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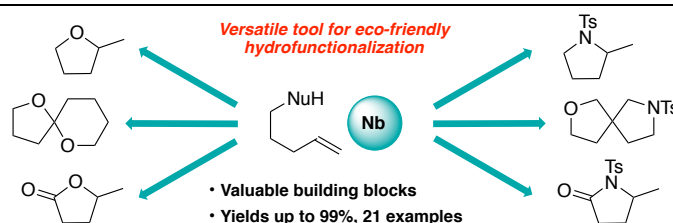
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Niobium-Catalyzed Intramolecular Addition of O–H and N–H Bonds to Alkenes: a Tool for Hydrofunctionalization

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Supporting Information Placeholder



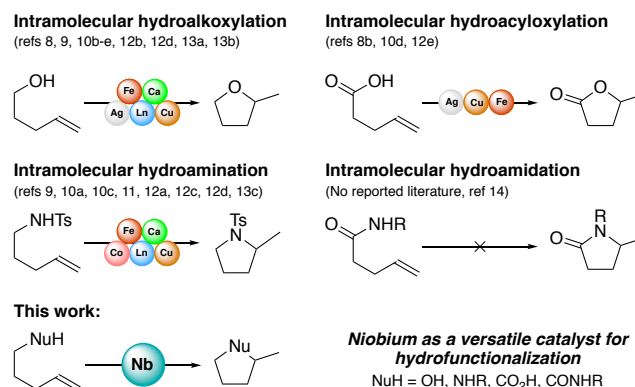
ABSTRACT: A convenient, versatile and easy to handle intramolecular hydrofunctionalization of alkenes (C–O and C–N bonds formation) is reported using a novel niobium-based catalytic system. This atom economic and eco-friendly methodology provides an additional synthetic tool for the straightforward formation 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 $\text{NbCl}_5 \cdot \text{DME}$ 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 $\text{NbCl}_3 \cdot \text{DME}$ 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

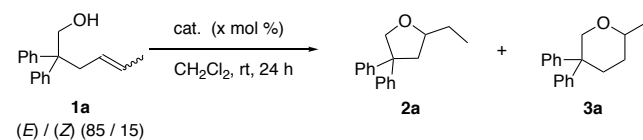


broad scope, low cost and low environmental impact are limited to the use of Ag,⁸ Ln,⁹ Cu,¹⁰ Co,^{10a, 11} Fe^{10a, 12} and Ca¹³ catalysis (Scheme 1). However, none of these metals exhibits

generality in each of the following cyclizations: unsaturated alcohols, amines, carboxylic acids and amides¹⁴ 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, zeolites 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 NbCl₅/AgNTf₂ 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 NbCl₅/AgNTf₂ 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 NbCl₅ or AgNTf₂ was not productive, emphasizing the

Table 1. Catalyst Screening and Optimization of the Reaction Conditions



entry	cat. (mol %)	conversion (2a + 3a / 1a) ^a	yield (%)	(2a / 3a) ^a
1	NbCl ₅ •DME (10)	(0 / 100)	nr ^b	–
2	NbCl ₅ (10)	(0 / 100)	nr	–
3	Nb(OEt) ₅ (10)	(0 / 100)	nr	–
4	NbCl ₅ •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 ¹H NMR analysis. ^b No reaction was observed. ^c Due to the modest conversion observed using AgSbF₆, AgNTf₂ was retained as additive of choice. However, additional studies were realized to further evaluate AgSbF₆ 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 NbCl₅/AgNTf₂ (Table 1, entries 13 and 14). Interestingly, this one-step pro-

cess 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).

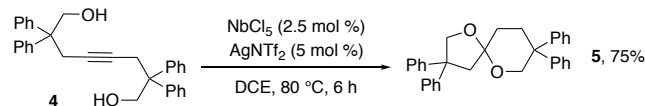
Table 2. Scope of Unsaturated Alcohols

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 ¹H 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



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 niobium¹⁷

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).

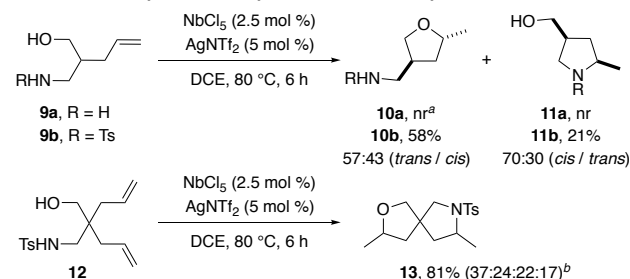
Table 3. Scope of Unsaturated Amines

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 chemoselectivity). 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 PhSiMe₃ 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)

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Notes

The authors declare no competing financial interest.

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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.; Ziolk, 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) Schlewitz, 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.; Hultsch, 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.; Lemièrre, 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.; Hultsch, 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.; Bénèteau, 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 $\text{NbCl}_5/\text{AgClO}_4$ 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.

