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A Pd/Cu-Free magnetic cobalt catalyst for C–N cross coupling reactions: synthesis of abemaciclib and fedratinib[†]

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Herein, the synthesis of a nano-catalytic system comprising magnetic nanoparticles as the core and edible natural ligands bearing functional groups as supports for cobalt species is described. Subsequent to its characterization, the efficiency of the catalyst was investigated for C–N cross-coupling reactions using assorted derivatives of amines and aryl halides. This novel and easily accessible Pd- and Cu-free catalyst exhibited good catalytic activity in these reactions using γ -valerolactone (GVL) at room temperature; good recyclability bodes well for the future application of this strategy. The introduced catalytic system is attractive in view of the excellent efficiency in an array of coupling reactions and its versatility is illustrated in the synthesis of abemaciclib and fedratinib, which are FDA-approved new and significant anti-cancer medicinal compounds that are prepared under green reaction conditions.

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Introduction

In recent decades, cross-coupling reactions using noble transition-metal catalysts have been gaining importance in academic and industrial synthetic chemistry.¹ More than half of all the C–C and C–heteroatom bond-forming reactions in drug discovery studies involve palladium-catalyzed cross-coupling reactions.² Due to the broad use of heterocyclic compounds in medicinally important derivatives and natural products, the development of facile approaches for the construction of C–N bonds has become one of the attractive research topics in the synthetic organic chemistry.^{3–6}

Conventionally, the Pd-catalyzed C–N coupling of amines and aryl halides is an efficient and versatile reaction procedure. Besides their high cost and scarcity, the use of palladium catalysts can lead to contamination of pharmaceutical compounds. These conditions provide a strong motivation for finding alternative valuable catalytic systems.⁷

In this regard, the use of inexpensive 3d transition-metals such as iron,⁸ nickel^{9,10} and copper^{11–19} has exhibited significant progress. However, various disadvantages of most of these methods limit their applications, for example, application of higher temperatures, longer reaction times, usage of stoichiometric amounts of metal catalysts, low catalyst efficiency, and consumption of volatile solvents and expensive ligands. Thus, the development of a more efficient, convenient Pd-free method is desirable. Although Cu is a known traditional catalyst for C-N and C-O cross-coupling reactions, the propensity of copper to promote oxidative homocoupling and the greater toxicity of Cu (safe value is set at around 5 mg kg⁻¹) in comparison with that of Co (safe value is set at around 150 mg kg⁻¹) motivated us to shift our research focus to the development of Cu-free catalytic systems.²⁰ Cobalt catalytic systems were found to be efficient and non-toxic, with cobalt being a stable metal and a low-cost alternative to palladium for deployment in organic chemistry.^{21–27}

Very recently, Szostak *et al.* reported the Kumada crosscoupling of aryl tosylates with alkyl and aryl Grignard reagents. They succeeded in introducing an efficient cobalt catalytic system, but it deployed expensive N-heterocyclic carbene ligands and suffered from non-reusability of the catalyst.²⁸

In 2020, Chu *et al.* developed the dehydrogenative coupling of aromatic diamines and primary alcohols catalyzed by the homogeneous $Co(\pi)$ complex.²⁹

Almost all available cobalt catalytic systems deploy homogeneous cobalt species; despite good efficiency, they suffer

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from disadvantages such as their high propensity for aggregation, low stability, and recycling problems which can lead to a reduction in their catalytic activities.

Various solid supports have been used to overcome these problems *via* immobilization of metal nanoparticles. In this regard, magnetic nanoparticles (MNPs) have attracted much attention as a supporting catalyst material due to their numerous merits such as low cost and toxicity, high surface area, facile separation process, ease of preparation, and easy functionalization procedure.^{30,31} Coating of MNPs with organic compounds is necessary to avoid MNP agglomeration during the catalytic reaction.

From the point of view of green chemistry, abundantly available natural carbohydrate compounds are suitable for coating the MNPs,^{32–36} and despite their various advantages namely their environmentally friendly nature, low cost, and stability, only a few reports on their applications are available.^{37–40}

Encouraged by our previous knowledge attained on the use of cobalt heterogeneous catalysts,^{41–45} herein, a novel, sustainable, and inexpensive heterogeneous cobalt catalyst was prepared using MNPs possessing various safe and readily available ligands including mannitol, sorbitol, xylitol, tartaric acid, malic acid, and citric acid. After preparation and appropriate characterization, their efficiency in C–N cross-coupling reactions was explored.

Over the past years, scientists have been encouraged to find alternative cleaner procedures for the traditional chemical syntheses by using greener solvents,^{46–53} and performing organic reactions in an eco-friendly manner using safe solvents is now of paramount interest. One of the non-toxic and very suitable solvent alternatives to classic polar aprotic solvents is γ -valerolactone (GVL). Moreover, it is accessible *via* a low-cost efficient process with many excellent properties which make it an ideal solvent of choice for large-scale synthesis.^{54,55}

Most of the reported cross-coupling reaction procedures require elevated temperatures and inert reaction conditions. While a few procedures have been conducted under room-temperature conditions,⁵⁶ this strategy is considered green as it avoids the generation of hazardous materials and by-products at elevated temperatures.^{57,58} Moreover, the avoidance of an inert atmosphere bodes well for its application on a large-scale, thus conforming to an upward trend in green chemistry.

One of the important pharmaceutical compounds, which have been synthesized through the C–N cross-coupling reaction is fedratinib, which is a JAK2 inhibitor anti-cancer agent that was recently approved by the FDA.^{59,60} A practical synthetic route for fedratinib preparation was developed in two steps based on the Pd-catalyzed C–N cross-coupling reaction by TargeGen Inc.⁶¹ Abemaciclib is another FDA approved pharmaceutical which is a cyclin-dependent kinase (CDK) selective ATP inhibitor used for the treatment of hormone-receptor-positive breast cancer and could be synthesized *via* a Pd-catalyzed C–N coupling reaction. The only accepted and efficient method for the large-scale preparation of these compounds involves the use of a palladium salt.⁶² Considering the

expensive nature and toxicity of Pd-based catalysts, the introduction of efficient, environmentally safe, and low-cost Pd-free catalysts is valuable. Herein, a thorough investigation of the efficiency of the synthesized magnetic cobalt catalyst in C–N coupling reactions was carried out and its synthetic applicability to produce the two aforementioned valuable drugs (Scheme 1) was evaluated.

Results and discussion

The catalyst preparation process is shown in Scheme 2. The magnetic nanoparticles were reacted with mannitol through a simple and mild protocol. Then, the magnetic hydroxyl-rich carbohydrate hybrid was reacted with CoCl₂ to generate the final solid catalyst which is termed Co-MTL@MNPs; detailed synthesis procedures are provided in the ESI.[†]

The process steps for the preparation of Co-MTL@MNPs were examined using the relevant analysis such as FT-IR, elemental analysis and TGA. The FT-IR spectrum of the catalyst preparation steps is given in Fig. 1.

In the spectra of pure MNPs (Fig. 1(a)), the Fe–O vibration mode is indicated by the appearance of bands at 572 cm⁻¹. In the spectra of b (MTL@MNPs), the bands at 1000–1300 cm⁻¹ are related to the C–O group vibrations, and the vibration mode of O–H appeared at 3431 cm⁻¹ (Fig. 1(b)). The FT-IR spectra of the catalyst are shown in Fig. 1(c) which affirms the expected structure.



Scheme 1 The structures of fedratinib and abemaciclib.



Scheme 2 Synthesis of the catalyst.

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Fig. 1 FT-IR spectra: (a) magnetic nanoparticles (MNPs); (b) mannitolcoated magnetic nanoparticles (MNPs@MNL); and (c) the final catalyst (MNPs@MNL-Co).

The TGA and elemental analysis are used to investigate the number of organic moieties in the catalyst. The TGA diagram, in Fig. 2a, shows the weight loss of the catalyst as a function of temperature in the range 30–800 °C. The first step of weight loss in these cases is related to the elimination of adsorbed water and the additional weight loss is attributed to the

removal of the organic species; these observations confirmed the stability of the catalyst at elevated temperatures. The total amount of organic moieties on the catalyst was 4.21 mmol g⁻¹, as determined by elemental analysis. The results of the TGA and elemental analysis showed acceptable agreement with the elemental analysis results. The phase of the catalyst was determined from its XRD spectrum. The characteristic diffraction peaks at 30.25°, 35.73°, 43.6°, 47.84°, 53.95°, 57.6°, 63.2°, and 67.4° were attributed to Fe₃O₄, and the peaks at 2 θ of 62.80°, 58.85, 37.70, and 33.50 were ascribed to the cobalt species (Fig. 2b). The magnetic properties of the catalyst were investigated by VSM. The reduction of the magnetic behaviour of the catalyst in comparison with that of raw magnetic nanoparticles (22.1 emu g⁻¹ vs. 69.4 emu g⁻¹) confirmed the organic coating of the catalyst (Fig. 2c).

The investigation of the XPS of cobalt in the catalyst showed two spin–orbit doublets arising from $2p_{3/2}$ and $2p_{1/2}$. The Co $2p_{3/2}$ component corresponded to Co^{3+} and Co_2^+ , thus, confirming the presence of the Co_2^+ and Co^{3+} species. Based on available knowledge, the presence of a shoulder is related to the presence of the CoO phase. The Fe 2p peak for Fe₃O₄ disintegrated into Fe²⁺ and Fe³⁺ peaks that confirmed the formation of Fe₃O₄.^{45,46} The Co loading of the catalyst was measured by ICP and it was about 1.38% (0.22 mmol g⁻¹) (Fig. 3).

The FE-SEM and TEM images were used for surface morphology characterization, and the images of the sizing diagram of the catalyst are shown in Fig. 4; the average-size of the nanoparticles was ~13 nm.



Fig. 2 (a) TGA thermogram; (b) XRD pattern; and (c) room temperature magnetization curve of the catalyst.



Fig. 3 The XPS spectra of the catalyst.



Fig. 4 TEM images; FE-SEM images; and the nanoparticle size diagram of the catalyst.

For catalytic studies and finding the most efficient catalyst, the magnetic nanoparticles were functionalized with the various mentioned hydroxyl-rich small carbohydrate molecules and their influence was studied in the C–N cross-coupling model reaction, the reaction of indole (1.0 mmol) and bromo-



^{*a*} Reaction carried out with indole (1.0 mmol) and bromobenzene (1.1 mmol), using 10 mg of catalyst (0.22 mol% Co) under the optimized reaction conditions, under air. ^{*b*} GC yields obtained by using decane as an internal standard.

benzene (1.1 mmol). The effect of various catalysts was examined, and the results are summarized in Table 1, entries 1-6; the best yield of the product was achieved using the catalyst containing the mannitol ligand. The model reaction was performed in the presence of cobalt supported on magnetic nanoparticles without any ligands (Table 1, entry 1), and poor product efficiency was observed, which confirmed the positive effect of the ligand in promoting the reaction. Next, the magnetic-free catalyst was also prepared and its efficiency was examined (Table 1, entry 7), and no significant difference between the operation of this catalyst and our best catalyst showed virtually no effect of the iron element on the improvement of the reaction. In further studies on the catalyst, the effect of various amounts of the catalyst was investigated in a model reaction, and 10 mg amount was found to be the suitable quantity (Table 2).

The same reaction was then conducted at various temperatures. Given that carrying out the reaction under mild reaction conditions was of importance, the reaction was performed at room temperature, and in comparison, no considerable improvement was achieved at 50 °C or at 80 °C. Then, the influence of different solvents was assessed, from the perspective of green chemistry, as finding an effective, environmentally-friendly and readily available solvent was a high priority. Among the various tested solvents, including DMA, DMF, NMP and GVL, GVL appeared to be the best option. The effect of the base was also investigated and K_2CO_3 was chosen as the suitable base. The optimized reaction conditions of the model reaction are presented in Table 2.

After finding the best reaction conditions, its generality and versatility in the synthesis of numerous amino derivatives was examined (Table 3). The aryl halides contain substituents with different electronic properties and they reacted efficiently with indole and high yields of the products were obtained.

Table 2 Optimization of the reaction conditions^a

	+ Br	Base, Solvent, T ^o		\bigcirc	
Entry	Catalyst (mg per Co mol%)	Base (mmol)	Solvent	Т (°С)	Yield ^b (%)
1	15 (0.33)	$K_3PO_4(4)$	DMF	120	97
2	10 (0.22)	$K_3PO_4(4)$	DMF	120	93
3	5 (0.11)	$K_3PO_4(4)$	DMF	120	88
4	10 (0.22)	$K_3PO_4(4)$	DMA	120	90
5	10 (0.22)	$K_3PO_4(4)$	NMP	120	87
6	10 (0.22)	$K_3PO_4(4)$	GVL	120	95
7	10 (0.22)	_	GVL	120	93
8	10 (0.22)	$NaHCO_3(4)$	GVL	120	89
9	10 (0.22)	$Na_2CO_3(4)$	GVL	120	_
10	10 (0.22)	$K_2CO_3(4)$	GVL	120	90
11	10 (0.22)	$K_2CO_3(3)$	GVL	120	82
12	10 (0.22)	$K_2CO_3(2)$	GVL	120	63
13	10 (0.22)	$K_2CO_3(5)$	GVL	120	91
14	10 (0.22)	K_2CO_3	GVL	90	88
15	10(0.22)	K_2CO_3	GVL	60	88
16	10(0.22)	K_2CO_3	GVL	45	87
17	10 (0.22)	K_2CO_3	GVL	r.t.	86
18	10 (0.22)	$K_2CO_3(4)$	PEG (200)	r.t.	82
19	10 (0.22)	K_2CO_3 (4)	H_2O	r.t.	64
20	10 (0.22)	$K_2CO_3(4)$	2-MeTHF	r.t.	51

^a The reaction was carried out with the model reaction of indole (1.0 mmol), bromobenzene (1.1 mmol), base (4 mmol), and solvent (3.0 mL), under air, for 8 h. b GC yields obtained by using decane as an internal standard.

According to the results, it appears that the electronic properties of the precursors had no significant influence on the reaction outcomes.

To expand the substrate range, the reactions of diphenylamine and several aryl halides were also explored under the optimized reaction conditions, and products were obtained with good to excellent conversions (Table 4). The generality of the reaction was studied by using a variety of aryl halides and imidazoles (Table 5). The reaction of imidazole with iodo- and bromobenzene resulted in the desired products in good yields.

Gratifyingly, the introduced easy-to-prepare heterogeneous catalytic system, created from the safe and easily available ligand and cobalt, exhibited high activity in multiple C-N





^a The reaction was carried out with indole (1.0 mmol), bromobenzene (1.1 mmol), K_2CO_3 (4 mmol), GVL (3.0 mL), and 10 mg catalyst, at r.t., under air, for 10 h. ^{*b*} GC yields obtained by using decane as an internal standard.

 Table 3
 N-Arylation
 of
 indole
 with aryl halides catalyzed by MNPs@MTL·Co^a

Table 5 N-Arylation of imidazole with aryl halides catalyzed by MNPs@MTL·Co²

> Co/MTL@MNPs K₂CO₃, GVL, r.t

> > R

Н

Н

 $4-OCH_3$

 $4-NO_2$

4-CN

 $3-CH_3$

 $4-NO_2$

 $4-OCH_3$

3-OCH₃

4-COCH₃

Х

Br

Br

Br

Br

Br

Br

Br

Cl

Cl

Cl

Entry

1 2

3

4

5

6

7

8

9 10

		$\underbrace{ \begin{array}{c} Co/MTL@MNPs \\ K_2CO_3, \text{GVL}, r.t \end{array}}$	N R
Entry	Х	R	$\mathrm{Yield}^{b}\left(\%\right)$
1	Br	4-OCH ₃	82
2	Br	Н	86
3	Br	$4-NO_2$	87
4	Br	4-CN	89
5	Br	4-COCH ₃	83
6	Br	$3-CH_3$	86
7	Br	3-OCH ₃	81
8	Cl	$4-OCH_3$	63
9	Cl	Н	66
10	Cl	$4-NO_2$	69

^a The reaction was carried out with indole (1.0 mmol), bromobenzene (1.1 mmol), K₂CO₃ (4 mmol), GVL (3.0 mL), and 10 mg catalyst, at r.t., under air, for 8 h. ^bGC yields obtained by using decane as an internal standard.

^a The reaction was carried out with indole (1.0 mmol), bromobenzene (1.1 mmol), K_2CO_3 (4 mmol), GVL (3.0 mL), and 10 mg catalyst, at r.t., under air, for 10 h. ^b GC yields obtained by using decane as an internal standard.

п

 $Yield^{b}(\%)$

91

89

84

80

82

81

85

71

68

73

Table 6 N-Arylation of aliphatic amines^a



^{*a*} The reaction was carried out with indole (1.0 mmol), bromobenzene (1.1 mmol), K_2CO_3 (4 mmol), GVL (3.0 mL), and 10 mg catalyst, at r.t., under air, 10 h. ^{*b*} GC yields obtained by using decane as an internal standard.

coupling reactions including indole (Table 3), diphenylamine (Table 4), and imidazole (Table 5) as substrates. This heterogeneous catalytic system also exhibited high activity in the coupling of aryl halides with aliphatic amines (Table 6). The corresponding products were obtained in moderate to excellent yields under extremely mild reaction conditions in greener media.

The efficiency of the prepared catalyst for the C–N reaction was compared with those of other similar Pd-free catalysts used for this reaction. These results are presented in Table 7 and they indicate the good performance of our heterogeneous catalyst in this context.

One of the serious problems with homogeneous catalysts as conventional promoters in these types of syntheses is the difficulty in separation, and hence the recyclability of the catalyst was studied using the model reaction.

After the completion of the reaction, the catalyst was easily separated *via* a magnetic bar, washed with hot ethanol, dried, and applied in the next catalytic cycle. Until its seventh reuse, no discernible decrease in activity could be detected (Table 8).

FT-IR, XRD, ICP and TEM analyses were deployed for the characterization of the reused catalyst, and the results are provided in the ESI.† In comparison with the analysis of fresh catalysts, very little changes can be seen. In the recovered catalyst, the cobalt content of the seven-time used catalyst was identified by ICP as 0.16 mmol g^{-1} which in comparison with a fresh one (0.22 mmol g^{-1}) indicates minor metal leaching. The TEM images of the reused catalyst are presented in the ESI;† the aggregation of the catalyst is not more than that of the fresh catalyst.

Table 8 Recyclability of the catalyst in the model reaction of C-N coupling reaction

Run	Yield ^a (%)	Run	$\operatorname{Yield}^{a}(\%)$
1	86	5	73
2	83	6	70
3	82	7	63
4	80	8	-

^a GC yields obtained by using decane as an internal standard.



Scheme 3 Fedratinib synthesis process.





Encouraged by these promising findings and considering the need to develop such methods for the synthesis of medicinal compounds, our optimized method was applied to the synthesis of fedratinib and abemaciclib, which are antitumor agents recently approved by the FDA. Fedratinib is a JAK2 inhibitor and is used for the oral treatment of adult patients with advanced myelofibrosis,⁶⁰ while abemaciclib is a drug used for the treatment for advanced breast cancers.⁶⁵ The structure and synthesis steps of these compounds are shown in Schemes 3 and 4. Accordingly, the introduced cobalt catalytic system was effectively applied to the synthesis of fedrati-

Table 7	Comparison of the	e catalytic activity o	f some reported Pd-free	heterogeneous	catalysts in N-a	ryl reactions
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Entry	Catalyst	Reaction conditions	Yield (derivative)	Ref.
1	Hexaphenylbenzene-Fe ₂ O ₃ -Cu ₂ O	EtOH/H ₂ O; <i>hv</i> ; K ₂ CO ₃ /6 h	85 (triphenylamine)	63
2	Cu/ascorbic acid@MNPs	H ₂ O, KOH, r.t./6 h	94 (diphenylamine)	37
3	Fe ₂ O ₃ /L-proline	DMSO, tBuONa, 135 °C/24 h	93 (1-phenyl-1 <i>H</i> -indole)	12
4	MNPs/melamine/Co	DMSO, KOH, 80 °C, 8 h	71 (1-phenyl-1 <i>H</i> -indole)	41
5	MC-81@Co/Cu	DMF, KOH, 80 °C, 8 h	65 (diphenylamine)	64
6	MNPs@MTL-Co	GVL, K ₂ CO ₃ , r.t., 8 h.	86 (indole)	This work

nib and abemaciclib with acceptable overall yields and the products obtained were purified by flash column chromatography. The characterization data of the products are available in the ESI. \dagger

Conclusions

Herein, a sustainable and low energy consuming method deploying an innovatively designed recyclable catalyst is successfully introduced for the general C–N cross-coupling reactions. A variety of derivatives obtained from these reactions have been readily synthesized in excellent yields. Moreover, this is the first report on the successful synthesis of fedratinib and abemaciclib (anti-cancer agents) using a Pd/Cu-free catalyst. Finally, the heterogeneity of the catalyst is confirmed through the recyclability assessments. In general, the introduced procedure is a facile, mild and green method that does not lead to hazardous metal pollution.

Conflicts of interest

There are no conflicts to declare.

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