Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Preparation of a ruthenium complex covalently bonded to multilayer graphene and its evaluation as photocatalyst

Lesly V. Rodríguez-Flórez,[a,b‡] María de Gracia Retamosa,[a,b] Miriam Navlani-García[$c] Diego Cazorla-Amorós,[c*] Carmen Nájera,[b] Miguel Yus[b] and José M. Sansano.[a*]

[a] Departamento de Química Orgánica e Instituto de Síntesis Orgánica (ISO). University of Alicante, E-03080 Alicante, Spain

[b] Centro de Innovación en Química Avanzada (ORFEO-CINQA). University of Alicante, E-03080 Alicante, Spain

[c] Departamento de Química Inorgánica and Instituto Universitario de Materiales, University of Alicante, E-03080 Alicante, Spain.

Table of Contents

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 N 1s spectrum was carried out by using Gaussian Lorentzian curves. FWHM of the peaks was kept between 1.0 and 1.7 eV and a Shirley line was used for estimating the background signal. MLG 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 N_2 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. ICP-MS analysis was performed in a Agilent-7700x (ICP-MS) apparatus. The microwave reactions were run in a MILESTONE microwave oven Start-S model using plastic-coated glass vessels with a valve operating up to 1.2 atm. The thermal method used consisted in a 5 min slope to reach 100 ºC and then, maintenance of the reaction at this temperature for 5 h. Then, the air-cooling flow allowed to raise the room temperature in, approximately, 15 min.

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 of about 0.3 mg/mL.

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

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 was 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 to the literature.[1] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3H, OCH_3), 4.43 (s, 2H, CH_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-[(pyridin-2-ylmethylene)amino]acetate (**1b**). The product was obtained according to the literature.[2] ^{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-(benzylideneamino)propanoate (**1c**). The product was obtained according to the literature [3] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.55 (d, *J* = 6.8, 3H, CCH_3), 3.76 (s, 3H, OCH_3), 4.18 (q, *J* = 7.6, C*H*Me), 7.40-7.45 (m, 3H, Ar*H*), 7.70-7.80 (m, 2H, Ar*H*), 8.36 (s, 1H, CN*H*).

3. General procedure for the synthesis of α-imino ester 1d.

A solution of 2-acetylpyridine (5.0 g, 0.041 mol) in acetic acid (11 mL) containing 32% hydrobromic acid (11 mL) was cooled to 0 °C, and a solution of tetrabutylammonium tribromide (12 g) in acetic acid (150 mL) was added and allowed to react at 60 °C for 6 h. The reaction system was cooled to room temperature, and diethyl ether (300 ml) was added to the system. After 12 h at 0 °C, the precipitates were filtered, washed with acetone and vacuum dried to yield 2-(bromoacetyl)pyridine as a yellow solid (9.0 g, >99%). Then, pyridine (5 mL) was added to a dispersion of 2-(bromoacetyl)pyridine in tetrahydrofuran (170 mL) under argon atmosphere, and the reaction mixture was stirred at 25°C for 6 h. The precipitate was filtered, washed with tetrahydrofuran and vacuum-dried to give salt **2** as a white solid (12.4 g). The obtained **2** was used for the preparation of compound **3** without further purification.[4]

Compound **2** (6.0 g, 21.5 mmol), ammonium acetate (7.0 g, 90.8 mmol), crotonaldehyde (3.53 mL, 43.0 mmol) and ethanol (170 mL) were added into a pressure flask. The solution was heated to 110 °C for 72 h. The solvent was then evaporated under reduced pressure and the black oil was extracted with petrol ether (10 mL×6). The combined organic layers were washed with saturated brine and dried over $MgSO_4$, filtered, and evaporated under vacuum obtaining compound **3** (1.4 g, 38%).[5]

Selenium dioxide (2.0 g, 18 mmol) was added to a solution of 4-methyl-2,2′-bipyridine **3**, (1.4 g, 8.0 mmol) in diethylene glycol dimethyl ether (25 mL), and the solution was mildly refluxed for 4.5 h. On cooling of the solution to 90-95 °C, water (5 mL) was added and a black solid was formed, separated, and washed twice with dioxane. The filtrate was evaporated to dryness and the resulting solid was dissolved in DCM (20 mL), and the solution was vigorously stirred with a solution of K_2CO_3 (5%, 10 mL) for 15 min. The water layer was separated and extracted with DCM (15 mL). The combined organic extracts were dried over $MgSO_4$ and evaporated, and the crude product was purified by column chromatography (hexane:ethyl acetate, 4:1 + 1% Et_3N) to afford the pure 2-formyl-2,2′-bipyridine **4** as a yellow pallid colored powder (0.95 g, 65%).[6]

The imino ester **1d** was prepared, quantitatively, according to the procedure described in section 2.

Methyl (*E*)-2-{([2,2'-bipyridin]-6-ylmethylene)amino}acetate (**1d**): ^{1}H NMR (300 MHz, Chloroform-*d*): δ = 3.77 (s, 3H), 4.47 (d, *J* = 1.3 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.85 – 7.71 (m, 2H), 8.41–8.35 (m, 2H), 8.63 (s, 1H), 8.69 – 8.65 (m, 1H), 8.73 (d, *J* = 5.0 Hz, 1H).

^{1}H NMR (101 MHz, $CDCl_3$): δ = 59.0 (CH_3), 70.5 (CH_2), 120.7, 121.2, 123.9, 124.0, 137.0, 137.1, 143.3, 149.2, 149.6, 149. 9 (Ar*C*), 163.9 (C=NH), 170.0 (C=O). IR (neat) ν_{max}: 1737.55, 1455.99, 1402, 1213.01, 788.743, 742.46, 613.252 cm^{-1} MS (EI) *m/z*: 255 (M^+, 8%), 240 (37), 196 (100), 182 (34), 169 (16). HRMS (ESI): *m/z* calcd for $C_{14}H_{13}N_3O_2$ [M^+] 255.1010; found: 255.0970.

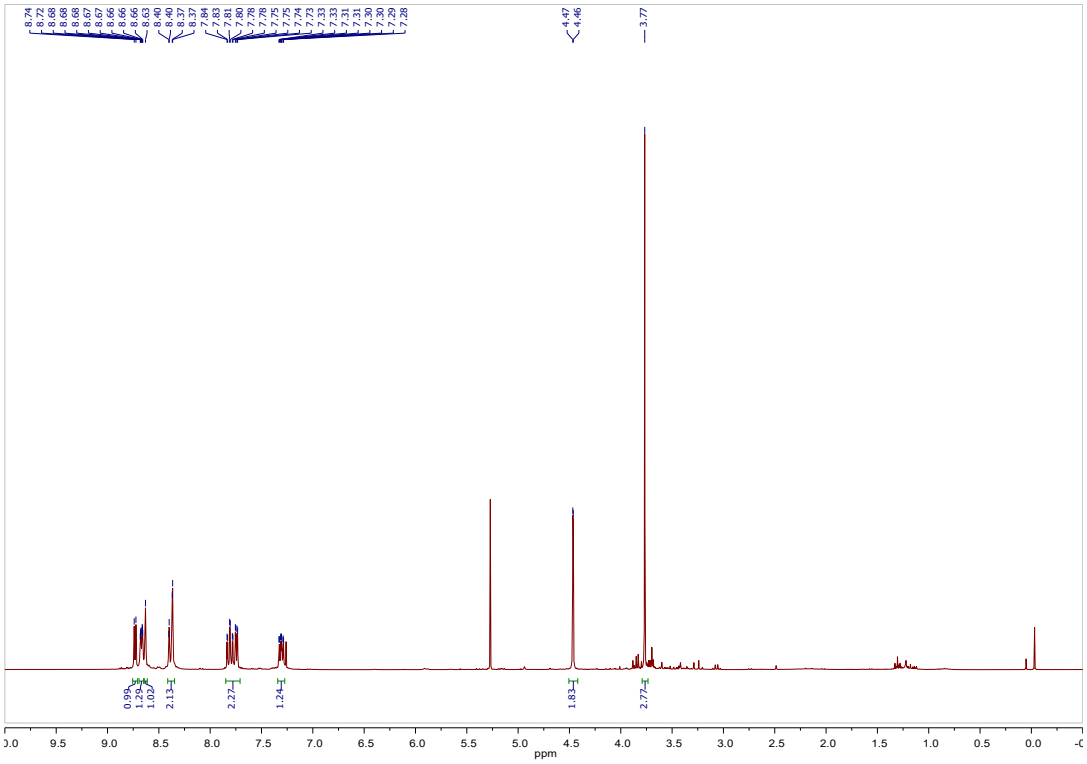


Figure 1S. ^{1}H NMR spectra of compound **1d**.

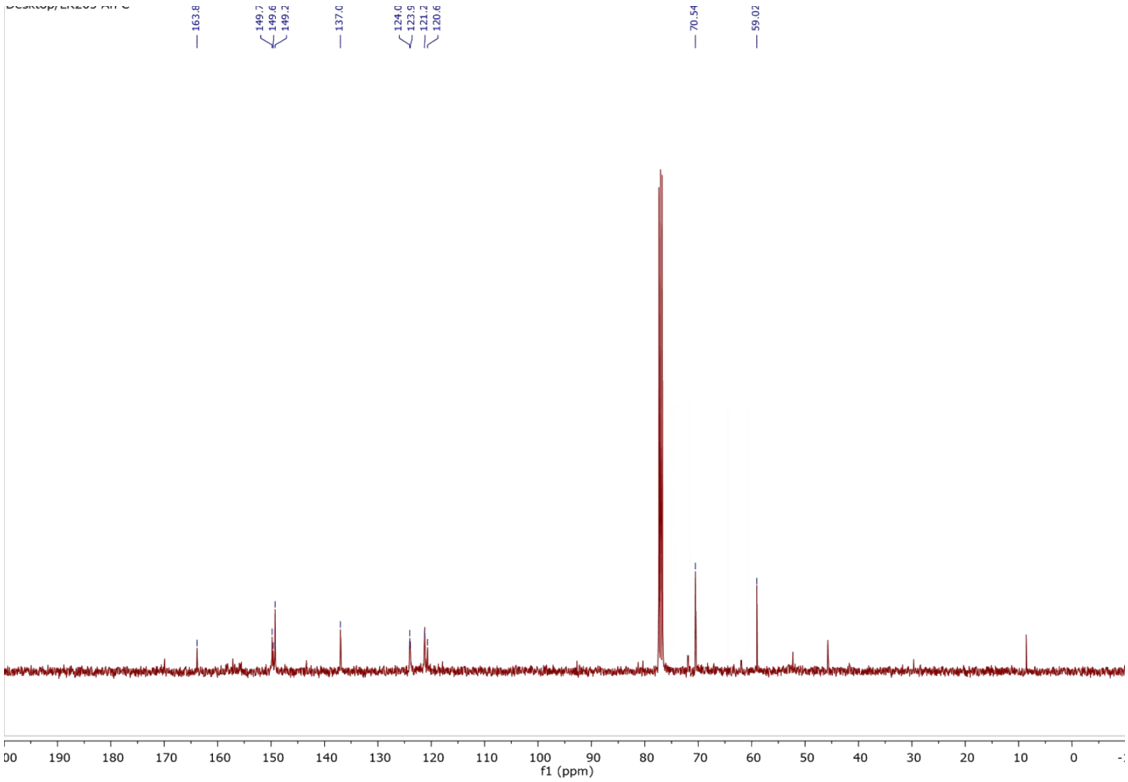


Figure 2S. ^{13}C NMR spectra of compound **1d**.

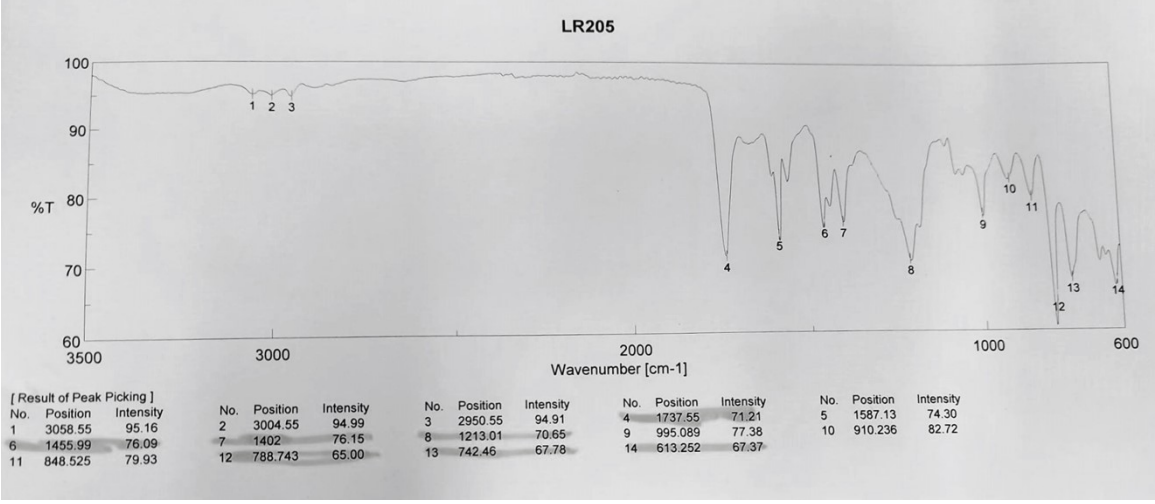


Figure 3S. IR Spectra of compound **1d**.

4. General procedure for the synthesis of cycloadducts MLG1a to MLG1d.

The plot of the mass lost (%) *versus* time (h) is plotted in the next Figure showing that the optimal reaction time using microwave-assisted heating was 5 h.

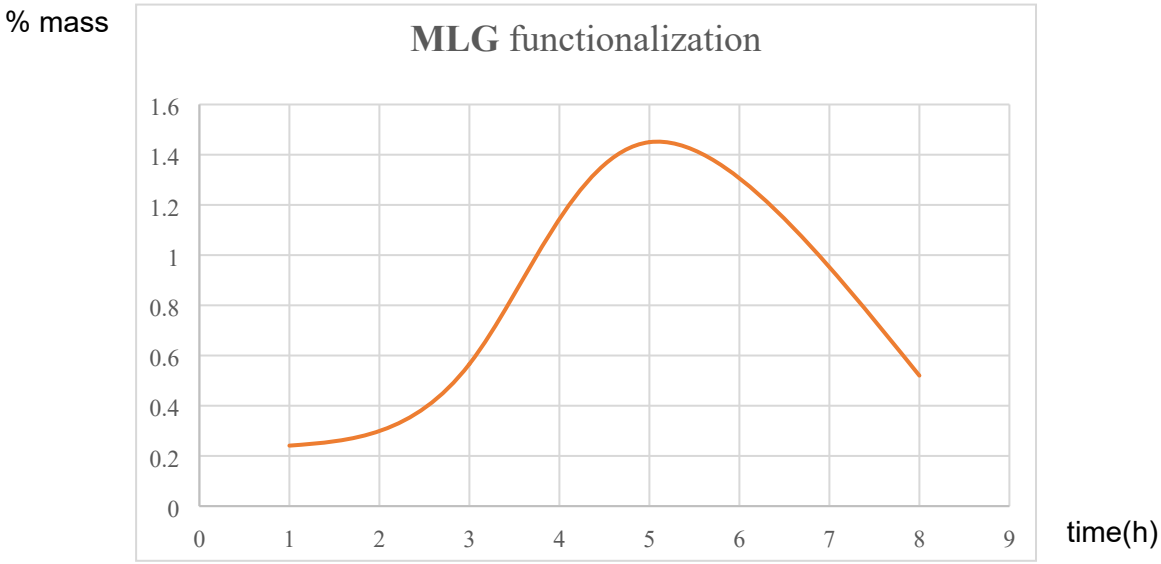


Figure 4S. Plot of the functionalization degree (% gained mass) of MLG *versus* time (h) under MW irradiation.

In a 100 mL round-bottomed flask 50 mL of **MLG** dispersion in NMP (0.3 mg/mL) and 120 mg of the freshly-prepared imino ester **1** were added. The resulting mixture was stirred at 100 ºC for 5 h in a microwave oven following the method described in the general section. 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 for 24 h. All the samples were characterized *via* thermogravimetric analysis (decomposition analyzed up to 900 ºC) and X-ray photoelectron spectroscopy (XPS). All the **MLG1a-d** derivatives display a common peak comprised between 400.1 to 400.7 eV, respectively, corresponding to the prolinate nitrogen. A second peak appears in the case of **MLG1b and MLG1d** 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. All the spectra present an almost negligible signal at around 401.0 eV due to some NMP adsorption.

A Raman spectra comparison between **MLG** and **MLG1a** was reported. It is almost identical to the results previously reported by our group.[7]

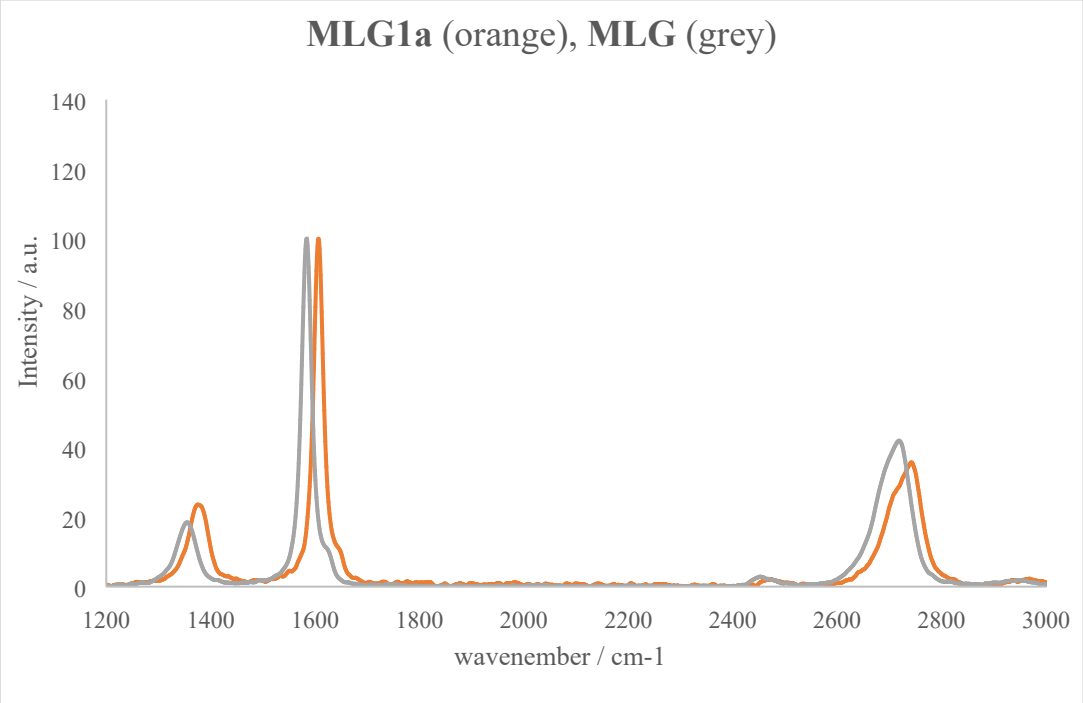


Figure 5S. Comparison between Raman spectra of **MLG** and **MLG1a**.

*Thermogravimetric analyses of **MLG1***

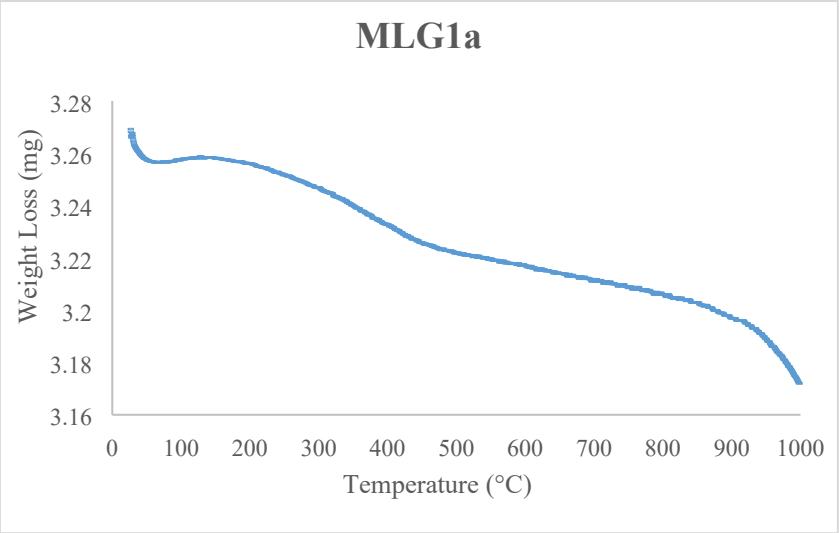


Figure 6S. Thermogravimetric analyses of **MLG1a**.

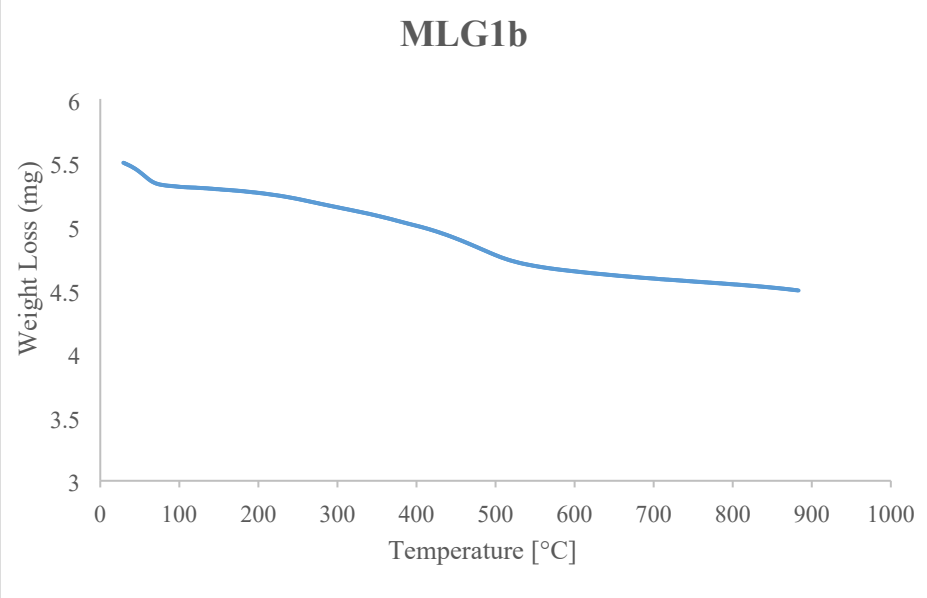


Figure 7S. Thermogravimetric analyses of **MLG1b.**

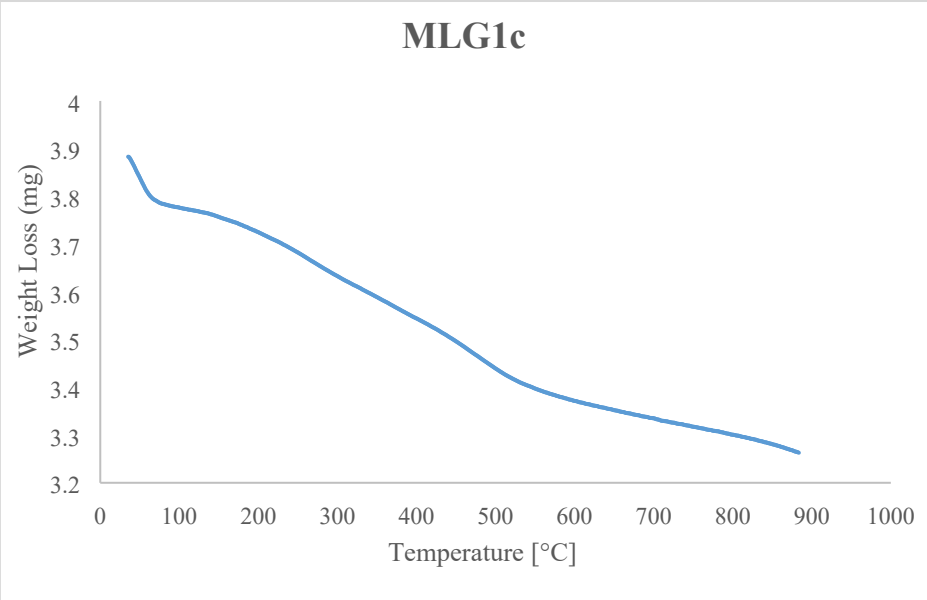


Figure 8S. Thermogravimetric analyses of **MLG1c**.

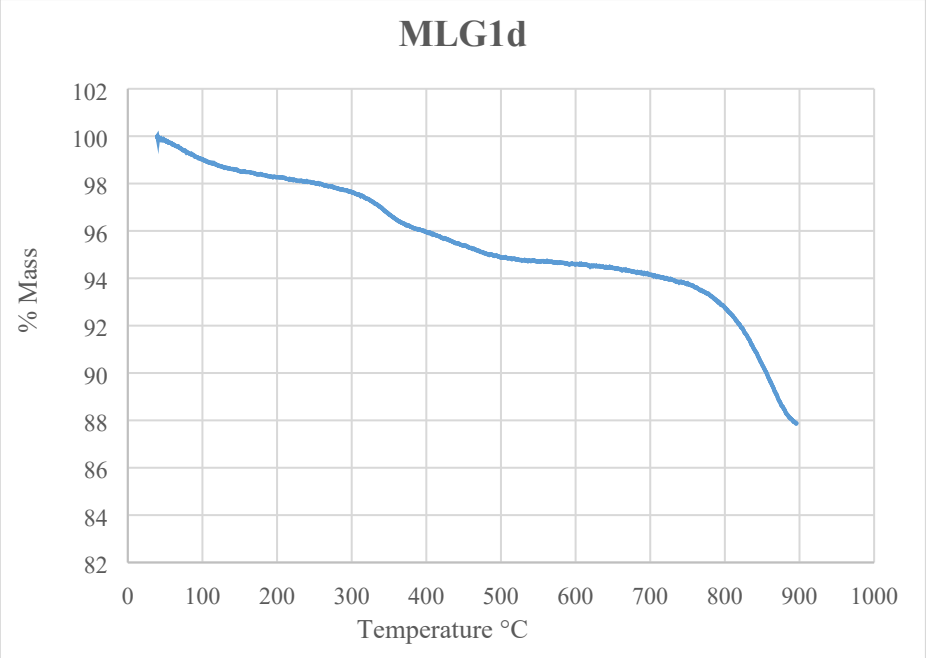
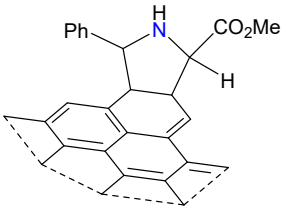
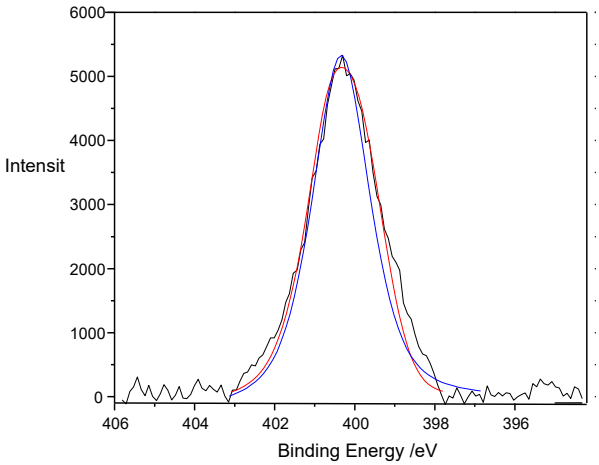


Figure 9S. Thermogravimetric analyses of **MLG1d**.

*XPS analyses of **MLG1***

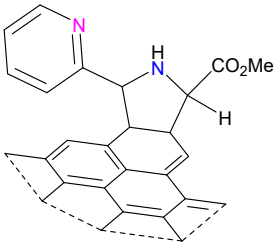


MLG1a

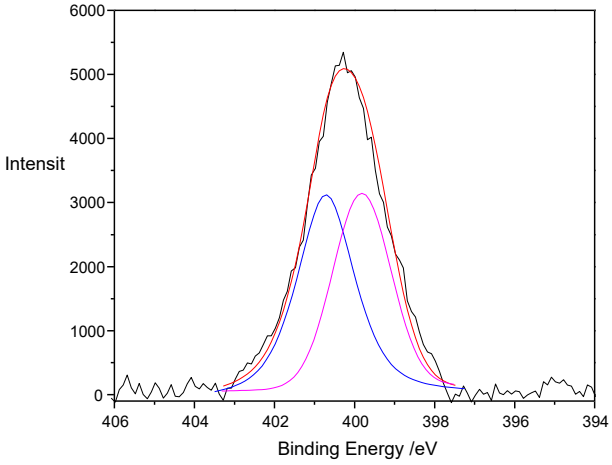


Peak	Position (eV)	Area	FWHM (eV)
1	400.1	2.550.000	1.650

Figure 10S. XPS plot of **MLG1a**.



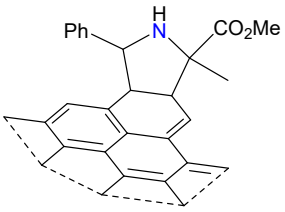
MLG1b



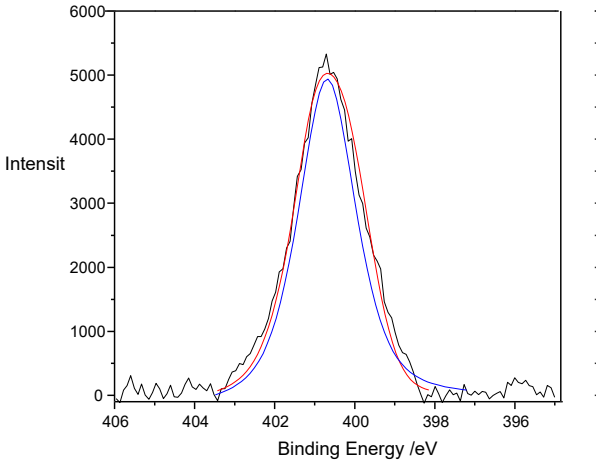
Peak	Position (eV)	Area	FWHM (eV)
0	399.8	6.100.000	1.700

1	400.7	6.300.000	1.600

Figure 11S. XPS plot of **MLG1b**.

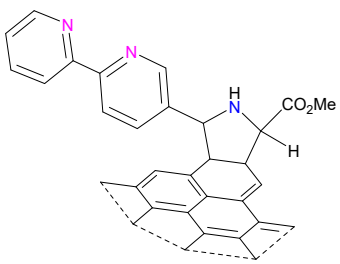


MLG1c

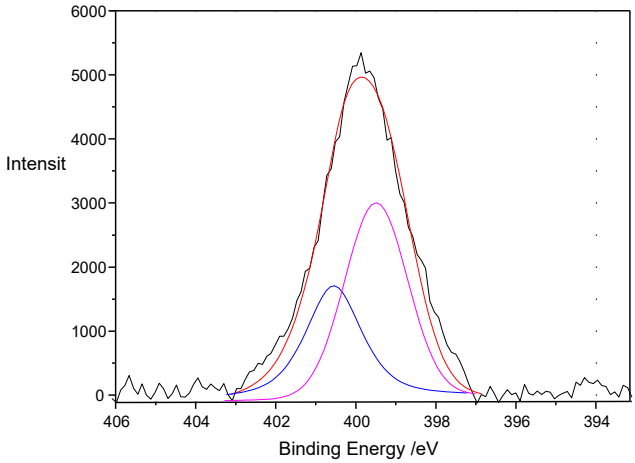


Peak	Position (eV)	Area	FWHM (eV)
1	400.1	6.550.000	1.650

Figure 12S. XPS plot of **MLG1c**.



MLG1d



Peak	Position (eV)	Area	FWHM (eV)
0	399.8	12.100.000	1.700
1	400.7	6.300.000	1.600

Figure 13S. XPS plot of **MLG1d**.

5. Preparation of MLG-Ru.

Functionalized graphene **MLG1d** (40mg), $Ru(Bpy)_2Cl_2 \cdot 2H_2O$ (40mg) and tetrachloroethane (20 mL) were added in a round bottom flask and then, the resulting suspension was refluxed for 48 h. After that, the solvent was distilled and the solid was dried under vacuum line. The graphene was collected and dispersed in 10 mL of methanol, and then centrifuged again. This procedure was repeated three times and then the graphene was dried under reduced pressure for 24 h.

ICP-MASS analysis: 0.80% in mass of Ru was obtained.

ICP-MASS analysis after reaction: 0.80% in mass of Ru was obtained.

*Comparative TG between **MLG1d** and **MLG-Ru***

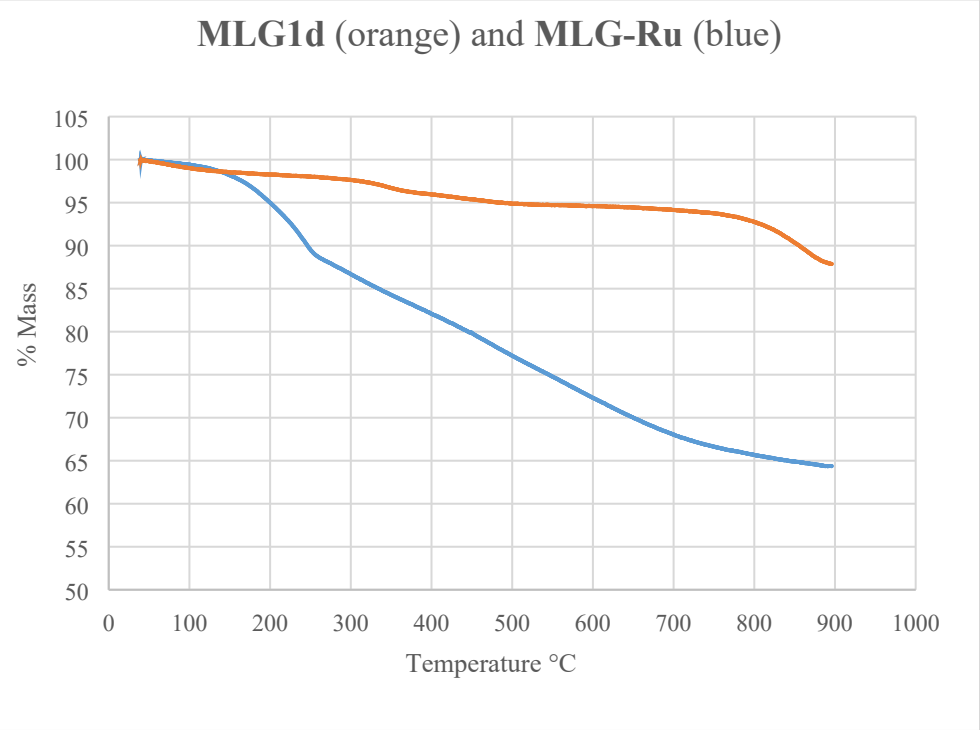


Figure 14S. Comparative TG between **MLG1d** and **MLG-Ru**.

SEM and Mapping-FSEM analysis

The analysis of mapping images indicated that Ru is well-dispersed and homogeneously distributed on the MLG.

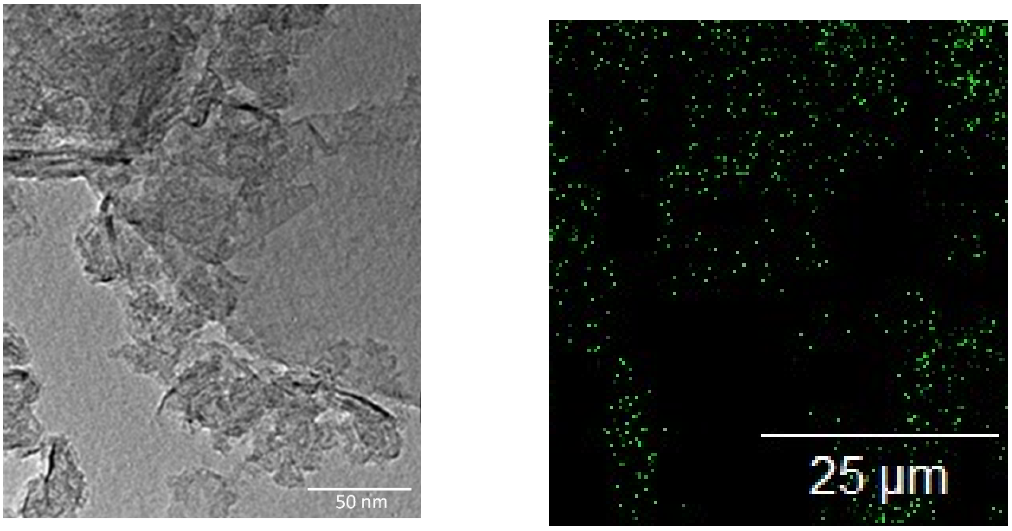


Figure 15S. a) SEM image of **MLG-Ru**. b) Mapping of Ru in **MLG-Ru**.

XPS analysis

Nitrogen atoms:

Three contributions centered at 398.7, 400.2, and 401.8 eV were identified in the N 1s spectrum. The latter contribution, which could be assigned to quaternary or positively charged nitrogen atoms usually appears in N 1s spectra because of the X-ray irradiation.

The positions of the peaks are slightly shifted compared to the Ru-free **MLG1d** sample, which might be due to the interaction between Ru and N atoms present in the **MLG-Ru** sample.

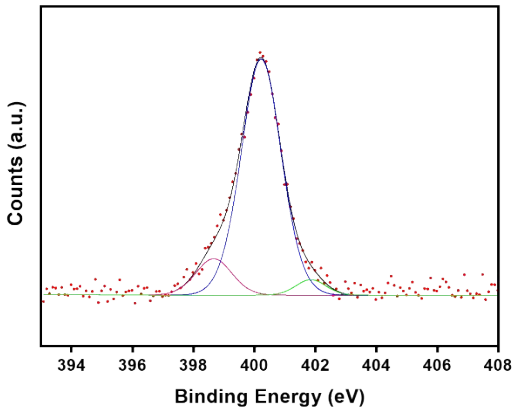


Figure 16S. XPS spectra of N 1s in **MLG-Ru**.

Ruthenium atoms:

XPS analysis revealed the presence of two contributions, located at 463.1 and 485.1 eV, which can be attributed to the presence of Ru(II) in the metal complex.

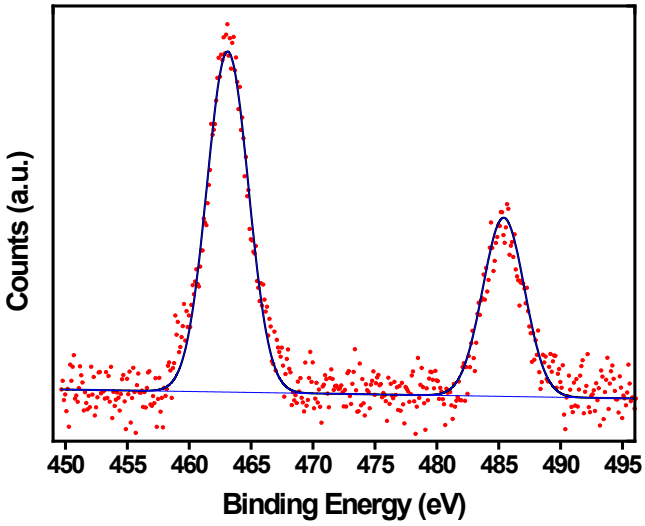


Figure 17S. XPS spectra of Ru 3p in **MLG-Ru**.

6. Catalytic aerobic oxidative hydroxylation of 4-methoxyphenylboronic acid. [8]

A suspension of **MLG-Ru** (20 mg) in DMF, 4-methoxyphenylboronic acid (**5**, 10.6 mg, 0.07 mmol), DIPEA (19.5 µL, 0.14 mmol), under an air atmosphere, was irradiated with a white LED light (14 W), at room temperature, for 72 h. The catalyst was then quantitatively recovered by centrifugation and the catalysis output was isolated by volatile evaporation under reduced pressure. The **MLG-Ru** recovered was reused again in the same reaction affording identical results. Routine GC-MS and ^{1}H NMR were performed to confirm the structure of the final compound.

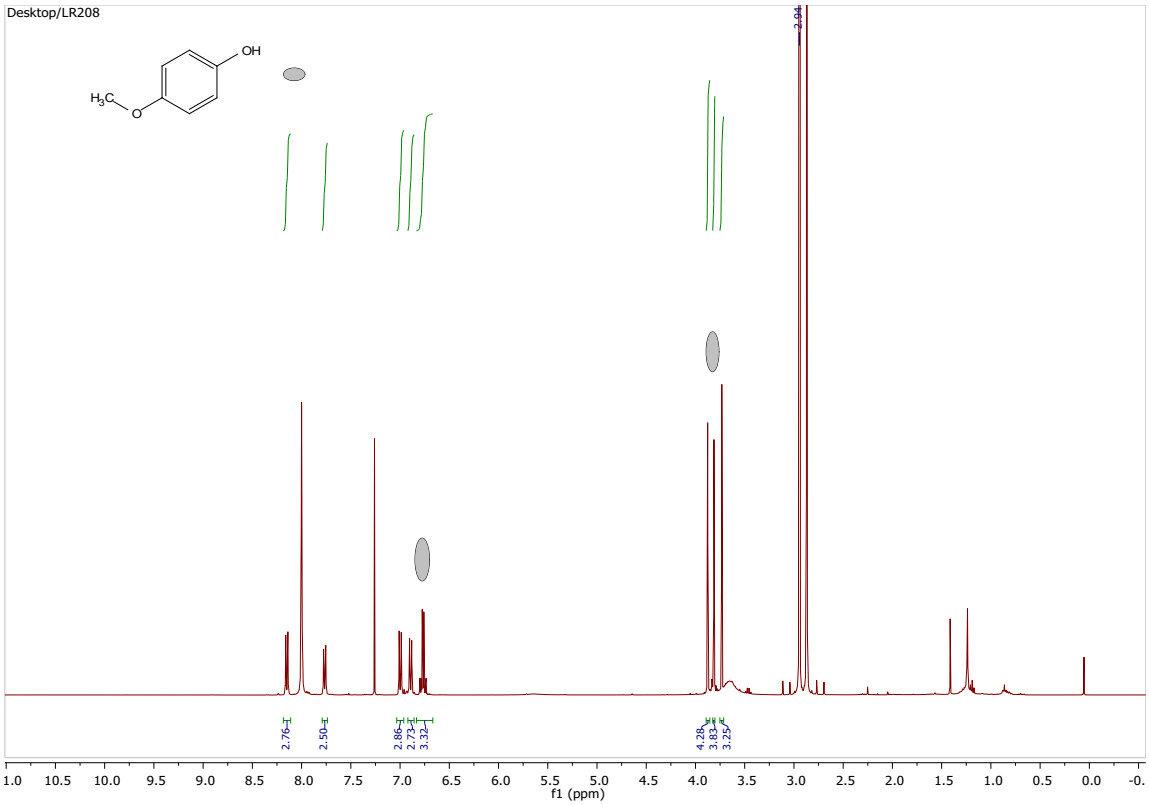


Figure 18S. ^{1}H NMR (300 MHz, $CDCl_3$) spectra from the reaction crude (without any purification) after 36 h. Solvent DMF as impurity.

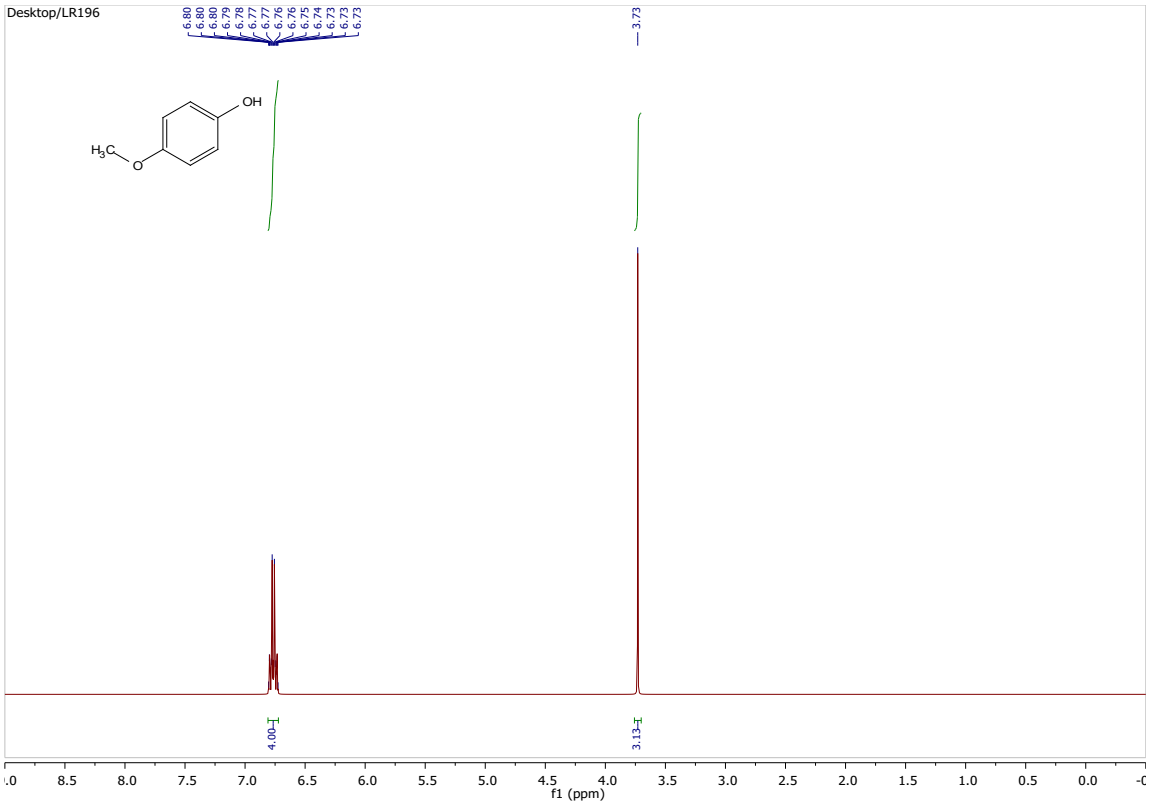


Figure 19S. ^{1}H NMR (300 MHz, $CDCl_3$) spectra from the catalytic oxidation of 4-methoxyphenol with freshly prepared **MLG-Ru** after 72 h, and also with the recovered **MLG-Ru** under the same conditions.

The recycled **MLG-Ru** was very robust according to the following analyses:

ICP-MASS analysis of the recycled sample: 0.80% in mass of Ru was obtained.

SEM and Mapping-FSEM analysis after the catalytic oxidative hydroxylation

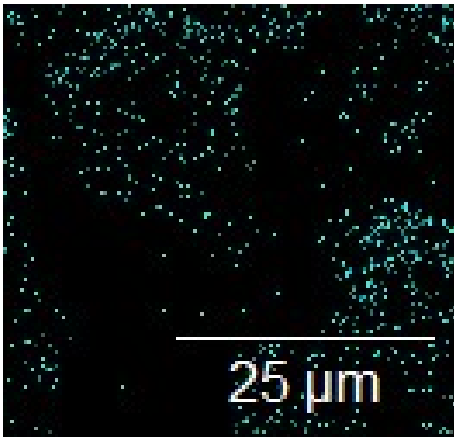


Figure 20S. a) SEM image of recovered **MLG-Ru** b) Mapping of Ru in recovered **MLG-Ru**

*XPS analysis of the recovered **MLG-Ru***

Nitrogen atoms:

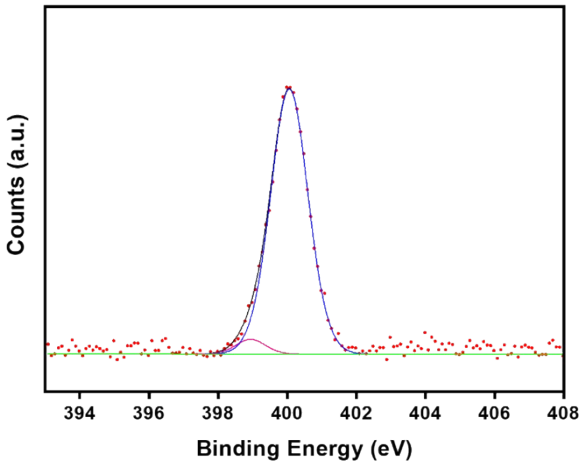


Figure 21S. XPS analysis (N 1s) of the recovered **MLG-Ru**

Ruthenium atoms

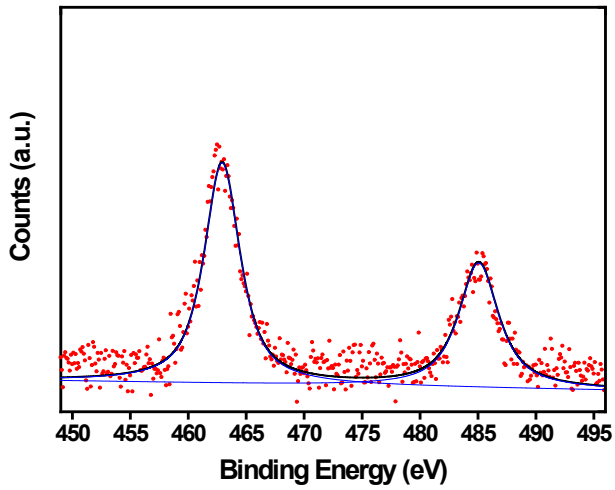


Figure 22S. XPS spectra of Ru 3p in recovered **MLG-Ru**.

Comparative study of XPS of ruthenium atoms in the recycled sample (down plot) *versus* XPS of the initially prepared supporting complex (up diagram). As can be seen, the electronic properties of the surface of the Ru species did not change during the reaction.

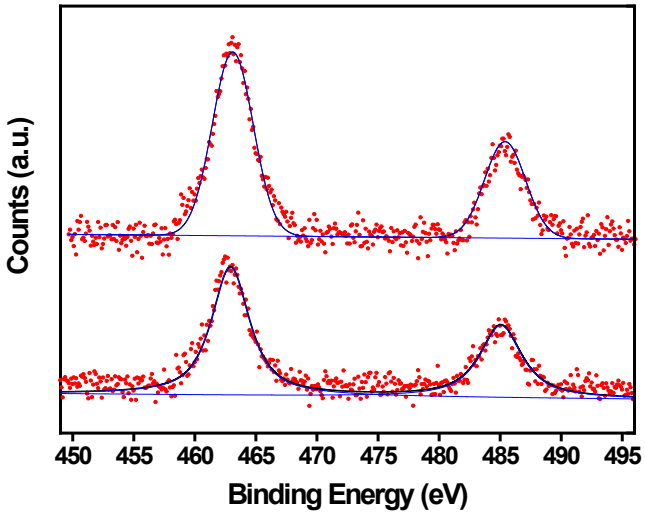


Figure 23S. Comparative analysis of XPS spectra of Ru 3p atoms in the recycled sample (down plot) *versus* XPS of the initially prepared supporting in **MLG-Ru**.

7. References

[1] A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc*. **2008**, *130* (31), 10084–10085.
[2] M. Ayerbe, A. Arrieta, F. P. Cossío, A. Linden, *J. Org. Chem*. **1998**, *63* (6), 1795–1805.
[3] K. V. Kudryavtsev, A. A. Zagulyaeva, *Russ. J. Org. Chem*. **2008**, *44*, 378–387.
[4] Y. Katoh, Y. Tsujimoto, C. Yamamoto, T. Ikai, M. Kamigaito, Y. Okamoto. *Polymer J.,* **2011**, 43, 84–90.
[5] Y. Huang, Q. Lin, J. Wu, N. Fu, *Dyes and Pigments*, **2013**, *99*, 699e704.

[6] P. Beer, F. Szemes, P. Passaniti, M. Maestri, M. *Inorganic Chemistry* **2004**, *43*, 3965-3975.
[7] G. Caleffi, O. Larrañaga, M. Ferrándiz-Saperas, P. Costa, C. Nájera, A. de Cózar, F. P. Cossío, J. M. Sansano, *J. Org. Chem.*, **2019**, *84*, 10593-10605.
[8] Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jørgensen, W.-J. Xiao *Angew. Chem. Int. Ed.,* **2012**, ***51***, 784 –788.