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Synthetic, spectral and catalytic activity studies of ruthenium bipyridine and terpyridine complexes: Implications in the mechanism of the ruthenium(pyridine-2,6-bisoxazoline)(pyridine-2,6-dicarboxylate)-catalyzed asymmetric epoxidation of olefins utilizing H_2O_2

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Abstract

Various $Ru(L_1)(L_2)$ (**1**) complexes (L_1 = 2,2′-bipyridines, 2,2′:6′,2″-terpyridines, 6-(4*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl-2,2′-bipyridinyl or 2,2′-bipyridinyl-6-carboxylate; L_2 = pyridine-2,6-dicarboxylate, pyridine-2-carboxylate or 2,2′-bipyridinyl-6-carboxylate) have been synthesized (or in situ generated) and tested on epoxidation of olefins utilizing 30% aqueous H_2O_2. The complexes containing pyridine-2,6-dicarboxylate show extraordinarily high catalytic activity. Based on the stereoselective performance of chiral ruthenium complexes containing non-racemic 2,2′-bipyridines including 6-[(4*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridinyl new insights on the reaction intermediates and reaction pathway of the ruthenium-catalyzed enantioselective epoxidation are proposed. In addition, a simplified protocol for epoxidation of olefins using urea hydrogen peroxide complex as oxidizing agent has been developed.
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Keywords: Ruthenium; Olefin; Epoxidation; Homogeneous catalysis; Mechanism

1. Introduction

Oxidation reactions constitute one of the core technologies which convert simple bulk raw materials, such as alkanes and olefins, to value-added products in higher oxidation states [1]. However, in the area of fine chemicals and pharmaceuticals they are less established on industrial scale compared to reductions and CC coupling reactions. For a more general application of oxidation reactions, the "ideal" oxidant should be in high atom-economy, environmentally benign, readily available and safe as well [2]. Air (molecular oxygen) is undoubtedly the perfect oxidant of choice for a number of oxidation reactions. However, only one oxygen atom of O_2 is productive for most oxidations (50% atom efficiency), thus such processes produce significant amount of waste from the co-reductant [3,4]. Apart from molecular oxygen, hydrogen peroxide (H_2O_2) has been shown to be a useful oxidant with respect to the criteria mentioned above [5,6]. Due to its handling and price it is particularly useful for liquid-phase oxidations for the synthesis of fine chemicals, pharmaceuticals, agrochemicals and electronic materials. Hence, developments on new catalytic systems using H_2O_2 are an important and challenging goal in oxidation chemistry [7,8].

With regard to enantioselective epoxidations of olefins, titanium (Sharpless epoxidation) [9] and manganese (Jacobsen–Katsuki epoxidation) [10] based catalysts are still in the state-of-the-art. Very recently Katsuki et al. demonstrated that a titanium schiff base catalyst showed very good activity and excellent ee in asymmetric epoxidation utilizing aqueous H_2O_2 [11]. In the last decade significant

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progress using organic catalysts based on chiral ketones (Shi, Yang and other's ketone catalysts) [12,13] has also been reported. Besides, the polypeptide-catalyzed stereoselective epoxidation of enones under phase transfer conditions seems to be an industrially applicable process [14]. Chiral Lewis acids [15] and chiral amines [16] catalyzed epoxidation of α,β-unsaturated olefins also have been demonstrated.

Generally, there are several problems associated with the use of H_2O_2 in asymmetric epoxidations [8]. For instance H_2O_2 usually decomposes to O_2 in the presence of transition metal catalysts. Over stoichiometric amount of H_2O_2 is often employed to solve this problem. However, the stability of the catalyst in high concentration of H_2O_2 as well as the selectivity, especially enantioselectivity, in the presence of water obviously could be problematic. It is also apparent that oxidative cleavage of the olefin competes with the productive epoxidation. Therefore, even after decades of extensive research efforts, the development of general and catalytic asymmetric epoxidation methods using H_2O_2 is still underway [16,11,17].

Our interest has been aroused by ruthenium-catalyzed oxidation reactions with its wide range of applicability and broad variation of ligand type especially in asymmetric epoxidation of olefins [18]. In this regard, we chose Ru(pyridine-2,6-bisoxazoline)(2,6-pyridinedicarboxylate) (**1**) as our starting point as it contains two different meridional ligands [19]. It is patently advantageous that by modifying the chiral (pybox) and the achiral (pydic) ligands separately, the reactivity and (enantio)selectivity should be possible to tune up easily. Applying this concept, we were able to make **1** to become a more practical epoxidation catalyst by adding a controlled amount of water to the reaction mixture [20a]. This also led to the development of enantioselective epoxidation protocols applying alkyl peroxides [20b] and hydrogen peroxide [20d,20e,20f]. Noteworthy, highly productive and robust ruthenium catalysts with turnover number (TON) up to 10 000 have also been developed for non-asymmetric epoxidation with 30% aqueous H_2O_2 [20c,20e]. Most recently, a ligand library of *N*,*N*,*N*-tridentate pyridinebisimidazolines, so-called pybim ligands, was also realized during the course of these studies [20f,21]. Fig. 1 shows four of more than 70 catalysts which we have tested in the epoxidation of olefins with H_2O_2.

In this paper, we describe our work on the synthesis of novel ruthenium(II) bipyridine and terpyridine complexes. Spectral and catalytic activity studies using these complexes shed light on the mechanism of the ruthenium-catalyzed asymmetric epoxidation. Besides a simplified protocol for the epoxidation of olefins utilizing urea hydrogen peroxide complex has been developed.

2. Results and discussion

In our previous studies, we have shown that various ruthenium complexes, such as **1** and **2** allow for the epoxidation of aromatic olefins with high selectivity (chemoselectivity up to 99%; enantioselectivity up to 85%) [22]. With regard to the mechanism of this novel asymmetric epoxidation, we have established the role of the protic solvent, the effect of acid additives, and the relative rate of different catalysts. In addition, competitive reactions with different olefins suggested an unsymmetric oxo-transfer transition state [22b]. Modelling studies on the reactivity of the core structure **1′** at the B3LYP/LANL2DZ density functional level of theory showed that an *N*-oxide coordinating intermediate is likely to be the most thermodynamically stable isomer of all possible intermediates. Scheme 1 shows a preliminary mechanistic picture of the reaction.

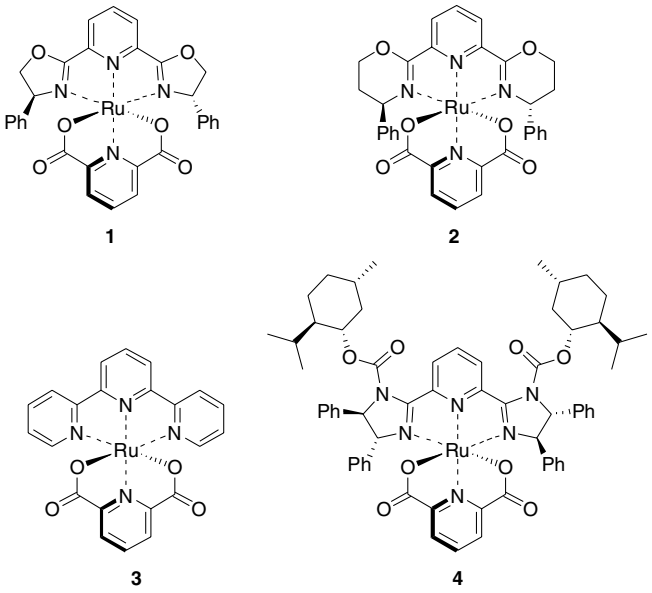
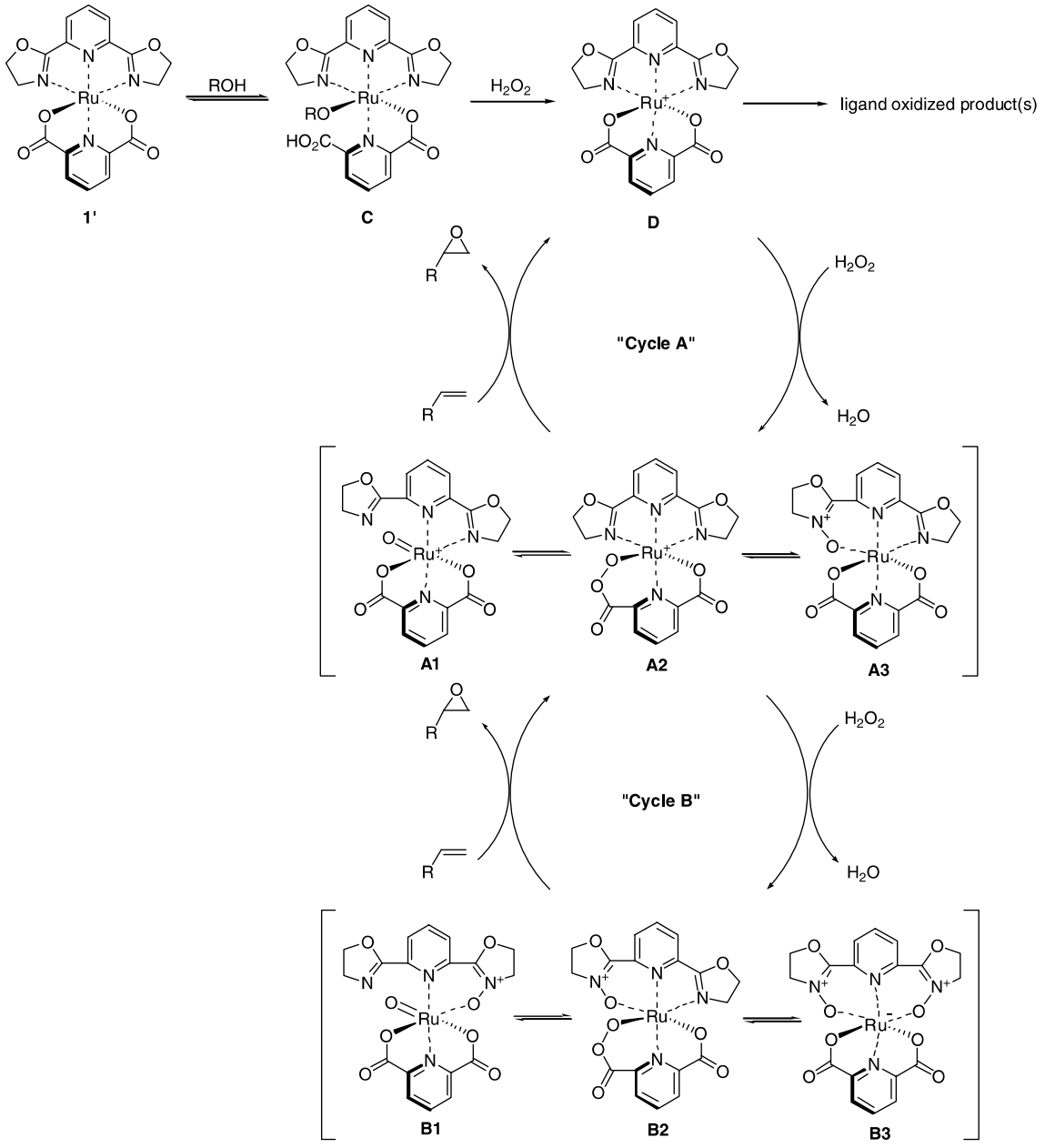


Fig. 1. Ruthenium catalysts for epoxidation of olefins with H_2O_2.

Initially, the carboxylate on **1′** dissociates in a protic solvent and makes the oxidation of the ruthenium center much faster. Hence, the ruthenium(III) species **D** forms, which is further oxidized to intermediates **A**. **A3** is the most stable one suggested by theoretical calculation. However, from the evidence of kinetic studies, **A1** is suspected to be the active oxo-transfer intermediate [23]. After epoxidation of the olefin **D** is regenerated (cycle A). Alternatively, intermediates **A** can be further oxidized to complexes **B** which transfer the oxygen atom to the olefin and regenerate intermediates **A** (cycle B).

Unfortunately, so far any isolation of ruthenium intermediates in higher oxidation state was not successful. Also initial attempts to synthesize the mono- or di-*N*-oxide of 2,6-bis-[(4*S*)-4-phenyl-4,5-dihydrooxazol-2-yl]pyridine (*S*,*S*-Ph_2-pybox) by oxidation with *m*-CPBA [24] or cyclization of (*S*)-2-hydroxy-amino-2-phenylethanol with dimethyl pyridine-2,6-dicarboximidate [25] did not yield the desired *N*-oxide ligands. Apparently *S*,*S*-Ph_2-pybox and its *N*-oxides are not stable in strong oxidizing and acidic conditions.

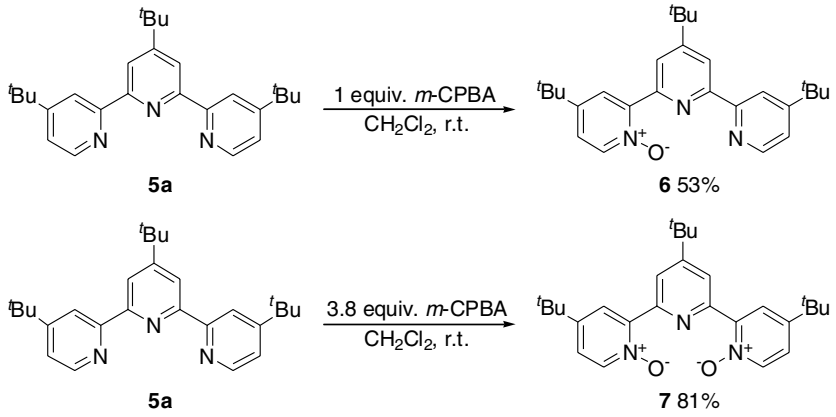
Therefore, we chose the more robust 2,2′:6′,2″-terpyridines as our model ligand system. Though the turnover



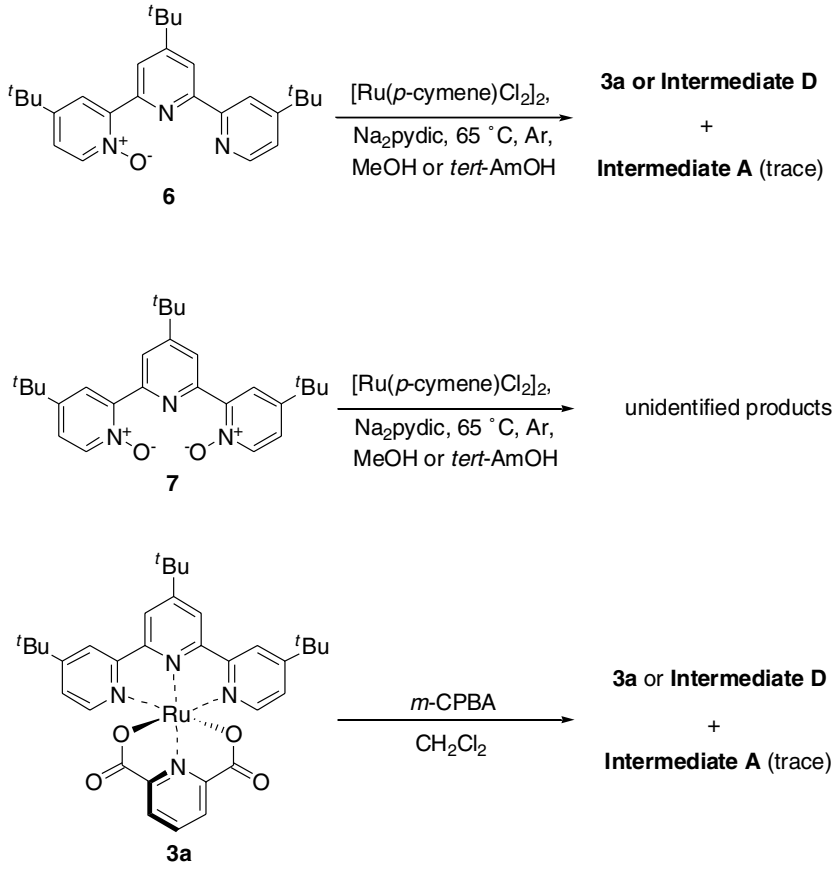
Scheme 1. Proposed mechanism for the Ru(pybox)(pydic)-catalyzed epoxidation of olefins.

number (TON) of the ruthenium terpyridine complex **3** is around 40 times larger than that of **1** (TON of **1** and **3** are ~200 and ~8000, respectively) [20d,20e], competition reactions showed that the relative rate of **3** is only 1.8–2.4 times faster than that of **1** [22b]. This shows good agreement with our hypothesis that the high productivity of **3** is due to its robustness and not electronic or steric reasons. Owing to better solubility, 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2′-terpyridine **5a** was subjected to selective oxidation with *m*-CPBA to yield **6** and **7** in 53% and 81%, respectively (Scheme 2) [26].

Next, **6** and **7** were reacted with $[Ru(p\text{-cymene})Cl_2]_2$ as illustrated in Scheme 3. In case of **6** only metal species with a molecular weight similar to **3a** have been observed in the electrospray ionization mass spectrometry (ESI-MS) after removal of solvent. Moreover, unidentified products were observed in the ESI-MS when **7** was used in the complexation reaction. Direct oxidation of **3a** with *m*-CPBA in CH_2Cl_2 turned the solution from violet to brown instantaneously. However, after removal of solvent, only a purple solid with molecular mass as **3a** was observed. Hence, titration of **3a** with *m*-CPBA monitored by UV–Vis spectroscopy in CH_2Cl_2 at 25 °C was then performed. As shown in Fig. 2 the absorption maxima at 526, 329, 321 nm were gradually decreased and the shoulder at 337 nm was increased when portions of *m*-CPBA solution was added (see Section 4). Isosbestic points were observed at 354 and 327 nm. This phenomenon indicates that a single



Scheme 2. Synthesis of terpyridine *N*-oxides.



Scheme 3. Attempts to synthesize catalytic intermediates A.

product was formed preferentially [27]. The ratio of **3a** to *m*-CPBA determined by the titration was approximately 1:1 in three different concentrations of **3a**.

The ESI-MS of the **3a**:*m*-CPBA 1:1 solution showed only the molecular ion peak similar to **3a**. No epoxide was observed even in the presence of a 10-fold excess of styrene. Reacting an excess of *m*-CPBA with **3a** in CH_2Cl_2 or CH_3CN gave only a weak molecular ion peak of $[(\mathbf{3a} + O + H)^+]$ and high intensity of $[(\mathbf{3a})^+]$ in the ESI-MS. Noteworthy, the molecular ion peak of $[(\mathbf{3a} + 2O)^+]$ has never been observed. In addition, there was no observable change in the UV–Vis spectrum when benzoic acid was added to the solution of **3a**. Hence, the UV–Vis absorption spectrum shift is not due to the formation of intermediate **A** nor protonation. Instead, we propose that **3a** is easily oxidized by *m*-CPBA to intermediate **D**. This is in agreement with the previous observation that **3** can be oxidized to a paramagnetic Ru(III) state in solution [28]. However, we could not exclude that intermediate **A** is generated in low concentration or it decomposed back

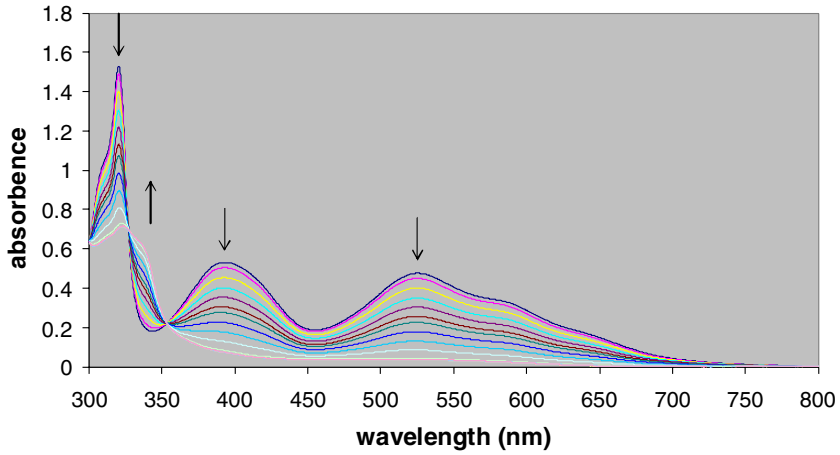


Fig. 2. UV–Vis titration of **3a** with *m*-CPBA.

to **3a** or intermediate **D**. In fact ruthenium (IV) oxo porphyrin has been reported to undergo disproportionation to give a ruthenium (II) porphyrin and a ruthenium (VI) dioxo porphyrin complex [29].

Thus, we computed the possible key intermediates aiming to have further insight about the decomposition pathways of the oxidized complex **3** (Scheme 4 and Table 1). All calculations were carried out by using the GAUSSIAN 03 program [30]. Structures were optimized at the B3LYP [31] density functional level of theory with the LANL2DZ basis set [32], and the nature of the optimized structures on the potential energy surface (PES) was characterized by the calculated number of imaginary frequency (NImag) at the same level of theory (B3LYP/LANL2DZ), i.e.; minimum structures without (NImag = 0) [33]. The corresponding frequency calculations provide also the thermal corrections to Gibbs free energies at 298 K. The energies for discussion and interpretation are the Gibbs free energies ($\Delta G = \Delta H - T\Delta S$). At B3LYP/LANL2DZ, the parent complex **3** has C_2 symmetry, and the mono- and di-oxidized species **3**(**O**) and **3**(**O**)$_2$ are C_1 and C_2 symmetrical, respectively. All three structures are energy minimums on the PES.

From the Gibbs free energy, both the bimolecular decomposition of mono-oxo complex **3**(**O**) to **3** and O_2 and self decomposition of di-oxo ruthenium complex **3**(**O**)$_2$ to **3** and O_2 are highly thermodynamically favourable

Table 1
B3LYP/LANL2DZ total electronic energies (E_{tot}, au) and total Gibbs free energies (G_{tot}, au, at 298 K) and number of imaginary frequencies (NImag)

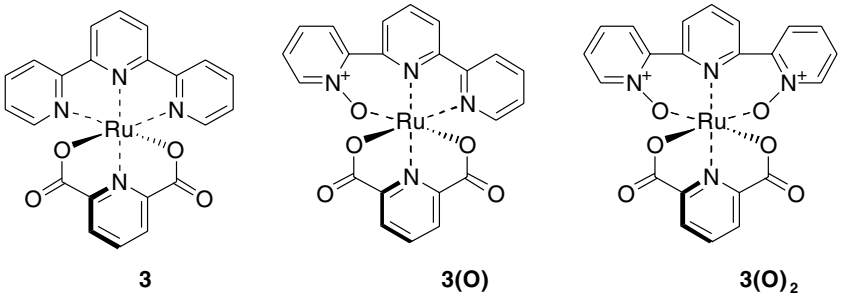
	E_{tot}	G_{tot}	NImag
3/C_2	−1460.51505	−1460.23975	0
3(**O**)/C_1	−1535.65806	−1535.38146	0
3(**O**)$_2$/C_2	−1610.79774	−1610.51774	0

$$2[\mathbf{3}(\mathbf{O})] \rightarrow 2[\mathbf{3}] + O_2 \quad \Delta G = -30.0 \text{ kcal mol}^{-1} \tag{1}$$

$$[\mathbf{3}(\mathbf{O})] \rightarrow 2[\mathbf{3}] + O_2 \quad \Delta G = -33.6 \text{ kcal mol}^{-1} \tag{2}$$

$$2[\mathbf{3}(\mathbf{O})] \rightarrow [\mathbf{3}] + [\mathbf{3}(\mathbf{O})_2] \quad \Delta G = +3.4 \text{ kcal mol}^{-1} \tag{3}$$

(about −30 kcal mol^{-1}). Disproportionation of **3**(**O**) to **3** and **3**(**O**)$_2$ is also not likely (+3.4 kcal mol^{-1}). The calculations suggest that the ruthenium oxo-transfer species is not **3**(**O**)$_2$ due to insufficient stability, though the rate of this decomposition is not so clear. Moreover, since the decomposition of **3**(**O**) is bimolecular, when the concentration of **3**(**O**) is low (as in the catalytic reaction conditions: H_2O_2 is dosed to the catalytic reaction slowly in 12 h and pre-catalyst is only in catalytic amount), the olefin acts as a good trap and epoxide forms. The bimolecular decomposition of two **3**(**O**) to molecular oxygen also explain the observation in the ESI-MS [very low intensity of **3**(**O**)] and the

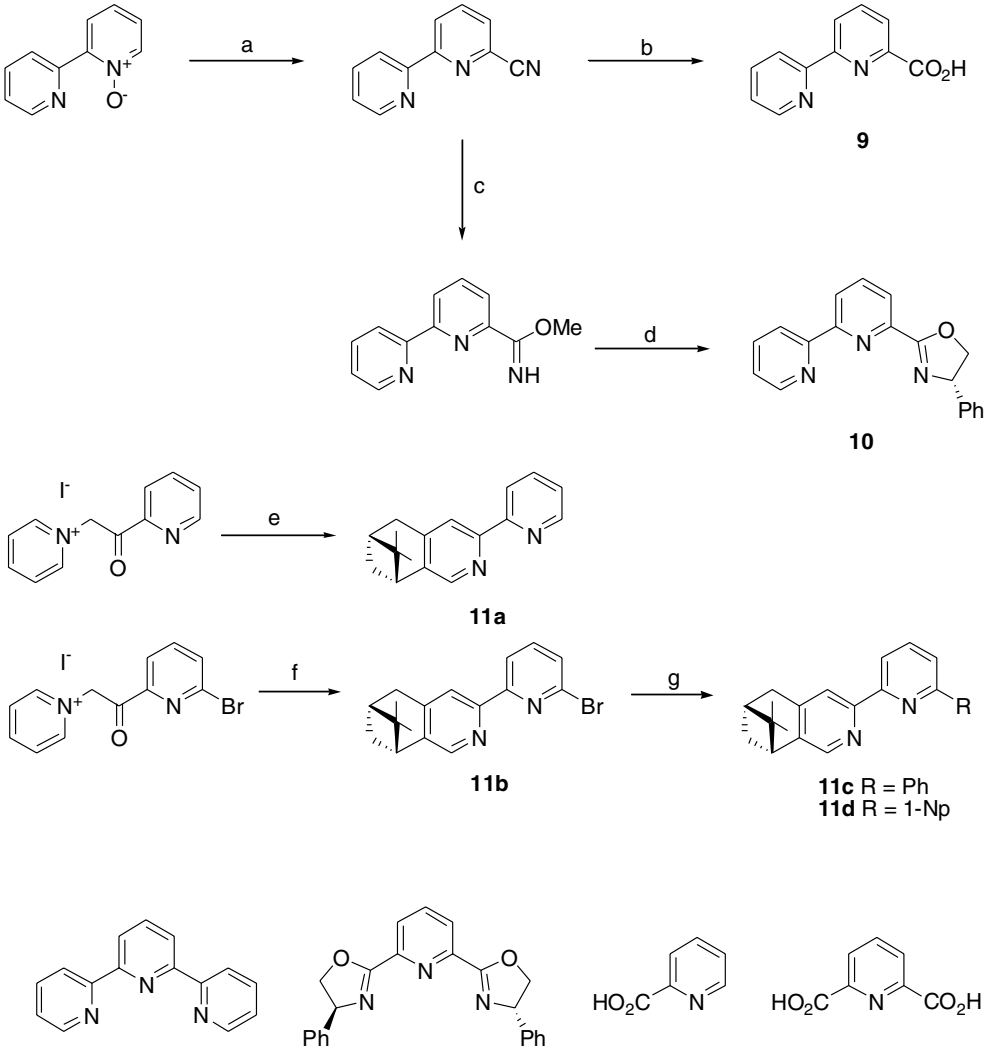


Scheme 4. Modeling of the decomposition reactions of **3**, **3**(**O**) and **3**(**O**)$_2$.

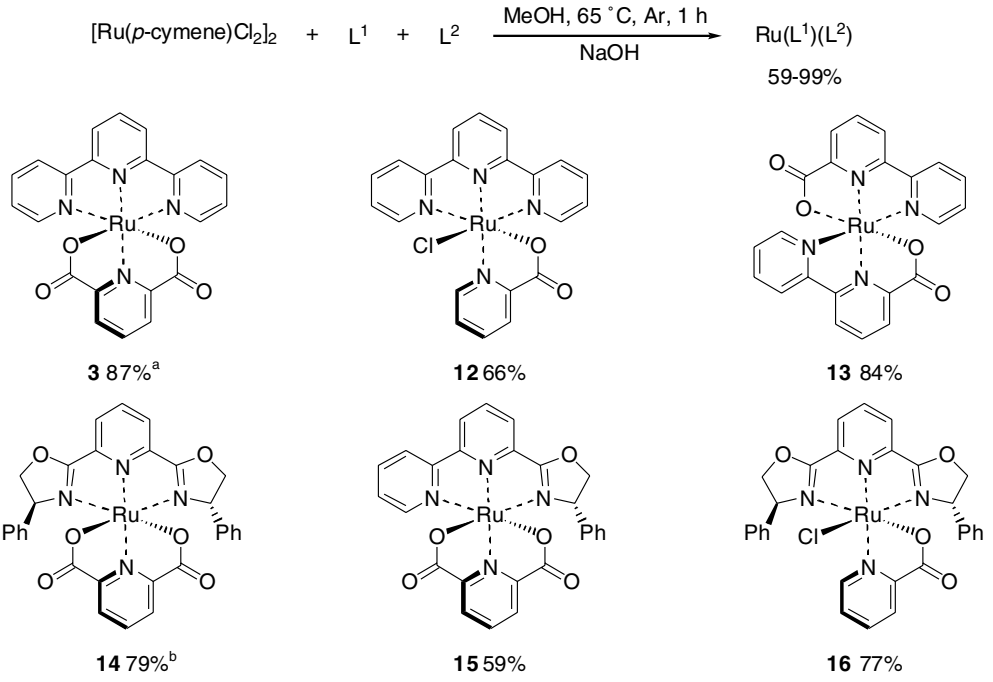
negative results in the attempts of isolating **3**(**O**) since concentrating of the solution of **3**(**O**) favours the bimolecular decomposition of **3**(**O**) to **3** and O_2 (infra supra).

In order to have a better understanding of the reactivity and transfer of chirality, we used the fragment-based approach to address the essential part of the catalysts. These C_2 symmetric catalysts contain two meridional ligands. Each of them contains four pyridine nitrogen and two carboxylate oxygen atoms. We decided to synthesize and test new catalysts with similar coordinating groups according to their possibility of modification, the availability of starting materials, and the ease of synthesis. Hence, different 2,2′-bipyridines functionalized in the 6-position were synthesized (Scheme 5). 2,2′-Bipyridine *N*-oxide was treated with TMSCN and benzoyl chloride at 0 °C to room temperature for 18 h to yield 2,2′-bipyridine-6-carbonitrile in 90% [34]. Hydrolysis of 2,2′-bipyridine-6-carbonitrile with HCl gave 2,2′-bipyridine-6-carboxylic acid in good yield (77%) [35].

Direct cyclization of unsymmetrical 6-[(4*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridinyl (**10**) with (*S*)-2-amino-2-phenylethanol and 2,2′-bipyridine-6-carbonitrile in refluxing anhydrous chlorobenzene using anhydrous $ZnCl_2$ as the catalyst showed inferior result and gave only a trace of the desired product. To our delight, **10** was obtained in good yield when methyl 2,2′-bipyridine-6-carboxyimidate was refluxed with (*S*)-2-amino-2-phenylethanol in CH_2Cl_2 for 48 h. Chiral non-racemic 2,2′-bipyridine (**11a**) was reported to induce good enantioselectivity in epoxidation of styrene with $PhI(OAc)_2$, though with low reactivity [36]. Therefore, we were interested to test this type of ligands in our reaction conditions [20d]. Hence, **11a** and **11b** were synthesized by Kröhnke condensation [37]. Subsequently, **11c** and **11d** were obtained in good yields using the Suzuki–Miyaura cross coupling reaction [37b]. Other commercially available ligands and co-ligands used in this study are also shown in Scheme 5.



Scheme 5. Synthesis of ligands and commercially available ligands in this study. Reagents and conditions: (a) TMSCN, PhCOCl, CH_2Cl_2, 0 °C to r.t., 18 h, 90%; (b) 37% HCl, reflux, 2 h, 77%; (c) Na, anhy. MeOH, Ar, r.t., 4 days, 99%; (d) (*S*)-2-amino-2-phenylethanol, anhy. CH_2Cl_2, Ar, reflux, 48 h, 92%; (e) (1*R*)-(−)-myrtenal, NH_4OAc, formamide, 75 °C, 6 h, 53%; (f) (1*R*)-(−)-myrtenal, NH_4OAc, HOAc, reflux, 6 h, 42%; (g) 0.2 mol% $Pd(PPh_3)_4$, $RB(OH)_2$, toluene/H_2O, K_2CO_3, 120 °C, 13 h, **11c**: 99%, **11d**: 84%.



Scheme 6. Synthesis of ruthenium catalysts: [a]Ref. [20e]; [b]Ref. [22a].

Scheme 7. Ruthenium-catalyzed epoxidation of styrene and *trans*-stilbene.

Next, six different ruthenium complexes have been synthesized in moderate to good yields by heating [Ru(*p*-cymene)Cl_2]$_2$ with the corresponding ligand in MeOH at 65 °C under Ar in the presence of NaOH (1 equiv. per carboxylic acid) for 1 h (see Section 4) (Scheme 6). All pre-catalysts were well characterized and subjected to two prototypical epoxidation reactions. The results are summarized in Scheme 7 and Table 2. In case of complexes with 2,2′-bipyridines

Table 2
Ruthenium-catalyzed epoxidation of styrene and *trans*-stilbene with H_2O_2[a]

Entry	Catalyst	Ph		Ph Ph	
		Yield (%)	Ee (%)	Yield (%)	Ee (%)
1	0.5 mol% **3**[a]	71	–	96	–
2	0.5 mol% **12**[b]	0	–	0	–
3	0.5 mol% **13**	9	–	26	–
4	5 mol% **14**[c]	70	+31[d]	100	−67[e]
5	5 mol% **15**	68	−1	>99	0
6	5 mol% **16**	18	n.d.[f]	14	n.d.
7	2.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 5 mol% **11a**, 5 mol% H_2pydic, 12 mol% Et_3N	67	+4	84	0
8	2.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 5 mol% **11b**, 5 mol% H_2pydic, 12 mol% Et_3N	40	−2	28	0
9	2.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 5 mol% **11c**, 5 mol% H_2pydic, 12 mol% Et_3N	29	−4	19	−3
10	2.5 mol% [Ru(*p*-cymene)Cl_2]$_2$, 5 mol% **11d**, 5 mol% H_2pydic, 12 mol% Et_3N	77	0	69	0

[a] Ref. [20e].
[b] See Section 4.
[c] Ref. [22b].
[d] "+" sign means (*R*)-(+)-styrene oxide is the major enantiomer.
[e] "−" sign means (*S*,*S*)-(−)-*trans*-stilbene oxide is the major enantiomer.
[f] Not determined.

11a–d and 2,6-pyridinedicarboxylic acid we used an in situ catalyst generation protocol [20a], due to the easy hydrolysis of the resulting complexes [36].

All catalytic experiments were run with 30% aqueous H_2O_2 at room temperature. Complex **3** has been shown to be a general and efficient catalyst because of its robustness [20e]. Surprisingly complexes **12** and **13**, which contain the same aromatic terpyridine unit as **3**, showed a drastic decrease of activity. Simply changing 2,6-pyridinedicarboxylate (pydic) to 2-pyridinecarboxylate, the resulting ruthenium complex **12** showed no reactivity at all. Even **13** containing four pyridine nitrogen and two carboxylate groups similar to **3** gave only poor yield for the epoxides [38]. Clearly, the chelating sub-unit "O–N–O" of pydic, which stabilizes the Ru(III) oxidation state by donating electron density to the metal center, plays a dominating role on the catalytic reactivity.

The importance of this "O–N–O" sub-unit is also reflected by the reduction and oxidation potentials of different ruthenium complexes (Table 3). It is with good agreement that the higher the oxidation potential of Ru^{2+}/Ru^{3+}, the lower the reactivity in the epoxidation reaction. On the other hand, the higher the $E_{1/2}$ (reduction potential) the higher the stability of the ligands towards reduction. Hence, **3** showed the highest reduction potential on terpyridine. Moreover, no reduction potential of pydic was observed [39]. As both terpyridine and "pydic" are more stable, the whole catalytic system becomes more robust.

Attempts to isolate catalysis intermediates from epoxidation reactions in the presence of Ru(*S*,*S*-Ph_2-pybox)(pydic) (**14**) resulted in the isolation of suspected Ru(*S*,*S*-Ph_2-pybox)(pydic)(O) complexes in low yield (<10%). The ^1H NMR spectrum of the isolated product showed diamagnetic behaviour and was not explainable. A careful analysis of the ultra high resolution mass spectrum showed three major peaks at $m/z = 636.05765$ ($C_{30}H_{22}N_4O_6Ru^+$), 650.03980 ($C_{30}H_{20}N_4O_7Ru^+$), and 652.05383 ($C_{30}H_{22}N_4O_7Ru^+$). We believe that **14** is oxidized to a Ru(III) species together with two Ru complexes with one oxygen atom more, in which one of them has an aromatized oxazoline ring. Catalytic tests with the chiral catalyst **15** demonstrated that even one aromatized oxazoline ring on the catalyst may lead to a total loss of enantioselectivity. In agreement with this observation, the suspected Ru(*S*,*S*-Ph_2-pybox)(pydic)(O) mixture gave a significantly lower enantioselectivity compared with the original catalyst **14**. The testing of in situ generated catalysts with chiral bipyridines **11a–d** resulted in 29–77% of *trans*-stilbene oxide, however none of the catalysts gave any reasonable ee (0–4%) (Scheme 8).

Finally, we were interested in improving our general epoxidation protocol. In our original procedure, 30% aqueous H_2O_2 was delivered to the olefin in *tert*-amyl alcohol in the presence of 0.5 mol% of **3** for 12 h by a syringe pump to prevent unproductive decomposition of H_2O_2.

For a laboratory procedure, it is advantageous to apply a solid oxidizing agent which can be dosed to the reaction mixture without any additional equipment. In case of a lower solubility of the solid oxidant in *tert*-amyl alcohol, unwanted decomposition of H_2O_2 to O_2 should be minimized. Hence, we tested common solid oxidants for the epoxidation of *trans*-stilbene (Table 4). To our delight, urea hydrogen peroxide complex deserves our hypothesis and gave an excellent yield of epoxide (>99%) in our model reaction in only 1 h. Next, we tested this simplified protocol and the results are shown in Table 5. UPH oxidized aromatic olefins in the presence of 0.5 mol% **3** with moderate to very good selectivity. Compared to the original proce-

Table 3
Redox potentials of various ruthenium terpyridine and pydic complexes

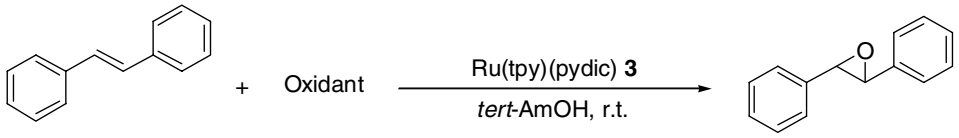
Complex	$E_{1/2}$ (oxidation) [V]	$E_{1/2}$ (reduction) [V]		Ref.
		1	2	
$Ru(tpy)^{2+}$	+1.31[a]	−1.24	−1.49	[38]
[Ru(tpy)(pic)][PF_6]	+0.88[b]	−1.39	−2.12	[39]
Ru(tpy)(bpyCO_2)	+0.90	−1.36	−1.63	[38]
Ru(tpy)(pydic) (**3**)	+0.60	−1.53	not observed	[39]
Ru(bpyCO_2)$_2$ (**13**)	+0.52	−1.49	−1.79	[38]
K$Ru(pydic)_2$	+0.21[c]	n.d.	n.d.	[40]

n.d., Not determined.
[a] Reduction potential vs. SCE.
[b] Initial reported reduction potentials were referenced to Fc/Fc^+ which is taken as +0.48 V here.
[c] Determined by potentiometric titration at pH 7.

Table 4
Screening of various solid oxidant for epoxidation of *trans*-stilbene

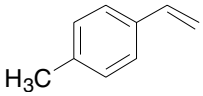
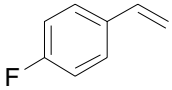
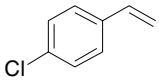
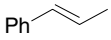
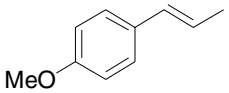
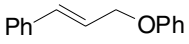
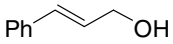
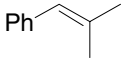
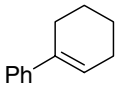
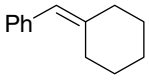
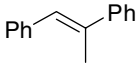
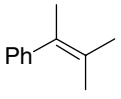
Entry	Oxidant	Time (h)	Conv. (%)	Yield (%)	Selec. (%)[a]
1	30% H_2O_2	12	100	96	96
2	UHP[b]	1	100	>99	>99
3	$Na_2CO_3 \cdot 1.5H_2O_2$	16	0	0	0
4	Oxone®[c]	16	9	4	44
5	$Ca(OCl)_2$	16	14	0	0

[a] Selectivity towards epoxide.
[b] Urea hydrogen peroxide complex.
[c] $2KHSO_4 \cdot KHSO_4 \cdot K_2SO_4$.



Scheme 8. Screening of various solid oxidant for epoxidation of *trans*-stilbene.

Table 5
Scope and limitations of Ru(tpy)(pydic) **3**-catalyzed epoxidation of olefin with UHP

Entry	Olefin	Time (h)	Conv. (%)	Yield (%)[a]	Selec. (%)[b]
1		3	41	39	95
2		3	81	74	91
3		3	49	39	80
4		3	40	28	71
5		3	100	>99	>99
6		3	100	95	95
7		3	100	92[c]	92
8		3	100	63	63
9		3	65	59	91
10		3	67	51	76
11		3	100	83	83
12		3	99	95	96
13		3	99	92	93
14		3	100	96[d]	96
15		3	53	48	91

[a] GC-yields.
[b] Chemoselectivity towards epoxide.
[c] Isolated yield.
[d] NMR yield.

dure the reaction time is shortened. Mono-, 1,1-di, *trans*- and *cis*-1,2-di-, tri- and even tetra-substituted olefins all have good to excellent selectivity towards the corresponding epoxides. Functional groups like alcohol and halogens are tolerant in the reaction system. Clearly, slow dosage of the oxidant is no longer needed for this method.

3. Conclusion

In summary, mechanistic studies of ruthenium-catalyzed epoxidations of olefins were performed experimentally and theoretically with high level density functional theory calculations. Mono-*N*-oxide **A3** and active oxo-transfer catalyst **A1** are possible intermediates in the reaction pathway. A fragment-based catalyst design showed that the 2,6-pyridinedicarboxylic acid ligand is essential for the reactivity. Moreover, a C_2 symmetric chiral ligand provides the necessary chiral induction. Hence, catalyst **15** gave no ee for the epoxidation of *trans*-stilbene and styrene. This suggests that a partial ligand oxidation of the catalyst is possibly one of the non-productive asymmetric epoxidation pathways. Moreover, a general simplified and more active ruthenium-catalyzed epoxidation procedure of olefins utilizing urea hydrogen peroxide complex has been developed. Further development towards asymmetric epoxidation reactions are under investigation in our laboratory.

4. Experimental

4.1. General

Unless specified, all chemicals are commercially available and used as received. Ru(tpy)(pydic) (**3**) [19], Ru(^{t}Bu$_3$-tpy)(pydic) (**3a**) [20e], bpyCO$_2$H (**9**) [32], 2,2′-bipyridines (**11a–d**) [37], Ru(bpyCO$_2$)$_2$ (**13**) [38], and Ru(*S*,*S*-Ph$_2$-pybox)(pydic) (**14**) [19], are synthesized according to the literature procedures. Qualitative analysis of reaction products was done on a gas chromatograph HP 5890 with mass selective detector HP 5989A (Hewlett-Packard) and a capillary column of type HP 5 was used for separation. For quantitative analysis of reaction mixture, the measurement was performed on a HP 6890 gas chromatograph (Hewlett-Packard) with flame ionization detector. The separation is obtained on a capillary column of type HP 5 (5% phenylmethylsiloxane, length 30 m, inner diameter 250 μm, film thickness 0.25) with argon as flowing gas. Enantiomeric excess of epoxides were determined with HP 1090 liquid chromatography (Hewlett-Packard) equipped with a DAD detector. UV–Vis spectroscopic measurements were performed with a Shimadzu UV-1601 spectrophotometer. Nuclear magnetic resonance spectra were recorded on Bruker ARX300 or ARX400 spectrometers. All NMR spectra were taken in pure deuteriated solvents, such as $CDCl_3$, CD_2Cl_2, etc. Chemical shifts (δ) are given in ppm and refer to residual solvent as internal standard. Signal multiplicity and coupling constants (J in Hz) are shown in the parentheses. For multiplicity the following abbreviations are used: s, singlet; d, duplet; dd, duplet of duplet; t, triplet and m, multiplet.

4.2. Ligand synthesis

4.2.1. Synthesis of 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine 1-N-oxide (6)

To the solution of 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (**5a**) (300 mg, 0.75 mmol) in CH_2Cl_2 (7.5 ml), *m*-CPBA (77%, 167 mg, 0.75 mmol) in CH_2Cl_2 (7.5 ml) was added dropwise. The reaction mixture was stirred at r.t. for 15 h. It was then diluted with CH_2Cl_2 (10 ml) and washed with $NaHCO_3$ (10 ml × 3). The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was chromatographed on silica gel (70–230 mesh) using ethyl acetate:Et_3N:MeOH 100:1:0 to 100:1:1 as the gradient eluent. An off-white solid was obtained after removal of solvent (165 mg, 53%). **6**: $R_f = 0.60$ (ethyl acetate:Et_3N:MeOH 100:1:10); ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.37$ (s, 9H), 1.38 (s, 9H), 1.42 (s, 9H), 7.25 (dd, $J = 6.9$, 3.0 Hz, 1H), 7.35 (dd, $J = 5.4$, 2.0 Hz, 1H), 8.23 (d, $J = 6.9$ Hz, 1H), 8.47 (d, $J = 3.0$ Hz, 1H), 8.53 (d, $J = 2.0$ Hz, 1H), 8.57 (d, $J = 1.7$ Hz, 1H), 8.62 (d, $J = 5.4$ Hz, 1H), 9.17 (d, $J = 1.7$ Hz, 1H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 30.46$, 30.67, 34.65, 35.08, 35.44, 116.29, 118.51, 118.95, 121.89, 122.37, 123.12, 124.86, 140.06, 146.35, 148.18, 148.93, 150.12, 154.52, 155.50, 161.82; IR (KBr) 1588, 1546, 1480, 1377, 1261, 1192, 1067, 895, 831; 728, 609; EI-MS *m/z* 417 (M^+); FAB-MS *m/z* 418 ($M + H^+$); HRMS Calc. for $C_{27}H_{36}ON_3$: 418.28583. Found: 418.28564.

4.2.2. Synthesis of 4,4′,4″-tri-tert-butyl-2,2′:6′,2″-terpyridine 1,1″-di-N-oxide (7)

To the solution of 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine (**5a**) (100 mg, 0.25 mmol) in CH_2Cl_2 (2.5 ml), *m*-CPBA (77%, 210 mg, 0.94 mmol) in CH_2Cl_2 (2.5 ml) was added in one portion. The reaction mixture was stirred at r.t. for 15 h. It was then diluted with CH_2Cl_2 (15 ml) and washed with $NaHCO_3$ (10 ml × 3). The organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was chromatographed on silica gel (70–230 mesh) using ethyl acetate:Et_3N:MeOH 100:1:0 to 100:1:3 as the gradient eluent. A white solid was obtained after removal of solvent (88 mg, 81%). **7**: $R_f = 0.23$ (ethyl acetate:Et_3N:MeOH 100:1:10); ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 1.34$ (s, 18H), 1.39 (s, 9H), 7.29 (dd, $J = 6.9$, 3.0 Hz, 2H), 8.18 (d, $J = 3.0$ Hz, 2H), 8.29 (d, $J = 6.9$ Hz, 2H), 8.96 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 30.44$, 30.56, 34.76, 35.38, 122.62, 123.71, 125.02, 139.94, 146.48, 149.23, 151.57, 160.87; IR (KBr) 1590, 1547, 1476, 1383, 1255, 1193, 887, 827; 709, 617, 604; EI-MS *m/z* 433 (M^+); FAB-MS *m/z* 434 ($M + H^+$); HRMS Calc. for $C_{27}H_{35}O_2N_3$: 433.27292. Found: 433.27271.

4.2.3. Synthesis of 6-[(4S)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridinyl (10)

4.2.3.1. Synthesis of 2,2′-bipyridine-6-carbonitrile. 2,2′-Bipyridine *N*-oxide (300 mg, 1.74 mmol) was dissolved in anhydrous CH_2Cl_2 (5 ml) under Ar. It was then cooled to 0 °C and TMSCN (1.0 ml, 8.71 mmol) was added. Benzoyl chloride (404 μl, 3.48 mmol) was added dropwise. The reaction mixture was stirred overnight. Then 10% Na_2CO_3 (10 ml) was added and the mixture was separated and the aqueous layer was extracted with CH_2Cl_2 (5 ml × 3). The combined organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was chromatographed on silica gel (70–230 mesh) using CH_2Cl_2 to CH_2Cl_2:ethyl acetate (10:1) as the gradient eluent. An off-white solid was obtained after removal of solvent (285 mg, 90%). 2,2′-bipyridine-6-carbonitrile: $R_f = 0.68$ (CH_2Cl_2:ethyl acetate 6:1); ^1H NMR (400.1 MHz, $CDCl_3$): $\delta = 7.37$ (ddd, $J = 7.5$, 4.8, 1.2 Hz, 1H), 7.68 (dd, $J = 7.6$, 0.9 Hz, 1H), 7.85 (unresolved ddd, 1H), 7.93 (unresolved dd, 1H), 8.45 (d, $J = 7.9$ Hz, 1H), 8.66–8.68 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 117.33$, 121.65, 124.27, 124.80, 128.17, 133.18, 137.41, 137.92, 149.09, 153.82, 157.44; MS (EI, 70 eV) *m/z* 181 (M^+).

4.2.3.2. Synthesis of methyl 2,2′-bipyridine-6-carboxyimidate. 2,2′-Bipyridine-6-carbonitrile (1.0 g, 5.5 mmol) was dissolved in anhydrous MeOH with gentle heating under Ar. After it was cooled to r.t., Na (13 mg, 0.58 mmol) was added. The reaction mixture was stirred for four days at r.t. HOAc (33 μl, 0.58 mmol) was then added. The solvent was removed under reduced pressure to give an off-white solid (1.17 g, 99%). Methyl 2,2′-bipyridine-6-carboxyimidate: m.p. 69.4–69.7 °C; ^1H NMR (300.1 MHz, d^7-DMF): $\delta = 3.99$ (s, 3H), 7.52 (ddd, $J = 7.5$, 4.8, 1.3 Hz, 1H), 7.91 (dd, $J = 7.6$, 1.0 Hz, 1H), 8.02 (ddd, $J = 7.7$, 7.7, 1.9 Hz, 1H), 8.13–8.19 (unresolved dd, 1H), 8.59 (dd, $J = 7.9$, 1.1 Hz, 1H), 8.67–8.70 (unresolved ddd 1H), 8.74 (ddd, $J = 4.8$, 1.8, 0.9 Hz, 1H); ^{13}C NMR (75.5 MHz, d^7-DMF): $\delta = 53.94$, 121.62, 121.67, 123.06, 124.31, 125.29, 138.03, 139.74, 147.37, 150.10, 155.51, 156.24, 166.61; MS (EI, 70 eV) *m/z* 213 (M^+); IR (KBr, cm^{-1}): 3290, 3050, 3002, 2951, 1976, 1654, 1185, 1099, 784, 748, 709; HRMS Calc. for $C_{19}H_{15}N_3O$ *m/z*: 213.0897. Found: 213.08844.

4.2.3.3. Synthesis of 6-[(4S)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridinyl (10). Methyl 2,2′-bipyridine-6-carboxyimidate (400 mg, 1.88 mmol) and (*S*)-2-amino-2-phenylethanol (257 mg, 1.88 mmol) were dissolved in anhydrous CH_2Cl_2 (8 ml) under Ar in a pressure tube. The mixture was then heated at 60 °C for three days. After removal of solvent, the crude product was chromatographed on silica gel (70–230 mesh) using CH_2Cl_2:Et_3N:-MeOH 100:1:0 to 100:1:2 as the gradient eluent. A pale yellow solid was obtained after removal of solvent (519 mg, 92%). Analytically pure product was obtained by slow evaporation of the etherate solution of **10** to yield an off-white product (310 mg, 55%). **10**: $R_f = 0.22$ (CH_2Cl_2:Et_3N: MeOH = 100:1:5); m.p. 108.0–111.8 °C; ^1H NMR (300.1 MHz, $CDCl_3$): $\delta = 4.37$–4.42 (unresolved dd, 1H), 4.91 (dd, $J = 10.2$, 8.6 Hz, 1H), 5.46 (dd, $J = 10.2$, 8.5 Hz, 1H), 7.25–7.37 (m, 6H), 7.79 (ddd, $J = 7.8$, 7.8, 1.8 Hz, 1H), 7.88–7.93 (unresolved dd, 1H), 8.17 (dd,

$J = 7.7$, 1.1 Hz, 1H), 8.52 (ddd, $J = 7.9$, 2.5, 1.1 Hz, 2H), 8.66 (ddd, $J = 4.8$, 1.8, 0.9 Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 70.31$, 75.36, 121.64, 123.11, 124.04, 124.31, 126.81, 127.71, 128.76, 136.97, 137.55, 141.84, 146.13, 149.09, 155.30, 156.22, 164.04; MS (EI, 70 eV) *m/z* 301 (M^+); $[\alpha]_D = -115.1°$ ($c = 0.50$, $CHCl_3$); IR (KBr, cm^{-1}): 3069, 3032, 2972, 2897, 1643, 1263, 1114, 787, 749, 700. Elementary analysis Calc. for $C_{19}H_{15}N_3O$: C, 75.73; H, 5.02; N, 13.94. Found: C, 75.69; H, 4.62; N, 14.03%.

4.3. Synthesis of ruthenium complexes

4.3.1. Synthesis of chloro-ruthenium (2,2′:6′,2″-terpyridine) (pyridine-2-carboxylate) complex (**12**)

[Ru(*p*-cymene)Cl_2]$_2$ (131 mg, 0.21 mmol) and 2,2′:6′,2″-terpyridine (100 mg, 0.43 mmol) were dissolved in MeOH (7 ml) at r.t. under Ar to form a deep violet solution. Sodium 2-pyridinecarboxylate (62 mg, 0.43 mmol) was dissolved in H_2O (3 ml) and MeOH (4 ml) was added. This solution was purged with Ar for ~15 min and then added dropwise to the reaction mixture via a cannular. The whole reaction mixture was heated at 70 °C for 1 h. It turned to deep purple in ~15 min at 70 °C. After the reaction mixture was cooled to r.t., CH_2Cl_2 (25 ml) and H_2O (25 ml) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 ml × 3). The combined organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. It was then chromatographed on silica gel (70–230 mesh) using CH_2Cl_2:MeOH 100:1 to 100:5 as the gradient eluent. After removal of solvent, a purple solid was obtained (140 mg, 66%). The product can be further purified by recrystallization in CH_2Cl_2/hexane to give a deep purple solid. The product was not soluble enough to give satisfactory ^{1}H and ^{13}C spectra. **12**: $R_f = 0.15$ (CH_2Cl_2/MeOH 100:5); UV–Vis (CH_2Cl_2, λ_{max}/nm, $\log\varepsilon$) 326 (4.40), 402 (3.94), 551 (3.82). HRMS Calc. for ($C_{21}H_{15}ClN_4O_2{}^{96}Ru$) *m/z*: 485.99611. Found: 485.99540. Elementary analysis Calc. $C_{21}H_{15}ClN_4O_2Ru{\cdot}CH_2Cl_2$ (%) C, 45.81; H, 2.97; N, 9.71. Found: C, 45.87; H, 3.21; N, 10.17.

4.3.2. Synthesis of ruthenium bis-(2,2′-bipyridine-6-carboxylate) complex (**13**) [38]

[Ru(*p*-cymene)Cl_2]$_2$ (46 mg, 0.075 mmol) and 2,2′-bipyridine-6-carboxylic acid (60 mg, 0.30 mmol) were dissolved in anhydrous MeOH (10 ml) under Ar at r.t. and Et_3N (42 μl, 0.30 mmol) was then added. The reaction mixture was heated at 65 °C for ~13 h and turned from pale orange to deep orange in color. After the reaction mixture was cooled to r.t., a purple solid precipitated with a clear orange solution. The purple solid was filtered, washed with MeOH and dried under high vacuum (63 mg, 84%). **13**: $R_f = 0.57$ (CH_2Cl_2/MeOH 10:1); ^{1}H NMR (300 MHz, d^6-DMSO, ppm) δ 7.10 (d, $J = 5.1$ Hz, 1H), 7.19–7.21 (m, 1H), 7.77–7.82 (m, 1H), 8.10–8.14 (m, 2H), 8.69 (d, $J = 7.2$ Hz, 1H), 8.91–8.97 (m, 1H); UV–Vis (EtOH:MeOH = 4:1, λ_{max}/nm, $\log\varepsilon$) 298 (4.69), 369 (3.89), 511 (4.11). HRMS Calc. for ($C_{22}H_{14}N_4O_4{}^{96}Ru$) *m/z*: 499.00868. Found: 499.008554.

4.3.3. Synthesis of ruthenium {6-[(4S)-4-phenyl-4,5-dihydro-oxazol-2-yl]-[2,2′]bipyridinyl} (2,6-pyridinedicarboxylate) complex (**15**)

[Ru(*p*-cymene)Cl_2]$_2$ (102 mg, 0.17 mmol) and **10** (100 mg, 0.33 mmol) were dissolved in MeOH (2 ml) at r.t. under Ar to form a deep violet solution. Disodium 2,6-pyridinedicarboxylate (70 mg, 0.33 mmol) was dissolved in H_2O (1 ml) and MeOH (1 ml) was then added. This solution was purged with Ar for ~15 min and then added dropwise to the reaction mixture via a cannular. The whole reaction mixture was heated at 65 °C for 1 h. It turned to deep red in ~5 min at 65 °C. After the reaction mixture was cooled to r.t., CH_2Cl_2 (50 ml) and H_2O (25 ml) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 ml × 3). The combined organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. It was then chromatographed on silica gel (70–230 mesh) using CH_2Cl_2:MeOH 100:3 to 100:7 as the gradient eluent. After removal of solvent, a purple solid was obtained (111 mg, 59%). The product can be further purified by recrystallization in CH_2Cl_2/hexane to give a deep purple solid. $R_f = 0.09$ (CH_2Cl_2/MeOH 100:5); ^{1}H NMR (300 MHz, $CDCl_3$, ppm) δ 4.63 (dd, $J = 10.6$, 8.9 Hz, 1H), 4.81–4.88 (unresolved dd, 1H), 5.17–5.23 (unresolved dd, 1H), 6.78 (d, $J = 7.2$ Hz, 2H), 7.07–7.22 (m, 4H), 7.35 (d, $J = 5.3$ Hz, 1H), 7.55–7.68 (m, 3H), 7.81 (t, $J = 7.7$ Hz, 1H), 8.04 (d, $J = 7.7$ Hz, 1H), 8.09–8.22 (m, 3H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 67.91, 78.18, 121.12, 121.90, 123.76, 126.10, 126.71, 126.90, 127.25, 127.98, 128.59, 129.18, 134.01, 134.81, 136.42, 146.70, 149.40, 150.23, 151.09, 158.32, 167.67, 171.40, 171.92; UV–Vis (CH_2Cl_2, λ_{max}/nm, $\log\varepsilon$) 399 (3.94), 514 (4.10). HRMS Calc. for ($C_{26}H_{18}N_4O_5{}^{102}Ru + H^+$) *m/z*: 569.03989. Found: 569.03990. Elementary analysis Calc. $C_{26}H_{18}N_4O_5Ru \cdot H_2O$: C, 53.33; H, 3.44; N, 9.57. Found: C, 52.89; H, 3.00; N, 9.35%.

4.3.4. Synthesis of chloro-ruthenium {bis[(4S)-4-phenyl-4,5-dihydro-oxazol-2-yl]-pyridine}(2,6-pyridinedicarboxylate) complex (**16**)

[Ru(*p*-cymene)Cl_2]$_2$ (83 mg, 0.14 mmol) and bis[(4*S*)-4-phenyl-4,5-dihydro-oxazol-2-yl]-pyridine (100 mg, 0.27 mmol) were dissolved in MeOH (2 ml) at r.t. under Ar to form a deep red solution. Disodium 2,6-pyridinedicarboxylate (70 mg, 0.33 mmol) was dissolved in H_2O (1 ml) and MeOH (1 ml) was then added. This solution was purged with Ar for ~15 min and then added dropwise to the reaction mixture via a cannular. The whole reaction mixture was heated at 65 °C for 1 h. It turned first to orange then brownish orange in color at 65 °C. After the reaction mixture was cooled to r.t., CH_2Cl_2 (20 ml) and H_2O (20 ml) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 ml × 3). The combined organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure. It was then chromatographed on silica gel (70–230 mesh) using CH_2Cl_2:MeOH 100:1 to 100:5 as the gradient eluent. After

removal of solvent, a purple solid was obtained (131 mg, 77%). The product can be further purified by recrystallization in CH_2Cl_2/hexane. $R_f = 0.20$ (CH_2Cl_2/MeOH 100:5); ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 4.49–4.69 (m, 3H), 4.93–5.00 (unresolved dd, 1H), 5.09–5.26 (m, 2H), 6.75 (d, $J = 7.0$ Hz, 2H), 6.89–7.16 (m, 9H), 7.38–7.39 (m, 2H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.75–7.80 (m, 2H), 8.96 (d, $J = 5.3$ Hz, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$, ppm) δ 68.35, 68.69, 78.22, 78.43, 123.23, 123.25, 124.99, 125.21, 127.01, 127.32, 127.99, 128.13, 128.32, 128.68, 134.24, 136.27, 136.80, 150.12, 150.16, 150.52, 150.80, 167.21, 167.64, 172.48; MS (EI 70 eV) m/z 627 (M^+). UV–Vis (CH_2Cl_2, λ_{max}/nm, $\log\varepsilon$) 378 (3.45), 506 (4.11). Elementary analysis Calc. $C_{29}H_{23}ClN_4O_4Ru{\cdot}H_2O$: C, 53.91; H, 3.90; N, 8.67. Found: C, 54.24; H, 4.21; N, 8.52%.

4.4. UV–Vis spectroscopic titration

Ru(^{t}Bu$_3$-tpy)(pydic) **3a** (2.70 mg, 4.04×10^{-3} mmol) was dissolved in CH_2Cl_2 (100.00 ml) in a volumetric flask. *m*-CPBA was purified according to literature before use [41]. *m*-CPBA (10.51 mg, 6.09×10^{-3} mmol) was dissolved in CH_2Cl_2 (10.00 ml) in a volumetric flask. A solution of **3a** (3.00 ml) was transferred to a Teflon stoppered 1.0 cm quartz cell. Then the initial UV–Vis spectrum was recorded. Next *m*-CPBA solution (2.0 μl) was added to the solution of **3a** and the reaction was monitored by UV–Vis spectroscopy. When there was no further change indicated by the absorption spectrum, further portions of *m*-CPBA solution (2.0 μl each) were given. The ratio between **3a** and *m*-CPBA was determined at different wave lengths (at least 5) other than the isosbestic points.

4.5. Catalytic reactions

All olefins and epoxides are known compounds. The conversions and yields were determined by comparing the authentic samples with an internal standard on GC-FID. The identities of the products were further confirmed by GC–MS.

4.5.1. Screening of different oxidants

4.5.1.1. General procedure for non-asymmetric epoxidation with hydrogen peroxide. In a 25 ml Schlenk tube, the catalyst (0.0025 mmol) and *trans*-stilbene (90.1 mg, 0.50 mmol) were stirred with gentle heating in *tert*-amyl alcohol (9 ml) until all *trans*-stilbene was dissolved. After the reaction mixture was cooled to r.t., dodecane (GC internal standard, 100 μl) was added. To this reaction mixture, a solution of 30% hydrogen peroxide (170 μl, 1.5 mmol) in *tert*-amyl alcohol (830 μl) was added over a period of 12 h by a syringe pump. After the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data.

4.5.1.2. General procedure for asymmetric epoxidation with hydrogen peroxide. In a 25 ml Schlenk tube, the catalyst (0.025 mmol) and *trans*-stilbene (90.1 mg, 0.50 mmol) were stirred with gentle heating in *tert*-amyl alcohol (9 ml) until all *trans*-stilbene was dissolved. After the reaction mixture was cooled to r.t., dodecane (GC internal standard, 100 μl) was added. To this reaction mixture, a solution of 30% hydrogen peroxide (170 μl, 1.5 mmol) in *tert*-amyl alcohol (830 μl) was added over a period of 12 h by a syringe pump. After the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data. The reaction mixture was then quenched with Na_2SO_3solution (~10 ml) and extracted with dichloromethane (10 ml × 2) and washed with water (~20 ml). The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude epoxide. It was then dissolved in *n*-hexane for HPLC measurement.

4.5.1.3. General procedure for in situ generation of catalyst in asymmetric epoxidation with hydrogen peroxide. In a 25 ml Schlenk tube, [Ru(*p*-cymene)Cl_2]$_2$ (7.7 mg, 0.013 mmol) and the chiral ligand (0.025 mmol) were dissolved in *tert*-amyl alcohol (2 ml) under Ar. To this solution, H_2pydic (4.2 mg, 0.025 mmol) and Et_3N (8.4 μl, 0.060 mmol) in *tert*-amyl alcohol (2 ml) were added dropwise via a cannular. The reaction mixture was heated at 65 °C for 1 h. *trans*-Stilbene (90.1 mg, 0.50 mmol) and *tert*-amyl alcohol (5 ml) were added and the whole reaction mixture was heated until all *trans*-stilbene was dissolved. After the reaction mixture was cooled to r.t., dodecane (GC internal standard, 100 μl) was added. To this mixture, a solution of 30% hydrogen peroxide (170 μl, 1.5 mmol) in *tert*-amyl alcohol (830 μl) was added over a period of 12 h by a syringe pump. After the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data. The reaction mixture was then quenched with Na_2SO_3 solution (~10 ml), extracted with dichloromethane (10 ml × 2) and washed with water (~20 ml). The combined organic layer was dried over $MgSO_4$ and evaporated to give the crude epoxide. It was then dissolved in *n*-hexane for HPLC measurement.

4.5.1.4. General procedure for screening of solid oxidants. In a 25 ml Schlenk tube, Ru(tpy)(pydic) (**3**) (0.0025 mmol) and *trans*-stilbene (90.1 mg, 0.50 mmol) were stirred with gentle heating in *tert*-amyl alcohol (10 ml) until all *trans*-stilbene was dissolved. After the reaction mixture was cooled to r.t., dodecane (GC internal standard, 100 μl) was added. To this reaction mixture, the solid oxidant (1.5 mmol) was added. After the addition, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data.

4.5.1.5. General procedure for epoxidation with urea hydrogen peroxide complex for solid olefins. In a 25 ml Schlenk tube, Ru(tpy)(pydic) **3** (0.0025 mmol) and olefin (0.50 mmol) were stirred with gentle heating in *tert*-amyl alcohol (10 ml) until it was dissolved. After the reaction mixture was cooled to r.t., dodecane (GC internal stan-

dard, 100 μl) was added. Urea hydrogen peroxide complex (47 mg, 0.50 mmol) was added in three portions at 0, 1, and 2 h as a total of (141 mg, 1.5 mmol). The reaction mixture was stirred at r.t. for an additional hour. Aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data.

4.5.1.6. General procedure for epoxidation with urea hydrogen peroxide complex for liquid olefins. In a 25 ml Schlenk tube, Ru(tpy)(pydic) (**3**) (0.0025 mmol) was stirred with gentle heating in *tert*-amyl alcohol (10 ml). After the reaction mixture was cooled to r.t., olefin (0.50 mmol) and dodecane (GC internal standard, 100 μl) were added. Urea hydrogen peroxide complex (47 mg, 0.50 mmol) was added in three portions at 0, 1 and 2 h as a total of (141 mg, 1.5 mmol). The reaction mixture was stirred at r.t. for an additional hour. Aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data.

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References

[1] K. Weissermel, H.-J. Arpe, Industrial Organic Chemistry, fourth ed., Wiley-VCH, Weinheim, 2003.
[2] (a) R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981;
(b) J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004.
[3] (a) L.I. Simándi, Catalytic Activation of Dioxygen by Metal Complexes, Kluwer Academic, Dordrecht, 1992;
(b) D.H.R. Barton, A.E. Bartell, D.T. Sawyer (Eds.), The Activation of Dioxygen and Homogeneous Catalytic Oxidation, Plenum Press, New York, 1993;
(c) F. Montanari, L. Casella (Eds.), Metalloporphyrins Catalyzed Oxidations, Kluwer, Dordrecht, 1994;
(d) L.I. Simándi (Ed.), Advances in Catalytic Activation of Dioxygen by Metal Complexes, Kluwer Academic, Dordrecht, 2003;
(e) for recent examples see: I.E. Markó, P.R. Giles, M. Tsukazaki, S.M. Brown, C.J. Urch, Science 274 (1996) 2044;
(f) G.-J. ten Brink, I.W.C.E. Arends, R.A. Sheldon, Science 287 (2000) 1636;
(g) B. Betzemeier, M. Cavazzini, S. Quici, P. Knochel, Tetrahedron Lett. 41 (2000) 4343;
(h) Y. Ishii, S. Sakaguchi, T. Iwahama, Adv. Synth. Catal. 343 (2001) 393;
(i) Y. Nishiyama, Y. Nakagawa, N. Mizuno, Angew. Chem. Int. Ed. 40 (2001) 3639;
(j) Y. Nishiyama, T. Hayashi, Y. Nakagawa, N. Mizuno, Stud. Surf. Sci. Catal. 145 (2003) 255;
(k) A.M. Khenkin, L.J.W. Shimon, R. Neumann, Inorg. Chem. 42 (2003) 3331;
(l) T. Nishimura, S. Uemura, Synlett (2004) 201.
[4] For examples in which both oxygen atoms are used see: (a) J.T. Groves, R. Quinn, J. Am. Chem. Soc. 107 (1985) 5790;
(b) I.R. Paeng, K. Nakamoto, J. Am. Chem. Soc. 112 (1990) 3289;
(c) I.E. Markó, P.R. Giles, M. Tsukazaki, I. Chellé-Regnant, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. 119 (1997) 12661;
(d) K.P. Peterson, R.C. Larock, J. Org. Chem. 63 (1998) 3185;
(e) K.S. Coleman, C.Y. Lorber, J.A. Osborn, Eur. J. Inorg. Chem. (1998) 1673;
(f) J. Christoffers, J. Org. Chem. 64 (1999) 7668;
(g) C. Döbler, G. Mehltretter, M. Beller, Angew. Chem. 111 (1999) 3211;
Angew. Chem. Int. Ed. 38 (1999) 3026;
(h) C. Döbler, G. Mehltretter, U. Sundermeier, M. Beller, J. Am. Chem. Soc. 122 (2000) 10289;
(i) G.M. Mehltretter, C. Döbler, U. Sundermeier, M. Beller, Tetrahedron Lett. 41 (2000) 8083;
(j) C. Döbler, G.M. Mehltretter, U. Sundermeier, M. Beller, J. Organomet. Chem. 621 (2001) 70;
(k) U. Sundermeier, C. Döbler, G.M. Mehltretter, W. Baumann, M. Beller, Chirality 15 (2003) 127.
[5] (a) G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic, Dordrecht, 1992;
(b) C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999.
[6] (a) B. Elvers, S. Hawkins, M. Ravenscroft, G. Schulz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, fifth ed., vol. A13, VCH, New York, 1989, p. 443;
(b) J.I. Kroschwitz, M. Howe-Grant (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., vol. 13, Wiley, New York, 1995, p. 961.
[7] Selected examples using H_2O_2 as oxidant: (a) W.A. Herrmann, R.W. Fischer, D.W. Marz, Angew. Chem., Int. Ed. Engl. 30 (1991) 1638;
(b) J. Rudolph, K.L. Reddy, J.P. Chiang, K.B. Sharpless, J. Am. Chem. Soc. 119 (1997) 6189;
(c) W.A. Hermann, R.M. Kratzer, H. Ding, W.R. Thiel, H. Glas, J. Organomet. Chem. 555 (1998) 293;
(d) R.W. Fischer, W.A. Herrmann, Trans. Metals Org. Synth. 2 (1998) 341;
(e) W.A. Herrmann, J.J. Haider, J. Fridgen, G.M. Lobmaier, M. Spiegler, J. Organomet. Chem. 603 (2000) 69;
(f) L. Shu, Y. Shi, J. Org. Chem. 65 (2000) 8807;
(g) M.C. White, A.G. Doyle, E.N. Jacobsen, J. Am. Chem. Soc. 123 (2001) 7194;
(h) Y. Shi, J. Synth. Org. Chem. Jpn. 60 (2002) 342;
(i) K.A. Srinivas, A. Kumar, S.M.S. Chauhan, Chem. Commun. (2002) 2456;
(j) M.K. Carter, J. Mol. Catal. A 200 (2003) 191;
(k) R. Noyori, M. Aoki, K. Sato, Chem. Commun. (2003) 1977;
(l) D.E. De Vos, B.F. Sels, P.A. Jacobs, Adv. Synth. Catal. 345 (2003) 457;
(m) S.Y. Jonsson, H. Adolfsson, J.-E. Bäckvall, Chem. Eur. J. 9 (2003) 2783;
(n) G. Maayan, R.H. Fish, R. Neumann, Org. Lett. 5 (2003) 3547;
(o) S. Velusamy, T. Punniyamurthy, Tetrahedron Lett. 44 (2003) 8955;
(p) M.V. Vasylyev, R. Neumann, J. Am. Chem. Soc. 126 (2004) 884.
[8] For reviews of H_2O_2 as epoxidation oxidant see: (a) G. Grigoropoulou, J.H. Clark, J.A. Elings, Green Chem. 5 (2003) 1;
(b) B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457;
(c) for a commentary see: M. Beller, Adv. Synth. Catal. 346 (2004) 107;
(d) for other asymmetric oxidations using H_2O_2 see: N. Komatsu, T. Murakami, Y. Nishibayashi, T. Sugita, S. Uemura, J. Org. Chem. 58 (1993) 3697;
(e) A. Gusso, C. Baccin, F. Pinna, G. Strukul, Organometallics 13 (1994) 3442;

(f) C. Bolm, F. Bienewald, Angew. Chem. Int. Ed. 34 (1996) 2640;
(g) M. Costas, A.K. Tipton, K. Chen, D.H. Jo, L. Que Jr., J. Am. Chem. Soc. 123 (2001) 6722;
(h) S.-I. Murahashi, S. Ono, Y. Imada, Angew. Chem. Int. Ed. 41 (2002) 2366;
(i) S.A. Blum, R.G. Bergman, J.A. Ellman, J. Org. Chem. 68 (2003) 150;
(j) J. Legros, C. Bolm, Angew. Chem. Int. Ed. 42 (2003) 5487;
(k) J. Legros, C. Bolm, Chem. Eur. J. 11 (2005) 1086.

[9] Reviews for Ti: (a) R.A. Johnson, K.B. Sharpless, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993 (Chapter 4.1);
(b) T. Katsuki, V.S. Martin, Org. React. 48 (1996) 1.

[10] Reviews for Mn: (a) E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993 (Chapter 4.2);
(b) T. Katsuki, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, second ed., Wiley-VCH, New York, 2000, p. 287;
(c) T. Katsuki, Adv. Synth. Catal. 344 (2002) 131.

[11] K. Matsumoto, Y. Sawada, B. Saito, K. Sakai, T. Katsuki, Angew. Chem. Int. Ed. 44 (2005) 4935.

[12] Reviews for asymmetric epoxidation mediated by chiral ketones see:
(a) D. Yang, Acc. Chem. Res. 37 (2004) 497;
(b) Y. Shi, Acc. Chem. Res. 37 (2004) 488;
(c) Y. Shi, in: J.-E. Bäckvall (Ed.), Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004 (Chapter 3) and references cited therein.

[13] For reviews of asymmetric epoxidation mediated by organic compounds see: (a) W. Adam, C.R. Saha-Möller, P.A. Ganeshpure, Chem. Rev. 101 (2001) 3499;
(b) P.I. Dalko, L. Moisan, Angew. Chem. Int. Ed. 40 (2001) 3726;
(c) P.I. Dalko, L. Moisan, Angew. Chem. Int. Ed. 43 (2004) 5138, and references cited therein.

[14] (a) S. Juliá, J. Masana, J.C. Vega, Angew. Chem. Int. Ed. 19 (1980) 929;
(b) S. Juliá, J. Guixer, J. Masana, J. Rocas, S. Colonna, R. Annuziata, H. Molinari, J. Chem. Soc. Perkin Trans. 1 (1982) 1317;
(c) S. Colonna, H. Molinari, S. Banfi, S. Juliá, J. Masana, A. Alvarez, Tetrahedron 39 (1983) 1635;
(d) J.R. Flisak, K.J. Gombatz, M.M. Holmes, A.A. Jarmas, I. Lantos, W.L. Mendelson, V.J. Novack, J.J. Remich, L. Snyder, J. Org. Chem. 58 (1993) 6247;
(e) A.M. Rouhi, Chem. Eng. News 82 (2004) 47.

[15] (a) M. Bougauchi, S. Watanabe, T. Arai, H. Sasai, M. Shibasaki, J. Am. Chem. Soc. 119 (1997) 2329;
(b) T. Nemoto, T. Ohshima, M. Shibasaki, J. Am. Chem. Soc. 123 (2001) 9474;
(c) S. Matsunaga, T. Kinoshita, S. Okada, S. Harada, M. Shibasaki, J. Am. Chem. Soc. 126 (2004) 7559.

[16] M. Marigo, J. Franzen, T.B. Poulsen, W. Zhuang, K.A. Jorgensen, J. Am. Chem. Soc. 127 (2005) 6964.

[17] Selected examples of asymmetric epoxidation using H_2O_2 as oxidant:
(a) R. Sinigalia, R.A. Michelin, F. Pinna, G. Strukul, Organometallics 6 (1987) 728;
(b) T. Schwenkreis, A. Berkessel, Tetrahedron Lett. 34 (1993) 4785;
(c) R. Irie, N. Hosoya, T. Katsuki, Synlett (1994) 255;
(d) P. Pietikäinen, Tetrahedron Lett. 35 (1994) 941;
(e) A. Berkessel, M. Frauenkron, T. Schwenkreis, A. Steinmetz, J. Mol. Catal. A 117 (1997) 339;
(f) C. Bolm, D. Kadereit, M. Valacchi, Synlett (1997) 687;
(g) M.B. Francis, E.N. Jacobsen, Angew. Chem. Int. Ed. 38 (1999) 937;
(h) R.M. Stoop, A. Mezzetti, Green Chem. 1 (1999) 39;
(i) R.M. Stoop, C. Bauer, P. Setz, M. Wörle, T.Y.H. Wong, A. Mezzetti, Organometallics 18 (1999) 5691;
(j) R.M. Stoop, S. Bachmann, M. Valentini, A. Mezzetti, Organometallics 19 (2000) 4117;
(k) C. Bolm, N. Meyer, G. Raabe, T. Weyhermüller, E. Bothe, Chem. Commun. (2000) 2435;
(l) P. Pietikäinen, J. Mol. Catal. A 165 (2001) 73;
(m) L. Shu, Y. Shi, Tetrahedron 57 (2001) 5213;
(n) R.I. Kureshy, N.-u. H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, Tetrahedron: Asymm. 12 (2001) 433;
(o) A. Lattanzi, P. Iannece, A. Vicinanza, A. Scettri, Chem. Commun. (2003) 1440;
(p) F. Hollmann, P.-C. Lin, B. Witholt, A. Schmid, J. Am. Chem. Soc. 125 (2003) 8209;
(q) J.-M. Lopez-Pedrosa, M.R. Pitts, S.M. Roberts, S. Saminathan, J. Whittall, Tetrahedron Lett. 45 (2004) 5073;
(r) J.-X. Ye, Y.-C. Wang, J.-P. Chen, X.-M. Liang, Adv. Synth. Catal. 346 (2004) 691;
(s) D.R. Kelly, S.M. Roberts, Chem. Commun. (2004) 2018.

[18] S.-I. Murahashi (Ed.), Ruthenium in Organic Synthesis, Wiley-VCH, Weinheim, 2004.

[19] H. Nishiyama, T. Shimada, H. Itoh, H. Sugiyama, Y. Motoyama, Chem. Commun. (1997) 1863.

[20] (a) M.K. Tse, S. Bhor, M. Klawonn, C. Döbler, M. Beller, Tetrahedron Lett. 44 (2003) 7479;
(b) S. Bhor, M.K. Tse, M. Klawonn, C. Döbler, W. Mägerlein, M. Beller, Adv. Synth. Catal. 346 (2004) 263;
(c) M. Klawonn, M.K. Tse, S. Bhor, C. Döbler, M. Beller, J. Mol. Catal. A 218 (2004) 13;
(d) M.K. Tse, C. Döbler, S. Bhor, M. Klawonn, W. Mägerlein, H. Hugl, M. Beller, Angew. Chem. 116 (2004) 5367;
Angew. Chem. Int. Ed. 43 (2004) 5255;
(e) M.K. Tse, M. Klawonn, S. Bhor, C. Döbler, G. Anilkumar, H. Hugl, W. Mägerlein, M. Beller, Org. Lett. 7 (2005) 987;
(f) S. Bhor, G. Anilkumar, M.K. Tse, M. Klawonn, B. Bitterlich, A. Grotevendt, M. Beller, Org. Lett. 7 (2005) 3393.

[21] G. Anilkumar, S. Bhor, M.K. Tse, M. Klawonn, B. Bitterlich, M. Beller, Tetrahedron: Asymm. 16, in press.

[22] For the synthesis of the ligands and complexes see: (a) M.K. Tse, S. Bhor, M. Klawonn, C. Döbler, G. Anilkumar, A. Spannenberg, H.-J. Jiao, W. Mägerlein, H. Hugl, M. Beller, submitted.;
(b) for the catalytic activity and mechanistic studies see: M.K. Tse, S. Bhor, M. Klawonn, C. Döbler, G. Anilkumar, A. Spannenberg, H.-J. Jiao, W. Mägerlein, H. Hugl, M. Beller, 2005, Part 2, submitted.

[23] (a) J.T. Groves, Y. Watanabe, J. Am. Chem. Soc. 108 (1986) 507;
(b) W.-C. Cheng, W.-Y. Yu, C.-K. Li, C.-M. Che, J. Org. Chem. 60 (1995) 6840;
(c) W.-H. Fung, W.-Y. Yu, C.-M. Che, J. Org. Chem. 63 (1998) 7715;
(d) C.-J. Liu, W.-Y. Yu, C.-M. Che, C.-H. Yeung, J. Org. Chem. 64 (1999) 7365.

[24] T.D. Lee, J.F.W. Keana, J. Org. Chem. 41 (1976) 3237.

[25] O. Tamura, K. Gotanda, J. Yoshino, Y. Morita, R. Terashima, M. Kikuchi, T. Miyawaki, N. Mita, M. Yamashita, H. Ishibashi, M. Sakamoto, J. Org. Chem. 65 (2000) 8544.

[26] R.P. Thummel, Y. Jahng, J. Org. Chem. 50 (1985) 3635.

[27] H.-H. Perkampus, UV–Vis Spectroscopy and its Applications, Springer, 1992.

[28] S.M. Couchman, J.M. Dominguez-Vera, J. Jerrery, Polyhedron 17 (1998) 3541.

[29] (a) J.T. Groves, K.-H. Ahn, Inorg. Chem. 26 (1987) 3833;
(b) I.R. Paeng, K. Nakamoto, J. Am. Chem. Soc. 112 (1990) 3289.

[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T.

Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, GAUSSIAN 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004.

[31] (a) A.D. Becke, J. Chem. Phys. 98 (1993) 5648;
(b) P.J. Stevens, R.J. Devlin, C.F. Chablowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.

[32] (a) P.J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 299;
(b) T.H. Dunning Jr., P.J. Hay, in: H.F. SchaeferIII (Ed.), Modern Theoretical Chemistry, Plenum, New York, 1976, p. 1.

[33] J.B. Foresman, Æ. Frisch, Exploring Chemistry with Electronic Structure Methods: A Guide to Using Gaussian, second ed., Gaussian, Inc., Pittsburgh, PA, 1996.

[34] F.R. Heintzler, Synlett (1999) 1206.

[35] J.E. Parks, E. Wagner, R.H. Holm, J. Organomet. Chem. 56 (1973) 53.

[36] W. Zou, H. Zhang, Y.-Q. Huang, Y.-Y. Li, Z.-R. Dong, Huaxuetongbao 66 (2003) 684.

[37] (a) P. Hayoz, A. von Zelewsky, H. Stoeckli-Evans, J. Am. Chem. Soc. 115 (1993) 5111;
(b) M. Düggeli, C. Goujon-Ginglinger, S.R. Ducotterd, D. Mauron, C. Bonte, A. von Zelewsky, H. Stoeckli-Evans, A. Neels, Org. Biomol. Chem. 1 (2003) 1894.

[38] T. Norrby, A. Börje, B. Åkermark, L. Hammarström, J. Alsins, K. Lashgari, R. Norrestam, J. Mårtensson, G. Stenhagen, Inorg. Chem. 36 (1997) 5850.

[39] S.M. Couchman, J.M. Dominguez-Vera, J.C. Jerffery, C.A. McKee, S. Nevitt, M. Pohlman, C.M. White, M.D. Ward, Polyhedron 17 (1998) 3541.

[40] N.H. Williams, J.K. Yandell, Aus. J. Chem. 36 (1983) 2377.

[41] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, fourth ed., Elsevier Science, Oxford, 2002.