Tetrahedron Letters 55 (2014) 992–995

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Synthesis of (*Z*)-*N*-alkenyl-β-arylselanyl imidazoles via additive-free nucleophilic addition of imidazole to arylselanylalkynes

Liane K. Soares, Renata G. Lara, Raquel G. Jacob, Eder J. Lenardão, Diego Alves, Gelson Perin *

LASOL, CCQFA, Universidade Federal de Pelotas, UFPel, PO Box 354, 96010-900 Pelotas, RS, Brazil

ARTICLE INFO

Article history:
Received 13 November 2013
Revised 12 December 2013
Accepted 14 December 2013
Available online 22 December 2013

Keywords:
Imidazole
Organoselenium compounds
Nucleophilic addition
Stereoselective
(*Z*)-Arylselanyl alkenes

ABSTRACT

We present herein our results on the nucleophilic addition of imidazole to a range of arylselanylalkynes by simple heating in DMF without any additives to give (*Z*)-1-(1-organyl-(2-arylselanyl)vinyl)-1H-imidazoles. The reactions were performed under mild conditions with a range of arylselanylalkynes in good yields and with high regio- and stereoselectivity to give the respective (Z)-arylselanyl alkene as the only isomer.

Heterocyclic nitrogen-containing substrates are common constituents of natural products, agrochemicals, pharmaceuticals and are also useful intermediates in a number of microbial transformations and industrial processes.[1,2] Imidazole rings are incorporated in a large number of well-known drugs, such as Alcaftadine, used for the prevention of itching associated with allergic conjunctivitis;[1a,3] Liarozole, used for the treatment of ichthyosis[4,5] and Zolpidem, used to treat anxiety and insomnia[6,7] (Fig. 1).

Among nitrogen-containing heterocycles, *N*-alkenyl imidazoles are a very interesting sub-group, both in organic synthesis, as a building block in intramolecular cyclizations,[8] and as antifungal agents.[9] In a general way, the described methods to synthesize *N*-alkenyl imidazoles are of two types: reactions involving the hydroamination of alkynes or the coupling of imidazole with vinyl halides. The hydroamination of alkynes using imidazole as nucleophile includes the reaction in the presence of phosphazene base (^{t}Bu-P4) and DMSO, which affords a mixture of (*E*)- and (*Z*)-*N*-alkenyl imidazoles.[10] By starting from alkynones and phenacyl sulfones, a mixture of (*E*)- and (*Z*)-β-(1-imidazolyl)enones was obtained in reasonable to good yields.[11] When NaOH/TBAI/DMSO were used instead Et_3N, (*E*)-*N*-alkenyl-β-phenacyl imidazole was obtained exclusively in 66% yield.[12] (*Z*)-*N*-Alkenyl-β-bromo imidazole was obtained as a co-product in the reaction of bromoalkynes with imidazole in the presence of CuO/KOH/1,4-dioxane[13] or CuI/Cs_2CO_3/PEG-400.[14] In these reactions, *N*-alkynyl substituted imidazoles were preferentially obtained, except when a bromide source [$(Bu)_4NBr$] was present.[14] Interestingly, if the mixture of imidazole and bromoalkyne is heated at 150 °C for 2–24 h, (Z)-*N*-alkenyl-β-bromo imidazoles are obtained exclusively in good yields.[15] In a similar approach, (Z)-*N*-alkenyl-β-(*p*-bromophenyl) imidazole was selectively prepared by the copper-catalyzed nucleophilic addition of imidazole to [(4-bromophenyl)ethynyl]trimethylsilane in the presence of BtH/KOH/DMSO.[16] The hydroamination of conjugated symmetrical 1,4-diaryl-1,3-diynes via a modified Ullmann condensation was efficiently used to prepare several *N*-alkenyl-β-alkynyl imidazoles. The reaction affords a mixture of *E* and *Z* isomers (with preference for the *Z* one) in good yields by heating the reagents at 100 °C for 16 h in the presence of 1,10-phenanthroline and Cs_2CO_3 in DMSO.[17] Electron-rich terminal arylalkynes reacted with imidazole in the presence of KOH/DMSO at 120 °C to afford (*Z*)-β-imidazolyl styrenes in good yields.[18] The addition of imidazole to alkynyl phosphonium salts (acetonitrile, 80 °C, 27.5 h) followed by base hydrolysis (aq NaOH, reflux, 13.5 h) afforded *gem*-*N*-alkenyl imidazole (26% yield, 2 steps).[19]

The methods starting from vinyl halides include the reaction of β-chloroenones with imidazole in the presence of Et_3N to prepare (*E*)-*N*-alkenyl-β-phenacyl imidazoles selectively.[11] Several catalysts and ligands were used to perform the coupling of vinyl bromides with imidazole, including CuI/DMEDA in the presence of Cs_2CO_3, TBAF.$3H_2O$ in DMF[20] and CuI/EDA/K_3PO_4.[21] Depending on the starting vinyl bromide, (*Z*)- or *gem*-*N*-alkenyl imidazoles were selectively obtained, but in moderated to poor yields, even after heating the mixture for 2 days at 110 °C.[21] The oxidative amination of styrene using a polymer-bound oxidovanadium(IV) complex[22] was also used to prepare *gem*-*N*-alkenyl imidazoles. In this case a

* Corresponding author. Tel./fax: +55 5332757533.
E-mail address: gelson_perin@ufpel.edu.br (G. Perin).

0040-4039/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2013.12.058

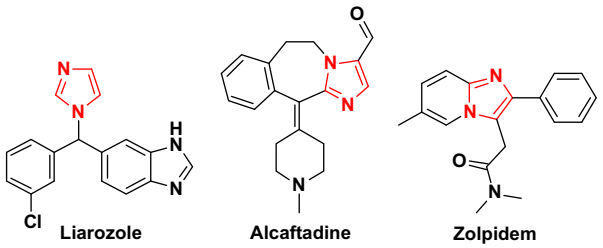


Figure 1. Drugs containing imidazolyl moiety in their structures.

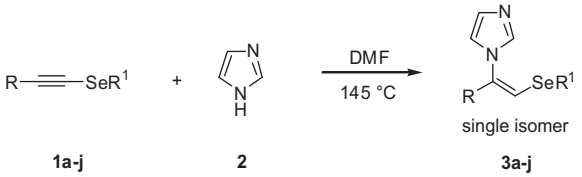
mixture of the Markovnikov and *anti*-Markovnikov adducts was obtained.

The biological activity[23] and usefulness of selenium-containing compounds in organic synthesis[24] are well documented, including a number of books[25] and reviews.[26] Of special interest are the nitrogen-functionalized organoselenium compounds, which present interesting pharmaceutical properties, including antimicrobial,[27] antioxidant,[28] and antidepressant-like.[29] Besides, catalytic amounts of optically active amino diselenides were used in the synthesis of valuable chiral building blocks in organic synthesis.[30] Thus, the search for general and selective methods to prepare highly functionalized nitrogen-containing organoselenium compounds has attracted the attention of organic synthetic chemists in the last years.

Recently, we have described the use of selanylalkynes as starting material in the hydrochalcogenation of alkynes to prepare vinyl chalcogenides.[31,32] The nucleophilic chalcogenolate anions were generated in situ by using the system $(RY)_2/NaBH_4$/PEG-400 (Y = S, Se, Te)[31] or KF/Al_2O_3.[32] In this context, we report herein the selective preparation of *N*-alkenyl-β-arylselanyl imidazoles by the additive-free nucleophilic addition of imidazole to arylselanylalkynes (Scheme 1).[33]

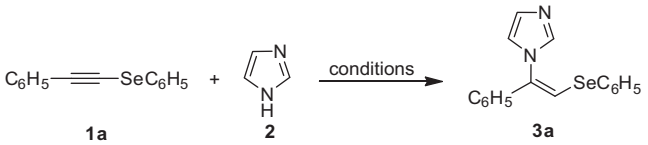
Initially, we chose 1-phenylselanyl-2-phenylethyne **1a** (0.5 mmol) and imidazole **2** (1.0 mmol) as the standard starting materials to establish the best reaction conditions for the synthesis of *N*-alkenyl-β-arylselanyl imidazole **3a** (Table 1). We examined the influence of temperature, solvent, as well as the amount of imidazole **2**. When the reaction was performed at 90 °C in DMF (5 mL) under air atmosphere, it proceeded slowly to give **3a** in 47% yield after stirring for 5 days and a large amount (49%) of starting 1-phenylselanyl-2-phenylethyne **1a** was recovered (Table 1, entry 1). The temperature was then increased to 120 °C and only 58% yield of **3a** was formed after a long reaction time (Table 1, entry 2). Fortunately, when the reaction was performed at 145 °C, the desired product (*Z*)-**3a** was obtained in 73% yield after stirring for 48 h (Table 1, entry 3). In this reaction, a small amount (13%) of starting 1-phenylselanyl-2-phenylethyne **1a** was isolated during the step of purification of the product. The yield of **3a**, however, remained almost the same even after stirring for more time at 145 °C.

Aiming to increase the yield of **3a** as well as the consumption of **1a**, we examined the influence of the amount of substrate **2** under



Scheme 1. General scheme of the reaction.

Table 1
Optimization of reaction conditions[a]



Entry	**2** (equiv)	Solvent	Temp. (°C)	Time (h)	Yield of **3a**[b] (%)
1	2.0	DMF	90	120	47
2	2.0	DMF	120	120	58
3	2.0	DMF	145	48	73
4	1.5	DMF	145	48	48
5	3.0	DMF	145	48	71
6	2.0	PEG-400	145	48	n.r.
7	2.0	DMSO	145	72	n.r.
8	2.0	THF	reflux	72	n.r.
9	2.0	DCM	reflux	72	n.r.

[a] Reactions performed using **1a** (0.5 mmol), imidazole **2** and solvent (5.0 mL).
[b] Yields are given for isolated product **3a**.

the same reaction conditions described in Table 1, entry 3. Unfortunately, when the reactions were performed using 0.75 mmol (1.5 equiv) of imidazole **2**, product **3a** was obtained only in 48% yield (Table 1, entry 4). When 1.5 mmol (3 equiv) of imidazole **2** was used, no increasing in yield was observed compared to the use of 2 equiv (Table 1, entries 5 vs 3). These results suggest that the use of an excess of imidazole is preferable to afford good yields of **3a**. The unreacted 1-phenylselanyl-2-phenylethyne **1a** was easily recovered to be used in further reactions. When the reactions were carried out using other solvents, such as PEG-400, DMSO, THF, and DCM, no product was observed after 72 h and compound **1a** was recovered (Table 1, entries 6–9).

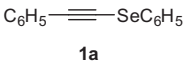
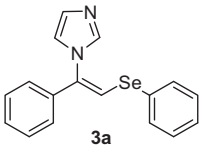
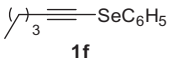
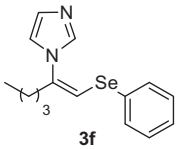
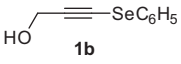
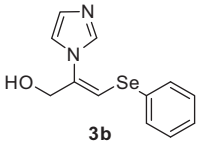
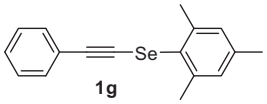
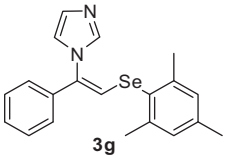
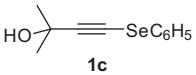
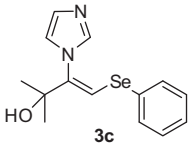
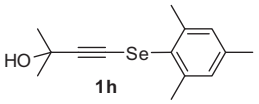
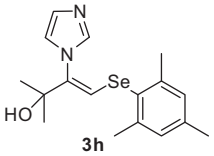
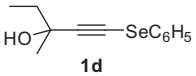
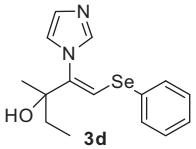
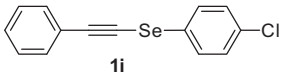
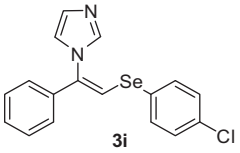
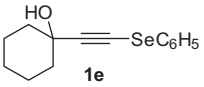
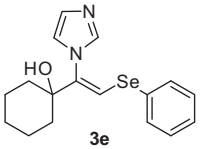
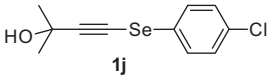
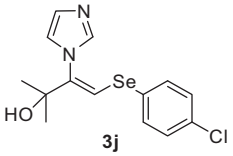
Thus, in an optimized reaction, 1-phenylselanyl-2-phenylethyne **1a** was reacted with imidazole **2** (2 equiv) in DMF at 145 °C during 48 hours under air atmosphere, yielding (*Z*)-1-(1-phenyl-(2-phenylselanyl)vinyl)-1*H*-imidazole **3a** in 73%. In contrast to the previously described methods to prepare *N*-alkenyl-imidazoles,[10–22] to our satisfaction the reaction described here was 100% stereo- and regioselective, giving exclusively the (*Z*)-alkene **3a**.

To evaluate the efficiency and generality of our protocol and to examine the reactivity of imidazole **2** against different arylselanylalkynes, the method was extended to different aromatic, propargylic (alcohol derivatives) and aliphatic alkynes and also a sort of arylselenides (Table 2).

Firstly, different phenylselanylalkynes **1a–f** were reacted with imidazole **2** under our optimal conditions (Table 2, entries 1–6). As it can be seen in Table 2, the reactivity of alkynol derivatives is influenced by steric effects. Thus, the unsubstituted phenylselanyl alkynol **1b** and the dimethylated derivative **2b** afforded, respectively **3b** and **3c** in 61 and 70% yields after 48 h (entries 2 and 3). When phenylselanyl alkynols containing sterically hindered substituents (**1d** and **1e**) were used, only reasonable yields of the respective alkenes **3d** and **3e** were isolated, even after 96 h of reaction (Table 2, entries 4 and 5). To our satisfaction, the reaction of **2** with hex-1-ynyl(phenyl)selanyl **1f** gave **3f** in 70% yield after 96 h (Table 2, entry 6). Despite a small amount of the *E*-isomer was observed here, *Z*:*E* ratio = 97:3, this is a very interesting result, once the selective preparation of vinyl selenides from low reactive aliphatic alkynes is not trivial.[26a]

The NOESY spectrum of **3c** (see in Support information) in $CDCl_3$ shows NOE cross peak of the vinylic hydrogen at 6.97 ppm (H-4, Fig. 2) to the methyl ones of the carbinol moiety at 1.31 ppm (H-1, Fig. 2). These observations corroborate for a

Table 2
Scope of the synthesis of *N*-alkenyl-β-arylselanyl imidazoles **3**[a]

Entry	Arylselanylalkyne **1**	Product **3**	Yield[b] (%)	Entry	Arylselanylalkyne **1**	Product **3**	Yield[b] (%)
1	 **1a**	 **3a**	73	6[c,d]	 **1f**	 **3f**	70
2	 **1b**	 **3b**	61	7[c]	 **1g**	 **3g**	61
3	 **1c**	 **3c**	70	8[c]	 **1h**	 **3h**	65
4[c]	 **1d**	 **3d**	56	9[c]	 **1i**	 **3i**	40
5[c]	 **1e**	 **3e**	47	10[c]	 **1j**	 **3j**	50

[a] Reactions were performed using **1a** (0.5 mmol), imidazole **2** (1.0 mmol) and DMF (5 mL) at 145 °C for 48 h under air atmosphere.
[b] Yield after purification by column chromatography. In these reactions a small amount (5–15%) of 1-phenylselanyl-2-phenylethyne **1a** was recovered.
[c] Reactions were performed for 96 h.
[d] *Z*:*E* ratio = 97:3.

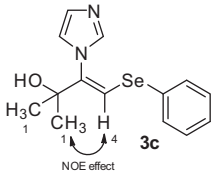


Figure 2. NOE correlation observed between CH_3-1 and vinylic H-4 in $CDCl_3$.

(*Z*)-stereochemistry in the double bond in **3c**, resulted of an *anti*-addition of the imidazole **2** to the triple bond in **1c**.

Following, we studied the effect of different substituents in the arylselanyl moiety of the arylselanylalkynes (Table 2, entries 7–10). The reaction works with both, electron-donating (–CH_3) and electron-withdrawing groups (–Cl) at the aromatic ring of the arylselanyl group. It was observed, however, that a longer reaction time was necessary for the aryl-substituted selanylalkynes. Thus, mesitylselanylalkyne **1g** and **1h** reacted with imidazole **2** to afford, after 96 h, the respective *N*-alkenyl-β-mesitylselanyl imidazoles **3g** and **3h** in 61% and 65% yield, respectively (entries 7 and 8). When *p*-chlorophenylselanylalkyne **1i** and **1j** were used, the yields of the respective alkenes **3i** and **3j** were slightly lower, of 40% and 50% (Table 2, entries 9 and 10).

It is important to point out that our protocol is suitable for both, aromatic and aliphatic selanylalkynes and, except for the alkene derived from hex-1-ynyl(phenyl)selanyl **1f**, all the products were obtained with 100% of regio- and stereoselectivity, giving exclusively the *N*-alkenyl-β-arylselanyl imidazoles **3**.[34] Besides, it is important to note that the previously described synthesis of *N*-alkenyl heteroarenes makes use of catalysts and others additives. More specifically, stereoselective methodologies to access imidazole-functionalized (*Z*)-arylselanyl alkenes were not reported yet. We believe that this good result suggest the *anti*-addition across the triple bond with abstraction of hydrogen of the second equivalent of imidazole to give the desired products **3** in excellent regio- and stereoselectivity.[35]

In conclusion, we have demonstrated for the first time the efficient synthesis of new (*Z*)-1-[1-organyl-(2-arylselanyl)vinyl]-1*H*-imidazoles by simple nucleophilic addition of imidazoles to a range of arylselanylalkynes. By this new protocol, under additive-free conditions and with simple experimental operation the products were obtained in good yields and with high regio- and stereoselectivitiy.

Acknowledgments

The authors are grateful to FAPERGS and CNPq (PRONEX 10/0005-1, PRONEM 11/2026-4 and PqG 11/0719-3), CAPES, and FINEP for the financial support.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.12.058.

References and notes

1. (a) Ding, H. X.; Liu, K. K.-C.; Sakya, S. M.; Flick, A. C.; O'Donnell, C. J. *Bioorg. Med. Chem.* **2013**, *21*, 2795; (b) Lawrence, S. A. In *Amines: Synthesis, Properties, and Applications*; Cambridge University Press: New York, 2004.; (c) Brossi, A. In *The Alkaloids: Chemistry and Pharmacology*; Cordell, G. A., Eds.; Academic Press: San Diego, 1993, Vol. 43, pp 119.; (d) Daly, J. W.; Garraffo, H. M.; Spande, T. F. In *The Alkaloids: Chemistry and Pharmacology*; Cordell, G. A., Eds.; Academic Press: San Diego, 1993, Vol. 43, pp 185.
2. (a) Stork, G.; Brizzolara, A.; Landesman, H.; Szmuszkovicz, J.; Terrell, R. *J. Am. Chem. Soc.* **1963**, *85*, 207; (b) Stork, G. *Med. Res. Rev.* **1999**, *19*, 370; (c) Cossy, J.; Belotti, D.; Bellosta, V.; Boggio, C. *Tetrahedron Lett.* **1997**, *38*, 2677; (d) Carey, J. S.; Laffan, D.; Thomson, C.; Williams, M. T. *Org. Biomol. Chem.* **2006**, *4*, 2337; (e) Wahi, A. K.; Singh, A. *Asian J. Biochem. Pharm. Res.* **2011**, *1*, 193; (f) Parshikov, I. A.; Netrusov, A. I.; Sutherland, J. B. *Appl. Microbiol. Biotechnol.* **2012**, *95*, 871.
3. Namdar, R.; Valdez, C. *Drugs Today* **2011**, *47*, 883.
4. Verfaille, C. J.; Vanhoutte, F. P.; Blanchet-Bardon, C.; van Steensel, M. A.; Steijlen, P. M. *Br. J. Dermatol.* **2007**, *156*, 965.
5. Bryson, H. M.; Wagstaff, A. J. *Drugs Aging* **1996**, *9*, 478.
6. Berson, A.; Descatoire, V.; Sutton, A.; Fau, D.; Maulny, B.; Vadrot, N.; Feldmann, G.; Berthon, B.; Tordjmann, T.; Pessayre, D. *J. Pharmacol. Exp. Ther.* **2001**, *299*, 793.
7. Harrison, T. S.; Keating, G. M. *CNS Drugs* **2005**, *19*, 65.
8. Reddy, V. P.; Iwasaki, T.; Kambe, N. *Org. Biomol. Chem.* **2013**, *11*, 2249.
9. (a) Ogata, M.; Matsumoto, H.; Hamada, Y.; Takehara, M.; Tawara, K. *J. Med. Chem.* **1983**, *26*, 768; (b) Ogata, M.; Matsumoto, H.; Shimizu, S.; Kida, S.; Tawara, K. *J. Med. Chem.* **1987**, *30*, 1348.
10. Imahori, T.; Hori, C.; Kondo, Y. *Adv. Synth. Catal.* **2004**, *346*, 1090.
11. Kashima, C.; Tajima, T. *Synthesis* **1980**, *11*, 880.
12. Shankar, R.; Jha, A. K.; Singh, U. S.; Hajela, K. *Tetrahedron Lett.* **2006**, *47*, 3077.
13. Das, B.; Reddy, G. C.; Balasubramanyam, P.; Salvanna, N. *Synthesis* **2011**, *5*, 816.
14. Burley, G. A.; Davies, D. L.; Griffith, G. A.; Lee, M.; Singh, K. *J. Org. Chem.* **2010**, *75*, 980.
15. Yamagishi, M.; Okazaki, J.; Nishigai, K.; Hata, T.; Urabe, H. *Org. Lett.* **2012**, *14*, 34.
16. Joshi, M.; Tiwari, R.; Verma, A. K. *Org. Lett.* **2012**, *14*, 1106.
17. Gupta, S.; Agarwal, P. K.; Saifuddin, M.; Kundu, B. *Tetrahedron Lett.* **2011**, *52*, 5752.
18. Joshi, M.; Patel, M.; Tiwari, R.; Verma, A. K. *J. Org. Chem.* **2012**, *77*, 5633.
19. Bagdasaryan, G. B.; Pogosyan, P. S.; Panosyan, G. A.; Asratyan, G. V.; Indzhikyan, M. G. *Russ. J. Gen. Chem.* **2006**, *76*, 1324.
20. Xu, H.; Gu, S.; Chen, W.; Li, D.; Dou, J. *J. Org. Chem.* **2011**, *76*, 2448.
21. Liau, Q.; Wang, Y.; Zhang, L.; Xi, C. *J. Org. Chem.* **2009**, *74*, 6371.
22. Maurya, M. R.; Kumar, U.; Correia, I.; Adão, P.; Pessoa, J. C. *Eur. J. Inorg. Chem.* **2008**, 577.
23. (a) Parnham, M. J.; Graf, E. *Prog. Drug Res.* **1991**, *36*, 9; (b) Mugesh, G.; du Mont, W. W.; Sies, H. *Chem. Rev.* **2001**, *101*, 2125; (c) Nogueira, C. W.; Zeni, G.; Rocha, J. B. T. *Chem. Rev.* **2004**, *104*, 6255; (d) Tiekink, E. R. T. *Dalton Trans.* **2012**, *41*, 6390.
24. Moro, A. V.; Nogueira, C. W.; Barbosa, N. B. V.; Menezes, P. H.; Rocha, J. B. T.; Zeni, G. *J. Org. Chem.* **2005**, *70*, 5257.
25. (a) Alberto, E. E.; Braga, A. L. In *Selenium and Tellurium Chemistry From Small Molecules to Biomolecules and Materials*; Derek, W. J.; Risto, L. Eds.; Springer: Berlin Heidelberg, 2011; (b) Wirth, T. *Organoselenium Chemistry: Synthesis and Reactions*; Wiley: Weinheim, 2011; (c) Menezes, P. H.; Zeni, G. Vinyl Selenides. In *Patai's Chemistry of Functional Groups*; Jonh Wiley & Sons: Oxford, 2011.
26. (a) Perin, G.; Lenardão, E. J.; Jacob, R. G.; Panatieri, R. B. *Chem. Rev.* **2009**, *109*, 1277; (b) Freudendahl, D. M.; Santoro, S.; Shahzad, S. A.; Santi, C.; Wirth, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 8409.
27. (a) Libero, F. M.; Xavier, M. C. D.; Victoria, F. N.; Nascente, P. S.; Savegnago, L.; Perin, G.; Alves, D. *Tetrahedron Lett.* **2012**, *53*, 3091; (b) Alberto, E. E.; Rossato, L. L.; Alves, S. H.; Alves, D.; Braga, A. L. *Org. Biomol. Chem.* **2011**, *9*, 1001.
28. Savegnago, L.; Vieira, A. I.; Seus, N.; Goldani, B. S.; Castro, M. R.; Lenardão, E. J.; Alves, D. *Tetrahedron Lett.* **2013**, *54*, 40.
29. Donato, F.; Gomes, M. G.; Goes, A. T. R.; Seus, N.; Alves, D.; Jesse, C. R.; Savegnago, L. *Life Sci.* **2013**, *93*, 393.
30. (a) Freudendahl, D. M.; Shahzad, S. S.; Wirth, T. *Eur. J. Org. Chem.* **2009**, 1649; (b) Braga, A. L.; Lüdtke, D. S.; Vargas, F. *Curr. Org. Chem.* **2006**, *10*, 1912; (c) Godoi, M.; Paixão, M. W.; Braga, A. L. *Dalton Trans.* **2011**, *40*, 11347.
31. Perin, G.; Borges, E. L.; Alves, D. *Tetrahedron Lett.* **2012**, *53*, 2066.
32. Lara, R. G.; Borges, E. L.; Lenardão, E. J.; Alves, D.; Jacob, R. G.; Perin, G. *J. Braz. Chem. Soc.* **2010**, *21*, 2125.
33. *General procedure for the preparation of compounds* ***3a–j****:* A mixture of arylselanylalkyne[36] 1 (0.5 mmol) and imidazole 2 (1.0 mmol) in DMF (5.0 mL) was stirred in a silicone bath maintained at 145 °C for the time indicated on Table 2. After being cooled to room temperature, the reaction mixture was diluted with NaOH 1 M (10 mL) and extracted with ethyl acetate (4 × 5 mL). The combined organic layers were washed successively with water (2 × 5 mL) and brine (2 × 5 mL), dried over MgSO4, and concentrated in vacuum to give a crude oil. The products were isolated by column chromatography using hexane/ethyl acetate as eluent. All the compounds were characterized and spectral data are listed in Supporting Information. *(Z)-1-(1-phenyl-2-(phenylselanyl)vinyl)-1H-imidazole (**3a**):* Yield: 0.119 g (73%); yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 7.56–7.57 (m, 1H), 7.48-7.51 (m, 2H), 7.25-7.27 (m, 3H), 7.20–7.24 (m, 3H), 7.14–7.15 (m, 1H), 7.07 (s, 1H), 7.01–7.04 (m, 2H), 6.95–6.96 (m, 1H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 137.5, 136.3, 135.4, 133.0, 129.6, 129.5, 129.3, 128.7, 128.6, 128.2, 125.3, 120.9, 119.4 ppm. MS *m*/*z* (rel int., %) 326 (M^+, 38.4), 258 (12.2), 178 (100), 157 (33.0), 77 (58.3). HRMS calcd. for $C_{17}H_{14}N_2Se$: [M+H]+ 327.0400. Found: 327.0390.
34. For more details, see in Support information the GC/MS analysis of the crude **3d** and **3i**.
35. Wong, V. H. L.; Hor, T. S. A.; Hii, K. K. *Chem. Commun.* **2013**, *49*, 9272.
36. Renard, M.; Hevesi, L. *Tetrahedron* **1985**, *41*, 5939.