**ChemCatChem**

Research Article
doi.org/10.1002/cctc.202200967

**Chemistry
Europe**
European Chemical
Societies Publishing

www.chemcatchem.org

# Improved Performance of a Europium-based Metal-Organic Framework for Cyanosilylation of Demanding Ketones

Juana M. Pérez+,[a] Estitxu Echenique-Errandonea+,[b] Sara Rojas,[c]
Duane Choquesillo-Lazarte,[d] José M. Seco,[b] Mireya E. López-Vargas,[a]
Antonio Rodríguez-Diéguez,*[c] and Ignacio Fernández*[a]

Solvothermally promoted assembly of the multifunctional 3-amino-4-hydroxybenzoic acid ligand with the corresponding Eu salt gives rise to the formation of a porous metal-organic framework with the general formula $\{[Eu_5L_6(OH)_3(H_2O)_3]\cdot 5DMF\}_n$ (1) that has been tested as heterogeneous catalyst for the cyanosilylation of a broad scope of ketones in solvent-free conditions, using the lowest catalyst loading of 0.5 mol% ever reported, and exhibiting no leak and high recyclability.

## Introduction

Cyanohydrins are versatile building blocks for the synthesis of a great variety of fine chemicals, agrochemicals and pharmaceuticals.[1] For the synthesis of this type of compounds, trimethylsilyl cyanide (TMSCN) has been imposed in order to replace the use of more toxic reagents such as NaCN, KCN or HCN, giving rise to the generation of the C—C bond with a greenest approach.[2] This is a preferred reagent due to its easy handling and most importantly, its higher atom economy without formation of side products. Moreover, it is environmentally friendly, cost-efficient and selective towards extremely versatile organic molecules, which is in total agreement with some of the twelve principles of green chemistry.[3]

Several efficient catalysts such as Lewis acids,[4,5] Lewis bases,[6,7] organic-inorganic salts,[8,9] or nucleophilic catalysts[10] among others[2] have been extensively investigated so far in the cyanosilylation reaction. All of which can play an important role in the activation of the carbonyl-containing substrates. In most of the studies, the reaction is catalyzed by homogeneous catalysts, in which separation difficulties and recyclability hinder the process. In order to solve these drawbacks, heterogeneous catalysis is presented as a very interesting alternative to solve this problem because of its several advantages, such as recyclability, easy processability and economic viability derived from its low cost and lack of catalyst contamination within the final product.

In this context, metal-organic frameworks (MOFs) have garnered significant attention by the scientific community as potential functional materials of use in heterogeneous catalysis.[11,12] The high degree of synthetic tunability in coordination modes and number, allowed to the synthesis of materials with different properties such as surface area, porosity, pore size and shape, density and stability.[13] MOFs main advantage lie in: i) their high internal surface area that allows a greater probability of interaction with substrates and therefore greater space for reactions to take place, ii) catalytic activity in which both the metallic and organic components of the MOF can intervene, iii) selectivity imposed by the nature of the well-defined channels or pores, iv) chemical stability by means of the metal-organic nature of the supramolecular assembly which v) makes them recyclable systems and used as catalysts.[14]

An interesting group of MOFs are those based on rare-earth metals, which include all lanthanides together with yttrium and scandium.[15] The coordination chemistry of these metals is very diverse, even though they enjoy small differences in terms of coordination numbers and geometries, and where contrary to *d*-block metals, geometry is mainly driven by more or less sterically demanding ligand backbones.[16] In recent years, various studies have been conducted towards the use of rare-earth MOFs as heterogeneous catalysts for organic reactions,

[a] Dr. J. M. Pérez,+ M. E. López-Vargas, Prof. I. Fernández
Department of Chemistry and Physics
Research Centre CIAIMBITAL
University of Almería,
Ctra. Sacramento, s/n
04120, Almería (Spain)
E-mail: ifernan@ual.es
Homepage: www.nmrmbc.com

[b] Dr. E. Echenique-Errandonea,+ Prof. J. M. Seco
Departamento de Química Aplicada
Facultad de Química
Universidad del País Vasco UP/EHU
Paseo Manuel Lardizabal N°3
20018 Donostia-San Sebastián (Spain)

[c] Dr. S. Rojas, Prof. A. Rodríguez-Diéguez
Departamento de Química Inorgánica
Facultad de Ciencias
Universidad de Granada
Av. Fuentenueva S/N
18071 Granada (Spain)
E-mail: antonio5@ugr.es
Homepage: www.antonio596.wixsite.com/misitio

[d] Dr. D. Choquesillo-Lazarte
Laboratorio de Estudios Cristalográficos
IACT, CSIC-UGR
Av. Las Palmeras n°4
18100 Granada (Spain)

[+] These authors contributed equally.

**ChemCatChem**

Research Article
doi.org/10.1002/cctc.202200967

**Chemistry**
**Europe**
European Chemical
Societies Publishing

being one of these benchmark transformations the cyanosilylation of carbonyl-containing compounds.[15] This reaction was firstly reported in 1994 by Fujita and coworkers using a Cd-MOF catalyst,[17] and here after, a plethora of diverse works have been applied to this specific reaction using metal-MOF such as based on Cu, Cr, Mn, Fe, Co, Zr, etc.[18–24] Placing the focus on lanthanide-based MOFs, no more than 15 examples have been reported so far, where the catalytic activity of the material is demonstrated by using catalyst loadings in the range of 1 to 10 mol%, and using in all of them reactive aldehydes as electrophiles.[25–38] There are only three examples where the use of less reactive ketones was studied with these rare-earth metal-MOFs giving rise to the formation of highly interesting quaternary centers. The first one, was reported by Gustafsson et al. in 2010,[39] in where Nd(btc)·$H_2O$ (btc = 1,3,5-benzenetricarboxylate) was used as catalyst in a 4.5 mol% loading at room temperature and dichloromethane (DCM) as solvent, reaching 91% of conversion after 18 h. To the best of our knowledge, this is the highest conversion reached so far when using ketones as electrophiles. Later on, Ce-MOF (3 mol%)[40] and Tm-BDC (BDC = 1,4-benzenedicarboxylate) (2 mol%)[41] catalysts where tested under solvent-free conditions being not able to overpass previous results yielding only an 8 or 31% of conversion, respectively.

With this background, and continuing with our research efforts focused on the design, synthesis and catalytic applications of new MOF systems,[42] we report herein the application and recyclability of a new **Eu-MOF** (**1**), based on 3-amino-4-hydroxybenzoate, to be used in this green organic process specially focused on the derivatization of less reactive substrates such as ketones.

## Results and Discussion

### Structure description

Single-crystal structure of **Eu-MOF** (**1**) {[$Eu_5L_6(OH)_3(H_2O)_3$]·5DMF}n (L = 3-amino-4-hydroxybenzoate) exhibit three-dimensional metal-organic framework that crystallizes in P63/m space group (Figure 1).

The asymmetric unit is comprised of two crystallographically independent $Eu^{3+}$ ions (Eu1 and Eu2, see below), a deprotonated ligand, a hydroxyl bridge acting as connector among metallic centers, and one coordinated water molecule.

Actually, 3-amino-4-hydroxybenzote ligand displays multiple coordinating groups, comprising the carboxylate, hydroxyl and amino functionalities, which make it an ideal candidate for the preparation of novel three metal-organic frameworks. In fact, this ligand belongs to the class of organic compounds known as hydroxybenzoic acid derivatives and is known to be a primary metabolite being directly involved in organism growth, development or reproduction.[43] Despite its promising potential in the synthesis of novel materials, relatively scarce examples of porous 3D-MOFs are found within this ligand. It was the group of Zhang *et al.* who reported the first example of a Zn based
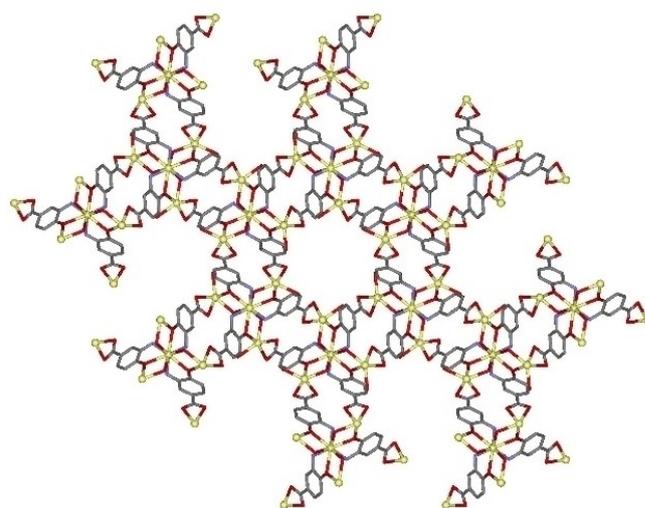


**Figure 1.** Perspective of **Eu-MOF** along *c* axes. Code color: Europium, carbon, oxygen; yellow, grey, red. Hydrogen atoms have been omitted for clarity.

material able to efficiently separate $C_2H_2$ from acetylene/carbon dioxide mixtures.[44]

Focusing in our structure, regarding metal environment, Eu1 atom renders a $EuN_3O_6$ environment which is established by three amino and three hydroxyl oxygen atoms from L ligand and three additional oxygen donor atoms belonging to hydroxyl bridges.

Eu2 exhibits an eight coordination $EuO_8$ surrounding where six of eight oxygen donor atoms belong to two carboxylate groups and two hydroxyl oxygen atoms from 3-amino-4-hydroxy benzoate dianionic ligand, one additional oxygen donor atom belongs to a coordination water molecule and the remaining one corresponds to the hydroxyl bridge. The nine and eight coordinated environments build spherical tricapped trigonal prism (TCTPR-9) and triangular dodecahedron (TDD-8) polyhedron, respectively according to SHAPE[45] calculations.

It is worth mentioning the key role that the coordinated water molecule of Eu2 site would play in the catalytic process. Its appropriate disposition pointing out the pore cavity made us think about the possibility of removing the coordinated solvent molecule to create vacant coordination sites (Figure S4) that could serve as active Lewis acid catalytic sites where the transformation of the incoming aldehyde or ketone would occur. Comparing with the yttrium-based structures (**GR-MOF-6** and **Y-MOF**) reported so far by our group[42,46] which were able to perform efficiently cyanosilylation of carbonyls, previous examples display DMF coordinated molecules which hinders solvent discoordination deriving in the slowing down of catalytic reaction.

Growing the structure along *c* axes leaves microchannels (as it is appreciable in Figure 1). Indeed, the appropriate pore size of (7.4 Å) allows the effective inclusion of solvent molecules. The aforementioned channels correspond to *ca.* 19% of the unit cell (according to the geometrical calculation of the pore volume with the PLATON-v1.18 program) and host crystallization DMF molecules. Finally, according to the connectivity

**ChemCatChem**

Research Article
doi.org/10.1002/cctc.202200967

**Chemistry Europe**
European Chemical
Societies Publishing

evaluated by TOPOS,[47] pentanuclear nodous are connected by 6-connected unimodal net displaying $\mathbf{4^9 \cdot 6^6}$ point symbol and *acs* net type.

Having all these facts in mind we decided to test compound **1** as heterogeneous catalyst for the cyanosilylation of a broad scope of ketones under very mild and solvent-free conditions.

### Chemical stability and electrophoretic behavior

Surface chemistry determines the stability, potential oxidation, and reactivity of a catalyst. Further, regarding particle size, it is generally considered that smaller particles will favor the catalytic reactions. Here, the colloidal stability of the **Eu-MOF** (**1**) material was assessed by means of electrophoretic mobility. ζ-potential, defined as the electric potential in the interfacial double layer at the location of the slipping plane relative to a point in the bulk medium,[48] was used as an indirect estimation of the surface charge density of our system. The ζ-potential helps to unravel repulsive interactions between colloidal particles and the tendency of aggregation. Systems with high ζ-potential (−/+) are electrically stable, whereas colloids with low ζ-potential (−/+) tend to coagulate or flocculate. Importantly, ζ-potential is deduced from the electrophoretic mobility, in our case via the Smoluchowski approximation (F(κa) is 1.5). All the experiments were performed at a fixed conductivity of 330 μS/cm, which is equivalent to a concentration of 3.7 mM NaCl (Figure S5). Negative values of ζ-potential suggest that dissociation of external acidic groups have occurred. This fact is produced at pH 10 with the lowest value of −25.0±0.6 mV (electrophoretic mobility of −1.957±0.048 μm·cm/V·s) (Figure 2 and Table S6) that implies that the MOF particles will tend to repel each other and there will be no tendency for the particles to come together at this basic pH. However, when reducing the pH the system under study showed lower ζ-potentials, evidencing an isoelectric point between pH 8 and 9, highlighting that the point where aggregation is most likely and therefore the system is least stable. Interestingly, at pHs lower than 7 the ζ-potential remained constant in the range of +2.4–1.1 mV, proving a non-very stable colloidal system. The fact that
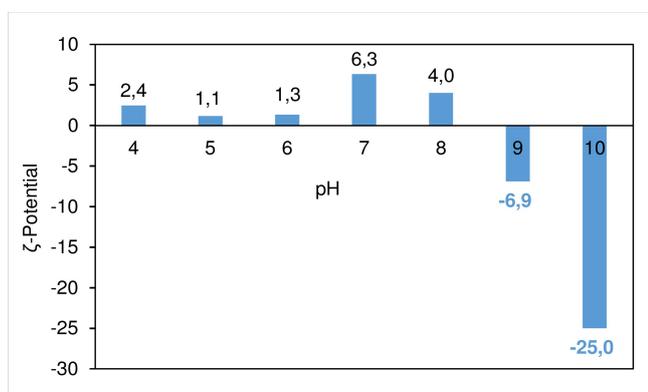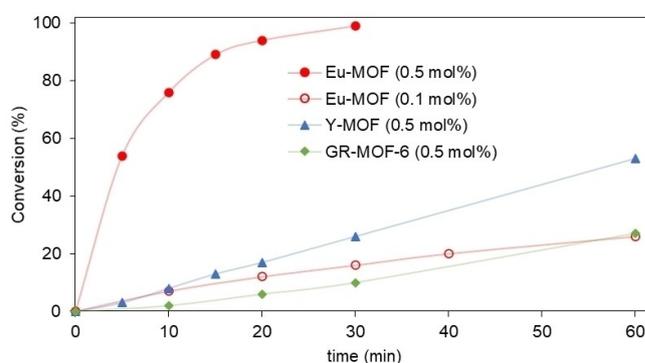
at pH 10 the system reached the highest absolute value of electrophoretic mobility, is related with a higher number of deprotonated functional groups that repelled each other favoring the system to remain in solution.

Standard DLS measurements were also carried out to the sample in order to establish the size of the particles under study. In this case, the colloids were found to have average diameters in the range of 2437±145 to 2756±229 nm all over the range of pH between 4 to 10, and PDI values centered at 0.3 (Figure S7), indicating that the size of the particles was not affected by surface charge and the overall contribution of the electrostatic repulsion is not enough to divide or aggregate the catalyst (Figure S6).

### Catalytic activity

For comparison issues within other MOF systems, whether described by some of us or by others, the benchmark reaction used benzaldehyde (**2a**), TMSCN, room temperature and no solvent. As already reported,[42] the blank reaction reached 8% conversion after 14 h of reaction under optimal conditions. The use of 0.5 mol% of **Eu-MOF** (**1**) gave full conversion only with 30 minutes of reaction (Figure 3). Under the same conditions, previous catalysts such as **Y-MOF**[42] or **GR-MOF-6**[46] yielded conversions of 26% and 10%, respectively, at the same time of 30 minutes (Figure 3). This performance could be ascribed to the eased discoordination of the water molecule comparing to the rest of the structures (**Y-MOF**[42] or **GR-MOF-6**[46]) which display coordinated DMF molecules. The latter statement does not consider the effect of the different ligands within the structure, and therefore a hypothetical **Eu-MOF** holding a DMF molecule instead of water would demonstrate its true effect. The synthesis of such MOF is currently undergoing in our laboratories.

When the **Eu-MOF** catalyst loading is reduced down to 0.1 mol%, its performance is comparable to those based on yttrium (**Y-MOF** and **GR-MOF-6**), but under the same loading our catalyst is five-fold faster.

**Figure 2.** ζ-potential of **1** as a function of pH. All the measurements were performed with constant conductivity of 330 μS/cm.

**Figure 3.** Kinetic profile of the reaction using 0.5 mol% (solid circles) and 0.1 mol% (empty circles) of **Eu-MOF** (**1**) catalyst, 0.5 mol% of **Y-MOF** (triangles) and 0.5 mol% of **GR-MOF-6** (diamonds) and a ratio **2a**/TMSCN 1:1.1 under inert nitrogen atmosphere at room temperature.

The turnover frequency (TOF) of catalyst **1** was calculated as a function of conversion (Figure S8a) for benzaldehyde substrate (**2a**), obtaining a maximum TOF of 1301 h$^{-1}$ at 5 min of reaction time (54% of conversion). These results remarkably overpass those found by our group with Y-based MOF catalysts but also those reported with any MOF based on lanthanides (Table S8). Remarkably, the amount of Europium metal is only 2.5 mol% when 0.5 mol% of catalyst loading is used, which is one of the most reduced metal loadings among the rest of described MOF catalysts based on Europium, which are usually in the range of 5 to 20 mol%. When the catalyst loading is reduced down to 0.1 mol% the achieved TOF after the same 5 min of reaction (13% of conversion) was as high as 783 h$^{-1}$ (Figure S8b).

The scope of the reaction was also explored by using an overall of 17 types of ketone (Table 1). A great variety of aryl alkyl ketones were tested (entries 4–12). Also, three different aldehydes were assayed just to check its utility in aldehydes. In all of them, aldehydes and ketones, high conversions were obtained after 24 h, only with a slight reduction when the aromatic ring contained electron-withdrawing groups whether at the *para*- or at the *ortho*-positions (entries 7 and 9–10), probably related with a decrease of the Lewis basicity of the oxygen atom of the carbonyl group.

The evaluation of diaryl ketones (entries 13–14) required 48 h to achieve moderate to good results, probably due to the steric hindrance of the substrate, thus decreasing its electrophilicity, or the increased volume of the substrate, thus disturbing its diffusion inside the pores of the **Eu-MOF**. This result also demonstrates that the reaction takes place mainly inside the pores of the MOF, so sterically demanding substrates somehow larger than 7.4 Å would have difficulties in entering the assembly and therefore their reactivity would be limited to take place just on the surface.

The use of α,β-unsaturated ketones (entry 15) was also assayed but unfortunately only a conversion of 58% was obtained, probably due to the fact that the substrate is rather not electrophilic enough. The use of aliphatic ketones (entries 16–17) provided full conversions after 24 h of reaction.

Finally, we decided to test cyclic ketones **2r**–**2t** (entries 18–20) which are usually less employed. In our hands, full conversion was obtained after 24 h, although an extra 24 hours were needed in order to fully convert the most sterically demanding 2-adamantanone **2t**.

The possibility of scaling-up the process was also pursued by performing the reaction with aldehyde **2j**, giving rise to the formation of almost a gram of product **3j** and an isolated yield of 98% (see general procedure in SI). This cyanohydrin silyl ether is of great interest in the agri-food sector since it has been described as a very useful precursor of 5-(2,4-difluoro-phenyl)-4-imino-5-methyl-3-(phenylamino)oxazolidin-2-one, a potent fungicide (Scheme 1).[49]

From a green chemistry point of view, the recyclability properties of a heterogeneous catalyst are of remarkable importance. For this reason, recyclability tests were also conducted using benzaldehyde (**2a**) and TMSCN as the model reaction (entry 1, Table 1). After completeness, the catalyst was easily separated from the reaction solution by centrifugation and washed with Et$_2$O. As shown in Figure S23 and Scheme 2, catalyst **1** could be reused seven times without any erosion on the catalytic activity.

To support the importance of the porous structure for the constructed **Eu-MOF**, we carried out several homogenous catalytic reactions using as catalysts the ligand itself, the europium precursor [Eu(NO$_3$)$_3$·5H$_2$O], and both of them. These experiments were performed with ketones **2i** and **2o**, in where our MOF could not promote quantitative results (entries 9 and
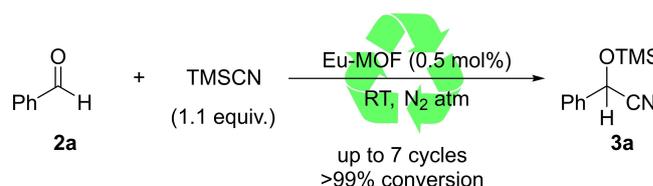
**Table 1.** Results of cyanosilylation of carbonyl-containing compounds in the presence of catalyst **1** at room temperature.[a]

| Entry | R | R' | No. | Time [h] | Conversion [%][b,c] |
|---|---|---|---|---|---|
| 1 | Ph | H | **3a** | 24 | >99 |
| 2 | 4-MeOC$_6$H$_4$ | H | **3b** | 24 | >99 |
| 3 | 4-ClC$_6$H$_4$ | H | **3c** | 24 | >99 |
| 4 | Ph | Me | **3d** | 24 | >99 (99) |
| 5 | 4-MeOC$_6$H$_4$ | Me | **3e** | 24 | >99 (98) |
| 6 | 4-$^t$BuC$_6$H$_4$ | Me | **3f** | 24 | >99 (91) |
| 7 | 4-ClC$_6$H$_4$ | Me | **3g** | 24 | 87 (82) |
| 8 | 3-ClC$_6$H$_4$ | Me | **3h** | 24 | >99 (93) |
| 9 | 2-ClC$_6$H$_4$ | Me | **3i** | 24 | 83 (80) |
| 10 | 2,4-F$_2$C$_6$H$_3$ | Me | **3j** | 24 | 91 (89) |
| 11 | 2-Pyridine | Me | **3k** | 24 | >99 (96) |
| 12 | 4-FC$_6$H$_4$ | CF$_3$ | **3l** | 24 | >99 (78) |
| 13 | Ph | Ph | **3m** | 48 | >99 |
| 14 | 2-MeC$_6$H$_4$ | Ph | **3n** | 48 | 57 (37) |
| 15 | PhCH=CH | Ph | **3o** | 48 | 58 (47) |
| 16 | C$_6$H$_{11}$ | C$_6$H$_{11}$ | **3p** | 24 | >99 |
| 17 | Et | Me | **3q** | 24 | >99 |
| 18 | (CH$_2$)$_5$ | - | **3r** | 24 | >99 (85) |
| 19 | (see structure) | - | **3s** | 24 | >99 |
| 20 | (see structure) | - | **3t** | 48 | 74 |

[a] Reaction carried out using substrates **2** (0.25 mmol) and TMSCN (34 μL, 0.275 mmol, 1.1 equiv.) with catalyst **1** (2.5 mg, 0.5 mol%) under inert N$_2$ atmosphere at room temperature. [b] Conversions (relative to compound **2**) determined by $^1$H NMR of the reaction crude. [c] Isolated yield in brackets.
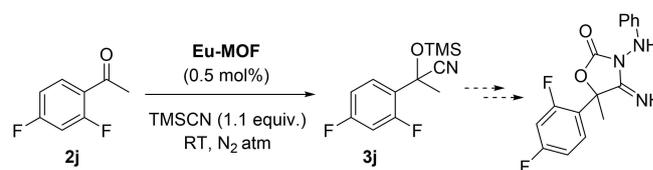


**Scheme 1.** Potential application of the cyanohydrin product **2j** towards the synthesis of a fungicidal active compound.



**Scheme 2.** Recyclability test of catalyst **Eu-MOF**.

**ChemCatChem**

Research Article
**doi.org/10.1002/cctc.202200967**

**Chemistry
Europe**
European Chemical
Societies Publishing

15, Table 1). These results are provided in Table 2 and as expected, the ligand alone did not afford significant yield within any of the two substrates. With the europium precursor [Eu(NO$_3$)$_3 \cdot$5H$_2$O], moderate to very good results were obtained, and therefore comparable to the results obtained with the heterogenous **Eu-MOF**. Interestingly, the presence of ligand under the same experimental conditions eroded the conversion in 8% and 12% for **2i** and **2o**, respectively, pointing out that the solid-state network establish by the europium salt and the ligand in the 3D MOF not only improves the catalytic outcome but also increase the recyclability of the catalyst as already mentioned.

Next, we were interested on evaluating any possible leak that our catalyst could have during its performance. For that, after the second and seventh reaction cycle, the reaction crude was centrifuged, and the supernatant filtered off through a plug of celite and dried under vacuum. Then, compound **2d** (117 μL, 1 mmol) and TMSCN (136 μL, 1.1 mmol, 1.1 equiv.) were added to the dried residue and the reaction crude stirred under inert N$_2$ atmosphere at room temperature for 24 hours (Scheme S2). $^1$H NMR spectra analysis of the final reaction crude indicated in both cases no traces of product **3d**, corroborating that no leaching of Eu take place all over the different cycles.

Importantly, to evaluate if the overall transformation is eco-friendly and overcome health and environmental problems derived from the chemical industry, green chemistry metrics[27,38,50,51] such as atomic economy (AE), mass intensity (MI), reaction mass efficiency (RME), and carbon efficiency (CE) were calculated through as previously described by Gómez et al..[27,38] These metrics considering all the substrates assayed in this work are provided in Table S9. The obtained values for the reaction using acetophenone (**2d**) as starting material were 100% of AE, 1.09 for MI, 95.7% for RME and 96.8% for CE, which are comparable to those described previously for related lanthanide-based MOFs.[27,38]

Two possible catalytic cycles for the cyanosilylation reaction are usually proposed.[42] In both of them, the coordination of the carbonyl-containing substrate to the metal center is proposed as the first step of the reaction, favoring the subsequent nucleophilic attack of the TMSCN. In order to corroborate this coordination ability, the analysis of the mixture of **Eu-MOF** as well as its precursor, i.e., Eu(NO$_3$)$_3 \cdot$6H$_2$O, were mixed with substrate **2e** in a mol ratio 1:1 and analyzed by FT-IR (ATR mode) (Figure S9-S10). As it could be observed, the signal corresponding to the carbonyl stretching [ν (C=O)] is shifted from 1664 cm$^{-1}$ to 1661 cm$^{-1}$ in the case of **Eu-MOF** and to 1654 cm$^{-1}$ in the europium salt, corroborating the expected Lewis acid character of our MOF. The latter statement is verified by monitoring the stretching C—O band associated to the methoxy group located at *para* position, since an elongation of the C=O double bond due to the europium coordination produces a shortening of the C—O bond resulting in a band shift opposite to the previous one, and therefore a shift from 1015 cm$^{-1}$ to 1023 cm$^{-1}$ in the case of **Eu-MOF** and to 1024 cm$^{-1}$ in the europium salt. The unaffected C(sp$^3$)-H stretching band associated with the methoxy group observed whether in the presence or in absence of Europium validates this approach, in where the observed shifts are diagnostic of the Lewis acid behavior. Other substrates such as **2c**, **2l**, and **2m**, were also mixed with **Eu-MOF** catalyst and examined thoroughly through IR (Figures S11-S13 and Table S7) obtaining signal shifts that corroborates the coordination of the different substrates with our MOF catalyst ad validating the first step of the two proposed mechanisms in where the Lewis acid character of the catalyst activate the carbonyl towards further reactions.

## Conclusion

In summary, we have synthesized and characterized a new europium-based metal-organic supramolecular porous system exhibiting the formula {[Eu$_5$L$_6$(OH)$_3$(H$_2$O)$_3$]$\cdot$5DMF}$_n$. This new material has been employed in the solvent-free cyanosilylation of 17 ketones and 3 aldehydes, avoiding the use of volatile organic compound as solvents, and favoring the transformation to the final product under green conditions and using the lowest catalyst loadings of europium-MOF (0.5 mol%) ever reported. Importantly, the reported catalyst is among those based on lanthanides, the one with highest activity in the

**Table 2.** Study of the reaction with catalyst precursors.[a]

| Catalyst precursor | No. | Conversion after 5 min [%][b] | Conversion after 12 h [%][b] | Conversion after 24 h [%][b] |
|---|---|---|---|---|
| Eu(NO$_3$)$_3 \cdot$5H$_2$O (1.25 mol%) | **3i** | 0 | 80 | 80 |
| Ligand (1.5 mol%) | **3i** | 0 | 0 | 0 |
| Eu(NO$_3$)$_3 \cdot$5H$_2$O (1.25 mol%) + Ligand (1.5 mol%) | **3i** | 0 | 72 | 72 |
| Eu(NO$_3$)$_3 \cdot$5H$_2$O (1.25 mol%) | **3o** | 0 | 49 | 57 |
| Ligand (1.5 mol%) | **3o** | 0 | 8 | 8 |
| Eu(NO$_3$)$_3 \cdot$5H$_2$O (1.25 mol%) + Ligand (1.5 mol%) | **3o** | 0 | 37 | 45 |

[a] Reaction carried out using substrates **2i** and **2o** (0.25 mmol) and TMSCN (34 μL, 0.275 mmol, 1.1 equiv.) under inert N$_2$ atmosphere at room temperature.
[b] Conversions (relative to compound **2**) determined by $^1$H NMR of the reaction crude.

cyanosilylation of ketones with a TOF value of 1301 h$^{-1}$, and with the impressive possibility of recyclability for at least seven cycles without any change on structure and with no leak during them.

## Experimental Section

**Preparation of {[Eu$_5$L$_6$(OH)$_3$(H$_2$O)$_3$]·5DMF}$_n$, Eu-MOF (1):** 0.010 g (0.0625 mmol) of 3-amino-4-hydroxybenzoic acid organic linker was dissolved in 0.2 mL of DMF containing 10 µL of Et$_3$N (0.072 mmol). 0.019 g (0.0434 mmol) of Eu(NO$_3$)$_3$·5H$_2$O, was dissolved into a 0.8 mL of distilled water in a separate vial. Once dissolved, 0.8 mL of H$_2$O was added to the ligand solution and 0.2 mL of DMF to the metal solution. Metal solution was added dropwise to the ligand solution keeping magnetic stirring. The resulting brownish-yellow solution was poured into a screw-capped vial (6 mL) and introduced to the oven at 100 °C for 2 hours to give rise hexagonal shaped single crystals. The scale up synthesis is described in the supporting information.

**General procedure for the cyanosilylation reaction:** In a 1 mL vial with a septum screw capped equipped with a stirring bar, Eu-MOF catalyst (2.5 mg, 0.5 mol%) was weighed Subsequently, the corresponding amount of carbonyl-containing compound **2** (0.25 mmol) was added followed by trimethylsilyl cyanide (TMSCN) (34 µL, 0.275 mmol, 1.1 equiv.) and the reaction was stirred under inert N$_2$ atmosphere at room temperature during the corresponding time. Once the reaction was finished the catalyst was removed by centrifugation (8000 rpm, 3 min) and washed with Et$_2$O (2 x 0.5 mL) obtaining the corresponding pure product **3** after removal of the solvent with rotary evaporator. When not fully conversion was reached the product was purified by column chromatography using hexane as eluent.

## *Conflict of Interest*

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

[1] R. J. H. Gregory, *Chem. Rev.* **1999**, *99*, 3649–3682.
[2] G. A. O. Tiago, K. T. Mahmudov, M. F, C. Guedes, A. P. C. Ribeiro, C. Branco, F. I. Zubkov, A. J. L. Pombeiro, *Catalysts* **2019**, *9*, 284–300.
[3] J. C. Anastas, P. T. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, New York, **1998**.
[4] P. Saravanan, R. Vijaya Ananad, V. K. Singh, *Tetrahedron Lett.* **1998**, *39*, 3823–3824.
[5] S. K. De, R. A. Gibbs, *J. Mol. Catal. A* **2005**, *232*, 123–125.
[6] S. K. Tian, L. Deng, *J. Am. Chem. Soc.* **2001**, *123*, 6195–6196.
[7] S. E. Denmark, W. Chung, *J. Org. Chem.* **2006**, *61801*, 4002–4005.
[8] X. Wang, S. K. Tian, *Tetrahedron Lett.* **2007**, *48*, 6010–6013.
[9] N. Kurono, M. Yamaguchi, K. Suzuki, T. Ohkuma, *J. Org. Chem.* **2005**, *70*, 6530–6532.
[10] Y. Suzuki, A. Bakar, M. D. K. Muramatsu, M. Sato, *Tetrahedron* **2006**, *62*, 4227–4231.
[11] M. Cabrero-Antonino, S. Remiro-Buenamanaña, M. Souto, A. A. Garciá-Valdivia, D. Choquesillo-Lazarte, S. Navalón, A. Rodríguez-Diéguez, G. Mínguez Espallargas, H. Garciá, *Chem. Commun.* **2019**, *55*, 10932–10935.
[12] J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
[13] A. Bavykina, N. Kolobov, I. S. Khan, J. A. Bau, A. Ramirez, J. Gascon, *Chem. Rev.* **2020**, *120*, 8468–8535.
[14] A. Alzamly, M. Bakiro, S. Hussein Ahmed, M. A. Alnaqbi, H. L. Nguyen, *Coord. Chem. Rev.* **2020**, *425*, 213543.
[15] F. Saraci, V. Quezada-Novoa, P. R. Donnarumma, A. J. Howarth, *Chem. Soc. Rev.* **2020**, *49*, 7949–7977.
[16] M. Seitz, A. G. Oliver, K. N. Raymond, *J. Am. Chem. Soc.* **2007**, *129*, 11153–11160.
[17] M. Fujita, S. Washizu, K. Ogura, Y. J. Kwon, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152.
[18] Z. Hu, D. Zhao, *CrystEngComm* **2017**, *19*, 4066–4081.
[19] O. Ohmori, M. Fujita, *Chem. Commun.* **2004**, *4*, 1586–1587.
[20] A. Henschel, K. Gedrich, R. Kraehnert, S. Kaskel, *Chem. Commun.* **2008**, 4192–4194.
[21] K. Iwanami, J. C. Choi, B. Lu, T. Sakakura, H. Yasuda, *Chem. Commun.* **2008**, 1002–1004.
[22] H. S, D. M, T. K, L. JR, *J. Am. Chem. Soc.* **2008**, *130*, 5854–5855.
[23] X.-P. P. Dai, Y.-Z. Z. Hou, J. Guan, L.-B. Bin Liu, H. Wang, L.-B. B. Zhou, *J. Clust. Sci.* **2020**, *31*, 1077–1085.
[24] F. Zhang, J. Zhang, B. Zhang, L. Zheng, X. Cheng, Q. Wan, B. Han, J. Zhang, *Green Chem.* **2020**, *22*, 5995–6000.
[25] R. F. Dvries, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla, M. A. Monge, *Cryst. Growth Des.* **2014**, *14*, 2516–2521.
[26] C. Pagis, M. Ferbinteanu, G. Rothenberg, S. Tanase, *ACS Catal.* **2016**, *6*, 6063–6072.
[27] G. E. Gomez, E. V. Brusau, J. Sacanell, G. J. A. A. Soler Illia, G. E. Narda, *Eur. J. Inorg. Chem.* **2018**, 2452–2460.
[28] P. K. Batista, D. J. M. Alves, M. O. Rodrigues, G. F. De Sá, S. A. Junior, J. A. Vale, *J. Mol. Catal. A* **2013**, *379*, 68–71.
[29] X. Wu, Z. Lin, C. He, C. Duan, *New J. Chem.* **2012**, *36*, 161–167.
[30] R. F. D. Vries, M. Iglesias, N. Snejko, E. Gutie, M. A. Monge, *Inorg. Chem.* **2012**, *51*, 11349–11355.
[31] P. Wu, J. Wang, Y. Li, C. He, Z. Xie, C. Duan, *Adv. Funct. Mater.* **2011**, *21*, 2788–2794.
[32] H. An, L. Wang, Y. Hu, F. Fei, *CrystEngComm* **2015**, *17*, 1531–1540.
[33] F. Fei, H. An, C. Meng, L. Wang, H. Wang, *RSC Adv.* **2015**, 18796–18805.
[34] X. Wang, L. Zhang, J. Yang, F. Liu, F. Dai, R. Wang, D. Sun, *J. Mater. Chem. A* **2015**, *3*, 12777–12785.
[35] O. R. Evans, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395–10396.
[36] C. Zhu, Q. Xia, X. Chen, Y. Liu, X. Du, Y. Cui, *ACS Catal.* **2016**, *6*, 7590–7596.
[37] R. F. Dvries, V. A. De La Peña-Oshea, N. Snejko, M. Iglesias, E. Gutiérrez-Puebla, M. Á. Monge, *Cryst. Growth Des.* **2012**, *12*, 5535–5545.

**ChemCatChem**

Research Article
**doi.org/10.1002/cctc.202200967**

**Chemistry Europe**
European Chemical
Societies Publishing

[38] G. E. Gomez, A. M. Kaczmarek, R. Van Deun, E. V. Brusau, G. E. Narda, D. Vega, M. Iglesias, E. Gutierrez-Puebla, M. Á. Monge, *Eur. J. Inorg. Chem.* **2016**, 1577–1588.

[39] M. Gustafsson, A. Bartoszewicz, B. Martiín-Matute, J. Sun, J. Grins, T. Zhao, Z. Li, G. Zhu, X. Zou, *Chem. Mater.* **2010**, *22*, 3316–3322.

[40] A. Karmakar, G. M. D. M. Rúbio, A. Paul, M. F. C. Guedes da Silva, K. T. Mahmudov, F. I. Guseinov, S. A. C. Carabineiro, A. J. L. Pombeiro, *Dalton Trans.* **2017**, *46*, 8649–8657.

[41] H. He, H. Ma, D. Sun, L. Zhang, R. Wang, D. Sun, *Cryst. Growth Des.* **2013**, *13*, 3154–3161.

[42] E. Echenique-Errandonea, J. M. Pérez, S. Rojas, J. Cepeda, J. M. Seco, I. Fernández, A. Rodríguez-Diéguez, *Dalton Trans.* **2021**, *50*, 11720–11724.

[43] Y. Li, S. J. Gould, P. J. Proteau, *Tetrahedron Lett.* **2000**, *41*, 5181–5185.

[44] L. Zhang, K. Jiang, L. Li, Y. P. Xia, T. L. Hu, Y. Yang, Y. Cui, B. Li, B. Chen, G. Qian, *Chem. Commun.* **2018**, *54*, 4846–4849.

[45] D. Llunell, M. Casanova, D. Cirera, J. Bofill, J. M. Alemany, P. Alvarez, S. Pinsky, M. Avnir, *SHAPE, v1.1b, Barcelona, Spain* **2005**, 1–35.

[46] J. M. Pérez, S. Rojas, A. García-García, H. Montes-Andrés, C. Ruiz Martínez, M. S. Romero-Cano, D. Choquesillo-Lazarte, V. K. Abdelkader-Fernández, M. Pérez-Mendoza, J. Cepeda, et al., *Inorg. Chem.* **2022**, *61*, 1377–1384.

[47] V. A. Blatov, A. P. Shevchenko, D. M. Proserpio, *Cryst. Growth Des.* **2014**, *14*, 3576–3586.

[48] R. J. Hunter, R. H. Ottewill, R. L. Rowell, *Zeta Potential in Colloid Science: Principles and Applications*, Elsevier Science, **2013**.

[49] J. B. Sternberg, Jeffrey Arthur, Adams, *Eur. Pat. Appl.* **1992**, 120.

[50] D. J. C. Constable, D. Curzons, V. L. Cunningham, *Green Chem.* **2002**, 521–527.

[51] B. M. Trost, *Science* **1991**, *254*, 1471–1477..