amount of iron(III) chloride (Table 1, entries 17−19). To optimize the reaction medium, other solvents were examined. Among the solvents tested, chloroform and acetonitrile delivered good cyclization conversion, while with toluene, nitromethane, ethanol, tetrahydrofuran and 1,4-dioxane lower yields of product were obtained (Table 1, entries 20−26). Next, other iron sources were considered under the cyclization conditions. The results obtained did not show any further improvement over the results obtained with iron(III) chloride (Table 1, entries 27−31). We followed the progress of the reaction by periodic analysis using TLC to determine the necessary reaction time for the complete consumption of the starting material. We observed that 1.0 h was the required time taken for the reaction to be completed (Table 1, entry 32). To minimize the amount of waste solvents, we tested the effect of concentration on the yield of reaction and good yields were still achieved using 2.0 mL of DCE instead of 5.0 mL (Table 1, entry 33). These last two experiments are significant because makes the present cyclization more economical and environmentally attractive in terms of energy efficiency. When we run the reaction of alkynol **1a** with diphenyl diselenide, in the absence of iron(III) chloride, 2-phenyselenyl-naphthalene **2a** was not obtained and only the starting material was recovered (Table 1, entry 34). The evaluation of reaction conditions studied showed that the addition of alkynol **1a** (0.25 mmol) to a previous prepared solution of diphenyl diselenide (0.6 equiv) and iron(III) chloride (0.75 equiv) in DCE (2 mL), under air atmosphere at 70 °C for 1 h, is the best condition to obtain the 2-phenyselenyl-naphthalene **2a** in higher yield (Table 1, entry 33). The distance between the nucleophilic carbon of the aromatic ring and the carbon−carbon triple bond could result in competition between the intramolecular 6-*endo*-dig cyclization and 5-*exo*-dig mode resulting in a mixture of isomers. The regiochemical outcome of the carbon attack was based on NMR analysis and proved by single-crystal X-ray diffraction of the 2-phenyselenyl-naphthalene **2a**, which confirmed that the reaction followed a 6-*endo*-dig process (Figure 1; the CCDC 1525289 contains the supplementary crystallographic data for the compound **2a**).

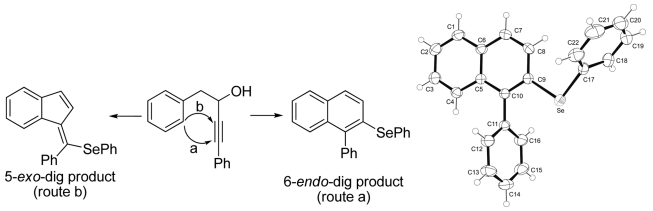

Figure 1. Competition between the intramolecular 6-*endo*-dig (route a) cyclization and 5-*exo*-dig mode (route b).

Scope of the Reaction. With the optimization conditions determined, they were expanded to a wide variety of alkynols **1** and diorganyl dichalcogenides and the results are shown in Table 2. To investigate the influence of diorganyl diselenides on the synthesis of 2-organoselenyl-naphthalenes **2**, we studied the reaction of alkynol **1a** with diorganyl diselenides bearing different substituents on the structure (Table 2, entries 1−13). When the alkynol **1a** was reacted with diaryl diselenides containing neutral or electron-donating groups on their aryl moieties, the corresponding naphthalene derivatives **2a−e** were obtained in good yields (Table 2, entries 1−5). An exception for these series was observed for diaryl diselenide having a methoxyl group at the *para* position (Table 2, entry 6). In this case no cyclization product was observed under the standard conditions and a significant amount of the diaryl selenide **4** was isolated together with alkynol **1a** (Scheme 2, eq 1). The generation of **4** could be explained in terms of iron selenol formation, which could undergo further C−Se bond formation by the coupling of selenol and diaryl diselenides.[10d,18] To prove this hypothesis we reacted the bis(4-methoxyphenyl) diselenide with iron(III) chloride in the absence of alkynol **1a**, under our standard reaction conditions (Scheme 2, eq 2). After 1 h we obtained the bis(4-methoxyphenyl) selenide quantitatively as the product. This result suggests that the reaction of alkynol **1a** with bis(4-methoxyphenyl) diselenide did not allow the cyclization even that using an excess of diselenide, reflux and a long reaction time, because the diselenide is consumed in a parallel reaction with iron salt (Scheme 2). Under the optimized reaction conditions, the diaryl diselenides containing electron-withdrawing groups gave good results on the cyclization of alkynol **1a** but with lower yields than those of diaryl diselenides containing electron-donating groups (Table 2, entries 7−9). In addition, the bulky diaryl diselenides gave the cyclized products **2j** and **2k** in moderate yields (Table 2, entries 10 and 11), suggesting that electronic and steric effects of substituents on the diselenides influence the yields of this cyclization process. The electronic and steric effects can restrict the selenium−selenium bond cleavage by iron salt. The reaction was therefore investigated using heteroaryl diselenides, such as bis(pyridyl) diselenide and bis(thienyl) diselenide; however, they failed to provide the desired naphthalene products (Table 2, entries 12 and 13). These negative results can be rationalized through the coordination of donor atoms of the heteroaryl diselenides with iron chloride giving an iron

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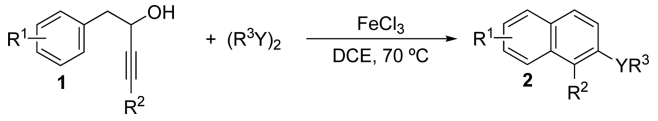
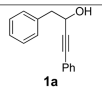
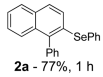
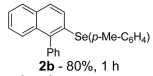
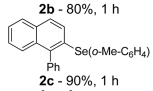
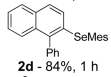
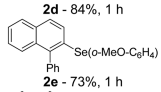
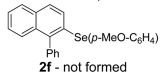
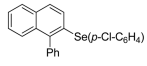
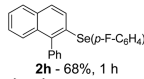
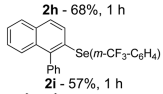
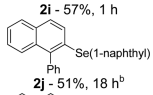
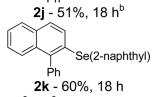
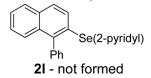
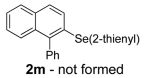
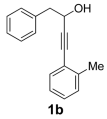
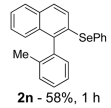
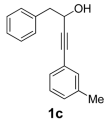
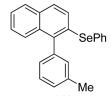
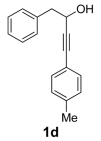
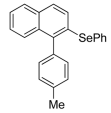
Table 2. Synthesis of 2-Organoselenyl-naphthalenes 2[a]



entry	alkynol **1**	$(R^3Y)_2$	2-organoselenyl-naphthalenes **2**-yields, reaction time
1	 **1a**	$(PhSe)_2$	 **2a** - 77%, 1 h
2	**1a**	$(p\text{-Me-}C_6H_4Se)_2$	 **2b** - 80%, 1 h
3	**1a**	$(o\text{-Me-}C_6H_4Se)_2$	 **2c** - 90%, 1 h
4	**1a**	$(SeMes)_2$	 **2d** - 84%, 1 h
5	**1a**	$(o\text{-MeO-}C_6H_4Se)_2$	 **2e** - 73%, 1 h
6	**1a**	$(p\text{-MeO-}C_6H_4Se)_2$	 **2f** - not formed
7	**1a**	$(p\text{-Cl-}C_6H_4Se)_2$	 **2g** - 68%, 1 h
8	**1a**	$(p\text{-F-}C_6H_4Se)_2$	 **2h** - 68%, 1 h
9	**1a**	$(m\text{-}CF_3\text{-}C_6H_4Se)_2$	 **2i** - 57%, 1 h
10	**1a**	$(1\text{-naphthyl-Se})_2$	 **2j** - 51%, 18 h[b]
11	**1a**	$(2\text{-naphthyl-Se})_2$	 **2k** - 60%, 18 h
12	**1a**	$(2\text{-pyridyl-Se})_2$	 **2l** - not formed
13	**1a**	$(2\text{-thienyl-Se})_2$	 **2m** - not formed
14	 **1b**	$(PhSe)_2$	 **2n** - 58%, 1 h
15	 **1c**	$(PhSe)_2$	 **2o** - 72%, 1 h
16	 **1d**	$(PhSe)_2$	 **2p** - 62%, 1 h

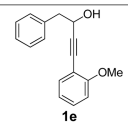
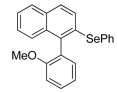
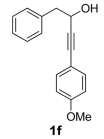
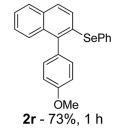
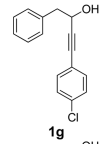
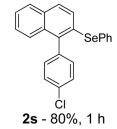
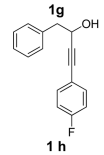
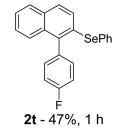
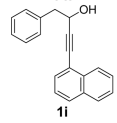
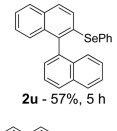
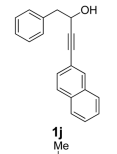
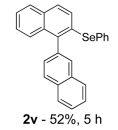
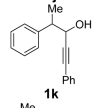
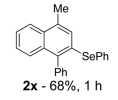
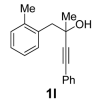
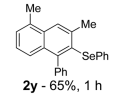
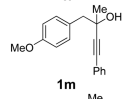
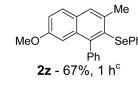
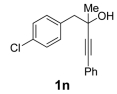
entry	alkynol **1**	$(R^3Y)_2$	2-organoselenyl-naphthalenes **2**-yields, reaction time
17	 **1e**	$(PhSe)_2$	 **2q** - 74%, 1 h
18	 **1f**	$(PhSe)_2$	 **2r** - 73%, 1 h
19	 **1g**	$(PhSe)_2$	 **2s** - 80%, 1 h
20	 **1 h**	$(PhSe)_2$	 **2t** - 47%, 1 h
21	 **1i**	$(PhSe)_2$	 **2u** - 57%, 5 h
22	 **1j**	$(PhSe)_2$	 **2v** - 52%, 5 h
23	 **1k**	$(PhSe)_2$	 **2x** - 68%, 1 h
24	 **1l**	$(PhSe)_2$	 **2y** - 65%, 1 h
25	 **1m**	$(PhSe)_2$	 **2z** - 67%, 1 h[c]
26	 **1n**	$(PhSe)_2$	**2aa** - 44%, 1 h
27	**1a**	$(BuSe)_2$	**2ab** - 70%, 1 h
28	**1o**	$(PhSe)_2$	**2ac** - 74%, 1 h
29	**1a**	$(MeS)_2$	**2ad** - 56%, 1 h[d]
30	**1a**	$(PhS)_2$	**2ae** - 41%, 1 h[e]

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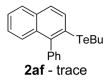
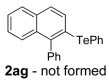
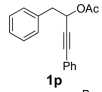
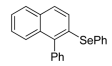
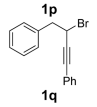
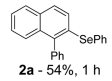
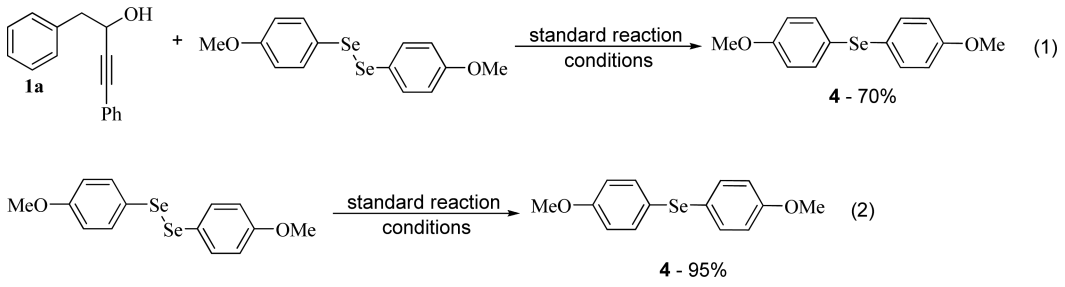
Table 2. continued

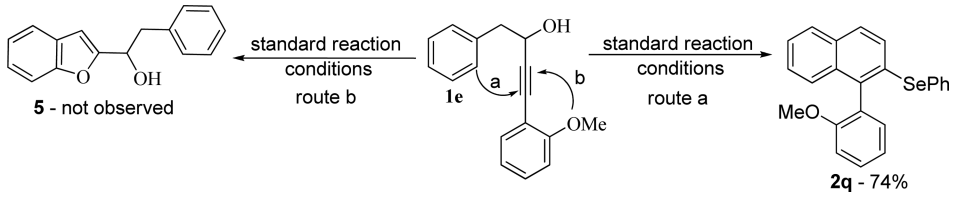
entry	alkynol **1**	$(R^3Y)_2$	2-organoselenyl-naphthalenes **2**- yields, reaction time
31	**1a**	$(BuTe)_2$	 **2af** - trace
32	**1a**	$(TePh)_2$	 **2ag** - not formed
33	 **1p**	$(PhSe)_2$	 **2a** - 44%, 1 h
34	 **1q**	$(PhSe)_2$	 **2a** - 54%, 1 h

[a]The reaction was performed by the addition of diorganyl dichalcogenide (0.6 equiv) to a solution of $FeCl_3$ (0.75 equiv) in DCE (2 mL), under air atmosphere, at room temperature. After 15 min, at this temperature, alkynol **1** (0.25 mmol) was added. The resulting mixture was stirred at 70 °C for the time indicated in Table 2. [b]The reaction was performed using diorganyl diselenide (1.5 equiv) and $FeCl_3$ (1.5 equiv). [c]The reaction was performed using $FeCl_3$ (1.5 equiv). [d]$(MeS)_2$ (8 equiv) was used. [e]K_2CO_3 (2 equiv) was used.

Scheme 2



Scheme 3



stable complex hampering the cyclization. We next examined the cyclization reaction of the substituted alkynols **1b–j**, each one bearing a substituent at the aromatic ring directly bonded to the triple bond (Table 2, entries 14–22). We reacted alkynols bearing methyl and methoxyl groups with diphenyl diselenide in order to investigate the influence of electron-donating groups on the aromatic ring. In all cases the corresponding organoselenyl-naphthalenes were obtained in high yields although, the alkynol **1b**, which has a bulky methyl group at the *ortho*-position, gave the desired product in moderate yields (Table 2, entries 14–18). The alkynol **1e**, which has the methoxyl and the aromatic ring competing as potential nucleophiles, could gave the naphthalene **2q**, benzofuran **5** or a mixture of them (Scheme 3). The ratio of products depends on several factors, including the nucleophilic character, the steric effects and polarization of the alkyne triple bond.[19] Using our protocol, the cyclization of alkynol **1e** gave the exclusive formation of product, resulting from participation of phenyl ring as nucleophile. This result is in agreement with the higher nucleophilicity of phenyl ring when compared to that of the methoxyl group.[20] The effects of electron withdrawing and bulky groups directly bonded to alkyne were also studied. When we used alkynol **1g**, which has chlorine at the *para*-position of this aromatic group, the cyclized product was obtained in 80% yield, whereas the presence of fluorine substituent at the *para*-position gave the naphthalene in a moderate 47% yield (Table 2, entries 19 and 20). The reaction showed to be sensitive to the presence of bulky naphthalene group giving the products **2u** and **2v** only in moderate yields (Table 2, entries 21 and 22). We next examined the cyclization of alkynols with a methyl group at the homopropargyl and propargyl positions. With these substrates we observed no difference in reactivity, whereas the reactions could be performed at 70 °C for 1 h affording **2x** and **2y** in 68 and 65% yields, respectively (Table 2, entries 23 and 24). With regard to the presence of substituents at the benzylic group, methyl and methoxyl groups lead to better yields than that of the electron withdrawing chlorine group (Table 2, entries 24–26). Replacing the diaryl diselenides by dialkyl diselenide had no negative effect on the yield, as the cyclization reaction of alkynol **1a** with dibutyl diselenide gave the 2-butylselenyl-naphthalene **2ab** in 70% yield (Table 2, entry 27). The cyclization reaction of alkynol **1o**, which has an alkyl chain bonded to alkyne was also investigated (Table 2, entry 28). It is well recognized in the literature that this reaction could be hampered when alkyl-substituted triple bonds are employed in electrophilic cyclization reaction.[21] This reaction could only give a moderate yield of cyclized product or in some cases the product of triple bond reduction was isolated as the exclusive product. This last product probably arises from the addition of electrophilic species to the carbon–carbon triple bond.[7] The hypothesis that the absence of π bonds next to the alkyne decreased the reactivity of the carbon–carbon bond is considered to explain the behavior of this substrate. However,

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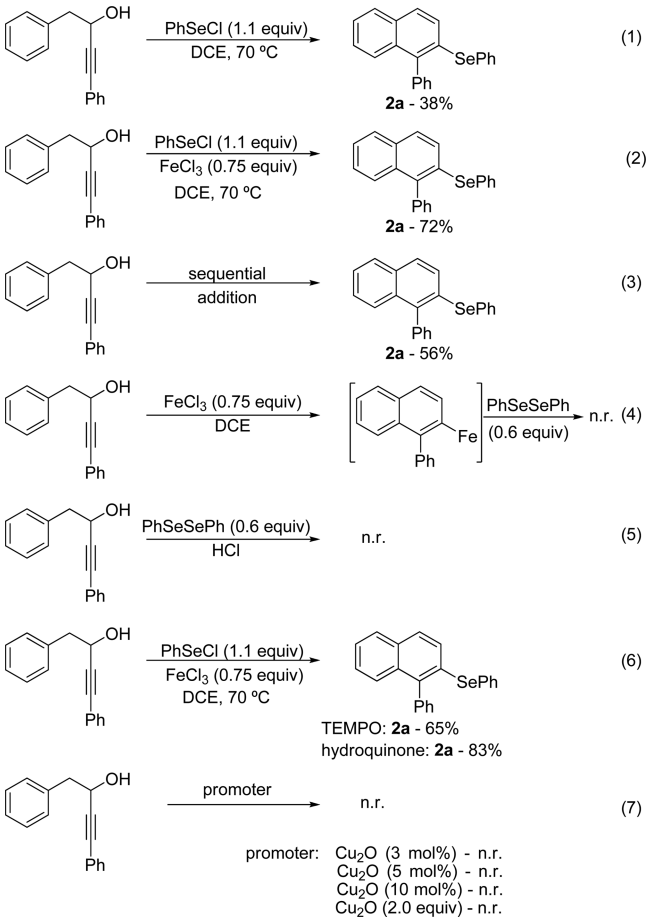
under our conditions the reaction of alkynol **1o** with diphenyl diselenides gave the naphthalene **2ac** in 74% yield (Table 2, entry 28). In an effort to extend the optimized reaction conditions to other diorganyl dichalcogenides, alkynol **1o** was reacted with diorganyl disulfides and diorganyl ditellurides. The diorganyl disulfides, upon cyclization conditions, afforded the products in moderate yields, whereas diorganyl ditellurides did not afford the products (Table 2, entries 29–32). The reactivity of disulfides in this cyclization reaction can be rationalized through the strength of the sulfur–sulfur bond that prevents its cleavage by iron salt. The negative results obtained for ditellurides are probably explained by the formation of polymeric iron tellurolate complex, which is very instable, decomposing via telluroxide elimination by oxidation.[17] Besides the alkynol, O-acyl and bromine groups at the propargyl position could also react well under the optimized reaction conditions to give the 2-phenylselenyl-naphthalenes **2a** in moderate yields (Table 2, entries 33 and 34).

Mechanism Discussion. To establish a plausible reaction mechanism, a number of control reactions were performed (Scheme 4): (i) Treatment of alkynol **1a** with PhSeCl, a

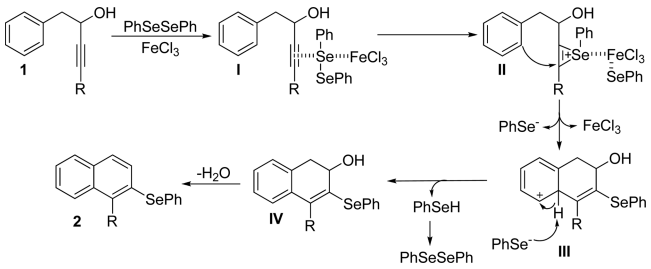
Scheme 4



selenium electrophilic species that could be formed in situ by reaction of diphenyl diselenide with iron(III) chloride, afforded the desired 2-phenyselenyl-naphthalene **2a** in 38% yield, together with product of PhSeCl addition to alkyne (Scheme 4, eq 1).[15] (ii) Treatment of alkynol **1a** with PhSeCl and iron(III) chloride under the optimized conditions delivered the corresponding naphthalene **2a** in 72% yield (Scheme 4, eq 2). (iii) The reaction running by sequential addition of all reagents, instead of previous mixture of iron(III) chloride and diphenyl diselenide, gave **2a** in only 56% yield (Scheme 4, eq 3). The experiments described in Scheme 4, eqs 1–3 suggest that a selenium electrophilic species alone is unable to promote the cyclization reaction and that the mutual action between iron(III) chloride and diphenyl diselenide is essential for the formation of **2a** in good yield. (iv) No reaction occurred when diphenyl diselenide was added to a previous prepared solution of iron(III) chloride and alkynol **1a** (Scheme 4, eq 4). This experiment implies that a $C(sp)^2$-Fe intermediated might not be the active species to promote cyclization of alkynol **1a**. (v) The reaction of alkynol **1a** with diphenyl diselenide in the presence of dry HCl gas and the absence of iron(III) chloride led to a complex mixture of unidentified products (Scheme 4, eq 5). This result excludes the action of HCl, released from decomposition of iron(III) chloride, as a cyclization promoter. vi) Upon adding radical inhibitors, such as TEMPO and hydroquinone, the reaction of alkynol **1a** with diphenyl diselenide, under optimized reaction conditions gave the product **2a** in 65% and 82% yields respectively, which suggests that a radical pathway does not contribute for the formation of **2a** (Scheme 4, eq 6). (vii) The reaction of alkynol **1a** with diphenyl diselenide using Cu_2O 3 mol %, 5 mol %, 10 mol % and 2 equiv as promoter did not result in conversion into the desired product (Scheme 4, eq 7). These studies confirm that iron(III) chloride is the real reactive species under the reaction conditions and that the active participation of Cu_2O as trace contaminant of the iron(III) chloride is discarded.[22]

Mechanism Proposal. On the basis of above investigation and the knowledge that iron salts react with diorganyl diselenides promoting the selenium–selenium bond heterogeneous cleavage to give an organoselenyl cation and an organoselenyl anion,[10d,17] a plausible mechanism for this reaction has been outlined in Scheme 5. The coordination of

Scheme 5



the carbon–carbon triple bond to the electrophilic portion of diphenyl diselenide generates the intermediate **I**. The iron(III) coordination with one selenium atom from diorganyl diselenide activates the other toward nucleophilic attack by the alkyne giving the seleniranium ion **II**. The antiattack of the electron cloud from the aromatic ring at the activated intermediate **II** produces the cyclized cationic intermediate **III** via a 6-*endo*-dig process. Deprotonation of intermediate **III** by selenolate anion restores the aromatic ring giving the dihydronaphthalene species **IV**, which can undergo dehydration to give 2-phenyselenyl-naphthalenes **2** (Scheme 5).

Reactivity of 2-Organoselenyl-Naphthalenes. The presence of $C(sp)^2$-Se bond on the organic substrates offers considerable potential for further elaboration, particularly in the formation of new carbon–carbon, carbon–metal, carbon–

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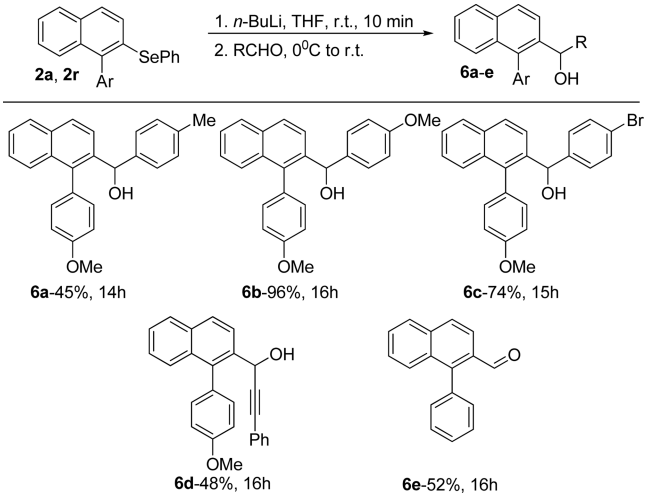
halogen and carbon−heteroatom formation via lithium intermediate[23] or applied as electrophiles in transition metal catalyzed reactions.[24] In this respect, the 2-organoselenyl-naphthalenes prepared is a straightforward option to regio- and stereoselectivity modification on naphthalene structures. To determine the reactivity of 2-organoselenyl-naphthalenes we envisioned that they could be treated with *n*-butyllithium to give lithium naphthalenide anion, via selenium−lithium exchange reactions, which would be trapped with aldehydes to furnish the corresponding alcohols. Thus, organolithium intermediate was generated by addition of *n*-butyllithium (1.1 equiv) to a solution of 2-organoselenyl-naphthalene (0.25 mmol) in THF (5 mL) and hexane (5 mL), at room temperature. The resulting solution was stirred for 10 min at this temperature and the aldehyde was added at 0 °C and reacted at room temperature for the time indicated in Scheme 6. The reactivity of different aldehydes having electron-

Scheme 6



withdrawing and electron-donating substituents on the aromatic ring afforded moderate to good yields of the desired secondary alcohols **6a−c**. The 3-phenylpropiolaldehyde was also suitable electrophile giving **6d** in 48% yield. The reaction of lithium naphthalenide anion with DMF under the reaction conditions, gave the corresponding aldehyde **6e** in 52%, after 16 h.

CONCLUSION

In summary, we have developed a strategy for the construction and functionalization of naphthalene rings by a sequential carbon−carbon/carbon−selenium bond cyclization of benzylic-substituted propargyl alcohols mediated by iron(III) chloride and diorganyl diselenides. The substrate scope of the reaction was studied, showing that a range of benzylic-substituted propargylic alcohols were compatible with the optimized reaction conditions, giving exclusively the 2-organoselenyl-naphthalenes in good yields following a 6-*endo*-dig process. The 2-organoselenyl-naphthalenes thus obtained further underwent the selenium−lithium exchange reactions with *n*-buthyllithium to give the lithium naphthalenide anion, which was trapped with aldehydes furnishing the corresponding alcohols. Considering that iron salts are easily available commercially, not expensive, relatively nontoxic and the reactions were carried out under open tube, and the carbon−carbon and carbon−selenium bonds were formed in a one step, this method could be considered an economic and eco-friendly protocol. The other advantage of this protocol is that the reaction gave the products in good yields, using 0.6 equiv of diorganyl diselenides, which indicates that the two portions of diselenides were incorporated in the final products, demonstrating a high atom economy and conversion efficiency of the cyclization reactions.

EXPERIMENTAL SECTION

Materials and Methods. Proton nuclear magnetic resonance spectra (^{1}H NMR) were obtained on a NMR spectrometer at 400 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$ or tetramethylsilane (TMS) as the external reference. Data are reported as follows: chemical shift (δ), multiplicity, coupling constant (J) in Hertz and integrated intensity. Carbon-13 nuclear magnetic resonance spectra (^{13}C NMR) were obtained on a 400 NMR spectrometer at 100 MHz. Spectra were recorded in $CDCl_3$ solutions. Chemical shifts are reported in ppm, referenced to the solvent peak of $CDCl_3$. Abreviations to denote the multiplicity of a particular signal are s (singlet), d (doublet), t (triplet), quart (quartet), quint (quintet), sex (sextet), dd (double doublet) and m (multiplet). High resolution mass spectra were recorded on a mass spectrometer using electrospray ionization (ESI). Column chromatography was performed using Silica Gel (230−400 mesh). Thin layer chromatography (TLC) was performed using Gel GF254, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Most reactions were monitored by TLC for disappearance of starting material. The following solvents were dried and purified by distillation from the reagents indicated: tetrahydrofuran from sodium with a benzophenone ketyl indicator. All other solvents were ACS or HPLC grade unless otherwise noted. Air- and moisture-sensitive reactions were conducted in flame-dried or oven-dried glassware equipped with tightly fitted rubber septa and under a positive atmosphere of dry nitrogen or argon. Reagents and solvents were handled using standard syringe techniques. The $FeCl_3$ was used in 99.99% purity purchased from commercial suppliers.

General Procedure for the Synthesis of 2-Organoselenyl-naphthalenes 2a−ag. To a 10 mL Schlenk tube with a magnetic stirring bar, at room temperature were charged $FeCl_3$ (0.03 g, 0.18 mmol), diorganyl dichalcogenides (0.15 mmol) and 1,2-dichloroethane (3 mL). The reaction mixture was stirred at room temperature for 15 min. After this time, appropriate substrate **1** (0.25 mmol) was added and the reaction was stirred at 70 °C for the time indicated in Table 2. The mixture was dissolved in ethyl acetate, washed with a saturated solution of NH_4Cl, dried with $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography over silica gel to provide the products **2**.

Phenyl(1-phenylnaphthalen-2-yl)selane ***2a***. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow solid. Yield: 0.069 g (77%); mp 100−101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81−7.76 (m, 1H), 7.66−7.61 (m, 1H), 7.53−7.38 (m, 7H), 7.37−7.24 (m, 7H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.9, 139.7, 135.0, 133.2, 132.3, 131.0, 130.7, 130.2, 129.4, 128.5, 128.3, 128.2, 127.9, 127.8, 126.5, 126.2, 125.5. MS (EI, 70 eV; m/z (relative intensity)) 362 ([M + 2], 14), 360 (63), 280 (60), 202 (100), 126 (03), 77 (09). HRMS calcd for $C_{22}H_{17}Se$ (ESI-TOF, $[M + H]^+$) 361.0495, found 361.0501.

(1-Phenylnaphthalen-2-yl)(p-tolyl)selane ***2b***. Title compound was isolated by column chromatography (hexane was eluent) as a yellow solid. Yield: 0.074 g (80%); mp 141.2−145.9 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79−7.73 (m, 1H), 7.64−7.58 (m, 1H), 7.54−7.27 (m, 10H), 7.25−7.19 (m, 1H), 7.13−7.06 (m, 2H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.7, 139.1, 138.2, 135.6, 133.1, 132.1, 131.7, 130.3, 128.5, 128.0, 127.9, 127.8, 127.6, 126.5, 126.4, 126.0, 125.3, 21.2. MS (EI, 70 eV; m/z (relative intensity)) 376 ([M + 2], 9), 374 (53), 294 (49), 279 (36), 207 (08),

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202 (100), 176 (06) 91 (20). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 375.0652, found 375.0660.

(1-Phenylnaphthalen-2-yl)(o-tolyl)selane **2c**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.084 g (90%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.80−7.74 (m, 1H), 7.64−7.57 (m, 1H), 7.55−7.45 (m, 4H), 7.44−7.29 (m, 5H), 7.27−7.19 (m, 2H), 7.15−7.05 (m, 2H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 141.7, 139.7, 139.6, 136.4, 133.2, 132.1, 131.1, 130.8, 130.3, 130.0, 128.7, 128.5, 128.1, 127.8, 127.8, 127.6, 126.7, 126.4, 126.0, 125.4, 22.7. MS (EI, 70 eV; *m*/*z* (relative intensity)) 376 ([M + 2], 21), 375 ([M + 1], 25)], 374 (100), 372 (54), 294 (13), 282 (18), 279 (14), 204 (69), 203 (68), 202 (90), 169 (11), 91 (15). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 375.0652, found 375.0661.

Mesityl(1-phenylnaphthalen-2-yl)selane **2d**. Title compound was isolated by column chromatography (hexane was eluent) as a yellow light solid. Yield: 0.084 g (84%); mp 112.5−116 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.76−7.69 (m, 1H), 7.58−7.45 (m, 4H), 7.44−7.26 (m, 5H), 6.98 (s, 2H). 6.82 (d, J = 8.7 Hz, 1H), 2.37 (s, 6H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 143.8, 139.8, 139.0, 138.0, 133.3, 132.0, 131.8, 130.1, 128.9, 128.6, 128.0, 127.9, 127.8, 127.8, 126.3, 125.5, 125.3, 124.9, 24.2, 21.0. MS (EI, 70 eV; *m*/*z* (relative intensity)) 404 ([M + 2], 22), 403 ([M + 1], 28), 402 (100), 400 (56), 399 (22), 282 (11), 204 (32), 203 (40), 202 (63), 200 (25), 198 (67), 196 (33), 119 (25), 91 (18). HRMS calcd for $C_{25}H_{23}Se$ (ESI-TOF, $[M + H]^+$) 403.0965, found 403.0973.

(2-Methoxyphenyl)(1-phenylnaphthalen-2-yl)selane **2e**. Title compound was isolated by column chromatography (eluent 1% EtOAc in hexane) as a light yellow viscous oil. Yield: 0.071g (73%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.83−7.78 (m, 1H), 7.69−7.64 (m, 1H), 7.50−7.38 (m, 6H), 7.37−7.30 (m, 3H), 7.27−7.20 (m, 2H), 6.87−6.78 (m, 2H), 3.76 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 158.2, 141.5, 139.9, 134.3, 133.2, 132.6, 130.1, 130.0, 129.2, 128.8, 128.3, 128.0, 127.8, 127.6, 126.4, 126.3, 125.6, 121.5, 120.9, 110.8, 55.8. MS (EI, 70 eV; *m*/*z* (relative intensity)) 392 ([M + 2], 20), 391 ([M + 1], 25), 390 (100), 388 (53), 387 (20), 386 (20), 310 (62), 295 (13), 282 (24), 203 (34), 202 (84), 77 (11). HRMS calcd for $C_{23}H_{19}OSe$ (ESI-TOF, $[M + H]^+$) 391.0601, found 391.0610.

(4-Chlorophenyl)(1-phenylnaphthalen-2-yl)selane **2g**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow solid. Yield: 0.066 g (68%); mp 118.2−119.4 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.82−7.77 (m, 1H), 7.69−7.63 (m, 1H), 7.52−7.45 (m, 3H), 7.45−7.40 (m, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.37−7.30 (m, 3H), 7.28 (d, J = 8.7 Hz, 1H), 7.23 (d, J = 8.6 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 140.2, 139.6, 136.0, 134.2, 133.1, 132.3, 130.3, 130.2, 129.6, 129.0, 128.5, 128.3, 128.3, 127.9, 126.6, 126.2, 125.7. MS (EI, 70 eV; *m*/*z* (relative intensity)) 394 (38), 314 (31), 278 (22), 207 (63), 202 (100), 176 (6), 138 (6), 112 (5), 77 (33). HRMS calcd for $C_{22}H_{16}ClSe$ (ESI-TOF, $[M + H]^+$) 395.0106, found 395.0112.

(4-Fluorophenyl)(1-phenylnaphthalen-2-yl)selane **2h**. Title compound was isolated by column chromatography (hexane was eluent) as light yellow solid. Yield: 0.061 g (68%); mp 123.2−124.1 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81−7.75 (m, 1H), 7.68−7.61 (m, 1H), 7.55−7.45 (m, 5H), 7.44−7.38 (m, 2H), 7.37−7.30 (m, 3 H), 7.25−7.19 (m, 1H), 6.98 (t, J = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 163.0 (d, J = 248 Hz), 139.5, 137.4 (d, J = 8.0 Hz), 133.2, 132.2, 131.1, 130.2, 128.5, 128.2, 127.9, 127.7, 126.5, 126.1, 125.6, 125.0, 125.0, 116.6 (d, J = 21 Hz). MS (EI, 70 eV; *m*/*z* (relative intensity)) 378 (34), 298 (29), 207 (100), 202 (89), 176 (5), 150 (4), 133 (26), 96 (42), 73 (53). HRMS calcd for $C_{22}H_{16}FSe$ (ESI-TOF, $[M + H]^+$) 379.0401, found 379.0408.

(1-Phenylnaphthalen-2-yl)(3-(trifluoromethyl)phenyl)selane **2i**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow oil. Yield: 0.061 g (57%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.86−7.77 (m, 1H), 7.75−7.65 (m, 2H), 7.62−7.54 (m, 1H), 7.53−7.40 (m, 6H), 7.40−7.25 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 141.0, 139.5, 137.3, 133.1, 132.5, 132.3, 131.8 (q, J = 32.4 Hz), 130.5 (q, J = 3.7 Hz), 130.1, 129.6, 129.3, 128.8, 128.5, 128.4, 127.9, 126.6, 126.4, 126.0, 124.3 (q, J = 3.7 Hz), 120.9 (q, J = 272.7 Hz). MS (EI, 70 eV; *m*/*z* (relative intensity)) 429 ([M + 1], 12), 428 (50), 348 (31), 282 (15), 203(51), 202 (100), 176 (6). HRMS calcd for $C_{23}H_{16}F_3Se$ (ESI-TOF, $[M + H]^+$) 429.0369, found 429.0373.

Naphthalen-1-yl(1-phenylnaphthalen-2-yl)selane **2j**. Title compound was isolated by column chromatography (hexane was eluent) as a brown solid. Yield: 0.052 g (51%); mp 98−100 °C. ^1H NMR ($CDCl_3$,. 400 MHz) δ (ppm) 8.25−8.21 (m, 1H), 7.91−7.86 (m, 2H), 7.85−7.82 (m, 1H), 7.73−7.69 (m, 1H), 7.59−7.53 (m, 2H), 7.52−7.30 (m, 10H), 6.94 (d, J = 8.7 Hz, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.6, 138.8, 135.8, 134.9, 134.2, 133.2, 132.0, 131.4, 130.2, 129.9, 129.1, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 127.3, 127.0, 126.4, 126.4, 126.0, 125.9, 125.3. MS (EI, 70 eV; *m*/*z* (relative intensity)) 410 ([M + 2], 100), 409 (16), 408 (52), 330 (68), 329 (67), 253 (67), 202 (93). HRMS calcd for $C_{26}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 411.0652, found 411.0665.

Naphthalen-2-yl(1-phenylnaphthalen-2-yl)selane **2k**. Title compound was isolated by column chromatography (hexane was eluent) as a brown solid. Yield: 0.06 g (60%); mp 96.9−100.1 °C. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.05−7.99 (m, 1H), 7.83−7.69 (m, 4H), 7.63−7.58 (m, 1 H), 7.55−7.27 (m, 12H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.9, 139.7, 134.2, 134.1, 133.2, 132.7, 132.3, 132.0, 131.0, 130.2, 128.8, 128.5, 128.4, 128.2, 128.0, 127.9, 127.9, 127.8, 127.6, 126.5, 126.4, 126.2, 125.5. MS (EI, 70 eV; *m*/*z* (relative intensity)) 410 (73), 331 (21), 330 (77), 329 (57), 281 (18), 253 (14), 202 (100), 163 (15), 115 (17). HRMS calcd for $C_{26}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 411.0652, found 411.0682.

Phenyl(1-o-tolylnaphthalen-2-yl)selane **2n**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.054 g (58%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81−7.76 (m, 1H), 7.67−7.61 (m, 1H), 7.56−7.51 (m, 2H), 7.44−7.36 (m, 3H), 7.35−7.21 (m, 7H), 7.21−7.16 (m, 1H), 2.02 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 138.9, 138.7, 136.9, 135.3, 132.8, 132.1, 131.4, 130.3, 130.2, 130.0, 129.4, 128.2, 128.0, 128.0, 127.8, 126.6, 126.1, 125.6, 125.5,19.7. MS (EI, 70 eV; *m*/*z* (relative intensity))376 ([M + 2], 20), 375 ([M + 1], 25), 374 (100), 372 (53), 295 (11), 294 (31), 280 (11), 217 (44), 216 (45), 215 (89), 202 (67), 189 (12). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 375.0652, found 375.0663.

Phenyl(1-m-tolylnaphthalen-2-yl)selane **2o**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.066 g (72%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79−7.74 (m, 1H), 7.64−7.59 (m, 1H), 7.53−7.48 (m, 2H), 7.46−7.36 (m, 3H), 7.35−7.23 (m, 6H), 7.17−7.12 (m, 2H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 140.0, 139.6, 138.0, 135.0, 133.2, 132.2, 130.9, 130.9, 130.8, 129.3, 128.5, 128.3, 128.3, 128.0, 127.8, 127.2, 126.4, 126.2, 125.4, 21.5. MS (EI, 70 eV; *m*/*z* (relative intensity)) 376 ([M + 2] 20), 375 (24), 374 (100), 372 (52), 294 (61), 293 (31), 282 (35), 280 (29), 279 (54), 278 (36), 217 (17), 216 (35), 215 (65), 202 (82), 189 (17), 163 (10), 77 (13). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 375.0652, found 375.0660.

Phenyl(1-p-tolylnaphthalen-2-yl)selane **2p**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.058 g (62%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.80−7.74 (m, 1H), 7.64−7.59 (m, 1H), 7.54−7.48 (m, 2H), 7.47−7.43 (m, 1H), 7.42−7.36 (m, 1H), 7.35−7.22 (m, 9H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.8, 137.5, 136.7, 135.0, 133.3, 132.2, 131.1, 130.7, 130.1, 129.4, 129.2, 128.1, 128.0, 127.9, 127.9, 126.4, 126.2, 125.4, 24.4. MS (EI, 70 eV; *m*/*z* (relative intensity)) 374(100), 372 (51), 294 (67), 279 (53), 215 (66), 207 (44), 202 (80), 189 (16), 77 (12). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 375.0652, found 375.0659.

(1-(2-Methoxyphenyl)naphthalen-2-yl)(phenyl)selane **2q**. Title compound was isolated by column chromatography (eluent 1% EtOAc in hexane) as a viscous dark orange oil. Yield: 0.072 g (74%). ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.78−7.74 (m, 1H), 7.65−7.61 (m, 1H), 7.49−7.35 (m, 6H), 7.34−7.28 (m, 1H), 7.24−7.16 (m, 4H), 7.10−6.99 (m, 2H), 3.64 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 157.4, 137.6, 134.2, 133.2, 132.4, 131.8, 131.4, 131.2, 129.5, 129.4, 129.2, 128.5, 128.1, 127.9, 127.4, 126.3, 126.2, 125.5, 120.6,

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111.3, 55.6. MS (EI, 70 eV; *m*/*z* (relative intensity)) 390 (17), 219 (17), 218 (100), 202 (16), 189 (51), 163 (18), 77 (8). HRMS calcd for $C_{23}H_{19}OSe$ (ESI-TOF, $[M + H]^+$) 391.0601, found 391.0608.

(1-(4-Methoxyphenyl)naphthalen-2-yl)(phenyl)selane **2r**. Title compound was isolated by column chromatography (eluent 1% EtOAc in hexane) as an orange solid. Yield: 0.071g (73%); mp 106.8−111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79−7.75 (m, 1H), 7.64−7.60 (m, 1H), 7.54−7.50 (m, 2H), 7.48−7.44 (m, 1H), 7.43−7.38 (m, 1H), 7.36−7.33 (m, 1H), 7.32−7.22 (m, 6H), 7.06−7.02 (m, 2H), 3.89 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 159.3, 139.4, 135.1, 133.5, 132.2, 131.9, 131.6, 131.4, 130.6, 129.4, 128.0, 127.9, 127.9, 126.4, 126.2, 125.4, 114.0, 55.3. MS (EI, 70 eV; *m*/*z* (relative intensity)) 392 ([M + 2], 20), 391 ([M + 1], 25), 390 (100), 388 (53), 310 (62), 295 (13), 202 (18), 189 (82), 163 (14), 77 (12). HRMS calcd for $C_{23}H_{19}OSe$ (ESI-TOF, $[M + H]^+$) 391.0601, found 391.0613.

(1-(4-Chlorophenyl)naphthalen-2-yl)(phenyl)selane **2s**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.078 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.79 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.50−7.45 (m, 4H), 7.45−7.40 (m, 1H), 7.40−7.34 (m, 2H), 7.33−7.24 (m, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 138.6, 138.0, 134.8, 133.9, 133.0, 132.2, 131.6, 131.0, 130.4, 129.4, 128.5, 128.4, 128.0, 126.7, 125.8, 125.7. MS (EI, 70 eV; *m*/*z* (relative intensity)) 396 ([M + 2], 43), 394 (100), 392 (50), 316 (24), 314 (62), 282 (33), 279 (62), 236 (22), 202 (100), 201 (40), 200 (50), 77 (13). HRMS calcd for $C_{22}H_{16}ClSe$ (ESI-TOF, $[M + H]^+$) 395.0106, found 395.0111.

(1-(4-Fluorophenyl)naphthalen-2-yl)(phenyl)selane **2t**. Title compound was isolated by column chromatography (hexane was eluent) as a white solid. Yield: 0.044 g (47%); mp 105.4−108 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81−7.77 (m, 1H), 7.67−7.63 (m, 1H), 7.51−7.47 (m, 2H), 7.45−7.39 (m, 1H), 7.38−7.36 (m, 1H), 7.36−7.27 (m, 7H), 7.23−7.16 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 162.5 (d, J = 247 Hz),138.8, 135.5, 135.5 (d, J = 3.5 Hz) 134.9, 133.3, 132.3, 132.0 (d, J = 8.1 Hz), 131.3, 130.5, 129.4, 128.4, 128.4, 128.0, 126.6, 125.9, 125.6, 115.5 (d, J = 21 Hz). MS (EI, 70 eV; *m*/*z* (relative intensity)) 380 ([M + 1], 9)], 379 (11), 378 (51), 376 (26), 298 (63), 297 (31), 220 (100), 77 (12). HRMS calcd for $C_{22}H_{16}FSe$ (ESI-TOF, $[M + H]^+$) 379.0401,found 379.0410.

1,1′-Binaphthyl-2-yl(phenyl)selane **2u**. Title compound was isolated by column chromatography (hexane was eluent) as a yellow viscous oil. Yield: 0.058 g (57%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.0−7.92 (m, 2H), 7.84−7.79 (m, 1H), 7.75−7.70 (m, 1H), 7.62−7.56 (m, 1H), 7.50−7.42 (m, 4H), 7.42−7.34 (m, 2H), 7.31−7.19 (m, 6H), 7.18−7.12 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 137.8, 137.3, 135.0, 133.8, 133.7, 132.5, 132.3, 132.2, 130.5, 129.3, 128.4, 128.4, 127.9, 126.6, 126.3, 126.3, 126.0, 125.9, 125.6, 125.5. MS (EI, 70 eV; *m*/*z* (relative intensity)) 410 (24), 253 (100), 252 (92), 250 (30), 126 (17), 77 (6). HRMS calcd for $C_{26}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 411.0652, found 411.0688.

1,2′-Binaphthyl-2-yl(phenyl)selane **2v**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow solid. Yield: 0.053g (52%); mp 80.8−83.5 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.98 (d, J = 8.4 Hz, 1H), 7.95−7.91 (m, 1H), 7.87−7.83 (m, 1H), 7.82−7.78 (m, 2H), 7.67 (d, J = 8.4 Hz, 1H), 7.56−7.45 (m, 5H), 7.45−7.38 (m, 2H), 7.35−7.23 (m, 5H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 139.7, 137.2, 135.0, 133.4, 133.3, 132.9, 132.3, 131.2, 130.6, 129.4, 129.4, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.9, 126.5, 126.2, 125.6. MS (EI, 70 eV; *m*/*z* (relative intensity)) 411[M + 1 (16)], 410 (59), 408 (32), 333 (20), 330 (45), 329 (38), 253 (64), 252 (100), 250 (36), 126 (12), 77 (9). HRMS calcd for $C_{26}H_{19}Se$ (ESI-TOF, $[M + H]^+$) 411.0652, found 411.0673.

(4-Methyl-1-phenylnaphthalen-2-yl)(phenyl)selane **2x**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.064 g (68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.98−7.91 (m, 1H), 7.52−7.39 (m, 7H), 7.38−7.16 (m, 7H), 2.57 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 140.0, 138.8, 134.6, 134.5, 133.3, 131.6, 131.0, 130.4, 130.1, 129.3, 129.2, 128.4, 127.6, 127.6, 126.9, 126.1, 125.4, 124.1,19.3. MS (EI, 70 eV; *m*/*z* (relative intensity)) 374 (100), 294 (60), 279 (41), 215 (45), 202 (58). HRMS calcd for $C_{23}H_{19}Se$ (ESI-TOF, $M + H^+$) 375.0652, found 375.0659.

(3,5-Dimethyl-1-phenylnaphthalen-2-yl)(phenyl)selane **2y**. Title compound was isolated by column chromatography (hexane was eluent) as a dark green solid. Yield: 0.063 g (65%); mp 149.1−153.2 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.98−7.95 (m, 1H), 7.41−7.35 (m, 3H), 7.34−7.30 (m, 1H), 7.26−7.14 (m, 4H), 7.12−7.05 (m, 3H), 7.05−6.99 (m, 2H), 2.72 (s, 3H), 2.60 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 147.4, 141.9, 139.2, 134.3, 133.4, 132.9, 132.0, 129.8, 129.0, 129.0, 127.8, 127.4, 127.1, 126.1, 125.5, 125.1, 124.6, 24.8, 19.6. MS (EI, 70 eV; *m*/*z* (relative intensity)) 388 (100), 386 (53), 308 (44), 293 (33), 229 (22), 215 (84). HRMS calcd for $C_{24}H_{21}Se$ (ESI-TOF, $M + H^+$) 389.0808, found 389.0817.

(7-Methoxy-3-methyl-1-phenylnaphthalen-2-yl)(phenyl)selane **2z**. Title compound was isolated by column chromatography (eluent 1% EtOAc in hexane) as a light green solid. Yield: 0.067 g (67%); mp 121.2−123.8 °C ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.73−7.64 (m, 2H), 7.41−7.31 (m, 3H), 7.22−7.10 (m, 3H), 7.10−6.97 (m, 5H), 6.66 (d, J = 2.3 Hz, 1H), 3.61 (s, 3H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 157.2, 145.7, 141.7, 136.9, 134.4, 132.9, 129.7, 129.7, 129.4, 129.0, 128.9, 128.6, 128.0, 127.9, 127.1, 125.4, 119.0, 106.2, 55.0, 24.1. MS (EI, 70 eV; *m*/*z* (relative intensity)) 404 (100), 402 (45), 324 (40), 231 (19), 202 (27), 188 (22). HRMS calcd for $C_{24}H_{21}OSe$ (ESI-TOF, $M + H^+$) 405.0758, found 405.0752.

(7-Chloro-3-methyl-1-phenylnaphthalen-2-yl)(phenyl)selane **2aa**. Title compound was isolated by column chromatography (hexane was eluent) as a light green solid. Yield: 0.045 g (44%); mp 151.5−154.1 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.75−7.68 (m, 2H), 7.41−7.35 (m, 4H), 7.35−7.32 (m, 1H), 7.17−7.12 (m, 2H), 7.10−7.05 (m, 3H), 7.03−6.98 (m, 2H), 2.55 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 146.2, 140.8, 139.9, 134.0, 132.6, 132.1, 131.5, 131.0, 129.9, 129.4, 129.0, 128.7, 128.1, 127.5, 127.5, 126.3, 125.8, 24.4. MS (EI, 70 eV; *m*/*z* (relative intensity))408 (96), 406 (49), 330 (15), 328 (37), 293 (29), 216 (44), 215 (100). HRMS calcd for $C_{23}H_{18}ClSe$ (ESI-TOF, $M + H^+$) 409.0262, found 409.0271.

Butyl(1-phenylnaphthalen-2-yl)selane **2ab**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.059 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.81 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.7 Hz, 1H), 7.60 (d, J = 8.7 Hz, 1H), 7.53−7.35 (m, 5H), 7.34−7.27 (m, 3H), 2.84 (t, J = 7.4 Hz, 2H), 1.63 (quint, J = 7.4 Hz, 2H), 1.37 (sex, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 140.3, 140.0, 133.2, 132.0, 130.3, 129.5, 128.4, 127.9, 127.8, 127.6, 127.3, 126.3, 126.0, 125.2, 31.9, 26.7, 23.0, 13.5. MS (EI, 70 eV; *m*/*z* (relative intensity)) 341 ([M + 1], 17), 340 (100), 338 (42), 284 (36), 204 (100), 203 (58), 202 (69). HRMS calcd for $C_{20}H_{21}Se$ (ESI-TOF, $M + H^+$) 341.0808, found 341.0813.

(1-Butylnaphthalen-2-yl)(phenyl)selane **2ac**. Title compound was isolated by column chromatography (hexane was eluent) as an orange oil. Yield: 0.063 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.01−8.02 (m, 1H), 7.78−7.73 (m, 1H), 7.61−7.57 (m, 1H), 7.53−7.47 (m, 2H), 7.47−7.39 (m, 3H), 7.26−7.18 (m, 3H), 3.34 (t,J = 7.3 Hz, 2H), 1.65 (quint, J = 7.3 Hz, 2H), 1.51 (sex, J = 7.3 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm)140.8, 133.3, 132.8, 132.3, 131.9, 131.6, 131.4, 129.3, 129.2, 129.1, 128.6, 127.7, 127.1, 127.0, 126.4, 125.6, 124.4, 32.9, 32.4, 23.2, 14.0. MS (EI, 70 eV; *m*/*z* (relative intensity)) 342 ([M + 2], 70), 340 (71), 295 (23), 217 (70), 216 (100), 215 (62), 141 (53), 115 (18). HRMS calcd for $C_{20}H_{21}Se$ (ESI-TOF, $M + H^+$) 341.0808, found 341.0814.

Methyl(1-phenylnaphthalen-2-yl)sulfane **2ad**. Title compound was isolated by column chromatography (hexane was eluent) as a light yellow viscous oil. Yield: 0.035 g (56%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.82 (t, J = 9.5 Hz, 2H), 7.56−7.43 (m, 4H), 7.41−7.27 (m, 5H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz) δ (ppm) 138.6, 137.3, 134.8, 132.9, 131.3, 130.5, 128.5, 128.1, 127.82, 127.7, 126.5, 125.7, 125.0, 123.4, 16.3. MS (EI, 70 eV; *m*/*z* (relative intensity)) 251 ([M + 1], 20), 250 (100), 235 (68), 234 (65), 202 (32), 117 (19).

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HRMS calcd for $C_{17}H_{15}S$ (ESI-TOF, $[M + H]^+$) 251.0894, found 251.0902.

Phenyl(1-phenylnaphthalen-2-yl)sulfane ***2ae***. Title compound was isolated by column chromatography (hexane was eluent) as a yellow oil. Yield: 0.032 g (41%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.83−7.79 (m, 1H), 7.72 (d, J = 8.7 Hz, 1H), 7.51−7.41 (m, 5H), 7.38−7.31 (m, 4H), 7.30−7.26 (m, 2H), 7.26−7.20 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 140.3, 138.7, 136.2, 133.2, 132.9, 132.3, 131.7, 130.4, 129.1, 128.3, 128.3, 127.8, 127.6, 127.0, 126.5, 126.4, 125.8. MS (EI, 70 eV; m/z (relative intensity)) 312 (100), 235 (23), 234 (37), 203 (48). HRMS calcd for $C_{22}H_{17}S$ 313.1051, found 313.1059.

General Procedure for the Reaction of 2-Organoselenylnaphthalenes with *n*-Butyllithium Followed by Different Electrophiles. To a two-necked round-bottomed flask, under argon, containing a solution of **2** (0.5 mmol) in THF (5 mL) and hexane (5 mL) at room temperature, was added dropwise *n*-BuLi (0.55 mmol, of a 2.5 M solution in hexane). The reaction mixture was stirred for 15 min, and then was gradually added a solution of the appropriate electrophilic species (0.55 mmol) in THF (2 mL), at 0 °C. The reaction mixture was allowed to stir at 25 °C for the time indicated in Scheme 6. After this time, the mixture was diluted in ethyl acetate (20 mL) and washed with a saturated aqueous solution of NH_4Cl (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum.

(1-(4-Methoxyphenyl)naphthalen-2-yl)(p-tolyl)methanol ***6a***. Title compound was isolated by column chromatography (eluent 4% EtOAc in hexane) as a yellow oil. Yield: 0.04 g (45%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.87−7.78 (m, 2H), 7.65 (d, J = 8.6 Hz, 1H), 7.42 (d, J = 5.4 Hz, 2H), 7.37−7.17 (m, 3H), 7.17−6.90 (m, 7H), 5.82 (s, 1H), 3.86 (s, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 158.9, 140.9, 139.1, 138.9, 137.4, 136.7, 133.0, 132.8, 131.8, 131.1, 130.3, 129.2, 128.8, 128.1, 127.8, 127.4, 126.9, 126.4, 125.9, 125.7, 124.5, 113.8,72.6, 55.2, 21.0. MS (EI, 70 eV; m/z (relative intensity)) 354 (60), 336 (100), 321 (30), 304 (22), 260 (23), 245 (16), 201 (27), 118 (58), 104 (23). HRMS calcd for $C_{25}H_{23}O_2$ (ESI-TOF, $[M + H]^+$) 355.1698, found 355.1706.

(4-Methoxyphenyl)(1-(4-methoxyphenyl)naphthalen-2-yl)methanol ***6b***. Title compound was isolated by column chromatography (eluent 7% EtOAc in hexane) as light yellow oil. Yield: 0.089 g (96%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.86−7.79 (m, 2H), 7.69 (d, J = 8.6 Hz, 1H), 7.45−7.39 (m, 2H), 7.35−7.28 (m, 1H), 7.28−7.20 (m, 1H), 7.09 (d, J = 8.4 Hz, 2H), 6.99 (ddd, J = 16.0, 8.4, 2.2 Hz, 2H), 6.91 (dd, J = 8.3, 2.5 Hz, 1H), 6.87−6.82 (m, 1H), 6.75 (d, J = 8.8 Hz, 2H), 5.79 (s, 1H), 3.85 (s, 3H), 3.72 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 159.0, 158.7, 139.0, 137.4, 136.2, 133.1, 132.9, 131.9, 131.1, 130.4, 128.5, 128.0, 127.8, 127.8, 126.9, 125.9, 125.7, 124.4, 114.0, 113.9, 113.7, 113.6, 72.5, 64.2, 55.3. MS (EI, 70 eV; m/z (relative intensity)) 370 (56) 352 (100), 337 (23), 320 (30), 260 (47), 202 (10), 201 (26), 188 (23), 135 (63), 94 (11), 77 (18). HRMS calcd for $C_{25}H_{23}O_3$ (ESI-TOF, $[M + H]^+$), 371.1647 found 371.1655.

(4-Bromophenyl)(1-(4-methoxyphenyl)naphthalen-2-yl)methanol ***6c***. Title compound was isolated by column chromatography (eluent 5% EtOAc in hexane) as an orange oil. Yield: 0.077 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 7.82 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 1H), 7.47−7.38 (m, 3H), 7.37−7.28 (m, 3H), 7.27−7.13 (m, 1H), 7.09−6.92 (m, 5H), 5.79 (s, 1H), 3.86 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 159.0, 142.8, 138.3, 137.7, 133.0, 132.9, 131.7, 131.5, 131.4, 131.2, 131.0, 130.1, 128.5, 128.5, 128.3, 128.2, 128.2, 127.8, 126.9, 126.5, 126.1, 125.9, 124.2, 121.0, 114.0, 113.8,72.2, 55.3. MS (EI, 70 eV; m/z (relative intensity)) 420 (61), 418 (71), 402 (100), 400 (85), 387 (19), 306 (20), 260 (28), 245 (31), 202 (23), 189 (55), 155 (30), 77 (38). HRMS calcd for $C_{24}H_{20}BrO_2$ (ESI-TOF, $[M + H]^+$), 419.0647, found 419.0653.

1-(1-(4-Methoxyphenyl)naphthalen-2-yl)-3-phenylprop-2-yn-1-ol ***6d***. Title compound was isolated by column chromatography (eluent 4% EtOAc in hexane) as an orange oil. Yield: 0.043 g (48%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 8.00 (d, J = 8.6 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.51−7.43 (m, 2H), 7.42−7.33 (m, 3H), 7.33−7.24 (m, 5H), 7.04 (d, J = 8.9 Hz, 2H), 5.62 (s, 1H), 3.88 (s, 3H), 2.30 (s, 1H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 159.2, 137.5, 136.3, 133.4, 133.1, 131.8, 131.7, 131.5, 129.7, 128.4, 128.4, 128.2, 127.9, 127.1, 126.1, 126.0, 124.4, 122.7, 113.9, 113.8, 89.7, 86.6, 62.8, 55.3. MS (EI, 70 eV; m/z (relative intensity)) 364 (59), 349 (20), 315 (27), 262 (79), 261 (29), 202 (31), 189 (65), 102 (100), 73 (16). HRMS calcd for $C_{26}H_{21}O_2$ (ESI-TOF, $[M + H]^+$), 365.1542 found 365.1549.

1-Phenyl-2-naphthaldehyde ***6e***. Title compound was isolated by column chromatography (eluent 1% EtOAc in hexane) as a light yellow solid. Yield: 0.03 g (52%); mp 98−101 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 9.89 (s, 1H), 8.06 (d, J = 8.7 Hz, 1H), 7.95−7.89 (m, 2H), 7.68−7.57 (m, 2H), 7.56−7.49 (m, 3H), 7.48−7.37 (m, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz) δ (ppm) 192.6, 146.5, 136.1, 135.3, 132.5, 131.3, 131.0, 128.7, 128.3, 128.3, 128.2, 128.2, 127.7, 126.8, 122.2. MS (EI, 70 eV; m/z (relative intensity)) 234 ([M + 2], 100), 216 (26), 214 (50), 205 (49), 202 (41), 189 (14), 156 (26), 129 (36), 108 (33), 94 (20). HRMS calcd for $C_{17}H_{13}O$ (ESI-TOF, $[M + H]^+$), 233.0966, found 233.0970.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00050.

Text, figures, spectroscopic data for all new compounds, X-ray results (PDF)

Crystal data (CCDC 1525289) (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: gzeni@ufsm.br.

ORCID

Gilson Zeni: 0000-0003-1290-6478

Notes

The authors declare no competing financial interest.

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