

Lanthanide(III) Tosylates as New Acylation Catalysts

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Lanthanide(III) complexes of *p*-toluenesulfonic acid ($\text{Ln}(\text{TOS})_3$) were prepared, characterized, and examined as catalysts for the acetylation of various alcohols in acetic acid solution. Examination of a series of $\text{Ln}(\text{TOS})_3$ catalysts in the acetylation of 2-phenylethanol revealed a clear correlation between the ionic radius of the lanthanide(III) ion and the yield of the reaction, with the heavier lanthanides being more effective. In the presence of 5 mol-% of $\text{Yb}(\text{TOS})_3$, a quantitative conversion of phenethyl alcohol to phenethyl acetate was achieved within 18 hours at 50 °C. Faster reaction was obtained under reflux conditions, in which case acetylation

was complete within 30 minutes and in the presence of only 2 mol-% of the $\text{Yb}(\text{TOS})_3$ catalyst. The $\text{Yb}(\text{TOS})_3$ catalyst was effective for acetylation of a range of primary, secondary, and tertiary alcohols. The $\text{Yb}(\text{TOS})_3$ catalyst was also effective for acylation of phenethyl alcohol with propionic acid and cyclohexanecarboxylic acid. The catalysts could be easily recovered and reused for further acetylation, with no apparent change in selectivity or efficiency.

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Introduction

The acetylation (or acylation in general) of hydroxyl groups is one of the most frequently used synthetic procedures in organic chemistry.^[1] Acetylation of alcohols is frequently performed with acid anhydride or acetyl chloride, in the presence of a basic catalyst such as triethylamine, pyridine, 4-(dimethylamino)pyridine, 4-pyrrolidinopyridine, or *N,N,N',N'*-tetramethylethylenediamine.^[2–4] Alternatively, various Lewis acid catalysts including zinc chloride, magnesium bromide, cobalt(II) chloride, chlorotitanium(IV) tris(trifluoromethanesulfonate), diorganotin dichloride, and tantalum(V) chloride, among others, could be applied.^[5–9] Although the Lewis acids are usually very efficient acylation catalysts, they have some major drawbacks: they need to be used in stoichiometric amounts, they are easily deactivated by water, and they cannot be recycled or reused.

An alternative approach is the use of ionic liquid solvents as media for Lewis acid-catalyzed acetylation. The development of “recyclable” ionic catalyst solutions offers new possibilities for “green” chemistry in the search for better alternatives to acid-/base-catalyzed reactions.^[10]

In recent years, various trifluoromethanesulfonates (so-called triflates) such as ytterbium(III) triflate,^[11] lanthanum(III) triflate,^[11] cerium(III) triflate,^[12] copper(II) triflate,^[13] scandium(III) triflate,^[11a,14] erbium(III) triflate,^[15] indium(III) triflate,^[16] and bismuth(III) triflate^[17] have been

described as efficient catalysts for the acetylation of various alcohols in the presence of acetic acid, acetic anhydride, or acetyl chloride. An important property of triflate salts is their compatibility with water and other protic solvents. After workup, the catalysts can be easily recycled and reused without significant loss of activity. However, the disadvantages of triflate salts include their relatively high cost and the fact that one needs to handle the corrosive triflic acid for their preparation.

In pursuit of lanthanide(III) catalysts that would not require the use of hazardous or costly compounds, we recently examined lanthanide(III) salts of noncorrosive aromatic sulfonic acids, such as *p*-toluenesulfonic acid and nitrobenzenesulfonic acids, as catalysts for the nitration of aromatic compounds.^[18–20] The aromatic sulfonic acids are much weaker acids than triflic acid, (*p*-toluenesulfonic acid, for example, is about 10^6 times weaker acid than triflic acid),^[21] and their complexes with lanthanides would therefore be expected to be significantly weaker Lewis acids than the lanthanide(III) triflates. Surprisingly, we found that their catalytic efficiency was comparable to that of the triflate salts.^[18–20] This prompted us to exploit the advantages of lanthanide(III) *p*-toluenesulfonate complexes (usually referred to as lanthanide(III) tosylates) over lanthanide(III) triflates, which include much cheaper costs and easier handling, and to explore lanthanide(III) tosylates further as catalysts for other types of organic reactions. In this study we demonstrate that lanthanide(III) tosylates can be used as efficient, inexpensive, recyclable, and environmentally friendly catalysts for the acetylation (and acylation in general) of various alcohols.

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Results and Discussion

Synthesis and Characterization of the Catalysts

Structural and thermal studies of lanthanide(III) tosylates (Figure 1) showed that complexes of this type initially crystallize with nine water molecules in the first coordination sphere, and that seven water molecules are lost upon heating to circa 55 °C.^[22] Since the coordination number of the trivalent lanthanide ion is commonly eight or nine, it has been suggested that the coordination mode of the sulfonate anions changes upon removal of the hydrated water molecules from the crystal, so that they act as multidentate ligands forming more metal–oxygen bonds in order to replace the removed water oxygen atoms in the first coordination sphere of the lanthanide(III) ion. The elemental analysis results of lanthanide(III) tosylate catalysts (see Experimental Section) indicated that some water of crystallization is lost upon drying of the crystalline solid at 50 °C in vacuo, but that the complexes still contain one to three molecules of water. Consequently, infrared spectra of the complexes showed strong and broad absorption in the 3200–3600 cm^{−1} region, corresponding to the –OH stretching frequency of water molecules.

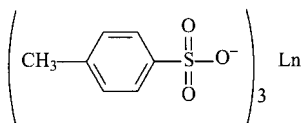
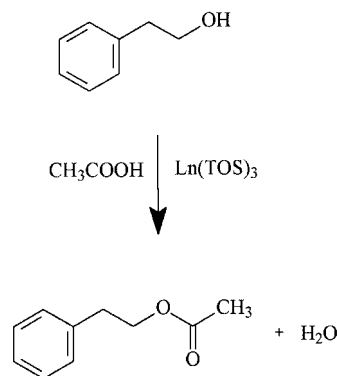


Figure 1. Chemical structure of Ln(TOS)₃ complexes.

Because it is known that *p*-toluenesulfonic acid is itself capable of promoting acylation reactions^[23] it is important to demonstrate the absence of trace amounts of free *p*-toluenesulfonic acid in the lanthanide(III) catalyst. The infrared spectra of lanthanide(III) complexes showed that the broad absorption between 2400 and 3100 cm^{−1}, typical of the OH stretching mode of protonated *p*-toluenesulfonic acid,^[24] was absent. Furthermore, aqueous solutions of lanthanide(III) complexes always had close to neutral pH, which further confirms the absence of free *p*-toluenesulfonic acid in the isolated catalysts.

Screening of the Lanthanide(III) Catalysts

In order to optimize the rate of the acylation reaction, a range of lanthanide(III) tosylates were examined as potential catalysts. The reaction we chose for the initial screening of the catalytic activity of the lanthanide(III) tosylates was the acetylation of phenethyl alcohol (2-phenylethanol) (Scheme 1) in acetic acid as the solvent. The use of acetic acid rather than acetyl chloride or acetic anhydride is both economically and environmentally beneficial.



Scheme 1.

As can be seen in Figure 2, all complexes exhibited catalytic activity, but noticeable differences in reactivity were observed. While lanthanum(III) tosylate gave only 26% conversion of phenethyl alcohol to phenethyl acetate after 18 hours of reaction at 50 °C, ytterbium(III) tosylate and erbium(III) tosylate yielded quantitative conversion under the same conditions.

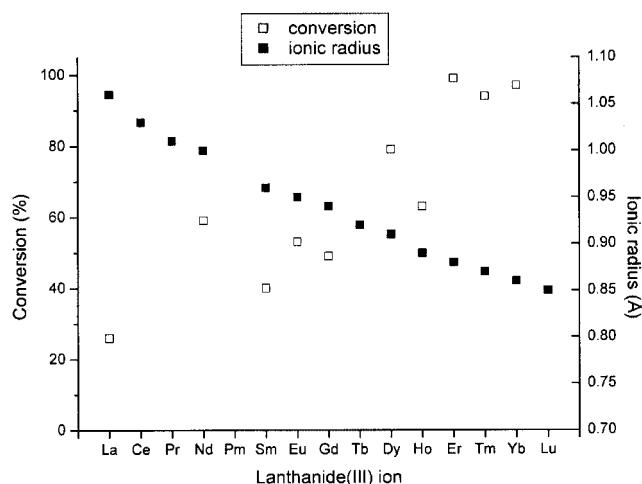


Figure 2. Effect of the lanthanide(III) ion in the tosylate salt on the catalyzed conversion of phenethyl alcohol into phenethyl acetate in the presence of acetic acid. The ionic radii of the lanthanide(III) ions are shown for comparison.

Apart from some scattered data points, there is a clear inverse correlation between the ionic radii of the lanthanide(III) ion and the yield of the acetylation reaction. Previous studies involving reactions catalyzed by lanthanide(III) triflates have revealed a similar trend.^[25] The smaller ionic radius of trivalent lanthanide ion leads to a greater charge to size ratio (Z/r), which in turn results in greater polarizing power of the lanthanide(III) center.

Effects of Reaction Time, Temperature, and Amount of Catalyst on the Extent of Acetylation

In order to optimize the catalytic reaction further, we first examined the effects of temperature and reaction time on the acylation reaction. Since the screening of the series

of lanthanide(III) catalysts had shown that ytterbium(III) tosylate was the most effective, all further acetylation experiments were performed with this catalyst. As can be seen in Table 1, acetylation of phenethyl alcohol was rather slow at room temperature, most probably due to the low solubility of the catalysts in acetic acid. Upon increasing the temperature to 50 °C, nearly quantitative conversion was achieved within 18 hours. The fastest reaction was obtained under reflux conditions, in which case acetylation was essentially complete in the time taken to bring the reaction mixture to reflux.

Table 1. Effects of temperature and reaction time on the acetylation of phenethyl alcohol with acetic acid in the presence of ytterbium(III) tosylate.^[a]

Yb(TOS) ₃ (mol-%)	Time (h)	T (°C)	Conversion (%) ^[b]
5	24	room temp.	35
—	24	room temp.	3
5	18	50	97
—	18	50	23
5	1	80	64
—	1	80	5
5	0.5	reflux	>98
—	0.5	reflux	39

[a] 1 mmol of phenethyl alcohol in 2 mL of acetic acid. [b] Determined by GC.

The acetylation reaction in the presence and in the absence of the catalyst was followed as a function of time, and the results shown in Figure 3 are consistent with pseudo-first order kinetics with one of the reactants (i.e., acetic acid) present in large excess. Fitting of the data revealed that the catalyzed reaction was at least an order of magnitude faster than the reaction run in the absence of the catalyst.

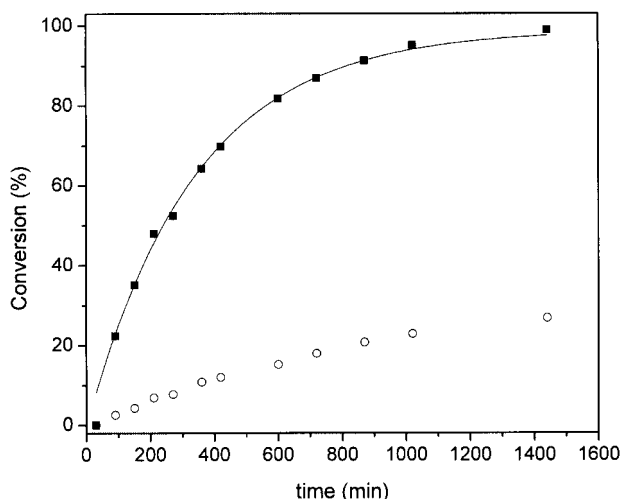


Figure 3. Conversion of phenethyl alcohol into phenethyl acetate in the presence of 5 mol-% of Yb(TOS)₃ (black squares) and in the absence of the catalyst (open circles). The fitting of the results for the catalyzed reaction yielded pseudo-first-order rate constant of $3.0 \times 10^{-3} \text{ min}^{-1}$.

Acylation of Alcohols Catalyzed by Yb(TOS)₃

The applicability of the acetylation reaction catalyzed by Yb(TOS)₃ was tested for different alcohols as the substrate. All acetylation reactions were performed with acetic acid acting both as the substrate and as the solvent. Treatment of an alcohol with acetic acid was performed at reflux temperature, in the presence of 5 mol-% of the catalyst. After the reaction mixture had been brought to reflux (approximately 30 minutes), the reaction was quenched by the addition of water and dichloromethane and the products were analyzed by gas chromatography or by ¹H NMR spectroscopy. As can be seen in Table 2, the acetylation of primary alcohols proceeded quantitatively under these conditions. As would be expected, the acetylation of secondary and tertiary alcohols was slower, and required longer reaction times for completion. It is also worth mentioning that no elimination products were observed.

Table 2. Acetylation of alcohols with acetic acid catalyzed by ytterbium(III) tosylate.^[a]

Alcohol or phenol	Yb(TOS) ₃ (mol-%)	Conversion (%) ^[b]
1-phenylethanol	5	>98
—	—	26
2-phenylethanol	5	>98
—	—	39
tetrahydropyran-2-methanol	5	>98
—	—	35
3-bromo-3-buten-1-ol	5	>98
—	—	28
benzyl alcohol	5	94
—	—	42
cyclohexanol	5	51
—	—	14
octan-1-ol	5	>98
—	—	33
octan-2-ol	5	62
—	—	12
butan-1-ol	5	95
—	—	37
butan-2-ol	5	74 ^[c]
—	—	29 ^[c]
adamantan-1-ol	5	76 ^[d]
—	—	trace ^[d]
phenol	5	43 ^[d]
—	—	2 ^[d]

[a] 1 mmol of alcohol in 2 mL of acetic acid, at reflux for 30 minutes. [b] Determined by GC and/or ¹H NMR. [c] At reflux for 1 hour. [d] At reflux for 18 hours.

Besides acetylation in acetic acid solutions, Yb(TOS)₃ was also an effective catalyst for the acylation of phenethyl alcohol in propionic acid and in cyclohexanecarboxylic acid solutions, although the latter reactions were somewhat slow, but could be completed within one or two hours (Table 3).

The effect of catalyst concentration on the reaction yields was examined for the acetylation reaction of phenethyl alcohol. Only 2 mol-% of the Yb(TOS)₃ catalyst in acetic acid solution were sufficient for the quantitative conversion of phenethyl alcohol into phenethyl acetate within 30 minutes. (Table 4).

Table 3. Acylation of phenethyl alcohol with carboxylic acids catalyzed by ytterbium(III) tosylate.^[a]

Acid	Yb(TOS) ₃ (mol-%)	Conversion (%) ^[b]	
		50 °C, 18 h	120 °C, 30 min
acetic acid	5	>98	>98
	–	23	39
propionic acid	5	67	86
	–	11	20
cyclohexane-carboxylic acid	5	49	59
	–	9	12

[a] 1 mmol of phenethyl alcohol in 2 mL of acid. [b] Determined by GC and/or ¹H NMR spectroscopy.

Table 4. The effect of the ytterbium(III) tosylate loading on the acetylation of phenethyl alcohol with acetic acid.^[a]

Catalyst load (mol-%)	Conversion (%) ^[b]
None	39
0.1	73
0.2	74
0.5	81
1	89
2	>98
5	>98

[a] 1 mmol of phenethyl alcohol in 2 mL of acetic acid, at reflux for 30 minutes. [b] Determined by GC.

Recovery and Reuse of the Yb(TOS)₃ Catalyst

Upon quenching of the reaction by addition of dichloromethane and water, the catalysts could easily be recovered from the aqueous phase by evaporation of the solvent under reduced pressure. The FT-IR spectra of the recycled catalysts were identical to spectra of freshly prepared Yb(TOS)₃. In addition, in the experiments performed with diamagnetic La(TOS)₃, the ¹H NMR spectra of the recovered catalysts were identical to the spectrum of freshly prepared La(TOS)₃. The recovered catalysts were shown to be active for further acetylation reaction with no apparent change in selectivity or in efficiency (Table 5). Because the catalyst was very effective for acetylation at a loading of only 2 mol-%, it is not surprising that the reaction goes to completion even after some loss of the catalyst during recycling.

Table 5. Recovery of ytterbium(III) tosylate after acetylation of phenethyl alcohol.^[a]

Run	Conversion (%) ^[b]	Recovery of catalyst (%)
1	>98	91
2	>98	84
3	>98	71

[a] 1 mmol of phenethyl alcohol in 2 mL of acetic acid, at reflux for 30 minutes, with 5 mol-% of Yb(TOS)₃ in the first run.

Postulated Mechanism for the Yb(TOS)₃-Catalyzed Acylation

Our initial work on lanthanide(III) tosylate and lanthanide(III) nosylate catalysts was mostly focused on nitrations of aromatic compounds.^[18–20] During the course of these

studies we discovered that the lanthanum(III) complexes, despite their much smaller polarizabilities, were more efficient catalysts than the corresponding ytterbium(III) complexes.^[18,20] Intriguingly, the reactivity trend observed in the acylation reactions is exactly the opposite: Yb(TOS)₃ is a more effective catalyst than La(TOS)₃. How can these findings, which on the first glance may seem contradictory, be rationalized?

The X-ray single-crystal structures of most of the lanthanide(III) tosylates have been reported, and they indicate distinct structural differences across the lanthanide(III) series.^[22,26] For example, in the La(TOS)₃·9H₂O complex, nine water molecules occupy the first coordination sphere and the tosylate counterions are merely spectator ions located in the second coordination sphere.^[26] In contrast, the structure of Yb(TOS)₃ is markedly different: the coordination environment around the ytterbium(III) is occupied by two oxygen atoms from the sulfonate group of TOS and six oxygen atoms from water molecules.^[22] The third TOS anion is not located in the first coordination sphere, but forms hydrogen bonds with one of the coordinated water molecules. Solution studies of Ln(TOS)₃ complexes have indicated that the solid-state structure is preserved in solution in noncoordinating or weakly coordinating solvents.^[27] This suggests that, in noncoordinating solvents, the interaction between the ytterbium(III) and the incoming substrate may be hindered through the steric hindrance associated with the bulky coordinated TOS ligands. Therefore, for reactions performed in noncoordinating solvents, (such as, for example, nitration of arenes), Yb(TOS)₃ is not the best catalyst. In the case of La(TOS)₃ this steric hindrance is absent and the interaction between the metal center and the substrate is facilitated. However, in strongly coordinating solvents such as water, the structures of all lanthanide(III) tosylates are the same, since the coordinating solvent replaces TOS ligand from the first coordination sphere.^[27]

The question, then, is what the structures of Ln(TOS)₃ complexes in acetic acid solutions are. In order to elucidate this problem, we recorded the ¹H NMR spectrum of Eu(TOS)₃ in deuterated acetic acid solution. X-ray single-crystal structures of Eu(TOS)₃ shows that this complex is isostructural with Yb(TOS)₃, so the coordination environment around the europium(III) is occupied by two oxygen atoms from the sulfonate group of TOS and six oxygen atoms from water molecules.^[28] Previous NMR studies of europium(III) complexes have revealed that this structure is preserved in weakly coordinating solvents so that the two sulfonate ligands bound to europium(III) each exhibited a large paramagnetic shift, while the third ligand appeared at the same chemical shifts as the fully dissociated sulfonic acid, implying that there was no binding to the lanthanide(III) ion.^[20] In acetic acid solution, however, only one set of proton resonances appeared in the region between 6.8 and 7.2 ppm typical of the fully dissociated *p*-toluenesulfonic acid (Figure 4). The ¹H NMR spectrum was taken over a large proton resonance range (from –30 to +30 ppm), and no presence of paramagnetically shifted protons was detected. This indicates that in acetic acid solution the tos-

ylate ligands are removed to the second coordination sphere and that the first coordination sphere around europium(III) is occupied by acetic acid ligands. It is reasonable to assume that other $\text{Ln}(\text{TOS})_3$ complexes also undergo this ligand substitution upon being dissolved in acetic acid.

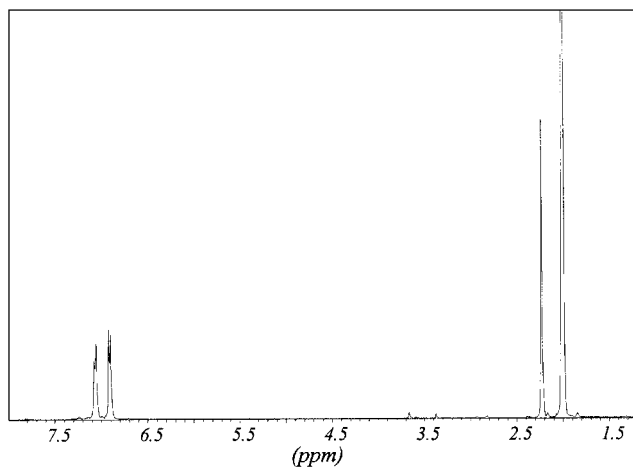


Figure 4. Proton NMR spectrum of $\text{Eu}(\text{TOS})_3$ in $[\text{D}_3]\text{acetic acid}$ solution at 80°C . The large peak at $\delta = 2.08$ ppm belongs to the solvent $[\text{D}_3]\text{acetic acid}$.

Since the acylation experiments have shown that there is a correlation between the charge to size ratio (Z/r) and the catalytic activity, there is obviously an interplay between the lanthanide(III) ion and acetic acid, in which an increasing electrostatic interaction results in greater reactivity. The mechanism can be postulated as follows: upon displacement of TOS and water molecules from the inner coordination sphere by acetic acid, the resulting strong polarization due to the lanthanide(III) ion results in polarization of the carbonyl group. This polarization increases the electrophilicity of the carbonyl carbon, making it more susceptible to nucleophilic attack by the oxygen atom of the alcohol. In this way an oxonium ion is formed, and this further reacts in classical manner to produce an ester. Thus, the experimentally observed correlation between the increasing charge to size ratios and the extent of esterification can be rationalized by noting that the nucleophilic attack of the alcohol becomes more facile as the metal becomes more polarizing.

Conclusions

In summary, we have demonstrated that efficient lanthanide(III) acylation catalysts can be easily prepared from noncorrosive and relatively inexpensive *p*-toluenesulfonic acid. Although the acidity of *p*-toluenesulfonic acid is about 10^6 times weaker than that of triflic acid, its complexes with lanthanide(III) ions are strong Lewis acids able to catalyze the acylation of alcohols with comparable efficiency. The use of *p*-toluenesulfonic acid over triflic acid for the preparation of lanthanide(III) catalysts is both environmentally and economically advantageous.

Experimental Section

Materials and Methods: Reagents were obtained from Aldrich Chemical Co. Inc., Acros Organics, or Rhodia Electronics and Catalysis, and were used without further purification. ^1H NMR spectra were run on a Bruker Avance 300, operating at 300 MHz. GC analyses were performed at ThermoFinnigan Trace GC. Elemental analysis was performed on a CE Instruments EA-1110 elemental analyzer.

General Procedure for the Synthesis of $\text{Ln}(\text{TOS})_3$ Complexes: The tosylate complexes were synthesized by the reaction of 1.1 equivalent of the corresponding lanthanide(III) oxide with six equivalents of *p*-toluenesulfonic acid in water. After the solution had been stirred in boiling water for 30 minutes, the excess of oxide was removed by filtration. The filtered solution was either left to crystallize or was evaporated to dryness and the resulting solid was dried in a vacuum oven at 50°C overnight.

Elemental Analysis Results for $\text{Ln}(\text{TOS})_3 \cdot x\text{H}_2\text{O}$: $\text{La}(\text{TOS})_3 \cdot 3\text{H}_2\text{O}$ ($\text{C}_{21}\text{H}_{27}\text{S}_3\text{O}_{12}\text{La}$) calcd. (found): C 35.70 (35.68), H 3.85 (3.76) %. $\text{Nd}(\text{TOS})_3 \cdot 2\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{25}\text{S}_3\text{O}_{11}\text{Nd}$) calcd. (found): C 36.47 (36.76), H 3.65 (3.36) %. $\text{Sm}(\text{TOS})_3 \cdot 3\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{27}\text{S}_3\text{O}_{12}\text{Sm}$) calcd. (found): C 35.05 (34.79), H 3.78 (3.73) %. $\text{Eu}(\text{TOS})_3 \cdot 3\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{27}\text{S}_3\text{O}_{12}\text{Eu}$) calcd. (found): C 35.00 (35.35), H 3.78 (3.74) %. $\text{Gd}(\text{TOS})_3 \cdot 3\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{27}\text{S}_3\text{O}_{12}\text{Gd}$) calcd. (found): C 34.76 (34.60), H 3.75 (3.70) %. $\text{Dy}(\text{TOS})_3 \cdot 2\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{25}\text{S}_3\text{O}_{11}\text{Dy}$) calcd. (found): C 35.34 (35.54), H 3.53 (3.30) %. $\text{Ho}(\text{TOS})_3 \cdot 3\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{27}\text{S}_3\text{O}_{12}\text{Ho}$) calcd. (found): C 34.43 (34.45), H 3.72 (3.62) %. $\text{Er}(\text{TOS})_3 \cdot 2\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{25}\text{S}_3\text{O}_{11}\text{Er}$) calcd. (found): C 35.25 (35.50), H 3.52 (3.87) %. $\text{Tm}(\text{TOS})_3 \cdot 2\text{H}_2\text{O}$, ($\text{C}_{21}\text{H}_{25}\text{S}_3\text{O}_{11}\text{Tm}$) calcd. (found): C 35.10 (35.13), H 3.51 (3.30) %. $\text{Yb}(\text{TOS})_3 \cdot \text{H}_2\text{O}$ ($\text{C}_{21}\text{H}_{23}\text{S}_3\text{O}_{10}\text{Yb}$) calcd. (found): C 35.75 (35.63), H 3.29 (3.69) %.

General Procedure for the $\text{Ln}(\text{TOS})_3$ -Catalyzed Acylation of Alcohols: The alcohol (1 mmol) was added to a solution of the respective lanthanide(III) catalyst (5 mol-%, 0.05 mmol) in glacial acetic acid (2 mL). The mixture was stirred and heated at reflux. After a given period of time the solution was cooled and diluted with water and with dichloromethane. The organic phase was dried with MgSO_4 , the solvent was evaporated, and the residue was analyzed by ^1H NMR or gas chromatography.

Acknowledgments

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