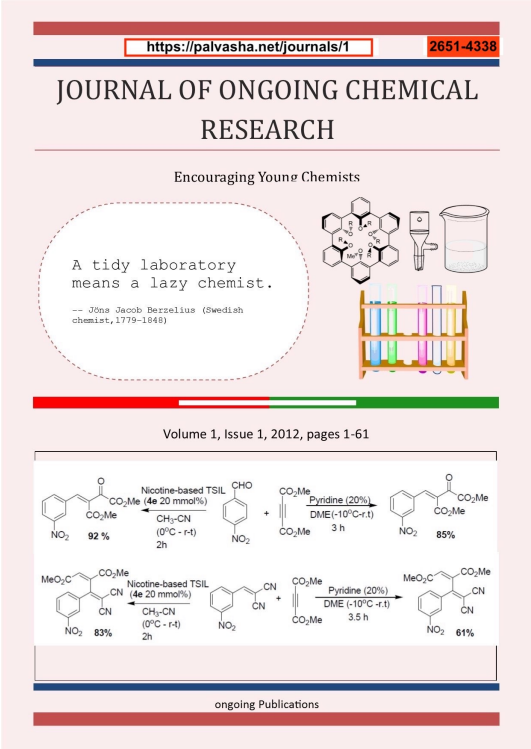
RECENT ADVANCES IN IRON CATALYZED REACTIONS IN ORGANIC SYNTHESIS



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Review

Recent Advances in Iron Catalyzed Reactions in Organic Synthesis

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Abstract

The transition metal catalyzed reactions are widely developed in current years. Most of the transition metals are expensive and are not easily available like; Gold (Au), Iridium (Ir), Palladium (Pd), Platinum (Pt), Ruthenium (Ru), Rhodium (Rh) etc. Iron is one of the highly plentiful, cheap and easily available transition metals. It has been consistently used in organic synthesis nowadays. In this review we have described the role of iron in organic reactions like C-C, C-O, C-N, C-S and N-S bond forming reactions. This review highlights the advancements in iron based organocatalysis from 2005 to 2020.

Keywords: Organic Synthesis, Catalysis, Green Chemistry, Heterocycles, Transition Metals, Bond Forming

The transition metals catalyzed reactions are an extremely helpful tools in organic-synthetic chemistry. The transition-metal-mediated organic processes are involved in the formation of carbon-carbon bonds and carbon-heteroatoms bonds that has become fundamental in the synthetic organic chemistry in few decades. The new methods for synthesis, reagents and catalysts have been developed in recent years to support in the synthesis of different chemical structures. The catalysts which have more reactivity, or the higher efficiency are playing an active role in chemicals research [1]. For a particular application the catalyst and organometallic reagent is selected based on different factors. For example, the compatibility with different functional groups and protecting groups, thermal stability of the substrate, the desire for stereo and regiospecificity, economic factor and operation ease [2]. The transition metals (like Palladium) catalyzed reactions make more than 60% carbon bond formations which are used in medicinal-chemistry these days [3]. The residual contamination issue is raised due to the use of palladium. This can cause the subsequent transformations and even patients health can be affected [4]. Many reactions reported to date require the use of precious-metals like; Palladium (Pd), Rhodium (Rh), Platinum (Pt), Gold (Au), and Ruthenium (Ru). The inherent toxicity and environmental impact is caused by these catalysts [5]. Therefore, the development of more sustainable and environment friendly reactions catalyzed through more benign-metal are needed to be investigated [6]. Iron can be of the appealing alternate to palladium as it is low cost, broadly available and have low toxicity [7-8]. Significant advances are made in the fields of iron catalyzed reactions in the past few years especially, in the carbon-carbon bond making, carbon-oxygens bond formation, carbon to nitrogens bond formation, nitrogen-sulfurs bond formations. These bond formation reactions have arisen as a powerful tool and various functionalized compounds like amino acids, ketones, carboxylic acids, and so on has been prepared [9-11].

Here we have described different iron catalyzed organic reactions which are divided into four parts. The part 1 includes the carbon carbon bonds formation reactions. In the second part of This review we have discussed Iron catalyzed carbon oxygen bond formations reaction. In the third part of this review, we have discussed the carbon nitrogen bond formation reactions which are catalyzed with iron. Here 2 articles are discussed. At last we have also discussed iron-catalyzed N-S bond formation.

1. C-C bond formation

1.1 Carbon−carbon oxidative homo-coupling of alkenyl-lithiums:

The coupling reaction of grignard reagents oxidatively catalyzed through iron-based transition metals have been actively investigated recently. Since 1969, the stoichiometric amount of $FeCl_3$ for oxidative homo-coupling of vinyllithium are reported. Z. Zhong et al. (2019), reported an effective iron catalyzed oxidative

homocoupling of alkenyl lithiums. These were produced via lithium−halide direct exchange or by acetylenic lithium reagent cyclization. Which were covering different 1,3-butadiene like, polycyclic or acyclic multi-substituted 1,3-butadienes. At the start they used stoichiometric amount of $FeCl_3$ and obtained the desired product of 1,3-buadiene in 86 % yield. They reported that by decreasing loading of $FeCl_3$ and absence of oxidant lead to lower yield. The DTBP (di-tert-butyl peroxide) was used as an oxidant which gave 86% yields. The solvent and temperatures were observed to have no role in yields improvement. They also observed that homocoupling of aryl groups with electron deficient substituents were slightly disrelished and lead to 49 to 58 % yield. Electron donating groups on aromatic rings increased the yield. Even the diene of natural product dimer was obtained in 47-77% yield. They observed that the tandem cyclization/oxidative coupling for acetylenic phenyl iodides led to higher yields than acetylenic alkyl iodides. Their work is shown in the figure 1 [12].

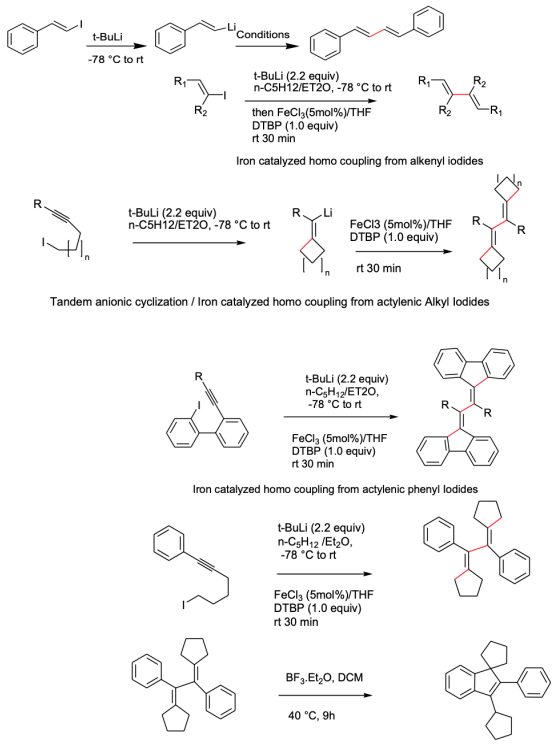

Figure 1. Oxidative homo-coupling of alkenyllithiums

1.2 Iron catalyzed α-alkylation of ketones with secondary alcohols:

Bettoni et al. (2020) reported the alkylation of sterically hinderd aromatic ketone with different secondary alcohol's by iron complex catalyzed phosphine free complex. They used hydrogen's autotransfer methodology which provide carbonyl compounds with β-branch in very good yield. The aliphatic alcohols and aromatic alcohols both can be used. The results from labelling study show that the source of hydride is secondary alcohol, while the alkylation in cobalt presence, no reversible step occur in this process. As a result, the alkylation will be diastereoselective. This work is shown in figure 2 [13].

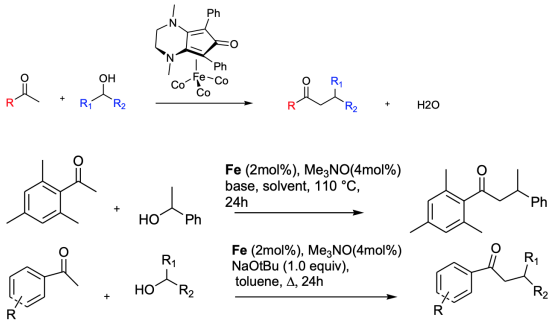

Figure 2. Iron-catalyzed α-alkylation of ketones with secondary alcohols

1.3 Iron-catalyzed β alkylation of alcohols:

Bettoni et al. (2019), prepared β-Branched alkylated alcohols with diaminocyclopentadienone iron tricarbonyl-complex Fe1. They performed alkylations of 2-arylethanol derivatives. Benzylic alcohols and methanol were used for alkylation under milder condition. They used iron catalyzed methylation' and benzylations of 2-arylethanol which gave β-methylated or β-benzylated alcohols in considerble yield.

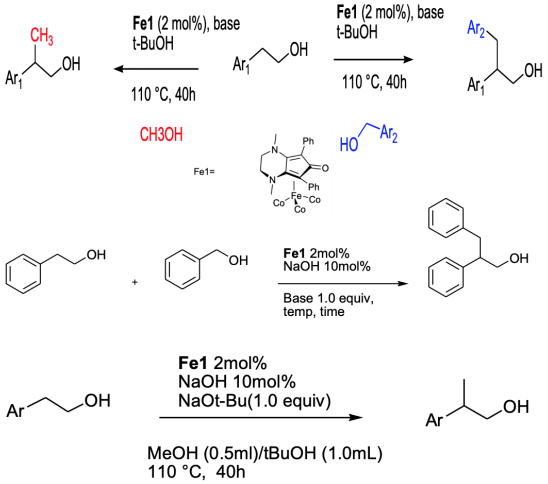

Figure 3. Iron catalyzed double hydrogen autotransfer alkylation

Different functionalities, like heterocyclic fragment,

can be inserted on the aryl rings. These results confirm the synthesis of functionalize alcohol. This pathway can be alternatively used for hydroformylation and hydrogenation sequence. Their work is shown in figure 3 [14].

1.4 Heteroaromatic sulfonates and phosphates as electrophiles in iron catalyzed cross-couplings:

Gogsig et al. (2009), used iron catalysis for heteroaromatic tosylates and heteroaromatic phosphates as the electrophile in cross coupling reactions to alkyl grignards reagent. These reactions proceeded at lower temperature which allowed high functional groups tollerance with complete conversion was achieved in lowest time. Their work is shown in figure 4 [15].

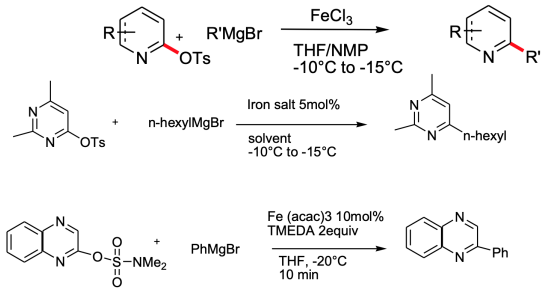

Figure 4. Heteroaromatic sulfamate in iron-catalyzed cross-couplings

1.5 Iron catalyzed synthesis of unnatural chiral amino acid derivatives:

Zhang and his coworkers worked on the iron catalyze synthesis to various amino acids derivative. They used three different Evans-oxazolidinones which were used as chiral auxiliaries. These were 1) (S)-4-benzyloxazolidin-2-one (a), 2) (S)-4-phenyloxazolidin-2-one (b), and 3) (S)-4-tert-butyloxazolidin-2-one (c). All these were used on N-phthaloyl dehydroalanene which gave matching 2-phthaloyl acrylamides (1a to c). The reaction of (1c) with (2a) yielded the highest (dr > 20:1) using a $Fe(acac)_3$ as catalyst with of 1,2-dichloroethane plus ethylene glycol mixed solvent in $PhSiH_3$ presence at room temperature. The (3a) of S-configuration can be isolated through column chromatography. The yield obtained only 31%. When(2a) was increased, the yield improved and alkene homocoupling occurred. Other iron-catalysts show poor results. The DCE and EG mixed solvent was found suitable. The diastereoselectivity decreased with temperature increase upto 80°C. They examined different alkenes with different-sized rings to check the scope of alkenes for un-natural and chiral α-amino acid derivatives (3) which showe high yields and more diastereoselectivity in which large cyclic substrate showing high diastereo-selectivity due to big steric hindrance effect. For noncyclic alkenes the smaller steric substituents bearing substrates like methyl showed slightly lower diastereoselectivity. The preparation of unnatural and chiral α-amino acid derivativesi(3) show the use of several functional group which include ethers, amide, hydroxyl groups and esters. Their work is shown in figure 5 [16].

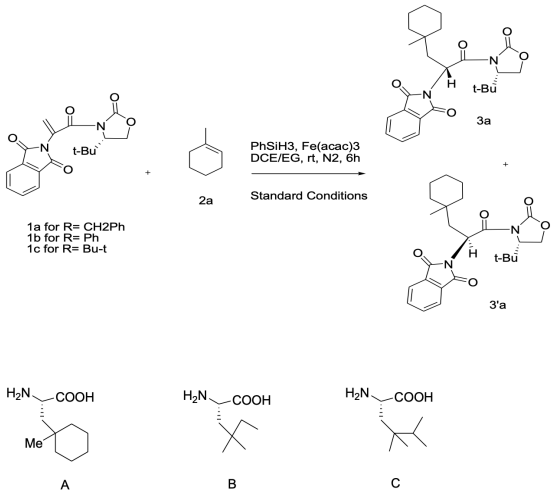

Figure 5. Diastereoselective synthesis of unnatural-chiral amino acid derivatives

1.6 Iron catalyzed reactions of alkyl grignards with aryl sulfamates and tosylates:

Agrawal et al. (2013) achieved the iron catalyzed crosscouplings of tosylates and the aryl sulfamates with primary and secondary alkyls grignard.

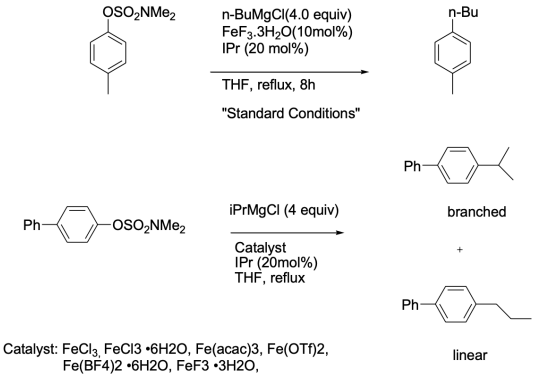

Figure 6. Cross-coupling reactions of alkyl Grignard with aryl sulfamates and tosylates

They used $FeF_3.3H_2O$ as catalyst. This reaction tolerated a lot of iron pre-catalysts. The iron counterion had a prominent effect on the branch to linear ratio with the secondary grignard reagents. This work is shown in figure 6 [17].

1.7 Iron catalyzed coupling of aryl sulfamates and aryl/vinyl tosylates with aryl grignards:

Agrawal and Cook. (2014), for the first time reported the iron catalyze coupling of arylsulfamate and tosylate to with aromatic grignards reagent. Their reaction provide a wide series of cross coupled product in excellent yield. These reaction's proceeded with lower level of grignards homocoupling irrespective of iron-source as shown in figure 7 [18].

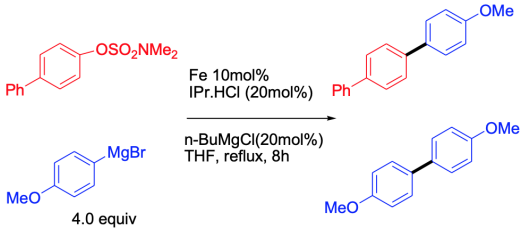

Figure 7. Coupling of aryl sulfamate and aryl/vinyl tosylate to aryl Grignard

1.8. Iron catalyzed C−H alkylation of heterocyclic C−H bonds:

Babu et al. (2016), used iron based catalyst for C−H alkylation of the thiazole, benzothiazoles, benzoxazoles with alkyl tert-butyl peresters and alkyl diacyl peroxides. The reaction was started with benzothiazole (1a), lauroyl peroxide (LPO) (2a). 2-undecylbenzothiazole (3a) was produced in 67% when the reaction condition was 10 mol% $Fe(OTf)_3$ in the 1,4-dioxane as solvent at 80°C . Metal catalysts like $Fe(OTs)_3$, $Zn(OTf)_2$, $In(OTf)_3$, $Cu(OTf)_2$, were used to catalyze the reaction, but they showed little efficiency. Acetonitrile proved the most suitable solvent. The reduction of catalyst amount as 5, 3, or 1 mol % led to less conversion of (1a). The reaction in which HOTf was taken as 30 mol % in place of using metal based catalyst produced (3a) in 51% yield. The electronic effect influence was observed on lauroyl peroxide reaction. Electron donating methoxy group on benzothiazole led to 90% yield, meanwhile electron withdrawing groups like nitro- and chloro-substituted alkylated benzothiazoles gave yield in 75% and 80% respectively. They proposed the mechanism of single electron transfer catalytic cycle for alkylation of benzothiazoles in which Fe(III) (B) would reduce to Fe(II) (A) through radicals and result in benzothiazole radical (C) as illustrated in figure 8 [19].

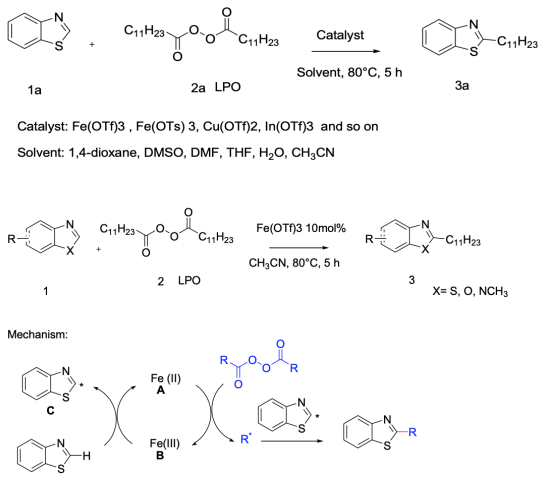

Figure 8. C−H alkylation of heterocyclic C−H bonds

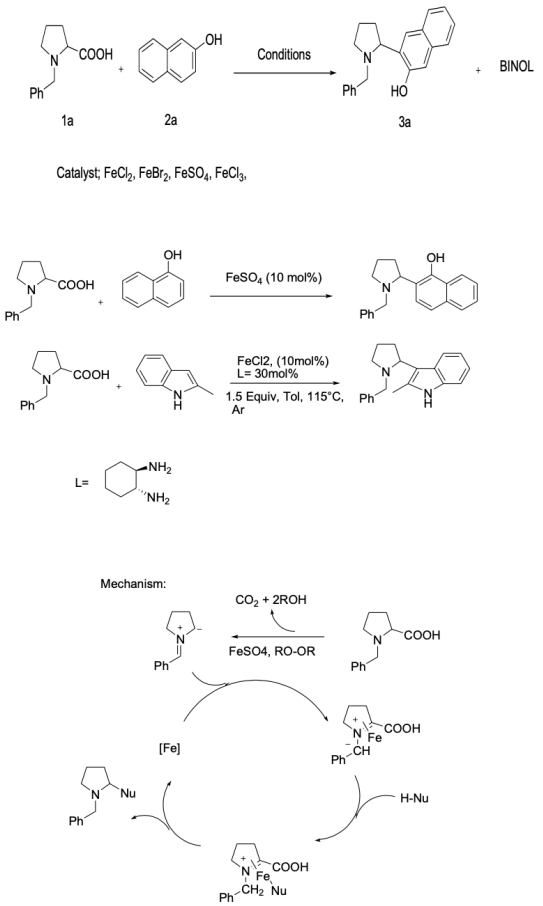

Figure 9. Decarboxylative C-C coupling of proline derivatives and naphthol

1.9 Iron-catalyzed decarboxylative C-C coupling of proline derivatives and naphthol:

Bi et al. (2009), developed an iron catalyzed decarboxylative C-C reaction. For this purpose proline derivatives were used. The Proline (1a) and 1.5 equiv of -naphthol (2a), 1.5 equiv of *tert*-butyl peroxide (4a) and 10 mol % $FeCl_2$ at 115°C kept under argon for one night. The 70 % yield of the required tertiary amino-naphthol (3a) was obtained. $FeSO_4$ gave the good yield as compared to some newer iron catalysts. Other oxidants like TBHP (*t*BuOOH) and dicumyl peroxide produced low desired product. The *trans*-1,2-diaminocyclohexane, a racemic ligand, gave excellent yields. an excellent yield was obtained when 1.0 equiv of (2a) and 1.5 equiv of (1a) were used. When iron catalyst was absent, yield reduced to 31%. An electron-donating group on the naphthol at C6, C7 reacted easily and products obtained in good yields as shown in figure 9 [20].

1.10. Iron-catalyzed homo-coupling of simple and functionalized arylmagnesium reagents:

Cahiez et. Al, 2005, developed an efficient iron catalyzed homo-coupling of simple functionalized aryl-magnesium reagents. The homo-coupling reaction was performed in THF, at reflux, using of 1,2-dichlororethane as oxidant.

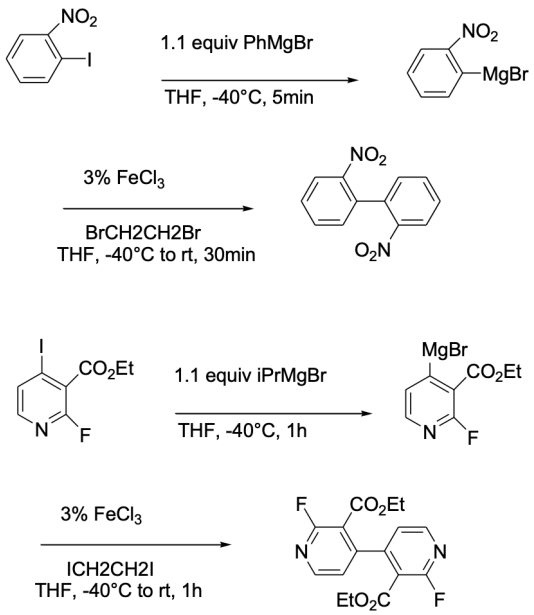

Figure 10. (1) Homo coupling of 2-nitrophenylmagnesium bromide (2) Homo coupling of 2-fluoro-3-carbethoxy-4-pyridylmagnesium bromide

The results show that this reaction could be performed in THF with 3% $FeCl_3$ at room temperature. The dichloroethane was taken as an oxidant in stoichiometric amount. The homo-coupling product was obtained in appreciable yield. This reaction is applicable to heteroaromatic grignard reagents as well. Under similar coupling conditions, 41% yield of 2,2′-dinitrobiphenyl was obtained from corresponding Grignard regents. These conditions were applied to functionalized pyridyl magnesium bromides. The 2-fluoro-3-iodopyridine gave 2-fluoro-3-carbethoxy-4-iodopyridine in 66% yield. It was reacted -40 °C with i-PrMgBr upto 1 hour to give grignard reagent. This was reacted with 1,2-diiodoethane and 3% $FeCl_3$ which give the 33% yield as shown in figure 10 [21].

1.11 Iron catalyzed Suzuki−Miyaura cross coupling reaction between alkyl halides and un-activated aryl-boronic esters:

Crockett et al. (2018), performed iron-based catalyzed coupling reaction (Suzuki−Miyaura reaction) of alkyl halide and arylboronic esters. In this process the activation of boronic ester to alkyl-lithium reagent or the magnesium additives is not required. A combination of researches showed that lithium amide bases were coupled to iron-complexes that were containing deprotonated cyanobis ligand.

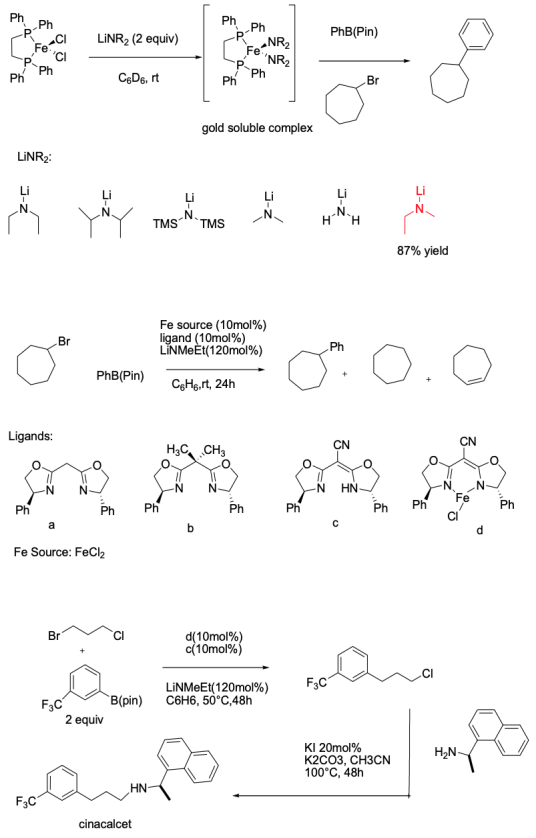

Figure 11. Synthesis of cinacalcet by iron-based alkyl-aryl Suzuki−Miyaura cross coupling reaction

The catalytic cross coupling reactions gave maximum yield of 89 %. The pharmaceutical Cinacalcet was prepared in shortest way through the new iron based Suzuki−Miyaura reactions. The most successful and effective conditions for Suzuki-Miyaura reactions were to avoid the iron aggregates formation. The anionic ligands and amide bases make transmetallation from boron to iron facile.The mononuclear iron species were found necessary for cross coupling reactions to be successful between unactivated arylboronic esters and alkyl halides, shown in figure 11 [22].

1.12 Iron catalyzed cross-coupling of non-activated secondary alkyl halides with alkynyl grignard reagents:

Cheung et al., 2014; developed the iron-catalyzed crosscoupling between non-activated secondary alkyl halides (alkyl bromides, alkyl iodides) and alkynyl grignard reagent in room temperature. They started crosscoupling of iodocyclohexane and 1-propynylmagnesium bromide in solvent N-methylpyrrolidone (NMP). This reaction was performed at room temperature. Different salts of iron(III) and iron(II) were tested as catalyst. The iron(II) bromide wasconsidered to be the optimal catalyst for this reaction. They achieved 86 % yield when 10 mol % $FeBr_2$ and 1.5 equiv of alkynyl grignard reagents in highly diluted solution. Without $FeBr_2$, no product formed suggesting that $FeBr_2$ is a genuine precatalyst. This work is placed in figure 12 [23].

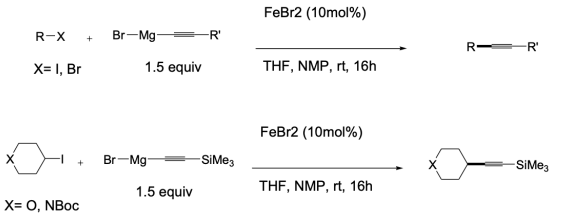

Figure 12. Iron-catalyzed cross-coupling of nonactivated secondary alkyl halides and alkynyl Grignard reagents

1.13 Iron catalyzed alkylation of aryl sulfamates and carbamates:

Silberstein et al. 2012, reported alkylation of aryl sulfamates and carbamates by using alkyl grignard reagent and iron catalyst to produce sp^2-sp^3 carbon carbon bonds. This transformation enable the alkylation of wide range of substrate like, electron rich arene, ortho substituted aromatic compounds and heterocyclic compounds. For alkylation of aryl-sulfamates and carbamates the alkyl grignard reagents are better coupling partners. The alkylated product (2) is formed when carbamate (1) couples to n-hexylmagnesium chloride in the presence of NHC as ligand (3). The addition of CH_2Cl_2 in substoichiometric concentration is necessary for higher yield. The experiments with no $FeCl_2$ gave <15% yield as shown in figure 13 [24].

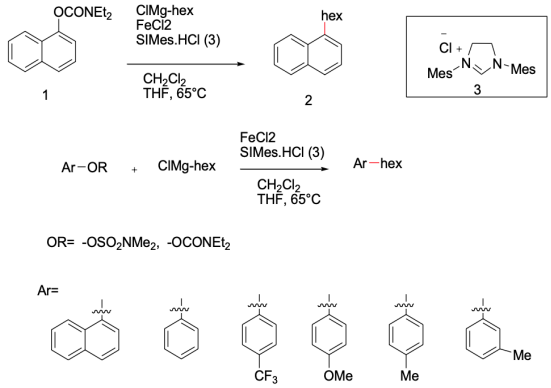

Figure 13. Iron catalyzed coupling of aryl carbamates and sulfamates to n-hexylmagnesium chloride

1.14 Iron catalyzed heterocycle and arene deprotonative alkylation:

The transition metal catalyzed alkylation of C-H bonds to convert sp^2 C-H bond to $C(sp^2)$-$C(sp^3)$ bonds have been developed. Several of them suffer from carbocation isomerization, regioselectivity problems and the polyalkylation which limits their synthetic applicability. Tran et al. 2010 developed alkylation of arene C-H bonds through alkyl iodides and bromides catalyzed by iron. In amide base presence, both primary, secondary alkyl halides could couple to thiophene, furan, pyridine derivatives and several arenes. The reaction optimization showed that crosscoupling of 2-lithiobenzothiophene and cyclohexyl bromide gave 20% yield while corresponding grignard reagent could couple with high yields. The HMTA/TMEDTA and *trans*-*N*,*N*′-dimethylcyclohexane-1,2-diamine were noted as best ligands to give high yields. The Iron(III) chloride was better than few other iron sources.The TMPMgCl·LiCl as base,10 mol % $FeCl_3$, 25 mol %*trans*-*N*,*N*′-1,2-dimethylcyclohexane-1,2-diamine ligand and THF(solvent) were the optimum conditions at room temperature for such type of reactions as shown in figure 14 [25].

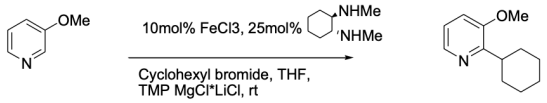

Figure 14. Iron catalyzed heterocycle and arene deprotonative alkylation

2. C-O bond formation

2.1 Iron catalyzed acyloxylation of aryl-2h azirines with hypervalent iodine(iii) reagents:

Wang et al. (2018), worked on the oxidation of 2H-azirines C-H bond with phenyliodine(III) diacetate (PIDA) through iron catalyst.

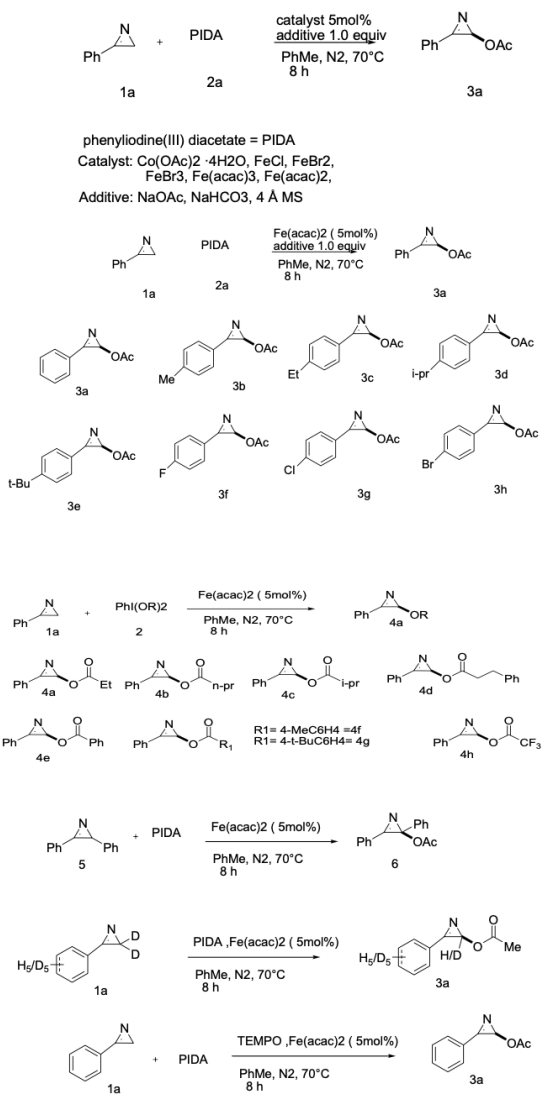

Figure 15. Iron-catalyzed acyloxylation of aryl□2-azirines with hypervalent iodine(iii) reagents

They carried the reaction of 3-phenyl-2H-azirine (1a) and PIDA (2a) and irradiated with green light for 10 hours in room temperature. The product (3a) was obtained in 13% yield. But their experiment showed that heating the reaction upto 70°C gave 11% yield and (1a) decomposed which means, that the reaction is not depending upon light. Some other salts of iron like, Fe (II), Fe (III) were applied on this reaction. This showed that the presence of coordinating anions in ferrous salts was necessary for 2H-azirine oxidation. The 65% yield of (3a) was obtained when $Fe(acac)_3$ was applied. The aprotic toluene was found to be the ideal medium. A family of HIRs (Hypervant iodine(iii) reagents) derived from PIDA were reacted to 3-phenyl-2H-azirine (1a) and inserted an aliphatic group on HIRs increased the oxidation ability and reaction was completed in 8 hours under iron catalysis giving higher yields from 4a-d. A sterically more hindered azirine (5) was prepared and used as an oxidant with PIDA. They didn't give product (6). The addition of a radical inhibitor, TEMPO(2,2,6,6-tetramethylpiperidin-1-yl)oxyl) didn't let to oxidize 2H-azirines. It confirms the radical mechanism in this reaction. This work is elaborated in figure 15 [26].

2.2. Iron-catalyzed, microwave-promoted, one-pot synthesis of 9-substituted xanthenes by a cascade benzylation-cyclization process:

Xiaobing Xu et al., 2010, investigated iron catalysis starting from 1-(2-bromophenyl)ethyl acetate, synthesized from already available methods. For screening of the experimental conditions, they performed the reaction of 1-(2-bromophenyl)ethyl acetate and 4-methyl phenol. This reaction was considered as model reaction. First, they carried the reaction using 5 mol% of $FeCl_3$ on 50°C. The microwave radiation was used as the catalyst. They observed that benzylation reaction was completed in only 10 minutes. The reaction mixture was put to cooling and 5.0 equiv of Cs_2CO_3 and DMF were added to this mixture.This mixture was put to another 10 minutes in microwave irradiation on 130°C. The 75% yield of required xanthene obtained. The reactions with no microwave irradiation resulted in very low yield of xanthene i.e. 46% only. The 4.0 equivalent of Cs_2CO_3 produced less product. They concluded that 5 mol % $FeCl_3$ is optimum catalyst for this reaction. This reaction was checked for the cascade benzylation and cyclization at these reaction conditions. The acetates having alkyl groups on benzylic position were reacting easily to produce xanthene alkylated at position 9. The variety of substitutes can be used for xanthene production. The benzylation-cyclization reaction can be carried out through banzyl-carbonates, benzyl-acetates and the benzyl-bromides. The Benzyl

bromides having methyl or phenyl substituent on benzylic position, reacted to phenols and gave higher yields of xanthene shown in figure 16 [27].

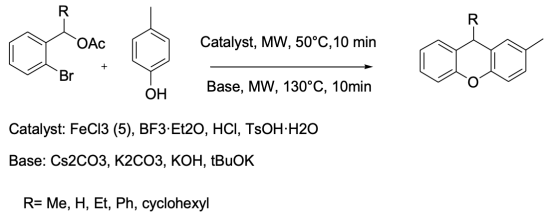

Figure 16. Synthesis of xanthenes from the reaction of phenols and benzyl acetates

2.3 Iron catalyzed 2-arylbenzoxazole formation from o-nitrophenols and benzylic alcohols:

Mingyue wu et al. (2012), worked on iron catalysts for the C-N bond creation. They reacted 2-nitrophenol (1a) and the benzyl alcohol (2a) on150 ^{o}C in toluene. In the absence of a catalyst, the 2-nitrophenol and 2.5 equivalent of benzyl alcohol didn't form the desired product (3a). Then they applied different iron salts like Fe_2O_3, $FeSO_4$, $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$.Which showed as ineffective catalysts for this reaction. Ferrocene and Fe(acac)3 led to 18% and 31% product respectively. While 5mol% of $FeCl_3$ and $FeCl_2$ improved the yield to 79% and 81%. The dppf (1,1 0-bis(diphenylphosphino)-ferrocene) showed the most effeciency forming (3a) in 82% yield. The chlorobenzene, anisole and P-xylene were among the good solvents for this reaction. The decreased loading of catalyst to 3 or 2 mol% resulted in higher yield. The decrease in temperature also decreased the yield. The electrons donating and withdrawing substituents on aromatic ring of benzylic alcohols led to the desired products in decent yield. Wu et al. detected that aliphatic alcohols were not suitable for such reactions under optimal conditions shown in figure 17 [28].

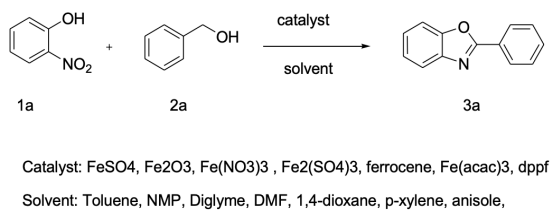

Figure 17. 2-arylbenzoxazole formation from o-nitrophenols and benzylic alcohols

2.4 Iron catalyzed intramolecular o-arylation: synthesis of 2-aryl benzoxazoles:

Bonnamour et al. (2008), performed iron catalyzed o-arylation reaction to synthesize 2-substituted benzoxazoles. They used *N*-(2-Bromophenyl) benzamide (1a) as model for optimization of the reaction conditions. The reagents like TMHD, FeCl3, Cs_2CO_3, and DMF were used in combination. At 135 °C benzamide (1a) cyclized smoothly and benzoxazole (2a) produced in 98% yield. In the absence of $FeCl_3$/TMHD the reaction gave (2a) in only 42% yield. The iron-catalyzed cyclization and nucleophilic substitution was suggested in the initial experiment to led to give higher yields of (2a). At lower temperatures, the lower yield of (2a) was obtained. The Cs_2CO_3 led to higher result and few bases like $K2CO_3$, $K3PO_4$, and NaO*t*-Bu resulted lower yields of (2a). No product was obtained in the absence of the base. Lower yields of (2a) obtained in solvents other than the DMF. Iron(III) sources like Fe_2O_3 and $FeCl_3 \cdot 6H_2O$ were showing compatibility in this reaction. The Iron in +2 oxidation state i.e. $Fe(OAc)_2$, $FeBr_2$, and $Fe(ClO4)_2$ were also applicable. In every way the benzoxazole (2a) was obtained in appreciable yields. The different substituted aromatic compounds at position (R2) were converted to benzoxazoles (2a) in good yield. The halobenzamides having the aliphatic or vinylic substituents didn't cyclize due to the steric hindrance. The aromatic amides with substituents at (R1) position resulted in good yields of benzoxazoles shown in figure 18 [29].

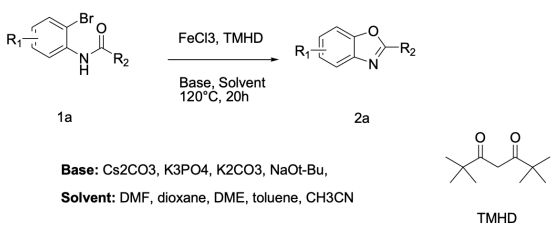

Figure 18. Synthesis of 2-aryl benzoxazoles

3. C-N bond Formation

3.1 Iron catalyzed intramolecular C−H amination of α-azidyl amides:

Zhao et al. (2019), used the $FeCl_2$ and β-diketiinate ligand for azidyl nitrogen insertion in the C-H bond of amidyl group. It produced the polysubstituted imidazolinones in good yield. The $FeCl_2$ or $FeBr_2$ were used alongwith β-diketiminate (L) which facilitated the reaction. They found that different 2-azido-N,N-diarylmethyl-2-methylpropanamides reacted easily to give the cyclized products in higher yield. The iron catalyzed C-H amination of azides were investigated

by Betley's group who used irondipyrrinato complexe as the catalyst. The iron(II) complex which is generated in situ from $FeCl_2$ and β-diketiminate ligand are believed as active catalysts in this reaction shown in figure 19 [30].

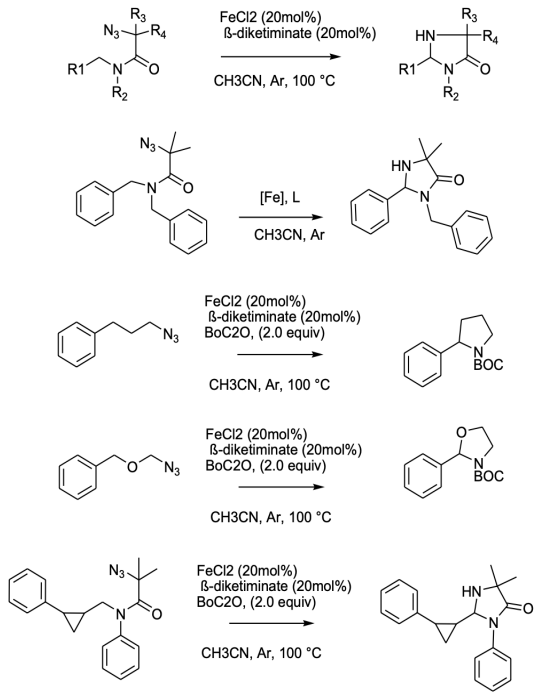

Figure 19. Iron catalyzed intramolecular C−H amination of azides

3.2 Iron catalyzed aerobic oxidation and annulation reaction of pyridine and α-substituted allenoate towards functionalized indolizine:

A lot of natural products and pharmaceutical products contain indolizines. These structures containing compounds show various biological activities like, antiviral activities, anti inflammatory and antitumor activities. Jin et al. (2018), reported a very important reaction between pyridine and allenoate (substituted). This reaction was catalyzed by iron giving functionalize indolizines derivative. The pyridine (1) and allenoate (2) were selected to be the model substrates for this type of renovation reaction. By using iron chloride and combination in air resulted to annulation product (3) oxidatively in 38% yield. They found that the reaction performance was improving by catalyst loading and product (3) yield can be increased upto 68 % if 30 mol % of catalyst loading is used. The different solvents like; DMF, CH_3CN and PhCl had no improving effect on product (3) yield respectively shown in figure 20 [31].

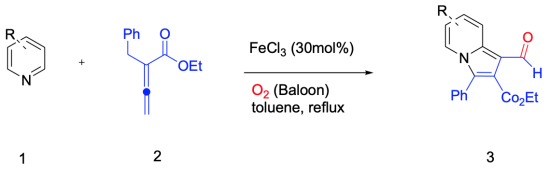

Figure 20. Formation of functionalized indolizine from of pyridine and α-substituted allenoate

4. N-S bond formation

4.1 Iron catalyzed imination of sulfoxides and sulfides:

Mancheno et al. (2006), investigated the iron (III) catalyzed imination of sulfoxides and sulfides to sulfonylamide in iodinanes presence. The high yields were obtained when $Fe(acac)_3$ was introduced as catalyst alongwith iodosyl-benzene. The reaction proceeded in the stereospecific way. The configuration was retained at sulfur atom. In this way enantiopure sulfoximine can be constituted from the respective sulfoxides. When the N-nosyl product is deprotected, it gives NH-sulfoximines without epimerization. At last the iron-nitrene complex was suggested to be the reactive intermediate in the reaction shown in figure 21 [32].

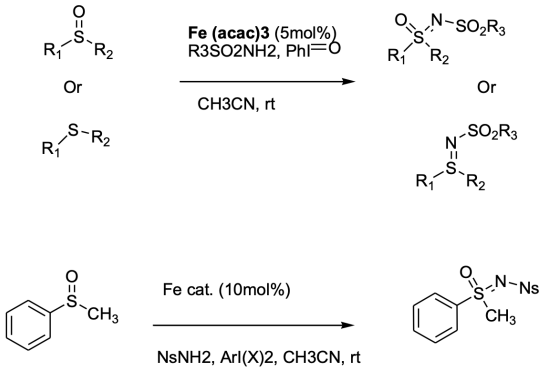

Figure 21. Imination of sulfoxides and sulfides

Conclusion and Future prospects

In our present work an effort has been made to summarize more promising and fascinating achievements from 2005-2020 in the synthesis of different organic compounds. we have described the role of iron in transition metal catalyzed reactions. Different bond forming reactions like; C-C, C-O, C-N and N-S are discussed. This will help researchers to use iron based catalysts in organocatalysis and advance synthesis. It will be helpful in complex organic reactions in natural products, pharmaceuticals

and different organic materials. which will be more economical and environment friendly. This field needs further to be explored.

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