

Supporting Information: Graphene Oxide-Supported Oxime Palladacycles as Efficient Catalysts for the Suzuki–Miyaura Cross-Coupling Reaction of Aryl Bromides at Room Temperature under Aqueous Conditions

Melania Gómez-Martínez, Alejandro Baeza and Diego A. Alonso

1. General

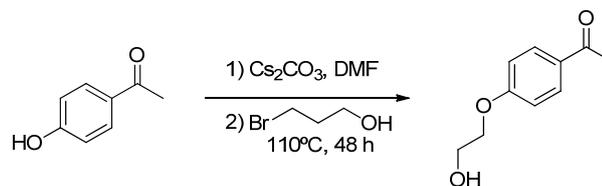
Unless otherwise noted, all commercial reagents and solvents were used without further purification. ¹H-NMR (300 MHz) and ¹³C-NMR (75 MHz) spectra were obtained on a Bruker AC-300, using CDCl₃ as solvent and TMS (0.003%) as reference, unless otherwise stated. Low-resolution mass spectra (MS) were recorded in the electron impact mode (EI, 70 eV, He as carrier phase) using an Agilent 5973 Network Mass Selective Detector spectrometer, being the samples introduced through a GC chromatograph Agilent 6890N equipped with a HP-5MS column [(5%-phenyl)-methylpolysiloxane; length 30 m; ID 0.25 mm; film 0.25 mm]. Analytical TLC was performed on Merck aluminum sheets with silica gel 60 F254. Silica gel 60 (0.04–0.06 mm) was employed for flash chromatography. The conversion of the reactions was determined by GC analysis on an Agilent 6890N Network GC system. Centrifugations were carried out in a Hettich centrifuge (Universal 320, 6000 rpm, 15 minutes). ICP-MS analyses were performed on an Agilent 7700x equipped with HMI (high matrix introduction) and He mode ORS as standard. Elemental analyses were determined with a CHNS elemental micro analyzer with Micro detection system TruSpec LECO.

X-ray Powder Diffraction (XRD) was performed in a Bruker D8-Advance with mirror Goebel (non-planar samples) with high temperature Chamber (up to 900°C), with a generator of x-ray KRISTALLOFLEX K 760-80F (power: 3000W, voltage: 20–60 KV and current: 5-80 mA) with a tube of RX with copper anode. X-ray photoelectron spectroscopy (XPS) was performed in a VG-Microtech Mutilab 3000 equipment equipped with a hemispherical electron analyzer with 9 channeltrons (with energy of passage of (2–200 eV) and an X-ray radiation source with Mg and Al anodes. Transmission electron microscopy (TEM) was performed in JEOL Model JEM-2010. This microscope features an OXFORD X-ray detector model INCA Energy TEM 100 for microanalysis (EDS). The image acquisition camera is of the brand GATAN model ORIUS SC600. It is mounted on the axis with the microscope at the bottom and is integrated into the GATAN Digital Micrograph 1.80.70 image acquisition and processing program for GMS 1.8.0. The supported catalyst were sonicated in a ultrasons P-Selecta (360W).

UV-Vis spectroscopy in solid state was performed in a JASCO V-670 dual-beam UV-Vis / NIR spectrometer covering the wavelength range from 190 to 2700 nm. The equipment has a single monochromator with double netting, one for the UV-Vis region (1200 grooves / mm) and one for the NIR region (300 grooves/mm). The detectors are a photomultiplier tube for the UV-Vis region and a PbS detector for the NIR region. The switching of both the detectors and the networks is automatically effected at a wavelength set by the user between 750 and 900 nm. The sources used are a deuterium lamp (190 to 350 nm) and a halogen lamp (330 to 2700 nm). On the other hand, the UV-Vis spectroscopy of oxime precursor of catalyst **1** was performed in ethanol solution (1.04 mg of oxime in 20 mL of ethanol aproxymately) in a SHIMAZU UV-1603 spectrophotometer covering the wavelength range from 190 to 2700 nm.

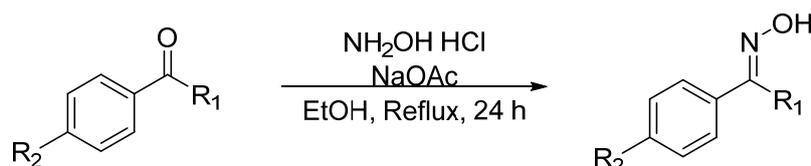
2. Typical Procedure for the Synthesis of Oxime-palladacycles Derivatives

2.1. Typical Procedure for the Synthesis of Ketone Precursor of Palladacycle 3



In a 25 mL round-bottom flask, 4-hydroxyacetophenone (313 mg, 2.30 mmol, 1eq) and cesium carbonate (1500 mg, 4.6 mmol, 2 eq) were added under argon atmosphere. Then, anhydrous DMF (5 mL) was introduced into the reaction flask. The reaction mixture was stirred at rt during 10 minutes and 2-bromoethanol was added. The resulting mixture was heated at 100 °C during 48 h. After this reaction time, the mixture was cooled to rt and 10 mL of H₂O and 10 mL of EtOAc were added. The aqueous layer was extracted with EtOAc (3 × 20 mL). The organic layers were washed with H₂O to completely remove the DMF and the combined organic layers were dried over MgSO₄. Then, the solvent was removed under vacuum. The obtained crude residue was purified by flash chromatography (Silica gel, Hexane/EtOAc: 6/2) to obtain 0.18 g of the desired ketone (45% yield).

2.2. Typical Procedure for the Synthesis of Oxime Derivatives¹



In a 250 mL round-bottom flask, the corresponding ketone (1 eq), hydroxylamine hydrochloride (3 eq) and sodium acetate (3 eq) were suspended in anhydrous ethanol (80 mL for 12.4 mmol of ketone). The reaction mixture was stirred under reflux conditions during 24 h. After this time, the reactions were cooled to rt. Then, saturated NaHCO₃ (8 mmol, 100 mL for 8 mmol of starting material) was added. The aqueous layer was extracted with diethyl ether (3 × 20 mL) and the organic layers were combined, washed with saturated NaHCO₃ solution, brine and dried over MgSO₄. The solvent was removed under vacuum. The corresponding oxime was obtained by recrystallization in ethanol at 5 °C.

3. Synthesis of Supported Oxime Palladacycles

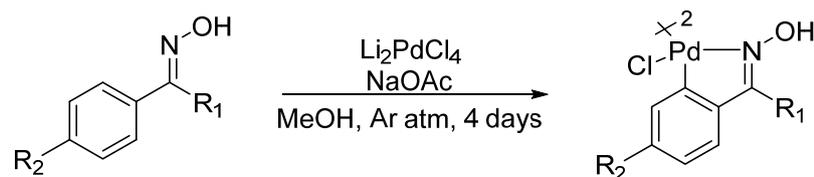
3.1. Typical Procedure for the Preparation of Lithium Tetrachloropalladate (0.5 M in Methanol)

A 0.5 M solution of lithium tetrachloropalladate (II) was prepared by stirring until obtaining a homogeneous solution (3–24 h) a mixture of palladium (II) chloride (1 eq) and lithium chloride (2 eq) in MeOH under Argon atmosphere.

3.2. Typical Procedure for Synthesis of Palladacycles²

¹ Ulbrich, H. K.; Luxenburger, A.; Prech, P.; Eriksson, E.E.; Soehnlein, O.; Rotzius, P.; Lindbom, L.; Dannhardt, G. A Novel Class of Potent Nonglycosidic and Nonpeptidic Pan-Selectin Inhibitors. *J. Med. Chem.* **2006**, *49*, 5988–5999

² Pacheco, M. C.; Alonso, D. A.; Najera, C. Oxime Palladacycles: Stable and Efficient Catalysts for Carbon–Carbon Coupling Reactions. *Org. Lett.* **2000**, *2*, 1823–1826



A MeOH (4.8 mL for 4.61 mmol of oxime derivative) solution of the corresponding oxime (1eq), sodium acetate (NaOAc, 1eq) and Li_2PdCl_4 (1eq, 0.5 M in MeOH) was stirred at room temperature under argon atmosphere during 4 days. Then, water was added to precipitate the corresponding palladium complex and subsequently, the palladacycle was filtered and washed with hexane. Finally, the catalyst was dried under reduced pressure overnight giving the corresponding oxime palladacycles 1-3.

3.3. Characterization of supported oxime palladacycle

Graphene oxide (GO) and reduce graphene oxide (rGO) have been provided by Nanoinnova Technologies S.L. Characterization of these materials can be found at (<http://www.nanoinnova.com/Product>) and it is shown below.

3.3.1. Characterization of graphene oxide (GO)

FTIR Spectroscopy

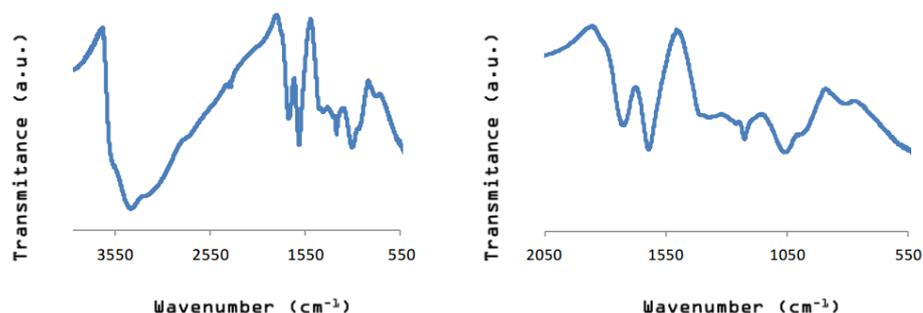


Figure 1. Left: full IR spectrum. Right: magnification between 2000 and 900 cm^{-1} wavenumbers. Assignment (cm^{-1}) 1713 C=O (carbonyl/carboxy); 1611 C=C (aromatics); 1388 C-O (carboxy); 1217 C-O (epoxy); 1043 C-O (alkoxy).

Scanning Electron Microscopy

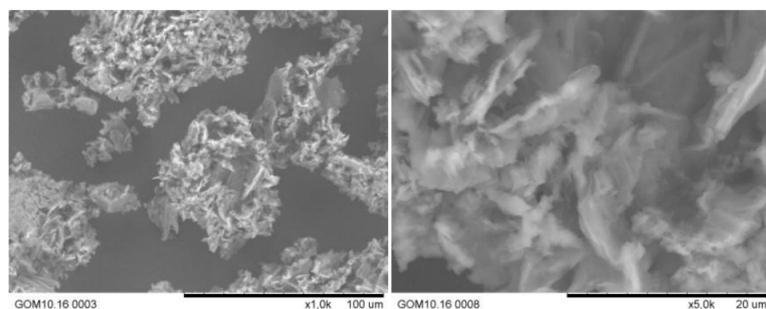


Figure 2. SEM images of GO.

Analysis Elemental

	%C	%H	%N	%S
GO	54.9	2.32	0.04	0.8

% Mn by ICP-OES

The residual amount of Mn in graphene oxide measured by ICP-OES is 0.05%.

X-ray Powder Diffraction (XRD)

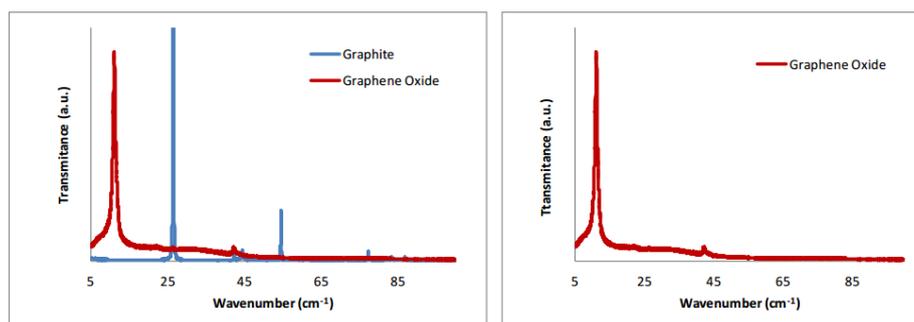


Figure 3. Left: XRD pattern for as-prepared graphene oxide bulk material. Right: comparison between XRD patterns of graphene oxide and graphite starting material evidencing that complete oxidation have occurred

Thermogravimetric analysis (TGA)

Experiment settings:

Temperature scanning rate: 1 C/min

Temperature range 20-800 °C

Purging inert gas: N₂

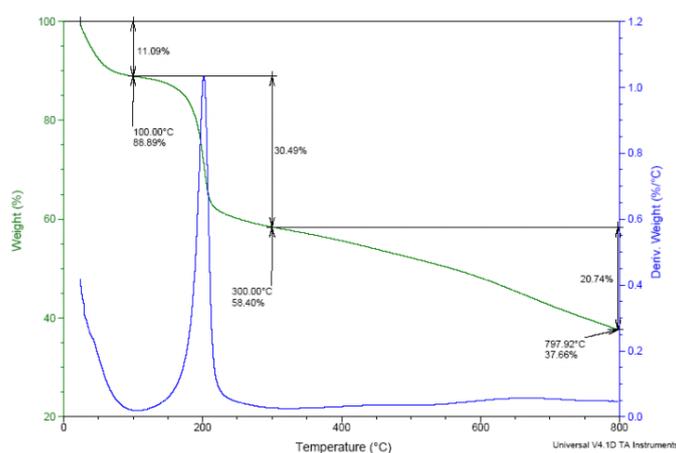


Figure 4. TGA of GO. The first 11.9% mass loss (approx 100 °C) it is due to water solvent molecules absorbed into the GO bulk material, the following 30.49% decrease at 300 °C stands for GO decarboxylation process. Decomposition takes place up to 800 °C

X-ray photoelectron spectroscopy (XPS)

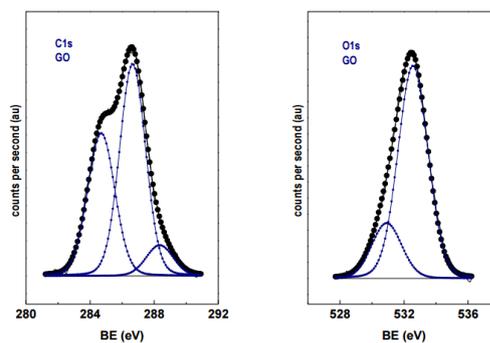


Figure 5. Left: XPS C1s of GO. Right: CPS O1s of GO.

	C1s	O1s	O/C Atomic Ratio
GO	284.8 (38%) 286.6 (54%) 288.3 (8%)	530.9 (21%) 532.5 (79%)	0.655

Atomic-force microscopy (AFM)

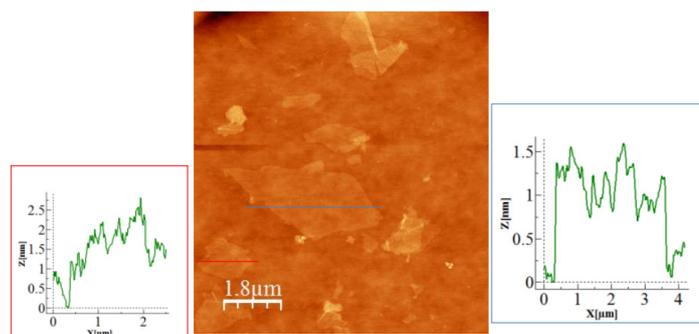


Figure 6. AFM topographic image and magnification of GO deposited onto a silicon wafer. The high profile of the observed GO flakes correlates accordingly calculated values (0.7–1.2 nm)

Solid State ^{13}C NMR

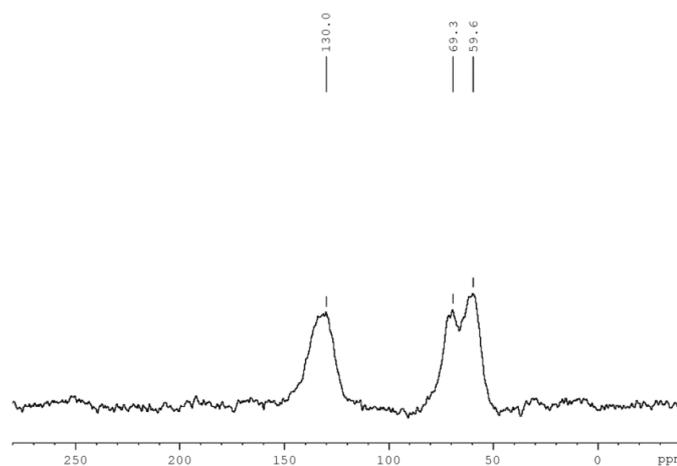


Figure 7. Solid State ^{13}C NMR of GO.

3.3.2. Characterization of reduced graphene oxide (rGO)

IR Spectroscopy

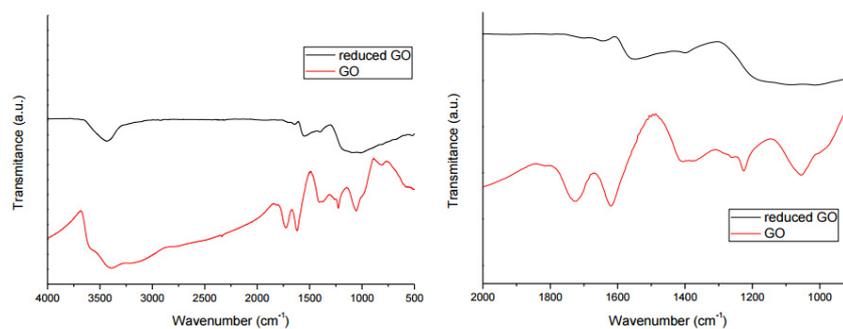


Figure 8. Assignment (cm⁻¹): for GO 1725 C=O (carbonyl/carboxy); 1618 C=C (aromatics); 1407 C-O (carboxy); 1225 C-O (epoxy); 1057 C-O (alkoxy). In comparison peaks due to oxygen functional groups are almost entirely removed in rGO.

Transmission Electron Microscopy (TEM)

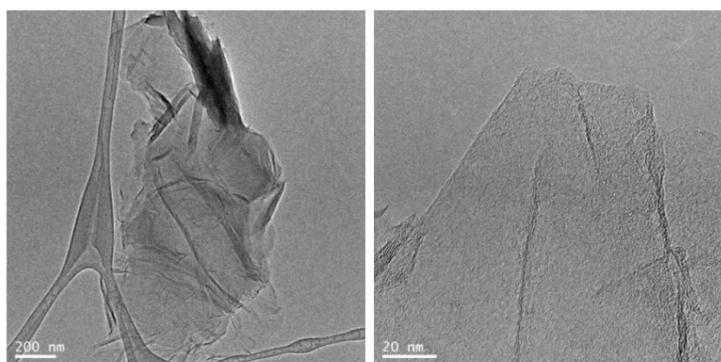


Figure 9. TEM images of rGO.

X-ray Powder Diffraction (XRD)

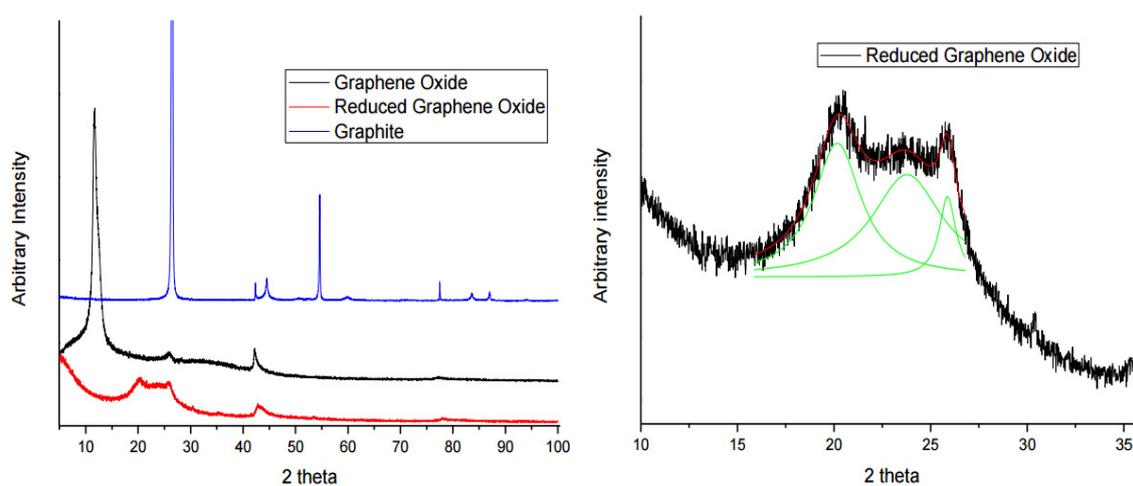


Figure 10. Left, XRD pattern of graphite, GO and rGO. Right, fitting curve for reduced GO (002) peak. In the XRD pattern of GO, the strong and sharp peak at $2\theta = 11.7^\circ$ corresponds to an interlayer distance of 7.6 \AA (d_{002}). rGO shows a broad peak that can be fitted by using a Lorentzian function into three peaks centered at $2\theta = 20.17^\circ$, 23.78° and 25.88° , corresponding to interlayer distances of 4.47, 3.82 and

3.53 Å, respectively. These XRD results are related to the exfoliation and reduction processes of GO and the processes of removing intercalated water molecules and the oxide groups.

Thermogravimetric analysis (TGA)

Experiment settings:

Temperature scanning rate: 1 °C/min

Temperature range 20-800 °C

Purging inert gas: N₂

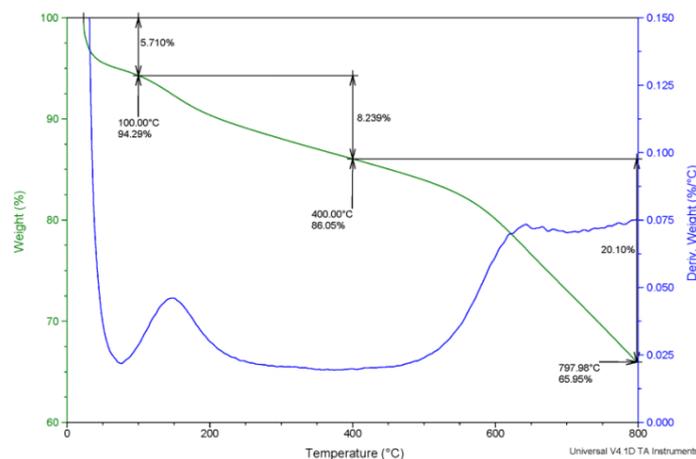


Figure 11. TGA of rGO. The first 5.71% mass loss (approx 100 °C) it is due to water solvent molecules absorbed into the reduced GO bulk material, the following 8.239% decrease (400 °C) stands for elimination of remaining functional groups, further decomposition takes place up to 800°C.

X-ray photoelectron spectroscopy (XPS)

	C1s	O1s	O/C Atomic Ratio
rGO	284.8 (69%)	532.4	0.142
	286.2 (21%)		
	287.8 (8%)		
	289.2 (2%)		

Binding energies (eV) and deconvoluted peaks (%) for C1s and O1s core levels. Assignment (eV): 284.8 C-C 532.4 C-O 286.2 C-O 287.8 C=O 289.2 C(O)O.

UV-VIS

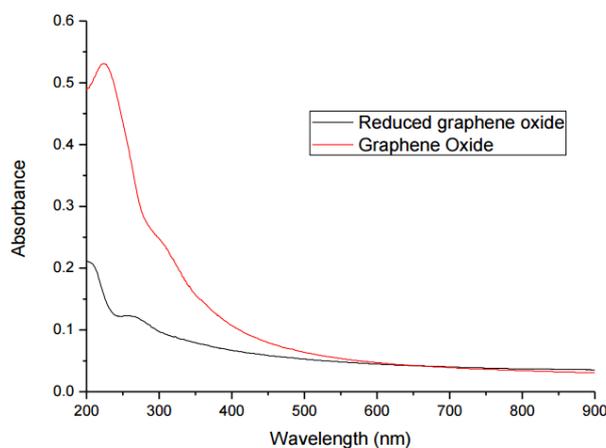


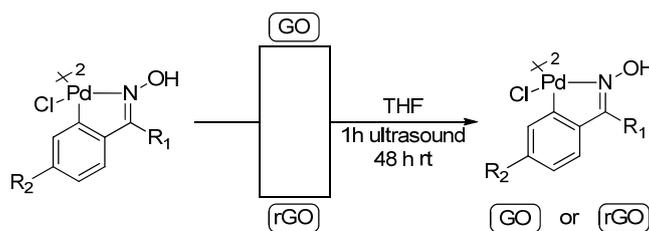
Figure 12. The UV-VIS spectra of GO exhibits a maximum absorption peak at about 223 nm, corresponding to π - π^* transition of aromatic C-C bonds. The absorption peak for reduced GO had

red shifted to 270 nm. This phenomenon of red shift has been used as a monitoring tool for the reduction of GO.

Elemental Analysis

	%C	%H	%N
rGO	76.38	1.44	3.72

3.4. Synthesis of supported palladacycles on graphene derivatives



Supported Catalyst	%Pd ^a
1-GO	THF → 2%
	H ₂ O → 1.35%
2-GO	2.72%
3-GO	2.98%
5-GO	3.22%
1-rGO	0.035%

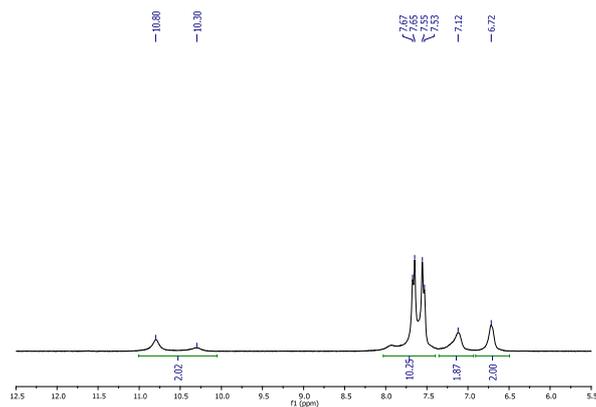
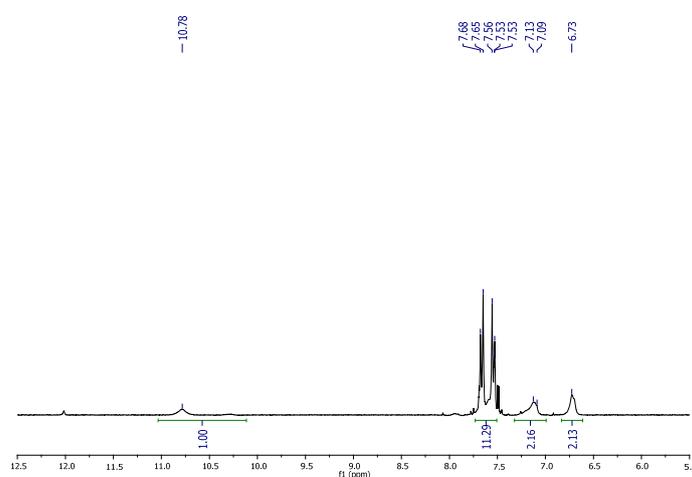
^a Palladium content determined by ICP-OES

3.4.1. Typical Procedure for the synthesis of supported palladacycles

A 10 mL glass vessel was charged with GO or rGO (200 mg) and the corresponding oxime palladacycle (**1**: 45.89 mg; **2**: 32.93 mg; **3**: 37.87 mg, **5**: 52.86 mg) Then, anhydrous THF (4 mL) was added and the reaction mixture was sonicated during 1h. Afterwards, the reaction was stirred at room temperature during 48 h. After this time, the catalyst was submitted to four washing (THF, 10 mL)-centrifugation (6000 rpm, 15 minutes) cycles, being the solvent eliminated after each cycle with a syringe equipped with a 4 mm/0.2 μm PTFE syringe filter. The residual solvent was completely removed under reduced pressure affording the Pd complex supported on graphene derivatives **1-GO**, **2-GO**, **3-GO**, **5-GO** and **1-rGO**. The amount of palladium was determined by ICP-OES.

3.4.2. Stability of oxime palladacycle 1

After the synthesis of supported oxime palladacycle **1-GO**, the eluted palladacycle was analyzed by ¹HNMR to study the stability of the oxime palladacycle. As seen in figures 13 and 14, no significant structural changes were observed in **1** confirming the stability of the complex.

Figure 13. ¹H NMR of 1 before supported step.Figure 14. ¹H NMR of washing/centrifugation solvent after synthesis of 1-GO.

3.4.3. XPS analysis of supported and non supported palladacycle^{3,4,5,6}

XPS analysis of 1

³ Singh, G.; botcha, V. C.; Sutar, D. S.; Talwar, S. S.; Srinivasa, R. S.; Major, S. S. Graphite mediated reduction of graphene oxide monolayer sheets. *Carbon* **2015**, *95*, 843-851

⁴ Yu, B.; Wang, X.; Qian, X.; Xing, W.; Yang, H.; Ma, L.; Lin, Y.; Jiang, S.; Song, L.; Hu, Y.; Lo, S. Functionalized graphene oxide/phosphoramidate oligomer hybrids flame retardant prepared via in situ polymerization for improving the fire safety of polypropylene. *RSC Adv.*, **2014**, *4*, 31782-31794

⁵ Lin, Y.; Pan, X.; Qi, W.; Zhang, B.; Su, D. S. Nitrogen-doped onion-like carbon: a novel and efficient metal-free catalyst for epoxidation reaction. *J. Mater. Chem. A*. **2014**, *2*, 12475-12483

⁶ Fath, R. H.; Hoseini, S. J. Covalently cyclopalladium(II) complex/reduced-graphene oxide as the effective catalyst for the Suzuki–Miyaura reaction at room temperature. *J. Organomet. Chem.* **2017**, *828*, 16-23

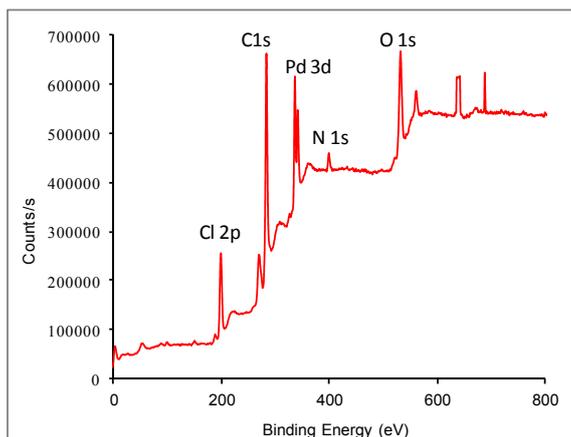
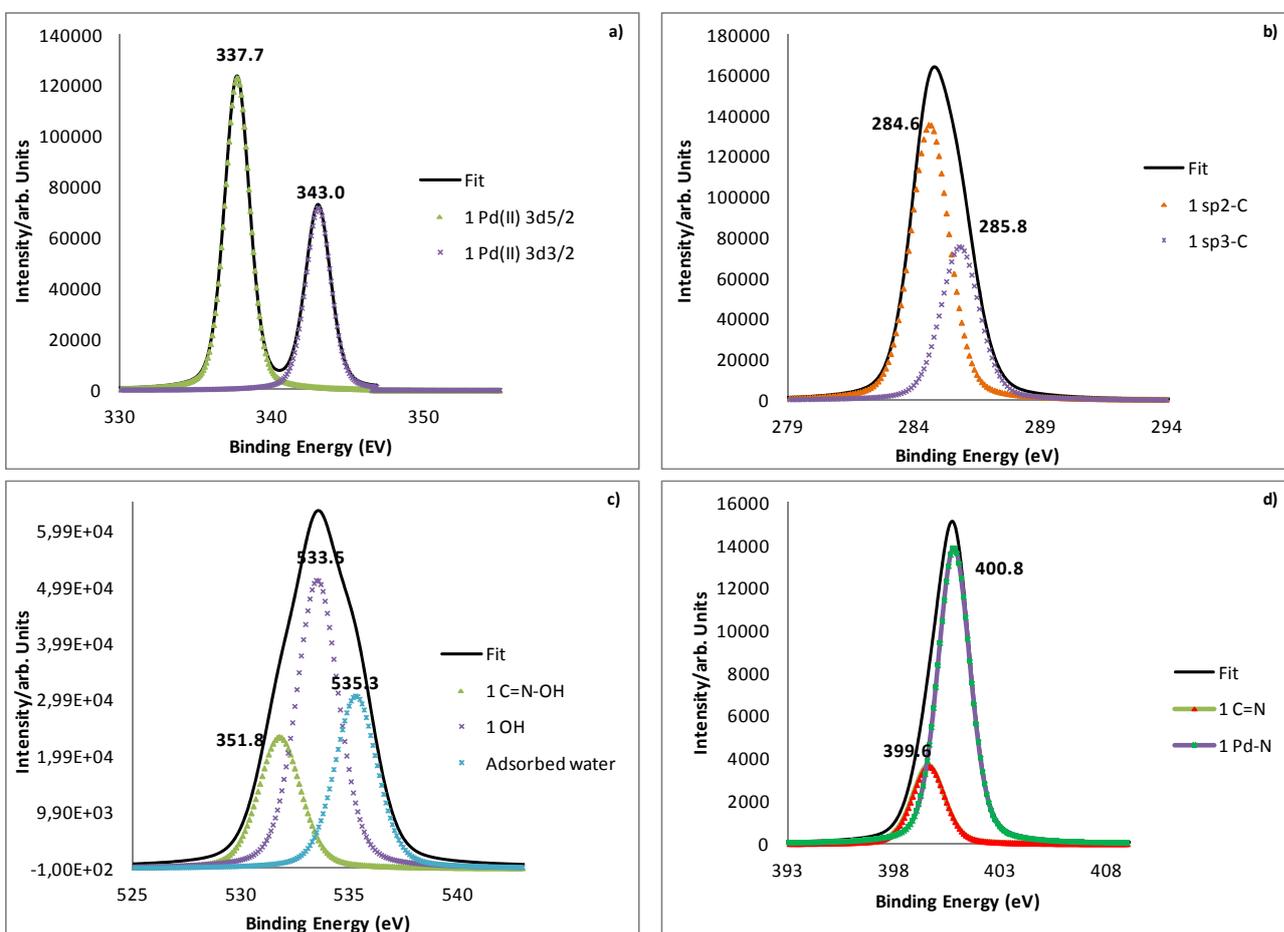


Figure 15. XPS full spectra of 1.



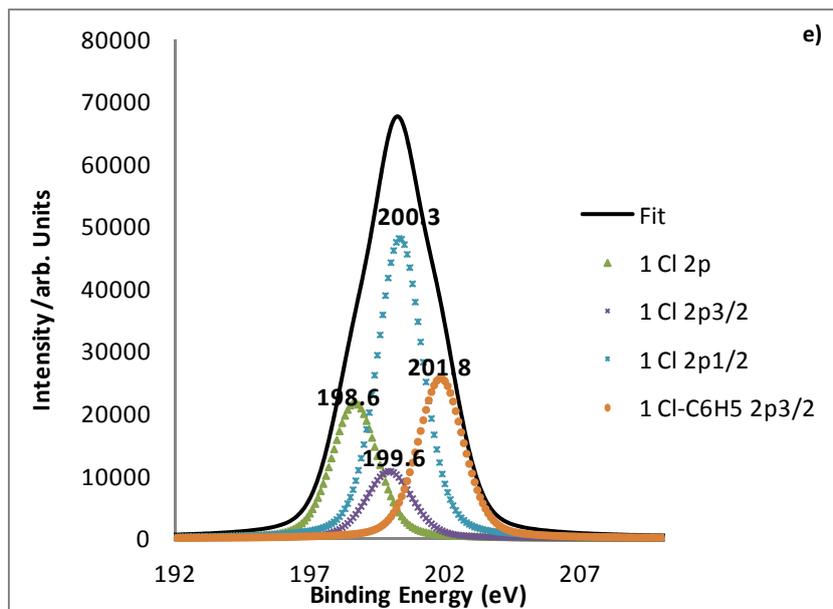


Figure 16. XPS spectra of 1: (a) Pd 3d; (b) O 1s; (c) C 1s; (d) N 1s; (e) Cl 2p and deconvoluted peaks (%) for Pd3d, O1s, C1s, N1s and Cl2p core levels.

XPS analysis of 1-GO

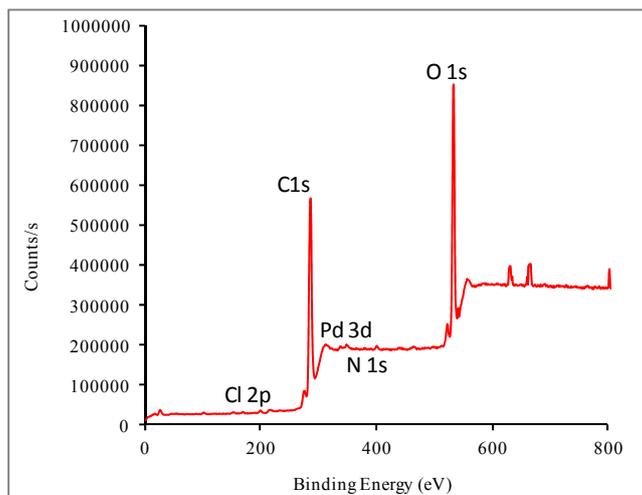


Figure 17. XPS full spectra of 1-GO.

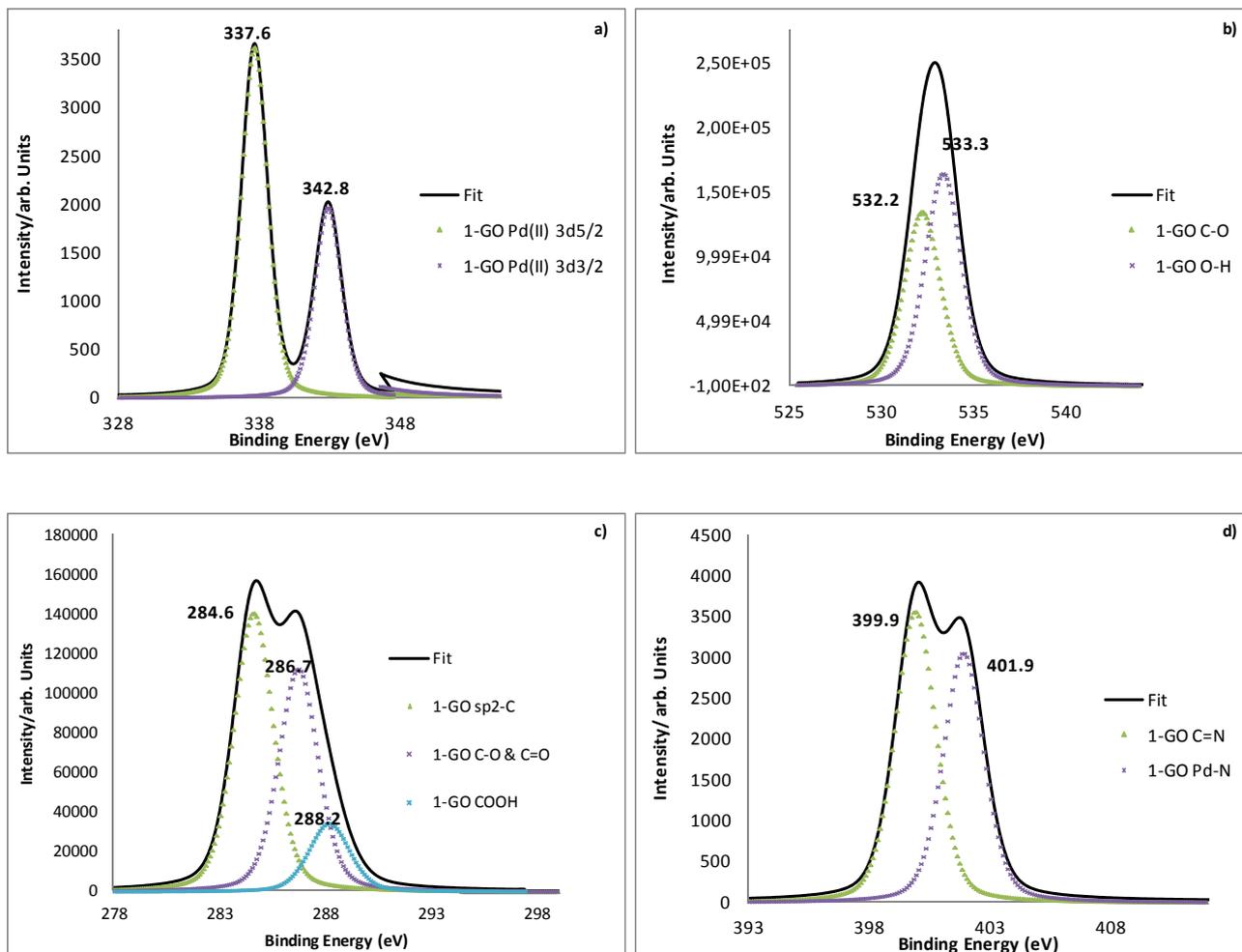


Figure 18. XPS spectra of 1-GO: (a) Pd 3d; (b) O 1s; (c) C 1s; (d) N 1s and deconvoluted peaks (%) for Pd3d, O1s, C1s and N1s core levels.

XPS analysis of 2

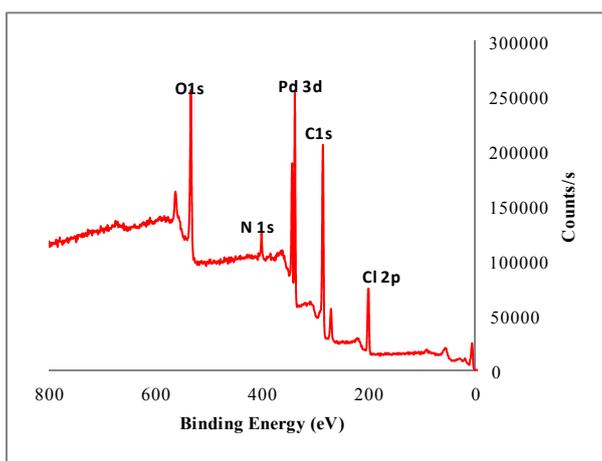


Figure 19. XPS full spectra of 2.

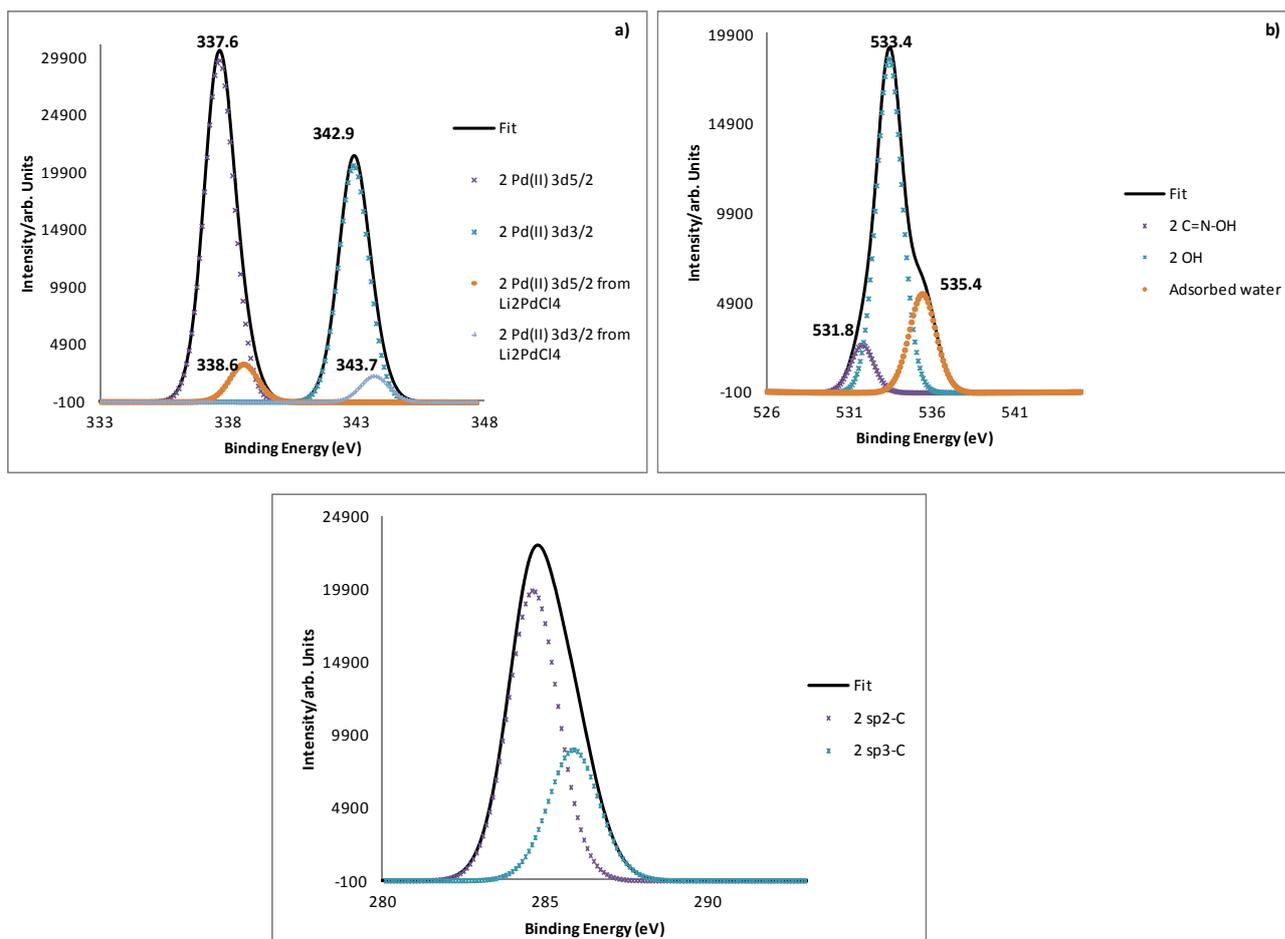


Figure 20. XPS spectra of 2: (a) Pd 3d; (b) O 1s; (c) C 1s; (d) N 1s and deconvoluted peaks (%) for Pd3d, O1s, C1s and N1s core levels.

XPS analysis of 2-GO

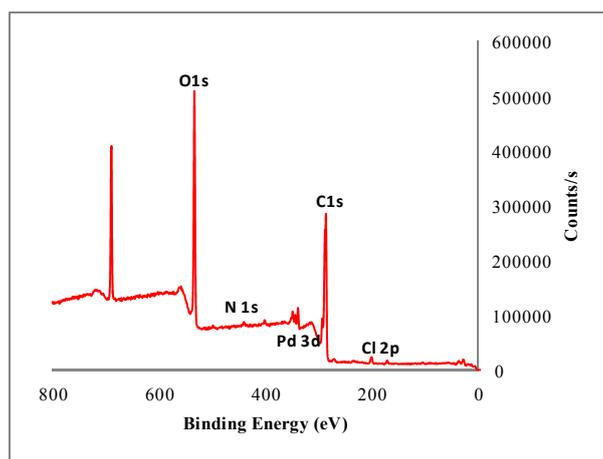


Figure 21. XPS full spectra of 2-GO.

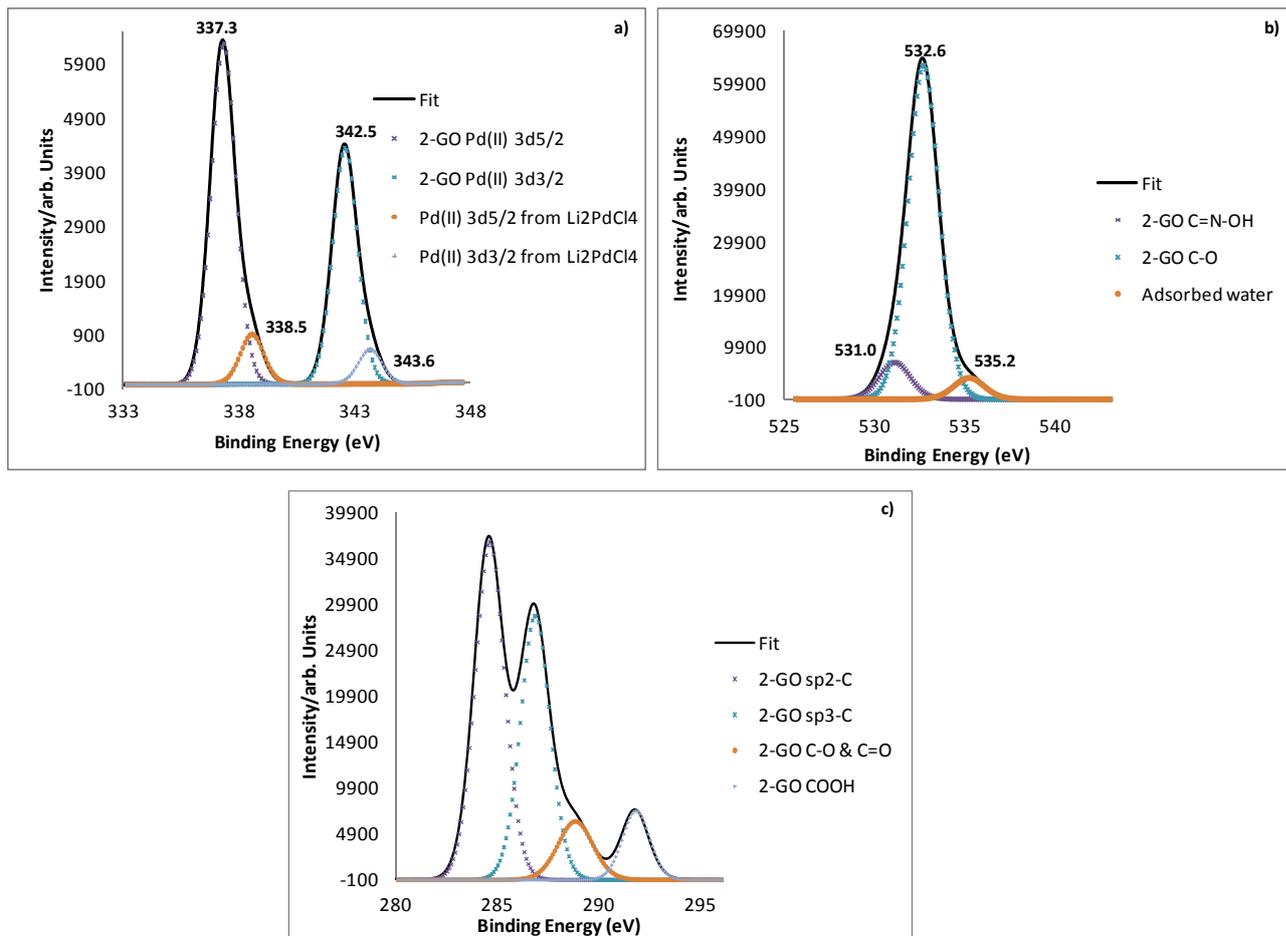


Figure 22. XPS spectra of 2-GO: (a) Pd 3d; (b) O 1s; (c) C 1s and deconvoluted peaks (%) for Pd3d, O1s and C1s core levels.

XPS analysis of 3

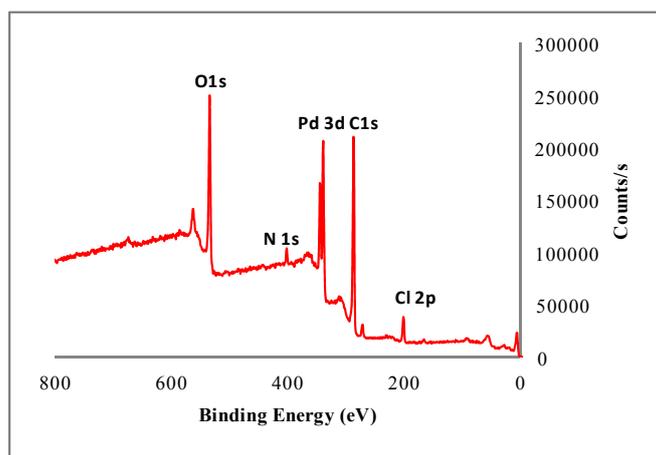


Figure 23. XPS full spectra of 3.

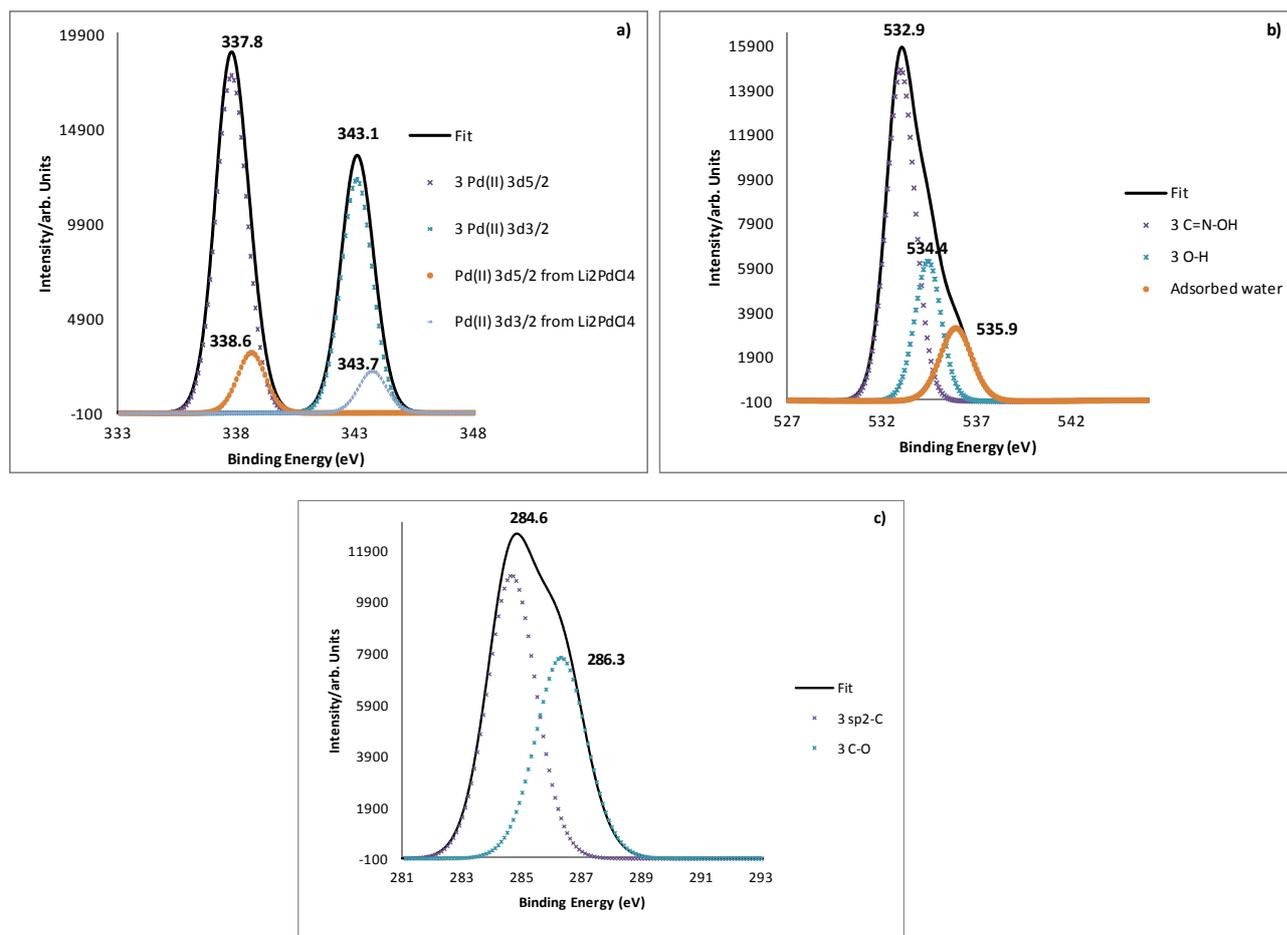


Figure 24. XPS spectra of 3: (a) Pd 3d; (b) O 1s; (c) C 1s and deconvoluted peaks (%) for Pd3d, O1s and C1s core levels.

XPS analysis of 3-GO

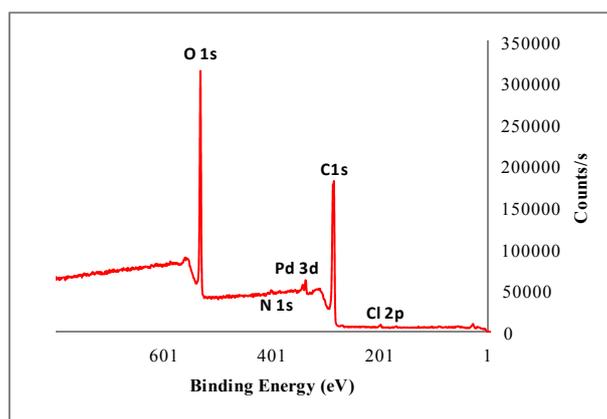


Figure 25. XPS full spectra of 3-GO.

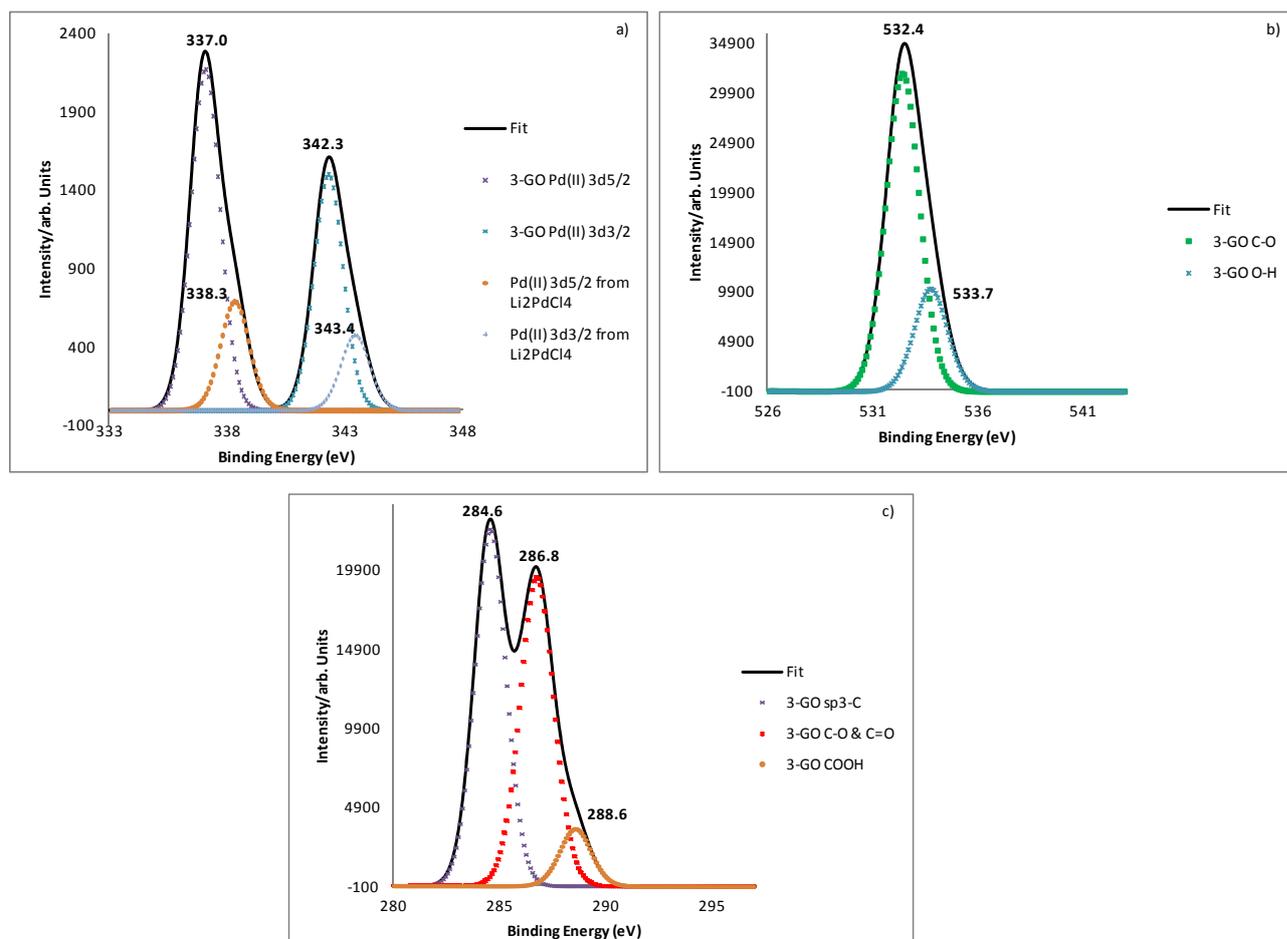


Figure 26. XPS spectra of 3-GO: (a) Pd 3d; (b) O 1s; (c) C 1s and deconvoluted peaks (%) for Pd3d, O1s and C1s core levels.

XPS analysis of Li₂PdCl₄

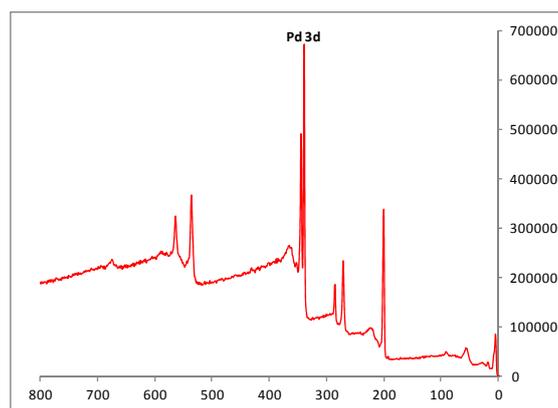


Figure 27. XPS full spectra of Li₂PdCl₄.

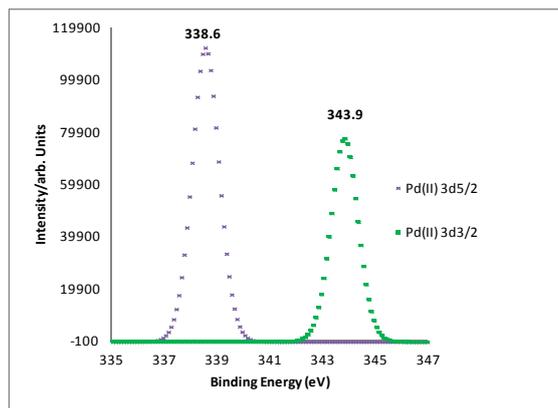
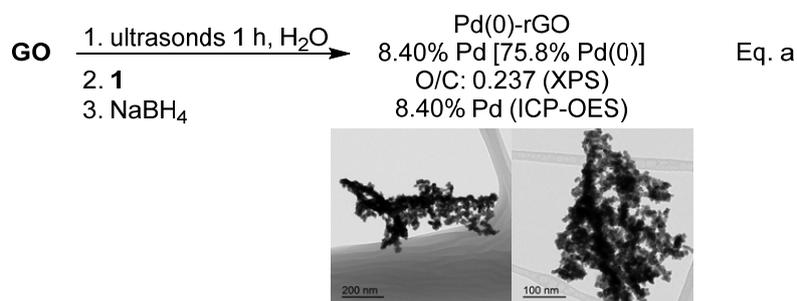


Figure 28. XPS spectra of Li_2PdCl_4 : Pd 3d and deconvoluted peaks (%) for Pd3d core levels

3.4.4. Typical procedure for the reduction of supported catalyst 1-GO

Method a



A 10 mL glass vessel was charged with GO (100 mg). Then, H_2O (100 mL) was added and the reaction mixture was sonicated until was observed (1-2 h). Afterwards, the corresponding oxime palladacycle **1** (38.24 mg) and NaBH_4 (215 μL , 150 mM) were added and the reaction mixture was stirred during 2 h at room temperature. Then, the catalyst was washed with water (3x20 mL) and the supernatant was separated by centrifugation (4500 rpm, 15 min). The properties of the catalyst were analyzed by XPS and ICP-MS.

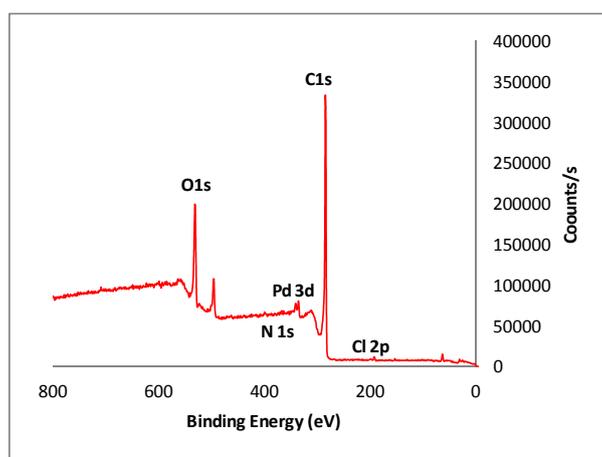


Figure 29. XPS full spectra of the reduction of **1-GO** by method A.

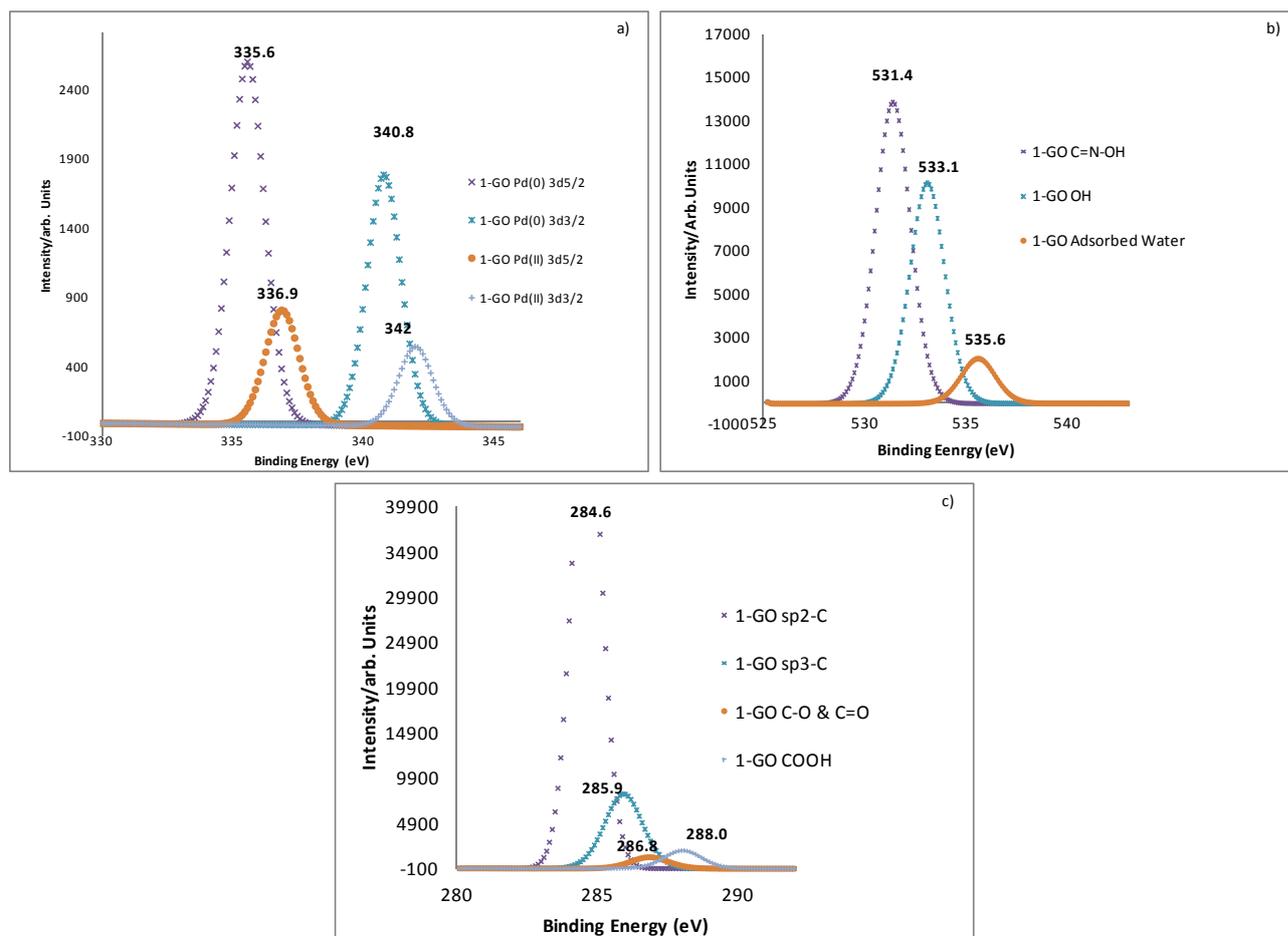
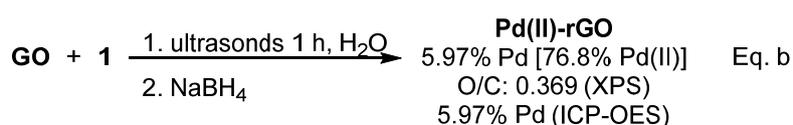


Figure 30. XPS spectra of reduction of 1-GO by method a: (a) Pd 3d; (b) O 1s; (c) C 1s and deconvoluted peaks (%) for Pd3d, O1s and C1s core levels

3.4.4.2. Method b



A 10 mL glass vessel was charged with GO (100 mg) and the corresponding oxime palladacycle **1** (38.24 mg). Then, H₂O (100 mL) was added and the reaction mixture was sonicated until a homogeneous solution was observed (1–2 h). Afterwards, NaBH₄ (215 μL, 150 mM) was added and the reaction mixture was stirred during 2 h at room temperature. Then, the catalyst was washed with water (3 × 20 mL) and the supernatant was separated by centrifugation (4500 rpm, 15 min). The properties of the catalyst were analyzed by XPS and ICP-MS.

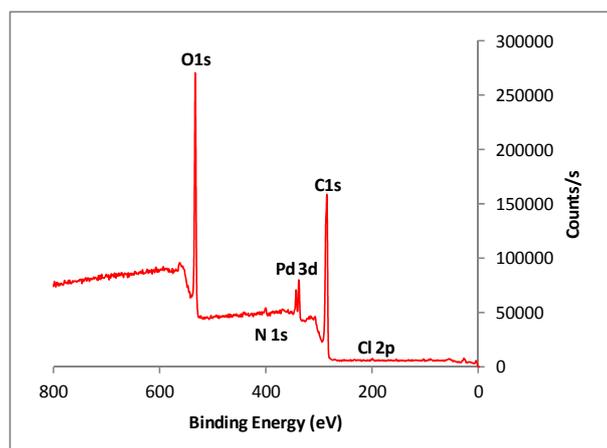


Figure 31. XPS full spectra of the reduction of 1-GO by method B

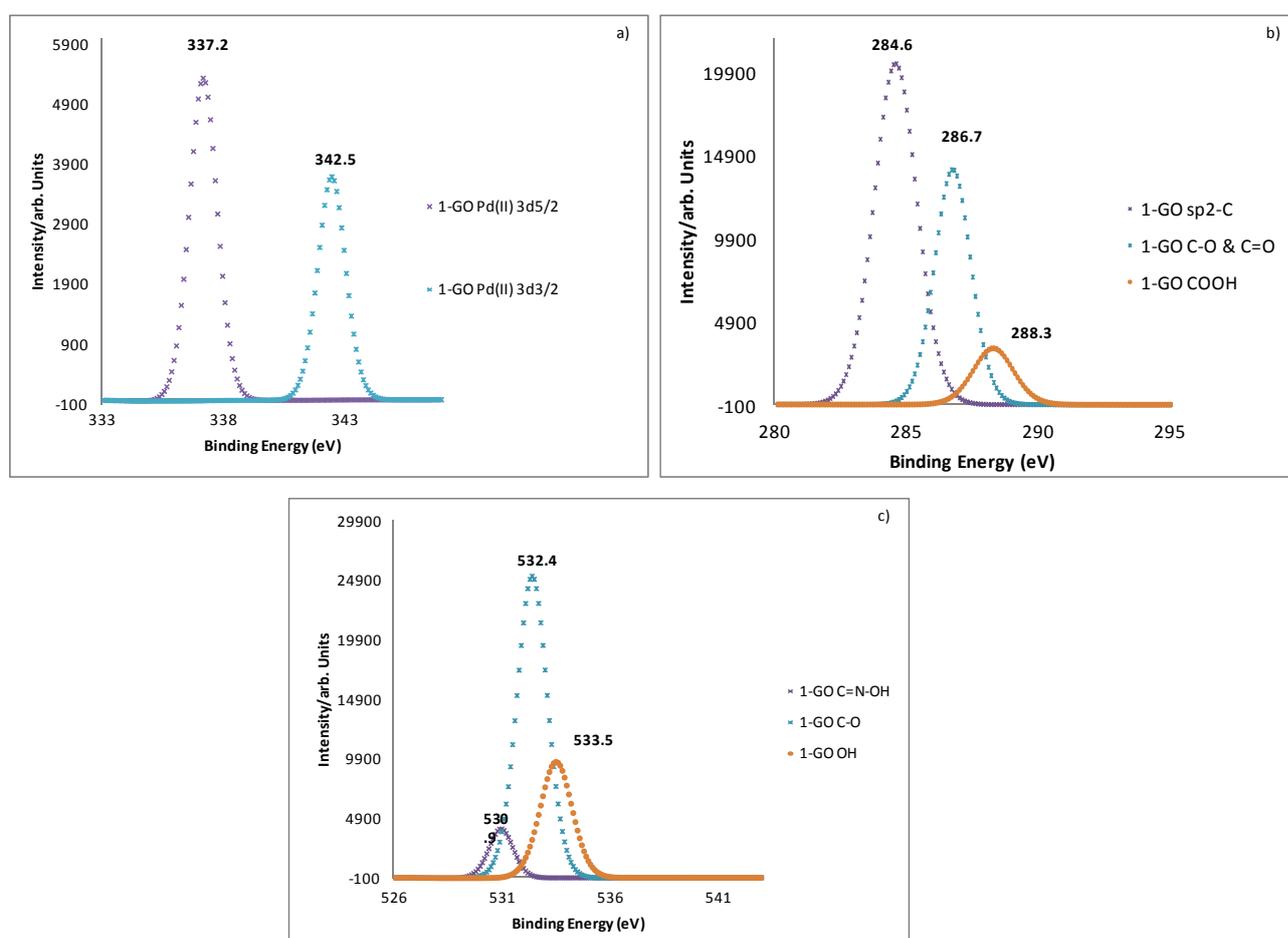
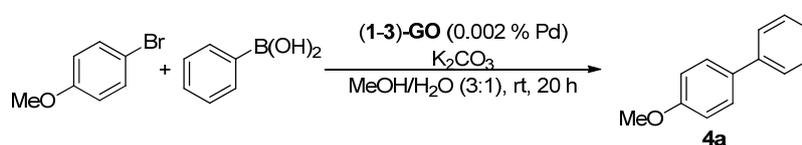


Figure 32. XPS spectra of reduction of 1-GO by method b: (a) Pd 3d; (b) O 1s; (c) C 1s and deconvoluted peaks (%) for Pd3d, O1s and C1s core levels.

4. Typical procedure for the Suzuki-Miyaura reaction catalyzed by palladacycles supported on graphene derivatives



A 10 mL glass vessel was charged with the corresponding supported palladacycle (0.002 mol% Pd, 1-GO: 0.198 mg, 2-GO: 0.098 mg, 3-GO: 0.089 mg,), 4-bromoanisole (156.5 μ L, 1.25 mmol, 1 eq), phenylboronic acid (190.2 mg, 1.56 mmol, 1.25 eq), K_2CO_3 (345.5 mg, 2.5 mmol, 2 eq) and MeOH/ H_2O : 3/1 (3 mL). The vessel was sealed with a pressure cap and the mixture was stirred at room temperature during 20 h. Then, H_2O (5 mL) and EtOAc (5 mL) were added and the liquid mixture was filtered with cotton and extracted with EtOAc (3×10 mL). The organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash chromatography (Silica gel, Hexane/EtOAc: 95/5).

5. Recovery of the catalyst in the Suzuki-Miyaura reaction catalyzed by palladacycles supported on graphene derivatives

5.1. Typical Procedure for the recovery of the catalyst

Once the reaction was finished, the mixture was suspended and stirred during 15 min in a 10 mL mixture of EtOAc/ H_2O : 1/1. Then, this mixture was centrifuged (6000 rpm, 20 minutes) and the solvent was eliminated using a syringe equipped with 4 mm/0.2 μ m PTFE syringe filter. The washing/centrifugation sequence was repeated four additional times until no product was detected in the liquid phase by thin layer chromatography. The residual solvent was completely removed under reduced pressure affording the supported palladacycle catalyst which was directly used in the same tube with fresh reagents for the next run. This procedure was repeated for every cycle and the conversion of the reaction was determined by GC using decane as internal standard.

Run	1	2	3	4	5
Yield (%)	99	99	61	65	16

5.2. ICP analysis of the solution after 5th run

ICP analysis was performed to determine the palladium content on the solution after 5th cycle, giving 66.78 ppb (0.16 % of Palladium).

5.3. XPS analysis of recovery of catalyst 1-GO

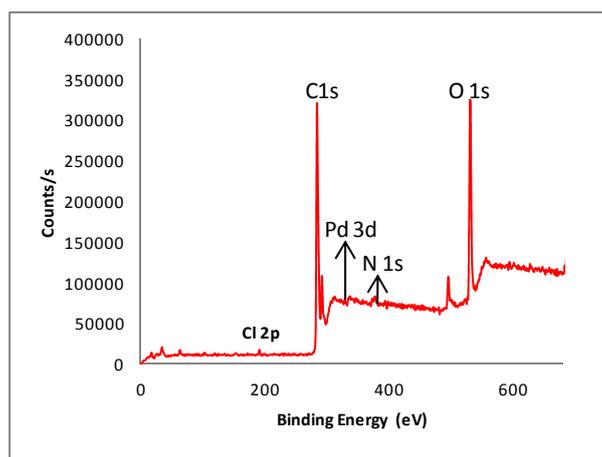


Figure 33. XPS full spectra of 1-GO 5th run

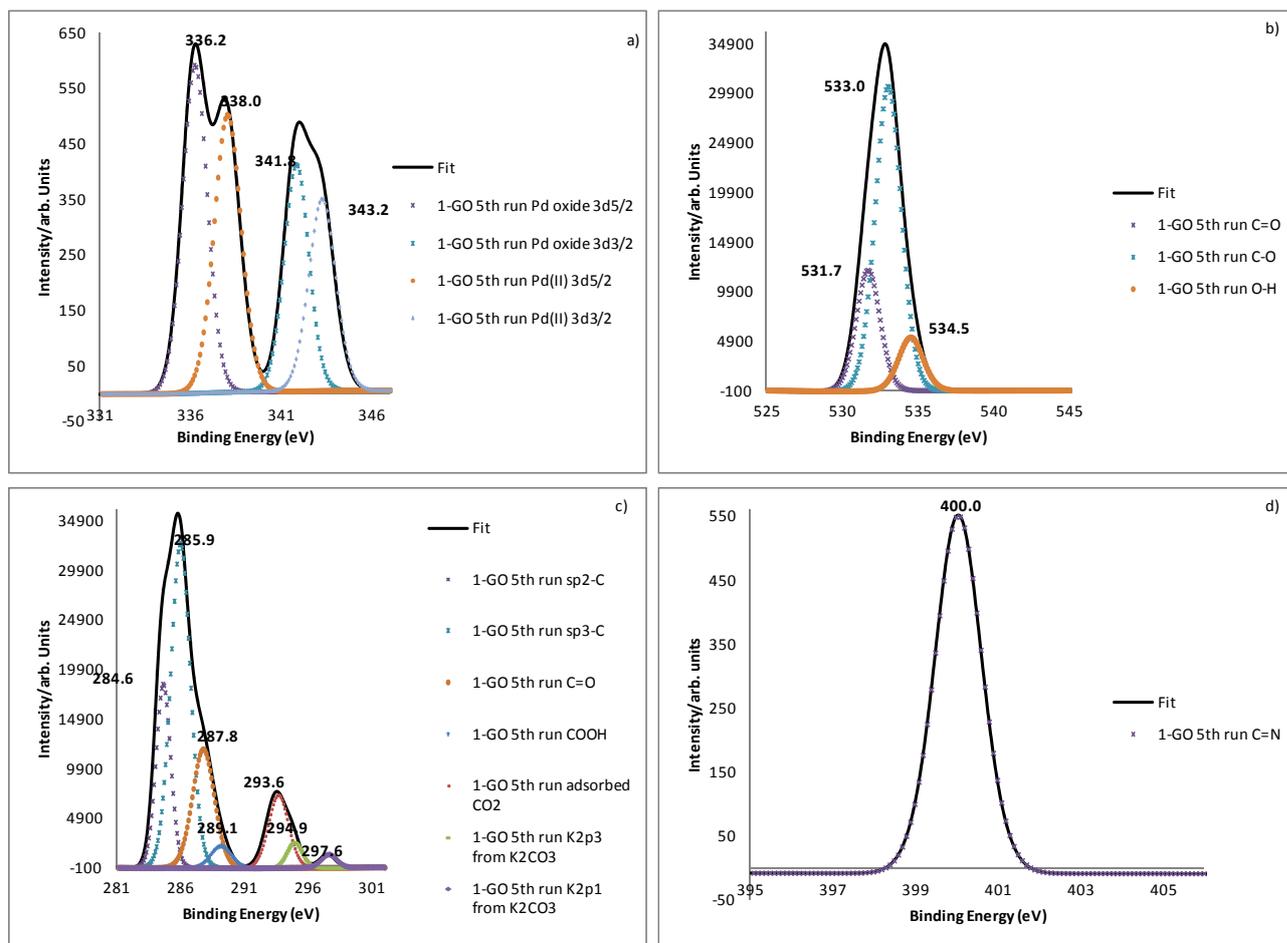
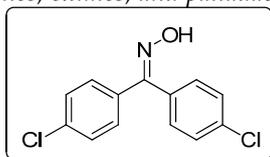


Figure 34. XPS spectra of 1-GO 5th run: (a) Pd 3d; (b) O 1s; (c) C 1s; (d) N 1s and deconvoluted peaks (%) for Pd3d, O1s, C1s and N1s core levels

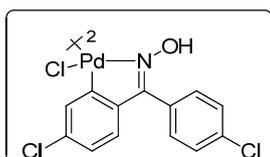
6. Physical and spectroscopic data

6.1. Physical and spectroscopic data of ketones, oximes, and palladacycles



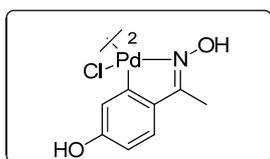
Bis(4-chlorophenyl)methanone oxime.1 White solid, Yield 99%

^1H NMR (300 MHz, DMSO- d_6) δ 11.63 (s, 1H), 7.56 – 7.49 (m, 2H), 7.47 – 7.26 (m, 6H).



Bis(4-chlorophenyl)methanone oxime palladacycle (1).² Yellow solid. Yield 47%. Pd content by ICP-OES: 2%

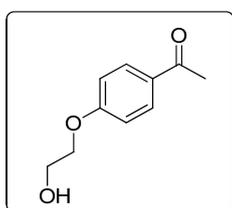
^1H NMR (300 MHz, DMSO- d_6) δ 10.97 – 10.18 (m, 2H), 7.76 – 7.46 (m, 10H), 7.12 (s, 2H), 6.72 (s, 2H).



(E)-1-(4-hydroxyphenyl)ethan-1-one oxime palladacycle (2). Yellow solid. Yield 43%, Melting Point: 222 °C (descomposition), Pd content by ICP-OES: 2.72%

^1H NMR (300 MHz, DMF- d_7) δ 9.55 (s, 1H), 7.29 (s, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.45 (dd, J = 8.1, 2.1 Hz, 1H), 2.16 (s, 3H).

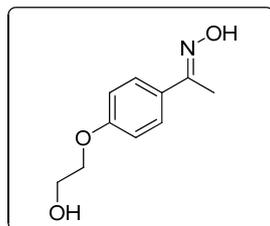
^{13}C NMR (75 MHz, DMF- d_7) δ 157.5, 154.3, 135.1, 126.7, 123.0, 111.1, 104.3, 11.2.



1-(4-(2-hydroxyethoxy)phenyl)ethan-1-one.⁷ White solid; Yield 53%, purified by flash chromatography (Silica, Hex/EtOAc: 6:2).

¹H NMR (300 MHz, CDCl₃) δ 7.94 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.16 (dd, *J* = 5.2, 3.8 Hz, 2H), 4.06 – 3.89 (m, 2H), 2.56 (s, 3H), 2.15 (t, *J* = 6.2 Hz, 1H).

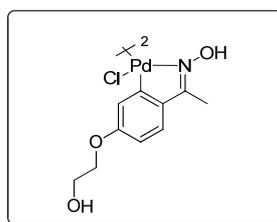
¹³C NMR (400 MHz, CDCl₃) δ 196.8, 162.5, 130.6, 130.5, 114.1, 69.3, 61.2, 26.3.



(E)-1-(4-(2-hydroxyethoxy)phenyl)ethan-1-one oxime. White solid. Yield 89%.

¹H NMR (300 MHz, DMSO-d₆) δ 10.98 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.90 (t, *J* = 5.5 Hz, 1H), 4.00 (t, *J* = 5.0 Hz, 2H), 3.72 (q, *J* = 5.0 Hz, 2H), 2.12 (s, 3H).

¹³C NMR (75 MHz, DMSO-d₆) δ 159.5, 152.8, 129.8, 127.3, 114.7, 70.0, 60.0, 11.9.

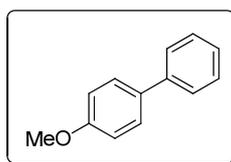


(E)-1-(4-(2-hydroxyethoxy)phenyl)ethan-1-one oxime palladacycle (3). Yellow solid. Yield 50%.

¹H NMR (300 MHz, DMF-d₇) δ 10.23 (s, 1H), 7.46 (s, 1H), 7.36 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.5 Hz, 0H), 4.21 (t, *J* = 4.9 Hz, 2H), 4.01 (t, *J* = 4.9 Hz, 2H), 2.46 (s, 3H).

¹³C NMR (75 MHz, DMF-d₇) δ 167.2, 157.9, 151.7, 135.4, 126.8, 109.5, 70.0, 60.5, 10.9.

6.2. Physical and spectroscopic data of Suzuki-Miyaura coupling products

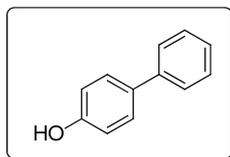


⁷ Mello, R.; Martínez-Ferrer, J.; Asensio, G.; González-Núñez, M.E. Oppenauer Oxidation of Secondary Alcohols with 1,1,1-Trifluoroacetone as Hydride Acceptor. *J. Org. Chem.* **2007**, *72*, 9376-9378

4-methoxy-1,1'-biphenyl (4a).⁸ White solid. Yield 73%, Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.58 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 1H), 3.89 (s, 4H).

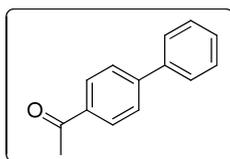
MS (EI) *m/z* 185 (*M*⁺¹, 15%), 184 (*M*⁺, 100), 169 (48), 152(10), 141(39), 139 (15), 115 (31).



[1,1'-biphenyl]-4-ol (4b).⁹ White solid. Yield 61%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.58 – 7.51 (dd, *J* = 2.6, 1.8 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 – 7.27 (m, 1H), 6.96 – 6.82 (m, 1H), 5.03 (s, 1H).

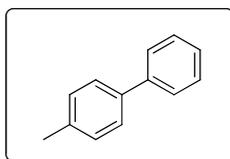
MS (EI): *m/z* 171 (*M*⁺¹, 14%), 170 (*M*⁺, 100), 141 (19), 115 (14)



1-([1,1'-biphenyl]-4-yl)ethan-1-one (4c).⁵ White solid. Yield 66%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 8.04 (d, *J* = 8.6 Hz, 2H), 7.76 – 7.56 (m, 4H), 7.44 (dd, *J* = 15.2, 7.3 Hz, 3H), 2.64 (s, 3H).

MS (EI) *m/z* 197 (*M*⁺¹, 9%), 196 (*M*⁺, 46), 181 (100), 152 (47), 151 (16).



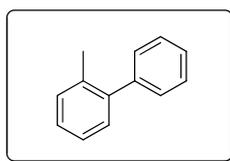
4-methyl-1,1'-biphenyl (4d).⁹ White solid. Yield 94%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.68 (dd, *J* = 7.2, 1.2 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.55 – 7.49 (m, 2H), 7.46 – 7.39 (m, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.49 (s, 3H).

⁸ Alacid, E.; Nájera, C. First cross-coupling reaction of potassium aryltrifluoroborates with organic chlorides in aqueous media catalyzed by an oxime-derived palladacycle. *Org. Lett.* 2008, *10*, 5011–5014

⁹ Baia, L.; Wang, J. W. Reusable, Polymer-Supported, Palladium-Catalyzed, Atom-Efficient Coupling Reaction of Aryl Halides with SodiumTetraphenylborate in Water by Focused Microwave Irradiation. *Adv. Synth. Catal.* **2008**, *350*, 315–320

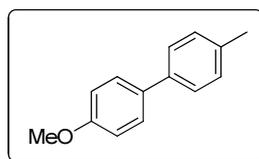
MS (EI): m/z 169 (M^{+1} , 13%), 168 (M^{+} , 100), 165 (25), 153 (14), 152 (19).



2-methyl-1,1'-biphenyl (4e).¹⁰ Yellow oil. Yield 42%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.43 – 7.36 (m, 2H), 7.35 – 7.28 (m, 3H), 7.27 – 7.21 (m, J = 8.5, 6.1 Hz, 4H), 2.26 (s, 1H).

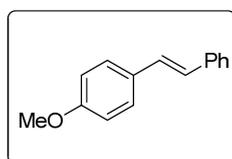
MS (EI) m/z 169 (M^{+1} , 15%), 168 (M^{+} , 100), 167 (85), 153 (41), 152 (29), 115 (10).



4-Methoxy-4'-methyl-1,1'-biphenyl (4g).¹¹ White solid. Yield 68%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.47 (dd, J = 18.1, 8.3 Hz, 4H), 7.22 (d, J = 8.3 Hz, 2H), 6.96 (d, J = 8.6 Hz, 2H), 3.83 (s, 3H), 2.38 (s, 3H).

MS (EI) m/z 199 (M^{+1} , 16%), 198 (M^{+} , 100), 184 (10), 183 (53), 155 (28), 153 (10), 152 (11).



(E)-1-methoxy-4-styrylbenzene (4i).¹² White solid. Yield 35%. Purified by flash chromatography (Hex/EtOAc: 95:5).

¹H NMR (300 MHz, CDCl₃) δ 7.56 – 7.46 (m, 4H), 7.37 (t, J = 7.5 Hz, 2H), 7.32 – 7.19 (m, 2H), 7.10 (d, J = 16.3 Hz, 1H), 7.00 (d, J = 16.4 Hz, 1H), 6.93 (d, J = 8.8 Hz, 1H), 3.86 (s, 3H).

MS (EI): m/z 211 (M^{+1} , 17%), 210 (M^{+} , 100), 195 (17), 167 (21), 166 (11), 165 (31), 152 (19).

¹⁰ Stevens, P. D.; Fan, J.; Gardimalla M. R.H.; Yen, M.; Gao, Y. Superparamagnetic Nanoparticle-Supported Catalysis of Suzuki Cross-Coupling Reactions. *Org.Lett.* 2005, 7, 2085-2088

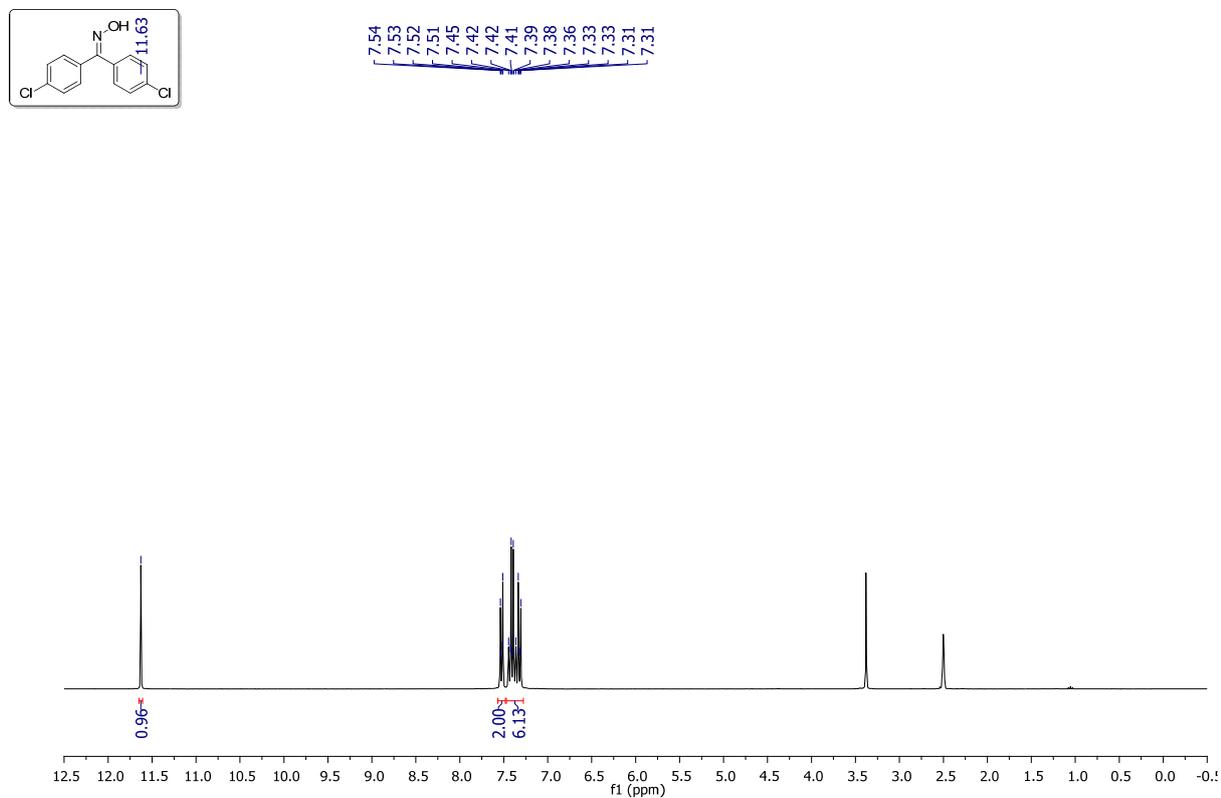
¹¹ Bo, L.; Chunling, F.; Shengming, M. Application of a readily available and air stable monophosphine HBF₄ salt for the Suzuki coupling reaction of aryl or 1-alkenyl chlorides. *Tetrahedron Lett.* 2010, 51, 1284-1286

¹² Huo, C.; He, X.; and Chan, T. H. Zwitterionic Phosphonium Sulfonates as Easily Phase-Separable Ion-Tagged Wittig Reagents. *J. Org. Chem.* 2008, 73, 8583-8586

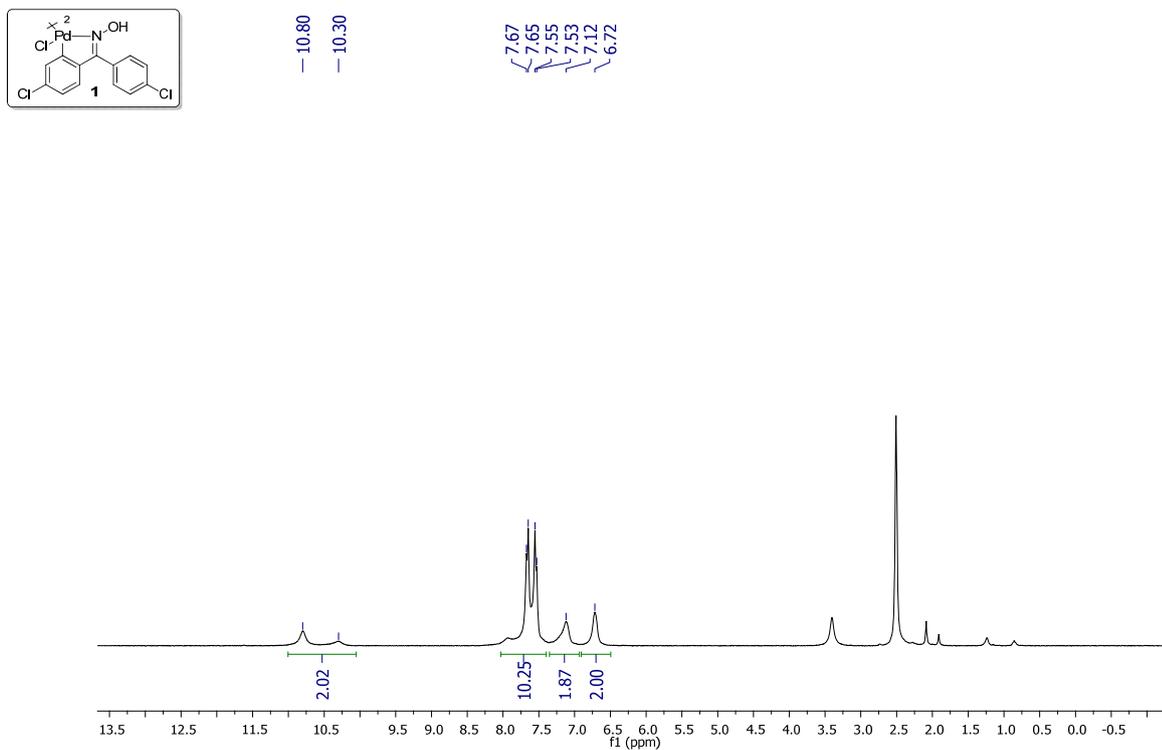
7. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra

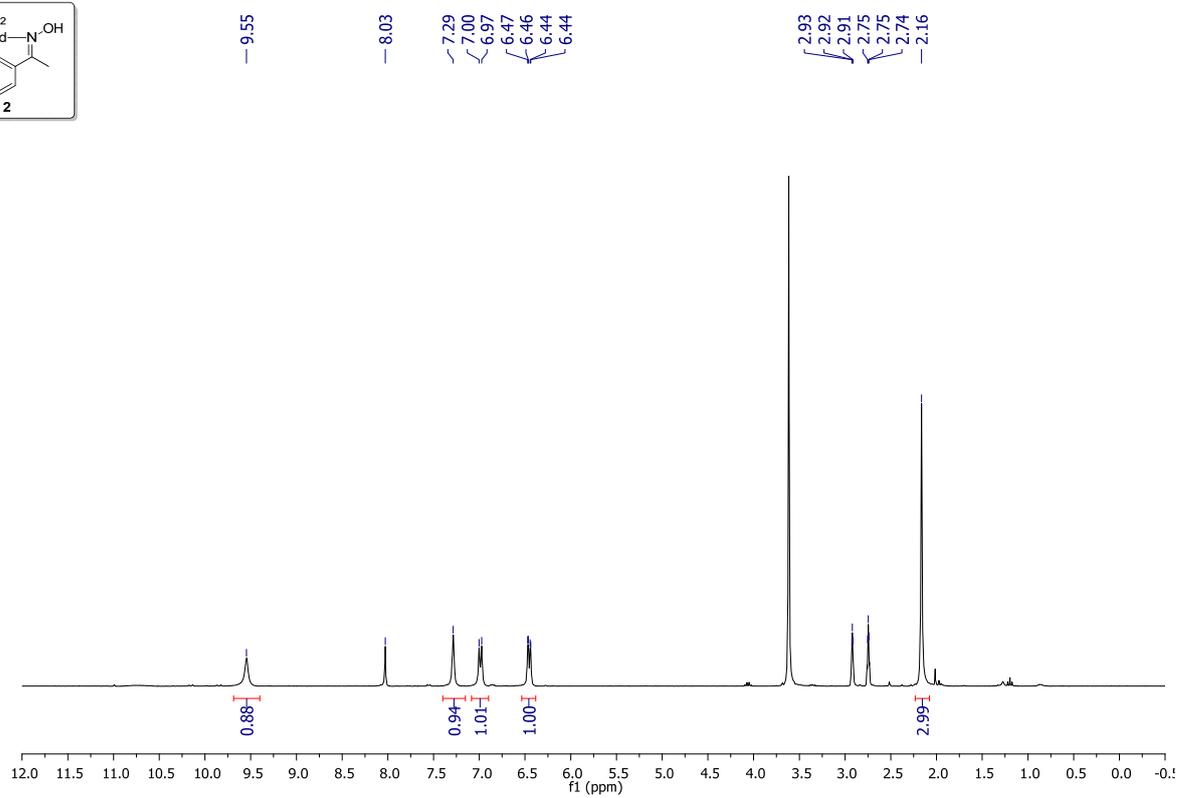
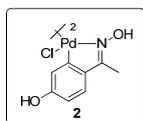
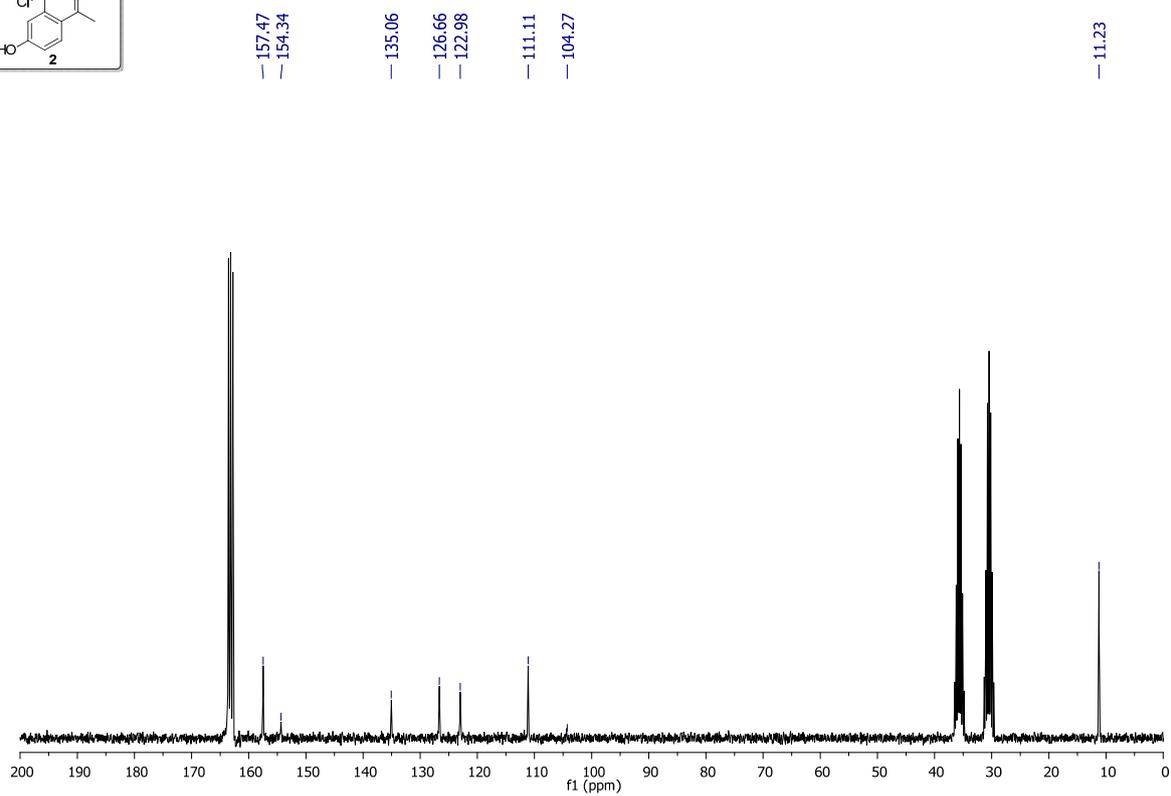
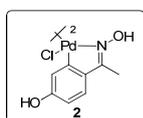
7.1. Ketone, oximes, and oxime palladacycles spectra

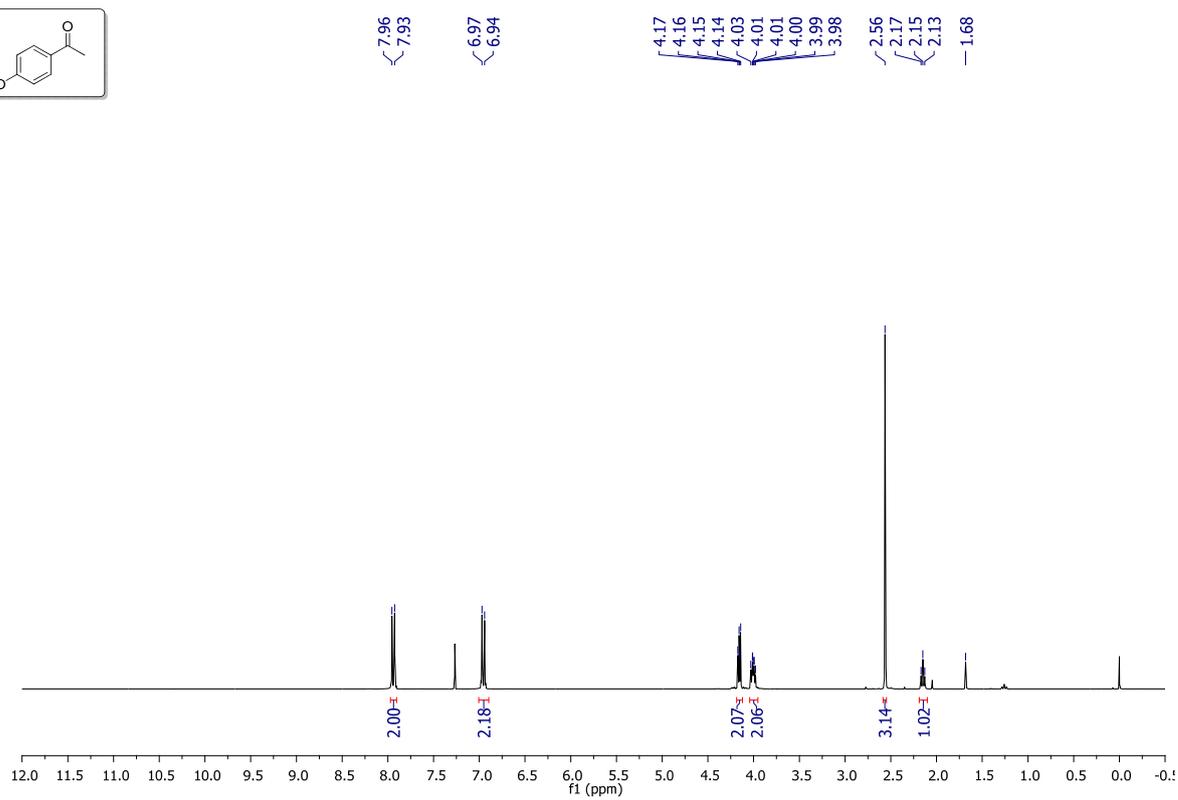
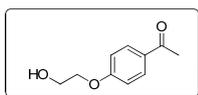
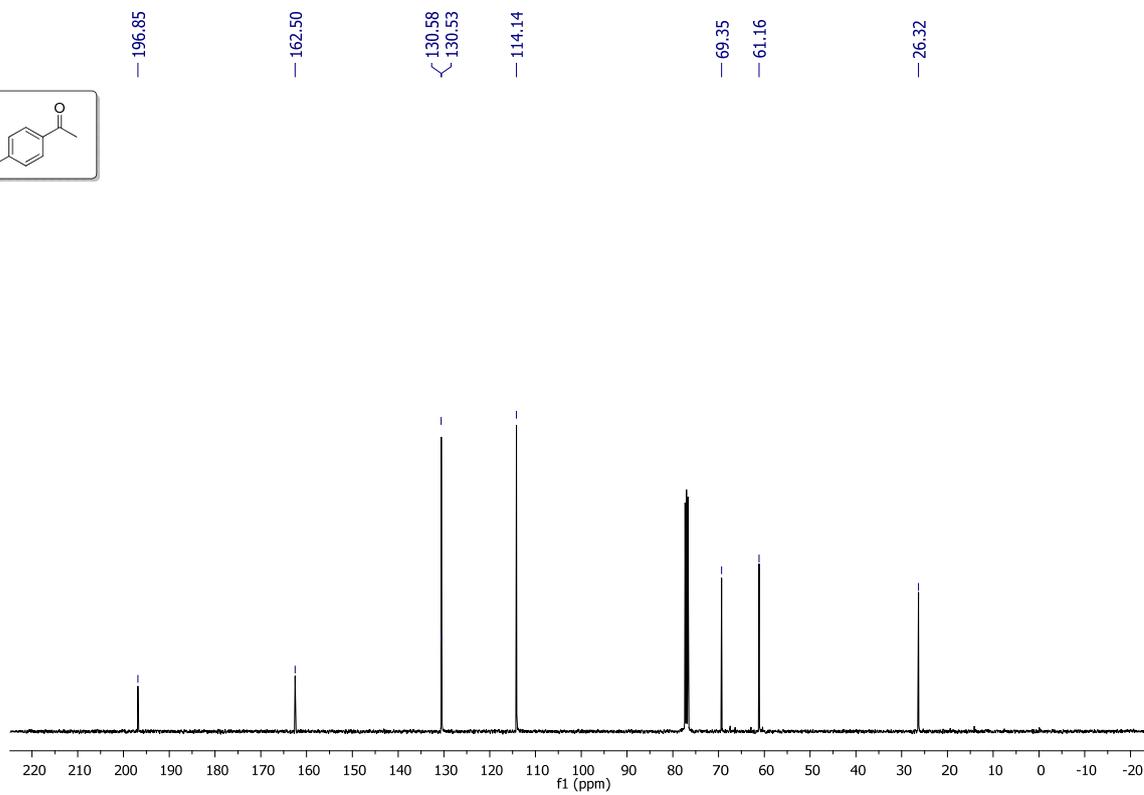
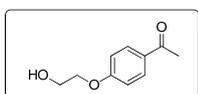
$^1\text{H-NMR}$



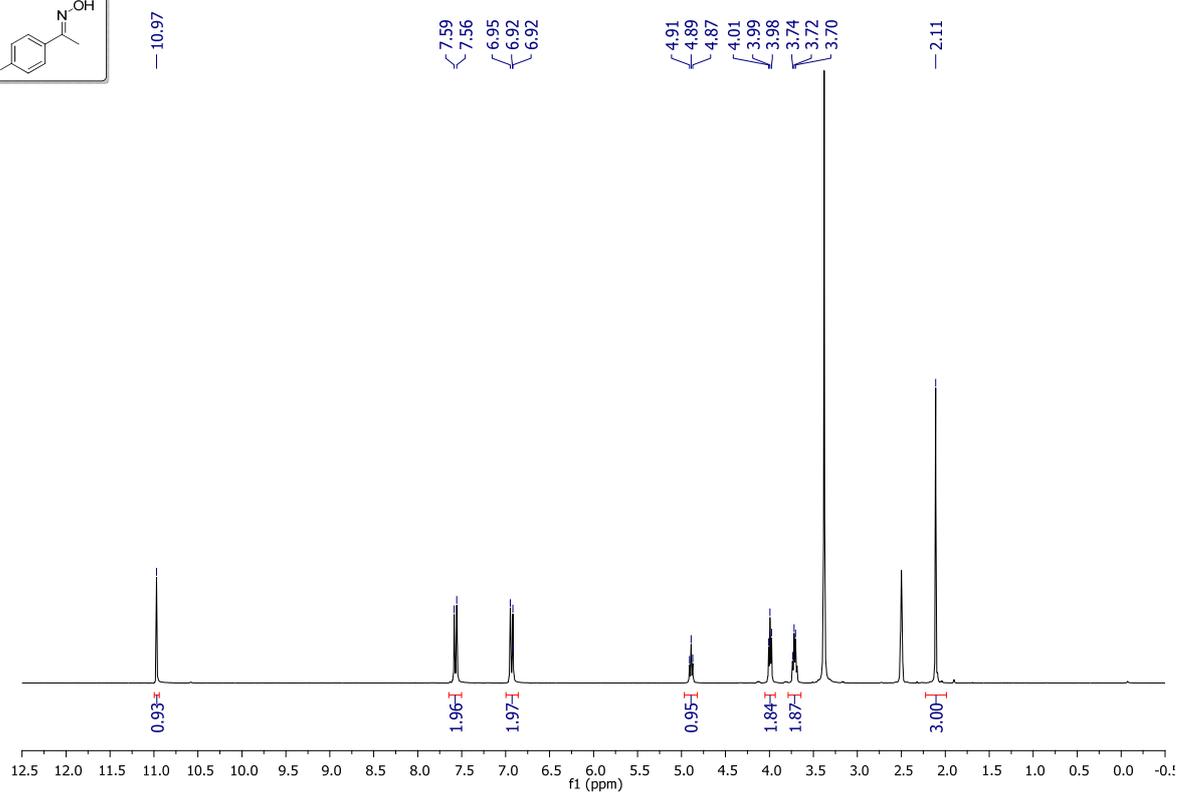
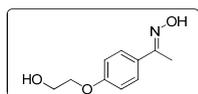
$^1\text{H-NMR}$



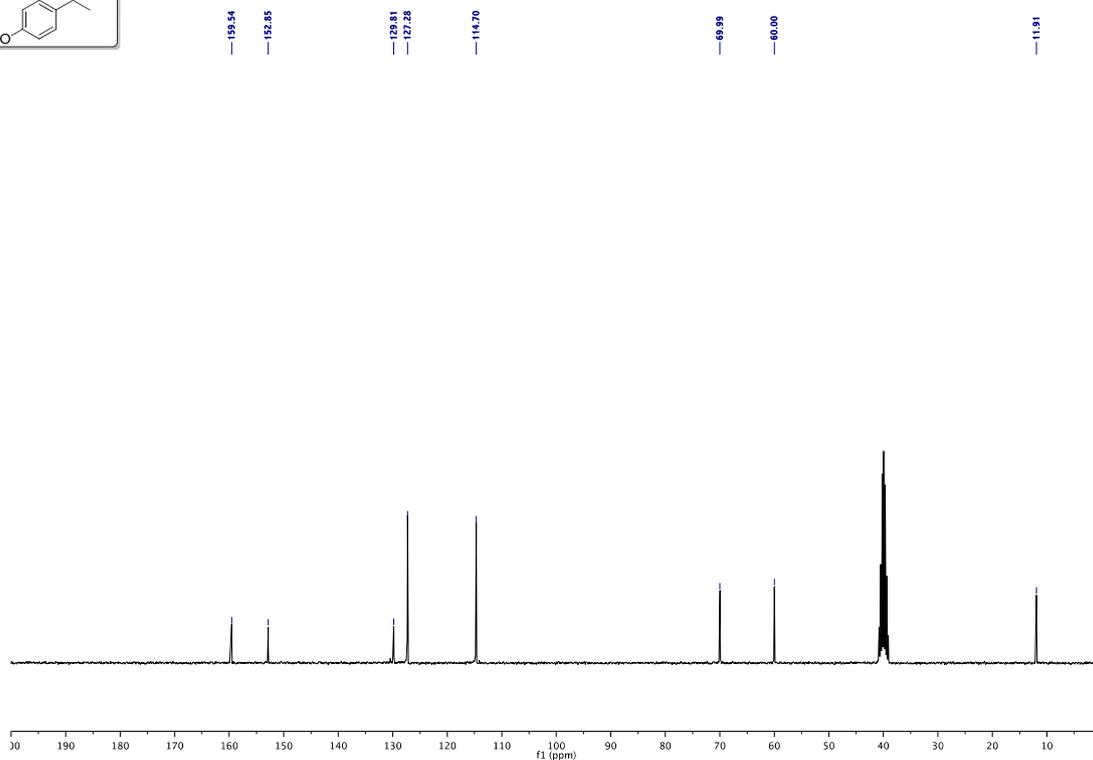
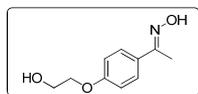
¹H NMR**¹³C NMR**

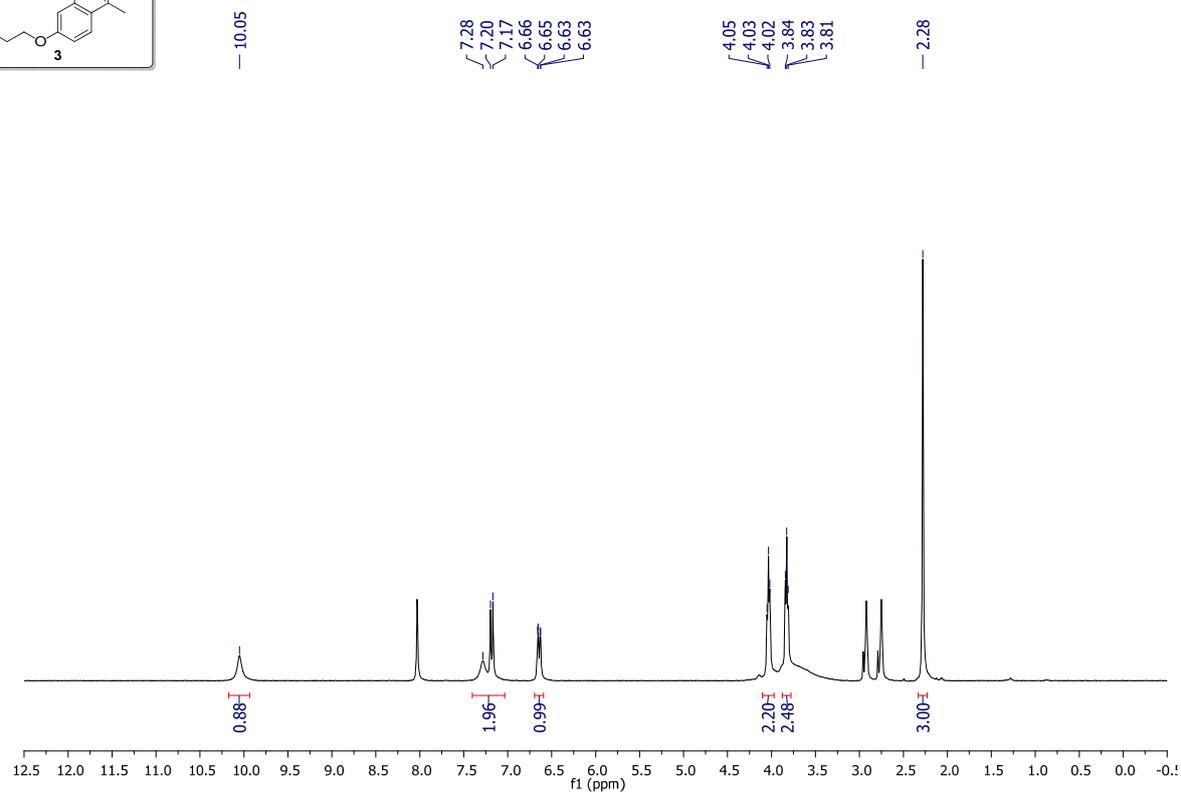
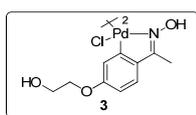
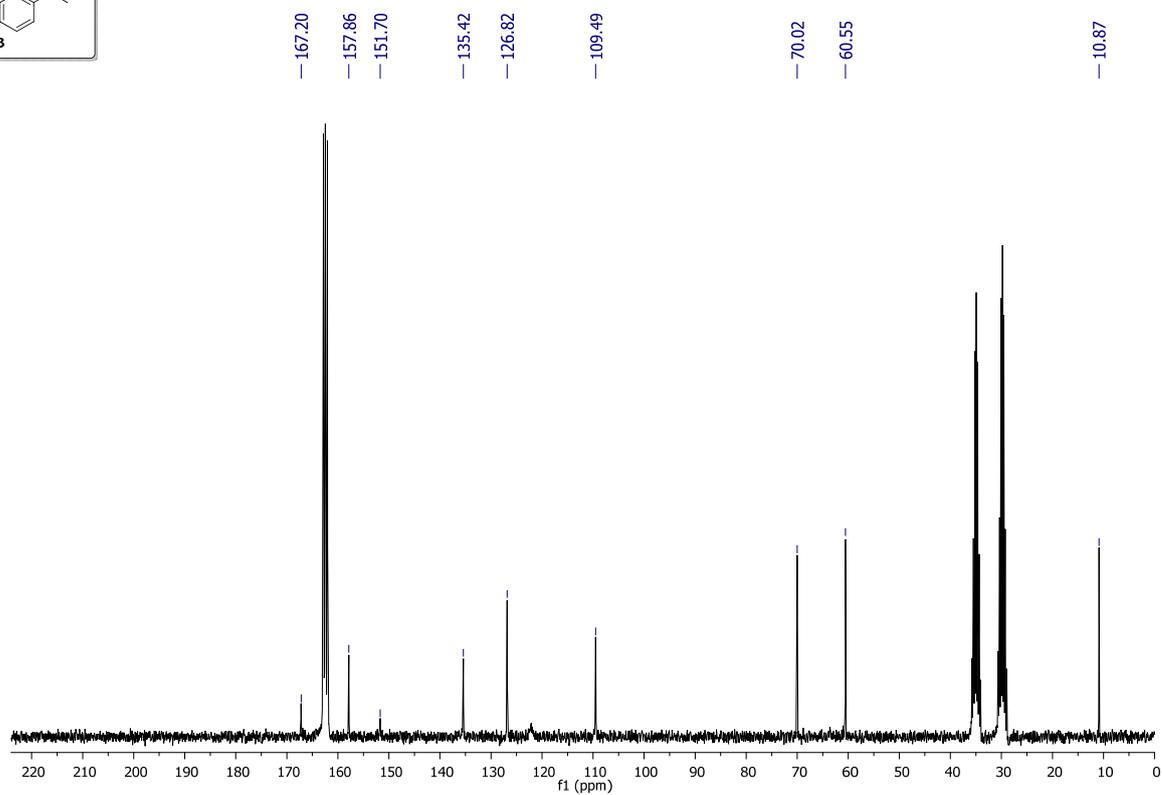
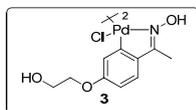
¹H NMR¹³C NMR

¹H NMR

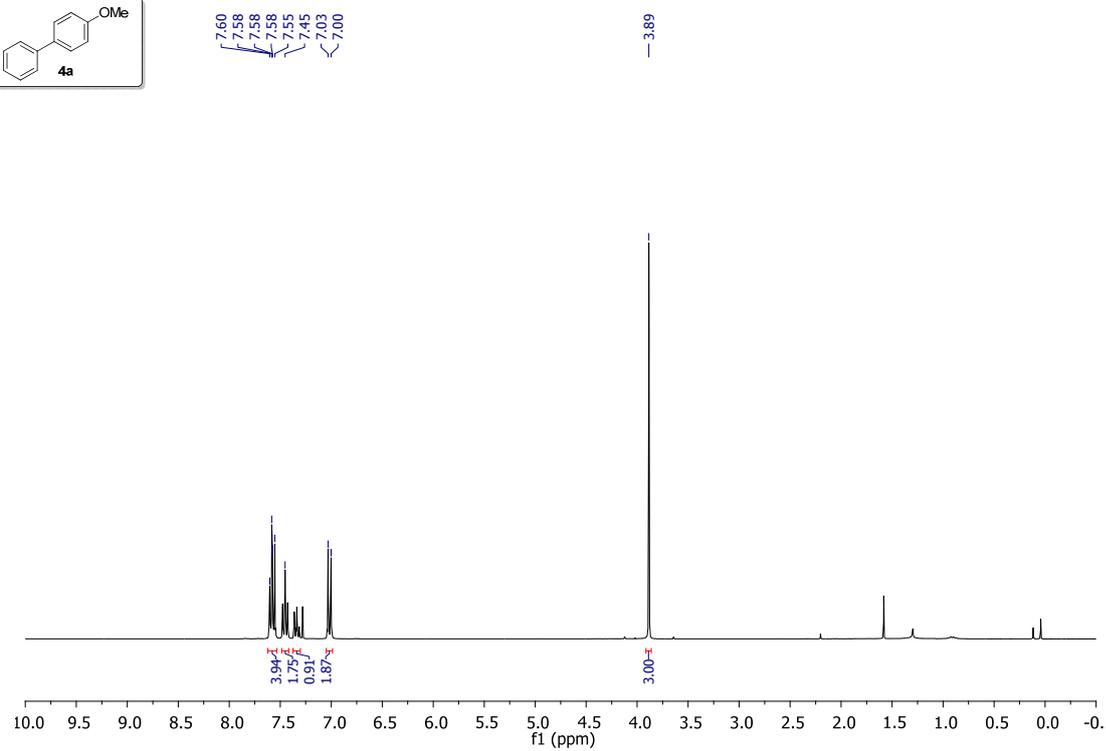
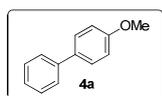
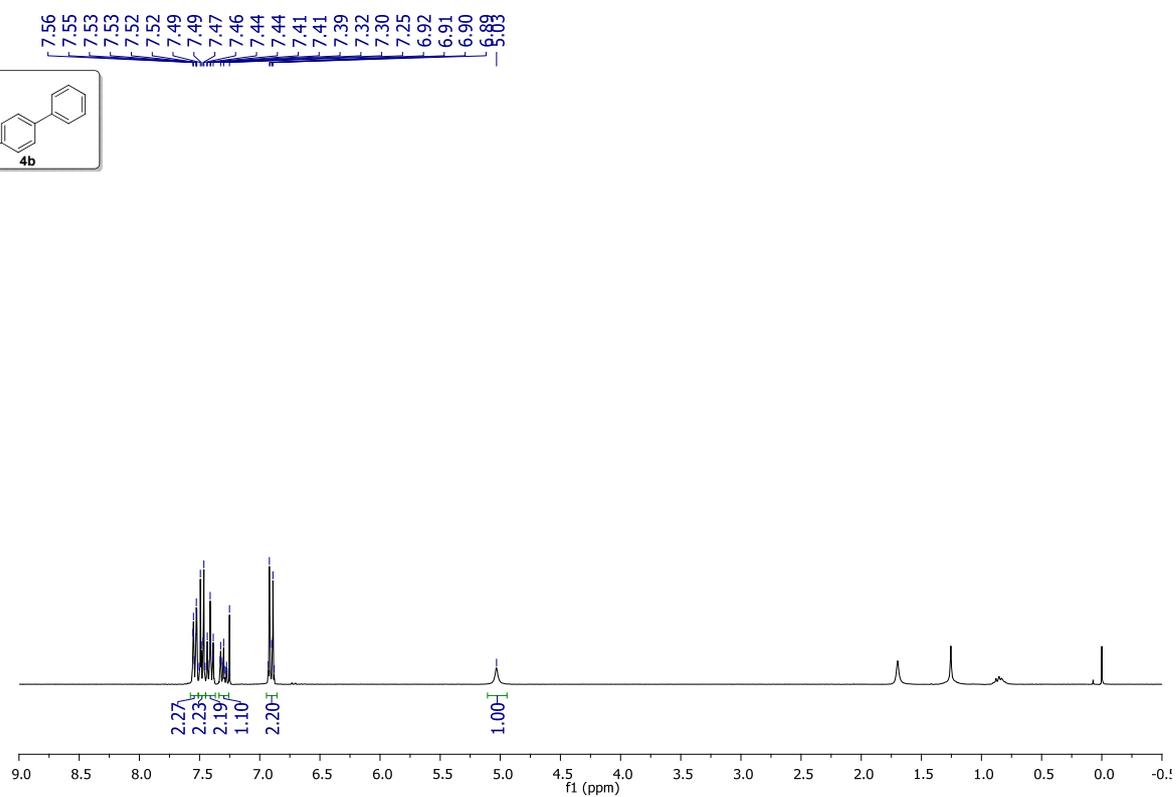
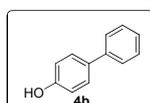


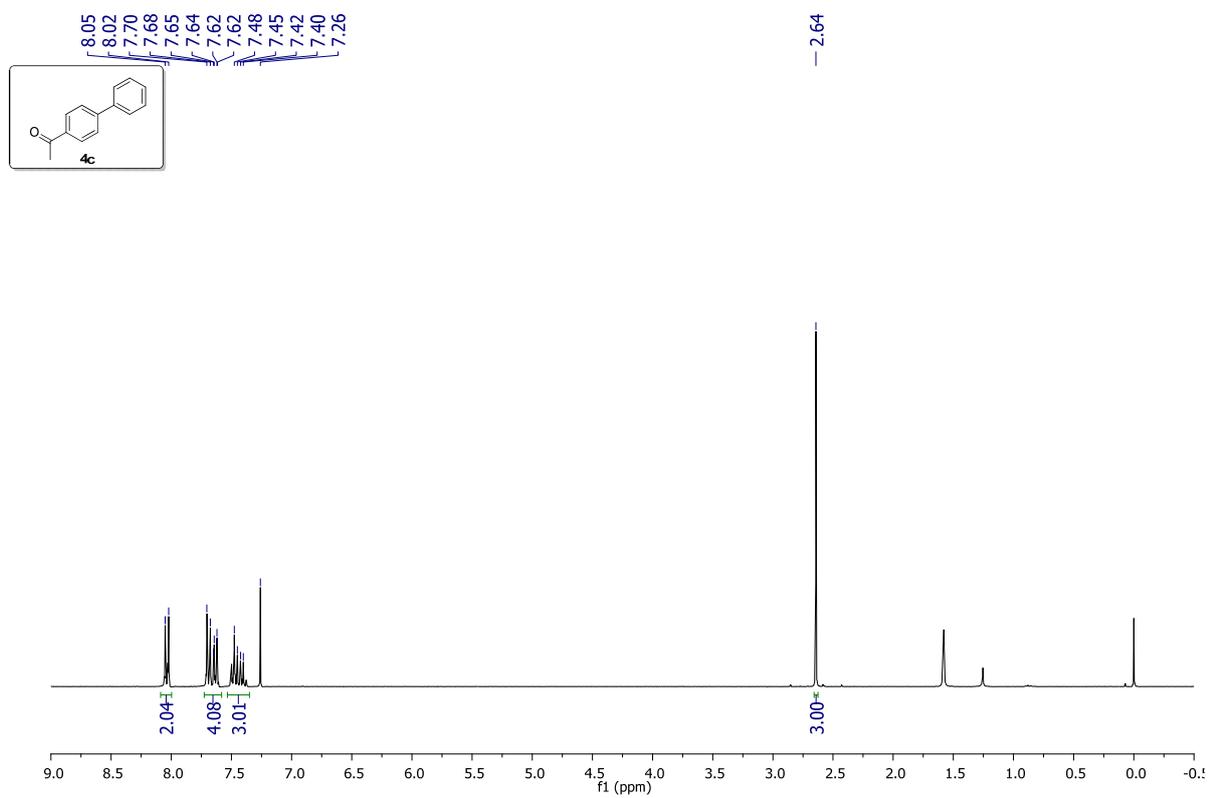
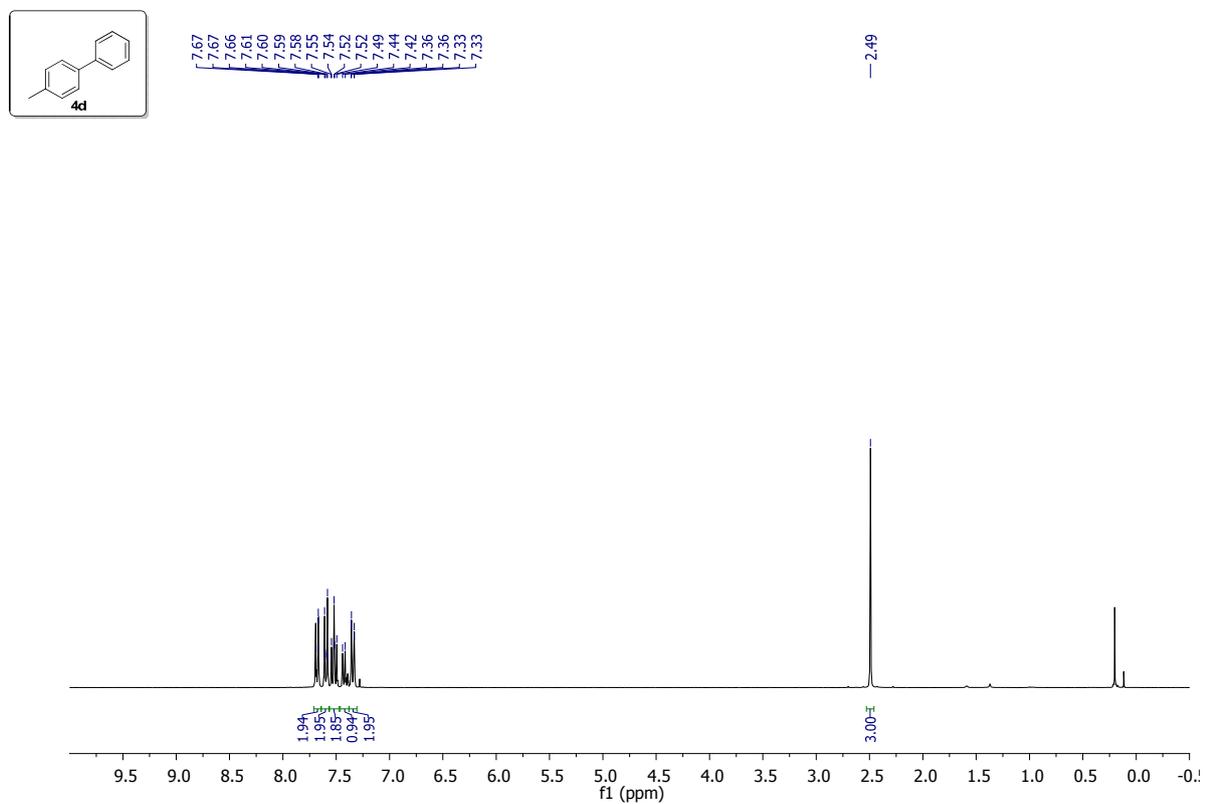
¹³C NMR



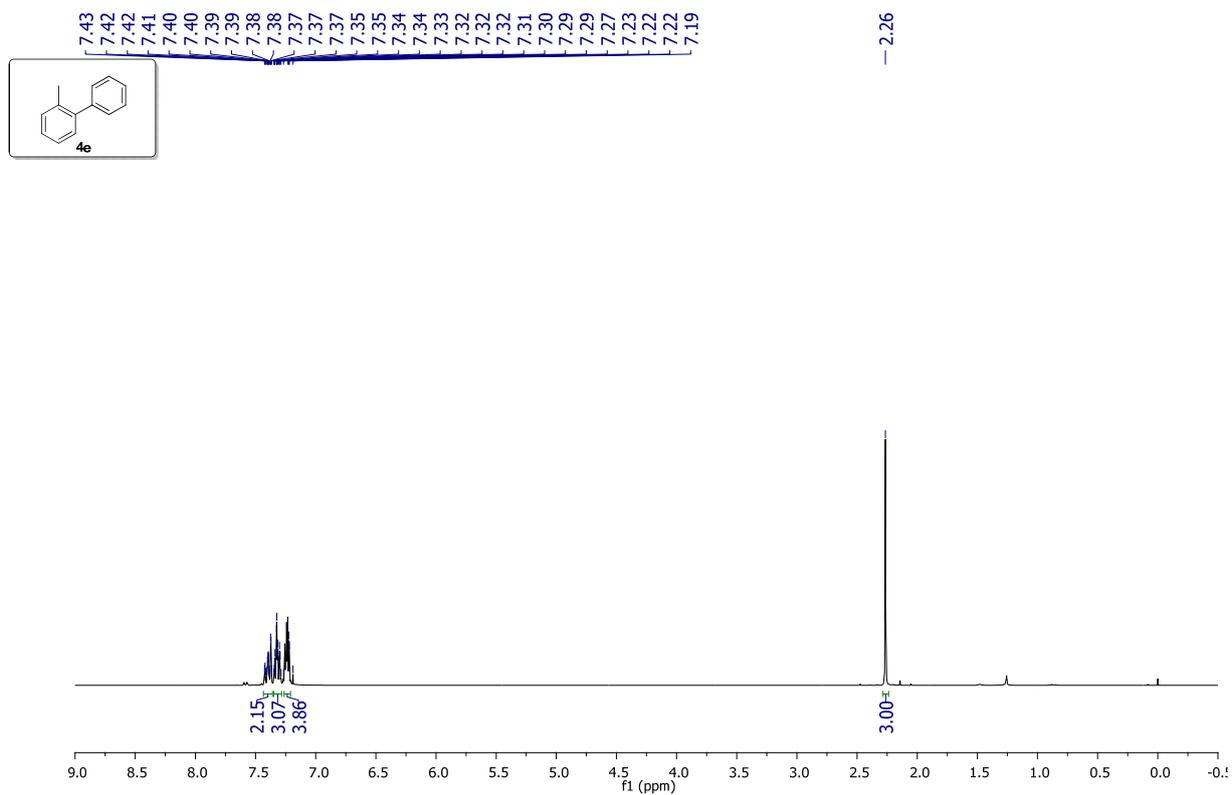
¹H NMR¹³C NMR

7.2. Suzuki-Miyaura coupling products spectra

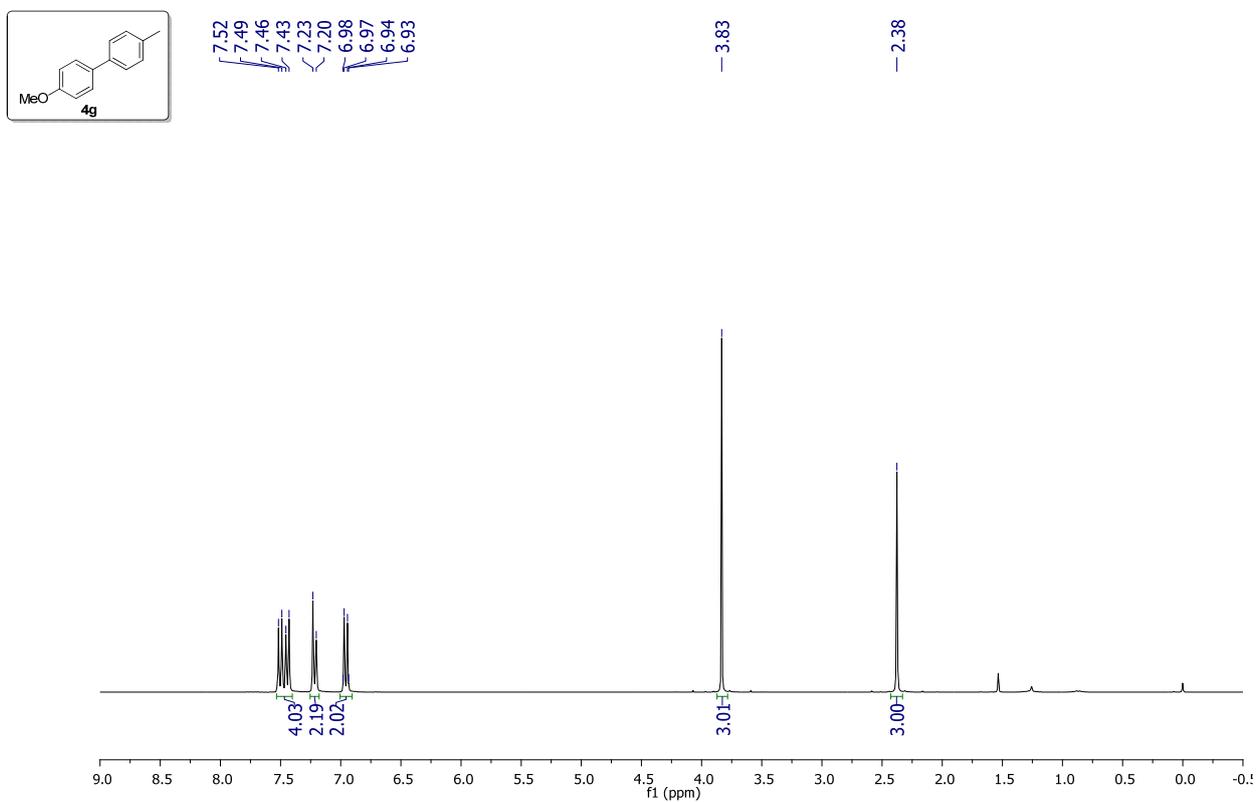
¹H NMR¹H RMN

¹H NMR¹H RMN

¹H NMR



¹H NMR



¹H RMN

