Design and synthesis of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ as a new and efficient mesoporous magnetic catalyst in carbon–carbon cross-coupling reactions

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In this paper, a new type of mesoporous material based on KIT-6 has been introduced. In this aim, magnetic Fe₃O₄ nanoparticles and mesoporous silica KIT-6 have been combined to obtain mesoporous MNPs. The prepared magnetic mesoporous catalyst has been applied in different carbon–carbon cross-coupling reactions including Mizoroki–Heck, Suzuki–Miyaura, and Stille reactions. This magnetic mesoporous compound is characterized by various techniques including FT-IR, BET, VSM, SEM, XRD, and TGA.

Mesoporous materials are solid and porous compounds with nanometer pore sizes and very high available surfaces area. These porous materials are made of two parts: cavities and walls. In the last few years, a different category of porous materials has been recognized and introduced to chemistry science, such as silica structures, metal oxides, silicon nanopores, carbon nanotubes, and porous carbon. The regular and porous silica structures were discovered in the 1990s¹–³. High specific level, selectivity, shape, and size are the most significant characteristics of these materials, which convert them to critical materials with a wide range of applications such as catalysis, filtration and isolation etc.⁴,⁵. Major applications of nanopores in chemistry are their use in the manufacture of chemical sensors and application as a surface for the stabilization of chemical and biochemical catalysts. The development of these materials in the future depends on the manufacture of engineered and controlled porosity for the given applications⁶–¹⁰. Based on the size of the channel diameters, nanoporous materials are divided into three main categories: macroporous, mesoporous and microporous. The most important members of mesoporous, which are named as M41S family, include MCM-41, MCM-48, and MCM-50 mesopores¹¹,¹².

The KIT-6 structure is a relatively new structure of mesoporous silica, which has first been synthesized by Rio et al. in 2003 that has a cubic bilateral structure of Ia₃d symmetry and cylindrical cavities and the advantage of this structure compared to other silica structures is the higher cavities volumes¹³,¹⁴. This three-dimensional silica grid can be a suitable host for various components, which can easily enter the cavity and spread out. KIT-6 has been recognized with wide applications including electrical, catalytic, and isolation applications¹⁵–¹⁸.

One of the most important chemists’ achievements is the discovery of the carbon–carbon coupling reactions in the presence of a complex containing transition metal such as copper, palladium, nickel, and iron. Among transition metals complexes, palladium is one of the best choices, due to its simple complex preparation, high activity, and selectivity in coupling reactions¹⁹–²⁴. In organic chemistry science, a variety of coupling reaction systems has been discovered, designed, and introduced: Heck reaction²⁵, Suzuki reaction²⁶, Negishi reaction²⁷, Stille reaction²⁸, Sonogashira reaction²⁹, Kumada coupling³⁰, Hiyama coupling reaction³¹, and Buchwald–Hartwig reaction³². Among them, Stille (coupling reaction of a tin organic compound with an electro-friendly organic compound)³³, Suzuki (coupling reaction of a phenylboronic acid derivative with various aryl halides)³⁴, and Heck reaction (coupling reaction of aryl of various halides with alkenes)³⁵ are main and generally applicable methods for the construction of carbon–carbon bonds³⁶,³⁷. Herein we have synthesized a new immobilized palladium complex on the modified magnetic mesoporous material (Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰) that acts as a versatile catalyst in cross-coupling reactions.

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Result and discussion

Preparation and characterization of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰. For the synthesis of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ catalyst, first Fe₃O₄ magnetic nanoparticles were synthesized by co-precipitation method. Subsequently, it was coated by KIT-6 to synthesize Fe₃O₄@SiO₂@KIT-6 nanoparticles. In the next step, obtained Fe₃O₄@SiO₂@KIT-6 modified by (3-chloropropyl) triethoxysilane. Finally, to obtain the final catalyst Fe₃O₄@SiO₂@KIT-6-nPrNH₂ condensed with dithizone followed by coordination with palladium as outlined in Fig. 1.

After designing and fabricating Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰, the structure of this magnetic mesoporous material is characterized by various techniques.

To consider the morphology of prepared magnetic mesoporous material, SEM (scanning electron microscopy) was applied. As it can be seen in Fig. 2, Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ particles are spherical with nano-sized particles.

Porosity analysis of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ studied by nitrogen absorption–desorption technique. Based on this analysis, the specific surface area of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ was 71.477 m²/g, its monolayer capacity (Vₙ) was 16.422 cm³ (STP) g⁻¹ and the total pore volume of the prepared magnetic mesoporous compound was 0.1188 cm³/g. The specific surface area was calculated by the Langmuir isotherm.

Figure 1. Stepwise preparation of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰.

Figure 2. SEM images of the Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ at different magnification.
Langmuir isotherm (Fig. 3) illustrated $a_{\text{Lang}} = 415.1 \text{ m}^2/\text{g}$ and $V_m = 95.372 \text{ cm}^3$ (stp) g$^{-1}$, respectively. Furthermore, the calculations related to BJH diagram from the adsorption and desorption branch of the nitrogen adsorption curve indicated that the pore sizes in these compounds were the same and the average pore diameter of Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$ is 2.41 nm.

To measure the exact amount of loaded Pd on the surface of Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ nanoparticles, induced coupled plasma (ICP) spectroscopy technique was used, which based on this technique, the exact amount of Pd is $1.069 \times 10^{-3}$ mol/g.

The XRD pattern of Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$ nanoparticles is displayed in Fig. 4. As it can be seen, the XRD pattern of synthesized nanoparticle shows characteristic peaks at $2\theta = 25.86^\circ$, $30.46^\circ$, $35.71^\circ$, $43.46^\circ$, $53.86^\circ$, $57.01^\circ$, $62.86^\circ$, and $74.16^\circ$ that are related to Fe$_3$O$_4$ and the extent peak appearing in $2\theta$ of 20.26$^\circ$ are related to the presence of a silica layer around the nanoparticles. The corresponding peaks at $2\theta = 39.91^\circ$, $45.16^\circ$ and $66.86^\circ$ 2$\theta$ is correspondence to Pd particles. These pieces of evidence show that Pd is well stabilized on the nanocatalyst.

The TGA diagram for magnetic mesoporous material (Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$) is shown in Fig. 5. Based on this analysis, the first weight loss under 200 $^\circ$C (about 10%) is related to the evaporation of physically adsorbed solvents and water. The second weight loss, which is about 9.5%, is between 200 to 800 $^\circ$C related to the removal of organic moieties on the surface of magnetic mesoporous support. The final weight loss is related to the phase change of Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$ nanoparticles.

Figure 3. N$_2$ adsorption–desorption isotherms of Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$.

Figure 4. The XRD pattern of the Fe$_3$O$_4@$SiO$_2@$KIT-6@DTZ-Pd$^0$. 

![Figure 3](image-url)  
![Figure 4](image-url)
The magnetic properties of the synthesized Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ were investigated by VSM analysis. As displayed in Fig. 6, the magnetic property of the nanocatalyst is 3.67 emu/g, which reflects the fact that the nanoparticle surface is coated with SiO₂ and organic groups. Nevertheless, by applying an external magnetic field, the catalyst can be easily separated from the reaction mixture.

The FT-IR spectra of Fe₃O₄@SiO₂@KIT-6 (Fig. 7a), Fe₃O₄@SiO₂@KIT-6@CPTES (Fig. 7b), Fe₃O₄@SiO₂@KIT-6@DTZ (Fig. 7c), Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ (Fig. 7d) and recovered Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ (Fig. 7e) are shown in Fig. 7. The FT-IR spectra of Fe₃O₄@SiO₂@KIT-6 (Fig. 7a) indicated several bands at 463 cm⁻¹, 637 cm⁻¹, which is related to stretching vibration of Fe–O bond, and a sharp peak at 1079 cm⁻¹ belongs to stretching vibration of Si–O–Si bond, two peaks at 1634 cm⁻¹ and 3433 cm⁻¹ related to bending vibration and stretching vibration OH groups, respectively. Several peaks about 2900 cm⁻¹ are related to C–H stretching vibration and the bending vibration for Si–O–Si bond appears at 1078 cm⁻¹ in the IR spectra of Fe₃O₄@SiO₂@KIT-6@CPTES (Fig. 7b). In the next spectra (Fig. 7c) the observed peaks at 3436 cm⁻¹ and 1650 cm⁻¹ are related to N–H and C=N bonds, also the observed peak at 1391 cm⁻¹ is related to the stretching vibration of C=S bond. The shifting of C=N peak from 1650 to 1634 cm⁻¹ in IR spectra of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd (Fig. 7d) indicating that palladium was successfully coordinated to dithizone. The FT-IR spectra of recovered Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ (Fig. 7e), after the four times recovery, do not show any significant change with the fresh catalyst.

Catalytic studies. Mizoroki–Heck cross-coupling reaction. After the characterization of the prepared magnetic mesoporous material, the catalytic activity of this compound was studied in carbon–carbon bond formation reactions.

Initially, the catalytic activity of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ was examined in Heck reaction. To obtain optimal conditions for this C–C cross-coupling reaction, the reaction of iodobenzene and butyl acrylate was investigated as a model reaction. The reaction was examined in the presence of various solvents such as PEG, DMF, DMSO, CH₂CN, different bases (KOH, NaOH, Na₂CO₃, Li₂CO₃), and different values of catalysts (4, 5, and 6 mg) at various temperature conditions.

The highest yield of product (95%) was obtained in PEG as the solvent, 3 mmol of K₂CO₃ as the base and 5 mg of catalyst at 100 °C (Table 1).

To develop the efficiency of described catalyst a variety of aryl halides reacted with butyl acrylate under obtained optimal reaction conditions (Scheme 1).
The results are summarized in Table 2. As it can be seen, aryl iodides are not significantly different from aryl bromides and chlorides in terms of the reaction yields, and only the reaction time with aryl bromides and aryl chlorides is slightly longer.

**Suzuki–Miyaura cross-coupling reaction.** To consider more activity of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ as the catalyst, the activity of the described catalyst was studied in the Suzuki cross-coupling reaction. The optimization experiment initiated the reaction of iodobenzene with phenylboronic acid in different conditions as a model substrate. Reaction conditions including base, solvent, temperature, the amount of catalyst were screened and the results are summarized in Table 3. The results demonstrated that the highest efficiency was achieved in Ethanol as the solvent, K₂CO₃ (2.5 mmol), and was 5 mg of catalyst at 75 °C.

The optimal conditions were applied for the reaction of a wide variety of aryl halides with phenylboronic acid (Scheme 2); the results are presented in Table 4.

**Stille cross-coupling reaction.** Herein in the final part of this research project, Stille cross-coupling reaction of various aryl halides and triphenyl tin chloride was investigated in the presence of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰. The reaction parameters (including solvent, temperature, type, and amount of base as well as the amount of catalyst) were considered for the cross-coupling of iodobenzene and triphenyl tin chloride. As is evident from Table 5 the highest product yield was obtained in PEG as solvent. Also, the highest yield and the
The shortest time for the mentioned cross-coupling reaction was obtained using K₂CO₃ as the base, 6 mg of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ at 80 °C.

To spread out the application of the described catalyst in the Stille reaction, triphenyl tin chloride reacted with a variety of aryl halides (including chloride, bromide, and iodide) under optimal conditions (Scheme 3). The results including yields and reaction times were brought in Table 6.

In order to compare the catalytic performance of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰ with the previously reported catalysts, the results of coupling of phenylboronic acid with iodobenzene by the previously reported methods are shown in Table 7. In this comparison, various parameters such as reaction time, reaction conditions, and efficiency with other catalysts were compared. In this work, the C–C bond formation reaction is performed in ethanol as a green solvent and this catalyst almost shows a shorter reaction time and higher performance than the other catalysts.

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### Table 1. Optimization conditions of Mizoroki–Heck cross-coupling reaction of iodobenzene and butyl acrylate. Significant values are in bold. *Isolated yield.

| Entry | Solvent | Base | Base (mmol) | Catalyst (mg) | Temperature (°C) | Time (min) | Yield (%) | a |
|-------|---------|------|-------------|---------------|-----------------|------------|-----------|---|
| 1     | PEG     | K₂CO₃ | 3           | 5             | 100             | 35         | 95        |   |
| 2     | DMSO    | K₂CO₃ | 3           | 5             | 100             | 35         | 67        |   |
| 3     | DMF     | K₂CO₃ | 3           | 5             | 100             | 35         | 65        |   |
| 4     | CH₃CN   | K₂CO₃ | 3           | 5             | Reflux          | 35         | 59        |   |
| 5     | PEG     | KOH   | 3           | 5             | 100             | 35         | 53        |   |
| 6     | PEG     | Na₂CO₃| 3           | 5             | 100             | 35         | 76        |   |
| 7     | PEG     | Li₂CO₃| 3           | 5             | 100             | 35         | 61        |   |
| 8     | PEG     | NaOH  | 3           | 5             | 100             | 35         | 45        |   |
| 9     | PEG     | K₂CO₃ | 3           | 6             | 100             | 35         | 96        |   |
| 10    | PEG     | K₂CO₃ | 3           | 4             | 100             | 35         | 54        |   |
| 11    | PEG     | K₂CO₃ | 1.5         | 5             | 100             | 35         | 63        |   |
| 12    | PEG     | K₂CO₃ | 3           | 5             | Reflux          | 35         | 96        |   |
| 13    | PEG     | K₂CO₃ | 3           | 5             | 80              | 35         | 65        |   |
| 14    | PEG     | K₂CO₃ | 3           | 5             | 60              | 35         | 33        |   |

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![Scheme 1. Mizoroki–Heck cross-coupling reaction.](image)

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### Table 2. Mizoroki–Heck cross-coupling reaction in the presence of a catalytic amount of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd⁰. *Isolated yield.

| Entry | X  | R     | Time (min) | Yield (%) | M.P (°C) | TON | TOF (h⁻¹) |
|-------|----|-------|------------|-----------|----------|-----|-----------|
| 1     | I  | H     | 35         | 95        | Oil³⁶    | 177.73 | 304.85 |
| 2     | I  | 4-CH₃| 20         | 92        | Oil³⁶    | 172.123 | 516.88 |
| 3     | I  | 4-OCH₃| 15        | 90        | Oil³⁶    | 168.381 | 673.52 |
| 4     | Br | 4-OCH₃| 40        | 90        | Oil³⁶    | 168.381 | 252.825 |
| 5     | Br | 4-CH₃| 75         | 87        | Oil³⁶    | 162.768 | 130.215 |
| 6     | Br | H     | 130        | 85        | Oil³⁶    | 159.027 | 61.164 |
| 7     | Br | 4-Cl  | 145        | 89        | Oil³⁶    | 166.510 | 68.92 |
| 8     | Br | 4-NO₂| 180        | 85        | 60–61³¹ | 159.027 | 53.009 |
| 9     | Cl | H     | 270        | 79        | Oil³¹    | 147.801 | 32.844 |
Reusability of the catalyst. According to the principles of green chemistry, the recovery of the catalyst at the end of the reaction and its reusability is a highly significant factor. In this aim, Suzuki cross-coupling reaction of iodobenzene and phenylboronic acid was investigated. After each run nanocatalyst was isolated from reaction media by applying a magnet and washed several times with ethanol, then dried and reused for the next experiment. As it can be seen from Fig. 8, the catalyst is recoverable at least up to four runs, with a negligible decrease in its activity.

Catalyst leaching study. To perform the hot filtration test, the Suzuki reaction was selected as the model reaction and two types of reactions were performed between iodobenzene and phenylboronic acid under opti-
mal reaction conditions. In the first reaction, the biphenyl product was obtained after 6 min (half the reaction time) with a yield of 69. Simultaneously in the second reaction, the same reaction was repeated, but at the half-reaction (after 6 min), the catalyst was removed from the reaction mixture by a magnet and the reaction mixture was allowed to run for another 6 min. The reaction efficiency at this stage was 72%. These experiments confirmed that Fe₃O₄@SiO₂@KIT-6@DTZ-Pd₀ was necessary to complete the reaction and that confirmed the leaching of palladium during the reaction didn’t occur.

**Conclusions**

In this research project, we have introduced a novel magnetic mesoporous material with two unique properties i.e. high porosity and magnetism. These two factors make this nanomaterial an efficient and versatile catalyst. The catalytic activity of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd₀ was examined in the variety of cross-coupling reactions.

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### Table 5. Optimization of Stille cross-coupling reaction of iodobenzene and triphenyl tin chloride. Significant values are in bold. *Isolated yield.

| Entry | Solvent | Base | Base (mmol) | Catalyst (mg) | Temperature (°C) | Time (min) | Yield (%)a |
|-------|---------|------|-------------|---------------|-----------------|------------|------------|
| 1     | PEG     | K₂CO₃ | 3           | 6             | 80              | 35         | 94         |
| 2     | DMSO    | K₂CO₃ | 3           | 6             | 80              | 35         | 64         |
| 3     | DMF     | K₂CO₃ | 3           | 6             | 80              | 35         | 67         |
| 4     | EtOH    | K₂CO₃ | 3           | 6             | Reflux          | 35         | 60         |
| 5     | CH₃CN   | K₂CO₃ | 3           | 6             | 80              | 35         | 55         |
| 6     | PEG     | KOH   | 3           | 6             | 80              | 35         | 75         |
| 7     | PEG     | Na₂CO₃| 3           | 6             | 80              | 35         | 71         |
| 8     | PEG     | NaOH  | 3           | 6             | 80              | 35         | 68         |
| 9     | PEG     | K₂CO₃ | 1.5         | 6             | 80              | 35         | 59         |
| 10    | PEG     | K₂CO₃ | 3           | 7             | 80              | 32         | 94         |
| 11    | PEG     | K₂CO₃ | 3           | 5             | 80              | 35         | 86         |
| 12    | K₂CO₃   | K₂CO₃| 3           | 6             | 100             | 30         | 93         |

### Scheme 3. Stille reaction by Fe₃O₄@SiO₂@KIT-6@DTZ-Pd₀.

**Table 6.** Stille cross-coupling reaction in the presence of a catalytic amount of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd₀. *Isolated yield.

| Entry | X     | R     | Time (min) | Yield (%)a | M.P (°C) | TON   | TOF (h⁻¹) |
|-------|-------|-------|------------|------------|----------|-------|-----------|
| 1     | I     | H     | 35         | 94         | 68–69⁴⁴  | 175.865| 301.655   |
| 2     | I     | 4-CH₃| 35         | 92         | 43–45⁴⁴  | 172.121| 288.819   |
| 3     | I     | 4-OCH₃| 20        | 90         | 85–86⁵²  | 168.381| 505.615   |
| 4     | Br    | 4-OH  | 55         | 89         | 162–163⁴⁹| 166.510| 181.78    |
| 5     | Br    | 4-OCH₃| 60         | 88         | 84–86⁵²  | 164.639| 164.639   |
| 6     | Br    | 4-CH₃| 70         | 85         | 42–43⁴⁹  | 159.027| 95.454    |
| 7     | Br    | 3-OCH₃| 75         | 87         | 86–88⁵²  | 162.768| 139.596   |
| 8     | Br    | H     | 100        | 90         | 69–70⁴⁴  | 168.381| 101.069   |
| 9     | Br    | 4-Cl  | 110        | 89         | 69–70⁴⁴  | 166.510| 90.989    |
| 10    | Br    | 4-NO₂| 125        | 88         | 112–114⁴⁰| 164.639| 79.039    |
| 11    | Cl    | H     | 240        | 74         | 68–69⁴⁴  | 138.447| 34.611    |

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including Heck, Suzuki, and Stille reactions. These coupling reactions are performed in environmental-friendly conditions with short reaction times and high efficiency and purity of products.

**Experimental**

**Preparation of Fe₃O₄@SiO₂@KIT-6.** For the synthesis of Fe₃O₄@SiO₂@KIT-6, initially, Fe₃O₄@SiO₂ nanoparticles were synthesized using the previously reported procedure in the literature. In the next step, P123 (1.25 g), Fe₃O₄@SiO₂ (1 g), HCl (37% wt) (2.4 mL), and 1.3 g of n-butanol (99.4% wt) were mixed in distilled water (45 mL) and stirred at 35 °C for an hour, then 2.7 g of TEOS was added and the mixture was stirring in the same temperature under nitrogen atmosphere. Finally, the resulting mixture was transmitted into an autoclave and placed in the oven for 24 h at 100 °C. The resulting mixture was washed with 300 mL of ethanol and 20 mL of HCl. Finally, Fe₃O₄@SiO₂@KIT-6 was calcified at 550 °C for 6 h.

**Preparation of Fe₃O₄@SiO₂@KIT-6@DTZ.** In a 100 mL balloon, Fe₃O₄@SiO₂@KIT-6 (1 g) sonicated for 30 min in toluene (25 mL), then, 1.5 mL of 3-chloropropyltriathoxycylanine (CPTES) was added and the resulting mixture was stirred for 24 h at 90 °C under nitrogen atmosphere. The obtained solid material was washed with dichloromethane (50 mL). Subsequently, Fe₃O₄@SiO₂@KIT-6@CPTES (1 g) was dispersed in 25 mL of DMF by sonication for 30 min, which was followed by adding 3 mmol of dithizone (diphenylthiocarbazone) and 3.5 mmol triethylamine. The resulting mixture was stirred for 48 h at 100 °C with. The obtained precipitate was then washed several times by organic solvents and dried at room temperature.

**Preparation of Fe₃O₄@SiO₂@KIT-6@DTZ-Pd.** In a 100 mL round-bottom flask Fe₃O₄@SiO₂@KIT-6@DTZ (1 g) dispersed in 50 mL ethanol via sonication for 20 min. Then, 0.5 g of Pd(OAc)₂ was added to the mixture and stirred for 20 h, at reflux conditions under nitrogen atmosphere. Finally, NaBH₄ (0.6 mmol) was added to the reaction mixture and stirred under the same conditions for 2 more hours. Then, the reaction mixture cooled down to room temperature, and magnetic mesoporous material (Fe₃O₄@SiO₂@KIT-6@DTZ-Pd) was isolated by a magnet and washed several times with ethanol.

**General procedure for Mizoroki–Heck cross-coupling reaction.** To perform Heck reaction, in a 5 mL round bottom flask, aryl halide (1 mmol), butyl acrylate (1.2 mmol), 3 mmol of potassium carbonate, and Fe₃O₄@SiO₂@KIT-6@DTZ-Pd (5 mg) were added to 2 mL of PEG and the mixture stirred at 100 °C. The progress of the reaction was followed by TLC. After completion of cross-coupling reaction, 10 mL water was added.
and catalyst separated by an external magnet. The corresponding product was extracted by ethyl acetate from a mixture of water and ethyl acetate.

*n-Butyl cinnamate.* mp: Oil (lit.ref Oil); 1H NMR (300 MHz, CDCl₃): δ 7.67–7.72 (d, J = 7.69, 1H, alkene), 7.52 (d, J = 7.52, 2H, ArH), 7.39–7.40 (t, J = 7.39, 2H, ArH), 7.37–7.38 (t, J = 7.38, 1H, ArH), 6.43–6.48 (d, J = 4.55, 1H, alkene), 4.22 (t, J = 4.22, 2H, CH₂), 1.70 (m, J = 1.68, 2H, CH₂), 1.43–1.46 (m, J = 1.44, 2H, CH₂), 0.96 (t, J = 0.97, 3H, CH₃) ppm (Fig. S1).

**General procedure for Suzuki–Miyaura cross-coupling reaction.** To a 5 mL round bottom flask, aryl halide (1 mmol), phenylboronic acid (1 mmol), potassium carbonate (2.5 mmol), catalyst (5 mg), and 2 mL of ethanol solvent were added. The reaction mixture was stirred for a specified time at 75 °C. After reaction completion, the catalyst was separated using an external magnet and the reaction mixture was transferred to a separating funnel and extracted with ethanol. The extracted organic phase was collected and dried. The obtained product was then spectrally analyzed after purification.

4-Methyl-1,1'-biphenyl. mp: 45–48 °C (lit.ref 50–51 °C); TLC (n-hexane); 1H NMR (500 MHz, DMSO-d₆) δ 7.62 (d, J = 7.63, 2H, ArH), 7.54 (d, J = 7.55, 2H, ArH), 7.44 (t, J = 7.44, 2H, ArH), 7.33 (t, J = 7.33, 1H, ArH), 7.27 (d, J = 7.26, 2H, ArH), 2.34 (s, 3H, CH₃) ppm (Fig. S2).

4-Nitrobiphenyl. mp: 113–114 °C (lit.ref 103–106 °C); TLC (n-hexane); 1H NMR (500 MHz, CDCl₃) δ 8.29–8.30 (d, J = 8.30, 2H, ArH), 7.72–7.76 (d, J = 7.74, 2H, ArH), 7.62–7.63 (d, J = 7.62, 2H, ArH), 7.51 (t, J = 7.52, 2H, ArH), 7.48 (t, 1H, ArH) ppm (Fig. S3).

**General procedure for Stille cross-coupling reaction.** In a 5 mL round bottom flask, aryl halide (1 mmol), triphenyl tin chloride (0.5 mmol), potassium carbonate (3 mmol), catalyst (6 mg), and 2 mL of PEG solvent were added. The reaction mixture was stirred for a specified time at 80 °C. The reaction progress followed by TLC. After the reaction completion, the catalyst was separated by an external magnetic field, and the mixture was transferred to a separating funnel and extracted with ethyl acetate and water. The obtained organic phase was collected and dried. The obtained product was then spectrally analyzed after purification.

[1,1'-Biphenyl]-4-ol. mp: 162–163 °C (lit.ref 161–164 °C); TLC (n-hexane); 1H NMR (500 MHz, DMSO-d₆) δ 9.60 (s, 1H, OH), 7.56 (d, J = 7.56, 2H, ArH), 7.48 (d, J = 7.49, 2H, ArH), 7.39 (t, J = 7.39, 2H, ArH), 7.26 (t, J = 7.26, 1H, ArH), 6.88 (d, J = 6.89, 2H, ArH) ppm (Fig. S4).

4-Chlorobiphenyl. mp: 69–70 °C (lit.ref 70–72 °C); TLC (n-hexane); 1H NMR (500 MHz, DMSO-d₆): δ 7.68 (d, J = 7.67, 2H, ArH), 7.66 (d, J = 7.64, 2H, ArH), 7.51 (d, J = 7.5, 2H, ArH), 7.46 (t, J = 7.46, 2H, ArH), 7.38 (t, J = 7.38, 1H, ArH) ppm (Fig. S5).

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**Author contributions**

Zahra Moradi did the experimental works, wrote the manuscript draft and drew the images, schemes and Figures. Arash Ghorbani-Choghamarani supervised the research project and is the corresponding author of the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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