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Facile Chan-Lam coupling using ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene

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Gajanan Rashinkar, Department of Chemistry, Shivaji University, Kolhapur, 416004, MS, India. Email: gsrchem@unishivaji.ac.in Ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene ([GrFemImi]NHC@Cu complex) has been synthesized by covalent grafting of ferrocenyl ionic liquid in the matrix of graphene followed by metallation with copper (I) iodide. The [GrFemImi]NHC@Cu complex has been characterized by fourier transform infrared (FT-IR), fourier transform Raman (FT-Raman), CP-MAS ¹³C NMR spectroscopy, transmission electron microscopy (TEM), thermogravimetric analysis (TGA), energy dispersive X-ray (EDX) analysis, X-ray photoelectron spectroscopy (XPS), Brunauer-Emmett-Teller (BET) surface area analysis and X-ray diffractometer (XRD) analysis. This novel complex served as a robust heterogeneous catalyst for the synthesis of bioactive *N*-aryl sulfonamides from variety of aryl boronic acids and sulfonyl azides in ethanol by Chan-Lam coupling. Recyclability experiments were executed successfully for six consecutive runs.

KEYWORDS

ferrocene, graphene, N-aryl sulfonamides, N-heterocyclic carbene, reusability

1 | INTRODUCTION

N-Heterocyclic carbenes (NHCs) have emerged as the powerful spectator ligands in transition metal (TM) catalysis.^[1] NHCs are electron–rich, excellent σ -donors and moderate π -acceptors, which make them ideal ligands for complexation with transition metals. An important attribute of NHC-TM complexes is their unexceptional stability that is often cited as one of the key advances of these ligands over their phosphine counterparts.^[2] In addition, they are remarkably stable towards air, heat and moisture. Moreover, their steric and electronic properties can be fine-tuned with the help of wingtip substituents in the ligand backbone thereby making them process compatible.^[3] The scrutiny of literature reveals

that majority of the NHC-TM complexes are homogenous in nature. The insight into these complexes has revealed some basic problems in terms of separation and recycling.^[4] In addition, the contamination of ligand residue in the product causes inevitable pollution and unfavorable economics when the precious metals are employed during complexation. These inherent limitations associated with homogenous NHC-TM complexes have sparked major research activity in the field of heterogenous analogs of these complexes.^[5] The heterogeneous NHC-TM complexes are usually prepared by immobilizing NHCs on high area support materials. A plethora of distinct protocols for synthesis of heterogeneous NHC-TM complexes by employing structurally diverse supports have been reported.^[6] However, despite

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tremendous advances, there is considerable scope for the further development especially using nanomaterials as a support in order to accomplish the aim of sustainable and environmentally benign processes.

Nanomaterials play a pivotal role in green chemistry as they enhance the environmental sustainability of processes producing negative externalities. They exhibit exciting features such as small size, large surface to volume ratio and ease of surface functionalization. Recognition of these inherent attributes has sparked flourishing research activity especially in the area of nanomaterial supported catalysis. Recently, graphene oxide (GO) has emerged as one of the most promising nanomaterial that has been widely applied in diverse areas including cancer therapy,^[7] catalysis,^[8] organic synthesis, electrochemistry,^[9] tissue engineering,^[10] imaging, diagnostics,^[11] sensors,^[12] drug delivery^[13] etc. Significant increase in research in the GO based nanomaterials is predominantly due to its extraordinary chemical, physical and electronic properties such as surface functionalizability, electroconductivity, surface enhanced Raman scattering (SERS) property, amphiphilicity, fluorescence quenching ability and excellent aqueous processability. The large surface area and chemical stability^[14a-c] of GO facilitate high loading of active sites and contribute to resistance to degradation in both acidic and basic media. These attributes have made GO as unparalleled 2D support in the synthesis of heterogeneous catalysts. The recent applications of GO supported catalysts in the realm of catalysis have demonstrated tremendous potential in the development of economical, efficient and environmentally benign organic synthesis.^[14d-f]

N-Aryl sulfonamides are privileged motifs that find prominent place in medicinal chemistry owing to their intriguing chemical properties and potential biological activities. They exhibit anticonvulsant, anticancer, antibacterial and HIV protease inhibitory activities. They are also employed in the treatment of diabetes mellitus, oedema and hypertension.^[15] Due to broad therapeutic potential, synthesis of N-aryl sulfonamides represents significant area of research in organic synthesis. Some of the most prominent methods for their synthesis include copper catalyzed reaction of sulfonyl azides or sulfonamides with boronic acids,^[16] Pd(OAc)₂ mediated N-arylation of sulfonamides using aryl halides or aryl triflates,^[17] copper promoted reaction of chloramine-T and arylboronic acids,^[18] Pd assisted cross-coupling of methanesulfonamide with aryl halides,^[19a] transition metal free reaction of o-silylaryl triflates with sulfonamides,^[19b] Pd promoted aminosulfonylation of aryl iodides^[19c] and iron mediated coupling of nitroarenes and sodium sulfonate.^[19d] Amongst these, copper catalyzed reaction of sulfonyl azides and boronic acids represents

most elegant protocol due to wide substrate scope, mild reaction conditions and potential synthetic utility. A variety of catalytic systems have been reported to improve efficiency of this protocol. However, there is a still scope to explore new methodology especially using a robust heterogeneous catalyst.

Based on aforementioned discussion and in continuation of our studies related to heterogeneous catalysis,^[20] we report herein preparation of ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene and its application in the synthesis of *N*-aryl sulfonamides.

2 | EXPERIMENTAL

2.1 | Materials and methods

All reactions were carried out under air atmosphere in dried glassware. FT-IR spectra were measured with a Perkin Elmer One FT-IR spectrophotometer. The samples were examined as KBr discs (~5% w/w). Raman spectroscopy was done using a Bruker:RFS 27 spectrometer. The thermal gravimetric analysis (TGA) curves were obtained using instrument TA SDT Q600 V20.9 Build 20 in the presence of static air at linear heating rate of 10 °C/min from 25 °C to 1000 °C. Elemental analyses were performed in a Perkin-Elmer 2400, Series II, CHNS/O analyzer and using an energy-dispersive X-ray spectroscopic facility attached to the field emission SEM instrument (Hitachi S 4800, Japan). ¹H NMR and ¹³C NMR spectra were recorded with a Bruker AC (300 MHz for ¹H NMR and 75 MHz for ¹³C NMR) spectrometer using CDCl₃ as solvent and tetramethylsilane as an internal standard. Chemical shifts are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz). The CP-MAS ¹³C NMR spectrum was recorded with a JEOL-ECX400 type FT-NMR spectrometer under prescribed operating conditions. Mass spectra were recorded with a Shimadzu QP2010 GC-MS. The materials were analyzed by TEM using a PHILIPS CM 200 model with 20-200 kV accelerating voltages. Melting points were determined using MEL-TEMP capillary melting point apparatus and are uncorrected. BET (Brunauer-Emmet-Teller) Quantachrome Nova Win surface area analyzer was used for surface area and pore size measurements by N_2 adsorption-desorption analysis. 1-N-Ferrocenylmethyl imidazole was synthesized following the literature procedure.^[21] Graphite (1) and all other chemicals were obtained from local suppliers and used without further purification. XPS was conducted with X-ray Photo Spectrometer and UPS equipped with Al Ka radiation.

2.2 | Preparation of graphite oxide (2)

The graphite oxide was synthesized by using modified Hummers and Offeman's method.^[22,23] A mixture of 1 (5.0 g), NaNO₃ (2.5 g) and conc. H₂SO₄ (115 ml) was stirred in an ice bath. Afterwards, KMnO₄ (15 g) was added gradually with constant stirring maintaining the temperature below 20 °C. The reaction mixture was then shifted to water bath at 35 °C and stirred for 30 min. to paste. Afterwards, distilled water produce thick (230 mL) was added slowly, which enhances the temperature to 98 °C and kept for 15 min. Further, reaction mixture was treated with distilled water (700 ml) and 30% H₂O₂ (50 mL). The residue of graphite oxide (2) was washed with water until the pH 7, separated by centrifugation and dried under vacuum at 50 °C.

IR (KBr, thin film): $\upsilon = 3400,\,1711,\,1611,\,1215,\,after\,1037~cm^{-1}.$

2.3 | Preparation of graphene oxide GO (3)

A mixture of (2) (1.0 g) and distilled water (250 ml) was sonicated for 30 min. Subsequently, 50% hydrazine hydrate (5 ml) was added slowly. The resulting mixture was refluxed in an oil bath. After 4 hr, insoluble product was separated by centrifugation, washed with water (6 \times 20 ml) and dried under vacuum at 50 °C to afford graphene oxide GO (3).

IR (KBr, thin film): v = 3437, 1710, 1060; Raman: v = 3036, 2129, 1974, 1596, 1293 cm⁻¹.

2.4 | Preparation of chloropropyl graphene (4)

A mixture of **3** (8.0 g) and (3-chloropropyl)triethoxysilane (10.8 ml, 45 mmol) in xylene (50 mL) was refluxed in an oil bath. After 24 hr, the mixture was cooled and the residue was separated by centrifugation washed with THF (3×5 ml) and dried under vacuum at room temperature to afford chloropropyl graphene **(4)**.

IR (KBr, thin film, v): 2945, 2885, 2375, 1698, 1426, 995, 792, 682 cm⁻¹; Raman: v = 3036, 2129, 1974, 1597, 1293 cm⁻¹; Loading: 0.26 mmol of functional group per gram of **4**.

2.5 | Preparation of [GrFemImi]Cl (6)

A mixture of **4** (8.0 g) and 1-*N*-ferrocenylmethyl imidazole (**5**) (3 g, 11 mmol) in DMF (25 ml) was heated at 80 °C in an oil bath. After 72 hr, the solid was separated by centrifugation, washed with DMF (3×50 ml), MeOH $(3 \times 50 \text{ ml})$ and CH_2Cl_2 $(3 \times 50 \text{ mL})$ and dried under vacuum at 50 °C for 24 hr to afford [GrFemImi]Cl (6).

IR (KBr, thin film): v = 3800, 3410, 2921, 2852, 1642, 1575, 1463, 1405, 1385, 1097, 1023, 657, 467 cm⁻¹. Raman: v = 3418, 2869, 2127, 1599, 1293 cm⁻¹. Elemental analysis observed: % C 59.34, % H 2.04, % N 4.65. Loading: 0.68 mmol functional group per gram of **6**.

2.6 | Preparation of [GrFemImi]NHC@Cu complex (7)

A mixture of **6** (9.0 g), CuI (1.9 g, 10 mmol) and NaOtBu (0.096 g, 10 mmol) in THF (50 ml) was stirred at room temperature under nitrogen for 6 hr. Afterwards, the mixture was separated by centrifugation, washed with THF (3×20 ml) and dried under vacuum for 24 hr to afford [GrFemImi]NHC@Cu complex **(7)**.

FT-IR (KBr, thin film, υ): 3410, 2921, 2852, 1642, 1575, 1463, 1385, 1022, 1023, 727, 470 cm⁻¹. Raman: υ = 3418, 2869, 2127, 1602, 1293 cm⁻¹. Elemental analysis observed: % C 67.27, % O 27.91, % Si 1.56, % Fe 1.43, % Cu 1.69, % I 0.15. ¹³C CP-MAS NMR (500 MHz): δ 193 (**C**=O groups of graphene), 169 (O=**C**-O), 101 (O-**C**-O), 130 (graphitic sp²-C), 70 (**C**-OH), 62 (epoxide), 177 (s, imidazolium **C**₂), 135 (s, imidazolium **C**₄), 120 (s, imidazolium **C**₅), 72 (s, non-substituted Cp ring carbon of ferrocene), 79 (s, substituted Cp ring carbon of ferrocene), 49 (s, 1**C**, =N-**C**H₂CH₂-CH₂), 28 (s, 1**C**, =N-CH₂**C**H₂-CH₂), 8 (s, 1**C**, -**C**H₂Si). Loading of copper: 0.26 mmol functional group per gram of **7** of graphene.

2.7 | General method for synthesis of *N*-aryl sulfonamides

A mixture of phenyl boronic acid (1.2 mmol), sulfonyl azide (1 mmol) and [GrFemImi]NHC@Cu complex (7) (70 mg) in ethanol (5 ml) was stirred at 70 °C. After completion of the reaction as monitored by the TLC, the reaction mixture was centrifuged to remove complex 7. Evaporation of solvent in vacuuo followed by column chromatography over silica gel using petroleum etherethyl acetate afforded pure products.

3 | RESULTS AND DISCUSSION

The preparation of the ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene is outlined in Scheme 1. Initially, purified graphite (1) was oxidized to graphite oxide (2) following modified Hummers and Offeman method.^[22,23] The ultrasound assisted exfoliation of 2 using hydrazine hydrate in



SCHEME 1 Preparation of [GrFemImi]NHC@Cu complex (7)

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aqueous medium afforded GO (3) which was subsequently treated with (3-chloropropyl)triethoxysilane to form chloropropyl graphene (4). The synthetically fertile chloro group in 4 allowed installation of azolium group in the graphene matrix through quaternization with *1-N*-ferrocenylmethyl imidazole (5) to yield heterogeneous salt acronymed as [GrFemImi]Cl (6) that served as precursor for preparation of NHC-Cu complex. Finally, the complexation of 6 with CuI yielded the desired ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene acronymed as [GrFemImi] NHC@Cu complex (7).

Fourier transform infrared (FT-IR), FT-Raman and cross polarization magic angle spinning (CP-MAS) ¹³C NMR spectroscopy were used to monitor reactions involved in the preparation of [GrFemImi]NHC@Cu complex (7). The FT-IR spectrum (Figure 1c) of 4 displayed characteristic peaks at 3437 cm⁻¹ (O-H stretching), 2885 cm⁻¹ (C-H stretching), 995 cm⁻¹ (Si-O stretching), 682 cm⁻¹ (C-Cl stretching).^[24] The quarternization of 4 with 5 was monitored by FT-IR spectroscopy. The vanishing of peak at 682 cm⁻¹ (C-Cl stretching) and appearance of peaks at 467 cm⁻¹ (Fe-Cp stretching band), 1385, 1463 and 1575 cm⁻¹ (ring stretching modes of

imidazolium ring), 2921 and 2852 cm⁻¹ (C-H stretching of Cp rings), 1642 cm⁻¹ (C=C stretching), 1575 cm⁻¹ (N-C-N stretching), 3410 cm⁻¹ (O-H stretching) demonstrated formation of **6** (Figure 1d). The shifting of characteristic IR absorption peaks to lower frequency values affirmed the formation of complex with copper (Figure 1e).^[25]



FIGURE 1 FT-IR spectra of (a) Graphite oxide; (b) Graphene oxide; (c) Chloropropyl graphene; (d) [GrFemImi]Cl; (e) [GrFemImi]NHC@Cu complex (7); (f) reused [GrFemImi] NHC@Cu complex (7)

The structural modifications in the preparation of [GrFemImi]NHC@Cu complex (7) were also reflected in the FT- Raman spectroscopy. Raman spectra of GO and 7 (Figure 2a) displayed characteristic D and G band. The D band is attributed to structural disorder at defect sites resulting from lattice vibrations and breathing mode of sp² carbon related to graphene edge or defect, whereas the G band arises from the vibration of the sp^2 bonded carbon atoms in planar configuration that constitutes graphene. It is observed that the G band shifts from 1596.51 in GO to 1599.14 cm^{-1} in [GrFemImi]Cl (6) with a further blue shift to 1602.85 in [GrFemImi]NHC@Cu complex (7). This upshift is probably due to gradually increased compressive local stress caused by covalent binding chains.^[26] This phenomenon also suggest an effective charge transfer from GO to 6 and 7.

The thermal stability profile of [GrFemImi]NHC@Cu complex (7) was assessed by TGA analysis over the temperature range of 25–1000 °C at heating rate of 10 °C/min (Figure 3a). The initial weight loss of 5.3% up to 185 °C is due to desorption of physically adsorbed water. The second key weight loss of 10.5% up to 308 °C is attributed to the weight loss of pendant ferrocenyl group and surface bound organic scaffolds.^[27] The third weight loss of 13.8% corresponds to the decomposition



FIGURE 2 (a) Raman spectra of GO (3) (black), [GrFemImi]Cl (6) (red), [GrFemImi]NHC@Cu complex (7) (green); (b) Raman spectrum of reused [GrFemImi]NHC@Cu complex (7) (blue)



FIGURE 3 (a) TGA curve of [GrFemImi]NHC@Cu complex (7) (b) TGA curve of reused [GrFemImi]NHC@Cu complex (7)

of the graphene by oxidative mode up to the 380.20 °C. The two combined weight losses of 30.6% and 18.1% are assigned to complete combustion of GO and carbon skeleton. The observations are in good agreement with TGA profile of GO reported in the literature.^[28a]

The X-ray diffraction (XRD) pattern of [GrFemImi] NHC@Cu complex (7) (Figure 4), displays two noticeable diffraction peaks at 26.0° and 43.3° corresponding to the (002) and (101) reflections of graphitized carbon, respectively, suggesting structural integrity of support.^[28b]

The amount of Cu in [GrFemImi]NHC@Cu complex (7) was quantified by using energy dispersive X-ray



FIGURE 4 XRD of [GrFemImi]NHC@Cu complex (7)

(EDX) analysis. The analysis revealed presence of 0.26 mmol of Cu per gm of **7**.

Brunauer–Emmett–Teller (BET) surface area analysis and was performed to evaluate the textural properties of [GrFemImi]NHC@Cu complex (7). The 7 showed BET surface area of 20.23 m²/g with the average pore diameter of 43 A°. The surface area, pore volume and pore size of 7 was significantly smaller as compared to pristine graphene oxide (77 m²/g, 23A°) indicating loss of micropores due to substantial grafting of functional groups on the surface.^[29]

Transmission electron microscopy (TEM) was employed to warrant morphological aspects of [GrFemImi]NHC@Cu complex (7) and GO (Figure 5a-c, 5f). The TEM micrographs displayed crumpling features with twisted nanosheets in disordered phase. The fold edges by virtue of sp³ carbon in nanosheets of GO carry immobilized NHC-Cu complex on both sides facilitating easy access of catalytic sites to the reactants. The selected area electron diffraction (SAED) pattern that exhibit bright dotted pattern persuades crystalline nature of GO nanosheets.^[30]

The X-ray photoelectron spectroscopy (XPS) was employed for structural investigations of immobilized species on GO. The XPS survey spectrum of [GrFemImi]NHC@Cu complex (7) displayed peaks of Fe, O, Si, C, N and Cu (Figure 6a). The core level XPS



FIGURE 5 TEM images of (a-c) [GrFemImi]NHC@Cu complex (7) with SAED pattern; (d-e) reused [GrFemImi]NHC@Cu complex (7); (f) TEM image of graphene oxide (GO)

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spectrum of Cu 2p displayed peaks at 933.52 eV and 953.44 eV respectively (Figure 6b). The energy difference of 19.92 eV between these peaks confirms existence of +1 oxidation state of Cu in $7^{[31]}$ In the core level XPS spectrum of C1s, the main peak is observed at 283.5 eV which is again deconvoluted into four peaks at 284.4, 285.3, 286.7, 287.6 eV (Figure 6c). The large peak area with binding energy 284.4 eV is ascribed to presence of bulky ferrocenyl group.^[32] A pronounced peak displayed with binding energy 286.7 eV confirms carbenic carbon bonded with copper metal (C₂ carbon of imidazolium ring).^[33] The peak at 285.3 eV designates C-C bonds (carbon sp³). Moreover, the peak at

287.6 represents C=O (carbonyl) and C-O-C (epoxy) interactions.^[34] A set of two isolated peaks is observed in core level XPS spectrum of N 1 s. The peak at 399.3 eV correlates with N atom bonded with sp³ hybridized C atoms (N- sp³C) whereas the peak at 400.6 eV is ascribed to N atom bonded with sp² hybridized C atoms (N-sp²C) (Figure 6d). These observations strongly suggest the coordination of NHC with Cu. The core level spectrum of oxygen displays peak with binding energy 531.5 eV which is indicative for oxygen bonded with Si (Figure 6e).^[35] Consequently, these structural investigations confirm the successful formation of **7**.



FIGURE 6 (a) XPS survey spectrum of [GrFemImi]NHC@Cu complex (7); (b) Core level XPS spectrum of Cu in [GrFemImi]NHC@Cu complex (7); (c) Core level XPS spectrum of C in [GrFemImi]NHC@Cu complex (7); (d) Core level XPS spectrum of N in [GrFemImi] NHC@Cu complex (7); (e) Core level XPS spectrum of O in [GrFemImi]NHC@Cu complex (7)

Our next task was to access the catalytic activity of [GrFemImi]NHC@Cu complex (7) in the synthesis of *N*-aryl sulfonamides (Scheme 2). In order to optimize reaction conditions, we executed an extensive screening of various parameters using phenyl boronic acid (8a; 1.2 mmol) and 4-toluenesulfonyl azide (9a; 1.0 mmol) as model substrates. In order to examine active site in [GrFemImi]NHC@Cu complex (7) responsible for catalytic cycle, the model reaction was performed by using varying amounts of CuI, ferrocene, 1-*N* ferrocenylmethyl imidazole (5) and [GrFemImi]Cl (6) (Table 1, entry 1–4). Interestingly, the reaction failed to proceed in all the catalytic runs. In the light of these observations, we

SCHEME 2 [GrFemImi]NHC@Cu complex (7) catalyzed synthesis of *N*-aryl sulfonamides

TON

5538

5577

5055

4423

TOF (h^{-1})

2552

3529

7659

6701

TABLE 1 Optimization of catalyst loading in synthesis of N-aryl sulfonamides^a

9a

Solvent EtOH

EtOH

EtOH

EtOH

EtOH

EtOH

EtOH

EtOH

B(OH)

8a

Entry

1

2

3

4

5

6

7

8

Catalyst

FemImi (5)

Ferrocene

[GrFemImi]Cl (6)

complex (7)

[GrFemImi]NHC@Cu

CuI

7

7

7

	9	7	EtOH	90 mg	37	92	3931	6444
	10	7	EtOH	100 mg	35	92	3538	6100
	11	7	EtOH	150 mg	30	93	2384	4768
	12	7	EtOH	200 mg	30	93	1788	3576
	13	7	DCM	70 mg	400	72	3956	594
	14	7	DMF	70 mg	540	69	3791	421
	15	7	THF	70 mg	270	87	4780	1062
	16	7	Toluene	70 mg	660	60	3296	299
	17	7	Xylene	70 mg	510	60	3296	387
	18	7	Methanol	70 mg	45	81	4450	5933
	19	7	Water	70 mg	2880	No product	-	-

[GrFemImi]NHC@Cu complex (7) Solvent_reflux

Amount of catalyst

10 mol%

10 mol%

10 mol%

10 mol%

50 mg

60 mg

70 mg

80 mg

^aReaction condition: Phenyl boronic acid (1.2 mmol), 4-toluenesulfonyl azide (1.0 mmol), ethanol (5 ml); ^bIsolated yields after chromatography.

believe that GO support in combination with ferrocene tethered *N*-heterocyclic carbene-copper complex exhibit synergistic effect in catalysis.

Initially, the influence of catalyst loading on *N*-aryl sulfonamides synthesis was investigated by employing various amounts of [GrFemImi]NHC@Cu complex (7). Use of 50 mg (0.013 mmol) and 60 mg (0.015 mmol) of 7 provided low yield of corresponding product viz 4-methyl-*N*-phenylbenzenesulfonamide (**10a**) even after prolonged reaction time (Table 1, entry 5–6). More efficient results were observed by increasing quantity to 70 mg (0.018 mmol), 80 mg (0.020 mmol), 90 mg (0.023 mmol) and 100 mg (0.026 mmol) as the yield of

10a

Yield (%)^b

<6

Trace

Trace

Trace

72

87

92

92

Time (Min.)

24 h

24 h

24 h

24 h

130

95

40

40

product was boosted to 92% under identical reaction conditions (Table 1, entry 7–10). Subsequently, further increase in the quantity of **7** did not show a substantial alteration in the yield of product and reaction time (Table 1, entries 11 and 12).

The next parameter in the optimization studies was the choice of solvent. A thorough screening of diverse range of solvents was undertaken (Table 1). The model reaction afforded good yields in polar aprotic solvents such as dichloromethane (DCM), dimethyl formamide (DMF) and polar aprotic tetrahydrofuran (THF) (Table 1, entries 13–15), whereas moderate yields were obtained in non-polar solvents like toluene and xylene (Table 1, entries 16–17). Good yields were achieved in polar protic solvents like methanol and ethanol (Table 1 , entries 18,7). To our surprise, the reaction could not be initiated in water (Table 1, entry 19). Amongst all the screened solvents, ethanol gave excellent yield of desired product and was selected for further studies. (Table 1, entry 7).

After the optimization of reaction conditions, the scope and generality of protocol was investigated by reacting sulfonyl azides with structurally diverse arylboronic acids (Table 2). Gratifyingly, the reaction proceeded smoothly in all the cases forming desired *N*-aryl sulfonamides in good to excellent yields (Table 2,

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entries **10 a-n**) without any side products. There was no influence of electronic effect of substituents as electron rich as well electron poor arylboronic acids reacted with equal efficiency furnishing the corresponding products in excellent yield.

A reasonable explanation for the notable catalytic activity of [GrFemImi]NHC@Cu complex (7) in Chan-Lam coupling is attributed to the tethered ferrocenyl group. It is now well established that electron rich NHC-metal complexes with the steric bulk incorporated on nitrogen aids to promote the reductive elimination which is the key step in coupling reaction.^[36,37] One of the reliable approach to design electron rich catalytic systems for cross coupling reactions is to tether an organometallic moiety like ferrocene at wingtip position in the ligand framework. In the present case, by virtue of its relatively steric bulk owing to unique cylindrical shape and powerful electron donor capacity accelerate the rate of reductive elimination, thus furnishing excelent results.^[38]

A plausible mechanism of [GrFemImi]NHC@Cu complex (7) catalyzed Chan-Lam coupling reaction based upon Cu(I)/Cu (II)/Cu (III) system.^[39] is outlined in Scheme 3 and is based on report by Kim and coworkers. Initially, **7** is air oxidized to afford **(I)**, which coordinates with sulfonyl azide generating intermediate **(II)**. Further, reaction

TABLE 2 [GrFemImi]NHC@Cu complex (7) catalyzed synthesis of *N*-aryl sulfonamides^a

		B(OH ₂) R + N ₃	o j="S=R' [GrFemImi]N Ö E	IHC@Cu complex (7) tOH, reflux	O NHS-R' O R		
		8	9	10) a-n		
Entry	R	R'	Product	Time (Min.)	Yield ^b (%)	TON	TOF (h^{-1})
a	н	<i>p</i> -MePh	10a	40	92	5055	7659
b	<i>p</i> -Me	<i>p</i> -MePh	10b	45	92	5055	6740
с	p-Cl	<i>p</i> -MePh	10c	35	89	4890	8383
d	<i>p</i> -Br	<i>p</i> -MePh	10d	40	76	4175	6327
e	3,5-diMe	<i>p</i> -MePh	10e	40	78	4285	6493
f	<i>p</i> -OMe	<i>p</i> -MePh	10f	45	88	4835	6446
g	m-Cl	<i>p</i> -MePh	10g	50	87	4780	5736
h	m-OMe	<i>p</i> -MePh	10h	40	90	4945	7492
i	Н	Me	10i	40	89	4890	7409
j	<i>p</i> -Me	Me	10j	35	92	5055	8666
k	p-Cl	Me	10k	40	88	4835	7326
1	<i>p</i> -Br	Me	101	40	78	4285	6493
m	m-OMe	Me	10m	35	82	4505	7724
n	p-OMe	Me	10n	45	88	4835	6446

^aReaction conditions: phenyl boronic acids (1.2 mmol), sulfonyl azides (1.0 mmol), ethanol (5 ml), [GrFemImi]NHC@Cu complex (70 mg), ^bIsolated yields after chromatography.



SCHEME 3 Plausible mechanism for the synthesis of N-aryl sulfonamides using [GrFemImi]NHC@Cu complex (7)

of arylboronic acid with **II** followed by transmetalation results in intermediate **(III)**. Finally, air oxidation of **III** affords higher oxidation state intermediate **(IV)** which undergo reductive elimination thereby resulting in the formation of desired *N*-aryl sulfonamides.^[40]

In order to confirm the heterogeneous nature of the [GrFemImi]NHC@Cu complex (7), hot filtration test was implemented employing model reaction. The complex was filtered off when 50% conversion was accomplished (GC). The filtrate of reaction mixture was stirred for additional 3 hr. Interestingly, there was no enhancement in the yield of product beyond 50%. In addition, inductively coupled plasma atomic emission spectroscopic (ICP-AES) analysis of filtrate shows absence of copper confirming the heterogeneous nature of **7**.

The reusability is one of the significant features of heterogeneous catalyst to determine their dynamic life span. The recyclability of [GrFemImi]NHC@Cu complex (7) was further scrutinized by repeating the model reaction (Figure 7). In brief, after completion of the reaction, the reaction mixture was centrifuged and recovered 7 was washed ethanol, dried in vacuuo at room temperature and used directly for the next cycle. It is noteworthy to

mention that the recovered complex could be reused for six cycles without significant loss in the yield of product.

The stability of recycled complex was studied by FT-Raman spectroscopy, FT-IR spectroscopy, TGA and EDX analysis as well as by TEM of fresh and recycled [GrFemImi]NHC@Cu complex (7). It is noteworthy to mention that, FT-IR (Figure 1f) and FT-Raman (Figure 2



FIGURE 7 Reusability of [GrFemImi]NHC@Cu complex (7) in the synthesis *N*-aryl sulfonamides

b) spectrum of reused **7** complex still retains the prominent peak pattern of the fresh **7**. The TGA of reused **7** (Figure 3 b) displayed mimicking pattern to the thermogram of fresh **7** (Figure 3a). The elemental EDX mapping of **7** after six catalytic cycles confirmed the integrity of the recycled complex. Moreover, TEM analysis of fresh (Figure 5 **a-c**) and reused **7** (Figure 5 d-e) designates that morphology is preserved even after six successive runs. The results of FT-Raman, FT-IR, TGA, EDX and TEM analysis of fresh and reused **7** confirmed that the structural rigidity and main characteristics of complex remain conserved, demonstrating stability of **7** after six consecutive runs.

4 | CONCLUSION

In conclusion, we have reported a facile synthesis of ferrocene tethered *N*-heterocyclic carbene-copper complex anchored on graphene. The complex was thoroughly characterized by FT-IR, FT-Raman, CP-MAS ¹³C NMR spectroscopy, XPS, TEM, TGA, EDX, BET and XRD analysis. The synthesized complex exhibits outstanding catalytic activity in the Chan Lam coupling of phenylboronic acids with sulfonyl azides affording *N*-aryl sulfonamides with high TON and TOF. In comparison with traditional methods,^[41] this protocol offers several striking advantages such as good yields, simple work up procedure, use of environmentally benign solvent and shorter reaction time.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

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SUPPORTING INFORMATION

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