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Sodium Hippurate as an Efficient Ligand for the Development of an Iron-Hippurato Complex Catalysing the Synthesis of 2-Arylbenzoxazoles: A Novel Approach

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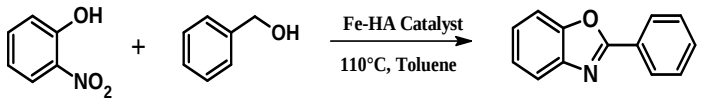
ABSTRACT

Organometallic catalysts have gained popularity due to their superior efficiency and cost-effectiveness when compared to standard metal catalysts. A new protocol for the development of iron catalysts using an in-house designed sodium hippurate ligand is described. This protocol allows the synthesis of 2-Arylbenzoxazoles from 2-Nitrophenols and Benzyl Alcohols via hydrogen transfer. Iron catalysts demonstrate high efficiency in benzoxazole synthesis without external reducing agents or acids, making the reaction simpler. This stable and cost-effective method is a good alternative to current synthetic protocols and provides a way to produce valuable heterocyclic compounds for medical and scientific applications.

Graphical abstract-



Keywords-Organometallic catalysts, Heterocyclic synthesis, Hippuric acid, Metal complex, Hydrogen transfer.

Abbreviations

NP: 2-Nitrophenol, BA: Benzyl Alcohol, BBA: 4-Bromobenzyl alcohol, PM:2-Pyridine methanol, PA: Picric acid, MBA: 4-Methoxybenzyl alcohol, RT: Room temperature, FNP: 4-Fluoro-2-Nitrophenol, NBA: 2-Nitrobenzyl alcohol, HA: Hippuric acid.

1. INTRODUCTION

Organometallic synthesis preceded synthetic chemistry.[1] Transition metals are readily available and have emerged as good candidates for catalysts. Despite their wide availability, iron-catalyzed reactions are not well understood.[2] Here we have developed metal-iron complexes with hippuric acid (HA) as an effective ligand. Aryl-substituted benzoxazoles are common building blocks for the synthesis of drugs, natural products, functional materials, agrochemicals, and antibiotic, antifungal, antimicrobial, and anticancer properties.[3-5] The developed catalyst is used for the synthesis of 2-arylbenzoxazole from the condensation of 2-nitrophenols and benzyl alcohol. It's crucial to synthesize benzoxazole molecules. Numerous beneficial advancements have been achieved in order to accomplish this goal. The synthesis from 2-nitrophenols and benzylic alcohols is one such example. The scientific community has witnessed a surge in interest regarding the activation of C-H bonds, particularly in facilitating the direct synthesis of C-C and C-heteroatom bonds. This area of research has attracted attention because of its potential applications in drug synthesis and catalysis. Aryl-substituted benzoxazoles have been synthesized via direct C-H coupling followed by C-C bond formation with aryl halides,

aryl silanes, and aromatic carboxylic acids.[6-8] Conventional methods for the synthesis of these important compounds are twofold. One method involves the metal-catalyzed intramolecular cyclization of O-haloanilides or their analogs. [9-12] Their second approach involves the hydrolysis of 2-aminophenol and carboxylic acid products under strong acid/high temperature. A new generation of catalytic systems has emerged, facilitating the direct conversion of nitroarenes and alcohols into C-N bonded compounds through hydrogen transfer reactions.[13-15] This method provides a shortcut for C-N bond formation using stable starting materials without any external reducing reagent or oxidant. However, noble metals such as ruthenium, palladium, or iridium were used in most cases. The use of cheap and nontoxic iron catalysts for C-N bond formation would be highly desirable.[16-17] Herein, we report an iron-catalyzed 2-arylbenzoxazoleformation from 2-nitrophenols and benzylic alcohols, affording the aryl-substituted benzoxazoles in high yields.

2.EXPERIMENTAL

2.1 Materials: –

2-Nitrophenol (99%, LOBA CHEM), $FeCl_2$ (98%, LOBA CHEM), Benzyl Alcohol (98.5%, LOBA CHEM), Hippuric acid (98%, LOBA CHEM), Toluene (99%, LOBA CHEM), Picric acid (99%, LOBA CHEM), 4-Bromobenzyl alcohol (99%, OTTOKEMI), 2-Pyridine methanol (98%, OTTOKEMI), 4-Methoxybenzyl alcohol (98%, OTTOKEMI), 4-Fluoro-2-Nitrophenol (99%, CHEMSWORTH.), 2-Nitrobenzyl alcohol (99%, SIGMA-ALDRICH), NaOH (97% LOBA CHEM.).

2.2 Characterization by using ATR-IR-

IR spectra of ligand and metal complex was procured using Perkin Elmer UATR two. Solid sample was mixed thoroughly with KBr and used for analysis.

2.3 Characterization by using NMR-

^{1}H NMR analysis of ligand and benzoxazole derivatives was conducted on Bruker ADVANCE NEO Nanobay,400 MHz and solvent used was DMSO. For sampling 20 mg sample in 600 ul DMSO.

2.4 Characterization by using XRD

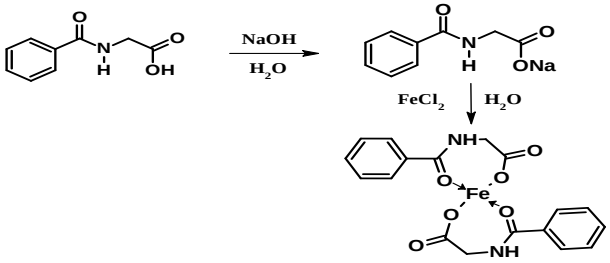
^{1}H NMR analysis of ligand was conducted on LYNXEYE XE T (1D mode): PSD counter.

2.5 Characterization by using GC-MS-

GC-MS on Shimadzu GCMS-QP2010 Ultra.

2.6 Scheme-1 i) The synthesis of Iron-Hippuric acid complex

To a round-bottom flask containing 10 mL of water, 3 grams of $FeCl_2$ was added and stirred until a clear solution formed. In a separate flask, 2 equivalents of hippuric acid were dissolved in 5 mL of water to form a slurry. Then, 2.1 equivalents of NaOH in 5 mL of water was added dropwise, yielding a clear sodium hippurate salt solution after 30 minutes of stirring. The ferric chloride solution was then added dropwise to the sodium hippurate salt solution, initially forming a clear solution that precipitated within minutes. After overnight stirring, the complex was filtered, washed with 60 mL of water, suction-dried for approximately an hour, and oven-dried until a constant mass of 1.8 grams was achieved. (Scheme.1)



Scheme 1: Synthesis of Fe-HA complex

ii) Characterization of Iron-Hippuric acid complex

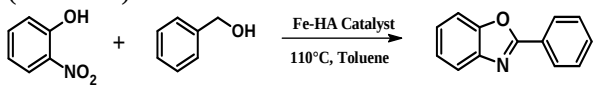
The structure of the novel complex was thoroughly elucidated using various analytical techniques. Infrared spectroscopy revealed the binding interactions between the metal center and distinct functional groups, while ^{1}H NMR spectroscopy determined the ligand structure. Additionally, X-ray diffraction (XRD) was employed to determine the crystal structure.

ii) Solubility of Complex-

Room temperature solubility studies of the Fe-HA complex were conducted in various solvents, including polar protic (methanol, ethanol), polar aprotic (DMSO, DMF, DCM, ethyl acetate, THF), and non-polar (petroleum ether) solvents. Notably, the Fe-HA complex exhibited solubility exclusively in DMSO.

2.7 Scheme 2. Condensation of 2-Nitrophenol and Benzyl Alcohol

Condensation of 2-Nitrophenol and Benzyl Alcohol (Scheme 2) was done at 110°C in toluene using metal catalyst (Fe-HA). The addition of catalyst to nitro compound and alcohol was done at R.T. and the temperature was increased to 110°C subsequently. The product was isolated by the filtration followed by concentrating organic layer. The product was extracted with petroleum ether, dried using sodium sulphate, and evaporated to get pure 2-Aryl benzoxazole (Scheme 2).



Scheme.2: Condensation of 2-Nitrophenol and Benzyl Alcohol

3. RESULTS AND DISCUSSION

3.1. Characterization of complex

3.1.1 NMR spectrum of Iron-Hippuric acid complex

The ^{1}H NMR spectrum of the complex provides crucial evidence for its formation, revealing key signals that confirm the presence of specific functional groups. In comparison with the NMR spectrum of the ligand the spectrum of complex shows a methylene group (-CH_2) signal at 4 ppm, aromatic ring signals at 7.6 ppm and 7.9 ppm, and an amide proton (-NH) signal at 9.5 ppm. Notably, the carboxylic group (-COOH) signal around 12.5 ppm is absent, indicating its involvement in coordination during complex formation. Additionally, a residual solvent peak of DMSO, is observed at 2.5 ppm.

3.1.2 Infrared spectrum of Iron-Hippuric acid complex

The interpretation of IR spectra reveals the formation of a complex by analysing various IR frequencies. Ligand sharp (C=O) stretching peak at 1740 cm^{-1} shifts to 1639 cm^{-1} in the complex, revealing (C=O) group participation. Additionally, the broad carboxylic acid peak around 3400 cm^{-1} disappears, confirming carboxylate group coordination with Fe. The presence of a sharp peak at 3295 cm-1 indicates (N-H) bond stretching in the amide group, while the peak at 735 cm^{-1} suggests the presence of a monosubstituted benzene ring.

3.1.3 XRD pattern of Iron-Hippuric acid complex:

The XRD pattern of Iron-Hippuric acid complex reveals sharp peaks, signifying its crystalline nature and well-ordered atomic arrangement. Specifically, the 2θ values of 12.86°, 17.42°, 21.18°, 23.1°, 27.61°, 32.5°, and 41.4° confirm the crystallographic conformation and purity of Iron-Hippuric acid complex . The results indicate that the complex, characterized by a highly organized three-dimensional molecular arrangement.

3.2 Characterisation of 2-Phenyl Benzoxazole

The structure of the 2-Phenyl Benzoxazole was thoroughly elucidated using various analytical techniques. Infrared spectroscopy revealed distinct functional groups, while ^{1}H NMR spectroscopy determined the molecular structure. Additionally, mass spectrum was employed to determine molecular composition.

3.2.1 NMR spectrum of 2-Phenyl Benzoxazole

The NMR spectra of 2-phenylbenzoxazole exhibit distinct signals that provide valuable information about its molecular structure. In the ^{1}H NMR spectrum, signals appear between 7.1-8.3 ppm, corresponding to protons on the oxazole ring, phenyl and benzene ring This NMR spectrum findings provides important information for structural elucidation and presence of key functional groups in the molecule, laying the groundwork for additional characterization and feature elucidation.

3.2.2 Infrared spectrum of 2-Phenyl Benzoxazole

The IR spectrum of 2-phenylbenzoxazole spectrum typically displays strong absorption bands around 1600-1630 cm^{-1} due to C=N stretching, while medium-strong bands appear between 1550-1600 cm^{-1} attributed to C=C stretching of the aromatic rings. Additionally, medium-intensity bands are observed around 1240-1270 cm^{-1} for C-O stretching, along with weaker bands in the 3050-3100 cm^{-1} region corresponding to C-H stretching of the aromatic rings, respectively.

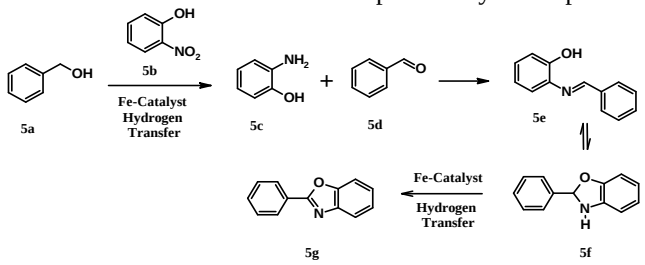
3.2.3 Mass spectrum of 2-Phenyl Benzoxazole

The mass spectrum of 2-Phenylbenzoxazole reveals a molecular ion peak at 196 m/z, confirming a molecular weight of 196, which aligns with the molecular formula $C_{13}H_9NO$. Notably, the base peak is observed at 195 m/z.

3.3 Possible mechanism for Condensation 2-Nitrophenol and Benzyl Alcohol

The reaction involves a series of steps, starting with the oxidation of compound **(5a)** to form aldehyde **(5d)** and reducing **(5a)** to **(5c)**. The aldehyde **(5d)** then condenses with **(5c)** to form imine **(5e)**, which exists in equilibrium with dihydrobenzazole **(5f)**. A hydrogen-transfer process from **(5f)** to **(5a)** ultimately yields the

desired product **(5g)**. The nitro group plays a crucial role, acting as a hydrogen acceptor in two separate instances. This mechanism enables the efficient formation of product by redox process.



3.4 Optimisation

3.4.1 Solubility of catalyst[a] -

The Fe-HA catalyst exhibited limited solubility, showing no dissolution in various common solvents such as Ethyl Acetate, Methanol, Dichloromethane (MDC), Tetrahydrofuran (THF), Ethanol, and N,N-Dimethylformamide (DMF). However, it demonstrated solubility in Dimethyl Sulfoxide (DMSO). This unique solubility profile suggests that DMSO's polar aprotic nature facilitates interaction with the Fe-HA catalyst.(Table no 3.1)

Table 3.1 : Solubility of catalyst[a] -

Sr no.	Catalyst	Solvent	Solubility[b]
1	Fe-HA	Ethyl Acetate	No
2	Fe-HA	Methanol	No
3	Fe-HA	MDC	No
4	Fe-HA	THF	No
5	Fe-HA	DMSO	Yes
6	Fe-HA	DMF	No
7	Fe-HA	Ethanol	No

[a]Reaction condition – Solubility was tested using 10 volumes of solvent.
[b]Solubility of catalysts.

3.4.2 Solvent Effect on Condensation Reaction[a]

The impact of Toluene, 1,4-Dioxane, O-Xylene, Anisole, DMSO, Chlorobenzene and water as solvents in the condensation reaction was examined, demonstrating that nearly all solvents yielded between 70 to 80%. Since toluene yields almost 95% in condensation reaction, it is chosen as the preferred solvent. (Table no 3.2)

Table 3.2 : Solvent Effect on Condensation Reaction[a]

Sr no.	Catalyst	Solvent	Yield[b,](%)
1	Fe-HA	Toluene	94
2	Fe-HA	1,4-Dioxane	72
3	Fe-HA	O-Xylene	75
4	Fe-HA	Anisole	80
5	Fe-HA	DMSO	77
6	Fe-HA	Chlorobenzene	81
7	Fe-HA	Water	70

[a]Reaction conditions : 2-Nitrophenol (1 mmol), Benzyl Alcohol (2.5 mmol), temp-110°C solvent (5 volumes), catalyst (20 wt %), time (24 hours)
[b]Isolated yield.

3.4.3 Effect of Temperature on Condensation Reaction[a]

The effect of temperature on reaction rate was examined, revealing initially slow reaction kinetics. when conducted at room temperature (RT). Nevertheless, the temperature was raised in order to supply sufficient activation energy for the reaction to occur. (Table no 3.3)

Table 3.3: Effect of Temperature on Condensation Reaction[a]-

Sr.No	Catalyst	Temperature (℃)	Time (hours)	Yield[b](%)
1	Fe-HA	RT	48	60

2	Fe-HA	60	48	65
3	Fe-HA	100	48	70
4	Fe-HA	110	24	95
5	Fe-HA	120	24	88

[a]Reaction conditions : 2-Nitrophenol (1 mmol), Benzyl Alcohol (2.5 mmol), temp-110°C, solvent (5 volumes), catalyst (20 wt %), time (24 hours) [b]Isolated yield.

3.4.4 Effect of Weight (%) of Catalyst[a]-

An investigation was carried out to find the best weight percentage of the catalyst for optimization. Findings showed that a 20 wt% percent catalyst resulted in a high yield, whereas using 20 wt% or 30 wt% percent showed similar results. (Table no 3.4)

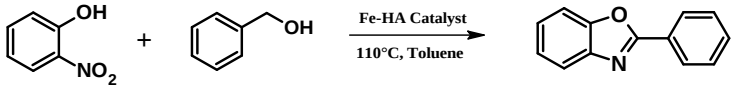
Table 3.4 : Effect of Weight (%) of Catalyst[a]-

Sr.No	Catalyst	Catalyst (weight %)	Time (hours)	Yield[b](%)
1	Fe-HA	5	48	40
2	Fe-HA	10	48	60
3	Fe-HA	15	48	75
4	Fe-HA	20	24	92
5	Fe-HA	30	24	88

[a]Reaction conditions : 2-Nitrophenol (1 mmol), Benzyl Alcohol (2.5 mmol), temp-110°C, solvent (5 volumes), catalyst (20 wt %), time (24 hours), [b]Isolated yield.

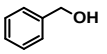
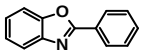
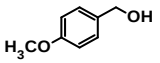
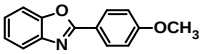
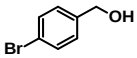
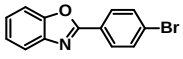
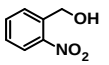
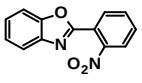
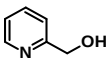
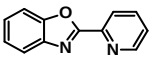
3.4.5 Reactions of 1a with Various Benzyl Alcohols Derivatives[a]-

The Fe-HA catalyst was effectively employed in the synthesis of 2-Arylbenzoxazoles via condensation of 2-Nitrophenol with Benzyl Alcohols in toluene at 110°C. Catalyst optimization yielded a 20 wt% loading, while a 1: 2.5 molar ratio of Benzyl alcohols to 2-Nitrophenol was maintained. The reaction conditions afforded remarkable conversion efficiencies 98%+ and more or less 90% isolated yield across all trials. (Table 3.5)



1a **2** **3**

Table 3.5 : Reactions of 1a with Various Benzyl Alcohols Derivatives[a]-

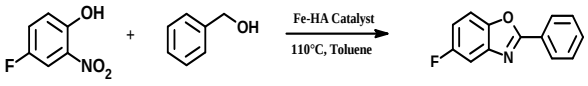
Entry	Alcohol		Product		Yield[b]
1		2a		3a	95
2		2b		3b	82
3		2c		3c	86
4		2d		3d	91
5		2e		3e	75

[a]Reaction conditions : 2-Nitrophenol (1 mmol), Benzyl Alcohols (2.5 mmol), temp-110°C, solvent (5 volumes), catalyst (20 wt %), time (24 hours), [b]Isolated yield

3.4.6 Reactions of 4a with Various Benzyl Alcohols Derivatives[a]-

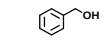
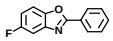
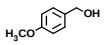
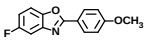
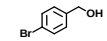
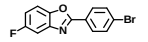
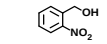
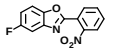
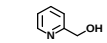
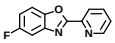
Utilizing the Fe-HA catalyst, 2-Arylbenzoxazoles were efficiently synthesized through the condensation of 4-Fluoro-2-Nitrophenol with Benzyl Alcohols in toluene at 110°C. Optimization studies revealed that a 20 wt% catalyst loading and a 1 : 2.5 Benzyl alcohol to 4-Fluoro-2-Nitrophenol molar ratio yielded exceptional results.

Consistently high conversion rates 98%+ and impressive isolated yields more or less 90% were achieved across multiple trials. (Table 3.6)



4a 5 6

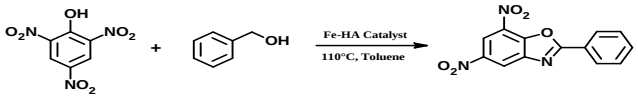
Table 3.6 : Reactions of 4a with Various Benzyl Alcohols Derivatives[a]-

Entry	Alcohol	Product	Yield[b]
1	 5a	 6a	85
2	 5b	 6b	81
3	 5c	 6c	87
4	 5d	 6d	90
5	 5e	 6e	84

[a]Reaction conditions : 4-Fluro-2-Nitrophenol (1 mmol), Benzyl Alcohols (2.5 mmol), temp-110°C, solvent (5volumes), catalyst (20 wt %), time (24 hours) [b]Isolated yield

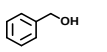
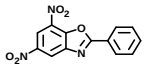
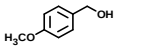
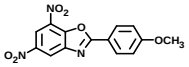
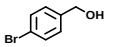
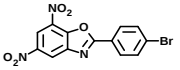
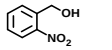
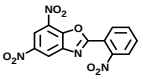
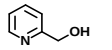
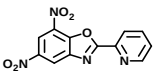
3.4.7 Reaction of 7a with Various Benzyl Alcohols Derivatives[a]-

A highly efficient synthesis of 2-Arylbenzoxazoles was achieved using the Fe-HA catalyst, which facilitated the condensation of Picric acid with Benzyl Alcohols in toluene at 110°C. By optimizing the catalyst loading to 20 wt% and maintaining a 1 : 2.5 molar ratio of Benzyl alcohol to Picric acid, exceptional results were consistently obtained, with conversion rates exceeding 98% and isolated yields approaching 80% across multiple trials. (Table 3.7)



7a 8 9

Table 3.7 : Reactions of 7a with Various Benzyl Alcohols Derivatives[a]-

Entry	Alcohol	Product	Yield[b]
1	 8a	 9a	80
2	 8b	 9b	81
3	 8c	 9c	86
4	 8d	 9d	82
5	 8e	 9e	88

[a]Reaction conditions : Picric acid (1 mmol), Benzyl Alcohol (2.5 mmol), temp-110°C, solvent (5volumes), catalyst (20 wt %), time (24 hours), [b]Isolated yield

3.5 Characterisation of 2-Phenylbenzoxazole Derivatives[a]-

The structure of the 2-Phenyl Benzoxazole was thoroughly elucidated using ^{1}H NMR spectroscopy determined the molecular structure. Additionally, mass spectrum was employed to determine molecular composition.

3.5.1 Spectral analysis of analog -3b

1.Mass spectrum: The mass spectrum of analog (3b) reveals a molecular ion peak at 225 m/z, confirming a molecular weight of 225.24, which aligns with the molecular formula $C_{14}H_{11}NO_2$. Notably, the base peak is observed at 210 m/z indicating a prominent fragment ion.

2.NMR Spectrum: The ^{1}H NMR spectrum of analog (3b) shows distinct signals that offer insights into its structure. The signals between 7.1-8.3 ppm are attributed to protons on the oxazole, phenyl, and benzene rings, while the signal at 3.8 ppm corresponds to methyl protons. These NMR findings provide crucial information for

structural elucidation, confirming the presence of key functional groups and laying the groundwork for further characterization.

3.5.2 Spectral analysis of analog -3c

1.Mass spectrum: The mass spectrum of analog (3c) shows molecular ion peaks at m/z 274 and 276 in a 1:1 ratio, characteristic of bromine-containing compounds due to the bromine isotopes. This confirms a molecular weight of 274.11, consistent with the molecular formula $C_{13}H_8NOBr$. The base peak appears at 195 m/z.
2.NMR Spectrum: The ^1H NMR spectrum of analog (3c) displays distinct signals that offer insights into its molecular structure. The signals between 7.1-8.3 ppm correspond to protons on the oxazole, phenyl, and benzene rings, providing crucial information for structural elucidation and confirming the presence of key functional groups. These findings lay the groundwork for further characterization and detailed structural analysis.

3.5.3 Spectral analysis of analog -3d
1.Mass spectrum: The mass spectrum of analog (3d) reveals a molecular ion peak at 240 m/z, confirming a molecular weight of 240, which aligns with the molecular formula $C_{13}H_8N_2O_3$. Notably, the base peak is observed at 105 m/z.
2.NMR Spectrum: The ^1H NMR spectrum of analog (3d) shows distinct signals between 7.1-8.3 ppm, attributed to protons on the oxazole and benzene rings. These signals provide valuable insights into the molecular structure and structure elucidation.

3.5.4 Spectral analysis of analog -3e
1.Mass spectrum: The mass spectrum of analog (3e) reveals a molecular ion peak at 196 m/z, confirming a molecular weight of 196, which aligns with the molecular formula $C_{11}H_8N_2O$.The base peak appears at 195 m/z.
2.NMR Spectrum: The ^1H NMR spectrum of analog (3e) shows distinct signals that offer insights into its molecular structure. Signals between 7.1-8.3 ppm correspond to aromatic protons, while a signal at 8.9 ppm is attributed to a proton on carbon directly linked to nitrogen. These findings provide valuable information for structural elucidation.

3.5.5 Spectral analysis of analog -6a
1.Mass spectrum: The mass spectrum of analog (6a) reveals a molecular ion peak at 213 m/z, confirming a molecular weight of 213.11, which aligns with the molecular formula $C_{13}H_8NOF$ and the base peak is observed at 213 m/z.
2.NMR Spectrum: The NMR spectra of analog (6a) exhibit distinct signals that provide valuable information about its molecular structure. In the ^1H NMR spectrum, signals appear between 7.1-8.3 ppm, corresponding to protons on the oxazole ring, phenyl and benzene ring This NMR spectrum findings provides important information for structural elucidation laying the groundwork for additional characterization and feature elucidation.

3.5.6 Spectral analysis of analog -6b
1.Mass spectrum: The mass spectrum of analog (6b) shows a molecular ion peak at 244 m/z, consistent with the molecular formula $C_{13}H_{10}NO_2F$ and molecular weight 243.99. The base peak is observed at 243 m/z.
2.NMR Spectrum: The ^1H NMR spectrum of analog (6b) shows signals between 7.1-8.3 ppm, suggesting aromatic protons of benzene and oxazole ring. A signal at 3.9 ppm corresponds to methyl protons, advising the presence of a methyl group in the molecule.

3.5.7 Spectral analysis of analog -6c
1.Mass spectrum: The mass spectrum of analog (6c) reveals a molecular ion peak at 371 m/z and 373 m/z in a 1:1 ratio, characteristic of bromine-containing compounds due to the bromine isotopes confirming a molecular weight of 371.79, which aligns with the molecular formula $C_{13}H_7NOFBr$. Notably, the base peak is observed at 279 m/z.
2.NMR Spectrum: The ^1H NMR spectrum of analog (6c) shows signals between 7.1-8.2 ppm, attributed to aromatic protons on the oxazole ring and benzene ring. These findings provide valuable insights into the molecular structure, confirming the presence of key functional group, facilitating further characterization of the analog.

3.5.8 Spectral analysis of analog -6d
1.Mass spectrum: The mass spectrum of analog (6d) reveals a molecular ion peak at 258 m/z, confirming a molecular weight of 257.99, aligning with the molecular formula $C_{13}H_7N_2O_3F$.and the base peak is observed at 105 m/z.
2.NMR Spectrum: The NMR spectra of analog (6d) exhibit distinct signals that provide valuable information about its molecular structure. In the ^1H NMR spectrum, signals appear between 7.1-8.4 ppm, corresponding to

protons on the oxazole ring, phenyl and benzene ring This NMR spectrum findings gives information for structural elucidation and presence of key functional groups.

3.5.9 Spectral analysis of analog -6e

1.Mass spectrum: The mass spectrum of analog (6e) confirms its molecular weight of 213.99 with molecular ion peak at 214 m/z, along the formula $C_{12}H_7N_2OF$ and base peak at 214 m/z.

2.NMR Spectrum: The ^1H NMR spectrum of compound (6e) shows signals between 7.1-7.8 ppm, corresponding to protons on the oxazole and benzene rings. A signal at 8.2 ppm is attributed to a proton present on carbon directly bonded to nitrogen. These findings show valuable insights into the molecular structure.

3.5.10 Spectral analysis of analog -9a

1.Mass spectrum: The mass spectrum of analog (9a) shows a molecular ion peak at m/z 285, consistent with the molecular formula $C_{13}H_7N_3O_5$ and confirming the molecular weight and base peak appears at m/z 105, indicates a prominent fragment ion.

2.NMR Spectrum: The ^1H NMR spectrum of analog (9a) displays characteristic signals that offer insights into its molecular structure. The aromatic protons on the oxazole, phenyl, and benzene rings resonate between 7.1-8.3 ppm. These spectral findings are crucial for confirming the structure and identifying key functional groups.

3.5.11 Spectral analysis of analog -9b

1.Mass spectrum: The mass spectrum of analog (9b) reveals a molecular ion peak at 315 m/z, confirming a molecular weight of 315, which aligns with the molecular formula $C_{14}H_9N_3O_6$.and the base peak is observed at 273 m/z.

2.NMR Spectrum: The NMR spectra of analog (9b) exhibit distinct signals that provide valuable information about its molecular structure. In the ^1H NMR spectrum, signals appear between 6.9-7.4 ppm, corresponding to protons on the oxazole ring, phenyl and benzene ring and signal at 3.8 ppm corresponds to methyl protons. 3.5.12 Spectral analysis of analog -9c

1.Mass spectrum: The mass spectrum of analog (9c) reveals a molecular ion peak at 444m/z, and 446 m/z in a 1:1 ratio, characteristic of bromine-containing compounds due to the bromine isotopes (^{79}Br and ^{81}Br).Notably spectrum shows base peak at 181 m/z suggesting a stable fragment ion. This matches with molecular formula $C_{13}H_6N_3O_5Br$ of the analog and molecular weight 443.8.

2.NMR Spectrum: The ^1H NMR spectrum of analog (9c) displays a range of distinct signals that offer crucial insights into its molecular architecture. Specifically, the aromatic protons on the oxazole, phenyl, and benzene rings resonate between 7.1 ppm to 8.1 ppm and signals 8.8 ppm and 9.2 ppm are of protons in vicinity of two nitro groups providing valuable information about the compound's structure and confirming the presence of these key functional groups. This spectral data plays a vital role in elucidating the molecular structure and facilitating further characterization.

3.5.13 Spectral analysis of analog -9d

1.Mass spectrum: The mass spectrum of analog (9d) reveals a molecular ion peak at 330 m/z confirming a molecular weight of 330 which aligns with the molecular formula C13H6N4O7 Notably, the base peak is observed at 105 m/z.

2.NMR Spectrum: The NMR spectra of analog (9d) exhibit distinct signals that appear between 7.1-8.4 ppm, corresponding to protons on oxazole, phenyl and benzene ring. This spectral data plays a vital role in elucidating the molecular structure.

3.5.14 Spectral analysis of analog -9e

1.Mass spectrum: The mass spectrum of analog (9e) shows a molecular ion peak at 286 m/z and base peak at 57m/z confirming a molecular weight of 286, which aligns with the molecular formula $C_{12}H_6N_4O_5$.

2.NMR Spectrum: The NMR spectra of analog (9e) exhibit distinct signals that provide valuable information about its molecular structure. In the ^1H NMR spectrum, signals appear between 7.1-8.2 ppm, corresponding to protons on the oxazole ring, phenyl and benzene ring. Two distinct at 8.4 ppm and 8.6 ppm are of protons in vicinity of two nitro groups. This NMR spectrum findings provides important information for structural elucidation.

4. CONCLUSION

A novel, efficient, and cost-effective method for synthesizing Fe-HA catalysts has been developed and characterized using infrared, NMR, and XRD spectroscopy. The catalyst's versatility was demonstrated through successful condensation reactions, exhibiting consistent efficacy across various substrates. Notably, nitro groups with electron-donating substituents outperformed those with electron-withdrawing groups. This approach offers a more convenient and practical alternative to existing industrially challenging protocols for generating

substituted benzoxazoles. This breakthrough lays the groundwork for developing new ligands with promising potential for future applications.\

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