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PII: S0040-4020(17)30086-8

DOI: 10.1016/j.tet.2017.01.051

Reference: TET 28421

To appear in: *Tetrahedron*

Received Date: 13 November 2016

Revised Date: 16 January 2017

Accepted Date: 23 January 2017

Please cite this article as: Zhu X, Li G, Xu F, Zhang Y, Xue M, Shen Q, Investigation and mechanistic study into intramolecular hydroalkoxylation of unactivated alkenols catalyzed by cationic lanthanide complexes, *Tetrahedron* (2017), doi: 10.1016/j.tet.2017.01.051.

## Graphical Abstract

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**Investigation and Mechanistic Study into IntramolecularHydroalkoxylation of Unactivated Alkenols Catalyzed by Cationic Lanthanide Complexes**

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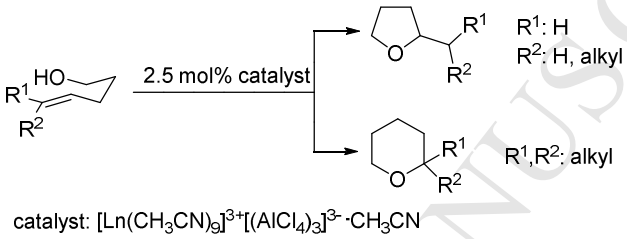
Xuehua Zhu,[†,‡] Guoyao Li,[†] Fan Xu,*[,†] Yong Zhang,[†] Mingqiang Xue,[†] Qi Shen*[,†]

*†College of Chemistry, Chemical Engineering and Materials Science Soochow University, Suzhou 215123, People's Republic of China*

*‡School of chemical biology and materials engineering Suzhou University of Science and Technology, Suzhou 215009, People's Republic of China*



# Investigation and Mechanistic Study into Intramolecular Hydroalkoxylation of Unactivated Alkenols Catalyzed by Cationic Lanthanide Complexes

Xuehua Zhu,[†,‡] Guoyao Li,[†] Fan Xu,*[,†] Yong Zhang,[†] Mingqiang Xue,[†] Qi Shen*[,†]

[†]College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People's Republic of China

[‡]School of chemical biology and materials engineering, Suzhou University of Science and Technology, Suzhou 215009, People's Republic of China

*gshen@suda.edu.cn; xufan@suda.edu.cn*

**Abstract:** Cationic lanthanide complexes of the type $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ (Ln = Pr, Nd, Sm, Gd, Er, Yb, Y) served as effective catalysts for the intramolecular hydroalkoxylation/cyclization of unactivated alkenols to yield the cyclic ethers with Markovnikov regioselectivity under mild conditions. Novel cationic complexes, $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ and $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$, were synthesized and evaluated for the intramolecular hydroalkoxylation/cyclization of unactivated alkenols for comparison. The active sequence of $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$ < $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ < $[Nd(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ observed indicated that both the cation and anion have great influence on the activity. Comparative study on the activity of $AlCl_3$ and its cationic complex $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ revealed the formation of the cationic Al center enhanced the activity greatly. The $^1H$ NMR studies indicated the activation of hydroxyl and olefin by the cationic $Ln^{3+}$ center were involved in the reaction pathways.

**Keywords:** alkenol, hydroalkoxylation, cationic lanthanide complex, reaction mechanism, catalysis

## 1. Introduction

Saturated oxygen heterocycles are recognized as important structural moieties that are found in a wide range of naturally occurring and biologically active molecules, such as polyethers,

antibiotics, acetogenins and prostaglandins.[1] Intramolecular addition of an O-H bond across an unsaturated C-C bond of a pendant olefin (intramolecular hydroalkoxylation) is an atom-economical, and therefore particularly attractive, approach for preparing saturated oxygen heterocycles. The hydroalkoxylation of alkenols traditionally involves reaction with a stoichiometric amount of a toxic metal ion, followed by reduction.[2] Catalytic processes for such transformations are limited, particularly for unactivated alkenols. Brønsted acids,[3] transition metals salts[4] such as those of gold,[4a] tin,[4b] ruthenium,[4c,4d,4h] and platinum,[4e] and some metal triflates[5] have been reported as effective catalysts for intramolecular and intermolecular hydroalkoxylation of olefins. However, these transition metal catalysts are either toxic or relatively expensive. Therefore, the development of new, efficient and cheaper methods for intramolecular and intermolecular hydroalkoxylation of olefins has attracted great attention.[6] Recently, Marks et al. reported that homoleptic lanthanide amido complexes ($Ln[N(SiMe_3)_2]_3$) are effective and selective precatalysts for the intramolecular hydroalkoxylation/cyclization of alkynyl and allenyl alcohols providing exocyclic enol ethers.[7] Lanthanide triflates ($Ln(OTf)_3$) also serve as efficient catalysts for the intramolecular hydroalkoxylation/cyclization of primary or secondary, and aliphatic or aromatic hydroxyalkenes at room temperature in ionic liquids, affording five- and six-membered oxygen heterocycles with Markovnikov-type selectivity.[8]

Cationic metal species are generally more electrophilic than their neutral forms, and thus are more active homogeneous catalysts. Cationic lanthanide alkyl complexes are well known to be more active and selective in catalyzing olefin polymerization and copolymerization with respect to their neutral analogs.[9] However, the use of cationic lanthanide complexes in organic transformations remains limited, and examples include intramolecular hydroamination,[10] dimerization of phenylacetylene[11] and hetero-Diels-Alder reaction.[12]

We previously reported that anhydrous lanthanide trichlorides ($LnCl_3$) react easily with anhydrous $AlCl_3$ in acetonitrile ($CH_3CN$), affording disconnected ion-pair Ln/Al complexes, $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$, in almost quantitative yields.[13] The lanthanide ions in these cationic complexes exhibit high electrophilicity and therefore can act as catalysts for styrene polymerization without the need for a co-catalyst.[14] These studies led us to investigate the intramolecular hydroalkoxylation of unactivated alkenols using these complexes as catalysts, with the aim of expanding the scope of cationic lanthanide complexes in organic synthesis. It was found that these complexes show good activity for a wide range of substrates, and we now disclose

these results. The syntheses and molecular structures of novel cationic complexes, $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ and $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$, and investigation of their catalytic activity in the intramolecular hydroalkoxylation of alkenols were studied to assess the influence of both the cation and the counteranion on the activity of this type of complex.

## 2. Results and Discussion

### 2.1 Optimization of the intramolecular hydroalkoxylation

*2.1.1 Syntheses of $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ (Ln= Pr **I**, Nd **II**, Sm **III**, Gd **IV**, Er **V**, Yb **VI** and Y **VII**) and the molecular structures of the Nd and Y complexes.* A series of cationic complexes, $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$, containing the early to later lanthanide metals were synthesized by the reaction of $LnCl_3$ and $AlCl_3$ in $CH_3CN$ according to a reported procedure (Scheme 1).[13]

**Scheme 1. Syntheses of $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$**

$$LnCl_3 + 3\,AlCl_3 \xrightarrow{CH_3CN} [Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\cdot CH_3CN$$

Ln = Pr **I**, Nd **II**, Sm **III**, Gd **IV**, Er **V**, Yb **VI**, Y **VII**

The solid state structures of the $[Nd(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ **II** and $[Y(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ **VII** complexes were determined by X-ray crystal structural analysis,[15] as they were unknown in the literature. They are isostructural and isomorphous, and their molecular structures are similar to that of the analogous Sm complex reported previously.[13] Both have an ion-pair structure consisting of one cation $[Ln(CH_3CN)_9]^{3+}$ and three anions of $(AlCl_4)^-$ (See Supplementary data).

*2.1.2 Solvent effects on the catalytic intramolecular hydroalkoxylation/cyclization of alkenols.* The intramolecular hydroalkoxylation/cyclizations of aromatic alkenol **1a** and aliphatic alkenol **1b** were investigated as model reactions, using 5 mol% of **II** in $CHCl_3$ at 65℃ for **1a**, and in DCE at 83℃ for **1b**. We were pleased to observe that the $[Nd(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ complex exhibited high catalytic activity in both reactions, affording 95% conversion of **1a** to cyclic ether **2a** (Table 1, entry 1), and 93% yield of cyclic ether **2b** (Table 2, entry 1) after 24 h. These encouraging results led us to examine the reactions further in various solvents. Thus, DCE, $CHCl_3$ and $CH_3CN$ for the

reaction of **1a**, and $CHCl_3$, DCE, $CH_3NO_2$ and toluene for the reaction of **1b** were investigated with a 5 mol% catalyst loading at different temperatures. The choice of solvent appeared to have a noticeable effect on both reactions. The hydroalkoxylation/cyclization reactions of **1a** in $CHCl_3$ at 65℃ and in DCE at 83℃ were almost complete after 24 h, affording **2a** in 95% and 90% yield, respectively (Table 1, entries 1 and 2). However, only a trace of **2a** was obtained when the reaction was carried out in $CH_3CN$ (Table 1, entry 3). Moreover, whereas reaction of unsaturated alcohol **1b** gave an almost quantitative yield of cyclic ether **2b** in DCE at 83℃ (93% yield, Table 2, entry 1), only 88% and 80% conversion of **1b** to **2b** was achieved when using toluene at 110℃ and $CH_3NO_2$ at 100℃, respectively (Table 2, entries 2 and 4). Only a 50% yield of **2b** was obtained in $CHCl_3$ at 65℃ (Table 2, entry 3). Thus, the optimal solv ent for this system is $CHCl_3$ for aromatic hydroxyalkenes, and DCE for aliphatic hydroxyalkenes.

The reaction concentration also affects the yield of the reaction. As illustrated in Table 1, the yield of **2a** decreased with an increase in the concentration of **1a** in a range from 0.5–2.0 mol/L (Table 1, entries 1, 4 and 5). The lowest-yielding reaction of **2a** was under solvent-free conditions (49%, Table 1, entry 6). This may be attributed to the poor solubility of the catalyst both in the substrate and the resulting product.

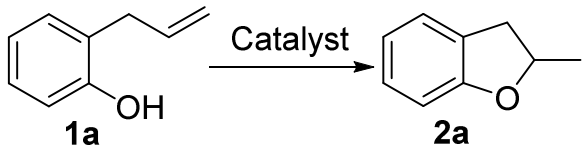
*2.1.3 Lanthanide metal effects on catalytic intramolecular hydroalkoxylation/cyclization of alkenols.* The influence of the lanthanide metal (Ln) on the model reactions of **1a** and **1b** was then screened in $CHCl_3$ at 65℃ for the former (Table 1), and in DCE at 83 ℃ for the latter (Table 2). As shown in Table 1, the activity of the complexes $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ increases substantially with a decrease in the Ln ionic radius. The reaction using the smallest ionic radius catalyst (Yb) afforded a quantitative yield of **2a**, medium-sized Ln catalysts (Sm and Gd) afforded 87–88% yields of **2a**, and 81–82% yields were achieved for the larger Nd and Pr metal catalysts (Table 1, entries 7–10 and 12). The activity of the Y complex is somewhat lower than that of the Yb complex (Table 1, entry 11). The sequence of Pr~Nd<Sm~Gd<Y<Yb observed here is consistent with an increasing trend of Lewis acidity of the Ln ions. This pattern parallels that of organolanthanide-catalyzed aminoalkyne hydroamination/cyclizations,[16] and $Ln(OTf)_3$-catalyzed hydroxyalkene hydroalkoxylation/cyclizations,[8] but not that of organolanthanide-catalyzed aminoalkene hydroamination/cyclizations,[17] or organolanthanide-catalyzed hydroxyalkyne and hydroxyallene hydroalkoxylation/cyclizations.[7c,18]

It is noteworthy that the complex **VI** showed a high activity in this transformation. The reaction

using 1.0 mol% of **VI** in $CHCl_3$ at 65℃ afforded a complete conversion of **1a** to **2a** after 24 h, and a 93% conversion after 18 h (Table 1, entries 13 and 14). The same reaction afforded **2a** in 81% yield after 24 h, even with a lower catalyst loading of 0.5 mol% (Table 1, entry 15).

An increasing activity with increasing Ln ionic radius was observed for the reaction of **1b** (Table 2, entries 5–11). The sequence of Yb<Y~Er~Gd<Sm~Nd~Pr here is in contrast to that found for the reaction of **1a**. The reason for such a substrate-dependent Ln metal effect is not clear, but the same outcome was also observed in the hydroalkoxylation/cyclization of unactivated alkenols catalyzed by $Ln(OTf)_3$.[8]

**Table 1 Screening of $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ complexes and solvents for intramolecular hydroalkoxylation/cyclization of 1a**[a]



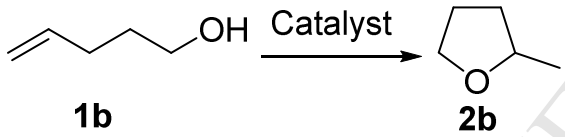

**1a** **2a**

| Entry | Ln catalyst (loading, mol%) | Solvent | GC yield (%) |
|---|---|---|---|
| 1 | **II** (5.0) | $CHCl_3$ | 95 |
| 2[b] | **II** (5.0) | DCE | 90 |
| 3[b] | **II** (5.0) | $CH_3CN$ | 8 |
| 4[c] | **II** (5.0) | $CHCl_3$ | 80 |
| 5[d] | **II** (5.0) | $CHCl_3$ | 73 |
| 6[e] | **II** (5.0) | - | 49 |
| 7 | **I** (2.5) | $CHCl_3$ | 81 |
| 8 | **II** (2.5) | $CHCl_3$ | 82 |
| 9 | **III** (2.5) | $CHCl_3$ | 87 |

| | | | |
|---|---|---|---|
| 10 | **IV** (2.5) | $CHCl_3$ | 88 |
| 11 | **VII** (2.5) | $CHCl_3$ | 95 |
| 12 | **VI** (2.5) | $CHCl_3$ | >99 |
| 13 | **VI** (1.0) | $CHCl_3$ | >99 |
| 14 | **VI** (1.0) | $CHCl_3$ | 93[f] |
| 15 | **VI** (0.5) | $CHCl_3$ | 81 |

[a] Reactions were conducted with 1 mmol of substrate in 2 mL of solvent at 65℃ for 24 h. [b] At 83℃. [c] The concentration of substrate was 1 mol/L. [d] The concentration of substrate was 2 mol/L. [e] Solvent free. [f] 18 h.

**Table 2 Screening of $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ complexes and solvents for intramolecular hydroalkoxylation/cyclization of 1b[a]**




**1b** **2b**

| Entry | Ln catalyst (loading, mol%) | Solvent | Temp. (℃) | GC yield (%) |
|---|---|---|---|---|
| 1 | **II** (5.0) | DCE | 83 | 93 |
| 2 | **II** (5.0) | toluene | 110 | 88 |
| 3 | **II** (5.0) | $CHCl_3$ | 65 | 50 |
| 4 | **II** (5.0) | $CH_3NO_2$ | 100 | 80 |
| 5 | **II** (2.5) | DCE | 83 | 90 |
| 6 | **I** (2.5) | DCE | 83 | 91 |

| | | | | |
|---|---|---|---|---|
| 7 | **III** (2.5) | DCE | 83 | 91 |
| 8 | **IV** (2.5) | DCE | 83 | 36 |
| 9 | **V**(2.5) | DCE | 83 | 40 |
| 10 | **VII** (2.5) | DCE | 83 | 39 |
| 11 | **VI** (2.5) | DCE | 83 | 31 |

[a] Reactions were conducted with 1 mmol of substrate in 2 mL of solvent for 24 h.

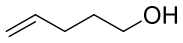
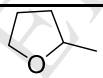
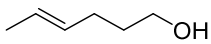
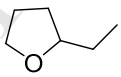
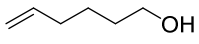
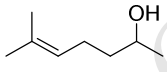
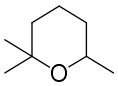
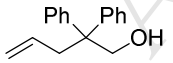
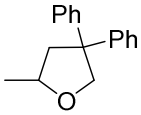
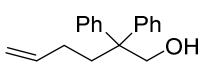
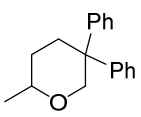
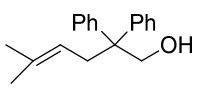
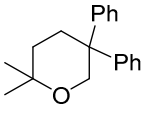
## 2.2 Scope of the catalytic intramolecular hydroalkoxylation/cyclization of alkenols

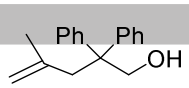
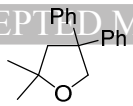
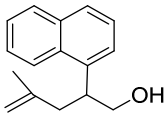
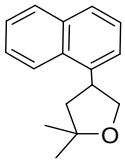
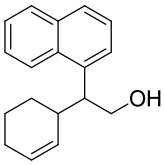
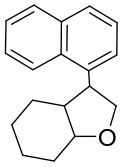
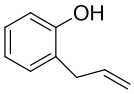
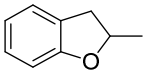
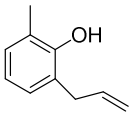
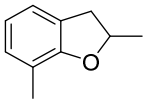
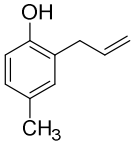
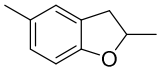
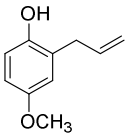
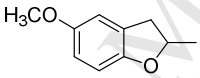
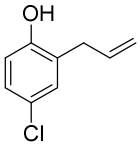
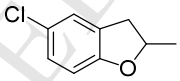
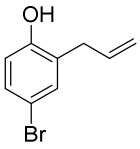
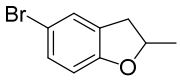
To probe the scope of the present catalytic hydroalkoxylation/cyclization process, the complex **II** (2.5 mol%) was chosen as the catalyst for the reactions of aliphatic hydroxyalkenes, and the complex **VI** (1 mol%) was used for the aromatic hydroxyalkenes. The reaction solvent and temperature were selected based on the substrates used (DCE, 83℃ for aliphatic hydroxyalkenes; $CHCl_3$, 65℃ for aromatic hydroxyalkenes). From the results in Table 3 it can be seen that $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ complexes serve as robust and effective catalysts for the hydroalkoxylation/cyclization of both aromatic and aliphatic hydroxyalkenes. The hydroalkoxylation/cyclization of hydroxyalkenes with a terminal double bond (**1b**, **1d**, **1f**, **1i**, and **1j**) proceeded smoothly to give the corresponding products in good to excellent yields (Table 3, entries 1, 3, 5, 8 and 9), except for **1g**. The ring-size dependence of the reaction activity on the substrates used here is 5>6, which is consistent with a sterically controlled ring-forming transition state, and is also observed for the other reported catalysts[8] (Table 3, entries 1 vs. 3, 5 vs. 6, and 8 vs. 7). The reactions of the unsaturated alcohols with a disubstituted terminal double bond, such as **1e** and **1h**, led exclusively to the formation of the corresponding tetrahydropyrans **2e** and **2h** (Table 3, entries 4 and 7), and no five-membered cyclic ether was observed. This indicates that the present hydroalkoxylation/cyclization proceeds at the more substituted carbon atom of the double bond with Markovnikov selectivity. This is similar to those found with the reported lanthanide (La, Sm, Yb),[8] aluminum, and other transition metal catalysts[4,5b]. In the case of an alcohol such as **1c**,

the cyclization was successful in refluxing DCE, regiospecifically affording the five-membered cyclic ether as the only product in quantitative yield (Table 3, entry 2). The intramolecular addition of the hydroxyl group to a cyclohexene also works, such as the reaction with **1k**, although the yield of the cyclic ether **2k** was somewhat low (Table 3, entry 10).

The $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ catalysts are also efficient in the hydroalkoxylation/cyclization of aromatic hydroxyalkenes such as **1a**, **1l**, **1m**, **1n, 1o** and **1p**. The present cyclization tolerated a number of functional groups at the phenyl ring including Me, MeO, Cl, and Br (Table 3, entries 13–16). The activity of the hydroxyalkenes with an electron-withdrawing group *para* to the hydroxyl (Table 3, entries 15 and 16) is higher than that of those with an electron-donating group at the same position (Table 3, entries 13 and 14). The efficiency of the $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$-catalyzed hydroalkoxylation/cyclization of aromatic hydroxyalkenes was sensitive to the group at the *ortho* position to the hydroxyl. For example, **1a** underwent cyclization in almost quantitative yield, but **1l** only afforded a moderate yield of the desired product (Table 3, entries 11 and 12). This may be due to the bulky group preventing the coordination of the hydroxyl group to the central metal atom.

**Table 3. Intramolecular hydroalkoxylation/cyclization of aliphatic and aromatic alkenols catalyzed by $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$[a]**

| Entry | Substrate | | Product | | GC yield (%) |
|---|---|---|---|---|---|
| 1 |  | **1b** |  | **2b** | 90 |
| 2 |  | **1c** |  | **2c** | >99 |
| 3 |  | **1d** |  | **2d** | 85 |
| 4 |  | **1e** |  | **2e** | 97/50[b] |
| 5 |  | **1f** |  | **2f** | 98/85[b] |
| 6 |  | **1g** |  | **2g** | 60 |
| 7 |  | **1h** |  | **2h** | 91 |

| | | | | | |
|---|---|---|---|---|---|
| 8 |  | **1i** |  | **2i** | 98/87[b] |
| 9 |  | **1j** |  | **2j** | 81/75[b] |
| 10 |  | **1k** |  | **2k** | 49[c] |
| 11[d] |  | **1a** |  | **2a** | >99/97[b] |
| 12[e] |  | **1l** |  | **2l** | 55 |
| 13[e] |  | **1m** |  | **2m** | 87/81[b] |
| 14[e] |  | **1n** |  | **2n** | 81/76[b] |
| 15[e] |  | **1o** |  | **2o** | 95/89[b] |
| 16[e] |  | **1p** |  | **2p** | 99/97[b] |

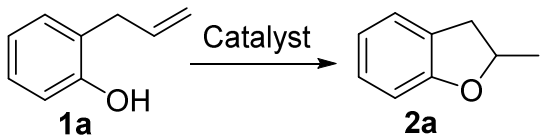
[a] Reactions were conducted with 1 mmol of substrate in 2 mL of DCE for 24 h catalyzed by 2.5 mol% **II** at 83℃. [b] Isolated yield. [c] 48 h. [d] 1 mol% **VI**, $CHCl_3$, 65℃. [e] 2.5 mol% **VI**, $CHCl_3$, 65℃.

## 2.3 Mechanistic study

To gain information on the true catalytic species, the hydroalkoxylation/cyclization reactions of **1a** catalyzed by anhydrous $YbCl_3$ (1 mol%), $AlCl_3$ (3 mol%) and a mixture of $YbCl_3$ (1 mol%) and $AlCl_3$ (3 mol%) were conducted in $CHCl_3$ at 65℃ as control experiments. The results are

summarized in Table 4.

**Table 4. Screening of $YbCl_3$ and $AlCl_3$ for the intramolecular hydroalkoxylation/cyclization of 1a[a]**




**1a** **2a**

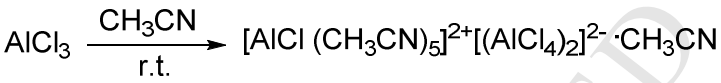
| Entry | Catalyst (loading, mol%) | GC yield (%) |
|---|---|---|
| 1 | $YbCl_3$ (1.0) | trace |
| 2 | $AlCl_3$ (3.0) | 30 |
| 3 | $YbCl_3$ (1.0) + $AlCl_3$ (3.0) | 31 |
| 4[b] | $CH_3CN$–treated $YbCl_3$ (1.0) | trace |
| 5[b] | $CH_3CN$–treated $AlCl_3$ (3.0) | 69 |

[a] Reactions were carried out at 65℃ in $CHCl_3$ for 24 h, the substrate concentration was 0.5 mol/L. [b] The catalyst was first treated with $CH_3CN$ at room temperature for 24 h, then evaporated to dry to catalyze the hydroalkoxylation/cyclization of 1a.

Anhydrous $YbCl_3$ alone was almost completely inactive in this transformation, and only a trace of **2a** was detected (Table 4, entry 1) under the same reaction conditions as those used for **VI** (Table 1, entry 13). Anhydrous $AlCl_3$ was also an inefficient catalyst, and the reaction using 3 mol% $AlCl_3$ in $CHCl_3$ afforded only a 30% yield of **2a** after 24 h (Table 4, entry 2). The reaction with a mixture of $YbCl_3$ and $AlCl_3$ as the catalyst afforded a 31% yield of **2a** (Table 4, entry 3)**,** which is probably due to the accumulation of the catalytic activities of the individual $YbCl_3$ and $AlCl_3$ species. The much higher activity exhibited by **VI** (>99% yield of **2a**, Table 1, entry 13) compared with that of the mixture of $YbCl_3$ and $AlCl_3$ demonstrates that the cationic complex did not decompose into a mixture of $YbCl_3$ and $AlCl_3$ during the reaction process. Indeed, **VI** is stable in the $CHCl_3$ solution of the phenol. After stirring a 1:1 mixture of **VI** and phenol in $CHCl_3$ for 24 h, the complex **VI** was recovered. Thus, the cationic complex **VI** itself may be the true catalyst for the present hydroalkoxylation/cyclization. Also, the much higher activity of the complex **VI** compared with that of $YbCl_3$ may be attributed to the formation of the more electrophilic cationic Yb metal species.

*2.3.1 Influence of the cation on the activity.* It is noteworthy that the yield of **2a** increased from 30% to 69% when the $AlCl_3$ was first treated with $CH_3CN$ at room temperature for 24 h, then evaporated to dryness (Table 4, entry 5). Conversely, no difference in the yield of **2a** was observed when the $CH_3CN$-treated $YbCl_3$ was used instead of the untreated $YbCl_3$ (Table 4, entry 4). To understand the reason for such a great difference in reaction with the $CH_3CN$-treated $AlCl_3$, the reaction of $AlCl_3$ with $CH_3CN$ at room temperature was investigated in detail. Stirring a suspension of $AlCl_3$ in $CH_3CN$ for 24 h afforded a clean, colorless solution. Concentrating the solution and crystallizing from a mixed solvent of $CH_3CN$ and hexane at room temperature led to the formation of colorless crystals in almost quantitative yield. X-ray crystal structural analysis revealed that the crystals are the cationic Al complex $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ **VIII**, which is composed of one cation $[AlCl(CH_3CN)_5]^{2+}$ and two anions $(AlCl_4)^-$ (Scheme 2).[19] The molecular structure of **VIII** is shown in Figure 1. The Al atom in the cation bonds to one Cl atom and five $CH_3CN$ molecules in a distorted octahedral geometry.

**Scheme 2. Synthesis of VIII**



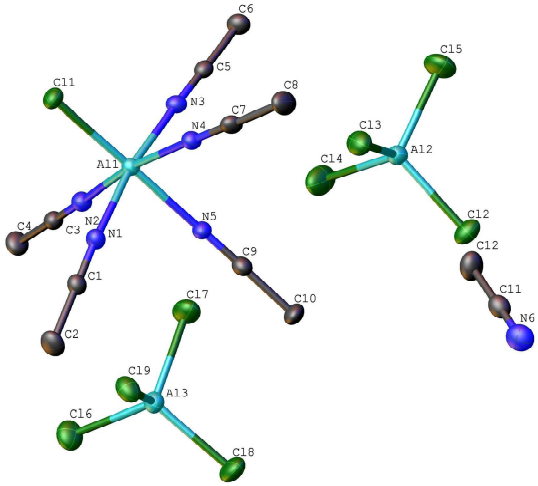
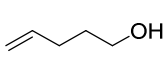
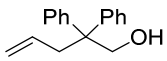
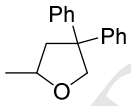
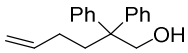
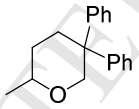
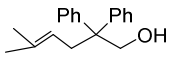
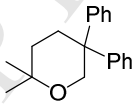
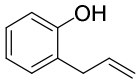
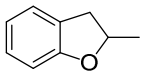
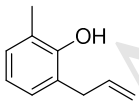
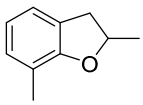




**Figure 1.** Molecular structure of **VIII**.

The complex **VIII** was then evaluated in the intramolecular hydroalkoxylation/cyclization of unactivated alkenols. As shown in Table 5, the reaction of **1a** with 1 mol% **VIII** in $CHCl_3$ at 65℃ yielded **2a** in 69% yield after 24 h (Table 5, entry 5). This is the same yield obtained with the $CH_3CN$-treated $AlCl_3$ (Table 4, entry 5), indicating that the formation of a cationic Al species leads to a large increase in activity. The yield of **2a** could be increased to 90% when the catalyst loading was increased to 5 mol% (Table 5, entry 5). Table 5 shows that **VIII** can serve as a catalyst for the transformation of unactivated alkenols to cyclic ethers; however, the activity is much lower than that of the $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ complexes. Moreover, the efficiency of the hydroalkoxylation/cyclization with **VIII** was very sensitive to the substrates used (Table 5, entries 3, 4 and 6). Comparing results between the two cationic complexes, $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ and **VIII**, demonstrates that the cation plays an important role in determining the efficiency of the complex.

**Table 5. Intramolecular hydroalkoxylation of alkenols catalyzed by VIII**[a]

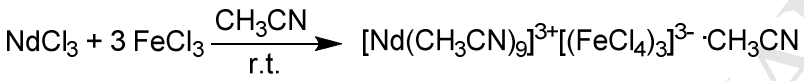
| Entry | Substrate | | Product | | GC yield (%) |
|---|---|---|---|---|---|
| 1 |  | **1b** |  | **2b** | 71/61[b] |
| 2 |  | **1f** |  | **2f** | 72 |
| 3 |  | **1g** |  | **2g** | 33 |
| 4 |  | **1h** |  | **2h** | 2.7 |
| 5[c] |  | **1a** |  | **2a** | 90[b]/69[d] |
| 6[c] |  | **1l** |  | **2l** | 38 |

[a] Reactions were catalyzed by 10 mol% **VIII** at 83℃ in DCE for 24 h, the substrate concentration was 0.5 mol/L. [b] Catalyst loading 5 mol%. [c] Solvent $CHCl_3$, reaction temperature 65℃. [d] Catalyst loading 1 mol%.

*2.3.2 Influence of the anion on the activity.* A novel cationic Nd/Fe complex

$[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$ **IX**[20] was prepared using a similar procedure, to investigate the influence of the anion on the activity. Addition of $CH_3CN$ to a mixture of $NdCl_3$ and $FeCl_3$ in a 1:3 molar ratio, followed by stirring the suspension at room temperature for 24 h, led to a clear purple solution, from which purple crystals were isolated in 43% yield upon crystallization. The crystals were characterized to be the expected cationic complex $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$ **IX** (Scheme 3). The solid state structure of **IX** was further determined by an X-ray crystal structural analysis. As shown in Figure 2, the complex consists of one cation of $[Nd(CH_3CN)_9]^{3+}$ and three anions of $(FeCl_4)^-$. The coordination geometry about the nine-coordinate metal center can be viewed as a distorted tricapped trigonal prism. Each Fe ion in the anion coordinates to four Cl atoms, forming a distorted tetrahedron. The molecular structure of **IX** is quite similar to that of the complex **II**.

**Scheme 3. Synthesis of IX**



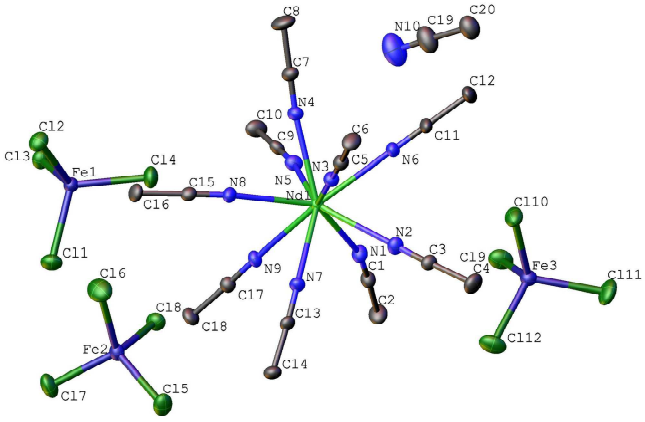
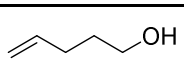
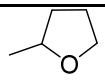
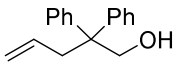
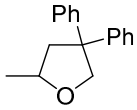
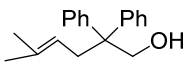
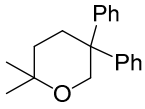
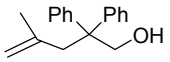
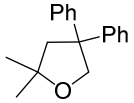
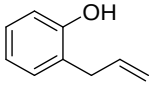
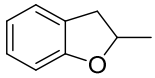
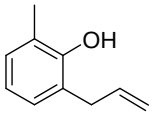
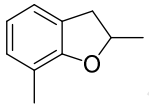




**Figure 2.** Molecular structure of **IX**.

The complex **IX** was then trialed in the hydroalkoxylation/cyclization of a range of alkenols. The results obtained under the same conditions as for the $[Nd(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ **II** catalyst (Table 3) are listed in Table 6. It can be seen that the complex **IX**, as an alternative cationic lanthanide catalyst, also catalyzes the hydroalkoxylation/cyclization of alkenols. However, the activity is lower than that of **II** (Table 6, entries 1–4 and Table 3, entries 1, 5, 7, 8), especially for aromatic alkenols (Table 6, entries 5, 6 and Table 3, entries 11, 12). The comparative study here

revealed the anion in these complexes is also crucial for determining the catalytic activity. It can be found from the crystallographic data of complexes **II** and **IX** that the average Nd–N bond distance in complex **II** is longer than that in **IX**, suggesting that the Ln center in the former is more positive than that in the latter. It may be the reason for the difference of catalytic activity between **II** and **IX**.

**Table 6. Intramolecular hydroalkoxylation of alkenols catalyzed by IX**[a]

| Entry | Substrate | | Product | | GC yield (%) |
|---|---|---|---|---|---|
| 1 |  | **1b** |  | **2b** | 61 |
| 2 |  | **1f** |  | **2f** | 92 |
| 3 |  | **1h** |  | **2h** | 46 |
| 4 |  | **1i** |  | **2i** | 91 |
| 5[b] |  | **1a** |  | **2a** | 6.7 |
| 6[b] |  | **1l** |  | **2l** | 4.1 |

[a] Reactions were catalyzed by 2.5 mol% **IX** at 83℃ in DCE for 24 h, the substrate concentration is 0.5 mol/L. [b] Solvent $CHCl_3$, reaction temperature 65℃.

*2.3.3 $^1H$ NMR spectroscopy study.* To gain an insight into which groups (hydroxyl group, C-C double bond or both) coordinate to the Ln metal, an in situ $^1H$ NMR spectroscopic experiment with **1b** was carried out in $CDCl_3$ at room temperature in the presence of 1 equiv. **VII**. As shown in Figure 3 (B and C), the signals corresponding to the α–carbon $H^1$ resonances ($\Delta\delta$ = 0.5 ppm) and olefinic $H^5$ resonances ($\Delta\delta$ = 0.06 ppm) were significantly displaced. This indicates that the $Ln^{3+}$ complexes to both the hydroxyl group and the double bond. As a control, an $^1H$ NMR experiment with **1b** and 1 equiv. **VIII** was also conducted under the same conditions (Figure 3A). A similar, but smaller, displacement of the $^1H$ resonances was observed ($\Delta\delta$ 0.02 ppm for the olefinic $H^5$, and $\Delta\delta$ 0.38 ppm for the α-carbon $H^1$). The smaller variation in the chemical shifts of the $^1H$ protons, compared with that for the case of **1b** + **VII**, may be attributed to the weaker interaction of the Al ion to the alkenol, versus that of the Ln ion to the alkenol. This might be the reason why **VIII** exhibits lower activity than the $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}$•$CH_3CN$ complex.

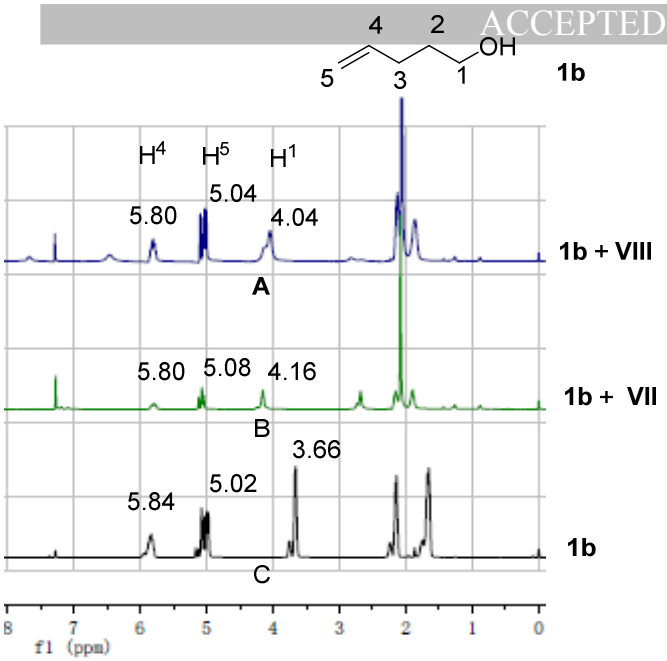
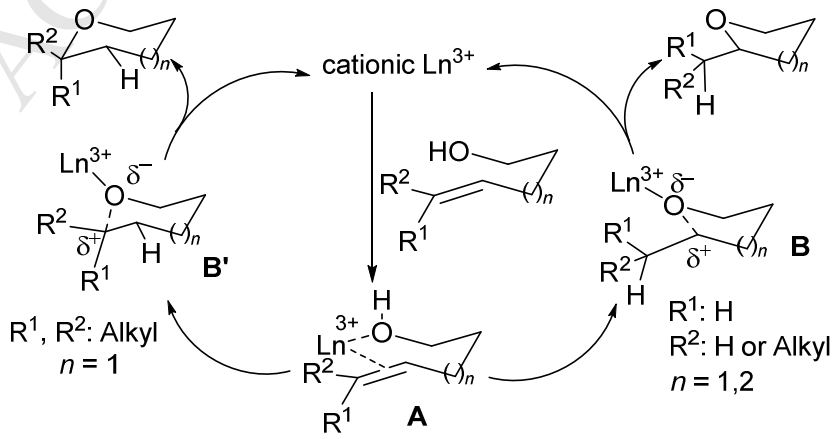



**Figure 3.** $^{1}$H NMR of **1b**, **1b** + **VII**, and **1b** + **VIII**.

Unfortunately, attempts to isolate the active species of the catalytic process by mixing **1a** and **VI** stoichiometrically in $CHCl_3$ were unsuccessful and no absolute complex was obtained.

A reaction pathway was suggested based on the above information, as proposed for the $Ln(OTf)_3$-catalyzed process[8b] (Scheme 4). The first step is the coordination of the cationic lanthanide center with both the hydroxyl group and the C=C double bond to yield intermediate **A**. Proton transfer then affords intermediate **B** or **B**' with Markovnikov selectivity. Subsequent alkoxide nucleophilic attack then produces the cyclic ethers and regenerates the catalyst.

**Scheme 4. Proposed catalytic pathways for $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}$•$CH_3CN$-catalyzed intramolecular hydroalkoxylation/cyclization of alkenols**



## 3. Conclusions

We have demonstrated for the first time that cationic lanthanide complexes $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ serve as efficient catalysts for the intramolecular hydroalkoxylation/cyclization of unactivated aromatic and aliphatic alkenols. The catalytic activity depends on the Ln metal ion size and solvent used. Various furan, pyran and benzofuran derivatives were selectively formed as Markovnikov regioselection products in moderate to excellent yields. A study comparing the activity of three types of cationic complexes, $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$, $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$, and $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$, revealed that both the cation and the anion have a great influence on the activity of the complex. The much greater activity observed for the cationic Al complex **VIII** over the neutral $AlCl_3$ supports the theory that an increased electron-deficiency of the central metal is the key to activating the hydroxyl and the C=C double bond.

## 4. Experimental Section

### 4.1 General information

All manipulations and reactions were performed under a purified argon atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. $LnCl_3$ were prepared according to the literature procedure.[21] $AlCl_3$ was sublimed before use. All solvents were predried and distilled before use. Substrates **1a**, **1b**, **1c**, **1d**, **1e** and **1l** were purchased from Alfa Aesar Co., dried over freshly activated Davison 4Å molecular sieves and were distilled under reduced pressure. Substrates **1f**,[4e] **1g**,[4e] **1h**,[4e] **1i**,[4e] **1j**,[5c] **1k**,[5c] **1m**,[6a] **1n**,[6a] **1o**[6a] and **1p**[6a] were prepared using reported methods. $^1H$ and $^{13}C$ NMR spectra were recorded on Varian System-300 and INOVA-400 spectrometers. Chemical shifts ($\delta$) were reported in ppm. Gas chromatography was performed on a Varian CP3800 gas chromatograph equipped with a 30 m HP-5 polydimethylsiloxane capillary column using the following conditions: 80℃ (3 min)//10℃/min//260℃ (10 min) gradient, detector t emperature 260℃. Crystals suitable for X-ray diffraction of complexes (**II**, **VII**, **VIII** and **IX**) were sealed, respectively, in a thin-walled glass capillary filled with argon for structural analysis. X-ray diffraction data were collected on a Rigaku

Saturn CCD area detector.

### 4.2 Catalyst syntheses

*4.2.1 $[Ln(CH_3CN)_9]^{3+}[(AlCl_4)_3]^{3-}\bullet CH_3CN$ (Ln = Pr, Nd, Sm, Gd, Er, Yb and Y).* This series of cationic complexes were synthesized by the reaction between $LnCl_3$ and $AlCl_3$ in $CH_3CN$ according to a reported procedure.[13] Take $Sm(CH_3CN)_9(AlCl_4)_3\bullet CH_3CN$ as an example: 0.9 g (6.74 mmol) of $AlCl_3$ was added to a slurry of 0.58 g (2.24 mmol) of anhydrous $SmCl_3$ in 20 mL $CH_3CN$ and the reaction mixture was stirred at room temperature for 20 h. The reaction solution was filtrated, concentrated and cooled to 0°C for crystallization, and finally 1.0 g yellow crystals of $Sm(CH_3CN)_9(AlCl_4)_3\bullet CH_3CN$ were collected. The solid state structures of **II** and **VII** were determined by X-ray crystal structural analysis, as no molecular structures for them had been reported.

*4.2.2 $[AlCl((CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$*. A suspension of $AlCl_3$ in $CH_3CN$ was stirred at room temperature for 24 h. The resulting clear solution was concentrated, and $[AlCl(CH_3CN)_5]^{2+}[(AlCl_4)_2]^{2-}\bullet CH_3CN$ **VIII** was obtained as colorless crystals by crystallization from a mixed solvent of $CH_3CN$ and hexane at room temperature in almost quantitative yield. The structure of the complex was determined by single-crystal X-ray analysis.

*4.2.3 $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$.* A certain amount of $CH_3CN$ was added to a mixture of $NdCl_3$ and $FeCl_3$ in a 1:3 molar ratio. The suspension was stirred at room temperature for 24 h and a clear purple solution was obtained. The solution was concentrated and cooled at 0℃ for several days to give $[Nd(CH_3CN)_9]^{3+}[(FeCl_4)_3]^{3-}\bullet CH_3CN$ **IX** as purple crystals in 43% yield. The structure of the complex was determined by single-crystal X-ray analysis.

### 4.3 Typical procedure for hydroalkoxylation of unactivated Alkenols (product 2b as an example)

Into a 10 mL of Schlenk tube under dried argon were added **II** (0.0265 g, 0.025 mmol), DCE (2.0 mL) and 4-pentenol (0.10 mL, 1.0 mmol). The resulting mixture was stirred at 83°C for 24 h. The reaction was cooled to room temperature and the catalyst was removed by filtration through a short pad of silica gel. Product **2b** was obtained by silica-gel column chromatography with pentane/diethyl ether or petroleum ether/ethyl acetate as an eluent. The GC yield of 90% was determined with nonane as internal standard.

### 4.4. Spectroscopic data

*4.4.1 2,3-dihydro-2-methylbenzofuran (**2a**).*[8] yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ =7.27–7.20

(m, 2 H), 6.97–6.89 (m, 2 H), 5.05–4.96 (m, 1 H), 3.41–3.35 (dd, *J* = 15.6, 8.8 Hz, 1 H), 2.93–2.87 (dd, *J* = 15.2, 7.6 Hz, 1 H), 1.58 (d, *J* = 6.4Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 154.5, 122.9, 121.9, 119.9, 115.1, 104.2, 74.3, 32.0, 16.7.

*4.4.2 2-methyltetrahydrofuran (**2b**).*[8] colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 3.88–3.82 (m, 2 H), 3.67–3.62 (m, 1 H), 1.93–1.91 (m, 1 H), 1.83–1.81 (m, 2 H), 1.36–1.30 (m, 1 H), 1.16 (d, *J* = 6.0 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 75.5, 68.0, 33.5, 26.3, 21.3.

*4.4.3 2-ethyltetrahydrofuran (**2c**).*[8] colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 3.88–3.82 (m, 1 H), 3.73–3.70 (m, 2 H), 1.99–1.92 (m, 1 H), 1.87–1.83 (m, 2 H), 1.62–1.56 (m, 1 H), 1.51–1.38 (m, 2 H), 0.93 (t, *J* = 7.6 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 81.5, 68.4, 31.6, 29.2, 26.4, 11.2.

*4.4.4 2-methyltetrahydropyran (**2d**).*[8] colorless oil. $^{1}$H NMR (300 MHz, $CDCl_3$): *δ* = 3.89–3.82 (m, 1 H), 3.75–3.68 (m, 2 H), 1.88–1.86 (m, 3 H), 1.63–1.56 (m, 1 H), 1.49–1.40 (m, 2 H), 0.91 (d, *J* = 7.5 Hz, 3 H). $^{13}$C NMR (75 MHz, $CDCl_3$): *δ* = 80.9, 67.8, 31.0, 28.6, 25.8, 10.6.

*4.4.5 2,2,6-trimethyltetrahydropyran (**2e**).*[8] colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 3.70–3.64 (m, 1 H), 1.63–1.52 (m, 4 H), 1.41–1.37 (m, 2 H), 1.21 (s, 3 H), 1.19 (s, 3 H), 1.10 (d, *J* = 8.0 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 67.1, 61.8, 31.4, 28.8, 27.4, 18.2, 17.4, 15.5.

*4.4.6 2-methyl-4,4-diphenyltetrahydrofuran (**2f**).*[8] off-white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 7.31–7.20 (m, 10 H), 4.60–4.58 (m, 1 H), 4.19–4.16 (m, 2 H), 2.66–2.61 (m, 1 H), 2.30–2.24 (m, 1 H), 1.29 (d, *J* = 6.4 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 146.9, 146.8, 128.9, 128.8, 127.7, 126.9, 126.7, 75.3, 55.9, 47.1, 30.2, 21.9.

*4.4.7 2-methyl-5,5-diphenyltetrahydropyran (**2g**).*[8] colorless oil. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 7.45–7.18 (m, 10 H), 4.66–4.63 (m, 1 H,), 3.59–3.16 (m, 2 H), 2.46–2.43 (m, 2 H), 1.58–1.54 (m, 1 H), 1.27–1.23 (m, 1 H), 1.19–1.18 (m, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 147.3, 146.4, 129.5, 128.8, 128.5, 127.5, 126.8, 126.2, 75.6, 74.6, 46.3, 35.3, 30.3, 22.2.

*4.4.8 2,2-dimethyl-5,5-diphenyltetrahydropyran (**2h**).*[5c] off-white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 7.29–7.22 (m, 8 H), 7.16–7.12 (m, 2 H), 4.02 (s, 2 H), 2.41–2.38 (m, 2 H), 1.38–1.35 (m, 2 H), 1.19 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 146.6, 128.2, 128.1, 126.1, 71.4, 69.1, 46.0, 32.7, 30.9, 26.5.

*4.4.9 2,2-dimethyl-5,5-diphenyltetrahydrofuran (**2i**).*[4e] white solid. $^{1}$H NMR (400 MHz, $CDCl_3$): *δ* = 7.27–7.24 (m, 8 H), 7.18–7.14 (m, 2 H), 4.43 (s, 2 H), 2.60 (s, 2 H), 1.18 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 147.0, 128.5, 127.4, 126.3, 81.6, 75.6, 56.9, 51.6, 29.4.

*4.4.10 2,2-dimethyl-4-Naphthyltetrahydrofuran (**2j**).*[5c] light yellow solid. $^{1}$H NMR (300 MHz, $CDCl_3$): *δ* = 8.14 (d, *J* = 6.0 Hz, 1 H), 7.89–7. 73 (m, 2 H), 7.55–7.44 (m, 4 H), 4.42–4.26 (m, 2 H), 4.02–3.97 (m, 1 H), 2.36 (t, *J* = 28.0 Hz, 1 H), 2.09 (t, *J* = 28.0 Hz, 1 H), 1.42 (s, 6 H). $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 137.9, 134.0, 132.2, 129.0, 127.2, 126.1, 125.6, 123.5, 122.9, 81.2, 72.6, 46.0, 41.3, 29.0, 28.5.

*4.4.11 3-naphthyloctahydrobenzofuran (**2k**).*[5c] light yellow solid. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ = 8.13 (d, *J* = 6 Hz, 1 H), 7.87–7.73 (m, 2 H), 7.52–7.38 (m, 4 H), 4.62–4.57 (m, 1 H), 4.40–4.36 (m, 2 H), 4.26–4.21 (m, 1 H), 2.46 (s, 1 H), 2.11–2.07 (m, 1 H), 1.59–1.46 (m, 5 H), 1.12–0.97 (m, 2 H), 0.66–0.62 (m, 1 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 133.9, 133.5, 132.6, 129.0, 127.2, 126.0, 125.6, 125.0, 123.7, 123.2, 78.8, 68.3, 45.2, 41.6, 28.9, 4.3.6, 23.2, 20.5.

*4.4.12 2,7-dimethyl-2,3-dihydrobenzofuran (**2l**).*[6a] yellow oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 6.99–6.91 (m, 2 H), 6.75–6.71 (m, 1 H), 4.94–4.86 (m, 1 H), 3.33–3.27 (m, 1 H), 2.84–2.78 (m, 1 H), 2.20 (s, 3 H), 1.48 (d, *J* = 8 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.5, 129.6, 126.7, 122.8, 120.5, 119.9, 79.6, 37.9, 22.4, 15.8.

*4.4.13 2,5-dimethyl-2,3-dihydrobenzofuran (**2m**).*[6a] colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 6.96 (s, 1 H), 6.89 (d, *J* = 8.1 Hz, 1 H), 6.64 (d, *J* = 8.0 Hz, 1 H), 4.98–4.74 (m, 1 H), 3.26 (dd, *J* = 15.4, 8.7 Hz, 1 H), 2.77 (dd, *J* = 15.4, 7.7 Hz, 1 H), 2.27 (s, 3 H), 1.45 (d, *J* = 6.2 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 157.5, 129.5, 128.3, 127.2, 125.7, 108.9, 79.6, 37.3, 21.8, 20.9.

*4.4.14 5-methoxy-2-methyl-2,3-dihydrobenzofuran (**2n**).*[6a] colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 6.74 (s, 1 H), 6.69–6.60 (m, 1 H), 4.96–4.78 (m, 1 H), 3.74 (s, 3 H), 3.27 (dd, *J* = 15.5, 8.6 Hz, 1 H), 2.79 (dd, *J* = 15.5, 7.8 Hz, 1 H), 1.45 (d, *J* = 6.2 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 154.0, 153.7, 128.1, 112.7, 111.4, 109.1, 79.7, 56.0, 37.7, 21.8.

*4.4.15 5-chloro-2-methyl-2,3-dihydrobenzofuran (**2o**).*[6a] colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.08 (s, 1 H), 7.03 (d, *J* = 8.5 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 5.06 –4.76 (m, 1 H), 3.27 (dd, *J* = 15.6, 8.8 Hz, 1 H), 2.78 (dd, *J* = 15.6, 7.6 Hz, 1 H), 1.44 (d, *J* = 6.3 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.3, 129.1, 127.9, 125.2, 116.1, 110.3, 80.3, 37.1, 21.8.

*4.4.16 5-bromo-2-methyl-2,3-dihydrobenzofuran (**2p**).*[6a] colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.21 (d, *J* = 8.5 Hz, 1 H), 7.17 (d, *J* = 8.5 Hz, 1 H), 6.61 (d, *J* = 8.4 Hz, 1 H), 5.01–4.80 (m, 1 H), 3.27 (dd, *J* = 15.6, 8.8 Hz, 1 H), 2.78 (dd, *J* = 15.6, 7.6 Hz, 1 H), 1.44 (d, *J* = 6.2 Hz, 3 H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 158.7, 130.7, 129.6, 127.9, 111.8, 110.8, 80.1, 36.9, 21.7.



## Acknowledgements

We are grateful to the National Natural Science Foundation of China (Grant Nos. 21272168 and 21372171) and Specialized Research Fund for the Doctoral Program of Higher Education (200802850003).

## Supplementary data

Supplementary data (crystallographic data for complexes **II**, **VII**, **VIII**, **and IX** and copies of $^1$H NMR and $^{13}$C NMR spectra of compounds **2a**-**2p**) related to this article can be found.

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