

## FULL PAPER

# Cellulose-supported N-heterocyclic carbene silver complex with pendant ferrocenyl group for diaryl ether synthesis

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A cellulose-supported N-heterocyclic carbene Ag(I) complex has been synthesized by covalent grafting of ferrocenyl ionic liquid in the matrix of cellulose followed by metallation with silver oxide. The complex was employed as a heterogeneous catalyst in the synthesis of diaryl ethers. Reactions of a variety of phenols with aryl halides afford corresponding diaryl ethers in moderate to good yields. Recyclability experiments were executed successfully for five consecutive runs.

**KEYWORDS**

diaryl ether, ferrocene, N-heterocyclic carbene, reusability

## 1 | INTRODUCTION

N-Heterocyclic carbenes (NHCs) are a versatile class of ancillary ligands that have garnered tremendous attention for their ability to effect various C–C, C–N and C–O bond formations.<sup>[1]</sup> This outstanding class of ligands has high activity and selectivity with increased stability towards air and moisture. NHCs allow manipulation of the catalytic performance through adjustment of electronic and steric parameters.<sup>[2]</sup> Compared to phosphorus-containing ligands, NHCs tend to bind more strongly with metals leading to stable metal–carbon bonds thereby avoiding the necessity for the use of excess ligand in catalytic reactions.<sup>[3]</sup> NHC–metal complexes have displayed superior catalytic activities in many useful organic transformations.<sup>[4]</sup> Insight into homogeneous NHC–metal complex catalytic systems has revealed some basic problems in terms of separation and recycling. This factor coupled with their ability to induce contamination of the ligand residue in products has triggered a flourishing interest in heterogenization of homogeneous NHC-based catalytic systems.<sup>[5]</sup> The built-in heterogeneous nature of NHCs allows for a robust recycling and provides excellent opportunity to prevent the contamination of the ligand thereby decreasing the environmental pollution caused by residual metals in the waste. The field of heterogeneous NHCs has witnessed impressive progress during the past few years.<sup>[6]</sup> Despite tremendous strides, a major driver

of current ground-breaking research is the development of new heterogeneous NHCs with different properties and reactivities.<sup>[1]</sup>

The recent quest towards green and sustainable development has spurred an extensive interest in the use of renewable bioresources in catalytic technology.<sup>[7]</sup> Cellulose is the most abundant renewable and biodegradable biopolymer with an annual world production of around 500 billion metric tons. Being abundant and outside the human food chain, it represents the most attractive and economic natural feedstock as per green chemistry principles. It is a long-chain linear polymer made up of repeating units of  $\beta$ -D-glucose linked by 1,4-glycosidic bonds. It has an unusual structure in which every other glucose monomer is flipped over and packed tightly as extended long chains which imparts rigidity and high tensile strength.<sup>[8]</sup> It is insoluble in water and most common solvents due to strong intramolecular and intermolecular hydrogen bonding between the individual chains.<sup>[9]</sup> In addition to the aforementioned properties, its high surface area, non-toxicity, stability in common organic solvents, unlimited availability as a renewable agro-resource and excellent biodegradability make cellulose an excellent renewable biopolymeric support for synthesis of heterogeneous catalysts.<sup>[10]</sup> The interesting properties of cellulose spurred us to investigate its feasibility in the synthesis of heterogeneous NHC–transition metal complexes with catalytic potential.

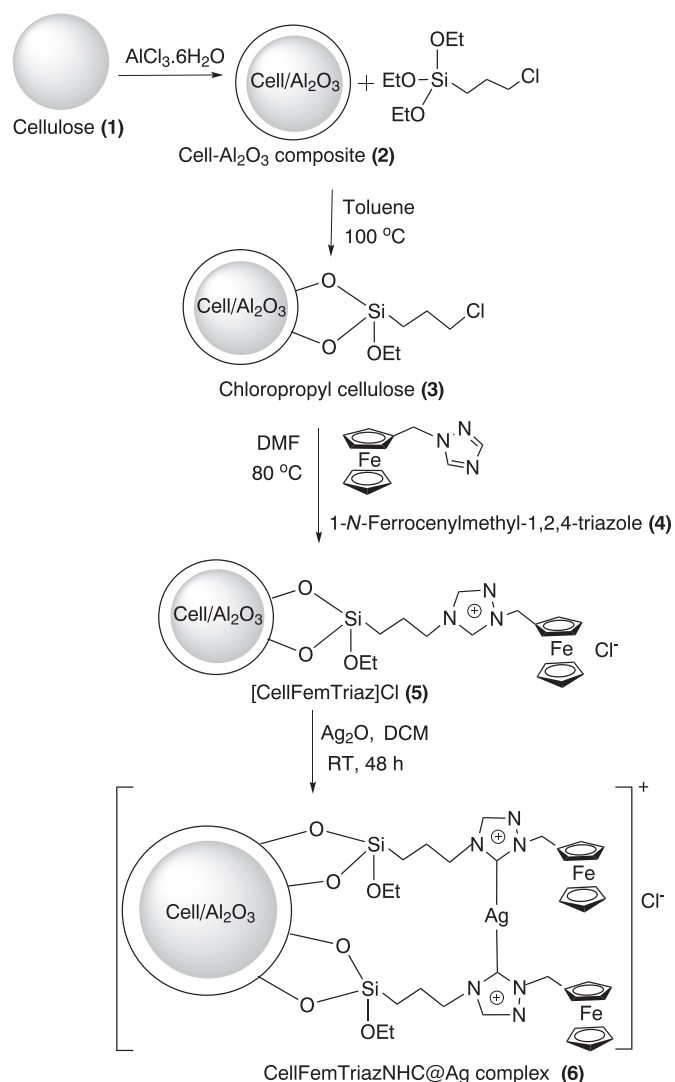
In the present paper, we report a conceptually new approach for the synthesis of a cellulose-supported NHC–silver complex with pendant ferrocenyl group. The complex constitutes a unique arrangement encompassing pendant ferrocenyl group that allows straightforward control of steric properties and natural feedstock-based backbone consisting of cellulose to achieve the goal of sustainability. In continuation of our work related to green chemistry,<sup>[11]</sup> we report herein the synthesis of diaryl ethers using CellFemTriazNHC@Ag complex **6** as catalyst.

## 2 | RESULTS AND DISCUSSION

The preparation of the cellulose-supported NHC–silver complex with pendant ferrocenyl group is outlined in Scheme 1. Initially, aluminium oxide was finely dispersed on the cellulose surface with a good degree of adhesion to form Cell–Al<sub>2</sub>O<sub>3</sub> composite (**2**). The tendency of surface Al–OH groups of **2** to form stable Al–O–Si bonds with Si–OCH<sub>2</sub>CH<sub>3</sub> groups of (3-chloropropyl)triethoxysilane allowed facile synthesis of chloropropylcellulose (**3**) with a considerable degree of organofunctionalization. The synthetically active chloro group in **3** allowed installation of azolium group in the cellulose matrix. This was achieved by quaternization of 1-*N* ferrocenylmethyl-1,2,4-triazole (**4**) with **3** to yield heterogeneous azolium salt [CellFemTriaz]Cl (**5**). Finally, the complexation of **5** with Ag<sub>2</sub>O yielded the desired cellulose-supported NHC–silver complex with pendant ferrocenyl group, namely CellFemTriazNHC@Ag complex (**6**).

Fourier transform infrared (FT-IR), FT-Raman and cross-polarization magic angle spinning (CP-MAS) <sup>13</sup>C NMR spectroscopies were employed to monitor the progress of reactions involved in the synthesis of complex **6**. The FT-Raman spectrum displayed peaks at 487 cm<sup>-1</sup> (Fe–Cp stretching band), 1360, 1494 and 1550 cm<sup>-1</sup> (ring stretching modes of triazole ring), 3142 and 3176 cm<sup>-1</sup> (C–H stretching of Cp rings) and the FT-IR spectrum displayed a strong intense band in the range 1350–1500 cm<sup>-1</sup> as a result of bonding of NHC carbon with silver metal ion and representative ‘four fingers’ pattern suggesting the formation of **6**. The formation of **6** was further corroborated by recording the CP-MAS <sup>13</sup>C NMR spectrum which demonstrated peaks at 161.87 (s, triazolium C<sub>2</sub>), 122.04 (s, triazolium C<sub>5</sub>), 105.72 (bs, C<sub>1</sub> of cellulose), 89.40 (bs, C<sub>4</sub> of cellulose), 72.05–75.30 (m, C<sub>2</sub>, C<sub>3</sub>, C<sub>5</sub> of cellulose), 65.81 (bs, C<sub>6</sub> of cellulose), 68.15 (s, non-substituted Cp ring carbon of ferrocene), 83.59 (s, substituted Cp ring carbon of ferrocene), 47.13 (s, 1C, =N–CH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>), 22.27 (s, 1C, =N–CH<sub>2</sub>CH<sub>2</sub>–CH<sub>2</sub>), 10.11 (s, 1C, –CH<sub>2</sub>Si) confirming the proposed structure.

Thermogravimetric analysis (TGA) was conducted to evaluate the thermal stability of complex **6**. The thermogram is shown in Fig. 1. Complex **6** displayed an initial weight loss of 5.35% ascribed to desorption of physically adsorbed water



SCHEME 1 Synthesis of CellFemTriazNHC@Ag complex (**6**)

below 100°C. The second key weight loss of 62.95% up to 301°C is attributed to combined weight loss of pendant ferrocenyl unit and other organic functional groups from the cellulose matrix. The third weight loss of 3.63% corresponds to the decomposition of the cellulose matrix by oxidative mode. These observations are in good agreement with TGA profile of cellulose reported in the literature.<sup>[12]</sup>

X-ray photoelectron spectroscopy (XPS) was used to investigate the elemental coordination state of Ag. The XPS spectrum of Ag 3d core level region for complex **6** displayed peaks of binding energy at 367.25 eV (3d<sub>5/2s</sub>) and 373.23 eV (3d<sub>3/2</sub>). These values corroborate the existence of Ag(I) in **6**.

The scanning electron microscopy (SEM) analysis of cellulose and complex **6** is exemplified in Fig. 2. The SEM images (Figs 2(a) and (b)) display particles of micrometre size and a clear change in morphology of cellulose was observed after anchoring of NHC–silver complex on cellulose.

To explore the catalytic efficiency of **6**, it was used in the synthesis of diaryl ethers which are core scaffolds of commercially very important structures often found in antibiotic,

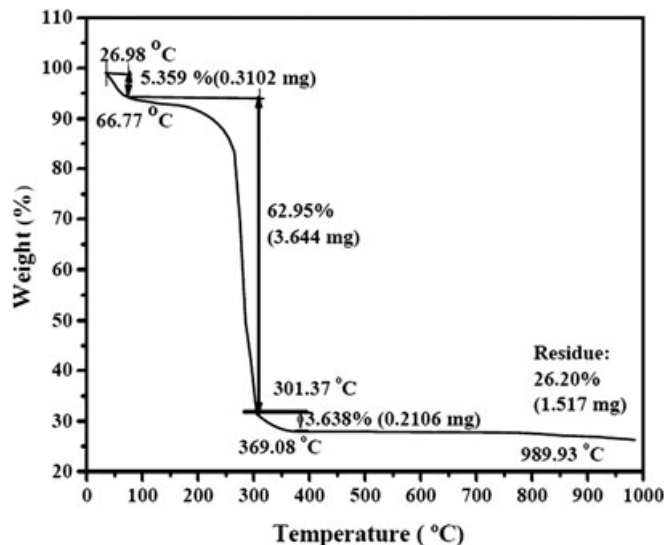


FIGURE 1 TGA curve of CellFemTriazNHC@Ag complex (6)

antitumor and anti-HIV agents<sup>[13a-c]</sup> and also constitute a significant class of organic compounds throughout various industrial fields in polymer, pharmaceutical, chemical and life sciences.<sup>[13d]</sup> In addition, they are versatile building blocks in the synthesis of natural products<sup>[13e]</sup> and valuable intermediates in organic synthesis.<sup>[13f]</sup> Several distinct protocols have been developed for the synthesis of diaryl ethers. One prominent method for diarylether synthesis includes reaction of alkyl halides and phenols. Several catalysts such as Cu(I)-USY zeolites,<sup>[14a]</sup> CuBr and supporting ligand (2-pyridyl)acetone,<sup>[14b]</sup> CuI and *N,N*-dimethylglycine,<sup>[14c]</sup> Cu<sub>2</sub>O and ligands (Chxn-Py-Al, Salox, DMG),<sup>[14d]</sup> Cu salt/aminophenol,<sup>[14e]</sup> CuI/picolinic,<sup>[14f]</sup> AgNO<sub>3</sub>/*N,N*-DMEDA<sup>[14g]</sup> as well as microwaves technique<sup>[14h]</sup> have been reported to expand the effectiveness of this protocol. However, there is a still scope for improvement especially towards developing a green procedure using heterogeneous catalysis. This prompted us to evaluate the catalytic activity of **6** in synthesis of diaryl ethers (Scheme 2). Initially, to optimize the reaction conditions, iodobenzene (**7a**; 1 mmol) and *p*-cresol (**8a**; 1.2 mmol) were chosen as model substrates for the synthesis of diaryl ether in the presence of a catalytic amount of **6** in toluene. Initially, the influence of catalyst loading on diaryl ether synthesis was investigated. The use of 25 mg (0.0071 mmol) of the catalyst provided a low yield of corresponding product (1-methyl-4-phenoxybenzene, **9a**) even after prolonged reaction time (Table 1, entry 1). When the catalyst quantity was increased to 50 mg (0.014 mmol), the product yield was boosted to 90% under identical reaction conditions (Table 1, entry 2). Subsequently, further increase in the quantity of catalyst from 100 to 150 mg did not show a substantial alteration in the yield of product and reaction time (Table 1, entries 3 and 4). The next parameter in the optimization studies was the choice of solvent. Screening of various organic solvents was carried out, and eventually it was found that the model reaction afforded good yields

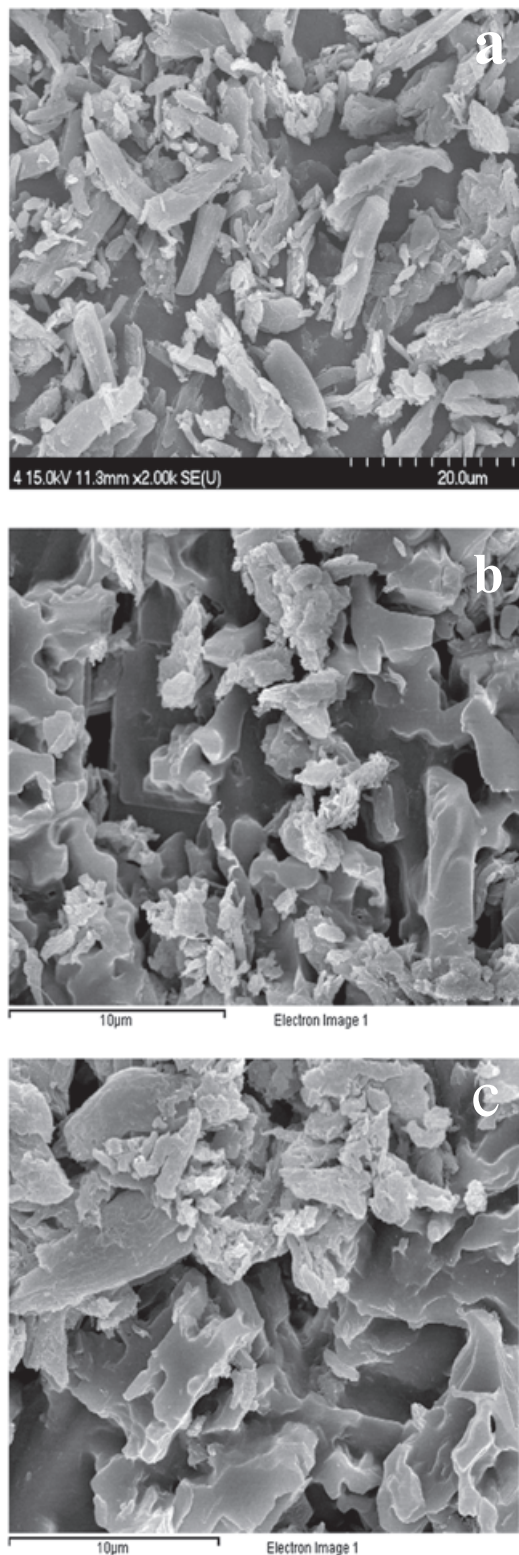
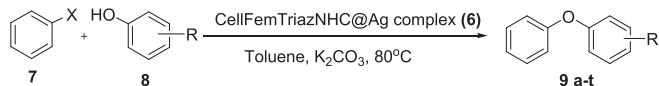


FIGURE 2 SEM images of (a) cellulose (b) fresh CellFemTriazNHC@Ag complex (**6**) and (c) recovered CellFemTriazNHC@Ag complex after fifth run

in solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO) (Table 2, entries 1 and 2). Better yields were achieved in solvents like acetonitrile and tetrahydrofuran (THF) (Table 2, entries 3 and 4), while moderate yields were obtained in dichloromethane and 1,4-dioxane solvents (Table 2, entries 5 and 6). Lower





**SCHEME 2** CellFemTriazNHC@Ag complex-catalysed diaryl ether synthesis

**TABLE 1** Catalyst optimization in CellFemTriazNHC@Ag complex-promoted synthesis of diaryl ethers<sup>a</sup>

| Entry | Catalyst (mg) | Time (h) | Yield (%) <sup>b</sup> | TON  | TOF (h <sup>-1</sup> ) |
|-------|---------------|----------|------------------------|------|------------------------|
| 1     | 25            | 5.00     | 57                     | 8028 | 1605                   |
| 2     | 50            | 4.45     | 90                     | 6428 | 1444                   |
| 3     | 100           | 4.45     | 91                     | 4272 | 960                    |
| 4     | 150           | 4.45     | 91                     | 3204 | 720                    |

<sup>a</sup>Optimal reaction conditions: **7a** (1 mmol), **8a** (1.2 mmol) and toluene (5 ml), K<sub>2</sub>CO<sub>3</sub> (2 eq.).

<sup>b</sup>Isolated yields after column chromatography.

yields were obtained in polar protic solvents such as water and ethanol (Table 2, entries 7 and 8). Toluene proved to be the best solvent as the yield of the desired product (**9a**) was highest amongst all the screened solvents (Table 2, entry 9). Screening of various bases (Table 3) revealed that the presence of base is essential for the reaction to proceed. Several bases were examined for the model reaction, but K<sub>2</sub>CO<sub>3</sub> (Table 3, entry 4) was found to give best yield as compared to other bases (Table 3, entries 1–3, 5 and 6). Thus, there is a cumulative effect of all parameters on yield of product.

With a reliable set of parameters in hand, we probed the general applicability of the protocol by reacting aryl halides with a variety of substituted phenols for the synthesis of diaryl ethers. The results are summarized in Table 4. Aryl iodides and aryl bromides reacted with structurally diverse

**TABLE 2** Solvent optimization in CellFemTriazNHC@Ag complex-promoted synthesis of diaryl ethers<sup>a</sup>

| Entry | Solvent                         | Time (h) | Yield (%) <sup>b</sup> | TON  | TOF (h <sup>-1</sup> ) |
|-------|---------------------------------|----------|------------------------|------|------------------------|
| 1     | DMF                             | 6.00     | 80                     | 5714 | 952                    |
| 2     | DMSO                            | 5.50     | 83                     | 5928 | 1077                   |
| 3     | CH <sub>3</sub> CN              | 10.0     | 57                     | 4071 | 407                    |
| 4     | THF                             | 7.00     | 20                     | 1428 | 204                    |
| 5     | CH <sub>2</sub> Cl <sub>2</sub> | 6.30     | 25                     | 1785 | 71                     |
| 6     | 1,4-Dioxane                     | 6.00     | 67                     | 4785 | 797                    |
| 7     | H <sub>2</sub> O                | 8.00     | 10                     | 714  | 89                     |
| 8     | EtOH                            | 7.45     | 20                     | 1428 | 191                    |
| 9     | Toluene                         | 4.45     | 90                     | 6428 | 1444                   |

<sup>a</sup>Optimal reaction conditions: **7a** (1 mmol), **8a** (1.2 mmol) and solvent (5 ml), K<sub>2</sub>CO<sub>3</sub> (2 eq.), CellFemTriazNHC@Ag complex (**6**) (50 mg).

<sup>b</sup>Isolated yields after column chromatography.

**TABLE 3** Base optimization in CellFemTriazNHC@Ag complex-promoted synthesis of diaryl ethers<sup>a</sup>

| Entry | Base                            | Time (h) | Yield (%) <sup>b</sup> | TON  | TOF (h <sup>-1</sup> ) |
|-------|---------------------------------|----------|------------------------|------|------------------------|
| 1     | K <sub>3</sub> PO <sub>4</sub>  | 6.40     | 77                     | 5500 | 859                    |
| 2     | Cs <sub>2</sub> CO <sub>3</sub> | 5.45     | 84                     | 6000 | 1100                   |
| 3     | Na <sub>2</sub> CO <sub>3</sub> | 7.00     | 55                     | 3928 | 561                    |
| 4     | K <sub>2</sub> CO <sub>3</sub>  | 4.45     | 90                     | 6428 | 1444                   |
| 5     | NaOH                            | 8.30     | 25                     | 1785 | 215                    |
| 6     | KOH                             | 6.45     | 18                     | 1285 | 199                    |

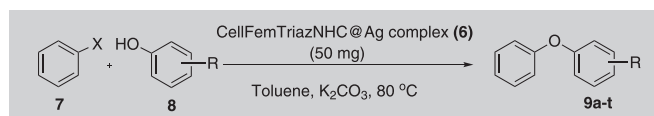
<sup>a</sup>Optimal reaction conditions: **7a** (1 mmol), **8a** (1.2 mmol) and toluene (5 ml), base (2 eq.), CellFemTriazNHC@Ag complex (**6**) (50 mg).

<sup>b</sup>Isolated yields after column chromatography.

phenols yielding corresponding diaryl ethers with the turnover number (TON) in the range 4642–6428 and turnover frequency (TOF) in the range 221–1995 h<sup>-1</sup> (Table 4, entries a–t). In general, the electronic nature of the substituents attached to the aromatic ring had an impact on the yield of the product. Phenols with electron-donating groups furnished higher yields than those with electron-withdrawing groups. It is worth noting that no reaction was observed under similar conditions in the absence of complex **6**.

A tentative reaction mechanism is proposed in Scheme 3 and is based on Ag(I)/Ag(III) catalytic system-promoted C–O cross-coupling reaction proposed by Ribas and co-workers.<sup>[15]</sup> Initially, facile oxidative addition of aryl halide to complex **6** forms aryl–Ag(III) intermediate which further reacts with phenol followed by reductive elimination furnishing desired diaryl ethers. The bulk of tethered ferrocenyl group plays a vital role in catalysis. It is now well established that activity and selectivity of NHC–metal complexes can be enhanced by a change of electronic and steric properties of substituents in the vicinity of a heterocyclic ring. The high electron density on the metal centre imparted by the NHC favours the oxidative addition step. In the present work the ferrocenyl moiety represents a relatively bulky group with a unique cylindrical shape, and electronically the powerful donor capacity of ferrocene generates an electron-rich NHC–Ag complex which undergoes faster oxidative addition which is a key step thereby resulting in an efficient synthesis of diaryl ethers.

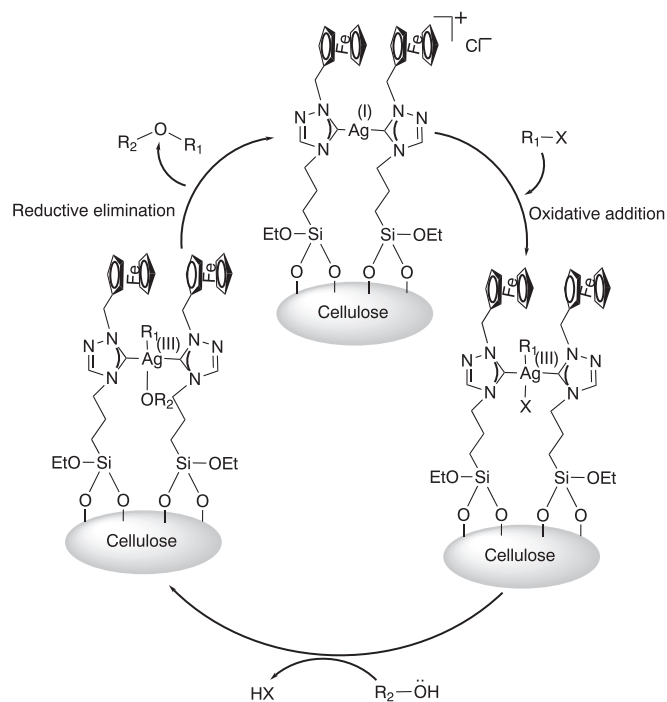
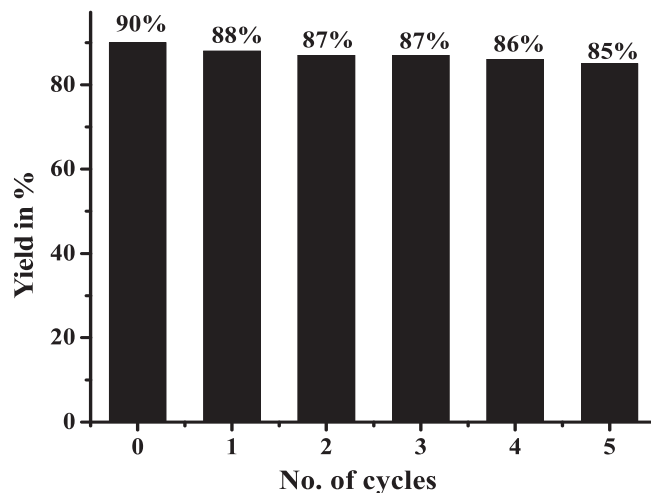
To verify heterogeneous nature of complex **6** a hot filtration test was performed using a model reaction. After 50% reaction completion, **6** was separated from reaction mixture by simple filtration. The filtrate was stirred for additional time. Interestingly, no substantial progress (GC–MS analysis) in the yield was noticed in absence of catalyst. Moreover, inductively coupled plasma atomic emission spectrometric analysis of a similar reaction mixture at the midpoint of reaction revealed the absence of metallic species present in the solution confirming the heterogeneous nature of **6**.

**TABLE 4** CellFemTriazNHC@Ag complex-catalysed synthesis of diaryl ethers<sup>a</sup>


| Entry | R                         | X  | Product   | Time (h) | Yield (%) <sup>b</sup> | TON  | TOF (h <sup>-1</sup> ) |
|-------|---------------------------|----|-----------|----------|------------------------|------|------------------------|
| a     | <i>p</i> -Me              | I  | <b>9a</b> | 4.45     | 90                     | 6428 | 1444                   |
| b     | <i>p</i> -Me              | Br | <b>9b</b> | 7.40     | 77                     | 5500 | 743                    |
| c     | <i>o</i> -Me              | I  | <b>9c</b> | 6.20     | 85                     | 6071 | 979                    |
| d     | <i>o</i> -Me              | Br | <b>9d</b> | 8.45     | 79                     | 5642 | 667                    |
| e     | <i>m</i> -Me              | I  | <b>9e</b> | 4.45     | 80                     | 5714 | 1284                   |
| f     | <i>m</i> -Me              | Br | <b>9f</b> | 5.15     | 71                     | 5071 | 984                    |
| g     | <i>o</i> -MeO             | I  | <b>9g</b> | 5.15     | 78                     | 5571 | 1081                   |
| h     | <i>o</i> -MeO             | Br | <b>9h</b> | 5.40     | 71                     | 5071 | 939                    |
| i     | <i>p</i> -MeO             | I  | <b>9i</b> | 3.15     | 88                     | 6285 | 1995                   |
| j     | <i>p</i> -MeO             | Br | <b>9j</b> | 4.45     | 74                     | 5285 | 1187                   |
| k     | H                         | I  | <b>9k</b> | 6.40     | 81                     | 5785 | 903                    |
| l     | H                         | Br | <b>9l</b> | 9.30     | 78                     | 5571 | 557                    |
| m     | <i>p</i> -NO <sub>2</sub> | I  | <b>9m</b> | 16.0     | 76                     | 5428 | 339                    |
| n     | <i>p</i> -NO <sub>2</sub> | Br | <b>9n</b> | 20.0     | 65                     | 4642 | 232                    |
| o     | <i>o</i> -NO <sub>2</sub> | I  | <b>9o</b> | 18.0     | 71                     | 5071 | 281                    |
| p     | <i>o</i> -NO <sub>2</sub> | Br | <b>9p</b> | 21.50    | 67                     | 4785 | 221                    |
| q     | <i>m</i> -NO <sub>2</sub> | I  | <b>9q</b> | 15.0     | 75                     | 5357 | 357                    |
| r     | <i>m</i> -NO <sub>2</sub> | Br | <b>9r</b> | 21.0     | 68                     | 4857 | 231                    |
| s     | <i>p</i> -CN              | I  | <b>9s</b> | 12.10    | 70                     | 5000 | 413                    |
| t     | <i>p</i> -CN              | Br | <b>9t</b> | 16.0     | 68                     | 4857 | 303                    |

<sup>a</sup>Optimal reaction conditions: **7** (1 mmol), **8** (1.2 mmol), toluene (5 ml) and CellFemTriazNHC@Ag complex (**6**) (50 mg), K<sub>2</sub>CO<sub>3</sub> (2 eq.).

<sup>b</sup>Isolated yields after column chromatography. All products were characterized by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS analyses.

**SCHEME 3** Plausible mechanism for the synthesis of diaryl ethers using CellFemTriazNHC@Ag complex (**6**)**FIGURE 3** Reusability of CellFemTriazNHC@Ag complex (**6**) in diaryl ether synthesis

The reusability of complex **6** was studied using the model reaction. After each cycle, catalyst was recovered by simple filtration; the recovered catalyst was washed with toluene and dried *in vacuo* at room temperature and used directly for the next cycle. The studies revealed a minimal loss in catalytic activity, as the catalyst could be reused for five cycles under optimal reaction conditions (Fig. 3). SEM analysis of reused catalyst shows no significant alteration in the morphology in comparison with fresh catalyst (Fig. 2(c)).

### 3 | CONCLUSIONS

We have reported the synthesis of a cellulose-supported NHC–silver complex with pendant ferrocenyl group. The synthesized complex exhibits outstanding catalytic activity in the synthesis of diaryl ethers with high TON and TOF. This protocol offers several noteworthy merits such as operational simplicity, clean reaction profile and good yields.

### 4 | EXPERIMENTAL

All reactions were carried out under air atmosphere in dried glassware. FT-IR spectra were measured with a PerkinElmer One FT-IR spectrophotometer. The samples were examined as KBr discs (*ca* 5% *w/w*). Raman spectroscopy was done using a Bruker FT-Raman (MultiRAM) spectrometer. The elemental compositions of materials were analysed using an energy-dispersive X-ray spectroscopic facility attached to the field emission SEM instrument (Hitachi S 4800, Japan). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker AC (300 MHz for <sup>1</sup>H NMR and 75 MHz for <sup>13</sup>C NMR) spectrometer using CDCl<sub>3</sub> 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 <sup>13</sup>C 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 analysed by SEM using a JEOL model JSM with 5 and 20 kV accelerating voltages. Melting points were determined using MEL-TEMP capillary melting point apparatus and are uncorrected. 1-*N*-(ferrocenylmethyl) triazole was synthesized following a literature procedure.<sup>[16]</sup> Cellulose (**1**) and all other chemicals were obtained from local suppliers and used without further purification. XPS was conducted with a KRATOS AXIC 165 equipped with Mg K $\alpha$  radiation.

#### 4.1 | Preparation of Cell-Al<sub>2</sub>O<sub>3</sub> composite (**2**)

A blend of microcrystalline cellulose **1** (15 g), aluminium chloride hexahydrate (15 g) in water (200 ml) was stirred for 12 h. The mixture was subsequently filtered and resultant solid was exposed to ammonia. Finally, it was washed with water and dried under vacuum at room temperature to afford Cell-Al<sub>2</sub>O<sub>3</sub> composite **2**. The amount of aluminium was determined by calcining 0.300 g of **2** to 600°C for 8 h and the residue weighed as Al<sub>2</sub>O<sub>3</sub>, which was found to be 3.27 wt%, corresponding to 0.69 mmol g<sup>-1</sup> aluminium.

#### 4.2 | Preparation of chloropropylcellulose (**3**)

A mixture of **2** (10.0 g) and (3-chloropropyl)triethoxysilane (9.6 ml, 40.0 mmol) in 25 ml of toluene was refluxed in an oil bath. After 24 h, the reaction mixture was cooled, and the product was filtered and washed with toluene (3 × 5 ml) and dried under vacuum at room temperature for 8 h to afford **3**.

FT-IR (KBr, thin film,  $\nu$ , cm<sup>-1</sup>): 3366, 2898, 1623, 1427, 1335, 1204, 1160, 1109, 1056, 1032, 707, 667. Loading: 0.59 mmol of functional group per gram of cellulose.

#### 4.3 | Preparation of [CellFemTriaz]Cl (**5**)

A mixture of **3** (7.0 g) and 1-*N*-ferrocenylmethyl-1,2,4-triazole (**4**; 3.76 g, 14 mmol) in DMF (25 ml) was heated at 80°C in an oil bath. After 72 h, the solid was filtered, washed with DMF (3 × 50 ml), MeOH (3 × 50 ml) and CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 ml) and dried under vacuum at 50°C for 24 h to afford **5**.

FT-IR (KBr, thin film,  $\nu$ , cm<sup>-1</sup>): 3345, 2901, 2136, 1639, 1541, 1508, 1428, 1372, 1336, 1317, 1281, 1235, 1202, 1161, 1111, 1059, 1034, 705, 665, 617, 560, 519. Raman (cm<sup>-1</sup>): 487, 755, 980, 1065, 1298, 1360, 1494, 1550, 2756, 2910, 3142, 3176. Elemental analysis observed (%): C, 30.03; N, 10.55; O, 58.36; Cl, 0.21; Si, 0.49; Fe, 0.36; Loading: 0.15 mmol of functional group per gram of cellulose.

#### 4.4 | Preparation of CellFemTriazNHC@Ag complex (**6**)

A mixture of **5** (5.0 g) and Ag<sub>2</sub>O (1.70 g) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) was stirred at room temperature for 48 h in the dark. Afterwards, the mixture was filtered and the residue was washed

with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 ml) and dried under vacuum for 48 h to afford complex **6**.

FT-IR (KBr, thin film,  $\nu$ , cm<sup>-1</sup>): 3346, 2900, 1623, 1427, 1383, 1372, 1356, 1316, 1280, 1247, 1235, 1203, 1161, 1111, 1056, 1034, 897, 704, 664, 617, 559, 520. Raman (cm<sup>-1</sup>): 490, 599, 978, 1086, 1318, 1379, 1487, 1592, 1657, 1786, 2803, 2959, 3146, 3197. Elemental analysis observed (%): C, 26.59; N, 26.38; O, 42.10; Al, 0.49; Si, 0.45; Fe, 0.95; Ag, 3.04. Loading: 0.28 mmol of Ag per gram of cellulose.

#### 4.5 | General method for synthesis of diaryl ethers

A mixture of phenol (1.2 mmol), aryl halide (1 mmol), K<sub>2</sub>CO<sub>3</sub> (2 eq.) and complex **6** (50 mg) in toluene (5 ml) was stirred at 80°C. The progress of the reaction was monitored by TLC. After completion, the reaction mixture was filtered to remove insoluble catalyst. Evaporation of solvent *in vacuo* followed by column chromatography over silica gel using petroleum ether-ethyl acetate afforded pure products.

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