PROJECT COMPLETION REPORT

1. Title of the Project: Development of Palladium- and Nickel-based Catalyst for Cross-Coupling reaction of Carboxylic Acid Derivatives

2. Principal Investigator: Dr. Tahshina Begum

3. Mentor: Prof. Nashreen S. Islam

4. Implementing Institution and other collaborating Institution(s): Tezpur University

5. Date of Commencement: 27/04/2022

6. Planned Date of Completion: 26/04/2025

7. Actual Date of Completion: 31/12/2024

8. Objectives as stated in the project proposal:

The main objective of the present proposal is to develop a series of highly active and selective nickel and palladium-based metal complexes with specified ligand systems such as Schiff-base, NHC (*N*-heterocyclic carbene) and oximes

i) To synthesize Pd- and Ni-based complexes involving NHC, Schiff-base and oxime ligands. Special emphasis would be given to develop catalysts having reduced reductive elimination rates and high tendency for C-O oxidative addition led decarbonylation. The set of electronically diverse ligands would include:

a) Monodentate and bidentate aryl- and alky-based phosphine ligands.

b) Heterocycles like quinoline, quinazoline, tetrazole, pyrimidine, imidazolidine, 1,3-azoles, triazole, benzimidazole etc.

c) Monodentate and bidentate N, N-donor, and N, O-donor Schiff-base ligands, and

d) Mono- and polycyclic-oxime derivatives.

e) Immobilization of above-prepared metal complexes on silica, metal oxides, and zeolites via coordination and encapsulation strategies.

ii) Optimization of the cross-coupling of carboxylic acid derivatives:

a) Synthetic methodologies towards biaryl and biaryl ketones: The prepared catalysts would be investigated for their prowess in the activation of C_{aryl}-O and C_{acyl}-O bonds of carboxylic acid derivatives towards coupling reaction.

b) To evaluate ideal reaction conditions: optimization will be done by screening solvents, base, reaction temperature and catalyst loading. Kinetic studies would be performed.

c) The mechanism and the probable reaction pathways will be investigated by DFT and computational calculations. Efforts would be made to implement the developed methods for the synthesis of targets like valsartan, boscalid, fingolimod, lasiodiplodin, sulisobenzone, naringenin and sofalcone, which have pharmaceutical/industrial significances.

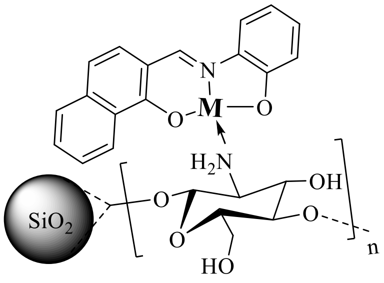
9. Deviation made from original objectives if any, while implementing the project and reasons thereof: No Deviation

10. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:

<u>Experiment 1:</u>

During the first year of the project, Cu(II) and Ni(II) metal complexes of tridentate Schiff Base ligand supported on silica chitosan were prepared. Wherein, Chitosan acts as co-ligand having covalently connected with silica. These complexes were characterized by EDX, SEM, FT-IR and Powder XRD. The catalytic activities of the complexes have been studied in some organic transformation reactions

The successful synthesis of the catalysts **SiO_2-CS-Metal** has been achieved by performing a three-step methodology. The first step involves the preparation of SiO_2-CS. This was obtained by reacting Chitosan dissolved in aqueous solution of acetic acid with silica using NH_3 as a base using previously reported literature. In the second step, a new Schiff base complex is synthesized by refluxing 2-hydroxy-1-napthaldehyde with 2-aminophenol in MeOH. The last step involves the formation of SiO_2-CS-Metal complex by simply mixing $Cu(OAC)_2$ or $Ni(OAc)_2$, SiO_2-CS and the Schiff base ligand in MeOH solution and is refluxed for two days. After that the resulting mixture was cooled. The precipitate was washed with methanol and dried to get a green-colored precipitate of the catalyst (**Figure 1**). The catalysts so obtained are non-hygroscopic, stable and can be stored for a longer period without any change in its catalytic efficiency.

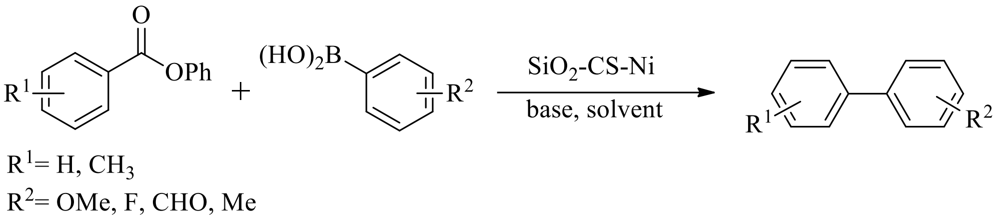


[M= Cu, Ni]

Figure 1: Proposed structure of the catalyst

Catalytic activity: Cross-coupling of Esters using SiO_2-CS-Ni catalyst

The utilization of aromatic esters in lieu of aryl halides in cross-coupling reactions offers advantages due to their easy accessibility, stability, and comparably less-toxicity. The synthesized catalyst (SiO_2-CS-Ni) exhibited excellent activity for the Suzuki-type decarbonylative arylation reaction of esters, using aryl boronic acids as coupling partners. This method proceeds with a recyclable catalytic system, offering an environmentally benign alternative to the existing protocols. The transformation tolerates structurally diverse aryl substituents on both coupling partners and shows high reactivity and excellent functional group tolerance.

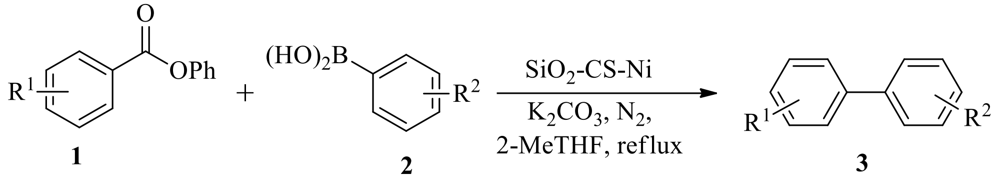


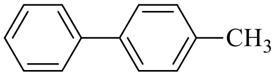
Scheme 4: Decarbonylative cross-coupling catalysed by **SiO_2-CS-N**i

The use of silica enhances nickel absorption, owing to its large surface/volume ratios, and excellent porosity; thereby increasing its catalytic activity and stability. Moreover, these SiO_2-CS-M complexes are air- and moisture-stable, which makes their handling operationally convenient and provides important benefits in terms of cost and safety. The resulting solid catalyst showed excellent catalytic activities in the cross-coupling between aromatic esters and arylboronic acids in 2-MeTHF, under low catalyst loading. To the best of our knowledge, it is the first report on the use of heterogeneous catalyst for such coupling reactions. After optimization of the reaction conditions, various electronically diverse aromatic esters and arylboronic acids were treated to provide high yield coupling products. Interestingly, the immobilized nickel complex is easily isolable after completion of the reaction and can be reused for substituent catalytic reactions without losing its catalytic efficiency.

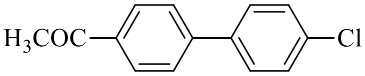
Various electronically diverse substrates were studied under the optimized reaction conditions which deliver excellent yields (**Table 1**). The remarkable advantage of this method is the use of practically water-immiscible solvent 2-MeTHF, which provides easy isolation of the crude mixture just by separation of 2-MeTHF for aqueous layers, and then evaporation of 2-MeTHF.

Table 1: Cross-coupling of Esters using SiO_2-CS-Ni catalyst

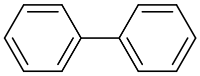




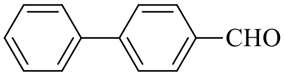
3a, 71%



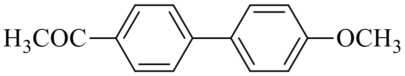
3b, 73%



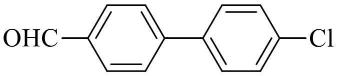
3c, 76%



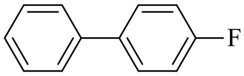
3d, 62%



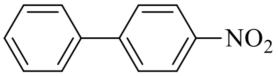
3e, 71%



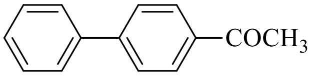
3f, 67%



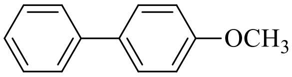
3g, 64%



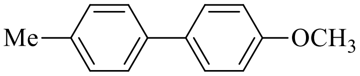
3h, 69%



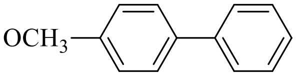
3i, 71%



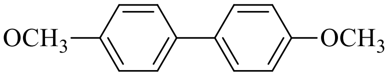
3j, 68%



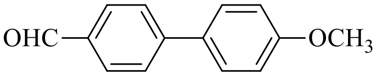
3k, 61%



3l, 72%



3m, 69%



3o, 61%

Regeneration of the catalyst

One of the important features of the catalyst is its heterogeneous nature. The solid catalyst was easy to recover from the spent reaction mixture by centrifugation. The recovered catalyst was washed with water and then acetone and allowed to dry for the next cycle. The recyclability of the catalyst was examined for five cycles under the optimized condition as depicted in Fig 1. The activity of the catalyst retained up to 3rd cycle. Although, 4th cycle onwards there is a slight decrease in the activity of the catalyst. These observations indicate the structural integrity of the catalyst.

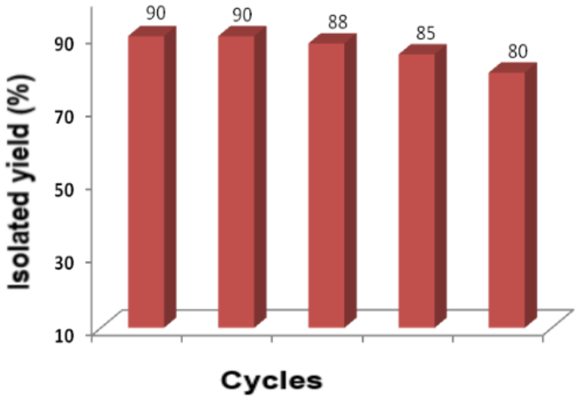


Fig. 1 Regeneration of the catalyst

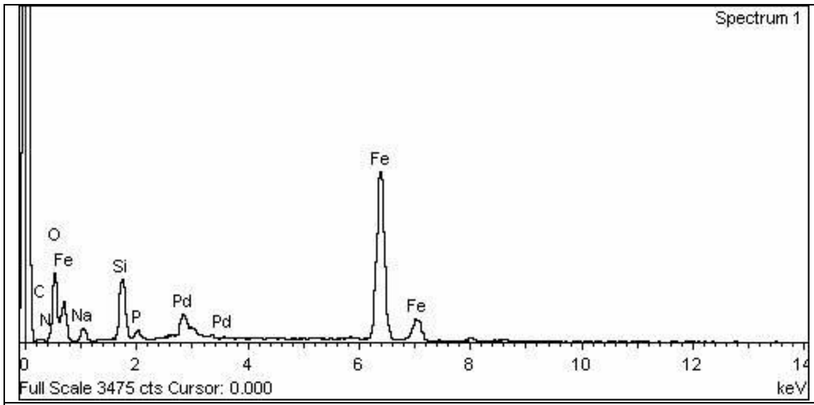
This work is under communication

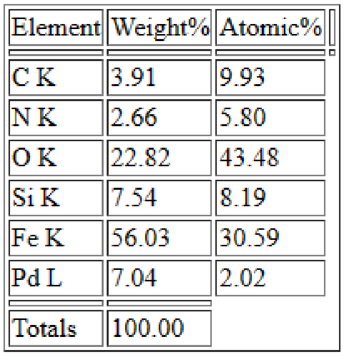
Experiment 2:

We have developed a magnetically separable, Fe_3O_4@TEOS-palladacycle which is oxime-based palladacycle complex and it is a very efficient and versatile catalyst for Suzuki-type decarbonylative cross-coupling of esters with phenylboronic acid in 2-MeTHF under refluxing condition. The novel catalyst was synthesized using a multi-step process involving surface modification, oxime-functionalization, and palladium immobilization, and characterized by FE-SEM, EDX, VSM, FT-IR, P-XRD, TEM, TGA, XPS, and ICP-OES analysis. The Fe_3O_4@TEOS-palladacycle was also used as an efficient catalyst for the preparation of Boscalid, a significant fungicide, via a decarbonylative approach. Moreover, the solid catalyst could be recovered easily and can be reused five times without significant loss of its catalytic activity. More importantly, the wide range of functional groups found to be compatible with the given reaction conditions are the main merits of this protocol**.**

Catalyst Characterization:

The energy dispersive X-ray is used to calculate the elemental composition. The magnetic Fe_3O_4 nanocatalyst's elemental compositions are shown below (**Figure 1**).





Element	Weight%	Atomic%
C K	3.91	9.93
N K	2.66	5.80
O K	22.82	43.48
Si K	7.54	8.19
Fe K	56.03	30.59
Pd L	7.04	2.02
Totals	100.00	

Figure 1: EDX spectra of Fe_3O_4@TEOS-palladacycle

The crystallinity of the synthesized Fe_3O_4 and Fe_3O_4@TEOS-palladacycle MNPs were investigated with PXRD techniques as shown in **Figure 2**. In the spectra of Fe_3O_4, the XRD pattern exhibited sharp reflection peaks at around 2θ= 30.1, 35.5, 43.1, 53.3, 56.9 and 62.7° corresponding to (220), (311), (400), (422), (511) and (440) planes of cubic lattice of Fe_3O_4, respectively (JCPDS no. 88-0866). However, in addition to the Fe_3O_4 peaks, the complex Fe_3O_4@TEOS-palladacycle shows some characteristic peaks at around 2θ= 40.2, 46.6, and 68.1 corresponding to (111), (200), and (220) planes of the face-centered cubic phase of palladium signifying that the as-prepared palladacycle MNPs have a high purity and high crystallinity. (JCPDS number: 46–1043).

Field-emission scanning electron microscopy (FE-SEM) to analyze the surface structure and morphology of the Fe3O4 and Fe3O4@TEOS-Palladium composite material. In **Figure 3**, it is evident that the catalyst particles exhibit a spherical shape, almost monodisperse, and are nano-scaled. However, there is some clustering of the sample attributable to magnetostatic interactions between the particles. Moreover, the representative TEM images of the Fe3O4 and Pd catalysts indicate well-defined spherical Pd nanoparticles dispersed on the surface of Fe3O4 nanoparticles. The average particle size of the Fe3O4 nanoparticles and Fe3O4@TEOS-palladacycle is ~10–13 and 6-7 nm respectively. (Fig. 4 and 5). **Fig. 6** illustrates the TEM image of the catalyst where, six bright circular rings that appeared in the selected area electron diffraction (SAED) pattern indicate diffraction of polycrystalline material and are corresponding to the crystallographic planes (220), (311), (422) and (440) of Fe3O4 and (200) and (220) of fcc-structured Pd nanoparticles which consistent with the XRD analysis of Fe3O4 and Pd nanoparticles. Furthermore, these findings are consistent with the particle-size distribution histogram of Pd catalyst, which are distributed within a narrow range of 3-10 nm with an average size of ~6 nm (Fig. 7). The magnetic properties of Fe_3O_4 and Fe_3O_4@TEOS-palladacycle were analyzed by vibrating sample magnetometer (VSM) using magnetization as a function of magnetic field strength at room temperature (Fig 8). Based on the magnetization curve, the saturation magnetization (Ms) value of Fe_3O_4 was found at 77.26 emu/g, while 0. 0770 kOe and 8.55 emu/g are the values of coercivity (Hc) and retentivity respectively (Fig. 8(a)). On the contrary, saturation magnetization (Ms), coercivity (Hc), and retentivity values of Fe_3O_4@TEOS-palladacycle are 24.08 emu/g, .0442 kOe, and 1.8 emu/g respectively (Fig. 8(b)). The superparamagnetic behavior of Fe_3O_4 in Fe_3O_4@TEOS-palladacycle remained unchanged as the coercivity values of Fe_3O_4 and Fe_3O_4@TEOS-palladacycle were almost identical and extremely close to zero. The low saturation magnetization of Fe_3O_4@TEOS-palladacycle in comparison to Fe_3O_4 MNPs, is due to the presence of non-magnetic silica and other functionalized groups onto the surface of Fe_3O_4 NPs. Moreover, the magnetization curve shows a weak hysteresis loop at room temperature, signifying the occurrence of superparamagnetic behavior in both samples.

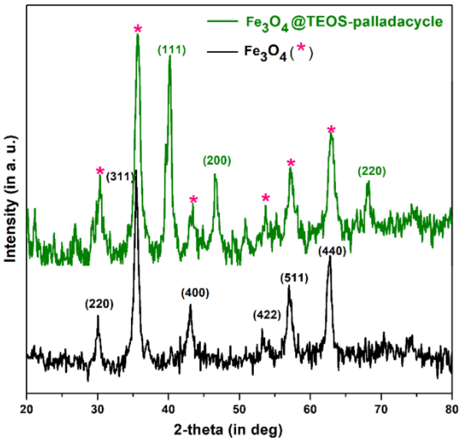


Fig. 2 XRD pattern of Fe_3O_4 and Fe_3O_4@TEOS-palladacycle

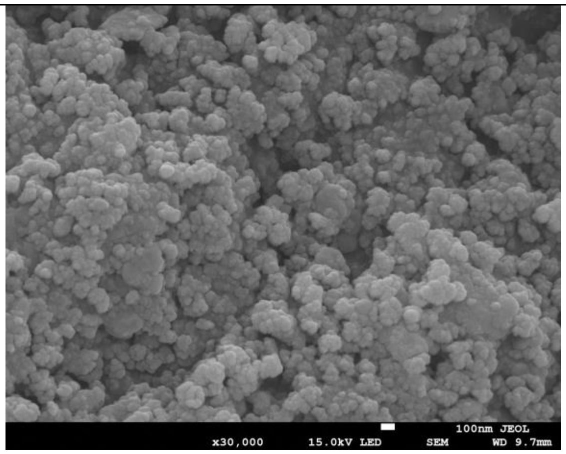
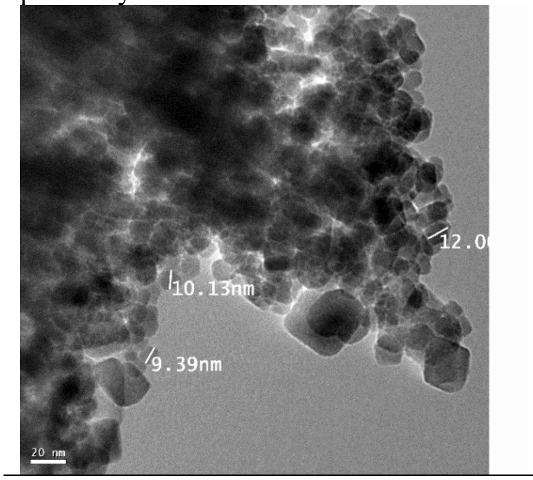


Fig 3: FESEM image of Fe_3O_4@TEOS-palladacycle;



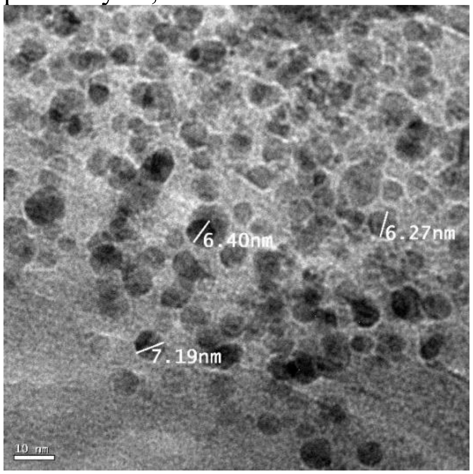


Fig. 4 TEM images of Fe_3O_4

Fig. 5 TEM image of Fe_3O_4@TEOS-palladacycle

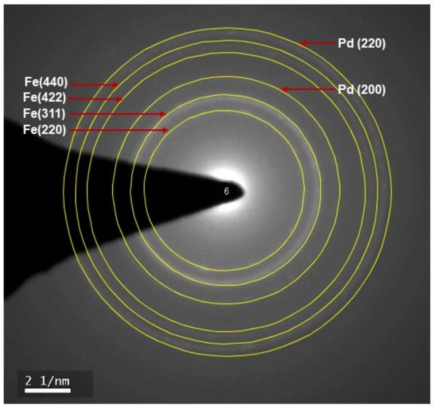


Fig. 6 SAED pattern of Fe_3O_4@TEOS-palladacycle

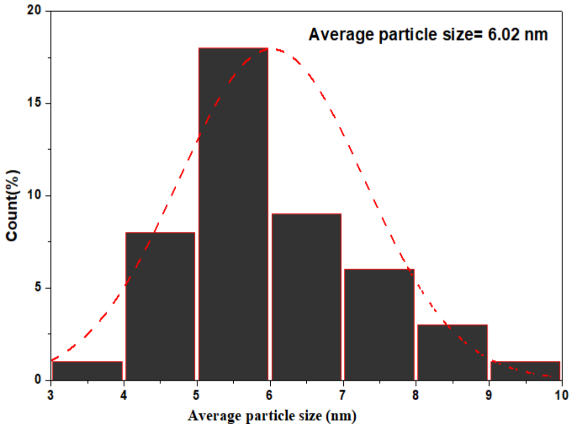


Fig. 7 Particle-size distribution for the catalyst

Even though this decreases the saturation magnetization of the palladium catalyst, the strength of its magnetic power is quite high and can be easily separated from the reaction mixture by using an external magnet.

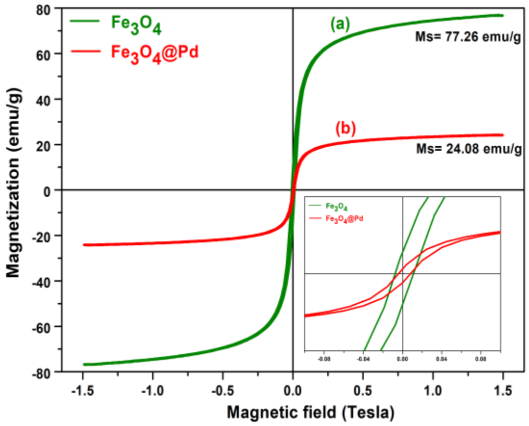


Fig. 8 Room temperature magnetization curve of (a) Fe_3O_4 and (b) Fe_3O_4@TEOS-palladacycle; weak hysteresis loop indicates the superparamagnetic nature of the prepared materials of Fe_3O_4 and Fe_3O_4@TEOS-palladacycle (inset).

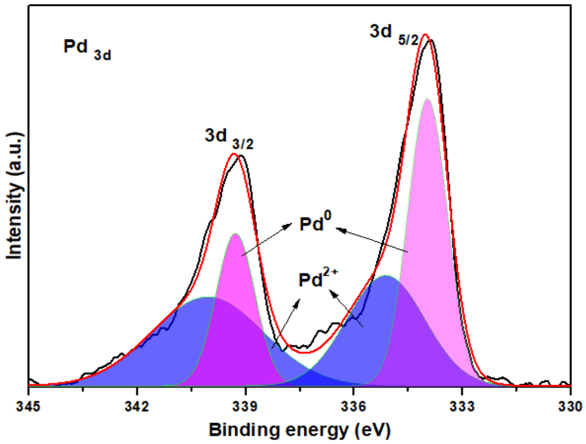
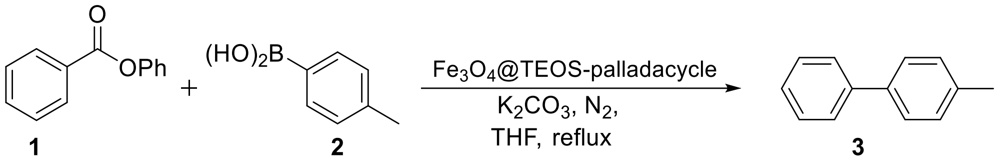


Fig. 9 XPS pattern of Pd 3d

The high-resolution XPS spectrum in the range of 330 to 345 eV (Fig. 9) confirms the effective coordination of palladium on functionalized Fe_3O_4 nanoparticles. The Pd 3d spectra in Fe_3O_4@TEOS-palladacycle consisted of clear doublet peaks that emerged at 339.3 eV and 334.0 eV, corresponding to the 3d3/2 and 3d5/2 peaks of Pd(0) respectively, which closely related to expected Pd(0) values mentioned in the literature (341.2 eV and 335.9 eV). The negative shift of 2.0 and 1.9 eV for Pd(0) of the complex suggests strong coordination between palladium and N-containing ligand with the functionalized Fe_3O_4. The low intensity and broad bands near 340.1 and 335.0 eV indicate a small fragment of palladium in the +2 oxidation state. This might be unreduced Pd(II) or palladium oxide (PdO), which are formed during XPS sample collection. It is expected that most of the Pd species in the catalyst would remain in the zerovalent system since the Pd (0) ratio is larger than the Pd (II) ratio.

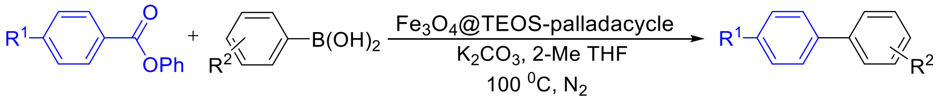
Catalytic activity: Cross-coupling of Esters using Fe_3O_4@TEOS-palladacycle nanocatalyst catalyst

During this period, we have synthesized a Pd-nanocatalyst and investigated its catalytic activity in cross-coupling of aryl esters with aryl boronic acid. To optimize the reaction conditions, a series of experiments under varied conditions in terms of solvents, base, catalyst amount, and temperature for a model cross-coupling reaction of phenyl benzoate **1** with 4-methyl phenylboronic acid **2** were carried out.



The utilization of aromatic esters in lieu of aryl halides in cross-coupling reactions offers advantages due to their easily accessibility, stability, and comparably less-toxicity. The synthesized catalyst (Fe_3O_4@TEOS-palladacycle) exhibited excellent activity for the Suzuki-type decarbonylative arylation reaction of esters, using aryl boronic acids as coupling partners. This method proceeds with a recyclable catalytic system, offering an environmentally benign alternative to the existing protocols. The transformation tolerates structurally diverse aryl substituents on both coupling partners and shows high reactivity and excellent functional group tolerance (Table 2).

Table 2: Scope of Pd-catalyzed Suzuki-Miyaura cross-coupling of esters



Entry	R^1	R^2	Time (h)	Yield^b
1	CH_3	4-CH_3	6.5	91
2	CH_3	H	6	89
3	CH_3	3-CH_3	7	83
4	CH_3	3-CN	8	82
5	CH_3	4-OCH_3	6	89
6	OCH_3	3-CH_3	7	80
7	OCH_3	4-Cl	8	78
8	OCH_3	4-OCH_3	6	89
9	OCH_3	H	6	88
10	OCH_3	4-NO_2	8	82
11	OCH_3	4-$COCH_3$	8	84

12	OCH_3	4-CHO	7	85
13	OCH_3	4-CH_3	6.5	88
14	H	3-CN	8.5	78
15	H	4-Cl	7	80
16	H	4-OCH_3	7	88
17	H	H	6.5	87
18	H	4-NO_2	7	84
19	H	3-CF_3	9	79
20	H	3-CH_3	8	80
21	H	4-$COCH_3$	8	85
22	H	4-CH_3	7	87
23	H	4-F	7.5	82

Scale-up Synthesis.

The decarbonylative cross-coupling reactions have wide applications in large-scale chemical industries due to the easy accessibility and broad functionality of aryl esters and organoboron derivatives. Thus, we have explored the scale-up scope to prepare grams instead of milligrams of biaryl derivatives. Thus, we carried out a gram-scale reaction involving **1** (1 g) and **2** in presence of Fe_3O_4@TEOS-Palladacycle catalyst (Pd mol%). Finally, we were able to isolate 0.9432 grams (94%) of 4-methyl-1,1'-biphenyl.

Hot filtration test:

A hot filtration test was performed in the Suzuki cross-coupling reaction of phenyl benzoate and 4-Me phenylboronic acid to investigate whether the reaction proceeded in a heterogeneous or a homogeneous pathway. After completion of 50% of the coupling reaction, the liquid phase is collected by filtration at the reaction temperature (**Figure 10**). The resulting filtration was stirred for an additional 3h. However, gas chromatography analysis showed negligible progress of the reaction (around 2%) upon further stirring of the catalyst-free solution. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) measurements showed that the leached palladium in the filtrate after removal of the catalyst was 0.00032 ppm. These studies demonstrated that palladium ions have strong coordination and stability to a considerable extent with the heterogeneous solid supports which prohibit metal leaching during the reaction.

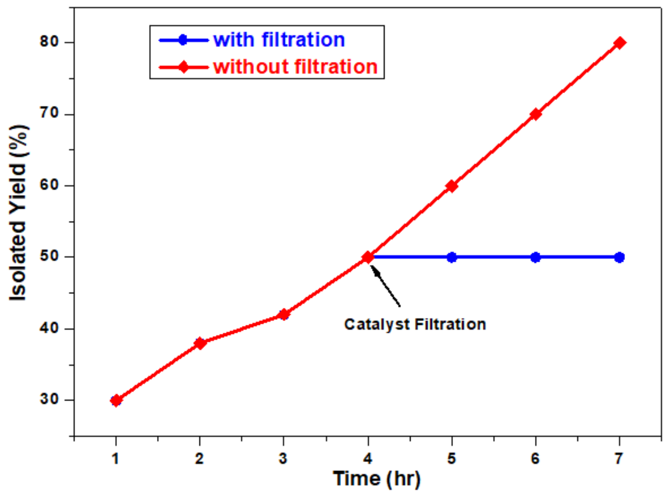


Figure 10: Hot-filtration test

This work is published in ***Catalysis Science and Technology (2025)***

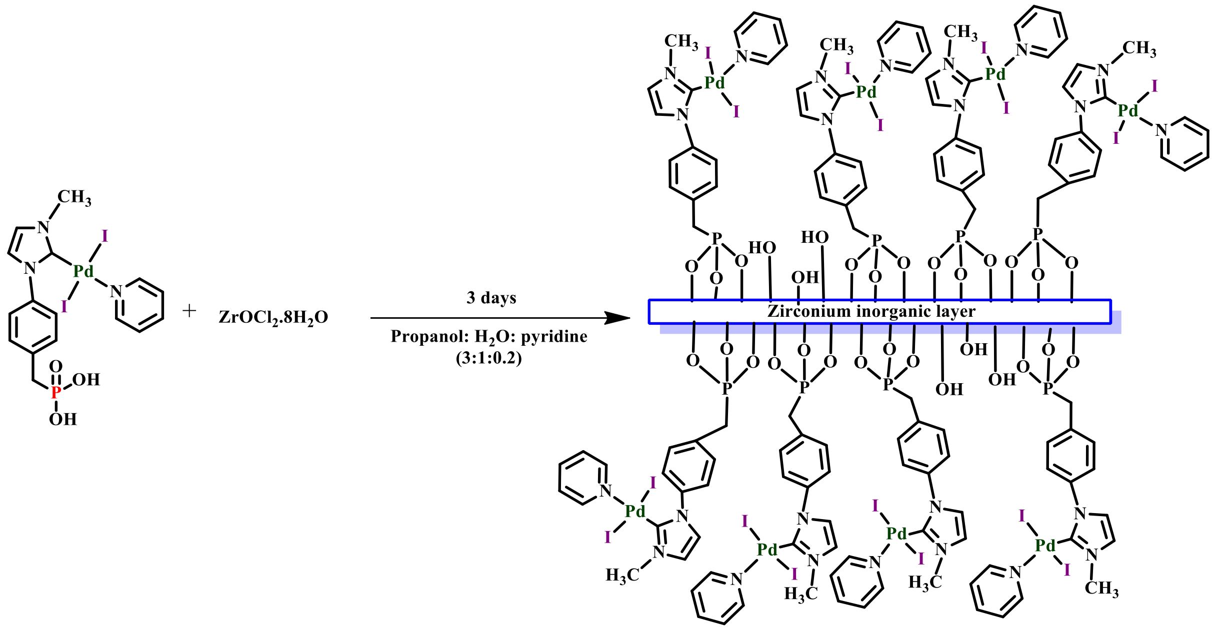
Experiment 3:

We have also established a rational bottom-up methodology for the development of catalytically active organometallic fragment, Pd(II)-NHC on layered Zr(IV) phosphonate. The layered Zr(IV) phosphonate containing dangling Pd(II)-NHC groups is characterized by using analytical, spectroscopic, structural and microscopic tools.The layered Zr(IV) phosphonate showed good catalytic activity in Suzuki-Miyaura cross-coupling reaction of aryl chlorides (up to 90% yield) and aryl bromides (up to 99% yield) with aryl boronic acids.The heterogeneous catalyst can be recycled up to nine catalytic cycles without any significant loss of catalytic efficacy. Further, it retains its integrity even after ninth catalytic cycles.

Catalyst synthesis:

We have recently reported a series of Pd(II)-PEPPSI complexes featuring dangling phosphonate ester or phosphonic acid functional groups [31]. These, complexes show reasonably good catalytic activity in Suzuki-Miyaura cross coupling reaction involving aryl chlorides and aryl bromides with aryl boronic acids under mild reaction conditions. Further, reaction of the precursor imidazolium ligand bearing phosphonic acid functionality with Zr(IV) salt affords layered Zr(IV) phosphonate framework where covalently linked imidazolium groups are uniformly present on the surface [32]. By employing the Pd(II)-PEPPSI complex bearing phosphonic acid functionality as the precursor ligand, $[Pd(L_1)(py)I_2]$, we have now accessed a layered zirconium(IV) phosphonate framework uniformly decorated with covalently anchored

Pd(II)-PEPPSI groups. Thus, reaction of the benzyl phosphonate, $RPO(OH)_2$ (R= Pd(II)-PEPPSI fragment shown in **Scheme 1**) bearing a dangling Pd(II)-PEPPSI group with $ZrOCl_2.8H_2O$ in presence of pyridine resulted a zirconium(IV) phosphonate, $[Zr(RPO_3)_{1.62}(OH)_{0.76}].nH_2O$ (**1**) as a yellow powder in near quantitative yield (**Scheme 1**). Elemental analysis, inductively coupled plasma-optical emission spectroscopy (ICP-OES), thermogravimetric analysis (TGA), energy dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) and solid-state ^{31}P NMR results conform well with the given formulation of the Zr(IV) phosphonate



[1]

Here, Suzuki-Miyaura cross-coupling reactions between various substituted aryl chlorides and aryl bromides along with different substituted boronic acids were investigated (**Table 1**). Up to 90% isolated yield of cross-coupling product is obtained even when aryl chlorides are used as substrates revealing the high catalytic efficacy of the present catalyst. Electronic effect of the substituents on the yield of cross-coupling product was studied, and higher yields are observed when electron donating substituents are present on the substrates.

Table 1: Suzuki-Miyaura reaction of different aryl boronic acid with aryl halides catalysed by Pd(II)-PEPPSI

$$\text{Ar-B(OH)}_2 \quad + \quad \text{Ar}'\text{-X} \quad \xrightarrow[\substack{{}^{i}\text{PrOH-H}_2\text{O (3:1), 60 }^{o}\text{C} \\ \text{2 hours}}]{\text{Catalyst (0.01 mol\%), K}_2\text{CO}_3} \quad \text{Ar-Ar}'$$

SL	-Ar	-X	-Ar′	% Yield[c]	TON	TOF (hr^{-1})
1	-Ph	-Cl	-Ph-4-Me	89	8900	4450
2	-Ph	-Cl	-Ph-3-Me	82	8200	4100
3	-Ph-4-Me	-Cl	-Ph-4-Me	90	9000	4500
4	-Ph-4-Me	-Cl	-Ph-3-Me	83	8300	4150
5	-Ph-4-Me	-Cl	-Ph-4-CN	88	8800	4400
6	-Ph-4-Me	-Cl	-Ph-3-CN	82	8200	4100
7	-Ph	-Cl	-Ph-4-CN	87	8700	4350
8	-Ph	-Br	-Ph-4-Me	95	9500	4750
9	-Ph	-Br	-Ph-3-Me	91	9100	4550
10	-Ph-4-Me	-Br	-Ph-4-Me	97	9700	4850
11	-Ph-4-Me	-Br	-Ph-3-Me	88	8800	4400
12	-Ph	-Br	-Naphthalene	95	9500	4750
13	-Ph-4-Me	-Br	-Ph-4-CN	99	9900	4950
14	-Ph-4-Me	-Br	-Ph-3-CN	97	9700	4850

Reaction condition: 0.24 mmol aryl boronic acid; 0.2 mmol aryl halide; 0.4 mmol K_2CO_3; temperature: 60 °C; time: 2 hours; catalyst: 0.01 mol %; [c] = isolated yield

This work is published in ***Molecular catalysis (2025)***

11. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject: The application of green chemistry principles to research addressing contemporary needs in synthetic chemistry and catalysis has recently attracted fresh attention. The design, development, and application of chemical products and processes to minimize the use and production of compounds that are harmful to the environment and human health is known as "green chemistry." These days, one of the most fascinating research projects for organic chemists is the growth of the field of green chemistry through organic reactions carried out in 2 Me-THF. It's interesting to note that 2-MeTHF has physical characteristics like toluene or THF and provides advantages over popular aprotic solvents in organometallic processes that are both cost-effective and environmentally benign. The fact that 2-MeTHF corresponds to several Green Chemistry principles is another factor contributing to its growing popularity. The third one (less hazardous chemical synthesis-permitted daily exposure of 2-MeTHF in humans is up to 6.2 mg day1), the fifth one (safer solvents and auxiliaries), the seventh one (use of renewable feedstocks-it can be obtained from biomass feedstock like furfural or levulinic acid derived from corncobs and sugarcane), and the tenth one (design for degradation—it degrades by factors like air and sunlight, probably via oxidation and ring opening) are among the ones that make it a suitable green solvent for both academia and industry. Additionally, from a business perspective, the inability to reuse such expensive homogeneous catalysts reduces the viability of their widespread or industrial application. Therefore, using a supported or impregnated heterogeneous catalyst will be a preferable option.

12. Conclusions summarizing the achievements and indication of scope for future work:

a) We have developed a nickel-based Schiff-based complex containing nitrogen-based ligands for the decarbonylative cross-coupling reactions of esters with arylboronic acids.

b) We have also developed the first example of bis-oxime palladacycle-derived silica immobilized palladium catalyzed decarbonylative cross-coupling reactions of esters with arylboronic acid for the synthesis of biaryls. Majority of earlier reports employ expensive homogeneous ligand-based palladium and nickel catalyst under harsh reaction conditions. The present solid catalyst was prepared by simple “anchoring-coordination to silica” methodology

c) We have also reported a series of Pd(II)-PEPPSI (PEPPSI = pyridine enhanced precatalyst preparation, stabilization and initiation) complexes bearing pendant phosphonate ester or phosphonic acid functionality. Here, a zirconium(IV) phosphonate framework is prepared by employing a Pd(II)-NHC complex, [Pd(L1)(py)I2], bearing dangling phosphonic acid functionality as precursor. The catalytic efficacy as well as recyclability of the resulting layered Zr(IV) phosphonate decorated with covalently anchored Pd(II)-NHC fragment are also investigated.

d) The remarkable benefit of the method is the use of 2-MeTHF as solvent system, which provides very simple isolation of the crude reaction mixture and the catalyst just by filtration or centrifugation.

e) The bis-oxime palladacycle complex has also been employed for the preparation of Boscalid, a agricultural fungicide, whose yearly production volume has been estimated >1000 metric tons.

f) With the merit of easily adaptable synthetic method of catalyst preparation using non-toxic and commercially available starting materials, low loading, rapid and ease of reaction, this protocol expands the synthetic portfolio of esters.

13. New Observations:

a) We have developed a magnetically separable, oxime-based palladacycle complex (Fe_3O_4@TEOS-palladacycle) and demonstrated that it is a very efficient and versatile catalyst for Suzuki-type decarbonylative cross-coupling of esters with phenylboronic acid in 2-MeTHF

b) The present catalytic system appears to be the first reported as a heterogeneous catalyst in decarbonylative cross-coupling reactions of esters with arylboronic acid without the use of additives. This catalytic system is compatible with a wide range of substrates, in addition, the catalyst is reusable and exhibits minimal metal leaching in the tested conditions.

c) The Fe_3O_4@TEOS-palladacycle was also used as an efficient catalyst for the preparation of Boscalid, a significant fungicide, via a decarbonylative approach.

d) The simple and rational methodology adopted to anchor organometallic fragment on the surface of Zr(IV) phosphonate is expected to provide easy access to highly active yet robust and recyclable heterogeneous organometallic catalysts.

14. Innovations: We have developed a magnetically separable, oxime derived palladacycle complex (Fe_3O_4@TEOS-palladacycle), which displays excellent catalytic activity in Suzuki-type decarbonylative cross-coupling of esters with arylboronic acid. Also, we have developed a zirconium(IV) phosphonate framework is prepared by employing a Pd(II)-NHC complex, [Pd(L_1)(py)I_2] (**chart 1**), bearing dangling phosphonic acid functionality as precursor. The catalytic efficacy as well as recyclability of the resulting layered Zr(IV) phosphonate decorated with covalently anchored Pd(II)-NHC fragment are also investigated.

15. Application Potential:

a. Immediate: 2-MeTHF can be used as a possible industrial solvent because of its interesting features including (i) it is derived from furfural, which is a renewable feedstock; (ii) Compared to THF, it has a higher boiling point, which is useful in several situations; and (iii) reaction phases can be separated easily from aqueous layers during the work-up procedure

b. Long Term: We have also attempted to implement the present catalytic system in the process development for the synthesis of industrially targeted "Boscalid", an important agricultural fungicide, whose yearly production volume has been estimated to be more than 1000 metric tons, that protects a wide range of crops including vegetables and other crops from grey and blue mold induced by Botrytis cinerea and Penicillium expansum. These strategies are also can be used for other new process developments for the synthesis of synthetic targets like valsartan, fingolimod, lasiodiplodin, sulisobenzone, naringenin and sofalcone, which have pharmaceutical/agrochemicals significances.

16. S&T benefits accrued:

a. List of Research publications

SL No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year
1	**Tahshina Begum**, Sazida Yasmin Sultana, Hasmita Hasin Mou, Nashreen S Islam	Oxime-palladacycle complex supported on magnetic nanoparticles: a recyclable catalyst for Suzuki-type decarbonylative cross-coupling of esters with aryl boronic acid	Catalysis Science & Technology	15	1247-1258	2025
2	Bagmita Bhattacharyya, Surangana	A convenient bottom-up route to covalently anchor Pd (II)-PEPPSI	Molecular Catalysis	569	114583	2024

	Kashyap, **Tahshina Begum**, Gorishmita Borah, Shashank Mishra, Nashreen S Islam, Nayanmoni Gogoi	on layered zirconium (IV) phosphonate: Efficient catalyst for Suzuki-Miyaura cross coupling of aryl chlorides				
3	Sazida Yasmin Sultana, Mitu Sharma, Hiya Talukdar, **Tahshina Begum**, Nand Kishor Gour, Bipul Sarma, Nashreen S Islam	New mixed ligand oxido-vanadium(V) complexes with O,O-donor and diimine ligands: Synthesis, crystal structure and catalytic activity in eco-friendly oxidation of olefins and phenol	Molecular Catalysis	565	114352	2024
4	Sazida Yasmin Sultana, Mitu Sharma, Hiya Talukdar, Gangutri Saikia, **Tahshina Begum,** Archana Sinha, Subrata Mishra, Bipul Sarma, Suman Dasgupta, Nashreen S Islam	Synthesis, structure, stability, lipophilicity and bio-relevant activities of new heteroleptic oxidovanadium (V) complexes	Journal of Inorganic Biochemistry	270	112939	2025

b. Manpower trained on the project

   i) Ph.D. produced: No

   ii) Other Technical Personnel trained: 3 (M.Sc. final year project)

c. Patents taken, if any: No

17. Financial Position:

S No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
1.	Salaries/ Manpower costs	Revised sanctioned amount (1st to 3rd year) 35,60,198/-	22,40,313/-	
2.	Equipment		96,965/-	
3.	Supplies & Materials		5,47,585/-	
4.	Contingencies		69,479/-	
5.	Travel		54,084/-	
6.	Overhead Expenses		2.22,989/-	
7.	Others, if any			
	Total	35,60,198/-	32,31,415/-	**90.76%**

18. Procurement/ Usage of Equipment
a)

S No	Name of Equipment	Make/ Model	Cost (FE/ Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance/ breakdown
1	**Dell laptop**	**Latitude 3430**	**78,531/-**	**March 2023**	**100%**	**They are all in good condition**
2	**Hot air gun**	**Bosch**	**2599/-**		**80%**	
3	**Canon Printer**	**G3010**	**15,835/-**		**100%**	

b) Plans for utilizing the equipment facilities in future: Currently research scholars are using these equipments.

Name and Signature with Date

Tahshina Begum

Tahshina Begum
(Principal Investigator)

b. N. S. Islam
(Mentor)

STATEMENT OF EXPENDITURE

1. Sanction Order No and Date: **DST/WOS-A/CS-23/2020 (G), 30/03/2022**
2. Total Project Cost: **31,75,902/-** (Rupees Thirty-one Lakh seventy-five thousand nine hundred two only)
3. Revised Project Cost (if applicable): 35,60,198/- (Rupees Thirty-five lakhs sixty thousand one ninety-eight only)
4. Date of Commencement: **27/04/2022**
5. Grant received in each year:
    a. 1st Year: **11, 44, 050/-** (Rupees Eleven lakh forty-four thousand fifty only)
    b. 2nd Year: **10,41,800/-** (Rupees ten lakhs forty-one thousand eight hundred only)
    c. 3rd Year: **11,81,818/-** (Rupees eleven lakhs eighty-one thousand eight hundred eighteen only)
    d. Interest, if any: **7185/-** (Rupees seven thousand one hundred eighty-five only)
    e. **Total (a+b+c+d): 33,74,853/-** (Rupees thirty-three lakhs seventy-four thousand eight hundred fifty-three only)

STATEMENT OF EXPENDITURE

(From 1/04/2024 to 31/12/2024)

S No (I)	Sanctioned Heads (II)	Sanctioned Cost (1st to 3rd year) (III)	Expenditure Incurred			Total Expenditure IV + V + VI (VII)	Balance as on (date) III – VII = (VIII)	Requirement of Funds up to 31st March next year	Remarks (if any)
			1st Year (27th April 2022 to 31st March 2023) (IV)	2nd Year (1st April 2023 to 31st March 2024) (V)	3rd Year (1st April 2024 to 31/12/2024) (VI)				
1.	Fellowship + HRA	25,22,696/-	6,12,333/- + 48,987/-	6,60,000/- + 52,800/-	7,83,000/- + 83,193/-*	22,40,313/-	2,82,383/-	---	Due to 'Vigyan Dhara' scheme, funds were returned without further payment. Therefore, payment of **Rs 51,093/-** towards consumables and contingency + **Rs. 4230/-** under overhead for analytical charges are still pending.
2.	Consumables	5,50,000/-	2,00,000	2,00,000/-	1,47,585/-	5,47,585/-	2415/-	37,014/-	
3.	Travel	75,000/-	17,184/-	16,114/-	20,786/-	54,084/-	20,916/-	---	
4.	Contingencies	75,000/-	25,000/-	25,000/-	19,479/-	69,479/-	5,521/-	14,079/-	
5.	Equipment	1,02,250	96,965/-	-----	-----	96,965/-	0**	---	
6.	Overhead expenses	2,35,252/-	79,000/-	79,000/-	64,989/-	2,22,989/-	12,263/-	4230/-	
7.	Total	**35,60,198/-**	**10,79,469/-**	**10,32,914/-**	**11,19,032/-**	**32,31,415/-**	**3,23,498/-**	**55,323/-**	

*This includes HRA (Rs 55,000 @1% from 27/04/2022 to 31/12/2024) & (Rs 12,000 @9% from 01/01/2023 to 31/12/2024)

** Non-recurring unspent balance of **Rs 5,285/-** deposited through **Bharatkosh, Transaction Id: 0311230002242**

 # Rs. 1,86,291/- was pulled back by DST

Dr. Tahshina Begum Tahshina Begum
Name and Signature of Principal Investigator:
Date: 30/07/2025

Signature of Competent financial authority: ____________

(with seal) Date:____________

Finance Officer
Tezpur University

FORM GFR 12A

GENERAL FINANCIAL RULES 2017
Ministry of Finance
Department of Expenditure

GFR 12 – A
[(See Rule 238 (1)]
FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR 2024-2025 (upto 31/12/2024) in respect
of Non-Recurring
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme : **Women Scientist Scheme –A (WOS-A)**
2. WOS-A Reference No : **DST/WOS-A/CS-23/2020 (G) and DST/WOS-A/CS-23/2020 (C)**
3. Principal Investigator : **Dr. Tahshina Begum**
4. Whether recurring or non-recurring grants : **Non-Recurring**
5. Grants position at the beginning of the financial year : **2024-2025**

(i) Cash in Hand/Bank: **5285/-**
(ii) Unadjusted advances:
(iii) Total: **5285**

6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment	Grant received during the year			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balances (5-6)
1	2	3	4			5	6	7
			Sanction No. (i)	Date (ii)	Amount (iii)			
5285/-	0	0	DST/WOS-A/CS-23/2020 (G)	--	-	**5285/-**	0	**5,285/-** (deposited through BharatKosh, Transaction ID:0311230002242)

Component wise utilization of grants:

Grant-in-aid–creation of capital assets (equipment) during financial year **2024-2025**	Total
0/-	**0/-**

Details of grants position at the end of the year
(i) Cash in Hand/Bank : **5,285/-**
(ii) Unadjusted Advances
(iii) Total: **5,285/- (Rupees Five thousand two hundred eighty-five only)** (deposited through BharatKosh, Transaction ID:0311230002242)

Tahshina Begum
Signature of PI
Date 30/07/2025

Signature
Name.........
Chief Finance Officer
(Head of the Finance) (With seal)
6/7/25
Finance Officer
Tezpur University

Signature
Name.........
Head of the Organisation
(With seal)
06/08/2025
Registrar
Tezpur University

Certified that I have satisfied myself that, the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

1) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.
2) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.
3) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.
4) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.
5) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.
6) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.
7) It has been ensured that the physical and financial performance under **DST Women Scientist-A** has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.
8) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)
9) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries are enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 30/07/2025
Place: Tezpur

TahshinaBegum
Signature of PI
Date 30/07/2025

Signature
31/7/25
Name……… Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
06/08/2025
Name ……Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

GFR 12 – A
[(See Rule 238 (1)]

FORM OF UTILIZATION CERTIFICATE
FOR AUTONOMOUS BODIES OF THE GRANTEE ORGANIZATION

UTILIZATION CERTIFICATE FOR THE YEAR 2024-2025 (from 1/04/2024 to 31/12/2024) in respect of **Recurring**
GRANTS-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1. Name of the Scheme	: **Women Scientist Scheme –A (WOS-A)**
2. WOS-A Reference No	: **DST/WOS-A/CS-23/2020 (G)**
3. Principal Investigator	: **Dr. Tahshina Begum**
4. Whether recurring or non-recurring grants	: **Recurring**
5. Grants position at the beginning of the financial year	: **2024-2025**

(i) Cash in Hand/Bank: **68,182/-**
(ii) Unadjusted advances:
(iii) Total: **68,182/-**

6. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received years [figure as at Sl. No. 3 (iii)]	Interest Earned thereon	Interest deposited back to the Govern-ment		Grant received during the year (01/04/2024 to 31/03/2025)			Total Available funds (1+2-3+4)	Expenditure incurred (from 01/04/2024 to 31/12/2024)	Amount pulled back	Closing Balances (5-6)
1	2	3		4			5	6	7	
				Sanction No. (i)	Date (ii)	Amount (iii)				
68,182/-	-	-		**DST/WOS-A/CS-23/2020 (G)**	**09/09/2024**	**11,81,818/-**	**12,50,000/-**	**11,19,032/-**	**1,86,291/-**	**(-)55,323/-**

Component wise utilization of grants:

Grant-in-aid– General	Grant-in-aid– Salary	Total
2,52,839/-	**8,66,193/-**	**11,19,032/-**

Details of grants position at the end of the year
(i) Cash in Hand/Bank: **(-)55,323/-**
(ii) Unadjusted Advances
(iii)Total: **(-)55,323/- (Rupees fifty five thousand three hundred twenty three only)**

Tahshina Begum
Signature of PI
Date 30/07/2025

Signature
Name.... 31/7/25
Chief Finance Officer
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
06/08/2025
Name........
Head of the Organisation
(With seal)
Date
Registrar
Tezpur University

Certified that I have satisfied myself that, the conditions on which grants were sanctioned have been duly fulfilled/are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

1) The main accounts and other subsidiary accounts and registers (including assets registers) are maintained as prescribed in the relevant Act/Rules/Standing instructions (mention the Act/Rules) and have been duly audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.
2) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.
3) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.
4) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.
5) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.
6) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.
7) It has been ensured that the physical and financial performance under **DST Women Scientist-A** has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes given at Annexure – I duly enclosed.
8) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry/Department concerned as per their requirements/specifications.)
9) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries are enclosed at Annexure –II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date: 30/07/2025
Place: Tezpur

Tahshina Begum
Signature of PI
Date 30/07/2025

Signature
Name .... Chief Finance Officer
24/7/25
(Head of the Finance)/ (With seal)
Date
Finance Officer
Tezpur University

Signature
Name ...... Head of the Organisation
06/08/2025
(With seal)
Date
Registrar
Tezpur University