

Proceedings

# Direct Arylation-Based Synthesis of Carbazoles Using an Efficient Palladium Nanocatalyst under Microwave Irradiation <sup>†</sup>

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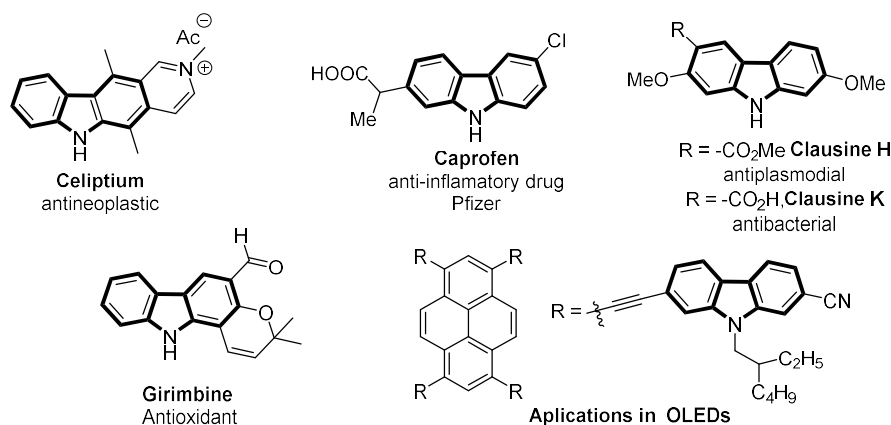
**Abstract:** Herein, an eco-friendly palladium-catalyzed tandem reaction for the one-pot synthesis of carbazoles under microwave irradiation is reported. This approach involves an amination and a direct arylation from available and inexpensive anilines and 1,2-dihaloarenes. For the development of this purpose, a novel recoverable palladium nanocatalyst supported on a green biochar under ligand-free conditions is used. Compared to other existing palladium-based protocols, the present synthetic methodology shows a drastic reduction in reaction times and excellent compatibility with different functional groups allowing to obtain a small library of carbazoles with high yields and regioselectivity. The novel heterogeneous palladium nanocatalyst can be recycled and reused up to 5 times without significant loss activity

**Keywords:** carbazoles; tandem reaction; microwave-assisted synthesis; palladium nanoparticles; green biochar

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## 1. Introduction

9H-carbazole constitutes a predominant nitrogen-containing heterocyclic compound present in both synthetic and naturally occurring alkaloids. Their planar structure is broadly distributed in natural bioactive products with significant biological properties including antibiotic and antimicrobial anti-inflammatory and antioxidant, neuroprotector and antitumoral [1,2]. In addition, carbazole scaffolds are useful  $\pi$ -extending building blocks for organic materials, such as polymeric light-emitting diodes (PLEDs) and organic light-emitting devices (OLEDs) (Figure 1) [3].

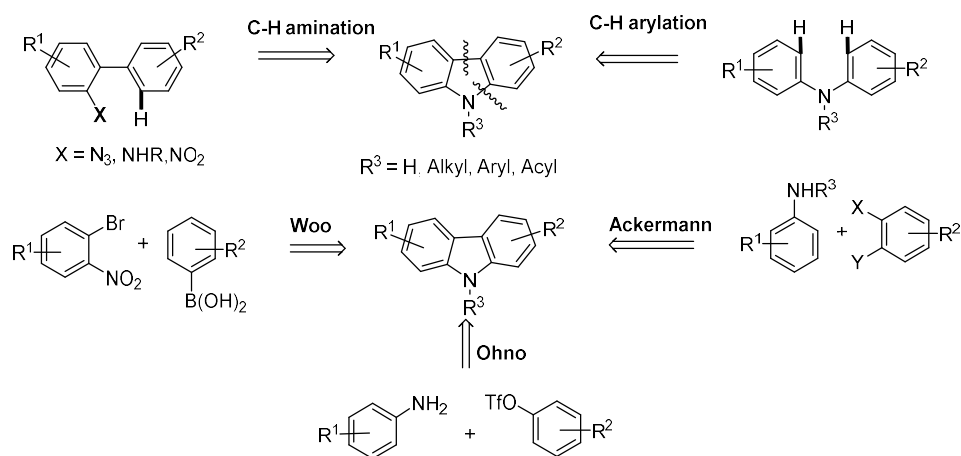


**Figure 1.** Relevance of carbazole motif in active alkaloids and organic materials.

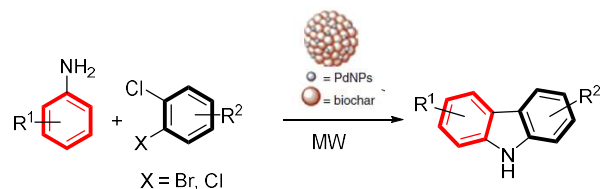
Owing to the relevance of the carbazole framework, it has emerged as an important molecular target in certain areas such as medicinal chemistry, science of materials and industry. An extensive amount of research has been dedicated to introducing structural modifications to natural occurring carbazoles; the synthesis of brand-new derivatives and finding new and efficient ways to obtain them from readily available, low-cost materials. In this context, direct-arylation of arenes is an outstanding strategy from an economic and environmental point of view in cross-coupling reactions, using stoichiometric quantities of organometallic reactants. Amongst the aryl halides, the most interesting would be the chlorides, due to their low costs and wide diversity [4].

Manifold synthetic approaches for the construction of the central pyrrole ring have been extensively reported in the last decade. This aim has been achieved by transition-metal catalyzed intramolecular C-H amination of substituted biaryls and intramolecular coupling of *N,N*-diarylamines through C-C bond formation (Figure 2) [5].

#### General approaches



#### This work



**Figure 2.** Approaches towards the synthesis of carbazole derivatives.

On the other hand, direct synthesis of carbazoles through sequential palladium catalysed cross-coupling C-N/C-C bond formation has emerged as an attractive synthetic approach in the last decade.

In 2009, Ohno and co-workers, reported an interesting *N*-arylation and oxidative biaryl coupling for the carbazole synthesis from anilines and aryl triflates under homogenous palladium (II) acetate as catalyst [6].

In 2016, Woo and co-workers reported the *one-pot* synthesis of carbazoles via Suzuki cross-coupling and consecutive reductive Cadogan cyclization employing *ortho*-halonitroarenes and arylboronic acids as starting materials [7]. Despite these considerable advances, they require complex precursors, drastic reaction conditions, expensive non-recoverable catalysts, and the presence of phosphine ligands and/or additives.

These drawbacks could be addressed by heterogeneous nanocatalysis based on transition metals which represent an enormous progress to both industry and academic areas, due to their advantages related to atomic economy, low toxicity, atomic efficiency, and eco-friendliness [8].

In this context, microwave-assisted organic synthesis (MAOS) denotes a mighty and useful tool in heterocyclic chemistry that allows to reduce reaction time and the generation of by-products, leading to an improvement in the overall yields. Therefore, the combination of MAOS and heterogeneous catalysis represents an attractive eco-friendly approach for the synthesis of functionalized carbazoles [9].

Ackerman and co-workers reported an elegant Palladium-catalyzed *N*-arylation and C-H activation leading to the synthesis of carbazoles from easily attainable anilines and 1,2-dihaloarenes [10]. The cited protocol is limited due to the need of activated anilines, long reaction times, the presence of phosphine as a ligand, and unrecoverable palladium catalysts.

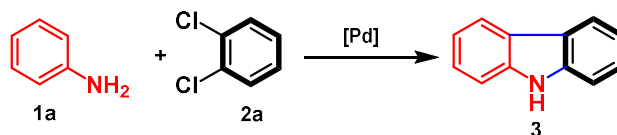
Inspired by these results, we herein propose an alternative, efficient, and straightforward palladium-catalyzed intermolecular C-N bond formation and intramolecular C-H arylation between anilines and 1,2-dihaloarenes, which allows the access to carbazole derivatives through a *one-pot* process. For this purpose, a novel palladium heterogeneous catalyst and microwave irradiation were employed. The nanoparticles of palladium are supported on biochar (henceforth referred to as PdNPs/BC); the solid residue of the pyrolysis of sunflower seed hulls, a plentiful and regional agricultural waste.

Moreover, through the application of microwave irradiation, the severe reaction conditions used by other known protocols have been improved and reaction times have been shortened from up to 18 h to barely 25 min.

## 2. Results and Discussion

We began our investigations using aniline 1a and 1,2-dichlorobenzene 2a as starting materials in the presence of a set of Palladium-based catalysts, both homogeneous and heterogeneous (Table 1). For this purpose, the reaction conditions proposed by Ackermann were used as a starting point {[Pd] (5 mol %), *N,N*-dimethylpyrrolidine (NMP), K<sub>3</sub>PO<sub>4</sub>, 130 °C, 18 h.} (Table 1). During control experiments, the tested homogeneous catalysts showed low activity and efficiency in the generation of our desired product. To improve these results, we made use of a powerful and versatile tool to decrease reaction times and limit the generation of by-products; microwave-assisted organic synthesis. No reaction progress was detected when the reaction was performed without catalyst (entry 1). To our satisfaction, the corresponding carbazole **3** was obtained in 19% yield when our novel PdNPs/BC was used under microwave irradiation (entry 7). In contrast, the thermal conditions both at 130 °C and 180 °C for 18 h led to carbazole in low yields (entries 7 and 10). An improvement of the yield (43%) was accomplished when the reaction was subjected at 200 W and 180°C for 25 min. Among the commercial homogeneous catalysts tested, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PdCl<sub>2</sub>(MeCN)<sub>2</sub> led to **3** in low yields (entry 2 and 3), whereas the Pd(PPh<sub>3</sub>)<sub>4</sub> and Pd<sub>2</sub>(dba)<sub>3</sub> showed less or no activity (entry 2 and 4). By increasing the temperature using the homogeneous PdCl<sub>2</sub>(MeCN)<sub>2</sub> no reaction progress was detected (entry 6). Additionally, other nanopalladium heterogeneous catalysts were tested. PdNPs/Al<sub>2</sub>O<sub>3</sub> led to **3** in low yields in both thermal and microwave conditions at 130 °C and 180 °C, whereas PdNPs/PbO were inactive in the same reaction conditions (entries 8 and 9).

The low reactivity of both PdNPs supported on Al<sub>2</sub>O<sub>3</sub> and PbO respectively by comparison with PdNPs/BC strongly suggest that BC is not an innocent support for the reaction. The reason why BC promotes Pd catalytic features would be related the peculiar surface chemistry of BC, which a highly functionalized material. Unrevealing the exact nature of BC surface and its role in reaction is beyond the scope of the present study, and will be discussed in future studies of our group.



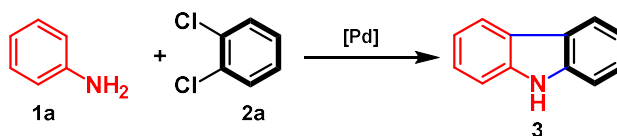
**Table 1.** Preliminary screening of Pd catalyst<sup>a</sup>.

Entry	[Pd]	Temperature (°C)	Yield (%) Thermal <sup>a</sup>	Yield (%) MW <sup>b</sup>
1	---	130	---	---
2	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	130	6	trace
3	Pd <sub>2</sub> (dba) <sub>3</sub>	130	-	trace
4	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	130	8	--
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	130	N.R.	N.R.
6	PdCl <sub>2</sub> (MeCN) <sub>2</sub>	160	N.R.	N.R.
7	PdNPs/BC	130	11	19 <sup>c</sup>
8	PdNPs/PbO	130	--	trace
9	PdNPs/Al <sub>2</sub> O <sub>3</sub>	130	traces	9
10	PdNPs/BC	180	18	43 <sup>c</sup>
11	PdNPs/Al <sub>2</sub> O <sub>3</sub>	180	10	12

**Standard reaction conditions:** [a] Aniline (1a) 1.2 mmol, 1,2-dichlorobenzene (2a) (1 mmol), K<sub>3</sub>PO<sub>4</sub> (3 mmol.). PdNPs/BC (5 mol %), NMP (10.0 mL), 18 h. [b] Reaction was conducted at 200 W, 25 min. Time reaction monitored by TLC and GC-MS.

Subsequently, various reaction conditions such as solvents, bases and PdNPs/BC loading were evaluated (Table 2). Upon decreasing the catalyst load to 2.5 mol % a low yield of 3 (16%) was obtained (entry 1). Surprisingly, when the reaction was carried out by using 15 mol % of the PdNPs/BC, the carbazole was obtained in 76% yield (entry 3). A moderate yield (57%) of carbazole was obtained when an intermediate load of catalyst (10 mol %) was used (entry 2). Next, several polar solvents with elevated boiling points were evaluated. Among the solvents tested, dimethyl sulfoxide (DMSO) at 180 °C demonstrated the best efficiency (entry 6), whereas *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMAc) showed no significant changes in comparison with *N*-Methyl-2-pyrrolidone (NMP) (entries 4 and 5). Finally, different bases were examined. The inorganic base KOAc showed the best performance (entry 9), whereas different carbonates and organic bases such as NaOt-Bu did not improve yields. (entries 8–11).

Additionally, the effect of irradiation time and power were also evaluated. When the reaction was subjected to 200 W for 25 min a complete conversion of starting materials was observed, whereas prolonged times led to an increase in the formation of by-products. Performing the reaction at 100 W led to no reaction progress both at reaction times 25 and 60 min. Irradiation power at 300 W for more than 25 min led to the carbazole in a lower yield. Therefore, the use of irradiation power at 200 W for 25 min was determined as the optimal condition.

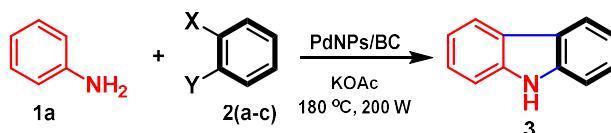


**Table 2.** Optimization of the reaction conditions for the one-pot synthesis of 9H-carbazole. <sup>[a]</sup>

Entry	PdNPs/BC (% mol)	Solvent	Base	Yield (%) <sup>b</sup>
1	2.5	NMP	K <sub>3</sub> PO <sub>4</sub>	16
2	10	NMP	K <sub>3</sub> PO <sub>4</sub>	57
3	15	NMP	K <sub>3</sub> PO <sub>4</sub>	76
4	15	DMF	K <sub>3</sub> PO <sub>4</sub>	71
5	15	DMAc	K <sub>3</sub> PO <sub>4</sub>	73
6	15	DMSO	K <sub>3</sub> PO <sub>4</sub>	85
7	15	DMSO	KOAc	88
8	15	DMSO	K <sub>2</sub> CO <sub>3</sub>	84
9	15	DMSO	Cs <sub>2</sub> CO <sub>3</sub>	82
10	15	DMSO	Na <sub>2</sub> CO <sub>3</sub>	81
11	15	DMSO	NaOt-Bu	61

**Reaction conditions:** [a] Aniline (1a) 1.2 mmol, 1,2-dichlorobenzene (1 mmol), (2a) (2.1 mmol), Base (3 mmol.). PdNPs/BC (mol %), solvent (5 mL) at 180 °C under microwave irradiation 200 W for 25 min. Time reaction monitored by TLC and GC-MS. [b] Isolated yield.

Under the optimized reaction conditions (Table 2, entry 9) we carried out the scope and limitations to our methodology by employing different 1,2-dihaloarenes and aniline (**1a**) (Table 3). When the reaction was carried out by using 1,2-dibromobenzene (**2c**), carbazole **3** was obtained in an excellent yield (90%). Besides, using 1-bromo-2-chlorobenzene (**2c**) as substrate, the desired product **3** was obtained in 81% yield. As shown Table 3, the formation of carbazole was not limited while resorting to 1,2-dihaloarenes bearing good leaving groups, such as bromine. In this context, it is important to note that the present methodology enables to obtain carbazole by using inexpensive aryl chlorides as electrophilic reagent. In addition, neither formation of homocoupling by-products, nor significant differences in term of yields were observed using aryl chlorides instead of aryl bromides.

**Table 3.** Substrate scope for the synthesis of 9H-carbazole. <sup>[a]</sup>

Entry	Aniline	1,2-dihalobenzene	9H-Carbazole	Yield (%) <sup>b</sup>
1				88
2	<b>1a</b>		<b>3</b>	81
3	<b>1a</b>		<b>3</b>	90 <sup>[c]</sup>

[a] **Reaction conditions:** aniline (1.2 mmol), *ortho*-dihalobenzene (1 mmol), PdNPs/BC (15 mol %), KOAc (3 mmol) in DMSO (5 mL) at 180 °C under MW (200 W) for 25 min. [b] Isolated yield. [c] homocoupling products were detected (<5%).



Isolated yield after purification (in parentheses). [b]The reaction was conducted using 1-bromo-2-chlorobenzene.

Finally, the recyclability of the PdNPs/BC catalyst was studied using the direct synthesis of carbazole **3** as reaction model. After completion of the reaction (monitoring monitored by TLC), the nanocatalyst was easily separated from the reaction mixture by filtration and washed several times with EtOAc and then dried under vacuum to be used directly for further catalytic reactions. As shows Figure 3, no significant loss of catalytic efficiency was observed up to five cycles.



**Figure 3.** Recyclability of the PdNPs/BC catalyst in the direct synthesis of carbazole **3**.

### 3. Conclusions

In conclusion, we have developed a practical, eco-friendly and selective methodology for the synthesis of carbazoles promoted by a catalytic system based on PdNPs supported on green biochar. The novel catalyst could be recycled up to at least until 5 times without significant loss activity. Additionally, the present methodology enabled us to access a variety of carbazoles by using inexpensive aryl chlorides as electrophiles and anilines as starting materials. Moreover, the prolonged reaction times were drastically reduced to minutes by using microwave irradiation. Furthermore, the present protocol is compatible with different functional groups and does not require the presence of ligands or additives as the traditional methods reported up to date.

### 4. Materials and Methods

#### 4.1. General Information

Unless otherwise noted, reagents were obtained commercially and used without further purification. Solvents were dried and distilled in accordance with standard procedure (ref). Reactions were monitored by thin-layer chromatography on silica gel plates (60F-254) visualized under UV light and/or using 5% phosphomolybdic acid in ethanol. All  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at room temperature in  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  on a Bruker Avance ARX-300 spectrophotometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) from tetramethylsilane (TMS) using the residual solvent resonance ( $\text{CDCl}_3$ : 7.26 ppm for  $^1\text{H}$  NMR, 77.16 ppm for  $^{13}\text{C}$  NMR. Multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; brs = broad signal). IR spectra were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrometer in the ATR mode at room temp. Melting points were determined using a Büchi 510 apparatus and are not corrected. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a GC Shimadzu (GC-14B) with a flame ionization detector equipped with a HP-5MS column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ) using nitrogen as carrier gas. High resolution mass spectra were recorded on Thermo Fisher LTQ Orbitrap XL, (for EI) and a Finnigen MAT 95 (for ESI). Flash column chromatography was performed using Macherey

Nagel MN silica gel 60M (0.040–0.063 mm/230–240 mesh ASTM). Microwave reactions were performed using microwave oven CEM Discover in sealed reaction vessels. The palladium loading of the catalyst was determined by Atomic Absorption Spectrometry (AAS) in a Perkin Elmer AAnalyst 700 equipment. Powder X-ray diffraction (XRD) patterns were recorded on a Philips PW1710 BASED Diffractometer, operating at 45 kV and 30 mA, fitted with a graphite monochromator getting Cu Ka 1 radiation ( $\lambda$  1/4 0.15406 nm). The samples were characterized by Transmission Electron Microscopy (TEM), employing a Joel 100 CX2 (Tokyo, Japan) apparatus. Approximately one hundred palladium particles were measured to perform the particle size distribution in order to obtain the mean particle size (d) [11]. Nitrogen adsorption/desorption isotherm at 77 K was obtained with a Nova 1200e Quantachrome Instrument. The specific surface areas were measured following the Brunauer-Emmette-Teller (BET) method.

#### 4.2. Microwave Reactions

All microwave reactions were carried out following the same procedure: Anilines (1.2 mmol), 1,2-dihaloarenes (1 mmol), KOAc (3 mmol), PdNPs/BC (15 mol %), and dry DMSO (5 mL) were added to a vessel tube with a magnetic stirring bar. The mixture resulting was heated at 180 °C under microwave irradiation (200 W) for 25 min. The progress of the reaction was monitored by TLC and GC-MS. The crude product was treated with EtOAc. The catalyst was recovered by filtration and washed several times with the same solvent. The filtrate was washed twice with a brine and then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure and the desired carbazole was purified by column chromatography using silica gel 60 as adsorbent.

**9H-Carbazole (3).** The title compound was prepared from aniline and 1,2-dichlorobenzene to give a white solid (0.14 g, 0.88 mmol, 88% yield), m.p. 245–246 °C. SiO<sub>2</sub> (hexane/EtOAc = 7:3). The spectral data were in accordance with those reported in the literature [12].

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  7.13 (t, *J* = 7.6 2 H), 7.35 (t, *J* = 7.6, 2H) 7.48 (d, *J* = 8.1 Hz, 2 H), 8.11 (d, *J* = 8 Hz, 2 H),  $\delta$  11.26 (s, 1 H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  110.9, 118.5, 120.1, 122.4, 125.5, 139.7. IR (KBr)  $\nu$  [cm<sup>-1</sup>] = 3392, 3049, 1625, 1449, 1327, 1240. HRMS (EI) for C<sub>12</sub>H<sub>9</sub>N: calcd. 167.0735; found: 167.0738.

**3-methoxy-9H-carbazole (4).** The title compound was prepared from 4-methoxyaniline and 1,2-dichlorobenzene to give a white solid (0.15 g, 0.77 mmol, 77% yield), m.p. 139–140 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 10:1). The spectral data were in accordance with those reported in the literature [13].

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.93 (s, 3H), 7.05 (dd, *J* = 8.8, 2.4, 1H), 7.19–7.23 (m, 1H), 7.34 (d, *J* = 8.8, 1H), 7.41 (d, *J* = 3.6, 2H), 7.56 (d, *J* = 2.4, 1H), 7.91 (brs, 1H), 8.04 (d, *J* = 8.0, 1H), <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  56.2, 103.2, 110.8, 111.4, 115.1, 119.1, 120.3, 123.4, 123.8, 125.9, 134.4, 140.3, 153.9. IR (KBr)  $\nu$  [cm<sup>-1</sup>] = 3404, 2925, 1612, 1460, 1310, 1255, 1041. HRMS (EI) for C<sub>13</sub>H<sub>11</sub>NO calcd. 197.0736; found 197.0736

**3-fluoro-9H-carbazole (5).** The title compound was prepared from 4-fluoroaniline and 1,2-dichlorobenzene to give a white solid (0.14 g, 0.76 mmol, 76% yield), m.p. 208–209 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 9:1). The spectral data were in accordance with those reported in the literature [13].

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.16 (td, *J* = 9.2, 2.4, 1H), 7.21–7.28 (m, 1H), 7.34 (dd, *J* = 8.8, 4.2, 1H), 7.40–7.48 (m, 2H), 7.73 (dd, *J* = 9.2, 2.4, 1H), 8.01–8.03 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  106.1 (d, *J*<sub>CF</sub> = 23.6), 110.9, 111.22 (d, *J*<sub>CF</sub> = 9.2), 113.7 (d, *J*<sub>CF</sub> = 25.6), 119.5, 120.6, 123.2 (d, *J*<sub>CF</sub> = 4.0), 123.9 (d, *J*<sub>CF</sub> = 9.6), 126.5, 135.8, 140.6, 157.6 (d, *J*<sub>CF</sub> = 235.6). <sup>19</sup>F NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  -124.4. IR (KBr)  $\nu$  [cm<sup>-1</sup>] = 3411, 3043, 1362, 1238, 807. HRMS (EI) for C<sub>12</sub>H<sub>8</sub>FN: calcd.184.0568; found 184.0562.

**3-methyl-9H-carbazole (6).** The title compound was prepared from 4-methylaniline and 1,2-dichlorobenzene to give a white solid (0.13 g, 0.71 mmol, 71% yield), m.p. 169–171 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 9:1). The spectral data were in accordance with those reported in the literature. [14].

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  2.54 (s, 3H), 7.17–7.28 (m, 2H), 7.32 (d, *J* = 8.0, 1H), 7.40 (d, *J* = 3.6, 2H), 7.89 (s, 1H), 7.94 (brs, 1H), 8.05 (d, *J* = 7.6, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  21.6, 110.4, 110.7, 119.3, 120.4, 120.3, 123.3, 123.6, 125.7, 127.3, 128.8, 137.8, 139.9. IR (KBr)  $\nu$  [cm<sup>-1</sup>] = 3404, 2921, 1459, 1333, 1217. HRMS (EI) for C<sub>13</sub>H<sub>11</sub>N: calcd. 181.0814; found 181.0819.



**2-Methyl-9H-carbazole (7).** The title compound was prepared from 3-methylaniline and 1-bromo-2-chlorobenzene to give a colorless solid (0.14 g, 0.80 mmol, 80% yield), m.p. 245–246 °C. SiO<sub>2</sub> (petroleum ether /EtOAc = 8:2). The spectral data were in accordance with those reported in the literature [15].

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.53 (s, 3H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.18–7.24 (m, 2H), 7.35–7.42 (m, 2H), 7.95 (d, *J* = 7.9 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 22.2, 110.6, 110.8, 119.5, 120.1, 120.1, 121.1, 121.2, 123.6, 125.4, 136.1, 139.6, 140.1. IR (KBr) ν [cm<sup>-1</sup>] = 3397, 3051, 2921, 1652, 1510, 1365, 1244. HRMS (EI) for C<sub>13</sub>H<sub>11</sub>N calcd. 181.0891; found 181.0894.

**3-carbonitrile-9H-carbazole (8).** The title compound was prepared from 4-aminobenzonitrile and 1,2-dichlorobenzene to give a colorless solid (0.13 g, 0.68 mmol, 68% yield), m.p. 188–189 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 6:4). The spectral data were in accordance with those reported in the literature [14].

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 7.25 (t, *J* = 7.6, 1H), 7.48 (t, *J* = 7.6, 1H), 7.57 (d, *J* = 8.0, 1H), 7.63 (d, *J* = 8.4, 1H), 7.75 (d, *J* = 8.4, 1H), 8.24 (d, *J* = 8.0, 1H), 8.71 (s, 1H), 11.81 (brs, 1H). <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>): δ 100.2, 111.6, 112.1, 119.9, 120.7, 121.0, 121.6, 122.7, 125.6, 127.06, 128.6, 140.3, 141.7. IR (KBr) ν [cm<sup>-1</sup>] 3293, 3097, 2220, 1620, 1465, 1326, 1242, 1127. HRMS (EI) for C<sub>13</sub>H<sub>9</sub>N<sub>2</sub>: calcd. 192.0585; found: 192.0588.

**1-(9H-carbazol-3-yl)ethan-1-one (9).** The title compound was prepared from 1-(4-aminophenyl)ethan-1-one and 1,2-dichlorobenzene to give a yellow solid 177–178 °C (0.16 g, 0.77 mmol, 77% yield). SiO<sub>2</sub> (petroleum ether/EtOAc = 7:3). The spectral data were in accordance with those reported in the literature [16]

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 2.73 (s, 3H), 7.28–7.33 (m, 1H), 7.42–7.47 (m, 3H), 8.03–8.10 (m, 2H), 8.50 (brs, 1H), 8.74 (d, *J* = 1.5, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 26.8, 110.4, 111.2, 120.51, 120.6, 122.0, 123.2, 123.5, 126.7, 126.8, 129.4, 140.1, 142.5, 198.1. IR (neat) ν [cm<sup>-1</sup>] 3294, 2924, 1660, 1329, 1246, 1015. HRMS (EI) for C<sub>14</sub>H<sub>11</sub>NO: calcd. 197.0841; found: 197.0839.

**2-Nitro-9H-carbazole (10).** The title compound was prepared from 3-nitroaniline and 2-bromo-1-chlorobenzene to give a white solid (0.14 g, 0.68 mmol, 68% yield), m.p. 202–203 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 10:1). The spectral data were in accordance with those reported in the literature [17].

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.30–7.36 (m, 1H), 7.49–7.59 (m, 2H), 8.13–8.17 (m, 3H), 8.36–8.39 (m, 1H), 8.41 (brs, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 106.8, 111.3, 115.0, 120.3, 120.8, 121.5, 122.0, 128.3, 128.5, 138.3, 141.6, 145.9. IR (KBr) ν [cm<sup>-1</sup>] = 3372, 3047, 1632, 1569, 1470, 1384, 1343, 1276, 804. HRMS (EI) for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>: calcd. 212.0658; found 212.0653.

**9H-pyrido[2,3-*b*]indole (11).** The title compound was prepared from 2-amino-pyridine and 2-bromo-1-chlorobenzene to give a white solid (0.13 g, 0.79 mmol, 79% yield), m.p. 214–215 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 40:1). The spectral data were in accordance with those reported in the literature [18].

<sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>): δ 7.17–7.25 (m, 2H), 7.42–7.48 (m, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 7.8 Hz, 1H), 8.41 (d, *J* = 4.8, 1.6 Hz, 1H), 8.49 (dd, *J* = 7.7, 1.6 Hz, 1H), 11.80 (s, 1H). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 75 MHz): δ 111.3, 115.0, 115.2, 119.4, 120.4, 121.2, 126.6, 128.4, 138.8, 146.1, 151.9. IR (KBr) ν [cm<sup>-1</sup>] = 3400, 3048, 1615, 1403, 1328, 1275. HRMS (EI) for calcd. C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>: 168.0766; found 168.0769.

**Methyl 9H-carbazole-3-carboxylate (12).** The title compound was prepared from aniline and 4-bromo-3-chlorobenzoate to give a white solid (0.13 g, 0.57 mmol, 57% yield), m.p. 170–172 °C. SiO<sub>2</sub> (petroleum ether/EtOAc = 6:4). The spectral data were in accordance with those reported in the literature [19].

<sup>1</sup>H NMR (acetone-*d*<sub>6</sub> 300 MHz): δ 3.92 (s, 3H), 7.25–7.29 (m, 1H), 7.44–7.48 (m, 1H), 7.58 (d, *J* = 8.3, 3.5 Hz, 2H), 8.09 (d, *J* = 8.6, 1.6 Hz, 1H), 8.26 (d, *J* = 7.8 Hz, 1H), 8.82 (s, 1H), 10.9 (br s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): 51.9, 110.1, 110.9, 120.3, 120.6, 121.4, 122.9, 123.1, 123.3, 126.5, 127.4, 139.9, 142.3, 167.9. IR (KBr) ν [cm<sup>-1</sup>] = 3344, 2947, 1710, 1590, 1497, 1327, 1244, 1286, 1119. HRMS (EI) for C<sub>14</sub>H<sub>11</sub>NO<sub>2</sub>: calcd. 225.0863; found: 225.0865.

**3-Nitro-6-methoxy-9H-carbazole (13).** The title compound was prepared from 3-methoxyaniline and 1,2-dichloro-4-nitrobenzene to give a yellow solid (0.15 g, 0.61 mmol, 61% yield). SiO<sub>2</sub> (petroleum ether/EtOAc = 7:3). The spectral data were in accordance with those reported in the literature [19].

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  3.93 (s, 3 H), 7.14 (dd,  $J = 8.5, 2.5$  Hz, 1 H), 7.39 (d,  $J = 9.0$  Hz, 1 H), 7.41 (d,  $J = 9.0$  Hz, 1 H), 7.58 (d,  $J = 2.5$  Hz, 1 H), 8.31 (dd,  $J = 9.0, 2.0$  Hz, 1 H), 8.96 (d,  $J = 2.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz):  $\delta$  56.2, 103.5, 110.5, 112.3, 117.37, 117.6, 121.8, 123.2, 123.9, 135.3, 141.1, 143.4, 155.2. IR (neat)  $\nu$  [ $\text{cm}^{-1}$ ] = 3420, 2825, 1636, 1483, 1325, 1295, 1171, 1032. HRMS (EI) for  $\text{C}_{13}\text{H}_{10}\text{N}_2\text{O}_3$ : calcd. 241.0613; found: 241.0617.

#### 4.3. Synthesis and Characterization of the Catalyst

Palladium catalyst supported on biochar (PdNPs/BC) was prepared following the precipitation-reduction method, employing  $\text{PdCl}_2$  as the metal precursor and biochar (BC) as the support BC was obtained as a product of the pyrolysis of lignocellulosic biomass [20,21].

Firstly, the BC was put in contact with a 10% nitric acid solution at room temperature for 2 h under stirring. The solid was extensively washed with deionized water. Afterwards, approximately 1 g of the sample was put in contact with a HCl aqueous solution of palladium chloride at 80 °C under stirring. A 37% formaldehyde solution and a 30% NaOH solution up to basic pH were added to attain palladium precipitation on support. Afterwards, the resulting solid was filtered and washed exhaustively with deionized water in order to remove the chloride. Finally, the catalyst was dried at 100 °C for 2 h and just before reaction it was calcined in air at 350 °C during 2 h.

A TEM study was carried out in order to determine palladium particle size. Highly dispersed spherical nanoparticles on BC, with an average particle size of 2.0 nm were observed.

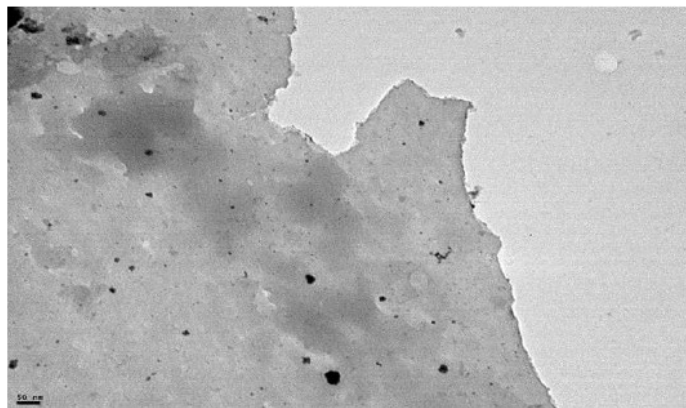


Figure 4. TEM micrograph of PdNPs/BC.

The XRD pattern showed peaks associated with char as well as the ones corresponding to palladium species.

The specific surface area of the PdNPs/BC, as measured by BET methodology, was 65m<sup>2</sup>/g.

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