Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2015

SUPPORTING INFORMATION

Cu(0)@Al_2O_3/SiO_2 NPs: An Efficient Reusable Catalyst for the Cross Coupling Reactions of Aryl Chlorides with Amines and Anilines

P. Linga Reddy,[a] R. Arundhathi,[b] Diwan S. Rawat[a,]*

[a]*Department of Chemistry, University of Delhi, Delhi-110007, India*
[b]*Corporate Research & Development Centre, Bharat Petroleum Corporation Limited, Greater Noida, Uttar Pradesh-201306*
**Corresponding author. Tel.: +91-40-27193510; Fax: +91-40-27160921.*
E-mail address: dsrawat@chemistry.du.ac.in

CONTENTS

1. General Remarks S-2

2. Preparation of the catalyst S-3

3. H_2-Temperature Programmed Reduction (H_2-TPR) S-4

4. Characterization of recycled catalyst S-5

5. SEM-EDAX spectrum of Cu(0)@Al_2O_3/SiO_2 S-6

6. Spectroscopic data of representative compounds S-6-S-18

7. References S-18-S-19

8. ^{1}H, ^{13}C, Mass spectra of representative compounds S-20-S-63

General Remarks:

All chemicals were purchased from Aldrich and were used as received. All solvents used were analytical grade and were used as received from Merck India Pvt. Ltd. Alumina/silica (Al_2O_3/SiO_2) was purchased from Sasol, Germany. X-ray powder diffraction (XRD) data were collected on a Simens/D-5000 diffractometer using Cu Kα radiation. The Cu weight percentage was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and SEM-EDAX (Philips XL30 electron micrograph). The particle size and external morphology of the samples were observed on a JEOL JEM-2010 high resolution transmission electron microscope (HRTEM). Brunauer, Emmett and Teller (BET) surface area of supported catalyst and specific surface area of metallic copper was performed using Quantachrome ASiQ instrument. Temperature programmed reduction (TPR) measurements were carried out on Automated chemisorption analyzer (ChemBET pulsar TPR/TPD, Quantachrome). XPS spectra were recorded on a Kratos AXIS 165 with a dual anode (Mg and Al) apparatus using the Mg Kα anode. The pressure in the spectrometer was about 10^{-9} Torr. For energy calibration, we have used the carbon 1s photoelectron line. The carbon 1s binding energy was taken to be 285.0 eV. Spectra were deconvoluted using the Sun Solaris based Vision 2 curve resolver. The location and the full width at half maximum (FWHM) for a species were first determined using the spectrum of a pure sample, The location and FWHM of the products, which were not obtained as pure species, were adjusted until the best fit was obtained. Symmetric Gaussian shapes were used in all cases. The Cu weight percentage was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). ^{1}H and ^{13}C spectra were recorded on a Jeol Spectrospin spectrometer at 400 MHz and 100 MHz respectively. Chemical shifts were reported in ppm relative to the residual $CDCl_3$ (δ 7.28 ppm ^{1}H; δ 75 ppm ^{13}C) Coupling constants (*J*) were reported in Hertz. Mass spectral data were recorded on a Jeol-AccuTOF JMS-T100LC and micromass LCT Mass Spectrometer/Data system. Copper nanoparticles on alumina/silica were prepared by wet impregnation method. ^{1}HNMR and ^{13}C NMR of the compounds were proved

either by comparison to the known compounds or the synthesized compounds according to the literature. ACME SILICA GEL (100-200 mesh) was used for column chromatography and thin layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates.

Preparation of catalysts:

(i) Typical procedure for synthesis of Cu(II)@Al_2O_3/SiO_2 NPs:

Cu(II)@Al_2O_3/SiO_2 was prepared as follows: $Cu(NO_3)_2.3H_2O$ (33.35 g, 0.138 moles) was suspended in doubly deionised water (500 ml) in 1 L four neck round bottom flask and stirred at 25 ^oC with overhead mechanical stirrer. To this 100 g of Al_2O_3-SiO_2 was added and aged at 65 ^oC for twelve hours. The solid product was isolated by filtration, washed thoroughly with doubly deionised water dried at 65 ^oC for 12 h to obtain 130 g of pale blue powder of Cu(II)@Al_2O_3/SiO_2 NPs.

(ii) Typical procedure for synthesis of CuO@Al_2O_3/SiO_2 NPs:

Cu(II)@Al_2O_3/SiO_2 (100 g) was taken in a crucible and calcined in the presence of air at a ramping temperature of 150 ^oC/1 h and 800 ^oC/3 h. The calcined catalyst was then cooled to room temperature to obtain 65 g of grey coloured CuO@Al_2O_3/SiO_2 NPs .

(iii)Typical procedure for synthesis of Cu(0)@Al_2O_3/SiO_2 NPs:

Cu(0)@Al_2O_3/SiO_2 (5 g) was taken in a SS reactor and reduced at 250 ^oC temperature and 10 bar hydrogen pressure with a flow rate of 1 L/h to obtain 4.8 g black colored Cu(0)@Al_2O_3/SiO_2.

Figure S1. Stainless steel (SS) units used for reduction of copper oxide on alumina/silica support.

The Cu loading on Cu(0)@Al_2O_3/SiO_2 was found to be 2.06 wt% from SEM-EDAX elemental analysis and particle size of Cu(0) on Al_2O_3/SiO_2 was estimated to be 4-6 nm which is well matched with high resolution transmission electron microscopy (HR-TEM).

H_2-Temperature Programmed Reduction (H_2-TPR)

Temperature programmed reduction (TPR) measurements were carried out on Automated chemisorption analyzer (Chem BET pulsar TPR/TPD, Quantachrome). Upon loading of 0.10 g of CuO@Al_2O_3/SiO_2 into a quartz U-tube, the sample was degassed at 200 °C for 30 min under helium. When the temperature dropped to 20 °C, the gas was changed to 9.9% H_2/Ar. Finally, the sample was heated from 20 °C to 800 °C with 10 °C min^{-1} in 9.9% H_2/Ar with a gas flow of 30 mL min^{-1}. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD). For H_2 consumption quantification, CuO (99.99%) was used as the calibration standard sample.

At low copper loading, copper was present as highly dispersed clusters or isolated Cu ions, which interact strongly with the alumina-silica-type oxide, thus requiring higher reduction temperature. Support effects on the dispersion and reducibility of copper oxide have been documented in the literature. [2,3] The H_2-TPR curves of the three samples, for the as synthesised Cu(II)@Al_2O_3/SiO_2 catalyst sample, the H_2 consumption peak was located between 150–300 °C and for calcined CuO@Al_2O_3/SiO_2 sample, it was in between 200–300 °C, while for the commercial CuO, it was in between 400–600 °C. These results indicates that the as synthesised Cu(II)@Al_2O_3/SiO_2 and calcined CuO@Al_2O_3/SiO_2 are much easier to reduce than the commercial CuO. But in our reaction conditions for the reduction of calcined CuO@Al_2O_3/SiO_2 catalyst we used higher reduction temperatures because of high dispersion of copper ions.

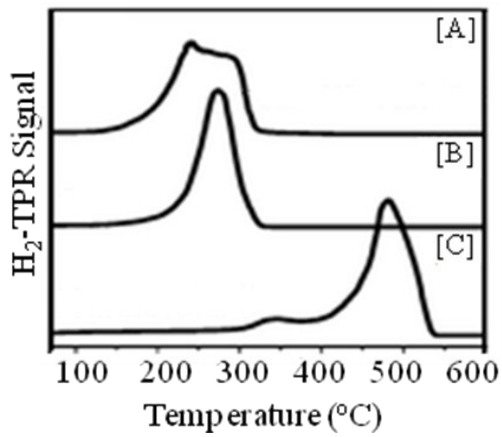


Figure S2. Hydrogen- Temperature Programmed Reduction [A] Cu(II)@Al_2O_3/SiO_2 [B] calcined CuO@Al_2O_3/SiO_2 and [C] Commercial CuO (Aldrich)

Characterization of the recycled catalyst:

X-ray photoelectron spectroscopy (XPS) of recycled Cu(0)@Al_2O_3/SiO_2 catalyst

The X-ray photoelectron spectroscopic analysis of 5th reused Cu(0)@Al_2O_3/SiO_2 catalyst revealed that there was no deviation in the binding energy values of copper Cu(0) $2p_{3/2}$ such as 932.48 and 952.11 eV, which conforms the presence of exclusively Cu(0) oxidation state as shown in Figure S2. The TEM analysis of recycled catalyst revealed the no change in the internal morphology of catalyst (Figure S3).

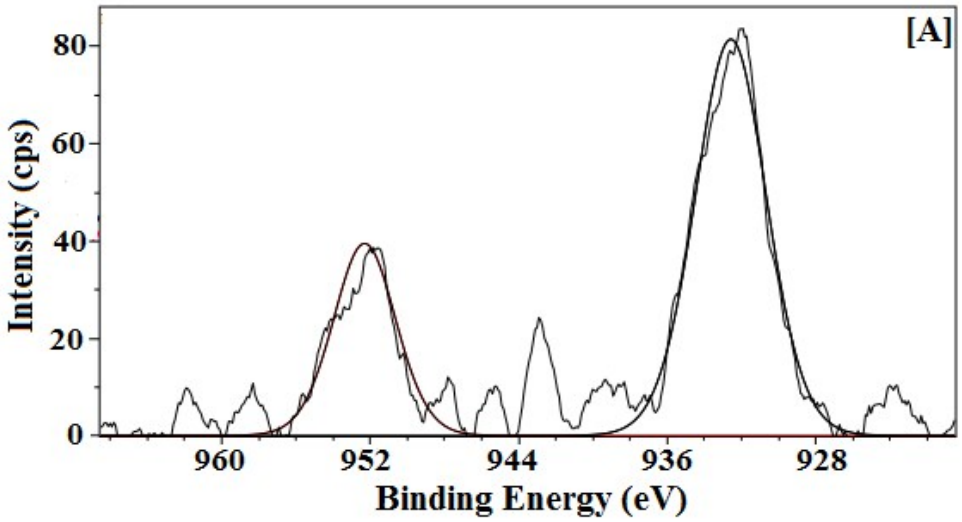


Figure S2. XPS spectra of recycled Cu(0)@Al_2O_3/SiO_2 (5th run, A).

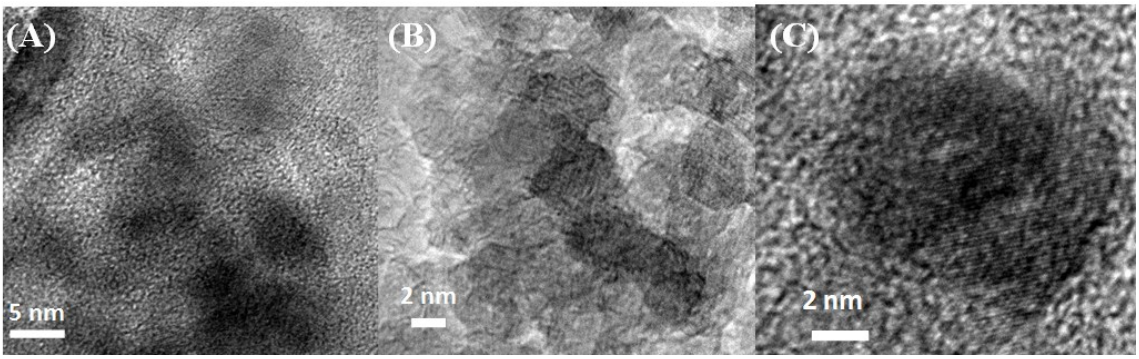


Figure S3. TEM pictures of reused Cu(0)@Al_2O_3/SiO_2 [A, B and C]

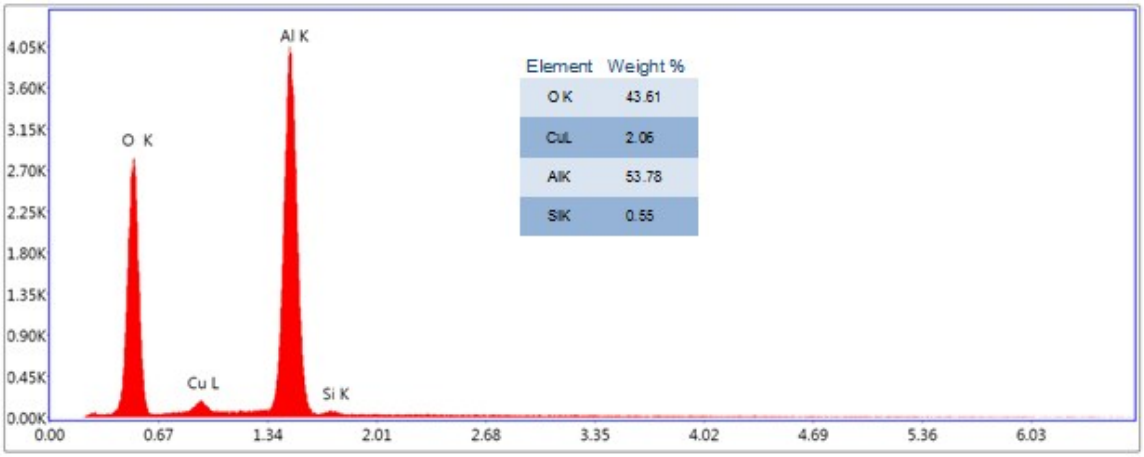
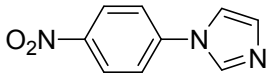


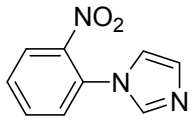
Figure S4: SEM-EDAX analysis of Cu(0)@Al_2O_3/SiO_2 (Cu(0): 2.06 wt%)

Spectroscopic data of representative compounds:



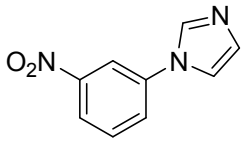
1a

1-(4-nitrophenyl)-1H-imidazole (Table 2, Entry 1a)[4]: Pale yellow solid, mp 197-200; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.38 (d, *J* = 9.16 Hz, 2H), 7.99 (s, 1H), 7.58 (d, *J* = 9.16 Hz, 2H), 7.38 (s, 1H), 7.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2, 141.9, 135.3, 131.7, 125.7, 121.0, 117.6.



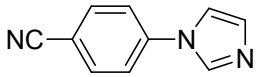
1b

1-(2-nitrophenyl)-1H-imidazole (Table 2, Entry 1b)[4]: Pale yellow solid, mp 95-97; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01 (dd, *J* = 8.39 Hz, 1.53 Hz, 1H), 7.74 (dt, *J* = 7.63 Hz, 1.53 Hz, 1H), 7.68-7.60 (m, 2H), 7.51-7.46 (m, 1H), 7.22 (s, 1H), 7.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.3, 137.2, 133.7, 130.5, 130.3, 129.6, 128.6, 125.3, 120.4.



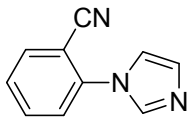
1c

1-(3-nitrophenyl)-1H-imidazole (Table 2, Entry 1c)[5]: white solid, mp: 107-109; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30-8.28 (m, 1H), 8.26-8.27 (m, 1H), 7.96 (s, 1H), 7.74-7.69 (m, 1H), 7.39-7.37 (m, 1H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.03, 138.17, 135.38, 131.40, 131.02, 126.76, 121.98, 117.89, 116.16.



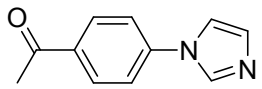
1d

4-(1H-imidazol-1-yl)benzonitrile (Table 2, Entry 1d)[4]: White solid, mp 151-154; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (s, 1H), 7.81 (d, *J* = 8.39 Hz, 2H), 7.54 (d, *J* =8.39 Hz, 2H), 7.34 (s, 1H), 7.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3, 135.2, 134.1, 131.2, 121.3, 117.7, 117.5, 111.1.



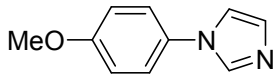
1e

2-(1H-imidazol-1-yl)benzonitrile (Table 2, Entry 1e)[6]: White solid, mp 145-147; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82-7.74 (m, 2H), 7.72-7.65 (m, 1H), 7.47 (t, *J* = 7.63 Hz, 1H), 7.40 (d, *J* = 7.63 Hz, 1H), 7.29 (s, 1H), 7.20 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 136.6, 134.5, 134.2, 130.7, 128.4, 125.6, 119.5, 115.7, 108.0.



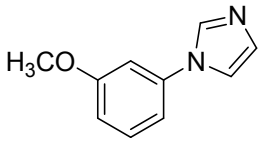
1f

1-(4-(1H-imidazol-1-yl)phenyl)ethanone (Table 2, Entry 1f)[6]: White solid, mp 112-114; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, *J* = 8.39 Hz, 2H), 7.95 (s, 1H), 7.47 (d, *J* = 8.39 Hz, 2H), 7.33 (s, 1H), 7.22 (s, 1H), 2.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 140.6, 135.7, 135.3, 131.0, 130.3, 120.6, 117.6, 26.6.



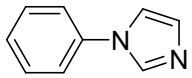
1g

1-(4-methoxyphenyl)-1H-imidazole (Table 2, Entry 1g)[4]: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.23 (d, *J* = 9.16 Hz, 2H), 7.14 (s, 2H), 6.91 (d, *J* = 9.16 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.8, 135.7, 130.5, 129.7, 123.1, 118.7, 114.8, 55.5.



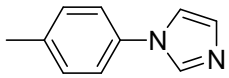
1h

1-(3-methoxyphenyl)-1H-imidazole (Table 2, Entry 1h)[7]: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.35-7.19 (m, 3H), 6.91 (d, *J* = 7.63 Hz, 1H), 6.84-6.81 (m, 2H), 3.86 (s, 3H); 160.64, 130.71, 113.66, 112.62, 107.72, 55.51.



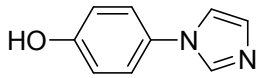
1i

1-phenyl-1H-imidazole (Table 2, Entry 1i)[4]: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (s, 1H), 7.47-7.40 (m, 2H), 7.37-7.29 (m, 3H), 7.24 (s, 1H), 7.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.1, 135.4, 130.3, 129.7, 127.4, 121.3, 118.1.



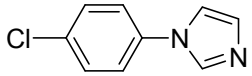
1j

1-(p-tolyl)-1H-imidazole (Table 2, Entry 1j)[6]: Off white mp 46-48; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.26 (s, 4H), 7.23 (s, 1H), 7.18 (s, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.4, 135.5, 134.9, 130.2, 130.1, 121.3, 118.3, 20.9.



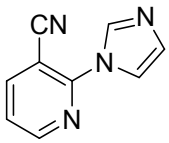
1k

4-(1H-imidazol-1-yl)phenol (Table 2, Entry 1k)[8]: Off white solid, mp 192-196; ^{1}H NMR (400 MHz, DMSO): δ = 9.70 (s, 1H, OH), 8.13 (s, 1H), 7.63 (s, 1H), 7.39 (d, *J* = 8.39, 2H), 7.13 (s, 1H), 6.85 (d, *J* = 8.39 Hz, 2H); ^{13}C NMR (100 MHz, DMSO): δ = 156.3, 128.9, 122.2, 116.0.



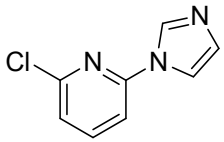
1l

1-(4-chlorophenyl)-1H-imidazole (Table 2, Entry 1l)[9]: Off white solid, mp 64-66; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (s, 1H), 7.41 (d, *J* =8.39 Hz, 2H), 7.30 (d, *J* = 8.39 Hz, 2H), 7.21 (s, 1H), 7.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.7, 135.4, 133.1, 130.5, 129.9, 122.6, 118.1.



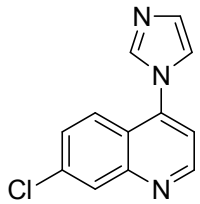
1m

2-(1H-imidazol-1-yl)nicotinonitrile (Table 2, Entry 1m)[10]: Off white solid, ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75-8.71 (m, 1H), 8.52 (s, 1H), 8.18-8.14 (m, 1H), 7.92 (s, 1H), 7.45-7.39 (m, 1H), 7.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.84, 149.27, 143.98, 136.41, 130.95, 121.72, 117.53, 115.48, 99.67.



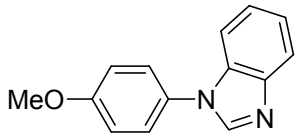
1n

2-chloro-6-(1H-imidazol-1-yl)pyridine (Table 2, Entry 1n)[11]: colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.33 (s, 1H), 7.82-7.76 (m, 1H), 7.62 (s, 1H), 7.28 (t, *J* = 6.87, 2H), 7.19 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.66, 148.63, 141.25, 134.95, 130.87, 122.16, 116.09, 110.21.



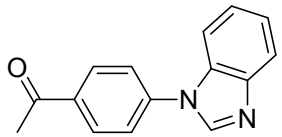
1o

7-chloro-4-(1H-imidazol-1-yl)quinolone (Table 2, Entry 1o)[12]: Off white solid, ; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (d, *J* = 5.34 Hz, 1H), 8.23 (d, *J* = 1.53 Hz, 1H), 7.85 (s, 1H), 7.79 (d, *J* = 8.39 Hz, 1H), 7.59 (dd, *J* = 9.16 Hz, *J* = 2.29 Hz, 1H), 7.39-7.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.61, 150.03, 141.85, 137.55, 130.74, 129.18, 129.07, 123.81, 121.93, 120.71, 116.90.



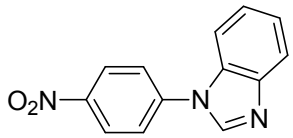
1p

1-(4-methoxyphenyl)-1H-benzo[d]imidazole (Table 2, Entry 1p)[13]: Pale yellow solid, mp 99-101; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.83-7.77 (m, 1H), 7.41-7.36 (m, 1H), 7.33 (d, *J* = 9.16 Hz, 2H), 7.28-7.23 (m, 2H), 7.0 (d, *J* = 9.16 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 143.6, 142.4, 134.1, 129.0, 125.6, 123.4, 122.5, 120.3, 115.0, 110.2, 55.5.



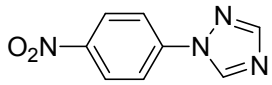
1q

1-(4-(1H-benzo[d]imidazol-1-yl)phenyl)ethanone (Table 2, Entry 1q)[13]: Pale yellow solid, mp 132-134; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21-8.16 (m, 3H), 7.93-7.87 (m, 1H), 7.65 (d, *J* = 8.70 Hz, 2H), 7.62-7.58 (m, 1H), 7.41-7.35 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.6, 144.2, 141.7, 140.2, 136.1, 133.0, 124.1, 123.3, 123.3, 120.8, 110.4, 26.6



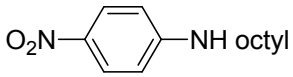
1r

1-(4-nitrophenyl)-1H-benzo[d]imidazole (Table 2, Entry 1r)[4]: Yellow solid, mp 185-187; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 9.16 Hz, 2H), 8.20 (s, 1H), 7.93-7.88 (m, 1H), 7.75 (d, *J* = 9.16 Hz, 2H), 7.64-7.59 (m, 1H), 7.44-7.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.4, 144.3, 141.6, 141.5, 132.7, 125.8, 124.5, 123.7, 123.6, 121.1, 110.2.



1s

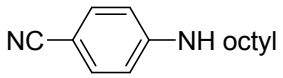
1-(4-nitrophenyl)-1H-1,2,4-triazole (Table 2, Entry 1s)[14]: White solid, mp 186-189; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (s, 1H), 8.41 (d, *J* = 9.16 Hz, 2H,), 8.17 (s, 1H), 7.93 (d, *J* = 9.16 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 146.7, 141.2, 125.5, 119.8.



2a

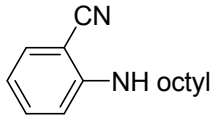
4-nitro-N-octylaniline (Table 3, Entry 2a)[15]: White solid, mp 66-68; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 9.16 Hz, 2H), 6.51 (d, *J* = 9.16 Hz, 2H), 4.54 (brs, 1H, NH), 3.2 (q, *J* = 6.87 Hz, 2H), 1.65 (m, 2H), 1.45-1.21 (m, 10H), 0.92-0.81 (m, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ = 153.4, 137.6, 126.4, 110.8, 43.3, 31.7, 29.2, 29.1, 29.0, 26.9, 22.5, 14.0.



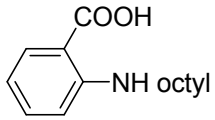
2b

4-(octylamino)benzonitrile (Table 1, Entry 2b)[16]: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, *J* = 9.16 Hz, 2H), 6.53 (d, *J* = 9.16 Hz, 2H), 4.16 (brs, 1H, NH), 3.13 (q, *J* = 7.63, 2H), 1.67-1.59 (m, 2H), 1.43-1.23 (m, 10H), 0.92-0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.4, 133.6, 120.5, 112.0, 98.3, 43.2, 31.7, 29.2, 29.1, 29.1, 27.0, 22.6, 14.0.



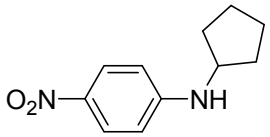
2c

2-(octylamino)benzonitrile (Table 3, Entry 2c)[16]: Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.34 (m, 2H), 6.68-6.61 (m, 2H), 4.52 (brs, 1H, NH), 3.18 (q, *J* = 6.10 Hz, 2H),1.72-1.62 (m, 2H), 1.45-1.32 (m, 10H), 0.98-0.88 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.5, 134.0, 133.8, 130.0, 127.1, 115.8, 113.4, 42.2, 33.8, 31.8, 29.4, 29.2, 26.8, 26.6, 14.0.



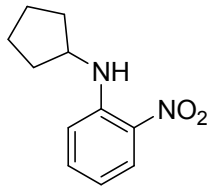
2d

2-(octylamino)benzoic acid (Table 3, Entry 2d)[17]: White solid, mp 82-84; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 7.63 Hz, 1H), 7.38 (t, *J* = 7.63 Hz, 1H), 6.67 (d, *J* = 8.39 Hz, 1H), 6.58 (t, *J* = 7.63 Hz, 1H), 3.19 (t, *J* = 7.63, 2H), 1.68 (m, 2H), 1.46-1.39 (m, 2H), 1.37- 1.19 (m, 10H), 0.92-0.82 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.9, 151.8, 135.4, 132.6, 114.2, 111.2, 108.4, 42.8, 31.7, 29.3, 29.2, 29.0, 27.1, 22.6, 14.0.



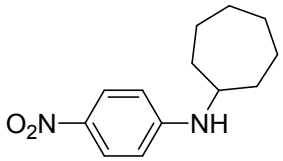
2e

N-cyclopentyl-4-nitroaniline (Table 3, Entry 2e)[18]: Thick yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 9.16 Hz, 2H), 6.48 (d, *J* = 9.16 Hz, 2H), 4.59 (brs, 1H, NH), 3.88-3.78 (m, 1H), 2.10- 1.99 (m, 2H), 1.78- 1.59 (m, 4H), 1.54-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.0, 137.4, 126.3, 111.2, 54.3, 33.3, 23.9.



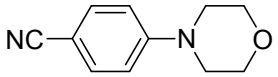
2f

N-cyclopentyl-2-nitroaniline (Table 3, Entry 2f)[19]: Thick yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (dd, *J* = 8.39 Hz, 1.53 Hz, 1H), 8.11 (brs, 1H, NH), 7.45-7.38 (m, 1H), 6.88 (d, *J* = 9.16 Hz, 1H), 6.61 (t, *J* = 9.16 Hz, 1H), 4.02-3.92 (m, 1H), 2.16-2.05 (m, 2H), 1.88-1.77 (m, 2H), 1.75-1.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 145.1, 135.9, 131.8, 126.8, 114.8, 114.6, 53.9, 33.5, 24.0.



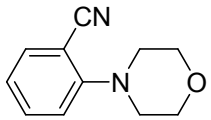
2g

N-(4-nitrophenyl)cycloheptanamine (Table 3, Entry 2g)[20]: Thick yellow liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 9.16 Hz, 2H), 6.45 (d, *J* =9.16 Hz, 2H), 4.48 (brs, 1H, NH), 3.59- 3.49 (m, 1H), 2.08-1.96 (m, 2H), 1.79-1.47 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.2, 137.3, 126.5, 112.2, 53.6, 34.5, 28.0, 24.1.



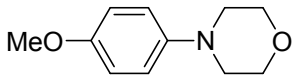
2h

4-morpholinobenzonitrile (Table 3, Entry 2h)[21]: Colorless solid, mp 74-76; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 9.16 Hz, 2H), 6.83 (d, *J* = 9.16 Hz, 2H), 3.82 (t, *J* = 4.58 Hz, 4H), 3.24 (t, *J* = 4.58 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.4, 133.6, 119.9, 114.1, 101.0, 66.4, 47.5.



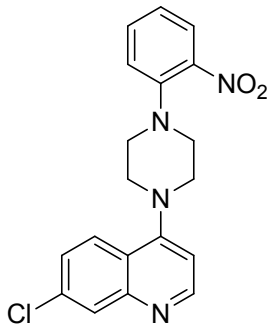
2i

2-morpholinobenzonitrile (Table 3, Entry 2h)[22]: Colorless solid, mp 82-84; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61-7.56 (m, 1H), 7.54-7.48 (m, 1H), 7.07-7.0 (m, 2H), 3.91 (t, *J* = 4.58 Hz, 4H), 3.21 (t, *J* = 4.58 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 134.3, 133.8, 122.1, 118.4, 118.2, 106.0, 66.8, 51.7.



2j

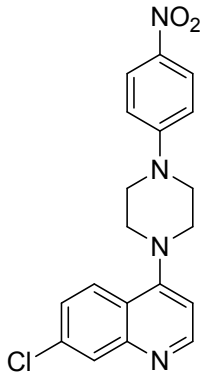
4-(4-methoxyphenyl)morpholine (Table 3, Entry 2j)[23]: Colorless solid, mp 66-68; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.91-6.83 (m, 4H), 3.85 (t, *J* = 5.34 Hz, 4H), 3.77 (s, 3H), 3.05 (t, *J* = 5.34 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.9, 145.6, 117.8, 114.4, 67.0, 55.5, 50.8.



2k

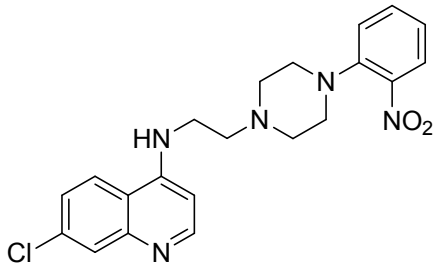
7-chloro-4-(4-(2-nitrophenyl)piperazin-1-yl)quinoline (Table 3, Entry 2k): Pale yellow solid, mp 177-179; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.76 (d, *J* = 5.04 Hz, 1H),

8.07 (d, J = 2.29 Hz, 1H), 7.99 (d, J = 8.70 Hz,1H), 7.82 (dd, J = 8.24 Hz, J = 1.83 Hz, 1H), 7.59-7.53 (m, 1H), 7.45 (dd, J = 8.70 Hz, J = 1.83 Hz, 1H), 7.30-7.27 (m, 1H), 7.18-7.11 (m, 1H), 6.91 (d, J = 5.04 Hz, 1H), 3.42-3.33 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6, 152.0, 150.1, 145.6, 144.0, 134.9, 133.5, 128.9, 126.3, 125.8, 124.9, 122.7, 121.8, 121.4, 109.3, 52.2, 51.8; ESI-HRMS (m/z) Anal. Calcd. for $C_{19}H_{18}ClN_4O_2$: 369.1113 $(MH)^+$; Found: 369.1119 (MH)+.



2l

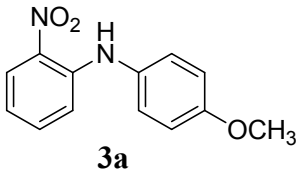
7-chloro-4-(4-(4-nitrophenyl)cyclohexyl)quinolone (Table 3, Entry 2l)[24]: Pale yellow solid, mp 235-237; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.77 (d, J = 5.34 Hz, 1H), 8.18 (d, J =9.16 Hz, 2H), 8.08 (d, J = 2.29 Hz, 1H), 8.0 (d, J = 9.16 Hz, 1H), 7.48 (dd, J = 9.16 Hz, 2.29 Hz, 1H), 6.97-6.89 (m, 4H), 3.70 (t, J = 5.34 Hz, 4H), 3.39 (t, J = 5.34 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.2, 154.7, 151.9, 150.1, 139.1, 135.2, 129.0, 126.6, 125.9, 124.7, 121.7, 113.1, 109.1, 51.6, 47.2.



2m

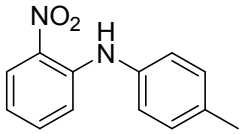
7-chloro-N-(2-(4-(2-nitrophenyl)piperazin-1-yl)ethyl)quinolin-4-amine (Table 3, Entry 2m): Pale yellow solid, mp 103-105; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 8.41 (s, 1H), 8.05 (s, 1H), 7.92 (d, J = 8.70 Hz, 1H), 7.79-7.75 (m, 1H), 7.53-7.47 (m, 1H), 7.38 (d, J = 8.70 Hz, 1H), 7.17 (d, J = 8.24 Hz, 1H), 7.07 (t, J = 7.79 Hz, 1H), 6.43 (d, J = 4.58 Hz, 1H), 3.73 (brs, 1H, NH), 3.51-3.44 (m, 2H), 3.18-3.10 (m, 4H), 2.90 (t, J = 5.50

Hz, 2H), 2.78-2.71(m, 4H); ^{13}C NMR (100 MHz, DMSO): δ = 151.9, 149.9, 149.0, 134.1, 133.3, 131.5, 128.7, 127.5, 125.6, 124.8, 124.1, 123.9, 117.3, 98.7, 56.5, 54.3, 45.6; ESI-HRMS (m/z) Anal. Calcd. for $C_{21}H_{23}ClN_5O_2$: 412.1535 $(MH)^+$; Found: 412.1549 $(MH)^+$.



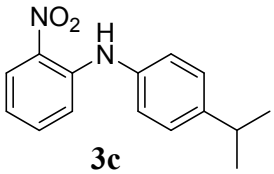
3a

N-(4-methoxyphenyl)-2-nitroaniline (Table 4, Entry 3a)[25]: Brown solid, mp 87-89; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.33 (brs, 1H, NH), 8.11 (d, *J* = 8.39 Hz, 1H), 7.28-7.22 (m, 1H), 7.12 (d, *J* = 8.39 Hz, 2H), 6.95-6.86 (m, 3H), 6.67-6.60(m, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.9, 144.4, 135.7, 132.2, 131.1, 127.1, 126.5, 116.7, 115.7, 114.9, 55.5.



3b

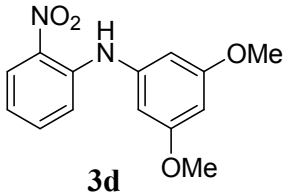
2-nitro-N-(p-tolyl)aniline (Table 4, Entry 3b)[25]: Brown solid, mp 68-70; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.45 (brs, 1H, NH), 8.22-8.17 (m, 1H), 7.37-7.29 (m, 1H), 7.22 (d, *J* = 8.39 Hz, 2H), 7.19-7.12 (m, 3H), 6.76-6.70 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 135.8, 135.7, 135.6, 132.7, 130.2, 126.6, 124.8, 117.0, 115.9, 20.9



3c

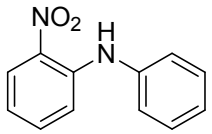
N-(4-isopropylphenyl)-2nitroaniline (Table 4, Entry 3c): Brown liquid; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 9.48 (brs, 1H, NH), 8.19 (dd, *J* = 8.70 Hz, *J* = 1.83 Hz, 1H), 7.37-7.32 (m, 1H), 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 6.77-6.71 (m, 1H), 3.00-2.88 (m, 1H), 1.32-1.24 (d, *J* = 6.87 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6, 143.6, 136.1,

135.6, 132.7,127.6, 126.5, 124.7, 117.0, 115.9, 33.6, 23.9; ESI-HRMS (m/z) Anal. Calcd. For $C_{15}H_{17}N_2O_2$: 257.1285 $(MH)^+$; Found: 257.1281.



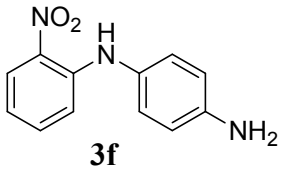
3d

3,5-dimethoxy-N-(2-nitrophenyl)aniline (Table 4, Entry 3d): Brown solid, mp 85-87; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 9.41 (brs, 1H, NH), 8.19 (d, *J* = 8.39 Hz, 1H), 7.42-7.30 (m, 2H), 6.78 (t, *J* = 7.63 Hz, 1H), 6.43 (d, *J* = 2.29 Hz, 2H), 6.33 (t, *J* = 2.29 Hz, 1H), 3.79 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 142.5, 140.4, 135.6, 133.3, 126.5, 117.6, 116.6, 102.1, 97.5, 54.4; ESI-HRMS (m/z) Anal. Calcd. For $C_{14}H_{15}N_2O_4$: 275.1026 $(MH)^+$; Found: 275.1056 $(MH)^+$.



3e

2-nitro-N-phenylaniline (Table 4, Entry 3e)[25]: Brown solid, mp 72-74; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.49 (s, 1H), 8.20 (d, *J* = 8.39 Hz, 1H), 7.46-7.34 (m, 3H), 7.32-7.20 (m, 4H), 6.81-6.74 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.0, 138.6, 135.6, 133.1, 129.7, 126.6, 125.6, 124.3, 117.4, 116.0.



3f

N^1-(2-nitrophenyl)benzene-1,4-diamine (Table 4, Entry 3g): Dark brown solid, mp 111-113; ^{1}H NMR (400 MHz, $CDCl_3$) : δ = 9.37 (brs, 1H, NH), 8.21-8.15 (m, 1H), 7.33-7.27 (m, 1H), 7.05 (d, *J* = 8.39 Hz, 1H), 6.97 (d, *J* = 8.39 Hz, 1H), 6.73 (d, *J* = 8.39 Hz,

2H), 6.71-6.65 (m, 1H), 3.74 (brs, 2H, NH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 135.6, 132.1, 129.0, 127.3,126.5, 116.3, 115.9, 115.8, 102.3; ESI-HRMS (m/z) Anal. Calcd. For $C_{12}H_{12}N_3O_2$: 230.0924 $(MH)^+$; Found: 230.0924 $(MH)^+$.

References:

1. X. Guo, C. Hao, G. Jin, H. Y. Zhu and X. Y. Guo, *Angew. Chem. Int. Ed.,* 2014, **53**, 1973.
2. W. P. Dow and T. J. Huang, *J. Catal*., 1994, **147**, 322.
3. W. P. Dow, Y. P. Wang and T. J. Huang, *J. Catal*., 1996, **160**, 155.
4. B. M. Choudary, C. Sridhar, M. L. Kantam , G. T. Venkanna and B. Sreedhar, *J. Am. Chem. Soc.* 2005, **127**, 9948.
5. R. A. Altman and S. L. Buchwald, *Org. Lett.,* 2006, **8**, 2779.
6. B. Sreedhar, R. Arundhathi, P. L. Reddy and M. L. Kantam, *J. Org. Chem.* 2009, **74**, 7951.
7. P. Suresh and K. Pitchumani, *J. Org. Chem.*, 2008, **73**, 9121.
8. R. A. Altman, E. D. Koval and S. L. Buchwald, *J. Org. Chem.* 2007, **72**, 6190.
9. P. Suresh and K. Pitchumani, *J. Org. Chem.* 2008, **73**, 9121.
10. J. M. Keith, *J. Org. Chem.*, 2008, **73**, 327.
11. A. Velavan, M. Dibyendu and S. Sachin, *Bull. Korean Chem. Soc*, 2013, **34**, 3459.
12. H. F. Motiwala , R. Kumar and A. K. Chakraborti, *Aust. J. Chem.*2006, **60**, 369.
13. M. Huang, X. Lin, X. Zhu, W. Peng, J. Xie and Y. Wan, *Eur. J. Org. Chem.* **2011**, *23*, 4523.
14. A. A. Farahat and D. W. Boykin, *Tetrahedron Letters*, 2014, ***55,*** 3049.

15. Q. Shen, T. Ogata and J. F. Hartwig, *J. Am. Chem. Soc.* ,2008, **130**, 6586.

16. S. Ge, R. A. Green and J. F. Hartwig, *J. Am. Chem. Soc.,* 2014, **136**, 1617.

17. M. L. Docampo, R. F. Pellón, A. Estevez-Braun and A. G. Ravelo, *Eur. J. Org. Chem,.,* 2007, **24**, 4111.

18. B. Sreedhar, R. Arundhathi, P. L. Reddy, M. A. Reddy and M. L. Kantam, Synthesis, 2009, **15**, 2517.

19. R. Arundhathi, D. C. Kumar and B. Sreedha, *Eur. J. Org. Chem.,* 2010, **19**, 3621.

20. Y. Liu and C. Chi-Ming, *Chem. Eur. J.,* 2010, **16**, 10494.

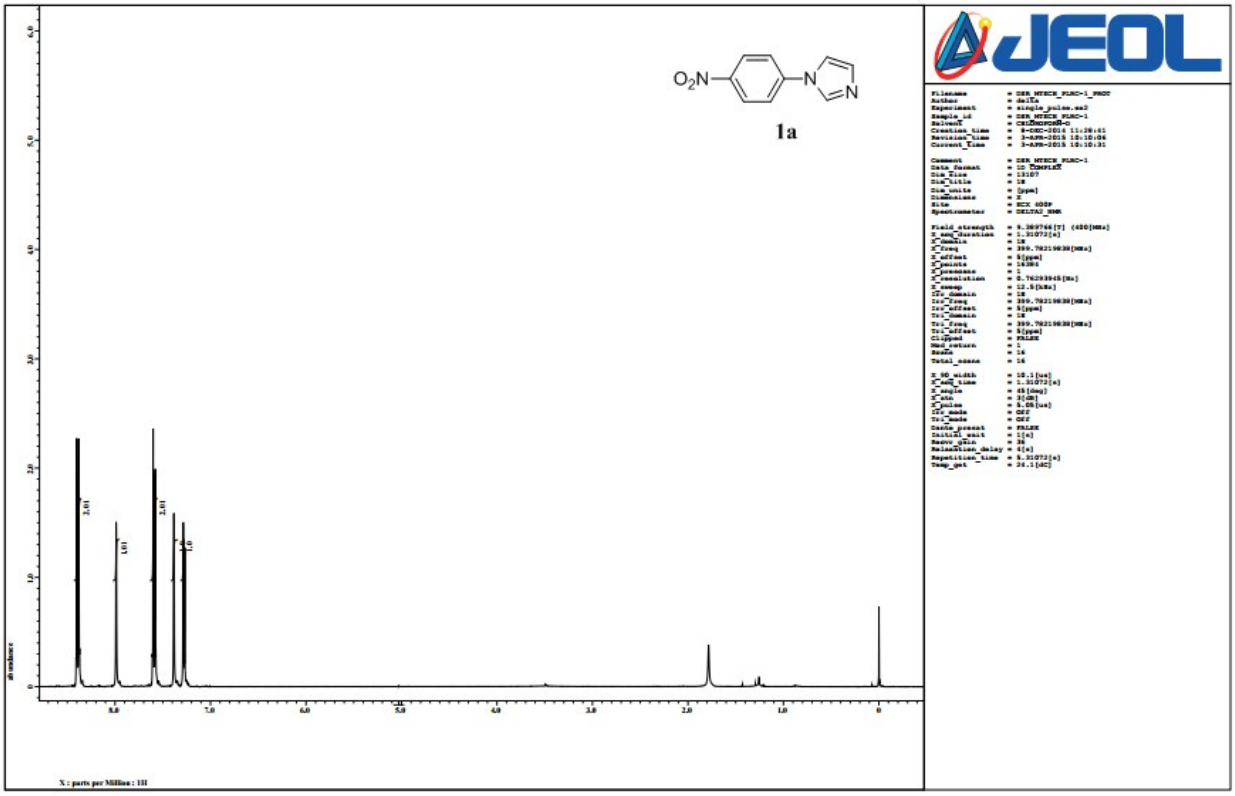
21. M. Al-Amin, S. Arai, N. Hoshiya, T. Honma, Y. Tamenori, T. Sato, M. Yokoyama, A. Ishii, M. Takeuchi, T. Maruko, S. Shuto and M. Arisawa, *J. Org. Chem.* 2013, **78**, 7575.

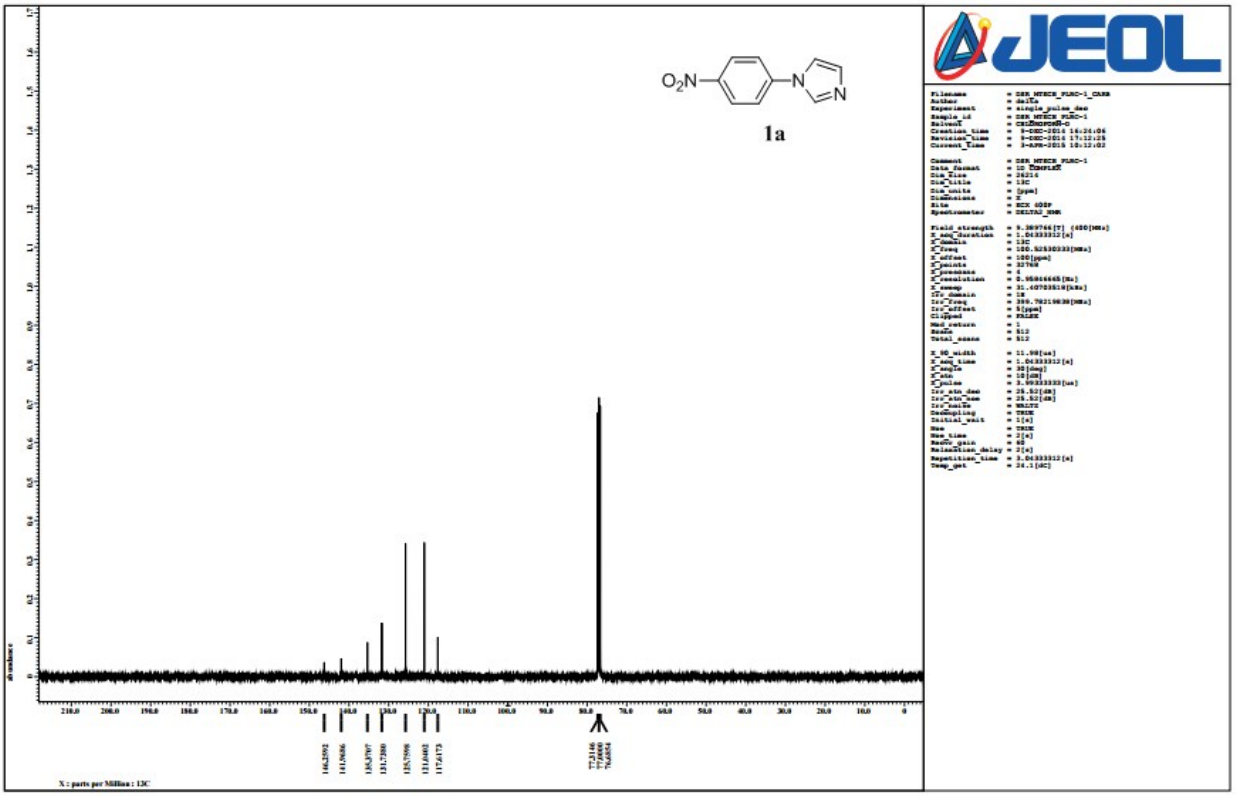
22. C. E. Hendrick, S. L. McDonald and Q. Wang, *Org. Lett.,* 2013, **15**, 3444.

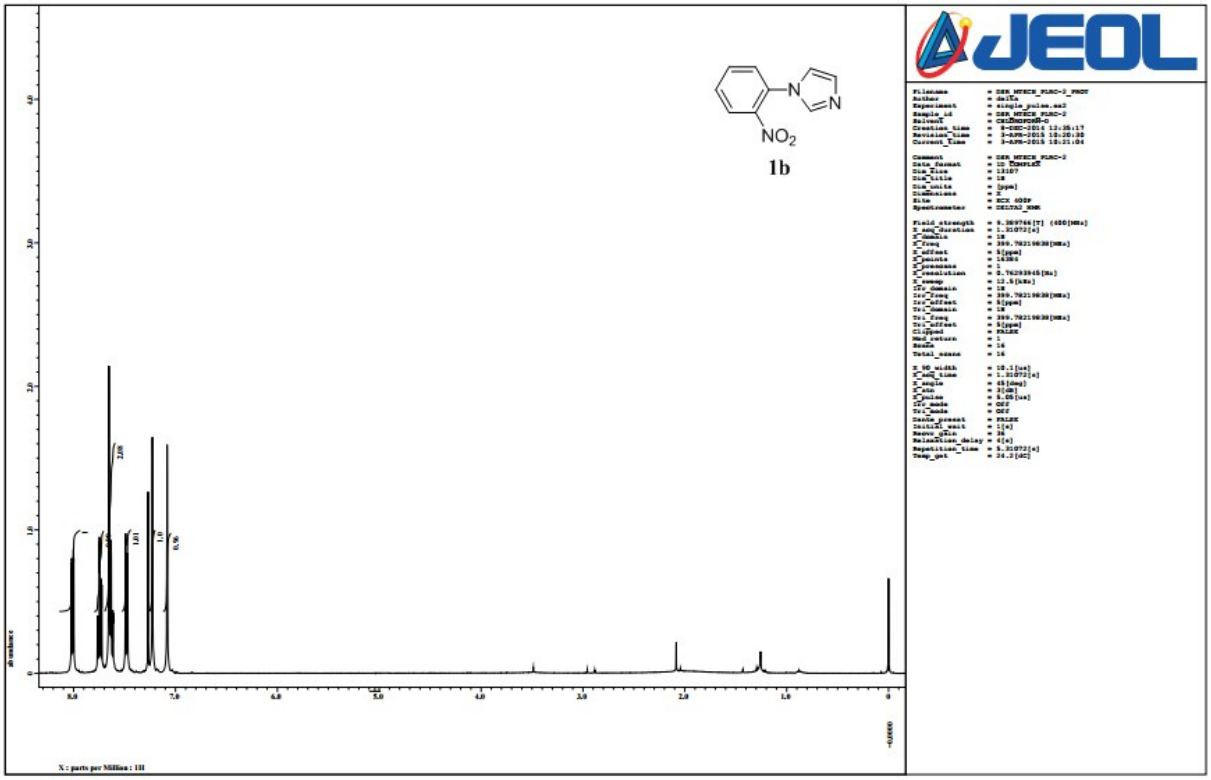
23. R. Pratap, D. Parrish, P. Gunda, D. Venkataraman and M. K. Lakshman, *J. Am. Chem. Soc.,* 2009, **131**, 12240.

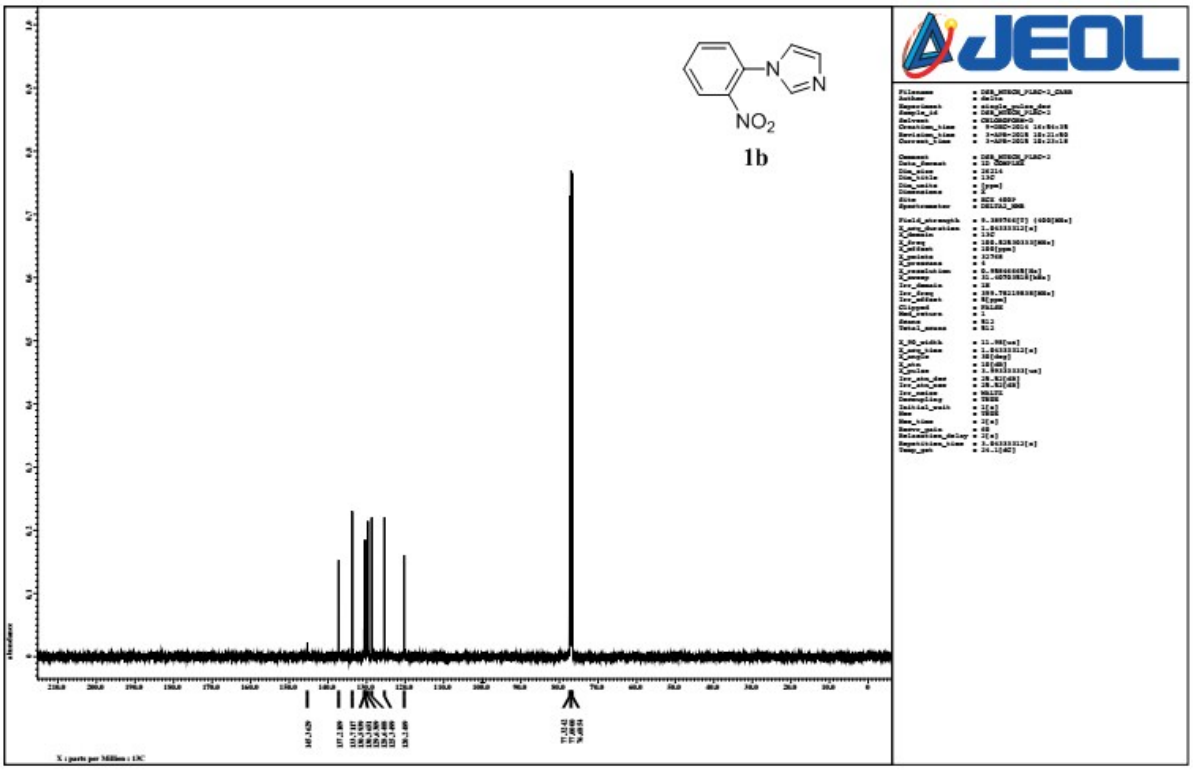
24. S. Abuzar, R. Dubey and S. Sharma, *Eur. J. Med. Chem.,* 1986, **21**, 5.

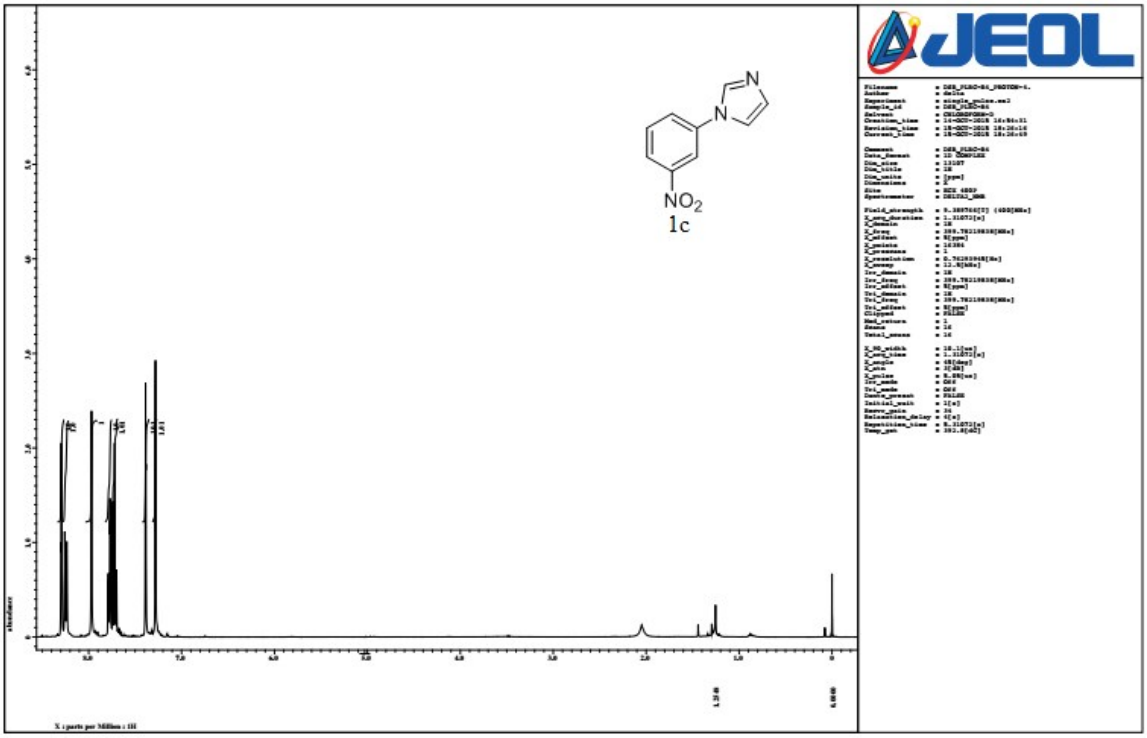
25. L. Z. Huang, P. Han, Y. Q. Li, Y. M. Xu, T. Zhang and Z. T. Du, *Int. J. Mol. Sci.* 2013, **14**, 18850.

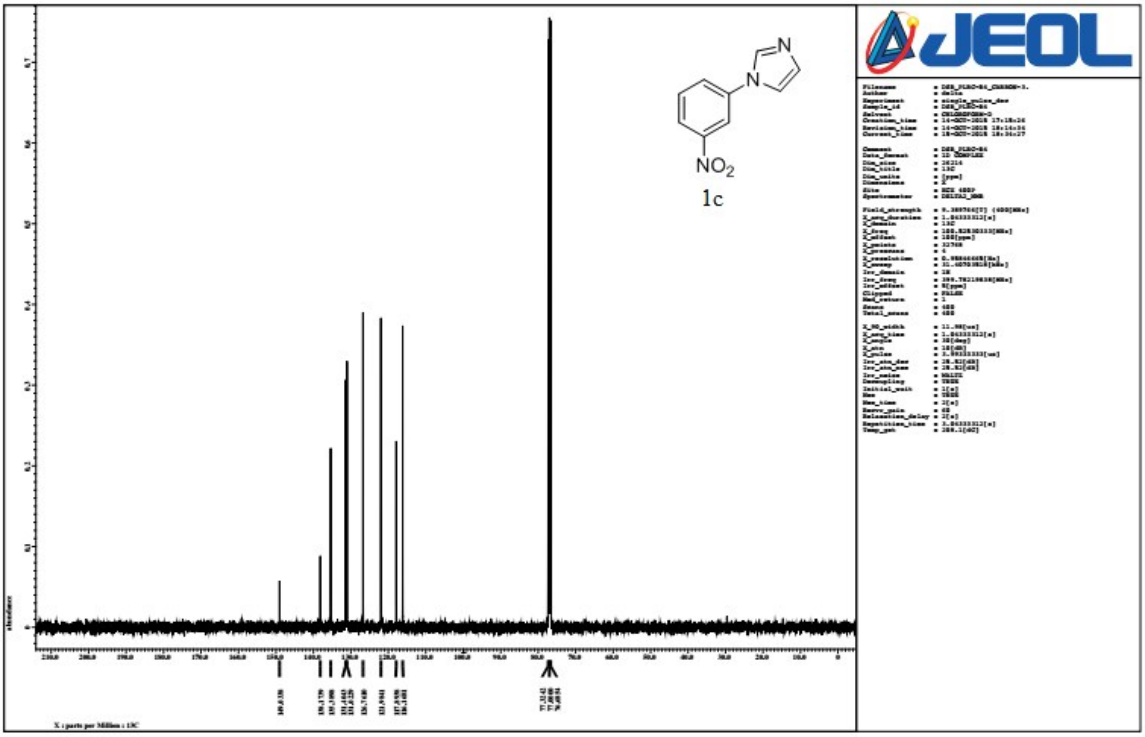

1a
X : parts per Million : 1H

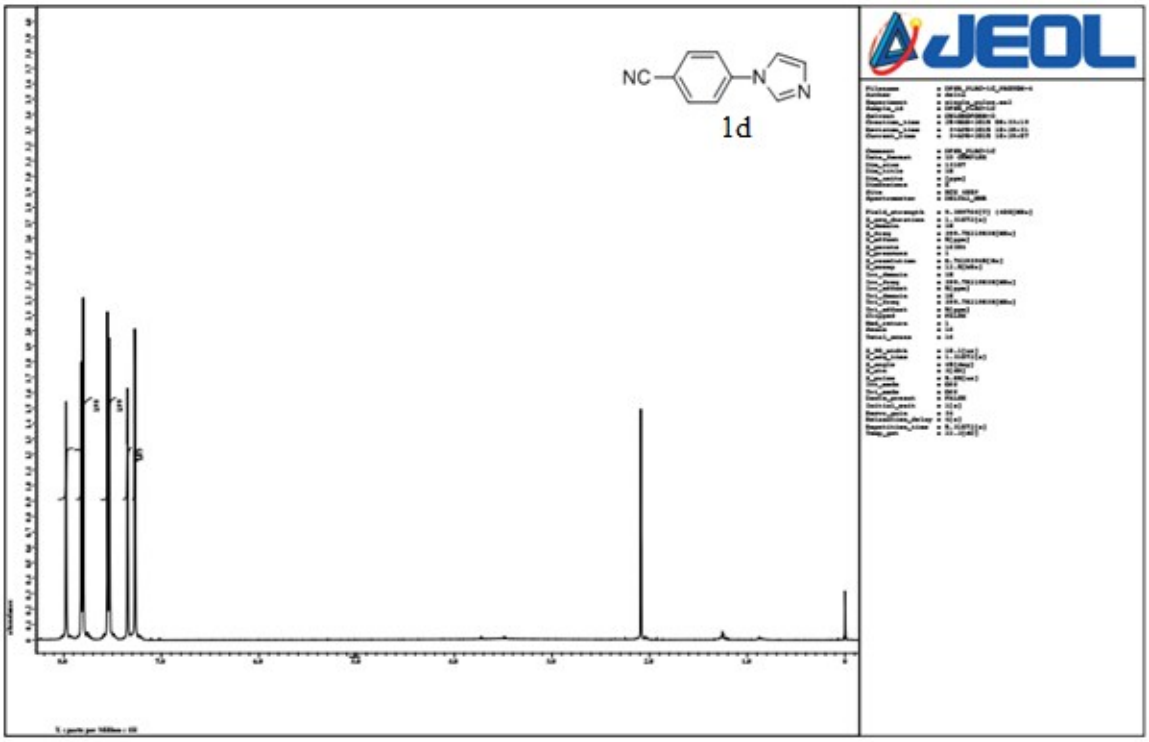

1a
X : parts per Million : 13C

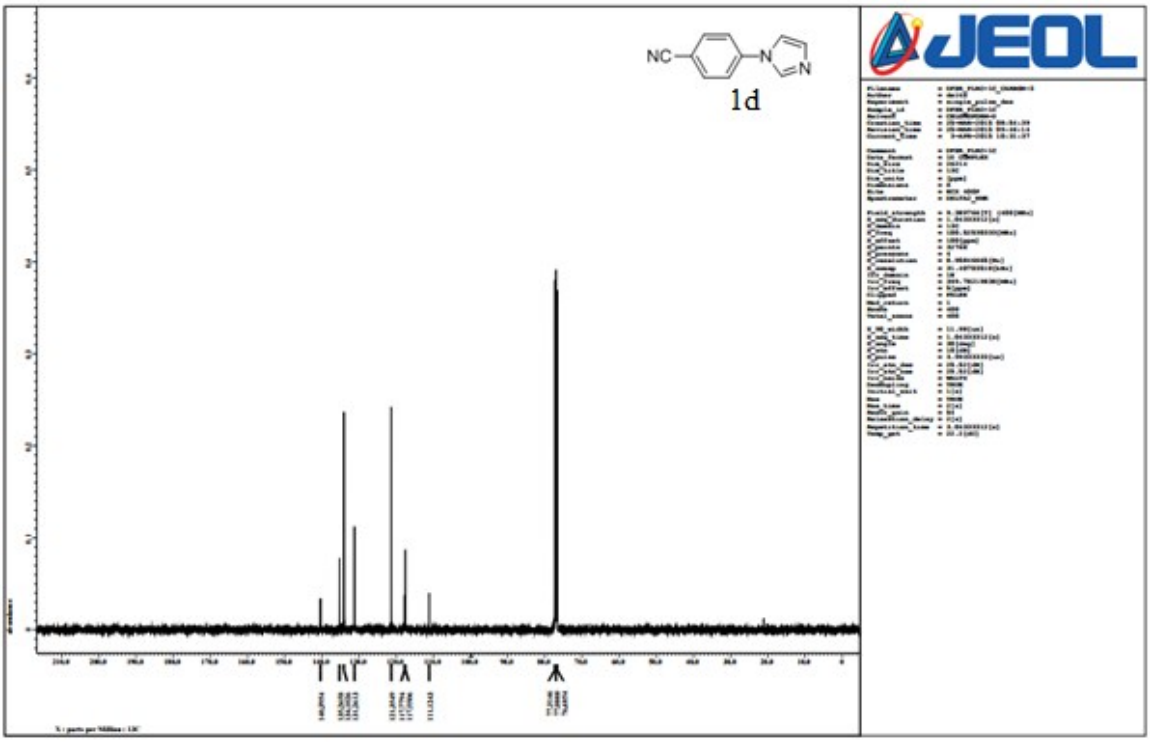

NO2
1b
JEOL
X : parts per Million : 1H

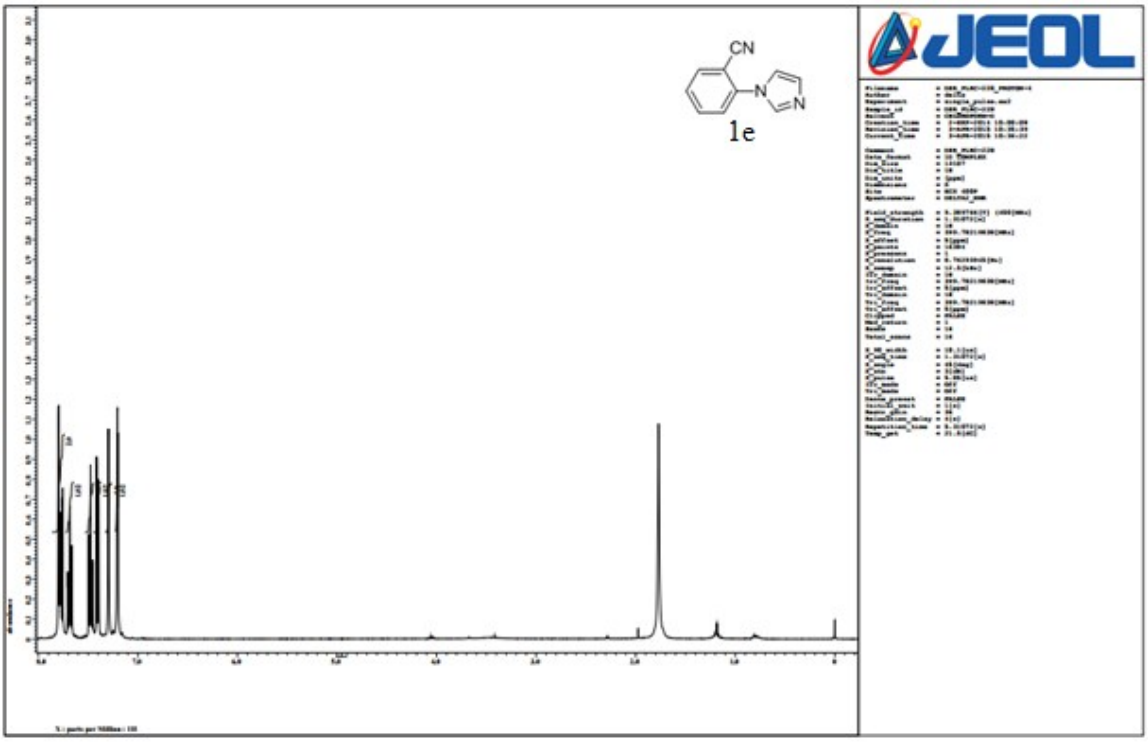

NO2
1b
JEOL
X : parts per Million : 13C

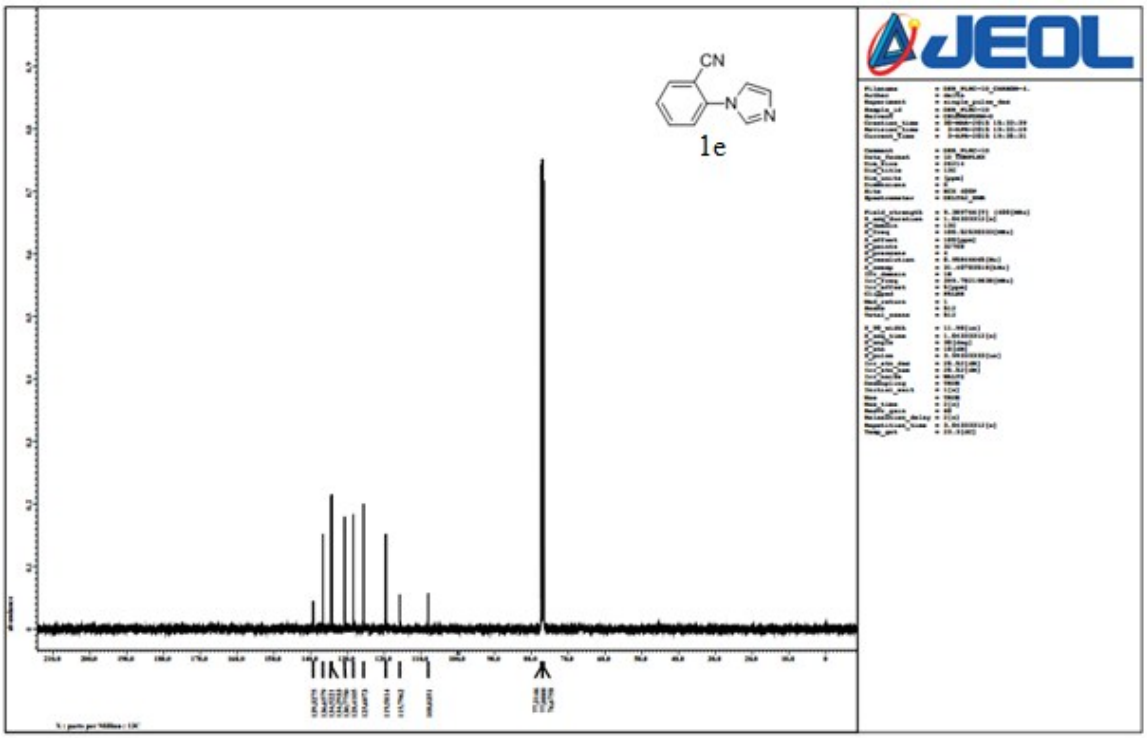

JEOL
NO2
1c

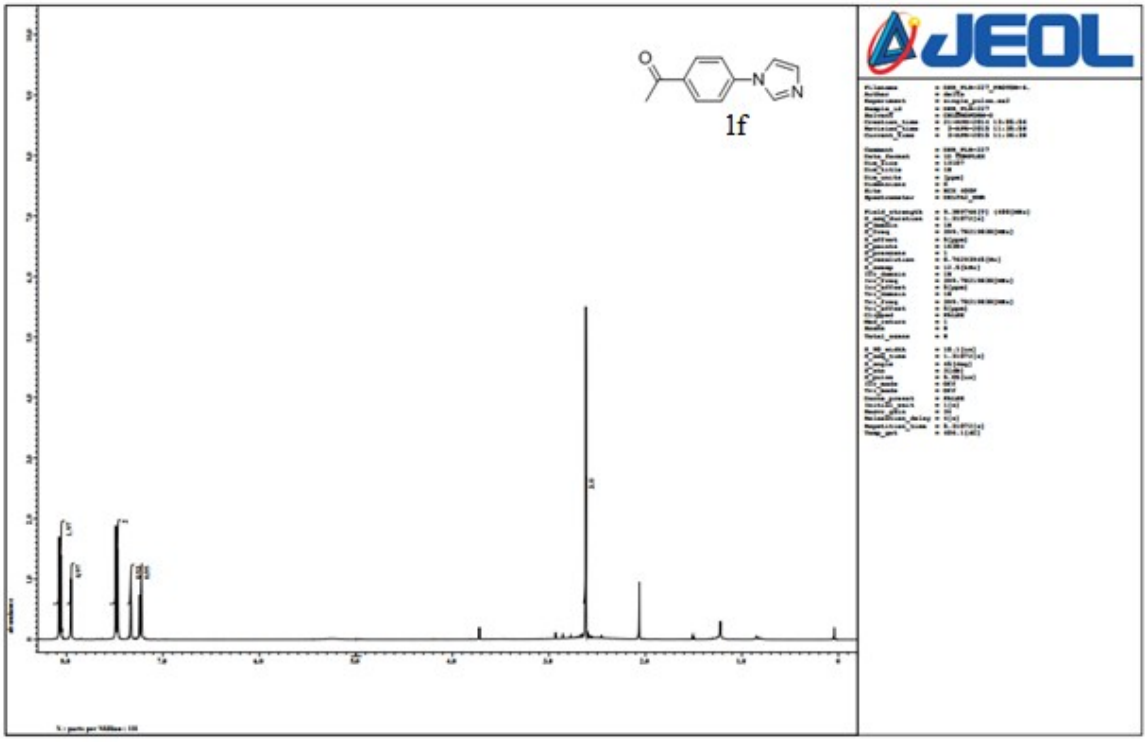

JEOL
NO2
1c

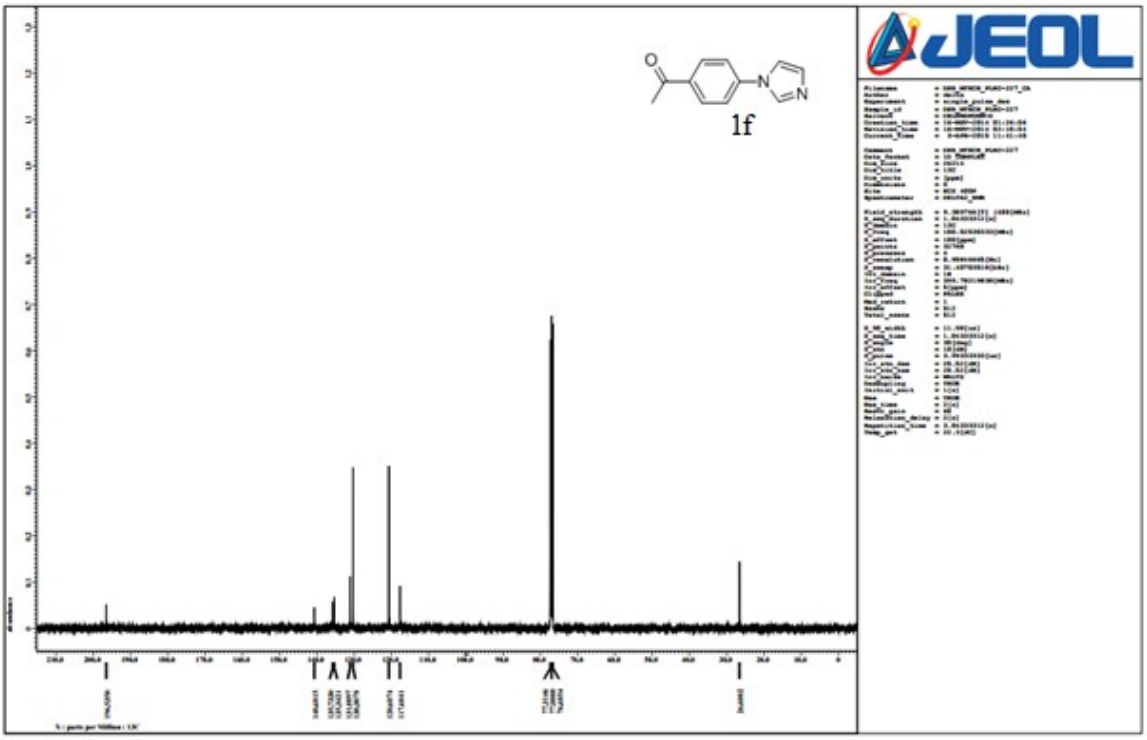

NC
N
N
1d
JEOL

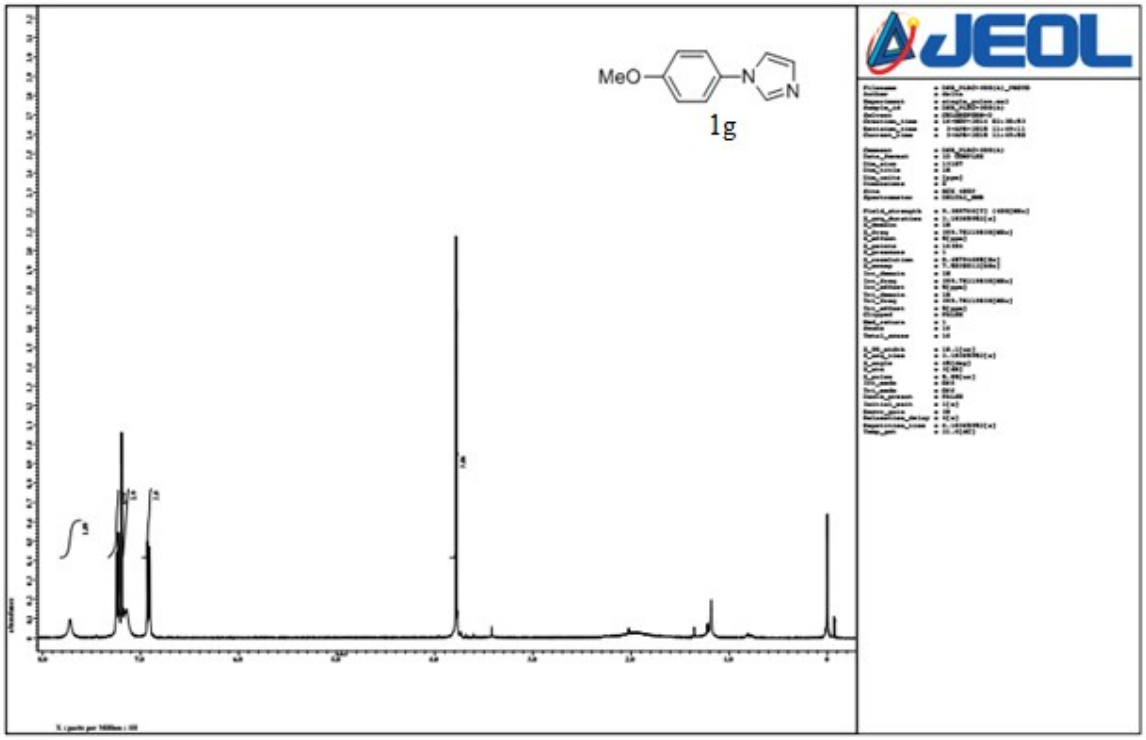

NC
N
N
1d
JEOL

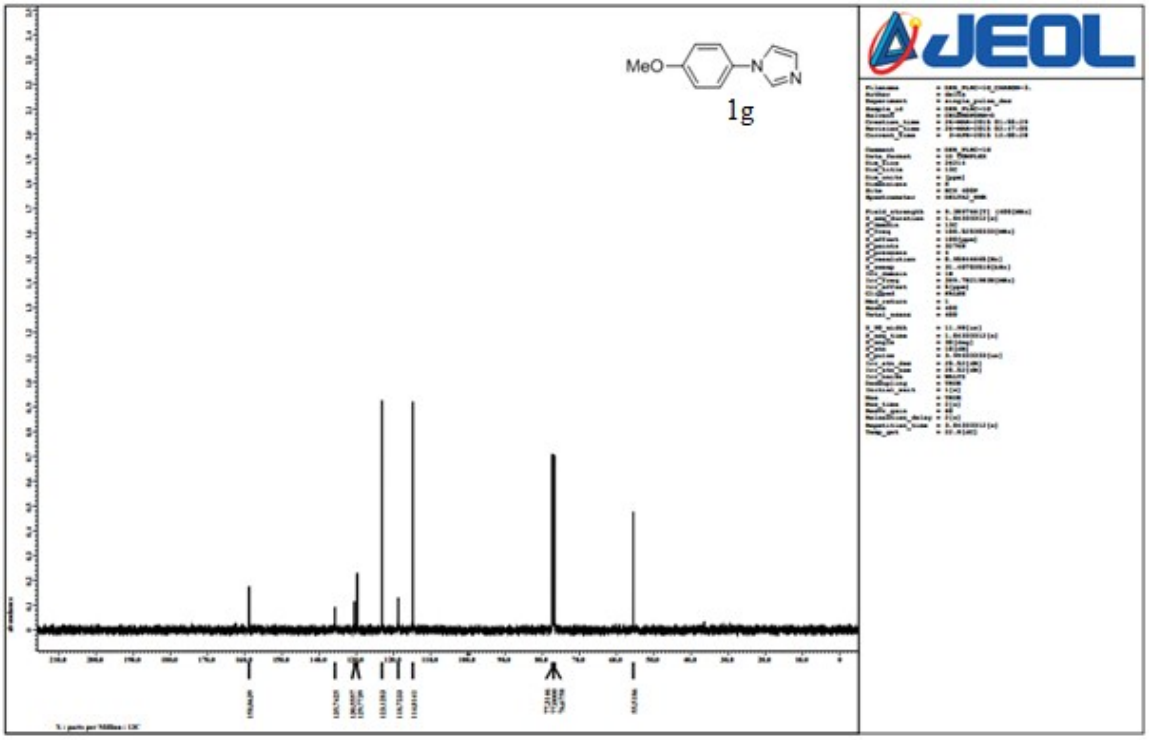

CN
N
N
1e
JEOL

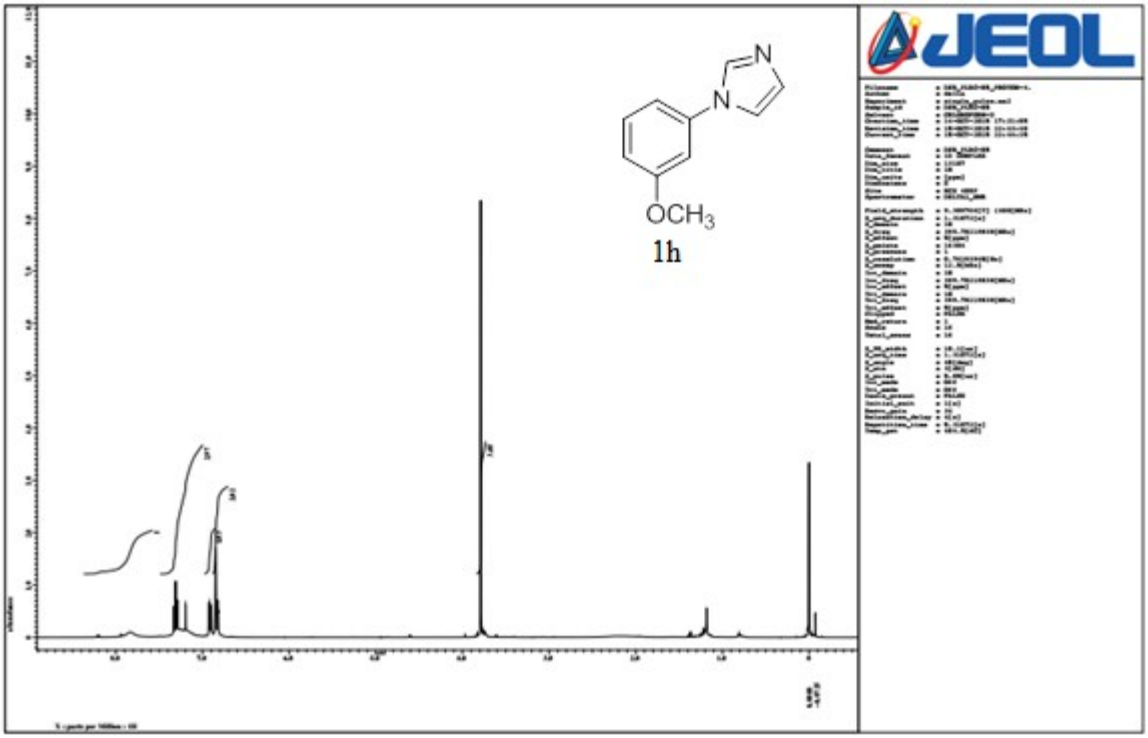

CN
N
N
1e
JEOL

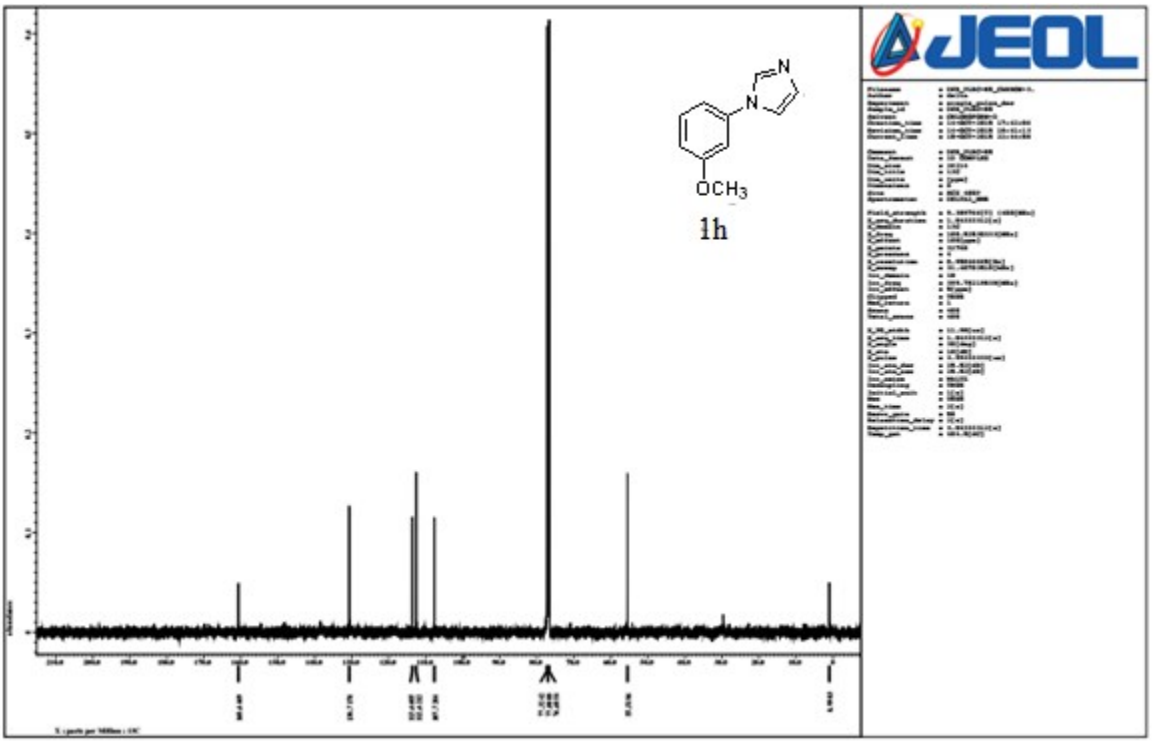

1f
JEOL

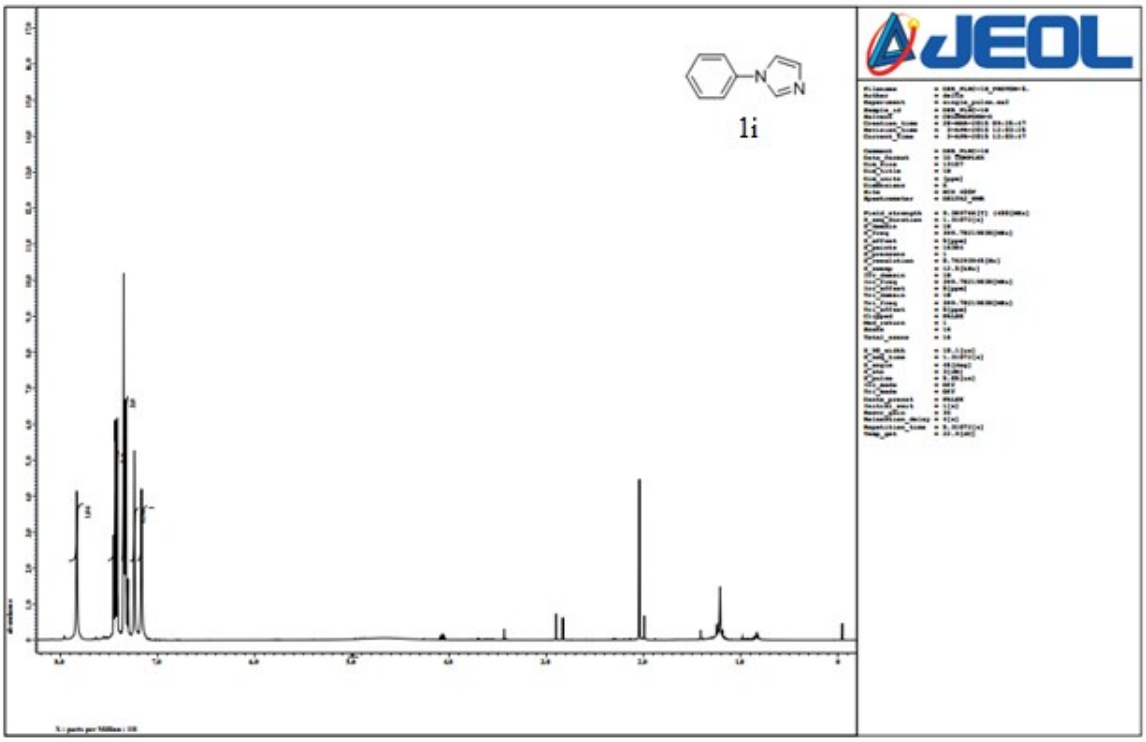

1f
JEOL

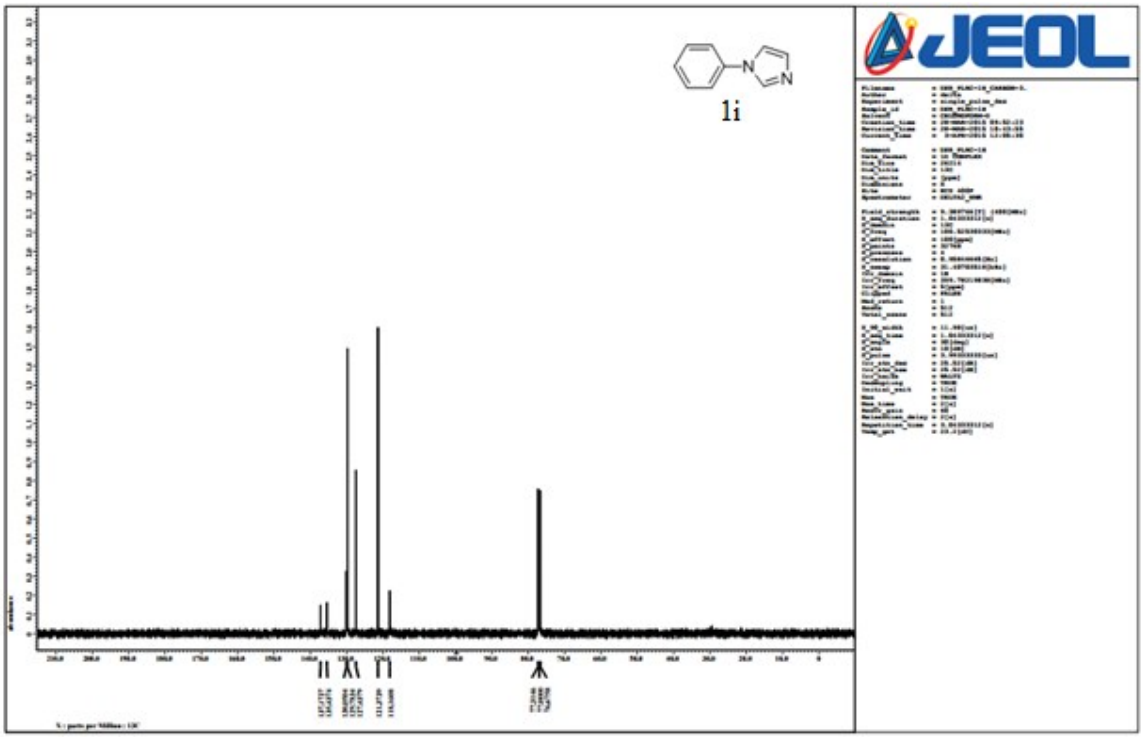

MeO
N
N
1g
JEOL

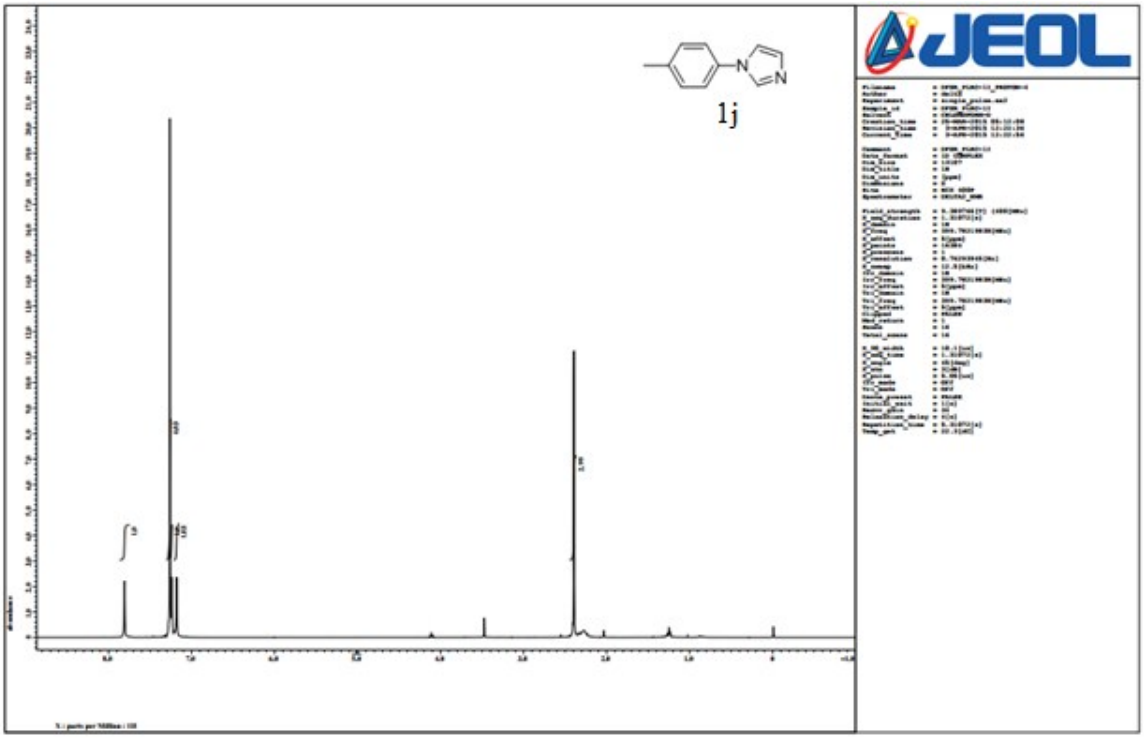

MeO
N
N
1g
JEOL

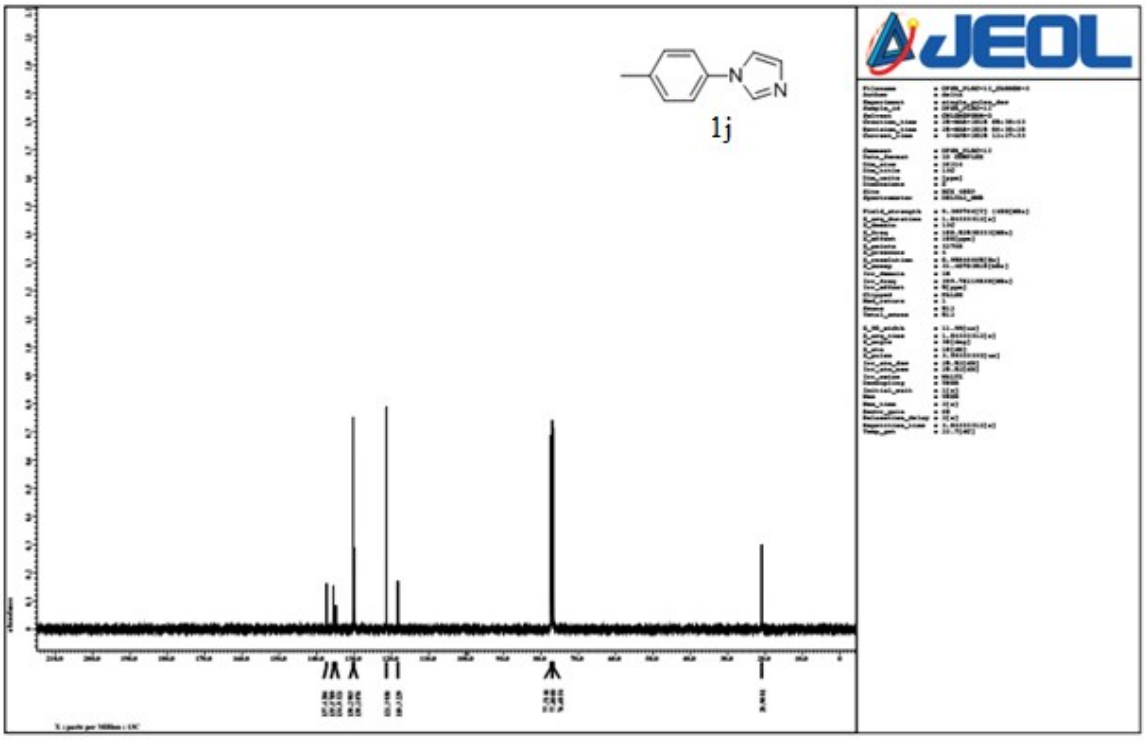

JEOL
N
N
OCH3
1h

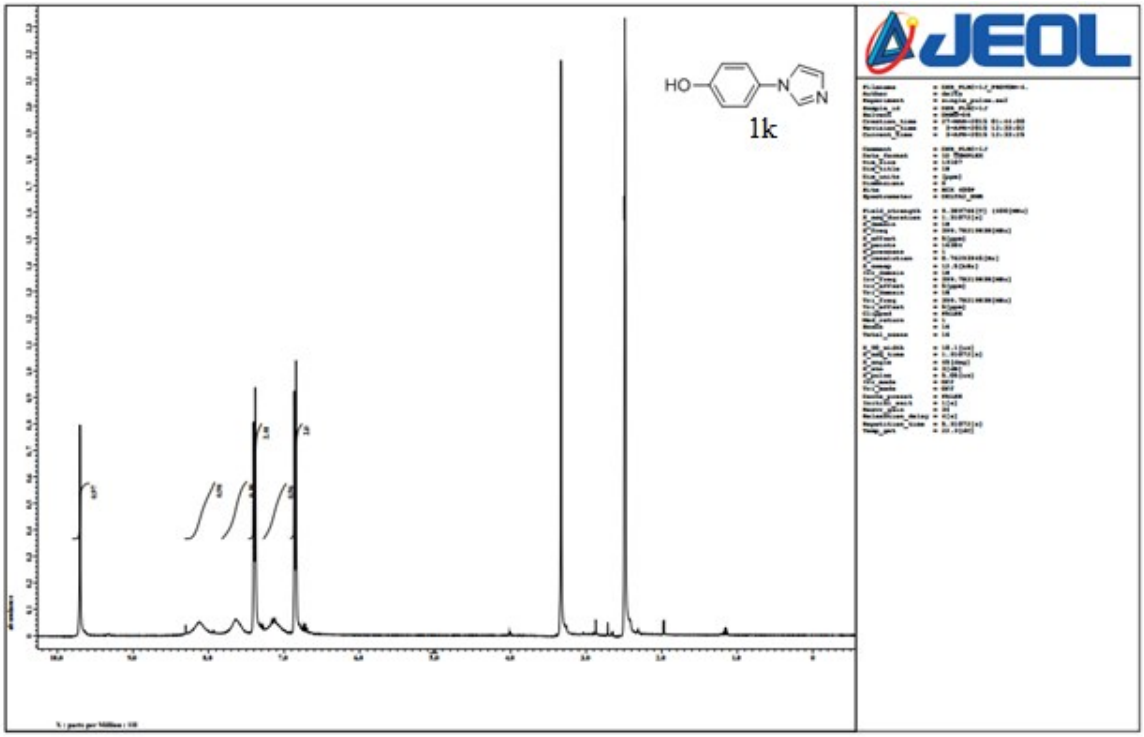

JEOL
N
N
OCH3
1h

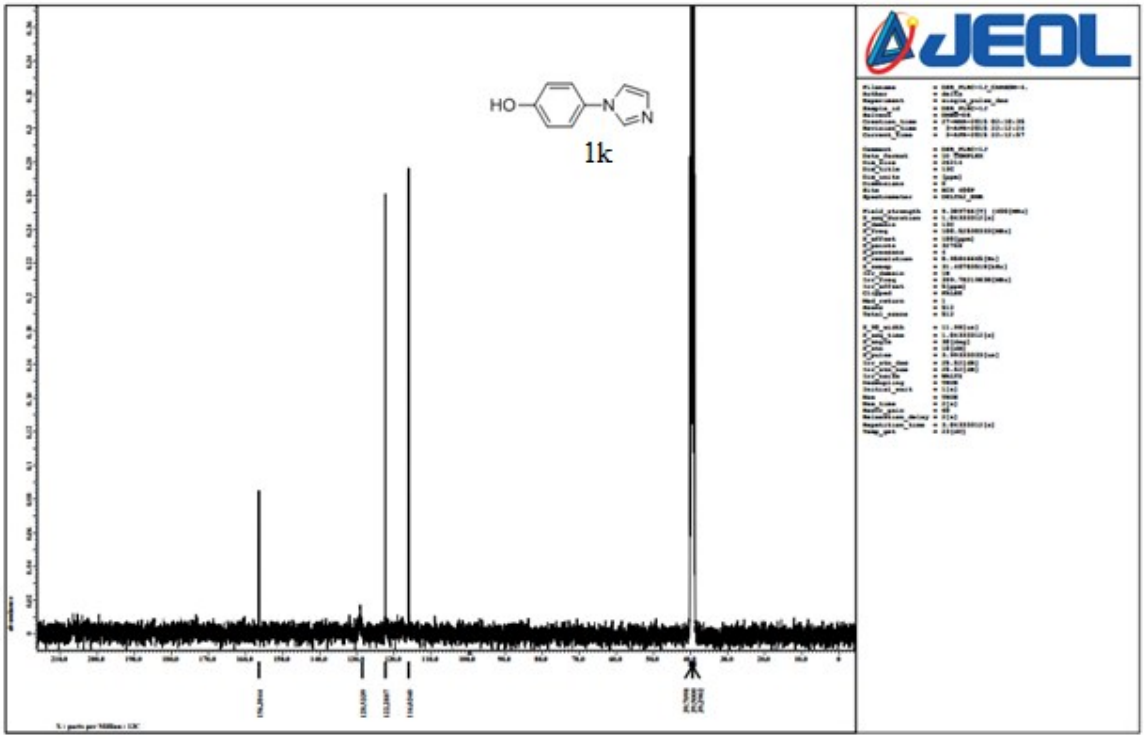

1i
JEOL

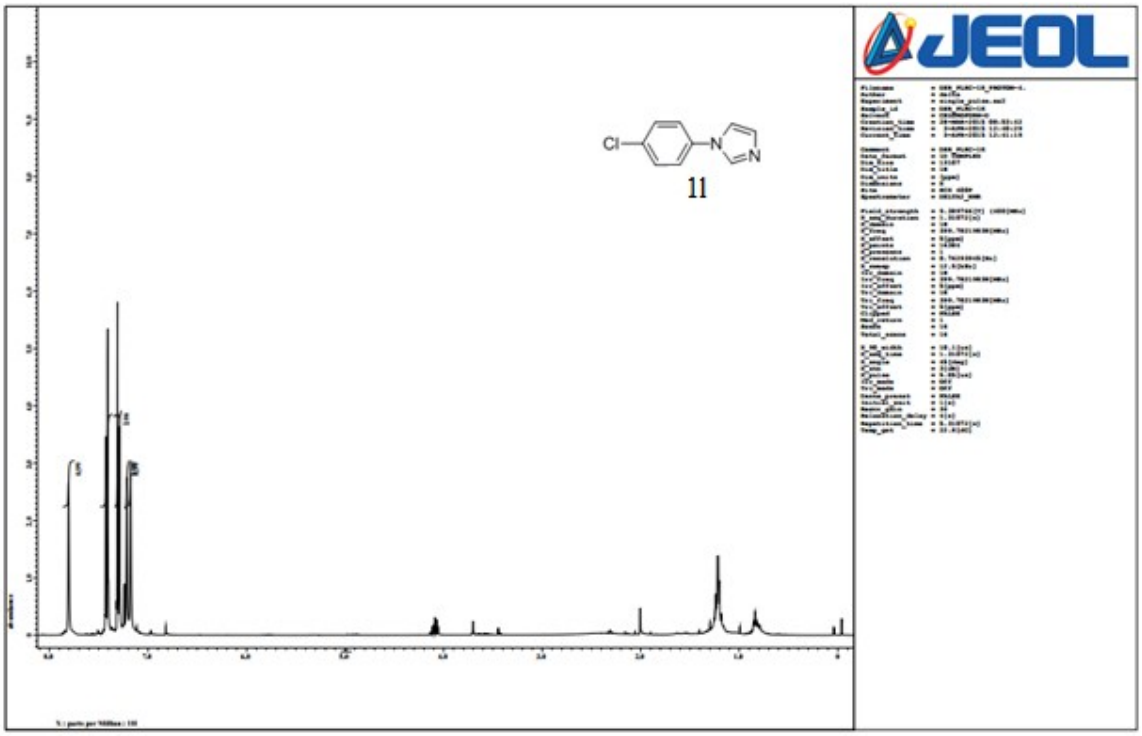

1i
JEOL

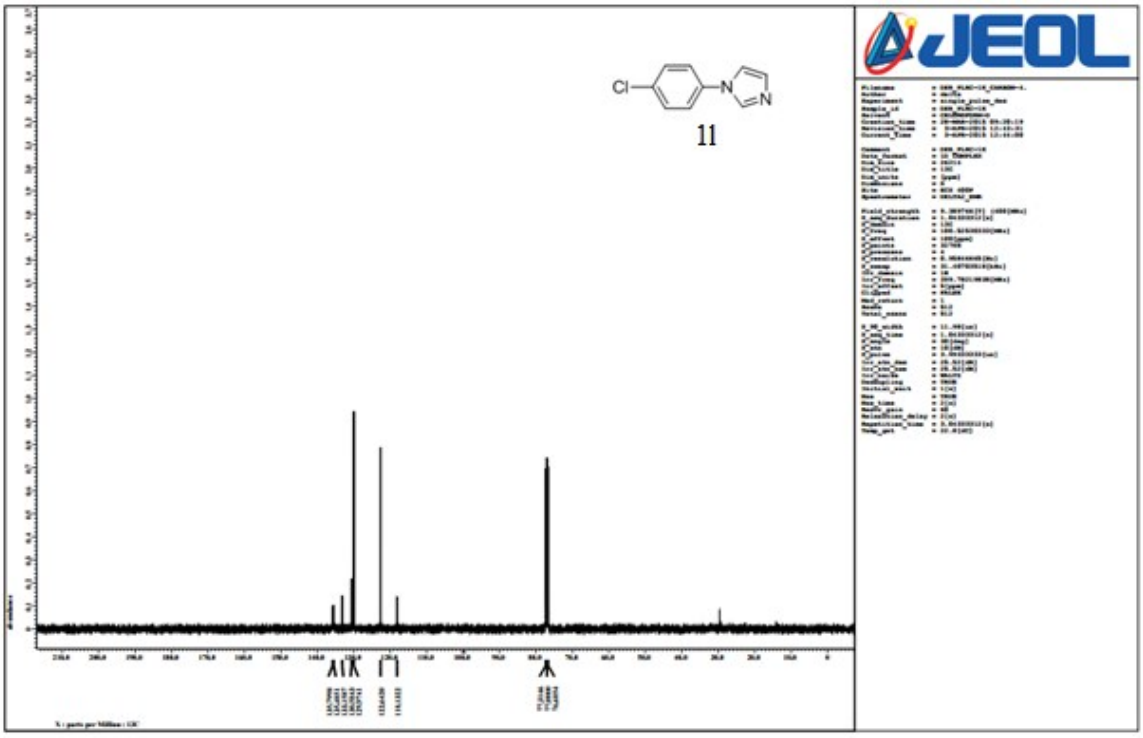

1j
JEOL

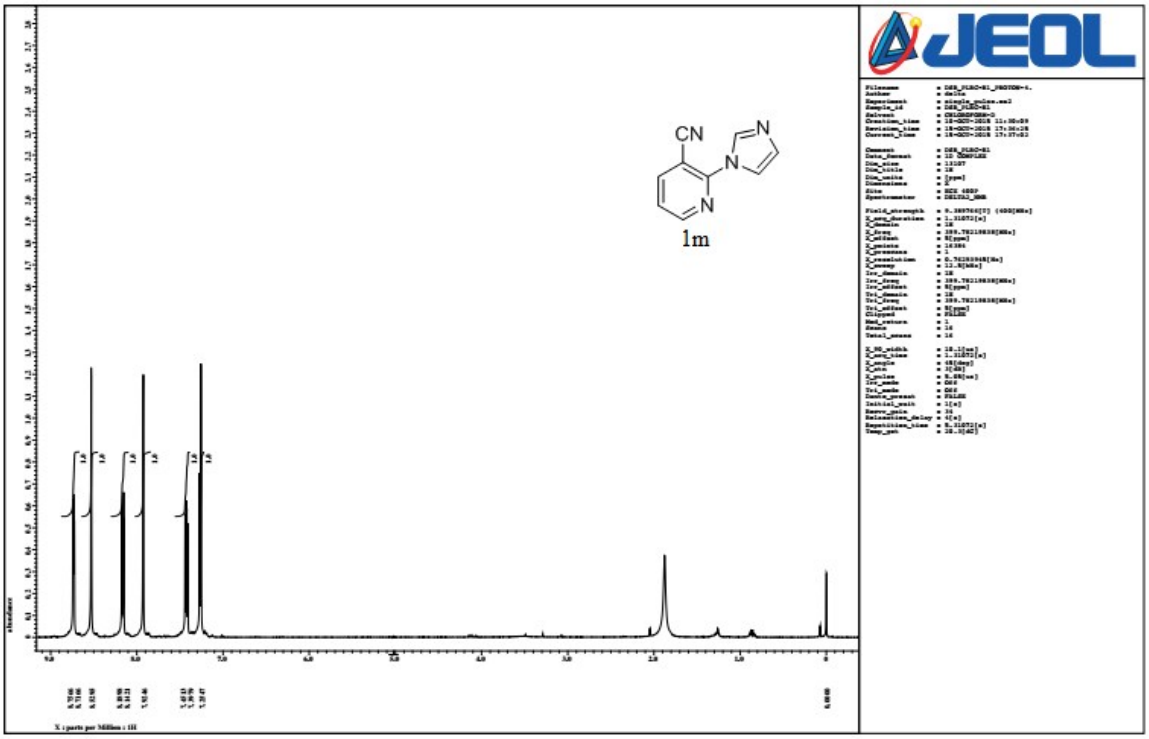

1j
JEOL

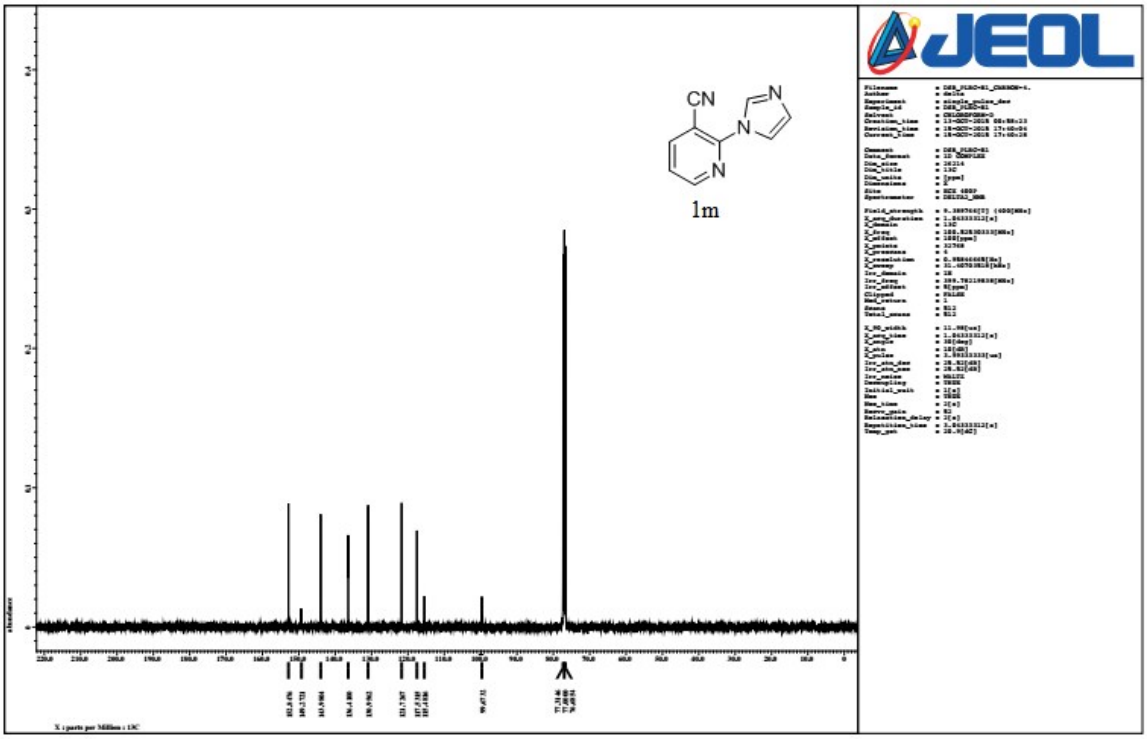

HO
N
N
1k
JEOL

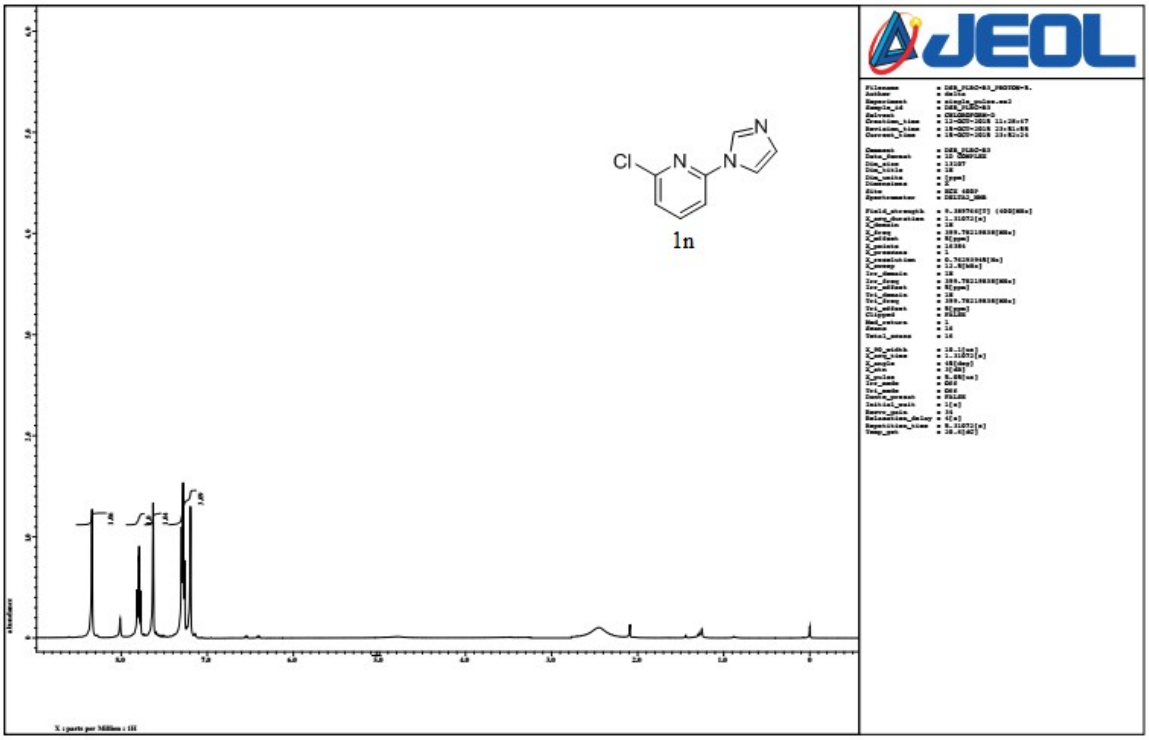

HO
N
N
1k
JEOL

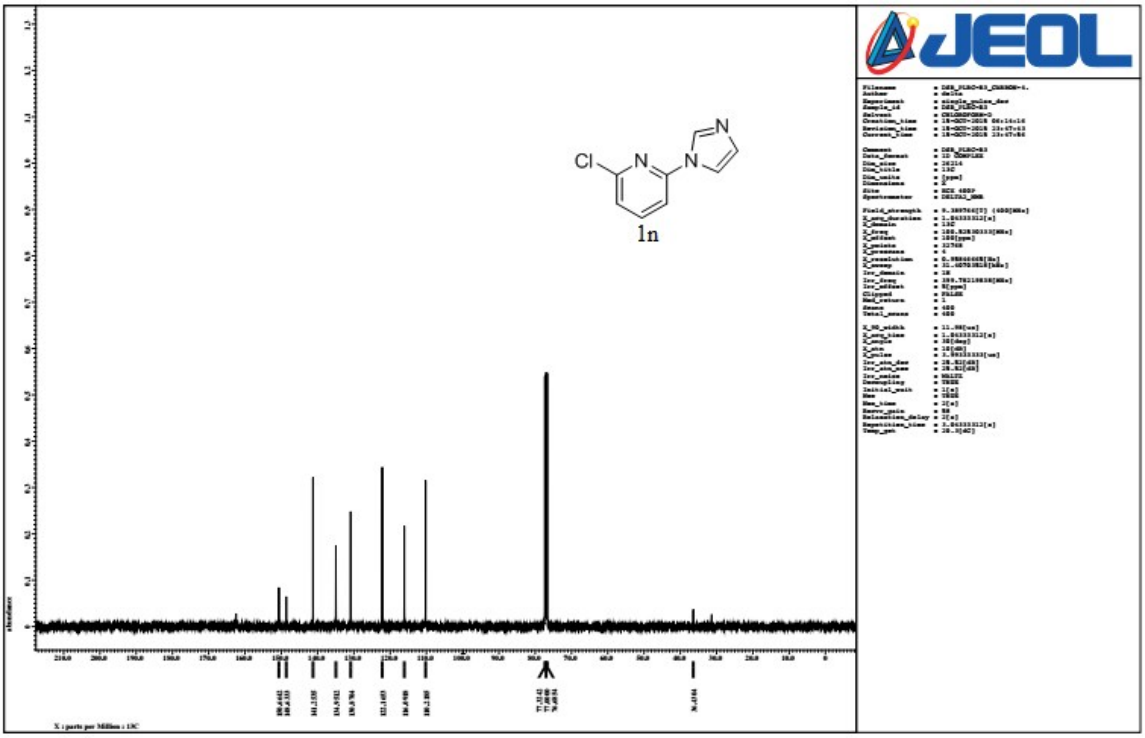

JEOL
Cl
N
N
11

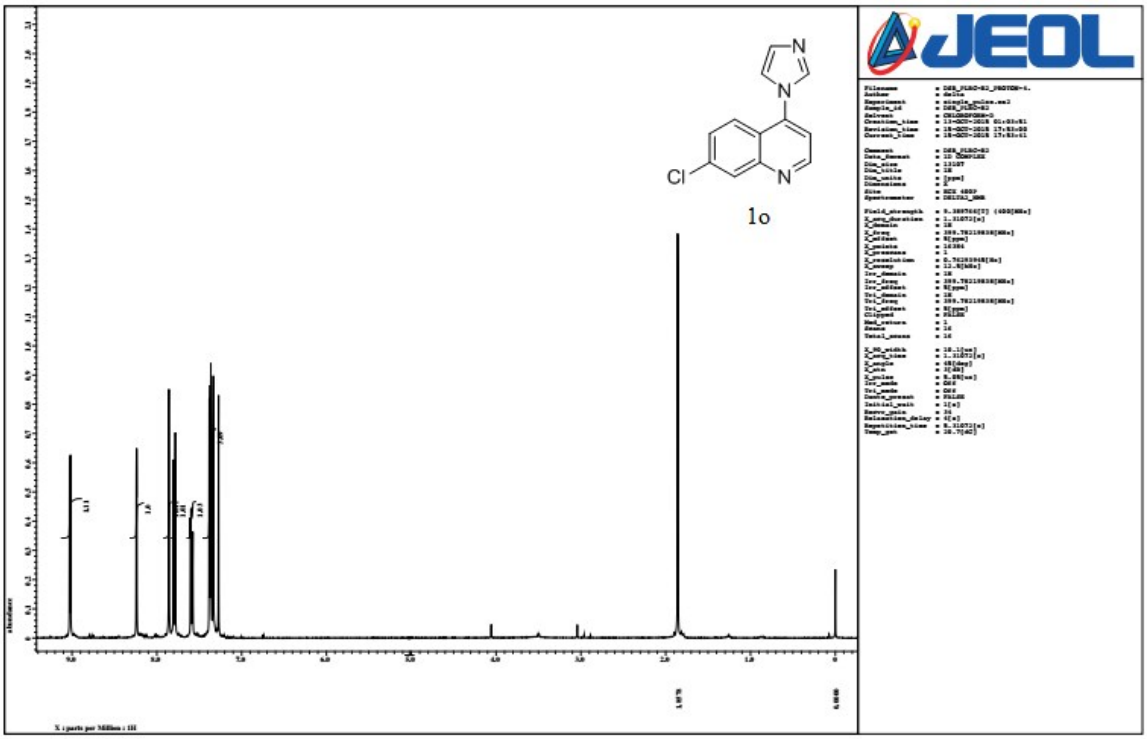

JEOL
Cl
N
N
11

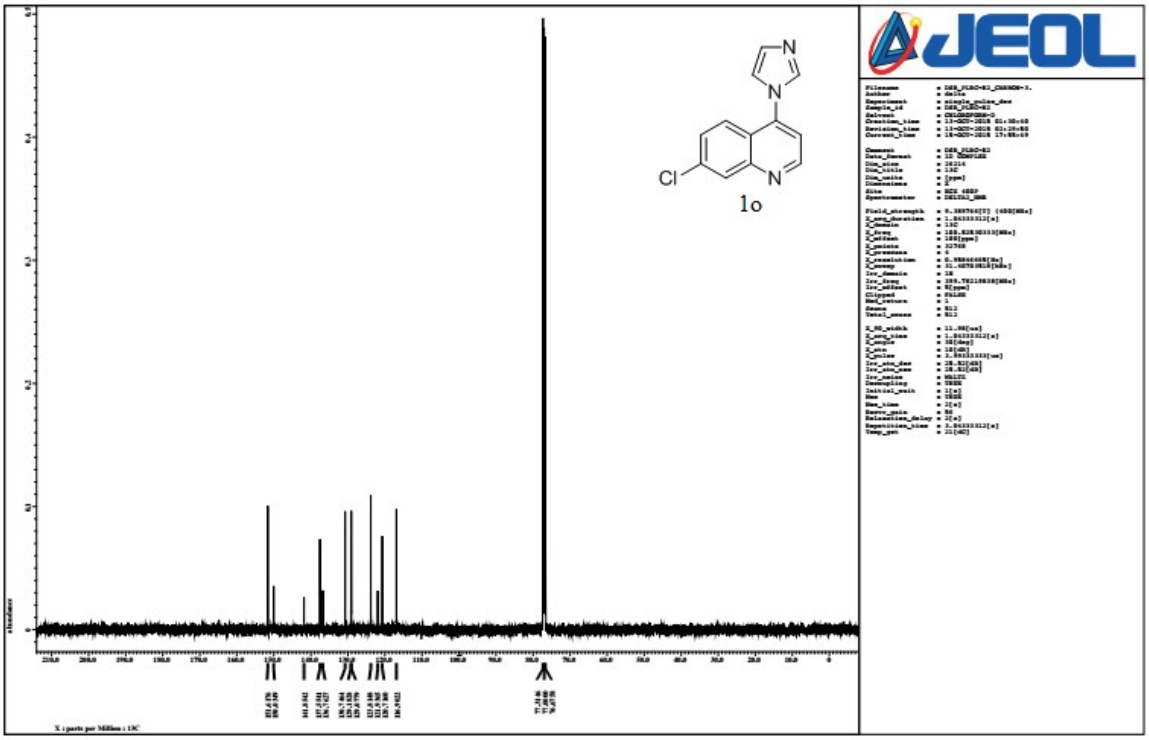

CN
N
N
N
1m
JEOL

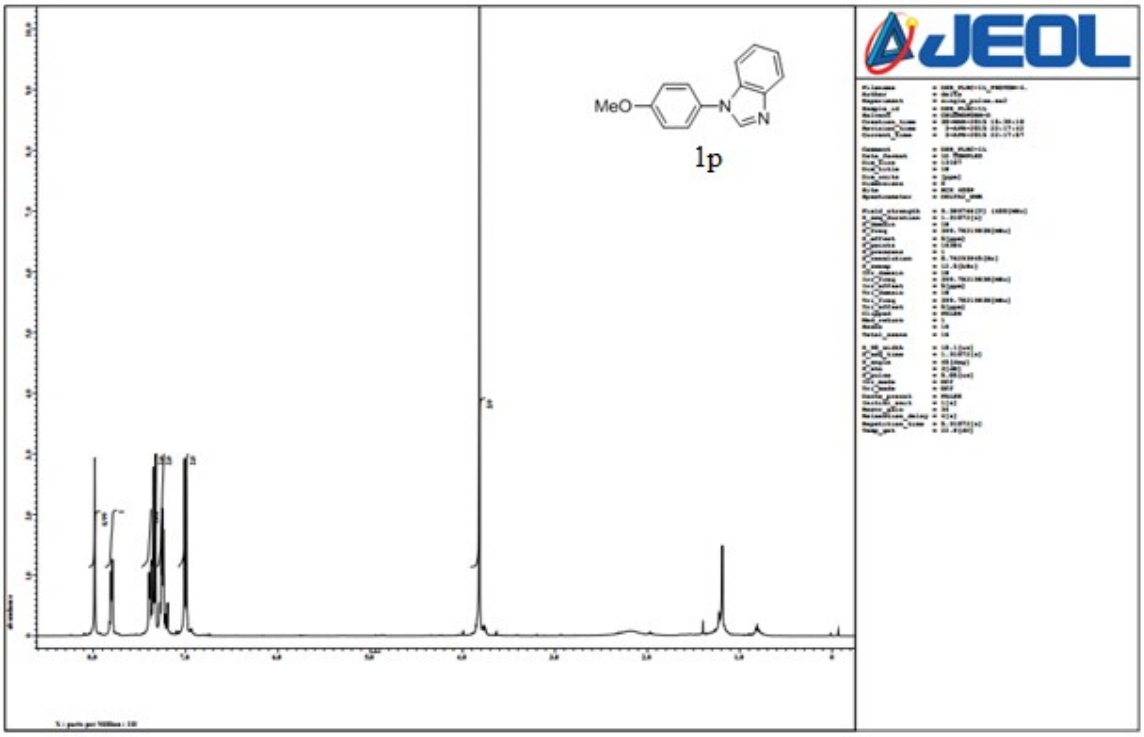

CN
N
N
N
1m
JEOL

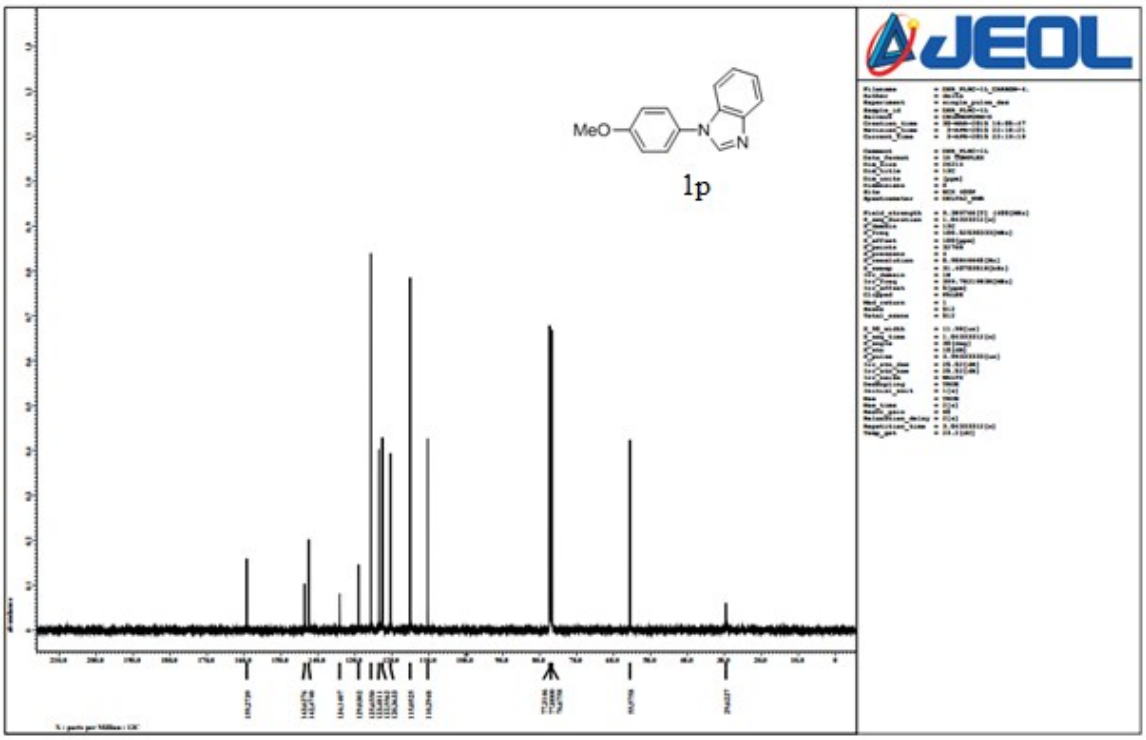

Cl
N
N
N
1n
JEOL

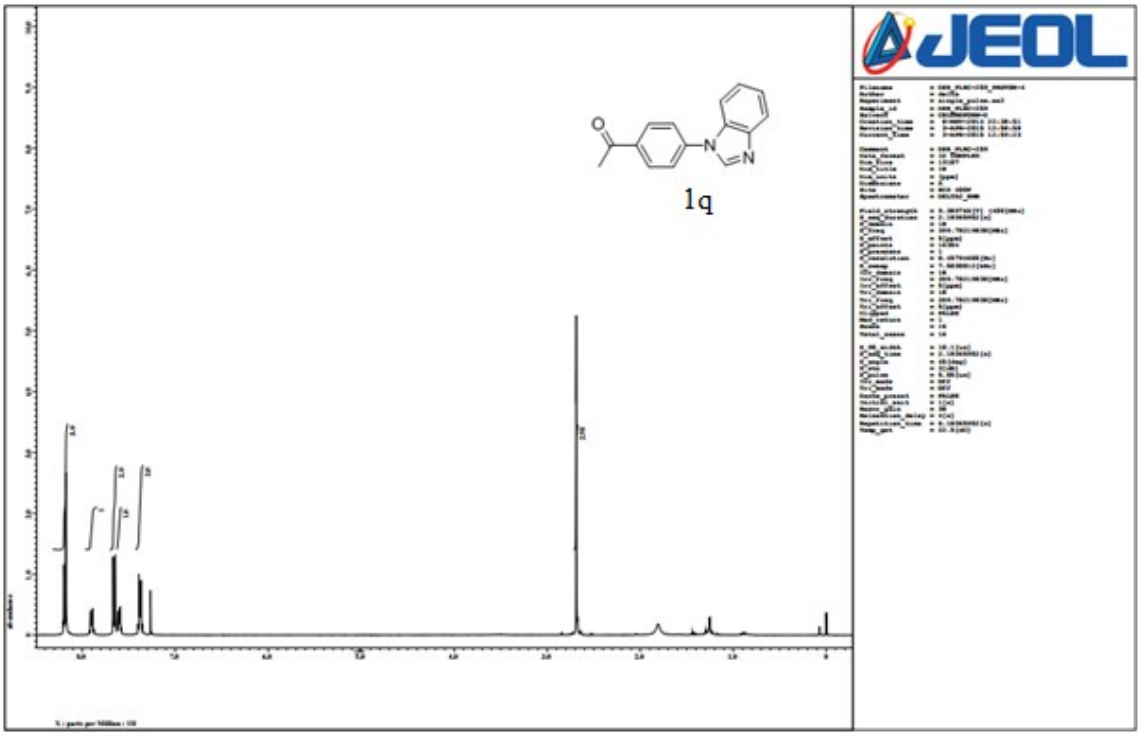

Cl
N
N
N
1n
JEOL

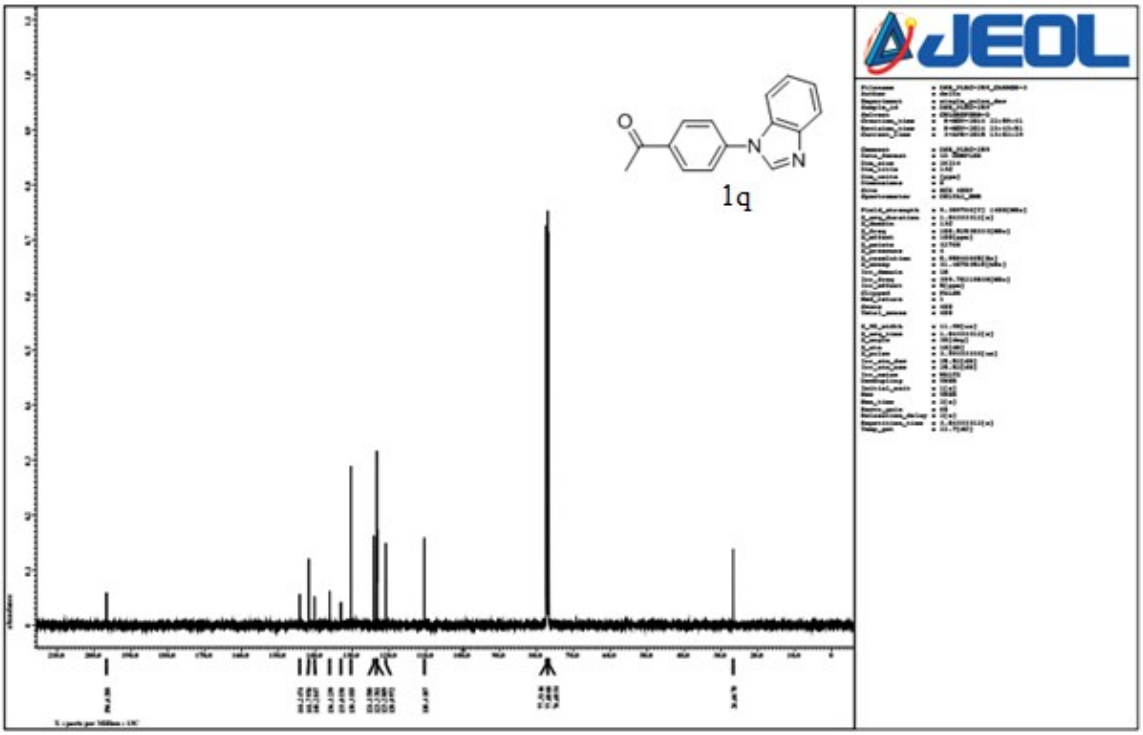

1o

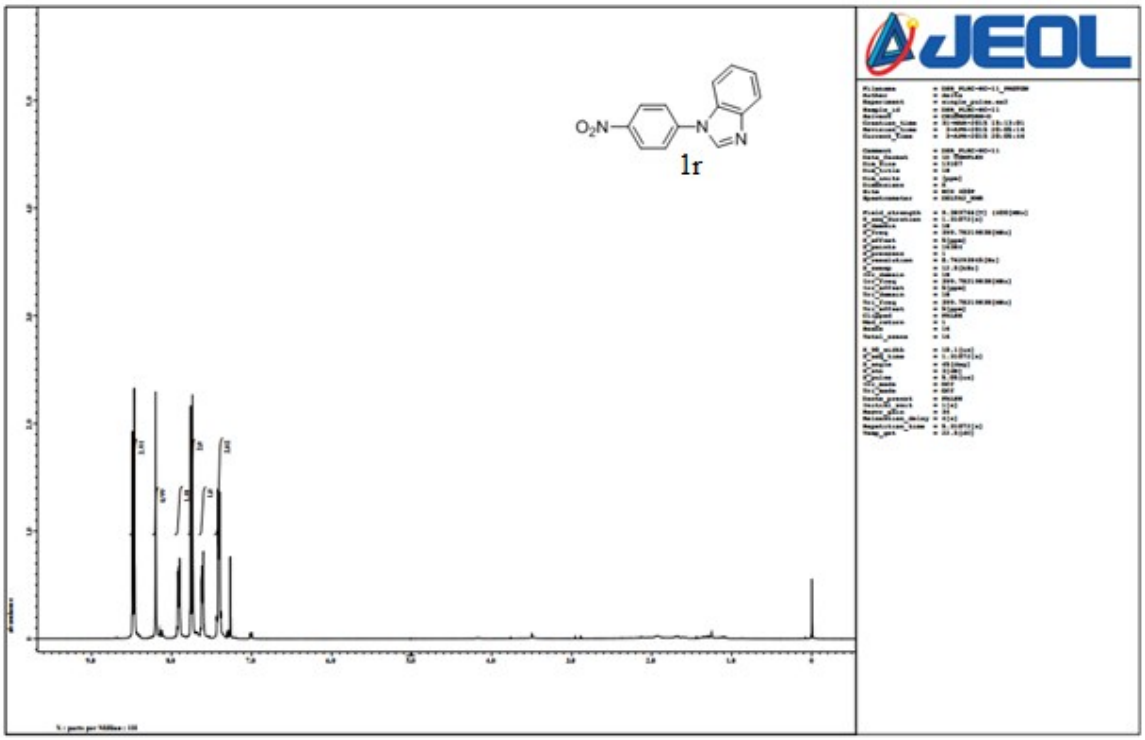

1o

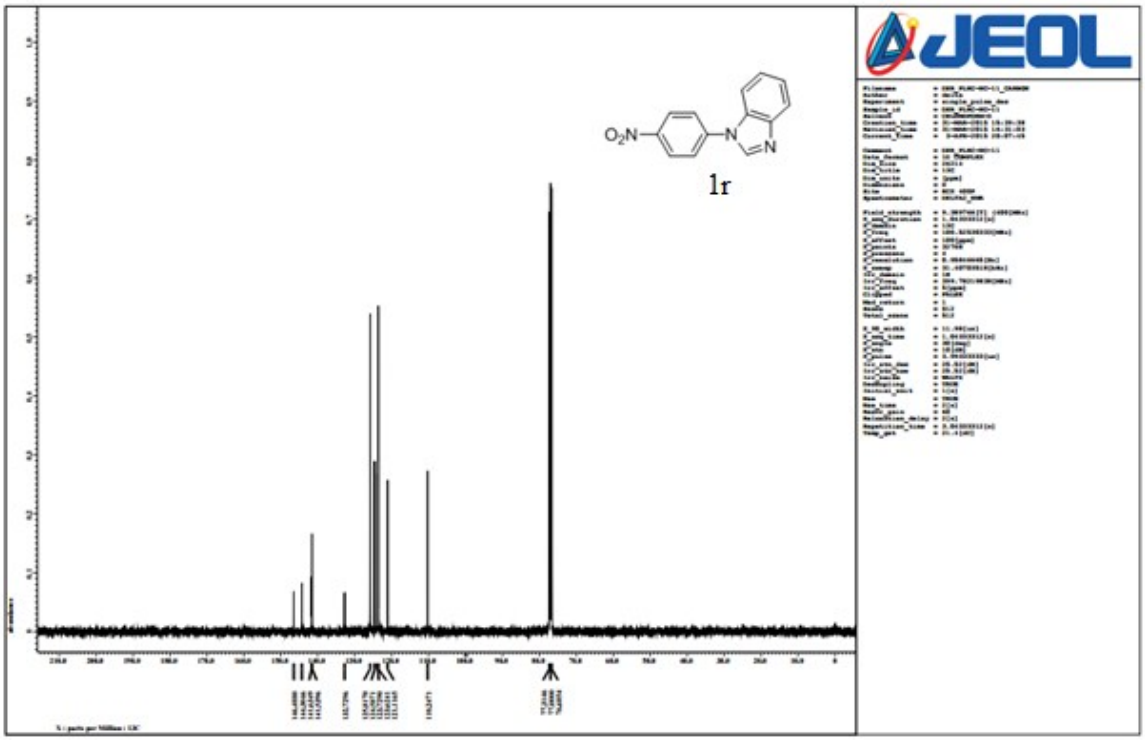

MeO
N
N
1p
JEOL

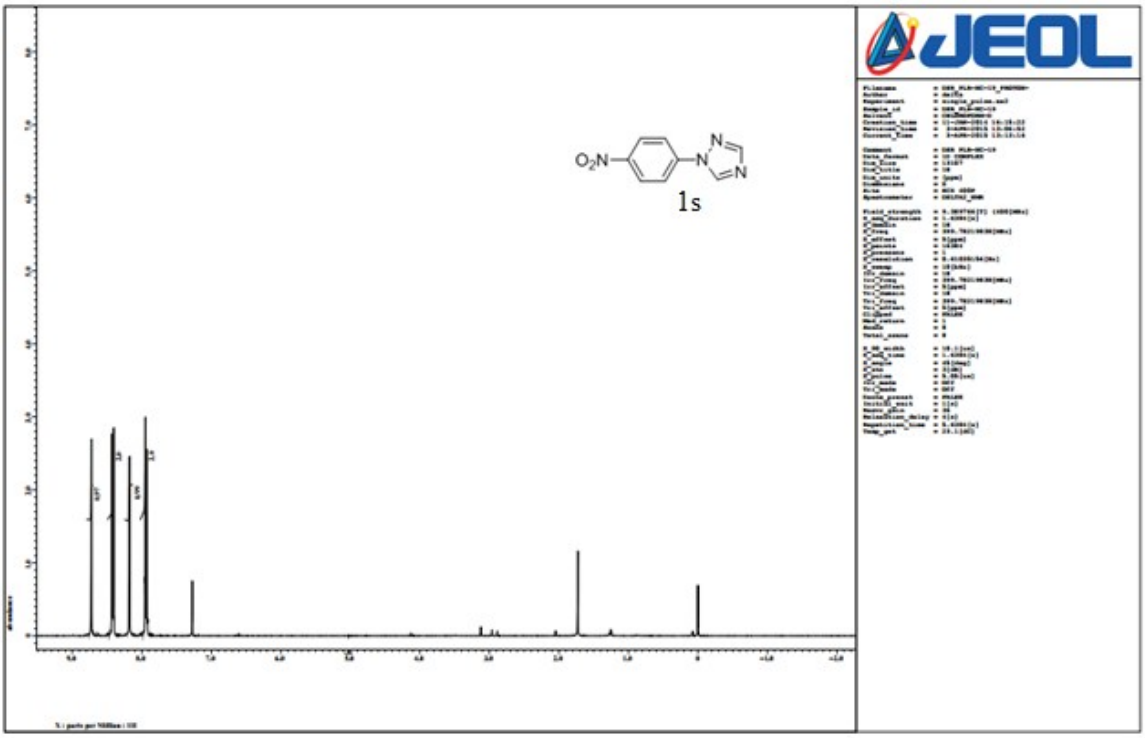

MeO
N
N
1p
JEOL

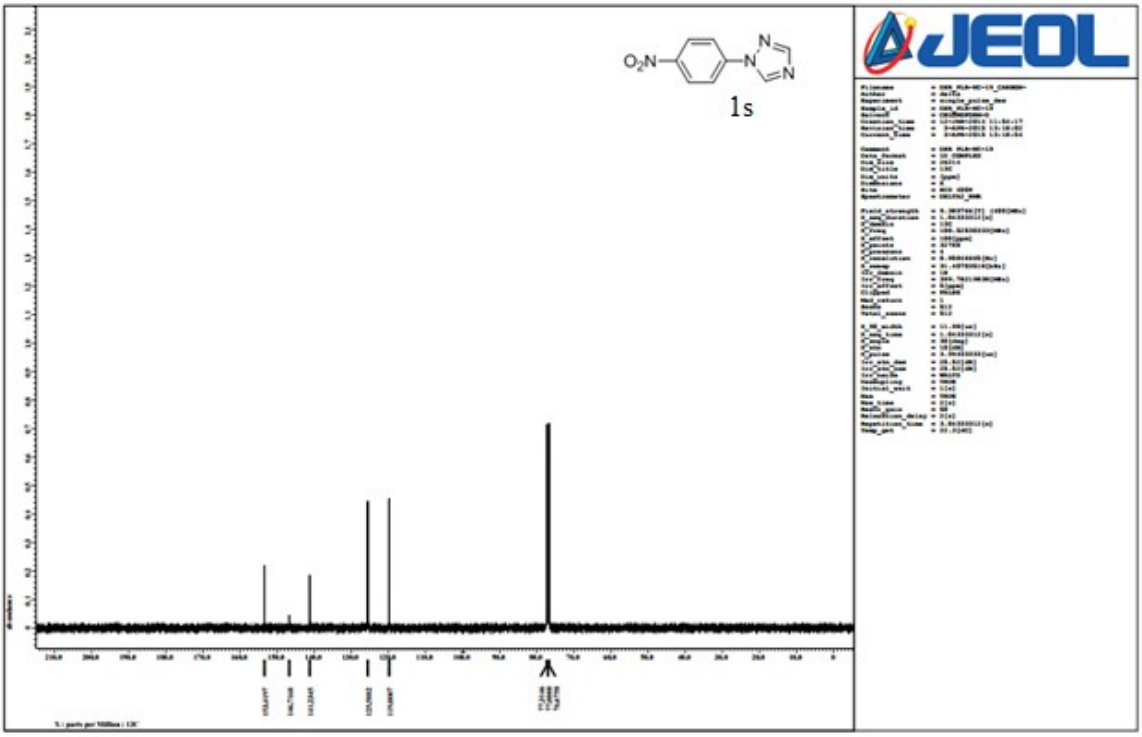

1q

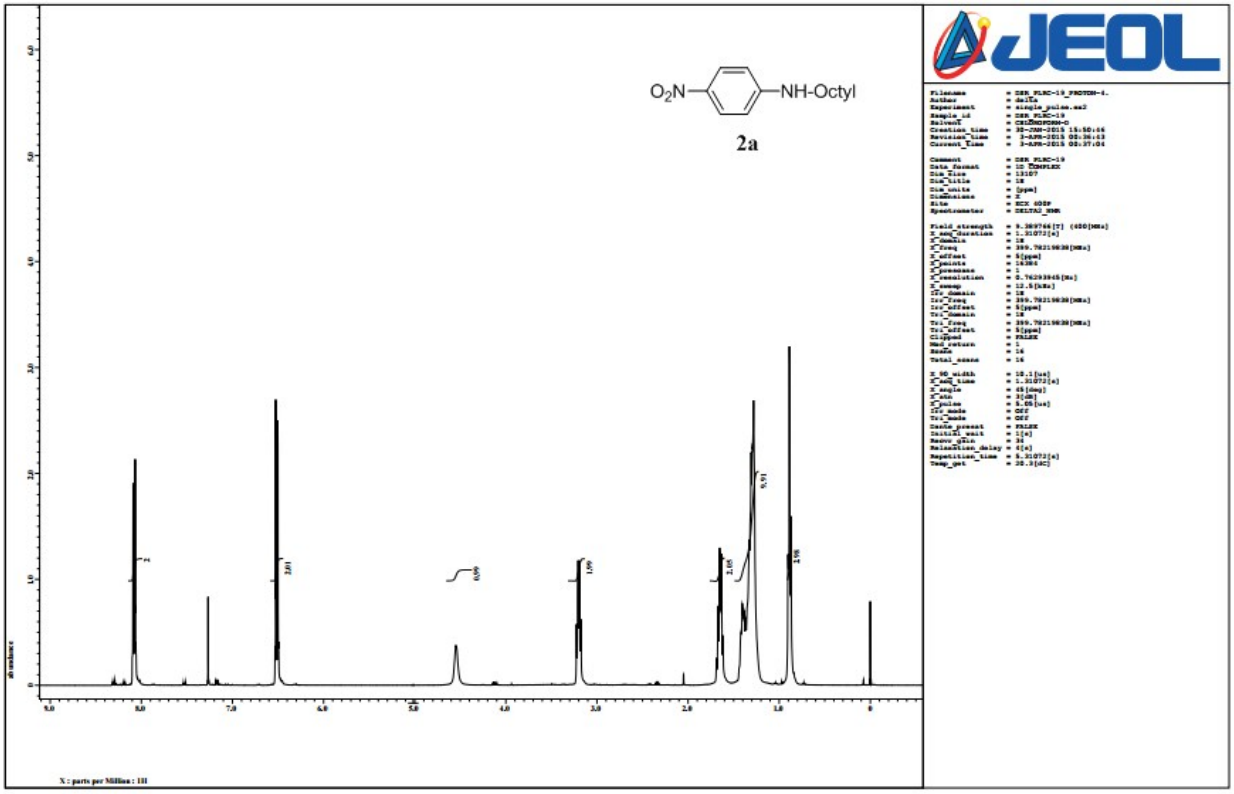

1q

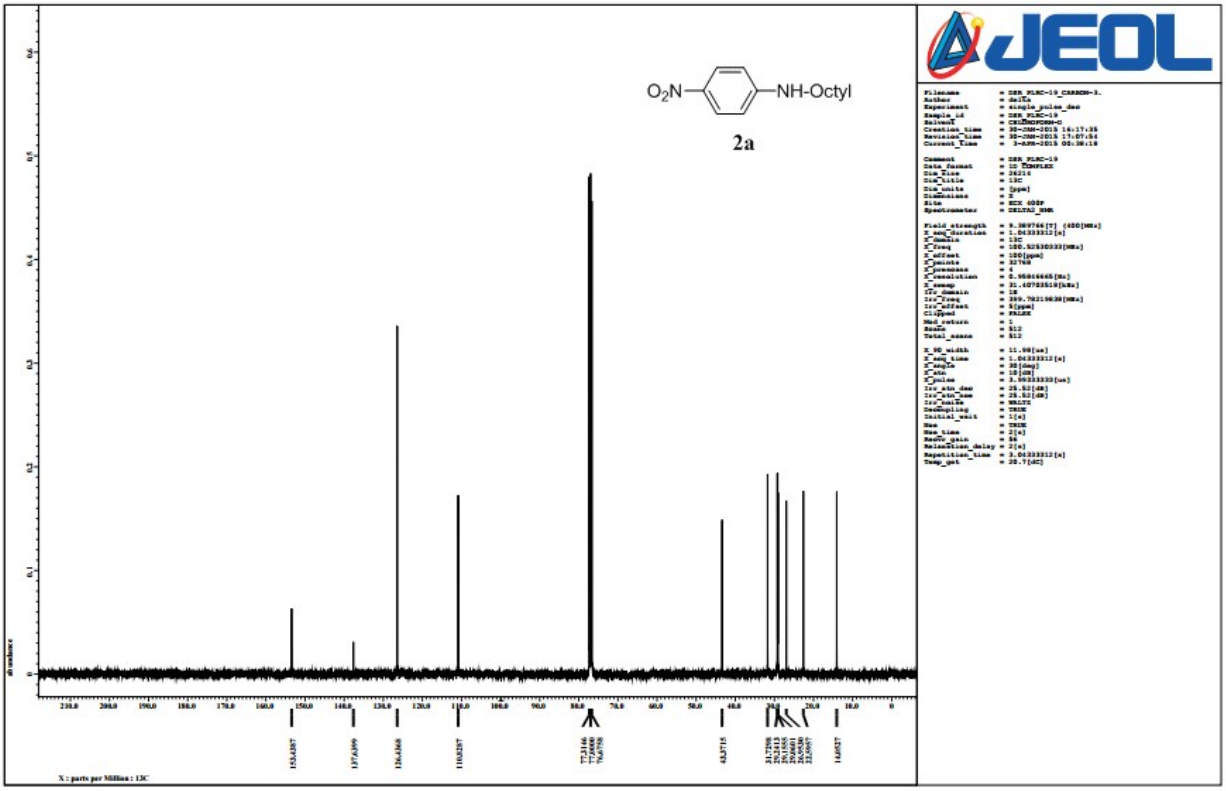

JEOL
1r

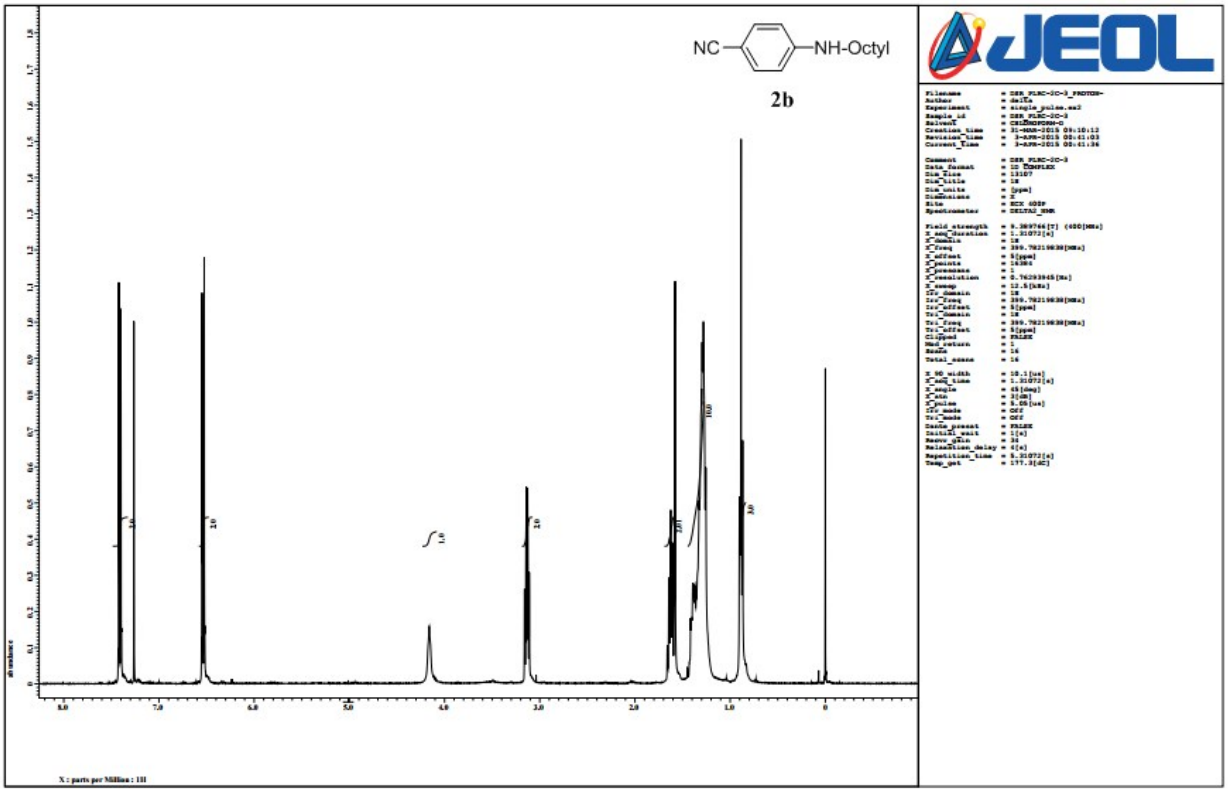

JEOL
1r

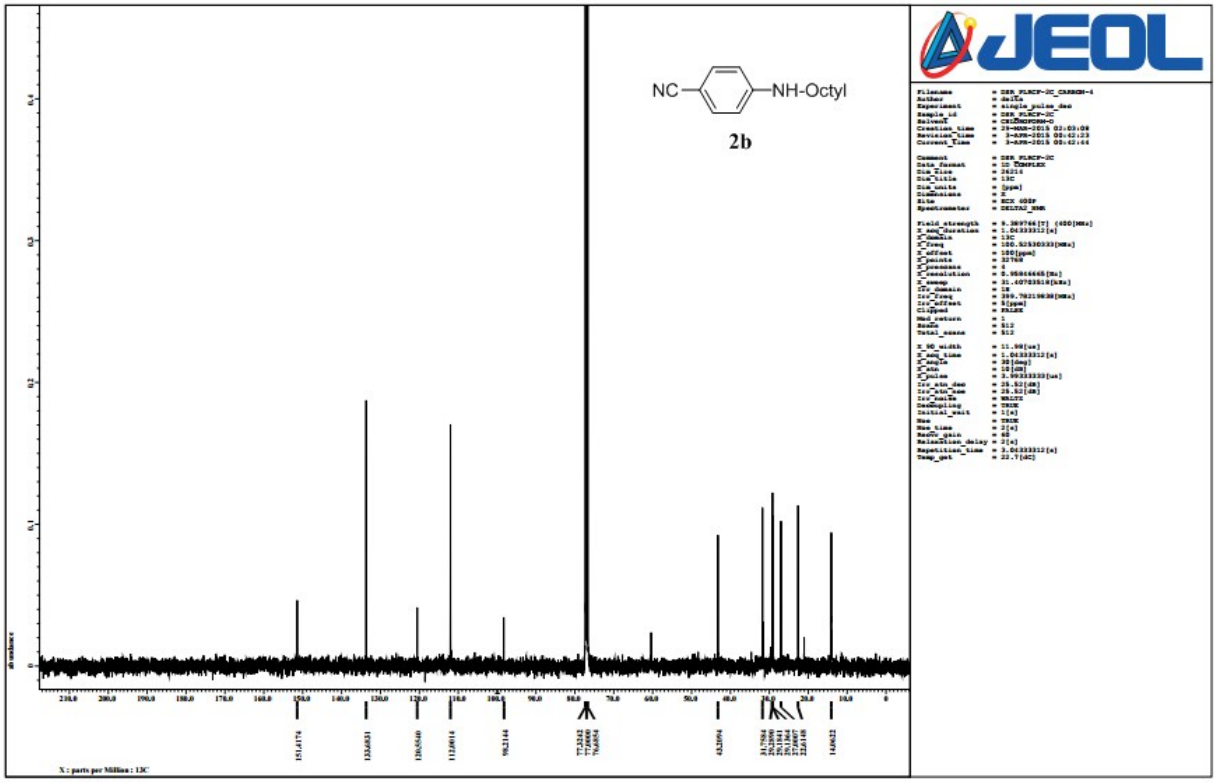

1s

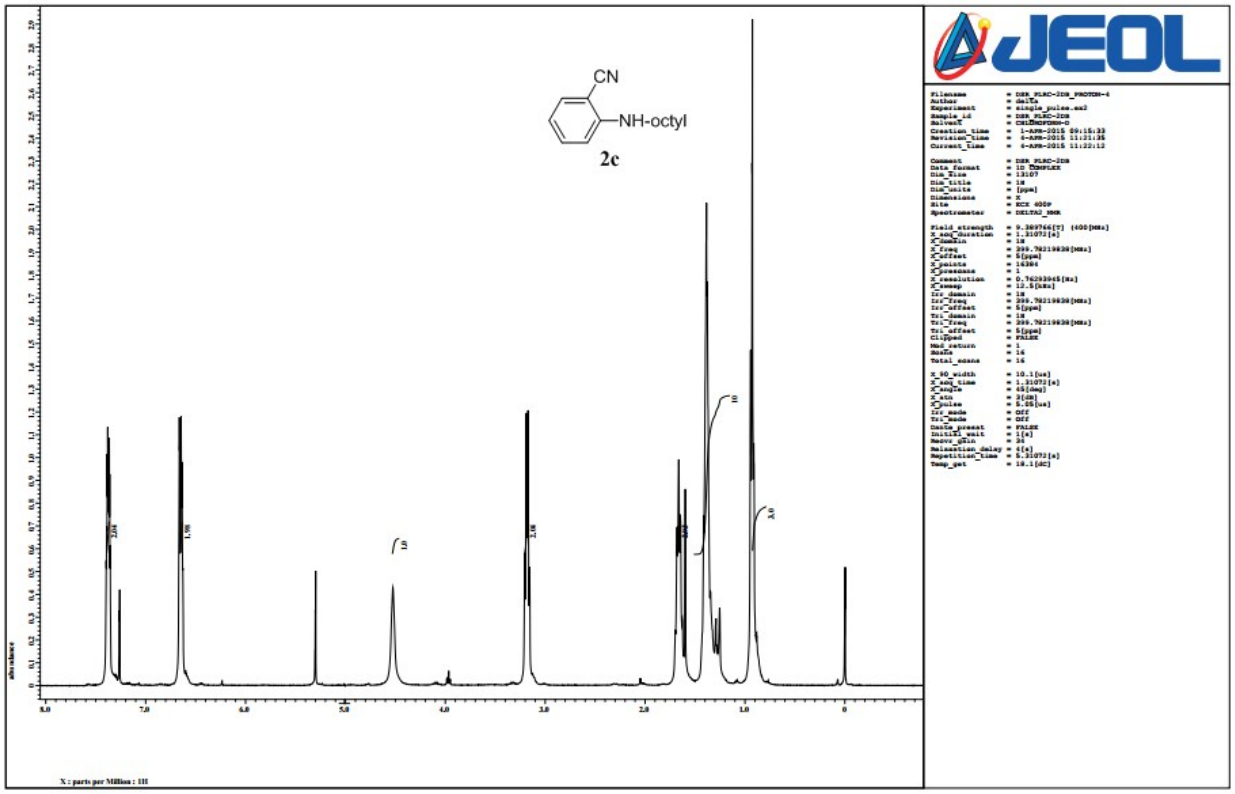

1s

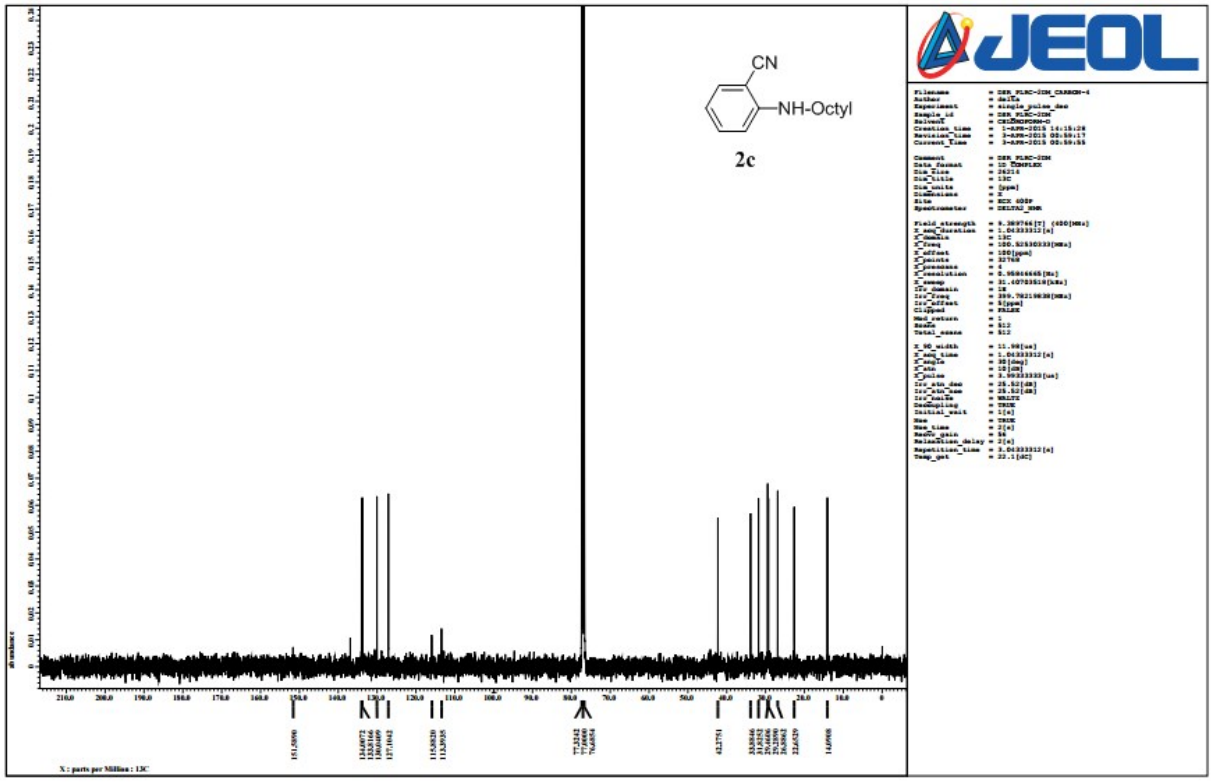

O2N
NH-Octyl
2a
JEOL
X : parts per Million : 1H

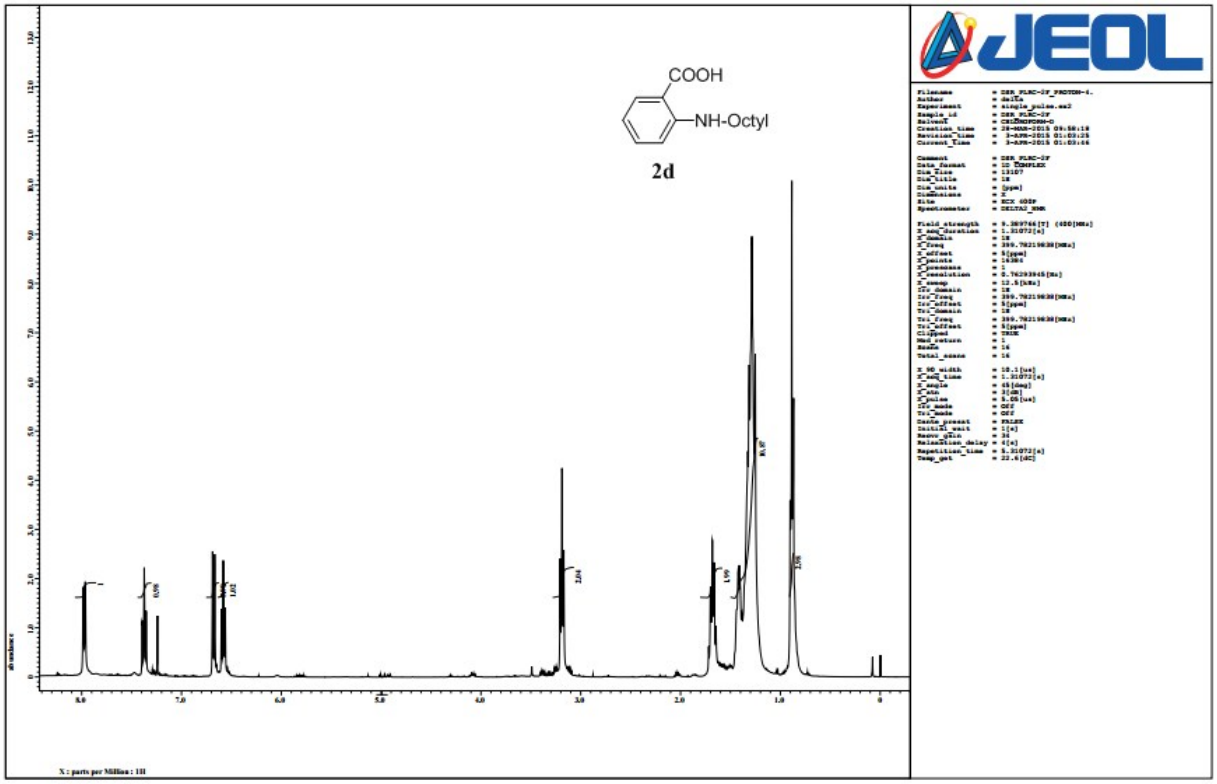

O2N
NH-Octyl
2a
JEOL
X : parts per Million : 13C

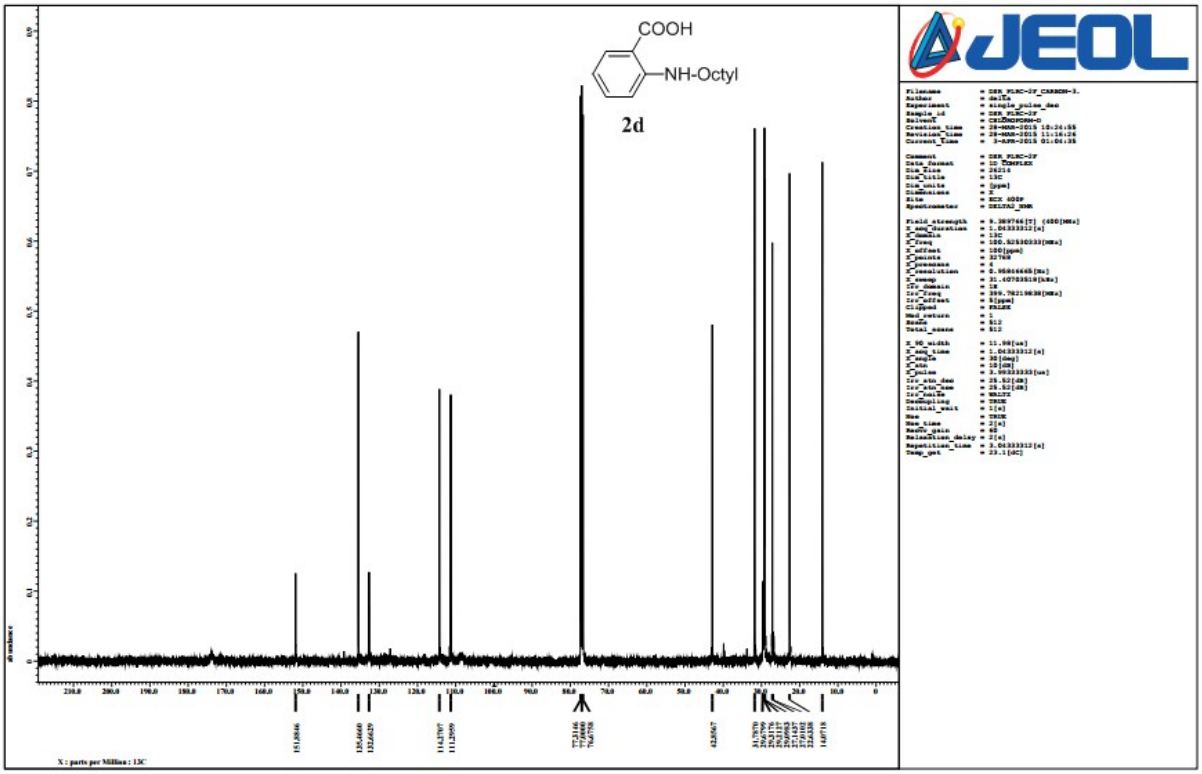

NC
NH-Octyl
2b
JEOL
X : parts per Million : 1H

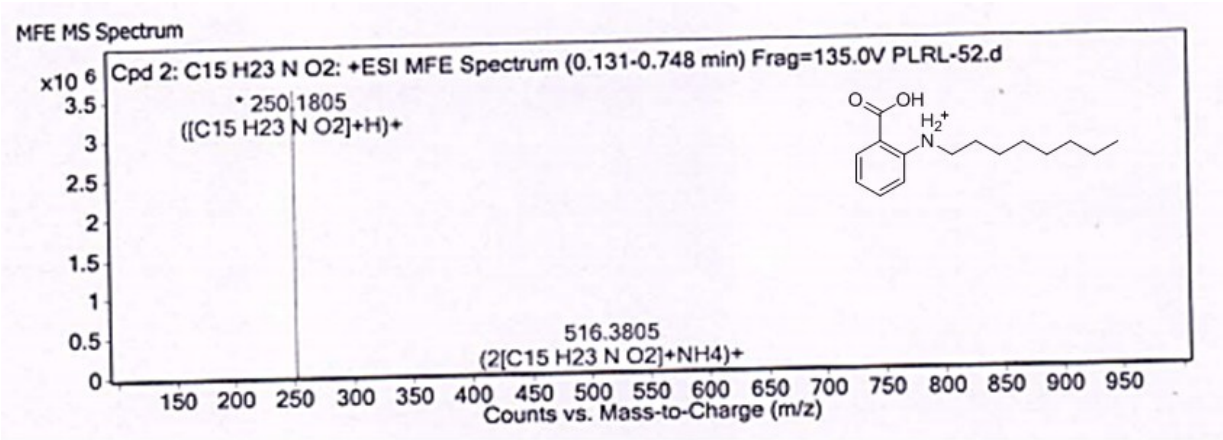

NC
NH-Octyl
2b
JEOL
X : parts per Million : 13C

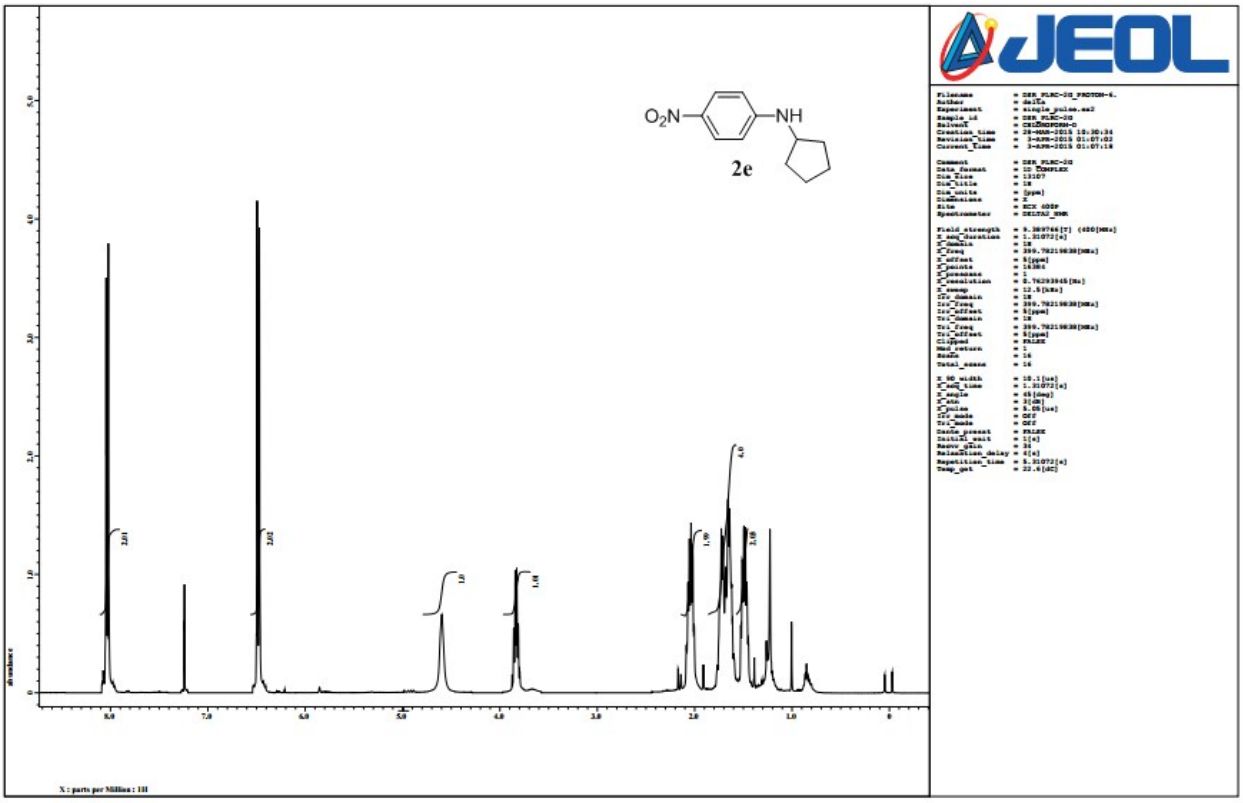

CN
NH-octyl
2c
JEOL
X : parts per Million : 1H

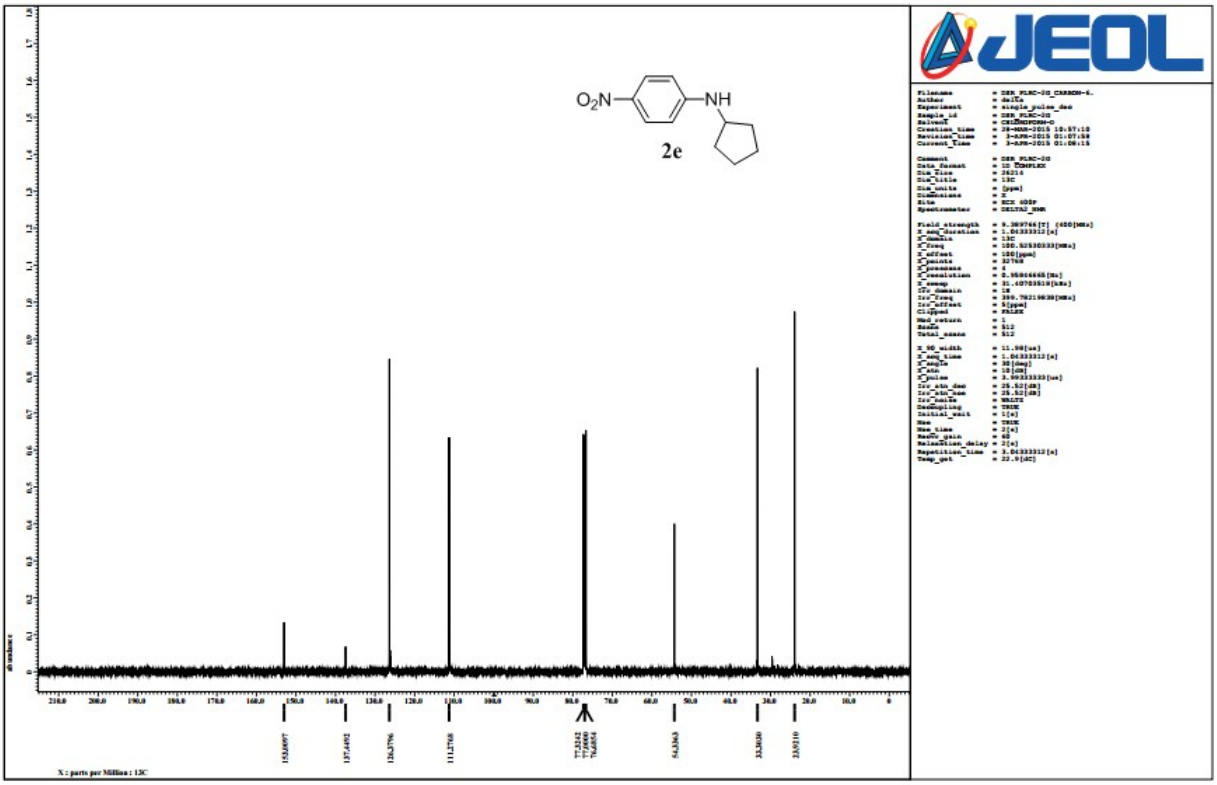

CN
NH-Octyl
2c
JEOL
X : parts per Million : 13C

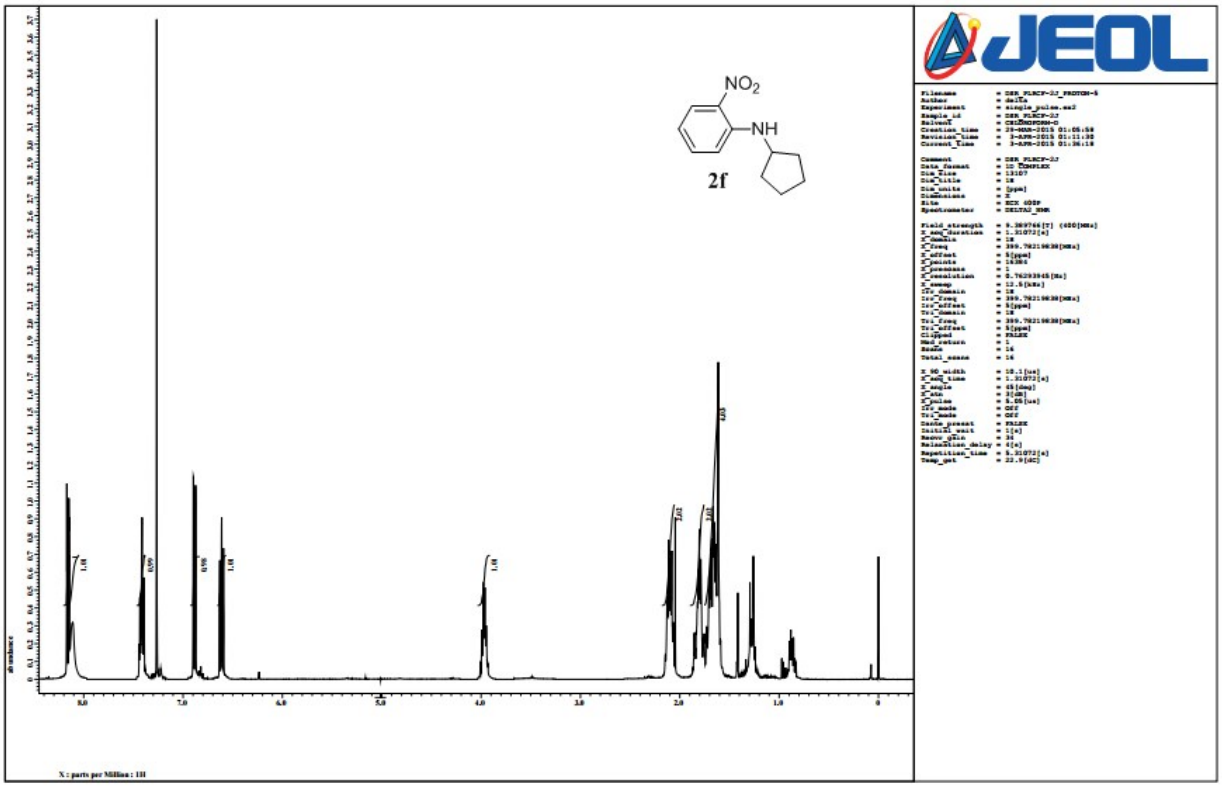

COOH
NH-Octyl
2d
JEOL
X : parts per Million : 1H

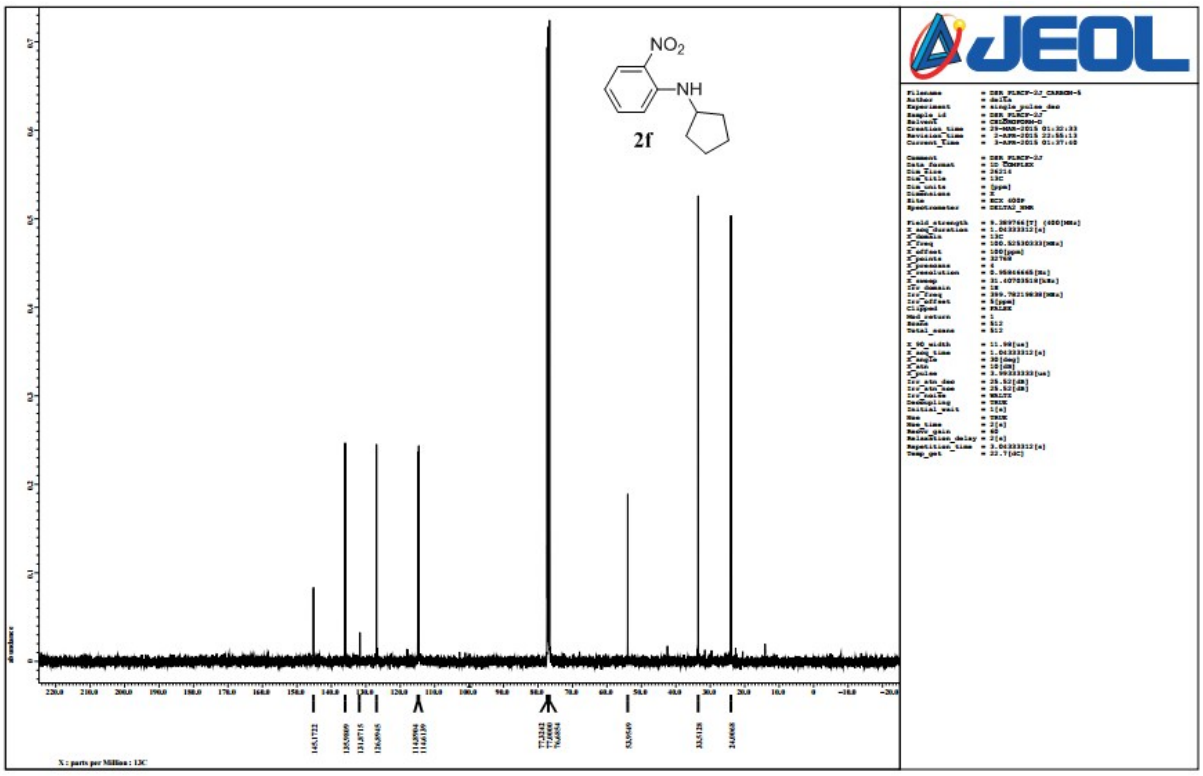

COOH
NH-Octyl
2d
JEOL
X : parts per Million : 13C

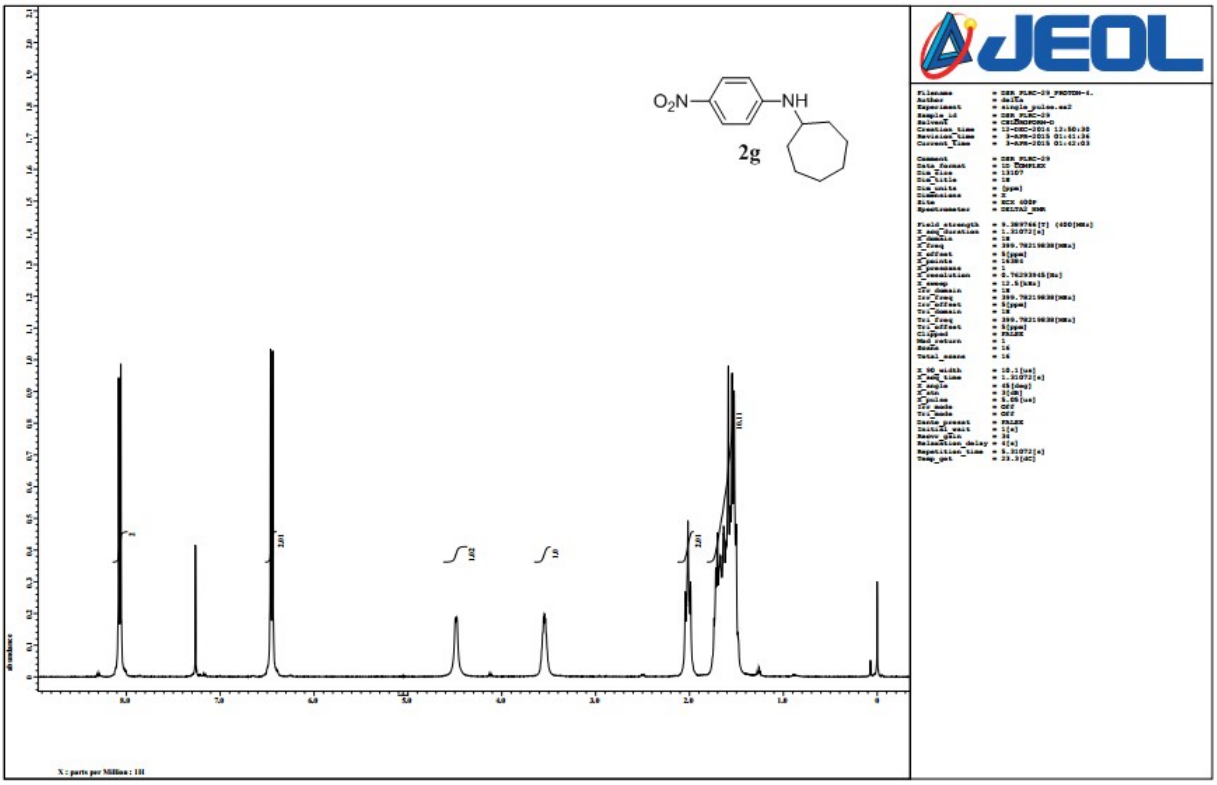

MFE MS Spectrum
Cpd 2: C15 H23 N O2: +ESI MFE Spectrum (0.131-0.748 min) Frag=135.0V PLRL-52.d
x10 6
3.5
3
2.5
2
1.5
1
0.5
0
250.1805
([C15 H23 N O2]+H)+
516.3805
(2[C15 H23 N O2]+NH4)+
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950
Counts vs. Mass-to-Charge (m/z)
O
OH
H2+
N

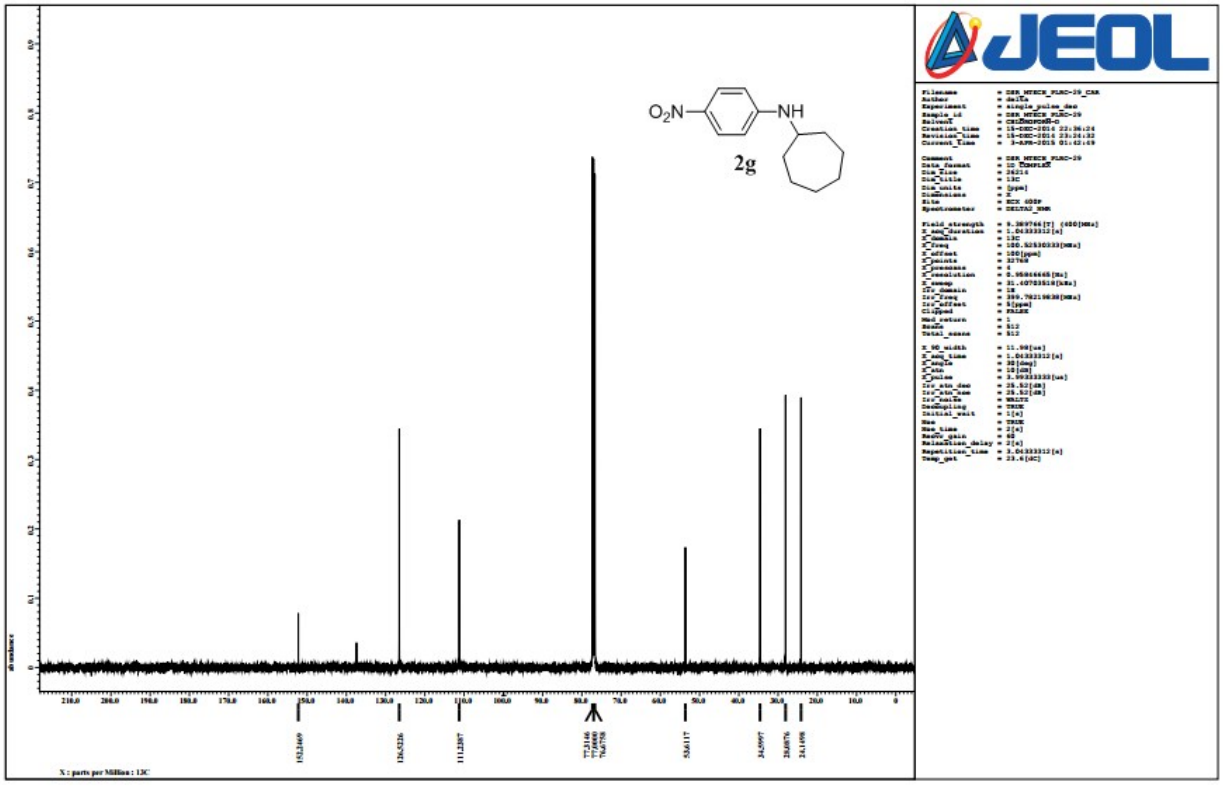

O2N
NH
2e
JEOL
X : parts per Million : 1H

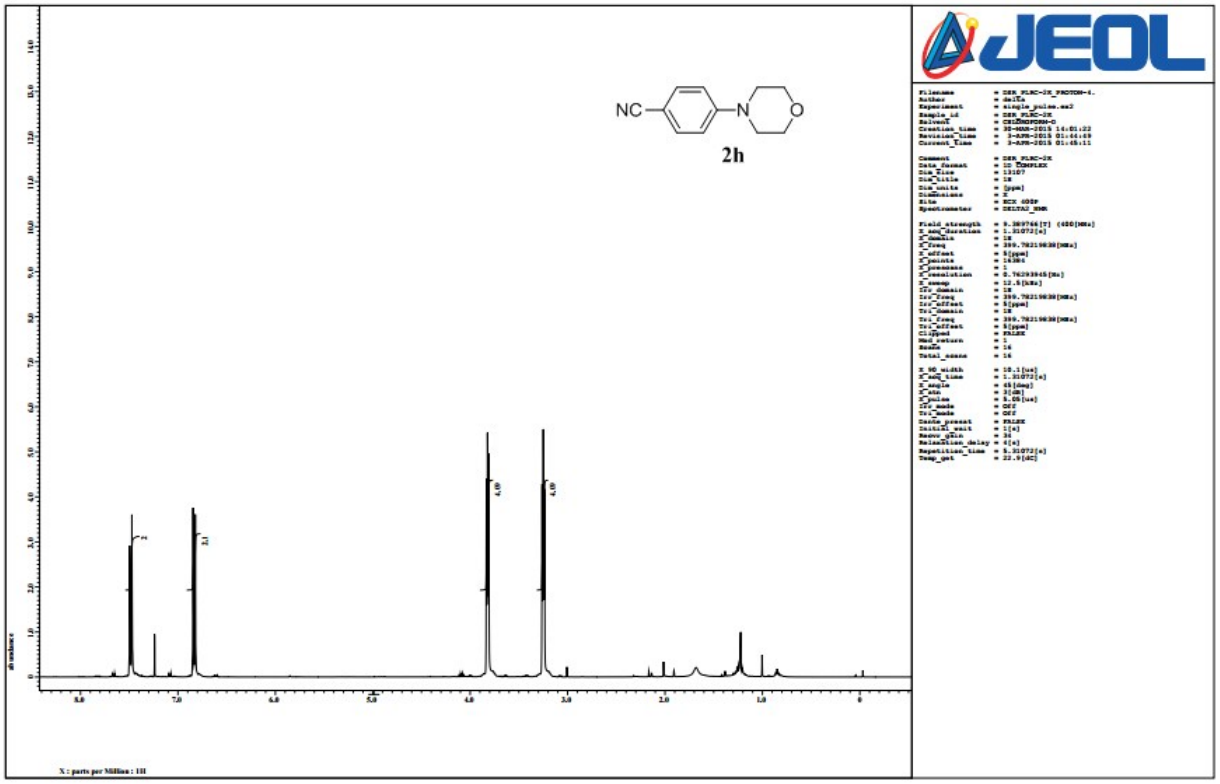

O2N
NH
2e
JEOL
X : parts per Million : 13C

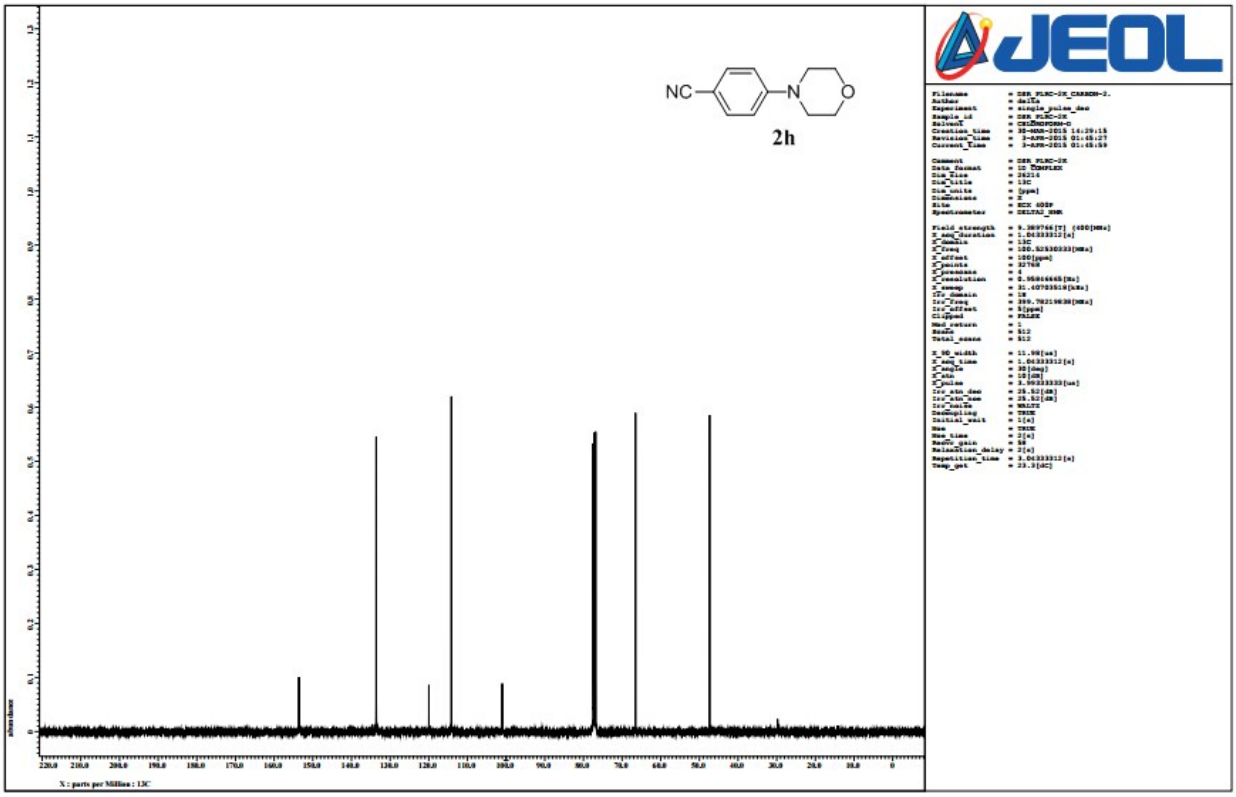

NO2
NH
2f
JEOL
X : parts per Million : 1H

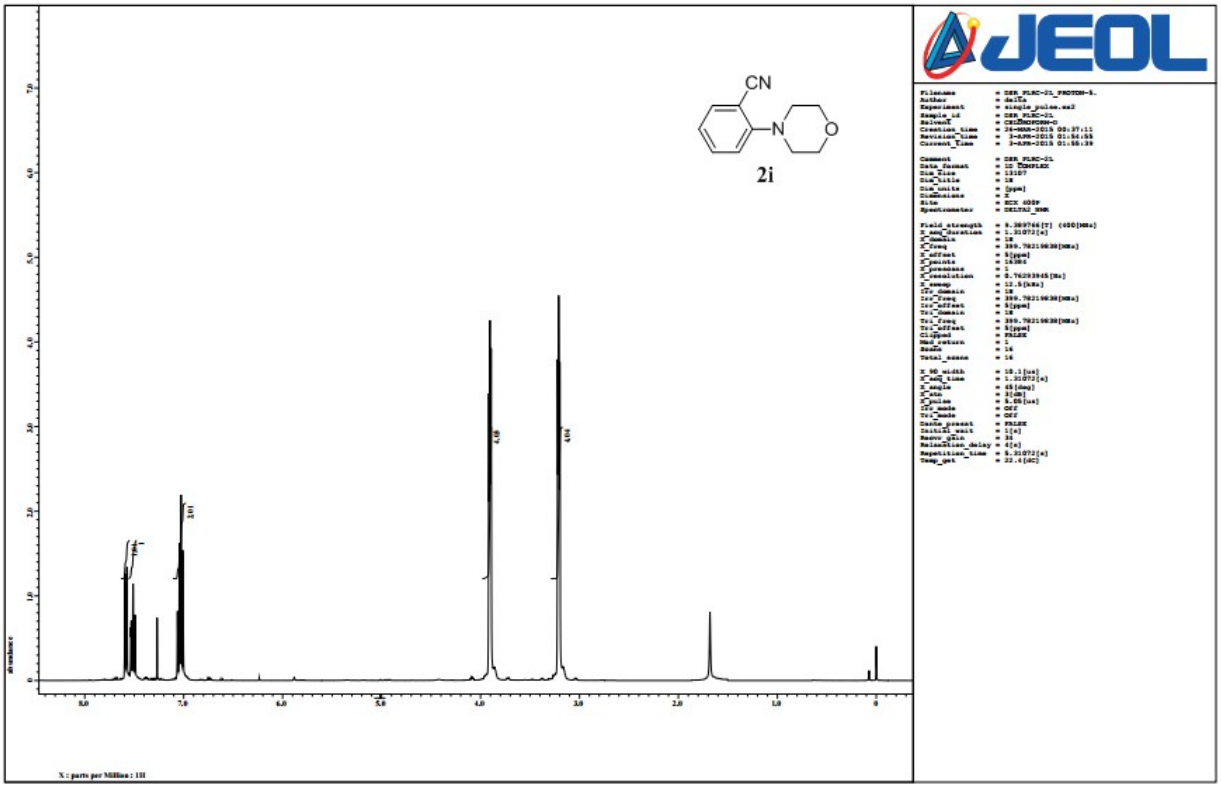

NO2
NH
2f
JEOL
X : parts per Million : 13C

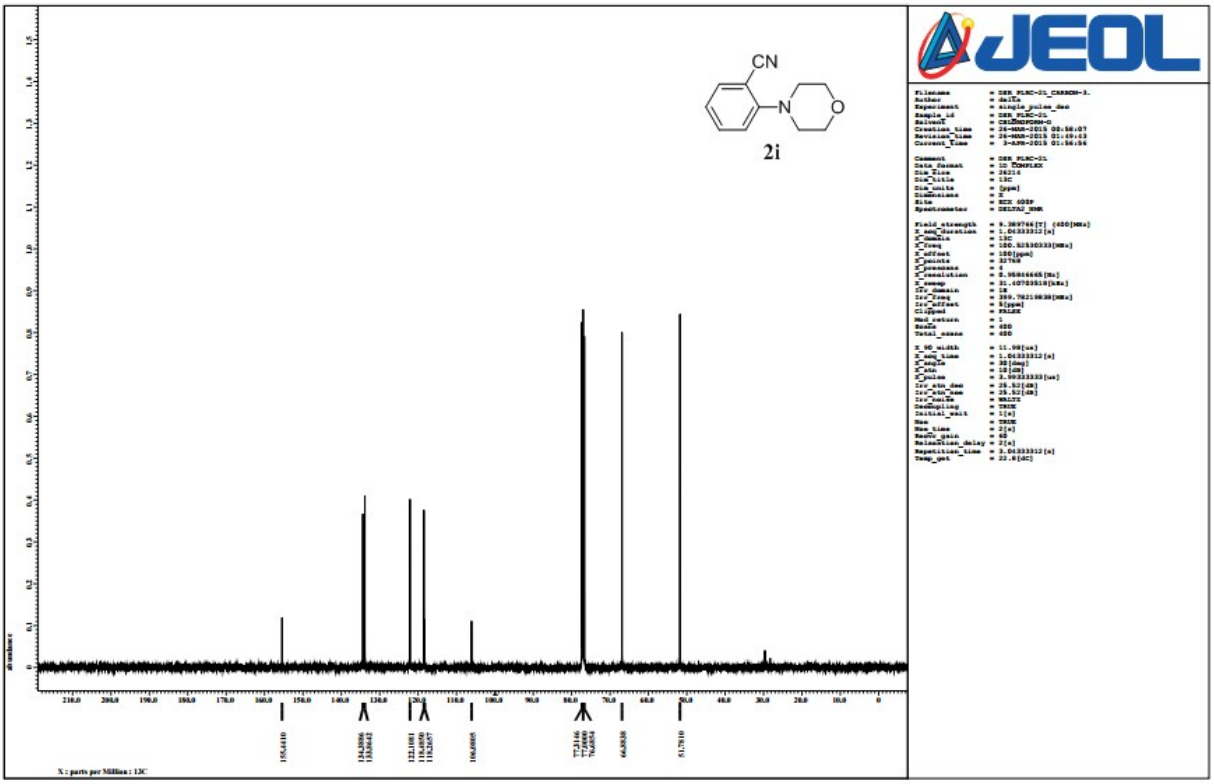

O2N
NH
2g
JEOL
X : parts per Million : 1H

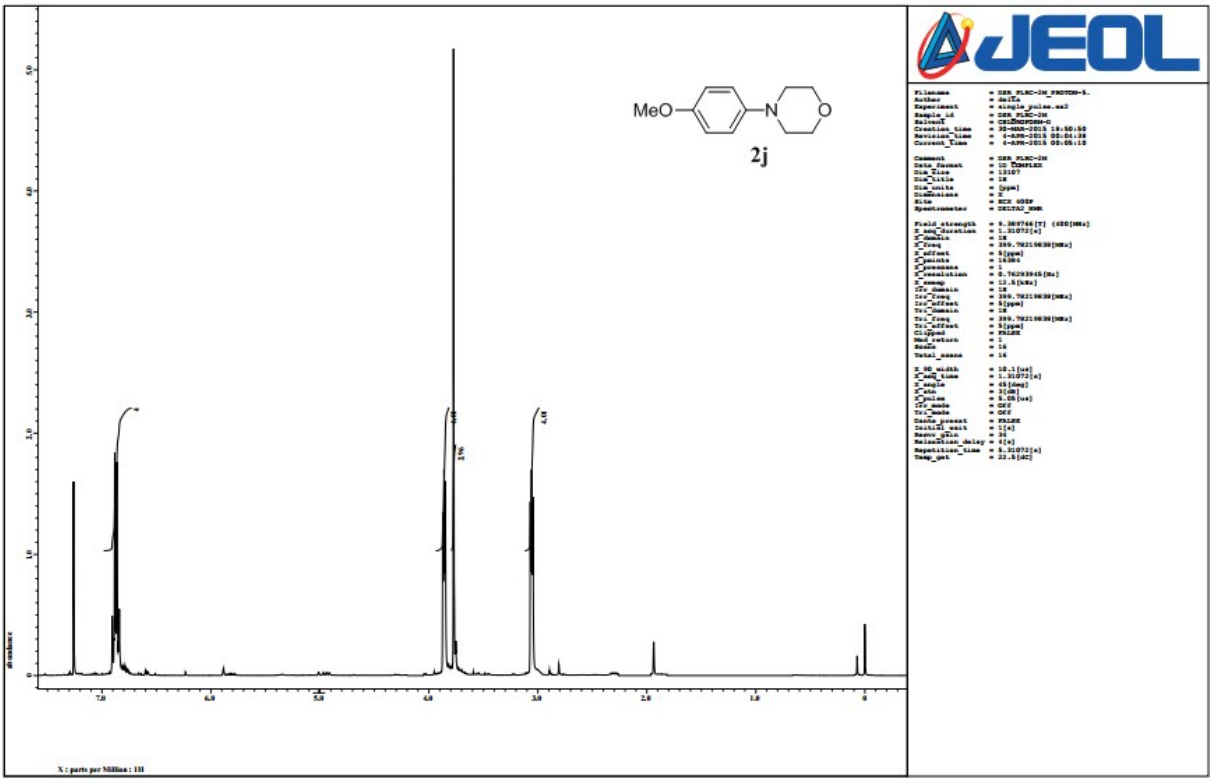

O2N
NH
2g
JEOL
X : parts per Million : 13C

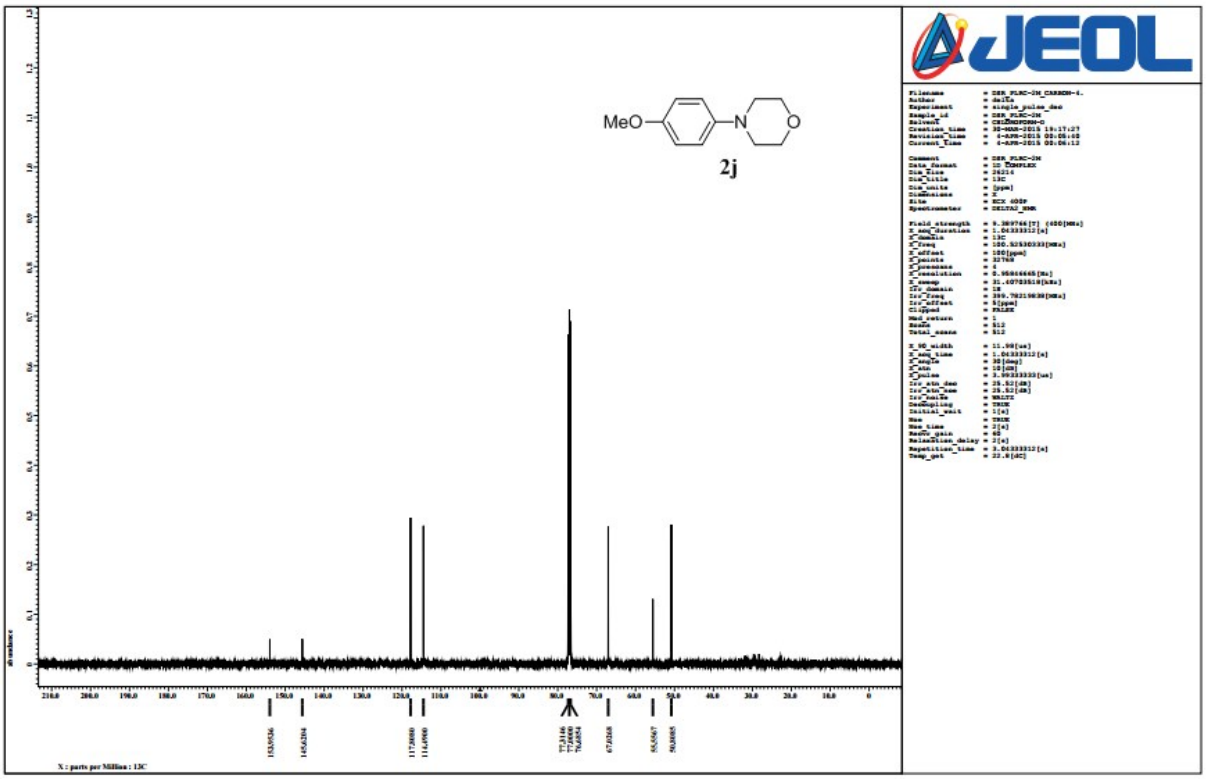

NC
N
O
2h
JEOL
X : parts per Million : 1H

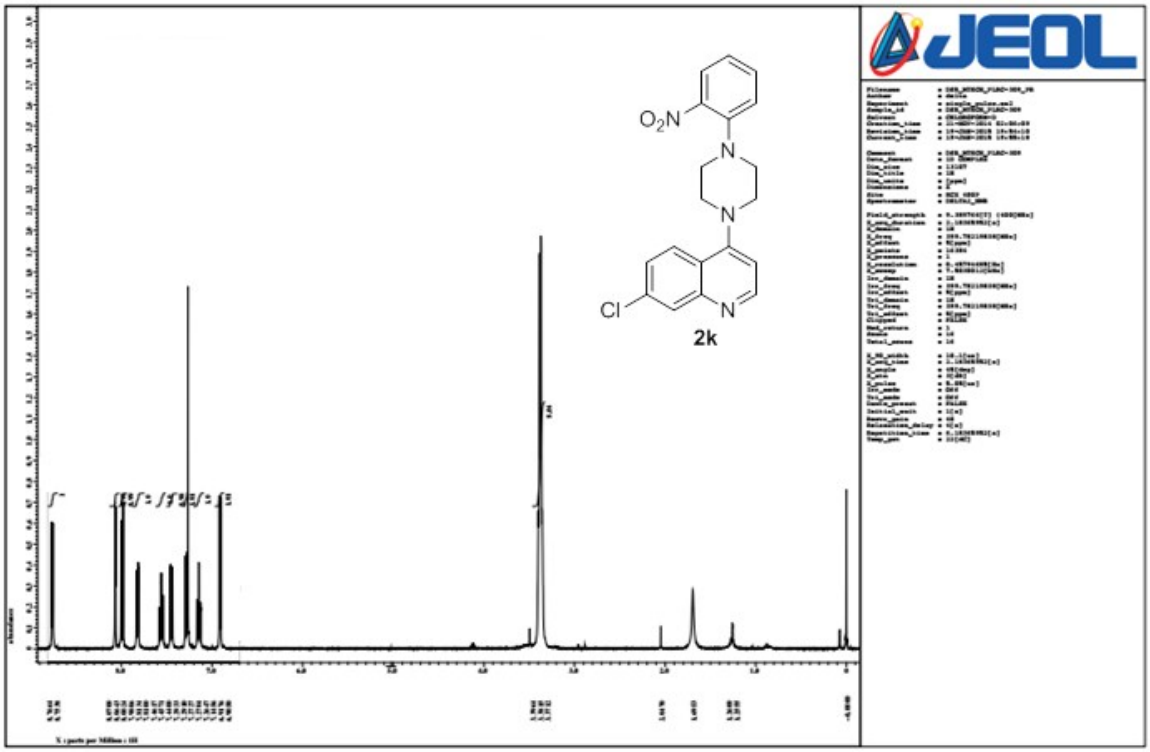

NC
N
O
2h
JEOL
X : parts per Million : 13C

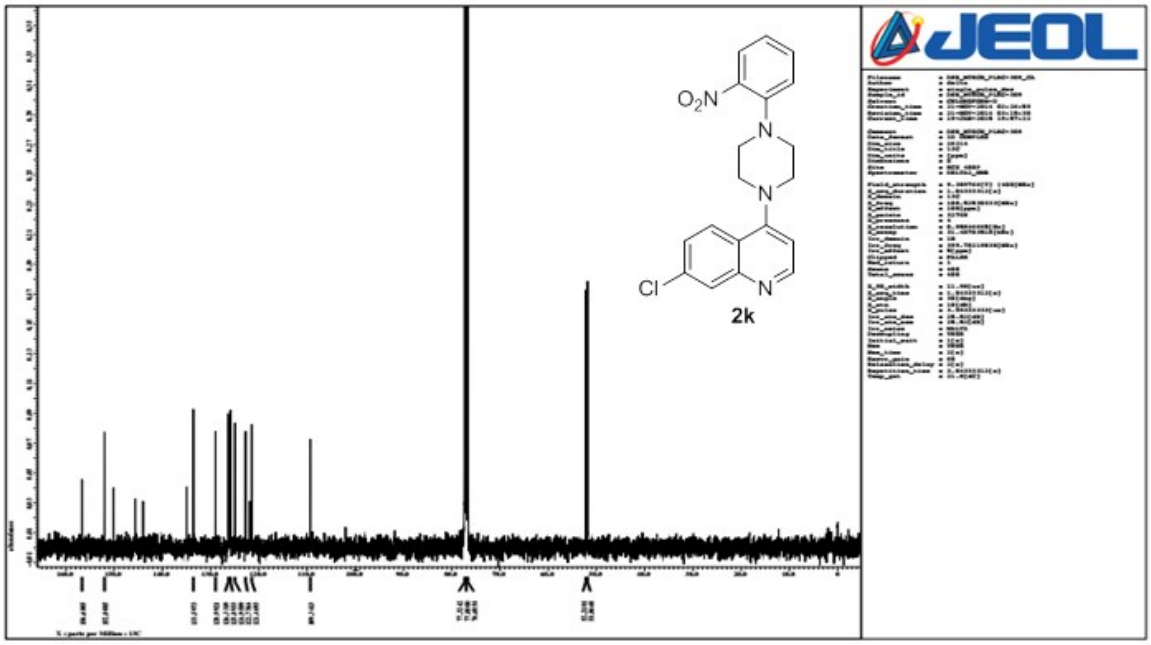

CN
N
O
2i
JEOL
X : parts per Million : 1H

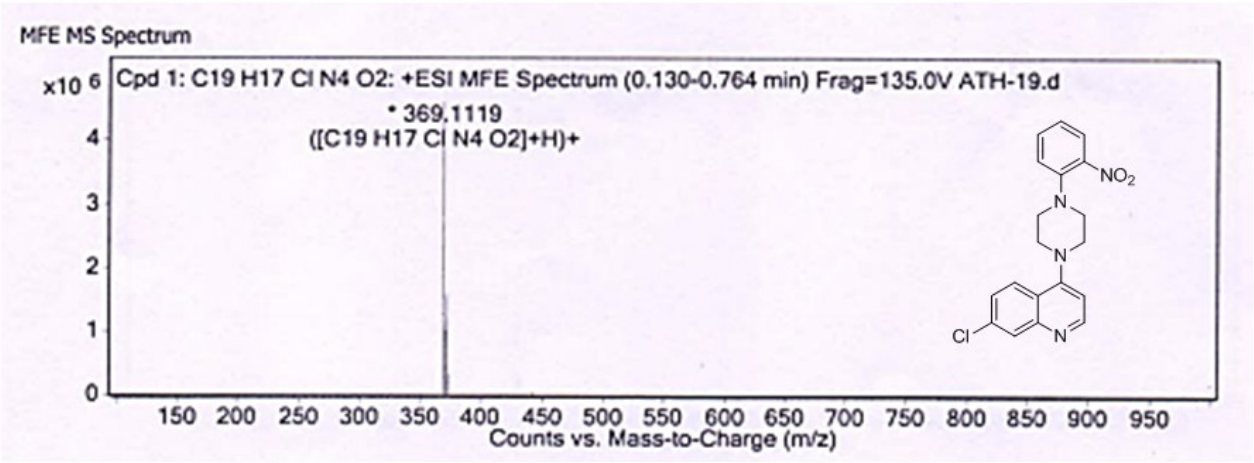

CN
N
O
2i
JEOL
X : parts per Million : 13C

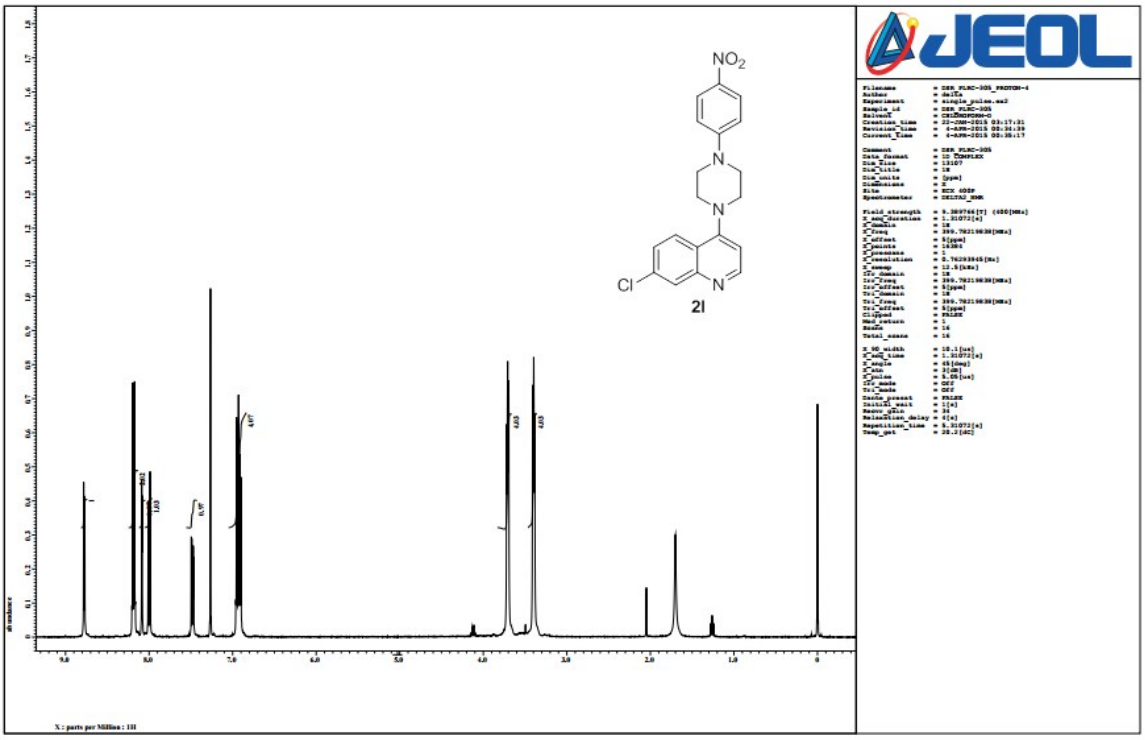

MeO
N
O
2j
JEOL
X : parts per Million : 1H

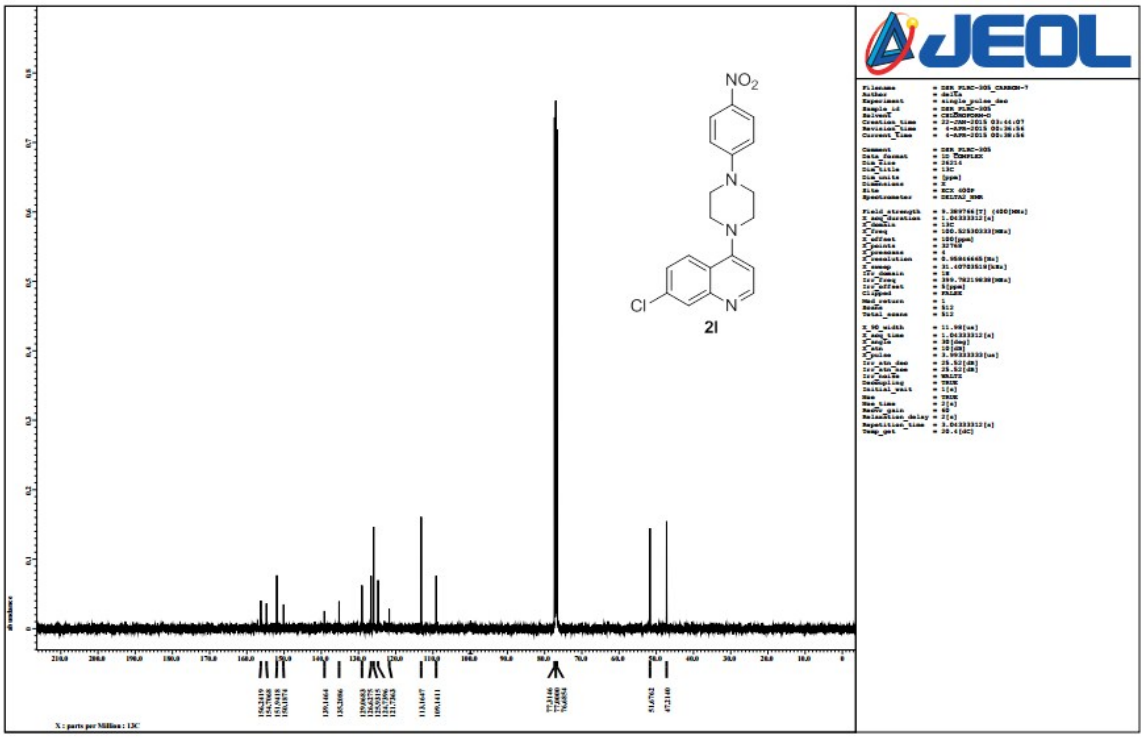

MeO
N
O
2j
JEOL
X : parts per Million : 13C

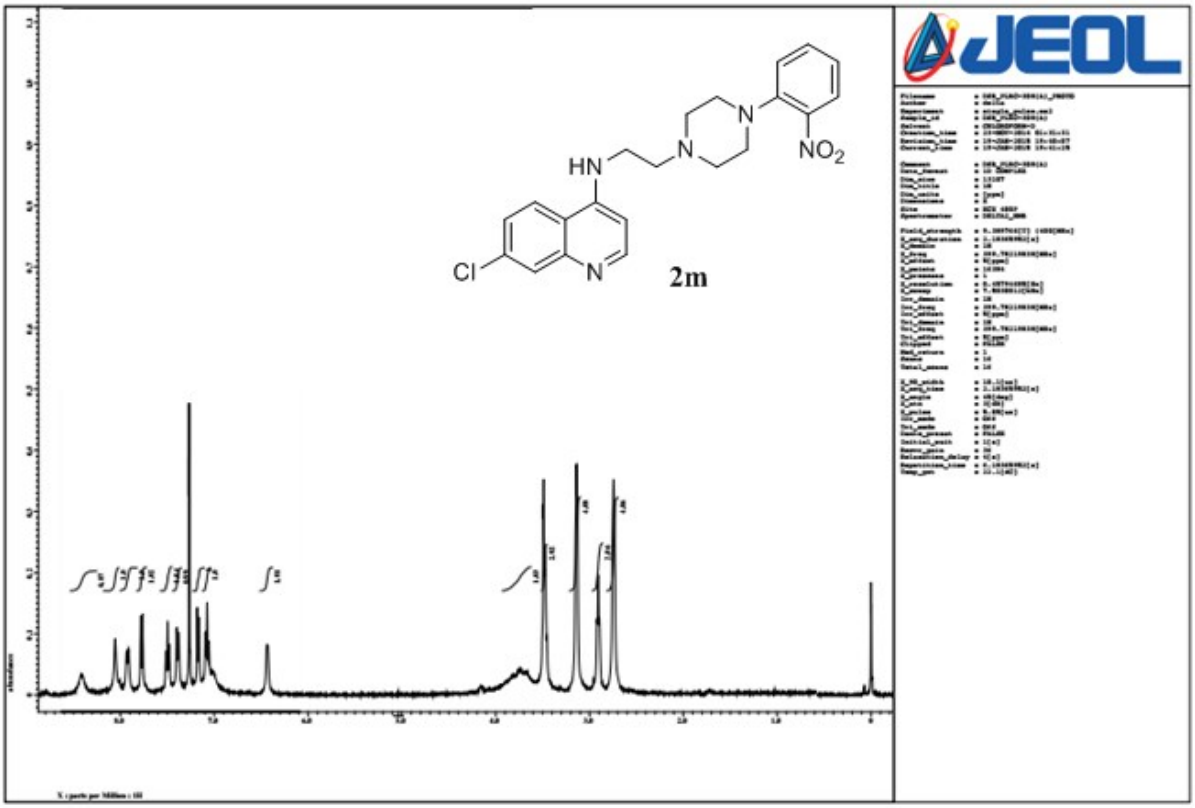

JEOL
O_2N
N
N
Cl
N
2k

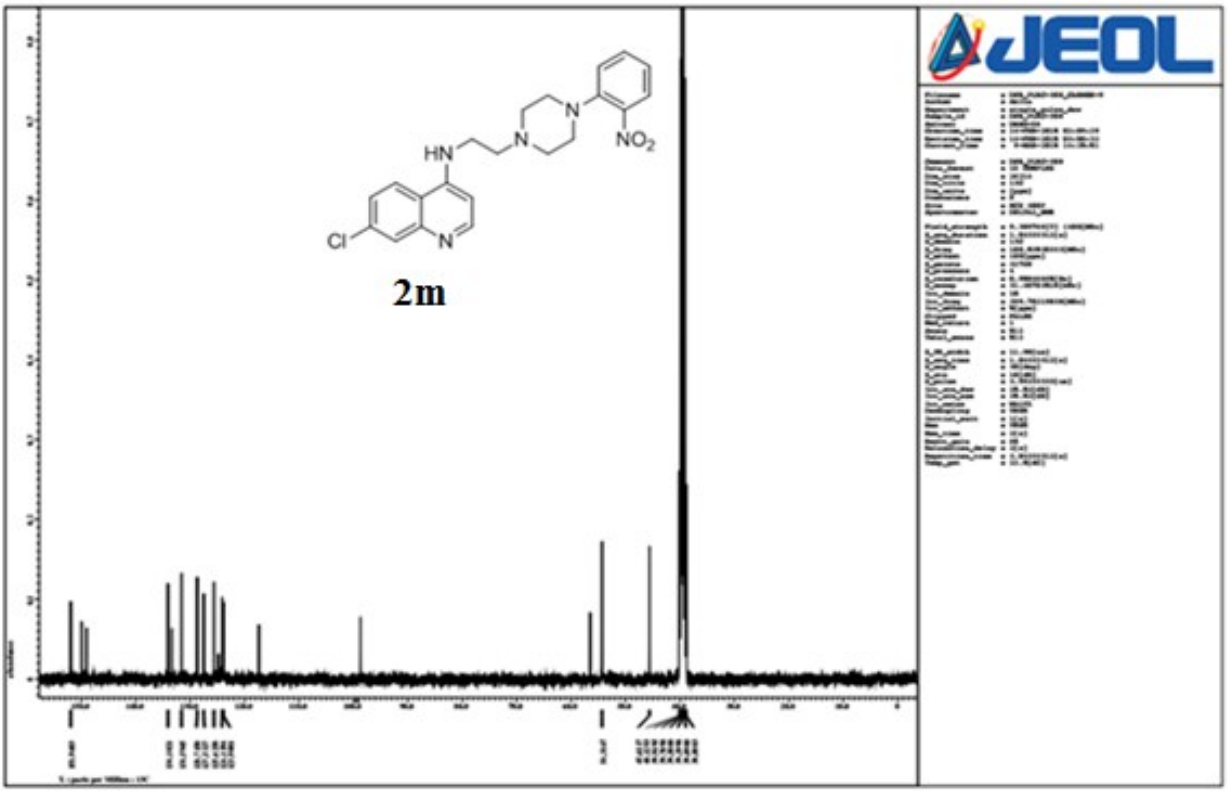

JEOL
O_2N
N
N
Cl
N
2k

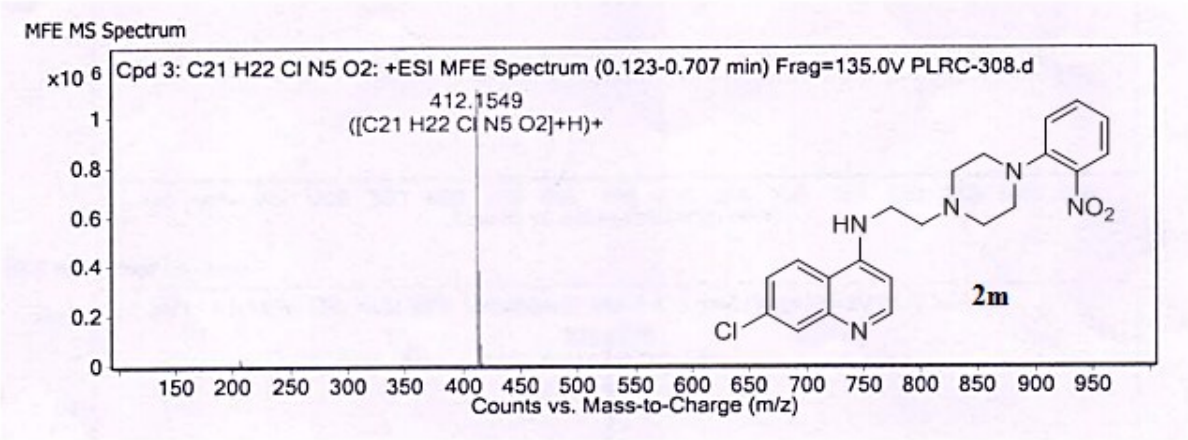

MFE MS Spectrum
Cpd 1: C19 H17 Cl N4 O2: +ESI MFE Spectrum (0.130-0.764 min) Frag=135.0V ATH-19.d
x10 6
* 369.1119
([C19 H17 Cl N4 O2]+H)+
4
3
2
1
0
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950
Counts vs. Mass-to-Charge (m/z)
NO2
N
N
Cl
N

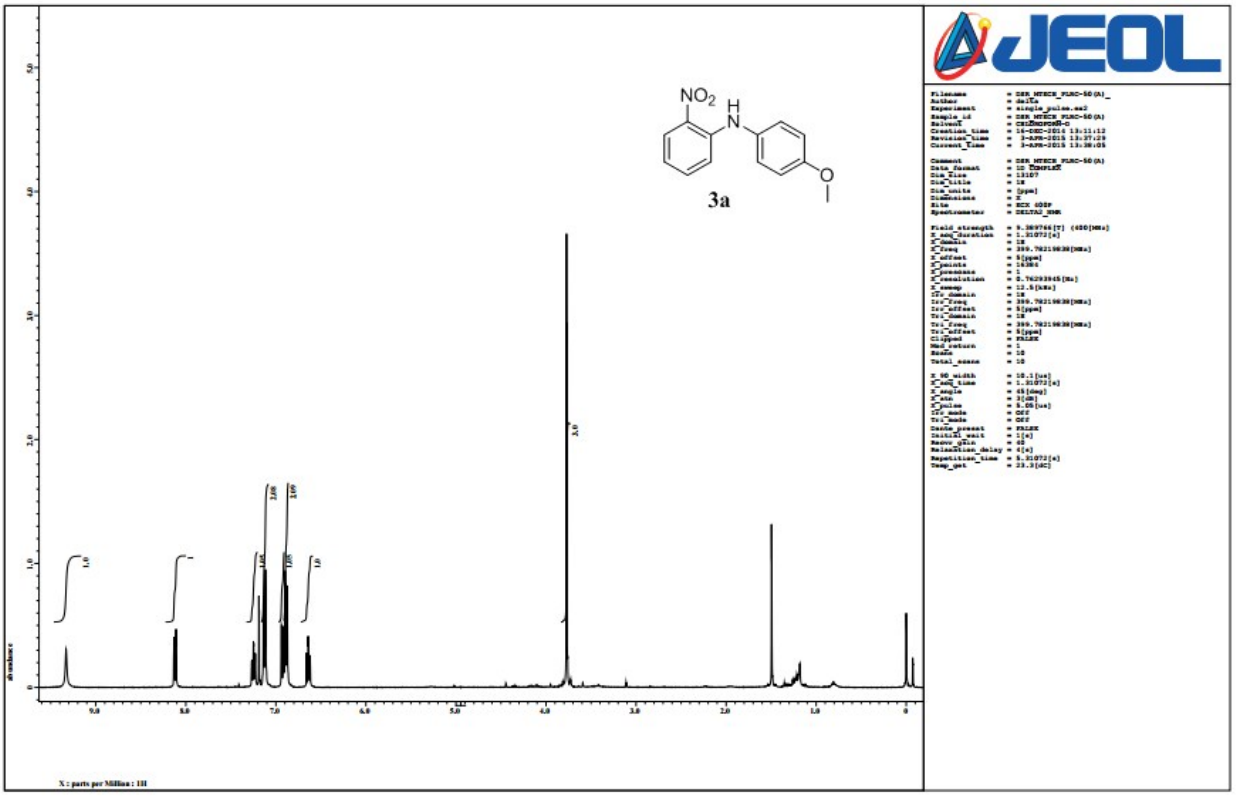

NO2
N
N
Cl
N
2l
JEOL
X : parts per Million : 1H

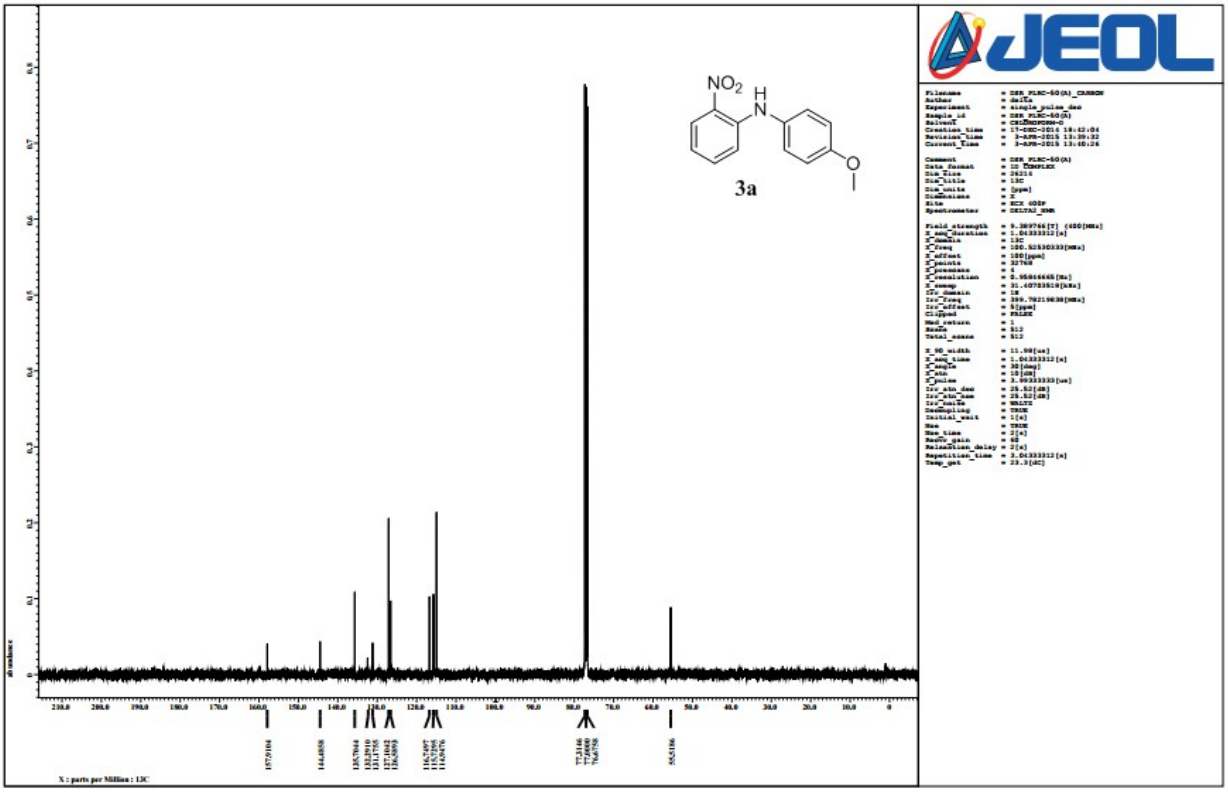

NO2
N
N
Cl
N
2l
JEOL
X : parts per Million : 13C

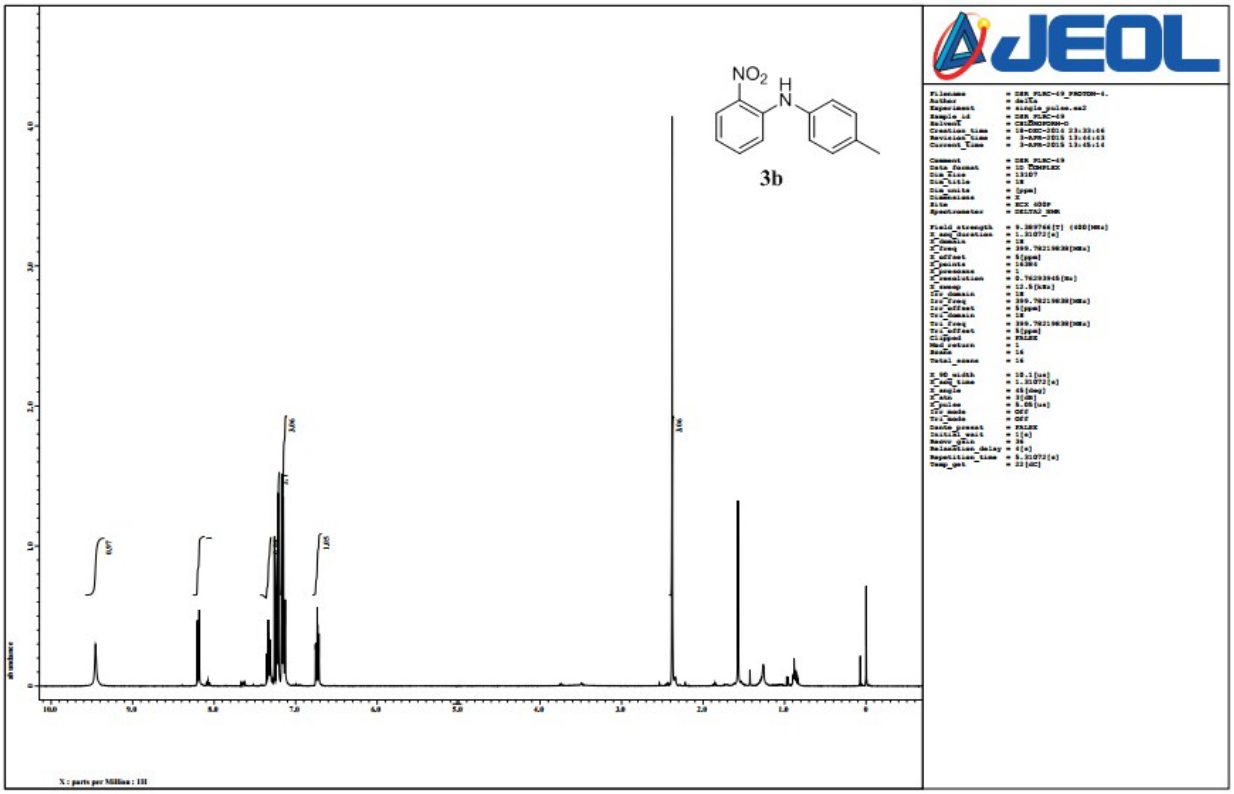

HN
N
N
NO2
Cl
N
2m
JEOL

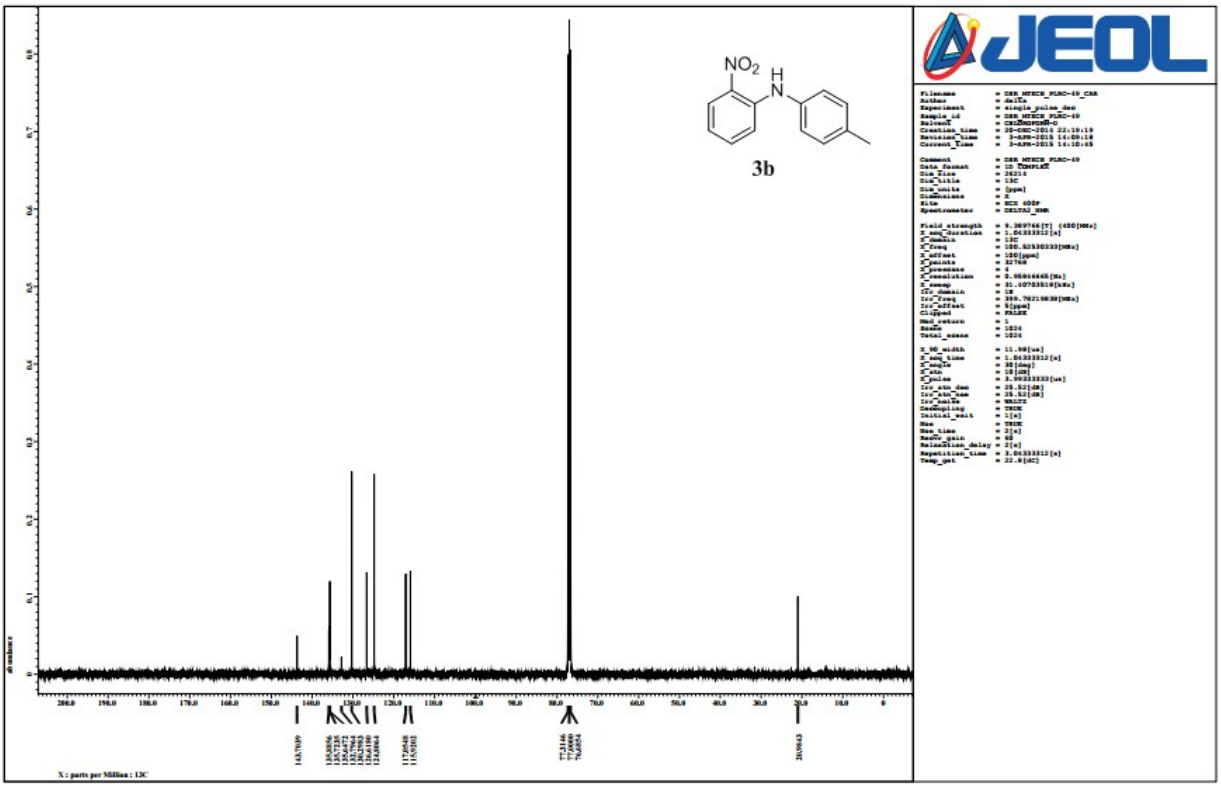

HN
N
N
NO2
Cl
N
2m
JEOL

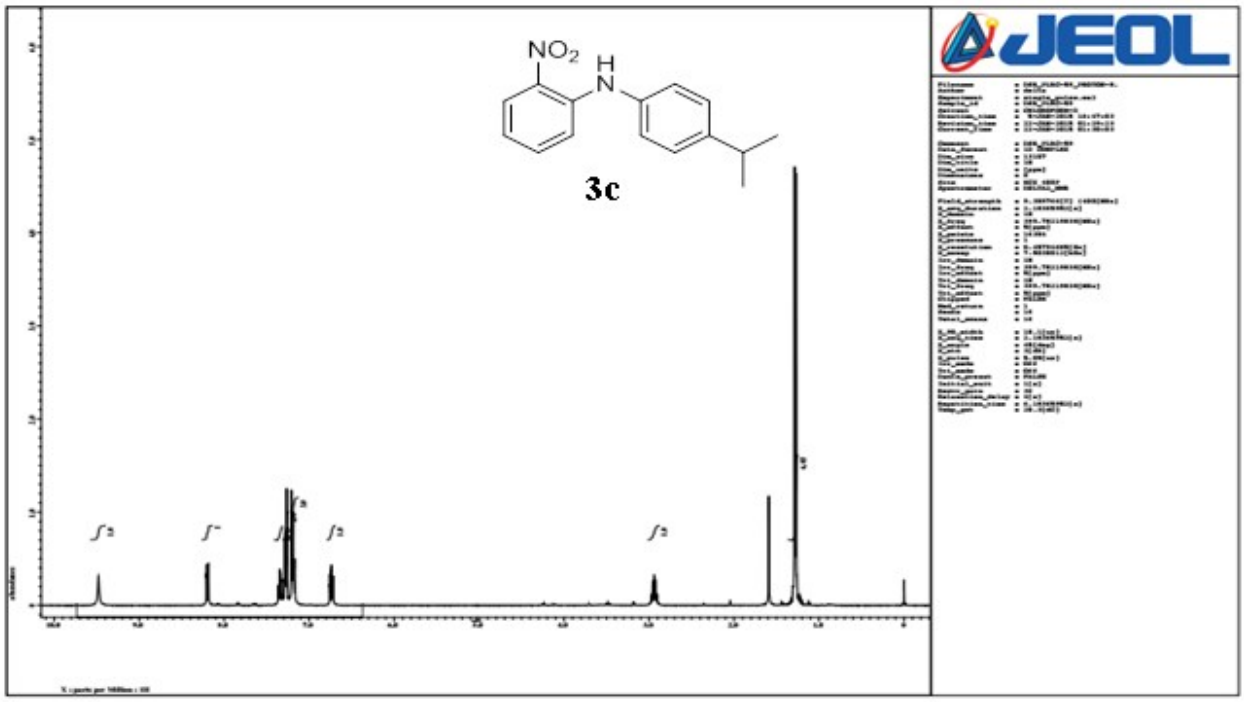

MFE MS Spectrum
Cpd 3: C21 H22 Cl N5 O2: +ESI MFE Spectrum (0.123-0.707 min) Frag=135.0V PLRC-308.d
x10 6
412.1549
([C21 H22 Cl N5 O2]+H)+
1
0.8
0.6
0.4
0.2
0
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950
Counts vs. Mass-to-Charge (m/z)
HN
N
N
NO2
Cl
N
2m

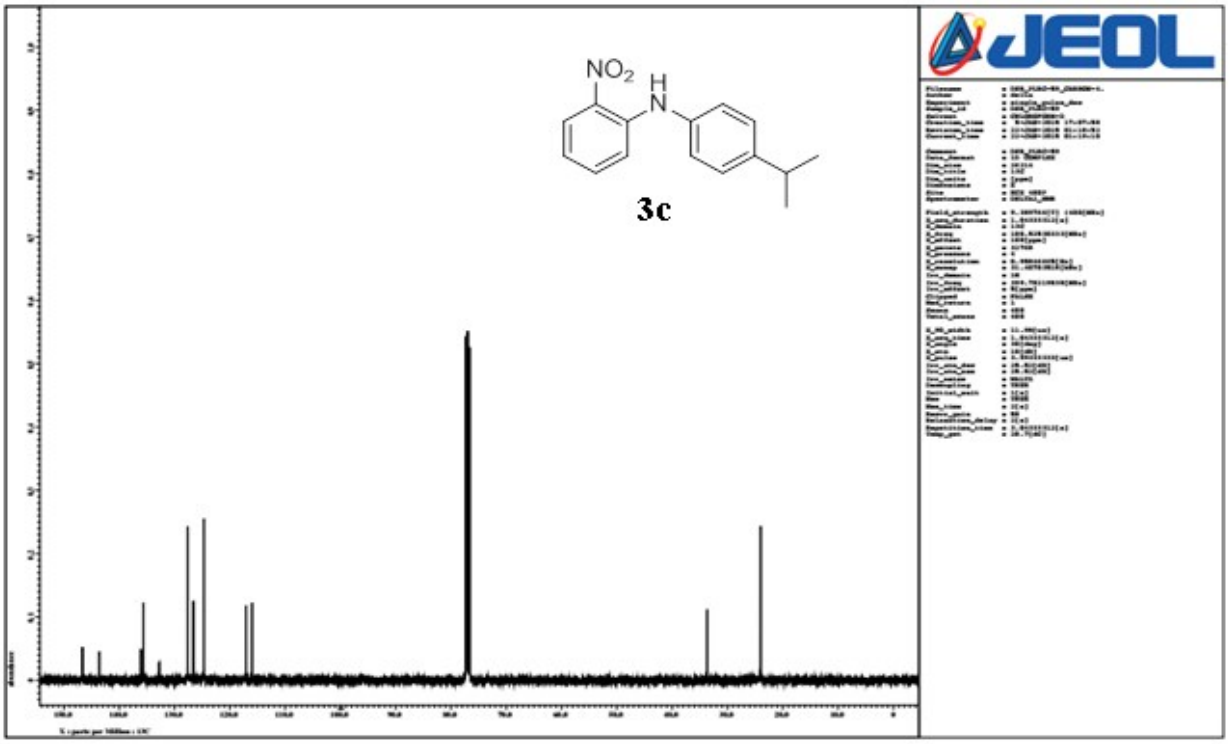

NO2
H
N
O
3a
JEOL
X : parts per Million : 1H

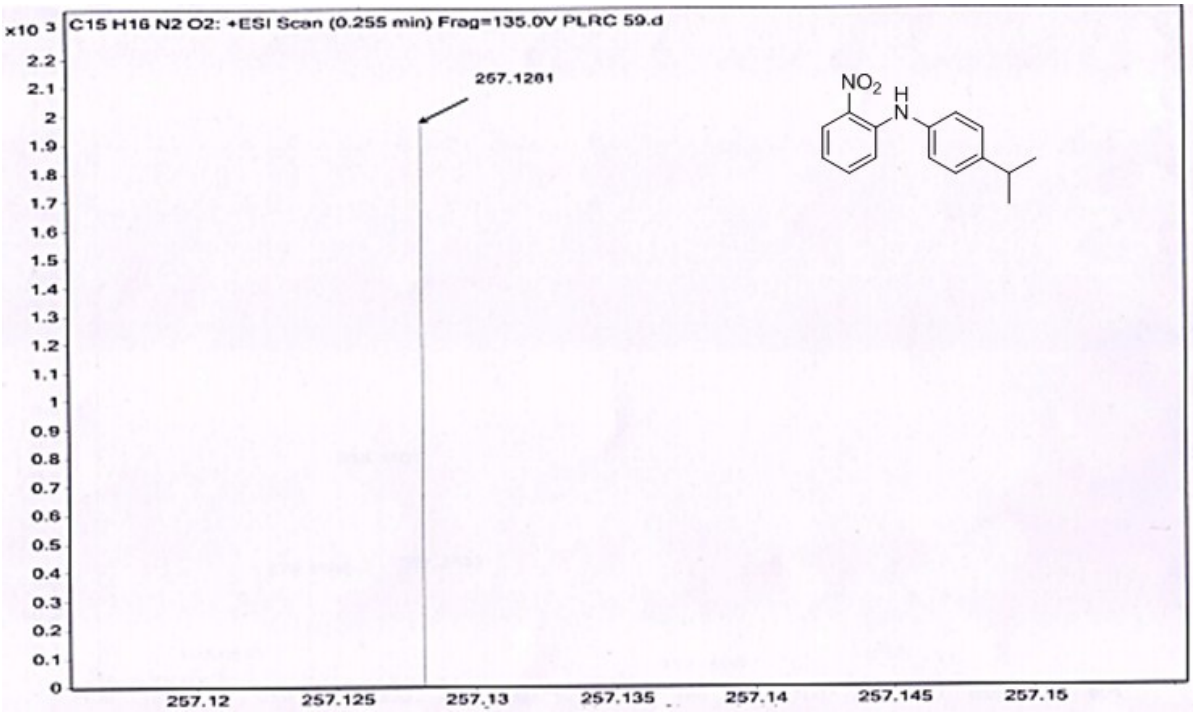

NO2
H
N
O
3a
JEOL
X : parts per Million : 13C

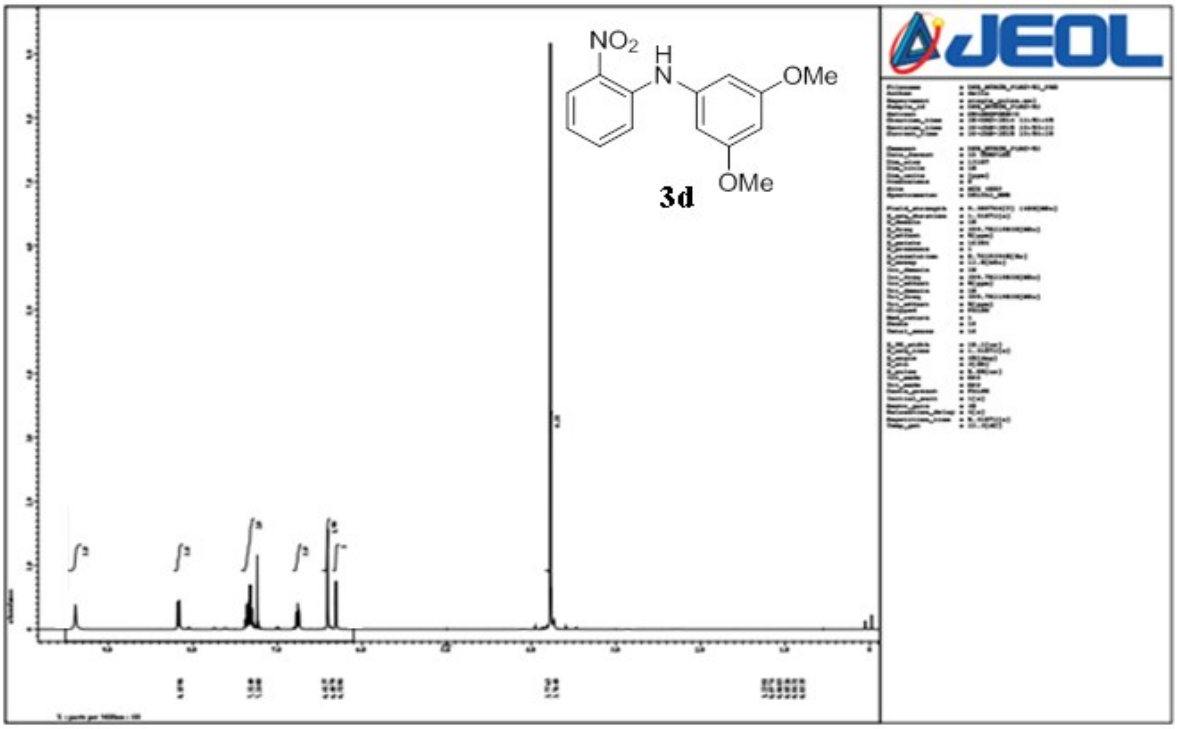

NO2
H
N
3b
JEOL
X : parts per Million : 1H

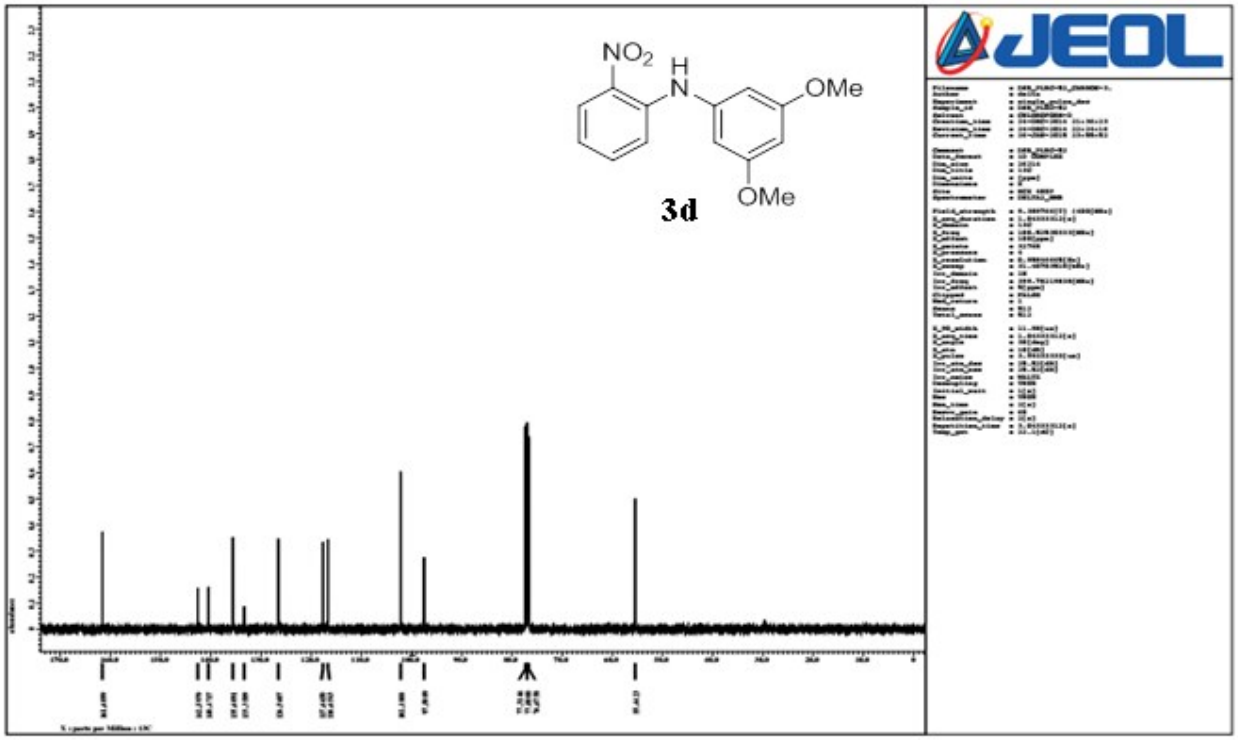

NO2
H
N
3b
JEOL
X : parts per Million : 13C

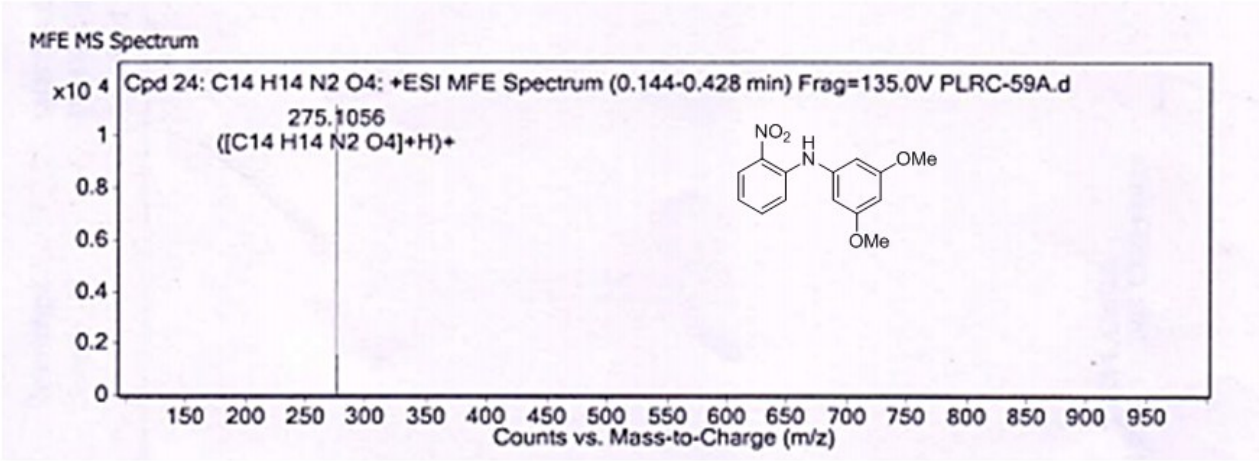

NO2
H
N
3c
JEOL

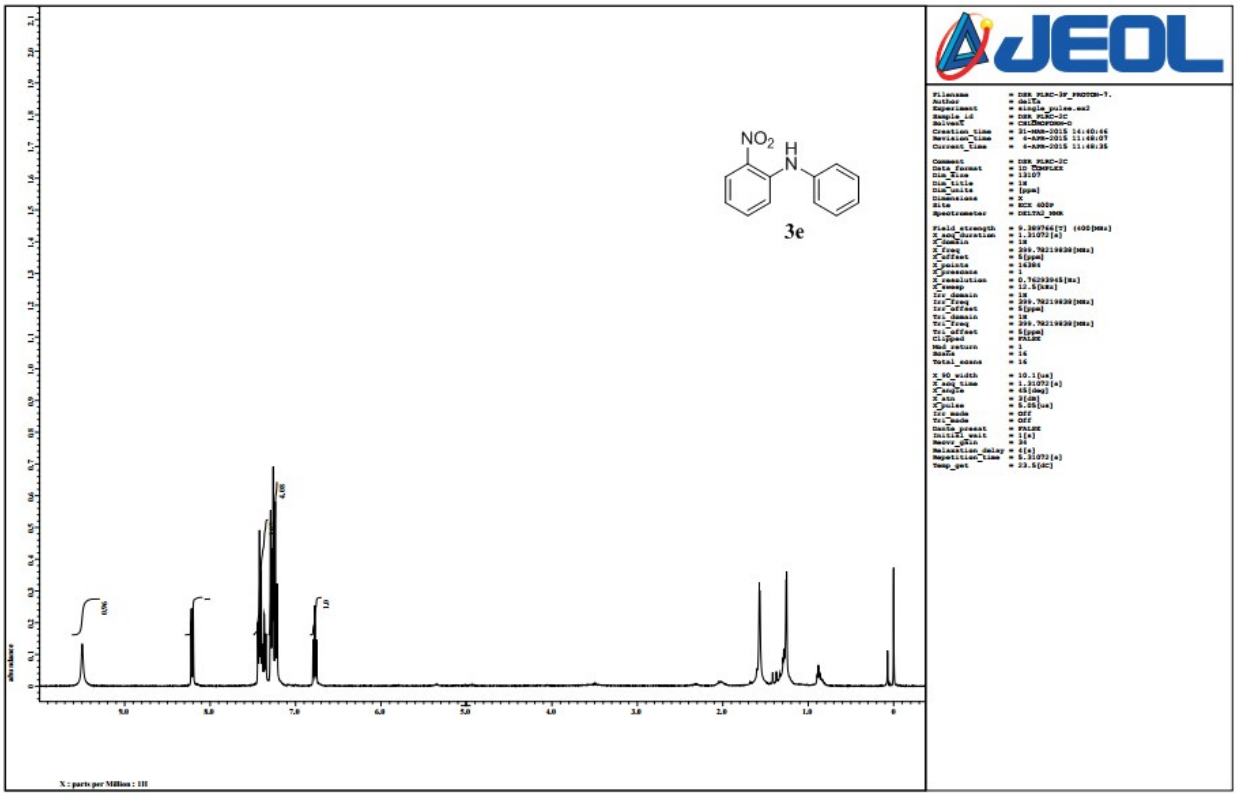

NO2
H
N
3c
JEOL

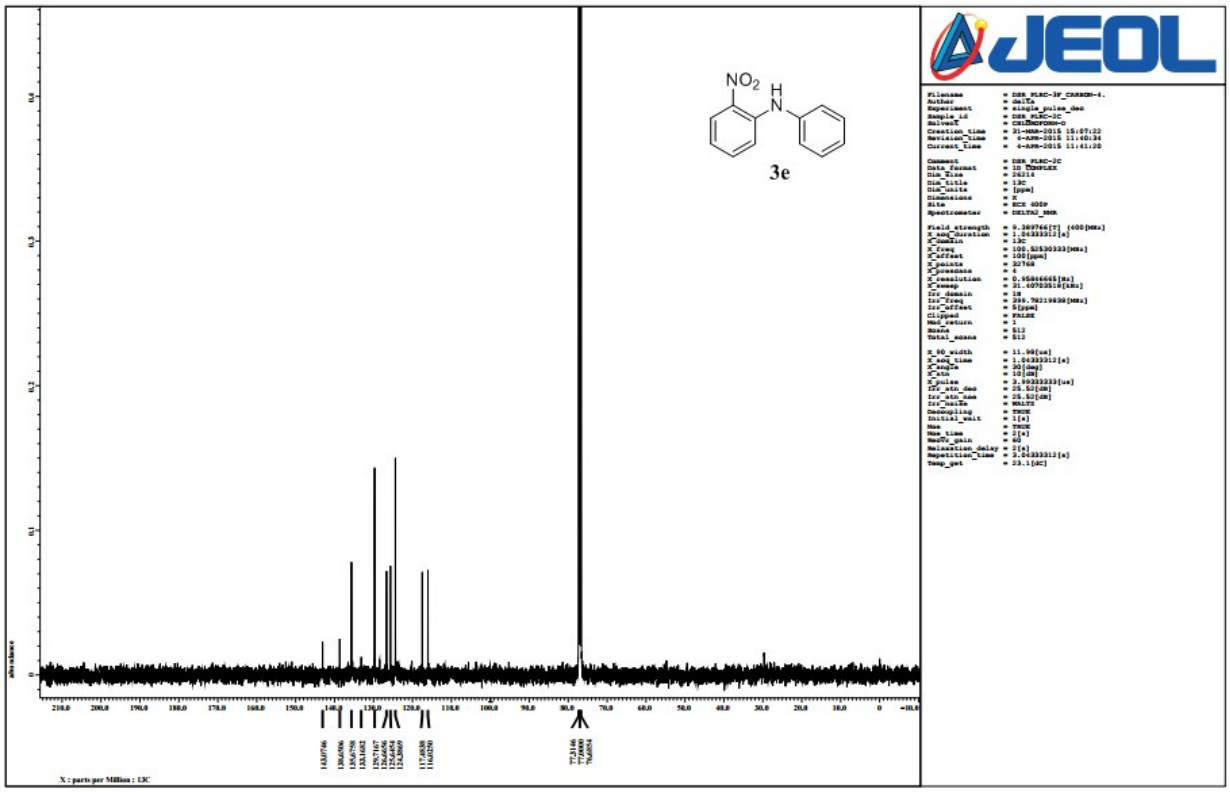

C15 H16 N2 O2: +ESI Scan (0.255 min) Frag=135.0V PLRC 59.d
x10 3
2.2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
257.1281
257.12
257.125
257.13
257.135
257.14
257.145
257.15
NO2
H
N

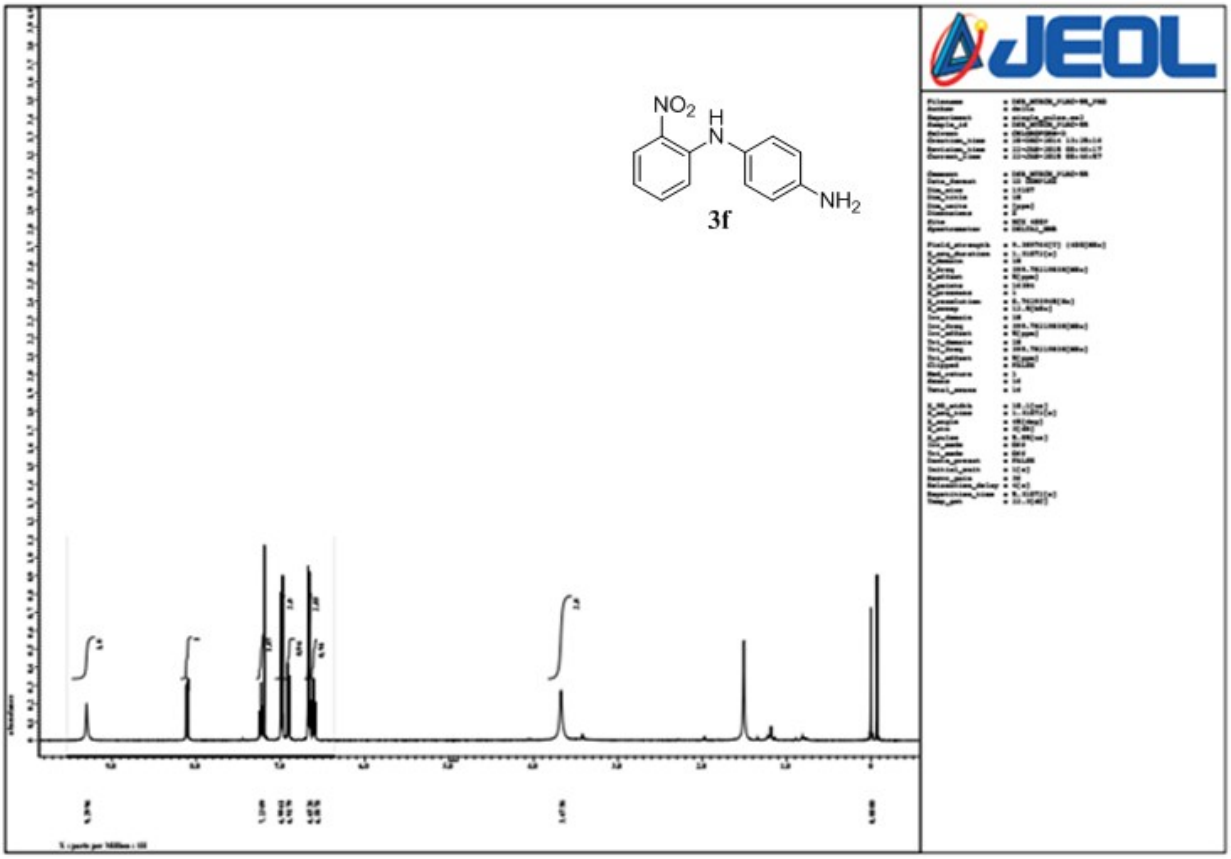

NO2
H
N
OMe
OMe
3d

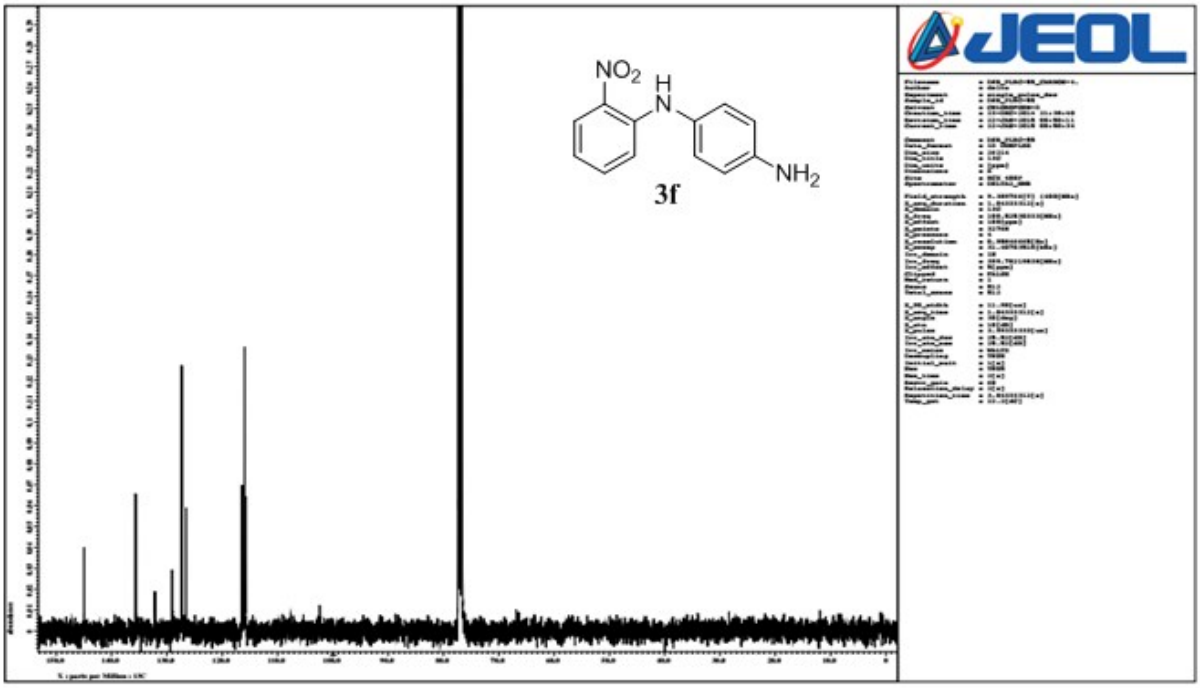

NO2
H
N
OMe
OMe
3d

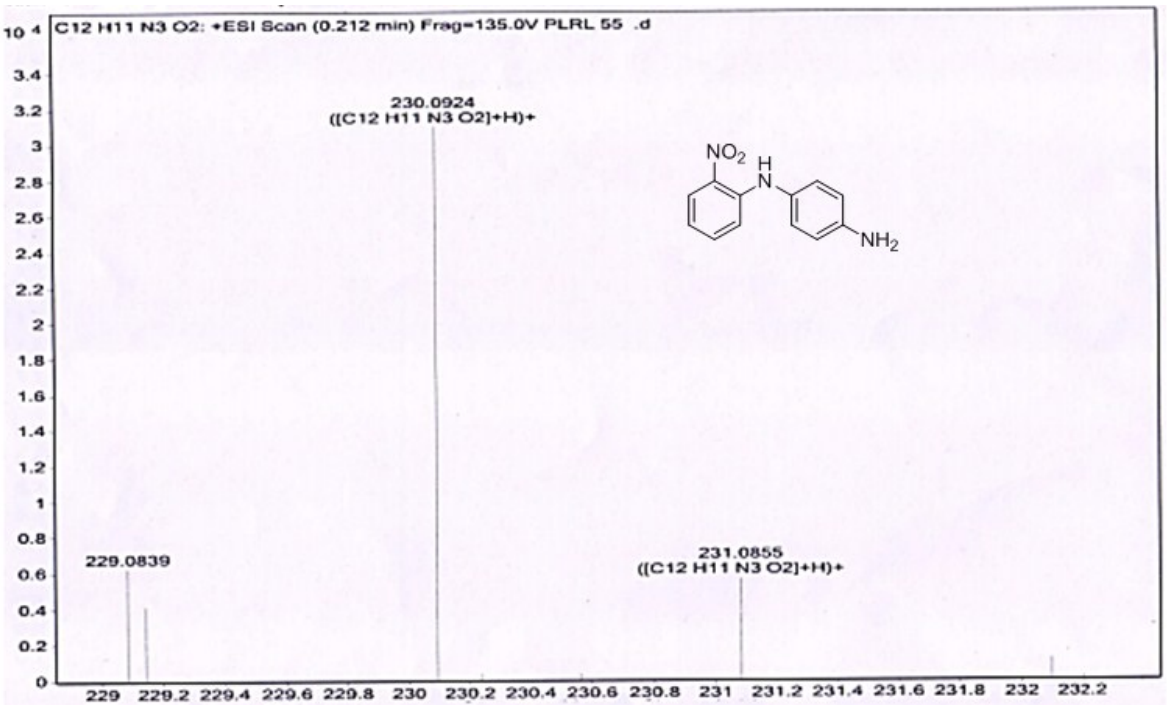

MFE MS Spectrum
Cpd 24: C14 H14 N2 O4: +ESI MFE Spectrum (0.144-0.428 min) Frag=135.0V PLRC-59A.d
x10 4
275.1056
([C14 H14 N2 O4]+H)+
NO2
H
N
OMe
OMe
1
0.8
0.6
0.4
0.2
0
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950
Counts vs. Mass-to-Charge (m/z)


NO2
H
N
3e
JEOL
X : parts per Million : 1H


NO2
H
N
3e
JEOL
X : parts per Million : 13C


NO2
H
N
NH2
3f


NO2
H
N
NH2
3f


C12 H11 N3 O2: +ESI Scan (0.212 min) Frag=135.0V PLRL 55 .d
230.0924
([C12 H11 N3 O2]+H)+
229.0839
231.0855
([C12 H11 N3 O2]+H)+
NO2
H
N
NH2