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The RuO_4-catalysed dihydroxylation, ketohydroxylation and mono oxidation—novel oxidation reactions for the synthesis of diols and α-hydroxy ketones†

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α-Hydroxy ketones are versatile intermediates for the synthesis of complex molecular architectures and subunits of a variety of natural products. Different approaches towards the synthesis of this important functional group combination have been elaborated. The present article summarises our research on the field of RuO_4-catalysed oxidations of alkenes that resulted in the development of the first RuO_4-catalysed ketohydroxylation of olefins. Mechanistic investigations of both dihydroxylation and ketohydroxylation led to the discovery of the first regioselective catalytic mono oxidation of *vic*-diols, which was applied in a two-step sequence of asymmetric dihydroxylation and regioselective mono oxidation to furnish enantiopure α-hydroxy ketones with both predictable regioselectivity and absolute configuration.

Introduction

The past thirty years have seen a tremendous development in the field of catalysis.[1] With regard to environmental and economical arguments the development of reactions in which new atom bonds are formed while using only small amounts of a recyclable reagent meets current criteria of sustainable development.[2] Among the catalytic transformations the introduction of oxygen occupies an important place. The fact that traditional oxidation reactions often use stoichiometric amounts of hazardous and poisonous oxidizing agents clearly indicates the need for the development of catalytic systems in which the active oxidant is formed in minor amounts and recycled by a non-toxic and non-explosive reoxidant. In the ideal case the final reoxidant would be oxygen. Hence, the development of new and improvement of already known oxygen transfer reactions still represents a challenging problem.[3]

The oxidation of *C*,*C*-double bonds occupies an important place among oxygen transfer reactions.[4] The transfer of only one oxygen in a catalytic hydroboration–oxidation[5] as well as the formation of two *C*,*O*-bonds in the catalytic epoxidation[6] and dihydroxylation[7] have been in the centre of research for the past years. However, when we started our research in the field of oxidation chemistry only a few reports dealt with the introduction of three *C*,*O*-bonds, a reaction that would allow the transformation of a *C*,*C*-double bond into a synthetically useful α-hydroxy ketone.[8] The present paper summarises our investigations aimed towards the development of a novel direct ketohydroxylation of olefins. Starting with the fundamental finding of a proton assisted rate acceleration in RuO_4-catalysed dihydroxylations[9] a transfer of these results subsequently led to the discovery of the first RuO_4-catalysed regioselective ketohydroxylation of olefins.[10] The observations made in both projects were applied in the development of the first catalytic regioselective mono oxidation of *vic*-diols, a reaction that was used for the simple preparation of enantiomerically enriched unsymmetrical acyloins.[11] Finally the mechanistic relationship between these three reactions will be discussed in detail.

The RuO_4-catalysed dihydroxylation

Among the so far known catalytic oxidation reactions the osmium tetraoxide-catalysed asymmetric dihydroxylation following the Sharpless protocol represents a benchmark reaction when it comes to generality and selectivity.[4] Despite its synthetic usefulness the toxicity, volatility and high cost of the osmium-catalyst have prevented a successful application of the reaction on industrial scale. Therefore, the search for alternative dihydroxylation-catalysts remains a challenging problem. Shing reported in 1994 the use of the isoelectronic ruthenium(VIII) oxide, prepared *in situ*

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Meike Niggemann (left) and Bernd Plietker (right)

Bernd Plietker studied chemistry in Münster, Germany, and received his diploma degree in 1995. He did his PhD under supervision of Peter Metz in the field of intramolecular Diels–Alder reactions first in Münster and later on at the Technische Universität Dresden, Germany. After finishing his PhD he did a first postdoc with Jan-Erling Bäckvall, Stockholm Universitet, Sweden, from 1999–2000 and second one with Barry M. Trost from 2000–2001 working in the field of Pd-catalysis. Since fall 2001 he has been working towards his habilitation in the group of Norbert Krause, Universität Dortmund, Germany. The research in his group focuses on the preparation of highly oxidised ruthenium compounds and their use in catalysis.

Meike Niggemann studied chemistry at Universität Dortmund, Germany, and received her diploma in 2003. During her studies she worked for six months as an undergraduate researcher at the University of Edinburgh, UK. Since October 2003 she has been studying for her PhD under the supervision of Bernd Plietker and Norbert Krause. Her research interests are in the field of ruthenium-catalysed dihydroxylation reactions.

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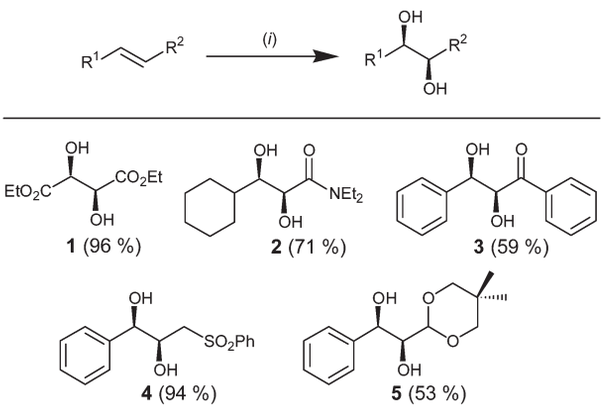
from inexpensive ruthenium(III) chloride as a promising alternative dihydroxylation catalyst.[12] However, because of the significantly higher redox potential of ruthenium(VIII) (E^0 (Ru(VIII)/Ru(VI)): 1.400 V) compared to osmium(VIII) (E^0(Os(VIII)/Os(VI)): 1.020 V) overoxidation and formation of fission products are common side reactions in ruthenium-catalysed dihydroxylations.[13] Despite these problems we envisioned RuO_4 not only to be a less toxic and expensive but also more potent oxidizing agent for the dihydroxylation of olefins known to be unreactive in osmium-catalysed oxidations. During intense investigations on factors influencing the selectivity of the reaction it was found that simple addition of catalytic amounts of protic acids led to a significant rate acceleration and consecutively to a drastically reduced catalyst loading from originally 7 mol% down to only 0.5 mol% (Scheme 1) while maintaining the short reaction times (s to min).[9]



Scheme 1 *Reagents and conditions*: (i) 0.5 mol% $RuCl_3$, 20 mol% H_2SO_4, 1.5 equiv. $NaIO_4$, EtOAc/CH_3CN/H_2O (6/6/1), 0 °C.

Due to the short reaction times acid labile functional groups, such as allylic halides, esters, and amides are compatible with the reaction conditions. Even acetals can be dihydroxylated under slightly adapted reaction conditions. The oxidation of allylic, benzylic or tertiary *C*,*H*-bonds as well as alkyne moieties was not observed on the time scale of the dihydroxylation reaction.

The acid-induced rate acceleration can be rationalised in analogy to the acid catalysed cleavage of carboxylic acid esters by an activation of the intermediate ruthenate **I** (Fig. 1) *via* coordination of a proton to one of the *Ru*,*O*-bonds. The resulting electron-deficient ruthenate **II** should react fast with the incoming water to give the desired diol **III** (for a detailed mechanistic discussion of the catalytic cycle see Fig. 3).

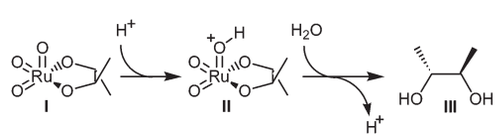


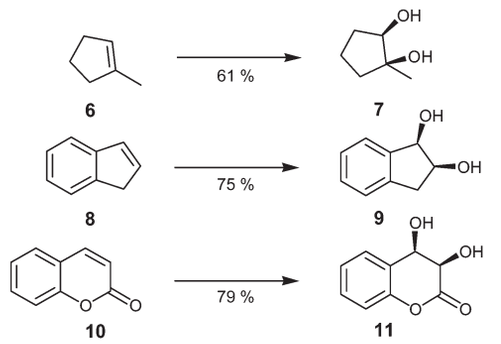
Fig. 1 Postulated activation of ruthenate **I** by protonation.

Due to a fast electrocyclic fragmentation favoured by the release of ring strain the conversion of cyclic olefins can be problematic in some cases, however a range of different cycloalkenes was dihydroxylated in moderate to good yields (Scheme 2).

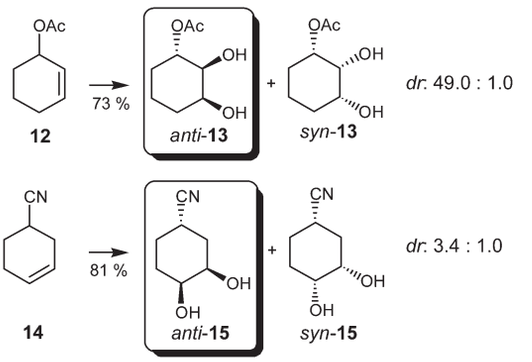
Oxidation of chiral cyclic olefins possessing stereocentres in allylic or homoallylic positions gave the corresponding *vic*-diols in good to excellent diastereoselectivity (Scheme 3). Apart from the fact, that the dihydroxylation follows the Kishi rules it is important to note that the simple stereoselectivity in RuO_4-catalysed oxidation is much higher compared to the analogous reaction using OsO_4.[14]

The RuO_4-catalysed ketohydroxylation

Knowing the beneficial influence of protons on the dihydroxylation we speculated that it would in principal be possible to use a different nucleophile than water to cleave the intermediate ruthenates. If this alternative nucleophilic agent possesses additional



Scheme 2 Dihydroxylation of cycloalkenes. *Reagents and conditions*: 0.5 mol% $RuCl_3$, 20 mol% H_2SO_4, 1.5 equiv. $NaIO_4$, EtOAc/CH_3CN/H_2O (6/6/1), 0 °C.



Scheme 3 Dihydroxylation of chiral cyclic olefins **12** and **14**. *Reagents and conditions*: 0.5 mol% $RuCl_3$, 20 mol% H_2SO_4, 1.5 equiv. $NaIO_4$, EtOAc/CH_3CN/H_2O (6/6/1), 0 °C.

oxidising properties a different mechanistic pathway eventually leads to the formation of α-hydroxy ketones instead of *vic*-diols. This dichotomy is shown in Fig. 2.

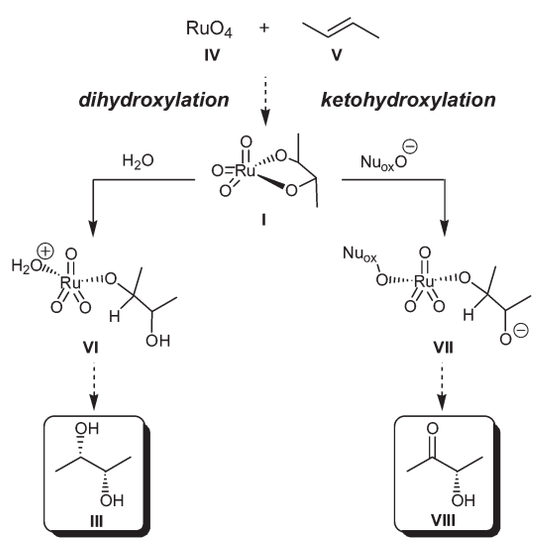
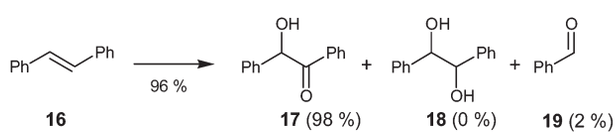


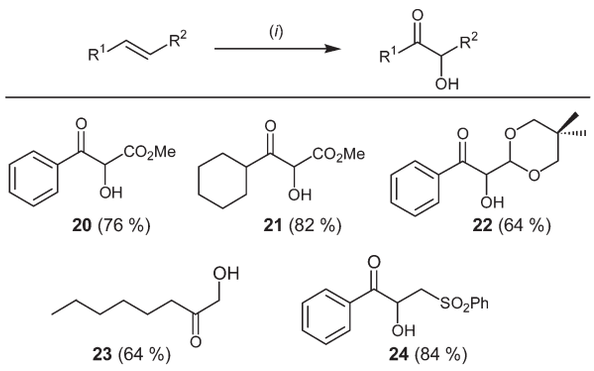
Fig. 2 Dihydroxylation *vs.* ketohydroxylation.

Indeed, upon treatment of stilbene **16** with a combination of Oxone ($2NaHSO_5$*$NaHSO_4$*Na_2SO_4) in the presence of catalytic amounts of $RuCl_3$ under slightly different conditions compared to the dihydroxylation an efficient direct oxidation of the *C*,*C*-double bond to benzoin **17** was achieved (Scheme 4).[13b,15]



Scheme 4 *Reagents and conditions*: $RuCl_3$ (1 mol%), Oxone (5 equiv.), $NaHCO_3$ (2.5 equiv.), EtOAc/CH_3CN/H_2O (6/6/1), rt.

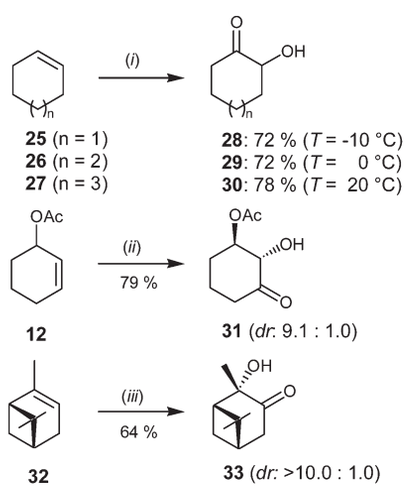
Detailed investigations on scope and limitations rendered this new oxidation method to be broadly applicable.[10] A variety of functional groups are tolerated. Most interestingly due to the very short reaction times even acid labile groups like acetals are compatible with the reaction conditions (Scheme 5).



Scheme 5 *Reagents and conditions*: $RuCl_3$ (1 mol%), Oxone (5 equiv.), $NaHCO_3$ (2.5 equiv.), EtOAc/CH_3CN/H_2O (6/6/1), rt.

We were pleased to find that this reaction is not only chemo- but also highly regioselective. Depending on the electronic properties of the substituents at the *C*,*C*-double bond regioselectivities ranging from 3.0 : 1.0 up to >10.0 : 1.0 were observed with the hydroxyl group ending up proximal to the most electron-withdrawing substituent.[10b]

The ketohydroxylation of cyclic olefins however proved to be less selective. These problems were overcome by varying the reaction temperature. Some representative examples are given in Scheme 6. As in the dihydroxylation the simple diastereoselectivity in the ketohydroxylation follows the Kishi rules indicating that the active catalyst is indeed RuO_4.



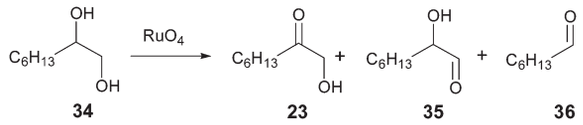
Scheme 6 *Reagents and conditions*: $RuCl_3$ (1 mol%), Oxone (5 equiv.), $NaHCO_3$ (2.5 equiv.), EtOAc/CH_3CN/H_2O (6/6/1); (i) temperatures are given in brackets, (ii) T = 20 °C; (iii) T = 0 °C.

The ketohydroxylation represents a novel straightforward direct oxidation of olefins to α-hydroxy ketones in a both highly regio- and diastereoselective way. The resulting unsymmetrical acyloins might serve as useful building blocks for the synthesis of more complex molecular architectures. However, the development of an asymmetric version of this new oxidation is our ultimate future goal. In the meantime we developed a simple two-step procedure of asymmetric dihydroxylation and regioselective mono oxidation that allows the preparation of unsymmetrical acyloins in good to excellent enantiopurity.

The RuO_4-catalysed mono oxidation

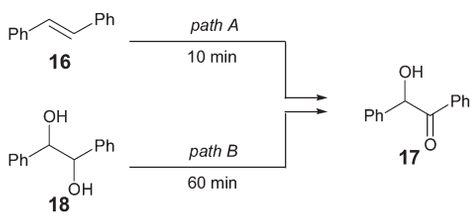
Having established the new ketohydroxylation protocol we were wondering whether this oxidation is a direct oxidation or the result of a two-step procedure of flash-dihydroxylation and subsequent overoxidation. Hence, two control experiments were performed (Scheme 7). The reaction rate of the direct oxidation of stilbene **16** (*path A*) was compared to the rate in the overoxidation of hydrobenzoin **18** (*path B*).[10a]

Table 1 Influence of the reoxidant



Entry	Reoxidant	**23** : **35** : **36**[a]	Conv. [%][a]
1	NaOCl	41 : 4 : 55	75
2	$NaIO_4$	12 : 0 : 88	98
3	$K_2S_2O_8$	n.d.	21
4	$KBrO_3$	15 : 0 : 85	47
5	Oxone/$NaHCO_3$	92 : 0 : 8	96

[a] Determined by GC-integration.



Scheme 7 *Reagents and conditions*: $RuCl_3$ (1 mol%), Oxone (5 equiv.), $NaHCO_3$ (2.5 equiv.), EtOAc/CH_3CN/H_2O (6/6/1), rt.

This test experiment clearly proved the ketohydroxylation to be much faster and hence to be a direct oxidation without formation of intermediate *vic*-diols. However, with regard to the good regioselectivities in ketohydroxylations we were wondering if the oxidation of *vic*-diols under identical conditions would result in the formation of acyloins with the same degree of regioselectivity. Different oxidising agents were used under the conditions developed for the ketohydroxylation. The results are listed in Table 1. Among the tested reoxidants only the combination of Oxone/$NaHCO_3$ allowed the regio- and chemoselective formation of α-hydroxy ketone **23**. Since the reaction is thought to proceed *via* a cyclic ruthenate **XI** (Fig. 3) these results indicate, that the cyclic nature of **XI** in combination with the use of Oxone as a nucleophilic reoxidant amplifies the electronic bias necessary for a regioselective oxidation. To the best of our knowledge this is the first example of a catalytic regioselective mono oxidation of *vic*-diols.[11]

With regard to the ketohydroxylation we thought that this transformation could provide first insights into the stability of α-hydroxy ketones under acidic ketohydroxylation conditions. Hence, a variety of enantiomerically enriched glycols were prepared according to the Sharpless-procedure and regioselectively oxidised using $RuCl_3$/Oxone/$NaHCO_3$. We were pleased to find that in all cases a complete conservation of enantiopurity was observed. Hence, this procedure allows the simple preparation of a variety of *enantiopure acyloins with predictable regioselectivity and absolute configuration* by using alkenes as α-ketol surrogates.[11] Thus, it complements the so far developed methods for the preparation of enantiomerically enriched acyloins, *e.g.* the asymmetric benzoin condensation,[16] the asymmetric dihydroxylation of enolethers[17] or the direct organocatalytic α-hydroxylation of carbonyl compounds using (L)-proline[8] as a catalyst. Representative examples are given in Scheme 8.

The remarkable stability of α-hydroxy ketones even under acidic conditions might be due to a stabilizing hydrogen bridge between hydroxy and carbonyl group. In the resulting almost planar five-membered ring chelate the σ(*C*,*H*)-molecular orbital is not coplanar to the π(*C*,*O*)-orbital of the carbonyl group. Thus, this hydrogen bridge might disturb the enantiodecreasing [1,3]-hydrogen shift between α-carbon and carbonyl oxygen.

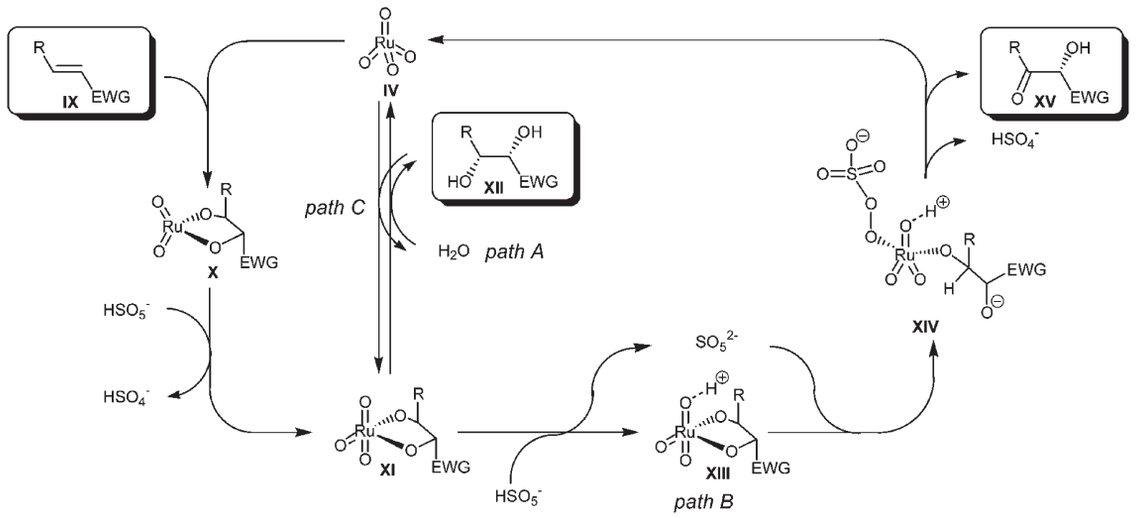
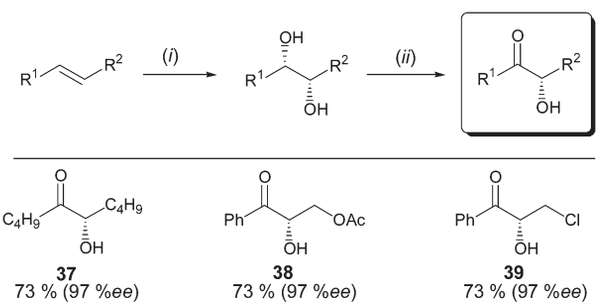


Fig. 3 Proposed mechanism for ruthenium-catalysed dihydroxylations (path A), ketohydroxylations (path B) and mono oxidations (path C).



Scheme 8 *Reagents and conditions*: (i) AD-Mix-α, $MeSO_2NH_2$ (1 equiv.), t-BuOH/H_2O (1/1), 0 °C; (ii) $RuCl_3$ (1 mol%), Oxone (5 equiv.), $NaHCO_3$ (2.5 equiv.), EtOAc/CH_3CN/H_2O (6/6/1), rt.

With regard to a future asymmetric development of the ketohydroxylation it is important to note, that (*i*) the asymmetric [3 + 2]-cycloaddition of a group(VIII)-metal oxide creates two new stereocentres with defined relative and absolute configuration, that (*ii*) only the combination of $RuCl_3$/Oxone/$NaHCO_3$ allows a regioselective formation of α-hydroxy ketones, and finally, that (*iii*) the enantiopure α-hydroxy ketones do not epimerise under acidic conditions.

Mechanistic proposal and future perspectives

Based upon observations made during the optimisations of these three RuO_4-catalysed oxidations a simplified mechanistic model is proposed. The mechanistic relationship between the different reactions is shown in Fig. 3. Starting with olefin **IX** an initial [3 + 2]-cycloaddition leads to ruthenium(VI)-compound which is oxidised to ruthenate **XI**. This cyclic ruthenium-ester plays a key role in all three transformations. On the one hand the nucleophilic addition of water leads to the formation of *vic*-diol **XII** (*path A*: the dihydroxylation). In the presence of Oxone as the alternative nucleophile activated ruthenate **XIII** is attacked by the SO_5^{2-} to give peroxo compound **XIV** collapsing to α-hydroxy ketone **XV** and RuO_4 (*path B*: the ketohydroxylation). During the optimisation of the dihydroxylation we found an acceleration of the glycol cleavage in the presence of RuO_4.[9] This observation and the results obtained in the mono oxidation process[11] indicate, that the hydrolysis of ruthenate **XI** is indeed a reversible process. Hence, a condensation of *vic*-diol **XII** with RuO_4 **IV** leads to cyclic ruthenate **XI**, which reacts with Oxone under the ketohydroxylation conditions to α-hydroxy ketone **XV** (*path C*: the mono oxidation). Thus, the future problem of enantioselectivity in these reactions can be reduced to the development of an enantioselective [3 + 2]-cycloaddition between RuO_4 and the olefin. While the π-bond geometry is directly translated into the relative stereochemistry at the two newly formed adjacent centres of chirality the remaining steps in the mechanism do not involve any further reaction at these stereocentres. In the ketohydroxylation one of the two new chirality centres is destroyed during the oxidation however the second centre ends up in the final product and does not epimerise under the reaction conditions.

Future work will focus on detailed investigations of mechanistic aspects by spectroscopic means. Kinetic and theoretical investigations might help to complement these results leading to an improved understanding of factors that influence the reactivity in RuO_4-catalysed oxidation reactions. This knowledge can be applied in the development of an asymmetric ruthenium catalysed di- and ketohydroxylation. Applications towards the synthesis of biological active natural products are on the way.

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