

Review

# Erbium Salts as Non-Toxic Catalysts Compatible with Alternative Reaction Media

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**Abstract:** Green catalysts must be non-toxic, easy to manage, able to be recovered and reused, active under alternative reaction conditions and cheap. Erbium salts meet all the previously listed characteristics and today they are emerging as a valuable catalytic solution to a number of organic transformations needing a Lewis acid catalyst in wet conditions or under alternative heating sources. This review aims to summarize the application of erbium salts in green organic transformations, with particular emphasis on their versatility under both homogeneous and heterogeneous conditions. The erbium salts' role in bifunctional catalysis is also presented.

**Keywords:** erbium chloride; erbium triflate; Lewis acid catalyst; bifunctional catalysts

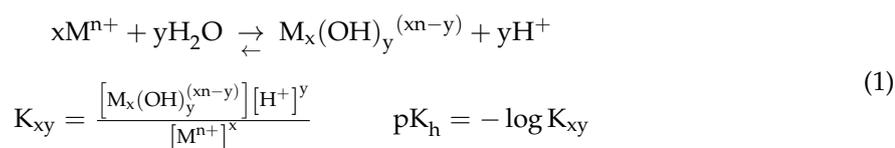
## 1. Introduction

Erbium is a lanthanide, a rare earth element originally separated by Mosander from the gadolinite mine in the Swedish town of Ytterby, from which it inherited its name, in 1848 [1].

You can find this and other information about erbium in the review published by Procopio et al. [2] about a decade ago. However, it is worth mentioning at least some of the peculiar chemical characteristics of this element here.

Lanthanide salts gained great importance as Lewis acids in green organic chemistry because of their stability and their low to moderate toxicity [3]. In the specific case of erbium, some observations reported in the literature make it preferable to other lanthanides.

Erbium(III) turned out to be one of the most active lanthanoid(III) derivatives, both in organic solvents and in water or wet solvents. Lewis acidity in dry organic solvents can be inferred by a study which evaluated the relative Lewis acidity of rare earth metal triflates from their competitive ligand dissociation from complexes by mass spectrometry. In that same study, Er(III) displayed a good Lewis acidity, slightly lower than that of Ytterbium, and a clear oxophylicity [4]. The behaviour of Er(III) salts in water has been extensively studied in terms of coordination number, exchange rate constant and hydrolysis constant [5–9]. Er<sup>3+</sup>, generated by the dissociation of erbium salts in water, coordinates water molecules with a coordination number of 8 [5,6]. The water molecules in the coordination sphere can be exchanged with other ligands, i.e., organic solvent molecules or reaction substrates. Alternatively, water can induce the hydrolysis reaction described in Equation (1):



where, in the case of  $Er^{3+}$ ,  $x = 1$  and  $y = 8$ .

In a comparative study performed by Kobayashi et al. on the lanthanides series, hydrolysis constants ( $pK_h$ ) and water exchange rate constants (WERC) have been correlated to Lewis acid strength, establishing that metal compounds which have  $pK_h$  values from 4.3 to 10.08 and WERC greater than  $3.2 \times 10^6 \text{ s}^{-1}$  are strong acids. Erbium(III), ( $pK_h = 7.9$  and  $WERC = 1.4 \times 10^8 \text{ s}^{-1}$ ), perfectly fits these parameters [6–9]. From a hard–soft theory point of view, Er(III) is a hard cation, much more oxyphilic than other metals; thus, its application as a catalyst in organic transformations involving oxygenated functional groups (such as epoxides, carboxylic groups, acetals and chetals etc.) has been largely discussed in the literature [4].

It has only been in the late 20th century that modern ion-exchange production techniques have made all rare-earth metals and their chemical compounds available, so papers about their employment in organic synthesis have started to appear only recently. For this reason, despite the interesting chemical characteristics of the erbium salts reported above, the Lewis acid powers of these compounds have not been completely exploited, although the number of their applications in organic synthesis has significantly increased over the last few decades. The most interesting characteristic of erbium salts is the fact that they are perfectly in line with the Green Chemistry principles, which refer to sustainable catalysts. Indeed, erbium salts can be used in aqueous solvents or in water without any deactivation; they can be easily recovered from the reaction medium by extraction and can be used several times without loss of activity. The present work contains a collection of the homogeneous phase applications in non-conventional solvents and under non-conventional heating methods of the two most used Er(III)salts, namely  $Er(OTf)_3$  and  $ErCl_3$ , taking into account the catalysts' efficiency, recovery and reusability. Moreover, the efforts to transform homogeneous Er(III) catalysts into heterogeneous ones have also been reviewed, as has the possibility of applying Er(III) to multifunctional catalysis to demonstrate the huge versatility and the modernity of erbium salts.

## 2. Er(III) Salts in Homogeneous Catalysis

### 2.1. Er(III) Triflate

One of the main features of erbium(III) is its capability to coordinate the oxygen atom [2]; as a consequence, the first and simplest application of Er(III) triflate [ $Er(OTf)_3$ ] in organic chemistry was its use as a catalyst in the transformation of epoxides.

Erbium triflate has been shown to catalyze the rearrangement of epoxides to carbonyl compounds and their reactions with various nucleophiles, in an extremely efficient and regioselective manner [10]. Good performance has been observed in the ring opening of epoxides using aliphatic as well as aromatic amines to afford  $\beta$ -amino alcohols [11]. The direct transformation of epoxides into 1,2-diacetates has also been successfully accomplished by mixing together the epoxide and acetic anhydride using Er(III) triflate as a catalyst [12].

The regio- and stereoselective ring opening of epoxides with oxygen or sulfur nucleophiles, such as water, alcohols and thiols, has been another interesting goal in the use of this lanthanide [13]. Procopio et al. described the  $Er(OTf)_3$ -catalyzed ring opening of unsymmetrically polarized epoxides that proceeds via cleavage of the C–O bond in a way that results in the best stabilization of the developing positive charge. The reactions of styrene oxide with alcohols or thiols in the presence of only 0.1 mol %  $Er(OTf)_3$  were carried out smoothly under mild conditions, with excellent conversion rates and with short reaction times (Figure 1, panel A1).

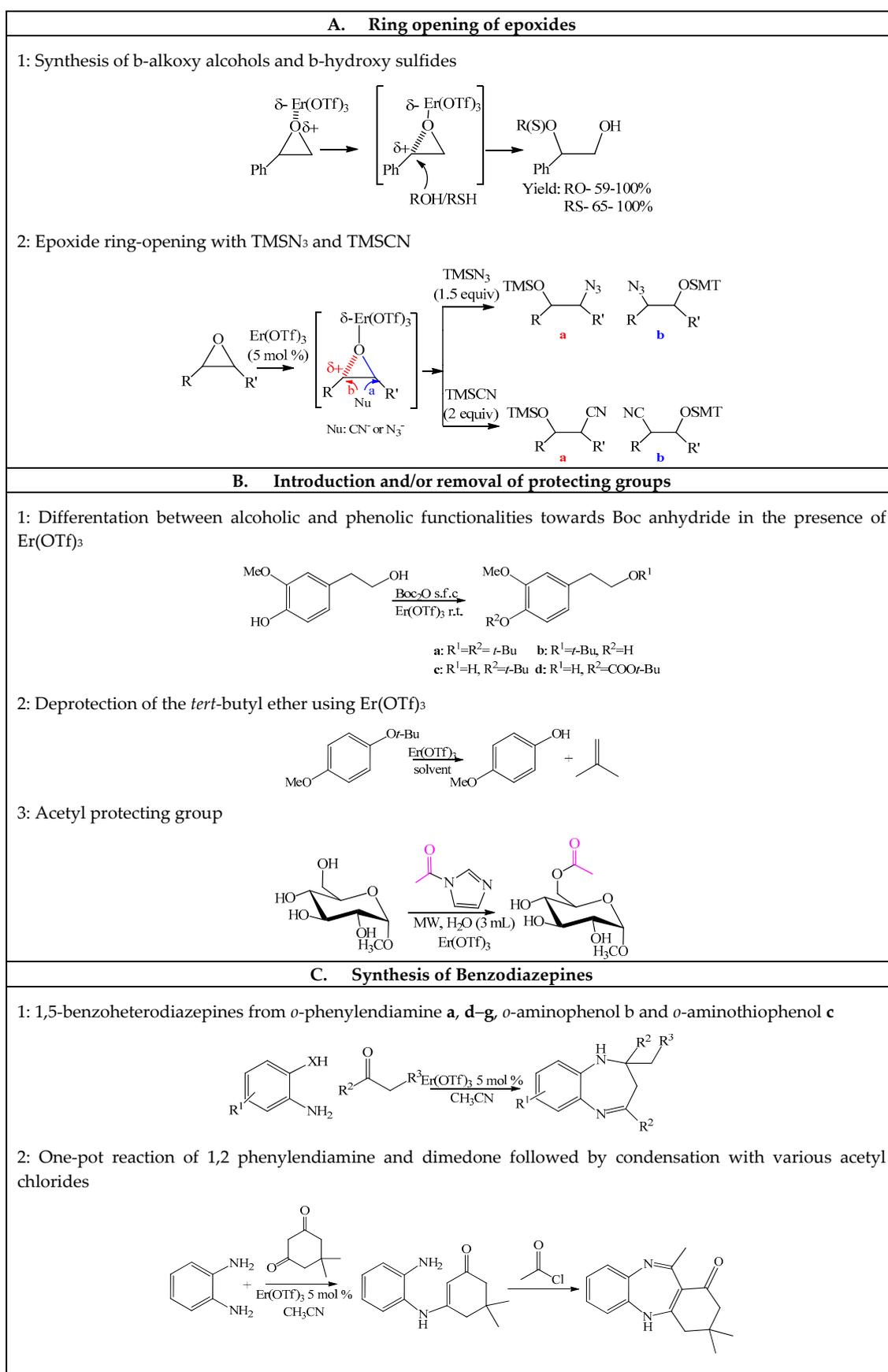
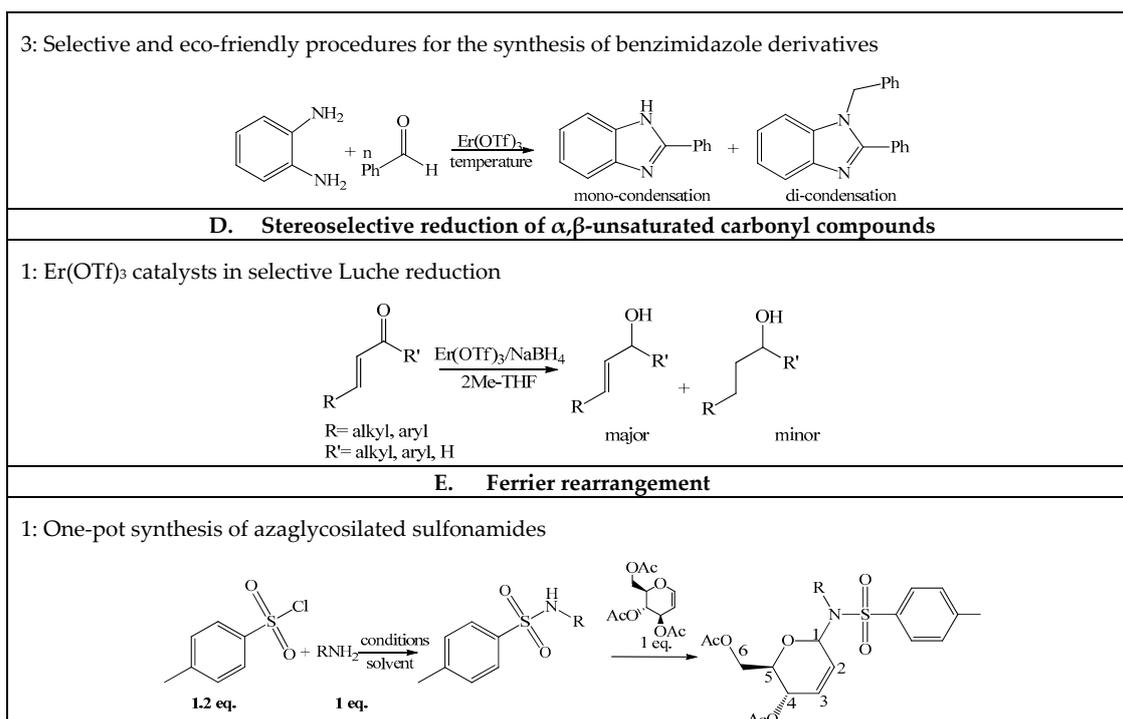


Figure 1. Cont.



**Figure 1.** Er(OTf)<sub>3</sub> in homogeneous catalysis.

The same authors demonstrated that Er(OTf)<sub>3</sub> is an excellent catalyst in the regio- and stereoselective ring opening of epoxide with trimethylsilylazide (TMSN<sub>3</sub>) and trimethylsilylcyanide (TMSCN) [14]. The  $\alpha$ -azido alcohols and  $\beta$ -hydroxynitriles produced are useful synthetic intermediates in organic synthesis, thanks to their versatile hydroxyl and azido or cyano moieties (Figure 1, panel A2). The observation that TMSCN was more reactive than TMSN<sub>3</sub> led to a better clarification of the mechanisms involved in the erbium(III) triflate-catalyzed ring opening, by expanding the knowledge about its interaction with other nucleophiles and validating the use of Er(OTf)<sub>3</sub> as a Lewis acid when coordinated with the oxygen atom. In a suggested mechanism of this reaction, authors envisaged that in an asymmetrical epoxide, the attack of –CN, which is a strong nucleophile, occurred during an early transition state. In this condition, the spatial arrangement of epoxide was still intact, and the substituents' positions highly influenced the attack. On the other hand, less nucleophilic N<sub>3</sub><sup>–</sup> was added at a late transition state while the ring opening proceeded, in order for the C–O bond cleavage to give the best stabilization of the developing positive charge. Thus, the  $\beta$ - and benzylic positions were the favored sites for nucleophilic attacks of CN and N<sub>3</sub>, respectively.

Er(OTf)<sub>3</sub> has largely been exploited as catalyst in the protection and deprotection of functional groups. The presence of a hydroxyl group in various biologically active compounds makes its protection a necessity during their synthesis and transformation. Consequently, several kinds of masking groups have been successfully used in this regard [15–19]. In the case of alcohols, the hydroxyl group may be protected by formation of an ether, an ester, or an acetal. Acetals, commonly used to protect 1,2- and 1,3-diols, have the obvious advantage that they can be used to simultaneously protect two hydroxyl groups and be removed under neutral conditions by either hydrogenolysis or strong acid hydrolysis.

Er(OTf)<sub>3</sub> proved to be a suitable agent for the deprotection of acetals and ketals under almost neutral conditions [18–20].

A frequently used protection method of alcohols and phenols is transformation into *tert*-butyl ethers. This strategy has always been considered with great interest by chemists, since *tert*-butyl ether

is one of the few stable ethers under commonly used basic conditions. Its scarce employment in organic synthesis is probably due to the harsh conditions required for its formation and its cleavage.

Procopio et al. investigated the application of an  $\text{Er}(\text{OTf})_3$  catalyst in the protection of the function of  $\text{OH}^-$  by forming a *tert*-butyl ether [21]. The use of 5 mol % of  $\text{Er}(\text{OTf})_3$  in combination with Boc anhydride enabled fast and efficient conversion of all tested alcohols and phenols, and good to excellent yields of *tert*-butyl ether derivatives were also recorded (Figure 1, panel B1). Performing the reaction in solvent free conditions made the reaction workup very simple, since the residual Boc anhydride was easily degraded to  $\text{CO}_2$  and isobutene, providing the products with satisfying purities, in most cases, without any chromatographic purification. The very low amount of catalyst required and the possibility of reusing the catalyst after a simple workup make this method highly eco-compatible. In the same study the authors demonstrated the ability of these Lewis acid catalysts to remove the acid-labile *tert*-butyl ether protection. Ether cleavage remains an integral functional group transformation, primarily as a deprotection step to unmask a hydroxyl group. The *tert*-butyl ethers were quantitatively and quickly cleaved in methanol, using 10 mol % of  $\text{Er}(\text{OTf})_3$  at 100 °C under microwaves (MW) irradiation (Figure 1, panel B2).

Acylation is another widely used method for the protection of hydroxyl (OH) groups [22,23], and regioselective acetylation has been tentatively developed in order to maximize the different reactivities of the primary hydroxyl groups in polyols and carbohydrates. Nevertheless, many of the reported methods involve the use of environmentally harmful or expensive reagents, anhydrous environments and the iterative blocking and de-blocking of all other potentially reactive OH functionalities in the molecule [24–31]. In a very recent paper, Procopio et al. suggested an effective procedure for the selective acetylation of biomolecules catalyzed by  $\text{Er}(\text{OTf})_3$  [32].

Considering the stability and catalytic activity of erbium(III) salts in water, which can be ascribed to their large ionic radii and an equilibrium between the Lewis acids and water [7–9], the authors tested the reactivity of 1-acetylimidazole and the catalytic activity of  $\text{Er}(\text{OTf})_3$ . The reaction was performed in water, using  $\text{Er}(\text{OTf})_3$  as a catalyst under MW irradiation. The use of 3 mmol of 1-acetylimidazole in the presence of 10% of  $\text{Er}(\text{OTf})_3$  resulted in a high reaction yield (Figure 1, panel B3). The procedure is quite generic, as a wide range of multifunctional natural compounds, such as methyl D-pyranosides, phenyl D-pyranosides, nucleosides, phenolic antioxidant compounds and aliphatic alcohols, were selectively acetylated.

As mentioned above, erbium(III)-based Lewis acids have exceptional similarities to carbonyl oxygens and carboxylates [4], thus allowing for structured transition states of the substrates bearing these moieties. This fact was utilized by Procopio and his research group for the development of the eco-friendly condensation of *o*-phenylenediamine with carbonyl compounds under MW irradiation [33].

The use of  $\text{Er}(\text{OTf})_3$  as a Lewis acid catalyst resulted in a remarkable amplification of an otherwise slow process for the synthesis of functionalized benzodiazepines. Benzodiazepines (BZDs) are psychoactive drugs whose core chemical structure is the fusion of a benzene ring and a diazepine ring. However, their biological activity is highly dependent on the nature of the BZD scaffold, including the conformation of the 1,4-diazepine ring and its substituents, the tendency of the hydrogen bond donor and acceptor, and the electrostatic profile [34]. Consequently, the development of expedient synthetic approaches to access new BZD scaffolds has attracted significant attention in the discovery of biologically active compounds. Compounds with a 1,5-benzodiazepine scaffold have recently received growing attention because of their pharmacological properties [35,36]. A greater therapeutic potential and lower incidence of side effects were described for 1,5-BZDs when compared to 1,4-BZDs.

An erbium(III) triflate catalyst was therefore used in the MW-assisted condensation reactions of *o*-phenylenediamine, *o*-aminophenol and *o*-aminothiophenol with carbonyl compounds to form functionalized 1,5-benzodiazepines, 1,5-benzoxazepines and 1,5-benzothiazepines. Five mmol of  $\text{Er}(\text{OTf})_3$  in ACN was found to be the best reaction conditions for the synthesis of such compounds in almost quantitative yields (Figure 1, panel C1).

The discovery of a novel class of 1,5-benzodiazepines as hepatitis C virus NS5B polymerase inhibitors prompted chemists to search for a suitable methodology for the synthesis of this category of benzodiazepines [37]. A one-pot procedure that involved the reaction of 1,2-phenylenediamine with dimedone in acetonitrile at room temperature in the presence of 5 mol %  $\text{Er}(\text{OTf})_3$ , followed by the addition of an equivalent of acyl or aryl chloride to perform the final cyclization (Figure 1, panel C2) was revealed to be a suitable method for providing important precursors of 1,5-benzodiazepine-type I in appreciably high yields and with short reaction times [38].

*o*-Phenylenediamines are widely featured scaffolds present in biologically active compounds and are frequently used substrates for the formation of heterocyclic compounds. The condensation of *o*-phenylenediamine with aldehydes readily produces benzimidazole derivatives. However, the reaction is not selective, producing both 2-substituted and 1,2-disubstituted benzimidazoles (Figure 1, panel C3).

$\text{Er}(\text{OTf})_3$  efficiently catalyzed the selective formation of benzimidazole derivatives, avoiding tedious work-up and procedures for product separation [39]. Two-substituted benzimidazoles were selectively obtained in high yields, with short reaction times, through the reaction of phenylenediamine with various aldehydes at a low temperature (1–2 °C), or at 80 °C in the case of electron-deficient aldehydes. The observed different reactivities, leading to the formation of either mono- or double-condensation products, were attributed to the calculated charge density located on the carbonyl group that is necessary for the coordination with the catalyst. Authors suggested that the calculated charge densities on oxygen could indicate the reactivity of these aldehydes. Moreover, the theoretical results predict that a charge density on the oxygen higher than  $-0.52$  favors coordination with the catalyst, therefore affording the products of double-condensation.

The affinity of Er(III) for the carbonyl oxygen was further exploited in a well-known lanthanide catalyzed reaction: the Luche reaction [40]. This is an organic reaction used to convert an  $\alpha,\beta$ -unsaturated ketone into an allylic alcohol, generally by using cerium trichloride, sodium borohydride, and an alcohol solvent. The role of the cerium is to coordinate the alcohol, making its proton more acidic so that it can be abstracted by the carbonyl oxygen of the ketone starting material. The  $\text{NaBH}_4$  starting reagent also reacts with the cerium activated alcohol to form a series of alkoxyborohydrides, and these “hard reagents” result in a 1,2-hydride attack on the protonated carbonyl, resulting in the final allylic alcohol product [41].

The need for stoichiometric amounts of salts and the use of conventional solvents are the main drawbacks of the Luche protocol. Thus, the use of catalytic amounts of  $\text{Er}(\text{OTf})_3$  was explored for the development of an eco-friendly, synthetic protocol for the reduction of  $\alpha,\beta$ -unsaturated carbonyl compounds [42]. Five mol % of erbium triflate and 1 equiv of  $\text{NaBH}_4$  enabled quantitative reduction of the carbonyl compounds. The reaction was performed in a green solvent, such as 2-MeTHF, thus allowing easy product isolation and improving the extraction yield by reducing the number of extraction steps (Figure 1, panel D1). The protocol, tested on chiral natural substrates, such as 3,5-dimethylcyclohex-2-enone, (*R*)-carvone and (*R*)-pulegone, displayed a significant diastereoselectivity towards the corresponding allyl alcohol with the *cis* configuration. This demonstrates that  $\text{NaBH}_4$  prefers to approach the carbonyl group axially by forming the equatorial alcohol [42].

Lewis acid catalysis is also involved in the Ferrier rearrangement that implicates the reaction of a suitably protected 1,2-glycal with an alcohol under Lewis acid catalysis to form the corresponding 2,3-unsaturated 1-*O*-glycosides [43]. Such 1-*O*-glycosides have been transformed into a variety of useful intermediates both in organic synthesis as well as specifically in carbohydrate chemistry. Since C-glycosides are stable analogs of O-glycosides and less prone to cleavage at the anomeric carbon, they have gained considerable importance over the last few decades. Among several approaches towards C-glycosides, the Ferrier rearrangement utilizing C-nucleophiles has been found to be quite useful. Several catalysts and nucleophiles have been introduced in the literature, addressing the mildness of the procedure, effects of the solvents, effects of the catalyst, and yields of products. The use

of  $\text{Er}(\text{OTf})_3$  as a catalyst for the Ferrier rearrangement has already been well established [44–46], and presents several advantages, which include high yields of products, clean reactions, short reaction times, mild reaction conditions, high stereoselectivity, wide applicability and recoverability of the catalyst.

In a more recent work, in view of the numerous biological properties of glycosides [47], Procopio and his research group investigated the role of  $\text{Er}(\text{OTf})_3$  in the Ferrier azaglycosylation of sulfonamides and amino acids with various nucleophiles to provide 2,3-unsaturated-*N*-pseudoglycals [48]. By considering the development of new eco-sustainable methods for the *N*-protection of amino acids and amines by carbonate and sulfonyl chlorides as protecting groups [49] and alkylation of amino groups with alternative methods [50,51], a synthetic method for the synthesis of 2,3-unsaturated-*N*-pseudoglycals has been developed.

$\text{Er}(\text{OTf})_3$  in 2-MeTHF has been revealed to be a useful catalyst for this purpose, allowing the *N*-glycosylation of *N*-tosyl-alanine methyl ester with 3,4,6-tri-*O*-acetyl- $\text{D}$ -glucal with an excellent yield. Glycal and various sulfonamides were coupled in the presence of  $\text{Er}(\text{OTf})_3$  (10 mol %) in 2-MeTHF, producing the corresponding *N*-glycosyl sulfonamides (Figure 1, panel E1). The same reaction carried out in the absence of  $\text{Er}(\text{III})$  did not lead to the formation of the product, thus confirming that the Lewis acid catalyst is essential for the Ferrier azaglycosylation reaction. In a hypothesized mechanism, the Ferrier process starts with the coordination of Er and one of the oxygen atom lone pairs of the glycal molecule, causing the release of a glycosylic group. A delocalized cation is formed and is then attacked by a nucleophile, forming the product [48].

All of the chemical transformations developed by using erbium triflate were also applied for the chemical manipulation of natural compounds (Figure 2). Natural product-based drug discovery, in fact, is characterized by using a starting point of an active compound, followed by individual manipulation of the structure so as to reach a drug criterion.

Procopio et al. applied their catalytic protocols to the chemical manipulation of a known natural product: oleuropein [52]. They successfully tested, and then patented, a very mild method to achieve selective Lewis acid catalyzed oleuropein hydrolysis. The selective hydrolysis of oleuropein is a challenging aim, due to the multifunctional chemical nature of the molecule. In the practical approach reported (Figure 2a), an aqueous acetonitrile oleuropein solution was treated with 10 mol % of erbium triflate under reflux, until the complete disappearance of the starting material was achieved. The complex product characterization was performed by means of LC-MS and  $^1\text{H}$  NMR analysis.

A simple acetylation protocol for obtaining the acetyl derivatives of oleuropein from the obtained aglycone and hydroxytyrosol was also developed (Figure 2b). Researchers have reported the biological evaluation and molecular modelling results of natural and semisynthetic oleuropein derivatives. All of the considered molecules have shown significant anti-inflammatory activity [53] and anti-proliferative and antioxidant effects on breast cancer cells [54], as well as antigrowth actions [55].

The same lanthanide is useful in the acylation of hydroxytyrosol with fatty acid chlorides (Figure 2c). Butyryl, decanoyl, elaidyl, linoleyl, oleyl, stearyl, and palmitoyl moieties have been conjugated to hydroxytyrosol, and permeation studies have been carried out through “in vitro” modeling, using Franz diffusion cells [56]. These conjugates have the potential to be administered as topical therapeutic agents for the treatment of cutaneous diseases as they permeated efficaciously through the Stratum Corneum Epidermis (SCE) membrane when applied in an “in vitro” Franz cell model.

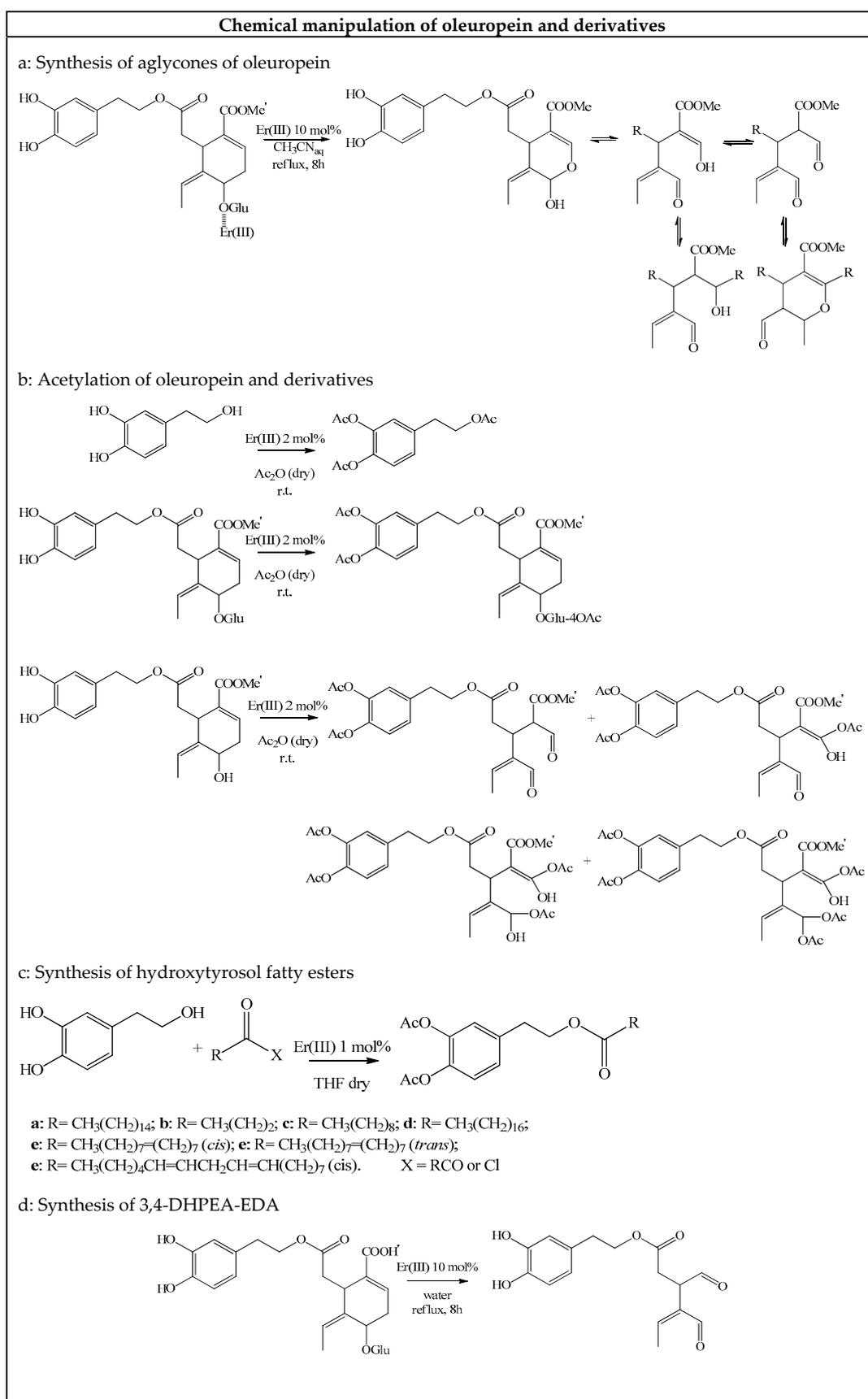
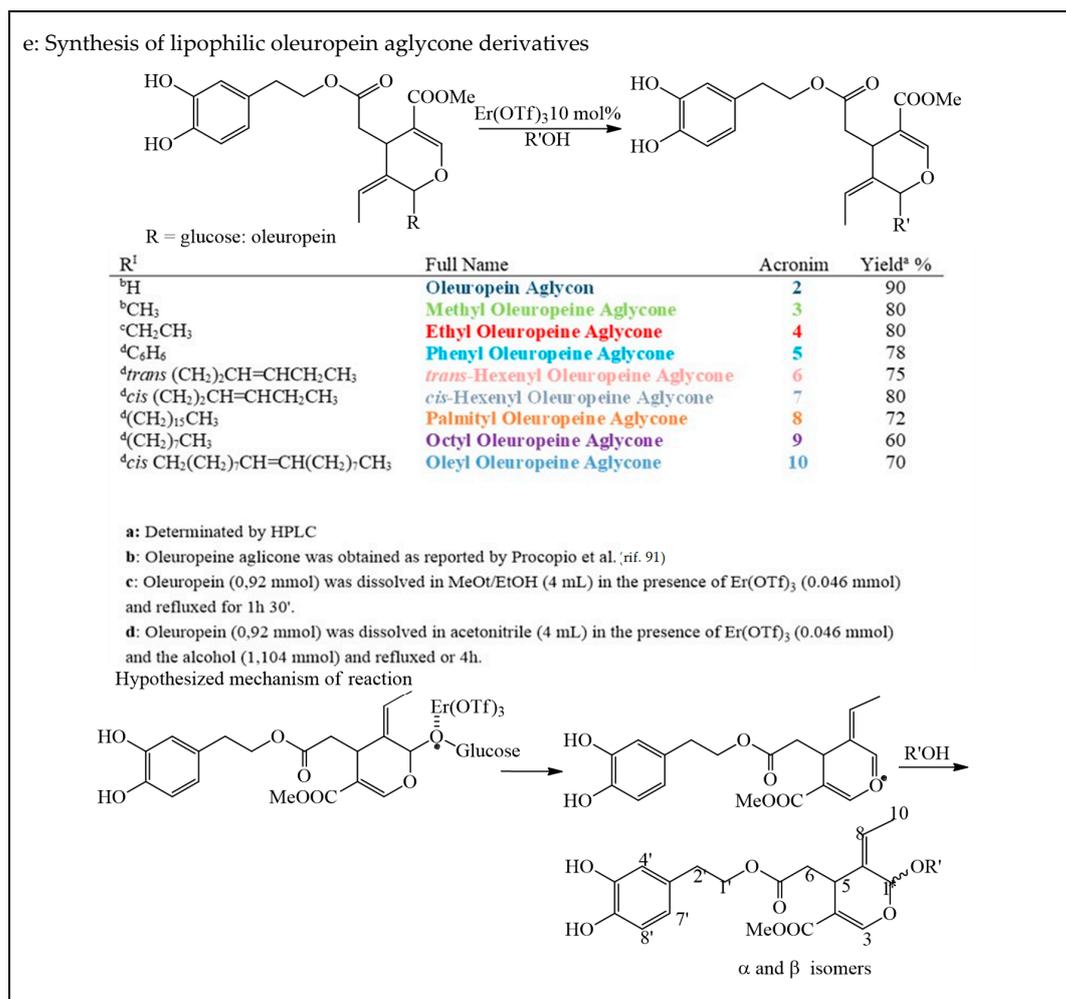


Figure 2. Cont.



**Figure 2.** Chemical manipulation of oleuropein with Er(III) as the catalyst.

In recent decades, exhaustive physicochemical data have been provided for the presence—in virgin olive oil and other oils—of two active principles characterized by a dialdehyde moiety conjugated with 2-(3,4-hydroxyphenyl) ethyl (3*S*,4*E*)-4-formyl-3-(2-oxoethyl)hex-4-enoate (3,4-DHPEA-EDA) and 2-(3,4-hydroxyphenyl) ethyl (3*S*,4*E*)-4-formyl-3-(2-oxoethyl)hex-4-enoate (*p*-HPEA-EDA) [57,58] that show peculiar sensory and health properties [59,60]. Remarkably, 3,4-DHPEA-EDA is associated with intense bitterness, attributed to VOO [58]. It is endowed with numerous beneficial effects on human health and its quantity in oil and olive waste water ranges from a few tens to some hundreds of mg/kg. Nevertheless, further detailed studies of the antioxidant and beneficial physiological effects of this individual compound have been hindered by the difficulty of isolating it as a pure compound in sufficient amounts for further investigation and dosages [61].

Considering the interesting pharmacological properties of 3,4-DHPEA-EDA and the many difficulties of isolating it as a pure compound in sufficient amounts, in a subsequent research, a synthetic strategy based on the catalytic role of erbium triflate produced this molecule with high purity and yield (Figure 2d) [62]. The synthetic compound was useful for developing a method to test the quantities of 3,4-DHPEA-EDA and *p*-HPEA-EDA in virgin olive oil [63].

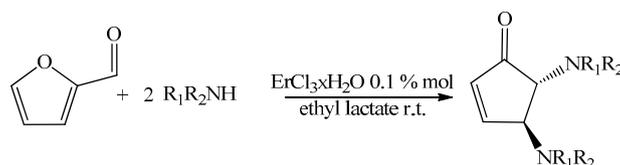
Exploiting the ability of erbium(III) to coordinate the oxygen atom, a new group of lipophilic oleuropein aglycone derivatives was synthesized through a transacetylation reaction with oleuropein and different fatty alcohols (Figure 2e) [64]. Oleuropein aglycone derivatives with long saturated and unsaturated alkyl chains were evaluated in terms of their lipophilicities and antioxidant capacities, both in chemical and biological environments, to establish whether they could be potentially used

as antioxidants in a fatty matrix and if augmented lipophilicities would correspond to better cellular internalization and antioxidant activity. Both the LC-MS and  $^1\text{H}$  NMR analyses of all the obtained compounds showed the presence of two isomeric products. Indeed, the hypothesized mechanism allows for the formation of an oxonium ion, which results in the formation of two diastereoisomers. These reactions occur through the anchimeric assistance of heterocyclic oxygen. Erbium coordinates acetal oxygen, resulting in the formation of the oxonium ion and subsequent attack of the nucleophilic alcohol (Figure 2e).

## 2.2. Er(III) Chloride

Among the lanthanide salts used as Lewis acids (LA) in organic chemistry, erbium(III) chloride plays a crucial role in green chemistry. It has been exploited for the development of new environmentally friendly protocols for the synthesis of compounds with potential pharmacological activity. It is much less expensive and toxic compared to the other lanthanide salts.

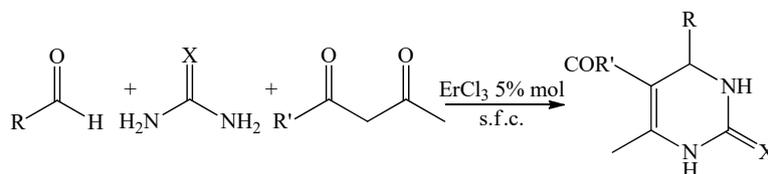
Various 4,5-diaminocyclopent-2-enones—structural motifs widely present in numerous natural and synthetic bioactive compounds—were efficiently prepared using only a very small catalytic amount of Er(III) chloride hexahydrate in ethyl lactate and avoiding strictly dry experimental conditions (Figure 3) [65].



**Figure 3.** Erbium(III) chloride in the synthesis of trans-4,5-diaminocyclopent-2-enones.

Conventionally, these compounds are synthesized from furaldehyde and primary or secondary amines, but in low yields and under harsh reaction conditions [66]. Procopio and co-workers demonstrated that the employment of only 0.1 mol % of  $\text{ErCl}_3 \times 6\text{H}_2\text{O}$  in ethyl lactate was enough to obtain a quantitative yield of diaminocyclopentenones in 30 min. The products were formed exclusively as transdiastereomers, consistent with thermal conrotatory  $\pi 4a$  electrocyclization, reminiscent of Nazarov cyclization [67].

The catalysis of this very mild and environmentally benign Lewis acid was further used in the well-known Biginelli reaction to produce 4-aryl-3,4-dihydropyrimidin-2(1H)-ones (DHPMs) in a simple one-pot condensation between ethyl acetoacetate, benzaldehyde, and urea [68]. Procopio and his co-workers [69] synthesized a library of dihydropyrimidinone derivatives, performing the Biginelli reaction under pressure, in solvent-free conditions and using 5% mol of Er(III)chloride (Figure 4) in a microwave or Q-tube reactor.



**Figure 4.** Synthesis of 4-aryl-3,4-dihydropyrimidin-2(1H)-ones (DHPMs) by the Biginelli Reaction.

## 3. Er(III) Salts in Heterogeneous Catalysis

Due to increasing environmental pressure, a general current interest is the transformation of homogeneous processes into heterogeneous ones. Heterogeneous catalysis offers several advantages in both organic synthesis and in industrial processes compared to homogeneous catalysis, because

catalyst recovery and recycling is often easier and does not lead to any reduction in reaction selectivity and yield [70]. Despite the extensive literature about Er(III) salts as catalysts in the homogeneous phase, relatively few reports have been produced regarding their use as heterogeneous catalysts. There are essentially two different strategies to make the conversion from a homogeneous to a heterogeneous catalyst (Figure 5); both of them have been successfully applied to Er(III) salts to include metals into metal-organic frameworks (MOFs) [71–74] or to support soluble catalysts on large-surface-area inorganic carriers [75–86].

Er(III) Heterogeneous Catalysts			
	Supported		Metal-Organic Frameworks (MOFs)
<i>Adsorption</i>	<i>Co-condensation</i>	<i>Post-calcination grafting</i>	Er <sub>6</sub> (OH) <sub>8</sub> (pydc) <sub>5</sub> (H <sub>2</sub> O) <sub>3</sub>
ErCl <sub>3</sub> /SiO <sub>2</sub>	Er <sup>3+</sup> /kenyanite	ErCl <sub>3</sub> /MCM-41	Er(BTC)(H <sub>2</sub> O)(DMF) <sub>1.1</sub>
ErCl <sub>3</sub> /SiO <sub>2</sub>		ErCl <sub>3</sub> /β-zeolite	MWNT-confined/Er-MOF
ErCl <sub>3</sub> /monmorillonite K10			

**Figure 5.** Strategies to convert Er(III)-based homogeneous catalysts into heterogeneous catalysts.

MOFs are an emerging class of micro- and mesoporous materials, characterized by a hybrid composition and an extended three-dimensional structure based on the network between inorganic metal centers and organic linkers in a heterogeneous coordination complex. The most important advantage of using MOFs as catalysts is the possibility of tuning their catalytic activity by acting on the coupling of the metal center and organic linker [71]. MOFs based on lanthanides are potent candidates for catalysis, because they display heterogeneous acid Lewis acidity due to their unsaturated metal sites in terms of coordination number and flexible coordination environments [72,73]. Er–MOFs have been assembled using aromatic linkers and used as catalysts in classical acid-catalyzed organic transformations, such as aldehyde protection or multi-component reactions [71–73]. In all cases, the Er–MOFs needed a thermal pre-activation step to induce the removal of coordinated and non-coordinated water molecules. They were thermally stable up to 350–400 °C and produced a number of four-five re-cycles before losing a significant amount of their activity. A nice solution for prolonging the lifetime of insoluble catalysts was proposed by Hashimoto et al. [74], who confined the unstable Er(III) heterogeneous catalyst—obtained by the MOF strategy—into multiwalled carbon nanotubes. In this way, they were able to produce a stable, heterogeneous Er(III) asymmetric catalyst, able to perform asymmetric Mannich type reactions in continuous-flow reactors. The continuous elution operated for 56 h to produce stereoselective Mannich products with a turnover number (TON) of 225, average conversion rate of 96% and 94% enantiomeric excess (ee). The best result, in terms of a potentially large-scale implementation, was reached by the solvent volume reduction of 98%, compared to the same reaction performed in a batch.

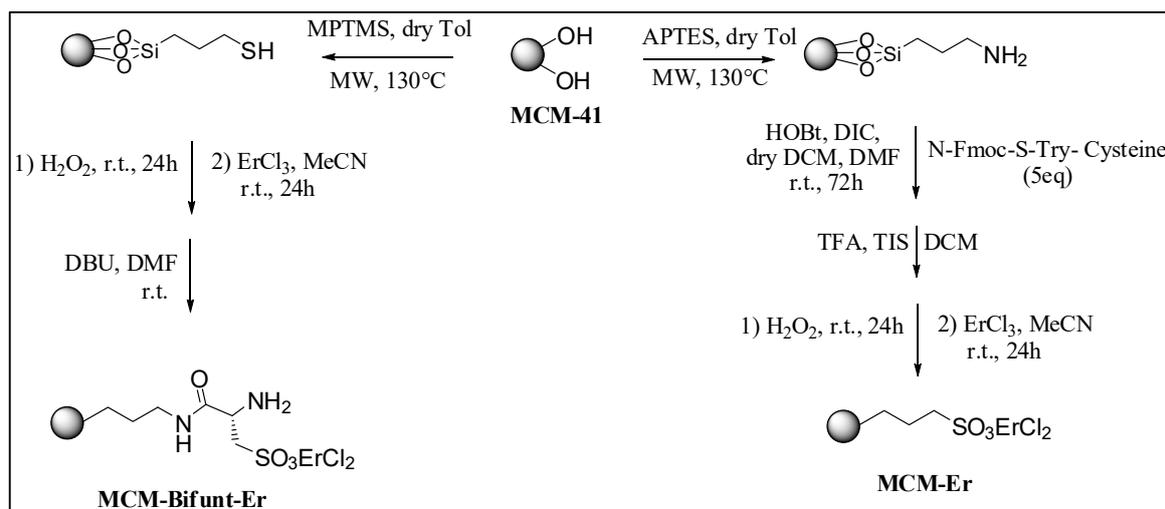
Concerning the possibility of supporting a homogeneous catalyst into a solid matrix, three different methods have been proposed for Er(III) catalysts: Er(III) adsorption over the solid support [75, 76], Er(III) co-condensation into the inorganic framework [77] and post-calcination Er(III) grafting on the solid surface [78–82].

Despite the protocol simplicity of the Er(III) salts' adsorption over solid supports—namely amorphous [75] and mesoporous silica [76]—the resulting heterogeneous catalysts display significant ion leaching after few reaction cycles, thus lowering the catalyst performance at a rate that is too fast for reliable large-scale implementation. Adsorbed Er(III) salts [76] and oxides [75] were used to perform oxidative conversions [75] as well as Lewis acid mediated conversions, such as the furfural reaction with secondary amines to obtain 4,5-diaminocyclopent-2-enones [76].

Co-condensation is the best way to limit metal leaching, as the active site is included in the inorganic framework and is easily accessible, thanks to the inorganic materials generally having meso- or macroporous structures. In particular, Er(III) ions were included into lamellar silicates, such as kenyaite and magadite, and their influence on catalytic performance was studied in a Knoevenagel

reaction. The results showed that the better catalytic performance of Er kenyaite was not only due to the weak acidity introduced by Er(III) ions on the silicate, but also due to a change that Er(III) cations induced in the silicate lattice of the layered solid, thus generating a coexistent acid-based redox pair [77].

Post-calcination grafting is a very useful method if the binding site of the catalyst has to be accessible on the surface, or if high loading is required, which can compromise the stability of the co-condensated structure [78]. An easy, fast and cheap microwave-assisted grafting method for synthesizing a mesoporous silica MCM-41 supported Er(III) catalyst (Figure 6) was described by Procopio et al. [79–82].



**Figure 6.** Synthetic schemes of MCM-Er catalyst and MCM-bifunctional Er catalysts, according to Procopio et al. [79–82].

They demonstrated that such a catalyst is resistant to several different alternative reaction conditions, such as batch solvent free conditions [79], continuous-flow conditions [80] and US-irradiation [81]. The catalyst was very efficient in the solvent free cyanosilylation of carbonyl compounds [79] and was evaluated in the continuous flow deprotection of benzaldehyde dimethylacetal. The high reaction conversions and rates suggested a good potential application for these materials in allowing a cleaner, continuous flow technique; at the same time, the leaching studies suggested that the efficiency of the method is strictly related to the reaction solvent. In particular, solvents like THF or  $\text{CH}_3\text{NO}_2$ , that potentially coordinate Er(III), generated higher Er(III) leaching than non-oxygenated solvents, such as toluene [80]. Ultrasound exposure did not cause the loss of Er(III) or any significant structural modification of the Er(III)-MCM-41 solid catalyst. This characteristic was demonstrated by its efficient application as a reusable solid catalyst in the solvent-free ultrasound-assisted synthesis of Boc-carbonate derivatives of a wide range of alcohols and phenols [80]. More recently, the same authors described an MW-assisted grafting method to successfully synthesize a bifunctional Er(III)-based metalorganic heterogeneous catalyst, by using a modified L-cysteine as ligand for Er(III) and as an amino group source [81]. The correct spatial arrangement of acid/base sites, which allows for their cooperation and peaceful co-existence on the silica surface, has been demonstrated. The catalyst showed good catalytic activity for C–C bond formation in the Henry reaction and aldol condensation; the activity was higher compared to separated acid and base catalysis or a mechanically mixed combination of Er(III) salt and amine.

An interesting application of the Er(III) heterogeneous catalyst as a Lewis acid mediator of cellulose hydrothermal degradation has also been reported [83,84]. In water, homogeneous Er(III) triflate and chloride are able to efficiently catalyze the conversion of pure microcrystalline cellulose into

lactic acid [85,86]. However, as using a homogeneous catalyst is far too labor consuming for a reliable lignocellulose conversion, two homogeneous versions of  $\text{ErCl}_3$  have been produced. Firstly,  $\text{ErCl}_3$  was adsorbed into montmorillonite K-10 using the ion exchange method, thus obtaining a heterogeneous catalyst able to efficiently convert cellulose into lactic acid (67.6% yield) in water and at 240 °C and 2 MPa. The same catalyst was recovered and reused only three times, and its loss of activity was due to a combination of metal leaching, deposition of carbon into solid pores and partial instability of the solid structure [83]. In order to limit the ion leaching, the same authors produced an  $\text{Er(III)}/\beta$ -zeolite catalyst, obtained by post-calcination grafting of the  $\text{Er(III)}$  salt [84]. Despite improved metal adhesion during the reaction, the new catalyst displayed worse catalytic efficiency without TON improving. The reason for the catalytic loss of efficiency was, in this case, the collapse of the  $\beta$ -zeolite structure and the carbon deposit due to the harsh reaction conditions [84]. In all the aforementioned reactions,  $\text{Er(III)}$  was the better cation for cellulose conversion compared to other lanthanides [83]; because of this, the search for new heterogeneous  $\text{Er(III)}$  based catalysts able to perform such conversions under milder reaction conditions and with better performances is still an open topic.

$\text{Er(III)}$  doped photocatalysts are a special case concerning the use of  $\text{Er(III)}$  cations in a heterogeneous phase. In this very recent application,  $\text{Er(III)}$  is far from playing an active catalytic role in photocatalysis, but it is essential to change the structural and electronic characteristics of well-known photocatalysts, thus improving their performances, especially under solar insolation [87–97]. It is well known, for example, that titania ( $\text{Ti}_2\text{O}$ ) is a semiconductor active as a photocatalyst in the UV range, and its applications in water splitting, pollutant removal and conversion of carbon dioxide into useful chemicals have been extensively studied [87]. The main drawback of titania use is the limitation of its bandgap in the UV range, making its use under solar insolation infeasible [88,89]. Doping titania, as well as other active semiconductors with lanthanides, is an interesting approach for increasing the use of low energy photons in photocatalysis. A good number of reports have concluded that  $\text{Er(III)}$  is the best lanthanide cation for improving the catalytic performance of  $\text{Ti}_2\text{O}$  [87–90],  $\text{BiVO}_4$  [91,92],  $\text{Bi}_2\text{WO}_6$  [93],  $\text{Bi}_2\text{O}_3$  [94] and  $\text{ZnO}$  [95], in the photocatalytic degradation of phenols under five different light conditions (UV, UV-vis, NIR, Vis-NIR and UV-vis-NIR). Moreover, the incorporation of  $\text{Er(III)}$  into  $\text{YVO}_4$  improved its photocatalytic activity by inducing a change in morphology and a better electron-hole separation mechanism, thus making this catalyst a promising candidate for water splitting reactions [96].  $\text{Er(III)}$  was finally used as a dopant to transform a wide band gap metal oxide ( $\text{ZrO}_2$ ) into a visible light active photocatalyst [97].

#### 4. $\text{Er(III)}$ in Multifunctional Catalysis

One of the most important goals of modern organic synthesis is to mimic the enzyme's key features to position the substrates in proximity to each other, and simultaneously enhance their reactivity by appropriately positioning the reacting functional groups in their asymmetric environment [98]. Molecular catalysts for the synthesis of optically active chiral compounds have undergone tremendous development over the last two decades, especially in the homogenous phase, since it is possible to modify their structures to improve their efficacy. Organo-transition metals or main-group organometallic compounds have been developed for different catalytic asymmetric C–C bond-forming reactions, with metalloenzymes as their models. Many multifunctional catalysts, especially bifunctional catalysts, were designed and applied to asymmetric catalysis, combining a metal ion, acting as Lewis acid moiety with a Lewis or Brønsted base in the form of an organic functional group [99–102]. Among them, Shibasaki et al. [103] reported the first example of an asymmetric Henry reaction using rare earth metal complexes prepared by the reaction of  $\text{H}_2\text{BINOL}$  with  $[\text{La}_3(\text{O}i\text{Bu})_9]$  in the presence of  $\text{LiCl}$  and water. Considering the lower ionization potential (ca. 5.4–6.4 eV) and the lower electronegativity (1.1–1.3) of rare earth elements [104], their alkoxides with (S)-BINOL have been successfully tested as asymmetric catalysts for the nitroaldol reaction. After the structure elucidation of this new heterobimetallic asymmetric catalyst [105], different combinations of rare earth and alkali metals have been employed in order to obtain a versatile framework for enantioselective

transformations [106]. The structure of the rare earth–alkali metal–BINOL (abbreviated as LnMB; Ln = rare earth metal, M = alkali metal, B = BINOL) complex is shown in Figure 7.

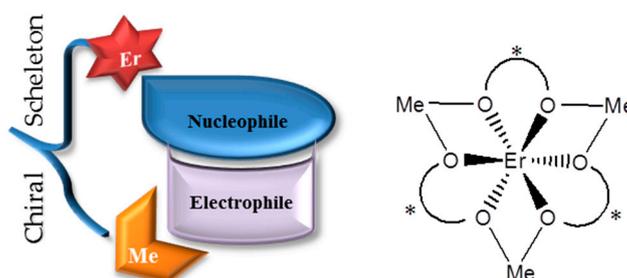


Figure 7. Schematic and functional structure of an Er–Me<sub>3</sub>–tris(binaphthoxide) (ErMB) catalyst.

These catalysts were also convenient from a sustainability point of view, considering that the active nucleophilic species were generated in situ from pronucleophiles, and the reactions proceeded with high atom economy through a simple proton transfer [107].

Although the lanthanide group elements are considered with homogenous characteristics in mind, differences in the ionic radius allow relevant differences both in reactivity and in enantioselectivity to be obtained, as reported by Shibasaki et al. [108]. In the nitroaldol reaction used as a reaction test, the same BINOL ligand and alkali metal were combined with different rare earth elements. It was observed that a small change in the Ln(III) radius generally resulted in increased catalytic activity and often in increased enantioselectivity. In this way, when the right pair is combined, it is possible to obtain good results for different enantioselective transformations, or, in some cases, to obtain a selected enantiomer, simply by changing the rare earth element in the catalyst. Regarding Er(III) based catalysts, only one, comprising a small amide-based ligand derived from an  $\alpha$ -amino acid, was developed, to obtain a *syn*-selective catalytic Mannich type reaction that was tunable into an *anti*-selective one by changing the Er(III) salt with a Sc(III) salt [109]. The amide-based ligands' characteristics, such as the rigidity of the planar amide and conformational flexibility of the  $\alpha$ -carbon, combined with the multiple coordination modes and coordination numbers of the rare earth element, provided flexible structural dynamics.

In principle, the use of a Lewis acid close to a Lewis base could lead to a self-quenching reaction, but by combining a Ln hard metal ion with the right soft base it is possible not only to avoid this side reaction but also to increase the reaction rate, as demonstrated by Aggarwal et al. [110]. Embedding a tertiary amino group into an aliphatic  $\beta$ -amino alcohol such as norephedrine was first tested by Tiseni and Peters as a chiral ligand for Er(III) [111]. This complex, formed in situ, catalyzed a [4 + 2] cycloaddition of  $\alpha,\beta$ -unsaturated acid chlorides with different aldehydes and provided a broad variety of  $\delta$ -lactones with high enantioselectivity. Er(OTf)<sub>3</sub> was chosen for its low price [112], due to its extensive use in the telecommunications industry [113], together with its small ionic radius that allows for a rigid transition state during the cycloaddition [114]. Er(III), which normally prefers a high coordination number, is able to bind both the ligand and the substrates at the same time in order to control reactivity and stereoselectivity. The fact that no self-quenching phenomena occurred and the great importance of the lanthanide counter ion were also highlighted, since ErCl<sub>3</sub> did not catalyze the product formation in the same reaction conditions.

Furthermore, the cooperative effect of Er(III) with a base amino group, over a relatively small distance and without self-quenching, has been observed in the heterogeneous Er(III) based bifunctional catalyst, as described in the previous section [82]. The great advantage of this catalyst is the possibility of recovering and reactivating it via acid/base wash, and reusing it without any significant loss of activity.

Finally, there are polynuclear Er(III) complexes with near-infrared (NIR) emission—structurally related but with different scopes—which are supramolecular aggregates of exoerbium(III) obtained

from a chemically modified Salen ligand. These complexes can not only be potentially applied in the telecommunications field, but also in bio-analysis and imaging [115].

## 5. Conclusions

Erbium(III) salts possess the most important characteristic of green catalysts: they are cheap, easily available, efficient Lewis acids in the homogeneous phase, allow reactions to proceed under mild conditions, are highly stable in aqueous media or sustainable solvents, and are easily recoverable and reusable several times without time consuming purification protocols or important loss in activity. Their catalytic efficiency has been proven in a huge number of reactions involving oxygenated functional groups and under non-conventional reaction conditions, such as microwave, ultrasound and light pressure assisted reactions. Their ability to function under mild reaction conditions make erbium salts the most suitable solution for the manipulation of chemical complex natural molecules, giving rise to several new classes of semisynthetic derivatives with improved biological activity. Some interesting applications in the heterogeneous phase as well as in multifunctional catalysis have also been studied, thus demonstrating the ability of erbium salts to preserve their versatility and efficiency. Nevertheless, many examples of Er(III)-based heterogeneous catalysis are still unexplored, compared to homogeneous catalysts, thus justifying future efforts in this direction. Exploring their application in the asymmetric catalysis after being coordinated with suitable asymmetric ligands, as well as optimizing the conditions for their application in multifunctional solid supports, such as zeolites, are still some of unresolved hot topics when it comes to erbium catalysis.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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