Silica-ferric chloride (SiO_2-$FeCl_3$) catalyzed selective synthesis of 2-substituted benzimidazole through $C_{sp}2$-$C_{sp}3$ bond cleavage of β-ketoester/amide

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Graphical Abstract

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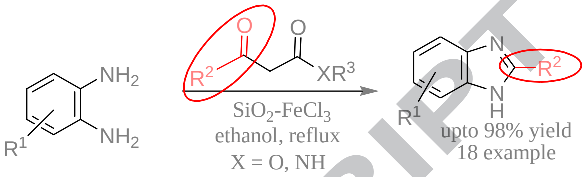

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Silica-ferric chloride (SiO_2-$FeCl_3$) catalyzed selective synthesis of 2-substituted benzimidazole through $C_{sp}2$-$C_{sp}3$ bond cleavage of β-ketoester/amide

Swapan Majumdar[a]*, Ankita Chakraborty[a], Subrata Bhattacharjee[a], Sudipto Debnath[b] and Dilip K. Maiti[b]

[a] *Department of Chemistry, Tripura University, Suryamaninagar, 799 022, INDIA*
[b] *Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata 700 009, INDIA*

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ABSTRACT

Silica-ferric chloride (SiO_2-$FeCl_3$) supported reagent was successfully utilized as recyclable catalyst for the general and highly efficient synthesis of 2-substituted benzimidazole by the condensation of 1,2-diamino benzene and β-ketoester/amide followed by original $C_{sp}2$-$C_{sp}3$ bond cleavage. Evidences in favour of C-C (α-β) bond cleavage of β-ketoesters/amides are established.

Solid supported reagents have much attention in organic synthesis owing to their characteristics properties such as enhanced reactivity and selectivity, simple work-up procedure, minimization of cost and waste generation and reuse of the catalysts with significant catalyst turnover.[1] Recently, iron compounds have drawn much attention for their outstanding catalytic activity, selectivity, cost-effectiveness, ready availability, sustainability, and environmentally friendly properties towards wide range of organic transformations[2] and synthesis of functionalized heterocycles. Over the past few years, silica supported ferric chloride was extensively used in several catalytic organic transformations[3a-f] with high efficiency.

N-heterocycles are the most abundant and integral scaffolds that occur ubiquitously in a large number of bioactive natural products, drug intermediates, pharmaceuticals, and agrochemicals. Benzimidazoles are a privileged class of compounds among the *N*-heterocycles with a diverse spectrum of biological activities and therapeutic potentialities.[4] Benzimidazole derivatives have found diverse applications in therapeutic areas[5] including anti-ulcers, anti-hypertensives, anti-virals, anti-fungals, anti-cancers, and anti-histaminics. In addition, benzimidazoles are very important intermediates in dyes and polymer synthesis[6a] and also widespread applications in fluorescence,[6b] chemosensing,[6c] crystal engineering,[6d] and corrosion science.[6e] Due to their wide spread use in different segment of science and technology, a number of methods have been reported for their synthesis. They are commonly prepared by the condensation of aromatic 1,2-diamine with aldehydes[7] using oxidants or carboxylic acid derivatives under harsh conditions. Recently, oxidative condensations of the alcohol or amines with aromatic 1,2-diamine have also been developed.[8] Copper (I) catalyzed coupling of o-haloacetanilide with amine/amidine to 2-substituted benzimidazoles is known in the litrature.[9] Bronsted acids such phosphoric acid (H_3PO_4) or *p*-toluene sulfonic acid (p-TsOH) catalyzed synthesis of benzimidazoles are successfully studied.[10] However, despite of some notable advances, they generally suffer from one or more drawbacks, such as requirement of stoichiometric or excess amounts of strong oxidants, high temperatures, high transition metal catalyst loading, harsh reaction conditions and also non-recyclability of the catalysts or protic acids. In the field of organic synthesis, C-C bond cleavage reaction is a topic of interest that allows C-C/C-N bond annulation to construct new molecules of interest. In spite of having lot of significant advances in this field, most of the methods rely on transition metal catalyzed processes. But recyclable metal catalyzed C-C bond cleavage reactions of eco-friendly in nature to achieve unstrained molecules are still in its infancy.

In the course of our ongoing research on the development of efficient methods for heterocycle synthesis[11] herein, we report that benzimidazoles can readily be obtained from the substituted o-phenylenediamines and β–ketoester or amide by the catalysis of silica supported ferric chloride in a very short reaction time through intermediate aminal formation followed by H-bond assisted selective C−C bond cleavage. This method has several advantages such as (i) oxidant free, (ii) very mind condition, (iii) low catalyst loading, (iv) no co-occurance of side product specially 1,2-disubstituted benzimidazole and (iv) catalyst recyclability etc. than direct synthesis of benzimidazoles from o-phenylenediamine and aldehyde. Recently, we have reported[11c] that ionic liquid could be utilized as an activator at high temperature (>120°C) for the synthesis of

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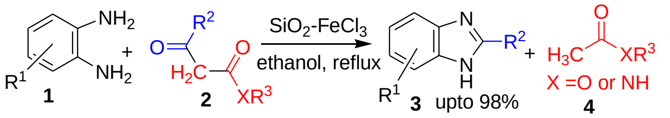
* Corresponding author. *Tel: +91-381-237-9070; Fax: +91-381-2374802*; e-mail: *smajumdar@tripurauniv.in*

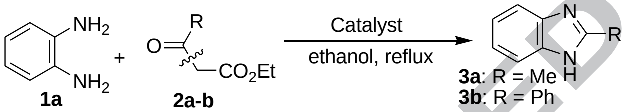
benzimidazoles from aromatic 1,2-diamines (**1**) and β-keto ester/amides (**2**) via thermolysis of intermediate 1,5-benzodiazepinone. In contrast to our previous method, the present method took place under mild conditions to produce both 2-alkyl (long alkyl chain) and 2-aryl-substituted benzimidazoles (**3**, Scheme 1) in excellent yields with a high tolerance to a variety of functional groups.



Scheme 1: SiO_2-$FeCl_3$ catalyzed synthesis of benzimidazole using β-keotester/amide as acyl source

To optimize the reaction condition, initially the reaction of o-phenylene diamine (**1a**) and ethyl acetoacetate (**2a**) was chosen as model using different heterogeneous catalysts. No reaction was observed in the absence or presence of silica-gel (230-400 Mesh) in refluxing ethanol (Table 1, entry 1). However, under identical condition SiO_2-$KHSO_4$ (40 mg, 10% $KHSO_4$),[12] SiO_2-$HClO_4$ (40 mg, 10% w/v)[13] and SiO_2-$FeCl_3$ (40 mg containing ~12.5% $FeCl_3$)[4] catalysts afforded 2-methyl benzimidazole (**3a**) in 83%, 90% and 98% respectively within 2 h (Table 1, entries 2-4). Reactions at room temperature in ethanol or DCM or in refluxing DCM with silica-$FeCl_3$ were not successful. Further decrease of the quantity of SiO_2-$FeCl_3$ also drops the yield dramatically (Table 1, entries 5). Our study revealed that 5 mol% $FeCl_3$ alone was affective for the synthesis of 2-methyl benzimidazole in refluxing ethanol with longer reaction time and lesser yield (Table 1, entry 6).

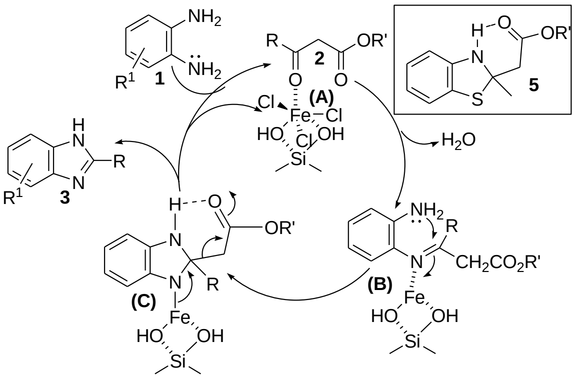
Table 1: Optimization of reaction condition and substrate scope[a]



Entry	Catalyst	Solvent	R	Time (h)	Yield (%)
1	SiO_2	EtOH	Me	2.0	NR
2	SiO_2-$KHSO_4$	EtOH	Me	2.0	83
3	SiO_2-$HClO_4$	EtOH	Me	1.5	90
4	**SiO_2-$FeCl_3$ (3 mol%)**	**EtOH**	**Me**	**1.5**	**98**
5	SiO_2-$FeCl_3$(2 mol%)	EtOH	Me	4.0	76
6	$FeCl_3$ (5 mol%)	EtOH	Me	5.0	75
7	Amberlyst 15	EtOH	Me	2.0	92[b]
8	Amberlite IR120 H^+	EtOH	Me	2.0	94[b]
9	nanoTS1	EtOH	Me	2.0	98[c]
10	SiO_2-$FeCl_3$ (3 mol%)	EtOH	Ph	3.0	92
11	Amberlite IR120 H^+	EtOH	Ph	48.0	73[b]
12	nanoTS1	EtOH	Ph	8.0	20
13	SiO_2-$FeCl_3$(3 mol%)	EtOH	Me	2.0	98[d]

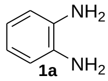
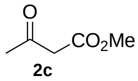
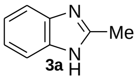
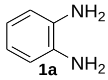
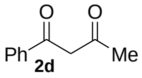
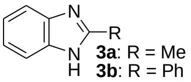
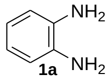
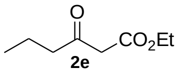
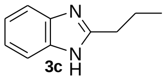
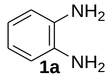
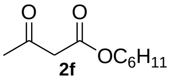
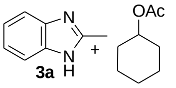
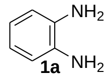
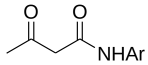
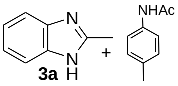
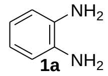
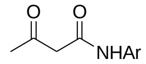
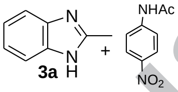
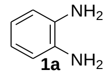
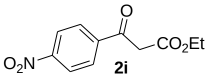
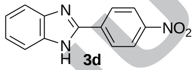
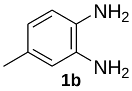
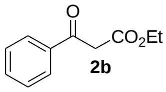
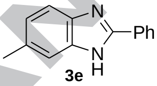
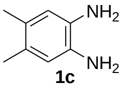
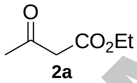
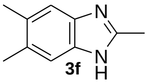
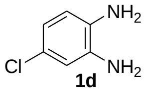
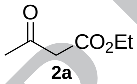
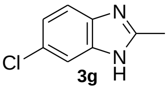
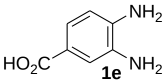
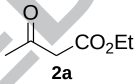
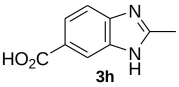
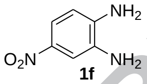
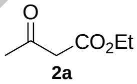
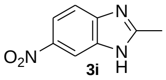
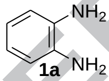
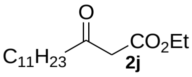
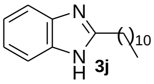
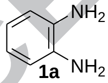
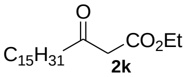
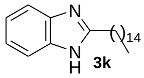
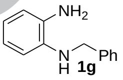
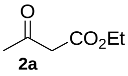
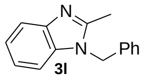
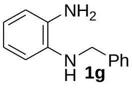
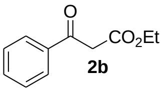
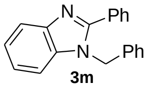
[a] reaction performed in 1 mmol scale; [b] 40 mg resin was used in each entries; [c] 5 mg nano TS1 was employed; [d] reaction was in 20 mmol scale

We have also investigated the reaction using commercially available two sulphonic acid resins (Amberlyst-15 and Amberlite IR $120H^+$) and nano titania-silica (TS1).[14] All of these immobilized catalysts shows promising activity in all most same level of efficiency (Table 1, entry 7-9) as like as silica-$FeCl_3$ catalyst. However, the resin catalyzed or TS1 catalyzed reactions are very slow and produced lesser yield in cases of other β-ketoesters **2b** (R = Ph, Table 1, entries 11, 12 vs entries 8, 9) although these catalysts showed excellent recyclability (results not shown). It is observed from the results assembled in Table 1 that SiO_2-$FeCl_3$ showed better catalytic activity for the synthesis of 2-methyl and 2-phenyl benzimidazoles (**3a-b**) in 98% and 92% yield respectively. The present protocol is also compatible for large scale synthesis (20 mmol) of 2-methyl benzimidazoles (Table 1, entry 13). Reaction under solvent free condition results incomplete conversion due to the deposition of solid product on the surface of solid catalyst which in turns shield catalyst from the reactants. To explore the generality of the present approach we have studied with various aromatic diamines and β-ketoesters under optimized condition (Table 1, entry 4). o-Phenylenediamine reacts with methyl acetoacetate (**2c**) in the presence of SiO_2-$FeCl_3$ (3 mol%) catalyst also produced 2-methyl benzimidazole but it reacts with benzoyl acetone (**2d**) under same conditions producing a mixture of 2-methyl benzimidazole (**3a**) and 2-phenyl benzimidazole (**3b**) in a ratio of 3:1 along with acetophenone as by product (Table 2, entry 2). Formation of acetophenone by-product indicated the cleavage of C-C bond in this reaction. Similarly, ethyl 3-oxo hexanoate (**2e**) afforded 2-propyl benzimidazoles (**3c**) in 90% yield (Table 2, entry 3). Isolation and characterisation of cyclohexyl acetate, 4-methyl acetanilide and 4-nitroacetanilide along with excellent yield of 2-methyl benzimidazole from the reactions (Table 2, entries 4-6) provide further evidences that the reaction proceed through C-C bond cleavage reaction of β-ketoesters or amides. β-Ketoesters containing aromatic ring with electron withdrawing (**2i**) substituent undergo same type of reaction that yielded benzimidazoles (**3d**) without difficulties (Table 2, entries 7). Diversity of the synthesis also observed in the cases of other aromatic o-phenylenediamines **1b-f** and highly substituted benzimidazoles **3e-i** were obtained in good to excellent yield (Table 2, entries 8-12). Benzimidazoles containing long alkyl chain at C-2 is very significant as so many studies have been carried out to explore their aggregation and other physical properties but they were prepared by heating aromatic diamines, fatty acid and PPA at very high temperature.[15] They were produced generally in very low yield, required inert condition and critical work up protocol made the process less interesting. In this context our method produced **3j** and **3k** in 90% and 92% yields respectively (Table 2, entry 13, 14). The N-mono substituted phenylenediamine (**1g**) also participated benzimidazole formation reaction that produced 1,2-disubtuted benzimidazoles **3l-m** (table 2, entris 15, 16). Unfortunately 2-amino phenol/thiophrnol failed to produce benzoxazole/benzothiazole. In the later case, thioaminal was produced in 60 % yield, no change was observed upon heating at 120 °C. Although the exact mechanism of the silica-supported ferric chloride catalyzed reaction is not clear to us but Lewis acid has major role during the heterocyclization with C-C cleavage. Adsorption of iron (III) chloride on the surface of silica is probably make polynuclear iron complex, which activates ketone carbonyl of β-keto esters/amides or diketone for nucleophilic attack (A). Thus aromatic dimines first produced imino ester (B) (equilibrium with enamine is also possible) which undergo ring closing by second amino group to form aminal (C) followed by H-bond assisted C-C bond cleavage produces benzimidazole (Scheme 2). Silica being water absorbent could facilitate the formation of **B**. Isolation of thioaminal intermediate **5** from the reaction 2-amino thiophenol



Scheme 2: Probable mechanism SiO_2-$FeCl_3$ catalysed reaction

Table 2: Diversity in the synthesis of substituted benzimidazoles using SiO_2-$FeCl_3$ (3-5 mol%) as recyclable catalyst.

Entry	Diamine (**1**)	β-ketoester/amide (**2**)	Product (**3**)	Time (h)	Yield (%)
1	 **1a**	 **2c**	 **3a**	1.0	94[11c]
2	 **1a**	 **2d**	 **3a**: R = Me **3b**: R = Ph	3.0	60 (**3a**) 15 (**3b**)[11c]
3	 **1a**	 **2e**	 **3c**	2.0	90[16]
4	 **1a**	 **2f**	 **3a**	1.5	85
5	 **1a**	 Ar = p-tolyl (**2g**)	 **3a**	1.0	90
6	 **1a**	 Ar = 4-nitrophenyl(**2h**)	 **3a**	2.0	88
7	 **1a**	 **2i**	 **3d**	4.0	78[11b]
8	 **1b**	 **2b**	 **3e**	1.5	77[11c]
9	 **1c**	 **2a**	 **3f**	1.0	87[11c]
10	 **1d**	 **2a**	 **3g**	1.5	82[11c]
11	 **1e**	 **2a**	 **3h**	2.0	84[11c]
12	 **1f**	 **2a**	 **3i**	2.5	78[11c]
13	 **1a**	 **2j**	 **3j**	3.0	90
14	 **1a**	 **2k**	 **3k**	3.0	92
15	 **1g**	 **2a**	 **3l**	2.0	87[17]
16	 **1g**	 **2b**	 **3m**	3.0	85[11b]

and ethyl acetoacetate supports our suggestion although this intermediate thioaminal (**5,** see SI) became inert to carbon-carbon bond cleavage because in this aminal N-H remains in the form of hydrogen bonded (Scheme 2, inset). Elimination of enolate has prevented due to poor donor activity of sulphur atom. Finally, we have investigated catalytic recyclability of the catalyst SiO_2-$FeCl_3$ (40 mg/mmol substrate) from the reaction of ethylacetoacetate and o-phenylenediamine (20 mmol). After completion of reaction catalyst was filtered, washed several times with dicloromethane and dried under vacuum and used for next cycle. The results (98% initial, 96%, 95%, 92% and 90%) evidently showed that the loss of catalytic efficiency is retained (Figure 1). In conclusion, we have developed a novel, non-conventional, very fast, simple and efficient method to synthesize highly substituted benzimidazoles from the reaction between β-ketoesters or amides and aromatic diamines through C-C bond cleavage using silica supported ferric chloride (3 mol%) as recyclable catalyst. On the basis of our results we were able to demonstrated mechanistic evidences in favour of the suggested mechanism. Our study also reveals that the catalyst can be recycled up to five cycles without significant loss of its activity.

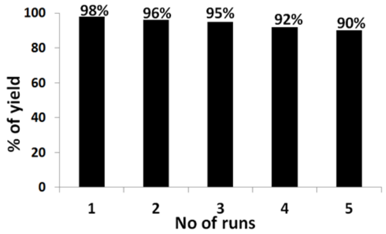


Figure 1: Test of recyclability of SiO_2-$FeCl_3$ reaction

Typical procedure for benzimidazole formation: To a solution of aromatic diamine (1 mmol), β-ketoester (1 mmol) in ethanol (5 mL) SiO_2-$FeCl_3$ (40 mg) was added followed by reflux for appropriate time indicated in Table 1 and Table 2. After completion of reaction (TLC), the catalyst was filtered through whatmann 42 filter paper; residue was washed several times with dichloromethane. The combined filtrate was evaporated to dryness to obtain crude product which was re-crystalized or passing through short pad silica-gel column to get analytically pure product. **2-n-Pentadecyl-1*H*-benzimidazole (3l):** Yield 92%, amorphous solid, m. p. 90-92^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (bs, 1H), 7.75-7.72 (m, 2H), 7.38-7.26 (m, 2H), 3.24 (t, *J* = 7.5 Hz, 2H), 2.0 (t, *J* = 7.2 Hz, 2H), 1.37-1.16 (m, 24H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.2, 132.5, 124.9, 114.0, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 28.0, 27.2, 22.7, 14.1 HRMS calcd for $C_{22}H_{36}N_2+H^+$ 329.2957; found 329.2957

Acknowledgments

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Title of the manuscript: **Silica-ferric chloride (SiO_2-$FeCl_3$) catalyzed selective synthesis of 2-substituted benzimidazole through $C_{sp}2$-$C_{sp}3$ bond cleavage of β-ketoester/amide**

Authors: Swapan Majumdar⁎, Ankita Chakraborty, Subrata Bhattacharjee, Sudipto Debnath and Dilip K. Maiti

Submitted to Tetrahedron Letters

HIGHLIGHTS

- SiO_2-$FeCl_3$ was found as effective catalyst for facile synthesis of benzimidazole
- Reaction proceed through C-N annulation followed by C-C bond cleavage
- The catalyst can be re-used upto five cycle without loss in catalytic activity.

⁎ Corresponding author. *Tel: +91-381-237-9070; Fax: +91-381-2374802*; e-mail: *smajumdar@tripurauniv.in*