Electronic Supplementary Material (ESI) for Dalton Transactions.

Immobilized Pd on magnetic nanoparticles bearing proline as highly efficient and retrievable Suzuki-Miyaura catalyst in aqueous media.

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Supporting informations

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2) Literature survey

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6) ^{1}H NMR spectrum of the crude mixture after catalysis

7) NMR spectra for products of the Suzuki-Miyaura cross coupling

1) Experimental details

Materials

Dopamine hydrochloride, (Boc)-L-Pro-OSu were purchased from Sigma-Aldrich. $Pd(OAc)_2$ was bought from Acros Organics. o-phthalaldehyde (OPA) reagent solution were purchased from Thermoscientific. Fluoraldehyde OPA reagent solution contains 0.8 mg mL_1 of o-phthalaldehyde. All the other reagents were obtained from commercial suppliers and were used without purification.
Water was purified with a millipore system (resistivity 18.2 MΩ cm).
^{1}H NMR spectra (400 MHz), proton-decoupled ^{13}C NMR spectra (100.63 MHz) were recorded on a Bruker Avance III 400 spectrometer. Chemical shifts are reported in parts per million (ppm) on the δ scale. The residual solvent peaks were used as internal references (^{1}H NMR: $CHCl_3$ 7.26 ppm, H_2O 4.79 ppm; ^{13}C NMR: $CDCl_3$ 77.2 ppm). Data are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, qt = quintuplet, m = multiplet and coupling constant(s) are given in Hz. FTIR spectra were recorded as KBr pellets or between NaCl plates (for liquid product) on a Thermo Scientific Nicolet 380 FTIR spectrophotometer and are reported in wavenumbers (cm^{-1}). High resolution Mass Spectrometry experiments were realized on a LTQ Orbitrap Velos (Thermo Scientific) in positive and negative modes using an ESI source. Specific optical rotation were measured on a Perkin Elmer 341 polarimeter at 26°C using a Hg lamp (λ = 589 nm) in water.
UV-visible spectra were recorded on a Varian Cary 50 Scan UV-Visible spectrophotometer. The number of particles was determined by UV from the iron concentration (ε_{480} = 420 L.mol-1.cm-1), considering an average diameter of 10 nm, a density value of 4.85 $g.cm^{-3}$, and a molecular weight of 160 $g.mol^{-1}$ for γ-Fe_2O_3.
The hydrodynamic diameter and the zeta potential of the nano complex were determined by dynamic laser light scattering (DLS) on a Nano-ZS (Red Badge) ZEN 3600 device (Malvern Instruments, Malvern, UK).
TEM images were obtained using a FEI CM10 microscope (Philips), and samples were prepared by depositing a drop of nanoparticles suspension on carbon-coated copper grids placed on a filter paper. The average particle diameters were deduced from TEM data measurements, simulating the diameter distribution with a log-normal function (g(d)):

$$g(d) = \frac{1}{\sigma d\sqrt{2\pi}} \exp\left(-\frac{\left(\ln \frac{d}{d_{med}} \right)^2}{2\sigma^2} \right)$$

σ corresponding to the distribution's length and $\ln(d_{med})$ to the medium of (d).
Quantification of Cat-Pro and Pd coating and grafting per particle was evaluated by Energy-dispersive X-ray (EDX), FTIR and thermogravimetric analysis (TGA) respectively. EDX microanalyses were performed using a TM 3000 tabletop microscope equipped with a Swift EDX-ray 3000 microanalysis system (Oxford Instruments). Samples were deposited as powder on a copper surface, and data were collected using a 15 kV accelerating voltage, studying ratio of iron vs Pd and knowing the average number of iron atoms/particles. The thermogravimetric analysis (TGA) curves were recorded using a LabsSys evo TG-DTA-DSC 16000 device manufactured by Setaram Instrumentation.
X-ray Photoelectron Spectroscopy (XPS) data were recorded on a PHI Versaprobe 5000 device and Al–K monochromated radiation (1486.6 eV, 50 W with a 200-µm-diameter spot size) was used as X-ray source. Pass energy is 200 eV for spectra and 60 eV for windows (quantifications and curve fitting are obtained from windows acquisitions). Powder samples were prepared by pressing the sample powder on an indium sheet. Neutralization was used to minimize charge effects and the adventitious carbon C1s peak at 284.5 eV was used as the reference. The pressure in analysis chamber during acquisition is around 8.10^{-8} Pa. Photoemission peak areas were calculated after background subtraction using a Shirley routine and all concentration calculations were done with Multipack software. Windows were decomposed into components by fitting with Gaussian (70%)-Lorentzian (30%) peaks. In the fitting procedure, Full-Widths at Half-Maximum (FWHMs) were set with Casa XPS software."
The magnetic behavior of the as-synthesized nanoparticles was characterized at room temperature using a vibrating magnetometer was characterized at room temperature using a vibrating magnetometer, VSM (Dautum Design, Versalab). The fluorescence measurements were performed with Spex Fluoromax spectrofluorometer (HORIBA jobin-Yvon, france) equipped with a Hamamatsu 928 photomultiplier.
Chemicals reaction under microwave irradiation were performed using Mono Wave 300 (Anton, Paar) in sealed vessel.

Chemical synthesis and characterization

***Cat-Pro** (S)-N-(3,4-dihydroxyphenethyl)pyrrolidine-2-carboxamide*

Dopamine hydrochloride (948 mg, 5 mmol) was solubilized with 10mL CH_2Cl_2 and N,N-diisopropylethylamine (1,74 mL, 10 mmol) was added to the mixture. Then 6 mL of a solution (Boc)-L-Pro-OSu (1,59 g, 5 mmol) in CH_2Cl_2 were added and the resulting mixture was stirred for 3 days at room temperature. The orange-yellow crystal clear solution was then extracted and washed twice with an acid solution (0.1M $KHSO_4$) and twice with 0.1 M NaOH. The crude product was evaporated to yield a yellow oil which was used without further purification.

Dopamine-(Boc)-L-Proline was then solubilized with 3 mL CH_2Cl_2 and 3mL of trifluoroacetic acid (TFA) were added. The mixture was stirred 30 min at room temperature and then CH_2Cl_2 and TFA were evaporated. After two washing with Et_2O, the product is filtered. The product is obtained as TFA salt and yielded a yellow oil (1.47 g, 81% global yield on the two steps).

RMN ^1H (D_2O, 25°C): δ = 6,8-6,56 (m, 3H) ; 4,17 (dd, 1H) ; 3.52-3.42 (m, 1H) ; 3,24-3,09 (m, 3H) ; 2,66-2,45 (m, 2H) ; 2,18-2,05 (m, 1H) ; 1.89-1.76 (m, 1H) ; 1.76-1.65 (m, 1H) ; 1.65-1.53 (m, 1H) ppm.

RMN $^{13}C\{^1H\}$ (D_2O, 25°C): δ = 169,09 ; 143.73 ; 142,28 ; 131,66 ; 121,17 ; 116,62 ; 116,11 ; 59,58 ; 46,29 ; 40,48 ; 35,59 ; 29,83, ; 23,49 ppm.

IR (NaCl): 3270,9 ; 3099.8, 2982.4 ; 1673.9 (TFA) ; 1603.9 ; 1567.0 ; 1441.3 (TFA) ; 1383.7 ; 1285.0 ; 1253.7; 1200.7 (TFA) ; 1137.5 (TFA) ; 337.8 ; 799.7 ; 722.6

HR-MS (ESI$^+$-Q Tof) $C_{10}H_{19}N_2O_8P_2S$: m/z $(M+H)^+$: 251.13908 ; calc: 251.13957.

$[\alpha]_D^{26°C}$ = -52.5°.

Nanoparticles synthesis and coating / immobilization of Palladium

The bare maghemite nanoparticles, γFe_2O_3 nanocrystals (average diameter 10.5 nm and size distribution σ = 0.2), were synthesized according to the following procedure (Lalatonne 2008). Dimethylamine ($(CH_3)_2NH$) was added to an aqueous solution of ferrous dodecyl sulfate ($Fe(DS)_2$). The final concentrations after the reactants were mixed were $1.4.10^{-2}$ $mol.L^{-1}$ and 1.4 $mol.L^{-1}$ respectively for $Fe(DS)_2$ and dimethylamine. The solution was stirred vigorously for 2 h at 28 °C. 12 mL of HCl (1 M) were then added in order to reach the isoelectric point (around pH = 7), inducing nanoparticle precipitation. The precipitate was isolated from the supernatant using magnetic separation. After 10 washings at neutral pH, the nanoparticles were then dispersed at pH=2 in distilled water. At this stage bare γ-Fe_2O_3 nanocrystals were produced.

The coating of γ-Fe_2O_3 nanocrystals with **Cat-Pro** was done following the protocols already described (Boley 2013). To 10 mL of an aqueous solution of **Cat-Pro** trifluoroacetate (1,35 mL, 0,58 mmol, pH = 11), 10 mL of an aqueous solution of γ-Fe_2O_3 nanoparticles ([Fe] = 0,20 M, pH = 10,5) were added. The resulting mixture is vigouresly stirred for 2 h at room temperature. The **γ-Fe_2O_3@Cat-Pro** particles are washed 5 times per magnetic separation in order to remove the excess of unbounded product. Particles are then dispersed in water at pH = 7.

The average number of Cat-Pro per nanocrystal was measured by thermogravimetric analysis and ortho-phthaldialdehyde (OPA) analysis. For the OPA method, 50 mL of the sample was diluted in 50 mL of NaOH 2 N and left overnight at 60°C. 1 mL of OPA reagent was added to the mixture and fluorescence measurement was recorded.

IR (KBr): 3424 ; 2922.1 ; 2851.9 ; 1631.1; 1539.8; 1409.5 ; 1384.2 ; 1118.5 ; 890.2 ; 794.9 ; 632.5 ; 586.3 ; 454.9 ; 447.1

The immobilization of the palladium onto **γ-Fe_2O_3@Cat-Pro** nanoparticles was realized adapting the protocol described by Allam et al. for Pd-Proline complex. Briefly, 2.5 mL of **γ-Fe_2O_3@Cat-Pro** nanoparticles ([Fe] = 0,12 M, pH = 7) were mixed with 1.5 mg of Pd(OAc) in 2.5 mL of MeOH and 2.5 µL of triethylamine. After 24 h mixing under vigorous stirring the **γ-Fe_2O_3@Cat-Pro(Pd)** nanoparticles were washed 5 times with water MeOH mixture and nanoparticles were then dispersed in water.

The average number of Pd per nanocrystal was determined by EDX-analysis by studying Iron/Palladium ratio.

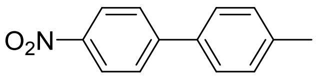
IR (KBr): 3435.0 ; 2925.2 ; 2847.5 ; 1666.5 ; 1634.7 ; 1574.7 ; 1411.8 ; 1386.4 ; 890.6 ; 633.7 ; 589.2 ; 448.4.

General procedure for Suzuki-Miyaura cross coupling :

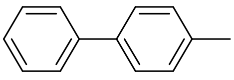
example of reaction of 4-tolylboronic acid with 4-iodonitrobenzene with 0.1 mol % Pd of the **γ-Fe_2O_3@Cat-Pro(Pd)** nanocatalyst

In a 10 mL MW vial, 30 µL of an aqueous solution of **γ-Fe_2O_3@Cat-Pro(Pd)** ([Fe] = 0.22 M ; [Pd] = 6.6 mM) was added to 1 mL of water. 49.8 mg of 4-iodonitrobenzene (0.20 mmole) and 30 mg of 4-tolylboronic acid

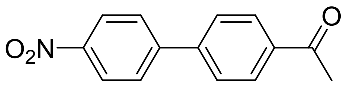
(0.22 mmole) and 80 µL of triethylamine (0.6 mmole) were then added. The glass walls of the vial were rinsed with 1 mL ethanol and a caps was fixed on the top of the vial. The vial was heated in a microwave appartus for 30 min. at 80°C using ruby thermometer (step 1: heat in 2 min. to 80°C, step 2 hold at 80°C for 28 min. Stirrer speed 1200 rpm for both steps). After cooling of the solution 1 mL of diethyl ether was added and the organic layer was extracted 5 times. The nanocatalyst was then washed using magnetic separation by 5 times 1 mL of ethanol and 5 times 1 mL of water. It can be then reused directly or stored in water. The product was then isolated by evaporation and purified by simple filtration over silica when conversion was total or purified by silica gel column chromatography using ethyl acetate hexane mixtures when starting halogenated reactants remained un reacted.



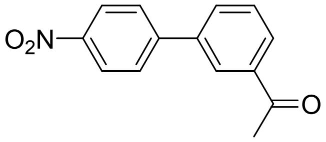
RMN ^{1}H (CDCl$_3$, 25°C): δ = 8.28 (d, J = 8.8 Hz, 2H) ; 7.72 (d, J = 8.8 Hz, 2H) ; 7.53 (d, J = 8.8 Hz, 2H) ; 7.30 (d, J = 8.8 Hz, 2H) ; 2.42 (s, 3H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 147.8 ; 147.0 ; 139.3 ; 136.0 ; 130.0 ; 127.7 ; 127.4 ; 124.3 ; 21.4 ppm.



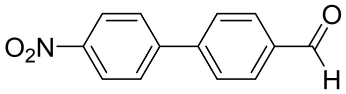
RMN ^{1}H (CDCl$_3$, 25°C): δ = 7.59 (d, J = 8.1 Hz, 2H) ; 7.50 (d, J = 8.1 Hz, 2H) ; 7.43 (t, J = 8.1 Hz, 2H) ; 7.33 (t, J = 8.1 Hz, 1H) ; 7.26 (d, J = 8.1 Hz, 2H) ; 2.40 (s, 3H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 141.3 ; 138.5 ; 129.6 ; 128.8 ; 127.1 ; 127.1 ; 21.2 ppm.



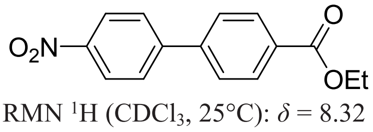
RMN ^{1}H (CDCl$_3$, 25°C): δ = 8.33 (d, J = 8.9 Hz, 2H) ; 8.08 (d, J = 8.8 Hz, 2H) ; 7.78 (d, J = 8.8 Hz, 2H) ; 7.72 (d, J = 8.8 Hz, 2H) ; 2.67 (s, 3H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 197.7 ; 147.8 ; 147.0 ; 146.4 ; 143.3 ; 137.2 ; 129.3 ; 128.3 ; 127.8 ; 124.4 ; 26.9 ppm.



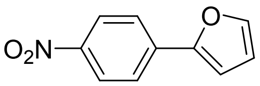
RMN ^{1}H (CDCl$_3$, 25°C): δ = 8.34 (d, J = 8.8 Hz, 2H) ; 8.22 (t, J = 1.7 Hz, 1H) ; 8.02 (td, J = 7.7 and 1.7 Hz, 1H) ; 7.82 (td, J = 7.7 and 1.7 Hz, 1H) ; 7.78 (d, J = 8.8 Hz, 2H) ; 7.62 (t, J = 7.7 Hz, 1H) ; 2.68(s, 3H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 197.8 ; 147.6 ; 146.7 ; 139.5 ; 138.1 ; 132.0 ; 129.7 ; 129.0 ; 128.2 ; 127.2 ; 124.4 ; 27.0 ppm.



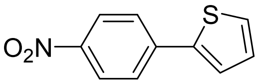
RMN ^{1}H (CDCl$_3$, 25°C): δ = 10.08 (s, 1H) ; 8.34 (d, J = 8.8 Hz, 2H) ; 8.00 (d, J = 8.8 Hz, 2H) ; 7.78 (d, J = 8.8 Hz, 4H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 191.8 ; 147.9 ; 146.2 ; 144.7 ; 136.4 ; 130.6 ; 128.4 ; 128.3 ; 124.5 ppm.



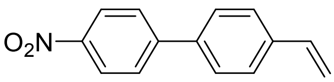
RMN ^{1}H (CDCl$_3$, 25°C): δ = 8.32 (d, J = 8.8 Hz, 2H) ; 8.170 (d, J = 8.8 Hz, 2H) ; 7.78 (d, J = 8.8 Hz, 2H) ; 7.69 (d, J = 8.8 Hz, 2H) ; 4.41 (q, J = 7.1 Hz, 2H) ; 1.43 (q, J = 7.1 Hz, 2H) ppm.
RMN ^{13}C{^{1}H} (D$_2$O, 25°C): δ = 166.2 ; 147.7 ; 146.5 ; 143.0 ; 130.5 ; 128.2 ; 127.5 ; 124.3 ; 61.4 ; 14.7 ppm.



RMN ^{1}H ($CDCl_3$, 25°C): δ = 8.25 (d, J = 8.9 Hz, 2H) ; 7.80 (d, J = 8.9 Hz, 2H) ; 7.58 (d, J = 1.3 Hz, 1H) ; 6.88 (d, J = 3.1 Hz, 1H) ; 6.56 (dd, J = 1.3 and 3.1 Hz, 1H) ppm.
RMN ^{13}C{^{1}H} (D_2O, 25°C): δ = 151.8 ; 146.5 ; 144.3 ; 135.6 ; 122.4 ; 122.0 ; 112.6 ; 109.1 ppm.



RMN ^{1}H ($CDCl_3$, 25°C): δ = 8.24 (d, J = 8.9 Hz, 2H) ; 7.75 (d, J = 8.9 Hz, 2H) ; 7.8 (dd, J = 1.1 and 3.7 Hz, 1H) ; 7.44 (dd, J = 1.1 and 4.0 Hz, 1H) ; 7.15 (dd, J = 3.1 and 4.0 Hz, 1H) ppm.
RMN ^{13}C{^{1}H} (D_2O, 25°C): δ = 148.8 ; 141.8 ; 140.8 ; 128.9 ; 127.9 ; 126.2 ; 125.9 ; 124.6 ppm.



RMN ^{1}H ($CDCl_3$, 25°C): δ = 8.30 (d, J = 8.8 Hz, 2H) ; 7.74 (d, J = 8.8 Hz, 2H) ; 7.61 (d, J = 8.4 Hz, 2H) ; 7.53 (d, J = 8.4 Hz, 2H) ; 6.77 (dd, J = 10.9 and 17.6 Hz, 1H) ; 5.84 (d, J = 17.6 Hz, 1H) ; 5.35 (d, J = 10.9 Hz, 1H) ppm.
RMN ^{13}C{^{1}H} (D_2O, 25°C): δ = 147.2; 147.3 ; 138.4 ; 138.1 ; 127.7 ; 127.1 ; 124.3 ; 115.1 ppm.

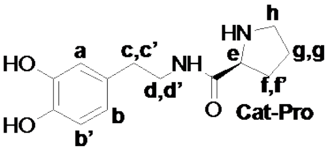
2) Literature survey

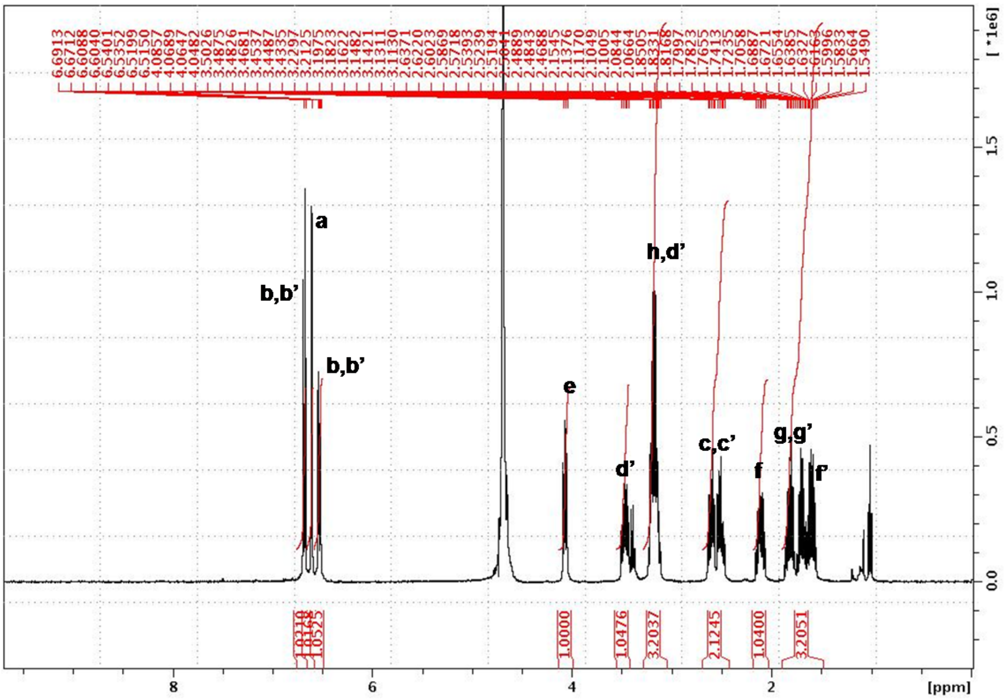
Selected Catalysts and Conditions used for Suzuki-Miyaura Cross-couplings extract from recent literature (for more examples see M. O. Sydnes *Current Organic Chemistry,* 2014, *18,* 312-326 or A. Fihri, Chem. Soc. Rev., 2011, 40, 5181–5203)

Catalysts	Conditions	TOF	references
$NiFe_2O_3$ Dopamine Pd	Cat. (1 mol %), K_3PO_4, DMF, TBAB, 36h, 110°C (X = Cl); 30h,65°C (X = Br); 20h,45°C (X = I)	5	B. Baruwati, *Org. Lett.*, **2007,** Vol. 9, No. 26
functionalized Fe_3O_4 NP with Pd(0) on surface	Cat. (0.816 mol%), K_3PO_4, MeOH 24h (X = Cl) 18h (X = Br)	7	A. Amali, *Green Chem.,* **2009**, 11, 1781-1786
Magnetic NP-supported (β-oxoiminato)(phosphanyl)Pd complex	Cat. (0.5 mol%), CsF, EtOH/H_2O (1:1), 50°C, 3h	67	M-J.Jin, *Angew. Chem. Int. Ed.* **2010**, 49,1119-1122.
Pd NP on a phosphine-functionalized magnetic support	Cat. (0.5 mol%), KOH, toluene, sealed tube, 100°C, 2h	100	N.J.S. Costa, *J. Catal*, **2010**, 276, 382-389
Co/C-ROMPgel Immobilized Pd-Complex	Cat. (1.1 mol%), K_3PO_4, H_2O/THF (2:1), 65°C	100	A.Schätz, *Adv.Funct.Mater.* **2010**, 20, 4223-4228
Magnetic NP-supported Pd	Cat. (0.1 mol%), KOH, DMF, 100°C, 2h	500	N.T.Bui, Cinh.*J.Cat*, **2011**, 32, 1667-1676
Pd on Fe_3O_4 NPs (diameter of Fe_3O_4 NPs between 25-50 nm)	Cat. (1 mol%), K_2CO_3, TBAB, DMA/H_2O (10:1), 80°C,10h (X = Br) 1h (X = I)	100	B.Wu, *Nano Today*, **2011**, 6, 75-90
Fe_3O_4@SiO_2-PPh_2 Pd	Cat. (0.5 mol%), K_2CO, CH_3OH, 60°C,1.5h	133	P. Li *Adv. Synth. Catal.* **2012**, 354: 1307–1318
Fe_3O_4@Dopa-PPh_2 Pd	Cat. (0.5 mol%), KOH, toluene, 100°C,6h	83	F. G. De Riveira, *Chem. Eur. J.* **2013**, 19, 11963 – 11974
Fe_3O_4@SiO_2@IL-NH2 Pd	Cat. (0.5 mol%), NaOH, , EtOH/H_2O 25°C,3h	67	J. Wang, *Tetrahedron Lett.* **2013**, 54, 238–241
Pd^0 NPs stabilized by tripodal based ligands (2.1 ± 0.4 nm)	Cat. (0.05 mol%), K_2CO_3, DMF/H_2O (1:1), 100°C, 3h (X = Br) 1h (X = I)	1800	B. Borah., *Catal. Today*, **2012**, 198, 174-183
Dendrimer-stabilized Pd NPs (2.3 ± 0.2 nm)	Cat. (0.01 mol%), K_3PO_4, EtOH/H_2O (1:1), 25°C,6h	1533	C. Ornelas, *Adv. Synth. Catal.*, **2008**, 350, 837-845
Pd/porous SiO2 yolk-shell NPs (Pd/pSiO_2)	Cat. (0.003 mol%), Cs_2CO_3,,DMF/H_2O (20:1), 200°C,3h	11000	J.Park, *J. Phy. Chem. C*, **2011**, 115, 14772-15777
MOF PI Pd	Cat. (0.025 mol%), K_2CO_3,EtOH/H_2O, 80°C,3h	1333	D. Saha *Langmuir* **2013**, 29, 3140−3151
Resin encapsulated Pd NP	Cat. (0.031 mol%), Na_2CO_3, EtOH/H_2O (3:2), MW (140°C, 100W), 8 min.	20000	H.Kaur, *Catal. Commun.* **2011**, 12, 1384-1388

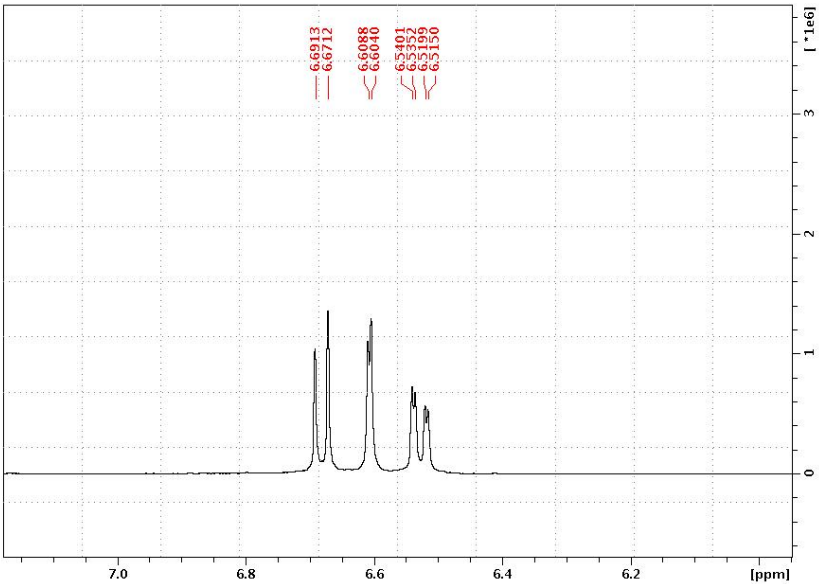
3) RMN, HRMS and FTIR spectra for Cat-Pro

RMN ^{1}H

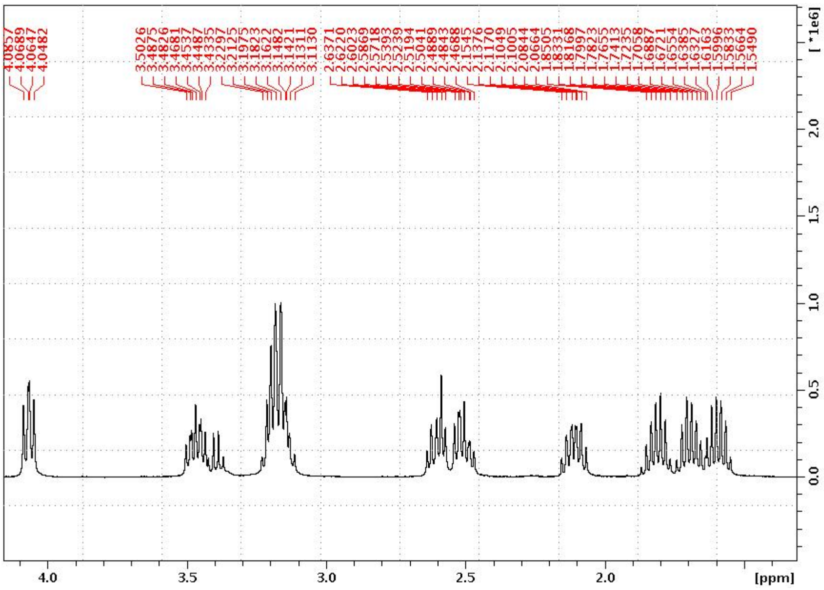




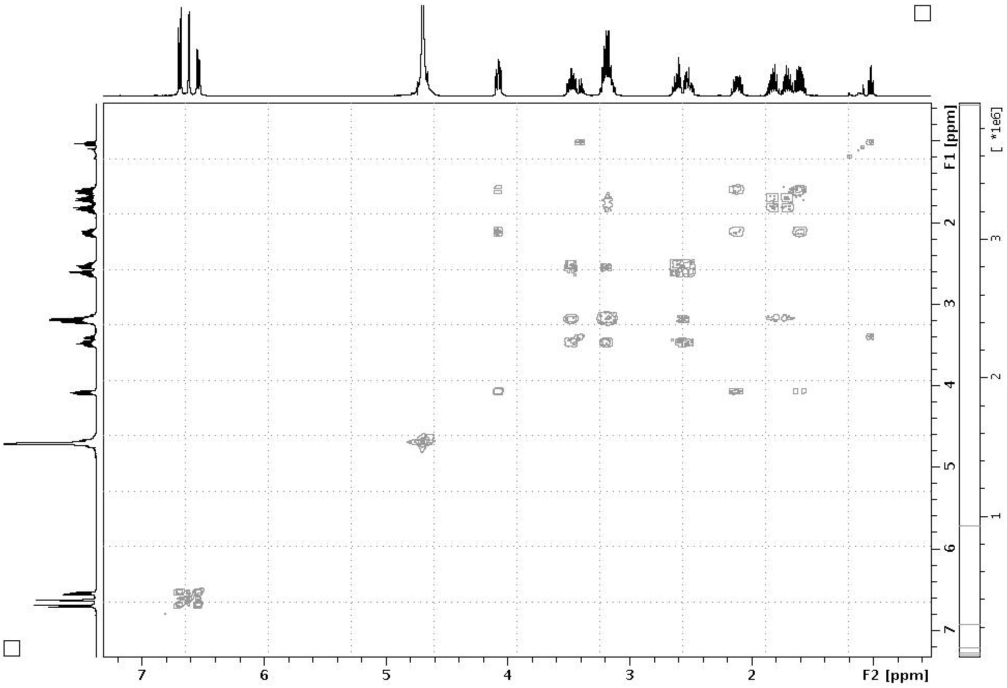
Zoom from 6-8 ppm



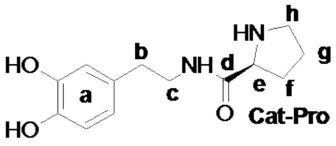
Zoom from 1-5 ppm

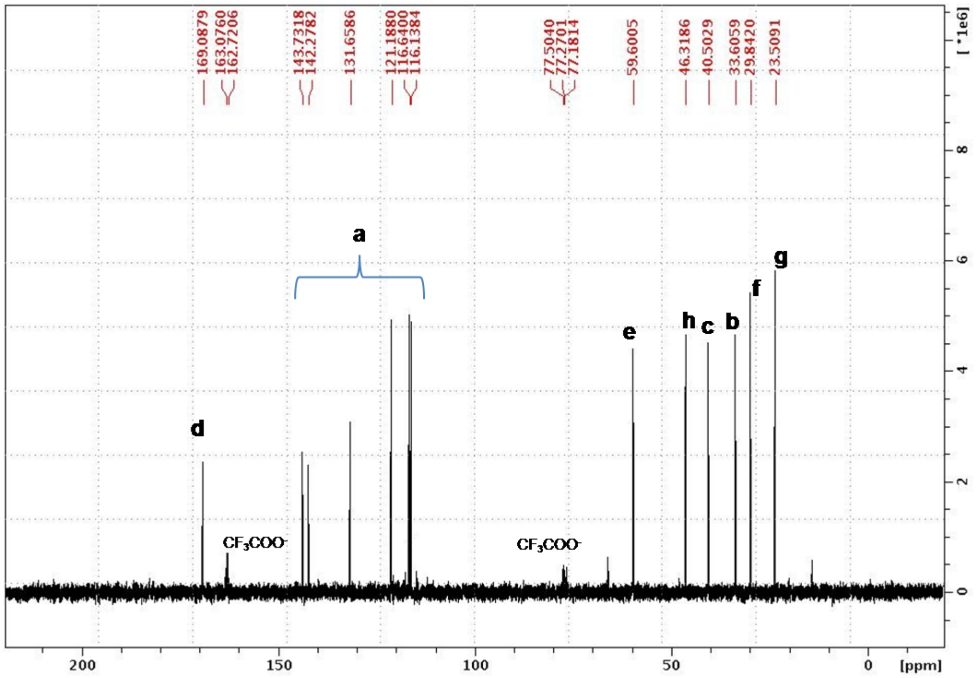


COSY



RMN ^{13}C


HO
HO
a
b
c
NH
d
O
HN
h
g
e
f
Cat-Pro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77.1814
59.6005
46.3186
40.5029
33.6059
29.8420
23.5091
a
d
CF$_3$COO$^-$
CF$_3$COO$^-$
e
h
c
b
f
g
[*1e6]
8
6
4
2
0
200
150
100
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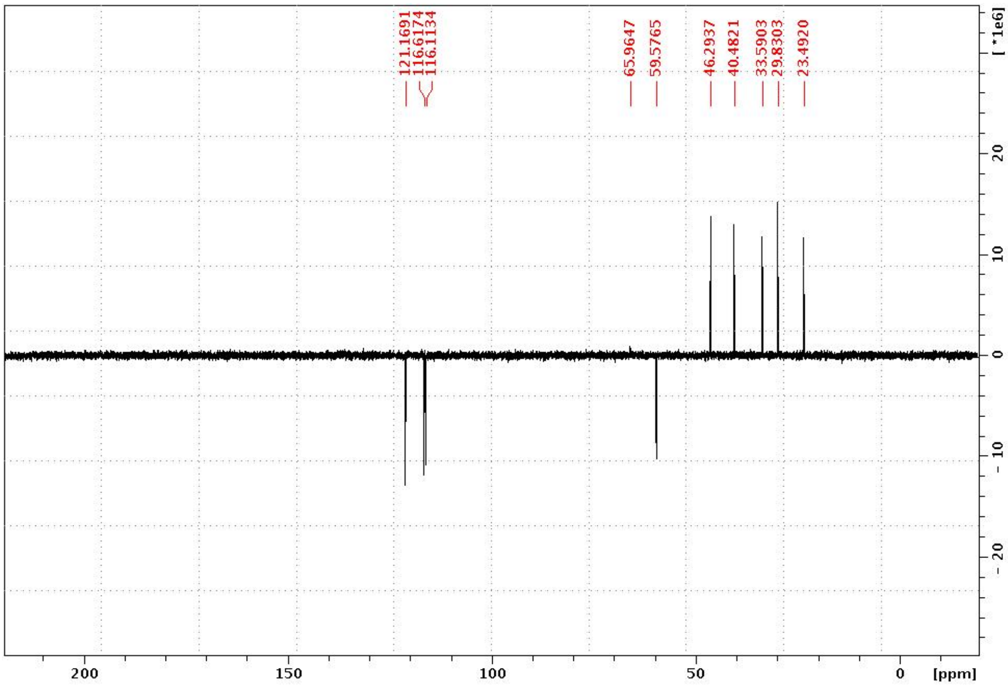
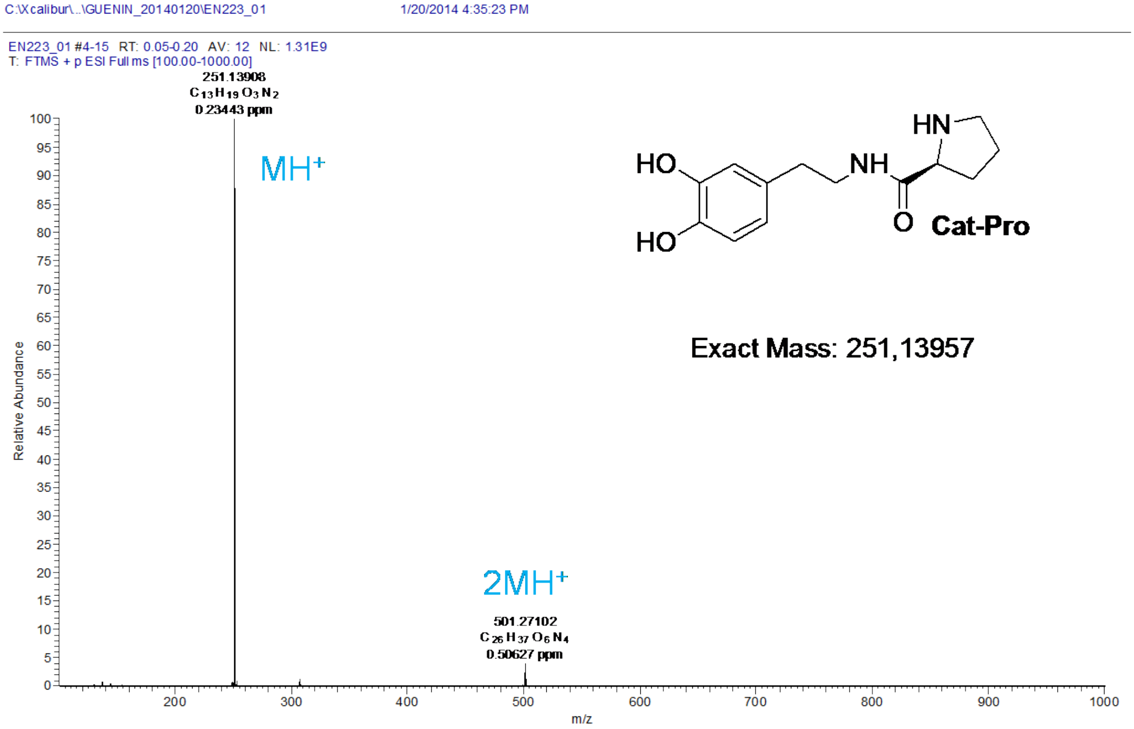
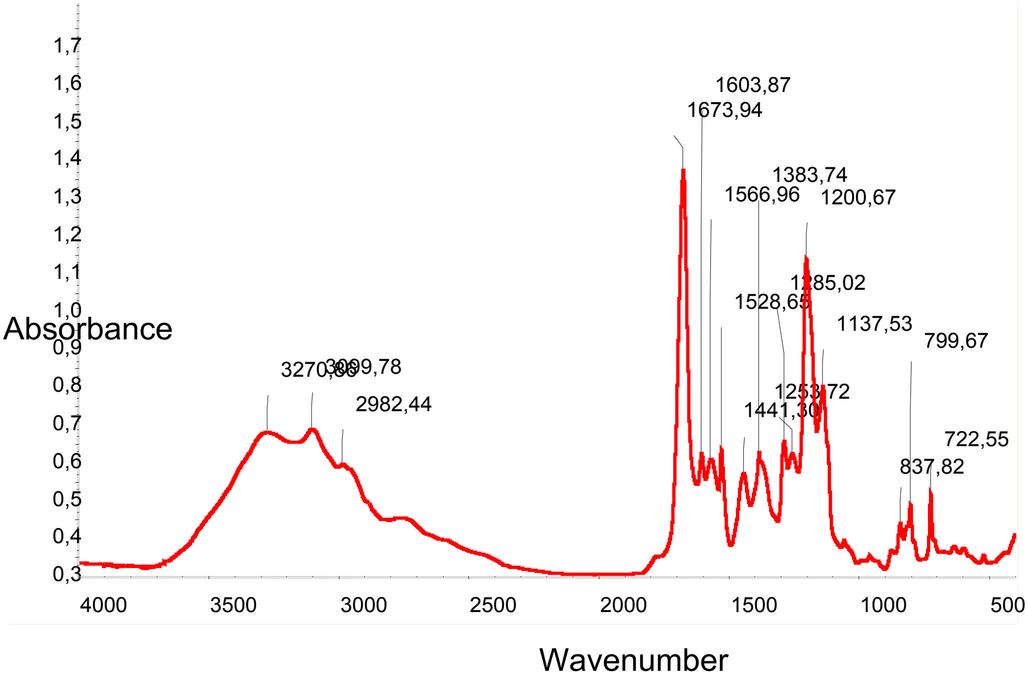
DEPT


121.1691
116.6174
116.1134
65.9647
59.5765
46.2937
40.4821
33.5903
29.8303
23.4920
[*1e6]
20
10
0
- 10
- 20
200
150
100
50
0
[ppm]

HRMS

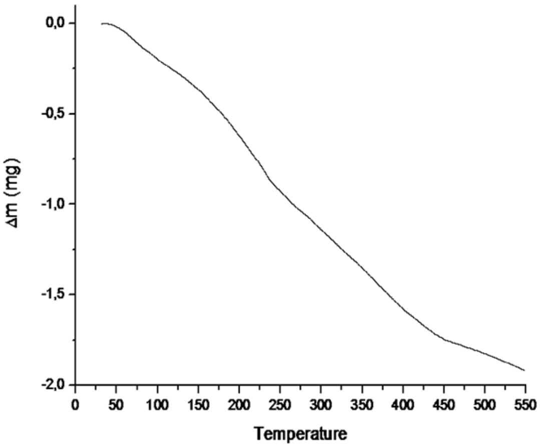

C:\Xcalibur\..\GUENIN_20140120\EN223_01
1/20/2014 4:35:23 PM
EN223_01 #4-15 RT: 0.05-0.20 AV: 12 NL: 1.31E9
T: FTMS + p ESI Full ms [100.00-1000.00]
251.13908
$C_{13}H_{19}O_3N_2$
0.23443 ppm
MH⁺
2MH⁺
501.27102
$C_{26}H_{37}O_6N_4$
0.50627 ppm
Relative Abundance
m/z
HO
HO
NH
HN
O
Cat-Pro
Exact Mass: 251,13957

FTIR

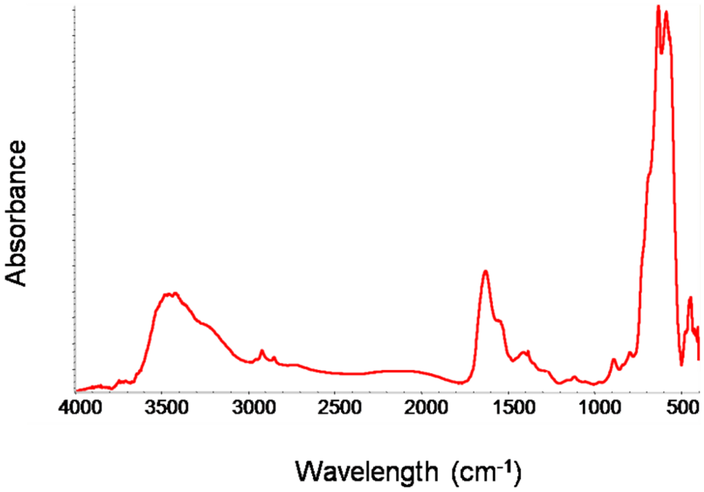

Absorbance
Wavenumber
1603,87
1673,94
1383,74
1566,96
1200,67
1285,02
1528,65
1137,53
799,67
3270,86
3099,78
2982,44
1253,72
1441,30
722,55
837,82

4) γ-Fe_2O_3@Cat-Pro

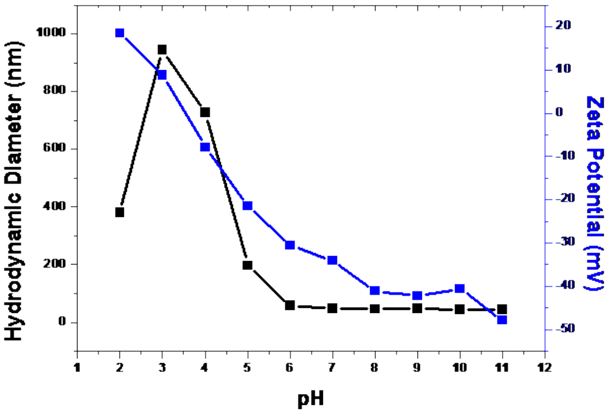
ATG



FTIR



hydrodynamic diameter and zeta potential evolution versus pH

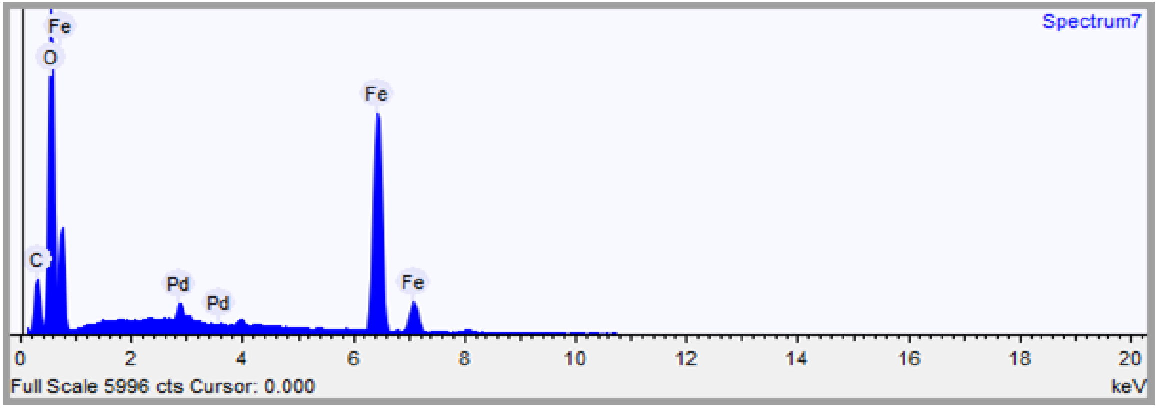


5) γ-Fe_2O_3@Cat-Pro(Pd)

EDX

Acquisition conditions

Acquisition time (s)	120.0
Process time	5
Accelerating voltage (kV)	15.0



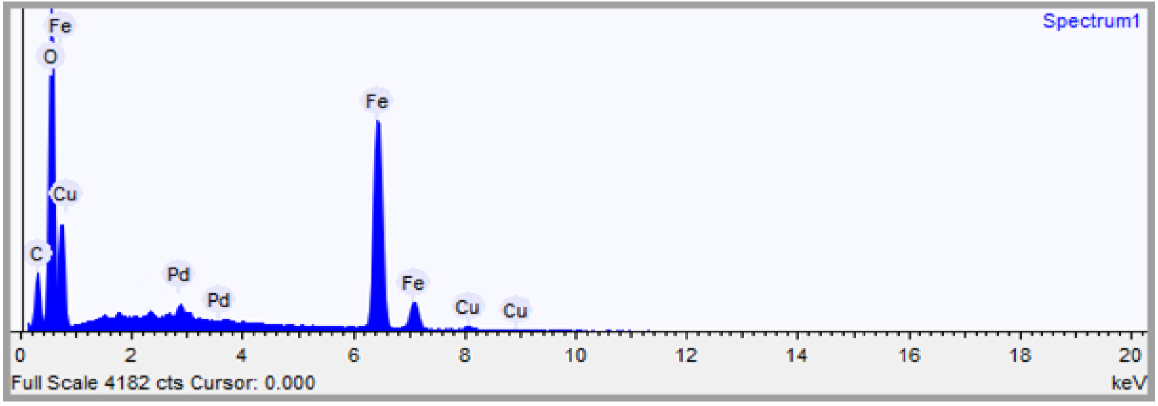
Summary results

Element	Weight %	Weight % σ	Atomic %
Carbon	13.481	0.837	27.332
Oxygen	32.834	0.388	49.874
Iron	51.021	0.543	22.202
Palladium	2.593	0.140	0.592

EDX after 8 runs

Acquisition conditions

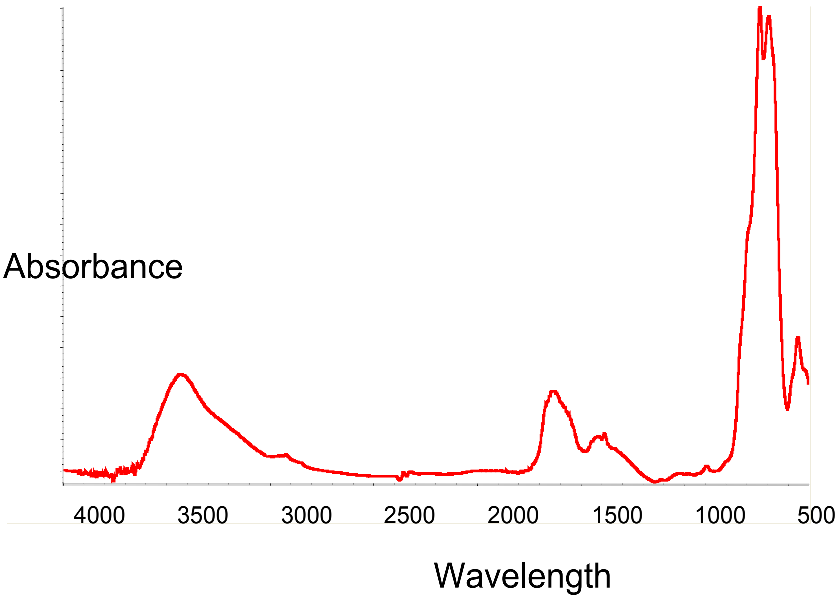
Acquisition time (s)	100.0
Process time	5
Accelerating voltage (kV)	15.0



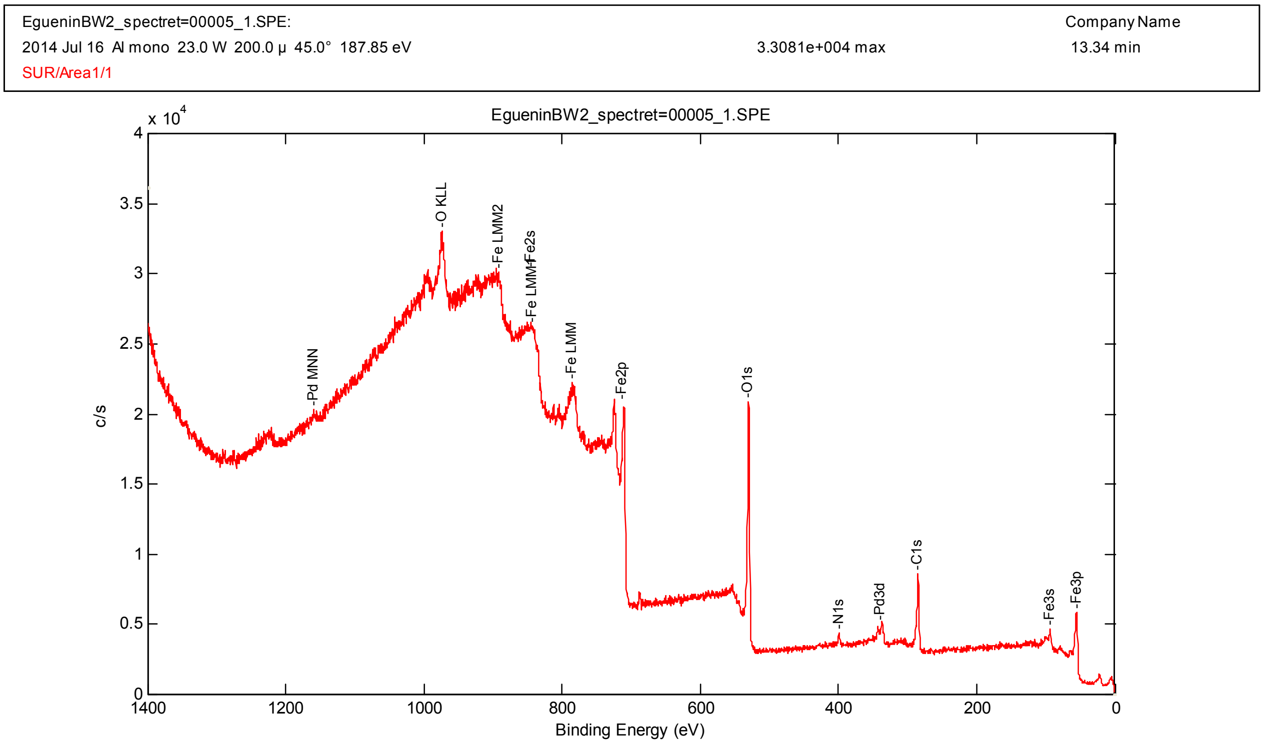
Summary results

Element	Weight %	Weight % σ	Atomic %
Carbon	14.318	1.009	28.370
Oxygen	33.421	0.475	49.713
Iron	49.826	0.646	21.233
Copper	0.000	0.000	0.199
Palladium	2.167	0.163	0.485

FTIR



XPS

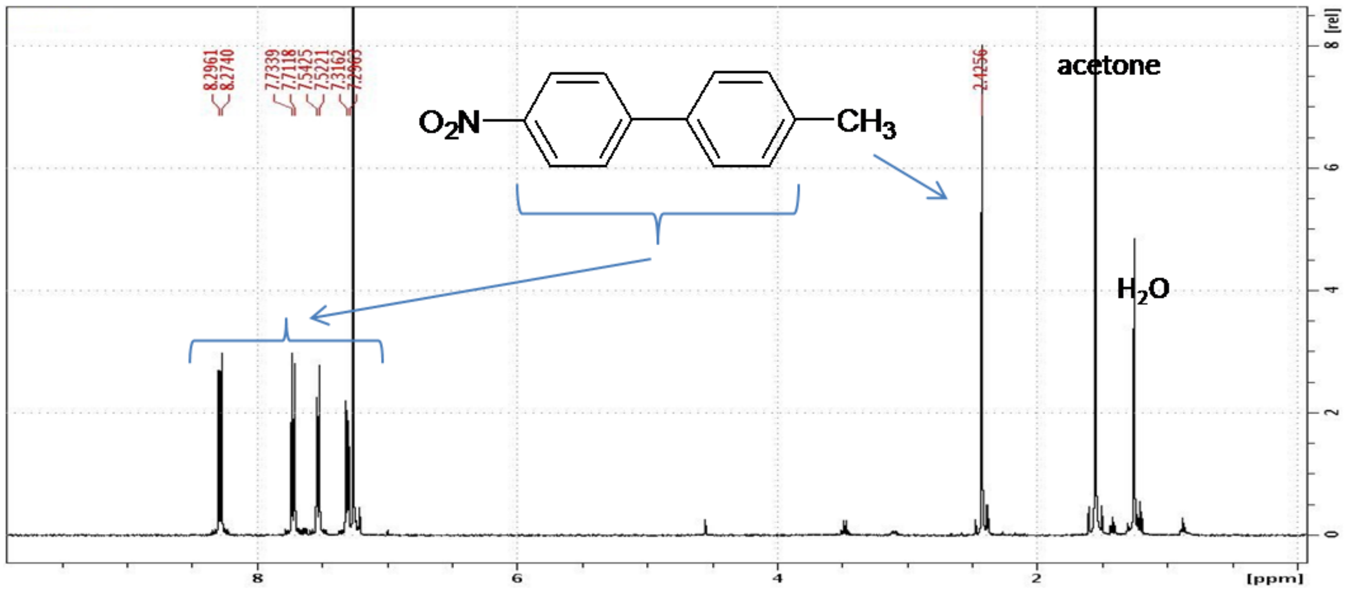


EgueninBW2_spectret=00005_1.SPE:
2014 Jul 16 Al mono 23.0 W 200.0 µ 45.0° 187.85 eV
SUR/Area1/1

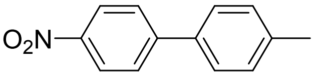
3.3081e+004 max

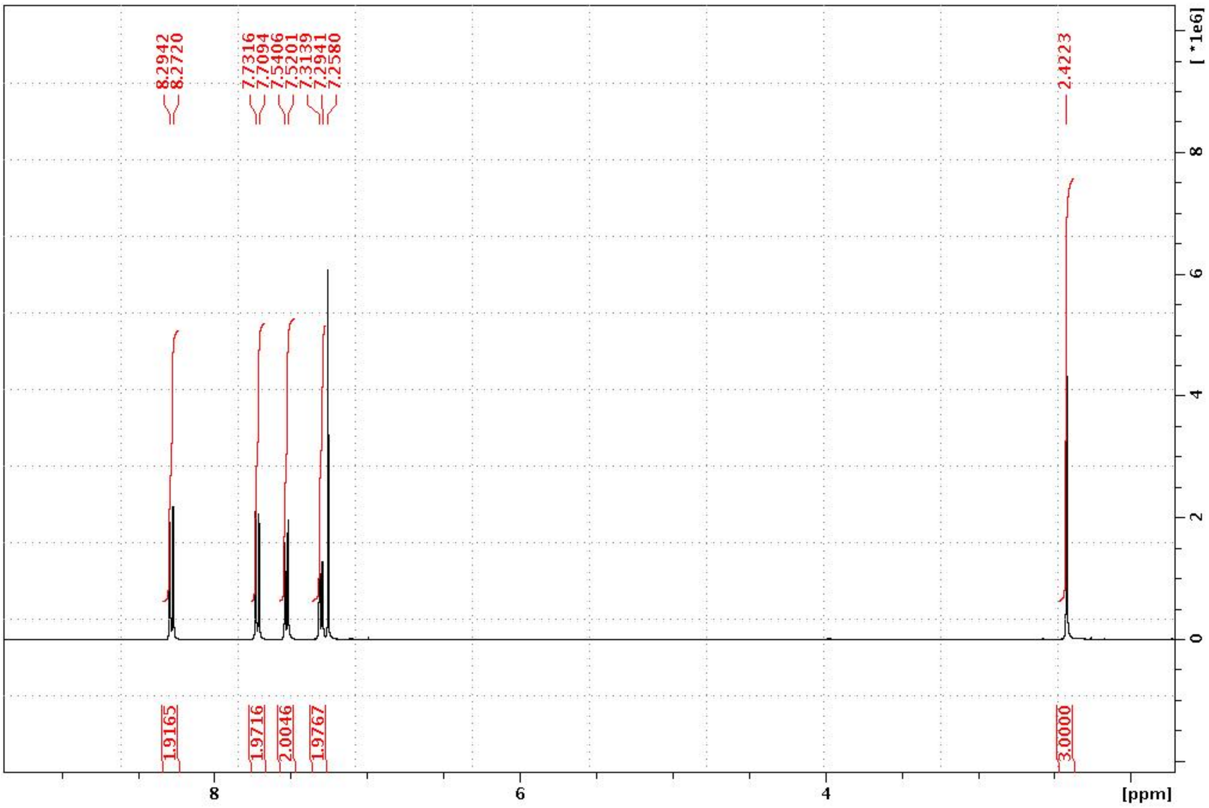
Company Name
13.34 min

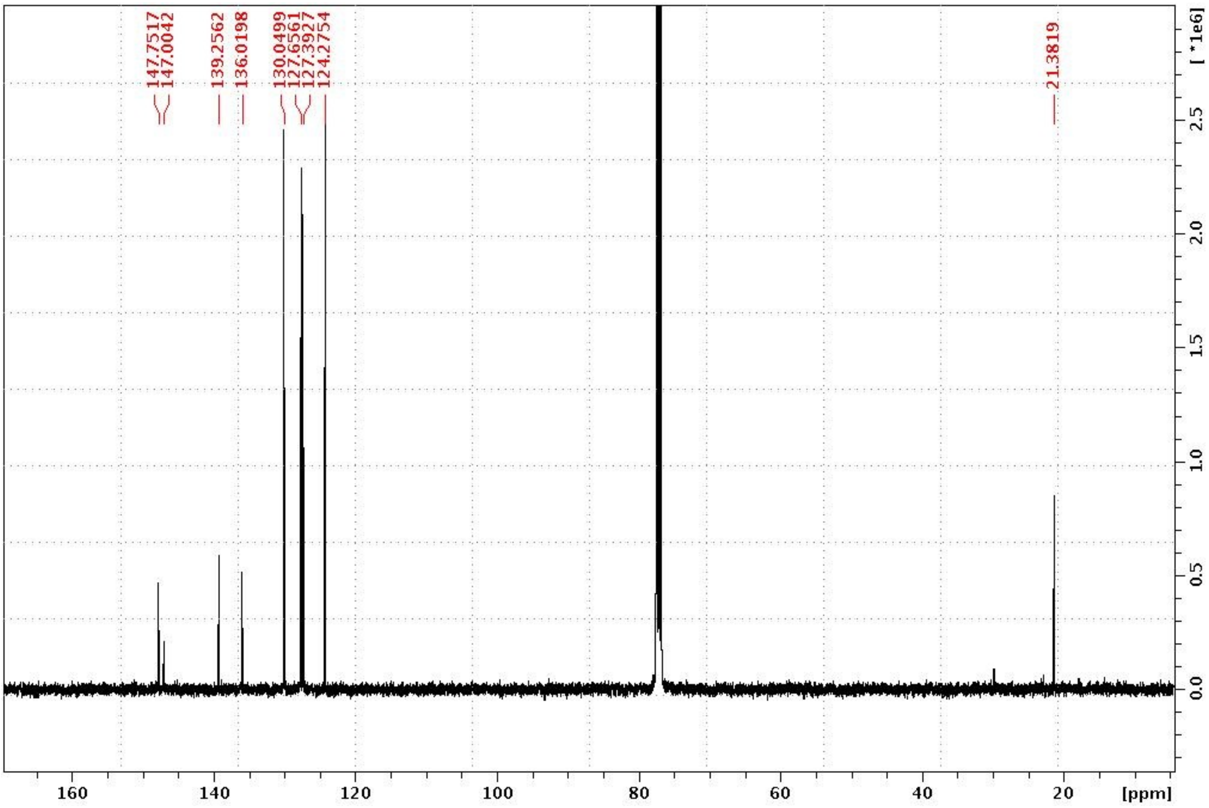
7) ^{1}H NMR spectrum of the crude mixture after catalysis (no purifications other than extraction from the media and evaporation were done)

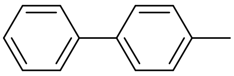


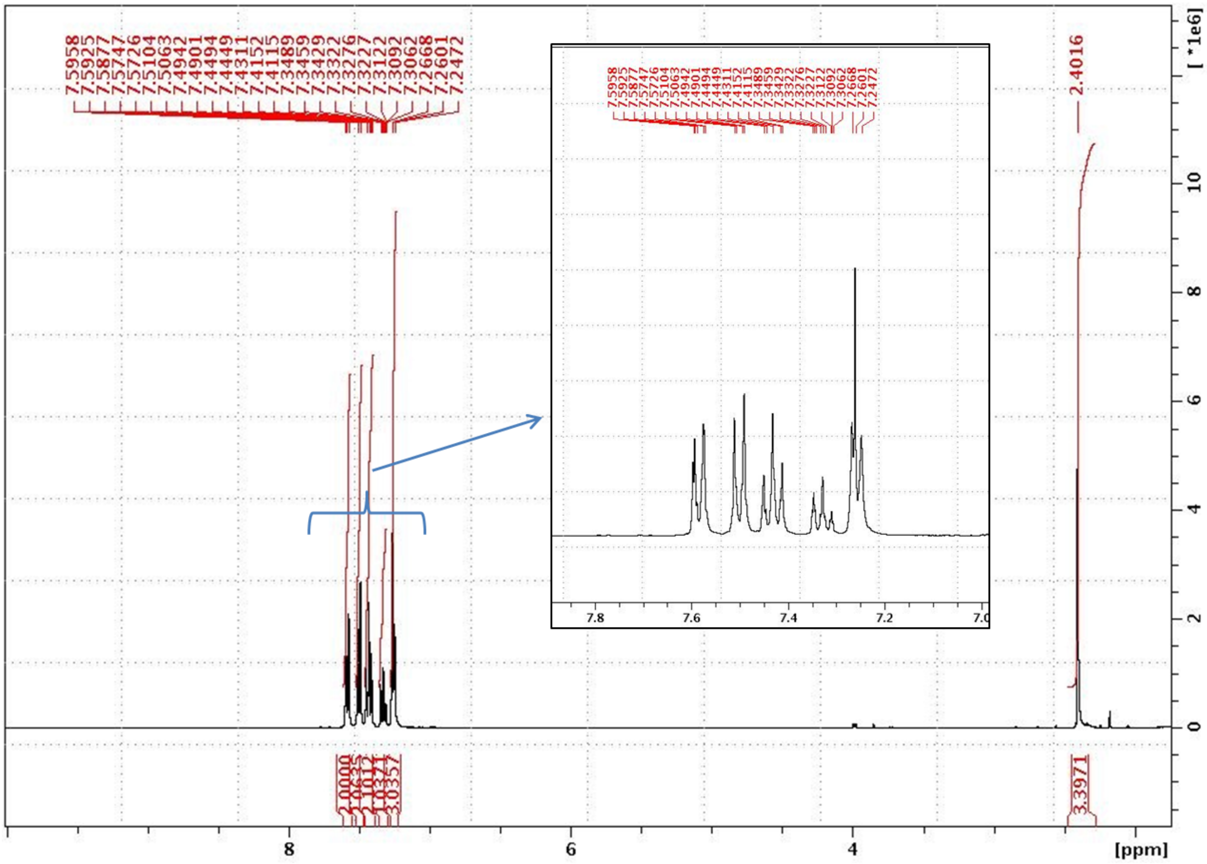
8) NMR spectra for products of the Suzuki-Miyaura cross coupling

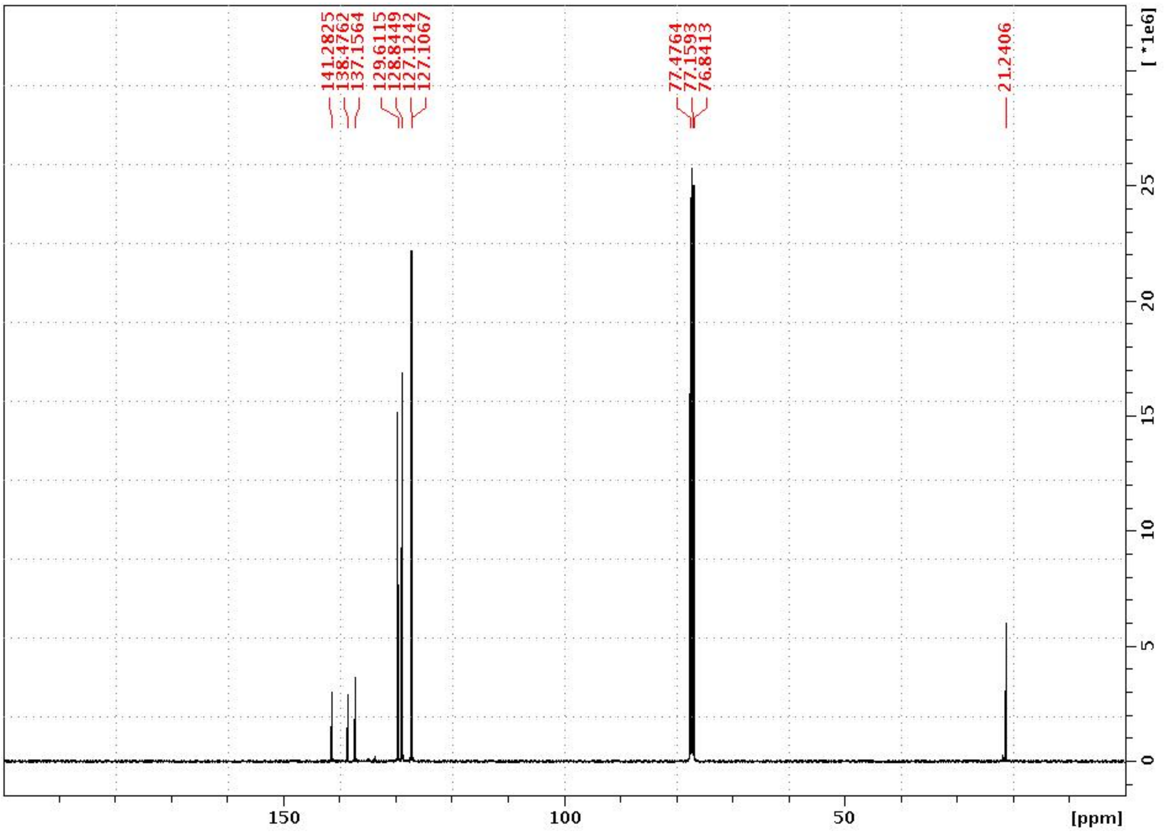


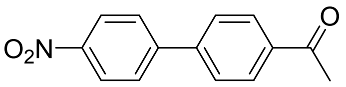


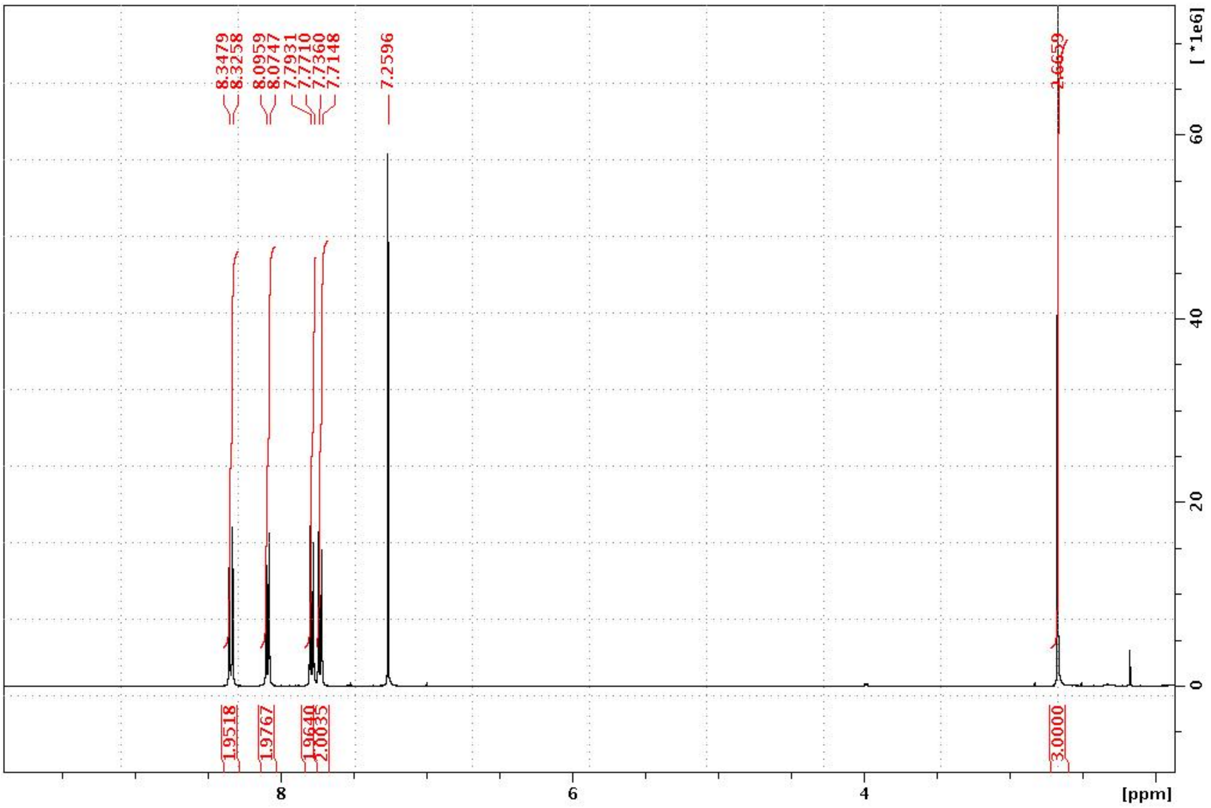


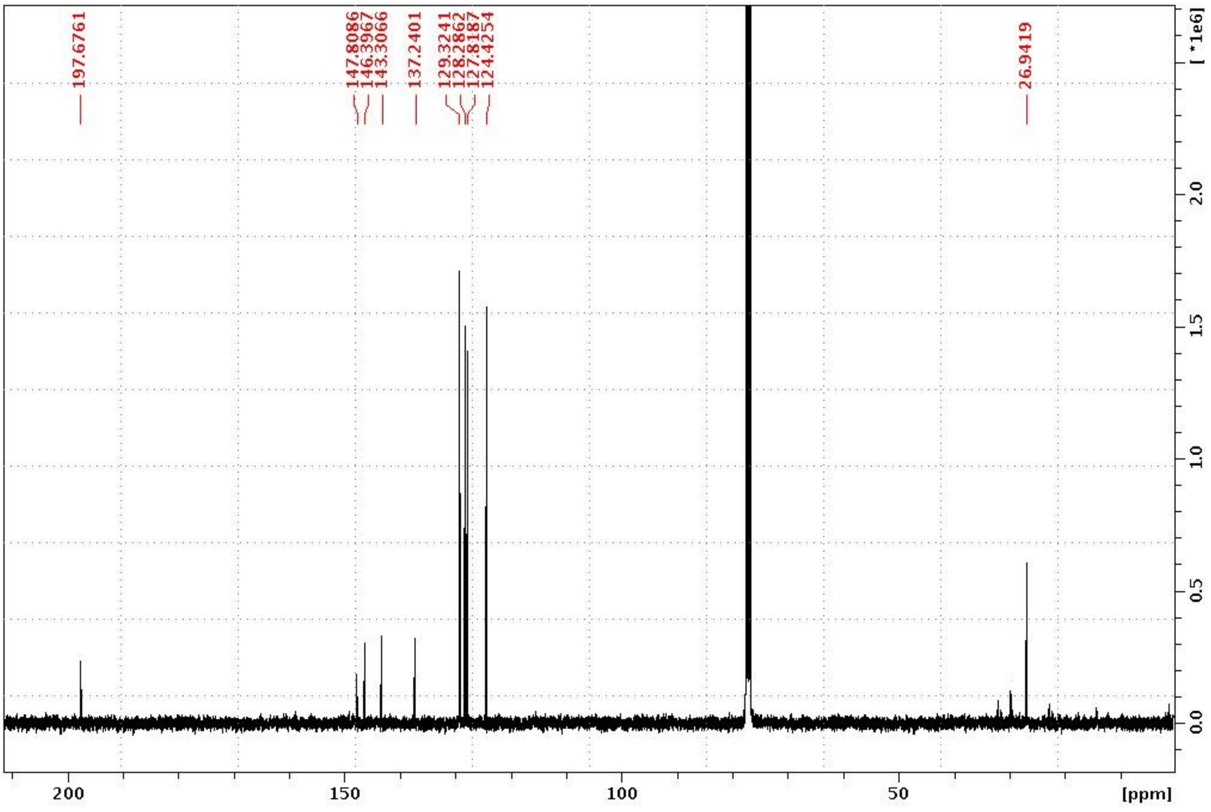


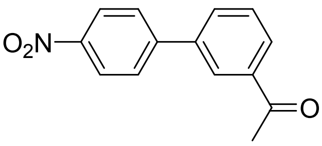

7.5958
7.5925
7.5877
7.5747
7.5726
7.5104
7.5063
7.4942
7.4901
7.4494
7.4449
7.4311
7.4152
7.4115
7.3489
7.3459
7.3429
7.3322
7.3276
7.3227
7.3122
7.3092
7.3062
7.2668
7.2601
7.2472
2.4016
[*1e6]
10
8
6
4
2
0
2.0000
1.9635
2.1012
1.0371
3.0357
3.3971
8
6
4
[ppm]
7.8
7.6
7.4
7.2
7.0

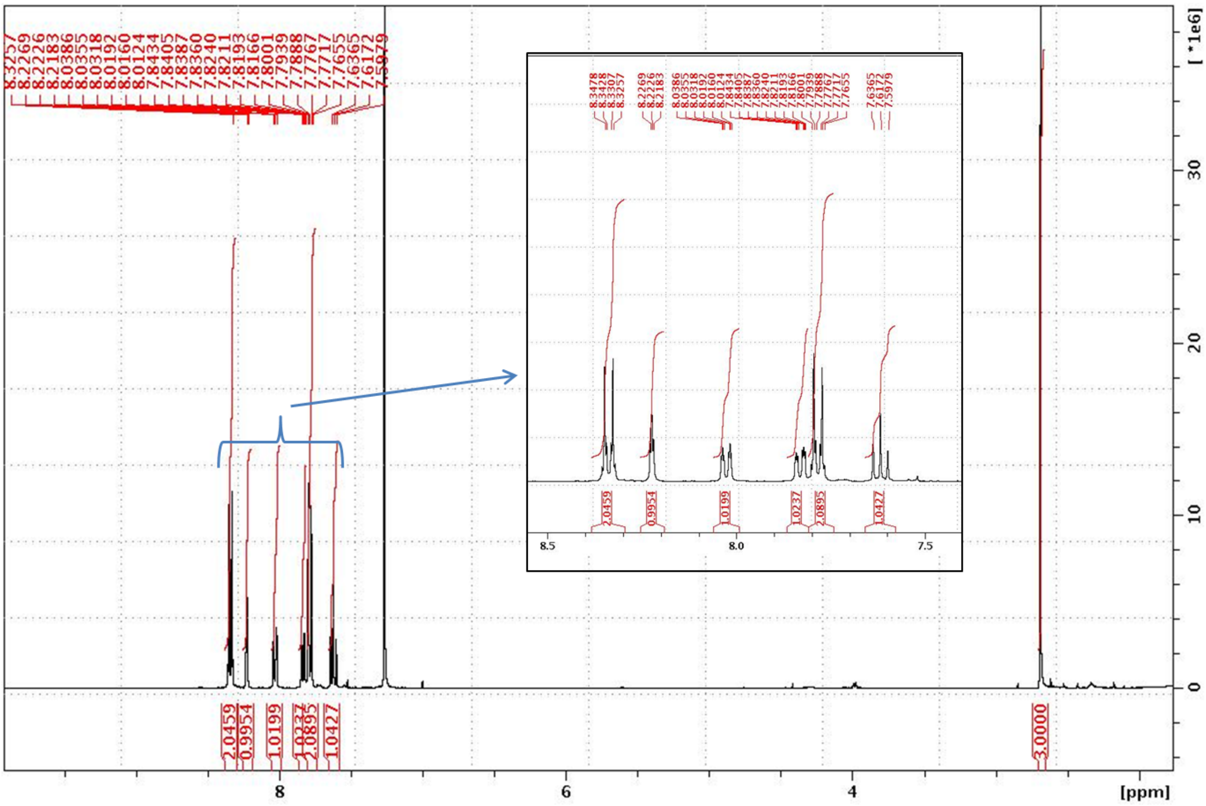

141.2825
138.4762
137.1564
129.6115
128.8449
127.1242
127.1067
77.4764
77.1593
76.8413
21.2406
[*1e6]
25
20
15
10
5
0
150
100
50
[ppm]

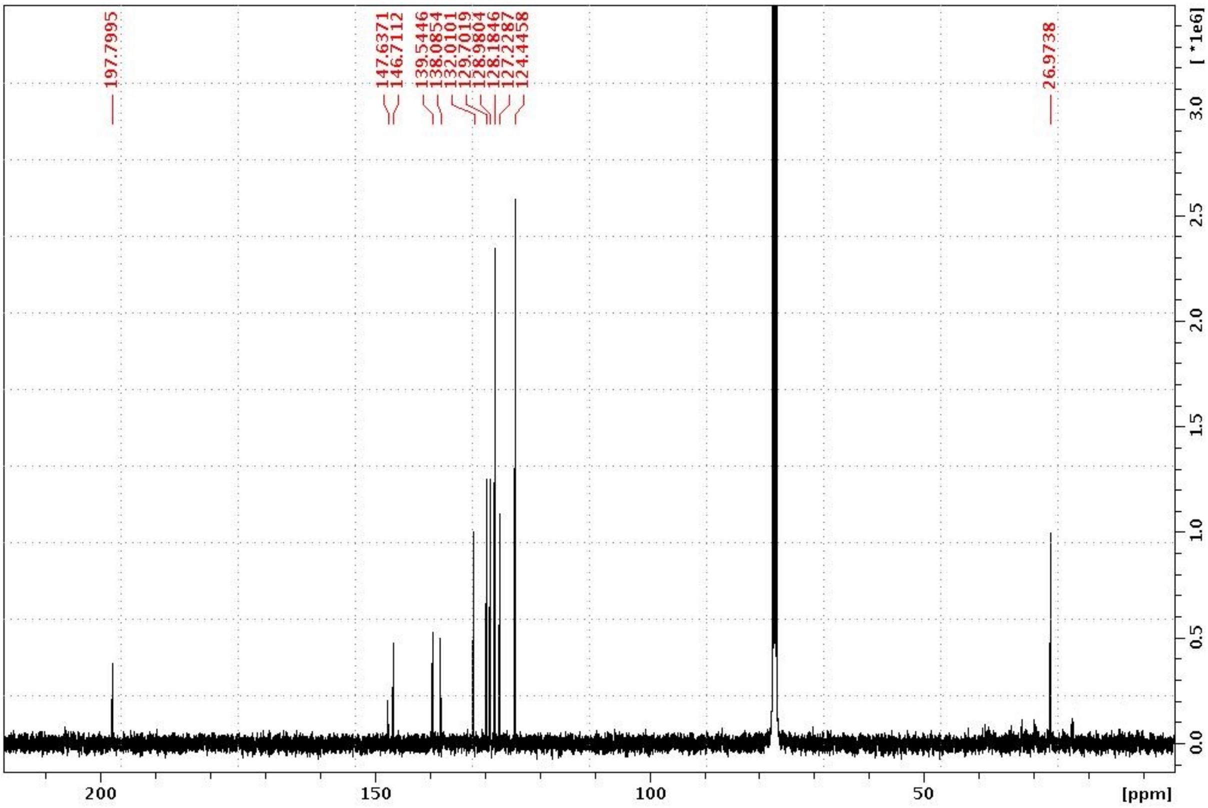

O
O2N

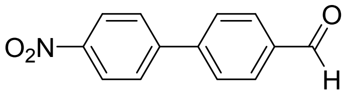

8.3479
8.3258
8.0959
8.0747
7.7931
7.7710
7.7360
7.7148
7.2596
2.6659
1.9518
1.9767
1.9640
2.0035
3.0000
[*1e6]
60
40
20
0
8
6
4
[ppm]

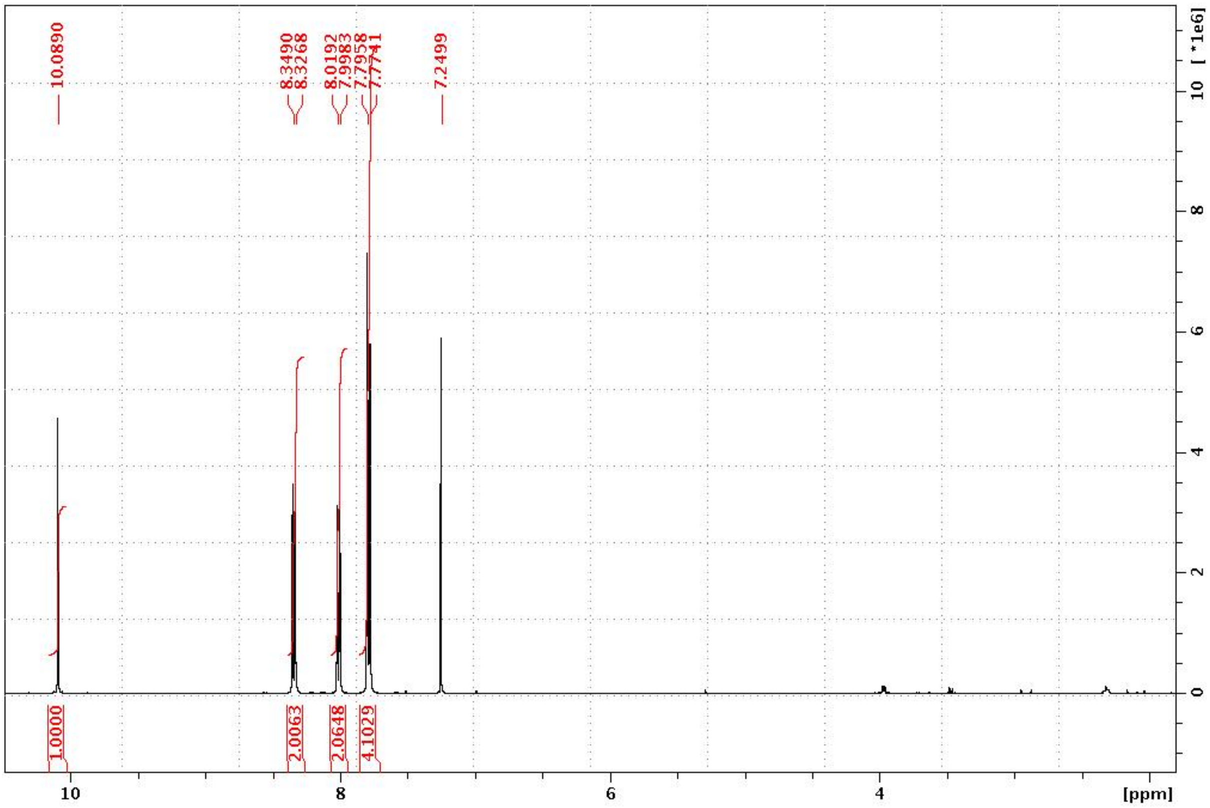

197.6761
147.8086
146.3967
143.3066
137.2401
129.3241
128.2862
127.8187
124.4254
26.9419
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
[ppm]

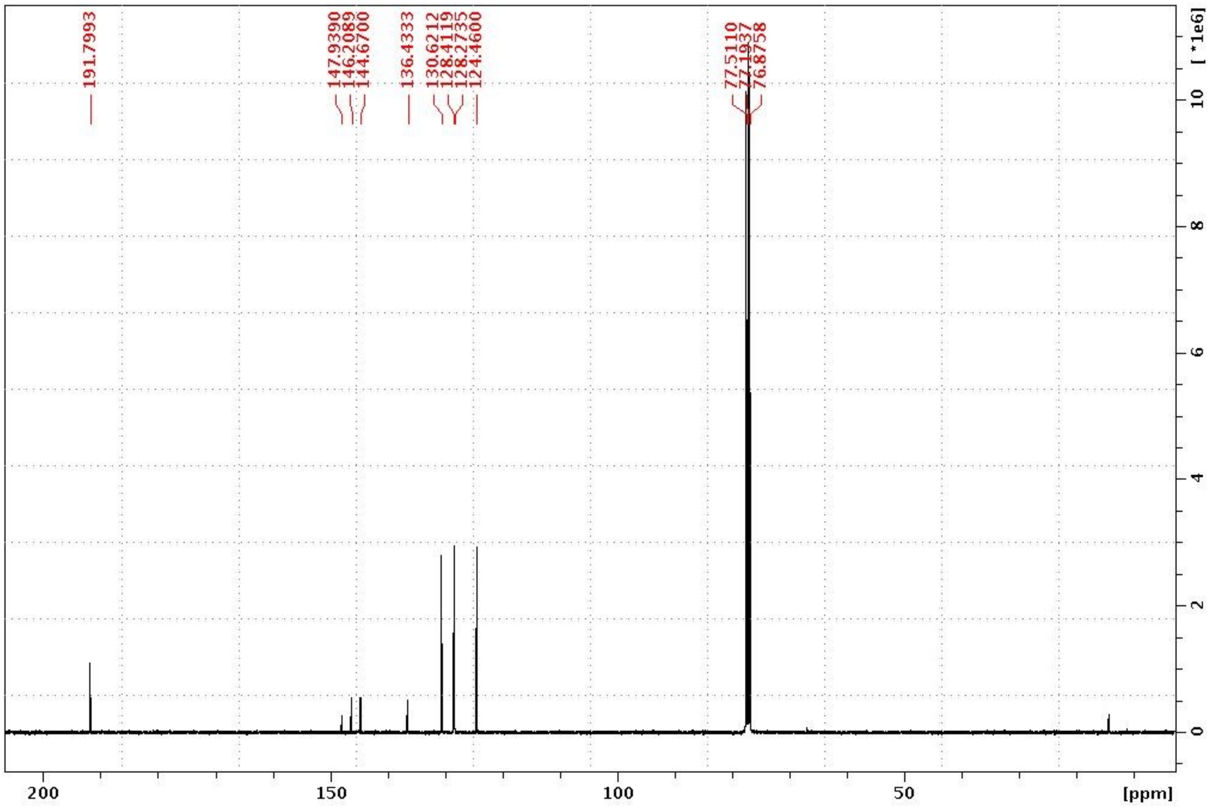

O2N
O

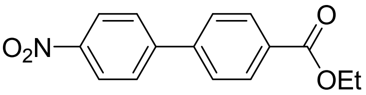

8.3257
8.2269
8.2226
8.2183
8.0386
8.0355
8.0318
8.0192
8.0160
8.0124
7.8434
7.8405
7.8387
7.8360
7.8240
7.8211
7.8193
7.8166
7.8001
7.7939
7.7888
7.7767
7.7717
7.7655
7.6365
7.6172
7.5979
8.3478
8.3428
8.3307
8.3257
2.0459
0.9954
1.0199
1.0237
1.0895
1.0427
3.0000
8.5
8.0
7.5
8
6
4
[ppm]
[*1e6]
30
20
10
0

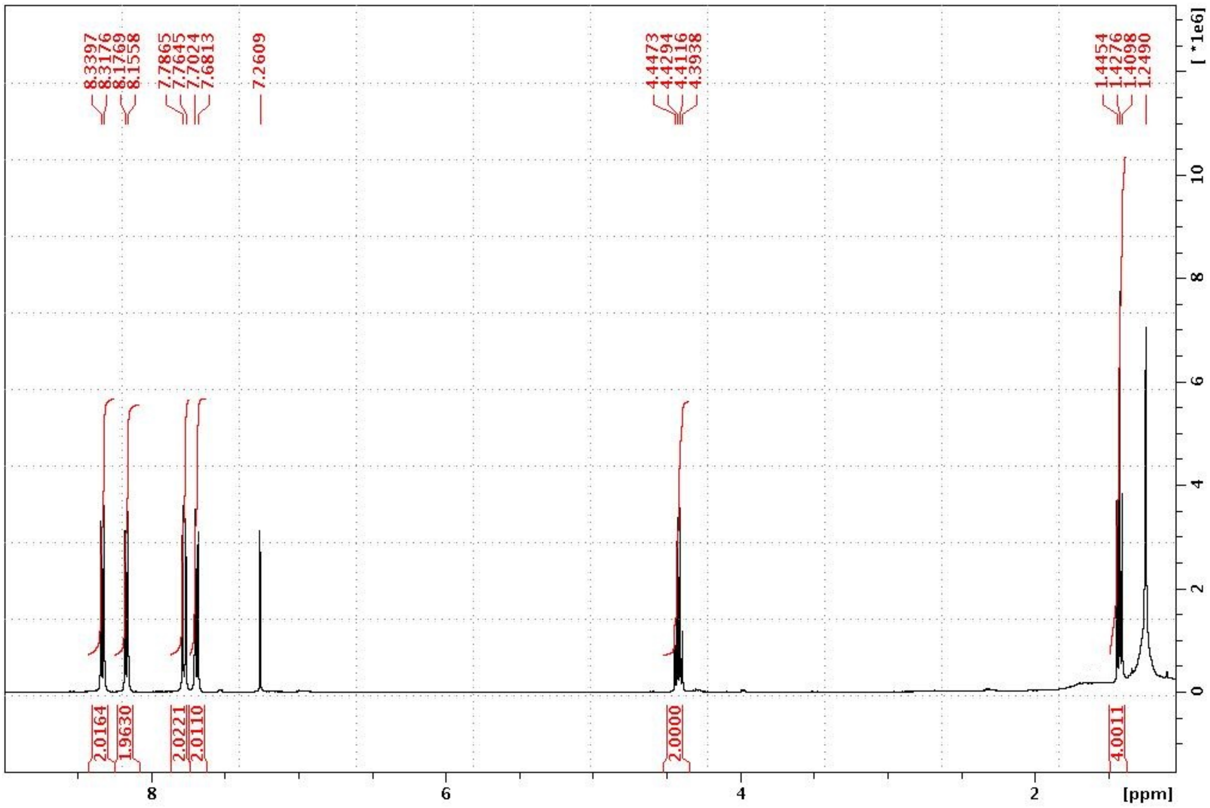

197.7995
147.6371
146.7112
139.5446
138.0854
132.0101
129.7019
128.9804
128.1846
127.2287
124.4458
26.9738
200
150
100
50
[ppm]
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0

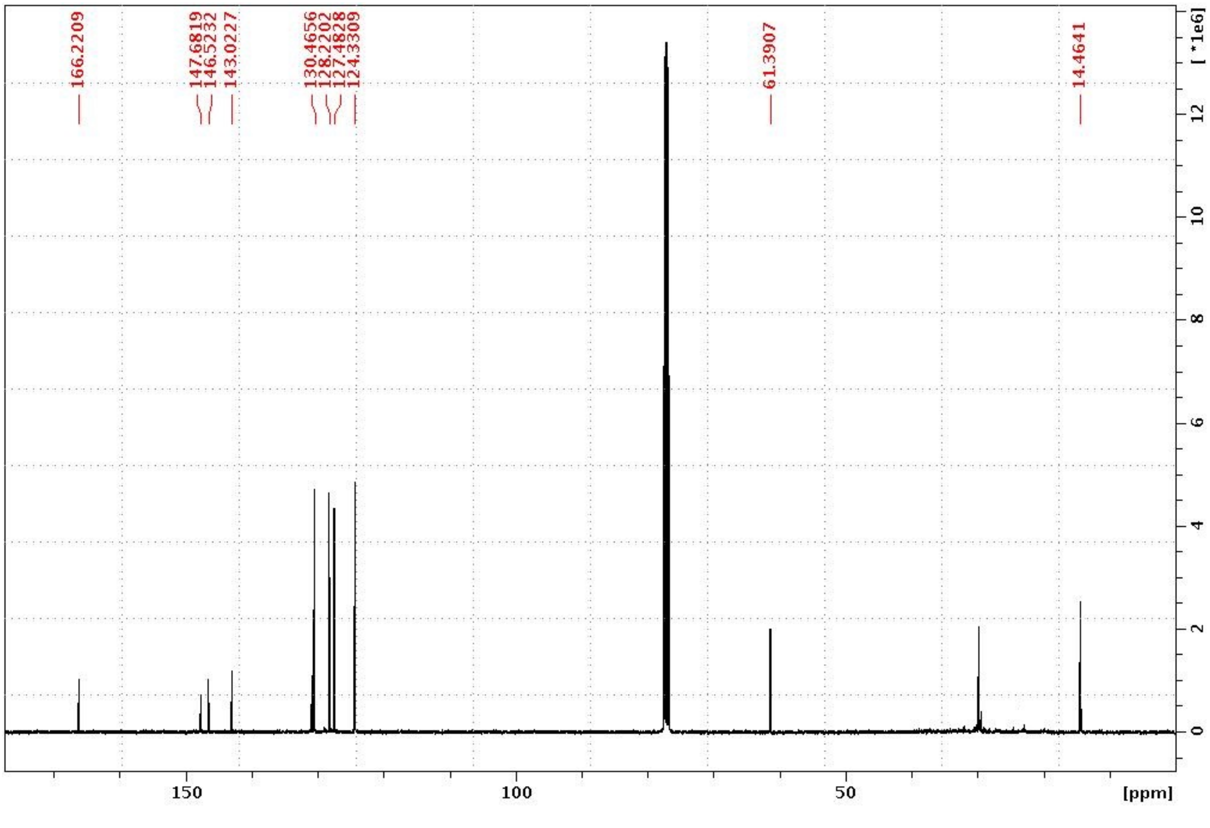

O
O2N
H


10.0890
8.3490
8.3268
8.0192
7.9983
7.7958
7.7741
7.2499
1.0000
2.0063
2.0648
4.1029
10
8
6
4
[ppm]
[*1e6]
10
8
6
4
2
0

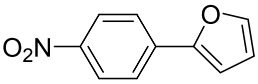

191.7993
147.9390
146.2089
144.6700
136.4333
130.6212
128.4119
128.2735
124.4600
77.5110
77.1937
76.8758
200
150
100
50
[ppm]
[*1e6]
10
8
6
4
2
0

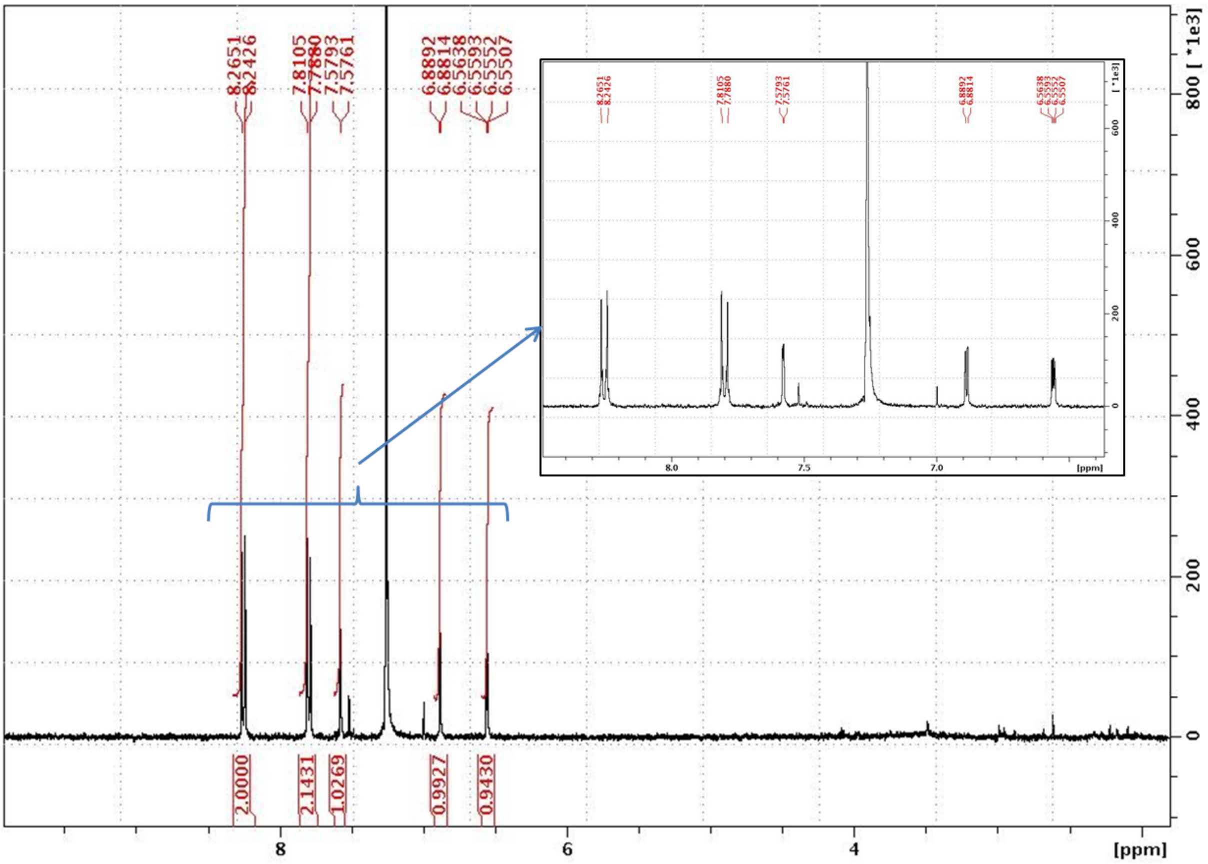






NB: acetone peak can be seen on both spectra


O
O_2N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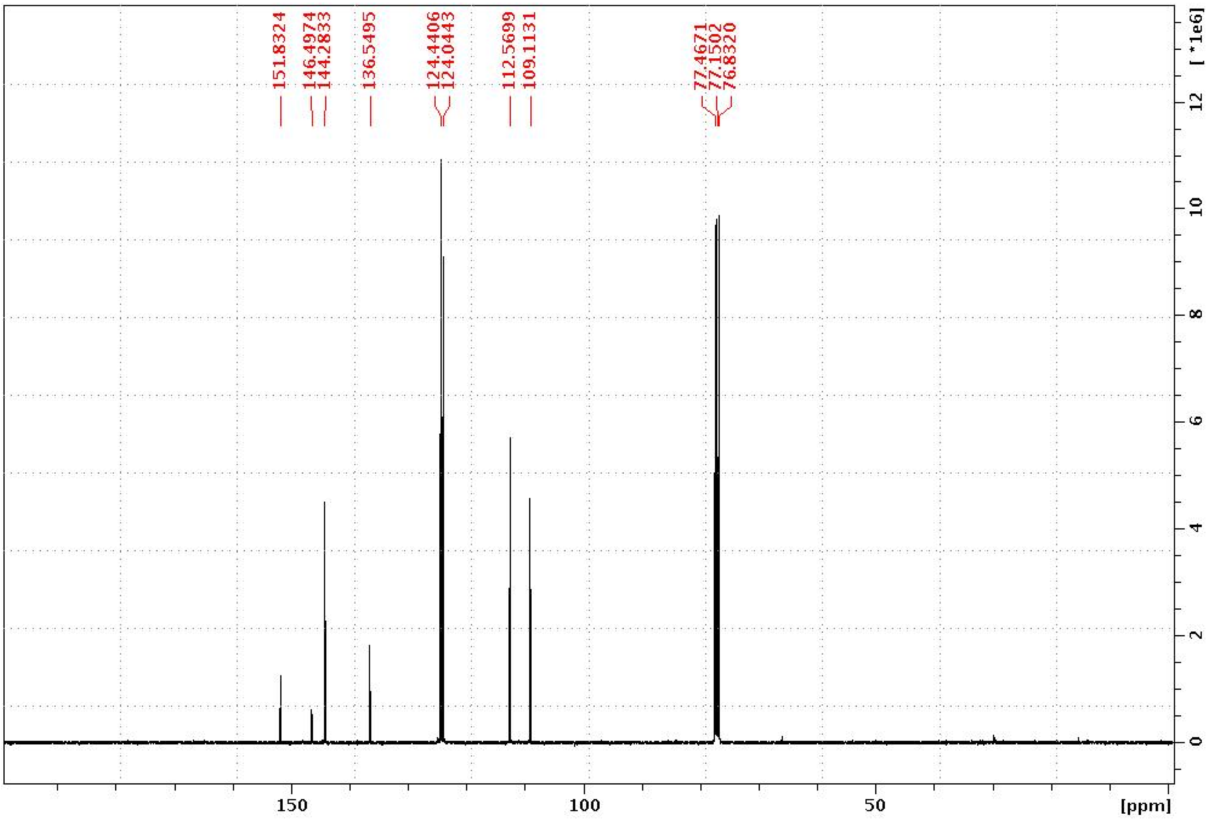
8.2426
7.8105
7.7880
7.5793
7.5761
6.8892
6.8814
6.5638
6.5593
6.5552
6.5507
2.0000
2.1431
1.0269
0.9927
0.9430
8
6
4
[ppm]
0
200
400
600
800 [*1e3]
8.0
7.5
7.0
[ppm]
[*1e3]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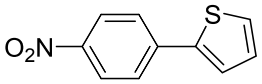
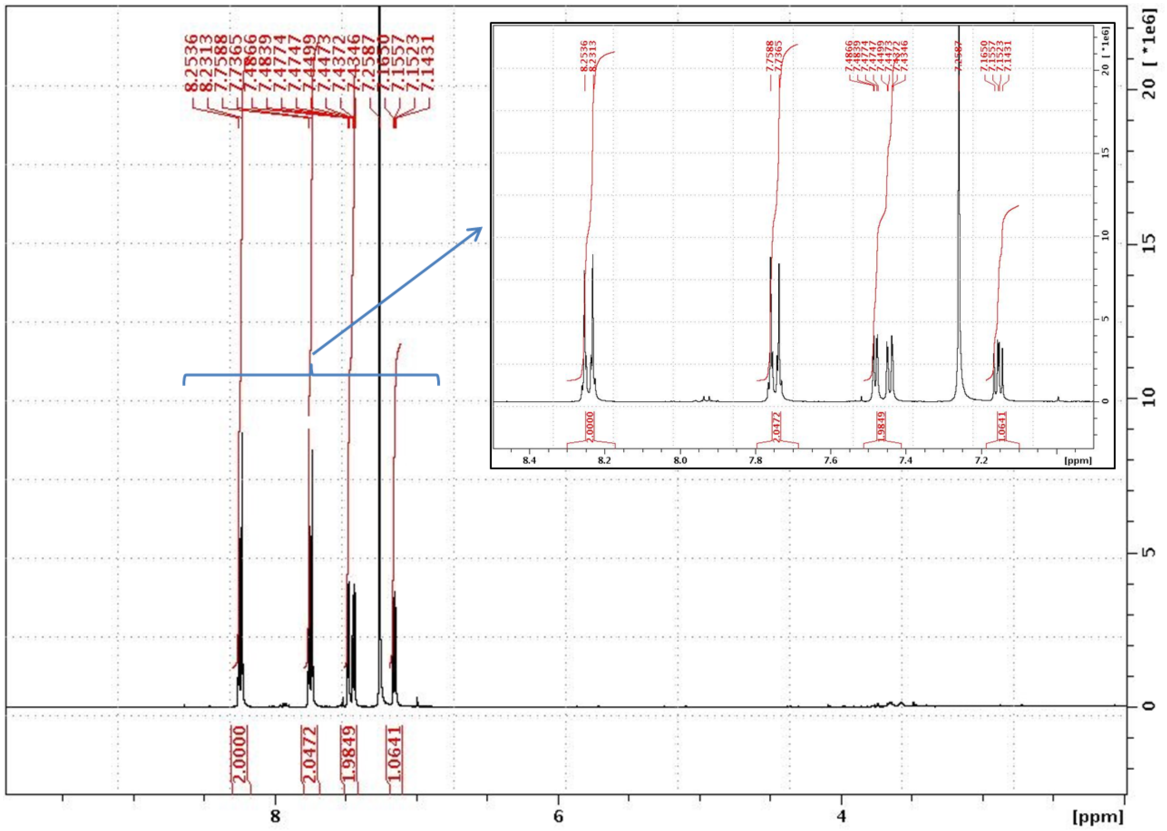
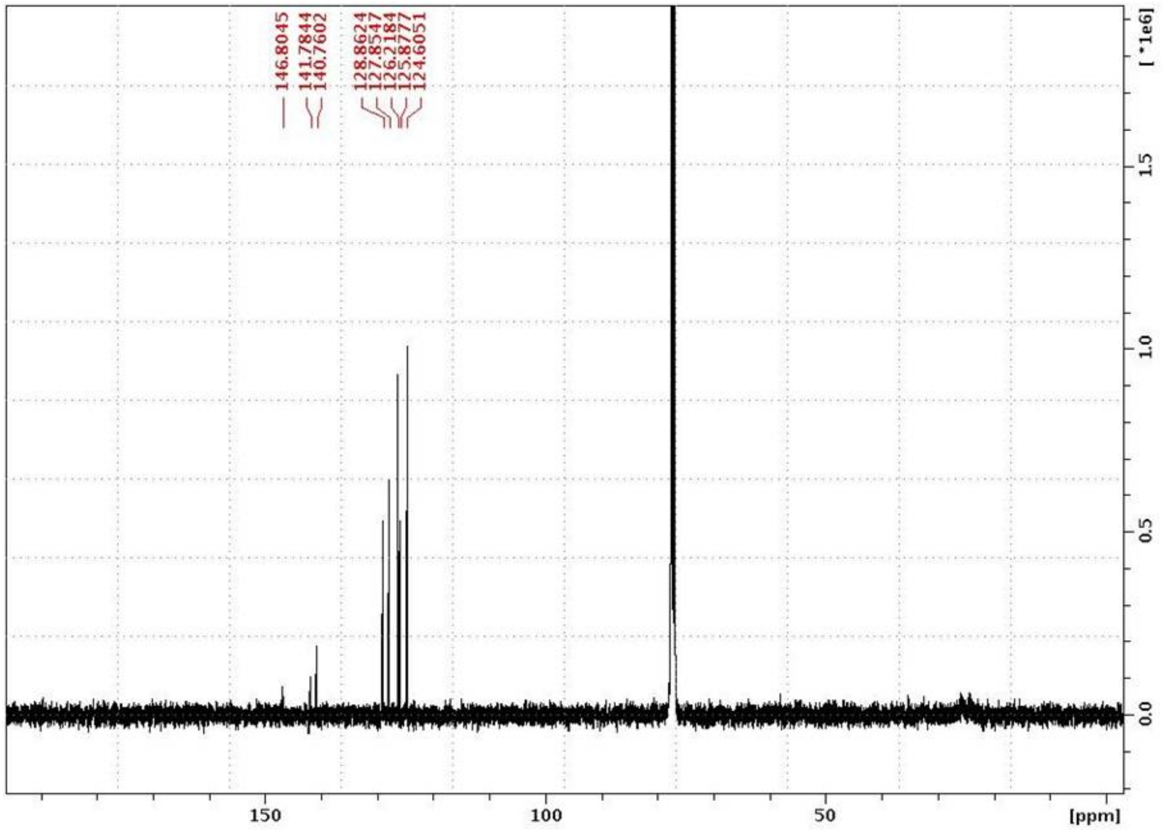
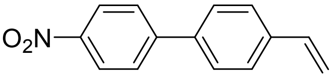
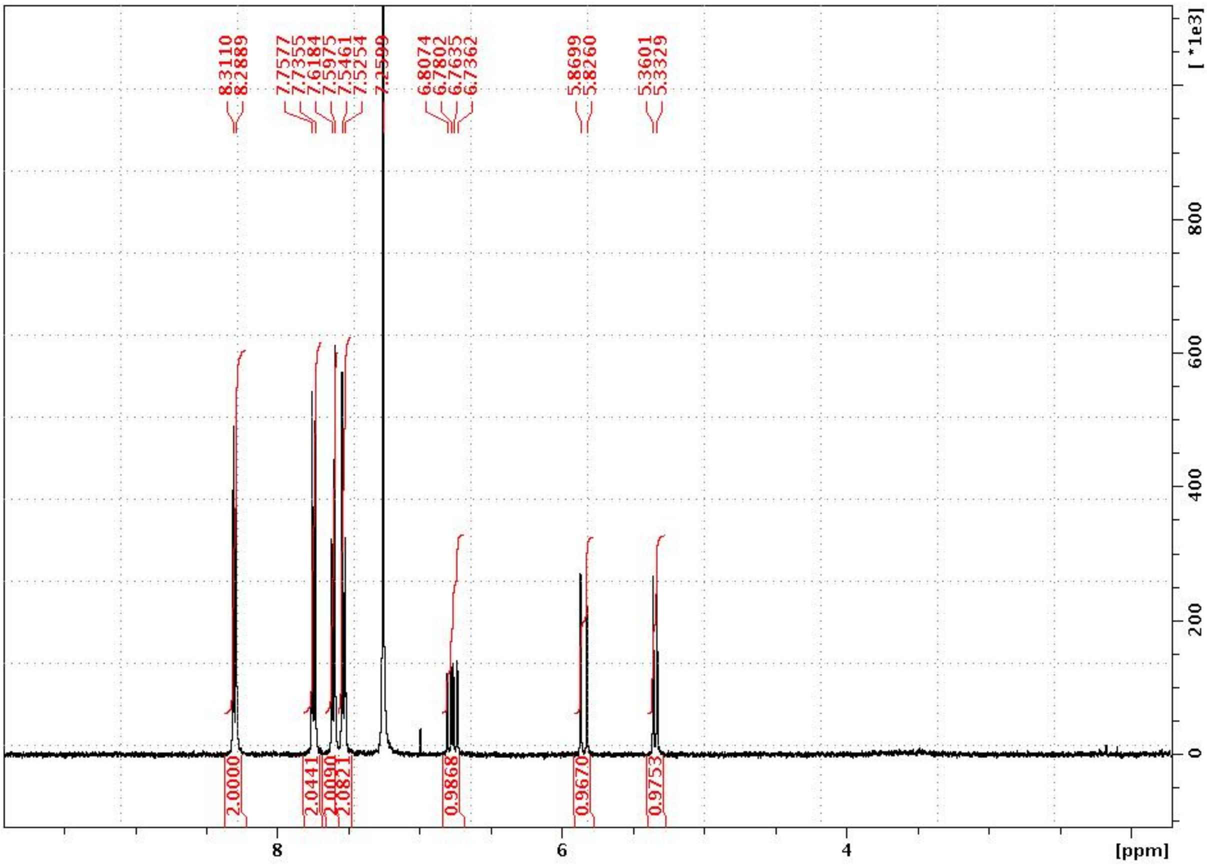
146.4974
144.2833
136.5495
124.4406
124.0443
112.5699
109.1131
77.4671
77.1502
76.8320
150
100
50
[ppm]
0
2
4
6
8
10
12
[*1e6]

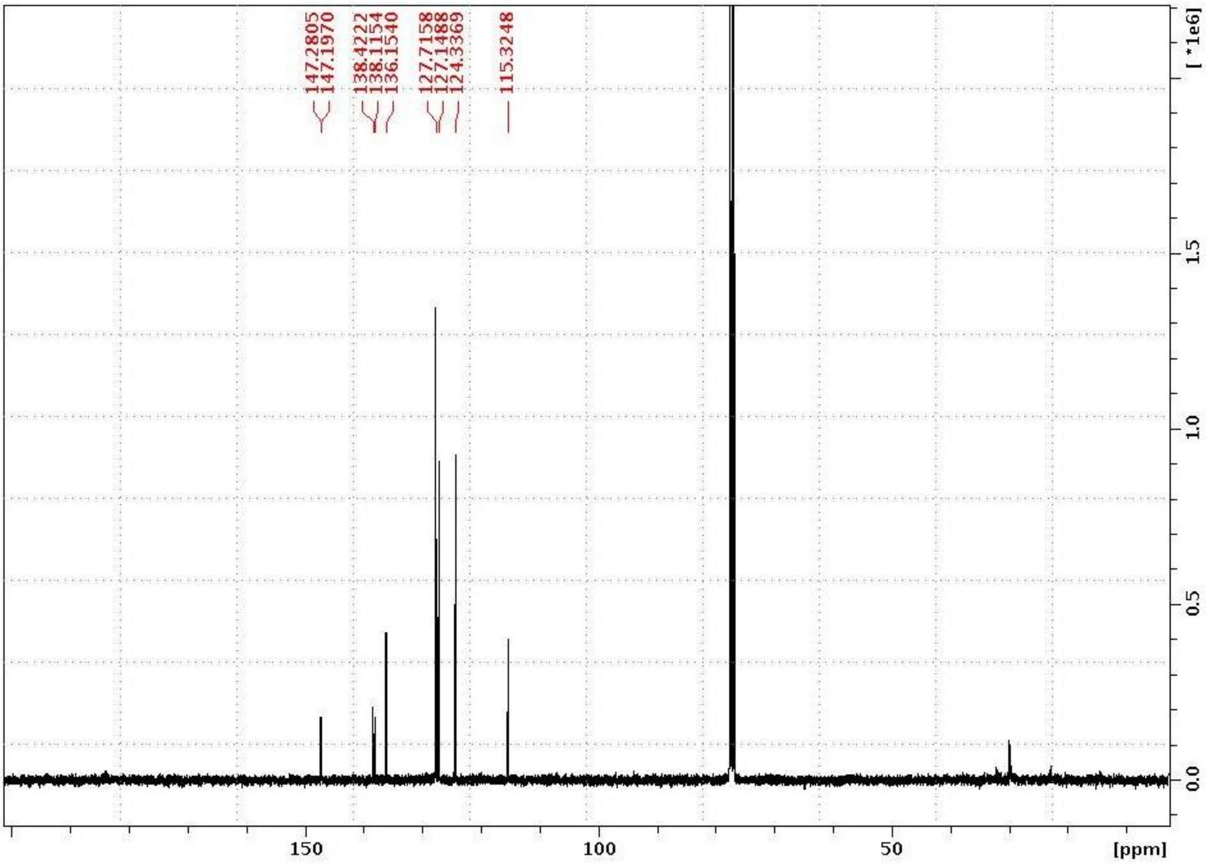

S
O2N


8.2536
8.2313
7.7588
7.7365
7.4866
7.4839
7.4774
7.4747
7.4499
7.4473
7.4372
7.4346
7.2587
7.1650
7.1557
7.1523
7.1431
2.0000
2.0472
1.9849
1.0641
8
6
4
[ppm]
0
5
10
15
20
[*1e6]
8.4
8.2
8.0
7.8
7.6
7.4
7.2
[ppm]


146.8045
141.7844
140.7602
128.8624
127.8547
126.2184
125.8777
124.6051
150
100
50
[ppm]
0.0
0.5
1.0
1.5
[*1e6]


O2N


8.3110
8.2889
7.7577
7.7355
7.6184
7.5975
7.5461
7.5254
7.2599
6.8074
6.7802
6.7635
6.7362
5.8699
5.8260
5.3601
5.3329
2.0000
2.0441
2.0090
2.0821
0.9868
0.9670
0.9753
[*1e3]
800
600
400
200
0
8
6
4
[ppm]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147.1970
138.4222
138.1154
136.1540
127.7158
127.1488
124.3369
115.3248
[*1e6]
1.5
1.0
0.5
0.0
150
100
50
[ppm]