Iron-Catalyzed/Mediated Oxidative Transformation of C-H Bonds

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Complete List of Authors:	Jia, Fan; Renmin University of China, Chemistry Li, Zhiping; Renmin University of China, Department of Chemistry

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Iron-Catalyzed/Mediated Oxidative Transformation of C-H Bonds

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Fan Jia and Zhiping Li*

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It has been a long time since C-H bond oxidations went into chemists' attention. In the last several decades, C-H bond oxidation has been extensively investigated and applied in chemistry. Transition-metal catalyzed C–H bond oxidative transformations presents one of the state-of-arts at the chemistry frontiers. Iron, as a cheap, readily accessible metal, has already showed its unique utilities. This review attempts to give focus on the way of C-H bond cleavage in the oxidative transformation via iron catalysis, as well as applications in synthetic chemistry.

1 Introduction

Carbon-hydrogen bond is one of the most common chemical bonds in organic molecules.[1] The oxidative transformations of such kind of bond play a vital role in modern scientific research.[2] In nature, many important biochemical processes involve the oxidation reactions. Such as oxidations catalyzed by enzyme within the cells of living organisms. In organic chemistry, generally, oxidation means *gain of oxygen and/or loss of hydrogen of an organic substrate*.[3] Due to the most of oxidation reactions are thermodynamically downhill, achieving high selectivity of such reactions have been the most challenging topics. Generally, C-H bond oxidations include oxygenation,[4] amination,[5] halogenation[6] (Figure 1) and dehydrogenation.[7]

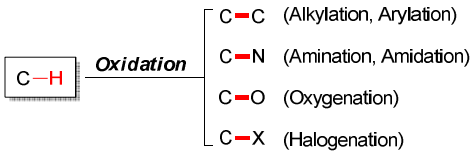
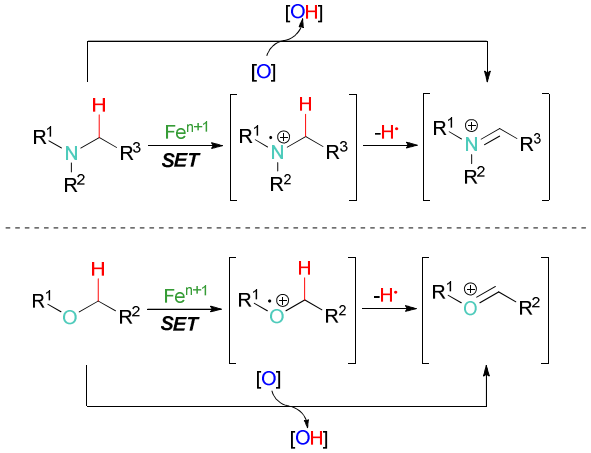


Figure 1 Representative oxidative transformations of C-H bonds.

Over the last several decades, utilizing transition metal as catalysis plays a vital role in the area of C-H activations.[8] Chemists gradually tend to use these 'magic' tools to transform C-H bonds into target functional groups. The vast majority of transition-metal catalyzed C–H oxidation reactions have focused on the transformation of C–H bonds into C–C bonds.[9] These powerful methods have been the subject of numerous review articles. Synthetically, the needed installations of functionalities have become great variety of instruments for total synthesis of natural products and pharmaceuticals.[10]

Iron, which is known one of the most abundant metals in earth, lies in the first transition series. On account of its electron configuration, iron has a wide range of oxidation states, −II to +VIII, although the potential full oxidation state never been reached for now. +II and +III are most common oxidation state for iron in general compounds. However, when iron coordinate to π-acidic ligands, such as CO, NO, bipy et al, it can reach 0, –I or –II oxidation state. In terms of positive oxidation states, iron has variable ones, +IV, +V and +VI, but they are all unstable high valent species and always act as oxidants. Ground on the nature properties of iron, catalysts based on iron have their unique utilities. In the last ten years, iron-catalyzed organic reactions have been widely developed and applied.[11] Resultingly, the vast majority of useful reviews have been written on this charming chemistry in different point of views.[12]

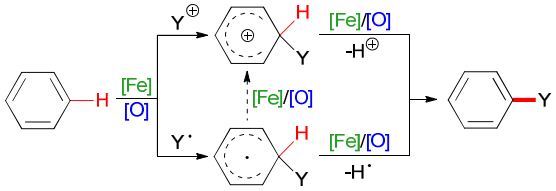
As one of the cheap, readily accessible and environmental benign metals, iron-catalyzed C-H bond oxidative transformation mainly results in the formation of C-C bond, C-N bond, and C-O bond. These transformations are the subject of this review, which will focus on the types of C-H bonds.



Scheme 1 General reaction pathways for reactive sp^3 C-H bond homolytic cleavage. (Adjacent to N or O atom)

C-H bonds with sp^3 hybridisation commonly divided into unreactive and reactive ones. The former is isolated and not adjacent to heteroatom, which termed as aliphatic C-H bonds. Ordinarily, this kind of C-H bond goes into homolytic cleavage in iron-catalyzed oxidation reactions. Activated sp^3 C-H bond is connecting with carbon which has other hybrid type (sp^2 or sp) or adjacent to heteroatoms (such as N or O). This class of C-H bond usually undergoes single electron transfer facilitated by iron followed by hydrogen atom abstraction which resulted in C-H bond homolytic cleavage (Scheme 1).

C-H bonds with sp^2 hybridisation exist in alkenes (belong to carbon-carbon double bond), aromatic compounds (which carbon located in aromatic ring) or other organic molecule (such as aldehyde C(O)-H bond). Such kinds of C-H bond can undergo the homolytic cleavage to form carbon-centered radical or through the heterolytic cleavage directly to generate carbon cation (Scheme 2).



Scheme 2 General pathways of sp^2 C-H bond cleavage at arenes after addition of cationic group or radical.

2 Oxidative Transformation of sp^3 C-H Bond

2.1 C-C Bond Formation

The generation of C-C bond is one of the most important topics in modern organic synthesis. Many significant contributions for this chemical bond architecture have been made in last several decades. As a most direct way to form C-C bond, oxidative coupling between sp^3 C-H bonds and other type of C-H bonds became a topical strategy. Cross-dehydrogenative coupling (also called CDC reaction), is a powerful strategy for the construction of C-C bond (Figure 2).[13]

2.1.1 Benzylic sp^3 C-H Bond

The first raw transition-metal catalysts are found to be reactive in the initiating research of CDC reactions, and then discovered that simple copper salts were the most popular catalyst.[14] In 2007, Li and co-workers reported the first example for the construction of a C-C bond by an $FeCl_2$-catalyzed CDC reaction between two sp^3 C-H bond (Scheme 3).[15] The method utilizing 1,3-dicarbonyl compounds as coupling partner goes through with benzylic C-H bond oxidation to synthesize α-branched alkyl-β-dicarbonyl compounds in 25-87% yield (17 examples).

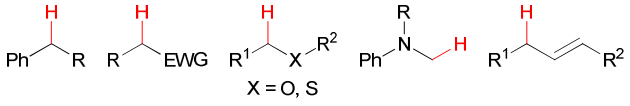
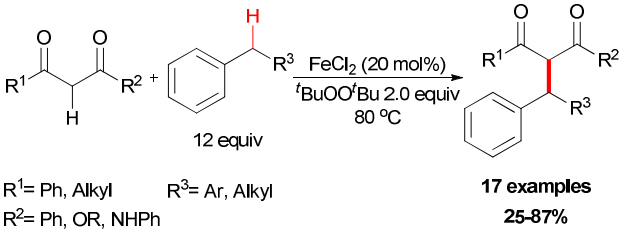
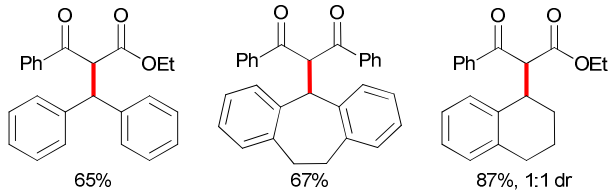


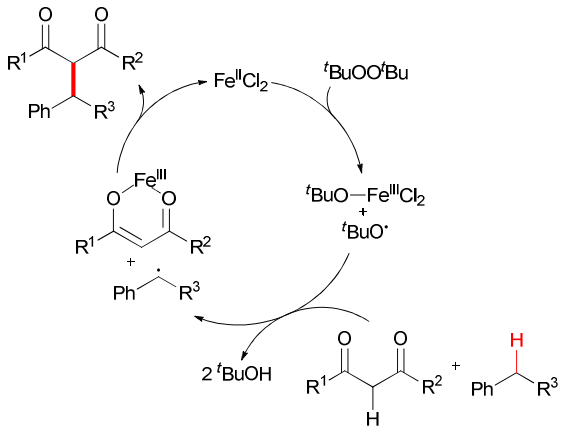
Figure 2 General substrate types for oxidative transformation of sp^3 C-H bonds.





Scheme 3 $FeCl_2$-catalyzed benzylic alkylation.

The reaction mechanism can be rationalized by initial homolytic cleavage of the peroxide bond (^{t}BuO-O^{t}Bu) of the stoichiometric oxidant di-*tert*-butyl peroxide by $FeCl_2$ to generate *tert*-butoxyl radical, which abstracts a hydrogen atom from benzyl substrate to form benzylic radical, whereas iron(III) compound could react with di-carbonyl compound leading to chelate Fe-enolate complex. The benzylic radical could then react with enolate to form the final product and regenerate the Fe(II) which undergoes the next cycle (Scheme 4). The reaction was also found to proceed efficiently at room temperature, and coupling product was isolated in 80% yield on extending the reaction time by using diphenylmethane and benzoylacetone as substrates. In the same year, Li and Zhang reported an Fe-catalyzed alkylation of activated methylenes using simple cycloalkanes as substrate in the presence of di-*tert*-butyl peroxide.[16] In contrast to aged Fenton-type initiation,[17] the active catalyst can also be the chelate Fe-enolate complex formed at start from $FeCl_2$ and dicarbonyl compounds.

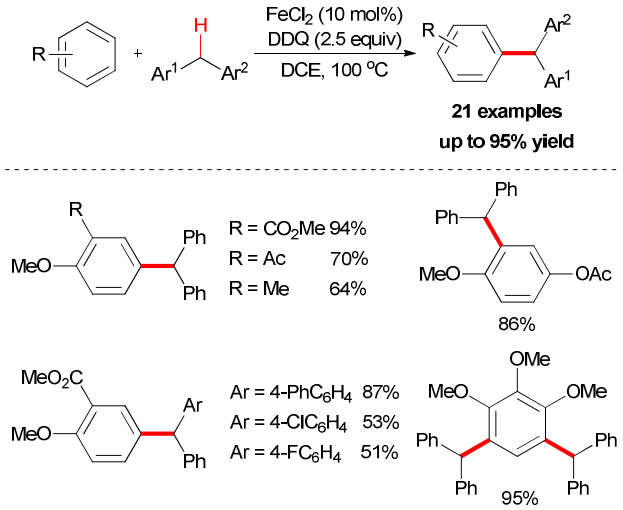


Scheme 4 Proposed mechanism for $FeCl_2$-catalyzed benzylic alkylation.

In Li's subsequent studies, simple toluene derivatives was further tested in the oxidative coupling reactions along with 1,3-dicarbonyl compounds.[18] The condition optimization indicated that $Fe(OAc)_2$ was the best catalyst and *tert*-butyl peroxide was the most efficient oxidant. Under the developed condition, various of toluene derivatives could couple with 1,3-dicarbonyl compounds in moderate to good yields. The

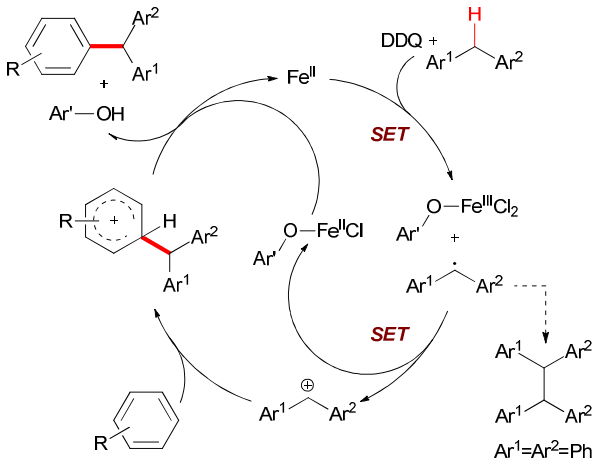
authours also performed the mechanistic studies and the results suggested that the benzylic radical addition to the benzoyl-methana-iron species could occur in the coupling reaction.

The Shi group reported the first example of direct oxidative arylation reactions of benzyl compounds.[19] They used a variety of electron-rich aromatic substrates as coupling partner. After catalysts screening, $FeCl_2$ was identified as the best choice. Combination with DDQ as oxidant, the desired oxidative coupling products were smoothly generated (Scheme 5).



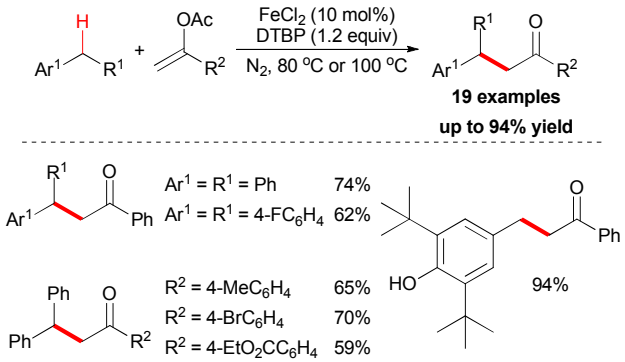
Scheme 5 Iron-catalyzed direct oxidative arylation of the benzylic C-H bond.

The authors also conducted mechanistic studies. Based on their experimental results, a possible mechanism was proposed (Scheme 6). The reaction is initiated by single-electron-transfer process (SET) assisted by the iron salt to generate the benzyl radical, which could be further oxidized to the benzyl cation. The subsequent Friedel-Crafts-type alkylation, followed by abstraction of the proton by the reduced hydroquinone, would release the coupling product and regenerate the catalyst to fulfil the catalytic cycle.



Scheme 6 Proposed mechanism of Fe-catalyzed arylation of benzylic C-H bond. Ar'OH stands for the reduced DDQ.

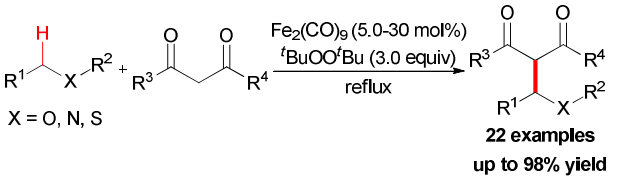
In the same year, the Shi group and the Gan group expanded their research into benzylic alkylation reaction. They used vinyl acetate as coupling partner to construct sp^3 C-C bond with benzyl compounds.[20] After reaction optimization, $FeCl_2$ was identified as the best catalyst and di-*tert*-butyl peroxide (DTBP) was the most efficient oxidant. Under the best condition, a series of benzyl compounds could react with vinyl acetate to give coupling products (19 examples, Scheme 7). Mechanistically, the authors proposed a radical pathway and a cationic pathway. However, the experimental results supported the radical mechanism. They also performed the intermolecular isotopic competitive study, and the result ($K_{H/D}$=2.4) indicated that the proton abstraction process may be involved in the rate determining step.



Scheme 7 Benzylic alkylation with vinyl acetates via iron-catalysis.

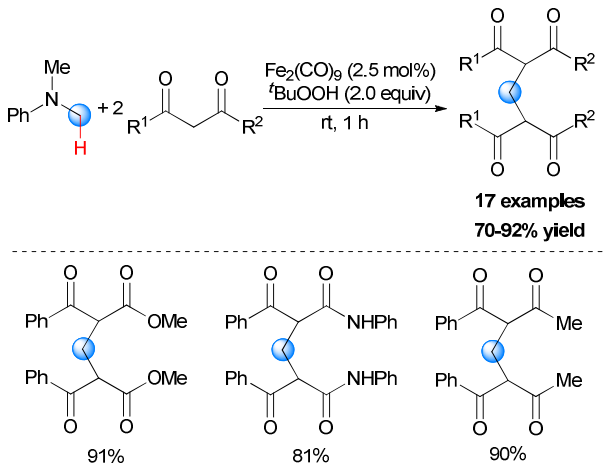
2.1.2 sp^3 C-H Bond Adjacent to Heteroatom

Instead of the sp^3 C-H bond on benzylic and activated methylene motifs, the sp^3 C-H bond adjacent to heteroatoms can also be utilized in oxidative coupling reactions to form the C-C bond. In 2008, Li and co-workers made a breakthrough in such area. Their report disclosed an oxidative cross-coupling reaction of ethers, sulphides, or tertiary amines with 1,3-dicarbonyl compounds (Scheme 8).[21] Diiron nonacarbonyl $Fe_2(CO)_9$, as an Fe(0) complex, proved to be the most efficient catalyst while the $Fe(OAc)_2$ shows almost the same efficiency in the present transformation. By using di-*tert*-butyl peroxide as the optimal oxidant, substrates can be smoothly underwent the CDC reaction.



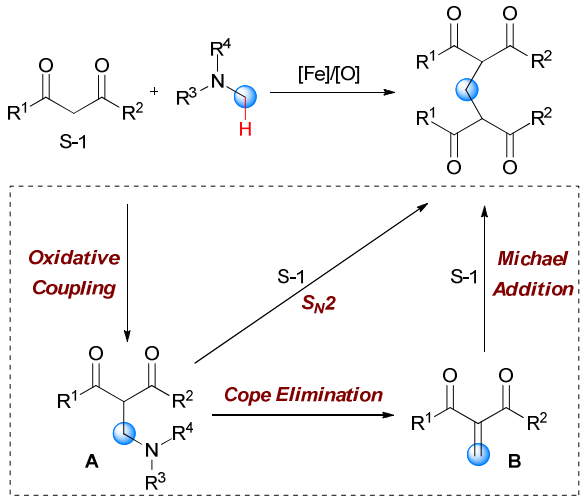
Scheme 8 Iron-catalyzed oxidative coupling reactions of 1,3-dicarbonyl compounds.

In Li's subsequent research, they reported an unprecedented dialkylation of the methylene group.[22] By using *N*,*N*-dimethylaniline as methylenic source and 2 equiv of 1,3-dicarbonyl compounds, the methylene-bridged bis-1,3-dicarbonyl compounds were smoothly constructed in high efficiency. The reaction condition optimization shows that $Fe_2(CO)_9$/TBHP was the best catalyst/oxidant combination (Scheme 9).



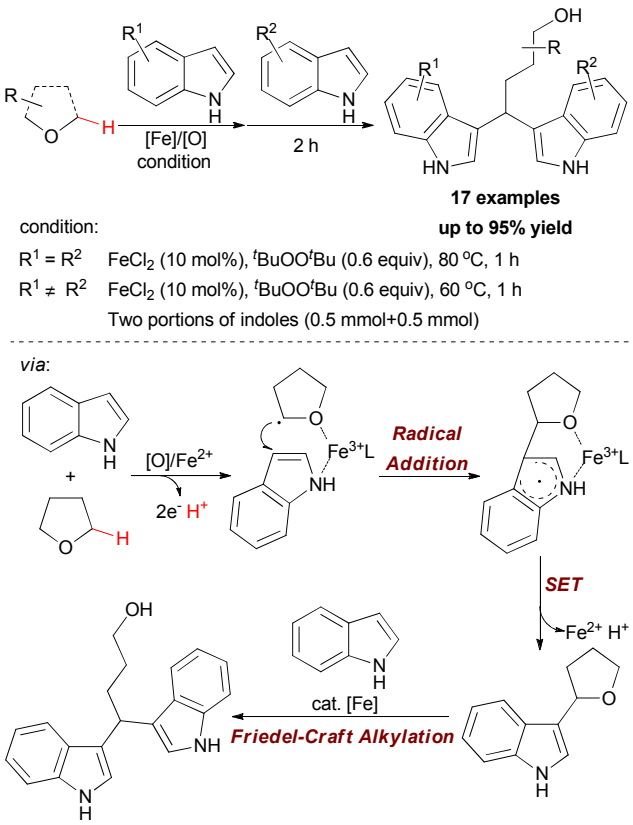
Scheme 9 Iron-catalyzed selective oxidation of *N*-methyl amines.

In Li's proposal, this oxidation reaction likely involves two different pathways (Scheme 10). Based on the previous work, the oxidative coupling intermediate A formed in $Fe_2(CO)_9$/TBHP system. A can undergo the direct S_N2 reaction attacked by the second molecular 1,3-dicarbonyl compound. Also, A may go the Cope elimination to give the intermediate B followed by the Michael addition to generate the final product. Notably, the authors found that the formation of formaldehyde in the present transformation by performing Nash test. This result gave the other potential mechanism which include the reaction between formaldehyde generated *in situ* and 1,3-dicarbonyl substrate. However, they could not fully exclude this pathway at that moment.



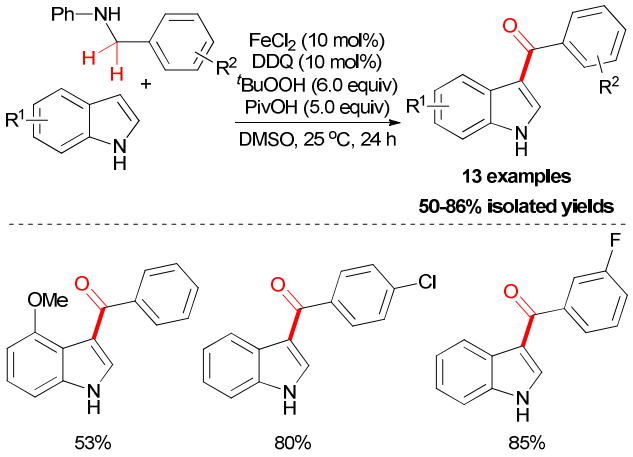
Scheme 10 Proposed pathways for iron-catalyzed selective oxidation of N-methyl amines.

Apart from using *N*,*N*-dimethylaniline as methylenic source, the sp^3 C-H bond adjacent to O-atom of ethers can also undergo oxidative coupling to link indoles. In 2009, Li and co-workers disclosed an one-pot synthetic protocol for constructing symmetric and unsymmetric 1,1-bis-indolylmethanes via tandem iron-catalyzed C-H bond oxidation and C-O bond cleavage (Scheme 11).[23]



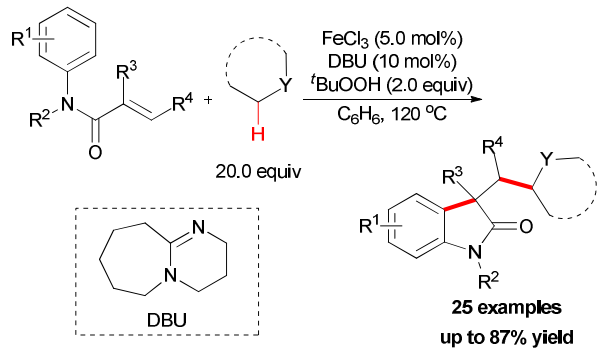
Scheme 11 Iron-catalyzed one-pot synthesis of symmetric and unsymmetric 1,1-bis-indolylmethanes via tandem C-H bond oxidation and C-O bond cleavage.

Amines are known to undergo the oxidations to form the iminium ion intermediate. However, this process could be utilized in acylation reaction of indoles. In 2011, Su and co-workers reported this kind of methodology.[24] In their research, anilines were used as carbonyl source to install benzoyl group onto 3-position of N-H free indoles through iron-catalyzed oxidative coupling. Under the optimized condition, several N-H free indoles could be acylated on 3-postion in moderate to good yields (Scheme 12) while the *N*-alkyl anilines failed in this reaction.

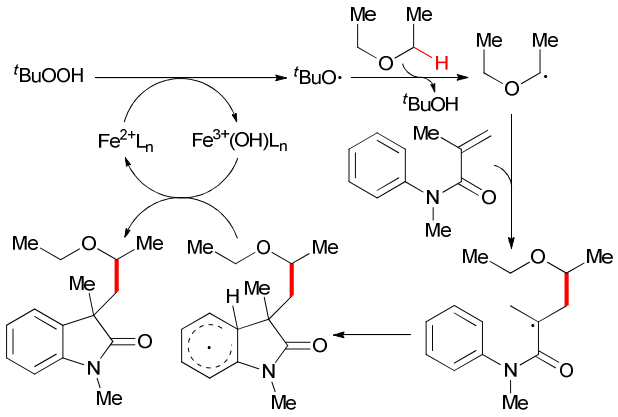


Scheme 12 $FeCl_2$-catalyzed acylation of N-H free indoles.

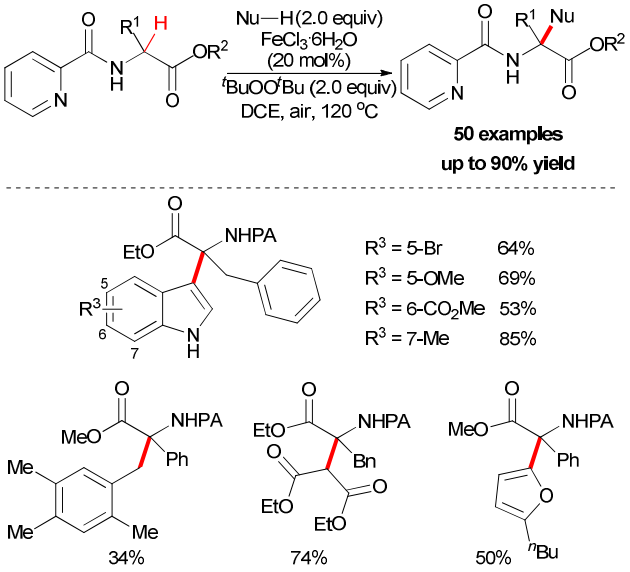
From 2009, several efficient methods have been developed to the synthesis of oxindoles through oxidative coupling.[25] Recently, Li and co-workers disclosed a novel $FeCl_3$-catalyzed oxidative 1,2-alkylarylation of acrylanilides initialled by sp^3 C-H bond homolytic cleavage in the presence of TBHP as oxidant (Scheme 13).[25a] Using this methodology, a series of 3-alkylated oxindoles was constructed. The authors also performed the control experiments and UV/Vis titration to explain the DBU as a ligand, not a base. But they cannot rule out that the alkalinity of DBU promotes the reaction. Through the designed controlled experiments and radical trapping reactions, a radical mechanism was proposed (Scheme 14).



Scheme 13 Iron-catalyzed oxidative 1,2-alkylarylation of activated alkenes.

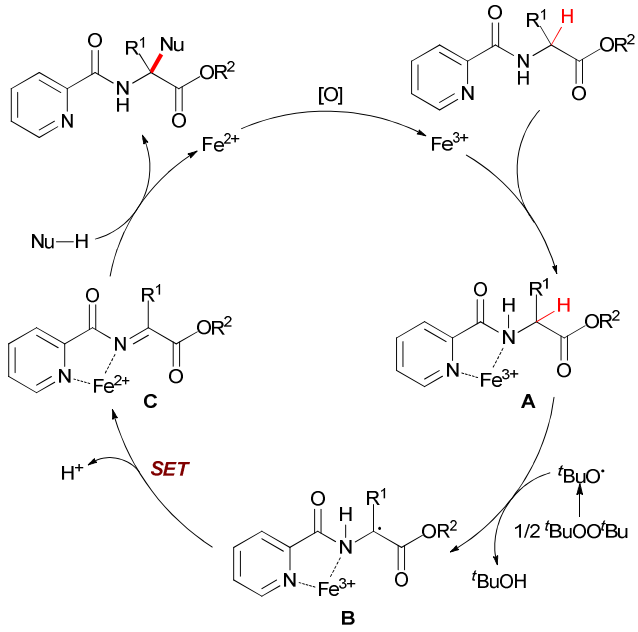


Scheme 14 Radical cyclization pathway for oxindole synthesis.



Scheme 15 Fe(III)-catalyzed oxidative functionalization of α-sp^3 C-H bonds of α-tertiary α-amino acid esters.

Very recently, You and co-workers reported an efficient route to furnish α-quaternary α-amino acid derivatives.[26] In this work, they used catalytic amount of $FeCl_3{\cdot}6H_2O$ and di-*tert*-butyl peroxide as oxidant. The oxidative sp^3 C-H bond coupling has exhibited a broad substrate scope for both α-amino acids and nucleophiles as well as good functional group tolerance (Scheme 15). When treated with 2,2,6,6-tetramethylpiperidine oxide (TEMPO) or 2,6-ditert-butyl-4-methylphenol (BHT), the coupling reaction of ethyl 3-phenyl-2-(picolinamido)propanoate with 1*H*-indole could be suppressed. Due to this experimental result, the authors proposed a possible mechanism involving a single-electron transfer process (Scheme 16).



Scheme 16 Possible mechanism of the α-sp^3 C-H bond functionalization of α-substituted α-amino acid esters.

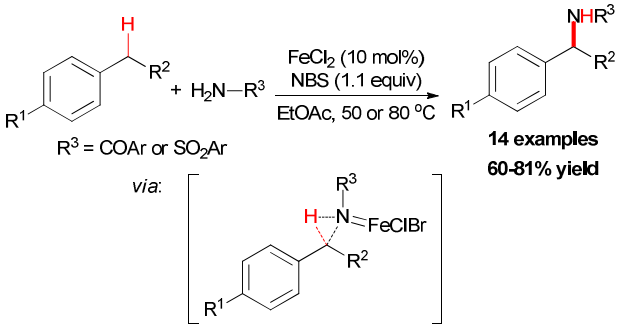
In their proposal (Scheme 16), 2-picolinamido α-tertiary amino acid ester coordinates with Fe^{III} to yield the intermediate A. Then the *tert*-butoxyl radical (*t*BuO·) which generated from di-*tert*-butyl peroxide (DTBP) abstracts the α-hydrogen atom of A to form the radical intermediate B. Next, the radical species B undergoes an intramolecular single-electron transfer (SET) process to give the α-ketimine intermediate C. Subsequently, the coordination of picolinamido group with Fe^{III} species activates the α-ketimine and facilitates the addition of nucleophile to intermediate C which results in releasing the desired α-quaternary α-amino acid ester product. The authors also performed the model reaction under N_2 atmosphere and the desired product generated in low yield (39% yield compared with 90% yield under the standard condition). This result indicated that the released Fe^{II} is reoxidized to Fe^{III} by air[27] as well as DTBP[28] to fulfill the catalytic cycle.

2.2 C-N Bond Formation

Oxidative C-H bond transformations to construct C-N bond are important processes to synthesis of nitrogen-containing compounds. In 1982, Breslow and Gellman reported the amidation of cyclohexane using PhI=NTs as a stoichiometric oxidant.[29] After their seminal report, many developed alternative nitrogen sources showed their utilities, such as chloramines-T,[30] bromamines-T,[31] and tosyloxycarbamates.[32] But the direct installation of nitrogen in oxidative C-H bond transformation process still remains challenge.

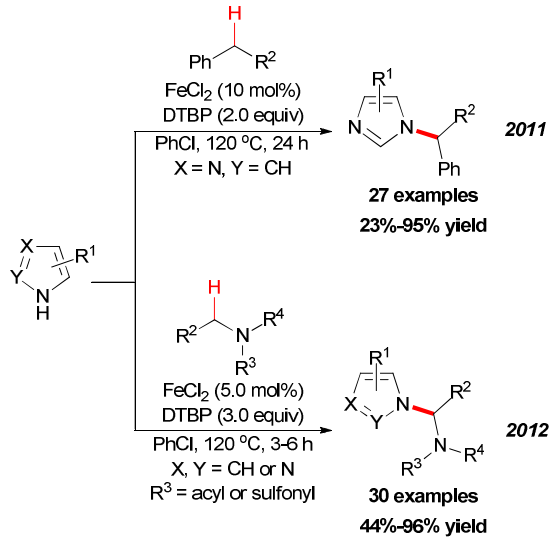
2.2.1 Benzylic sp^3 C-H Bond

In 2008, Fu and co-workers reported the first example of amidation of benzylic sp^3 C-H bonds by using an efficient, inexpensive and air-stable $FeCl_2$/NBS as catalyst/oxidant system.[33] Under the best reaction condition, series of the benzylic reagents underwent amidation reaction in reasonable yields (Scheme 17) utilizing carboxamides and sulphonamides as amidation reagents. The activity order of the benzylic reagents is diphenylmethane > ethylbenzene > 4-bromoethylbenzene.



Scheme 17 Iron-catalyzed benzylic sp^3 C-H bond amidation.

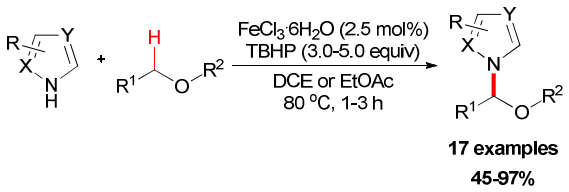
In 2011, Chen and Qiu reported a direct C-N coupling method between imidazoles and benzylic compounds through iron-catalyzed oxidative transformation of sp^3 C-H bonds (Scheme 18, top).[34] The reaction utilized the inexpensive $FeCl_2$/DTBP combination which is suitable for the oxidative coupling of a serious of benzylic sp^3 C-H bonds with imidazoles. In Chen's subsequent research, they extended their strategy into *N*-alkylation of azoles via oxidative cleavage of a sp^3 C-H bond adjacent to *N*-atom in amides and sulphonamides (Scheme 18, bottom).[35] Under the optimized condition, a wide range of amides and sulphonamides could be used as substrate for *N*-alkylation of azoles.



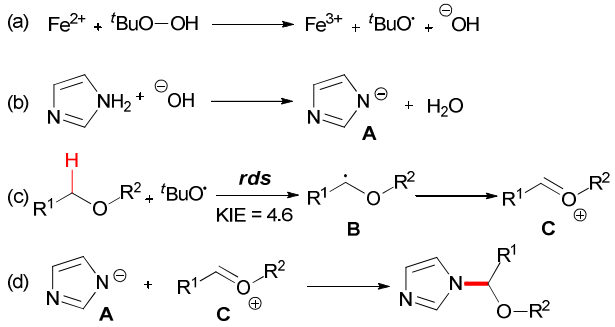
Scheme 18 Iron-catalyzed sp^3 C-H bond oxidation and C-N bond formation.

2.2.2 sp^3 C-H Bond Adjacent to Heteroatom

In 2010, Li and co-workers reported an iron-catalyzed *N*-alkylation of azoles via oxidation of a sp^3 C-H bond adjacent to oxygen atom (Scheme 19).[36] This methodology extended their previous work from C-C bond formation to C-N bond formation. The latter process is one of the valuable goals for the preparation of various nitrogen-containing compounds.



Scheme 19 Iron-catalyzed *N*-alkylation of azoles.



Scheme 20 Plausible pathways for the iron-catalyzed *N*-alkylation of azoles.

The proposed mechanism (Scheme 20) showed that TBHP decomposed into *tert*-butoxyl radical and hydroxyl anion in the presence of the ferrous catalyst (step a). Deprotonation of azole gave the anion species A (step b). On the other side, a hydrogen abstraction of C-H bond adjacent to an oxygen atom afforded B,

which could be trapped by TEMPO, and followed by ferric oxidation to generate oxonium ion C (step c). Finally, the nucleophilic addition of A to C provided the desired coupling product (step d). Overall, the Fe^{2+}-Fe^{3+} redox process played a key role in the present C-N bond formation reaction, which were the reductive heterolytic cleavage of O-O bond in the peroxide (step a) and the oxidation of the carbon-centered radical to oxonium (step c).

2.3 C-O Bond Formation

The direct oxygenation of sp^3 C-H bonds presents a powerful approach to alcohol products,[1] which is one of the most important organic synthetic intermediates.

2.3.1 Unactivated sp^3 C-H Bonds

Due to the catalytic properties of metal catalysis, the two mechanisms for the direct oxygenation of alkanes are labelled as 'organometallic' and 'coordination' ways.[37] Iron, as an aged metal in alkane oxidations, its catalytic pattern is often considered as 'coordination' way.[37,38]

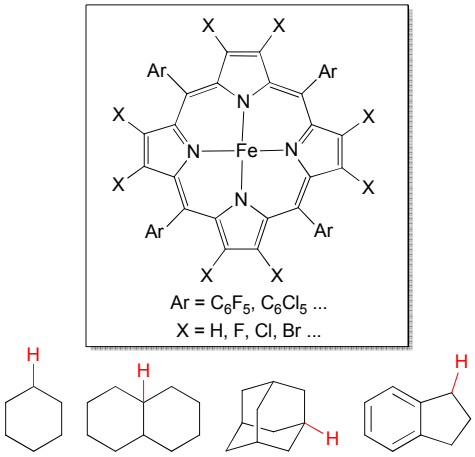


Figure 3 General structures for porphyrin-based iron catalyst and benchmark substrates for direct oxygenation of sp^3 C-H bonds.

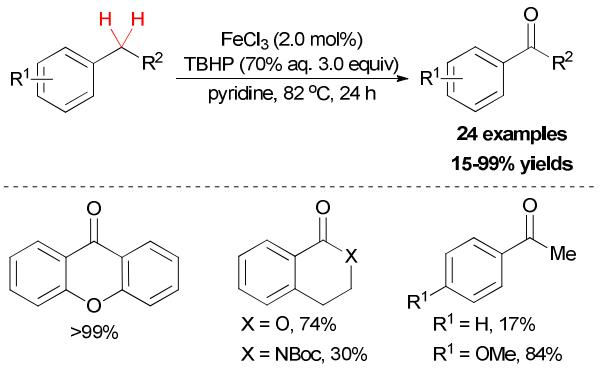
As a chemical model for cytochrome P450 mono-oxygenase,[39] porphyrin-based iron catalysts show their powerful utilities in aliphatic C-H bond oxidations (Figure 3). This oxidation chemistry has been broadly reviewed.[38,40] In contrast, iron-based non-heme complexes also have been developed for alkane hydroxylations, but the mechanism of such reactions remains debate.

In 1983, Barton introduced a particular type of aliphatic oxidation reaction using iron catalyst (termed as Gif chemistry). After that, large numbers of studies focus on elucidating mechanistic and kinetic details rather than on using the concept for synthetic applications.[41] Moreover, Gif chemistry also provoked a long-term mechanistic controversy.

In synthetic field, the White group did a series of contributions on aliphatic C-H bond oxidations.[42]

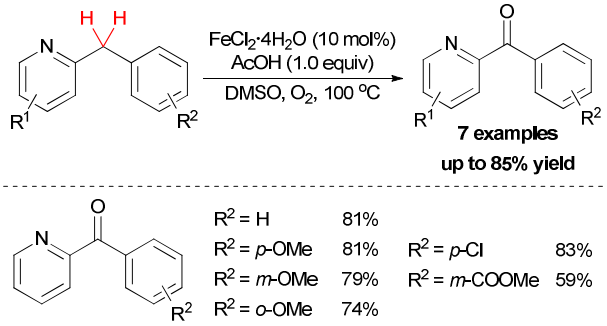
2.3.2 Activated sp^3 C-H Bonds

Recently, C-H bond oxidation/oxygenation has had a breakthrough. In 2007, Bolm and co-workers reported an alternative oxidation method, which using a small amount of $FeCl_3$ (2 mol%) catalyzed benzylic oxidations with *tert*-butyl hydroperoxide (TBHP, 70% in water) as cheap and convenient oxidant in pyridine (Scheme 21).[43] Under the optimized conditions, various benzyl compounds were subjected and the corresponding carbonyl products were formed in good to excellent yields.



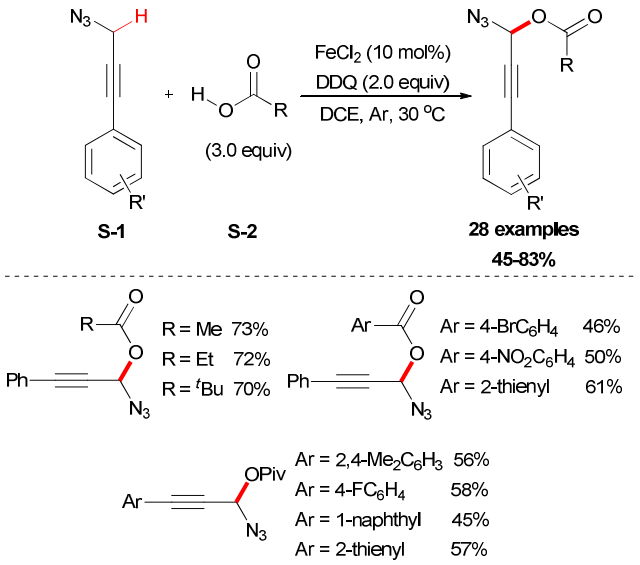
Scheme 21 Iron-catalyzed benzylic oxidation with aqueous *tert*-butyl hydroperoxide.

Except for using hydroperoxide as oxidant in sp^3 C-H bond oxidation/oxygenation, dioxygen could also act as terminal oxidant in such kind of reactions. In 2012, Maes and co-workers developed a sustainable oxidation method for synthesis of aryl(di)azinyl ketones.[44] After condition's optimization, $FeCl_2{\cdot}4H_2O$ shows the best catalytic property among other simple iron salts. Under the best condition, serious substrates which bearing both electron-donating and electron-withdrawing groups could be oxidized to corresponding ketone in moderate to good yields (Scheme 22).



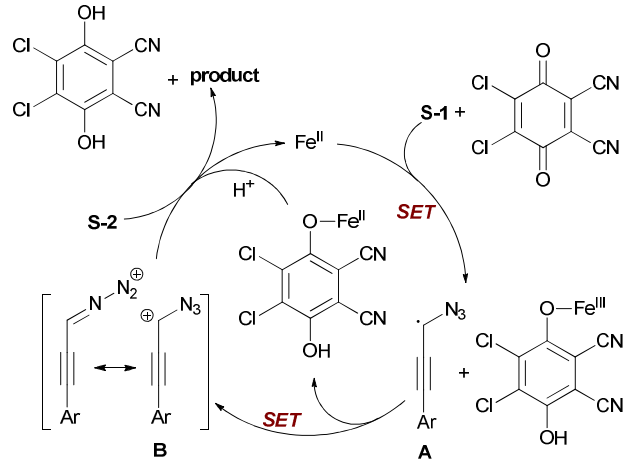
Scheme 22 Oxidation of the methylene group of aryl(di)azinyl-methanes.

Except for using environmental unfriendly organic solvents, water used as reaction media became an attractive topic in green chemistry.[45] Recently, Novák and co-workers reported a benzylic oxidation in water.[46] They used solution of sodium dodecylsulphate (SDS) to build up the iron-surfactant nanocomposite catalytic system. Simple iron(III) salts ($Fe_2(SO_4)_3$ and $FeCl_3$) were used as catalyst source and aqueous TBHP (70 wt% aq.) as cheap oxidant. Under the optimized reaction condition, a series of benzylic compounds were smoothly transformed to ketons (30 examples, 21-99% yield).



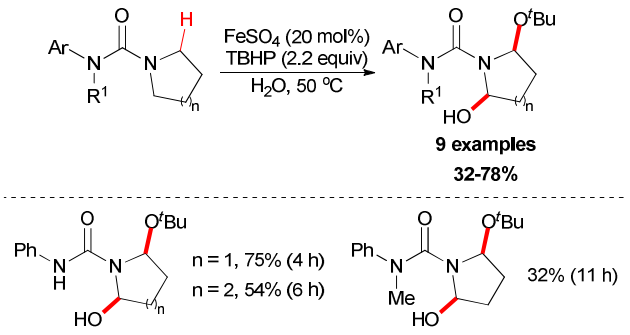
Scheme 23 Iron-facilitated oxidative dehydrogenative C-O bond formation.

In 2012, Jiao group reported an iron-facilitated oxidative dehydrogenative C-O bond formation reaction.[47] They used aryl propargyl azides as substrates which generated *in situ* followed the oxidative coupling with carboxylic acids (Scheme 23). Iron salts showed their activities and $FeCl_2$ was the most effective catalyst. The oxidative coupling reaction performed smoothly using DDQ as oxidant in DCE solvent (28 examples, up to 83% yield). Attempting to use other oxidants and solvents were not successful. This methodology also showed its useful synthetic applications, as the reaction products are useful synthons for a wide range of synthetic targets such as 4,5-disubstituted-1,2,3-triazoles, 3-alkoxyenals, and benzotriazoles.



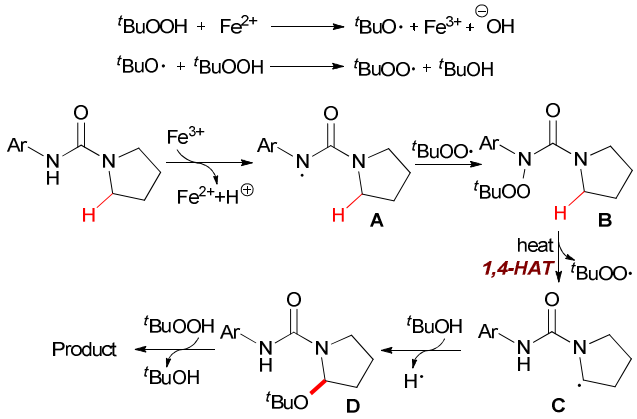
Scheme 24 Proposed mechanism of iron-catalyzed oxidative dehydrogenative C-O bond formation.

The authors proposed a tentative mechanism showing in Scheme 24. Initially, substrate S-1 undergoes the hydrogen abstraction through an iron-facilitated single-electron transfer (SET) with DDQ to form the radical species A, which may be stabilized by the azido group. Then the radical species A was further oxidized to give the aryl propargyl cation B. Next, nucleophilic attack of cation B by carboxylic acid (S-2) gave the desired product with the regeneration of the catalyst.

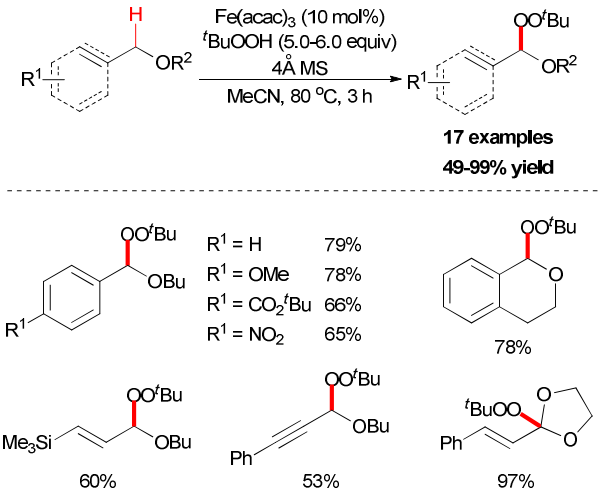


Scheme 25 Iron-catalyzed oxidation of sp^3 C-H bonds adjacent to a nitrogen atom of unprotected arylureas.

Instead of the C-C and C-N bond formation through an oxidative transformation of a C-H bond adjacent to heteroatom. In 2011, Liang and co-workers reported a C-O bond formation by iron(II)-catalyzed oxidation of sp^3 C-H bonds adjacent to a nitrogen atom of unprotected arylureas with *tert*-butyl hydroperoxide (TBHP) in water (Scheme 25).[48] The authors separated and identified an *N*-*tert*-butylperoxylated intermediate B under the standard reaction condition, which indicated that peroxyl radical could react with aminyl radical derived from the oxidation of the arylurea. The elimination of the *tert*-butylperoxy radical generated a new carbon-centered radical C via 1,4-hydrogen atom transfer (1,4-HAT),[49] which was trapped by *tert*-butanol to give a α-*tert*-butoxylated urea D and regenerated TBHP. Finally, a hydroxyl group was introduced to the other α-position of D via hydrogen abstraction by TBHP and released the final product (Scheme 26).

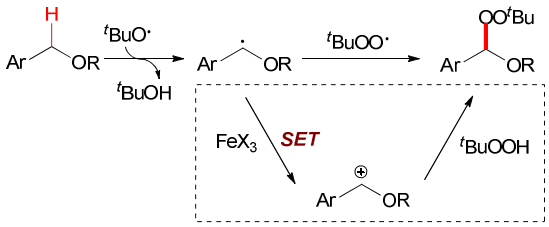


Scheme 26 Proposed mechanism for iron-catalyzed oxidation of sp^3 C-H bonds adjacent to a nitrogen atom.



Scheme 27 Synthesis of *tert*-butyl peroxyacetals via iron-catalyzed sp^3 C-H bond oxidative functionalization.

In 2012, Urabe and co-workers reported an iron-promoted C-H bond oxygation reaction for the synthesis of *tert*-butyl peroxyacetals. Under the optimized condition, series of *tert*-butyl peroxyacetals were synthesized in good to excellent yields (Scheme 27).[50] Mechanistically, the authors proposed two possible pathways to explain the formation of *tert*-butyl peroxyacetals (Scheme 28). The initiation step generated *tert*-butyl peroxy radical may start efficiently in the presence of Fe catalyst. Then the peroxy radical abstracted a hydrogen atom on ether substrate to form the benzyl radical. This benzyl radical could go through two pathways to form the final product.



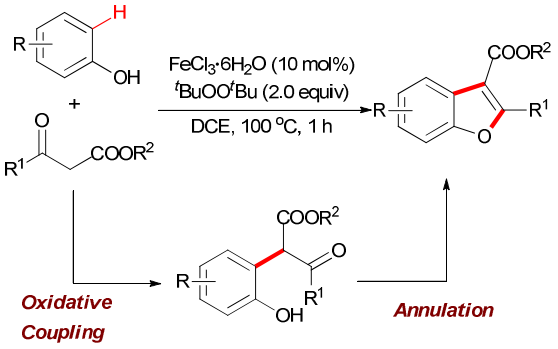
Scheme 28 Nucleophilic attack and radical coupling pathways.

3 Oxidative Transformations of sp^2 C-H Bonds

3.1 C-C Bond Formation

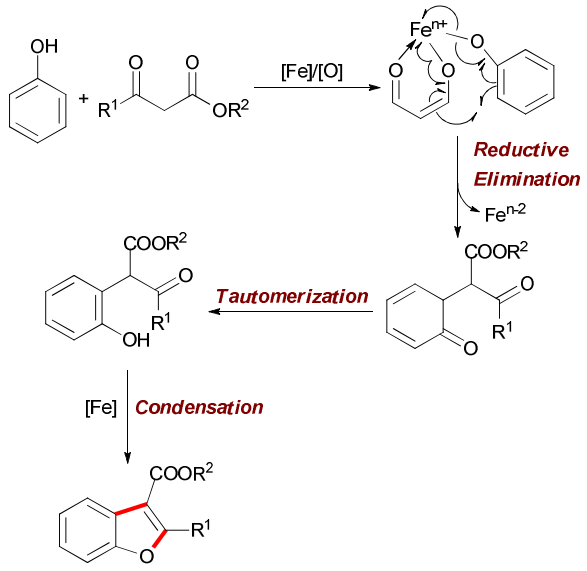
3.1.1 sp^2 C-H Bond of Phenols

In 2009, Li and co-workers reported an unprecedented methodology for the construction of polysubstituted benzofurans through iron-catalyzed tandem oxidative couping and annulation between phenols and β-keto esters (Scheme 29).[51] In this reaction, various iron salts were tested and the results showed there were no significant effects in efficiency of the reaction. It noteworthy the water in iron catalyst is essential for the present reaction and adding 4Å molecular sieve can dramatically stop the reaction. Mechanistically, the authors proposed a tentative mechanism of the iron-catalyzed oxidative reaction of phenols and β-keto esters (Scheme 30).

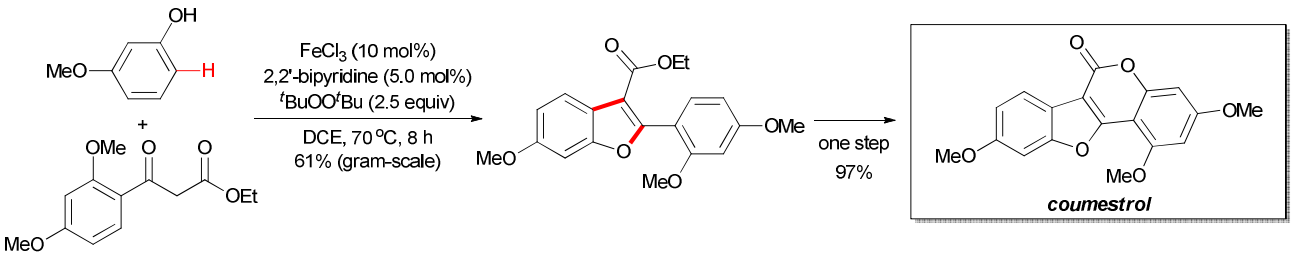


Scheme 29 Iron-catalyzed tandem oxidative couping and annulation to construct polysubstituted benzofurans.

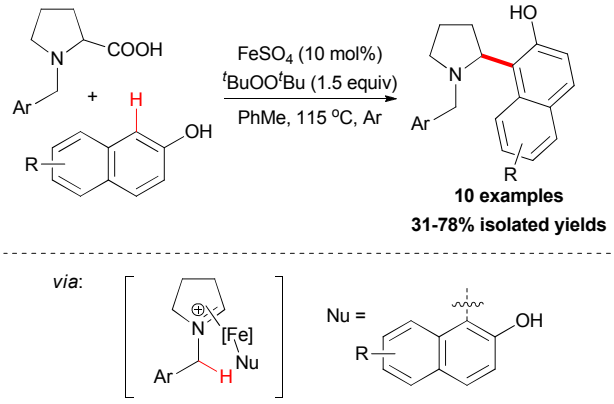
The above methodology presented an efficient approach to synthesis polysubstituted benzofuran. Such kind of heterocyclic motifs are important structural units and widely found in biological and medical compounds. Recently, Pappo and co-workers applied this concept in the total synthesis of coumestrol.[52] Based on their previous work[53] and the Li group's pioneering work,[51] the oxidative coupling reaction occurred successfully by using ethyl 2-(2,4-dimethoxybenzoyl)acetate and 3-methoxyphenol under the modified reaction condition. The desired benzofuran was obtained in 61% yield (gram-scale yield). The transformation of benzofuran to coumestrol was carried out by using one-pot protocol and the natural product was smoothly constructed. Notably, the present method for total synthesis of coumestrol can scale-up in 10 mmol and 59% overall yield was achieved in only two steps (Scheme 31).



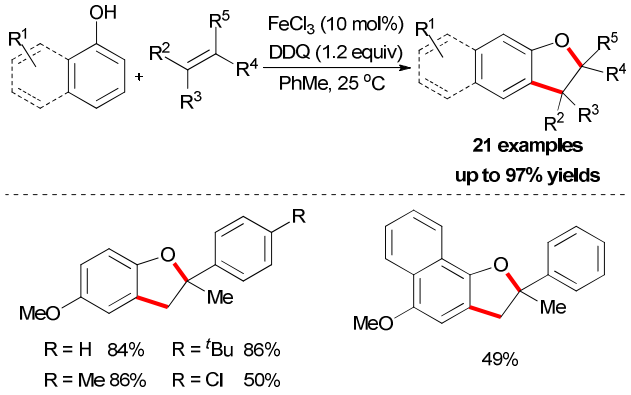
Scheme 30 Tentative mechanism of the iron-catalyzed oxidative reaction of phenols and β-keto esters.



Scheme 31 Total synthesis of coumestrol via oxidative coupling between phenol and β-keto ester.



Scheme 32 Iron-catalyzed decarboxylative coupling of proline derivatives with β-naphthols.



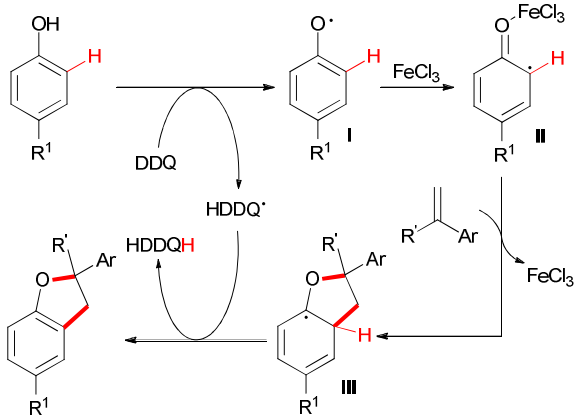
Scheme 33 Iron-catalyzed oxidative radical cross coupling-cyclization between phenols and olefins.

The sp^2 carbon adjacent to OH group in β-naphthols could also act as nucleophile in decarboxylative coupling reaction. In 2009, Li and co-workers disclosed the first example of iron-catalyzed intermolecular decarboxylative coupling reaction.[54] Proline derivatives and β-naphthols could couple smoothly under the developed reaction condition (Scheme 32). The tentative mechanism showed that the iron-coordinated imine ion was the key intermediate in coupling process, which then attacked by β-naphthol followed by releasing coupling product.

Decarboxylative couplings have recently emerged as a promising concept for bond formation reactions.[55] However, such an area using simple and easily handed iron salts as catalyst still undeveloped. As such, iron-based catalysts might play a role in future studies on decarboxylative chemistry.

The sp^2 C-H bonds which located in aromatic ring of phenol and catechol derivatives are known to undergo the oxidation reactions by using simple iron salts, especially $FeCl_3$.[13i] This kind of reaction usually generates the homo-coupled products, higher-molecular-weight polymers or C,O-connected phenol portions undesirably. However, such traditional process could be altered when olefins and external oxidants were introduced into reaction. Recently, Lei and co-workers reported a novel $FeCl_3$-catalyzed oxidative coupling reaction of phenols and olefins.[56] Under the optimized conditions, the highly selective oxidative coupling/cyclization reaction occurred at room temperature (Scheme 33).

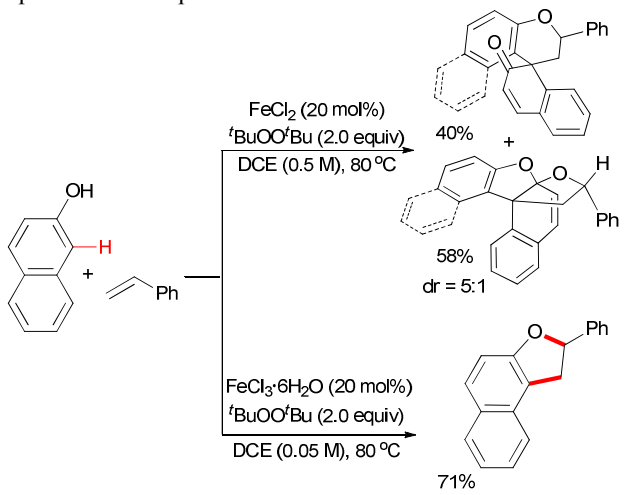
Based on the radical trapping experiment, EPR and operando IR studies, the authors proposed a radical pathway (Scheme 34). First, DDQ oxidized phenol to generate the corresponding phenol radical **I**.[57] As a Lewis acid, $FeCl_3$ was more likely to coordinate with O-atom which could stabilize the resonance structure of the phenol as well increased the activity of the radical **II** to react with alkenes. The resulting radical **III**[58] underwent the H-atom abstraction by HDDQ radical to form the final product.



Scheme 34 Proposed mechanism for synthesis dihydrobenzofuran.

Meantime, Pappo and co-workers disclosed another strategy to construct 2,3-dihydrobenzofuran motif (Scheme 35).[59] The present reaction is sensitive to both the iron source and the reaction concentration. By utilizing $FeCl_2$ as catalyst, the tandem coupling reaction occurred. However, when $FeCl_3 \cdot 6H_2O$ was used as catalyst under the diluted solution, the desired 2,3-dihydrobenzofuran formed. The former result could

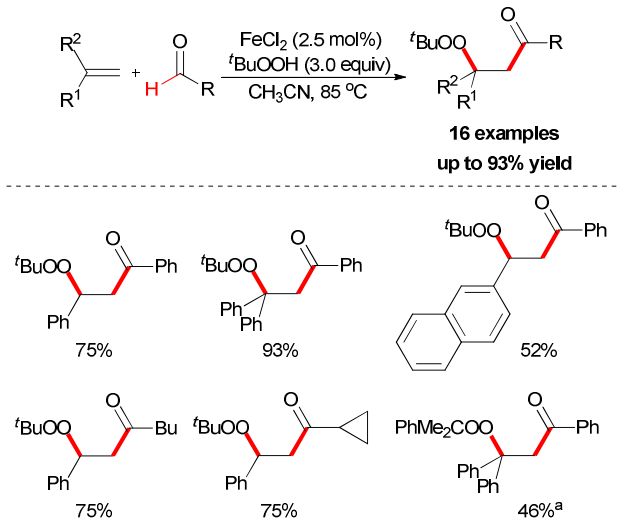
be explained by the formation of BINOL via homo-coupling of 2-naphthol followed by a rapid oxidative/addition dearomatization reaction with styrene under the same condition. Using anhydrous $FeCl_3$ (20 mol%) as catalyst, the furan product was isolated in low yield, which indicated water might play a role in the proton transfer process of the reaction.[51]



Scheme 35 Iron-catalyzed oxidative cross-coupling of phenols and alkenes.

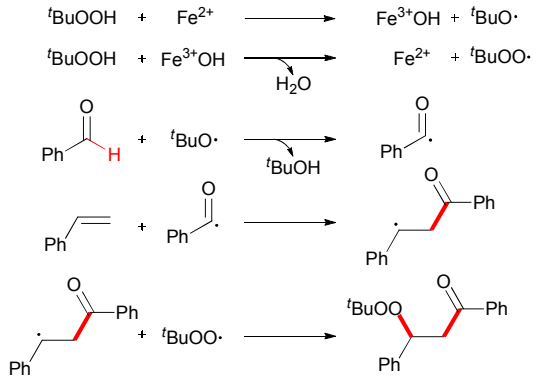
3.1.2 Aldehyde C(O)-H Bond

In 2011, Li and co-workers reported a novel and practical protocol of iron-catalyzed carbonylation-peroxidation of alkenes.[60] A series of β-peroxy ketones were selectively and efficiently constructed by the three-component reaction of alkenes, aldehydes, and hydroperoxide (Scheme 36).



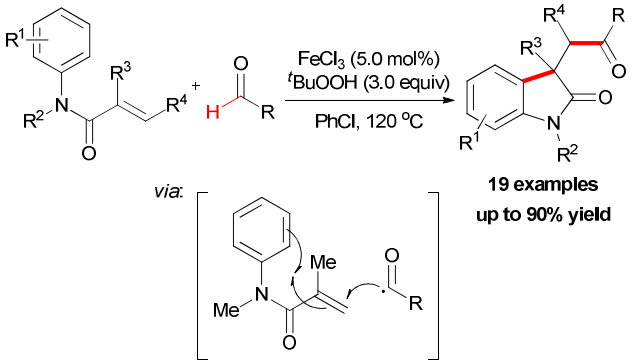
Scheme 36 Iron-catalyzed carbonylation-peroxidation of alkenes. [a.] Using $PhMe_2COOH$ instead of TBHP as oxidant.

When TEMPO was introduced into the reaction, the formation of β-peroxy ketone product was completely suppressed while the TEMPO-adduct aldehyde was isolated in quantitative yield. This experimental result indicated that acyl radical[61] was generated under the standard conditions while the reaction is unlikely involved cationic pathway.[62] Scheme 37 showed a tentative pathway for iron-catalyzed carbonylation-peroxidation reaction. Alkyloxy and alkylperoxy radicals were generated from $FeCl_2$/TBHP system, and followed by the hydrogen abstraction by oxyl radical via sp^2 C-H bond homolytic cleavage. The final β-peroxy ketone product was formed after radical addition and then the radical coupling reaction. In the subsequent research, Li and co-workers expended this concept to the synthesis of α-ester-β-keto peroxides.[63]



Scheme 37 A proposed mechanism for iron-catalyzed carbonylation-peroxidation.

Recently, after reporting of carbonylation-peroxidation of alkenes, Li and co-workers disclosed an iron-catalyzed carbonylation-arylation of activated alkenes (Scheme 38).[64] Although a 68% yield of desired product was obtained in the absence of a catalyst,[25j] using $FeCl_3$ as catalyst is beneficial to the efficiency of the reaction. However, other metal salts (such as $CuCl_2$ and $CoCl_2$) showed the low catalytic ability. Alkene substrates bearing alkyl, aryl protecting groups on the nitrogen were excellent for this transformation, and both α-substituted olefins and internal olefins were compatible with the reaction conditions. Many aldehyde substrates could be abstracted a hydrogen atom by oxy radical initialled with the combination of $FeCl_3$/TBHP system via sp^2 C-H bond homolytic cleavage. The resulting acyl radical, which is nucleophilic in nature, is known to add more easily to electron-deficient alkenes than normal alkenes.[65] Then the generated radical underwent an intramolecular 5-*exo*-trig cyclization[66] and followed by the oxidation step to form the final oxindole.

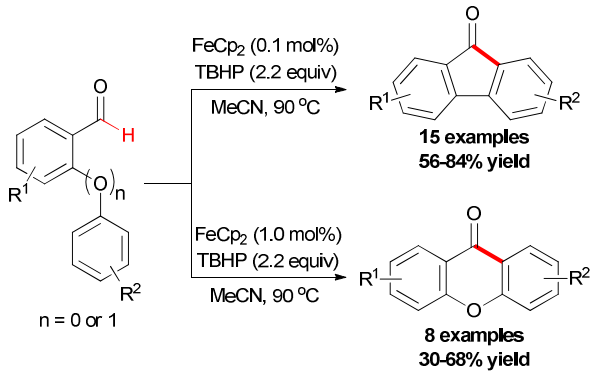


Scheme 38 Iron-catalyzed carboylation-arylation of alkenes.

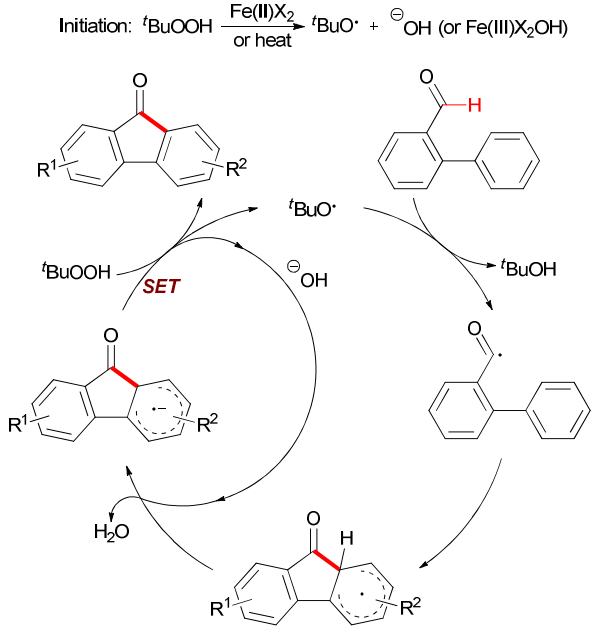
Recently, the Studer group reported a synthetic methodology for constructing fluorenones and xanthones (Scheme 39).[67] The condition screening indicated that $FeCp_2$ was the best radical initiator and *tert*-butyl peroxide was the most efficient oxidant.

Under the developed conditions, various readily available *ortho*-formyl biphenyls and *ortho*-formyl biphenylethers were tested. In contrast, radical chains were shorter and a higher iron salt loading was necessary in the fluorenone synthesis. Therefore, lower yields were achieved.

Mechanistically, the author proposed a base promoted homolytic aromatic substitution (BHAS) pathway (Scheme 40).[68] Initiation occured by reducing TBHP with Fe(II) to generate the *tert*-butoxyl radical and Fe(III) complex. The *tert*-butoxyl radical underwent the hydrogen atom abstraction from the aldehyde to give the acyl radical, which then attacked the arene to form the cyclohexadienyl radical. Deprotonation with the basic hydroxide anion resulted in forming the biaryl radical anion. Then this radical anion reduced TBHP by single-electron transfer (SET) to give the final product and *tert*-butoxyl radical which underwent the next radical chain reaction.

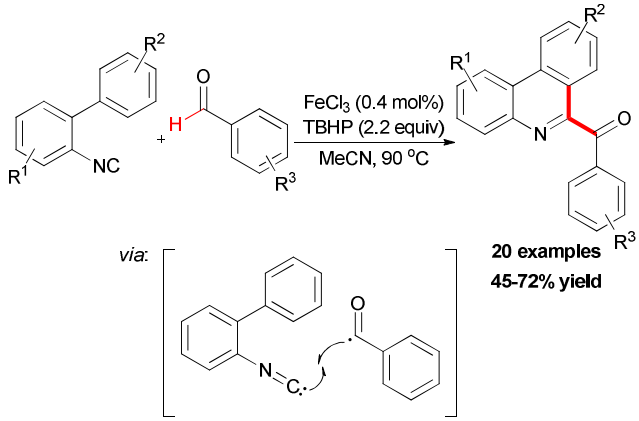


Scheme 39 Iron-catalyzed CDC reaction via base promoted homolytic aromatic substitution (BHAS).



Shcme 40 Suggested mechanism for BHAS reaction.

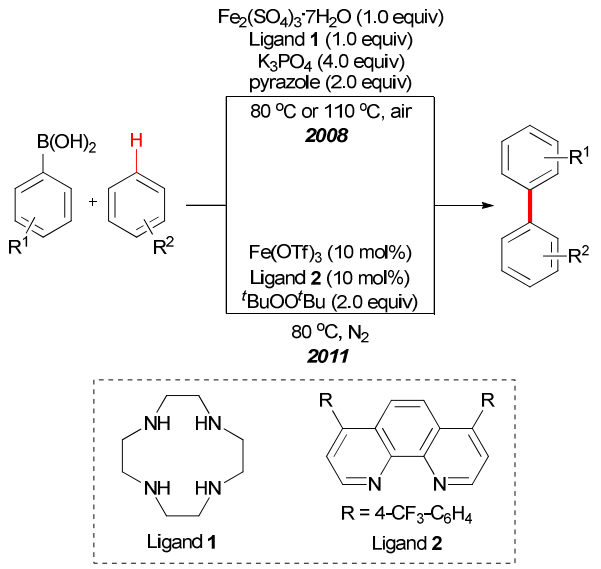
In Studer's subsequent research, they applied this BHAS concept in constructing 6-aroylated phenanthridines (Scheme 41).[69] Readily available 2-isocyanobiphenyls and aromatic aldehydes were used as substrates. By introducing small amounts of ferric chloride as radical initiator and TBHP as efficient oxidant, series of 6-aroylated phenanthridines were smoothly constructed through the radical cascade reaction. In radical initiation step, the Fe(III) chloride was first reduced to Fe(II) chloride through ligand exchange to give $FeCl_2OO^tBu$ species. This iron-peroxyl intermediate underwent the homolytic Fe-O bond cleavage to form $FeCl_2$ and the *tert*-peroxyl radical which could also abstract H-atom from aldehydes. It is known that aliphatic acyl radical can undergo the decarbonylation reaction to generate alkyl radical. Interestingly, when valeraldehyde was used as acyl radical precursor in this reaction, no 6-butylphenanthridine product was observed and target product formed in relative low yield (39%). However, when cyclohexanecarbaldehyde was introduced as substrate, the decarbonylated 6-cyclohexylphenanthridine was observed alone with the 6-acylated product (44% combined yield, ratio 57:43).



Scheme 41 Synthesis of 6-aroylated phenanthridines via BHAS.

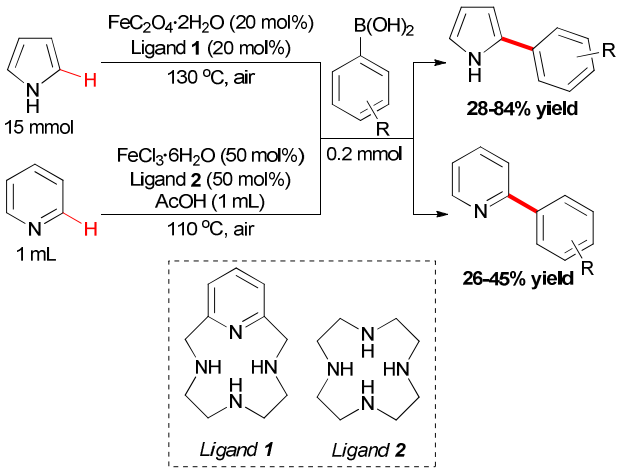
3.1.3 sp^2 C-H Bond of Arenes and Heteroarenes

In 2008, Yu and co-workers reported an important method for iron-mediated direct arylation of unactivated arenes with arylboronic acids.[70] Under the developed conditions, various arylboronic acids can coupling with arenes in moderate to good yield (Scheme 42, top). Mechanism studies indicated that the oxygen in air act as sacrificial oxidant for the reaction and no radical species involved in the coupling process. Although the C-H bond cleavage is the rate-determining step, the detailed mechanism is still unknown. Later on, Shirakawa, Hayashi and co-workers disclosed an alternative method for constructing biaryls.[71] In this reaction, they established that $Fe(OTf)_3$ coordinated with ligand **2** (phenanthroline, Scheme 42, bottom) catalyzed the oxidative coupling of arylboronic acids with arenes via homolytic aromatic substitution (HAS) mechanism. Under the optimized condition, various arylboronic acids could couple with benzene derivatives in moderate to good yields.

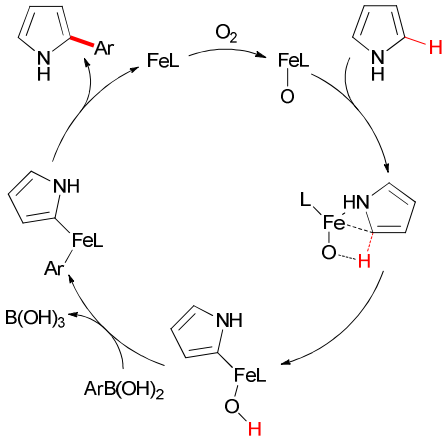


Scheme 42 Iron-mediated/catalyzed direct arylation of unactivated arenes.

In Yu's subsequent research, they extended their study by utilizing electron-rich and electron-deficient heteroarenes (pyrrole and pyridine) as substrates.[72] Coupling reactions could successfully occur with the arylboronic acids as coupling partners and combining $FeC_2O_4{\cdot}2H_2O$/MCPA ligand as catalytic system (Scheme 43). When pyrroles used as substrates, the amounts of iron catalyst could be decreased to 20 mol% by employing O_2 as indispensable oxidant. It worth noted that the arylation selectively occurred at the C2 position of pyrroles.



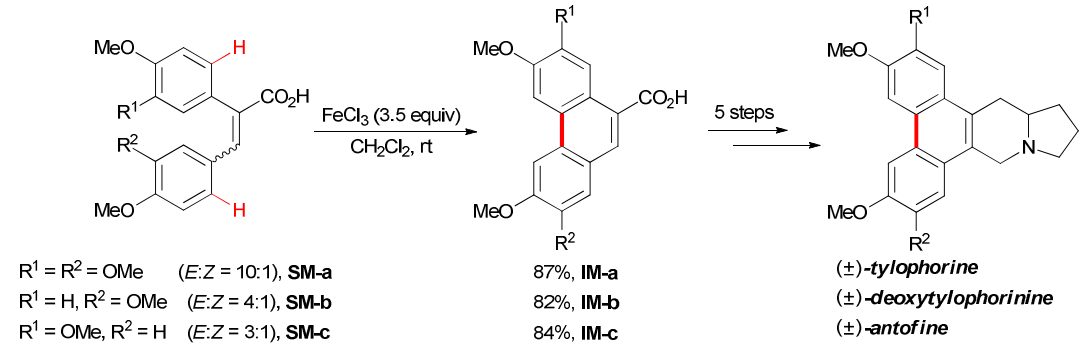
Scheme 43 Iron-catalyzed *ortho*-arylation of pyrrole and pyridine.



Scheme 44 Proposed catalytic cycle of the iron-catalyzed direct Suzuki-Miyaura coupling. (L = ligand).

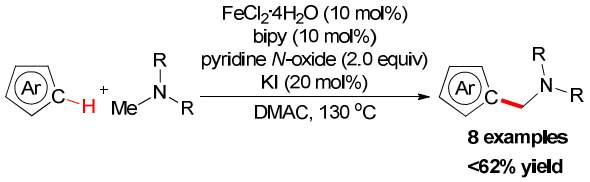
Mechanistically, the authors proposed that the oxoiron complex might be the active species in the present reaction. And DFT calculations indicated the C-H activation through σ-bond metathesis. The full catalytic cycle was showed in Scheme 44.

In 2008, Wang and co-workers reported an iron-mediated oxidative cyclization for the total synthesis of (±)-antofine, (±)-deoxytylophorinine and (±)-antofine.[73] Using a mixture of *E* and *Z* isomers SM-a, SM-b and SM-c as starting materials to undergo the oxidative coupling by utilizing 3.5 equiv of $FeCl_3$, the desired phenanthrene products were smoothly synthesized (Scheme 45). In authors' later report, they proposed a tentative mechanism involved a radical initiation and heterolytic cleavage of sp^2 C-H bond on phenyl ring.[74]



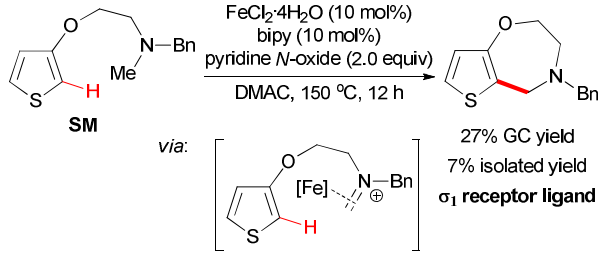
Scheme 45 Total syntheses of (±)-antofine, (±)-deoxytylophorinine and (±)-antofine via oxidative phenolic coupling.

In 2009, Itami group and Wünsh group reported an iron-catalyzed oxidative coupling of heteroarenes with methyl-amines by using Fe(II) as catalyst and pyridine *N*-oxide as oxidant.[75] The oxidative coupling reaction could be used for the intermolecular coupling of thiophenes, furans, and indoles with methylamines (Scheme 46). Although the detailed mechanism was still unknown, the authors proposed a tentative mechanism involving the iron-bound iminium species which could undergo electrophilic substitution on the thiophene moiety (Scheme 47).[11a]



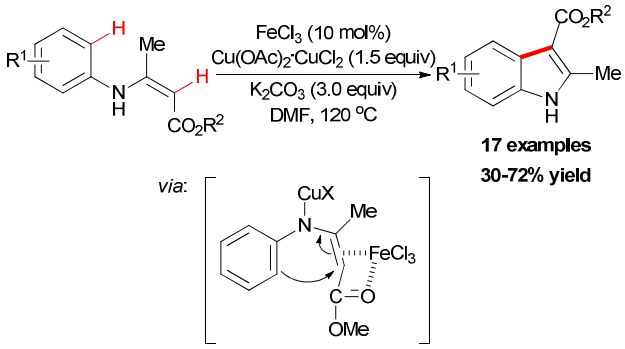
Scheme 46 Iron-catalyzed oxidative coupling of heteroarenes and methylamines.

When intramolecular oxidative coupling was performed using thiophene SM as substrate, the benzazepine-like bicyclic nitrogen heterocycle was formed, albeit in low yield (Scheme 47). The authors also identified the coupling product has a good binding affinity toward the σ_1 receptor protein. The difficulty of cyclizing seven member rings may be one of the reasons for the low efficiency.



Scheme 47 Intramolecular oxidative coupling for constructing new σ_1-receptor ligand.

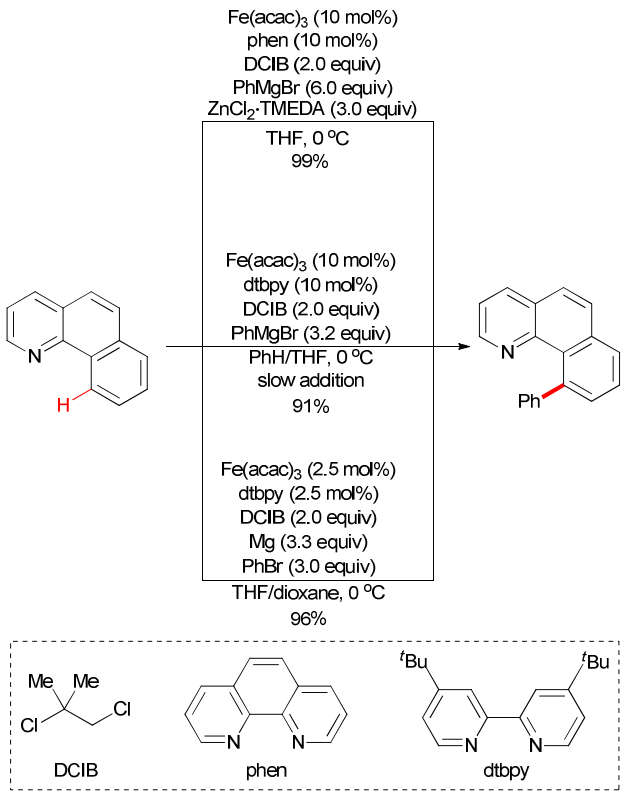
In 2010, Liang and co-workers reported an iron catalyzed direct intramolecular oxidative coupling reaction for the synthesis of indoles (Scheme 48).[76] In their studies, the best catalyst was $FeCl_3$ and the highly active $Cu(OAc)_2{\cdot}CuCl_2$ was used as oxidant.



Scheme 48 $FeCl_3$-catalyzed direct oxidative coupling for the preparation of indoles.

Direct arylation of aryl C-H bonds are not limit at using arylboronic acids as coupling partners. In recent years, iron-catalyzed direct arylation of aryl C-H bond with organometallic reagents was developed (Scheme 49). The Nakamura group did a lot of contributions in such an area.[77] In 2008, they reported the first iron-catalyzed direct arylation of aryl C-H bond (Scheme 49, top).[77k] In the initial study, they used organozinc reagents generated *in situ* from aryl Grignard reagents and $ZnCl_2$ in the presence of the proper ligand. The extensive optimizations showed that $Fe(acac)_3$/phen/DCIB was the best catalytic system. In this reaction, substrate arene displaying Lewis-basic directing group could be regioselectively functionalized at remarkably low reaction temperatures through chelation control. It is noteworthy that the proper ligand was essential for this coupling reaction and the oxidant dihalide was converted to the corresponding olefin.

Obviously, the above reaction has an unattractive feature, that is, it requires the use of large amounts of the zinc salt (3 equiv) and the aryl Grignard reagent (6 equiv) for the *in situ* generation of the reactive arylzinc reagent. In Nakamura's subsequent research, they successfully overcome this disadvantage. The key elements of the development were the use of an aromatic co-solvent, such as chlorobenzene and benzene, and the slow addition of the Grignard reagent (Scheme 49, middle).[77f]



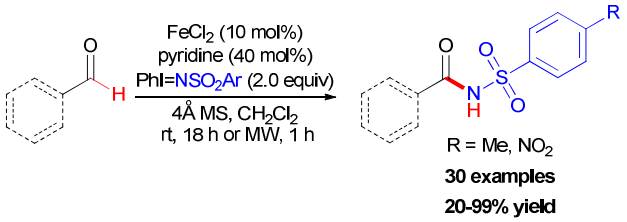
Scheme 49 Iron-catalyzed direct phenylation of α-benzoquinoline through directed C-H bond activation.

In contrast with using organozinc regents or Grignard reagents, metallic magnesiums could also be utilized in such coupling reaction. The use of a 1:1 mixture of tetrahydrofuran and 1,4-dioxane is essential for this C-H bond activation reaction (Scheme 49, bottom).[77e]

3.2 C-N Bond Formation

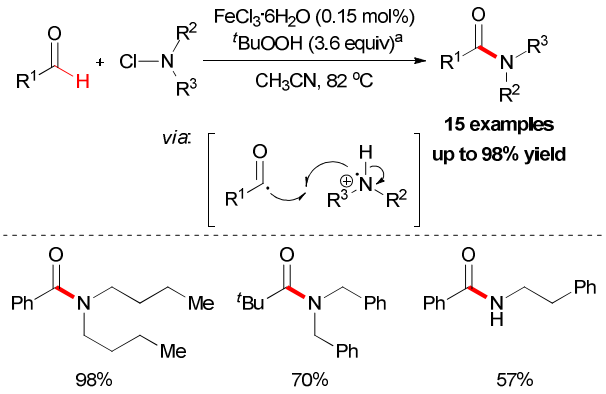
3.2.1 Aldehyde C(O)-H Bond

In 2011, Chan and co-workers reported a method for the amidation of aldehydes with PhI=NTs/PhI=NNs as the nitrogen source.[78] They used $FeCl_2$/pyridine as the *in situ* formed precatalyst and the reaction was accomplished in moderate to excellent yields (Scheme 50). The mechanistic studies showed that $[Fe(py)_4Cl_2]$ formed *in situ* and thus facilitated the insertion of a putative iron-nitrene/imido group to the formylic C-H bond of aldehyde.



Scheme 50 Iron(II)-catalyzed amidation of aldehydes with iminoiodinanes.

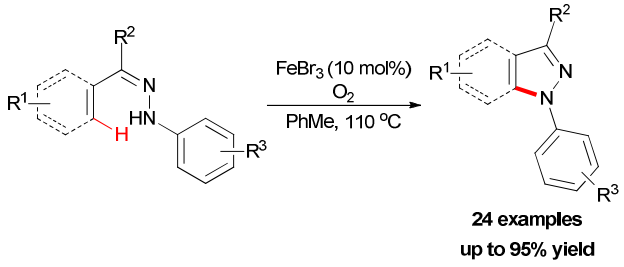
In 2012, Luca and co-workers reported an iron-catalyzed amidation of aldehydes with *N*-chloroamines (Scheme 51).[79] In this methodology, they gave a new example on coupling of acyl radical and nitrogen-centered radical. $FeCl_3{\cdot}6H_2O$ is the best choice while $FeCl_2{\cdot}4H_2O$ shows almost the same efficiency in this amidation reaction. Introducing the radical trapping regent, such as TEMPO resulted in the formation of TEMPO-adduct aldehyde product. This result indicated that the acyl radical may generate in the initiation step via homolytic sp^2 C-H bond cleavage in aldehyde substrates.



Scheme 51 Amidation of aldehydes with *N*-chloroamines. [a.] 70 wt% solution in water.

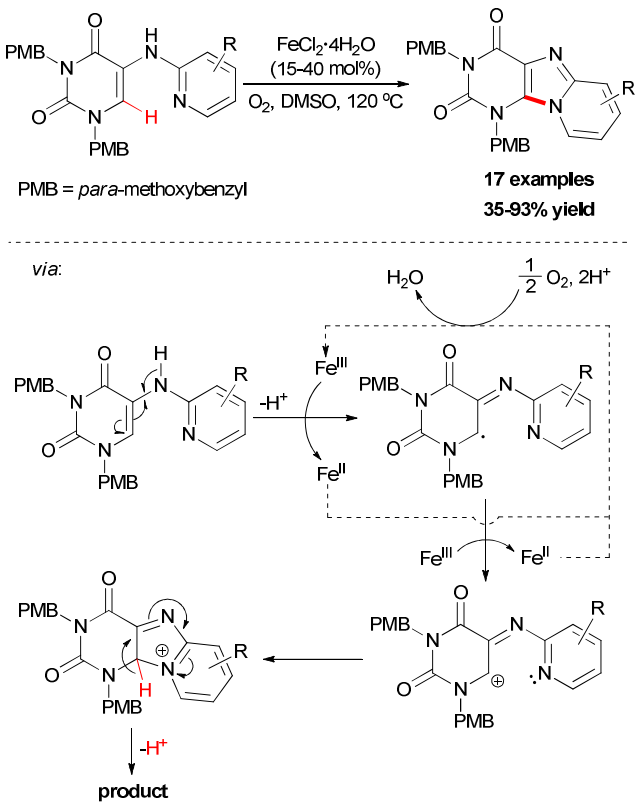
3.2.2 sp^2 C-H Bond of Arenes and Alkenes

Recently, Bao and co-workers disclosed a synthetic methodology of 1*H*-indazoles and 1*H*-pyrazoles via iron-mediated oxidative intramolecular C-H amination (Scheme 52).[80] After optimization of reaction conditions, the authors found that $FeBr_3/O_2$ was the best catalyst/oxidant combination. Through this method, a series of 1,3-diaryl-substituted indazoles and trisubstituted pyrazoles were achieved in moderate to excellent yields.



Scheme 52 $FeBr_3/O_2$ mediated intramolecular sp^2 C-H amination.

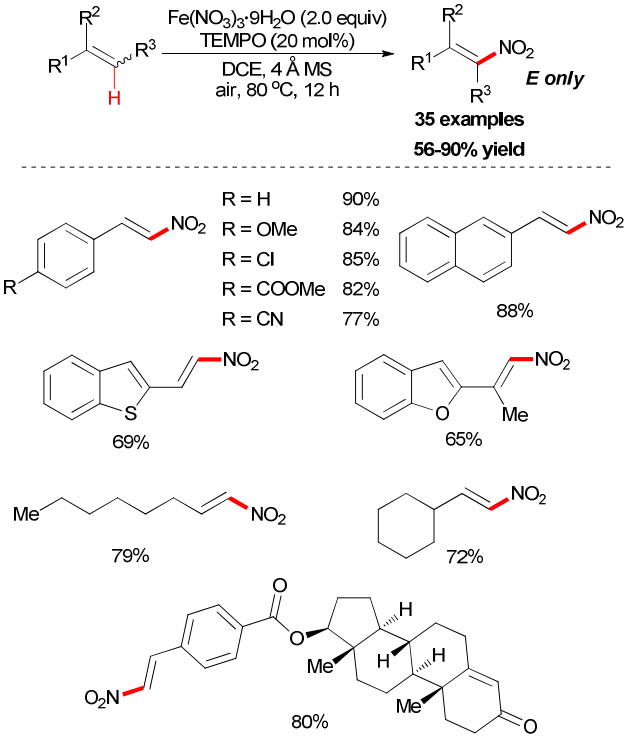
More recently, Maes and co-workers reported iron-catalyzed sp^2 C-H amination for the construction of C8-N9 annulated purines.[81] Catalyst screening indicated that $FeCl_2{\cdot}4H_2O$ was the best choice, while the $FeCl_3{\cdot}6H_2O$ gave a similar result. However, copper salts showed the low catalytic ability. Using O_2 as oxidant, a series of easily accessible 5-(pyridin-2-ylamino)pyrimidine-2,4 (1*H*,3*H*)-dione substrates underwent direct amination reaction to form the substituted pyrido [1,2-*e*]purines (Scheme 53). The addition of TEMPO to the cyclization reaction gave a significant reduction in conversion suggesting that radical might involve in the reaction mechanism. Based on the experimental results and previous reports, the catalytic cycle was proposed and showed in Scheme 53.



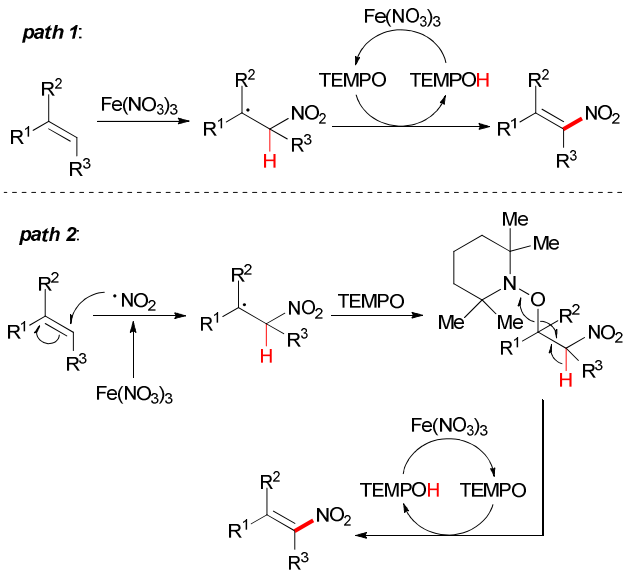
Scheme 53 Iron-catalyzed sp^2 C-H amination for constructing of C8-N9 annulated purines.

Maiti and co-workers reported an important methodology for constructing nitroolefins via a predictably selective nitration of olefins with $Fe(NO_3)_3{\cdot}9H_2O$ and TEMPO (Scheme 54).[82] The condition screening indicated that $Fe(NO_3)_3{\cdot}9H_2O$ was the best nitrating agent along with catalytic TEMPO. Notably, the nature of the solvent had a significant effect on the nitration reaction as less/nonpolar solvents were tested to be better choice compared to polar solvents.

Under the developed condition, a wide variety of aromatic, aliphatic, and heteroaromatic olefins were smoothly underwent nitration in region- and steroselective manner. Synthetically, the present reaction provided nitro-olefins in preparatively useful yields with excellent *E*-selectivity. Based on the authors' previous work,[83] two tentative pathways were proposed (Scheme 55). Initially, the nitro radical ($NO_2^{\cdot}$) could be generated from $Fe(NO_3)_3{\cdot}9H_2O$ under thermal conditions.[84] Then the nitro radical would react with olefin at the less-hindered side to form the carbon-centered radical. This nitroalkane radical could be transformed to final product via two possible ways. In path 1, TEMPO could directly abstract a hydrogen radical, which released the nitro-olefin. In path 2, TEMPO acted as a radical trapping regent after the formation of carbon-centered radical followed by oxidation to generate the final product.



Scheme 54 Iron-mediated selective nitration of olefins.



Scheme 55 Proposed pathways for steroselective nitration.

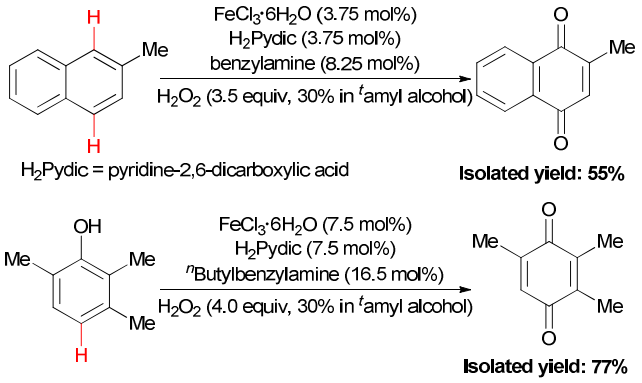
3.3 C-O Bond Formation

Direct oxidation of arenes to phenols is a difficult reaction. One reason is that many metal complexes capable of arene sp^2 C-H bond activation could not survive under the oxidizing conditions. In addition, because phenols are more electron-rich than the substrate arene, over-oxidation is also a complicated problem.

One hundred years ago, in 1900, the first example of the direct hydroxylation of arenes to phenols was reported.[85] The benzene was oxidized to phenol under a mixture of $FeSO_4$ and hydrogen peroxide (Fenton's reagent).[17] After the seminal

report, many optimized systems were developed. However, no significant progress could apply in synthetic fields.

In 2010, the Beller group disclosed the first example of iron-catalyzed selective oxidation of the sp^2 C-H bond of arenes and phenols.[86] Under two types of three component catalytic system ($FeCl_3{\cdot}6H_2O/H_2Pydic/amine$ = 1/1/2.2), oxidations of 2-methyl-naphthalene and TMP (2,3,6-trimethylphenol) took place in 55% and 77% yield (Scheme 56), respectively. This oxidation reaction offered an important method for the synthesis of vitamin E intermediates and vitamin K_3.



Scheme 56 Iron-catalyzed selective oxidation of arenes and phenols with hydrogen peroxide.

4 Future Challenges

Although many significant developments have been reported in the iron-catalyzed/mediated C-H bond oxidative transformations, this attractive field still remain many challenges. The problems could mainly divide into three aspects: reactivity, selectivity and mechanistic studies.[87]

Due to the strength of general C-H bonds, reactivity in their oxidative transformation becomes the very important challenge. Iron, as discussed above, has already showed its unique power in such transformations, but more reactive catalyst and less catalyst loading are much needed in this area.

Generally, most organic molecules involve the C-H bonds with different chemical environments. The target C-H bond should be selectively transformed and leave the other C-H bonds retard. Moreover, because most oxidation reactions are thermodynamically downhill, avoiding over-oxidation may be a potential challenge. As such, the regioselectivity and chemoselectivity may attract much more organic chemists' focus. In addition, the synthesis of chirality-containing compounds will encourage the chemists to find more methods to transform C-H bonds in high stereoselectivity.

As mentioned above, the mechanisms of many oxidation processes still unclear. Further researches towards the design of more powerful catalytic cycle should base on the mechanistic studies. The combination of iron-catalyst/oxidant may also play a vital role in the design of new reactions.

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