Received: 26 December 2018 | Revised: 5 May 2019 | Accepted: 8 May 2019

DOI: 10.1002/aoc.5066

FULL PAPER

WILEY Applied Organometallic Chemistry

Intramolecular O-arylation using nano-magnetite supported *N*-heterocyclic carbene-copper complex with wingtip ferrocene

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Funding information
Science and Engineering Research Board, Grant/Award Number: SB/FT/CS-060/2014

Nano-magnetite supported *N*-heterocyclic carbene-copper complex with wingtip ferrocene has been prepared *via* multi-step procedure. The complex has been characterized by various analytical techniques such as fourier transform infrared (FT-IR), fourier transform Raman (FT-Raman), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) analysis. The catalytic activity of the complex has been exploited in intramolecular O-arylation of *o*-iodoanilides under heterogeneous conditions. The complex could be successfully recycled up to twelve consecutive cycles.

KEYWORDS

ferrocene, intramolecular O-arylation, nano-magnetite, *N*-heterocyclic carbenes, reusability

1 | INTRODUCTION

N-Heterocyclic carbenes (NHCs) have emerged as a versatile class of ligands with enormous applications.[1] The selection of NHCs as best ligands can be rationalized by their coordinative unsaturation, incomplete electron octet, which promise comparatively weak π-acceptor property, strong σ-donor capability, strong binding with transition metals and sterically demanding structure.[2] In addition, owing to flexible design of NHCs and ease of convenience to their azolium salt precursors, tailor made NHCs are readily offered.[3] Moreover, the steric and electronic properties of NHCs can be systematically fine-tuned with the assistance of wingtip substituents on the ligand backbone.[4] It is well recognized that tethering organometallic fragment like ferrocene at wingtip site in ligand backbone can have notable influence on steric and spatial properties of NHCs.[5] Ferrocene, by virtue of its unique cylindrical shape and powerful electron donor capacity causes expedient stabilization of NHCs. Additionally, ferrocene is non-toxic, easily accessible and can be installed by simple synthetic manipulation in backbone of NHCs.[6] These unique properties of ferrocene have focused a quest towards progress of new methods for synthesis of ferrocenyl NHC-transition metal complexes in the field of catalysis.[7a–f]

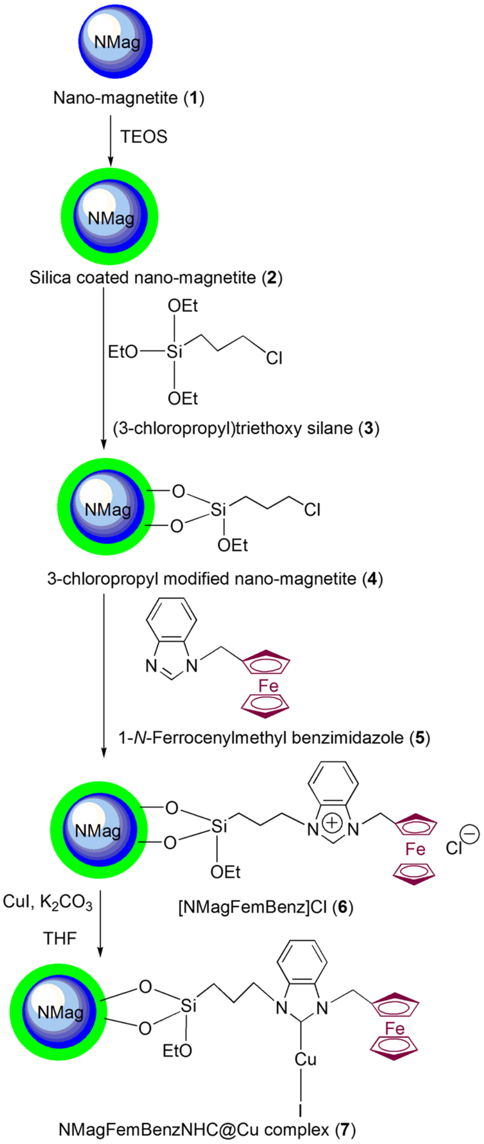
In recent years, magnetic nanoparticles (MNPs) are intensely researched in the catalysis arena, as magnetic based nanocatalysts have been contributing significantly to meet requirements of green chemistry standpoints.[7g–o] The bridge between heterogeneous and homogeneous catalysts can be accomplished through the use of MNPs.[7p] Out of various MNPs, nano-magnetite finds a myriad of applications in the diverse areas including catalysis,[8] bioengineering,[9a–d] drug delivery,[9e] sensing,[9f] environmental treatment,[10] bioseparation,[11] biomaterials[12] and food analysis.[13] The ease of surface functionalization of nano-magnetite with desired precursors have provided significant versatility to design task specific catalytic systems.[14a] Amongst various precursors, organosiloxane precursors have been extensively employed for coating of silica on nano-magnetite which serves as a shell and hydroxyl-rich surface for high degree of organofunctionalization.[8p] Owing to unique physicochemical properties such as good dispersivity, high surface area, low toxicity, superparamagnetic behavior and biocompatibility, nano-magnetite has emerged as promising support material.[14b, c] Consequently, nano-magnetite supported catalytic systems have received significant attention in synthetic chemistry.[15] In addition, facile retrievability by external magnet have sparked the interest of scientific community in the recognizing the goal of magnetically separable catalysis and sought to become a promising option for application in fixed-bed technologies.[16] Despite remarkable progress, research toward applications of nano-magnetite in the synthesis of magnetically retrievable NHCs is still in its infancy and therefore warrants immediate attention.

Benzoxazoles have acquired more importance in recent years due to their many applications in medicinal chemistry. They possess a wide range of pharmaceutical properties including anticancer,[17] antibiotic,[18] antimycobacterial,[19] antiparasitic[20] and inhibitory activities.[21] In addition to these, they are used as key synthons for the synthesis of bioactive molecules[22] and natural products.[23] Moreover, they are renowned as a central scaffold to build materials,[24] novel ligands[25] as well as exploited in agrochemicals, metal sensors, engineering plastics and as optical brightener for textiles.[24a, 26] Based on their significance, the development of new methods for the ecofriendly and facile synthesis of benzoxazoles is highly anticipated. A plethora of strategies have been reported for the synthesis of benzoxazoles, which involve condensation of 2-aminophenol with aldehydes,[27] transition metal-mediated direct arylation of bezoxazoles with aryl halides,[3b, 28] intramolecular cyclization of *o*-halobenzanilides[29] and ring-opening-coupling-recyclization of benzoxazoles with benzoyl chloride or aromatic aldehydes.[30] Amongst these, transition metal catalyzed intramolecular cyclization of *o*-haloanilides represents most elegant protocol due to potential synthetic utility, wide substrate scope and mild reaction conditions. A large number of protocols for the synthesis of 2-aryl benzoxazoles *via* intramolecular cyclization have been developed.[31] However, there is a still scope to develop an efficient protocol especially using robust heterogeneous catalyst.

Considering aforementioned discussion and in continuation of our studies related to green chemistry,[32] we report herein the preparation of nano-magnetite supported NHC-copper complex with wingtip ferrocene and its application as a heterogeneous catalyst in intramolecular O-arylation of *o*-iodoanilides.

2 | RESULTS AND DISCUSSION

The synthesis of nano-magnetite supported NHC-Cu complex is outlined in Scheme 1. Initially, bare nano-magnetite (**1**) was prepared by conventional co-precipitation followed by coating with a silica layer using sol–gel method to afford silica coated nano-magnetite (**2**). The tendency of surface Si-OH groups of **2** to form stable Si-O-Si bonds with alkoxy groups of (3-chloropropyl) triethoxy silane (**3**) allowed a facile synthesis of 3-chloropropyl modified nano-magnetite (**4**) with high degree of organofunctionalization. The 1-*N*-ferrocenylmethyl benzimidazole (**5**) was covalently tethered on **4** *via* quaternization to afford heterogeneous azolium salt abbreviated as [NMagFemBenz]Cl (**6**). The complexation of **6** with copper iodide in the presence of



SCHEME 1 Preparation of NMagFemBenzNHC@Cu complex (**7**)

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K_2CO_3 afforded the desired nano-magnetite supported NHC-Cu complex with wingtip ferrocene acronymed as NMagFemBenzNHC@Cu complex (**7**) (Scheme 2).

FT-IR and FT-Raman spectroscopy were used to monitor the progress of the reactions involved in the synthesis of NMagFemBenzNHC@Cu complex (**7**). The FT-IR spectrum of pristine nano-magnetite (**1**) demonstrated Fe-O stretching vibration band at 592 cm^{-1}. The FT-IR spectrum of nano-magnetite (**2**) showed peaks at 792 (Si-O-Si symmetric stretching modes), 941 (Si-O symmetric stretching modes) and 1060 cm^{-1} (Si-O-Si asymmetric stretching modes) suggesting the formation of silica coated nano-magnetite (**2**) (Figure 1a).[33] The FT-IR spectrum of 3-chloropropyl modified nano-magnetite **(4)** (Figure 1b) displayed characteristic peak at 2948 cm^{-1} attributed to the C-H stretching vibration of propyl group.[34] The covalent tethering of 1-*N*-ferrocenylmethyl benzimidazole **(5)** on **4** was evident from strong bands at 1637 (C=C stretching) and 477 (Fe-Cp stretching) observed in the FT-IR spectrum of [NMagFemBenz]Cl **(6)** (Figure 1c). The formation of NMagFemBenzNHC@Cu complex (**7**) was confirmed by FT-IR spectroscopy on the basis of strengthening of C=N ring stretching bands in the range of 1350–1500 cm^{-1} suggesting binding of carbenic carbon with Cu metal (Figure 1d), which is in accordance to the literature.[35] In addition, FT-Raman spectrum of **7** exhibited signals at 472 cm^{-1} (Fe-Cp stretching band), 1238, 1341, 1412, 1466 cm^{-1} (ring stretching modes of benzimidazolium ring), 3141 and 3105 cm^{-1} (C-H stretching of Cp rings) confirming the proposed structure. The energy dispersive X-ray (EDX) analysis was employed to investigate elemental loading. The analysis revealed 0.28 mmol of Cu per gram of **7**.

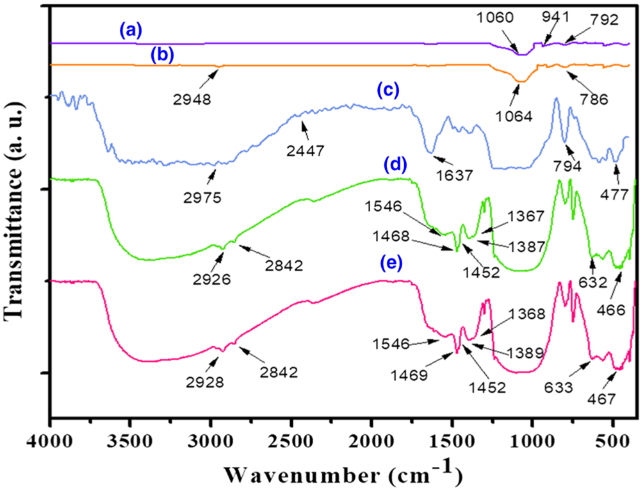

FIGURE 1 FT-IR Spectra of (**a**) silica coated nano-magnetite (**2**); (**b**) 3-chloropropyl modified nano-magnetite (**4**); (**c**) [NMagFemBenz]Cl (**6**); (**d**) NMagFemBenzNHC@Cu complex (**7**); (**e**) reused NMagFemBenzNHC@Cu complex (**7**) after twelfth catalytic run

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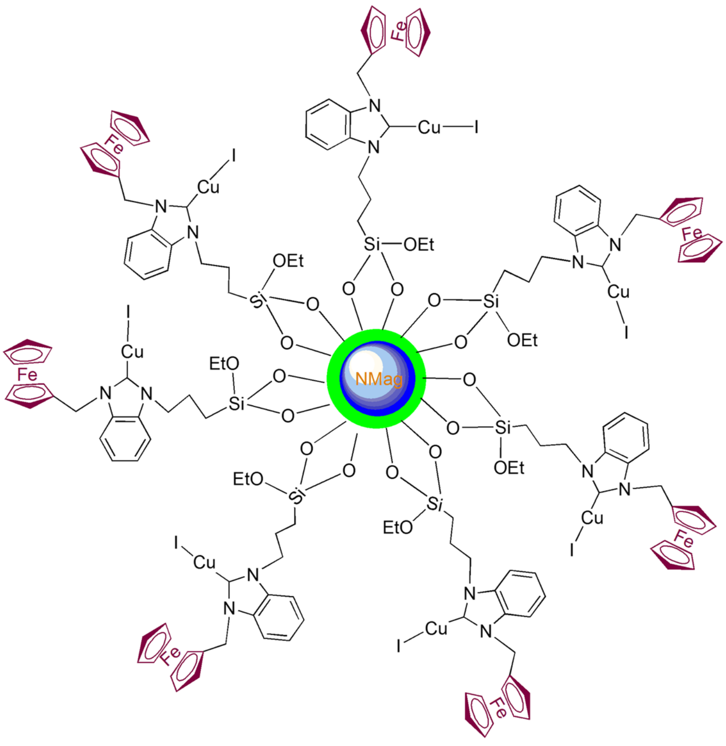
The thermogravimetric analysis (TGA) of NMagFemBenzNHC@Cu complex (7) was carried out over the temperature range of 25–1000 °C at a heating



NMagFemBenzNHC@Cu complex (**7**)

SCHEME 2 Structure of NMagFemBenzNHC@Cu complex (**7**)

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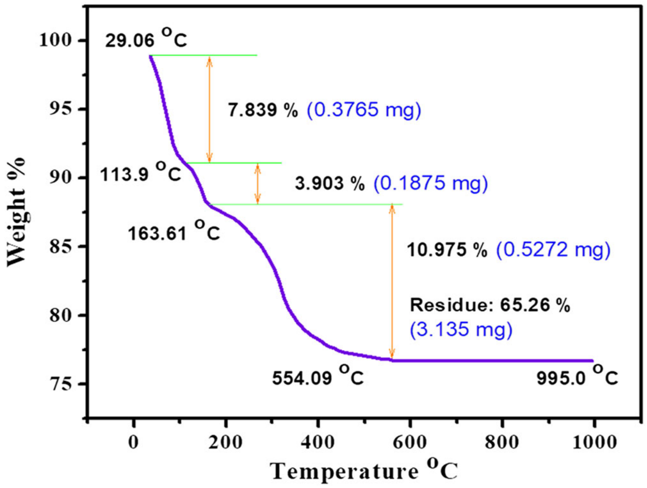

FIGURE 2 TGA curve of NMagFemBenzNHC@Cu complex (**7**)

rate of 10 °C/min (Figure 2). The thermogram displayed an initial weight loss of 7.83% centered at 113 °C ascribed to evaporation of physically adsorbed water followed by a cramped weight loss of 3.90% up to 163 °C and a steep weight loss of 10.97% at 554 °C owing to the thermal decomposition of covalently anchored organic moieties. Finally, the residual weight is ascribed to the formation of silica and metallic oxides which possess high thermal stability.

Transmission electron microscopy (TEM) analysis was employed to warrant the morphology of the NMagFemBenzNHC@Cu complex (**7**) and is shown in Figure 3a-c. The TEM micrographs appeared to have spheres with non-smooth surface. Moreover, encapsulated dark magnetite nanocores surrounded by grey shell were seen in TEM micrographs (Figure 3a-b).[36] A bright dotted pattern assured the single crystalline nature of magnetite nanocores in the selected area electron diffraction (SAED) pattern (Figure 3(c)).

The powder X-ray diffraction (XRD) pattern was employed to ascertain retention of crystal structures of nano-magnetite in NMagFemBenzNHC@Cu complex (**7**). The well indexing of diffractogram with JCPDS card no. 19–629 affirmed the single-phase inverse cubic spinel structure of standard magnetite nanocore with high phase purity and crystallinity (Figure 4a). The characteristic peaks at 2θ values of 18.38°, 30.28°, 35.62°, 57.15°, 62.77°, 66.21°, 73.83° and 86.70° assigned to (1 1 1), (2 2 0), (3 1 1), (5 1 1), (4 4 0), (5 3 1), (5 3 3), (6 4 2) crystallographic planes of magnetite nanocore respectively were observed. The most intense peak at 2θ value 35.62° is ascribed for (3 1 1) plane. The crystallite size calculated with respect to most intense peak is found to be 21 nm by using Debye–Scherrer equation. The XRD analysis revealed preservation of crystallographic structure of magnetite in **7** even after multi-step functionalization.

The X-ray photoelectron spectroscopy (XPS) was employed for structural investigations of immobilized species in NMagFemBenzNHC@Cu complex (**7**). The

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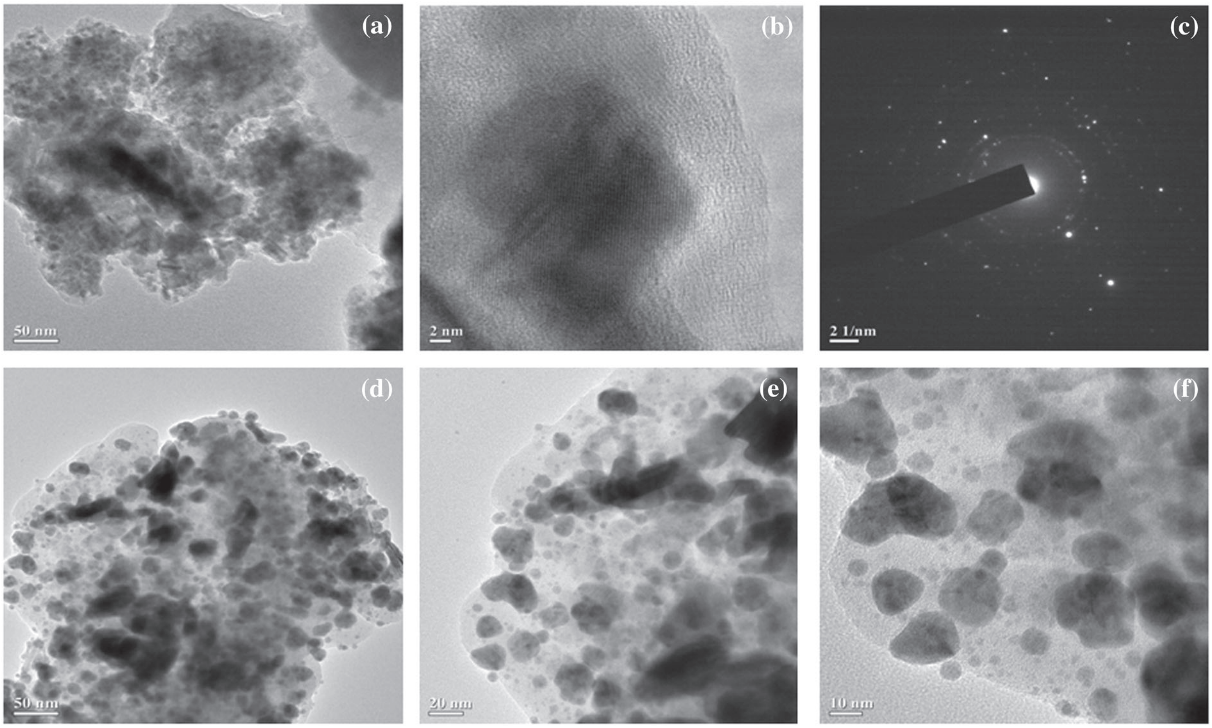

FIGURE 3 TEM images of (**a-c**) NMagFemBenzNHC@Cu complex (**7**) with SAED pattern; (**d-f**) reused NMagFemBenzNHC@Cu complex (**7**) after twelfth catalytic run

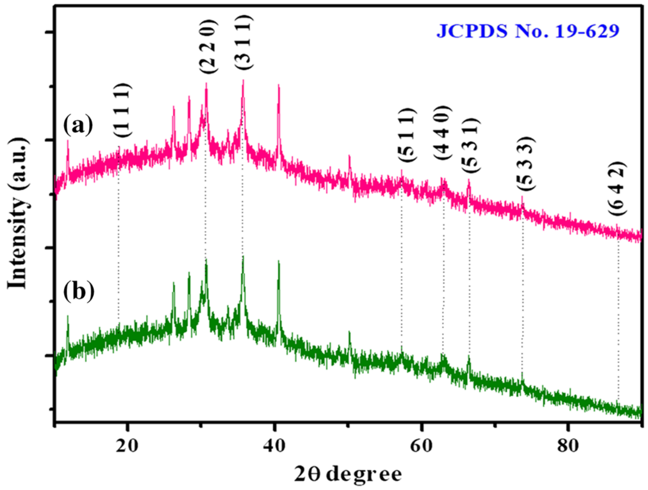

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FIGURE 4 XRD pattern of (**a**) NMagFemBenzNHC@Cu complex (**7**); (**b**) reused NMagFemBenzNHC@Cu complex (**7**) after twelfth catalytic run

XPS survey spectrum of **7** displayed peaks due to Cu, C, N, O, Fe and Si (Figure 5a). The core level XPS spectrum of Cu 2p displayed peaks at 933.0 eV ($2p_{3/2}$) and 952.8 eV ($2p_{1/2}$) respectively (Figure 5b). These peaks corroborate existence of +1 oxidation state of Cu in **7**. In the core level XPS spectrum of C1s, the main peak is observed at 283.2 eV which is again deconvoluted into three peaks at 283.1, 284.4, 286.6 eV (Figure 5c). The peak at 283.1 eV shows bonding interactions of carbon and silicon. This fact is again confirmed by a peak around 100.6 eV in the Si 2p region (Figure 5g).[37] The peaks exhibited with binding energies at 284.4 and 286.6 eV are assigned to ferrocenyl carbons and carbenic carbon (C_2 carbon of benzimidazolium ring) bonded with Cu respectively.[38] In addition, the large peak area with binding energy 284.4 eV reaffirms existence of bulky ferrocenyl group. Moreover, the core level spectrum of Fe 2p demonstrate peaks with binding energy 708.1 eV and 719.6 eV, also designates existence of wingtip ferrocenyl group (Figure 5f).[39] A set of two isolated peaks is perceived in core level XPS spectrum of N 1 s. The peak at 398.2 eV corresponds to N atom bonded with sp^3 hybridized C atoms (N- sp^3C), whereas the peak at 400.9 eV is attributed to N atom bonded with sp^2 hybridized C atoms (N- sp^2C) (Figure 5d).[40] These observations strongly support the coordination of NHC with Cu. The core level spectrum of oxygen displays peaks with binding energies 528.9 and 530.7 eV which are indicative for oxygen in magnetite and oxygen bonded with Si (Figure 5 e).[41] Consequently, these structural investigations affirm the successful formation of **7**.

The magnetization measurements of pristine nanomagnetite (**1**) and NMagFemBenzNHC@Cu complex (**7**) were assessed by vibrating sample magnetometer (VSM) at room temperature (Figure 6). The magnetic saturation of **1** is found to be 30 emug^{-1}, whereas that of **7** is 14 emug^{-1}. The lower saturation magnetization of **7** is attributed to functionalization of non-magnetic layers on surface of **1** during multistep-functionalization.[42] Despite of decline in the saturation magnetization of **7**, it can be still efficiently and easily removed with external magnet.

Our next task was to evaluate the catalytic efficiency of NMagFemBenzNHC@Cu complex (**7**) in intramolecular O-arylation of *o*-iodoanilides. Intramolecular O-arylation of *N*-(2-iodophenyl)benzamide was chosen as a model reaction for the optimization of reaction conditions. Initially, the effect of catalyst loading on model reaction was investigated. To standardize the reaction conditions, a series of experiments were carried out by varying amounts of **7** in ethanol using Cs_2CO_3 as a base at 70 °C. The reaction was sluggish in the presence of 25 mg of **7** affording the corresponding product, 2-phenylbenzimidazole (**9a**) in 47% yield after prolonged reaction time of 6 hr (Table 1, entry 1). Increasing the quantity to 50 mg elevated the yield significantly affording **9a** in 94% in 4 hr (Table 1, entry 2). However, further increase in the quantity of **7** did not found to have profound effect on the yield of product (Table 1, entries 3, 4). In addition, control experiments demonstrate that the model reaction does not occur in the absence of **7** signifying that complex has definite role in cycle.

The base is a crucial parameter for intramolecular *O*-arylation reaction. Therefore, the effect of different bases on model reaction was assessed (Table 2). Excellent yields were observed with Cs_2CO_3 (Table 2, entry 4). All tested inorganic bases including K_3PO_4, KOH, ^{t}BuOK and K_2CO_3 give much better yields (Table 2, entries 1, 2, 5 and 7) in comparison with other organic bases DIPEA and TEA (Table 2, entries 3,6). These results implied that among all the screened bases Cs_2CO_3 was found to be superior in view of reaction time and product yield.

Next, we investigated the effect of various solvents on model reaction. An array of solvents was employed for this purpose. Reactions in polar-aprotic solvents such as DMF, DMSO and acetonitrile afforded desired product with moderate yields (Table 3, entries 1–3), whereas non-polar solvents like 1,4-dioxane, toluene provided the better yields (Table 3, entries 4–5). On the contrary, the polar solvents such as ethanol, DMAC improved the yield significantly (Table 3, entries 6–7). Ethanol is found to be the best solvent (Table 3, entry 6) as the yield of desired product was elevated among all the screened solvents.

The active site in NMagFemBenzNHC@Cu complex (**7**) responsible for catalytic cycle was explored by performing several catalytic runs with varying amounts

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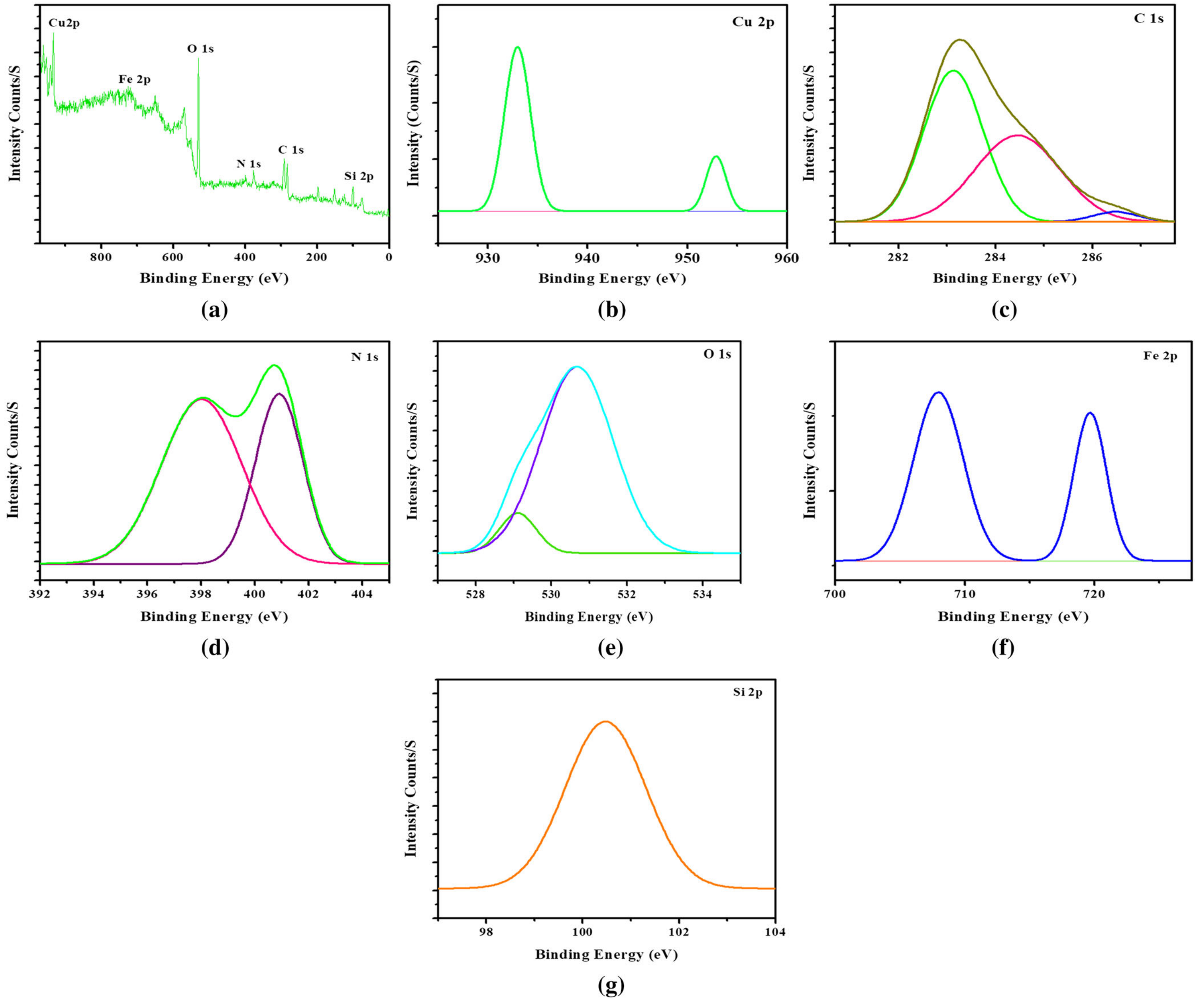

FIGURE 5 **(a)** XPS survey spectrum of NMagFemBenzNHC@Cu complex (**7**); **(b)** Core level XPS spectrum of Cu in (**7**); (**c**) Core level XPS spectrum of C in (**7**); (**d**) Core level XPS spectrum of N in (**7**); (**e**) Core level XPS spectrum of O in (**7**); (**f**) Core level XPS spectrum of Fe in (**7**); (**g**) Core level XPS spectrum of Si in (**7**)

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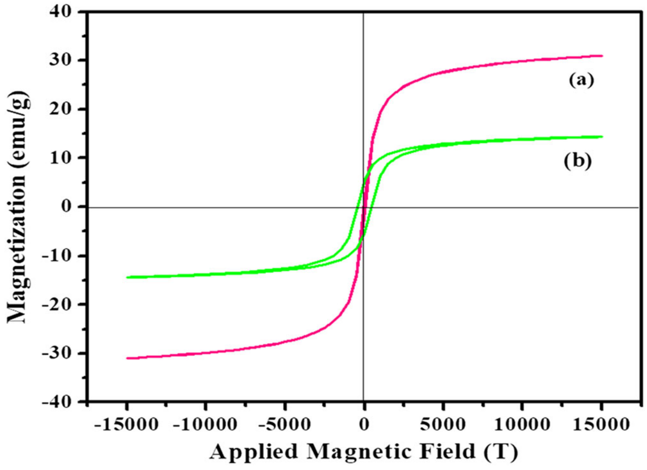
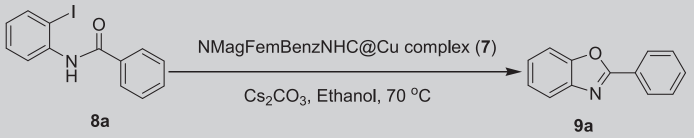


FIGURE 6 Magnetic curves of a) bare nano-magnetite (**1**); b) NMagFemBenzNHC@Cu complex (**7**)

of ferrocene, nano-magnetite (**1**), silica coated nano-magnetite (**2**) and [NMagFemBenz]Cl (**6**). Excitingly, the reaction failed to proceed in all the catalytic runs. Under the scenario of these observations, we believe that Cu is the active site in **7** for catalytic run.

After the optimization of reaction conditions, the generality of protocol was explored by reacting series of *o*-iodoanilides under the optimized reaction conditions. As shown in Table 4, the protocol was proved to be effective for both *o*-iodoanilides bearing electron-donating groups (Table 4, entries 8b, 8e, 8f, 8h, 8i and 8l) as well as electron-withdrawing groups (Table 4, entry 8c) affording anticipated products in good to excellent yields. The electronic effect on the *o*-iodoanilides has no influence on the reaction rate as well as yield. Sterically hindered *o*-iodoanilides also

TABLE 1 Catalyst optimization in NMagFemBenzNHC@Cu complex (**7**) promoted intramolecular O-arylation of *o*-iodoanilide[a]

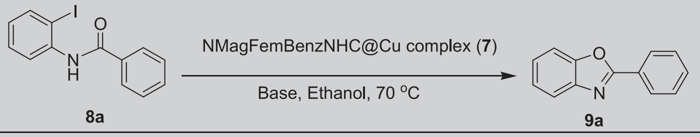


Entry	Catalyst mg (mol%)	Time (h)	Yield[b] (%)
1	25 (0.70 mol%)	6	47
2	**50 (1.40 mol%)**	**4**	**94**
3	75 (2.11 mol%)	4	95
4	100 (2.81 mol%)	4	95

[a] Reaction conditions: **8a** (1 mmol), Cs_2CO_3 (2 mmol), NMagFemBenzNHC@Cu complex (**7**) and ethanol (5 ml).

[b] Isolated yield after column chromatography.

TABLE 2 Screening of bases in NMagFemBenzNHC@Cu complex (**7**) catalyzed intramolecular O-arylation of *o*-iodoanilide[a]

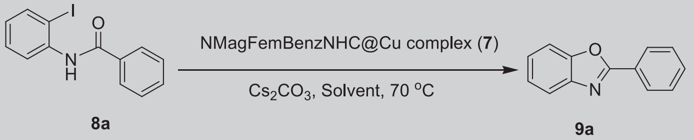


Entry	Base	Time (h)	Yield[b] (%)
1	K_3PO_4	15	47
2	KOH	14	72
3	DIPEA	24	44
4	**Cs_2CO_3**	**4**	**94**
5	^{t}BuOK	19	61
6	TEA	21	39
7	K_2CO_3	7	79

[a] Reaction conditions: **8a** (1 mmol), base (2 mmol), NMagFemBenzNHC@Cu complex (**7**) (50 mg; 1.40 mol%) and ethanol (5 ml).

[b] Isolated yield after column chromatography.

TABLE 3 Screening of solvents in NMagFemBenzNHC@Cu complex (**7**) catalyzed intramolecular O-arylation of *o*-iodoanilide[a]

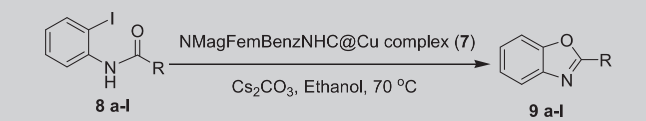


Entry	Solvent	Time (h)	Yield[b] (%)
1	DMF	12	69
2	DMSO	13	71
3	Acetonitrile	18	62
4	1,4-Dioxane	16	50
5	Toluene	19	48
6	**Ethanol**	**4**	**94**
7	DMAC	7	77

[a] Reaction conditions: **8a** (1 mmol), Cs_2CO_3 (2 mmol), NMagFemBenzNHC@Cu complex (**7**) (50 mg; 1.40 mol%) and solvent (5 ml).

[b] Isolated yield after column chromatography.

TABLE 4 NMagFemBenzNHC@Cu complex (**7**) catalyzed intramolecular O-arylation of *o*-iodoanilides[a]



Entry	-R	Products (9)	Time (h)	Yield[b] (%)
a	C_6H_5	**9a**	4	94
b	C $(CH_3)_3$	**9b**	4.5	85
c	4-$O_2NC_6H_4$	**9c**	5	82
d	Pyridin-4-yl	**9d**	5	85
e	4-$MeOC_6H_4$	**9e**	5	87
f	4-$C_2H_5C_6H_4$	**9f**	4.5	89
g	2,6-$(MeO)_2C_6H_3$	**9g**	6.0	82
h	4-MeC_6H_4	**9h**	4.5	87
i	3,4-$(Me)_2C_6H_3$	**9i**	4.0	79
j	2-MeC_6H_4	**9j**	5.5	77
k	Pyridin-3-yl	**9k**	5.0	75
l	4-OHC_6H_4	**9l**	5.0	80
m	Furan-2-yl	**9m**	5.0	78

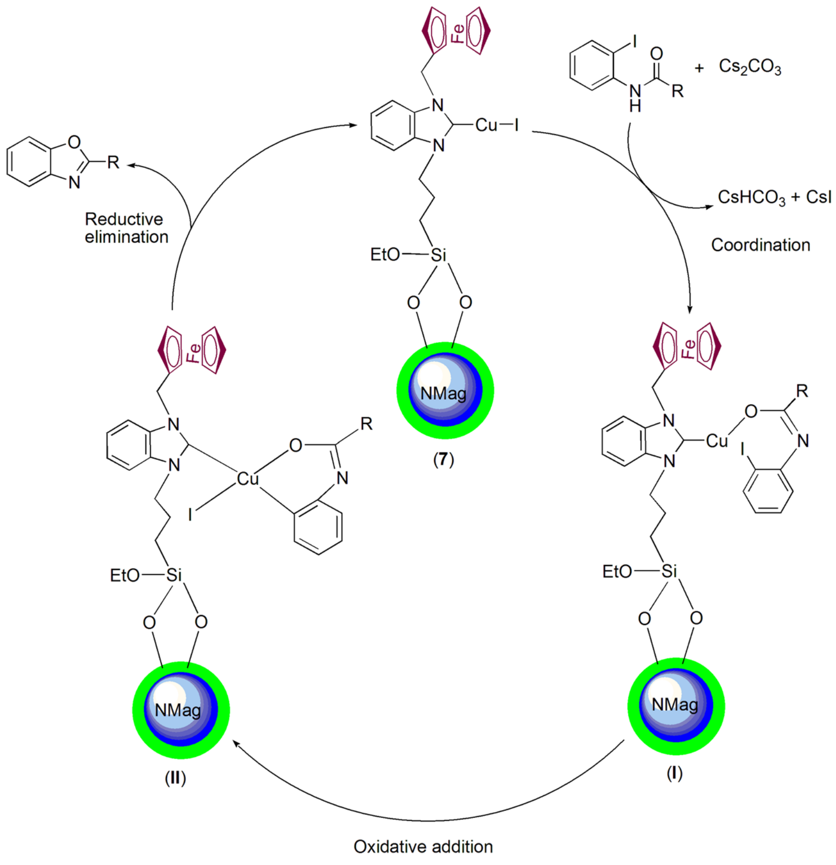
[a] Reaction conditions: **8** (1 mmol), Cs_2CO_3 (2 mmol), NMagFemBenzNHC@Cu complex (**7**) (50 mg; 1.40 mol%) and ethanol (5 ml).

[b] Isolated yield after column chromatography.

performed well and produced corresponding products in high yields (Table 4, entries 8g, 8j). Moreover, *o*-iodoanilides bearing heteroatom such as *N*-(2-iodophenyl)isonicotinamide, *N*-(2-iodophenyl)nicotinamide, *N*-(2-iodophenyl)furan-2-carboxamide (Table 4, entries 8d, 8k, 8m) underwent smooth reactions furnishing the corresponding products in good yields.

The structures of all the products were confirmed on the basis of FT-IR, ^1H and ^{13}C NMR spectroscopy as well as by mass spectrometry. The spectroscopic data is consistent with the proposed structures.

A plausible mechanistic rational for NMagFemBenzNHC@Cu complex **(7)** promoted intramolecular O-arylation of *o*-iodoanilides is depicted in scheme 3 and is based on report of Batey *et al.*[43] Initially, **7** coordinates with *o*-iodoanilide to form intermediate (**I**) which is followed by a oxidative addition step providing the oxo-copper complex (**II**). Finally, reductive elimination of (**II**) results into formation of desired product. It is noteworthy to mention that the bulky ferrocenyl group at wingtip position of NHC backbone plays a crucial role in catalysis. It is anticipated that powerful donor capacity of ferrocene generates electron rich NHC-Cu complex that facilitates oxidative addition which is a key step in the mechanism. Moreover, the bulk of the ferrocenyl group shows substantial improvements in the permeability of the substrate into the catalyst matrix,



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SCHEME 3 Plausible mechanism for NMagFemBenzNHC@Cu complex (**7**) catalyzed intramolecular O-arylation of *o*-iodoanilide thereby improving the accessibility of reactants to the active sites which ultimately facilitates the catalyst performance.[44]

To check the heterogeneity of NMagFemBenzNHC@Cu complex **(7)**, split test was performed on model reaction. The **7** was separated from reaction with the aid of external magnet after 50% conversion (GC). The resultant filtrate was subsequently allowed to stir under similar reaction conditions for 5 hr and the GC–MS analysis revealed no further increment in product formation. Additionally, the ICP-OES analysis of reaction mixture revealed no copper leaching suggesting that reactions continue under heterogeneous conditions.

Heterogeneous catalysis has become a crucial point of synthetic interests because of the profound merits of straightforward recovery and *reuse* of the *catalyst*. In order to perform reusability studies, the model reaction was carried out under optimized reaction conditions. After each cycle, NMagFemBenzNHC@Cu complex (**7**) was recovered simply with the aid of external magnet. The recovered complex was washed with ethanol and dried under vacuum at 50 °C and reused for next cycle. The complex displayed appreciable reusability as the corresponding yields initiated at 94% and reached at 69% at the twelfth run (Figure 7). The structural and morphological stability of **7** was further confirmed by various analytical techniques such as XRD, TEM analysis and FT-IR spectroscopy of both fresh as well as recycled complex. The TEM images of **7** after twelfth catalytic run did not show a substantial alteration in its morphology (Figure 3 d-f), which confirms the retention of the catalytic activity after recycling. The matching of peaks in the X-ray diffraction pattern of the fresh and reused **7** with JCPDS card no. 19–629 also revealed retention of single-phase inverse cubic spinel structure of Fe_3O_4 nanocore (Figure 4a, 4b). It is noteworthy to mention that, the peak pattern of FT-IR spectra (Figure 1d, 1e) of both fresh and reused **7** revealed conservation of peaks even after twelve successive cycles. The results of FT-IR, XRD and TEM analysis of fresh and reused complex revealed that **7** is stable and do not undergo any physical or chemical alteration during recycling even after reuse for twelve times.

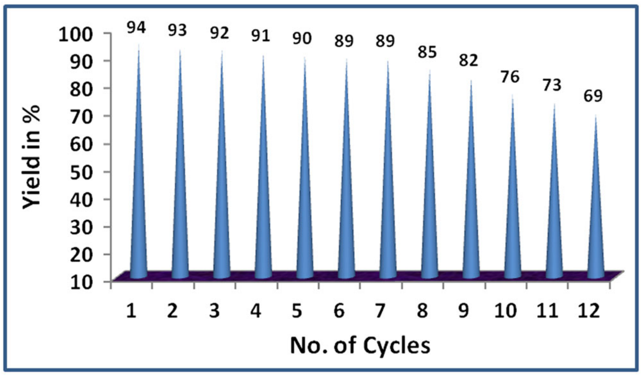

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FIGURE 7 Reusability of NMagFemBenzNHC@Cu complex (**7**) in intramolecular O-arylation of *o*-iodoanilide

Table 5 shows the merits of NMagFemBenzNHC@Cu complex (**7**) in comparison with those of previously reported methods for synthesis of 2-phenylbenzoxazole (**9a**). The comparison of results clearly proves that **7** is a superior catalyst in terms of catalyst loading, short reaction time and product yields as compared to many of the reported catalysts.

3 | CONCLUSION

In conclusion, we have developed simple, highly efficient and eco-friendly strategy of nano-magnetite supported *N*-heterocyclic carbene-copper complex promoted intramolecular O-arylation of *o*-iodoanilides. The complex could be magnetically separated and successfully recycled for twelve times. The fresh and recycled complex after twelfth cycles was characterized by variety of analytical techniques. The morphology and structure of reused complex were conserved after twelve consecutive recycles without leaching of copper confirming the heterogeneity and stability of the complex. The operational simplicity, low catalyst loading, high yields, clean reaction profile, ecofriendly reaction conditions, facile magnetic separation and recyclability are noteworthy merits of this strategy.

TABLE 5 Comparison of different catalysts for synthesis of **9a**

Sr. No.	Catalyst	Quantity	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	CuI	10 mol%	120 °C	8	88	[31a]
2	CuI	10 mol%	90 °C	12	87	[31f]
3	$FeCl_3$	10 mol%	120 °C	20	92	[31g]
4	CuO nanoparticles	5 mol%	110 °C	7	>99	[31h]
5	**NMagFemBenzNHC@Cu complex** (**7**)	**1.40 mol%**	**70 °C**	**4**	**94**	**This work**

4 | EXPERIMENTAL

4.1 | Materials and methods

All reactions were carried out under air atmosphere in dried glassware. Infrared 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 by using Bruker FT-Raman (MultiRAM) spectrometer. The elemental composition was analyzed by an energy-dispersive X-ray spectra (EDS) attached to the field emission scanning electron microscope (Oxford Instruments). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are expressed in δ parts per million (ppm) values and coupling constants are expressed in hertz (Hz). Mass spectra were recorded on a Shimadzu QP2010 GCMS. The materials were analyzed by TEM using a JEOL JEM 2100 (200 kV). Melting points were determined on MEL-TEMP capillary melting point apparatus and are uncorrected. X-ray photoelectron spectrum (XPS) was recorded on a PHI 5000 Versa Prob II, FEI Inc. Magnetic measurements were performed on Lakeshore magnetometer, USA, Model 7407 (Chennai, Tamilnadu). Nano-magnetite (**1**),[45] silica coated nano-magnetite (**2**)[46] and 1-*N*-ferrocenylmethyl benzimidazole (**5**)[47] were synthesized following the literature procedure. All other chemicals were obtained from local suppliers and used without further purification.

4.2 | Preparation of 3-chloropropyl modified nano-magnetite (4)

A mixture of silica coated nano-magnetite **(2)** (1 g) and (3-chloropropyl)triethoxy silane (**3**) (1 ml, 5 mmol) in dry xylene (50 ml) was refluxed in an oil bath. After 24 hr, the reaction mixture was cooled, product was isolated by magnetic separation and washed with xylene (4 x 25 ml), methanol (4 x 25 ml), deionised water (4 x 25 ml) and dried under vacuum at 50 °C for 12 hr to afford 3-chloropropyl modified nano-magnetite (**4**). FT-IR (KBr, Thin Film, υ, cm^{-1}): 2948, 1665, 1488, 1443, 1333, 1064, 786, 698, 637.

4.3 | Preparation of [NMagFemBenz]Cl (6)

A mixture of **4** (1 g) and 1-*N*-ferrocenylmethyl benzimidazole (**5**) (0.94 g, 3 mmol) in DMF (25 ml) was heated at 80 °C in an oil bath. After 72 hr, the product was separated by external magnet, washed with DMF (3 x 50 ml), methanol (3 x 50 ml), CH_2Cl_2 (3 x 50 ml) and dried under vacuum at 50 °C for 24 hr to yield [NMagFemBenz]Cl (**6**). FT-IR (KBr, Thin Film, υ, cm^{-1}): 3444, 2975, 2447, 1885, 1637, 1389, 1102, 794, 583, 477. Elemental analysis observed (%): C, 10.76; H, 1.96; N, 1.11; Loading: 0.39 mmol of benzimidazolium units g^{-1} of **6**.

4.4 | Preparation of NMagFemBenzNHC@Cu complex (7)

A mixture of **6** (2 g), copper iodide (0.176 g, 1 mmol) and K_2CO_3 (0.138 g, 1 mmol) in THF (25 ml) was refluxed for 24 hr. Afterwards, the mixture was separated with external magnet and subsequent washed with diethyl ether to afford NMagFemBenzNHC@Cu complex **(7)**. FT-IR (KBr, Thin Film, υ, cm^{-1}): 3406, 2926, 2842, 1611, 1546, 1468, 1452, 1387, 1367, 1068, 632, 466. FT-Raman (cm^{-1}): 472, 1238, 1341, 1412, 1466, 3105, 3141. Elemental analysis observed (%): C, 9.87; O, 56.75; Si, 17.91; Fe, 9.27; Cu, 1.79; Loading: 0.28 mmol Cu g^{-1} of **7**.

4.5 | General method for intramolecular O-arylation of *o*-iodoanilides

A mixture of *o*-iodoanilide (1 mmol), Cs_2CO_3 (2 mmol) and NMagFemBenzNHC@Cu complex (**7**) (50 mg; 1.40 mol%) in ethanol (5 ml) was stirred at 70 °C. The progress of reaction was monitored by TLC. After the completion of reaction, **7** was separated by external magnet. Evaporation of solvent in vaccuo followed by column chromatography over silica gel using petroleum ether/ethyl acetate afforded pure products. The products were identified by FT-IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy.

ACKNOWLEDGMENTS

We gratefully acknowledge Science and Engineering Research Board (SERB), New Delhi for providing financial support for this research work under the scheme of Start-Up Research Grant (Young Scientists) –Chemical Sciences (NO. SB/FT/CS-060/2014).

CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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How to cite this article: Naikwade A, Jagadale M, Kale D, Gajare S, Bansode P, Rashinkar G. Intramolecular O-arylation using nano-magnetite supported *N*-heterocyclic carbene-copper complex with wingtip ferrocene. *Appl Organometal Chem*. 2019;e5066. https://doi.org/10.1002/aoc.5066