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Full Paper

High Catalytic Activity of Peptide Nanofibres Decorated with Ni and Cu Nanoparticles for the Synthesis of 5-Substituted 1*H*-Tetrazoles and *N*-Arylation of Amines

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A rapid development of a new methodology for decarboxylative *N*-arylation of carboxylic acids and the preparation of 5-substituted 1*H*-tetrazoles catalysed by peptide nanofibres decorated with Cu and Ni nanoparticles is presented. Compared with conventional aryl halides, benzoic acids are extremely interesting and environmentally friendly options for the synthesis of secondary aryl amines.

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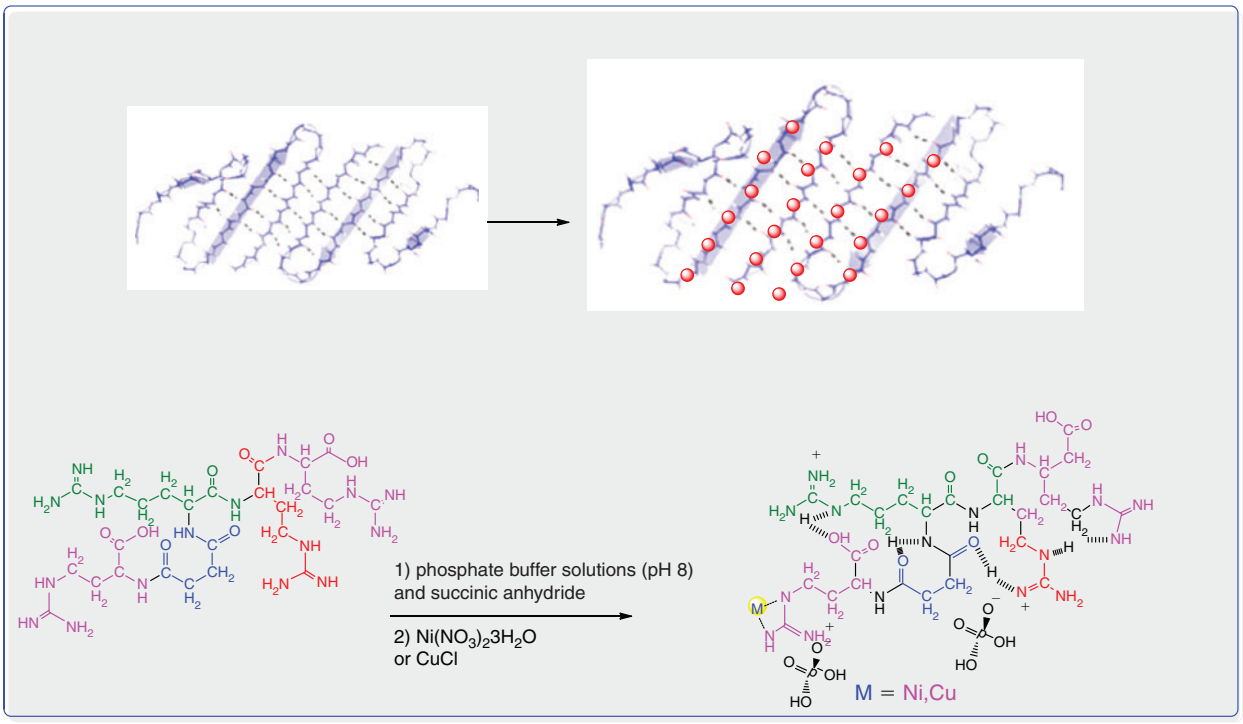
Introduction

The development of mild and general procedures for C–N bond formation via *N*-arylation coupling reactions catalysed by transition metals has attracted significant attention in recent years.[1–4] On the other hand, nickel-catalysed *N*-arylation reactions have received less attention. There is still a growing interest to use inexpensive copper and nickel catalysts instead of costly effective palladium catalysts (including toxic phosphate-containing ligands) for C–N bond formation. In addition, when the term '*N*-arylation chemistry' is stated, the fundamental concern is the use of aryl halides or arylboronic acids as electrophiles, which catalytically react with amines in the presence of transition metals. However, aryl halides present several problems, such as needing stoichiometric amounts of catalyst,



Scheme 1. Schematic synthesis of Ni and Cu nanoparticles supported on the peptide nanofibre.

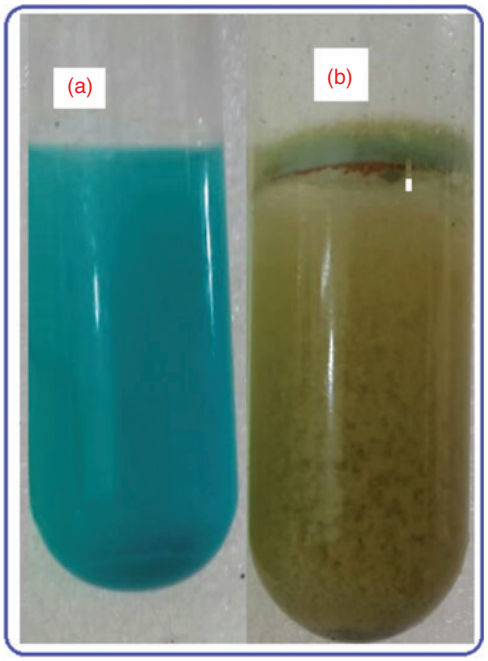


Fig. 1. (a) Phosphate buffer solution containing peptide nanofibre and CuCl (pH 8 by adding succinic anhydride which the final pH of the solution was found to be 7). (b) Phosphate buffer solution containing CuCl (pH 7 without adding succinic anhydride).

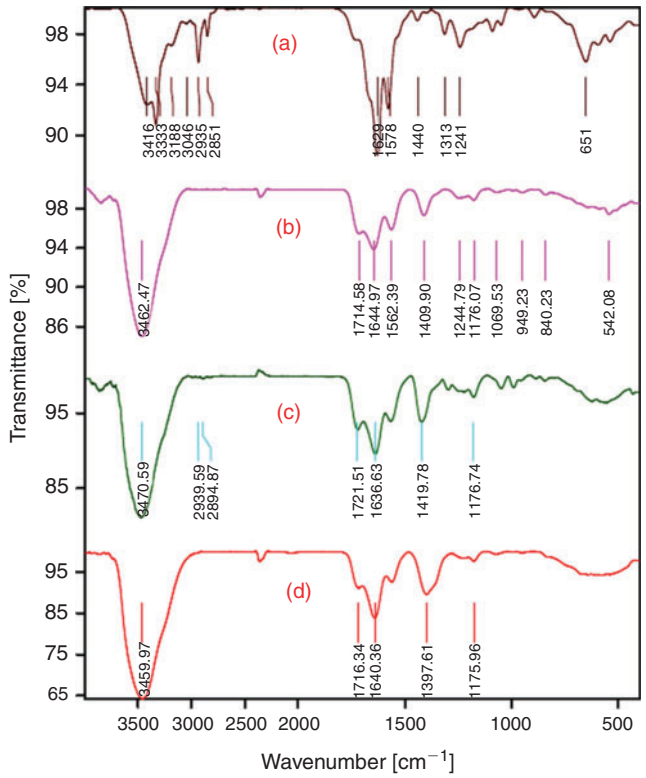


Fig. 2. FT-IR spectra of (a) peptide powder, (b) peptide nanofibre, (c) peptide nanofibres decorated with Cu nanoparticles, and (d) peptide nanofibres decorated with Ni noparticles.

high temperature reaction media, being environmental pollutants, producing by-products that need isolation and purification processes of the desired products.[5] Although aryl halides are

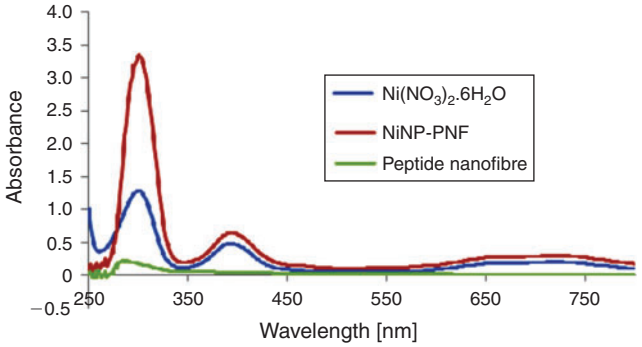


Fig. 3. UV-Visible absorption spectra for $Ni(NO_3)_2{\cdot}6H_2O$, peptide nanofibre, and NiNP-PNF.

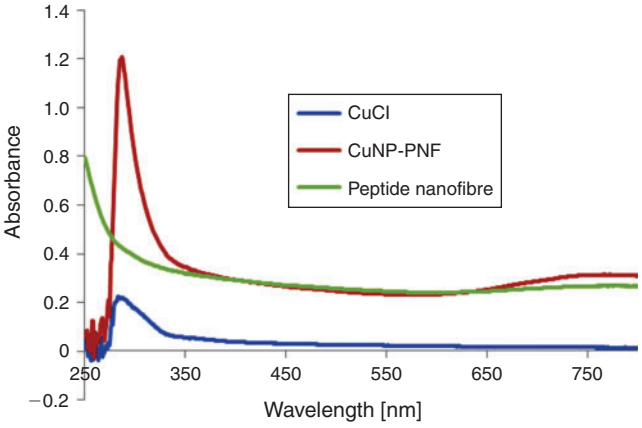


Fig. 4. UV-Visible absorption spectra for CuCl, peptide nanofibre, and CuNP-PNF.

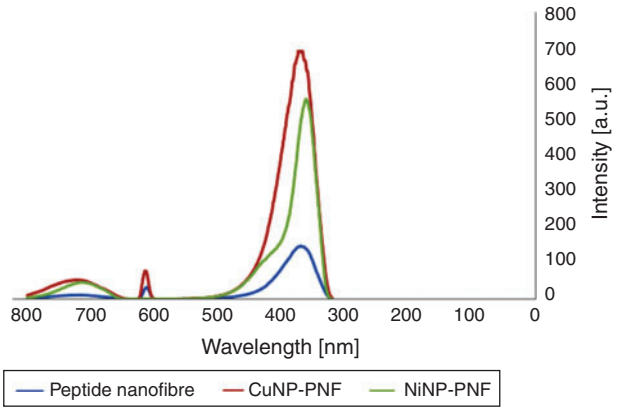


Fig. 5. Fluorescence spectra of peptide nanofibre and NiNP-PNF and CuNP-PNF.

still the main substrates to the intended *N*-arylation products, boronic acids likewise have attracted broad attention for this aim. Unfortunately use of these compounds are also accompanied with some drawbacks such as: the tricoordinate nature of these compounds makes them highly moisture sensitive, to minimise atmospheric oxidation and autoxidation, they should be stored under an inert atmosphere, and their reaction needs isolation and purification because of the formation of boroxines that are easily produced by the simple dehydration of boronic acids.[6] Therefore, in order to overcome the above mentioned drawbacks there is still a great interest to find a new electrophilic

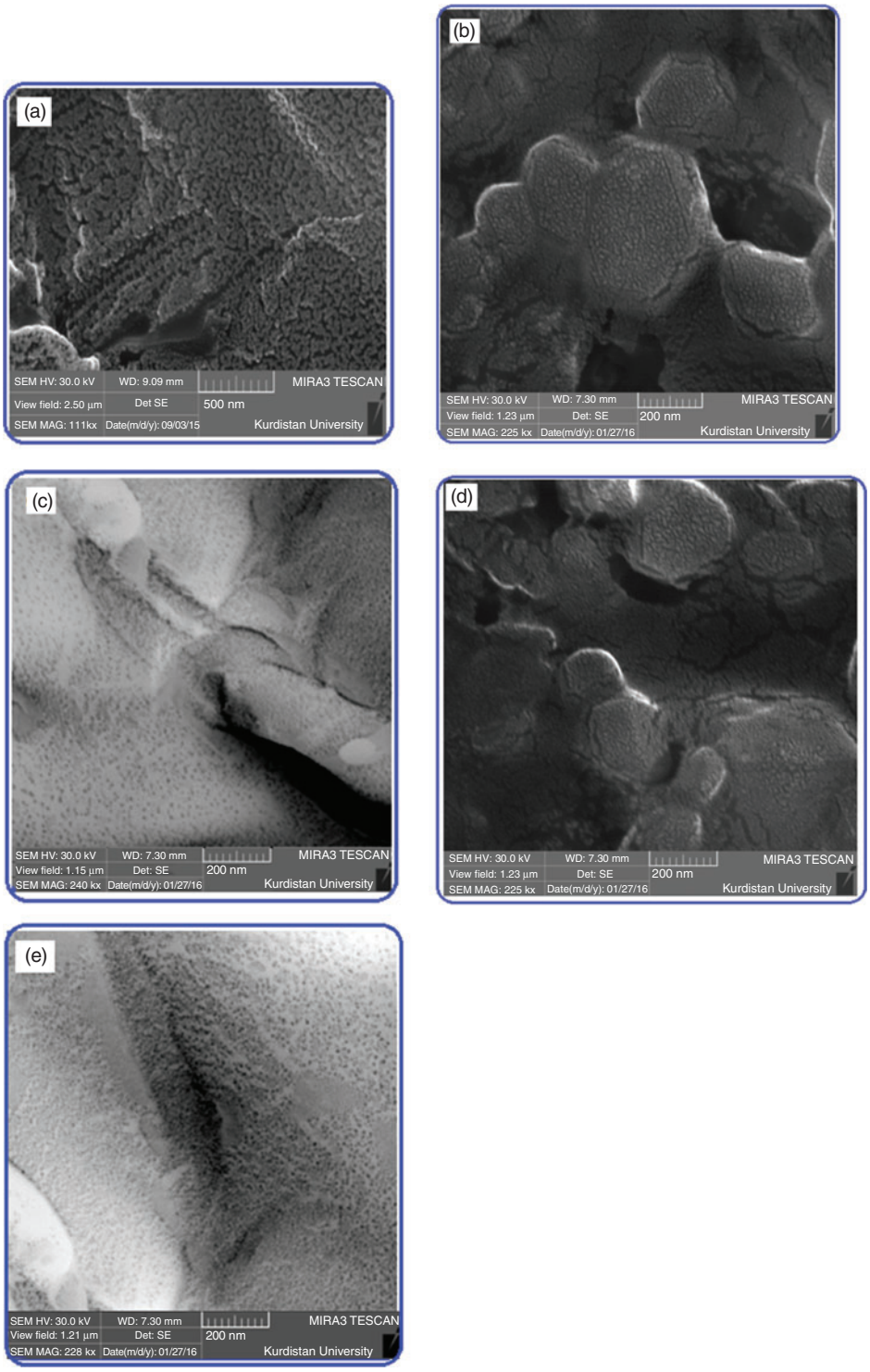
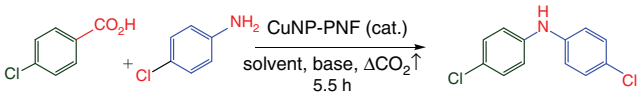


Fig. 6. SEM images of (a) peptide nanofibre, (b, c) immobilised Ni nanoparticles and (d, e) immobilised Cu nanoparticles on the surface of the woven nanofibers.

reagent. Among nitrogen-containing heterocyclic compounds, 1*H*-tetrazoles are a class of synthetic organic compounds that have been widely studied due to their wide range of applications in photography and information recording systems,[7] pharmaceutical syntheses,[8] etc. So far, several procedures have been introduced for the synthesis of 5-substituted 1*H*-tetrazoles. The most important approaches are: (i) condensation of hydrazoic acid with isocyanides,[9] (ii) the addition of sodium nitrite to amino guanidines,[10] (iii) the three-component reaction of primary amines with sodium azide and triethyl orthoformate,[11] and (iv) reaction of sodium azide to carbodiimides.[12] In general, the most versatile method used for the synthesis of 5-substituted 1*H*-tetrazoles is based on [3 + 2] cycloaddition of the azide ion and organic nitriles in the presence of a catalyst such as $AgNO_3$,[13] SiO_2–H_3BO_3,[14] BF_3–OEt_2,[15] $Zn(OTf)_2$,[16] Pd-2A3HP-MCM-41 (Pd-(0)-2-amino-3-hydroxypyridine grafted onto mesoporous

Table 1. Optimisation of the reaction conditions for the C–N coupling reaction in the presence of CuNP-PNF



Entry[A]	Solvent	Temp. [°C]	Base	Base [mmol]	Yield [%]
1	DMSO	130	KOH	7	90
2	DMF	130	KOH	7	N.R.
3	PEG	130	KOH	7	N.R.
4	H_2O	130	KOH	7	N.R.
5	DMSO	130	–	–	N.R.
6	DMSO	130	K_2CO_3	7	N.R.
7	DMSO	130	Na_2CO_3	7	N.R.
8	DMSO	130	Et_3N	7	N.R.
9	DMSO	100	KOH	7	23
10	DMSO	80	KOH	7	N.R.
11	DMSO	130	KOH	5	51
12	DMSO	130	KOH	2	23
13	DMSO	130	KOH	7	11[B]

[A]Reaction conditions: benzoic acid (1.3 mmol), amine (3 mmol), CuNP-PNF (200 µL), and solvent (3 mL). N.R. = no reaction.
[B]Reaction catalysed with CuCl in the absence of peptide nanofibre.

MCM-41),[17] Fe_3O_4@SiO_2@L-arginine,[18] $AlCl_3$,[19] $CdCl_2$,[20] and montmorillonite.[21]

Recently, considerable attention has been given to the design and immobilisation of different catalysts on various supports, such as polymeric and inorganic materials, including zeolites,[22] metal oxides,[23] mesoporous silica,[24] activated carbon,[25] carbon nanotubes,[26] and peptide nanofibres (PNFs).[27] Among these supports, PNFs are the best choice due to their unique properties such as a high surface area-to-volume ratio.[28] Among the applications of PNFs, their catalytic applications in organic reactions have attracted broad attention; hence, as a part of our research program towards the utility of PNFs, herein we report the preparation of Cu nanoparticles (NPs) and Ni NPs immobilised on PNFs, which were used as catalysts for the decarboxylative *N*-arylation of substituted benzoic acids as well as the synthesis of 5-substituted 1*H*-tetrazoles. Decarboxylation of carboxylic acids by loss of carbon dioxide (as a green and completely non-toxic by-product) has recently emerged as a promising coupling agent in organic synthesis such as for the formation of a bond between an aryl ring and an sp^2 carbon,[29] and for the formation of carbon–sulfur bonds via a palladium–copper-catalyzed decarboxylative cross-coupling reaction between a 2-substituted arene carboxylic acid and a thiol or a disulfide in the presence of an electron-withdrawing group on the arene carboxylic acid.[30] Recently decarboxylative etherification has been reported, for which the desired products have been achieved only for substrates with σ-electron-withdrawing substituents.[31] It is particularly noteworthy that amide bonds are typically formed from the reaction of amines and pre-activated carboxylic acid derivatives such as acid chlorides. Zhang also reported direct *N*-arylation of aryl carboxylic acids with *ortho*, *meta*, or *para*-electron-withdrawing groups with amines.[32] In a recent publication we reported the synthesis of PNFs using arginine as a building block (Scheme 1) and we showed that a self-assembled peptide was formed at pH 7.[27] The PNF's features led us to investigate the activity of nanofibres with Cu and Ni ions as an effective catalyst for the decarboxylative *N*-arylation of substituted benzoic acids as well as for the synthesis of 5-substituted 1*H*-tetrazoles. The PNFs were used as templates for the synthesis of NPs and Fig. 1 shows their effect on NP formation.

Results and Discussion

Characterisation of Supported Cu and Ni NPs on the PNFs

The interactions between the PNF and Ni and Cu NPs were investigated by IR spectroscopy, fluorescence spectroscopy, ultraviolet-visible (UV-vis) spectroscopy, and scanning electron microscopy (SEM) techniques.

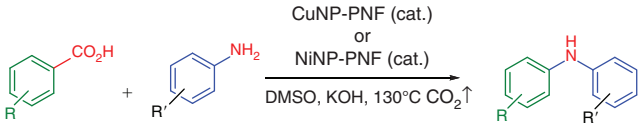
Fig. 2 shows a typical FTIR spectrum of the PNF (CuNP-PNF and NiNP-PNF). In the spectra (Fig. 2a) the peak at 1644 cm^{-1} corresponds to the bending vibration of NH groups for the PNF while this peak for CuNP-PNF and NiNP-PNF shifted to 1635 and 1640 cm^{-1}, respectively. The lowering in this frequency in the PNF indicates coordination of the nitrogen with metal. UV-Vis absorption spectroscopy is the most widely used method for characterising the optical properties of NPs. Figs 3 and 4 show the UV-vis absorption spectra of a PNF, CuCl, $Ni(NO_3)_2{\cdot}6H_2O$, CuNP-PNF, and NiNP-PNF. The adsorption of metal on the PNF could be invoked to explain the increase of the UV absorption and the peak shape changes. The visible spectra of the NiNP-PNF and CuNP-PNF show a maximum absorption compared with the free PNF and metallic salts. This may be due to a d–d electron transition or charge-transfer transition.[33] Also, enhancement of fluorescence through complexation could be observed (Fig. 5). In the absence of metal ions the fluorescence of the ligand is probably quenched by the occurrence of a photoinduced electron transfer (PET) process due to the presence of lone pairs of electrons of the donor atoms in the ligand, thus the fluorescence intensity may be greatly enhanced by the coordination with metals (Ni or Cu). The chelation of the ligand to metals increases the rigidity of the ligand and thus reduces the loss of energy by thermal vibrational decay.[34] The SEM images show that the Cu and Ni NPs were regularly immobilised on the surface of woven PNFs (Fig. 6).

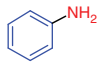
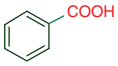
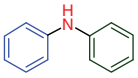
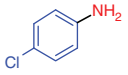
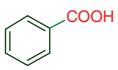
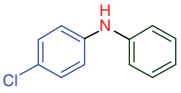
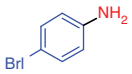
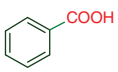
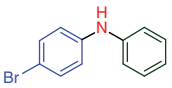
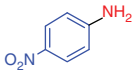
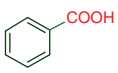
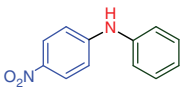
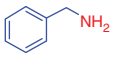
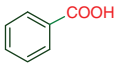
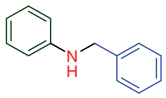
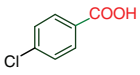
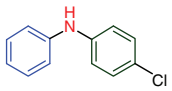
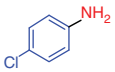
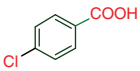
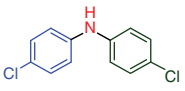
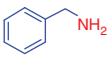
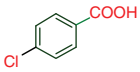
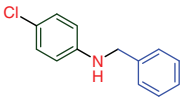
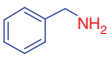
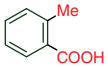
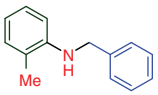
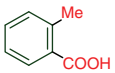
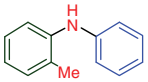
Catalytic Studies

After the preparation and characterisation of Cu and Ni NPs supported on the PNF, the catalytic activity of these compounds was investigated for the synthesis of secondary amines from the reaction of carboxylic acids and amines. In this study, a direct synthesis of aliphatic and aromatic amines via combination of carboxylic acids and amines in the presence of PNFs decorated with Cu and/or Ni NPs without production of amide as by-product has been presented. Initially, the reaction of 4-chlorobenzoic acid with 4-chloroaniline in the presence of Cu NPs supported on the PNF as a catalyst was selected as a model reaction, and different parameters including the type of base, solvent, and temperature were optimised (the results are summarised in Table 1). It was found that the influence of base type and solvent significantly affect the performance of a reaction. The reaction rate was also increased by increasing the reaction temperature. It is noteworthy that the reaction was also conducted in the presence of CuCl without PNF, and the observed yield of product was very low.

With optimal conditions in hand, a variety of secondary amines was synthesised using a combination of benzoic acid and amine at 130°C (Table 2).

Table 2. Synthesis of secondary amines via reaction of substituted benzoic acids and amines catalysed by Cu or NiNP-PNF in DMSO



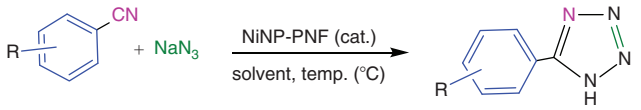
Entry[A]	Amine	Acid	Product	Time [h]		Yield [%][B]	
				Ni	Cu	Ni	Cu
1				6	5	85	80
2				9	8.5	65	75
3				15	14	55	65
4				3	2	75	78
5				5	5	44	53
6				10	8.5	75	88
7				5.5	5	90	90
8				4.5	4.5	38	45
9				9	7.5	45	43
10				20	18	53	57

[A]Reaction conditions: benzoic acids (1.3 mmol), amine (3 mmol), CuNP-PNF (200 µL), KOH (7 mmol), and DMSO (3 mL).
[B]Isolated pure product.

One of the important aspects of this methodology is the successful reaction of sterically hindered benzoic acids and amines; for example 2-methyl benzoic acid gives the desired products in good yield. Meanwhile, *ortho*-substituted benzoic acids require longer reaction times and give relatively lower product yields than *para*-substituted. The obtained results from Table 2 showed that the *N*-arylation reaction in the presence of CuNP-PNF in comparison with NiNP-PNF proceeds more rapidly and efficiently. A suggested mechanism for the decarboxylative C–N cross-coupling reaction is outlined in Scheme 2.

In order to further investigate the catalytic activities of these two new catalysts, the synthesis of 5-substituted 1*H*-tetrazole was studied as well. Initially, the reaction of 2-hydroxy-benzonitrile with sodium azide in the presence of Ni NPs supported on the

Table 3. Optimisation of the reaction conditions for the synthesis of 1,5-tetrazole



Entry[A]	Solvent	Temp. [°C]	Catalyst [µL]	Time [h]	Yield [%]
1	DMSO	120	200	30 min	80
2	DMF	120	200	50 min	65
3	H_2O	120	200	1	N.R.
4	PEG	120	200	20 min	90
5	PEG	100	200	1	90
6	PEG	80	200	2	66
7	PEG	120	100	20 min	40

[A]Reaction conditions: sodium azide (1.2 mmol), 2-hydroxy-benzonitrile (1 mmol), NiNP-PNF (200 µL), solvent (2 mL). N.R. = no reaction.

PNF as a catalyst was selected as a model reaction and different parameters including the solvent type and temperature were considered to develop the scope of this reaction further and the results are summarised in Table 3. After optimising the reaction conditions, it is worth noting that, among the examined organic solvents (H_2O, DMSO, DMF, polyethylene glycol (PEG)) we found that PEG gave the desired product in a good yield under heating at 120°C for 20 min (Table 3, entry 4). Also, the reaction rate was increased by increasing the reaction temperature. To understand the scope and effectiveness of the catalyst (PNFs decorated with Ni or Cu NPs) different substituted benzonitriles (Table 4) were selected and used under the determined conditions. Results show that benzonitriles containing electron-donating groups, such as 2-hydroxy-benzonitrile, gave very good yields in a shorter reaction time than electron-withdrawing containing ones (Table 4, entry 10), probably because of the chelating effect of the hydroxy group to the copper or nickel catalyst, which facilitated the catalysis to the desired product. On the other hand, the reaction yields were sensitive to steric effects on the benzonitriles. The sterically hindered *ortho*-substituted benzonitriles were proved to be problematic for this catalytic system and produced the corresponding products with much longer times (Table 4, entries 1, 2, 3).

The obtained optimised conditions for the Ni catalyst were applied for the synthesis of a variety of 5-substituted 1*H*-tetrazoles synthesised using sodium azide (1.2 mmol) and a nitrile compound (1 mmol) in the presence of CuNP-PNF at 120°C (Table 4). As it can be seen from Table 4, CuNP-PNF is more effective in comparision with NiNP-PNF.

The details of the reaction mechanism are not clear at this time, but one simple hypothesis is presented in Scheme 3. The first step involves coordination of the nitrile nitrogen atoms to Ni or Cu to form complex **A**, which accelerates the cyclisation step. It seems that the [3 + 2] cycloaddition between the two metal-coordinated C≡N bonds of the nitrile compound and azide ion takes place readily to form the intermediate **B**. Finally, acidic work-up affords desired products **C** and **D** (Scheme 2).

The recoverability and reusability of the Ni NP supported on the PNF in an *N*-arylation reaction over four successive runs, was investigated (see Experimental). It was found that NiNP-PNF could be reused multiple times without a significant decrease in its catalytic activity (Fig. 7).

Comparison of Catalysts

To evaluate the catalytic activity of PNFs decorated with Ni and Cu NPs, we compared the results for the synthesis of 5-(4-bromophenyl)-1*H*-tetrazole and diphenylamine in the presence of these catalysts with previously reported procedures (Tables 5 and 6). This catalyst leads to a good reaction time and higher yield than other reported catalysts. More importantly, compared with other catalysts, NiNP- and CuNP-PNF are easily prepared and can be reused four times without any significant loss of their activity.

Conclusions

In summary, we demonstrate an effective route for the C–N cross coupling reaction via decarboxylative *N*-arylation of substituted carboxylic acids without use of halocarbon precursors. The synthesis of substituted tetrazoles has also been studied. Copper and nickel as cost effective and non-toxic metals immobilised on woven peptide nanofibres are successfully applied to catalyse the described reactions.

Experimental

Instrumentation

NMR spectra were acquired on a Bruker Avance III 400 MHz. Melting points were measured with an Electrothermal 9100 apparatus. The particles size and morphology were investigated by a JEOL JEM-2010 scanning electron microscope on an accelerating voltage of 200 kV. Vertex 70 Fourier-transform infrared (FT-IR), Varian Cary 300 Bio UV-Vis, and Varian Cary spectrofluorimeter spectrometers were used for analysis of PNFs, CuCl, $Ni(NO_3)_2{\cdot}6H_2O$, CuNP-PNF, and NiNP-PNF which were studied at room temperature in aqueous solution.

Preparation of PNFs

The PNFs were prepared by a published procedure.[27]

Synthesis of NiNP-PNFs

PNF (30.14 mg, 0.04 mmol) was dissolved in 0.2 mL of doubly distilled water and 0.8 mL of phosphate buffer solution (pH 8) was added. The solution was then sonicated for a few minutes. This mixture was stirred overnight at 80°C. In the next step Ni $(NO_3)_2{\cdot}3H_2O$ (6.5 mg, 0.02 mmol) was added to the reaction mixture and stirred for 12 h at 80°C to obtain NiNP-PNF quantitatively.

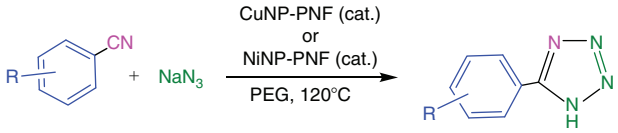
Synthesis of CuNP-PNFs

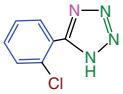
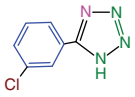
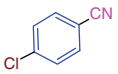
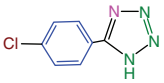
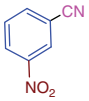
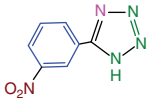
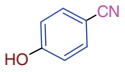
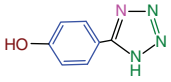
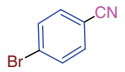
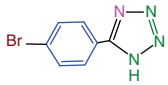
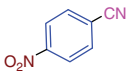
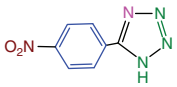
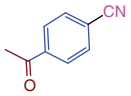
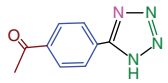
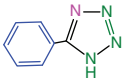
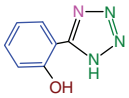
PNF (30.14 mg, 0.04 mmol) was dissolved in 0.2 mL of doubly distilled water and 0.8 mL phosphate buffer solution (pH 8). The solution was then sonicated for a few minutes. The reaction was allowed to continue at 80°C overnight. In the next step CuCl (2.2 mg, 0.02 mmol) was added to the reaction mixture and heated to 80°C for 12 h to obtain CuNP-PNF quantitatively.

General Procedure for the Synthesis of 1,5-Substituted Tetrazoles

To a stirred mixture of sodium azide (1.2 mmol) in PEG-400 (2 mL), a nitrile compound (1 mmol) and NiNP-PNF (200 µL) were added and heated at 120°C under atmospheric conditions. The reaction progress was monitored by TLC. Upon reaction completion, the mixture was allowed to cool to ambient temperature and then filtered and extracted with ethyl acetate. The

Table 4. Synthesis of tetrazoles catalysed by NiNP- or CuNP-PNF in PEG



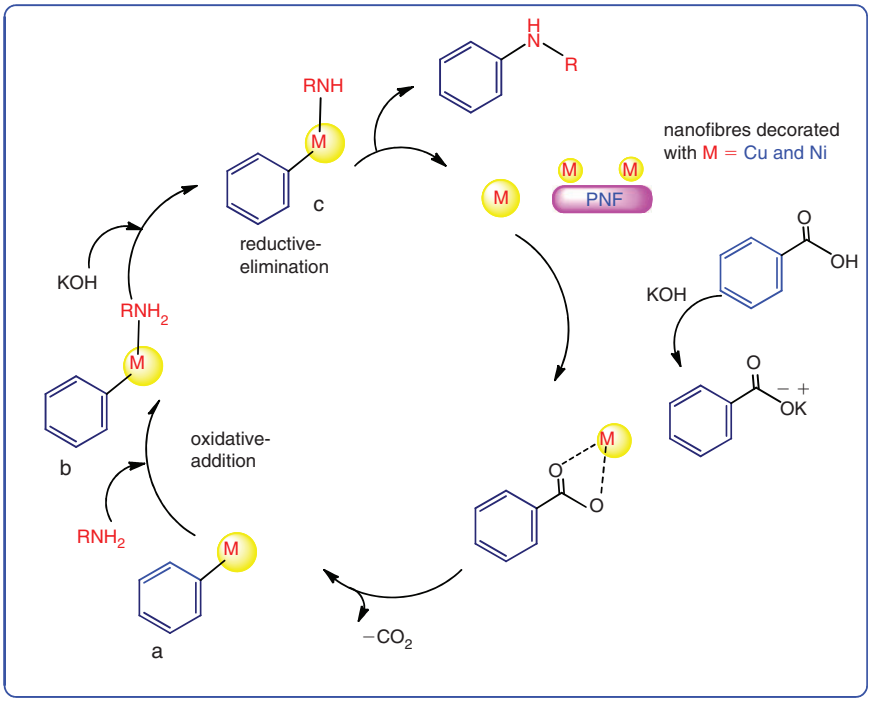
Entry[A]	Nitrile compound	Product	Time [h]		Yield [%][B]	
			Cu	Ni	Cu	Ni
1			7	3.5	71	75
2			6	3	85	90
3			3	2	90	95
4			8	5	75	93
5			6.5	2	82	95
6			3	4.5	90	85
7			8.5	8	80	73
8			10	8	78	73
9			4	2.5	90	95
10			20 min	15 min	85	87

[A]Reaction conditions: sodium azide (1.2 mmol), nitrile compound (1 mmol), CuNP- or NiNP-PNF (200 μL), and PEG (2 mL).
[B]Pure isolated yield.

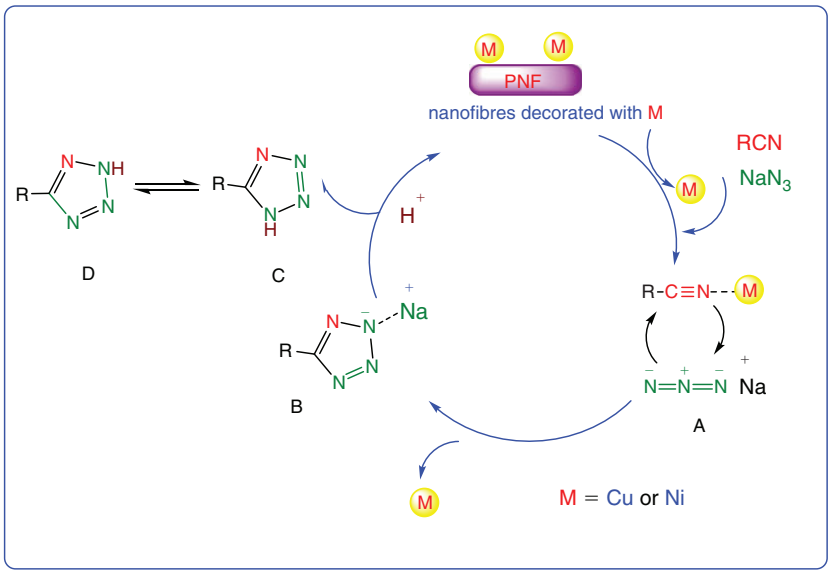
organic layer was washed with 1 N HCl, dried with anhydrous Na_2SO_4, and filtered to afford pure 5-substituted tetrazoles.

General Procedure for the Synthesis of Secondary Amines

The reaction was conducted at 130°C in DMSO (3 mL) with substituted amine (3 mmol), substituted benzoic acid (1.3 mmol), KOH (7 mmol), and 200 μL of the solution containing CuNP- or NiNP-PNF. The progress of the reaction was monitored by TLC. After reaction completion, the mixture was cooled to room temperature and was extracted with ethyl acetate (2 × 20 mL). The organic extract was washed twice with water and dried with anhydrous Na_2SO_4, and then filtered and the solvent was evaporated to give the corresponding aryl amine. The crude product was purified by preparative TLC.



Scheme 2. Proposed mechanism for the synthesis of secondary amines through cross-coupling reaction of benzoic acids with amines catalysed by peptide nanofibres decorated with Cu or Ni nanoparticles.



Scheme 3. Proposed mechanism for the synthesis of 5-substituted tetrazole catalysed by peptide nanofibres decorated with Ni or Cu nanoparticles.

4-Chloro-N-phenylaniline (Table 2, entry 3)

The title compound was obtained as a colourless solid. Mp 69.0°C (lit. 62–63°C[44]), δ_H (300 MHz, $CDCl_3$) 7.82–7.68 (m, 1H), 7.55–7.50 (m, 1H), 7.39–7.30 (m,4H), 7.1–6.90 (m,1H), 6.71 (s, 1H).

4-Bromo-N-phenylaniline (Table 2, entry 3)

The title compound was obtained as a pale yellow solid, mp 87–89°C (lit. 88°C[45]), δ_H (400 MHz, $CDCl_3$) 7.91–7.93 (d, *J* 8, 2H), 7.53–7.55 (t, *J* 8.2, 2H), 4.41–7.43 (d, *J* 8, 2H), 7.10–7.12 (t, *J* 5.2, 1H), 7.70–7.72 (t, *J* 8, 2H), 5.33 (br s, 1H, NH).

N-Benzylaniline (Table 2, entry 5)

The title compound was obtained as a colourless oil,[46] δ_H (400 MHz, $CDCl_3$) 7.66–7.68 (m, 4H), 7.33–7.38 (m, 6H), 3.72 (s, 2H), 3.44 (br s, 1H, NH).

2-Methyl-N-phenylaniline (Table 2, entry 9)

The title compound was obtained as a yellow oil,[47] δ_H (400 MHz, $CDCl_3$) 7.49–7.58 (m, 6H), 7.28–7.30 (m, 3H), 6.89 (br s, 1H, NH), 1.61 (s, 3H). δ_C (100 MHz, $CDCl_3$) 151.7, 150.2, 131, 129.1, 128.7, 127.4, 122.9, 120.5. ν_{max} (KBr)/cm^{-1} 3450,

3199, 3078, 2925, 2857, 1583, 1427, 1369, 1222, 1147, 1084, 1004.

Diphenylamine (Table 2, entry 1)

The title compound was obtained as a pale yellow solid, mp 54°C (lit. 52–53°C[48]), δ_H (400 MHz, $CDCl_3$) 7.95–7.97 (d, *J* 7.3, 2H), 7.49–7.56 (m, 2H), 7.29 (br s, 1H, NH). δ_C (100 MHz, $CDCl_3$) 150.2, 139.7, 139.5, 129.7126.2, 124.7, 121.9, 113.7. ν_{max} (KBr)/cm^{-1} 3695, 3059, 2925, 2857, 1581, 1453, 1294, 1216, 1150, 1069, 1015, 921, 771, 687, 525.

4-Nitro-N-phenylaniline (Table 2, entry 4)

The title compound was obtained as a yellow solid, mp 135–136°C (lit. 132–135°C[49]), δ_H (400 MHz, $CDCl_3$) 8.14–8.16 (d, *J* 8.7, 2H),7.42–7.44 (t, *J* 7.2, 2H), 7.23–7.25 (m, 3H), 6.96–6.98 (d, *J* 9.2, 2H), 6.36 (br s, 1H). δ_C (100 MHz, $CDCl_3$) 150.2, 139.8, 139.5, 129.8, 126.3, 124.7, 121.9, 113.7.

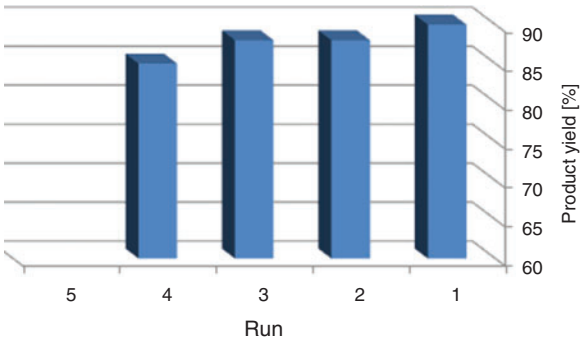


Fig. 7. Reusability of the Ni (II) immobilized on peptide nanofibre for the synthesis of bis (p-chlorophenyl) amine.

ν_{max} (KBr)/cm^{-1} 3508, 3101, 2919, 2854, 2690, 2617, 2547, 1608, 1521, 1439, 1346, 1156, 1101, 1024, 991, 951, 854, 721.

Bis(4-chlorophenyl)amine (Table 2, entry 7)

The title compound was obtained as a yellow solid, mp 77–78°C. (lit. 77°C[49]), δ_H (400 MHz, DMSO) 7.39 (d, *J* 7.6, 2H, ArH), 7.17 (d, *J* 7.6, 2H, ArH), 4.29 (s, 1H). ν_{max} (KBr)/cm^{-1} 3437, 2925, 2857, 1600, 1500, 1391, 1330, 1133, 1084, 831, 713, 540.

N-Benzyl-2-methylbenzenamine (Table 2, entry 7)

The title compound was obtained as a yellow solid, mp 57–60°C (lit. 59–60°C[50]). δ_H (300 MHz, $CDCl_3$) 7.94–7.88 (m, 4H), 7.74–7.68 (m, 1H), 7.61–7.40 (m, 1H), 4.20 (s, 2H), 2.3 (s, 3H).

5-(3-Chlorophenyl)-1H-tetrazole (Table 4, entry 2)

The title compound was obtained as a white solid, mp 132–134°C (lit. 137°C[51]), δ_H (400 MHz, DMSO) 8.07 (m, 1H), 8.01–8.04 (m, 1H), 7.63–7.60 (m, 2H), 6.13 (s, 1H).

5-(3-Nitrophenyl)-1H-tetrazole (Table 4, entry 4)

The title compound was obtained as a white solid, mp 149–151°C (lit. 154–156°C[51]), δ_H (400 MHz, DMSO) 8.82 (s, 1H), 8.44–8.4 (m, 1H), 7.10 (d, *J* 7.2, 1H), 7.89 (t, *J* 8, 1H). ν_{max} (KBr)/cm^{-1} 3852, 3308, 3085, 2975, 2894, 2752, 1621, 1524, 1348, 1243, 1156, 1076, 1011, 912, 865, 819, 727.

5-(4-Bromophenyl)-1H-tetrazole (Table 4, entry 6)

The title compound was obtained as a white solid, mp 265°C (lit. 264°C[52]), δ_H (400 MHz, DMSO) 7.97–8.00 (m, 2H), 7.82–7.86 (m, 2H). ν_{max} (KBr)/cm^{-1} 3443, 2956, 2923, 2861, 2766, 1601, 1423, 1317, 1152, 1055, 998, 734.

Table 5. Comparison of CuNP- and NiNP-PNF for the synthesis of 5-(4-Bromophenyl)-1*H*-tetrazole with previously reported procedures

Entry	Catalyst	Solvent	Yield [%][A]	Time [h]	Ref.
1	MCMBSA	DMF	78	12	[35]
2	Cu^{II} immobilized on Fe_3O_4@SiO_2@L-arginine	PEG	95	3	[18]
3	copper(I) chloride	DMF	90	12	[36]
4	nano-$TiCl_4.SiO_2$	DMF	91	2	[37]
5	$AlCl_3$ on γ-Al_2O_3	DMF	96	1.5	[38]
6	CuNP-PNF	PEG	95	2	This work
7	NiNP-PNF	PEG	90	3	This work

[A]Isolated yields.

Table 6. Comparison of CuNP- and NiNP-PNF for the synthesis diphenylamine with previously reported procedures

Entry	Catalyst	Phenylating reagent	Solvent	Base	Yield [%][A]	Temp. [°C]	Time [h]	Ref.
1	CuI	PhI	DMF	K_2CO_3	79	110	20	[39]
2	$Pd(OAc)_2$	$PhGeMe_3$	toluene	NaOAc	83	100	10	[40]
3	CuI (Ligand)	PhI	DMSO	K_3PO_4	94	80	17	[41]
4	Ni $(cod)_2$	Aryl imidazolylsulfonates	DMF	NaOt-Bu	94	105	16	[42]
5	Cu^{II}TMHD	PhI	toluene	KOtBu,	94	120	1.5	[43]
6	CuNP-PNF	benzoic acid	DMSO	KOH	80	120	6	This work
7	NiNP-PNF	benzoic acid	DMSO	KOH	85	120	5	This work

[A]Isolated yields.

5-(4-Nitrophenyl)-1H-tetrazole (Table 2, entry 3)

The title compound was obtained as a yellow solid, mp 214–217°C (lit. 218°C[52]), δ_H (500 MHz, DMSO) 8.55 (d, *J* 8.8, 1H), 8.29 (d, *J* 8.65, 1H). ν_{max} (KBr)/cm^{-1} 3508, 3101, 2967, 2919, 2854, 2547, 1646, 1608, 1521, 1349, 1156, 1101, 1024, 991, 721, 696.

5-Phenyl-1H-tetrazole (Table 2, entry 8)

The title compound was obtained as a white solid, mp 225–227°C (lit. 214–216°C[52]), δ_H (500 MHz, DMSO) 8.04–8.02 (m, 2H), 7.61–7.57 (m, 3H).

2-(1H-Tetrazol-5-yl) phenol (Table 4, entry 10)

The title compound was obtained as a white solid, mp 224°C (lit. 224–225°C[51]), δ_H (400 MHz, DMSO) 8.00–8.02 (m, 1H), 7.40–7.44 (m, 1H), 7.08–7.11 (m, 1H), 6.99–7.03 (m, 1H), 11.10 (br, 1H), 15.73 (br, 1H).

Recoverability and Reusability of NiNP-PNF

The reaction was performed in DMSO at 130°C, using 4-chlorobenzoic acid (1.3 mmol), 4-chloroaniline (3 mmol), and KOH (7 mmol) in the presence of NiNP-PNF (200 µL). Upon completion of the reaction, the mixture was cooled to room temperature. The organic layer was extracted with ethyl acetate (2 × 20 mL), which led to the precipitation of NiNP-PNF. The resulting precipitate was washed with ethyl acetate (2 × 20 mL) and dried before being used in the next run.

Conflicts of Interest

The authors declare no conflicts of interest.

Acknowledgement

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References

[1] J. Safaei-Ghomi, Z. Akbarzadeh, B. Khojastehbakht-Koopaei, *RSC Adv.* **2015**, *5*, 28879. doi:10.1039/C5RA01915J
[2] K. Karami, N. Haghighat Naeini, *Turk. J. Chem.* **2015**, *39*, 1199. doi:10.3906/KIM-1502-86
[3] P. Ruiz-Castillo, S. L. Buchwald, *Chem. Rev.* **2016**, *116*, 12564. doi:10.1021/ACS.CHEMREV.6B00512
[4] N. Barot, S. B. Patel, H. Kaur, *J. Mol. Catal. Chem.* **2016**, *423*, 77. doi:10.1016/J.MOLCATA.2016.06.009
[5] M. Mondal, S. K. Bharadwaj, U. Bora, *New J. Chem.* **2015**, *39*, 31. doi:10.1039/C4NJ01293C
[6] A. P. Liesen, A. T. Silva, J. C. Sousa, P. H. Menezes, R. A. Oliveira, *Tetrahedron Lett.* **2012**, *53*, 4240. doi:10.1016/J.TETLET.2012.06.011
[7] T. Habu, N. Mii, K. Kuge, H. Manto, Y. Takamuki, *J. Imaging Sci.* **1991**, *35*, 202.
[8] A. H. Davulcu, D. D. McLeod, J. Li, K. Katipally, A. Littke, W. Doubleday, Z. M. Xu, C. W. McConlogue, C. J. Lai, M. Gleeson, M. Schwinden, R. L. Parsons, *J. Org. Chem.* **2009**, *74*, 4068. doi:10.1021/JO9003508
[9] D. M. Zimmerman, R. A. Olofson, *Tetrahedron Lett.* **1969**, *10*, 5081. doi:10.1016/S0040-4039(01)88889-4
[10] W. G. Finnegan, R. A. Henry, E. Lieber, *J. Org. Chem.* **1953**, *18*, 779. doi:10.1021/JO50013A002
[11] D. Habibi, M. Nasrollahzadeh, L. Mehrabi, S. Mostafaee, *Monatsh. Chem.* **2013**, *144*, 725. doi:10.1007/S00706-012-0871-9
[12] A. R. Kazemizadeh, N. Hajaliakbarib, R. Hajianb, N. Shajaria, A. Ramaza, *Helv. Chim. Acta* **2012**, *95*, 594. doi:10.1002/HLCA.201100327
[13] P. Mani, A. K. Singh, S. K. Awasthi, *Tetrahedron Lett.* **2014**, *55*, 1879. doi:10.1016/J.TETLET.2014.01.117
[14] M. Parveen, F. Ahmad, A. M. Malla, S. Azaz, *New J. Chem.* **2015**, *39*, 2028. doi:10.1039/C4NJ02079K
[15] A. Kumar, R. Narayanan, H. Shechter, *J. Org. Chem.* **1996**, *61*, 4462. doi:10.1021/JO952269K
[16] S. Hajra, D. Sinha, M. Bhowmick, *J. Org. Chem.* **2007**, *72*, 1852. doi:10.1021/JO062432J
[17] M. Nikoorazm, A. Ghorbani-Choghamarani, M. Khanmoradi, *Appl. Organomet. Chem.* **2016**, *30*, 705. doi:10.1002/AOC.3494
[18] A. Ghorbani-Choghamarani, L. Shiri, G. Azadi, *RSC Adv.* **2016**, *6*, 32660.
[19] D. Habibi, M. Nasrollahzadeh, Y. Bayat, *Synth. Commun.* **2011**, *41*, 2135. doi:10.1080/00397911.2010.497728
[20] G. Venkateshwarlu, A. Premalatha, K. C. Rajanna, P. K. Saiprakash, *Synth. Commun.* **2009**, *39*, 4479. doi:10.1080/00397910902917682
[21] A. N. Chermahini, A. Teimouri, F. Momenbeik, A. Zarei, Z. Dalirnasab, A. Ghaedi, M. Roosta, *J. Heterocycl. Chem.* **2010**, *47*, 913. doi:10.1002/JHET.382
[22] M. Zaarour, M. El Roz, B. Dong, R. Retoux, R. Aad, J. Cardin, C. Dufour, F. Gourbilleau, J.-P. Gilson, S. Mintova, *Langmuir* **2014**, *30*, 6250. doi:10.1021/LA5006743
[23] R. Kou, Y. Shao, D. Mei, Z. Nie, D. Wang, C. Wang, J. Liu, *J. Am. Chem. Soc.* **2011**, *133*, 2541. doi:10.1021/JA107719U
[24] C. M. Crudden, M. Sateesh, R. Lewis, *J. Am. Chem. Soc.* **2005**, *127*, 10045. doi:10.1021/JA0430954
[25] M. Egashira, H. Takatsuji, S. Okada, J. Yamaki, *J. Power Sources* **2002**, *107*, 56. doi:10.1016/S0378-7753(01)00980-6
[26] B. Xue, P. Chen, Q. Hong, J. Lin, K. L. Tan, *J. Mater. Chem.* **2001**, *11*, 2378. doi:10.1039/B100618P
[27] A. Ghorbani-Choghamarani, Z. Taherinia, *RSC Adv.* **2016**, *6*, 9410.
[28] S. Zhang, *Biotechnology* **2004**, *22*, 151.
[29] H. Zhao, Y. Wei, J. Xu, J. Kan, W. Su, M. Hong, *J. Org. Chem.* **2011**, *76*, 882. doi:10.1021/JO102175F
[30] Z. Duan, S. Ranjit, P. Zhang, X. Liu, *Chem. – Eur. J.* **2009**, *15*, 3666. doi:10.1002/CHEM.200900133
[31] S. Bhadra, W. Dzik, L. Gooßen, *Angew. Chem. Int. Ed* **2013**, *52*, 2959. doi:10.1002/ANIE.201208755
[32] Y. Zhang, S. Patel, N. Mainolfi, *Chem. Sci.* **2012**, *3*, 3196. doi:10.1039/C2SC20606D
[33] W. Xin, D. Zhu, G. Liu, Y. Hua, W. Zhou, *Int. J. Photoenergy* **2012**, *2012*, 767905. doi:10.1155/2012/767905
[34] C. Anitha, C. D. Sheela, P. Tharmaraj, R. Shanmugakala, *Int. J. Inorg. Chem.* **2012**, *2012*, 7.
[35] A. Najafi Chermahini, M. K. Omran, H. A. Dabbagh, G. Mohammadnezhad, A. Teimouri, *New J. Chem.* **2015**, *39*, 4814. doi:10.1039/C5NJ00211G
[36] I. Esirden, E. Basar, M. Kaya, *Chem. Pap.* **2015**, *69*, 1231. doi:10.1515/CHEMPAP-2015-0124
[37] L. Zamani, B. B. F. Mirjalili, K. Zomorodian, S. Zomorodian, S. Afr, *J. Chem.* **2015**, *68*, 133.
[38] H. M. Nanjundaswamy, H. Abrahamse, *Heterocycles* **2014**, *89*, 2137. doi:10.3987/COM-14-13048
[39] X. Guo, H. Rao, H. Fu, Y. Jiang, Y. Zhao, *Adv. Synth. Catal.* **2006**, *348*, 2197. doi:10.1002/ADSC.200606198
[40] Q. Zhang, C. Liu, J. Shi, Q. Xu, L. Jin, C. Zhao, T. Zhang, *Synlett* **2016**, *27*, 1945. doi:10.1055/S-0035-1562104
[41] R. A. Altman, K. W. Anderson, S. L. Buchwald, *J. Org. Chem.* **2008**, *73*, 5167. doi:10.1021/JO8008676
[42] L. Ackermann, R. Sandmann, W. Song, *Org. Lett.* **2011**, *13*, 1784. doi:10.1021/OL200267B
[43] N. S. Nandurkar, M. J. Bhanushali, M. D. Bhor, B. M. Bhanage, *Tetrahedron Lett.* **2007**, *48*, 6573. doi:10.1016/J.TETLET.2007.07.009

[44] M. A. Carroll, R. A. Wood, *Tetrahedron* **2007**, *63*, 11349. doi:10.1016/J.TET.2007.08.076
[45] L. Rout, P. Saha, S. Jammi, T. Punniyamurthy, *Adv. Synth. Catal.* **2008**, *350*, 395. doi:10.1002/ADSC.200700480
[46] F. Y. Kwong, A. Klapars, S. L. Buchwald, *Org. Lett.* **2002**, *4*, 581. doi:10.1021/OL0171867
[47] P. Spagnolo, P. Zanirato, *J. Chem. Soc., Perkin Trans. 1* **1988**, 2615. doi:10.1039/P19880002615
[48] H. Rao, H. Fu, Y. Jiang, Y. Zhao, *J. Org. Chem* **2005**, *70*, 8107. doi:10.1021/JO051221W
[49] D. Maiti, B. P. Fors, J. L. Henderson, Y. Nakamura, S. L. Buchwald, *Chem. Sci.* **2011**, *2*, 57. doi:10.1039/C0SC00330A
[50] S. Miyano, N. Abe, A. Uno, *Chem. Pharm. Bull.* **1966**, *14*, 731. doi:10.1248/CPB.14.731
[51] M. Abdollahi Alibeik, A. Moaddeli, *New J. Chem.* **2015**, *39*, 2116. doi:10.1039/C4NJ01042F
[52] M. Zarghani, B. Akhlaghinia, *RSC Adv.* **2015**, *5*, 87769. doi:10.1039/C5RA16236J