Revised: 15 February 2020

4

FULL PAPER



Applied Organometallic WILEY Chemistry

Air-Stable Fe₃O₄@SiO₂-EDTA-Ni(0) as an Efficient Recyclable Magnetic Nanocatalyst for Effective Suzuki-Miyaura and Heck Cross-Coupling via Aryl Sulfamates and Carbamates

Iman Dindarloo Inaloo¹ [©] Mohsen Esmaeilpour¹

Iman Dindarloo Inaloo¹ | Sahar Majnooni² | Hassan Eslahi¹ |

¹Chemistry Department, College of Sciences, Shiraz University, Shiraz, Iran ²Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran

Correspondence

I. Dindarloo Inaloo, Chemistry Department, College of Sciences, Shiraz University, Shiraz, Iran. Email: iman.dindarlooinaloo@gmail.com The synthesis of inexpensive and novel air-stable Ni(0) nanoparticles immobilized on the EDTA-modified $Fe_3O_4@SiO_2$ nanocatalyst was investigated in Suzuki-Miyaura and Heck cross-coupling reactions. This catalytic system displayed a greatly improved substrate scope for the carbon–carbon bond formations starting from a wide range of green and economical electrophiles aryl and heteroaryl carbamates and sulfamates via highly efficient method under mild, operationally simple reaction conditions. The synthesized heterogeneous catalyst was also fully characterized by FT-IR, TEM, XRD, DLS, FE-SEM, UV–Vis, EDX, XPS, TGA, NMR, VSM, ICP and elemental analysis techniques. The heterogeneous magnetic nanocatalyst can easily be recovered by an external magnetic field and reused for the next reactions for at least seven times with negligible leaching of catalyst and no substantial decrement in the activity. All these highlights have made the present protocol an interesting, simple and environmentally benign process with low catalyst loading and easy manipulations.

K E Y W O R D S

C-O activation, cross-couplings, magnetic nanoparticles, nickel Nanocatalyst; carbamates; Sulfamates

1 | INTRODUCTION

Transition metal catalyzed cross-coupling reactions have become one of the most useful achievements for the synthesis of aromatic compounds in the last century.^[1] Having the importance of these compounds, they ubiquitously are observed in pharmaceuticals, agrochemicals, electronics and dyes.^[2] In addition, the discovery and development of effective and eco-friendly methods for the C-C bond formation are of researcher's priority.^[3] The most common and popular techniques to access such couplings are the usage of Pd catalyzed reaction between nucleophiles and aryl halides (I, Br, Cl) as the electrophile.^[4] In the view of polyfunctionalized aromatics importance in our lives, the high cost and toxicity of palladium metal and the stoichiometric quantity of halide waste generated from these reactions, their application is limited in both academic researches and industrial productions importantly in medicinal and agricultural applications.^[5] In recent years, the promising approach for the development of sustainable and environmentally benign cross-coupling processes has been noted using aryl halides, nontoxic and safe electrophiles, and significantly low cost and non-toxicity metals.^[6] Thus, a wide library 2 of 17 WILEY Organometallic Chemistry

of Nickel-catalyzed C-C bond formations starting from aryl boronic acids as nucleophilic coupling partners and aromatic rings such as aryl ethers,^[7] esters,^[8] tosylates,^[9] sulfamates,^[10] triflates,^[11] phosphates,^[12] carbonates^[13] and carbamates^[14] as aryl halide surrogates have been intensely investigated (Figure 1). As a result of these studies, aryl carbamates and sulfamates were considered ideal precursors because of their extensive derivatives, availability, high stability and more efficiency under a variety of reaction conditions.^[15]

Despite these significant advances that happened in recent years,^[16–19] however, this reaction suffers from several limitations including high catalyst loading, long reaction times, elevated temperature regime and the necessity to employ additional quantities of the phosphine ligands.^[17] It should be noted that the use of large quantities of ligands and metals as catalytic systems create a remarkable complexity in the purification, increase waste materials, decrease the safety of reaction and low to modest yields have resulted in the most cases.^[18] Besides, most of the phosphorus ligands that are necessary for doing these reactions have some drawbacks such as thermal and air instability, high prices and difficulty in the synthesis which are the main reasons for the growing interests in phosphine-free coupling reactions.^[19]

In the world ahead, we can follow the progress of nanotechnology especially nanomaterials in biomedicine, biodetections, bioimaging, and drug delivery systems due to their modified structure, increased activity, and surface area to volume ratio.^[20] They have also many appealing applications in advanced industries such as textile, medicine, and cosmetic industries.^[21]

Magnetic Fe_3O_4 nanoparticles (MNPs) are non-toxic, biodegradable, and biocompatible particles that have been attracted much attention giving to surface functionalization ability makes them an exciting option for the separation point of view.^[22] They are interesting candidates for ongoing researches owing to their unique physiochemical properties and outstanding usages including medical diagnostics and therapeutics,^[23]



FIGURE1 Conventional phenol derivatives in cross-coupling reactions

hyperthermia,^[24] data storage,^[25] magnetic resonance imaging (MRI),^[26] biomedical protection,^[27] sensor applications,^[28] magnetic inks for jet printing,^[29] and catalysis.^[30]

Scientists are commonly faced to the aggregation of MNPs resulting from anisotropic dipolar attractions that make them unstable in the reaction conditions.^[31] To surmount such drawbacks, they need some stabilizers as protecting layer to solve the difficulty stabilizing of which. These protection layers are vital to improve the dispersibility of Fe₃O₄ NPs and to ensure the chemical stability of them.^[32] Magnetic core-shells, bearing both advantages of cores and a wide spectrum of shells, have absorbed much attention in the intensive researches.^[33] So far, many stabilizers have been reported as the shell for this challenge such as Fe₃O₄/carbon,^[34] Fe₃O₄/meso-silica,^[35] Fe₃O₄/polymer,^[36] Fe₃O₄/MOF,^[37] and Fe₃O₄@SiO₂.^[38]

Abundant reports have been published in the literature using Fe₃O₄@SiO₂ core-shells as ingredient of heterogeneous catalysts.^[39] Although the heterogeneous catalysts are usually less reactive than homogeneous ones, they removed many limitations attributed to homogeneous catalysts including tedious workup and separation, contamination by the residual catalyst, low reusability, expensive reaction conditions, and high-cost preparation.^[40] As a result, we found such heterogeneous catalysts based on magnetic nanoparticles as applicable catalysts for our ongoing researches.^[41] Therefore, in this work, we reported nickel nanoparticles immobilized on EDTA-modified Fe₃O₄@SiO₂ (Fe₃O₄@SiO₂-EDTA-Ni(0) NPs) to catalyze the Suzuki-Miyaura and Heck cross-couplings via aryl carbamates and sulfamates without using any external ligand and the reducing agents (Scheme 1).

2 | EXPERIMENTAL

2.1 | Chemicals and instrumentation

All chemicals and solvents were purchased from Sigma-Aldrich and Merck chemicals and were used with no more purifications. The purity of the products and the



SCHEME 1 Suzuki-Miyaura and Heck Cross-Couplings of Aryl Carbamates and Sulfamates

progress of reactions were accomplished by TLC on silica-gel Polygram SILG/UV254 plates. The FT-IR spectra were recorded in the range of 500–3800 cm^{-1} using a potassium bromide matrix with a Shimadzu FTIR-8300 spectrophotometer. NMR spectra were recorded on a Bruker Advance DPX 250 MHz spectrometer using deuterated CDCl₃ as solvent and TMS as the internal standard. X-ray diffraction patterns of the powder samples are obtained with a Bruker AXS D8-advance X-ray diffractometer using Cu K α ($\lambda = 1.5418$) radiation. Transmission electron microscopy (TEM) was performed on a Philips EM208 transmission electron microscope at an acceleration of 100 kV. Field emission scanning electron microscopy (FESEM) pictures were observed on a Philips XL-30ESEM. Dynamic light scatterings (DLS) were performed using a HORIBA-LB550. The X-ray photoelectron spectra (XPS) were analyzed on the PHI 5300x multi-technique system with an Mg K α X-ray source. N₂ adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2000 instrument. UV-vis spectra were recorded on a PerkinElmer Lambda 25 UV/Vis spectrometer having a quartz cuvette. The elements in the samples were probed by an energydispersive X-ray (EDX) spectroscopy accessory to the Philips scanning electron microscopy (SEM). The magnetic property of the catalyst was measured with a BHV-55 vibrating sample magnetometer from -6000 Oe to +6000 Oe at room temperature. Thermogravimetric analysis (TGA) was performed with a TGA/SDTA851e under air atmosphere from 50 to 700 $^{\circ}$ C, with a heating rate of 20 °C min⁻¹ and an airflow rate of 30 ml min⁻¹. Elemental analysis was done on a Thermo Finnigan Flash EA-1112 CHNSO rapid elemental analyzer. The nickel content was measured by inductively coupled plasma (ICP, Varian, Vista-pro). Melting points were determined in open capillaries using an Electrothermal 9100 apparatus.

2.2 | General procedure

2.2.1 | Preparation of silica-coated magnetic nanoparticles (Fe₃O₄@SiO₂NPs)

Naked Fe_3O_4 nanoparticles were prepared by chemical coprecipitation based on our previous report.^[41] In a typical procedure, 1.3 g of FeCl₃.6H₂O (4.8 mmol) was dissolved in 30 ml of water to form a clear solution. Then, 1.0 g of polyvinyl alcohol (PVA 15000) as a surfactant and 0.9 g of FeCl₂.4H₂O were added and the resultant mixture was stirred for 0.5 hr at 80 °C. Next, hexamethylenetetramine (HMTA) (1.0 mol/L) was added drop by drop with vigorous stirring until pH 10 and a black product was obtained. Afterward, the resulting nanomaterial (Fe₃O₄)

was magnetically separated, washed with ethanol several times and dried at 80 °C for 10 hr. The coating of the magnetic nanoparticles with silica was performed according to the Stöber method. Briefly, in a typical process, prepared Fe₃O₄ particles (0.5 g) were dispersed in a mixture of deionized water (5 ml), ethanol (50 ml), and tetraethoxy silane (TEOS) (0.20 ml) by ultrasonication for 0.5 min. Subsequently, 5.0 ml of NaOH (10 wt%) was added dropwise. After being stirring for 30 min, the obtained magnetic particles (Fe₃O₄@SiO₂) were separated with the magnet, washed with deionized water and ethanol 3 times and dried at 80 °C for 10 hr.

2.2.2 | Preparation of Fe₃O₄@SiO₂ coated by (3-aminopropyl)-triethoxysilane (Fe₃O₄@SiO₂-NH₂ MNPs)^[41]

The obtained $Fe_3O_4@SiO_2$ NPs powder (1 g) was dispersed in 10 ml ethanol by sonicating for 5 min, and then, 3-aminopropyl (triethoxy)silane (0.25 ml, 1 mmol) was added to the mixture. After mechanical agitation under the reflux conditions for 12 hr, the obtained amino-functionalized $Fe_3O_4@SiO_2$ NPs were separated by magnetic decantation, washed with distilled water and ethanol several times and finally, dried at 80 °C for 6 hr.

2.2.3 | Preparation of Fe₃O₄@SiO₂-TCT NPs

The synthesis procedure for the magnetic $Fe_3O_4@SiO_2$ -TCT composite nanoparticles is schematically illustrated in Scheme 1. At the first, 1 g of $Fe_3O_4@SiO_2$ -NH₂ (1 g) and cyanuric chloride (TCT, 1 mmol, 0.185 g) were mixed with 10 mL of THF using mechanical stirring to produce a homogeneous suspension. Then, 0.17 mL diisopropylethylamine (DIPEA, 1 mmol) was added to which by using a syringe. In the next, the reaction was stirred at room temperature for 16 hr with continuously mechanical stirring. The functionalized cyanuric chloride by $Fe_3O_4@SiO_2$ NPs were separated by the magnet and subsequently washed with deionized water and hot ethanol to remove the residue substrates. Finally, the sample was dried in an oven at 60 °C for 4 hr.

2.2.4 | Preparation of Fe₃O₄@SiO₂-TCT-NH₂ NPs

1 g of Fe_3O_4 @SiO₂-TCTnanoparticles were dispersed in 5 ml of DMF in a 25 ml single-necked flask. Then, 0.25 ml of bis(3-aminopropyl)amine (2 mmol) and 0.35 ml of DIPEA (2 mmol) were added to the mixture and it was stirred at 80 $^{\circ}$ C for 12 hr. The final particles were separated from the solution with an external magnetic field, washed three times with ethanol and water, and dried at 70 $^{\circ}$ C for 4 hr.

2.2.5 | Preparation of Fe₃O₄@SiO₂-EDTA-Ni(0) NPs

For the synthesis of Fe₃O₄@SiO₂-EDTA NPs, 0.58 g of EDTA (2 mmol) was dispersed in 20 ml of DMSO and then, thionyl chloride (SOCl₂, 2 mmol) was added dropwise over 10 min through a constant pressure drop funnel. Next, 1.5 g of Fe₃O₄@SiO₂-TCT-NH₂ was added to the mixture and stirred for 2 hr at room temperature. The functionalized ethylenediaminetetraacetic acid by Fe₃O₄@SiO₂-TCT-NH₂ nanomaterial was then isolated by an external magnet, washed with sodium carbonate solution (0.1 mol L^{-1}), acetone and deionized water, and dried under vacuum at 60 °C for 2 hr. The resultant Fe₃O₄@SiO₂-EDTA (1.5 g) was dispersed in 10 ml methanol. Afterward, 1 g of nickel (II) acetate tetrahydrate (4 mmol) was added to the mixture and stirred for 2 hr under the reflux conditions. In the next step, 15 ml of N_2H_4 · H_2O (1 equiv.) was slowly added to the obtained mixture and it was allowed to be stirred for more 2 hr. The resulting solid of Fe₃O₄@SiO₂-EDTA-Ni(0) was separated from the reaction mixture by an external magnet, washed with ethanol and THF for three times, and dried at 60 °C for 3 hr to afford the final catalyst.

2.3 | General procedure for the crosscoupling reaction of aryl carbamate and/or aryl Sulfamates with aryl Boronic acids (Suzuki-Miyaura cross-couplings) (3a-3x)

Aryl carbamate and/or aryl sulfamate (1.0 mmol), arylboronic acid (1.0 mmol), potassium phosphate (2.0 mmol, 430 mg), Fe_3O_4 @SiO₂-EDTA-Ni(0) NPs (0.018 g, 1 mol %) and ethylene glycol (3.0 ml) were added into a round-bottomed flask and stirred at 120 °C for 6 hr under the air atmosphere. The reaction process was monitored by TLC using petroleum ether/ethyl acetate and/or GC. After the completion of the reaction, the reaction mixture was cooled to room temperature and the nanocatalyst was separated from the mixture with an external magnetic field. Then, 10 ml of distilled water was added and the crude was subsequently extracted with ethyl acetate (3 × 10 ml). The organic phase was dried over anhydrous MgSO₄ and the crude product was obtained after removing the ethereal solution by a rotary

evaporator. The product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (9:1) as the solvent or recrystallized (See supporting information for ¹H and ¹³C NMR of the products).

2.4 | General procedure for the crosscoupling reaction of aryl carbamate and/or aryl Sulfamates with olefins (heck crosscoupling) (5a-5 t)

Aryl carbamate and/or aryl sulfamate (1.0 mmol), olefin (1.0 mmol), potassium phosphate (2.0 mmol, 430 mg), Fe₃O₄@SiO₂-EDTA-Ni(0) NPs (0.018 g, 1 mol %) and ethylene glycol (3.0 ml) were added into a round-bottomed flask and stirred at 120 °C for 6 hr under the air atmosphere. The reaction process was monitored by TLC using petroleum ether/ethyl acetate and/or GC. After the completion of the reaction, the reaction mixture was cooled to room temperature and the nanocatalyst was separated from the mixture with an external magnetic field. Then, 10 ml of distilled water was added and the reaction mixture was subsequently extracted with ethyl acetate $(3 \times 10 \text{ ml})$. The organic phases were dried over anhydrous MgSO₄ and the crude product was obtained after removing the ethereal solution by a rotary evaporator. The product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (9:1) (See supporting information for ¹H and ¹³C NMR of the products).

3 | RESULTS AND DISCUSSION

The whole preparation route to Fe₃O₄@SiO₂-EDTA-Ni(0) NPs includes five steps is illustrated in Scheme 2. The Fourier transform infrared (FT-IR) spectra of all synthetic approaches of the final catalyst are shown in Figure 2a-g. The FT-IR spectrum of Fe₃O₄ MNPs demonstrates a band at 570 cm⁻¹ due to the stretching vibration of Fe-O and also, a broad band at 3441 cm⁻¹ is attributed to the presence of surface hydroxyl groups (Figure 2a). The broad and intense band at 1090 cm⁻¹ in the spectrum of Fe₃O₄-SiO₂ is assigned to the asymmetric stretching bands of Si-O-Si in the silica shell. Furthermore, the band at 801 cm⁻¹ is assigned to the Si-O-Si symmetric stretch (Figure 2b). The presence of the anchored NH₂ and CH₂ groups, originating from the amino-propyl moiety of APTES was confirmed by vibrations 3300-3370 cm⁻¹ stretching at and 2810–2986 cm⁻¹, respectively (Figure 2c). After the modification with cyanuric chloride (Fe₃O₄@SiO₂-TCT, Figure 2d), the appearance of new bands at 1511, 1564 and 1711 cm^{-1} correspond to C=N stretching vibration.



SCHEME 2 Preparation steps for fabricating nickel nanoparticles immobilized on EDTA-modified Fe₃O₄@SiO₂

Furthermore, on the spectrum of Fe₃O₄@SiO₂-TCT, the C-Cl absorption bands disappear due to interference from the core-shell Si-O-Si band. The FT-IR spectrum of Fe₃O₄@SiO₂-TCT-NH₂ (Figure 2e) showed new peaks at 2871-3057, 1451 and 1257 cm⁻¹ that are attributed to C-H (symmetric and asymmetric stretching vibrations), CH₂ (bending) and C-N (stretching vibration), respectively. After functionalization with EDTA, the spectra of Fe₃O₄@SiO₂-EDTA showed the characteristic bands at 1736 cm^{-1} (C=O carboxylic stretching vibration), 1628 cm⁻¹ (C=O amide stretching vibration) and 2885–3070 cm⁻¹ (C-H stretching vibrations) (Figure 2f). These results implied that EDTA was successfully immobilized on the Fe₃O₄@SiO₂-TCT-NH₂ nanoparticles. The sharp band at 1736 cm^{-1} (Figure 2f) is assigned to C=O (carboxyl group) stretching bond that has shifted to the 1722 cm^{-1} (Figure 2g) in the spectra of the complex indicating the coordination of oxygen to nickel. These results confirm that the catalyst had been successfully prepared.

Figure 3 shows the XRD patterns of Fe_3O_4 , Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-EDTA-Ni(0) MNPs. All three samples exhibit the peaks at $2\theta = 30.1^{\circ}$, 35.4° , 43.1° , 53.4° , 57° and 62.6° , attributable to (220), (311), (400), (422), (511), and (440) Bragg reflection revealing the cubic spinel structure of Fe₃O₄ which are in agreement with standard magnetite XRD patterns (reference JCPDS card no. 19-629). These results clearly show that the surface modification of the Fe₃O₄ nanoparticles does not lead to their phase change. It is found that the diffraction peaks of composite magnetic particles decrease in the intensity in comparison with those of bare magnetic particles, probably due to the amorphous silica coating (Figure 3b). In addition, the XRD pattern of Fe₃O₄@SiO₂-EDTA-Ni(0) contains a series of peaks (44.5°, 51.7° and 76.6°) which are indexed as the crystal planes of Ni(0) on the surface of Fe₃O₄@SiO₂ NPs (Figure 3c) around (111), (200) and (220) (JCPDS, no. 03-1051). Moreover, the average crystal size of Fe₃O₄ NPs cores was calculated to be 11 nm using the Debye–Scherrer equation $(D = K\lambda/\beta \cos\theta)$.

5 of 17



FIGURE 2 FT-IR spectra of (a) $Fe_3O_4@SiO_2$, (b) $Fe_3O_4@SiO_2$ -NH₂, (c) $Fe_3O_4@SiO_2$ -TCT, (d) $Fe_3O_4@SiO_2$ -TCT-NH₂, (e) $Fe_3O_4@SiO_2$ -EDTA and (f) $Fe_3O_4@SiO_2$ -EDTA-Ni(0) NPs

However, to obtain exact information about the oxidation state of Ni species, X-ray photoelectron spectroscopy (XPS) was performed (Figure 4). Results showed the presence of an intense doublet at a binding energy of 853.9 eV and 871.7 eV, whichcan be assigned to Ni(0) $2p_{3/2}$ and Ni(0) $2p_{1/2}$, respectively.^[42] The small shoulder peaks at 860.7 eV and 878.3 eV is also observed which could be indexed to Ni (II) $2p_{3/2}$ and Ni (II) $2p_{1/2}$, respectively. From the peak position it can be easily concluded that Ni(0) is present at the surface of the catalyst.^[42]

Figure 5a-c showed TEM micrographs of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$, and (c) $Fe_3O_4@SiO_2$ -EDTA-Ni(0) NPs. As it can be found in transmission electron microscopy (TEM) analysis (Figure 5a), the magnetite microspheres have been successfully obtained as acclaimed previously. After being coated with silica, a thickness of the layer was increased that can be observed as the pallid layer on the outer shell of the Fe_3O_4 cores in comparison with the dark inner core (Figure 5b). After coating with organic compounds and nickel immobilization, the obtained



FIGURE 3 XRD pattern of (a) Fe_3O_4 , (b) Fe_3O_4 @SiO₂ and (c) Fe_3O_4 @SiO₂-EDTA-Ni(0) NPs



FIGURE 4 X-ray photoelectron spectroscopy of Fe₃O₄@SiO₂-EDTA-Ni(0) catalyst

nanoparticles show a rougher surface than Fe_3O_4 @SiO₂ nanoparticles and become slightly larger in diameter (~ 30 nm, Figure 5c).

Furthermore, the nanoparticle size and morphology of Fe_3O_4 , $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$ -EDTA-Ni(0) catalyst were investigated by field emission scanning electron microscopy (FE-SEM) (Figure 5d-f). The FE-SEM image of Fe_3O_4 confirmed that the particles are nearly spherical (Figure 5d and 5g). However, after



FIGURE 5 TEM images of (a) Fe_3O_4 , (b) $Fe_3O_4@SiO_2$ and (c) $Fe_3O_4@SiO_2$ -EDTA-Ni(0) NPs (b); FE-SEM images of (d) Fe_3O_4 , (e) $Fe_3O_4@SiO_2$ and (f) $Fe_3O_4@SiO_2$ -EDTA-Ni(0) NPs and the size distributions of (g) Fe_3O_4 , (h) $Fe_3O_4@SiO_2$ and (i) $Fe_3O_4@SiO_2$ -EDTA-Ni(0) NPs, respectively

coating with SiO₂, clear spherical shaped nanoparticles were observed and the Fe₃O₄@SiO₂ NPs become a bit more aggregated than those in Fe₃O₄ NPs (Figure 5e). Also, FE-SEM imaging of Fe₃O₄@SiO₂-EDTAcatalyst confirmed the spherical shape of Ni(0)nanoparticles with slight agglomeration (Figure 5f). Moreover, the particle size distribution histogram of Fe₃O₄, Fe₃O₄@SiO₂ and Fe₃O₄@SiO₂-EDTA-Ni(0) magnetic nanoparticles is centered at 12, 20, and 33 nm, respectively (Figure 5 g-i).

Energy-dispersive X-ray spectroscopy (EDX) analysis provides local information about various elements. EDX analysis of Fe_3O_4 @SiO₂-EDTA-Ni(0) shows the presence of elements C, N, O, Si, Fe and Ni in the catalyst (Figure 6A).

The magnetic properties of nanoparticles were measured at room temperature using VSM analysis (Fig. 6Bb). The results show that Fe_3O_4 and $Fe_3O_4@SiO_2$ -EDTA-Ni(0) have saturated magnetization values of 64.8 and 27.1 emu g⁻¹, respectively. Neither remanence nor

coercivity was observed indicating that these particles were superparamagnetic. The immobilizing of amorphous silica nanoparticles and organic compounds was observed in the reduction of the magnetic strength of composite on the account of weight contribution from the nonmagnetic portion (Figure 6B). It should be noted that the magnetization saturation value of Fe₃O₄@SiO₂-EDTA-Ni(0) is lower than that of Fe₃O₄, however, it still shows strong magnetization, which provided an easy and efficient route to separate nanoparticles from a suspension system using an external magnetic field (Figure 6C.) Accordingly, the magnetic separation was quickly fulfilled by supplying an external magnetic field and also, nanoparticles could be re-dispersed quickly with a slight shake once the magnetic field was removed.

It was studied the stability of the Fe_3O_4 @SiO₂-EDTA-Ni(0) nanoparticles using thermal gravimetric analyses (TGA) and their corresponding thermal decomposition curves are obtained as shown in Figure 7. The curves were identified by two regions of weight loss. The first



FIGURE 6 (A) EDS analysis of Fe_3O_4 @SiO₂-EDTA-Ni(0) MNPs; (B) Magnetization curves obtained by VSM at room temperature for (a) Fe_3O_4 @SiO₂-EDTA-Ni(0) NPs; (C) Separation of the magnetically supported catalyst by an external magnet



FIGURE 7 (A) Thermogravimetric analysis (TGA) of (a) $Fe_3O_4@SiO_2-NH_2$, (b) $Fe_3O_4@SiO_2-TCT$, (c) $Fe_3O_4@SiO_2-TCT$ - NH_2 and (d) $Fe_3O_4@SiO_2-EDTA-Ni(0)$ NPs

region that has occurred upon heating in the temperature range of 50–150 °C can be assigned to the desorbed water or other organic solvents had been applied in the preparation of nanocatalyst. In the second region, the observed major weight loss between 150–600 °C could be attributed to the decomposition of organic materials. In addition, according to the weight losses between 150 and 600 °C in the TGA curve of Fe₃O₄@SiO₂-EDTA-Ni(0) (Figure 7d), it is calculated that the content of organic compounds on the surface of Fe₃O₄@SiO₂ NPs is about 41.5 wt%. Furthermore, TGA shows that the catalyst has high thermal stability of over 150 °C.

Additionally, the Ni loading of the catalyst was confirmed by the ICP analyzer. For this purpose, the catalyst (1 g) was stirred in aq. HCl (37%), then the magnetic nanocomposite was separated by an external magnetic field and the remaining solution was analyzed by ICP to determine the content of nickel. The amount of Ni on the support was determined as (0.55) mmol per gram of the catalyst.

After the preparation of Nickel-based nanocatalyst, we initiated our efforts for the applicability of this catalyst in different coupling reactions. We began our investigations by examining the reactivity of phenyl carbamate (1a) with the phenylboronic acid (2a) under nickel catalysis as the model reaction for finding the best reaction conditions (Table 1). Before all, we found that when the phenyl carbamate was applied in the blank test, there was observed no homocoupling product based on GC and HPLC analyses. However, when the phenylboronic acid was used in the blank test, we observed insignificant amount of homocoupling product After that, various reaction parameters including the amount of catalyst, base, solvent, and temperature were screened. Firstly, the solvent effect in the model reaction was investigated (Table 1, entries 1-12). These studies showed that the best yield was observed when the ethylene glycol was used as the solvent (Table 1, entry 4). In the next step, to find the most effective base and also the amount of which, the model reaction was performed in the presence of various bases including, KOH, NaOH, NaO^tBu, K₃PO₄, K₂CO₃, Cs₂CO₃, DBU and DABCO (Table 1, entries 4, 13-23). Although all bases were effective to produce the desired product, the best result was obtained in the presence of KOH (2.0 mmol) (Table 1, entry 4). Subsequently, the model reaction was carried out with different amounts of the catalyst (Table 1, entries 24-27). In the absence of the catalyst, no product formation was observed even after 48 hr (Table 1, entry 24). This result indicates that the catalyst exhibits high catalytic activity in this transformation. It was found that 1 mol% of the catalyst was sufficient to catalyze the reaction efficiently

TABLE 1 Optimization Studies for Cross-Coupling of phenyl carbamate with phenylboronic acid^a



Entry	Catalyst (mol %)	Base (equiv.)	Solvent	Temp [°C]	Tim [h]	Yield (%) ^b
1	1	KOH (2.0)	H ₂ O	reflux	6	71
2	1	KOH (2.0)	Ethanol	reflux	6	73
3	1	KOH (2.0)	PrOH	reflux	6	78
4	1	KOH (2.0)	EG	120	6	93
5	1	KOH (2.0)	Propane-1,2-diol	120	6	79
6	1	KOH (2.0)	Glycerol	120	6	82
7	1	KOH (2.0)	Dioxane	reflux	6	54
8	1	KOH (2.0)	Toluene	reflux	6	59
9	1	KOH (2.0)	CH ₃ CN	reflux	6	42
10	1	KOH (2.0)	DMF	reflux	6	49
11	1	KOH (2.0)	DMSO	120	6	51
12	1	KOH (2.0)	NMP	120	6	44
13	1	NaOH (2.0)	EG	120	6	90
14	1	$NaO^{t}Bu(2.0)$	EG	120	6	89
15	1	K ₃ PO ₄ (2.0)	EG	120	6	78
16	1	K_2CO_3 (2.0)	EG	120	6	80
17	1	$Cs_2CO_3(2.0)$	EG	120	6	82
18	1	DBU (2.0)	EG	120	6	81
19	1	DABCO(2.0)	EG	120	6	78
20	1	КОН (1.0)	EG	120	6	63
21	1	KOH (1.5)	EG	120	6	81
22	1	КОН (2.5)	EG	120	6	93
23	1	КОН (3.0)	EG	120	6	92
24	-	КОН (2.0)	EG	120	48	0
25	0.5	КОН (2.0)	EG	120	6	64
26	1.5	КОН (2.0)	EG	120	6	92
27	2	KOH (2.0)	EG	120	6	93
28	1	КОН (2.0)	EG	80	6	73
29	1	КОН (2.0)	EG	100	6	79
30	1	КОН (2.0)	EG	140	6	89
31	1	КОН (2.0)	EG	120	4	78
32	1	КОН (2.0)	EG	120	8	93
33	1	KOH (2.0)	EG	120	12	93

^aReaction conditions: phenyl carbamate (1 mmol), phenylboronic acid (1 mmol), base, Ni catalyst, 3 ml of solvent. ^bIsolated yield.

and there was no progress in the reaction yields using more amounts of catalyst. Additionally, the time and temperature of the reaction were checked (Table 1, entries 28–33). According to these experiments, we determined the best reaction conditions to be aryl carbamates (1 mmol), aryl boronic acids (1 mmol), and KOH (2 mmol) in the presence of Ni-based catalyst (1 mol %) in ethylene glycol (3 ml) at 120 $^{\circ}$ C. In the next step, the effect of some available stable nickel (II) and nickel(0) catalysts such as NiBr₂, NiCl₂, Ni (OAc)₂, NiCl₂(dppe), NiCl₂(dppf), Ni (acac)₂, NiCl₂(PPh₃)₂, Ni (cod)₂, Ni[P (OPh)₃]₄ and Ni[P (OEt)₃]₄ were surveyed and evaluated in the model reaction in the optimized reaction conditions. Based on the results exhibited in Table 2, the reaction preceded well and afforded the coupling product but in lower yields. Moreover, the usage of Ni (II) catalysts instead of the Ni(0) catalysts in the model reaction at the same conditions leads to lower product yield.

In the next step, various derivatives of phenol-based electrophiles and phenyl halides have been successfully used in the same reaction conditions to show the further versatility of the catalytic system (Table 3).

Respecting to the observed data, howsoever, aryl methyl ether (Table 3, entry 4) as electrophile was not feasible under the present reaction conditions and it was observed low yields using iodobenzene as the substrate (Table 3, entry 1). The moderate results were obtained when bromobenzene, phenyl acetate, phenyl mesylate, phenyl tosylate and phenyl triflate as the coupling partners (Table 3, entries 2, 6, and 8–10). Although chlorobenzene, phenyl pivalate and *tert*-butyl phenyl carbonate provided smooth alkylation products in high yield (Table 3, entries 3, 5 and 7), the use of carbamate and

TABLE 2 Ni catalyst effect in cross-coupling reaction of phenyl carbamate with phenylboronic acid^a

	t ₂ (HO) ₂ B	$\Rightarrow \bigcirc_{3a} \bigcirc_{3a}$
Linu y	ViD:	Tielu (%)
1	NIBr ₂	/0
2	NiCl ₂	63
3	Ni (OAc) ₂	73
4	NiCl ₂ (dppe)	78
5	NiCl ₂ (dppf)	81
6	Ni (acac) ₂	56
7	NiCl ₂ (PPh ₃) ₂	77
8	Ni (cod) ₂	69
9	Ni[P (OPh) ₃] ₄	81
10	Ni[P (OEt) ₃] ₄	78
11	Ni(0) catalyst	93

^aReaction conditions: phenyl carbamate (1 mmol), phenylboronic acid (1 mmol), KOH (2 mmol), Ni catalyst (1 mol %), EG (3 ml), 120 $^{\circ}$ C, 6 hr. ^bIsolated yield.

TABLE 3 Survey of Halide and Pseudohalide Substrates^a

1×+ (HO) ₂ B	Ja Ja
Entry	Х	Yield (%) ^b
1	Ι	78
2	Br	48
3	Cl	24
4	OMe	trace
5	OPiv	83
6	OAc	54
7	OCO ₂ ^t Bu	81
8	OMs	56
9	OTs	60
10	OTf	51
11	OSO ₂ NEt ₂	89
12	OCONEt ₂	93

^aReaction conditions: phenol-based electrophile (1 mmol), phenylboronic acid (1 mmol), KOH (2 mmol), Ni catalyst (1 mol %), EG (3 ml), 120 °C, 6 hr. ^bIsolated yield.

sulfamate substrates are more attractive and desirable (Table 3, entries 11 and 12).

After identifying the optimized reaction conditions, we then examined the generality and limitations of aryl sulfamates, aryl carbamates and arylboronic acid derivatives in this reaction (Table 4).

At first, a library of aryl carbamates and sulfamates were investigated using phenylboronic acid as the partner of C-C coupling among optimized reaction conditions. As shown in Table 4, the derivatives of aryl carbamates and sulfamates bearing an electron-donating substituent such as methyl and methoxy groups exhibited very good compatibility and all of which showed excellent yields (Table 4, entries 3b-3c and 3e). It should be noted that aryl carbamate and sulfamate bearing ortho-methyl or -methoxy substituents could be effectively coupled to give the corresponding products in the satisfactory yields (Table 4, entries 3d and 3f). However, substrates with the electron-withdrawing groups including CN, NO₂, CHO and CH₃CO on the benzene ring can be also coupled to phenylboronic acid furnishing the desired products in high yields (Table 4, entries 3 g-3j). Additionally, the heterocyclic aryl carbamates and sulfamates could also be employed to afford the desired products in good to excellent yields (Table 4, entries 3 k-3 m). Furthermore, the generality of this coupling reaction with various arylboronic acids has been investigated. As it can be

Applied Organometallic_WILEY^{11 of 17} Chemistry

TABLE 4 The coupling of aryl carbamates and sulfamates with aryl boronic acids^a





^aReaction conditions: aryl carbamates or sulfamates (1 mmol), arylboronic acid (1 mmol), KOH (2 mmol), Ni catalyst (1 mol %, 0.018 g) EG (3 ml), 120 °C, 6 hr. ^bIsolated yield.

found in Table 4, arylboronic acids bearing electrondonating groups coupled smoothly with a variety of aryl carbamate and sulfamate substrates under the present catalytic system (Table 4, entries 3n-3r). To our disappointment, heteroaryl boronic acids are less reactive under the coupling conditions (Table 4, entries 3 s-3v). Unfortunately, when the reaction was performed using (4-fluorophenyl) boronic acid and (4-trifluoromethyl) boronic acid as the coupling partners, the desired products were obtained in significantly low yields (Table 4, entries 3w-3x).

Subsequently, observed highly effective results in the Suzuki-Miyaura cross-coupling convinced us to examine the performance of this catalytic system in Heck coupling reaction under the same reaction conditions. As expected, very interesting results were achieved in this study (Table 5).

As shown in Table 5, the electron-neutral, electronrich and electron-poor aryl carbamate and sulfamate react with styrene efficiently to produce corresponding coupled products in good to excellent yields (Table 5, entries 5a-5e); but when the heterocyclic carbamate and sulfamate were applied, the desired products were obtained in insignificantly lower yields (Table 5, entries 5f-5 h). The C-C cross-coupling reactions of phenyl carbamate and sulfamate were also studied among the diverse range of substituted olefins. The electron-poor and electron-rich styrene derivatives can easily take part in the Heck reactions with substituted alkenes affording the coupling products in excellent yields (Table 5, entries 5i-5 l). Besides, aliphatic olefins such as butyl acrylate and cyclohexene were investigated under the optimized conditions. Fortunately, aryl carbamates and sulfamates with both electron-withdrawing and electron-releasing substituents react with butyl acrylate to afford the expected coupling products in good to moderate yields. The same results were obtained in the case of heterocyclic carbamate and sulfamate (Table 5, entries 5 m-5 s). Unexpectedly, no product was formed in the reactions of cyclohexene with phenyl carbamate and sulfamate as in addition to using higher temperatures and more catalyst amounts presented (Table 5, entry 5 t).

In analogy with the data reported in the literature,^[43] there were proposed the plausible catalytic mechanisms for the Suzuki-Miyaura and Heck cross-coupling reactions in scheme 3. In the Suzuki-Miyaura mechanism, the catalytic cycle starts with the oxidative addition of Ni(0) to aryl carbamates or aryl sulfamates to generate the intermediate (2) in situ. This complex subsequently reacts with arylbronic acid in the transmetalation process to reach diaryl intermediate (3). Finally, the reductive elimination step probiaryl product and regenerated duces the the Ni(0) based nanocatalyst. It was also proposed the mechanism for the Heck cross-coupling reaction in the second circle in which the intermediate (2) will be afforded after passing the oxidative addition of aryl carbamates or aryl sulfamates to Ni(0). The addition of olefin moiety presents π -complex (4) and then, the formation of the complex (5) is considered after passing the σ -complex formation step. Finally, a reductive elimination in the intermediate (6) regenerates the active Ni(0) nanocatalyst in the presence of KOH.

In addition to all attractive features of this catalyst system that expressed in the past sections, other advantages of the catalyst are rapid and efficient separation by

Applied Organometallic_WILEY 13 of 17 Chemistry

TABLE 5 The coupling of aryl carbamates and sulfamates with olefins^a



^aReaction conditions: Aryl carbamates and sulfamates (1 mmol), olefins (1 mmol), KOH (2 mmol), Ni catalyst (1 mol %, 0.018 g) EG (3 ml) 120 °C, 6 hr. ^bIsolated yield.



SCHEME 3 Proposed mechanism for the Suzuki-Miyaura and Heck cross-coupling reactions in the presence of Fe₃O₄@SiO₂-EDTA-Ni(0) NPs

using an appropriate external magnet and using this catalyst for more runs. Therefore, the recyclability of this catalvst was examined in the model reaction under the optimized reaction conditions. After the completion of the reaction, the catalyst was recovered from the reaction mixture by magnetic separation, washed with ethyl acetate, dried at 80 °C and then, reused in the next run. As can be seen in Figure 8, after seven consecutive cycles. the catalyst did not exhibit any significant loss of catalytic activity.

14 of 17

The morphology and stability of the catalyst against the aggregation have been investigated after 7th run



FIGURE 8 Reuse of Fe₃O₄@SiO₂-EDTA- Ni(0) NPs in the model reaction

(Figure 9). As shown in Figure 9a and 9b, the TEM and FE-SEM images of recovered magnetic nanoparticles after the sixth cycle revealed that almost all Fe₃O₄@SiO₂-EDTA-Ni(0) particles are spherical in the shape as the same as fresh catalyst indicating that the aggregation of nanoparticles is venial. Moreover, the hydrodynamic diameter of the catalyst was studied by the DLS technique (Figure 9c) in which insignificant aggregation was observed for reused nanocatalyst and the size distribution is centered at around 37 nm.

Additionally, the catalyst was investigated by ICP analysis after the last run to determine the amount of nickel leaching. Accordingly, the amount of loaded nickel on the recovered catalyst was measured to be 0.54 mmol/g. Propitiously, the ICP analysis after the seventh run showed less than 1% leaching of nickel. Moreover, to determine the responsibility of nickel moiety for carrying out the model reaction, the hot filtration test was performed. When the reaction time of model reaction reached the half time of reaction quenching, the catalyst nanoparticles were taken out from the reaction mixture by an external magnetic field, the residue was allowed to stir under the reaction conditions. The monitoring of reaction mixture by TLC did not show any considerable progress. These results showed that only a few species of nickel may exist in the solution phase and the main responsible species that catalyzes the model reaction, is the Fe₃O₄@SiO₂-EDTA-Ni(0) nanoparticles. All of these data confirmed the high stability and reusability of the catalyst under these reaction conditions.



5 0 29 31 33 35 37 39 41 43

Diameter (nm)

FIGURE 9 TEM (a), FE-SEM (b) and DLS (c) images ofFe₃O₄@SiO₂-EDTA-Ni(0) after seventh recycling experiment

CONCLUSION 4

In summary, we have designed and developed a novel, effective, and eco-friendly nickel(0)-based catalyzed protocol for Suzuki-Miyaura and Heck couplings of phenol derivatives such as aryl carbamates and sulfamates which is stable and easy to prepare and manipulate. In the Applied Organometallic_WILEY Chemistry 15 of 17

synthetic point of view, these results open new possibilities for exploiting these reactions, since aryl carbamates and sulfamates can be prepared from cheap, green and easily available phenols as starting materials. Therefore, the attractive features and broad scopes of aryl sulfamates and carbamates in the C-C coupling reactions and simple workup make this methodology attractive to be applied in the various industries especially pharmaceuticals. This methodology is more attractive because it is very cheap compared with other commercially available palladiumbased catalysts. Besides, the absence of any external ligands especially phosphine ligands, not using reducing agents in the catalytic and high ability to be recovered and reused without losing efficiency are of other advantages of this catalytic system

ACKNOWLEDGMENTS

Authors gratefully acknowledge the financial support of this work by the Research Council of University of Shiraz.

ORCID

Iman Dindarloo Inaloo D https://orcid.org/0000-0003-0087-4210

REFERENCES

- [1] a) A. H. Cherney, N. T. Kadunce, S. E. Reisman, Chem. Rev. 2015, 115, 9587; b) F. S. Han, Chem. Soc. Rev. 2013, 42, 5270; c) W. Shi, C. Liu, A. Lei, Chem. Soc. Rev. 2011, 40, 2761; d) C. Liu, H. Zhang, W. Shi, A. Lei, Chem. Rev. 2011, 111, 1780; e) A. Taheri Kal Koshvandi, M. M. Heravi, T. Momeni, Appl. Organomet. Chem. 2018, 32, e4210.
- [2] a) A. Rudolph, M. Lautens, Angew. Chem. Int. Ed. Engl. 2009, 48, 2656; b) A. Piontek, E. Bisz, M. Szostak, Angew. Chem. Int. Ed. Engl. 2018, 57, 11116; c) L. J. Gooßen, G. Deng, L. M. Levy, Science 2006, 313, 662; d) J. Magano, J. R. Dunetz, Chem. Rev. 2011, 111, 2177; e) P. Devendar, R. Y. Qu, W. M. Kang, B. He, G. F. Yang, J. Agric, Food Chem. 2018, 66, 8914; f) M. S. Schiedel, C. A. Briehn, P. Bäuerle, J. Organomet. Chem. 2002, 653, 200.
- [3] a) D. J. Cardenas, Angew. Chem. Int. Ed. Engl. 2003, 42, 384; b) A. Suzuki, J. Organomet. Chem. 2002, 653, 83; c) L. Ackermann, Chem Commun. 2010, 46, 4866.
- [4] a) T. Y. Luh, M. K. Leung, K. T. Wong, Chem. Rev. 2000, 100, 3187; b) R. Jana, T. P. Pathak, M. S. Sigman, Chem. Rev. 2011, 111, 1417; c) N. Miyaura, T. Yanagi, A. Suzuki, Synth. Commun. 1981, 11, 513; d) N. Kambe, T. Iwasaki, J. Terao, Chem. Soc. Rev. 2011, 40, 4937; e) M. T. Chen, W. R. Wang, Y. J. Li, Appl. Organomet. Chem. 2019, 33, e4912; f) B. Bhattacharyya, J. P. Biswas, S. Mishra, N. Gogoi, Appl. Organomet. Chem. 2019, 33, e5017.
- [5] a) S. R. Dubbaka, P. Vogel, Angew. Chem. Int. Ed. Engl. 2005, 44, 7674; b) M. R. Netherton, G. C. Fu, Adv. Synth. Catal. 2004, 346, 1525; c) S. H. Cho, J. Y. Kim, J. Kwak, S. Chang, Chem. Soc. Rev. 2011, 40, 5068; d) T. Mesganaw, N. K. Garg, Org. Process Res. Dev. 2013, 17, 29; e) M. Pagliaro, V. Pandarus,

16 of 17 WILEY Organometallic

R. Ciriminna, F. Beland, P. Demma Carà, *ChemCatChem* **2012**, *4*, 432.

- [6] a) T. M. Shaikh, C. M. Weng, F. E. Hong, Coord. Chem. Rev. 2012, 256, 771; b) K. W. Quasdorf, M. Riener, K. V. Petrova, N. K. Garg, J. Am. Chem. Soc. 2009, 131, 17748; c) A. Ohtaka, J. M. Sansano, C. Nájera, I. Miguel-García, Á. Berenguer-Murcia, D. Cazorla-Amorós, ChemCatChem 2015, 7, 1841; d) Y. P. Budiman, A. Friedrich, U. Radius, T. B. Marder, ChemCatChem 2019. https://doi.org/10.1002/cctc.201901220; e) M. Gholinejad, Appl. Organomet. Chem. 2013, 27, 19; f) X. Lei, K. A. Obregon, J. Alla, Appl. Organomet. Chem. 2013, 27, 419.
- [7] a) M. Tobisu, T. Shimasaki, N. Chatani, Angew. Chem. Int. Ed. Engl. 2008, 47, 4866; b) X. J. Li, J. L. Zhang, Y. Geng, Z. Jin, J. Org. Chem. 2013, 78, 5078; c) I. D. Inaloo, S. Majnooni, Chem 2018, 42, 13249; d) B. Karimi, F. Mansouri, H. M. Mirzaei, ChemCatChem 2015, 7, 1736.
- [8] a) N. Yoshikai, H. Matsuda, E. Nakamura, J. Am. Chem. Soc.
 2009, 131, 9590; b) J. Wang, T. Qin, T. G. Chen, L. Wimmer, J. T. Edwards, J. Cornella, B. Vokits, S. A. Shaw, P. S. Baran, Angew. Chem. Int. Ed. Engl. 2016, 55, 9676; c) N. A. LaBerge, J. A. Love, Eur. J. Org. Chem. 2015, 2015, 5546.
- [9] a) D. Zim, V. R. Lando, J. Dupont, A. L. Monteiro, Org. Lett.
 2001, 3, 3049; b) X. H. Fan, L. M. Yang, Eur. J. Org. Chem.
 2010, 2457; c) A. R. Sardarian, I. D. Inaloo, A. R. Modarresi-Alam, Mol. Diversity 2018, 22, 863; d) H. Gao, Y. Li,
 Y. G. Zhou, F. S. Han, Y. J. Lin, Adv. Synth. Catal. 2011, 353, 309.
- [10] a) Z. Y. Tang, Q. S. Hu, J. Am. Chem. Soc. 2004, 126, 3058; b)
 M. Baghbanzadeh, C. Pilger, C. O. Kappe, J. Org. Chem. 2011, 76, 1507; c) G. J. Chen, F. S. Han, Eur. J. Org. Chem. 2012, 2012, 3575.
- [11] a) M. A. Huffman, N. Yasuda, Synlett 1999, 1999, 471;
 b) X. Liao, Z. Weng, J. F. Hartwig, J. Am. Chem. Soc. 2008, 130, 195;
 c) I. D. Inaloo, S. Majnooni, New J. Chem. 2019, 43, 11275.
- [12] a) H. Chen, Z. Huang, X. Hu, G. Tang, P. Xu, Y. Zhao,
 C. H. Cheng, J. Org. Chem. 2011, 76, 2338; b) Y. Nan, Z. Yang,
 Tetrahedron Lett. 1999, 40, 3321; c) L. Liu, S. Zhang, H. Chen,
 Y. Lv, J. Zhu, Y. Zhao, Chem. Asian J. 2013, 8, 2592.
- [13] a) J. Y. Yu, R. Kuwano, Org. Lett. 2008, 10, 973; b) R. Kuwano,
 M. Yokogi, Org. Lett. 2005, 7, 945; c) I. Dindarloo Inaloo,
 S. Majnooni, ChemistrySelect 2019, 4, 7811.
- [14] a) L. Xu, B. J. Li, Z. H. Wu, X. Y. Lu, B. T. Guan, B. Q. Wang, K. Q. Zhao, Z. J. Shi, Org. Lett. 2010, 12, 884; b) M. R. Harris, L. E. Hanna, M. A. Greene, C. E. Moore, E. R. Jarvo, J. Am. Chem. Soc. 2013, 135, 3303; c) A. R. Sardarian, I. D. Inaloo, RSC Adv. 2015, 5, 76626; d) A. R. Modarresi-Alam, I. D. Inaloo, E. Kleinpeter, J. Mol. Struct. 2012, 1024, 156.
- [15] a) K. W. Quasdorf, A. Antoft-Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus, N. K. Garg, J. Am. Chem. Soc. 2011, 133, 6352; b) K. W. Quasdorf, X. Tian, N. K. Garg, J. Am. Chem. Soc. 2008, 130, 14422; c) I. D. Inaloo, S. Majnooni, ChemistrySelect 2018, 3, 4095; d) L. Chen, H. Lang, L. Fang, M. Zhu, J. Liu, J. Yu, L. Wang, Eur. J. Org. Chem. 2014, 2014, 4953; e) X. H. Fan, L. M. Yang, Eur. J. Org. Chem. 2011, 2011, 1467.
- [16] a) E. Gandolfo, X. Tang, S. Raha Roy, P. Melchiorre, Angew. Chem. Int. Ed. Engl. 2019. https://doi.org/10.1002/anie.

201910168; b) T. G. Chen, H. Zhang, P. K. Mykhailiuk,
R. R. Merchant, C. A. Smith, T. Qin, P. S. Baran, *Angew. Chem. Int. Ed. Engl.* 2019, 58, 2454; c) V. Murugesan,
V. Balakrishnan, R. Rasappan, J. Catal. 2019, 377, 293;
d) B. H. Shih, R. S. Basha, C. F. Lee, *ACS Catal.* 2019, 9, 8862;
e) R. Sun, Y. Qin, S. Ruccolo, C. Schnedermann, C. Costentin,
D. G. Nocera, J. Am. Chem. Soc. 2018, 141, 89.

- [17] a) Z. T. Ariki, Y. Maekawa, M. Nambo, C. M. Crudden, J. Am. Chem. Soc. 2017, 140, 78; b) Y. A. Ho, M. Leiendecker, X. Liu, C. Wang, N. Alandini, M. Rueping, Org. Lett. 2018, 20, 5644; c) J. E. Russell, E. D. Entz, I. M. Joyce, S. R. Neufeldt, ACS Catal. 2019, 9, 3304.
- [18] a) M. S. Hofmayer, F. H. Lutter, L. Grokenberger, J. M. Hammann, P. Knochel, *Org. Lett.* 2018, *21*, 36; b) J. Tang, L. Lv, X. J. Dai, C. C. Li, L. Li, C. J. Li, *Chem Commun.* 2018, 54, 1750; c) T. Hostier, Z. Neouchy, V. Ferey, D. Gomez Pardo, J. Cossy, *Org. Lett.* 2018, *20*, 1815.
- [19] a) C. Xu, W. H. Guo, X. He, Y. L. Guo, X. Y. Zhang, X. Zhang, *Nat. Commun.* 2018, *9*, 1170; b) Y. Yamazaki, N. Arima, T. Iwai, M. Sawamura, *Adv. Synth. Catal.* 2019, *361*, 2250; c) L. Guo, W. Srimontree, C. Zhu, B. Maity, X. Liu, L. Cavallo, M. Rueping, *Nat. Commun.* 2019, *10*, 1957; d) Y. Monguchi, K. Sakai, K. Endo, Y. Fujita, M. Niimura, M. Yoshimura, T. Mizusaki, Y. Sawama, H. Sajiki, *ChemCatChem* 2012, *4*, 546.
- [20] a) Q. Hu, H. Li, L. Wang, H. Gu, C. Fan, *Chem. Rev.* 2018, 119, 6459; b) J. A. Darr, J. Zhang, N. M. Makwana, X. Weng, *Chem. Rev.* 2017, 117, 11125; c) Y. Gu, W. Sun, G. Wang, N. Fang, *J. Am. Chem. Soc.* 2011, 133, 5720; d) A. R. Sardarian, I. D. Inaloo, A. R. Modarresi-Alam, E. Kleinpeter, U. Schilde, *J. Org. Chem.* 2019, 84, 1748.
- [21] a) H. Nambu, I. Shimokawa, T. Fujiwara, T. Yakura, *Asian J. Org. Chem.* 2016, *5*, 486; b) L. Rodriguez-Arco, I. A. Rodriguez, V. Carriel, A. B. Bonhome-Espinosa, F. Campos, P. Kuzhir, J. D. G. Duran, M. T. LopezLopez, *Nanoscale* 2016, *8*, 8138.
- [22] G. Simonsen, M. Strand, G. Øye, J. Pet. Sci. Eng. 2018, 165, 488.
- [23] a) S. Mornet, S. Vasseur, F. Grasset, E. Duguet, *J. Mater. Chem.* **2004**, *14*, 2161; b) C. Alexiou, R. Jurgons, C. Seliger, H. Iro, *J. Nanosci. Nanotechnol.* **2006**, *6*, 2762; c) Y. Zhu, L. P. Stubbs,
 F. Ho, R. Liu, C. P. Ship, J. A. Maguire, N. S. Hosmane, *ChemCatChem* **2010**, *2*, 365.
- [24] a) A.-H. Lu, E. L. Salabas, F. Schuth, Angew. Chem. Int. Ed. 2007, 46, 1222; b) Y. Ren, H. Zhang, B. Chen, J. Cheng, X. Cai, R. Liu, G. Xia, W. Wu, S. Wang, J. Ding, C. Gao, Int. J. Nanomed. 2012, 7, 2261.
- [25] a) T. Hyeon, Chem. Commun. 2003, 8, 927; b) G. Reiss,
 A. Hütten, Nat. Mater. 2005, 4, 725.
- [26] a) V. F. Cardoso, A. Francesko, C. Ribeiro, M. Bañobre-López, P. Martins, S. Lanceros-Mendez, *Adv. Healthcare Mater.* 2017, *7*, 1700845; b) N. Lee, T. Hyeon, *Chem. Soc. Rev.* 2012, *41*, 2575.
- [27] a) L. Sarma, N. Aomoa, T. Sarmah, S. Sarma, A. Srinivasan, G. Sharma, A. Gupta, V. R. Reddy, B. Satpati, D. N. Srivastava, S. Deka, L. M. Pandey, M. Kakat, J. Alloys Compd. 2018, 749, 768; b) J. Gao, H. Gu, B. Xu, Acc. Chem. Res. 2009, 42, 1097.
- [28] a) Y. Hu, S. Wang, Z. Guo, Y. Hu, H. Xie, *ChemElectroChem* **2018**, 5, 2449; b) T. A. Rocha-Santos, *Chem* **2014**, *62*, 28.

- [29] a) C. P. Park, D.-P. Kim, Angew. Chem., Int. Ed. 2010, 49, 6825;
 b) P. Tartaj, T. Gonzmlez-Carreæo, C. J. Serna, Adv. Mater. 2001, 13, 1620.
- [30] a) P. Hu, J. V. Morabito, C.-K. Frank Tsung, ACS Catal. 2014,
 4, 4409; b) I. D. Inaloo, S. Majnooni, M. Esmaeilpour, Eur. J. Org. Chem. 2018, 2018, 3481.
- [31] a) Y. Li, H. Chen, J. Wu, Q. He, Y. Li, W. Yang, Y. Zhou, *Appl. Surf. Sci.* 2018, 447, 393; b) D. Kim, N. Lee, M. Park, B. Y. Kim, K. An, T. Hyeon, *J. Am. Chem. Soc.* 2009, 131, 454.
- [32] Y. Hu, J. Li, Z. Zhang, H. Zhang, L. Luo, S. Yao, Anal. Chim. Acta 2011, 698, 61.
- [33] Q. Gao, D. Luo, J. Ding, Y.-Q. Feng, J. Chromatogr. A. 2010, 1217, 5602.
- [34] P. Hojati-Talemi, J. Azadmanjiri, G. P. Simon, *Mater. Lett.* 2010, 64, 1684.
- [35] J. Zhang, W. Sun, L. Bergman, J. M. Rosenholm, M. Lindén, G. Wu, H. Xu, H.-C. Gu, *Mater. Lett.* **2012**, *67*, 379.
- [36] H. Chen, C. Deng, X. Zhang, Angew. Chem. Int. Ed. 2010, 49, 607.
- [37] F. Ke, L. G. Qiu, Y. P. Yuan, X. Jiang, J. F. Zhu, J. Mater. Chem. 2012, 22, 9497.
- [38] Z. Chang, Z. Wang, J. Yue, H. Xing, L. Li, M. Ge, M. Li, H. Yan, H. Hu, D. Shao, Q. Xu, D. Jin, W.-F. Dong, ACS Appl. Mater. Interfaces 2018, 10, 10656.
- [39] a) J. Wang, S. Zheng, Y. Shao, J. Liu, Z. Xu, D. Zhu, J. Colloid Interface Sci. 2010, 349, 293; b) H. L. Ding, Y. X. Zhang, S. Wang, J. M. Xu, S. C. Xu, G. H. Li, Chem. Mater. 2012, 24, 4572; c) Y. Deng, D. Qi, C. Deng, X. Zhang, D. Zhao, J. Am. Chem. Soc. 2008, 130, 28.
- [40] a) E.-Y. Jeong, M. B. Ansari, S.-E. Park, ACS Catal. 2011, 1, 855; b) M. Shokouhimehr, Y. Piao, J. Kim, Y. Jang, T. Hyeon, Angew. Chem. Int. Ed. 2007, 46, 7039.

- [41] a) A. R. Sardarian, M. Zangiabadi, I. D. Inaloo, *RSC Adv.* 2016, 6, 92057; b) A. R. Sardarian, I. D. Inaloo, M. Zangiabadi, *New J. Chem.* 2019, 43, 8557; c) I. DindarlooInaloo, S. Majnooni, *Eur. J. Org. Chem.* 2019, 6359; d) M. Esmaeilpour, S. Zahmatkesh, N. Fahimi, M. Nosratabadi, *Appl. Organomet. Chem.* 2018, 32, e4302.
- [42] a) T.-Y. Yung, L.-Y. Huang, T.-Y. Chan, K.-S. Wang, T.-Y. Liu, P.-T. Chen, C.-Y. Chao, L.-K. Liu, *Nanoscale Res. Lett.* 2014, *9*, 444; b) D. Özhava, N. Z. Kılıcaslan, S. Özkar, *Appl. Catal. B Environ.* 2015, *162*, 573.
- [43] a) J. Y. Song, Y. Liu, H. Y. Zhao, H. T. Han, Z. F. Li,
 W. H. Guo, W. Y. Chu, Z. Z. Sun, New J. Chem. 2017, 41, 12288; b) Ö. Metin, S. Özkar, J. Mol. Catal. Chem. 2008, 295, 39; c) Z. Li, L. Liu, Chin. J. Catal. 2015, 36, 3.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Dindarloo Inaloo I, Majnooni S, Eslahi H, Esmaeilpour M. Air-Stable Fe₃O₄@SiO₂-EDTA-Ni(0) as an Efficient Recyclable Magnetic Nanocatalyst for Effective Suzuki-Miyaura and Heck Cross-Coupling via Aryl Sulfamates and Carbamates. *Appl Organomet Chem.* 2020;e5662. <u>https://doi.org/10.1002/aoc.</u> 5662