

Supplementary Material for

Simplified preparation of graphene-co-shelled Ni/NiO@C nano-catalyst and its application in the N-di-methylation synthesis of amines under mild conditions

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Fig. S3 to XPS spectra before and after reaction of Ni/NiO@C-700-200-2 h-EtOH.

Table S1 to EDS element before and after reaction of Ni/NiO@C-700-200-2 h-EtOH.

NMR and GC-MS spectra.

S1. Methods and materials

All aldehydes and amines were obtained commercially from various chemical companies. 1,3,5-trimethoxybenzene was purchased from Sigma Aldrich Co., Ltd.; Ni(NO₃)₂•6H₂O (AR, 98%), anhydrous citric acid (AR, ≥99.5%), CDCl₃ (99.8% D, stabilized with Ag) were obtained from Shanghai Macklin Biochemical Co., Ltd.; H₂SO₄ (GR, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; Al₂O₃ (basic, 200~300 meshes), ethanol (AR, 99.7%), methanol (GC, >99.9%) were purchased from Aladdin (Shanghai) Chemical Technology Co., Ltd.; Deionized water ($\sigma < 5 \mu\text{S}/\text{m}$) was self-made in the laboratory. Before using, the purity of aldehydes and amines has been checked.

GC of products was recorded by GC-2014C (Shimadzu, Japan) with HP5 column (30 m × 250 mm × 0.25 μm) and FID detector. GC-MS of products was determined by TRACE 1300ISQ GC-MS (Thermo Fisher Scientific, America) with TG-5MS column (30 m × 250 mm × 0.25 μm). ¹H NMR of products were recorded on a Bruker Avance III (400 MHz) spectrometer (Bruker BioSpin, Germany) with CDCl₃ as solvent at 400 MHz. The TEM measurements were conducted on a JEM-2100F microscope (JEOL, Japan) operated at 200 kV. The SEM images were obtained on Analytical SEM SU-70 (Hitachi, Japan) microscope operated at 10 kV. XPS measurements were performed on an Escalab250 Xi photoelectron spectrometer (Thermo Fisher Scientific, America) with Al Kα X-ray radiation with scan number of 5. XRD powder patterns were recorded on an X’Pert Pro MPD diffractometer (PANalytical, Netherlands) using the Cu Kα radiation at 40 kV and 20 mA ($\lambda = 1.5406 \text{ \AA}$). Processing and assignments of the powder patterns were conducted on the software Jade 6.0 using the Powder Diffraction File (PDF) database of the International Centre of Diffraction Data (ICDD). Nitrogen adsorption isotherms were measured at -196 °C on a Quadrasorb SI nitrogen adsorption apparatus (Quantachrome, America) by using the BET method.

S2. General preparation of catalysts

S2.1. Preparation of Ni@C-H₂O

In a typical synthesis procedure, nickel (II) nitrate hexahydrate (Ni (NO₃)₂•6 H₂O, 0.03 mol) and citric acid (C₆H₈O₇, 0.03 mol) were dissolved in deionized water (5 mL). The mixture was then aged at 70 °C for 8 h under stirring (300 rpm) until to obtain a transparent greenish gel, followed by drying at 100 °C for 72 h in a drying oven to remove the excess water. The obtained greenish solid was then calcining at fixed bed at 600 or 700 °C for 3 h under a high-purity N₂ (99.999 %) flow of 40 mL min⁻¹. The heating rate was controlled at 2 °C min⁻¹. The obtained black solids were treated in 1 M H₂SO₄ aqueous solution at 70 °C until the solution colorless to remove the insecure and uncovered Ni particles. The black solids were then full washed with deionized water until pH of waste solution was 7. Then, the black solids were dried at -48 °C for 12 h in vacuum by using a freeze dryer. The dried black solids denoted as Ni@C-x-H₂O, where x is calcining temperature of greenish gel, such as Ni@C-600-H₂O or Ni@C-700-H₂O.

S2.2. Preparation of Ni@C-EtOH

In a typical synthesis procedure, nickel nitrate hexahydrate (Ni (NO₃)₂•6 H₂O, 0.03 mol) and citric acid (C₆H₈O₇, 0.03 mol) were dissolved in anhydrous ethanol (5 mL). The mixture was then aged at 70 °C for 4 h under stirring (300 rpm) until to obtain a bubble-shaped greenish gel, followed by drying at 100 °C for 24 h in a drying oven to remove the excess solvent. The obtained greenish solid was then calcining at fixed bed at 600 or 700 °C for 3 h under a high-purity N₂ (99.999 %) flow of 40 mL·min⁻¹. The heating rate was controlled at 2 °C·min⁻¹. The obtained black solids were treated in 1 M H₂SO₄

aqueous solution at 70 °C until the solution colorless to remove the insecure and uncovered Ni particles. The black solids were then full washed with deionized water until pH of waste solution was 7. Finally, the black solids were dried at -48 °C for 12 h in vacuum by using a freeze dryer. The dried black solids denoted as Ni@C-x-EtOH, where x is calcining temperature of greenish gel, such as Ni@C-600-EtOH and Ni@C-700-EtOH.

S2.3. Preparation of Ni-NiO@Cs

In a typical synthesis procedure, Ni@C-H₂O and Ni@C-EtOH were grinded and sieved to powders of 800 meshes and then were heated at fixed bed at 200 °C for 1 or 2 h under argon (containing 1 vol% O₂) flow of 30 mL·min⁻¹. All these materials were labeled as M1/M2@C-x-y-z-s, where M1=Ni; M2=NiO; x denotes the pyrolysis temperature; y denotes the oxidation temperature; z denotes the oxidation time; and s denotes the solvent, respectively.

S3. Procedure for the synthesis of N-methylamines

S3.1. Reductive N-methylation of amines and aldehydes

The reaction was conducted in a stainless-steel autoclave (Anhui Kemi Machinery Technology Co., Ltd, China) with six wells (10 mL per well), one thermocouple and one circulating water-cooling equipment. Each well has a glass lining, in which were loaded with one 10 mm magnetic stirring bar, 0.5 mmol corresponding amine, 3 mmol corresponding aldehyde, 0.05 mmol 1,3,5-trimethoxybenzene, 10 mg catalyst, and 5 mL methanol. Then, the autoclave was sealed and purged with H₂ three times at 2 MPa pressure and was pressurized with 2 MPa H₂. The autoclave was placed into a heating mantle and the stirring rate was set at 300 rpm. The autoclave was preheated from room temperature to target temperature (inside temperature detected by thermocouple) at rate of 2 °C·min⁻¹. The target temperature was used as the reaction temperature. The reaction was proceeded at the reaction temperature for require time. After the reaction, the remaining gas was discharged after the autoclave was cooled down to room temperature. The reaction solutions were collected with a dropper and filtered. The catalyst was immobilized on the magnetic stirring bar and washed thoroughly with ethanol and water. The catalyst (together with magnetic stirring bar) was then dried at -48 °C for 12 h in vacuum by using a freeze dryer.

The reaction products were identified by GC-MS and ¹H NMR and the yields of reaction products were determined by GC with 1,3,5-trimethoxybenzene as internal standard. For ¹H NMR analysis, about 2 mL reaction solutions were concentrated by rotary evaporation, and then added with 0.6 mL of CDCl₃ (preneutralized with basic Al₂O₃).

S3.2. Procedure for the gram scare reaction

In a 500 mL stainless steel autoclave (WATTCAS, China) with one thermocouple, 1 g corresponding amine, corresponding aldehyde (3 mmol per 0.5 mmol amine), 1 mmol 1,3,5-trimethoxybenzene, one 30 mm magnetic stirring bar, Ni/NiO@C-700-200-2 h-EtOH (10 mg per 0.5 mmol amine) and methanol (5 mL per 0.5 mmol amine) were loaded. Then, the autoclave was sealed and purged with H₂ three times at 2 MPa pressure and was pressurized with 2 MPa H₂. The autoclave was placed into a heating mantle and the stirring rate was set at 300 rpm. The autoclave was preheated from room temperature to target temperature (inside temperature detected by thermocouple) at rate of 2 °C·min⁻¹. The target temperature was used as the reaction temperature. The reaction was proceeded at the reaction temperature for require time. After the reaction, the remaining gas was discharged after the autoclave was cooled down to room temperature. The reaction solutions were collected and filtered. The catalyst was immobilized on the magnetic stirring bar and washed thoroughly with ethanol and

water. The catalyst (together with magnetic stirring bar) was then dried at -48 °C for 12 h in vacuum by using a freeze dryer.

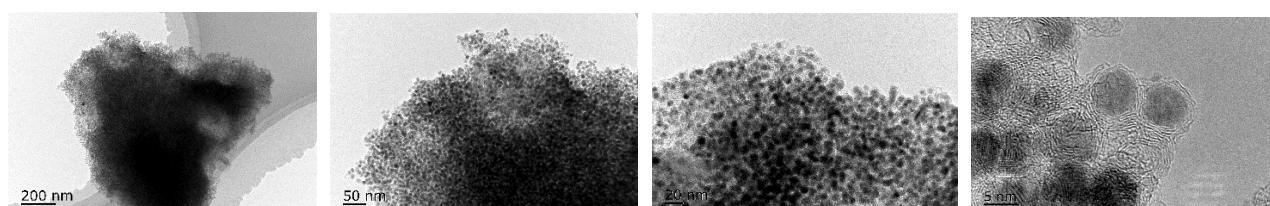
S3.3. Procedure for the Ni/NiO@C-700-200-2 h-EtOH recycling

The stability test of Ni/NiO@C-700-200-2 h-EtOH was performed in a stainless-steel autoclave (Anhui Kemi Machinery Technology Co., Ltd, China) with six wells (10 mL per well), one thermocouple and one circulating water-cooling equipment. The procedure of reaction and product analysis were similar to the S3.1 section. After one batch reaction, the collected catalyst (together with magnetic stirring bar) was thoroughly washed with ethanol and water. The catalyst (together with magnetic stirring bar) was dried at -48 °C for 12 h in vacuum by using a freeze dryer and was used for the next cycle of reaction.

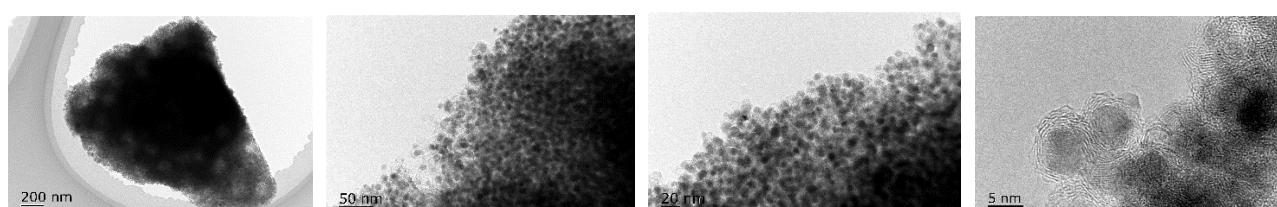
S3.4. Procedure for the two-step continuous reaction catalyzed by Ni/NiO@C-700-200-2 h-EtOH

The reaction was conducted in a stainless-steel autoclave (Anhui Kemi Machinery Technology Co., Ltd, China) with six wells (10 mL per well), one thermocouple and one circulating water-cooling equipment. Each well has a glass lining, in which were loaded with one 10 mm magnetic stirring bar, 0.5 mmol corresponding aldehyde, 5 ml ammonia solution (2 M in methanol), 0.05 mmol 1,3,5-trimethoxybenzene, 10 mg catalyst. Then, the autoclave was sealed and purged with H₂ three times at 2 MPa pressure and was pressurized with 2 MPa H₂. The autoclave was placed into a heating mantle and the stirring rate was set at 300 rpm. The autoclave was preheated from room temperature to target temperature (inside temperature detected by thermocouple) at rate of 2 °C·min⁻¹. The target temperature was used as the reaction temperature. The reaction was proceeded at the reaction temperature for require time. After the reaction, the remaining gas was discharged after the autoclave was cooled down to room temperature. Open the reactor, add 3 mmol formaldehyde to each lining, seal the reactor again and purged with H₂ three times at 2 MPa pressure and was pressurized with 2 MPa H₂. The autoclave was preheated from room temperature to target temperature (inside temperature detected by thermocouple) at rate of 2 °C·min⁻¹. The target temperature was used as the reaction temperature. The reaction was proceeded at the reaction temperature for require time. After the reaction, the remaining gas was discharged after the autoclave was cooled down to room temperature. The reaction solution was collected with a dropper and filtered.

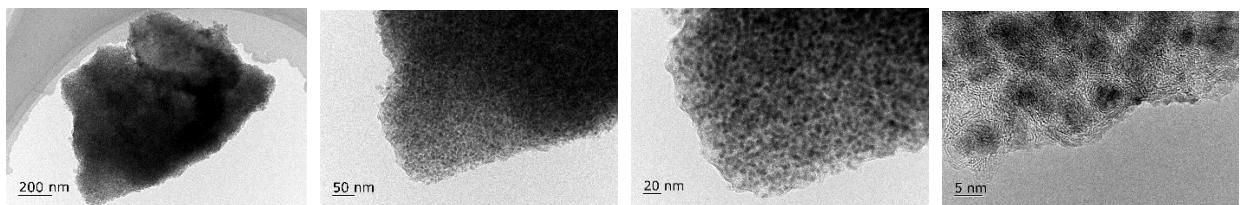
S4. TEM spectra before and after reaction of Ni/NiO@C-700-200-2 h-EtOH



a. Ni/NiO@C-700-200-2 h-EtOH catalyst before the reaction

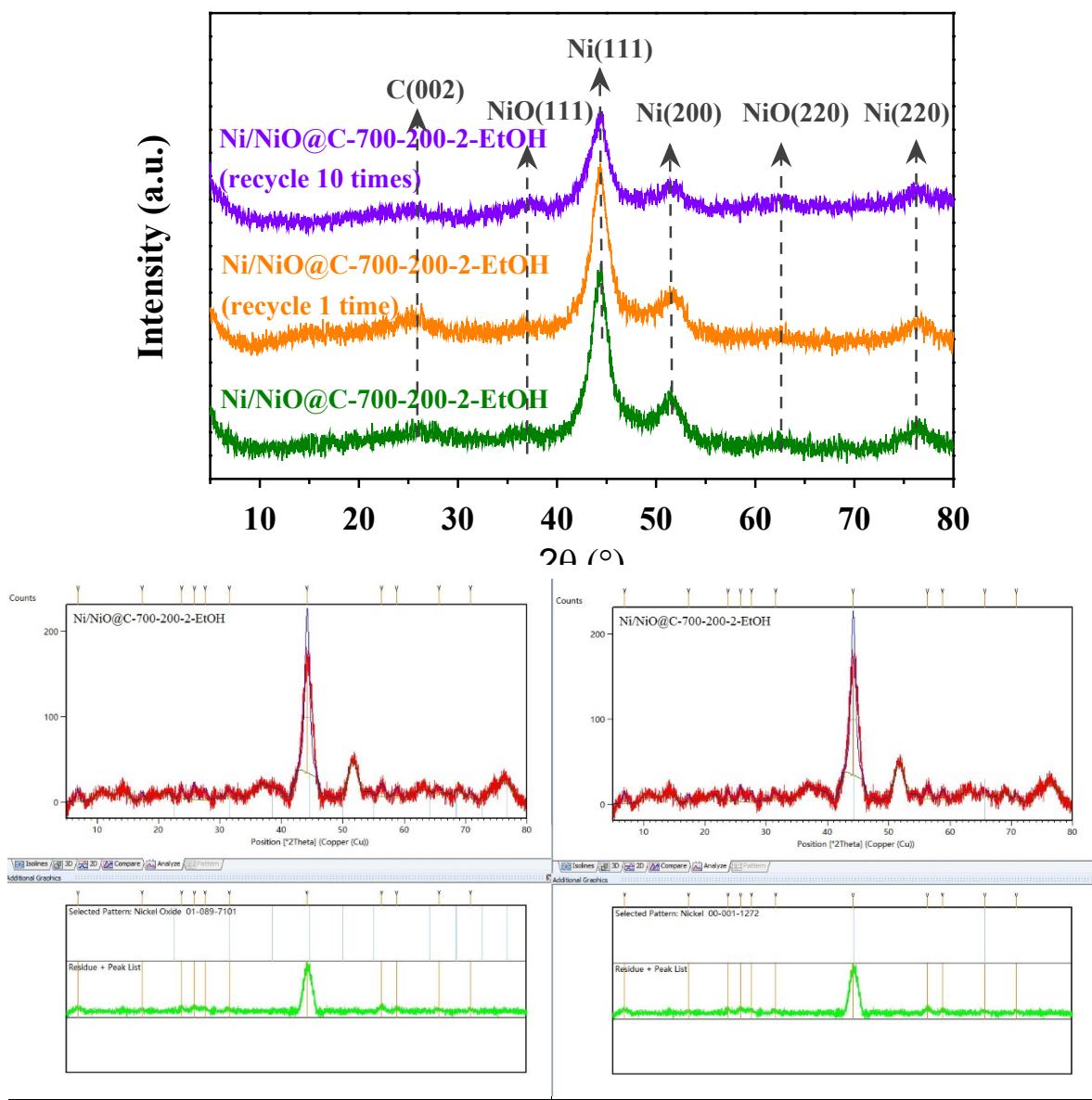


b. Ni/NiO@C-700-200-2 h-EtOH catalyst after the reaction

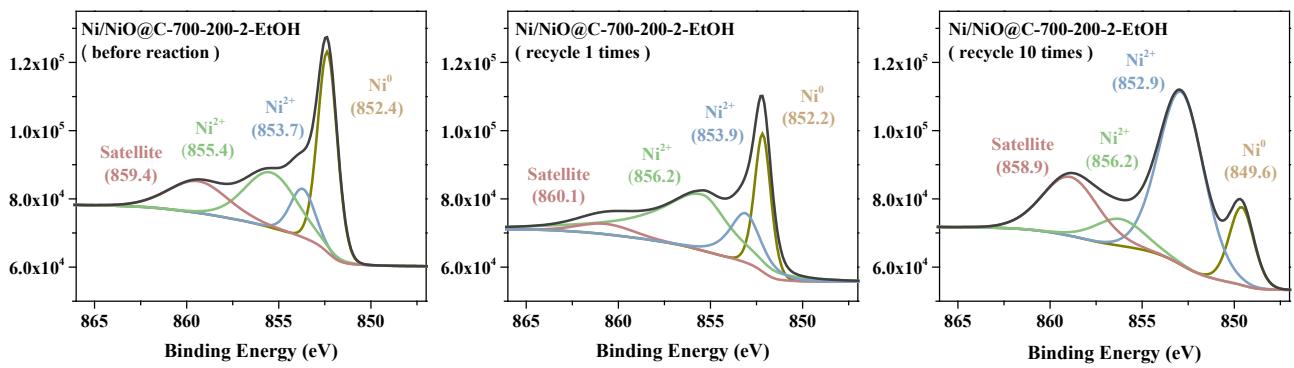


c. Ni/NiO@C-700-200-2 h-EtOH catalyst after the 10 times recycle reaction

S5. XRD spectra before and after reaction of Ni/NiO@C-700-200-2 h-EtOH



S6. XPS spectra before and after reaction of Ni/NiO@C-700-200-2 h-EtOH

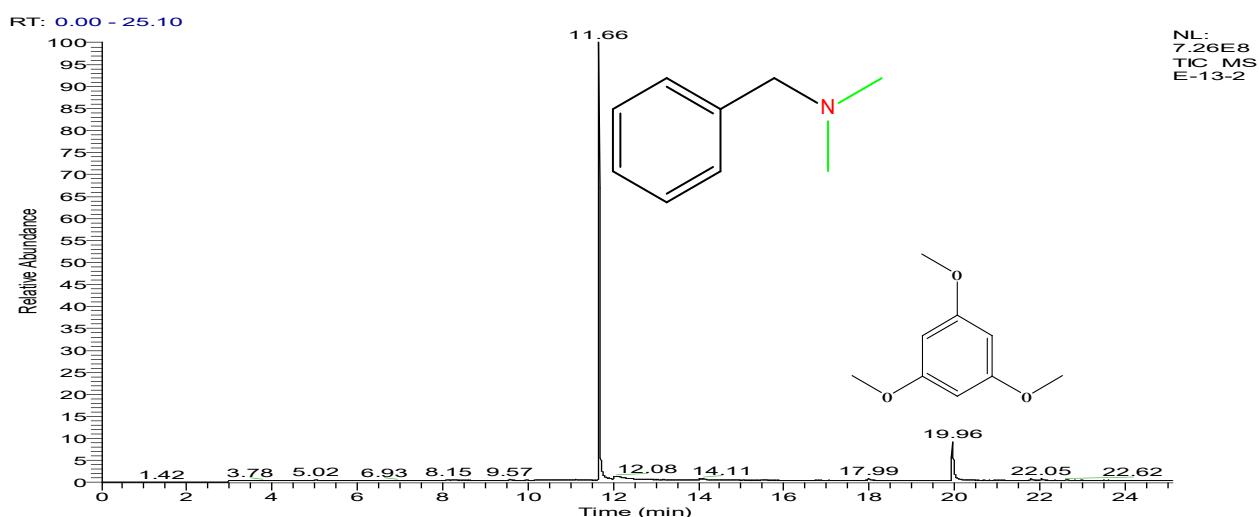
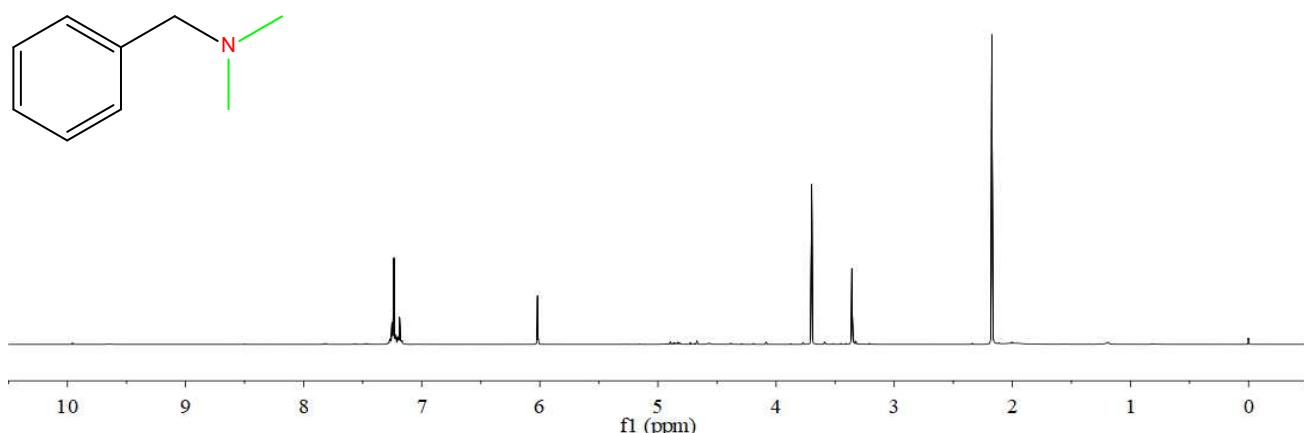


S7. EDS element before and after reaction of Ni/NiO@C-700-2 h-EtOH

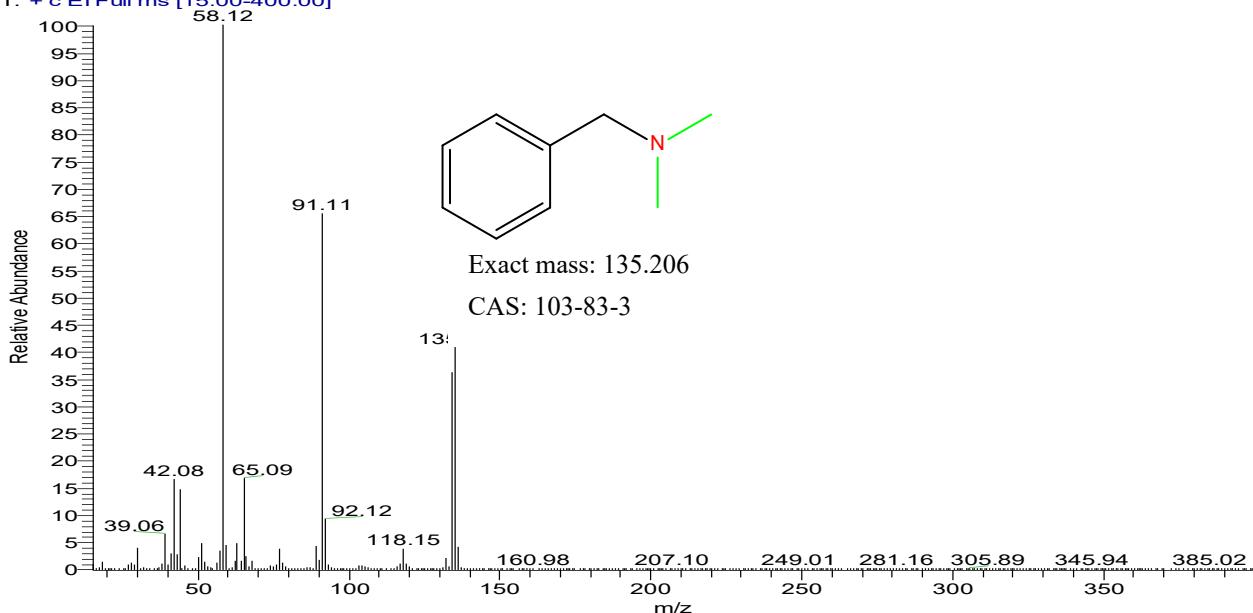
catalyst	C(%)	O(%)	S(%)	Ni(%)
before the reaction	18.78	2.31	0.16	78.75
after the reaction	32.35	5.31	0.08	62.27
recycle 10 times	37.36	7.25	0.28	55.12

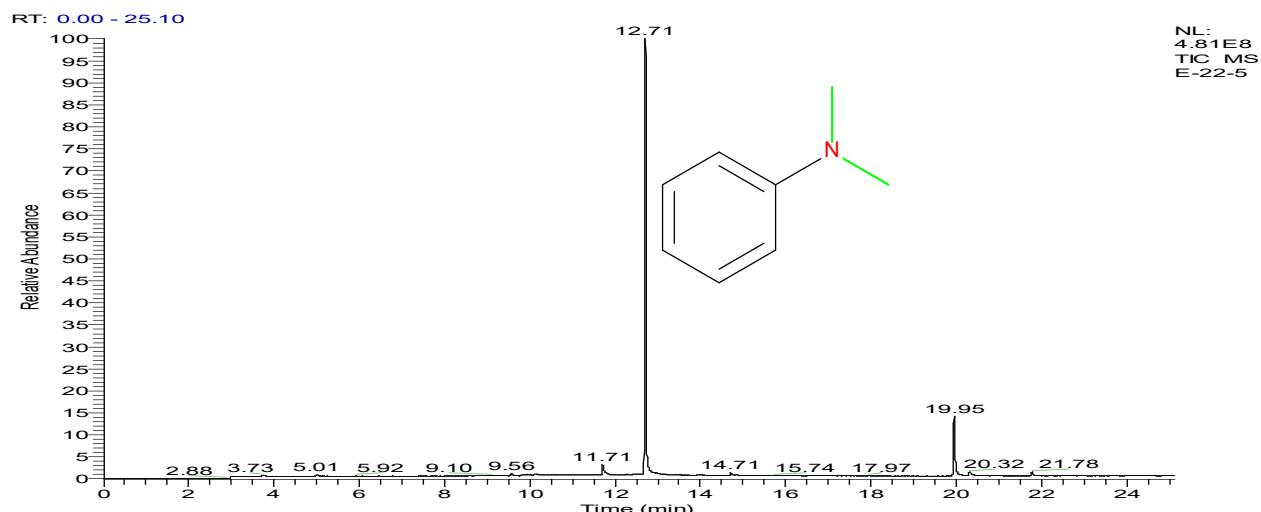
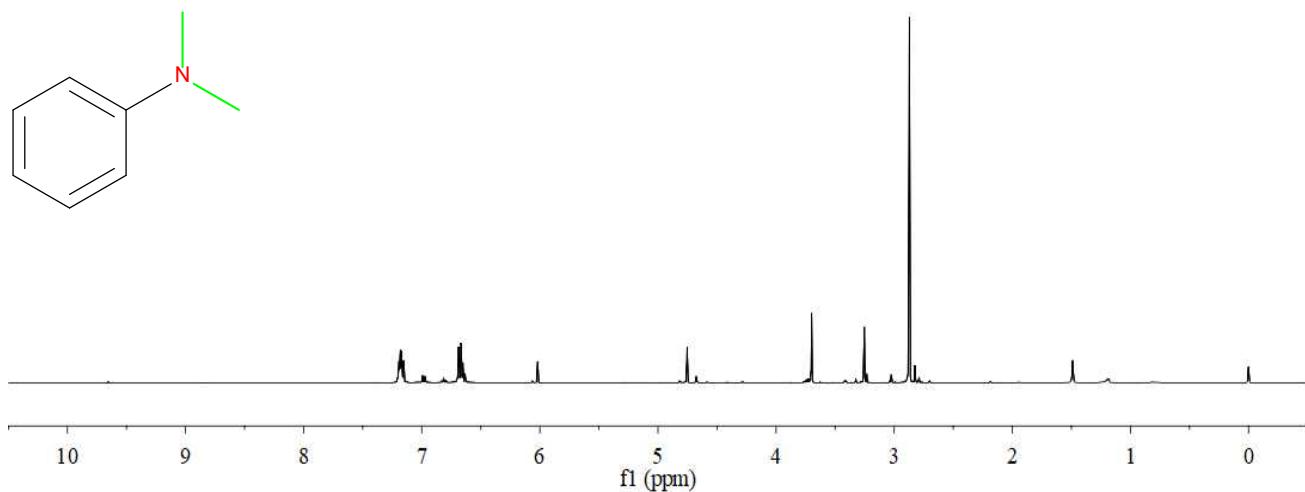
S8. NMR and GCMS spectra (In our GC-MS procedure, the first 3 min is held at 40 °C to stabilize the baseline and to evaporate the methanol solution, so that this part is deleted in our result to emphasize the main peak for target products)

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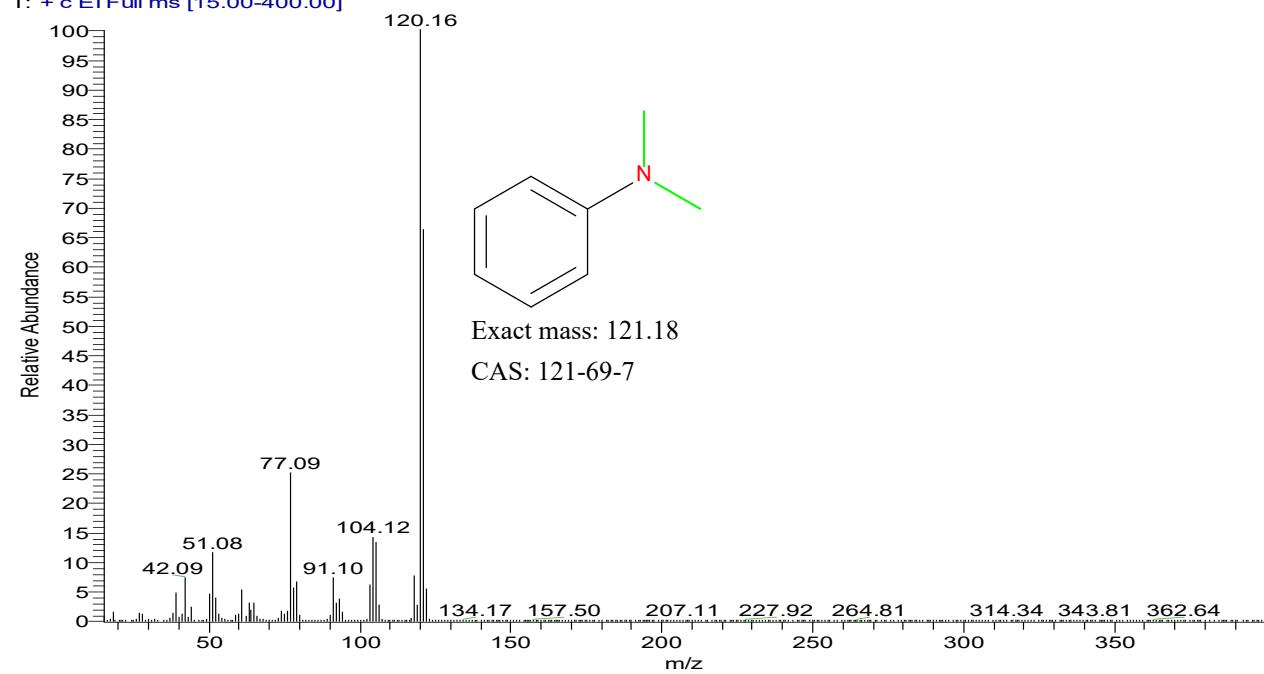


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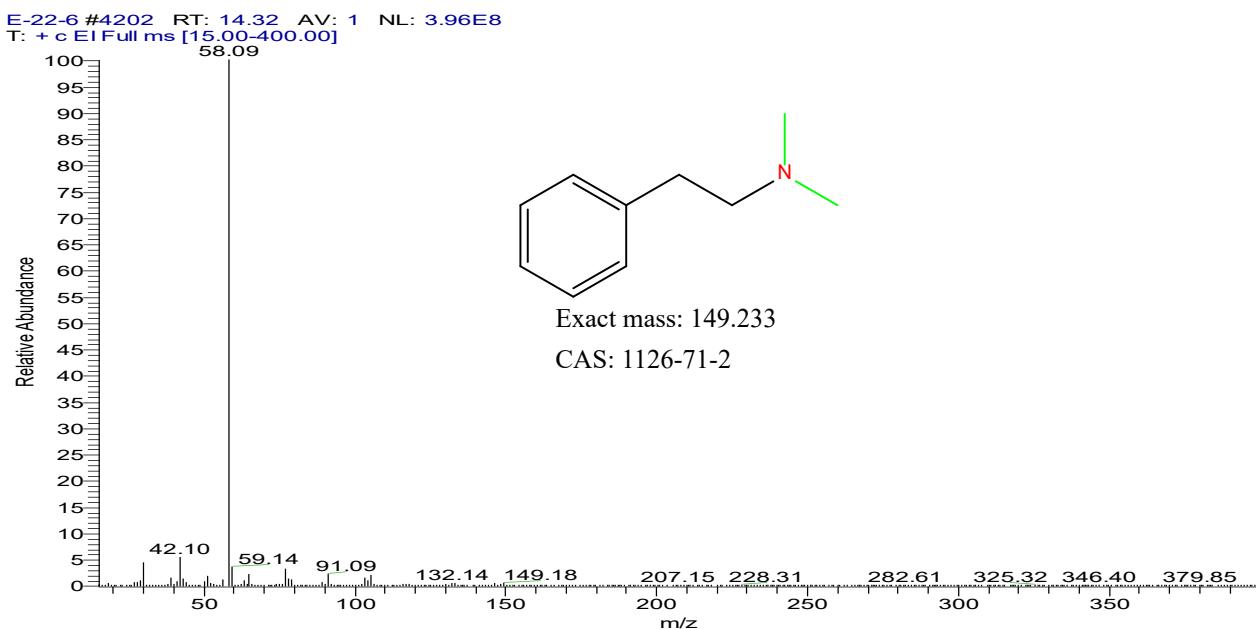
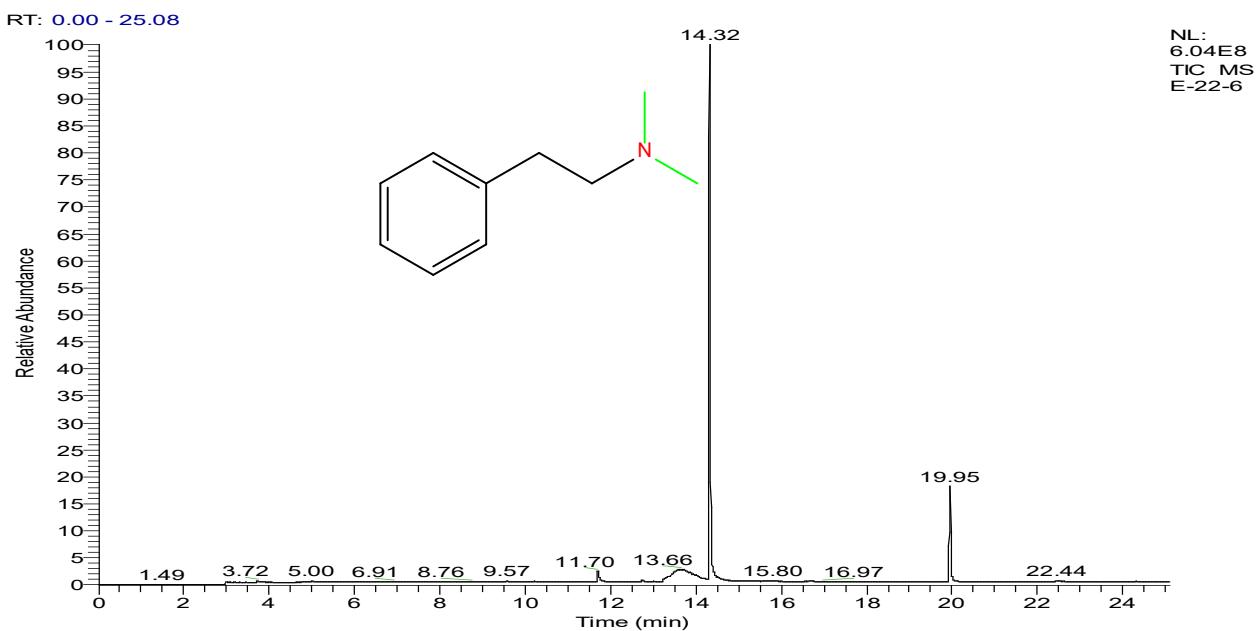
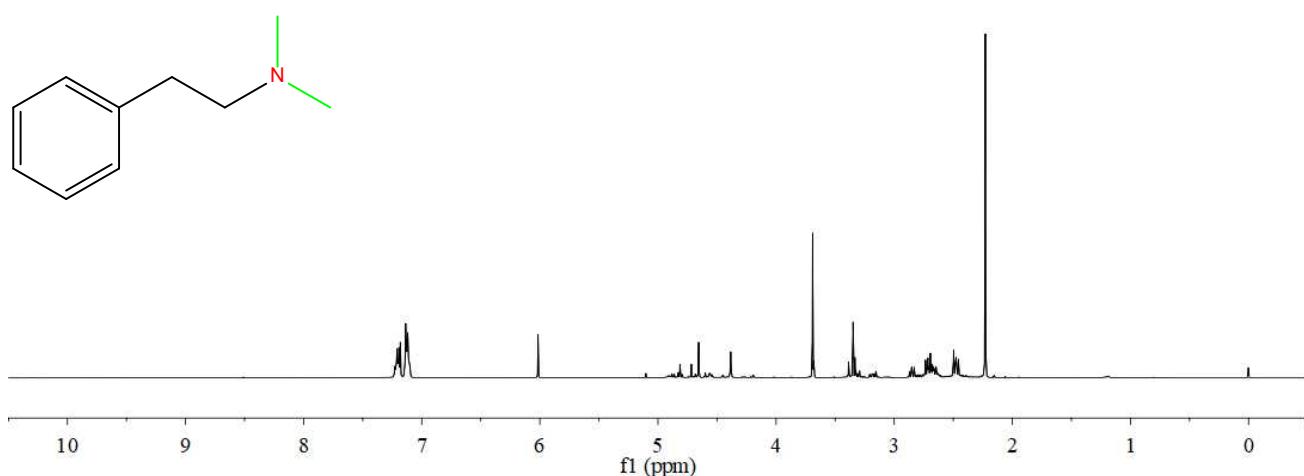




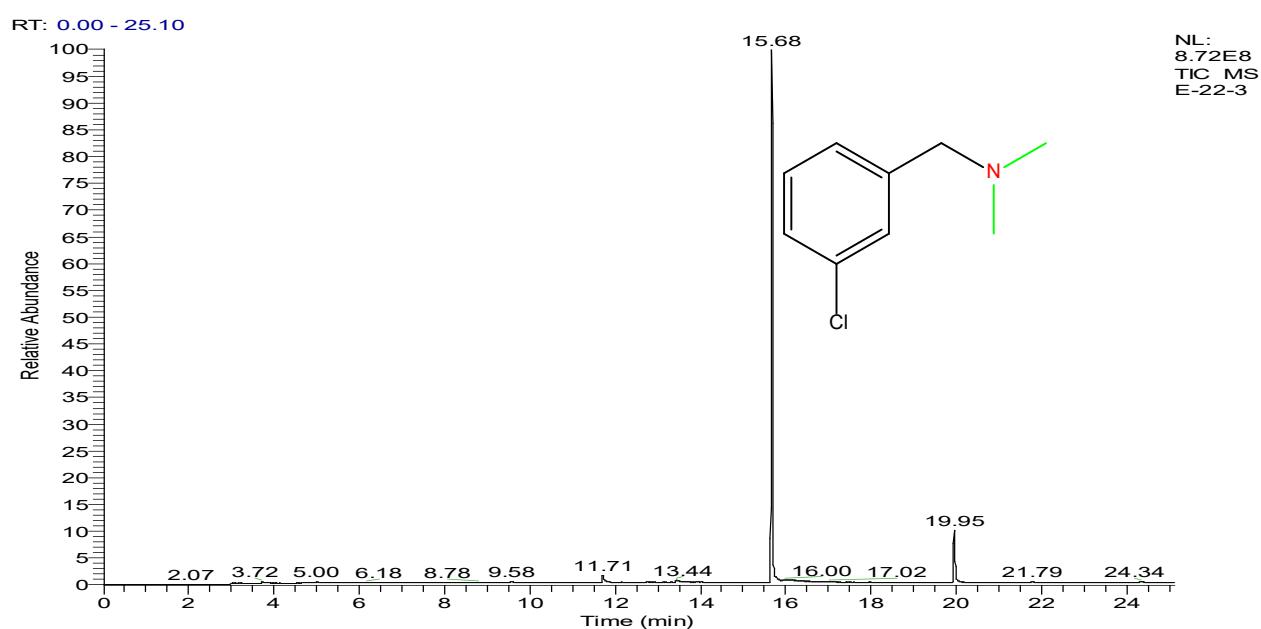
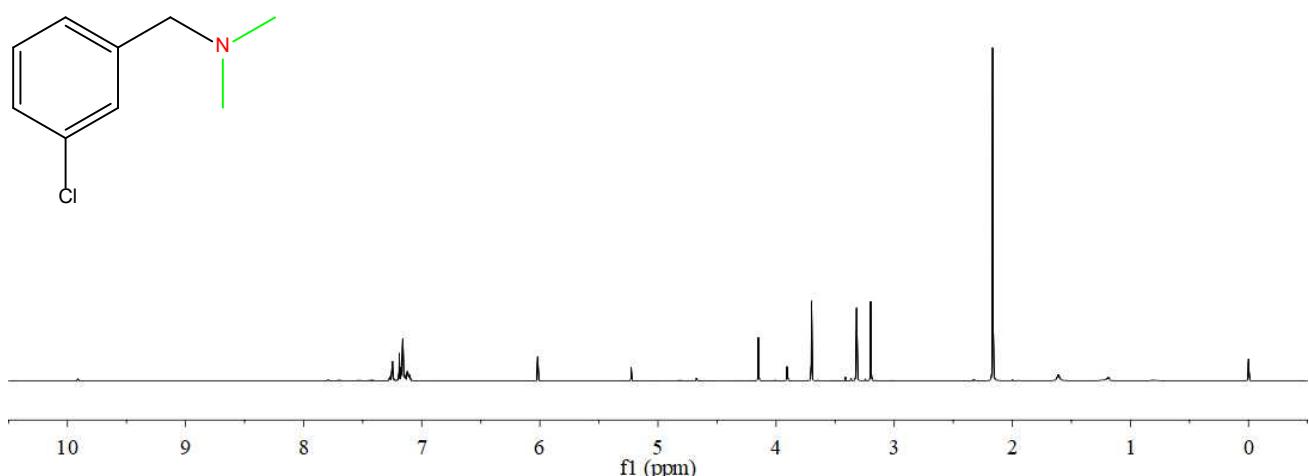
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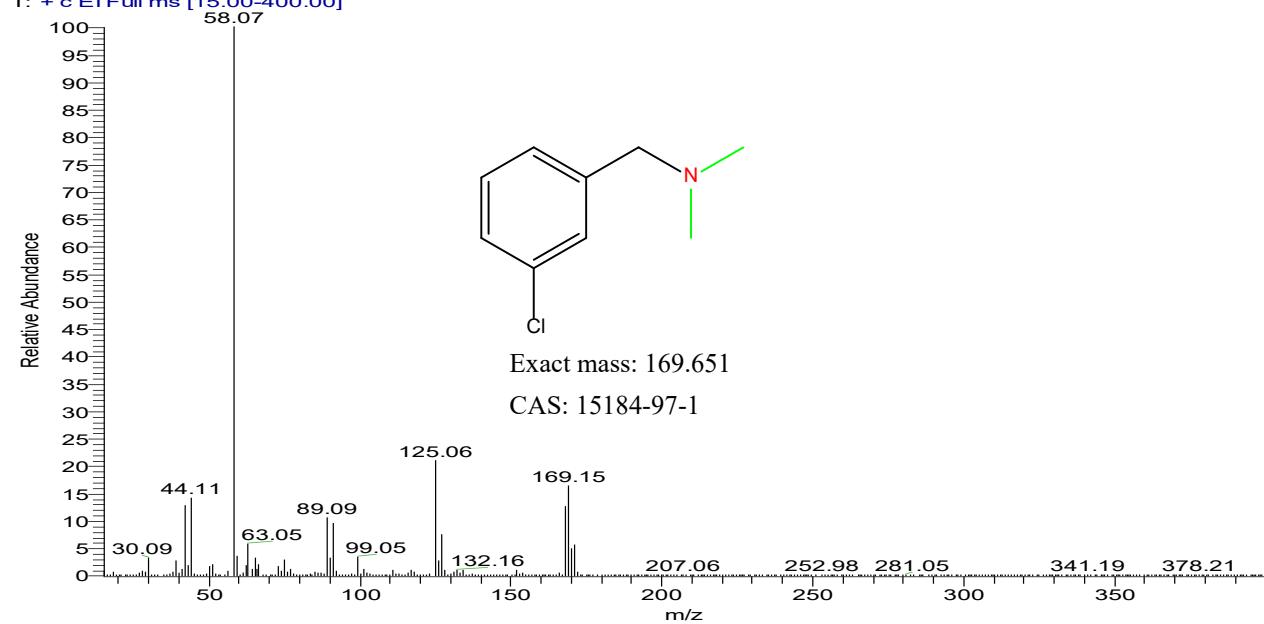
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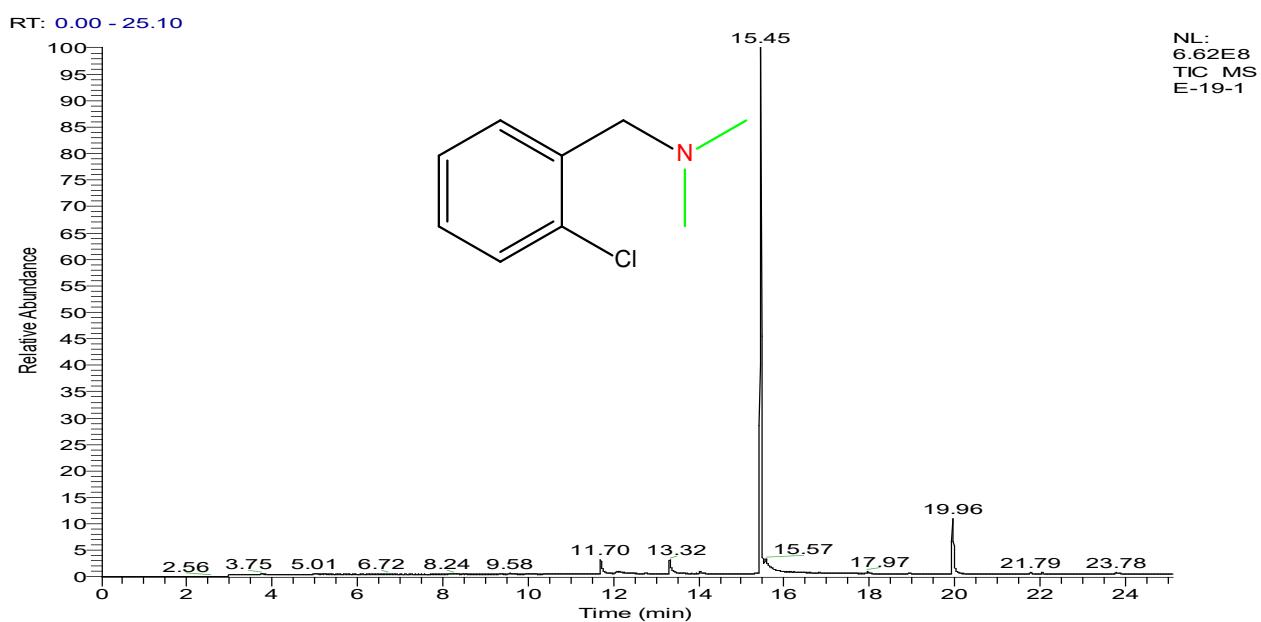
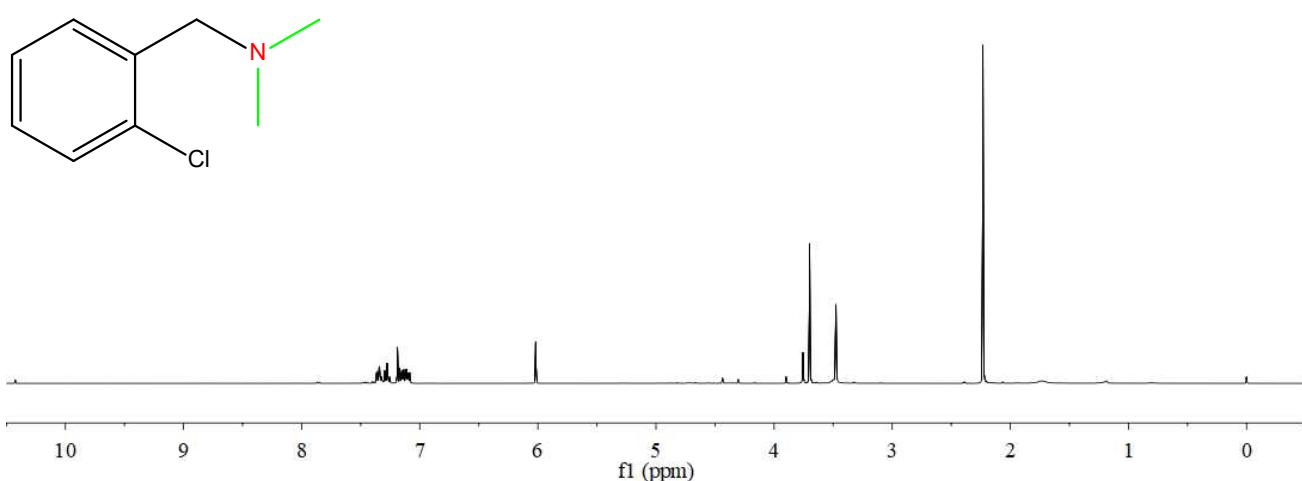
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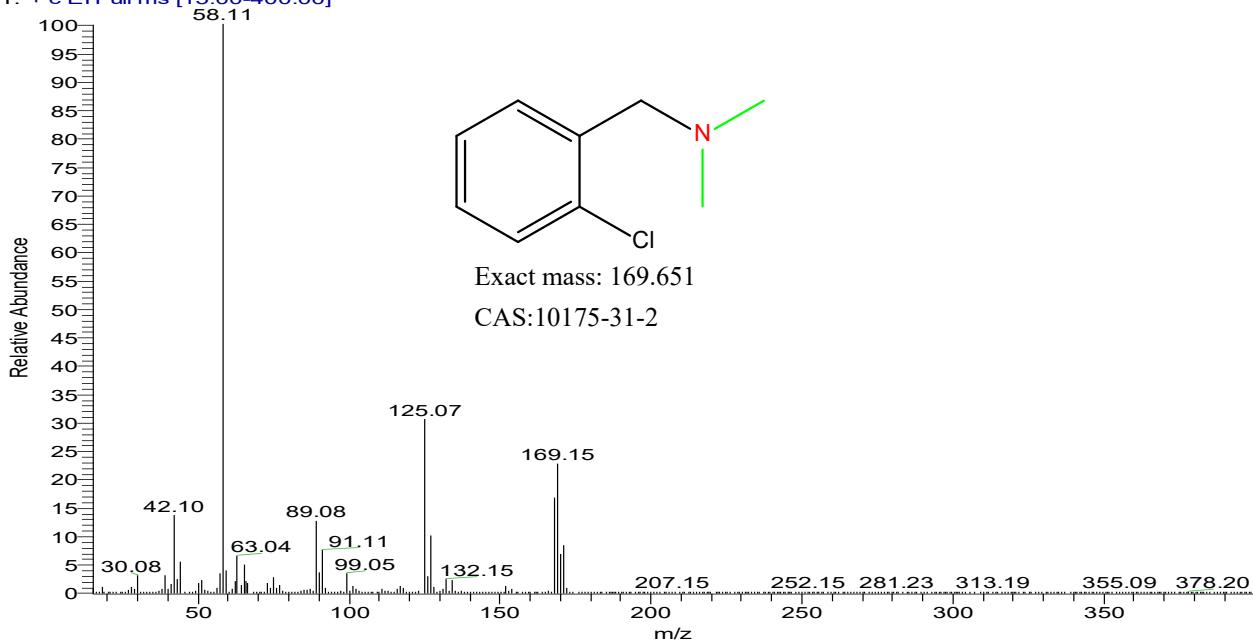
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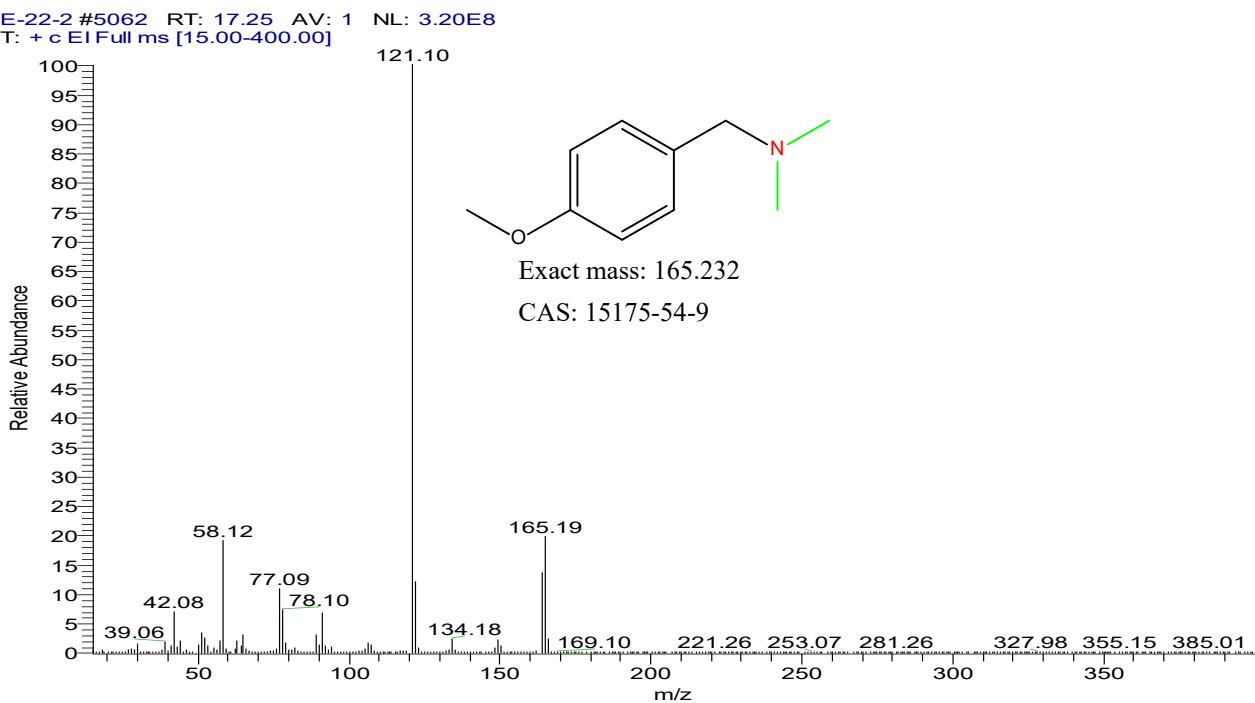
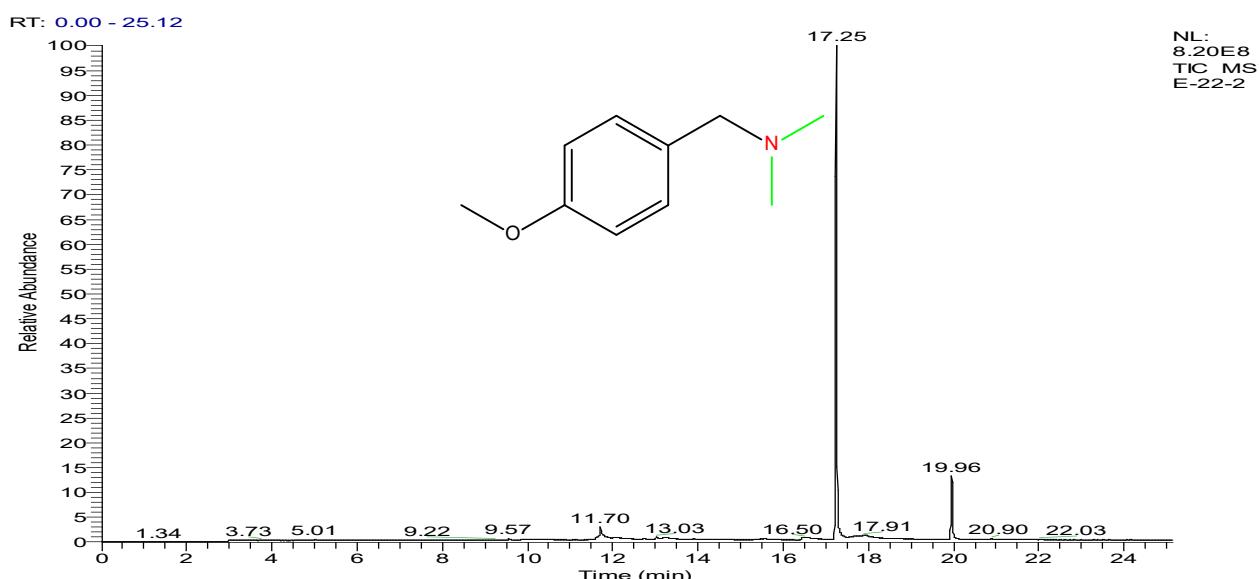
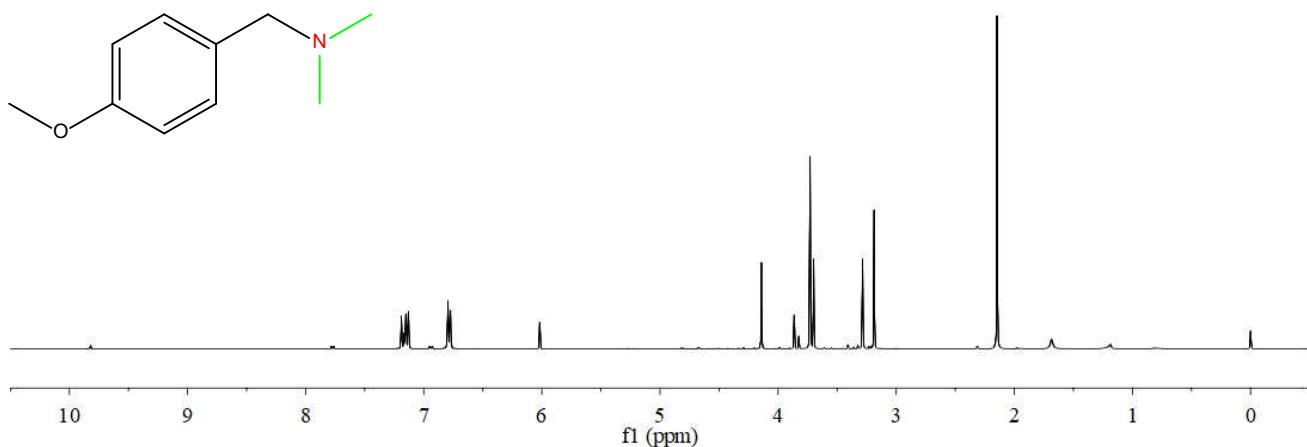


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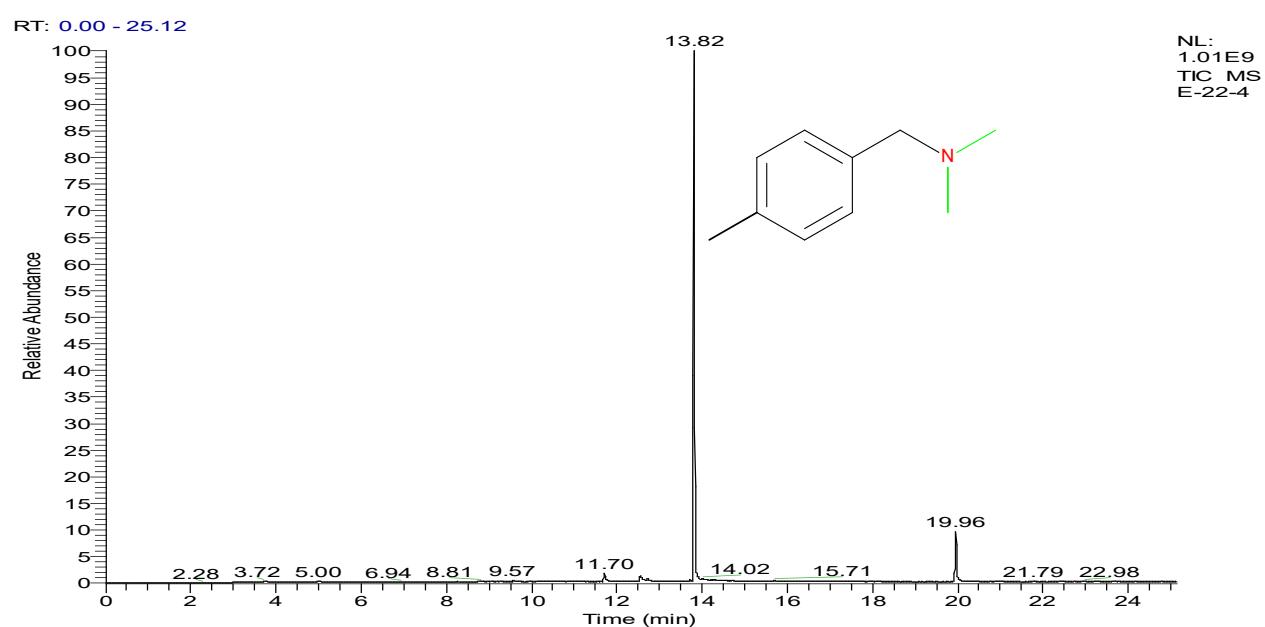
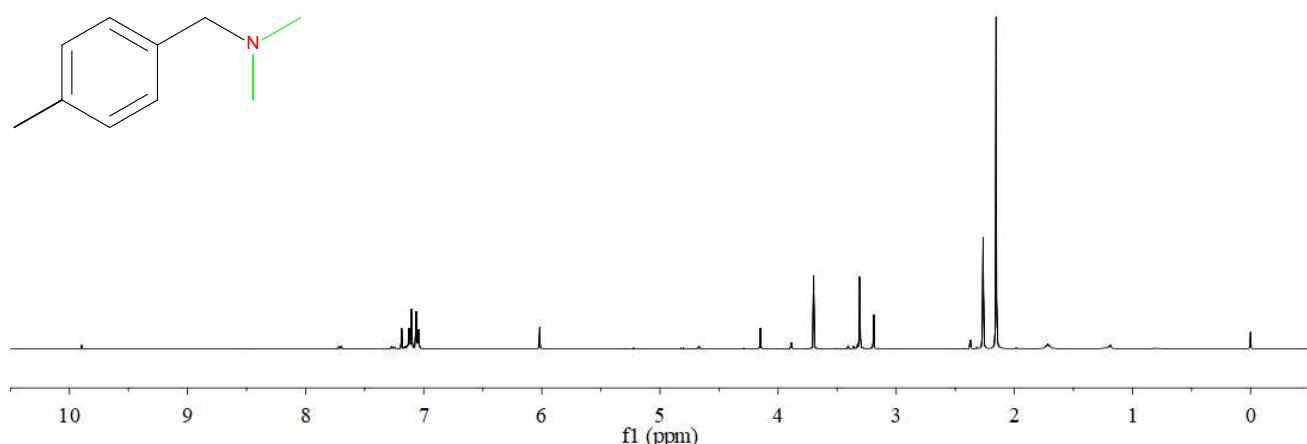


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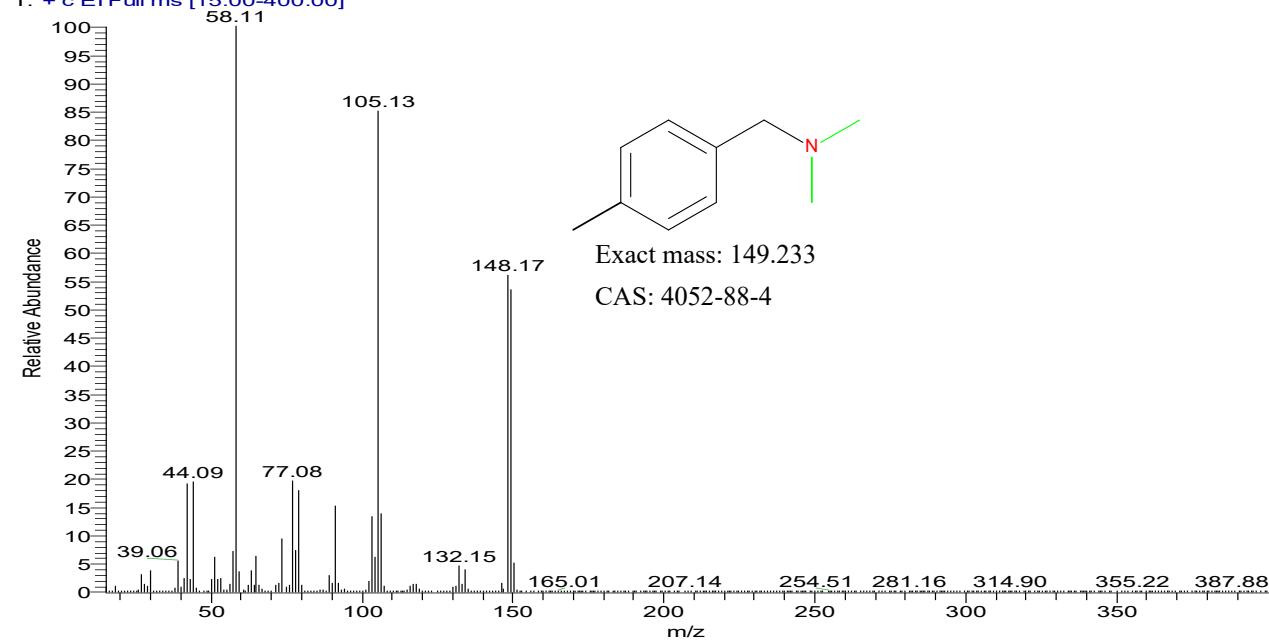


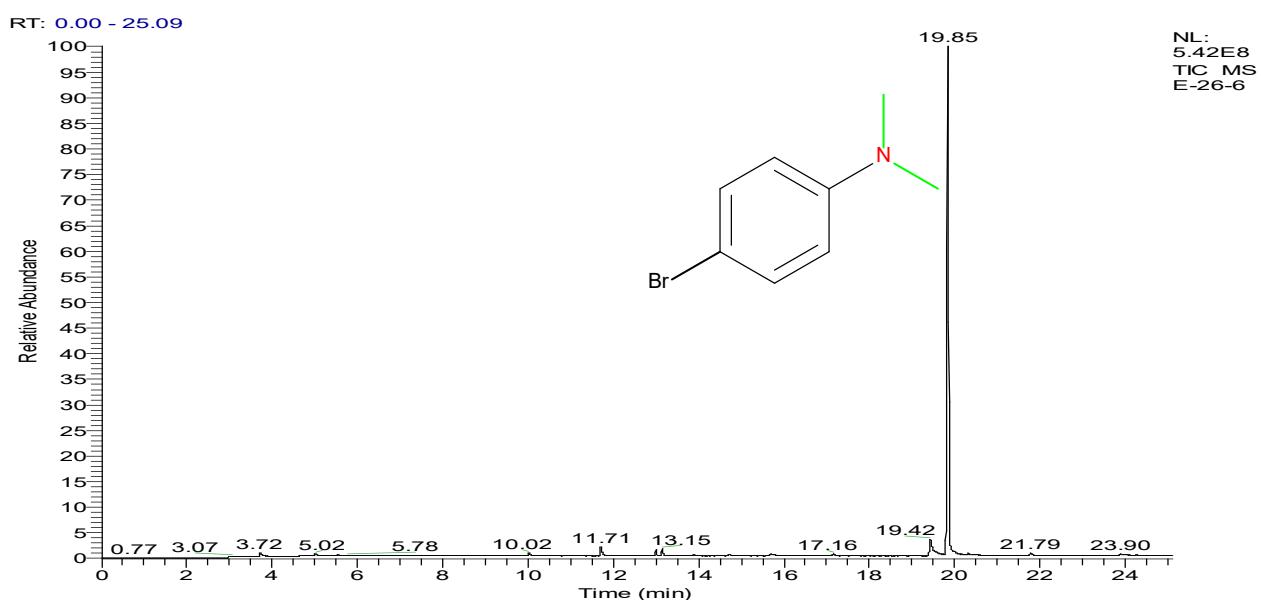
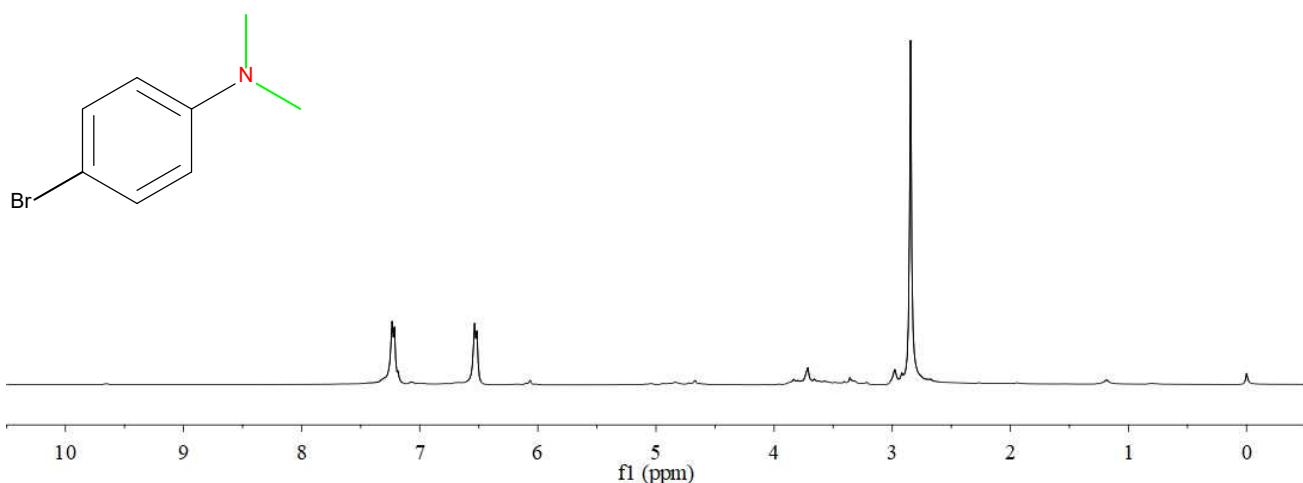


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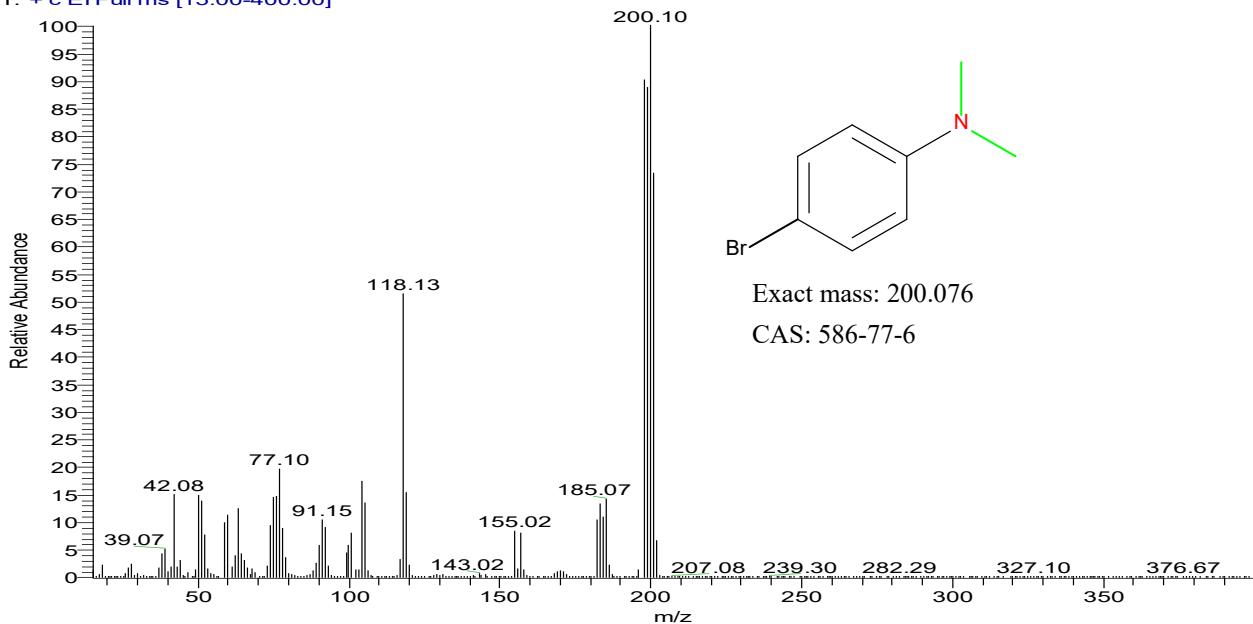


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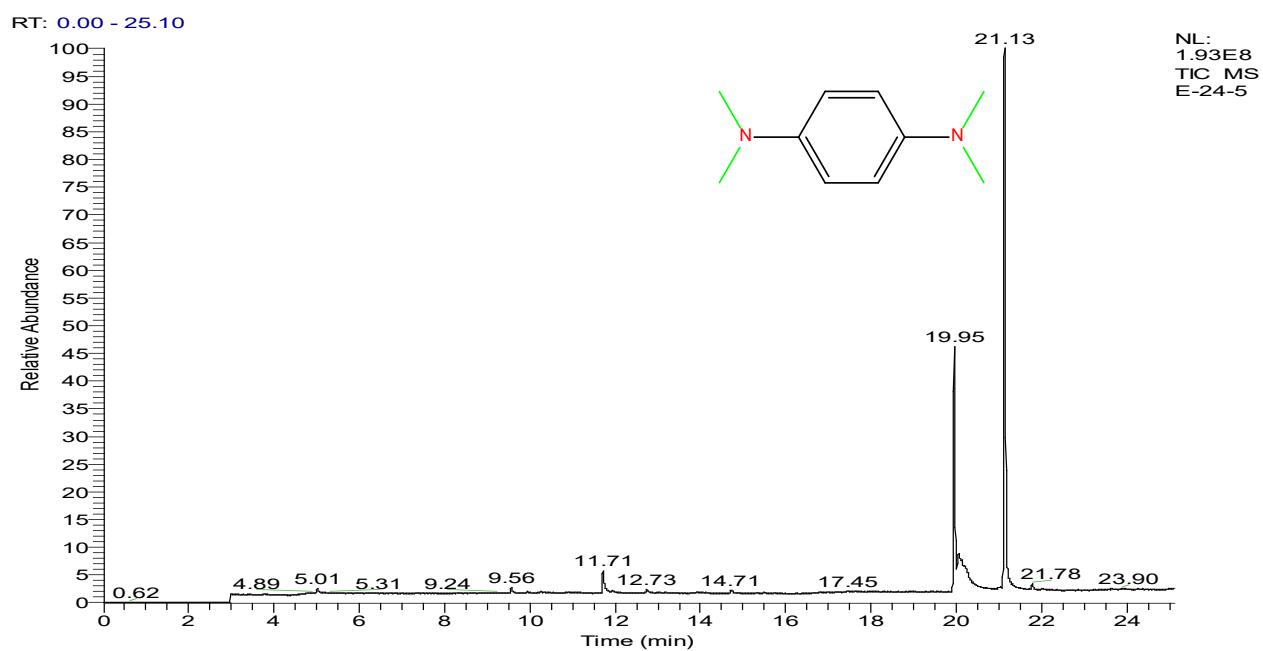
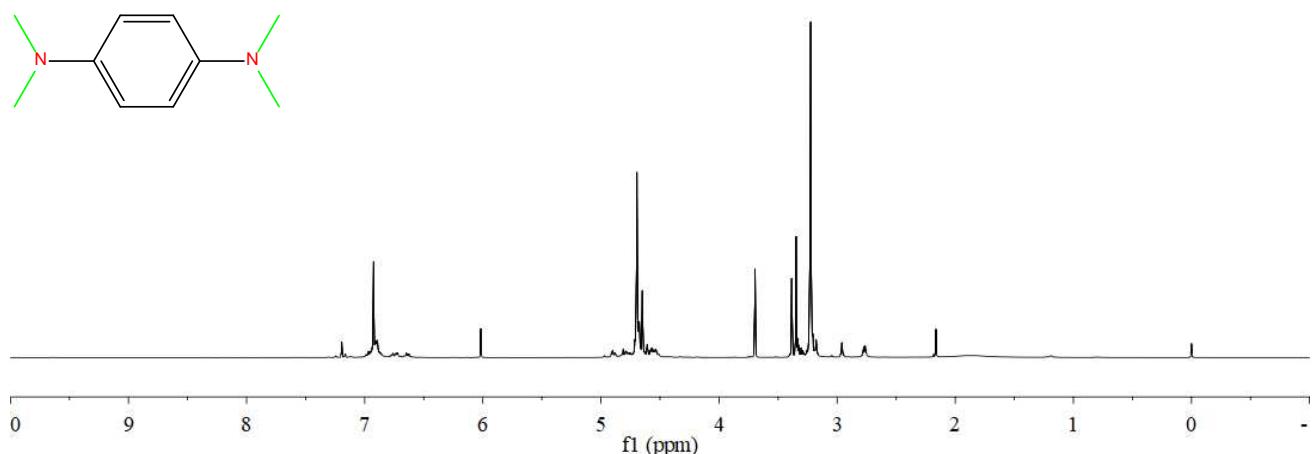




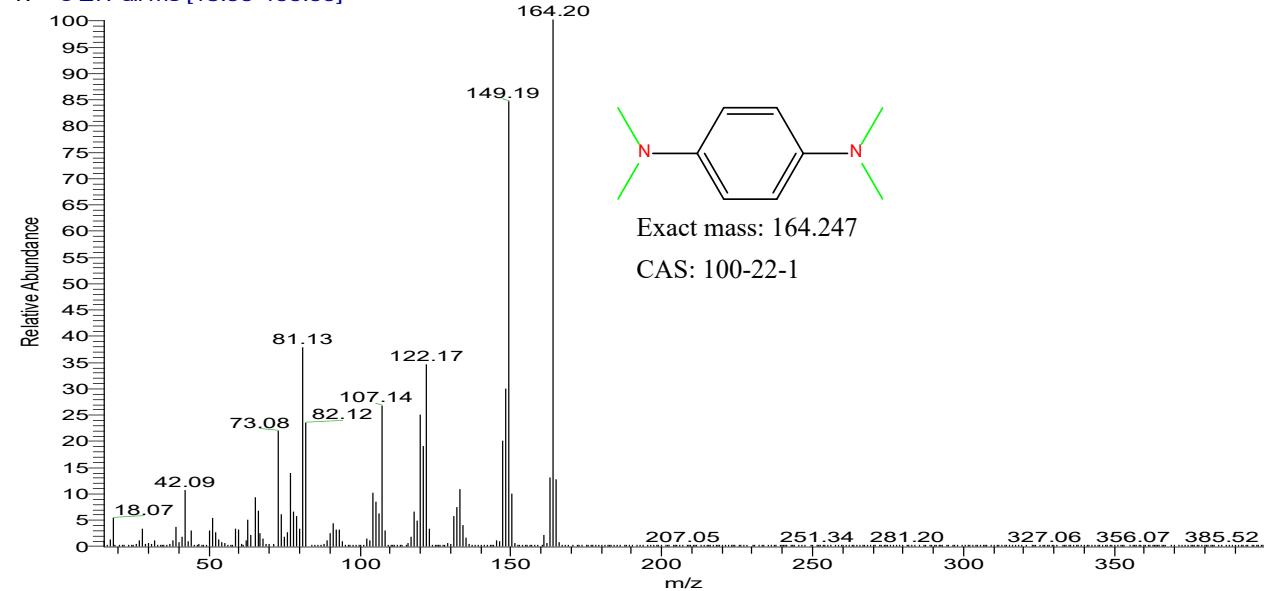
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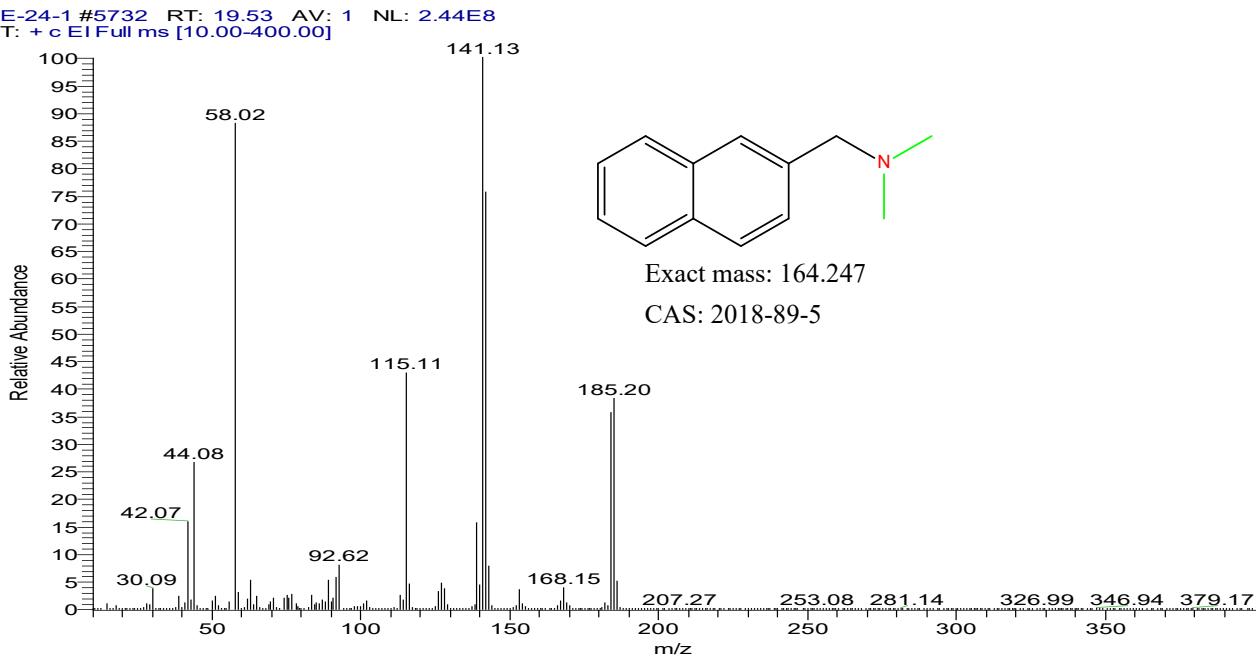
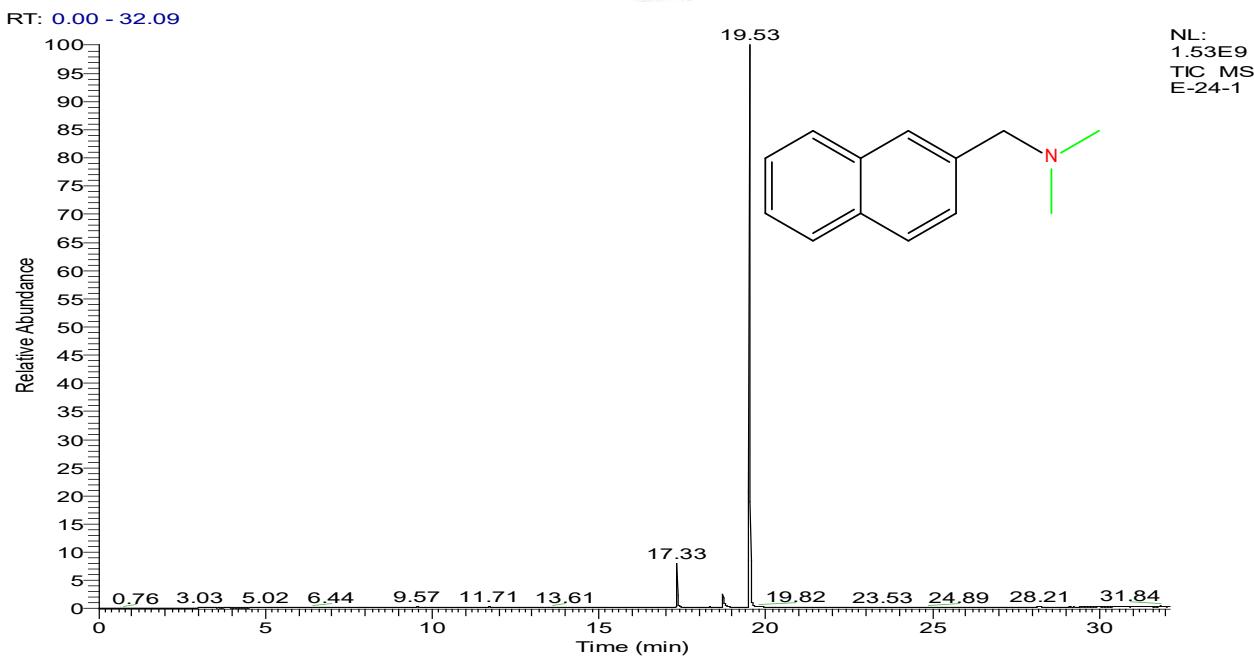
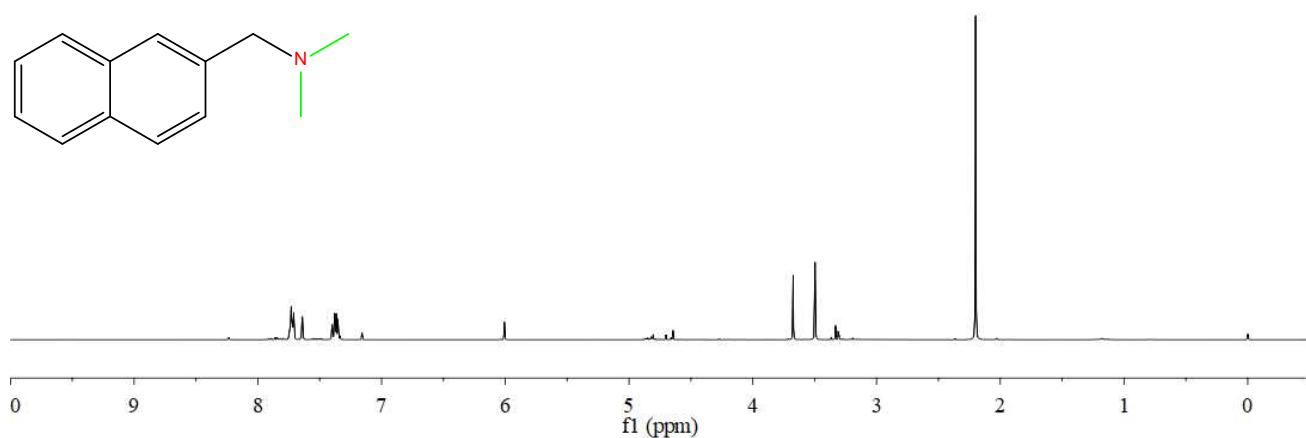
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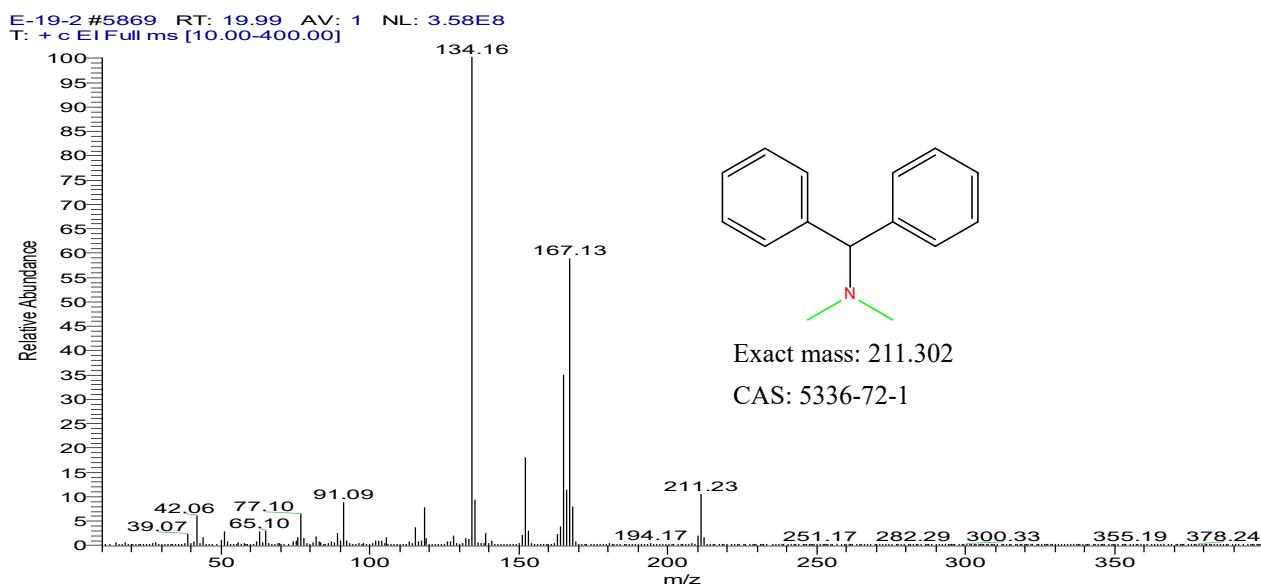
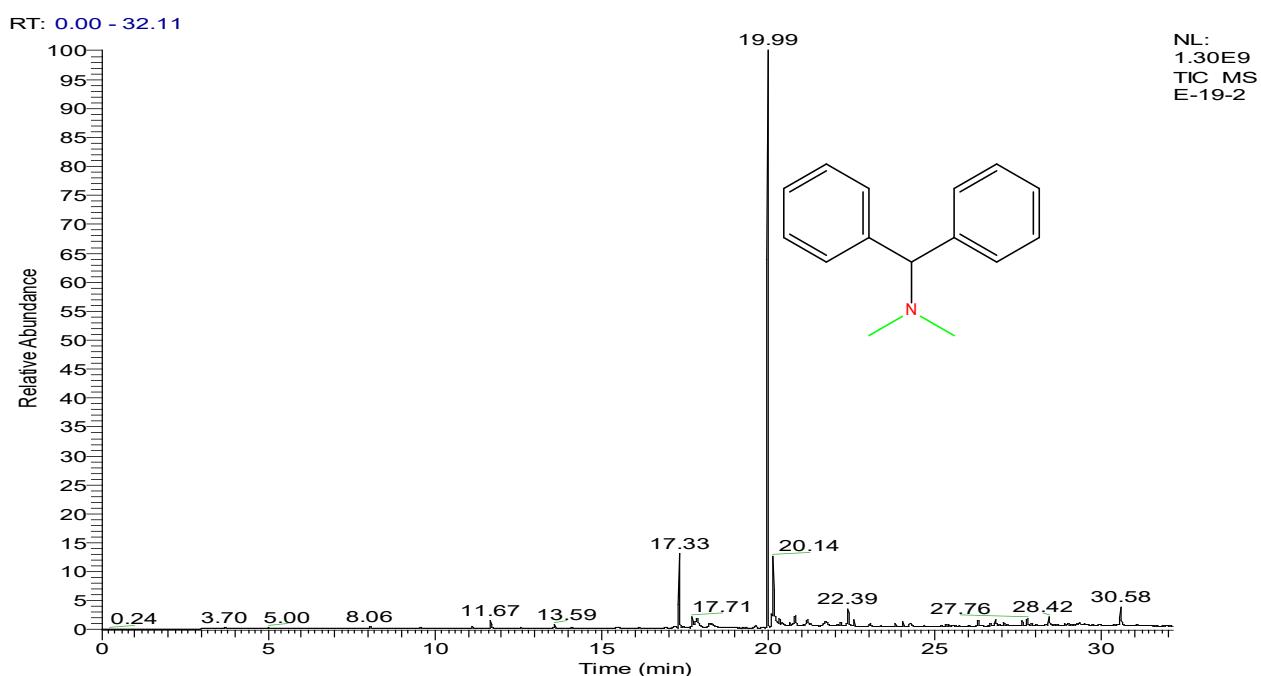
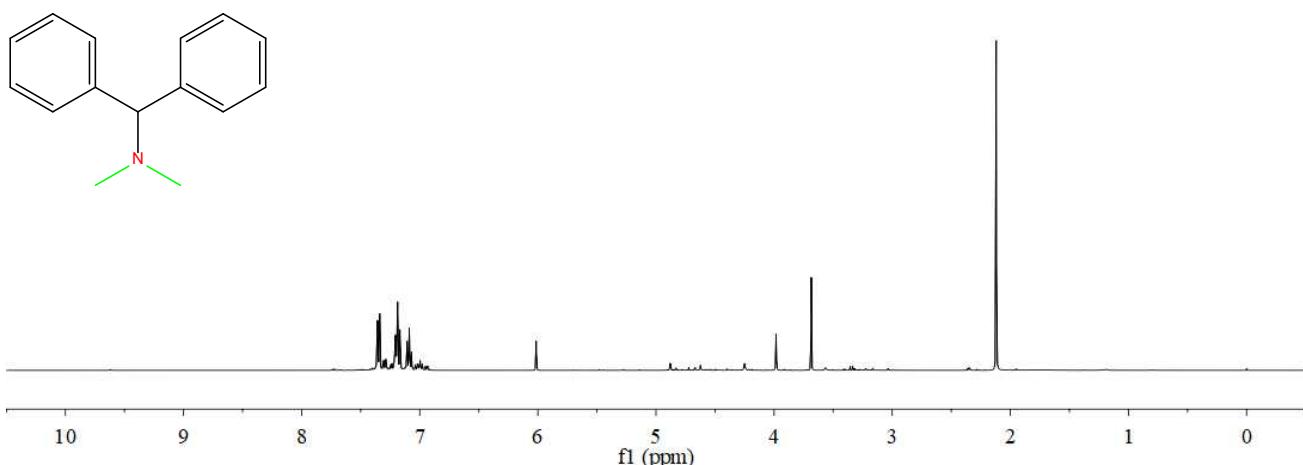
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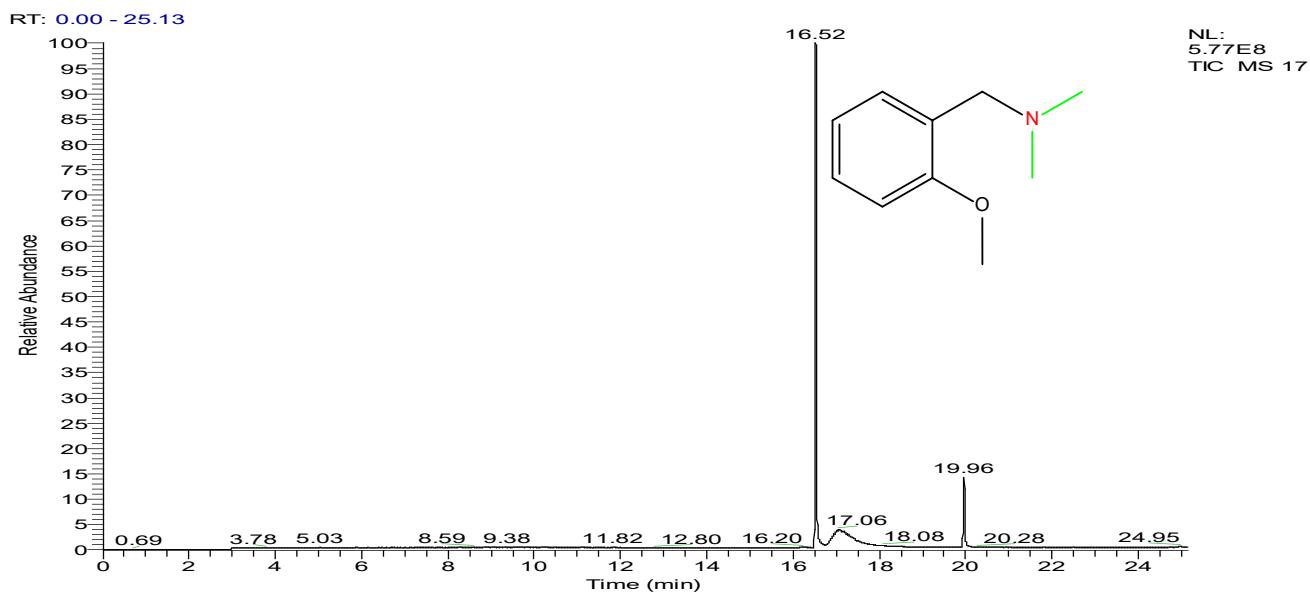
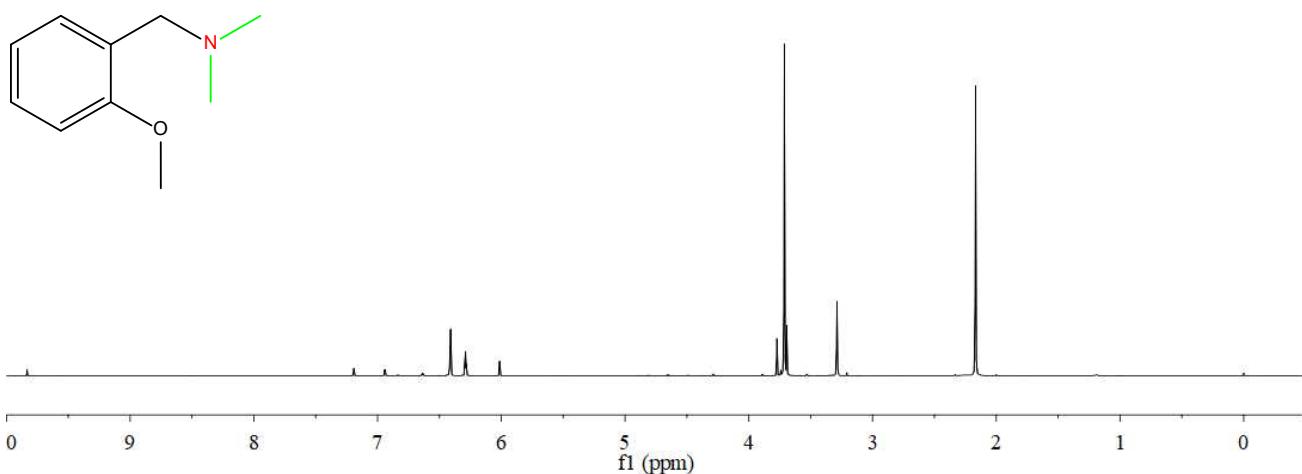
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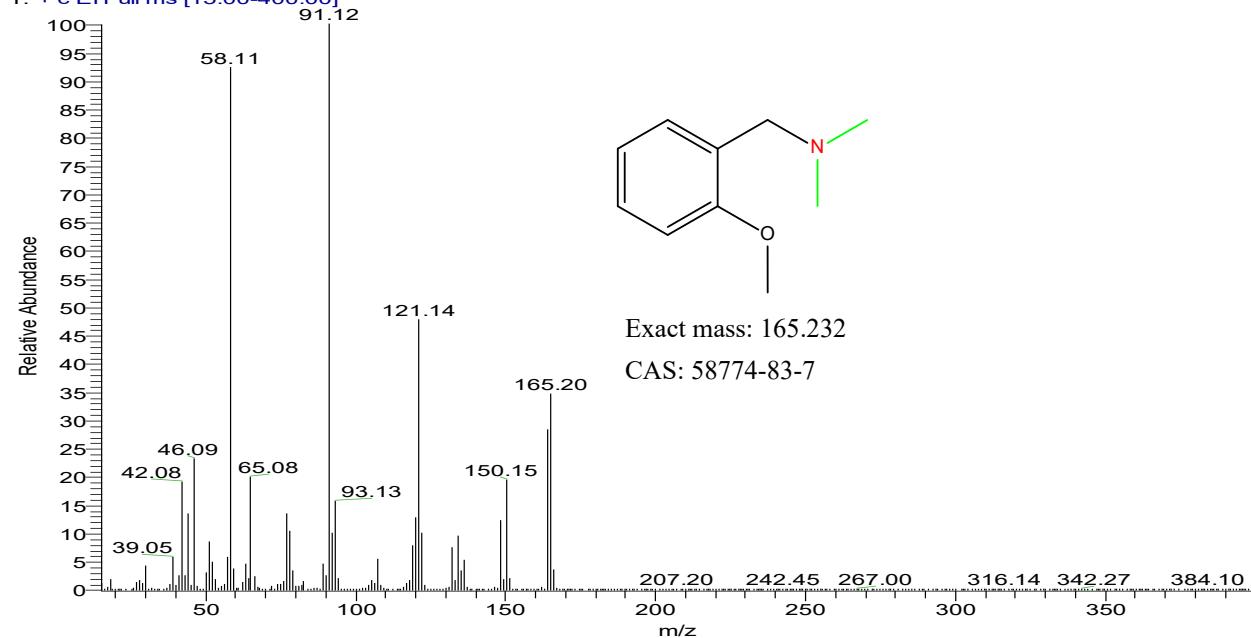
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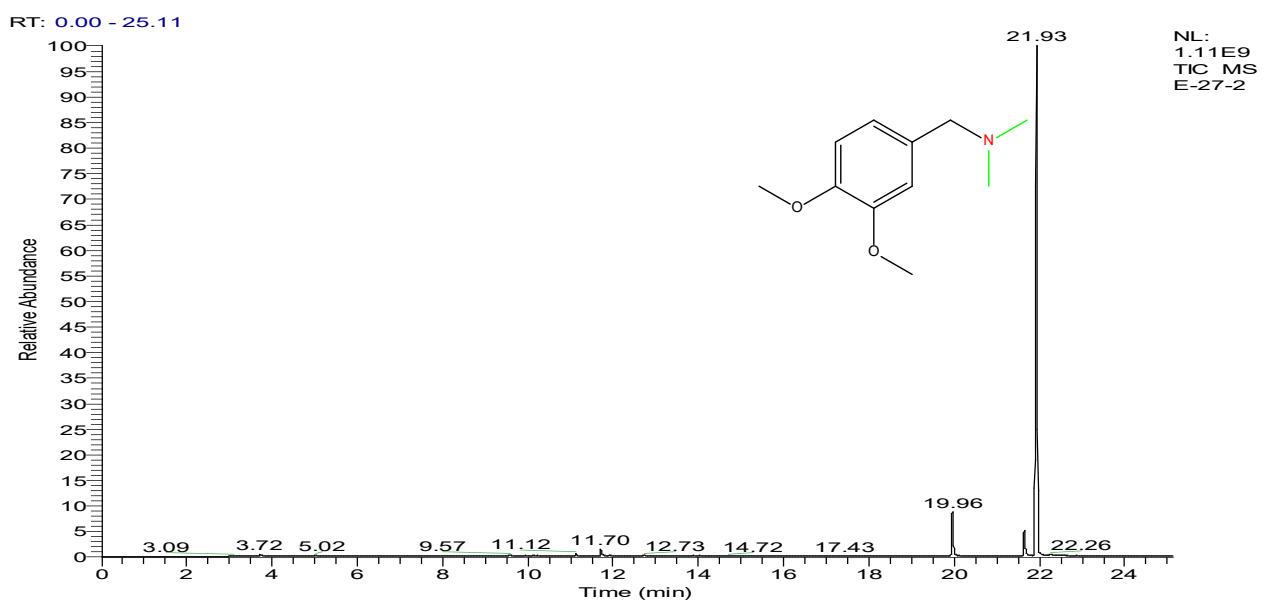
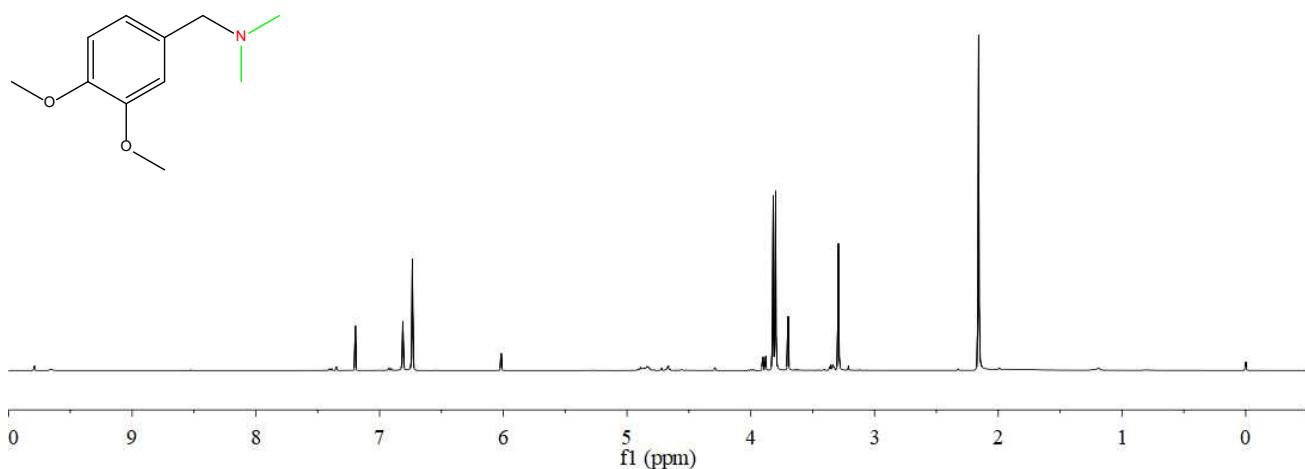
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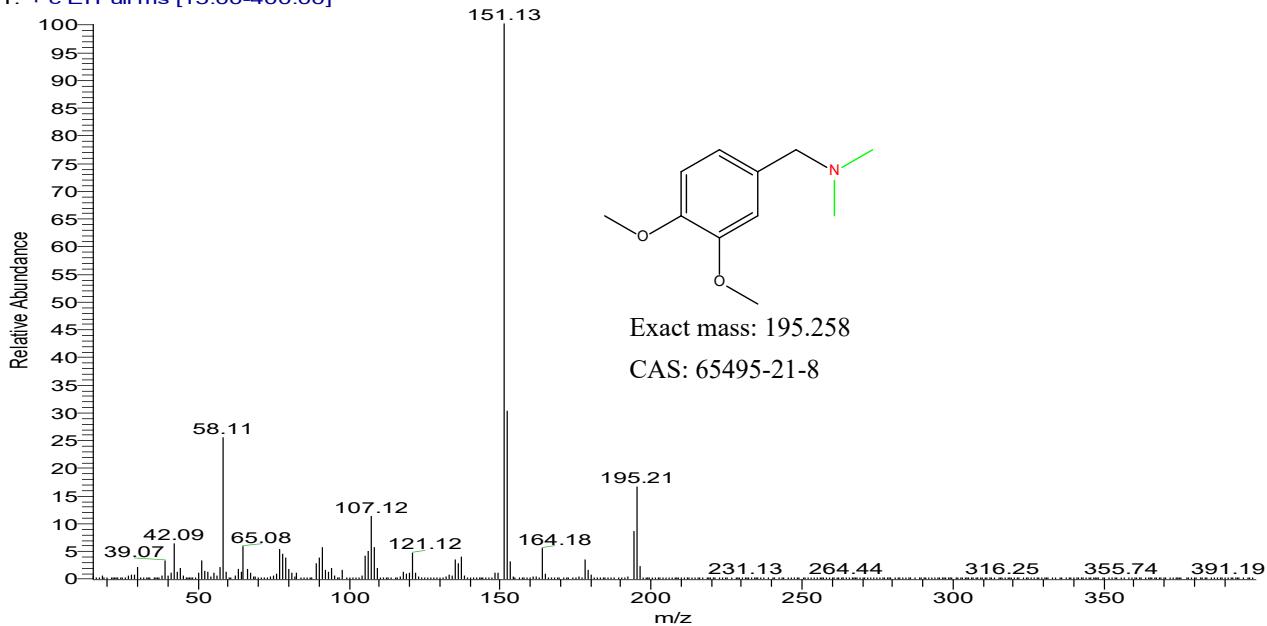
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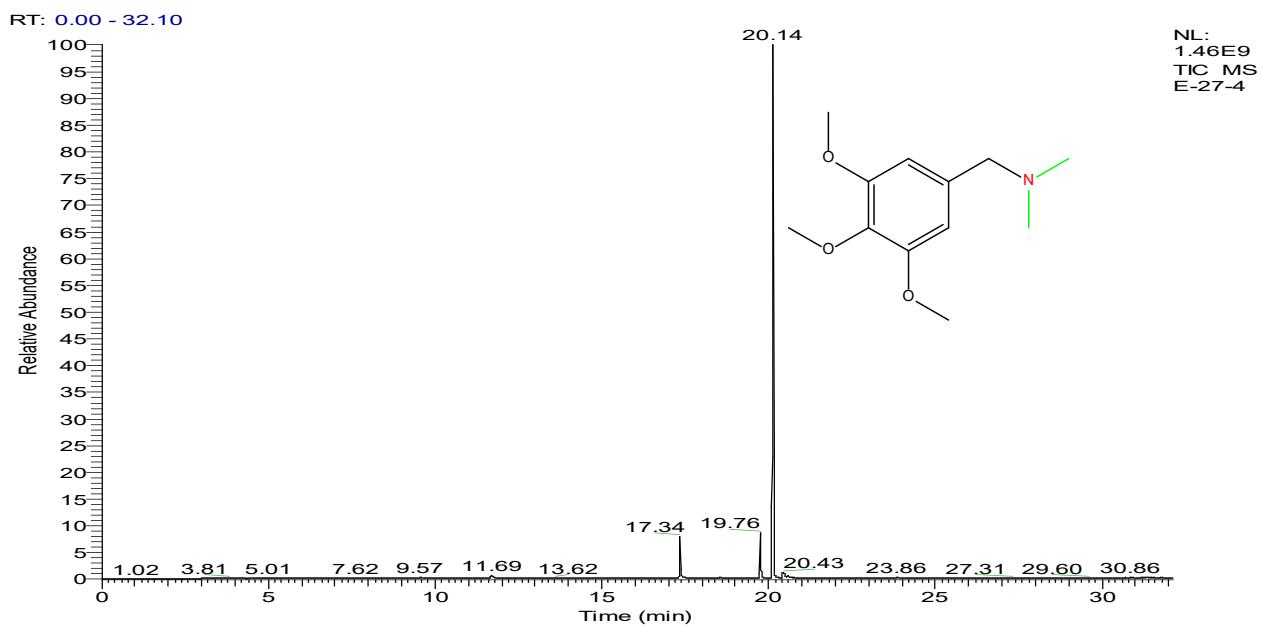
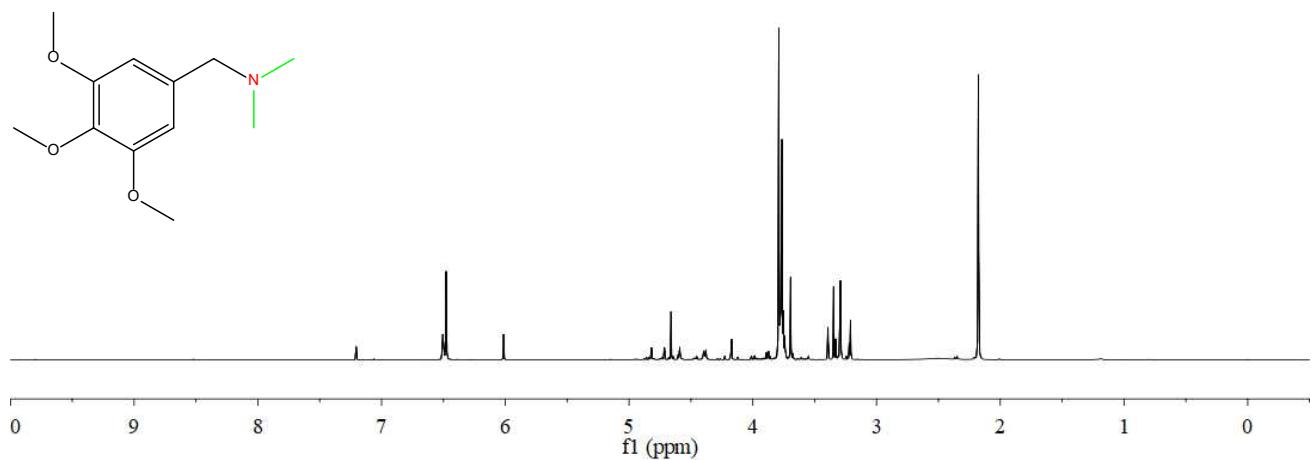


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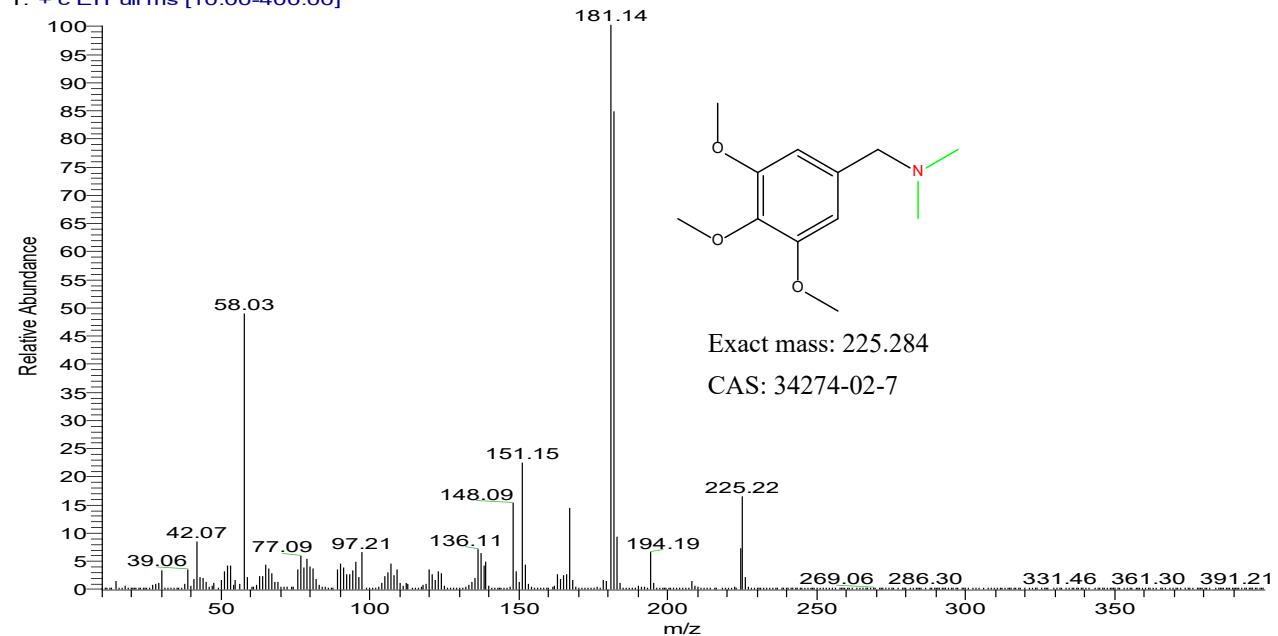


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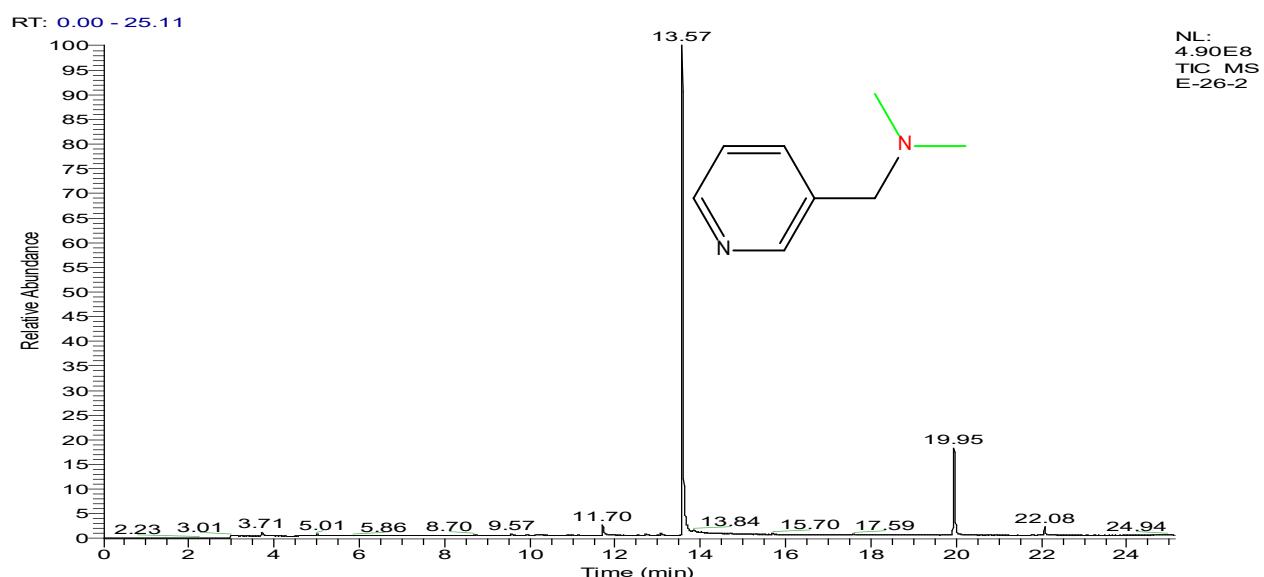
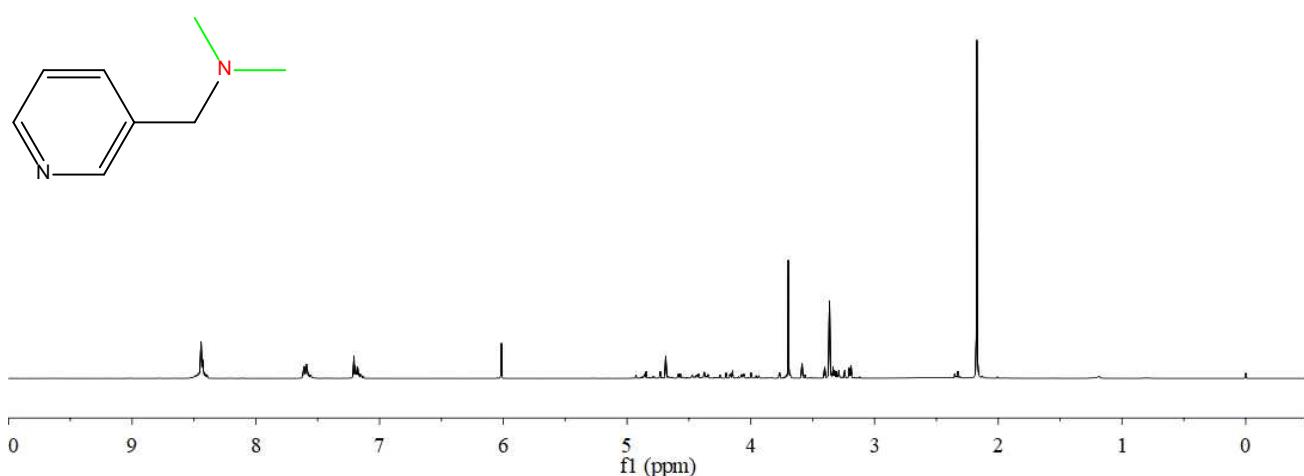




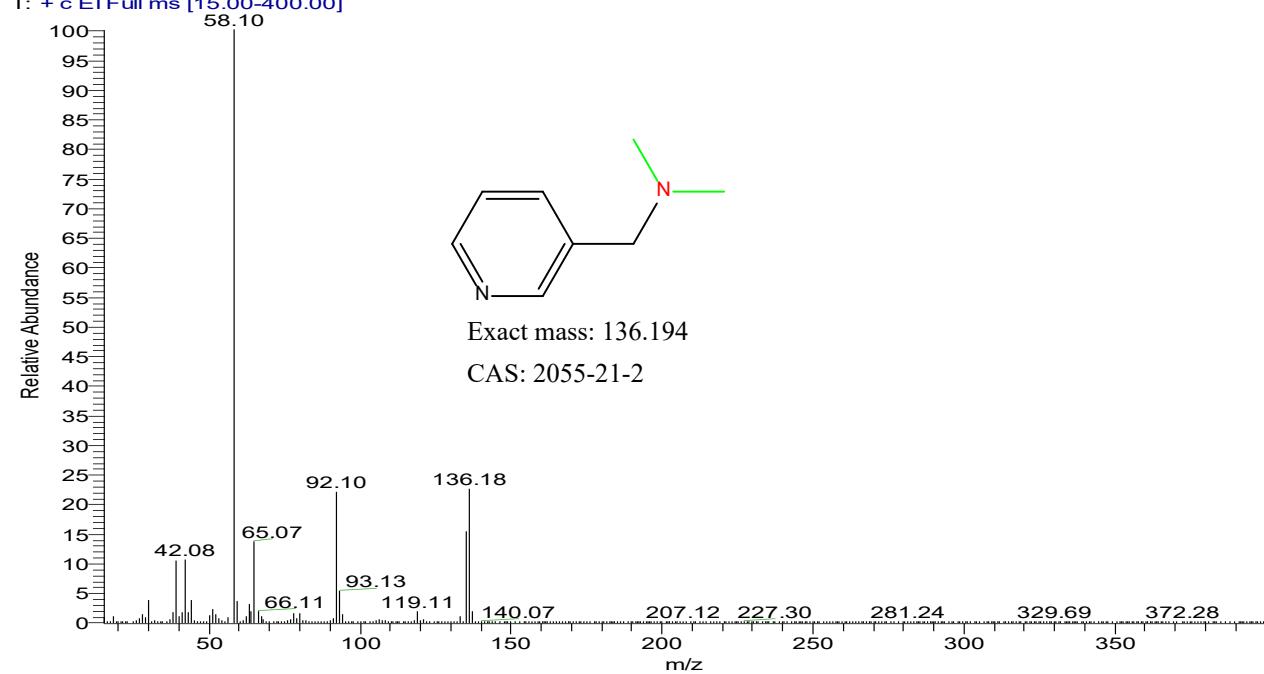
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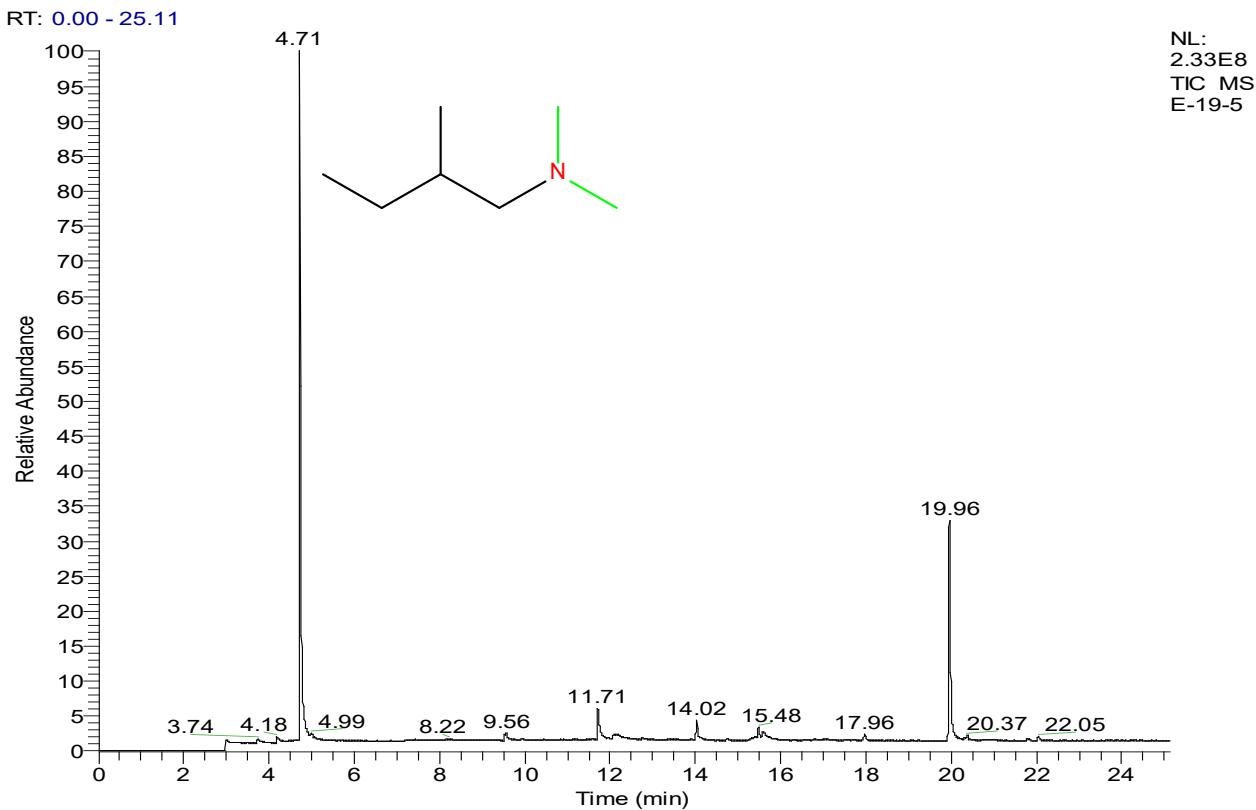
15



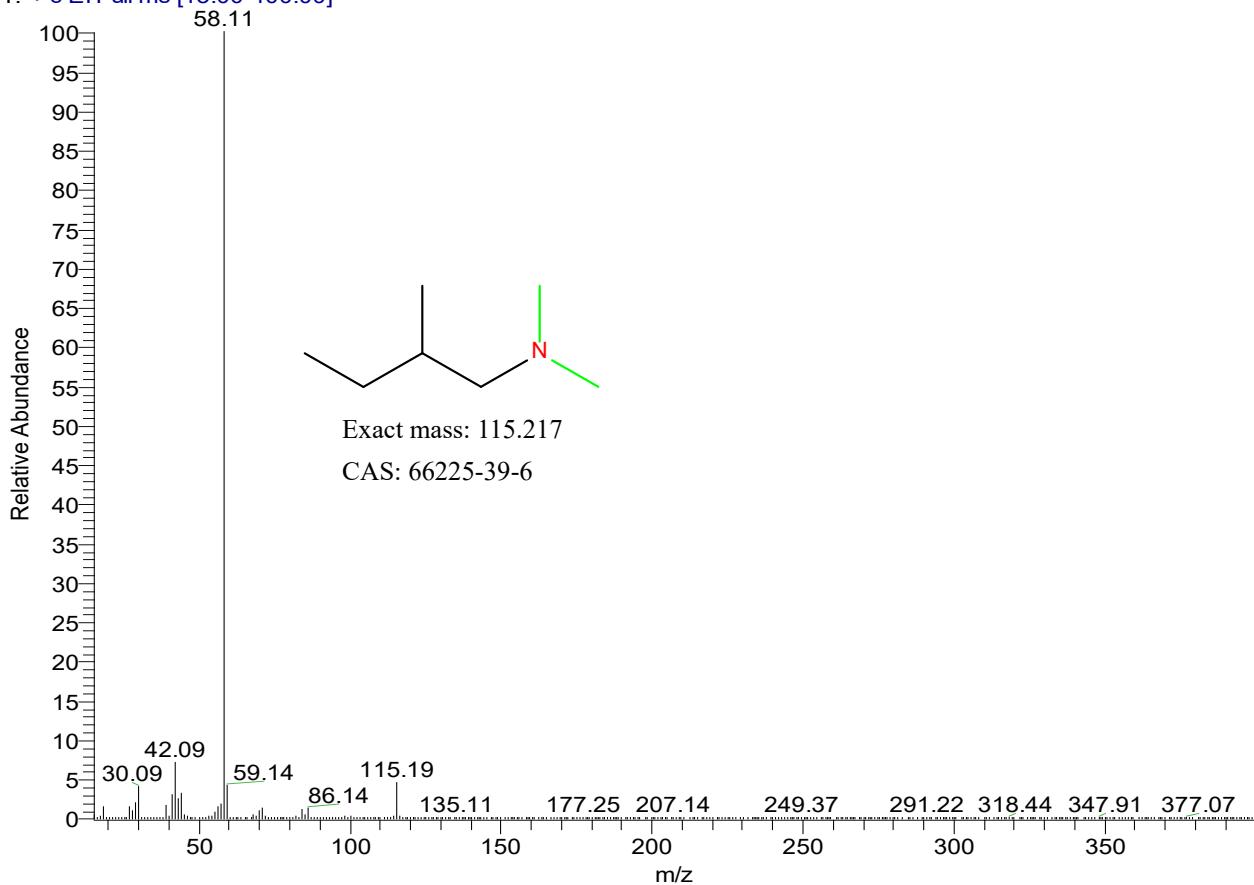
E-26-2 #3982 RT: 13.57 AV: 1 NL: 1.92E8
T: + c EI Full ms [15.00-400.00]



16



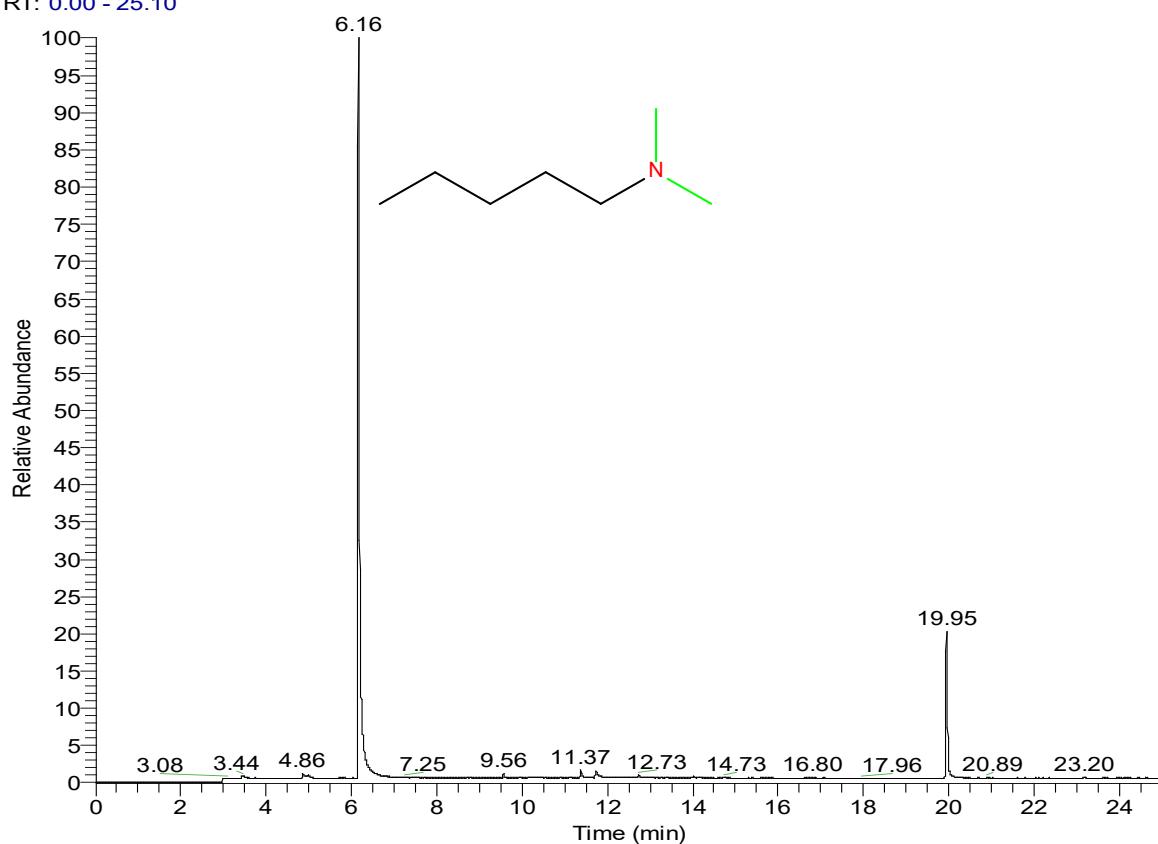
E-19-5 #1375 RT: 4.71 AV: 1 NL: 1.55E8
T: + c EI Full ms [15.00-400.00]



17

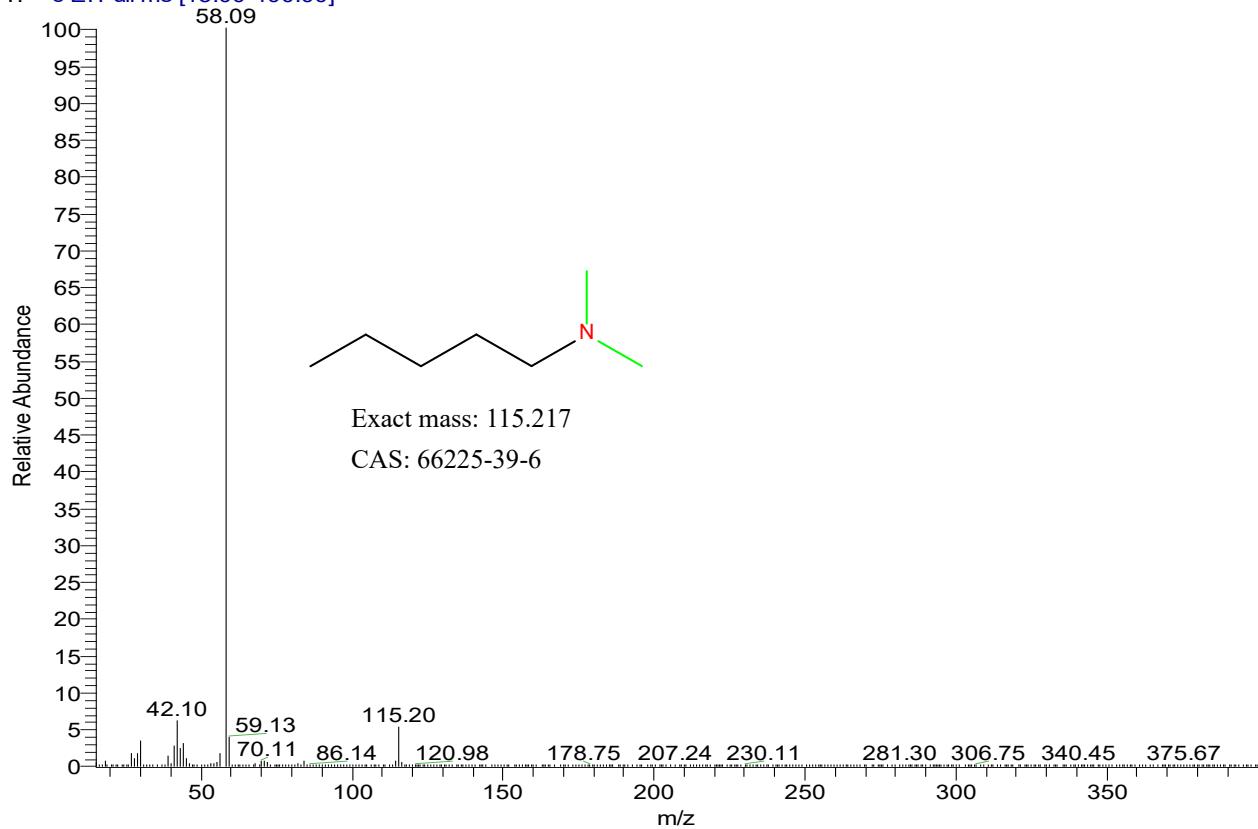
RT: 0.00 - 25.10

NL:
5.00E8
TIC MS
E-24-2

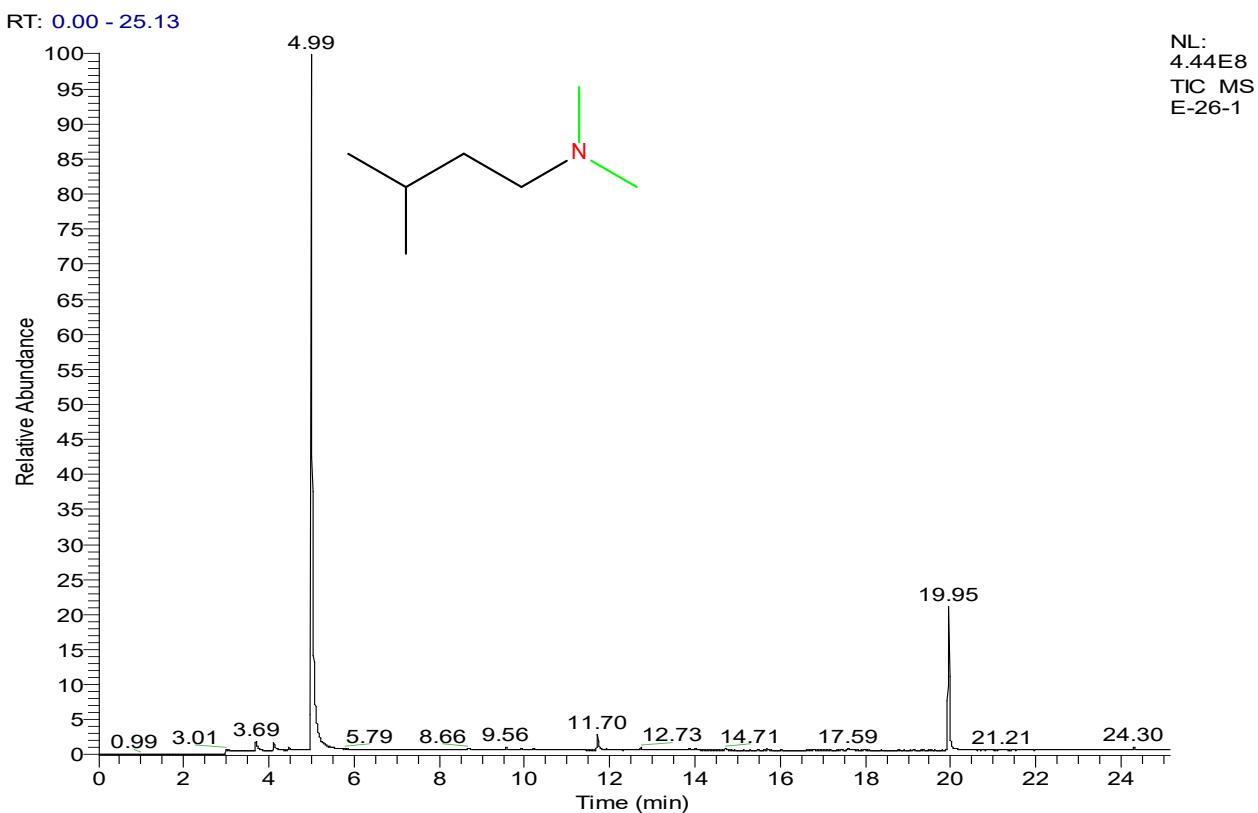


E-24-2 #1802 RT: 6.16 AV: 1 NL: 3.51E8

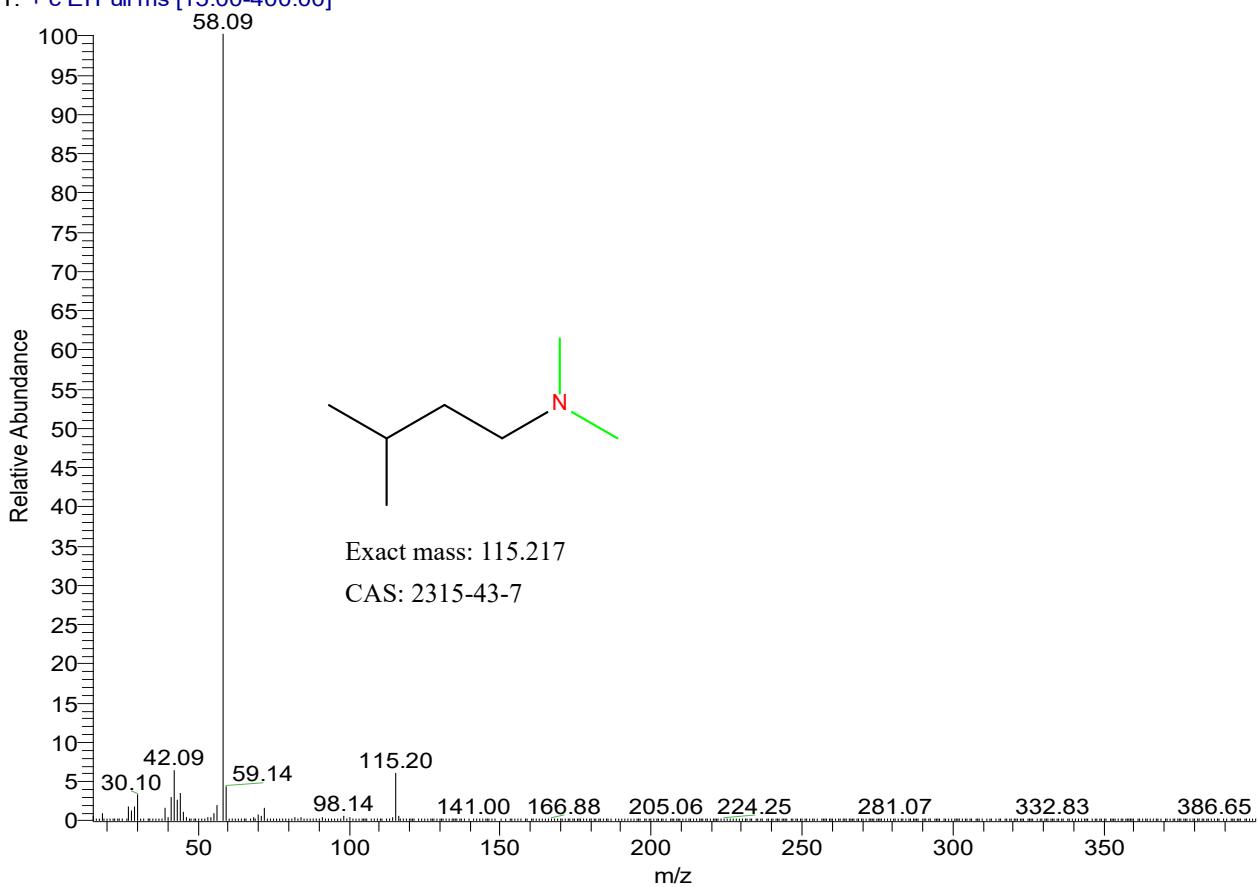
T: + c EI Full ms [15.00-400.00]



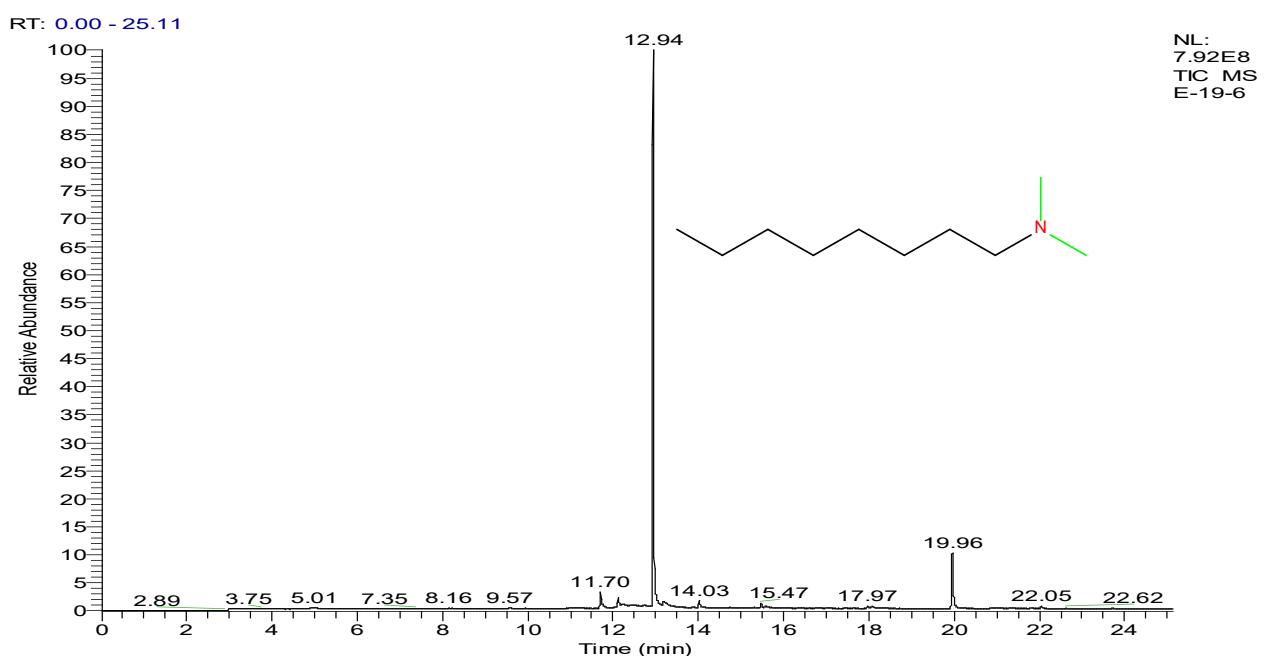
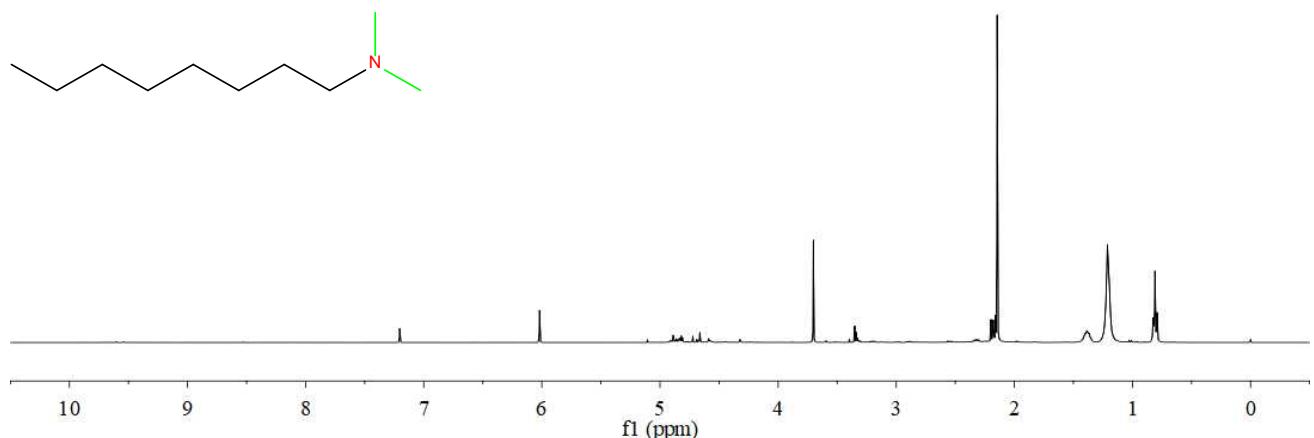
18



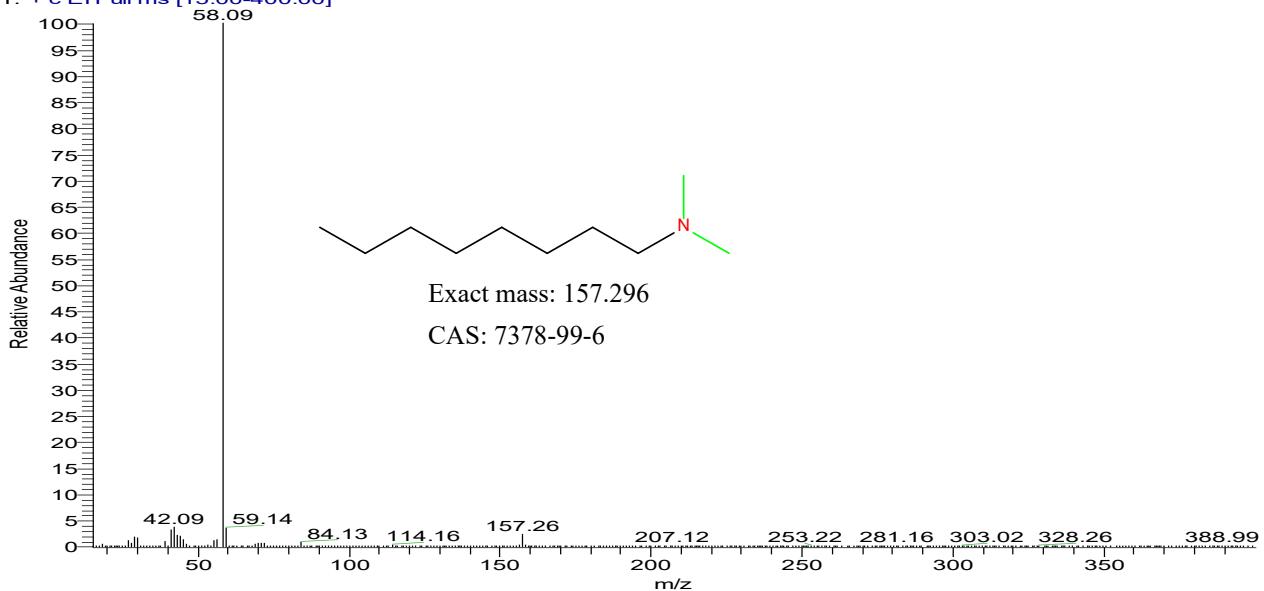
E-26-1 #1457 RT: 4.99 AV: 1 NL: 2.86E8
T: + c EI Full ms [15.00-400.00]

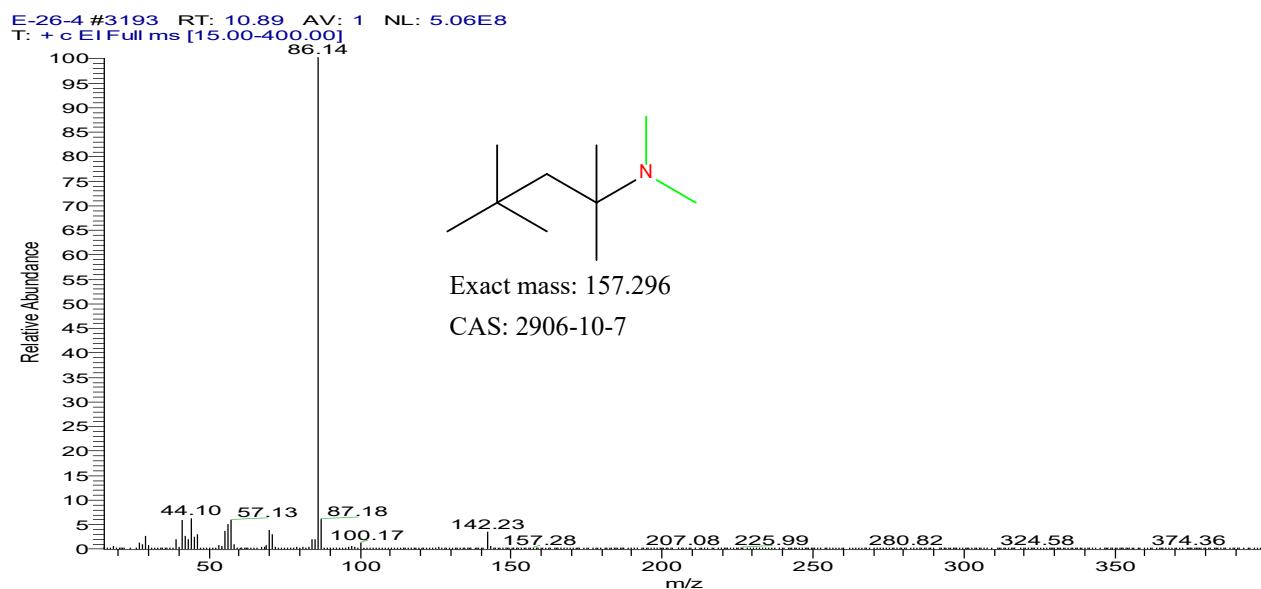
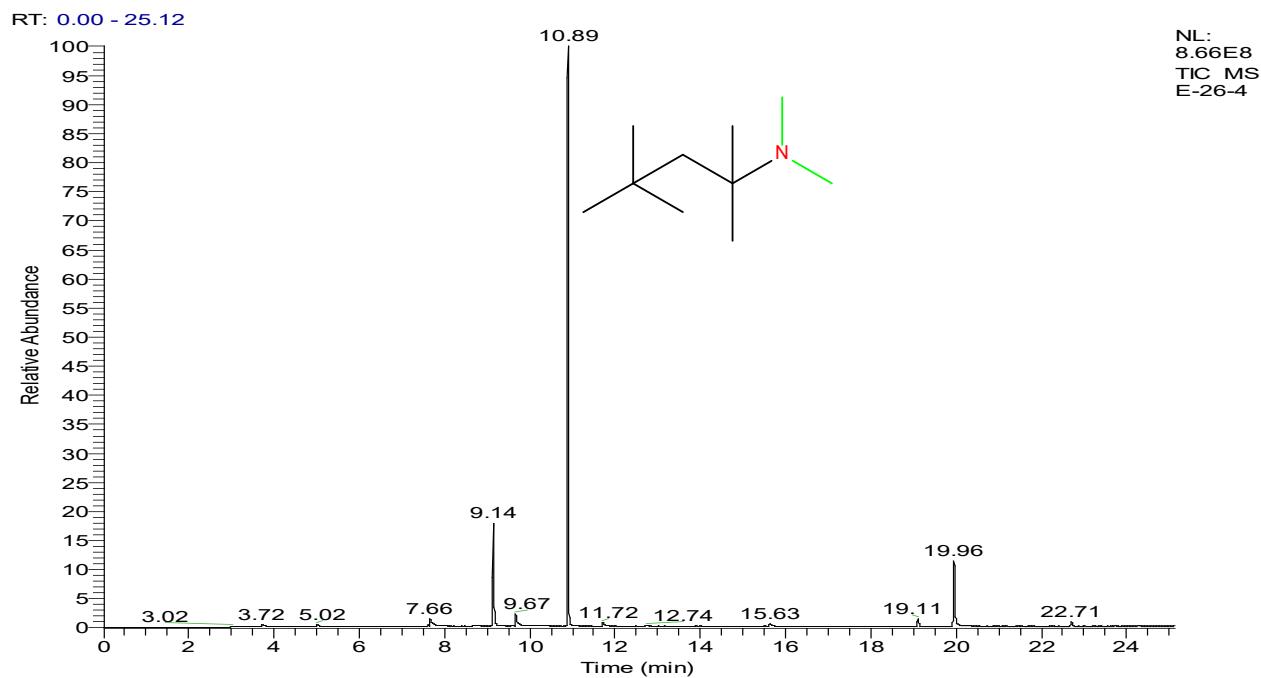
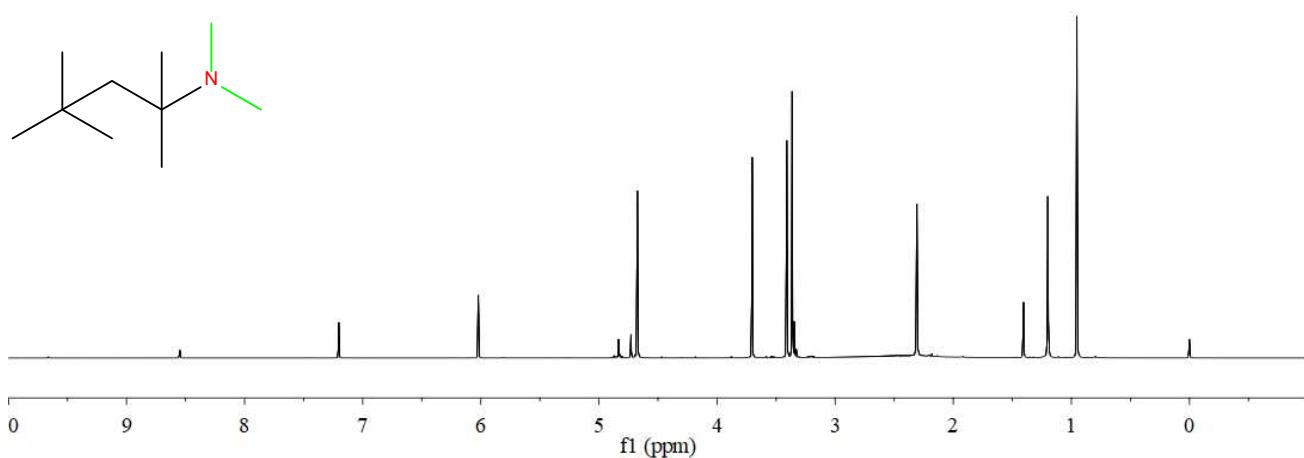


19

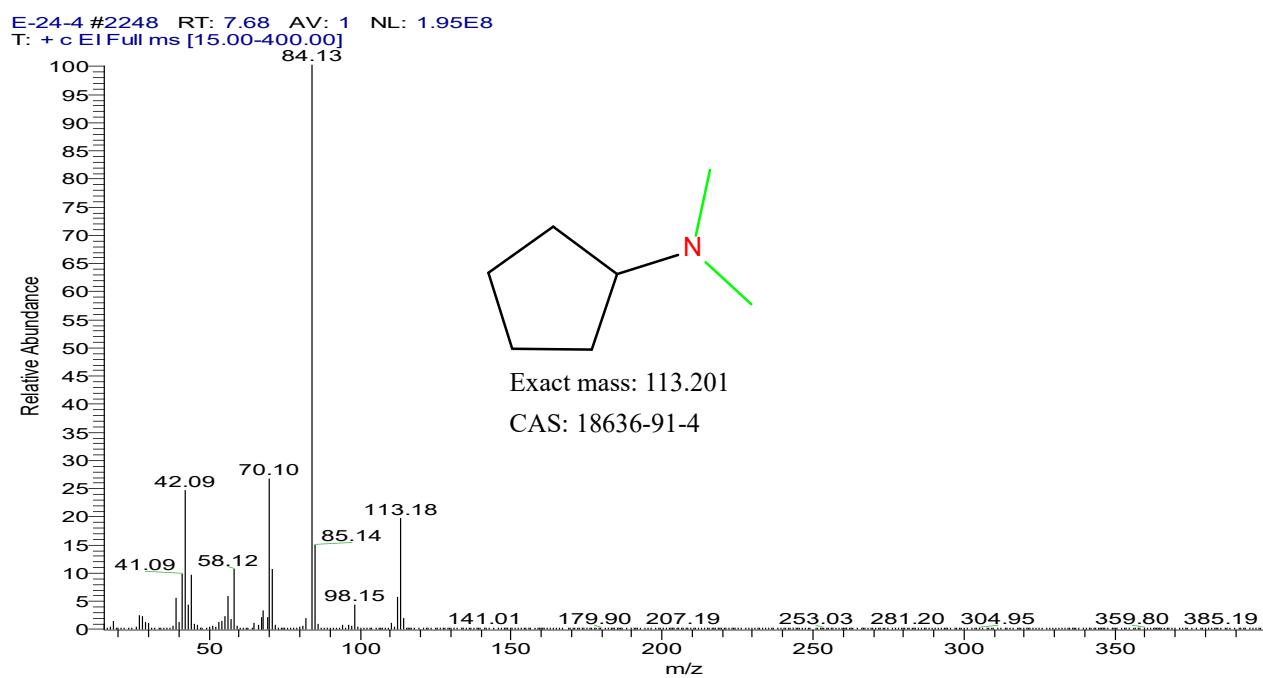
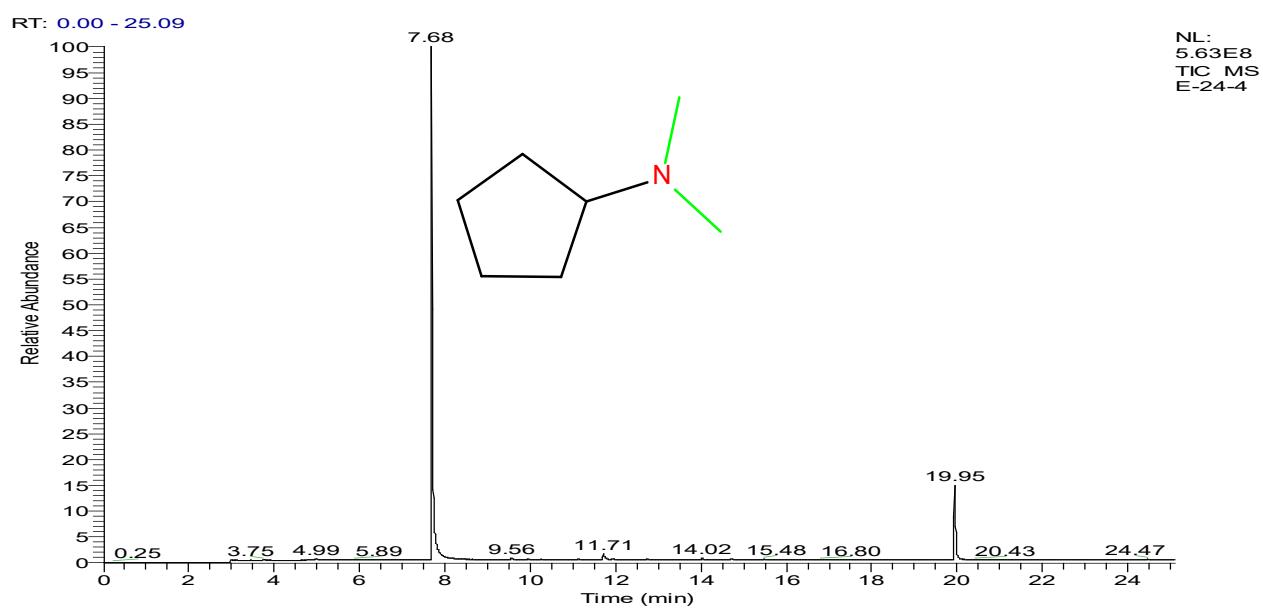
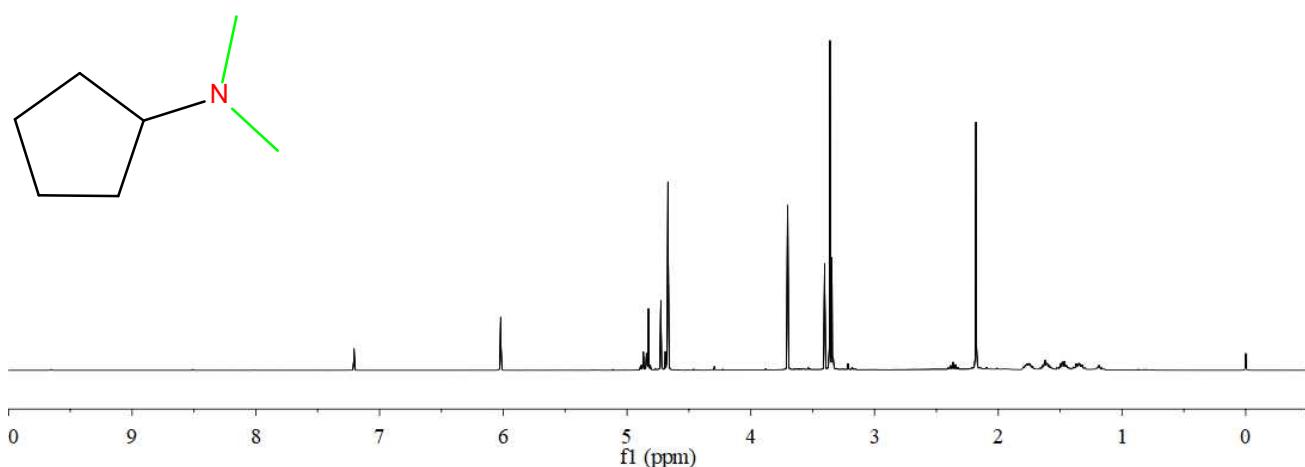


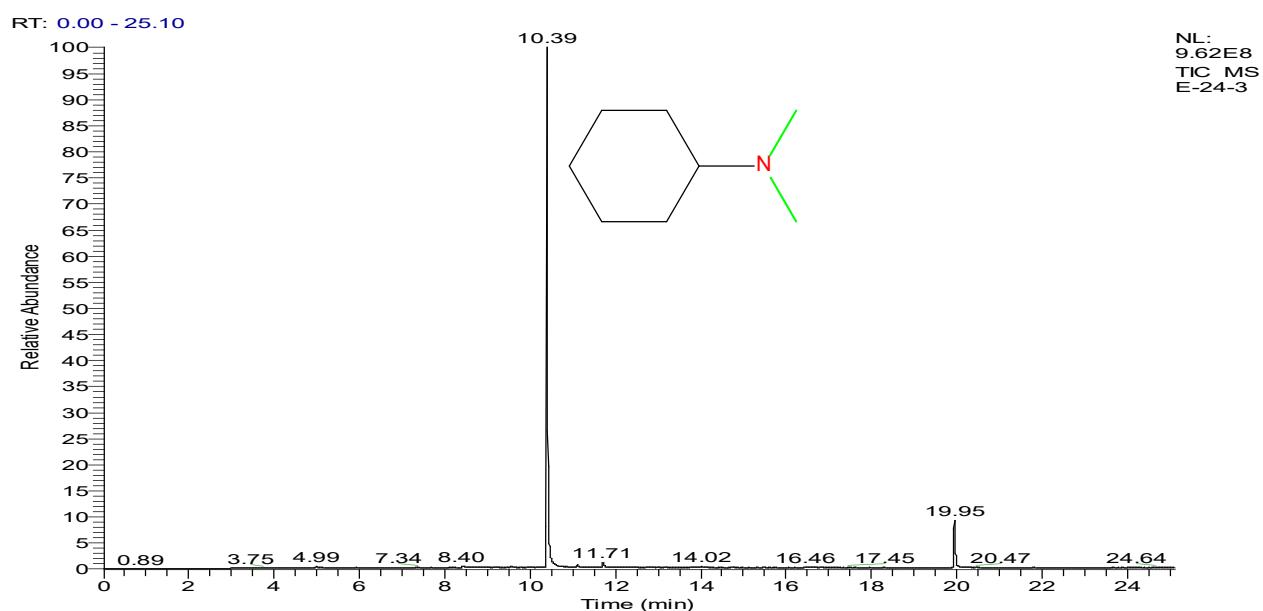
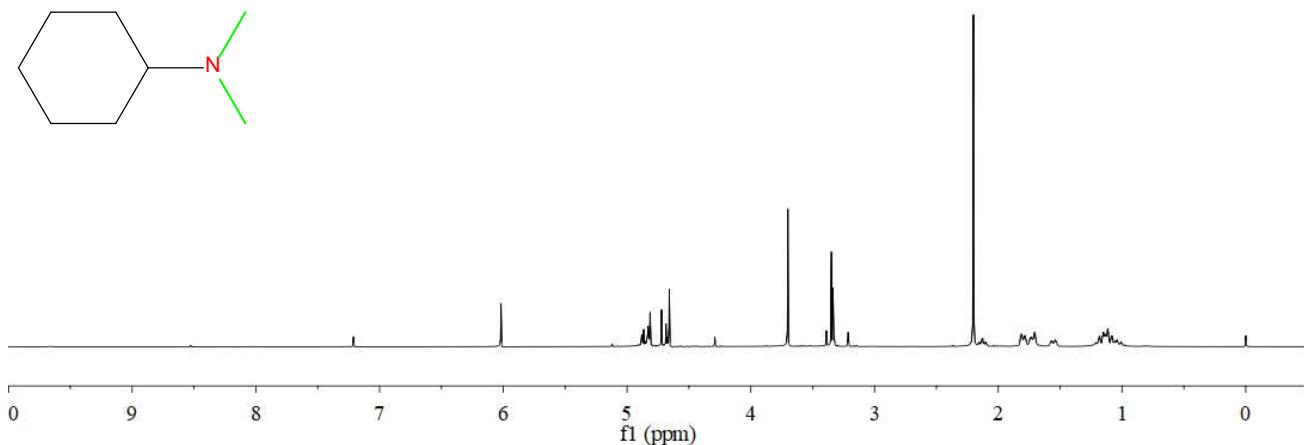
E-19-6 #3794 RT: 12.94 AV: 1 NL: 5.72E8
T: + c EI Full ms [15.00-400.00]



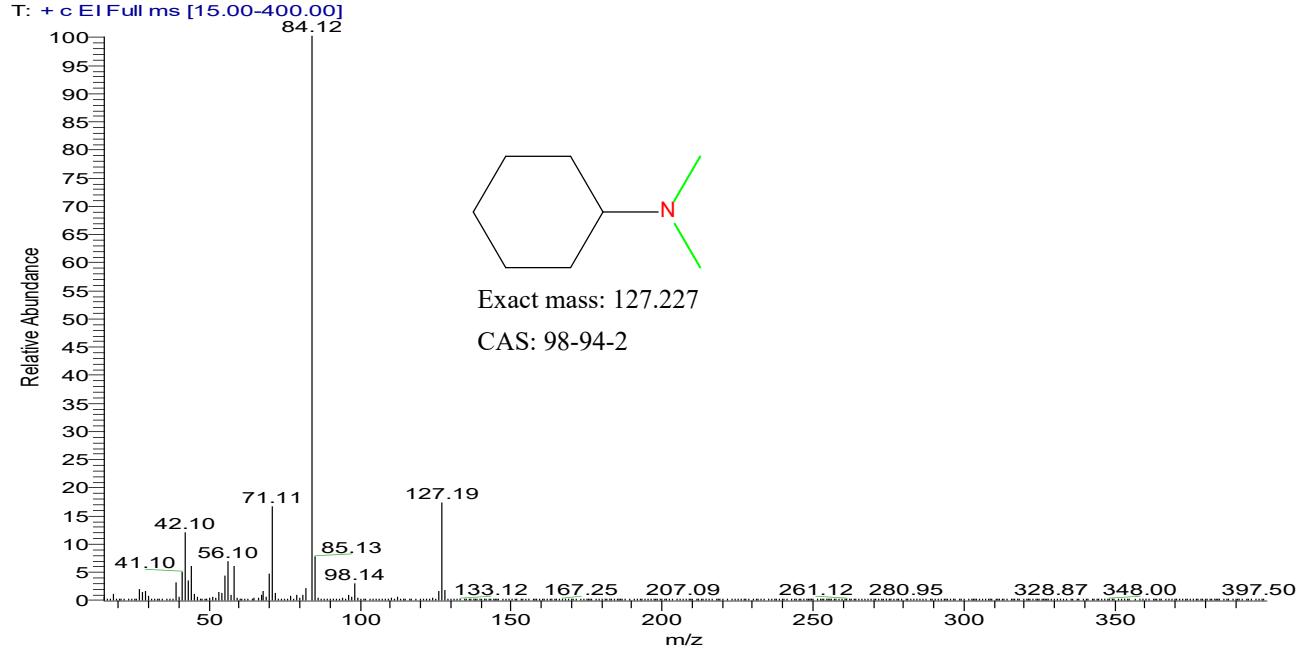


21

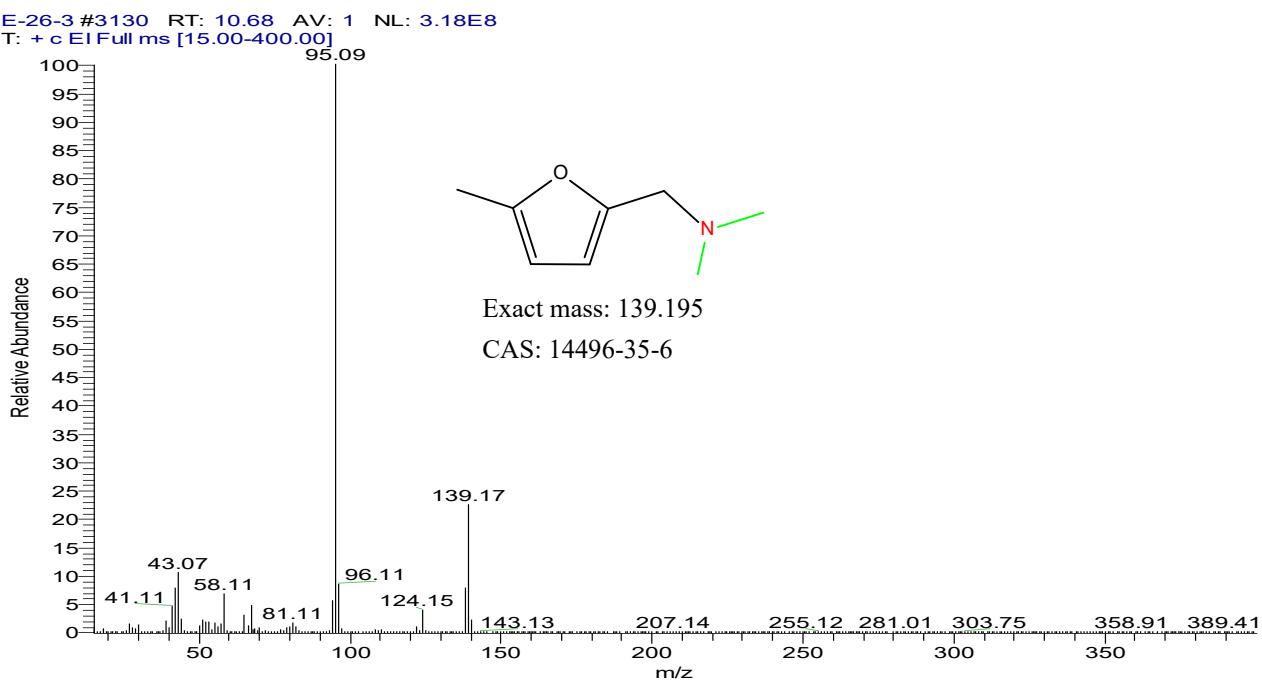
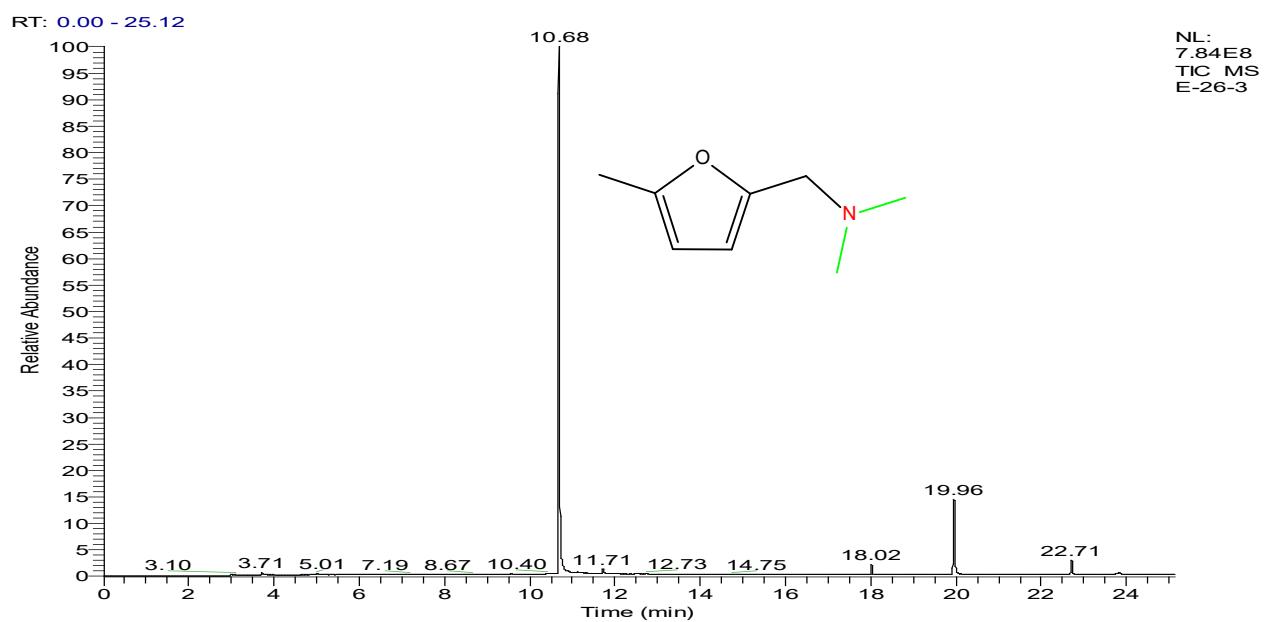
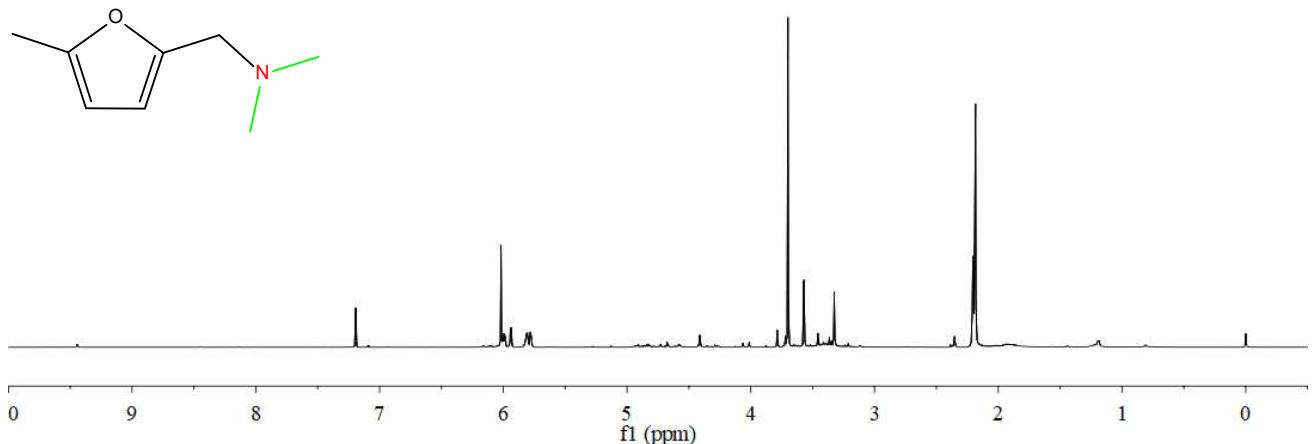


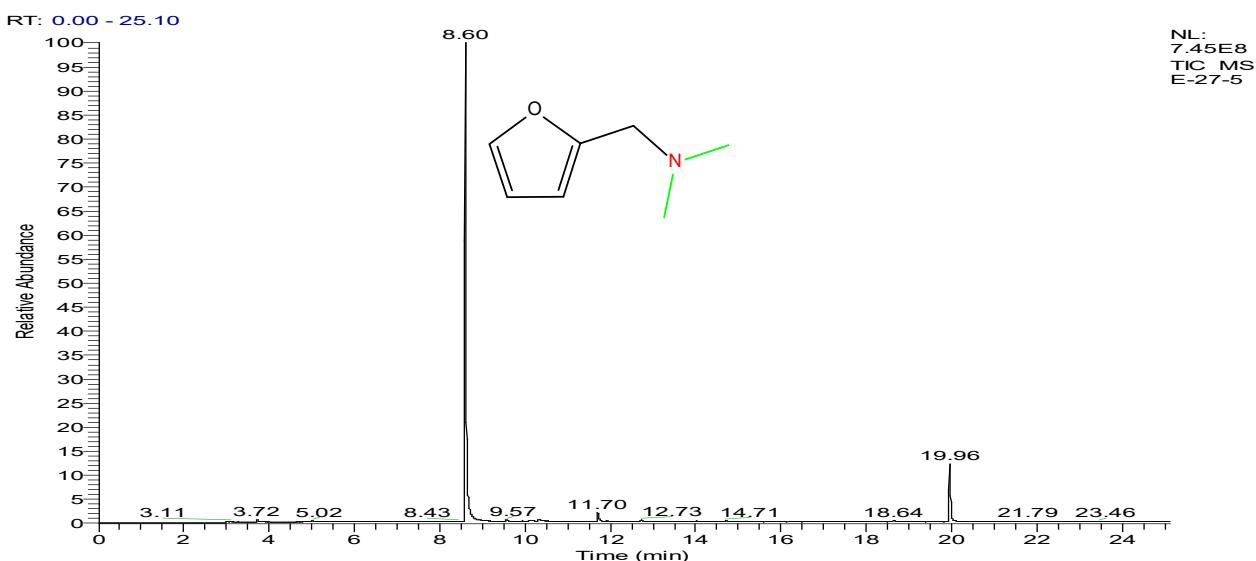
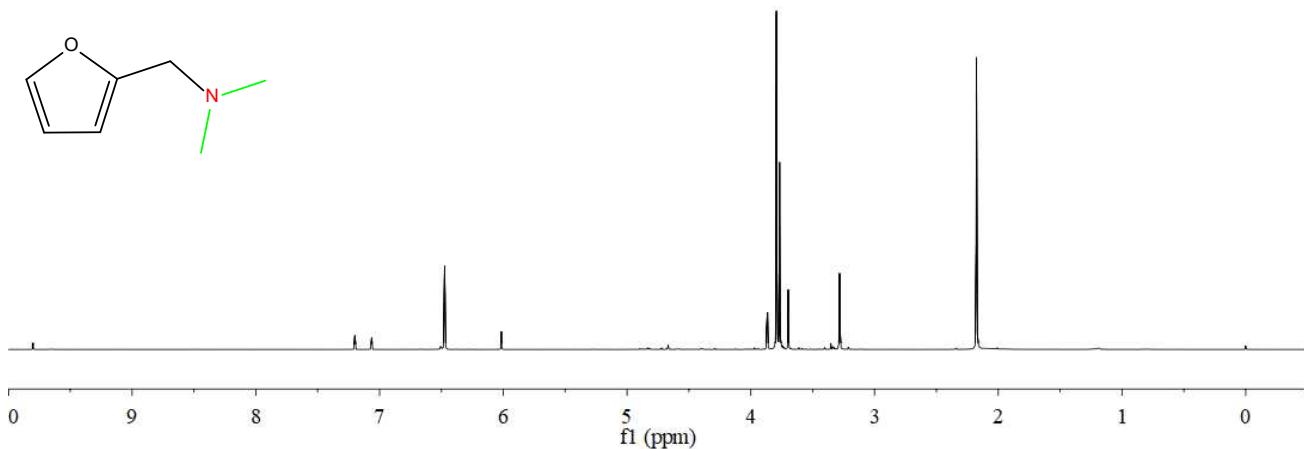


E-24-3 #3045 RT: 10.39 AV: 1 NL: 2.64E8
T: + c EI Full ms [15.00-400.00]

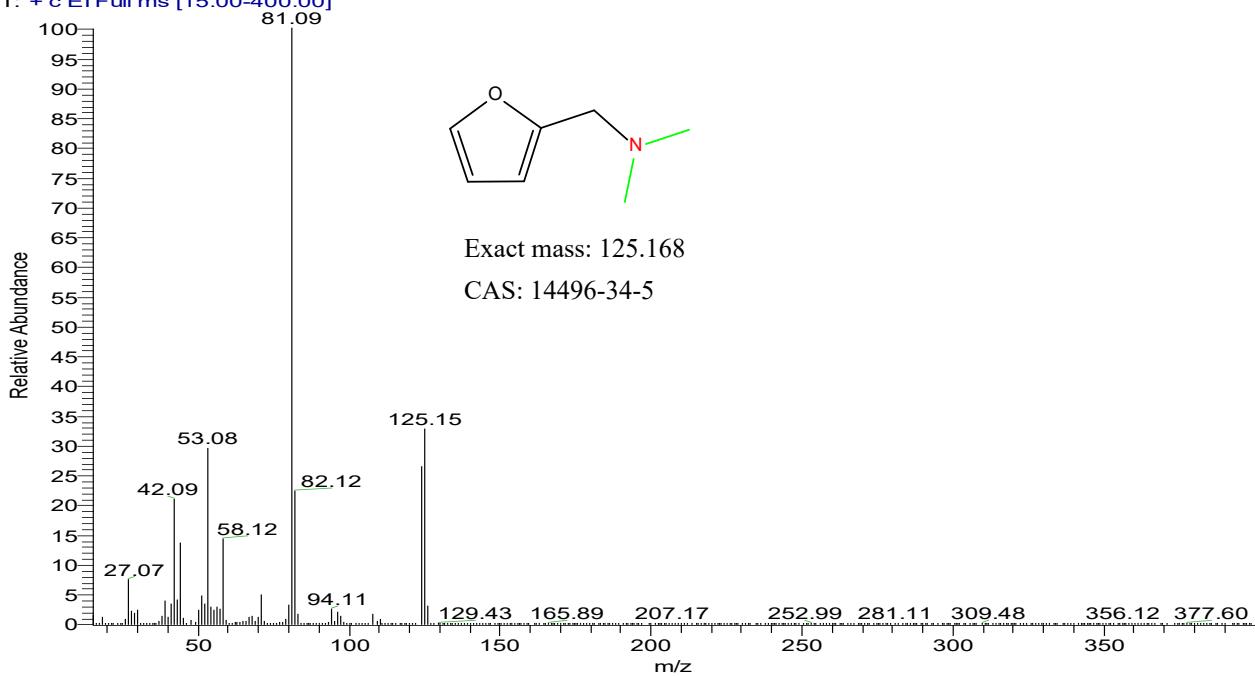


23

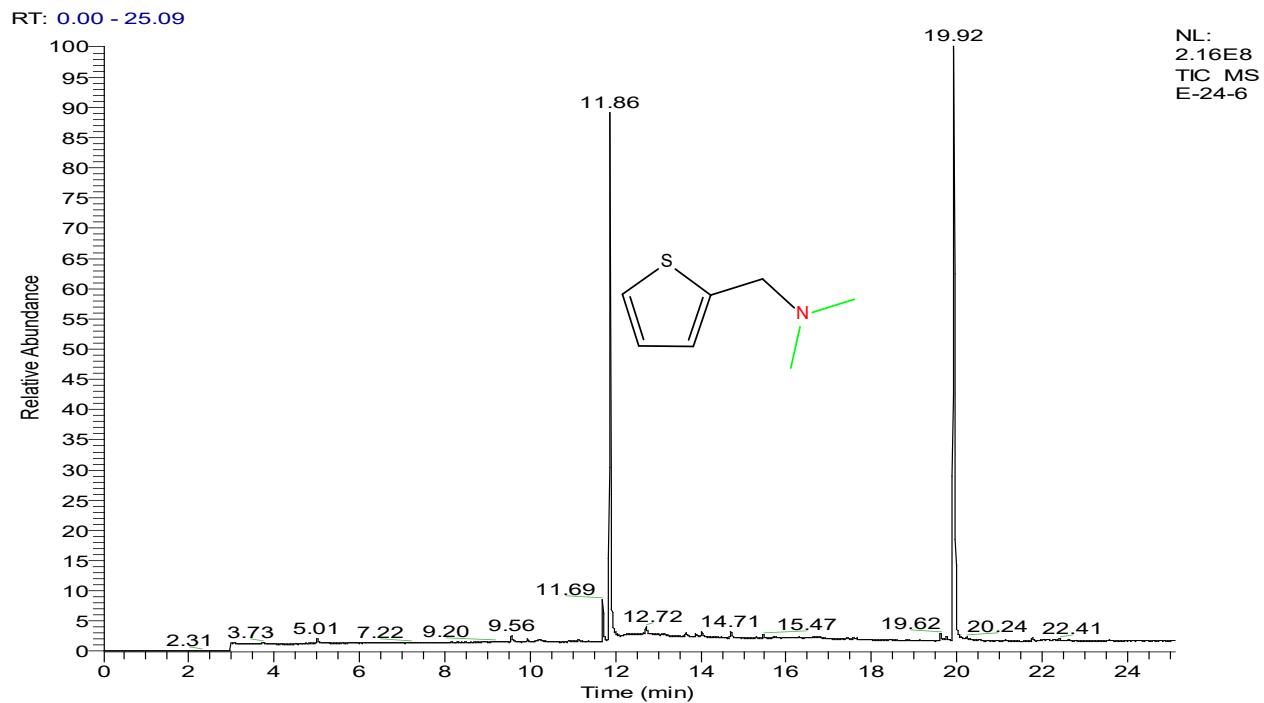
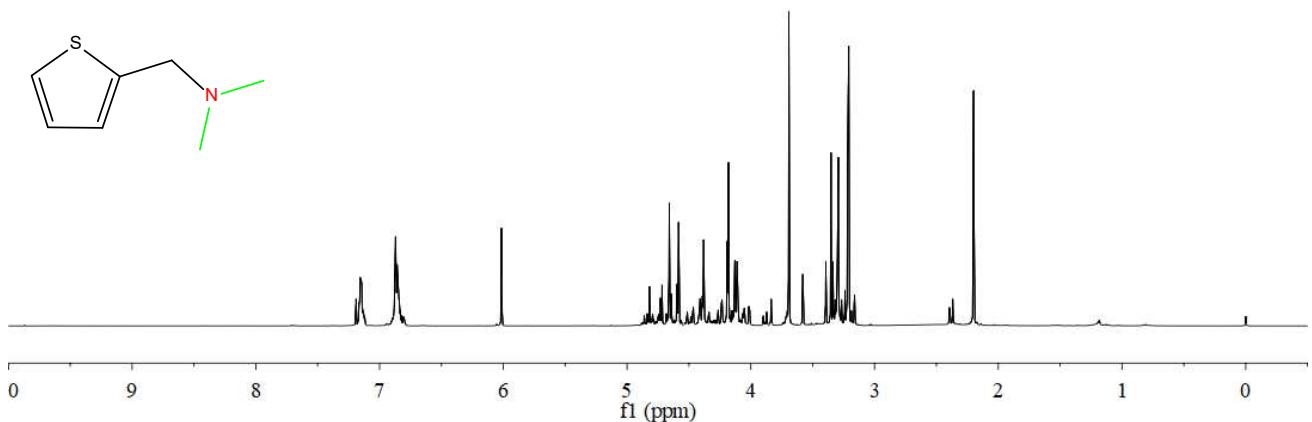




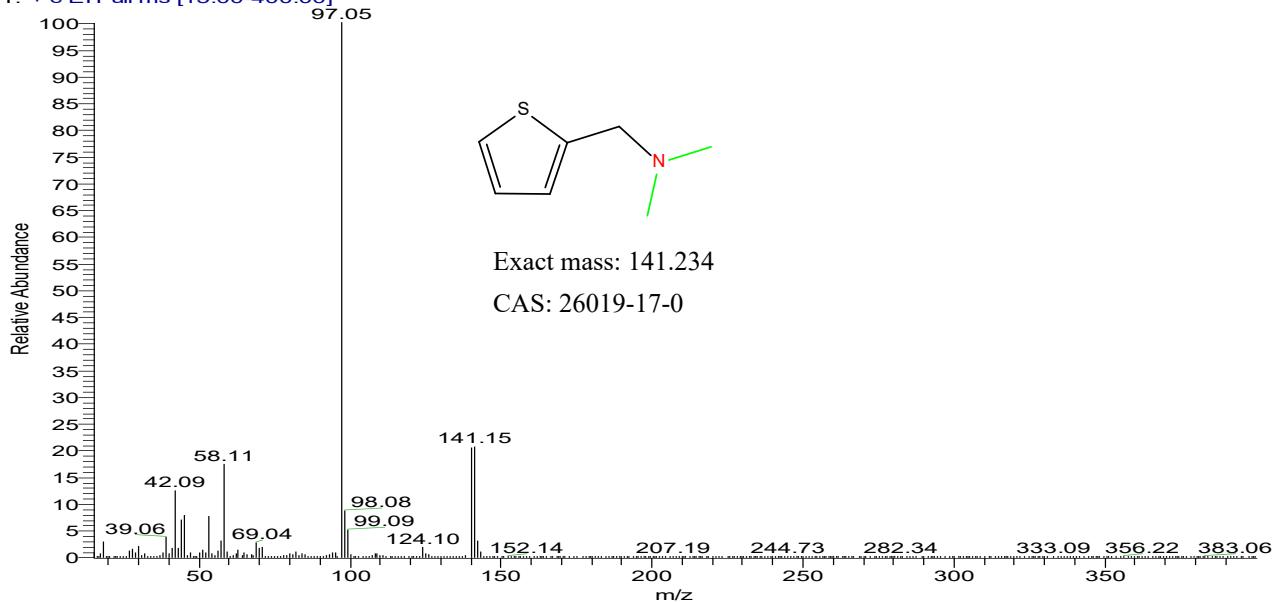
E-27-5 #2520 RT: 8.60 AV: 1 NL: 2.16E8
T: + c EI Full ms [15.00-400.00]



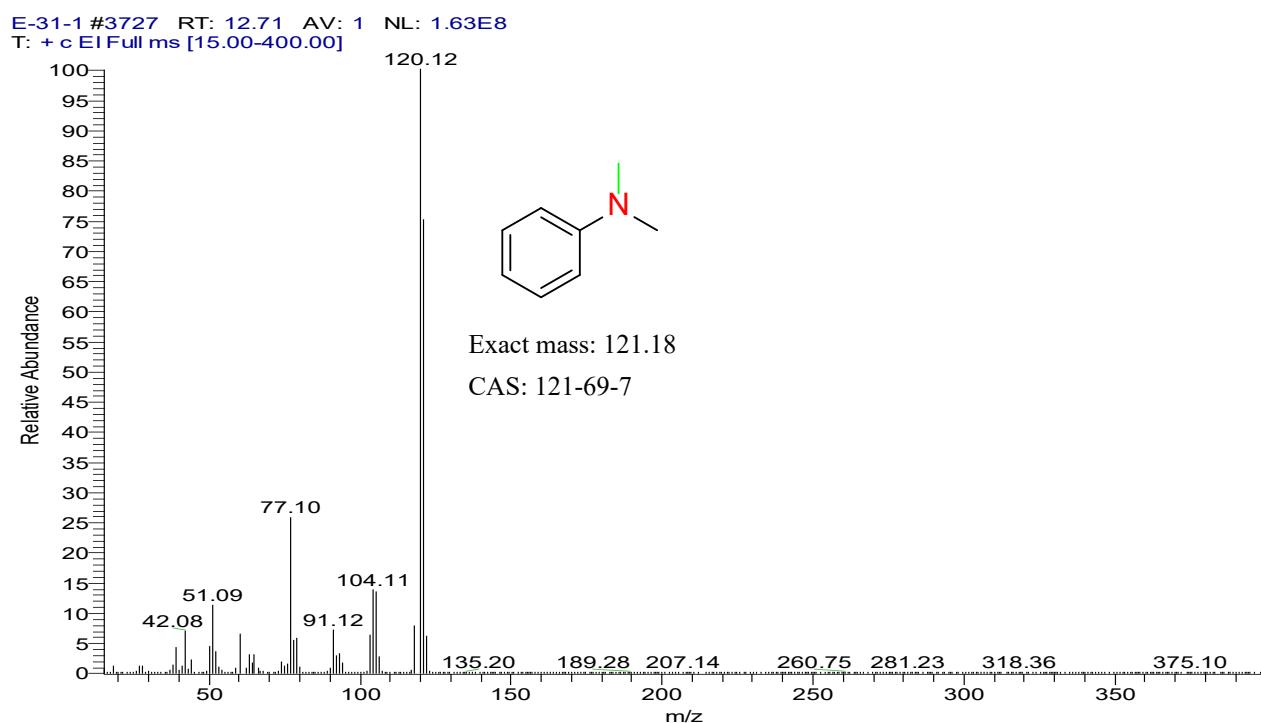
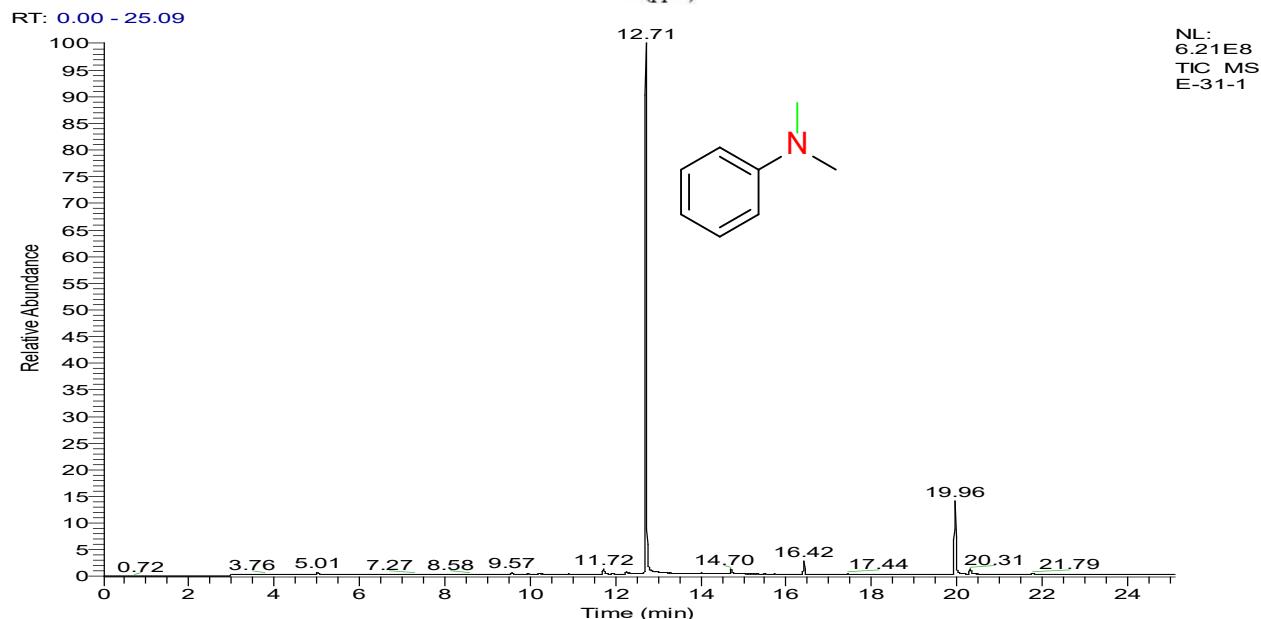
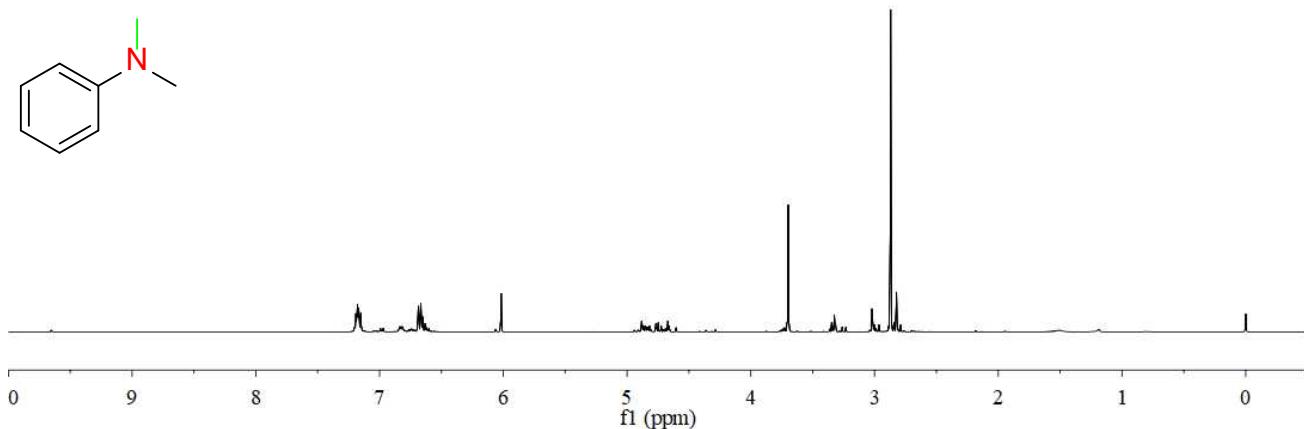
25

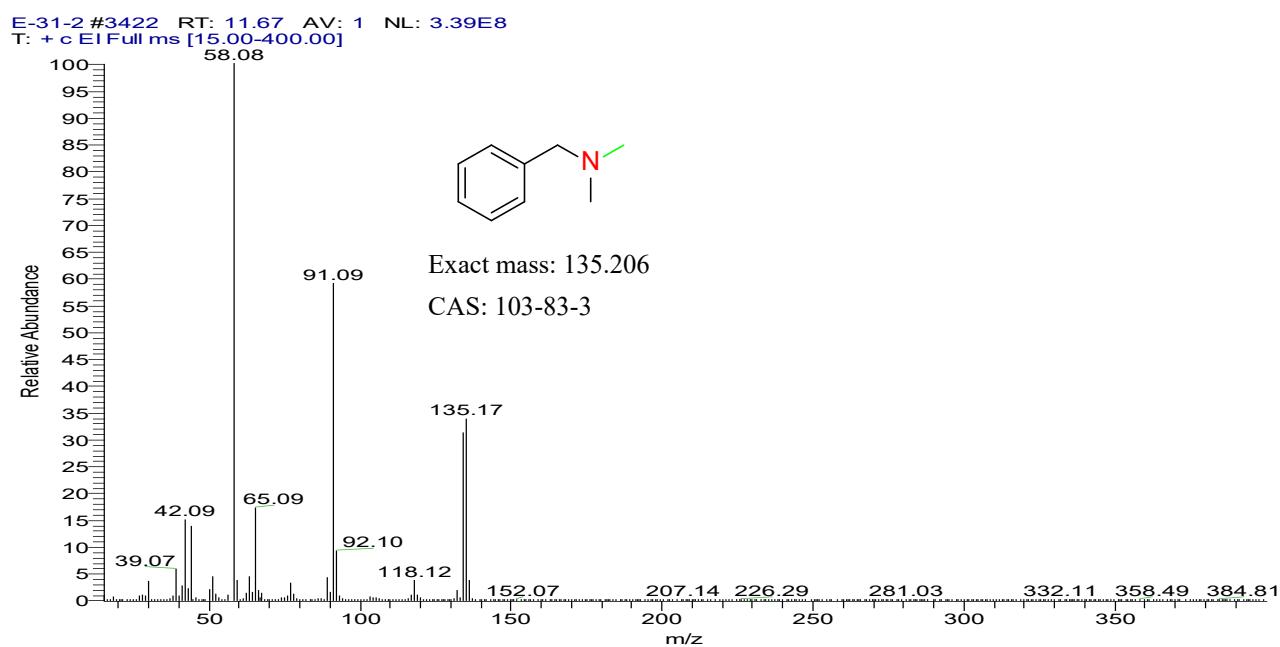
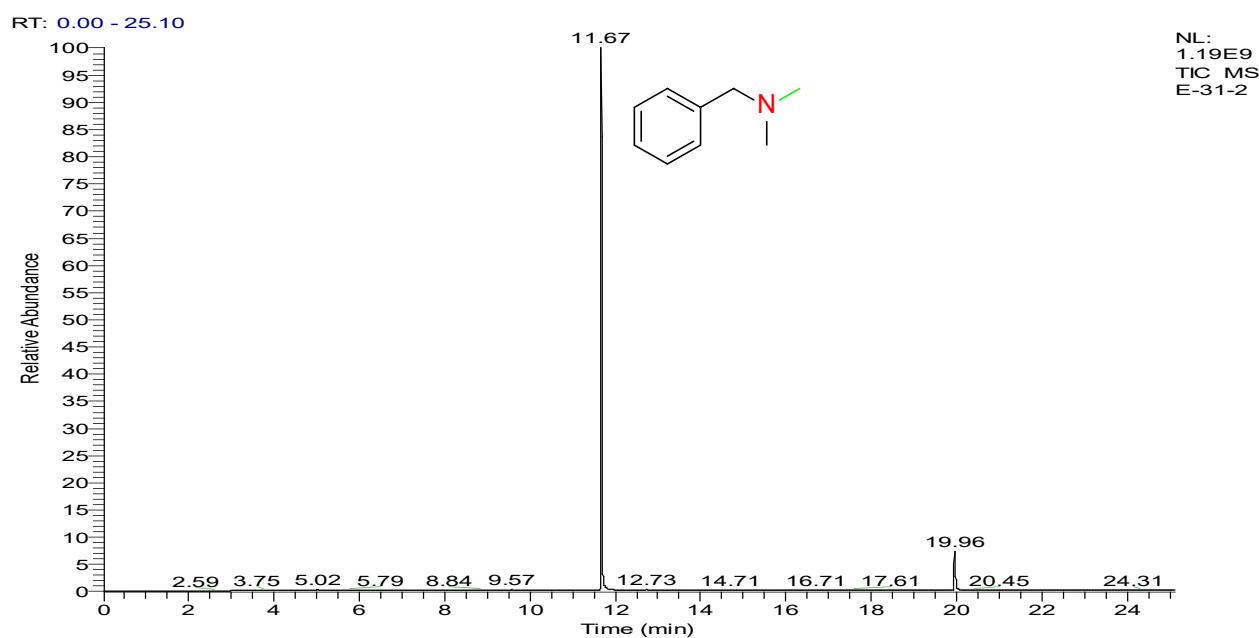
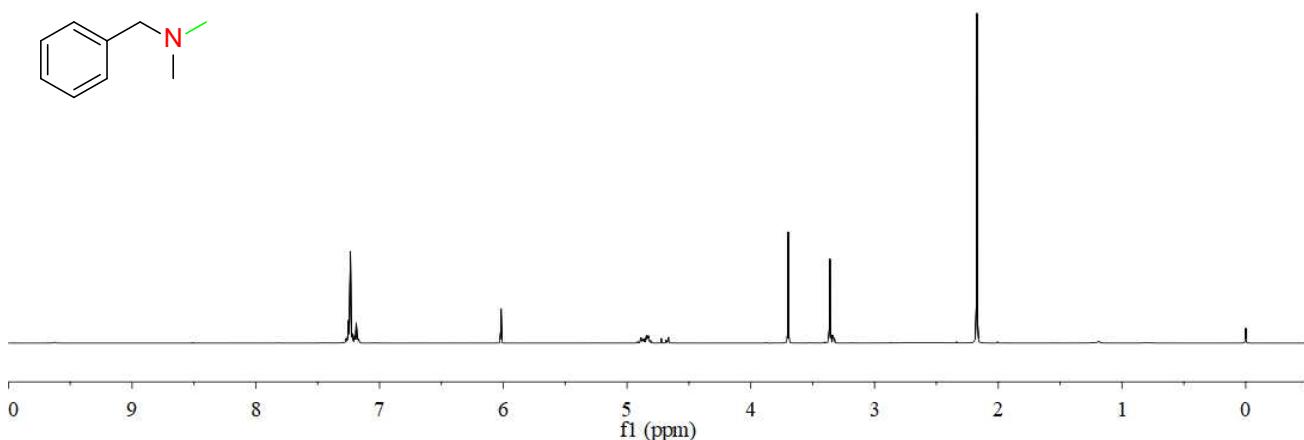


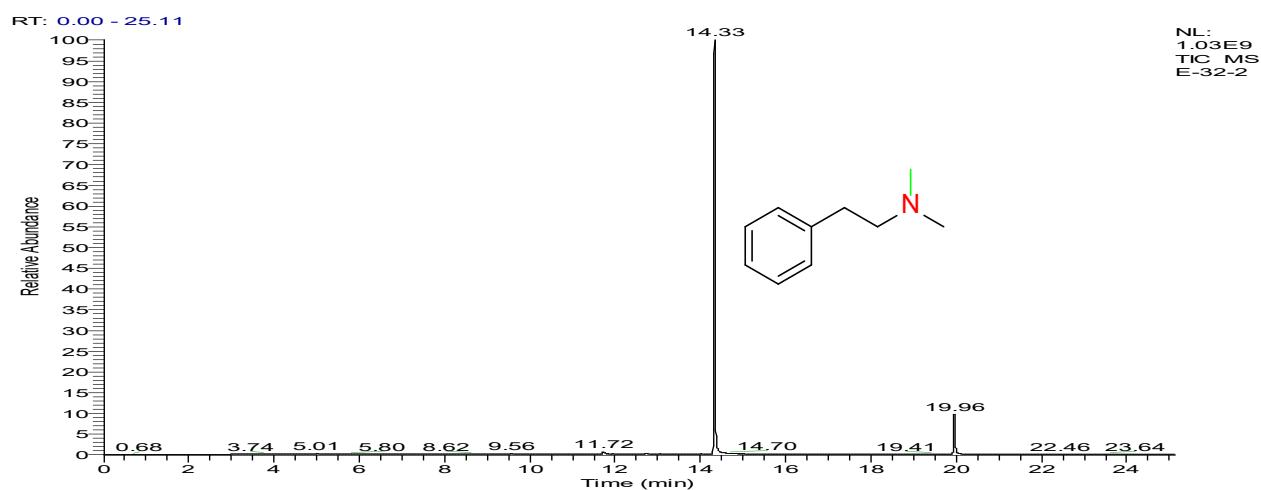
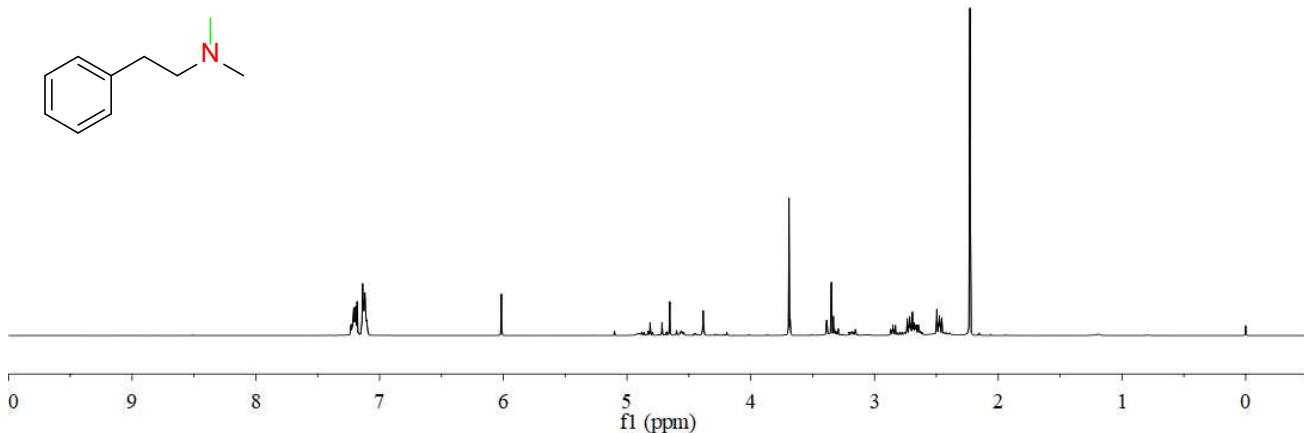
E-24-6 #3477 RT: 11.86 AV: 1 NL: 5.66E7
T: + c EI Full ms [15.00-400.00]



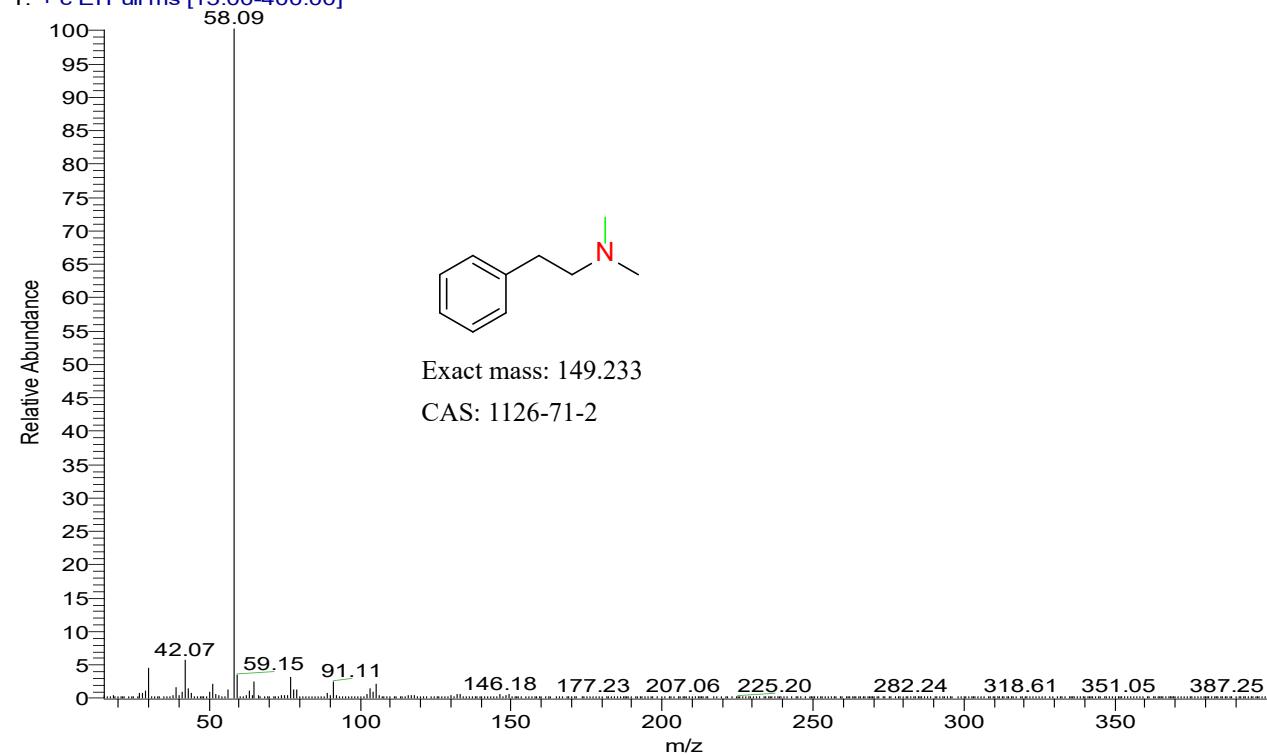
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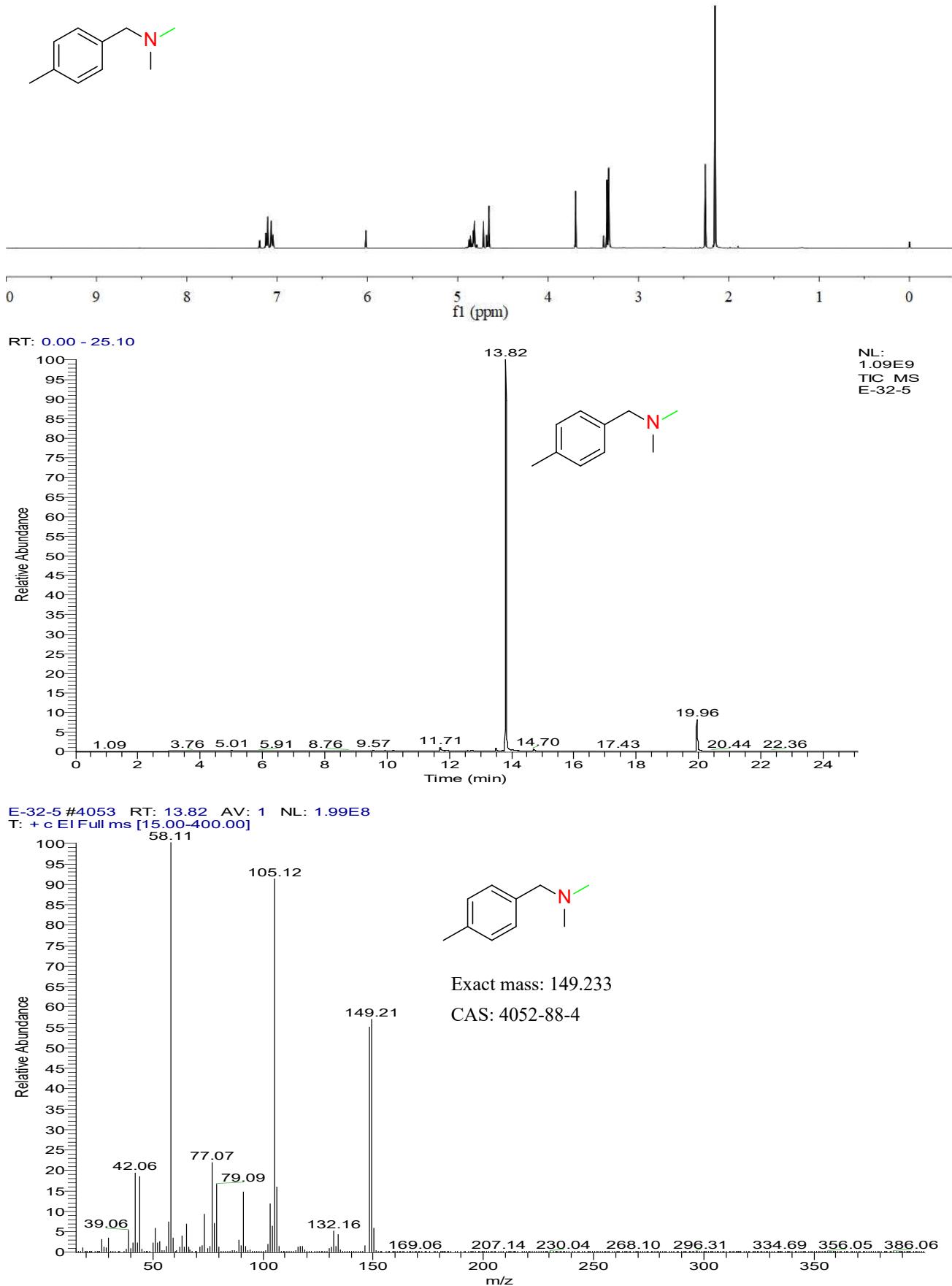


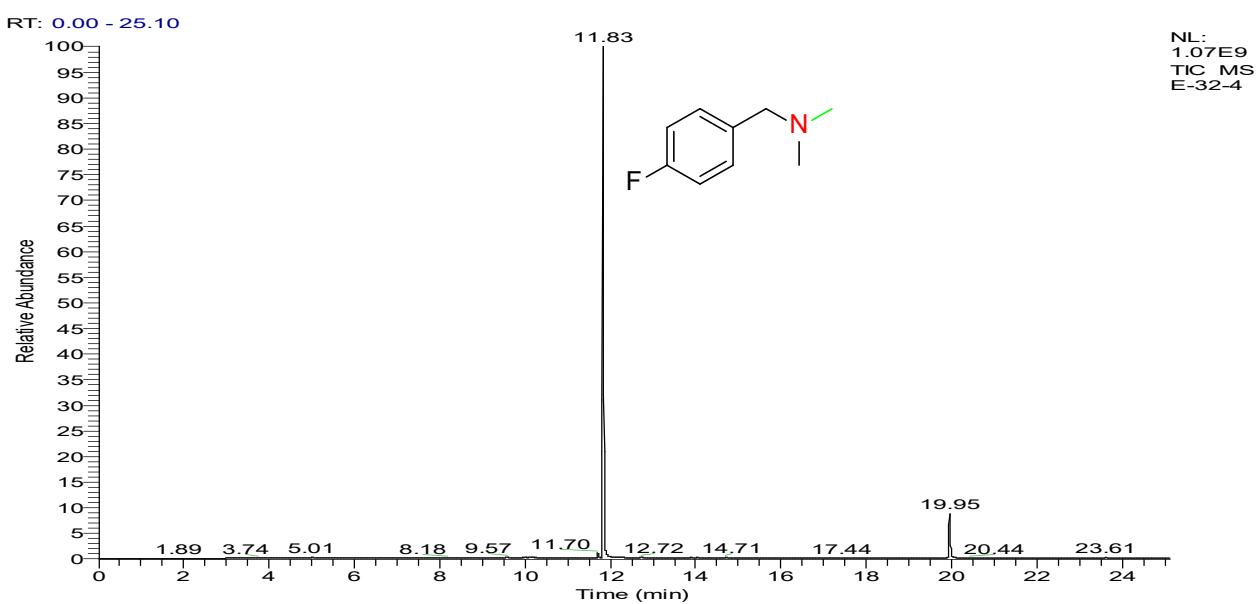
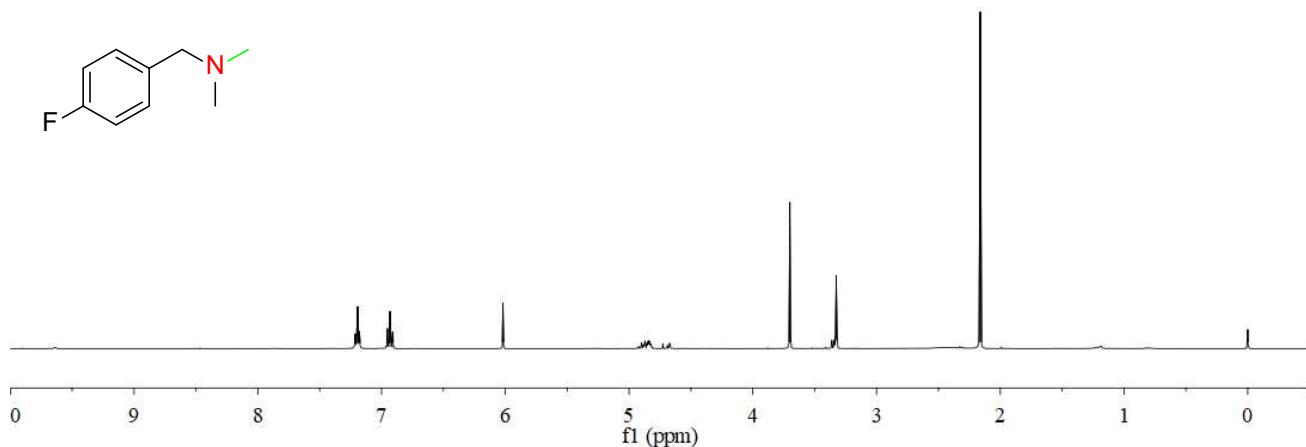
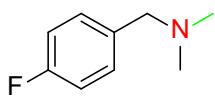


E-32-2 #4204 RT: 14.33 AV: 1 NL: 6.98E8
T: + c EI Full ms [15.00-400.00]

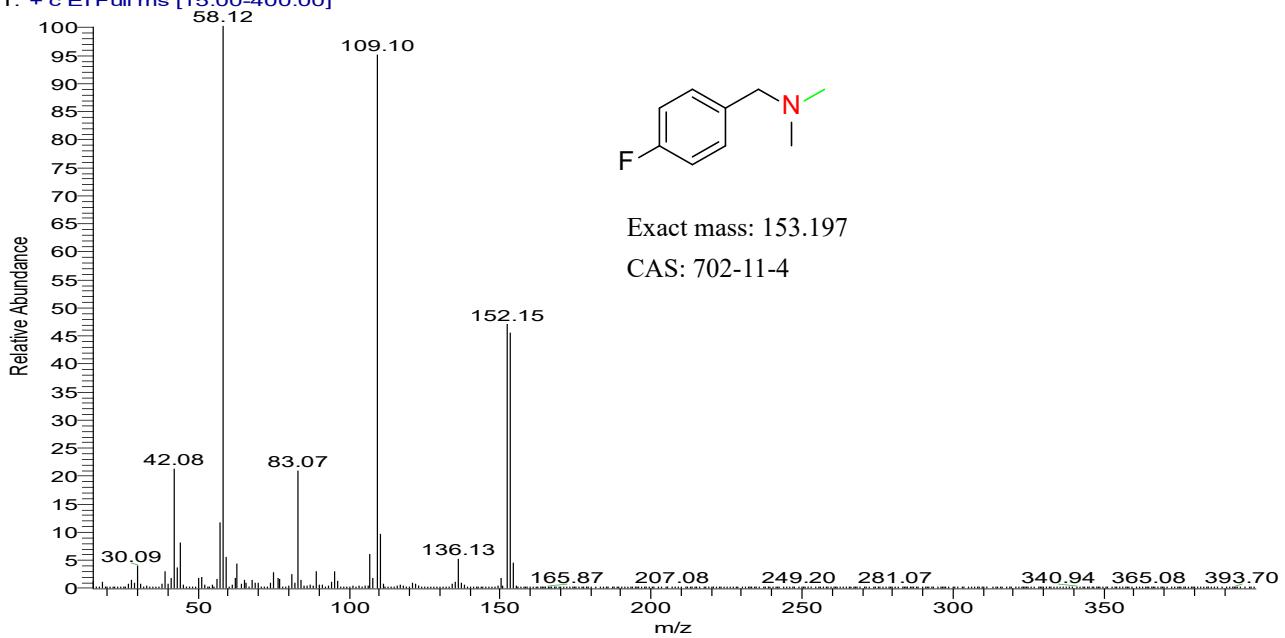


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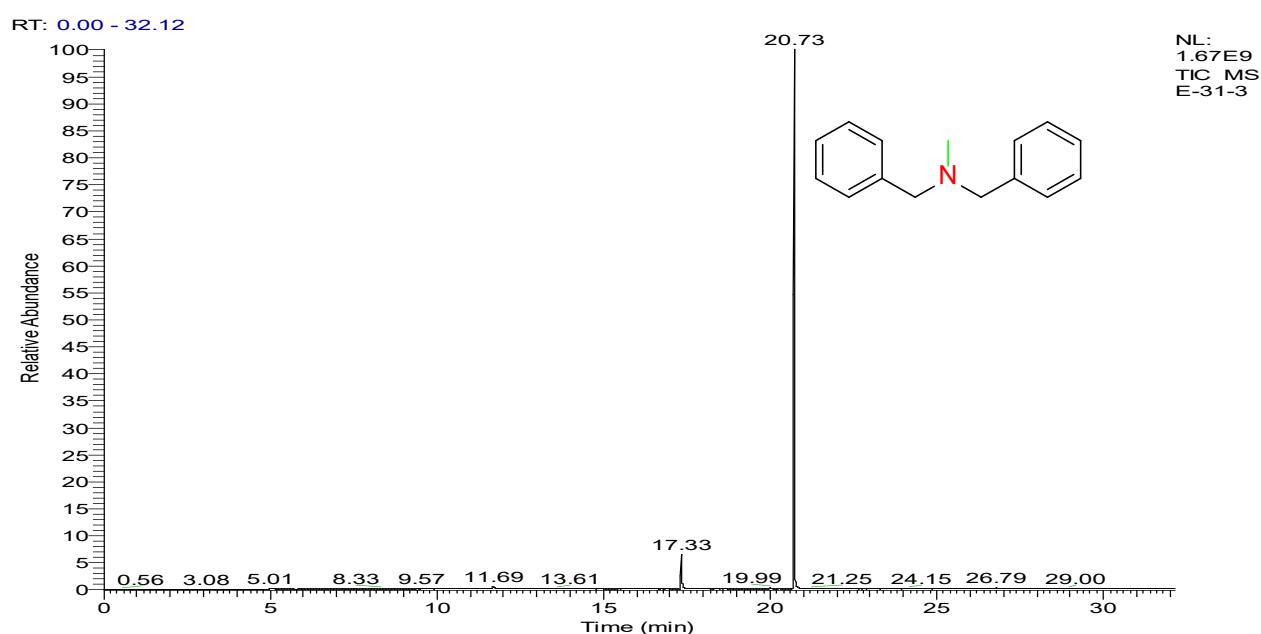
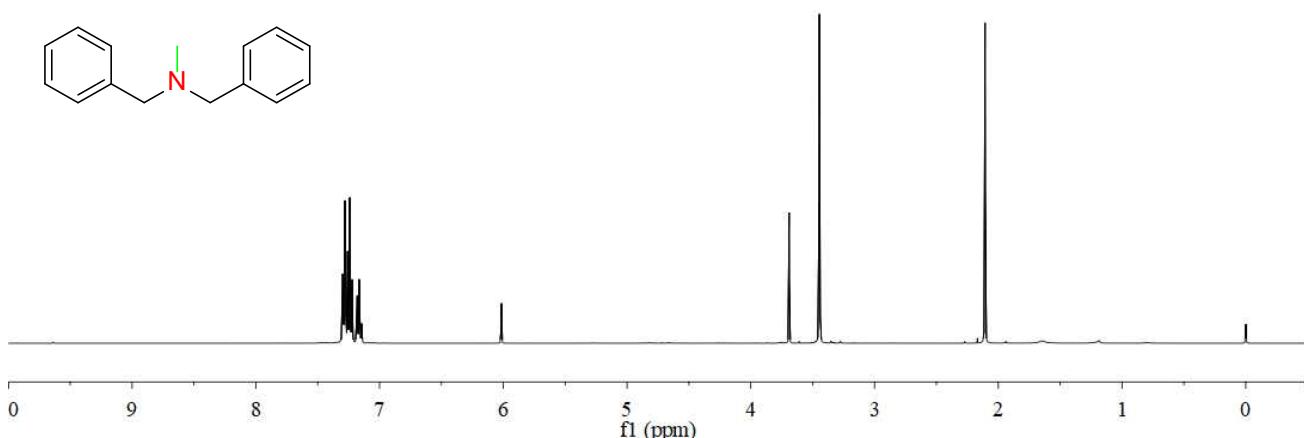




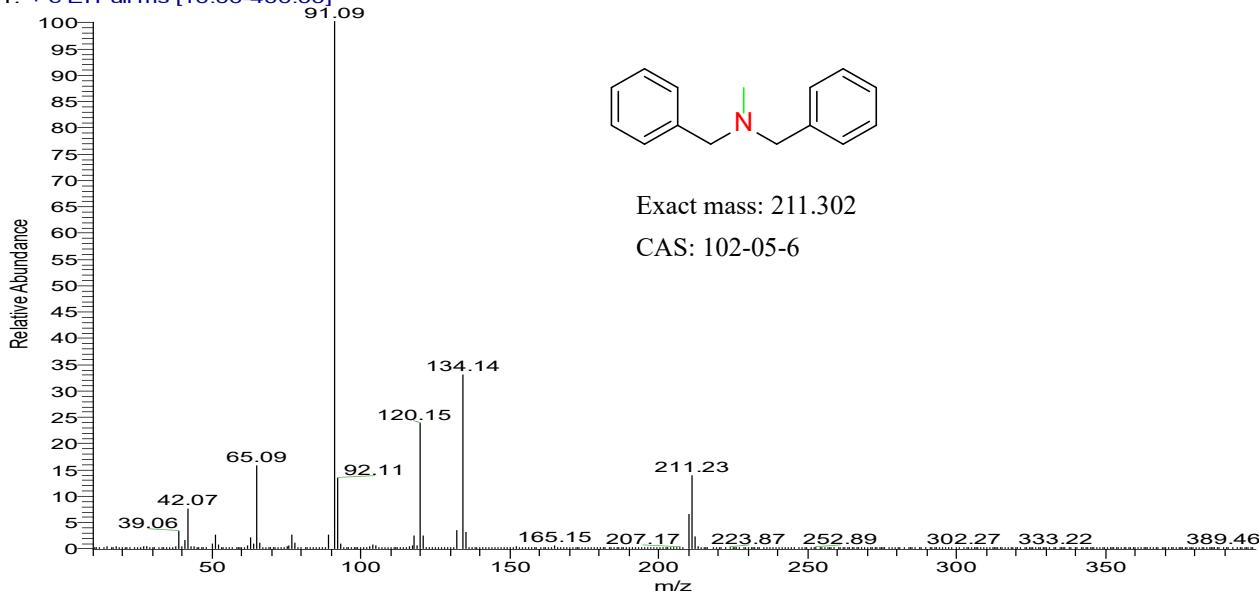
E-32-4 #3469 RT: 11.83 AV: 1 NL: 2.31E8
T: + c EI Full ms [15.00-400.00]
58.12

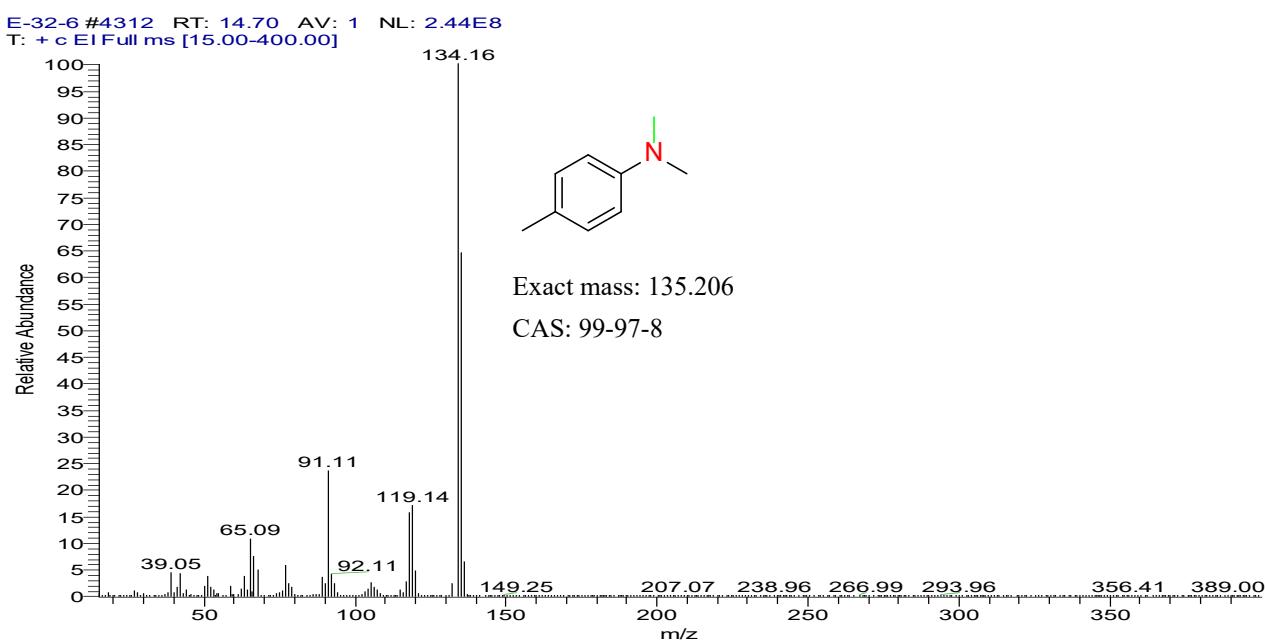
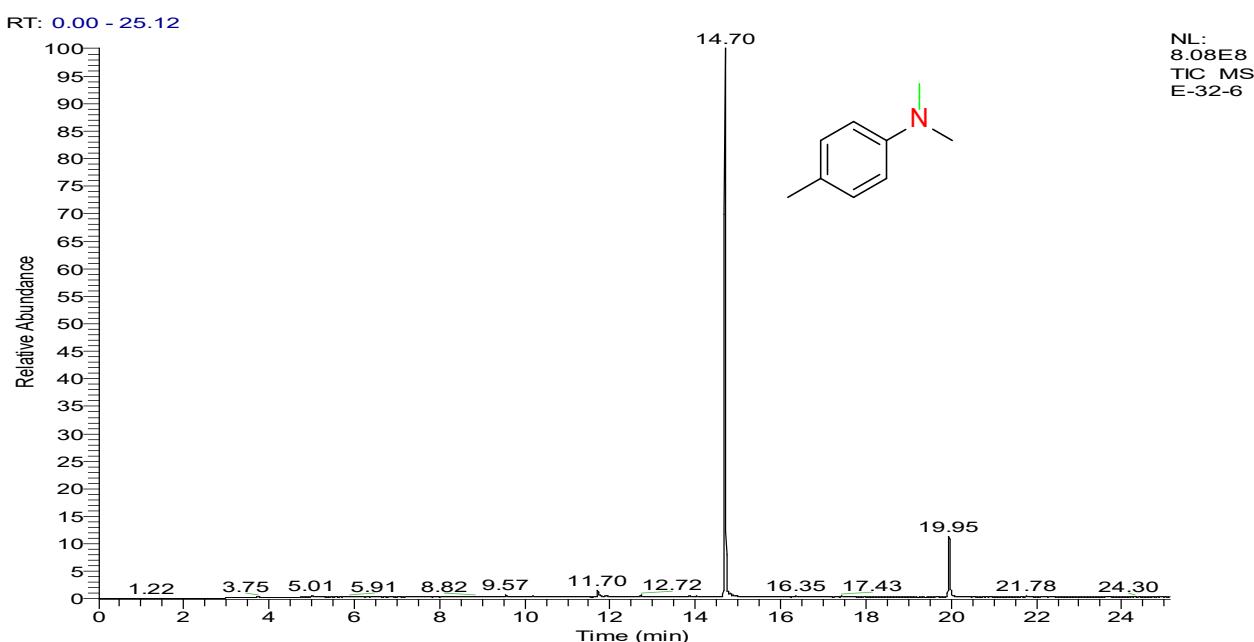
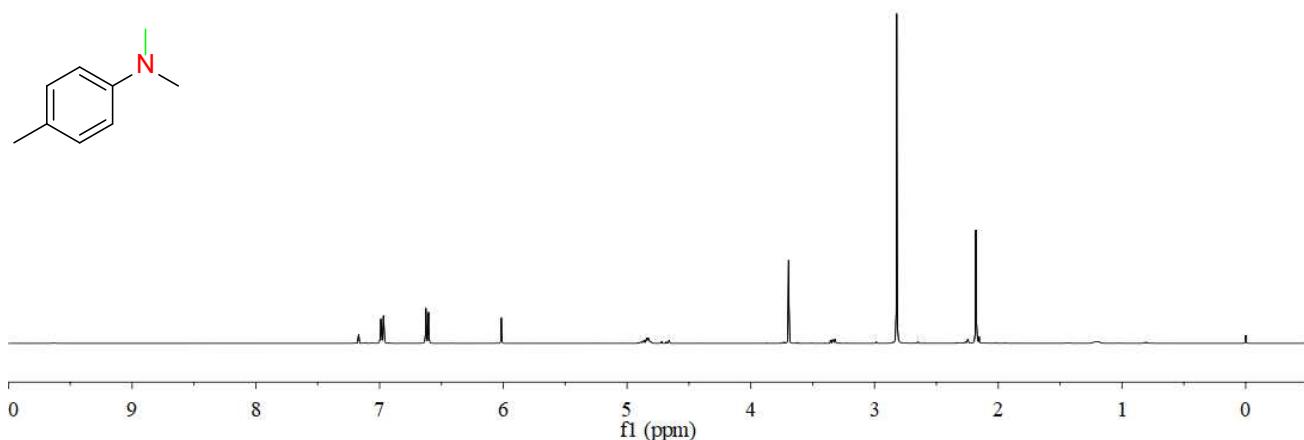


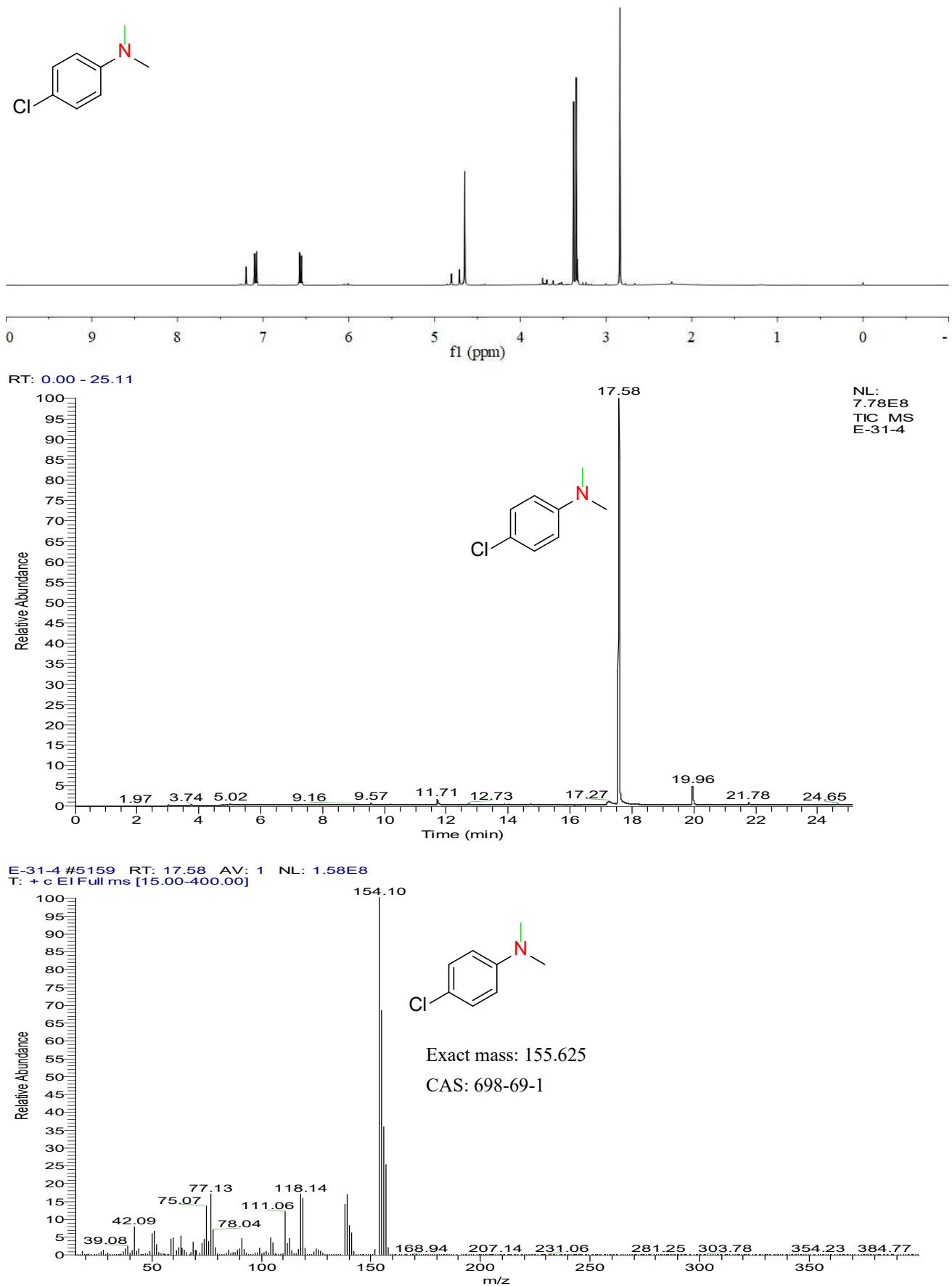
31

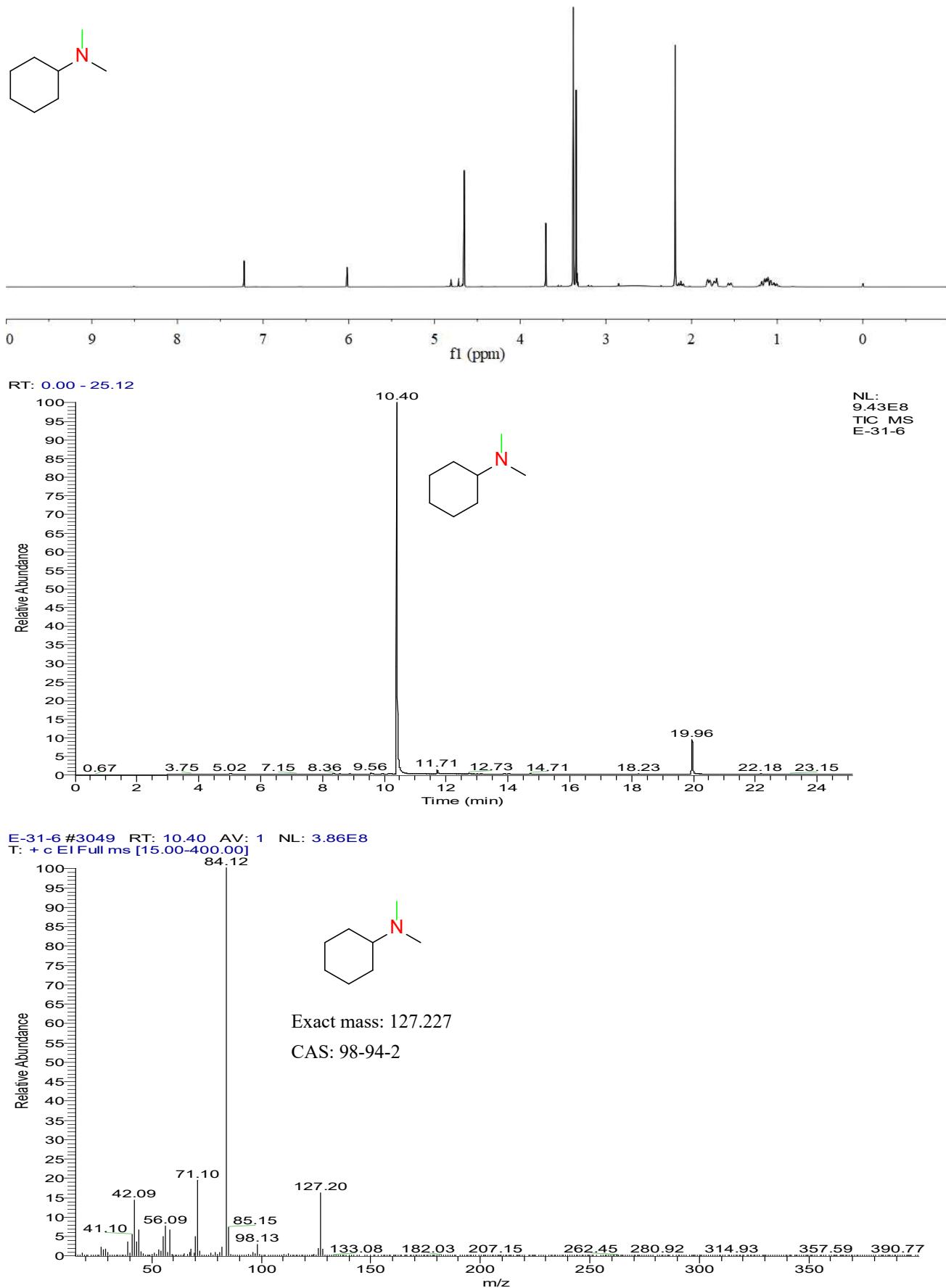


E-31-3 #6085 RT: 20.73 AV: 1 NL: 6.50E8
T: + c EI Full ms [10.00-400.00]

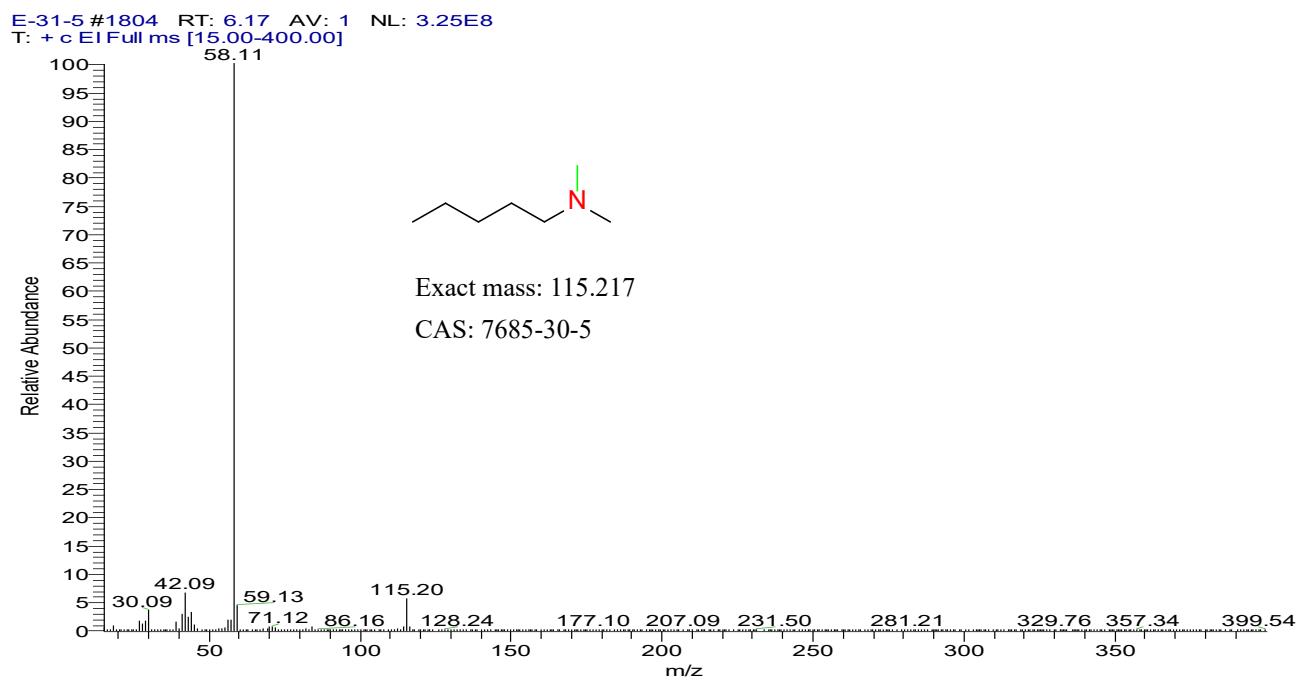
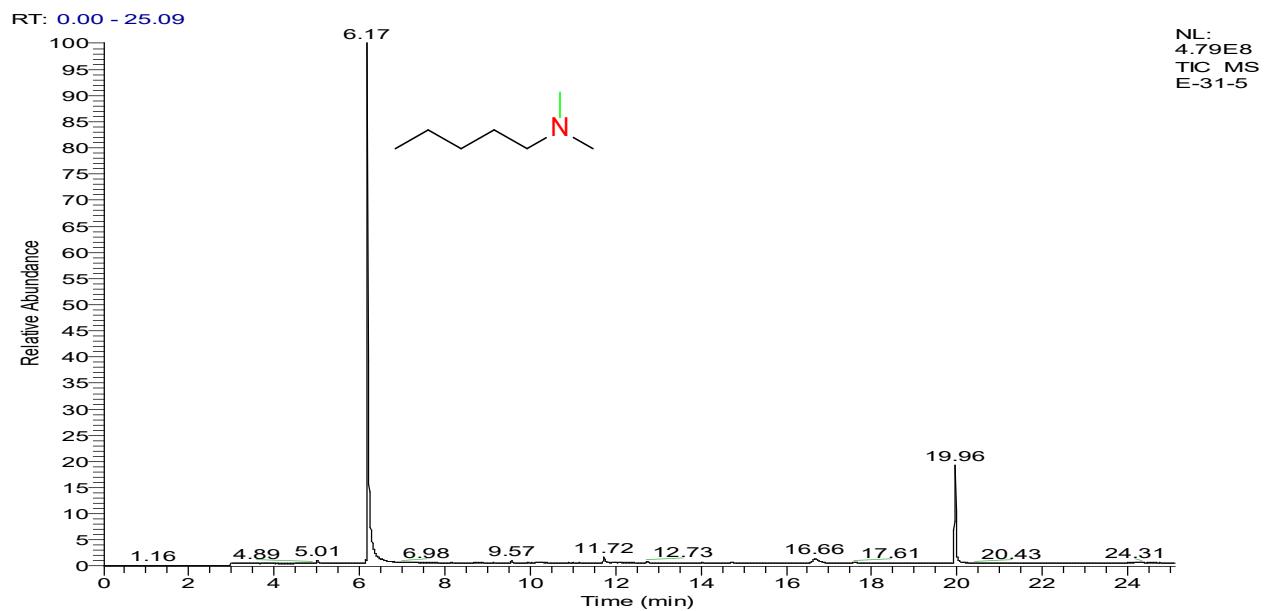
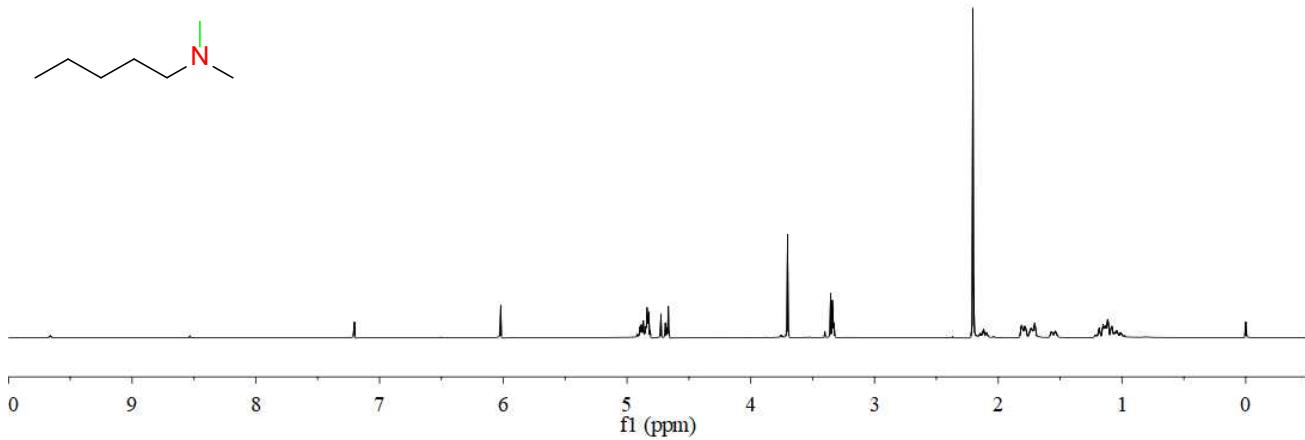


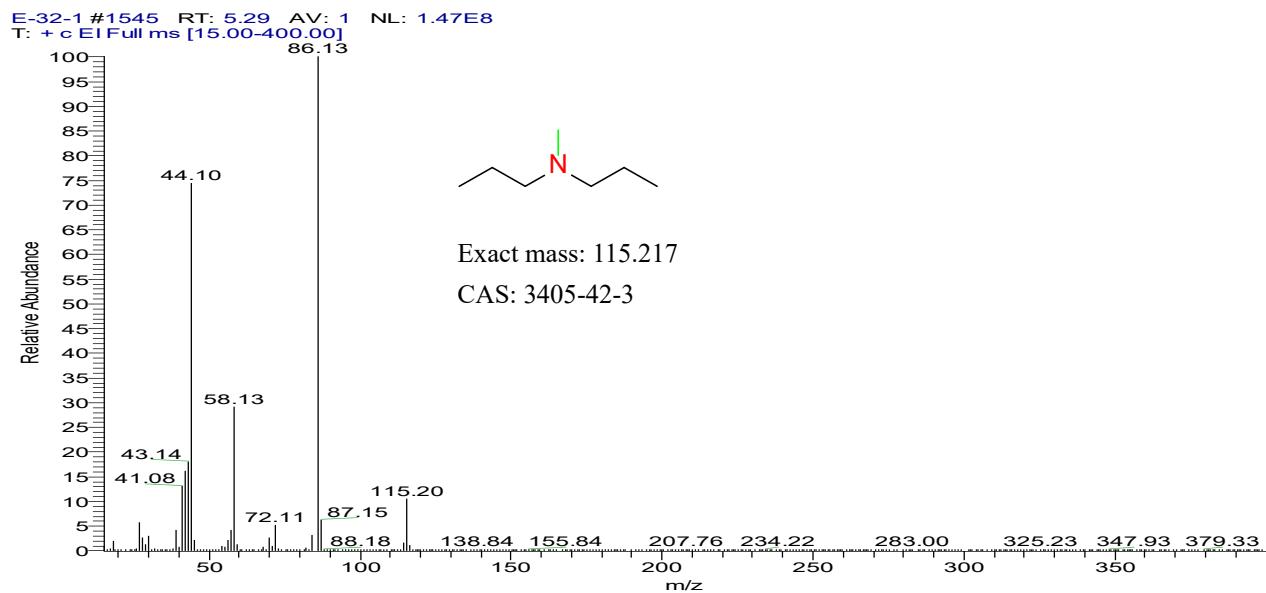
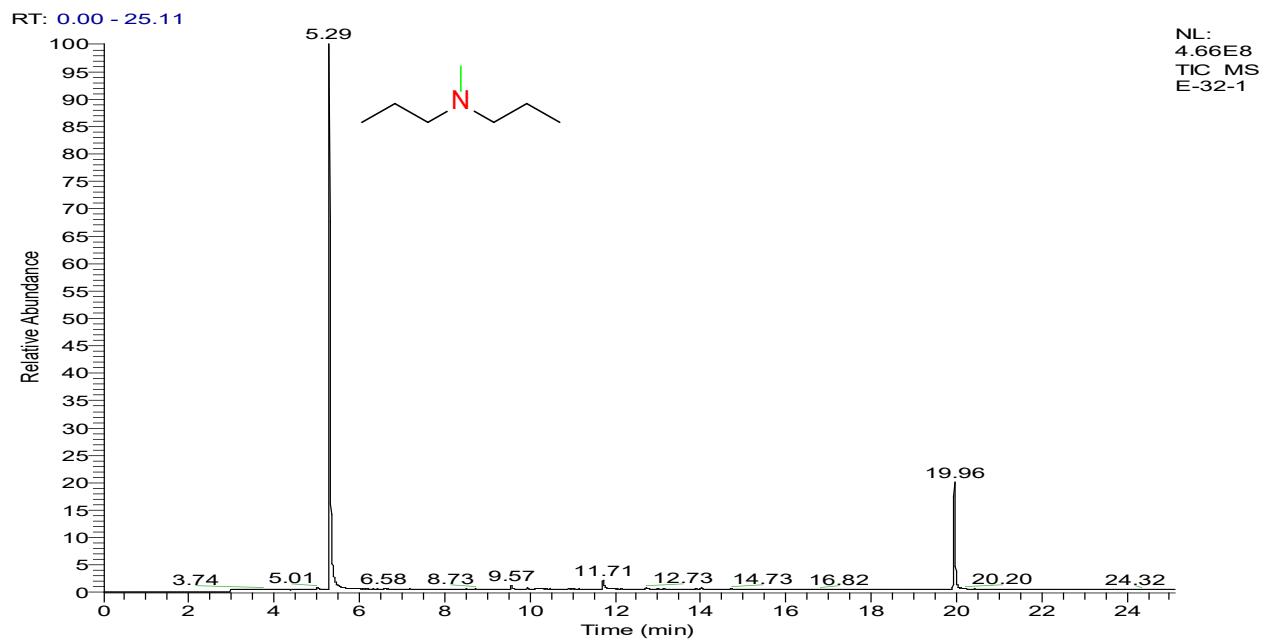
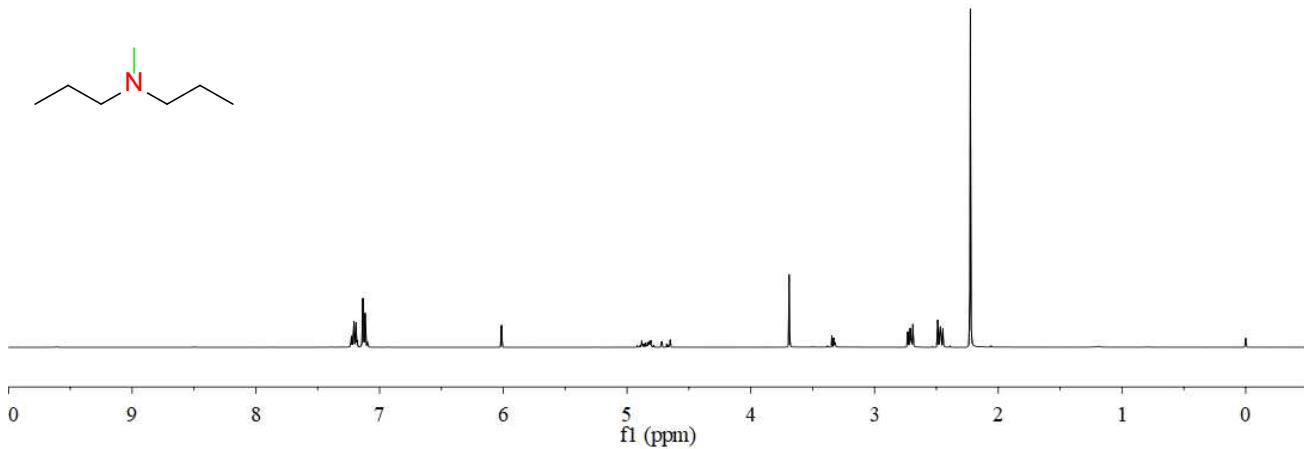


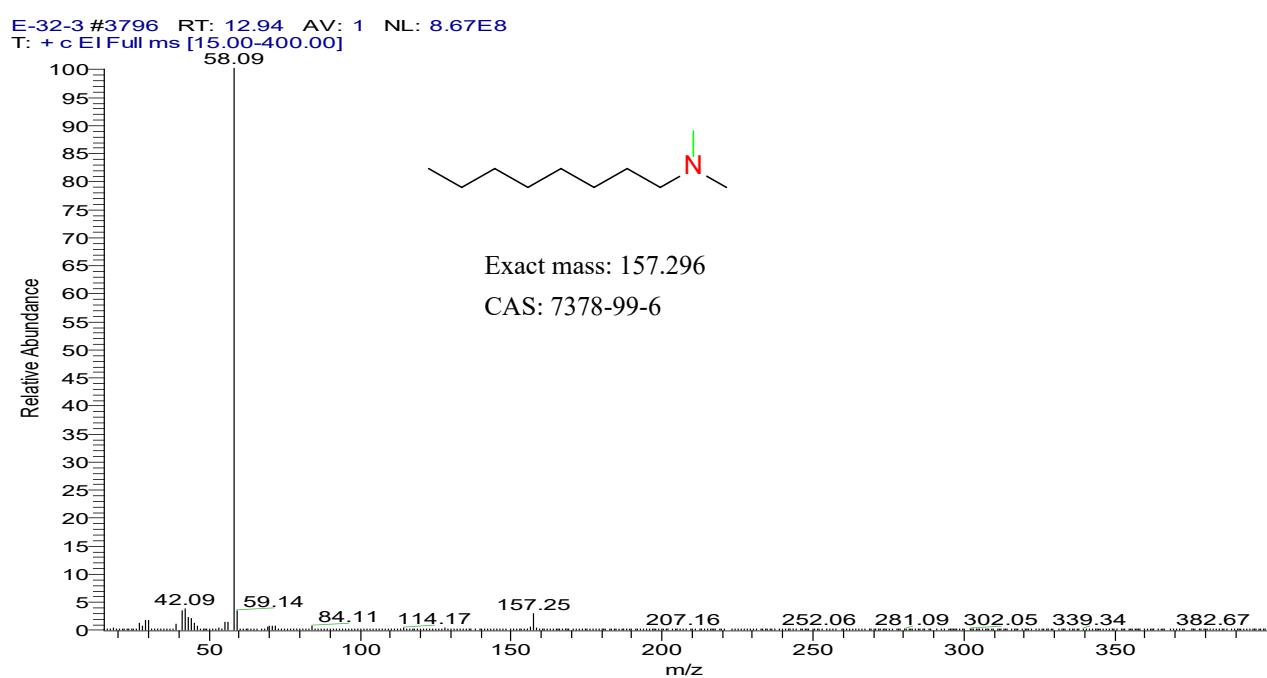
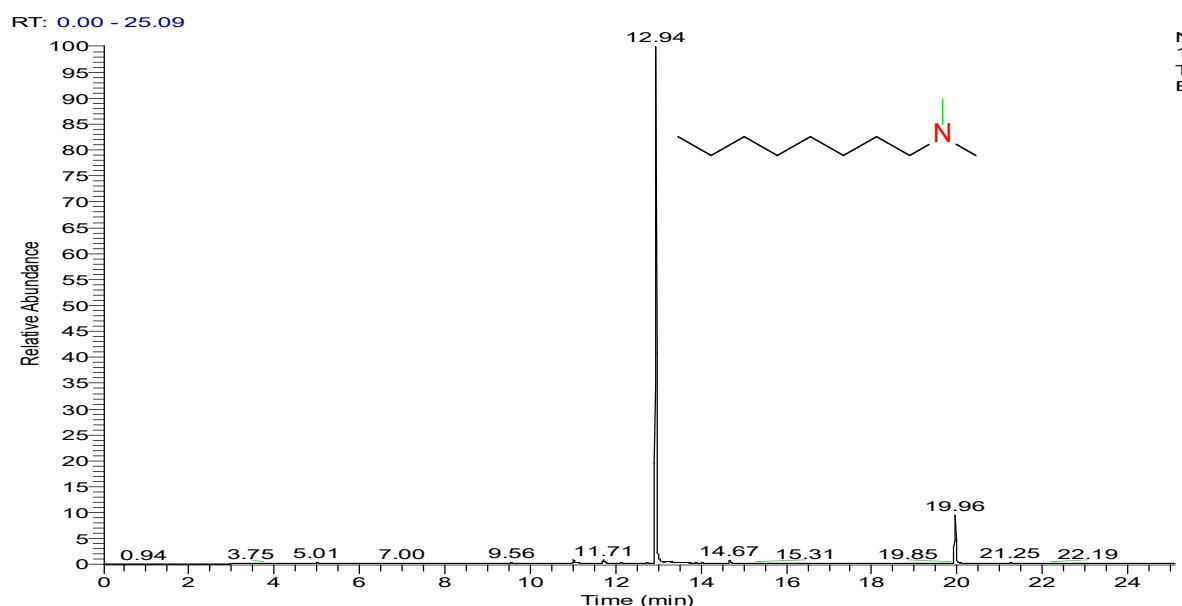
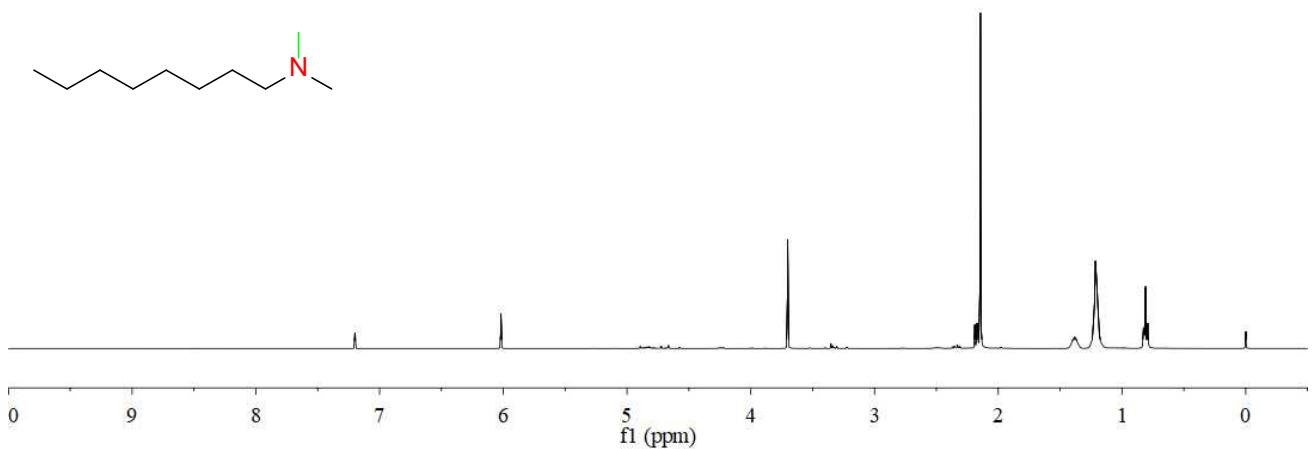


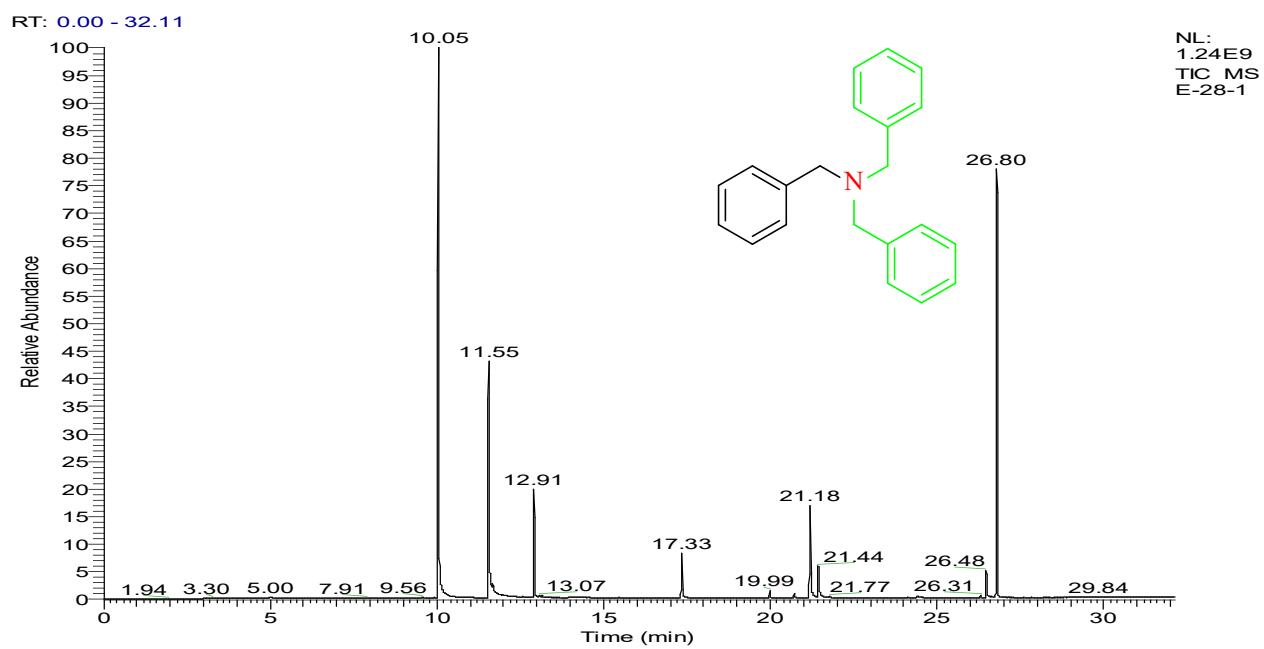
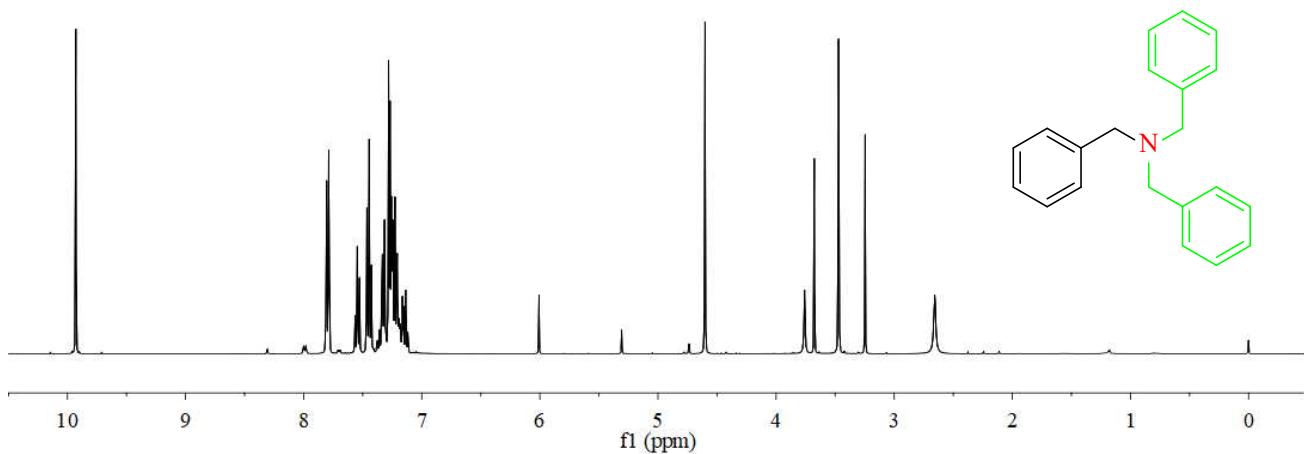


35

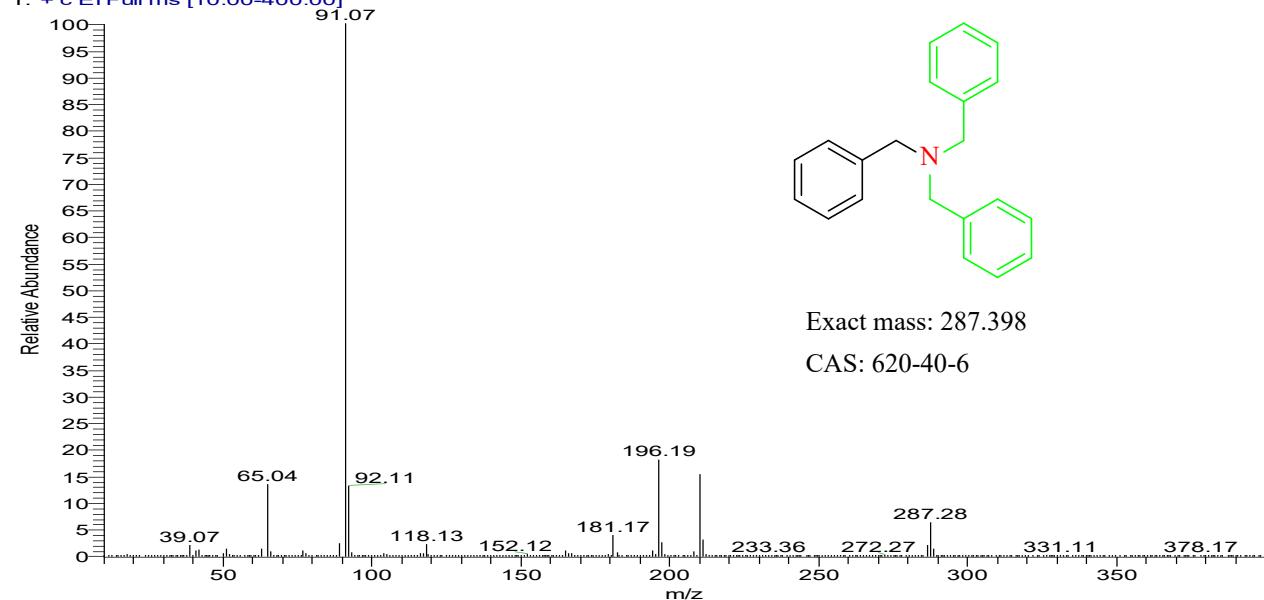


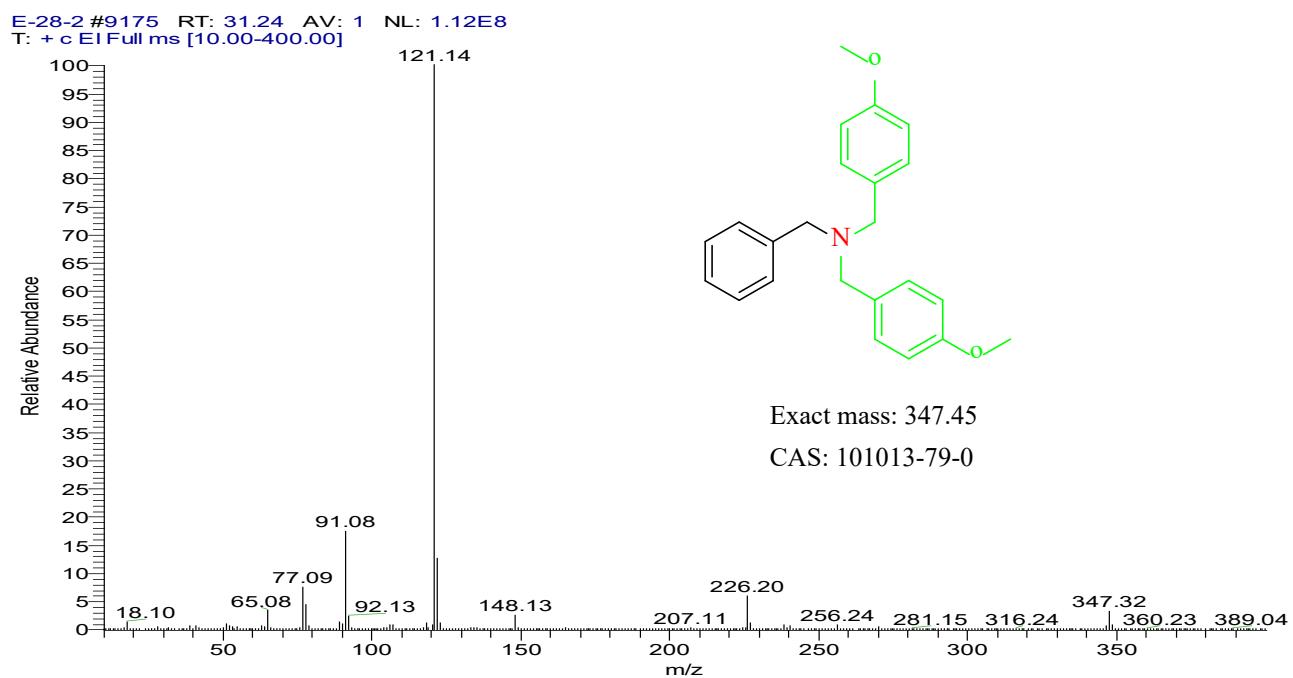
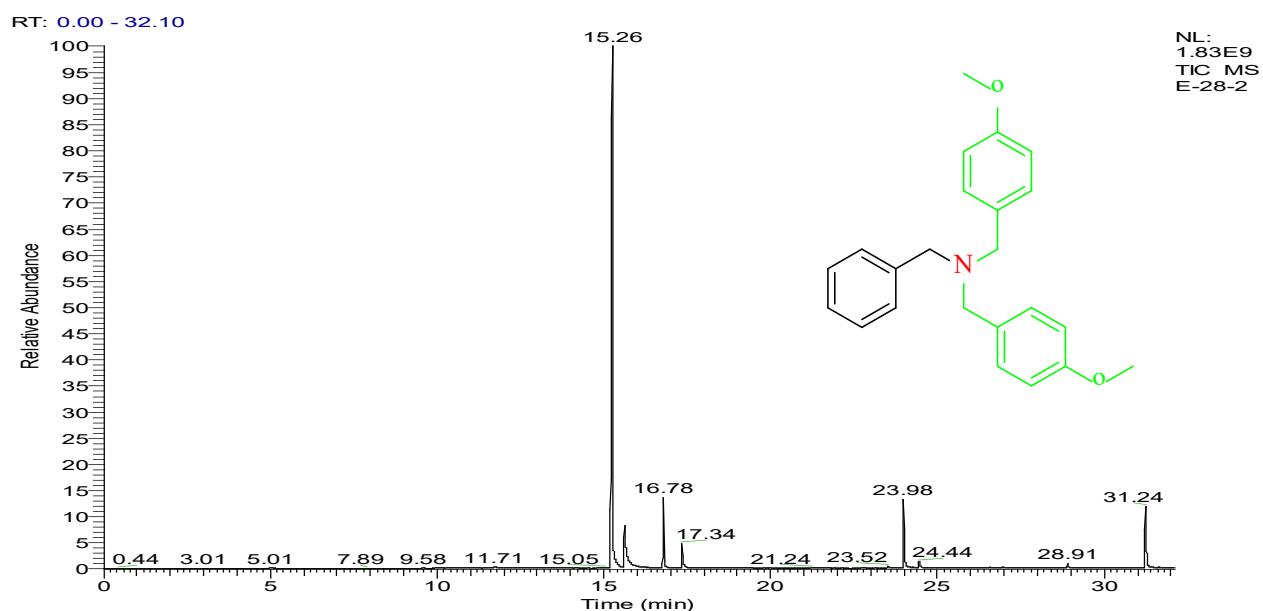
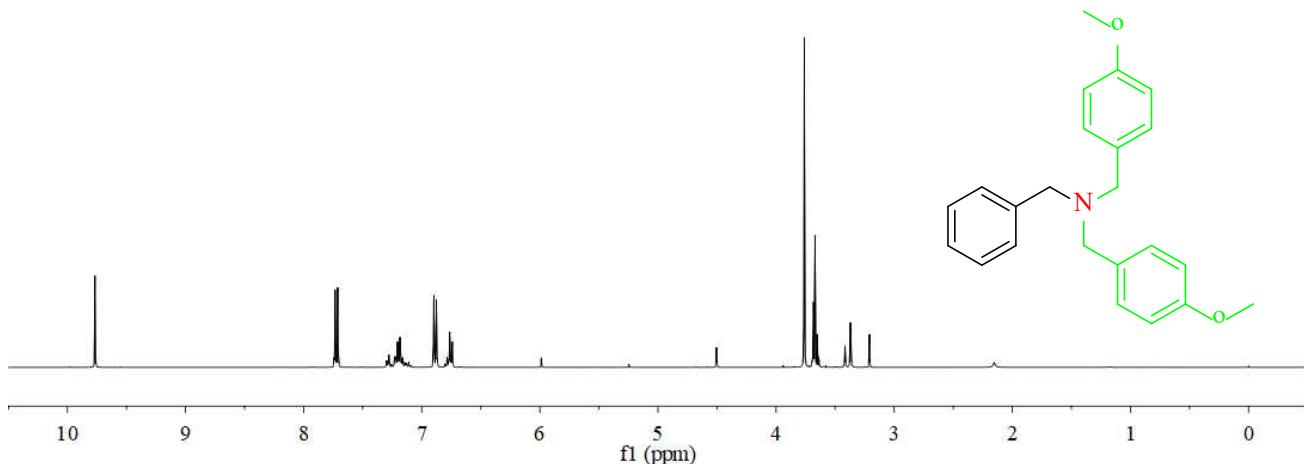


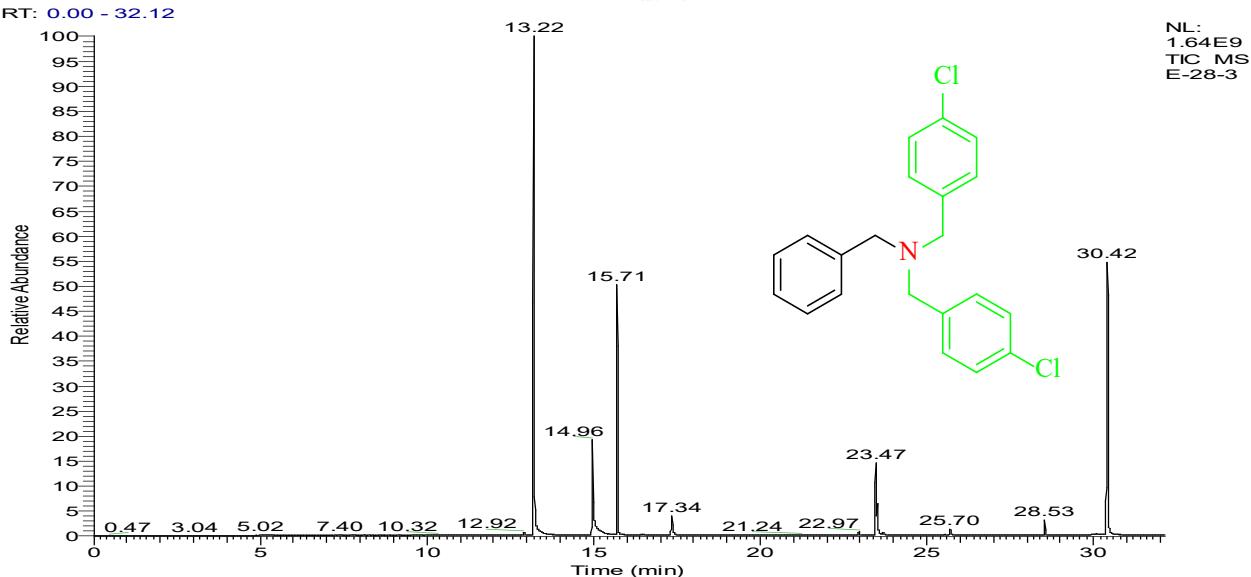
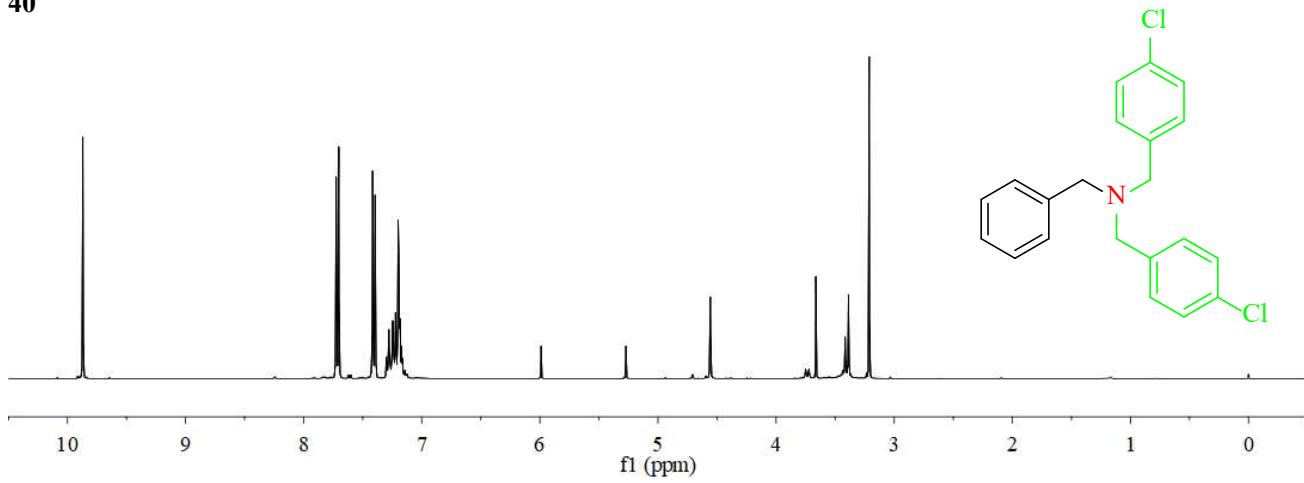




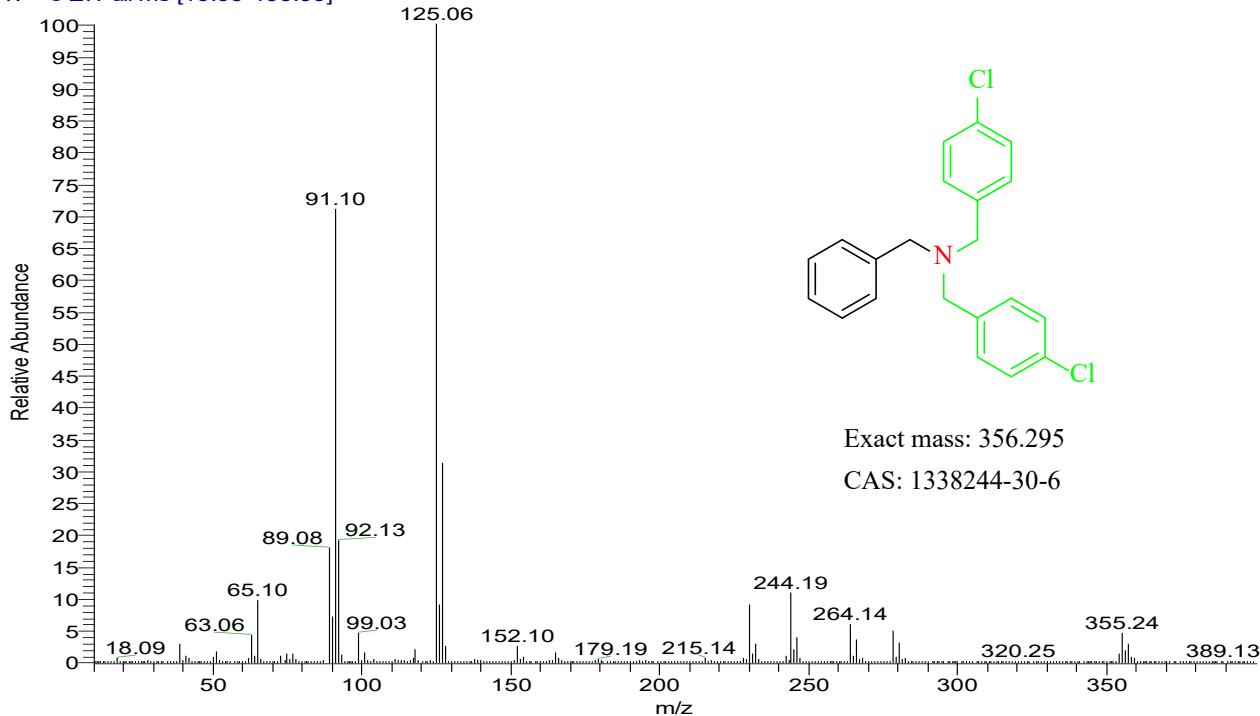
E-28-1 #7869 RT: 26.80 AV: 1 NL: 4.73E8
T: + c EI Full ms [10.00-400.00]

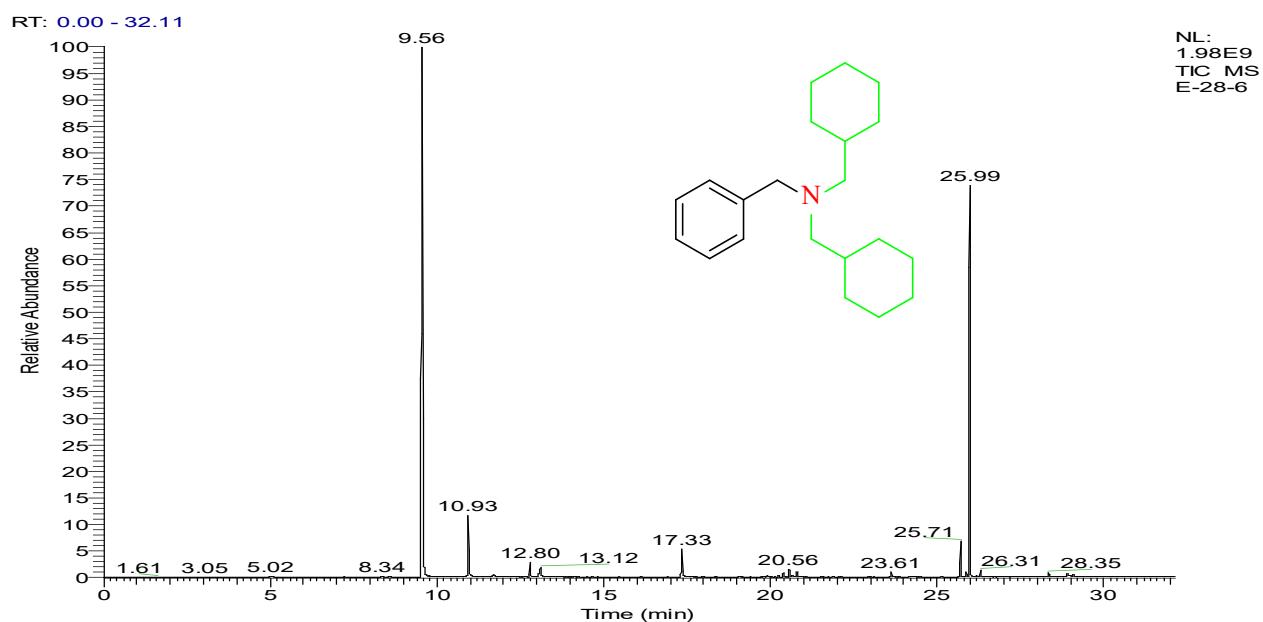
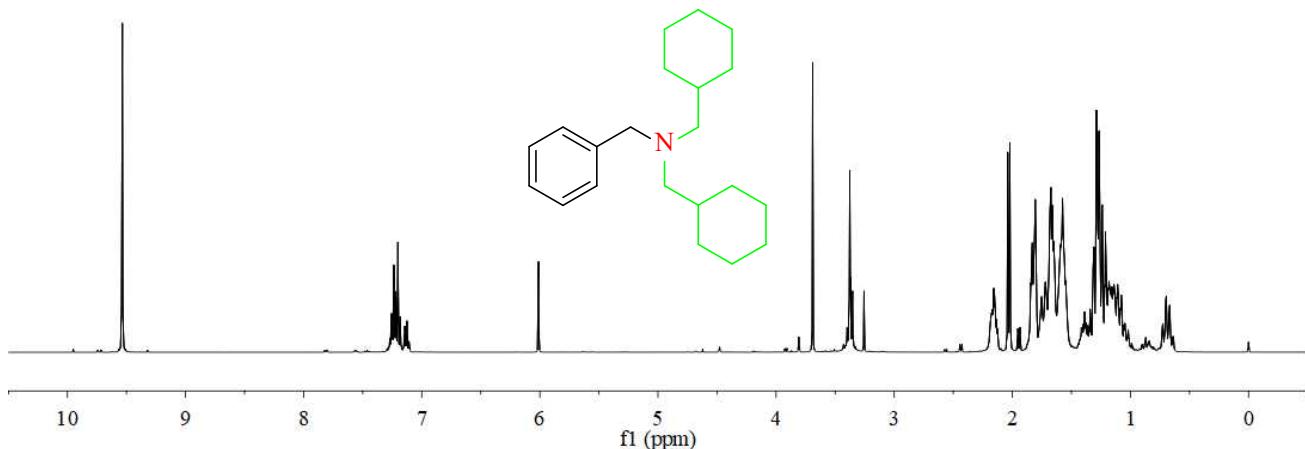




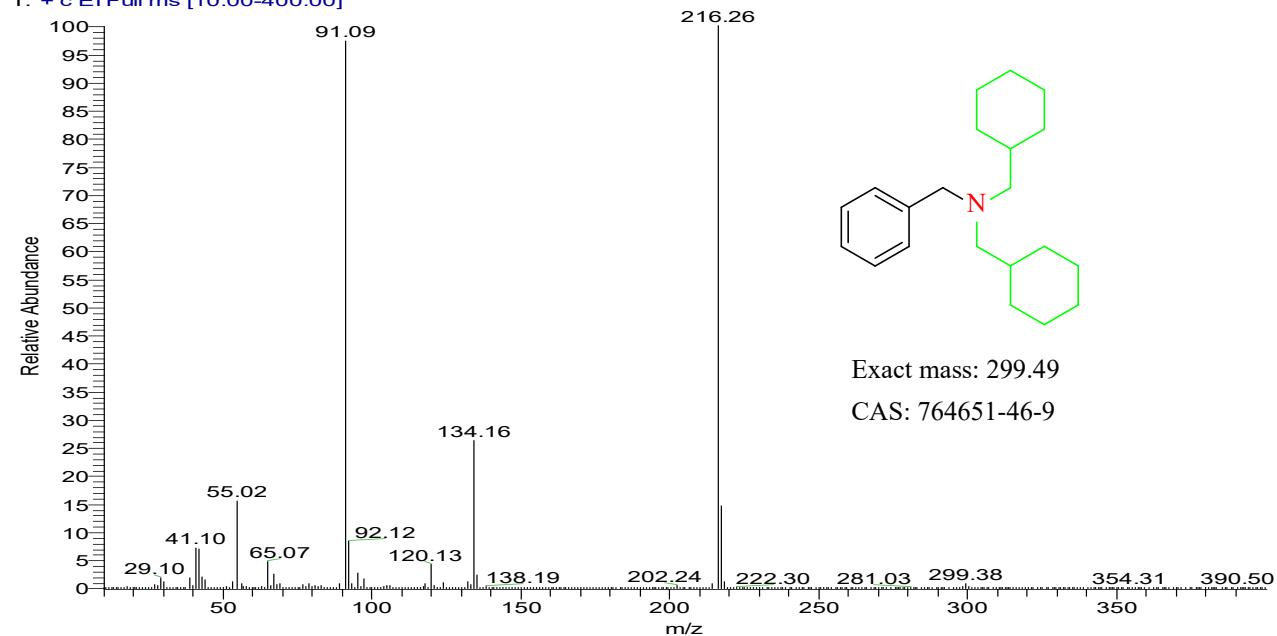


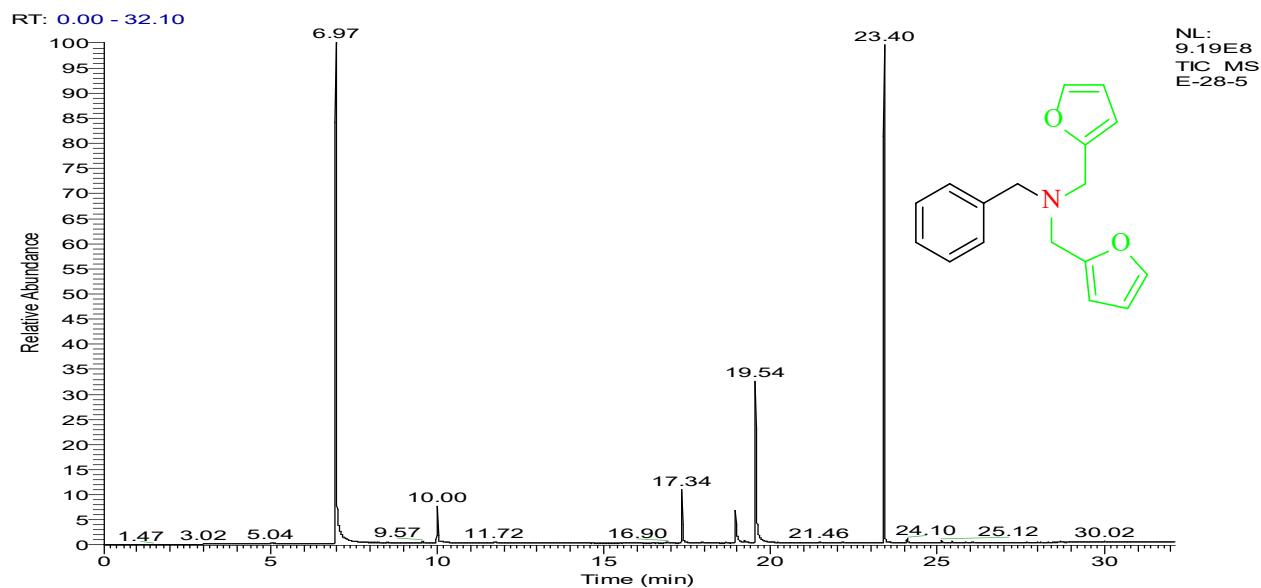
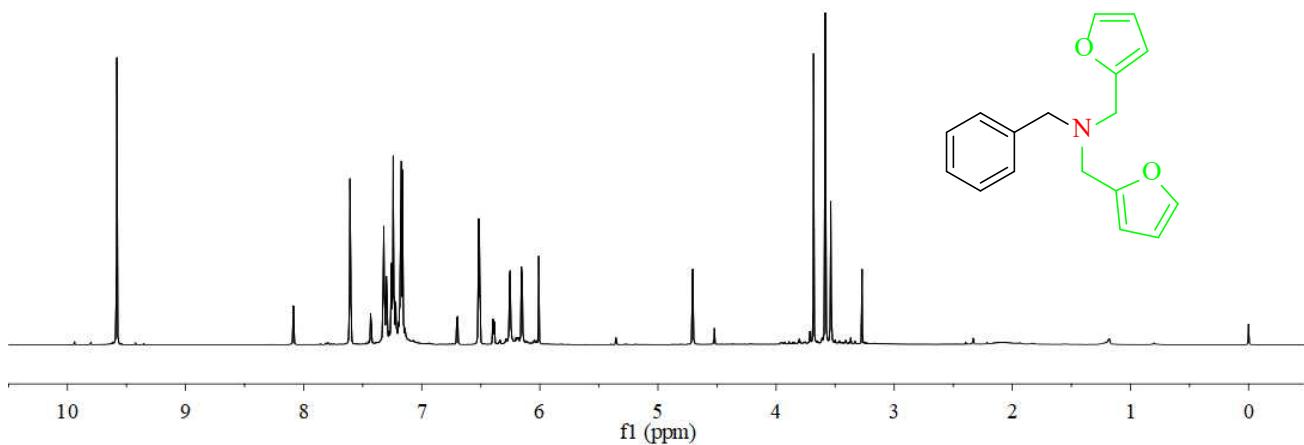
E-28-3 #8936 RT: 30.42 AV: 1 NL: 2.29E8
T: + c EI Full ms [10.00-400.00]



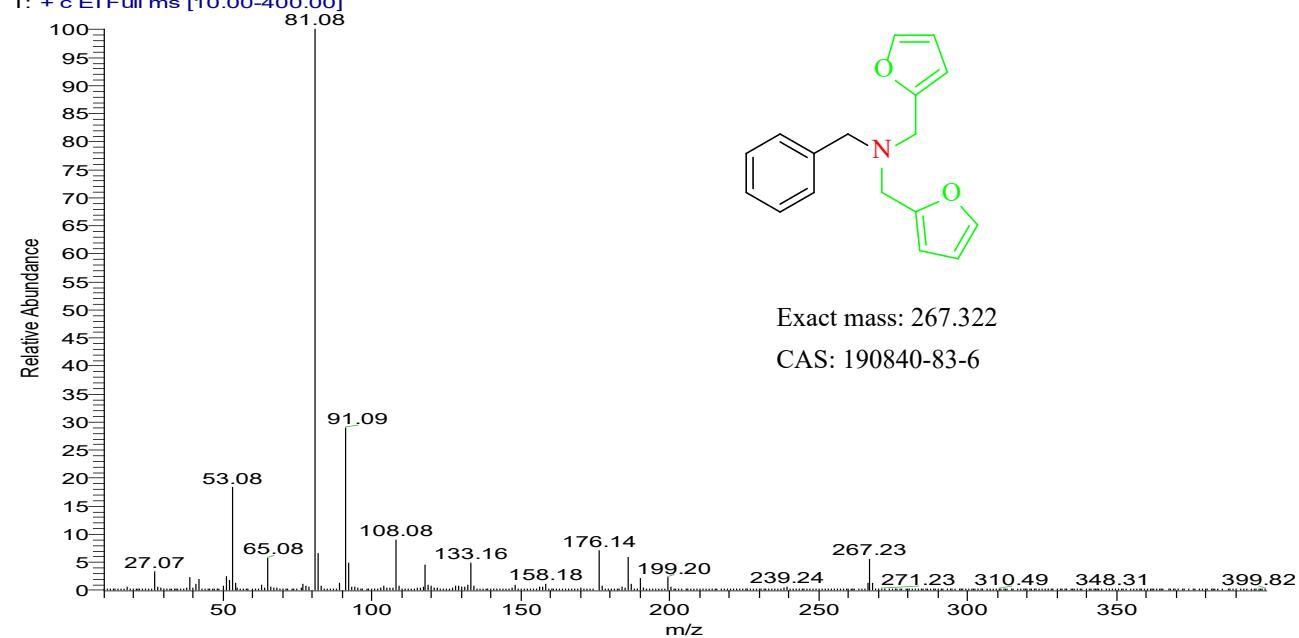


E-28-6 #7631 RT: 25.99 AV: 1 NL: 4.49E8
T: + c EI Full ms [10.00-400.00]

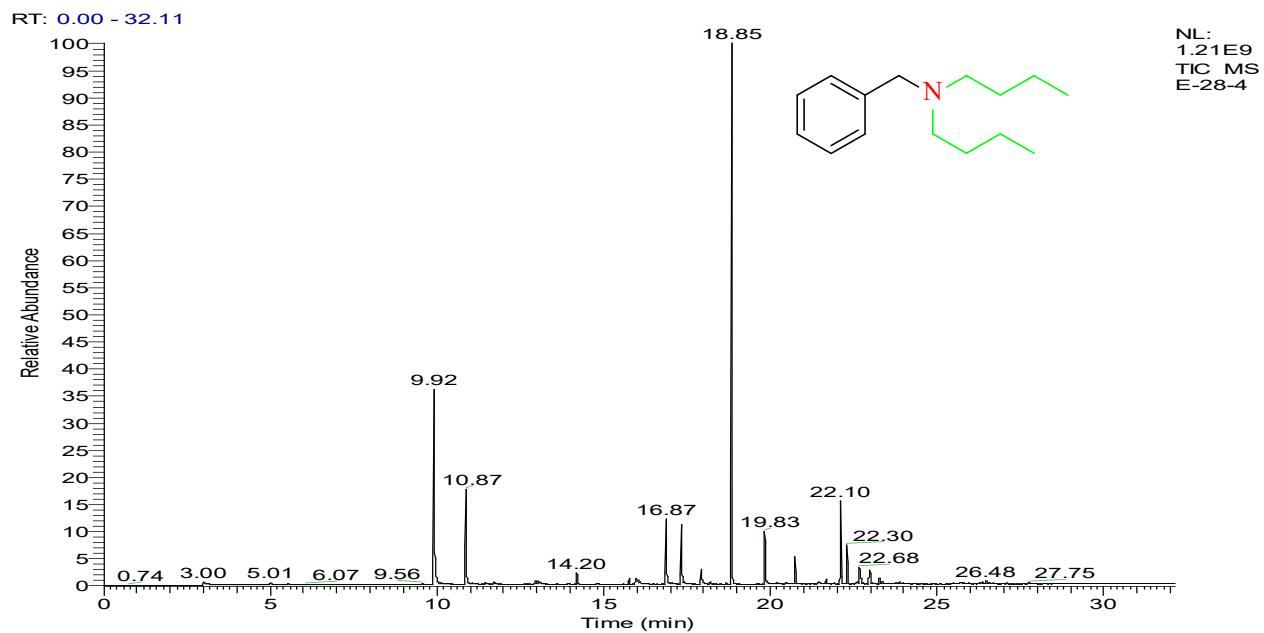
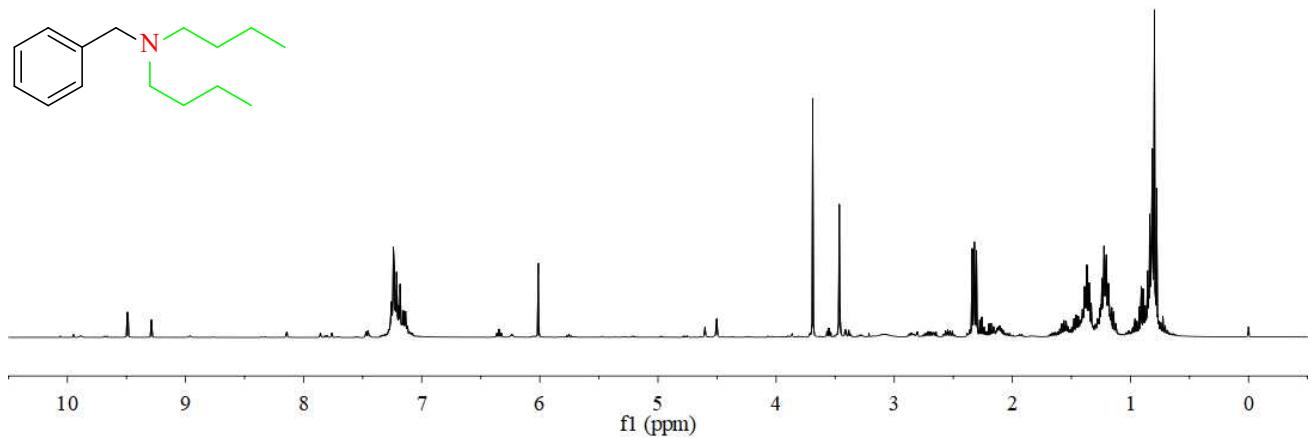




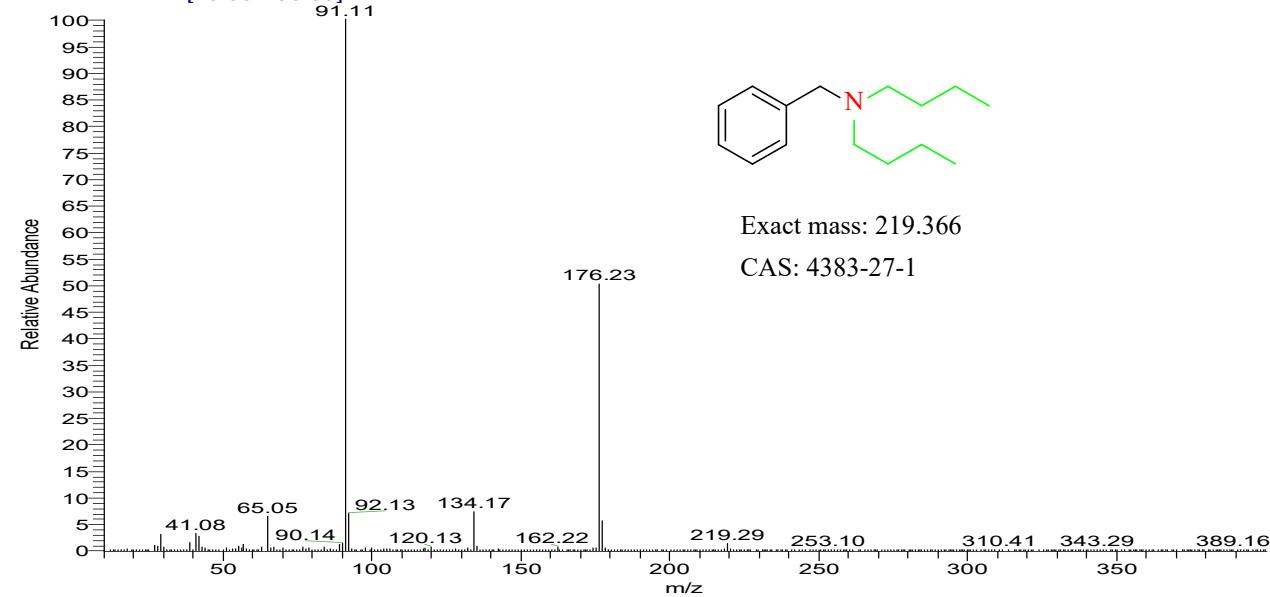
E-28-5 #6870 RT: 23.40 AV: 1 NL: 3.01E8
T: + c EI Full ms [10.00-400.00]

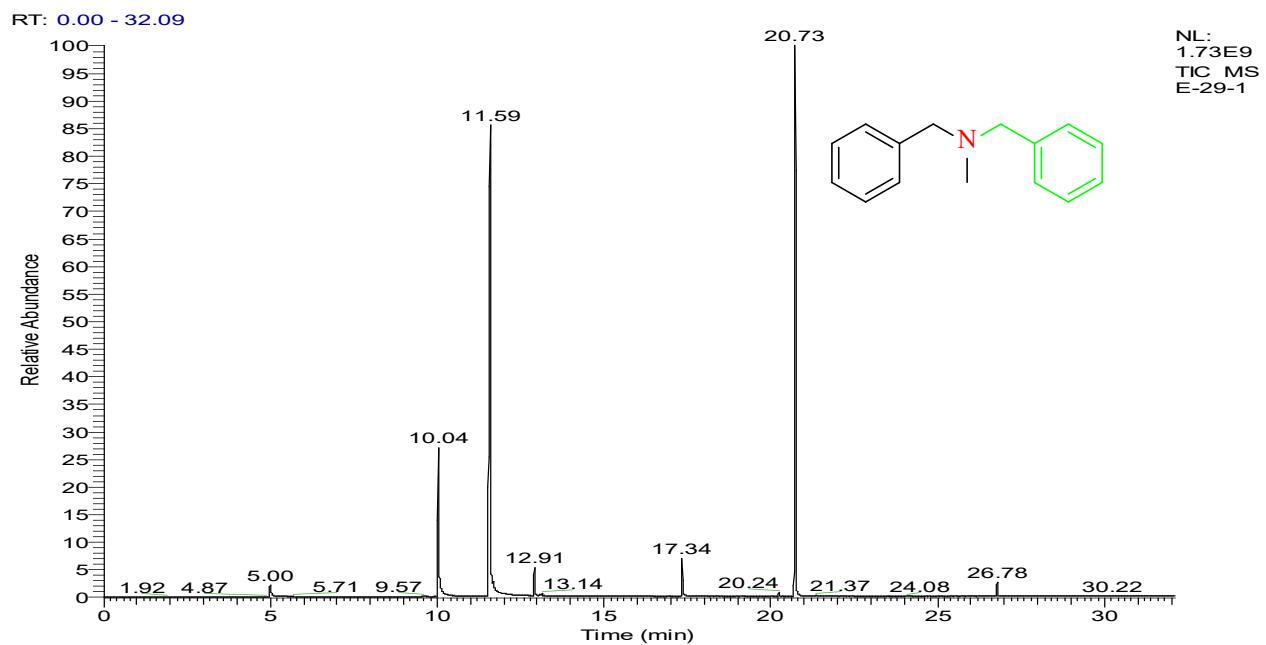
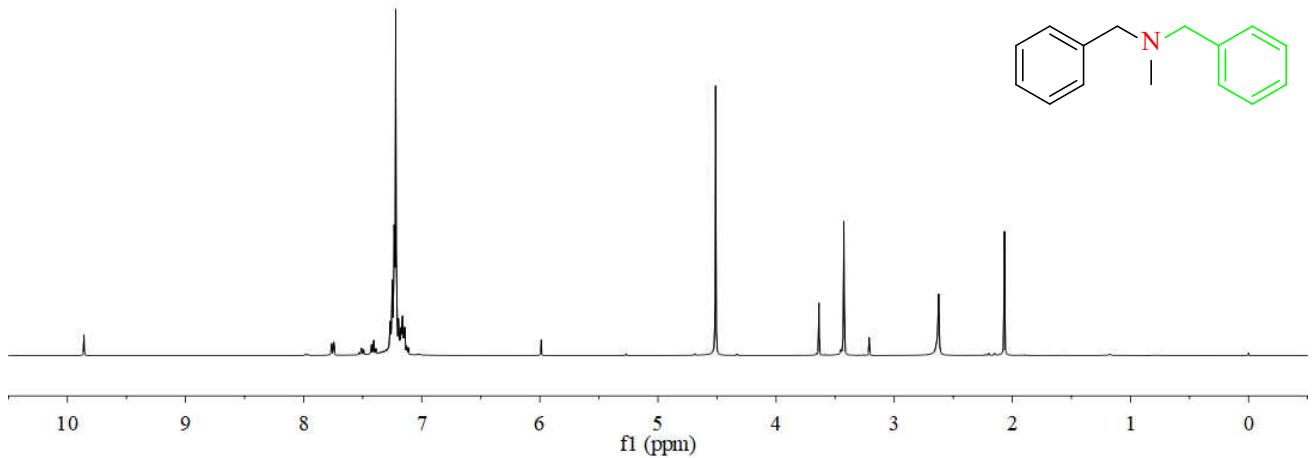


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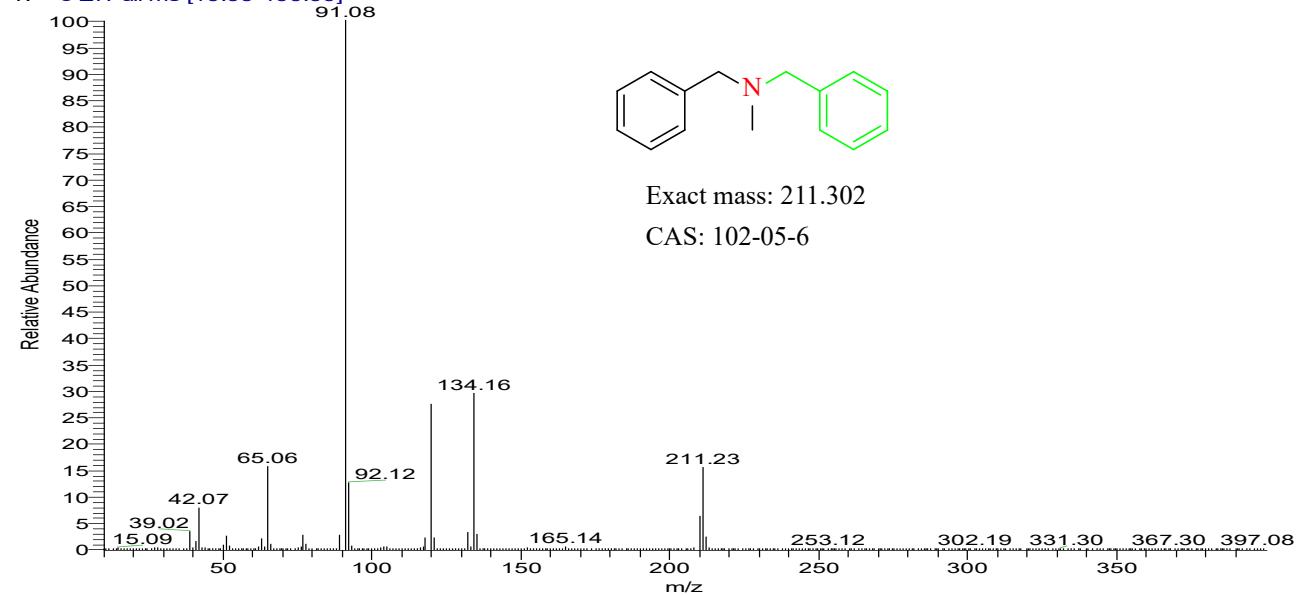


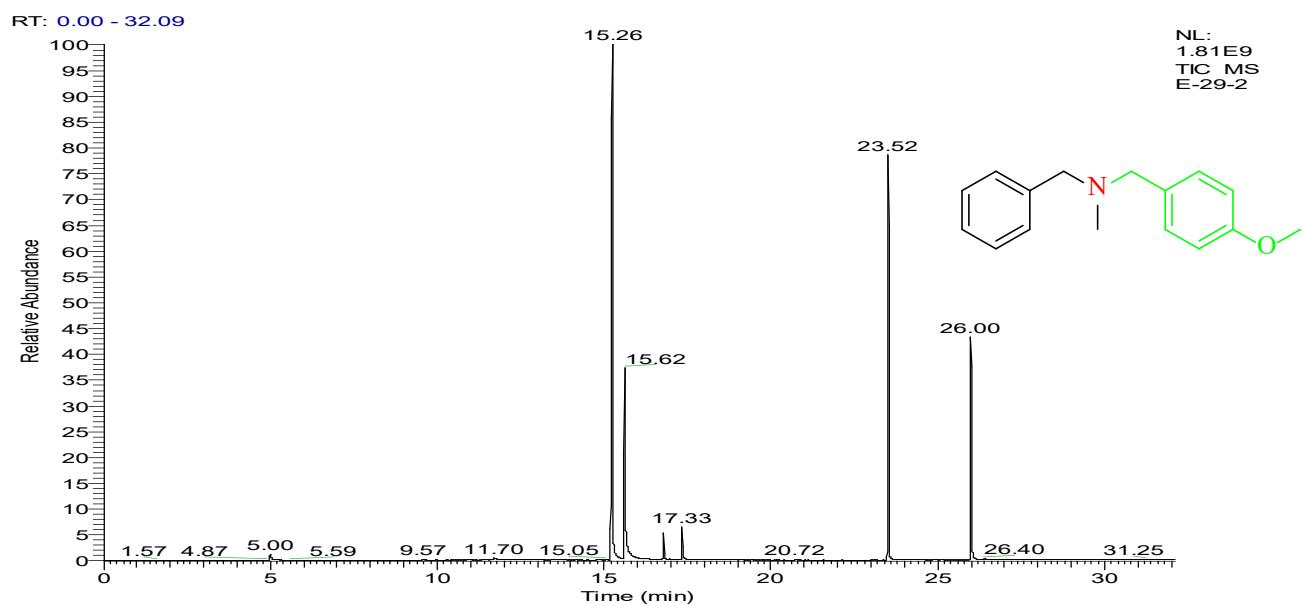
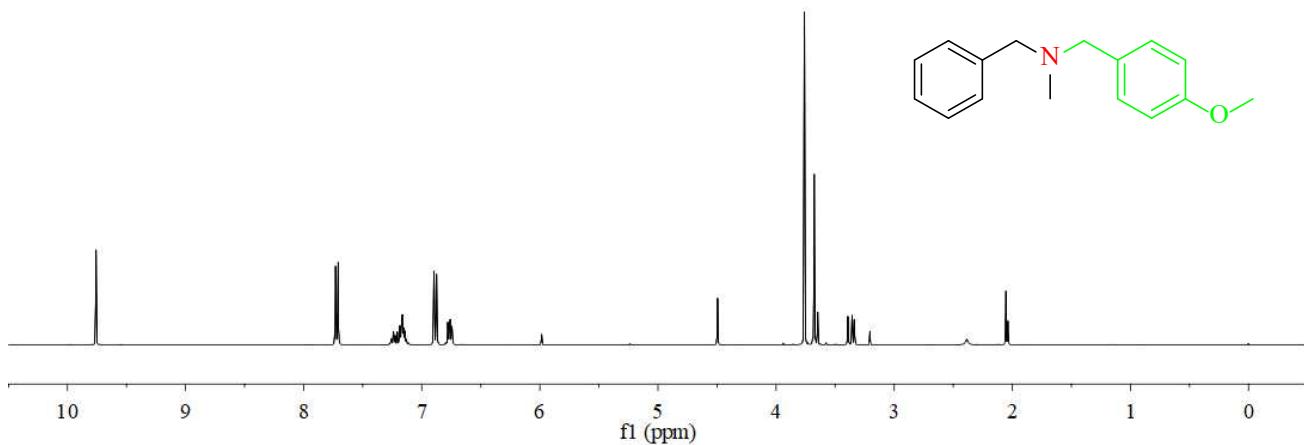
E-28-4 #5532 RT: 18.85 AV: 1 NL: 5.71E8
T: + c EI Full ms [10.00-400.00]



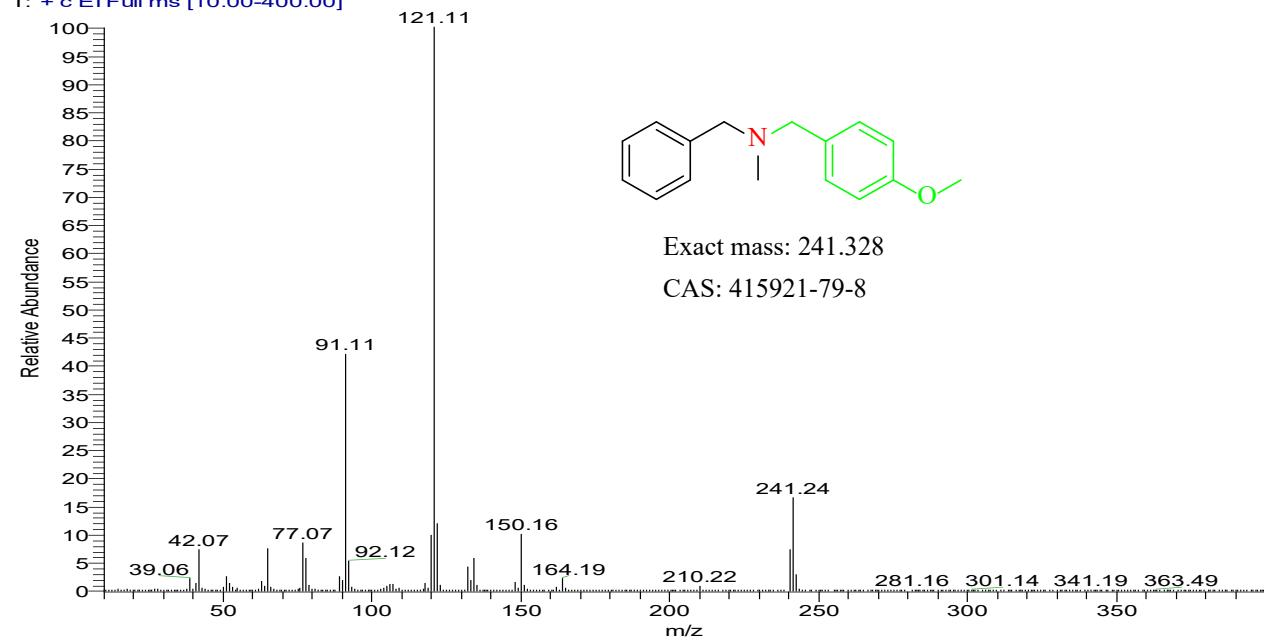


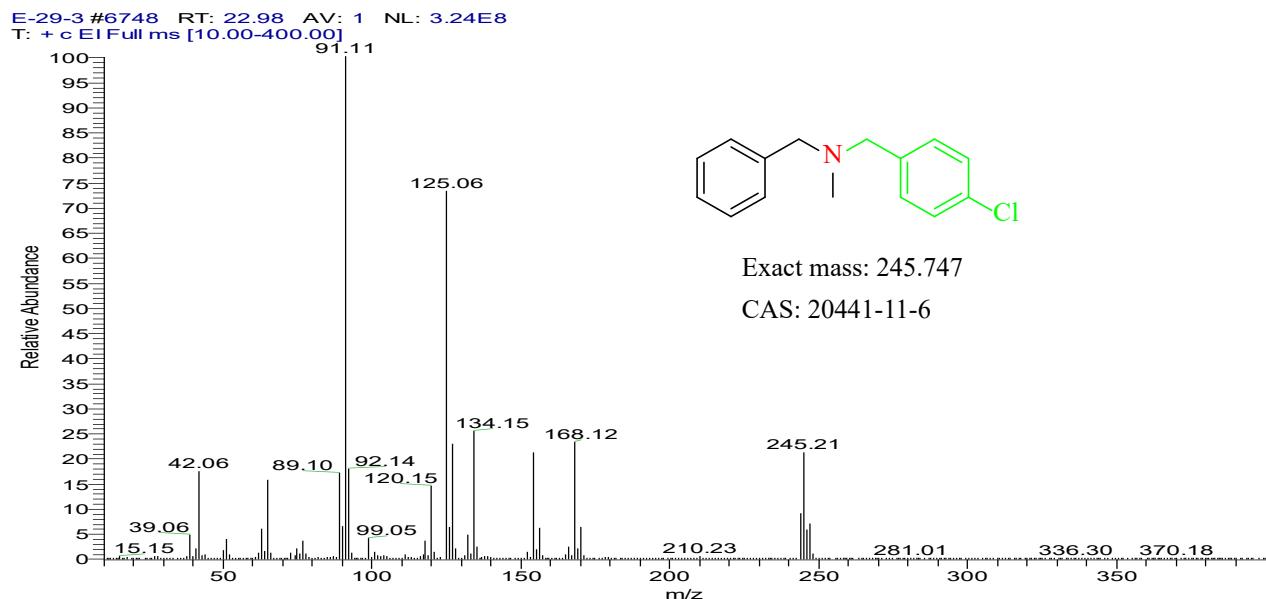
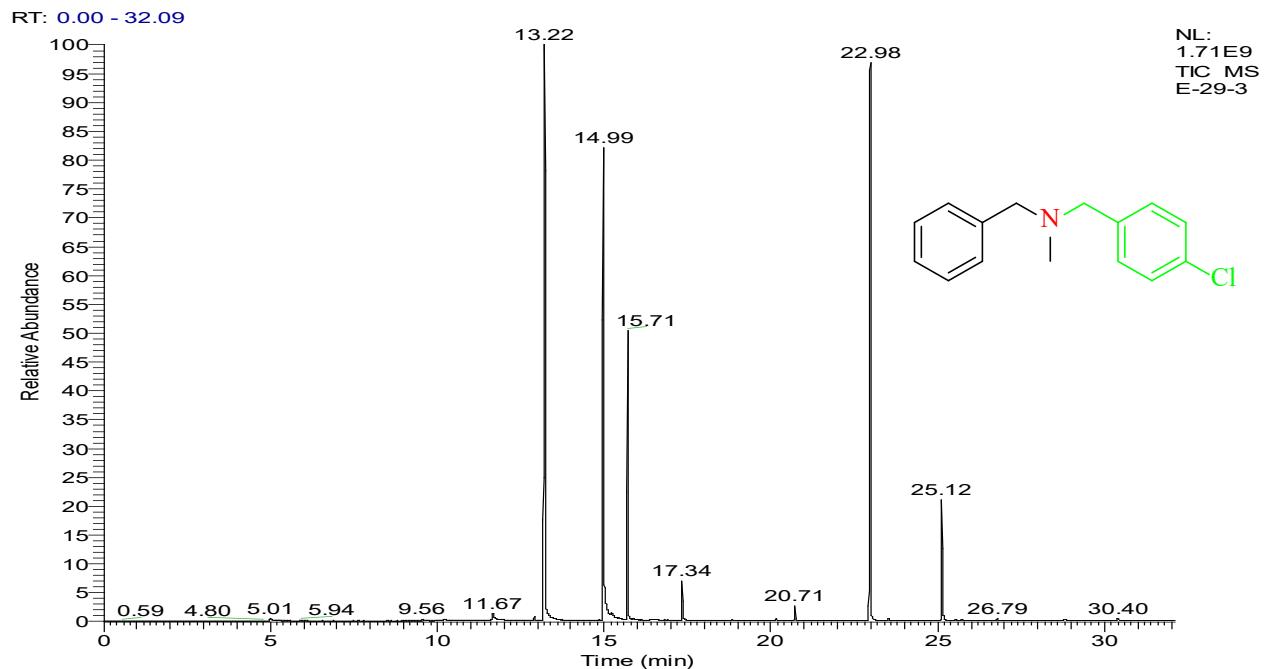
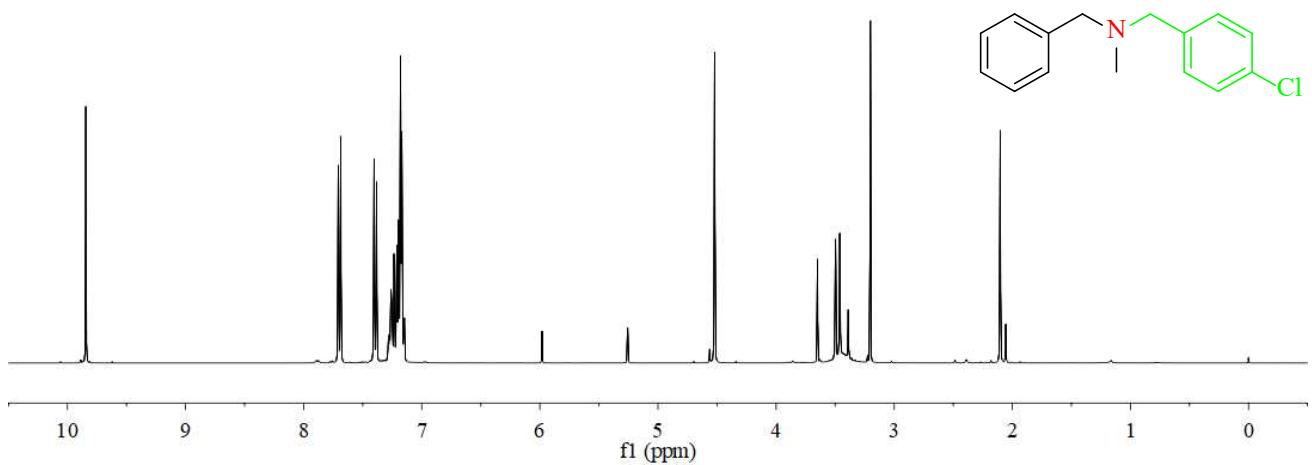
E-29-1 #6085 RT: 20.73 AV: 1 NL: 6.59E8
T: + c EI Full ms [10.00-400.00]

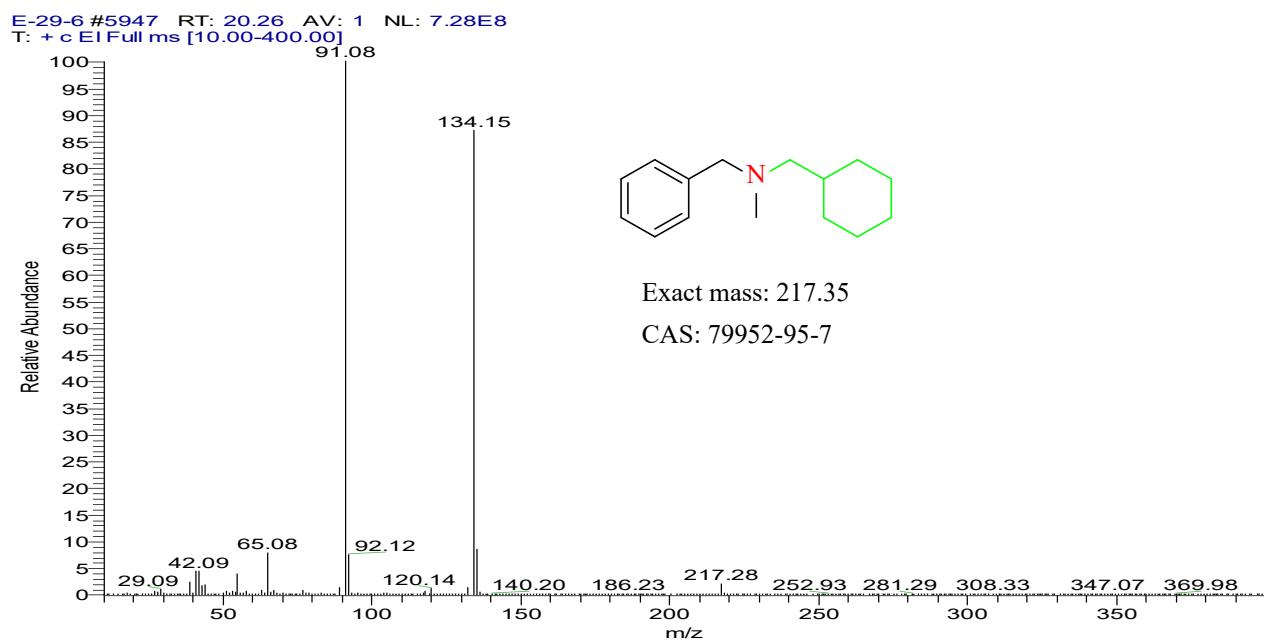
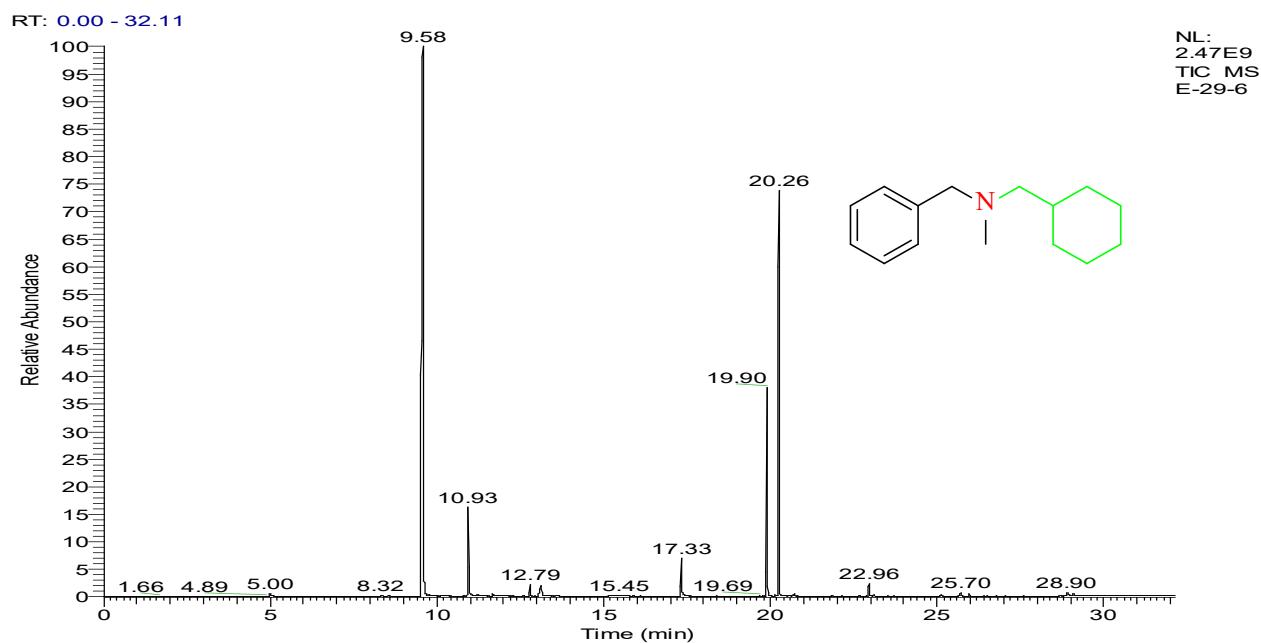
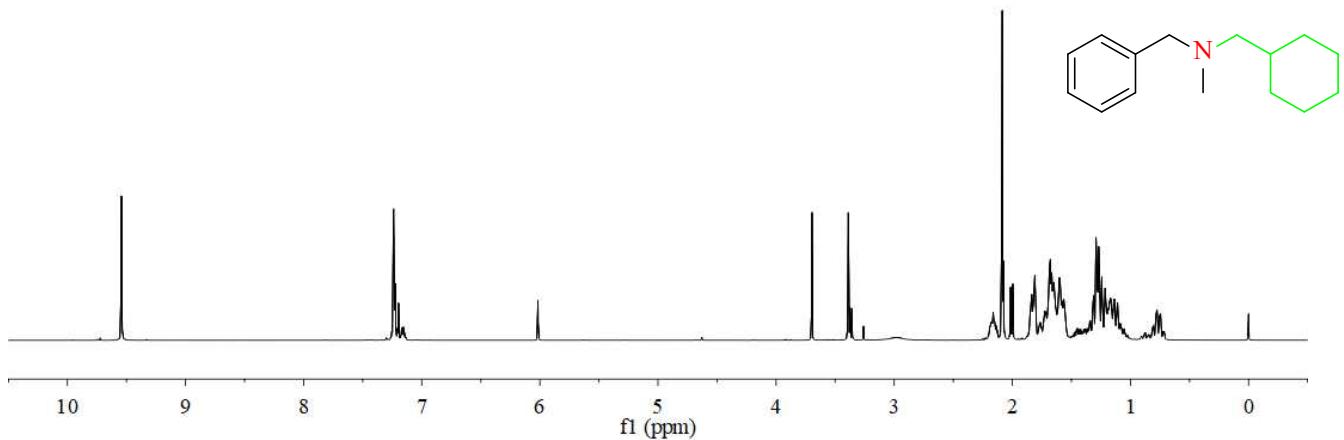


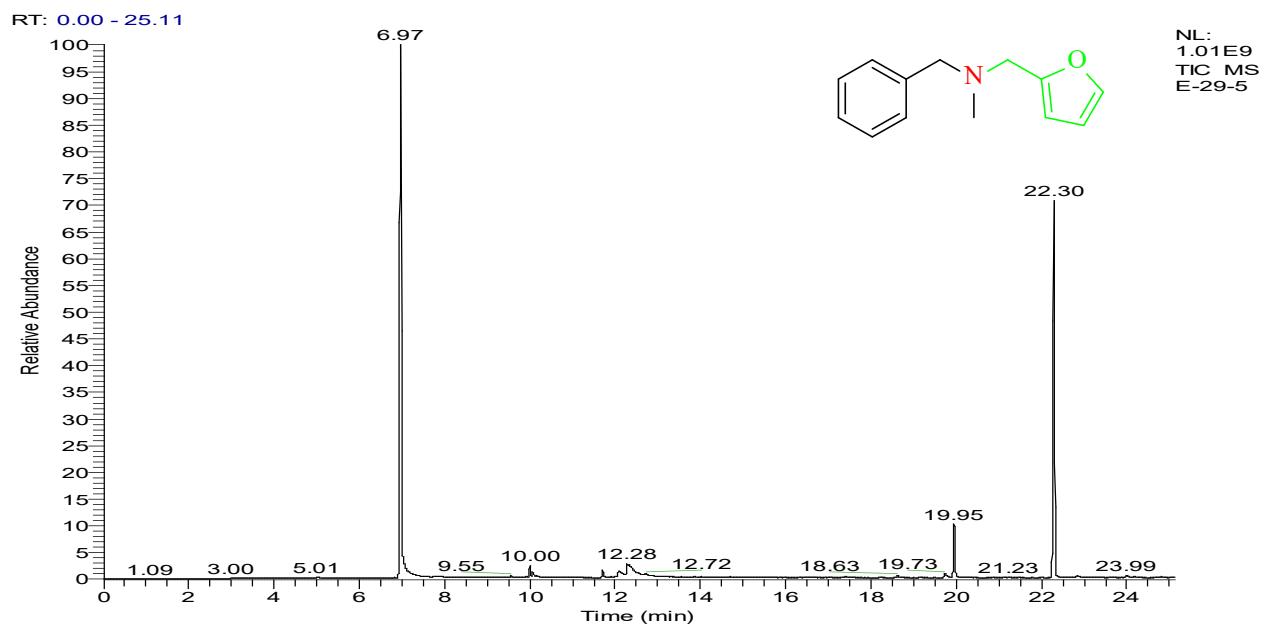
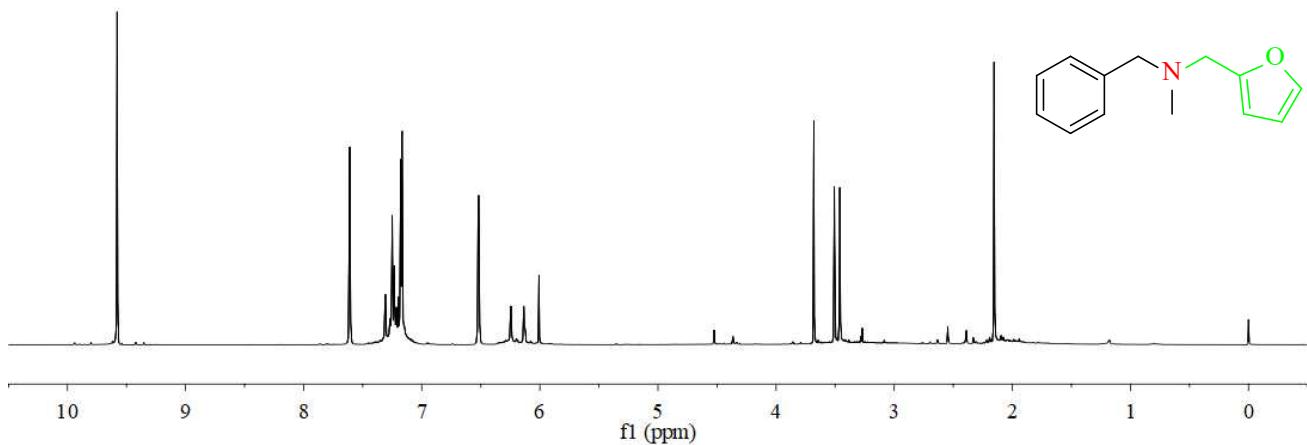


E-29-2 #6907 RT: 23.52 AV: 1 NL: 4.96E8
T: + c EI Full ms [10.00-400.00]

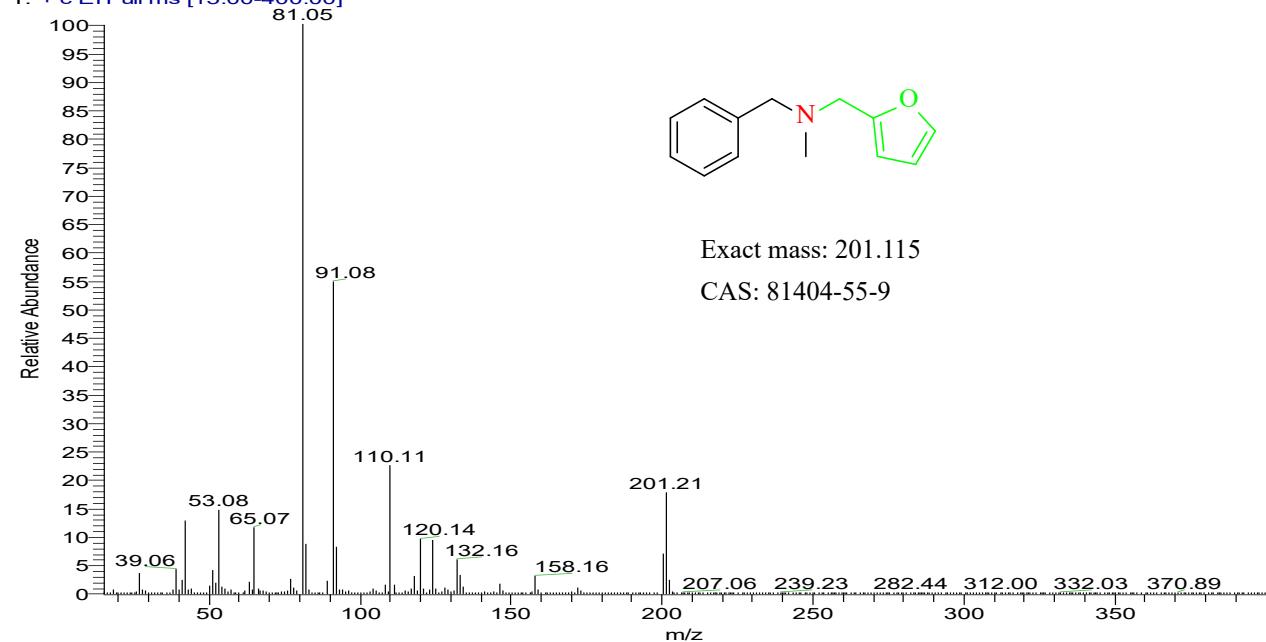




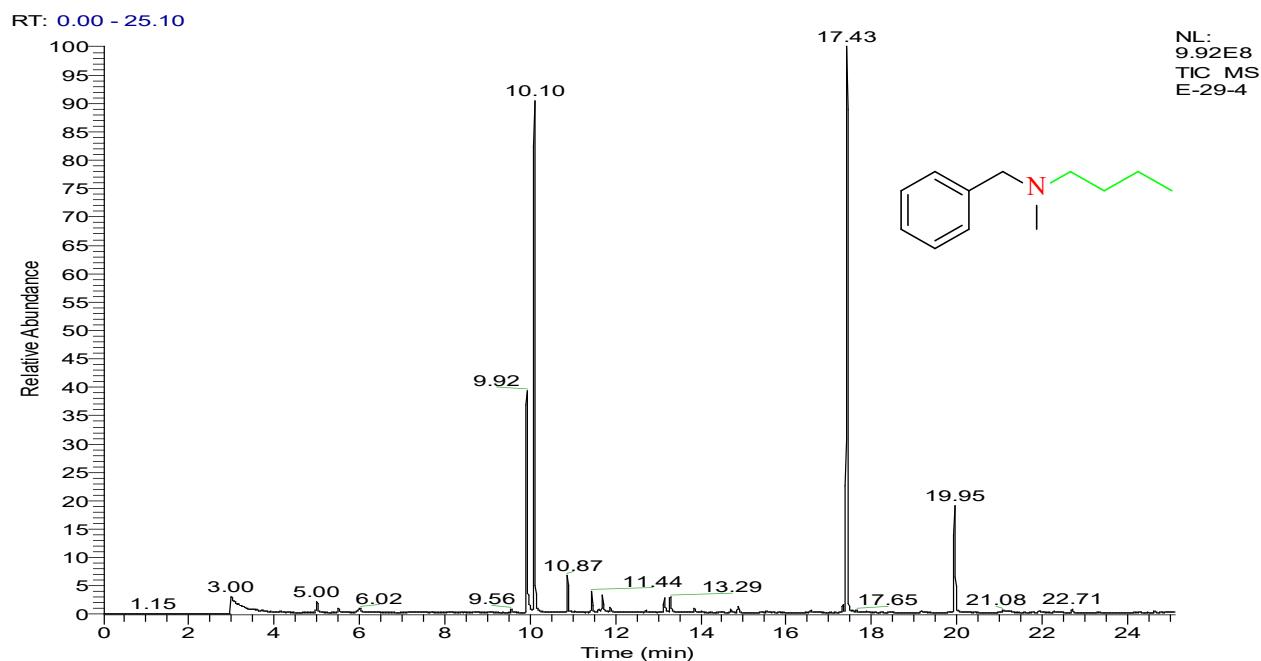
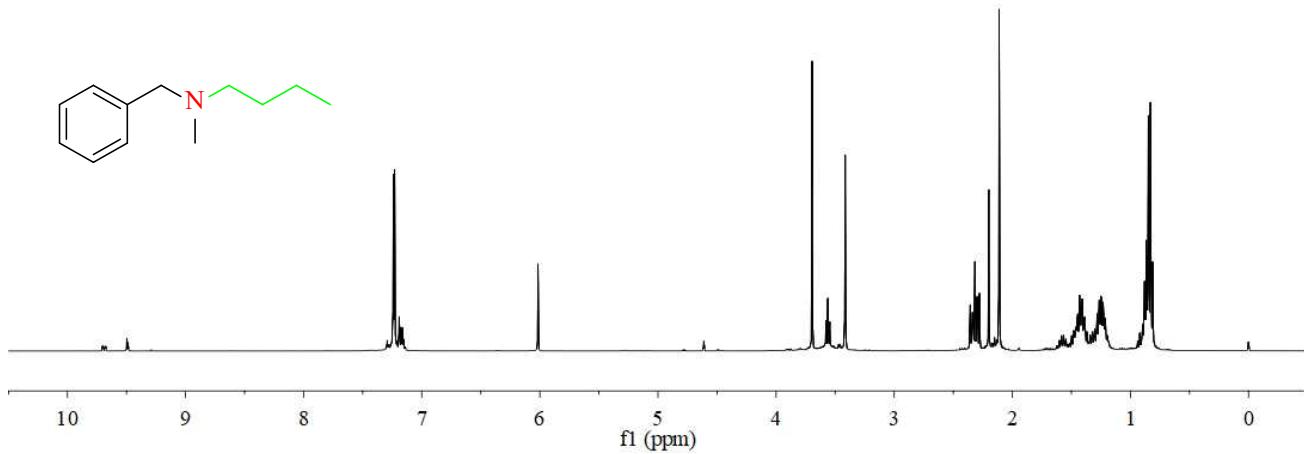




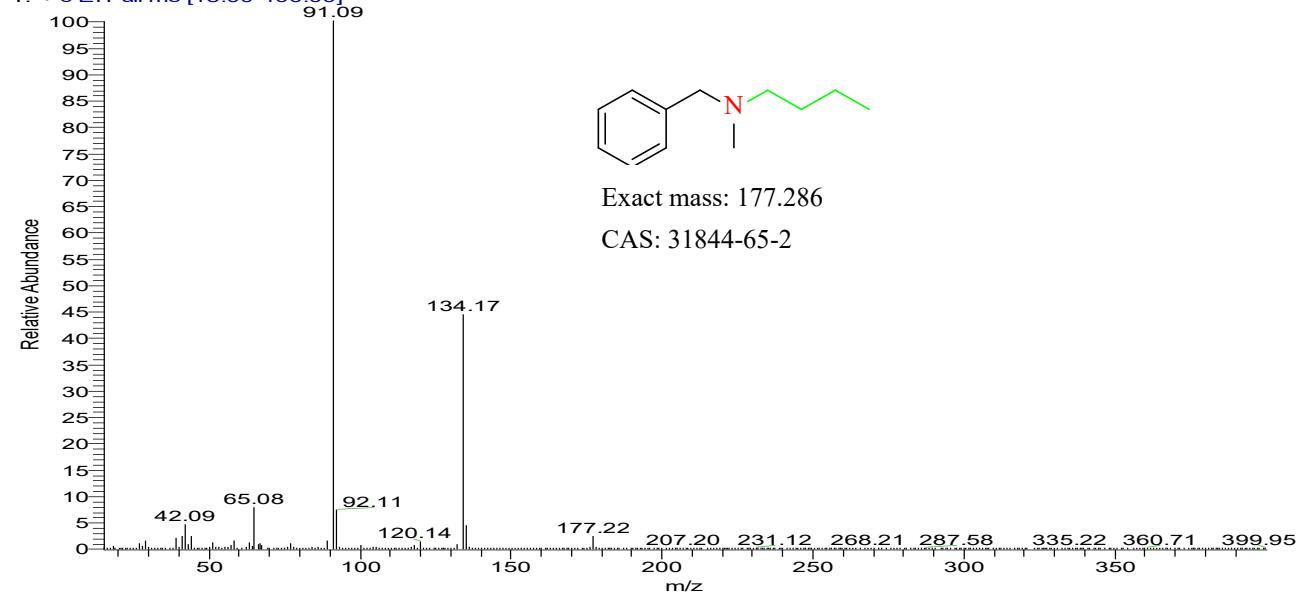
E-29-5 #6546 RT: 22.30 AV: 1 NL: 2.03E8
T: + c EI Full ms [15.00-400.00]

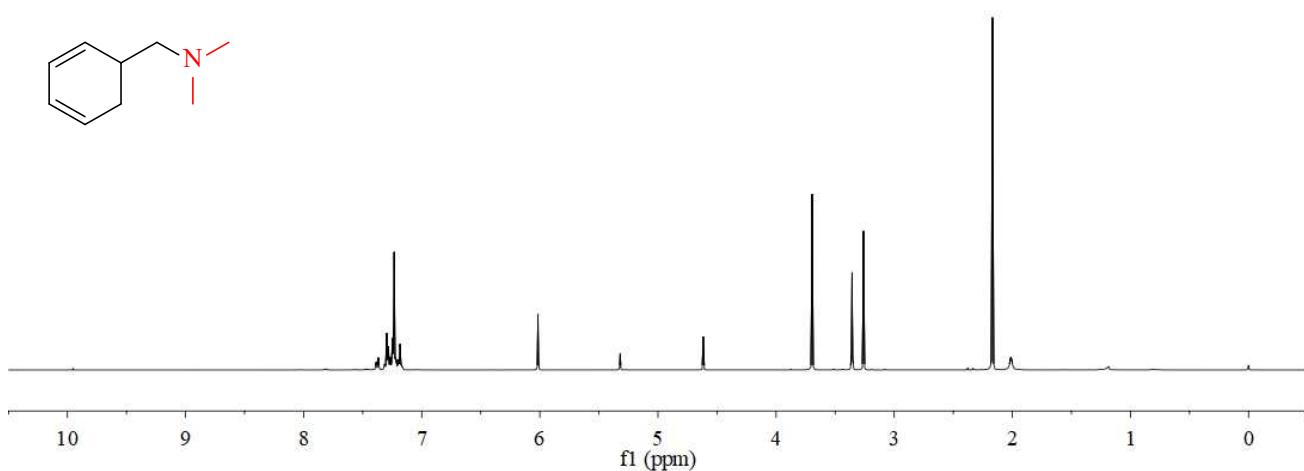
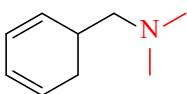


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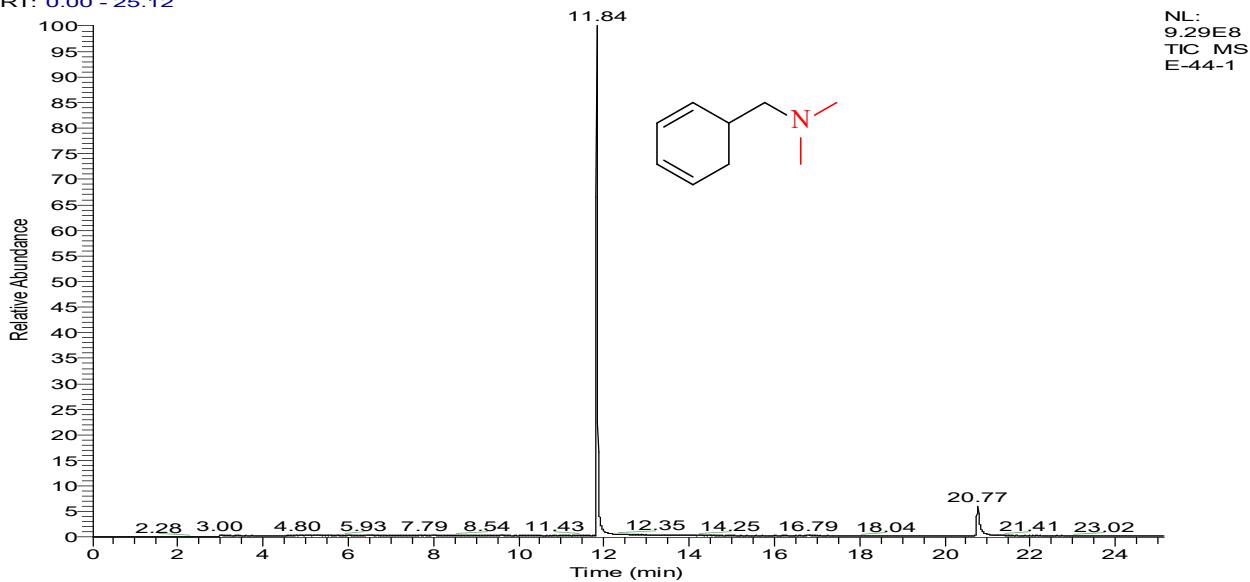


E-29-4 #5116 RT: 17.43 AV: 1 NL: 4.92E8
T: + c EI Full ms [15.00-400.00]

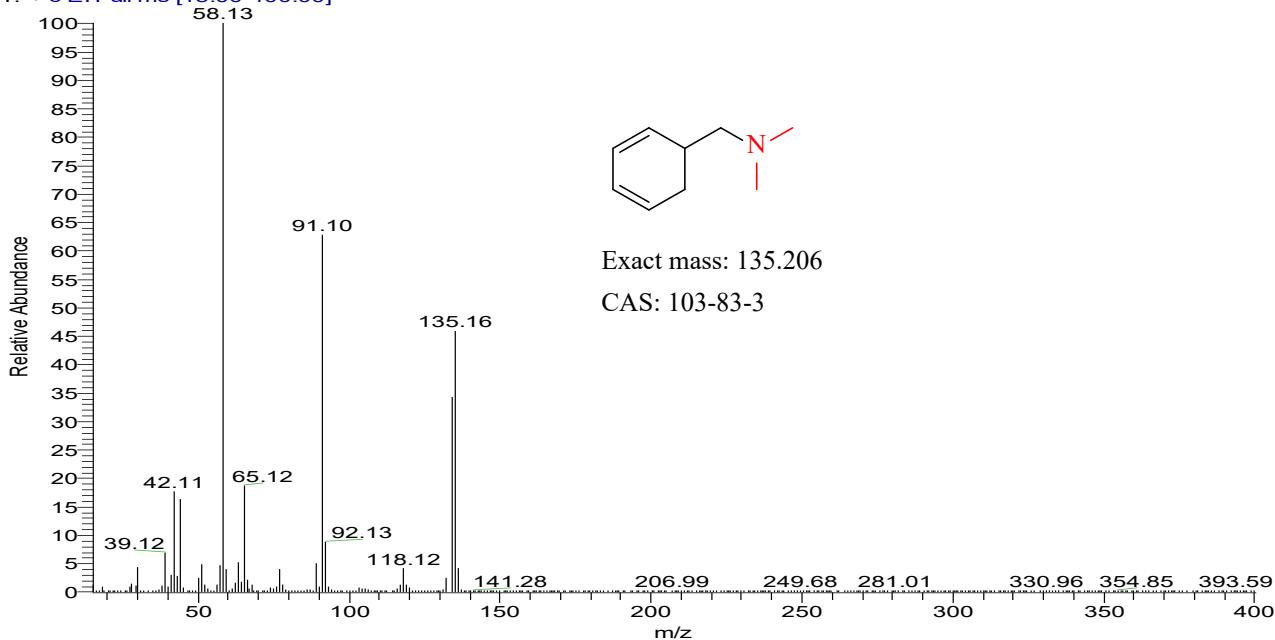




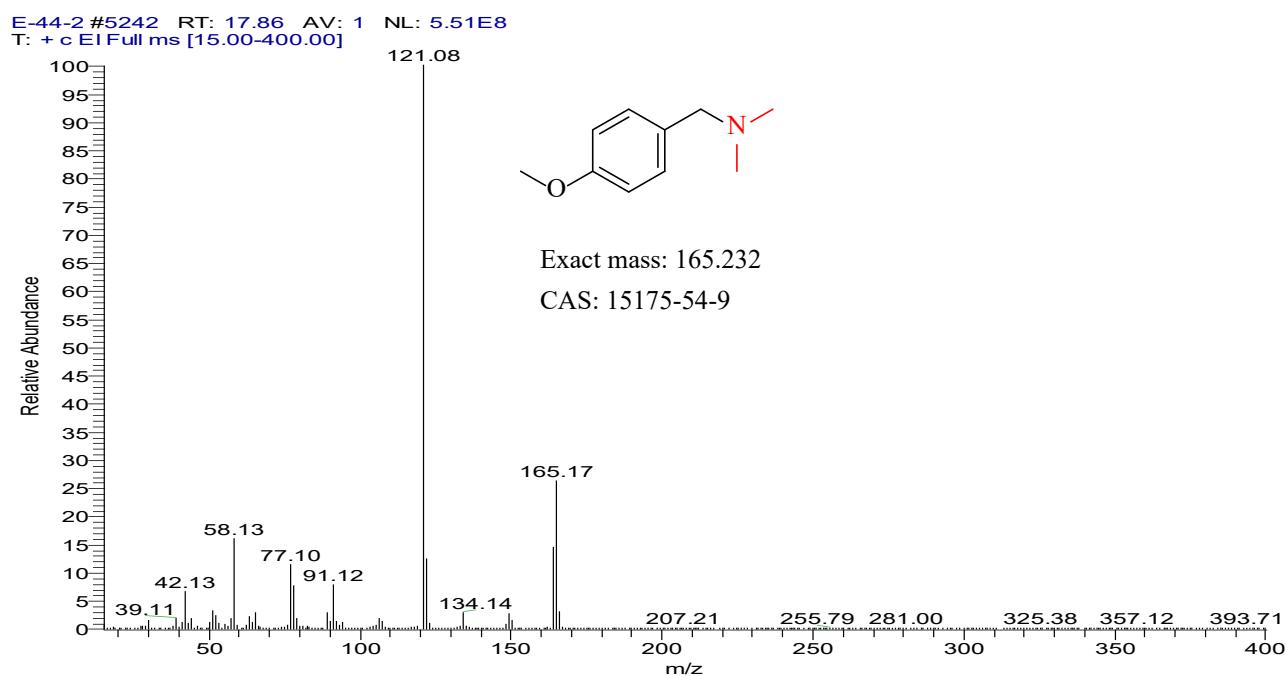
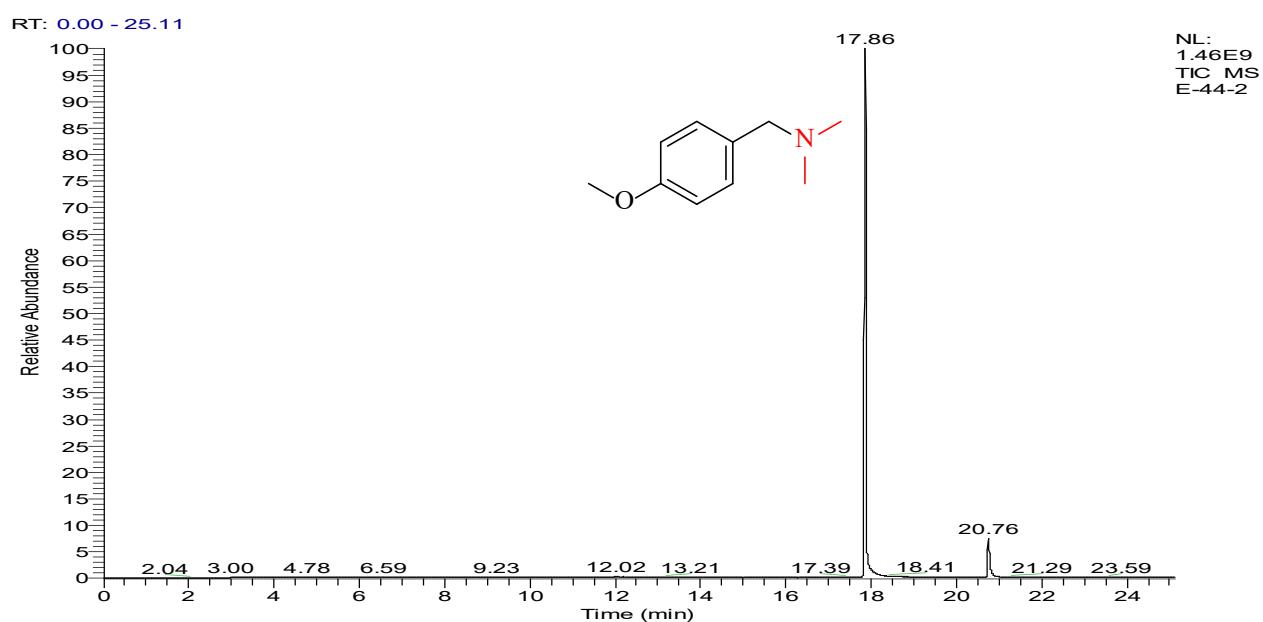
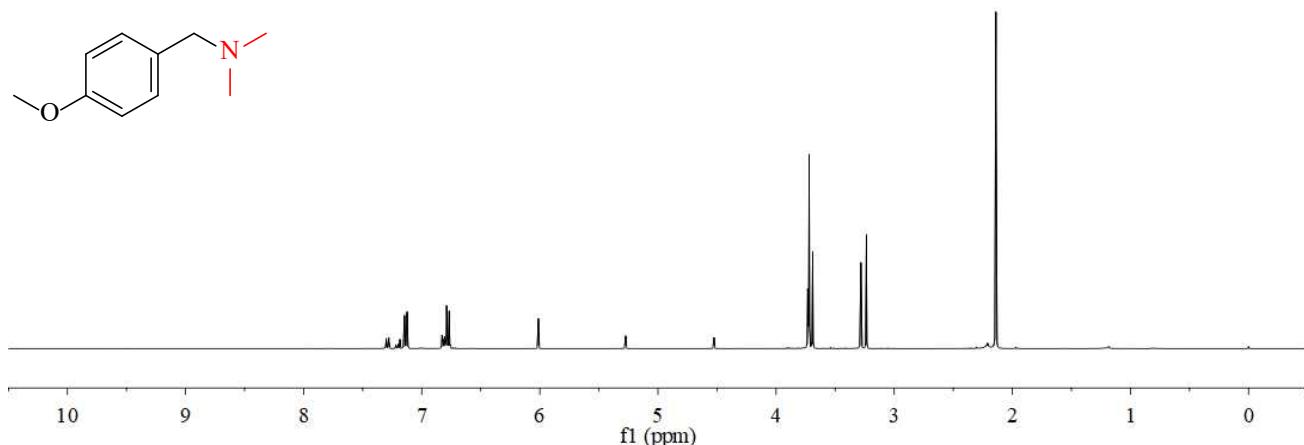
RT: 0.00 - 25.12

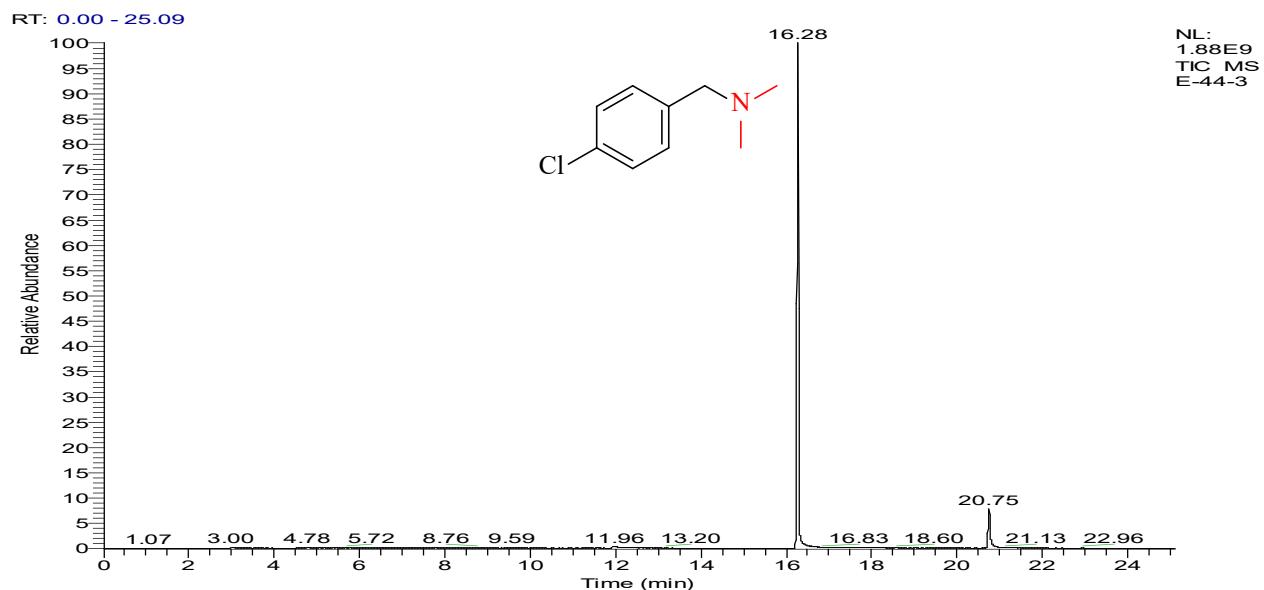
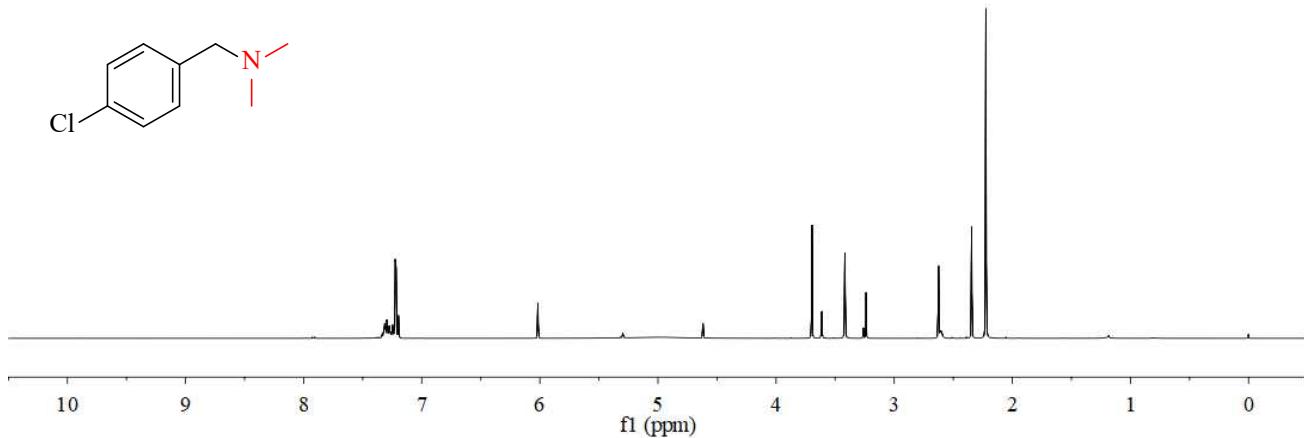


E-44-1 #3472 RT: 11.84 AV: 1 NL: 2.34E8
T: + c EI Full ms [15.00-400.00]
50-12

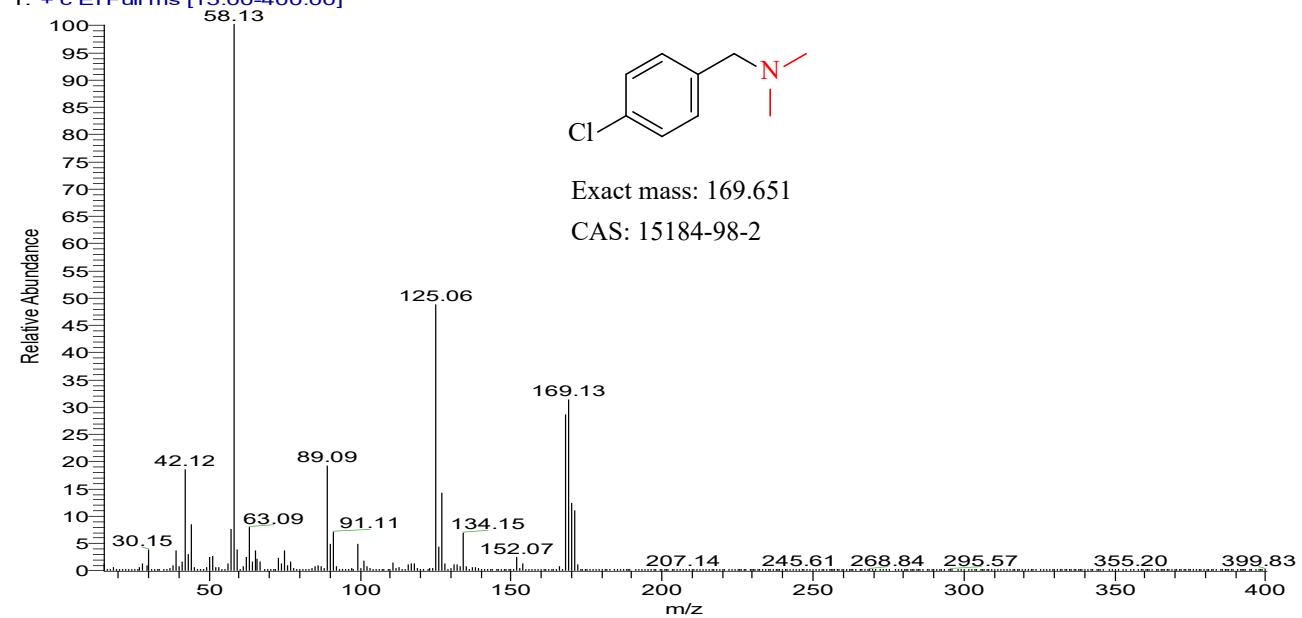


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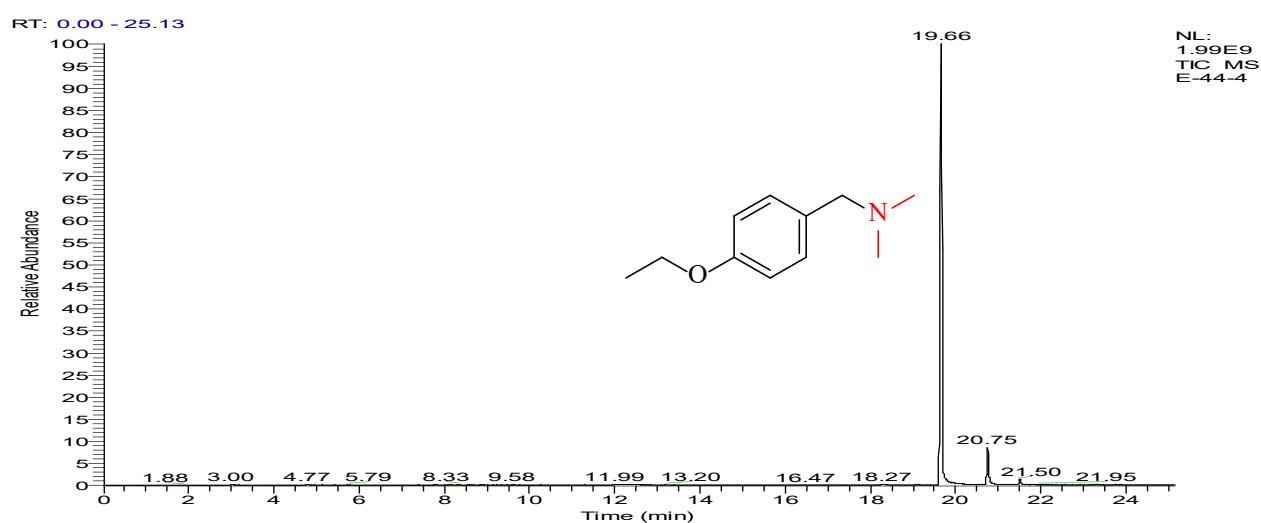
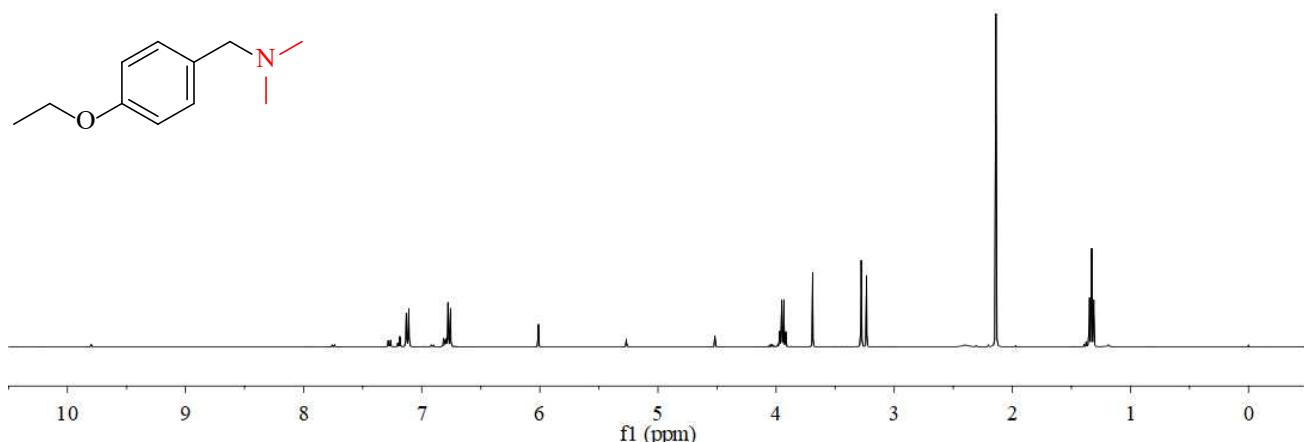




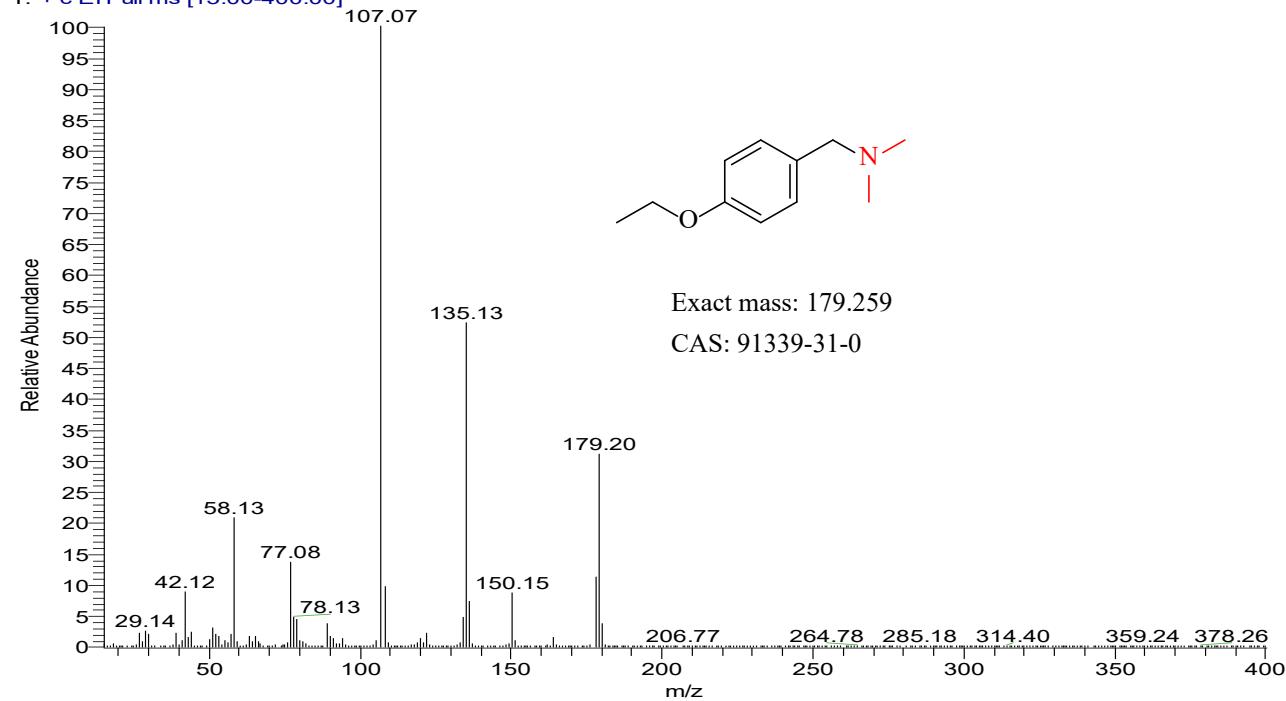
E-44-3 #4776 RT: 16.28 AV: 1 NL: 4.60E8
T: + c EI Full ms [15.00-400.00]

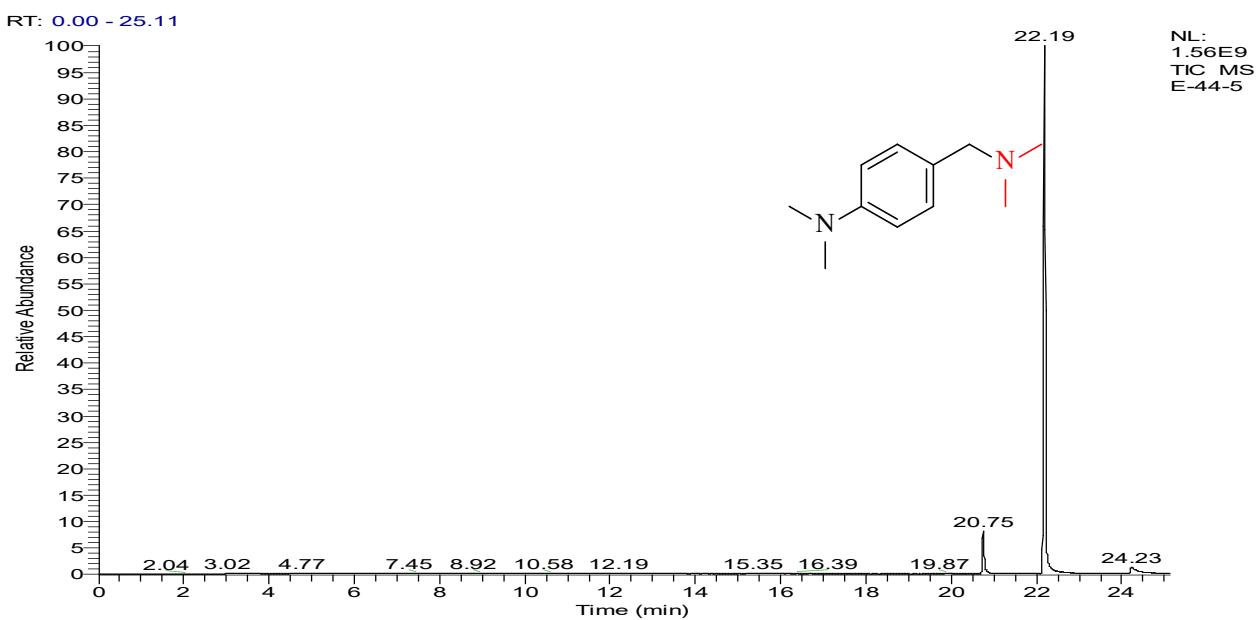
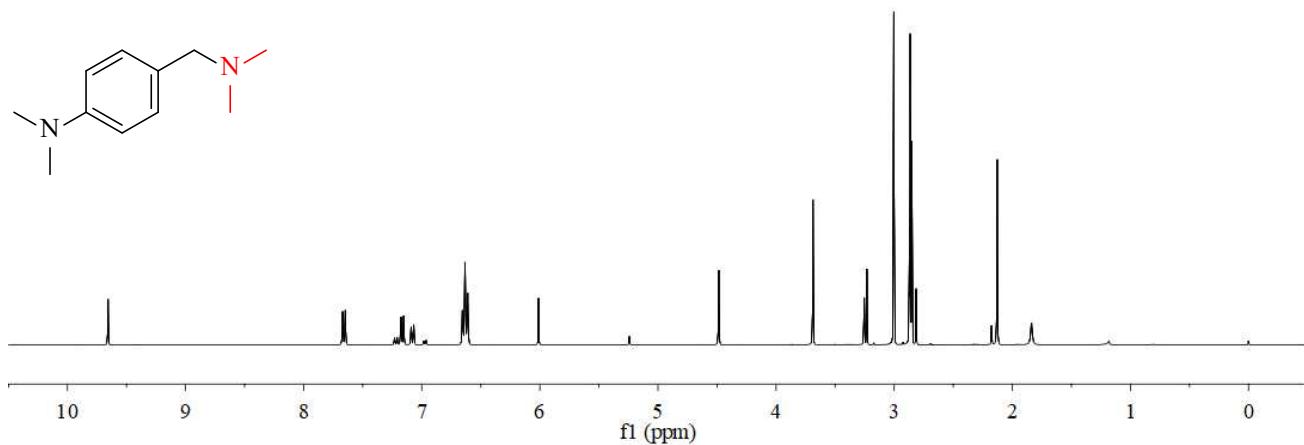


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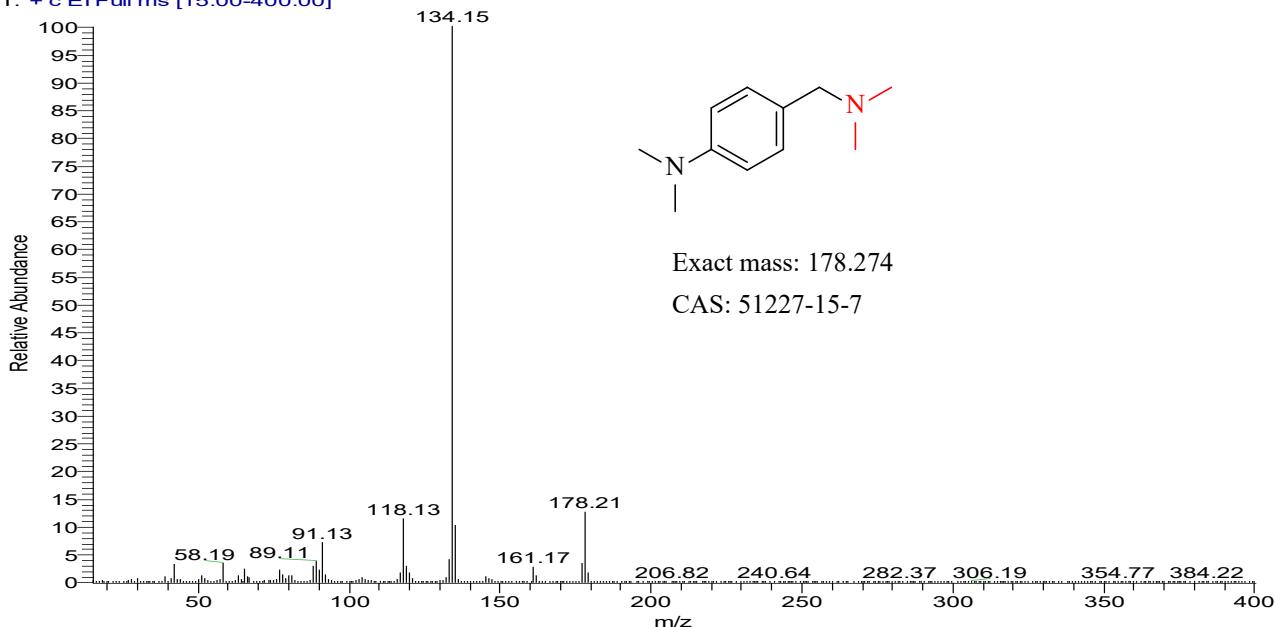


E-44-4 #5770 RT: 19.66 AV: 1 NL: 5.42E8
T: + c EI Full ms [15.00-400.00]

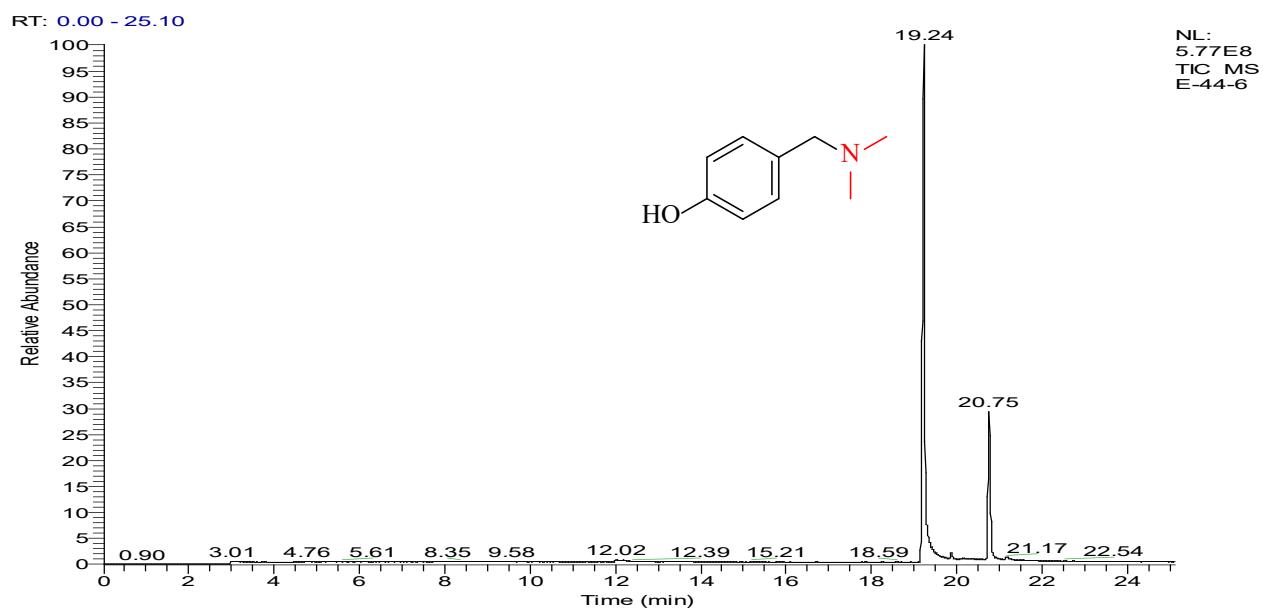
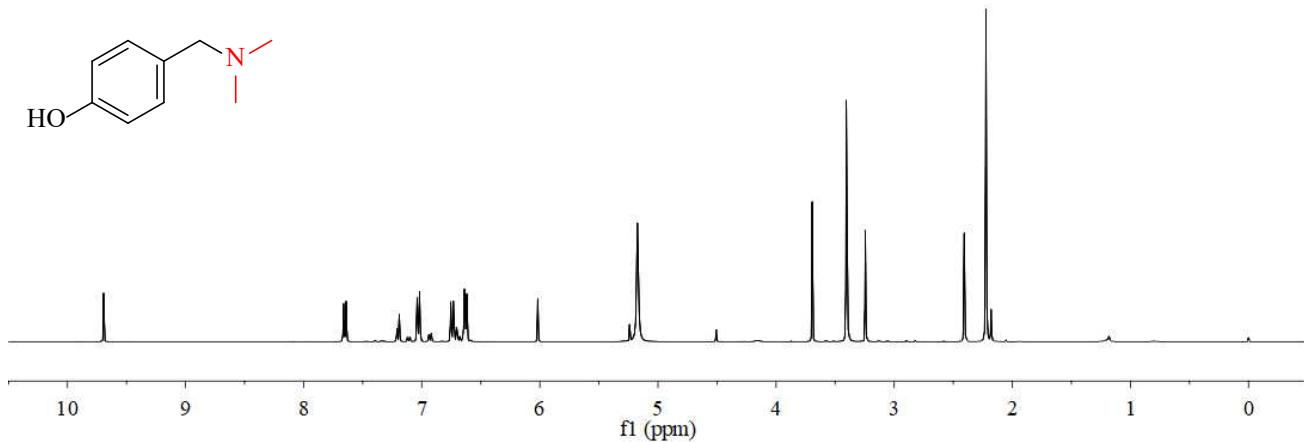




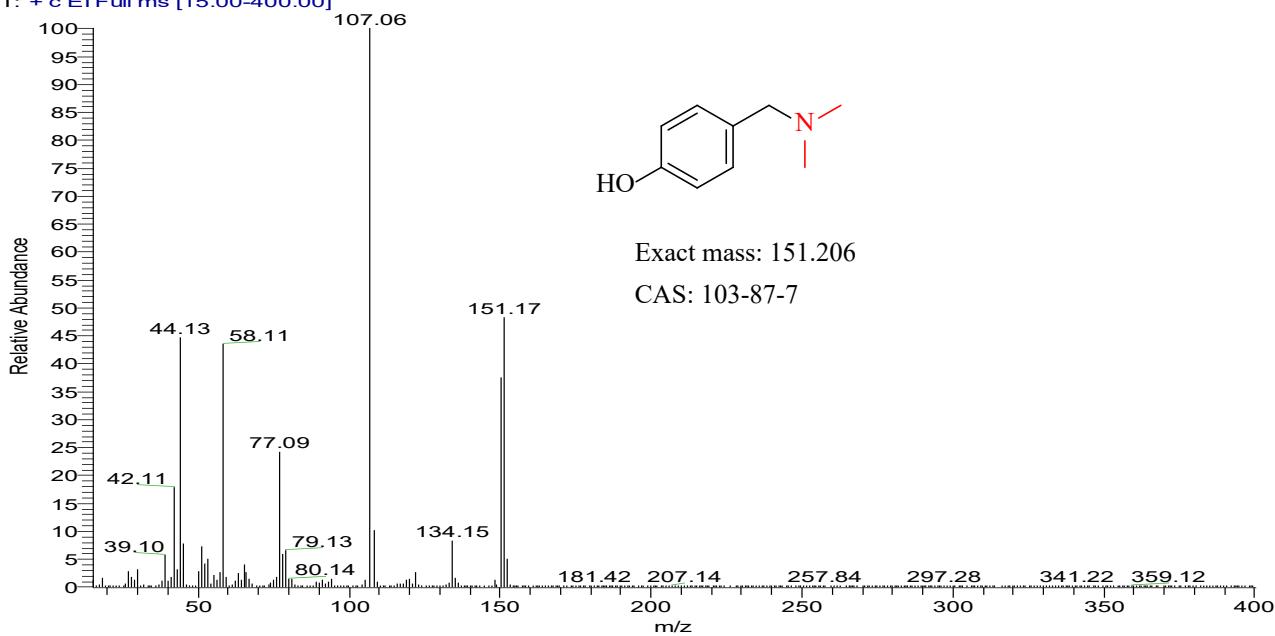
E-44-5 #6514 RT: 22.19 AV: 1 NL: 7.02E8
T: + c EI Full ms [15.00-400.00]

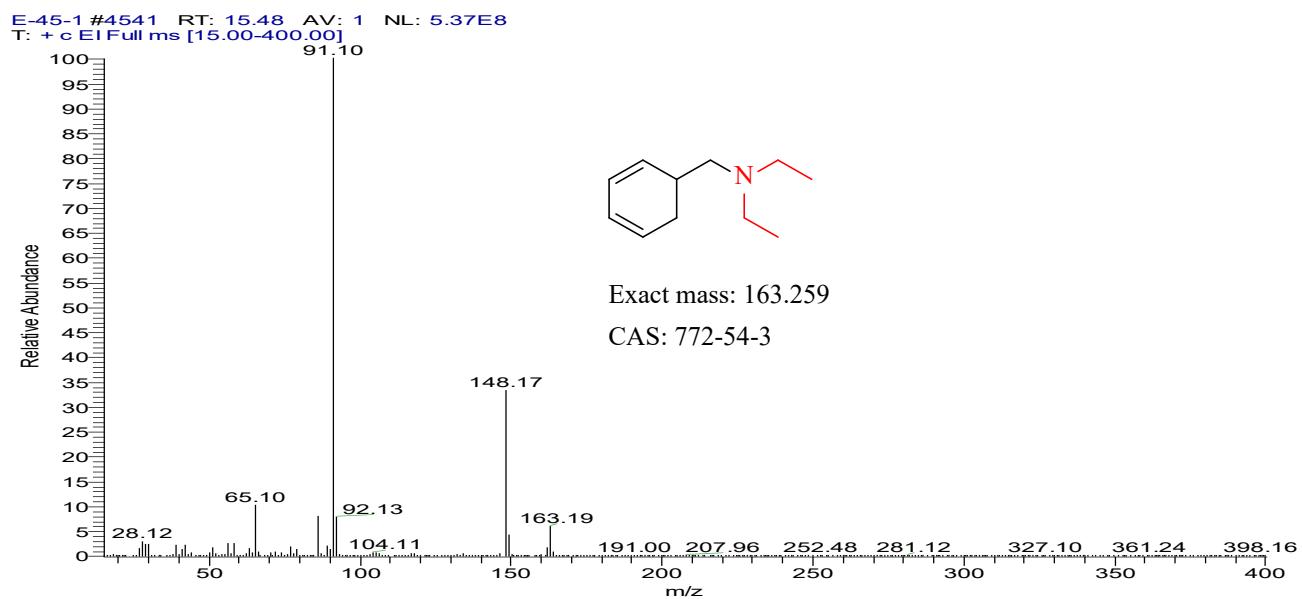
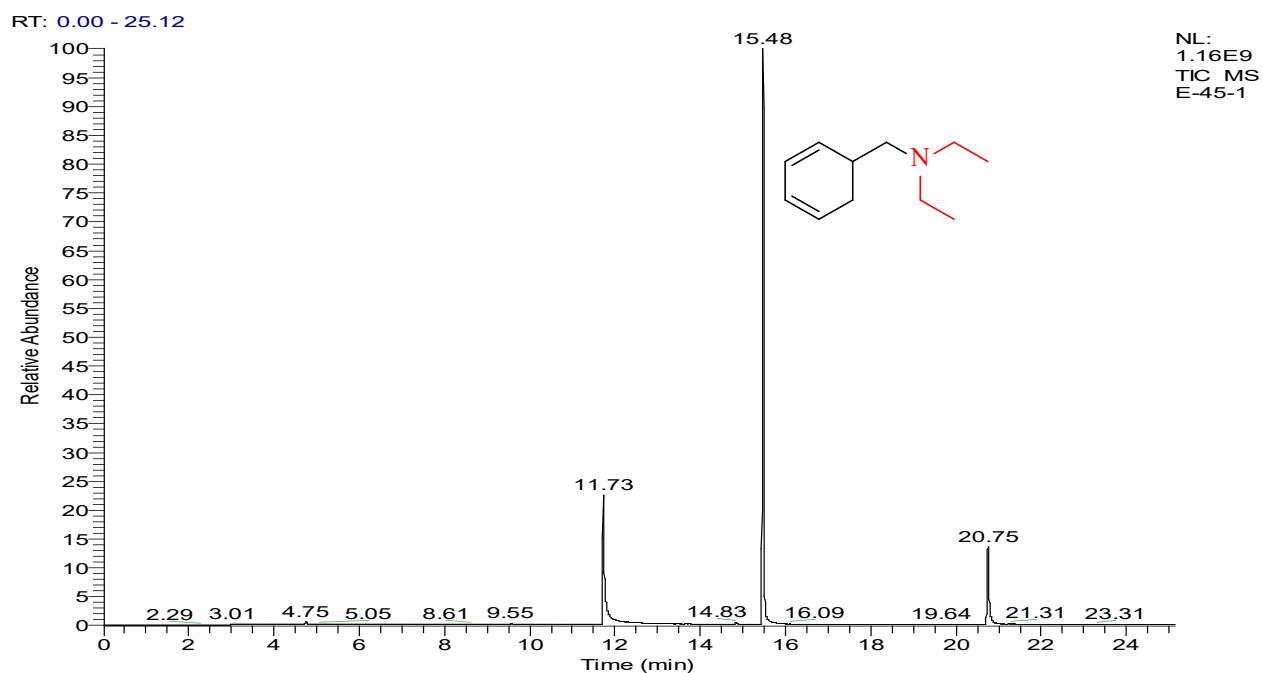
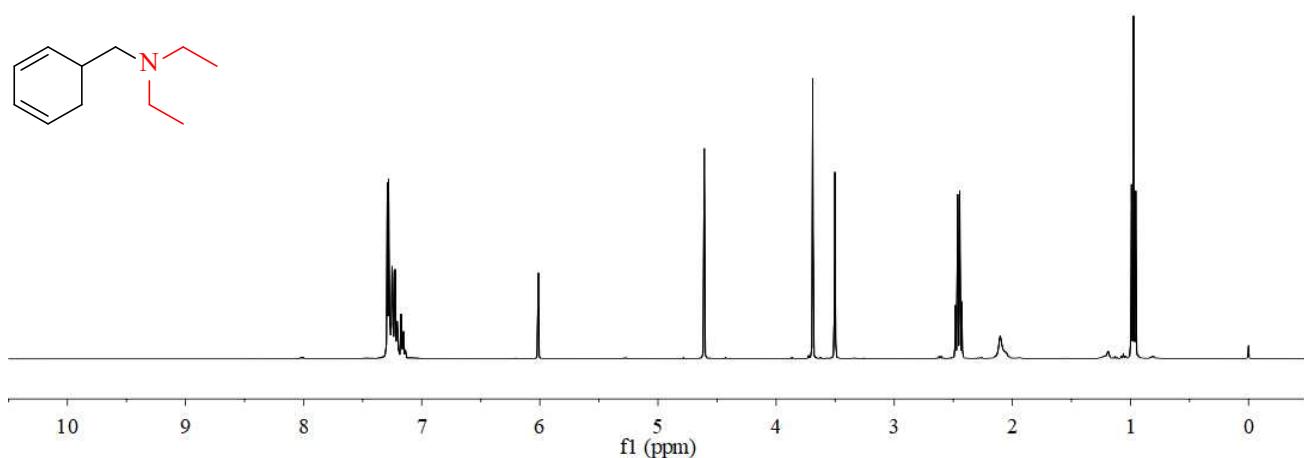


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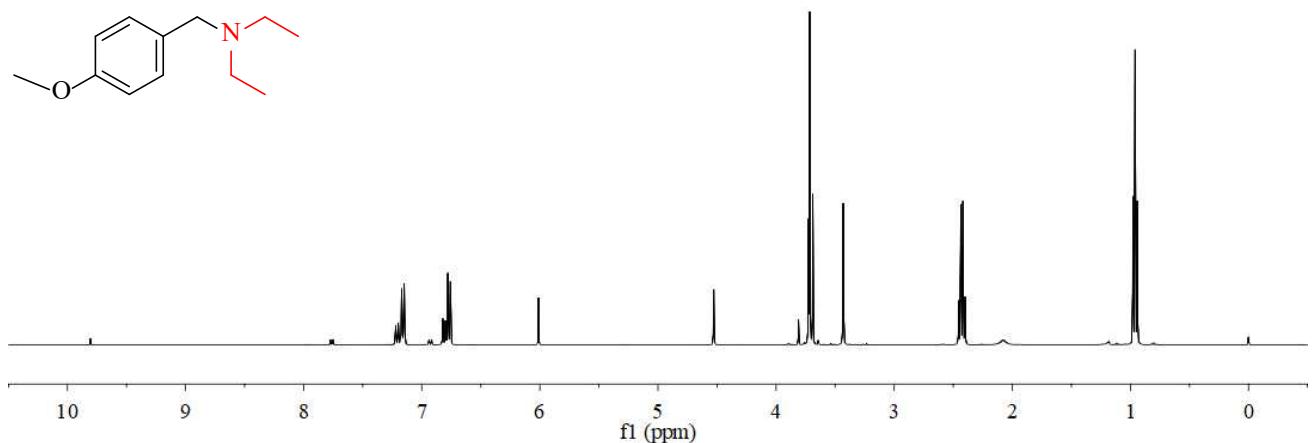


E-44-6 #5649 RT: 19.24 AV: 1 NL: 1.22E8
T: + c EI Full ms [15.00-400.00]

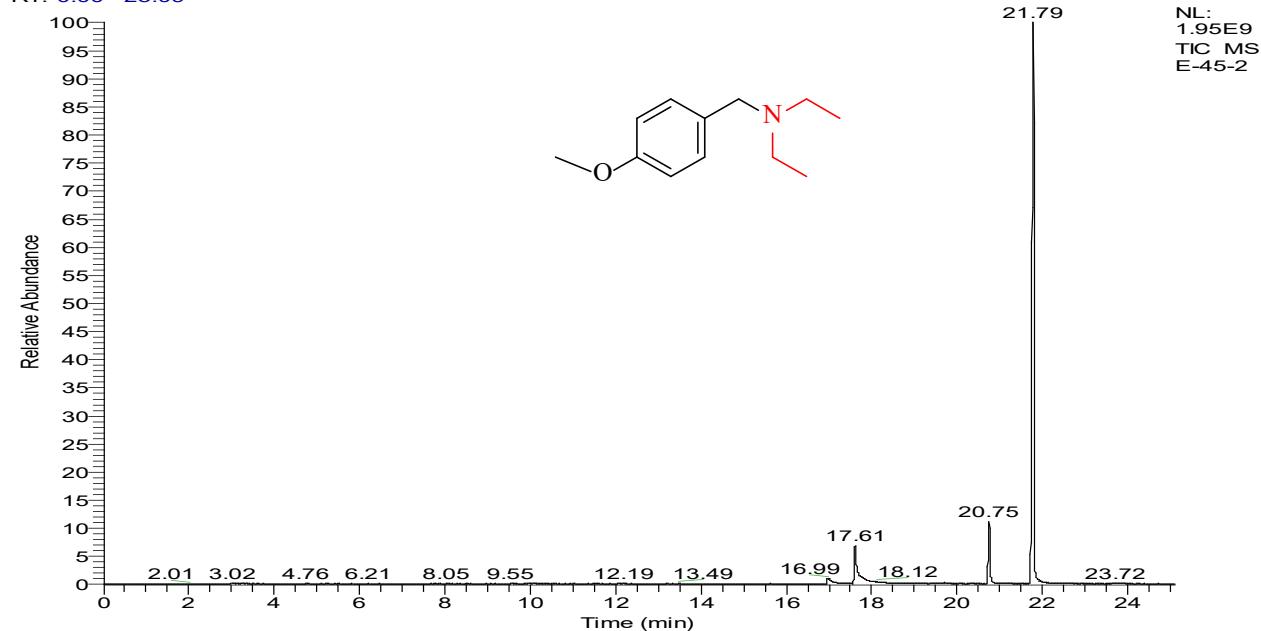




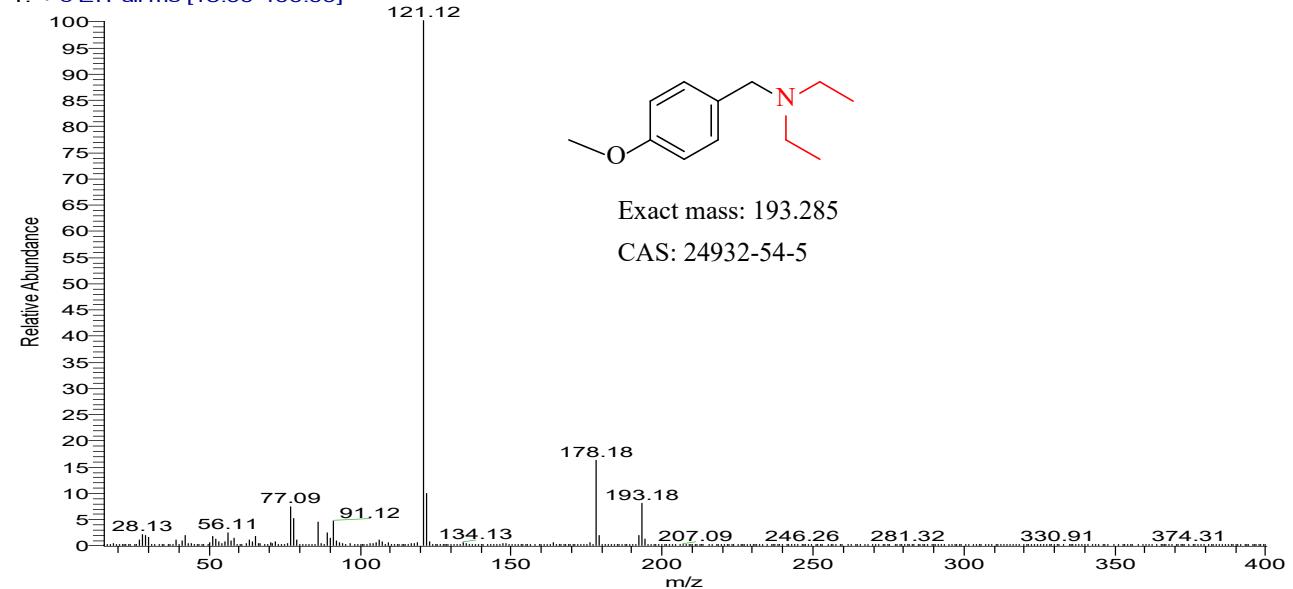
57



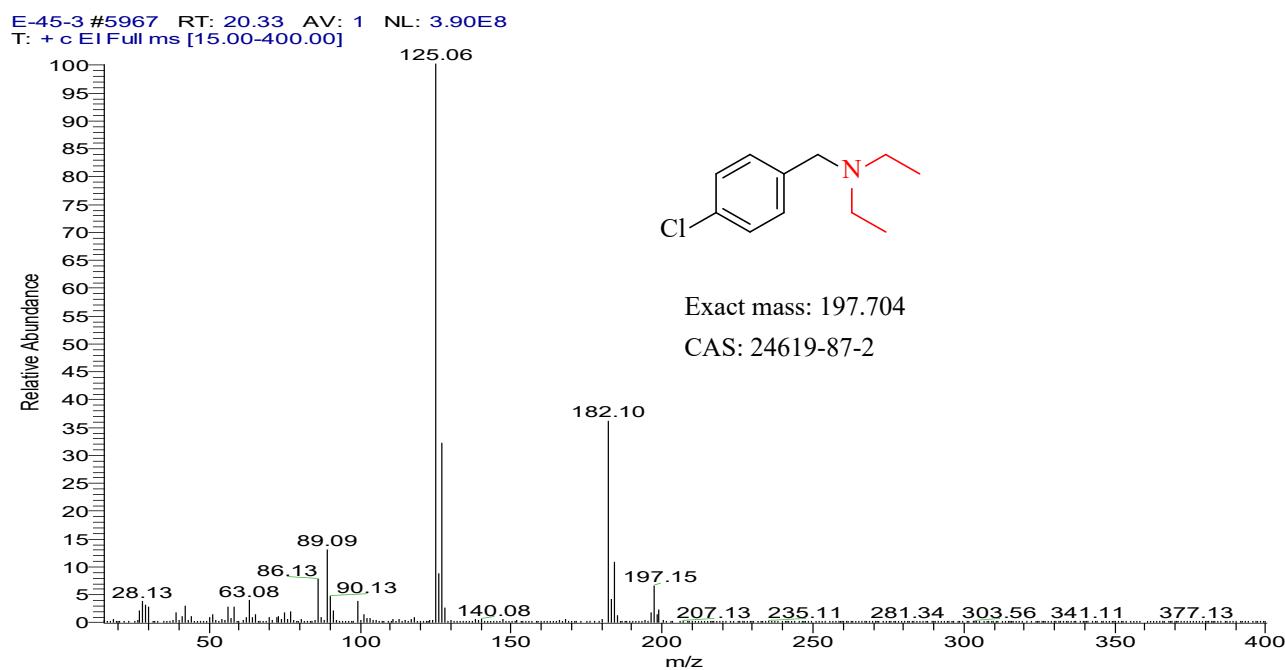
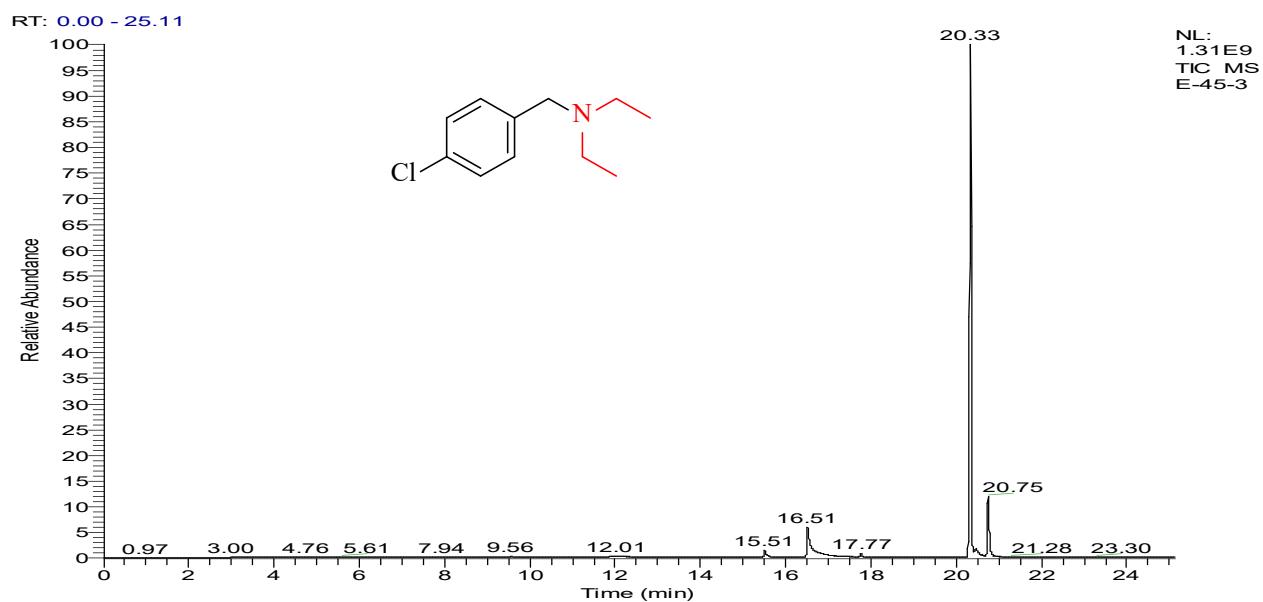
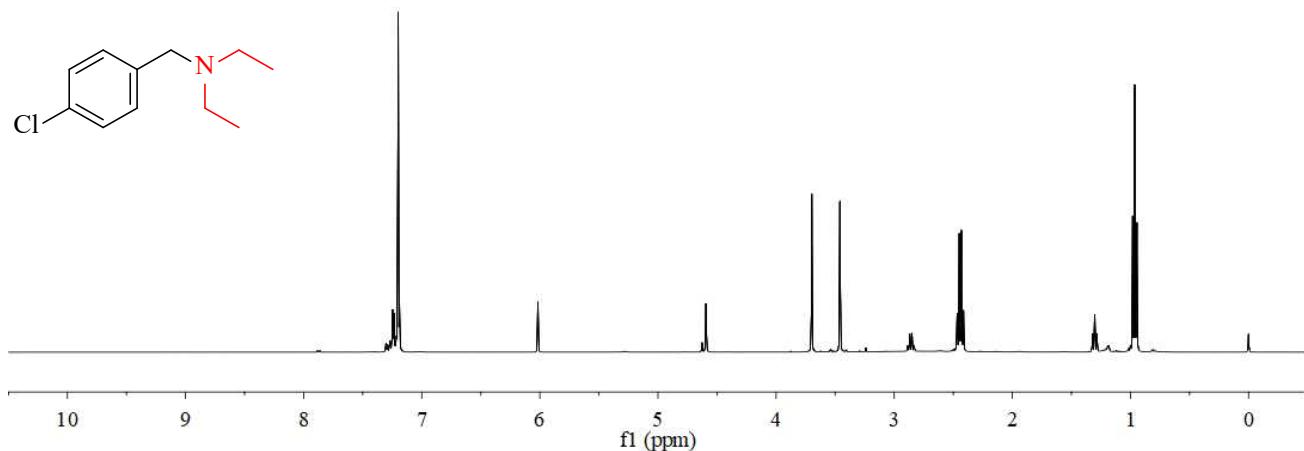
RT: 0.00 - 25.09



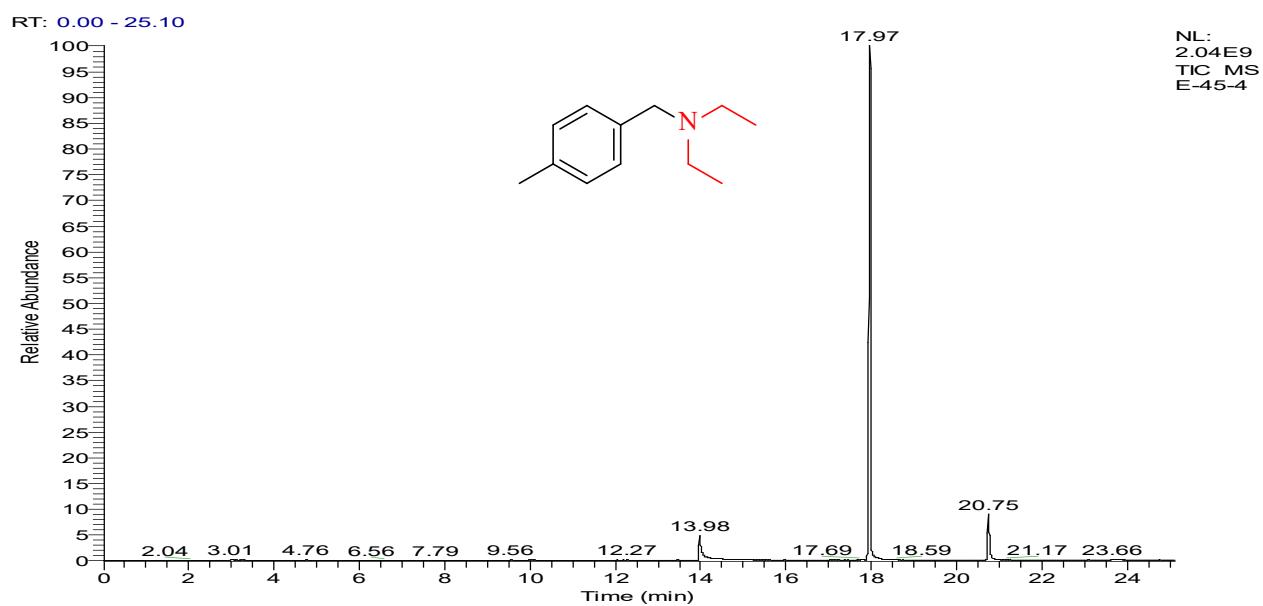
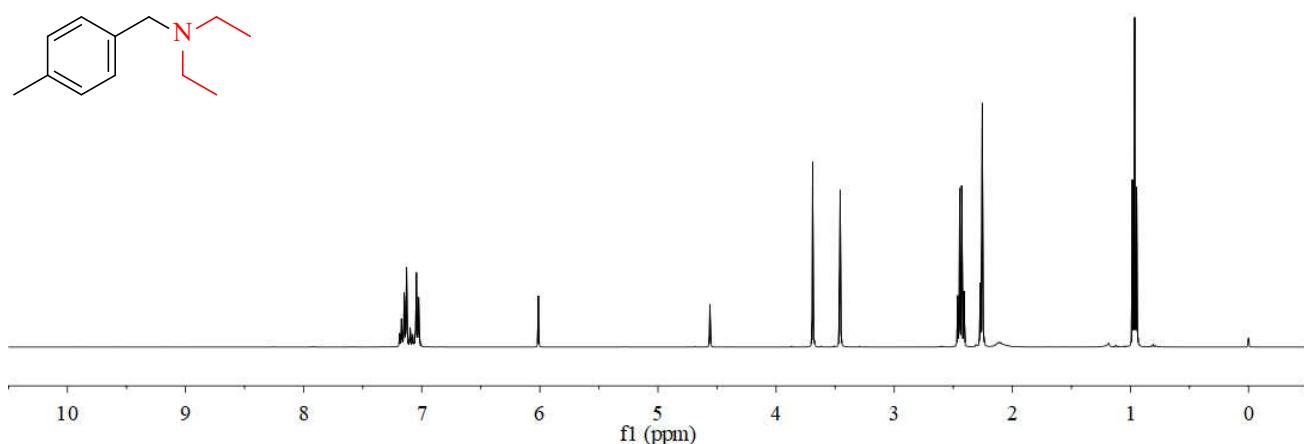
E-45-2 #6396 RT: 21.79 AV: 1 NL: 9.68E8
T: + c EI Full ms [15.00-400.00]



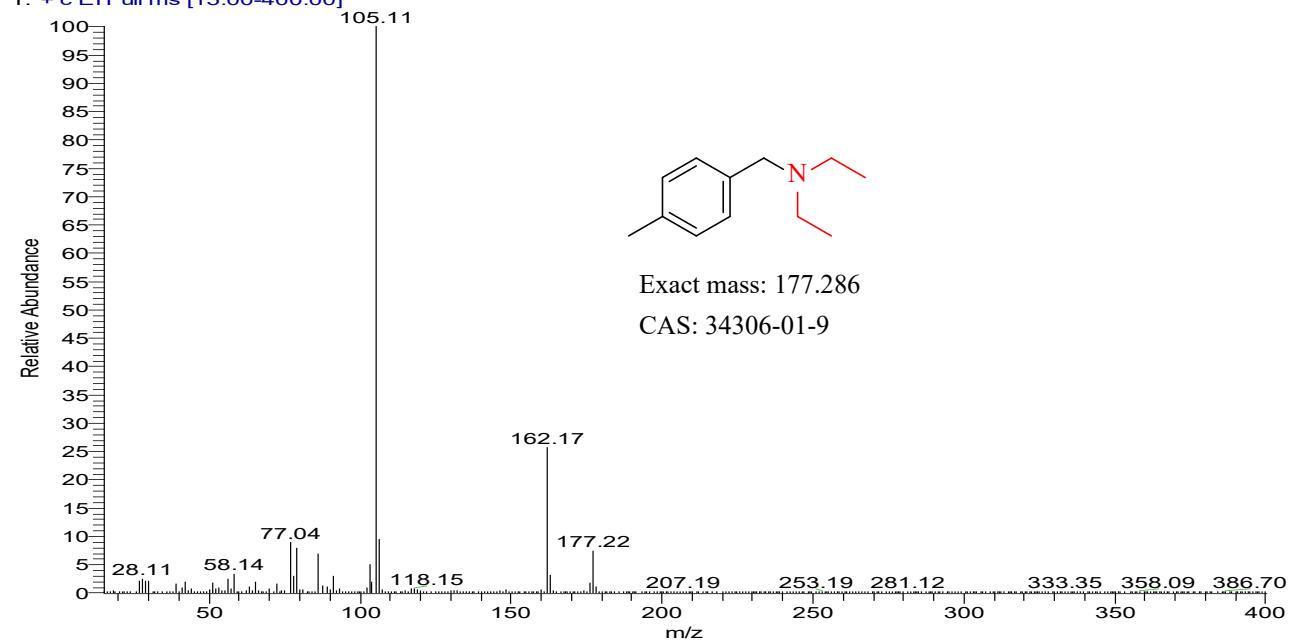
58

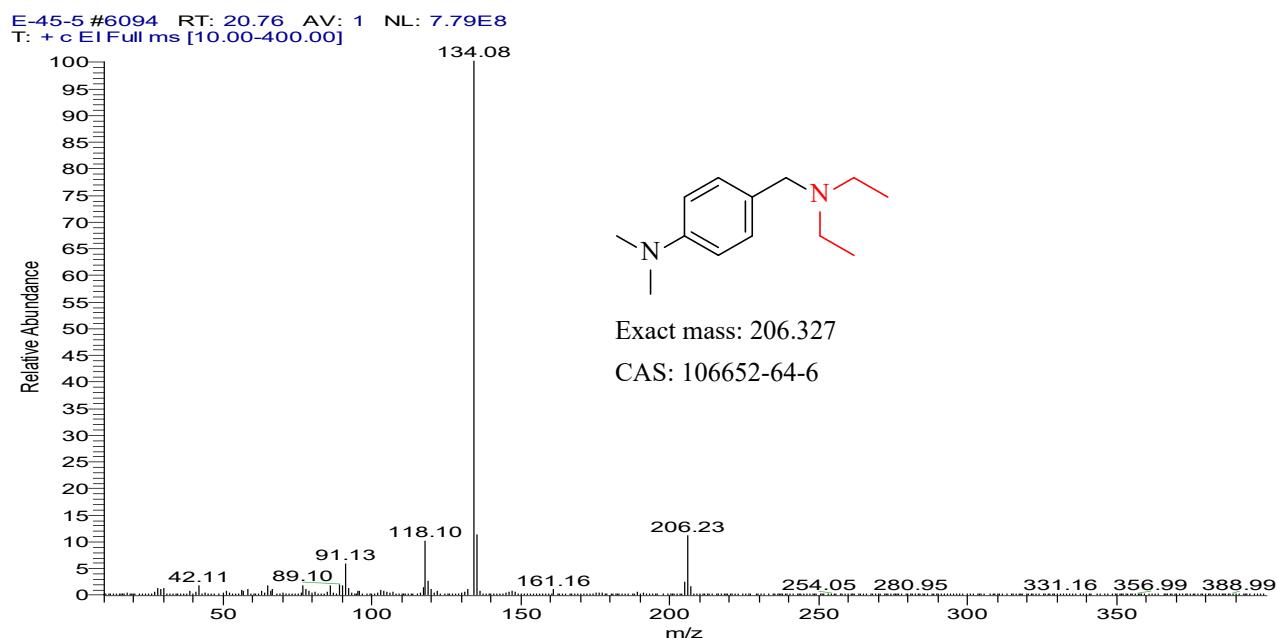
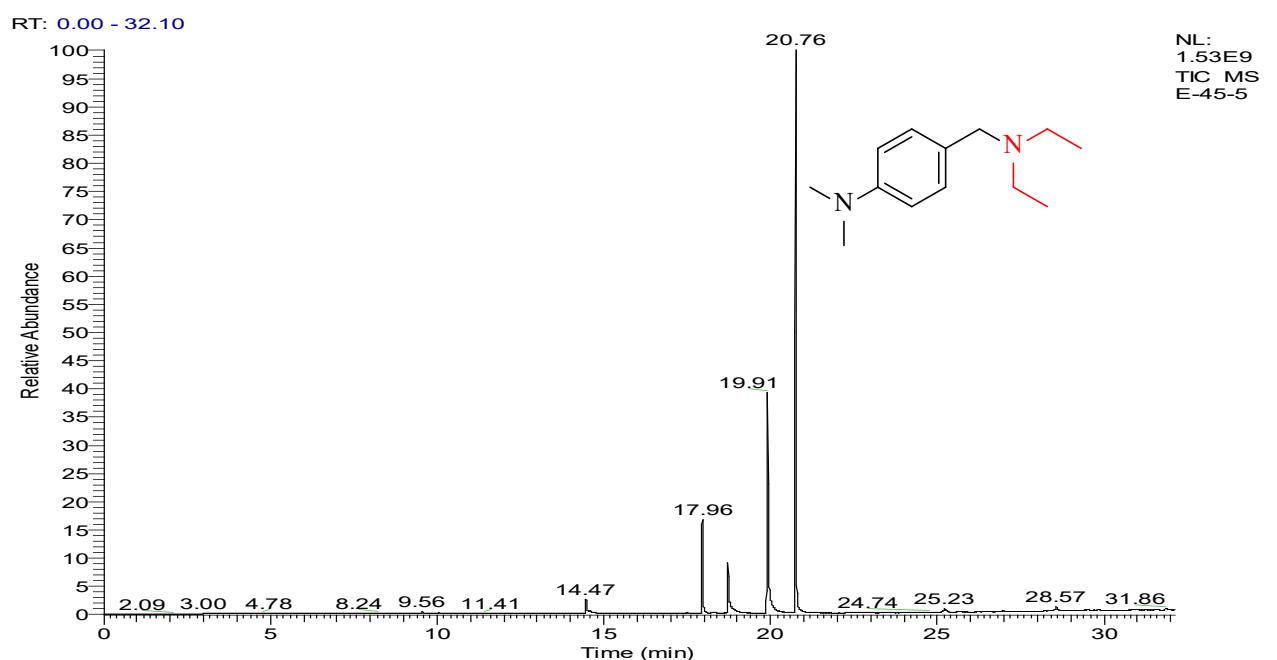
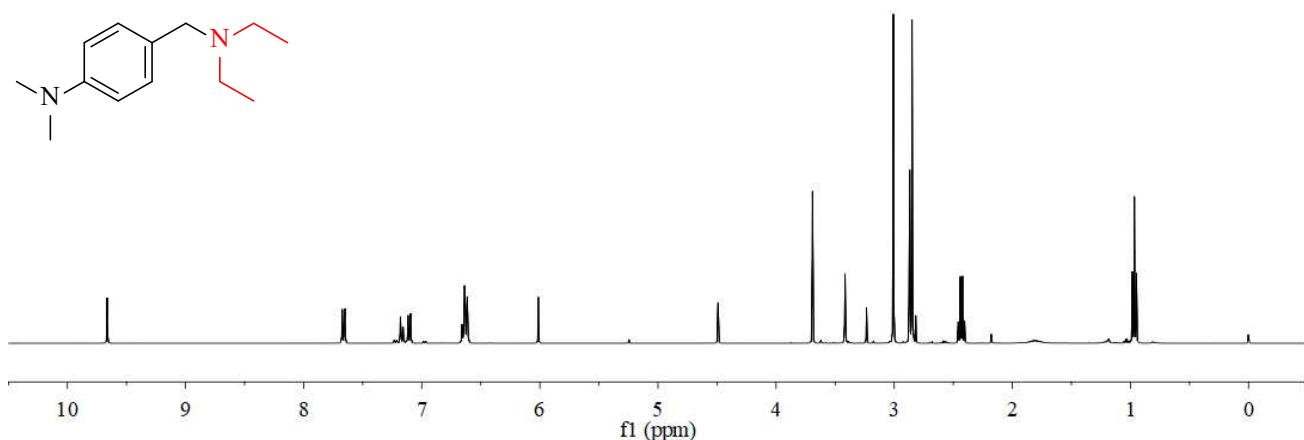


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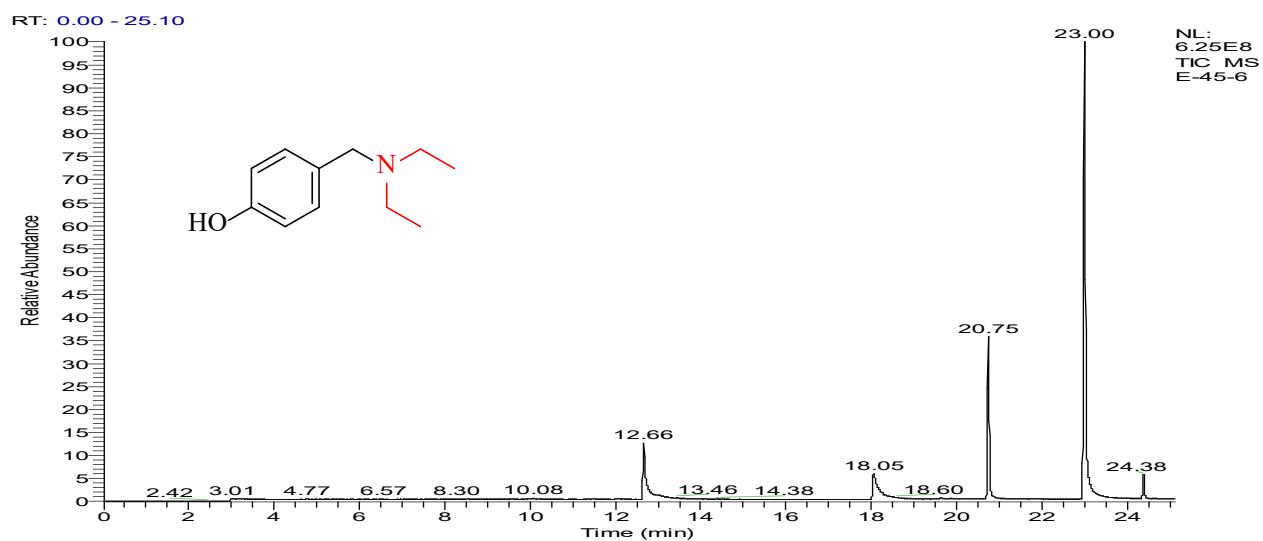
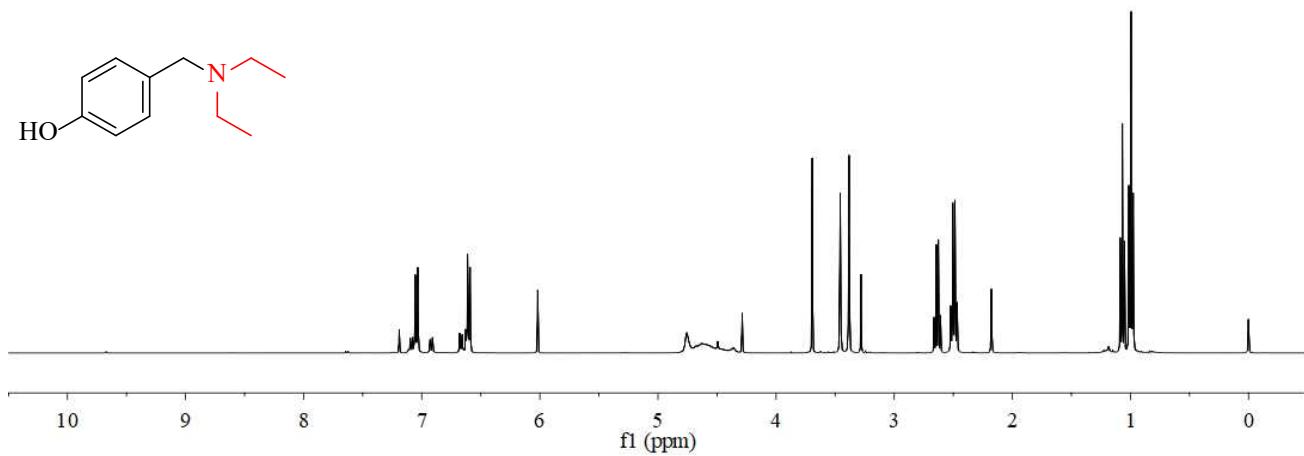


E-45-4 #5273 RT: 17.97 AV: 1 NL: 8.94E8
T: + c EI Full ms [15.00-400.00]

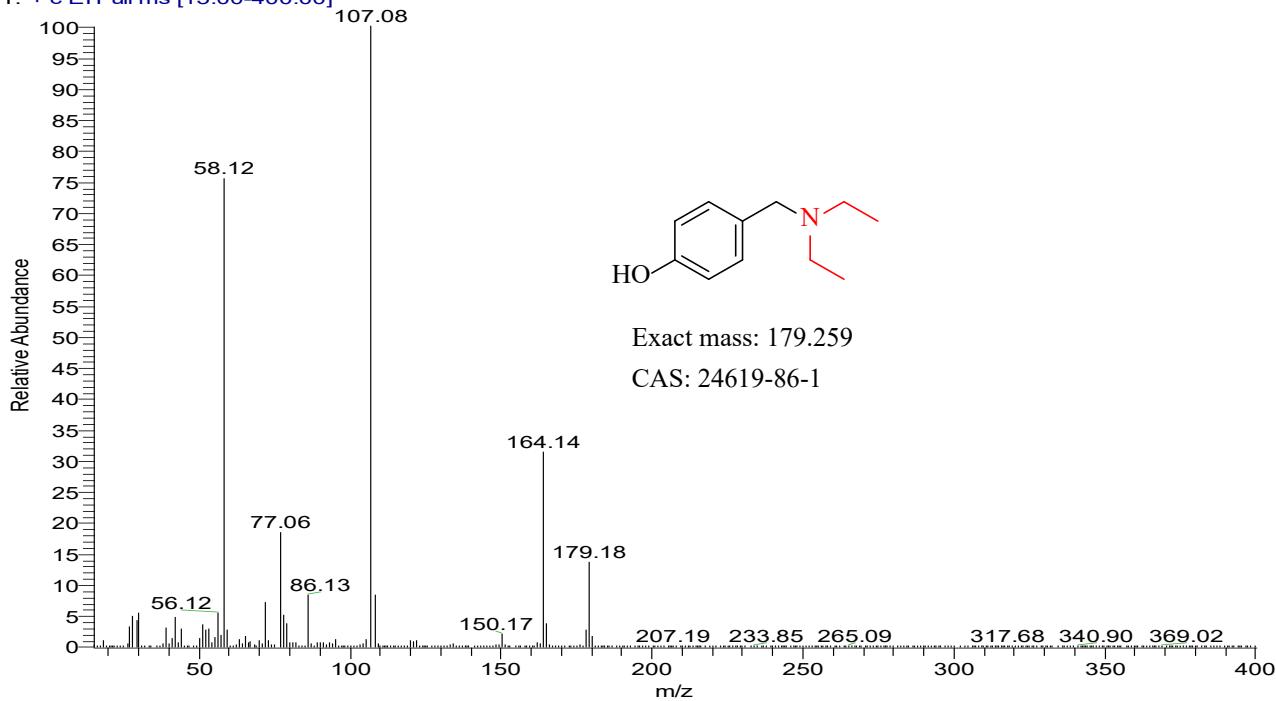


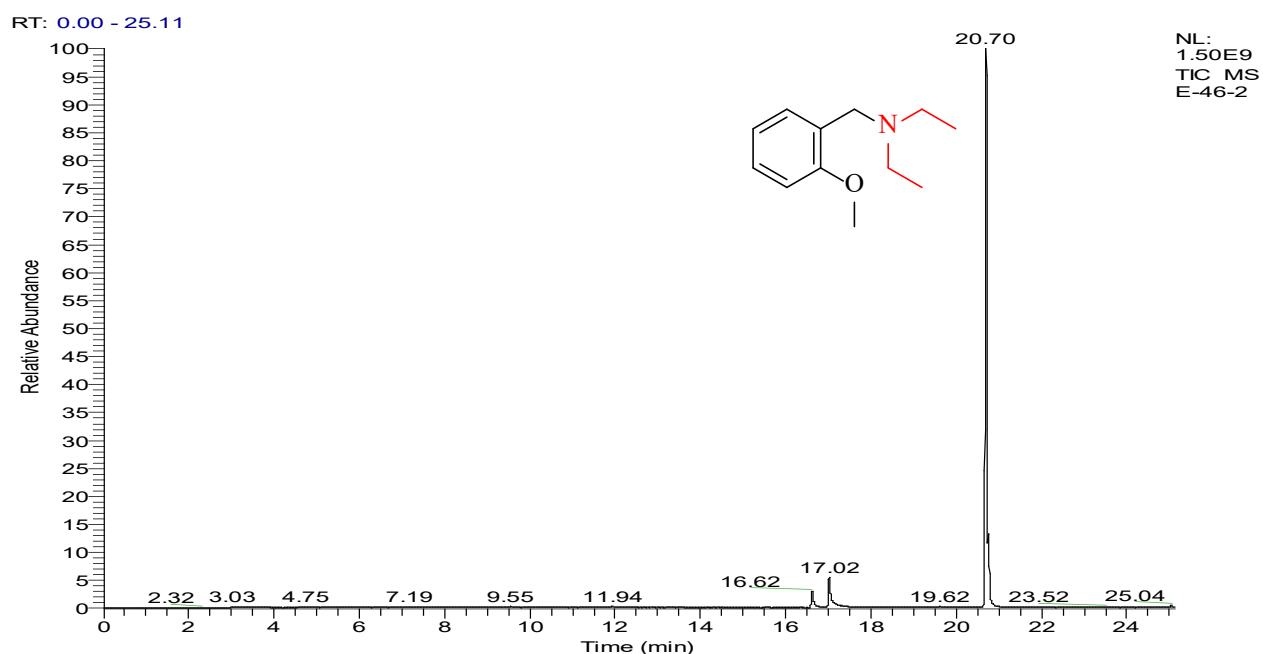
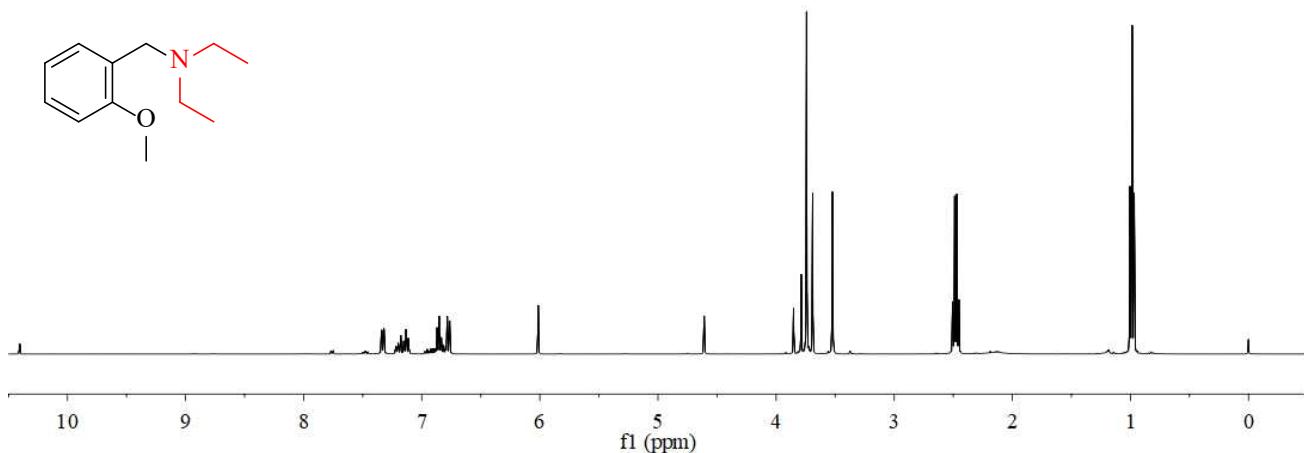


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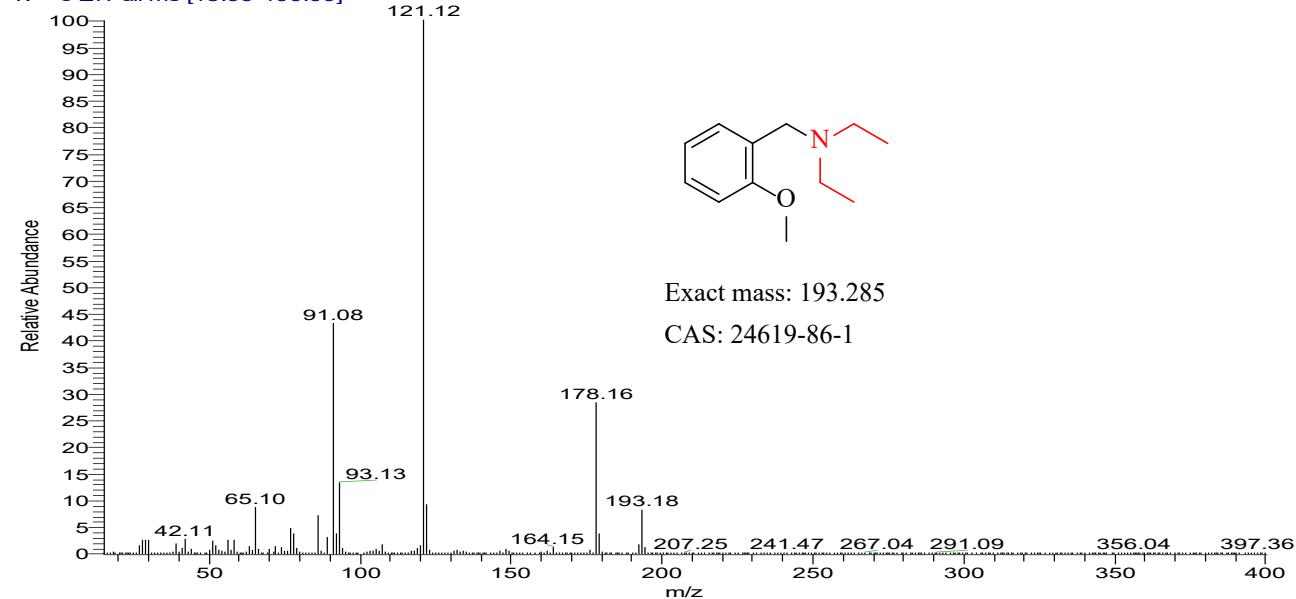


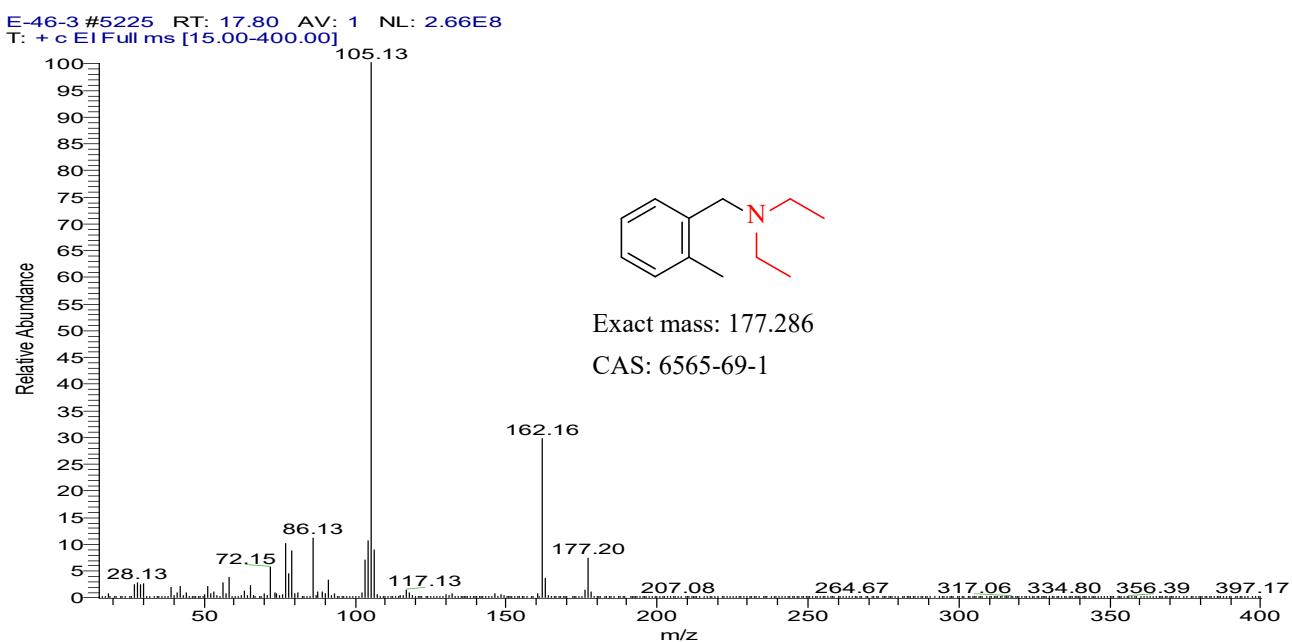
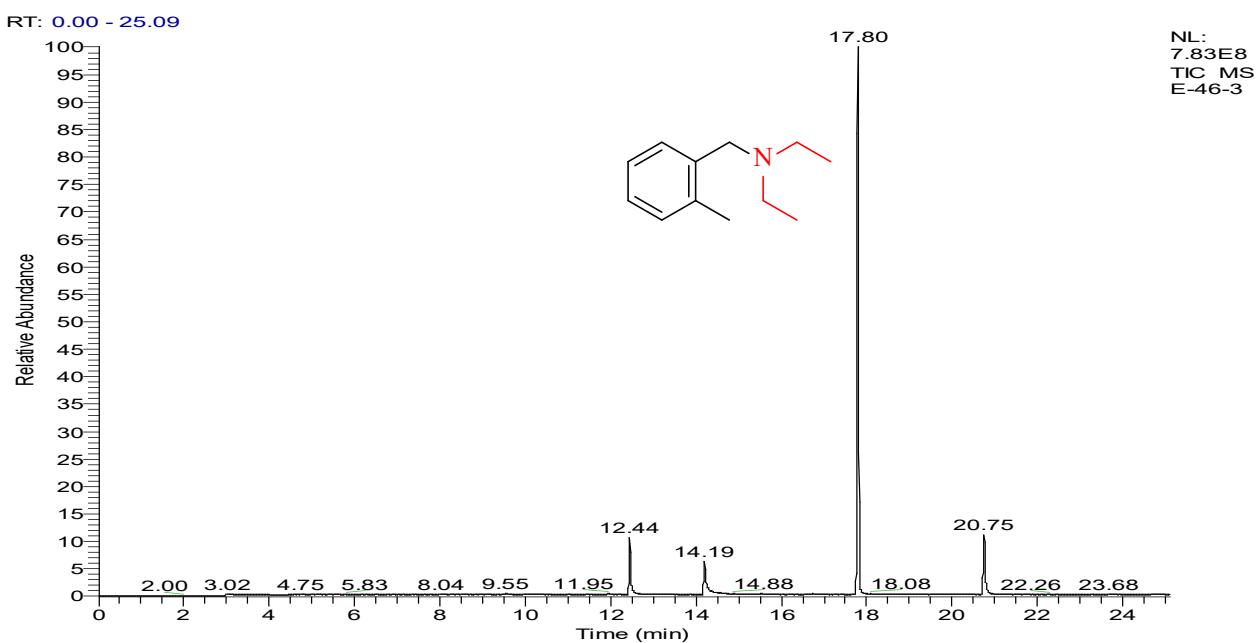
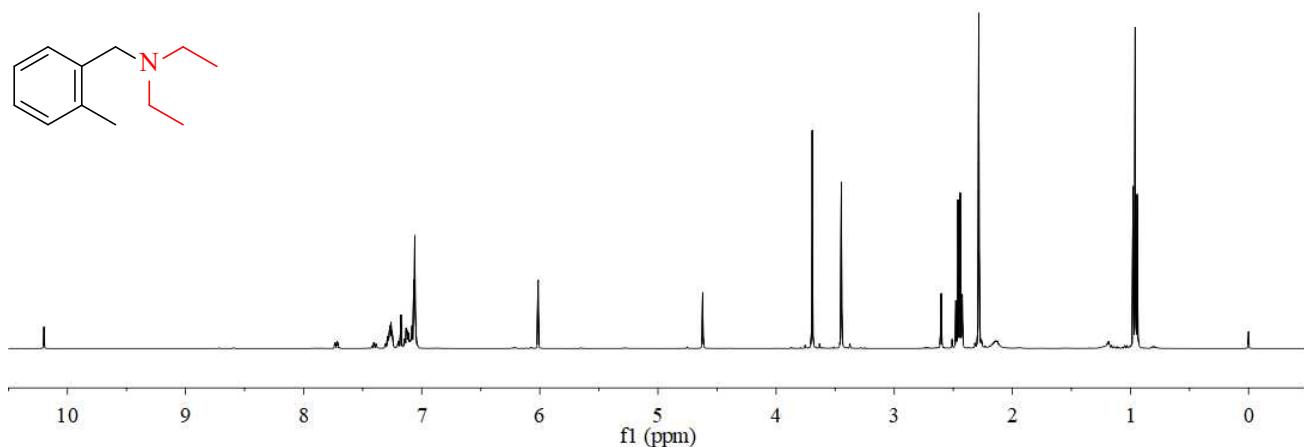
E-45-6 #6753 RT: 23.00 AV: 1 NL: 1.68E8
T: + c EI Full ms [15.00-400.00]

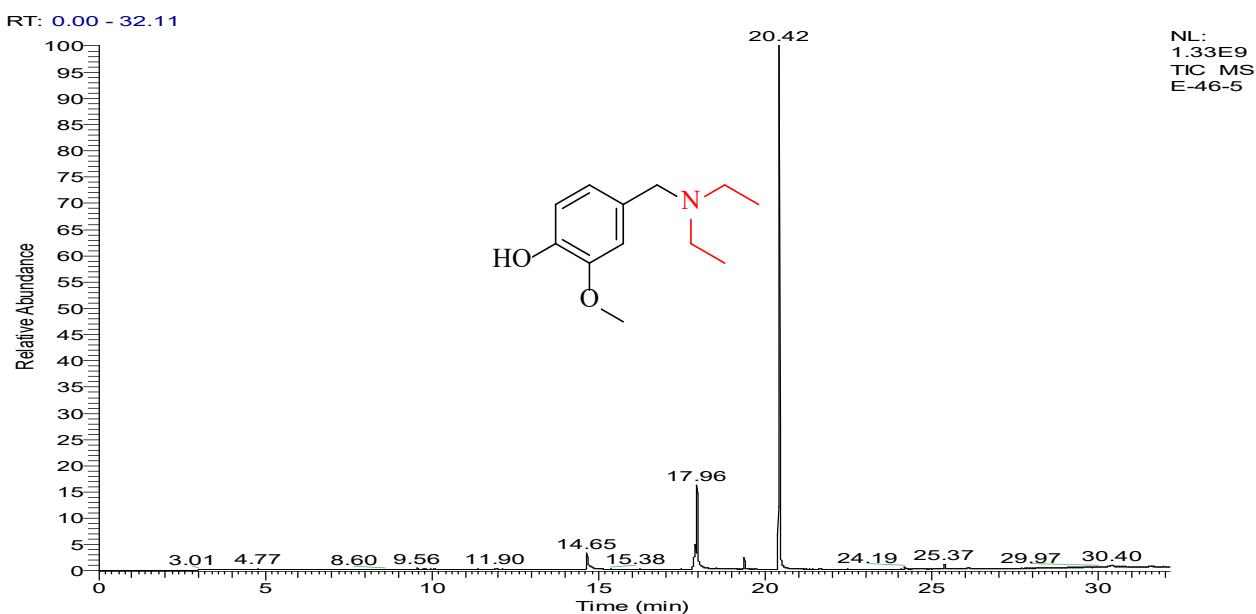
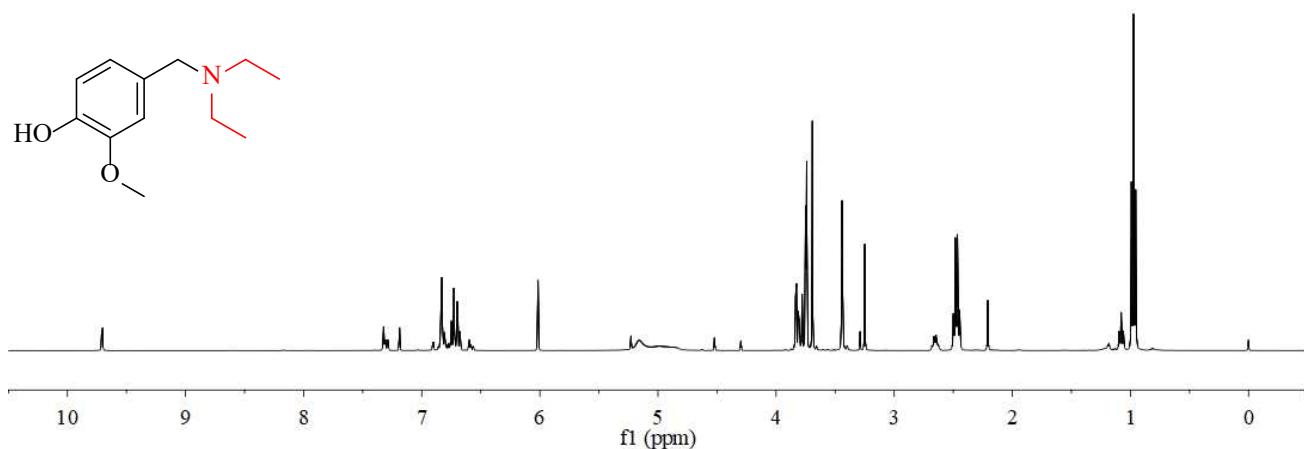




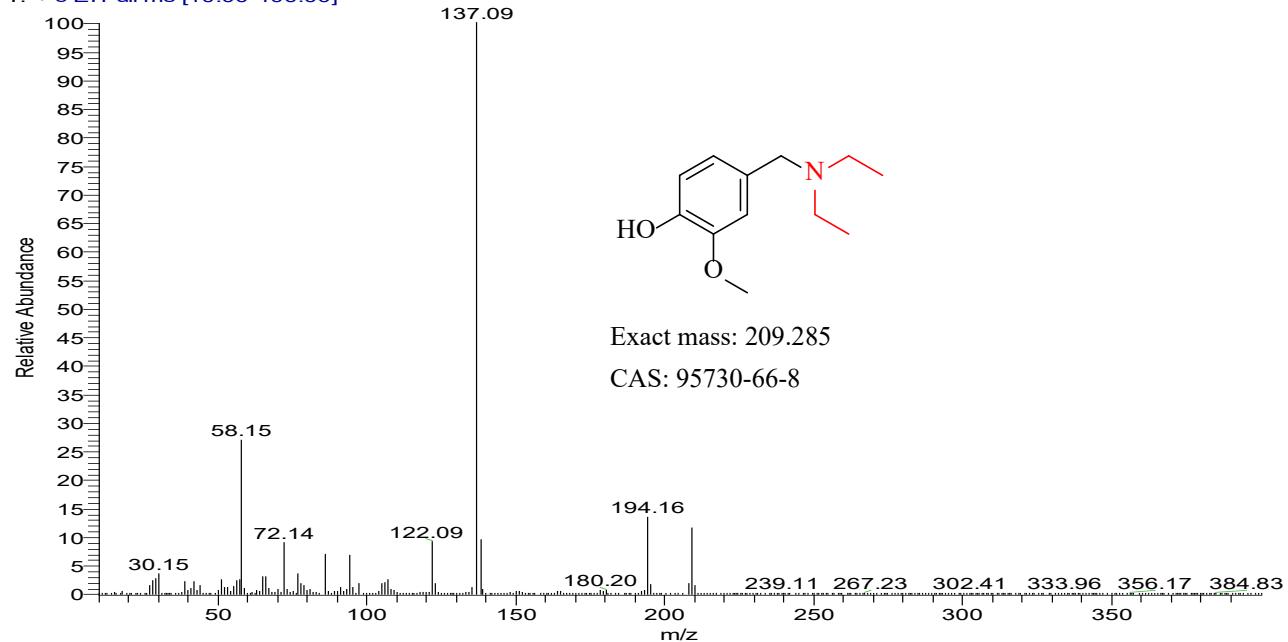
E-46-2 #6076 RT: 20.70 AV: 1 NL: 4.58E8
T: + c EI Full ms [15.00-400.00]



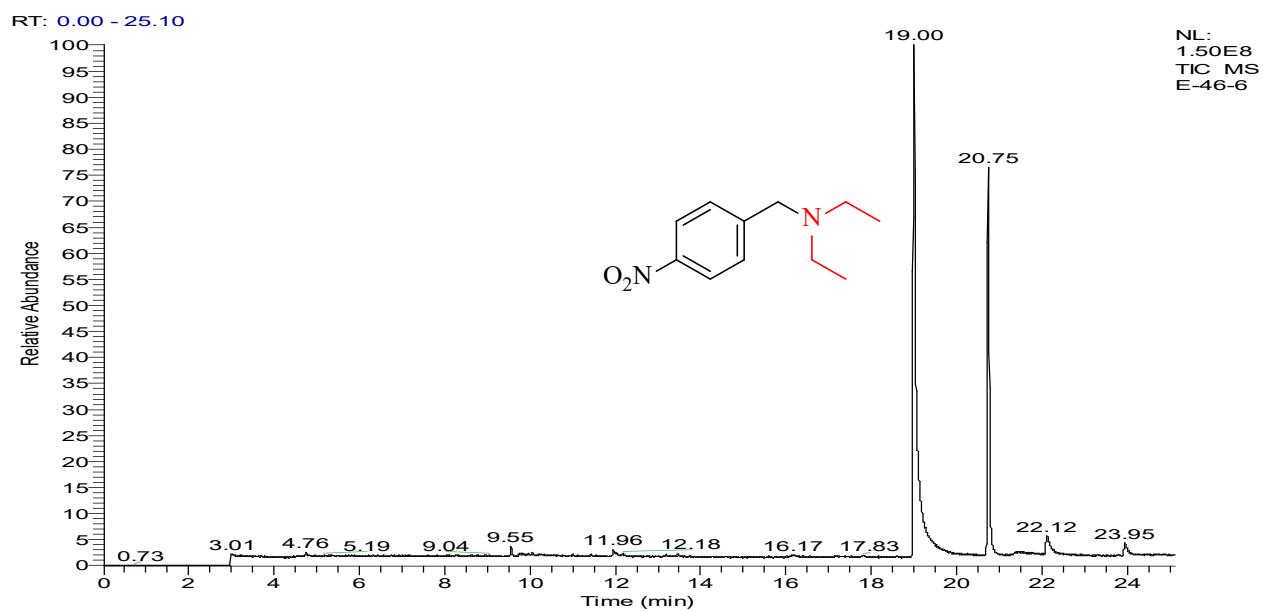
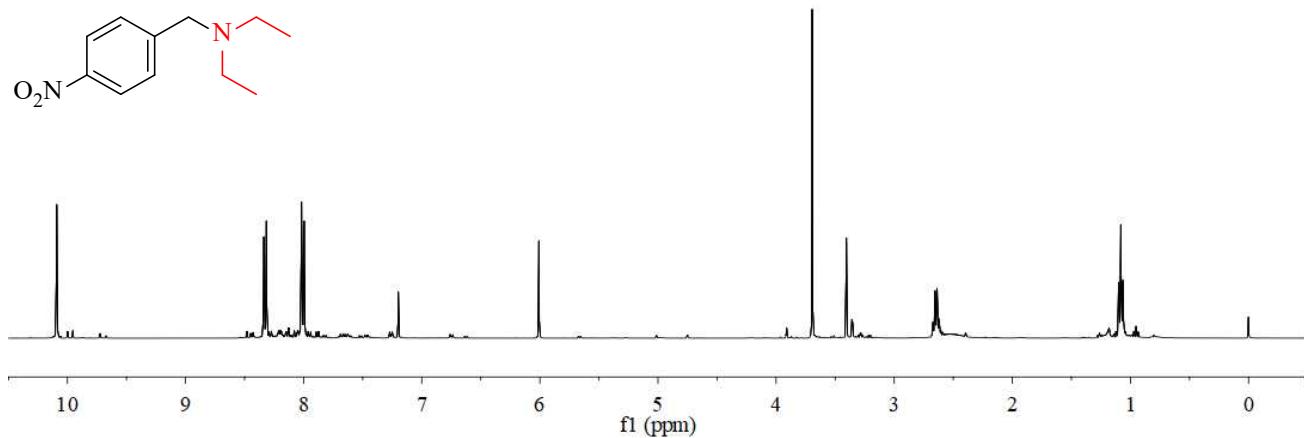




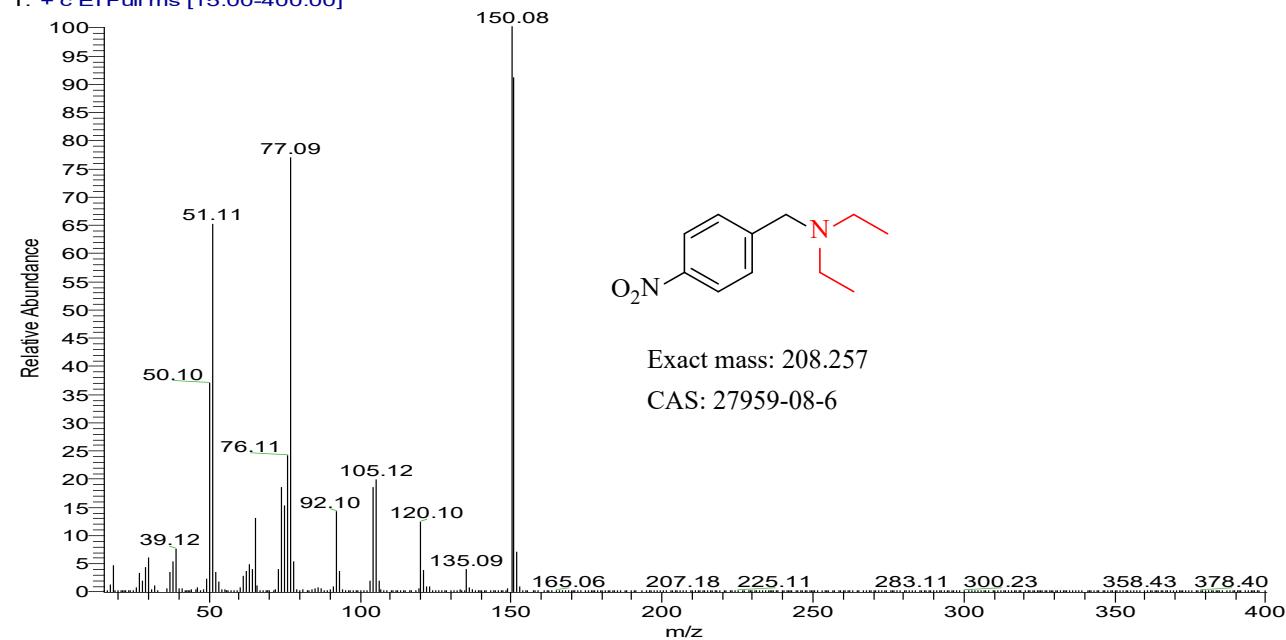
E-46-5 #5994 RT: 20.42 AV: 1 NL: 4.79E8
T: + c EI Full ms [10.00-400.00]

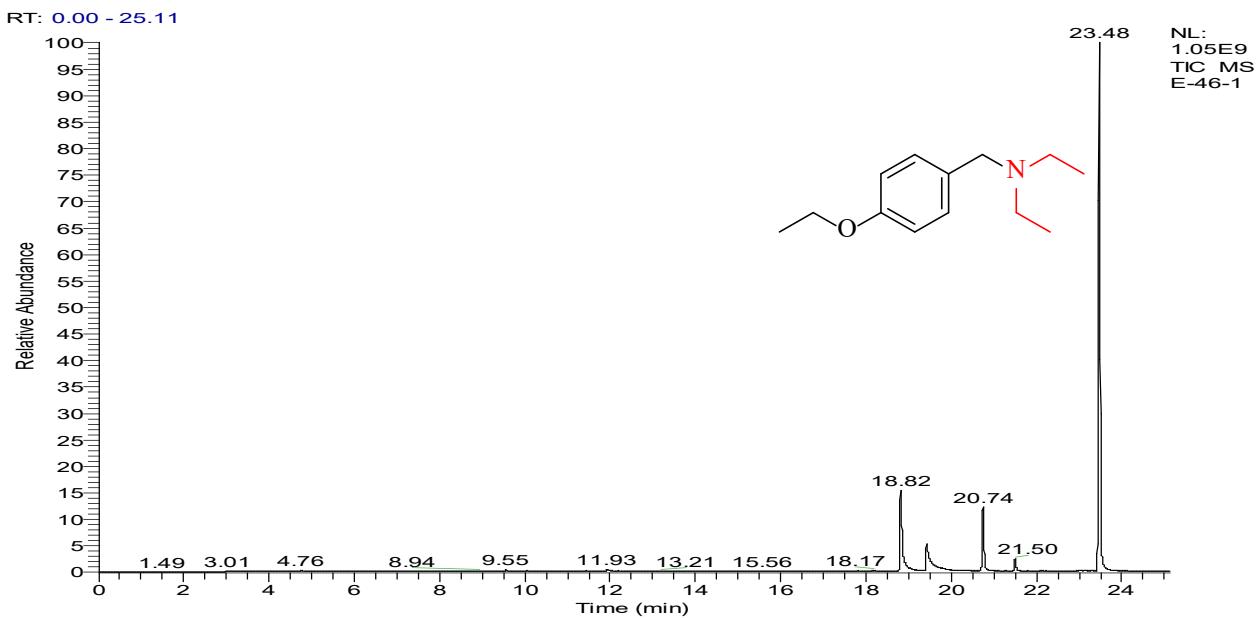
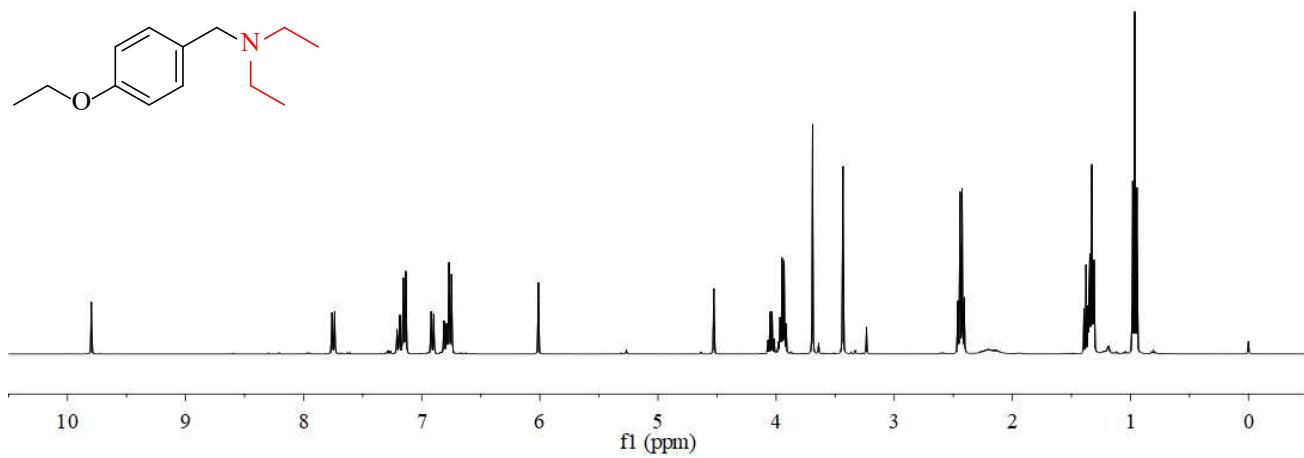


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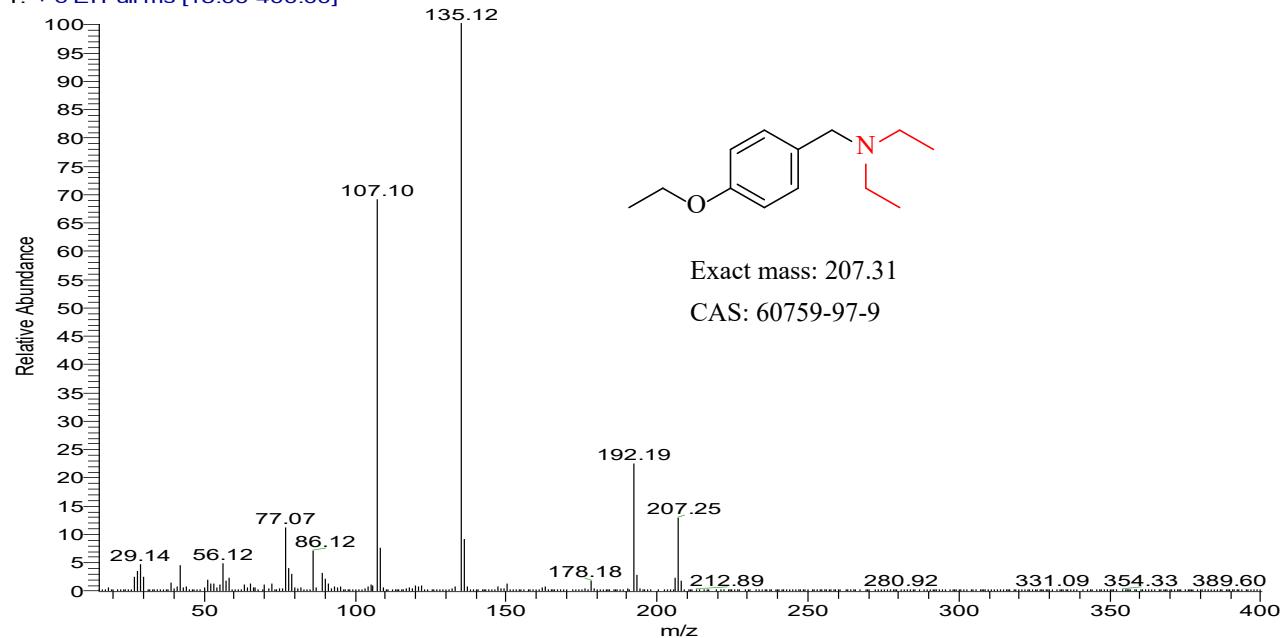


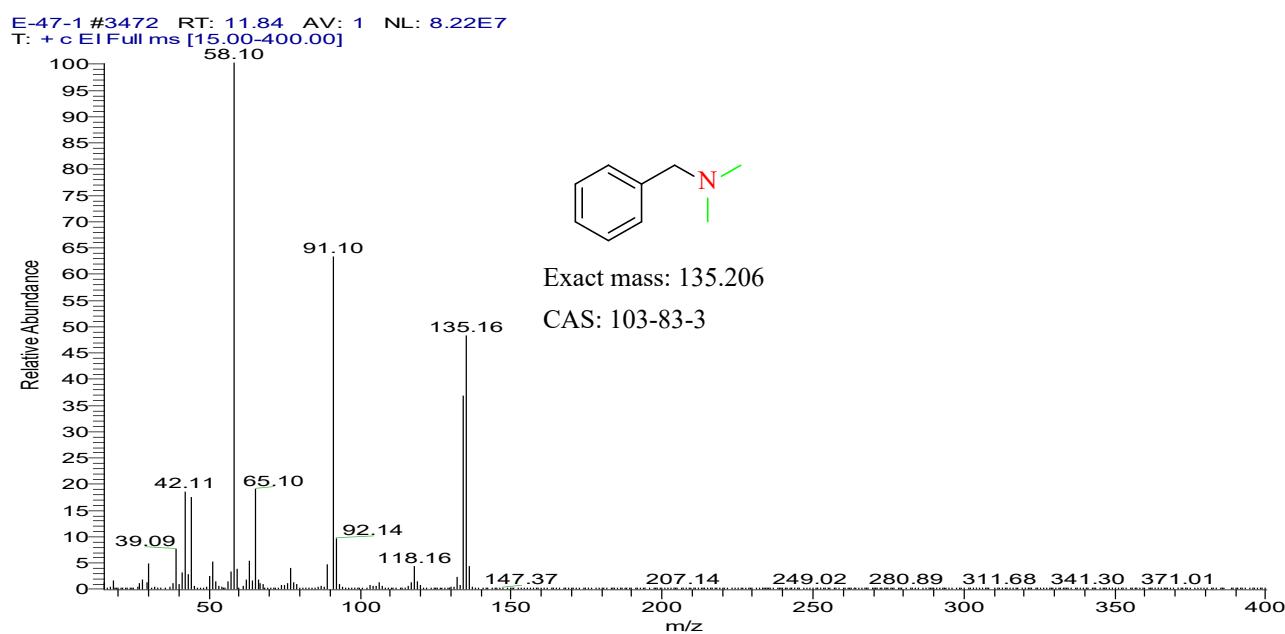
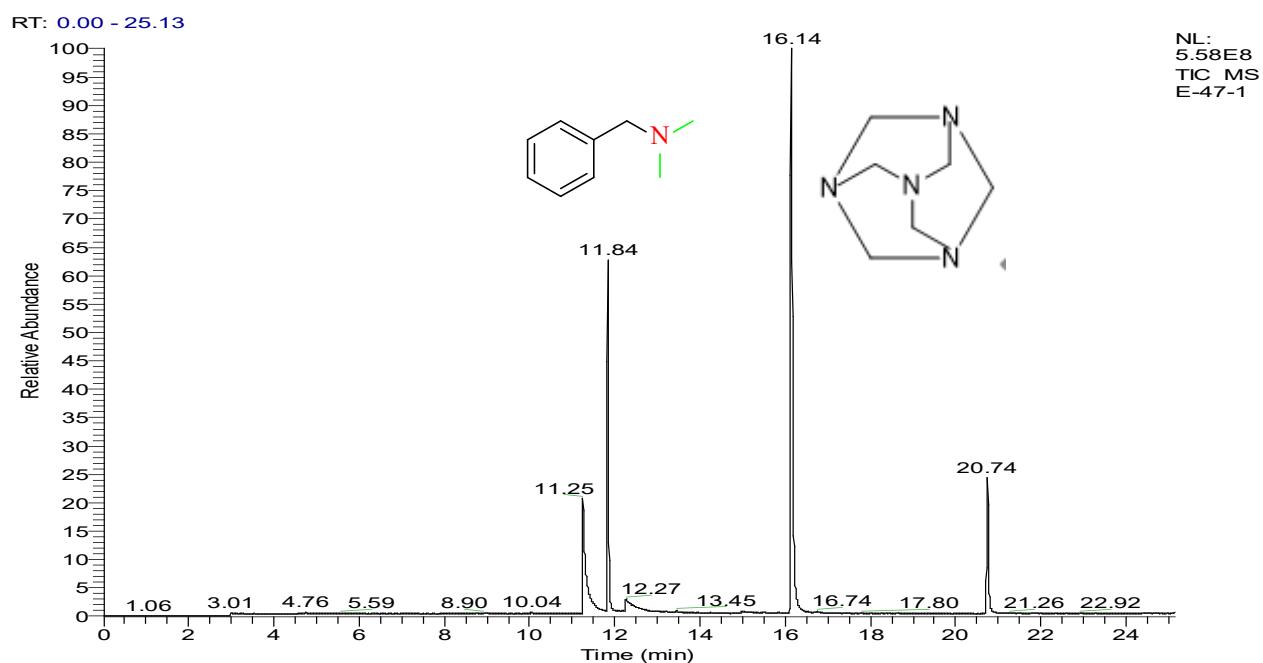
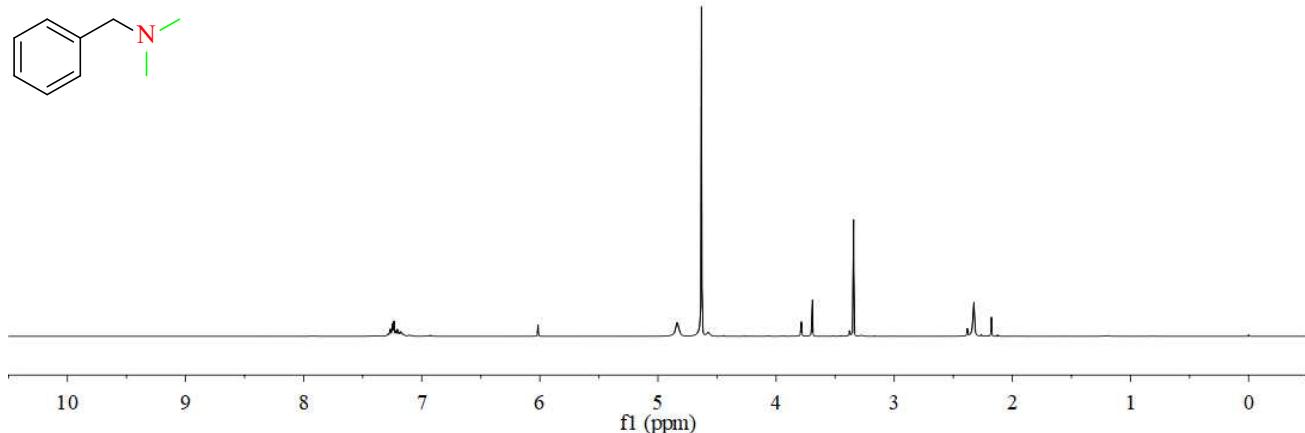
E-46-6 #5578 RT: 19.00 AV: 1 NL: 2.38E7
T: + c EI Full ms [15.00-400.00]

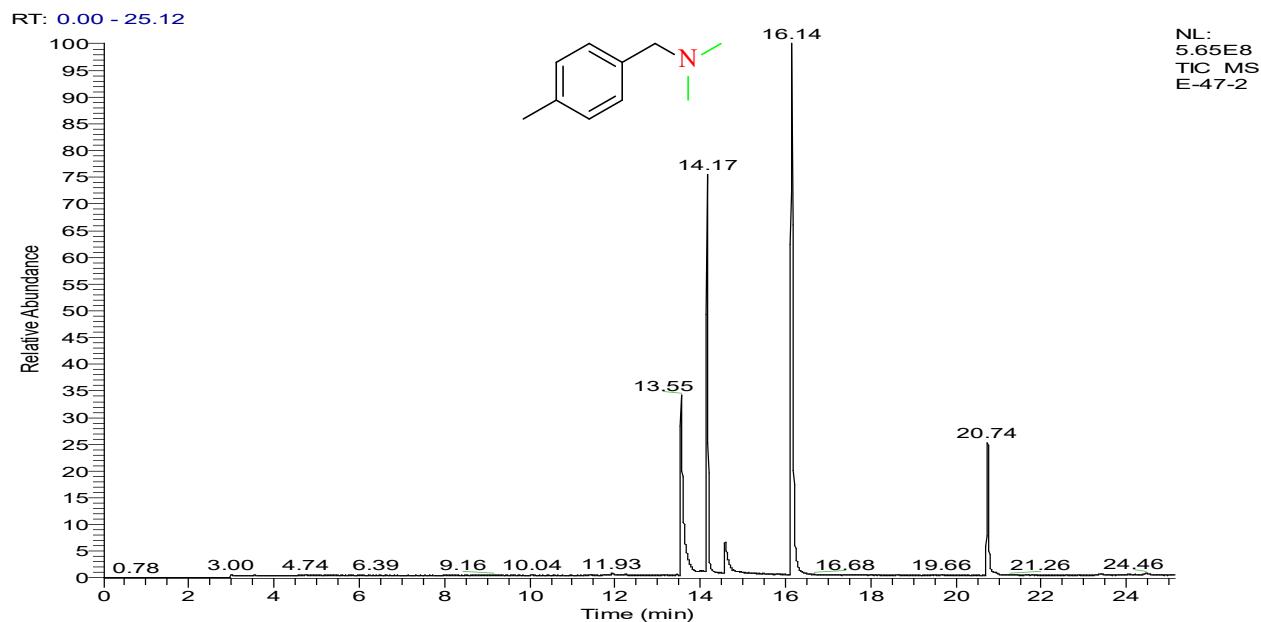
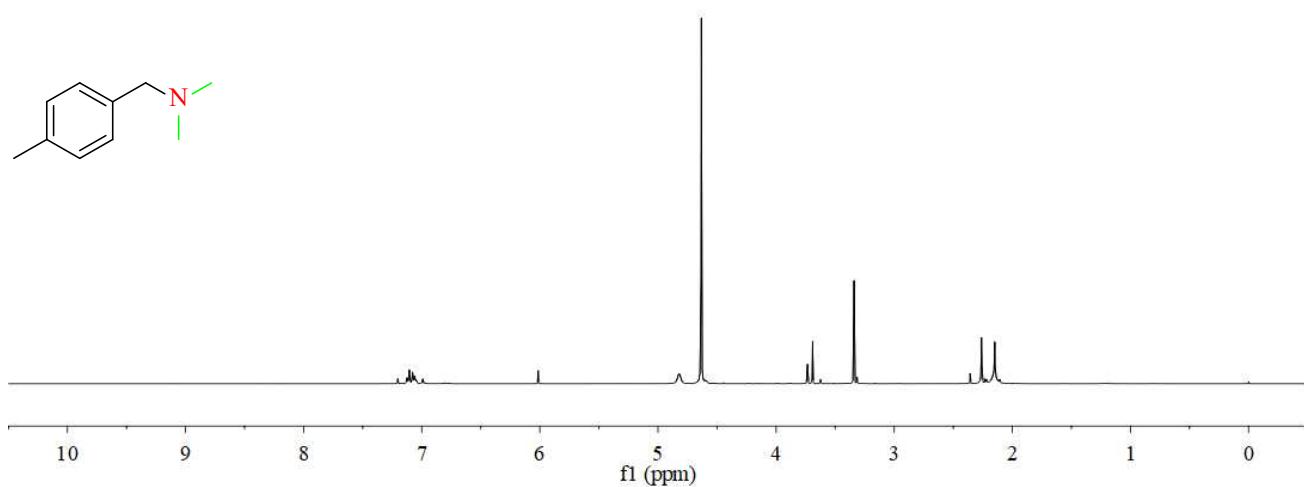




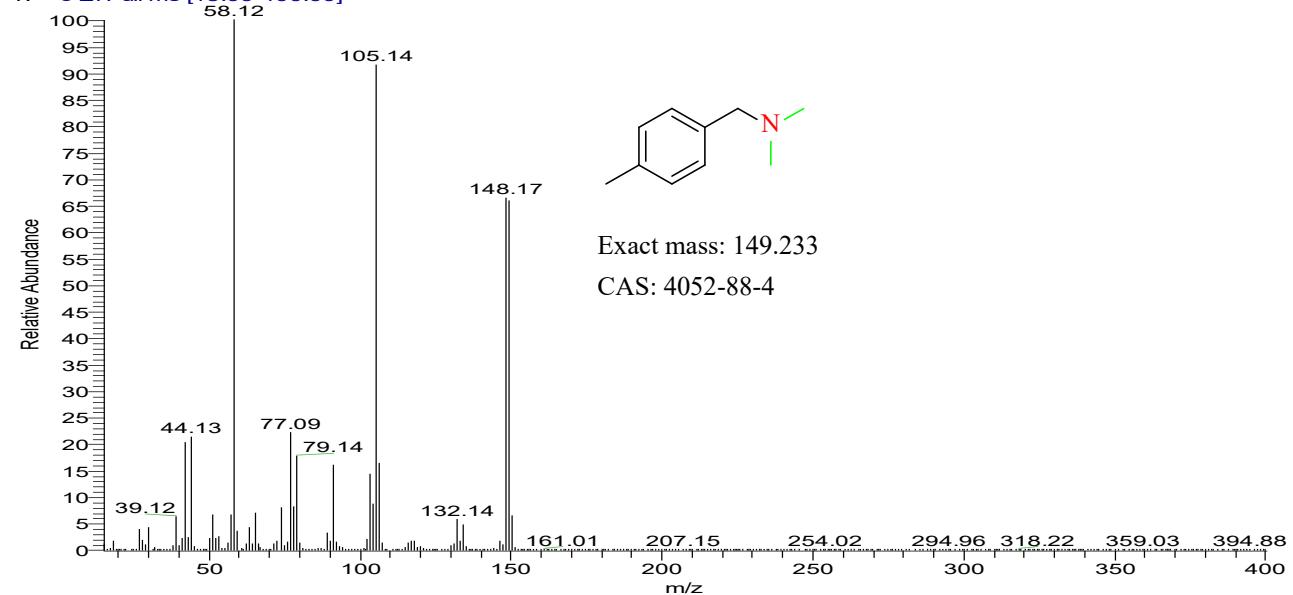
E-46-1 #6893 RT: 23.48 AV: 1 NL: 3.20E8
T: + c EI Full ms [15.00-400.00]



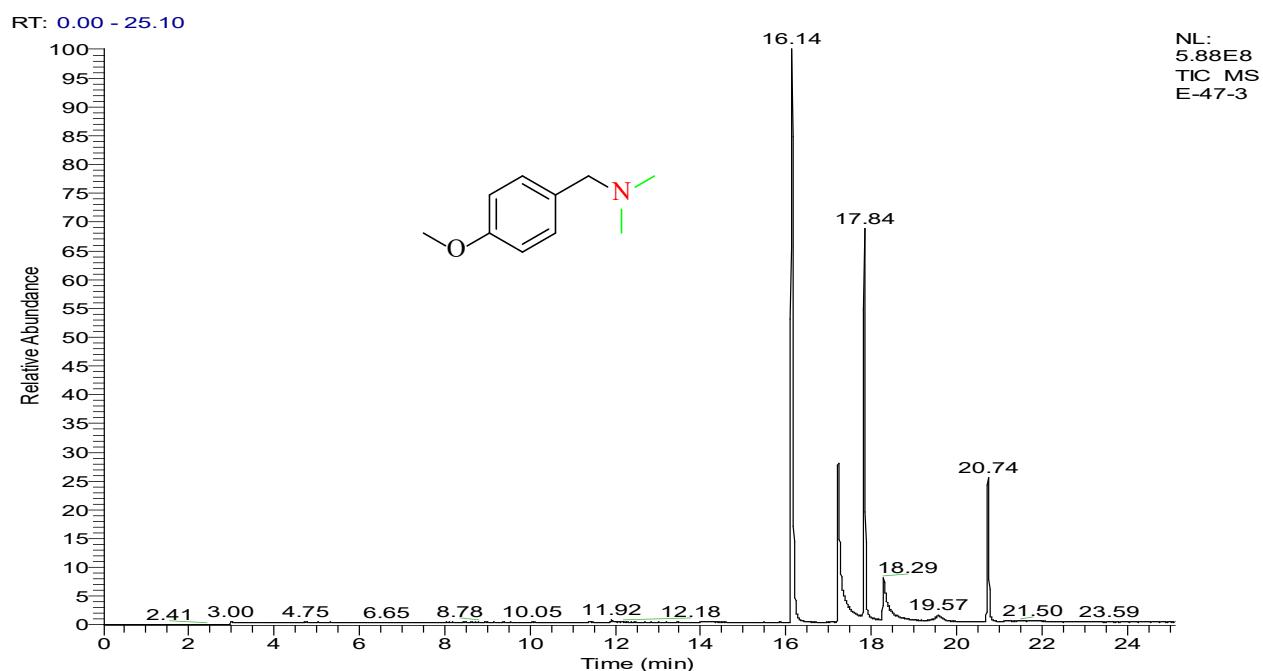
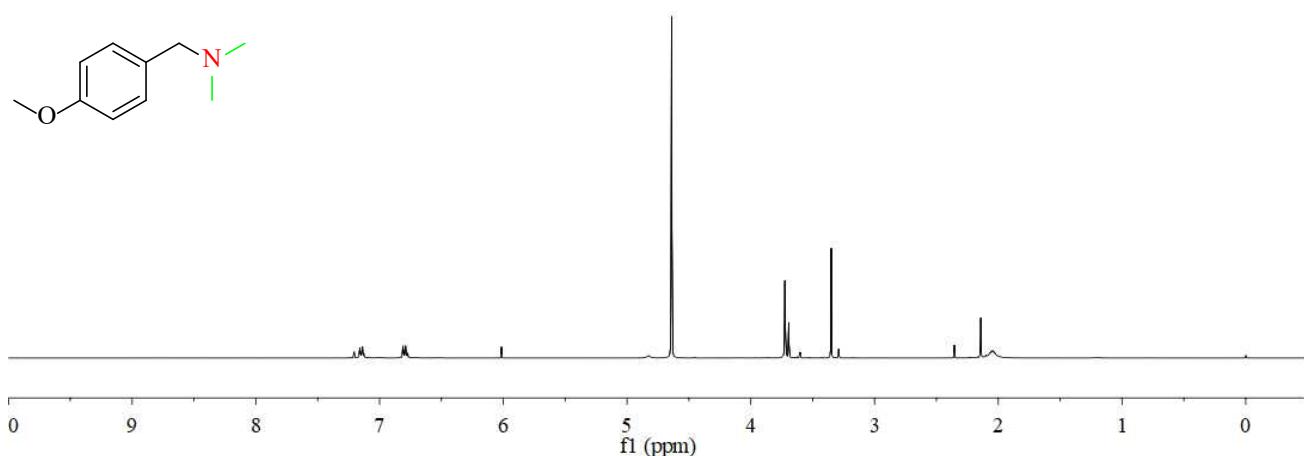




E-47-2 #4156 RT: 14.17 AV: 1 NL: 7.18E7
T: + c EI Full ms [15.00-400.00]

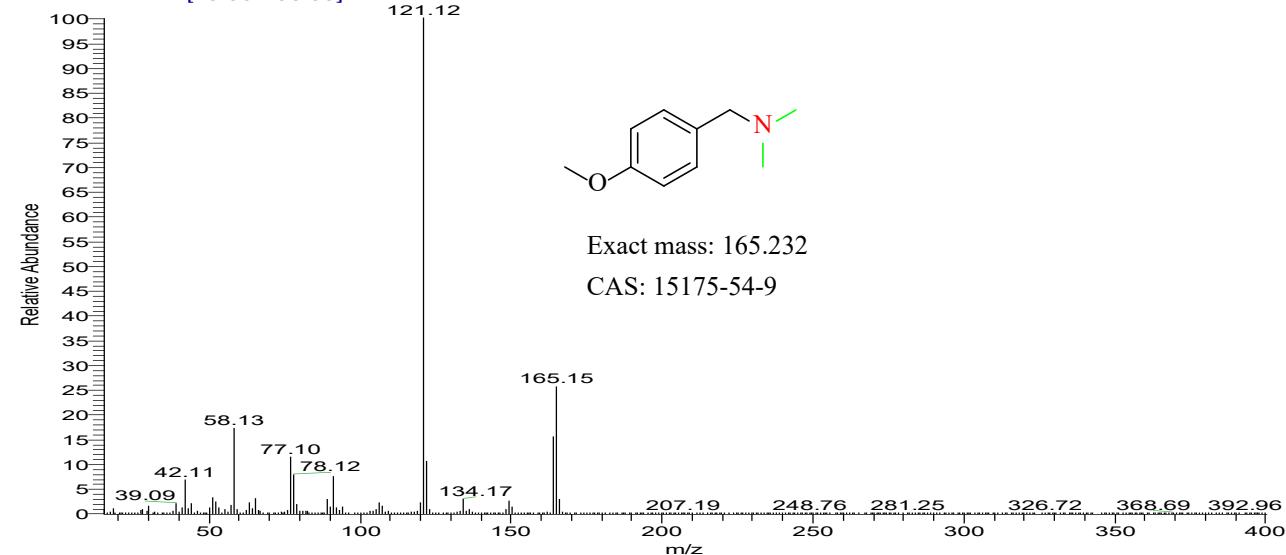


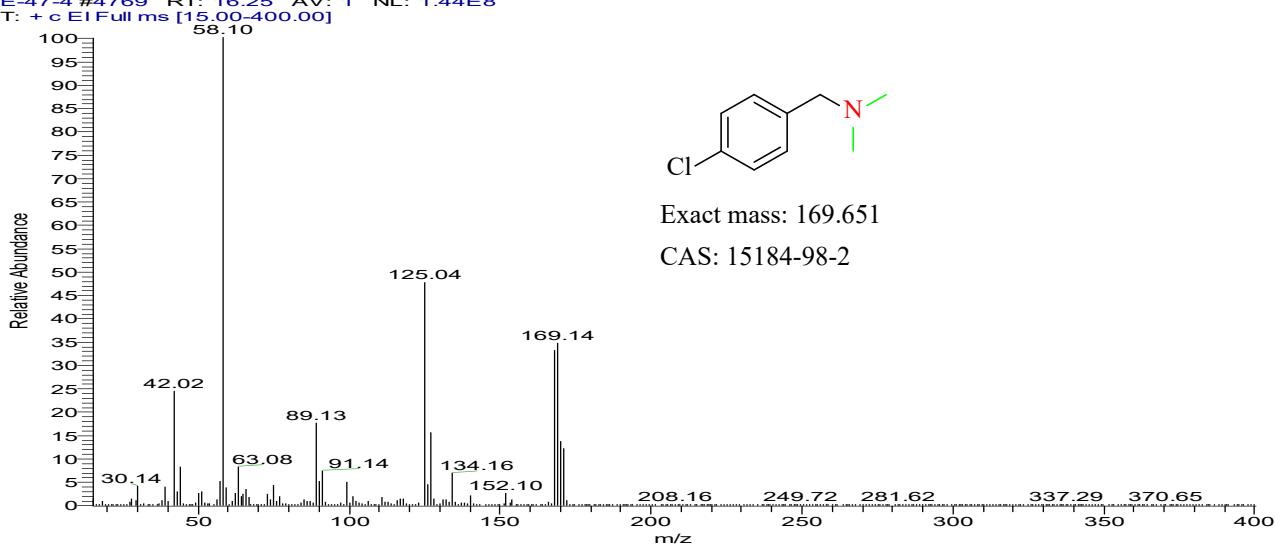
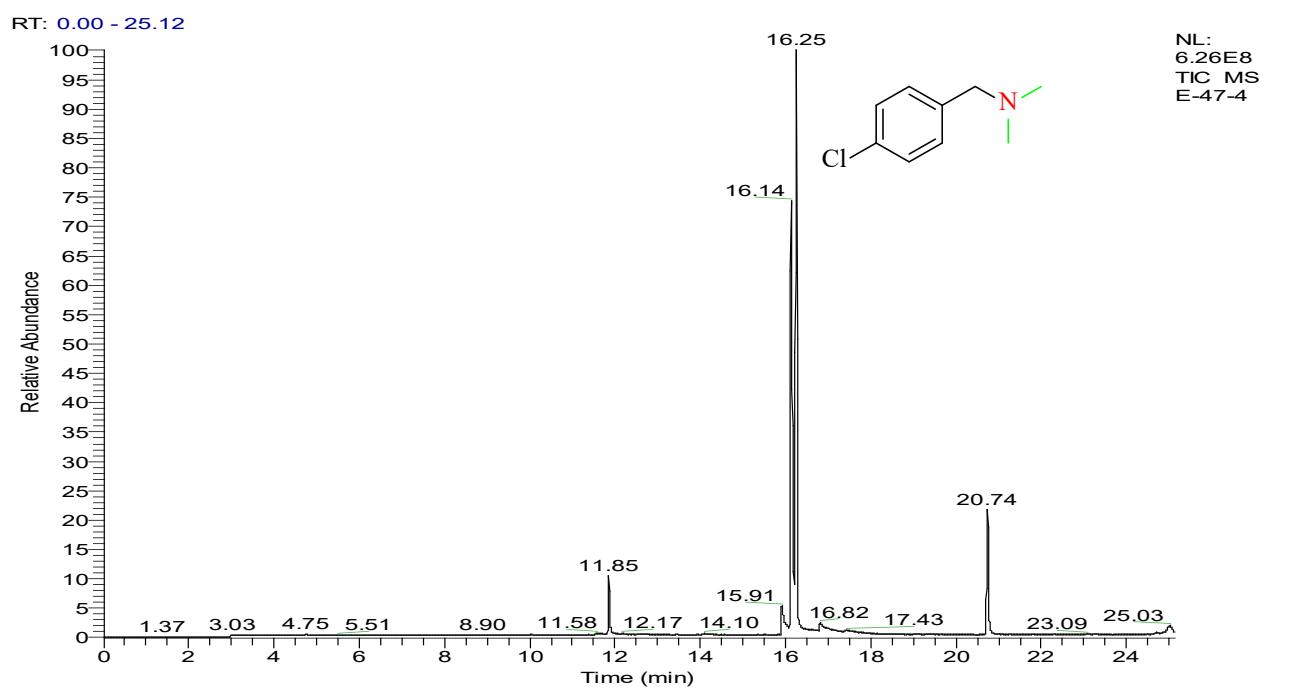
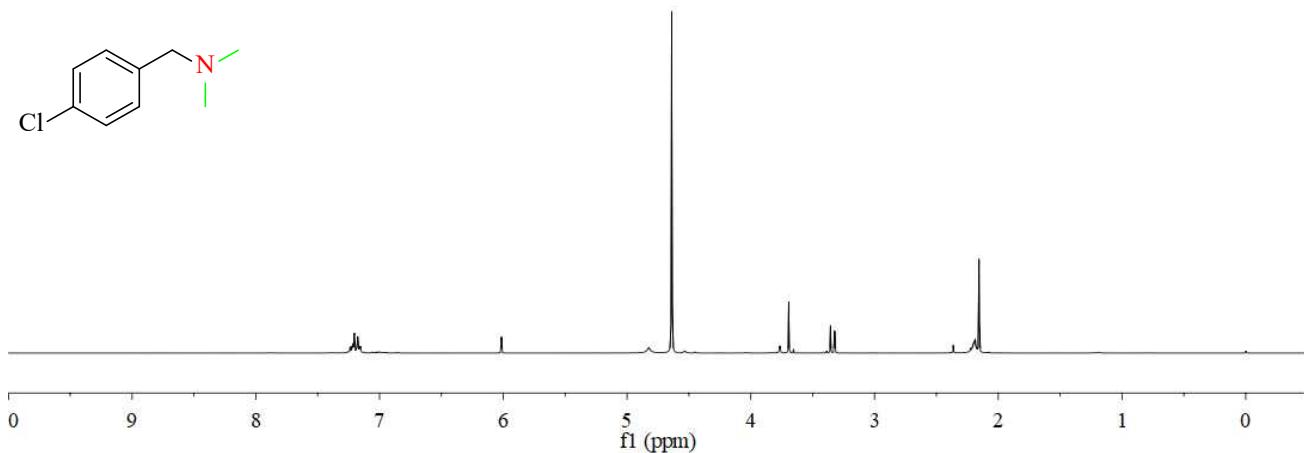
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E-47-3 #5235 RT: 17.84 AV: 1 NL: 1.29E8

T: + c EI Full ms [15.00-400.00]





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