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PAPER

Selective base-promoted synthesis of substituted selenophenes by carbocyclization of (*Z*)-benzylselenoenynes†

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We herein described the synthesis of several 3-benzyl-2,5-diarylselenophene derivatives in moderate to good yields using (*Z*)-benzylselenoenynes as starting material in carbocyclization reactions. The reactions were carried out under mild conditions using only *t*-BuOK as base, in the complete absence of transition metals or additives. The cyclized 3-benzyl-2,5-diarylselenophenes obtained in the current protocol appear highly promising and attractive intermediates for the synthesis of polysubstituted selenophenes. For instance, 3-benzyl-2,5-diphenylselenophene was treated with Br_2 provided the corresponding 3-benzyl-4-bromo-2,5-diphenylselenophene in high yield. 4-Bromoselenophene derivative was applied as substrate in the palladium catalyzed cross-coupling reactions with boronic acids to give the Suzuki type products in excellent yields.

Introduction

Carbocyclization of unsaturated species, particularly alkenes and alkynes, is an effective synthetic method for the synthesis of a variety of carbo and heterocyclic compounds.[1] Enynes have been also employed as key substrates in carbocyclization reactions[2] for the construction of ring systems and these reactions usually proceed with high efficiency and selectivity. In this context, transition metals such as Pd,[3] Pt,[4] Au,[5] Co,[6] Ni[7] and Rh,[8] are generally used to promote these carbocyclization reactions. Traditionally, alkenyl and alkynyl tethers attached to a nucleophilic heteroatom have been cyclized in the presence of palladium salts.[9] Some of these methods, however, do require a significant number of steps for preparation of the starting materials, employ toxic metal reagents for the cyclization event and sometimes display intolerance to some functionalities or proceed with a lack of regioselectivity. During the last years the electrophilic cyclization has been developed for converting alkenes, alkynes, allenes, conjugated dienes and other carbon-carbon multiple bonds, bearing an internal nucleophile, such as imines,[10] ketones,[11] esters,[12] amides,[13] benzyl sulfides,[14] alkyl selenides,[15] anisoles,[16] thioanisole,[17] alkynyl selenides[18] into heterocycles. This is a very versatile method which can be applied to a wide variety of substrates employing electrophiles, like I_2, ICl, chalcogen derivatives,[19] gold[20] and silver.[21] Another emerging area in the heterocycles chemistry is the preparation of selenophene and their derivatives. The role of selenophene compounds in organic synthesis is well established and in recent years much effort has been devoted to the study of the electrical properties, thermal and environmental stability, reactivity and their application in organic synthesis.[22] Selenoheterocycles, specially selenophenes are important and central structural units present in various biologically active compounds. Some selenophene derivatives have shown antioxidant,[23] antinociceptive[24] and anti-inflammatory properties,[25] as well as efficacy as a maturation inducing agents.[26]

In addition, during the past years there has been an impressive increasing attention in the development of environmentally benign protocols and the great challenge for chemists is to apply cost effective, green, mild and alternative methodologies.[27] Selenium stabilized carbanions from selenoacetals, α-alkylseleno or α-arylselenocarbonyl compounds, benzyl and vinyl selenides, generated by bases, can be an useful and environmental strategy for the construction, in few synthetic steps, of complex molecules, including high substituted Se-heterocycles.[28] As a part of our ongoing research in this area,[29] combined with the fact that base-promoted cyclization[30] of (*Z*)-benzylselenoenynes as substrate remains unexplored, in this paper, we reported an inexpensive and environmentally friendly synthetic method for the synthesis of selenophene derivatives. Our work hypothesis is outlined in Scheme 1, which consisted of the base-promoted cyclization of (*Z*)-benzylselenoenyne precursors **3**, through a C–C bond formation process, leading to a broad range of selenophenes **4** in complete absence of transition metals or additives (Scheme 1).

Results and discussion

Unfortunately, the scope of benzylselenoenynes **3**, needed for cyclization, appear limited to relatively different substituents in the structure. This limitation prompted us to investigate a complete

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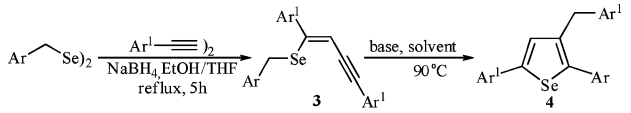
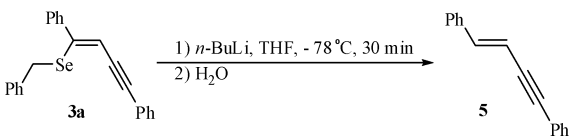


Ar = Ph, *p*-MeC_6H_4, 1-naphthyl, 2-naphthyl; Ar^1= Ph, *p*-MeC_6H_4, *m*-MeC_6H_4, 2-naphthyl

Scheme 1

study in the preparation of these compounds. In the course of studies designed to expand the scope of (*Z*)-benzylselenoenynes **3** to the more substituted structures, a hydroselenation of alkynes process[31] was envisioned as a highly efficient and selective method for the formation of *Z*-double bond required. Treatment of a variety of dibenzyl diselenides **1** bearing methyl, methoxyl and naphthyl groups with different diynes **2** using $NaBH_4$ in ethanol–THF, under reflux, gave the corresponding (*Z*)-benzylselenoenynes **3** as the only isomer (Table 1). Many functional groups were compatible with the reaction conditions. In general, all the reactions proceeded smoothly with good results. Most important, the hydroselenation turned out to be general with respect of a diverse array of functionalities. Inspecting Table 1, we can observe a significant decrease in yields of (*Z*)-benzylselenoenynes when the reaction was performed with bulky diynes (Table 1, entries 4 and 6) or bulky dinaphthyl diselenide (Table 1, entry 14).

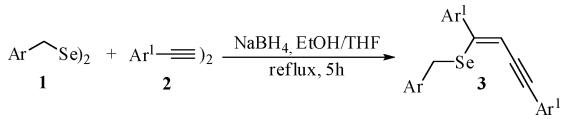
Since the Se/Li exchange reaction occurs with total retention of configuration,[32] the *Z* stereochemistry of benzylselenoenynes was readily determined by the multiplicity of the vinylic hydrogen signals of compound **5**, which was prepared by addition of *n*-BuLi (1.1 equiv) to a solution of benzylselenoenyne **3a** (0.5 mmol) in THF (3 mL) at –78 °C. After 30 min, the reaction was quenched by H_2O, producing the corresponding *Z*-enyne **5** as a single isomer (Scheme 2). The stereochemistry of **5** was clearly indicated by coupling constant (J = 16 Hz) of the doublets attributed to the vinylic hydrogens, which is characteristic of *trans* vinyl coupling.



Scheme 2

After the success in the synthesis of (*Z*)-benzylselenoenynes **3**, we next focus our attention on the development of an optimum set for the base-promoted intramolecular cyclization. For this purpose, the reaction of **3a** with bases in DMSO as solvent was chosen as a model system. Thus, the substrate **3a** (0.4 mmol) was reacted with KOH (1 equiv) as base in DMSO (4 mL) at 90 °C, yielding the desired product **4a** in 55% (Table 2, entry 1). Encouraged by this result, we further investigated the reaction behavior with other bases and solvents with the aim to improve the protocol. The outcome of this study and an investigation of other reaction parameters are depicted in Table 2. A comparison of the effectiveness of bases showed that all of them were effective to give the cyclized product (Table 2, entries 1–12), whereas *t*-BuOK was the most efficient since the product was obtained in 67% yield (Table 2, entry 12). It is important to note that when the amount of base was changed from 1.0 to 2.0 equiv or when the reaction was carried out at room temperature a decrease in the yields was observed (Table 2, entries 13 and 14).

Table 1 Synthesis of (*Z*)-benzylselenoenynes **3**[a]



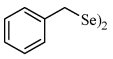
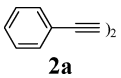
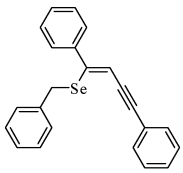
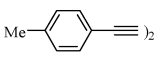
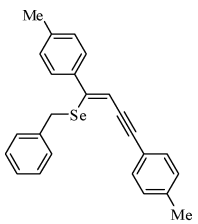
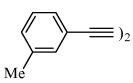
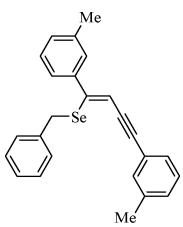
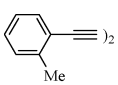
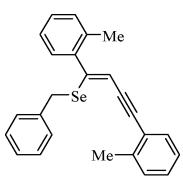
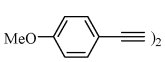
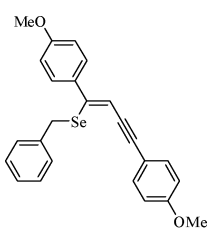
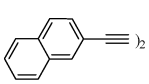
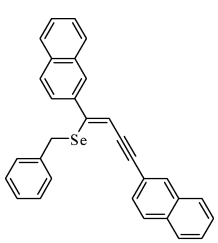
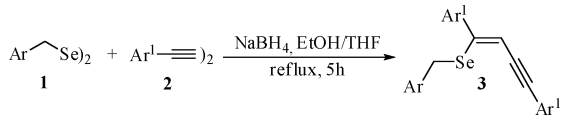
#	Dibenzyl diselenide	Diyne	Product yield (%)[b]
1	 **1a**	 **2a**	 **3a** (70%)
2	**1a**	 **2b**	 **3b** (85%)
3	**1a**	 **2c**	 **3c** (73%)
4	**1a**	 **2d**	 **3d** (51%)
5	**1a**	 **2e**	 **3e** (84%)
6	**1a**	 **2f**	 **3f** (52%)

Table 1 *(Contd.)*



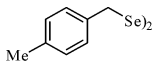
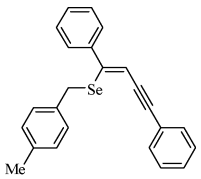
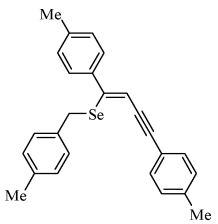
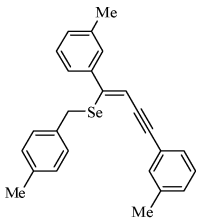
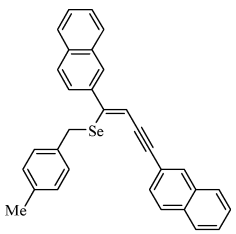
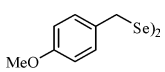
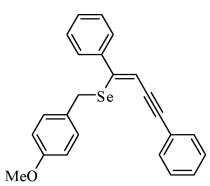
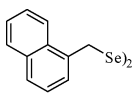
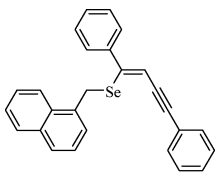
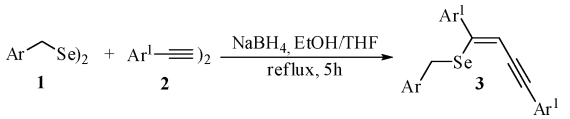
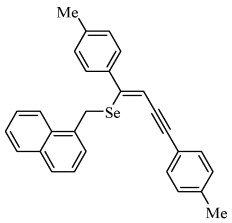
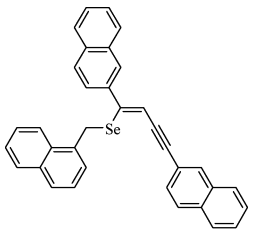
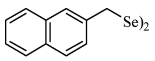
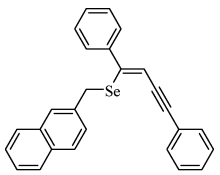
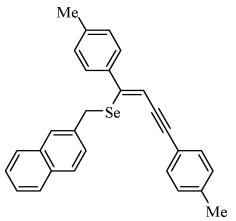
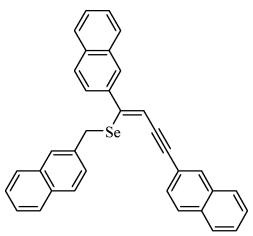
#	Dibenzyl diselenide	Diyne	Product yield (%)[b]
7	 **1b**	**2a**	 **3g** (55%)
8	**1b**	**2b**	 **3h** (80%)
9	**1b**	**2c**	 **3i** (63%)
10	**1b**	**2f**	 **3j** (69%)
11	 **1c**	**2a**	 **3k** (69%)
12	 **1d**	**2a**	 **3l** (74%)

Table 1 *(Contd.)*

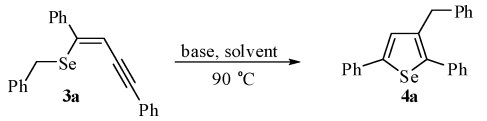


#	Dibenzyl diselenide	Diyne	Product yield (%)[b]
13	**1d**	**2b**	 **3m** (75%)
14	**1d**	**2f**	 **3n** (23%)
15	 **1e**	**2a**	 **3o** (65%)
16	**1e**	**2b**	 **3p** (60%)
17	**1e**	**2f**	 **3q** (70%)

[a] Reactions were performed with dibenzyl diselenide **1** (1 mmol), diyne **2** (2 mmol), EtOH (25 mL), THF (10 mL) and $NaBH_4$ (3.2 mmol) at reflux for 5 h. [b] Yields correspond to isolated products.

The study to screen the solvent showed the best results were obtained with DMSO and DMF (Table 2, entries 12 and 15) while toluene, 1,4-dioxane, CH_2Cl_2 and acetonitrile gave the target products in unacceptable yields (Table 2, entries 16–19).

Table 2 Optimization of reaction conditions[a]



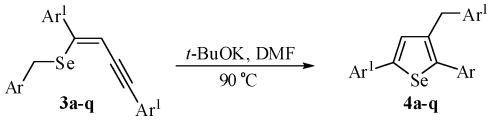
Entry	Base	Solvent	Yield (%)[b]
1	KOH	DMSO	55 (54)[c]
2	KOH[d]	DMSO	24
3	NaOH	DMSO	23
4	K_3PO_4	DMSO	23
5	K_3PO_4/H_2O	DMSO	22
6	Na_2CO_3	DMSO	15
7	Cs_2CO_3	DMSO	33
8	K_2CO_3	DMSO	14
9	Et_3N	DMSO	15
10	Pyrrolidine	DMSO	14
11	Pyridine	DMSO	14
12	*t*-BuOK	DMSO	67
13	*t*-BuOK[d]	DMSO	16
14	*t*-BuOK[e]	DMSO	59
15	*t*-BuOK	DMF	70 (67)[c]
16	*t*-BuOK	Toluene	15
17	*t*-BuOK	1,4-Dioxane	14
18	*t*-BuOK	CH_2Cl_2[f]	14
19	*t*-BuOK	CH_3CN	22

[a] Reaction performed in the presence of **3a** (0.4 mmol), base (1equiv) and 4 mL of solvent at 90 °C. [b] Yields are given by GC analysis. [c] Yields in parentheses correspond to isolated products. [d] Reaction performed using 2 equiv of *t*-BuOK. [e] Reaction was performed at room temperature. [f] Reaction was performed at 40 °C.

Thus, the careful analysis of the optimized reactions revealed that the best conditions for this carbocyclization reaction were found to be the use of (*Z*)-benzylselenoenyne **3a** (0.4 mmol), 1 equiv of *t*-BuOK as base in DMF (4 mL) at 90 °C. Using this reaction condition we were able to prepare the selenophene **4a** in 70% yield. In order to demonstrate the efficiency of this protocol, we explored the generality of our method extending the conditions to several (*Z*)-benzylselenoenynes **3a–q** and these results are summarized in Table 3.

Studies defining the scope and limitations of this reaction led us to a good understanding of this process. First, to determine the real influence of the substituent at aromatic ring of alkyne, we kept the selenobenzyl group directly bonded to double bond invariable. The results demonstrated that the cyclization efficiency was significantly influenced by the steric effects of aromatic ring, since the cyclization reaction gave lower yields with aromatic rings having a methyl substituent at *orto* position or a bulky naphthyl group than those having no substituent (Table 3, entries 1–6). We also observed that the reaction was sensitive to electronic effects of aromatic ring. For example, no product was obtained with (*Z*)-benzylselenoenynes having an aromatic ring with a MeO group, directly bonded to C*sp* of alkyne (Table 3, entry 5). In addition, the reactions of (*Z*)-benzylselenoenynes containing different substituents at benzyl group directly bonded to the selenium atom were also investigated. In most cases the corresponding selenophenes **3** were obtained in good yields. Inspecting Table 3, we can observe that the methodology showed only a limitation to (*Z*)-benzylselenoenynes having a methoxyl group bonded to the benzyl group (Table 3, entry 11).

Table 3 Synthesis of 3-benzyl-2,5-diarylselenophenes **4** *via* carbocyclization of (*Z*)-benzylselenoenynes **3**[a]



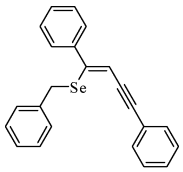
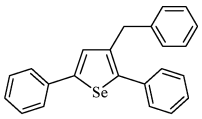
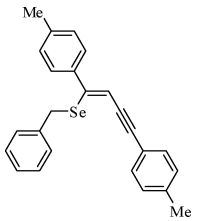
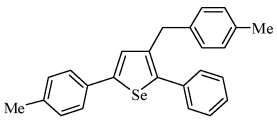
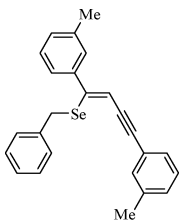
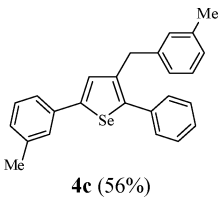
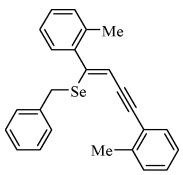
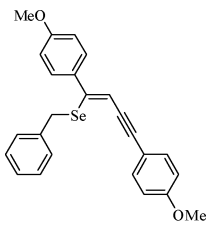
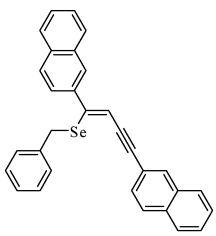
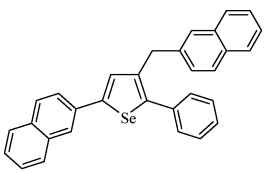
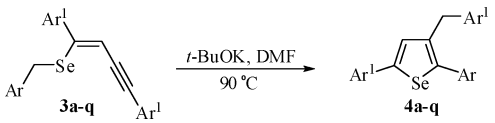
#	Substrate	Time (h)	Product yield (%)[b]
1	 **3a**	2	 **4a** (70%)
2	 **3b**	2	 **4b** (55%)
3	 **3c**	4	 **4c** (56%)
4	 **3d**	5	Trace
5	 **3e**	4	n.r.[c]
6	 **3f**	2	 **4f** (40%)

Table 3 *(Contd.)*



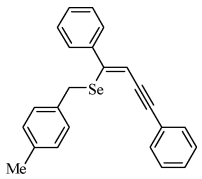
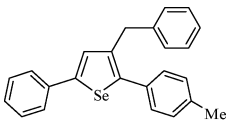
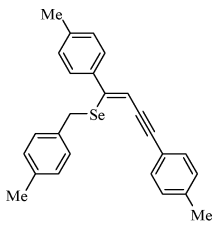
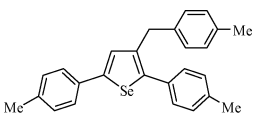
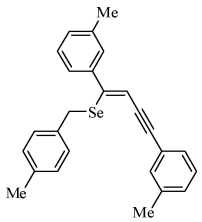
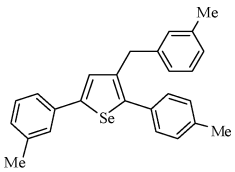
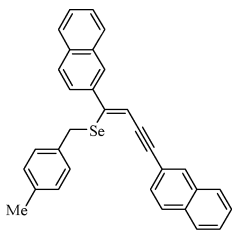
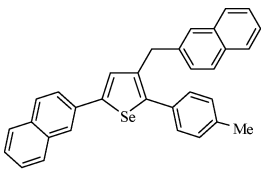
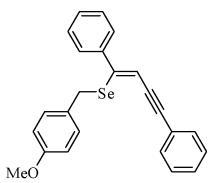
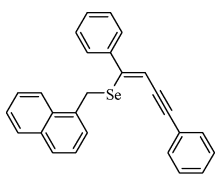
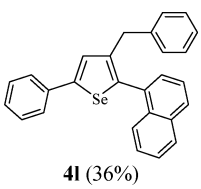
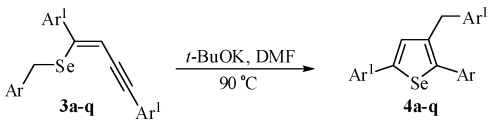
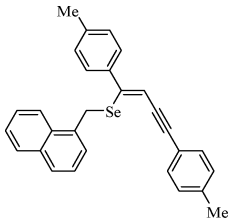
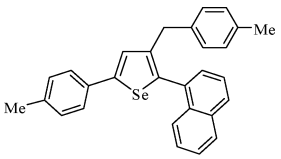
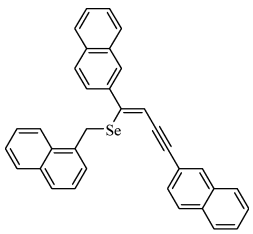
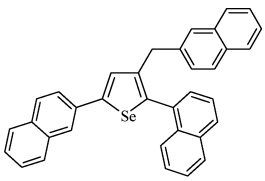
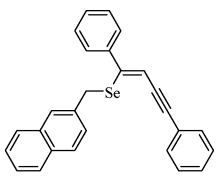
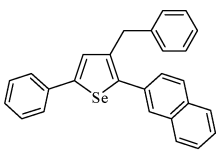
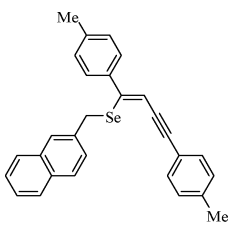
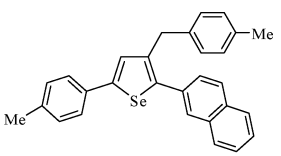
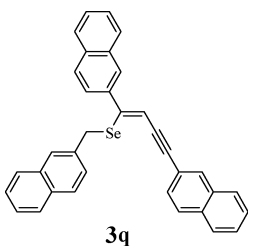
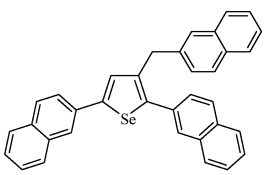
#	Substrate	Time (h)	Product yield (%)[b]
7	 **3g**	2	 **4g** (70%)
8	 **3h**	2	 **4h** (64%)
9	 **3i**	2	 **4i** (25%)
10	 **3j**	3	 **4j** (20%)
11	 **3k**	3	n.r.[c]
12	 **3l**	3	 **4l** (36%)

Table 3 *(Contd.)*

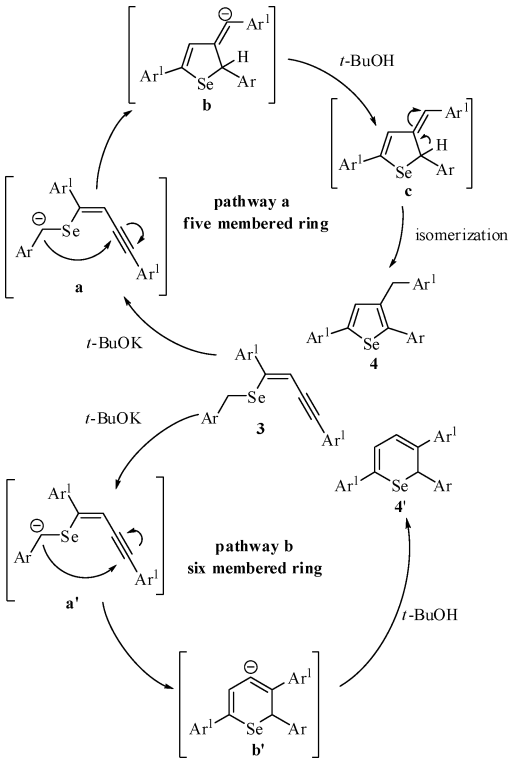


#	Substrate	Time (h)	Product yield (%)[b]
13	 **3m**	6	 **4m** (58%)
14	 **3n**	3	 **4n** (38%)
15	 **3o** (65%)	2	 **4o** (88%)
16	 **3p**	2	 **4p** (76%)
17	 **3q**	3	 **4q** (38%)

[a] Reactions performed in the presence of (*Z*)-benzylselenoenynes **3** (0.4 mmol), *t*-BuOK (0.4 mmol) and DMF (4 mL) at 90 °C. [b] Yields of **4a–q** are given for isolated products. [c] No reaction observed.

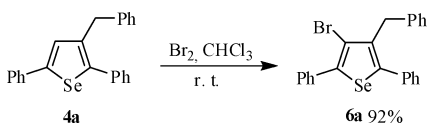
We believe that the mechanism of this carbocyclization reaction involves; (i) deprotonation of **3** by *t*-BuOK to generate selenium stabilized carbanion **a**; (ii) intramolecular nucleophilic attack of carbanion on the carbon-carbon triple bond produces

intermediate **b**; (iii) subsequent protonation of **b** by the conjugate acid *t*-BuOH provides the intermediate **c**; (iv) isomerization of **c** gives the selenophene product 4 (Scheme 3). Regarding the possibility to form five (pathway a, Scheme 3) *versus* six (pathway b, Scheme 3) membered ring, it is important to point out that the unique regioisomer obtained during the curse of this cyclization was the five-membered selenophene derivatives, which were determined by the presence of a signal from 3.65 to 4.16 ppm in H^1 NMR spectra referring to two hydrogens (Ha) from the benzyl group at 3-selenophene, observed for all compounds prepared (Scheme 3).



Scheme 3

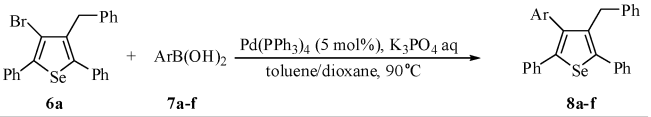
Since haloselenophenes[15,33] are important derivatives that provide an useful opportunity for the further functionalization, we wonder if it would be possible to obtain 4-bromoselenophenes from 2,5-diarylselenophenes prepared by our methodology. Gratifyingly, we found that the reaction of 3-benzyl-2,5-diphenylselenophene **4a** (1 equiv) with Br_2 (2,5 equiv) in $CHCl_3$ at room temperature gave the 3-benzyl-4-bromo-2,5-diphenylselenophene **6a** in 92% yield (Scheme 4).[34]



Scheme 4

The 3-benzyl-4-bromo-2,5-diphenylselenophene **6a** obtained appear highly attractive as intermediate for the preparation of polysubstituted selenophenes. This class of compound plays an important role in organic synthesis because many of them are useful compounds for both pharmaceutical[35] and material sciences.[36]

Table 4 Cross-coupling reaction of 3-benzyl-4-bromo-2,5-diphenylselenophene **6a** and boronic acids **7a–f**[a]



#	Substrate	Ar	Product	Yield (%)[b]
1	**6a**	**7a**		86
2	**6a**	**7b**	**8b**	93
3	**6a**	**7c**	**8c**	89
4	**6a**	**7d**	**8d**	80
5	**6a**	**7e**	**8e**	95
6	**6a**	**7f**	**8f**	90

[a] Reaction performed in the presence of **6a** (0.4 mmol), **7a–f** (0.6 mmol), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4 (1 mmol) in H_2O (0.6 mL), dioxane (1.6 mL), toluene (1.6 mL) at 90 °C. [b] Yields of **8a–f** are given for isolated products.

Thus, the potential of the compound **6a** as precursor for increasing molecular complexity by palladium-catalyzed Suzuki cross-coupling reaction was briefly investigated (Table 4). The Suzuki cross-coupling[37] was carried out using 4-bromoselenophene **6a** (0.4 mmol) with boronic acids **7a–f** (0.6 mmol), $Pd(PPh_3)_4$

(5 mol%) as catalyst and aqueous solution of K_3PO_4 (1 mmol) as base, in a mixture of and dioxane (1.6 mL)/toluene (1.6 mL) as solvent at 90 °C. The results, summarized in Table 4, showed that the reaction worked well for a variety of arylboronic acids. A closer inspection of the results revealed that the reaction was not sensitive to the electronic effects of an aromatic ring attached in the arylboronic acid. For example, the aromatic rings having neutral **7a**, electron-donating **7b–c** or electron-withdrawing **7d–f** substituents gave the desired products **8a–f** in similar yields (Table 4, entries 1–6). Most importantly, this method well tolerates ketone, nitro and halogen functional groups; the corresponding products **8a–f** have been isolated in 80–95% yields.

Conclusion

In summary, we have demonstrated the synthesis of several (*Z*)-benzylselenoenynes which were used as starting material in carbocyclization reactions establishing an alternative route to obtain 3-benzyl-2,5-diarylselenophenes in moderate to good yields. The reaction was carried out under mild conditions using only *t*-BuOK as base, in the complete absence of transition metals or additives. The 3-benzyl-2,5-diarylselenophenes obtained in the current protocol appear highly promising and attractive intermediates for the synthesis of polysubstituted selenophenes. For instance, 3-benzyl-2,5-diphenylselenophene was treated with Br_2 provided the corresponding 3-benzyl-4-bromo-2,5-diphenylselenophene in high yield. The 4-bromo-selenophene derivatives were applied as substrate in the palladium catalyzed cross-coupling reactions with boronic acids, to give the Suzuki type products in high yields.

Experimental section

General procedure for the preparation of the (*Z*)-benzylselenoenynes 3a–q. To a solution of the diyne (2.0 mmol) in THF (10 mL) and appropriate dibenzyl diselenide (1 mmol) in 95% ethanol (25 mL) under an argon atmosphere, $NaBH_4$ (0.12 g; 3.2 mmol) was added at room temperature, under vigorous stirring. Gas evolution was observed during addition. The reaction mixture was stirred under reflux for 5 h, allowed to reach room temperature, diluted with ethyl acetate (30 mL) and washed with brine (3 × 20 mL) and water (3 × 20 mL). After drying the organic phase over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel using hexane as eluent.

(*Z*)-Benzyl(1,4-diphenylbut-1-en-3-ynyl)selane (3a). Yield: 0.524 g (70%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.60–7.28 (m, 9H), 7.23–7.04 (m, 6H), 6.23 (s, 1H), 3.87 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 140.0, 138.3, 131.4, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 126.7, 123.3, 111.6, 97.3, 88.3, 30.5. MS (relative intensity) *m*/*z*: 373 (28), 282 (13), 202 (50), 126 (5), 91 (100), 77 (5). Elem. Anal. (%) Calcd for $C_{23}H_{18}Se$: C 73.99, H 4.86. Found: C 74.26, H 4.92.

(*Z*)-Benzyl(1,4-di*m*-tolylbut-1-en-3-ynyl)selane (3c). Yield: 0.584 g (73%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.45–7.02 (m, 13H), 6.21 (s, 1H), 3.87 (s, 2H), 2.36 (s, 3H), 2.33 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.6, 140.0, 138.5, 138.1, 137.9, 131.9, 129.2, 129.1, 128.9, 128.5, 128.3, 128.2, 126.7, 125.4, 123.2, 111.4, 97.3, 87.9, 30.6, 21.3, 21.2. MS (relative intensity) *m*/*z*: 402 (49), 296 (24), 229 (27), 215 (45), 115 (15), 91 (100). HRMS calcd for $C_{25}H_{22}Se$: 420.0887. Found: 402.0890.

(*Z*)-(1,4-Diphenylbut-1-en-3-ynyl)(4-methyl)selane (3g). Yield: 0.423 g (55%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.52–7.45 (m, 4H), 7.38–7.30 (m, 6H), 7.25–7.23 (m, 1H), 7.02 (s, 3H), 6.22 (s, 1H), 3.84 (s, 2H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.9, 140.1, 136.4, 135.1, 131.4, 129.0, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 123.4,, 111.4, 97.2, 88.3, 30.4, 21.0. MS (relative intensity) *m*/*z*: 388 (13), 202 (16), 105 (100), 77 (9). Elem. Anal. (%) Calcd for $C_{24}H_{20}Se$: C 74.41, H 5.20. Found: C 74.68, H 5.16.

(*Z*)-(1,4-Di(naphtalen-2-yl)but-1-en-3-ynyl)(4methylbenzyl)-selane (3j). Yield: 0.669 g (69%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.02 (s, 1H), 7.95 (s, 1H), 7.87–7.77 (m, 6H), 7.66–7.47 (m, 6H), 7.08–6.96 (m, 4H), 6.41 (s, 1H), 3.89 (s, 2H), 2.27 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 147.9, 137.5, 136.4, 135.1, 133.2, 133.2, 133.0, 132.8, 131.2, 129.1, 128.8, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 126.6, 126.5, 126.4, 126.0, 120.7, 112.1, 97.9, 97.5, 88.9, 30.6, 21.0. MS (relative intensity) *m*/*z*: 488 (20), 384 (14), 302 (28), 151 (10), 105 (100). Elem. Anal. (%) Calcd for $C_{32}H_{24}Se$: C 78.84, H 4.96. Found: C 78.79, H 4.92.

(*Z*)-(1,4-Diphenylbut-1-en-3-ynyl)(naphthalen-2ylmethyl)selane (3o). Yield: 0.551 g (65%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.77–7.58 (m, 3H), 7.51–7.17 (m, 14H), 6.20 (s, 1H), 4.01 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.5, 139.9, 135.7, 133.1, 132.3, 131.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.3, 127.2, 125.9, 125.6, 123.4, 111.7, 97.3, 88.3, 30.9. MS (relative intensity) *m*/*z*: 424 (84), 344 (31), 282 (11), 141 (100), 77 (15). Elem. Anal. (%) Calcd for $C_{27}H_{20}Se$: C 76.59, H 4.76. Found: C 76.72, H 4.80.

General procedure for the preparation of the 3-benzyl-2,5-diarylselenophenes 4a–q. To a Schlenck tube, under argon, containing the appropriate (*Z*)-benzylselenoenyne **3** (0.4 mmol) in DMF (4 mL) was added the *t*-BuOK (0.4 mmol) and the resulting solution was stirred at 90 °C for 2–6 h. After this the mixture was diluted with ethyl acetate (10 mL), and washed with brine (3 × 10 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane as the eluent.

3-Benzyl-2,5-diphenylselenophene (4a). Yield: 0.104 g (70%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.53–7.16 (m, 16H), 3.99 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.4, 144.1, 140.8, 138.6, 136.2, 136.1, 129.2, 128.9, 128.8, 128.6, 128.5, 128.4, 127.6, 127.5, 126.0, 125.9, 35.7. MS (relative intensity) *m*/*z*: 370 (100), 293 (19), 212 (43), 114 (11), 90 (14). Elem. Anal. (%) Calcd for $C_{23}H_{18}Se$: C 73.99, H 4.86. Found: C 74.03, H 4.90.

3-Benzyl-5-phenyl-2-*p*-tolylselenophene (4g). Yield: 0.105 g (70%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50–7.48 (m, 2H), 7.36–7.29 (m, 5H), 7.27–7.23 (m, 3H), 7.22–7.17 (m, 5H), 3.98 (s, 2H), 2.37 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.9, 144.3, 140.9, 138.4, 137.4, 136.3, 133.2, 129.3, 129.1, 128.9, 128.8, 128.5, 128.4, 127.4, 126.0, 125.9, 35.77, 21.2. MS (relative intensity) *m*/*z*: 388 (100), 311 (11), 215 (39), 115 (13), 91 (17). Elem. Anal. (%) Calcd for $C_{24}H_{20}Se$: C 74.41, H 5.20. Found: C 74.46, H 5.24.

5-(Napthalen-2-yl)-3-(naphthalen-2-ylmethyl)-2-*p*-tolylselenophene (4j). Yield: 0.038 g (20%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.92–7.75 (m, 5H), 7.65–7.31 (m, 6H), 7.26–7.07 (m,

8H), 3.68 (s, 2H), 2.32 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.1, 144.6, 138.5, 138.3, 137.5, 136.2, 136.1, 133.6, 133.2, 132.7, 132.1, 129.3, 129.2, 129.1, 128.9, 128.3, 128.1, 127.9, 127.7, 127.6, 127.3, 126.6, 126.5, 125.9, 125.8, 125.3, 124.4, 124.3, 36.1, 21.1. MS (relative intensity) *m/z*: 487 (100), 315 (26), 265 (30), 141 (23), 115 (24). Elem. Anal. (%) Calcd for $C_{32}H_{24}Se$: C 78.84, H 4.96. Found: C 78.92, H 5.01.

3-Benzyl-2-(naphthalen-2-yl)-5-phenylselenophene (4o). Yield: 0.150 g (88%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (s, 1H), 7.86–7.79 (m, 3H), 7.59–7.56 (m, 1H), 7.54–7.46 (m, 4H), 7.37–7.31 (m, 4H), 7.30–7.26 (m, 2H), 7.22–7.19 (m, 3H), 4.05 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 148.6, 144.0, 140.8, 138.9, 136.1, 133.4, 133.2, 132.4, 129.0, 128.8, 128.5, 128.4, 128.1, 128.0, 127.9, 127.6, 127.5, 127.4, 126.4, 126.1, 126.0, 125.9, 35.8. MS (relative intensity) *m/z*: 424 (100), 346 (15), 265 (45), 252 (20), 91 (14). Elem. Anal. (%) Calcd for $C_{27}H_{20}Se$: C 76.59, H 4.76. Found: C 76.29, H 4.71.

2,5-Di(naphthalen-2-yl)-3-(naphthalen-2-ylmethyl)selenophene (4q). Yield: 0.080 g (76%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.95 (s, 2H), 7.89–7.77 (m, 9H), 7.67–7.62 (m, 3H), 7.52–7.34 (m, 8H), 4.05 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 148.8, 144.5, 139.0, 138.4, 133.7, 133.6, 133.5, 133.3, 132.7, 132.6, 132.1, 129.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.7, 126.6, 126.5, 126.3, 126.0, 125.9, 125.4, 124.5, 124.3, 36.2. MS (relative intensity) *m/z*: 523 (100), 315 (59), 302 (16), 141 (19), 128 (28). Elem. Anal. (%) Calcd for $C_{35}H_{24}Se$: C 80.30, H 4.62. Found: C 80.52, H 4.70.

General procedure for the preparation of the 3-benzyl-4-bromo-2,5-diphenylselenophene (6a)[31]

A solution of bromine (2.0 g, 12.5 mmol) in $CHCl_3$ (15 mL) was added dropwise to a solution of 3-benzyl-2,5-diphenylselenophene **4a** (1.870 g, 5 mmol) in $CHCl_3$ (40 mL) at room temperature. After the addition was complete, the reaction was stirred at room temperature for 1 h. After this the mixture was diluted with CH_2Cl_2 (30 mL), and washed with brine (3 × 20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using hexane as the eluent.

3-Benzyl-4-bromo-2,5-diphenylselenophene (6a). Yield: 2.079 g (92%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.66–7.61 (m, 2H), 7.45–7.28 (m, 9H), 7.22–7.12 (m, 4H), 4.11 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.2, 142.2, 139.8, 136.8, 135.7, 135.2, 129.5, 128.9, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 125.9, 112.4, 36.2. MS (relative intensity) *m/z*: 452 (100), 373 (19), 293 (72), 215 (92), 138 (22), 91 (58). Elem. Anal. (%) Calcd for $C_{23}H_{17}Se$: C 61.08, H 3.79. Found: C 61.25, H 3.82.

General procedure for the palladium-catalyzed coupling reaction of 6a with arylboronic acids. To a Schlenck tube, under argon, containing a solution of 3-benzyl-4-bromo-2,5-diphenylselenophene **6a** (0.180 g, 0.40 mmol) in Toluene/Dioxane (1 : 1, 3.2 mL) was added to $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol). The resulting solution was stirred for 30 min at room temperature. After this time appropriate arylboronic acid (0.6 mmol) and a solution of K_3PO_4 (0.211 g, 1 mmol) in H_2O (0.5 mL) were added. The mixture was stirred at 90 °C for 3 h. After this the mixture was diluted with ethyl acetate (20 mL), and washed with brine (3 × 20 mL). The organic phase was separated, dried over $MgSO_4$, and concentrated under vacuum. The residue was purified by flash chromatography on silica gel using ethyl acetate–hexane (8 : 2) as the eluent.

3-Benzyl-2,4,5-triphenylselenophene (8a). Yield: 0.155 g (86%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.52–7.47 (m, 2H), 7.41–7.28 (m, 4H), 7.18–7.03 (m, 10H), 6.96–6.92 (m, 2H), 6.78–6.73 (m, 2H), 3.84 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.1, 144.3, 142.3, 140.8, 138.5, 138.4, 136.6, 136.3, 130.5, 129.5, 129.2, 128.5, 128.2, 128.0, 127.9, 127.8, 127.5, 126.8, 126.7, 125.4, 35.0. MS (relative intensity) *m/z*: 450 (100), 370 (14), 291 (39), 145 (29), 91 (19). Elem. Anal. (%) Calcd for $C_{29}H_{22}Se$: C 77.50, H 4.93. Found: C 77.69, H 4.99.

3-Benzyl-4-(4-methoxyphenyl)-2,5-diphenylselenophene (8b). Yield: 0.177 g (93%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.51–7.43 (m, 3H), 7.39–7.28 (m, 3H), 7.17–7.05 (m, 7H), 6.98–6.72 (m, 4H), 6.69–6.62 (m, 2H), 3.83 (s, 2H), 3.74 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 158.6, 145.0, 144.1, 142.0, 141.0, 138.7, 136.7, 136.5, 131.5, 130.8, 129.4, 129.2, 128.5, 128.2, 128.1, 127.9, 127.7, 127.5, 125.4, 113.5, 55.1, 35.0. MS (relative intensity) *m/z*: 480 (100), 291 (12), 191 (14), 153 (14), 91 (15). Elem. Anal. (%) Calcd for $C_{30}H_{24}OSe$: C 75.15, H 5.05. Found: C 75.28, H 5.17.

3-Benzyl-2,5-diphenyl-4-*p*-tolylselenophene (8c). Yield: 0.160 g (89%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.50–7.45 (m, 2H), 7.37–7.22 (m, 3H), 7.19–7.01 (m, 8H), 6.94–6.72 (m, 6H), 3.83 (s, 2H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 144.8, 144.1, 142.2, 140.9, 138.4, 136.5, 136.3, 136.2, 135.1, 130.1, 129.3, 129.2, 128.6, 128.5, 128.1, 128.0, 127.8, 127.4, 126.7, 125.3, 34.8, 21.2. MS (relative intensity) *m/z*: 464 (100), 384 (12), 291 (21), 191 (15), 145 (29). Elem. Anal. (%) Calcd for $C_{30}H_{24}Se$: C 77.74, H 5.22. Found: C 77.85, H 5.29.

1-(4-(4-Benzyl-2,5-diphenylselenophen-3-yl)-phenyl)ethanone (8d). Yield: 0.152 g (80%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.70 (d, J = 8.5 Hz, 2H), 7.52–7.47 (m, 2H), 7.42–7.32 (m, 3H), 7.13 (s, 5H), 7.08–7.02 (m, 5H), 6.77–6.72 (m, 2H), 3.84 (s, 2H), 2.54 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 197.6, 145.7, 145.0, 143.6, 141.1, 140.4, 137.7, 136.2, 135.8, 135.5, 130.7, 129.4, 129.2, 128.5, 128.2, 128.1, 127.9, 127.8, 127.7, 127.1, 125.5, 34.9, 26.3. MS (relative intensity) *m/z*: 492 (100), 291 (39), 191 (22), 145 (27), 91 (41). Elem. Anal. (%) Calcd for $C_{31}H_{24}OSe$: C 75.76, H 4.92. Found: C 75.91, H 4.98.

3-Benzyl-4-(4-chlorophenyl)-2,5-diphenylselenophene (8e). Yield: 0.180 g (95%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.51–7.45 (m, 2H), 7.40–7.26 (m, 3H), 7.21–7.03 (m, 10H), 6.86–6.70 (m, 4H), 3.82 (s, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 145.4, 144.5, 140.7, 140.5, 137.9, 136.7, 136.2, 135.8, 132.7, 131.7, 129.3, 129.2, 128.5, 128.2, 128.1, 128.0, 127.9, 127.6, 127.0, 125.5, 34.9. MS (relative intensity) *m/z*: 484 (100), 291 (36), 191 (20), 145 (72), 91 (27). Elem. Anal. (%) Calcd for $C_{29}H_{21}Se$: C 71.98, H 4.37. Found: C 72.21, H 4.43.

3-Benzyl-4-(3-nitrophenyl)-2,5-diphenylselenophene (8f). Yield: 0.162 g (90%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.02–7.96 (m, 1H), 7.78–7.74 (m, 1H), 7.55–7.46 (m, 2H), 7.44–7.31 (m, 10H), 6.75–6.70 (m, 2H), 3.83 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.8, 146.5, 145.3, 140.2, 140.0, 139.5, 137.6, 136.6, 136.0, 135.4, 129.5, 129.3, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9,

127.4, 125.8, 125.4, 121.7, 35.1. MS (relative intensity) m/z: 495 (100), 289 (35), 169 (21), 145 (37), 91 (33). HRMS calcd for $C_{29}H_{21}NO_2Se$: 495.0738. Found: 495.0742.

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