SUPPORTING INFORMATION

Multilayer graphene functionalized through thermal 1,3-dipolar cycloadditions with imino esters. A versatile platform for supported ligands in catalysis

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1. General procedures.

The graphite powder KS4 was supplied by TIMREX. All reagents and solvents were obtained from commercial suppliers (Aldrich, Acros Organics, Alfa-Aesar) and used without further purification, except aldehydes, which were distilled prior to use. NMR spectra were obtained using a Bruker AC-300 or AC-400 and were recorded at 300 or 400 MHz for ^{1}H NMR and 75 or 100 MHz for ^{13}C NMR, using $CDCl_3$ as the solvent and TMS as internal standard (0.00 ppm) unless otherwise stated. The following abbreviations are used to describe peak patterns where appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved and br s = broad signal. All coupling constants (*J*) are given in Hz and chemical shifts in ppm. ^{13}C NMR spectra were referenced to $CDCl_3$ at 77.16 ppm. The ultrasound bath is Argo Lab AU-32 and the centrifuge is Hettich Zentrifugen (universal 320). Atomic force microscopy analysis was performed on a microscope NT-MDT, model NTEGRA PRIMA, while the TEM images were recorded on a microscope JEOL model JEM-2010. XPS analyses were performed using a VG-Microtech Multilab 3000 spectrometer, equipped with an Al anode. The deconvolution of N1s spectrum was carried out by using Gaussian Lorentzian curves. FWHM of the peaks was kept between 1.4 and 1.7 eV and a Shirley line was used for estimating the background signal. MLG **G2** was obtained as dispersion in NMP according to the literature. Raman spectra were obtained with a Jobin-Yvon Horiba LabRam spectrometer coupled to an upright microscope Olympus BX30. The spectra were collected with 532 nm excitation. Each spectrum was acquired for 60 s. Lorentzian curves were used for deconvolution. TG analyses were recorded in a METTLER TOLEDO TGA/SDTA851e/SF/1100 series whilst the subtracted FTIR experiments (not shown in this SI) were carried out in a Nicolet 510 P-FT and BRUKER IFS 66/S.

Graphene exfoliation.

500 mg of graphite were heated at 930 ºC for 1 h under 100 mL min^{-1} flow of nitrogen. Then, graphite was dispersed in 100 mL of NMP and sonicated in an ultrasound bath for 2 h at 360 W. The resultant dispersion was then let stand at ambient conditions for 5 days in order to settle out any insoluble particle. The supernatant, corresponding to about 70% of the volume was then carefully collected and used in the functionalization reaction. The dispersion presented a concentration of MLG **G2** of about 0.3 mg/mL.

2. General procedure for the synthesis of α-imino esters 1a to 1g.

A suspension of alkyl amino ester hydrochloride (1 mmol) and Et_3N (1 mmol), in dry DCM (5 mL) was stirred at room temperature for 15-30 minutes. Then, aldehyde (1 mmol) was added. After 12 h at room temperature the mixture was filtered off and water was added. The organic layer was separated and the aqueous phase extracted with DCM (3x10 mL). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure to afford the corresponding final product.

Methyl (*E*)-2-(benzylideneamino)acetate (**1a**).The product was obtained according with the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3H, OC*H*$_3$), 4.43 (s, 2H, C*H*$_2$), 7.40-7.46 (m, 3H, Ar*H*), 7.73-7.80 (m, 2H, Ar*H*), 8.29 (s, 1H, C*H*).

Methyl (*E*)-2-[(4-cyanobenzylidene)amino]acetate (**1b**). The product was obtained according with the literature.[2] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3H, OC*H*$_3$), 4.47 (s, 2H, C*H*$_2$), 7.56 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.89 (d, *J* = 8.4 Hz, 2H, Ar*H*), 8.35 (s, 1H, C*H*).

Methyl (*E*)-2-[(3-cyanobenzylidene)amino]acetate (**1c**). The product was obtained according with the literature.[3] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OCH_3), 4.47 (s, 2H, CH_2), 7.56 (t, *J* = 7.8 Hz, 1H, Ar*H*), 7.68-7.82 (m, 1H, Ar*H*), 7.91-8.04 (m, 1H, Ar*H*), 8.09 (s, 1H, Ar*H*), 8.33 (s, 1H, C*H*).

Methyl (*E*)-2-[(2-cyanobenzylidene)amino]acetate (**1d**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.80 (s, 3H, OCH_3), 4.52 (s, 2H, CH_2), 7.48-7.55 (m, 1H, Ar*H*), 7.62-7.68 (m, 1H, Ar*H*), 7.70-7.75 (m, 1H, Ar*H*), 8.23 (d, *J* = 7.9 Hz, 1H, Ar*H*), 8.69 (s, 1H, C*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 52.4 (*C*H_3), 61.9 (*C*H_2), 127.8, 131.4, 133.1, 137.7 (Ar*C*), 161.4 (*C*=NH), 170.1 (*C*=O). IR (neat) υ_{max}: 2229, 1733, 1208, 1159, 981, 831, 732 cm^{-1}.MS (EI) m/z: 203 (M^+, 4%), 202 (8), 149 (12), 144 (22), 143 (100), 142 (15), 116 (93), 89 (53), 74 (86), 70 (13). HRMS calculated for $C_{11}H_{10}N_2O_4$: 202.0742; found: 202.0735.

Methyl (*E*)-2-[(pyridin-2-ylmethylene)amino]acetate (**1e**). The product was obtained according with the literature.[4] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3H, OCH_3), 4.47 (s, 2H, CH_2), 7.32-7.40 (m, 1H, Ar*H*), 7.69-7.88 (m, 1H, Ar*H*), 8.08-8.15 (m, 1H, Ar*H*), 8.39 (s, 1H, C*H*), 8.63-8.69 (m, 1H, Ar*H*).

Methyl (*E*)-2-[(4-cyanobenzylidene)amino]-3-phenylpropanoate (**1f**). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.15 (dd, *J* = 13.6, 9.1 Hz, 1H, C*H*), 3.38 (dd, *J* = 13.6, 4.8 Hz, 1H, C*H*), 3.76 (s, 3H, OCH_3), 4.52 (m, 1H, NC*H*COOCH_3), 7.67 (d, *J* = 8.5, 1H, Ar*H*), 7.77 (d, *J* = 8.6, 1H, Ar*H*), 7.88 (s, 1H, C*H*). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 39.7 (CH_2), 52.5 (*C*H_3), 74.9 (*C*H), 114.4, 118.5, 126.8, 128.5, 128.9, 129.8, 132.5, 137.1 (Ar*C*), 161.9 (*C*=NH), 171.7 (*C*=O). IR (neat) υ_{max}: 2229, 1734, 1205, 1159, 831, 697 cm^{-1} MS (EI) m/z: 292 (M, 4%), 231 (34), 201 (100), 146 (14), 142(26), 141 (18), 91 (28). HRMS calculated for $C_{18}H_{16}N_2O_2$: 292.1212; found: 292.1218.

tert-Butyl (*E*)-2-[(4-cyanobenzylidene)amino]acetate (**1g**). The product was obtained according with the literature.[5] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.47 (s, 9H, (CH_3)$_3$), 4.20 (s, 2H, CH_2), 7.48-7.85 (m, 2H, Ar*H*), 7.47-7.83 (m, 2H, Ar*H*), 8.21 (s, 1H, C*H*).

3. General procedure for the synthesis of cycloadducts G2a to G2g.

In a 250 mL round bottomed flask were added 35-40 mL of graphene dispersion in NMP (**G2**, 0.3 mg/mL), 50 mL of mixture of xylene isomers and 100 mg–120 mg of the freshly-prepared corresponding imine. The resulting mixture was stirred at 85-95 ºC for 4-5 days, and an extra aliquot of 100 mg–120 mg of the corresponding imine was added to the dispersion each day. Then, the resulting mixture was centrifuged for 30 minutes at 6000 rpm. The functionalized MLG was collected, re-dispersed in 10 mL of AcOEt and centrifuged again. This process was repeated three times. Eventually, the product was dried under reduced pressure 24 h. All the samples were characterized via N1s X-ray photoelectron spectroscopy, XPS (see Table 1 and 2). All the **G2a-g** derivatives display a common peak comprised between 400.1 to 400.7 eV, respectively, corresponding to the prolinate nitrogen as shown in Figure 1 for **G2a** (see S.I. for **G2b-g**). A second peak appears in the case of **G2b-g** samples where another nitrogen is present in the cycloadduct, and its binding energy, respectively ranging from 399.4 and 399.8 eV, depends on the nature of the corresponding nitrogen. In every case, the area of the signals is coherent with the stoichiometry of the derivative (see S.I). All the spectra present an almost negligible signal at around 401.0 eV due to some NMP adsorption.

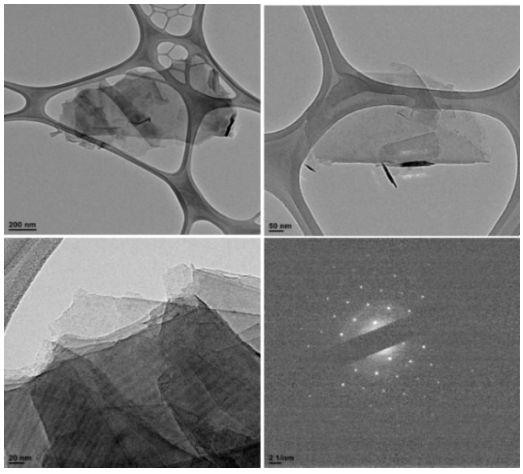
4. Iridium graphene metalation (G3a).

In a 250 mL round bottomed flask was added **G2a** and acetone with a ratio of 1 mL/mg. Then was added 1 mL of NaOH (0.1 M) per mg of graphene. The mixture was homogenized by ultrasound for 10 minutes and let react for 12 h, at room temperature under stirring. The resulting dispersion was centrifuged for 30 minutes at 6000 rpm. The graphene was collected and dispersed in 10 mL of methanol, then centrifuged again. This procedure was repeated three times and then the graphene was dried under reduced pressure for 24 h. Next, 30 mg of the dried graphene were added in a 50 mL round bottomed flask together with 10 mL dry DCM, and 5 mg of (pentamethylcyclopentadienyl)iridium(III) chloride dimer under argon atmosphere. The mixture was dispersed in ultrasound for 10 minutes and then stirred at room temperature for 18 h. The graphene was then collected and dispersed in 10 mL of DCM then centrifuged again. This procedure was repeated three times and then **G3a** was dried under reduced pressure for 24 h. ICP-MASS analysis: 0.8% in mass of Ir. N1s XPS of **G3a** is showed in Figure 2. This spectrum displayed a principal peak at 402.2 eV, corresponding to a highly oxidized nitrogen, which is in agreement with a prolinate nitrogen coordinated to Ir centers. This signal is flanked by a second one, less intense, at 400.10 eV, that corresponds to some unreacted prolinate nitrogen. The ratio between the area of these two peaks allowed to estimate the yield of the coordination reaction to about 75%. An almost negligible signal at 401.2 eV due to some NMP adsorption on the MLG edges is also found. The presence in the sample of traces of NaCl, coming from the ester hydrolysis, prevents the iridium XPS characterization, as sodium shares the same spectral window of the highest intensity signal from iridium

5. Catalytic reduction test of acetophenone and catalyst recovery.

A suspension of (37 mg) Iridium-graphenepyrrolidine (**G3a**), K_2CO_3 (103.7 mg), acetophenone (0.15 mL) and isopropanol (1.0 mL) was bubbled with argon for 15 min and then homogenized *via* ultrasound for 5 min. The resulting mixture was refluxed for 30 h. The catalyst was then quantitatively recovered by centrifugation and the catalysis output was isolated by volatile evaporation under reduced pressure and characterized by ^{1}H NMR. The MLG recovered after centrifugation was reused again in the same reaction.

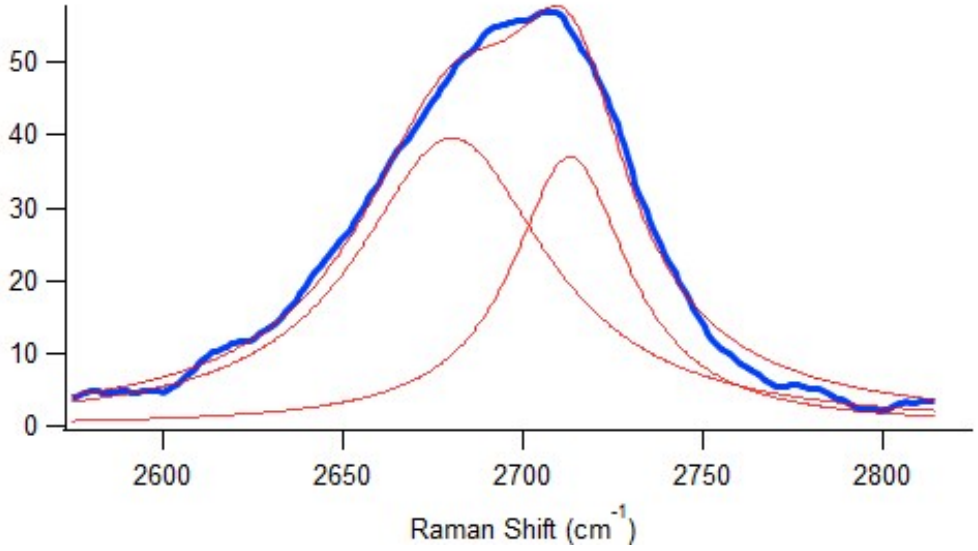
6. TEM images of the starting MLG



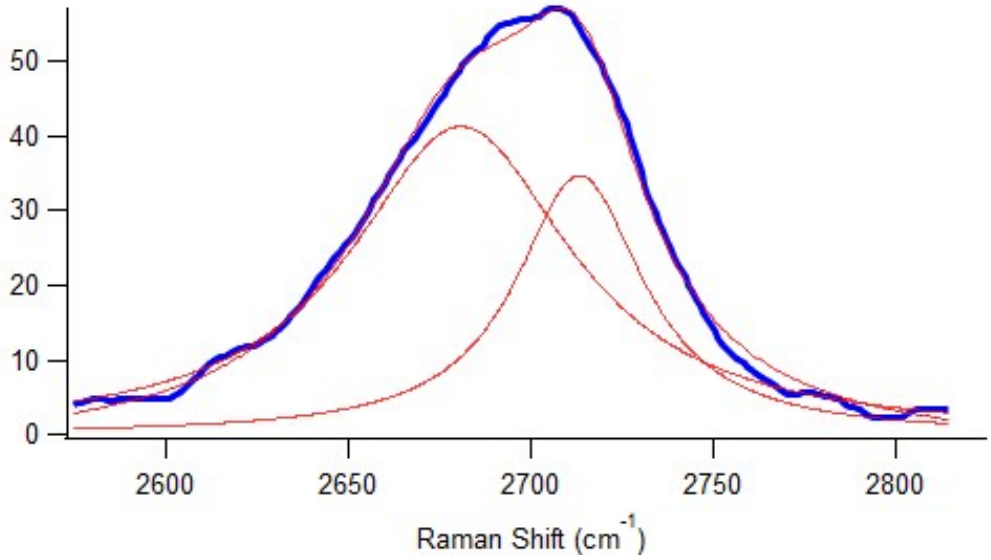
TEM images of MLG **G1**.

7. Raman spectra for G1 and comparison with Raman spectra of G2a

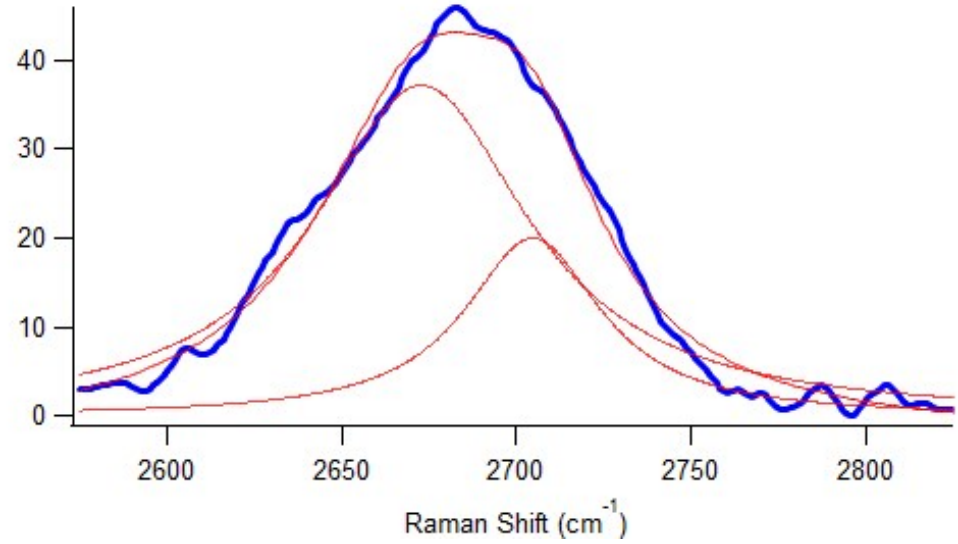
a) Measurement 1



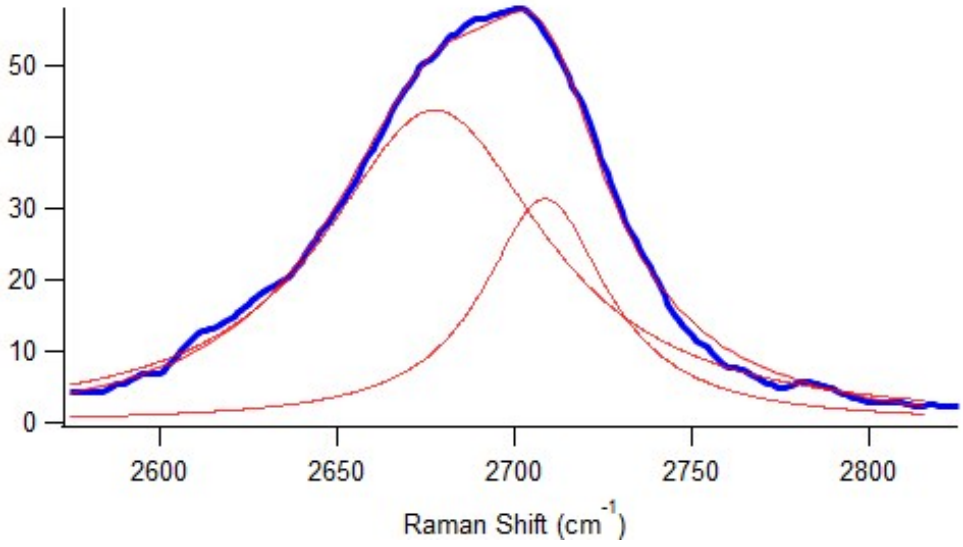
b) Measurement 2



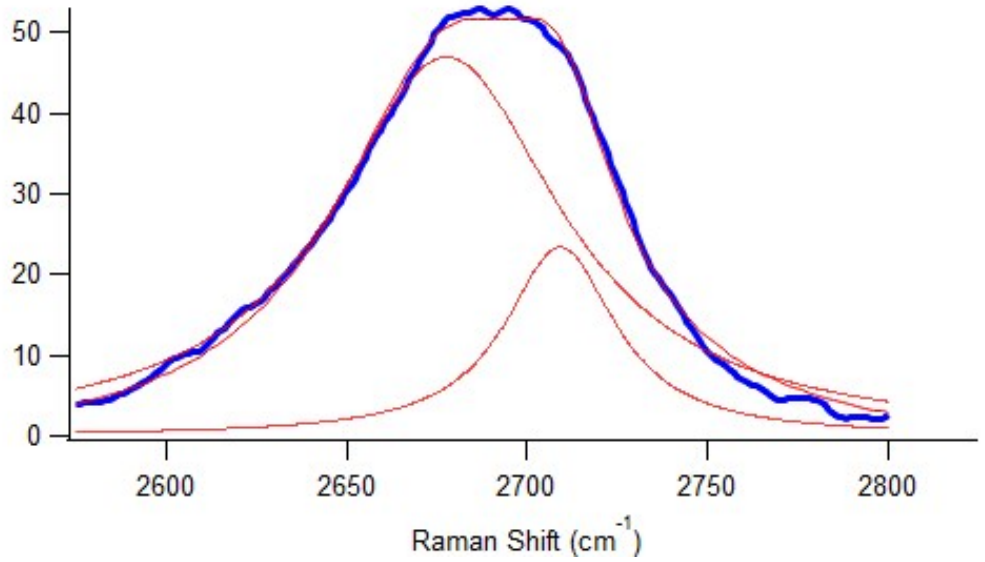
c) Measurement 3



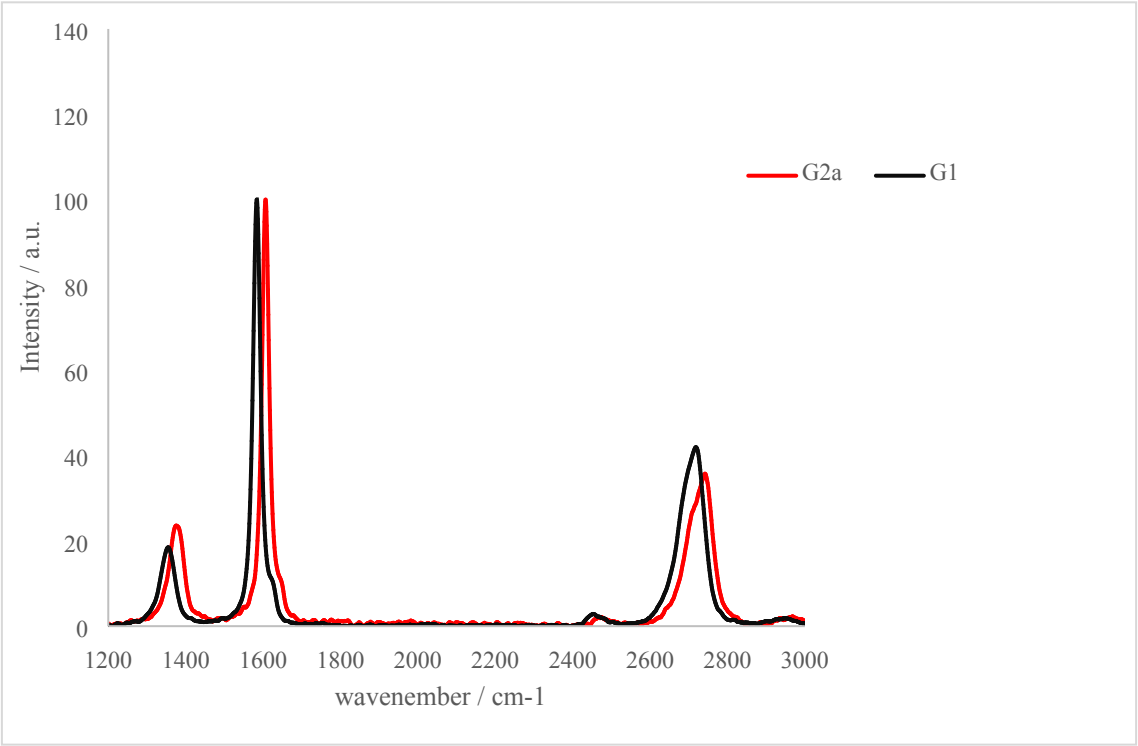
d) Measurement 4

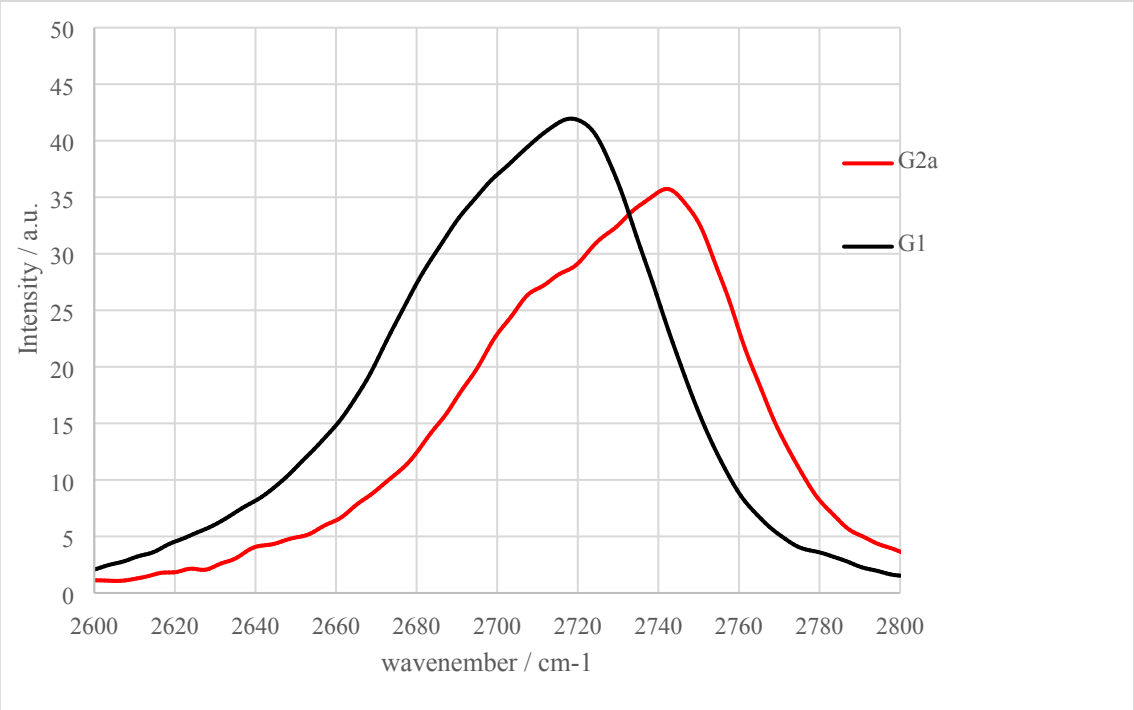


e) Measurement 5



f) Raman spectra of MLG G1 and functionalized MLG G2a.

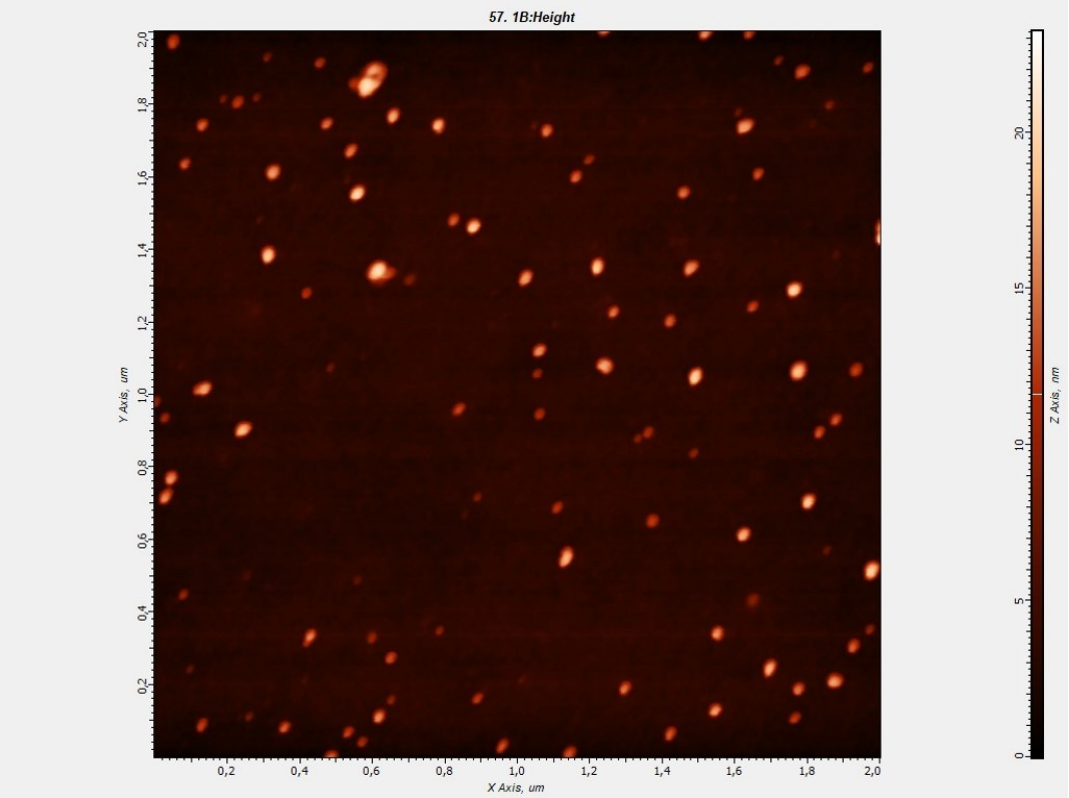




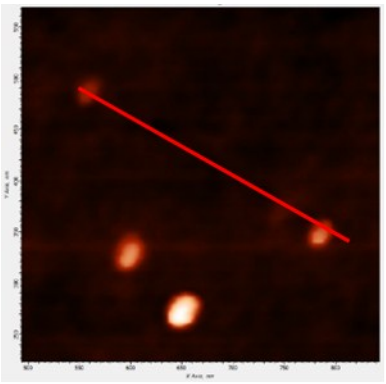
Expanded 2D region of the Raman spectra of MLG **G1** and functionalized MLG **G2a**.

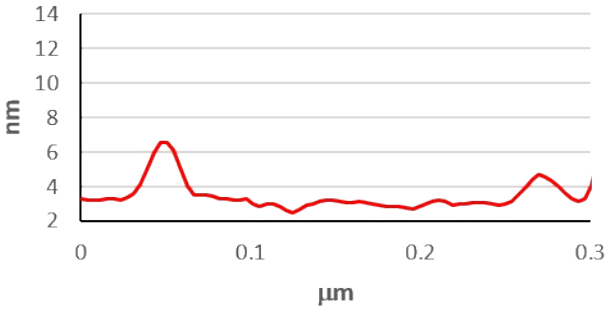
8. AFM images

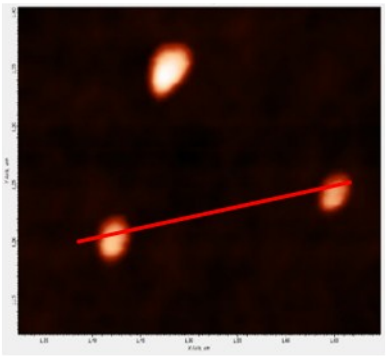
Homogeneous distribution of MLG onto a silicon support

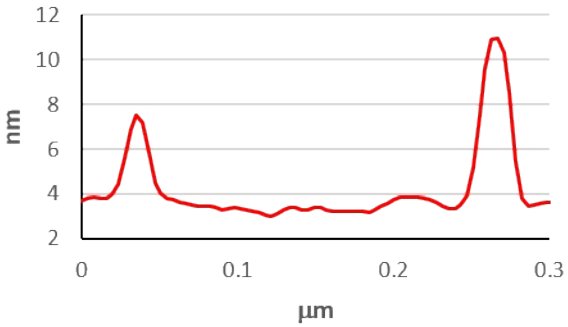


MLG 9 sheets **MLG 5 sheets**





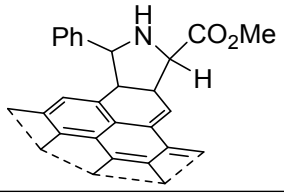
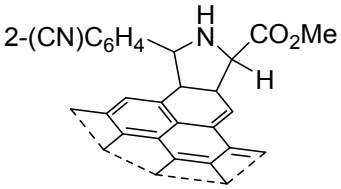
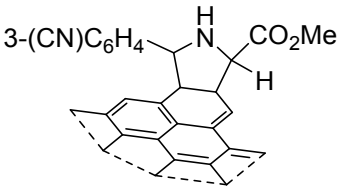
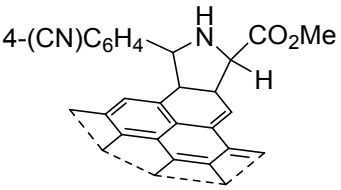
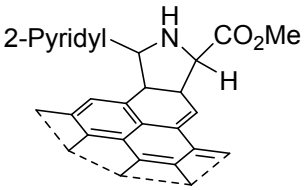
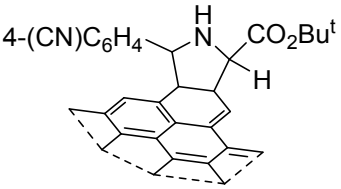
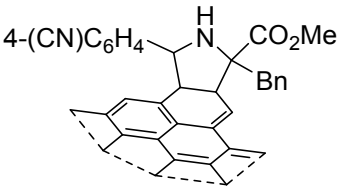




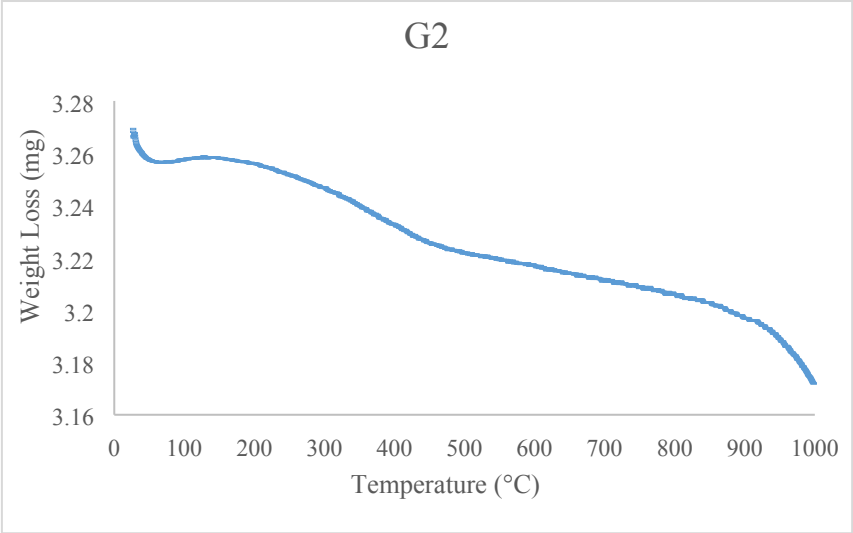
MLG 9 sheets **MLG 18 sheets**

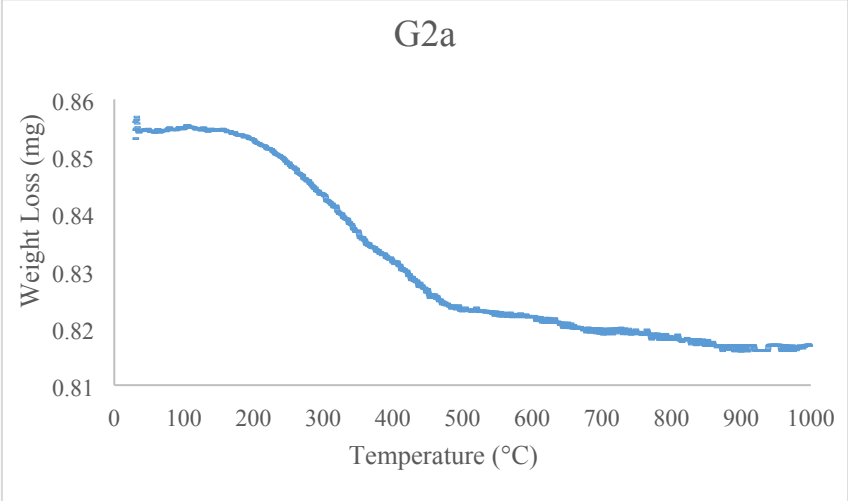
9. Thermogravimetric analysis

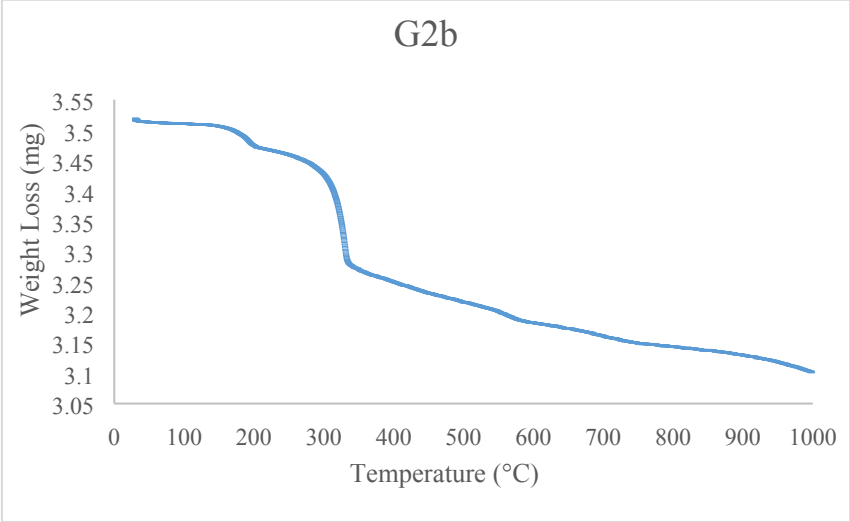
Determined by calcultation of the mass lost from rt to 900 ºC estimating a complete decomposition of the functional groups introduced during the 1,3-DC.

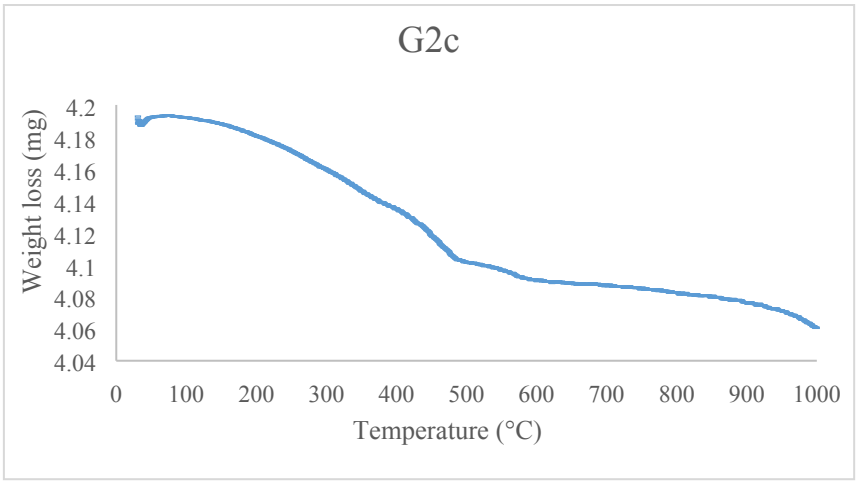
	% Total Nitrogen	% Total Carbon	% Total Oxygen	Chemical yield(%)[a]
	0.37	2.93	0.86	1.15
	1.46	6.88	1.67	2.61
	0.36	1.72	0.41	0.59
	0.50	2.35	0.56	0.82
	1.51	5.83	1.73	2.60
	0.61	3.37	0.69	0.80
	0.81	6.18	0.93	1.99

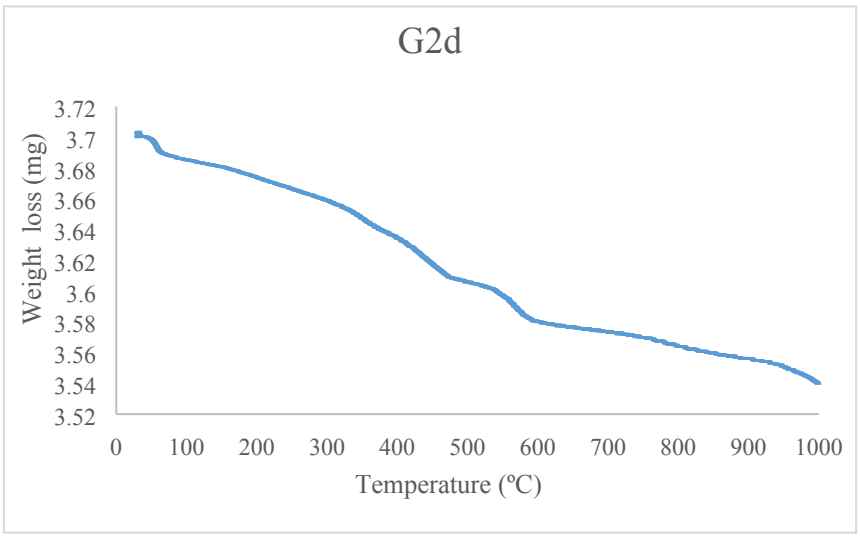
[a] Estimated chemical yield considering iminoester incorporated *versus* the initial amount of starting imino ester **1**.

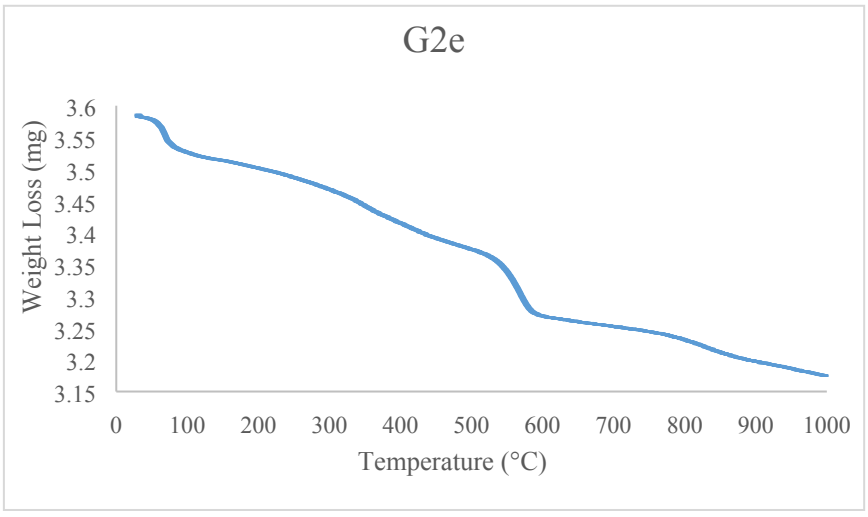

G2
Weight Loss (mg)
3.28
3.26
3.24
3.22
3.2
3.18
3.16
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

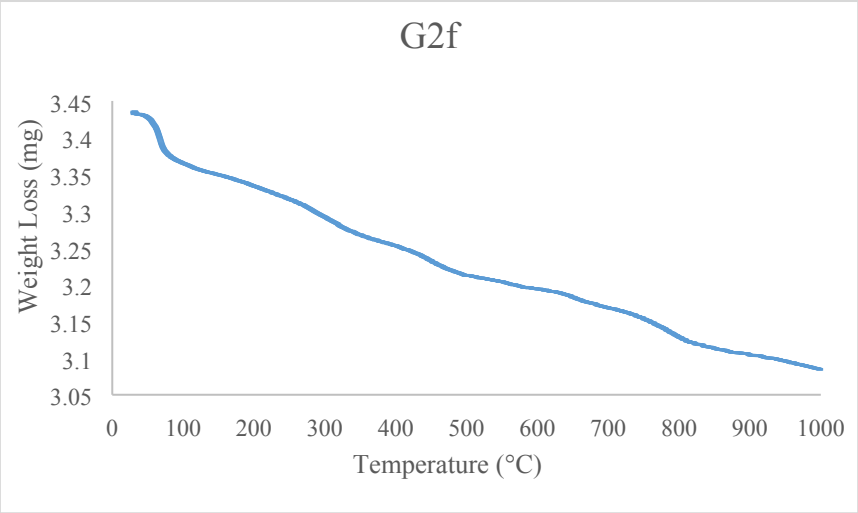

G2a
Weight Loss (mg)
0.86
0.85
0.84
0.83
0.82
0.81
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)

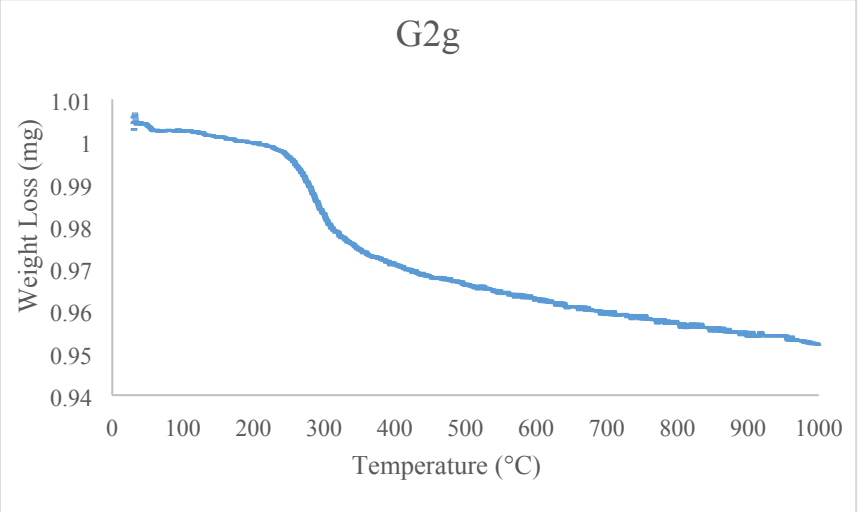

G2b
Weight Loss (mg)
3.55
3.5
3.45
3.4
3.35
3.3
3.25
3.2
3.15
3.1
3.05
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)


G2c
Weight loss (mg)
4.2
4.18
4.16
4.14
4.12
4.1
4.08
4.06
4.04
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)


G2d
Weight loss (mg)
3.72
3.7
3.68
3.66
3.64
3.62
3.6
3.58
3.56
3.54
3.52
0
100
200
300
400
500
600
700
800
900
1000
Temperature (ºC)

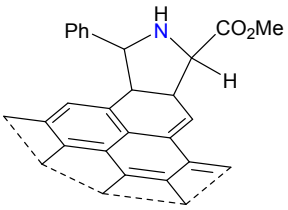

G2e
Weight Loss (mg)
3.6
3.55
3.5
3.45
3.4
3.35
3.3
3.25
3.2
3.15
0
100
200
300
400
500
600
700
800
900
1000
Temperature (°C)



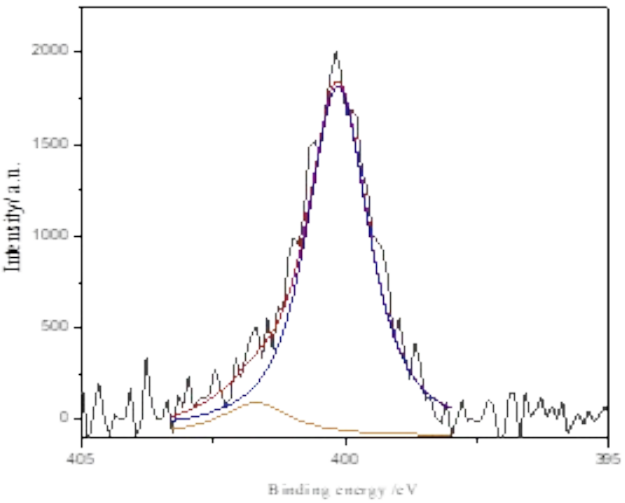


G3a ICP-MASS analysis: 0.80% in mass of Ir.

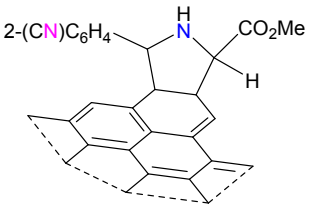
10. N1s XPS spectra of compounds G2a-g



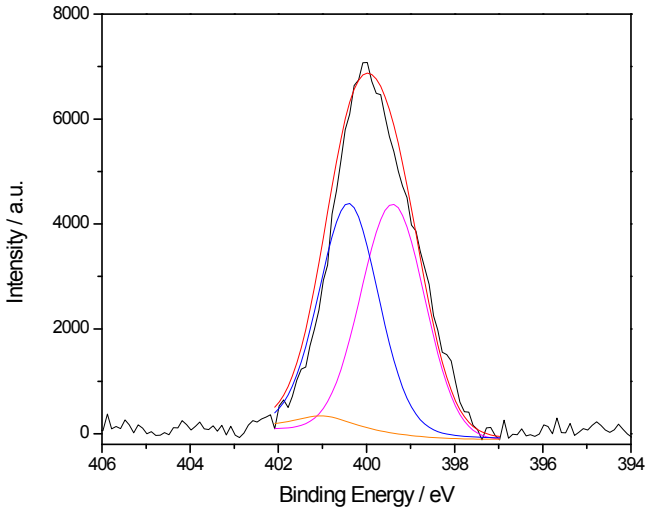
G2a



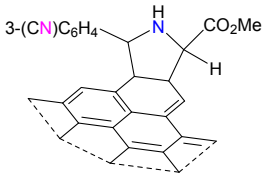
Peak	Position (eV)	Area	FWHM (eV)
1	400.1	2.550.000	1.650
2	401.0	350.000	1.600



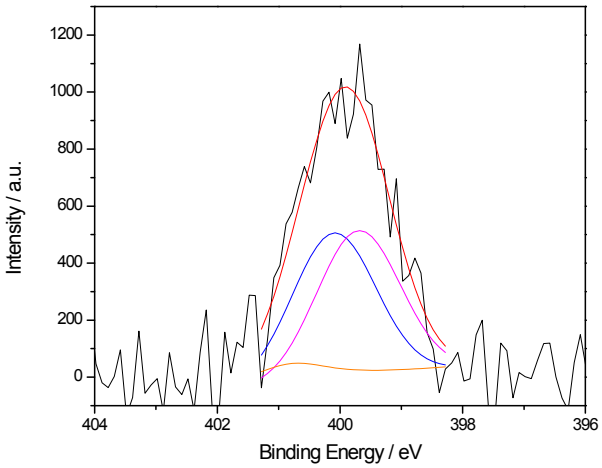
G2b



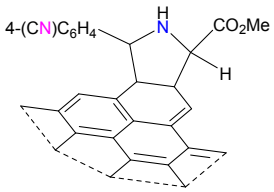
Peak	Position (eV)	Area	FWHM (eV)
0	399.4	8.000.000	1.700
1	400.4	8.000.000	1.600
2	401.0	700.000	1.700



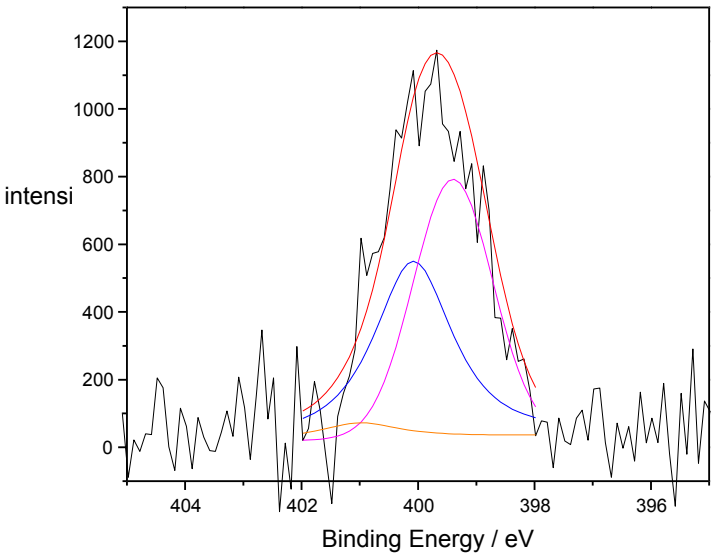
G2c



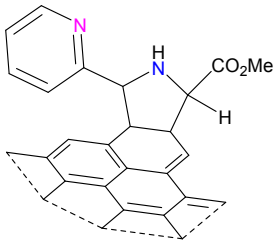
Peak	Position (eV)	Area	FWHM (eV)
0	399.4	1.259.353	1.600
1	400.1	1.300.353	1.600
2	401.0	130.353	1.700



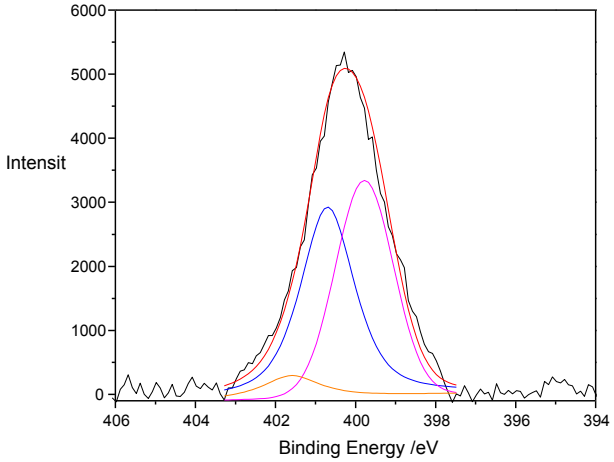
G2d



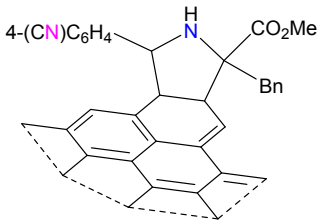
Peak	Position (eV)	Area	FWHM (eV)
0	399.4	1.270.353	1.600
1	400.1	1.300.353	1.600
2	401.0	130.353	1.700



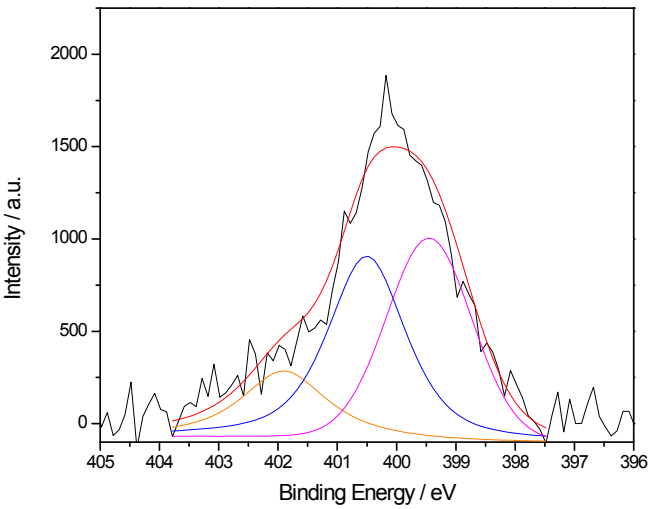
G2e



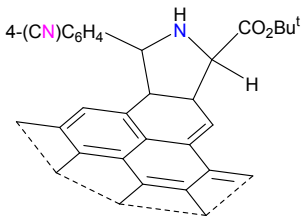
Peak	Position (eV)	Area	FWHM (eV)
0	399.8	6.100.000	1.700
1	400.7	6.300.000	1.600
2	401.4	900.000	1.700



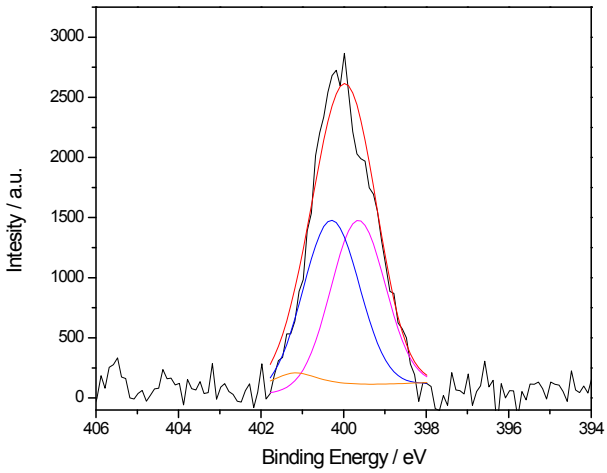
G2f



Peak	Position (eV)	Area	FWHM (eV)
0	399.4	2.050.000	1.700
1	400.5	2.100.000	1.550
2	401.7	900.000	1.700

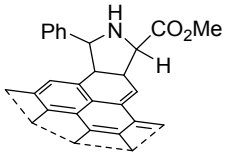
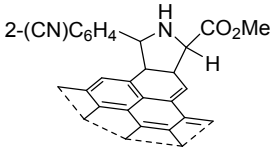
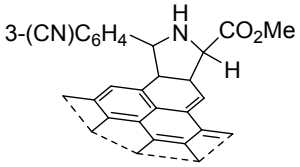
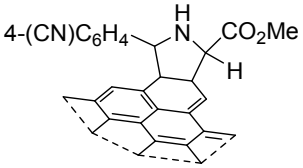
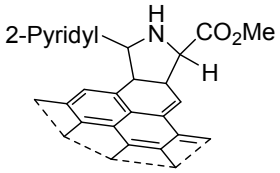
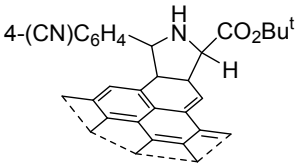
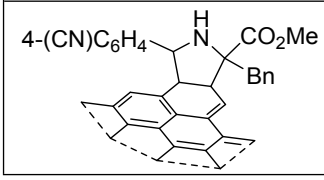


G2g



Peak	Position (eV)	Area	FWHM (eV)
0	399.6	2300	1.55
1	400.3	2400	1.6
2	401.2	400	1.6

11. Chemical analysis by XPS.

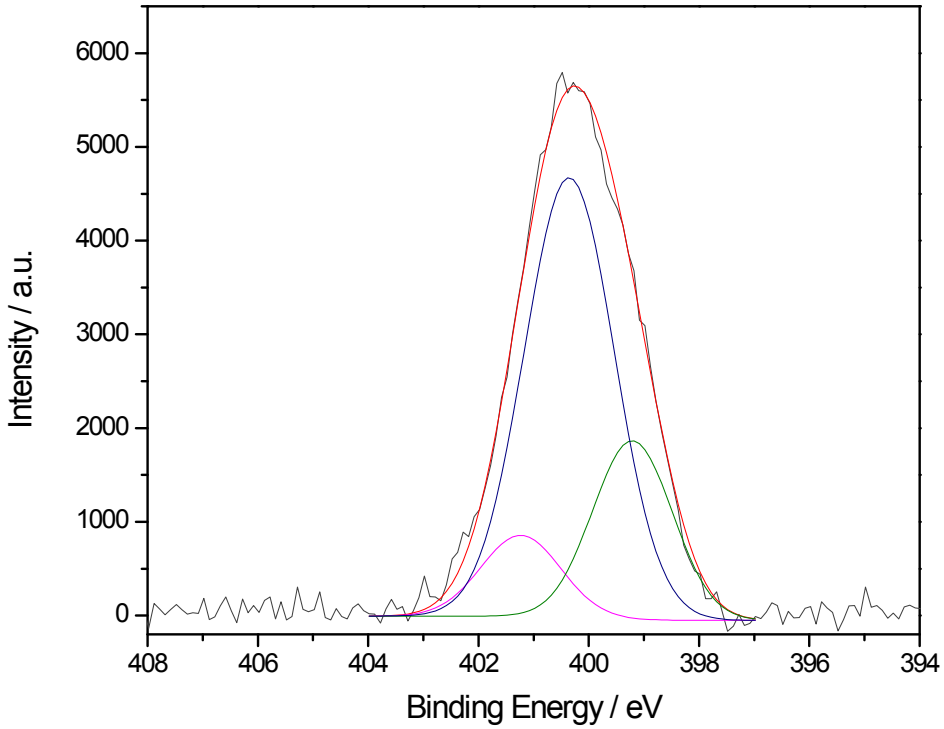
	% Total Nitrogen	% Total Carbon	% Total Oxygen	B.E (Ev) Pic1	B.E (Ev) Pic2	FD [a]	Yield (%)[b]
	1	95.07	3.93	-	400.3	0.97	2.97
	4.2	88.9	6.90	399.4	400.4	4.17	7.5
	0.57	96.99	2.44	399.4	400.1	0.54	0.94
	0.59	96.99	2.44	399.4	400.1	0.56	0.97
	3.68	86.99	9.33	399.8	400.7	3.65	6.25
	1.6	93.76	4.64	399.6	400.3	1.57	2.1
	1.24	91.64	7.11	399.4	400.5	1.21	3.05

[a] Functionalization degree (FD) calculated according to the procedure described in the literature.[6]

[b] Estimated chemical yield (based in XPS data) considering iminoester incorporated *versus* the initial amount of starting imino ester **1**.

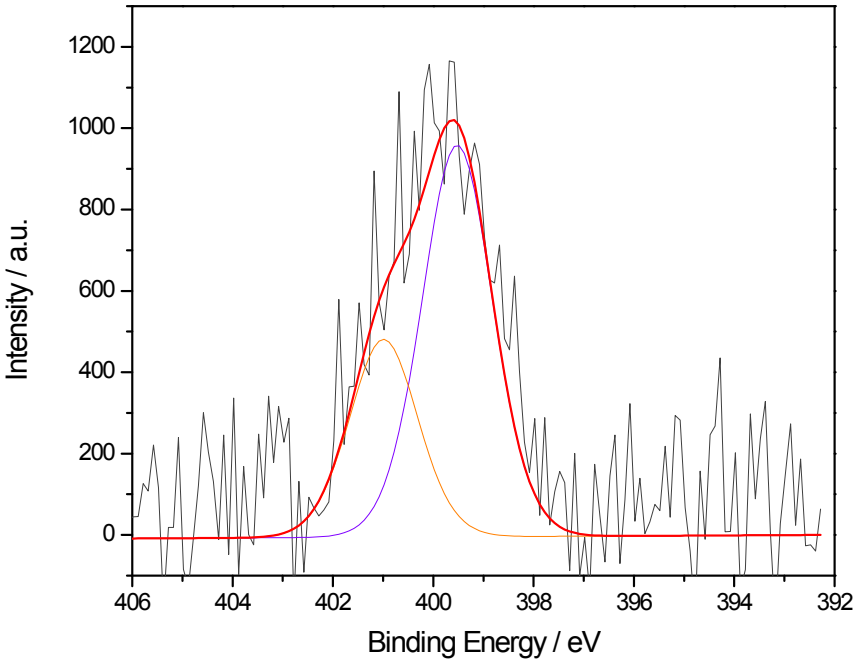
12. N1s XPS of G1a.

G1a present three nitrogen peaks: one (blue) is the prolinic nitrogen deriving from the 1,3 dypolar cycloaddition and two, minor contributions due to some nitrogen incorporation on the edges of the MLG, during the sonication step with pyridine (see below).

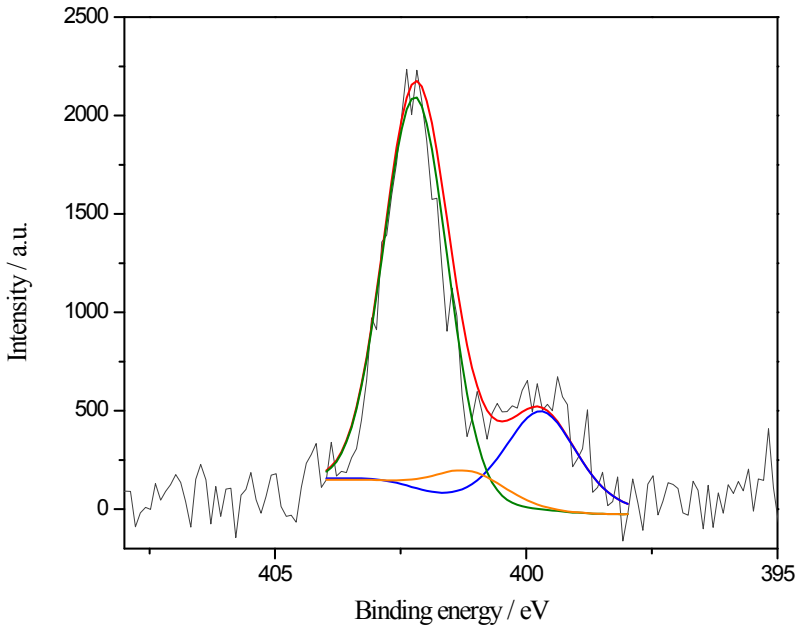


13. N1s XPS blank experiment: graphene sonicated in pyridine.

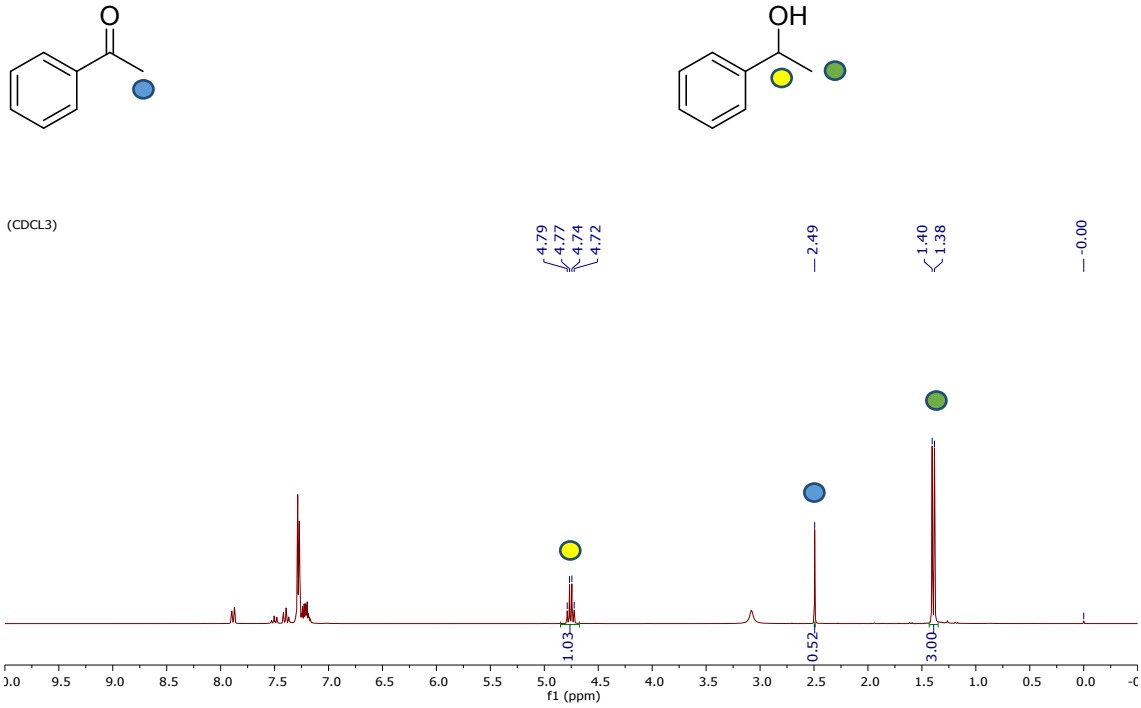
Exfoliation of graphite in pyridine afforded MLG sheets decorated with quaternary nitrogen (about 401 eV) and amine groups (about 399.5 eV). Overall nitrogen incorporation was about 0.30 at.%



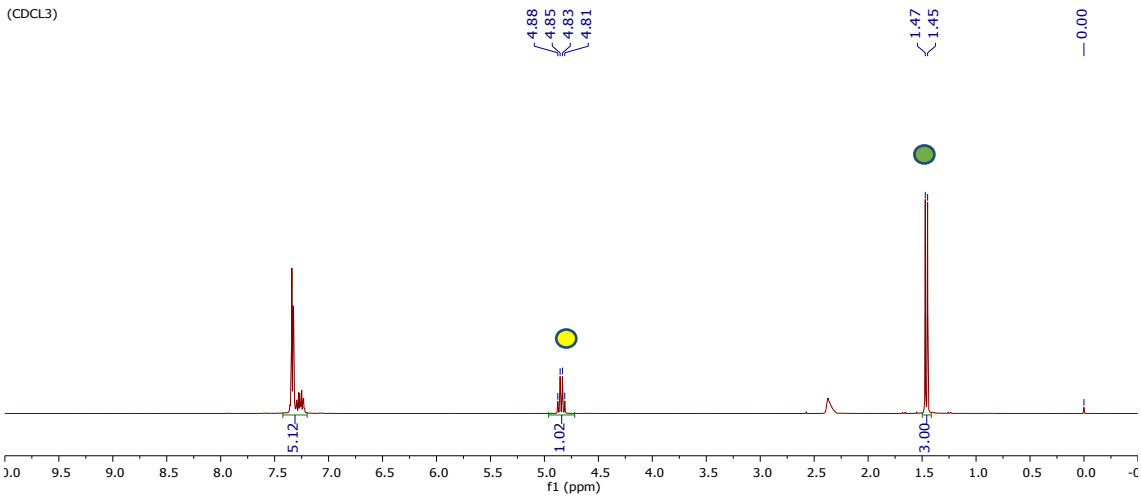
14. N1s XPS spectra of G3a.



15. Representative ^{1}H-NMR spectra: Reduction of acetophenone



^{1}H NMR (300 MHz, $CDCl_3$) spectra from the reaction crude (without any purification) of acetophenone catalyzed by **G3a.**



^{1}H NMR (300 MHz, $CDCl_3$) spectra from the reaction (with purification) of acetophenone catalyzed by **G3a.**

16. References

[1] A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc*. **2008**, *130* (31), 10084–10085.
[2] R. Lasch, M. R. Heinrich, *Tetrahedron* **2015**, *71* (25), 4282–4295.
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[6] D. D. Chronopoulos, A. Bakandritsos, P. Lazar, M. Pykal, K. Čépe, R. Zbořil, M. Otyepka. *Chem.Mater.* **2017**, *29*, 926−930.