Reduced Graphene Oxide Supported Piperazine in Aminocatalysis

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Electronic Supplementary information

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1. General methods

NMR spectra were acquired using $CDCl_3$ or Acetone-d_6 as the solvent, running at 300 and 75 MHz for ^1H and ^{13}C respectively. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^1H NMR, and 77.0 ppm for ^{13}C NMR; Acetone-d_6, 2.05 ppm for ^1H NMR and 206.1 ppm for ^{13}C NMR). In all ^1H NMR spectra, multiplicity is indicated as follows: bs (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) or m (multiplet). Coupling constant values (in Hertz) and number of protons for each signal are also indicated.

Melting points were measured using *Gallenkamp melting point apparatus* in open capillary tubes. Optical rotation was recorded in cells with 10 cm path length on a Perkin-Elmer 241 MC polarimeter. For thin layer chromatography (TLC) Supelco silica gel plates with fluorescence indicator 254 nm were used and compounds were visualized by irradiation with UV light and/or by treatment with a solution of $KMnO_4$ (1.5g), K_2CO_3 (10g), and 10% NaOH (1.25 mL) in H_2O (200 mL) or a solution of phosphomolybdic acid (12g), in EtOH (250 mL) followed by heating. Flash column chromatography (FCC) was performed using Fluka pore 60 Å, 40-63 μm silica gel and compressed air.

Mass spectra were obtained in a *VG AutoSpec Spectrometer* (TOF MS EI+). Obtained data are expressed in mass/charge (m/z) units. Values between parentheses indicate relative intensities with regard to the base peak.

ATR-FTIR spectrum was taken on a Perkin Elmer Spectrum 65 FT-IR spectrometer. FT-IR essays were carried out in a Nicolet Magna-IR 750 spectrometer. The thermogravimetric analysis was performed with a TGA Q-500 (TA Instruments) at 5ºC/min (from 25ºC until 900ºC) under nitrogen atmosphere. Elemental analyses were performed with a Leco CHNS- 932.

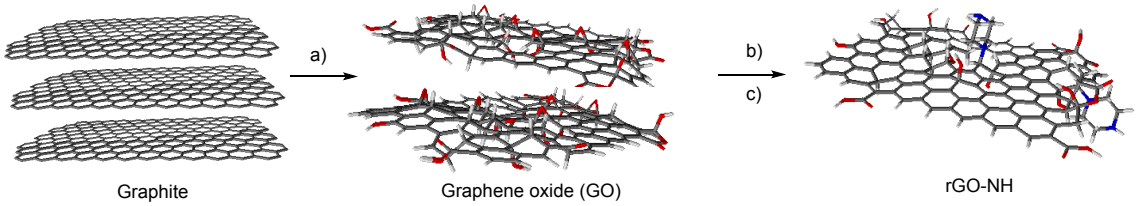
Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser and a Mg Kα (hv = 1254.6 eV) X-ray source, powered at 120 W. Binding energies were calibrated relative to the C 1s peak at 284.8 eV. High-resolution spectra envelopes were obtained by curve fitting synthetic peak components using the software “XPS peak.” Symmetric Gaussian–Lorentzian curves were used to approximate the line shapes of the fitting components. Atomic ratios were computed from experimental intensity ratios and normalized by atomic sensitivity factor.

X-ray diffraction was performed using a Panalytical X’Pert PRO θ/θ system, using CuKa-radiation, and X´Celerator detector. Samples were scanned between 5 and 100º (2θ) using a step size of 0.0167º (2θ) and a count time of 100s.

SEM images were acquired in a Hitachi Tabletop Microscope TM-1000-151.

Hexane and EtOAc were supplied by *Scharlau* and were used without previous purification. All the other reactants were bought in *Aldrich, Fluka* or *Alfa Aesar*. Cinnamaldehyde **2e** was diluted in Et_2O (1mL of **2e** in 10 mL of Et_2O) and this organic solution was washed twice with an aqueous $NaHCO_3$ saturated solution, brine and dried over $MgSO_4$.Et_2O was eliminated under reduced pressure and Cinnamaldehyde **2e** was freshly used for the corresponding reactions.

2. Synthesis of rGO-NH and derivatives



a) i. $NaNO_3$, H_2SO_4, $KMnO_4$, H_2O_2/H_2O; ii. US;
b) Piperazine, H_2O/EtOH, 100 ^oC, 24h;
c) NH_2NH_2, NH_4OH (pH 10), 100 ^oC, 1h

Scheme S1

a) Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized using a modified Hummers' method.[1] In a typical synthesis, 10g of graphite powder was added into 230 mL of concentrated H_2SO_4 in an ice bath, followed by adding 5g of $NaNO_3$ into the above mixture under stirring and cooling in an ice bath. The mixture was continuous stirred and 30g of $KMnO_4$ was added slowly so as to keep the temperature of mixture below 20 ℃. Then the mixture was kept at 30°C for 1.5h, followed by adding 400 mL of deionized water while stirring without intermitting, and the temperature would rise up to 95 °C. The mixture was kept stirring for a further 15 min, and 700 mL of deionized water and 6mL of 30% H_2O_2 were added in sequence. The oxidized material was then filtered and washed with deionised water until neutral pH. The collected product was dried under vacuum at 40°C. The GO was obtained thereafter.

b) Reaction of graphene oxide with piperazine

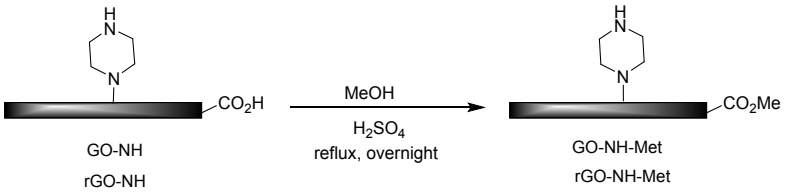
Modification with piperazine was carried out by GO´s epoxide opening.[2] 10g of GO was dispersed in 500 mL of water, followed by the addition of 30g of piperazine in 500 mL of ethanol. The mixture was allowed to stir for 24 h under reflux before isolation of the resulting derivative GO-NH (filtration, washing with water and ethanol, and drying at 80ºC).

c) Reduction of GO-NH

Reduction with hydrazine hydrate:[3] briefly 10g of material were dispersed in 1L of water and 7mL of hydrazine hydrated were added, pH was adjusted to 10 with NH_3. The mixture was stirred at 100ºC for 1h. Finally the suspension was filtered, washed with water and ethanol and dried at 80ºC for 6h to afford rGONH.

[1] W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339.
[2] A. B. Bourlinos, D. Gournis, D. Petridis, T. Szabó, A. Szeri, and I. Dékány, *Langmuir*, 2003, **15**, 6051.
[3] D. Li, M. B. Müller, S. Gilje, R. B. Kaner and G. G. Wallace, *Nature Nanotechnology*, 2008, **3**, 101.

Preparation of rGO-NH-Met and GO-NH-Met: Esterification of GO-NH and rGO-NH.



Scheme S2

In a 250 mL round bottom flask, 1g of GO-NH or rGO-NH obtained according to the previous method, 100 mL of ethanol and two drops of concentrated sulfuric acid were added. The mixture was stirred overnight under reflux before isolation of the resulting derivative GO-NH-Met and rGO-NH-Met respectively. The solvent was removed by filtration under vacuum. The material collected was washed with $NaHCO_3$ (5 x 20 mL, until pH = 9-10), water until pH=7 was reached and finally with acetone. The resulting solid was dried in the heater (1 h, 100 ºC).

3. Characterization of the material

X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS) mapping,

The **XRD** (X-ray diffraction) pattern of GO exhibits a strong peak at 2θ = 12º due to the presence of oxygen functionalities. After reduction with hydrazine, this peak completely disappears (Figure S1). Compared to graphite, the broad diffraction peaks of rGO and rGO-NH at 2θ = 26º indicate poor ordering of the sheets along the stacking direction, which implies that the samples were comprised from few layers of graphene. This could be confirmed by **FE-SEM** of rGO-NH images showing typical wrinkled structure (Figure S2). To verify the composition of rGO-NH, **EDS** mapping of C, O, and N was performed (Figure S3). Quantitative analysis gave 78.76 wt% C, 11.50 wt% O and 9.79 wt% N.

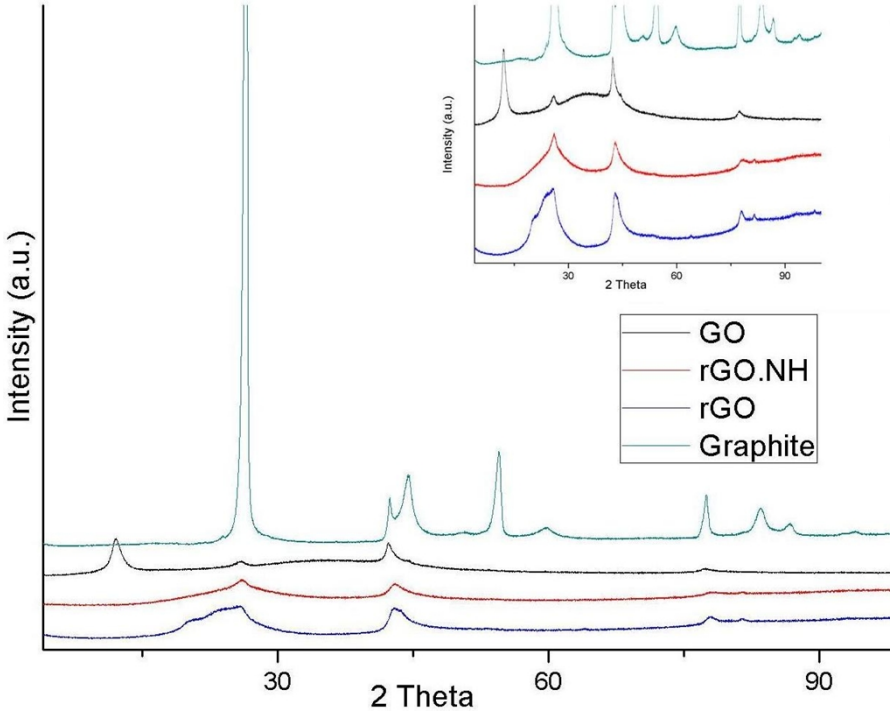


Figure S1. XRD of GO, rGO, rGO-NH and graphite

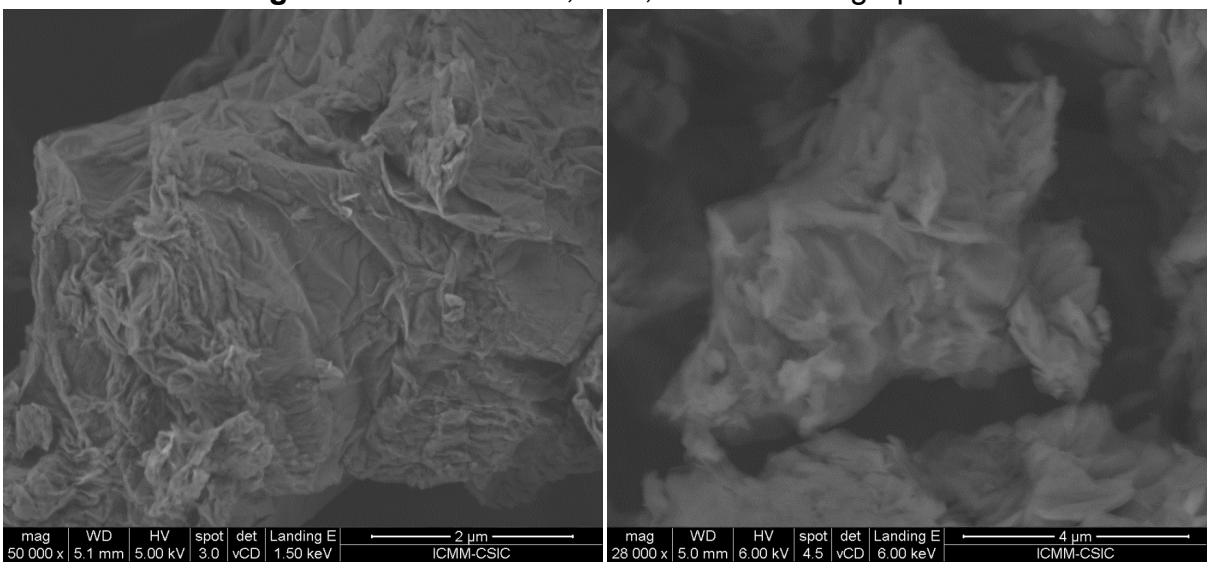
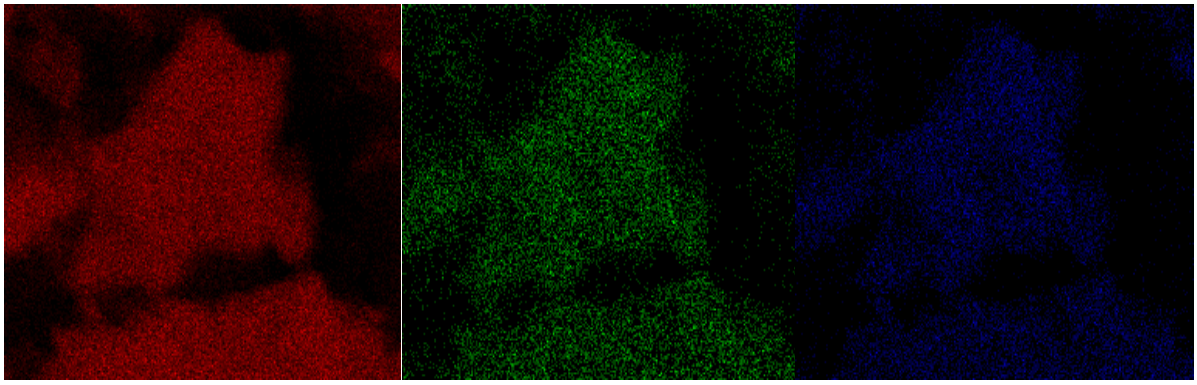


Figure S2. FE-SEM of rGO-NH images showing typical wrinkled structure



Carbon (Red dots), **Nitrogen (Green dots)** **Oxygen (Blue dots).**

Figure S3. Energy Dispersive Spectroscopy (EDS) mapping

X-ray photoelectron spectroscopy (XPS)

The nature and quantity of surface groups present in GO and rGO-NH samples, was revealed by **XPS** (Figure S4). The high resolution C1s, N1s and O1s core-level spectra are displayed above. The C1s peak was satisfactorily fitted into three components: a major component at 284.8 eV, which corresponds to sp^2 C-C bonds in graphitic carbon; a second one at 286.3 eV was associated to C-O/C-N bonds; and third minor one at 288.0 eV was assigned to C=O bonds. Consistently, the O1s peak showed two components at 531.5 eV and 532.9 eV associated to C=O and C-O bonds, respectively. In addition, the N1s emission showed two components at 399.8 and 401.7 eV due to C-N and protonated $C\text{-}NH^+$ moieties, respectively. Atomic composition was also deduced from XPS spectra. The C, O and N atomic percentages were 80.6, 12.7 and 6.7 %, respectively.

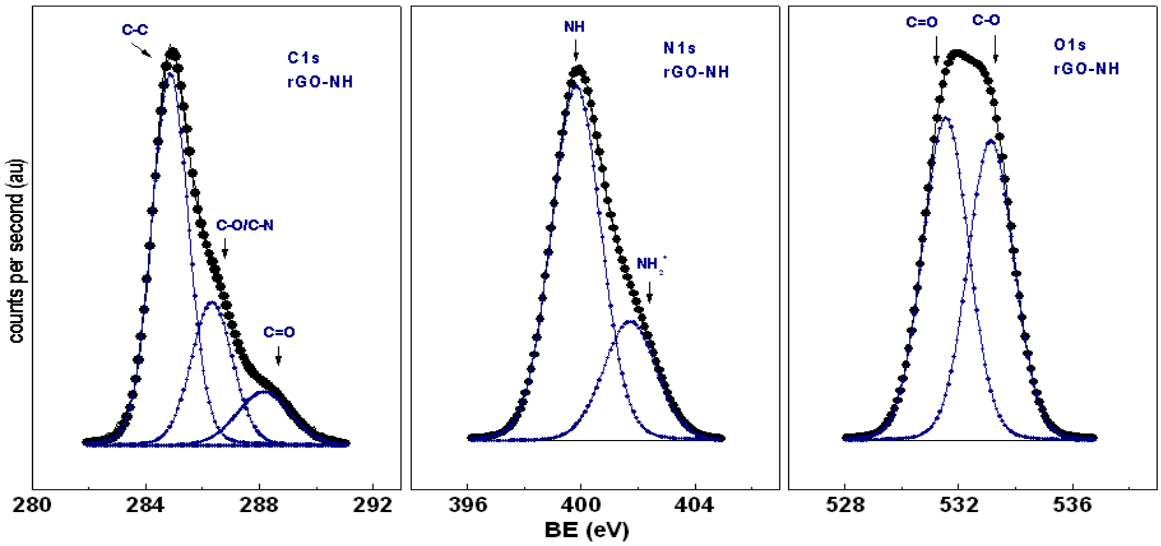


Figure S4. XPS data of rGO-NH

Thermogravimetric analysis (TGA)

Focusing on GO-TGA curve (green in Figure S5), it can observed an initial loss of weight due to the removal of adsorbed water and a higher loss of mass attributed to the decomposition of the oxygenated groups. rGO (dark blue in Figure S5) presents lower loss of weight, as it contains less functional groups and improve the thermal stability of GO. The curve corresponding to rGO-NH (light blue in Figure S5) lies between the previous two, since the material has less oxygen-containing groups than GO but it is not as stable as rGO.

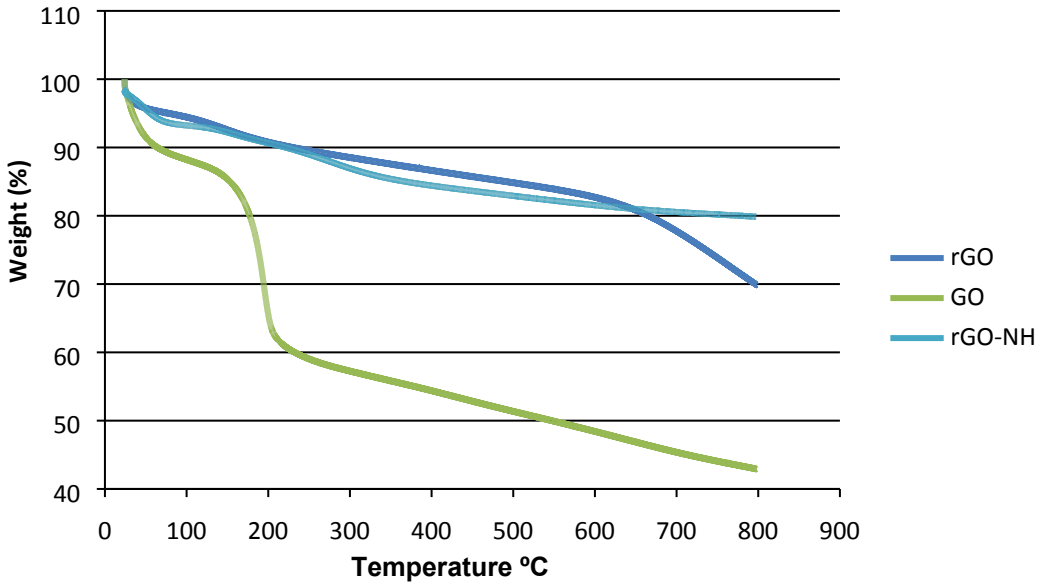


Figure S5. TGA curves of GO, rGO and rGO-NH.

Figure S6 shows TGA curve of rGO-NH. We can observe a small mass loss (4%) at around 100 ºC due to the removal of adsorbed water and a significant loss of weight which represent 10% of total mass at around 300 ºC corresponding to the piperazine anchored on rGO.

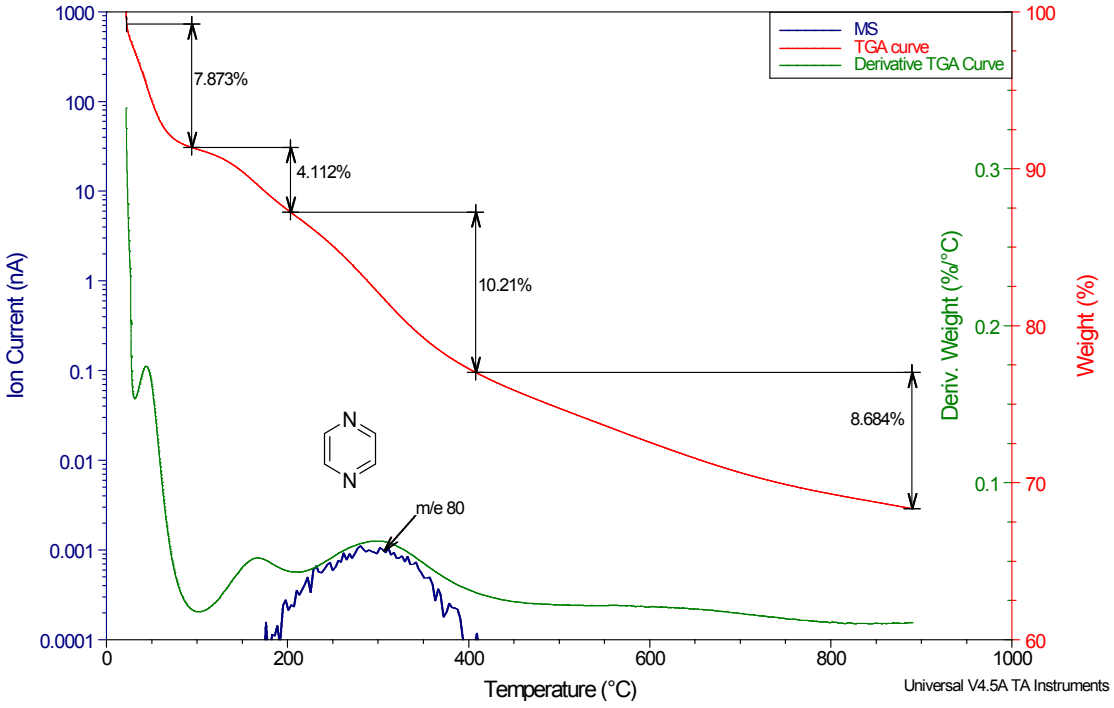


Figure S6. TGA-MS of rGO-NH.

In order to check if piperazine was anchored by covalent bond or just adsorbed on graphene oxide, we represent TGA curves for rGO-NH and rGO and piperazine (prepared by stirring rGO for 1 hour with piperazine in diethylether as solvent). Figure S7 shows a notable difference between both curves, indicating that piperazine should be anchored to the support through covalent bond.

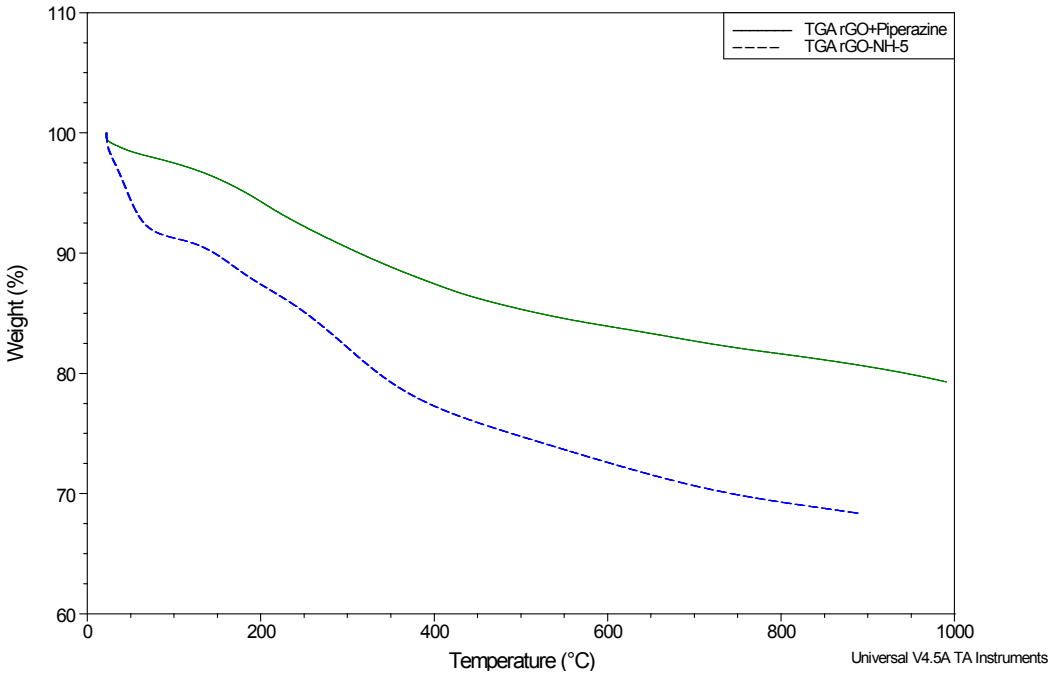


Figure S7. TGA-MS of rGO-NH and a mixture of rGO and piperazine.

FT-IR

We have not been able to obtain a clear IR spectrum of rGO-NH, probably due to its conductive properties. Nevertheless, we could obtain a good spectrum of GO-NH precursor.

In order to appreciate the difference between GO (the starting material) and GO-NH (functionalized material) both FT-IR spectra are shown in Figure S8. The 1800-1000 cm^{-1} area shows a decrease of the oxygenated groups in GO-NH (blue) compare with original GO (red), indicating a covalent interaction between the graphene oxide and piperazine.

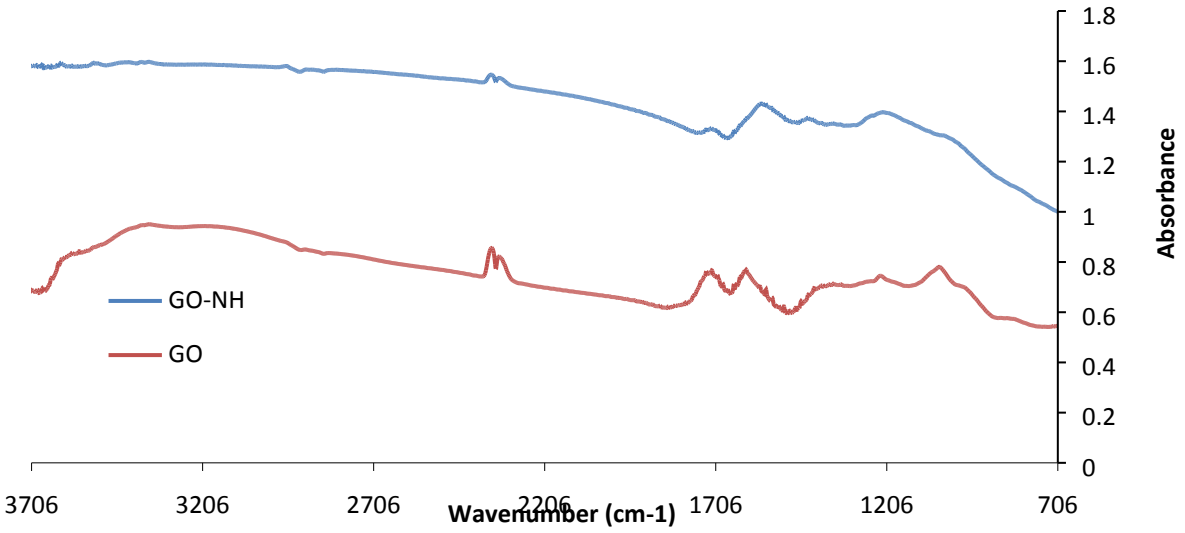


Figure S8. FT-IR of GO and GO-NH.

The most striking change is the disappearance of peaks at 1220[4] and 1055[5] cm^{-1}, which correspond to the epoxy groups existing in GO and the appearance of signals at 1569**5**, 1436 and 1250[6] cm^{-1} in GO-NH spectrum generated by bending and stretching of amine group. These observations as a whole could be considered as an empirical evidence of the opening of the epoxides of GO with piperazine through a nucleophilic attack (see expansion in Figure S9).

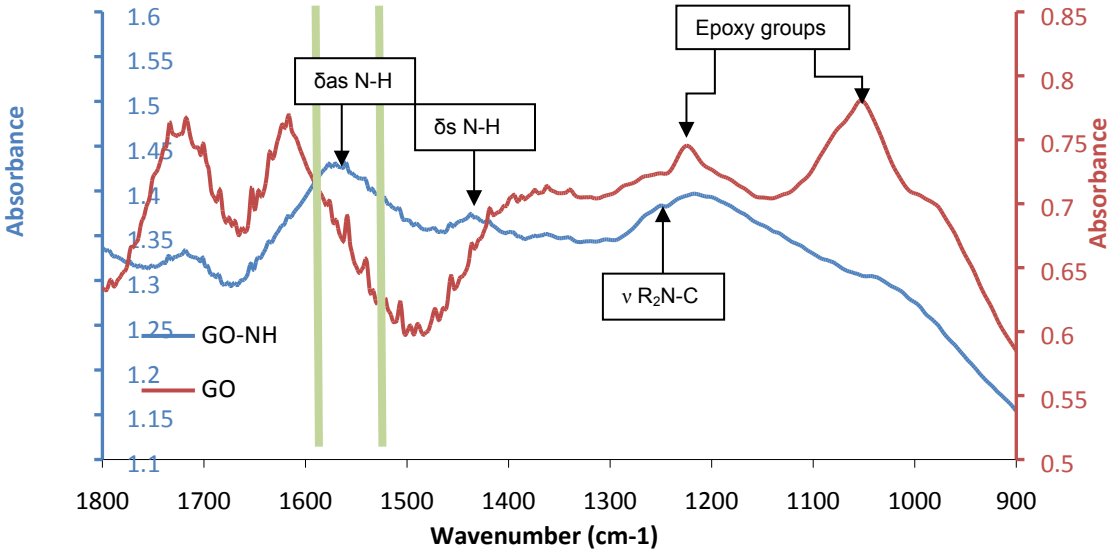


Figure S9. Expansion of overlaping FT-IR of GO and GO-NH

Interestingly, other differences between both materials may indicate that not only epoxides but also other oxygen-containing functional groups present in GO were affected under the functionalization conditions. The GO spectra shows two bands at approximately 1722 and 1617[7] cm^{-1} attributed to the C=O stretch in carboxylic acids and quinones respectively which decrease in the GO-NH spectra, as well as the signal around 1370[8] cm^{-1} assigned to the stretching vibration of C-O in alcohols (see Table 1). The greater width of the band appearing at 1580-1540 cm^{-1} in the spectrum of GO-NH respect to GO could be explained taking into account a greater contribution of C = C stretch in the GO-NH. This could be due to a recovery of aromaticity in some oxidized positions in GO for the possible removal of hydroxyl groups resulting from the opening of the epoxide with piperazine. This also agrees with the higher absorbance of GO-NH than GO precursor.

Table S1. Comparison of IR signals of GO and GO-NH

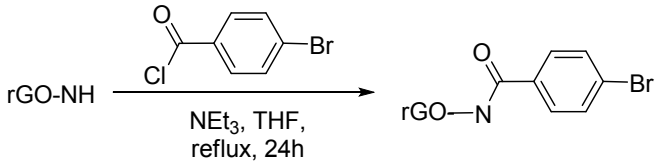
GO (cm^{-1})	GO-NH (cm^{-1})	Assignment
1722	1722	ν C=O (-COOH)8
1617	1617	ν C=O (quinone)**6**
-	1569	δas N-H (amine)**5** + ν C=C[9]
-	1436	δs N-H (amine)
1370	-	ν C-O (alcohols)**8**
-	1250	ν C-N (amine)**6**
1220	-	ν epoxy groups**8**
1055	-	epoxy groups or C-O (alcohols)
850	-	δ epoxy groups**8**

[4] E. Pretsch, T. Clero, J. Seibl y W. Simon, *Tablas para la elucidación estructura de compuestos orgánicos por métodos espectroscópicos*, Ed. Alhambra 1980.
[5] F. Zhang, H. Jiang, X. Li, X. Wu, H. Li, *ACS Catal.,* 2014, **4**, 394
[6] S. Biniak, G. Szymanski, J. Siedlewski, A. Swiatkowski, *Carbon,* 1997, **35**, 1799
[7] N. Lakshmi, N. Rajalakshmi, K-S. Dhathathreyan, *J. Phys. D: Appl. Phys.,* 2006, **39**, 2785
[8] A. Ambrosi, C. K. Chua, A. Bonanni, M. Pumera *Chem. Mater.*, 2012, **24**, 2292
[9] M. M. Antunes, P. A. Russo, P. V. Wiper, J. M. Veiga, M. Pillinger, L. Mafra, D. V. Evtuguin, N. Pinna, A. A. Valente, *ChemSusChem*, 2014, **7**, 804

Total reflection X-Ray Spectroscopy (TXRF)

With the different techniques used to characterize rGO-NH, it is possible to roughly deduce the minimum amount of piperazine contained in rGO-NH. It is important to note that when GO is reduced with hydrazine, a small ratio of nitrogen is incorporated to the material,[10] therefore all the nitrogen detected does not belong to the anchored piperazine.

The reaction of rGO-NH with 4-bromobenzoyl chloride should occur through the NH free groups of the anchored piperazine:



500 mg of rGO-NH were dispersed in THF (50 mL) under sonication for 1h. Triethylamine (1 mL) and 4-bromobenzoyl chloride (50 mg) were added and the mixture was stirred under reflux for 24 hr. After that time, the dispersion was filtered and washed with THF (2 × 25 mL).

For bromine quantification, a dispersion in milliQ water (1000 mg/L) was prepared by sonication for 1h and the dispersion was analyzed by total reflection X-Ray Spectroscopy (**TXRF**) (excitation Mo K radiation, voltage 50 kV) giving 10.676 mg of bromine/L. A loading of 0.13 mmol/g of piperazine was calculated with this value.

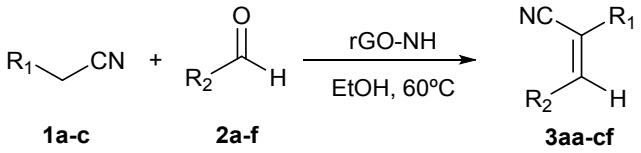
Elemental analysis of rGO-NH was: C: 66.58, H: 2.83, N: 5.27, S: 0.05

For all the reactions described in this publication, the catalyst **loading** used was 50 mg of rGO-NH for each 0.3 mmol of electrophile.

[10] S. Park, Y. Hu, J. O. Hwang, E-S. Lee, L. B. Casabianca, W. Cai, J. R. Potts, H-W. Ha, S. Chen, J. Oh, S. O. Kim, Y-H. Kim, Y. Ishii and R. S. Ruoff, *Nat. Commun*, 2012, **3**. 638

4. Experimental procedure for the Knoevenagel reaction

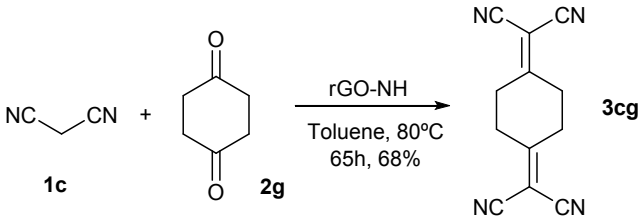
General procedure



1a-c **2a-f** **3aa-cf**

A vial equipped with a magnetic stirring bar was charged with nucleophile **1a-c** (0.31 mmol), aldehyde **2a-f** (0.3 mmol), rGO-NH (50 mg) and 2 mL of EtOH. The suspension was heated at 60ºC and stirred during the time indicated in each case (Table 1), whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The filtrate was concentrated under reduced pressure to afford the corresponding Knoevenagel products **3aa-cf**.

Preparation of 3cg



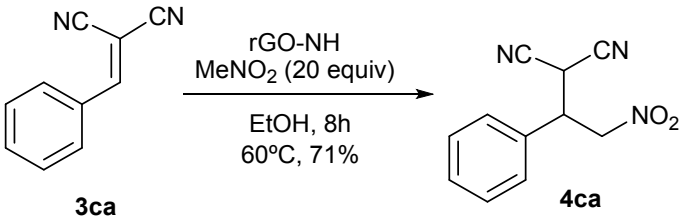
1c **2g**

A vial equipped with a magnetic stirring bar was charged with nucleophile **1c** (39.6 mg, 0.6 mmol), 1, 4 ciclohexadione (22.4 mg, 0.2 mmol), rGO-NH (33 mg) and 1.5 mL of Toluene. The suspension was heated at 80ºC and stirred during 65h, whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The dark green filtrate was concentrated under reduced pressure and purified by flash column chromatography (Hexane: EtOAc 5:1 to 3:1) to afford 28 mg (Yield: 68%) of the corresponding Knoevenagel product **3cg.**

Recovery of rGO-NH

We have proven, in the preparation of **3cc**, that the material might be recovered and used without losing efficiency at least after 3 cycles. Catalyst was recovered following this procedure: The mixture of the reaction was filtered under vacuum through a sintered glass filter and washed with acetone several times. The recovered solid was placed in a vial and dried in a heater at 100ºC during 1 hour.

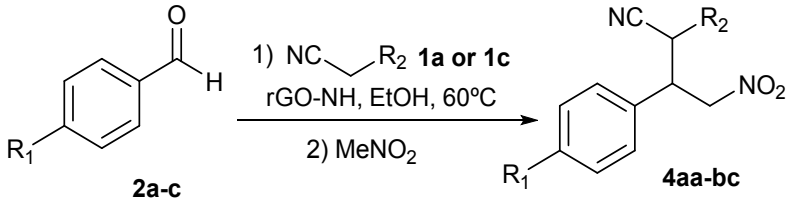
5. Experimental Procedure for the Michael addition (*via* base activation)



3ca **4ca**

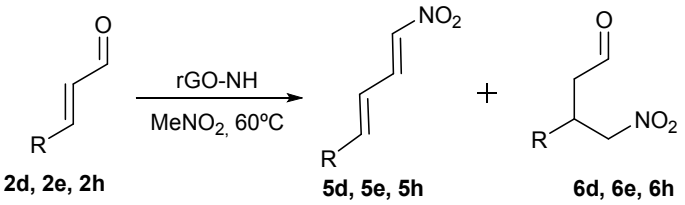
A vial equipped with a magnetic stirring bar was charged with compound **3ca** (46.2 mg, 0.3 mmol), 50 mg of rGO-NH and 1.5 mL of EtOH, whereupon 320 µL (5.4 mmol, 20 equiv) of $MeNO_2$, were added. The suspension was heated at 60ºC and stirred during 8h, whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The filtrate was concentrated under reduced pressure and purified by flash column chromatography (Hexane 7:1 EtOAc) to afford 46 mg (Yield: 71%) of product **4ca.**

6. Experimental Procedure for the one-pot Knoevenagel-Michael addition



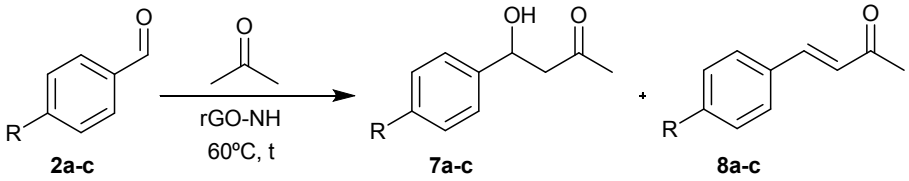
A vial equipped with a magnetic stirring bar was charged with nucleophile **1a** or **1c** (0.16 mmol), aldehyde **2a-c** (0.15 mmol), rGO-NH (25 mg) and 1 mL of EtOH. The suspension was heated at 60ºC and stirred during the time indicated in each case (Table 2). After that time, the indicated equivalents of $MeNO_2$ (Table 2), were added to the suspension, which was stirred at 60ºC during the time indicated in each case (Table 2), whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The filtrate was concentrated under reduced pressure and purified by flash column chromatography in the eluent indicated in each case.

7. Experimental Procedure for the Michael addition of nitromethane to enals (*via* iminium activation)



A vial equipped with a magnetic stirring bar was charged with 0.3 mmol of aldehyde **2d**, **2e** or **2h** and 50 mg of rGO-NH and 2 mL of $MeNO_2$. The suspension was heated at 60ºC and stirred during the time indicated in each case (Table 3), whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The filtrate was concentrated under reduced pressure and, if necessary, purified by flash column chromatography in the eluent indicated in each case.

8. Experimental Procedure for the Aldol Condensation



A vial equipped with a magnetic stirring bar was charged with 0.3 mmol of aldehyde, 50 mg of rGO-NH and 2 mL of acetone. The mixture was stirred at 60ºC during the time indicated in each case (Table 4), whereupon it was allowed to cool to room temperature. The solution is filtered off to remove the catalyst, washing several times with acetone. The filtrated was concentrated under reduced pressure and purified by flash column chromatography in the eluent indicated in each case.

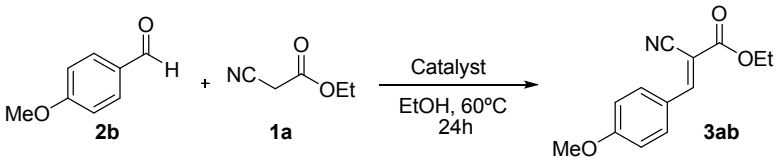
9. Other experiments: Comparison of the behavior of rGO-NH as catalyst and precursors

Knoevenagel reaction

To check the efficiency of the catalyst rGO-NH**,** we carried out the experiments depicted in Table S2. We first discarded the background reaction, i.e. the Knoevenagel reaction was performed with **1a** and **2b** the absence of catalyst affording product **3ab** with a 12% conversion after 24h of reaction (Entry 1). When the same reaction was performed with nucleophile **1c** and aldehyde **3c,** only traces of product **3cc** were observed in the crude after 3h of reaction, whereas with catalyst **I** the reaction was completed after that time.

We also tested different materials for the reaction between **1a** and **2b.** We found that GO seems to inhibit the reaction (compare entries 1 and 2) whereas rGO, the support used to anchored piperazine, was less effective than rGO-NH (compare entries 3 and 4). GO-NH, piperazine and *N*-methylpiperazine[11] afforded almost complete conversion after 24h of reaction.

Table S2. Knoevenagel Reaction with different materials.

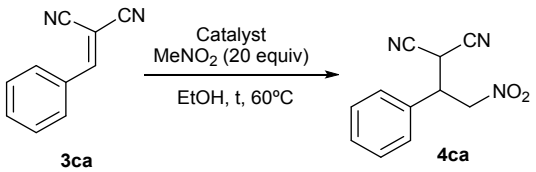


Entry	Catalyst	Conversion (**3ab**)
1	No Catalyst	12%
2	GO	0%
3	Graphite	14%
4	rGO	56%
5	rGO-NH	91%
6	GO-NH	>95%
7	Piperazine	>95%
8	*N*-Methylpiperazine	>95%

Michael addition (*via* basic activation)

This reaction was also performed using different catalysts. In this case, rGO-NH was the most effective catalyst. GO-NH and a mixture of rGO and piperazine also afforded the final product, but with lower yields (Table S3).

Table S3. Michael addition



Entry	Catalyst	Time	Conversion (**4ca**)	Yield (**4ca**)
1	rGO-NH	8h	> 95%	71%
2	rGO	24h	35%	n.d.
3	GO-NH	8h	> 95%	62%
4	Piperazine	24h	Complex mixture	---
5	rGO / Piperazine	8h	>95%	57%

[11] As rGO-NH features a secondary and tertiary amines we also tested the role of *N*-methylpiperazine

Michael addition of nitromethane to enals (*via* iminium activation)

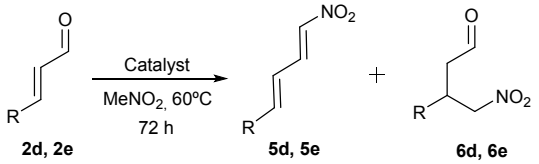
We have shown in the manuscript the comparative results using cinnamaldehyde (**2e**) as enal. Herein we gather the comparative experiments carried out using crotonaldehyde (**2d**) as enal (Table S4). In some of the cases, the alcohol from 1,2 addition was observed along with the diene **5d** derived from 1,2 addition**.** For simplicity**,** both ratios has been added and included in the table as a single number as '1,2 product' in the ratio column.

We proved that the support rGO was unsuccessful as catalyst (Entry 1). Contrary to the case of cinnamaldehyde (see table 3, manuscript) free piperazine is not able to catalyze the reaction. Nevertheless, in the presence of rGO piperazine is able to catalyze the reaction, what indicates a cooperative role between both components. This ratio contrast with the one obtained when using rGO-NH (compare entries 1 and 2), indicating an effect of the rGO support. Interestingly, when piperazine and rGO were introduced in the same reaction vessel, the ratio of the 1,4-adduct increased with respect to piperazine itself (compare entries 2 and 3). A similar effect was observed when *N*-methylpiperazine[11] itself and in the presence of rGO (entries 4 and 5), indicating a role of the support either due to the electronic properties and/or the acidic groups. We also evaluated the behavior of (piperazine-PS = piperazine supported on polistyrene) but a low conversion was also obtained (entry 6). GO-NH, precursor of rGO-NH, which should present less conductivity that rGO-NH afforded a higher conversion but a lower ratio of the 1,4 adduct (entry 7). Entry 8 shows the result obtained with rGONH.

In the case of cinnamaldehyde **2e**, some other experiments than those gathered in table 3 have been also performed (Table S4, entries 9-14). *N*-Methylpiperazine[11] afforded a low ratio of the 1,4 product that slightly increased in the presence of rGO (entries 9 and 10). Piperazine-PSc afforded similar ratio of 1,2 and 1,4 products (entry 11).

In order to also evaluate the role of the acids on the rGO-NH and GO-NH catalysts, the reaction of rGO-NH-Met and GO-NH-Met (where the acids were transformed into esters see SI 3) were also tested (entries 12 and 13). The lower ratio of the 1,4 product compare with rGONH (entry 14) could be due to a lower turnover of the catalyst as the enamine resulting from the attack of the nucleophile must be hydrolyze to the final product liberating the final product and the catalyst. The absence of acids slows down the 1,4-adition reaction via iminium ion activation.

Table S4. Michael addition of nitromethane to enals



2d, 2e **5d, 5e** **6d, 6e**

Entry	Aldehyde[a]	Catalyst	Conv	Ratio **1,2/1,4**	Yield **1,4** (**6**) (%)
					6d
1	**2d** (R = Me)	rGO[b]	f	No reaction	---
2	**2d** (R = Me)	Piperazine[c]	f	100/0	0
3	**2d** (R = Me)	rGO + Piperazine[d]	f	51/49	17
4	**2d** (R = Me)	*N*-Methylpiperazine[c]	f	Complex mixture	n.d
5	**2d** (R = Me)	rGO /*N*-Methylpiperazine[d]	f	57/43	12
6	**2d** (R = Me)	Piperazine-PS[c]	f	0/100	20
7	**2d** (R = Me)	GO-NH[e]	f	22/78	26
8	**2d** (R = Me)	rGO-NH[e]	f	8/92	58
					6e
9	**2e** (R = Ph)	*N*-Methylpiperazine[c]	37	81/19	n.d
10	**2e** (R = Ph)	rGO /*N*-Methylpiperazine[d]	39	68/32	9
11	**2e** (R = Ph)	Piperazine-PS[c]	61	59/41	17
12	**2e** (R = Ph)	rGO-NH-Met[e]	34	37/63	n.d
13	**2e** (R = Ph)	GO-NH-Met[e]	53	43/57	n.d
14	**2e** (R = Ph)	rGO-NH[e]	77	27/73	45

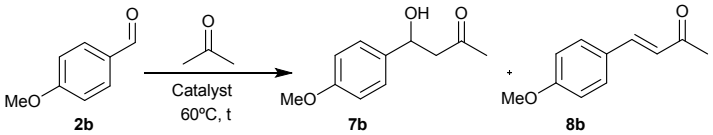
[a]0.3 mmol of aldehyde were used; [b]50 mg of rGO were used; [c]5 mol% was used; [d]50 mg of rGO and 5 mol% of piperazine were used; [e]50 mg were used;[f] As crotonaldehyde is volatile, conversion was not determined.

The higher ratio of the 1,4-products when using rGO as additive and in more extend when is directly anchored to the catalyst (rGO-NH), suggest a possible stabilization of the iminium ion intermediate due to the electronic density of the surface of the graphene derivative.

Aldol Condensation

The aldol condensation was also performed using *N*-methylpiperazine as catalyst, affording comparable results with the ones obtained with piperazine. The results are shown in Table S5.

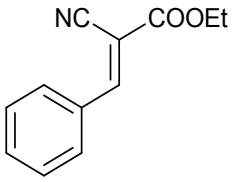
Table S5. Aldol condensation



Entry	Aldehyde	Catalyst	Time (h)	Conversion (%)	Ratio **7b/8b**	Yield **8b** (%)
1	**2b** (R = OMe)	*N*-Methylpiperazine	72	35	<2:98	57
2	**2b** (R = OMe)	rGO / *N*-Methylpiperazine	72	23	<2/98	53

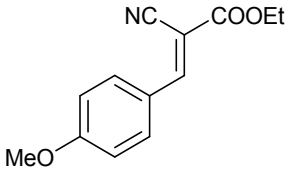
9. Data of Products 3-8

(E)-Ethyl-2-Cyano-3-phenylacrylate (3aa)



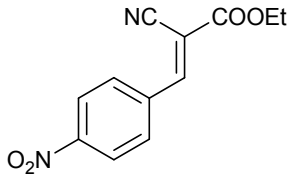
50 mg (Yield = 83%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.88 (d, *J* = 6.9 Hz, 2H), 7.48-7.29 (m, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). The spectroscopic data are in agreement with the literature.11

(E)-Ethyl-2-Cyano-3-(4-methoxyphenyl)acrylate (3ab)



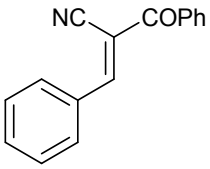
54 mg (Yield = 78%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.98 (d, *J* = 8.9 Hz, 2H), 6.97 (d, *J* = 8.9 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). The spectroscopic data are in agreement with the literature.[12]

(E)-Ethyl-2-Cyano-3-(4-nitrophenyl)acrylate (3ac)



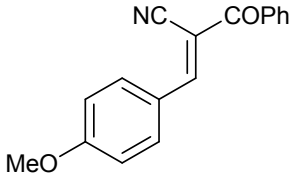
59 mg (Yield = 80%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.7 Hz, 2H), 8.29 (s 1H), 8.12 (d, *J* = 8.7 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). The spectroscopic data are in agreement with the literature.11

(E)-2-Benzoyl-3-phenylacrylonitrile (3ba)



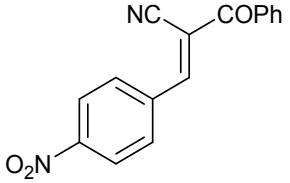
61 mg (Yield = 88%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.92 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46-7.38 (m, 5H). The spectroscopic data are in agreement with the literature.[13]

(E)-2-Benzoyl-3-(4-methoxyphenyl)acrylonitrile (3bb)



71 mg (Yield = 90%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.91 (s, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 2H). The spectroscopic data are in agreement with the literature.[14]

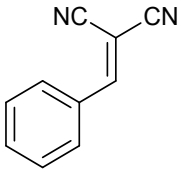
(E)-2-Benzoyl-3-(4-nitrophenyl)acrylonitrile (3bc)



Purified by flash column chromatography (Hexane: EtOAc, 12:1 to 7:1) 69 mg (Yield = 83%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H), 8.14 (s, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.73 (t, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H). The spectroscopic data are in agreement with the literature.[12]

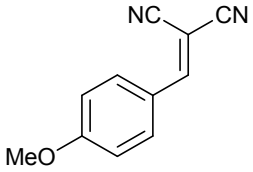
2-Benzylidenmalononitrile (3ca)

[12] J. S. Yadav, B. V. S. Reddy, A. K. Basak, B. Visali, A. Narsaiah and K. Nagaiah, *Eur. J. Org. Chem*., 2004, 546
[13] T. T.Kao, S. E. Syu, Y. W. Jhang, W. Lin, *Org. Lett*. 2010, **12**, 3066
[14] M. A. Kolosov, V. D. Orlov, N. N. Kolos, O. V. Shishkin and R. I. Zubatyuk, *ARKIVOC*, 2007, 187



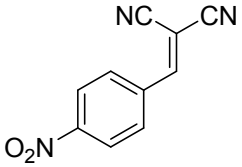
40 mg (Yield = 86%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.4 Hz, 2H), 7.71 (s, 1H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H). The spectroscopic data are in agreement with the literature.[15]

2-(4-Methoxybenzyliden)malononitrile (3cb)



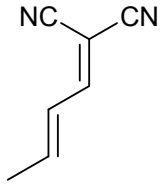
45 mg (Yield = 81%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.58 (s, 1H), 6.94 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H). The spectroscopic data are in agreement with the literature.[14]

2-(4-Nitrobenzyliden)malononitrile (3cc)



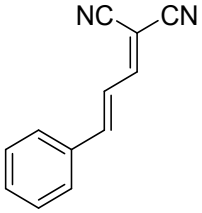
52 mg (Yield = 87%); **^{1}H RMN** (300 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 2H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.83 (s, 1H). The spectroscopic data are in agreement with the literature.[16]

(E)-2-(But-2-enylidene)malononitrile (3cd)



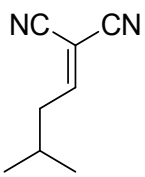
The crude was purified by flash column cromatography (Hexane : EtOAc 8:1 to 6:1). 31 mg (Yield = 88%); **^{1}H RMN:** (300 MHz, Acetone-d_6) δ 7.94 (d, *J* = 11.5 Hz, 1H), 6.94 (m, 1H), 6.68 (m, 1H), 2.80 (d, *J* = 7.1 Hz, 3H). The spectroscopic data are in agreement with literature.[17]

(E)-2-(3-Phenilallyldien)malononitrile (3ce)



45 mg (Yield = 83%). **^{1}H RMN:** 7.50-7.19 (m, 8H). The spectroscopic data are in agreement with the literature.[18]

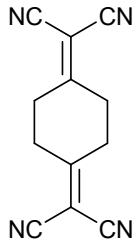
2-(3-Metylbutyliden)malononitrile (3cf)



36 mg (Yield = 89%). **^{1}H RMN** (300 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.9 Hz, 1H), 2.49 (dd, *J* = 7.9 and 6.9 Hz, 2H), 1.93 (m, 1H), 1.00 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.9 (CH), 112.2 (CN), 110.7 (CN), 90.4 (C), 41.5 (CH_2), 28.2 (CH), 22.2 (2 CH_3). **MS** (*TOF MS*): m/z 134 (M^+, 2), 119 (6), 92 (100), 65 (26). **HRMS** (*TOF MS*): calculated for $C_8H_{10}N_2$: 134.0044; found: 134.0042.

2, 2'-(Cyclohexane-1,4-diyliene)dimalononitrile (3cg)

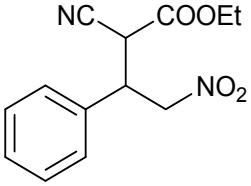
[15] J. Y. Liu, Y.J. Jang, W. W. Lin, J. T. Liu and C. F. Yao, *J. Org. Chem.*, 2003, **68**, 4030
[16] G. Postole, B. Chowdhury, B. Karmakar, K. Pinkib, J. Banerji, and A. Auroux, *J. Catal*. 2010, **269**, 110
[17] G. Krishnamoorthy, S. Schieffer, S. Shevyakov, A. Asato, K. Wong, J. Head and R. S. H. Liu, *Res. Chem. Intermed*. 2004, **30**, 397
[18] M. Zhang, A. Q. Zhang, H. H Chen, J. Chen and H. Y. Chen, *Synth. Commun.* 2006, **36**, 3441



Dark red solid. M.p. = 212-215 ºC. 28 mg (Yield = 68%). **^{1}H RMN** (300 MHz, Acetone-d_6) δ 3.14 (s, 8H). **^{13}C NMR** (75 MHz, Acetone-d_6) δ 181.2 (2C), 112.3 (4CN), 85.2 (2C), 31.6 ($4CH_2$). **MS** (*TOF MS*): m/z 208 (M^+, 30), 181 (24), 154 (18), 143 (100), 114 (13). **HRMS** (*TOF MS*): calculated for $C_{12}H_8N_4$: 208.0749; found: 208.0742.

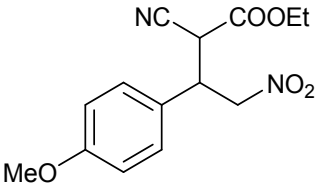
This compound has been synthesized previously in the literature[19], but NMR data had not been described.

Ethyl 2-Cyano-4-nitro-3-phenylbutanoate (4aa)



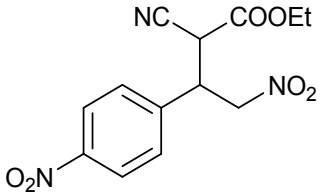
Purified by flash column chromatography (Hexane: EtOAc, 8:1 to 3:1). 31 mg (Yield = 78%). Mixture of diasteromers. **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.40-7.21 (m, 10H), 5.07-4.73 (m, 4H), 4.28-4.05 (m, 7H), 3.92 (d, *J* = 5.7 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). The spectroscopic data are in agreement with the literature.[20]

Ethyl 2-Cyano-3-(4-methoxyphenyl)-4-nitrobutanoate (4ab)



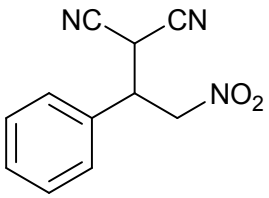
Purified by flash column chromatography (Hexane: EtOAc, 8:1 to 6:1). 32 mg (Yield = 74%). Mixture of diasteromers. **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.27-7.16 (m, 4H), 6.92-6.83 (d, *J* = 8.4 Hz, 4H), 5.04-4.68 (m, 4H), 4.32-3.99 (m, 7H), 3.88 (d, *J* = 5.7 Hz, 1H), 3.78 (s, 6H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). The spectroscopic data are in agreement with the literature.[19]

Ethyl 2-Cyano-4-nitro-3-(4-nitrophenyl)butanoate (4ac)



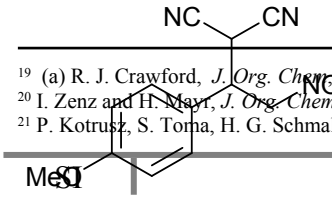
Purified by flash column chromatography (Hexane 6:1 EtOAc). 36 mg (Yield = 79%). Mixture of diasteromers. **^{1}H RMN.** (300 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 4H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H) 5.11-4.81 (m, 4H), 4.46- 4.13 (m, 7H), 3.98 (d, *J* = 5.7 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 163.4 (C), 163.2 (C), 148.5 (C), 148.4 (C), 141.6 (C), 140.7 (C), 129.4 (CH), 128.9 (CH), 124.6 (CH), 124.4 (CH), 113.8 (CN), 113.8 (CN), 75.7 (CH_2), 75.4 (CH_2), 64.1 (CH_2), 63.9 (CH_2), 42.5 (CH), 42.1 (CH), 41.0 (CH), 40.9 (CH), 13.9 (CH_3).

2-(2-Nitrophenylethyl)malononitrile (4ca)



Purified by flash column chromatography (Hexane 8:1 EtOAc). 23 mg (Yield = 72%). **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.42-7.38 (m, 3H), 7.28-7.25 (m, 2H), 4.96-4.78 (m, 2H), 4.37 (d, *J* = 5.9 Hz, 1H), 4.05-3.97 (m, 1H). The spectroscopic data are in agreement with the literature.[21]

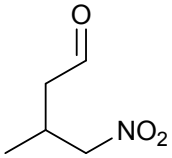
2-((1-(4-Methoxyphenyl)-2-nitroethyl)malononitrile (4cb).



[19] (a) R. J. Crawford, *J. Org. Chem.* 1983, **48**, 1366; (b) D. S. Acker, and R. W. Hertler, *J. Am. Chem. Soc.*, 1962, **84**, 3370
[20] I. Zenz and H. Mayr, *J. Org. Chem.*, 2011, **76**, 9370
[21] P. Kotrusz, S. Toma, H. G. Schmalz and A. Adler, *Eur. J. Org. Chem.,* 2004, 1577

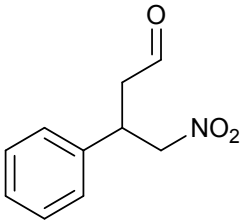
Purified by flash column chromatography (Hexane 8:1 EtOAc). 26 mg (Yield = 70%).**^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.20 - 6.90 (m, 4H), 4.84 (m, 2H), 4.32 (d, *J* = 5.8 Hz, 1H), 3.97 (q, *J* = 6.1 Hz, 1H), 3.76 (s, 3H). The spectroscopic data are in agreement with the literature.[22]

3-(Nitromethyl)butanal (6d)



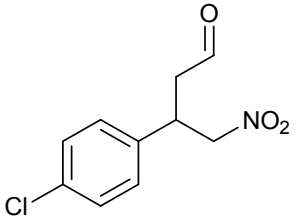
23 mg (Yield = 58%). **^{1}H RMN** (300 MHz, $CDCl_3$) δ 9.75 (s, 1H), 4.55-4.24 (m, 2H), 3.00-2.74 (m, 1H), 2.58 (m, 2H), 1.09 (d, *J* = 6.8 Hz, 3H). The spectroscopic data are in agreement with the literature. [23]

4-Nitro-3-phenylbutanal (6e)



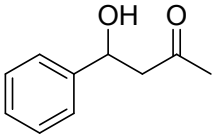
Purified by flash column chromatography (Hexane : EtOAc 10:1 to 4:1). 27 mg (Yield = 59%. Based on recovered starting material) **^{1}H RMN** (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.21 (m, 5H), 4.78-4.22 (m, 2H), 4.00 (q, *J* = 7.2 Hz, 1H), 2.87 (d, *J* = 7.1 Hz, 2H). The spectroscopic data are in agreement with the literature.[24]26

3-(4-Chlorophenyl)-4-nitrobutanal (6h)



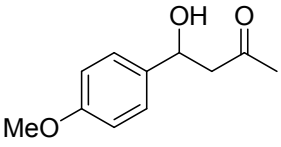
Purified by flash column chromatography (Hexane : EtOAc 20:1 to 4:1). 28 mg (Yield = 59%, based on the recovered starting material). **^{1}H RMN** (300 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 4.63 (m, 2H), 4.17-3.96 (m, 1H), 2.94 (d, *J* = 7.1 Hz, 2H). The spectroscopic data are in agreement with the literature.[25]

4-Phenyl-4-hydroxybutan-2-one (7a)



Purified by flash column chromatography (Hexane : EtOAc 8:1 to 3:1). 19 mg (Yield = 39%). **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.45-7.12 (m, 5H), 5.15 (dd, *J* = 8.8 and 3.6 Hz, 1H), 3.24 (bs, 1H), 2.95-2.73 (m, 2H), 2.19 (s, 3H). The spectroscopic data are in agreement with the literature.[26]

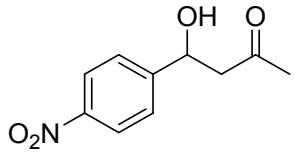
4-(4-Methoxyphenyl)-4-hydroxybutan-2-one (7b)



Purified by flash column chromatography (Hexane : EtOAc 8:1 to 3:1). 4 mg (Yield = 15%. Based on recovered starting material). **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 7.42-6.84 (m, 4H), 5.15 (dd, *J* = 9.0 and 3.5 Hz, 1H), 3.84 (s, 3H), 3.23 (bs, 1H), 2.98-2.78 (m, 2H), 2.23 (s, 3H). The spectroscopic data are in agreement with the literature.[25]

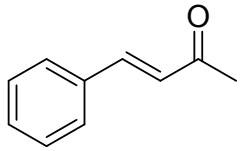
4-(4-Nitrophenil)-4-hydroxybutan-2-one (7c)

[22] G. Srihari and M. M. Murthy, *Synth.Commun*., 2009, **39**, 896
[23] W. Yongcan, L. Pengfei, L. Xinmiao L., Y. Z. Tony and Y. Jinxing, *Chem. Commun.*, 2008, **44**, 1232.
[24] C. Andreu and G. Asensio, *Tetrahedron,* 2011, **67**, 7050
[25] N. Solin, L. Han, S. Che and O. Terasaki, *Catal. Commun*., 2009, **10,** 1386
[26] K. Aelvoet, A. S. Batsanov, A. J. Blatch, C. Grosjean, L.G. F. Patrick, C. A. Smethurst and A. Whiting *Angew. Chem. Int. Ed.,* 2008, **47**, 768



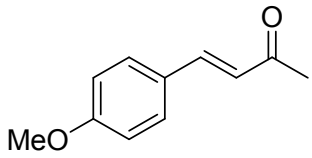
Purified by flash column chromatography (Hexane : EtOAc 10:1 to 1:1). 41.6 mg (Yield = 77%) **^{1}H NMR:** (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H), 5.25 (m, 1H), 3.63 (bs, 1H), 2.85 (m, 2H), 2.21 (s, 3H). The spectroscopic data are in agreement with the literature.[23]

4-Phenyl-3-buten-2-one (8a)



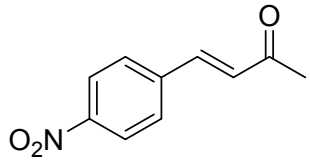
Purified by flash column chromatography (Hexane : EtOAc 8:1 to 3:1). 16 mg (Yield = 37%). **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.50-7.44 (m, 2H), 7.34-7.31 (m, 1H), 7.31-7.25 (m, 3H), 6.64 (d, *J* = 16.3 Hz, 1H), 2.30 (s, 3H). The spectroscopic data are in agreement with the literature.[27]

4-(4-Methoxyphenyl)-3-buten-2-one (8b)



Purified by flash column chromatography (Hexane : EtOAc 8:1 to 3:1). 10.5 mg (Yield = 47%, based on the recovered starting material). **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 7.43-7.36 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 15.5 Hz, 1H), 3.75 (s, 3H), 2.27 (s, 3H). The spectroscopic data are in agreement with the literature.[24]

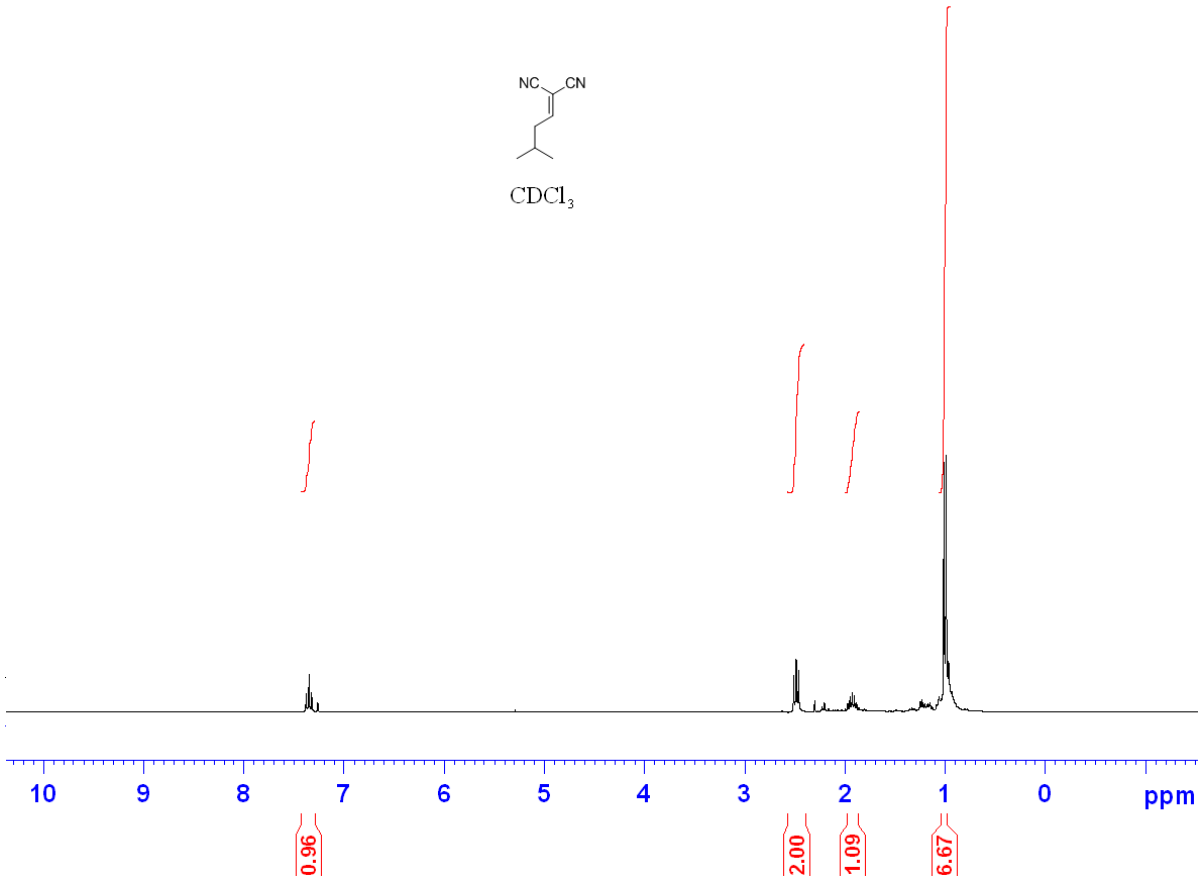
4-(4-Nitrophenyl)-3-buten-2-one (8c)

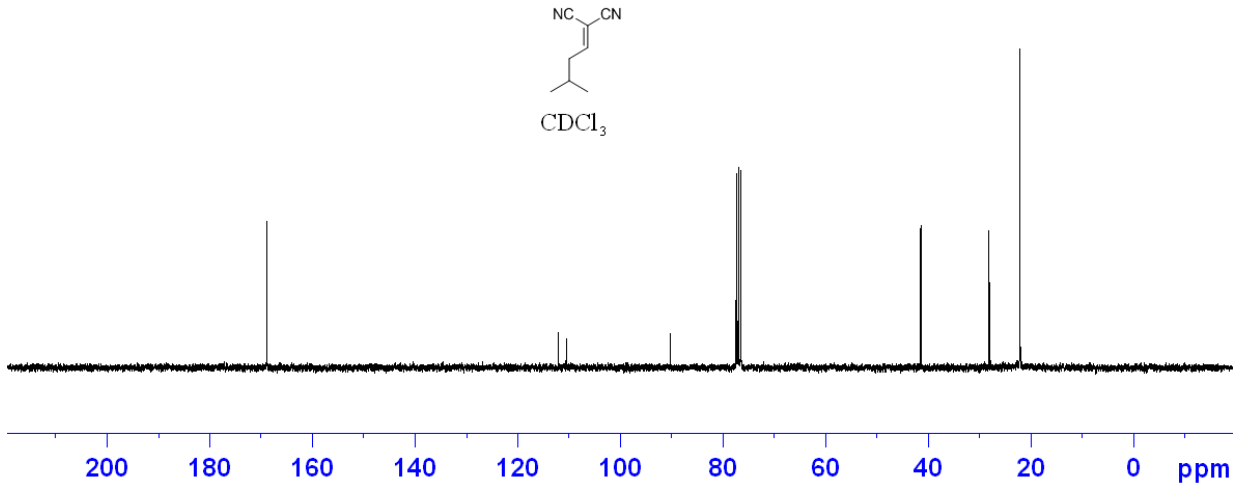


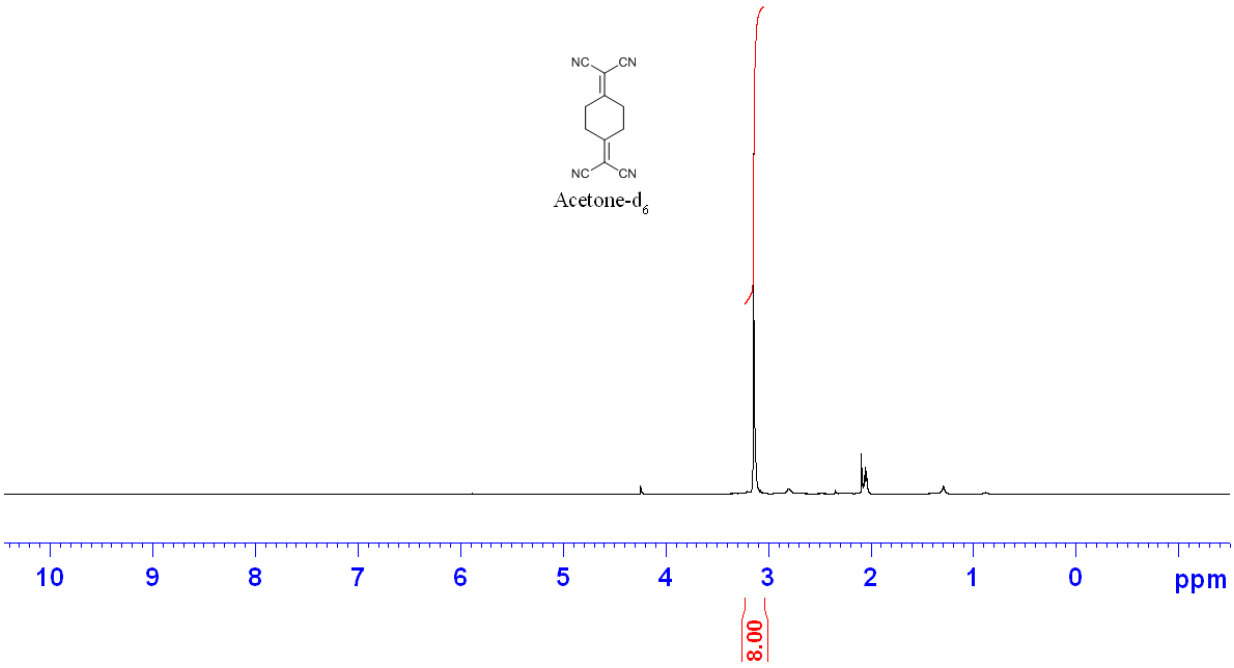
Purified by flash column chromatography (Hexane : EtOAc 10:1 to 1:1). 8.4 mg (Yield = 15%). **^{1}H RMN:** (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 1H), 6.80 (d, *J* = 16.3, 1H), 2.40 (s, 3H). The spectroscopic data are in agreement with the literature.[23]

[27] H. Gotoh, H. Ishikawa and Y. Hayashi, *Org. Lett.*, 2007, **9**, 5307.

10. NMR Spectra of the Products



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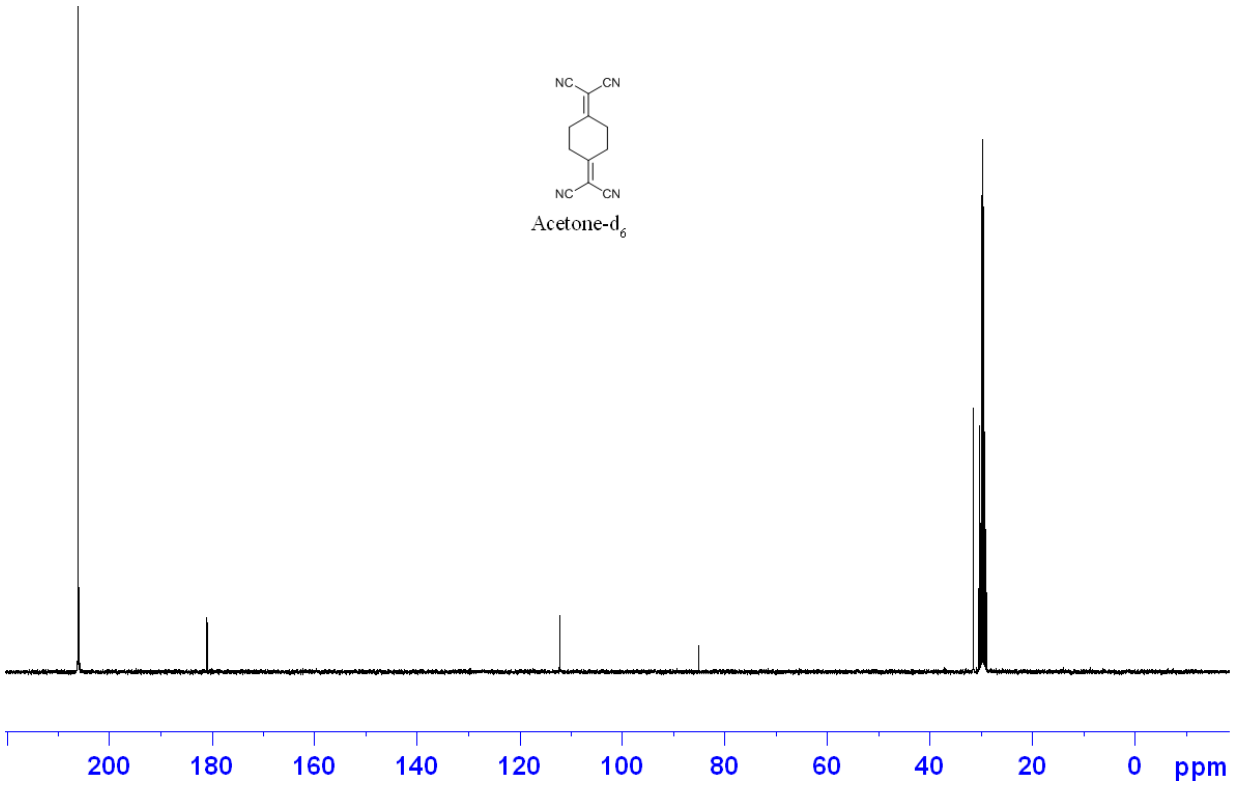
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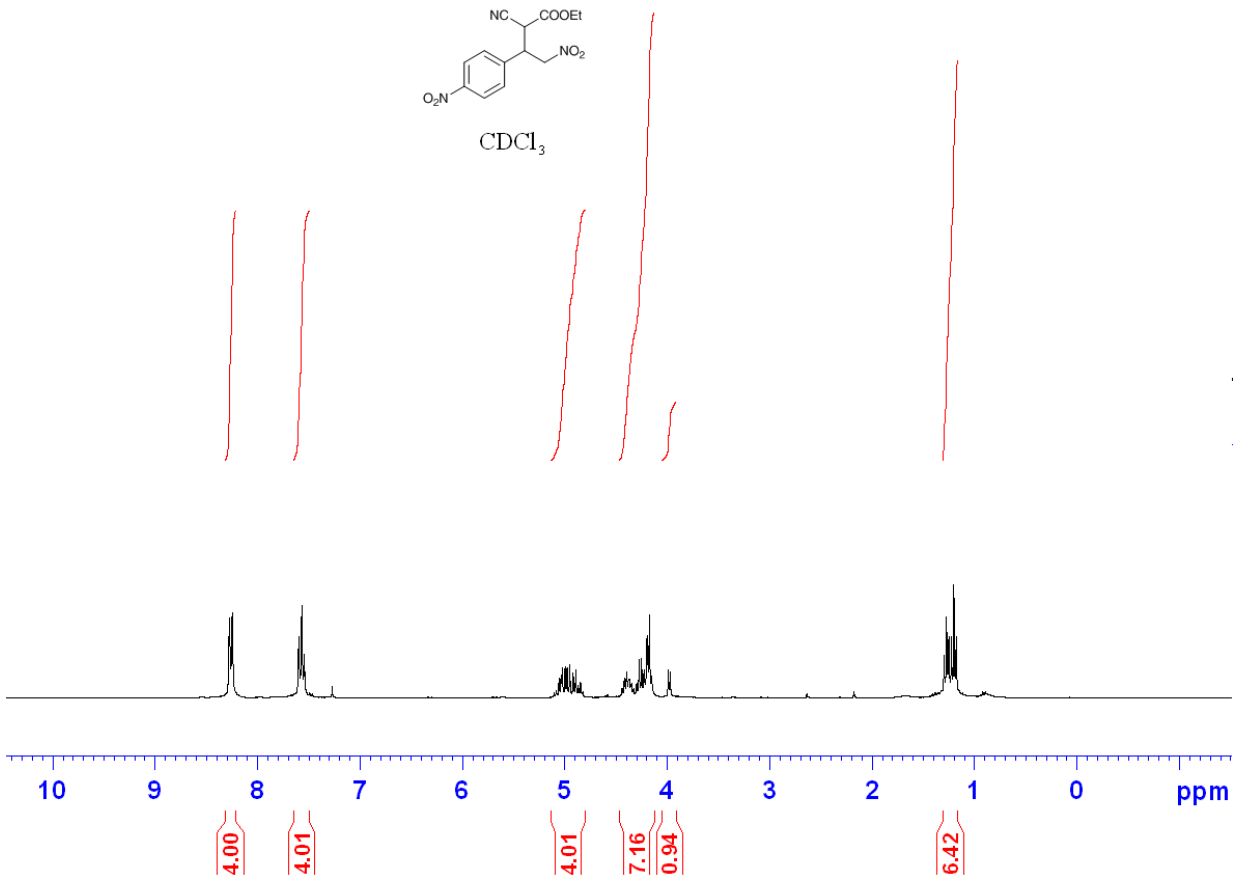
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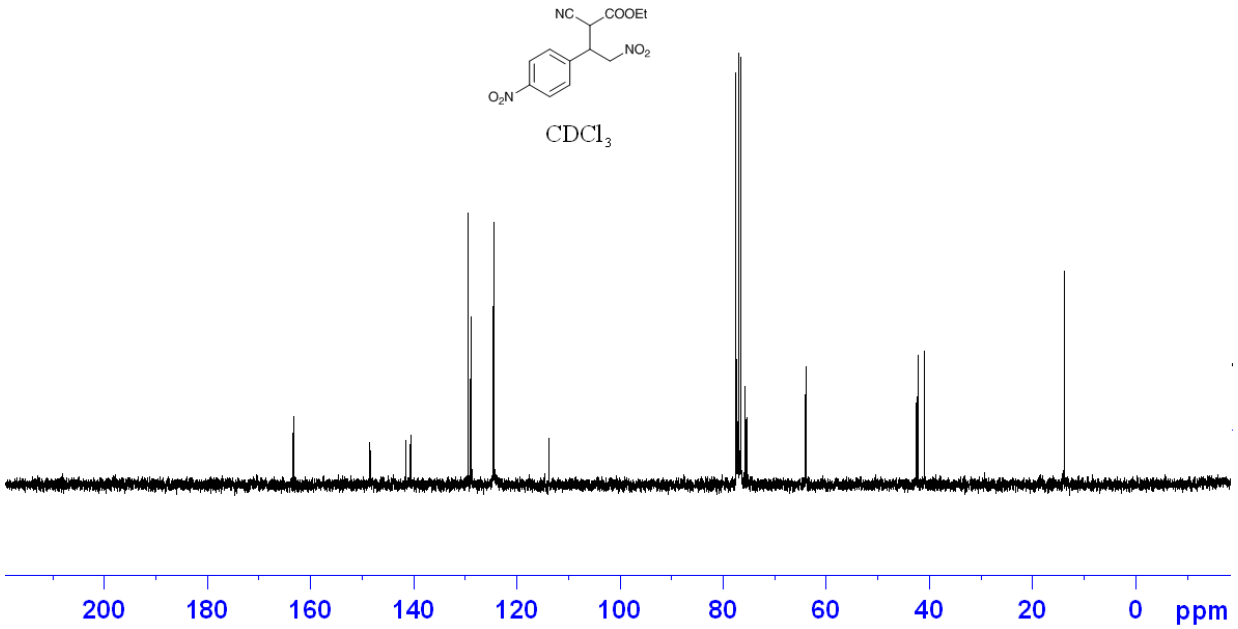
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