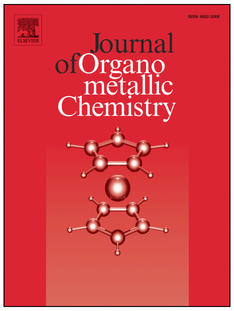

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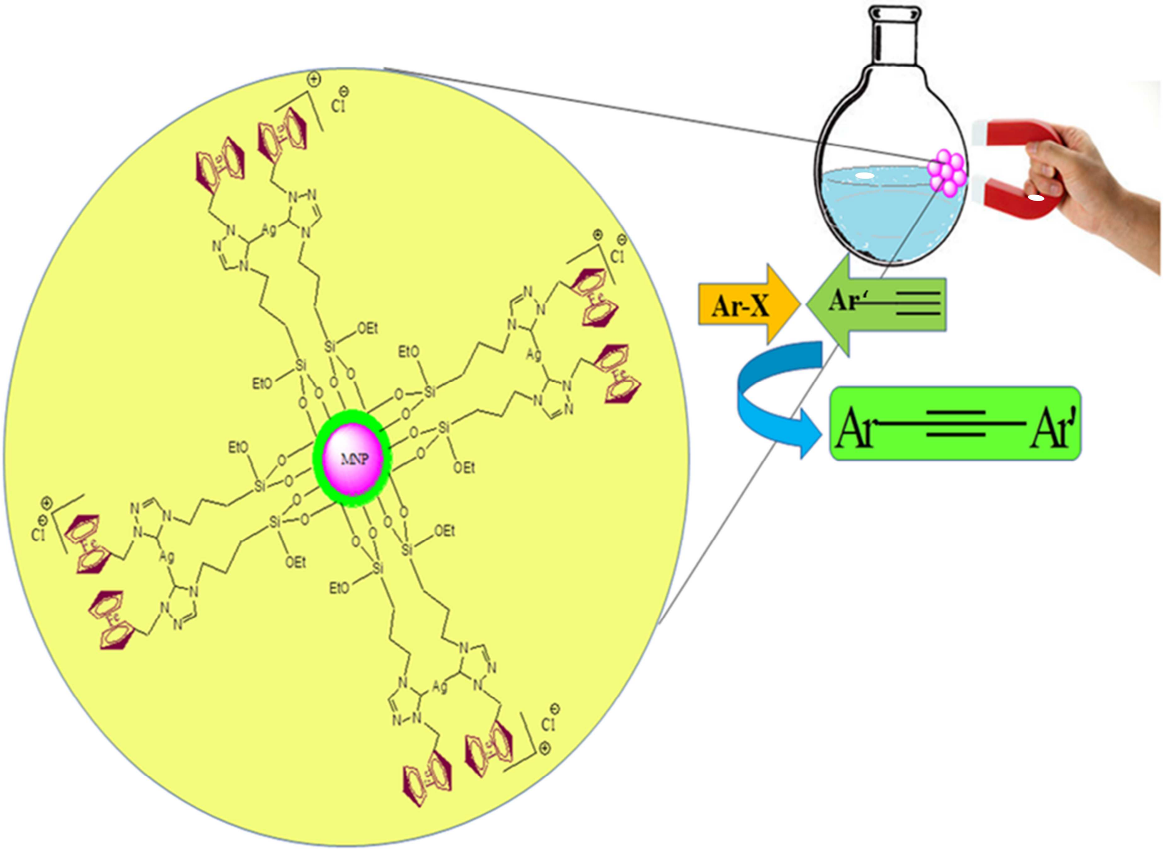

Magnetically retrievable *N*-heterocyclic carbene-silver complex with wingtip ferrocenyl group for Sonogashira coupling

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Abstract: A new magnetically retrievable *N*-heterocyclic carbene-silver complex with wingtip ferrocenyl group has been prepared by multi-step procedure. The formation of complex was confirmed on the basis of analytical techniques such as FT-IR, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), X-Ray diffraction (XRD), transmission electron microscopy (TEM), VSM (vibrating sample magnetometer) analysis. The complex was successfully employed as an efficient heterogeneous catalyst for Sonogashira coupling reaction of aryl halides with terminal alkynes. The catalyst could be separated easily by applying external magnet. The reusability studies of catalyst revealed that complex can be reused up to eight times without significant decrease in catalytic activity.

Keywords: *N*-Heterocyclic carbenes; Fe_3O_4 nanoparticles; ferrocene; Sonogashira coupling; reusability.

1. Introduction

N-Heterocyclic carbenes (NHCs) are pervasive class of ancillary ligands with myriad of applications, most conspicuously in transition metal catalysis [1]. By virtue of their significantly increased donor capacity, NHCs coordinate to a large number of transition elements yielding rigid NHC-metal complexes with unprecedented catalytic activity [2]. The remarkable catalytic efficiency of NHCs is ascribed to their strong σ-donor and comparatively weak π-acceptor properties as well as sterically demanding structure [3]. Another important attribute that explains versatility of the NHCs in catalysis is systematic alteration in their steric and electronic properties by simple synthetic methods which allow preparation of tailor made NHCs for specific catalytic performance. The steric properties of NHCs have been modulated by using different approaches [4]. One potentially powerful approach for tuning steric demand of NHCs relies on tethering bulky fragments at wingtip position of heterocyclic ring in the ligand backbone [5]. Over the past few years, substantial efforts have been devoted to develop new NHCs with bulky wingtip groups [6]. In this regard, ferrocenyl moiety represents a relatively bulky group with a unique cylindrical shape, and the electronically powerful donor capacity of ferrocene generates an electron-rich NHC–metal complexes [7]. The unique properties of ferrocene have driven a quest towards development of new approaches for synthesis of ferrocenyl NHC-transition metal complexes in the field of catalysis [8].

In the recent years, magnetic nanoparticles (MNPs) have attracted considerable attention due to their extensive use in the technological and chemical applications [9]. Among them, Fe_3O_4 MNPs are emerging as promising nanomaterials for development of advanced materials for catalytic applications [10]. Due to high surface area and facile retrievability by external magnetic field, Fe_3O_4 MNPs have emerged as excellent support material in heterogeneous catalysis [11].

Moreover, easy access to surface functionalized Fe_3O_4 MNPs using desired functionalities have added significant versatility for such materials in task specific catalytic systems [12]. The unique physical properties such as high surface area, superparamagnetism, low toxicity of Fe_3O_4 MNPs have sparked substantial of interest in the scientific community for realizing the goal of magnetically retrievable catalysis. However, despite substantial progress, research toward applications of Fe_3O_4 MNPs in NHC-TM catalysis is still in its infancy and therefore warrants immediate exploration.

Sonogashira coupling involving reaction of vinyl or aryl halides with terminal alkynes in the presence of Pd(II) / Cu(I) catalytic system is one of the most powerful tools for creating C-C bonds [13]. Sonogashira coupling has been extensively used in the diverse range of academic areas including natural products, material science, medicinal, biological and supramolecular chemistry as well as in catalysis [14]. The traditional Songashira coupling is associated with drawbacks such as homocoupling of terminal alkynes and use of costly palladium catalyst. These concerns have spurred extensive interest in the development of novel alterative catalytic systems for Sonogashira coupling. Towards this end, a large number of modifications in traditional catalytic system including silver promoted protocols have been reported [15]. However, despite impressive progress, research into development of novel catalysts for Sonogashira coupling continues apace with aim to find more efficient and robust catalytic system as compared to the existing methods.

Considering aforementioned discussion and in continuation of our research on the applications of green chemistry principles in synthetic chemistry [16], we report herein the preparation of a new magnetically retrievable NHC-silver complex with wingtip ferrocenyl group and its application as catalyst in the Sonogashira coupling of phenyl acetylenes with aryl halides.

2. Experimental

2.1 Materials and methods

All reactions were carried out under air atmosphere in dried glassware. Infrared spectra were measured with a Perkin-Elmer one FTIR spectrophotometer. The samples were examined as KBr discs~5% w/w. Raman spectroscopy was done by using Bruker FT-Raman (MultiRAM) spectrometer. The XRD analysis was carried out by using X-ray diffractometer Bruker-AX8. The elemental compositions of material were analyzed by an energy-dispersive X-ray spectra (EDS) attached to the field emission scanning electron microscope (OXFORD, Instruments). The correction of EDS data was performed on the basis of ZAF correction procedure included in the INCA Energy software. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC (300 MHz for ^{1}H NMR and 75MHz 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 analysed 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 Lake shore Magnetometer, USA, Model 7407. X-ray photoelectron spectrum (XPS) was recorded on a PHI 5000 Versa Prob II, FEI Inc. Fe_3O_4 MNPs [17], silica coated Fe_3O_4 MNPs [18] and 1-*N*-(ferrocenylmethyl)triazole [19] were synthesized following the literature procedure. All other chemicals were obtained from local suppliers and used without further purification.

2.2 Preparation of chloropropyl modified Fe_3O_4 (3)

A mixture of Fe_3O_4 MNPs **(2)** (1g) and 3-chloropropyltriethoxysilane (1 mL, 5 mmol) in dry xylene (50 mL) was refluxed in an oil bath. After 24 h, the reaction mixture was cooled and residue 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 ^oC for 12 h to afford chloropropyl modified Fe_3O_4 **(3)**. FT-IR (KBr, Thin Film, υ): 2939, 1459, 1070, 949, 790, 669, 631, 597, 568, 548, 528, 502 cm^{-1}. Loading: 0.42 mmol functional group g^{-1} of MNPs based on Cl content.

2.3 Preparation of [MNPFemTriaz]Cl (5)

A mixture of **3** (1 g), 1-*N*-ferrocenylmethyl-1,2,4-triazole **(4)** (0.80 g, 3 mmol) in DMF (25 mL) was heated at 80 °C in an oil bath. After 72 h, 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 h to yield [MNPFemTriaz]Cl **(5)**. FT-IR (KBr, Thin Film, υ): 2939, 1644, 1553, 1238, 1032, 798, 683, 626, 606, 519, 486, 464, 443, 385 cm^{-1}. Elemental analysis observed (%): C, 0.92; N, 1.34; H, 0.56. Loading: 0.39 mmol of triazolium units g^{-1} of **5**.

2.4 Preparation of MNPFemTriazNHC@Ag complex (6)

A mixture of **5** (1 g), silver acetate (0.332 g, 2 mmol), K_2CO_3 (0,345 g, 2.5 mmol) in THF (25 mL) was stirred at reflux for 24 h in dark. Afterwards, the mixture was separated with external magnet and washed with diethyl ether to afford MNPFemTriazNHC@Ag complex **(6)**. FT-IR (KBr, Thin Film): 3256, 2959, 1642, 1544, 1506, 1406, 1340, 1260, 1013, 843, 792, 632, 552 cm^{-1}. FT-Raman: 479, 567, 741, 1025, 1243, 1369, 1505, 1558, 1352, 2137, 2356, 2596, 2803, 3032, 3151, 3185, 3479, 3665, 3796 cm^{-1}. Elemental analysis observed (%): C, 19.93; O, 50.93; Si, 15.15; Fe, 9.30; Ag, 1.25; Loading: 0.116 mmol Ag g^{-1} of **6**.

2.5 General method for Sonogashira coupling Reaction

A mixture of aryl halide (1 mmol), terminal alkyne (1 mmol), K_2CO_3 (2 mmol) and MNPFemTriazNHC@Ag complex **(6)** (100 mg) in DMF (5 mL) was stirred at 100 ºC. The progress of reaction was monitored by TLC. After completion, the reaction mixture was quenched in ice cold water and **6** was separated by external magnet. The reaction mixture was extracted with ethyl acetate (3 x 25 mL). Evaporation of solvent in vaccuo followed by column chromatography over silica gel using petroleum ether/ethyl acetate afforded desired Sonogashira coupling products.

3 Results and Discussion

The synthetic route for magnetically separable *N*-heterocyclic carbene silver complex is shown in Scheme 1. Initially unmodified Fe_3O_4 MNPs **(1)** were prepared by using chemical co-precipitation followed by coating with a silica layer using sol-gel method. The condensation of silica coated Fe_3O_4 MNPs **(2)** with 3-chloropropyltriethoxysilane afforded chloropropyl modified Fe_3O_4 **(3)**. The chloropropyl group in **3** allowed the introduction of azolium unit by quaternization reaction with 1-*N*-ferrocenylmethyl-1,2,4-triazole **(4)** to afford heterogeneous azolium salt abbreviated as [MNPFemTriaz]Cl **(5)** which served as precursor for the synthesis of NHC-Ag complex. The complexation of **5** with silver acetate in the presence of K_2CO_3 afforded the desired magnetically retrievable NHC-Ag complex with wingtip ferrocenyl group acronymed as MNPFemTriazNHC@Ag complex **(6)**.

The functionalization of Fe_3O_4 MNPs was examined by employing FT-IR spectroscopy. The FT-IR spectrum of bare Fe_3O_4 MNPs (**1**) displayed band at 592 cm^{-1} which is attributes to stretching vibrations of Fe-O. The formation of silica coated Fe_3O_4 MNPs **(2)** was confirmed by peaks displayed at 793, 949 and 1070 cm^{-1} related to the Si-O-Si symmetric, Si-O symmetric and Si-O-Si asymmetric stretching modes respectively [20]. In FT-IR spectrum of 3-chloropylmodified MNPs **(3)**, showed a characteristic band at 2939 cm^{-1} indicates stretching vibration of the C–H of propyl group [21]. The covalent anchoring of 1-*N*-ferrocenylmethyl-1,2,4-triazole **(4)** on **3** was realised from bands at 1644 (C=N), 1553 (C-N) and 464 (Fe-Cp) observed in the FT-IR spectrum of [MNPFemTriaz]Cl **(5).** The formation of MNPFemTriazNHC@Ag complex **(6)** was confirmed by FT-IR spectrum which displayed characteristic "four fingers (f.fs)" pattern in the range 1350-1500 cm^{-1} owing to the stretching modes of vibrations of traizole ring ue to the presene of –CH=N- module [22-24]. In addition, the FT-Raman spectrum of **6** displayed signals at 479 cm^{-1} (Fe-Cp stretching band), 1369, 1505, 1558 cm^{-1} (ring stretching modes of triazole ring), 3151 and 3185 cm^{-1} (C-H stretching of Cp rings) confirming the proposed structure.

The elemental loading was investigated by energy dispersive X-ray (EDS) analysis. The analysis revealed 0.116 mmol of Ag per gram of MNPFemTriazNHC@Ag complex **(6)**. The thermal stability of MNPFemTriazNHC@Ag complex **6** was examined by employing thermogravimetric analysis (TGA) over the temperature range of 25-1000 °C at a heating rate of 10 °C/min (Fig. 1). The thermogram displayed an initial weight loss of 5.11 % up to 210 ^oC which is ascribed to the evaporation of physically adsorbed water. The further weight losses of 2.74 % within the range 210-262 ^oC and steep weight loss about 33.04 % in the range 262-554 ^oC are attributed to the loss of immobilized organic moieties on the surface of silica coated magnetite cores. Finally, the large residual weight is ascribed to the silica and Fe_3O_4 which possesses high thermal stability.

The morphology of MNPFemTriazNHC@Ag complex **(6)** was probed by transmission electron microscopy (TEM) and is shown in Fig. 2. The TEM images displayed granules having spherical shape with non-smooth surface. In addition, TEM images show embedded Fe_3O_4 nanocores in **6** as dark spot Fig. 2(b) [25]. The selected area electron diffraction (SAED) pattern exhibits a bright dotted pattern suggesting the single crystalline nature of Fe_3O_4 MNPs Fig. 2(c).

The evidence for retention of crystal structure of Fe_3O_4 MNPs in MNPFemTriazNHC@Ag complex **6** was further investigated by X-ray diffraction (XRD). The well indexing of all the peaks in diffractogram to the JCPDS card No. 86-1339 agreed retention of single phase inverse spinel structure of Fe_3O_4 nanocore with high phase purity and crystallinity (Fig. 3). The peaks at 2θ, 30°, 35.74°, 38.33°, 47.67°, 61.96°, 64.35° and 87.40° corresponding to the (2 2 0), (3 1 1), (2 2 2), (3 3 1), (4 4 0), (5 3 1), (6 4 2) crystallographic planes of Fe_3O_4 nanocore respectively were observed in the diffractogram. The most intense peak is observed for (3 1 1) plane at 2θ value 35.74°. The crystallite size calculated with respect to most intense peak is found to be 46 nm by using Debye-Scherrer equation. The XRD analysis revealed preservation of crystallographic structure of Fe_3O_4 in **6** even after multi-step functionalization.

The X-ray photoelectron spectroscopy (XPS) was employed for structural investigations of immobilized species on silica coated Fe_3O_4 MNPs. The XPS survey spectrum of MNPFemTriazNHC@Ag complex **6** displayed peaks of Fe, O, Si, C, N and Ag (Fig.4). The core level XPS spectrum of Ag 3d displayed peaks at 372.13 eV ($3d_{3/2}$) and 366.09 eV ($3d_{5/2}$) respectively (Fig. 4.1). The energy difference of 6.04 eV between these peaks confirms existence of +1 oxidation state of Ag in **6**. In the core level XPS spectrum of C1s, the main peak is observed at 283.3 eV which is again deconvoluted into thee peaks at 283.1, 284.3, 287.3 eV (Fig.

4.2). The peak at 283.1 eV designates bonding interactions of carbon and silicon. This fact is again reaffirmed by a peak around 101.6 eV in the Si 2p region (Fig.4.6) [26]. The peaks displayed with binding energies at 284.3 and 287.3 eV are assigned to ferrocenyl carbons and $C_{3,}$ C_5 carbons of triazolium ring respectively. The large area of peak with binding energy 284.3 eV confirms presence of bulky ferrocenyl group. In addition, the core level spectrum of Fe2p displays peaks with binding energy 708.4 eV and 719.9 eV which also designates existence of wingtip ferrocenyl group (Fig. 4.5) [27]. The core level spectrum of N 1s showing a set of two isolated peaks at 397.1, 398.6 eV with 1:2 area ratio is ascribed to bare nitrogen N_2 and the two nitrogen atoms (N_1 and N_4) of triazolium ring (Fig. 4.3). These observed binding energy values are in well agreement with skeletons of NHC [28, 29]. The core level spectrum of oxygen displays peaks with binding energies 529.2 and 531.2 eV which are suggestive for oxygen in Fe_3O_4 and oxygen bonded with Si (Fig. 4.4) [30]. The XPS confirm the successful formation of **6**.

Magnetic properties of bare Fe_3O_4 MNPs (**1**) and MNPFemTriazNHC@Ag complex (**6**) were investigated by vibrating sample magnetometer (VSM) as shown in Fig. 5. The saturation magnetization value of pristine MNPs is found to be 67 emug^{-1}. On the contrary, **6** displayed comparatively low saturation magnetization value of 21 emug^{-1}. The surface magnetic moments in **6** are quenched by non-magnetic layers on surface of **1** formed during functionalization [31]. However, magnetization exhibited by **6** was fair enough for effective separation by external magnet.

To evaluate catalytic efficiency of MNPFemTriazNHC@Ag Complex **6**, Sonogashira coupling between iodobenzene (**7a**; 1 mmol) and phenyl acetylene (**8a**; 1 mmol) in DMF was chosen as a model reaction. Initial studies were directed towards optimization of catalyst loading on the model reaction. It is noteworthy to mention that, reaction did not proceed in the absence of catalyst. However, in the presence of 50 mg of **6**, the reaction proceeded sluggishly furnishing the corresponding coupling product in 53 % yield in 18 h (Table 1, entry 1). The yield of the product elevated with increasing amount of catalyst from 50 to 100 mg (Table 1, entries 1-2). However, further increase in the catalyst quantity did not show any substantial gain in product yield (Table 1, entries 3, 4). Thus, 100 mg of **6** was selected as optimum catalyst loading for further studies.

Next, we probed the effect of various solvents on the efficiency of model reaction (Table 2). An array of solvents was employed for this purpose. Solvents like ethanol, THF, isopropanol, acetonitrile and xylene afforded moderate conversions (Table 2, entries 4, 6-9) whereas better yields were accomplished in solvents such as DMSO and 1,4-dioxane (Table 2, entries 1, 2). DMF turned out to be the best solvent as the yield of the desired product was most elevated among all the screened solvents (Table 2, entry 5). Further, screening of various bases affirmed that presence of base is crucial factor for reaction to proceed (Table 3, entry 8). Several bases were tested for the model reaction. The organic bases such as DIPEA, TEA, DEA were found to be less potent (Table 3, entries 4-6). Whereas inorganic bases like KOH, NaOH and K_3PO_4 were found to be substantially less efficient (Table 3, entries 1, 2 and 7). The use of K_2CO_3 led to quantitative yield (Table 3, entry 3) and therefore was selected for further studies.

With these encouraging results, the expansion of scope of protocol was established by reacting phenyl acetylene with diversely substituted aryl halides. As evident from the results in Table 4, the protocol tolerated an array of functionality furnishing excellent yields of corresponding Sonogashira coupling products. It is noteworthy that substituted aryl iodides and aryl bromides bearing both electron withdrawing and electron donating groups displayed high reactivity towards phenyl acetylene (Table 4, entries a-k). To our delight, the catalyst **6** could also be successfully applied for reactions of aryl chlorides (Table 4, entries l-o), albeit giving moderate yields of the corresponding products. To expand the scope of protocol, substituted terminal alkyne was also used as coupling partner. To our delight, the reactions of 4-methoxy phenyl acetylene with various aryl halides occurred successfully affording the desired coupling products in moderate to good yields (Table 4, entries p-t).

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

In order to explore active site in MNPFemTriazNHC@Ag complex **(6)** responsible for catalytic cycle, the model reaction was performed by using varying amounts of ferrocene, silica coated Fe_3O_4 MNPs **(2)** and [MNPFemTriaz]Cl **(5).** Interestingly, the reaction failed to proceed in all the catalytic runs. In the light of these observations, we believe that that Ag is the active site for catalytic performance of **6.**

A plausible mechanism for Sonogashira coupling reaction using MNPFemTriazNHC@Ag Complex **(6)** is depicted in Scheme 2 and is based on mechanistic understandings of Ag(I)/Ag(III) redox cycle in coupling reaction proposed by Ribas et al. [32]. Initially, **6** undergoes oxidative addition with aryl halide to form aryl-Ag (III) intermediate (I) which is followed by substitution reaction with terminal alkyne to form an intermediate (II). Finally, reductive elimination of (II) results into the formation of corresponding product. It is noteworthy to mention that the bulky ferrocenyl group at wingtip position of NHC backbone plays a vital role in catalysis. It is anticipated that powerful donor capacity of ferrocene generates electron rich NHC-Ag complex that facilitates oxidative addition which is a key step in the mechanism.

In order to confirm heterogeneous nature of MNPFemTriazNHC@Ag complex **(6)**, hot filtration test was performed on model reaction. After 50 % of reaction completion (GC), **6** was easily separated from reaction mixture by external magnet. The subsequent GC-MS analysis did not show further progress in the course of reaction. Moreover, the ICP-OES analysis of reaction mixture showed absence of metallic moiety signifying that silver is not leached out from the catalyst revealing that reactions proceed under heterogeneous conditions.

In view of economical and green chemistry standpoints, recyclability of catalyst plays a crucial role. To address this issue, the model reaction was carried out under optimized conditions. After each cycle, the catalyst was recovered simply by applying external magnetic field on reaction vessel. The recovered catalyst was washed with DMF and dried under vacuum at 50 ^{o}C and reused for next cycle. Recycling experiments revealed that there is no loss in catalytic activity up to eight consecutive runs (Fig. 6).

In order to demonstrate the merits of MNPFemTriazNHC@Ag complex **(6)**, we have summarized some of the previous reports for Sonogashira coupling in Table 5. The comparison of results clearly proves that MNPFemTriazNHC@Ag complex **(6)** is superior over other reported catalysts in terms of reaction time and yields of products.

4 Conclusion

In conclusion, we have synthesized magnetically retrievable *N*-heterocyclic carbene silver complex with wingtip ferrocenyl group). The complex showed excellent catalytic activity in Sonogashira coupling reaction of aryl halides and terminal alkynes. This protocol offers precious eminence in view of green chemistry standpoints such as facile magnetic separation and recyclability.

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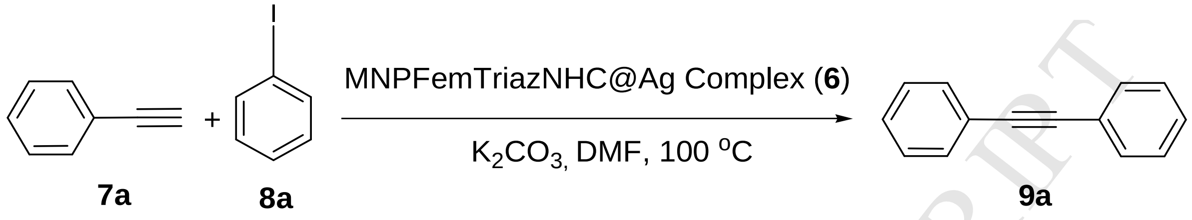
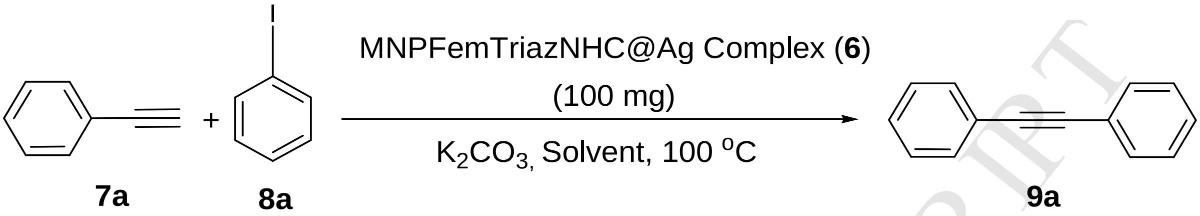
Table 1 Catalyst optimization in MNPFemTriaz@Ag complex (**6**) catalysed Sonogashira coupling reaction[a]



Entry	**Catalyst (mg)**	**Time (h)**	**Yield[b] (%)**
1	50	18	53
2	**100**	**12**	**91**
3	150	12	92
4	200	12	93

[a]Reaction conditions: **7a** (1 mmol), **8a** (1mmol), K_2CO_3 (2 mmol) and DMF (5 mL). [b] Isolated yield after column chromatography.

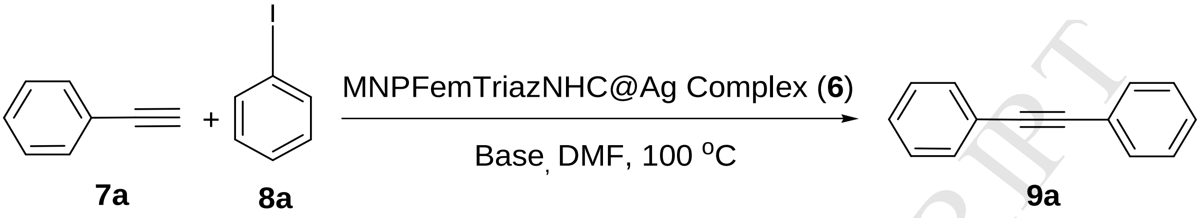
Table 2 Screening of solvents in MNPFemTriaz@Ag complex (**6**) promoted Sonogashira coupling reaction[a]



Entry	Solvent	Time (h)	Yield [b] (%)
1	DMSO	19	82
2	1,4-Dioxane	17	77
3	DMF: H_2O 1:1	24	Trace
4	Ethanol	20	43
5	**DMF**	**12**	**91**
6	THF	16	54
7	Isopropanol	19	52
8	Acetonitrile	18	48
9	Xylene	15	39

[a] Reaction conditions: **7a** (1mmol), **8a** (1 mmol), K_2CO_3 (2 mmol), MNPFemTriazNHC@Ag complex (**6**) (100 mg) and solvent (5 mL). [b] Isolated yield after column chromatography.

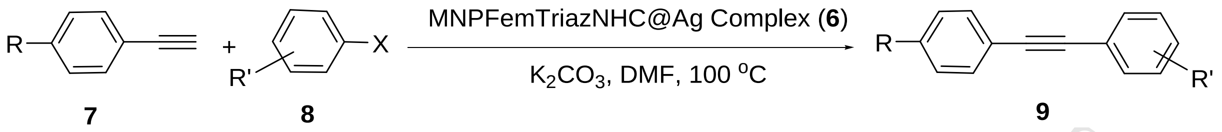
Table 3 Screening of bases in MNPFemTriaz@Ag complex (**6**) promoted Sonogashira coupling reaction[a]

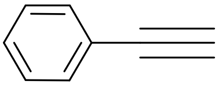
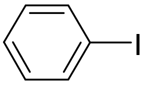
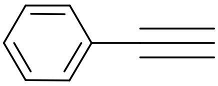
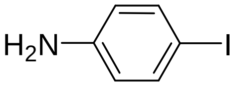
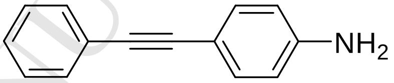
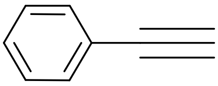
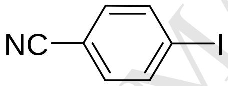
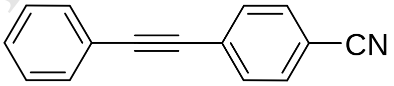
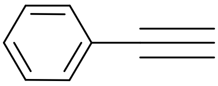
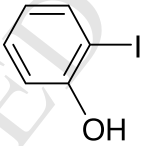
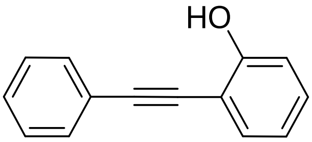
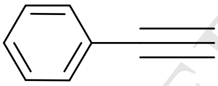
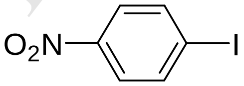
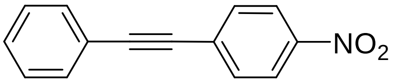
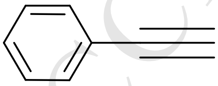
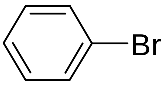
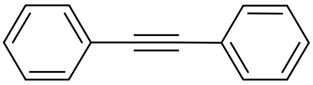
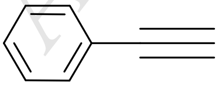
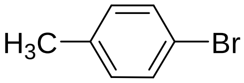
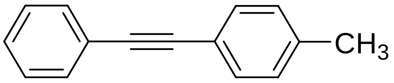
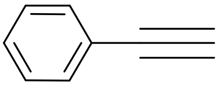
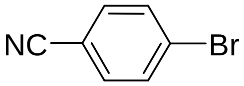
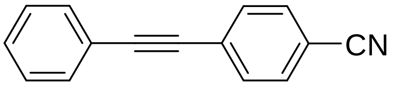


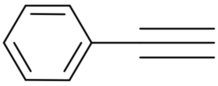
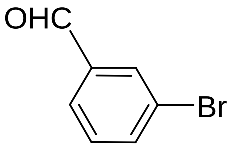
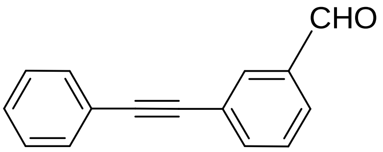
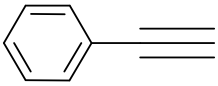
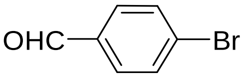
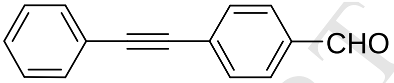
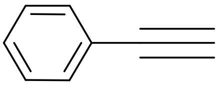
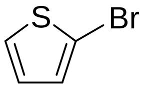
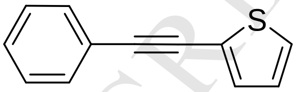
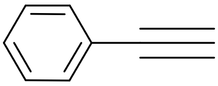
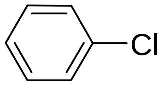
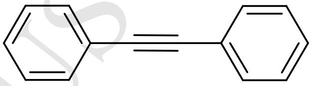
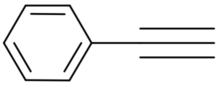
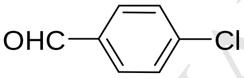
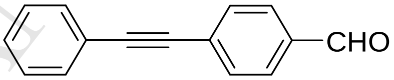
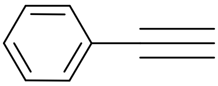
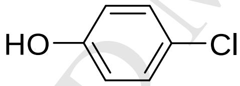
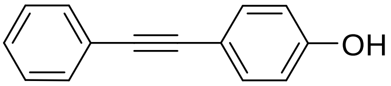
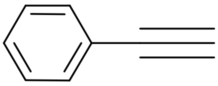
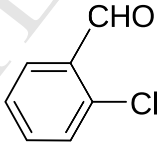
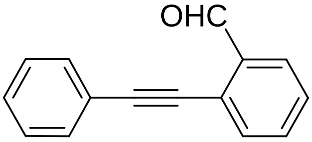
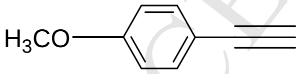
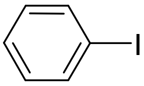
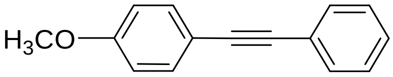
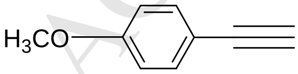
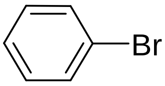
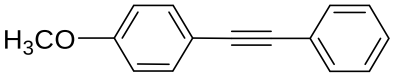
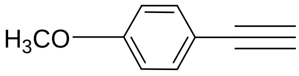
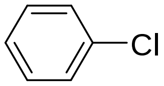
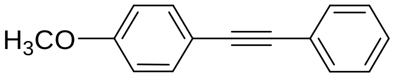
Entry	Base	Time (h)	Yield [b] (%)
1	KOH	14	72
2	NaOH	15	76
3	**K_2CO_3**	**12**	**91**
4	DIPEA	16	42
5	TEA	19	64
6	DEA	21	58
7	K_3PO_4	18	73
8	No Base	24	No Reaction

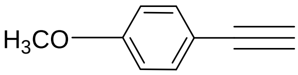
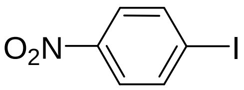
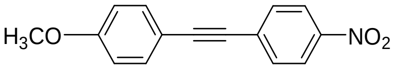
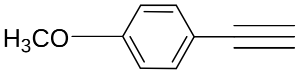
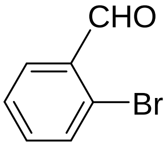
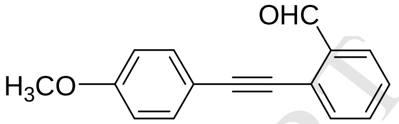
[a] Reaction conditions: **7a** (1mmol), **8a** (1mmol), base (2 mmol), MNPFemTriazNHC@Ag complex (**6**) (100 mg) and DMF (5 mL). [b] Isolated yield after column chromatography

Table 4 MNPFemTriazNHC@Ag complex (**6**) catalysed Sonogashira coupling reaction[a]



Entry	Phenyl acetylene (7)	Aryl halide (8)	Product (9)	Time (h)	Yield %[b]
a				12	91
b				13	90
c				11	92
d				14	80
e				12	92
f				13	87
g				14	85
h				12	88

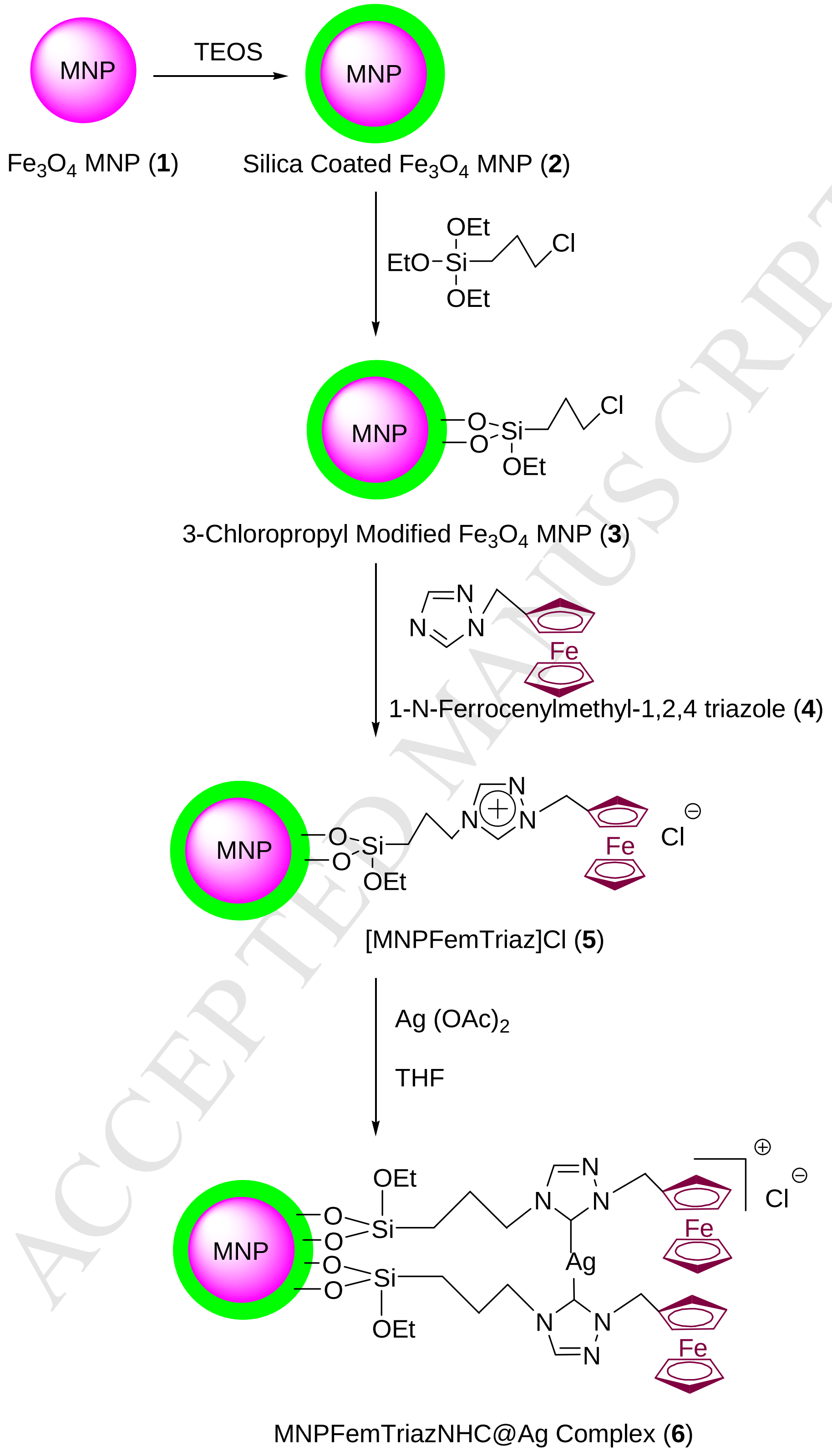
i				13	86
j				12	88
k				18	74
l				18	63
m				16	69
n				19	58
o				22	54
p				12	86
q				13	82
r				19	60

s				11	85
t				13	84

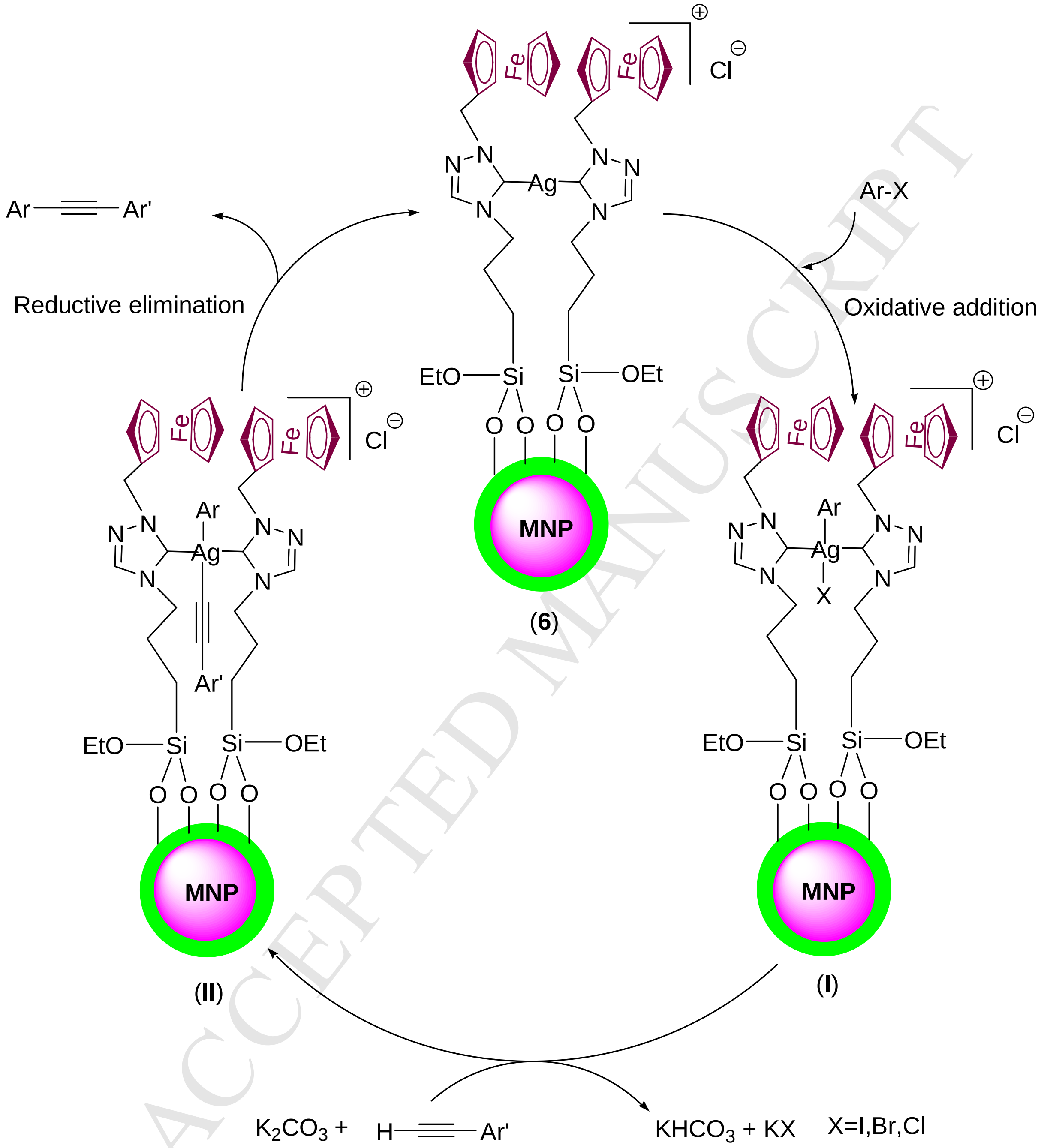
[a]Reaction conditions: **7** (1 mmol), **8** (1 mmol), K_2CO_3 (2 mmol), MNPFemTriazNHC@Ag complex (**6**) (100 mg) and DMF (5 mL), [b]Isolated yield after column chromatography.

Table 5. Comparison of different catalysts for synthesis of **9a**

Sr. No.	**Catalytic System**	**Solvent**	**Temp.**	**Time (h)**	**Yield [b] (%)**	**Ref.**
1	AgI (10 mol%), PPh_3 (30 mol%)	DMF	100 °C	8	95	15b
2	$[Ag_4(BPTC)]_n$ (2 mol%), PPh_3 (20 mol%)	DMF	100 °C	12	72	33
3	$Pd(OAc)_2$ (3 mol%), 2-aminopyrimidine-4,6-diol (6 mol%)	CH_3CN	R.T.	6	98	34
4	$PdCl_2$, (1 mol %), Pyrrolidine (10mol%)	H_2O	50°C	24	94	35
5	MNPFemTriazNHC@Ag complex **(6)**	DMF	100 °C	12	91	This work


MNP
TEOS
Fe3O4 MNP (1)
Silica Coated Fe3O4 MNP (2)
OEt
EtO-Si
OEt
Cl
O
Si
OEt
3-Chloropropyl Modified Fe3O4 MNP (3)
N
Fe
1-N-Ferrocenylmethyl-1,2,4 triazole (4)
[MNPFemTriaz]Cl (5)
Ag (OAc)2
THF
Ag
MNPFemTriazNHC@Ag Complex (6)

Scheme 1



Scheme 2. Plausible mechanism for Sonogashira coupling reaction using MNPFemTriazNHC@Ag complex **(6)**

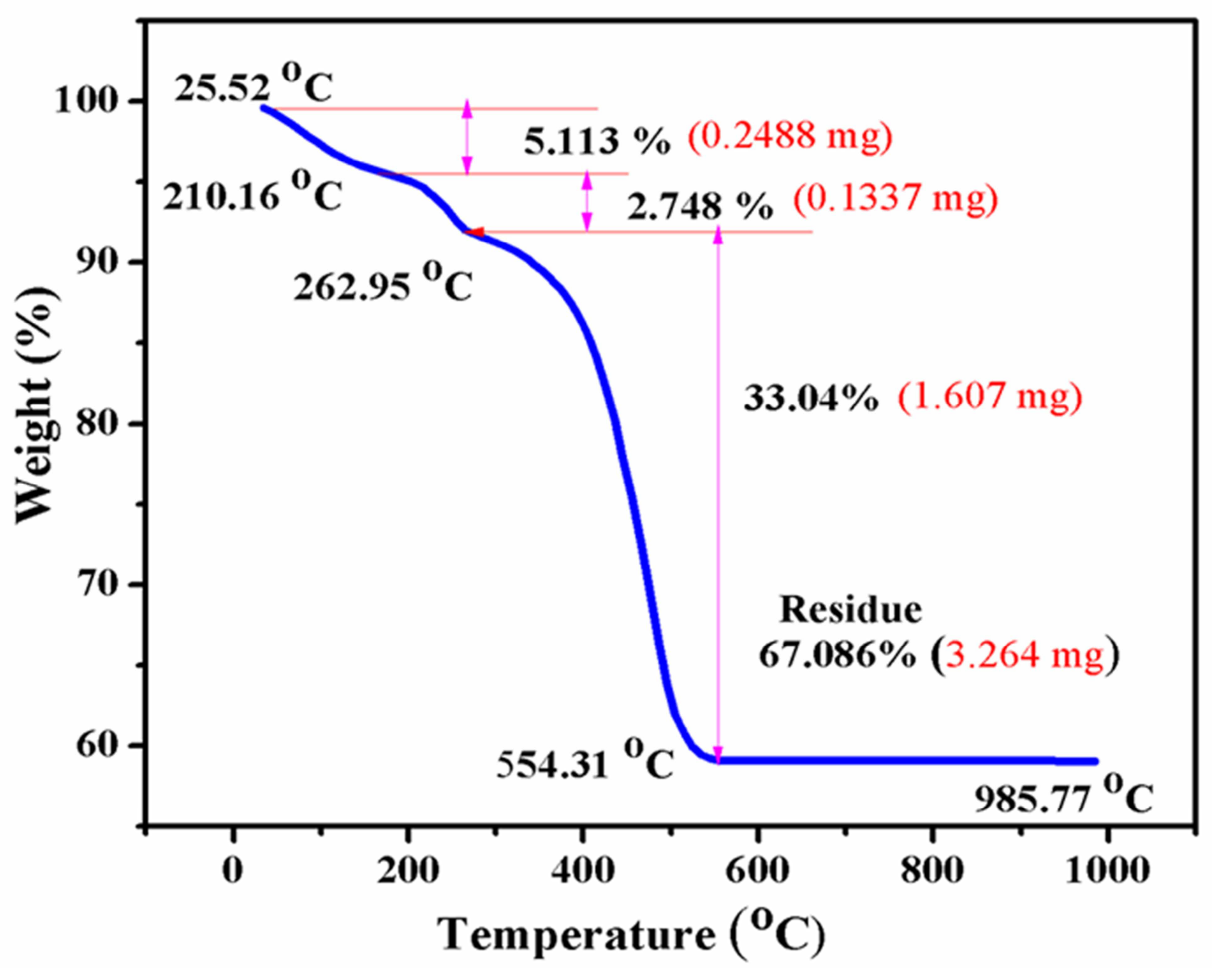


Fig. 1. TGA curve of MNPFemTriazNHC@Ag complex **(6)**

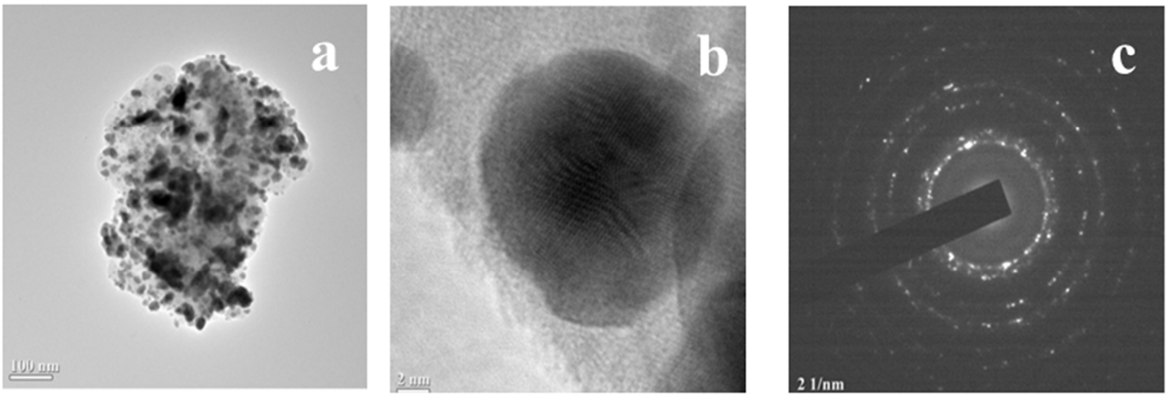


Fig. 2. TEM images of MNPFemTriazNHC@Ag complex **(6)** with SAED pattern

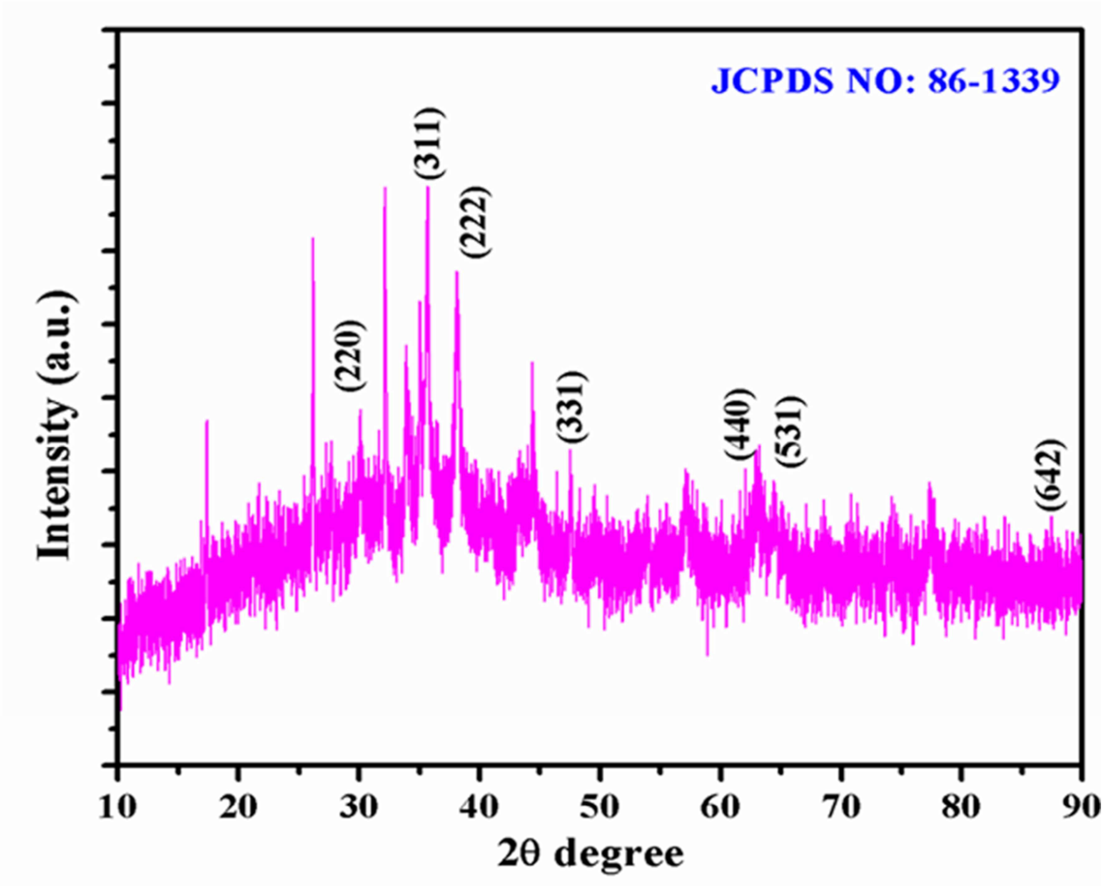


Fig. 3. XRD pattern of MNPFemTriazNHC@Ag complex **(6)**

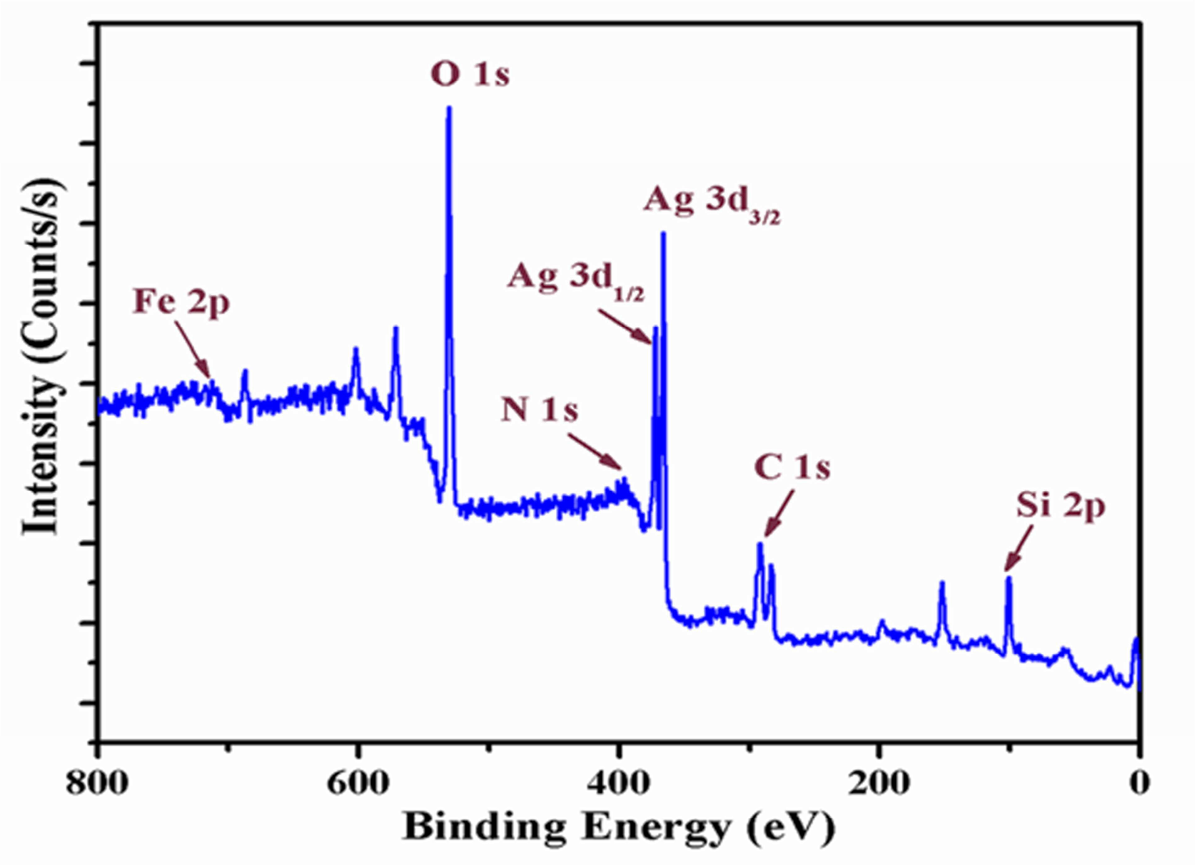


Fig. 4. XPS survey spectrum of MNPFemTriazNHC@Ag complex **(6)**

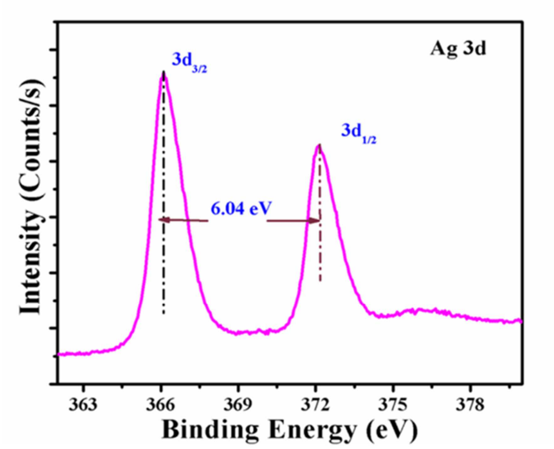


Fig. 4.1 Core level XPS spectrum of Ag in **(6)**

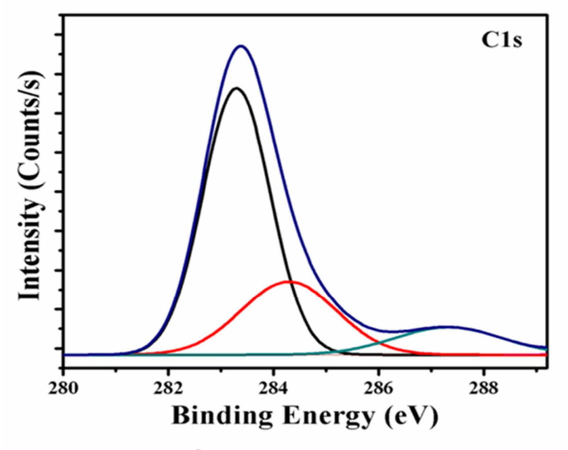


Fig. 4.2 Core level XPS spectrum of C in **(6)**

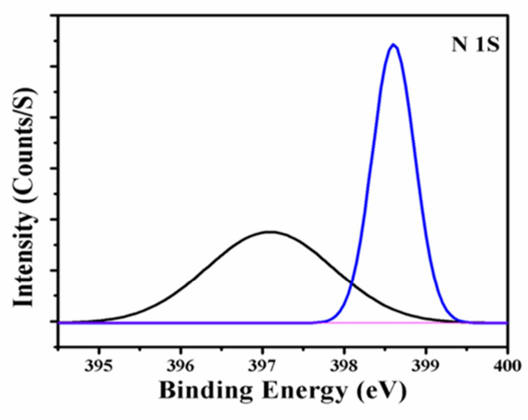


Fig. 4.3 Core level XPS spectrum of N in **(6)**

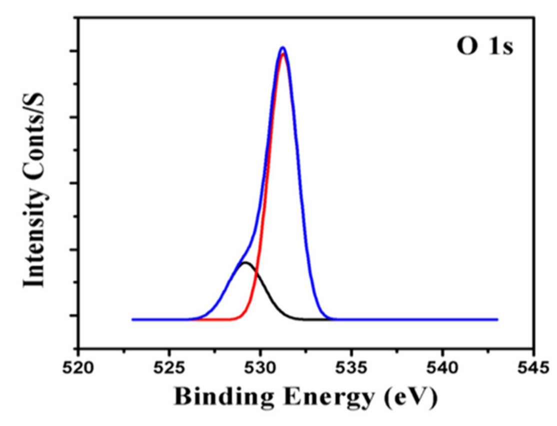


Fig. 4.4 Core level XPS spectrum of O in **(6)**

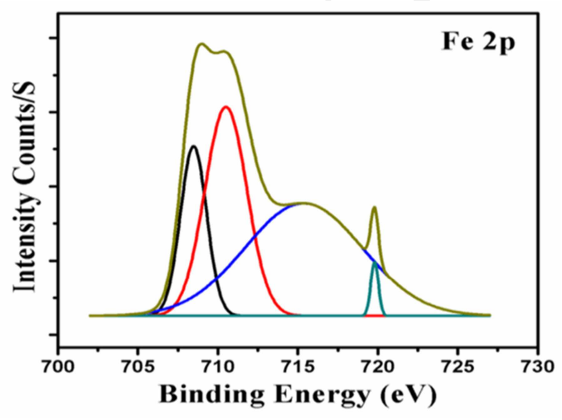


Fig. 4.5 Core level XPS spectrum of Fe in **(6)**

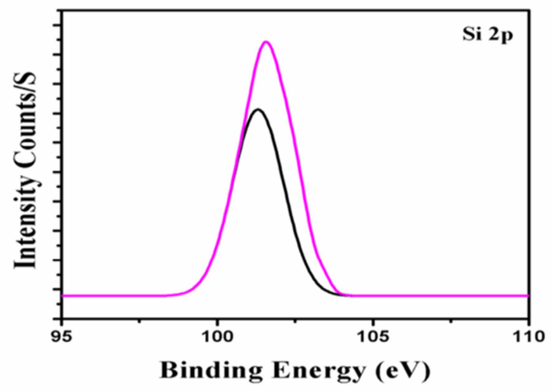


Fig. 4.6 Core level XPS spectrum of Si in **(6)**

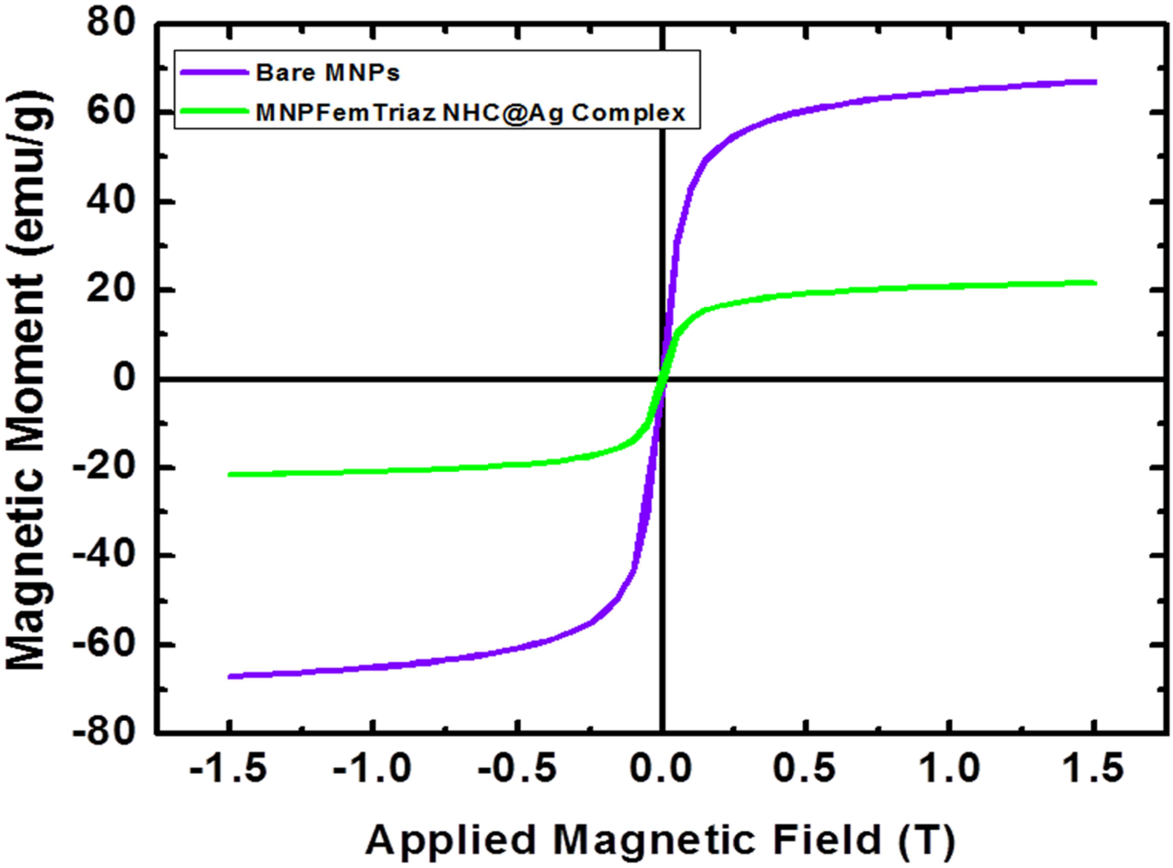


Fig. 5. Magnetic curves of bare MNPs and MNPFemTriazNHC@Ag complex **(6)**

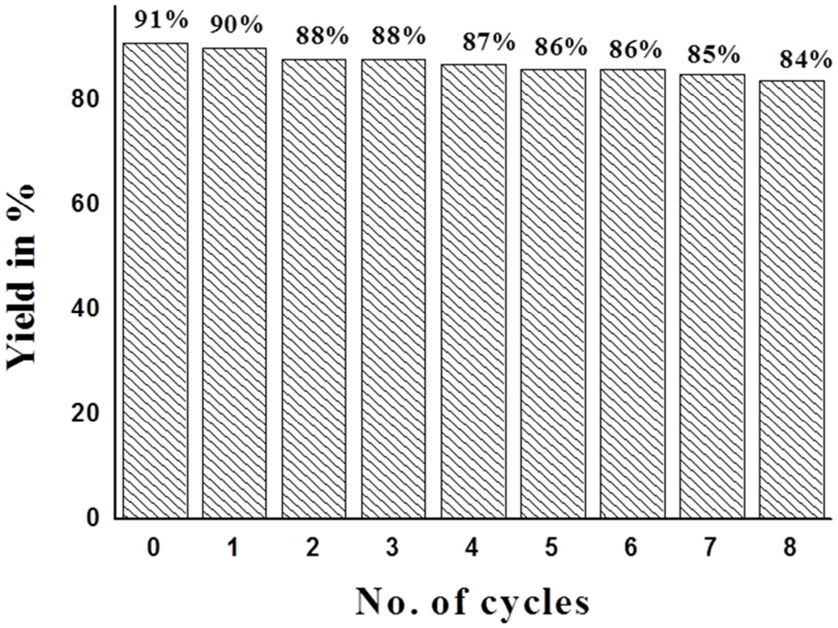


Fig. 6. Reusability of MNPFemTriazNHC@Ag complex **(6)** in Sonogashira Coupling

Highlights:

- Magnetically retrievable *N*-heterocyclic carbene-silver complex with wingtip ferrocenyl group was synthesized.
- The catalyst was employed efficiently for Sonogashira Coupling reaction of terminal alkynes and aryl halides.
- The catalyst can be reused up to eight consecutive runs without loss in catalytic activity.