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# Lanthanide bis(trifluoromethanesulfonyl)amides, synthesis, characterization and catalytic activity

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#### Abstract

The synthesis of lanthanum, neodymium and ytterbium bis(trifluoromethanesulfonyl)amides, named triflimidates, from acetates, carbonates and oxides is investigated. When the synthesis is performed in water, all the salts contain one molecule of water and the lanthanum and neodymium salts synthesized from the acetates also contain one molecule of acetic acid. After removal of the water and acetic acid in refluxing ethanol, the salts are obtained anhydrous but associated for lanthanum and neodymium, whereas the ytterbium salt is monomeric and volatile. When the synthesis is performed directly in ethanol, the neodymium salt contains two molecules of coordinated ethanol.

In non-hazardous solvents, these triflimidates are better catalysts than the analogous triflates toward either Friedel–Crafts acylations, or Fries transpositions or Baeyer–Villiger oxidations. Unexpectedly, the cerium(IV) triflimidate catalyzes the oxidation of aromatic ketones to give the corresponding acids.

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# 1. Introduction

Bis(trifluoromethanesulfonyl)amides of lanthanum [1], ytterbium, yttrium [2] and scandium [3]:  $Ln[N(SO_2CF_3)_2]_3$  have been described as strong Lewis acids, more powerful catalysts for Diels–Alder [1,2], or acylation reactions [3,4] than the analogous triflates.

These salts were obtained after reaction of the corresponding oxides, acetates, or carbonates with bis(trifluoromethanesulfonyl)amine in water [5,6] and after removal of the remaining water under reduced pressure. Nevertheless, as it was impossible to isolate suitable crystalline species for an X-ray structural analysis, the characterization of the isolated products remained uncertain, the structure of the salt seemed to be different according to the element and to the nature of the starting material. The lanthanum salt was described as monohydrated La[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>·H<sub>2</sub>O, whereas the scandium salt obtained from scandium acetate, contained ca. 1.5 equivalent of acetic acid:  $Sc[N(SO_2CF_3)_2]_3$ , 1.5AcOH and nothing was reported concerning the presence of ancillary ligands for the ytterbium and yttrium complexes.

To obtain more information about the exact structure of these salts and the eventual influence of the additional ligands on their catalytic activity, the synthesis and the characterization of bis(trifluoromethanesulfonyl)amides of three representative lanthanides: lanthanum, neodymium and ytterbium, was investigated. The catalytic activity of these salts was tested and compared to the activity of the analogous triflates in three reactions catalyzed by Lewis acids: the Friedel–Crafts acylation, the Fries transposition and the Baeyer–Villiger oxidation.

# 2. Results and discussion

# 2.1. Syntheses and qualitative analyses

The synthesis of lanthanide bis(trifluoromethanesulfonyl)amides (abbreviated as triflimidates:  $Ln(NTf_2)_3$ )

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D.B. Baudry et al. / Journal of Fluorine Chemistry 121 (2003) 233-238

$$\begin{array}{c} \text{Ln}(\text{CH}_{3}\text{CO}_{2})_{3}, n(\text{H}_{2}\text{O}) & \frac{3 \text{ HNTf}_{2}}{\text{H}_{2}\text{O}, 20^{\circ}, 30 \text{ min.}} & \text{Ln}(\text{NTf}_{2})_{3}, x(\text{H}_{2}\text{O}), y(\text{CH}_{3}\text{CO}_{2}\text{H}) \\ \text{H}_{2}\text{O}, 20^{\circ}, 30 \text{ min.} & \text{Ln}(\text{NTf}_{2})_{3}, x(\text{H}_{2}\text{O}) \\ \text{H}_{2}\text{O}, 20^{\circ}, 30 \text{ min.} & \text{Ln}(\text{NTf}_{2})_{3}, x(\text{H}_{2}\text{O}) \\ \text{H}_{2}\text{O}, 20^{\circ}, 30 \text{ min.} & \text{Ln}(\text{NTf}_{2})_{3}, x(\text{H}_{2}\text{O}) \\ \text{H}_{2}\text{O}, 100^{\circ}, 1 \text{ hour} & \text{Ln}(\text{NTf}_{2})_{3}, x(\text{H}_{2}\text{O}) \end{array}$$

Ln = La, Nd, Yb; x = 0, 1; y = 0, 1

Scheme 1.

was performed from the corresponding acetates, carbonates, or oxides.

From the acetates, 3 equivalent of the very strong acid bis(trifluoromethanesulfonyl)amine:  $H(NTf_2)$  were added and the solution was stirred for 30 min at room temperature. From the carbonates, only 2.75 equivalent of  $H(NTf_2)$  were used and the excess of carbonate was eliminated by filtration after 30 min stirring at room temperature. The reaction with the oxides needed 5.5 equivalent of  $H(NTf_2)$  and 1 h refluxing in water; the excess of acid was removed under vacuum (Scheme 1).

After removal of the water, the salts were dried for 24 h at 110 °C under reduced pressure. The extremely hygroscopic white powders thus obtained were stored in a glove box.

For clarity, the following notation will be used to designate the salts: the symbol of the element is followed by Ac for acetate, Car for carbonate, Ox for oxide. The solvents used for treatment will be designated as follow: water, W; water then ethanol, W/Et; ethanol alone: Et. For example, the lanthanum salt obtained from the acetate in water solution, then treating it with ethanol is called  $[La]_{Ac/W/Et}$ .

The pH of these salts dissolved in distilled water was measured. It is worthy noting that the lanthanum and neodymium salts obtained from the acetates,  $[La]_{Ac/W}$  and  $[Nd]_{Ac/W}$ , remained strongly acidic (pH 3.7). The ytterbium salt,  $[Yb]_{Ac/W}$ , was much less acidic (pH 4.5), whereas the salts obtained from carbonates,  $[La]_{Car/W}$ ,  $[Nd]_{Car/W}$ ,  $[Yb]_{Car/W}$ , or oxides,  $[Yb]_{Ox/W}$ , were near neutral (pH 5.5–6.5).

Thus,  $[La]_{Ac/W}$  and  $[Nd]_{Ac/W}$  contained a significant quantity of acetic acid. This fact was confirmed by <sup>1</sup>H NMR (singlet at 2 ppm in D<sub>2</sub>O) and also by IR spectroscopy (C=O stretching peaks at 1682 and 1672 cm<sup>-1</sup>). The presence of coordinated water in these complexes was also established by IR spectroscopy (peaks at 3450 and 1630 cm<sup>-1</sup> [7]).

The coordination of acetic acid to lanthanum and neodymium was unexpected and precluded the use of the classical method using methylorthoformate [8] to obtain anhydrous salts, formic acid being able to coordinate lanthanides in the same manner as acetic acid.

To obtain anhydrous salts, removal of the water by ethanol was performed; after drying, the salts were dissolved in absolute ethanol and the solution was evaporated under reduced pressure. The operation was repeated three times, and the white powders,  $[Ln]_{Ac/W/Et}$ ,  $[Ln]_{Car/W/Et}$ ,  $[Ln]_{Ox/W/Et}$ (Ln = La, Nd), were finally dried under vacuum for 24 h at 110 °C. All attempts to obtain the ytterbium salts failed, affording viscous brown oils.

The IR spectra of the salts did not show the peaks of water and their <sup>1</sup>H NMR spectra established the absence of coordinated ethanol. The pH of the aqueous solutions was near neutral.

An interesting fact was the absence of the peak at  $1320 \text{ cm}^{-1}$  (S=O stretching) in the spectra of these anhydrous compounds, whereas a strong peak appeared at ca.  $1270 \text{ cm}^{-1}$  (instead of a weak peak in the coordinated compounds). This lowering of the S=O frequency could be attributed to an Ln–O=S coordination in an associated structure.

An attempt to obtain the anhydrous neodymium salt directly by the addition of  $H(NTf_2)$  to a solution of neodymium acetate in ethanol (Scheme 2) afforded a white powder containing coordinated ethanol after work-up.

The <sup>19</sup>F NMR spectra of the isolated salts were recorded in deuteriated acetone. For the CF<sub>3</sub> groups, they all show a unique signal at ca. -78.8 ppm. These values are very close to this reported for the magnesium salt: -78.6 ppm [6] and ca. 1.8 ppm downfield compared to the free bis(trifluoromethanesulfonyl)amine [9]. It is very interesting that the diamagnetic lanthanum and the paramagnetic neodymium and ytterbium salts show the same chemical shift, in accordance with the fact that these complexes were dissociated in solution.

It appears that the structure of the bis(trifluoromethanesulfonyl)amide of the lanthanides depends on the ionic radius of the element and also on the experimental procedure, so quantitative analyses were performed to establish their structure accurately.

$$\text{Ln}(\text{CH}_3\text{CO}_2)_3, \text{n}(\text{H}_2\text{O}) \xrightarrow{3 \text{ HNTf}_2} \text{Ln}(\text{NTf}_2)_3, \text{x}(\text{EtOH})$$

$$\text{EtOH}, 20^\circ, 30 \text{ min.}$$

 Table 1

 Thermal decomposition of the lanthanum and neodymium salts

Compound	Loss (%, 20–150 °C)	Loss (%, 150-330 °C)	Loss (%, 330-450 °C)	Residue (%)
[La] <sub>Ac/W</sub>	0.7	5.57 (200)	76.6 (385; 400)	17.1
[La] <sub>Ac/W/Et</sub>	0.4	0.5	78.7 (394)	20.4
[La] <sub>Car/W/Et</sub>	0.8	1.2	78.0 (374; 404)	19.2
[La] <sub>Ox/W/Et</sub>	0.9 (120)	0.8 (260)	79.2 (391; 411)	19.0
[Nd] <sub>Ac/W</sub>	0.8	7.5 (210)	75.2 (369; 392)	16.5
[Nd] <sub>Ac/W/Et</sub>	1.2 (116)	0.1	77.6 (372; 386)	21.1
[Nd] <sub>Ac/Et</sub>	9 (154)	9 (154)	72.6 (368 388)	18.4
[Nd] <sub>Car/W/Et</sub>	0.6	0.8	81.2 (374; 386)	17.3
[Nd] <sub>Ox/W/Et</sub>	0.4	0.4	81.3 (379)	17.9

200 °C: Temperature corresponding to the maximum of weight loss.

# 2.2. Quantitative analyses

The amount of coordinated water was measured by Karl Fischer titration; the results are in very good accordance with the expected formulae. The  $[Ln]_{Ac/W}$  salts contained ca. 1.8% of water, corresponding to one molecule of coordinated H<sub>2</sub>O, whereas the  $[Ln]_{Ac/W/Et}$  salts were anhydrous (ca. 0.2% of water).

Thermogravimetric analysis was used to characterize the lanthanide triflates [10,11], more particularly to estimate the number of molecules of coordinated water in the adducts and also to study the decomposition process.

Atmospheric water, which is absorbed during the handling of hygroscopic species, is eliminated between 70 and 120 °C, whereas the coordinated molecules of solvent were successively eliminated between 150 and 300 °C. The following step was the decomposition of the salt and finally a stable residue was obtained. The behavior of the lanthanum and neodymium salts is summarized in Table 1. It is clear that the weight loss corresponding to the loss of the coordinated molecules, which occurs in the 150–330 °C range, is in good accordance with the previous results: 1H<sub>2</sub>O and 1CH<sub>3</sub>CO<sub>2</sub>H for  $[La]_{Ac/W}$  and  $[Nd]_{Ac/W}$ , and 2EtOH for  $[Nd]_{Ac/Et}$  (Fig. 1). For the "anhydrous" salts, the plateau



Fig. 1. Thermogram of the Nd[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>OH)<sub>2</sub>: [Nd]<sub>Ac/Et</sub> adduct.



appears as near horizontal, suggesting the presence of a very small amount of coordinated water or of a slow decomposition process.

Rapid decomposition of the salts, resulting in a sharp weight loss, occurred between 360 and 450 °C and proceeded in two steps and a horizontal plateau was obtained after the complete thermal decomposition. X-Ray electron microprobe analysis (EDX analysis) established that the residues were the trifluorides, LaF<sub>3</sub> and NdF<sub>3</sub>. Neither LaOF nor NdOF were detected. These results are very similar to those reported for the ytterbium and lanthanum triflates [10,11]; the fluorides were finally obtained and a two step process was also observed in the thermal decomposition of the ytterbium triflate.

The behavior of the ytterbium salts is different, a decomposition process began at a lower temperature with a maximum at ca. 300 °C and a small amount (2.8%) of residue was finally obtained. Thus, the ytterbium triflimidate is a volatile salt and a sublimation experiment was performed. At 240 °C,  $10^{-2}$  Torr, a microcrystalline product, ([Yb]<sub>Ac/W/</sub>sub), was obtained. The <sup>1</sup>H and <sup>19</sup>F NMR spectra of this product were identical to those of [Yb]<sub>Ac/W</sub> and the analysis corresponded to the anhydrous salt. The easy sublimation of this salt establishes the existence (at least at the sublimation temperature) of a monomeric form. This is a new class of volatile fluorinated lanthanide complexes; generally volatile lanthanides containing fluorine are  $\beta$ -diketonates [12] or alkoxides [13].

All these results allow the attribution of the following formulae for these salts.

- 1. For the salts obtained from the acetates:  $Ln[N(SO_2-CF_3)_2]_3(H_2O)(CH_3CO_2H)$  (Ln = La, Nd).
- 2. For the neodymium salt obtained in ethanol: Ln[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>(CH<sub>3</sub>CH<sub>2</sub>OH)<sub>2</sub>.
- For the anhydrous salts: {Ln[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>}<sub>x</sub> (Ln = La, Nd).
- 4. For the ytterbium salt obtained in water: Yb[N(SO<sub>2</sub>-CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>·H<sub>2</sub>O.
- 5. For the sublimated ytterbium salt:  $Yb[N(SO_2CF_3)_2]_3$ .

# 2.3. Reactivity

The catalytic activity of the lanthanide triflimidates has been tested in Friedel–Crafts acetylation of anisole. This reaction has been performed in a acetic acid–acetic anhydride mixture, rather than the very hazardous nitromethane [3] with 1% or less of catalyst [14]. Only a weak loss of reactivity is observed when monohydrated salts or crude salts containing acetic acid are used instead of the anhydrous salt. In the same conditions, phenetole afforded ethoxyacetophenone in similar yield.

The Fries transposition of  $\alpha$ -naphthyl acetate was also investigated (Scheme 3). It had previously been reported that scandium triflate (5 mol.%) was an efficient catalyst for this reaction, whereas lower yields were obtained with ytterbium triflate [15]. The catalytic activity of ytterbium triflimidate, [Yb]<sub>Ac/W</sub>, neodymium triflimidate, [Nd]<sub>Ac/W/Et</sub>, and ytterbium triflate, Yb(OTf)<sub>3</sub>, were compared (Table 2); Ytterbium triflate is a better catalyst than ytterbium triflate affording 70% versus 45% of 2-hydroxyacetonaphthone and also than neodymium triflimidate (15% yield).

Lanthanide triflates are known to catalyze the Baeyer– Villiger oxidation [16]. Ytterbium triflimidate is also a good catalyst, giving similar yields (98 versus 95%) in the oxidation of cyclohexanone or 4-methylacetophenone.

Cerium(IV) triflate was widely used to oxidize toluene, alkyl benzenes or benzylic alcohols to give the corresponding aldehydes [17–19]. These reactions need at least 2

Table 2

Yields in Fries transposition with ytterbium and neodymium triflimidates and ytterbium triflate as  $catalysts^a$ 

Catalyst	2-Hydroxyacetonaphthnone yield (%)	α-Naphthol yield (%)
NdAcW/Et	15	8
YbAcW	70	18
Yb(Otf) <sub>3</sub>	45	5

 $^a$  5 mol.% catalyst, 1 M solution of  $\alpha\text{-naphthyl}$  acetate in toluene, 24 h refluxing.



Scheme 4.

equivalents of cerium salt. Unexpectedly, a small amount of cerium(IV) triflimidate catalyzes the oxidation of 4-methylacetophenone to give 4-methylbenzoic acid (Scheme 4). The best results (85% yields) are obtained with 10% of salt and 3 equivalents of H<sub>2</sub>O<sub>2</sub>. Other aromatic ketones: 4-nitroacetophenone, 1,4-diacetylbenzene, propiophenone, give also the corresponding acids.

# 3. Conclusion

The synthetic results are in good accordance with the decreasing ability, connected to the decreasing ionic radius of the lanthanides, of coordinating ancillary ligands: large lanthanum or neodymium are able to coordinate two molecules of a solvent and, after removal of this solvent, the anhydrous salts only exist in an associated non-sublimable form. On the contrary, the small ytterbium coordinates only one molecule of water. By heating, this adduct gives a monomeric anhydrous salt.

As expected, these salts are efficient catalysts for reactions usually catalyzed by Lewis acids, the presence of a small amount of coordinated water having only a small effect on their catalytic activity. The lanthanum salt, less soluble than its neodymium or ytterbium analogues, is also less efficient. But the most interesting reaction is the selective oxidation of aromatic ketones catalyzed by the cerium salt. This reaction is currently being investigated and complete results will soon be published.

# 4. Experimental

# 4.1. General experimental procedures

# 4.1.1. Analytical techniques

The handling and storage of the hygroscopic materials were performed in a Jacomex glove box under purified argon atmosphere.

The infrared spectra were recorded in nujol mulls on a Bruker IFS 66V spectrometer. The <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded on a Bruker AC 300 apparatus in D<sub>2</sub>O or CDCl<sub>3</sub>. The elemental analyses were carried out on a Fisons Instruments EA 1108 CHNS-O. The Karl Fischer analyses were performed by using a Metrohm KF 684 coulometer. The thermogravimetric analyses were performed by using a TA Instruments 2960 apparatus at a heating rate of 20 °C/min under nitrogen atmosphere or under atmospheric conditions. The EDX analyses were performed by using an Oxford EDX microprobe coupled to a Jeol JSM 6400F scanning electron microscope. The composition and yields of the reaction products were determined with a Fisons Instruments GC 9000 gas chromatograph equipped with a flame ionization detector a data jet integrator and a  $30 \text{ m} \times 0.53 \text{ mm}$  OV 624 or a  $50 \text{ m} \times 0.32 \text{ mm}$  HP-FFAP capillary column.

#### 4.1.2. Materials

The bis(trifluoromethanesulfonyl)amine was supplied by Rhodia Chemical and purified by sublimation (50 °C, 0.1 Torr) before use. The lanthanide acetates, carbonates, oxides and triflates were supplied by Rhodia Chemical and used without any further purification. Anisole,  $\alpha$ -naphthyl acetate, cyclohexanone, 4-methylacetophenone were purchased from Aldrich and used without purification.

#### 4.2. Syntheses of bis(trifluoromethanesulfonyl)amides

# 4.2.1. From the acetates: $La[N(SO_2CF_3)_2]_3$ ( $H_2O$ )( $CH_3CO_2H$ ) [La]<sub>Ac/W</sub>

An amount of 2.44 g (6.96 mmol) of lanthanum acetate hydrate were dissolved in 5 ml water, 5. 87 g (20.88 mmol) of bis(trifluoromethanesulfonyl)amine were added and the solution was stirred for 30 min. After removal of the water, the viscous oil was dried for 24 h at 110 °C under vacuum  $(10^{-2}$  Torr). The white powder (7.20 g, 98% yield) was stored in the glove box.

 $Nd[N(SO_2CF_3)_2]_3 \cdot H_2O(CH_3CO_2H)$  and  $Yb[N(SO_2-CF_3)_2]_3 \cdot H_2O$  were obtained in the same manner.

# 4.2.2. $\{La[N(SO_2CF_3)_2]_3\}_x$ : $[La]_{Ac/W/Et}$

The crude product obtained after the removal of water, as above, was dissolved in 20 ml ethanol, after 10 min stirring, the solvent was evaporated and the residue was dried for 2 h at room temperature under vacuum. The operation was repeated two times and the salt was finally dried under vacuum for 24 h at 110 °C to give 6.45 g and 95% yield of white powder.

Analytically calculated for  $C_6O_{12}N_3S_6F_{18}La$ : C, 7.35; N, 4.29; S, 19.61; Found: C, 6.95; N, 4.53; S, 19.48. {Nd[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub>}<sub>x</sub> was obtained in the same manner.

# 4.2.3. Nd[N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>]<sub>3</sub> (CH<sub>3</sub>CH<sub>2</sub>OH)<sub>2</sub>: [Nd]<sub>Ac/Et</sub>

To a stirred suspension of 1.70 g (5 mmol) of neodymium acetate hydrate in 20 ml ethanol, 4.22 g (15 mmol) of bis-(trifluoromethanesulfonyl)amine were added at room temperature. After 30 min stirring, the solution was evaporated and the residue was dried under vacuum for 2 h at room temperature, then for 24 h at 110 °C. The 5.22 g, 97% yield of white powder were obtained.

#### 4.2.4. From the carbonates (general procedure)

To a stirred suspension of 1 g (2.2 mmol) of lanthanum carbonate,  $La_2(CO_3)_6$ , in 5 ml water, 3.42 g (12.2 mmol) of bis(trifluoromethanesulfonyl)amine were added at room temperature. After 30 min stirring, the excess of carbonate was filtered out and the solution was evaporated, then treated as above to obtain  $[La]_{Car/W}$ ,  $[Nd]_{Car/W}$ ,  $[Yb]_{Car/W}$ ,  $[La]_{Car/W/Et}$ , and  $[Nd]_{Car/W/Et}$ .

# 4.2.5. From the oxides (general procedure)

To a stirred suspension of 1 g (3.06 mmol) of lanthanum oxide,  $La_2O_3$ , in 10 ml water, 4.78 g (17 mmol) of bis(trifluoromethanesulfonyl)amine were added and the mixture was refluxed for 1 h. The clear solution was evaporated, then treated as above to obtain  $[Yb]_{Ox/W}$ ,  $[La]_{Ox/W/Et}$ , and  $[Nd]_{Ox/W/Et}$ .

# 4.3. Reactivity

#### 4.3.1. Acetylation of anisole (general procedure)

In the glove box, 50.6 mg (0.05 mmol) of  $Nd(NTf_{2})_3$  ([Nd]<sub>Ac/W/Et</sub>) were weighed in a 50 ml vessel. The vessel was connected to a nitrogen inlet; anisole: 0.54 g (5 mmol), acetic anhydride: 2.83 g (30 mmol) and acetic acid: 2.77 g (46.2 mmol) were added with a syringe and the mixture was magnetically stirred at 120 °C for 3 h. After cooling, 20 ml of diethyl ether were added and the solution was washed with a saturated solution of sodium hydrogen carbonate until neutral. The organic layer was dried over magnesium sulfate and the solvent was removed. A sample was taken and analyzed by GC. Yield ca. 95%.

# 4.3.2. Fries transposition of $\alpha$ -naphthyl acetate

In the glove box, 414 mg (0.4 mmol) of Yb(NTf<sub>2</sub>)<sub>3</sub> ([Yb]<sub>Ac/W</sub>) were weighed in a 50 ml vessel, 1.52 g (8.18 mmol) of  $\alpha$ -naphthyl acetate and 4 ml of toluene were added and the mixture was refluxed for 24 h. CG analysis: 2hydroxyacetonaphthone, 70% yield,  $\alpha$ -naphthol, 18% yield.

#### 4.3.3. Baeyer–Villiger oxidation of cyclohexanone

In the glove box, 196 mg (0.19 mmol) of Yb(NTf<sub>2</sub>)<sub>3</sub> ([Yb]<sub>Ac/W</sub>) were weighed in a 50 ml vessel, 185 mg (1.9 mmol) of cyclohexanone, 654 mg (3.8 mmol) of metachloroperbenzoic acid (MCPBA) and 10 ml of dichloromethane were stirred for 2 h at room temperature. GC analysis:  $\alpha$ -caprolactone, 98% yield.

# *4.3.4. Oxidation of 4-methylacetophenone by cerium triflimidate*

In the glove box, 203 mg (0.16 mmol) of  $Ce(NTf_2)_x$  were weighed in a 50 ml vessel; 210 mg (1.57 mmol) of 4-methylacetophenone and 16 ml of acetic acid were added and the mixture was stirred and refluxed under atmospheric pressure of oxygen. After 30, 60 and 90 min, 20 µl of H<sub>2</sub>O<sub>2</sub> (30 wt.%) are added for a total amount of 0.5 mmol. After 6 h, the solvent was evaporated under reduced pressure, the residue was subsequently dissolved in 25 ml of diethyl ether. A sample was taken and analyzed by GC after esterification of the 4-methylbenzoic acid with trimethylchlorosilane, 85% yield.

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