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Efficient Intramolecular Hydroalkoxylation/Cyclization of Unactivated Alkenols Mediated by Lanthanide Triflate Ionic Liquids

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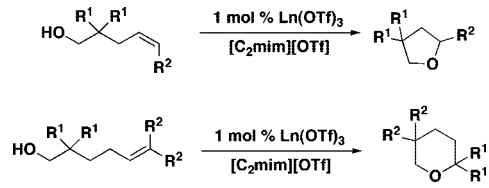
ABSTRACT



Lanthanide triflates, $Ln(OTf)_3$, serve as efficient catalysts for the intramolecular hydroalkoxylation (HO)/cyclization of primary/secondary and aliphatic/aromatic hydroxyalkenes in room temperature ionic liquids (RTILs). Cyclizations are effective in the formation of five- and six-membered oxygen heterocycles with Markovnikov-type selectivity. Reaction rates exhibit first-order dependence on $[Ln^{3+}]$ and [substrate].

The regioselective intramolecular addition of an O−H bond across C−C unsaturation is an atom-economical route to constructing both simple and complex oxygen-containing heterocycles,[1] including important structural components of a wide array of naturally occurring and biologically active molecules, such as acetogenins and polyether antibiotics.[2] Currently, cyclic ethers are accessible either by direct catalytic Wacker oxidative cyclization[2] or intramolecular hydroalkoxylation (HO),[3−6] with the latter being a relatively unexplored area involving a limited number of reported catalysts.[3−6] Catalytic approaches to intramolecular HO processes have implemented Brønsted acid,[3] transition metal,[4] and metal triflate[5] catalysts with varying degrees of success. Due to the limitations of the current synthetic methods, for example, high catalyst cost[4,5] and metal toxicity, development of new, efficient catalytic methods for cyclic ether synthesis presents an intriguing challenge.

Lanthanide complexes are known to be highly active hydrofunctionalization catalysts.[6−8] Recently, lanthanide triflates have emerged as important reagents/catalysts in a

(1) (a) Tani, K.; Kataoka, V. *Catalytic Heterofunctionalization*; Togni, A., Grützmacher, H., Eds.; Wiley-VCH: Weinheim, Germany, 2001.

(2) (a) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons: Chichester, 2004; pp 27−103. (b) Pei, T.; Wang, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2003**, *125*, 648–649. (c) Muñiz, K. *Adv. Synth. Catal.* **2004**, *346*, 1425–1428. (d) Hirai, Y.; Watanabe, J.; Nozaki, T.; Yokoyama, H.; Yamaguchi, S. *J. Org. Chem.* **1997**, *62*, 776–777. (e) Rönn, M.; Bäckvall, J. E.; Andersson, P. G. *Tetrahedron Lett.* **1995**, *36*, 7749–7752.

(3) For examples of Brønsted acid-mediated alkene hydroalkoxylation, see: (a) Rosenfeld, D. C.; Shekhar, S.; Tameiyama, A.; Utsunomiya, M. *Hartwig Org. Lett.* **2006**, *8*, 4179–4182. (b) Coulombel, L.; Duñach, E. *Green Chem.* **2004**, *6*, 499–501. (c) Linares-Palomino, P. J.; Salido, S.; Altarejos, J.; Sánchez, A. *Tetrahedron Lett.* **2003**, *44*, 6651–6655.

(4) For examples of transition metal-mediated alkene hydroalkoxylation, see: (a) Coulombel, L.; Rajzmann, M.; Pons, J.-M.; Olivero, S.; Duñach, E. *Chem.−Eur. J.* **2006**, *12*, 6356–6365. (b) Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2005**, *127*, 6966–6967. (c) Oe, Y.; Ohta, T.; Ito, Y. *Synlett* **2005**, *1*, 179–181. (d) Qian, H.; Han, X.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2004**, *126*, 9536–9537. (e) Marotta, E.; Foresti, E.; Marcelli, T.; Peri, F.; Righi, P.; Scardovi, N.; Rosini, G. *Org. Lett.* **2002**, *4*, 4451–4453.

(5) For examples of metal triflate-mediated alkene hydroalkoxylation, see: (a) Komeyama, K.; Morimoto, T.; Nakayama, Y.; Takaki, K. *Tetrahedron Lett.* **2007**, *48*, 3259–3261. (b) Yang, C.-G.; Reich, N. W.; Shi, Z.; He, C. *Org. Lett.* **2005**, *7*, 4553–4556. (c) Coulombel, L.; Rajzmann, M.; Pons, J.-M.; Olivero, S.; Duñach, E. *Chem.−Eur. J.* **2006**, *12*, 6356–6365.

(6) Hydroalkoxylation:(a) Seo, S.; Yu, X.; Marks, T. J. *J. Am. Chem. Soc.* **2009**, *131*, 263–276. (b) Yu, X.; Seo, S.; Marks, T. J. *J. Am. Chem. Soc.* **2007**, *129*, 7244–7245.

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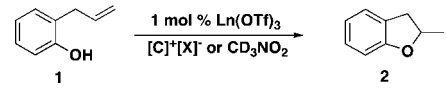
wide range of organic transformations.[9] Only substoichiometric amounts of catalyst are sufficient for complete conversions, and catalysts can be readily recycled.[9] Nevertheless, $Ln(OTf)_3$-catalyzed processes typically require toxic, highly polar, moderately coordinating solvents, which incur significant safety and cost-associated disadvantages.[9]

The use of room temperature ionic liquids (RTILs), thermally stable fluids comprised solely of ions, as chemical reaction media in place of conventional volatile organic solvents, has grown dramatically in recent years.[10] In addition to low volatility, a potential environmental benefit, ionic liquids are extremely polar, usually aprotic, and often afford unique reaction efficiencies and selectivities.[11] For $Ln(OTf)_3$-mediated intramolecular HO/cyclization of alkenols, RTILs based on noncoordinating anions might be expected to provide increased Ln^{3+} Lewis acidity, due to minimal solvent coordination to the Ln^{3+} center, and to offer catalyst and ionic liquid recyclability, as well as ease of product separation. In this contribution we report that lanthanide triflates in RTIL media are very efficient and selective catalysts for the HO/cyclization of unactivated alkenols, and present a preliminary discussion of reaction scope, selectivity, and kinetics for this new catalytic process.

The efficiency of the $Ln(OTf)_3$-catalyzed **1** → **2** conversion was first optimized as a function of solvent (Table 1), and an optimum protocol was identified. Initial screening of $Ln(OTf)_3$-mediated intramolecular HO/cyclization of **1** in nitromethane revealed exclusive formation of **2** (eq 1, Table 1); the formation of β-hydride elimination /isomerization products is not observed. $Ln(OTf)_3$ complexes exhibit modest catalytic activity for conversion **1** → **2** in nitromethane (Table 1, entries 1−3), with relative ordering of catalytic activity, $Yb^{3+} > Sm^{3+} > La^{3+}$.

In marked contrast to the catalytic results in nitromethane, the **1** → **2** catalytic conversion in RTILs based on weakly coordinating OTf^- and NTf_2^- anions proceeds with large rate enhancements, as reflected by ∼70-fold increases in turnover frequencies (Table 1, entries 6−11). The marked rate sensitivities to the nature of the solvent can be attributed to differences in the Ln^{3+} Lewis acidity in solvents that differ in cation-coordinating strength.[12] Nitromethane is a polar, aprotic, moderately cation-coordinating solvent,[12] which through coordination to Ln^{3+}, is expected to decrease the Lewis acidity. RTILs based on OTf^- and NTf_2^- anions are highly polar yet relatively noncoordinating,[10] thus likely enhancing Ln^{3+} Lewis acidity/unsaturation as suggested by the increased turnover frequencies (Table 1, entries 6−9). The present large rate enhancements in the hydrophilic[10] ionic liquid, $[C_n\text{mim}][OTf]$, vs the hydrophobic[10] $[C_n\text{mim}][NTf_2]$ analogues (Table 1, entries 9,10) are reasonably attributable to differences in solvation.[11b]

Table 1. Screening of $Ln(OTf)_3$ Complexes and Reaction Media for Intramolecular Hydroalkoxylation/Cyclization of **1**



1 2 (1)

entry	Ln^{3+} (mol %)	M^{3+} (Å)	solvent	time (h)	N_t h^{-1} (°C, yield %)[a,b]
1.	La(5)	1.172	CD_3NO_2	18	0.01(100,1)[c]
2.	Sm(5)	1.098	CD_3NO_2	18	0.04(100,2)[c]
3.	Yb(5)	1.008	CD_3NO_2	18	0.10(100,9)[c]
4.	–	–	$[C_2\text{mim}][OTf]$[d]	18	–(120,-)
5.	–	–	$[C_1\text{dbu}][OTf]$[e]	18	–(120,-)
6.	La(1)	1.172	$[C_1\text{dbu}][OTf]$[e]	3	0.67(120,48)
7.	Yb(1)	1.008	$[C_1\text{dbu}][OTf]$[e]	3	5.37(120,88)
8.	Yb(1)	1.008	$[C_2\text{mim}][OTf]$[d]	3	6.37(120,93)
9.	Yb(1)	1.008	$[C_4\text{mim}][OTf]$[f]	3	6.01(120,86)
10.	Yb(1)	1.008	$[C_2\text{mim}][NTf_2]$[g]	3	1.18(120,59)
11.	Yb(1)	1.008	$[C_4\text{mim}][NTf_2]$[h]	3	1.07(120,52)

[a] Turnover frequencies determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as internal standard. [b] Isolated yield of the purified product. [c] Percent formation of the final product was determined by ^{1}H NMR integration vs internal standard due to low observed product formation. [d] 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate. [e] 1-Methyl-1,3-diazabicyclo[5.4.0]undec-7-enium trifluoromethanesulfonate. [f] 1-Butyl-3-methyl imidazolium trifluoromethanesulfonate. [g] 1-Ethyl-3-methylimidazolium trifluoromethanesulfonyl amide. [h] 1-Ethyl-3-methylimidazolium trifluoromethanesulfonyl amide.

Investigating the scope of $Ln(OTf)_3$-catalyzed HO/cyclization of primary/secondary aliphatic/aromatic alkenols (Table 2) reveals efficacy for the formation of five- and six-membered oxygen heterocycles with the Markovnikov-type selectivity also observed in Ru-,[4c] Pt-,[4d] Au-,[4b] and Brønsted acid[5c]-based catalytic systems. Cyclizations of diverse alkenyl alcohols proceed with near-quantitative conversions and reasonably large turnover frequencies at 1 mol % $Ln(OTf)_3$ loading in 1−24 h at 60−120 °C. The final product can be isolated either by simple diethyl ether extraction or by vacuum transfer, thus allowing efficient catalyst and ionic liquid recycle.

The reaction scope study was designed to probe a variety of structural effects on this catalytic transformation. The

(7) Hydroamination: (a) Hong, S.; Marks, T. J. *Acc. Chem. Res.* **2004**, *37*, 673–686. (b) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *J. Org. Chem.* **2004**, *69*, 1038–1052. (c) Hong, S.; Marks, T. J. *J. Am. Chem. Soc.* **2002**, *124*, 7886–7887. (d) Ryu, J.-S.; Marks, T. J.; McDonald, F. E. *Org. Lett.* **2001**, *3*, 3091–3094. (e) Arredondo, V. M.; McDonald, F. E.; Marks, T. J. *Organometallics* **1999**, *18*, 1949–1960. (f) Li, Y.; Marks, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 1757–1771. (g) Gagné, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 275–294.

(8) Hydrophosphination: (a) Kawaoka, A. M.; Douglass, M. R.; Marks, T. J. *Organometallics* **2003**, *22*, 4630–4632. (b) Douglass, M. R.; Ogasawara, M.; Hong, S.; Metz, M. V.; Marks, T. J. *Organometallics* **2002**, *21*, 283–292. (c) Douglass, M. R.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **2001**, *123*, 10221–10238.

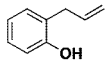
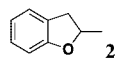
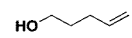
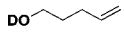
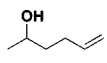
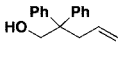
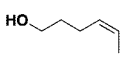
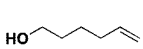
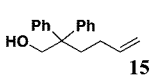
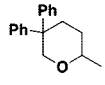
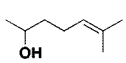
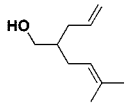
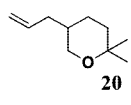
(9) (a) Li, C.-J.; Chen, L. *Chem. Soc. Rev.* **2006**, *35*, 68–82. (b) Li, C. *Chem. Rev.* **2005**, *105*, 3095–3165. (c) Kobayashi, S. *Chem. Rev.* **2002**, *102*, 2227–2302. (d) Kobayashi, S.; Manabe, K. *Acc. Chem. Res.* **2002**, *35*, 209–217. (e) *Topics in Organometallic Chemistry. Lanthanides: Chemistry and Use in Organic Synthesis*; Kobayashi, S., Ed.; Springer-Verlag: Berlin, 1999; Vol. 2, Chapter 2.

(10) (a) *Ionic Liquids: Industrial Applications to Green Chemistry*; ACS Symposium Series 818; Rogers, R. D., Seddon, K. R., Eds.; Oxford University Press: Oxford, 2002. (b) Parvulescu, V. I.; Hardacre, C. *Chem. Rev.* **2007**, *107*, 2615–2665. (c) Harper, J. B.; Kobrak, M. N. *Mini-Rev. Org. Chem.* **2006**, *3*, 253–269. (d) Cocalia, V. A.; Gutowski, K. E.; Rogers, R. D. *Coord. Chem. Rev.* **2006**, *250*, 755–764. (e) Dupont, J.; Suarez, P. A. Z. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2441–2452. (f) Welton, J. *Chem. Rev.* **1999**, *99*, 2071–2083.

(11) (a) Karshtedt, D.; Bell, A. T. T.; Tilley, T. D. *J. Am. Chem. Soc.* **2005**, *127*, 12640–12646. (b) Brunet, J. J.; Chu, C. N.; Diallo, O.; Mothes, E. *J. Mol. Catal. A* **2003**, *198*, 107–110.

(12) Reichardt, S. *Solvents and Solvent Effects in Organic Chemistry*; Wiley-VCH: Weinheim, 1990.

Table 2. Catalytic Alkenol Hydroalkoxylation/Cyclization Mediated by $Ln(OTf)_3$ Complexes (1 mol %) in $[C_2mim][OTf]$

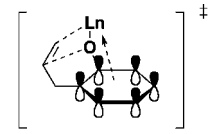
entry	Ln^{3+}	substrate	product	N_t h^{-1} (^oC, yield %)[a,b]
1.	La			0.82(120, 62)
2.	Sm			1.58(120, 80)
3.	Yb	1	2	6.37(120, 93)
4.	La			0.12(120, -)
5.	Sm			0.52(120, 53)
6.	Yb	3	4	4.78(120, 78)
7.	Yb	 5	 6	1.92(120, 49)[c]
8.	La			0.51(120, 40)
9.	Sm			1.14(120, 67)
10.	Yb	7	8	9.24(120, 89)
11.	La			0.57(120, 61)
12.	Sm			1.37(120, 82)
13.	Yb	9	10	46.97(120, 95)
14.	La			0.012(90, 2)[d]
15.	Sm			0.019(90, 3)[d]
16.	Yb	11	12	0.023(90, 8)[d]
17.	La			0.36(120, -)
18.	Sm			0.62(120, 73)
19.	Yb	13	14	1.89(120, 88)
20.	La			0.09(120, -)
21.	Sm			0.24(120, -)
22.	Yb	15	16	9.52(120, 90)
23.	La			4.88(90, 98)
24.	Sm			2.97(90, 89)
25.	Yb	17	18	0.52(90, 55)
26.	La			6.48(60, 98)
27.	Yb	19	20	3.25(60, 80)

[a] Turnover frequencies are determined by ^1H NMR integration vs internal standard. [b] Isolated yield of the purified product. [c] Percent formation of the final product was determined by ^1H NMR integration vs internal standard to avoid H/D exchange. [d] Percent formation of the final product was determined by ^1H NMR integration vs internal standard due to low observed product formation. [e] For more details see Supporting Information.

effects of Ln^{3+} ionic radius variation on the aliphatic/aromatic hydroxyalkene cyclization turnover frequencies clearly follow lanthanide contraction trends[13] (Table 2, entries 4−22), with the smallest and most Lewis acidic Ln^{3+} center being the most efficient. This pattern parallels that of organolathanide-catalyzed aminoalkyne hydroamination/cyclization but not that of aminoalkenes.[7] Interestingly, the ionic radius related N_t variations observed here are markedly smaller than the $\sim 10^3$-fold observed in organolanthanide-mediated amino alkene hydroamination/cyclization processes, presumably reflecting significant steric impediment/differences in the transition states.[7] The above observation argues for development in the present case of a transition state with more modest steric demands as discussed below.

The ring size dependence of $Ln(OTf)_3$/RTIL-catalyzed cyclization rates for the present primary hydroxyalkenes is 5 > 6, consistent with a classical, sterically controlled ring-forming transition state (Table 2, entry 2 vs 5, entry 6 vs 8). In the case of 5-membered ring formation, the **3** → **4** and **9** → **10** conversions (N_t = 4.78 h^{-1} and N_t = 46.97 h^{-1}, respectively) proceed somewhat more rapidly than analogous 6-membered molecules **13** → **14** and **15** → **16** (N_t = 1.89 h^{-1} and 9.52 h^{-1}, respectively) with an N_t increase of 3−10×. The same trend is observed in organolanthanide-mediated hydroamination, but with larger rate differences than observed here.[7h]

In the hydroalkoxylation/cyclization of primary hydroxy alkenes, there is a slight difference in cyclization rate between linear and aromatic hydroxyalkenes (Table 1, entries 3,6). The cyclization rate of the aryl-functionalized hydroxyalkene **1** (N_t = 6.37 h^{-1}) is slightly more rapid than that of the linear hydroxyalkene **3** (N_t = 4.78 h^{-1}). This suggests a transition state configuration in which the aryl-functionalized hydroxyalkene may have more accessible, preorganized structure involving interaction of the electrophilic lanthanide center with the electron-rich arene π system (**A**).[14]



A

For substrates bearing geminal diphenyl substituents on the carbon backbone, significant rate enhancements are attributed to angle compression effects (the "Thorpe-Ingold effect", Table 2, entries 9−13, 20−22).[7h,15] Thus, the **9** → **10** cyclization proceeds more rapidly than the analogous parent molecule **3** → **4** (N_t = 46.97 h^{-1} vs 4.78 h^{-1}, respectively) with N_t increased ∼10×. The cyclizations of alkenyl alcohols **13** and **15** to form 6-membered rings also exhibit Thorpe-Ingold effects (N_t = 1.89 h^{-1} vs 21.57 h^{-1}, respectively), but with diminished rates versus the 5-membered rings.

The catalytic sensitivity to olefin substituent steric encumbrance for conversions **17** → **18** and **19** → **20** (Table 2, entries 23−26) is consistent with the superiority of the larger ionic radius Ln^{3+} catalyst, as reflected in a 3-fold increase in N_t. This argues for a slightly sterically demanding transition state, reflecting subtle changes in the catalyst coordination environment.[7] Interestingly, the regiochemistry of the **17** → **18** and **19** → **20** cyclizations is different from what is expected in conventional lanthanide insertion/protonolysis processes (see more below);[7] in the **17** → **18** and **19** → **20** cyclizations, formation of 5-membered ring products is not observed.

Kinetic data aquired in the study of the **1** → **2** hydroalkoxylation/cyclization were acquired using the $Yb(OTf)_3$ catalyst. The kinetic data yield the empirical rate law $\nu \approx$

(13) Cotton, S. *Lanthanide and Actinide Chemistry*; Wiley: Chichester, England, 2006.

(14) For Ln^{3+}-arene complexes, see: (a) Cotton, A.; Schwotzer, W. *Organometallics* **1987**, *6*, 1275–1279. (b) Cotton, A.; Schwotzer, W. *J. Am. Chem. Soc.* **1986**, *108*, 4657–4568.

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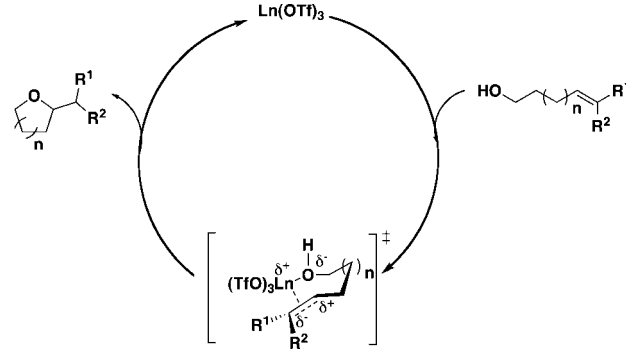
k[catalyst]^1[substrate]^1. This first-order dependence on substrate is different from the zero-order dependence generally observed in homoleptic lanthanide amido-mediated hydroamination/cyclization and hydroalkoxylation/cyclization processes.[6,7] The zero-order dependence in substrate observed in the aformentioned cases argues for turnover-limiting olefin insertion into Ln-N/Ln-O bond,[6,7] and agrees with thermodynamic considerations[17] and DFT level quantum chemical calculations.[18] The rate law observed here is most plausibly consistent with either turnover-limiting olefin intermolecular insertion or Ln^{3+}-hydroxyalkene complexation.

Kinetic isotope effect data (-OH versus -OD) were acquired for the cyclization **5** → **6** (Table 2, entries 6,7) as assayed by ^{1}H NMR spectroscopy, and yield $k_H/k_D = 2.48$ (9), which is suggestive of a primary effect. ^{2}H NMR spectra of the cyclized product **6** shows it to be monodeuterated at the 2-methyl position. Proton transfer processes typicaly exhibit KIEs of 2.5−7.0.[16] Although NH/ND labeling studies for analogous organolanthanide-catalyzed alkene hydroamination processes also exhibit a primary KIE with same deuterium regioselectivity,[7g] a number of pathways yielding the same regioselectivity can be envisioned for H^+ transfer in the present case, for example, olefin insertion into Ln-O bond followed by inter/intramolecular proton transfer, as for $Ln(OR)_3$-catalyzed processes,[6] or Ln^{3+}-coordinated oxygen nuceophilic attack with pre/post inter/intramolecular proton transfer, as proposed for possibly analogous $Al(OTf)_3$-catalyzed processes.[5c]

Recently our group reported that homoleptic lanthanide amides, $La[N(SiMe_3)_2]_3$, are effective precatalysts for the intramolecular HO/cyclization of alkyne- and allene-bearing alcohols.[6] Homoleptic lanthanide amides, Ln- $[N(SiMe_3)_2]_3$, are found to undergo instantaneous protonolysis by C−C unsaturated alcohols at 25 °C to form the corresponding alkoxides and free $HN(SiMe_3)_2$.[6] Turnover-limiting alkyne or allene insertion into the Ln−O bond is followed by rapid Ln−C protonolysis.[6] Although bond-energetic considerations[18] for alkene-, alkyne-, and allene-lanthanide alkoxide catalytic cycles predict net exothermic processes for all of these unsaturated alcohols, the very large Ln–O bond enthalpy[17] renders the insertive step rather endothermic for alkenyl alcohols, and thus intramolecular hydroxy alkene HO/cyclization has not yet been observed with these catalysts.[6]

For the present $Ln(OTf)_3$/RTIL catalysts, the cyclization rate dependence on ring size, Ln^{3+} ionic radius, and Thorpe-Ingold substituents are consistent with a classical olefin insertion process.[6,7] However, the regiochemistry of **17** → **18** and **19** → **20** cyclization products deviates from that expectation and is suggestive of a more cationic transition state. It is conceivable that varying charge distribution along the reaction coordinate can yield either a conventional insertive transition state,[6,7] or one that approaches a carbocationic one depending on the substrate[5c] (e.g., Scheme 1). Preliminary proton trapping experiments rule out the proton-catalyzed catalytic pathway, however they do suggest an involvement of a proton transfer.[19]

Scheme 1. Possible $Ln(OTf)_3$ -Mediated Intramolecular HO/Cyclization Pathway



In summary, we have demonstrated an efficient $Ln(OTf)_3$-mediated catalytic hydroalkoxylation/ cyclization of alkenols in imidazolium-based ionic liquids. This atom-economical route is remarkably clean and benefits from catalyst and reaction medium recyclability. Current efforts are directed toward further exploring reaction scope and mechanism.

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Supporting Information Available: Experimental details, kinetic and mechanistic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) The rate of $Ln(OTf)_3$-mediated cyclization of 2-allylphenol in the presence of 0.5 equiv of 2,6-di(*tert*-butyl)pyridine is significantly retarded. However, ^{19}F NMR analysis of the vacuum-transferred volatiles from the $Ln(OTf)_3$- and TfOH-catalyzed preparative scale reactions reveal the presence of significant quantities of TfOH only in the latter reaction (see Supporting Information).