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RESEARCH ARTICLE

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A mild and efficient procedure for alkenols oxyselenocyclization by using ionic liquids

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Abstract

A mild and efficient procedure for the oxyselenocyclization of unsaturated alcohols by treatment with phenylselenyl chloride using ionic liquids as solvents/catalyzers has been developed. The reaction proceeds instantaneously under mild conditions with absolute regioselectivity, using primary, secondary, tertiary, and aromatic alcohols, as well as monosubstituted, disubstituted, and trisubstituted alkenols. This procedure provides a new method for the synthesis of substituted tetrahydrofurans and tetrahydropyrans ethers, the precursors of many biologically active metabolites, avoiding the use of toxic and corrosive catalysts. There are no previous reports of selenium-mediated cyclofuncionalization reactions in ionic liquids. Taking into the account the good results obtained with [MMIM][MSO_4], its ease preparation, low viscosity, low price, and its capacity to be recovered and reused, it was selected as the solvent/catalyzer. Quantum-chemical calculations (MP2(fc)/6-311 + G**//B3LYP/6-311 + G**) has shown that the intramolecular cyclization is promoted by the hydrogen bond formed between the ionic liquid anion and the hydroxyl group of the alkenol.

KEYWORDS

catalysis, ionic liquids, oxyselenocyclization, quantum-chemical calculations, sustainable chemistry

1 | INTRODUCTION

Selenium is a fundamental element in life sciences; it can be found in many active and natural compounds such as carbohydrates, amino acids, and peptides.[1] Due to their biological and pharmacological properties, organoselenium compounds have emerged as important therapeutic compounds, acting as antioxidant,[2,3] anti-inflammatory, antitumor,[4] antimicrobial, or antiviral agents.[1,5] During the last decades, organoselenium compounds have also appeared as important reagents and intermediates in organic synthesis.[6,7] They can participate in a wide number of reactions, usually under relatively mild conditions[8] and presenting chemo-, regio-, or stereo-selectivity.[9] Thus, organoselenium compounds have been widely employed as intermediates in the

synthesis of complex molecules and in the development of asymmetric synthesis.[8,10–15]

Phenylselenyl halides (such as PhSeCl, PhSeBr, etc) are some of the most studied organoselenium compounds in organic synthesis; they have been widely employed as electrophilic promoters in cyclofunctionalization reactions. In particular, the synthesis of substituted tetrahydrofuran and tetrahydropyran cyclic ethers, which are the key structural elements of many metabolites from marine organisms, mycotoxins, and macrolides,[16–18] can be approached by the cyclization of alkenes with accessible hydroxyl groups induced by electrophilic selenium species (reaction termed selenoetherification).[19] The most commonly described selenocyclization reaction involves the use of an excess of a phenylselenyl halide (PhSeCl or PhSeBr) in CH_2Cl_2 as solvent, with temperatures ranging from −78°C to room temperature.[20–23] However, the use of phenylselenyl halides can give rise to the undesired addition reaction on the double bond of the unsaturated substrate, a process that gives smaller yields of the cyclic products decreasing the reaction chemoselectivity. Studies on these types of reactions have shown that the presence of equimolar amounts of bases (such as pyridine, triethylamine, or anhydrous potassium carbonate) can catalyze the reaction, increasing the rates and the yields to almost quantitative.[24] This is especially evident for secondary and tertiary unsaturated alcohols, where increased steric demands around the carbinol atom induces the selenocyclization to proceed in smaller extent.

Safety and environmental concerns demand new sustainable synthetic methods that can operate under mild reaction conditions while leading to high yields and selectivity without undesired by-products. Under this context, ionic liquids (ILs) have been successfully applied as alternative reaction media in a wide range of chemical reactions, often showing better yields, reaction rates, and selectivity than molecular solvents.[25,26] Their unique properties such as negligible vapor pressure, wide liquid range, chemical and thermal stability, recyclability, and high resistance to flammability make them a safer and more environmentally friendly reaction media compared with traditional molecular solvents.

A series of reactions of organoselenium compounds employing ILs have been tested. Potewar et al described the condensation of selenourea with different phenacyl bromides employing mixtures of different alkylimidazolium ILs with water.[27] Different groups prepared diorganyl selenides and selenolesters in a series of dialkylimidazolium ILs employing different promoters and catalysts as Zn dust,[28,29] ZnO nanopowder,[30] CuO nanopowder,[9,13] $NaBF_4$,[31] Indium[32] and InI,[33] triphenyl phosphine,[34] palladium,[35] or the bimetallic reagent Sn(II)/Cu(II).[14] The use of [bmim][BF_4] and [bmim][PF_6] in the synthesis of diaryl selenides by electrophilic substitution in arylboron reagents with phenylselenyl halides has been also described.[36] In addition, a series of chiral seleno amino derivatives have been synthesized employing CuO nanopowder in the IL [bmim][BF_4].[8] Finally, 3-arylselenylindoles have been prepared in the selenium-based IL [bmim][$SeO_2(OCH_3)$].[37] Those reactions were usually performed with high yields allowing the recovery and recycling of the IL. Nevertheless, to our knowledge, there are no previous reports of selenium-mediated cyclofuncionalization reactions in ILs.

As a continuation of our work on the application of ILs as solvents and/or catalysts in organic synthesis,[38–41] we report herein the use of different ILs as solvents/catalyzers in the cycloetherification reaction of unsaturated alcohols by means of phenylselenyl chloride. To investigate the IL effect on the reaction mechanism, quantum-chemical methods (MP2(fc)/6-311 + G**// B3LYP/6-311 + G**) have been applied.

2 | EXPERIMENTAL

2.1 | Synthesis

All chemicals used in the synthesis were purchased from Acros or Aldrich and used without any further pre-treatment or prepurification. Two unsaturated alcohols (1-phenyl-4-penten-1-ol and 1-phenyl-5-hexen-1-ol) were prepared by the procedures described in literature.[42,43] All ILs used in these studies (1-methyl-3-methylimidazolium methyl sulfate [MMIM][MSO_4],[38,44] 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [MMIM][NTf_2],[45] 1,2,3-trimethyl imidazolium methyl sulfate [MMMIM][MSO_4],[46] 1,1,3,3-tetramethylguanidinium trifluoro acetate [TMG][TFA],[40] bis(trifluoromethylsulfonyl)imide [Chol][NTf_2],[47] N-butylpyridinium bis(trifluoromethanesulfonyl)imide [BPy][NTf_2],[48] and N-butylpyridinium dicyanamide [BPy][DCA][49]) were prepared by procedures previously described in literature. Thus, sulfates were obtained by a direct quaternization reaction with a diakyl sulfate, trifluoroacetate derivative by treatment of the amine with and acid, and the rest by treatment with and alkyl halide followed by a methatesis reaction.

The detailed synthetic procedures as well as ^{1}H NMR, ^{13}C NMR, and HRMS spectral data of the synthesized compounds, are available in Supplementary Information (SI).

2.2 | Computational details

All structures were fully optimized at B3LYP/6-311 + G** and characterized as local minimum or transition state structures by computation of vibrational frequencies (for transition state structures, exactly one imaginary frequency is present, NImag = 1).[50] Being well aware of the limitations of Density Functional Theory (DFT) calculations,[51] we evaluated the energies by MP2(fc)/6-311 + G** calculations (MP2(fc)/6-311 + G**//B3LYP/6-311 + G** + ZPE(B3LYP/6-311 + G**)).[52] Gaussian 16 suites of programs were used throughout.[53]

3 | RESULTS AND DISCUSSION

A series of ILs derived from different cations (imidazolium, pyridinium, guanidinium, and cholinium) and different anions (methylsulfate, bistriflamide, dicyanoamide, and trifluoracetate) (Figure 1) were synthesized according to procedures previously described as indicated in the Section 2.

The study of phenylselenocyclofunctionalization in ILs was initially tested with the reaction of the primary alkenol pent-4-en-1-ol **1** with PhSeCl (1.1 equiv.) in the presence of each of the previously synthesized ILs as solvents/catalyzers room temperature. The reaction mixture was stirred for a certain time as required to complete the reaction (monitored by Thin Layer Chromatography (TLC)), and the reaction product was extracted with an appropriate solvent. The collected organic phases were washed and dried, and after the removal of the solvent, the residue was purified by column chromatography. The results are shown in Table 1. As it can be seen, the best reaction conditions were obtained when [MMIM][NTf_2] (time: less than 1 min, yield: 92%) and [MMIM][MSO_4] (time: 7 min, yield: 95%) were used as solvents/catalyzers. In view of the successful results, a recycling study with these two ILs was performed, observing that both ILs can be reused up to five times without loss of activity.

A comparison between the results obtained in entries 4, 5, and 6, keeping the same anion combined with different cations, indicated that in this process the main IL catalytic effect resides in the anion. Modifying the cation of an IL has shown to not affect the outcome of some other reactions, as for example S_N2.[54]

To investigate the scope of the reaction, it was also carried out with other substrates, using primary, secondary, tertiary, and aromatic alcohols, as well as monosubstituted, disubstituted, and trisubstituted alkenols (Table 2). Taking into the account the good results obtained with [MMIM][MSO_4] in the first reaction, its ease of preparation, low viscosity, and price, it was selected to be used as solvent. As it can be observed in Table 2, low reaction times and high yields were obtained for all substrates. In addition, a very high level of regioselectivity was achieved, since none other products were observed by TLC. The reaction products structures were determined by ^1H and ^{13}C NMR spectroscopy and

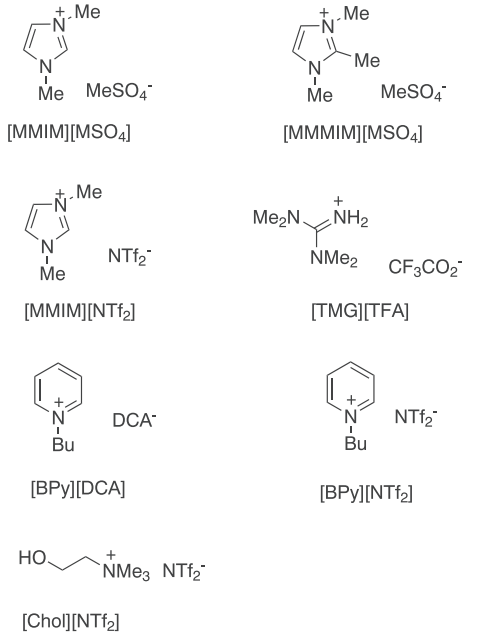
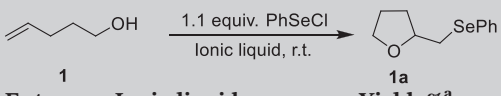


FIGURE 1 Structure of ionic liquids (ILs) synthesized to be used in this work

TABLE 1 Optimization of the reaction conditions for the ionic liquid-mediated phenylselenocyclofunctionalization



1 1a

Entry	Ionic liquid	Yield, %[a]	Time, min
1	[MMIM][MSO4][b]	95	7
2	[MMMIM][MSO4]	55[c]	10
3	[TMG][TFA]	65	360
4	[Chol][NTf2]	Not isolated[d]	1
5	[MMIM][NTf2][b]	92	<1
6	[BPy][NTf_2]	82	<1
7	[BPy][DCA]	78	90

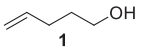
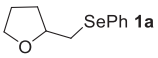
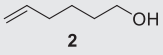
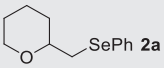
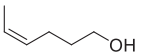
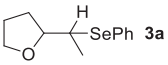
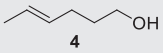
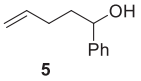
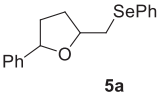
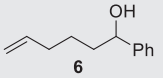
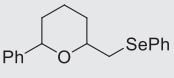
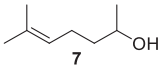
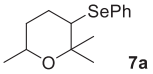
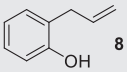
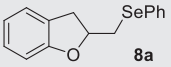
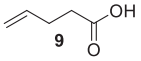
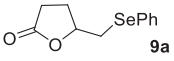
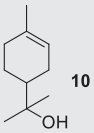
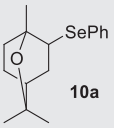
[a]TLC and NMR evaluation showed complete transformation of starting material, while presented yields correspond to the yields determined after purification by column chromatography.

[b][MMIM][MSO_4] and [MMIM][NTf_2] were reused up to five times without significant loss of activity.

[c]The lower yield was due to difficulties encountered to extract the product from the IL.

[d]The product extraction was not possible due to the high IL solubility in all tested solvents.

TABLE 2 Phenylselenocyclofunctionalization reaction of different unsaturated alcohols in [MMIM][MSO_4]

Substrate	Product	Yield, %[a]	Time, min	Ref.
 1	 **1a**	95	7	Konstantinovic et al[22] and Bugarčić et al[55]
 2	 **2a**	88	10	Konstantinovic et al[22] and Bugarčić et al[55]
 3	 **3a**	86[b]	5	Konstantinovic et al[22]
 4	 **4a**	91 (52:48)[c]	1	Konstantinovic et al[22]
 5	 **5a**	81 (50:50)[c]	10	Tiecco et al[56]e
 6	 **6a**	77 (45:55)[c]	20	-
 7	 **7a**	88	60	Konstantinovic et al[22]
 8	 **8a**	76[d]	90	Nicolaou[20]
 9	 **9a**	79	30	Nicolaou[21]
 10	 **10a**	71[d]	120	Wodrich et al[57]

[a]Yields determined after purification by column chromatography.

[b]*Erythro*-2-(1-phenylselenoethyl)tetrahydrofuran.

[c]Ratio of *cis/trans* isomers determined by NMR from crude reaction mixture.

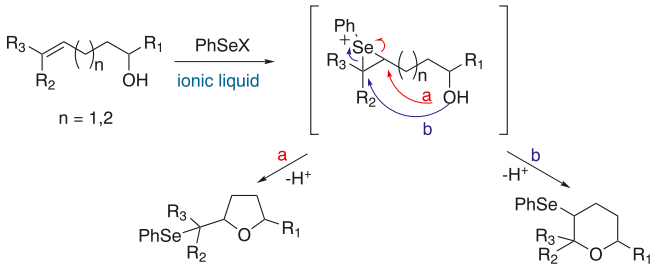
[d]The reaction was performed in the presence of 1 equivalent of pyridine.

[e]Our compound was obtained as mixture of *cis*- and *trans*- while in the referenced article the 4 enantiomers are described separately.

confirmed by comparison with the data previously report in literature, except in the case of **6a** whose data were not found in the bibliography. Its structure was confirmed by ^{1}H and ^{13}C NMR spectroscopy as well as high resolution mass spectrometry.

The accepted mechanism for the organoselenium-mediated cyclization reactions between unsaturated alcohols and electrophilic selenium reagents as PhSeCl involves the initial formation of a cyclic seleniranium ion intermediate by the electrophilic attack on the double bond. The later intramolecular nucleophilic attack of the hydroxyl group at one of the carbons of the seleniranium ring gives the cyclic ether product. As result of the seleniranium intermediate formation, the reaction is antistereospecific.[58] Depending on the chain length and the substitution pattern of the alkenol, the reaction can follow an exo- and/or endo-pathway to give a five or a six membered cyclic ether (Scheme 1).

A comparative study of the results obtained in this work with those previously described using a different reaction medium showed that the effect of the IL is very similar to that observed when the reaction is carried out in CH_2Cl_2 and an equimolecular amount of pyridine.[24] Thus, primary (**1**, **3**), secondary (**5**), and aromatic (**8**) Δ^4-alkenols gave five-membered cyclic ethers (**1a**, **3a**, **5a**, and **8a**), except when the terminal double bond is E disubstituted (**4**) or trisubstituted (**7**), that favor the tetrahydropyran derivative (**4a** and **7a**). The cyclic tertiary Δ^4-alkenol with a trisubstituted double bond **10** also gave the six-membered cyclic ether (**10a**). Quantum-chemical calculations on the phenylselenoetherification of (Z) and (E)-hex-4-en-1-ols (**3** and **4**)[55] have shown that the cyclization of (Z)-hex-4-en-1-ol (**3**) is kinetically controlled by the activation energy to afford the five-membered cyclic ether (**3a**), while the cyclization of the (E)-alkenol (**4**) is thermodynamically controlled to yield the more stable



SCHEME 1 General accepted mechanism of the phenylselenocyclofunctionalization reaction between unsaturated alcohols and PhSeX

six-membered tetrahydropyran cyclic ether (**4a**). As expected, the γ,δ-unsaturated carboxylic acid **9** yields the corresponding seleno-substituted lactone **9a**, showing the efficiency of the procedure when using unsaturated carboxylic acids instead of alkenols.

In the case of Δ^5-alkenols, primary (**2**), or secondary (**6**), the reaction always affords a six-membered cyclic ether (**6a**).

Although the reaction yields when using ILs or CH_2Cl_2/Py as solvents/catalyzers are very similar, and both proceed at room temperature, the use of ILs affords a series of advantages. Thus, besides avoiding the use of the traditional contaminating volatile organic solvents and toxic bases, they can be recycled and reused without losing their activity.

Mechanistic studies of cycloetherifications of pent-4-en-ols by treatment with PhSeCl in the presence of a base (pyridine, trimethylamine, quinolone, and 2,2′-bipyridine) have shown that the catalytic effect of the base is caused by the hydrogen bond formed with the hydroxyl group, which increases the oxygen nucleophilic character.[59,60] It has been also reported that solvents with higher polarity can better stabilize the charged transition state for the cyclization, increasing the reaction rate. Similar effects can be attributed to the catalytic role of the ILs, which present a very high polarity and would form hydrogen bonds with the hydroxyl group through the anion.

In order to determine the effect of the cation when acidic protons are present (H-2 of 1,2-dimethylimidazolium cation), the reaction between pent-4-en-1-ol **1** and PhSeCl in 1,2,3-trimethylimidazolium sulfate ([MMMIm][MSO_4]) was carried out (Table 1, entry 2), but no significant differences were observed in the reaction rate.

As mentioned above, the decision to investigate reactions in [MMIm][$MeSO_4$] was driven by the economical demands for the preparation of ILs, as well as by the reaction yields and rates observed during the optimization process. However, a pertinent effect of the NTf_2-based ILs on the reaction rates still remained to intrigue our research attention. As it can be seen in Table 1, the application of all NTf_2-based ILs as reaction media have afforded almost instantaneous formation of the cyclic ether product, regardless cationic part of the IL applied.

Therefore, we decided to perform additional quantum chemical calculations at molecular level in order to get deeper insight into the NTf_2 influence on the reaction pathway. For comparability with our previously published results for uncatalyzed- and pyridine-facilitated selenoetherification of pent-4-en-1-ol,[60] the same level of theory (B3LYP/6-311 + G**) has been utilized for our quantum chemical calculation of the NTf_2-suported reaction. Again, the same concept as already successfully applied was followed. The mechanistic survey started with the seleniranium ion formation (Figures 2A and 3A).

As it was expected, there is no significant difference for the bond lengths at this point in the reaction and very similar values have been obtained. The length of C–C bond of 1.44 Å in newly formed seleniranium intermediate is identical to those observed in unsupported- and pyridine-facilitated reactions.[60] Slightly different bond lengths have been noticed for the Se–CCH– bond, which is 2.23 Å (unsupported reaction: 2.13 Å; with pyridine: 2.17 Å) and for the C4-O distance (2.56 Å for IL-mediated reaction, 2.79 Å for the unsupported reaction, and 2.64 Å in pyridine case). Through the molecular rearrangement

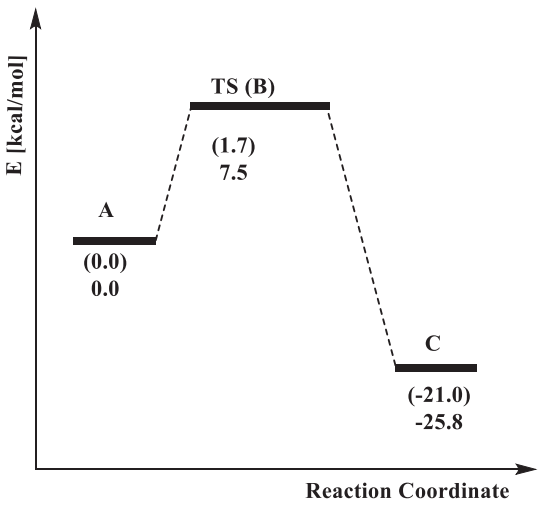


FIGURE 2 Calculated reaction pathway (MP2(fc)/6-311 + G**// B3LYP/6-311 + G** + ZPE(B3LYP/6-311 + G**) for the cycloselenoetherification of pent-4-en-1-ol mediated by the Ph-Se^+ with hydrogen bond bound [NTf_2] anion (Values in brackets: B3LYP/6-311 + G** + ZPE(B3LYP/6-311 + G**

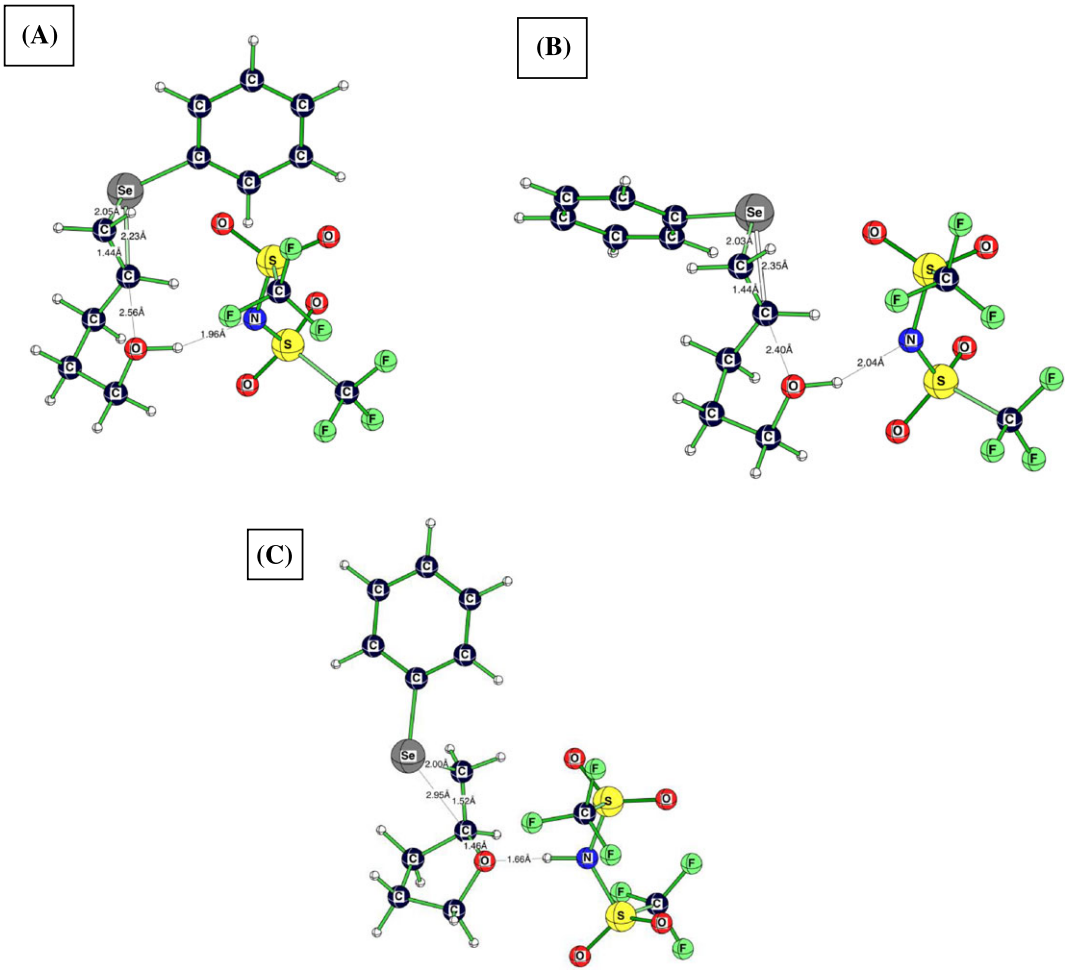


FIGURE 3 B3LYP/6-311 + G**-calculated (A) seleniranium ion; (B) transition state; and (C) cyclic ether product for the cycloselenoetherification mediated by the Ph-Se$^+$ with hydrogen bond bound NTf_2 anion

required for the final formation of the cyclic ether product, the first significant differences for unsupported and NTf_2-faciliated reaction are disclosed at the transition state (Figures 2B and 3B). The transition state of the unsupported reaction is associated with an energy barrier of 8.8 kcal/mol (B3LYP/6-311 + G**) (11.8 kcal/mol for MP2(fc)), while the presence of NTf_2 hydrogen bound by the OH group in the structure influences the significant decrease of energetic demands—more precisely, a barrier of 1.7 kcal/mol at the B3LYP level of theory (or 7.5 kcal/mol in the case of MP2(fc)) is calculated. It is noteworthy to mention that such differences in the activation barriers are already mentioned in literature for the B3LYP and MP2(fc) calculation and are not unexpected.[52]

The distance of the C4–O bond that is responsible for the cyclic ether formation is getting shorter in transition state by around 0.1 Å and reduces to the 1.47 Å in the final selenocyclic product C (Figures 2 and 3). Another relevant conclusion has been derived from the observation of energetic destiny for the hydrogen bond between nitrogen form NTf_2-anion and OH-alkenol group. Although in the framework of the seleniranium ion-transition state pass, this bond does not change its length, the migration of the proton from OH group to the negatively charged nitrogen in NTf_2 in the cyclic product is likely to have strong influence on the stability of calculated pathways. The liberated energies of 19 kcal/mol (B3LYP) and 18 kcal/mol (MP2(fc)) for the formation of the five-membered heterocyclic product C are very similar to those achieved by the pyridine-supported concept (around 20 kcal/mol). In contrast to the stabilization of the cyclic ether product caused by the NTf_2 acceptance of the proton, the protonated cyclic ether form in unsupported reaction is energetically very unfavorable in its transformation to the final product by later deprotonation. This behavior has been observed for other reported reactions in ILs, where the IL effect is correlated with the hydrogen bond accepting ability of the IL anion,[61] as well as the transition state IL solvation.[62]

4 | CONCLUSIONS

A new application of ILs in organic synthesis is reported. The oxyselenocyclization of unsaturated alcohols by treatment with phenylselenyl chloride is carried out by using ILs as solvents/catalyzers, without the need of any other promoter. The reaction proceeds in a regiospecific fashion, mild conditions, broad scope, and in general very good yields, using primary, secondary, tertiary, and aromatic alcohols, as well as monosubstituted, disubstituted, and trisubstituted alkenols. Taking into the account the good results obtained with [MMIM][MSO_4], its ease preparation, low viscosity, low price, and its capacity to be recovered and reused, it was selected to be used as the solvent/cataliser. This procedure provides an improved method for the synthesis of substituted tetrahydrofurans and tetrahydropyrans ethers, the precursor of many biologically active metabolites isolated from marine organisms, polyene mycotoxines, and macrolides. The reaction mechanism was investigated by Quantum-chemical calculations (MP2(fc)/6-311 + G**//B3LYP/6-311 + G**), which has shown that the intramolecular cyclization is promoted by the hydrogen bond formed between the IL anion and the HO group of the alkenol.

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REFERENCES

[1] G. Mugesh, W.-W. de Mont, H. Sies, *Chem. Rev.* **2001**, *101*, 2125.

[2] a) C. W. Nogueira, G. Zeni, J. B. T. Rocha, *Chem. Rev.* **2004**, *104*, 6255. b) V. K. Jain, K. I. Priyadarsini, *Organoselenium Compounds in Biology and Medicine: Synthesis, Biological and Therapeutic Treatments*, The Royal Society of Chemistry, Croydon (UK) **2018**.

[3] V. De Silva, M. M. Woznichak, K. L. Burns, K. B. Grant, S. W. May, *J. Am. Chem. Soc.* **2004**, *126*, 2409.

[4] Y. Kumar, R. Green, K. Z. Borysko, D. S. Wise, L. L. Wotring, L. B. Townsend, *J. Med. Chem.* **1993**, *36*, 3843.

[5] M. Soriano-Garcia, *Curr. Med. Chem.* **2004**, *11*, 1657.

[6] a) C. Paulmier, *Selenium Reagents and Intermediates in Organic Synthesis*, Pergamon, Oxford **1986**. b) E. J. Lenardão, C. Santi, L. Sancineto, *New Frontiers in Organoselenium Compounds*, Springer **2018**.

[7] T. G. Back, *Organoselenium Chemistry, A Practical Approach*, Oxford University Press, Oxford **1999**.

[8] S. M. Salman, S. Narayanaperumal, R. S. Schwab, C. R. Bender, O. E. D. Rodrigues, L. Dornelles, *RSC Adv.* **2012**, *2*, 8478.

[9] D. Singh, E. E. Alberto, O. E. D. Rodrigues, A. L. Braga, *Green Chem.* **2009**, *11*, 1521.

[10] N. Petragnani, H. A. Stefani, C. J. Valduga, *Tetrahedron* **2001**, *57*, 1411.

[11] M. Tiecco, in *Topics in Current Chemistry: Organoselenium Chemistry*, (Ed: T. Wirth) Vol. 208, Springer-Verlag, Berlin **2000** 7.

[12] G. Perin, D. Alves, R. G. Jacob, A. M. Barcellos, L. K. Soares, E. J. Lenardao, *ChemistrySelect* **2016**, *1*(2), 205.

[13] D. Singh, S. Narayanaperumal, K. Gul, M. Godoi, O. E. D. Rodrigues, A. L. Braga, *Green Chem.* **2010**, *12*, 957.

[14] K. Gul, S. Narayanaperumal, L. Dornelles, O. E. D. Rodrigues, A. L. Braga, *Tetrahedron Lett.* **2011**, *52*, 3592.

[15] D. M. Freudendahl, S. A. Shahzad, T. Wirth, *Eur. J. Org. Chem.* **2009**, *1649*.

[16] J. W. Blunt, B. R. Copp, M. H. G. Munro, P. T. Northcote, M. R. Prinsep, *Nat. Prod. Rep.* **2004**, *21*(1), 1.

[17] T. Yasumoto, M. Murata, *Chem. Rev.* **1993**, *93*, 1897.

[18] A. Bermejo, B. Figadere, M. C. Zafra-Polo, I. Barrachina, E. Estornell, D. Cortes, *Nat. Prod. Rep.* **2005**, *22*(2), 269.

[19] Z. M. Bugarcic, M. D. Kostic, V. M. Divac, *Current Org. Chem* **2016**, *20*(7), 777.

[20] K. C. Nicolaou, R. L. Magolda, W. J. Sipio, W. E. Barnette, Z. Lysenko, M. M. Joullie, *J. Am. Chem. Soc.* **1980**, *102*(11), 3784.

[21] K. C. Nicolaou, *Tetrahedron Lett.* **1981**, *37*(23), 4097.

[22] S. Konstantinovic, Z. Bugarčič, S. Milosavljevič, G. Schroth, M. L. Mihailovič, *Liebigs Ann. Chem.* **1992**, *1992*(3), 261.

[23] M. Gruttadauria, C. Aprile, S. Riela, R. Noto, *Tetrahedron Lett.* **2001**, *42*, 2213.

[24] Z. M. Bugarčić, B. M. Mojsilovic, V. M. Divac, *J. Mol. Catal. A: Chem.* **2007**, *272*, 288.

[25] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508.

[26] C. J. Clarke, W.-C. Tu, O. Levers, A. Bröhl, J. P. Hallett, *Chem. Rev.* **2018**, *118*, 747.

[27] T. M. Potewar, S. A. Ingale, and K. V. Srinivasan, ARKIVOC, **2008**, xii, 117.

[28] S. Narayanaperumal, E. E. Alberto, K. Gul, O. E. D. Rodrigues, A. L. Braga, *J. Org. Chem.* **2010**, *75*, 3886.

[29] S. Narayanaperumal, E. E. Alberto, K. Gul, C. Y. Kawasoko, L. Dornelles, O. E. D. Rodrigues, A. L. Braga, *Tetrahedron* **2011**, *67*, 4723.

[30] S. Narayanaperumal, K. Gul, C. Y. Kawasoko, D. Singh, L. Dornelles, O. E. D. Rodrigues, A. L. Braga, *J. Braz. Chem. Soc.* **2010**, *21*(11), 2079.

[31] E. J. Lenardão, L. C. C. Gonçalves, S. R. Mendes, M. T. Saraiva, D. Alves, R. G. Jacob, G. Perin, *J. Braz. Chem. Soc.* **2010**, *21*(11), 2093.

[32] G. Tabarelli, E. E. Alberto, A. M. Deobald, G. Marin, O. E. D. Rodrigues, L. Dornelles, A. L. Braga, *Tetrahedron Lett.* **2010**, *51*, 5728.

[33] S. Narayanaperumal, E. E. Alberto, F. Molinos de Andrade, E. J. Lenardao, P. S. Taube, A. L. Braga, *Org. Biomol. Chem.* **2009**, *7*, 4647.

[34] S. Banerjee, L. Adak, B. C. Ranu, *Tetrahedron Lett.* **2012**, *53*, 2149.

[35] H. Zhao, W. Hao, Z. Xi, M. Cai, *New J. Chem.* **2011**, *35*, 2661.

[36] C. S. Freitas, A. M. Barcellos, V. G. Ricordi, J. M. Pena, G. Perin, R. G. Jacob, E. J. Lenardao, D. Alves, *Green Chem.* **2011**, *13*, 2931.

[37] E. G. Zimmermann, S. Thurow, C. S. Freitas, S. R. Mendes, G. Perin, D. Alves, R. G. Jacob, E. J. Lenardão, *Molecules* **2013**, *18*, 4081.

[38] F. Santamarta, P. Verdía, E. Tojo, *Cat. Com.* **2008**, *9*, 1779.

[39] P. Verdía, F. Santamarta, E. Tojo, *Molecules* **2011**, *16*, 4379.

[40] M. Vilas, E. Tojo, *Tetrahedron Lett.* **2010**, *51*, 4125.

[41] V. Fernández-Stefanuto, P. Verdía, E. Tojo, *New J. Chem.* **2017**, *41*, 12830.

[42] B. Janza, A. Studer, *Org. Lett.* **2006**, *8*, 1875.

[43] E. C. Ashbym, R. N. DePriest, A. B. Goel, B. Wenderoth, T. N. Pham, *J. Org. Chem.* **1984**, *49*, 3545.

[44] P. Verdía, F. Santamarta, E. Tojo, *J. Chem. Educ.* **2017**, *94*, 505.

[45] E. Bodo, L. Gontrani, R. Caminiti, N. V. Plechkova, K. R. Seddon, A. Triolo, *J. Phys. Chem. B* **2010**, *114*, 16398.

[46] J. D. Holbrey, W. M. Reichert, R. P. Swatloski, G. A. Broker, W. R. Pitner, K. R. Seddon, R. D. Rogers, *Green Chem.* **2002**, *4*, 407.

[47] K. R. Harris, M. Kanakubo, *J. Chem. Eng. Data* **2016**, *61*, 2399.

[48] M. Potangale, A. Das, S. Kapoor, S. Tiwari, *J. Mol. Liq.* **2017**, *240*, 694.

[49] X. Xu, H. Li, Y. Wang, *ChemCatChem* **2014**, *6*, 3328.

[50] a P. J. Stevens, F. J. Devlin, C. F. Chablowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623. b A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. c C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785. d W. Koch, M. C. Holthausen, *A Chemist's Guide to Density Functional Theory*, 2nd ed., Wiley-VCH, Weinheim **2001**, Ch. 13, 239.

[51] a M. D. Wodrich, C. Corminboeuf, P. von Ragué Schleyer, *Org. Lett.* **2006**, *8*, 3631. b P. R. Schreiner, A. A. Fokin, R. A. Pascal, A. P. de Meijere, *Org. Lett.* **2006**, *8*, 3635. c S. Grimme, M. Steinmetz, M. Korth, *J. Org. Chem.* **2007**, *72*, 2118. d M. D. Wodrich, C. Corminboeuf, P. Schreiner, A. A. Fokin, P. von Ragué Schleyer, *Org. Lett.* **2007**, *9*, 1851. e P. R. Schreiner, *Angew. Chem. Int. Ed.* **2007**, *46*, 4217.

[52] W. J. Hehre, L. Radom, P. V. R. Schleyer, J. A. Pople, *Ab Initio Molecular Orbital Theory*, Wiley, New York **1986**.

[53] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings,B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16 (Revision A.03), Gaussian Inc., Wallingford CT, **2016**.

[54] E. E. L. Tanner, H. M. Yau, R. R. Hawker, A. K. Croft, J. B. Harper, *Org. Biomol. Chem.* **2013**, *11*, 6170.

[55] Z. M. Bugarčić, V. M. Divac, M. D. Kostić, N. Ž. Janković, F. W. Heinemann, N. S. Radulović, Z. Z. Stojanović-Radić, *J. Inorg. Biochem.* **2015**, *143*, 9.

[56] M. Tiecco, L. Testaferri, L. Bagnoli, V. Purgatorio, A. Temperini, F. Marini, C. Santi, *Tetrahedron: Asymmetry* **2004**, *15*, 405.

[57] M. D. Rvovic, V. M. Divac, N. Z. Jankovic, Z. M. Bugarcic, *Monatsh. Chem.* **2013**, *144*(8), 1227.

[58] V. A. Soloshonok, D. J. Nelson, *Beilstein J. Org.Chem* **2011**, *7*, 744.

[59] V. M. Divac, R. Puchta, Z. M. Bugarčić, *J. Phys. Chem. A* **2012**, *116*, 7783.

[60] M. D. Rvovic, V. M. Divac, R. Puchta, Z. M. Bugarčić, *J. Mol. Model.* **2011**, *17*, 1251.

[61] R. R. Hawker, R. S. Haines, J. B. Harper, *Org. Biomol. Chem.* **2018**, *16*, 3453.

[62] S. T. Keaveney, B. P. White, R. S. Haines, J. B. Harper, *Org. Biomol. Chem.* **2016**, *14*, 2572.

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