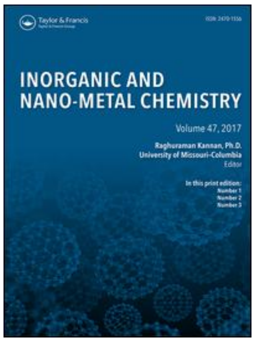

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SHORT COMMUNICATION

Synthesis and characterization of copper nanoparticles on walnut shell for catalytic reduction and C-C coupling reaction

Asghar Zamani[a], Ahmad Poursattar Marjani[b], Abbas Nikoo[b], Mojtaba Heidarpour[a], and Ahmad Dehghan[a]

[a]Department of Nanotechnology, Urmia University, Urmia, Iran; [b]Department of Organic Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran

ABSTRACT
Walnut shell-stabilized copper nanoparticles (CuNP/WS) were successfully prepared by a simple reaction of copper sulfate and Sodium borohydride. Formation of copper nanoparticles in this bio-nanocomposite was observed by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscope (EDX). CuNP/WS was found to be an efficient, inexpensive, easy to prepare, green and reusable catalyst in the reduction of aromatic nitro and nitrile compounds to their corresponding amines with $NaBH_4$ at 35 °C in aqueous medium. We continued our studies on the application of this nanocomposite in the classic Ullman reaction to synthesize biaryl. This method has the advantages of high yields, elimination of expensive stabilizer and homogeneous catalysts, simple methodology and easy work up. The catalyst can be recovered from the reaction mixture and reused several times without any significant loss of catalytic activity.

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Nanocatalysis; nitros and nitriles; Ullman reaction; biomass; green synthesis

Introduction

The catalytic hydrogenation of nitroarenes and nitriles to the corresponding amines is one of the most fundamental transformations because of the wide-spread application of amine containing structures as important building blocks of agrochemicals, dyes, polymers, rubbers, pharmaceuticals, photographic developers and corrosion inhibitors.[1] The conventional routes for the reduction of nitroarenes and nirtiles proceed through chemical reductions that many of these processes use gaseous hydrogen at a high pressure and temperature,[2,3] or harmful mineral acids.[4,5] Noteworthy is that the chemoselectivity of these methods in the presence of other functional groups is the critical challenge.[6] Thus, from the standpoint of environmental and economic concerns, catalytic reduction with safer reducing agents is the preferred approach, especially heterogeneous catalyst system.[7–9]

On the other hand, Due to the advantages of metal nanoparticles (MNPs) such as great ratio of surface atoms and high activity compared to traditional heterogeneous catalysts, increasing interest has recently been directed toward these materials as nanocatalysis.[10] Because of high surface-energy of naked MNPs (meta stable state), they tend to rapidly aggregate together to form larger, more thermodynamically stable particles which results in the decrease of catalytic efficiency of NPs.[11] Various organic and inorganic supports have been used to stabilize the nanoparticles.[12,13] Although supported MNPs have recently emerged as exceedingly efficient catalysts for the selective reduction of aromatic nitro compounds.[14–16] only a few examples of copper nanoparticle (CuNP)-catalyzed ones were described in the literature.[17–19]

In the recent years, bio-based economy and use of renewable biomass as the raw material have been considered as sustainable options to tackle the problems associated with local and global pollutions. Along this line, Lignocellulose-rich biomass as one of the most abundantly available agricultural wastes has been advocated as a choice for the production of fine chemicals.[20] One of opportunities in order to apply greener method for the synthesis of MNPs by the reduction of transition metal salts is the use of green stabilizer. Since in this regard, these renewable and low cost biomasses appear to be promising candidate for stabilizing of MNPs.

In the present work, we wish to report here utilizing walnut shell (WS) which contains cellulose and lignin,[21] in the stabilizing of copper nanoparticles and application of this green *nanocomposite* (CuNP/WS) as a reusable and efficient catalyst in the reduction of nitroarenes benzonitriles to corresponding amines with $NaBH_4$ at room temperature in aqueous phase. Also due to importance of Cu catalyzed formation of biaryl “Ullmann reaction” for preparing numerous natural compounds, pharmaceutical products and polymers in the material science industries,[22] we study catalytic properties of this nanocomposite by applying it as a catalyst in the classic Ullman reaction to synthesize biaryl in

CONTACT Asghar Zamani a.zamani@urmia.ac.ir Department of Nanotechnology, Urmia University, Urmia, Iran; Ahmad Poursattar Marjani a.poursattar@urmia.ac.ir Department of Organic Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran.

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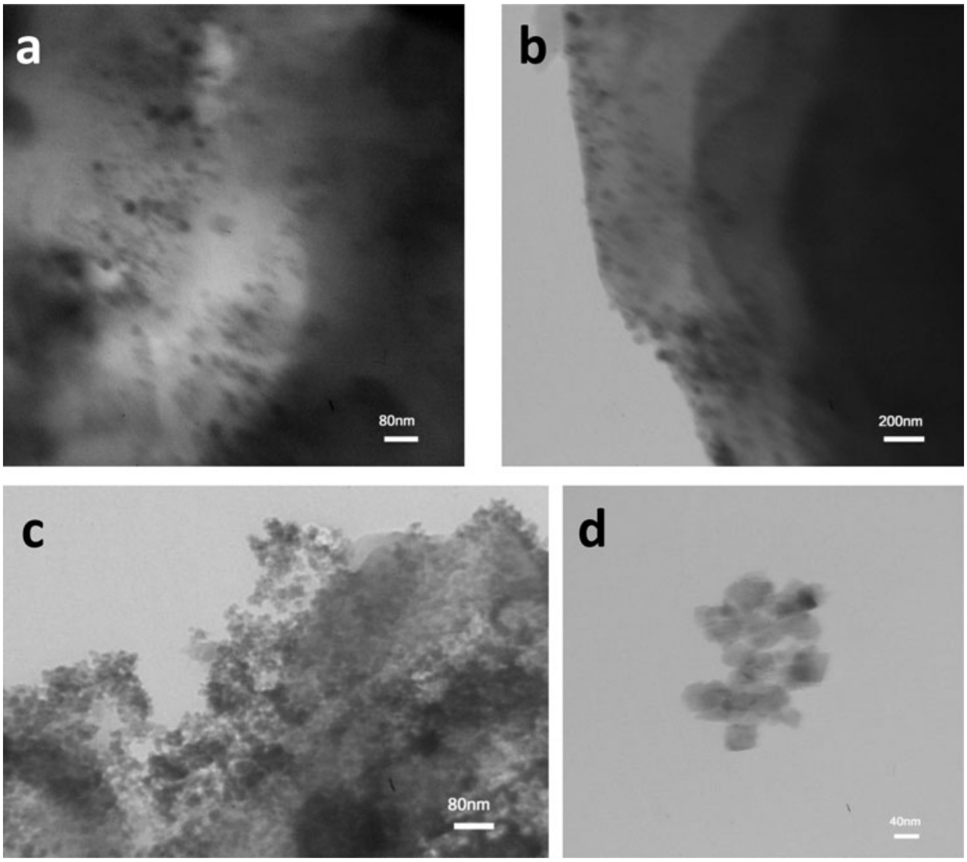


Figure 1. The TEM image of (A) CuNP/WS-1 (B) CuNP/WS-2 (C and D) CuNP/WS-3.

optimized reaction conditions which gave maximum yield with high purity.

Experimental

General Remarks

Chemicals were purchased from Merck and Fluka chemical companies. The products were characterized by comparison of their physical data with those of known samples or by their spectral data. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Advance DPX 400 MHz spectrometer in $CDCl_3$ or DMSO-$_{d6}$ as the solvent and TMS as internal standard. Most of the products are known, and all of the isolated products gave satisfactory UV-vis, IR and NMR spectra. FT-IR spectra of the powders were recorded using Thermo Nicolet Nexus 670 FT-IR spectrometer. UV-vis spectra were recorded using a *Biochrom* WPA 80-3003-75 *Biowave II* UV/vis spectrophotometer TEM analysis was performed with an instrument CM30, Philips, using an accelerating voltage of 150 kV.

Catalyst preparation

The walnut shells used in this work was obtained from a local walnut tree in Urmia, Iran. The walnut shells were washed and dried at room temperature and crushed using a high-speed rotary cutting mill and screened to collect the particles with a size smaller than 0.45 mm. 10 g of WS and 100 mL of $CuSO_4$ aqueous solution (0.03 M, 0.07 M and 0.14 M) were mixed in the flasks and in 50 °C for 2 h, followed by evaporation of water in a rotary evaporator. The reduction of Cu^{2+} was carried out by the drop-wise addition of 0.25 M ethanol solution of $NaBH_4$ (30 ml, 70 ml, 140 ml) to the *ethanol mixture of* obtained solid and intensive stirring was continued for 3 h. After filtering and washing the mixture, we obtained Cu loading on WS was 1.35% (CuNP/WS-1), 3.03% (CuNP/WS-2) and 8.14% (CuNP/WS-3), respectively, based on Atomic Absorption Spectroscopy (AAS) analysis.

General procedure for the reduction of nitroarenes and benzonitriles

In a 25 mL round bottom flask, CuNP/WS was added into a mixed solution containing 5 mL doubly distilled water and1 mmol nitroarene or benzonitrile. Next, 4 mmol $NaBH_4$ was added in 4 portions to the reaction mixture and stirred at room temperature for the appropriate amount of time. The progress of the reaction was monitored by TLC [using ethyl acetate/n-hexane as eluent: 1/5]. After completion of the reaction, the reaction mixture was filtered off and the catalyst rinsed twice with dichloromethane. The organic extracts were washed with H_2O, dried over $MgSO_4$ and evaporated in vacuo to give corresponding amines.

General procedure for the classic Ullman reaction

Iodoarene (1 mmol), CuNP/WS and DMF (10 mL) were added to a round bottomed flask fitted with a reflux

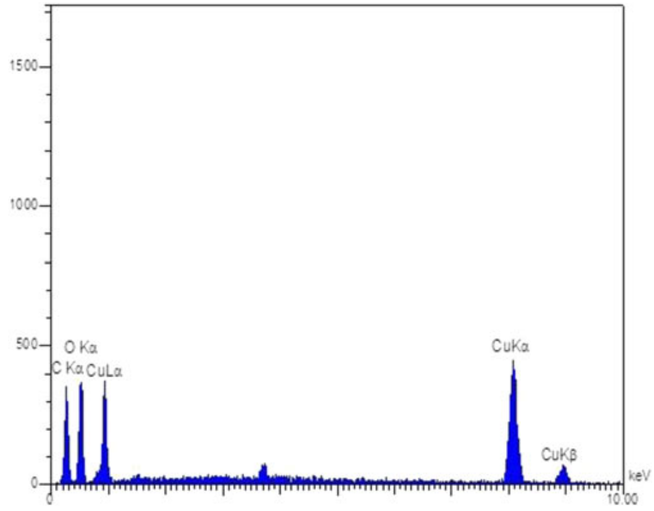


Figure 2. EDX spectroscopy of CuNP/WS-1.

condenser and a small stirring bar was added to the flask. The resulting mixture was refluxed in an oil bath and progress of the reaction was monitored by TLC (25% CH_2Cl_2 in hexane). After complete conversion of aryl iodide, mixture cooled to room temperature and the nanocomposite Cu catalyst was separated using filtration and were washed several times with DMF. Finally the residue was diluted with water and extracted with diethyl ether. The organic phase were washed with brine and dried over $MgSO_4$ and evaporated in vacuo and the crude product was purified by flash column chromatography to yield pure crystal of biaryl.

Results and discussion

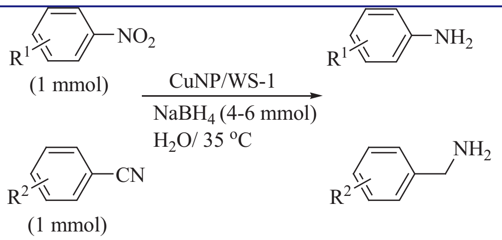
The copper catalyst was easily synthesized by stirring of the copper precursor, $CuSO_4$, with WS in water followed by the evaporation of solvent and reduction of metal with ethanolic solution of $NaBH_4$. The copper content was determined by atomic absorption spectroscopy.

Charactrization of the catalyst

High resolution transmission electron microscopy (HRTEM) studies of the copper supported catalyst, was carried out before and after the reduction experiments in order to understand the decrease in the catalytic activity encountered during the recycling experiments. TEM images of the as-prepared CuNP/WS-1, CuNP/WS-2, CuNP/WS-3 showed 15–22 (Figure 1a) and 60–80 nm (Figure 1b) particles respectively and extensive aggregation of metallic nanoparticles and non-supported ones were observed in the case of CuNP/WS-3 (Figure 1c and d). EDX can offer clear evidence about the elements present in the samples. Figure 2 showed the EDX patterns of CuNP/WS-1 which confirms that the nanoparticles are Cu. The carbon and oxygen peaks arise from the walnut shell.

FT-IR spectrum of CuNP/WS-3 is presented in electronic supplementary material. The peak at 1622 cm^{-1} are due to carboxylate ions (-COO^-) responsible for stabilization of copper(I) oxide NPs and the peak at 622 cm^{-1} correspond to Cu-O vibration of Cu_2O nanoparticles.[23] In addition based on the XPS analysis (electronic supplementary material) $Cu2p_{3/2}$ and $Cu2p_{1/2}$ signals centered at 932.7 and 952.6 eV respectively were consistent with Cu^0 or Cu^+ (Cu_2O).[24] The structure stability of CuNP/WS-1samples was investigated by the thermogravimetric (TGA) under air (electronic supplementary material).The TGA of this nanocomposite showed the first mass decrease below 100 °C due to desorption of physisorbed water. This was followed by a weight-reduction of ca. 90wt% in the temperature range between 200 °C to 500 °C that was attributed to the decomposition of nanocomposite. Thus, this TGA result showed that CuNP/WS sample is stable up to 200 °C.

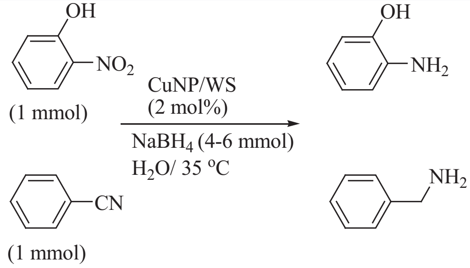
Table 1. Reduction of nitroarenes and benzonitriles in water.



Entry	R1	R2	Time (h)	Cat. (gr)	Yield (%)[a]
1	H	–	3	0.1	93
2	2-OH	–	5	0.1	99
3	3-OH	–	4	0.1	90
4	4-OH	–	2	0.1	91
5	4-Me	–	3	0.1	100
6	4-CHO	–	6	0.2	89[b]
7	4-CN	–	3	0.1	95[c]
8	4-NH_2	–	5	0.1	88
9	3-NH_2	–	6	0.1	90
10	2,3- di Me	–	6	0.2	98
11	4-CO_2H	–	2	0.1	93
12	–	H	1	0.1	100
13	–	Ph_2HC	1	0.1	75[d]
14	–	2-Cl	1.5	0.2	85
15	–	3-Cl	5	0.4	98
16	–	4-Cl	5		97
17	–	2,4-di Cl	4	0.2	96

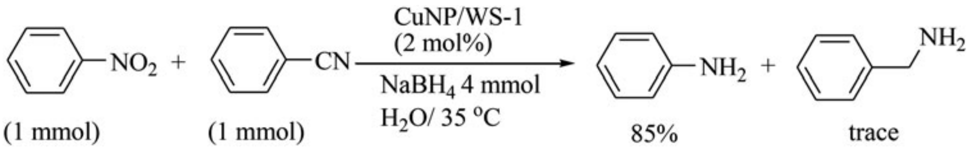
[a] GC yield.
[b] 4-Amino benzaldehyde as product.
[c] 4-Cyano aniline as product.
[d] 2,2-Diphenylethenamine as product

Table 2. Size-dependence of CuNP/WS catalysts in reduction reactions

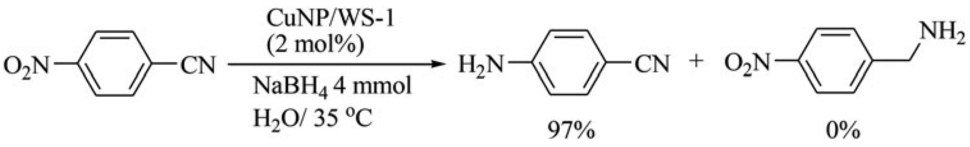


Entry	Catalyst (2 mol%)	Time (h)/ yield (%)[a]	
		benzonitrile	2-nitrophenol
1	CuNP/WS-1	1/100	5/99
2	CuNP/WS -2	2.5/91	5/85
3	CuNP/WS -3	10/93	6/88

[a] GC yield.



Scheme 1. Competitive reduction of nitrobenzene and benzonitrile using CuNP/WS-1.



Scheme 2. Selective reduction of *p*-nitrobenzonitrile to *p*-aminobenzonitrile using CuNP/WS-1.

Table 3. Comparison of our protocol with different CuNP-based catalytic systems.[a]

Entry	Conditions	Substrate	Temp. (°C)	Time (h)	yield (%)[b]	Ref.
1	$CuBr_2$ (10 mol%), EtOH	nitrobenzene	r.t.	5	90	[17]
2	Cu NP@ magnetic carbon (16 mol%), H_2O	4-nitrophenol	r.t.	0.5[c]	–	[18]
3	Sodium dodecyl benzene sulfonate stabilized CuNPs (10 mol%), THF/H_2O	nitrobenzene	50	2	98	[19]
4	Our protocole: CuNP/WS-1 (2 oml%), H_2O	nitrobenzene	35	3	93	
		4-nitrophenol	35		91	
				2		

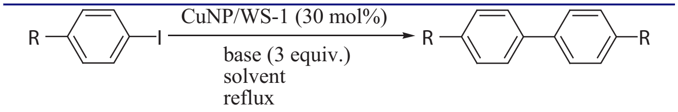
[a]All cases, in the presence of $NaBH_4$.
[b]GC yield.
[c]Conversion: 100%.

Catalytic reduction of nitroarenes and benzonitriles with copper supported catalysts

To test the catalytic activity of CuNP/WS-1 as a heterogeneous we selected the reduction of different nitroarenes and benzonitriles in aqueous medium. In a typical experiment, nitrobenzene (1 mmol) and $NaBH_4$ (4–5 mmol) were stirred at 35 °C in water (Table 1). The reduction of nitroarenes and benzonitriles carrying activated and deactivated groups such as OH, NH_2, Me, Cl, CHO and CN took place efficiently and easily to give the corresponding aniline and benzylamines as exclusive products according to TLC and GC. The scope and generality of this process is demonstrated with wide variety of nitroarenes and benzonitriles and the results are summarized in Table 1. Reaction of $NaBH_4$ and 2,2-diphenylacetonitrile yields 2,2-diphenylethenamine through imine-enamine tautomerism (Table 1, Entry 13). By using the reduction reaction of benzonitrile, it was found that this supported catalyst has been recovered and reused up to 4 times (yield of 1st run: 100% 1 h, 2nd run: 99% 1 h, 3rd run: 95% 1 h, 4th run: 89% 1 h, 5th run: 41%, 2 h). We have investigated the effect of Cu particle size on catalytic performances of the CuNP/WS catalysts in the reduction of benzonitrile and 2-nitrophenol (Table 2). It is of interest that different size of CuNPs exhibit different catalytic activity but in comparison with 2-nitrophenol, reduction of benzonitrile is more dependent to the size of CuNPs. However, CuNP/WS-1 contains smaller metal nanoparticles (15–22 nm) exhibited the highest activity in reduction of both substrates. The efficiency of CuNP/WS-1 was also demonstrated in the reduction of nitrobenzene in the presence of benzonitrile (Scheme 1). Notably, nitrobenzene was efficiently converted to aniline while benzonitrile was not reduced at all. Also CuNP/WS-1 was employed in the selective reduction of *p*-nitrobenzonitrile to *p*-aminobenzonitrile (Scheme 2). Because of diverse applications and uses of *p*-aminobenzonitrile in pharmaceuticals, agrochemicals, and fine chemicals, high selectivity to this target amine product is challenging[25].

In order to show the importance of this protocol for the reduction of nitroarenes and benzonitriles, Table 3 describes other CuNP-based catalytic systems previously reported in the literature. In addition to green dimensions of catalyst, to the best of our knowledge, it is the first report on CuN Pacting as a catalyst for the reduction of benzonitriles. On the other hand, the advantages of CuNP/WS-1 catalyst is more apparent in terms of higher yield at low catalyst loading (2 mol%) compared to other CuNP-based catalysts.

Table 4. C-C Ullmann coupling reaction.



Entry	R	Solvent	Base	Time (h)	Yield (%)[a]
1	H	DMF	K_3PO_4	5	88
2	H	DMF	NaOAC	5	27
3	H	DMF	Na_2CO_3	5	30
4	H	DMF	$NaHCO_3$	5	35
5	H	DMF	K_2CO_3	5	69
6	H	DMSO	K_3PO_4	24	11
7	H	H_2O	K_3PO_4	24	N.R.
8	H	PhMe	K_3PO_4	24	N.R.
9	Me	DMF	K_3PO_4	8	91
10	Ac	DMF	K_3PO_4	3	99
11	Cl	DMF	K_3PO_4	5	95
12	MeO	DMF	K_3PO_4	24	33
13	H	DMF	K_3PO_4	5	45[b]
14	H	DMF	K_3PO_4	5	9[c]

[a]GC yield.
[b]cat.: CuNP/WS-2.
[c]cat.: CuNP/WS-3.

Classic Ullman reaction catalyzed by with copper supported catalysts

In the next step, we tested the catalytic activity of CuNP/WS-1 for the C-C Ullmann coupling reaction. To find out the optimum reaction conditions, we initially selected phenyl iodide as a model reaction and studied the effects of the solvents and base on that. Among the different bases such as K_3PO_4, NaOAc, Na_2CO_3, $NaHCO_3$ and K_2CO_3, K_3PO_4 showed the maximum yield for homocoupling of phenyliodide to give biphenyl in 88% yield in DMF as solvent under reflux conditions (Table 4, entry 1). On the other hand, among various solvents that were used, such as DMF, DMSO, toluene and water, it turned out that DMF led to much better results in terms of product yields (Table 4, entries 1, 6–8).

To demonstrate the general applicability of the CuNP/WS-1 nanocomposite for Ullmann coupling different substituted aryliodides were examined. As shown in Table 4, the homocoupling reaction of different iodobenzenes including electron-rich and electron-poor substrates proceeded smoothly using as low as 30 mol% of catalyst to give the corresponding products in excellent yields (Table 4, entries 1, 9–12). For electron-neutral and electron-rich aryl iodides, good yields of the homocoupling products were obtained at 5–24 h (Table 4, entries 1, 9 and 12). Electron-poor iodobenzenes reacted under the present reaction conditions to produce the corresponding biaryls in excellent yields at 3–5 h (Table 4, entries 10 and 11). By using the Ullmann coupling of iodobenzene, it was found that this nanocomposite catalyst has been recovered and reused up to 3 times (yield of 1st run: 100% 5 h, 2nd run: 99% 8 h, 3rd run: 95% 15 h, 4th run: 89% 24 h). Also a size-dependence study showed that the catalytic efficiency of larger Cu nanoparticles was much lower than that of smaller ones under similar reaction conditions (Table 4, entries 13 and 14).

Conclusion

In conclusion, we have presented a new green, simple and inexpensive method of making copper nanoparticle catalyst supported on walnut shell. This material was characterized by TEM, EDX, TGA and AAS. It showed the isolated copper 15–22 nm nanoparticles were formed and immobilized onto the walnut shell. This catalyst was found to be efficient for reduction of aromatic nitro and nitrile with $NaBH_4$ in water and recovering and reusing of the catalyst happens to be easy. Also we have developed a green and economic catalyst system for the classic Ullmann reaction of iodoarenes by walnut shell-stabilized copper nanoparticles (CuNP/WS-1) as the catalyst in DMF. The homocoupling reactions of iodoarenes, produce the corresponding coupling products in good to excellent yields at the present reaction conditions.

Acknowledgements

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NMR data for some of the products

4-Bromoaniline: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.68$ (br, 2H, NH_2), 6.56 (d, 2H), 7.23 ppm (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 110.15$, 116.65, 131.90, 145.33 ppm.

Benzene-1,2-diamine: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.35$ (br, s, 4H, $2\times NH_2$), 6.58 ppm (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 116.75$, 138.50 ppm.

2,2-Diphenylethenamine: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.56$ (br, 2H, NH_2), 6.67 (br, 1H), 7.16 (m, 5H), 7.35 ppm (m, 5H); ^{13}C NMR (100 MHz, CDCl3) δ = 123.11, 124.8, 128.3, 127.9, 131.4, 132.1, 130.5, 139.1, 139.8 ppm.

4,4′-Dichloro-1,1′-biphenyl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.43$ (d, 4H), 7.50 ppm (d, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 128.25$, 129.07, 133.77, 138.45 ppm.

4,4′-Dimethoxy-1,1′-biphenyl: ^1H NMR (400 MHz, $CDCl_3$): $\delta = 3.89$ (s, 6H, $2\times$OMe), 7.00 (d, 4H), 7.52 ppm (d, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta = 55.36$, 114.20, 127.76, 133.51, 158.73 ppm.

Funding

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