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REVIEW

Recent Advances Review on Iron Complexes as Catalyst in Oxidation Reactions of Organic Compounds

E. THAMARAI SELVI[1,*], G. KAVINILAVU[1] and A. SUBRAMANI[2]

[1]Department of Chemistry, Anna Adarsh College for Women, Chennai-600040, India
[2]Department of Chemistry, Apollo Arts and Science College, Poonamallee, Chennai-600105, India

*Corresponding author: E-mail: thamaraithirumaran72@gmail.com; sjaaresearchgroup@gmail.com

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The complexes of iron are found to be too reactive and are too diverse in their reactivity, when compared to the other neighbouring metals in the group. Iron complexes are used in various catalytic reactions such as oxygenation of C–H bonds, the oxidation of alcohols to aldehydes, ketones (or) carboxylic acids, the epoxidation or dihydroxylation of alkenes and oxidative coupling reactions. Efforts are taken to avoid certain disadvantages taking place during enzymatic catalysis such as the temperature and solvent sensitivity, narrow substrate scope, restricted accessibility and so on observed while using other catalysts *via* iron enzymes. This helped in the various synthesis of complex molecules by increase in the number of iron catalyst systems for the oxidation reactions.

Keywords: Iron complexes, Oxidation reaction, Catalyst.

INTRODUCTION

Organic synthesis, a transformative science which is highly helpful in selective molecular engineering, assembly and architecture with various applications in biochemistry, material sciences, agrochemical, pharmaceutical industries and others [1-7]. For this organic synthesis, the transition metals are widely used, to be specific 3*d*-transition metals [8-11].

An important field in both academic and industrial research is catalysis, because it leads to more efficient reactions in terms of energy consumption and waste production. The formation of a catalytically active species is the common feature of these processes, in turn which forms reactive intermediates by coordination of an organic ligand and thus decreases the activation energy. The product formation should occur with regeneration of the catalytically active species. The efficiency of the catalyst is often described by its turnover number, providing a measure of what percentage catalytic cycles are gone by one molecule of catalyst [12,13]. For efficient regeneration, the catalyst forming the labile intermediates with the substrate should be used. This concept is often realized using transition metal complexes because metal-ligand bonds are generally weaker than covalent bonds. The transition metals often exist in several oxidation states with only moderate differences in their oxidation potentials, thus offering the likelihood of switching reversibly between the various oxidation states by redox reactions [14-16].

For Fe^{2+} complexes ([Ar]$3d^6 4s^0$), a coordination number of six with an octahedral ligand sphere is preferred. Fe^{3+} ([Ar]$3d^5 4s^0$) can coordinate three to eight ligands and often exhibits an octahedral coordination [17]. Comparing other trans-ition metals, iron has higher number of advantageous points to be noted in the field of catalysis, to be specific high abundance, less cost, low toxic [18,19], apart from these advantages, the main reason is that the variable oxidation states possessed by the metal (-II to +VI), of which the most important oxidation states +6, 0, -1 and -2.

Fe^{3+} generally is a harder Lewis acid than Fe^{2+} and thus binds to hard Lewis bases. Fe^0 mostly coordinates five or six ligands with trigonal bipyramidal and octahedral geometry. Iron in low oxidation states is most interesting for organometallic chemistry and in particular for iron-catalyzed reactions because they can form more reactive complexes than their Fe^{2+} and Fe^{3+} counterparts. Therefore, Fe^0 and Fe^{2-} compounds are favoured

for iron catalysis. Iron carbonyl complexes are of special interest due to their high stability with an Fe^0 centre capable of coordinating complex organic ligands, which represents the basis for organoiron chemistry [20,21].

The complexes of iron are found to be too reactive and diverse in their reactivity, when compared to the other neighbouring metals in the group [22], which results in the reduction and oxidation reactions which are in-turn used in various applications [23-28]. The difficulty in removing other metal residues from the merchandise induced the look for iron-catalyzed reactions. However, iron complexes can play different roles in catalytic processes *e.g.* (i) as substrate and/or product, (ii) as ligands for other transition metal catalysts to achieve activation and stereo-control and (iii) as catalytically active species.

Hence, this metal has been highly used in the research activity for more than two decades [29]. Catalytic reactions such as carbon-carbon coupling reactions [30], reduction [31,32], oxidation [33-35], carbon-heteroatom coupling reactions [20, 36], polymerization [37,38], C-H insertion, C-H functionalization [39-42], sigmatropic rearrangements [43], cyclopropanation [44,45], N-H insertion [46-48], S-H insertion [49], B-H insertion [50-52], *etc.* are greatly achieved through the iron catalysts of various types. The pioneers in the field of iron catalysis are reported by Kharasch & Fields [53] in 1940s, and Tamura & Kochi [54] in 1970s. Nakamura *et al.* [55] found a new field of metal-catalyzed cross-coupling chemical reactions before the nickel and palladium cross-coupling reactions.

Iron-based enzymes, which are naturally occurring have been largely used in the oxidation reactions under required conditions [56-58]. These enzymes are generally classified as heme systems and non-heme systems; heme enzymes contain a porp-hyrin co-factor, the most common example is the cytochrome P450 family [59,60]. Methyl monooxygenase and Rieske dioxygenase are the examples for non-heme systems (without porphyrin group) [61-63]. In 1970s, the reaction between polyhalogenated methanes with porphyrins were first reported. This was the visionary for the iron-porphyrin carbene (IPC) system [64]. Efforts are highly taken to avoid certain disadvantages taking place during enzymatic catalysis such as the temperature and solvent sensitivity, narrow substrate scope, restricted accessibility and so on observed while using other catalysts *via* iron enzymes [65,66]. This helped in the various synthesis of complex molecules by increase in the number of iron catalyst systems for the oxidation reactions [34,67-70].

Catalytic C-H aminations emerged as a new research field in the past 10 years [71]. The transition metal-catalyzed amination reactions can take place in either of the following two ways: (i) firstly, the metal-based catalyst is inserted into a C-H bond *via* oxidation and followed by amination resulting in a metal-complex species, complex formed is made to undergo reductive elimination through which C-N bond is formed (Fig. 1); (ii) the metal complex can also take part in a reverse reaction by introducing a nitrene species. The amination is carried out over the metal-nitrene complex resulting a C-H amination reaction [72]. Recent methods in amination involves *in situ* generated nitrenes where azides are used as the precursors for nitrenes,

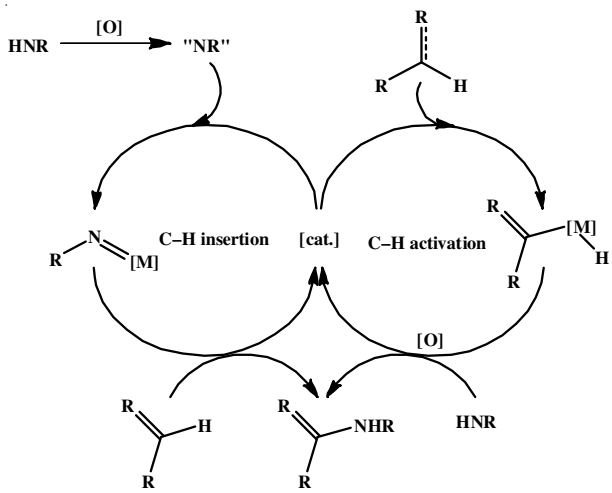


Fig. 1. Transition metal-catalyzed animation reaction

along with electron-deficient amides combined with strong external oxidative agents mainly Fe-based molecular catalysts [73,74].

Cross-coupling reactions through the metal catalyst are extensively used for the C-C bond formation and it has applications in many areas [75-77]. An alternative way of traditional cross-coupling reactions is the decarboxylative coupling which involves organometallic reagents [78]. In 2007, iron-catalyzed cross dehydrogenative coupling reaction was reported [79].

Similarly, many other reactions are extensively studied with the use of iron catalysts. In this article, various oxidation reactions have been discussed which are carried out through the numerous iron catalysts; their applications in research and industrial purposes, pharmaceutical industries, polymer synthesis and so other fields are also accounted.

Oxidation: The iron-catalyzed oxidation reactions have very important place in the synthesis of organic compounds, for the usage of most compounds in the pharmaceutical industry, agricultural chemistry and other important industries [80-82]. Most of the biological transformations depend on the enzymatic oxidation of various functional groups, which are quite hard to be achieved through the synthetic methods [60,66].

The iron-catalyzed oxidation reactions are made possible by the compounds such as heme-containing oxygenase's, cytochrome P450 enzymes, mono-nuclear non-heme containing enzymes and non-heme diiron enzymes [62,65,83]. Iron complexes are used in various catalytic reactions such as oxygenation of C-H bonds [65,84-87], the oxidation of alcohols to aldehydes, ketones (or) carboxylic acids [68,88,89], the epoxidation or dihydroxylation of alkenes [69,90-93] and oxidative coupling reactions [34,35,70,94-96].

If using iron-catalyzed oxidative reagents, then some selectivity should be maintained, since a large number of functional groups are oxidizable. When strong and powerful oxidizing reagents are used it may over-oxidize the reactants, while mild reagents may not oxidize the reactant. Hence, the selectivity is very much important. Mostly selectivity is done through the parameters such as temperature, concentration, *etc.* [97].

Iron-catalyzed oxidation reactions in which peroxides (or) oxygen used as an oxidizing agent, they can proceed through two different pathways: (i) radical mechanism; (ii) iron based

oxidizing species [34] and (iii) iron is very much useful in radical chain oxidation reactions, Fenton's reagent very well-known for more than a century (**Scheme-I**) [97,98].

Fenton reaction (1894)

$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + OH^\bullet$

$OH^\bullet + R{-}H \longrightarrow R^\bullet + HO{-}H$ (119 kcal/mol)

Autoxidation

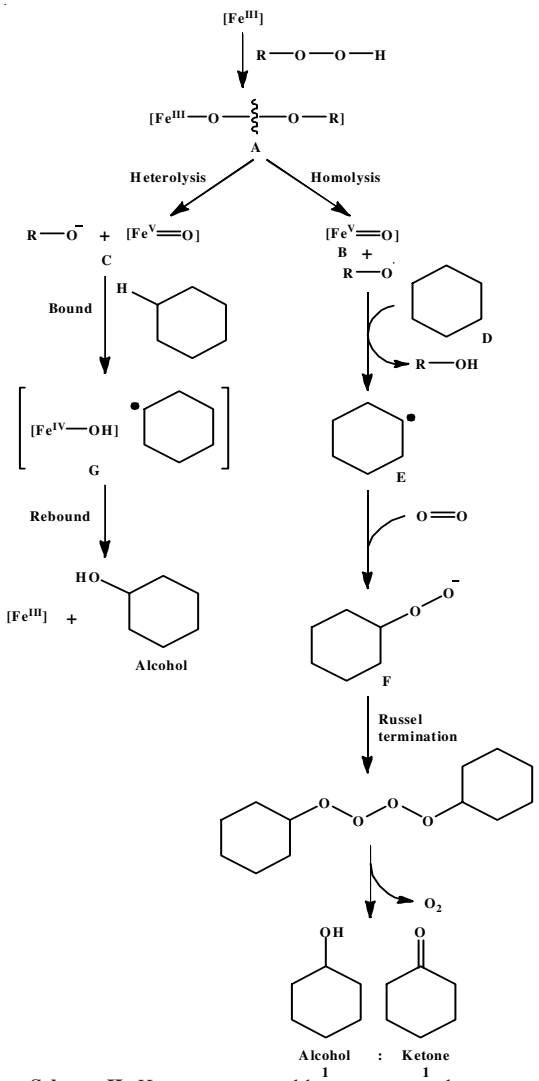
$R^\bullet + O_2 \longrightarrow RO^\bullet$

$RO^\bullet + R{-}H \longrightarrow R^\bullet + RO{-}H$ (104 kcal/mol)

Scheme-I: Radical chain oxidation reactions

Both the iron catalysts and peroxide oxidants proceed through same pattern in the mechanism, as like the scheme with cyclohexane as the substrate to be oxidized.

First, iron peroxide species is formed [Fe^{III}-O-O-R] in the presence of a peroxide R-O-O-R. Then there are probability of two pathways (**Scheme-II**) *i.e.*



Scheme-II: Homogeneous and heterogeneous cleavage

(a) A homogeneous O-O cleavage takes place forming an Fe^{IV}=O species and R-O^* radical (*OH if H_2O_2 is preferred instead of ROOR), which can abstract the hydrogen from the cyclohexane. The cyclohexane radical abstracts the oxygen from air and forms a peroxide species, Russel termination results in the formation of alcohol and ketone [1:1] [99]. More, the involvement of radicals, lower the alcohol/ketone ratio [100]. This ratio obtained will be used to obtain information about the radicals.

(b) A heterogeneous cleavage takes place, Fe^{V}=O is formed which is assisted by water. Peroxo species Fe-O-O-H is a poor oxidant [101]. The Fe^{V}=O oxo species has good oxidizing effect, either it will add oxygen or abstract a hydrogen from the substrate [102]. The C-H oxygenation step is often referred to as bound/rebound, when Fe^{IV}-OH firstly abstracts a proton, it is bound and after that it transfers an -OH radical to the substrate which is called as rebound [34,96]. It was found that if iron-centered species were used, it resulted in high ketone-alcohol ratio [102]. In this, rebound step occurred very fast, since no epimerization or rearrangement took place [34].

Kinetic isotope effects (KIE) and the investigation of regioselectivities are the other ways to distinguish between radical and iron-centered mechanisms. The C-H and C-D bonds are not efficiently discriminated by *OH radicals formed from the H_2O_2, which results in low KIE values (1-2), if deuterated substrates are employed [102]. High valent Fe=O species end in higher KIE value above 3, which indicates that the hydrogen abstraction is that the rate-determining step.

Substrates if contains both the secondary and tertiary carbon atoms, for instance adamantane (Fig. 2), it can potentially be oxidized in both the available positions. Tertiary position is less supported by radical intermediates than the iron-centered oxidants [102]. Loss of stereochemical information upon oxidation tells the radical mechanism, as epimerization occurs at tertiary, carbon-centered radicals, *cis*-1,2-dimethylcyclohexane is frequently used as a test substrate [103-105], the catalyst efficiency can be investigated by the iron-catalyzed oxidative degradation of dyes by means of spectroscopic methods [106-112].

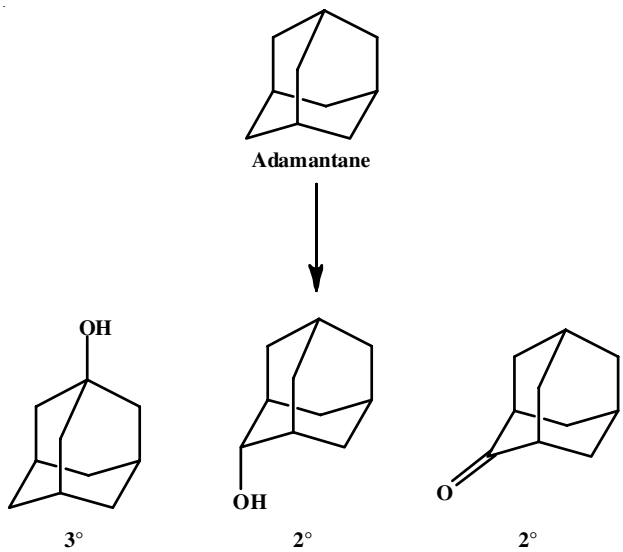
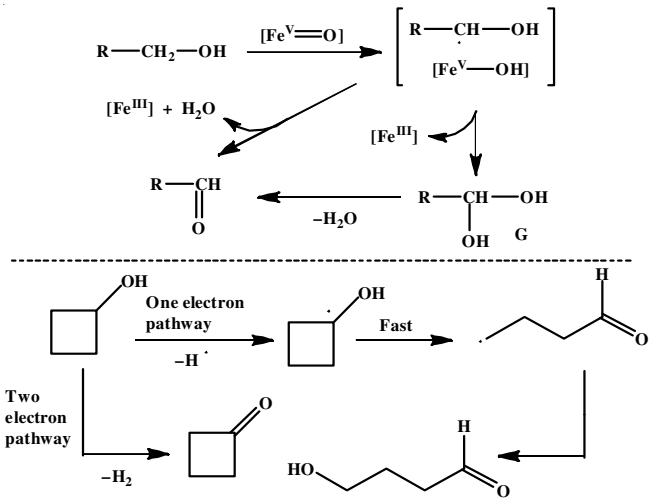


Fig. 2. Structure of adamantine and its stereoisomers

The oxidation of alcohols can also proceed through either radical (or) iron-centered mechanism which involves the Fe=O species of high valent [113-116]. In the below example, the metal-centered Fe=O species first abstract the α-hydrogen to give the corresponding radical, it rebounds to give a *gem.*-dihydroxide (**Scheme-III**), which loses water to give the carbonyl product [117]. A hydride transfer followed by an electron transfer is another probability [118]. This hydrogen transfer can be a one-electron or a two electron process, which is explained using cyclobutanol as an example. One-electron process will result in a cyclobutanol radical, which rapidly result in ring-opening [119]. Iron catalysts form hydride complexes, they can oxidize alcohols through hydride abstraction which is similar to that of oppenauer oxidation [120-122].



Scheme-III: Oxidation of alcohols

The mechanistic studies of iron-based catalyst systems helped in developing new catalysts. The guidance for how to increase the selectivity of iron-catalyzed reactions by investigating the formation, stabilization, reactivity and decay of high-valent Fe^{IV}=O and Fe^{V}=O species. But these mechanistic investigations also have their own limitations. Some of them are performed at very low temperatures in order to identify intermediates. A test reaction to investigate the involvement of radicals in the oxidation of cyclohexane to cyclohexanol, in which excess of the cyclohexane substrates is often applied to avoid over-oxidation [102], which is not practical in the synthesis of fine chemicals, also it cannot be denied that a variety of oxidizing species are used in the reaction mixtures and the reaction may proceed through several pathways [123]. The investigation of new iron catalyst systems along with computational and mechanistic studies have led to a variety of catalyst systems and such effort must continue to determine more efficient and selective catalyst systems.

Iron catalyst systems: More intense research activities in the field have resulted in a number of iron-based catalyst systems to perform a variety of oxidation reactions [34,35, 70,90-96]. Iron porphyrin complexes have been investigated early and it has been observed more progress in the field of oxidation [124,125]. The relatively rigid porphyrin backbone allows only for limited number of modifications, it also appears that more vigorous research activity currently occurs in the area of non-heme iron complexes, which exhibits a higher level of structural variety. Some examples of iron-complexes are:

(i) $[Fe(OTf)_2(tpa)]$ [126-128], $[Fe(BPMEN)(CH_3CN)_2](SbF_6)_2$ [129], tpa-*tris*(picolyl)amine BPMEN-N,N′-dimethyl-N,N′-*bis*(2-pyridylmethyl)ethylene-1,2-diamine

(ii) White's catalyst: $[Fe(S,S'\text{-PDP})(CH_3CN)_2](SbF_6)_2$ [130,131] or $[Fe(N_4Py)_2(CH_3CN)](ClO_4)_2$ [32], *etc*.

It is evident not only from these complexes and also other iron-complexes containing amine, pyridine (or) imine units in it are very good catalytic agents for oxidation reactions [34,35, 70,94-96,133,134].

Two-open sites preferably in *cis*-positions holds to be a good oxidant, [134,135] imine groups are prone to hydrolysis and CH_2NR_2 units can be oxidized to O=CNR_2. Though having potential decomposition pathways, amine and imine units can be very often seen in catalytically active iron-complexes. Complexes containing amide groups in their coordination sphere were found to be catalytically very active. Example, tetraamido macrocyclic ligands (TAML), form efficient iron complexes for selective cyclohexene oxidations [65,136-138].

Mechanistic studies, which were developed earlier on iron coordination complexes as functional models of non-heme oxygenases led to key discoveries that paved way for the evolution of synthetic non-heme iron catalysts competent for the selective oxidation of alkane and alkene moieties. In a series of studies, mononuclear iron complexes $[Fe(tpa)(CH_3CN)_2]^{2+}$ and $[Fe(men)(CH_3CN)_2]^{2+}$ react with H_2O_2, generating a highly reactive but selective oxidant, inconsistent with the production of hydroxyl radicals [128,139]. The metal-based nature of such oxidant was reflected by a high A/K ([cyclohexanol]/[cyclohexanone]) ratio (5:11) and a relatively high kinetic isotopic effect (KIE > 3) in cyclohexane oxidation, a high regioselectivity towards the tertiary C–H bond in adamantane oxidation (3°/2° normalized selectivity > 15) and a high retention of configuration in 1,2-*cis*-dimethylcyclohexane hydroxylation (> 94%) (Fig. 3) [139]. Moreover, isotopic labelling experiments demonstrated that the O-atom incorporated into the substrates derived from H_2O_2 and H_2O and not from O_2 (Fig. 3).

This observation discards the implication of carbon-centred radicals, because they're known to react with O_2 at diffusion-controlled rates and thus incorporate O-atoms from atmospheric oxygen. The stereo-retentive nature of the hydroxylation reaction and thus the shortage of O_2 incorporation into oxidation products provided conclusive evidence that C–H bond hydroxylation occurs *via* a mechanism that doesn't imply formation of a carbon centered free-diffusing radical. Therefore, these complexes react with H_2O_2 and override the Fe^{II}/Fe^{III} Fenton cycle, but produce a metal-based oxidant, proposed to be a high-valent iron-oxo (Fe^{V}=O) species that's competent for the selective oxidation of organic substrates. Parallel studies on the oxidation of olefins mediated by the same iron catalysts, bearing tetradentate ligands that leave two *cis*-labile sites, provided further evidence in favour of the formation of a high-valent iron-oxo species in these reactions [135].

These reactions provided epoxides and *syn*-1,2-diols and thus the mechanistic interrogation of both processes pointed

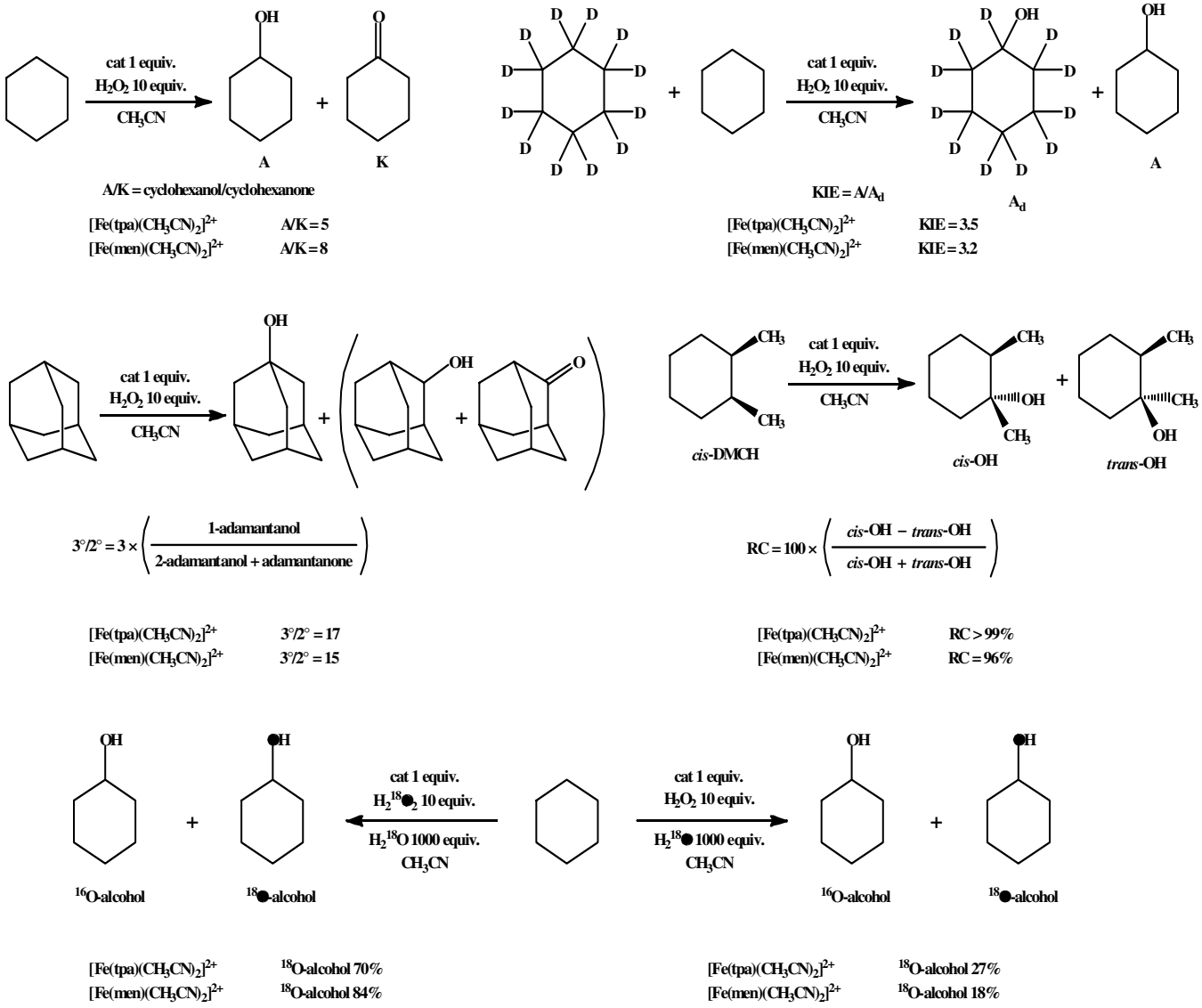


Fig. 3. Reactions of mononuclear iron complexes with H_2O_2

again towards a metal-based oxidation. First, stereo-retentive *syn*-dihydroxylation is incompatible with any radical reaction mechanism. Second, isotopic labelling in olefin oxidation reactions showed that oxygen atoms incorporated into oxidation products originate from H_2O_2 and H_2O but not O_2. Eventually, the epoxidation was also demonstrated to be a stereo retentive process (Fig. 4).

These pioneering studies were focused on the elucidation of the reaction mechanisms and employed large excesses of substrate. Therefore, their potential utility in chemical synthesis was very limited. However, they acknowledged that the reaction of those complexes with H_2O_2 forms a strong yet selective metal based oxidant, barren of free diffusing radicals. This finding rapidly raised the interest of the synthetic chemistry community in developing catalytic methodologies for selective alkane and alkene oxidation.

Essential structure-activity correlations: The most thoughtfully explored iron complexes in oxidation catalysis are based on tetradentate amine ligands. Representative examples

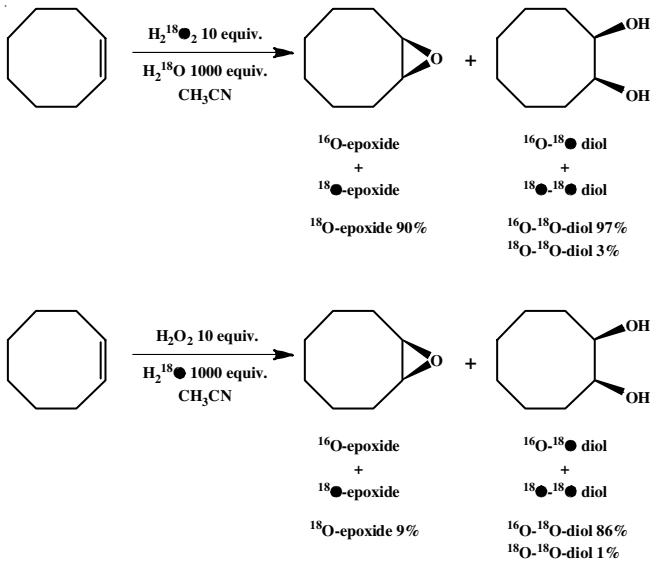
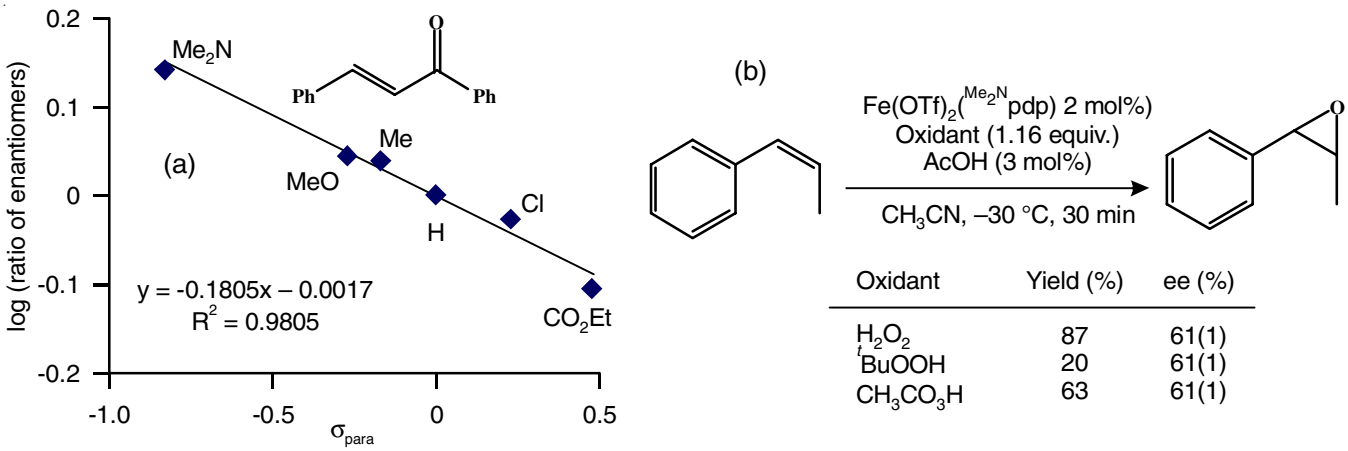


Fig. 4. Epoxidation



Oxidant	Yield (%)	ee (%)
H_2O_2	87	61(1)
^tBuOOH	20	61(1)
CH_3CO_3H	63	61(1)

Fig. 5. Oxidation catalysis in tetradentate amine ligands

are shown in Fig. 5. In general, the activity of these complexes in oxidation catalysis is dictated by two main aspects: (i) the presence of two *cis*-labile sites within the coordination sphere of the iron centre and (ii) the stability of the complex and the ligand against oxidative and hydrolytic degradation. With only a few exceptions, two *cis*-labile sites are required for H_2O_2 activation and subsequent formation of a metal-based oxidant ready to engage in selective oxidation of organic substrates (vide infra).

When these sites are blocked by a non-labile ligand (for instance chloride), the reaction occurs through a Fenton pathway [139,140]. A similar reactivity was reported also for complexes bearing pentadentate polyamine ligands or complexes where the 2 labile sites are trans to every other, further highlighting the importance of two *cis*-labile sites ([Fe(N_4Py)(CH_3CN)]-(ClO_4)$_2$ and [Fe(OTf)$_2$(TMC)], respectively, Fig. 5) [128,139, 141,142]. Iron catalysts showing optimal stability usually contain tetradentate aminopyridine ligands and form three five membered chelate rings upon binding to a ferrous centre. Although the resting state within the catalytic cycle is usually considered to be a ferric complex, Fe(II) precursors are convenient to use, as they're easily prepared and may be isolated as pure mononuclear iron complexes containing labile sites. Indeed, the oxophilicity of Fe(III) rapidly leads to the formation of oxobridged dimers, which are often catalytically inactive. On the other hand, ligands based on O or S donors [143,144], aromatic diamines [144] or imines [35,145] tend to form less stable complexes and do not usually show good catalytic activity. Methyl groups or halogens on the pyridine α-position (the closest to the metal), as well as replacement of pyridine donors with quinoline ones, weaken the Fe–N(py) bond, enforcing a high-spin configur-ation on the corresponding iron complexes. These high-spin complexes tend to deactivate rapidly, presumably because of the high lability of the metal-ligand bonds. In stark contrast, substitutions in positions 3, 4 or 5 are well tolerated and the ones in the 4th position allow the manipulation of electronics of the iron complex [85,146]. In general, electron poor complexes behave as less efficient oxidation catalysts [147,148].

O_2 activation: Although iron complexes are known to react with dioxygen, the utilization of O_2 in catalytic oxidations poses the innate challenge of coupling its 4e$^-$ reduction with the 2e$^-$ oxidation of a substrate [149]. Some strategies are suggested with the aim of developing oxidation methods that employ O_2 as oxidant, but the sector remains in its infancy. The simplest thanks to address this issue consists within the use of a sacrificial reductant to supply two electrons to activate O_2 by reducing it to the peroxide level. The peroxide is then further activated by the metal centre, generating a metal-based oxidant which engages within the 2e$^-$ oxidation of the substrate.

However, such a reductant also can compete with the substrate for the metal-based oxidant, or open up some undesired reactivity which ends up in formation of byproducts. Enzymes overcome this problem by precisely controlling the injection of electrons in the metal centre where the O_2 reduction/activation process takes place, but this is more difficult to achieve in synthetic systems. Inspiration for this approach came from α-ketoglutarate dependent non-heme iron oxygenases. These enzymes couple the 2e$^-$ oxidative decarboxylation of an α-ketoglutarate molecule with the 4e$^-$ O_2 reduction to make an oxidant capable of the 2e$^-$ substrate oxidation [150,151].

Complex [Fe(TpPh2)(Bz)] can be considered a synthetic model of these enzymes, although it cannot undergo turnover. It couples α-hydroxy acid (or α-keto acid) decarboxylation with O_2 activation to yield an Fe–oxygen intermediate (Fig. 6a), which has not been directly detected but leads to intramolecular ligand oxidation [152]. However, it's possible to inter-cept this intermediate with several substrates and therefore the authors suggest that it's an Fe^{IV}=O species with nucleophilic character. Addition of a Brønsted or a Lewis acid switched its reactivity towards that of an electrophilic oxidant capable of C–H hydroxylation, olefin dihydroxylation and sulphide oxidation [153]. Interestingly, this complex was recently reported to catalyze alcohol oxidation within the presence of excess deprotonated α-keto acid with up to five turnovers [154].

An example of catalytic O_2 activation including substrate oxidation was also described by Limberg & Siewert [155]. Complex [Fe(TpMe$_2$)(Phmal)] (Fig. 6b), where Phmal = diethyl phenyl malonate anion, was found to act as a structural and functional mimic of acetylacetone dioxygenase, a nonheme iron enzyme that catalyses the oxidative decarboxylation of acetylacetone. This complex mediated the oxidative

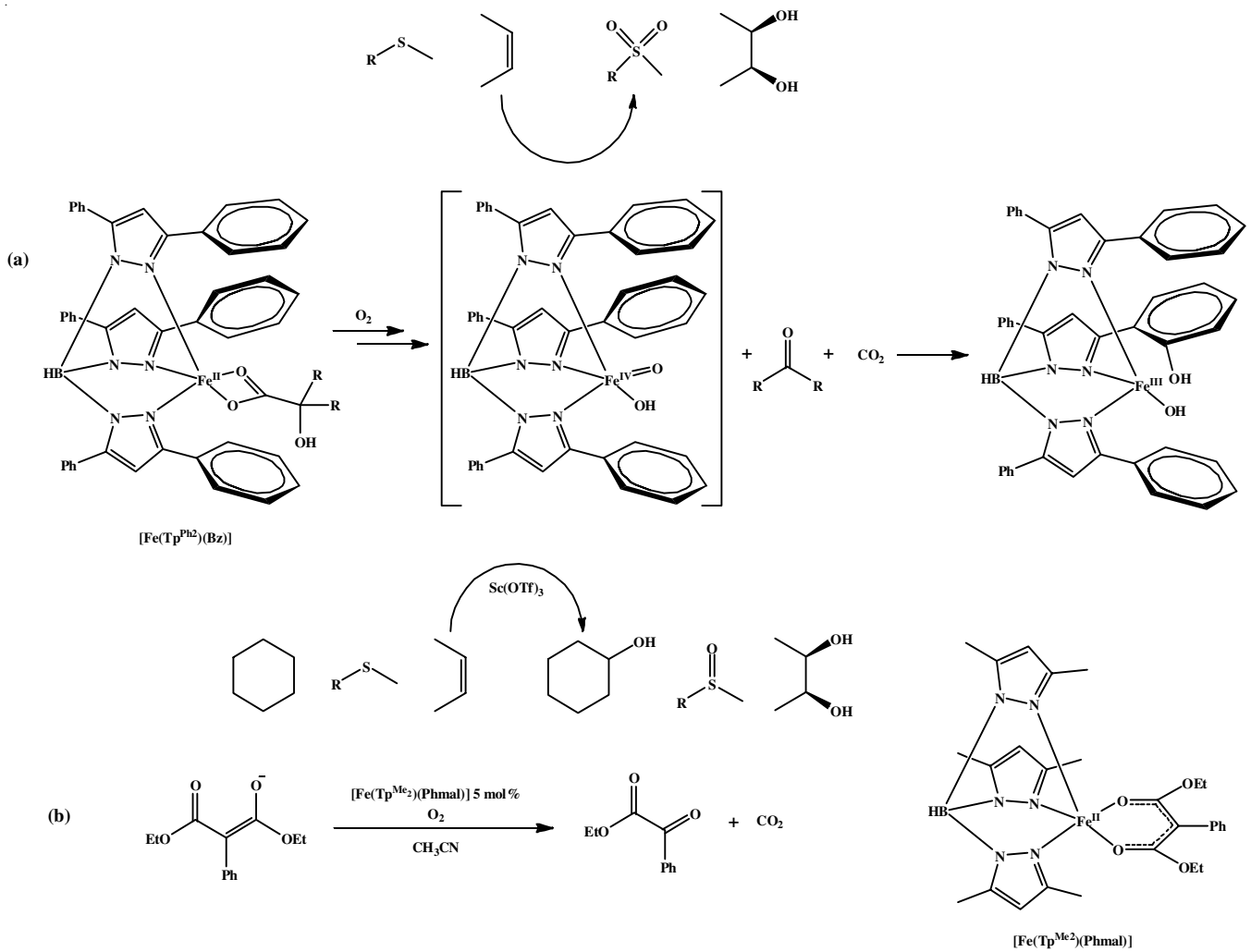


Fig. 6. Catalytic O_2 activation

decarboxylation of Phmal, an analog of acetylacetone (Fig. 6b) and was able to perform several catalytic cycles with a turnover frequency of 55 h^{-1} [55].

Catalytic aerobic oxidation has been described also by Gif systems, with Zn or Fe powder or H_2S as the sacrificial reductants [156-160]. However, these systems showed a peculiar alkane oxidation selectivity, which pointed to a radical oxidation mechanism that limits their value for selective oxidations [71]. Catalytic aerobic epoxidation was reported in 2011 [161,162]. The O_2 activation catalyzed by a simple catalytic system, 1:10 $FeCl_3$: imidazole mixture (Fig. 7) was coupled with reductive decarboxylation of a readily available β-ketoester to achieve olefin epoxidation in good yields. Remarkably, very low amounts of byproducts are observed, highlighting the potential of this technique. A similar aerobic epoxidation reactivity was described also with a different iron complex and aldehydes as sacrificial reductants [163]. These reports provided proof-of-principle that synthetically useful aerobic oxidations could be accomplished with carbonyl compounds as external reductants. The reaction mechanisms followed in these reactions are not completely understood. It is sure that oxidized products are formed not only through a metal-based process but also from free radical autoxidation chains.

Obviously, it would be highly desirable to avoid the use of sacrificial reductants; for example, by designing reactions where the substrate undergoes $4e^-$ oxidation, or by coupling the $4e^-$ O_2 reduction with the $2e^-$ oxidation of two equivalents of the substrate. The latter reactivity has been described by Nam *et al.* [164], who accomplished aerobic phosphine oxidation with [Fe(OTf)$_2$(TMC)] catalyst through the intermediary of an Fe^{IV}=O species.

Substrate oxidation regenerates the initial Fe^{II} complex, although with only a few turnovers [165]. More recently, Xiao & Castro [163] found that a mononuclear, tricoordinated Fe^{II} complex with a bulky ligand (Pybisulfide, Fig. 7b,c) dehydrogenative oxidizes cyclic ethers into lactones with impressive TONs (up to 412) using molecular oxygen (Fig. 7b). The three labile coordination sites on the catalyst are proposed to host the O_2 molecule and two ethereal substrates. The Fe^{III} superoxide would evolve to form an invoked Fe^{IV} dihydride species, which ulti-mately releases H_2 and regenerates the initial Fe^{II} complex. Therefore, coupling of ether oxidation with substrate dehydrogenative H_2 production was found to be the key for catalytic O_2 activation. The Fe^{III} complex of the same ligand was later reported to efficiently cleave the C=C double bond of styrene to yield two terminal carbonyl compounds (Fig. 7c), again without external reductants [164].

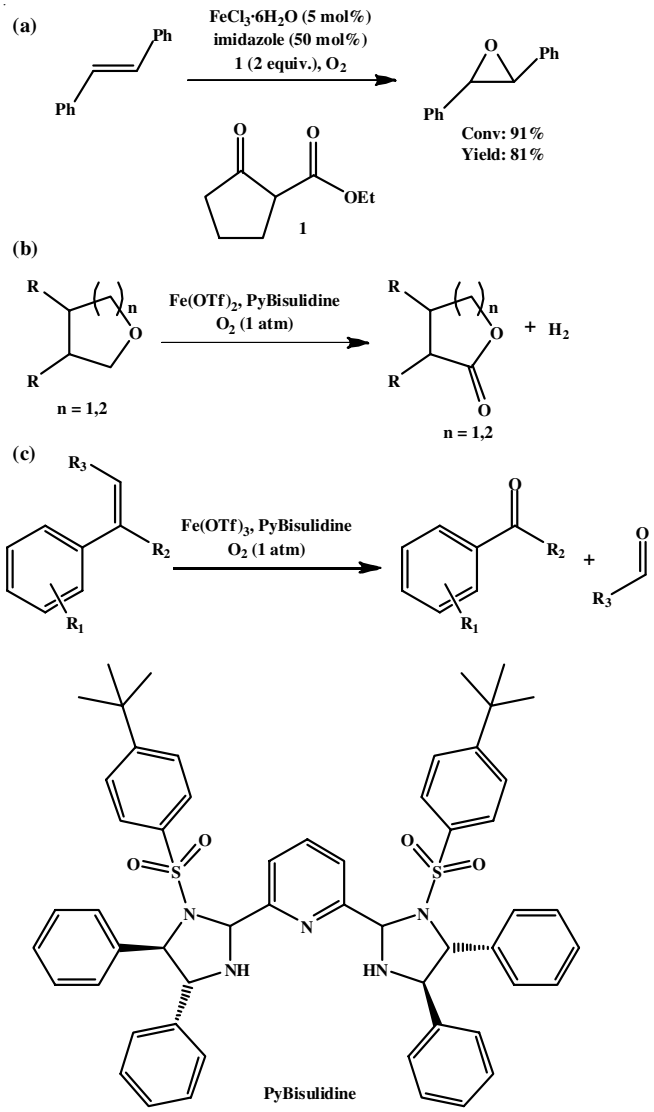


Fig. 7. Substrate oxidation

A different strategy has been reported by Wolff & Muhldorf [165], who used a riboflavin derivative as photocatalyst to scale back O_2, forming H_2O_2 and to catalytically oxidize alkyl aromatics. The produced H_2O_2 is used by an iron catalyst to oxidize the substrate. The mechanism of H_2O_2 formation in these reactions is interesting and entails oxidation of a sacrificial e^- donor by the photoexcited flavin, which then engages in reduction and protonation of the O_2 molecule, finally forming H_2O_2. The high redox potential of the photo-excited flavin also can oxidize e^- rich arenes, which, therefore, are often also used as electron donors within the generation of H_2O_2. Overall, this technique operates not only *via* O_2 activation, but also performs direct oxidation of the substrate *via* electron transfer. Nevertheless, this work delineates a really promising approach towards the utilization of O_2 because the terminal oxidant.

Important reactions: In 2019, Han *et al.* [166] reported an iron-catalyzed efficient methodology for the oxidation of methylarenes and alkylarenes to deliver arylaldehydes, aryl ketones and aryl esters efficiently. They employed a combination of iron(II) phthalocyanine (1 mol%) and ferrocene (10 mol%) as a catalyst in the presence of $K_2S_2O_8$ (1 equiv.) as an oxidant, together with polymethyl hydroxy silane (PMHS) as an activator. Moreover, the reaction was carried out in a CH_3CN /H_2O (1:1) solvent mixture under ambient air (1 atm of O_2) at 80 °C (Fig. 8).

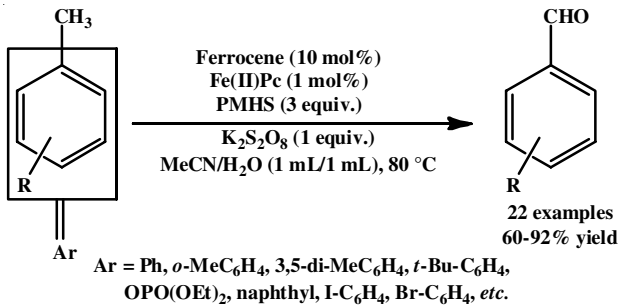


Fig. 8. Iron-catalyzed oxidation of methyl aromatics

Interestingly, toluenes bearing electron-donating groups such as methyl, polymethyl, 4-*tert*-butyl and diethyl phenyl phosphate produced the desired selective oxidized product in high yield (86-92% yield). Also, electron-withdrawing substituents (bromo, iodo, sulfonyl, *etc.*) containing toluene derivatives provided the desired aryl aldehyde at a slow reaction rate with high yield (60-94% yield) in the presence of an increased amount of oxidant (3 equiv. of $K_2S_2O_8$). Remarkably, the one-step oxidation of methylthiophenes to the corresponding then aldehydes (90% yields) was achieved using this reaction protocol. Importantly, then aldehydes are widely used for the synthesis of chemotherapeutic medicine teniposide, a common hepatoprotectant tenylidone and the insectifuge pyrantel.

Most intriguingly, the present methodology has been found to be compatible in the presence of unprotected boronic acids, which are very sensitive towards reagents such as bases, organic acids and oxidants due to unstable tricoordination nature of the boron centre. Thus, the present protocol chemo selectively oxidizes the aromatic methyl moiety in the presence of boronic acid to generate carbonyl compounds in good to excellent yields. Notably, for this particular type of reaction, they utilized FeCl (10 mol%) as the catalyst instead of the combination of ferrocene, iron(II) phthalocyanine and tetrabutylammonium bromide (TBAB), in the presence of the same oxidant/PMHS/solvent system. Notably, aldehydoarylboronic acids have high synthetic versatility due to the presence of both nucleophilic (C–B bond) and electrophilic (C=O bond) moieties. The robustness of this reaction protocol leads to the late-stage oxidation of complex molecules such as dehydroabetic acid, gemfibrozil and tocopherol nicotinate.

Mechanistically, the reaction is initiated *via* oxidation of Fe(II) center by persulfate to form Fe(III) species and sulphate radical anion I (Fig. 9). Notably, this Fe(III) species is further reduced for the regeneration of Fe(II) species in the presence of PMHS. Then, radical I react with alkylarenes *via* the single-electron transfer mechanism (SET) to generate alkyl aromatic cation II. This cation is highly acidic and readily eliminates benzylic hydrogen for the further formation of intermediate radical III. Notably, the formation of radical intermediate III was confirmed by trapping it with the radical scavenger 2,2,6,6-

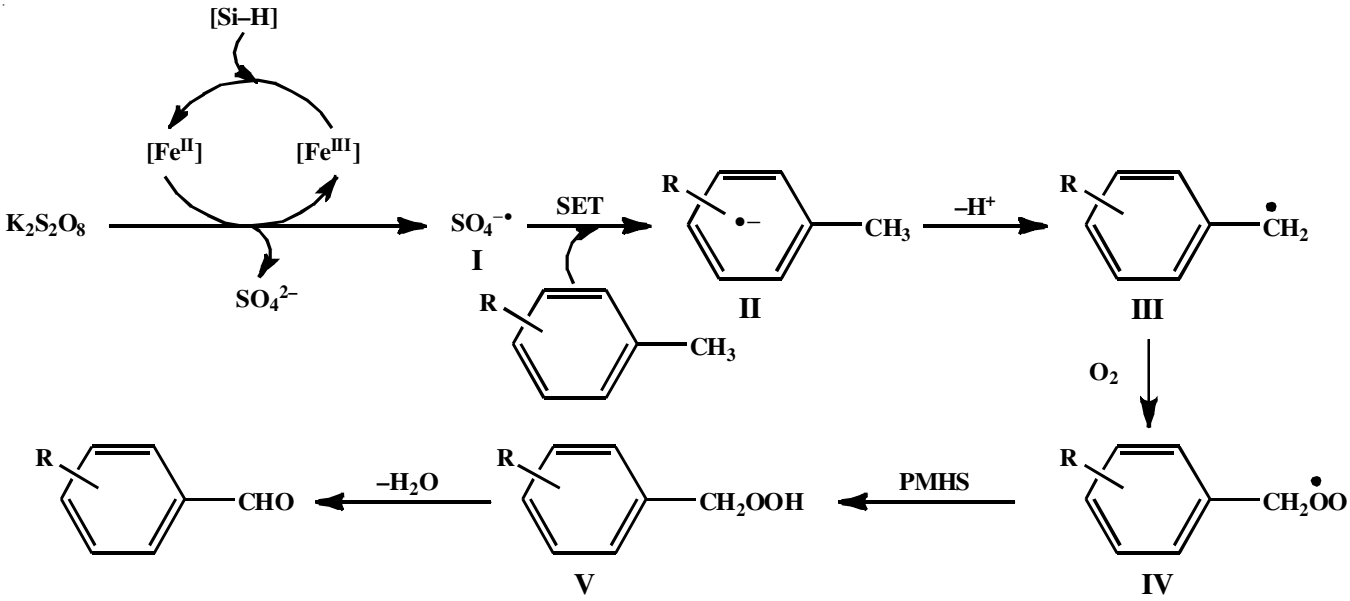


Fig. 9. Mechanistic pathway of iron-catalyzed oxidation of methyl aromatics

tetramerthylpiperodinooxy (TEMPO). Subsequently, radical intermediate III reacts with molecular oxygen to form benzyl peroxide radical IV followed by abstraction of hydrogen from PMHS. Thereafter, hydroperoxide V undergoes the elimination of water molecule for the formation of desired aryl aldehydes [167]. However, the possibility of self-reaction of two benzyl peroxide radicals IV cannot not be excluded during the formation of aldehyde [168,169].

Recently in 2020, Costas *et al.* [103,104,170] introduced another synthetic method describing an iron complex, (R,R)-Fe^{tips}PDP-(OTf)$_2$ (Λ-^{tips}2), catalyzed site and product chemoselective aliphatic C–H bond oxidation of polyfunctional substrates in the presence of hydrogen peroxide as a terminal oxidant and fluorinated alcohol as solvent (Fig. 10). The reaction is performed in the presence of a fluorinated solvent such as 1,1,3,3,3,3-hexafluoro-2-propanol (HFIP), exhibiting a strong

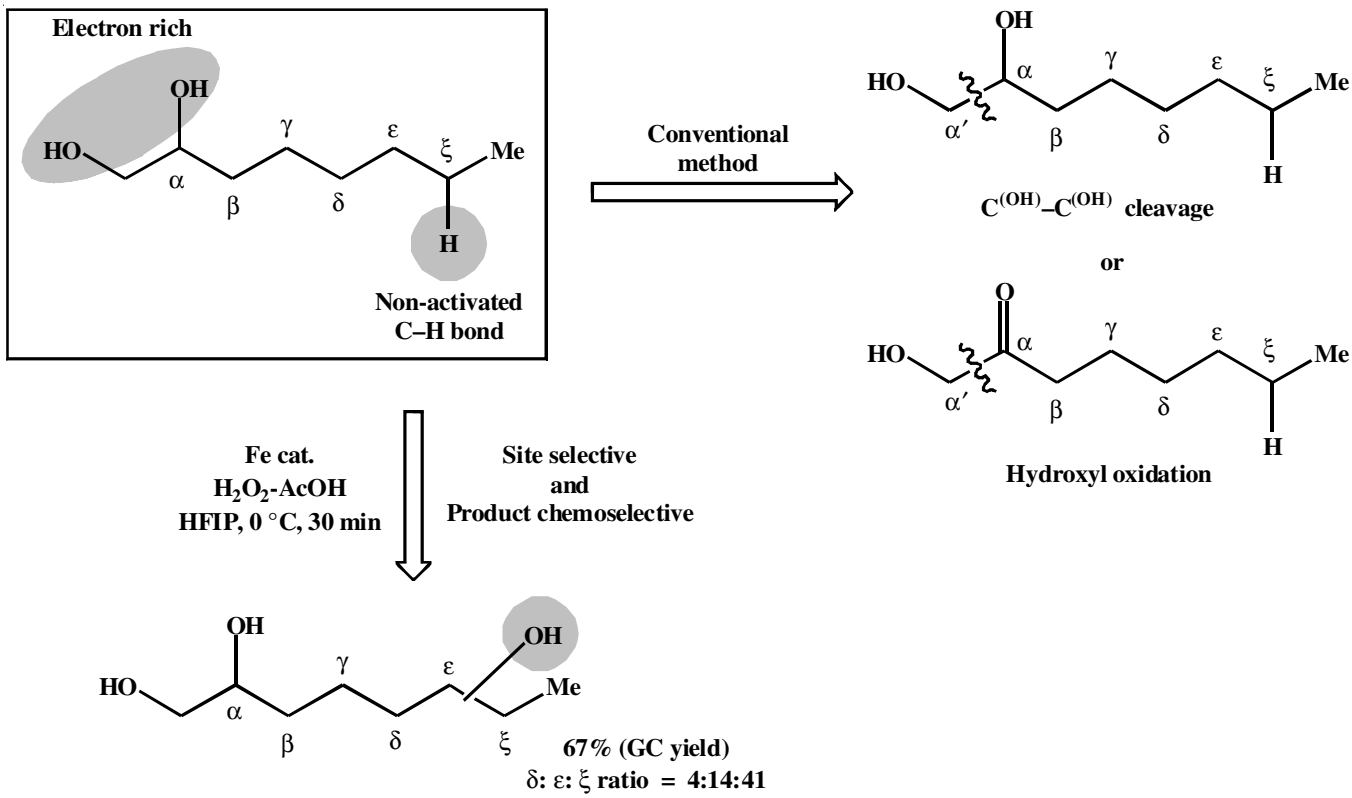


Fig. 10. C–H oxidation of polyhydroxylated molecules and its possible mechanism

polarity reversal in the hydroxyl moiety of 1,2-diols due to hydrogen bonding. This hydrogen bonding strongly deactivates the proximal C–H bonds and thus inhibits proximal C–H bond oxidation. Further, this methodology provides access to the predominant hydroxylation of remote and non-activated C–H bonds, providing orthogonal chemo-selectivity to existing alcohol oxidation methods (Fig. 10).

Furthermore, this reaction protocol was successfully applied for executing C–H oxidation of sugars, steroids and other densely functionalized substrates without protecting the hydroxyl functionalities. For example, anticancer drug capecitabine composed of a highly polar functional group-enriched core together with an oxidation-sensitive five-membered cyclic ether possessing a tertiary C–H bond at the γ-position and *syn* 1,2-diol at the α- and β-positions are well tolerated under the standard reaction conditions. Noteworthily, the cyclic ether moiety is connected to a fluorinated *N*-heterocyclic moiety connected to an alkyl carbamate moiety. Also, several 4,5,6-membered metal chelating units are present, having the ability to deactivate the metal catalyst (Fig. 11). However, despite these complexities, capecitabine undergoes hydroxylation (50% yields) at the remote methylenic sites of the alkyl chain (68% conversion) together with the formation of 12% of the corresponding carbonyl compound, keeping the densely functional core intact.

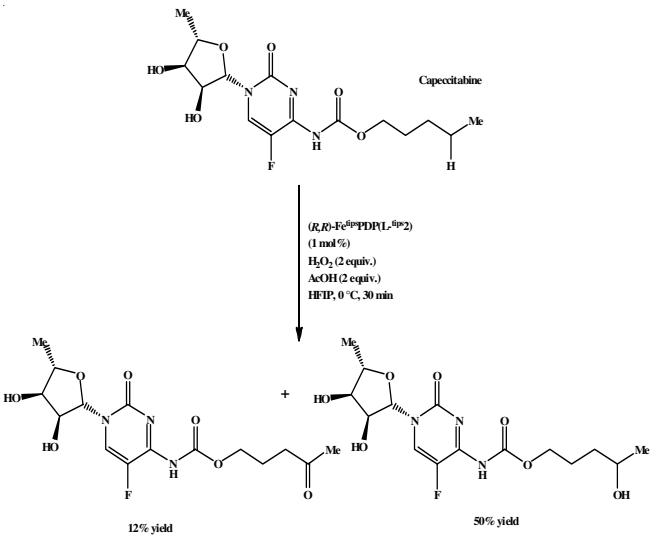


Fig. 11. Iron-catalyzed oxidation of capecitabine

Wacker-type oxidation: Although, Pd catalyzed Wacker oxidation for the formation of carbonyl compounds from olefin compounds is well known, the late transition metal Pd is very toxic, inexpensive and has low abundance in the earth's crust. Therefore, the development of alternative catalysts based on the cheap, non-toxic, earth abundant transition metals is of immense importance. Although iron-catalyzed Wacker oxidations are very rare, Che *et al*. [172] reported the iron-catalyzed anti-Markovnikov oxidation of terminal alkenes to aldehydes using iodosylbenzene as an oxidant *via* a tandem epoxidation–isomerization (E–I pathway) pathway. The iron(III) porphyrin complex [(2,6-Cl_2TPP) Fe(OTf)] was employed as the catalyst, delivering the desired product regioselectively in good yield (Fig. 12).

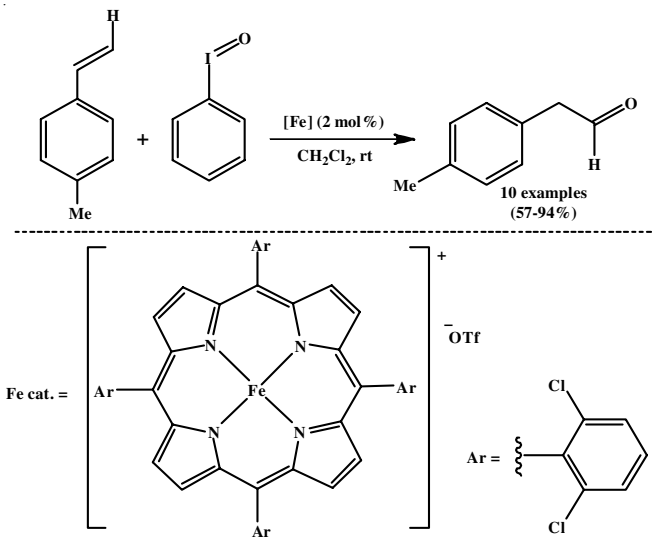


Fig. 12. Iron-catalyzed Wacker-type oxidation of styrene using iodosyl benzene

Lahiri *et al.* [175] reported an efficient method of iron-catalyzed regioselective oxidation of styrene with the anti-Markovnikov formation of acetal [102]. This method utilizes an iron catalyst, $Fe(BF_4)_2{\cdot}6H_2O$, in the presence of pyridine-2,6-dicarboxylic acid as the supporting ligand and iodobenzene diacetate [$PhI(OAc)_2$] as an oxidant in methanol under aerial circumstances (Fig. 13). Further, the use of a dehydrating agent, molecular sieves, in the reaction is crucial to achieve better yield of the desired product by minimizing the rearranged product. A wide range of different aromatic and aliphatic cyclic olefins are well tolerated chemoselectively to provide the terminal acetals. In contrast to the anti-Markovnikov selectivity observed in the present method, the palladium-catalyzed acetilization reaction provides Markovnikov selectivity [173].

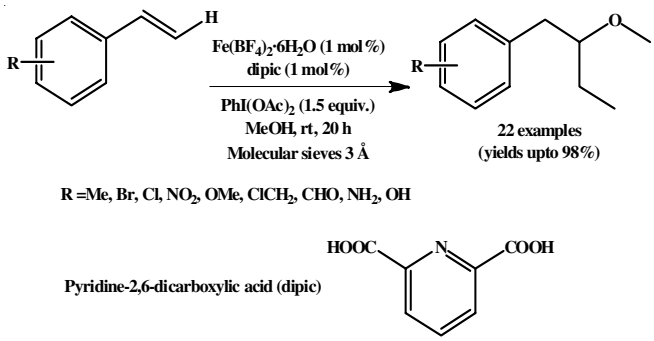


Fig. 13. Iron catalysed regioselective oxidation of styrene with anti-Markovnikov selectivity

It is believed that the reaction proceeds *via* the generation of iron-oxo intermediate I, which reacts with the olefin in a side-way approach to generate intermediate II, followed by a 1,2-hydride shift and two successive solvent nucleophilic attacks at the β position from intermediate III, leading to the formation of the desired product (Fig. 14).

In same year, they developed another method of regioselective oxidation of terminal alkenes to aldehyde using the same iron catalyst and supporting ligand in the presence

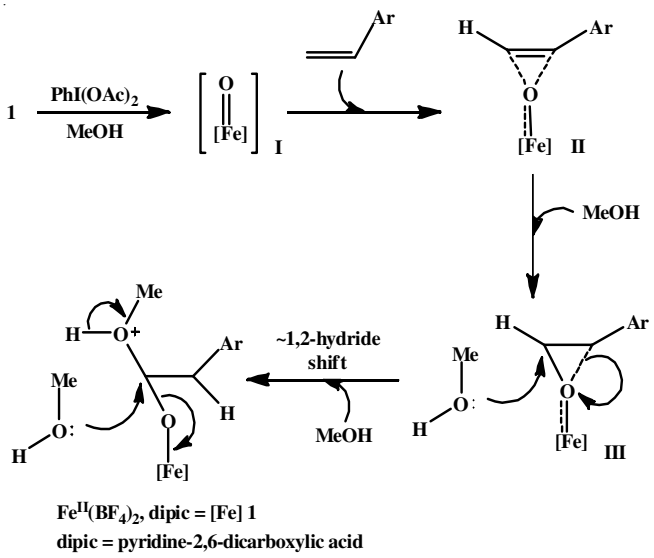


Fig. 14. Generation of iron-oxo intermediate

of iodosyl benzene as the oxidant in chloroform [172,173]. Different aromatic, aliphatic and terminal olefins together with alkenyl olefins were found to be compatible under the standard reaction conditions (Fig. 15). The tentative mechanism of the reaction was proposed, involving two possible pathways, namely tandem epoxidation-isomerization (pathway a) and pinacol like rearrangement (pathway b) (Fig. 16) [174-176].

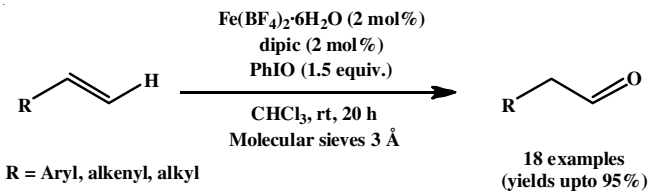


Fig. 15. Standard reaction conditions for iron-catalyzed oxidation to olefins

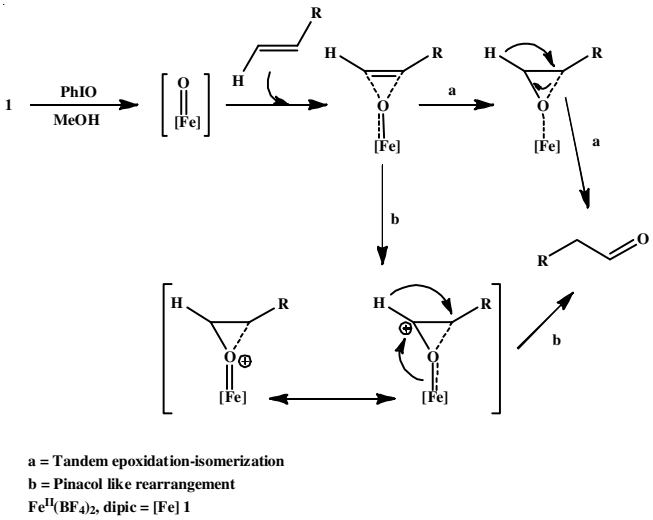


Fig. 16. Reaction pathways for iron-catalyzed oxidation to olefins

Earlier in 2011, Che *et al*. [177] studied the iron-porphyrin catalyzed anti-Markovnikov oxidation of both terminal aryl and aliphatic olefins to aldehyde using PhIO as an oxidant. However, due to the shortcoming of using PhIO as an oxidant, in 2014, they synthesized an iron-catalyst, [Fe^{III}(TF_4DMAP)-OTf], in the presence of H_2O_2 as the terminal oxidant for the anti-Markovnikov oxidation of terminal aryl alkenes to aldehydes (Fig. 17) [171]. It has been presumed that initially $[Fe(Por)]^+$ is converted to [Fe(O)(Por)] complex in the presence of H_2O_2, which takes part in the reaction with terminal aryl alkenes to afford the corresponding epoxide, followed by the regeneration of $[Fe(Por)]^+$ complex, inducing isomerization of the epoxide to the desired product.

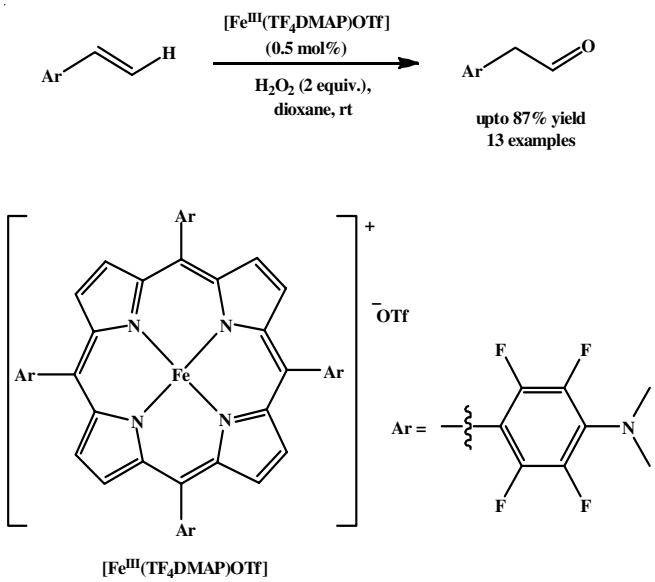


Fig. 17. Iron-catalyzed anti-Markovnikov addition of terminal alkenes

Significantly, similar to C–H oxidation, iron co-factor containing artificial metalloenzymes can also be used in the anti-Markovnikov oxidation of olefins. In 2017, Arnold *et al.* [178] reported the high-valent metal–oxo-mediated anti-Markovnikov oxidation of alkenes using an engineered cytochrome P-450 (aMOx) enzyme in combination with alcohol dehydrogenase (ADH) and oxygen as a terminal oxidant. Generally, the high-valent metal–oxo-mediated reaction proceeds *via* the concerted epoxidation pathway having a low energy barrier, resulting in the formation of the epoxidation product. However, this reaction also provides the direct anti-Markovnikov oxidation product when it proceeds *via* the formation of the high energy carbocationic intermediate (Fig. 18). This unstable intermediate is stabilized *via* 1,2-hydride migration, which was also confirmed by an isotopic labelling study.

Noteworthily, the asymmetric induction in the case of this methodology arises due to the 1,2-hydride migration. Moreover, the enantioselectivity originates from the locked arrangement of the substrates in a specific conformation, which aligns one of the C–H bonds coplanar to the empty *p*-orbital of the carbocation intermediate. A wide variety of styrenes are oxidized to the anti-Markovnikov carbonyl product with a TTN of 3800 and 81% selectivity. The *para*-substituted styrenes are converted into the desired products with high selectivity, while that with *meta* and *ortho* substitutions exhibit a lower level of selectivity (Fig. 19). Accordingly, this suggests that the direct anti-Markovnikov

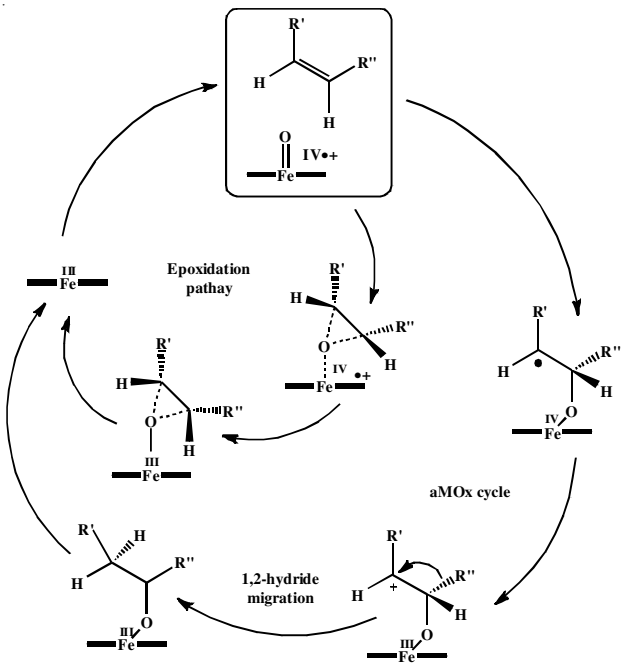


Fig. 18. Mechanistic pathway of epoxidation and anti-Markovnikov oxidation

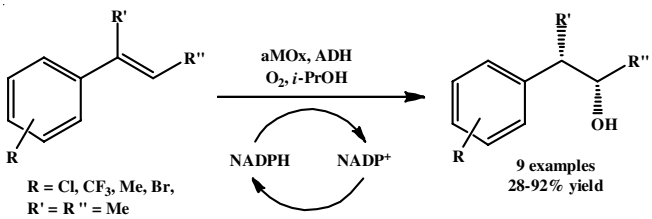


Fig. 19. Anti-Markovnikov hydration of alkenes *via* aMOx

oxidation is a catalyst-controlled process, which depends on the exact orientation of the substrate to prevail over epoxidation.

Subsequently, influenced by the chemistry of cytochrome P-450 [80,179-181] and the recent reported by Baran and co-workers [182-192], Han *et al.* [193] first developed an iron-catalyzed highly efficient and selective oxidation protocol. Here, polymethyl hydroxy silane (PMHS) is used as the reductant in alcohol for the aerobic oxidation of styrene, internal olefins and electron deficient aryl olefins to ketones (Fig. 20).

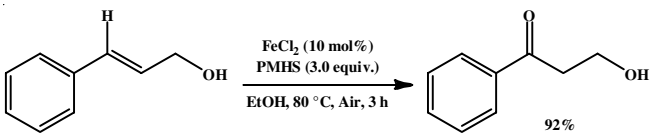


Fig. 20. Iron-catalyzed Wacker-type oxidation in ambient air

Subsequently, the substrate scope was tested under the optimized reaction conditions. A series of styrenes that are normally challenging substrates for the Wacker oxidation were found to afford the desired product in good to excellent yield with excellent selectivity. Substrates having electron donating substituents and electron-withdrawing substituents in the aryl rings give a comparative yield. Moreover, a wide range of functional groups such as halo groups (Cl, Br and I), esters, benzyl chloride, nitro group and carboxylic acids are well tolerated. Particularly, the presence of several readily oxidizable groups such as aldehyde, phenol, silane and aryl boronic acids and strong coordinating pyridyl groups are well tolerated. Notably, under slightly modified conditions, *i.e.* using $Fe(acac)_2$ as the catalyst and *t*-BuOH as the solvent, aliphatic terminal olefins undergo smooth conversion into the expected ketone with complete Markovnikov selectivity. In contrast to Pd-catalyzed Wacker-type oxidation, electron-deficient internal alkenes such as *trans*-benzylideneacetone and heterocyclic *trans*-4-(2-thienyl)-but-3-en-2-one undergo the reaction to produce the desired product. Additionally, an aliphatic internal alkene, (3Z)-hept-3-en-1-ol, which is completely unreactive, was reported by Sigman *et al.* [194] and Liu & Han [195] to be an efficient substrate exhibiting sufficient reactivity. Moreover, this synthetic protocol is applied for the oxidation of natural products and synthetic compounds with high complexity. For instance, a derivative of the antibacterial drug pleuromutilin underwent the reaction protocol to deliver the desired oxidized product in 70% yield. The mechanistic pathway of the iron-catalyzed Wacker-type oxidation of olefins to ketones using molecular oxygen as the sole oxidant in presence of reductive silane (Fig. 21).

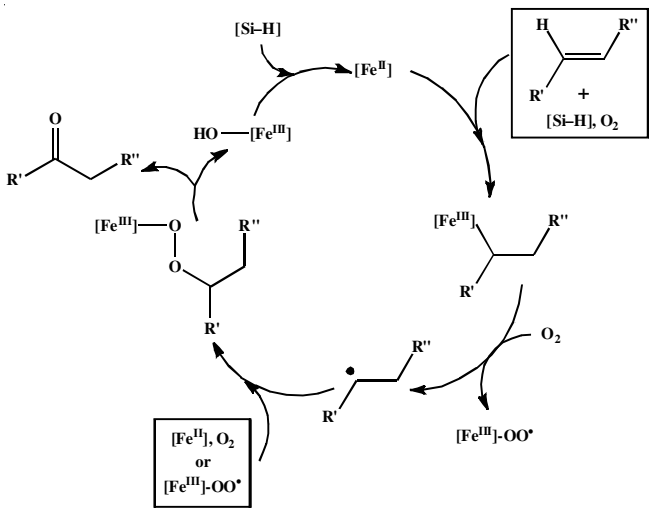


Fig. 21. Proposed mechanistic pathway of iron-catalyzed aerobic Wacker-type oxidations of olefins

Baeyer–Villiger-type oxidation: Baeyer & Villiger [196] discovered the oxidation of menthone to the corresponding lactone employing a mixture of sodium persulfate and concentrated vitriol. Thereafter, this persulphuric acid was replaced by other organic per-acids such as *meta*-chloroperoxybenzoic acid (*m*-CPBA), trifluoro peracetic acid and per benzoic acid. Thus, the conversion of ketone into the ester in the presence of per-acid as an oxidant has become one of the most well-known and widely applied organic reactions, which is known as Baeyer-Villiger oxidation. However, the organic peracids utilized in the oxidation reactions are hazardous and expensive. Hence, the usage of clean and inexpensive oxidants is extremely significant and attractive from an environmental and economic viewpoint. The aerobic Baeyer-Villiger oxidation of ketones in the presence of aldehyde was reported using Fe_2O_3 and Fe–MCM-41 under heterogeneous conditions [196].

However, the drawback of MCM-41 system is its unidirectional pore system. Thus, to overcome this drawback, Subramanian & Koodali *et al*. [197] discovered a highly active mesoporous catalyst, Fe-MCM-48, for the Baeyer-Villiger oxidation of cyclohexanones and the bulky molecule 2-adamantanone system. The catalyst are often reused for a minimum of three catalytic cycles with none loss in activity. It is specially observed that cubic MCM-48 with its interwoven and continuous 3D regular pore system provides favourable mass-transfer kinetics and is a better molecule for catalytic applications. Powder XRD and diffuse reflectance (DR) studies indicated the incorporation of Fe^{3+} into the silica pore wall in a tetrahedral position. Moreover, this material has a large surface area (1979 $m^2\ g^{-1}$) and large pore volume (1.2 $cm^3\ g^{-1}$).

In biology, oxygenase enzymes such as cytochrome P-450 carry out the oxygenation of different biomolecules [197]. Inspired by these enzymes, Ji *et al.* [198] in 2008 reported the highly efficient selective Baeyer-Villiger oxidation for the first time using iron(III)–*meso*-tetraphenyl porphyrin-[(TPP)Fe^{III}Cl] with molecular oxygen in the presence of benzaldehyde for the conversion of ketones into lactones (Fig. 22). Notably, the oxidation of cyclohexanone catalyzed by iron metalloporphyrin involves the radical species. Thus, due to the reluctance to undergo radical addition toluene was used as the solvent for the transformation. However, although different metals (Ru, Mn, Fe and Co) were tried with the TPP ligand, iron showed the best efficacy for the oxidation reaction. The reason for this is often that the catalytic activity and selectivity of various metalloporphyrin depend upon the steadiness of the various valences of their metal atoms and their electric potentials. Notably, cyclic ketones are more efficiently oxidized than acyclic ketones. Moreover, six-membered cyclic ketones are the foremost efficient among the cyclic ketones to get the corresponding oxidized products. The turnover number (TON) of the (TPP)FeCl catalyst can be maximized to 71,000 for the large scale oxidation of cyclohexanone.

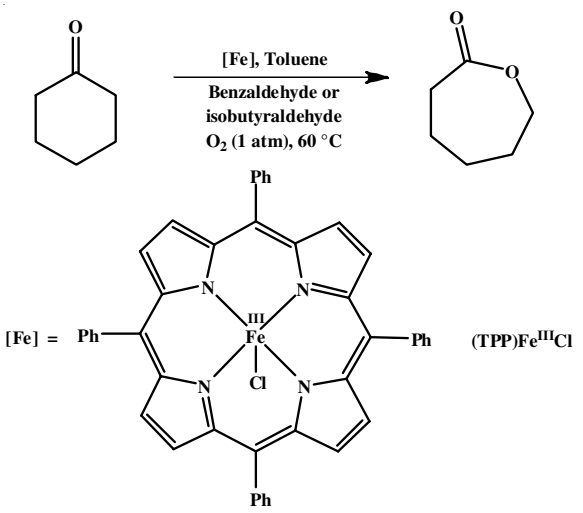


Fig. 22. Aerobic oxidation of ketones catalyzed by iron(III) *meso*-tetraphenyl porphyrin chloride

Here, ε-caprolactone was obtained in 96% yield in the presence of benzaldehyde, while the use of isobutyraldehyde afforded the product in only 11% yield. To investigate this difference, they further studied the mechanistic pathway. Based on the results of *in situ* FTIR, UV-vis spectroscopy and starch/KI experiments, they proposed the mechanistic pathway (Fig. 23) [198,199]. In the initial step of the mechanistic pathway, the iron porphyrin reacts with the aldehyde to get the acyl radical, which reacts with the molecular oxygen to offer the acyl peroxy radical. The resultant acyl peroxy radical as a carrier within the chain mechanism reacts with another molecule of aldehyde to get peroxybenzoic acid. The peroxybenzoic acid is involved in two pathways, A and B, in the presence of benzaldehyde and isobutyraldehyde, respectively. In the presence of benzaldehyde (pathway A), it reacts with another iron porphyrin molecule to generate a high valent iron(V) porphyrin intermediate *via* the elimination of benzoic acid. Then, the intermediate combines with cyclohexanone to require part within the oxygen transfer step, affording ε-caprolactone. However, in the presence of isobutyraldehyde (pathway B), peroxybenzoic acid attacks the activated ketone to generate a Criegee adduct, followed by protolysis to afford a lactone (Fig. 23).

Conclusion

The increasing use of iron-catalyzed organic reactions has led to the development of highly efficient procedures covering a large number of common organic transformations. Iron catalysis has great potential for use in natural product synthesis and has been used on a number of reactions to carry out difficult reactions on complex molecules. Iron-catalyzed transformations have enabled shorter synthetic routes, often giving higher yields, whilst also replacing more expensive or toxic reagents. It is expected that the future will see further uses of iron compared to other precious metals, particularly in the heavily developed area of iron-catalyzed cross-coupling reactions. The practicality and efficiency of these reactions has already been demonstrated by application to a number of complex natural product syntheses and will likely continue to be used extensively for this purpose. During the past 20 years, the C-H bond activations have inherit focus for organic chemists. Oxidative C-C bond forming reactions by cross-dehydrogenative couplings are very attractive as they allow a straightforward construction of new carbon skeletons without pre-functionalization of the substrates. But also, the functionalization of non-activated C-H bonds with heteroatom containing groups is a useful extension of classical reaction principles. The area is still dominated by palladium, rhodium, ruthenium, copper and iridium catalysts, but very promising iron-catalyzed variants have been developed. For example, the activation of sp^3-carbon atoms adjacent to nitrogen and oxygen atoms for C-C bond forming reactions *via* oxidation to iminium and oxonium species or radical processes, may be developed to a flexible tool for the development of complex molecules. Bioinspired iron-catalyzed oxidations are another area that had not received significant attention until recently, but are showing huge potential for use in biomimetic natural product synthesis. The use of iron-catalysts to mimic the multitude of enzyme-driven oxidation processes that occur in nature is likely to continually increase. There are still drawbacks to the use of iron in organic chemistry, namely operational difficulties,

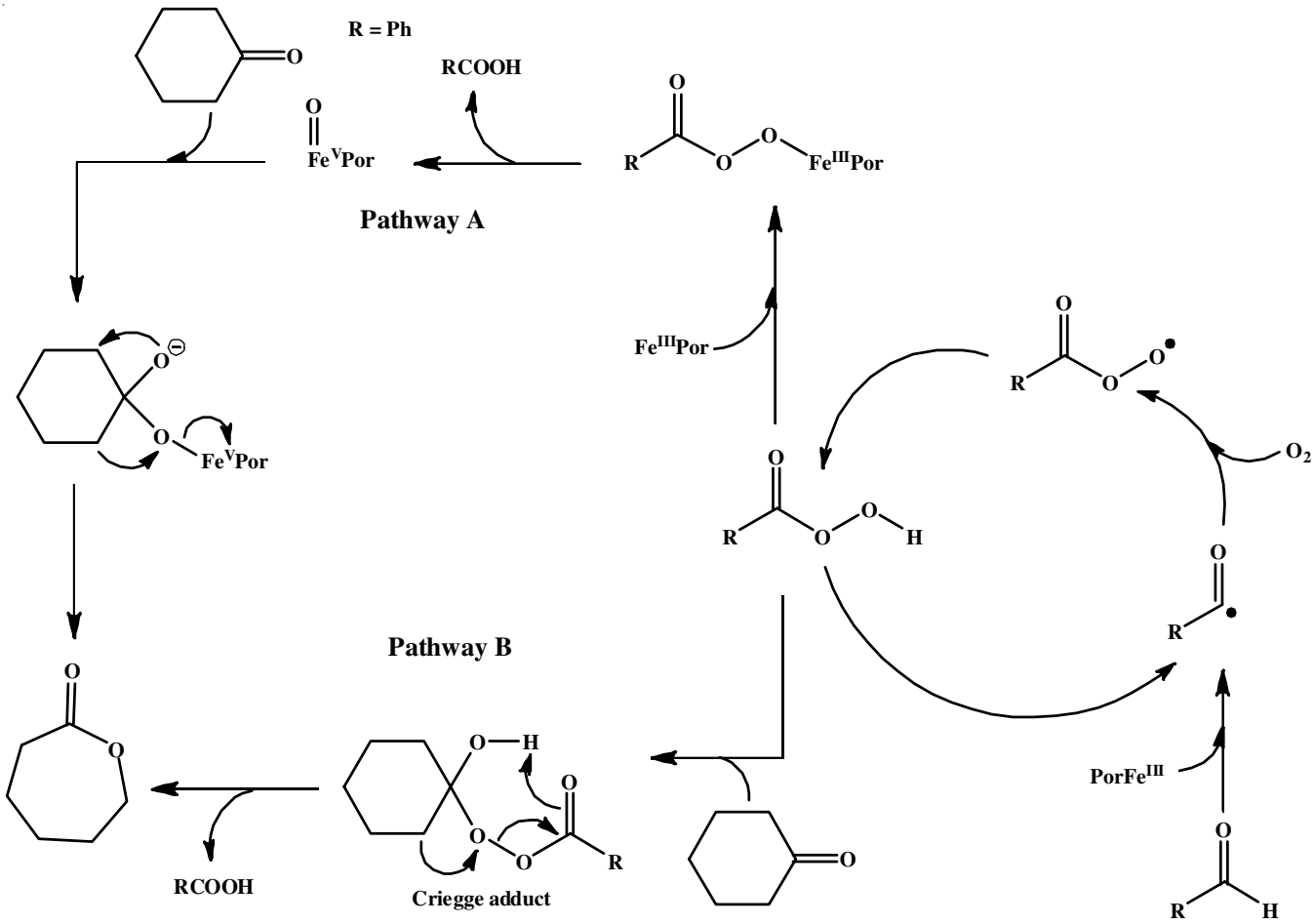


Fig. 23. Mechanistic pathway of cyclohexanone to ε-caprolactone (probable)

but the field is developing rapidly and considering the range of applications, low cost, low toxicity and ready availability of iron, there is immense potential for use in organic synthesis and natural product chemistry. Besides the fascinating developments mentioned above, there's a variety of further highly promising iron-catalyzed transformations. Further improvements of known iron-catalyzed reactions and new discoveries will fill the drawbacks which partly still exist compared to the more established noble metal catalyzed processes used in organic synthesis.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. A. Suzuki, *Angew. Chem. Int. Ed.*, **50**, 6722 (2011); https://doi.org/10.1002/anie.201101379
2. E. Negishi, *Angew. Chem. Int. Ed.*, **50**, 6738 (2011); https://doi.org/10.1002/anie.201101380
3. C.C.C.J. Seechurn, M.O. Kitching, T.J. Colacot and V. Snieckus, *Angew. Chem. Int. Ed.*, **51**, 5062 (2012); https://doi.org/10.1002/anie.201107017
4. A. Biffis, P. Centomo, A. Del Zotto and M. Zecca, *Chem. Rev.*, **118**, 2249 (2018); https://doi.org/10.1021/acs.chemrev.7b00443
5. F. Christoffel and T.R. Ward, *Catal. Lett.*, **148**, 489 (2018); https://doi.org/10.1007/s10562-017-2285-0
6. D. Roy and Y. Uozumi, *Adv. Synth. Catal.*, **360**, 602 (2018); https://doi.org/10.1002/adsc.201700810
7. P. Ruiz-Castillo and S.L. Buchwald, *Chem. Rev.*, **116**, 12564 (2016); https://doi.org/10.1021/acs.chemrev.6b00512
8. F. Kallmeier and R. Kempe, *Angew. Chem. Int. Ed.*, **57**, 46 (2018); https://doi.org/10.1002/anie.201709010
9. A. Rosas-Hernandez, C. Steinlechner, H. Junge and M. Beller, *Top. Curr. Chem.*, **376**, 1 (2018); https://doi.org/10.1007/s41061-017-0179-7
10. P.T. Wolczanski, *Organometallics*, **37**, 505 (2018); https://doi.org/10.1021/acs.organomet.7b00753
11. N. Rajesh, N. Barsu and B. Sundararaju, *Tetrahedron Lett.*, **59**, 862 (2018); https://doi.org/10.1016/j.tetlet.2018.01.065
12. D. Wei and C. Darcel, *Chem. Rev.*, **119**, 2550 (2019); https://doi.org/10.1021/acs.chemrev.8b00372
13. E.B. Bauer, *Isr. J. Chem.*, **57**, 1131 (2017); https://doi.org/10.1002/ijch.201700050
14. A. Correa, O.G. Mancheño and C. Bolm, *Chem. Soc. Rev.*, **37**, 1108 (2008); https://doi.org/10.1039/B801794H
15. S. Dadashi-Silab and K. Matyjaszewski, *ACS Macro Lett.*, **8**, 1110 (2019); https://doi.org/10.1021/acsmacrolett.9b00579
16. P.I. Dalko and L. Moisan, *Angew. Chem. Int. Ed.*, **43**, 5138 (2004); https://doi.org/10.1002/anie.200400650.
17. W. Huang, W.-H. Xu, W.H.E. Schwarz and J. Li, *Inorg. Chem.*, **55**, 4616 (2016); https://doi.org/10.1021/acs.inorgchem.6b00442
18. J.-B. Lu, J. Jian, W. Huang, H. Lin, J. Li and M. Zhou, *Phys. Chem. Chem. Phys.*, **18**, 31125 (2016); https://doi.org/10.1039/C6CP06753K

19. W.M. Reiff and G.J. Long, Mössbauer Spectroscopy Applied to Inorganic Chemistry, In: Mössbauer Spectroscopy and the Coordination Chemistry of Iron, Springer, pp. 245-283 (1984).
20. S.K. Ghorai, V.G. Gopalsamuthiram, A.M. Jawalekar, R.E. Patre and S. Pal, *Tetrahedron*, **73**, 1769 (2017); https://doi.org/10.1016/j.tet.2017.02.033
21. P. Chirik, *Angew. Chem. Int. Ed.*, **56**, 5170 (2017); https://doi.org/10.1002/anie.201611959
22. N. Yoshikai and E. Nakamura, *Chem. Rev.*, **112**, 2339 (2012); https://doi.org/10.1021/cr200241f
23. I. Bauer and H.-J. Knölker, *Chem. Rev.*, **115**, 3170 (2015); https://doi.org/10.1021/cr500425u
24. C. Bolm, J. Legros, J. Le Paih and L. Zani, *Chem. Rev.*, **104**, 6217 (2004); https://doi.org/10.1021/cr040664h
25. B. Plietker, Iron Catalysis. Fundamentals and Applications; Topics in Organometallic Chemistry, Springer: Heidelberg, vol. 33 (2011).
26. E.B. Bauer, Iron Catalysis II; Topics in Organometallic Chemistry, Springer International Publishing: Cham, vol. 50 (2015).
27. R.M. Bullock, Catalysis without Precious Metals, Wiley-VCH: Weinheim (2010).
28. I. Marek and Z. Rappoport, The Chemistry of Organoiron Compounds; Wiley: Chichester (2014).
29. E.B. Bauer, *Top. Organomet. Chem.*, **50**, 1 (2015); https://doi.org/10.1007/3418_2015_107
30. R.B. Bedford and P.B. Brenner, *Top. Organomet. Chem.*, **50**, 19 (2015); https://doi.org/10.1007/3418_2015_99
31. X. Du and Z. Huang, *ACS Catal.*, **7**, 1227 (2017); https://doi.org/10.1021/acscatal.6b02990
32. C. Darcel and J.-B. Sortais, *Top. Organomet. Chem.*, **50**, 173 (2015); https://doi.org/10.1007/3418_2015_104
33. H. Wójtowicz-Mlochowska, *Arkivoc*, 12 (2017); https://doi.org/10.3998/ark.5550190.p009.578
34. G. Olivo, O. Cussó, M. Borrell and M. Costas, *J. Biol. Inorg. Chem.*, **22**, 425 (2017); https://doi.org/10.1007/s00775-016-1434-z
35. R.V. Ottenbacher, E.P. Talsi and K.P. Bryliakov, *Molecules*, **21**, 1454 (2016); https://doi.org/10.3390/molecules21111454
36. J.-L. Renaud and S. Gaillard, *Top. Organomet. Chem.*, **50**, 83 (2015); https://doi.org/10.1007/3418_2015_103
37. B. Burcher, P.-A.R. Breuil, L. Magna and H. Olivier-Bourbigou, *Top. Organomet. Chem.*, **50**, 217 (2015); https://doi.org/10.1007/3418_2015_101
38. W. Zhang, W.-H. Sun and C. Redshaw, *Dalton Trans.*, **42**, 8988 (2013); https://doi.org/10.1039/C2DT32337K
39. P. Dydio, H.M. Key, A. Nazarenko, J.Y.-E. Rha, V. Seyedkazemi, D.S. Clark and J.F. Hartwig, *Science*, **354**, 102 (2016); https://doi.org/10.1126/science.aah4427
40. H.M. Key, P. Dydio, D.S. Clark and J.F. Hartwig, *Nature*, **534**, 534 (2016); https://doi.org/10.1038/nature17968
41. D.A. Vargas, A. Tinoco, V. Tyagi and R. Fasan, *Angew. Chem. Int. Ed.*, **57**, 9911 (2018); https://doi.org/10.1002/anie.201804779
42. R.K. Zhang, K. Chen, X. Huang, L. Wohlschlager, H. Renata and F.H. Arnold, *Nature*, **565**, 67 (2019); https://doi.org/10.1038/s41586-018-0808-5
43. V. Tyagi, G. Sreenilayam, P. Bajaj, A. Tinoco and R. Fasan, *Angew. Chem. Int. Ed.*, **55**, 13562 (2016); https://doi.org/10.1002/anie.201607278
44. K. Chen, S.Q. Zhang, O.F. Brandenberg, X. Hong and F.H. Arnold, *J. Am. Chem. Soc.*, **140**, 16402 (2018); https://doi.org/10.1021/jacs.8b09613
45. A.L. Chandgude, X. Ren and R. Fasan, *J. Am. Chem. Soc.*, **141**, 9145 (2019); https://doi.org/10.1021/jacs.9b02700
46. Z.J. Wang, N.E. Peck, H. Renata and F.H. Arnold, *Chem. Sci.*, **5**, 598 (2014); https://doi.org/10.1039/C3SC52535J
47. G. Sreenilayam and R. Fasan, *Chem. Commun.*, **51**, 1532 (2015); https://doi.org/10.1039/C4CC08753D
48. M.W. Wolf, D.A. Vargas and N. Lehnert, *Inorg. Chem.*, **56**, 5623 (2017); https://doi.org/10.1021/acs.inorgchem.6b03148
49. V. Tyagi, R.B. Bonn and R. Fasan, *Chem. Sci.*, **6**, 2488 (2015); https://doi.org/10.1039/C5SC00080G
50. S.B.J. Kan, X. Huang, Y. Gumulya, K. Chen and F.H. Arnold, *Nature*, **552**, 132 (2017); https://doi.org/10.1038/nature24996
51. X. Huang, M. Garcia-Borras, K. Miao, S.B.J. Kan, A. Zutshi, K.N. Houk and F.H. Arnold, *ACS Cent. Sci.*, **5**, 270 (2019); https://doi.org/10.1021/acscentsci.8b00679
52. K. Chen, X. Huang, S.-Q. Zhang, A. Zhou, S.B.J. Kan, X. Hong and F. Arnold, *Synlett*, **30**, 378 (2019); https://doi.org/10.1055/s-0037-1611662
53. M.S. Kharasch and E.K. Fields, *J. Am. Chem. Soc.*, **63**, 2316 (1941); https://doi.org/10.1021/ja01854a006
54. M. Tamura and J.K. Kochi, *J. Am. Chem. Soc.*, **93**, 1487 (1971); https://doi.org/10.1021/ja00735a030
55. E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies and M. Nakamura, *Org. React.*, **83**, 1 (2013); https://doi.org/10.1002/0471264180.or083.01
56. A. Rühlmann, D. Antovic, T.J.J. Müller and V.B. Urlacher, *Adv. Synth. Catal.*, **359**, 984 (2017); https://doi.org/10.1002/adsc.201601168
57. X. Engelmann, I. Monte-Pérez and K. Ray, *Angew. Chem. Int. Ed.*, **55**, 7632 (2016); https://doi.org/10.1002/anie.201600507
58. G.-D. Roiban and M.T. Reetz, *Chem. Commun.*, **51**, 2208 (2015); https://doi.org/10.1039/C4CC09218J
59. A.B. McQuarters, M.W. Wolf, A.P. Hunt and N. Lehnert, *Angew. Chem. Int. Ed.*, **53**, 4750 (2014); https://doi.org/10.1002/anie.201402404
60. P.R. Ortiz de Montellano, *Chem. Rev.*, **110**, 932 (2010); https://doi.org/10.1021/cr9002193
61. E.P. Talsi and K.P. Bryliakov, *Coord. Chem. Rev.*, **256**, 1418 (2012); https://doi.org/10.1016/j.ccr.2012.04.005
62. P.C.A. Bruijnincx, G. van Koten and R.J.M. Klein Gebbink, *Chem. Soc. Rev.*, **37**, 2716 (2008); https://doi.org/10.1039/b707179p
63. T.D.H. Bugg and S. Ramaswamy, *Curr. Opin. Chem. Biol.*, **12**, 134 (2008); https://doi.org/10.1016/j.cbpa.2007.12.007
64. D. Mansuy, M. Lange, J.C. Chottard, P. Guerin, P. Morliere, D. Brault and M. Rougee, *Chem. Soc., Chem. Comm.*, 648 (1977); https://doi.org/10.1039/c39770000648
65. L. Que Jr. and W.B. Tolman, *Nature*, **455**, 333 (2008); https://doi.org/10.1038/nature07371
66. M. Costas, M.P. Mehn, M.P. Jensen and L. Que Jr., *Chem. Rev.*, **104**, 939 (2004); https://doi.org/10.1021/cr020628n
67. F. Napoly, R. Kieffer, L. Jean-Gérard, C. Goux-Henry, M. Draye and B. Andrioletti, *Tetrahedron Lett.*, **56**, 2517 (2015); https://doi.org/10.1016/j.tetlet.2015.03.115
68. M.N. Kopylovich, A.P.C. Ribeiro, E.C.B.A. Alegria, N.M.R. Martins, L.M.D.R.S. Martins and A.J.L. Pombeiro, *Adv. Organomet. Chem.*, **63**, 91 (2015); https://doi.org/10.1016/bs.adomc.2015.02.004
69. O.Y. Lyakin, R.V. Ottenbacher, K.P. Bryliakov and E.P. Talsi, *ACS Catal.*, **2**, 1196 (2012); https://doi.org/10.1021/cs300205n
70. H. Wójtowicz-Mlochowska, *Arkivoc*, 12 (2017); https://doi.org/10.3998/ark.5550190.p009.578
71. Y. Park, Y. Kim and S. Chang, *Chem. Rev.*, **117**, 9247 (2017); https://doi.org/10.1021/acs.chemrev.6b00644
72. F. Collet, R.H. Dodd and P. Dauban, *Chem. Commun.*, 5061 (2009); https://doi.org/10.1039/b905820f
73. M. Shen and T.G. Driver, *Org. Lett.*, **10**, 3367 (2008); https://doi.org/10.1021/ol801227f
74. J. Bonnamour and C. Bolm, *Org. Lett.*, **13**, 2012 (2011); https://doi.org/10.1021/ol2004066
75. P.Y. Choy, S.M. Wong, A. Kapdi and F.Y. Kwong, *Org. Chem. Front.*, **5**, 288 (2018); https://doi.org/10.1039/C7QO00693D

76. D.A. Colby, R.G. Bergman and J.A. Ellman, *Chem. Rev.*, **110**, 624 (2010); https://doi.org/10.1021/cr900005n
77. M. Nagamoto and T. Nishimura, *ACS Catal.*, **7**, 833 (2017); https://doi.org/10.1021/acscatal.6b02495
78. R. Shang and L. Liu, *Sci. China Chem.*, **54**, 1670 (2011); https://doi.org/10.1007/s11426-011-4381-0
79. Z. Li, L. Cao and C.J. Li, *Angew. Chem. Int. Ed.*, **46**, 6505 (2007); https://doi.org/10.1002/anie.200701782
80. B. Meunier, S.P. de Visser and S. Shaik, *Chem. Rev.*, **104**, 3947 (2004); https://doi.org/10.1021/cr020443g
81. W. Nam, Y.-M. Lee and S. Fukuzumi, *Acc. Chem. Res.*, **47**, 1146 (2014); https://doi.org/10.1021/ar400258p
82. D. Lee and S.J. Lippard, Eds.: J.A. McCleverty and T.J. Meyer, Comprehensive Coordination Chemistry II: From Biology to Nanotechnology; Pergamon: Oxford, vol. 8, pp 309 (2003).
83. M.M. Abu-Omar, A. Loaiza and N. Hontzeas, *Chem. Rev.*, **105**, 2227 (2005); https://doi.org/10.1021/cr040653o
84. O. Martínez-Ferraté, G.J.P. Britovsek, C. Claver and P.W.N.M. van Leeuwen, *Inorg. Chim. Acta*, **431**, 156 (2015); https://doi.org/10.1016/j.ica.2014.12.016
85. G. Olivo, G. Arancio, L. Mandolini, O. Lanzalunga and S. Di Stefano, *Catal. Sci. Technol.*, **4**, 2900 (2014); https://doi.org/10.1039/C4CY00626G
86. M. Canta, D. Font, L. Gómez, X. Ribas and M. Costas, *Adv. Synth. Catal.*, **356**, 818 (2014); https://doi.org/10.1002/adsc.201300923
87. J. England, R. Gondhia, L. Bigorra-Lopez, A.R. Petersen, A.J.P. White and G.J.P. Britovsek, *Dalton Trans.*, 5319 (2009); https://doi.org/10.1039/b901390c
88. M. Lenze and E.B. Bauer, *Chem. Commun.*, **49**, 5889 (2013); https://doi.org/10.1039/c3cc41131a
89. B. Join, K. Möller, C. Ziebart, K. Schröder, D. Gördes, K. Thurow, A. Spannenberg, K. Junge and M. Beller, *Adv. Synth. Catal.*, **353**, 3023 (2011); https://doi.org/10.1002/adsc.201100210
90. I. Prat, D. Font, A. Company, K. Junge, X. Ribas, M. Beller and M. Costas, *Adv. Synth. Catal.*, **355**, 947 (2013); https://doi.org/10.1002/adsc.201200938
91. E.A. Mikhalyova, O.V. Makhlynets, T.D. Palluccio, A.S. Filatov and E.V. Rybak-Akimova, *Chem. Commun.*, **48**, 687 (2012); https://doi.org/10.1039/C1CC15935F
92. S.R. Iyer, M.M. Javadi, Y. Feng, M.Y. Hyun, W.N. Oloo, C. Kim and L. Que, *Chem. Commun.*, **50**, 13777 (2014); https://doi.org/10.1039/C4CC06164K
93. K. Suzuki, P.D. Oldenburg and L. Que Jr., *Angew. Chem. Int. Ed.*, **47**, 1887 (2008); https://doi.org/10.1002/anie.200705061
94. G. Shul'pin, *Catalysts*, **6**, 50 (2016); https://doi.org/10.3390/catal6040050
95. G. Olivo, O. Lanzalunga and S. Di Stefano, *Adv. Synth. Catal.*, **358**, 843 (2016); https://doi.org/10.1002/adsc.201501024
96. A.C. Lindhorst, S. Haslinger and F.E. Kühn, *Chem. Commun.*, **51**, 17193 (2015); https://doi.org/10.1039/C5CC07146A
97. F. Gozzo, *J. Mol. Catal. A*, **171**, 1 (2001); https://doi.org/10.1016/S1381-1169(01)00099-1
98. H.J.H. Fenton, *J. Chem. Soc. Trans.*, **65**, 899 (1894); https://doi.org/10.1039/CT8946500899
99. G.A. Russell, *J. Am. Chem. Soc.*, **79**, 3871 (1957); https://doi.org/10.1021/ja01571a068
100. J. Kim, R.G. Harrison, C. Kim and L. Que Jr., *J. Am. Chem. Soc.*, **118**, 4373 (1996); https://doi.org/10.1021/ja9542303
101. M.S. Seo, T. Kamachi, T. Kouno, K. Murata, M.J. Park, K. Yoshizawa and W. Nam, *Angew. Chem. Int. Ed.*, **46**, 2291 (2007); https://doi.org/10.1002/anie.200604219
102. F.T. de Oliveira, A. Chanda, D. Banerjee, X. Shan, S. Mondal, L. Que Jr., E.L. Bominaar, E. Münck and T.J. Collins, *Science*, **315**, 835 (2007); https://doi.org/10.1126/science.1133417
103. K. Chen, M. Costas and L. Que Jr., *J. Chem. Soc., Dalton Trans.*, 672 (2002); https://doi.org/10.1039/b108629d
104. M. Costas, K. Chen and L. Que Jr., *Coord. Chem. Rev.*, **200-202**, 517 (2000); https://doi.org/10.1016/S0010-8545(00)00320-9
105. J. Serrano-Plana, W.N. Oloo, L. Acosta-Rueda, K.K. Meier, B. Verdejo, E. García-España, M.G. Basallote, E. Münck, L. Que Jr., A. Company and M. Costas, *J. Am. Chem. Soc.*, **137**, 15833 (2015); https://doi.org/10.1021/jacs.5b09904
106. Y. Song, H.-G. Mayes, M.J. Queensen, E.B. Bauer and C.M. Dupureur, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, **174**, 130 (2017); https://doi.org/10.1016/j.saa.2016.11.030
107. W. Ma, J. Li, X. Tao, J. He, Y. Xu, J.C. Yu and J. Zhao, *Angew. Chem. Int. Ed.*, **42**, 1029 (2003); https://doi.org/10.1002/anie.200390264
108. A. Theodoridis, J. Maigut, R. Puchta, E. Kudrik and R. van Eldik, *Inorg. Chem.*, **47**, 2994 (2008); https://doi.org/10.1021/ic702041g
109. X. Chen, W. Ma, J. Li, Z. Wang, C. Chen, H. Ji and J. Zhao, *J. Phys. Chem. C*, **115**, 4089 (2011); https://doi.org/10.1021/jp110277k
110. J.A. Miller, L. Alexander, D.I. Mori, A.D. Ryabov and T.J. Collins, *New J. Chem.*, **37**, 3488 (2013); https://doi.org/10.1039/c3nj00525a
111. M. Cheng, W. Song, W. Ma, C. Chen, J. Zhao, J. Lin and H. Zhu, *Appl. Catal. B*, **77**, 355 (2008); https://doi.org/10.1016/j.apcatb.2007.08.006
112. J. Kruid, R. Fogel and J.L. Limson, *Chemosphere*, **175**, 247 (2017); https://doi.org/10.1016/j.chemosphere.2017.02.051
113. L. Cheng, J. Wang, M. Wang and Z. Wu, *Phys. Chem. Chem. Phys.*, **12**, 4092 (2010); https://doi.org/10.1039/b917906b
114. M. Ghosh, Y.L.K. Nikhil, B.B. Dhar and S.S. Gupta, *Inorg. Chem.*, **54**, 11792 (2015); https://doi.org/10.1021/acs.inorgchem.5b01937
115. W.A. Donald, C.J. McKenzie and R.A.J. O'Hair, *Angew. Chem. Int. Ed.*, **50**, 8379 (2011); https://doi.org/10.1002/anie.201102146
116. J.H. Han, S.-K. Yoo, J.S. Seo, S.J. Hong, S.K. Kim and C. Kim, *Dalton Trans.*, 402 (2005); https://doi.org/10.1039/b414603d
117. É. Balogh-Hergovich and G. Speier, *J. Mol. Catal. A*, **230**, 79 (2005); https://doi.org/10.1016/j.molcata.2004.12.013
118. N.Y. Oh, Y. Suh, M.J. Park, M.S. Seo, J. Kim and W. Nam, *Angew. Chem. Int. Ed.*, **44**, 4235 (2005); https://doi.org/10.1002/anie.200500623
119. O. Pestovsky and A. Bakac, *J. Am. Chem. Soc.*, **126**, 13757 (2004); https://doi.org/10.1021/ja0457112
120. T.N. Plank, J.L. Drake, D.K. Kim and T.W. Funk, *Adv. Synth. Catal.*, **354**, 597 (2012); https://doi.org/10.1002/adsc.201100896
121. M.G. Coleman, A.N. Brown, B.A. Bolton and H. Guan, *Adv. Synth. Catal.*, **352**, 967 (2010); https://doi.org/10.1002/adsc.200900896
122. S.A. Moyer and T.W. Funk, *Tetrahedron Lett.*, **51**, 5430 (2010); https://doi.org/10.1016/j.tetlet.2010.08.004
123. M. Newcomb, D. Aebisher, R.E.P. Chandrasena, P.F. Hollenberg, R. Shen and M.J. Coon, *J. Am. Chem. Soc.*, **125**, 6064 (2003); https://doi.org/10.1021/ja0343858
124. P. Böhm and H. Gröger, *ChemCatChem*, **7**, 22 (2015); https://doi.org/10.1002/cctc.201402331
125. C. Marchi-Delapierre, L. Rondot, C. Cavazza and S. Ménage, *Isr. J. Chem.*, **55**, 61 (2015); https://doi.org/10.1002/ijch.201400110
126. G.J.P. Britovsek, J. England and A.J.P. White, *Inorg. Chem.*, **44**, 8125 (2005); https://doi.org/10.1021/ic0509229
127. S.V. Kryatov, S. Taktak, I.V. Korendovych, E.V. Rybak-Akimova, J. Kaizer, S. Torelli, X. Shan, S. Mandal, V.L. MacMurdo, A. Mairata i Payeras and L. Que, *Inorg. Chem.*, **44**, 85 (2005); https://doi.org/10.1021/ic0485312

128. K. Chen and L. Que Jr., *Chem. Commun.*, 1375 (1999); https://doi.org/10.1039/a901678c
129. O.V. Makhlynets, W.N. Oloo, Y.S. Moroz, I.G. Belaya, T.D. Palluccio, A.S. Filatov, P. Müller, M.A. Cranswick, L. Que Jr. and E.V. Rybak-Akimova, *Chem. Commun.*, **50**, 645 (2014); https://doi.org/10.1039/C3CC47632D
130. M.S. Chen and M.C. White, *Science*, **327**, 566 (2010); https://doi.org/10.1126/science.1183602
131. M.S. Chen and M.C. White, *Science*, **318**, 783 (2007); https://doi.org/10.1126/science.1148597
132. E. Andris, R. Navrátil, J. Jašík, T. Terencio, M. Srnec, M. Costas and J. Roithová, *J. Am. Chem. Soc.*, **139**, 2757 (2017); https://doi.org/10.1021/jacs.6b12291
133. M. Grau and G.J.P. Britovsek, *Top. Organomet. Chem.*, **50**, 145 (2015); https://doi.org/10.1007/3418_2015_100
134. D.P. de Sousa and C.J. McKenzie, *Top. Organomet. Chem.*, **50**, 311 (2015); https://doi.org/10.1007/3418_2015_108
135. K. Chen, M. Costas, J. Kim, A.K. Tipton and L. Que Jr., *J. Am. Chem. Soc.*, **124**, 3026 (2002); https://doi.org/10.1021/ja0120025
136. L.L. Tang, M.A. DeNardo, C. Gayathri, R.R. Gil, R. Kanda and T.J. Collins, *Environ. Sci. Technol.*, **50**, 5261 (2016); https://doi.org/10.1021/acs.est.5b05518
137. L.L. Tang, M.A. DeNardo, C.J. Schuler, M.R. Mills, C. Gayathri, R.R. Gil, R. Kanda and T.J. Collins, *J. Am. Chem. Soc.*, **139**, 879 (2017); https://doi.org/10.1021/jacs.6b11145
138. G.R. Warner, M.R. Mills, C. Enslin, S. Pattanayak, C. Panda, T.K. Panda, S.S. Gupta, A.D. Ryabov and T.J. Collins, *Chem. Eur. J.*, **21**, 6226 (2015); https://doi.org/10.1002/chem.201406061
139. K. Chen and L. Que Jr., *J. Am. Chem. Soc.*, **123**, 6327 (2001); https://doi.org/10.1021/ja010310x
140. Y. Mekmouche, S. Ménage, C. Toia-Duboc, M. Fontecave, J.-B. Galey, C. Lebrun and J. Pécaut, *Angew. Chem. Int. Ed.*, **40**, 949 (2001); https://doi.org/10.1002/1521-3773(20010302)40:5<949::AID-ANIE949>3.0.CO;2-4
141. R. Mas-Balleste, M. Costas, T. van den Berg and L. Que Jr., *Chem. Eur. J.*, **12**, 7489 (2006); https://doi.org/10.1002/chem.200600453
142. G. Roelfes, M. Lubben, R. Hage, L. Que Jr. and B.L. Feringa, *Chem. Eur. J.*, **6**, 2152 (2000); https://doi.org/10.1002/1521-3765(20000616)6:12<2152::AID-CHEM2152>3.0.CO;2-O
143. J. England, G.J.P. Britovsek, N. Rabadia and A.J.P. White, *Inorg. Chem.*, **46**, 3752 (2007); https://doi.org/10.1021/ic070062r
144. J. England, C.R. Davies, M. Banaru, A.J.P. White and G.J.P. Britovsek, *Adv. Synth. Catal.*, **350**, 883 (2008); https://doi.org/10.1002/adsc.200700462
145. G.J.P. Britovsek, J. England and A.J.P. White, *Dalton Trans.*, 1399 (2006); https://doi.org/10.1039/b513886h
146. I. Prat, A. Company, T. Corona, T. Parella, X. Ribas and M. Costas, *Inorg. Chem.*, **52**, 9229 (2013); https://doi.org/10.1021/ic4004033
147. G. Olivo, O. Lanzalunga, L. Mandolini and S. Di Stefano, *J. Org. Chem.*, **78**, 11508 (2013); https://doi.org/10.1021/jo4020744
148. O. Cussó, I. Garcia-Bosch, X. Ribas, J. Lloret-Fillol and M. Costas, *J. Am. Chem. Soc.*, **135**, 14871 (2013); https://doi.org/10.1021/ja4078446
149. S. Sahu and D.P. Goldberg, *J. Am. Chem. Soc.*, **138**, 11410 (2016); https://doi.org/10.1021/jacs.6b05251
150. C. Krebs, D. Galonic Fujimori, C.T. Walsh and J.M. Bollinger Jr., *Acc. Chem. Res.*, **40**, 484 (2007); https://doi.org/10.1021/ar700066p
151. S. Sinnecker, N. Svensen, E.W. Barr, S. Ye, J.M. Bollinger Jr., F. Neese and C. Krebs, *J. Am. Chem. Soc.*, **129**, 6168 (2007); https://doi.org/10.1021/ja067899q
152. S. Paria, L. Que Jr. and T.K. Paine, *Angew. Chem. Int. Ed.*, **50**, 11129 (2011); https://doi.org/10.1002/anie.201103971
153. S. Chatterjee and T.K. Paine, *Angew. Chem. Int. Ed.*, **54**, 9338 (2015); https://doi.org/10.1002/anie.201502229
154. D. Sheet and T.K. Paine, *Chem. Sci.*, **7**, 5322 (2016); https://doi.org/10.1039/C6SC01476C
155. I. Siewert and C. Limberg, *Angew. Chem. Int. Ed.*, **47**, 7953 (2008); https://doi.org/10.1002/anie.200802955
156. D.H.R. Barton, R.S. Hay-Motherwell and W.B. Motherwell, *Tetrahedron Lett.*, **24**, 1979 (1983); https://doi.org/10.1016/S0040-4039(00)81821-3
157. D.H.R. Barton, J. Boivin, M. Gastiger, J. Morzycki, R.S. Hay-Motherwell, W.B. Motherwell, N. Ozbalik and K.M. Schwartzentruber, *J. Chem. Soc., Perkin Trans. 1*, 947 (1986); https://doi.org/10.1039/p19860000947
158. D.H.R. Barton and T. Li, *Chem. Commun.*, 821 (1998); https://doi.org/10.1039/a800552d
159. K. Schroder, B. Join, A.J. Amali, K. Junge, X. Ribas, M. Costas and M. Beller, *Angew. Chem. Int. Ed.*, **50**, 1425 (2011); https://doi.org/10.1002/anie.201004623
160. Q.F. Cheng, X.Y. Xu, W.X. Ma, S.J. Yang and T.P. You, *Chin. Chem. Lett.*, **16**, 1467 (2005).
161. P. Stavropoulos, R. Celenligil-Cetin and A.E. Tapper, *Acc. Chem. Res.*, **34**, 745 (2001); https://doi.org/10.1021/ar000100+
162. A. Gonzalez-de-Castro, C.M. Robertson and J. Xiao, *J. Am. Chem. Soc.*, **136**, 8350 (2014); https://doi.org/10.1021/ja502167h
163. A. Gonzalez-de-Castro and J. Xiao, *J. Am. Chem. Soc.*, **137**, 8206 (2015); https://doi.org/10.1021/jacs.5b03956
164. S.O. Kim, C.V. Sastri, M.S. Seo, J. Kim and W. Nam, *J. Am. Chem. Soc.*, **127**, 4178 (2005); https://doi.org/10.1021/ja043083i
165. B. Muhldorf and R. Wolf, *Angew. Chem. Int. Ed.*, **55**, 427 (2016); https://doi.org/10.1002/anie.201507170
166. P. Hu, M. Tan, L. Cheng, H. Zhao, R. Feng, W.-J. Gu and W. Han, *Nat. Commun.*, **10**, 2425 (2019); https://doi.org/10.1038/s41467-019-10414-7
167. G.A. Molander and N. Ellis, *Acc. Chem. Res.*, **40**, 275 (2007); https://doi.org/10.1021/ar050199q
168. Y. Ishii, S. Sakaguchi and T. Iwahama, *Adv. Synth. Catal.*, **343**, 393 (2001); https://doi.org/10.1002/1615-4169(200107)343:5<393::AID-ADSC393>3.0.CO;2-K
169. E. Gaster, S. Kozuch and D. Pappo, *Angew. Chem. Int. Ed.*, **56**, 5912 (2017); https://doi.org/10.1002/anie.201702511
170. M. Borrell, S. Gil-Caballero, M. Bietti and M. Costas, *ACS Catal.*, **10**, 4702 (2020); https://doi.org/10.1021/acscatal.9b05423
171. J.R. Griffin, C.I. Wendell, J.A. Garwin and M.C. White, *J. Am. Chem. Soc.*, **139**, 13624 (2017); https://doi.org/10.1021/jacs.7b07602
172. G.-Q. Chen, Z.-J. Xu, C.-Y. Zhou and C.-M. Che, *Chem. Commun.*, **47**, 10963 (2011); https://doi.org/10.1039/c1cc13574k
173. A. Dutta Chowdhury and G. Kumar Lahiri, *Chem. Commun.*, **48**, 3448 (2012); https://doi.org/10.1039/c2cc17889c
174. A.M. Balija, K.J. Stowers, M.J. Schultz and M.S. Sigman, *Org. Lett.*, **8**, 1121 (2006); https://doi.org/10.1021/ol053110p
175. A.D. Chowdhury, R. Ray and G.K. Lahiri, *Chem. Commun.*, **48**, 5497 (2012); https://doi.org/10.1039/c2cc32051g
176. J. Chen and C.-M. Che, *Angew. Chem. Int. Ed.*, **43**, 4950 (2004); https://doi.org/10.1002/anie.200460545
177. Y.-D. Du, C.-W. Tse, Z.-J. Xu, Y. Liu and C.-M. Che, *Chem. Commun.*, **50**, 12669 (2014); https://doi.org/10.1039/C4CC05972G
178. S.C. Hammer, G. Kubik, E. Watkins, S. Huang, H. Minges and F.H. Arnold, *Science*, **358**, 215 (2017); https://doi.org/10.1126/science.aao1482

179. P.R.O. de Montellano, Cytochrome P-450 Structure, Mechanism and Biochemistry, Plenum Press: New York (1986).
180. D. Mansuy, *Pure Appl. Chem.*, **59**, 759 (1987); https://doi.org/10.1351/pac198759060759
181. I. Tabushi, M. Kodera and M. Yokoyama, *J. Am. Chem. Soc.*, **107**, 4466 (1985); https://doi.org/10.1021/ja00301a016
182. J. Gui, C.-M. Pan, Y. Jin, T. Qin, J.C. Lo, B.J. Lee, S.H. Spergel, M.E. Mertzman, W.J. Pitts, T.E. La Cruz, M.A. Schmidt, N. Darvatkar, S.R. Natarajan and P.S. Baran, *Science*, **348**, 886 (2015); https://doi.org/10.1126/science.aab0245
183. J.C. Lo, J. Gui, Y. Yabe, C.-M. Pan and P.S. Baran, *Nature*, **516**, 343 (2014); https://doi.org/10.1038/nature14006
184. J.C. Lo, D.Y. Kim, C.-M. Pan, J.T. Edwards, Y. Yabe, J.H. Gui, T. Qin, S. Gutiérrez, J. Giacoboni, M.W. Smith, P.L. Holland and P.S. Baran, *J. Am. Chem. Soc.*, **139**, 2484 (2017); https://doi.org/10.1021/jacs.6b13155
185. J.C. Lo, Y. Yabe and P.S. Baran, *J. Am. Chem. Soc.*, **136**, 1304 (2014); https://doi.org/10.1021/ja4117632
186. H.T. Dao, C. Li, Q. Michaudel, B.D. Maxwell and P.S. Baran, *J. Am. Chem. Soc.*, **137**, 8046 (2015); https://doi.org/10.1021/jacs.5b05144
187. S.W.M. Crossley, C. Obradors, R.M. Martinez and R.A. Shenvi, *Chem. Rev.*, **116**, 8912 (2016); https://doi.org/10.1021/acs.chemrev.6b00334
188. T. Hashimoto, D. Hirose and T. Taniguchi, *Angew. Chem. Int. Ed.*, **53**, 2730 (2014); https://doi.org/10.1002/anie.201308675
189. E.K. Leggans, T.J. Barker, K.K. Duncan and D.L. Boger, *Org. Lett.*, **14**, 1428 (2012); https://doi.org/10.1021/ol300173v
190. T. Taniguchi, N. Goto, A. Nishibata and H. Ishibashi, *Org. Lett.*, **12**, 112 (2009); https://doi.org/10.1021/ol902562j
191. T. Sugimori, S. Horike, S. Tsumura, M. Handa and K. Kasuga, *Inorg. Chim. Acta*, **283**, 275 (1998); https://doi.org/10.1016/S0020-1693(98)00090-5
192. M. Takeuchi, M. Kodera, K. Kano and Z. Yoshida, *J. Mol. Catal. Chem.*, **113**, 51 (1996); https://doi.org/10.1016/S1381-1169(96)00047-7
193. B. Liu, F. Jin, T. Wang, X. Yuan and W. Han, *Angew. Chem. Int. Ed.*, **56**, 12712 (2017); https://doi.org/10.1002/anie.201707006
194. R.J. DeLuca, J.L. Edwards, L.D. Steffens, B.W. Michel, X. Qiao, C. Zhu, S.P. Cook and M.S. Sigman, *J. Org. Chem.*, **78**, 1682 (2013); https://doi.org/10.1021/jo302638v
195. B. Liu and W. Han, *Synlett*, **29**, 383 (2018); https://doi.org/10.1055/s-0036-1591532
196. S. Srinivasan and W.T. Ford, *J. Mol. Catal.*, **64**, 291 (1991); https://doi.org/10.1016/0304-5102(91)85139-S
197. H. Subramanian and R.T. Koodali, *React. Kinet. Catal. Lett.*, **95**, 239 (2008); https://doi.org/10.1007/s11144-008-5352-0
198. X.T. Zhou, H. B. Ji, L. X. Pei, Y. B. She, J. C. Xu and L.F. Wang, *Chin. J. Org. Chem.*, **27**, 1039 (2007).
199. B. Meunier, Biomimetic Oxidations Mediated by Metal Complexes, Imperial College Press: London (2000).