

Supporting Information

Assessment of amination reactions via nucleophilic aromatic substitution using conventional and eco-friendly energies

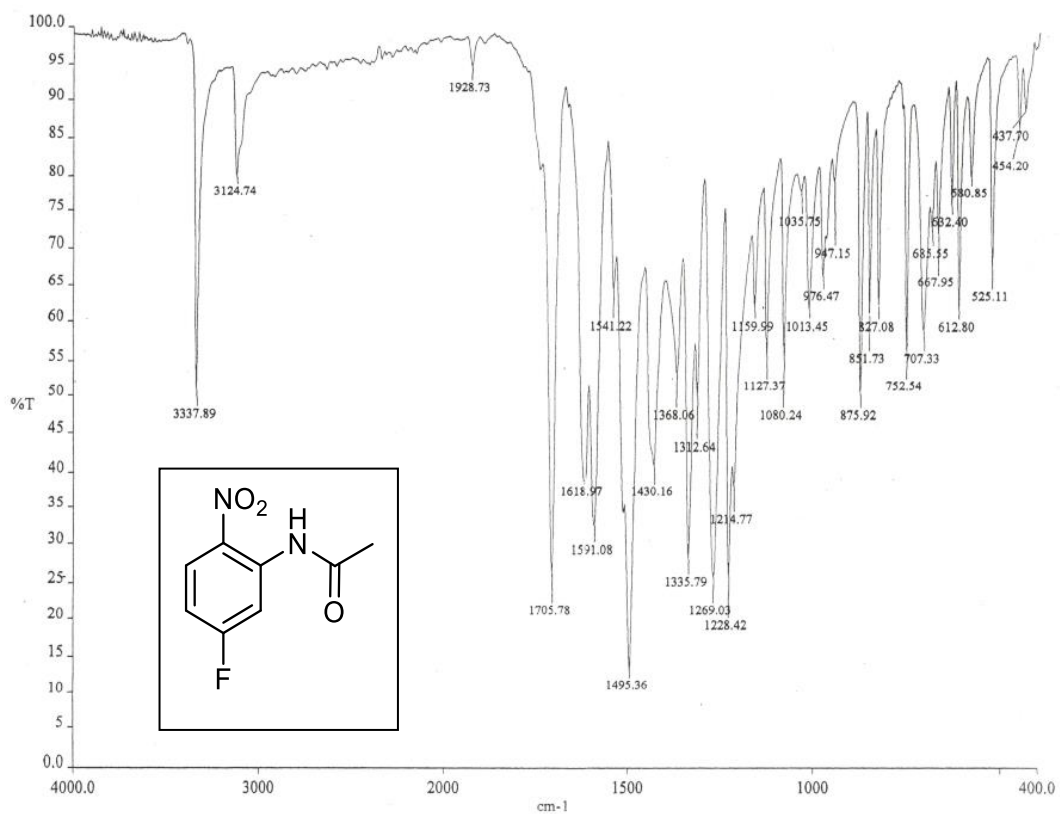
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Fernando Ortega-Jiménez^a, Hulme Ríos-Guerra^a, Jessica V. González-Carrillo^a,
Francisco Barrera-Téllez ^a Javier Perez-Flores^b, José G. Penieres-Carrillo ^{a,*}

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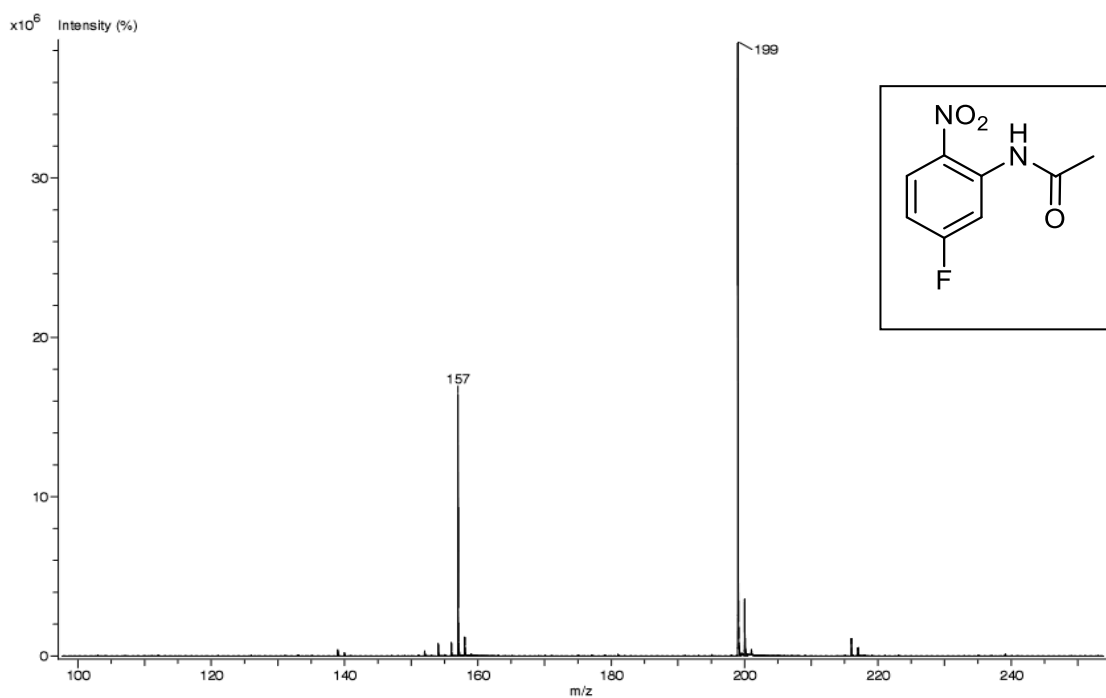
^b Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán, Cd. de México, México, C.P. 04510

penieres@unam.mx

Tel.: 0052-555-623-2024



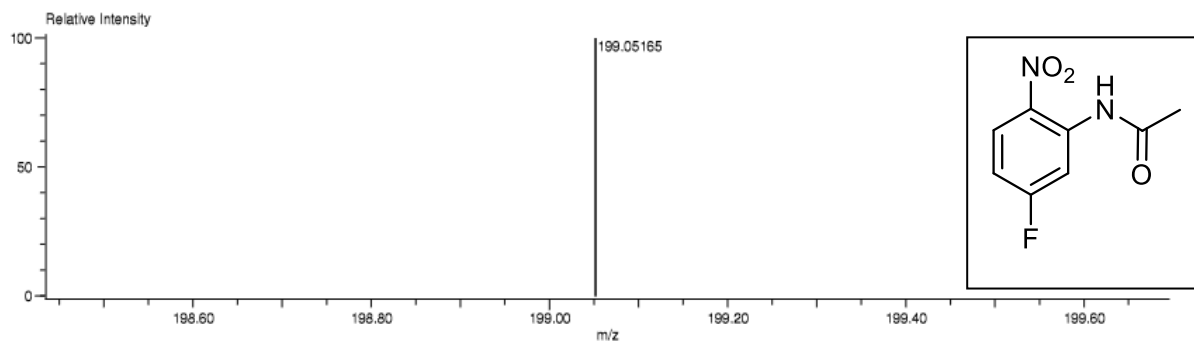
N-(5-Fluoro-2-nitrophenyl)acetamide **1a**



N-(5-Fluoro-2-nitrophenyl)acetamide **1a**

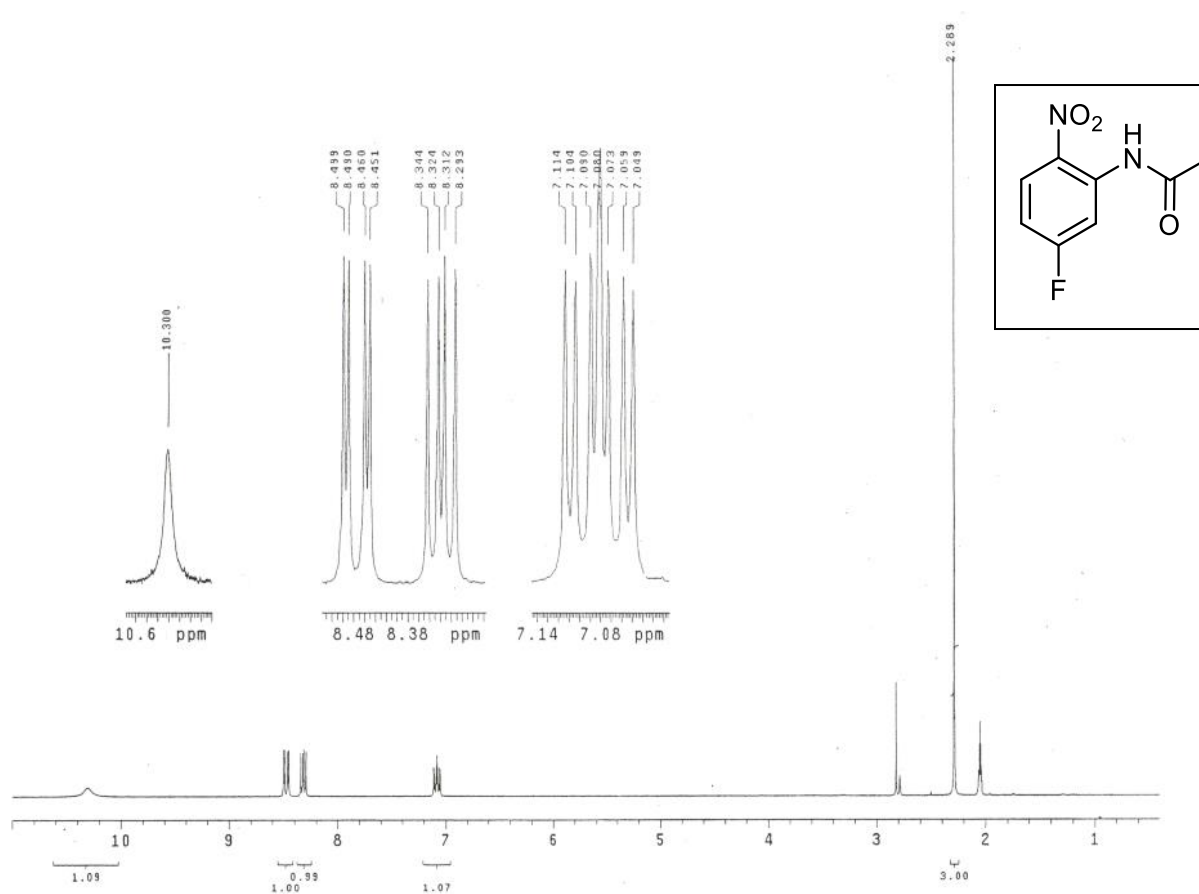
Charge number:1
 Element:¹²C:0 .. 50, ¹H:0 .. 200, ¹⁹F:1 .. 1, ¹⁴N:0 .. 2, ¹⁶O:3 .. 3

Unsaturation Number:0.0 .. 20.0 (Fraction:Both)

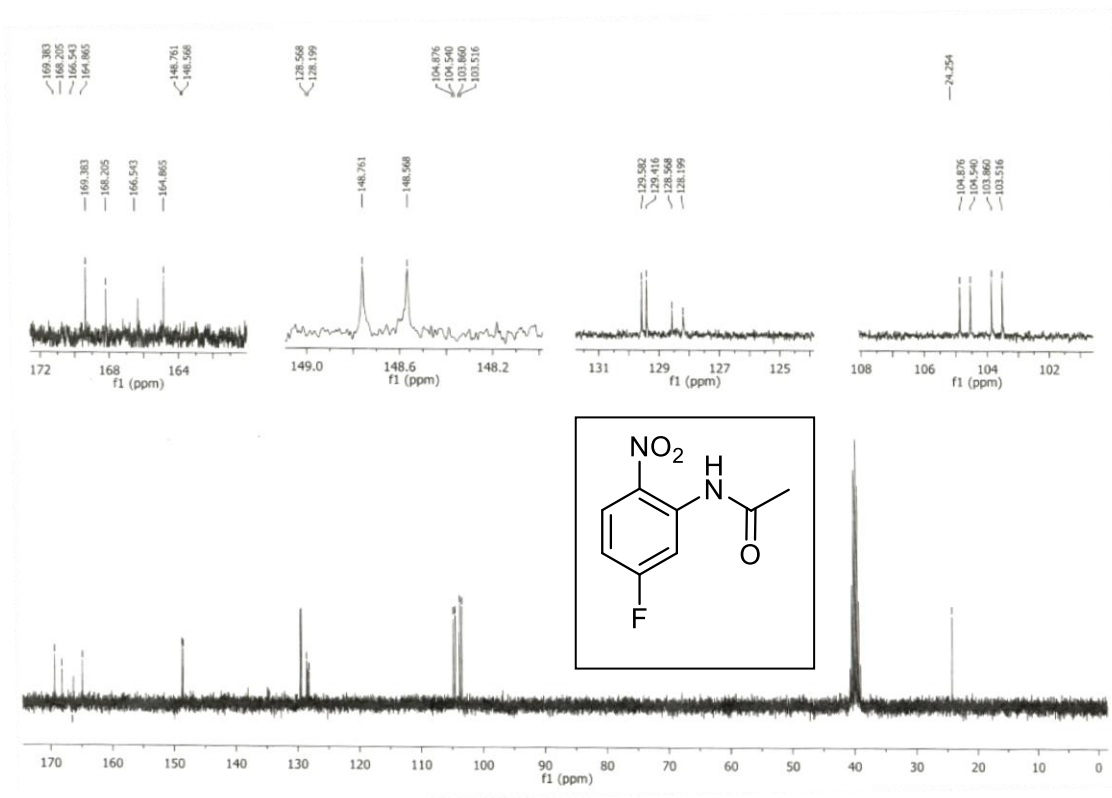


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
199.05165	182405.88	199.05190	-0.24	-1.22	¹² C ₈ ¹ H ₆ ¹⁹ F ₁ ¹⁴ N ₂ ¹⁶ O ₃	5.5

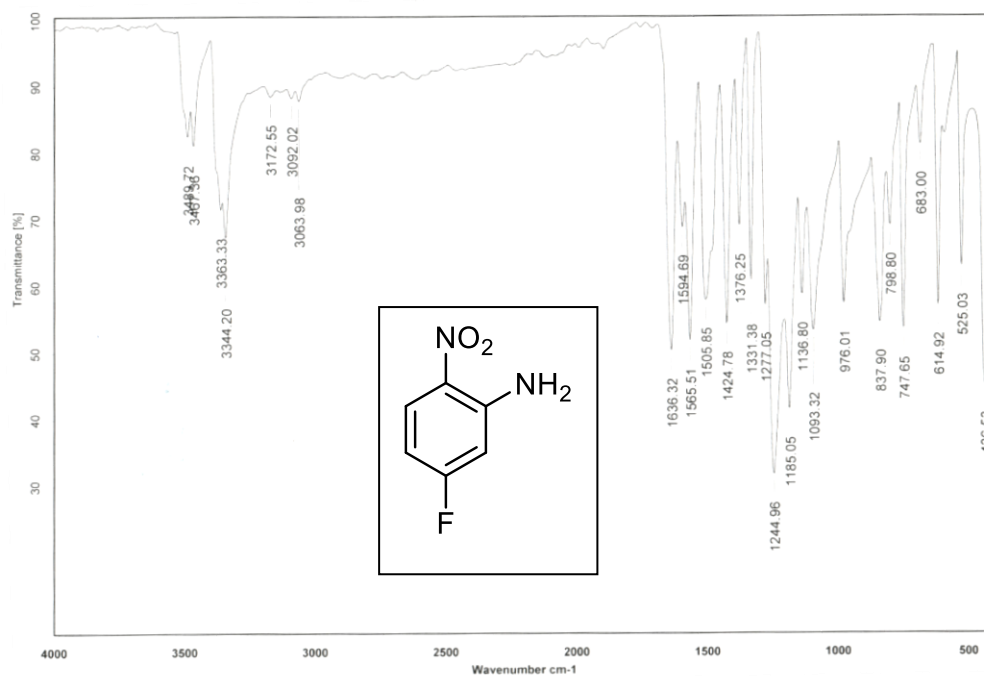
N-(5-Fluoro-2-nitrophenyl)acetamide **1a**



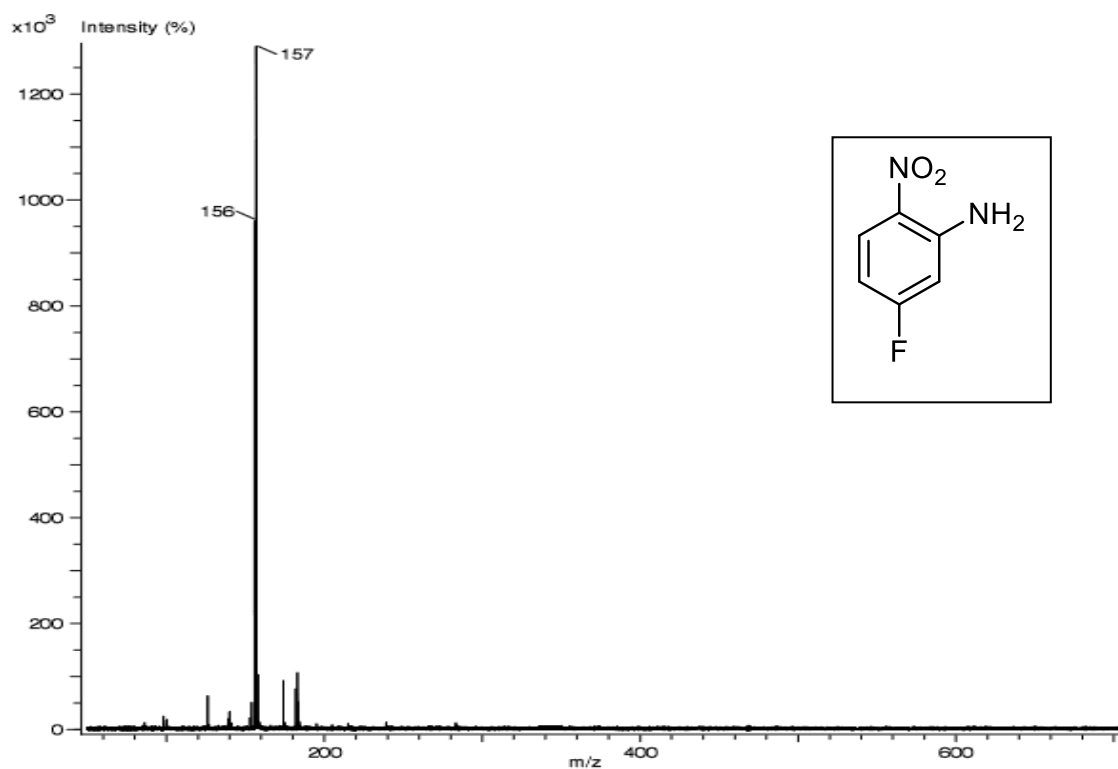
N-(5-Fluoro-2-nitrophenyl)acetamide **1a**



N-(5-Fluoro-2-nitrophenyl)acetamide **1a**

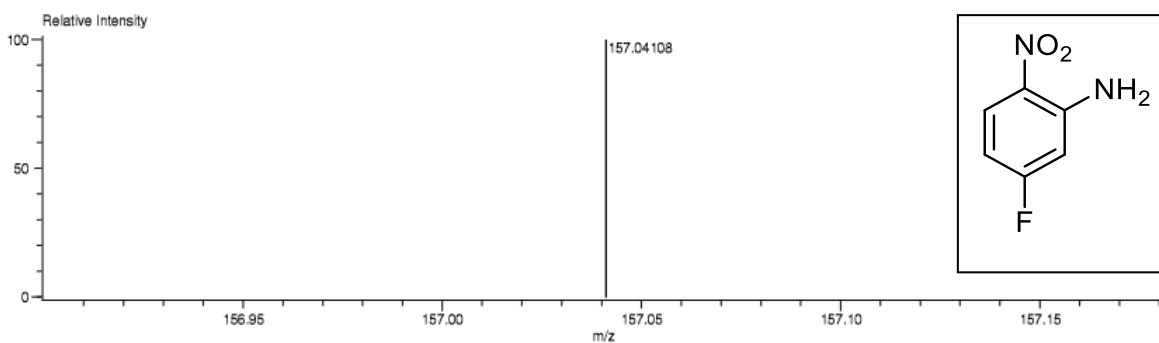


5-Fluoro-2-nitroaniline **4a**



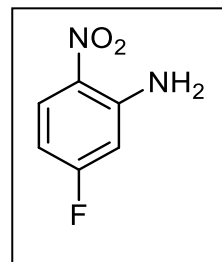
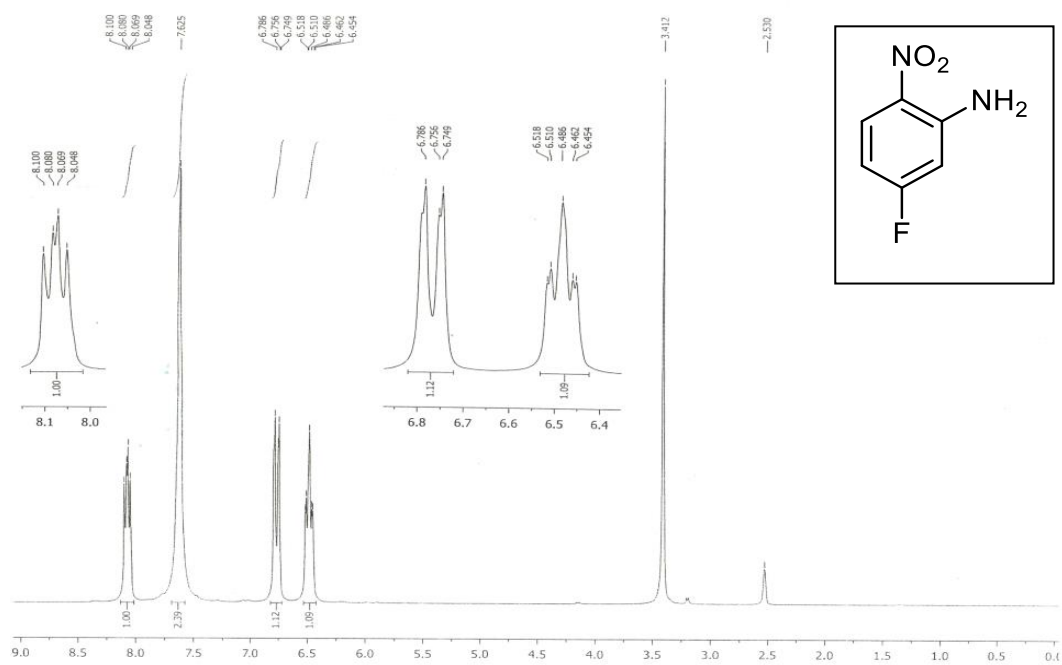
5-Fluoro-2-nitroaniline **4a**

Charge number:1 Tolerance:3.00(mmu) Unsaturation Number:0.0 .. 14.0 (Fraction:Both)
 Element:¹²C:0 .. 12, ¹H:0 .. 200, ¹⁹F:1 .. 1, ¹⁴N:0 .. 3, ¹⁶O:0 .. 3

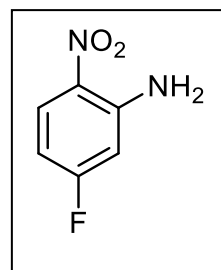
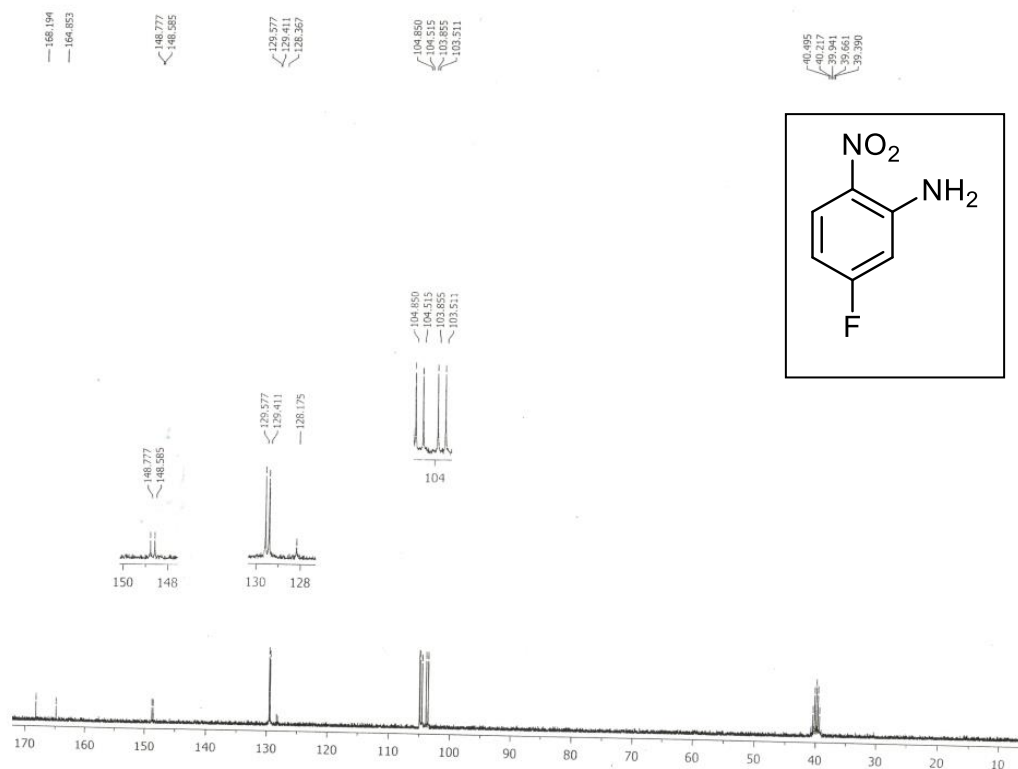


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
157.04108	5744.00	157.04133	-0.25	-1.59	¹² C ₆ ¹ H ₅ ¹⁹ F ¹⁴ N ₂ ¹⁶ O ₂	4.5

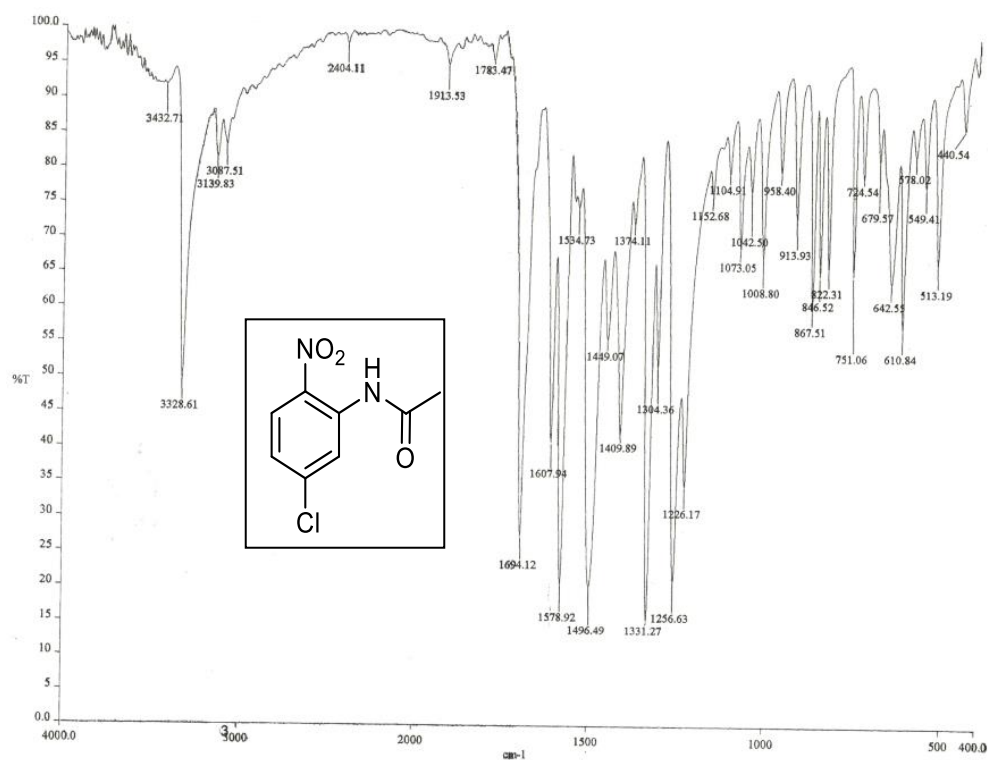
5-Fluoro-2-nitroaniline **4a**



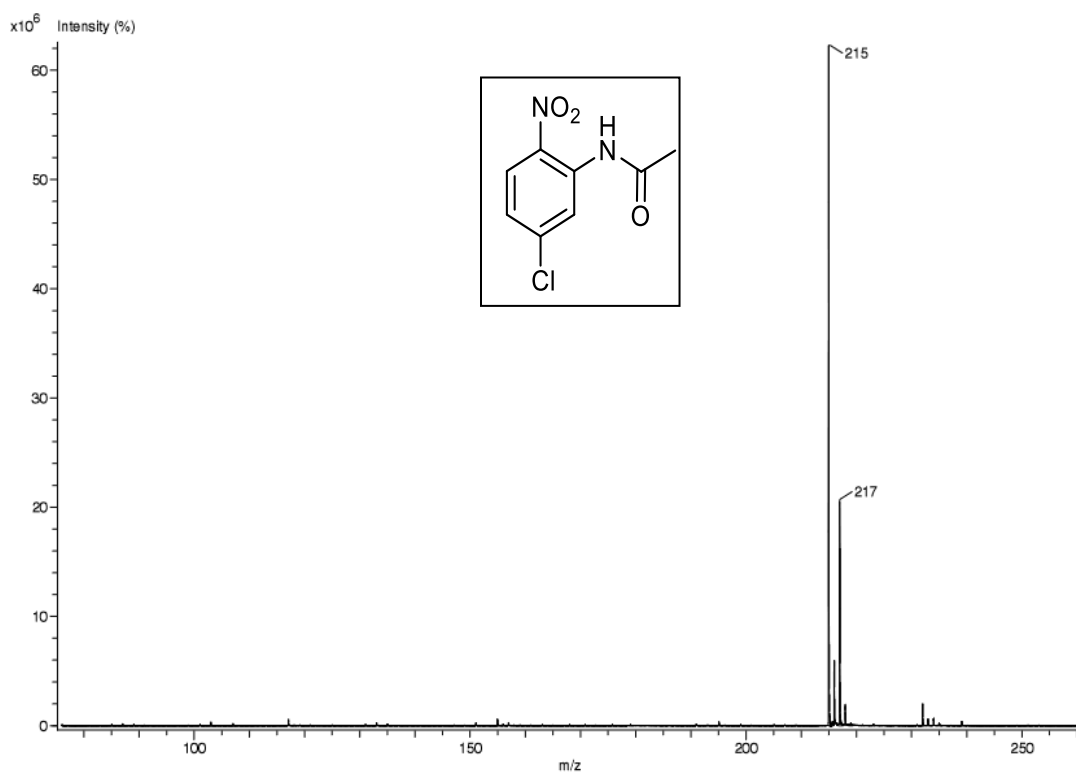
5-Fluoro-2-nitroaniline **4a**



5-Fluoro-2-nitroaniline **4a**



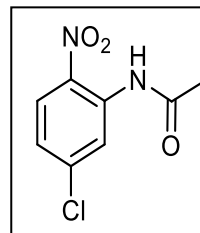
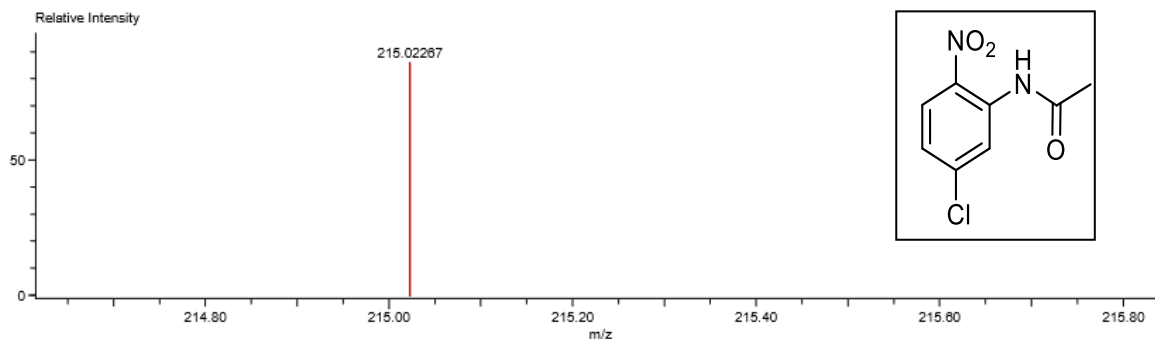
N-(5-Chloro-2-nitrophenyl)acetamide **1b**



N-(5-Chloro-2-nitrophenyl)acetamide(**1b**)

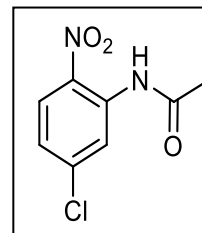
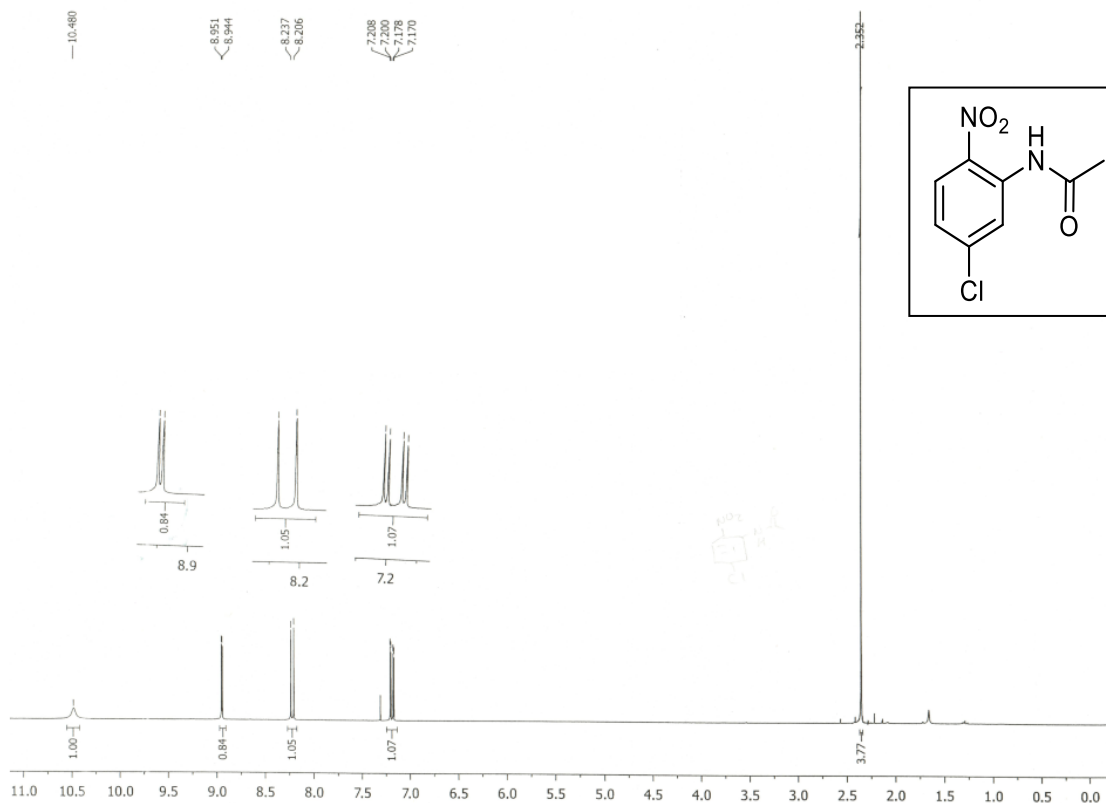
Charge number:1
 Element: ^{12}C :0 .. 50, ^1H :0 .. 100, ^{35}Cl :0 .. 1, ^{14}N :0 .. 2, ^{16}O :0 .. 6

Tolerance:3.00(mmu)
 Unsaturation Number:0.0 .. 12.0 (Fraction:.5)

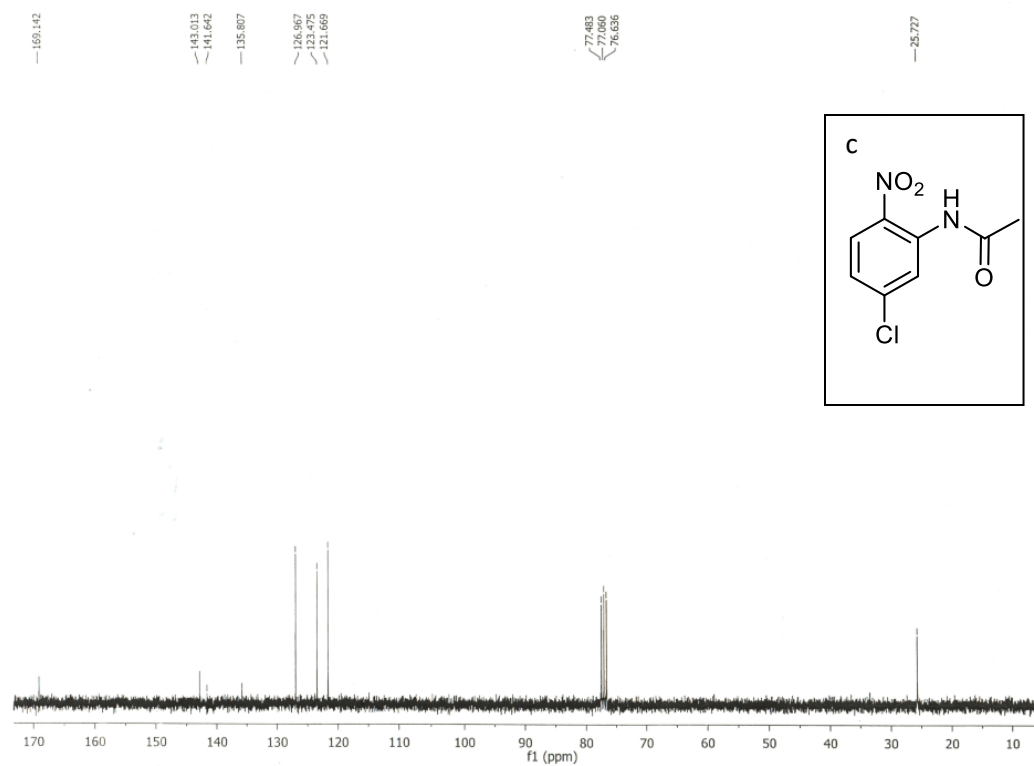


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
215.02267	102033.13	215.02234	0.33	1.51	$^{12}\text{C}_8^{1}\text{H}_8^{35}\text{Cl}_1^{14}\text{N}_2^{16}\text{O}_3$	5.5

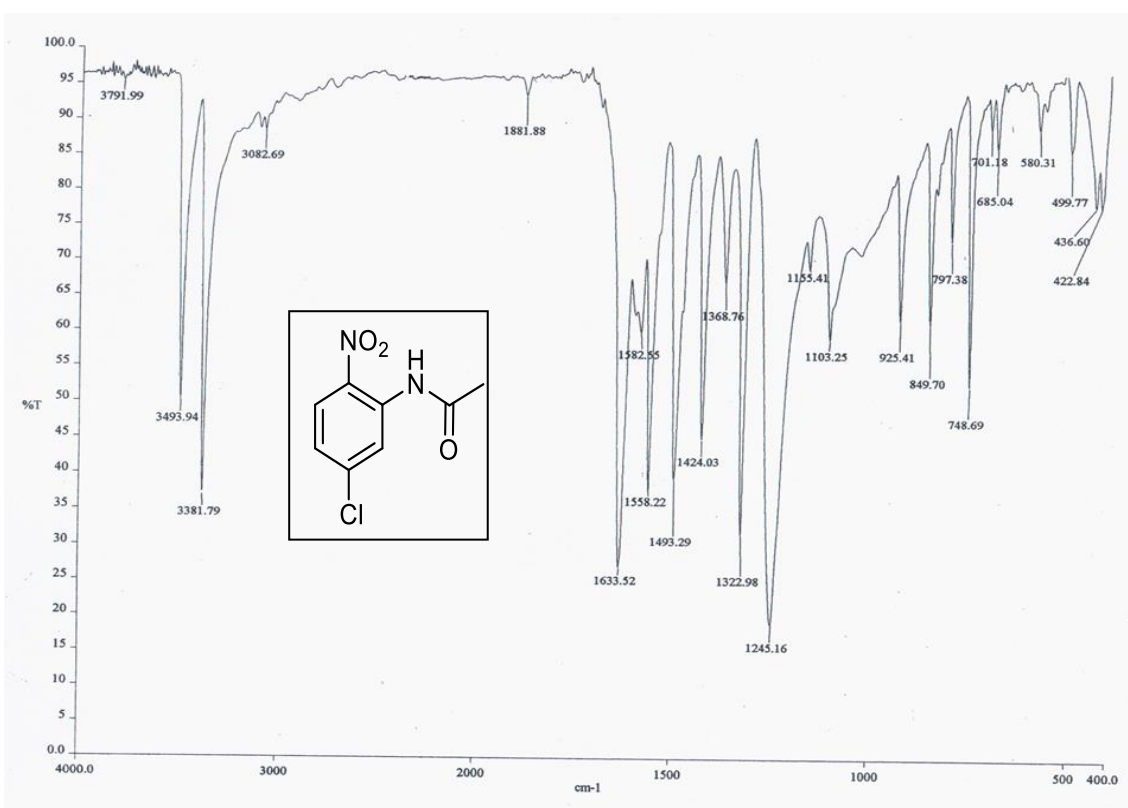
N-(5-Chloro-2-nitrophenyl)acetamide **1b**



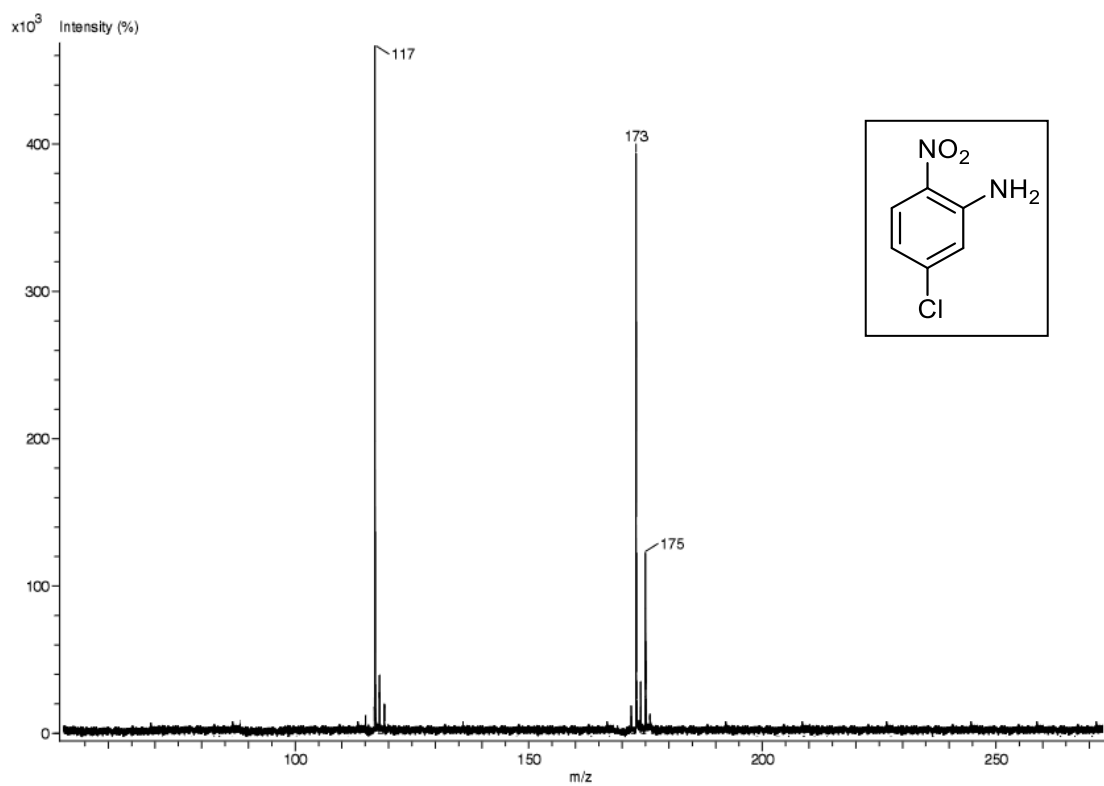
N-(5-Chloro-2-nitrophenyl)acetamide **1b**



N-(5-Chloro-2-nitrophenyl)acetamide **1b**

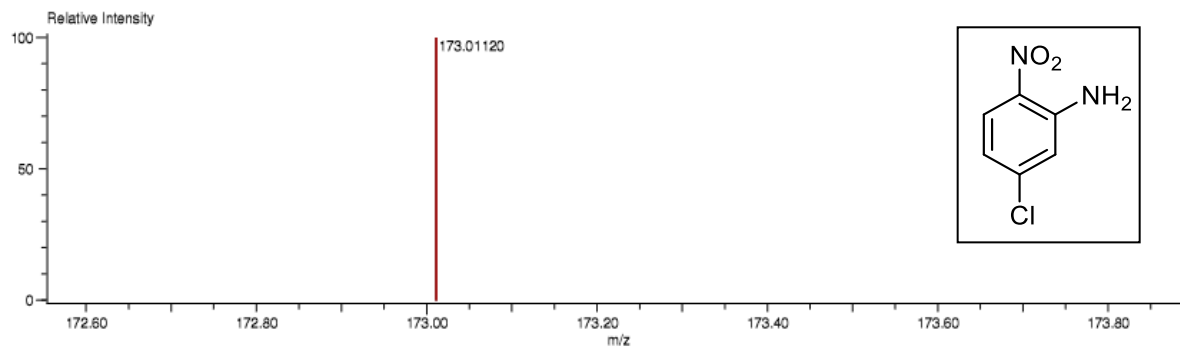


5-Chloro-2-nitroaniline **4b**



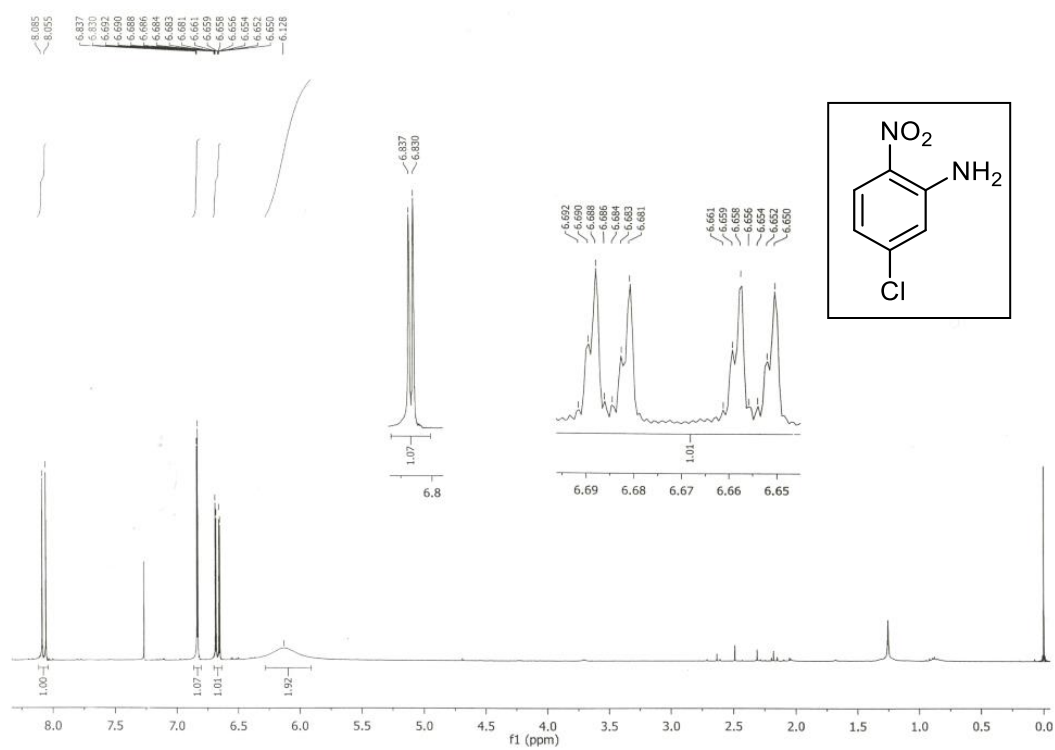
5-Chloro-2-nitroaniline **4b**

Charge number:1 Tolerance:3.00(mmu) Unsaturation Number:0.0 .. 30.0 (Fraction:Both)
 Element: ^{12}C :0 .. 10, ^1H :0 .. 200, ^{35}Cl :0 .. 1, ^{14}N :0 .. 2, ^{16}O :0 .. 2

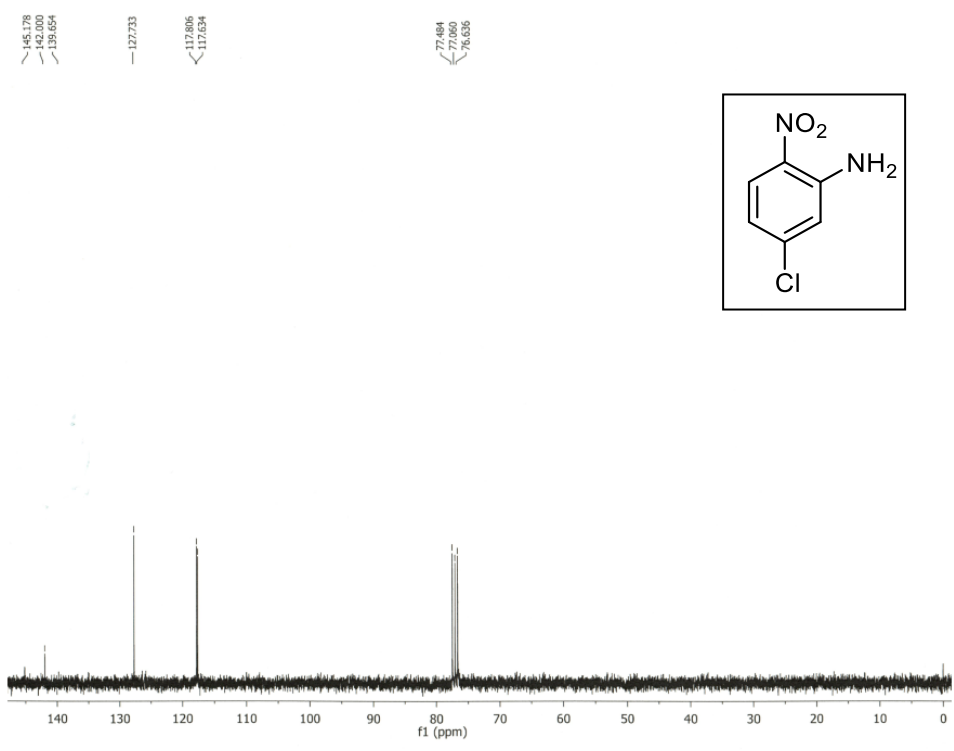


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
173.01120	1433254.00	173.01178	-0.58	-3.33	$^{12}\text{C}_8\text{H}_8\text{Cl}\text{N}_2\text{O}_2$	4.5

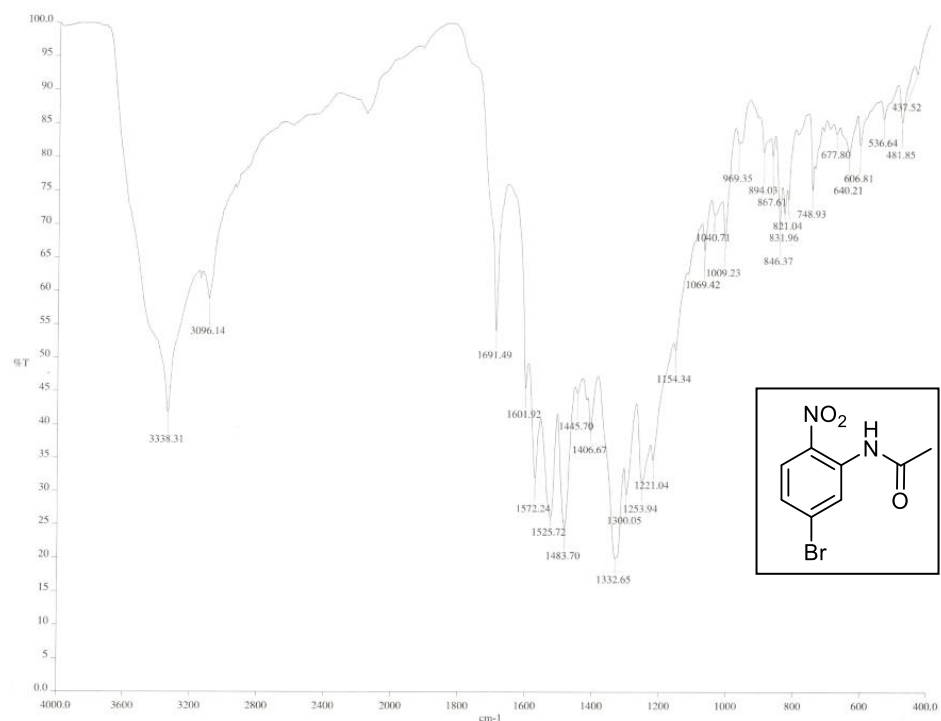
5-Chloro-2-nitroaniline **4b**



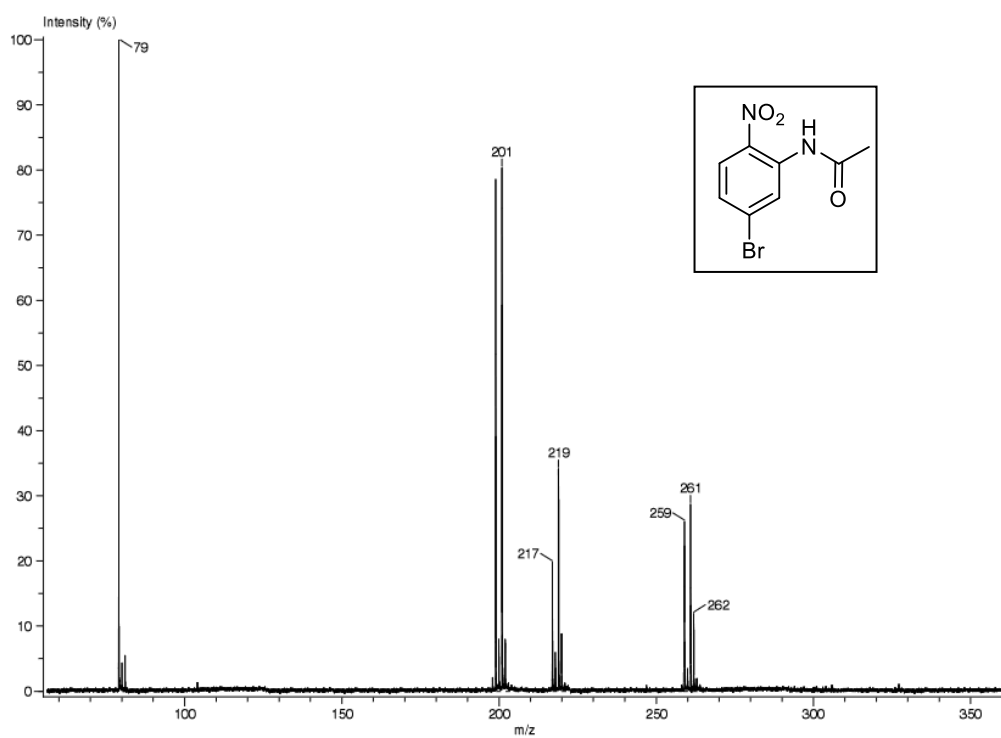
5-Chloro-2-nitroaniline **4b**



Chloro-2-nitroaniline **4b**



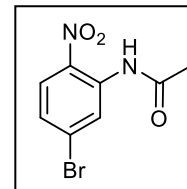
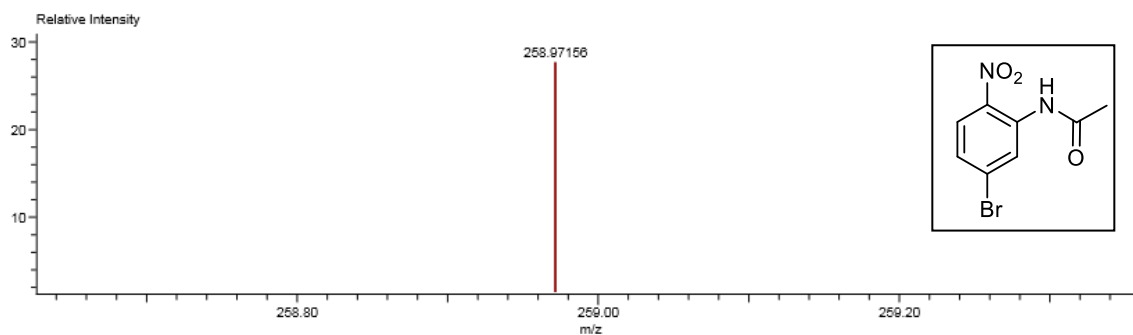
N-(5-Bromo-2-nitrophenyl)acetamide **1c**



N-(5-Bromo-2-nitrophenyl)acetamide **1c**

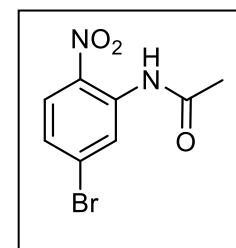
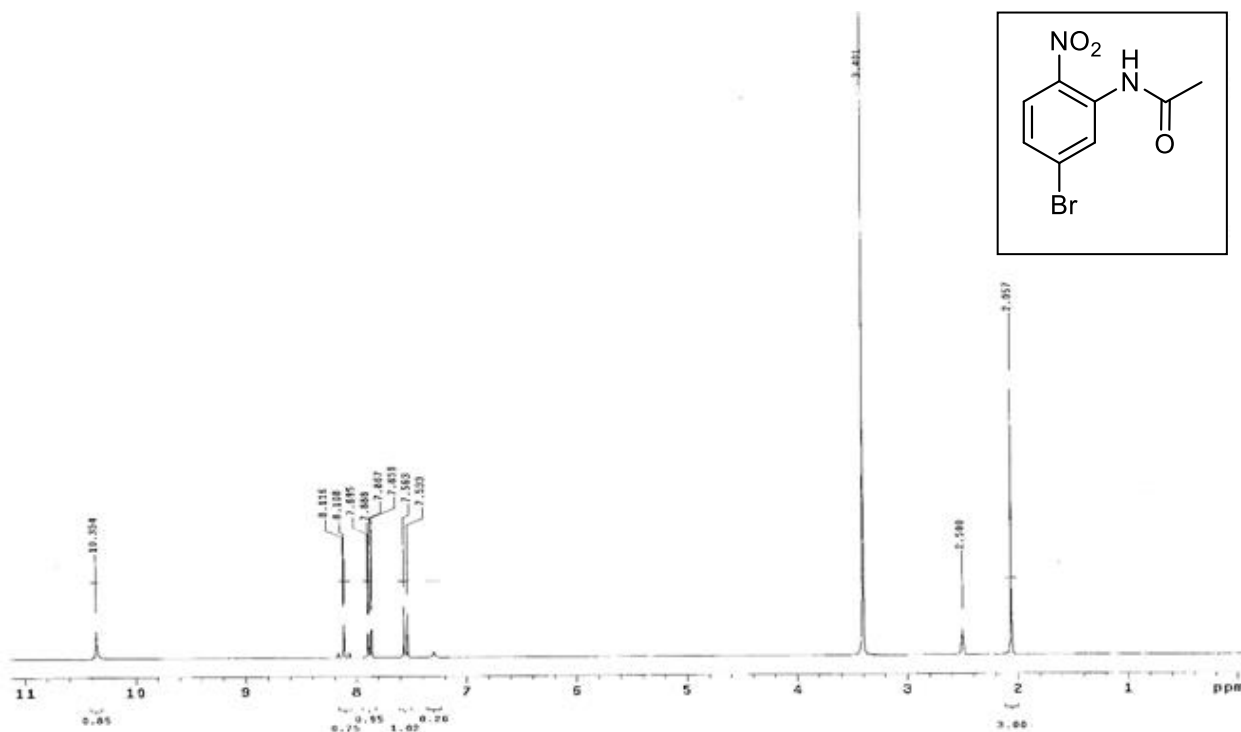
Charge number:1
 Element:¹²C:0 .. 30, ¹H:0 .. 42, ⁷⁹Br:1 .. 1, ¹⁴N:0 .. 3, ¹⁶O:0 .. 4

Tolerance:3.00(mmu)
 Unsaturation Number:0.0 .. 9.0 (Fraction:Both)

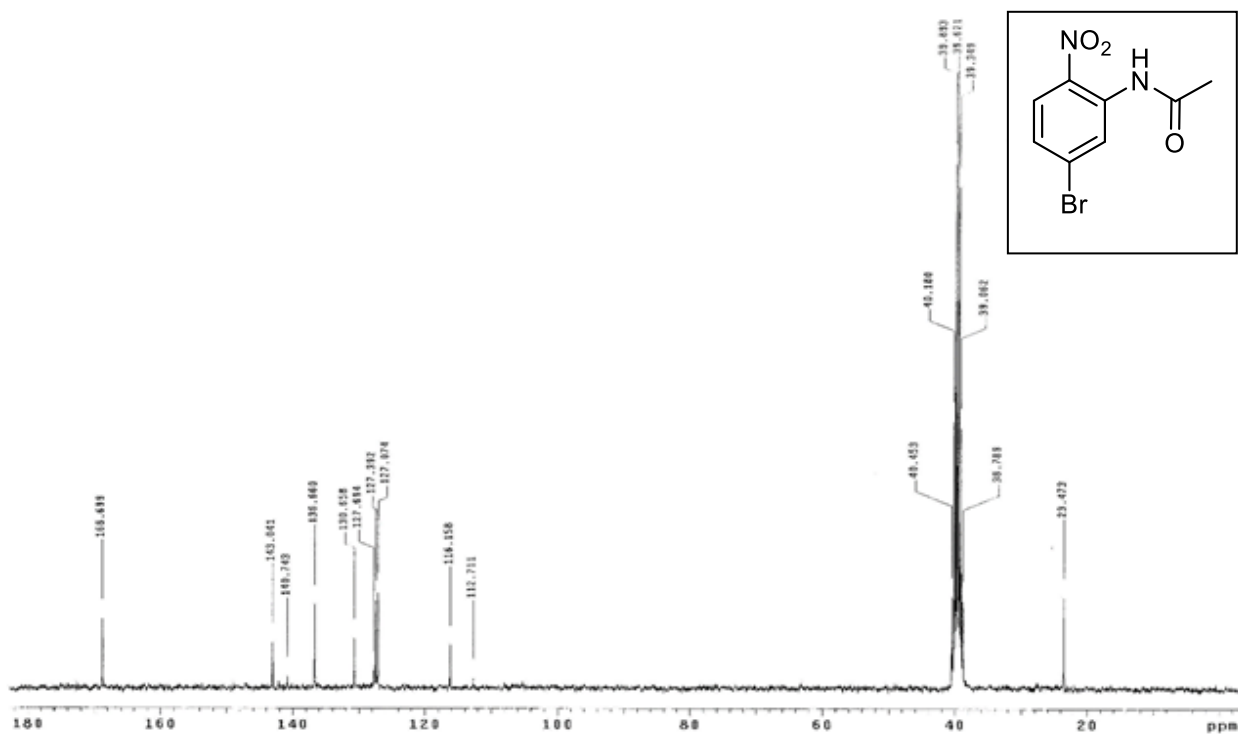


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
258.97156	105486.35	258.97183	-0.27	-1.03	¹² C ₈ ¹ H ₆ ⁷⁹ Br ₁ ¹⁴ N ₂ ¹⁶ O ₃	5.5

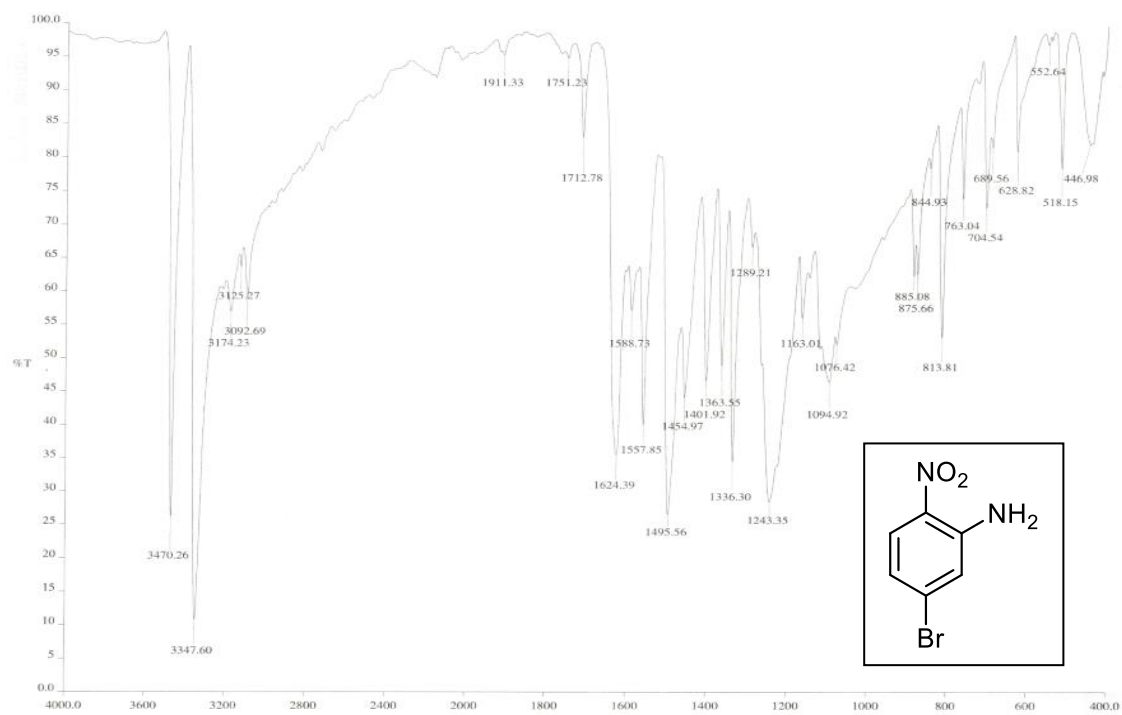
N-(5-Bromo-2-nitrophenyl)acetamide **1c**



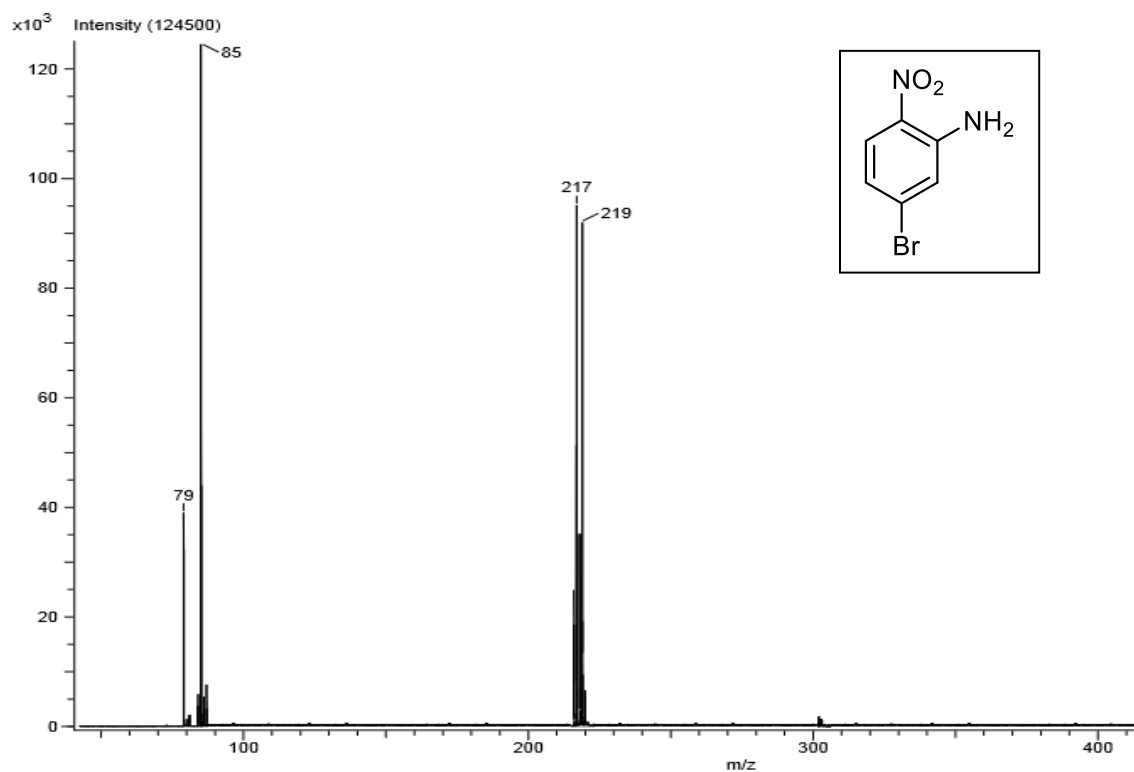
N-(5-Bromo-2-nitrophenyl)acetamide **1c**



N-(5-Bromo-2-nitrophenyl)acetamide **1c**



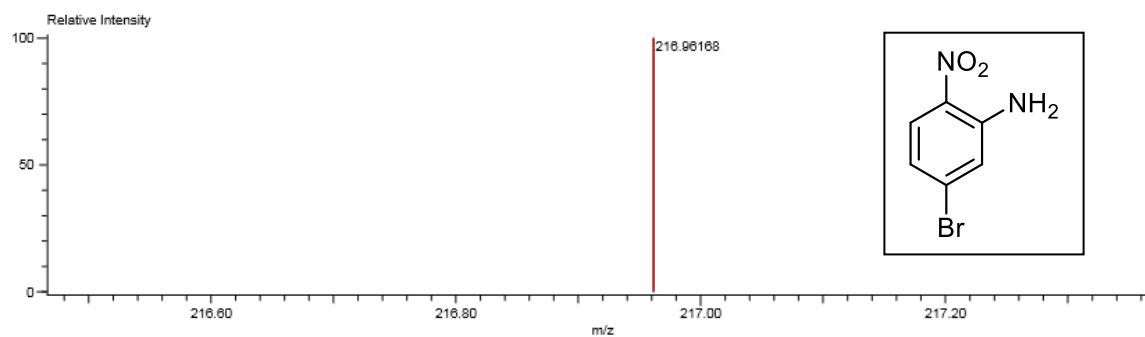
5-Bromo-2-nitroaniline **4c**



5-Bromo-2-nitroaniline **4c**

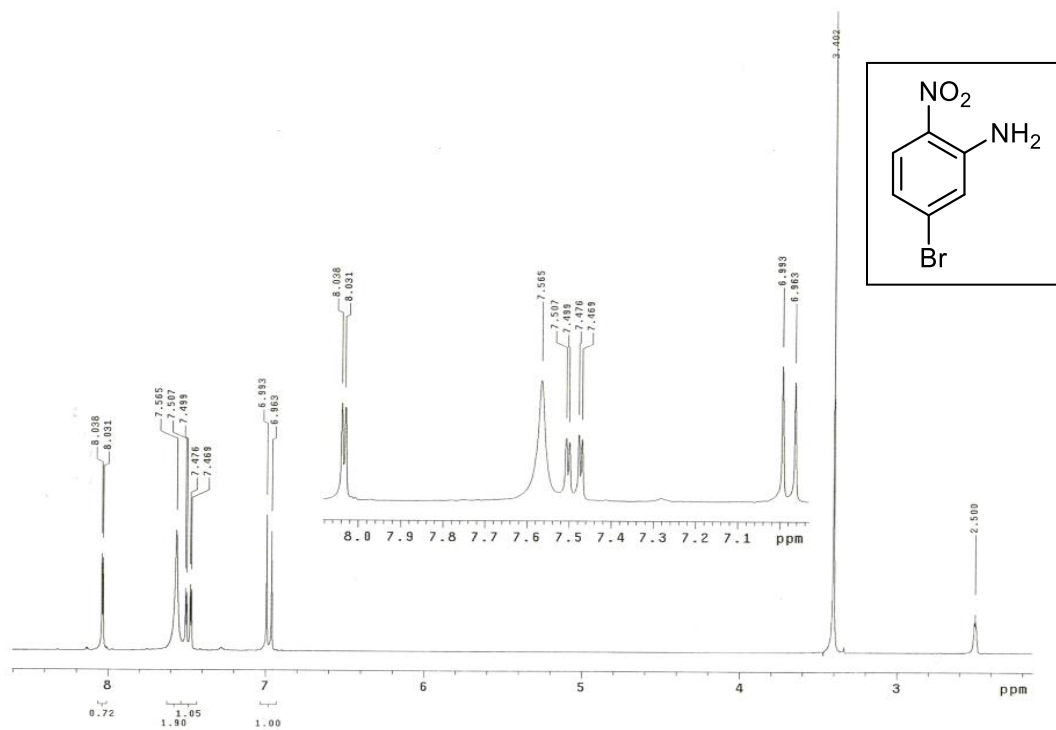
Charge number:1
 Element: ^{12}C :0 .. 30, ^1H :0 .. 42, ^{79}Br :1 .. 1, ^{14}N :0 .. 3, ^{16}O :0 .. 4

Unsaturation Number:0.0 .. 9.0 (Fraction:Both)

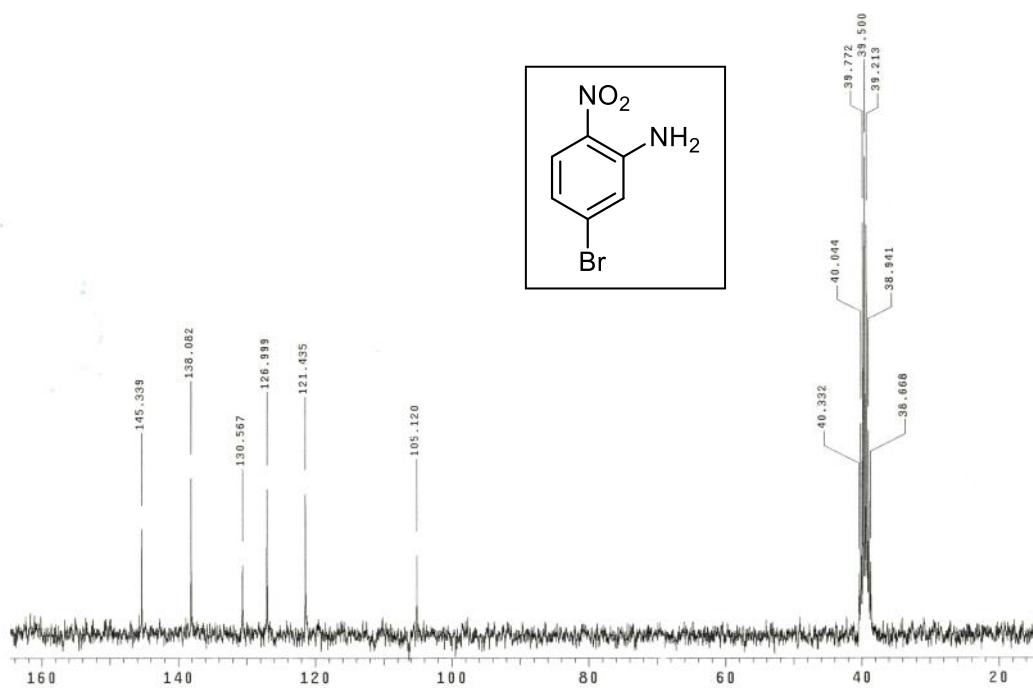


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
216.96168	381471.03	216.96127	0.41	1.91	$^{12}\text{C}_6\text{H}_5\text{Br}^{79}\text{Br}^{14}\text{N}_2\text{O}_2$	4.5

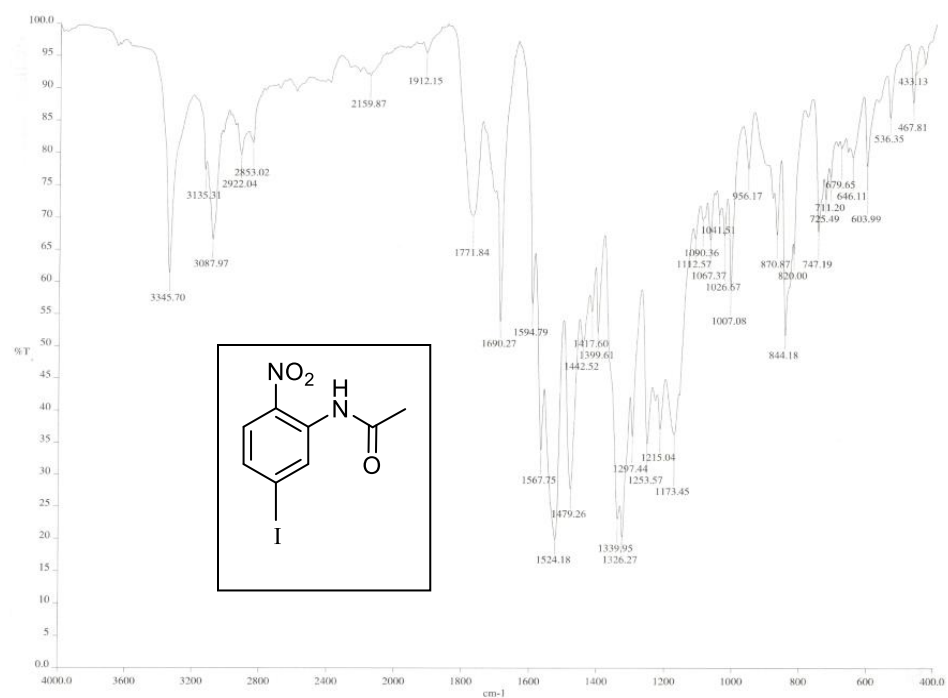
5-Bromo-2-nitroaniline **4c**



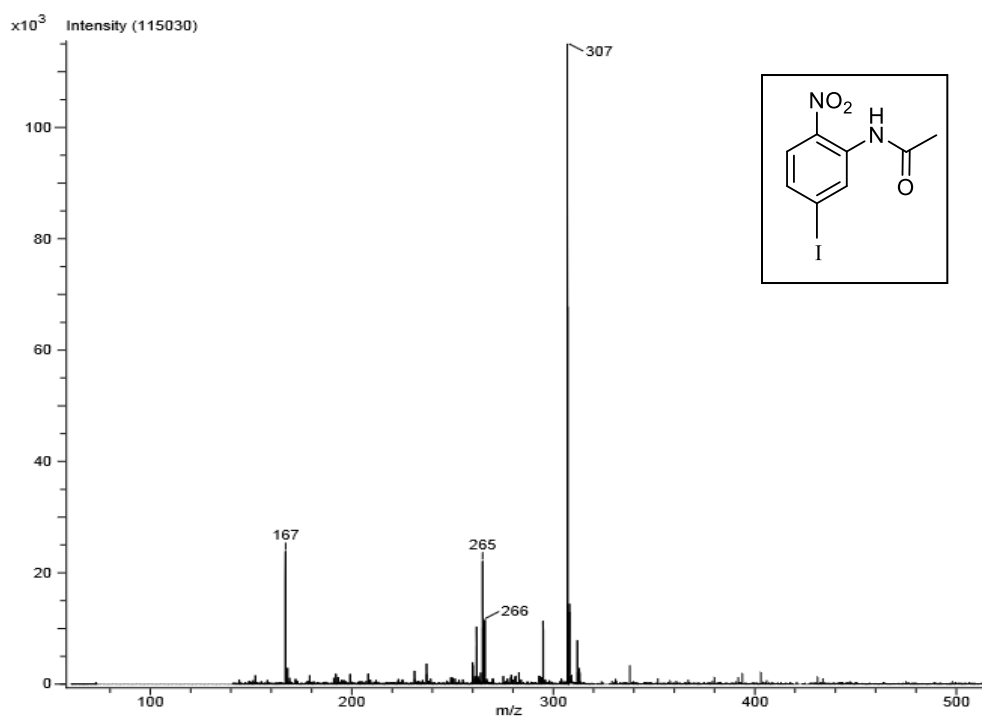
5-Bromo-2-nitroaniline **4c**



5-Bromo-2-nitroaniline **4c**



N-(5-Iodo-2-nitrophenyl)acetamide **1d**

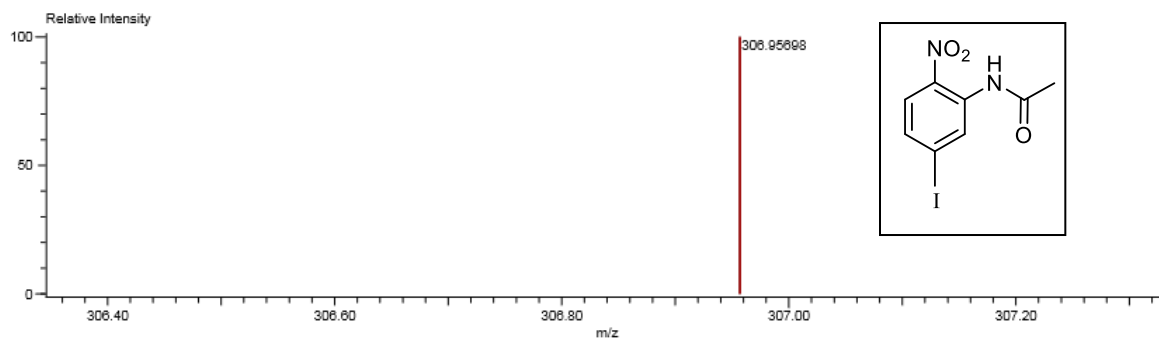


N-(5-Iodo-2-nitrophenyl)acetamide **1d**

Charge number:1
 Element:¹²C:1 .. 20, ¹H:1 .. 40, ¹²⁷I:0 .. 1, ¹⁴N:0 .. 2, ¹⁶O:0 .. 4

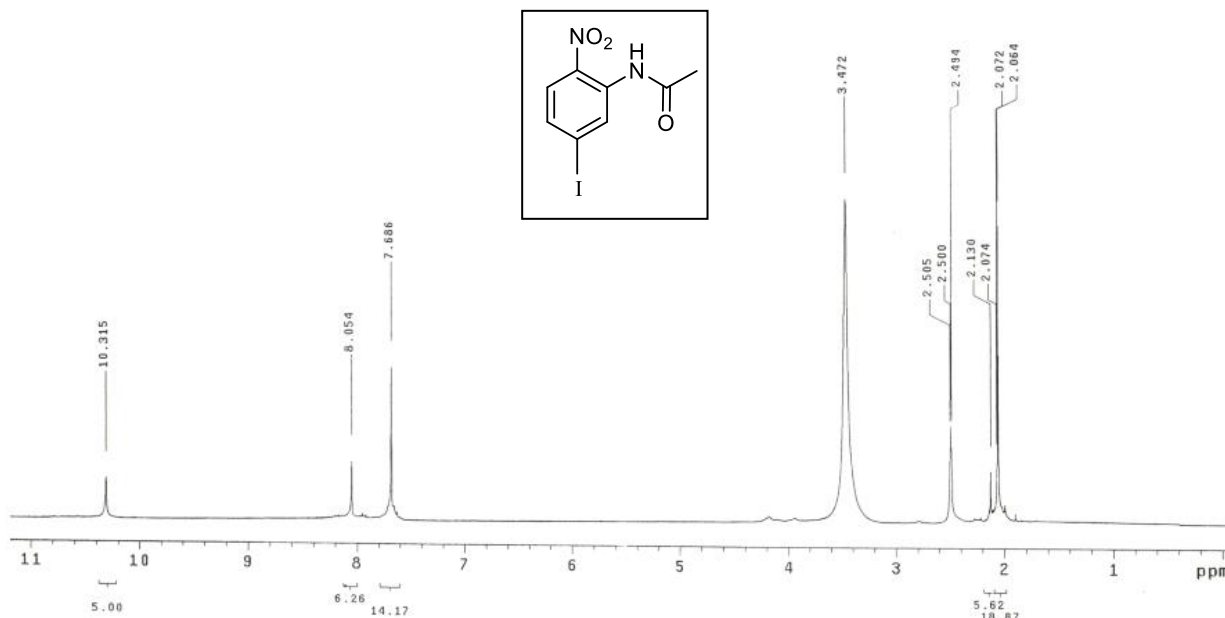
Tolerance:2.50(mmu)

Unsaturation Number:0.0 .. 15.0 (Fraction:Both)

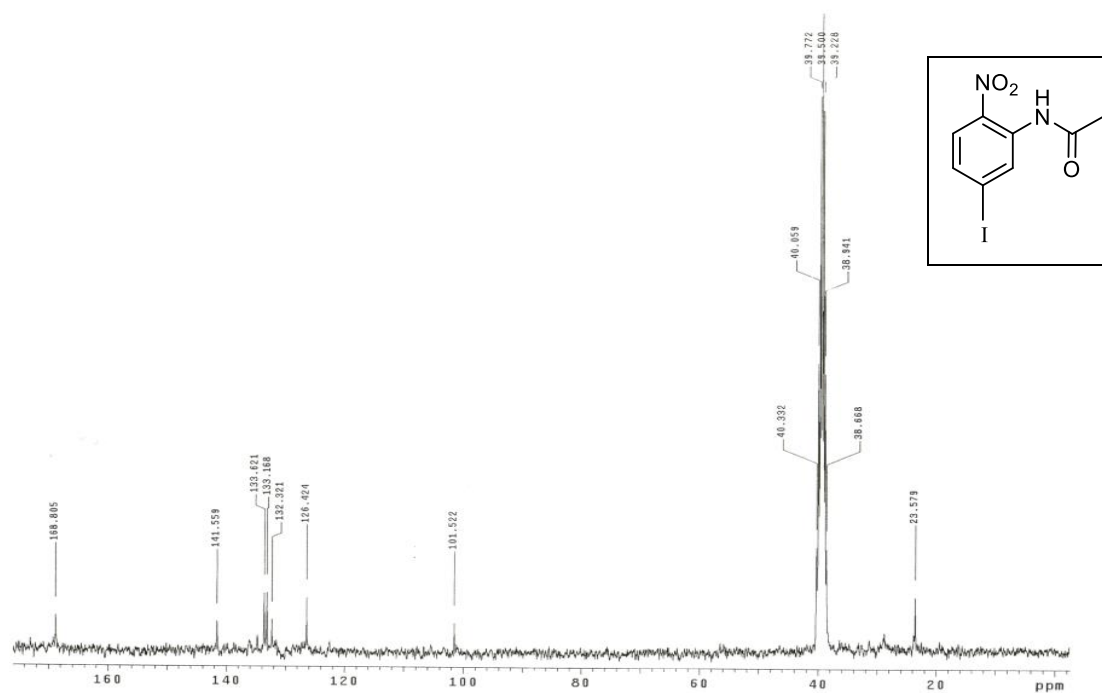


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
306.95698	396880.56	306.95796	-0.98	-3.20	¹² C ₉ ¹ H ₈ ¹²⁷ I ₁ ¹⁴ N ₂ ¹⁶ O ₃	5.5

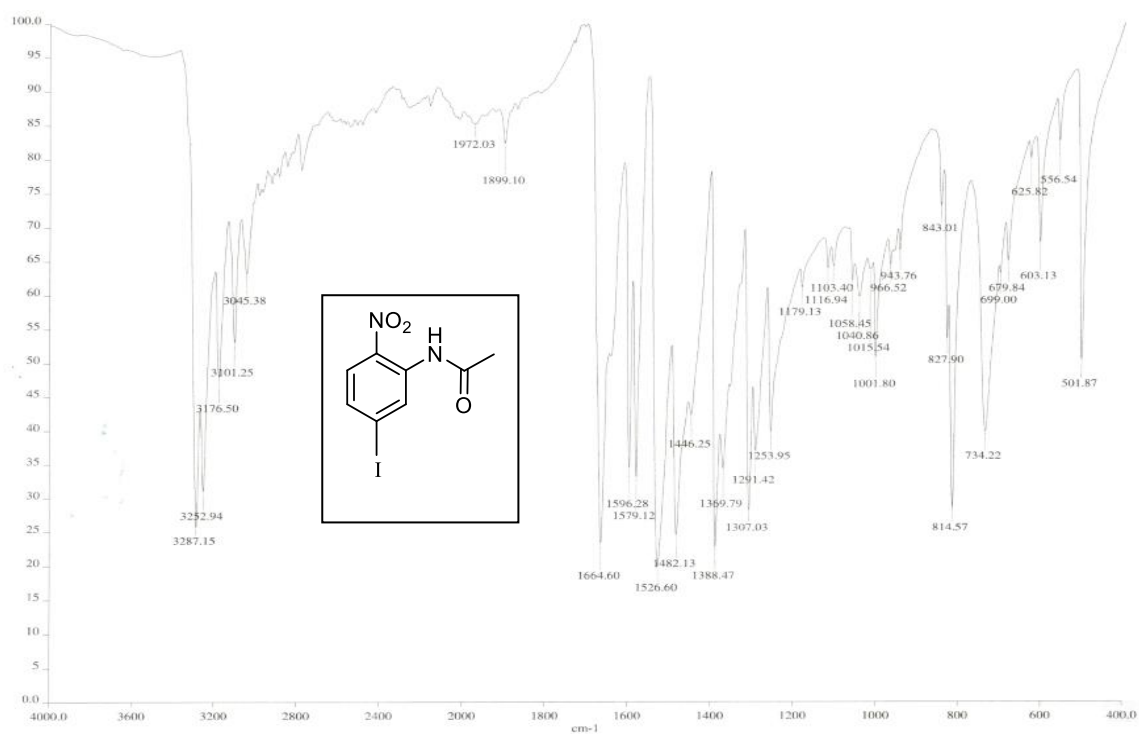
N-(5-Iodo-2-nitrophenyl)acetamide **1d**



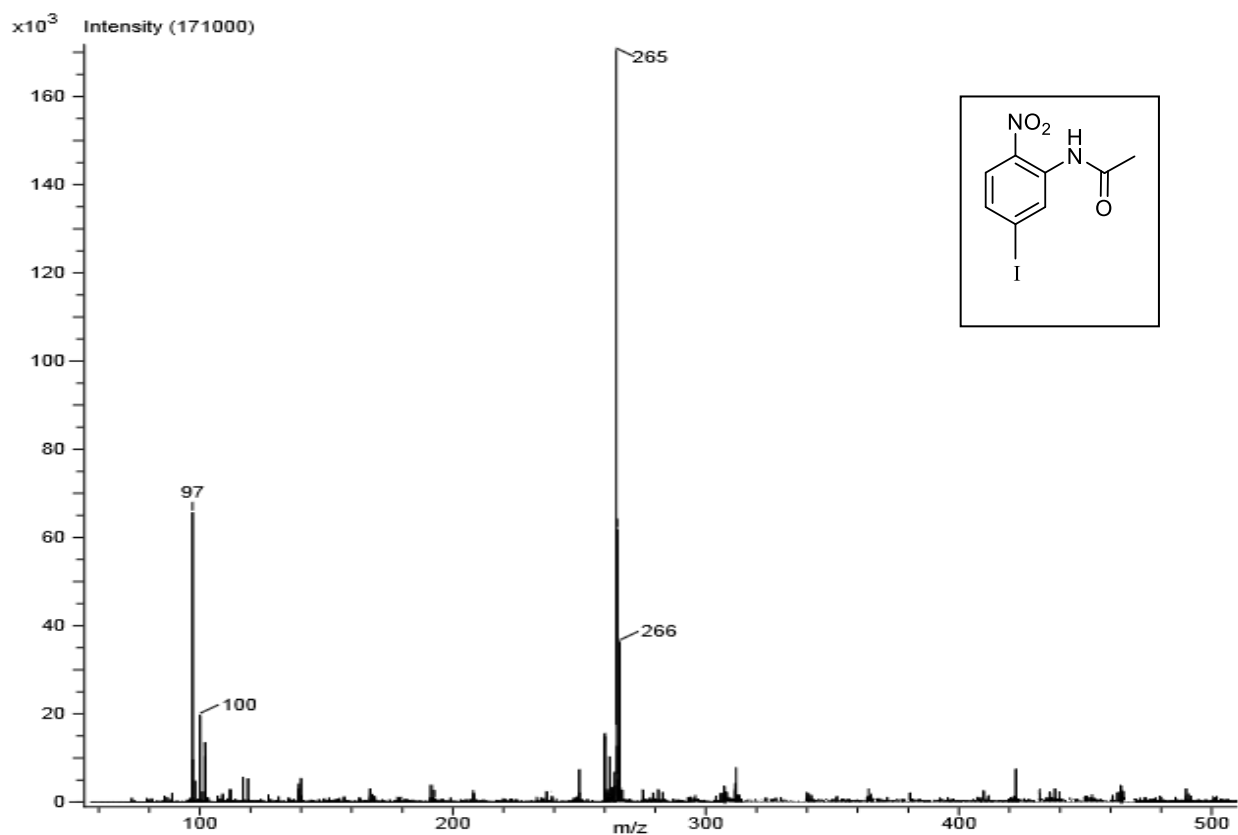
N-(5-Iodo-2-nitrophenyl)acetamide **1d**



N-(5-Iodo-2-nitrophenyl)acetamide 1d

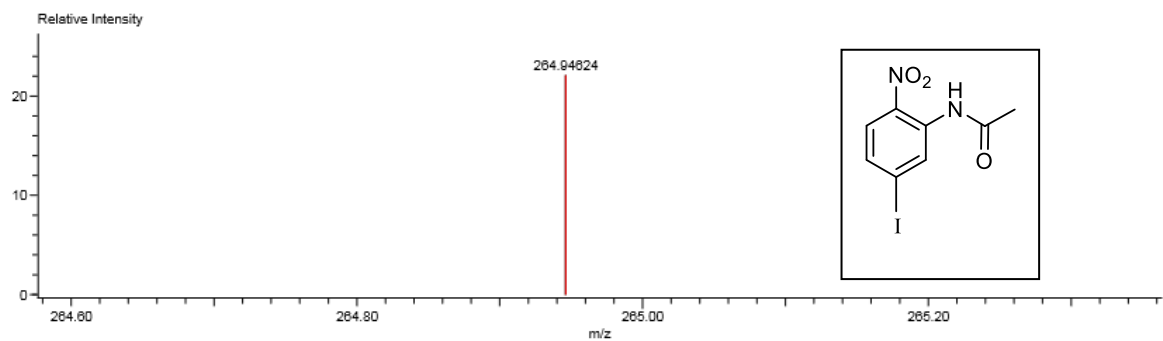


5-Iodo-2-nitroaniline 4d



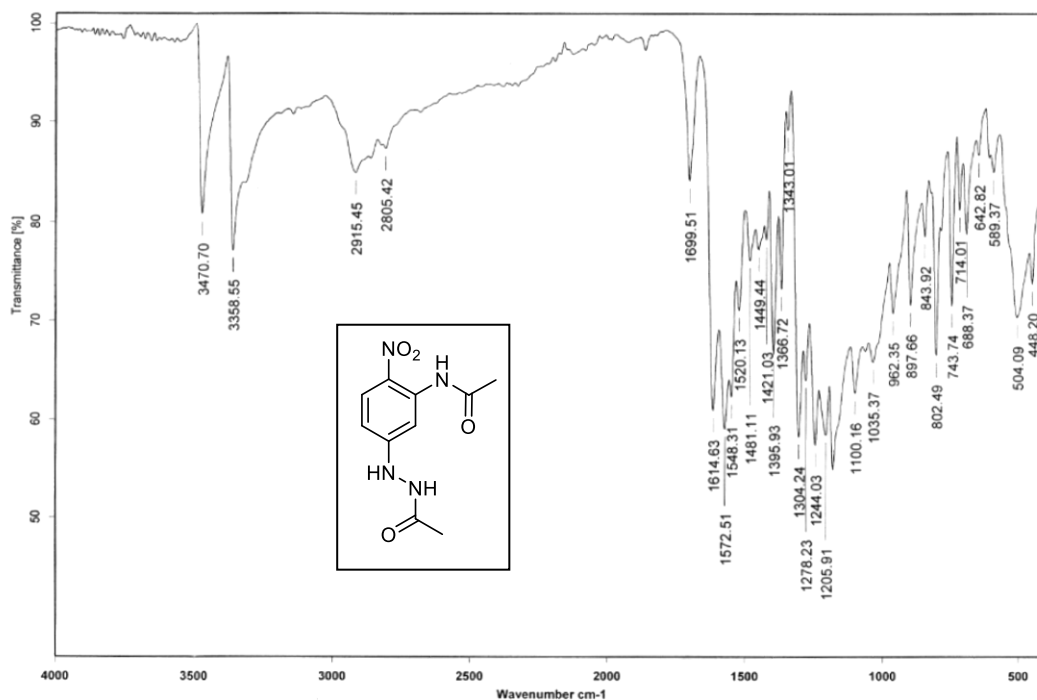
5-Iodo-2-nitroaniline **4d**

Charge number: 1 Tolerance: 3.00 (mmu) Unsaturation Number: 0.0 .. 15.0 (Fraction: Both)
 Element: ^{12}C : 1 .. 20, ^1H : 1 .. 40, ^{127}I : 0 .. 1, ^{14}N : 0 .. 2, ^{16}O : 0 .. 2

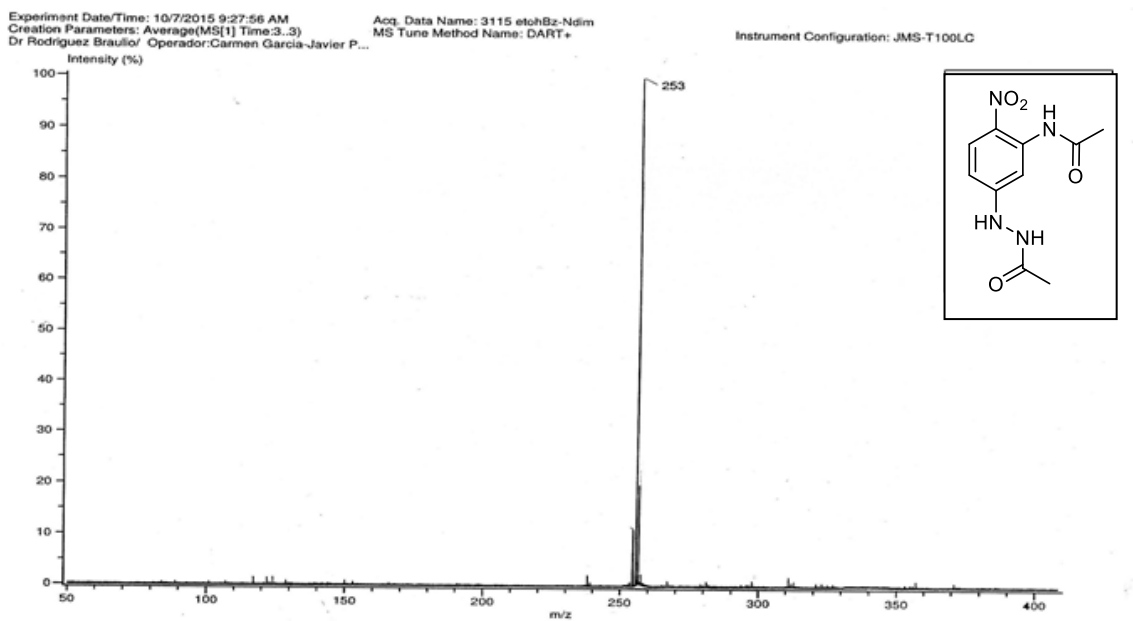


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
264.94624	264648.50	264.94739	-1.15	-4.35	$^{12}\text{C}_6\text{H}_6\text{I}^{127}\text{I}_1\text{N}_2\text{O}_2$	4.5

5-Iodo-2-nitroaniline **4d**



N-(5-(2-Acetylhydrazino)-2-nitrophenyl)acetamide **3a**



N-(5-(2-Acetylhydrazino)-2-nitrophenyl)acetamide **3a**

Data: F14

Sample Name:

Description:

Ionization Mode: ESI+

History: Determine m/z [Peak Detect [Centroid, 30, Area], Correct Base [10.0%], Correct Base [5.0%], Average (MS [1] 0..0)

Acquired: 5/24/2016 9:29:45 AM

Operator: AccuTOF

Mass Calibration data: Cal PEG 600

Created: 5/31/2016 6:40:45 PM

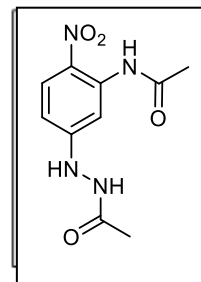
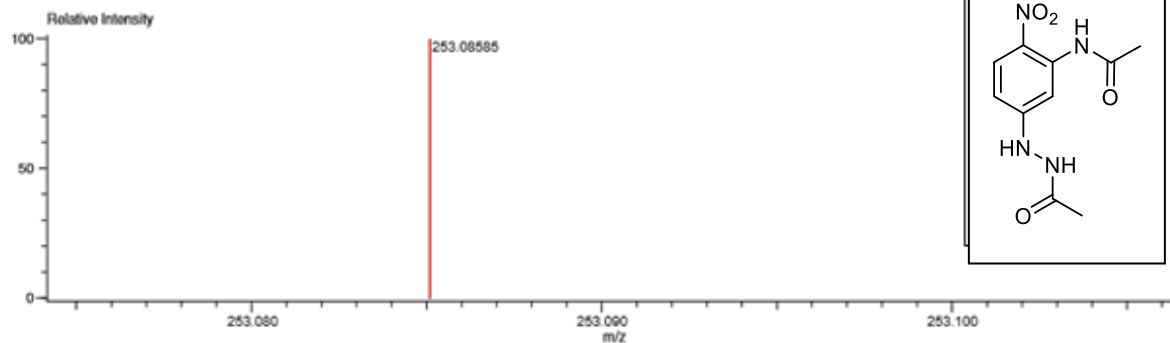
Created by: AccuTOF

Charge number: 1

Tolerance: 3.00 (mmu)

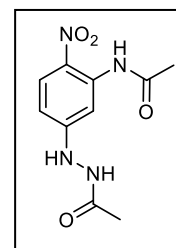
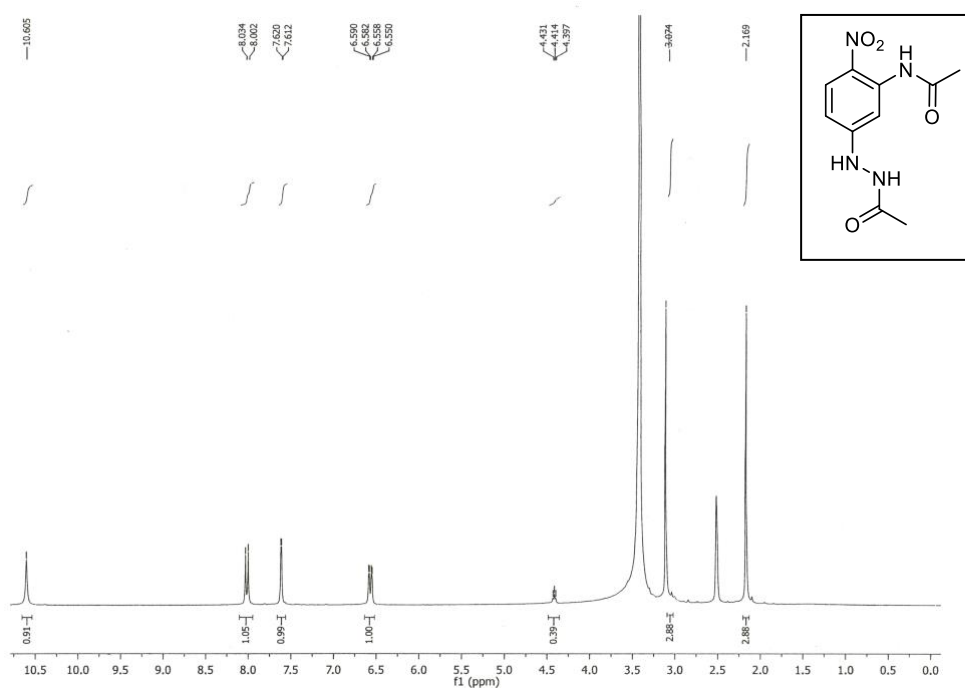
Unsaturation Number: 0.0 .. 20.0 (Fraction: 5)

Element: ^{12}C : 0 .. 50, ^1H : 0 .. 100, ^{14}N : 0 .. 3, ^{16}O : 0 .. 2



Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
253.08550	2369.51	253.08585	0.30	1.34	$^{12}\text{C}_{10}\text{H}_{12}\text{N}_4\text{O}_6$	5.5

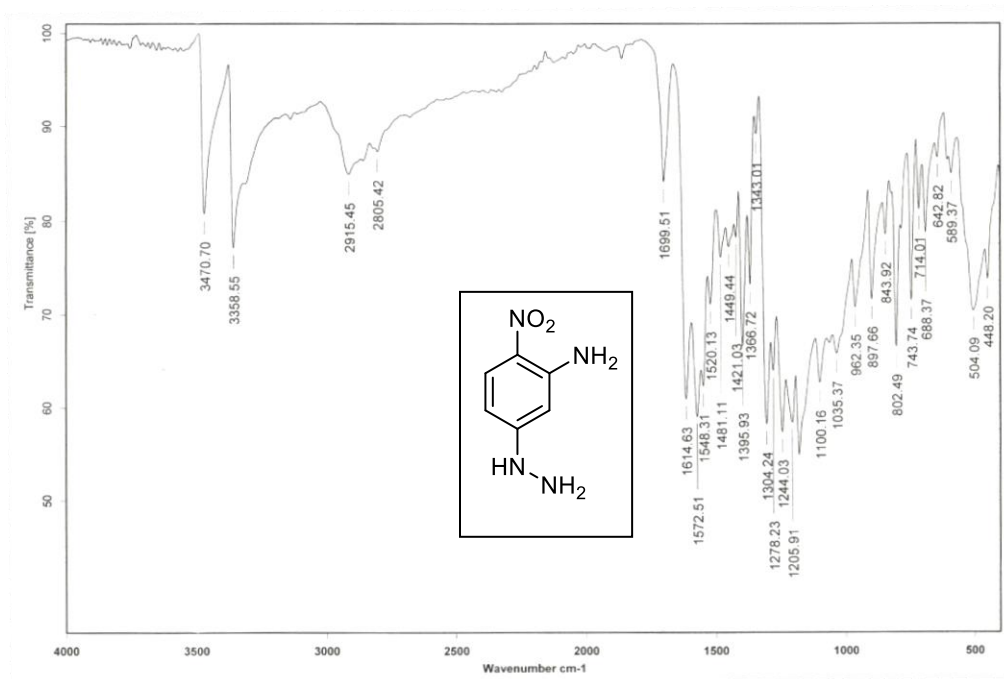
N-(5-(2-Acetylhydrazino)-2-nitrophenyl)acetamide **3a**



N-(5-(2-Acetylhydrazino)-2-nitrophenyl)acetamide **3a**



N-(5-(2-Acetylhydrazino)-2-nitrophenyl)acetamide 3a

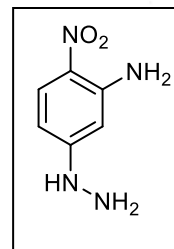
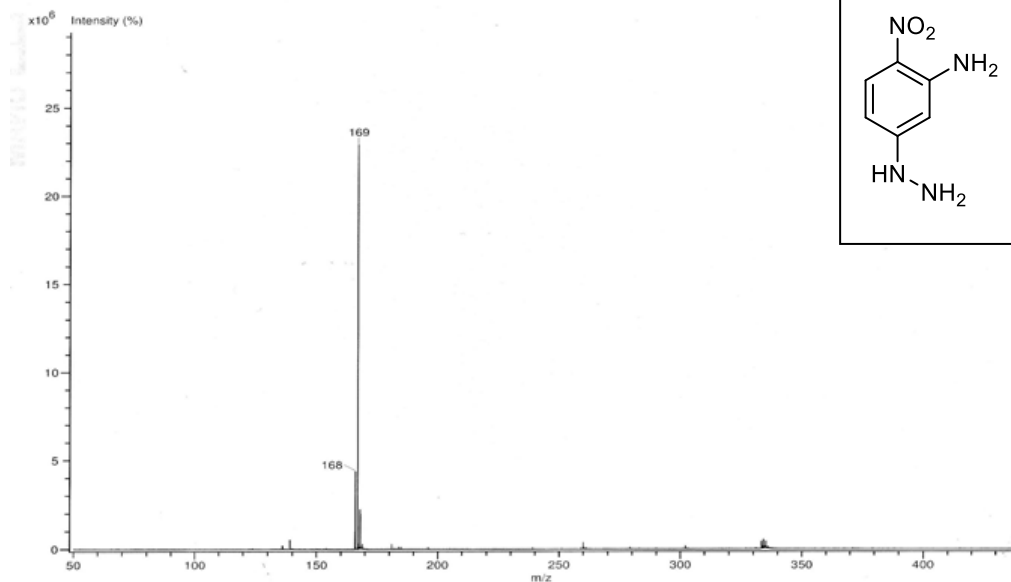


3-Amino-4-nitrophenylhydrazine 5a

Experiment Title: -
Creation Parameters: Average(MS[1] Time:0.20..0.20)

Acq. Data Name: 168 MS Tune
Method Name: DART+

Experiment Date/Time: 5/21/2016 11:27:06 AM



3-Amino-4-nitrophenylhydrazine **5a**

Data:169

Sample Name:Javier

Description:

Ionization Mode:ESI+

History:Determine m/z[Peak Detect(Centroid,30,Area);Correct Base[5.0%];Correct Base[5.0%];Average(MS[1] 0..0)

Acquired:2/26/2016 11:39:02 AM

Operator:AccuTOF

Mass Calibration data:PEG600

Created:3/10/2016 6:30:36 PM

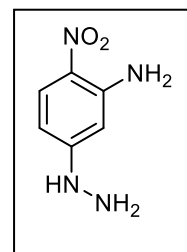
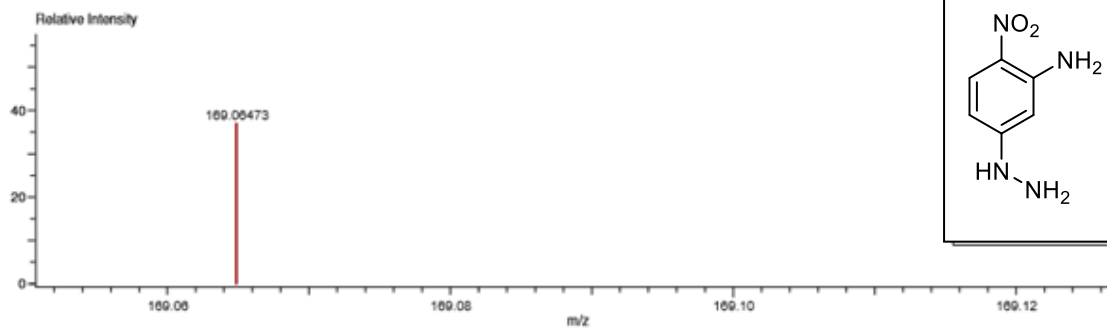
Created by:AccuTOF

Charge number:1

Tolerance:3.00(mmu)

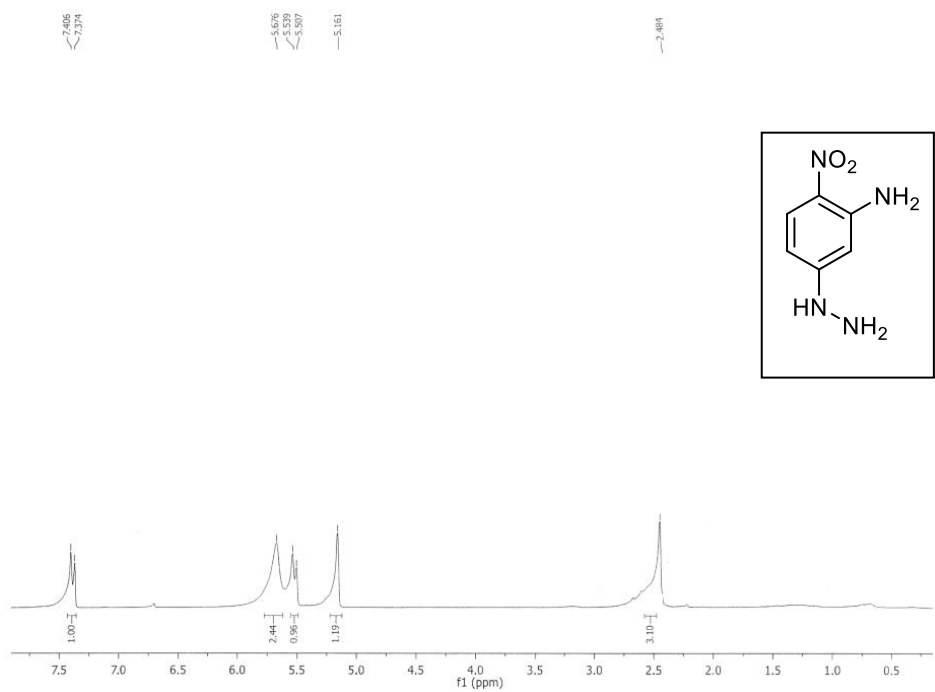
Unsaturation Number:0.0 .. 12.0 (Fraction:.0)

Element:¹²C:0 .. 50, ¹H:0 .. 100, ¹⁴N:0 .. 3, ¹⁶O:0 .. 3

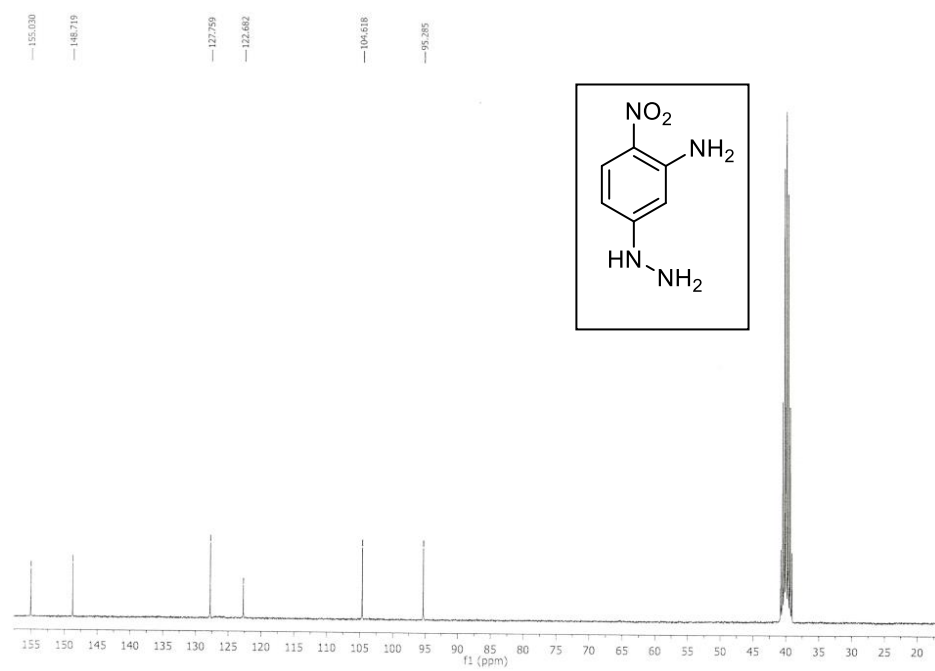


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
169.06473	751800.75	169.06451	0.22	1.31	¹³ C ₈ ¹ H ₈ ¹⁴ N ₄ ¹⁶ O ₂	5.0

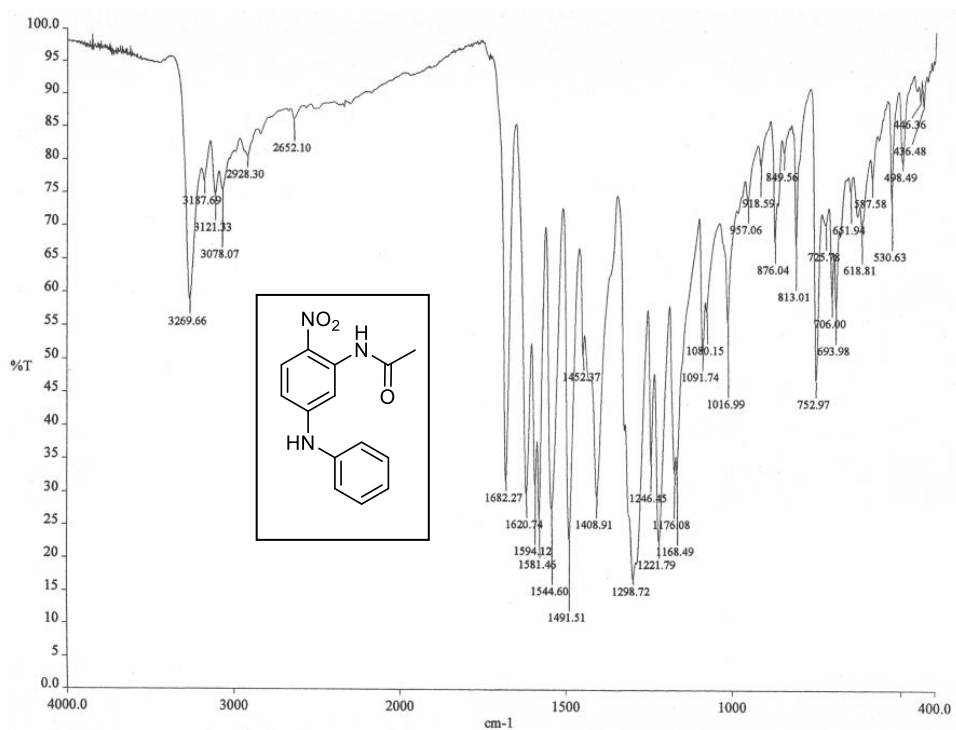
3-Amino-4-nitrophenylhydrazine **5a**



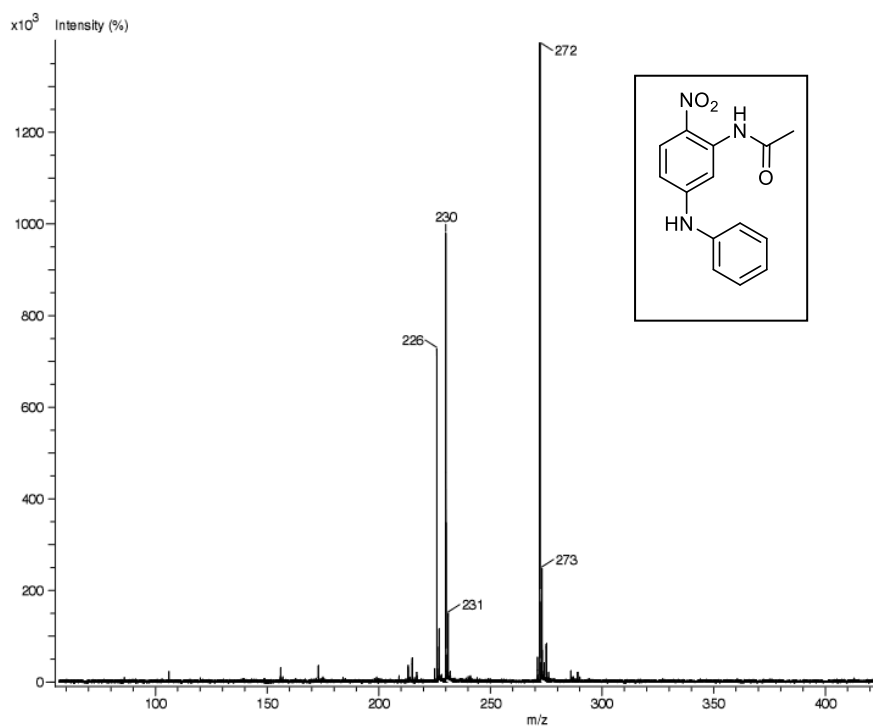
3-Amino-4-nitrophenylhydrazine **5a**



3-Amino-4-nitrophenylhydrazine **5a**



N-(2-Nitro-5-(phenylamino)phenyl)acetamide **3b**

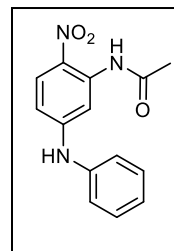
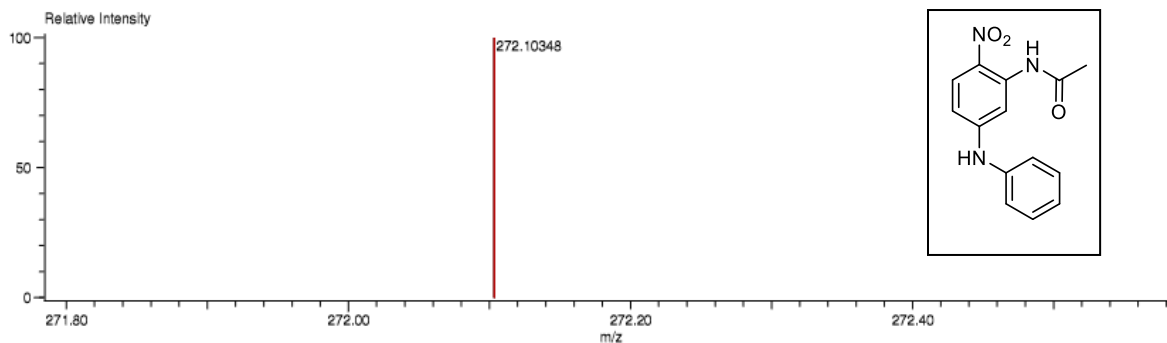


N-(2-Nitro-5-(phenylamino)phenyl)acetamide **3b**

Charge number:1
 Element:¹²C:0 .. 100, ¹H:0 .. 200, ¹⁴N:0 .. 3, ¹⁶O:0 .. 3

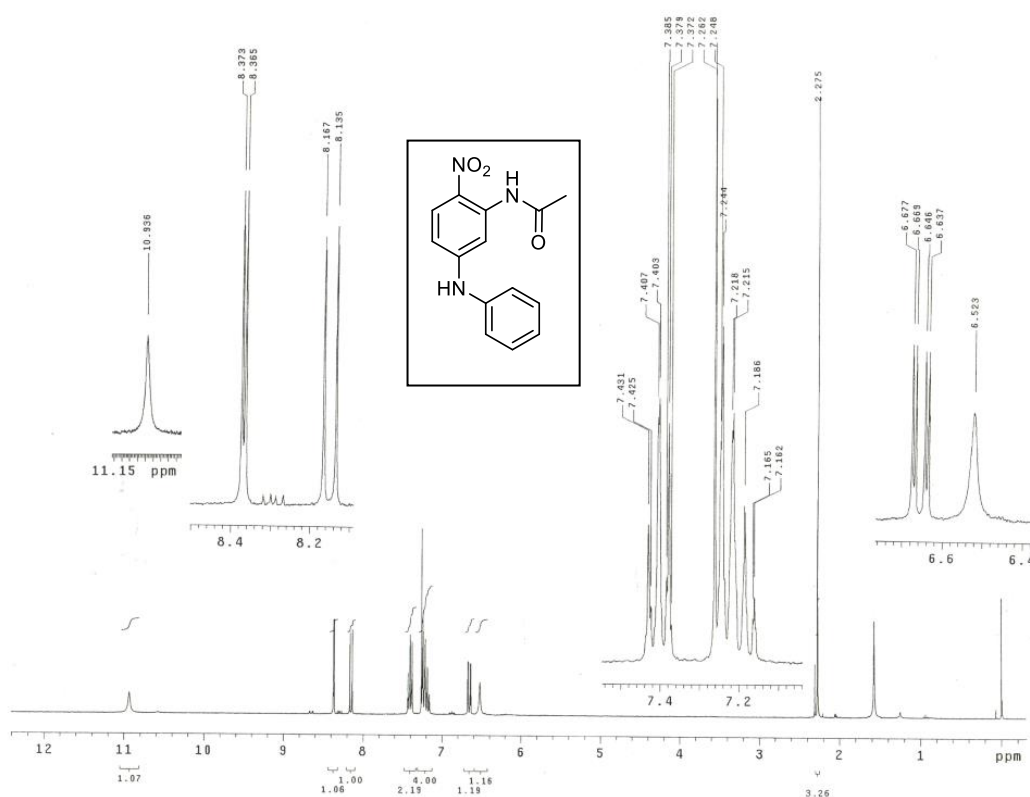
Tolerance:3.00(mmu)

Unsaturation Number:0.0 .. 14.0 (Fraction:Both)

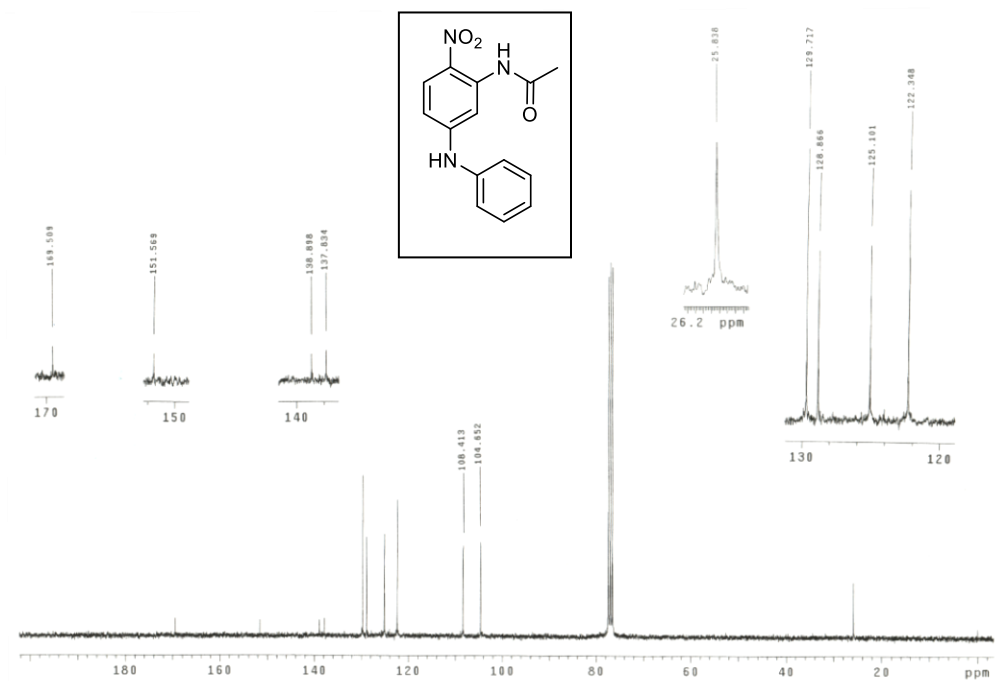


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
272.10348	54445.25	272.10352	-0.04	-0.13	¹² C ₁₄ ¹ H ₁₄ ¹⁴ N ₃ ¹⁶ O ₃	9.5

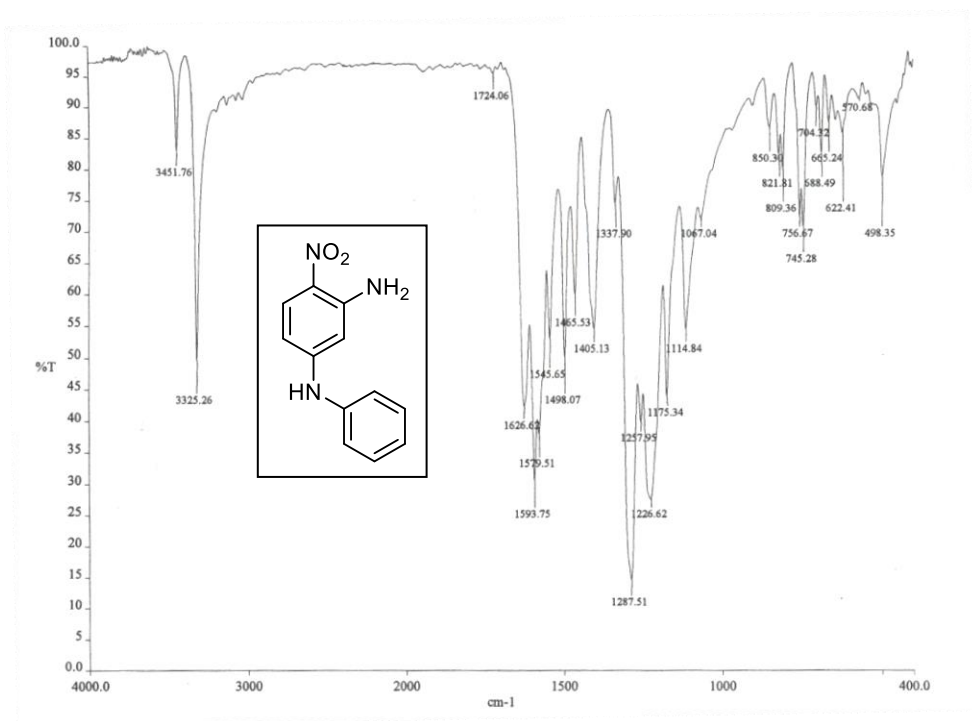
N-(2-Nitro-5-(phenylamino)phenyl)acetamide **3b**



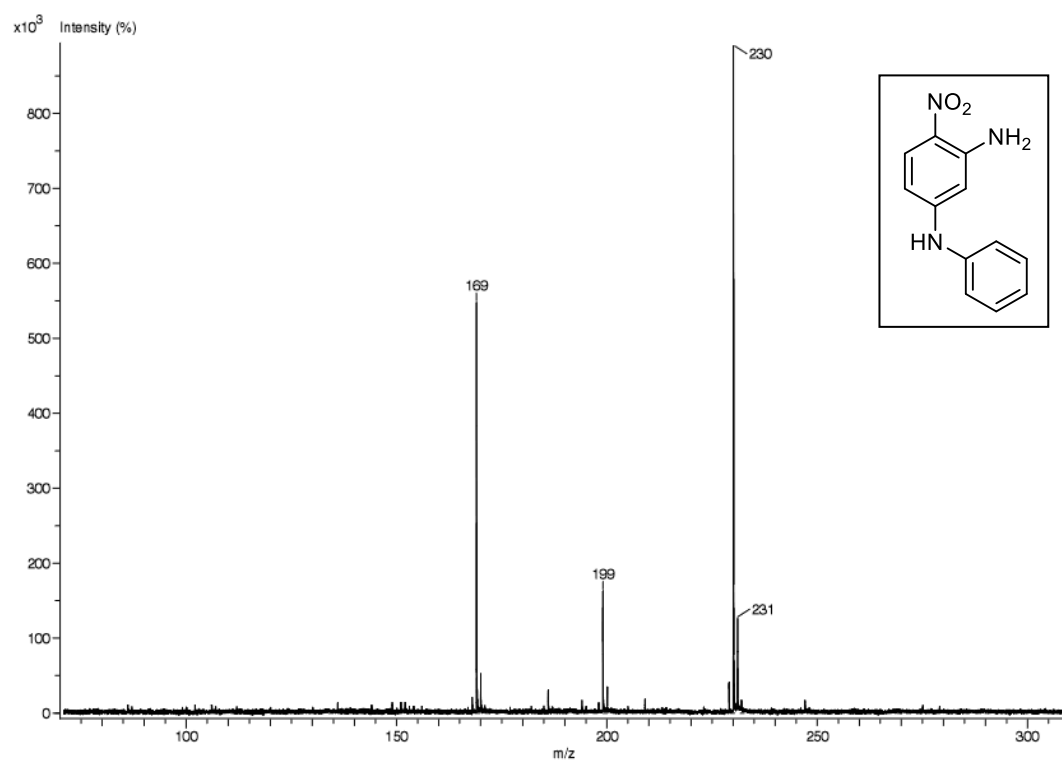
N-(2-Nitro-5-(phenylamino)phenyl)acetamide **3b**



N-(2-Nitro-5-(phenylamino)phenyl)acetamide **3b**



2-Nitro-5-anilinoaniline **5b**

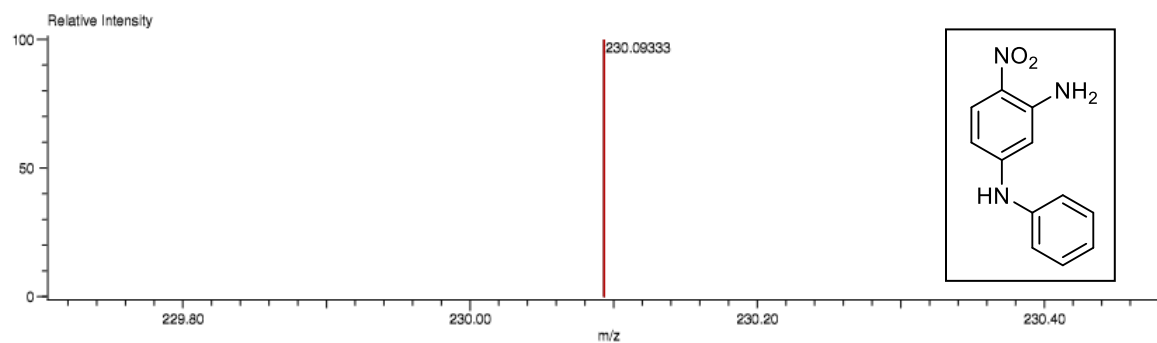


2-Nitro-5-anilinoaniline **5b**

Charge number:1
Element:¹²C:0 .. 12, ¹H:0 .. 200, ¹⁴N:0 .. 3, ¹⁶O:0 .. 3

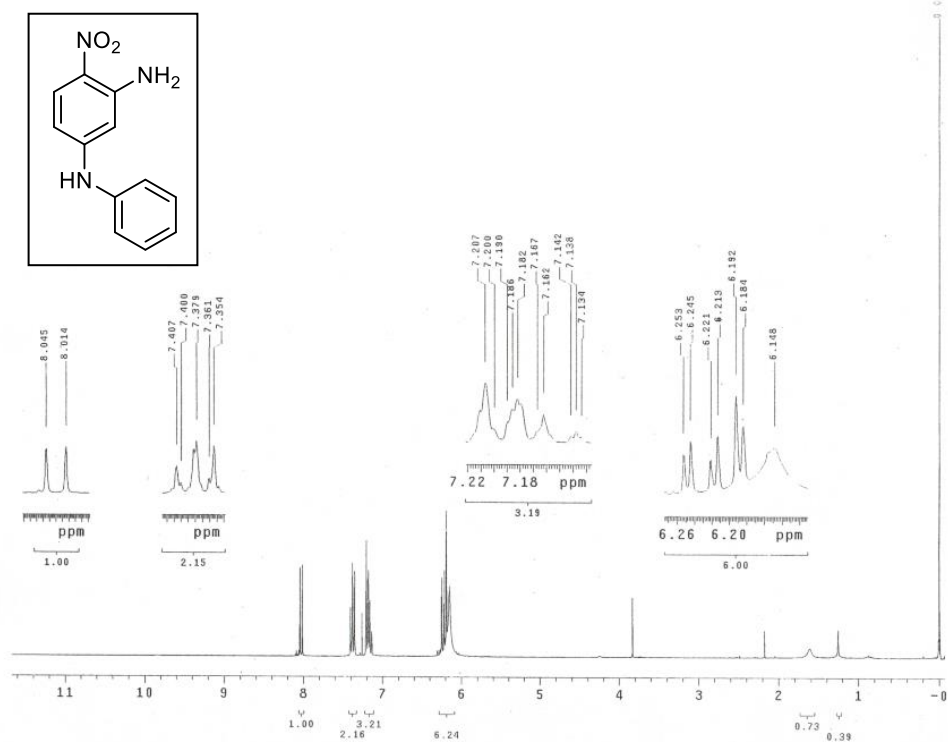
Tolerance:3.00(mmu)

Unsaturation Number:0.0 .. 14.0 (Fraction:Both)

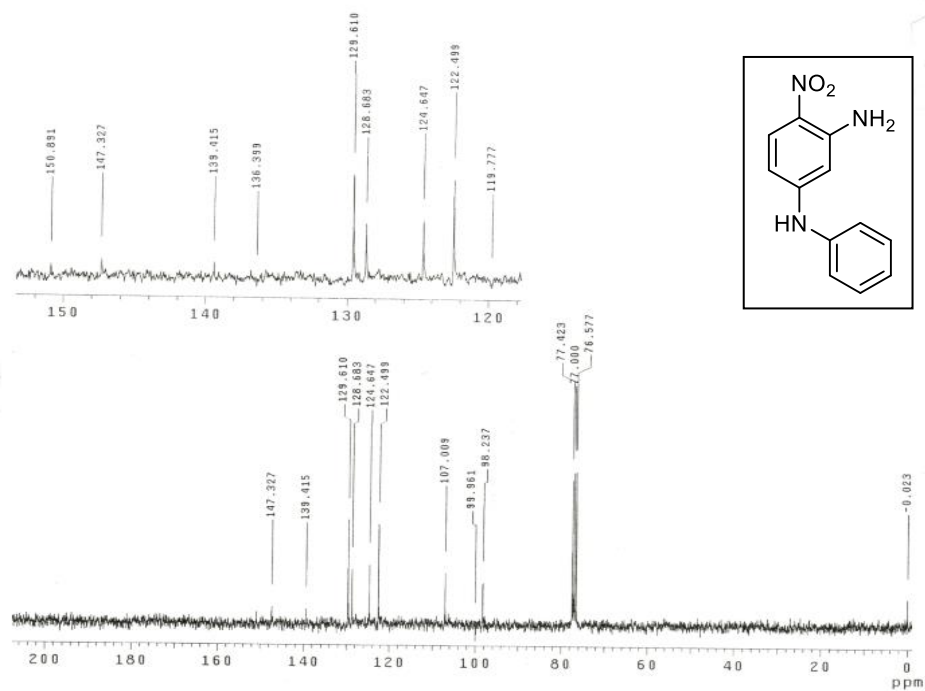


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
230.09333	48614.38	230.09295	0.38	1.67	¹² C ₁₂ ¹ H ₁₂ ¹⁴ N ₃ ¹⁶ O ₂	8.5

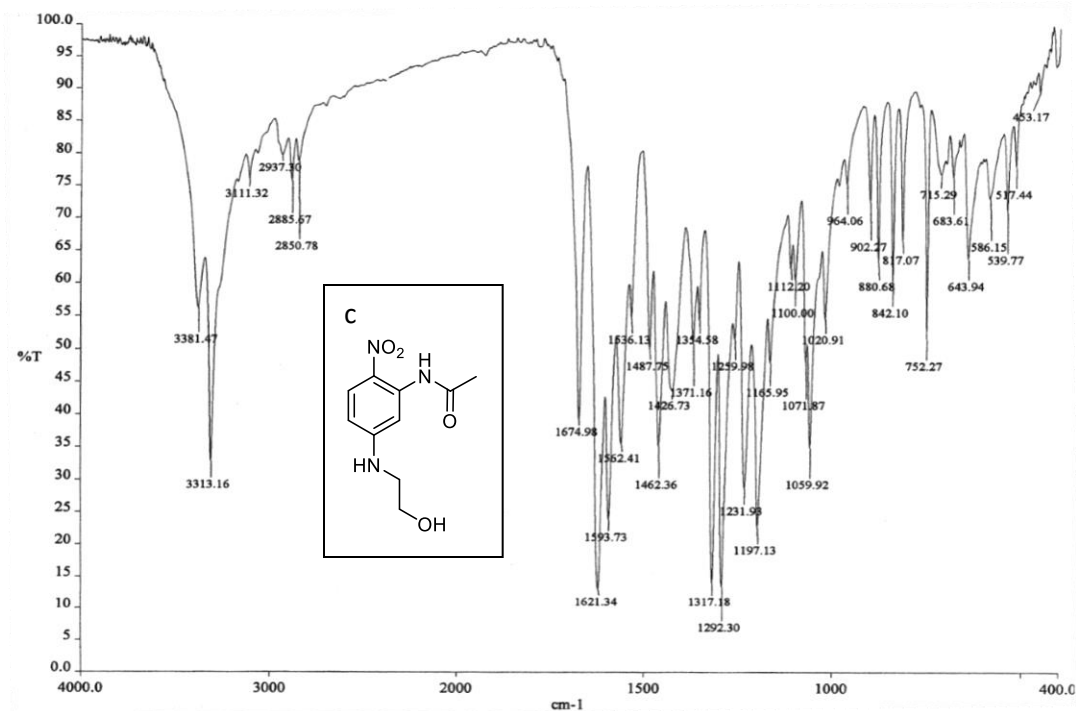
2-Nitro-5-anilinoaniline **5b**



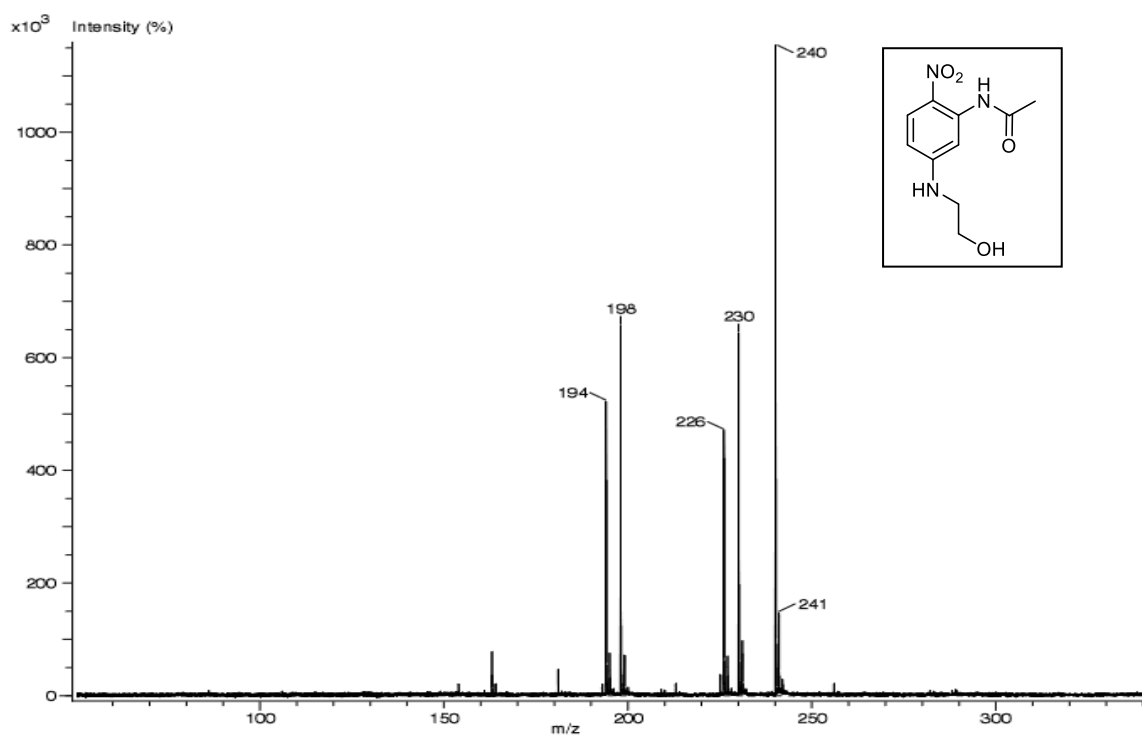
2-Nitro-5-anilinoaniline **5b**



2-Nitro-5-anilinoaniline **5b**



N-(5-(2-Hydroxyethylamino)-2-nitrophenyl)acetamide **3c**

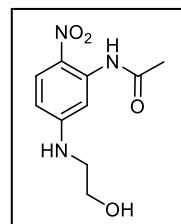
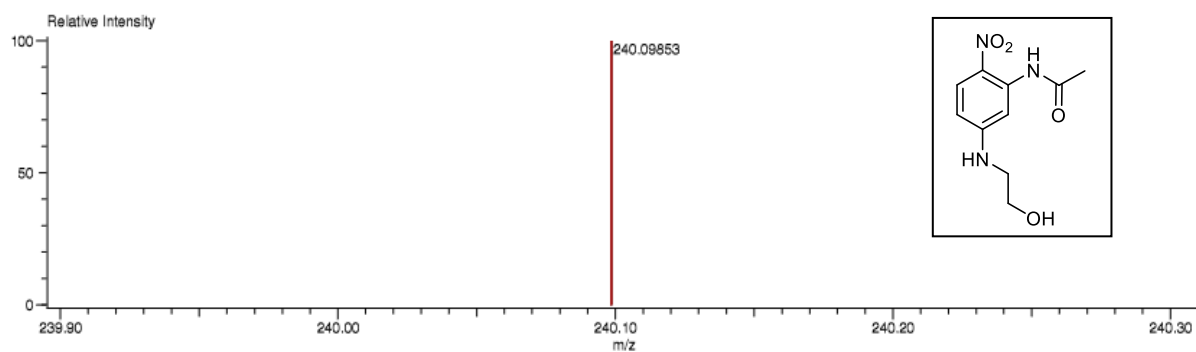


N-(5-(2-Hydroxyethylamino)-2-nitrophenyl)acetamide **3c**

Charge number:1
 Element:¹²C:0 .. 12, ¹H:0 .. 200, ¹⁴N:0 .. 4, ¹⁶O:0 .. 4

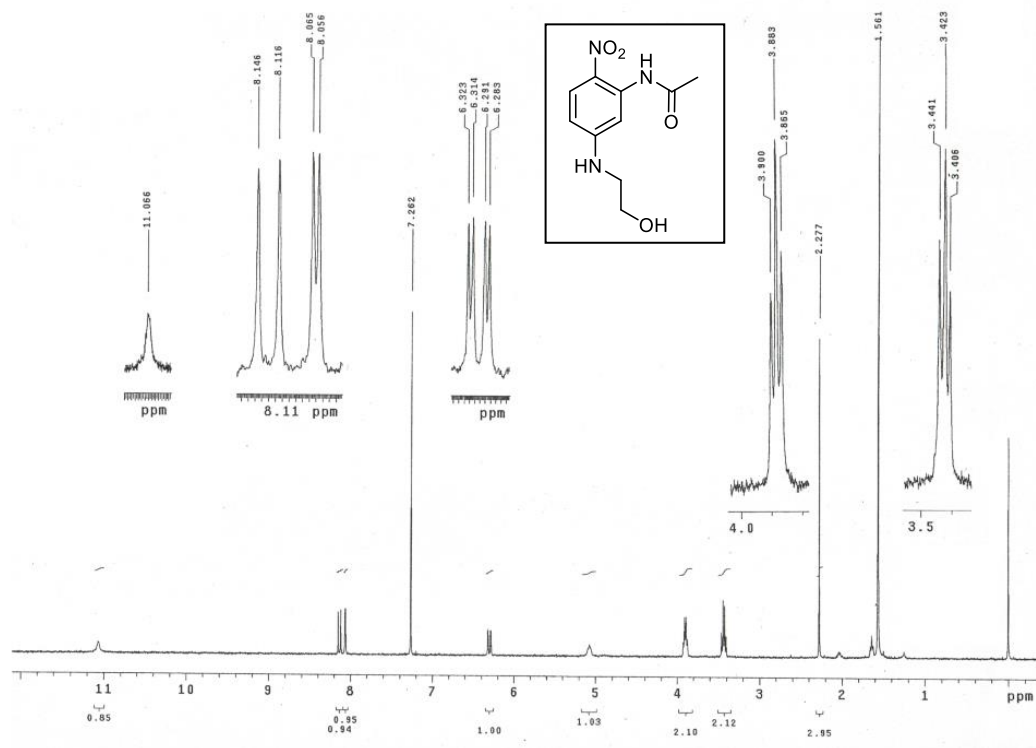
Tolerance:3.00(mmu)

Unsaturation Number:0.0 .. 14.0 (Fraction:Both)

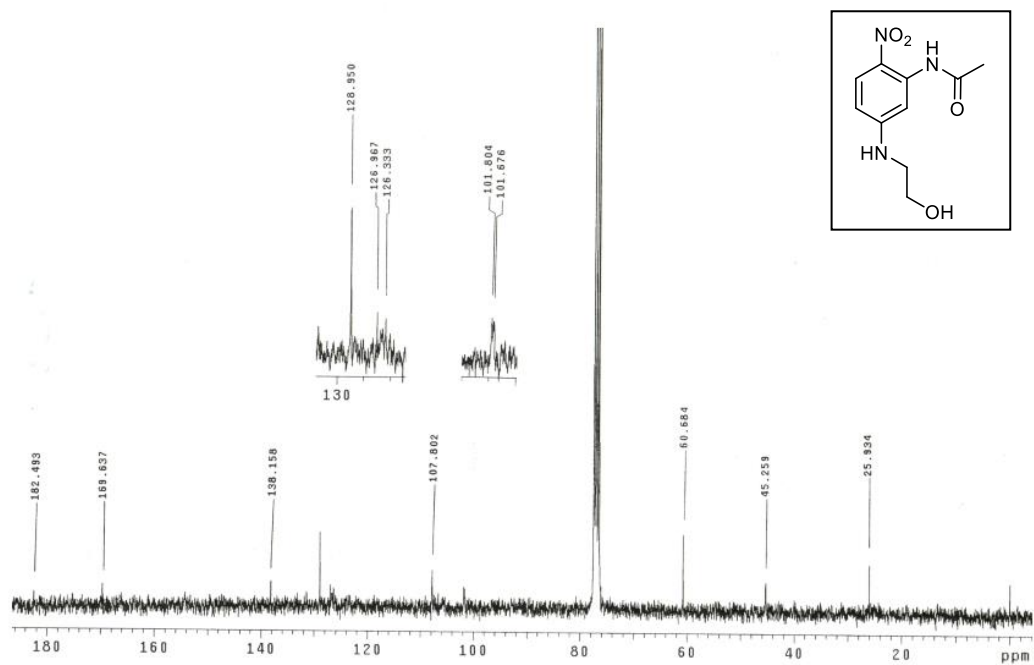


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
240.09853	23085.75	240.09843	0.10	0.42	¹² C ₁₀ ¹ H ₁₄ ¹⁴ N ₃ ¹⁶ O ₄	5.5

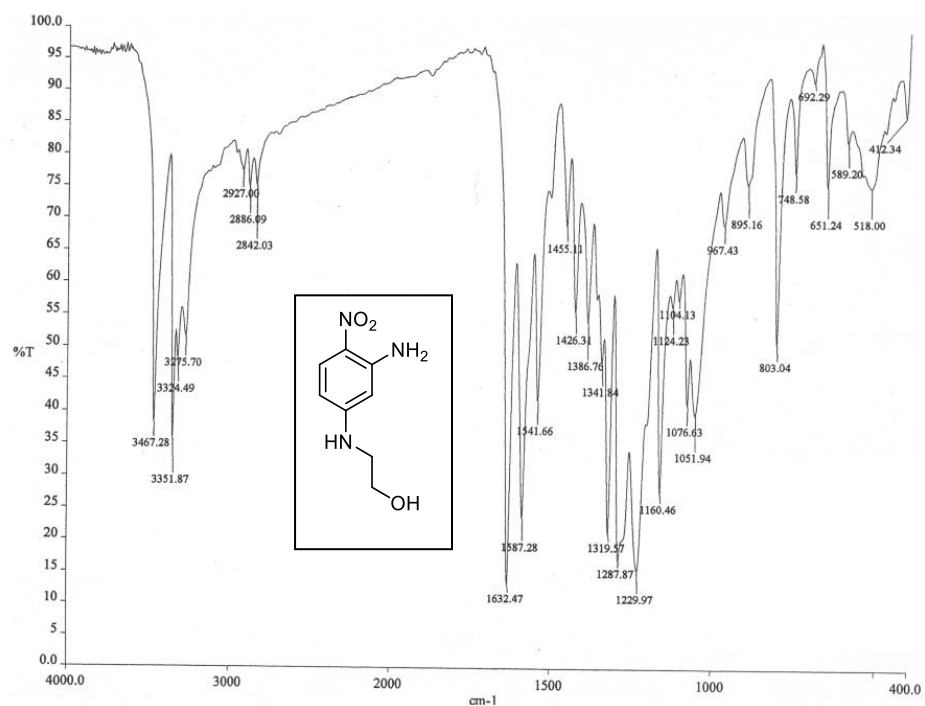
N-(5-(2-Hydroxyethylamino)-2-nitrophenyl)acetamide **3c**



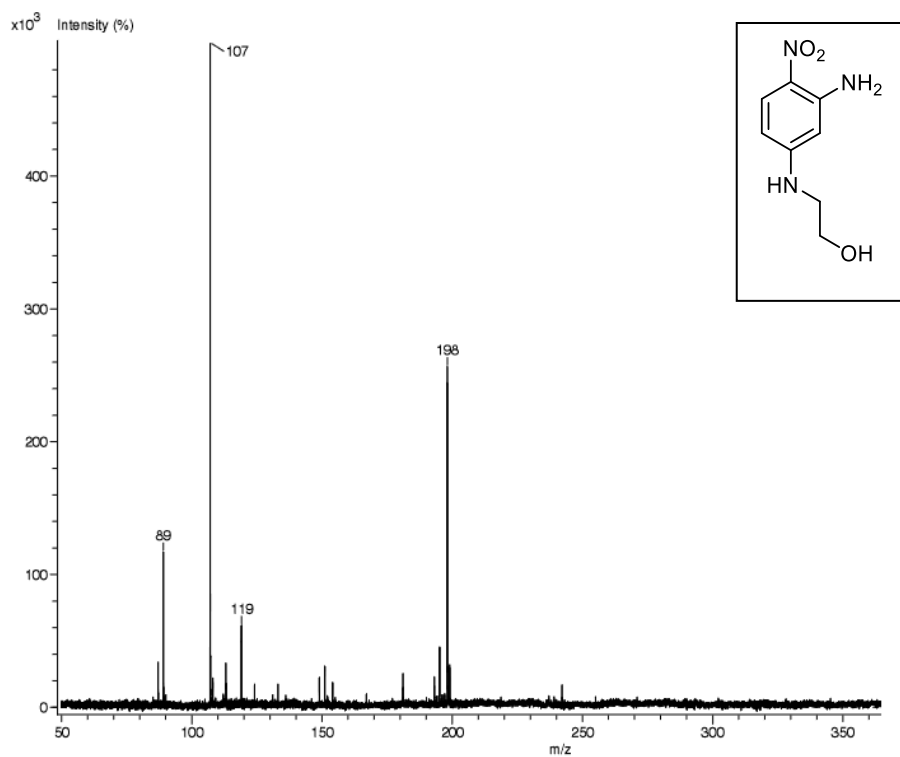
N-(5-(2-Hydroxyethylamino)-2-nitrophenyl)acetamide **3c**



N-(5-(2-Hydroxyethylamino)-2-nitrophenyl)acetamide **3c**

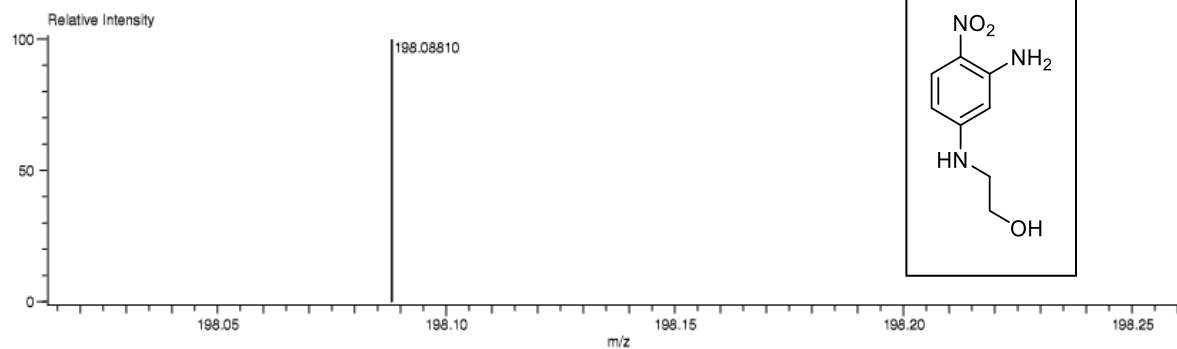


5-(2-Hydroxyethylamino)-2-nitroaniline **5c**



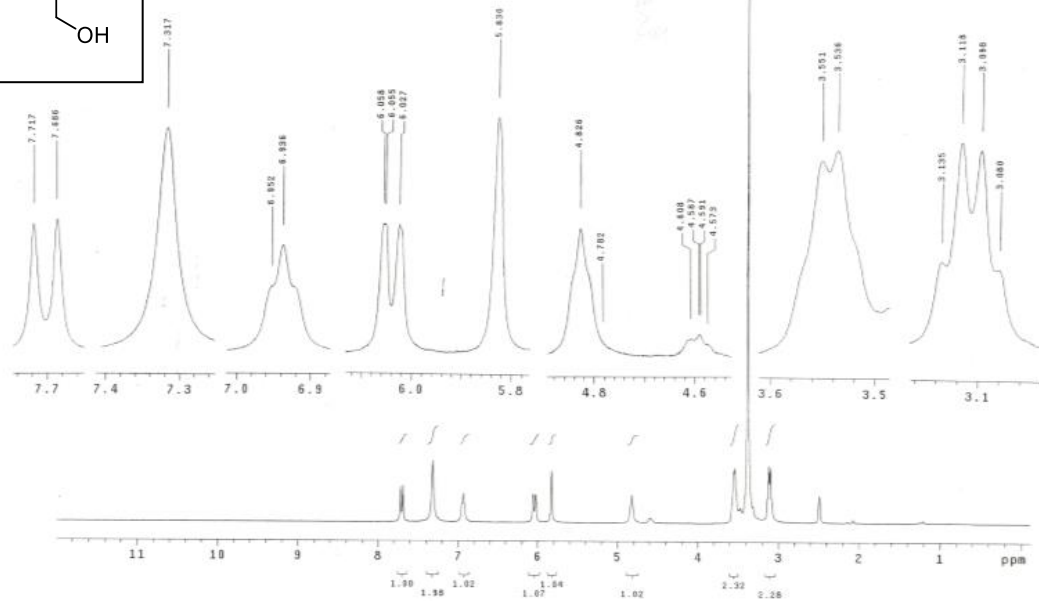
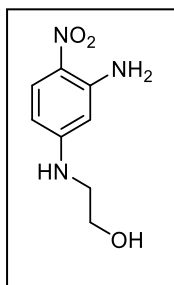
5-(2-Hydroxyethylamino)-2-nitroaniline 5c

Charge number:1 Tolerance:3.00(mmu) Unsaturation Number:0.0 .. 14.0 (Fraction:Both)
 Element:¹²C:0 .. 8, ¹H:0 .. 200, ¹⁴N:0 .. 3, ¹⁶O:0 .. 4



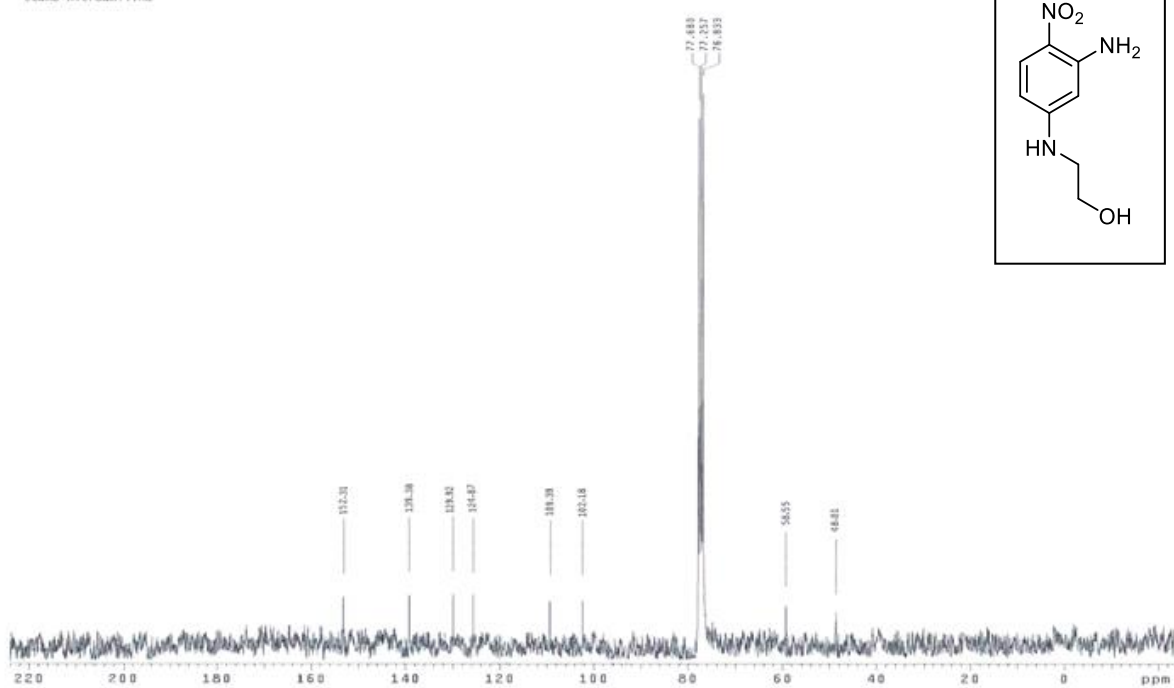
Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
198.08810	16035.25	198.08787	0.24	1.20	¹² C ₈ ¹ H ₁₂ ¹⁴ N ₃ ¹⁶ O ₃	4.5

5-(2-Hydroxyethylamino)-2-nitroaniline 5c

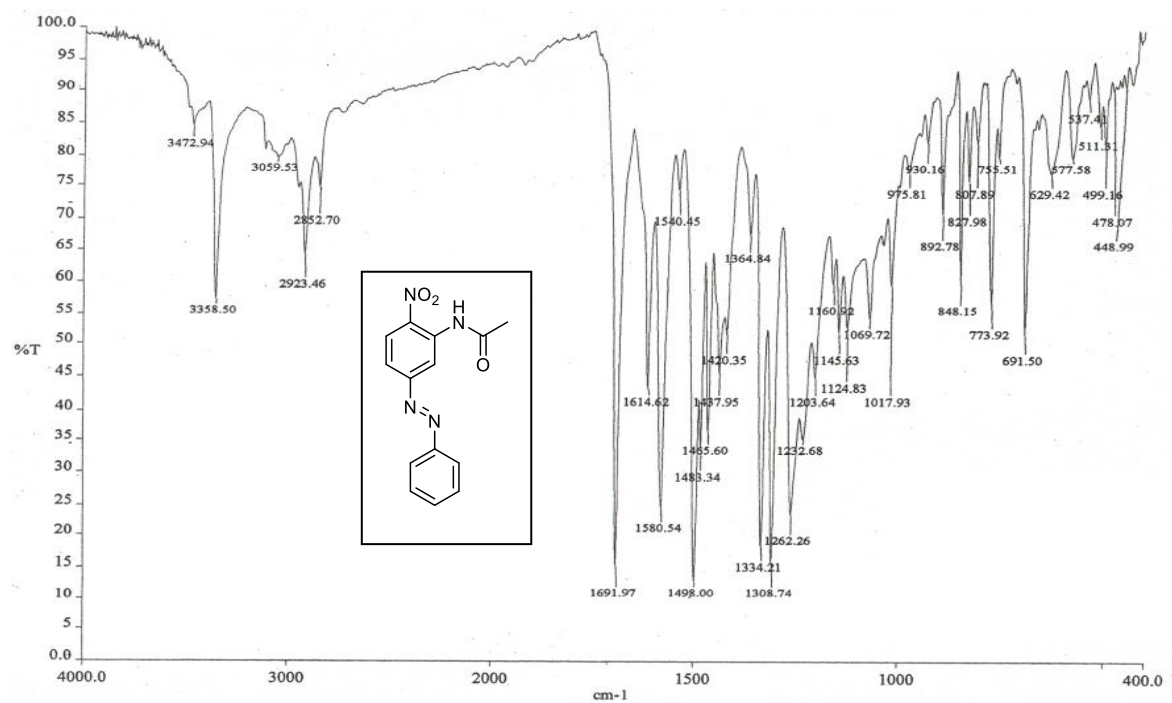


5-(2-Hydroxyethylamino)-2-nitroaniline 5c

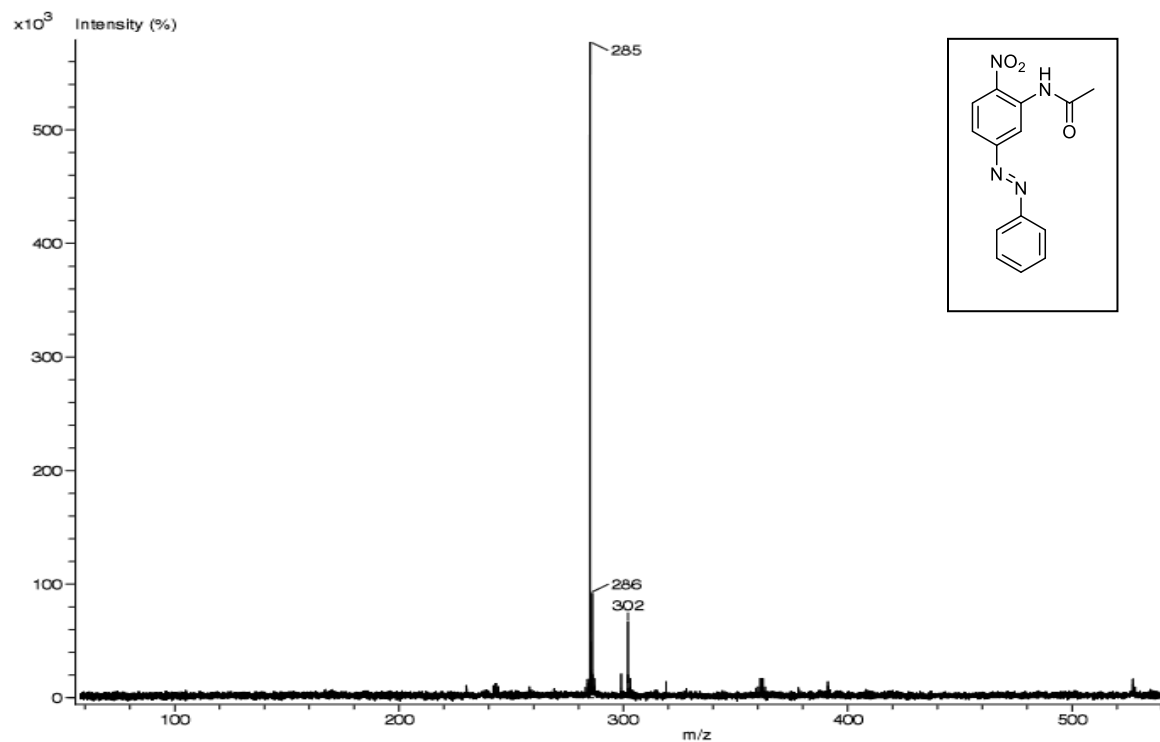
5-nitro-2-nitroaniline



5-(2-Hydroxyethylamino)-2-nitroaniline 5c



N-(2-Nitro-5-(phenyldiazenyl)phenyl)acetamide **3d**

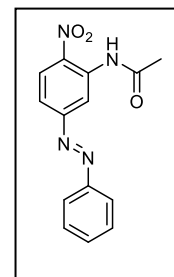
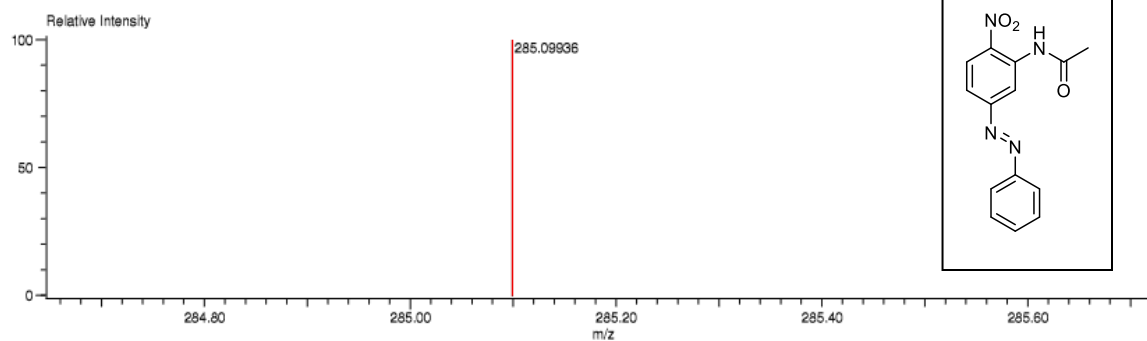


N-(2-Nitro-5-(phenyldiazenyl)phenyl)acetamide **3d**

Charge number:1
 Element:¹²C:0 .. 100, ¹H:0 .. 200, ¹⁴N:0 .. 4, ¹⁶O:0 .. 3

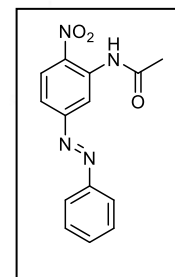
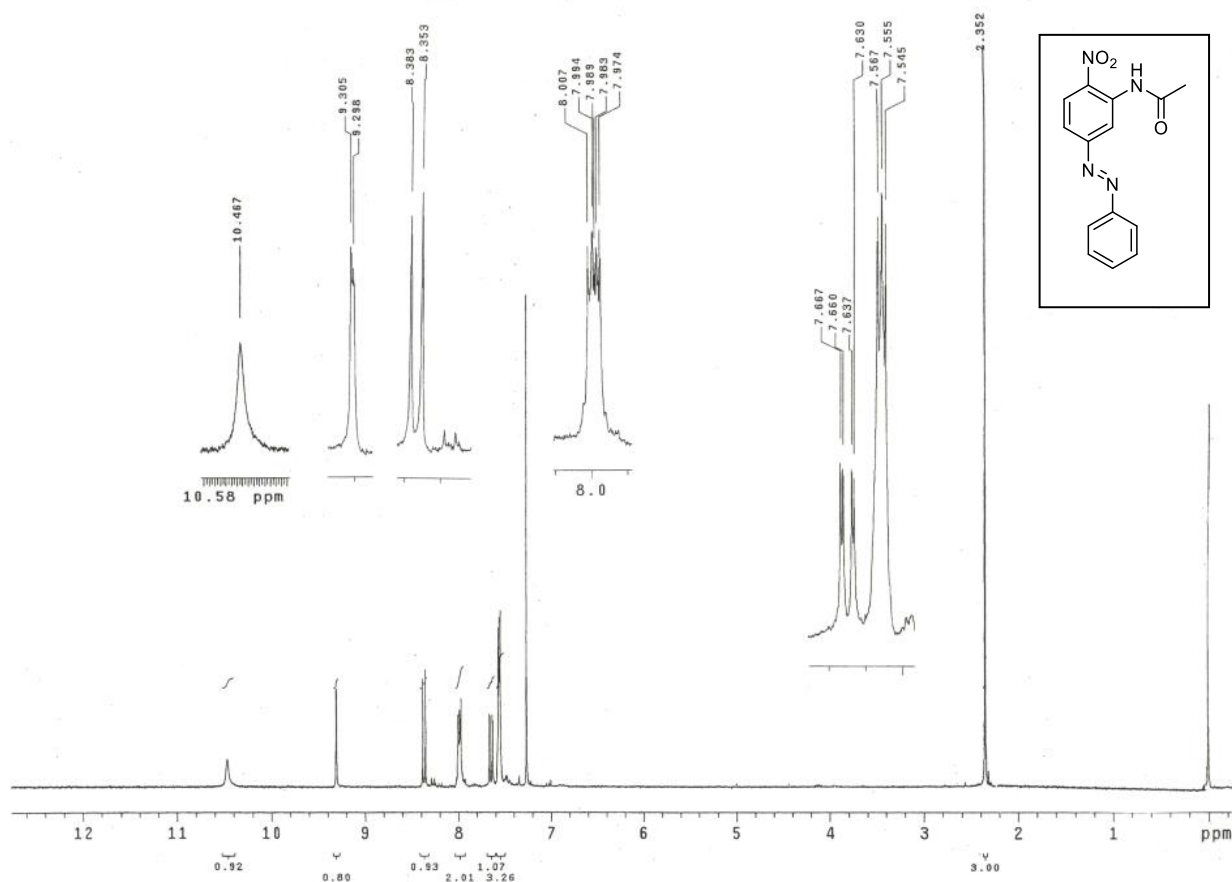
Tolerance:3.00(mmu)

Unsaturation Number:0.0 .. 14.0 (Fraction:Both)

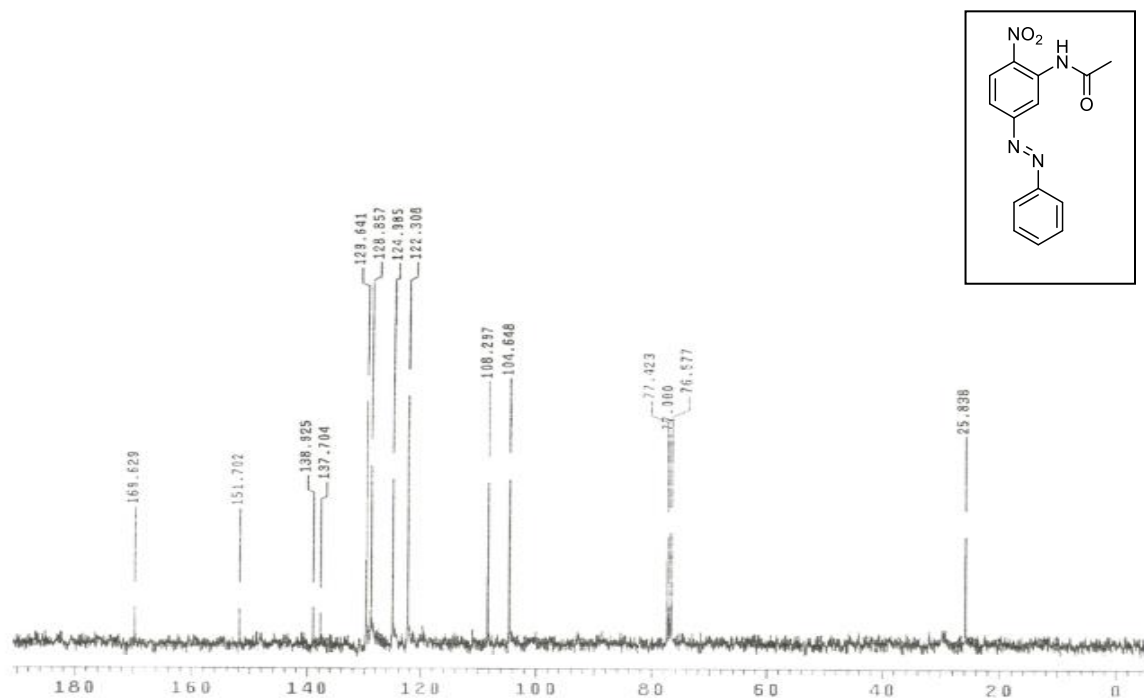


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
285.09936	33896.50	285.09876	0.59	2.07	¹² C ₁₄ ¹ H ₁₃ ¹⁴ N ₄ ¹⁶ O ₃	10.5

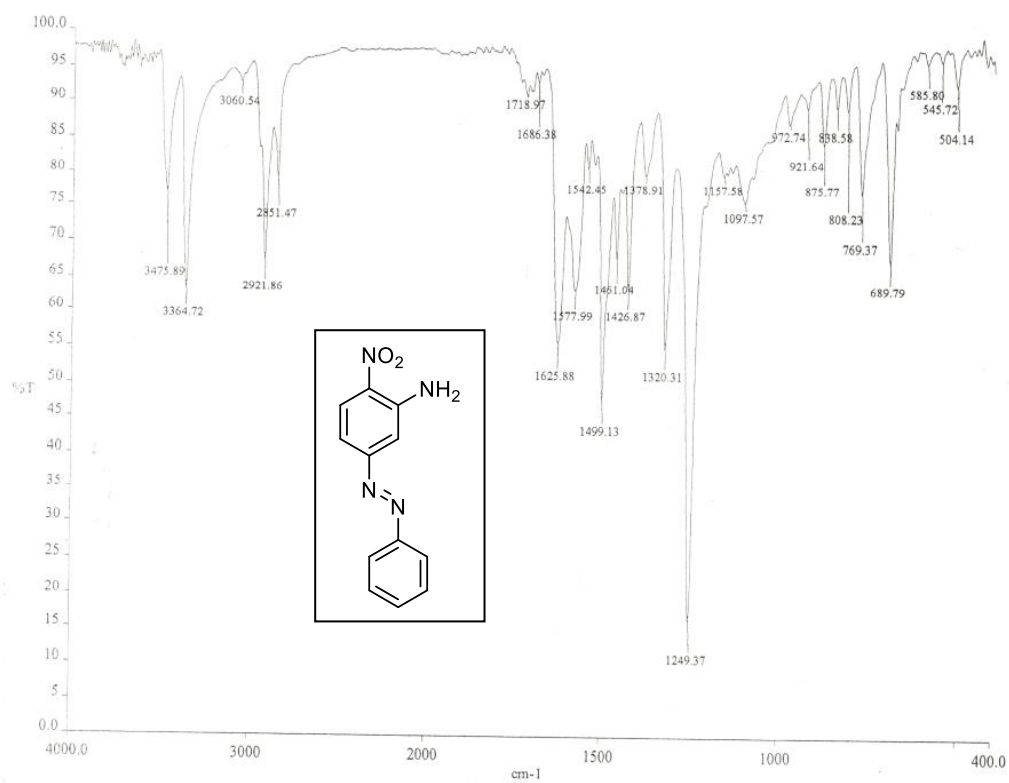
N-(2-Nitro-5-(phenyldiazenyl)phenyl)acetamide **3d**



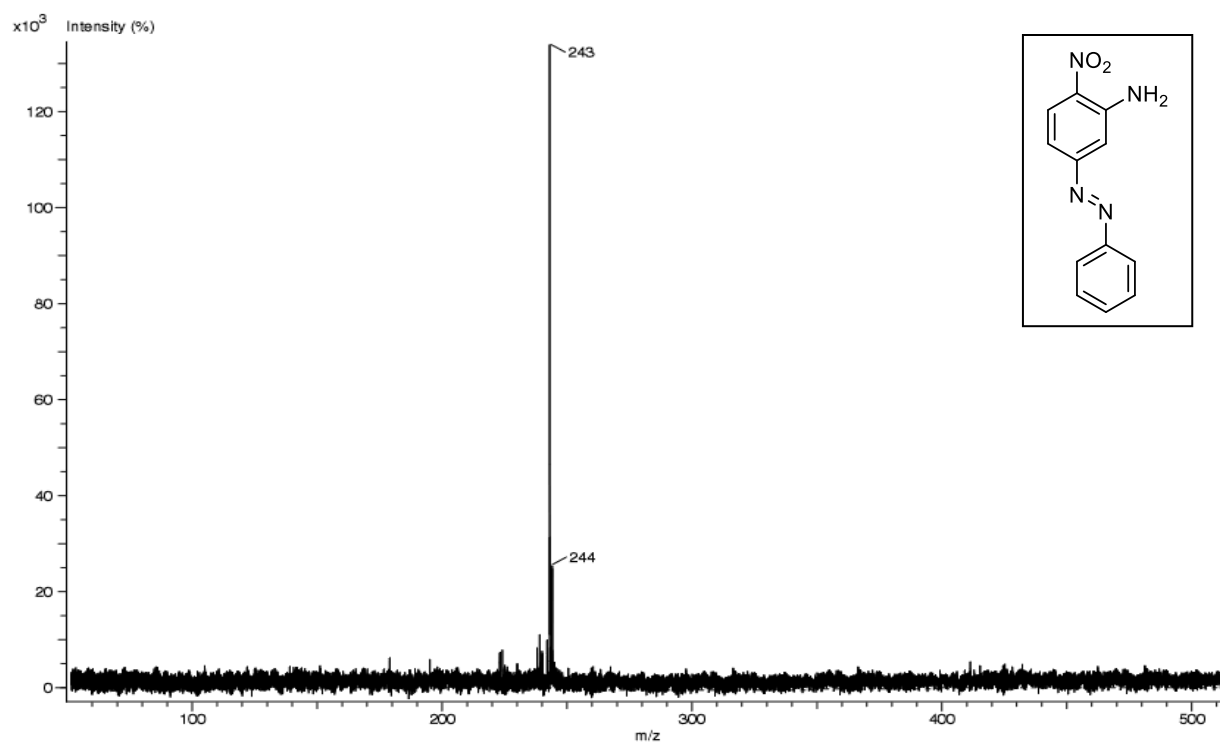
N-(2-Nitro-5-(phenyldiazenyl)phenyl)acetamide **3d**



N-(2-Nitro-5-(phenyldiazenyl)phenyl)acetamide 3d

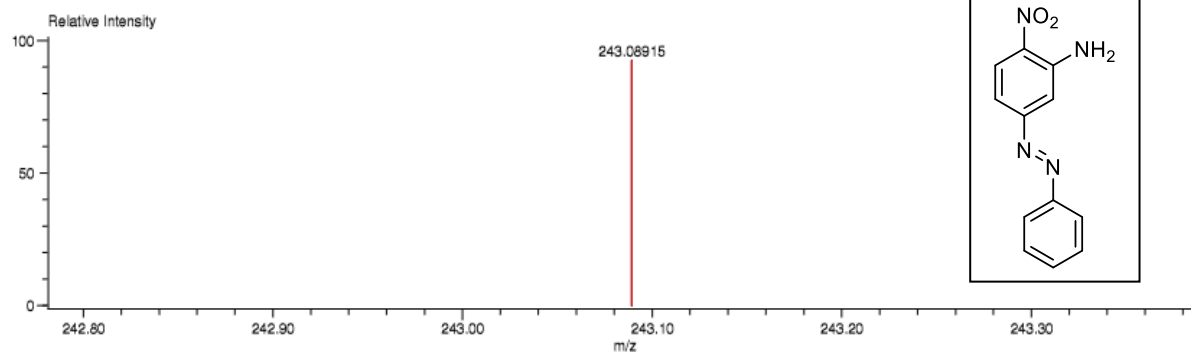


2-Nitro-5-(phenyldiazenyl)aniline 5d



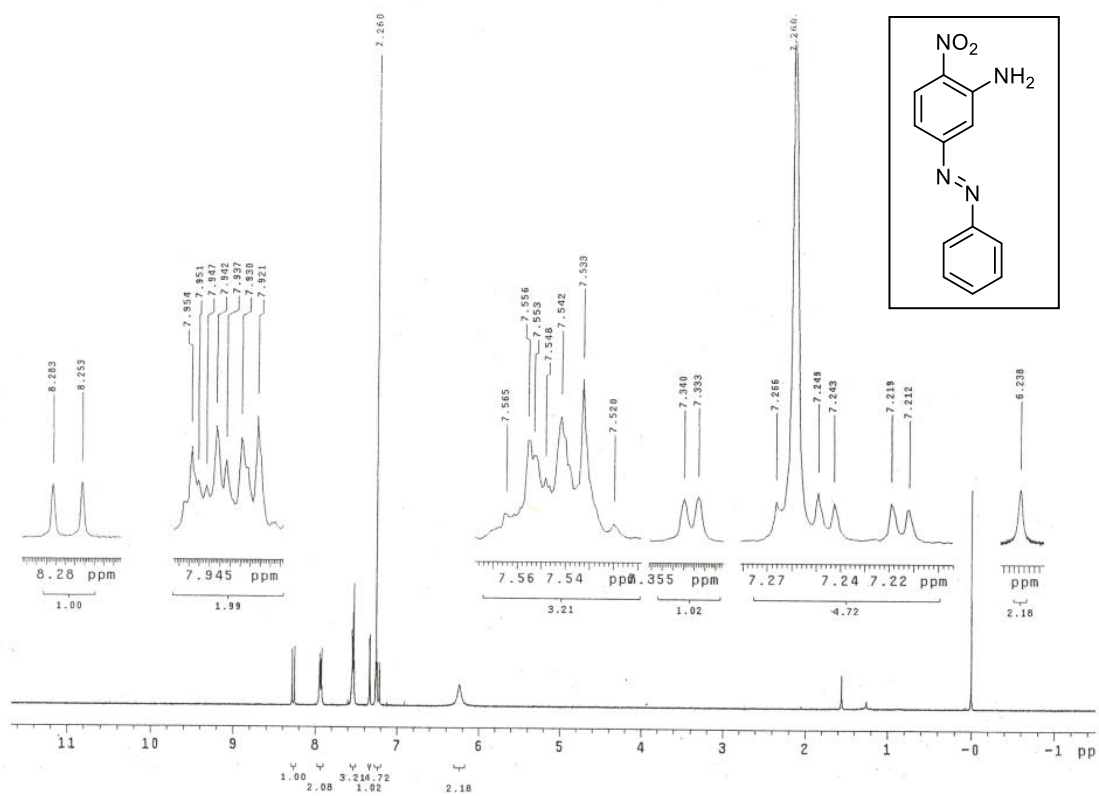
2-Nitro-5-(phenyldiazenyl)aniline **5d**

Charge number:1
 Element:¹²C:0 .. 12, ¹H:0 .. 200, ¹⁴N:0 .. 4, ¹⁶O:0 .. 3
 Tolerance:3.00(mmu)
 Unsaturation Number:0.0 .. 14.0 (Fraction:Both)

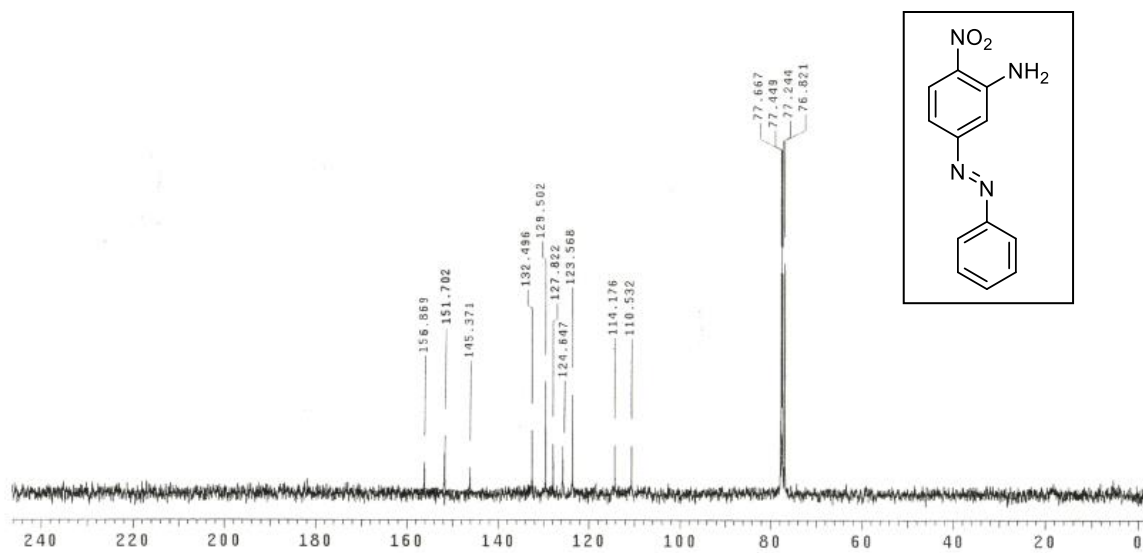


Mass	Intensity	Calc. Mass	Mass Difference (mmu)	Mass Difference (ppm)	Possible Formula	Unsaturation Number
243.08915	1080.13	243.08820	0.95	3.90	¹² C ₁₂ ¹ H ₁₁ ¹⁴ N ₄ ¹⁶ O ₂	9.5

2-Nitro-5-(phenyldiazenyl)aniline **5d**



2-Nitro-5-(phenyldiazenyl)aniline **5d**



2-Nitro-5-(phenyldiazenyl)aniline **5d**