

RESEARCH PAPER

The Suzuki-Miyaura Reaction of Phenylboronic Acid with Different Aryl Halides Catalyzed with Cu (II) Salen Complex@KCC-1 as a Recyclable Heterogeneous Catalyst

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ABSTRACT

The carbon-carbon bond formation reactions have always been interesting for scientists because of their wide range of uses in organic chemistry. The Suzuki-Miyaura reaction is a famous reaction for the C-C bond formation. The Suzuki-Miyaura reaction is applied to synthesize a wide range of pharmaceutical and biological compounds. In this research, a Cu (II) Salen complex supported on KCC-1 (Cu (II) Salen complex@KCC-1) has been synthesized and characterized for the C-C bond formation reaction. The synthesized catalyst was determined to be an effective heterogeneous catalyst for the coupling reaction of Suzuki-Miyaura. The synthesized catalyst was characterized via XRD, FT-IR, TEM, and EDX, and the organic compound was identified with melting-point, FT-IR, and ¹H NMR techniques. Cu (II) Salen @ KCC-1 complex can be separated and reused simply in the reaction mixture and reused several consecutive runs without significantly reducing the catalyst's performance. To identify each product, FT-IR, ¹H NMR, and melting point techniques were applied.

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INTRODUCTION

Schiff base (as well known as azomethine or imine) is an exceptional ligands category using diverse donor atoms demonstrating interesting coordination to many metal ions [1,2]. In preparing their metal complexes the adaptability by Schiff base chelation including transition metal ions is utilized. Schiff's base metal complex is famous because of their broad application, easy synthesis, and stability [3,4].

Metal complex comprising ligand based on

Schiff-base have been investigated for their fascinating and significant features like their capability binding by oxygen, antibacterial, antifungal and photochromism attribute, complexing and hydrogenation ability to some poisonous metals, and catalytic activity in olefins [5,6].

Cross-coupling reaction using the transition metal catalysts is unquestionably widely used to form C-N [7], C-C [8], C-S [9], and C-O [10], bonds in the synthesis of organic compounds. Scientists are

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attempting to expand easy, rapid, inexpensive, and much more efficient methods for diverse coupling reactions [11]. The Suzuki–Miyaura reaction is among the utmost utilized cross-coupling reaction in contemporary organic synthesis, whereas in the presence of the catalyst, the biphenyl molecule is synthesized by coupling the reaction of an aryl halide or triflate with phenylboronic acid [12]. Complexes of palladium are typical catalysts in the Suzuki–Miyaura reaction [13–16].

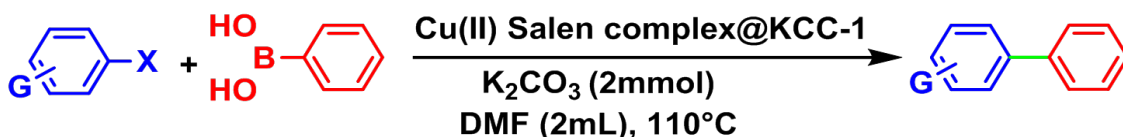
Regardless of the prevalent catalytic applications, the complexes of palladium have restricting aspects like poisonousness and more expensive, which caused the restriction of those on industrial-scale applications [17]. As a workable alternative to palladium, lately, Cu-based catalyst has drawn very consideration because of their biocompatibility and reduced cost in addition to their catalytic capability in cross-coupling reaction [18–20]. Notwithstanding these benefits, just some Suzuki–Miyaura (SM) cross-coupling reactions including Cu-catalyzed has been reported. These copper-based catalysts are such as 3D MOF {[Cu (4-tba)₂](solvent)}_n [21], copper nano colloid [22], Pd-Cu@Carbon [23], and Cu@molecular sieve [24]. Therefore, in order to extend the Suzuki–Miyaura coupling reaction catalyzed by copper, the development of novel and effective copper-based nanocatalysts is required. Therefore, the usage of new materials as supports for the heterogeneous catalysts is necessary. The immobility of copper species onto solid-supports in heterogeneous catalysts facilitates separation, thereby decreasing pollution and reuse of costly catalysts. For the preparation of heterogeneous catalysts, a variety of solid support includes zeolite, polymers, carbon nanotubes, and silica has been used [25–32]. The nature of the support can affect the reactivity and selectivity of the catalyst, consequently, careful selection of support could lead to the development of novel heterogeneous catalyst. As a proposition, KCC-1 is a compound

that can be used as a solid-support. Fibrous nano-silica (KCC-1), which attributes a high surface area and the effortless access *via* its fiber (as opposed to the traditional usage of pores), described by Polshettiwar et al. [33]. This would be a perfect catalyst support candidate for the manufacture of excellent metal-based catalysts that show high availability of active sites and superb catalytic activity. In this article, we synthesized copper (II) immobilized on Schiff base-functionalized KCC-1. In this procedure, in the beginning step, the KCC-1 was prepared and then Salen ligand was attached to the KCC-1 and ultimately, copper was coordinated to the Salen ligand and the corresponding catalyst was synthesized. In the next step, the efficiency of Cu (II) Salen complex@KCC-1 has been studied in Suzuki–Miyaura cross-coupling reaction (Fig. 1). Moreover, the amount of catalyst which has been used in the reaction and its effect on the product yields, as well as the ability to recovery have been studied. The other promising points of the presented methodology are inexpensive and readily available catalyst, operational simplicity, usage of environmentally benign solvents, high isolated yields of the pure products, mild reaction conditions, no formation of by-products, and finally, agreement with some of the green chemistry protocols.

MATERIALS AND METHODS

Using cetyltrimethylammonium bromide (CTAB), urea, tetraethyl orthosilicate (TEOS), and 1-panthenol, KCC-1 was synthesized. Then, salicylaldehyde and (3-Aminopropyl) trimethoxysilane (APTMS) was added drop by drop to obtain Salen ligand. In the next step, using Cu (II) acetate and NaOH, the homogenous copper was obtained. Lastly, the immobilizing of homogeneous Cu (II) Salen complex on the KCC-1 was done.

Fourier transform infrared (FT-IR), energy dispersive X-ray (EDX), powder X-ray diffractometric



X = Cl, Br, I

G = electron-withdrawing or electron-donating

Fig. 1. Suzuki–Miyaura cross-coupling reaction catalyzed via Cu(II) Salen complex@KCC-1

(XRD), BET & BJH, Transmission electron microscopy (TEM) were utilized to characterize the Cu (II) Salen complex loaded on KCC-1.

Preparation of the catalyst

Preparation of KCC-1

Dissolve 2 g of cetyltrimethylammonium bromide (CTAB) (5.48 mmol) and 2.4 g of urea (39.96 mmol) in 100 mL of water and stirred for 15 minutes. Then mix 10 mL of tetraethyl orthosilicate (TEOS) (44.78 mmol) with 10 mL of cyclohexane and drop by drop to the above solution and stirrer again for 15 minutes on a magnetic stirrer. Subsequently, 6 mL of 1-panthenol was added to it and this time it was placed on a magnetic stirrer at room temperature for 20 minutes. Then put the solution in the microwave for 1 hours at 120 °C and then dry at room temperature to form a precipitate. The corresponding precipitate is washed and separated by centrifugation and

water and ethanol solvents and placed in an oven at 80 °C for 8 hours to dry [34].

Preparation of Salen ligand

Mix 0.106 mL of salicylaldehyde (0.95 mmol) with 2 mL of ethanol Merck and transfer the mixture to a balloon and 0.218 mL of (3-Aminopropyl)trimethoxysilane (APTMS) (0.93 mmol) was added drop by drop to the balloon. The reaction mixture was then refluxed for 3 hours, after which the solvent was removed by rotary and the corresponding ligand was obtained [35].

Preparation of Cu (II) Salen complex

Then, to synthesize the Cu (II) Salen complex, add 20 mL of ethanol to the 1 mmol of the Salen ligand, and then 0.66 gr of NaOH (1.65 mmol) and 0.199 gr of copper (II) acetate (1.095 mmol) was added respectively and refluxed for 2 hours at 80 °C. After purification, the product was dried at 80

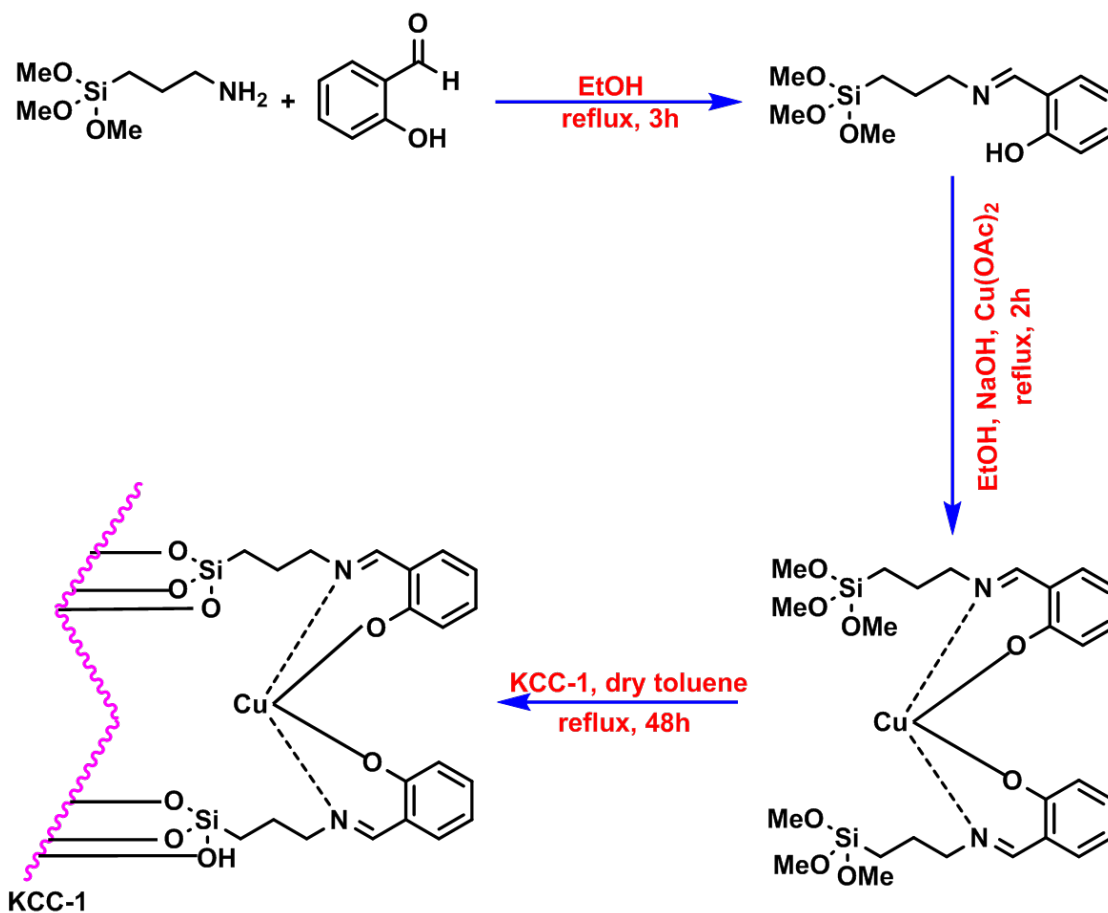


Fig. 2. Preparation of catalyst (Cu (II) Salen complex@KCC-1)

°C in a vacuum oven for 8 hours [36,37].

Preparation of Cu (II) Salen complex@KCC-1

Dissolve 0.5 g of KCC-1 in 50 mL of dry toluene and the mixture mentioned was sonicated for 30 min. Then, 0.25 g of Cu (II) Salen complex was added and the mixture was stirred under reflux for 48 hours. After purifying the precipitate, it was placed in a vacuum oven at 70 °C for 8 hours.

RESULTS AND DISCUSSION

Using cetyltrimethylammonium bromide (CTAB), urea, tetraethyl orthosilicate (TEOS), and 1-panthenol, KCC-1 was synthesized. Then, salicylaldehyde and (3-Aminopropyl) trimethoxysilane (APTMS) was added drop by drop to obtain Salen ligand. In the next step, using Cu (II) acetate and NaOH, the homogeneous copper was obtained. Lastly, the immobilizing of homogeneous Cu (II) Salen complex on the KCC-1 was done (Fig. 2).

Fourier transform infrared (FT-IR), energy dispersive X-ray (EDX), powder X-ray diffractometric (XRD), and Transmission electron microscopy (TEM) were utilized to characterize the Cu (II) Salen complex loaded on KCC-1.

FT-IR spectroscopy

The FT-IR was studied at 4000 to 400 cm^{-1} for KCC-1, ligand, Cu(II) Salen complex, and Cu(II) Salen complex@KCC-1 via FT-IR spectroscopy. The infrared spectra of all stages of Cu Salen complex @ KCC-1 synthesis are shown in the figure below (Fig. 3). In Fig. 3a spectrum shows the KCC-1 infrared spectrum, with vibrations in the 808, 915, and 3300 cm^{-1} regions, which are Si and OH, respectively. The above vibrations emphasize KCC-1 synthesis [38]. Spectrum 3b represents the infrared spectrum of Salen ligand that vibrations at about 1100, 1690, 3323 cm^{-1} correspond to Si, C=N, and OH respectively [39,40]. The 3c spectrum, the infrared spectrum of the Cu(II) Salen, shows that the stretching band vibrations in the region of 1115 and 2889 cm^{-1} are related to Si and methylene rings, respectively, and also the stretching band vibration of the C=N bond is observed in 1626 cm^{-1} [40]. The spectrum 3d represents the infrared spectrum of the heterogeneous catalyst (Cu (II) Salen complex @ KCC-1). The new band at 1585 cm^{-1} has appeared in the heterogeneous catalyst, which together with the 1099 cm^{-1} band related to Si-O-Si indicates the successful immobilization of the homogeneous Cu (II) Salen complex on the

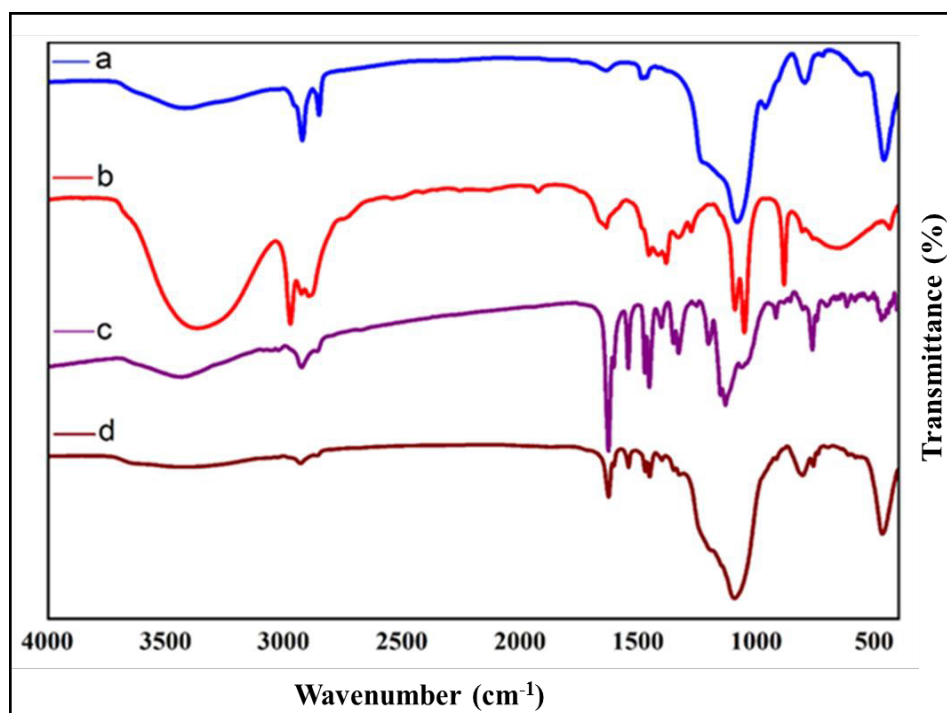


Fig. 3. FT-IR spectra of: KCC-1(a), Salen ligand (b), Cu(II) Salen complex (c), Cu(II) Salen complex@KCC-1(d)

surface of KCC-1.

Transmission Electron Microscopy (TEM)

The TEM images of KCC-1 (a) and Cu (II) Salen complex@KCC-1 (b) are shown in Fig. 4. As the images show, the nanoparticles are spherical.

X-ray diffraction (XRD) analysis

Fig. 5 presents the XRD patterns of synthesized KCC-1 (a) Cu(II) Salen complex@KCC-1 (b) nanoparticles. In the Cu (II) Salen complex @ KCC-1 X-ray diffraction pattern, the peak intensity decrease relative to the KCC-1 X-ray diffraction pattern could indicate the presence of a Salen

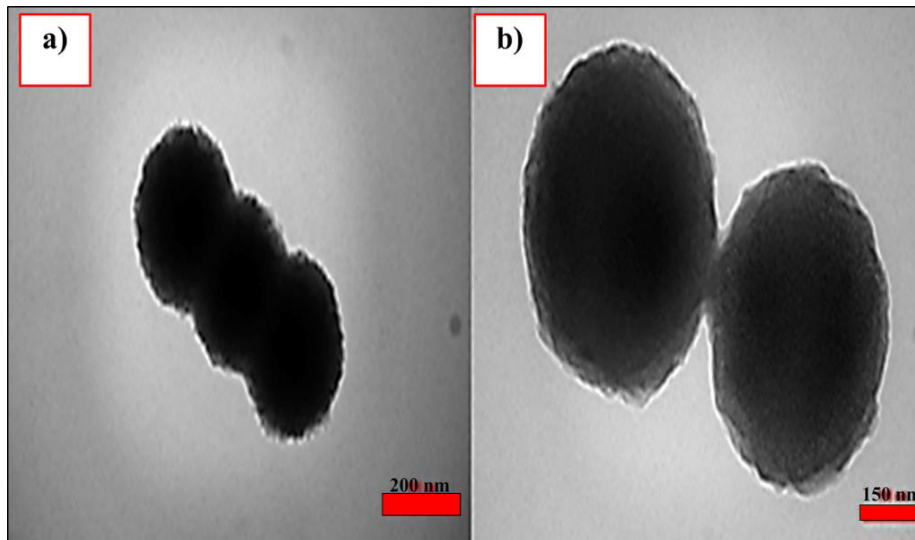


Fig. 4. TEM images of KCC-1 (a) Cu(II) Salen complex@KCC-1 (b)

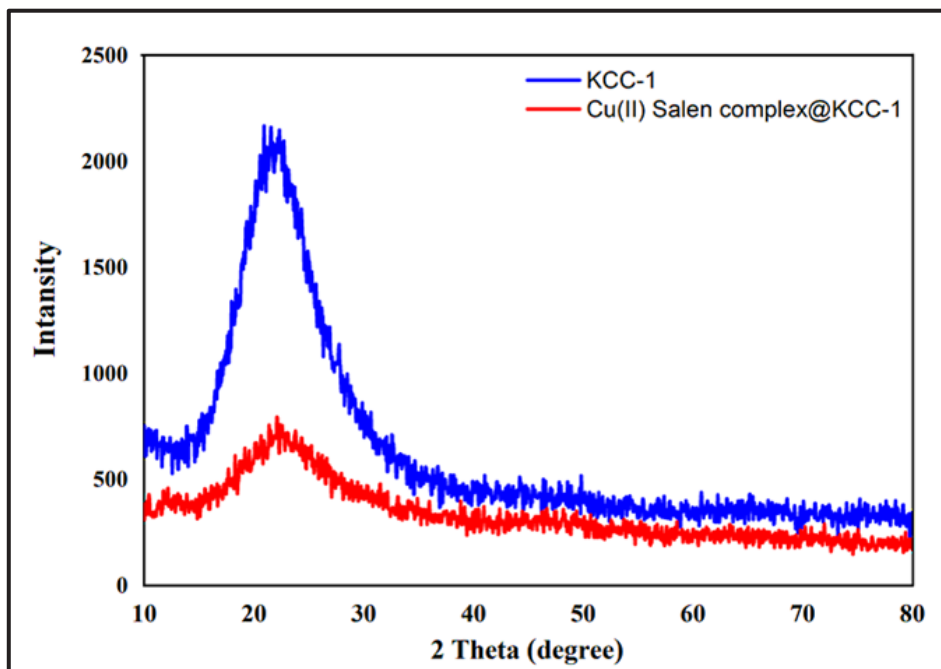


Fig. 5. XRD pattern of KCC-1 (a) Cu(II) Salen complex@KCC-1 (b)

complex immobilized on KCC-1. Also, a decrease in peak intensity of $2\theta = 22.13^\circ$ can be evidence of Salen complex coating on a KCC-1 substrate [34-38].

Energy dispersive X-ray (EDX)

Fig. 6 shows the energy-dispersive X-ray spectroscopy (EDX) of Cu (II) Salen complex@KCC-1 nanoparticle. The presence of the copper atom in nanoparticle was confirmed by EDX spectroscopy analysis. Peaks of C, O, Si elements are also clearly visible in this spectrum, which is a testament to the successful synthesis of this nanoparticle (Cu

(II) Salen complex@KCC-1).

BET surface area

The N_2 adsorption–desorption isotherm of Cu(II) Salen complex@KCC-1 revealed a characteristic type IV curve with a typical H3 hysteresis loop (Fig. 7). As for Cu(II) Salen complex@KCC-1, the BET surface area and average pore diameter are obtained as $698 \text{ m}^2 \text{ g}^{-1}$ and 3.41 nm respectively.

General procedure for catalytic Suzuki–Miyaura coupling

To 1.2 mmol of phenylboronic acid, 1 mmol of

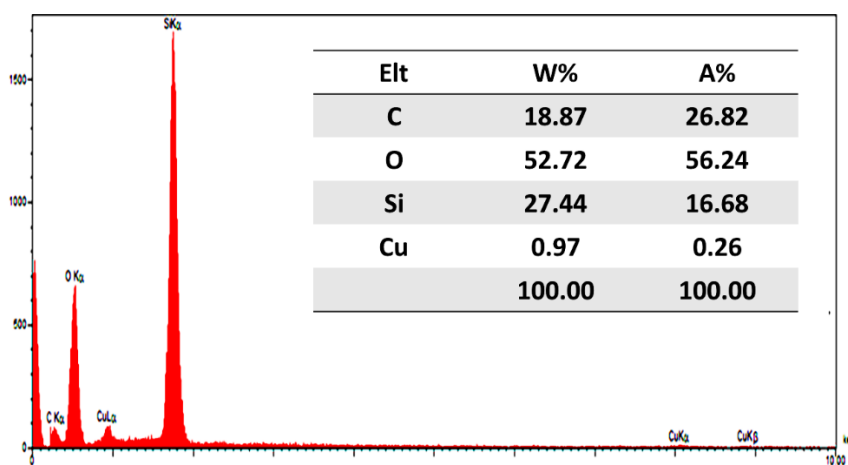


Fig. 6. EDX of Cu(II) Salen complex@KCC-1

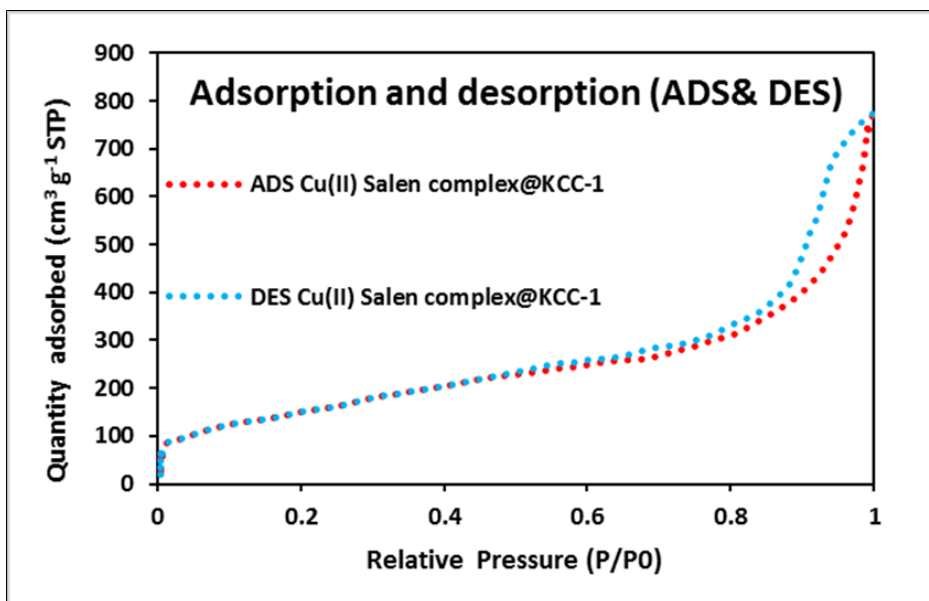


Fig. 7. Nitrogen adsorption–desorption isotherms of Cu(II) Salen complex@KCC-1

aryl halide and 2 mmol of K_2CO_3 , 2 mL of DMF as a solvent, and 0.07 g of Cu (II) Salen complex@KCC-1 were added and the resulting mixture was refluxed at 110 °C for a suitable time, the reaction progress was monitored by TLC. After the reaction was completed, the products were separated and purified, the best reaction efficiency was reported to be 95% after 4 hours. Structural assignments of the products are according to their 1H NMR spectra.

Analytical Data

1,1'-Biphenyl: White solid; M.P.= 68-70°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3044, 2971, 2835, 1889, 1611, 1483, 1251, 1193, 1114, 1029, 834, 754, 684; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.63 – 7.58 (m, 4H, Ar), 7.49 – 7.41 (m, 4H, Ar), 7.39 – 7.32 (m, 2H, Ar).

3-Nitro-1,1'-biphenyl: Yellow solid; M.P.= 58-59°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3081, 2923, 1626, 1568, 1352, 1065, 852, 749; 1H NMR (300 MHz, DMSO): δ (ppm) = 8.42 (t, J = 2.0 Hz, 1H, Ar), 8.24-8.13 (m, 2H, Ar), 7.79-7.74 (m, 3H, Ar), 7.57 – 7.44 (m, 3H, Ar).

4-Bromo-1,1'-biphenyl: White solid; M.P.= 87-90°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3051, 1949, 1907, 1753, 1658, 1471, 1389, 1069, 996, 823, 751, 684; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.59 – 7.54 (m, 4H, Ar), 7.48 – 7.34 (m, 5H, Ar).

4-Methyl-1,1'-biphenyl: White to yellow solid; M.P.= 44-47°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3029, 2941, 1594, 1483, 1431, 1406, 1169, 1117, 1032, 911, 823, 753, 691; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.50 – 7.43 (m, 3H, Ar), 7.41 – 7.29 (m, 4H, Ar), 7.28 – 7.17 (m, 2H, Ar), 2.28 (s, 3H, CH_3).

2-Methyl-1,1'-biphenyl: Colorless liquid; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3674, 3523, 3441, 2922, 2855, 1733, 1452, 1262, 1095, 803; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.34 – 7.21 (m, 5H, Ar), 7.17-7.13

(m, 4H, Ar), 2.18 (s, 3H, CH_3).

4-Methoxy-1,1'-biphenyl: White solid; M.P.= 87-89°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3041, 2958, 2833, 18979, 1601, 1483, 1244, 1196, 1121, 1034, 832, 754, 683; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.63 – 7.56 (m, 4H, Ar), 7.50 – 7.44 (m, 2H, Ar), 7.40 – 7.32 (m, 1H, Ar), 7.06 – 7.00 (m, 2H, Ar), 3.88 (s, 3H, OCH_3).

1,1'-Biphenyl-4-carbonitril: White solid; M.P.= 85-88°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 842, 761, 723, 695; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.76 – 7.66 (m, 4H), 7.62 – 7.57 (m, 2H), 7.53 – 7.39 (m, 3H).

4-Acetylbiphenyl: White solid; M.P.= 119-121°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3053, 3029, 2991, 2913, 1681, 1613, 1421, 1401, 1352, 1261, 1125, 1074, 961, 833, 764, 721, 694; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 8.07 – 8.02 (m, 2H, Ar), 7.72 – 7.62 (m, 4H, Ar), 7.52 – 7.38 (m, 3H, Ar), 2.65 (s, 3H, CH_3).

4-ethyl-1,1'-biphenyl: White solid; M.P.= 33-35°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3033, 2961, 2931, 1484, 1451, 1407, 833, 751, 692; 1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.69 – 7.60 (m, 4H, Ar), 7.54 – 7.49 (m, 2H, Ar), 7.45 – 7.36 (m, 3H, Ar), 2.79 (q, J = 7.6 Hz, 2H, CH_2), 1.37 (t, J = 7.6 Hz, 3H, CH_3).

4-Phenylbiphenyl: White solid; M.P.= 214-15°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3038, 2975, 2833, 1891, 1617, 1488, 1255, 1198, 1117, 1032, 831, 753, 679; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.70 – 7.62 (m, 8H, Ar), 7.50-7.43 (m, 4H, Ar), 7.39 – 7.31 (m, 2H, Ar).

4-ethyl-4'-methoxy-1,1'-biphenyl: White solid; M.P.= 73-74°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3109, 2968, 2921, 2841, 1895, 1611, 1492, 1453, 1252, 1179, 1133, 1032, 816, 653; 1H NMR (250 MHz, $CDCl_3$): δ (ppm) = 7.54 – 7.45 (m, 4H, Ar), 7.27-7.24 (m, 2H, Ar), 7.00-6.94 (m, 2H, Ar), 3.85 (s, 3H, OMe), 2.72 – 2.64 (m, 2H, CH_2), 1.31 – 1.23 (m, 3H, CH_3).

4-ethyl-4'-nitro-1,1'-biphenyl: White solid; M.P.= 82-84°C; FT-IR (thin film, cm^{-1}): $\bar{\nu}$ = 3081,

Table 1. The effect of diverse the solvents in the Suzuki–Miyaura cross-coupling reaction by Cu(II) Salen complex@KCC-1

Entry	Solvent	Time (h)	Yield (%)
1	DMF	4	95
2	DMSO	5	92
3	H ₂ O	14	7
4	EtOH	6	65
5	Toluene	7	33
6	THF	7	40
7	CH ₃ CN	8	50

Reaction conditions: phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), Cu(II) Salen complex@KCC-1 (0.07 g), K_2CO_3 (2 mmol), solvent (2 mL), at 110 °C

2983, 2852, 1575, 1513, 1442, 1341, 1315, 1109, 854, 834, 751; ^1H NMR (250 MHz, CDCl_3): δ (ppm) = 8.31-8.26 (m, 2H, Ar), 7.75-7.54 (m, 4H, Ar), 7.35-7.31 (m, 2H, Ar), 2.77 – 2.68 (m, 2H, CH_2), 1.32-1.25 (m, 3H, CH_3).

[1,1'-biphenyl]-4-amine: Pale yellow solid; M.P.= 52-54°C; FT-IR (KBr, cm^{-1}): $\bar{\nu}$ = 3421, 3209, 2924, 1623, 1481, 1261, 831; ^1H NMR (300 MHz, DMSO): δ (ppm) = 7.55 (d, J = 8.1 Hz, 2H, Ar), 7.41 – 7.36 (m, 4H, Ar), 7.22 (t, J = 6.7 Hz, 1H, Ar), 6.67 (d, J = 8.6 Hz, 2H, Ar), 5.25 (s, 2H, NH_2).

[1,1'-Biphenyl]-2-amine: Pale yellow solid; M.P.= 53-55°C; FT-IR (neat, cm^{-1}): $\bar{\nu}$ = 3474, 3378, 3020, 1609, 1478, 1433, 1286, 1286, 1147, 1061, 1002, 920, 753; ^1H NMR (300 MHz, DMSO): δ (ppm) = 7.47 – 7.35 (m, 5H, Ar), 7.10 – 7.01 (m, 2H, Ar), 6.82 – 6.65 (m, 2H, Ar), 4.79 (s, 2H, NH_2).

The catalyst performance of the Cu (II) Salen complex@KCC-1 in the cross-coupling reaction of Suzuki-Miyaura

The catalytic properties of Cu (II) Salen complex@KCC-1 was investigated to form a carbon-carbon bond through Suzuki-Miyaura (SM) cross-coupling of phenylboronic acid (PBA) with aryl halide as the model reaction. The

important reaction parameters, such as solvent, base, the catalyst amount, and temperature, were compared to attain the optimal conditions.

A variety of solvents with different properties and polarity were tested (Table 1, entries 1-7). DMF had the best effect by providing 95% efficiency at 110 °C (Table 1, entry 1), and after that, DMSO yielded an efficiency of 92%.

The results of Table 2 demonstrate that the basic medium is likewise important for the Suzuki-Miyaura (SM) cross-coupling reaction (Table 2, entry 8). Accordingly, to study its effect, many organic and inorganic bases were examined from the Suzuki-Miyaura (SM) cross-coupling reaction of phenylboronic acid (1.2 mmol) and iodobenzene (1 mmol) using all the Cu(II) Salen complex@KCC-1 (0.07 g) in DMF (2 mL) at 110 °C.

The ordinary organic bases like Et_3N usually utilized for the Suzuki-Miyaura reaction (SMR) have proven that in the corresponding reaction, it showed less efficiency (Table 2, entry 6). The identical treatment was also detected using sodium bicarbonate foundation (Table 2, entry 3) and hydroxide ion (Table 2, entries 1,2) because in both cases reactions need more time (7 and 8 hours, respectively). By comparison, carbonate

Table 2. The effect of diverse bases in the Suzuki-Miyaura cross-coupling reaction by Cu(II) Salen complex@KCC-1

Entry	Base	Time (h)	Yield (%)
1	KOH	8	50
2	NaOH	8	45
3	NaHCO_3	7	65
4	K_2CO_3	4	95
5	pyridine	10	65
6	Et_3N	12	60
7	Na_2CO_3	5	78
8	No base	25	N.R.

Reaction conditions: phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), Cu(II) Salen complex@KCC-1 (0.07 g), base (2 mmol), DMF (2 mL), at 110 °C

Table 3. The effect of different amount of Cu(II) Salen complex@KCC-1 catalysts on the Suzuki-Miyaura cross-coupling reaction

Entry	Catalyst (g)	Time (h)	Yield (%)
1	0.09	4	97
2	0.07	4	95
3	0.05	6.5	72
4	0.01	10	40
5	no catalyst	24	N.R.
6	Salen Cu	4	86

Reaction conditions: phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), Cu(II) Salen complex@KCC-1, K_2CO_3 (2 mmol), DMF (2 mL), at 110 °C

base, i.e., K_2CO_3 and Na_2CO_3 , given excellent results (Table 2, entries 4,7). Therefore, we've chosen K_2CO_3 as the ideal base for more optimization.

The reaction was performed when different amounts of heterogeneous Cu (II) Salen complex@KCC-1 were present at 110 °C. Using 0.07 g of Cu (II) Salen complex@KCC-1, the maximum

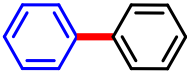
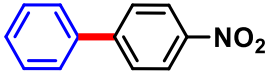
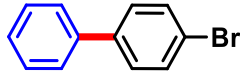
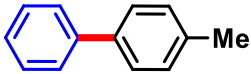
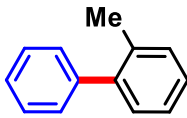
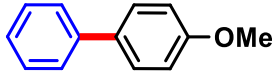
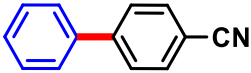
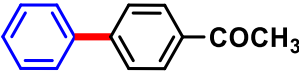
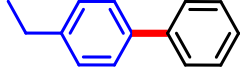
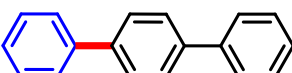
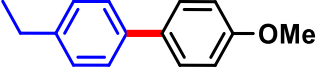
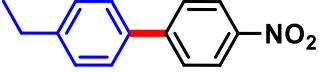
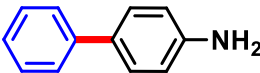
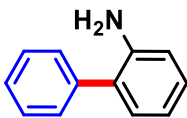
performance for the relevant product in a brief time was got. Efficiency declined at lower values and at higher value (0.09 g) no negative or positive effects on efficiency were observed (Table 3, entry 1). To compare the homogeneous Salen Cu was also studied under the obtained optimum circumstances (Table 3, entry 6).

Table 4. The effect of diverse temperatures in the Suzuki–Miyaura cross-coupling reaction by Cu(II) Salen complex@KCC-1

Entry	Temperature	Time (h)	Yield (%)
1	r.t	24	10
2	50	10	20
3	80	6	50
4	100	7	75
5	110	5	95

Reaction conditions: phenylboronic acid (1.2 mmol), iodobenzene (1 mmol), Cu(II) Salen complex@KCC-1 (0.07 g), K_2CO_3 (2 mmol), DMF (2 mL)

Table 5. Suzuki–Miyaura cross-coupling reaction of various aryl halides catalyzed by Cu(II) Salen complex@KCC-1

 4.0 h, 95%, X=I 5.0 h, 91%, X=Br 6.0 h, 71%, X=Cl	 4.0 h, 95%, X=I 5.0 h, 86%, X=Br 6.0 h, 79%, X=Cl	 4.0 h, 91%, X=I 5.0 h, 89%, X=Br 6.0 h, 81%, X=Cl
 4.0 h, 88%, X=I 5.0 h, 85%, X=Br 6.0 h, 71%, X=Cl	 4.0 h, 89%, X=I 5.0 h, 85%, X=Br 6.0 h, 71%, X=Cl	 4.0 h, 92%, X=I 5.0 h, 87%, X=Br 6.0 h, 71%, X=Cl
 4.0 h, 90%, X=I 5.0 h, 84%, X=Br 6.0 h, 69%, X=Cl	 4.0 h, 90%, X=I 5.0 h, 84%, X=Br 6.0 h, 71%, X=Cl	 4.0 h, 84%, X=I 5.0 h, 81%, X=Br 6.0 h, 72%, X=Cl
 4.0 h, 86%, X=I 5.0 h, 72%, X=Br 6.0 h, 67%, X=Cl	 4.0 h, 84%, X=I 5.0 h, 76%, X=Br 6.0 h, 71%, X=Cl	 4.0 h, 95%, X=I 5.0 h, 91%, X=Br 6.0 h, 86%, X=Cl
 4.0 h, 87%, X=I 5.0 h, 81%, X=Br 6.0 h, 74%, X=Cl	 4.0 h, 84%, X=I 5.0 h, 75%, X=Br 6.0 h, 72%, X=Cl	

Reaction conditions: phenylboronic acid (1.2 mmol) and derivatives of aryl halides (1 mmol), Cu(II) Salen complex@KCC-1 (0.07 g), K_2CO_3 (2 mmol), DMF (2 mL), at 110 °C

To elucidate the particular catalyst performance of Cu (II) Salen complex@KCC-1 in the Suzuki-Miyaura cross-coupling reaction (SMR), the reaction under the obtained optimized conditions was carried out in the absence of the catalyst. When the heterogeneous catalyst is not present, we do not see any product (Table 3, entry 5).

On the other hand, temperature represents an important role in the performance of the reaction. Different temperatures (25, 50, 80, 100, and 110 °C) on the model reaction was performed in dimethylformamide as a solvent and K_2CO_3 in the presence of Cu (II) Salen complex@KCC-1. There was a significant reduction in performance at 25 °C (Table 4, entry 1). The reaction proceeds more rapidly at 50 °C than at 25 °C. Nevertheless,

at temperatures above 50 °C (80, 100, and 110 °C), a clear increase in the performance of the corresponding reaction (Table 4, entries 3-5) was observed. We decided that the best temperature is 110 °C.

Various structurally different aryl iodide, bromide, and chloride react *via* phenylboronic acid (PBA) were converted to the corresponding products by the catalyst under obtained optimized conditions. The results are summarized in Table 5, where good to excellent yields are observed for aryl bromides (ArBr) and aryl iodides (ArI).

The model reaction of the Suzuki-Miyaura has been performed by using 0.07 g Cu (II) Salen complex@KCC-1 in the reaction of iodobenzene, phenylboronic acid, and K_2CO_3 in 110°C *via* DMF

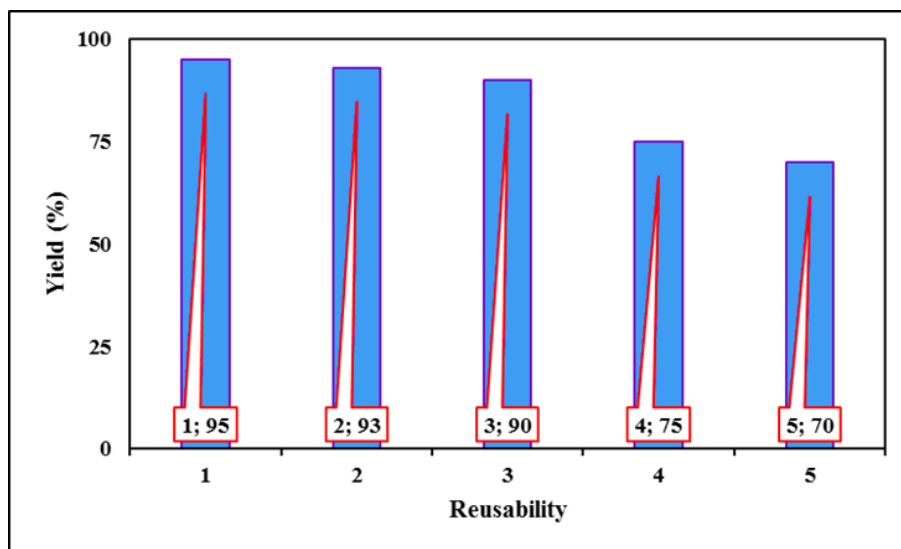


Fig. 8. Recyclability of Cu(II) Salen complex@KCC-1 for the model Suzuki-Miyamura reaction

Table 6. Comparison of the efficiency of Cu(II) Salen complex@ KCC-1 with diverse catalysts

Entry	Catalyst	Solvent	T (°C)	Yield (%)	Ref
1	Cu_2O^a	$H_2O, EtOH$	65	73	[40]
2	Nickel(II) Complex	dioxane	110	88	[41]
3	MCM-48-Py-Pd	$H_2O, EtOH$	90	92	[42]
4	Pd/SBA-15	$H_2O, EtOH$	85	88	[43]
5	SBA-Cu ^b	PEG	80	94	[44]
6	Cu(II) Salen complex@KCC-1 ^a	DMF	110	95	This work

Reaction conditions: aryl halide, olefin, base, solvent, in diverse temperature and time.

^a K_2CO_3 as a base.

^b Na_2CO_3 as a base.

as a solvent to observe reusability of the catalyst. Based on the tests, the outcomes which are shown in (Fig. 8) demonstrate that after four cycles, there is no particular reduction in the yield.

To comprehend the particularities of Cu (II) Salen complex@KCC-1, we compare the outcomes of the Suzuki-Miyaura (SM) reaction with other heterogeneous catalysts as presented in Table 6. This table demonstrates that the KCC-1 @ Salen Cu shows improved activity for the Suzuki-Miyaura reaction.

CONCLUSION

A novel, cost-effective, general and efficient method has been developed for transformation of various aryl halides (ArX) and phenylboronic acid (PBA) to the relevant product with a recyclable Cu (II) Salen complex@KCC-1. The characteristics of the catalyst was studied *via* several analyses including TEM, FTIR, BET&BJH, EDX, and XRD. The catalyst was highly effective in performing the Suzuki-Miyaura (SM) reaction with a variety of different electronic substrates. Also, tests of catalyst proved that Cu (II) Salen complex@KCC-1 is the most active in DMF at 110 °C *via* K₂CO₃ for the Suzuki-Miyaura (SM) reaction. Besides, the heterogeneous catalyst determined good recoverability and could be recycled for five consecutive cycles without any remarkable reactivity loss. The other promising points of the presented methodology are inexpensive and readily available catalyst, operational simplicity, usage of environmentally benign solvents, high isolated yields of the pure products, mild reaction conditions, no formation of by-products, and finally, agreement with some of the green chemistry protocols.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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