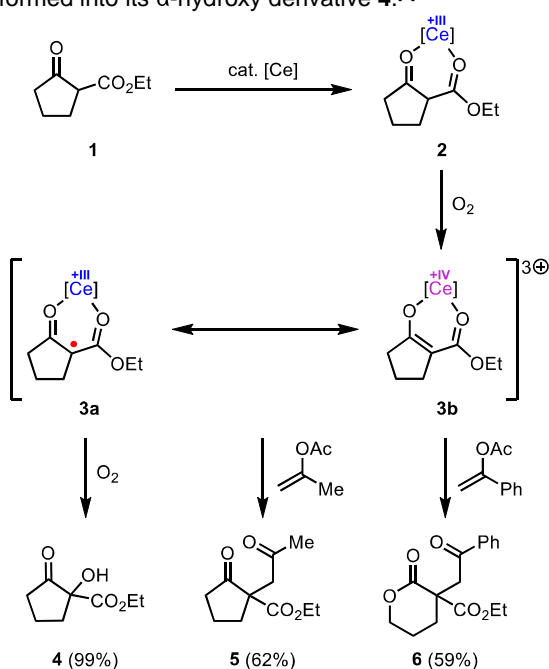


The use of a non-toxic cerium catalyst and atmospheric oxygen presents a considerable advantage for sustainability in synthetic organic chemistry. A novel 1,3-diketone ligand was developed to oxidize cerium(III) to cerium(IV) without being consumed as a substrate. This offers the opportunity to develop cerium-catalyzed oxidation reactions.

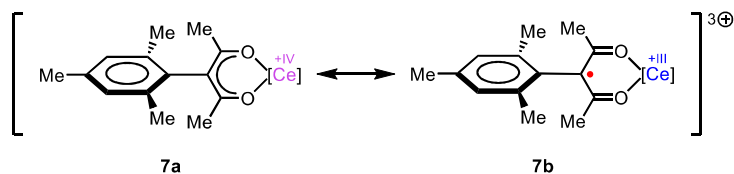
Previous Work

Our group pioneered the use of cerium as a catalyst metal for reactions, such as coupling β -oxoesters, like compound **1**, with enol esters to prepare δ -lactones **6** or 1,4-diketones **5**.^[1,2] This environmentally sustainable method utilizes a non-toxic cerium catalyst with atmospheric oxygen, where substrate **1** serves as a ligand for the catalyst, facilitating the oxidation of cerium(III) to cerium(IV) (species **3a** and **3b**). In the absence of an enol ester, β -oxoester **1** is transformed into its α -hydroxy derivative **4**.^[3]

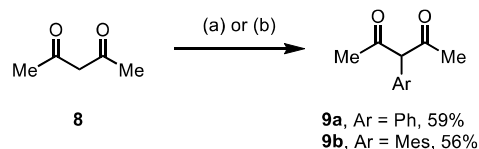


Concept and Synthesis

We have now proceeded towards the development of a novel type of 1,3-diketone ligand, designed to oxidize cerium(III) to cerium(IV) (species **7a** and **7b**) without consumption as a substrate. This would open up possible pathways for numerous cerium-catalyzed oxidation reactions.



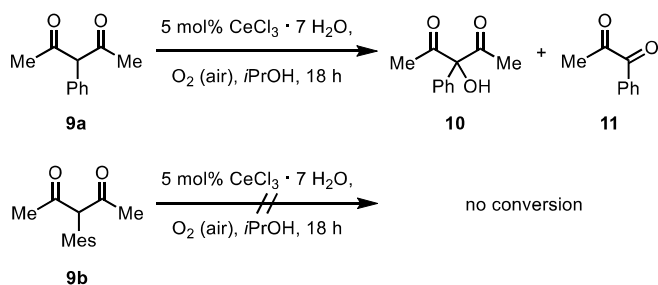
The ligand was synthesized via a three-step process, in which a triaryl bismuthane is prepared by Grignard reaction from BiCl_3 . Followed by oxidative halogenation with sulfuryl chloride, to then employ the resulting $\text{Mes}_3\text{BiCl}_2$ in the α -arylation of acetylacetone, which gave the ligand **9b** in 56% yield. Its phenylated congener **9a** was obtained by Ullmann coupling of iodobenzene and acetylacetone with copper iodide in a 59% yield.



(a) Ar = Ph: CuI , L-Pro, K_2CO_3 , PhI, *abs.* DMSO, 100°C , 18 h
(b) Ar = Mes: $\text{Mes}_3\text{BiCl}_2$, TMG, *abs.* THF, r.t., 48 h

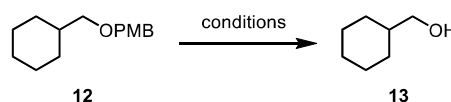
Stability Tests

To investigate the stability of the synthesized ligand **9b** it was exposed to conditions for cerium-catalyzed oxidations. In contrast to the decomposition of the phenyl derivate **9a** to the α -hydroxy compound **10** and a 1,2-diketone **11**, the mesitylated derivative **9b** remains stable.



Preliminary Results of Catalytic Activity

Catalytic activity was evaluated through the model reaction of PMB ether deprotection. Experiments were controlled by GLC and GC-MS analysis, tracking the conversion of starting material **12**, formation of cyclohexylmethanol **13** and any byproducts. The traditional method of using stoichiometric CAN posed as a comparison.



Conditions	Results
a) 2 equiv. CAN, ACN/ H_2O , 9:1, r.t.	✓
b) 5 mol% $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$, <i>i</i> PrOH, O_2 (air), r.t.	✗
c) 5 mol% $\text{CeCl}_3 \cdot 7 \text{H}_2\text{O}$, 15 mol% 9b , TFE, O_2 (1 atm), r.t.	✓

[1] I. Geibel, A. Dierks, T. Müller, J. Christoffers, *Chem. Eur. J.* **2017**, *23*, 7245–7254.

[2] (a) M. Rössle, T. Werner, A. Baro, W. Frey, J. Christoffers, *Angew. Chem. Int. Ed.* **2004**, *43*, 6547–6549; *Angew. Chem.* **2004**, *116*, 6709–6711. (b) I. Geibel, J. Christoffers, *Eur. J. Org. Chem.* **2016**, 918–920.

[3] J. Christoffers, T. Werner, *Synlett* **2002**, 119–121.