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Proceeding Paper

Carbocatalytic Synthesis of Azines by Oxidized Multiwalled Carbon Nanotubes [†]

Matías Blanco [1,2,*], Miguel A. Valle-Amores [1], Stefano Agnoli [3], Alberto Fraile [1,2] and José Alemán [1,2,4]

[1] Organic Chemistry Department, Universidad Autónoma de Madrid, 28049 Madrid, Spain; miguel.valle@uam.es (M.A.V.-A.); alberto.fraile@uam.es (A.F.); jose.aleman@uam.es (J.A.)
[2] Institute for Advanced Research in Chemical Sciences (IAdChem), Universidad Autónoma de Madrid, 28049 Madrid, Spain
[3] Dipartimento di Scienze Chimiche and Consorzio Interuniversitario Reattività Chimica e Catalisi-CIRCC, Università degli Studi di Padova, 35131 Padova, Italy; stefano.agnoli@unipd.it
[4] Center for Innovation in Advanced Chemistry (ORFEO-CINQA), Universidad Autónoma de Madrid, Spain
* Correspondence: matias.blanco@uam.es

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Abstract: We present the carbocatalytic synthesis of azines (*N-N* linked diimines) by mild-oxidized multiwalled carbon nanotubes (**oxMWNT**). The material is able to catalyze a room-temperature metal-free condensation of aldehydes with hydrazine to obtain, in just 3 h, a wide library of symmetric and asymmetric azines in excellent yields, even in the gram scale, showing too high selectivity for aromatic substrates. Azines with applications in nonlinear optics, organic materials and biological active compounds crafting can be synthetized through this method. **oxMWNT** owns full recyclability upon the recovery of the catalyst in the azine formation reaction. In addition, we have developed the one-pot synthesis of azines starting from benzyl alcohols.

Keywords: azines; oxidized carbon nanotubes; carbocatalysis; biological relevant molecules; recyclability

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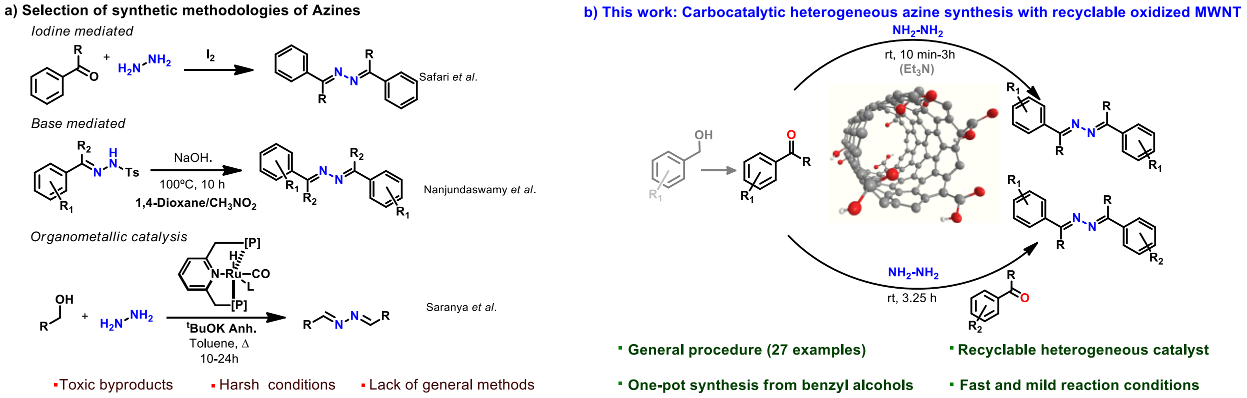
1. Introduction

Azines [1], molecules that contain the R-C=N-N=C-R′ functionality, have gathered increasing attention since they find application in several fields, such as nonlinear optics, liquid crystals as twisted-nematic displays, drug designing (antibacterial, anticancer or antifungal agents) and the synthesis of organic materials as covalent organic frameworks (COFs) [2]. Azines should be prepared by simple condensation of an aldehyde with hydrazine. Nevertheless, this direct approach requires, in many cases, reflux conditions and/or the presence of promoters such as strong Brönsted or Lewis acids, or iodine too. Furthermore, transition-metal organometallic complexes together with reductants and strong bases, using long reaction times are frequently found to promote azine synthesis (Scheme 1a). Carbenes, supercritical or electrochemical techniques, and ultrasound or microwave protocols were also reported [3–7]. To the best of our knowledge, general methods for the synthesis of azines are lacking, and even more, symmetric azines (R = R′) are yielded by some procedures while non symmetric azines (R ≠ R′) require a completely different protocol. In this context, carbon nanomaterials have started to be employed as catalytic materials in the recent times, obtaining comparable or better results than the traditional procedures, and with the advantage that they can be recycled and synergy is usually observed [8]. Indeed, there are reports where nanocarbons catalysed aldol and Knoevenagel condensation reactions, redox reactions and Michael additions [9–12]. Graphene oxide has been employed as benchmark carbocatalyst for this reactivity, but several graphene oxide formulations can be found in the literature where the generated material presents diverse parameters and properties depending on the synthesis conditions, thus preventing a general employment [13]. Conversely, carbon nanotubes (CNTs) are more controllable materials with similar properties to graphene [14]. The oxidation methodologies that deploy the required surface oxygen chemistry to trigger the carbocatalytic character are also well established [15], implying that CNTs would be valid candidate as potential carbocatalyst [16].

In this work we describe the synthesis of symmetric and asymmetric azines by a new versatile, carbocatalytic, and metal-free method using hydrazine and aldehydes with only 5 %wt. of mild-oxidized multiwalled carbon nanotubes as catalyst (**oxMWNT**, see Scheme 1b). Furthermore, **oxMWNT** is also able to carry out the one-pot synthesis but starting from alcohols, employing nitric acid as co-catalyst only. **oxMWNT** generates, a large family of symmetric and asymmetric azines, even in the gram scale and it is a fully recyclable material. The displayed catalytic performance is traced back to a combined action of the surface chemistry with the material's aromatic network.



Scheme 1. (**a**) Previous azines obtaining methods compared with (**b**) this work.

2. Methods

Catalyst preparation: 12 mg of purified MWNT (treated with HCl at 60 °C for 2 h and then water washed [15]) were reacted with 6 mL of concentrated HNO_3 under magnetic stirring at 80 °C for 20 min [17]. Reaction was then cooled down and the black powder was washed with water by centrifugation till reaching neutral pH to yield sample **oxMWNT. oxMWNT*** was prepared identically but maintaining the reaction with HNO_3 for 1 h, while **oxMWNT-TR450** was obtained by thermal reduction at 450 °C during 1 h in a horizontal quartz furnace under an Ar flux of 200 mL min^{-1} (heating ramp: 5 °C min^{-1}) [18].

Azine formation: 0.25 mmol of aldehyde, 0.125 mmol of hydrazine hydrate and 5 %wt. of **oxMWNT** were stirred in 1,4-dioxane at room temperature for a desired time, typically 3 h. Filtration of reaction mixture (and washing for recovery and recycling the catalyst by filtration methods over PTFE membranes), concentration of the filtrate and purification by flash chromatography, when necessary, achieved symmetric azines 3. Gram scale experiments were done with 10 mmol of substrates. Asymmetric azines 5 were obtained identically but employing 0.25 mmol of aldehyde with 0.25 mmol of hydrazine for 20 min, followed by the addition of the second aldehyde and allowed the reaction to proceed for 3 h.

One-pot synthesis: 0.25 mmol of benzyl alcohols, 0.5 mmol of HNO_3 and 5 %wt. of oxMWNT were stirred in 1,4-dioxane at 80 °C for 2 h [10]. Then, cooling down, acid-quenching with Et_3N and general azine synthetic procedure yielded the one-pot azines 3.

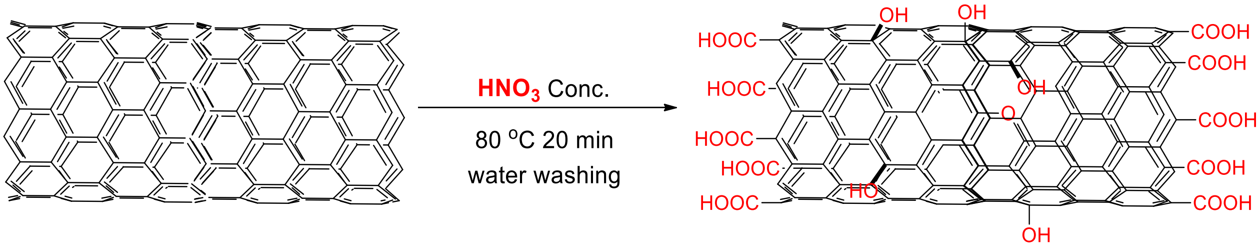
Characterizations: Nuclear Magnetic Resonance (NMR) spectra were acquired on a BRUKER AVANCE spectrometer running at 300 MHz for ^1H. Electrospray Ionization Mass Spectra (ESI-MS) were obtained on an Agilent Technologies 6120 Quadrupole

LC/MS coupled with a Supercritical Fluid Chromatograph (SFC) Agilent Technologies 1260 Infinity Series instrument. Transmission Electron Microscopy (TEM) images were acquired with a JEOL-JEM 2100F instrument. For the elemental analysis measurements, a LECO CHNS-932 Analyser (Model NO: 601-800-500) was used. Qualitative and quantitative Total Reflected X-Ray Fluorescence analyses (TXRF) were performed with a benchtop S2 PicoFox TXRF spectrometer from Bruker Nano (Germany). Fourier Transformed IR (FTIR) were recorded on a FT-IR 4100 JASCO spectrometer, equipped with a Globar source, a DGTS detector and KBr optics with the ATR accessory. X-ray photoemission spectroscopy (XPS) data were acquired in a custom designed UHV system equipped with an Omicron EA125 electron analyzer and a non-monochromatized Al K source (DAR400) at room temperature.

3. Results and Discussion

3.1. Catalyst Preparation

Multiwalled carbon nanotubes (MWNT) of 10 nm in diameter and several µm in length were purified by a treatment with HCl in order to remove the metals responsible of the nanotubes' growth and assess its true carbocatalytic character [15]. Upon this metal etching, TXRF measurements found values of metals below 6 ppm for cobalt or molybdenum, while 1 order of magnitude lower was found for the other metallic impurities present in the sample. Nevertheless, oxygen was present up to 16%. A further increase of the oxygen chemistry at the MWNT surface was accomplished with a more powerful oxidizing agent such as concentrated HNO_3 (Scheme 2) to yield the sample **oxMWNT**.



Scheme 2. MWNT oxidation to yield **oxMWNT**.

The HR-TEM revealed **oxMWNT** nanotubes with irregular carbon walls and amorphous carbon surrounding the tubular material (Figure 1a). The procedure was not very aggressive since the nanotube was firmly conserved, being difficult to find any disruption along the carbon scaffold. The oxidation was demonstrated by elemental analysis, where the oxygen content increased from 16 % to 25 % in the oxidized **oxMWNT** sample. The presence of oxygenated functional groups was determined employing FTIR (Figure 2a), which showed a band at around 1100 cm^{-1} related to C-O bonds. Moreover, the shoulder at ~ 1200 cm^{-1} could inform about the presence of epoxy groups [19]. Furthermore, an important fraction belonged to COOH functions, which were assigned by the detected band at 1720 cm^{-1} corresponding to the C=O vibrations of carboxylic acids, were found [17]. XPS confirmed the FTIR and elemental analysis results (Figure 1b), because a tiny quantity (< 7.5%) of hydroxyl or epoxide groups (C-O, 286.5 eV of BE) was present on pristine MWNT sample. Conversely, carbonyls (287.8 eV) or carboxylic acids (289.1 eV) were only barely detectable (<2%) [20]. On the other hand, the surface defects and oxygen chemistry got incremented till doubling the amount in sample **oxMWNT** (22.1% vs. 11.8%). Carboxyls and carbonyls showed a relative intensity of 3.5% and 6.4%, respectively, and the hydroxy/epoxy moieties were also increased to a noTable 12.2%. Therefore, the three techniques employed indicated that, after treatment with the HNO_3 agent, an enrichment in surface oxygen was produced on the **oxMWNT** walls.

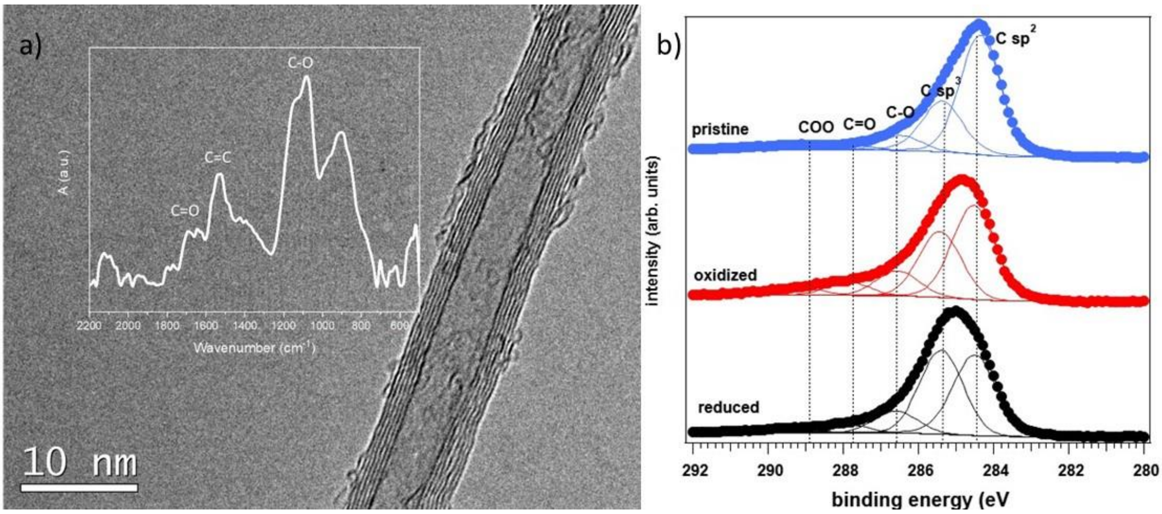


Figure 1. (**a**) Representative TEM image of **oxMWNT**. Inset: FTIR spectrum of **oxMWNT**; (**b**) C 1s XPS core level region of the nanotube carbocatalysts with the corresponding fitting into individual components.

3.2. Mechanistic Insights

As starting reaction point, we mixed benzaldehyde **1a** (0.25 mmol) with hydrazine hydrate **2** (0.5 equivalents) at room temperature in 1,4-dioxane in the presence of 5 % wt. loading of **oxMWNT** (1.3 mg), aiming to yield a hydrazone. However, the reaction afforded the azine **3a** in excellent yield (93%) after 3 h (Figure 2). Even though the hydrazone formation does not need to be catalyzed, further condensations to form an azine are not trivial, due to the large delocalization of the free electron-pair at the hydrazone, which produces lower nucleophilicity, making challenging its further condensation [21]. We initially monitored the condensation reaction withdrawing aliquots at regular intervals. The NMR tracking showed a *pseudo*-first order evolution in the azine formation, suggesting that the azine is likely formed by reaction of the immediately generated hydrazone in the presence of **oxMWNT**. On the other hand, the aldehyde was consumed after the first hour, while the hydrazone was progressively transformed in the final product in the last 100 min of reaction. This behaviour made us think that the nanotubes may play an important role in the formation of the azine. The employment of the "non-oxidized" MWNT sample showed just 60 % conversion of azine after 150 min of reaction. The amount of condensed azine obtained decreased to 20 % in a reaction performed without the carbon material (Figure 2). Interestingly, the overoxidized catalyst **oxMWNT*** (31 % oxygen) was able to finish the condensation in just 10 min of reaction, while the reduced **oxMWNT-TR450** (8% oxygen) just achieved 75 % conversion in the standard **3a** azine formation reaction. Therefore, the surface oxygen groups decorating the nanotube walls likely interact with the reactants by non-covalent interactions (typical Lewis acid behaviour [22]), which drives the reactivity towards the generation of the intended products. Nevertheless, other possible mechanisms could also take place, such as radical pathways. We performed the standard azine **3a** condensation in the presence of 3.6 equivalents of the radical scavenger TEMPO and we obtained the azine **3a** with a very similar performance, thus discarding a radical mechanism. On the other hand, the water molecules released at the condensation could also influence the reaction. Thus, we carried out the condensation in absence of water using $MgSO_4$ as desiccant. This test afforded the azine **3a** with the same performance as the standard run. Finally, starting from the corresponding hydrazone **4a** in absence or in the presence of the stoichiometric amounts of water resulted in the same full conversion reaction to the azine **3a**. These tests showed that the presence of water has no effect on the formation of azines catalyzed by **oxMWNT** because the aromatic azine formation reaction mainly takes place at the surface of the nanotubes, implying that the mechanism might be a surface version of a classic condensation.

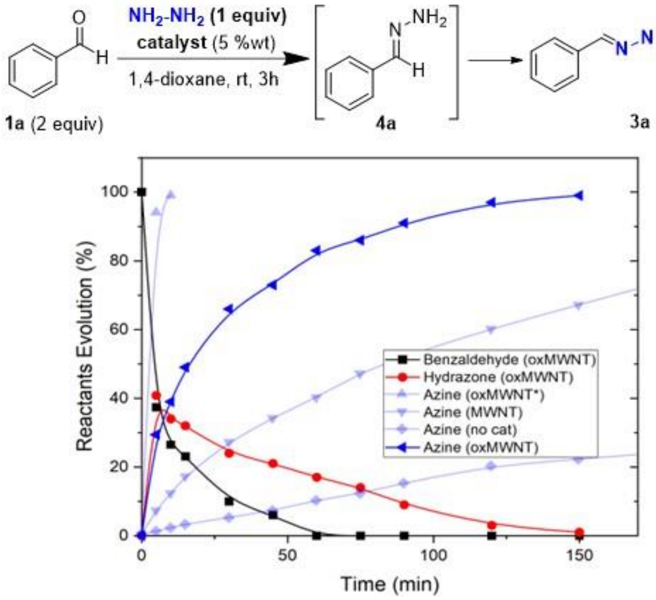
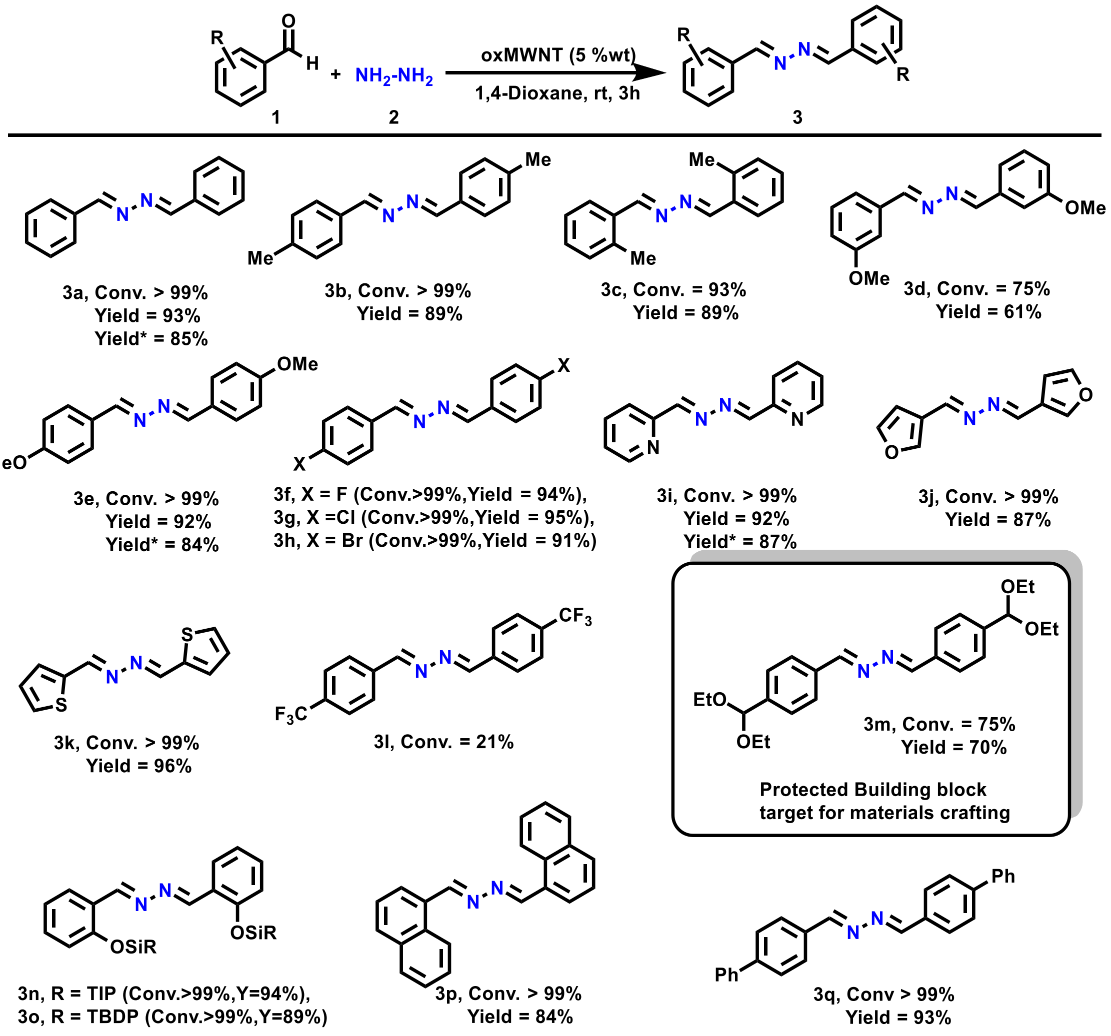


Figure 2. Time evolution of diphenyl azine formation catalysed by the different CNTs (lines are guide for the eyes).

3.3. Catalyst Scope and Recycling

Once known how **oxMWNT** performs in the azine condensation reaction, we challenge our catalyst to synthetize a large family of azines **3** using the same general procedure reported in Table 1. The reaction tolerated electron-donating groups irrespectively of their relative position at the phenyl ring. Hence, *o*-methyl and *p*-methyl aromatic azines could be generated with good yields (**3b** and **3c**, 89%). In addition, *m*-methoxy and *p*-methoxy symmetric azines (**3d** and **3e**) ranged from 61% to 92% yields, respectively. Azine **3e** could be obtained in the gram scale with an 84% yield. A halogen atom in the aldehyde precursor was either tolerated in the azine formation reaction (**3f-h** for -F, -Cl and -Br, respectively) with very good performance (91–95% yield). **oxMWNT** catalyst was also able to smoothly convert pyridine, furan and thiophene aldehydes into the corresponding azines (**3i-k**) with yields ranging from 87% to 96%. The pyridine azine **3i** was also obtained in the gram scale with a yield of 87%. However, the azine formation method owned some limitations. For example, the CF_3 azine **3l** was obtained in 21% conversion. Nevertheless, the protected aldehyde allowed the synthesis of azine **3m** in 70% yield, which potentially can be used for organic materials crafting [2]. On the other hand, the method did not work with aldehydes with protic groups. Conversely, this limitation could be overcome employing a simple protection pre-step with silanes as tri-isopropyl silane (TIPS) or *tert*-butyl diphenyl silane (TBDPS) (**3n** and **3o**), obtaining excellent yields (89% and 94%, respectively). Finally, other substrates such as a naphthyl aromatic ring (**3p**) or biphenyl (**3q**) could be tolerated in the formation of a more steric demanding azines in high yield (84% and 93%). We also tried to synthesize alkyl azines, but only the corresponding hydrazones were obtained in almost full conversion. Thus, the selectivity of the catalyst for aromatic substrates agrees with the mechanism explained above, highlighting the adsorption of the substrate at the nanotube wall as key step. Indeed, electron-rich substrates π-π stick more efficiently than the electron poor substrates, which is reflected in the reactivity in strong contrast with the known electrophilicity of the non-converted electron poor aldehydes in this surface-mediated reaction.

Table 1. Symmetric (**upper**) and asymmetric (**lower**) azine scope catalyzed by **oxMWNT**.



3a, Conv. > 99%
Yield = 93%
Yield* = 85%

3b, Conv. > 99%
Yield = 89%

3c, Conv. = 93%
Yield = 89%

3d, Conv. = 75%
Yield = 61%

3e, Conv. > 99%
Yield = 92%
Yield* = 84%

3f, X = F (Conv.>99%,Yield = 94%),
3g, X =Cl (Conv.>99%,Yield = 95%),
3h, X = Br (Conv.>99%,Yield = 91%)

3i, Conv. > 99%
Yield = 92%
Yield* = 87%

3j, Conv. > 99%
Yield = 87%

3k, Conv. > 99%
Yield = 96%

3l, Conv. = 21%

3m, Conv. = 75%
Yield = 70%

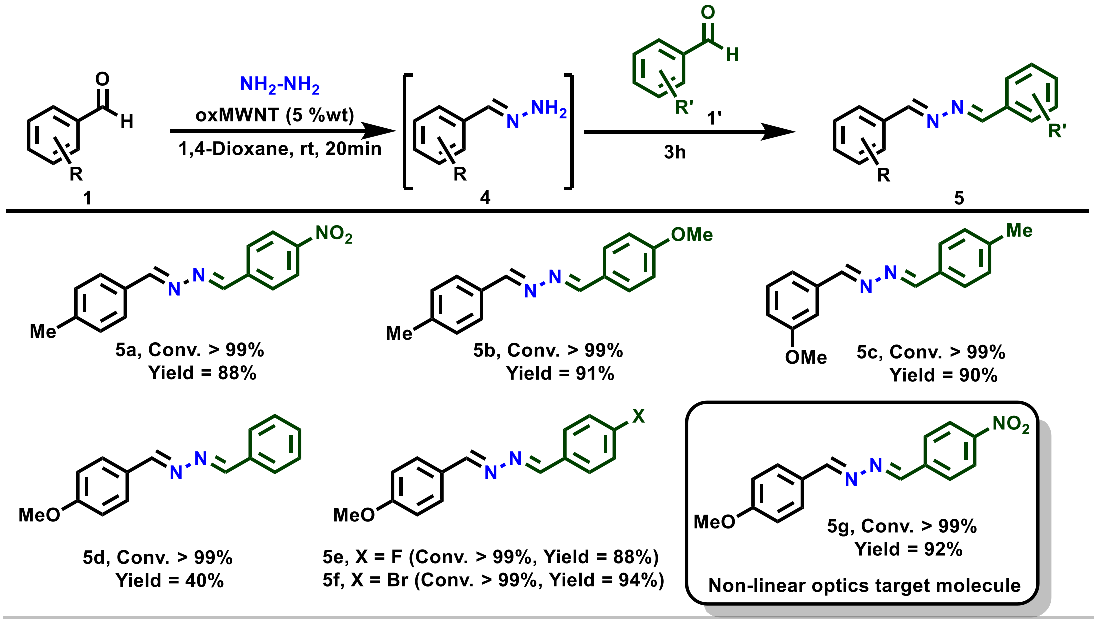
Protected Building block
target for materials crafting

3n, R = TIP (Conv.>99%,Y=94%),
3o, R = TBDP (Conv.>99%,Y=89%)

3p, Conv. > 99%
Yield = 84%

3q, Conv > 99%
Yield = 93%

a) Reaction conditions: 0.25 mmol of aldehyde, 0.125 mmol of hydrazyne hydrate, 0.5 M 1,4-dioxane, 5 %wt. **oxMWNT**, for 3h at room temperature. Conv. stands for conversion (determined by ^{1}H-NMR). Yield* refers to a 10 mmol reaction

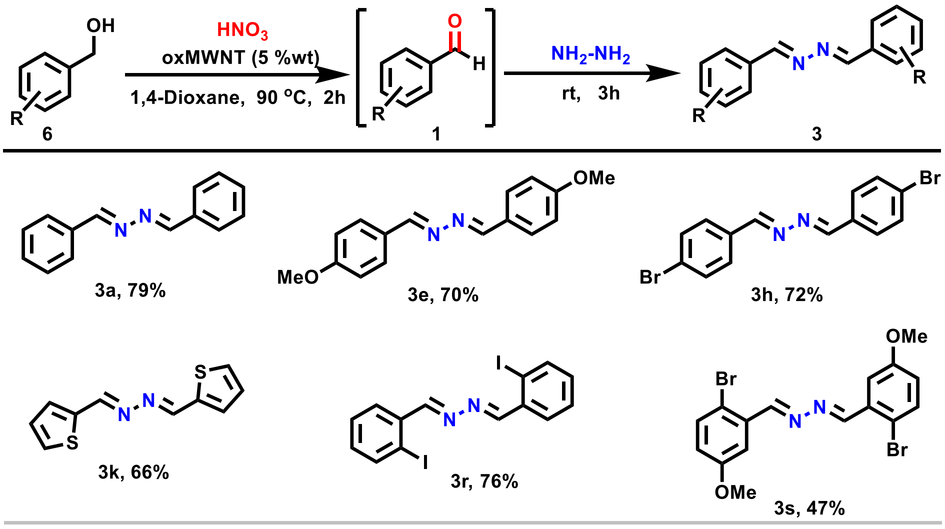


Reaction conditions: 0.25 mmol of aldehyde, 0.25 mmol of hydrazyne hydrate, 0.5 M 1,4-dioxane, 5 %wt. oxMWNT, for 20 min at room temperature. Then, 0.25 mmol of second aldehyde for 3 h. Conv. stands for conversion (determined by ^{1}H-NMR).

Asymmetric azines **5** could be synthetized following the general azine formation reaction, but using 1 equivalent of hydrazine hydrate **2**, stopping after 20 min and immediately adding a second aldehyde to this mixture, allowing them to react for 3 more hours. Thus, the limitations from the symmetric azine synthesis method could be surpassed and the reactivity was expanded to different substituents in both phenyl units. For instance, the azine **5a**, with a *p*-methyl and a *p*-nitro at each aromatic ring, could be synthesized with a yield of 88%. It is worthy to mention that the relative position of the substituents (*metha* or *para*) did not change the reaction outcome since an azine, where one phenyl ring contained a methoxy group and the other phenyl ring owned a *p*-methyl unit, was synthetized in an excellent 91–90% yield (**5b** and **5c,** respectively). The presence of halogens atoms at the aromatic rings also afforded derivatives **5e** and **5f** in good yields. In addition, the electron-rich hydrazone bearing a *p*-methoxy group reacted with the electron-poor *p*-nitrobenzaldehyde to give the azine **5g** with a 92% yield, which can be potentially applied for nonlinear optics [2]. Finally, using our conditions, but without the presence of the **oxMWNT** (or not waiting 20 min), azine **5g** could not be obtained with good results.

We also challenged the **oxMWNT** catalyst to perform an azine one-pot synthesis starting from benzylic alcohols. After formation of corresponding aldehydes **1** via oxidation catalysed too by **oxMWNT** using nitric acid as co-oxidant and acid neutralization [10], the mixture was treated with hydrazine hydrate **2** and additionally reacted for 3 h, obtaining the final azines with overall yields from 48 to 80% (see Table 2). Using this method, we were able to synthetize symmetric azines, in a one-pot manner, with a phenyl (**3a**) (79% yield), a *p*-bromophenyl (**3h**) and an *o*-iodophenyl (**3r**) group (72% and 76 % yield, respectively), a *p*-methoxy-C_6H_4 (**3e**) (70% yield), a thienyl group (**3k**) (66%) and a more substituted azine bearing bromo and methoxy moieties in the aryl ring (**3s**) (47% yield). We also added value to our methodology accomplishing the synthesis of azines with biological interest (Figure 3) [2], such as the antibacterial azine **5q**, obtained with an excellent 78% of global yield or the antifungal azine **3u,** which was obtained in almost quantitative yield (91% global yield, 3 steps). Finally, we studied the recyclability of the carbocatalyst, collecting by filtration the black catalyst at the end of each experiment, and washing the recovered solid with water and organic solvents and setting for a new oxidation-condensation reaction. No loss of activity was detected when performing a cycling study on benzyl alcohol (**6a**) oxidation-condensation runs to form the azine **3a** (see Figure 3).

Table 2. One-pot formation of azines from benzyl alcohols catalysed by **oxMWNT**.



Reaction conditions: Step 1: 0.25 mmol of alcohol, 0.5 mmol of HNO_3, 0.5 M 1,4-dioxane, 5 %wt. oxMWNT, for 2h at 90 °C. Step 2: Reactor cooled to room temperature, 0.5 mmol of Et_3N and 0.125 mmol of hydrazine hydrate, for 3 h at room temperature. Values stand for total isolated yield

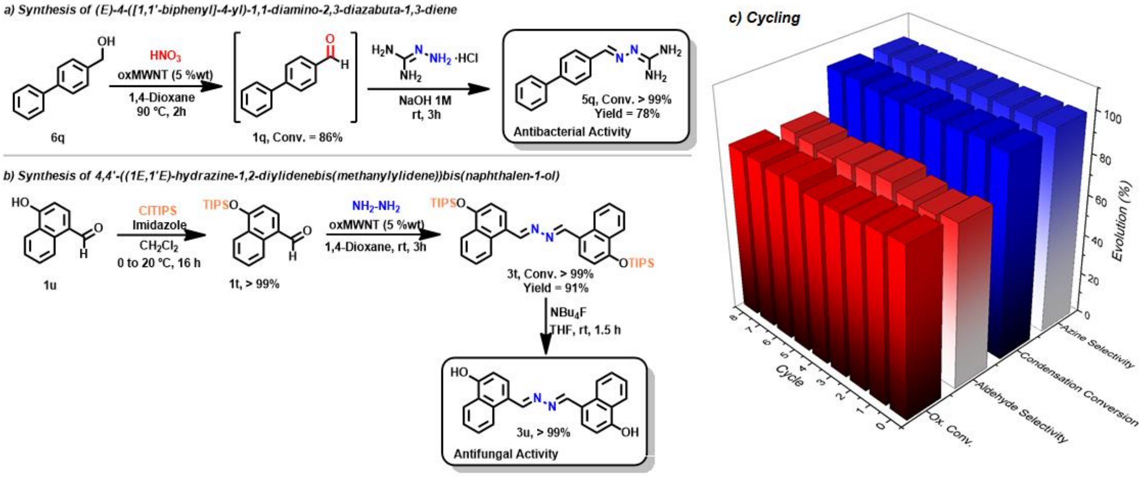


Figure 3. Synthesis of biological relevant azines with **oxMWNT**, including the cycling study.

4. Conclusions

This work describes a carbocatalytic method for the synthesis of a wide library of azines using as catalyst mildly acid oxidized multiwalled carbon nanotubes. The azine synthesis was performed mixing an aldehyde with hydrazine hydrate using as catalyst loading 5 % wt. of **oxMWNT**. The reaction can be scaled up to the gram scale. **oxMWNT** is able to yield symmetric and asymmetric azines within reaction times typically of 3 h as a function of the surface oxygen chemistry. In addition, these azines can be synthetized carrying out one-pot methods using as substrate the corresponding alcohol with total yields as high as 80%. Regarding the mechanism, aromatic aldehydes strongly stack to the nanotube wall and could be condensed, while aliphatic substrates were not physisorbed and therefore not converted. The data suggest that the substrates are able to react following this surface version of the general condensation once fixed at the **oxMWNT** surface and transformed through the oxygen surface chemistry.

Author Contributions: M.B.: Conceptualization, Writing—review & editing, Supervision. M.A.V.-A.: Investigation, Formal analysis. S.A.: Investigation, Formal analysis. A.F.: Conceptualization,

Writing—review & editing, Supervision. J.A.: Conceptualization, Writing—review & editing, Supervision. All authors have read and agreed to the published version of the manuscript.

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