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A straightforward approach to multifunctional graphene

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Abstract

Graphene has been covalently functionalized through a one-pot reductive pathway using graphite intercalation compounds (GICs), in particular KC_8 , with three different orthogonally-protected derivatives of 4-aminobenzylamine. This novel multifunctional platform exhibits excellent bulk functionalization homogeneity (H_{bulk}) and degree of addition while preserving the chemical functionalities of the organic addends through different protecting groups, namely: tert-butyloxycarbonyl (Boc), benzyloxycarbonyl (Cbz) and phthalimide (Pht). We have employed (temperature-dependent) statistical Raman spectroscopy (SRS), X-ray photoelectron spectroscopy (XPS), magic angle spinning solid state ^{13}C NMR (MAS-NMR), and a characterization tool consisting of thermogravimetric analysis coupled with gas chromatography and mass spectrometry (TG-GC-MS) to unambiguously demonstrate the covalent binding and the chemical nature of the different molecular linkers. This work paves the way for the development of smart graphene based materials of great interest in biomedicine or electronics, to name a few, and will serve as a guide in the design of new 2D multifunctional materials.

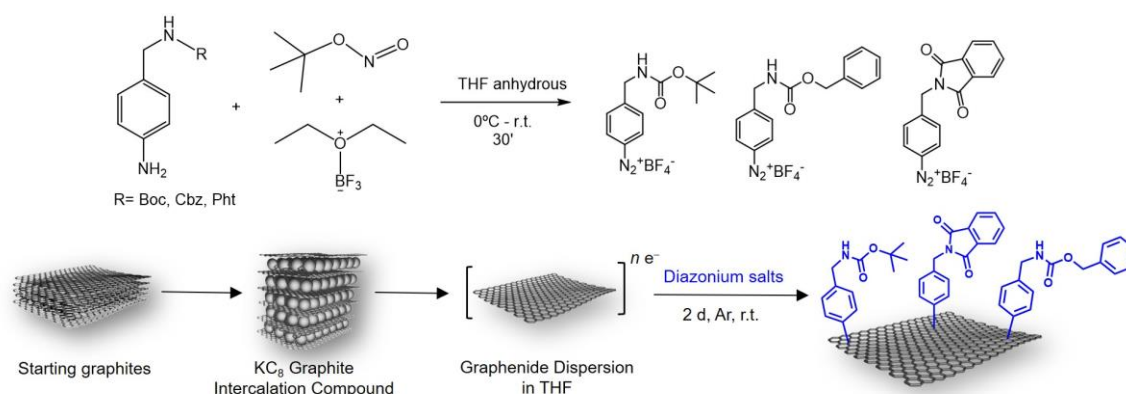
Introduction

Since its discovery, the chemical functionalization of graphene has been investigated with the purpose to tune its unique electrical properties and improve the functionalities of the material.^[1] The development of functional materials can be considered one of the great challenges on the chemistry of graphene, with the purpose to increase the performances of this 2D material. The reactivity of graphene has shown to be strongly correlated to the number of layers constituting each sheet, and it decreases dramatically with the increasing of the number of layers.^[2-4] For this reason, an extensive variety of organic reactions has been reported in the literature for monolayered graphene,^[4-7] but not all these reactions can be applied satisfactory for a scale-up production from bulk graphene. In this context, the reduction of graphite using alkaline metals yielding graphite intercalation compounds (GICs), followed by the quenching of the intermediately generated graphenides^[8] with electrophiles, is an appropriate alternative to enhance the functionalization degree in bulk graphene dispersions.^[9-12] The reactivity of intercalated graphenide species is higher respect to few layer graphene, and strongly dependent on the ratio between carbon and metal atoms, leading to different degree of functionalization.^[12] Besides these fundamental studies, one of the most important synthetic challenges in graphene chemistry that remains to be addressed is to develop a straightforward approach for the bulk synthesis of graphene functionalized with several molecules, each of them endowed with specific functions (*i.e.* multifunctionalization). Along this front, herein we have investigated the multifunctionalization in one-step reaction of bulk graphene, taking advantage of the reductive route using potassium-intercalated KC_8 GICs.^[11] This approach allowed us to obtain a multifunctional platform with a high level of functionalization and in elevate quantities, suitable for the development of smart graphene-based materials. In particular, we focused our attention on the characterization of the multifunctional material obtained. Thanks to the cross-use of several high-end complementary techniques including statistical Raman spectroscopy (SRS), X-ray photoelectron spectroscopy (XPS), magic-angle-spinning solid state NMR (MAS-NMR), thermogravimetric analysis coupled with gas chromatography and mass spectrometry (TGA/GC/MS) and Kaiser test, we were able to recognize and quantify the presence of the three different functional groups introduced on the surface of graphene. Our results demonstrate that it is possible to synthesize in one pot a multifunctional graphene derivative with three different orthogonally-protected derivatives of 4-aminobenzylamine,

while obtaining a high degree of addition and excellent bulk homogeneity. This will facilitate the future development of unprecedented smart graphene-based materials endowed with multiple functionalities.

Results and discussion

Our approach to the preparation of a multifunctional graphene (mf-G) started with the synthesis of three different orthogonally-protected derivatives of 4-aminobenzylamine (see Supporting Information),^[13] followed by the synthesis and isolation of the corresponding diazonium salts (Scheme 1). With these reagents in hands, we then intercalated pristine natural graphite (synthetic spherical graphite, SGN18) with metallic potassium,^[11,14] yielding KC_8 , an intermediate reduced form of graphite. Intercalated graphite, as widely described in literature is highly reactive respect to exfoliated few layers graphene and its preparation requires inert atmosphere and complete absence of water.^[12,14–17] KC_8 was sonicated in dry and degassed THF by tip sonication for 5 min to favour the almost complete exfoliation of graphene in monolayers, leading to a graphenide dispersion.^[8,18,19] One equivalent (constituted of 1/3 of each derivative) of the diazonium salts was mixed with KC_8 and reacted for 2 d at room temperature. After this time, benzonitrile (PhCN) was added under argon atmosphere, as scavenger for the residual negative charges to avoid side reactions, such as oxidation with atmospheric O_2 during the work-up, due to an incomplete charge-quenching of the graphenides.^[12,19,20] The material was then washed with dichloromethane, ethanol and water, to remove the organic species present in the mixture. Each reaction batch was carried out on an amount of ~ 80 mg KC_8 as starting material.



Scheme 1: Synthesis of the diazonium salt derivatives and functionalization of KC_8 . Boc, *tert*-butyloxycarbonyl; Cbz, benzyloxycarbonyl; Pht, phthalimide. Starting graphite is melted with

potassium to form KC_8 stage I graphite intercalation compound (GIC). The dispersion of KC_8 in THF using sonication leads to the formation of a graphenide solution. The quenching of the negatively charged graphenides with the three different diazonium salts leads to the covalently multifunctionalized graphene.

The evaluation of the functionalization of graphene started with statistical Raman spectroscopy (SRS). The analysis of the average Raman spectra revealed an increasing of the intensity of the D band respect to the G band of the bulk graphite (I_D/I_G ratio 0.1), and the appearance of the D' band. Moreover, the typical 2D band at $\sim 2690\text{ cm}^{-1}$ is overlapped by the appearing of a D+D' band at $\sim 2900\text{ cm}^{-1}$. This phenomenon is in agreement with the data reported in the literature and is as consequence of the A_{1g} mode-breathing vibrations of six-membered sp^2 carbon rings, which becomes Raman active after the symmetry of the nearby lattice is reduced (sp^2 carbons are converted to sp^3 hybridization) by the covalent functionalization with the diazonium salts.^[12,21–23] The calculation of the intensity I_D/I_G distribution functions between the D band ($\sim 1350\text{ cm}^{-1}$) and the G band ($\sim 1582\text{ cm}^{-1}$) resulted in a value of 1.3, analyzing three different areas of the sample (Figure 1a). The narrow statistical distribution of the I_D/I_G shows a residual contribution of pristine unreacted graphite and high homogeneity of the entire bulk functionalization (H_{bulk} , Figure 1b).^[24]

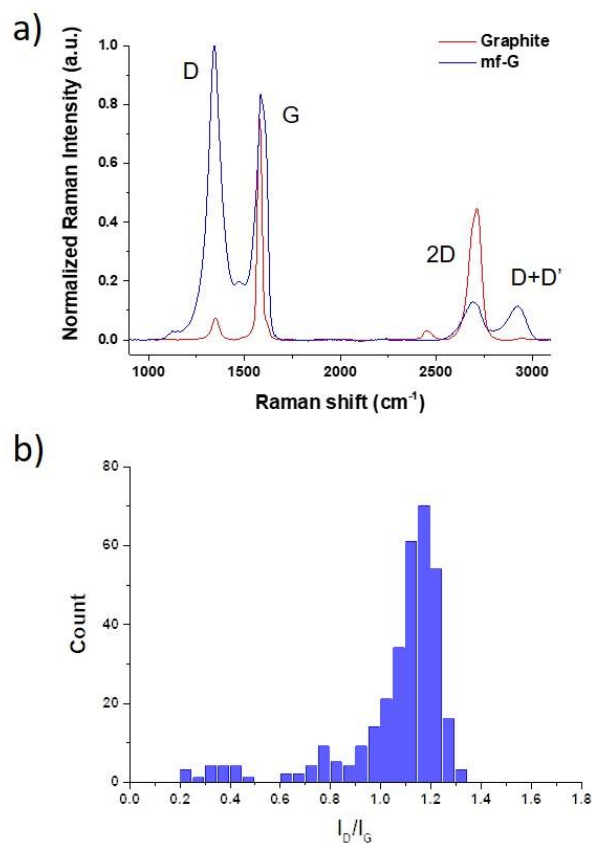


Figure 1: a) Comparison between mean Raman spectra (~500 single-point spectra) of graphite and mf-G; b) Distribution of I_D/I_G ratio from the Raman statistical analysis.

To assure that the drastic conditions of the reactions on graphene and that the functionalization do not affect the morphology of the layers, mf-G was dispersed in DMF by bath sonication and observed by transmission electron microscopy (TEM), confirming the typical shape of 2D materials (Figure 2).

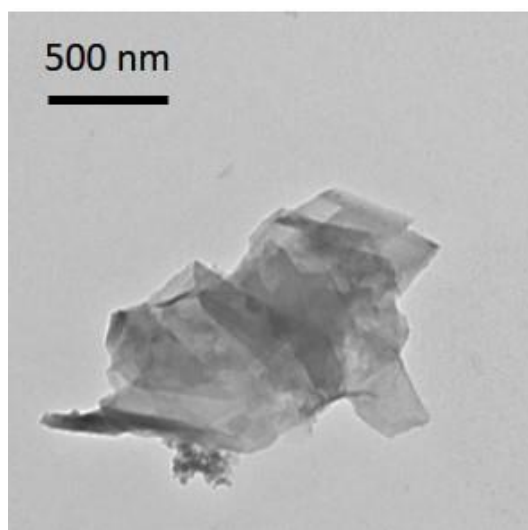


Figure 2: Low-magnification TEM image of mf-G.

Subsequently, we investigate, through temperature-dependent statistical Raman spectroscopy (T-SRS), the thermal evolution of the material between 25 and 450 °C. The I_D/I_G ratio, slowly diminish until 200 °C and then starts to decrease dramatically reaching mean I_D/I_G values of 0.45 at 425 °C (Figure 3a). This phenomenon is due to the detachment of the functional groups from the surface of graphene and corresponds to the rehybridization from sp^3 to sp^2 of the carbon atoms, thus restoring of graphitic configuration. In addition, it is also remarkable the increase of the 2D band and the decrease of the D+D' band, confirming that the defunctionalization process of the diazonium salt derivatives was occurring (Figure 3b). The observation of the detachment of covalently bound moieties was corroborated by the thermogravimetric analysis (TGA). The weight loss profile (Figure 3a) is stable until 220 °C, temperature above which the drastic weight loss begun. To well understand the slight difference on the defunctionalisation temperature observed between the two above-mentioned techniques, we must consider that the warming-up ramp programs present small differences. TGA program warm-up the samples at 10°C/min uniformly, while during Raman analysis the sample is warmed-up in successive steps, keeping stable the settled temperature during the scanning time. We can then affirm that the overall defunctionalization starts between 200° and 220° C.

Moreover, the observed weight loss of ~ 15% is in good agreement with the I_D/I_G ratio value of 1.3, corresponding to a high degree of functionalization of graphene.^[12] In addition, these results suggest the absence of secondary products, in good agreement with combined thermogravimetry gas chromatography and mass spectrometry analysis (*vide infra*). The high reactivity of KC_8 species was compared to the neutral route, *i.e.* the reaction to form mf-G performed starting from pristine few layers graphene exfoliated in NMP (see Supporting Information for the details). Graphene was reacted with a mixture of the same diazonium salts used to modify KC_8 following two different paths, one forming *in situ* the salts (mf-G_{situ}) using isopentyl nitrite, and the second using the preformed and well-characterised diazonium salts (mf-G_{pre}). As reported by the group of Hirsch,^[11] the functionalization of few layer graphene with diazonium salts requires a high ratio between graphene and the functional molecules (~ 1:6 eq.) to obtain materials with an elevated degree of functionalization. Besides, the use of high amount of reactive species is leading to side reactions, such as modification of the introduced functional groups or quenching of the reactive species by radical recombination.^[25]

Following the previous protocol, we performed the reaction in a ratio of 1:4 and 1:6 between graphene and the diazonium salts, obtaining a much lower degree of functionalization than in the case of KC_8 . The Raman analysis allowed us to measure an I_D/I_G mean ratio of 0.36 and 0.41 for mf-G_{situ} and mf-G_{pre}, respectively, starting from the value of 0.21 for the exfoliated graphene (Figure S1). Then, TGA analysis showed for both reactions a weight loss value of ~7 % (Figure S2). Both techniques confirmed the low degree of functionalization of these materials, which was not satisfactory and suitable for further applications of mf-G.

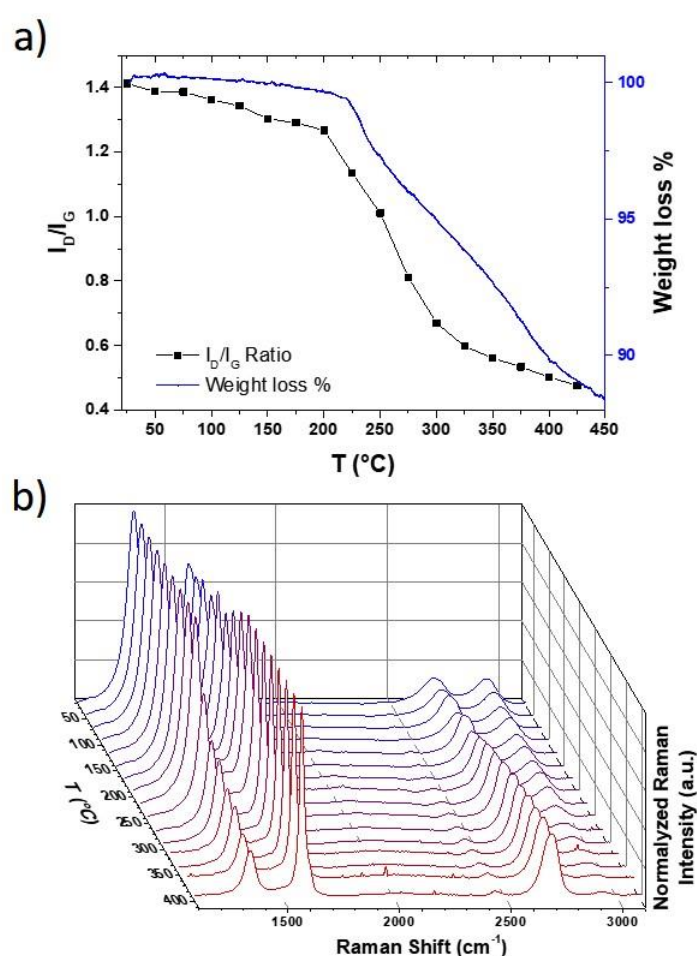


Figure 3: Temperature-dependent statistical Raman spectroscopy (TSRS) of mf-G in the temperature region between 25 and 450 °C. a) I_D/I_G ratio plotted respect to temperature and TGA analysis of mf-G. b) Means of the Raman temperature depending spectra.

The data obtained from the Raman analysis and the TGA are relative to the quantity of defects introduced on graphene surface during the functionalisation reactions but do not provide information about the chemical nature of these defects. To verify the effective functionalization with the different diazonium salt derivatives, several techniques were applied. First, the presence of N element was investigated by X-ray photoelectron

spectroscopy (XPS). The atomic percentage composition of mf-G was measured, revealing a ratio between C, O and N of 86.2%, 10.8% and 3.00% for the mf-G, respectively, and of 94.5%, 5.2% and 0.35%, respectively, for graphene after the initial potassium intercalation. The increment of N is the first advice that the increase of the defects observed by Raman spectroscopy is related to the grafting of the new functional groups and not due to a simple oxidation of graphene. In order to obtain a direct and unique confirmation of the presence of the functional groups on graphene, the Kaiser test was performed on mf-G.^[26,27] This test consists in a quantitative analysis of primary amines evaluated by UV-Vis spectroscopy.^[28] Each protecting group was selectively removed (see Supporting Information for details) and the test performed on graphene dispersions. The obtained results of 76, 42 and 46 $\mu\text{mol/g}$ for Boc, Cbz and Pht protected amines, respectively, are the proof of the presence of the expected functional groups grafted on graphene. The abundance of Boc protected amine respect to Cbz and Pht is due to the reactivity of the species, similarly to the data that we previously reported (Boc>Pht>Cbz).^[13]

To further explore the presence of the functional groups on the graphene structure, we analysed mf-G using MAS-NMR. ^{13}C solid state NMR on graphitic samples,^[29,30] and particularly in the case of single graphene sheets, is known to be rather challenging as it faces specific issues lying on high electric conductivity. Electric conductivity causes probe tuning problems,^[29,31] and very often gives rise to extremely wide lines^[32] that may become undetectable or indistinguishable from probe background signal when using DP/MAS (Direct Polarization/Magic Angle Spinning). As in pure graphene sheets no protons are available to perform CP/MAS experiments (Cross Polarization/Magic Angle Spinning) we recorded here a series of DP/MAS on a 750MHz spectrometer (17.8 Tesla) with a spin-echo sequence^[33] that cures the background signal problem and gives flat baselines and undistorted line shapes. We performed and compared the spectra of graphene after the intercalation of potassium (KC_8), of KC_8 mixed with the starting reagent (G_{mixed}) and of the final mf-G. In the case of the KC_8 sample, as expected for graphene, we had to finely mix it with an insulating powder (SiO_2 in a ratio of 1:4 graphene to SiO_2) to avoid the sample behaves as a bulk conductor^[29] and to achieve correct probe tuning and fast sample spinning. In addition, no clear signal of functional carbon atoms was detected (Figure 4, bottom), which may be an indication of KC_8 ^{13}C nuclei strongly affected by their interactions with conductive electrons.^[30,34] It appears that when compared with the residual probe background signal (Figure 4, bottom) very small

contribution could be ascribed to KC_8 while most of the spectral bands are resulting from the probe/spinner system. Clearly both signals, probe background and KC_8 , are much wider than the filter size used in the spin-echo sequence and they were mostly removed together by the filter. As first evidence of the occurred modification of graphene surface, the electrical conductivity in mf-G results to be much lower if not negligible respective to KC_8 . The probe was perfectly tuning, and the spectrum was collected without mixing with any insulating powder. Three peaks, at 7.0, 49.0 and 103 ppm (Figure 4, top) with rather wide (5 kHz) but detectable lines, are visible. This clearly implies a structural modification that cannot be due to simple stacking of reagents on graphene surface: the case is given in G_{mixed} spectrum (Figure S3 top) where the pure reagents (Figure S3 bottom) mostly keep their chemical shifts (30.0 ppm, 81.3 ppm and 146.2 ppm) together with a small line widening (50 Hz), probably due to magnetic susceptibility effects arising from KC_8 . It is important to note that mf-G presents the same peak series than G_{mixed} , but with big differences in chemical shift. Such difference in mf-G and G_{mixed} spectral features strongly pleads in favour of the covalent functional groups grafting. Indeed, these kind of unexpected variations in chemical shifts are not uncommon in graphene systems and have been ascribed to magnetic susceptibility effect,^[31] knight shift effects (due to electronic conductivity) or to the nucleus independent chemical shift (NICS), due to graphene sheet curvature.^[35] It has also been recently shown that the presence of local structural distortions in graphene can affect the values of the ^{13}C isotropic shielding constant leading to additional shifts in the same orders than those found for mf-G.^[36] However, due to this shifts variance, it is resulting arduous a confident assignment of a peak to a functional group. Nevertheless, based upon our experience, we hypothesized that the peak at 7.0 ppm can be assigned to the aliphatic carbon atoms, likely corresponding to the CH_3 of Boc protecting group. The second peak at 49.0 ppm can correspond to the carbon atoms bound to oxygen ($\text{CH}_2\text{-O}$) and the last at 103 ppm could be related to carbon atoms arranged in aromatic rings. As a confirmation of the covalent grafting of the functional groups, this last assignment is corroborated by the hypothesis that with the increasing of defects on graphene surface, the aromatics rings could result as more localized on the structure.

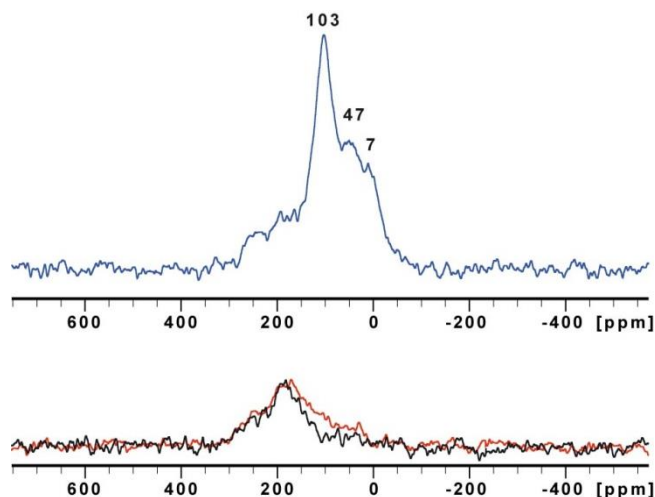


Figure 4: ^{13}C SS NMR spectra of mf-G and KC_8 . Top: DP spin-echo on mf-G. Peaks at 7, 47 and 103 ppm superimpose with probe background signal (bottom, black). Bottom: KC_8 (red) and probe background signal (black) in the same conditions.

Last but not least, to face the problem of the direct identification of the functional groups grafted onto graphene, we analyzed the mf-G with a technique based on the coupling between TGA, gas chromatography and mass spectroscopy (TG-GC-MS).^[12,37] We collected and eluted by GC the molecules and fragments in gas phase generated by the TGA at different temperature of the analysis, to evaluate the composition of the samples. In conventional TG-MS experiments the interpretation of the MS spectra collected is not easy because of the difficulty to predict the evolution of the organic moieties during the TGA process. Not all the m/z fragments collected could be assigned with certainty to a correspondent functional group. In this sense, GC allowed the separation and the mass analysis of each molecule developed during the TGA process, enhancing the interpretation of the MS spectra, a process that is crucial in the case of multifunctionalised materials. From the chromatogram of the gas injected at the temperature of 320 °C (Figure 5), evidence of the presence of Boc protecting group was derived from the characteristic mass signal at m/z 57 eluted with the peak at 3.57 min (Figure S5a). Moreover, two different peaks at 8.60 and 9.72 min were detected. From the chromatogram of the gas injected at 200 °C is it possible to predominantly observe the peak at 4.37 min, corresponding to THF adsorbed on mf-G (Figure S4).

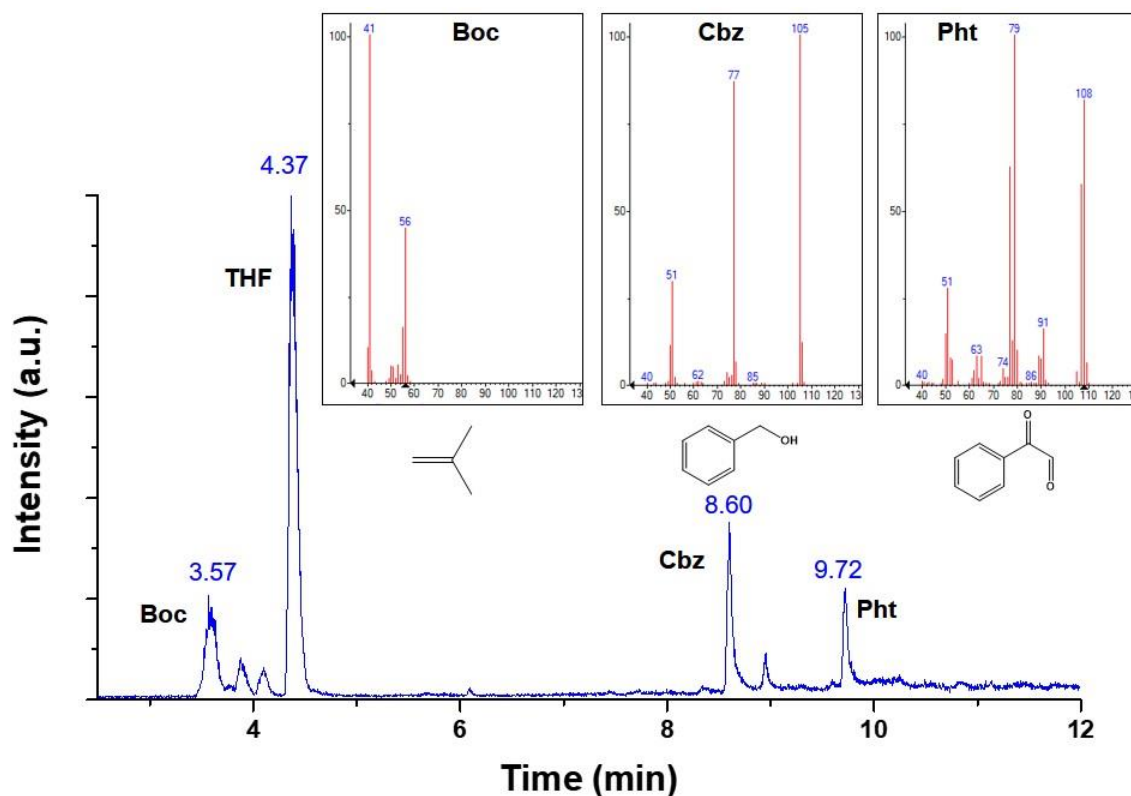


Figure 5: GC-MS spectrum from the TG-GC-MS measurement. Injection at 320 °C: the peaks at 3.57, 8.6 and 9.72 s were associated to Boc, Cbz and Pht, respectively.

The peak at 8.60 min contains mass fragments with m/z ratio of 51, 77 and 105 (Figure S5b). Comparing our MS spectra with a library of spectra, we could observe that these fragments match with the spectra of phenylglyoxal. This molecule is a structural isomer of the fragment of Cbz protecting group. To verify if the observed peak was really related to Cbz fragmentation, we prepared a control experiment consisting of functionalised graphene with only the Cbz diazonium salt derivate, observing the appearance of the same peak at 8.60 min, thus confirming the presence of this functional group. Finally, the peak at 9.72 min showed fragments with m/z of 77 and 108 (Figure S5c), matching with the MS spectra of benzyl alcohol. We hypothesised that this fragment could be generated from a rearrangement of the structure of the phenyl protecting group during the TGA process, after losing a NHCO group. Thanks to the coupling between TGA, GC and MS it was possible to observe fragments with similar m/z at different retention times and assign each one of these to the correspondent functional group on graphene, that would be impossible without the elution of GC. In light of these results we have direct evidence about the presence of the occurred functionalization by the three diazonium salts.

Conclusions

In summary, we developed a one-pot multifunctionalization of graphene with three different orthogonally-protected derivatives of 4-aminobenzylamine obtaining high degrees of addition and bulk homogeneity. We followed a reductive route using KC_8 graphite intercalation compound as activated precursor and an equimolecular mixture of different diazonium salts as electrophiles. Overall, the combination of advanced analytical tools allowed for the detailed identification of the covalently bound organic addends, proving the versatility of this synthetic approach. This work may serve as a guideline for the design of 2D multifunctional materials of great interest in biomedicine, electronics, sensing, or energy storage and conversion.

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Supporting Information

1. Experimental section

Materials

Synthetic spherical graphite (SGN18, 99.99 % C, TGA residue 0.01 % wt—Future Carbon, Germany) mean grain size of 18 μm , specific surface area of $6.2 \text{ m}^2\cdot\text{g}^{-1}$ was used after annealing under vacuum (300 °C) for 24 h. Graphite powder (powder < 20 μm , Sigma Aldrich, code: 282863) was used after exfoliation in N-methyl-2-pyrrolidone (NMP) (see description below) from SigmaAldrich Chemical and solvents were used purchased by Sigma Aldrich Co. and were used as received. Tetrahydrofuran (THF) were stored under Ar over molecular sieve (4 Å) for 3 days. Afterwards the dry solvent (H_2O <10 ppm, determined by using the “Karl Fischer” method) was pump-frozen 8 times to eliminate oxygen residue and then was introduced in the glovebox. Omnipore membrane filters 0.1 μm JH was used for the filtration of all the solutions of graphene. Bath sonicator Elmasonic P at 37 MHz, 100% power was used for preparing graphene dispersions.

$^1\text{H-NMR}$

$^1\text{H-NMR}$ spectra were recorded on Bruker DPX 300 instrument. The peak values were obtained as ppm (δ) and referenced to the solvent. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), m (multiplet).

Glovebox

Graphene functionalization was carried out in an argon-filled LABmasterpro sp glovebox (MBraun), equipped with a gas purifier and solvent vapor removal unit (oxygen and water content lower than 0.1 ppm).

Raman spectroscopy

Raman spectroscopic characterization was carried out on on a Horiba LabRAM Aramis confocal Raman microscope ($\lambda_{\text{exc}}=532 \text{ nm}$) with a laser spot size of *ca.* 1 μm , and equipped with an automated XYZ table using 0.80 NA objectives. The incident laser power was kept as low as possible to avoid structural sample damage. Spectra were obtained with a CCD array at $-70 \text{ }^\circ\text{C}$, and using a grating of 600 grooves per mm. Temperature-depending Raman measurements were performed in a Linkam stage THMS 600, equipped with a liquid nitrogen pump TMS94 for temperature stabilization under a constant flow of nitrogen. The

measurements were carried out on Si/SiO₂ substrates (300 nm oxide layer) with a heating rate of 10 K·min⁻¹.

Thermogravimetric analysis (TGA) combined with gas-chromatographic separation (GC) and coupled with a mass spectrometer (MS)

Thermogravimetric analysis was carried out on a PerkinElmer Pyris 1 TGA instrument. Time-dependent temperature profiles in the range of 20 and 700 °C (20 K·min⁻¹ gradient) were recorded under a constant flow of N₂ (70 mL min⁻¹). About 2.0 mg initial sample mass were used. The evolved gases detached from the respective sample in combination with the N₂ carrier gas is transferred into the GC system through a TL9000 TG-IR-GC interface at a constant temperature of 280 °C. The gas-chromatographic separation was achieved by a GCClaruss 680 with a polysiloxane-coated Elite-5MS capillary column: 30 m length, 0.25 mm diameter, 0.25 μm film thickness. A GC injection fraction of 150 μL was collected at the selected TG temperature (in the range of 200–300 °C), parameters: injector zone = 280 °C, detection zone = 250 °C, flow rate helium = 10 mL·min⁻¹, temperature profile = 34 min total run time, dynamic ramp = 24 min, 40–280 °C with a 10 K·min⁻¹ gradient followed by an isothermal step of 10 min at 280 °C. The obtained data was processed with the TurboMass Software and Bibliographic searches were performed with NIST MS Search 2.0.

Transmission electron microscopy (TEM)

TEM images were collected with an Hitachi 7500 transmission electron microscope (TEM) (Hitachi High Technologies Corporation, Tokyo, Japan) equipped with an AMT Hamamatsu digital camera (Hamamatsu Photonics, Hamamatsu City, Japan)

Solid-State NMR experiments

¹³C Solid-State NMR experiments were performed at room temperature on an AVANCE 750 MHz wide-bore spectrometer (Bruker™) operating at a frequency of 188.5 MHz for ¹³C. All the samples were spun at 30 kHz in a double resonance MAS probe designed for 2.5 mm o.d. zirconia rotors (closed with Kel-F caps). In order to filter out probe background signal and also to get undistorted lineshapes and baselines we used a spin-echo experiment,^[1] synchronized with the rotation (echo time = 6 rotation periods = 200 μs). Durations were 2.22 μs and 4.44 μs for π/2 and π pulses respectively, ensuring proper spectral coverage for such wide lines

(113 kHz ^{13}C B_1 field). Proton decoupling during acquisition was done using the SPINAL-64^[2] decoupling scheme at a 105 kHz RF field and the recycle time was set to 4 s. The spectral width was set to 250 kHz and 16384 transients per FID were acquired on 8192 time domain points. A 1 kHz Lorentzian filter was applied prior to Fourier transform without zero filling. Chemical shift are given respective to tetramethylsilane (TMS) using adamantane as a secondary reference.

Deprotection of protected amines^[3]

Pht deprotection^[4]

mf-G was suspended (concentration 1 mg/mL) in a solution of hydrazine hydrate in ethanol (1:25 v/v). The mixture was sonicated for 5 min in a bath sonicator to disperse the graphene and stirred for 17 h at r.t. in the dark. After this time, the dispersion was filtered and washed with 20 mL of dichloromethane (DCM), EtOH and water. The resulting solid was dried under vacuum. Kaiser test was performed on a dispersion of the obtained powder to evaluate the amount of free amines, compared to mf-G protected (46 $\mu\text{mol/g}$ of primary amines).

Boc deprotection

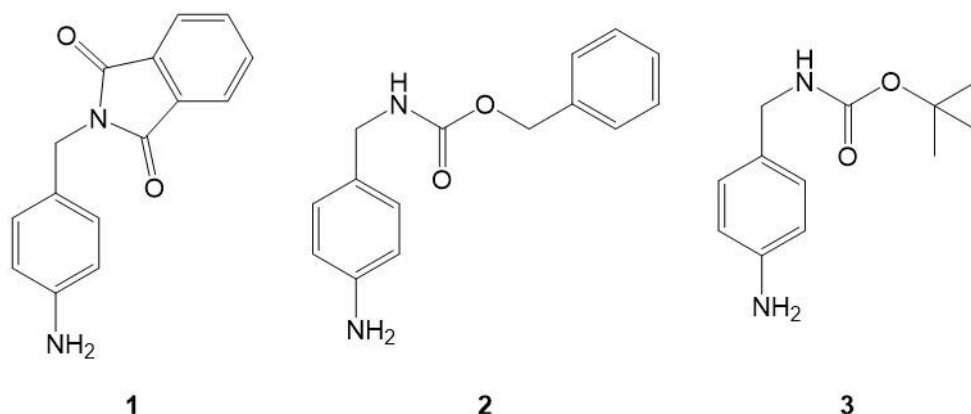
mf-G was suspended (concentration 1 mg/mL) in a solution of HCl 4 M in 1,4-dioxane (purchased Sigma Aldrich). The suspension was sonicated for 5 min in a bath sonicator and stirred for 17 h at r.t. in the dark. After this time, the dispersion was filtered and washed with 20 mL of dichloromethane (DCM), EtOH and water. The resulting solid was dried under vacuum. Kaiser test was performed on a dispersion of the obtained powder to evaluate the amount of free amines, compared to mf-G protected (76 $\mu\text{mol/g}$ of primary amines).

Cbz deprotection

A solution of trifluoroacetic acid (TFA), TMSOTf and *p*-cresol (ratio 3.8:1 v/v and 10 mg *p*-cresol) was prepared. mf-G was dispersed in the solution and sonicated for 5 min in bath sonicator and stirred for 15 h at r.t. in the dark. After this time the dispersion was filtered and washed with 20 mL of dichloromethane (DCM), EtOH and water. The resulting solid was dried under vacuum. To evaluate the amount of amines deprotected from Cbz protecting group, the deprotection was performed on the mf-G Boc deprotected. The amount of Cbz deprotected amines was evaluated subtracting the amount of Boc deprotected amines from the values

obtained through the Kaiser test on the contemporary Boc and Cbz deprotected graphene (118 $\mu\text{mol/g}$ of primary amines total, 46 $\mu\text{mol/g}$ of Cbz protected amines).

2. Synthesis of the reagents^[5]



2-(4-amino-benzyl)-isoindole-1,3-dione (**1**).

To a solution of 4-aminobenzylamine (2.5 g, 20.5 mmol, 1 eq.) in acetonitrile (40 mL) were added mono-methyl phthalate (3.69 g, 1 eq.), BOP reagent (benzotriazol-1-yloxytris(dimethylamino)-phosphonium hexafluorophosphate) (9 g, 1 eq.), and *N,N* diisopropylethylamine (11.4 mL, 3 eq.). The reaction was monitored by TLC (100% dichloromethane). After stirring for 3h, a solution of sodium carbonate (4.1 g) in deionized water (60 mL) was added. The mixture was vigorously stirred over the night, a yellow solid was formed and recover by filtration. The solid was used without further purification. 3.5 g of 2-(4-amino-benzyl)-isoindole-1,3-dione **1** was obtained as a yellow solid (yield: 75%). ¹H NMR (400 MHz, [D₆]-DMSO) δ =4,56 (s, 2 H), 5.03 (s, 2 H), 6.49 (d, J=8.36 Hz, 2 H), 6.98 (d, J=8.32, 2 H), 7.81-7.87 (m, 4 H)

(4-amino-benzyl)-carbamic acid benzyl ester (**2**).

To a solution of 4-aminobenzylamine (2 g, 16.4 mmol, 1 eq.) in 1,4-dioxane (15 mL) was added triethylamine (2.51 mL, 1.1 eq.). A solution of *N*-(benzyloxy carbonyloxy) succinimide (4.29 g, 1.05 eq.) in 1,4-dioxane (18 mL) was added dropwise. The reaction was monitored by TLC. After stirring for 5.5 h, the reaction mixture was evaporated *in vacuo*. The residue was dissolved in dichloromethane and deionized water was added. The two phases were

separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with deionized water and with brine, dried over sodium sulphate, filtered and evaporated *in vacuo*. The residue was purified by chromatography on silica gel using ethyl acetate/cyclohexane 3:7 to 4:6 as eluant. 3.72 g of (4-amino-benzyl)-carbamic acid benzyl ester **2** was obtained as a brown solid (yield: 93%). ¹H NMR (400 MHz, [D₆-DMSO]) δ=3.33 (s, 1 H), 4.03 (d, *J*=6.12 Hz, 2 H), 4.93 (s, 2 H), 5.03 (s, 2 H), 6.50 (d, *J*=8.3, 2 H), 6.91 (d, *J*=8.2 Hz, 2 H), 7.31-7.37 ppm (m, 5 H)

(4-amino-benzyl)-carbamic acid tert-butyl ester (3).

To a solution of 4-aminobenzylamine (2 g, 16.4 mmol, 1 eq.) in tetrahydrofuran (15 mL) was added dropwise a solution of di-tert-butyl dicarbonate (3.93 g, 1.1 eq.) in tetrahydrofuran (18 mL). The reaction was monitored by TLC. After stirring for 5 h, the reaction mixture was evaporated *in vacuo*. The residue was purified by chromatography on silica gel using ethyl acetate/cyclohexane 3:7 as eluant. 3.26 g of (4-amino-benzyl)-carbamic acid tert-butyl ester **2** was obtained as a yellow solid (yield: 90%). ¹H NMR (300 MHz, CDCl₃) δ=1.45 (s, 9 H), 3.647 (broad s, 2 H), 4.18 (d, *J*=5.4 Hz, 2 H), 4.73 (broad s, 1 H), 6.64 (d, *J*=8.4 Hz, 2 H), 7.07 ppm (d, *J*=8.1 Hz, 2 H)

General synthesis of diazonium salts^[6]

A solution of **1**, **2** or **3** (2 mmol, 1 eq.) in anhydrous THF (20 mL) under Ar atmosphere was cooled at 0 °C and boron trifluoride diethyl etherate (8 mmol, 4 eq.) was added dropwise through a syringe. Tert-butyl nitrite (6 mmol, 3 eq.) in 5 mL of THF was added dropwise to the solution and stirred vigorously in the dark at room temperature. The reaction was monitored by TLC. After 30 min an orange solid was formed. The mixture was poured in 100 mL of ethyl ether, filter and washed with ethyl ether (100 mL). The yellowish solid was dried in vacuum and correspond to the pure diazonium salt derivate with 99 % yield reaction.

Boc-protected derivate: ¹H NMR (400 MHz, CD₃OD) δ=1.35 (s, 9H), 4.36 (s, 2H), 7.75 (d, *J*=8.52, 2H), 8.46 (d, *J*=8.56, 2H).

Pht-protected derivate: (400 MHz, [D₆]-DMSO) δ=5.03 (s, 2 H), 7.88-7.38 (m, 6 H), 8.60 (d, *J*=8.80, 2 H)

Cbz protected derivate: (400 MHz, [D₆]-DMSO) δ=4.46 (d, *J*=6.00, 2 H), 5.07 (s, 2 H), 7.33-7.45 (m, 5 H), 7.82 (d, *J*= 8.7, 2 H), 8.61 (d, *J*=8.7, 2 H).

Exfoliation of Sigma-Aldrich Graphite

One g of graphite was dispersed in 200 mL of NMP and sonicated for 1 h. After sonication the dispersion was centrifuged at 1500 g for 45 minutes, the supernatant containing the exfoliated graphene sheets was collected, filter and re-dispersed in 40 mL of NMP, to obtain a dispersion with a final concentration of 0.8 mg/mL.

3. Characterization of the materials

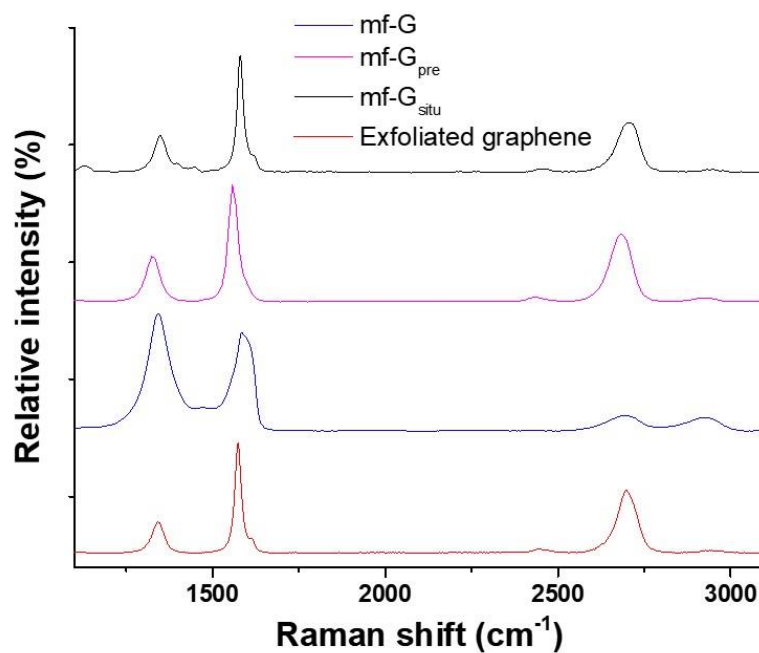


Figure S1: Raman spectra of mf-G_{situ}, mf-G_{isol} and mf-G.

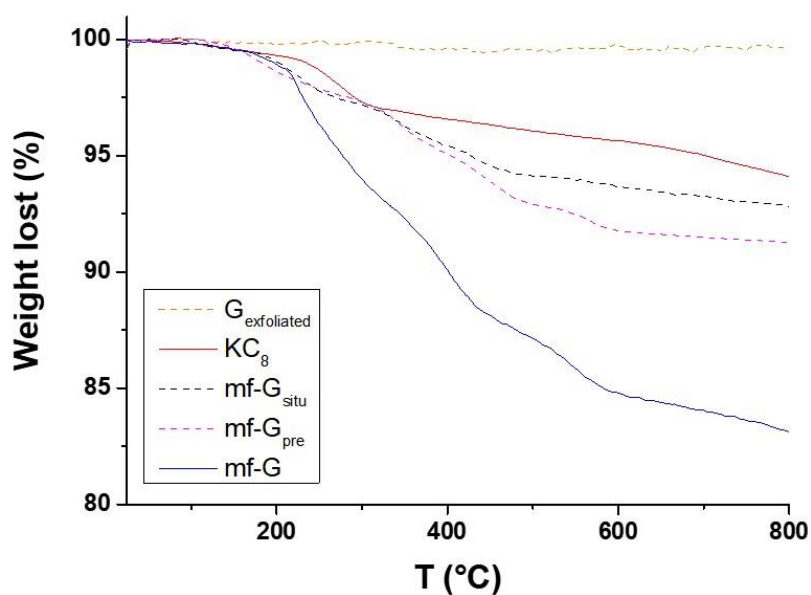


Figure S2: TGA spectra of graphene and mf-G. Dotted lines: exfoliated graphene and mf-G from exfoliated graphene. Straight lines: KC₈ and mf-G.

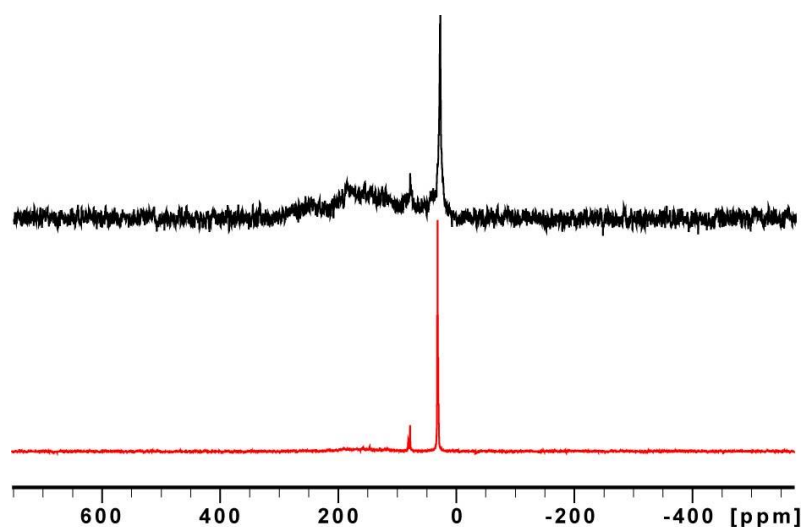


Figure S3: ¹³C SS NMR spectra of G_{mixed} (fine mixture of KC₈ with reagents) and pure reagents. Top: DP spin-echo on G_{mixed} (KC₈ + reagents). Broad lines between 100 and 300ppm are mainly probe background residuals. Comparison with pure reagents (bottom, red) shows quite no differences except small effects on linewidths (50Hz increase) together with a big change in the ratio peaks/background signal as there is much less reagents in the G_{mixed}.

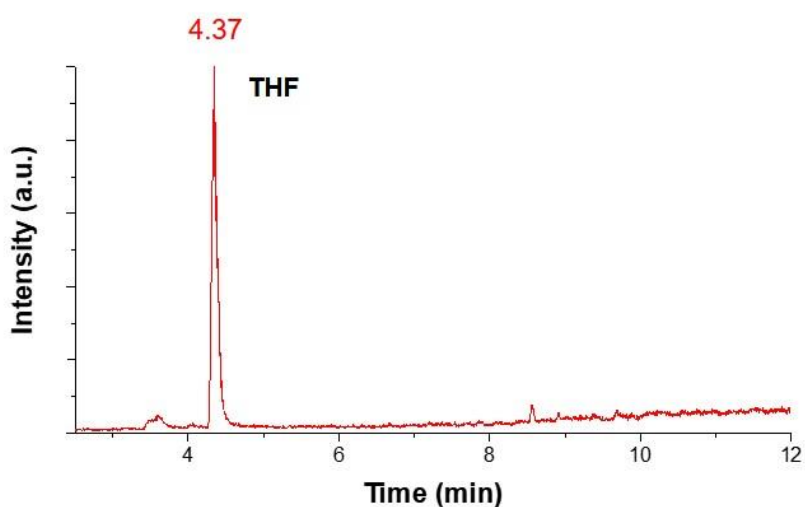


Figure S4: Chromatogram of GC-MS coupled TGA after injection at 220 °C, the peak at 4.37 min corresponds to THF adsorbed on mf-G.

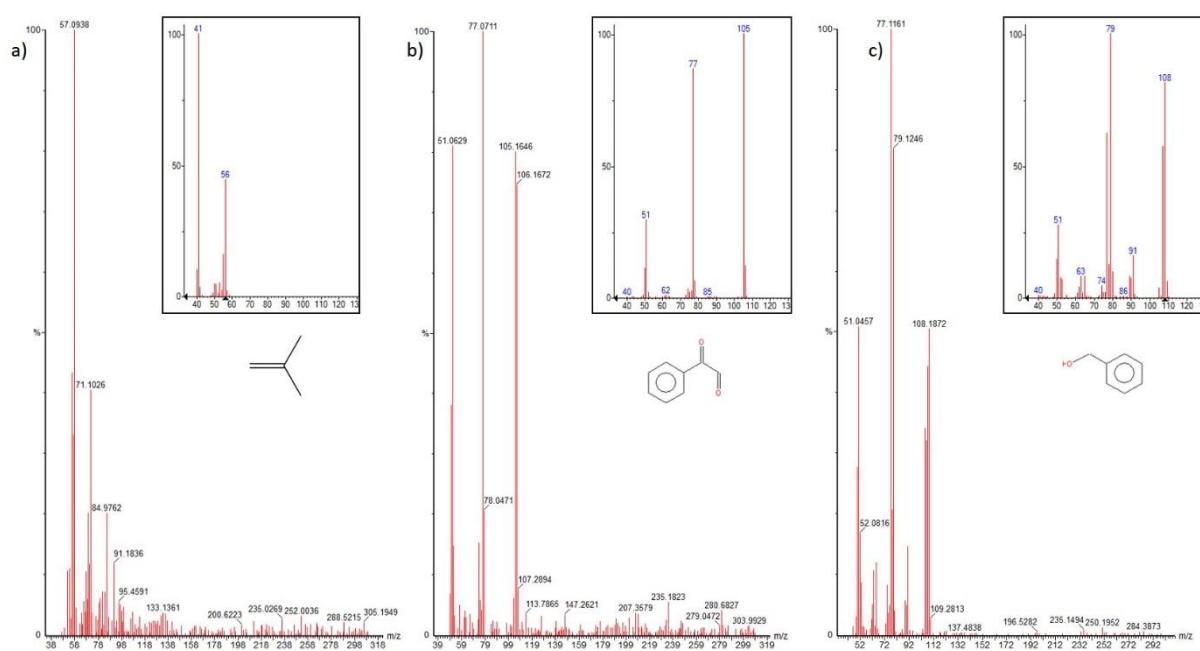


Figure S5: Mass spectra of a) Boc fragment at 3.57 min; b) Cbz MS fragment at 8.60 min, small spectra: MS spectra corresponding to phenylglyoxal; c) Pht MS fragment at 9.72 min, small spectra: MS spectra of benzyl alcohol.

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