IOSR Journal of Applied Chemistry (IOSR-JAC)
e-ISSN : 2278-5736 Volume 9, Issue 3 Ver. 1 (Mar. 2016), PP 40-65
www.iosrjournals.org

Iron-catalyzed synthesis of heterocycles

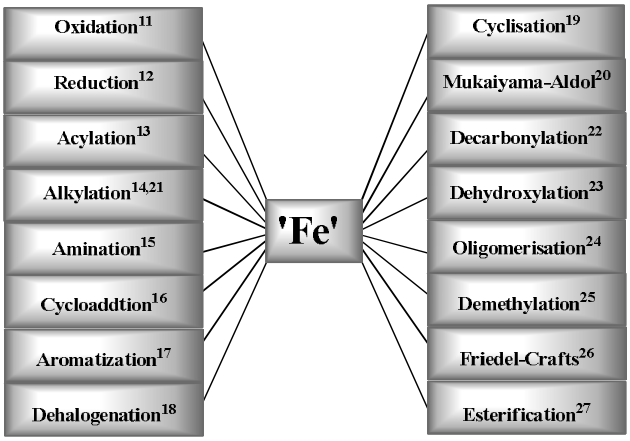
Samir K. Mandal*[1,2] and Asoke P. Chattopadhyay[1]
[1](Department of Chemistry/University of Kalyani, Nadia, India 741235)
[2](Current affiliation: Department of Chemistry, Saldiha College/University of Burdwan.
E-mail: samirmandal2004@gmail.com; Tel: +91-94-3335-6499)

Abstract: *Heterocycle synthesis using the transition metal based catalysts has several advantages. In recent years, iron catalysts have been used extensively in the development of synthetic methodologies for this purpose. Different salts of iron can assist bond formations due to their potential as Lewis acids, as oxidizing agents and as convenient catalysts. Fabrications of heterocycles proceed either via C-C bond or C-hetero bond formation from the corresponding acyclic compounds. This review summarises recent contributions from various authors working in this field.*

Keywords - *Iron Catalyst • heterocycles • eco-friendly • non-toxic • transition metal*

1. INTRODUCTION

Items essentials for human survival such as, food, medicine etc. are produced by chemical reactions directly or indirectly in nature or in industry. Other items such as cosmetics, which are also deemed essentials in affluent societies, are also obtained by above means. It is the biggest challenge in the modern society to maintain good supply line of these products by applying the advanced research, at the same time creating strategies to meet the critical needs of growing population of the world. Chemists have used catalysts, *esp*. transition metal catalysts, for the last few decades to achieve reactions which were almost impossible by the traditional methods. They would also try to maintain a greener environment by reducing the waste production and generation of the hazardous substances, while improving energy and atom efficiency and reducing reaction time. Transition metal catalysts play a key role in this context. One cannot visualize typical metal catalyzed coupling reactions such as Heck,[1] Suzuki,[2] Kumada,[3] Negishi,[4] Stille,[5] Hiyma,[6] Sonogashira[7] without a transition metal e.g. Pd, Ni etc. Major drawbacks of these catalysts are their toxicity, cost and low abundance. Hence these catalysts are unsuitable for the large-scale application, leaving aside their environmental impact. There has been recent interest in the iron as a catalyst. After almost 40 years, it seems that the iron may be the best alternative as it is one of the most abundant metal on the earth and is eco-friendly as well.[8] As it is available commercially at relatively low cost, it is expected to be used more.[9] However, except in the last couple of decades, reports on the iron as catalyst has been moderated in comparison to the other metals.[10] The rapid increase in application of the iron on catalysis in oxidation,[11] reduction,[12] acylation,[13] alkylation,[14] amination,[15] cycloaddition,[16] aromatization,[17] dehalogention,[18] cyclization,[19] Mukaiyama-aldol,[20] allylation,[21] decarbonylation,[22] dehydroxylation,[23] oligomerization,[24] demethylation,[25] Friedel–Crafts,[26] and esterification[27] reactions are quite informative. Iron as a catalyst is in serious competition with the Pd and Ni, *esp.* in C-H functionalization[28] to form C-C,[29] C-N,[30] C-O,[31] C-S,[32] C-B,[33] Si-O[34] to their asymmetric version including the nano-catalysis.[35]



The utility of the iron as a metalloenzyme for different redox reactions including oxygen transport,

hydroxylation, epoxidation, mono-oxygenation, addition, substitution, cycloaddition, hydrogenation, rearrangement, polymerization and cross coupling reactions are already well-documented.[36] Its effect in reducing use of toxic metals and their release in the environment is less discussed. This aspect has already been considered in the pro-drug[37] formulation. With an aim to increase attention on the iron catalyzed transformations, as well as providing a glimpse of further developments to come, this review offers to present a comprehensive report on recent developments in the iron-catalyzed transformations to the synthesis of heterocyclic compounds up to the end of 2014. Although it is well nigh impossible to summarize all such works in a single review, we hope to assemble at least one example of each type of the reaction as categorized below. We also expect that it will be of help to synthetic chemists, and offer an alternative to catalyst currently in vogue.

2. MECHANISM

Transition metal can assume multiple oxidation states, in the presence or absence of ligands, important on their catalytic process, by the virtue of their incomplete d-subshell. Although the iron can act as a Lewis acid or an oxidising agent, cross-coupling mechanism suggested in the literature typically cite the palladium and nickel as catalyst. However, highly reactive nucleophilic and paramagnetic nature of the iron-organo complexes makes them competitive in the field. Presence of more than one active species due to multiple exchange and disproportionation of the organo-iron intermediate do not hinder38 the determination of the reaction pathway accurately. Product formation is also ensured in most cases. Typical iron-catalyzed processes take place extremely rapidly even at the low temperature, let alone at room temperature. The mechanisms suggested here are based on direct or indirect experimental evidences.39 Corroboration is almost impossible in each case due to lack of elementary knowledge about electronic structure and the reactivity of intermediate low-valent iron species.

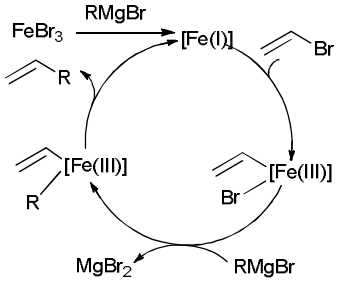


Fig. 1 *Kochi's Mechanistic proposal.*

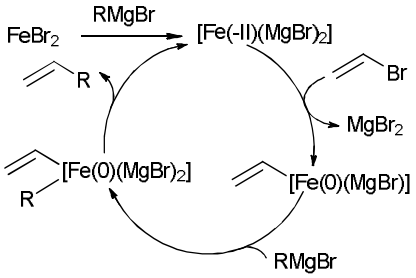


Fig. 2 *Früstner's mechnistic proposal*

Kochi, the pioneer of work on iron catalyzed reactions, proposed the mechanism by considering Fe(I)40 as the active species based on his experiments (Fig. 1). According to him, the active component is metastable which on standing in absence of reactant loses its catalytic activity. This was contradicted by Bogdanovic´ and other who proposed that the active iron species is Fe(-II) (Fig. 2).41 Three different mechanisms are extant at present. All state that the pre-catalyst is either Fe(II) or Fe(III), which is reduced by the organic nucleophile. Current proposals accept a formal Fe(-2) / Fe(0)41 rather than an Fe(+1)/Fe(+3) or Fe(0)/Fe(+2)42 as the redox couple. Although Fe(0) is considered to be the active catalyst, Fe-powder is not catalytically efficient and must be ligated to a source of nucleophile.

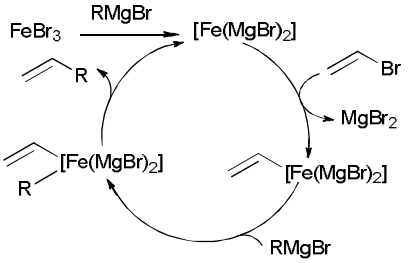


Fig. 3 *Most Accepted mechanism based on low-valent intermetallic catalyst.*

3. REACTIONS

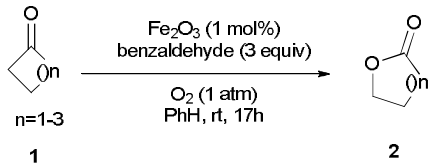
3.1. Oxygen Heterocycles

Methodologies leading to the formation of ring systems with one or more hetero-atoms have been explored using transition metals via C-C or C-O bond formation reaction on several occasions.[43] In many occasion, iron has also been used as the catalyst for oxidative purpose and useful instead of toxic reagents such

as Cr, Mn, Ni, Cu and Pd-complexes. Heterocycles containing oxygen[44] *e.g.* furan or pyran is of much interest as these are key substructures of several medicinal compounds.

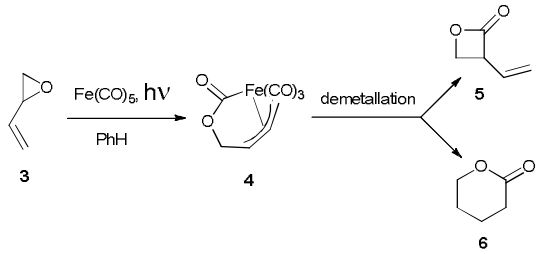
3.1.1. Lactone derivatives

Lactones such as β, γ, δ-lactones are important units of many natural products having medicinal value. Typical Baeyer Villiger oxidation[45] reaction (Scheme 1) of cycloalkanone (**1**) in the presence of non-toxic and inexpensive ferric oxide under aerobic condition was shown to result in biologically active lactone (**2**). The resence of an aldehyde is crucial to the reaction, as in the presence of Fe_2O_3 and molecular oxygen, the aldehyde forms an acylperoxy radical which subsequently abstracts a H-radical from another aldehyde to form a peracid. The in situ generated peracid reacts with the ketone in a similar way to produce the lactone.



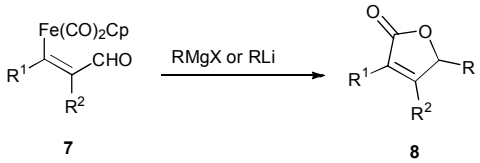
Scheme 1 *Synthesis of lactone ring* ***2***

The η^1-allyl-$CpFe(CO)_2$ complex prepared from allyl halide and $[Cp(CO)_2Fe]^-Na^+$ underwent [3+2]-cycloaddition reaction with electron deficient alkene to give $CpFe(CO)_2$ substituted cyclopentane derivative.[46] Removal of $CpFe(CO)_2$ becomes easy under oxidative cleavage to afford the cyclopentane derivative. On the other hand, β-lactone (**5**) or δ-lactone (**6**) were achieved via cationic η^3-allyltetracarbonyliron complex (**4**) prepared from 2-vinyloxirane (**3**) and pentacarbonyliron under photolysis followed by oxidative demetallation (Scheme 2). The two different product distributions are due to attachment of two different allyl termini to the metal.[47] The same strategy has been used in preparation of lactam.



Scheme 2 *Synthesis of lactone ring* ***5*** *&* ***6***

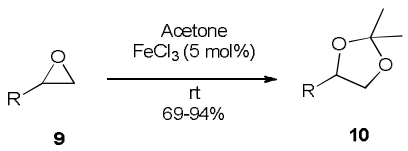
Similarly γ-lactone (**8**) has been achieved from $CpFe(CO)_2$ substituted enone or enal (**7**) via cyclocarbonylation in presence of metal hydride or metal alkyl (Scheme 3).[48] Use of organometallic compound such as alkyl lithium or Grignard reagent is crucial for such cyclocarbonylations.



Scheme 3 *Synthesis of lactone ring* ***8***

3.1.2. Acetonide derivatives

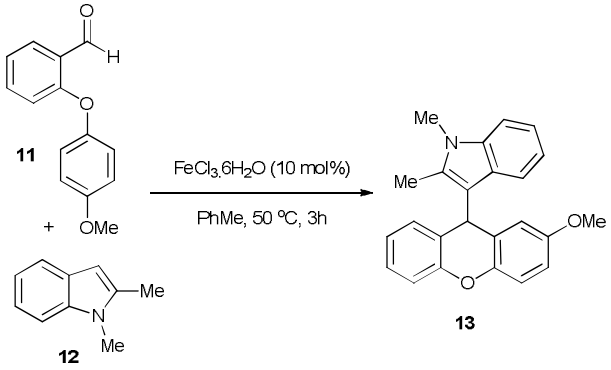
Synthetic use of masked diols is significant in carbohydrate chemistry. Iron(III) chloride was used as good catalyst for conversion of epoxide (**9**) into acetonide (1,3-dioxolane) (**10**) under mild and rapid condition (Scheme 4).[49] This method is useful for conversion of alkene into masked diol and subsequently to aldehyde without using well known toxic and harsh reagents, such as osmium tetroxide or Brønsted acid media. The reaction showed high regio- and stereo-selectivity at room temperature.



Scheme 4 *Synthesis of 1,3-dioxolane* ***10***

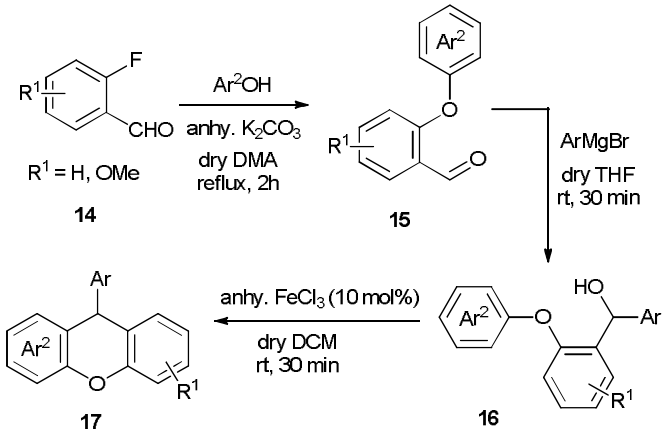
3.1.3. Xanthenes derivatives

Although several transition metal based reagents including iron have been exploited for C-C bond formation reaction, the reverse has not been fully explored. Carbon-carbon bond activation has been investigated by Li and co-workers using iron as catalyst. They reported C-C bond activation of tri-aryl methane produced in situ upon reaction of aldehyde (**11**) and N-methyl indole (**12**). This protocol has been shown to be useful in synthesis of 9-indolyl-substituted xanthene (**13**) using iron catalyst (Scheme 5).[50]



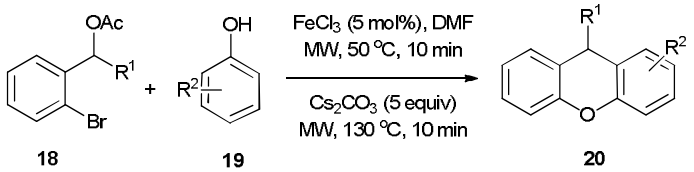
Scheme 5 *Synthesis of xanthene* ***13***

Synthesis of symmetrical and unsymmetrical 9-arylxanthenes (**17**) has been achieved through sequential aromatic nucleophilic substitution of commercially available 2-fluorobenzaldehydes (**14**) with arenoxides and proceeded through formation of arenoxybenzaldehydes (**15**) and carbinol (**16**) after Grignard reaction and $FeCl_3$-catalyzed intramolecular diarylmethylation in high yield (Scheme 6).[51] Similar strategy has also been applied for synthesis of 9-arylthioxanthenes. The reaction took place via cationic activation of diaryl carbinols in ambient condition.



Scheme 6 *Synthesis of 9-arylxanthenes* ***17***

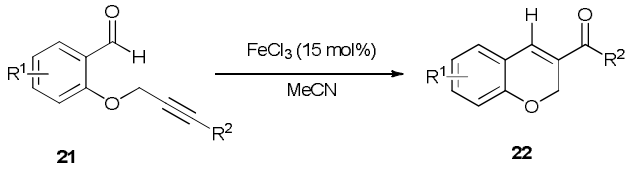
This result encouraged Li et al. to further development of 9-alky-substituted xanthenes. They achieved microwave-assisted one-pot synthesis of 9-substituted xanthene by a cascade benzylation-cyclization reaction using iron(III) chloride as catalyst (Scheme 7).[52] In this protocol, the reaction was claimed to be smooth for acetate (**18**) with an alkyl group at the benzylic position with various phenols (**19**) to afford 9-alkyl-substituted xanthene (**20**). In addition to benzyl acetate, benzyl bromide and benzyl carbonate were also suitable for this reaction scheme, but when benzyl alcohol was used as the benzylating agent only 29% yield was obtained.



Scheme 7 *Synthesis of xanthene* ***20***

3.1.4. 2*H*-Chromene derivatives

Biologically important functionalized chromenes are useful as precursors of flavonols, amines, and other important targets. Alkyne-aldehyde metathesis has been utilized for synthesis of functionalized 2*H*-chomene (**22**) via intramolecular alkyne-aldehyde metathesis (Scheme 8).[53] The reaction works well for both alkyl and aryl substituted alkyne (**21**), but was found unsuitable for terminal alkynes. A series of substituted 2*H*-chromenes have been synthesized and remained compatible toward a wide range of functional groups, such as methoxy, fluoro, chloro, bromo and phenyl groups. The reaction was expected to follow formal [2+2] cycloaddtion scheme to form oxetane intermediate, followed by cycloreversion to produce 2*H*-chromene completely regioselectively. One pot preparation of 3-nitrochromene was also shown to be efficient in presence of $FeCl_3$-piperidine under refluxing condition in toluene through sequential nitroalkene/Michael addition/aldol condensation reactions.[54]

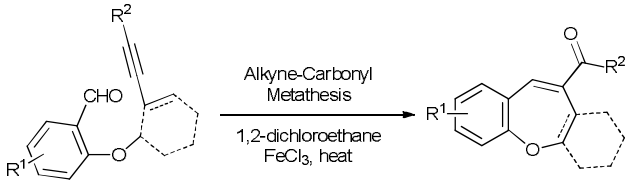


21 **22**

Scheme 8 *Synthesis of substituted 2H-chromene* ***22***

3.1.5. Benzo[b]oxepine derivatives

Later on, the same group has extended the alkyne-aldehyde metathesis procedure for synthesis of dibenzo[*b*,*f*]oxepine and benzo[*b*]oxepine (**24**) derivatives using $FeCl_3$ catalyst with high regio- and chemoselectivity (Scheme 9).[55] This method worked well for both electron-donating and electron-withdrawing aryl substituted alkyne (**23**), but did not work for alkyl substituted alkyne. This method proved to be selective and useful over the normal 8-*endo*-trig cyclization.



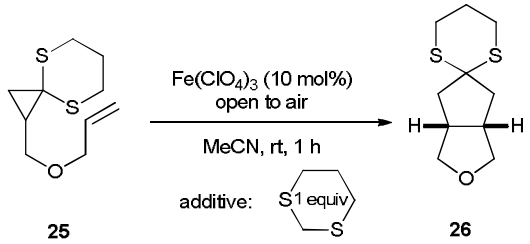
23 **24**

yield 53-95%

Scheme 9 *Synthesis of benzo[b]oxepine* ***24***

3.1.6. Tetrahydrofuran derivatives

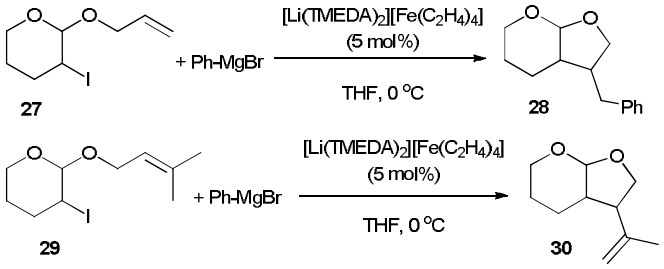
Oxidative cyclization of two or more unsaturation part of a molecule via stoichiometric amount of Fe-complex mediated reaction had been utilized for the past two to three decades.[56] Strained rings like cyclopropane (**25**) underwent indirect oxidative cleavage in presence of 10 mol% iron-perchlorate in open air condition and cyclised in presence of suitable acceptor unit, alkene to form bicyclic compound (**26**) through the C-C bond opening and bond forming reaction (Scheme 10).[57] The reaction was supposed to undergo on SET induced C-C bond cleavage reaction. 1,3-Dithiane was important to reduce the side reaction by reducing the intermediate properly.



25 **26**

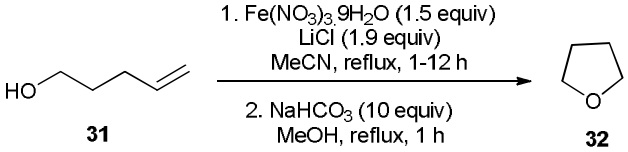
Scheme 10 *Synthesis of tetrahydrofuran* ***26***

The remarkable efficiency of cross coupling reaction of organic nucleophile with organic electrophile has led to combination of a smaller unit into a larger unit avoiding stepwise synthesis. Alkyl halide (**27** or **29**) and Grignard reagent underwent cross-coupling reaction in presence of iron catalyst at low temperature to afford bicyclic hexahydro-2H-furo[2,3-b]pyran skeletal (**28** or **30**) in good yield (Scheme 11).[58]



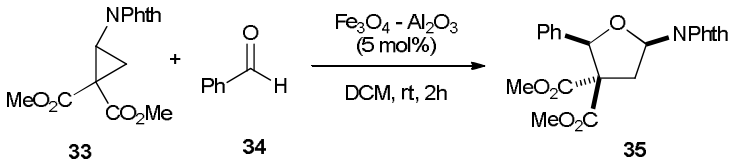
Scheme 11 *Synthesis of tetrahydrofurans* ***28 & 30***

The reaction possibly followed a radical pathway. The same reaction product was shown to be feasible in presence of catalyst $FeCl_2$ and alkyl bromide.[59]



Scheme 12 *Synthesis of tetrahydrofuran* ***32***

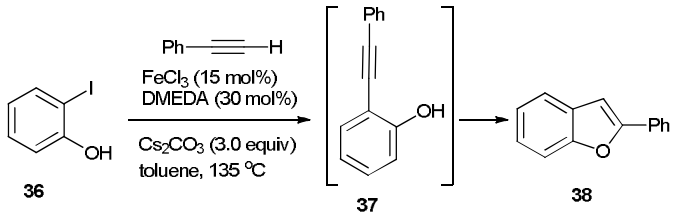
Tetrahydrofuran (**32**) was synthesized effectively via sequential chloronitration, elimination and Michael addition reaction from suitably substituted alkene (**31**) using $Fe(NO_3)_3$ as catalyst (Scheme 12).[60] This method was exclusively used for synthesis of pyrrolidine. An intramolecular ring expansion strategy of epoxide has been utilised using Fe-NHC catalytic condition, where $FeCl_2$ was used as pre-catalyst.[61] 2-Aminotetrahydrofuran is the common structural motif of nucleosides and are useful as therapeutic agents for the treatment of cancer, infections, and viral diseases. Iron(III) chloride mediated stereoselective [3+2] annulations and atom economic route for synthesis of 2-aminotetrahydrofuran (**35**) from aminocyclopropane (**33**) and aldehyde (**34**) has been described.62 This reaction is effective for a number of aldehydes with excellent yield (Scheme 13). Here aminocyclopropanes act as three-carbon zwitterionic synthons and subsequently underwent cycloaddition reaction with aldehyde to afford 2-aminotetrahydrofurans.



Scheme 13 *Synthesis of tetrahydrofuran* ***35***

3.1.7. Furan derivatives

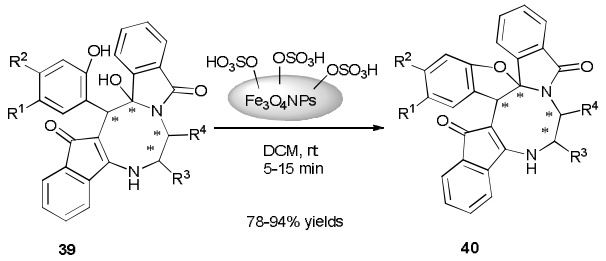
Iron complex [$FeCl_3$-DMEDA] catalyzed double domino reaction with halo-phenol (**36**) and alkyne results in benzofuran (**38**) and indole via cross-coupling and cycloisomeristion processes.[63]



Scheme 14 *Synthesis of benzofuran* ***38***

Cross-coupling results in the intermediate compound **37** which subsequently cycloisomerises to benzofuran with moderate yield (Scheme 14).

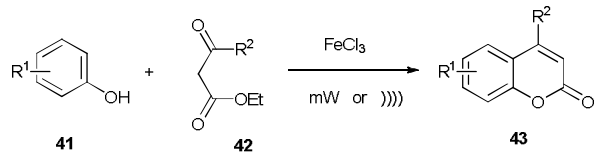
Fe_3O_4–SO_3H nanoparticles have been recognized as effective catalysts for synthesis of dihydrofuran (**40**) fused with cyclooctanoid via dehydration reaction of dihydroxy cyclo-octanoid heterocylce (**39**) (Scheme 15).[64] In this process, the catalyst remains active after five cycles and worked well even for acid sensitive groups like amide under ambient conditions. The short reaction time and high yield also makes the method smart in terms of higher member ring rupture and avoids tedious purification procedure.



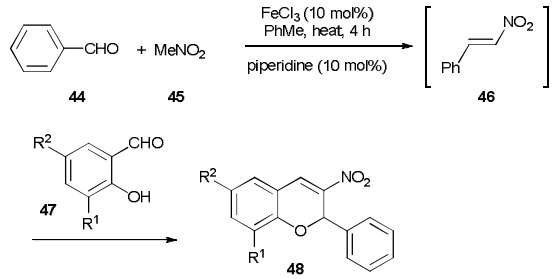
Scheme 15 *Synthesis of dihydrofuran* ***40***

3.1.8. Coumarin derivatives

Natural 3-oxo-3H-benzopyrans,[65] commonly termed as coumarins, are well known pharmaceutical, aromatic, agrochemical and insecticidal agents. 4-substituted coumarin (**43**) from phenol (**41**) and 1,3-diketone (**42**) has been synthesized under solvent free condition using ultra-sound assisted $FeCl_3$ catalyst with high efficiency (Scheme 16). With this protocol, the use of hazardous materials was minimized to make the process environmentally friendly for Pechmann reaction. They have shown high yield of coumarins at 100 ^oC using 150W within 1-20 min. The same catalyst was shown to useful for synthesis of 3-nitrochromene (**48)** from sequential formation of nitroalkene (**46**) from aldehyde (**44**) and nitromethane (**45**)/Michael addition/aldol condensation reactions with salicylaldehyde **(47)** (Scheme 17)[96]



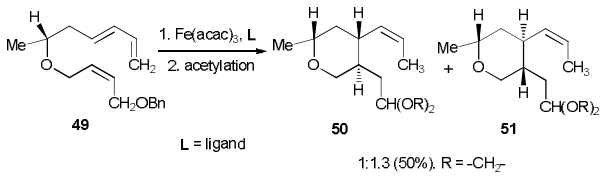
Scheme 16 *Synthesis of coumarin* ***43***



Scheme 17 *Synthesis of 3-nitrochromene* ***48***

3.1.9. Tetrahydropyran derivative

Takacs and co-worker have reported the stereoselective synthesis of bicyclic ring in presence of Fe-catalyst using enediene carbocyclization. This tool was shown to be useful for synthesis of several hetero-bicyclic ring compounds, *e.g.* tetrahydropyran, indolizidine and quinolizidine which was effective for the substrate undergoing Fe-enediene complexation.[66] The enediene carbocyclization of **49** occurs smoothly to yield tetrahydropyrans (**50, 51)** in 1:1.3 ratio (Scheme 18). Thus stereoselectivity and product formation are solely dependent on the substituted ring attached to the enediene and the nature of the ligand used with the pre-catalyst, $Fe(acac)_3$. It was claimed that the reaction proceeded through oxidative cyclization and the bisoxazoline-modified catalyst was superior under the reaction condition.



Scheme 18 *Synthesis of tetrahydropyran* ***50*** *&* ***51***

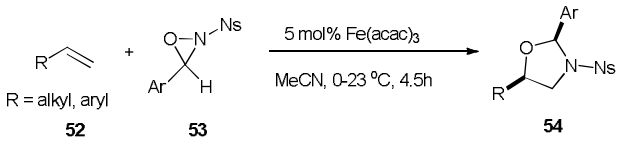
3.2. Nitrogen-Oxygen Heterocyles

3.2.1. Oxazolidine derivatives

Osmium-catalyzed[67] Sharpless aminohydroxylation is a well established method in this area. Atom

economy is demonstrated, and hazardous transition metals like Os, Pd, Cu have been replaced by appropriate choice of inexpensive, non-toxic first row transition metal Fe as catalyst in aminohydroxilation of alkene. The aminohydroxylation reactions have been reported either via intramolecular[68] reaction or via intermolecular[69] reaction with activation of N-O bond to form either substituted oxazolidine or substituted oxazolidin-2-one.

The first Fe-catalyzed aminohydroxylation reaction was discovered by Williamson and Yoon in 2010 via oxaziridine activation reaction. *N*-sulfonyl oxaziridine (**53**) reacted with alkene (**52**) in presence of 5 mol% $Fe(acac)_3$ to afford 2,5-substituted oxazolidine (**54**) which is regioisomeric with 2,4-substituted oxazolidine form in presence of a copper catalyst (Scheme 19).[70]

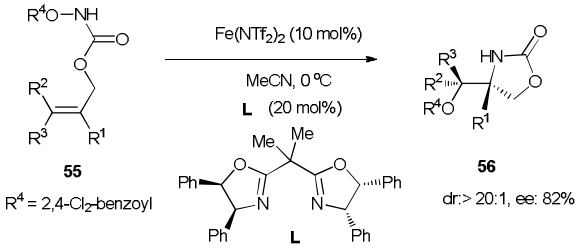


Scheme 19 *Synthesis of oxazolidine* ***54***

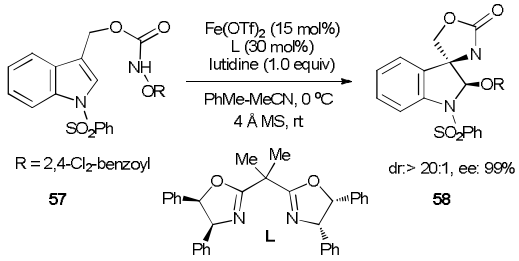
3.2.2. Oxazolidinone derivatives

Similar to aminochlorination, intramolecular aminohydroxylation of olefins with functionalized hydroxylamine (**55**) catalyzed by iron(II)-complex have been reported in 2013 (Scheme 20).[68] This method is useful for synthesis of amino alcohols with excellent selectivity (*dr* up to > 20:1), although selectivity depends on the selection of counteranion/ligand combinations. Based on the experimental results, it was assumed that the reaction proceeds via iron nitrenoid intermediate to form substituted oxazolidin-2-one (**56**).

The same protocol worked well when it was applied to indole system for conversion of **57** to **58** with high enantioselectivity although diastereo-selectivity and yields were slightly lower (Scheme 21).[71] This reaction, catalyzed by iron(II)–chiral bisoxazoline (BOX) complexes, is useful for asymmetric synthesis of a series of biologically active 3-amino oxindoles and 3-amino indolanes.

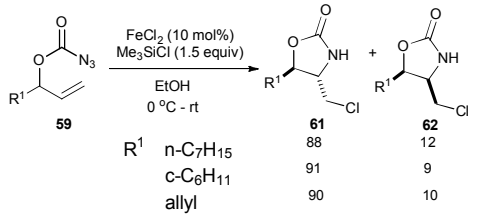


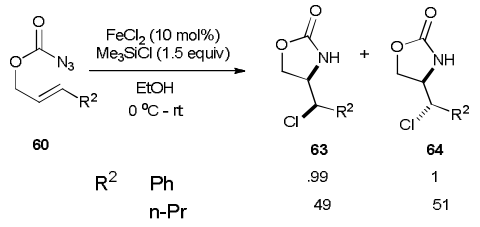
Scheme 20 *Synthesis of oxazolidinone* ***56***



Scheme 21 *Synthesis of oxazolidinone* ***58***

Aminochlorination of olefins has been shown to be productive by Fe(II)-catalyzed intramolecular reaction.[72] Substituted olefins has been transformed to oxazolidinones (**61-64**) diastereoselectively using catalytic amount of $FeCl_2$ in the presence of trimethylsilylchloride (Scheme 22). Although monosubstituted olefin (**59**) gave high diastereoselectivity, for the compound (**60**) having internal double bond, diastereoselectivity depends on the substitutents.

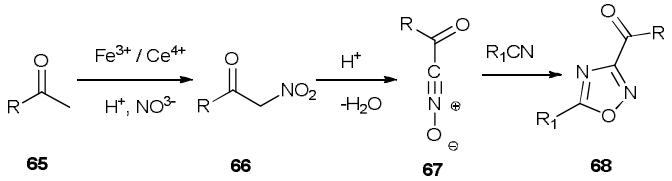




Scheme 22** Synthesis of oxazolidinones **61-64

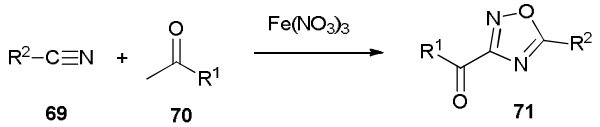
3.2.3. Oxadiazole derivatives

In last few years, 1,2,4-oxadiazoles are being used as ligands for metal catalyzed reactions.[73] 1,2,4-oxadiazoles are also biologically important, as recently 5-keto-1,2,4-oxadiazoles were established as anti-inflammatory agents.[74] The amidoxime route is well established for synthesis of 1,2,4-oxadiazoles.[75] New alternative one-pot iron(III) nitrate catalyzed synthesis of 3-acyl-1,2,4-oxadiazole (**68**) has been demonstrated from methyl ketone (**65**) (Scheme 23).[76] It has been considered that initially formed α-nitro ketone (**66**) underwent dehydration reaction to form nitrile oxide (**67**) and then nitrile underwent 1,3-dipolar cycloaddition reaction with nitrile oxide to form 1,2,4-oxadiazole (**68**).



Scheme 23** Synthesis of oxadiazole **68

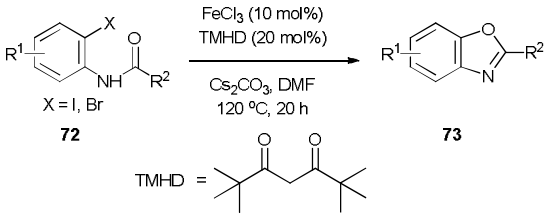
Iron(III) nitrate catalyzed reaction of nitrile (**69**) and acetophenone (**70**) at 80 °C also gave the corresponding 3-benzoyl-1,2,4-oxadiazole (**71**) derivative similar to cerium(IV) ammonium nitrate or via reductive process (Scheme 24).[77,78] This reaction was shown to be valuable for acetone to result 3-acetyl-1,2,4-oxadiazole derivatives as well.



Scheme 24** Synthesis of oxadiazole **71

3.2.4. Oxazoles derivatives

Medicinally significant benzoxazoles are privileged organic compounds due to their extraordinary biological activity.[79] The most common method for their synthesis involves toxic and harsh reaction condition with ortho-aminophenols.[80] More sustainable method under very mild condition has been reported using iron-catalyzed intramolecular O-arylation reaction, which yielded 2-substituted benzoxazoles. N-(2-Halophenyl)benzamide (**72**) underwent intermolecular O-arylation reaction in presence of $FeCl_3$ and 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) as catalytic combination, Cs_2CO_3 as base in DMF solvent at 120 °C to afford 2-substituted benzoxazole (**73**) in excellent yield (Scheme 25).[81]

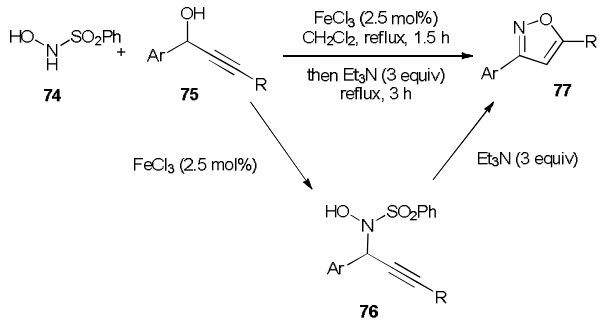


Scheme 25** Synthesis of benzoxazole **73

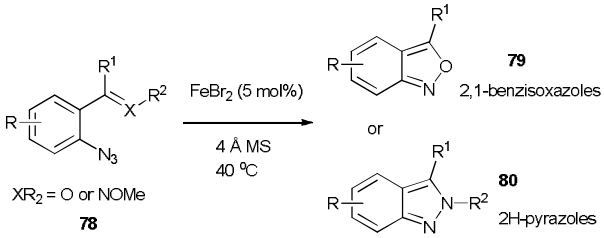
3.2.5. Isoxazole derivatives

Synthesis of isoxazole derivatives has been depicted by precious catalyst like $NaAuCl_4 \cdot 2H_2O$.[82] This has been replaced by one-pot $FeCl_3$ catalyzed reaction from N-hydroxy-benzene sulphonamide (**74**) and propargylic alcohol (**75**) in presence of Et_3N.[83] Bi-nucleophile N-hydroxy-benzene sulfonamide produced

propargyl hydroxylamine (**76**) in presence of 2.5 mol% $FeCl_3$, which then underwent cyclization to form isoxazole (**77**) in presence of 3.0 equivalent of Et_3N as confirmed from isolated steps (Scheme 26).



Scheme 26 *Synthesis of isoxazole **77***

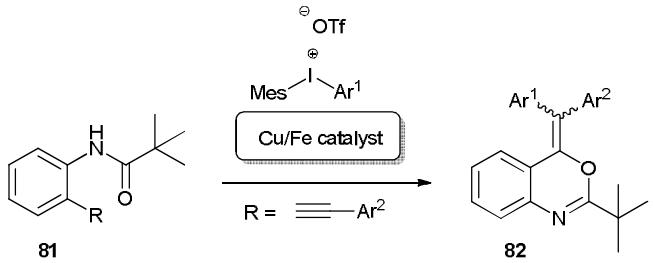


Scheme 27 *Synthesis of benzisoxazole **79** & pyrazole **80***

An Iron(II) catalyzed intramolecular N-O or N-N bond formation has been utilized for synthesis of 2,1-benzisoxazole (**79**), indazoles, or pyrazole (**80**) from vinyl and aryl azide (**78**) with ketone or methyl oxime substituents in *ortho*-position (Scheme 27).[84] Author claimed that reaction showed tolerance against a variety of functional groups, and proceed through the formation of Fe-azide complex leading to nucleophilic attack to the ketone or oxime. The scope of 2,1-benzisoxazoles in the synthesis of quinolines was shown.

3.2.6. Oxazines derivatives

Oxidative carboarylation ring closure protocols for synthesis of benzoxazine (**82**) from compound **81** have been demonstrated using copper on iron catalyst (Scheme 28).[85] The yield for such reaction is moderate. The reaction proceeds through the formation of C-O bond to form benzannulated oxazine.



Scheme 28 *Synthesis of oxazine **82***

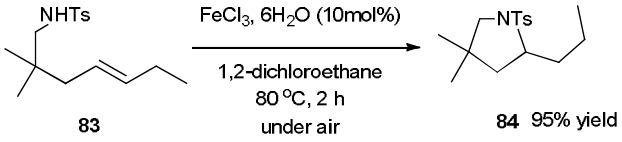
3.3. Nitrogen Heterocyles

Synthesis of indigenous natural scaffolds such as pyrimidine, quinoline, pyrole or indole is one of the most useful protocols using iron as catalyst as they can mimic actions of many biocatalysts. These heterocycles are not only useful in designing life-saving drugs, but are also useful in industry as well. Moreover, these processes are relatively fast, as products can be separated by either aqueous means or magnetically.

3.3.1. Pyrrolidine derivatives

Since the discovery of pyrrolinone in 1994[86] using $Fe(CO)_5$ via [4+1] cycloaddition reaction, synthesis of pyrrolidine heterocycle (**84**) via intramolecular hydroamination of γ-alkenyl sulphonamide (**83**) catalyzed by iron-catalyst have been reported in 2006 (Scheme 29).[87] This reaction showed higher functional-group compatibility and resistance to air and moisture. Very recently, Wang et al.[88] reported the synthesis of functionalized 2-pyrrolines from 2-phenyl-1-tosylaziridine with arylalkyne. The use of nitromethane as solvent at lower temperature gave better conversion with excess phenyl acetylene and no product with alkyl acetylene.

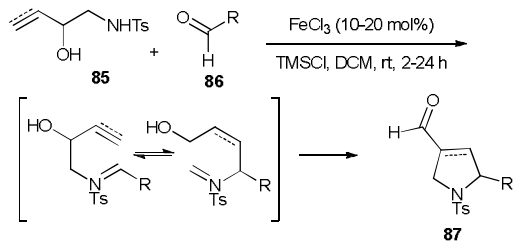
Interestingly, aziridine synthesis has also been developed from alkene and aryl azide using tetracarbene iron complex.[89]



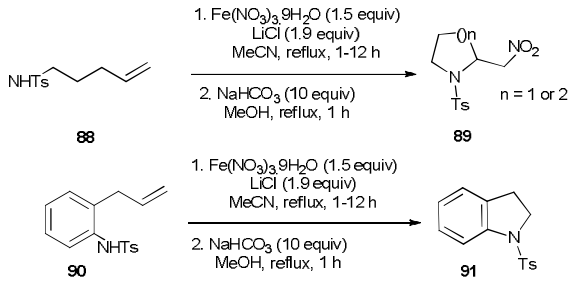
Scheme 29 *Synthesis of pyrrolidine* ***84***

Synthesis of *trans*-3,5-dialkyl pyrrolidines and 3,5-dialkyl-2,5-dihydro-1H-pyrroles has been reported using alkene aza-Cope-Mannich cyclization between 2-hydroxy homoallyl tosylamine (**85**) and aldehyde (**86**) in the presence of iron(III) salts as catalyst to afford 3-alkyl-1-tosyl pyrrolidine (**87**). The process is equally effective for stoichiometric and catalytic amount of iron(III) chloride under open air condition. Isolation of the product *trans* pyrrolidine-carbaldehyde became problematic due to instability, which has been minimized after reduction followed by isolation. This reaction condition is also suitable for alkyne aza-Cope-Mannich reaction between 2-hydroxy homopropargyl tosylamine and aldehydes to obtain 3-formyl-R,-unsaturated pyrrolidine (Scheme 30).[90]

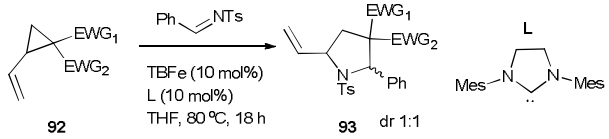
Similar to tetrahydrofuran, synthetic route of heterocycles such as pyrrolidine (**89**), piperidine and indoline (**91**) have been achieved using iron catalyst in one pot via sequential chloronitration, elimination and Michael addition reaction (Scheme 31). It was presumed that $Fe(NO_3)_3$ underwent decomposition to form NO_2^+ and the extreme reactivity of NO_2^+ is the main reason for this reaction with the alkenes **88** and **90**.[91]



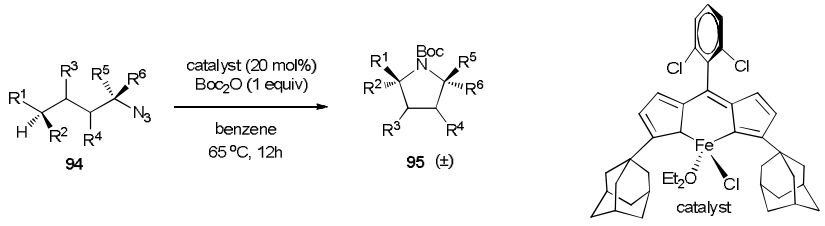
Scheme 30 *Synthesis of pyrrolidine* ***87***



Scheme 31 *Synthesis of pyrrolidine* ***89*** *and indoline* ***91***



Scheme 32 *Synthesis of pyrrolidine* ***93***



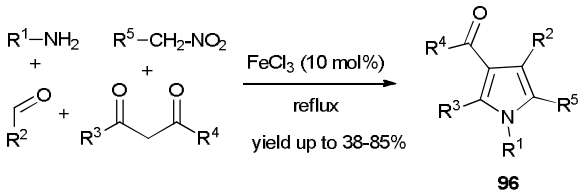
Scheme 33 *Synthesis of pyrrolidine* ***95***

On the other hand, vinyl cyclopropane (**92**) was subjected to [3 + 2] cycloaddition reaction with imines in presence of catalytic TBAFe {$Bu_4N[Fe(CO)_3(NO)]$} and NHC ligand to afford the pyrrolidine (**93**) derivative in good yield (Scheme 32).[92]

It is always a concern to make C(sp^3)-H reactive under any circumstances. Scientific development makes it possible even in chemical synthesis. Recently, the most attractive method has been shown by Betley in the synthesis of N-heterocycle (**95**) using iron-dipyrrinato catalyst via direct amination of aliphatic C-H activation (**94**) (Scheme 33).[93]

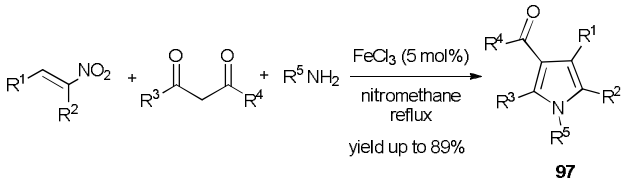
3.3.2. Pyrrole derivatives

$FeCl_3$ catalyst has been effective and simple to handle for four-component coupling synthesis of highly functionalized pyrrole (**96**) from 1,3-dicarbonyl compound, amine, aromatic aldehyde, and nitroalkane (Scheme 34).[94] This method is superior compared to the existing methods due to inexpensive and environmentally friendly catalyst, inexpensive and readily available components, direct introduction of functional group, moderate to high yielding products, and tolerance against a number of functional groups.



Scheme 34 *Synthesis of pyrrole* ***96***

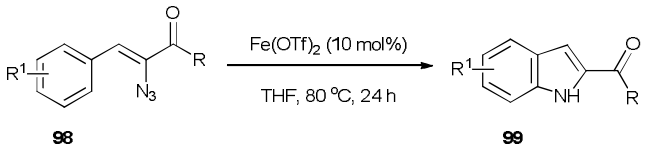
Modified three-component coupling synthesis of varieties of N-aryl substituted pyrrole (**97**) has been also described by the same workers in 2013 (Scheme 35).[95] This method described a straightforward approach for the synthesis of N-aryl substituted pyrroles from easily accessible starting materials such as nitroalkenes such as β-nitrostyrene derivatives, 1,3-dicarbonyl compounds such as ethyl acetoacetate, methyl acetoacetate, acetyl acetone and primary aromatic amines. The Fe(III)-catalyzed reaction proceeds through sequential amination-Michael-cycloisomerization reactions. Synthesis of N-arylpyrrole has been shown to be effective under almost same catalytic conditions in refluxing condition from aromatic aldehyde, nitromethane, aromatic amine and 1,3-diketone using toluene as solvent.[96]



Scheme 35 *Synthesis of pyrrole* ***97***

3.3.3. Indole derivatives

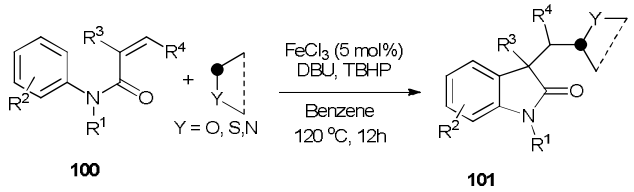
Intramolecular C-H amination is one of the best protocols for synthesis of N-heterocycles. The earliest synthetic method of biologically important compound *e.g.* indole was Fischer indole synthesis and has been abandoned due to low yield. Thermolysis of azide has been used for this purpose quite impressively, which proceeded through nitrene insertions but high exothermic nature of the reaction led researchers to seek alternatives on several occasions.[97] Bonnamour and Bolm (Scheme 36) have shown that iron salts can be effective for activation of azide (**98**) and thereby are useful for synthesis of indole derivatives (**99**).[98]



Scheme 36 *Synthesis of indole* ***99***

Synthesis of bio-active popular oxoindole[99] unit has been of great interest from ortho-functionalized anilines and noble-metal catalysts. Due to commercially non-availability of ortho-functionalized anilines, Li and his coworkers have established iron catalyzed oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp^2)-H and a C(sp^3)-H bond adjacent to a heteroatom for selective synthesis of functionalized 3-(2-oxoethyl)indolin-2-ones.[100] In this reaction $FeCl_3$ was used as catalyst, TBHP as oxidant and DBU as ligand. Investigation of reaction mechanism suggest that there was no kinetic isotope effect and the reaction proceeded

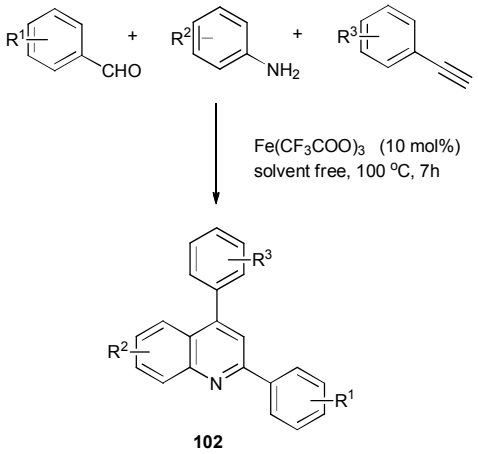
through the formation of radical intermediate after C(sp^3)-H bond activation with TBHP. The generated radical adds to the activated alkene (**100**) followed by intramolecular cyclization with aryl ring result arenium radical and subsequent aromatization result oxindole (**101**) (Scheme 37).



Scheme 37 *Synthesis of oxoindole* ***101***

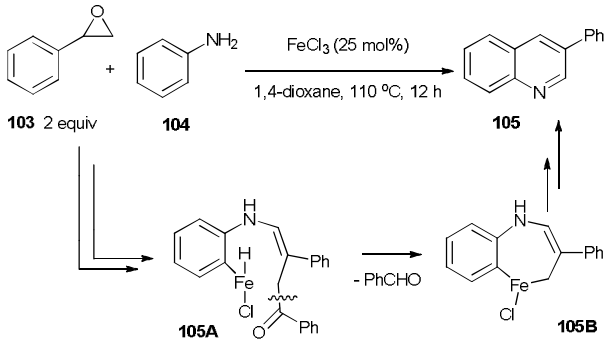
3.3.4. Quinoline derivatives

Nitrogen-containing heterocycles, particularly quinolines either hydrogenated or non-hydrogenated, are important structural motifs of several biologically active molecules.[101] Very recently, multicomponent synthesis of 2,4-diaryl substituted quinolines (**102**) have been achieved using $Fe(CF_3COO)_3$[102] and $Fe(OTf)_3$[103] via activation of a terminal alkyne C–H bond and formation of C-C bond under solvent-free conditions (Scheme 38).

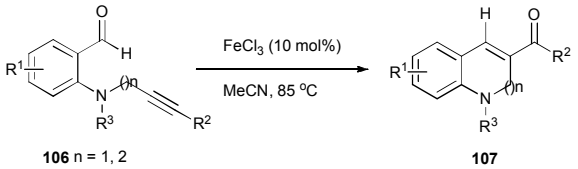


Scheme 38 *Synthesis of quinoline* ***102***

Quinoline derivative was effectively produced by $FeCl_3$ catalyzed reaction of styrene epoxide (**103**) and aniline (**104**).[104] The reaction proceeded through the C-H bond activation. Initially formed **105A** converted to cyclometalated species (**105B**), which underwent reductive elimination followed by oxidation to give the desired product **105** (Scheme 39). On the other hand, Jana et al. reported the synthesis of 1,2-dihydroquinoline and dihydrobenzo[b]-azepine derivative (**107**) using the same catalyst in acetonitrile solvent via intramolecular alkyne–aldehyde metathesis from **106** (Scheme 40).[105] This method has been extended for the synthesis of 3,4-substituted 1,2-dihydroquinolines via intramolecular alkyne–ketone metathesis. Similar to 2*H*-chromene, the reaction follows formal [2+2] cycloaddtion to form oxetane intermediate, followed by cycloreversion producing 1,2-dihydroquinoline or benzo[b]azepine completely regioselectively.

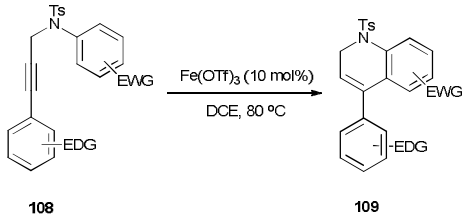


Scheme 39 *Synthesis of quinoline* ***105***



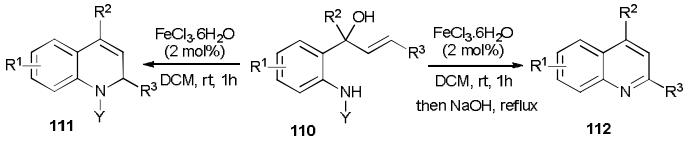
Scheme 40 *Synthesis of dihydroquinoline* ***107***

Intramolecular hydroarylation of electron deficient arene was found to be effective for the formation of 1,2-dihydroquinoline derivative and virtually ineffective for electron rich arene.[106] However, *N*-propargyl electron rich aryl ring (**108**) significantly accelerated the reaction rate for the formation of 1,2-dihydroquinoline derivative (**109**). This Friedel-Craft type iron triflate catalyzed reaction in dichloroethane proceeded through exclusive 6-*endo*-dig-cyclization via the formation of vinyl cationic intermediate (Scheme 41). Hydroarylation of o-alkynyl biaryls system worked well under the similar reaction condition but with longer time to result phenathene unit.



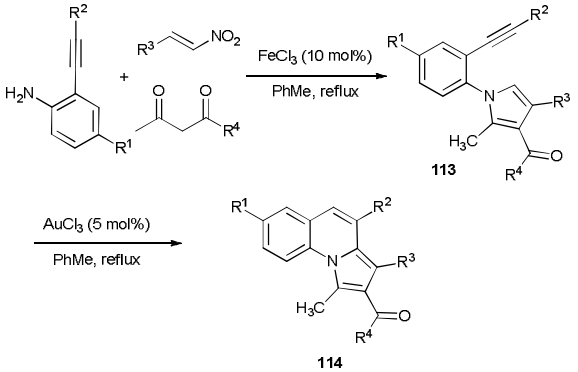
Scheme 41 *Synthesis of 1,2-dihydroquinoline* ***109***

Substituted 1,2-dihydroquinolines and quinolines have been reported using $FeCl_3.6H_2O$ via intramolecular allylic amination of *N*-protected 2-aminophenyl-1-en-3-ols (**110**).[107] The reaction proceeded in similar manner as that of intermolecular *N*-alkylation of allylic alcohol.[108,112] This method is almost equally efficient for preparation of substituted 1,2-dihydroquinoline (**111**) as that of substituted quinoline (**112**) in the same reaction vessel after treatment with NaOH in ambient air (Scheme 42).



Scheme 42 *Synthesis of 1,2-dihydroquinoline* ***111*** *and quinoline* ***112***

Polyfunctional pyrrolo[1,2-a]-quinoline derivatives (**114**) were achieved through sequential condensation-Michael addition-cyclization reactions.[109] The iron(III)-catalyzed three-component coupling of nitro-olefine, 1,3-dicarbonyl compound and 2-alkynylaniline derivative to form **113**, followed by second metal-catalyzed intramolecular hydroarylation of the alkyne unit, produced the tricyclic compound **114** in moderate to good yield (Scheme 43).

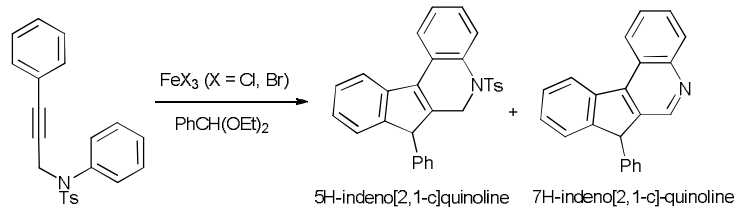


Scheme 43 *Synthesis of pyrrolo[1,2-a]-quinoline* ***114***

However, tandem carboarylation/cyclization of propargylaniline (**115**) with diethyl benzaldehyde acetal afforded the tetracyclic core of indeno[2,1-c]quinolines in presence of iron(III) salt (Scheme 44).[110]

Loading of catalyst and different temperature alter the ratio of products. Low catalyst loading resulted 5-tosyl-6,7-dihydro-5*H*-indeno[2,1-c]quinoline (**116**) whereas higher one furnished 7*H*-indeno[2,1-c]-quinoline (**117**) at optimized temperature (80 ^{o}C). Nonetheless, $FeBr_3$ acted more efficiently than $FeCl_3$ or $FeCl_3.6H_2O$ at the optimized temperature. Arylpropargylaniline bearing *p*-OMe substitution gave lower yield of 5*H*-indeno[2,1-c]quinoline and undesired pathways with acetals heterocyclic aromatic aldehydes.

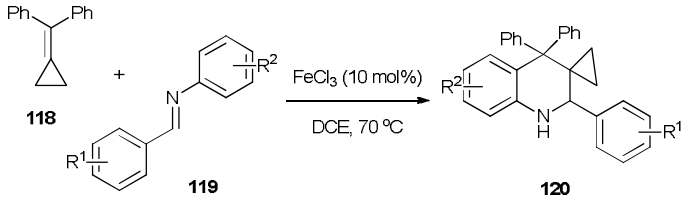
Entry	[Fe] equiv.	Temp (^{o}C)	5*H*-indeno[2,1-c] quinoline	7*H*-indeno[2,1-c] quinoline
1	$FeCl_3$ (0.3)	80	75	18
2	$FeCl_3$ (3.0)	80		73
3	$FeBr_3$ (3.0)	80		82
4	$FeBr_3$ (3.0)	100		69
5	$FeBr_3$ (3.0)	25	34	31



Scheme 44 *Synthesis of 5H-indeno[2,1-c]quinoline* ***116*** *and 7H-indeno[2,1-c]quinoline* ***117***

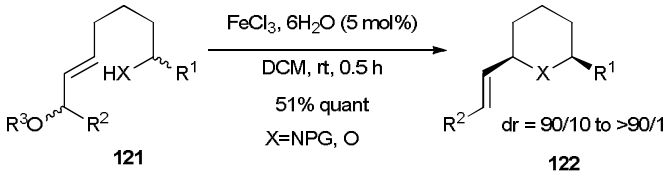
3.3.5. Piperidine derivatives

Lewis acid catalyzed aza-Diels–Alder reaction of methylenecyclopropane (**118**) with imine (**119**) affords well recognized method for synthesizing tetrahydroquinoline. Lewis acids of high cost and toxic nature prompted search for a low-cost and eco-friendly catalyst. In this regard, iron(III) chloride was used as an efficient catalyst for synthesizing natural-product-like molecule, tetrahydroquinoline (**120**) with a spirocyclopropyl (Scheme 45).[111]

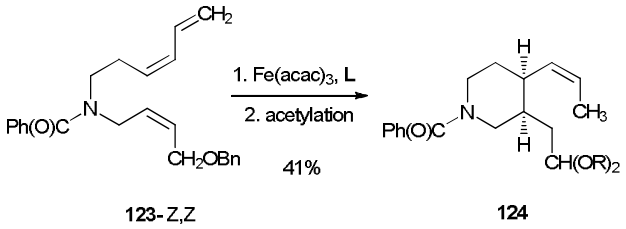


Scheme 45 *Synthesis of tetrahydroquinoline* ***120***

Diastereoselective synthesis of substituted *cis*-2,6-piperidine and *cis*-2,6-tetrahydropyran derivative (**122**) using eco-friendly reaction condition have been described by Cossy and co-workers (Scheme 46).[112] They have used inexpensive iron(III) chloride to activate allylic acetates or allylic alcohol of ζ-amino and ζ-hydroxy allyl alcohol derivative (**121**) through the formation of carbocation, which was confirmed from the formation of more thermodynamically stable *cis*- product exclusively.



Scheme 46 *Synthesis of piperidine* ***122***



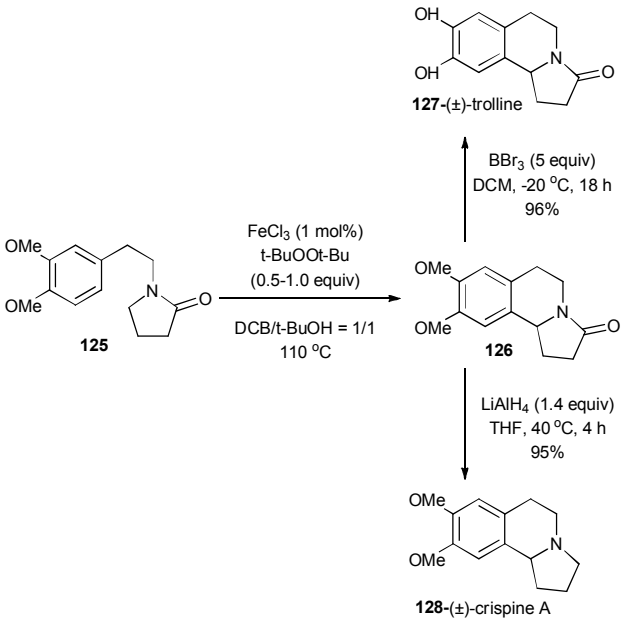
123- Z,Z **124**

Scheme 47 *Synthesis of piperidine* ***124***

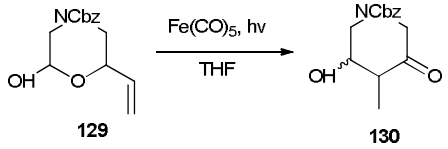
However, configuration of allylic double bond has no influence on the *cis*/*trans* ratio of the double bond of piperidines. Similar to the synthesis of tetrahydropyrans (**50, 51**), synthesis of *syn*-substituted piperidine (**124**) has been achieved from **123** using $Fe(acac)_3$ and bipyridine ligand via [4+2] cycloddition (Scheme 47).[66]

During their synthetic development of iron-catalyzed oxidative coupling of alkylamide with aromatic compound through oxidation of alkylamide, Shirakawa et al. extended the synthesis of isoquinoline alkaloids (±)-trolline (**127**) or (±)-crispine A (**128**).[113] Pyrrolidinone (**125**) forms tetrahydropyrrolo[2,1-a]isoquinolinone derivative (**126**) via ferric chloride catalyzed reaction under elevated temperature (Scheme 48).

Mac et al. have shown iron-catalyzed intramolecular tandem isomerization-aldolization process of **129** for synthesis of 4-methyl-3-piperidone (**130**). In this process they used 10 mol% $Fe(CO)_5$ as the catalyst to get aldols as mixture of stereoisomers (Scheme 49).[114]

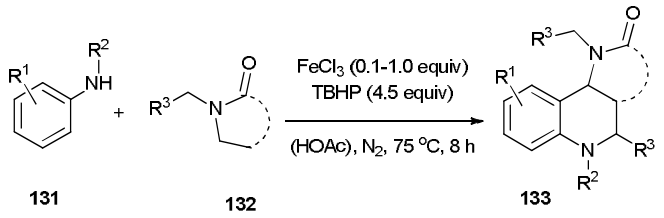


Scheme 48 *Synthesis of isoquinoline alkaloids* ***127*** *&* ***128***



Scheme 49 *Synthesis of piperidone* ***130***

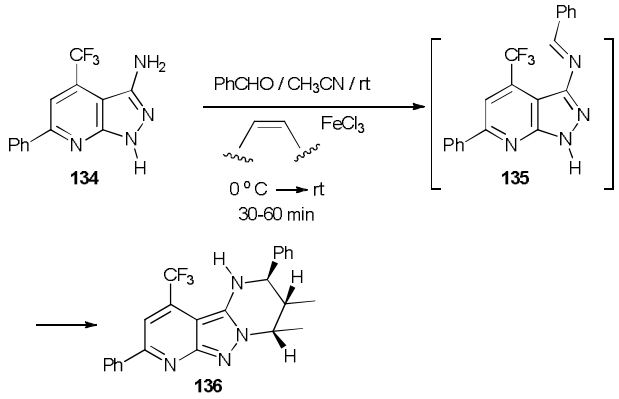
Recently, ring-fused tetrahydroquinoline derivative (**133**) has been synthesized from arylamine (**131**) and N-substituted lactam (**132**) through one pot multiple cross-dehydrogenative-coupling using TBHP as oxidant and iron(III) chloride as catalyst (Scheme 50).[115] In this process, two C–C bonds and one C–N bond were formed and one C–N bond was cleaved to form ring-fused tetrahydroquinoline derivatives.



Scheme 50 *Synthesis of tetrahydroquinoline* ***133***

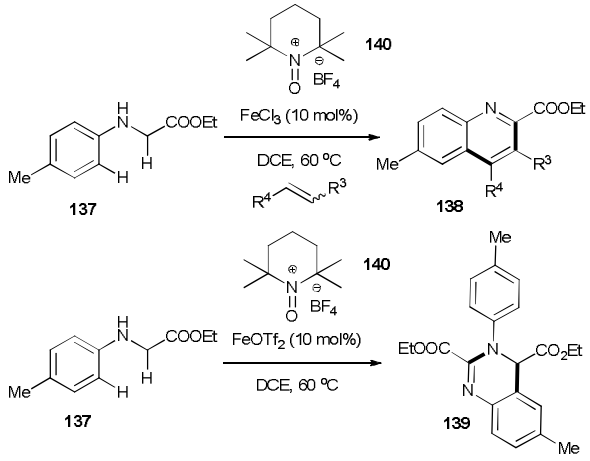
3.3.6. Pyrimidine derivatives

Iron(III) chloride catalyzed one-pot three component Grieco condensation of 3-aminopyrazolo[3,4-b]pyridine (**134**), formaldehyde/benzaldehyde and electron rich alkene produced tetrahydropyrido[2',3':3,4]pyrazolo[1,5-a]pyrimidine (**136**).[116] The reaction proceeded through the formation of intermediate imine **135** (Scheme 51)**.** The reaction is highly regioselective in nature and follows aza-Diels Alder type reaction at room temperature. Recently, synthesis of H-pyrazolo[5,1-a]isoquinolines has been achieved from the reaction of N_9-(2-alkynylbenzylidene)hydrazide with tertiary amine via C-H activation. The reaction was shown to be effective in presence of silver triflate and an iron catalyst with TBHP.[117]



Scheme 51 *Synthesis of tetrahydro pyrimidine* ***136***

3.3.7. Quinazoline derivatives

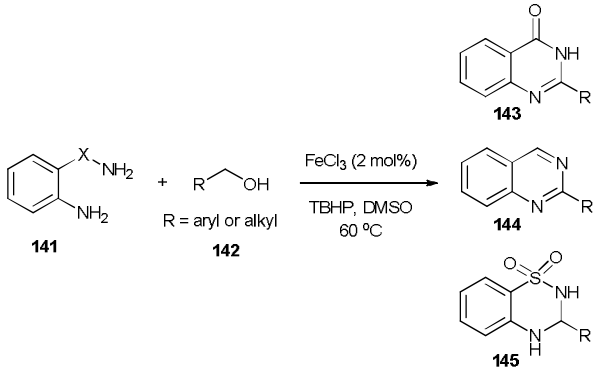


Scheme 52 *Synthesis of quinoline* ***138*** *and quinazoline* ***139***

Divergent oxidative tandem syntheses of quinoline (**138**) and dihydroquinazoline (**139**) from N-alkylaniline (**137**) have been reported using iron-catalyzed reaction in presence of TEMPO oxoammonium salt (**140**) (Scheme 52).[118] Different products are formed depending on choice of the iron catalyst. The reaction proceeds through C(sp^3)-H activation followed by C-C or C-N bond formation. Then dehydrogenative cyclization-oxidation afforded the corresponding products. The same protocol was shown to be useful for one-pot synthesis of quinolines from anilines, aldehydes, and olefins (Scheme 52).

Quinazolinone synthesis from 2-halobenzoic acid derivative with amidines under microwave heating,

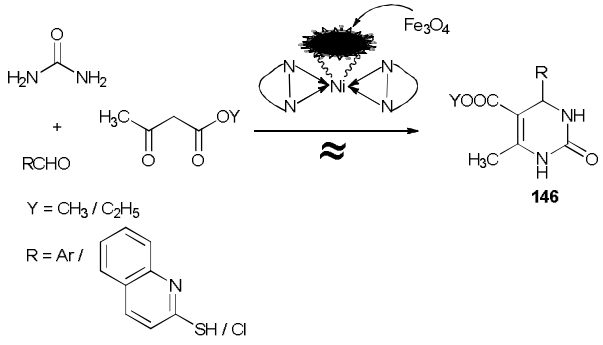
with or without ligand in water or DMF as solvent, has been reported by a group of workers in **2009**.[119] A general method for synthesis of quinazolinone (**143**), quinazoline (**144**) and 3,4-dihydro-2*H*-1,2,4-benzothiadiazine-1,1-dioxide (**145**) derivatives has been developed using iron-catalyzed one-pot one-step oxidative system (Scheme 53) from alcohol (**142**) and suitable aryl amine derivatives (**141**).[120]



Scheme 53 *Synthesis of quinazolinone* ***143,*** *quinazoline* ***144*** *and dihydro-benzothiadiazine-dioxide* ***145***

3.3.8. Pyrimidine derivatives

In 2014, Girija et al. have shown the synthesis of 3,4-dihydropyrimidine (**146**) using Fe_3O_4 nanoparticle supported Ni(II) complexes (Scheme 54).[121] The catalyst used in the Biginelli reaction has been recovered magnetically and remained active up to five cycles without significant loss of activity.

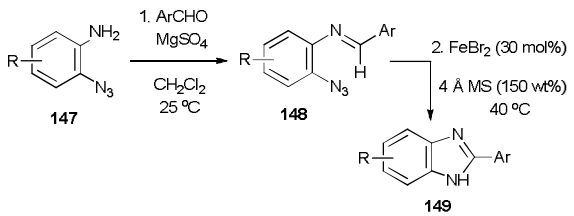


Scheme 54 *Synthesis of dihydropyrimidine* ***146***

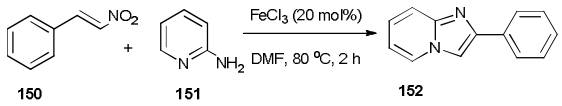
3.3.9. Imidazole derivatives

Thermolysis or photolysis of azides typically produces highly reactive intermediate nitrene, which subsequently reacts with olefin and C-H bond resulting in less selective products. In large scale, the reaction is ineffective due to its explosive nature.[122] Under thermal conditions, azide has been exploited in several C-N bond formation reactions.[123] But transition metal catalyzed reaction of azide gives low temperature reaction with selective reaction. Imine (**148**), ortho to aryl azide produced from **147,** facilitated the formation of benzmidazole (**149**) in presence of Iron(II) bromide (Scheme 55).[124]

Synthesis of imidazo-[1,2-a]pyridine (**152**) from nitroolefin (**150**) and 2-aminopyridine (**151**) has been described in one-pot cascade reaction catalyzed by Fe(III) chloride in DMF solvent (Scheme 56).[125] Here, nitroolefins act as bielectrophiles and 2-aminopyridines acts as binucleophiles. This reaction proceeds through sequential Michael addition-cyclization-elimination process. Formal synthesis of the drug Zolimidine has also been reported using this methodology. Further one pot multi-component strategy have also shown using the same reaction sequence by the same group.[126]



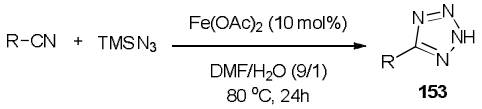
Scheme 55 *Synthesis of benzmidazole* ***149***



Scheme 56 *Synthesis of imidazo-[1,2-a]pyridine* ***152***

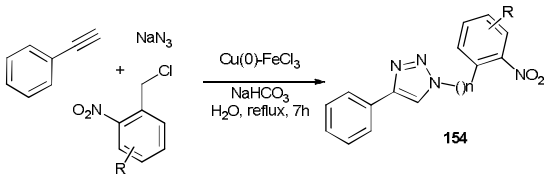
3.3.10. Tetrazole and triazole derivatives

Pharmaceutically and synthetically important tetrazole (**153**) can be synthesised from azide and nitrile via [2+3]-cycloaddition reaction (Scheme 57). There are several synthetic approaches using Zn(II)-salts,[127] Cu_2O,[129] TBAF[129] etc. Bonnamour and Bolm showed that iron(II) acetate was as effective as Cu_2O in 9:1 DMF/MeOH solvent at 80 °C when used with TMS-azide and aryl nitrile.[130] This method is high yielding for electron-rich aryl azide even in DMF/H_2O system. The method is highly demanding in its course of isolation process.



Scheme 57 *Synthesis of tetrazole* ***153***

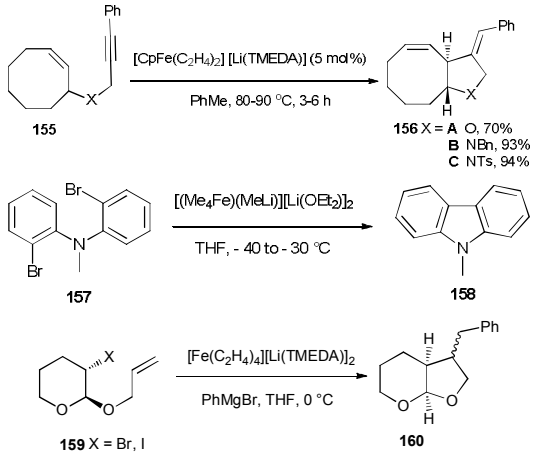
Kundu and co-workers have accomplished one-pot multicomponent reaction in water for the formation of triazole (**154**) using combined copper/iron catalyst (Scheme 58).[131] In this case, iron was suggested to serve as modulator for the oxidation state of copper. The reaction followed [3+2] cycloaddition reaction.



Scheme 58 *Synthesis of triazole* ***154***

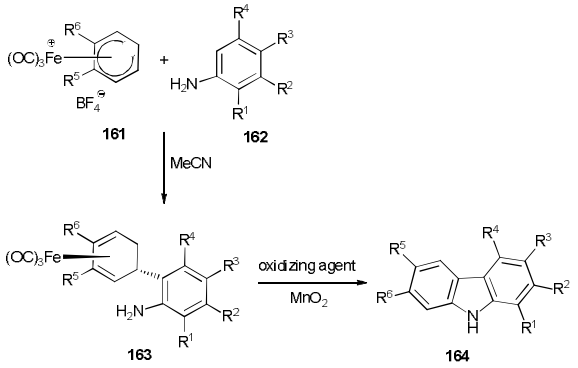
3.3.11. Carbazole derivatives

Characterization of the actual catalyst was found to be difficult in the cross-coupling reaction catalyzed by in situ generated low valent Fe-species from Fe(III) and excess RMgX. To avoid this, Früstner used Fe(0)-ate and Fe(II)-ate complexes to study the reaction mechanism and found that these surrogates worked well even for aryl magnesium halides.[132] These electron-rich systems could catalyse Alder-ene type reaction with enynes (Scheme 59). Enynes with cyclooctene (**155**) or cycloheptene gave *trans* annulated bicyclic oxygen or nitrogen heterocyclic compounds (**156A**) with Z-exocyclic double bond in presence of lithium ferrate complexes (LFC).[133] LFC are effective even in cross coupling reaction for organic halides like chloride and bromide in so called metal-like Pd, Ni-catalysts. LFC acted as single electron transfer (SET) agent which induces the homo-coupling reaction of aryl bromide (**157**) to give low valent iron-catalyzed cross coupling reaction to yield carbazole (**158**). Single electron transfer by LFC also helped the cyclization of halo acetal (**159**) in presence of alkene or alkyne through 5-*exo*-trig or dig ring closure with or without subsequent cross coupling to form furopyran (**160**).[134]



Scheme 59 *Synthesis of bicyclic* ***156,*** *carbazole* ***158,*** *furopyran* ***160***

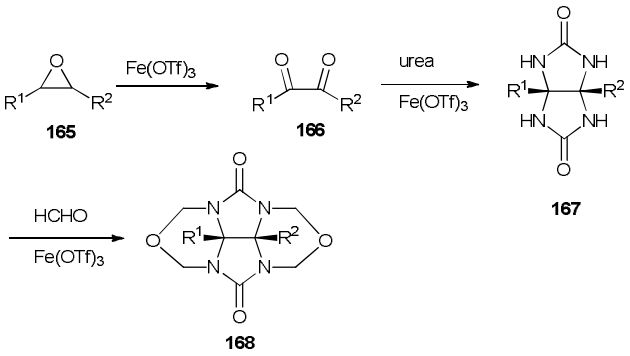
Synthesis of carbazoles from cationic tricarbonyl(η^5-cyclohexadienyl)iron complex (161) with aromatic amine (162) has been afforded (Scheme 60). The reaction proceeds through oxidative cyclization and subsequent aromatization in presence of oxidizing agents.[135] Initial oxidation of the arylamine to a quinonimine (163) followed by oxidative cyclization to an iron-coordinated 4b,8a-dihydrocarbazol-3-one and demetallation to a 3-hydroxycarbazole (164) has been described (Scheme 60).[136]



161 162 163 164

Scheme 60 *Synthesis of carbazole* ***164***

3.3.12. Glycoluril derivatives



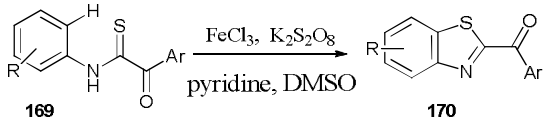
165 166 167 168

Scheme 61 *Synthesis of glycoluril diether* ***168***

$Fe(OTf)_3$ has been shown to be effective for three different reactions to produce an α-diketone from epoxide (**165**), in oxidative ring-opening reaction, to give glycoluril (**167**) from urea, in α-diketone (**166**) condensation, and in glycoluril diether (**168**) synthesis by formaldehyde condensation (Scheme 61).[137] The reaction is convenient for synthesis of α-hydroxy ketone from simple substrate like alkene over other oxidation protocol.

3.3.13. Benzothiazole derivatives

Pharmaceutically important heterocyclic compounds such as benzothiazole derivative (**170**) has been synthesized from N-phenylethanethioamide (**169**) using ferric chloride as catalyst (Scheme 62).[138] Use of pyridine as additive was shown to be more crucial than heat. High selectivity and mild reaction condition of this process was shown to be practical for scaling up of the synthetic step due to low waste product and easy separation process.



169 170

Scheme 62 *Synthesis of benzothiazole* ***170***

4. CONCLUSION

In this review, we have summarized recent progress in iron-catalyzed reactions in heterocyclic chemistry. Although there have been impressive developments in applications of such catalysts owing to their inexpensive nature, ready availability, eco-friendliness and stability in air and moisture, iron catalyst should have more widespread application in organic synthesis in the near future. Because of variations of reaction

conditions and flexibility of use, understanding of mechanisms of these reactions has indeed become an intellectual puzzle. But we are hopeful that future chemists will certainly be able to shine more light in this area and find new and more fruitful activity using these and other iron catalysts.

Acknowledgements

We thank all co-workers involved in use of iron in catalysis for their precious contributions. Many names have been included in the references, but we may still miss out a few. We sincerely apologise for such omission. We thank the University of Kalyani for infrastructural facility and DST-SERB for the research fellowship grant #SB/FT/CS-192/2013. Dr. Mandal also thanks Saldiha College for assistance in various purposes. We also thank support received from DST FIST, DST PURSE and UGC SAP (DRS) funds.

REFERENCES

[1] H. A. Dieck and R. F. Heck, Palladium-catalyzed conjugated diene synthesis from vinylic halides and olefinic compounds, *J. Org. Chem., 40(8),* 1975, 1083-1090.

[2] J. Suzuki, Stereoselective synthesis of arylated (E)-alkenes by the reaction of alk-1-enylboranes with aryl halides in the presence of palladium catalyst, *J. Chem. Soc. Chem. Commun., (19),* 1979, 866-867.

[3] M. Kumada, Nickel and palladium complex catalyzed cross-coupling reactions of organometallic reagents with organic halides, *Pure. Appl. Chem., 52(3),* 1980, 669-679.

[4] S. Baba and E. Negishi, A novel stereospecific alkenyl-alkenyl cross-coupling by a palladium- or nickel-catalyzed reaction of alkenylalanes with alkenyl halides, *J. Am. Chem. Soc., 98(21),* 1976, 6729-6731.

[5] D, Milstein and J. K. Stille, A general, selective, and facile method for ketone synthesis from acid chlorides and organotin compounds catalyzed by palladium, *J. Am. Chem. Soc., 100(11),* 1978, 3636-3638.

[6] Y. Hatanaka and T. Hiyama, Cross-coupling of organosilanes with organic halides mediated by a palladium catalyst and tris(diethylamino)sulfonium difluorotrimethylsilicate, *J. Org. Chem., 53(4),*1988, 918-920.

[7] K. Sonogashira, Y. Tohda and N. Hagihara, A convenient synthesis of acetylenes: catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes and bromopyridines, *Tetrahedron Lett*., *16(50),* 1975, 4467-4470.

[8] F. A. Cotton and G. Wilkinson, *Anorg. Chem.* 4th ed.; Verlag Chemie: Weinheim, 1982; p 767.

[9] C. Bolm, A new iron age, *Nature Chem., 1(5),* 2009, 420.

[10] *Iron Catalysis in Organic Chemistry: Reactions and Applications*, B. Plietker (Ed.), Wiley-VCH, Weinheim, 2008; *Iron-Catalyzed Cross-Coupling Reactions*, L. Ilies, E. Nakamura, Patai's Chemistry of Functional Groups. John Wiley & Sons, Ltd. 2012; *Iron-Catalyzed Cross-Coupling Reactions*, L. Ilies, E. Nakamura, in The Chemistry of Organoiron Compounds, (Eds.: I. Marek, Z. Rappoport), John Wiley & Sons, Ltd.: Chichester, UK 2014, pp 539-567; E. Nakamura, T. Hatakeyama, S. Ito, K. Ishizuka, L. Ilies, M. Nakamura, *Iron-Catalyzed Cross-Coupling Reactions*, Organic Reactions, vol. 83, Chapter 1 (Ed.: S. E. Denmark), John Wiley & Sons, Inc. 2014.

[11] T. Borowski, A. Bassan and Per E. M. Siegbahn, 4-Hydroxyphenylpyruvate Dioxygenase: A hybrid density functional study of the catalytic reaction mechanism, *Biochemistry, 43,* 2004, 12331-12342; D. Tetard and J.-B. Verlhac, Alkane hydroxylation reactions catalyzed by binuclear manganese and iron complexes, *J. Mol. Catal. A: Chem., 113(1-2),* 1996, 223-230; E. Baciocchi and S. Belvedere, Oxidation of α-alkylbenzyl alcohols catalysed by 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin iron(III) chloride. Competition between C-H and C-C bond cleavage, *Tetrahedron Lett., 39(26),* 1998, 4711-4714.

[12] M. Beller, N. S. Shaikh and K. Junge, A convenient and general iron-catalyzed hydrosilylation of aldehydes, *Org. Lett., 9(26),* 2007, 5429-5432; M. Beller, S. Enthaler and K. Junge, Sustainable metal catalysis with iron: From rust to a rising star? *Angew. Chem. Int. Ed., 47(18),* 2008, 3317-3321; A. Furuta and H.Nishiyama, An iron-catalysed hydrosilylation of ketones, *Chem. Commun.* 2007, *760*-762; N. S. Shaikh, S. Enthaler, K. Junge and M. Beller, Iron-catalyzed enantioselective hydrosilylation of ketones, *Angew. Chem. Int. Ed., 47(13),* 2008, 2497-2501; B. K. Langlotz, H. Wadepohl and L. H. Gade, Chiral Bis(pyridylimino)isoindoles: A highly modular class of pincer ligands for enantioselective catalysis, *Angew. Chem. Int. Ed., 47(25),* 2008, 4670-4674.

[13] C. B. Rao, D. C. Rao, D. C. Babu and Y. Venkateswarlu, Retro-Claisen condensation with Fe(III) as catalyst under solvent-free conditions, *Eur. J. Org. Chem., (15),* 2010, 2855-2859.

[14] S. Pan, J. Liu, H. Li, Z. Wang, X Guo and Z. Li, Iron-catalyzed N-alkylation of azoles via oxidation of C−H bond adjacent to an oxygen atom, *Org. Lett., 12(9),* 2010, 1932-1935.

[15] R. S. Srivastava and K. M. Nicholas, Iron-catalyzed allylic amination by nitroorganics, *Chem. Commun.,* 1998, 2705-2706.

[16] K. Gao, Y. Li, H. Sun, R. Fan and J. Wu, $FeCl_3$-catalyzed aza-diels–alder reactions of methylenecyclopropanes with imines, *Synthetic Commun., 37(24)*, 2007, 4425-4437.

[17] M. Filipan-Litvić, M. Litvić and V. Vinković, A highly efficient biomimetic aromatization of Hantzsch-1,4-dihydropyridines with t-butylhydroperoxide, catalysed by iron(III) phthalocyanine chloride, *Bioorg. Med. Chem., 16(20),* 2008, 9276-9282.

[18] K. Paul, K. Bera, S. Jalal, S. Sarkar and U. Jana, Fe-Catalyzed novel domino isomerization/cyclodehydration of substituted 2-[(indoline-3-ylidene)(methyl)]benzaldehyde derivatives: An Efficient approach toward Benzo[b]carbazole derivatives, *Org. Lett., 16(8),* 2014, 2166-2169.

[19] W. M. Czaplik, S. Grupe, M. Mayer and A. J. von Wangelin, Practical iron-catalyzed dehalogenation of aryl halides, *Chem. Commun., 46,* 2010, 6350-6352.

[20] Rodríguez-Gimeno, A. B. Cuenca, J. Gil-Tomás, M. Medio-Simón, A. Olmos and G. Asensio, $FeCl_3 \cdot 6H_2O$-Catalyzed Mukaiyama-Aldol type reactions of enolizable aldehydes and acetals, *J. Org. Chem., 79(17),* 2014, 8263-8270.

[21] P. Chakraborty and S. C. Roy, $FeCl_3$-catalysed Zn-mediated allylation of cyclic enol ethers in water, *J. Chem. Sci., 124(2),* 2012, 509-512.

[22] S. Maetani, T. Fukuyama, N. Suzuki, D. Ishihara, I. Ryu, Iron-catalyzed decarbonylation reaction of aliphatic carboxylic acids leading to α-olefins, *Chem. Commun*., *48*, 2012, 2552-2554.

[23] L. Y. Chan, J. S. K. Lim, S. Kim, Iron-catalyzed reductive dehydroxylation of benzylic alcohols using polymethylhydrosiloxane (PMHS), *Synlett, (19),* 2011, 2862-2866.

[24] Boudier, P. -A. R. Breuil, L. Magna, C. Rangheard, J. Ponthus, H. Olivier-Bourbigou, P. Braunstein, Novel catalytic system for ethylene oligomerization: an iron(III) complex with an anionic N,N,N ligand, *Organometallics*, *30(10)*, 2011, 2640-2642.

[25] G. B. Kok, P. J. Scammells, Further investigations into the N-demethylation of oripavine using iron and stainless steel, *Org. Biomol. Chem., 9,*2011, 1008-1011.

[26] E. Shirakawa, N. Uchiyama, T. Hayashi, Iron-catalyzed oxidative coupling of alkylamides with arenes through oxidation of alkylamides followed by friedel–crafts alkylation, *J. Org. Chem., 76,* 2011, 25-34.

[27] J. N. Rosa, R. S. Reddy, N. R. Candeias, P. M. S. D. Cal, P. M. P. Gois, NHC–Iron-catalyzed aerobic oxidative aromatic esterification of aldehydes using boronic acids, *Org. Lett*., *12(12)*, 2010, 2686-2689.

[28] S. –Y. Zhang, Y. –Q. Tu, C. –A. Fan, F. –M. Zhang, L. Shi, Iron-catalyzed C(sp3)-C(sp3) bond formation through C(sp3)-H functionalization: A cross-coupling reaction of alcohols with alkenes, *Angew. Chem. Int. Ed., 48(46),* 2009, 8761-8765.

[29] J. Norinder, A. Matsumoto, N. Yoshikai, E. J. Nakamura, Iron-catalyzed direct arylation through directed C–H bond activation, *Am. Chem. Soc., 130(18),* 2008, 5858-5859; K. Bera, S. Sarkar, S. Jalal, U. Jana, Synthesis of substituted phenanthrene by iron(iii)-catalyzed intramolecular alkyne–carbonyl metathesis, *J. Org. Chem.,77(19),* 2012, 8780-8786; R. B. Bedford, M. Nakamura, N. J. Gower, M. F. Haddow, M. A. Hall, M. Huwe, T. Hashimoto, R. A. Okopie, Iron-catalysed Suzuki coupling? A cautionary tale, *Tetrahedron Lett., 50(45),* 2009, 6110-6111.

[30] Y. Cheng, W. Dong, L. Wang, K. Parthavearathy, C. Bolm, Iron-catalyzed hetero-cross-dehydrogenative coupling reactions of sulfoximines with diarylmethanes: a new route to n-alkylated sulfoximines, *Org. Lett., 16(7),* 2014, 2000-2002; A. Correa, C. Bolm, Iron-catalyzed N-arylation of nitrogen nucleophiles, *Angew. Chem. Int. Ed., 46(46),* 2007, 8862-8865; A. Correa, A. Bolm, A. Iron-catalyzed C-N cross-coupling of sulfoximines with aryl iodides, *Adv. Synth. Catal., 350(3),* 2008, 391-394; A. Correa, S. Elmore, C. Bolm, Iron-catalyzed N-arylations of amides, *Chem. - Eur. J., 14(12),* 2008, 3527-3529.

[31] O. Bistri, A. Correa, C. Bolm, Iron-catalyzed C-O cross-couplings of phenols with aryl iodides, *Angew. Chem. Int. Ed., 47(3),* 2008, 586-588.

[32] Correa, M. Carril, C. Bolm, Iron-catalyzed S-arylation of thiols with aryl iodides, *Angew. Chem. Int. Ed., 47(15),* 2008, 2880-2883; H. Tian, C. Zhu, H. Yang, H. Fu, Iron or boron-catalyzed C–H arylthiation of substituted phenols at room temperature, *Chem. Commun., 50,* 2014, 8875-8877.

[33] F. Labre, Y. Gimbert, P. Bannwarth, S. Olivero, E. Duñach, P.Y. Chavant, Application of cooperative iron/copper catalysis to a palladium-free borylation of aryl bromides with pinacolborane, *Org. Lett., 16(9),* 2014, 2366-2369; G. Yan, Y. Jiang, C. Kuang, S. Wang, H. Liu, Y. Zhang and J. Wang, Nano-Fe_2O_3-catalyzed direct borylation of arenes, *Chem. Commun., 46,* 2010, 3170-3172.

[34] J. M. S. Cardoso, R. Lopes and B. Royo, Dehydrogenative silylation of alcohols catalysed by half-sandwich iron N-heterocyclic carbene complexes, *J. Organomet. Chem., 775,* 2015, 173-177.

[35] M. Stein, J. Wieland, P. Steurer, F. Tolle, R. Mulhaupt and B. Breit, Iron nanoparticles supported on chemically-derived graphene: catalytic hydrogenation with magnetic catalyst separation, *Adv. Synth. Catal., 353(4),* 2011, 523-527; S. M. Roopan, F. R. N. Khan and B. K. Mandal, Fe nano particles mediated C–N bond-forming reaction: Regioselective synthesis of 3-[(2-chloroquinolin-3-yl)methyl]pyrimidin-4(3H)ones, *Tetrahedron Lett., 51(17),* 2010, 2309-2311.

[36] S. P. de Visser, D. Kumar, *Iron-Containing Enzymes: Versatile Catalysts of Hydroxylation Reactions in Nature*, Royal Society of Chemistry, Cambridge, 2011; B. Plietker, *Iron Catalysis in Organic Chemistry*, Wiley-VCH, Weinheim, 2008; C. Bolm, J. Legros, J. Le Paih, L. Zani, Iron-catalyzed reactions in organic synthesis, *Chem. Rev., 104(12),* 2004, 6217-6254; W. Nam, S.-Y. Oh, Y. J. Sun, J. Kim, W.-K. Kim, S. K. Woo, W. Shin, Factors affecting the catalytic epoxidation of olefins by iron porphyrin complexes and H_2O_2 in protic solvents, *J. Org. Chem., 68(20),* 2003, 7903-7906; F. G. Gelalcha, Biomimetic iron-catalyzed asymmetric epoxidations: Fundamental concepts, challenges and opportunities, *Adv. Synth. Catal., 356(2-3),* 2014, 261-299.

[37] J. –B. Galey, O. Destre´e, J. Dumats, S. Ge´nard, P. Tachon, Protection against oxidative damage by iron chelators: Effect of lipophilic analogues and prodrugs of N,N‘-Bis(3,4,5-trimethoxybenzyl)ethylenediamine- N,N‘-diacetic acid (OR10141), *J. Med. Chem., 43(7),* 2000, 1418-1421.

[38] B. D. Sherry, A. Fürstner, PATAI'S Chemistry of Functional Groups, Online 2009–2012 John Wiley & Sons, Ltd.; B. D. Sherry, A. Fürstner, The promise and challenge of iron-catalyzed cross coupling, *Acc. Chem. Res*., *41(11)*, 2008, 1500-1511.

[39] J. Kleimark, A. Hedström, P.-F. Larsson, C. Johansson, P.-O. Norrby, Mechanistic investigation of iron-catalyzed coupling reactions, *ChemCatChem, 1(1),* 2009, 152-161; J. Kleimark, P.-F. Larsson, P. Emamy, A. Hedström, P.-O. Norrby, Low temperature studies of iron-catalyzed cross-coupling of alkyl grignard reagents with aryl electrophiles, *Adv. Synth. Catal., 354(2-3),* 2012, 448-456; M. Tamura, J. K. Kochi, Vinylation of Grignard reagents. Catalysis by iron, *J. Am.Chem. Soc., 93(6),* 1971, 1487-1489; S. C. Bart.; K. Chlopek,E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, Electronic structure of bis(imino)pyridine iron dichloride, monochloride, and neutral ligand complexes: A combined structural, spectroscopic, and computational study, *J. Am. Chem. Soc., 128(42),* 2006, 13901-13912; A. Fürstner, R. Martin, H. Krause, G. Seidel, G. Goddard, C. W. Lehmann, Preparation, structure, and reactivity of nonstabilized organoiron compounds. implications for iron-catalyzed cross coupling reactions, *J. Am. Chem. Soc., 130(27),* 2008, 8773-8787.

[40] J. K. Kochi, Homo coupling, disproportionation and cross coupling of alkyl groups. Role of the transition metal catalyst, *J. Organomet. Chem., 653(1-2),* 2002, 11-19; R. S. Smith, J. K. Kochi, Mechanistic studies of iron catalysis in the cross coupling of alkenyl halides and Grignard reagents, *J. Org. Chem., 41(3),* 1976, 502-509.

[41] B. Bogdanovic´and M. Schwickardi, Transition metal catalyzed preparation of grignard compounds, *Angew. Chem. Int. Ed., 39(24)*, 2000, 4610-4612; L. E. Aleandri, B. Bogdanovic´, P. Bons, C. Dürr, A. Gaidies, T. Hartwig, S. C. Huckett, M. Lagarden, U. Wilczok, R. A. Brand, Inorganic Grignard reagents. Preparation and their application for the synthesis of highly active metals, intermetallics, and alloys *Chem. Mater., 7(6),* 1995, 1153-1170; A. Fürstner, A. Leitner, M. Méndez, H. Krause, Iron-catalyzed cross-coupling reactions, *J. Am. Chem. Soc., 124(46),* 2002, 13856-13863; G. Cahiez, S. Marquais, Cu-catalyzed alkylation and Fe catalyzed alkenylation of organomanganese reagents, *Pure Appl. Chem., 68(1),* 1996, 53; G. Cahiez, S. Marquais, Highly chemo- and stereoselective Fe-catalyzed alkenylation of organomanganese reagents, *Tetrahedron Lett., 37,* 1996, 1773-1776.

[42] S. M. Neumann, J. K. Kochi, Synthesis of olefins. Cross-coupling of alkenyl halides and Grignard reagents catalyzed by iron complexes, *J. Org. Chem., 40(5),* 1975, 599-606; R. S. Smith, J. K. Kochi, Mechanistic studies of iron catalysis in the cross coupling of alkenyl halides and Grignard reagents, *J. Org. Chem., 41(3),*1976, 502-509.

[43] R. Surasani, D. Kalita, A. V. D. Rao, K. B. Chandrasekhar, Palladium-catalyzed C–N and C–O bond formation of N-substituted 4-bromo-7-azaindoles with amides, amines, amino acid esters and phenols, *Beilstein J. Org. Chem., 8,* 2012, 2004-2018; N. Miyaura , A. Suzukínt, Palladium-catalyzed cross-coupling reactions of organoboron compounds, *Chem. Rev., 95(7),* 1995, 2457-2483; X.-F. Cheng, Y. Li, Y.-M. Su, F. Yin, J.-Y. Wang, J. Sheng, H. U. Vora, X.-S. Wang, J.-Q. Yu, Pd(II)-catalyzed enantioselective C–H activation/C–O bond formation: Synthesis of chiral benzofuranones, *J. Am. Chem. Soc., 135(4),* 2013, 1236-1239; C. J. Diez-Holz, C. Böing, G. Franciò, M. Hölscher, W. Leitner, Phosphoramidite quinaphos-type ligands for highly selective Ni-catalysed asymmetric C–C bond forming reactions, *Eur. J. Org. Chem., (18),* 2007, 2995-3002; H. Cao, H. Zhan, J. Cen, J. Lin, Y. Lin, Q. Zhu, M. Fu, H. Jiang, Copper-catalyzed C–O bond formation: An efficient one-pot highly regioselective synthesis of furans from (2-furyl)carbene complexes, *Org. Lett., 15(5),* 2013, 1080-1083; B. H. Lipshutz, S. Huang, W. W. Y. Leong, G. Zhong, N. A. Isley, C–C Bond formation via copper-catalyzed conjugate addition reactions to enones in water at room temperature, *J. Am. Chem. Soc., 134(49),* 2012, 19985-19988; S. Z. Tasker, E. A. Standley, T. F. Jamison, Recent advances in homogeneous nickel catalysis*Nature*, *509*, 2014, 299-309.

[44] M. Murata, T. Yasumoto, The structure elucidation and biological activities of high molecular weight algal toxins: maitotoxin, prymnesins and zooxanthellatoxins, *Nat. Prod. Rep., 17(3),* 2000, 293-314; S. S. Bhagwat, P. R. Hamann, W. C. Still, S. Buntiny, F. A. Fitzpatrick, *Nature*, *315*, 1985, 511; V. N. Kale, D. L. J. Clive, Studies related to thromboxane A2: a formal synthesis of optically active 9.alpha., 11.alpha.-thiathromboxane A2 methyl ester from levoglucosan, *J. Org. Chem.* 1984, *49(9)*, 1554-1563; R. S. Ward, Lignans neolignans, and related compounds, *Nat. Prod. Rep., 10(1),* 1993, 1-28; *12*, 1995, 183-205; *14*, 1997, 43-74.

[45] S.-I. Murahashi, Y. Oda, T. Naota, Fe_2O_3-catalyzed Baeyer-Villiger oxidation of ketones with molecular oxygen in the presence of aldehydes, *Tetrahedron Lett., 33(49),* 1992, 7557-7560.

[46] M. Rosenblum, Organoiron complexes as potential reagents in organic synthesis, *Acc. Chem. Res.*, *7(4)*, 1974, 122-128.

[47] L. R. Cox, S. V. Ley, Tricarbonyliron complexes: an approach to acyclic stereocontrol, *Chem. Soc. Rev., 27,* 1998, 301-314.

[48] C. Möller, M. Mikulás, F. Wierchem, K. Rück-Braun, Synthesis of 5-Substituted α,β-Butenolides by Iron-promoted Intramolecular Cyclocarbonylation: Addition of organometallic reagents to iron-substituted enals, *Synlett*, (2), 2000, 182-184.

[49] S. Saha, S. K. Mandal, S. C. Roy, Fe(III) chloride catalyzed conversion of epoxides to acetonides, *Tetrahedron Lett., 49(41),* 2008, 5928-5930.

[50] H. Li, J. Yang, Y. Liu, Y. Li, Iron-catalyzed cascade arene−aldehyde addition/cyclizations for the highly efficient synthesis of xanthenes and its analogous: Observation of a C–C bond cleavage in indole-based triarylmethanes, *J. Org. Chem.* 2009, *74(17)*, 6797-6801.

[51] S. K. Das, R. Singh, G. Panda, A New Synthetic Route to Unsymmetrical 9-Arylxanthenes, *Eur. J. Org. Chem., (28),* 2009, 4757-4761.

[52] X. Xu, X. Xu, H. Li, X. Xie, Y. Li, Iron-catalyzed, microwave-promoted, one-pot synthesis of 9-substituted xanthenes by a cascade benzylation - cyclization process, *Org. Lett*., *12(1)*, 2010, 101-103.

[53] K. Bera, S. Sarkar, S. Biswas, S. Maiti, U. Jana, Iron-catalyzed synthesis of functionalized 2h-chromenes via intramolecular alkyne–carbonyl metathesis, *J. Org. Chem., 76(9),* 2011, 3539-3544.

[54] S. Jalal, S. Sarkar, K. Bera, S. Maiti, U. Jana, Synthesis of nitroalkenes involving a cooperative catalytic action of iron(iii) and piperidine: a one-pot synthetic strategy to 3-alkylindoles, 2h-chromenes and n-arylpyrrole, *Eur. J. Org. Chem.,* 2013, 4823-4828.

[55] K. Bera, S. Jalal, S. Sarkar, U. Jana, $FeCl_3$-catalyzed synthesis of functionally diverse dibenzo[b,f]oxepines and benzo[b]oxepines via alkyne–aldehyde metathesis, *Org. Biomol. Chem., 12,* 2014, 57-61.

[56] J. M. Takacs, J. J. Weidner, P. W. Newsome, B. E. Takacs, R. Chidambaram, R. Shoemaker, Catalytic iron-mediated enediene carbocyclizations: Investigations into the stereoselective formation of bicyclic ring systems, *J. Org. Chem., 60(11),* 1995, 3473-3486.

[57] H. Ohara, K. Kudo, T. Itoh, M. Nakamura, E. Nakamura, Fe(III)-catalyzed radical cyclization of cyclopropanone thioacetal, *Heterocycles*, *52(2)*, 2000, 505-510.

[58] R. Martin, A. Fürstner, Cross-coupling of alkyl halides with aryl grignard reagents catalyzed by a low-valent iron complex, *Angew Chem. Int. Ed*., *43(30)*, 2004, 3955-3957.

[59] Furstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, Preparation, structure, and reactivity of nonstabilized organoiron compounds. implications for iron-catalyzed cross coupling reactions, *J. Am. Chem. Soc., 130(27),* 2008, 8773-8787.

[60] T. Taniguchi, T. Fujii, H. Ishibashi, Iron-mediated one-pot formal nitrocyclization onto unactivated alkenes, *Org. Biomol. Chem.*, *9*, 2011, 653-655.

[61] G. Hilt, P. Bolze, I. Kieltsch, An iron-catalysed chemo- and regioselective tetrahydrofuran synthesis, *Chem. Commun*. 2005, 1996-1998.

[62] F. Benfatti, F. de Nanteuil, J. Waser, Iron-catalyzed [3 + 2] annulation of aminocyclopropanes with aldehydes: stereoselective synthesis of aminotetrahydrofurans, *Org. Lett.*, *14(1)*, 2012, 386-389.

[63] M. Carril, A. Correa, C. Bolm, Iron-catalyzed Sonogashira reactions, *Angew Chem. Int. Ed., 47(26),* 2008, 4862-4865; C. M. R. Volla, P. Vogel, Iron/copper-catalyzed C–C cross-coupling of aryl iodides with terminal alkynes, *Tetrahedron Lett., 49(41),* 2008, 5961-5964; N. Panda, A. K. Jena, S. Mohapatra, Ligand-free Fe–Cu cocatalyzed cross-coupling of terminal alkynes with aryl halides, *Chem. Lett., 40(9),* 2011, 956-958.

[64] S. Pathak, K. Debnath, Md. M. R. Mollick, A. Pramanik, Facile cyclization in the synthesis of highly fused diaza cyclooctanoid compounds using retrievable nano magnetite-supported sulfonic acid catalyst, *RSC Adv., 4,* 2014, 23779-23789.

[65] K.C. Prousis, N. Avlonitis, G. A. Heropoulos, T. Calogeropoulou, FeCl3-catalysed ultrasonic-assisted, solvent-free synthesis of 4-substituted coumarins. A useful complement to the Pechmann reaction, *Ultrason. Sonochem., 21(3),* 2014, 937-942.

[66] J. M. Takacs, J. J. Weidner, P. W. Newsome, B. E. Takacs, R. Chidambaram,, R. Shoemaker, Catalytic iron-mediated enediene carbocyclizations: Investigations into the stereoselective formation of bicyclic ring systems, *J.Org. Chem., 60(11),* 1995, 3473-3486.

[67] K. B. Sharpless, A. O. Chong, J. Oshima, Osmium-catalyzed vicinal oxyamination of olefins by Chloramine-T, *J. Org. Chem., 41(1),* 1976, 177-179.

[68] G. –S. Liu, Y. –Q. Zhang, Y. –A. Yuan, H. Xu, Iron(II)-catalyzed intramolecular aminohydroxylation of olefins with functionalized hydroxylamines, *J. Am. Chem. Soc., 135(9),* 2013, 3343-3346.

[69] K. S. Williamson, T. P. Yoon, Iron-catalyzed aminohydroxylation of olefins, *J. Am. Chem. Soc., 132(13),* 2010, 4570-4571.

[70] D. J. Michaelis, K. S. Williamson, T. P. Yoon, Oxaziridine-mediated enantioselective aminohydroxylation of styrenes catalyzed by copper(II) bis(oxazoline) complexes, *Tetrahedron*, *65(26)*, 2009, 5118-5124; D. J. Michaelis, C. J. Shaffer, T. P. Yoon, Copper(II)-catalyzed aminohydroxylation of olefins, *J. Am. Chem. Soc., 129(7),* 2007, 1866-1867.

[71] Y. –Q. Zhang, Y. –A. Yuan, G. –S. Liu, H. Xu, Iron(II)-catalyzed asymmetric intramolecular aminohydroxylation of indoles, *Org. Lett., 15(15),* 2013, 3910-3913.

[72] T. Bach, B. Schlummer, K. Harms, Iron(II)-catalyzed intramolecular aminochlorination of alkenes, *Chem. Commun., (4),* 2000, 287-288; T. Bach, B. Schlummer, K. Harms, *Chem.–Eur. J., 7(12),* 2001, 2581-2586.

[73] J. Childs, D. C. Craig, M. L. Scudder, H. A. Goodwin, Structural and Electronic Properties of the Iron(II) and Nickel(II) Bis(ligand) Complexes of 6-(5-Methyl-1,2,4-oxadiazol-3-yl)-2,2′-bipyridine— a Terpyridine-Based Tridentate, *Aust. J. Chem., 52(7),* 1999, 673-680; C. Richardson, P. J. Steel, The first metal complexes of 3,3′-bi-1,2,4-oxadiazole: A curiously ignored ligand, *Inorg. Chem. Commun.* 2007, *10(8)*, 884-887.

[74] J. Garfunkle, C. Ezzili, T. J. Rayl, D. G. Hochstatter, I. Hwang, D. L. Boger, Optimization of the central heterocycle of α-ketoheterocycle inhibitors of fatty acid amide hydrolase, *J. Med. Chem., 51(15),* 2008, 4392-4403.

[75] V. Maftei, E. Fodor, P. G. Jones, M. H. Franz, G. Kelter, H. Fiebig, I. Neda, Synthesis and characterization of novel bioactive 1,2,4-oxadiazole natural product analogs bearing the N-phenylmaleimide and N-phenylsuccinimide moieties, *Beilstein J. Org. Chem.* 2013, *9(11)*, 2202-2215.

[76] K. Itoh, H. Sakamaki, C. A. Horiuchi, *Synthesis*, (12), 2005, 19351938.

[77] A. P. Piccionello, A. Guarcello, S. Buscemi, N. Vivona, A. Pace, Synthesis of amino-1,2,4-triazoles by reductive ANRORC rearrangements of 1,2,4-oxadiazoles, *J. Org. Chem., 75 (24),* 2010, 8724–8727.

[78] A. Horiuchi, S. Kiji, A new α-iodination of ketones using iodine-ammonium cerium(IV) nitrate in alcohol or acetic acid, *Bull. Chem. Soc. Jpn.* 1997, *70(2)*, 421-426.

[79] M. H. Potashman, J. Bready, A. Coxon, T. M. Jr. DeMelfi, L. DiPietro, N. Doerr, D. Elbaum, J. Estrada, P. Gallant, J. Germain, Y. Gu, J. -C. Harmange, S. A. Kaufman, R. Kendall, J. L. Kim, G. N. Kumar, A. M. Long, S. Neervannan, V. F. Patel, A. Polverino, P. Rose, S. Van der Plas, D. Whittington, R. Zanon, H. Zhao, Design, synthesis, and evaluation of orally active benzimidazoles and benzoxazoles as vascular endothelial growth factor-2 receptor tyrosine kinase inhibitors, *J. Med. Chem., 50(18),* 2007, 4351-4373.

[80] Y. Kawashita, N. Nakamichi, H. Kawabata, M. Hayashi, Direct and practical synthesis of 2-arylbenzoxazoles promoted by activated carbon, *Org. Lett., 5(20),* 2003, 3713-3715; J. A. Seijas, M. P. Vázquez-Tato, M. R. Carballido-Reboredo, J. Crecente-Campo, L. Romar-Lo´pez, Lawesson's reagent and microwaves: A new efficient access to benzoxazoles and benzothiazoles from carboxylic acids under solvent-free conditions, *Synlett, (2),* 2007, 313-317.

[81] J. Bonnamour, C. Bolm, Iron-catalyzed intramolecular O-arylation: Synthesis of 2-aryl benzoxazoles, *Org. Lett.,* 2008, *10(13)*, 2665-2667.

[82] O. Debleds, C. DalZotto, E. Vrancken, J. -M. Campagne, P. Retail-leau, A dual gold-iron catalysis for a one-pot synthesis of 2,3-dihydroisoxazoles from propargylic alcohols and N-protected hydroxylamines, *Adv. Synth. Catal., 351(11-12),* 2009, 1991-1998.

[83] O. Debleds, E. Gayon, E. Ostaszuk, E. Vrancken,, J. –M. Campagne, A versatile iron-catalyzed protocol for the one-pot synthesis of isoxazoles or isoxazolines from the same propargylic alcohols, *Chem. Eur. J., 16(40),* 2010, 12207-12213.

[84] B. J. Stokes, C. V. Vogel, L. K. Urnezis, M. Pan, T. G. Driver, Intramolecular Fe(II)-catalyzed N–O or N–N bond formation from aryl azides, *Org. Lett., 12(12)*, 2010, 2884-2887.

[85] Székely, Á. Sinai, E. B. Tóth, Z. Novák, Utilization of a copper on iron catalyst for the synthesis of biaryl systems and benzoxazines via oxidative arylation of anilide derivatives, *Synthesis* 2014, *46(14)*, 1871-1880.

[86] M. S. Sigman, B. E. Eaton, The first iron-mediated catalytic carbon-nitrogen bond formation: [4 + 1] Cycloaddition of allenyl imines and carbon monoxide, *J. Org. Chem., 59(24),* 1994, 7488-7491.

[87] K. Komeyama, T. Morimoto, K. Takaki, A simple and efficient iron-catalyzed intramolecular hydroamination of unactivated olefins, *Angew. Chem. Int. Ed., 45(18),* 2006, 2938-2941.

[88] J. Fan, L. Gao, Z. Wang, Facile construction of highly functionalized 2-pyrrolines viaFeCl3-catalyzed reaction of aziridines with arylalkynes, *Chem. Commun*. 2009, 5021-5023.

[89] S. A. Cramer, D. M. Jenkins, Synthesis of aziridines from alkenes and aryl azides with a reusable macrocyclic tetracarbene iron catalyst, *J. Am. Chem. Soc., 133(48),* 2011, 19342-19345.

[90] R. M. Carballo, M. Purino, M. A. Ramírez, V. S. Martín, J. I. Padrón, Iron(III)-catalyzed consecutive Aza-Cope-Mannich cyclization: Synthesis of trans-3,5-dialkyl pyrrolidines and 3,5-dialkyl-2,5-dihydro-1H-pyrroles, *Org. Lett*. 2010, *12(22)*, 5334-5337.

[91] T. Taniguchi, T. Fujii, H. Ishibashi, Iron-mediated one-pot formal nitrocyclization onto unactivated alkenes, *Org. Biomol. Chem., 9(3),* 2011, 653-655.

[92] P. Dieskau, M. S. Holzwarth, B. Plietker, Fe-catalyzed allylic C-C-bond activation: vinylcyclopropanes as versatile a1,a3,d5-synthons in traceless allylic substitutions and [3 + 2]-cycloadditions, *J. Am. Chem. Soc., 134(11),* 2012, 5048-5051.

[93] T. Hennessy, T. A. Betley, Complex N-heterocycle synthesis via iron-catalyzed, direct C-H bond amination, *Science, 340(6132),* 2013, 591-595.

[94] S. Maiti, S. Biswas, U. Jana, Iron (III)-catalyzed four-component coupling reaction of 1, 3-dicarbonyl compounds, amines, aldehydes, and nitroalkanes: a simple and direct synthesis of functionalized pyrroles, *J. Org. Chem., 75(5),* 2010, 1674-1683.

[95] S. Sarkar, K. Bera, S. Maiti, S. Biswas, U. Jana, Three-component coupling synthesis of diversely substituted N-aryl pyrroles catalyzed by iron (III) chloride, *Synthetic Commun., 43(11),* 2013, 1563-1570.

[96] S. Jalal, S. Sarkar, K. Bera, S. Maiti,, U. Jana, Synthesis of nitroalkenes involving a cooperative catalytic action of iron(III) and piperidine: A one-pot synthetic strategy to 3-alkylindoles, 2H-chromenes and N-arylpyrrole, *Eur. J. Org. Chem., (22),* 2013, 4823-4828.

[97] H. Hemetsberger, D. Knittel, Synthese und thermolyse von α-azidoacrylestern, *Monatsh. Chem., 103(1),* 1972, 194-204; D. Knittel, Verbesserte synthese von α-azidozimtsäure-estern und 2H-azirinen, *Synthesis, (2),* 1985, 186-188.

[98] J. Bonnamour, C. Bolm, Iron(II) triflate as a catalyst for the synthesis of indoles by intramolecular C–H amination, *Org. Lett., 13(8),* 2011, 2012-2014.

[99] Deak, M. Doda, L. Gyorgy, L. Hazai, L. Sterk, A new type of anticonvulsant: 1-aryl-3-oxotetrahydroisoquinolines, *J. Med. Chem., 20(11)*, 1977, 1384-1388; A. Numata, P. Yang, C. Takahashi, R. Fujiki, M. Nabae, E. Fujita, Cytotoxic triterpenes from a Chinese medicine, Goreishi, *Chem. Pharm. Bull., 37(3),* 1989, 648-651; C. V. Galliford, K. A. Scheidt, Pyrrolidinyl-spirooxindole natural products as inspirations for the development of potential therapeutic agents, *Angew. Chem. Int. Ed., 46(46),* 2007, 8748-8758; J. E. M. N. Klein, R. J. K. Taylor, Transition-metal-mediated routes to 3,3-disubstituted oxindoles through anilide cyclisation, *Eur. J. Org. Chem., (11),* 2011, 6821-6841; T. Piou, L. Neuville, J. Zhu, Activation of a C(sp3)-H bond by a transient σ-alkylpalladium(II) complex: Synthesis of spirooxindoles through a palladium-catalyzed domino carbopalladation/C(sp3)-C(sp3) bond-forming process, *Angew. Chem. Int. Ed., 51(46),* 2012, 11561-11565; P. Tolstoy, S. X. Y. Lee, C. Sparr, S. V. Ley, Synthesis of enantiomerically enriched 3-amino-2-oxindoles through a palladium-mediated asymmetric intramolecular arylation of α-ketimino amides, *Org. Lett., 14*, 2012, 4810-4813; Y. Nakao, S. Ebata, A. Yada, T. Hiyama, M. Ikawa, S. Ogoshi, Intramolecular arylcyanation of alkenes catalyzed by nickel/AlMe2Cl, *J. Am. Chem. Soc., 130(39),* 2008, 12874-12875.

[100] W.-T. Wei, M.-B. Zhou, J.-H. Fan, W. Liu, R.-J. Song, Y. Liu, M. Hu, P. Xie, J.-H. Li, Synthesis of oxindoles by iron-catalyzed oxidative 1,2-alkylarylation of activated alkenes with an aryl C(sp2)-H bond and a C(sp3)-H bond adjacent to a heteroatom, *Angew. Chem. Int. Ed., 52(13),* 2013, 3638-3641.

[101] R. Katritzky, Introduction: Heterocycles, *Chem. Rev.* 2004, *104(5)*, 2125-2126; K. Kaur, M. Jain, R. P. Reddy, R. Jain, Quinolines and structurally related heterocycles as antimalarials, *Eur. J. Med. Chem., 45(8),* 2010, 3245-3264; J. P. Michael, Quinoline, quinazoline and acridone alkaloids, *Nat. Prod. Rep., 25,* 2008, 166-187; J. C. Craig, P. E. Person, Potential antimalarials. 7. Tribromomethylquinolines and positive halogen compounds, *J. Med. Chem., 14(12),* 1971, 1221-1222; L. Zhi, C. M. Tegley, M. Christopher, K. B. Marschke, D. E. Mais, T. K. Jones, K. Todd, 5-Aryl-1,2,3,4-tetrahydrochromeno[3,4-f]quinolin-3-ones as a novel class of nonsteroidal progesterone receptor agonists: Effect of a-ring modification, *J. Med. Chem., 42(8),* 1999, 1466-1472; B. Lockhart, N. Bonhomme, A. Roger, G. Dorey, P. Casara, P. Lestage, Protective effect of the antioxidant 6-ethoxy-2,2-pentamethylen-1,2-dihydroquinoline (S 33113) in models of cerebral neurodegeneration., *Eur. J. Pharmacol., 416(1-2),* 2001, 59-68.

[102] M. Zhang, T. Wang, B. Xiong, F. Yan, X. Wang, Y. Ding, Q. Song, Efficient synthesis of 2,4-diarylquinolines via Fe(III) trifluoroacetate catalyzed three-component reactions under solvent-free conditions, *Heterocycles,* 2012, *85(3)*, 639-649.

[103] C. Yao, B. Qin, H. Zhang, J. Lu, D. Wang, S. Tu, One-pot solvent-free synthesis of quinolines by C–H activation/C–C Bond formation catalyzed by recyclable iron(III) triflate, *RSC Adv., 2,* 2012, 3759-3764.

[104] Y. Zhang, M. Wang, P. Li, L. Wang, Iron-promoted tandem reaction of anilines with styrene oxides via c–c cleavage for the synthesis of quinolines, *Org. Lett., 14(9)*, 2012, 2206-2209.

[105] S. Jalal, K. Bera, S. Sarkar, K. Paul, U. Jana, Efficient synthesis of functionalized dihydroquinolines, quinolines and dihydrobenzo [b] azepine via an iron (iii) chloride-catalyzed intramolecular alkyne–carbonyl metathesis of alkyne tethered 2-amino benzaldehyde/acetophenone derivatives, *Org. Biomol. Chem., 12(11),* 2014, 1759-1770.

[106] K. Komeyama, R. Igawa, K. Takaki, Cationic iron-catalyzed intramolecular alkyne-hydroarylation with electron-deficient arenes *Chem. Commun., 46,* 2010, 1748-1750.

[107] Z. Wang, S. Li, B. Yu, H. Wu, Y. Wang, X. Sun, $FeCl_3 \cdot 6H_2O$-catalyzed intramolecular allylic amination: Synthesis of substituted dihydroquinolines and quinolines, *J. Org. Chem., 77(19)*, 2012, 8615-8620.

[108] U. Jana, S. Maiti, S. Biswas, An efficient $FeCl_3$-catalyzed amidation reaction of secondary benzylic and allylic alcohols with carboxamides or p-toluenesulfonamide, *Tetrahedron Lett., 49(5),* 2008, 858-862.

[109] S. Sarkar, K. Bera, S. Jalal, U. Jana, Synthesis of structurally diverse polyfunctional pyrrolo[1,2-a]quinolines by sequential iron-catalyzed three-component coupling and gold-catalyzed hydroarylation reactions, *Eur. J. Org. Chem., (27),* 2013, 6055-6061.

[110] Q. Yang, T. Xu, Z. Yu, Iron-mediated carboarylation/cyclization of propargylanilines with acetals: A concise route to indeno[2,1-c]quinolines, *Org. Lett., 16(2),* 2014, 6310-6313.

[111] K. Gao, Y. Li, H. Sun, R. Fan, J. Wu, $FeCl_3$-catalyzed aza-diels–alder reactions of methylenecyclopropanes with imines, *Synthetic Commun.*, 37, 2007, 4425-4438.

[112] Guérinot, A. Serra-Muns, C. Gnamm, C. Bensoussan, S. Reymond, J. Cossy, FeCl3-catalyzed highly diastereoselective synthesis of substituted piperidines and tetrahydropyrans, *Org. Lett.* 2010, *12(8)*, 1808-1811.

[113] E. Shirakawa, N. Uchiyama, T. Hayashi, Iron-catalyzed oxidative coupling of alkylamides with arenes through oxidation of alkylamides followed by Friedel–Crafts alkylation, *J. Org. Chem., 76(1),* 2011, 25-34.

[114] D. H. Mac, A. Sattar, S. Chandrasekhar, J. S. Yadav, R. Grée, Synthesis of new 4-methyl-3-piperidones via an iron-catalyzed intramolecular tandem isomerization–aldolisation process, *Tetrahedron,* 2012, *68(43)*, 8863-8868.

[115] M. Sun, T. Zhang, W. Bao, $FeCl_3$-Catalyzed cascade cyclization in one pot: synthesis of ring-fused tetrahydroquinoline derivatives from arylamines and N-substituted lactams, *J. Org. Chem., 78(16),* 2013, 8155-8160.

[116] S. R. Kanth, G. V. Reddy, D. Maitraie, B. Narsaiah, P. S. Rao, K. R. Kumar, B. Sridhar, Iron(III) chloride catalysed three-component Grieco condensation: Synthesis of tetrahydropyrido[2′,3′:3,4]pyrazolo[1,5-a]pyrimidines/quinazolines, *J. Fluorine Chem.* 2006, *127(9)*, 1211-1221.

[117] C. Ye, X. Yu, G. Qiu, J. Wu, Reaction of N-(2-alkynylbenzylidene)hydrazide with : A concise synthesis of H-pyrazolo[5,1-a]isoquinolines, *RSC Adv., 2,* 2012, 5961-5963.

[118] R. Rohlmann, T. Stopka, H. Richter, O. G. Mancheño, Iron-catalyzed oxidative tandem reactions with TEMPO oxoammonium salts: Synthesis of dihydroquinazolines and quinolines, *J. Org. Chem., 78(12),* 2013, 6050-6064.

[119] X. Zhang, D. Ye, H. Sun, D. Guo, J. Wang, H. Huang, X. Zhang, H. Jiang, H. Liu, Microwave-assisted synthesis of quinazolinone derivatives by efficient and rapid iron-catalyzed cyclization in water, *Green Chem., 11,* 2009, 1881-1888.

[120] D. Zhao, Y.-R. Zhou, Q. Shena, J.-X. Li, Heavy element doping for enhancing thermoelectric properties of nanostructured zinc oxide, *RSC Adv., 4,* 2014, 6486-6468.

[121] D. Girija, H.S. B. Naik, B. V. Kumar, C. N. Sudhamani, K.N. Harish, Fe_3O_4 nanoparticle supported Ni(II) complexes: A magnetically recoverable catalyst for Biginelli reaction, *Arabian J. Chem.,* 2014, 10.1016/j.arabjc.2014.08.008

[122] B. C. G. Söderberg, Synthesis of heterocycles via intramolecular annulation of nitrene intermediates, *Curr. Org. Chem., 4(7)*, 2000, 727-764; C. J. Moody, *Comprehensive Organic Synthesis;* B. M. Trost, I. Fleming, S. Ley, Eds.; Pergamon: Oxford, 1991; Vol. 7, p 21.

[123] L. Milligan, C. J. Mossman, J. Aubé, Intramolecular Schmidt reactions of alkyl azides with ketones: Scope and stereochemical studies, *J. Am. Chem. Soc., 117(42),* 1995, 10449-10459; V. Gracias, G. L. Milligan, J. Aubé, Efficient nitrogen ring-expansion process facilitated by in situ hemiketal formation. an asymmetric Schmidt reaction, *J. Am. Chem. Soc., 117(30),* 1995, 8047-8048; W. H. Pearson, R. Walavalkar, J. M. Schkeryantz, W.-K. Fang, J. D. Blickensdorf, Intramolecular Schmidt reactions of azides with carbocations: synthesis of bridged-bicyclic and fused-bicyclic tertiary amines, *J. Am. Chem. Soc., 115(22),* 1993, 10183-10184.

[124] M. Shen, T. G. Driver, Iron(II) bromide-catalyzed synthesis of benzimidazoles from aryl azides, *Org. Lett., 10(15),* 2008, 3367-3370.

[125] S. Santra, A. K. Bagdi, A. Majee, A. Hajra, Iron(III)-catalyzed cascade reaction between nitroolefins and 2-aminopyridines: synthesis of imidazo[1,2-a]pyridines and easy access towards zolimidine, *Adv. Synth. Catal., 355(6),* 2013, 1065-1070.

[126] S. Santra, S. Mitra, A. K. Bagdi, A. Majee, A. Hajra, Iron(III)-catalyzed three-component domino strategy for the synthesis of imidazo[1,2-a]pyridines, *Tetrahedron Lett., 55(37),* 2014, 5151-5155.

[127] F. Himo, Z. P. Demko, L. Noodleman, K. B. Sharpless, Why is tetrazole formation by addition of azide to organic nitriles catalyzed by Zinc(II) salts*? J. Am. Chem. Soc., 125(33),* 2003, 9983-9987.

[128] T. Jin, F. Kitahara, S. Kamijo, Y. Yamamoto, Copper-catalyzed synthesis of 5-substituted 1H-tetrazoles via the [3+2] cycloaddition of nitriles and trimethylsilyl azide, *Tetrahedron Lett., 49(17),* 2008, 2824-2827.

[129] D. Amantini, R. Beleggia, F. Fringuelli, F. Pizzo, L. Vaccoro, TBAF-catalyzed synthesis of 5-substituted 1H-tetrazoles under solventless conditions, *J. Org. Chem., 69(8),* 2004, 2896-2898.

[130] J. Bonnamour, C. Bolm, Iron salts in the catalyzed synthesis of 5-substituted 1H-tetrazoles, *Chem. Eur. J., 15(18),* 2009, 4543-4545.

[131] B. Saha, S. Sharma, D. Sawant, B. Kundu, Cu-$FeCl_3$-mediated one-pot multicomponent reaction leading to N-aryl- and N-alkyltriazoles in water, *Synlett, (7),* 2007, 1591-1594.

[132] R. Martin, A. Fürstner, Cross-coupling of alkyl halides with aryl grignard reagents catalyzed by a low-valent iron complex, *Angew. Chem. Int. Ed*., *43*, 2004, 3955-3957.

[133] Fürstner, R. Martin, K. Majima, Cycloisomerization of enynes catalyzed by iron(0)−ate complexes, *J. Am. Chem. Soc., 127(35),* 2005, 12236-12237.

[134] Fürstner, R. Martin, H. Krause, G. Seidel, R. Goddard, C. W. Lehmann, Preparation, structure, and reactivity of nonstabilized organoiron compounds. implications for iron-catalyzed cross coupling reactions, *J. Am. Chem. Soc.* 2008, *130(27)*, 8773-8787.

[135] H.-J. Knölker, *In Transition Metals for Organic Synthesis – Building Blocks, Fine Chemicals*, Vol. 1, 2nd edn. ed. M. Beller, C. Bolm, Wiley-VCH, Weinheim, 2004, Chap. 3.11, p. 585; H.-J. Knölker, M. Wolpert, Transition metal complexes in organic synthesis. Part 68: Iron-mediated total synthesis of mukonine and mukonidine by oxidative cyclization with air as the oxidizing agent, *Tetrahedron, 59(28)*, 2003, 5317-5322; H.-J. Knölker, T. Hopfmann, Transition metal complexes in organic synthesis. Part 65: Iron-mediated synthesis of carazostatin, a free radical scavenger from Streptomyces chromofuscus, and O-methylcarazostatin, *Tetrahedron, 58(44)*, 2002, 8937-8945.

[136] H.-J. Knölker, M. Bauermeister, J.-B. Pannek, M. Wolpert, Transition metal-diene complexes in organic synthesis, Part 22.The iron-mediated quinone imine cyclization: A general route to 3-hydroxycarbazoles, *Synthesis, (4),* 1995, 397-408.

[137] V. Mandadapu, F. Wu, A. I. Day, $Fe(OTf)_3$ versus $Bi(OTf)_3$ as mild catalysts in epoxide oxidative ring-opening, urea α-diketone condensation, and glycoluril diether synthesis, *Org. Lett., 16(5),* 2014, 1275-1277.

[138] X. Feng, Q. Wang, Z.-B. Huang, D.-Q. Shi, Fe-promoted oxidative cyclization of α-benzoylthioformanilides for the synthesis of 2-benzoylbenzothiazoles, *RSC Adv., 4,* 2014, 54719-54724.