Bimetallic Au-Pd nanoparticles supported on silica with tunable core@shell structure: Enhanced catalytic activity of Pd(core)-Au(shell) over Au(core)-Pd(shell)

*Gauravjyoti D. Kalita[a], Podma P. Sarmah[a], Golap Kalita[b], Pankaj Das[a]**

[a]Department of Chemistry, Dibrugarh University, Dibrugarh, Assam, India, 786004.
[b]Department of Physical Science and Engineering, Nagoya Institute of Technology (NiTech), Nagoya, Aichi, Japan-466-8555.

Supporting Information

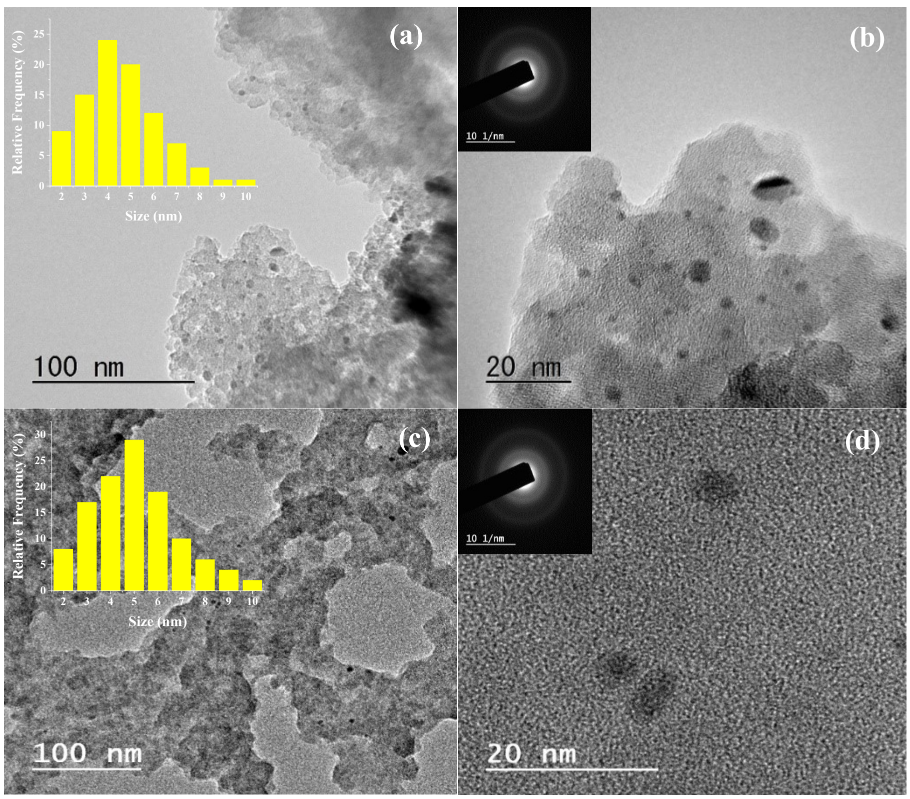


Fig. S1 (a) TEM image and size-distribution histogram (50 particles per site count) of SiO_2@Au with corresponding **(b)** HRTEM image and SAED pattern depicted on inset; **(c)** TEM image and size-distribution histogram (50 particles per site count) of SiO_2@Pd with corresponding **(d)** HRTEM image and SAED pattern depicted on inset

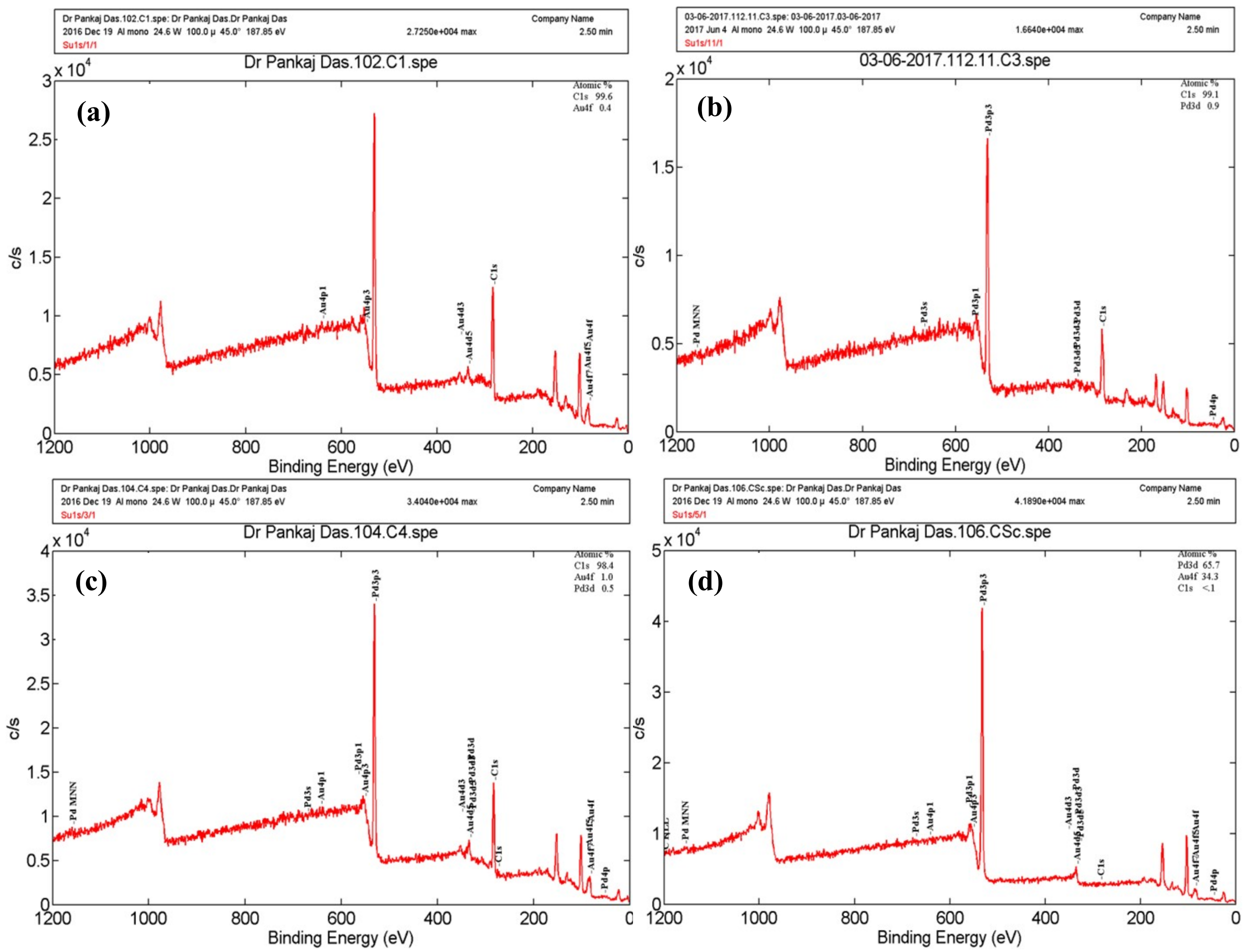


Fig. S2 XPS survey spectrum of the as prepared **(a)** SiO_2@Au, **(b)** SiO_2@Pd **(c)** Pd@Au-SiO_2 and **(d)** Au@Pd-SiO_2 materials

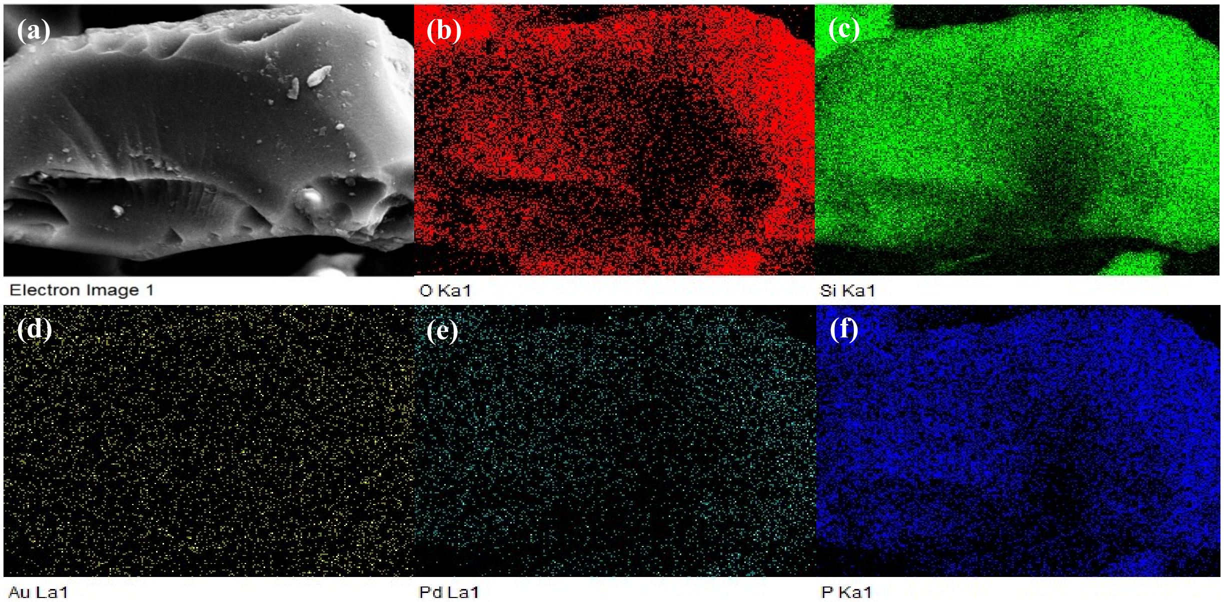


Fig. S3 FESEM-EDS images **(a)** electron image with corresponding elemental distributions **(b)** O Ka 1 **(c)** Si Ka1 **(d)** Au La1 **(e)** Pd La1 **(f)** P Ka1 of nanoparticle incorporated Pd@Au-SiO_2 material

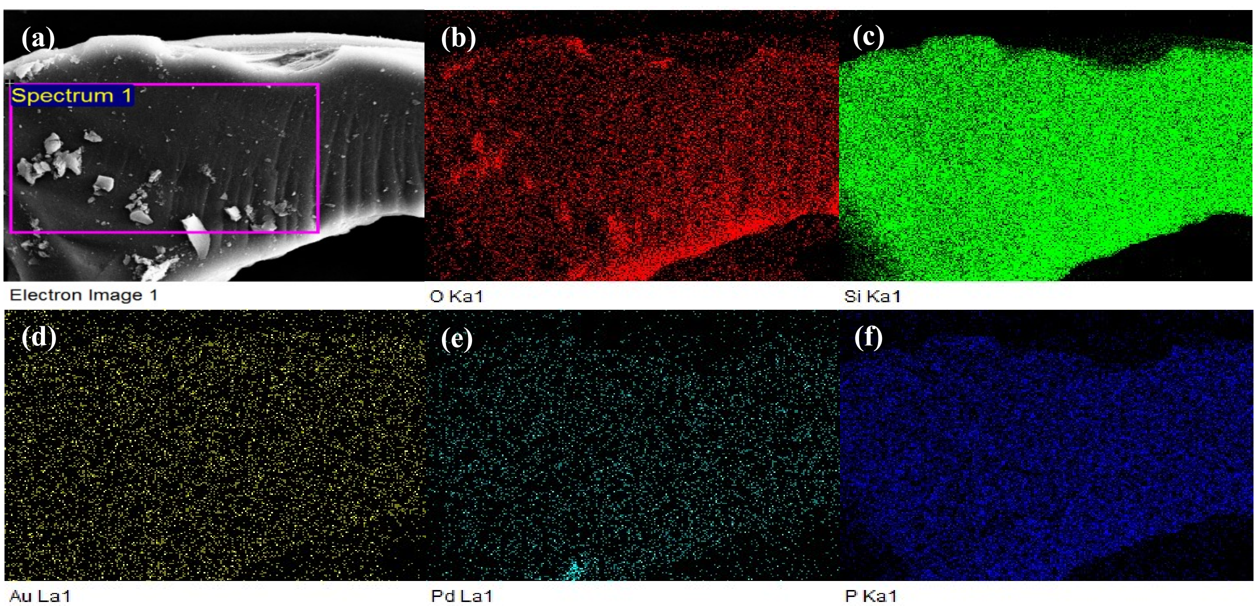


Fig. S4 FESEM-EDS images **(a)** electron image with corresponding elemental distributions **(b)** O Ka 1 **(c)** Si Ka1 **(d)** Au La1 **(e)** Pd La1 **(f)** P Ka1 of nanoparticle incorporated Au@Pd-SiO_2 material

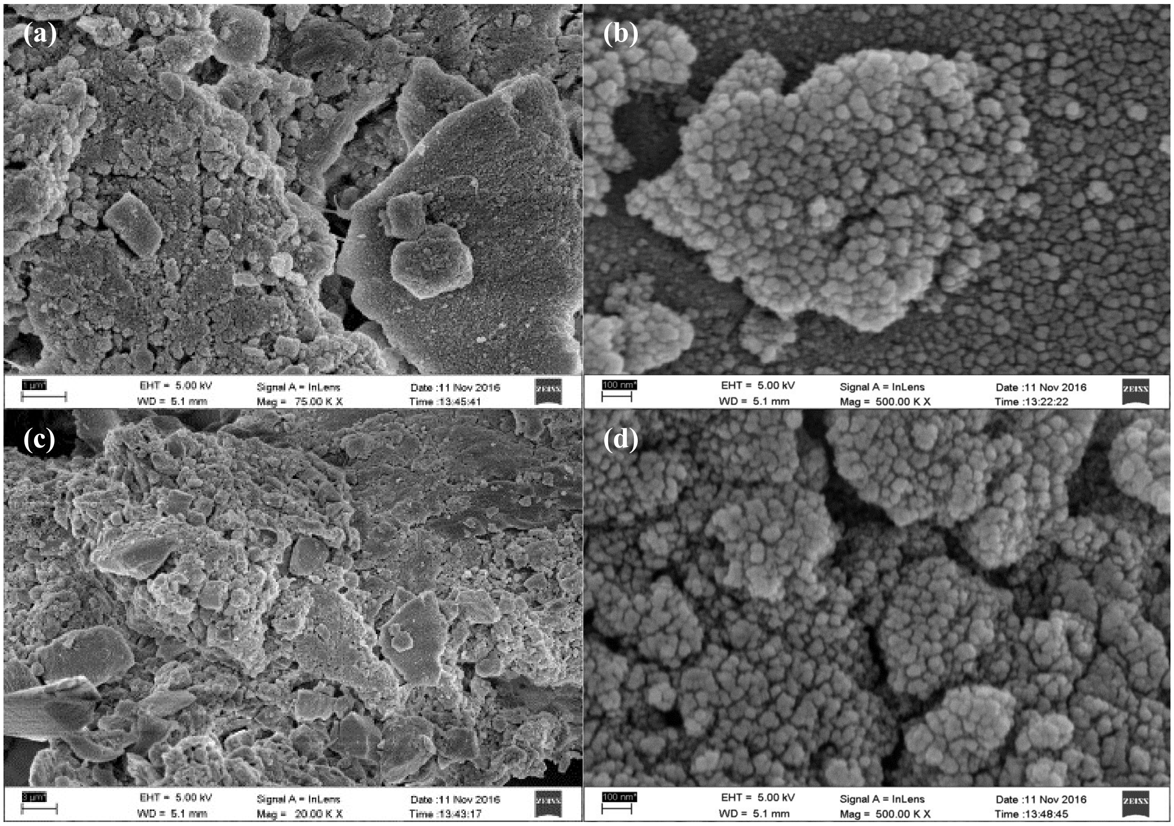


Fig. S5 FESEM images **(a)** and **(b)** for Pd@Au-SiO_2; and **(c)** and **(d)** for Au@Pd-SiO_2

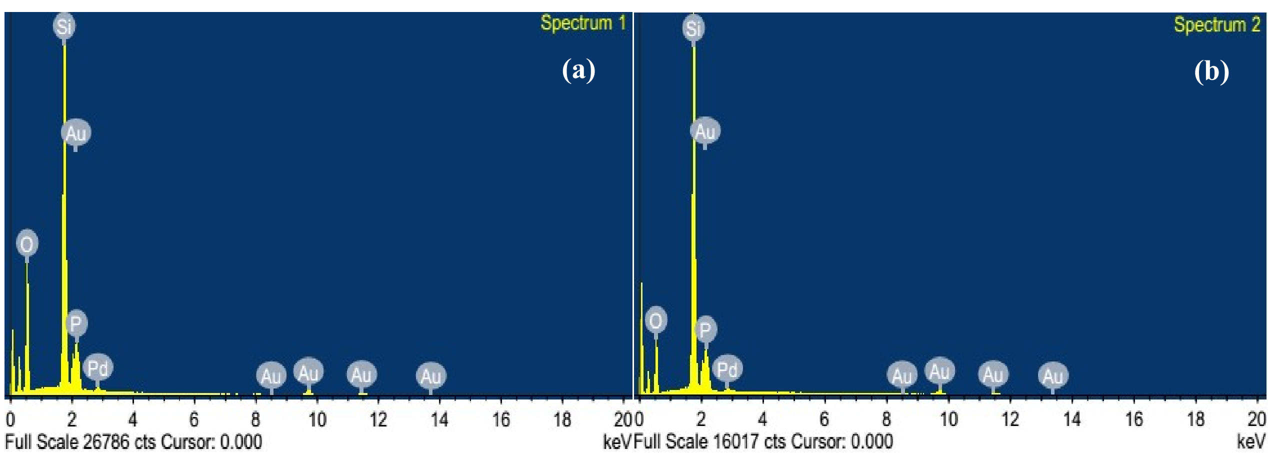


Fig. S6 FESEM-EDX spectra of **(a)** Pd@Au-SiO_2 and **(b)** Au@Pd-SiO_2

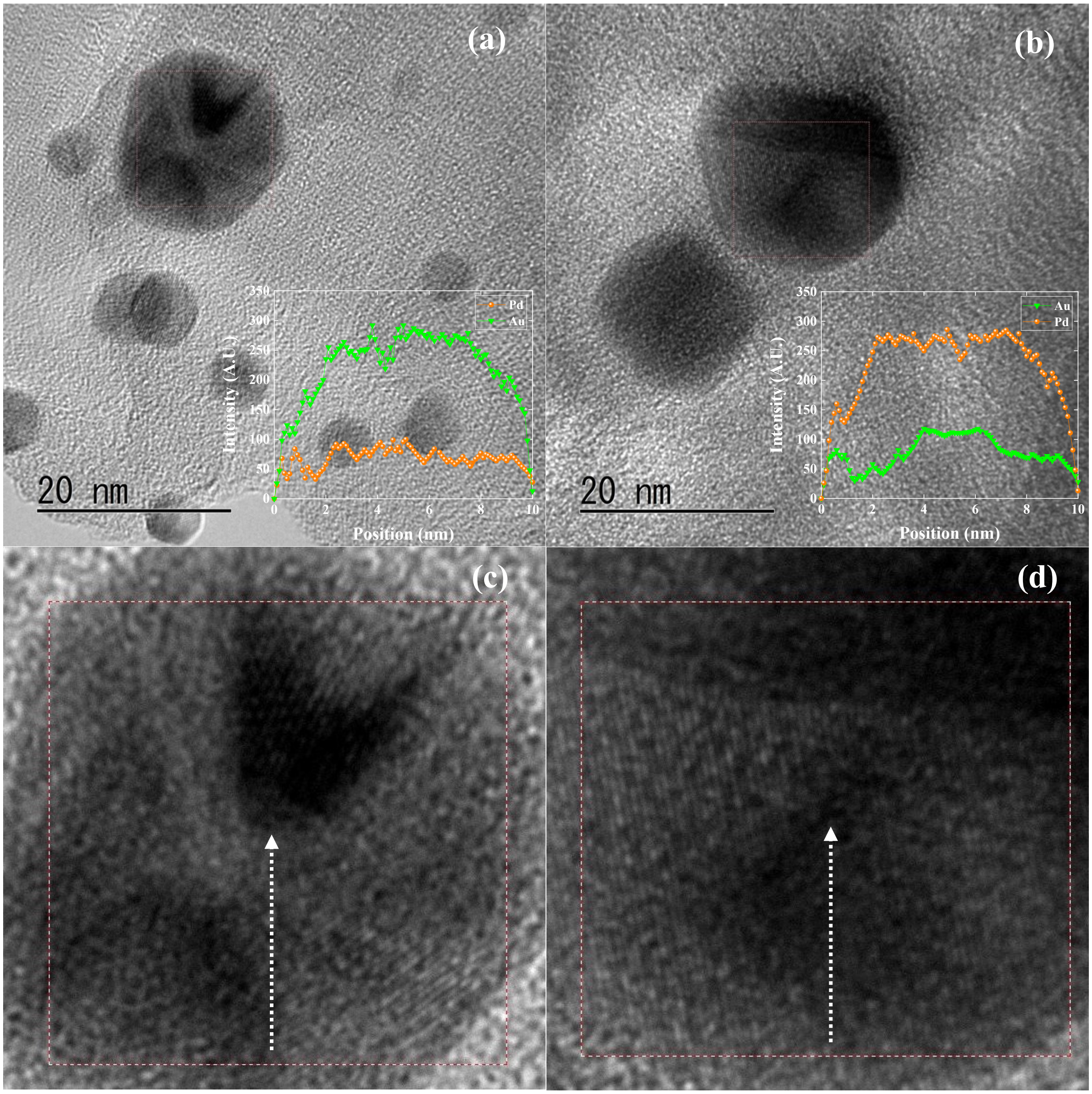


Fig. S7 TEM micrographs and line scan profiles (inset) for **(a)** Au@Pd-SiO_2 and **(b)** Pd@Au-SiO_2 along with the respective scanned cross-sections for **(c)** Au@Pd-SiO_2 and **(d)** Pd@Au-SiO_2

Table S1 Hydrogenation of 4-CNB with Pd@Au-SiO_2 core-shell nanoparticles as catalysts under liquid phase conditions [a]

Entry	Solvent	Reductant	Substrate (mmol)	Time (h)	Conversion [%] [b]	Selectivity [%] [b, c]
1	EtOH	NH_3. BH_3	2	5	44	86
2	EtOH	$HCOONH_4$	2	1	18	99
3	EtOH	HCOOH	2	1	20	99
4	EtOH	H_2	2	1	4	99
5	EtOH	N_2H_4. H_2O	2	0.5	42	99
6	EtOH	N_2H_4. H_2O	2	1	88	98
7	EtOH	N_2H_4. H_2O	2	2	98	88
8	EtOH	N_2H_4. H_2O	4	1	76	96
9	EtOH	Ethanol	2	5	NR	-
10	*i*-PrOH	*i*-PrOH	2	5	NR	-
11	EtOH	$NaBH_4$	2	3	35	80
12	EtOH	Ascorbic acid	2	24	2	99

[a] Reaction conditions: Pd@Au-SiO_2 [Au (0.13 mol%), Pd (0.15 mol%)], ethanol (5 mL), 400 rpm at 80°C, **[b]** Determined by GC-MS analysis, **[c]** Aniline (AN) was formed as the sole by-product **[d]** H_2 gas pressure was maintained at 1 bar.

Table S2 Comparison of catalytic efficiency of Pd@Au-SiO_2 with different solvents for hydration of benzonitrile [a]

Entry	Solvent (ratio)	Time (h)	Conversion (%) [c]	Selectivity (%) [c]
1	H_2O (Neat)	24	-	99
2	EtOH: H_2O (1:1)	10	64	99
3	EtOH: H_2O (1:10)	10	Trace	99
4	DMSO	8	62	99
5	MeOH: H_2O (1:1)	5	89	99
6	MeOH: H_2O (1:10)	12	60	99
7	^{i}PrOH: H_2O (1:1)	1	90	99
8[b]	^{i}PrOH: H_2O (1:1)	1	95	99
9	^{i}PrOH: H_2O (1:5)	1	36	99
10	^{i}PrOH: H_2O (1:10)	1	Trace	99

[a] Reaction conditions: Benzonitrile (0.5 mmol), Pd@Au-SiO_2 [Au (0.09 mol%), Pd (0.11 mol%)], solvent (4 mL), 400 rpm, 50^{o}C, **[b]** 60^{o}C, **[c]** Determined by GC-MS analysis.

Table S3 Hydration of benzonitrile with Pd@Au-SiO_2 core-shell nanoparticles as catalysts under liquid phase conditions [a]

Entry	Substrate (mmol)	Temperature (^{o}C)	Time (min)	Conversion [%] [b]	Selectivity [%] [b]
1	0.5	40	60	78	99
2	0.5	50	60	90	99
3	0.5	60	20	34	99
4	0.5	60	40	69	99
5	0.5	60	60	95	99
6	1	60	60	85	99
7	0.5	70	60	97	99
8	0.5	80	60	96	99

[a] Reaction conditions: Pd@Au-SiO_2 [Au (0.09 mol%), Pd (0.11 mol%)], ^{i}PrOH: H_2O (1:1) (4 mL) and 400 rpm, **[b]** Determined by GC-MS analysis

Calculation of shell widths from XPS peak intensities

High-resolution XPS spectra were taken (Figure 5b and 5c), from which the peak areas of C 1s, Pd 3d and Au 4f were measured and the ratios A_C/A_{Pd}, A_C/A_{Au} and A_{Pd}/A_{Au} were calculated.

where, A_C = Absorption intensity of C_{1s} peak,

A_{Pd} = Absorption intensity of $Pd_{3d_{3/2}}$ peak, and

A_{Au} = Absorption intensity of $Au_{4f_{5/2}}$ peak.

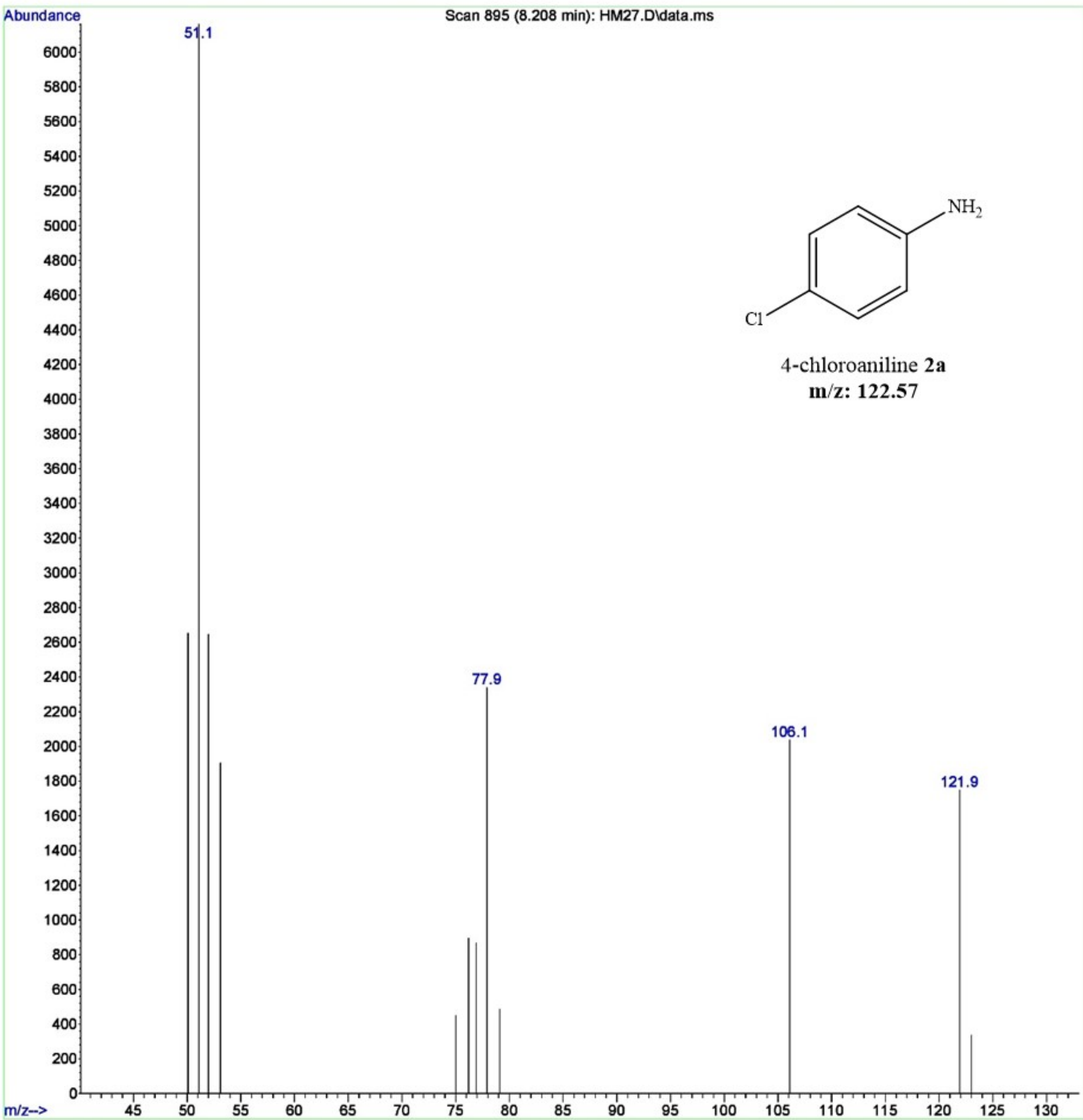
This reference method was adopted from a recent work by Yan et al.[1] that involved a similar calculation[2] with XPS binding energies for thiol functionalized Au NPs.

GC-Mass spectra of Products

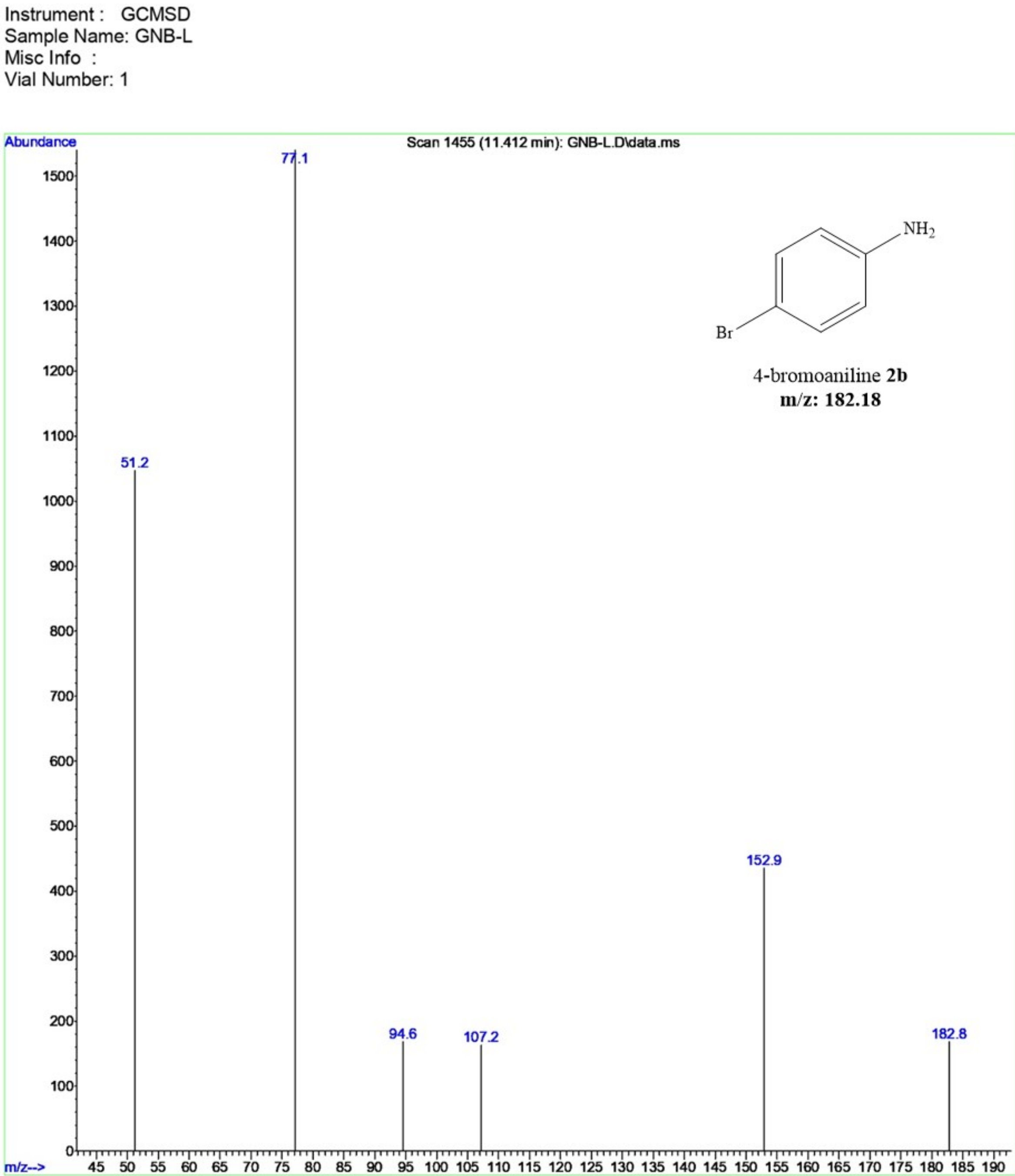
Hydrogenation

4-chloroaniline

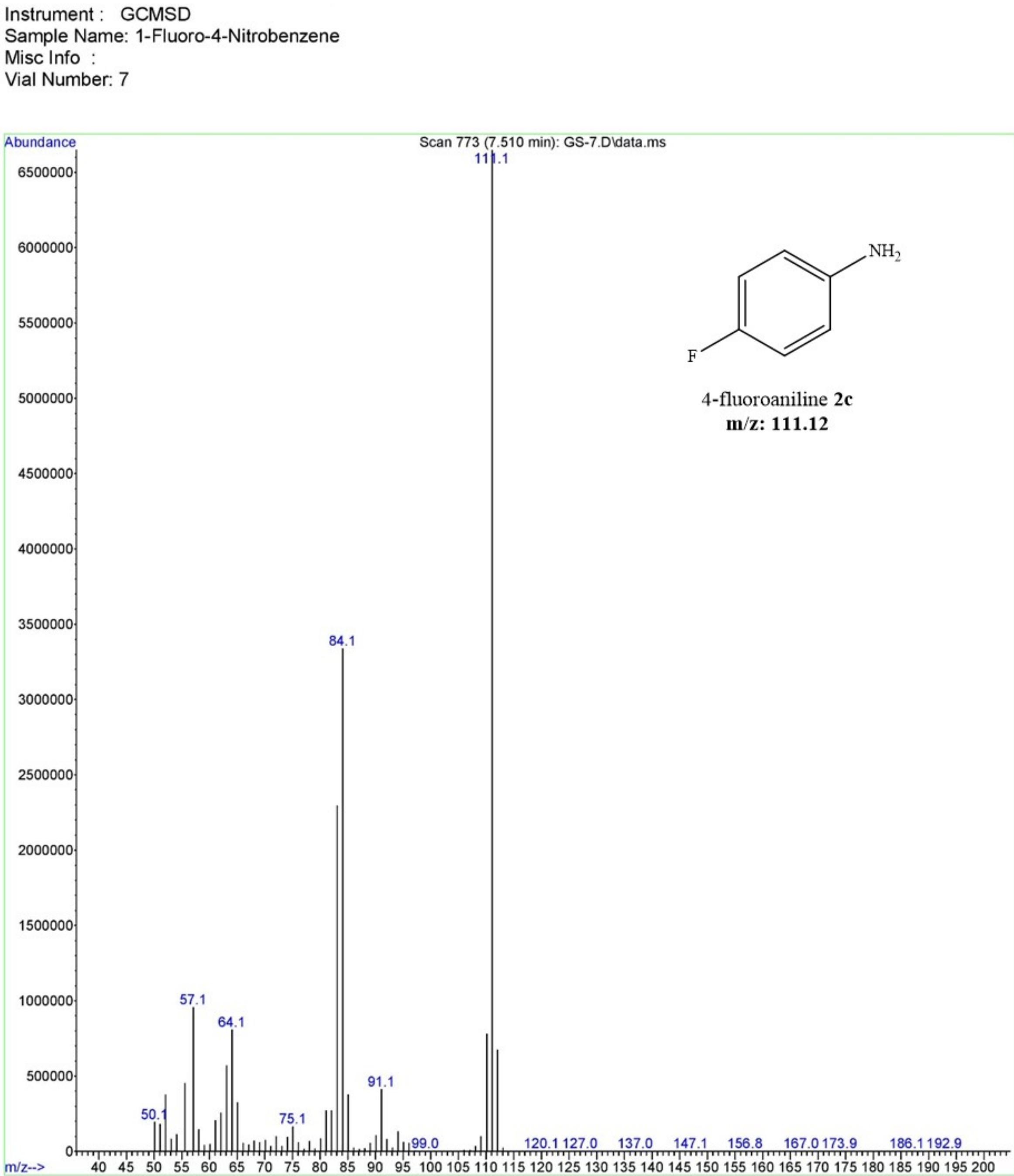
Instrument : GCMSD
Sample Name: HM27
Misc Info :
Vial Number: 1



4-bromoaniline

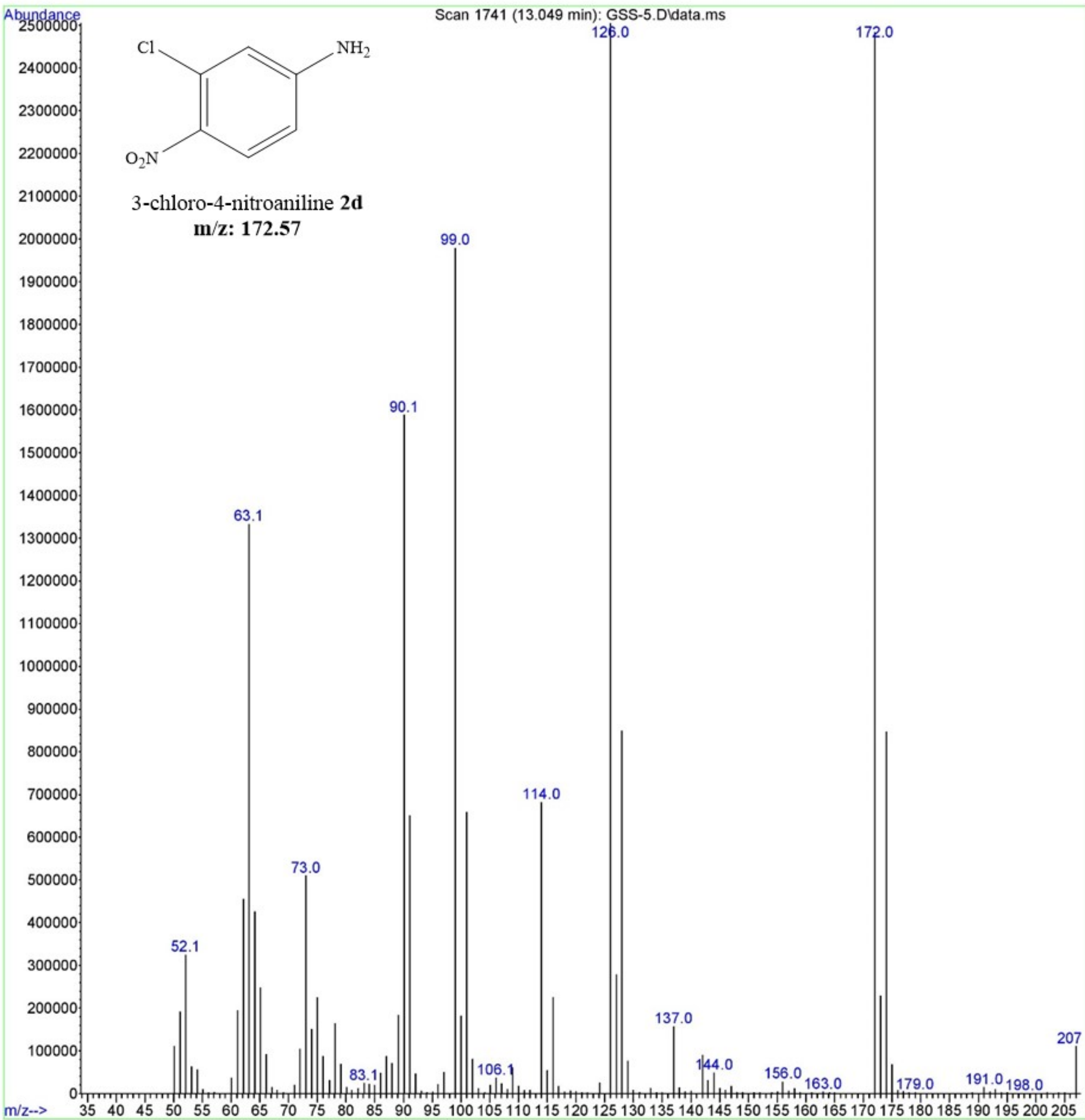


4-fluoroaniline



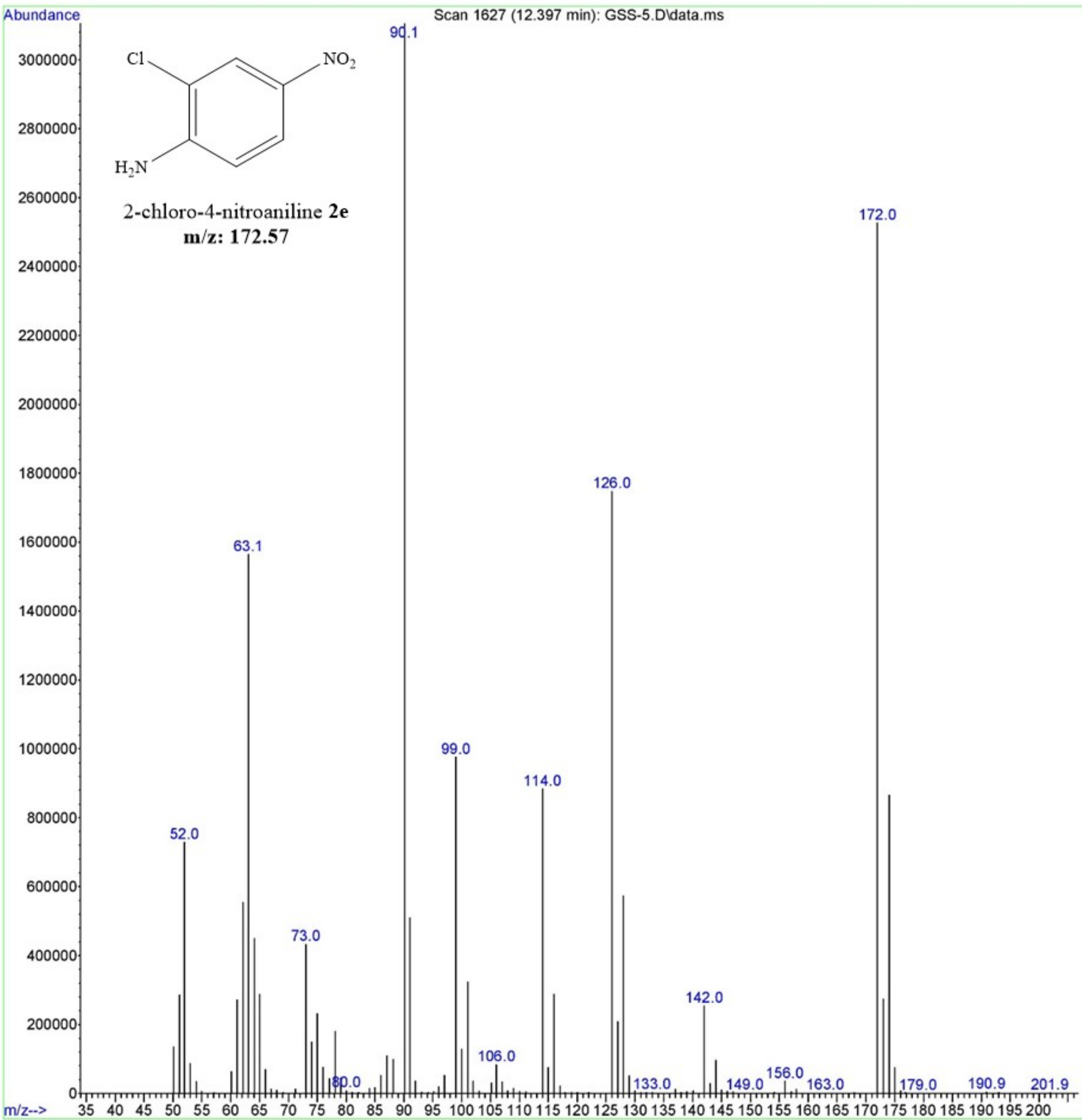
3-chloro-4-nitroaniline

Instrument : GCMSD
Sample Name: 1-Chloro-2,5-Dinitrobenzene
Misc Info :
Vial Number: 5



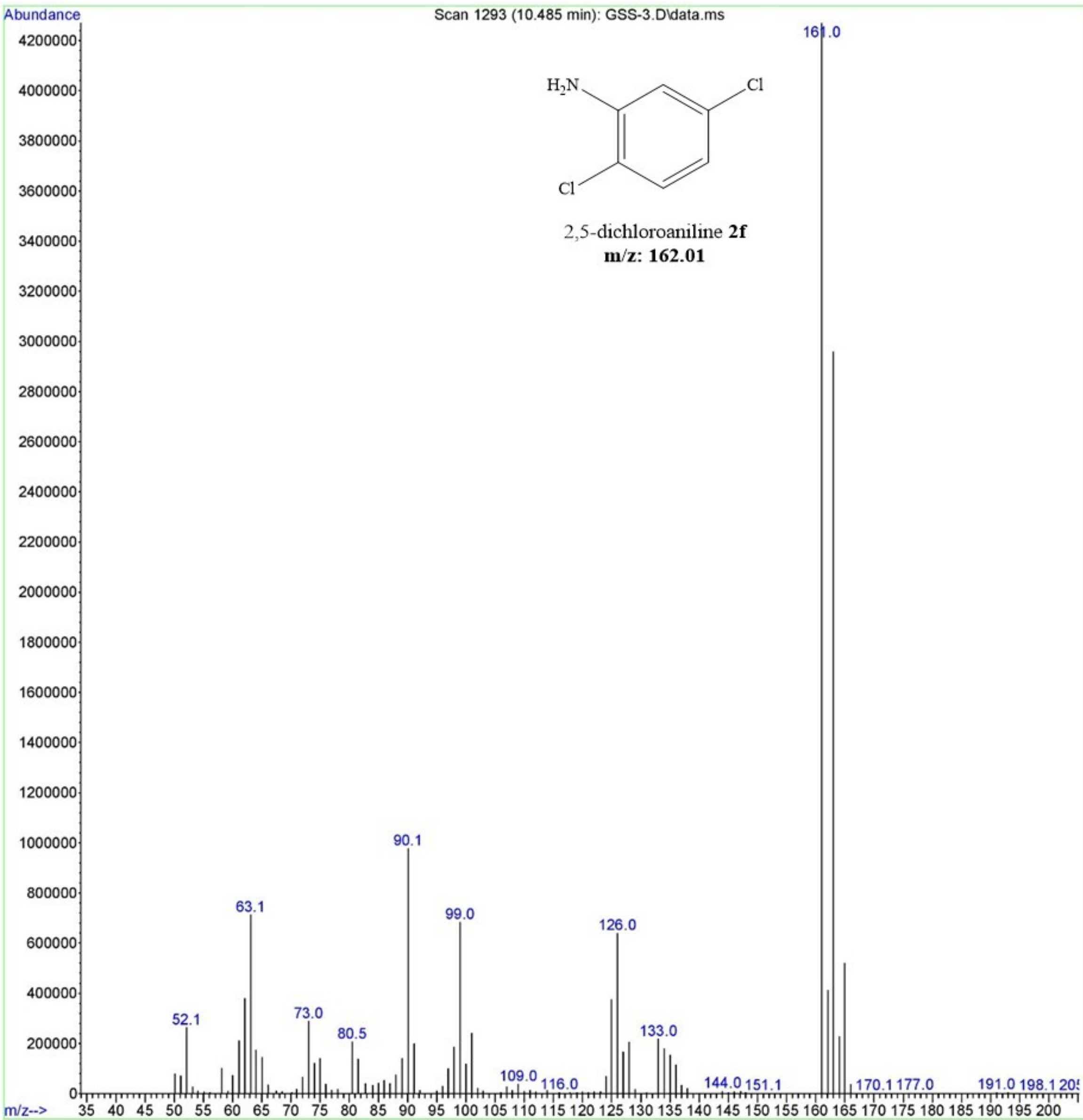
2-chloro-4-nitroaniline

Instrument : GCMSD
Sample Name: 1-Chloro-2,5-Dinitrobenzene
Misc Info :
Vial Number: 5



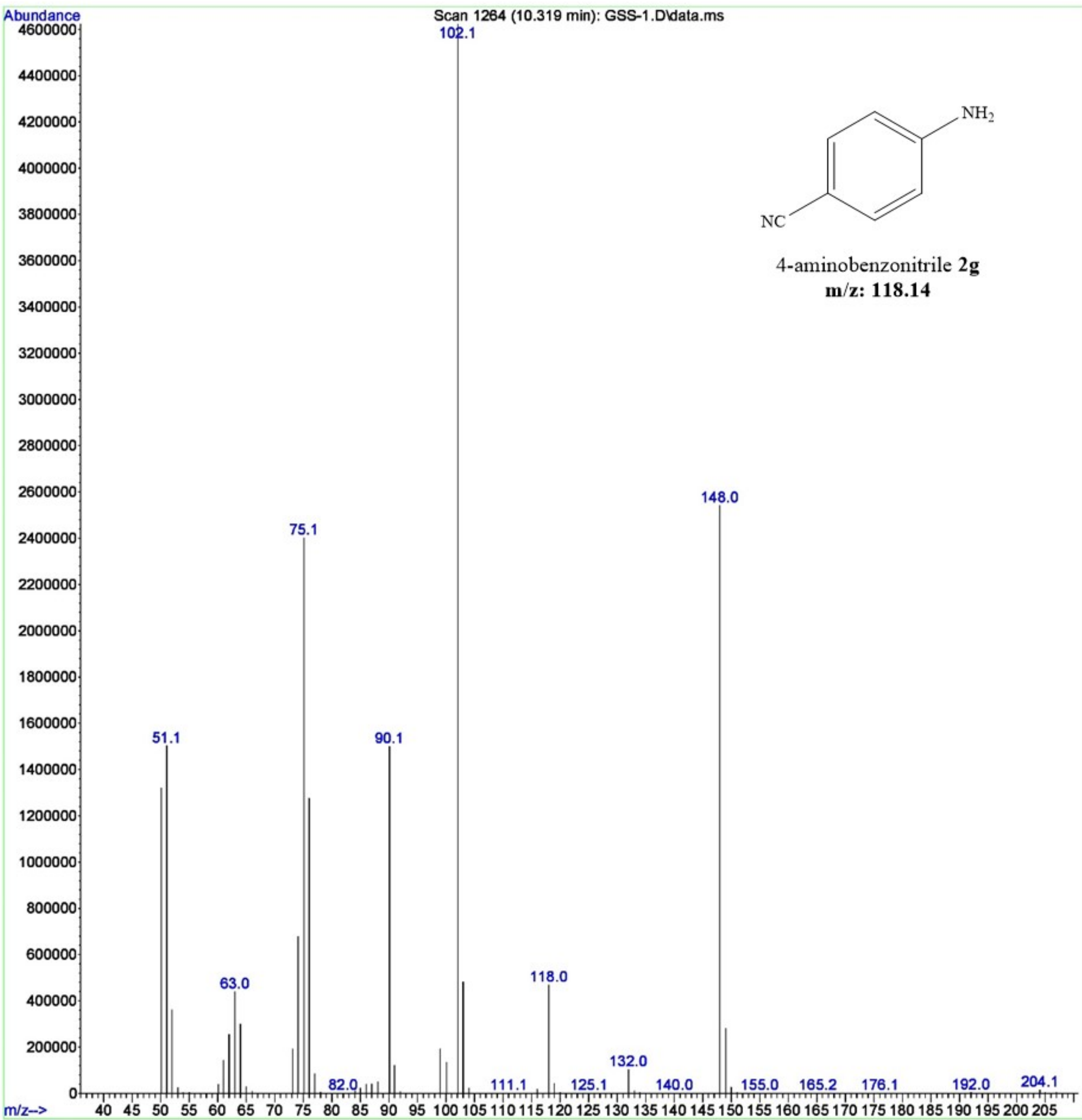
2,5-dichloroaniline

Instrument : GCMSD
Sample Name: 2,5-Dichloro-1-Nitrobenzene
Misc Info :
Vial Number: 3



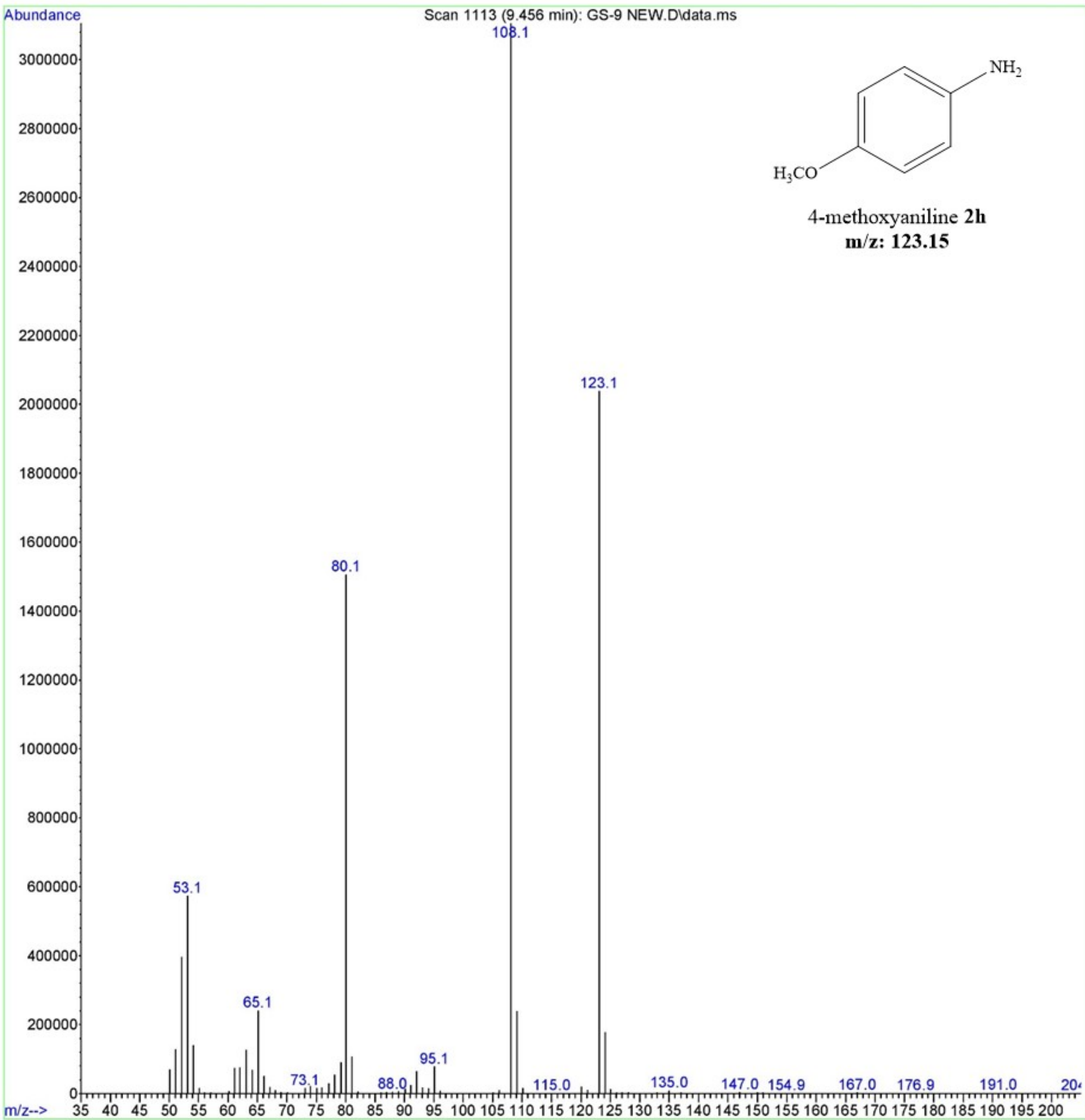
4-aminobenzonitrile

Instrument : GCMSD
Sample Name: 4-Nitrobenzonitrile
Misc Info :
Vial Number: 1



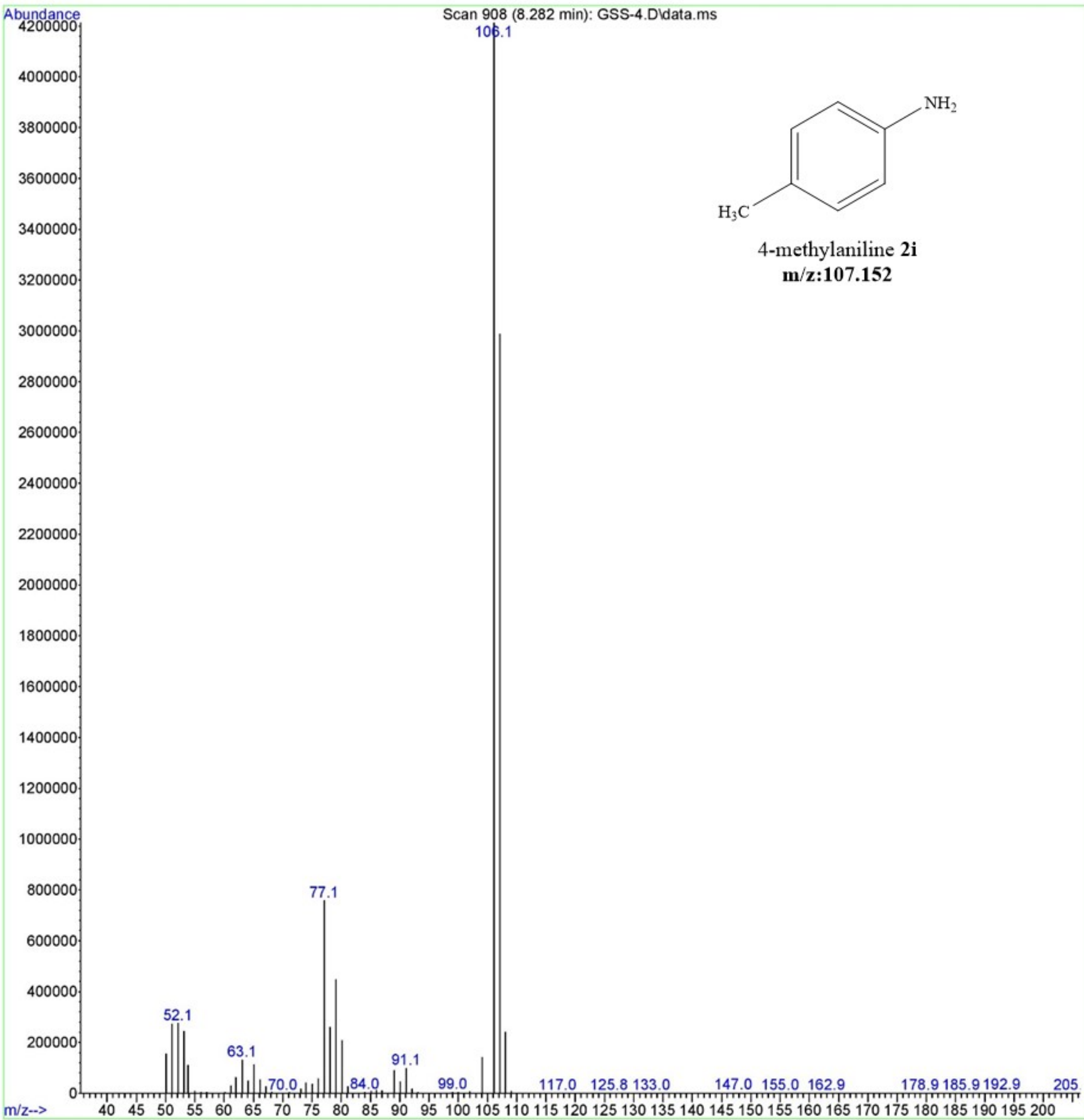
4-methoxyaniline

Instrument : GCMSD
Sample Name: 4-Nitroanisole
Misc Info :
Vial Number: 9



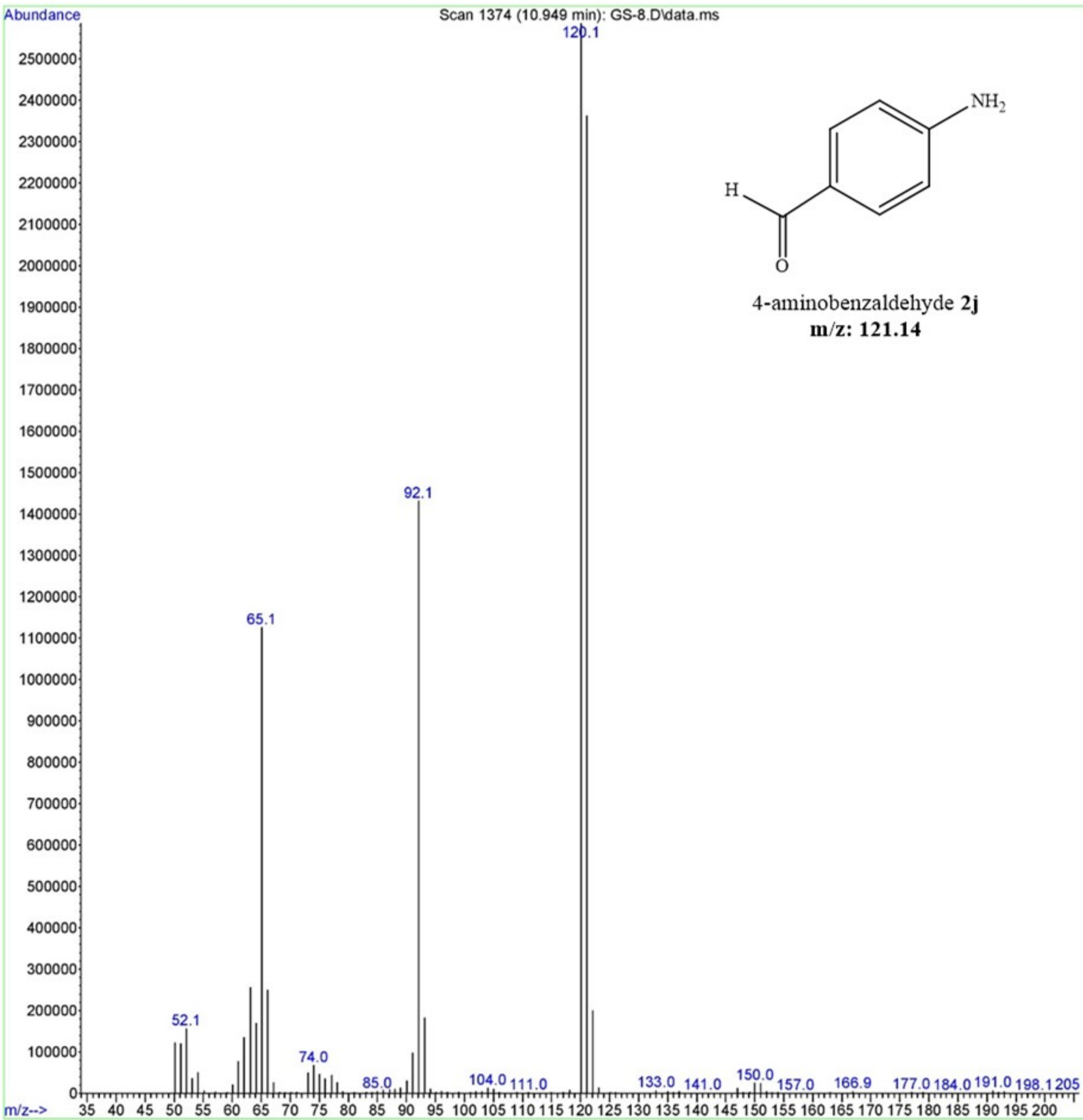
4-methylaniline

Instrument : GCMSD
Sample Name: 4-Nitrotoluene
Misc Info :
Vial Number: 4



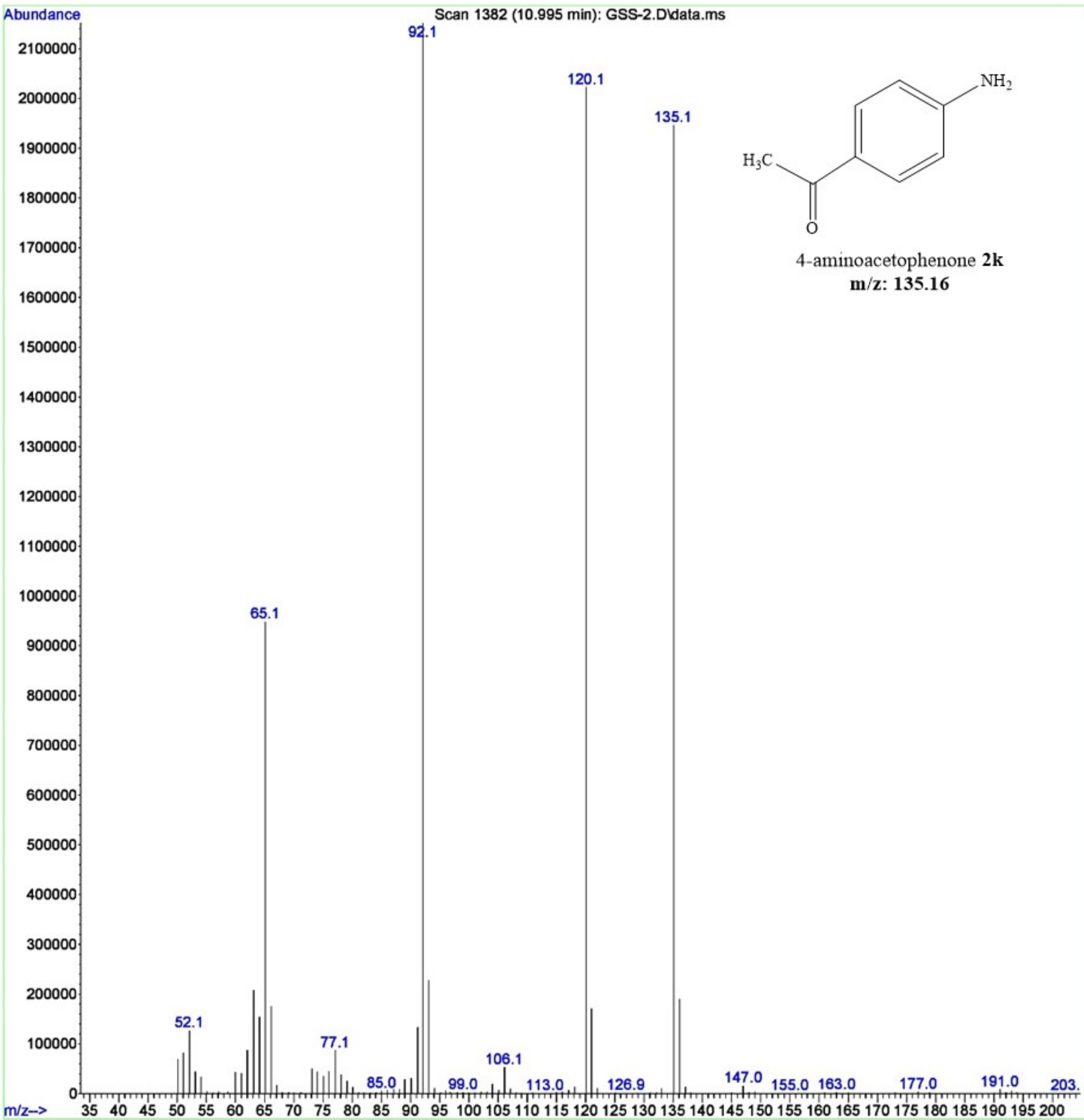
4-aminobenzaldehyde

Instrument : GCMSD
Sample Name: 4-Nitrobenzaldehyde
Misc Info :
Vial Number: 8



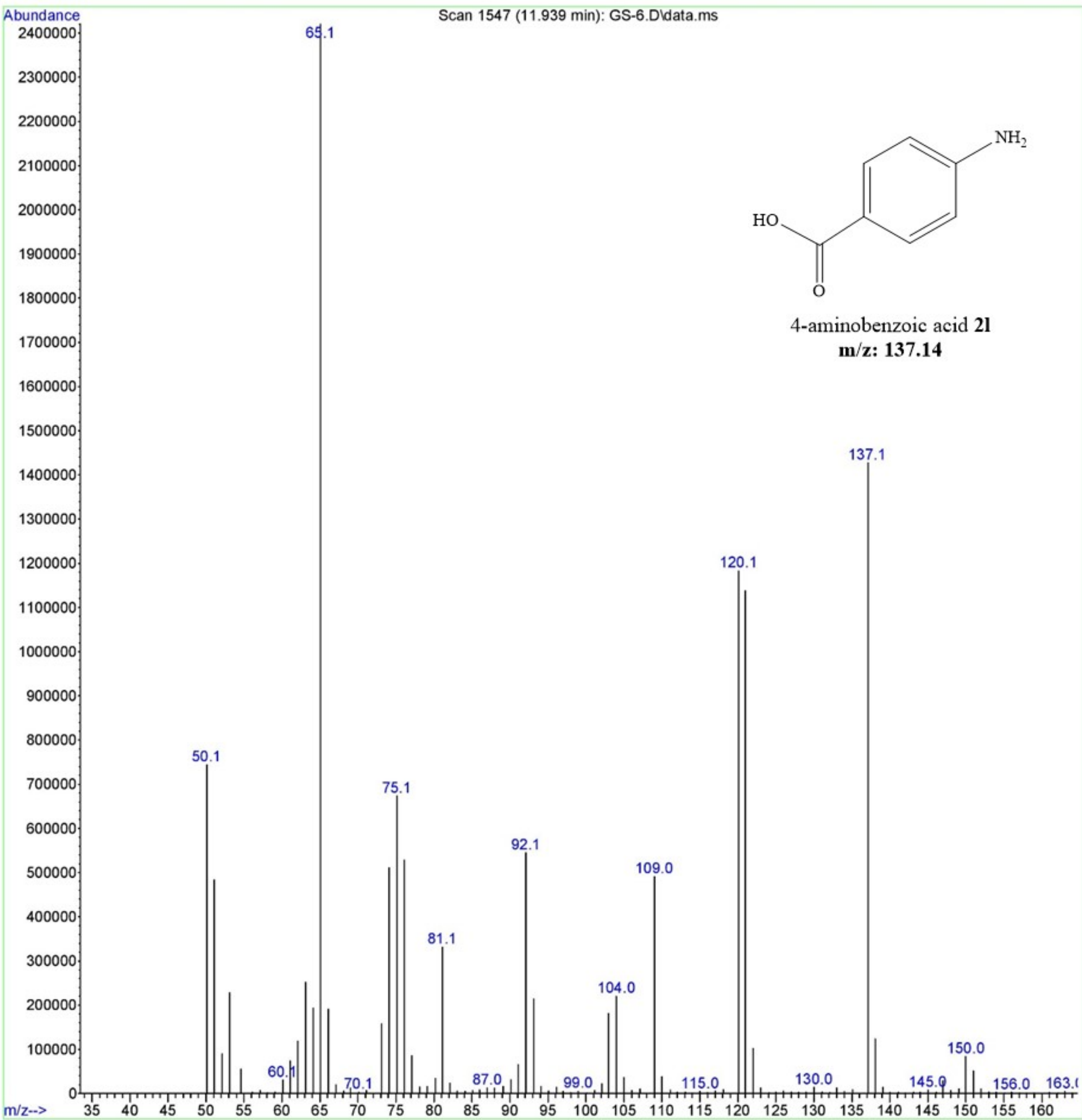
4-aminoacetophenone

Instrument : GCMSD
Sample Name: 4-Nitroacetophenon
Misc Info :
Vial Number: 2



4-aminobenzoic acid

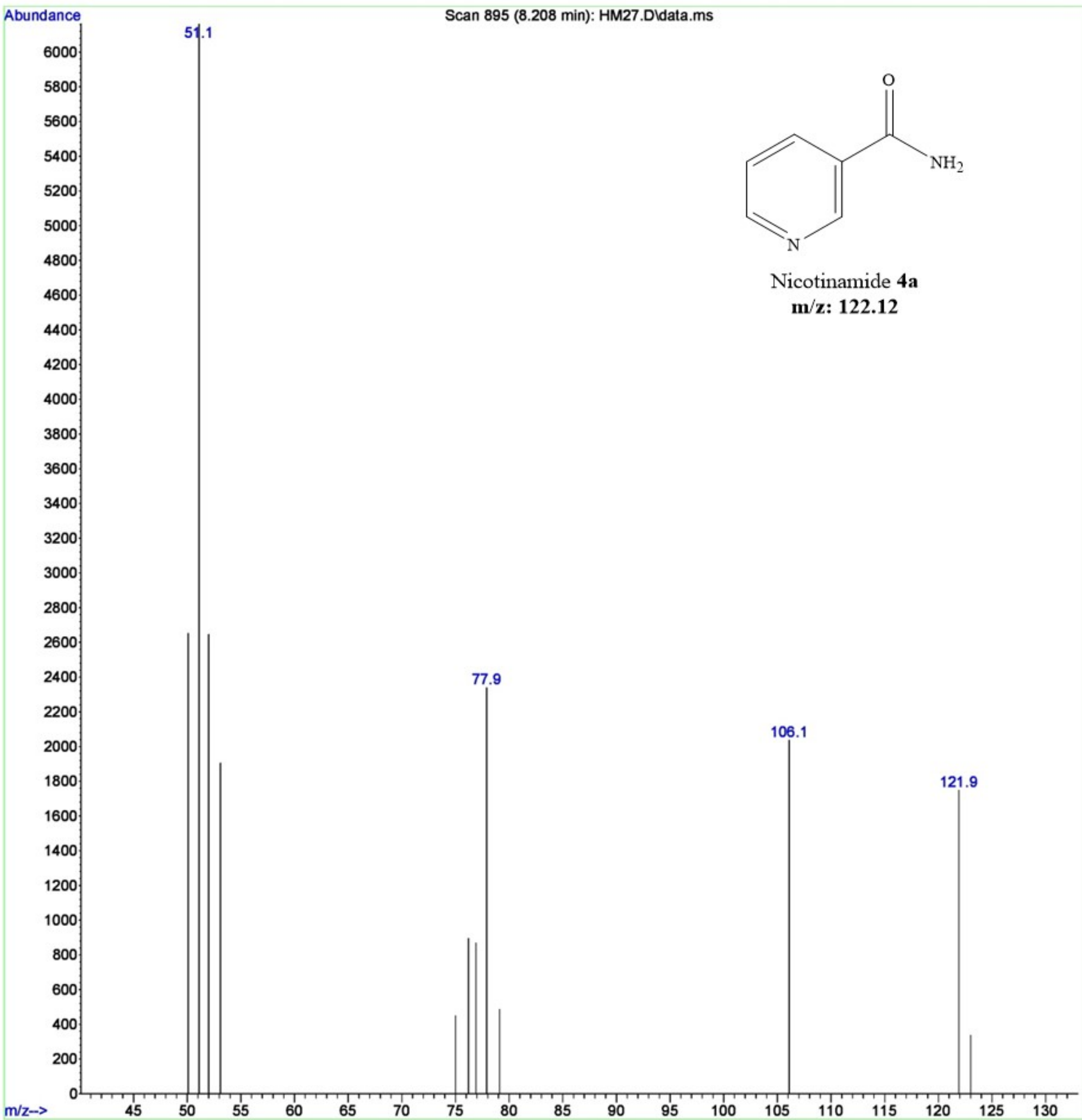
Instrument : GCMSD
Sample Name: 4-nitrobenzoic acid
Misc Info :
Vial Number: 6



Nitrile Hydration

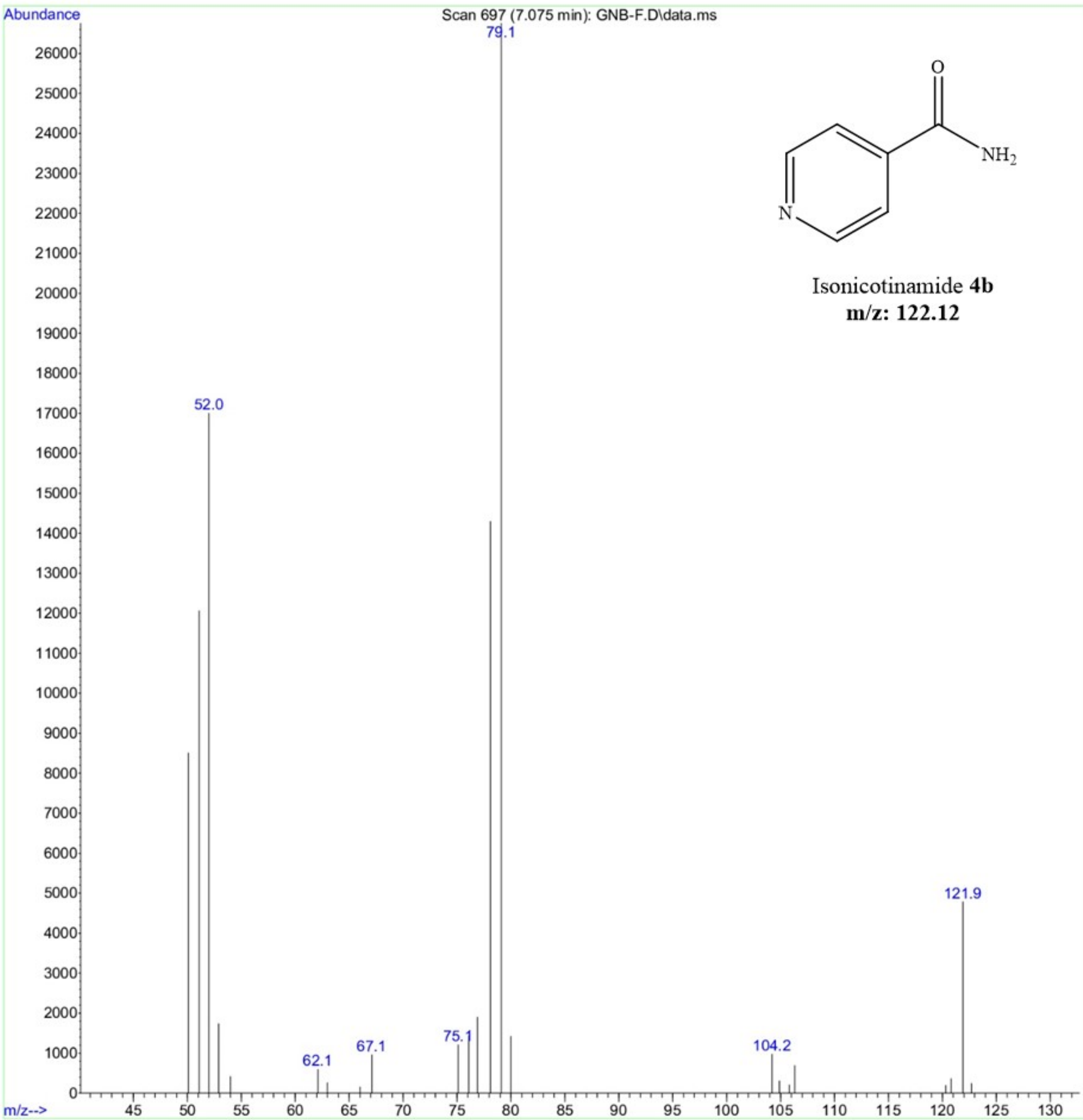
Nicotinamide

Instrument : GCMSD
Sample Name: HM27
Misc Info :
Vial Number: 1



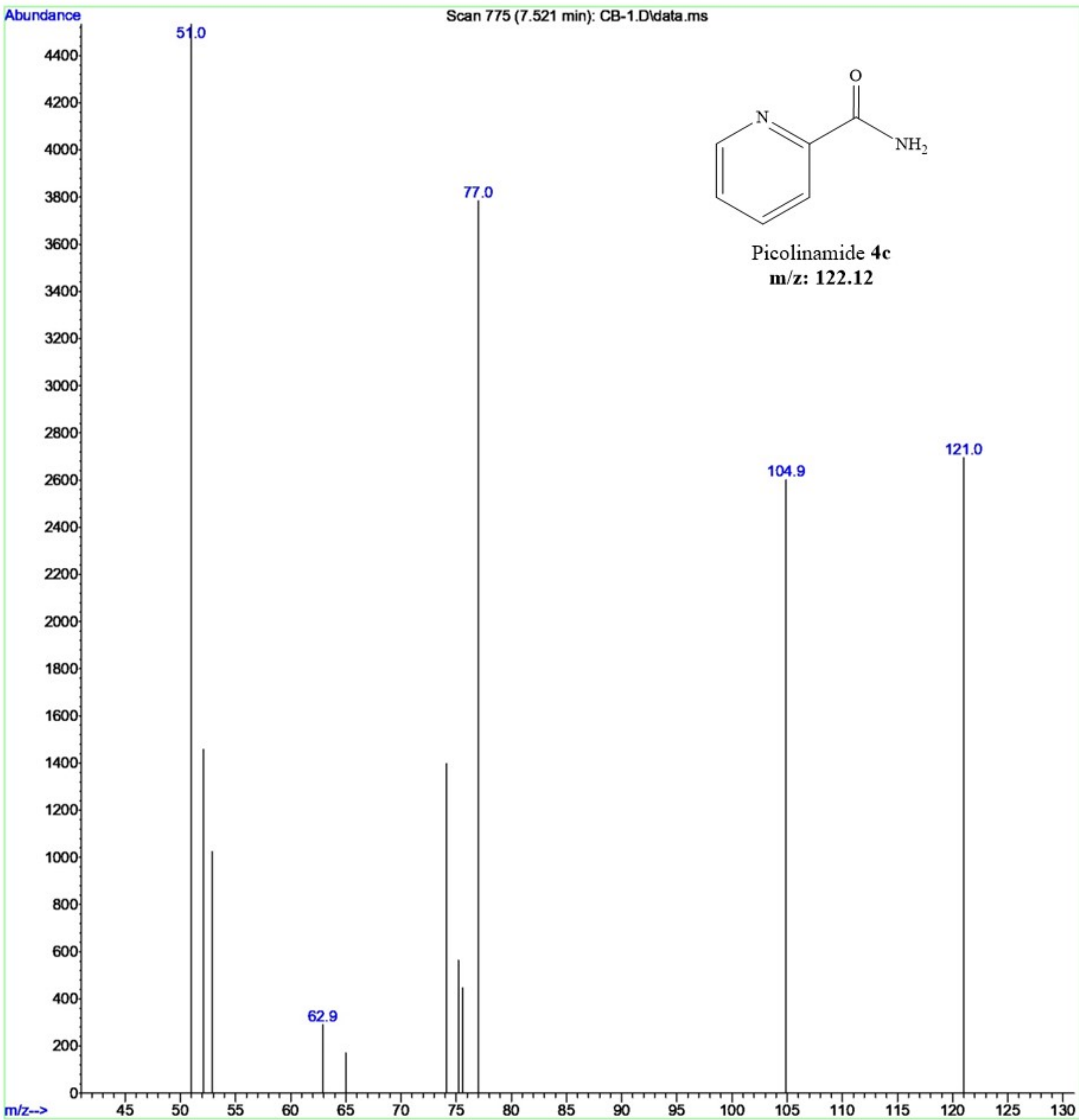
Isonicotinamide

Instrument : GCMSD
Sample Name: GNB-F
Misc Info :
Vial Number: 1



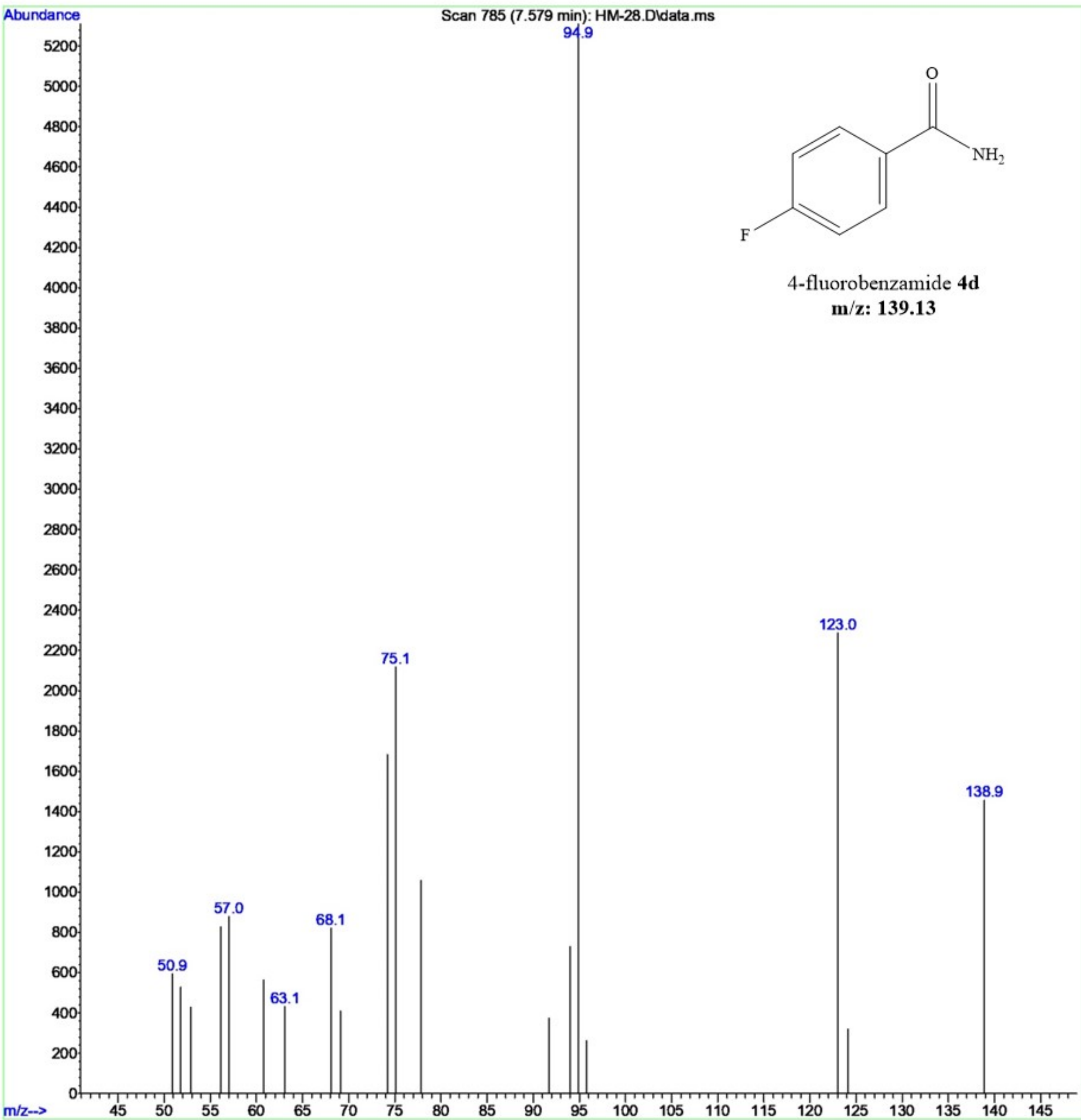
Picolinamide

Instrument : GCMSD
Sample Name: CB-1
Misc Info :
Vial Number: 1



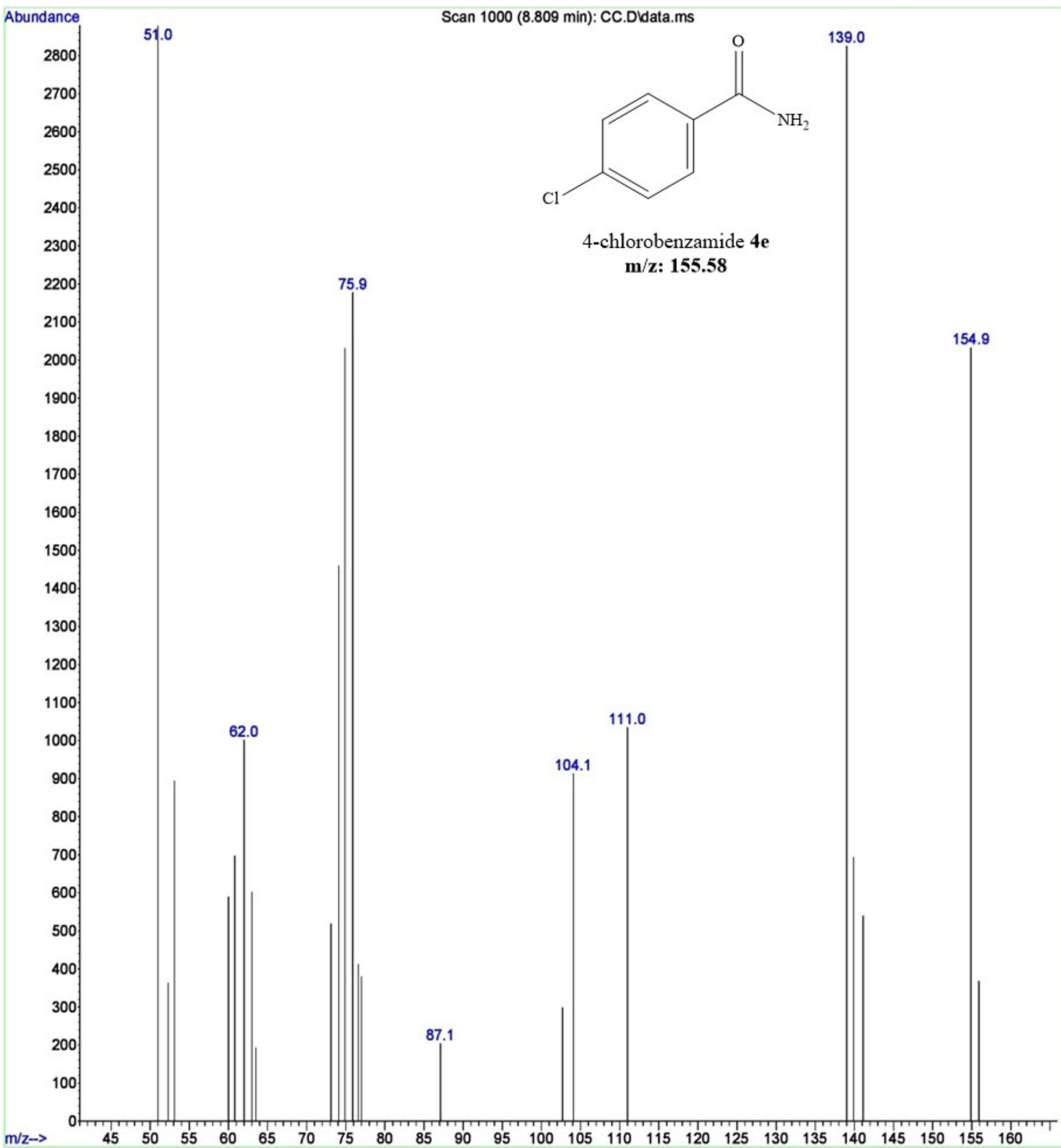
4-fluorobenzamide

Instrument : GCMSD
Sample Name: HM-28
Misc Info :
Vial Number: 1



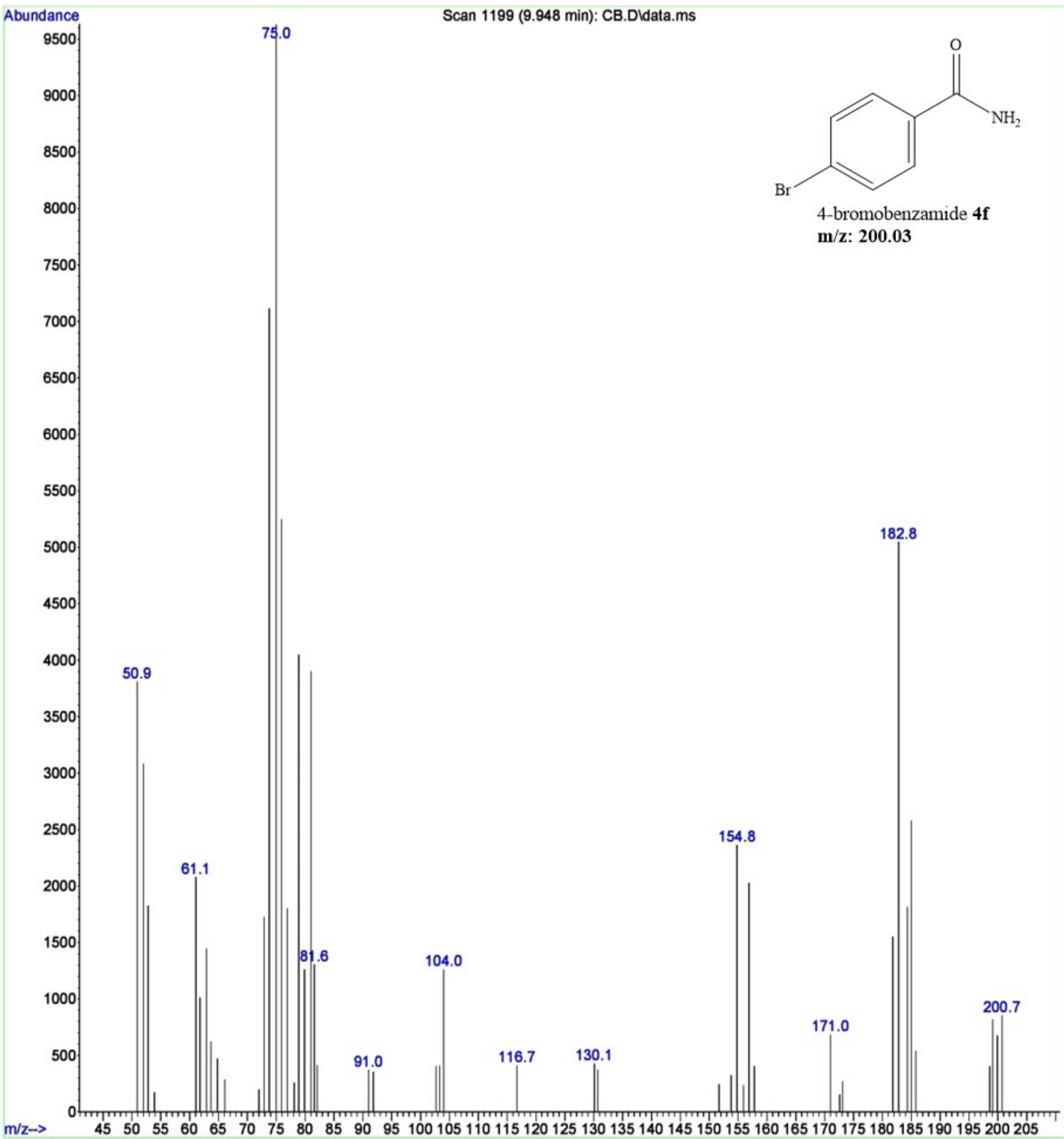
4-chlorobenzamide

Instrument : GCMSD
Sample Name: CC
Misc Info :
Vial Number: 1



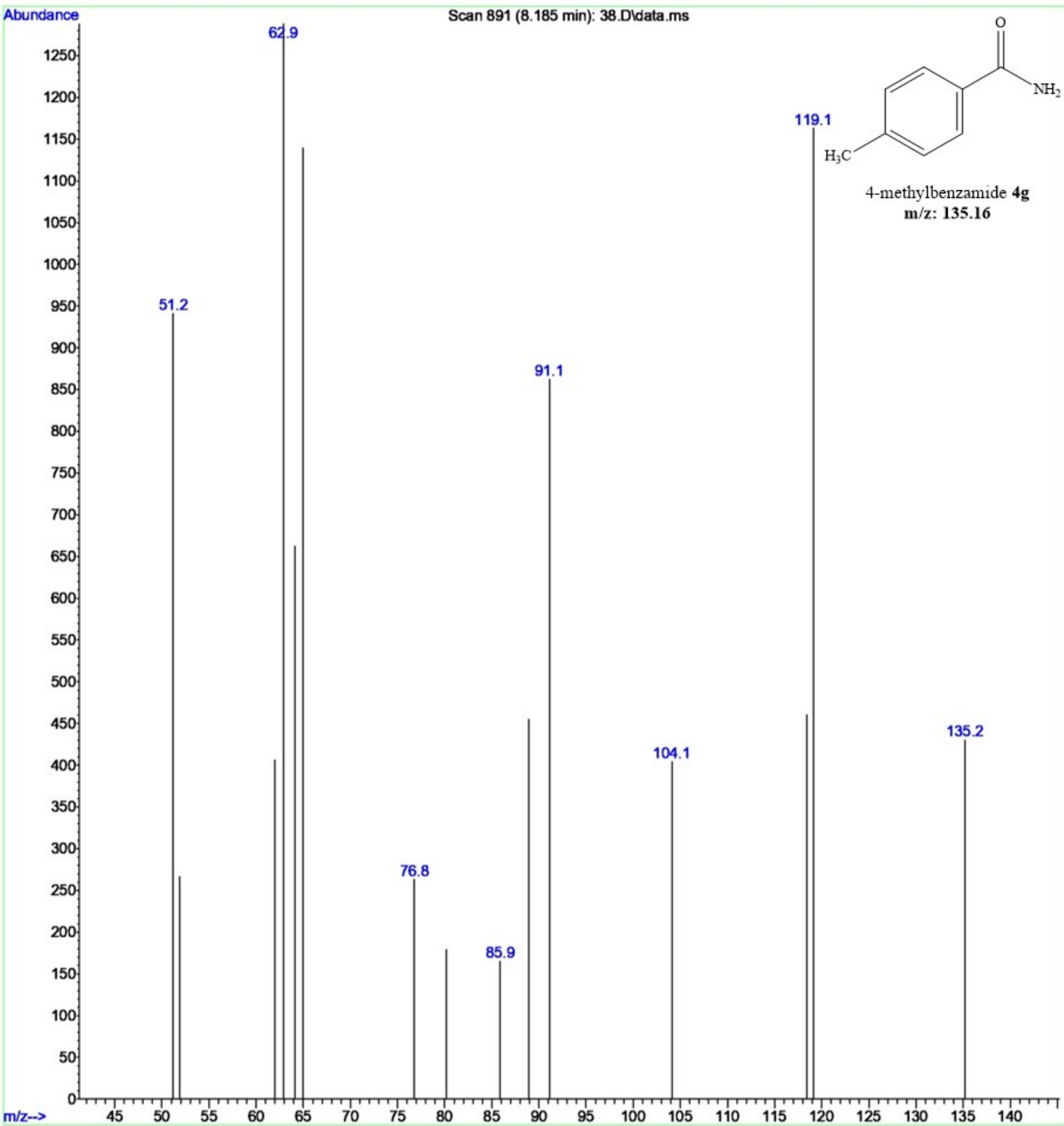
4-bromobenzamide

Instrument : GCMSD
Sample Name: CB
Misc Info :
Vial Number: 1

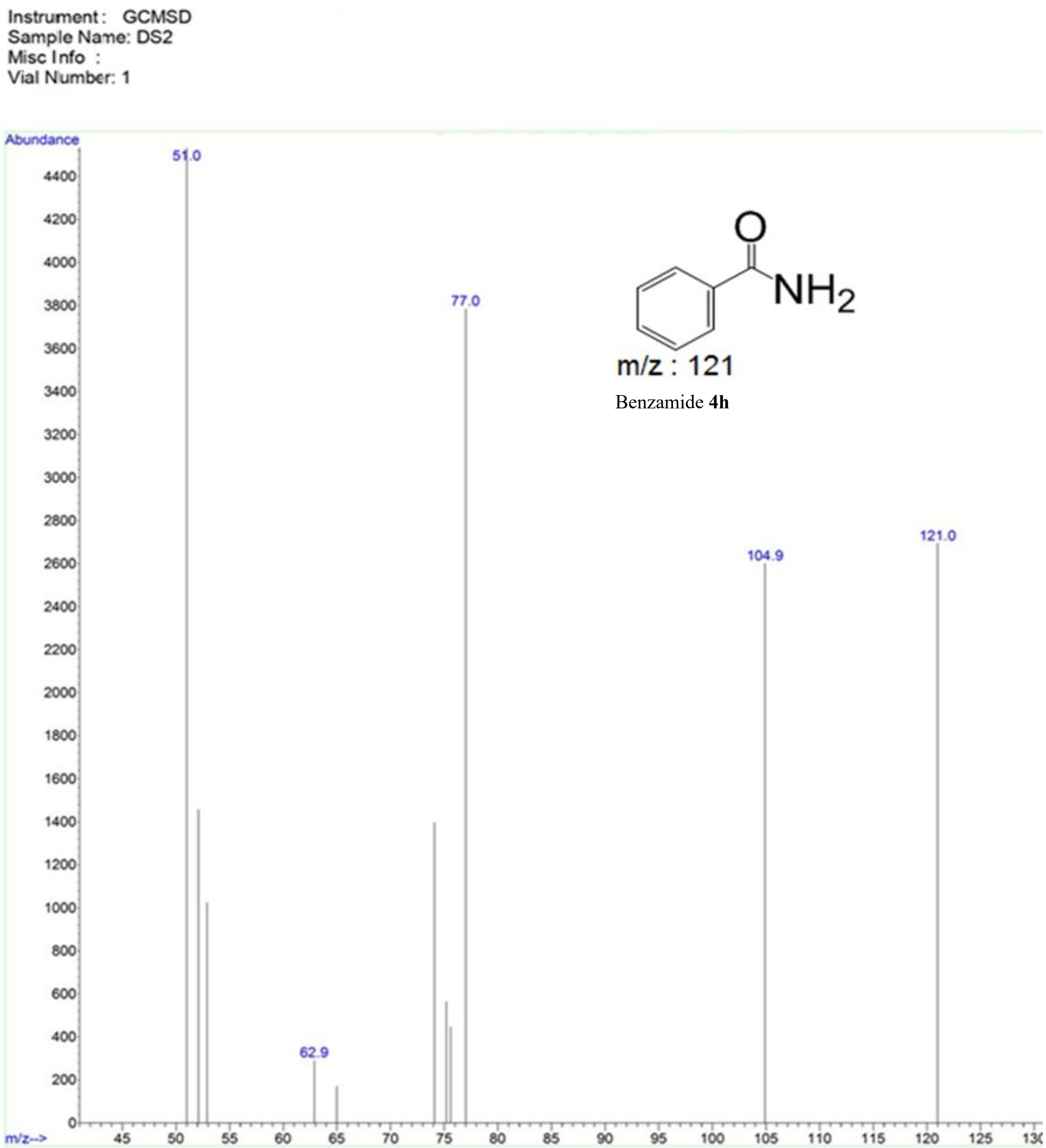


4-methylbenzamide

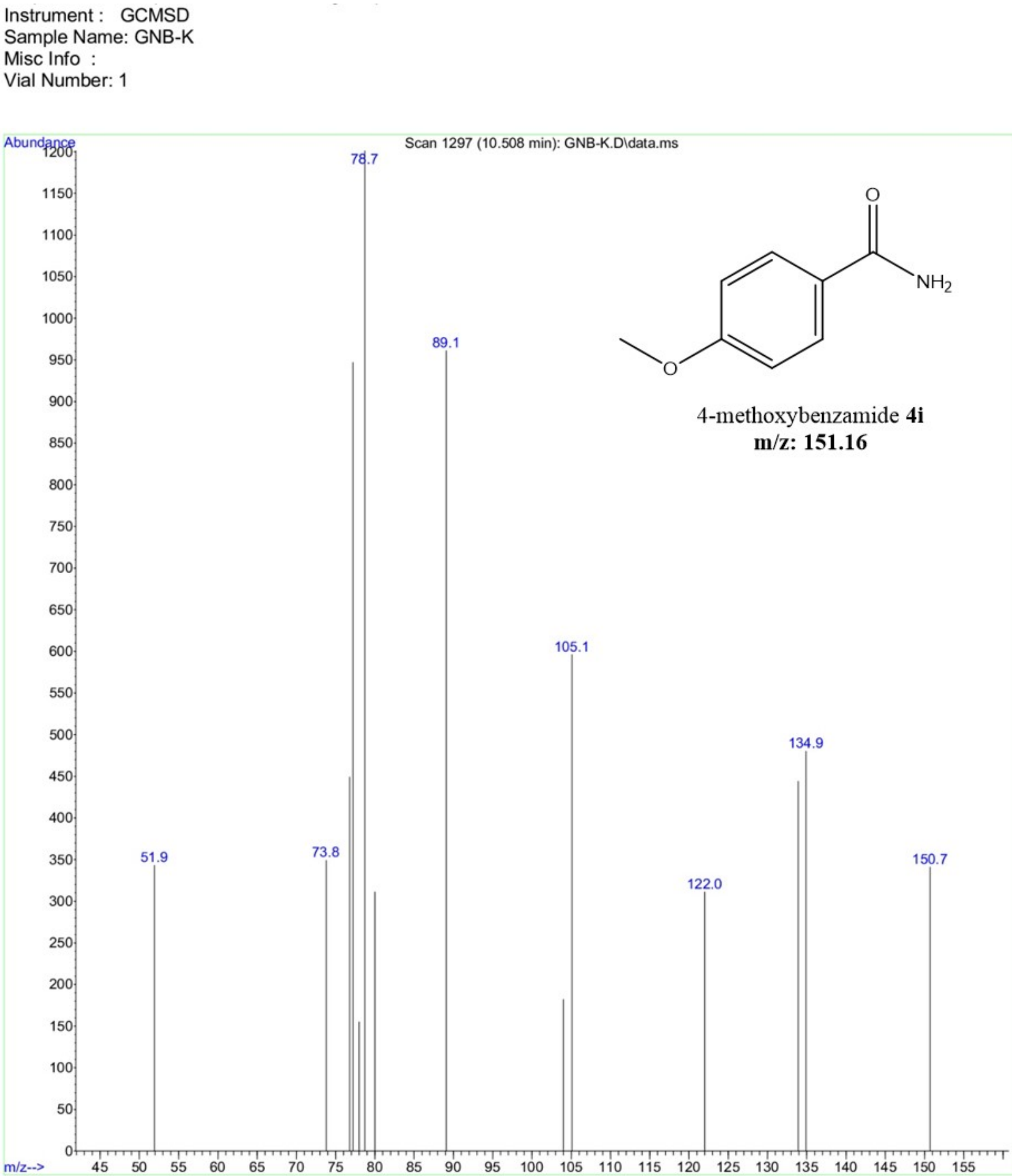
Instrument : GCMSD
Sample Name: 38
Misc Info :
Vial Number: 1



Benzamide

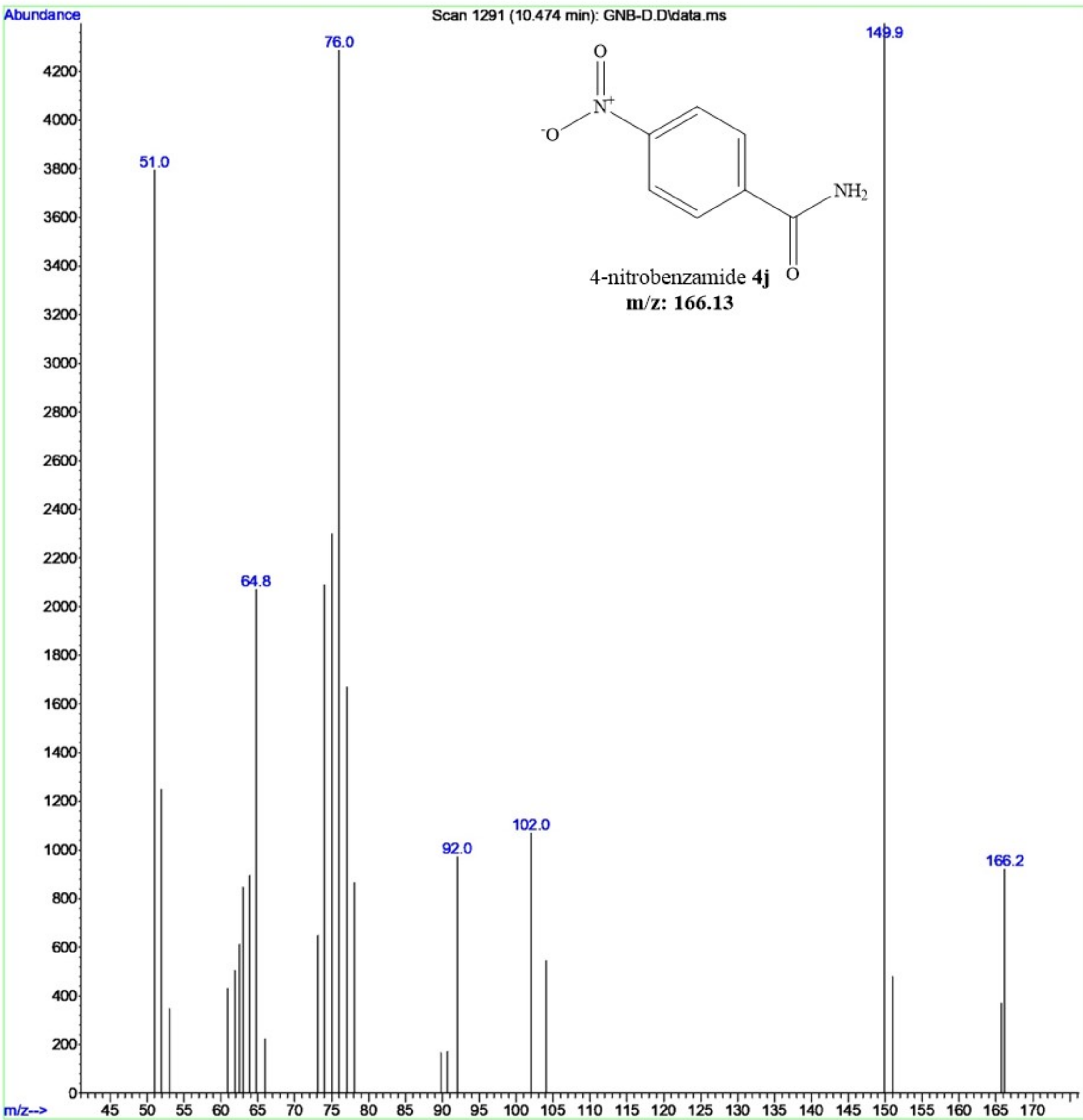

Instrument: GCMSD
Sample Name: DS2
Misc Info :
Vial Number: 1
Abundance
m/z-->
51.0
77.0
104.9
121.0
62.9
NH2
m/z : 121
Benzamide 4h

4-methoxybenzamide



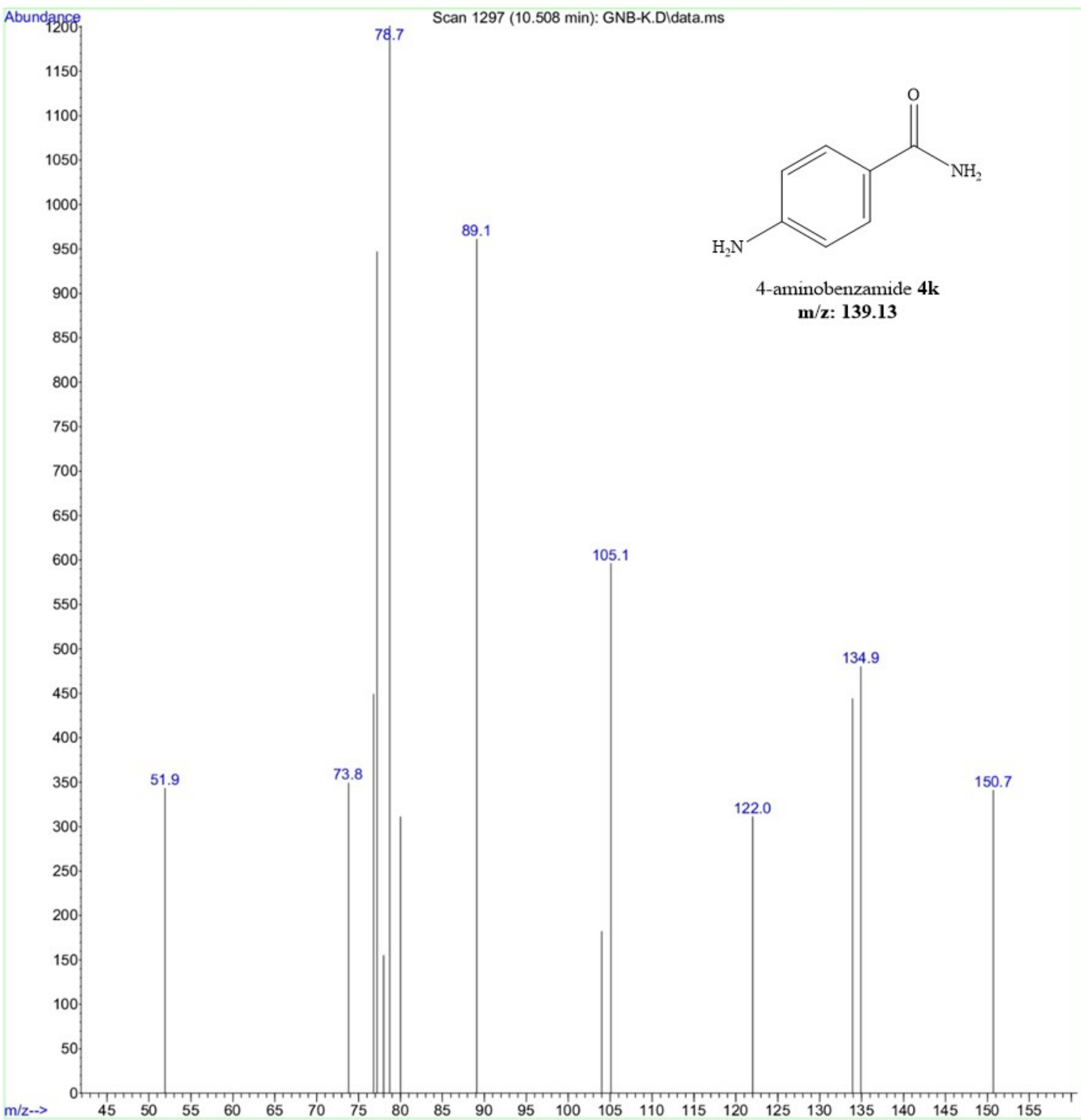
4-nitrobenzamide

Instrument : GCMSD
Sample Name: GNB-D
Misc Info :
Vial Number: 1



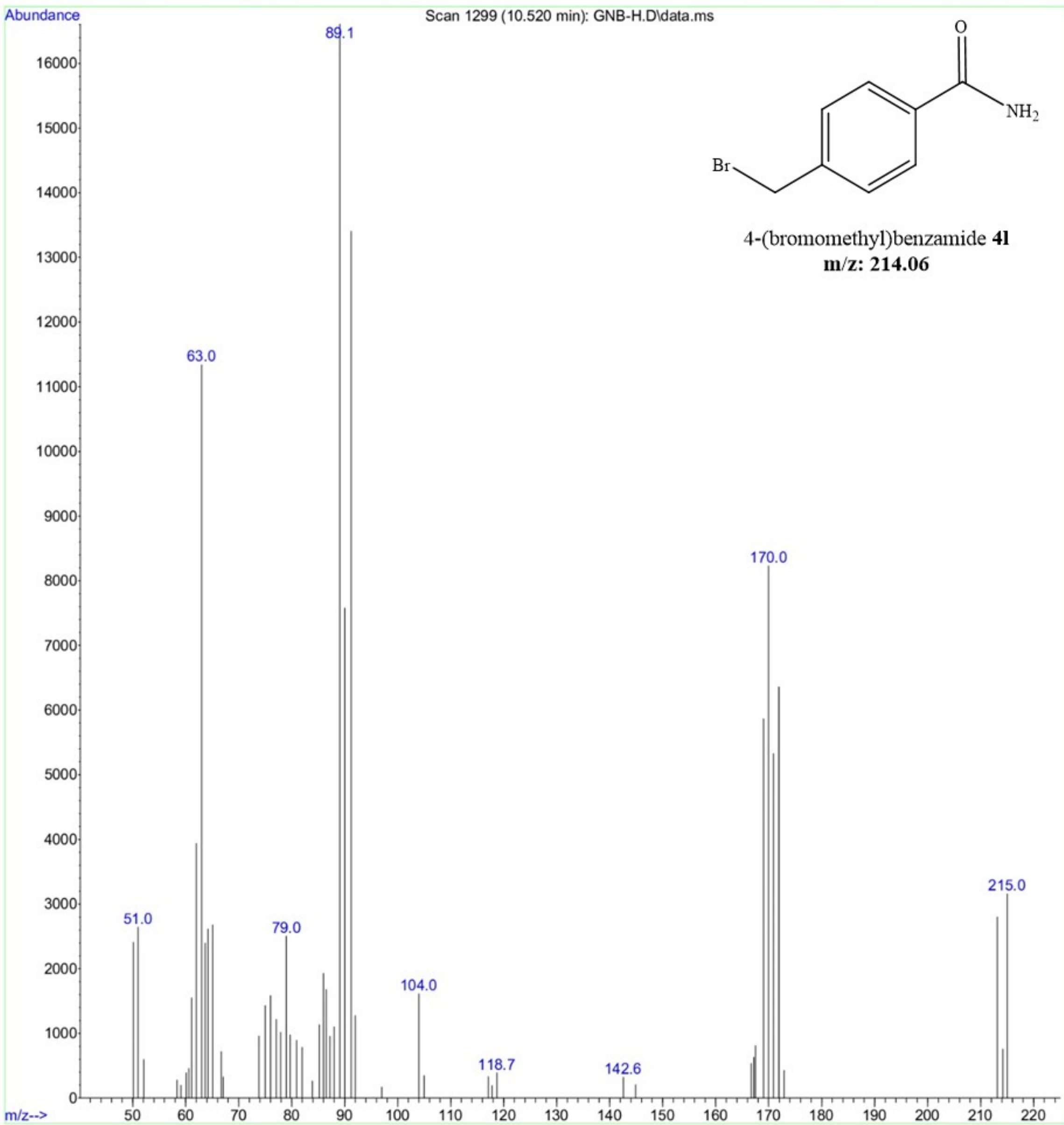
4-aminobenzamide

Instrument : GCMSD
Sample Name: GNB-K
Misc Info :
Vial Number: 1



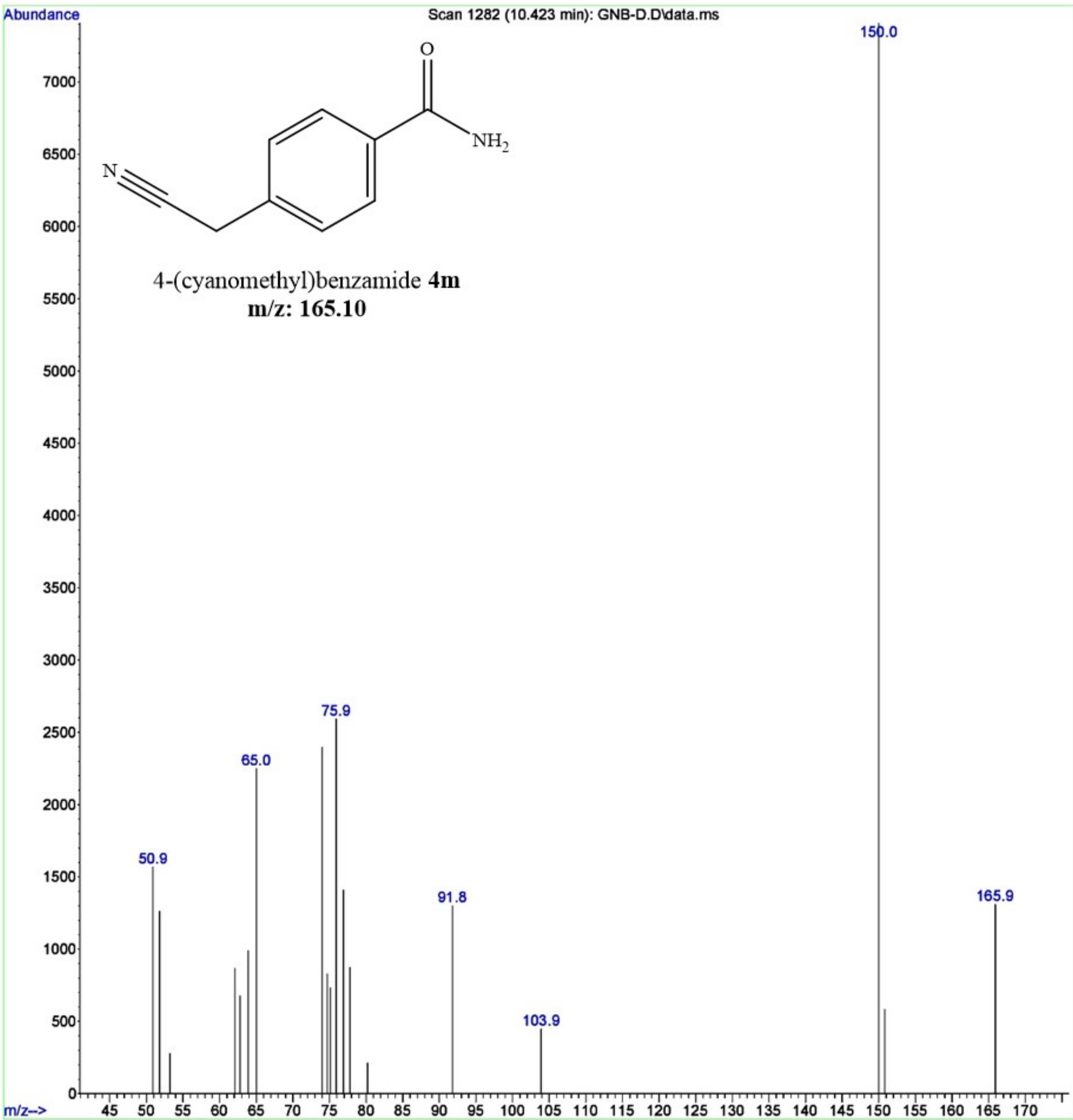
4-(bromomethyl)benzamide

Instrument : GCMSD
Sample Name: GNB-H
Misc Info :
Vial Number: 1



4-(cyanomethyl)benzamide

Instrument : GCMSD
Sample Name: GNB-D
Misc Info :
Vial Number: 1



Notes and references

1 Y. M. Jayawardena H. S. N., Liyanage Sajani H., Rathnayake K., Patel U., *Anal. Chem.*, 2021, **93**, 1889–1911.

2 A. Müller, T. Heinrich, S. Tougaard, W. S. M. Werner, M. Hronek, V. Kunz, J. Radnik, J. M. Stockmann, V. D. Hodoroaba, S. Benemann, N. Nirmalananthan-Budau, D. Geißler, K. Sparnacci and W. E. S. Unger, *J. Phys. Chem. C*, 2019, **123**, 29765–29775.