HAL
open science

Niobium-Catalyzed Intramolecular Addition of O–H and N–H Bonds to Alkenes: A Tool for Hydrofunctionalization

Laura Ferrand, Yue Tang, Corinne Aubert, Louis Fensterbank, Virginie Mouriès-Mansuy, Marc Petit, Muriel Amatore

To cite this version:

Laura Ferrand, Yue Tang, Corinne Aubert, Louis Fensterbank, Virginie Mouriès-Mansuy, et al.. Niobium-Catalyzed Intramolecular Addition of O–H and N–H Bonds to Alkenes: A Tool for Hydrofunctionalization. Organic Letters, 2017, 19 (8), pp.2062-2065. 10.1021/acs.orglett.7b00657 . hal-01520376

HAL Id: hal-01520376

https://hal.sorbonne-universite.fr/hal-01520376

Submitted on 10 May 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

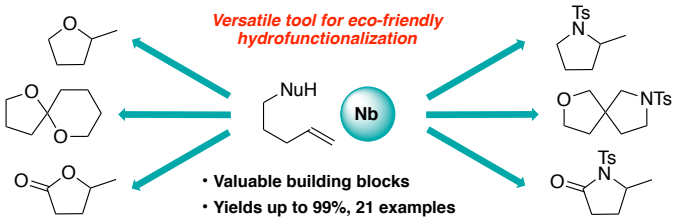
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Niobium-Catalyzed Intramolecular Addition of O–H and N–H Bonds to Alkenes: a Tool for Hydrofunctionalization

Laura Ferrand, Yue Tang, Corinne Aubert, Louis Fensterbank, Virginie Mouriès-Mansuy, Marc Petit* and Muriel Amatore*

Sorbonne Université, UPMC Univ Paris 06, Institut Parisien de Chimie Moléculaire, UMR CNRS 8232, Case 229, 4 Place Jussieu, 75252 Paris Cedex 05, France

Supporting Information Placeholder

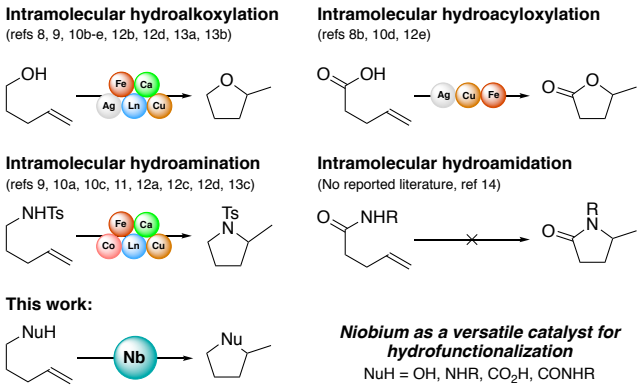


ABSTRACT: A convenient, versatile and easy to handle intramolecular hydrofunctionalization of alkenes (C–O and C–N bonds formation) is reported using a novel niobium-based catalytic system. This atom economic and eco-friendly methodology provides an additional synthetic tool for the straightforward formation of valuable building blocks enabling molecular complexity. Various pyran, furan, pyrrolidine, piperidine, lactone, lactam derivatives as well as spirocyclic compounds are produced in high yields and selectivities.

Development of environmentally friendly and economical processes is absolutely critical for the construction of valuable synthetic targets. Over the last decades, catalysis has proven to be an effective strategy to rapidly access molecular complexity with consideration of step/atom economy, energy and resources saving or waste minimization. While associated with limited availabilities, expensive costs and identified toxicity, noble metals catalysis has been nevertheless behind most of the commonly used methodologies. With this in mind, the exploitation of inexpensive, non-toxic and abundant low-valent transition metals in catalysis is an ongoing field of research. Inspired by Obora's work,[1] we recently identified $NbCl_3$•DME as a competent catalyst for the unprecedented [2+2+2] cycloaddition of fully substituted benzosilacyclobutenes.[2] Despite its valuable benefits in terms of sustainability, toxicity and cost, niobium chemistry is still in its infancy and most of the reported literature is dedicated to the formation of coordination complexes and materials mainly for industrial applications.[3] Because of their unusual reactivity compared to other transition metal halides, niobium complexes such as $NbCl_5$ or $NbCl_3$•DME have received a particular attention either as Lewis acid or as precursor of reactive Nb(III)-alkyne or -imine complexes, and some niobium-mediated processes have been developed.[2, 4]

With a goal of broadening the toolbox for synthetic chemists, we set out to more deeply explore the reactivity of $NbCl_5$ as catalyst for the intramolecular hydrofunctionalization of unactivated alkenes (C–O and C–N bonds formation, Scheme 1).[5] Such completely atom economic transformations promoted either by various and often precious transition metals (Au, Pt, Ru, Re, Zr, Ti, Al, Bi, Mg, …)[6] or Brønsted acids[7] have been deeply studied showing contrasting results. Unfortunately, despite their great potential, only few transition metal based catalytic systems have shown suitable versatility regarding substrates and the direct use of strong organic acids often demonstrates inferior catalytic performance due to their inherent instability and difficulty to handle. Indeed, to the best of our knowledge, processes matching

Scheme 1. Eco-Friendly Hydrofunctionalization of Alkenes

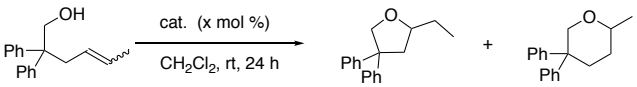


broad scope, low cost and low environmental impact are limited to the use of Ag,[8] Ln,[9] Cu,[10] Co,[10a, 11] Fe[10a, 12] and Ca[13] catalysis (Scheme 1). However, none of these metals exhibits

generality in each of the following cylizations: unsaturated alcohols, amines, carboxylic acids and amides[14] and the success of the reactions often requires high catalyst loadings (up to 25 mol %), excess of additives (silver salts up to 30 mol %, bases, disiloxanes, oxidants, ammonium or pyridinium salts), ionic liquids, zeolithes and sophisticated ligands. In this context, niobium catalysis emerges as a novel eco-friendly alternative for the construction of molecular complexity. Indeed this metal offers low toxicity, is affordable and relatively abundant in earth's crust.[3, 15]

We first selected unsaturated alcohol **1a** as a hydroalkoxylation model substrate. Comparison of the cyclization efficiency using catalytic amounts of niobium(III) or (V) catalysts clearly demonstrated the supremacy of the cationic $NbCl_5/AgNTf_2$ system at room temperature (Table 1, entries 1-7, see Supporting Information, parts 2 and 3 for more detailed optimization studies).[16] After screening various types of solvent, chlorinated solvents gave the best efficiency with dichloroethane (DCE) as best candidate (Table 1, entries 6 and 8). Further tuning of the stoichiometry of $NbCl_5/AgNTf_2$ catalytic system was realized and it was found that using a (1:2) ratio delivered a mixture of cyclized compounds **2a** and **3a** in 75% yield with high selectivity (Table 1, entries 8 and 9). Increasing the reaction temperature to 80 °C led to a full conversion of **1a** and in that case catalyst loadings could be decreased with only a slight loss of yield (Table 1, entries 10 and 11). Finally, **1a** underwent smooth hydroalkoxylation at 50 °C affording a mixture of **2a** and **3a** after 6 h in good yield (70%) and selectivity (94 / 6) (Table 1, entry 12). In contrast, conducting the reaction in the absence of $NbCl_5$ or $AgNTf_2$ was not productive, emphasizing the

Table 1. Catalyst Screening and Optimization of the Reaction Conditions



1a (*E*) / (*Z*) (85 / 15) **2a** **3a**

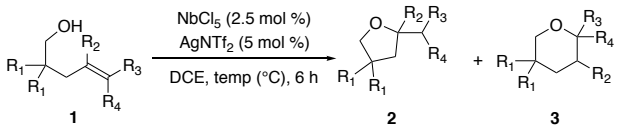
entry	cat. (mol %)	conversion (**2a** + **3a** / **1a**)[a]	yield (%)	(**2a** / **3a**)[a]
1	$NbCl_3$•DME (10)	(0 / 100)	nr[b]	–
2	$NbCl_5$ (10)	(0 / 100)	nr	–
3	$Nb(OEt)_5$ (10)	(0 / 100)	nr	–
4	$NbCl_3$•DME / $AgClO_4$ (10)	(13 / 87)	10	(91 / 9)
5	$NbCl_5$ / $AgClO_4$ (10)	(58 / 42)	41	(88 / 12)
6	$NbCl_5$ / $AgNTf_2$ (10)	(54 / 46)	51	(95 / 5)
7[c]	$NbCl_5$ / $AgSbF_6$ (10)	(21 / 79)	12	(100 / 0)
8[d]	$NbCl_5$ / $AgNTf_2$ (10)	(71 / 29)	62	(96 / 4)
9[d]	$NbCl_5$ (10) / $AgNTf_2$ (20)	(87 / 13)	75	(94 / 6)
10[d, e]	$NbCl_5$ (10) / $AgNTf_2$ (20)	(100 / 0)	69	(90 / 10)
11[d, f]	$NbCl_5$ (2.5) / $AgNTf_2$ (5)	(92 / 8)	63	(93 / 7)
12[d, g]	$NbCl_5$ (2.5) / $AgNTf_2$ (5)	(90 / 10)	70	(94 / 6)
13[d, g]	$NbCl_5$ (2.5)	(0 / 100)	nr	–
14[d, g]	$AgNTf_2$ (5)	(0 / 100)	nr	–
15[d, h]	$NbCl_5$ (1) / $AgNTf_2$ (2)	(90 / 10)	74	(94 / 6)

[a] The conversion (**2a + 3a** / **1a**) and ratio (**2a** / **3a**) were determined by ^{1}H NMR analysis. [b] No reaction was observed. [c] Due to the modest conversion observed using $AgSbF_6$, $AgNTf_2$ was retained as additive of choice. However, additional studies were realized to further evaluate $AgSbF_6$ efficiency on this reaction as a cheaper alternative (see Supporting Information, part 4). [d] The reaction was conducted in dichloroethane (DCE). [e] Reaction was conducted at 80 °C for 10 min. [f] The reaction was conducted at 80 °C for 30 min. [g] Reaction was conducted in DCE for 6 hours at 50° C. [h] Reaction was performed on 1g-scale in DCE for 24 hours at 50° C.

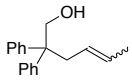
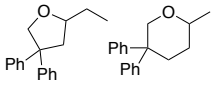
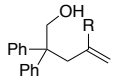
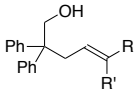
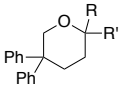
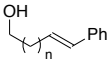
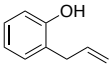
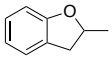
benefic effect of the catalytic combination $NbCl_5/AgNTf_2$ (Table 1, entries 13 and 14). Interestingly, this one-step process was readily gram-scalable and the catalyst loading could be reduced to 1 mol % of niobium at the cost of a prolonged reaction time (Table 1, entry 15).

After optimization of our catalytic system, we investigated its performance in terms of substrate scope. The direct access to substituted tetrahydrofurans and tetrahydropyrans was first envisaged (Table 2). The cyclization of unsaturated alcohols **1a-h** proceeded smoothly at 50 or 80 °C in 6 hours (Table 2, entries 1-8). The features of the process appeared closely related to the substitution pattern of the double bond and a highly regioselective cyclization generally occurred at the most substituted carbon. To our great delight, quantitative yields of tetrahydrofurans **2b** and **2c** were obtained (Table 2, entries 2 and 3). The substitution on the tether had only an influence on the reaction rate and unsubstituted alcohols **1f** and **1g** were cyclized with satisfactory yields up to 97% at 80 °C (Table 2, entries 6 and 7). Finally, the terminal 2- allylphenol **1h** could afford the corresponding cyclized compound **2h** with 66% yield and a complete regioselectivity (Table 2, entry 8).

Table 2. Scope of Unsaturated Alcohols



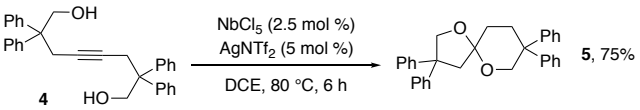
1 **2** **3**

entry	substrate **1**	products **2** / **3**, yield (%)
1	 **1a**	 **2a** / **3a**, 70[a, b]
2	 **1b**, R = Me	**2b**, > 99[b]
3	**1c**, R = H	**2c**, > 99[b]
4	 **1d**, R = R' = Me	 **3d**, 70[b]
5	**1e**, R = Ph, R' = H	**3e**, 74[b]
6	 **1f**, n = 2	**3f**, 68[c]
7	**1g**, n = 1	**2g**, 97[c]
8	 **1h**	 **2h**, 66[c]

[a] The ratio **2a** / **3a** (96 / 4) was determined by ^{1}H NMR analysis. [b] Reaction was carried out at 50 °C. [c] Reaction was carried out at 80 °C.

The reactivity of alkynes was also tested in this niobium-catalyzed hydroalkoxylation reaction. Interestingly, spirocyclization of diol **4** proceeded efficiently and yielded the valuable spiro-(5,6) compound **5** as the sole product (Scheme 2).

Scheme 2. Niobium-Catalyzed Spiro-Compound Synthesis

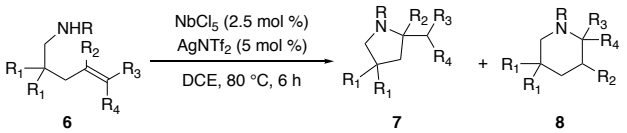


4 **5**, 75%

To explore the full scope of this reaction, we investigated the ability of unsaturated amines to undergo cyclization (Table 3). Unfortunately, no hydroamination occurred with unprotected primary amine **6a** presumably due to reaction inhibition through strong but non-productive coordination to niobium[17]

preventing any activation of the amine moiety or through non-desired trapping of a proton source that could be *in situ* delivered (Table 3, entry 1, see SI, part 6 for preliminary mechanistic investigations). Identically, most of *N*-protecting groups proved unsuccessful (**6b-d**, Bn, Bz, Boc, Table 3, entry 2). Gratifyingly, this niobium catalytic system could catalyze the desired cyclization with nucleophiles such as sulfonamides **6e-i** (Table 3, entries 3-7). While the corresponding pyrrolidines **7e-g** (Table 3, entries 3-5) and piperidine **8i** (Table 3, entry 7) could be isolated with high selectivities and excellent yields up to 99%, the reaction of sulfonamide **6h** featuring a prenyl moiety gave product **8h** in low yield with isolation of an undesired compound **8h'** as major product arising from a hydroarylation reaction (Table 3, entry 6).

Table 3. Scope of Unsaturated Amines

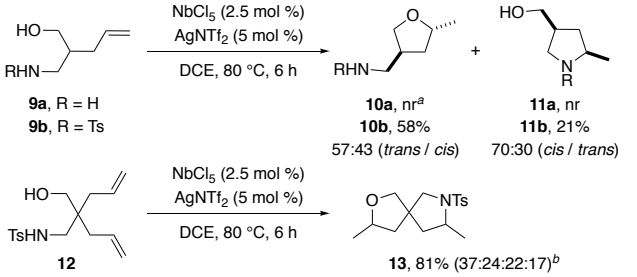


entry	substrate **6**	products **7** / **8**, yield (%)
1	**6a**, R = H	**7a**, nr[a]
2	**6b-d**, R = Bn, Bz, Boc	**7b-d**, nr[a]
3	**6e**, R = Ts	**7e**, 68
4	**6f**, R = Me	**7f**, 99
5	**6g**, R = H	**7g**, 99
6	**6h**, R = Ph, R' = R'' = Me	**8h**, 24[b] / **8h'**, 66[c]
7	**6i**, R = Me, R' = Ph, R'' = H	**8i**, 91

[a] No reaction was observed. [b] Full conversion was observed. [c] Product **8h'** arising from undesired hydroarylation.

We next examined the outcome of the reaction of unsaturated amino-alcohols under our catalytic conditions (Scheme 3). Once again, reaction was totally suppressed when using non-protected amino-alcohol **9a**. As seen previously, hydroxy-sulfonamide **9b** was the best candidate and afforded heterocyclic compounds **10b** and **11b** in good yields with hydroalkoxylation as favored pathway (see SI, part 5 for additional studies on reaction chemioselectivity). Finally, the synthetic potential of our method was highlighted by the possibility to readily form spirocyclic compound **13** in 81% yield as valuable scaffold.

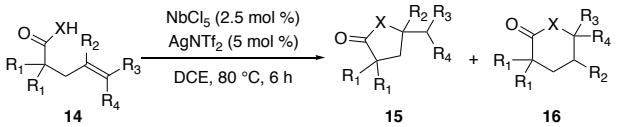
Scheme 3. Hydroalkoxylation *versus* Hydroamination



[a] No reaction was observed. [b] Compound **13** was obtained as an inseparable mixture of four diastereoisomers and ratios could not be attributed.

Encouraged by these results we further explored the versatility of our method by conducting hydrocarboxylation and hydroamidation reactions (Table 4). The optimized conditions could be applied to a variety of unsaturated carboxylic acids and amides yielding the corresponding lactones (Table 4, entries 1-3) and lactams (Table 4, entries 4 and 5) thus illustrating the synthetic potential of our methodology. Surprisingly and in marked contrast to previous results, the cyclization of the carboxylic acid homolog of **1a** led to low selectivity (Table 4, entry 1). However, high regioselectivities and satisfactory yields were achieved by modifying the substitution pattern of the double bond (Table 4, entries 2 and 3) or switching to amide-type analogs (Table 4, entries 4 and 5).

Table 4. Scope of Unsaturated Carboxylic Acids and Amides



entry	substrate **14**	products **15** / **16**, yield (%)
1	**14a**	**15a**, 38 / **16a**, 29
2	**14b**, R = Me	**15b**, 94
3	**14c**, R = H	**15c**, 94
4	**14d**, R = Me	**15d**, 56
5	**14e**, R =H	**15e**, 84

In summary, we have established an atom economic method for the intramolecular hydrofunctionalization of alkenes with high yields and selectivities. Being an efficient strategy for the straightforward synthesis of a large panel of heterocyclic compounds as valuable scaffolds for natural products and pharmaceuticals, this niobium-catalyzed reaction provides a nice and attractive contribution to the synthetic toolbox. While our given methodology, centered on a relatively inexpensive niobium-based catalyst, is convenient, versatile and easy to use, the exact nature of the niobium active species and the reaction mechanism are still to determine and are subject to further investigations (see SI, part 6 for preliminary mechanistic investigations). As initial results, control experiments using $PhSiMe_3$ as an efficient non-coordinative proton scavenger have suggested a mechanism involving a direct interaction between the metallic species and the substrate in contrast to a hidden Brønsted acid catalytic pathway. Gaining better insight into the reaction mechanism is necessary to explore the full potential of this method and to develop some more attractive asymmetric versions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures and spectral data for all products are provided (PDF)

AUTHOR INFORMATION

Corresponding Author

* E-mail: muriel.amatore@upmc.fr
* E-mail: marc.petit@upmc.fr

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by CNRS, MRES and UPMC, which we gratefully acknowledge.
We thank L. Vernhes (ENSCM) and C. Chalhoub (UPMC) for late-stage experimental contribution and O. Khaled (IPCM, UPMC) for HRMS analysis.

REFERENCES

(1) For seminal works: (a) Du Toit, C. J.; Du Plessis, J. A. K.; Lachmann, G. *J. Mol. Catal*. **1989**, *53*, 67–78. (b) Kakeya, M. ; Fujihara, T. ; Kasaya, T. ; Nagasawa, A. *Organometallics* **2006**, *25*, 4131–4137. For relevant references on Obora's work: (c) Satoh, Y.; Obora, Y. *Eur. J. Org. Chem*. **2015**, 5041–5054. (d) Yasuda, K.; Obora, Y. J. *Organomet. Chem*. **2015**, *775*, 33–38.

(2) Simon, C.; Amatore, M.; Aubert, C.; Petit, M. *Org. Lett*. **2015**, *17*, 844–847.

(3) Selected references: (a) Cardin, D. J. *Niobium.* In *Dictionary of Organometallic Compounds*, 2nd ed.; Chapman and Hall, 1995, vol. 3. (b) Nowak, I.; Ziolek, M. *Chem. Rev*. **1999**, *99*, 3603–3624. (c) Eckert, J. *Niobium and Niobium Compounds* In *Ullmann's Encyclopedia of Industrial Chemistry*, **2012**. (d) Coles, M. P. *Annu. Rep. Prog. Chem., Sect. A* **2007**, *103*, 147–158. (e) Schlewtiz, J. E. *Niobium and Niobium Compounds* In *Kirk-Othmer Encyclopedia of Chemical Technology* **2009**. (f) Otero, A; Antinolo, A.; Lara, A. *Niobium organometallics* In *Comprehensive Organometallic Chemistry III*, Eds: Mingos, D.; Michael, P.; Crabtree, R. H. **2007**, *5*, 61–100.

(4) Selected references: (a) Chandrasekhar, S.; Ramachandar, T.; Shyamsunder, T. *Indian J. Chem. B*. **2004**, *43B*, 813–838. (b) Andrade, C. K. Z. *Curr. Org. Synth*. **2004**, *1*, 333–353. (c) Lacerda, Jr. V.; Araujo dos Santos, D.; da Silva-Filho, L. C.; Greco, S. J.; Bezerra dos Santos, R. *Aldrichim. Acta* **2012**, *45*, 19–27. (d) Marchetti, F.; Pampaloni, G. *Chem. Commun*. **2012**, *48*, 635–653. (e) Arpini, B. H.; Bartolomeu, A. A.; Andrade, C. K. Z.; da Silva-Filho, L. C.; Lacerda, V. *Curr. Org. Synth*. **2015**, *12*, 570–583. (f) Arai, S.; Sudo, Y.; Nishida, A. *Tetrahedron* **2005**, *61*, 4639–4642. (g) de Souza Siqueira, M.; da Silva-Filho, L. C. *Tetrahedron Lett*. **2016**, *57*, 5050–5052.

(5) A previous work has been reported for the synthesis of β-lapachone using stoichiometric $NbCl_5$: Bian, J.; Deng, B.; Zhang, X.; Hu, T.; Wang, N.; Wang, W.; Pei, H.; Xu, Y.; Chu, H.; Li, X.; Sun, H.; You, Q. *Tetrahedron Lett*. **2014**, *55*, 1475–1478.

(6) Selected references: (a) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev*. **2004**, *104*, 3079–3159. (b) Barreiro, E. M.; Adrio, L. A.; Hii, K. K.; Brazier, J. B. *Eur. J. Org. Chem*. **2013**, 1027–1039. (c) Bernoud, E.; Lepori, C.; Mellah, M.; Schulz, E.; Hannedouche, J. *Catal. Sci. Technol*. **2015**, *5*, 2017–2037. (d) *Hydrofunctionalizations* In *Topics in Organometallic Chemistry*, Springer-Verlag Berlin Heidelberg, Eds: Ananikov, V. P.; Tanaka, M. **2013**. (e) Coman, S. M.; Parvulescu, V. I. *Org. Process Res. Dev*. **2015**, *19*, 1327–1355. (f) Patil, N. T.; Kavthe, R. D.; Shinde, V. S. *Tetrahedron* **2012**, *68*, 8079–8146. (g) Reznichenko, A. L.; Hultzsch, K. C. *Top. Organomet. Chem*. **2013**, *43*, 53–114. (h) Rodriguez-Ruiz, V.; Carlino, R.; Bezzenine-Lafollée, S.; Gil, R.; Prim, D.; Schulz, E.; Hannedouche, J. *Dalton Trans*. **2015**, *44*, 12029–12059. (i) Zeng, X. *Chem. Rev*. **2013**, *113*, 6864–6900. (j) Chong, E.; Garcia, P.; Schafer, L. L. *Synthesis* **2014**, 2884–2896. (k) Ondet, P.; Lemière, G.; Duñach, E. *Eur. J. Org. Chem*. **2017**, 761–780. (l) Antoniotti, S.; Poulain-Martini, S.; Duñach, E. *Synlett* **2010**, 2973–2988. (m) Ackermann, L.; Sandmann, R.; Kaspar, L. T. *Org. Lett*. **2009**, *11*, 2031–2034. (n) Ackermann, L.; Kaspar, L. T.; Gschrei, C. J. *Org. Lett.* **2004**, *6*, 2515–2518. (o) Ackermann, L. *Organometallics* **2003**, *22*, 4367–4368. (p) Anthunes, M. A.; Augusta, M. R. F.; Alves, L. G.; Schafer, L. L.; Martins, A. M. *J. Organomet. Chem*. **2010**, *696*, 2–6. (q) Watson, D. A.; Chiu, M.; Bergman, R. G. *Organometallics* **2006**, *25*, 4731–4733. (r) Gribkov, D. V.; Hultzsch, K. C. *Angew. Chem. Int. Ed*. **2004**, *43*, 5542–5546.

(7) Selected references: (a) Yamamoto, H. *Top. Organomet. Chem*. **2013**, *43*, 315–334. (b) Akiyama, T. *Chem. Rev*. **2007**, *107*, 5744–5758. (c) Yamamoto, H.; Boxer, M. B. *Chimia* **2007**, *61*, 279–281. (d) Cheon, C. H.; Yamamoto, H. *Chem. Commun*. **2011**, *47*, 3043–3056. (e) Coulombel, L.; Duñach, E. *Green Chem*. **2004**, *6*, 499–501. (f) Linares-Palomino, P. J.; Salido, S.; Altarejos, J.; Sánchez, A. *Tetrahedron Lett*. **2003**, *44*, 6651–6655. (g) Jeong, Y.; Kim, D. -Y.; Choi, Y.; Ryu, J. -S. *Org. Biomol. Chem*. **2011**, *9*, 374–378.

(8) Selected references: (a) Dang, T. T.; Boeck, F.; Hintermann, L. *J. Org. Chem*. **2011**, *76*, 9353–9361. (b) Yang, C. –G.; Reich, N. W.; Shi, Z.; He, C. *Org. Lett*. **2005**, *7*, 4553–4556. (c) Borghèse, S.; Drouhin, P.; Bénéteau, V.; Louis, B.; Pale, P. *Green Chem*. **2013**, *15*, 1496–1500.

(9) Selected references: (a) Dzudza, A.; Marks, T. J. *Chem. Eur. J*. **2010**, *16*, 3403–3422. (b) Dzudza, A.; Marks, T. J. *Org. Lett*. **2009**, *11*, 1523–1526. (c) Weiss, C. J.; Marks, T. J. *Dalton Trans*. **2010**, *39*, 6576–6588

(10) Selected references: (a) Lepori, C.; Hannedouche, J. *Synthesis* **2017**, *49*, 1158–1167. (b) Murayama, H.; Nagao, K.; Ohmiya, H.; Sawamura, M. *Org. Lett*. **2015**, *17*, 2039–2041. (c) Miller, Y.; Miao, L.; Hosseini, A. S.; Chemler, S. R. *J. Am. Chem. Soc*. **2012**, *134*, 12149–12156. (d) Ohmiya, H.; Yoshida, M.; Sawamura, M. *Synlett* **2010**, 2136–2140. (e) Adrio, L. A.; Shuyi Queck, L.; Taylor, J. G.; Hii, K. K. *Tetrahedron* **2009**, *65*, 10334–10338.

(11) Selected references: (a) Shigehisa, H.; Hayashi, M.; Ohkawa, H.; Suzuki, T.; Okayasu, H.; Mukai, M.; Yamazaki, A.; Kawai, R.; Kikuchi, H.; Satoh, Y.; Fukuyama, A.; Hiroya, K. *J. Am. Chem. Soc*. **2016**, *138*, 10597–10604. (b) Shigehisa, H.; Koseki, N.; Shimizu, N.; Fujisawa, M.; Niitsu, M.; Hiroya, K. *J. Am. Chem. Soc*. **2014**, *136*, 13534–13537.

(12) Selected references: (a) Komeyama, K.; Morimoto, T.; Takaki, K. *Angew. Chem. Int. Ed*. **2006**, *45*, 2938–2941. (b) Komeyama, K.; Morimoto, T.; Nakayama, Y.; Takaki, K. *Tetrahedron Lett*. **2007**, *48*, 3259–3261. (c) Pérez, S. J.; Purino, M. A.; Cruz, D. A.; López-Soria, J. M.; Carballo, R. M.; Ramírez, M. A.; Fernández, I.; Martín, V. S.; Padrón, J. I. *Chem. Eur. J*. **2016**, *22*, 15529–15535. (d) Greenhalgh, M. D.; Jones, A. S. Thomas, S. P. *ChemCatChem* **2015**, *7*, 190–222. (e) Komeyama, K.; Mieno, Y.; Yukawa, S.; Morimoto, T.; Takaki, K. *Chem. Lett*. **2007**, *36*, 752–753.

(13) Selected references: (a) Diba, A. K.; Bégouin, J. -M.; Niggemann, M. *Tetrahedron Lett*. **2012**, *53*, 6629–6632. (b) Bégouin, J. -M.; Niggemann, M. *Chem. Eur. J*. **2013**, *19*, 8030–8041. (c) Crimmin, M. R.; Casely, I. J.; Hill, M. S. *J. Am. Chem. Soc*. **2005**, *127*, 2042–2043.

(14) To the best of our knowledge, only precious metals such as Ir, Rh, Ru, Pd, Au and Pt are able to catalyze the intramolecular cyclization of unsaturated amides (a) Miller, D. C. ; Choi, G. J. : Orbe, H. S. ; Knowles, R. *J. Am. Chem. Soc*. **2015**, *137*, 13492–13495. (b) Zhu, L.; Xiong, P.; Mao, Z. -Y. ; Wang, Y. -H. ; Yan, X. ; Lu, X. ; Xu, H. -C. *Angew. Chem. Int. Ed.* **2016**, *55*, 2226–2229. (c) Huang, L.; Arndt, M.; Gooßen, K.; Heydt, H.; Gooßen, L. J. *Chem. Rev*. **2015**, *115*, 2596–2697.

(15) Cost for 100 g of > 99 % purity metal powder calculated from Strem Chemicals: Au (12150 €), Ag (320 €) and Nb (104 €). For crustal abundance and prices see the following websites as selected references: (a) http://www.rsc.org/periodic-table/element/41/niobium. (b) https://www.americanelements.com/nb.html. (c) http://www.metal.com/metals/productinfo/201102250606.

(16) The $NbCl_5/AgClO_4$ cationic system was first tested at room temperature with satisfactory results as reported by Nishida and coworkers (see ref 4f). A large screening of silver salts (AgOTs, $AgBF_4$, AgOTf, $AgPF_6$, Ag_2O, Ag_2CO_3, $AgNO_3$) or sodium salts ($NaClO_4$, $NaBPh_4$) was realized with no conversion of **1a** after 24 h at room temperature.

(17) Bondi, R.; Marchetti, F.; Pampaloni, G.; Zacchini, S. *Polyhedron*, **2015**, *100*, 192–198.