

**Poly(4-vinylpyridine)-Nitrating Mixture Complex (PVP-NM): Solid Nitrating
Mixture Equivalent for Safe and Efficient Aromatic Nitration**

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General Remarks: Unless otherwise mentioned, all chemicals were purchased from commercial sources and used as received. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on a Varian NMR at 400 MHz. ^1H NMR chemical shifts were determined relative to tetramethylsilane (TMS) as the internal standard at δ 0.0 ppm. ^{13}C NMR chemical shifts were determined relative to CDCl_3 at δ 77.0 ppm while ^{19}F NMR chemical shifts were determined relative to CFCl_3 as the internal standard at δ 0.0 ppm. Gas chromatograms were recorded on Bruker 450-GC and mass spectra were recorded on Bruker 300-MS in the ESI mode. The products were characterized by comparing their spectral data with those reported in the literature. The *ortho*, *meta* and *para* isomeric ratios of the products were determined based on ^1H NMR, ^{19}F NMR and GC. Scanning Electron Microscope images were obtained from a JEOL JSM6610 instrument at the Center for Electron Microscopy and Microanalysis, University of Southern California.

Typical Preparation of PVP- HNO_3 (1:7.5) complex: Fuming nitric acid (purum p.a., $\geq 99\%$, Sigma Aldrich; 0.75 mol) was cooled to $-78\text{ }^\circ\text{C}$ in a 500 mL Nalgene bottle. Cross-linked (with 2% divinylbenzene) poly(4-vinylpyridine) (0.1 mol, based on the monomer) was then slowly added with constant swirling and cooling to ensure a controlled and uniform reaction. After a fluffy, white solid was obtained, the bottle was allowed to come to room temperature, capped and then stored in a refrigerator ($-20\text{ }^\circ\text{C}$) for further use. PVP- H_2SO_4 was also prepared in a similar fashion to yield a fluffy, cream colored solid.

Typical Preparation of Nitrating Mixture (NM): Fuming nitric acid (purum p.a., $\geq 99\%$, Sigma Aldrich; 0.75 mol) was weighed in a 500 mL Nalgene bottle equipped with a stir bar and cooled to 0°C . Concentrated sulfuric acid (0.75 mol), weighed separately in a glass vial was slowly

added via a pipette to the stirring nitric acid. The Nalgene bottle was then capped and stored in a refrigerator (-20 °C) for further use.

Typical Preparation of PVP-NM (1:7.5) complex: Cross-linked (with 2% divinylbenzene) poly(4-vinylpyridine) (0.2 mol) was gradually added to the nitrating mixture (prepared previously) with constant swirling until a fluffy solid was obtained. The Nalgene bottle was then capped and stored in a refrigerator (-20 °C) for several hours before experimental use of the PVP-NM.

General Procedure for the Nitration of Aromatic Compounds with 1:1 mixture of PVP-HNO₃ and PVP-H₂SO₄: To a stirring solution of a selected arene (1 mmol) in dichloromethane (5 mL), PVP-HNO₃ (0.5 g, 2 mmol) was added and the solution was stirred for 5 min. PVP-H₂SO₄ (0.5 g, 2 mmol) was then gradually added, the reaction vessel was sealed and the mixture was stirred for the required time. Reactions at room temperature were carried out in glass vials while those requiring heating were carried out in glass pressure tubes. All reactions were monitored by thin layer chromatography or GC/MS. Upon completion, the reaction mixture was diluted with dichloromethane (5 mL) and filtered, washing with more dichloromethane (10 mL). The filtrate was washed with saturated NaHCO₃ solution (15 mL), saturated NaCl solution (15 mL) and water (15 mL), and dried over anhydrous Na₂SO₄. Removal of the solvent under reduced pressure afforded the product in pure form, as verified by ¹H NMR and GC/MS. The ratio of *ortho*, *meta* and *para* isomers was determined by ¹H NMR and GC/MS.

General Procedure for the Nitration of Aromatic Compounds with PVP-NM: To a stirring solution of a selected arene (1 mmol) in dichloromethane (5 mL), Nitrating Mixture (0.805 g, 5 mmol) was added and the mixture was stirred for the length of times as mentioned in Table 2.

Reactions were carried out in glass vials at room temperature and in glass pressure tubes at elevated temperatures. At the end of the times as mentioned in Table 2, the reaction mixtures were diluted with dichloromethane (5 mL), washing with more dichloromethane (10 mL). The filtrate was washed with saturated NaHCO₃ solution (15 mL), saturated NaCl solution (15 mL) and water (15 mL), and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure for analysis of the product by ¹H NMR and GC/MS. The ratio of *ortho*, *meta* and *para* isomers was determined by ¹H NMR and GC/MS. For comparison, reactions were repeated using pure nitrating mixture, keeping amount of the nitration mixture similar.

Recyclability Test for PVP-NM: PVP-NM (11.16 g) was added to a solution of ethylbenzene (1.48g, 13.93 mmol) in dichloromethane (45 mL) and stirred at room temperature. Upon completion of the reaction (1.5 h), the reaction mixture was diluted with dichloromethane (20 mL) and filtered, washing with more dichloromethane (20 mL). The filtrate was washed with saturated NaHCO₃ solution (50 mL), saturated NaCl solution (50 mL) and water (50 mL) and dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the product was analyzed by ¹H NMR and GC/MS which confirmed the product as a mixture of isomers of mononitrated ethylbenzene (95% yield). The solid polymer residue left after the extraction of the product from the reaction mixture was made basic (pH ~8) by the addition of saturated NaHCO₃. The basic mixture was vacuum-filtered, washing with water (50 mL) and the solid residue (recovered solid polymer) was dried in air for two days. Out of the recovered PVP (1.743 g), 1.717 g (0.0163 mol) was mixed with the nitrating mixture of HNO₃ (3.8 g, 0.06 mol) and H₂SO₄ (5.92 g, 0.06 mol) to make PVP-NM (recycled) (10.75g, 96% recovery). PVP-NM (recycled) (1.05 g) was added to a solution of ethylbenzene (124 mg, 1.16 mmol) in dichloromethane (5

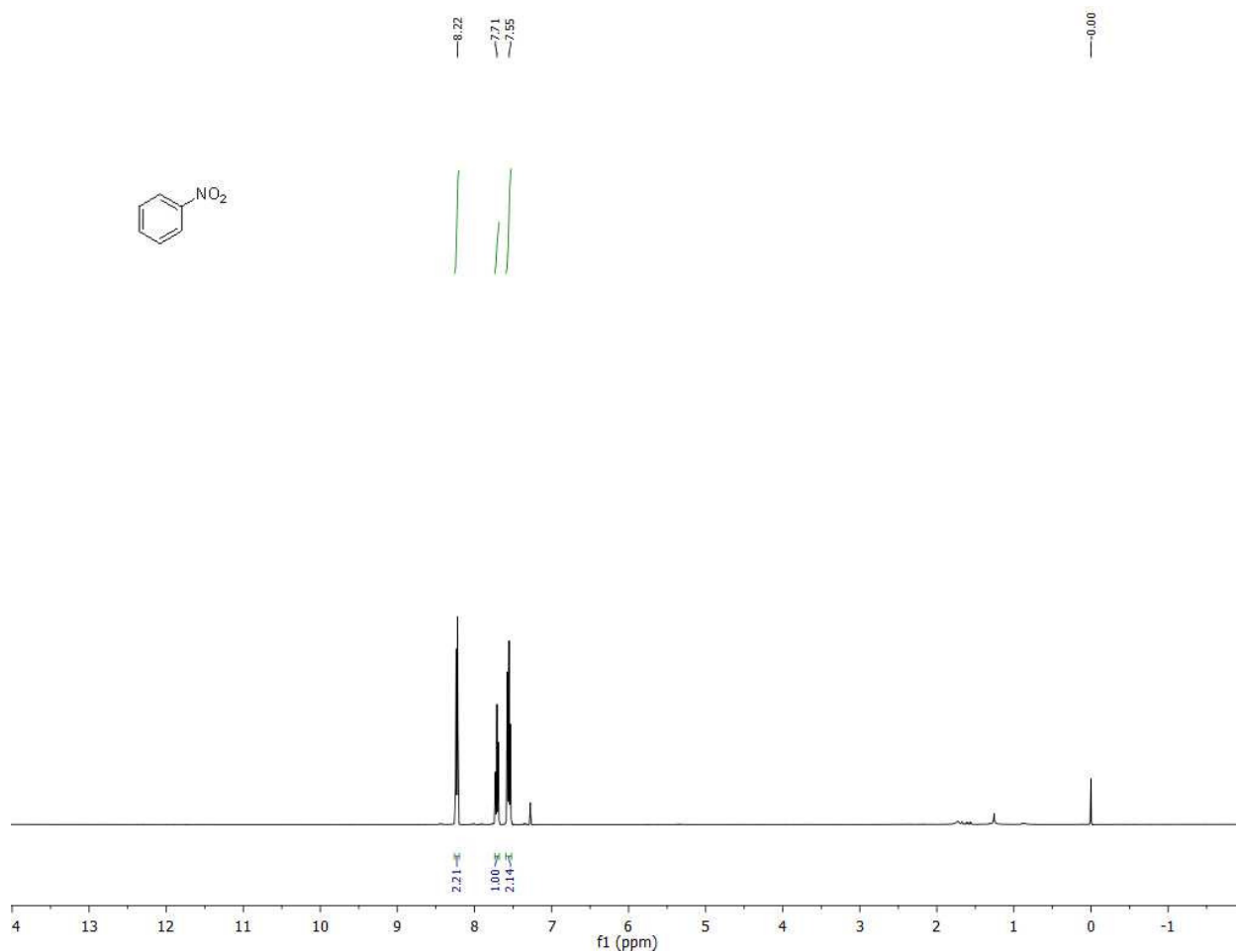
mL) and stirred for 1.5 h. The reaction was worked up as before to obtain nitroethylbenzene (167 mg, 1.10 mmol) as a mixture of its *ortho*, *meta* and *para* isomers in 95% yield.

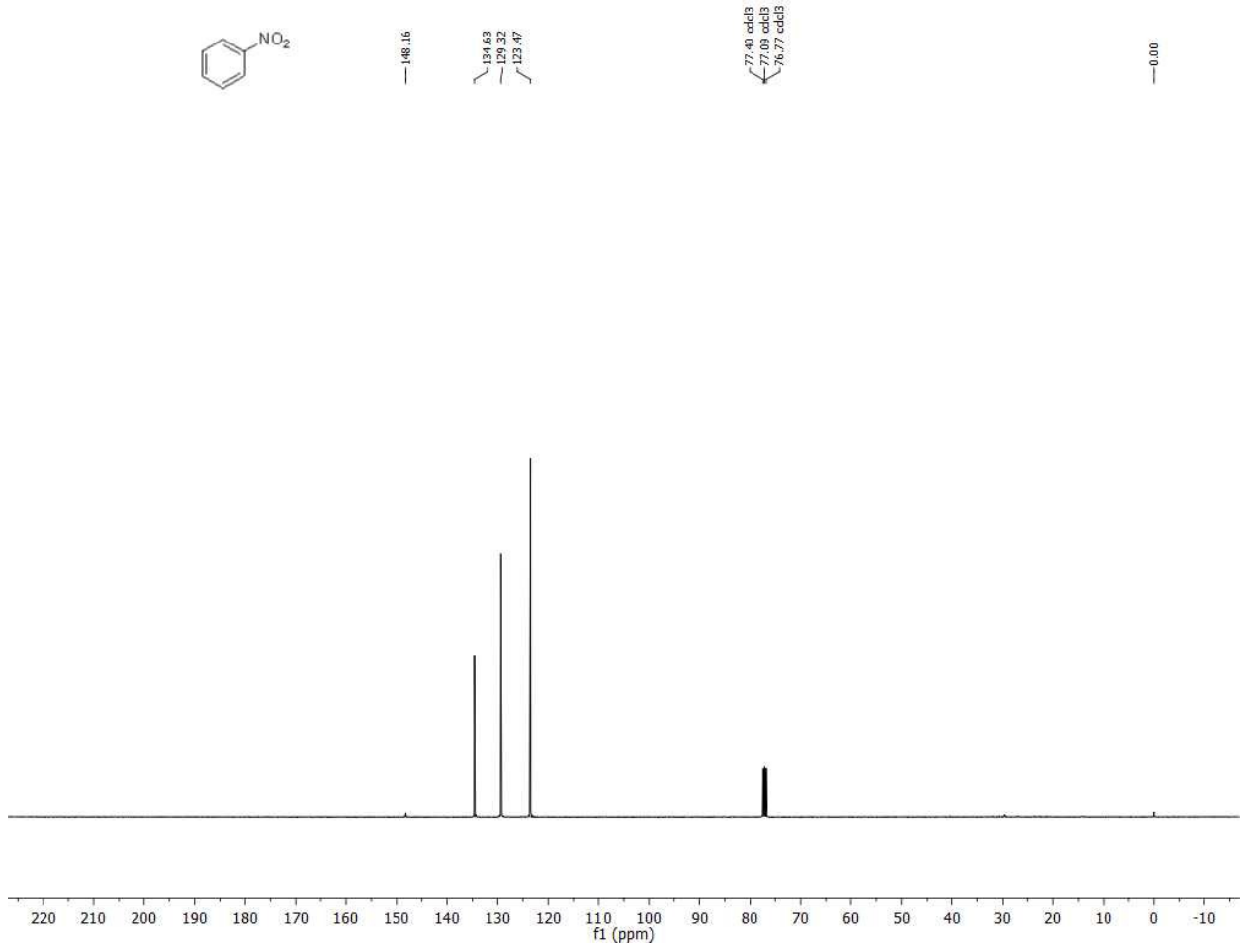
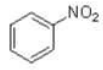
Spectral Data

1. Nitrobenzene¹

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.53-7.57(m, 2H), 7.71 (tt, $J=7.0$ Hz, 1.2 Hz, 1H), 8.19 – 8.26 (m, 2H).

¹³C NMR (400 MHz, Chloroform-*d*) δ = 123.47, 129.32, 134.63, 148.16



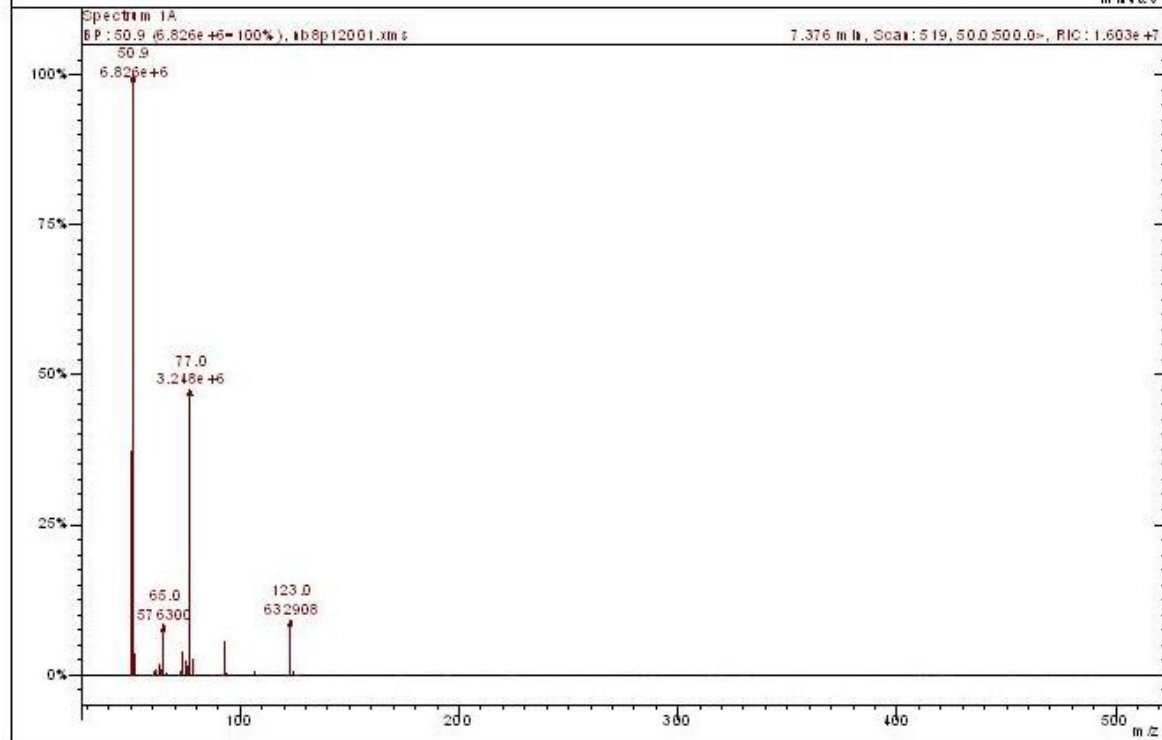
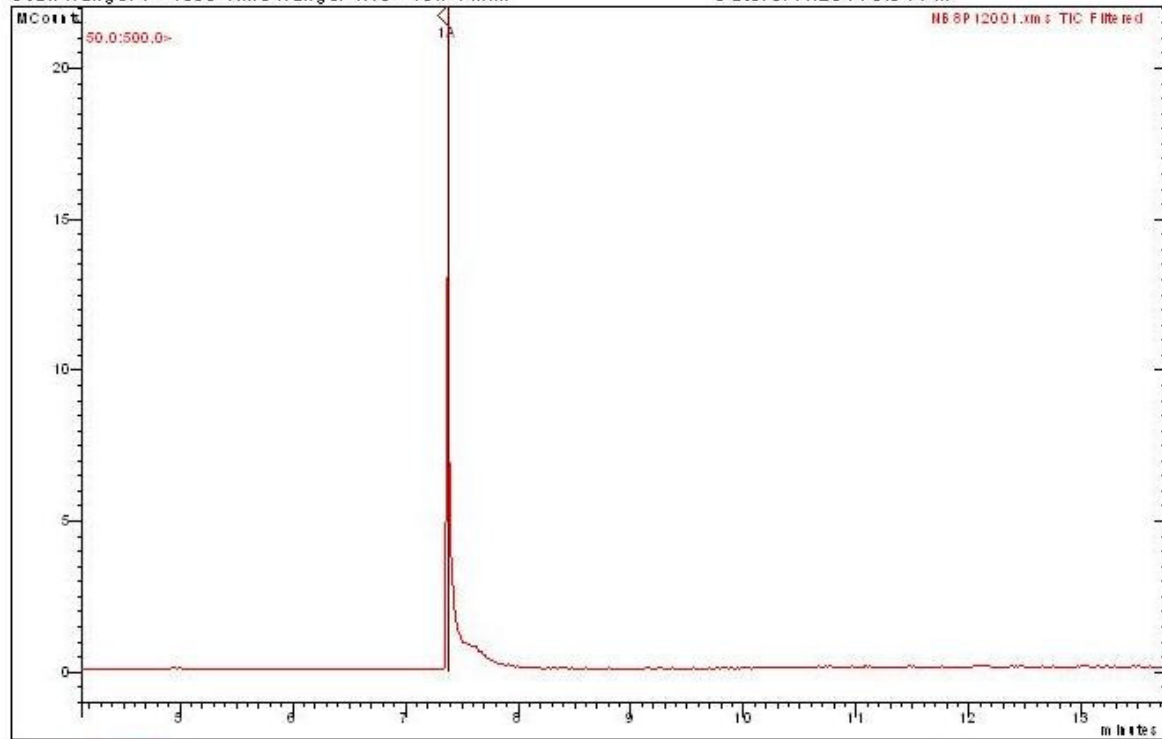


Nitrobenzene:

MS Data Review All Plots - 10/6/2014 6:32 PM

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Sample: NB8P12
Scan Range: 1 - 1533 Time Range: 4.13 - 13.74 min.

Operator: Laxman Gurung
Date: 8/11/2014 9:04 PM



2. Nitrotoluene

o-Nitrotoluene²

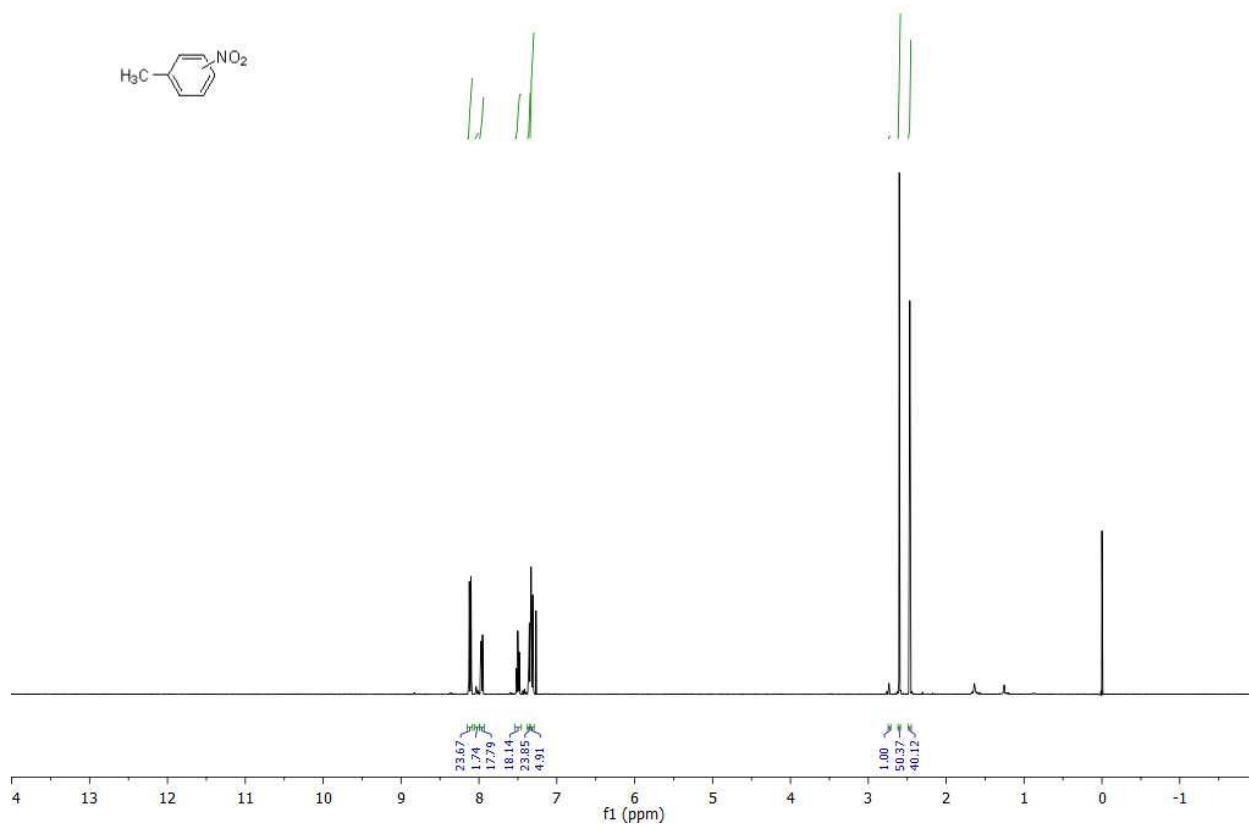
¹H NMR (400 MHz, Chloroform-*d*) δ = 2.47(s, 3H), 7.34-7.36 (m, 2H), 7.50 (td, $J=7.5$ Hz, 1.3 Hz, 1H), 7.96 (dd, $J=8.5, 1.3, 1$ H).

m-Nitrotoluene^{2a}

The amount of *m*-isomer was too low relative to other isomers, hence not visible in the NMR spectrum. However, it is observed in the GC (vide infra).

p-Nitrotoluene²

¹H NMR (400 MHz, Chloroform-*d*) δ = 2.60(s, 3H), 7.30 – 7.34 (m, 2H), 8.11 (d, $J=8.7$ Hz, 2H).

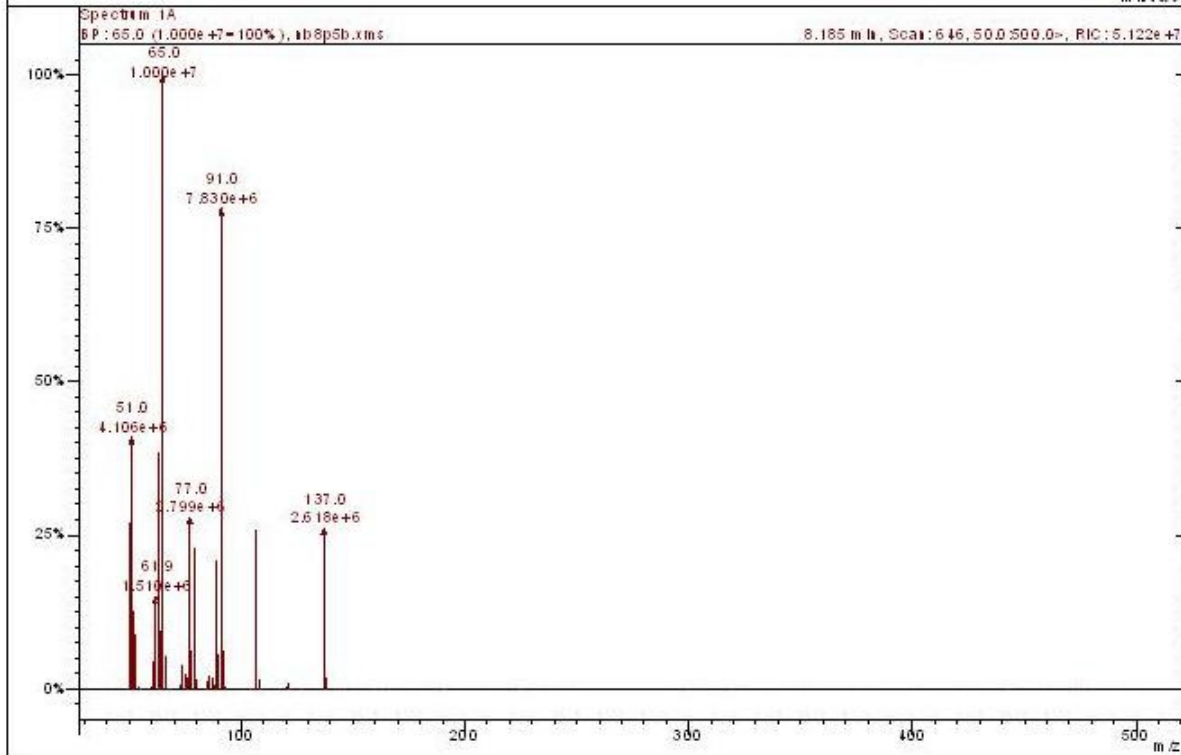
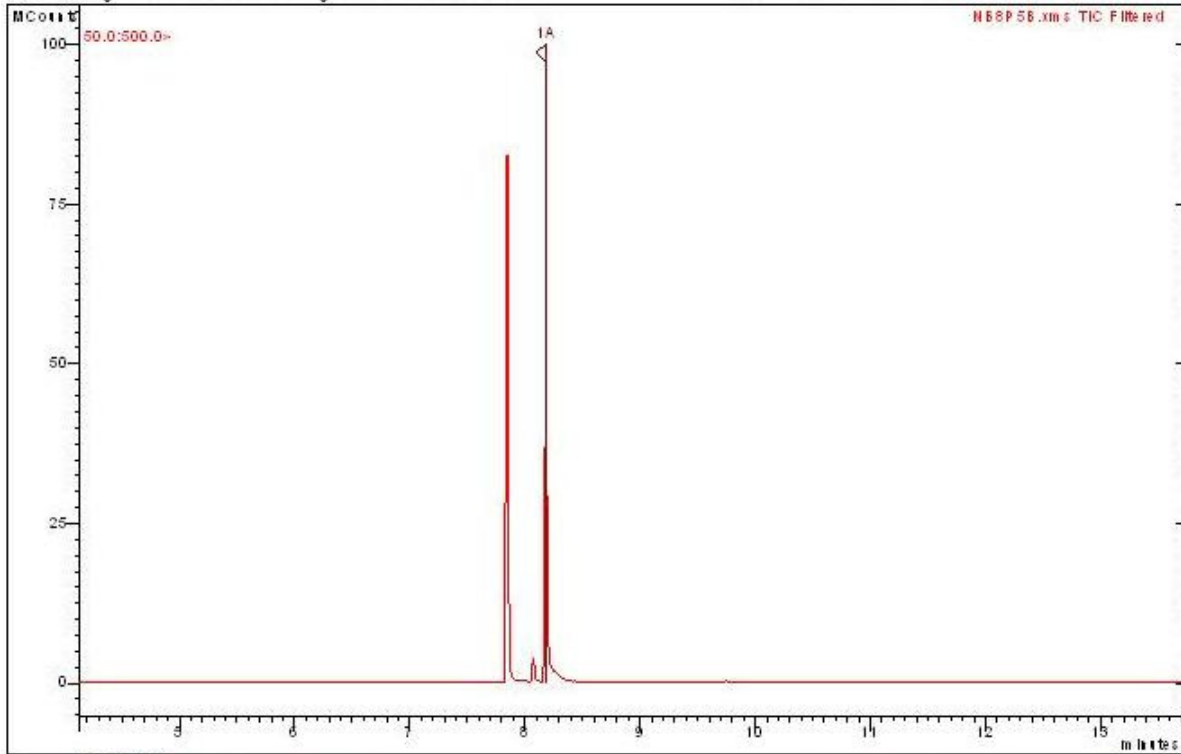


***o*-Nitrotoluene (selected peak) in a mixture of its isomers:**

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Operator: Laxman Gurung
Date: 8/19/2014 3:42 PM

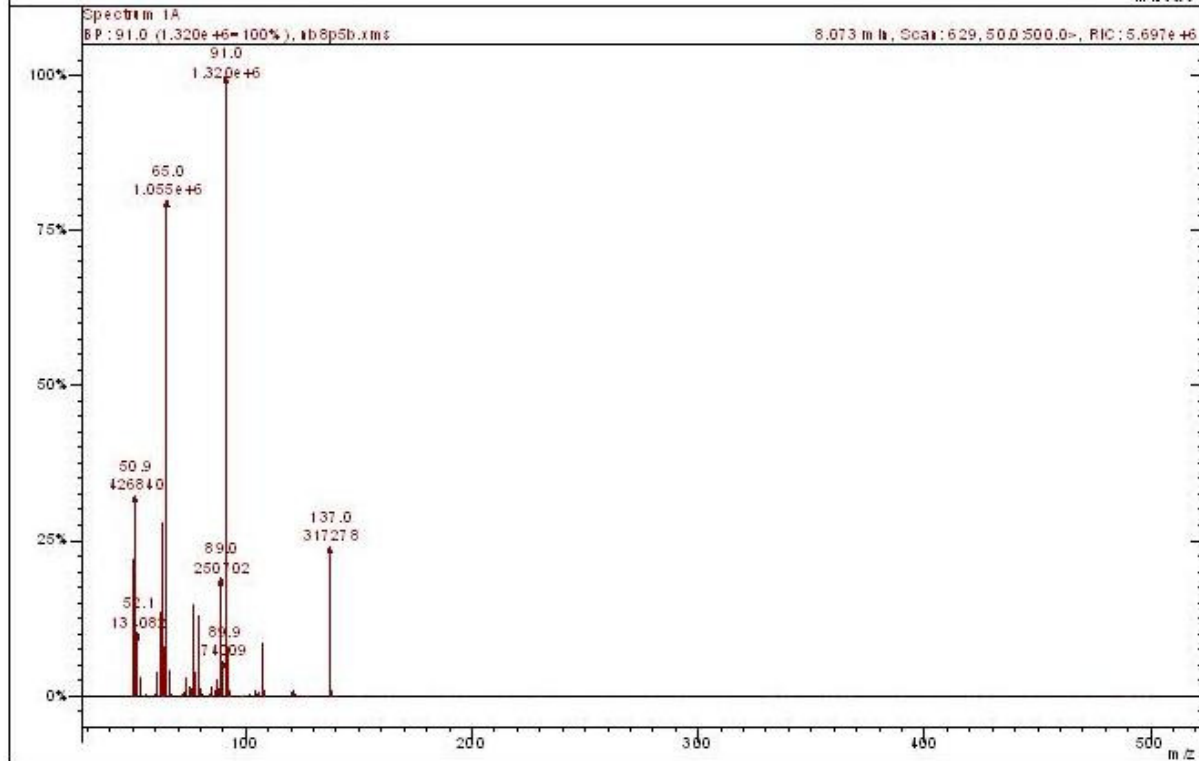
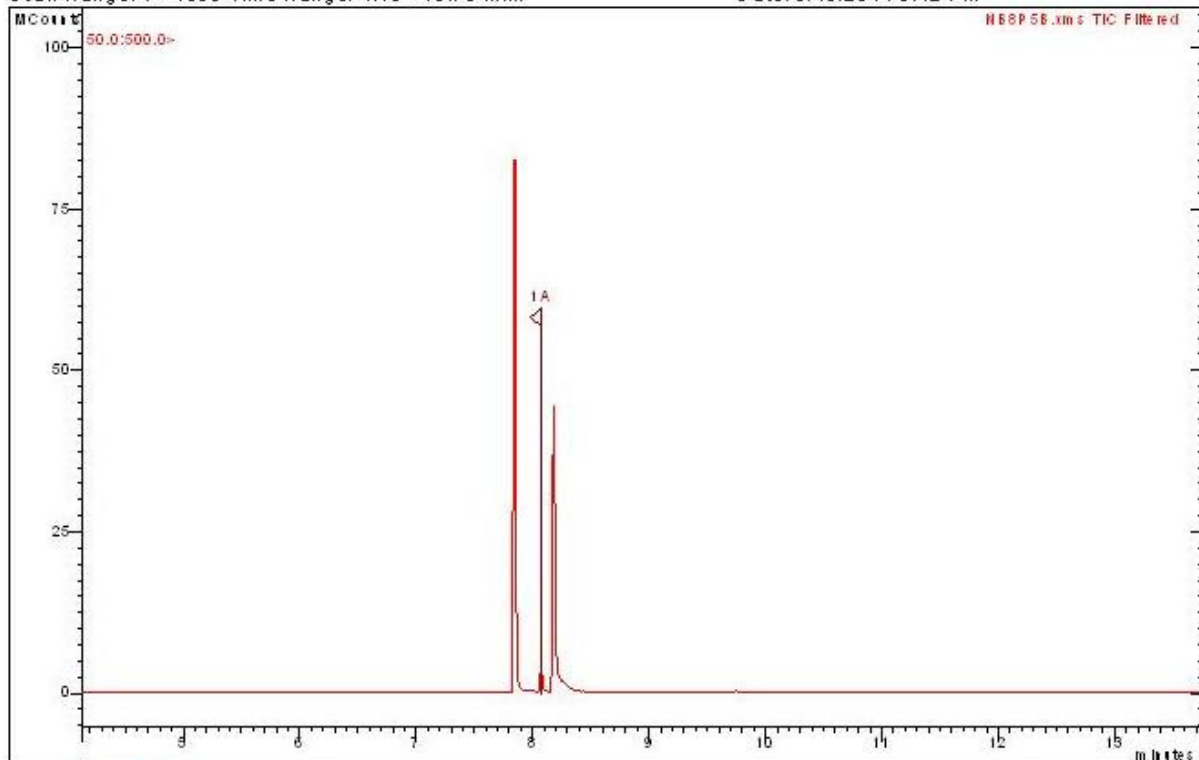


***m*-Nitrotoluene (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/6/2014 6:30 PM

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Sample: NB8P5B
Scan Range: 1 - 1533 Time Range: 4.13 - 13.75 min.

Operator: Laxman Gurung
Date: 8/19/2014 3:42 PM

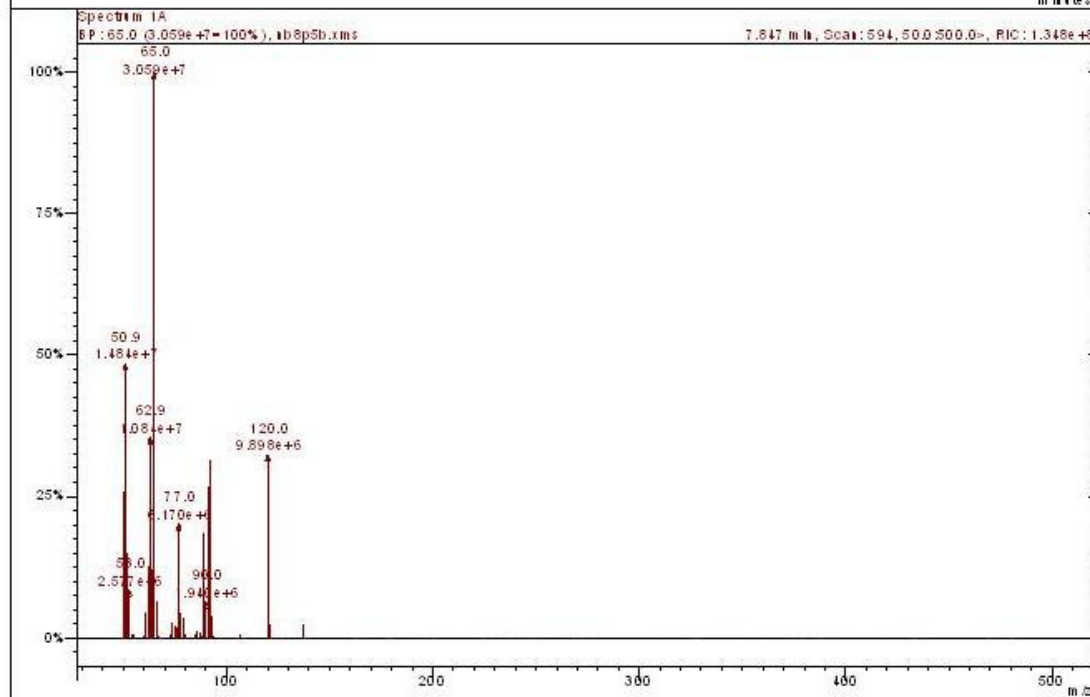
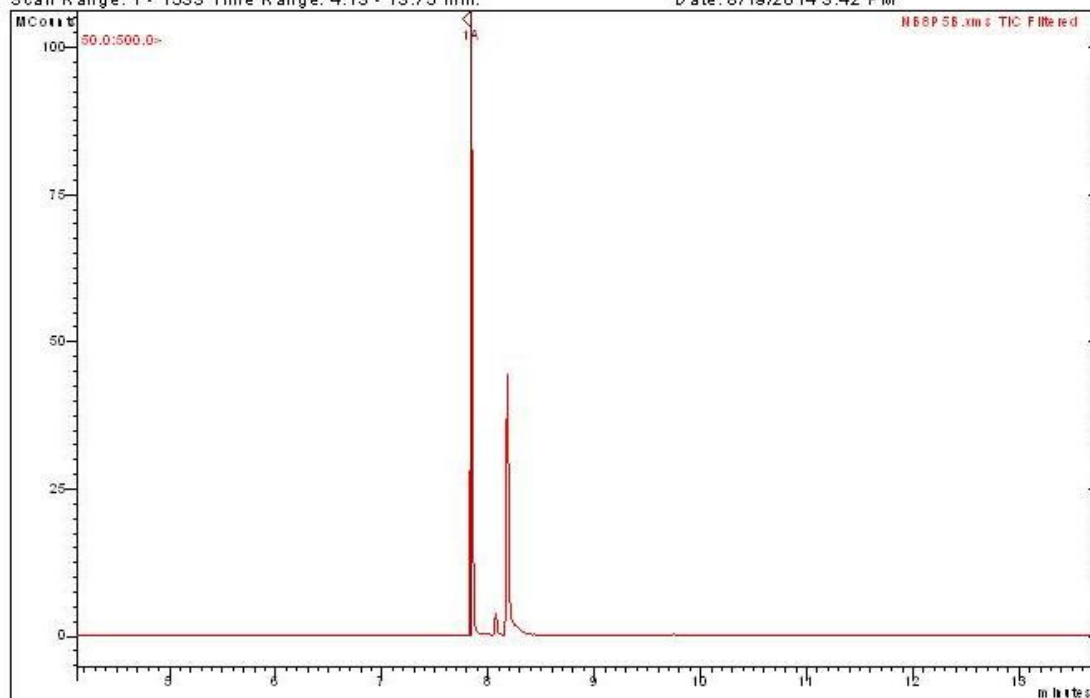


p-Nitrotoluene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:30 PM

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Sample: NB8P5B
Scan Range: 1 - 1533 Time Range: 4.13 - 13.75 min.

Operator: Laxman Gurung
Date: 8/19/2014 3:42 PM



3. Nitroethylbenzene

o-Nitroethylbenzene^{2a,3}

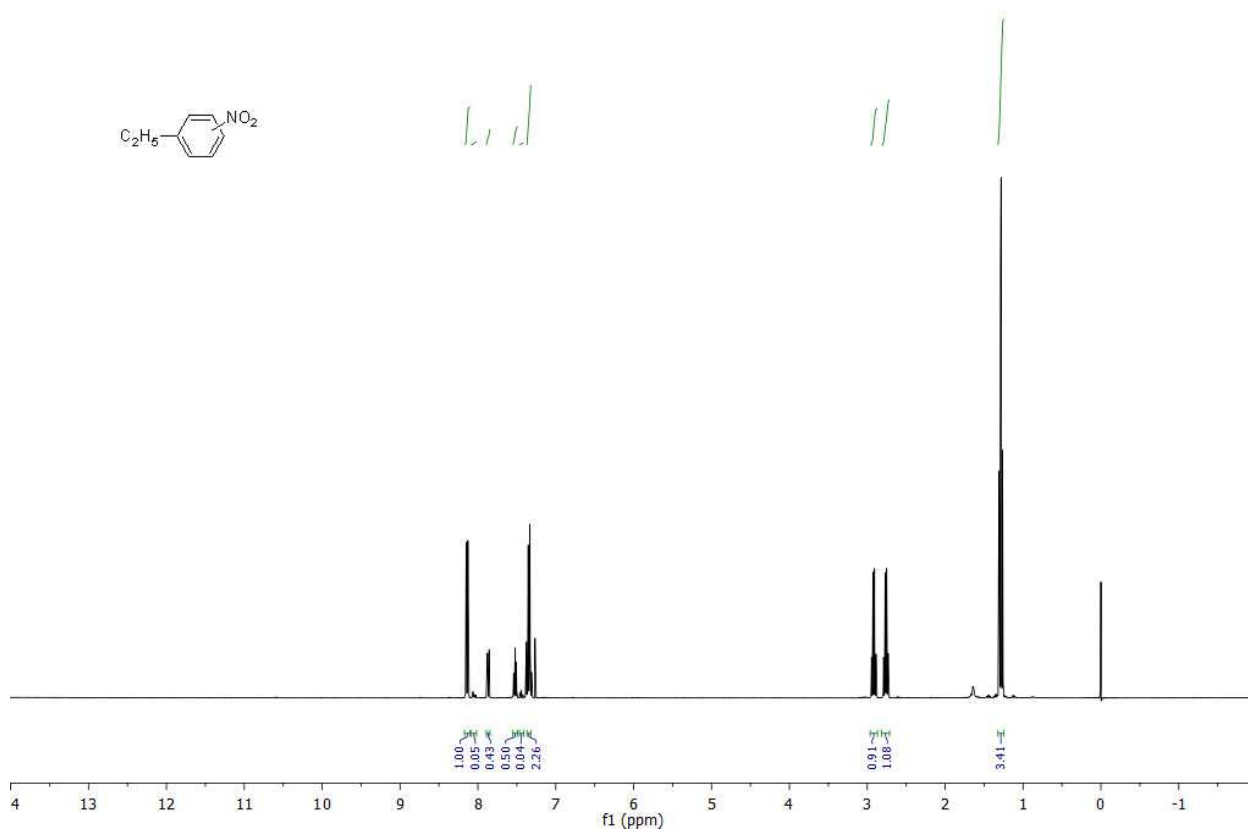
¹H NMR (400 MHz, Chloroform-*d*) δ = 1.29 (t, J = 3.1 Hz, 3H), 2.92 (q, J =7.6 Hz, 2H), 7.37 – 7.40 (m, 2H), 7.52 (td, J =7.6 Hz, 1.3 Hz, 1H), 7.87 (dd, J =8.1 Hz, 1.3 Hz, 1H).

m-Nitroethylbenzene⁴

¹H NMR (400 MHz, Chloroform-*d*) δ = 1.29 (t, J =9 Hz, 3H), 2.76 (q, J = 9 Hz, 2H) (the expected triplet and quartet were too small for observation), 7.44 (t, J =7.8 Hz, 2H), 8.01 – 8.09 (m, 2H)

p-Nitroethylbenzene^{2a}

¹H NMR (400 MHz, Chloroform-*d*) δ = 1.29 (t, J = 3.1 Hz, 3H), 2.76 (q, J =7.5 Hz, 2H), 7.24 – 7.41 (m, 2H), 8.14 (d, J =8.7 Hz, 2H).

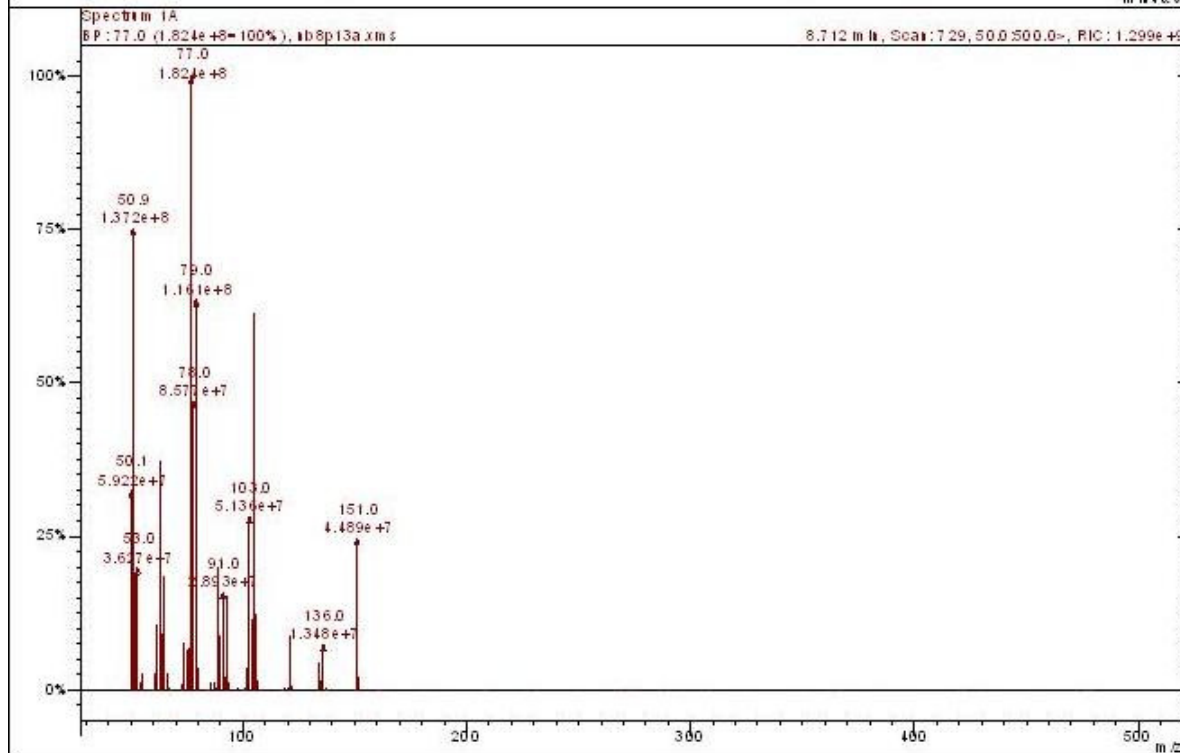
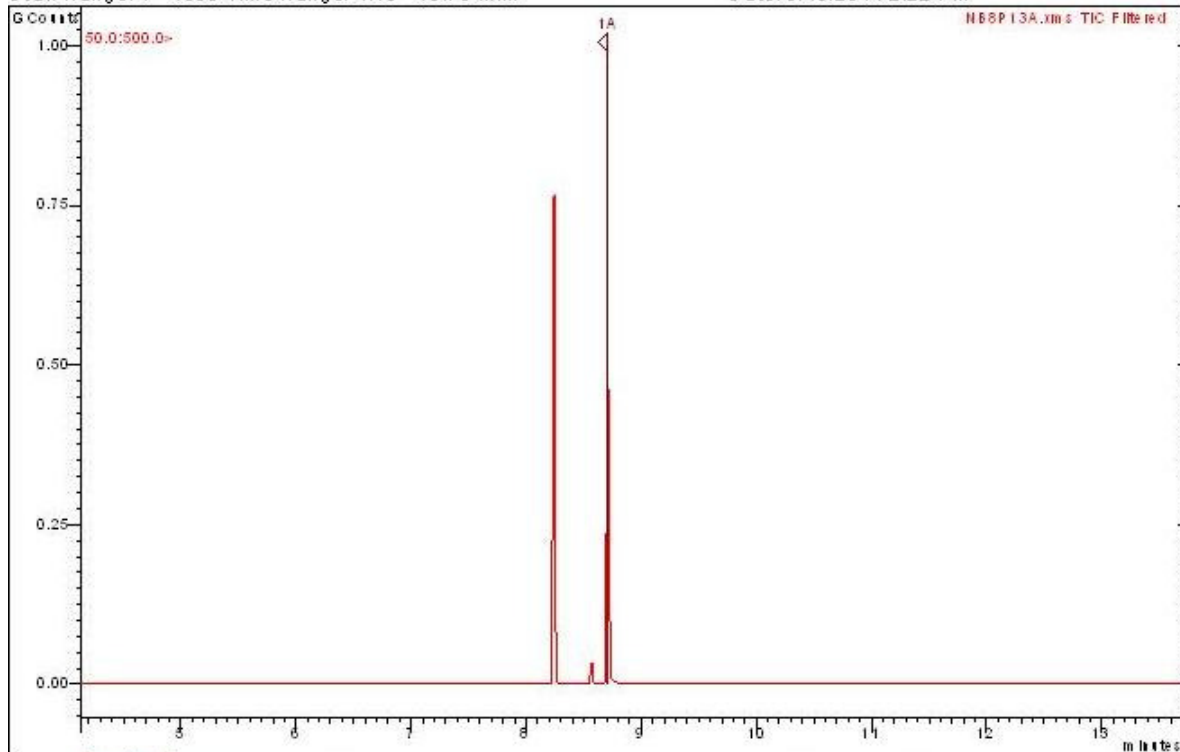


o-Nitroethylbenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:28 PM

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Sample: NB8P13A
Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

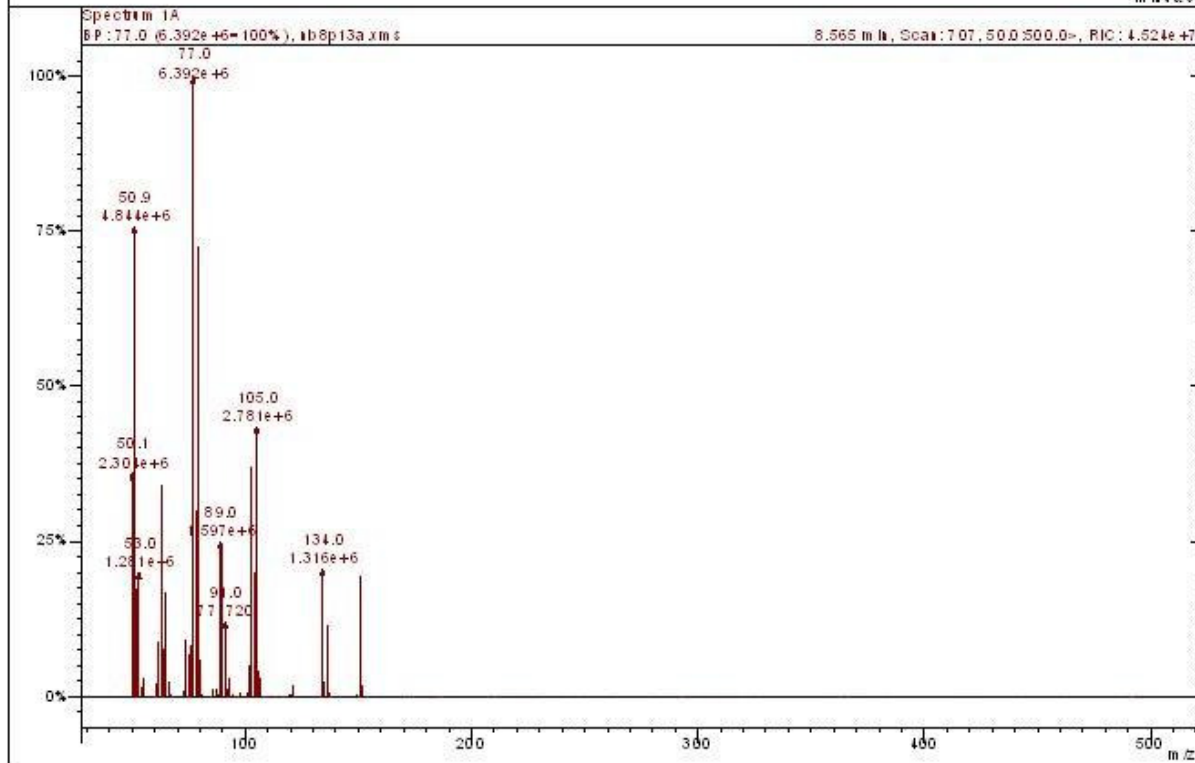
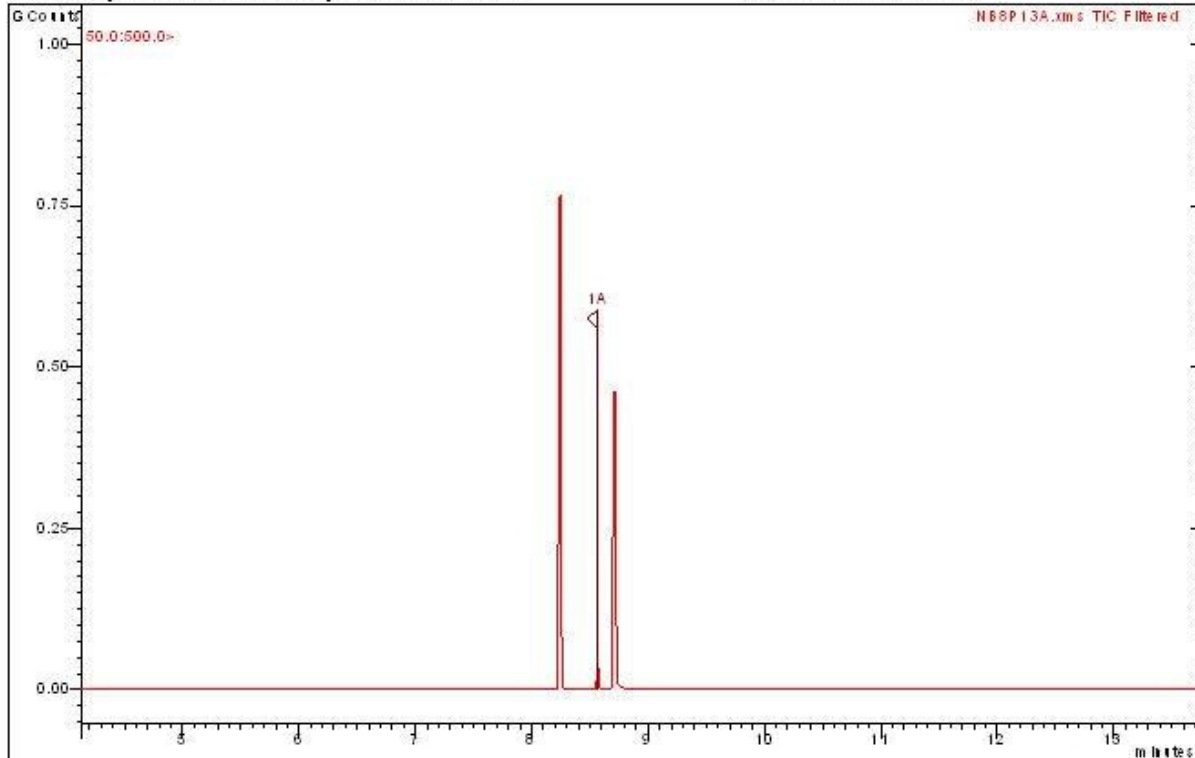
Operator: Laxman Gurung
Date: 8/13/2014 2:22 PM



***m*-Nitroethylbenzene (selected peak) in a mixture of its isomers:**
MS Data Review All Plots - 10/6/2014 6:28 PM

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Sample: NB8P13A
Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

Operator: Laxman Gurung
Date: 8/13/2014 2:22 PM

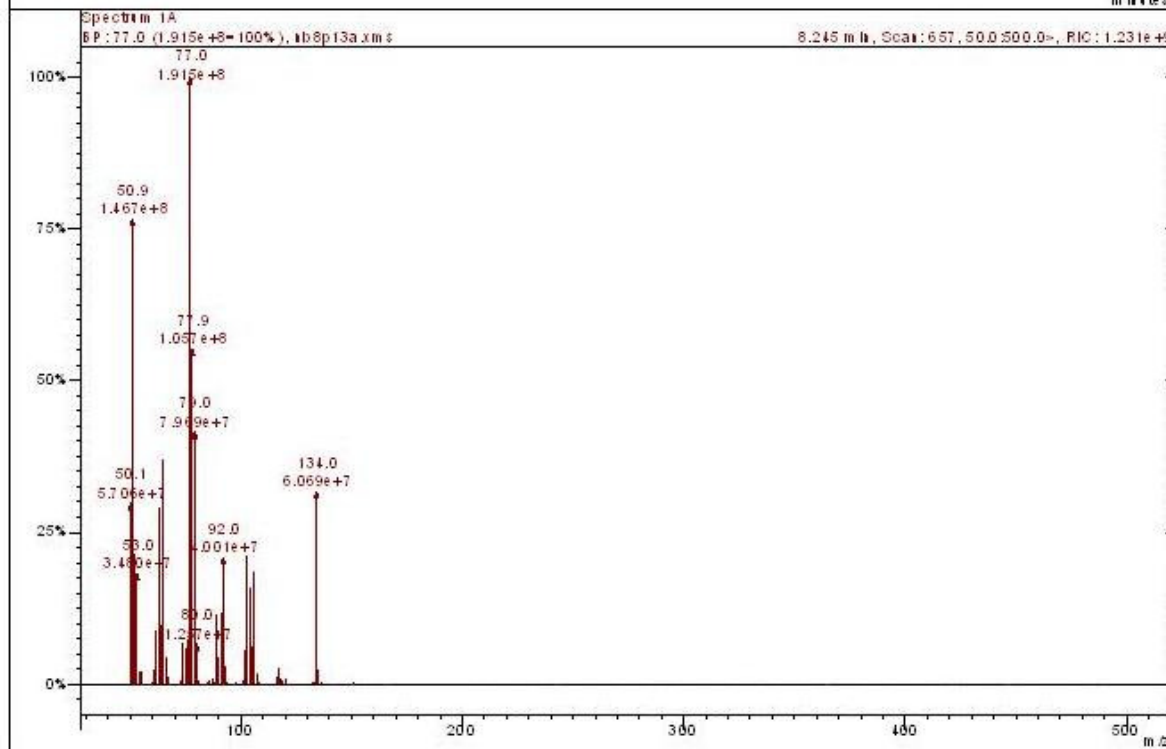
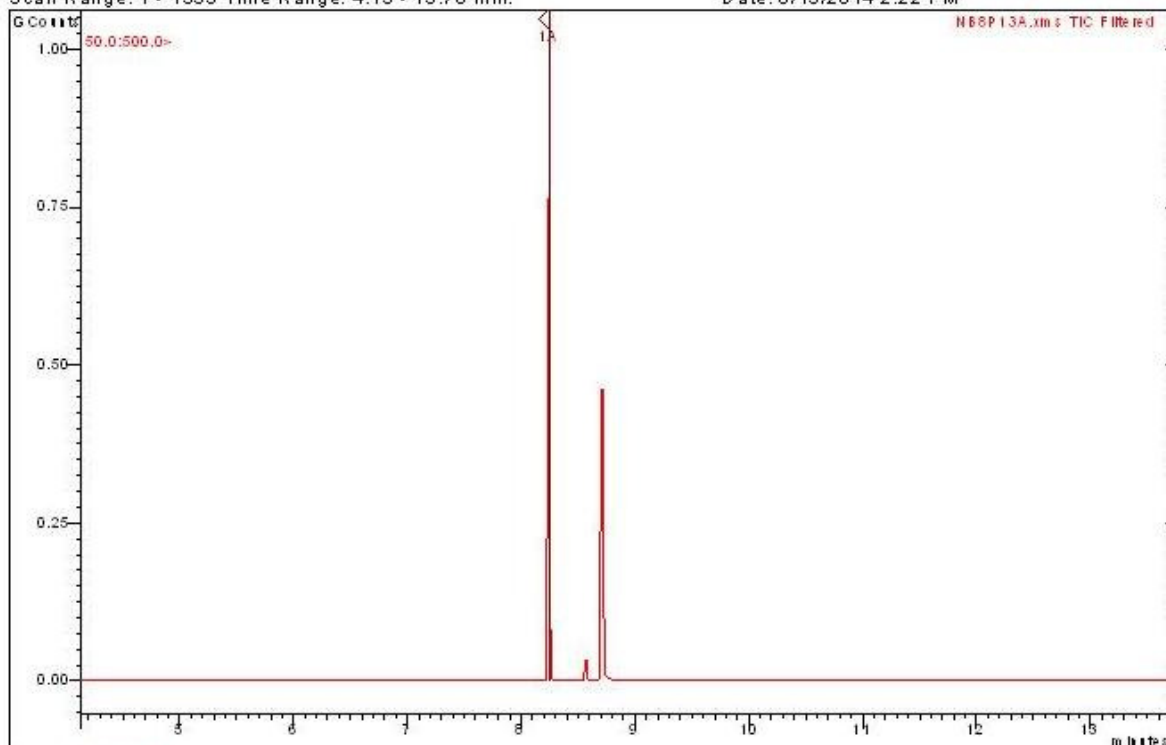


p-Nitroethylbenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:27 PM

File: c:\bruker\ms\data\laxman\pvp-nm kevin\nb8p13a.xms
Sample: NB8P13A
Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

Operator: Laxman Gurung
Date: 8/13/2014 2:22 PM



4. Nitropropylbenzene

o-Nitropropylbenzene^{5a}

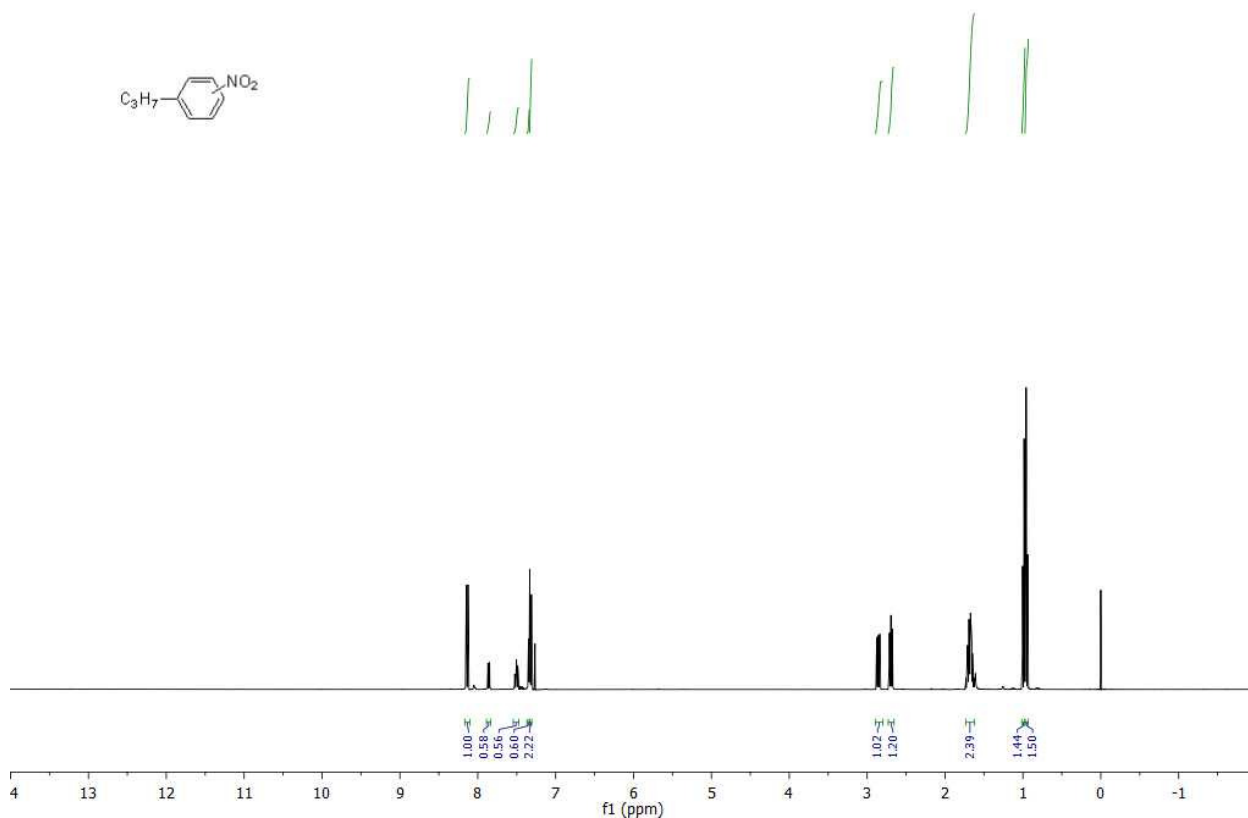
¹H NMR (400 MHz, Chloroform-d) δ = 0.99 (t, J =7.35 Hz, 3H), 1.61 – 1.77 (m, 2H), 2.82 – 2.90 (m, 2H), 7.34 – 7.37 (m, 2H), 7.50 (td, J =7.9 Hz, 1.3, 1H), 7.82 – 7.91 (m, 1H).

m-Nitropropylbenzene^{5b}

¹H NMR (400 MHz, Chloroform-d) δ = 7.43 (m, 2H), 8.05 (m, 2H). The expected peaks at 1.29 (t, J = 9 Hz, 3H) and 2.76 (q, J =9 Hz, 2H)^{6b}, were not observed either due to overlapping with peaks from the *o*- and *p*- isomers or due to the low concentration of the compound relative to these isomers.

p-Nitropropylbenzene^{5c}

¹H NMR (400 MHz, Chloroform-d) δ = 0.96 (t, J =7.35 Hz, 3H), 1.61 – 1.77 (m, 2H), 2.65 – 2.75 (m, 2H), 7.10 – 7.58 (m, 2H), 8.14 (d, J =8.8 Hz, 2H).



***o*-Nitropropylbenzene (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/6/2014 6:26 PM

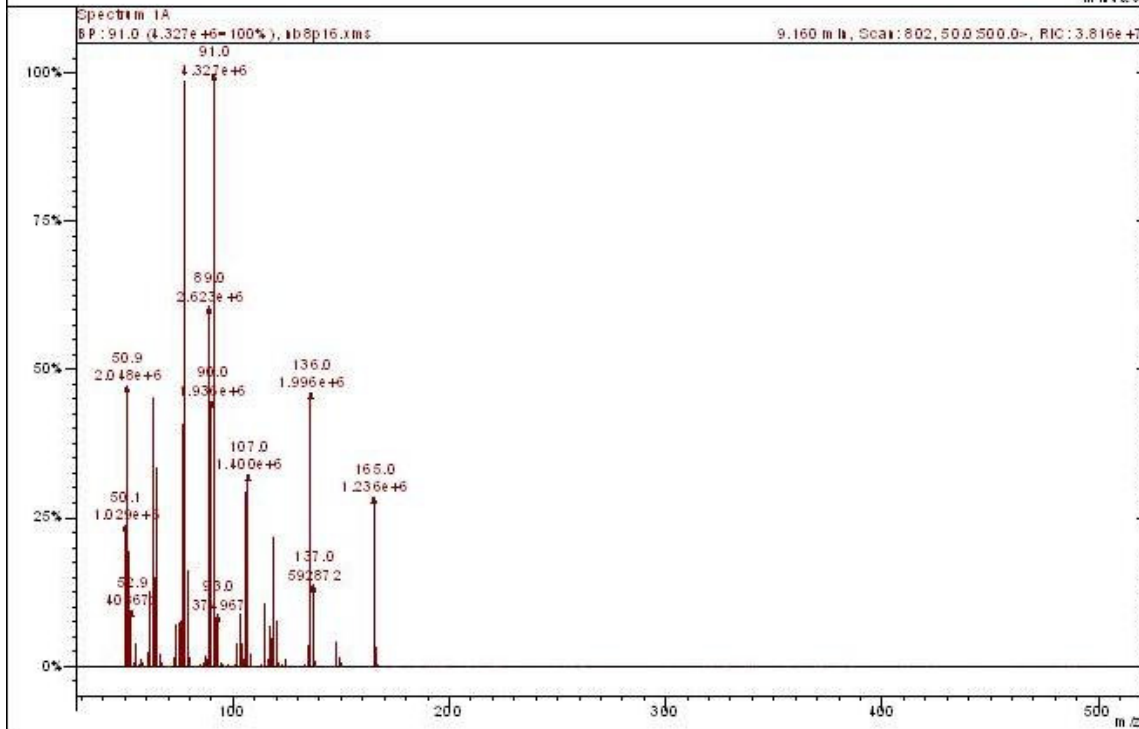
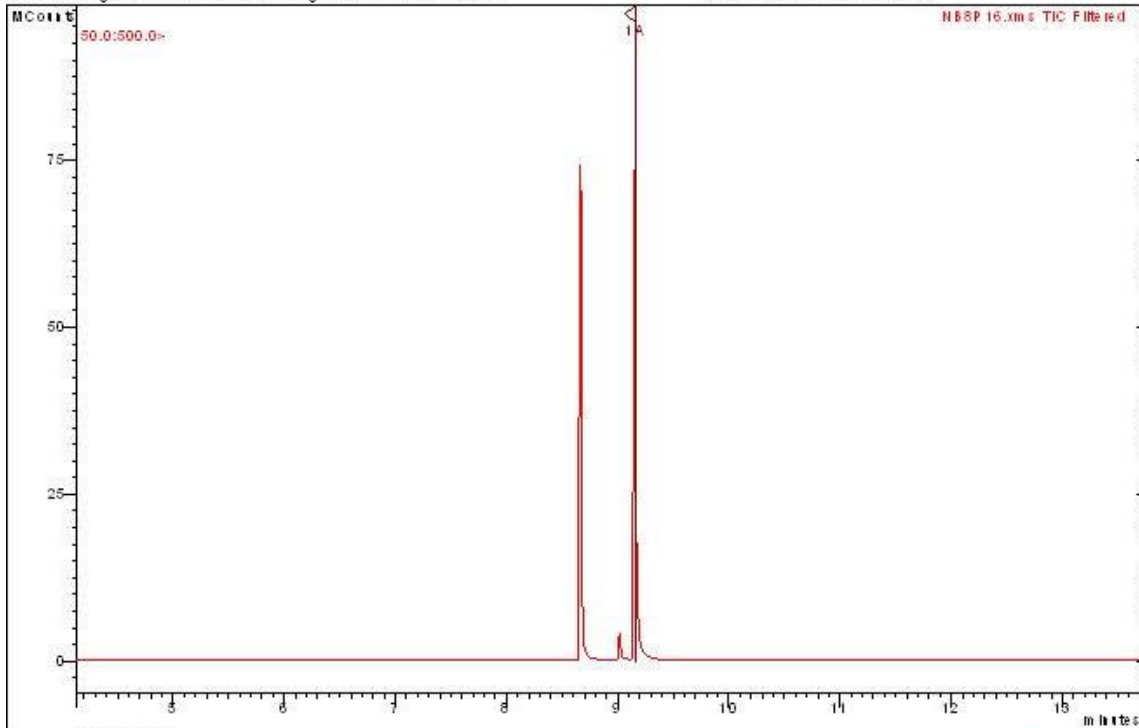
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Sample: NB8P16

Operator: Laxman Gurung

Scan Range: 1 - 1536 Time Range: 4.13 - 13.76 min.

Date: 8/19/2014 1:55 PM

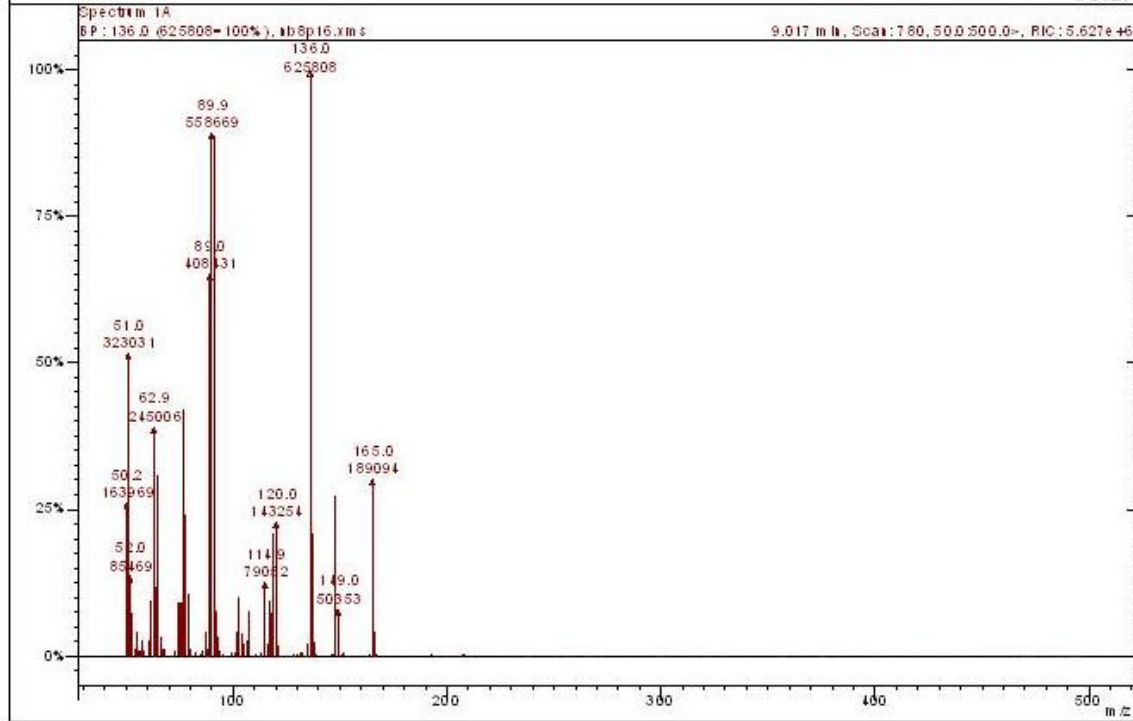
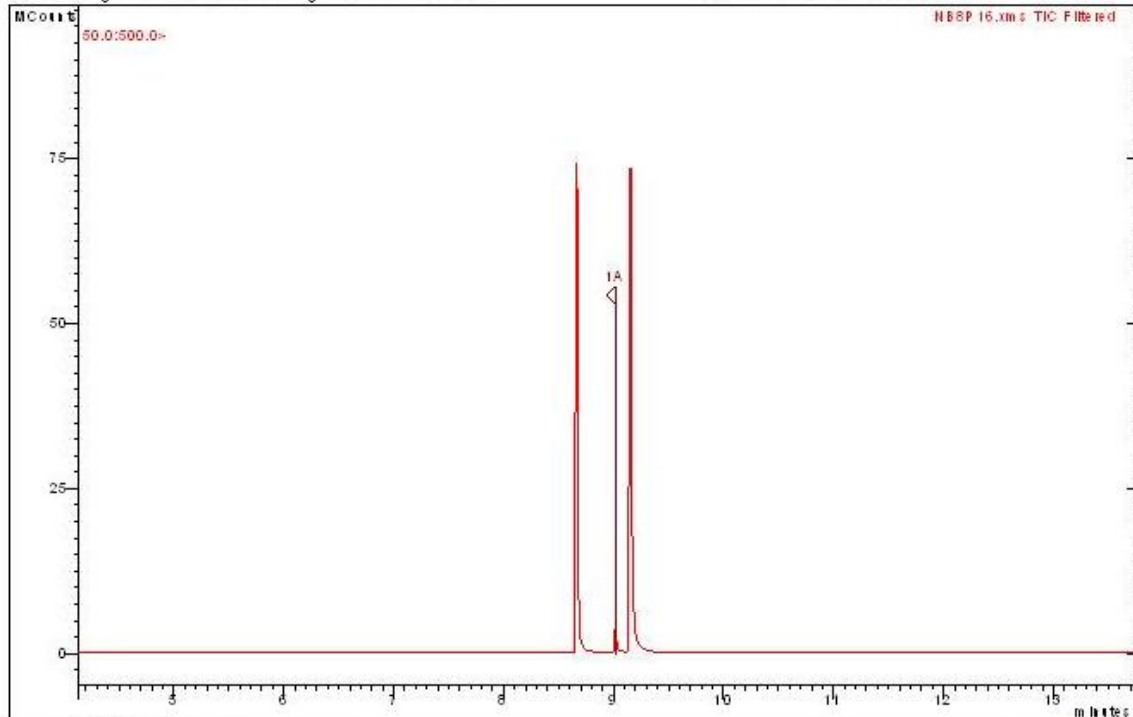


***m*-Nitropropylbenzene (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/6/2014 6:25 PM

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Sample: NB8P16
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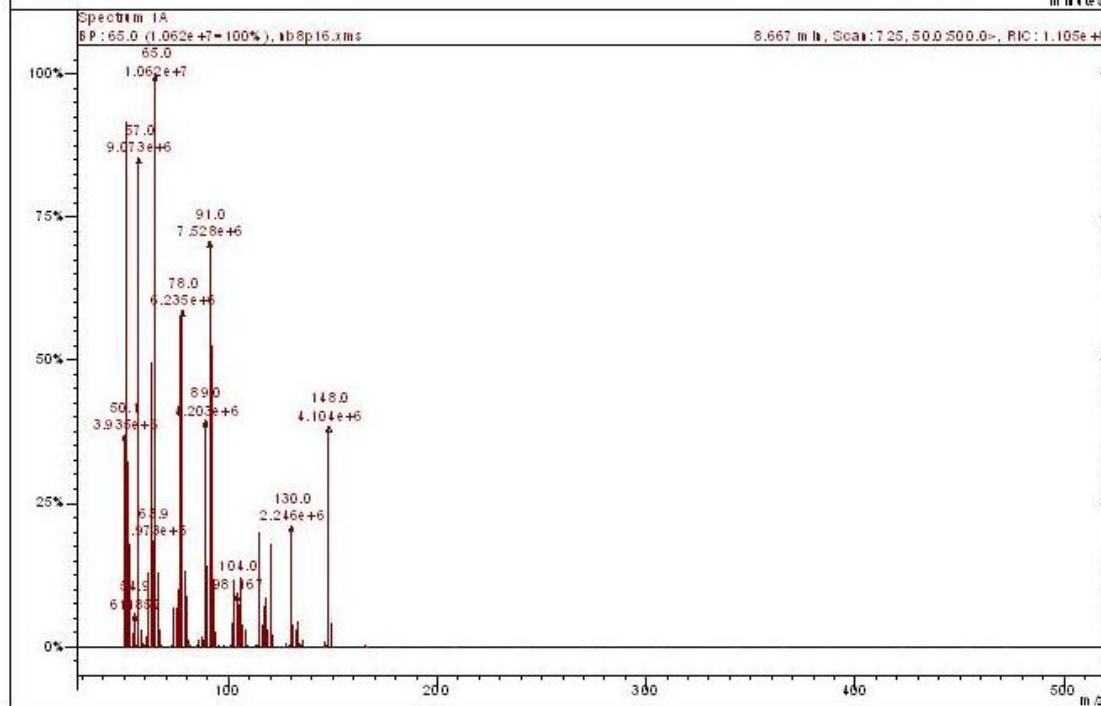
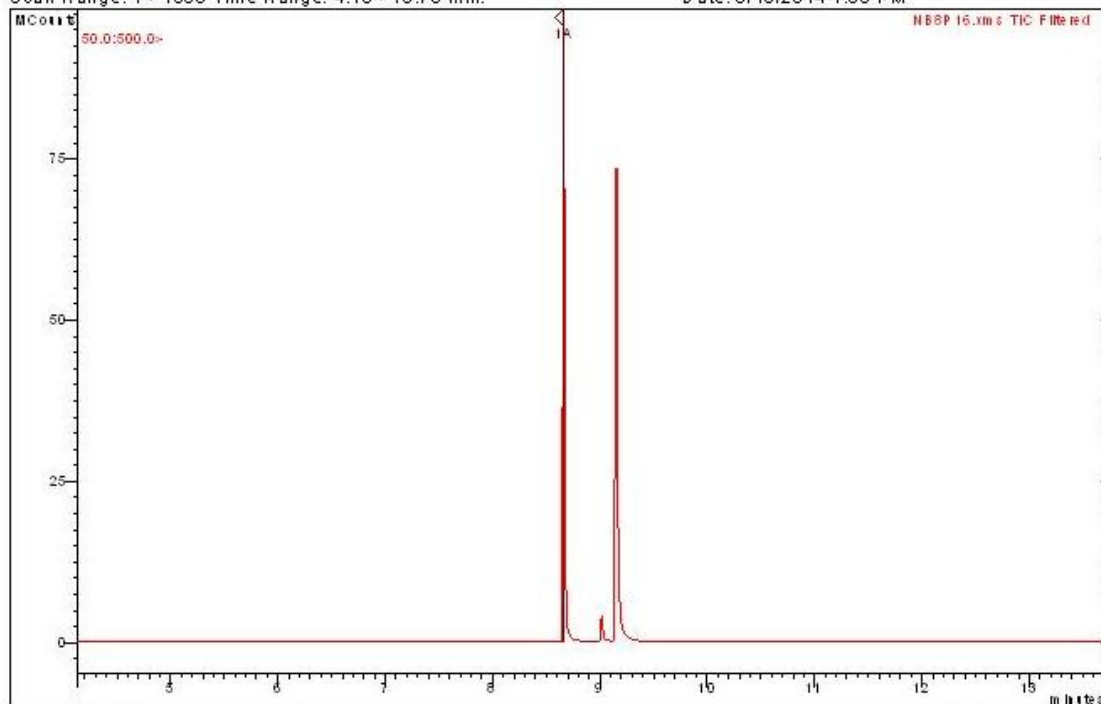
Operator: Laxman Gurung
Date: 8/19/2014 1:55 PM



***p*-Nitropropylbenzene (selected peak) in a mixture of its isomers:**
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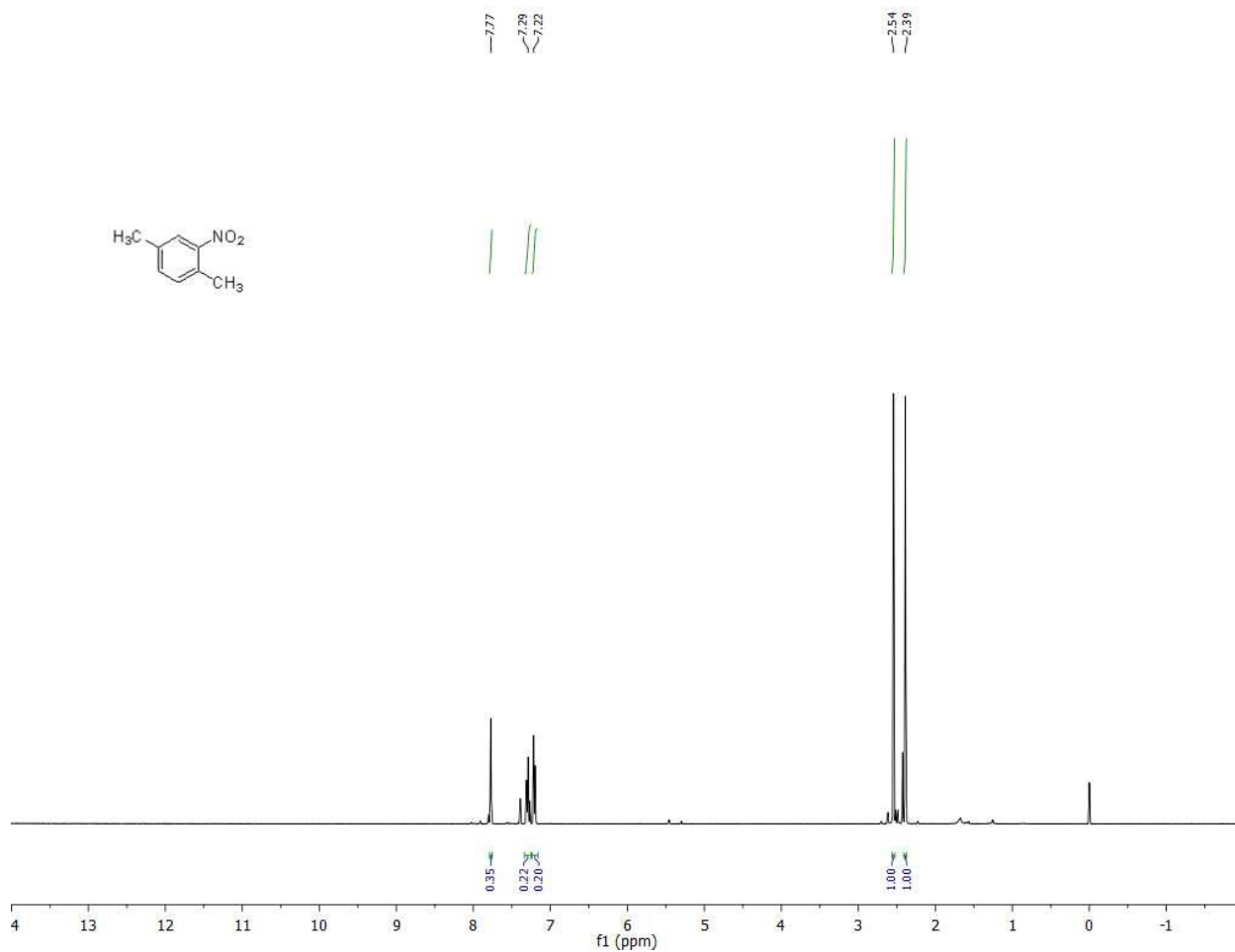
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 Date: 8/19/2014 1:55 PM

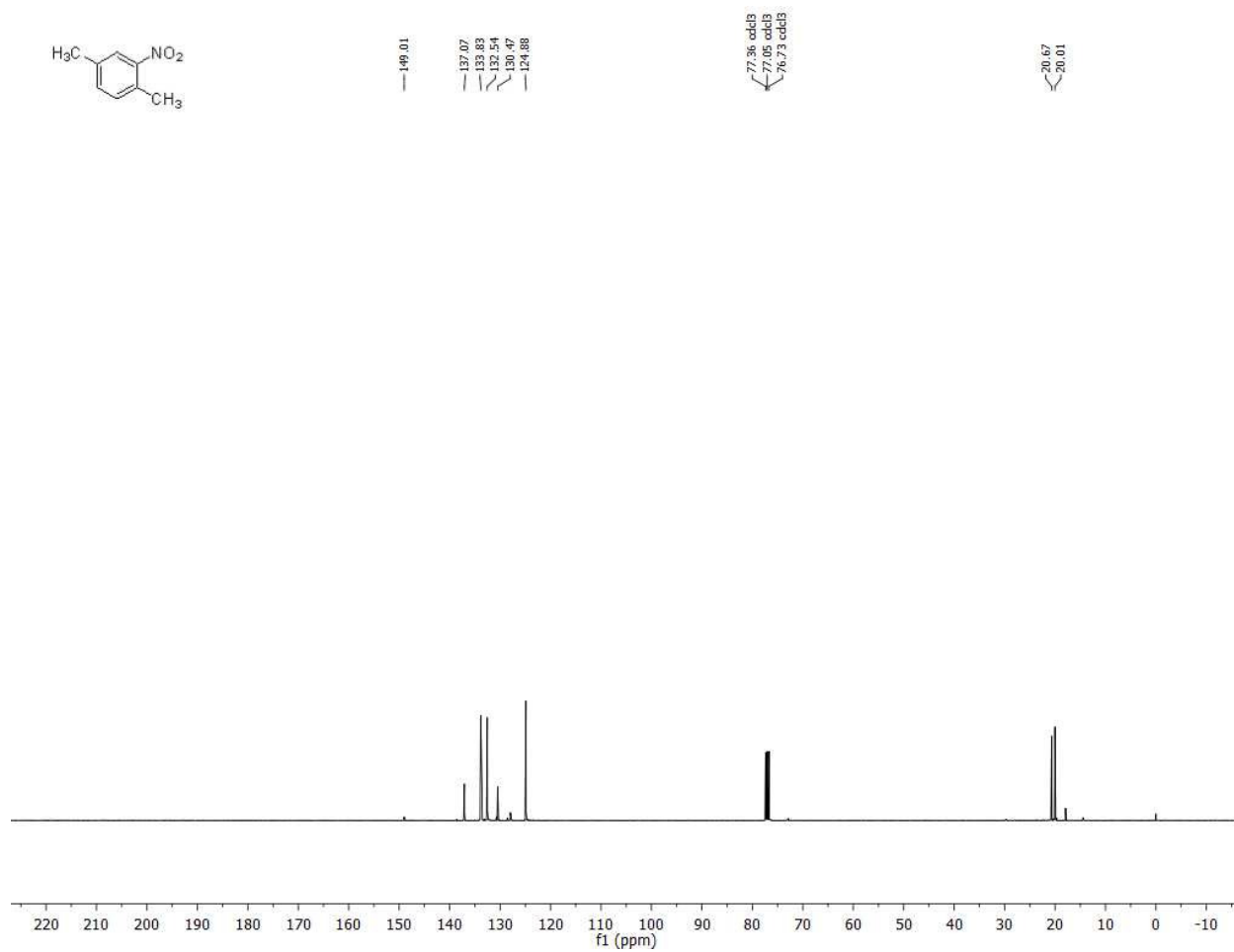
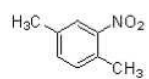


5. 2-Nitro-*p*-xylene^{2a, 6}

¹H NMR (400 MHz, Chloroform-*d*) δ = 2.39(s, 3H), 2.54(s, 3H), 7.20-7.22(m, 1H), 7.29-7.31(m, 1H), 7.77 (s, 1H)

¹³C NMR (400 MHz, Chloroform-*d*) δ = 20.01, 20.67, 124.88, 130.47, 132.54, 132.83, 137.07, 149.01





2-Nitro-*p*-xylene:

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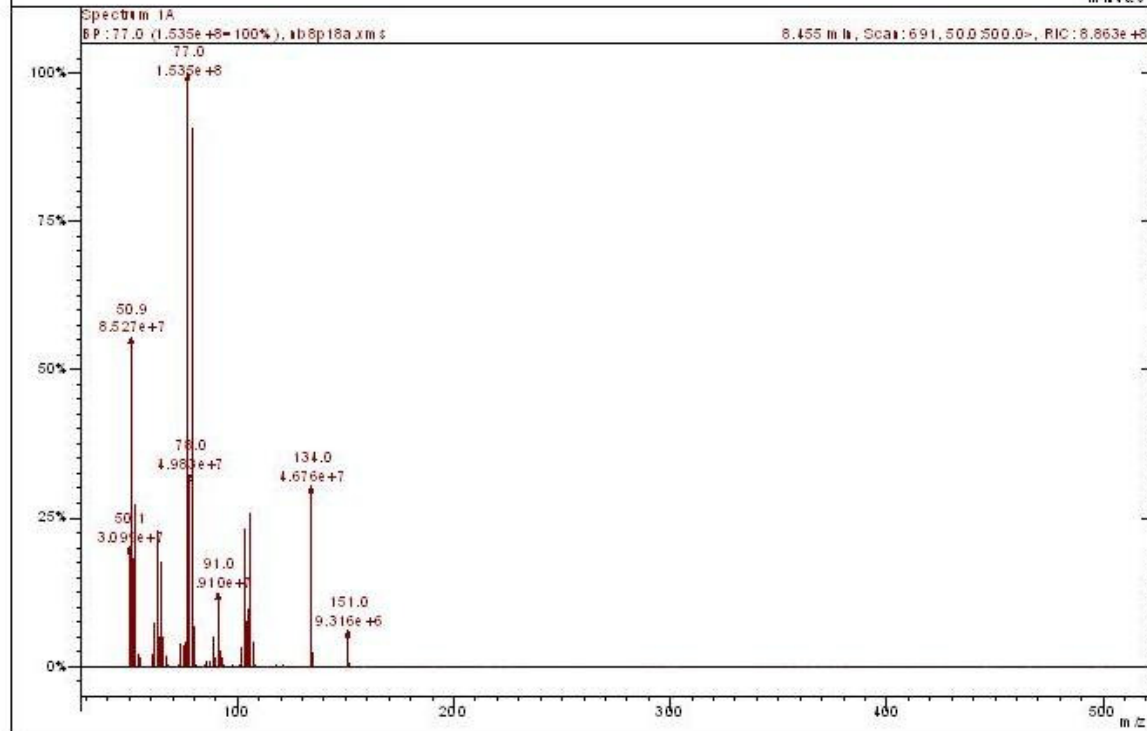
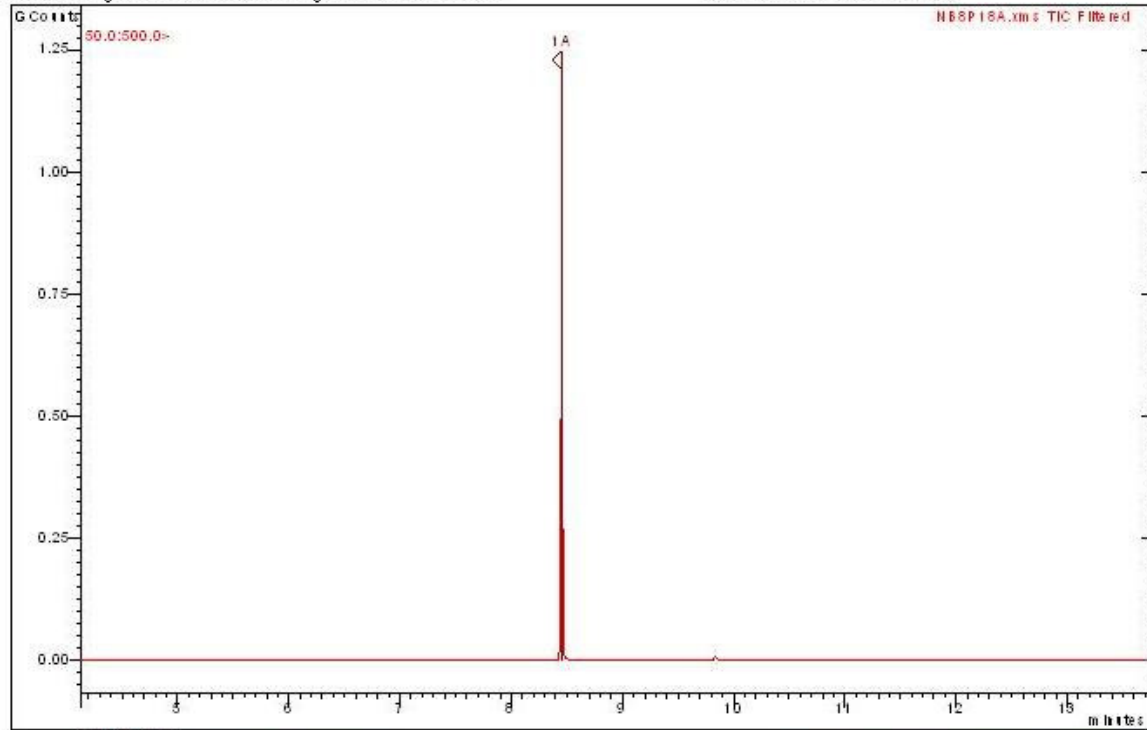
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Sample: NB8P18A

Operator: Laxman Gurung

Scan Range: 1 - 1536 Time Range: 4.13 - 13.76 min.

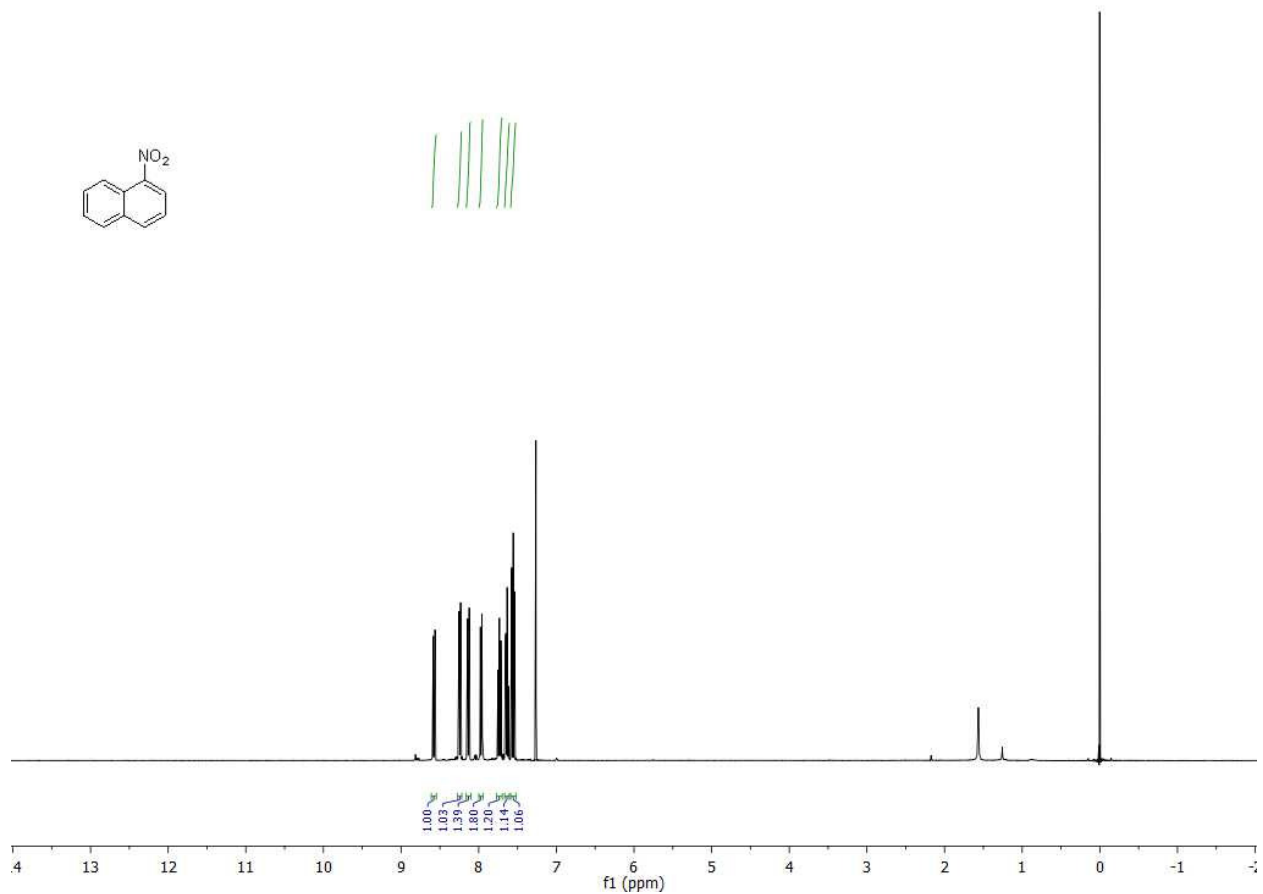
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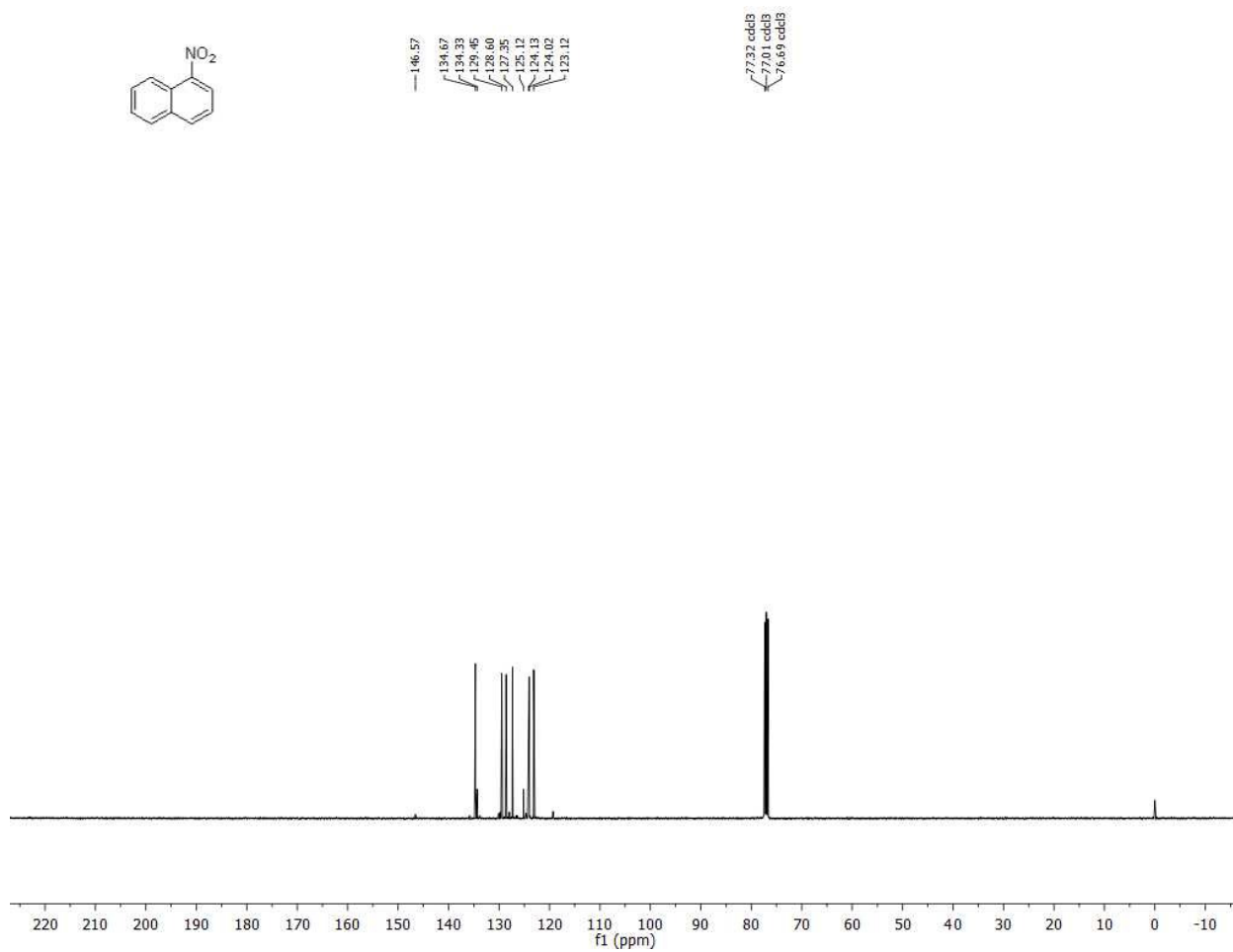


6. 1-Nitronaphthalene^{2a,7}

¹H NMR (399 MHz, Chloroform-*d*) δ = 7.55 (t, $J=8.1$ Hz, 1H), 7.63 (t, $J=8.1$ Hz, 1H), 7.73 (t, $J=8.1$ Hz, 1H), 7.97 (dt, $J=8.1$ Hz, 0.7 Hz, 2H), 8.13 (d, $J=8.1$ Hz, 1H), 8.24 (dd, $J=8.1$ Hz, 1.2 Hz, 1H), 8.58 (dq, $J=8.1$ Hz, 0.9, 1H).

¹³C NMR (100 MHz, cdcl₃) δ = 123.12, 124.02, 124.13, 125.12, 127.35, 128.60, 129.45, 134.33, 134.67, 146.57.



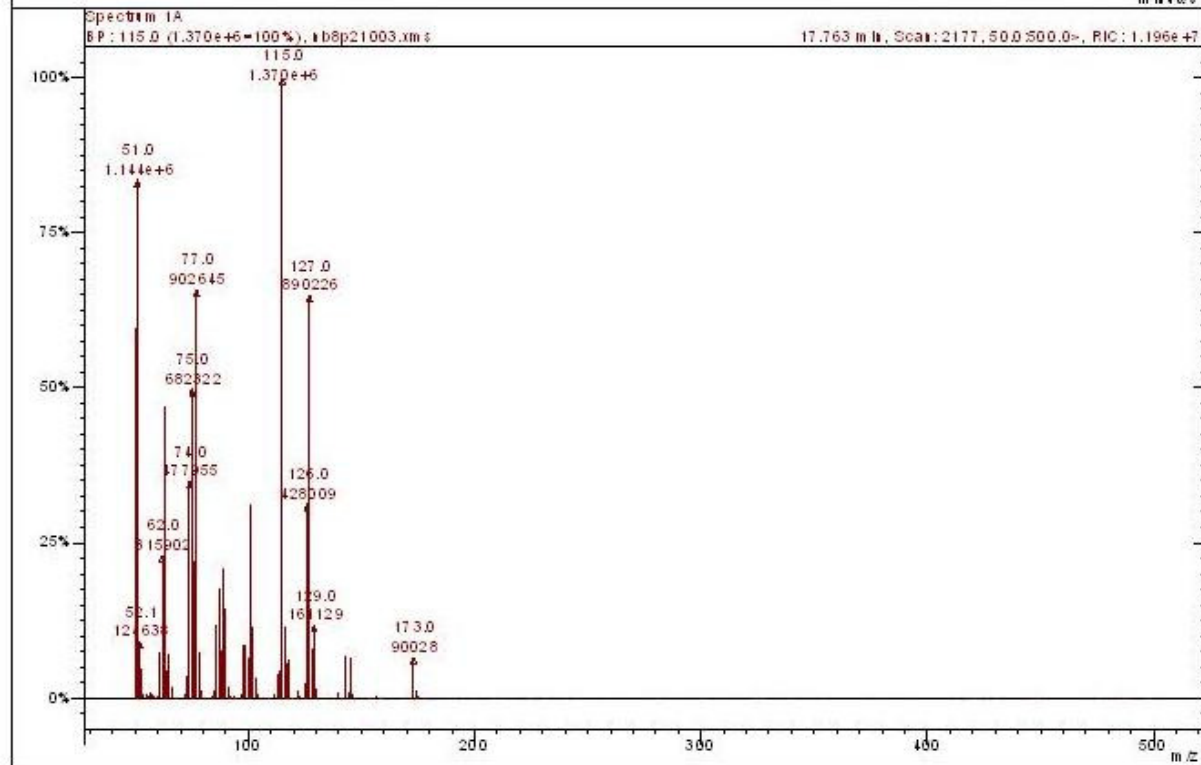
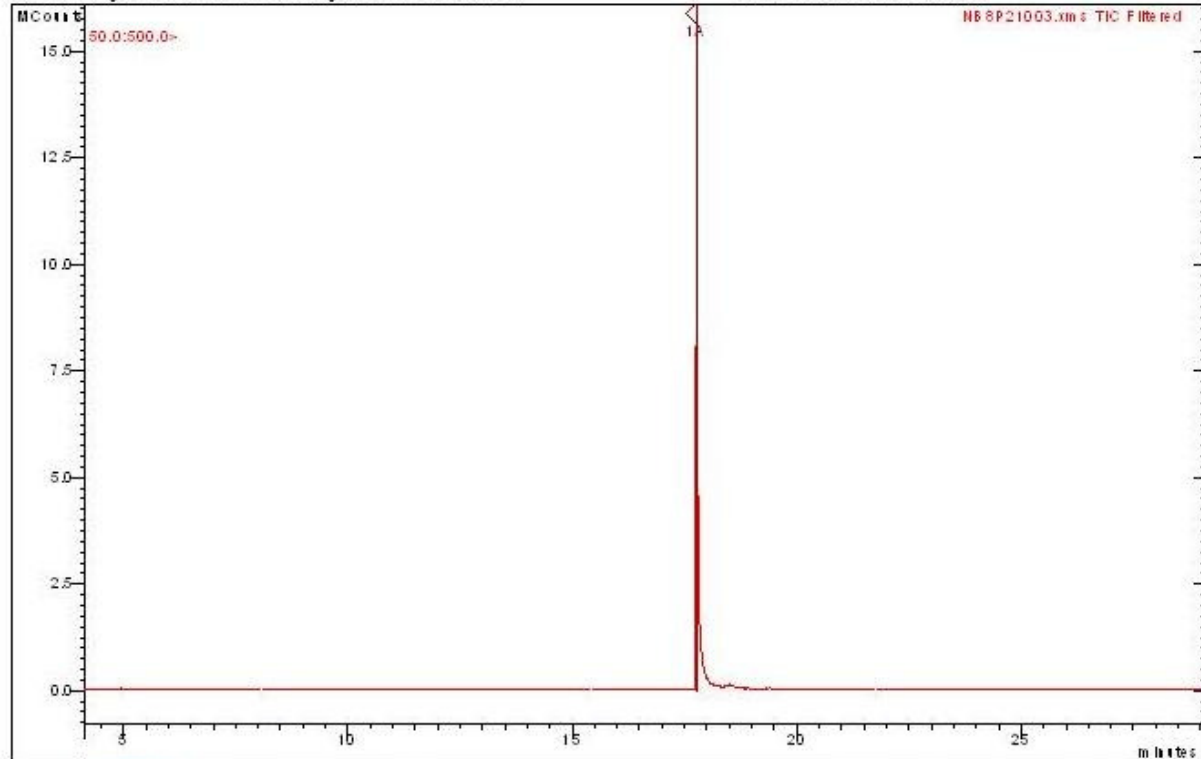


1-Nitronaphthalene:

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Operator: Laxman Gurung
Date: 8/22/2014 2:56 PM



7. Nitrofluorobenzene

o-Nitrofluorobenzene¹

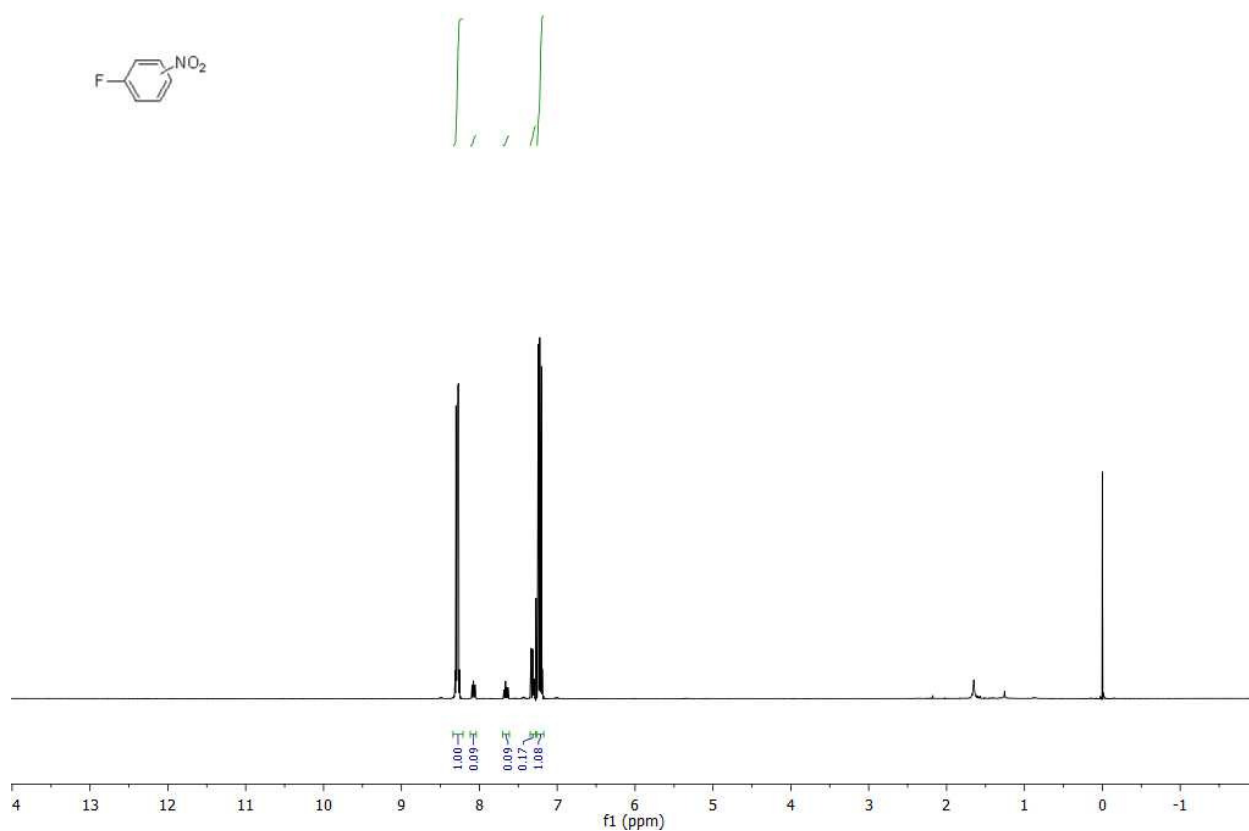
¹H NMR (400 MHz, Chloroform-*d*) δ = 7.28 – 7.38 (m, 2H), 7.59 – 7.73 (m, 1H), 8.03 – 8.13 (m, 1H).

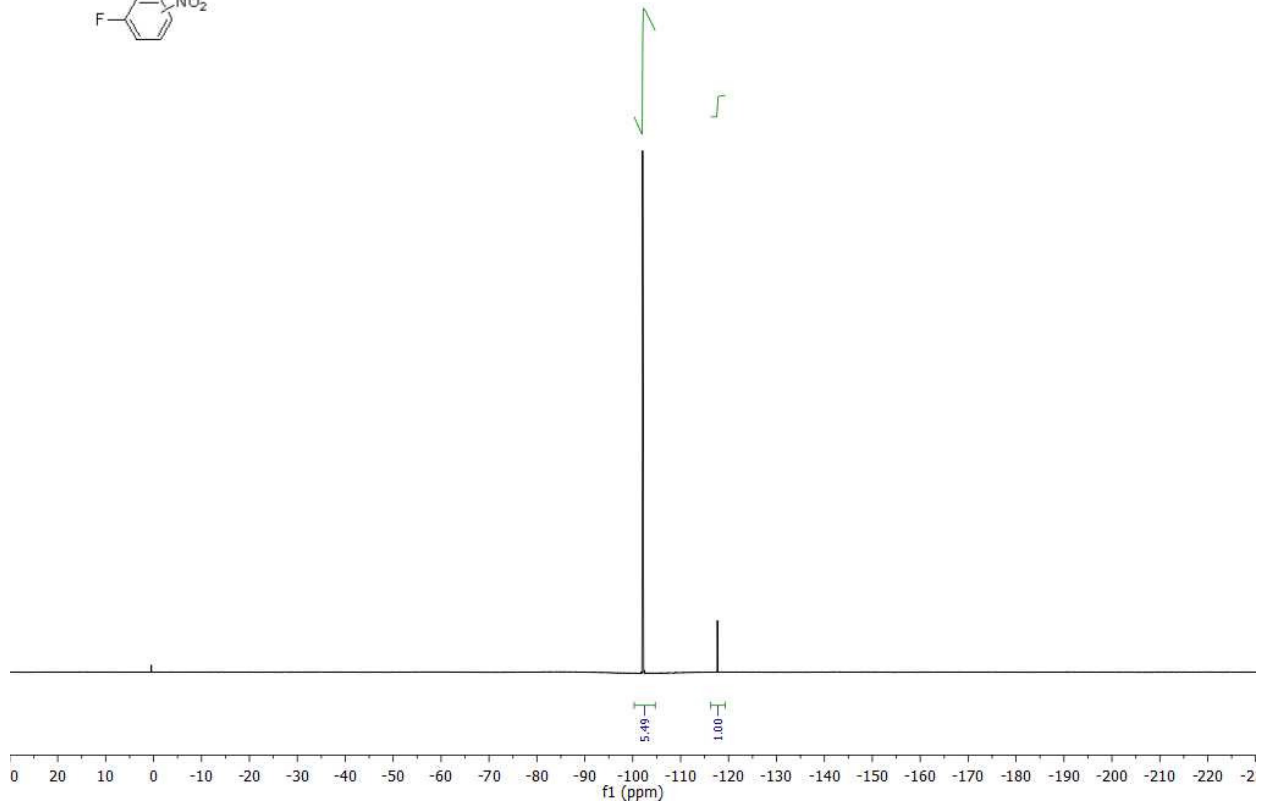
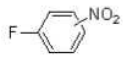
¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -117.69 - -117.63 (m, 1F)

p-Nitrofluorobenzene¹

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.22 (dd, $J=9.3$ Hz, 7.7, 1H), 8.28 (dd, $J=9.3$ Hz, 4.7 Hz, 1H).

¹⁹F NMR (376 MHz, Chloroform-*d*) δ = -102.10 - -102.08 (m, 1F)





***o*-Nitrofluorobenzen (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/6/2014 6:35 PM

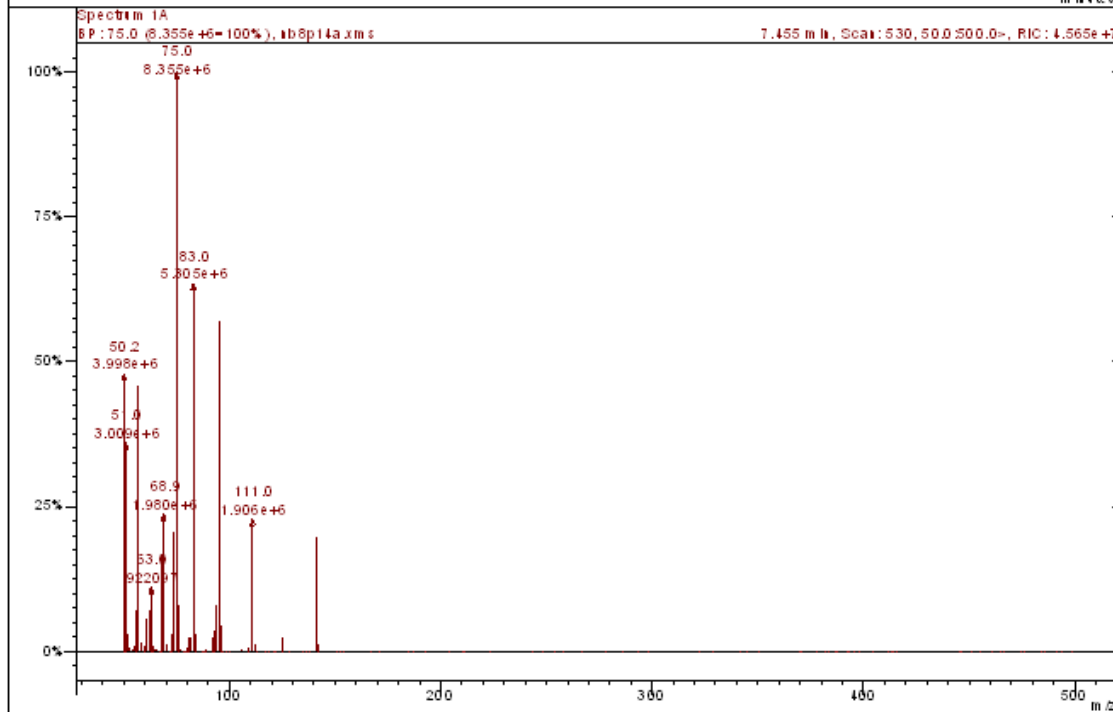
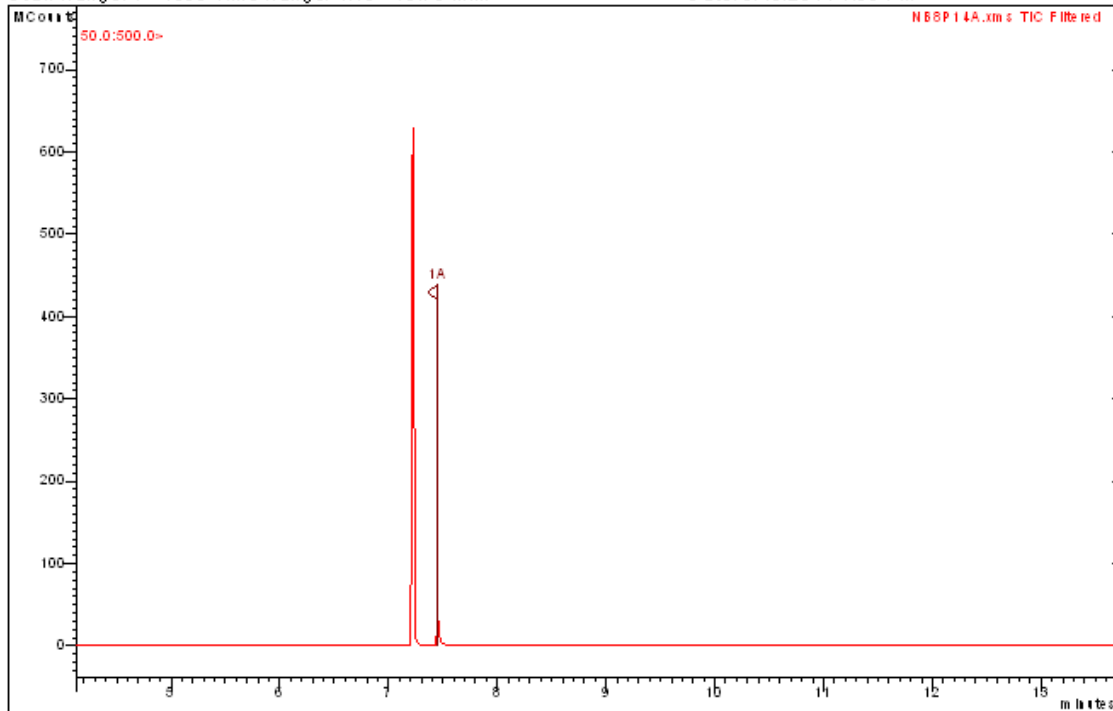
File: c:\brukerw\data\laxman\pvp-nm kevin\nb8p14a.xms

Sample: NB8P14A

Operator: Laxman Gurung

Scan Range: 1 - 1533 Time Range: 4.13 - 13.75 min.

Date: 8/13/2014 1:30 PM



p-Nitrofluorobenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:17 PM

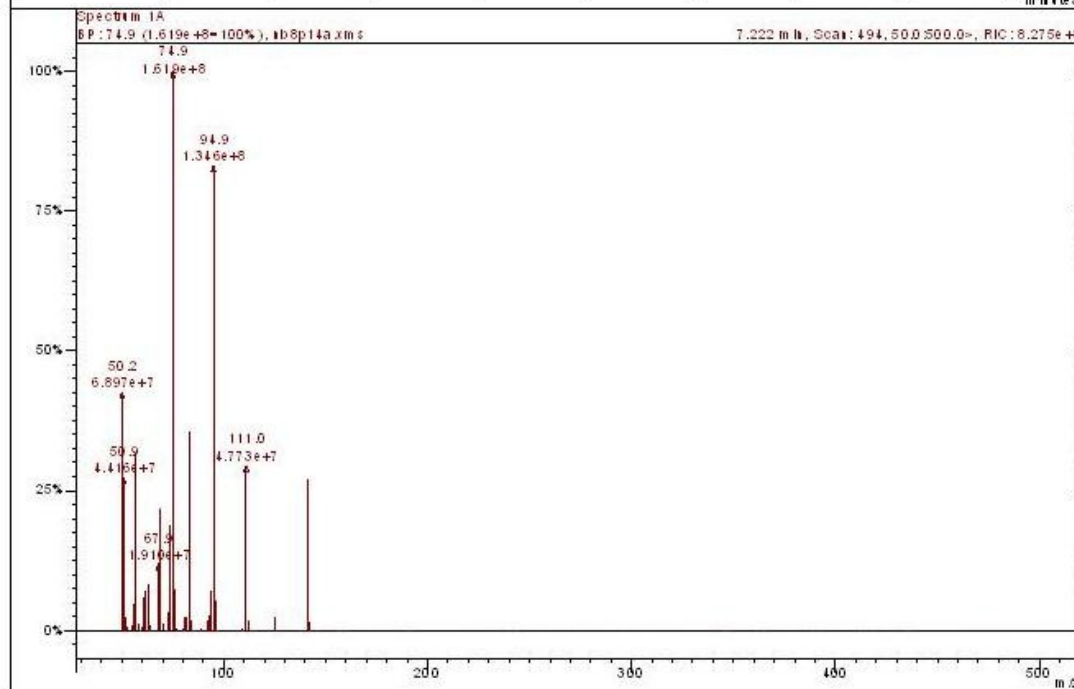
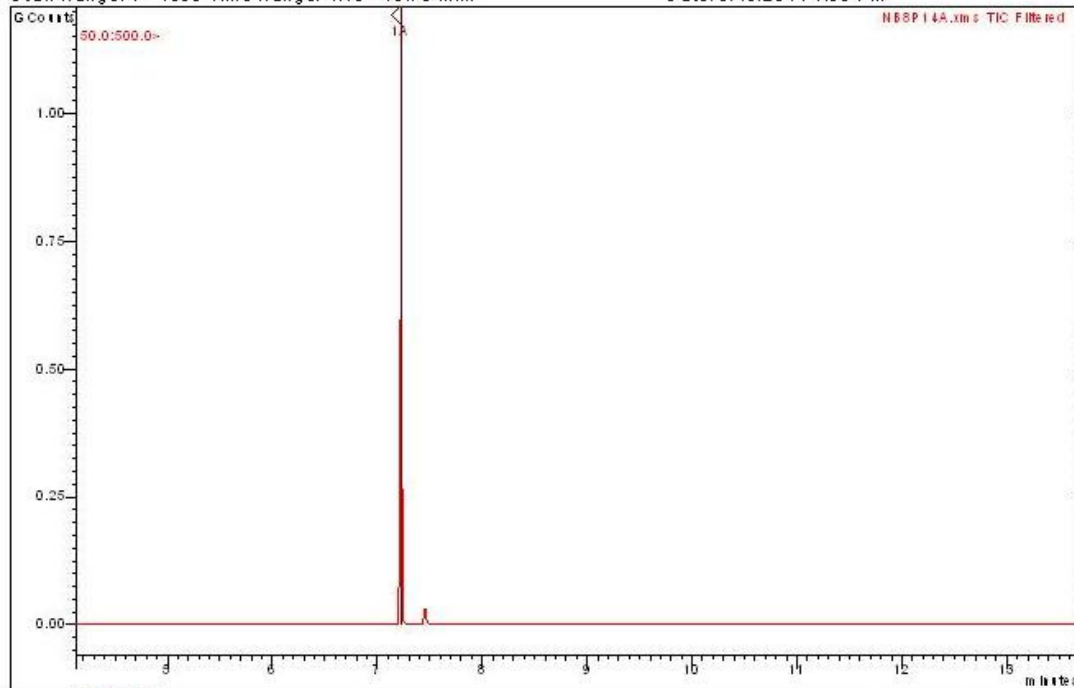
File: c:\bruker\ms\data\laxman\pvp-nm kevin\nb8p14a.xms

Sample: NB8P14A

Operator: Laxman Gurung

Scan Range: 1 - 1533 Time Range: 4.13 - 13.75 min.

Date: 8/13/2014 1:30 PM



8. Nitrochlorobenzene

o-Nitrochlorobenzene⁸

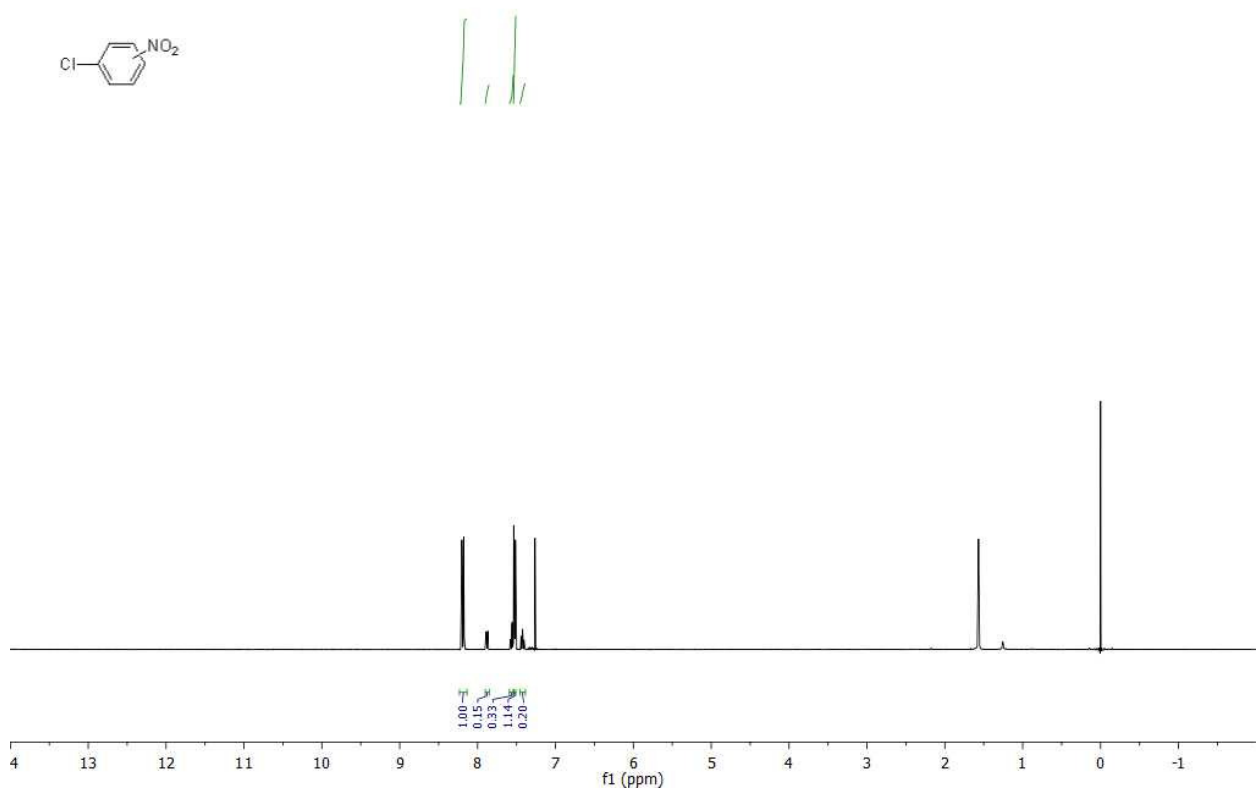
¹H NMR (400 MHz, Chloroform-*d*) δ = 7.40-7.44 (m, 1H), 7.55 – 7.61 (m, 2H), 7.86 (d, $J=8.7$ Hz, 1H).

m-Nitrochlorobenzene

The amount of *m*-isomer was too low relative to other isomers, hence not visible in the NMR spectrum. However, it is observed in the GC (vide infra).

p-Nitrochlorobenzene^{1,8}

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.52 (d, $J=9$ Hz, 2H), 8.19 (d, $J= 8.7$ Hz, 2H).

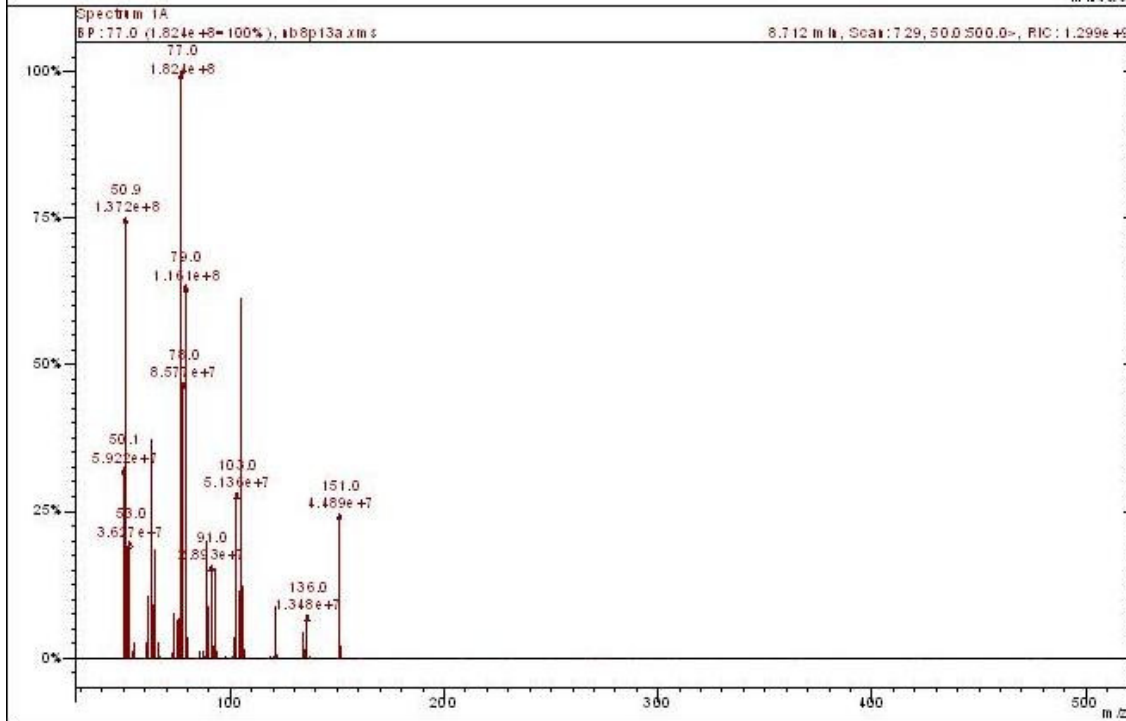
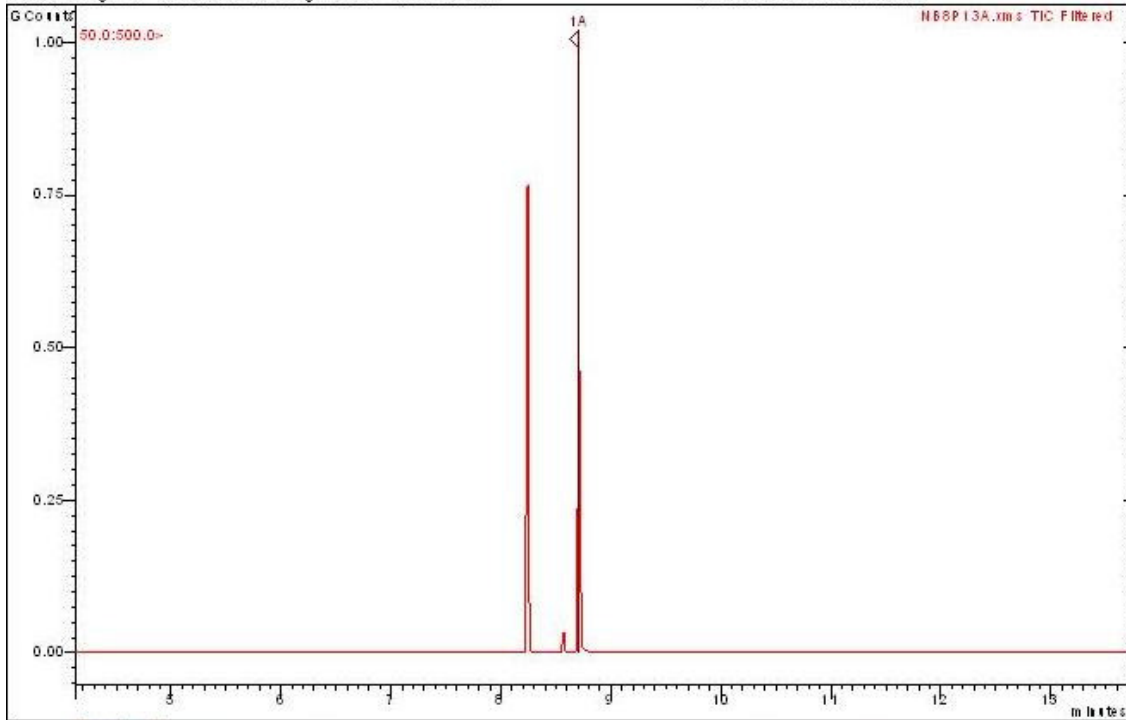


***o*-Nitrochlorobenzene (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/6/2014 6:28 PM

File: c:\bruker\erw\data\Maxman\pvp-nm.kevin\mb8p13a.xms
Sample: NB8P13A
Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

Operator: Laxman Gurung
Date: 8/13/2014 2:22 PM



m-Nitrochlorobenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:28 PM

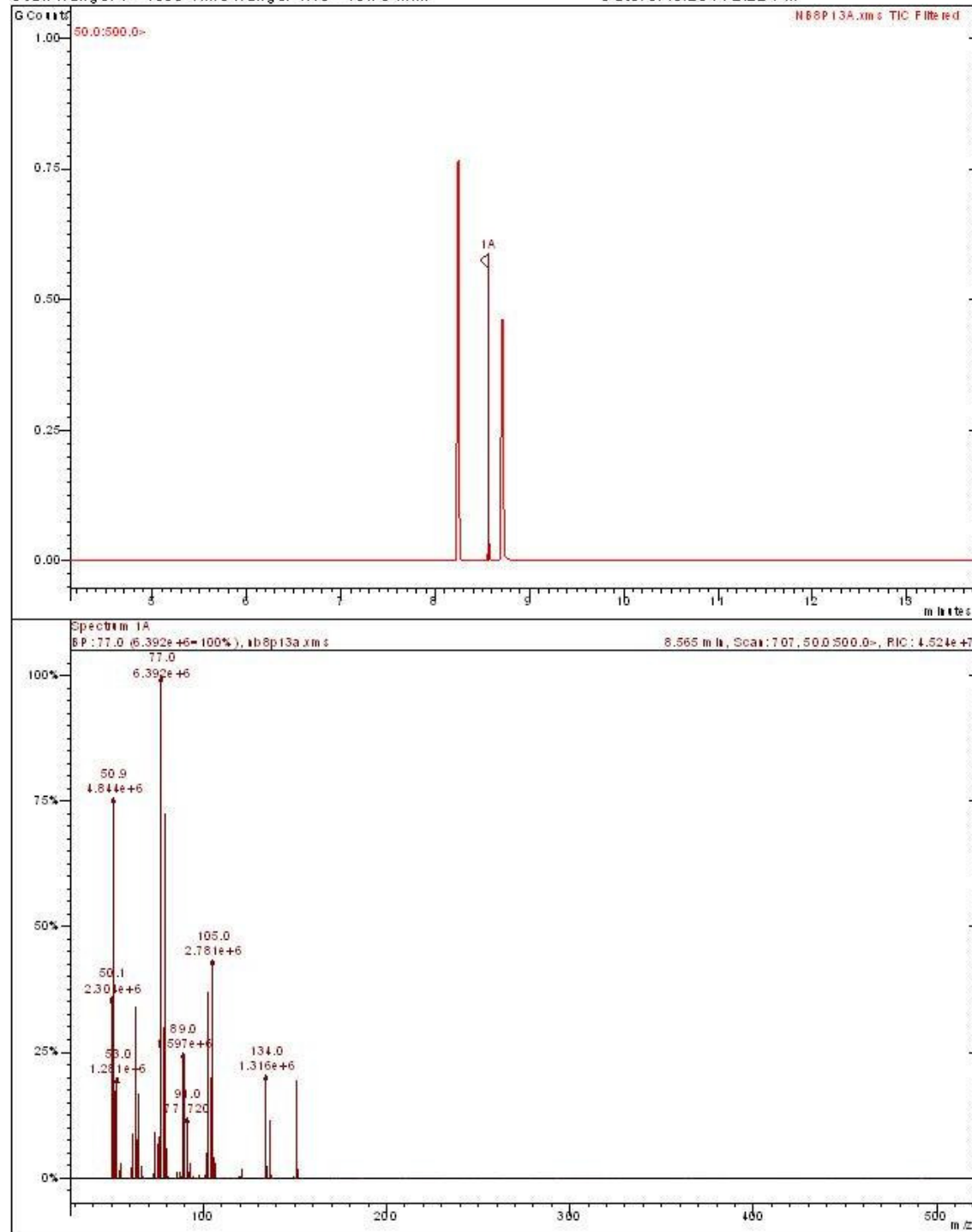
File: c:\brukerms\data\laxman\pvp-nm kevin\nb8p13a.xms

Sample: NB8P13A

Operator: Laxman Guring

Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

Date: 8/13/2014 2:22 PM



p-Nitrochlorobenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:27 PM

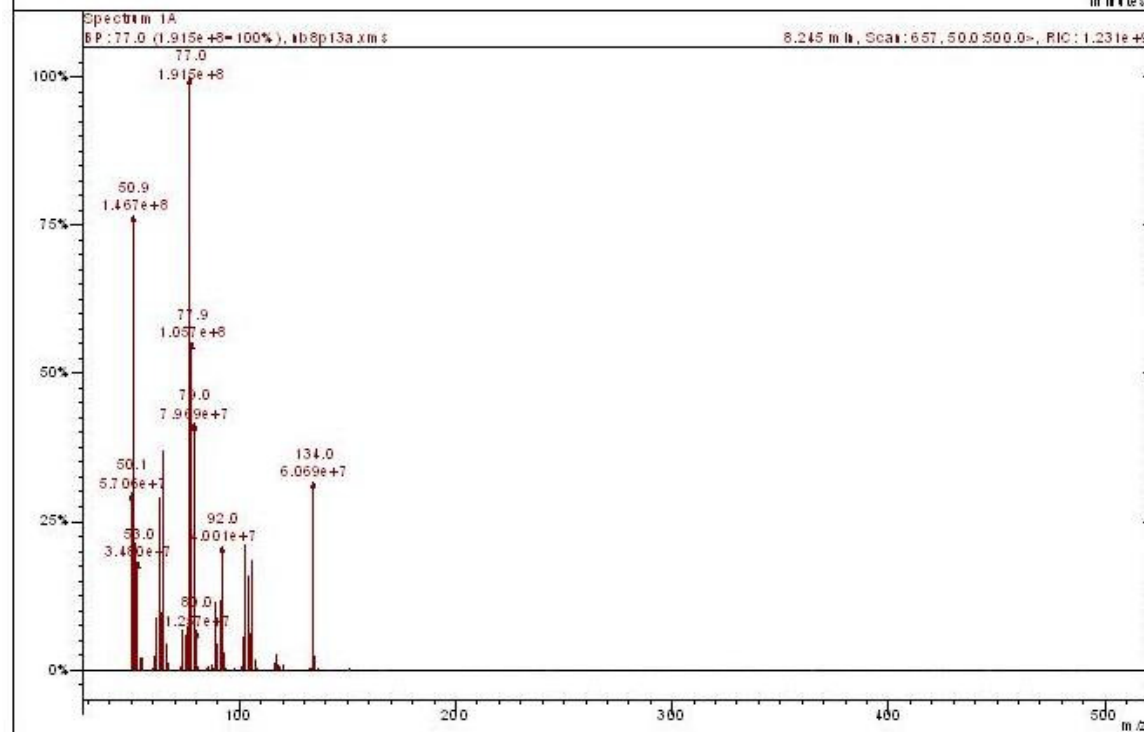
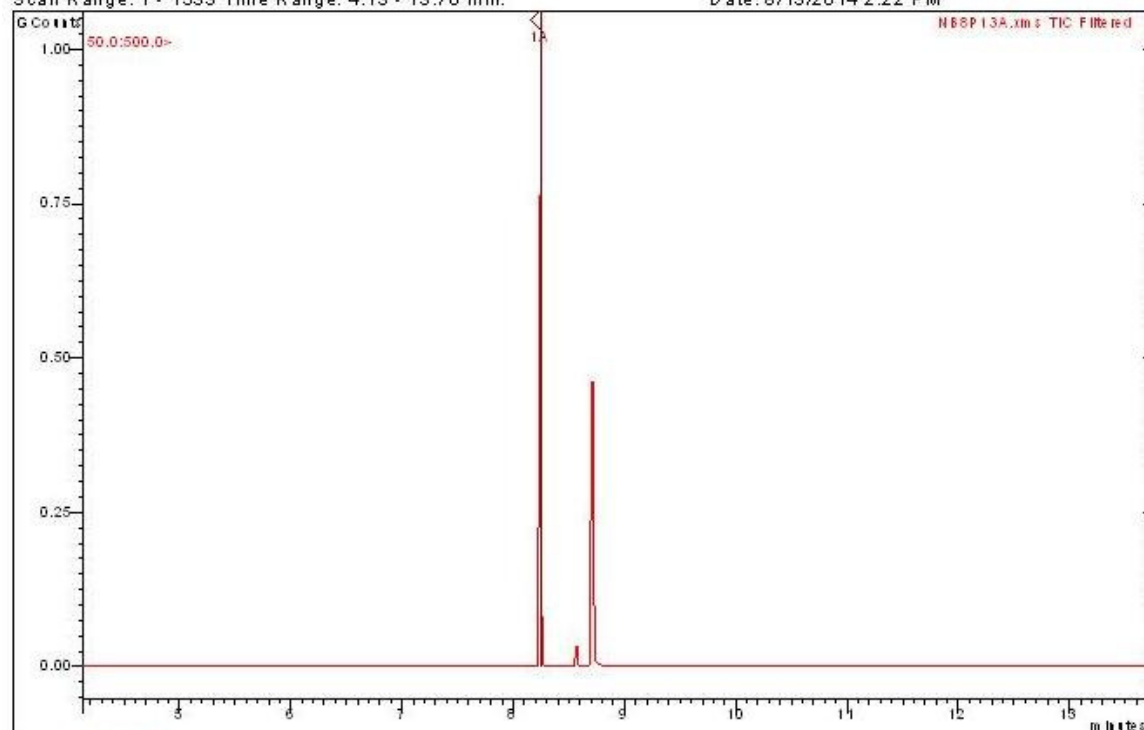
File: c:\brukerms\data\laxman\pvp-nm kevin\hb8p13a.xms

Sample: NB8P13A

Scan Range: 1 - 1533 Time Range: 4.13 - 13.76 min.

Operator: Laxman Gurung

Date: 8/13/2014 2:22 PM



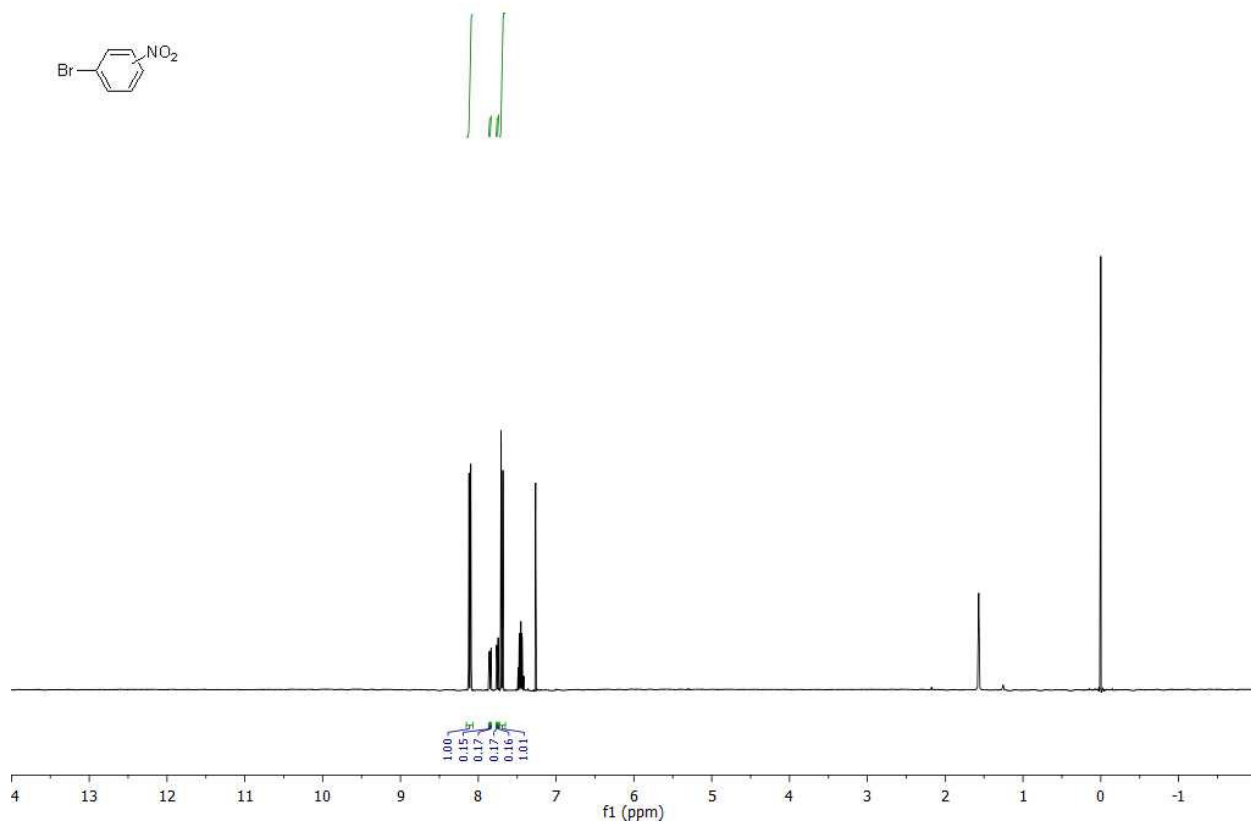
9. Nitrobromobenzene

o-Nitrobromobenzene⁸

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.74 (d, J =2.2 Hz, 1H), 7.75 – 7.77 (m, 1H), 7.83 – 7.85 (m, 1H), 7.86 (d, J =2.2 Hz, 1H).

p-Nitrobromobenzene⁸

¹H NMR (400 MHz, Chloroform-*d*) δ = 7.69 (d, J =9.1 Hz, 1H), 8.11 (d, J =9.1 Hz, 1H).



***o*-Nitrobromobenzene (selected peak) in a mixture of its isomers:**

MS Data Review All Plots - 10/7/2014 1:47 PM

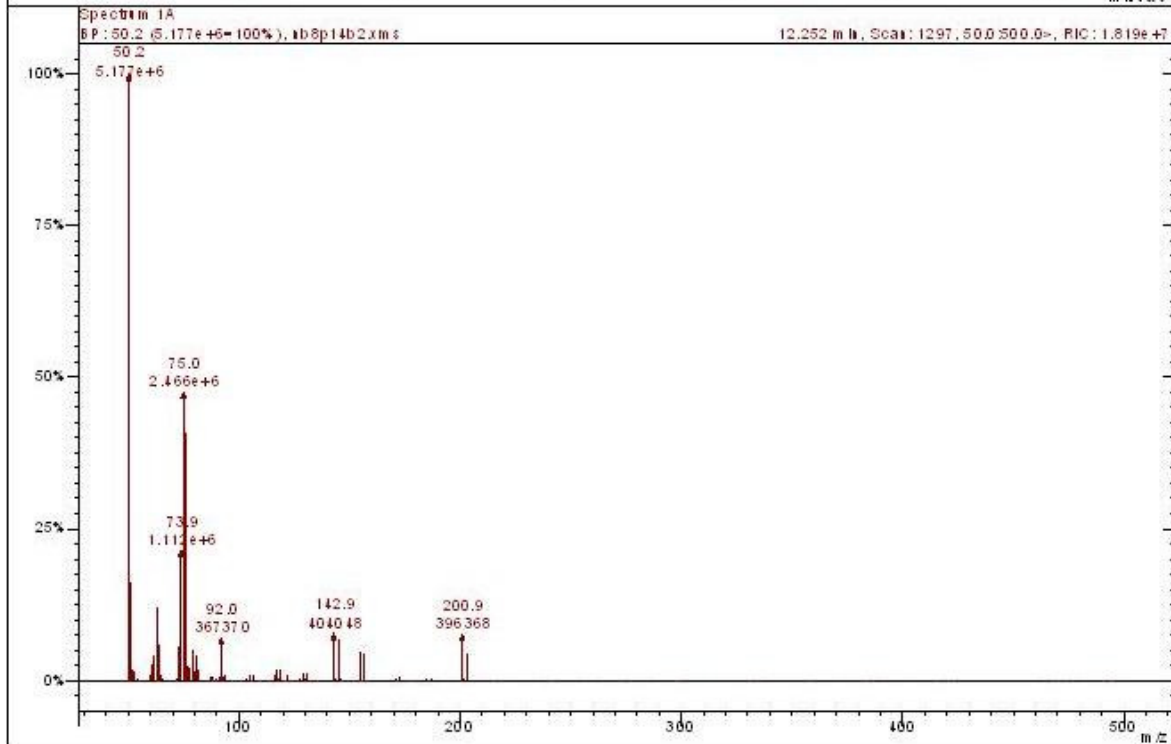
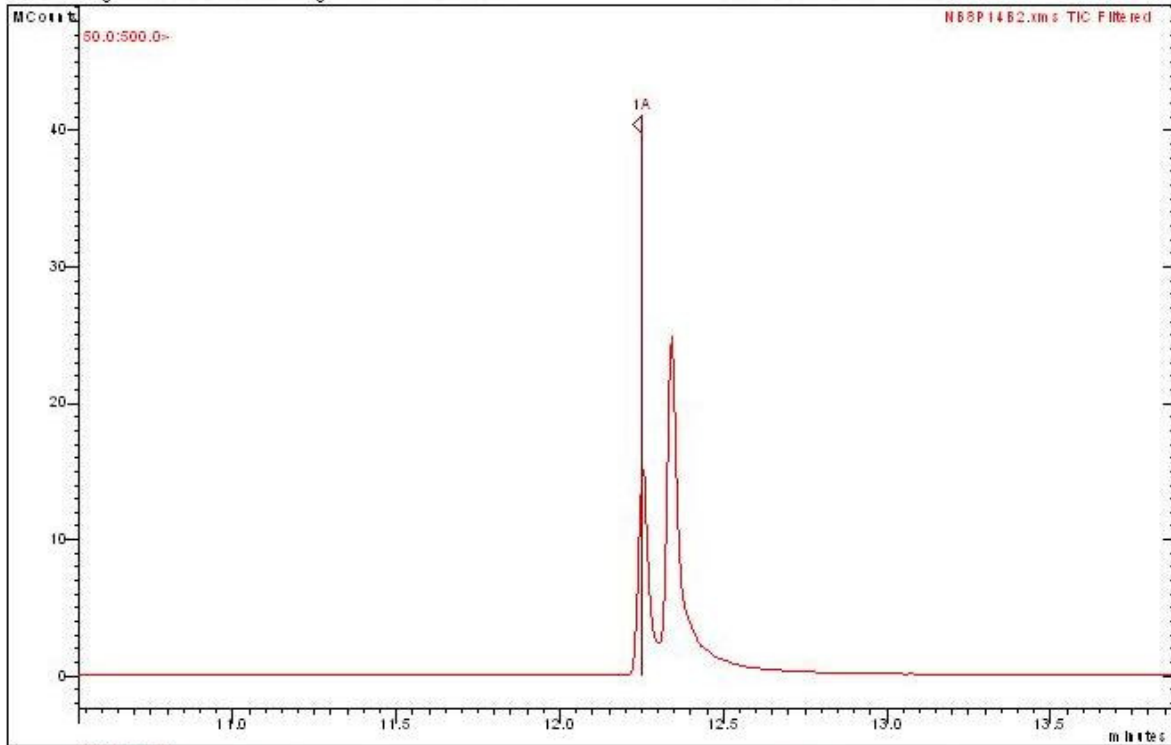
File: c:\bruker\ms\data\laxman\pvp-nm kevin\lb8p14b2.xml

Sample: NB8P14B2

Scan Range: 1 - 3663 Time Range: 4.13 - 27.08 min.

Operator: Laxman Gurung

Date: 8/13/2014 4:30 PM



p-Nitrobromobenzene (selected peak) in a mixture of its isomers:

MS Data Review All Plots - 10/6/2014 6:13 PM

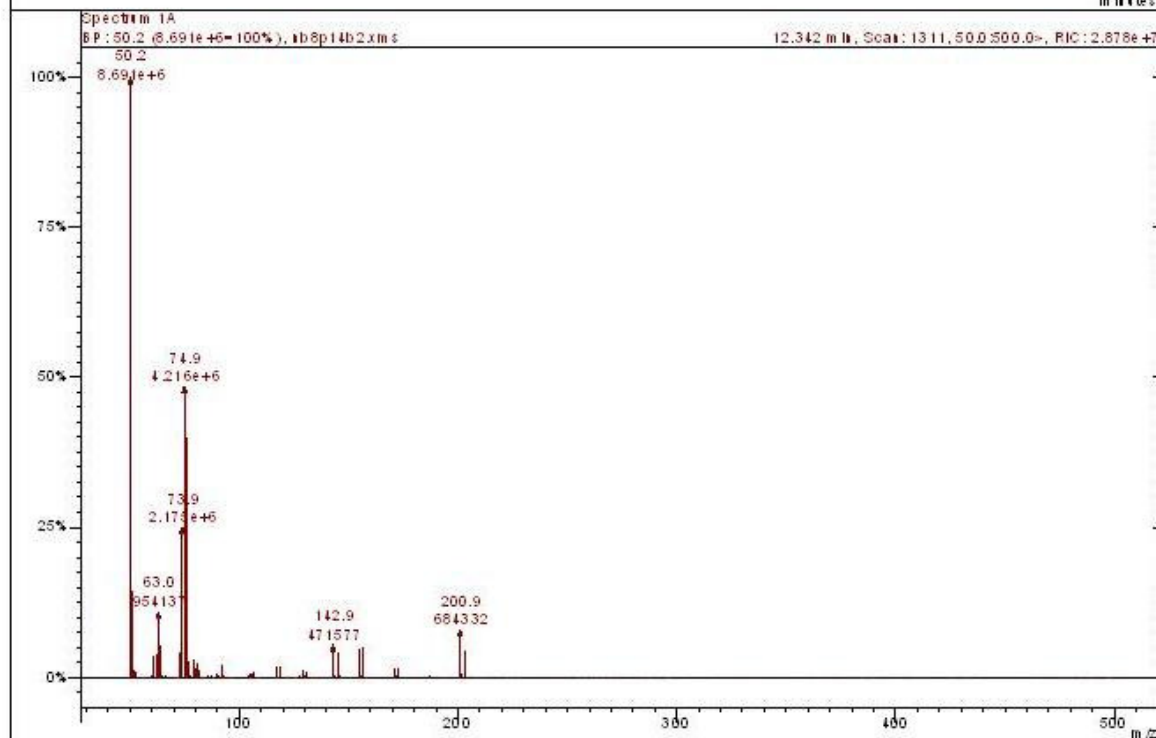
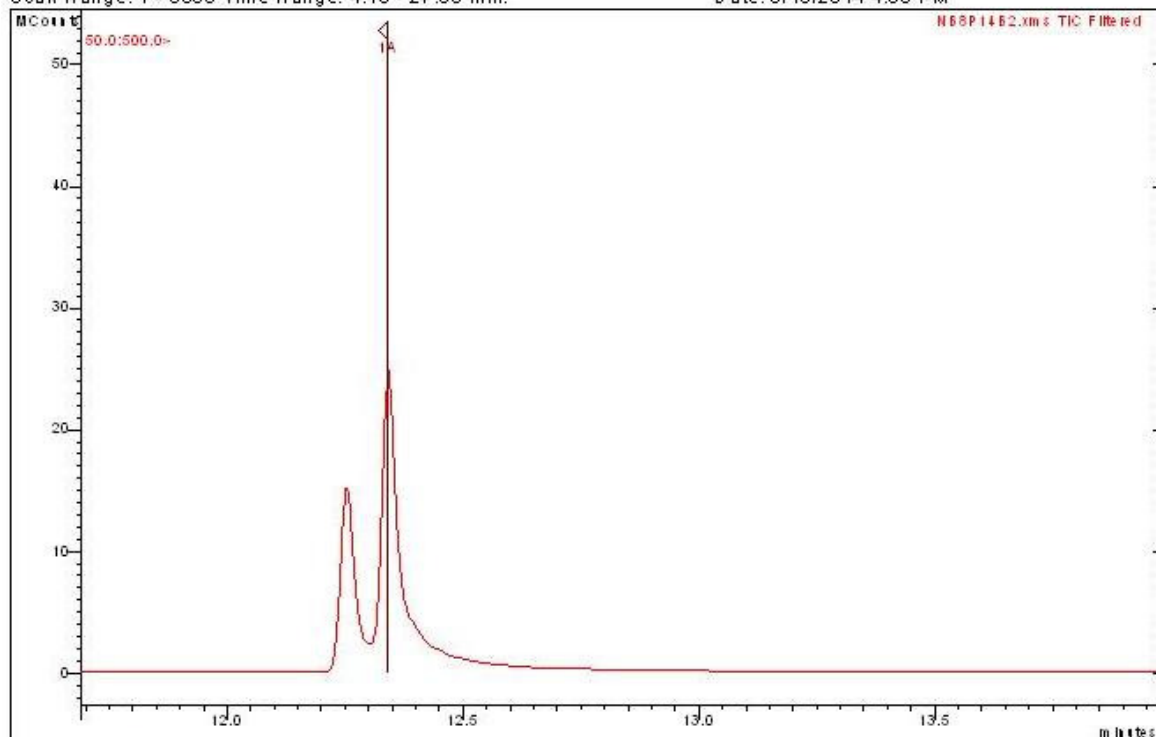
File: c:\bruker\ms\data\laxman\pvp-nm kevin\lb8p14b2.xml

Sample: NB8P14B2

Operator: Laxman Gurung

Scan Range: 1 - 3663 Time Range: 4.13 - 27.08 min.

Date: 8/13/2014 4:30 PM



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