

Supplementary Material

N-dimethylation and N-functionalization of amines using Ru nanoparticles catalyst and formaldehyde or functional aldehydes as carbon source

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S1. Methods and materials

All aldehydes and amines were obtained commercially from various chemical companies. 1,3,5-trimethoxybenzene and Nickel(II) oxide catalyst were purchased from Sigma Aldrich Co., Ltd.; Al₂O₃ (basic, 200~300 meshes), Methanol (GC, >99.9%), 5 wt% Pd/C, 5 wt% Rh/C, Raney-nickel and Raney-cobalt catalysts were purchased from Aladdin (Shanghai) Chemical Technology Co., Ltd.; 5 wt% Ru/C, 5 wt% Pt/C, CDCl₃ (99.8% D, stabilized with Ag) were applied by Macklin (Shanghai) Chemical Technology Co., Ltd. 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, respectively. 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 10kV. 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. Procedure for the synthesis of N-methylamines

S2.1. 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 2.5 MPa pressure and was pressurized with 2.5 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 proceeding 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 0.5 mL of CDCl₃ (preneutralized with basic Al₂O₃).

S2.2. Procedure for the gram scare reaction

In a 500 mL stainless steel autoclave (WATTCAS, China) with one thermocouple, 0.5 or 1 g corresponding amine, corresponding aldehyde (3 mmol per 0.5 mmol amine), 0.5 mmol 1,3,5-

trimethoxybenzene, one 30 mm magnetic stirring bar, 5%Ru/C (5 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 2.5 MPa pressure and was pressurized with 2.5 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 proceeding 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.

S2.3. Procedure for the 5%Ru/C recycling

The stability test of 5%Ru/C 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 S2.1 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. TEM spectra

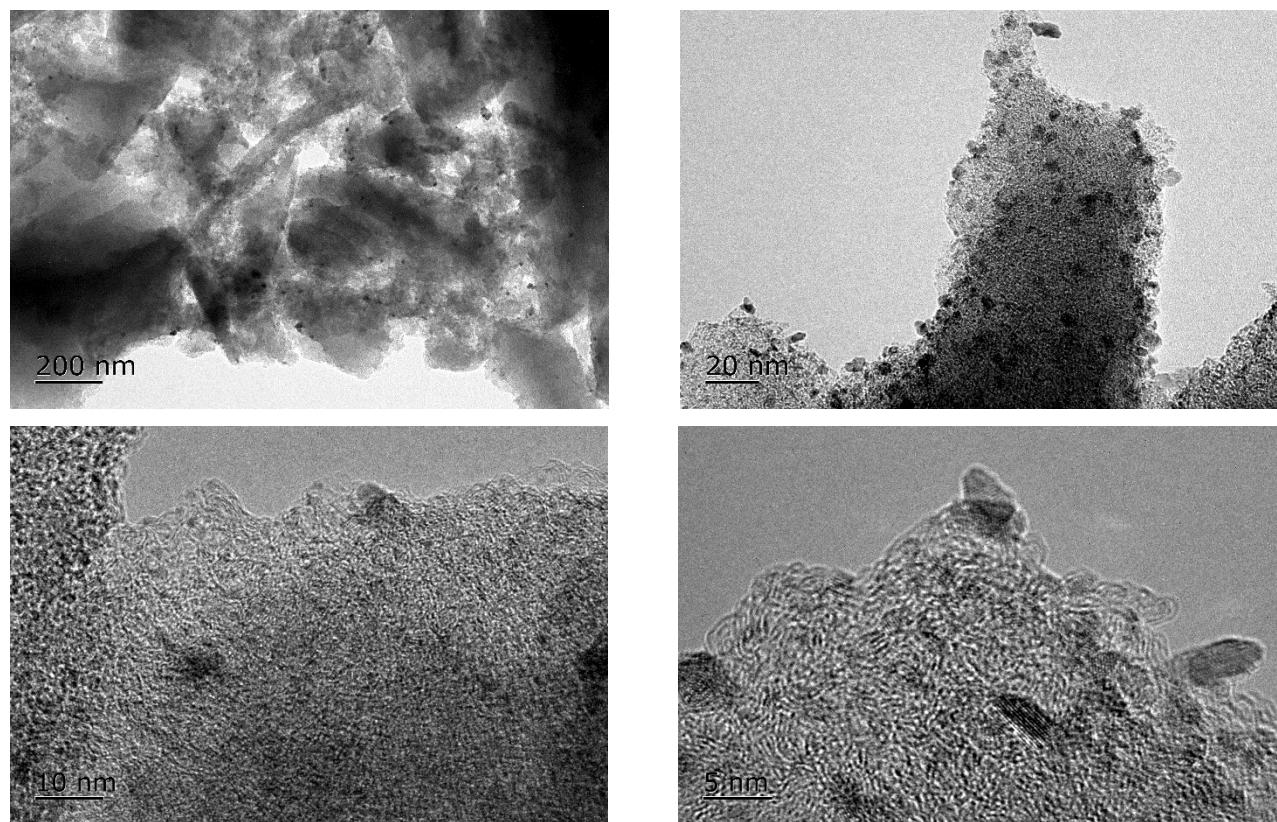


Figure S1. TEM images of 5%Ru/C.

S4. SEM spectra

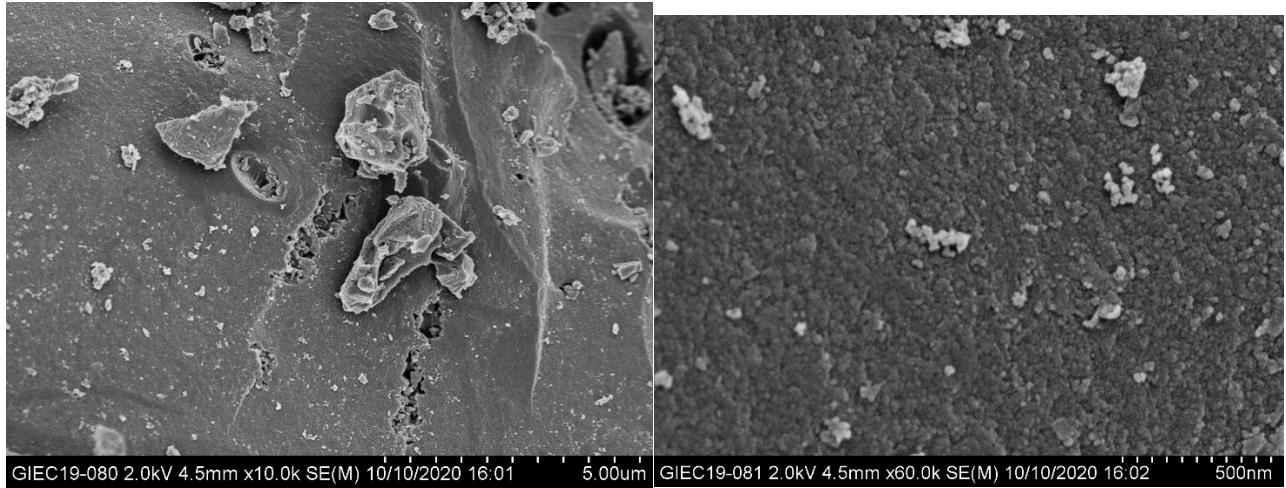


Figure S2. SEM images of 5%Ru/C.

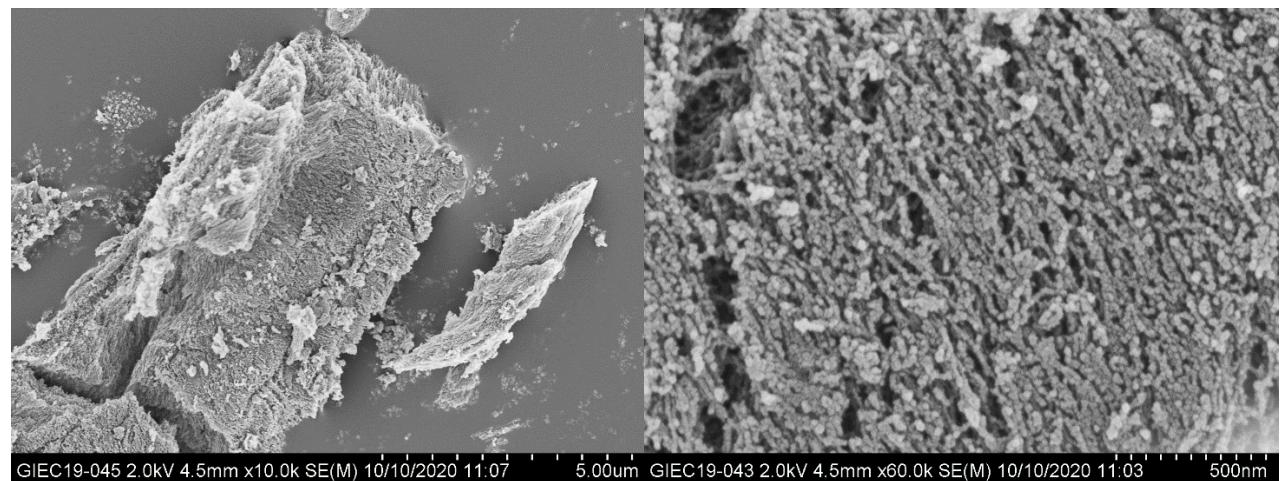


Figure S3. SEM images of 5%Rh/C.

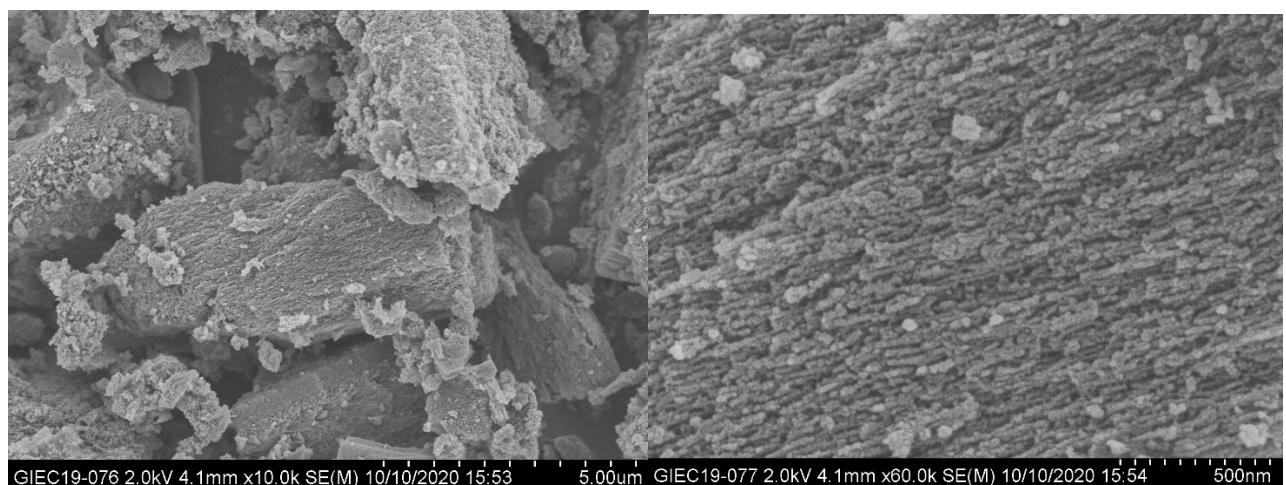


Figure S4. SEM images of 5%Pt/C.

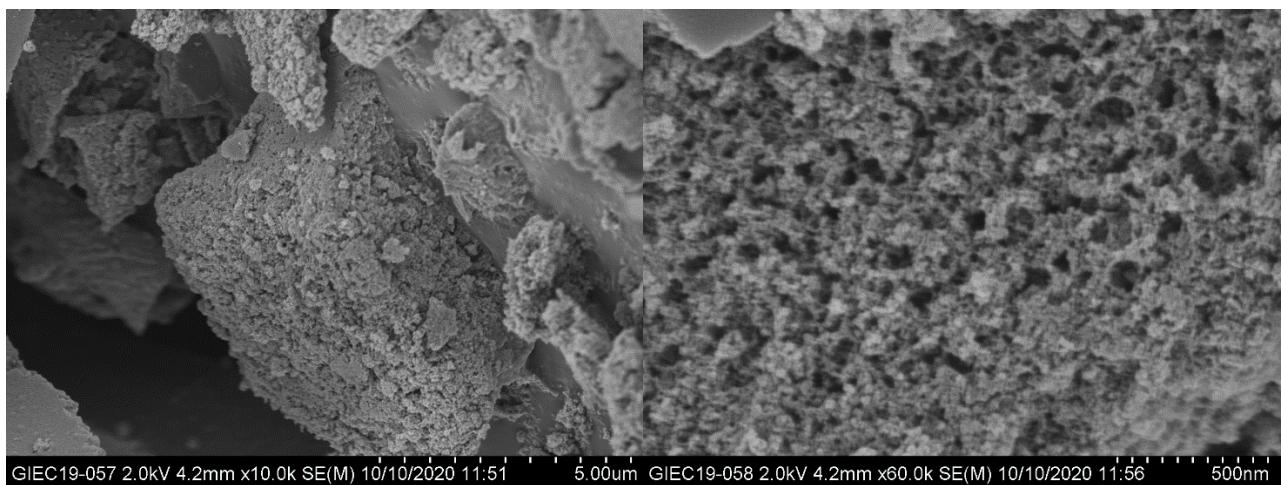


Figure S5. SEM images of 5%Pd/C.

S5. BET measurements

Table S1. BET measurements of Ru/C

Catalyst	Pore size (nm)	Surface area (m^2/g)	Total volume (cm^3/g)
5%Ru/C	1.8747	1061.804	0.4976

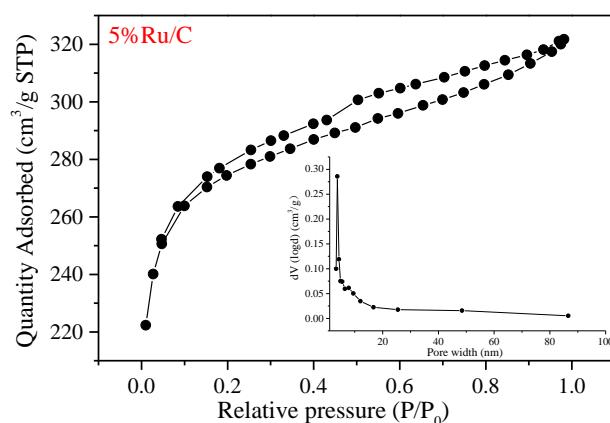


Figure S6. BET measurements of catalysts 5%Ru/C; N_2 adsorption and desorption isotherm curves and pore size distribution profile of the 5%Ru/C.

S6. XRD spectra

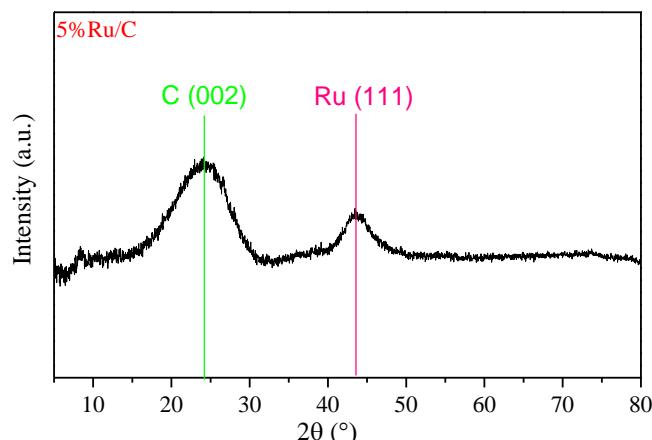


Figure S7. XRD images of 5%Ru/C.

S7. EDS element analysis

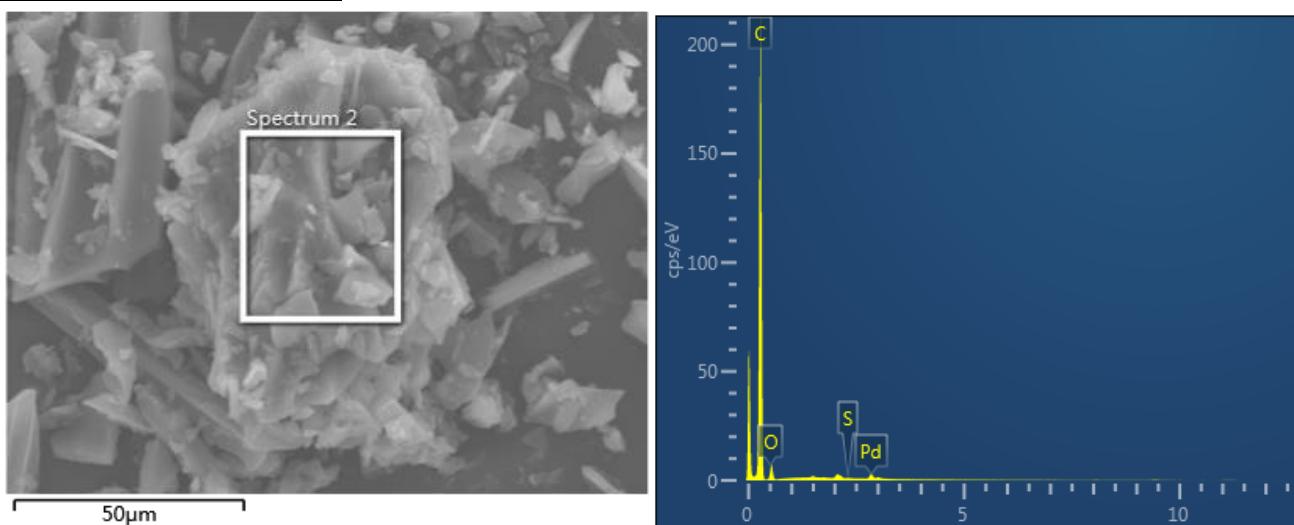


Figure S8. EDS element analysis of Pd/C

Table S2. EDS element analysis of Pd/C

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	131.99	1.31988	82.58	0.21	87.44	C Vit	Yes	
O	K series	9.97	0.03355	15.49	0.20	12.31	SiO2	Yes	
S	K series	0.08	0.00069	0.04	0.01	0.02	FeS2	Yes	
Pd	L series	3.20	0.03203	1.89	0.05	0.23	Pd	Yes	
Total:				100.00		100.00			

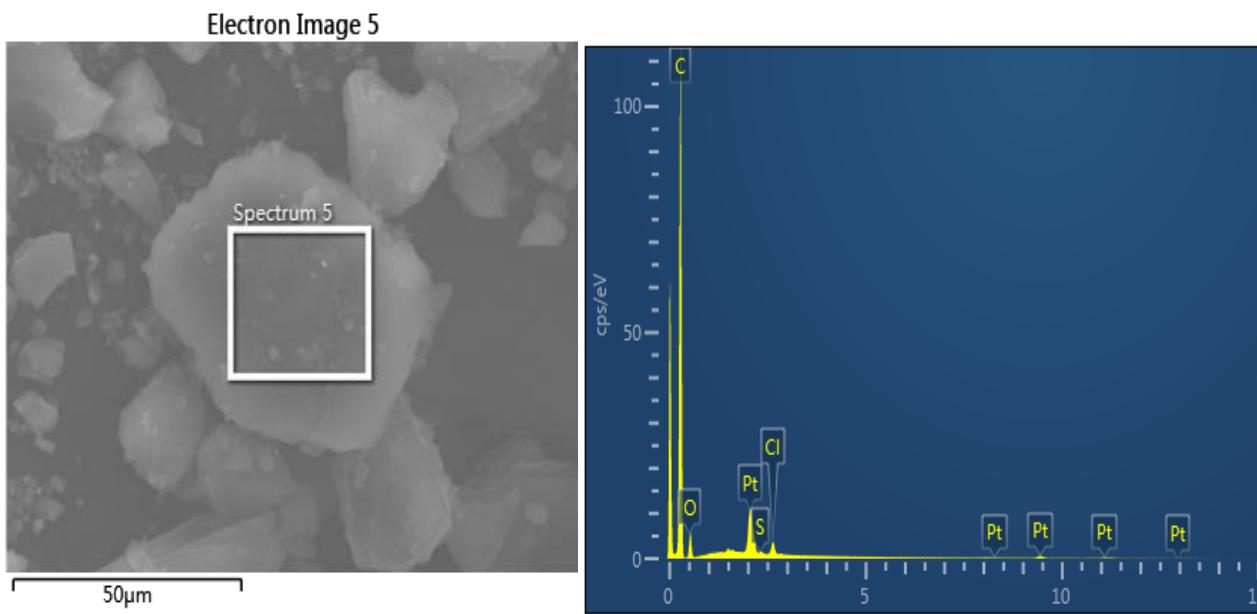


Figure S9. EDS element analysis of Pt/C

Table S3. EDS element analysis of Pt/C

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	117.53	1.17531	82.18	0.14	90.27	C Vit	Yes	
O	K series	8.66	0.02913	10.90	0.13	8.99	SiO2	Yes	
S	K series	0.12	0.00106	0.05	0.01	0.02	FeS2	Yes	
Cl	K series	1.84	0.01608	0.82	0.02	0.31	NaCl	Yes	
Pt	M series	12.87	0.12872	6.04	0.08	0.41	Pt	Yes	
Total:				100.00		100.00			

Electron Image 1

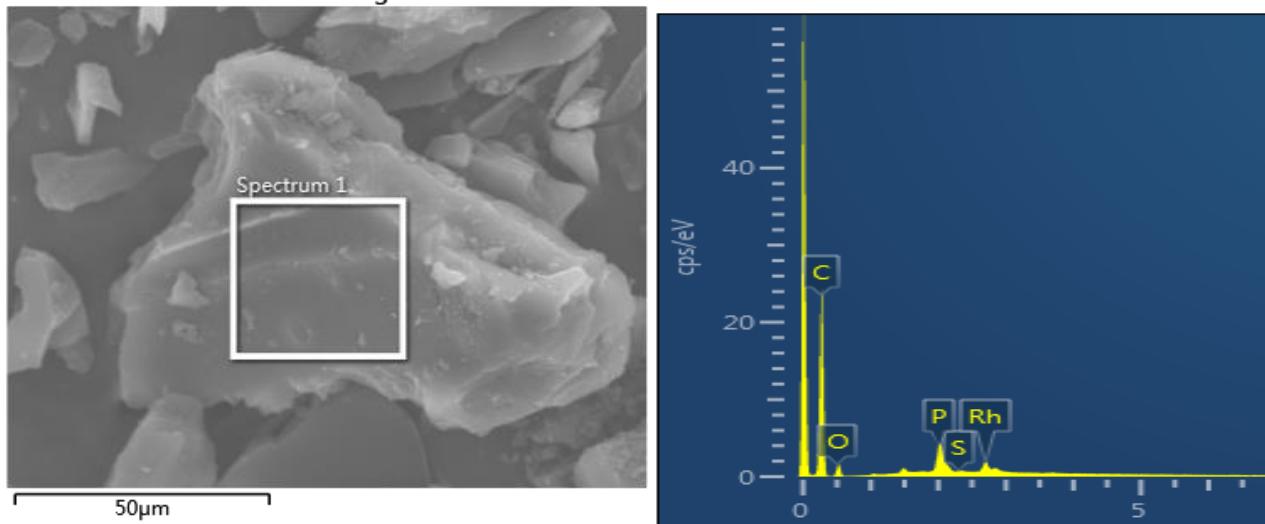


Figure S10. EDS element analysis of Rh/C

Table S4. EDS element analysis of Rh/C

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	30.67	0.30673	81.73	0.30	88.51	C Vit	Yes	
O	K series	2.38	0.00802	12.19	0.28	9.91	SiO ₂	Yes	
P	K series	2.47	0.01384	2.68	0.06	1.13	GaP	Yes	
S	K series	0.04	0.00036	0.07	0.03	0.03	FeS ₂	Yes	
Rh	L series	1.78	0.01780	3.33	0.13	0.42	Rh	Yes	
Total:				100.00		100.00			

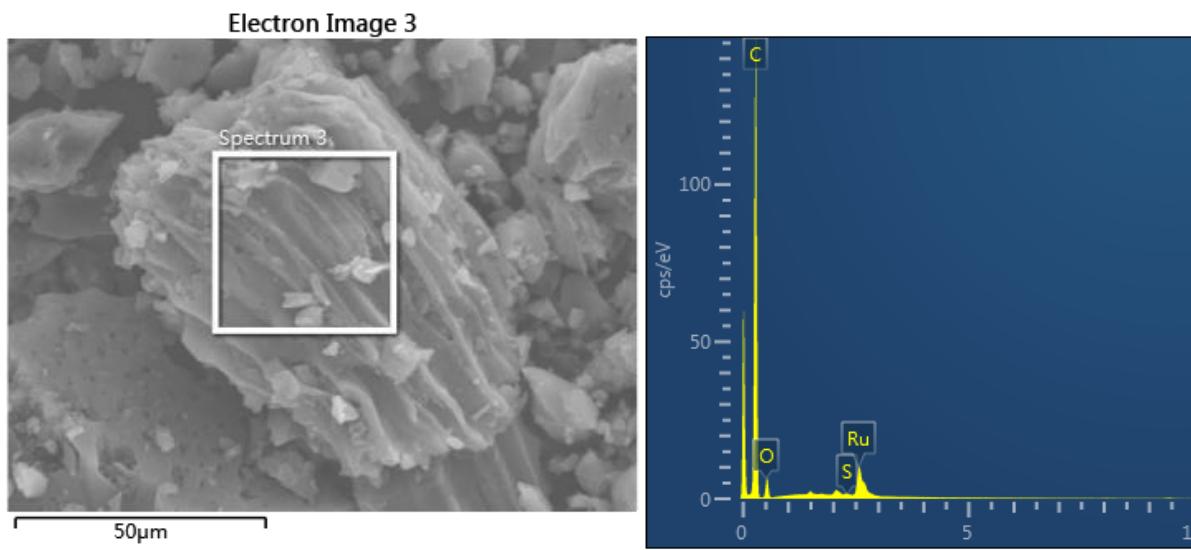


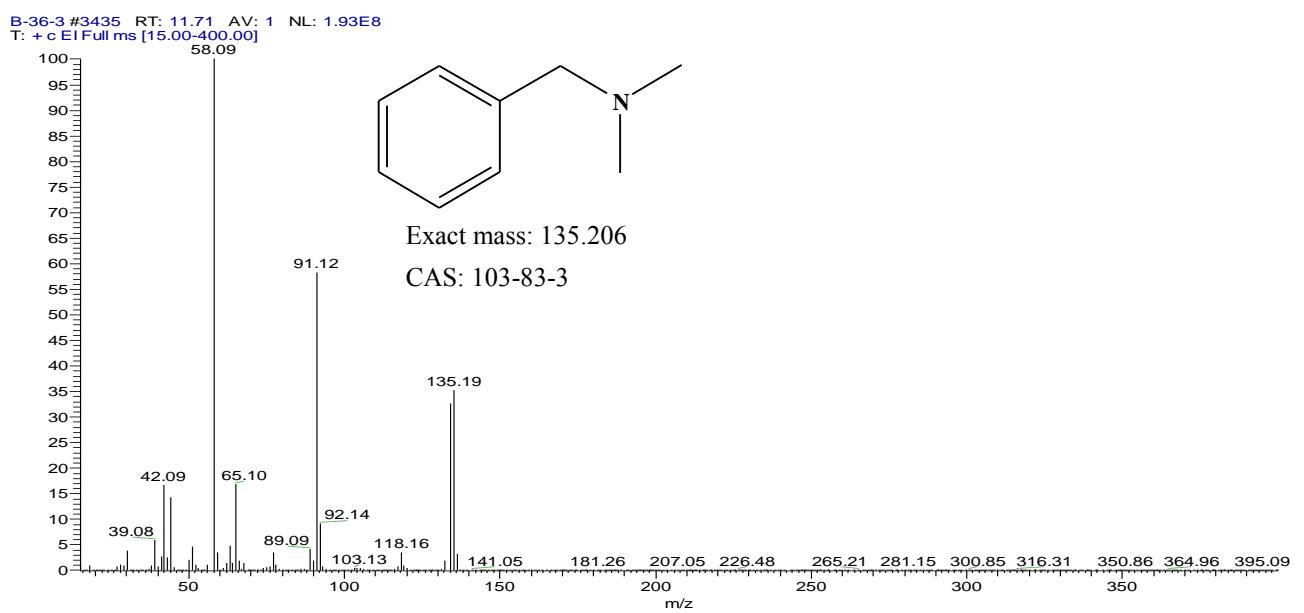
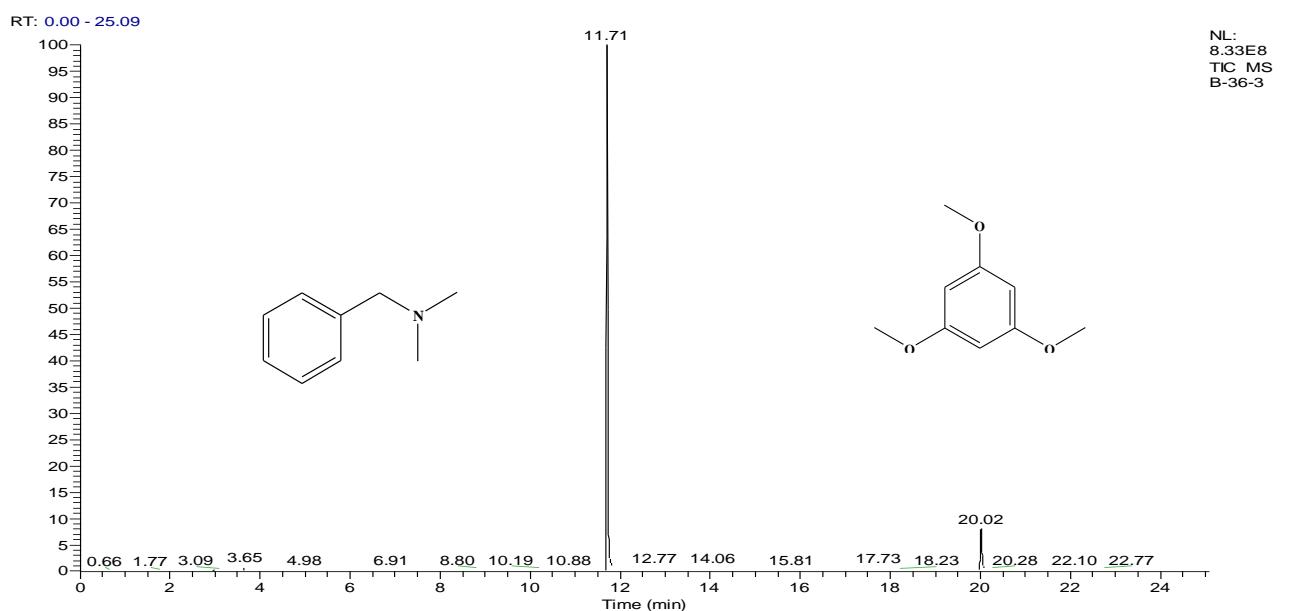
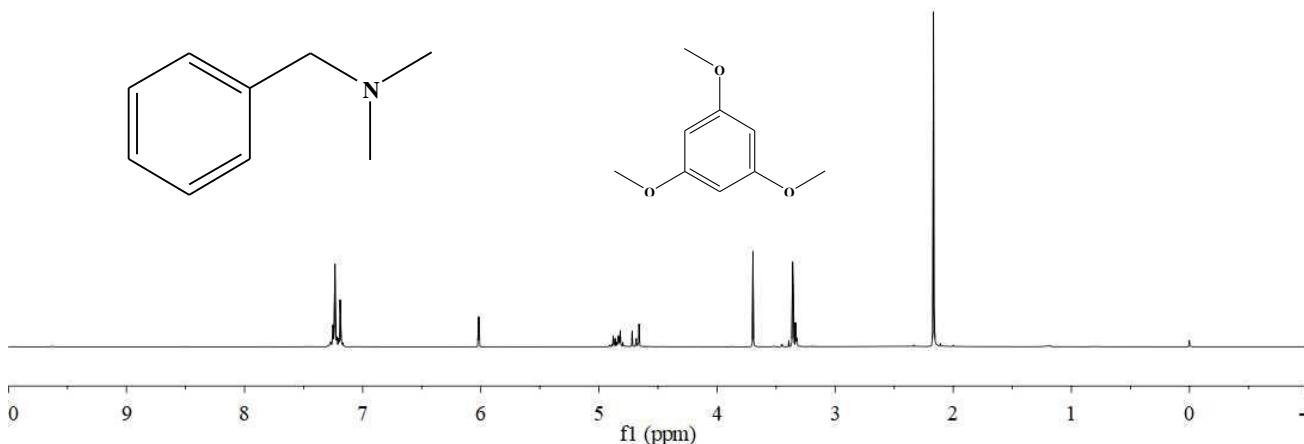
Figure S11. EDS element analysis of Ru/C

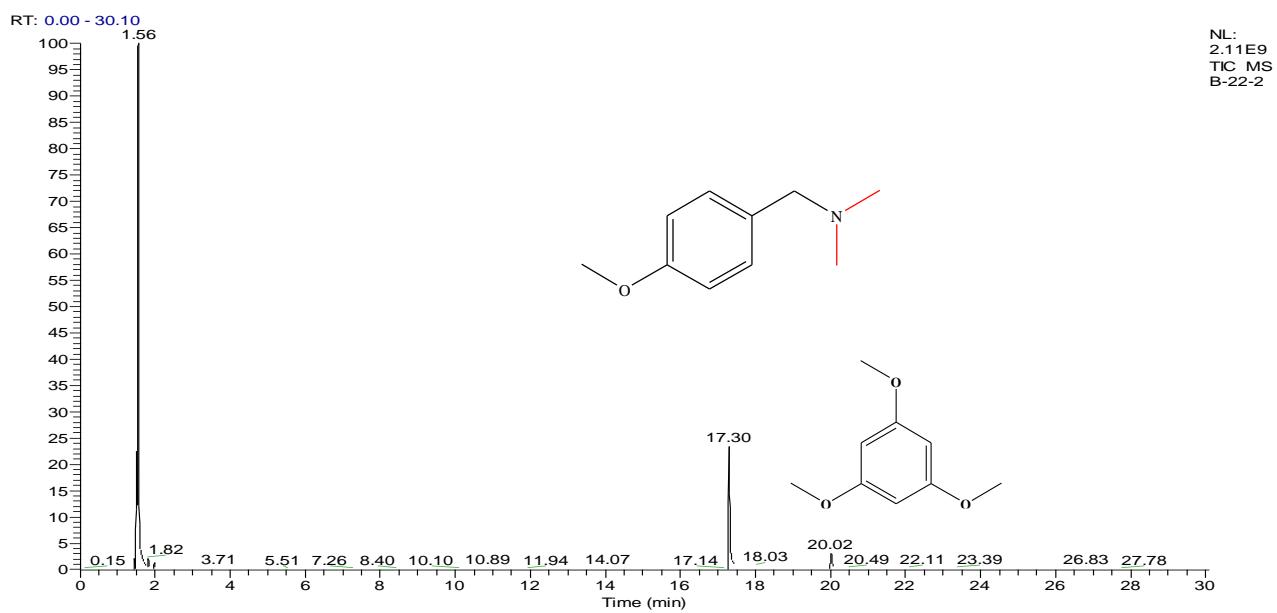
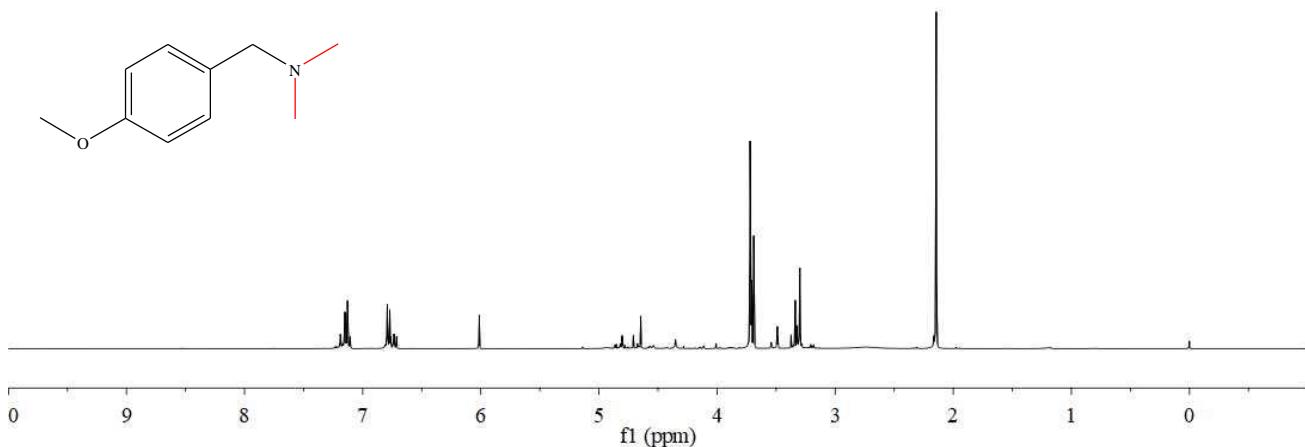
Table S5. EDS element analysis of Ru/C

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Atomic %	Standard Label	Factory Standard	Standard Calibration Date
C	K series	151.45	1.51453	80.93	0.16	88.29	C Vit	Yes	
O	K series	9.57	0.03221	13.35	0.16	10.94	SiO ₂	Yes	
S	K series	0.30	0.00256	0.13	0.01	0.05	FeS ₂	Yes	
Ru	L series	11.06	0.11056	5.59	0.07	0.72	Ru (v)	Yes	
Total:				100.00		100.00			

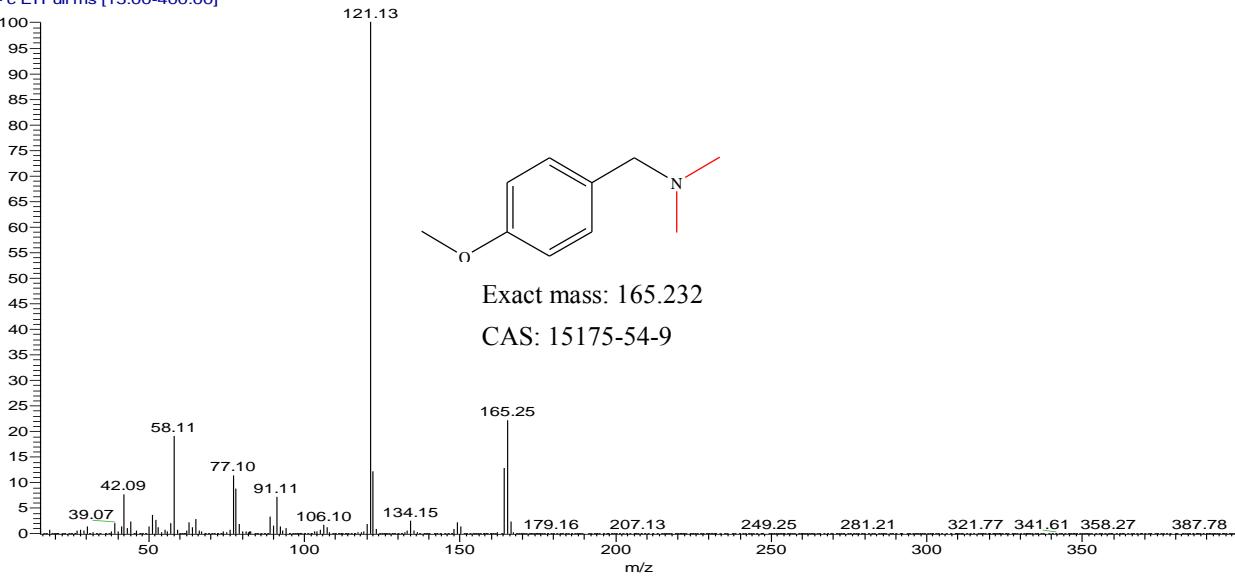
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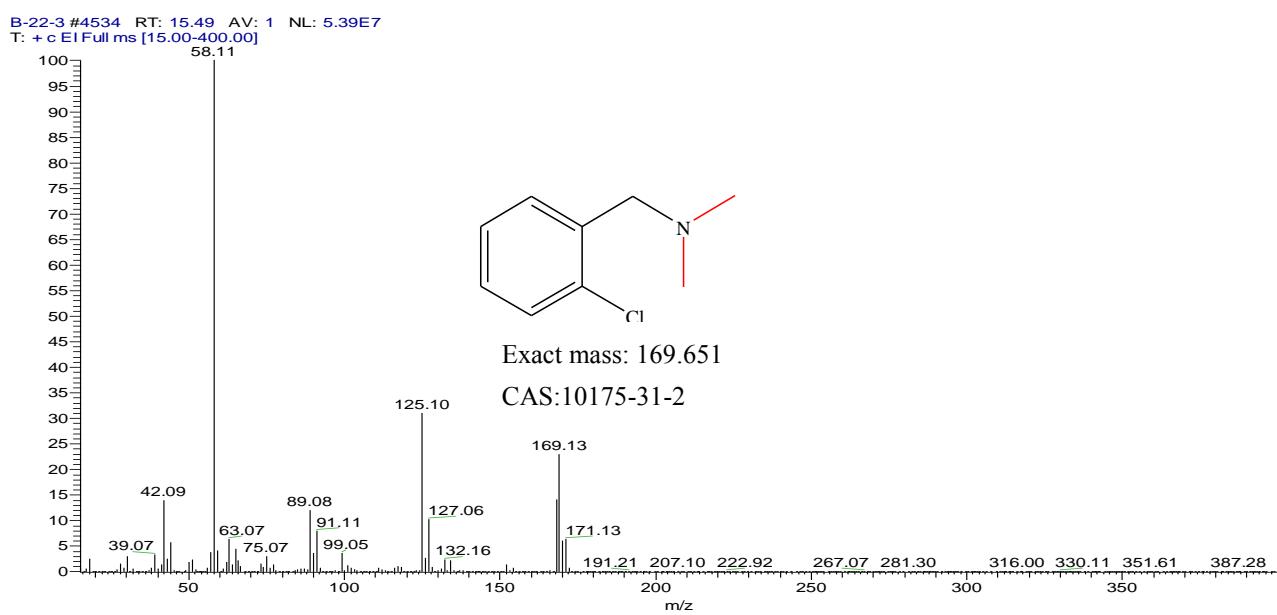
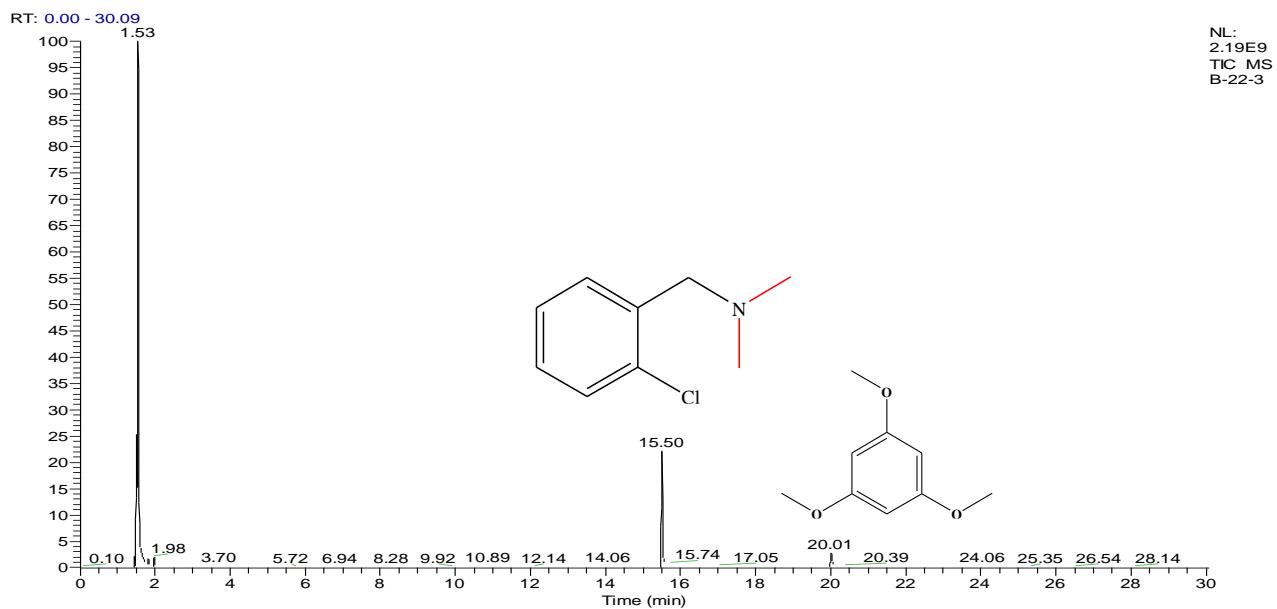
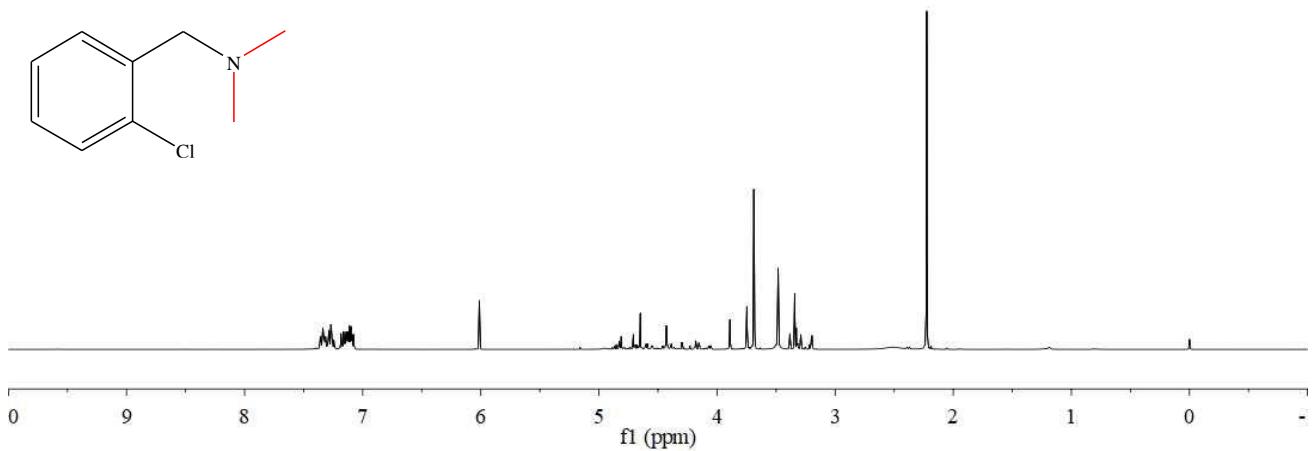
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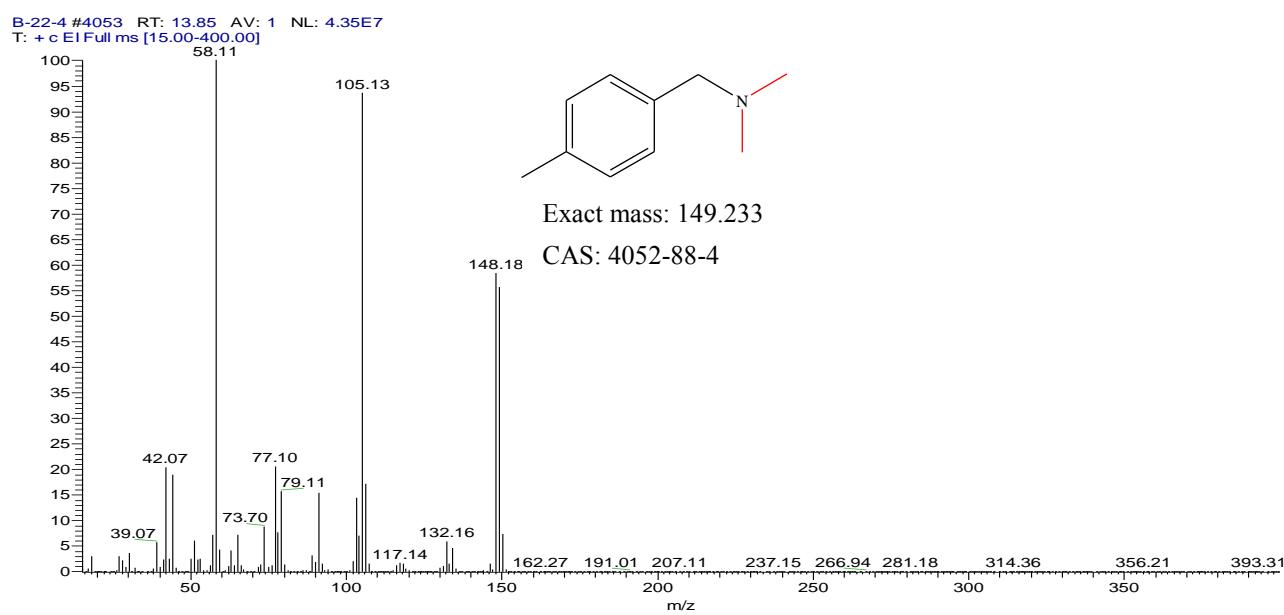
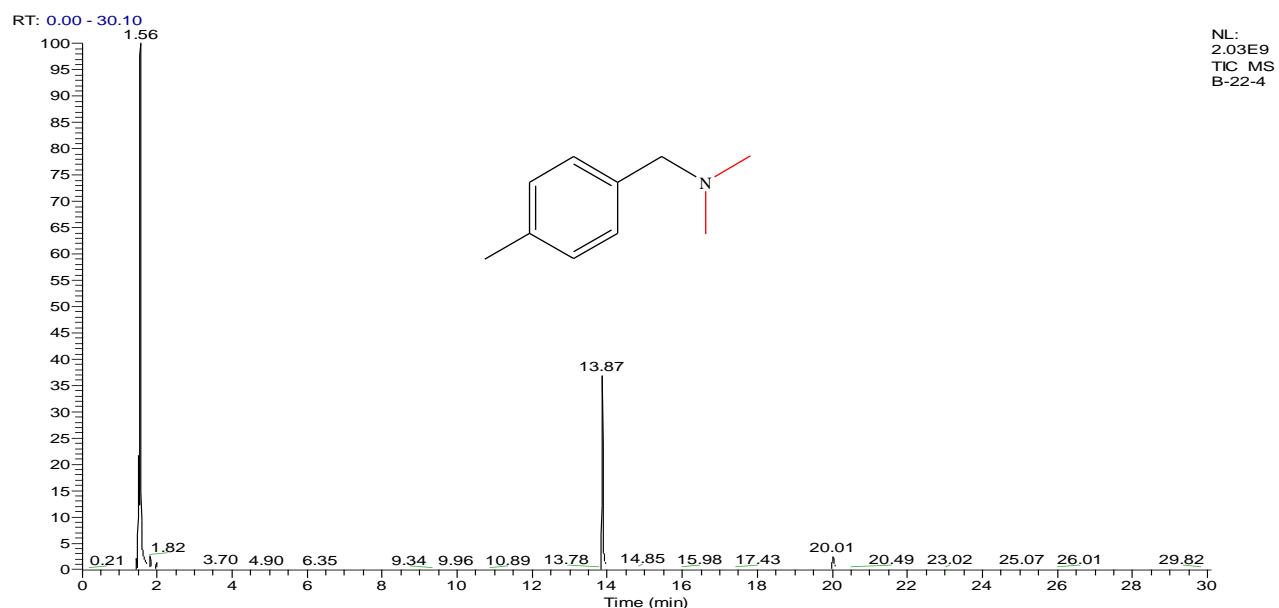
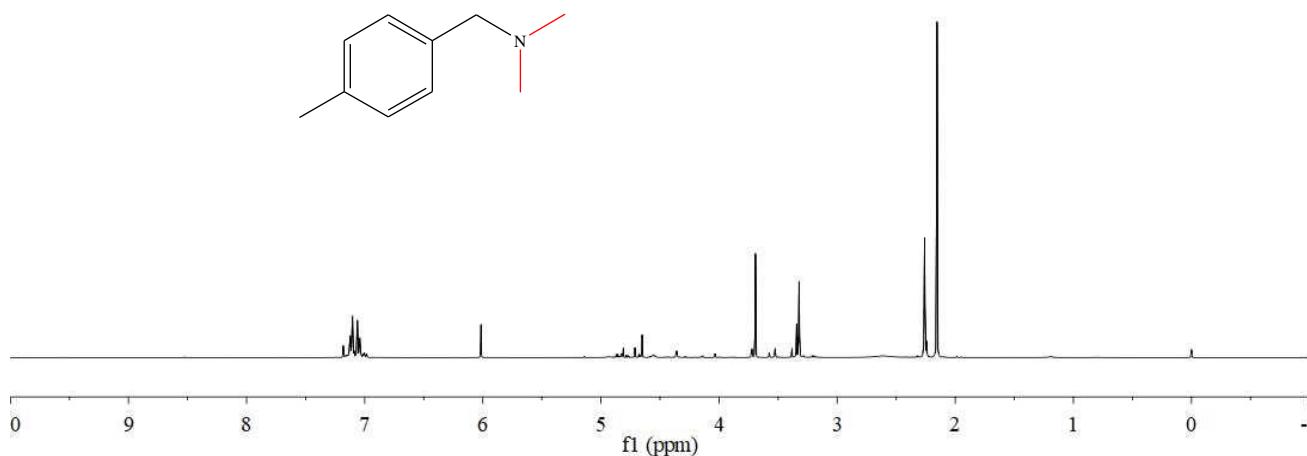


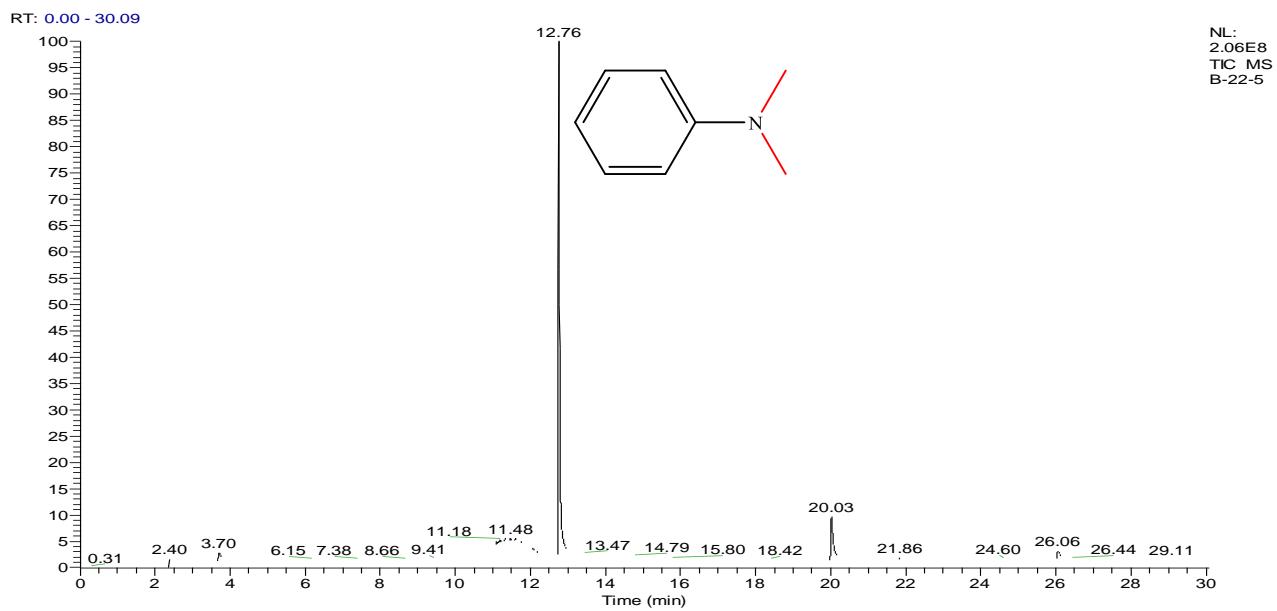
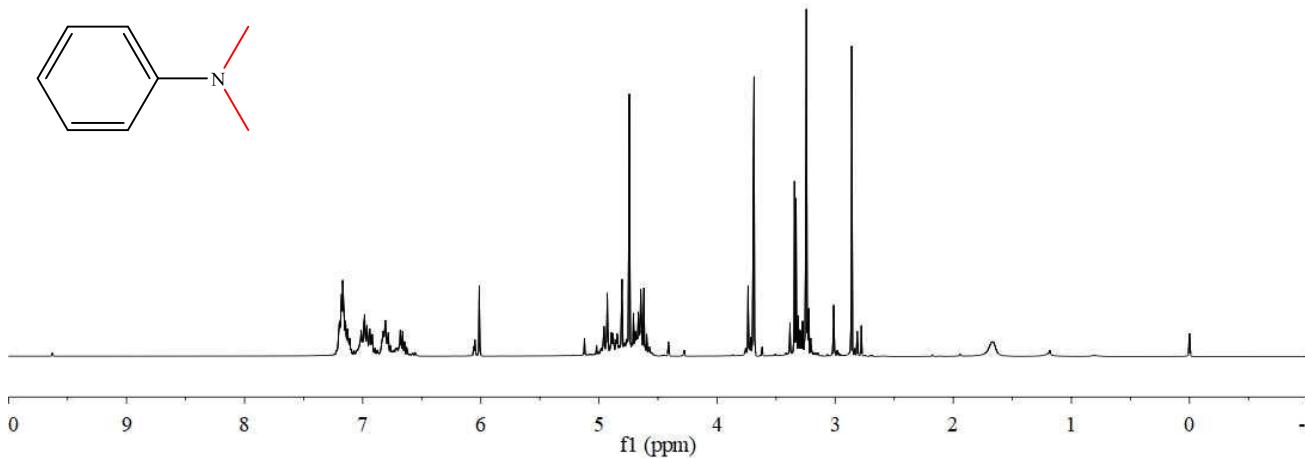


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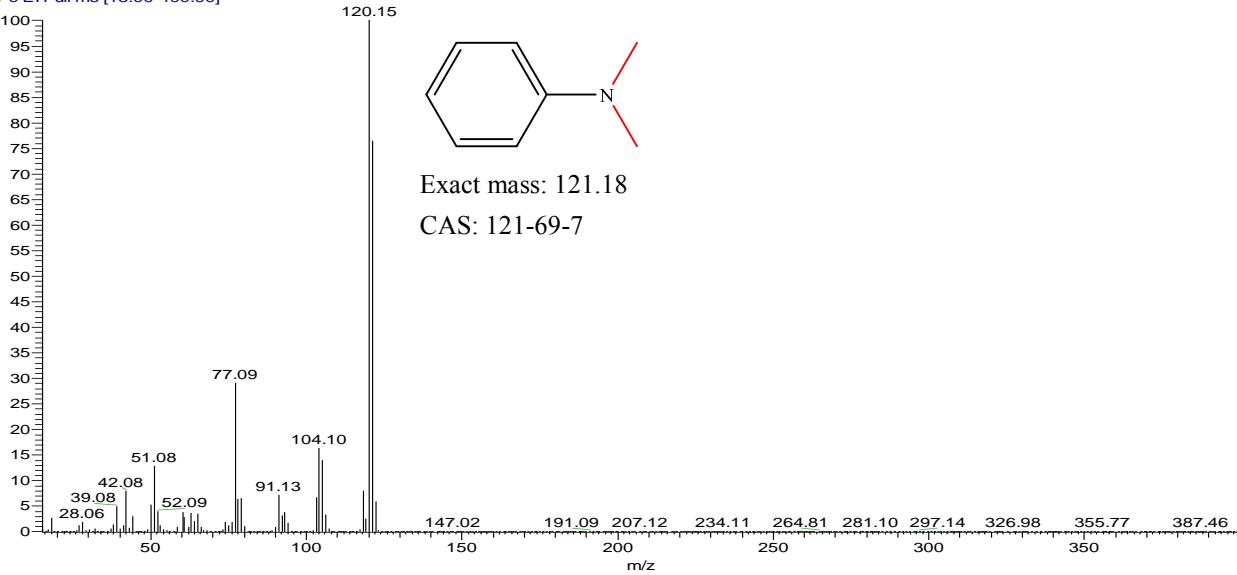


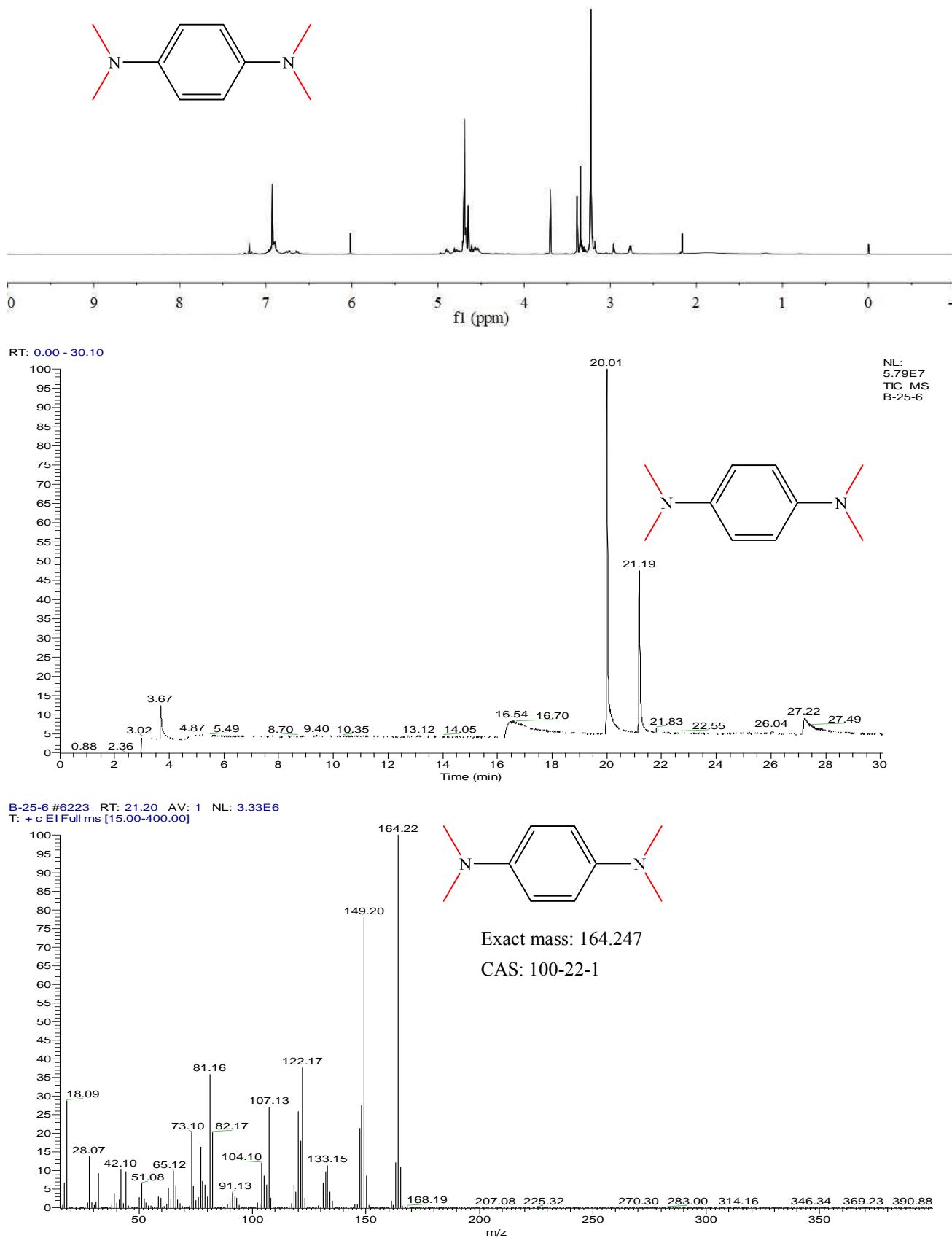


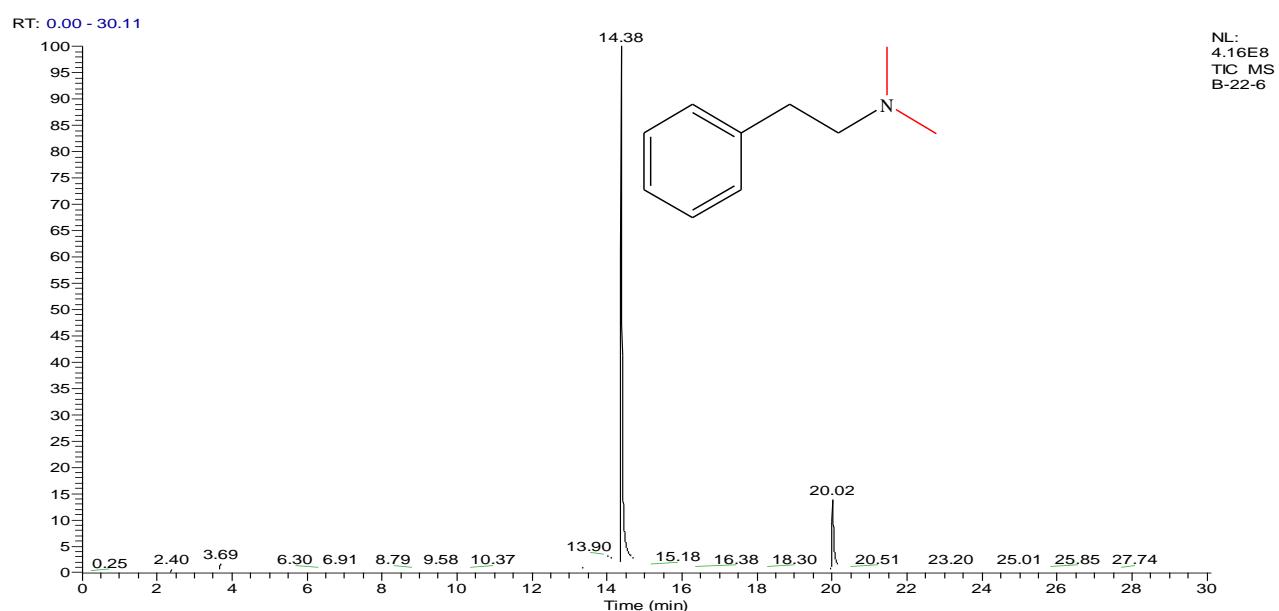
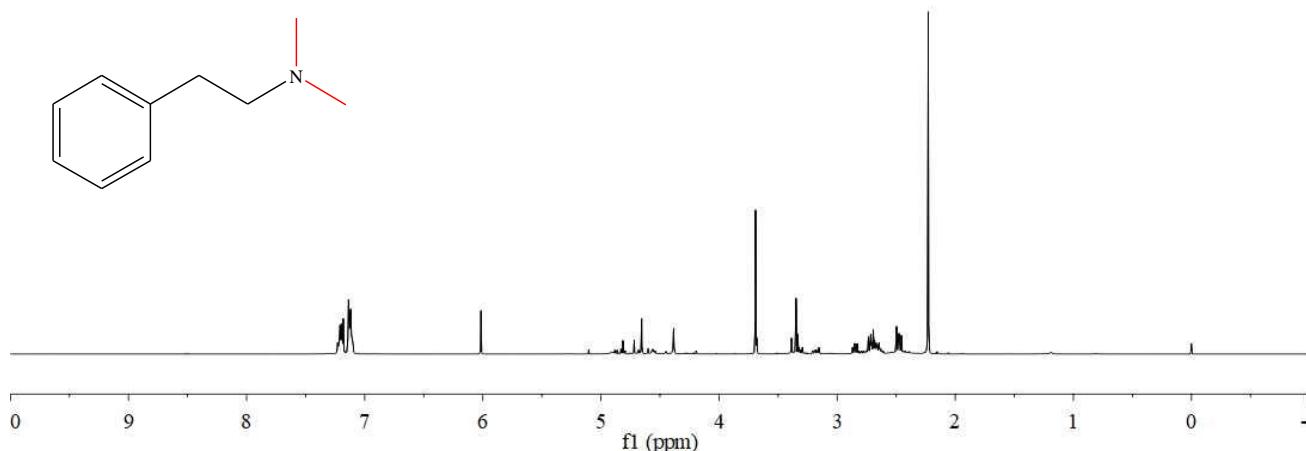


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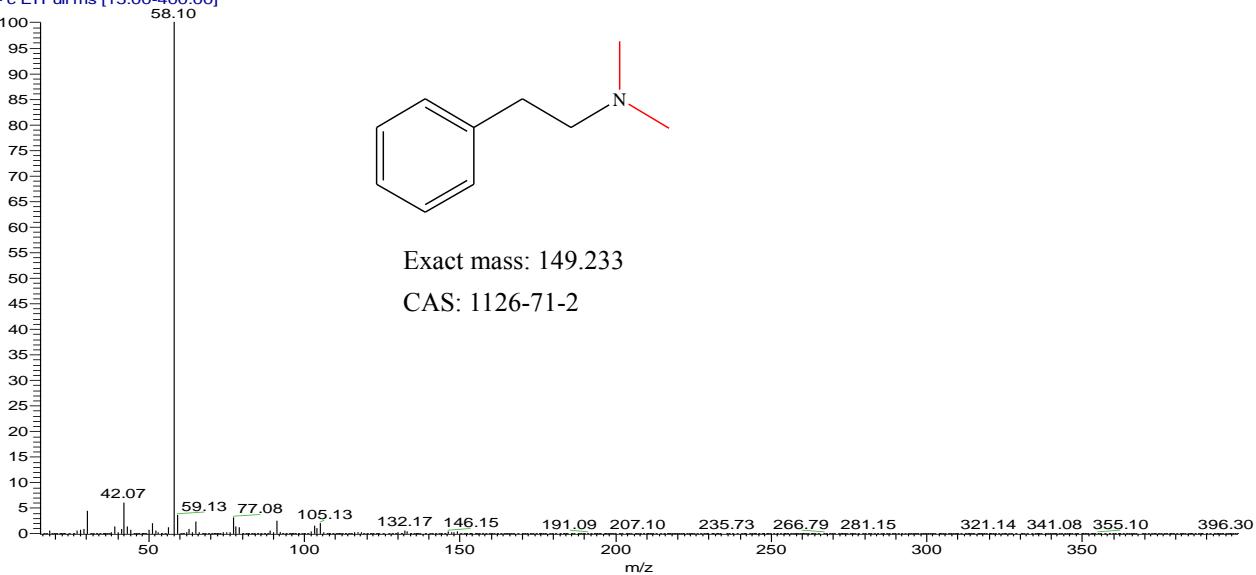
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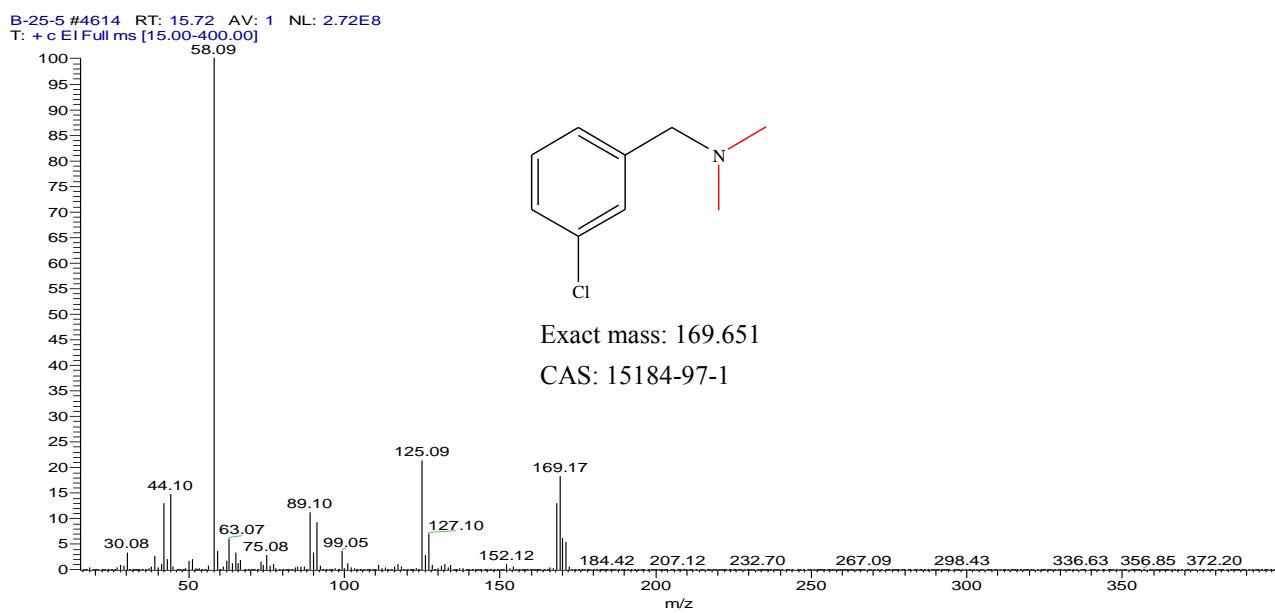
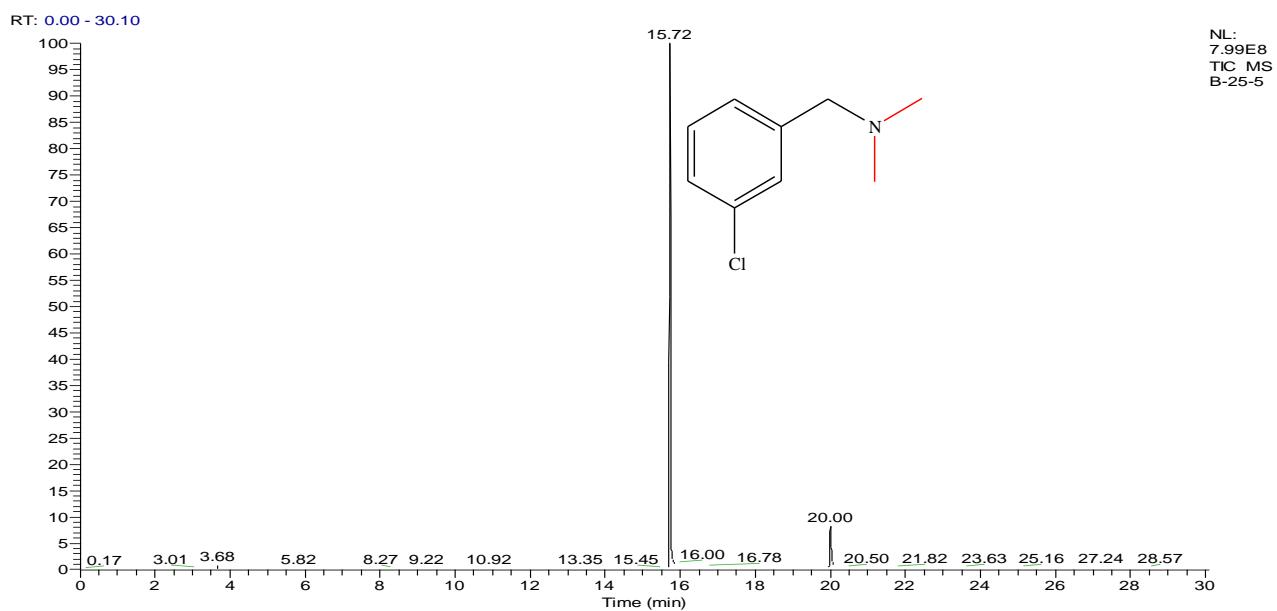
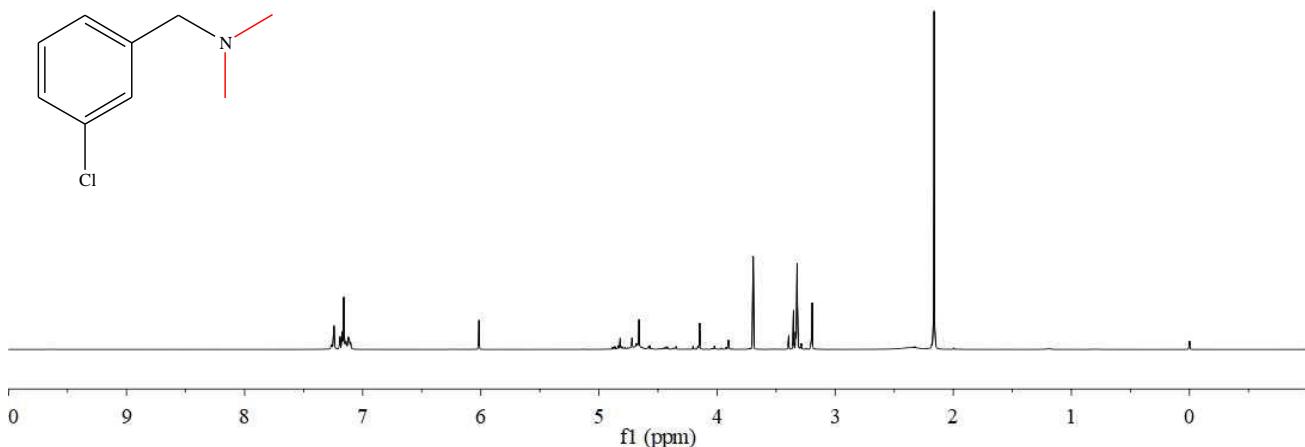


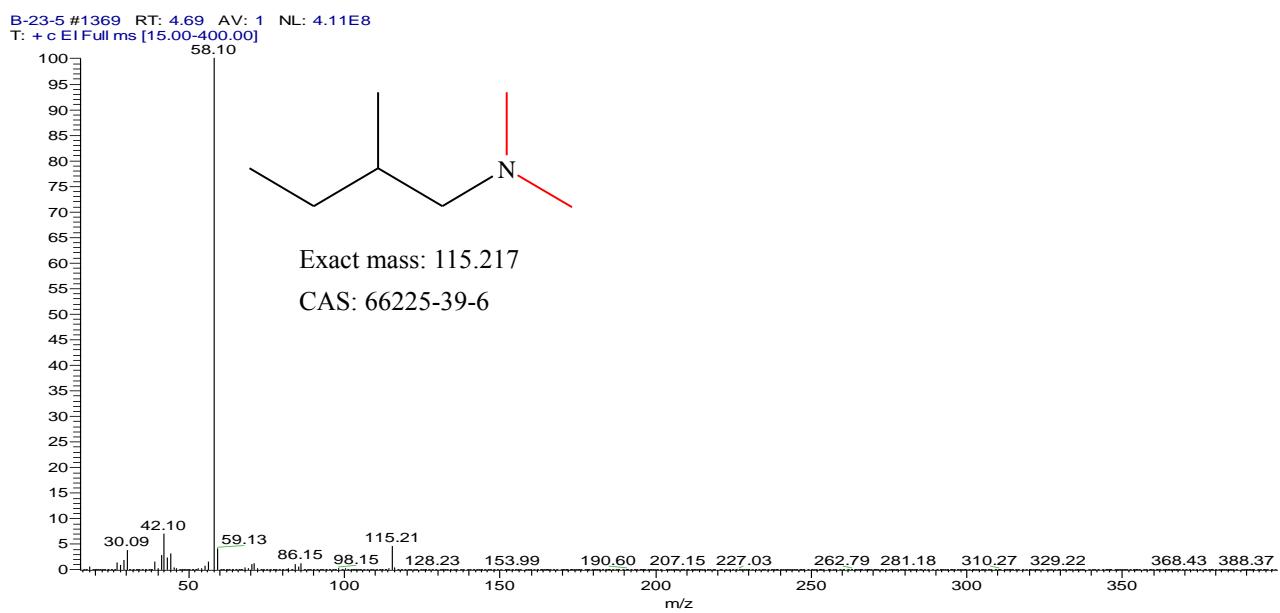
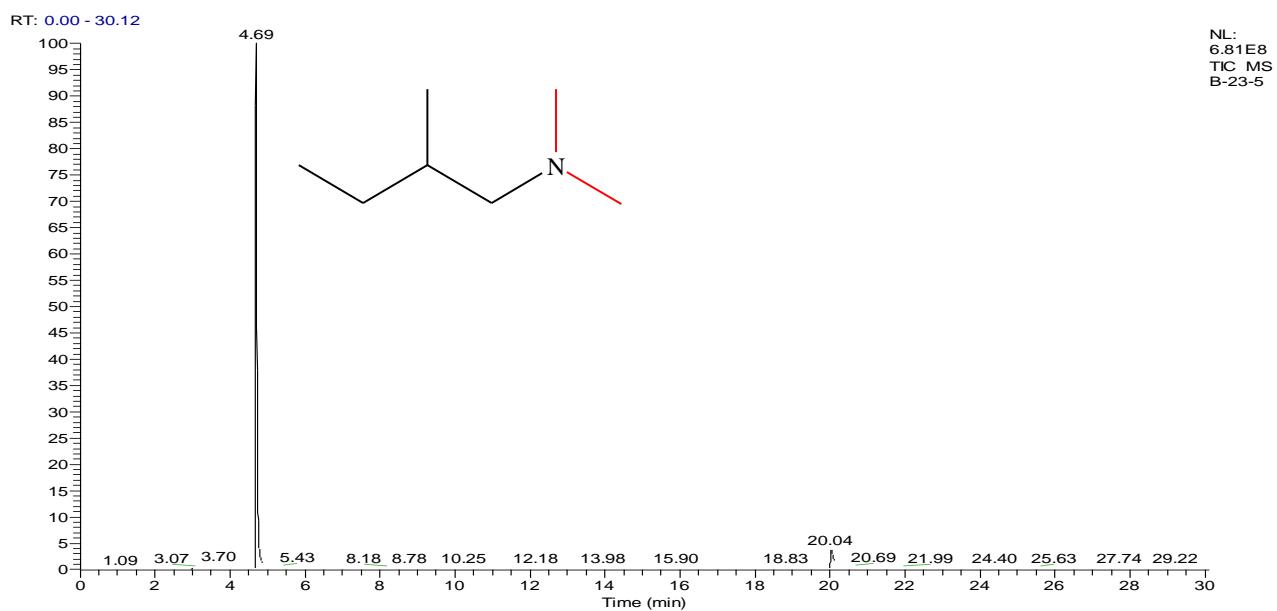
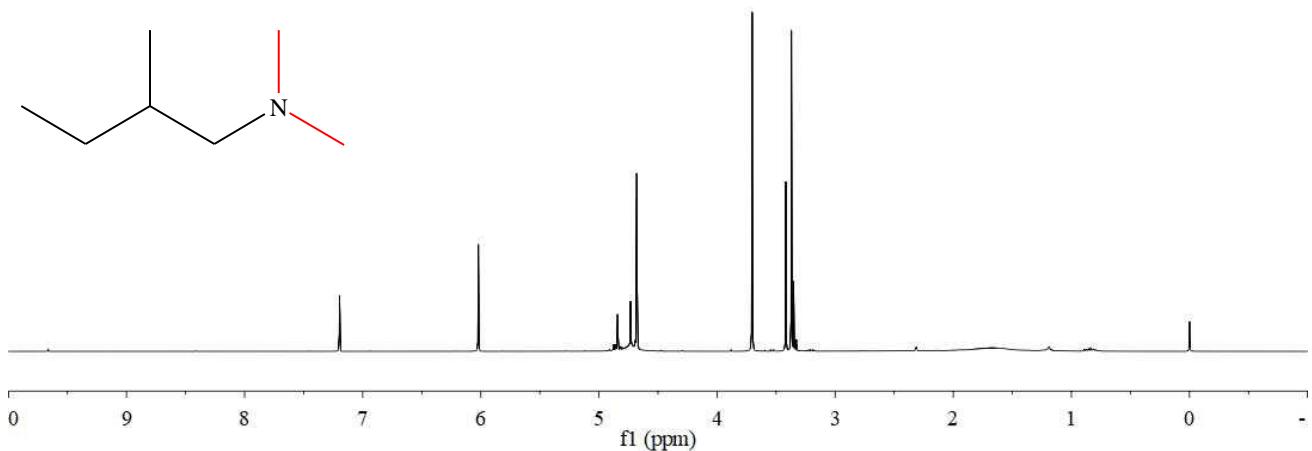


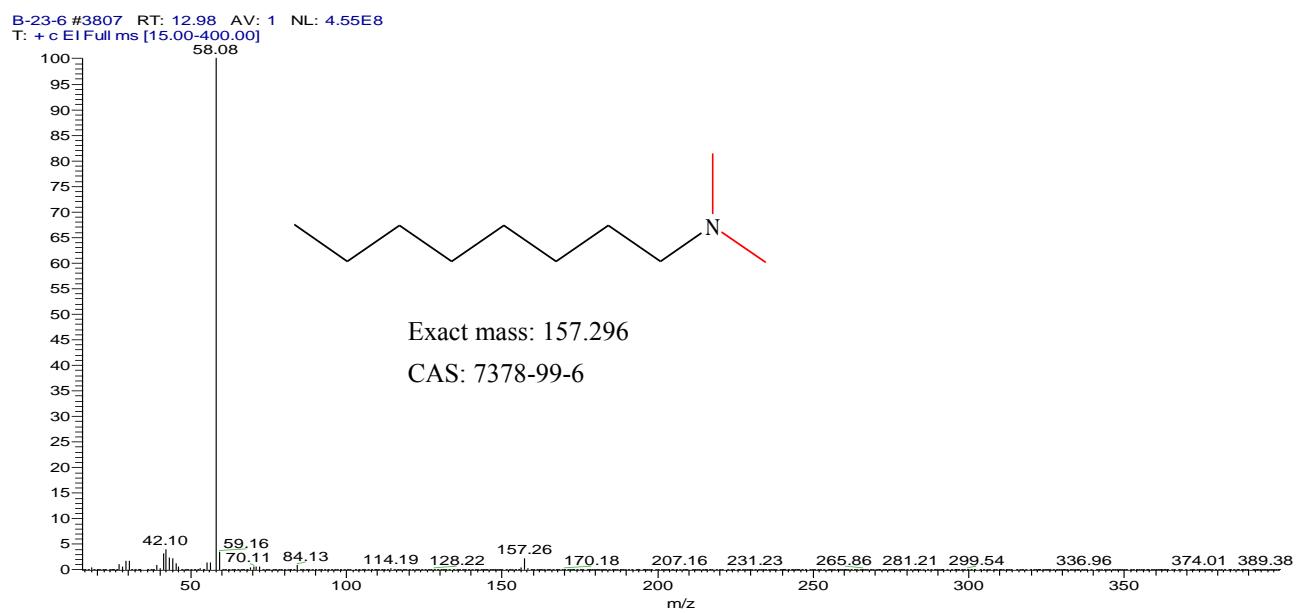
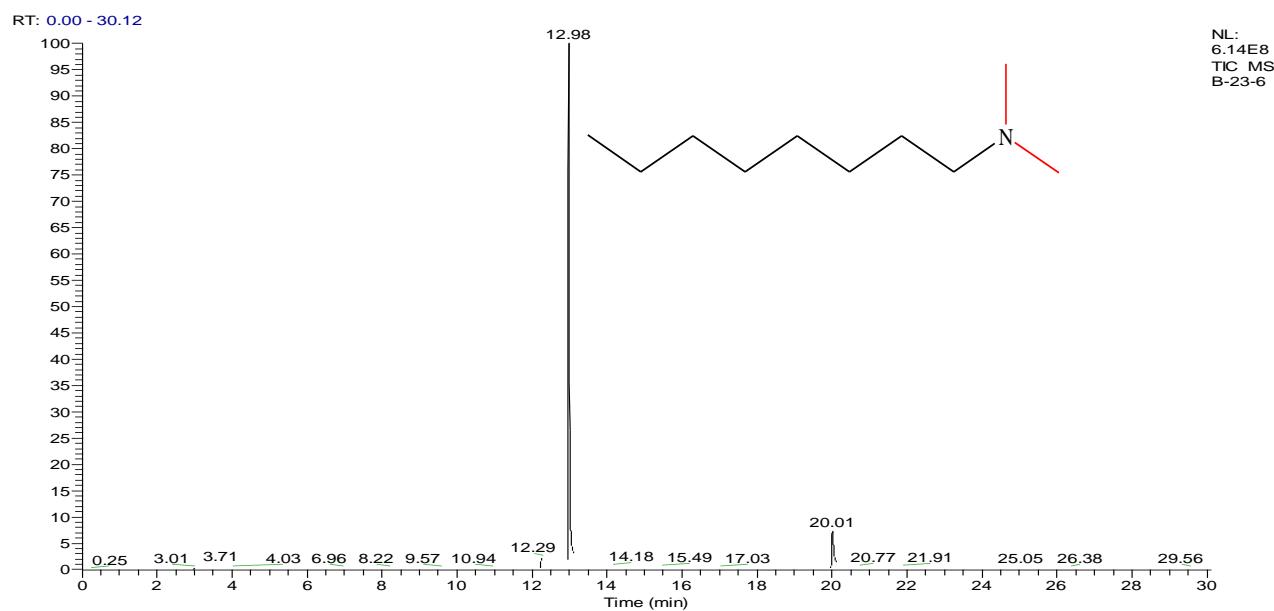
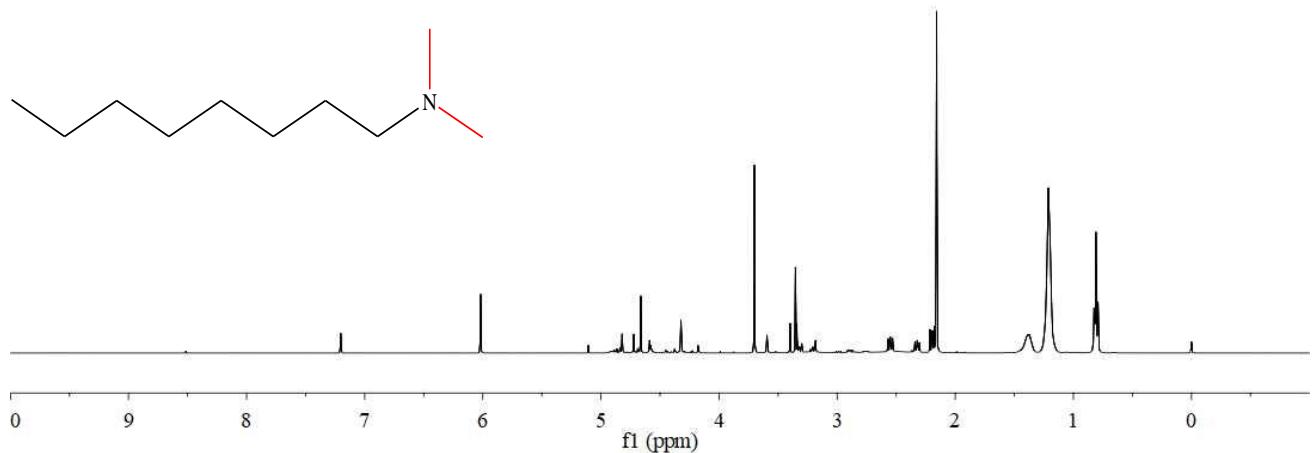


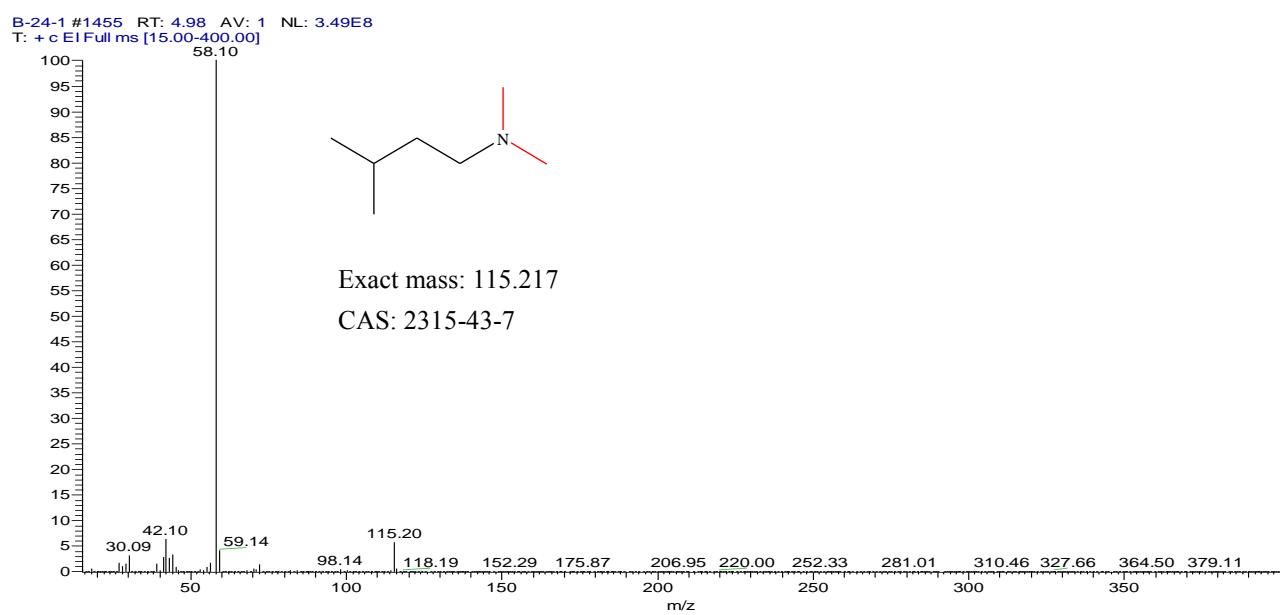
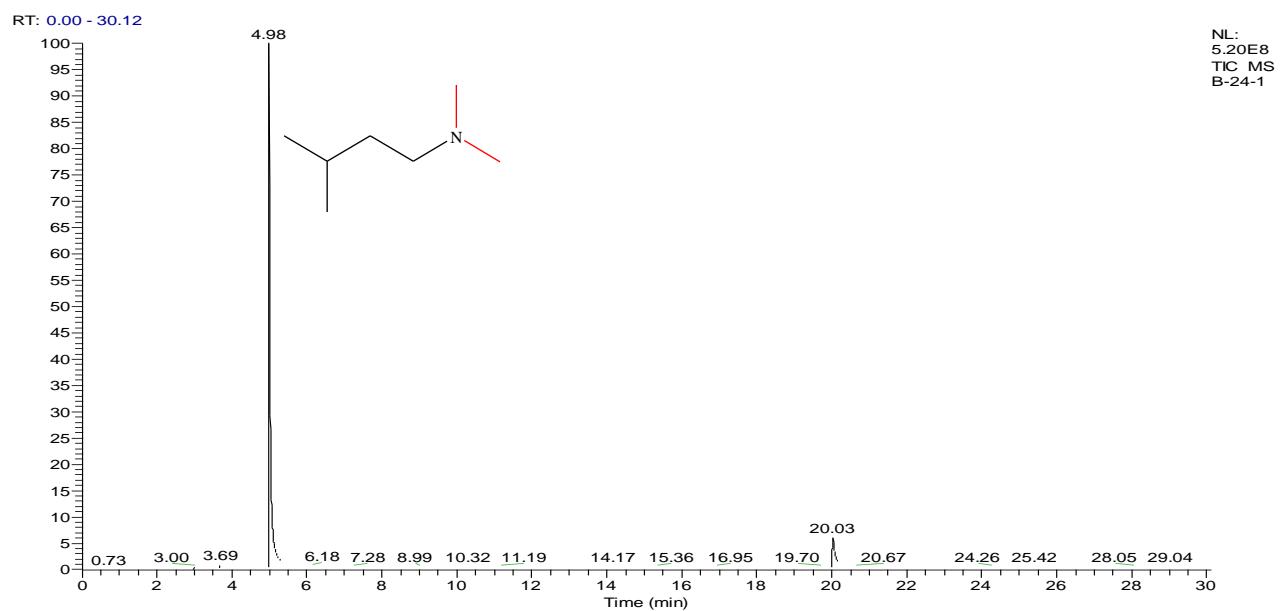
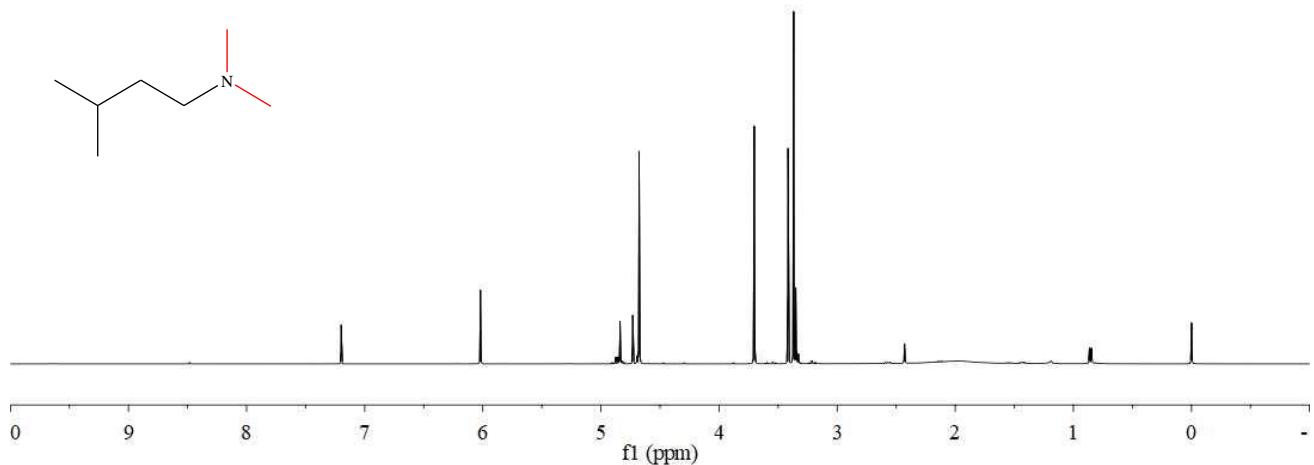
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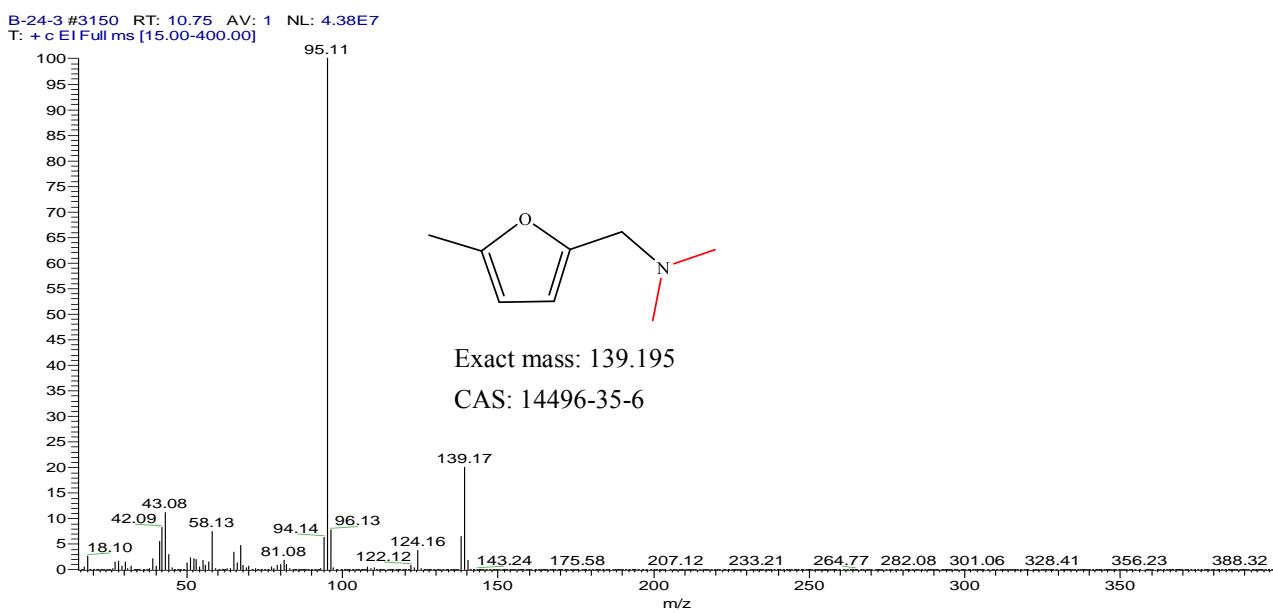
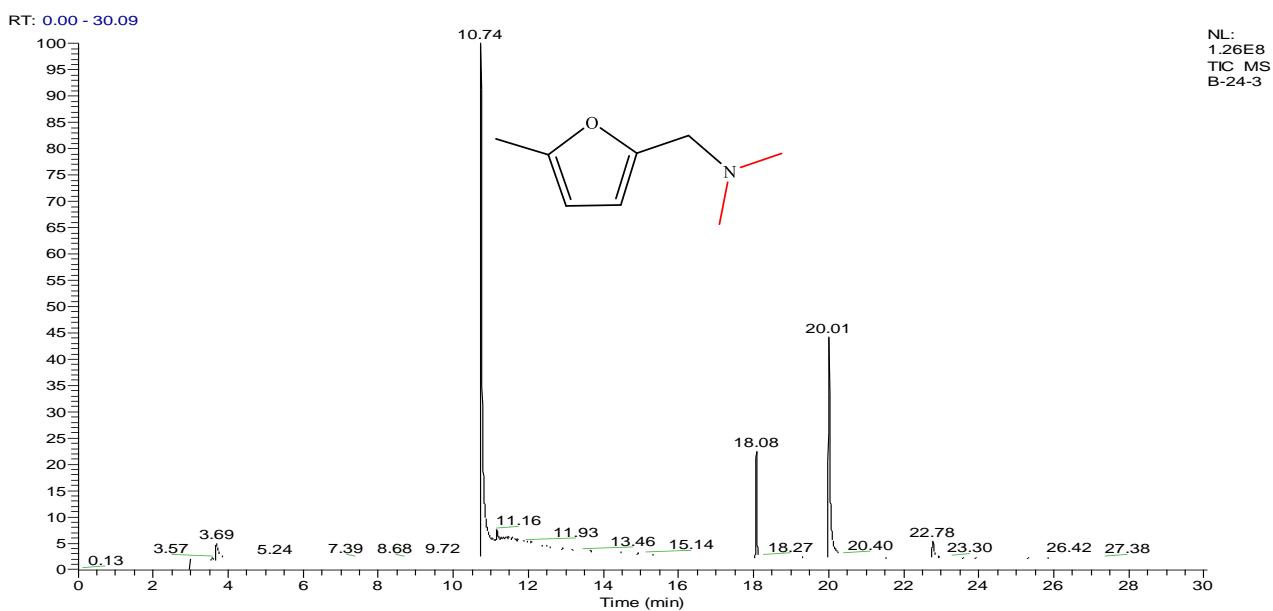
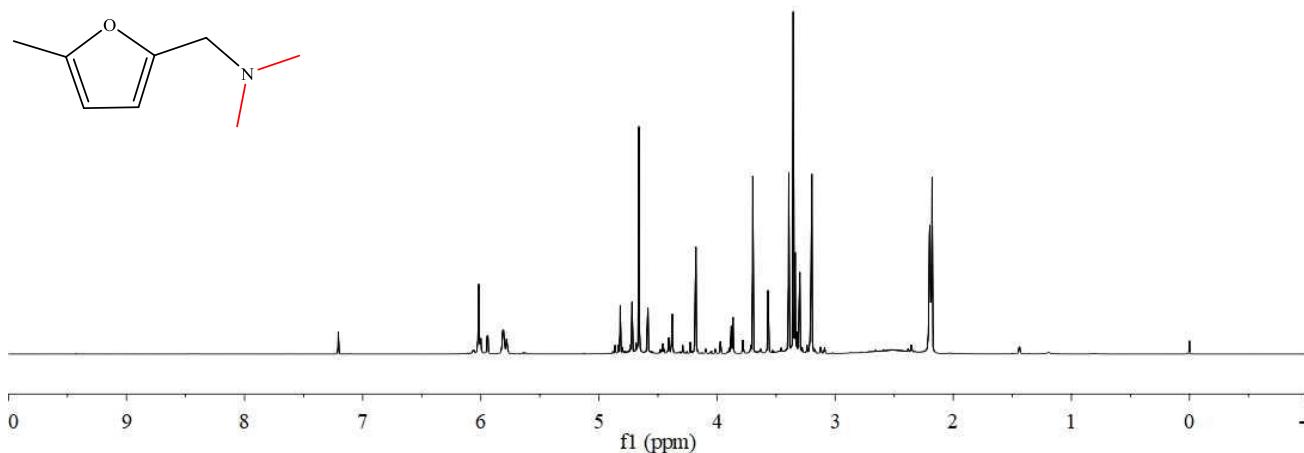


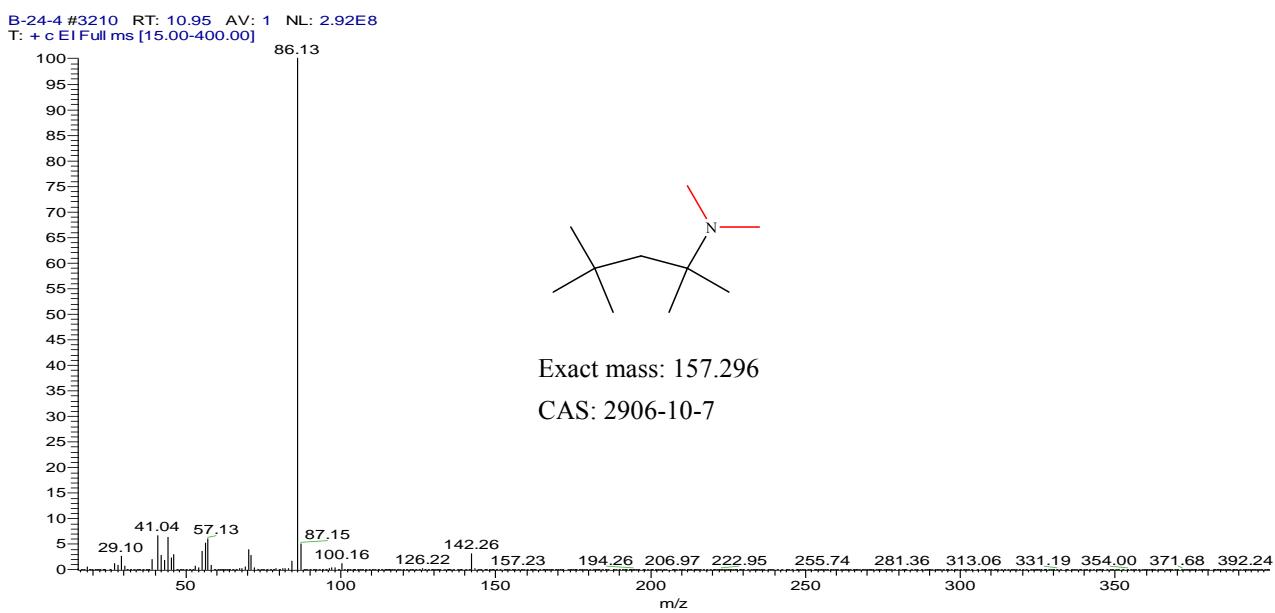
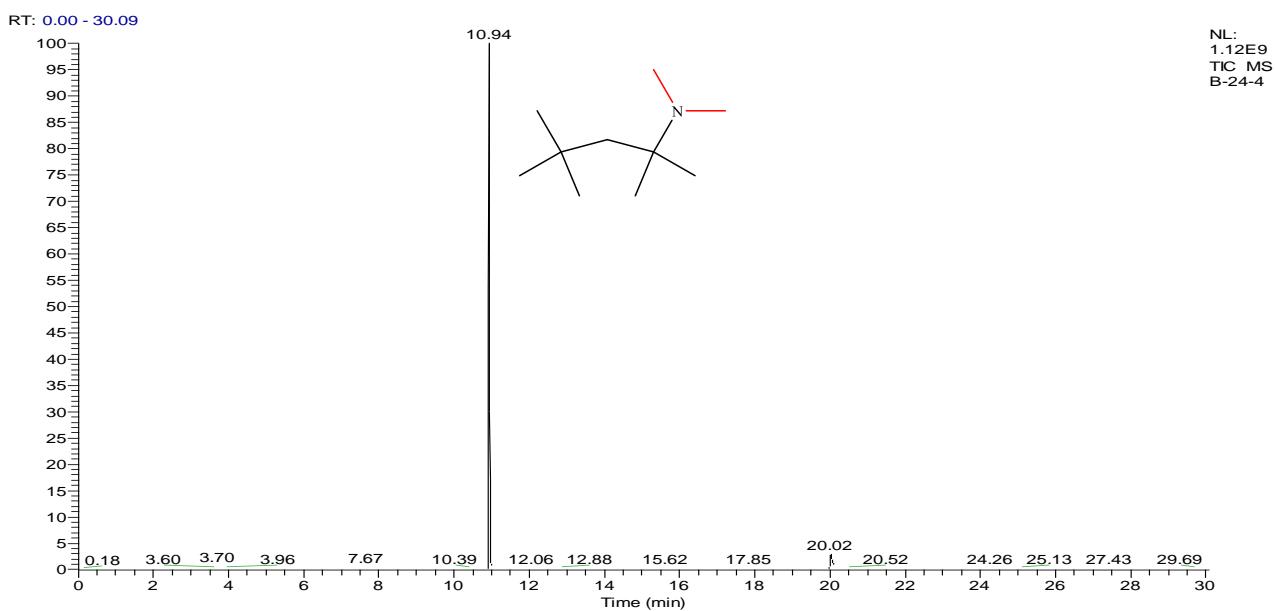
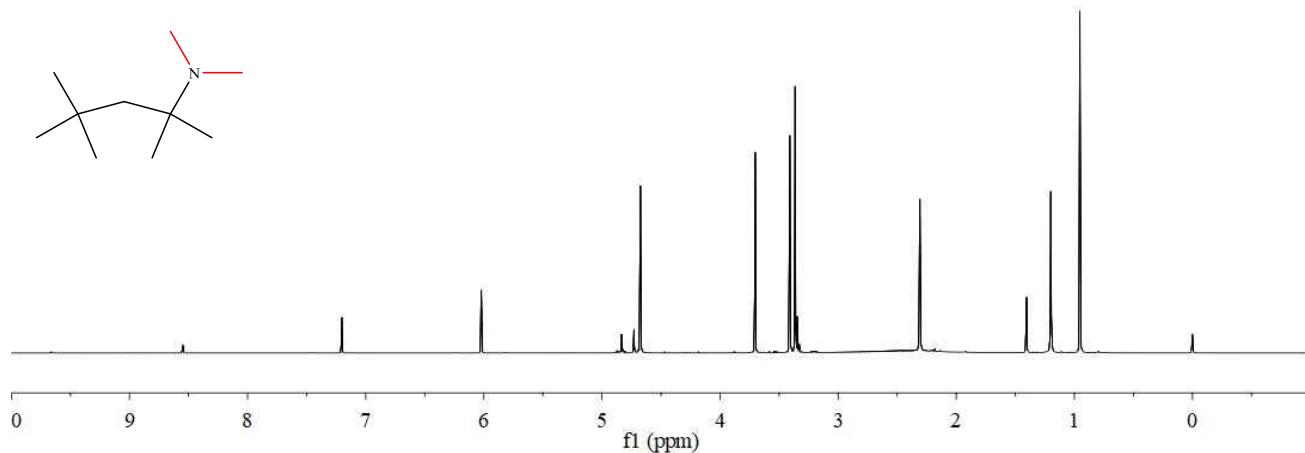


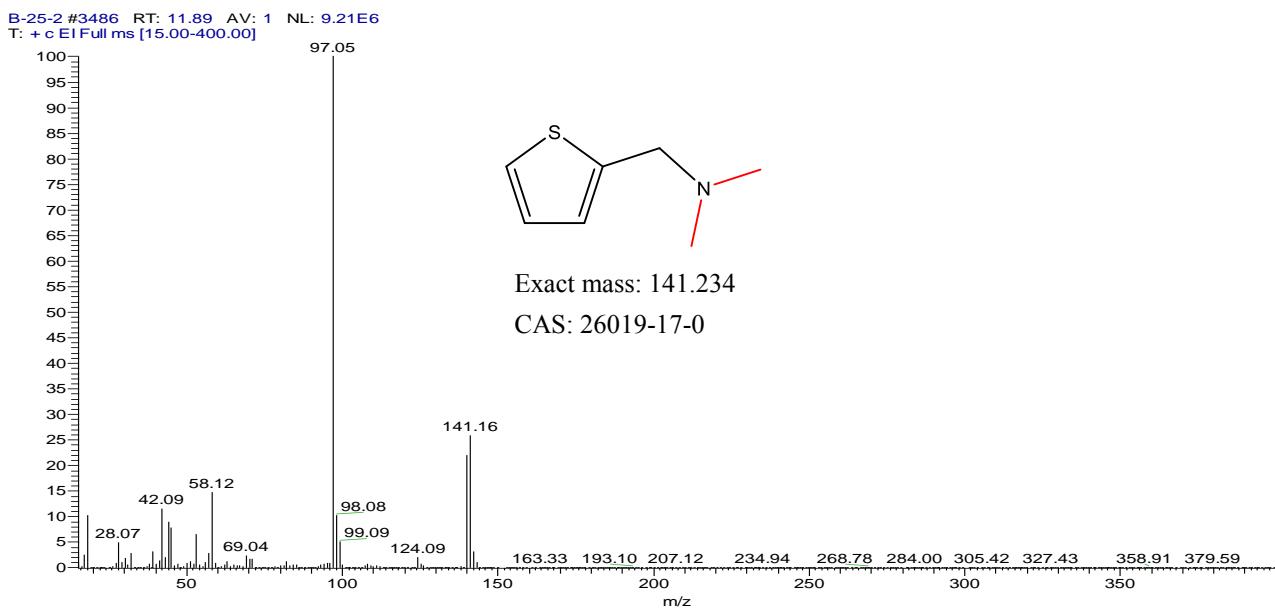
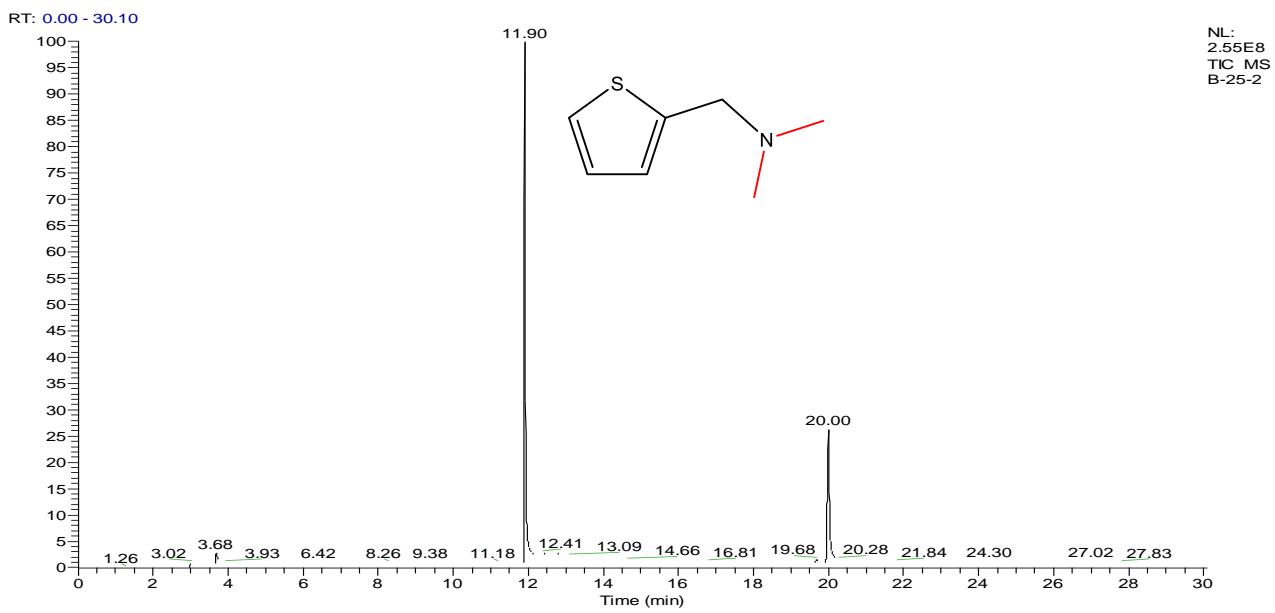
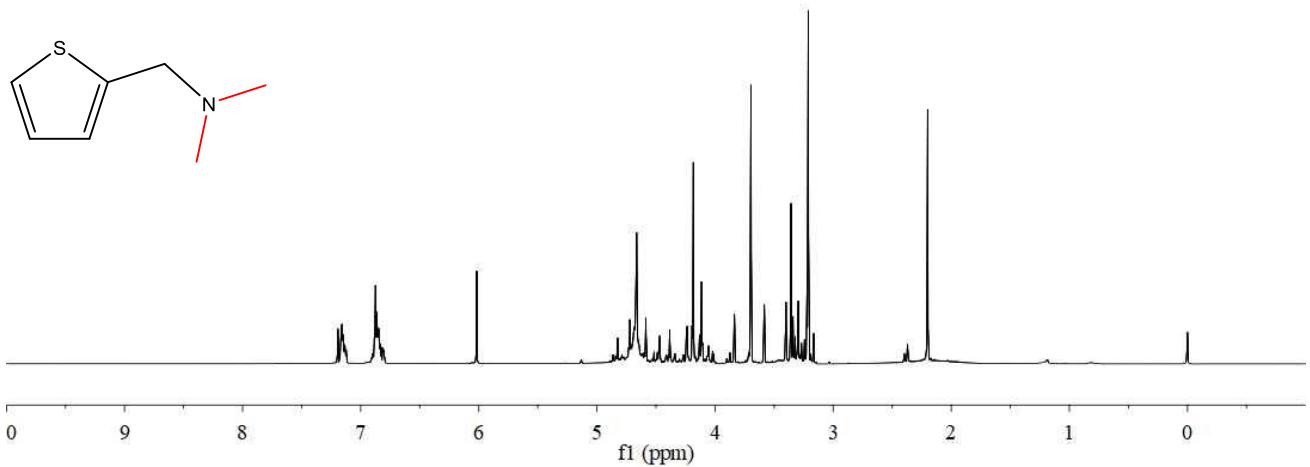


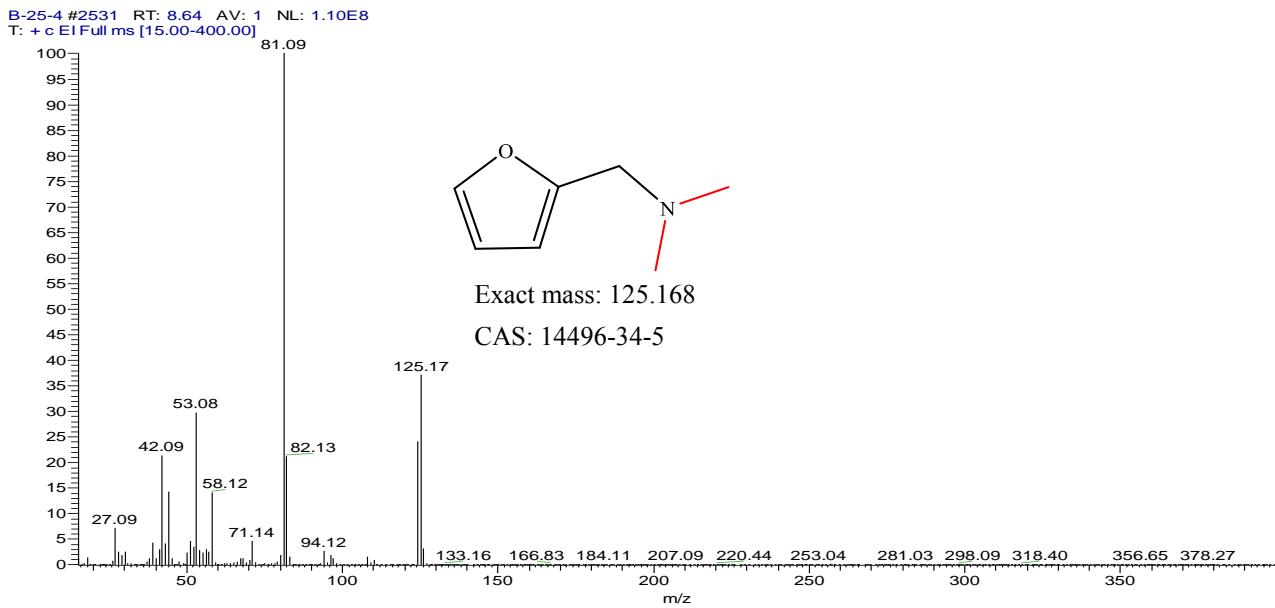
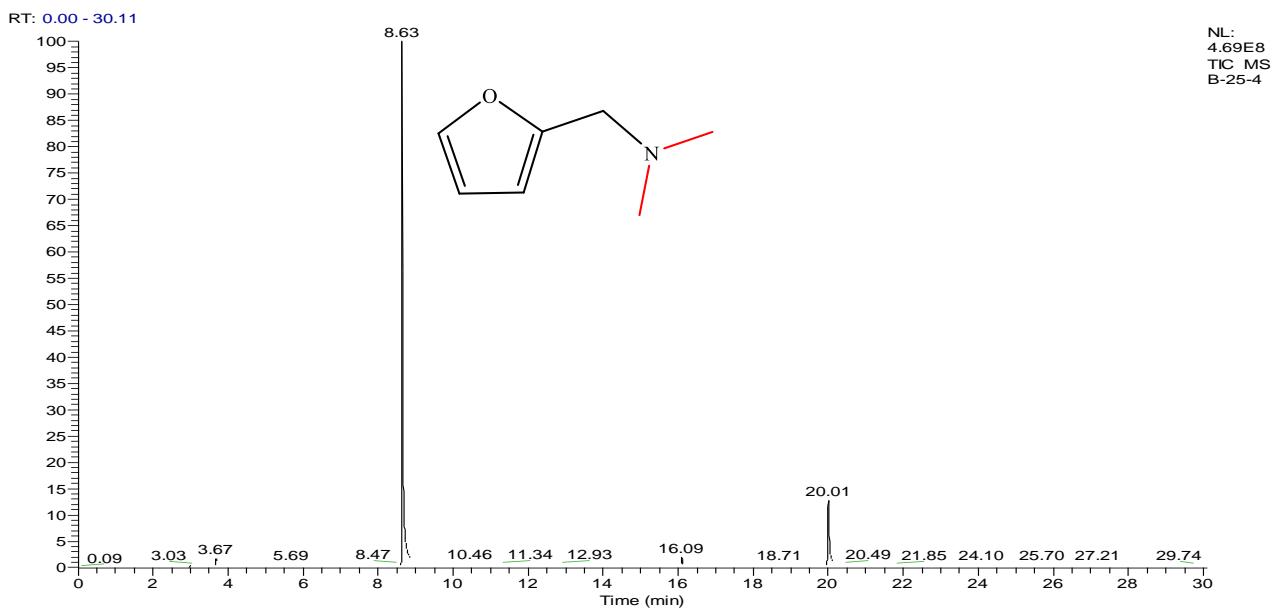
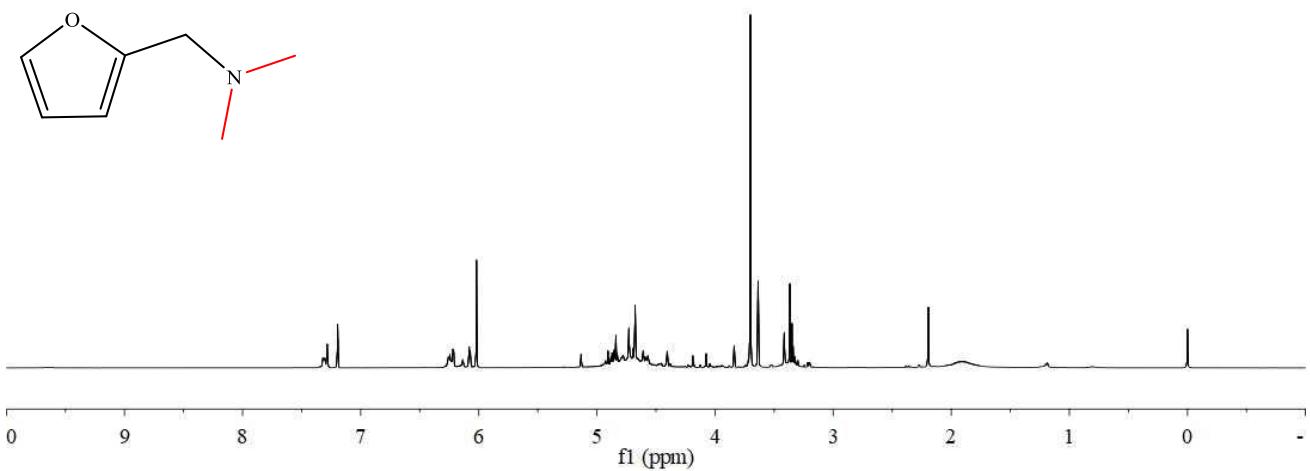


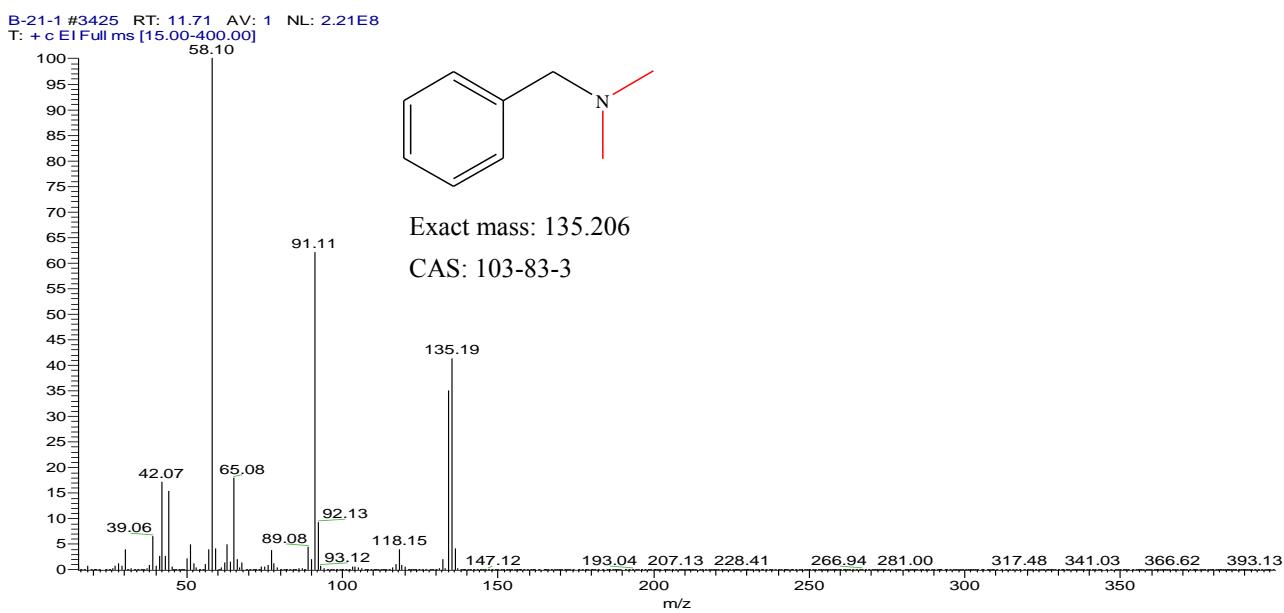
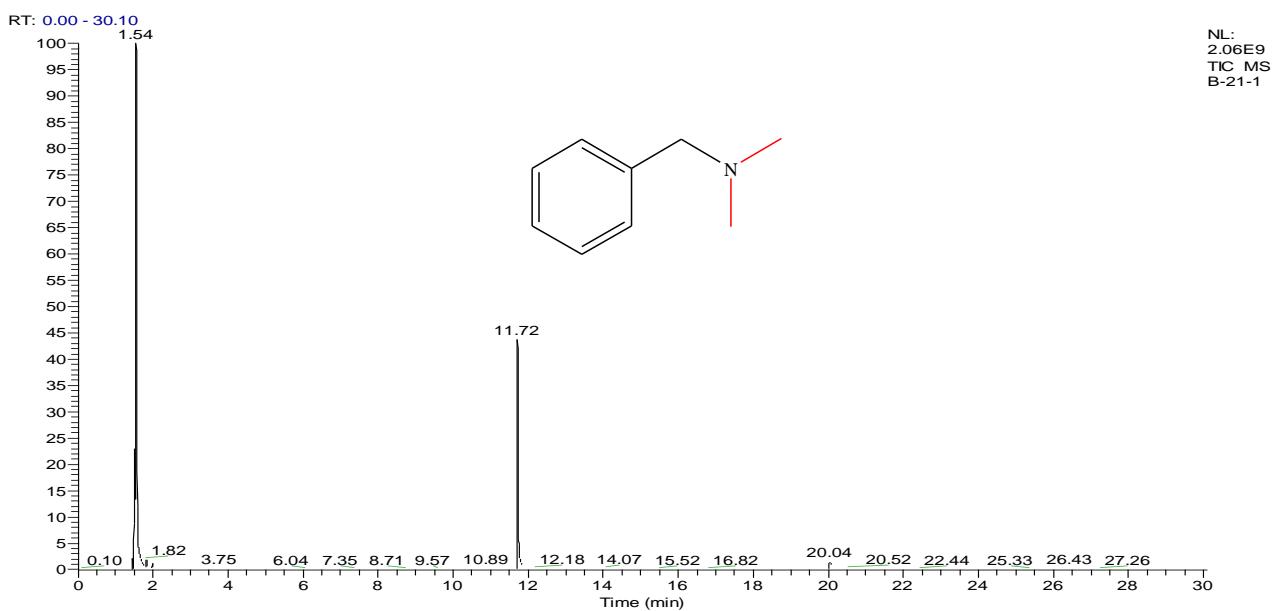
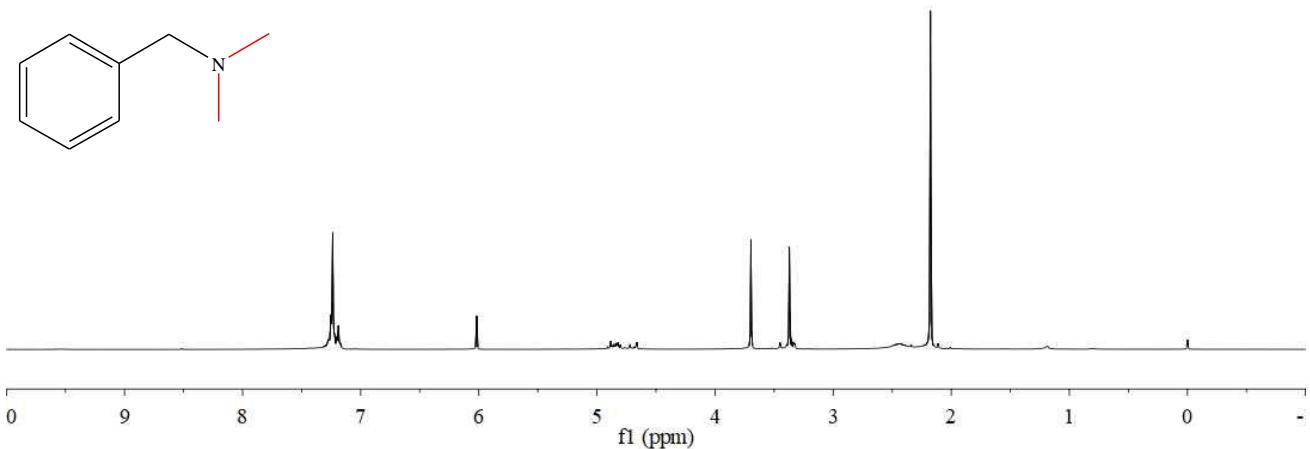


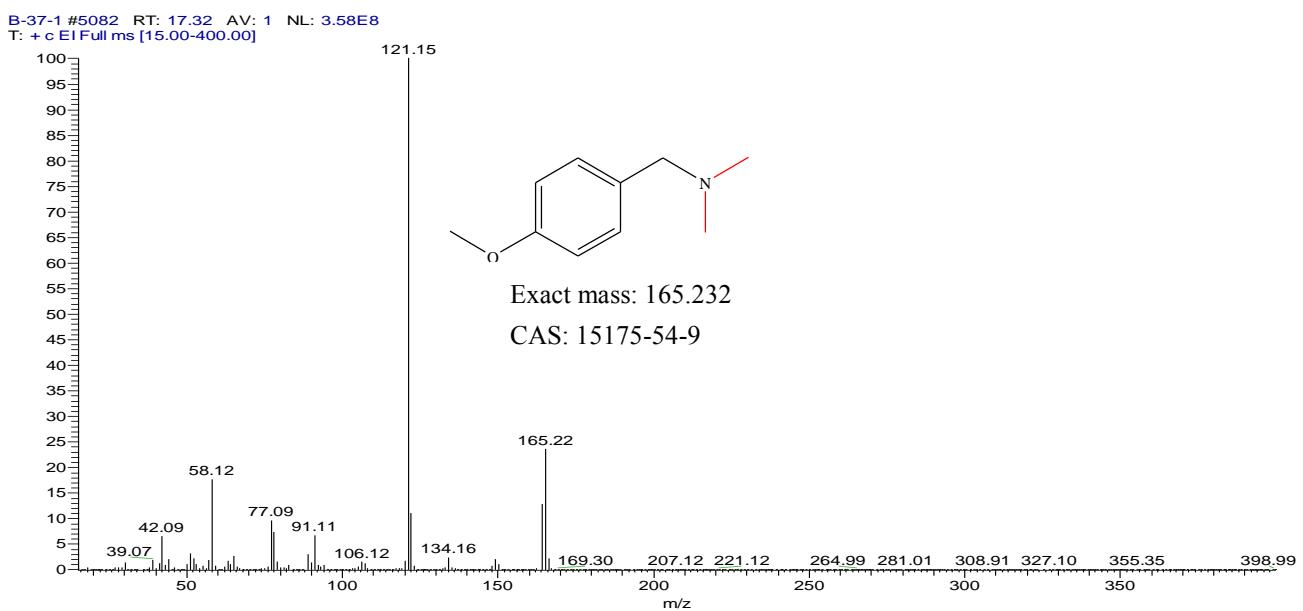
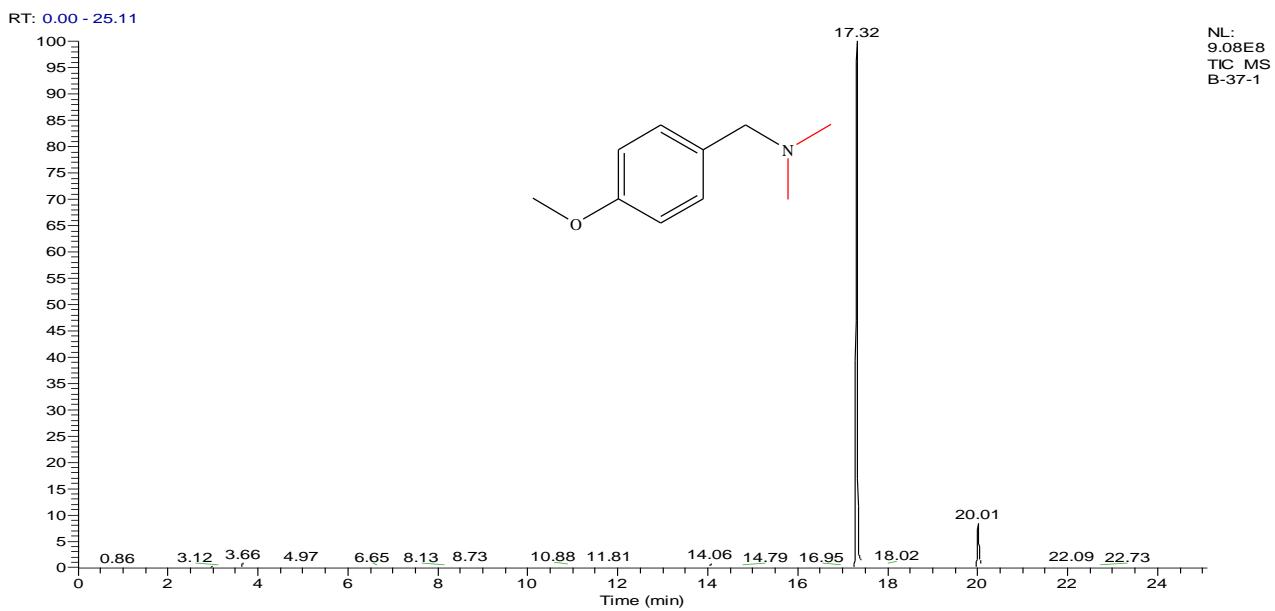
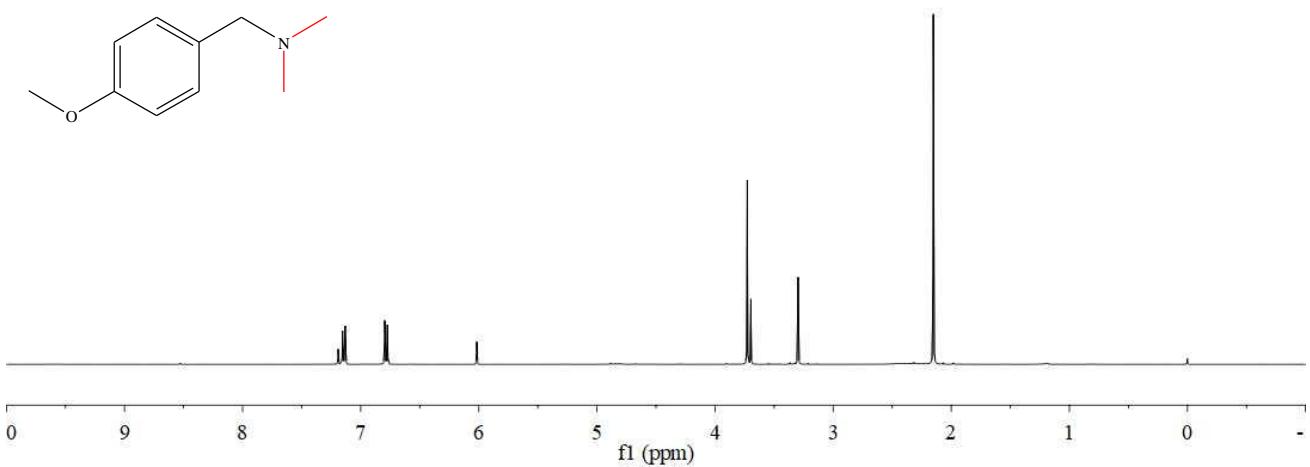


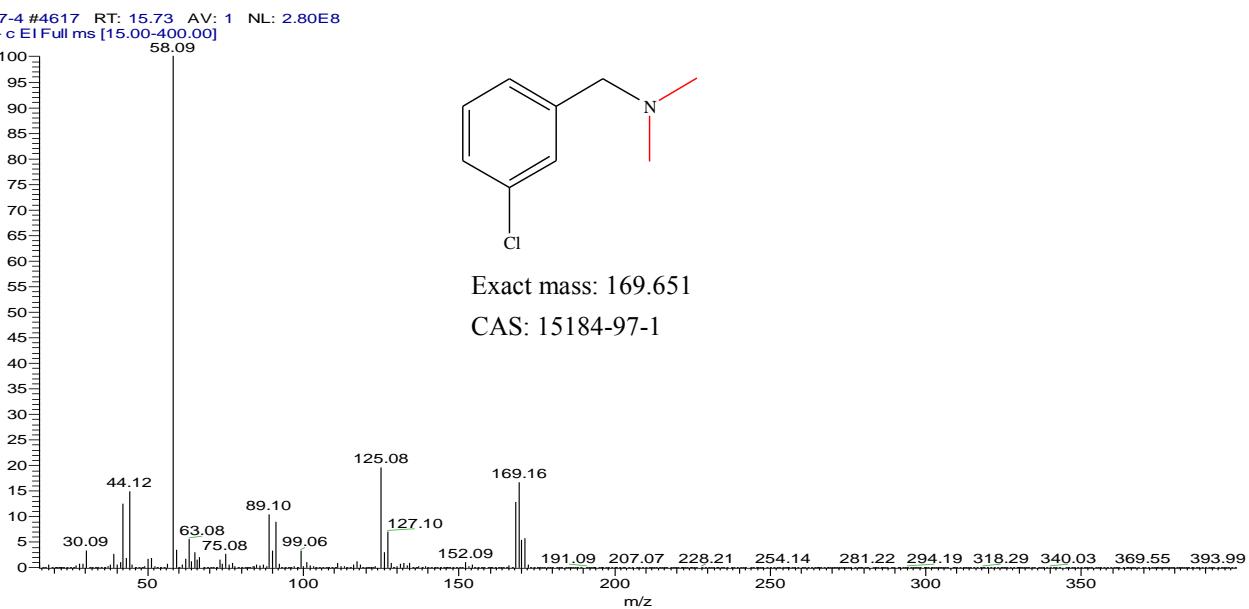
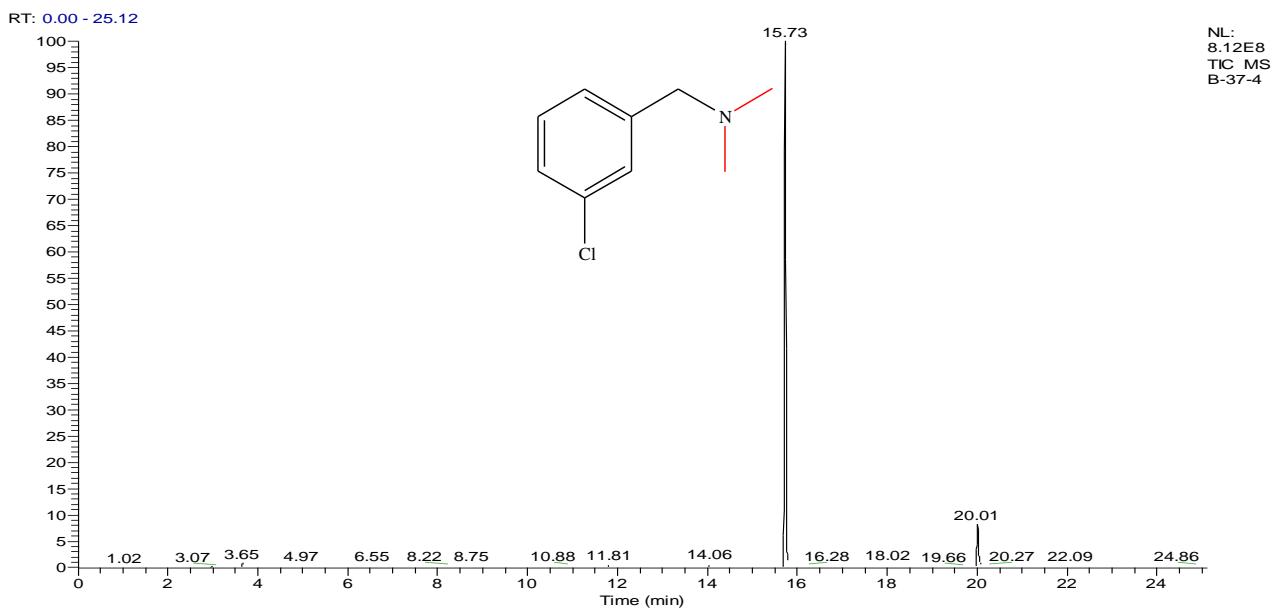
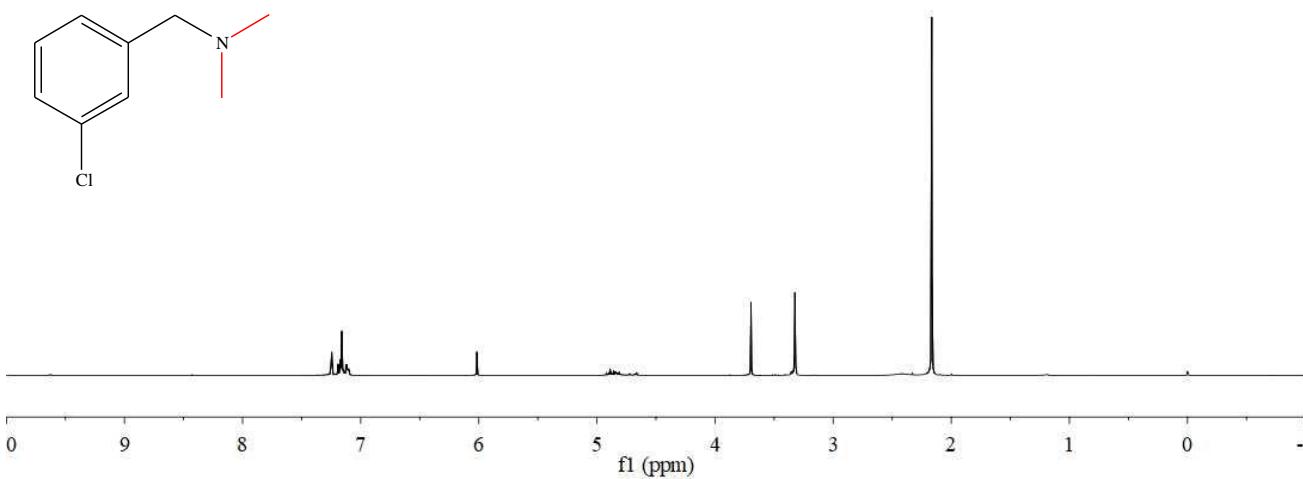


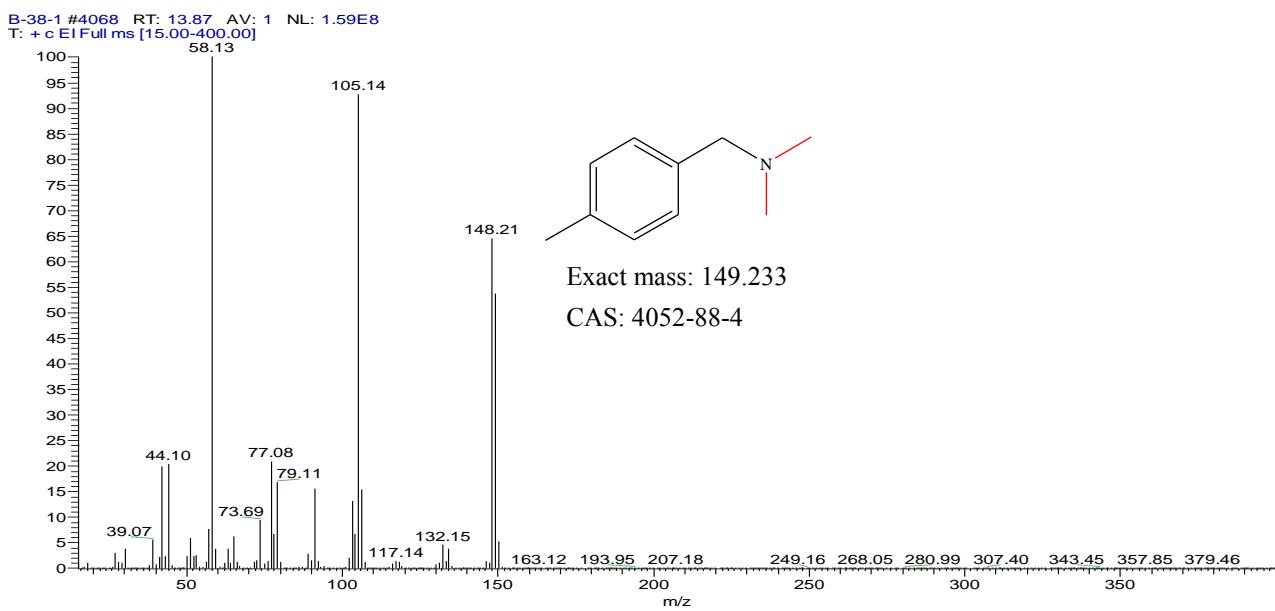
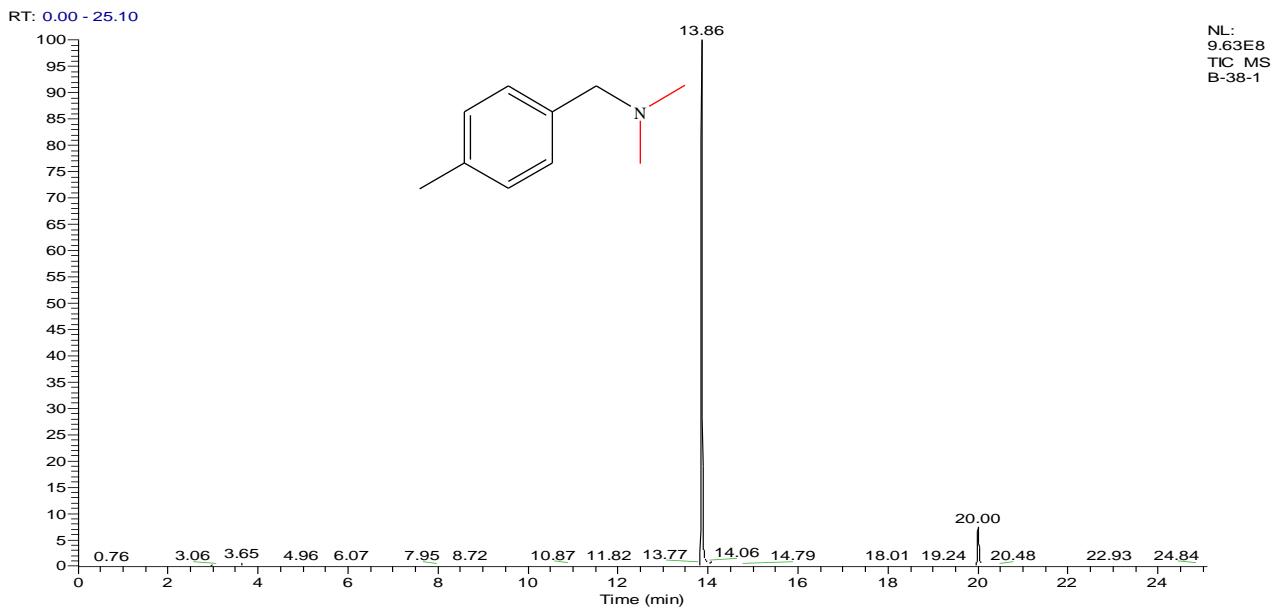
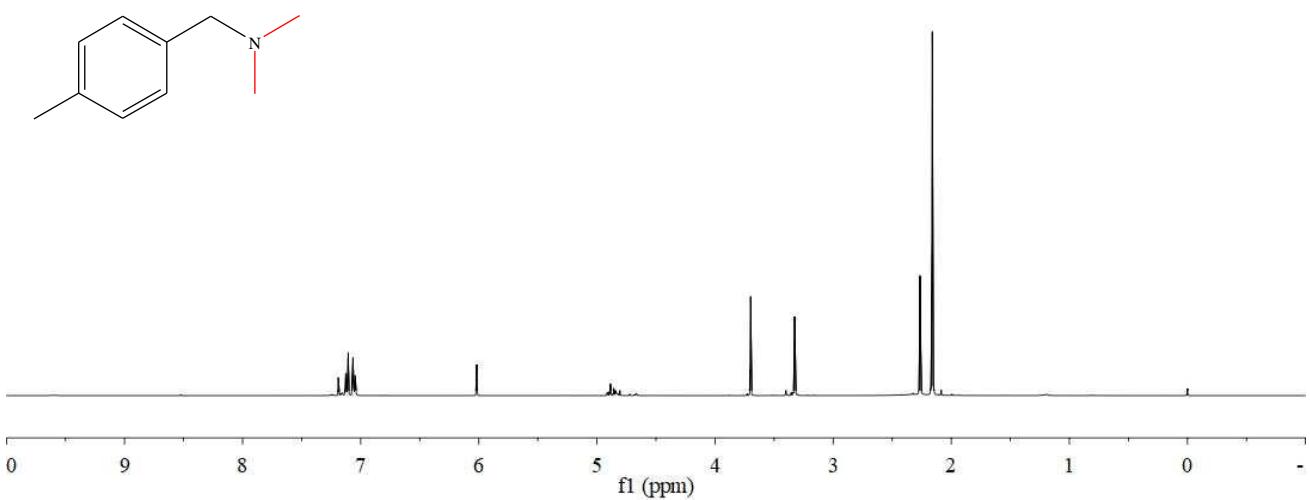


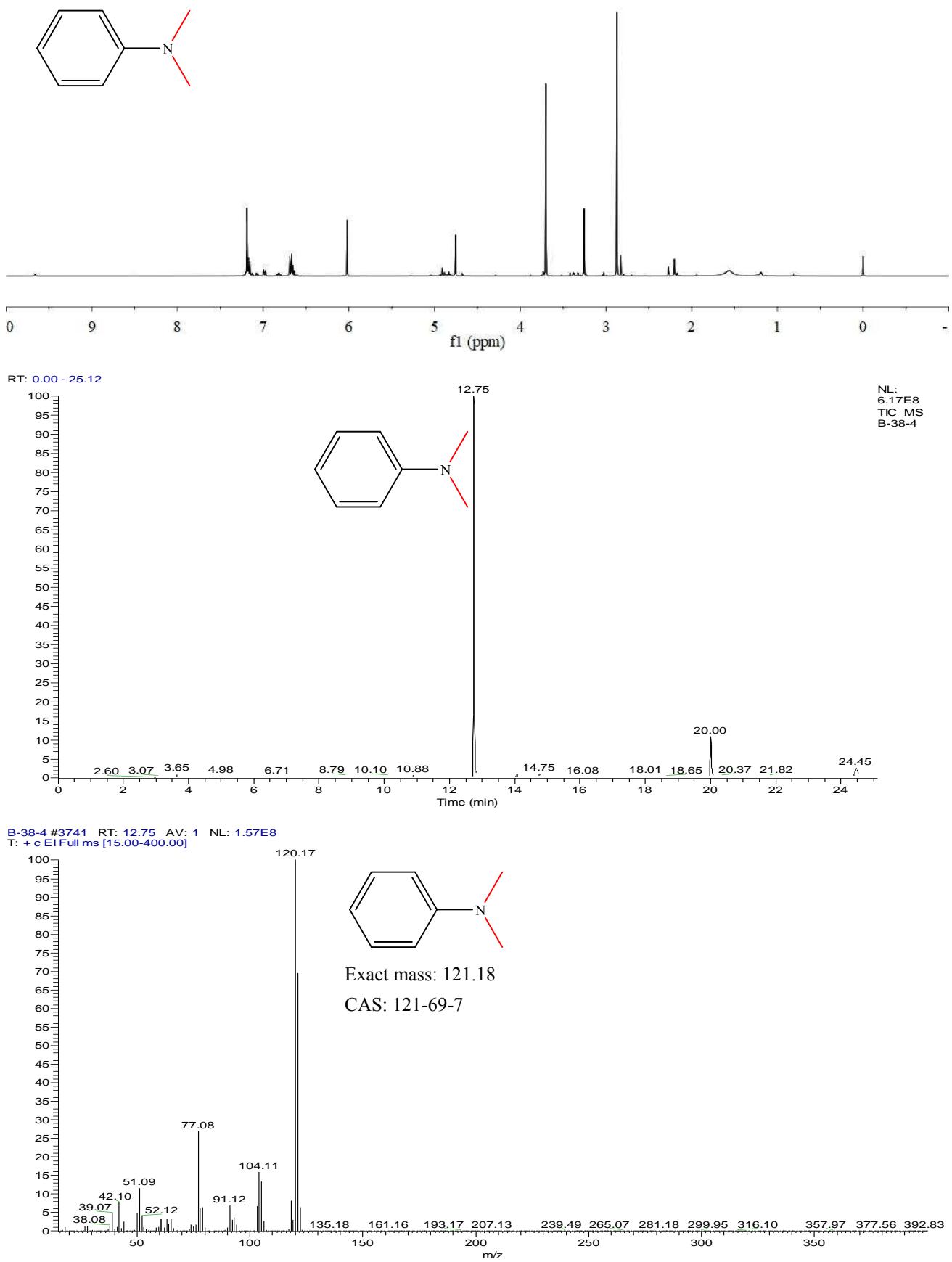


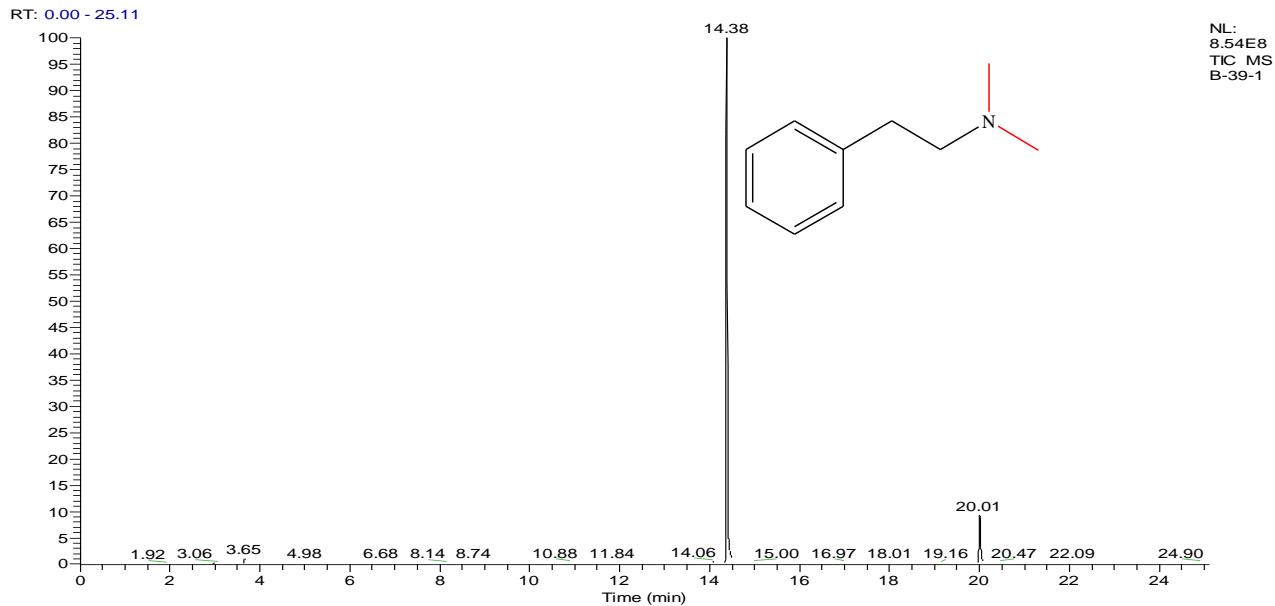
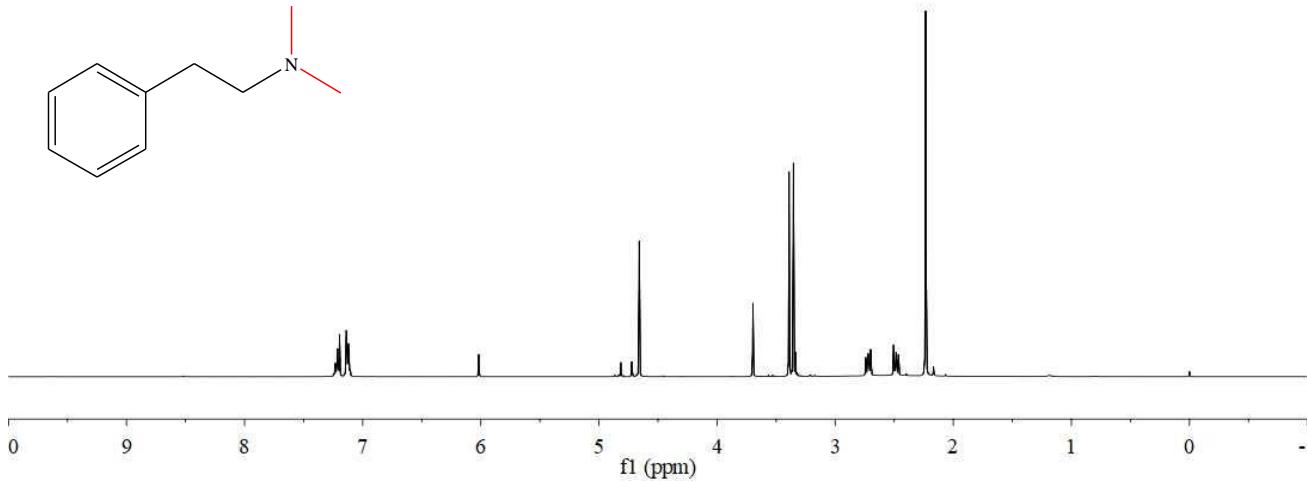


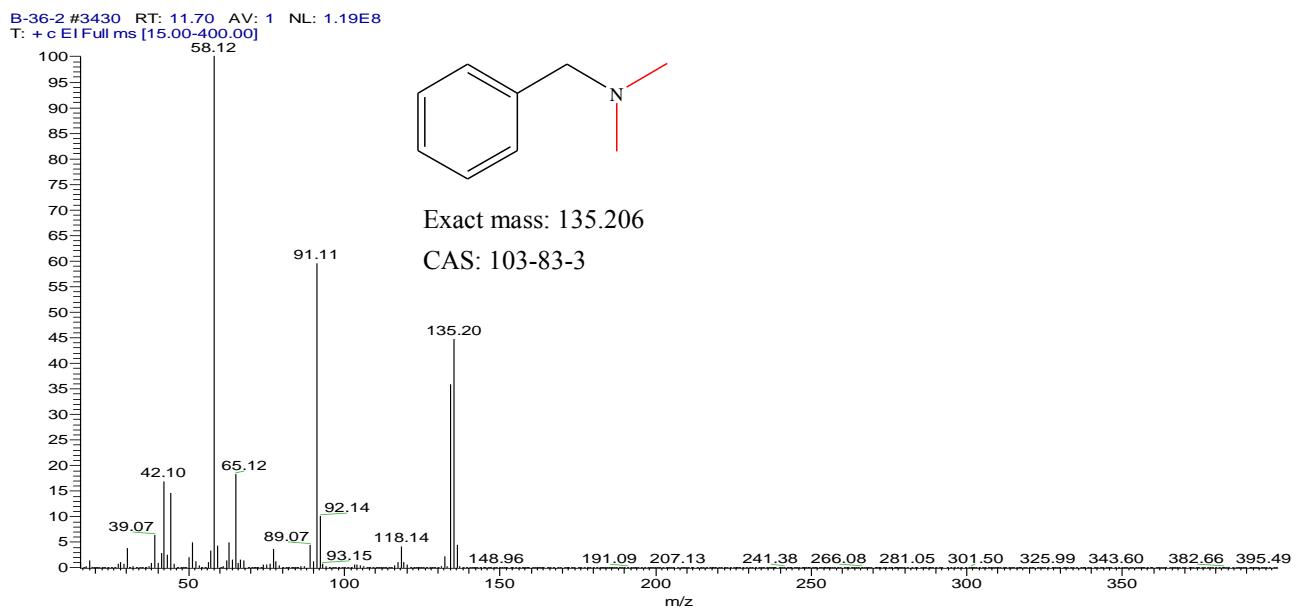
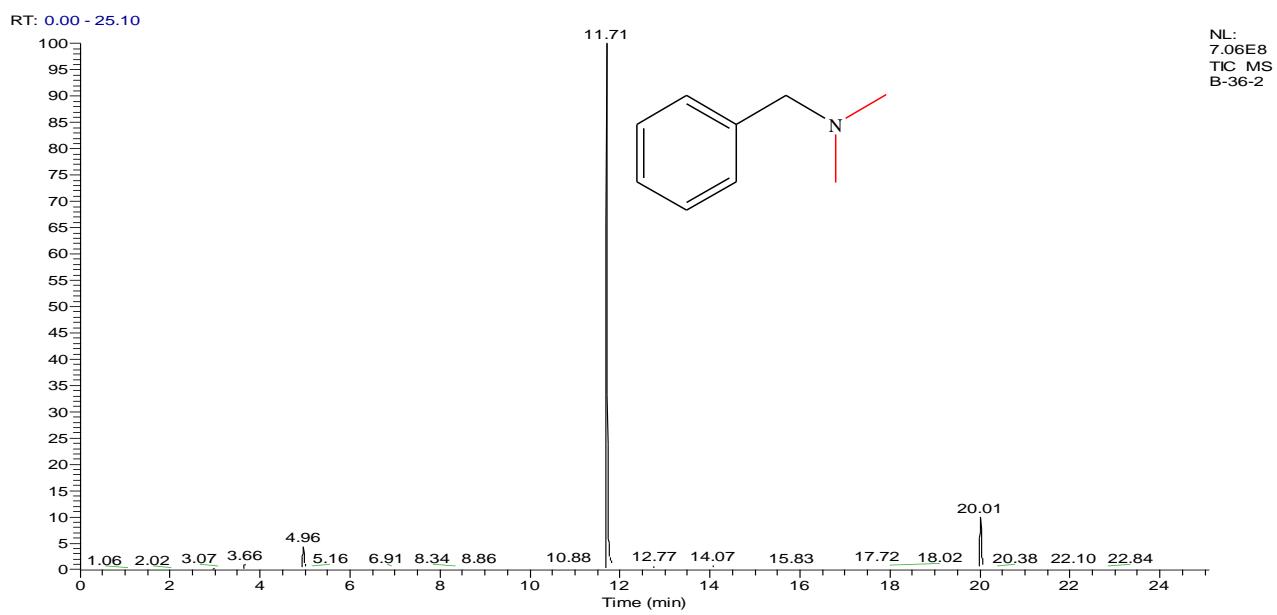
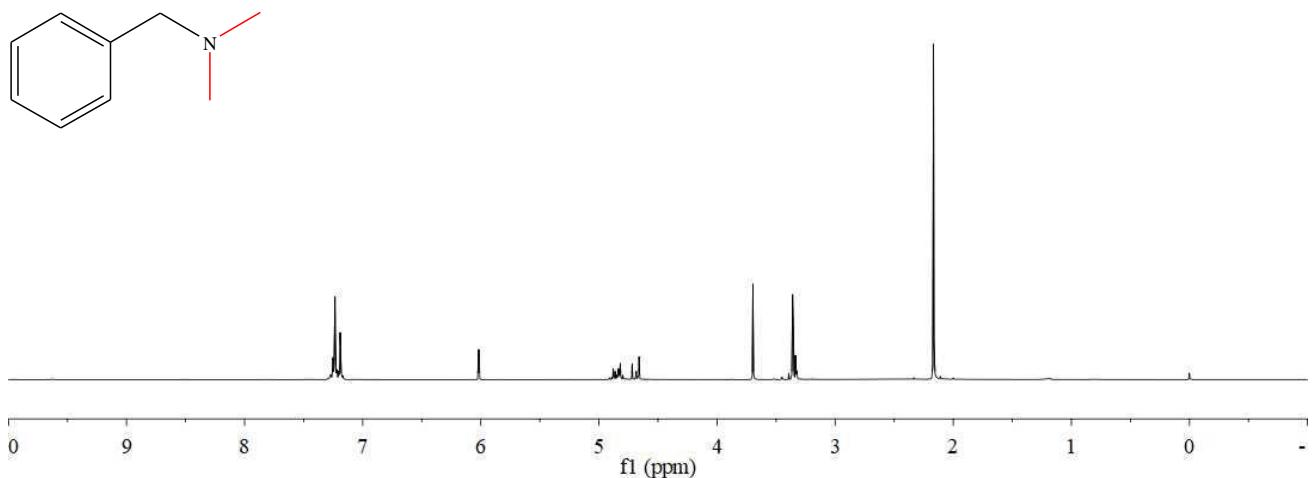


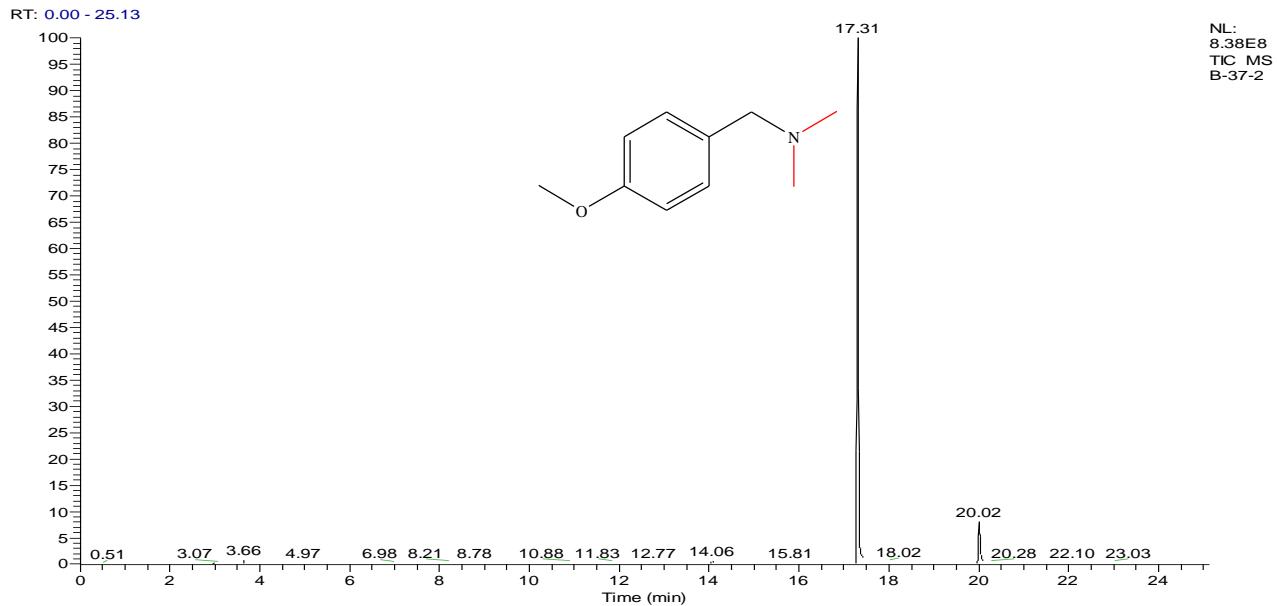
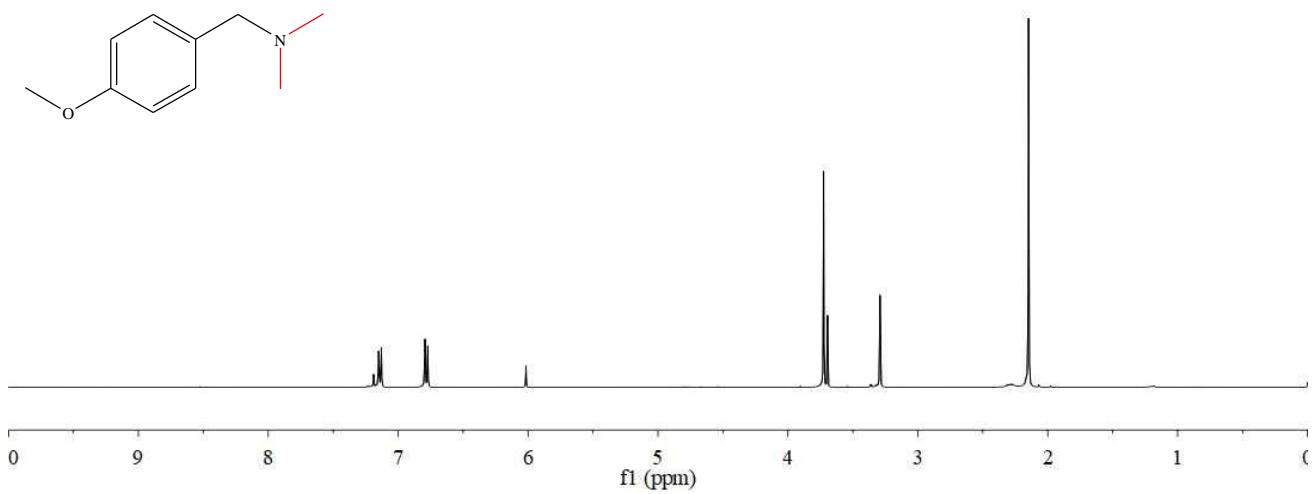




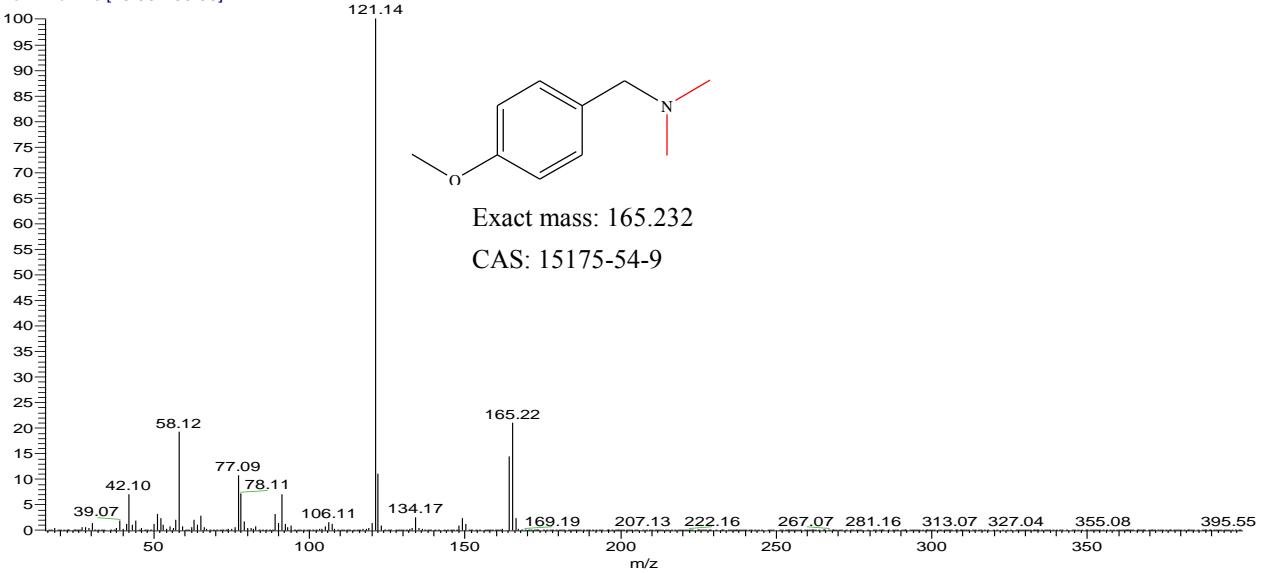


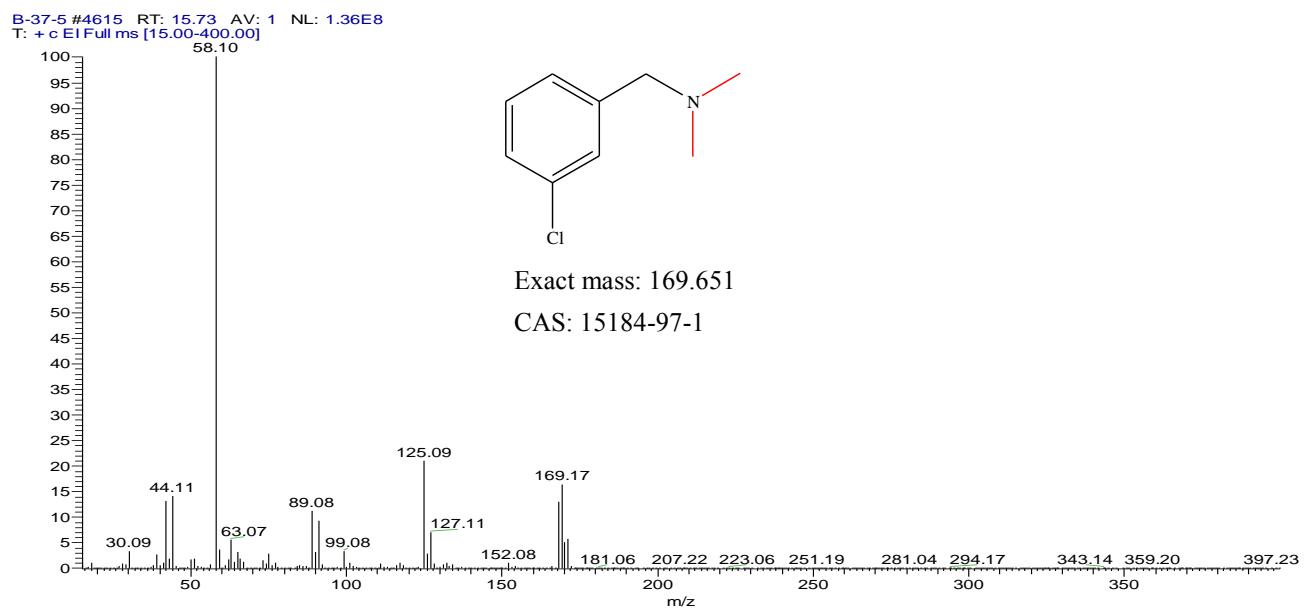
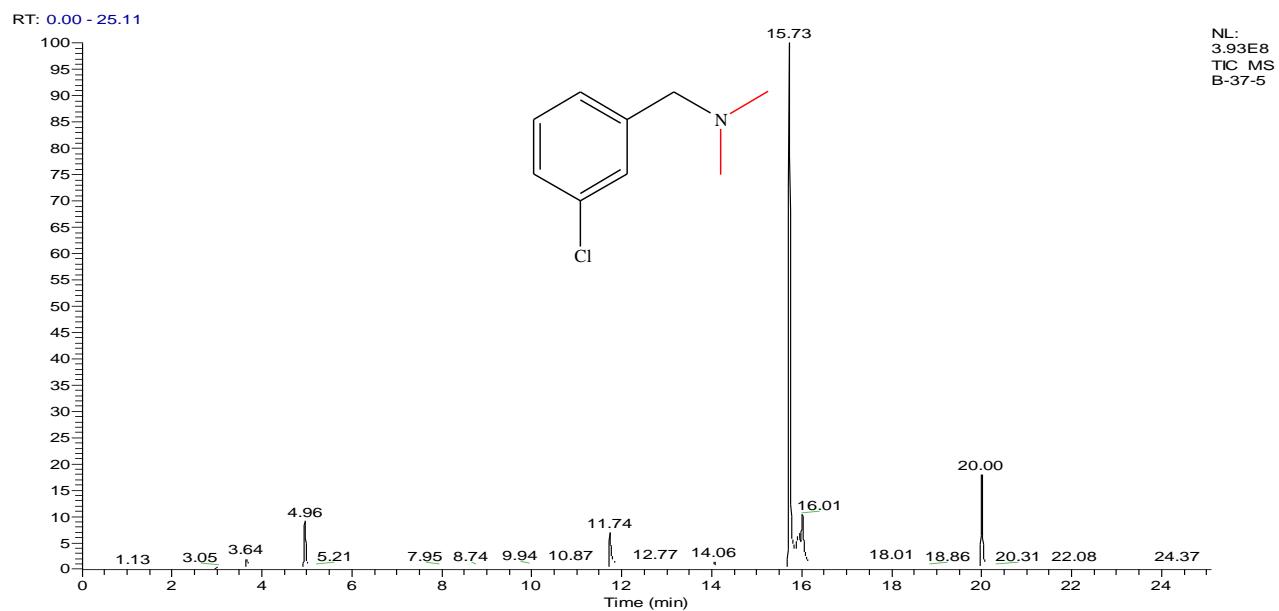
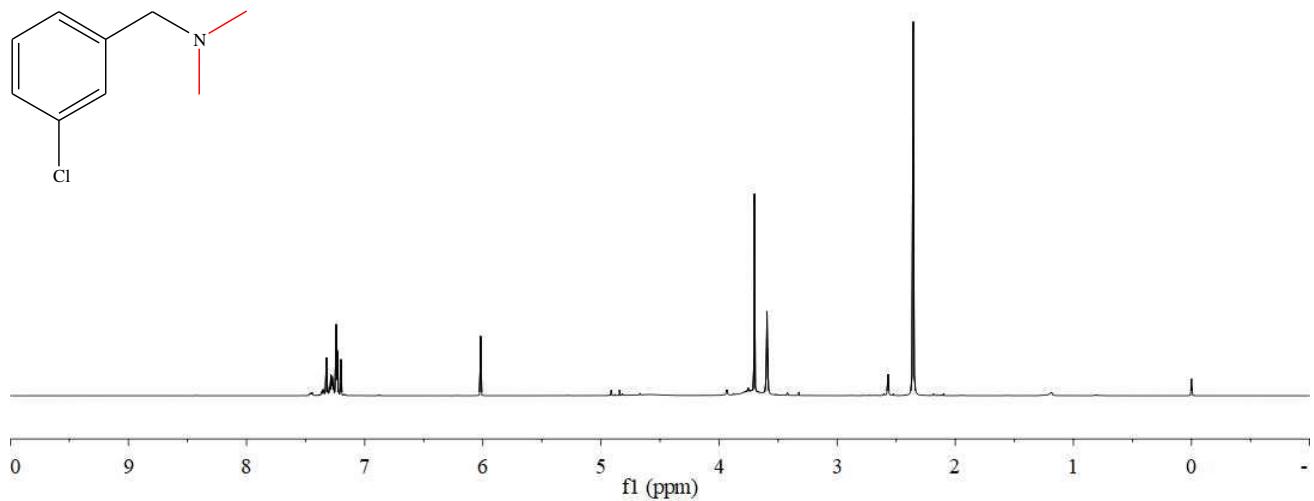


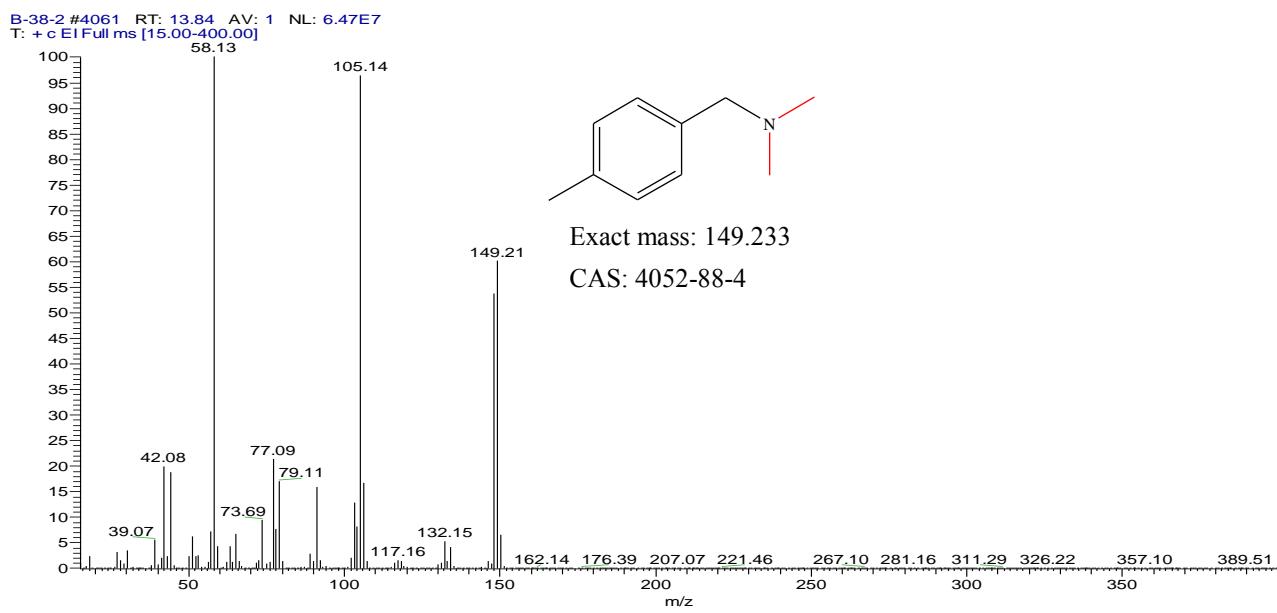
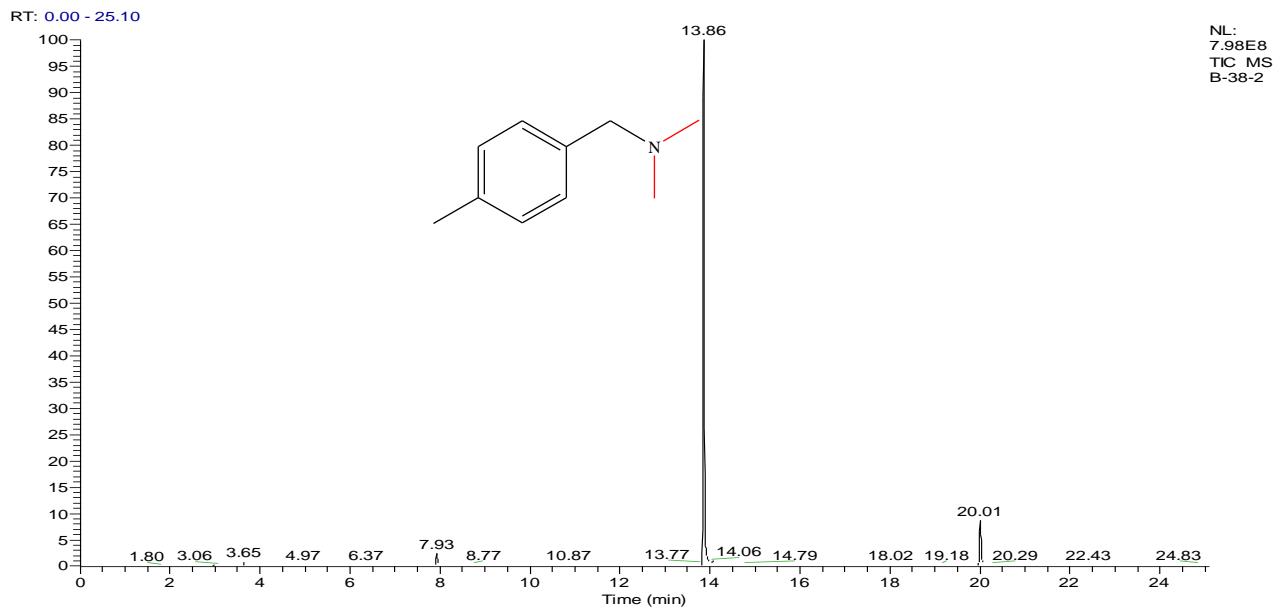
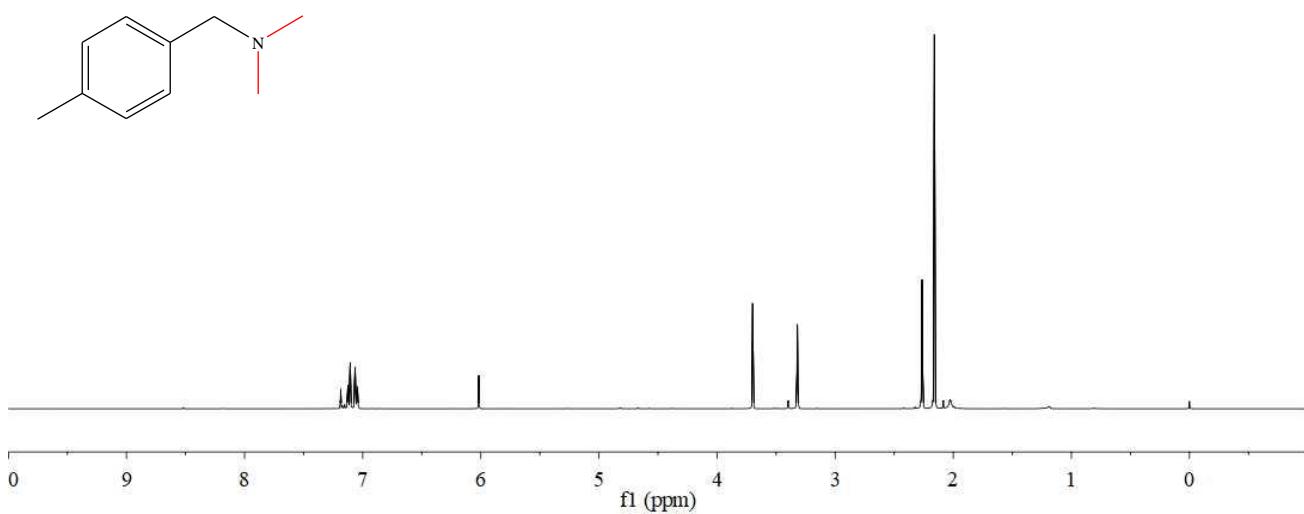


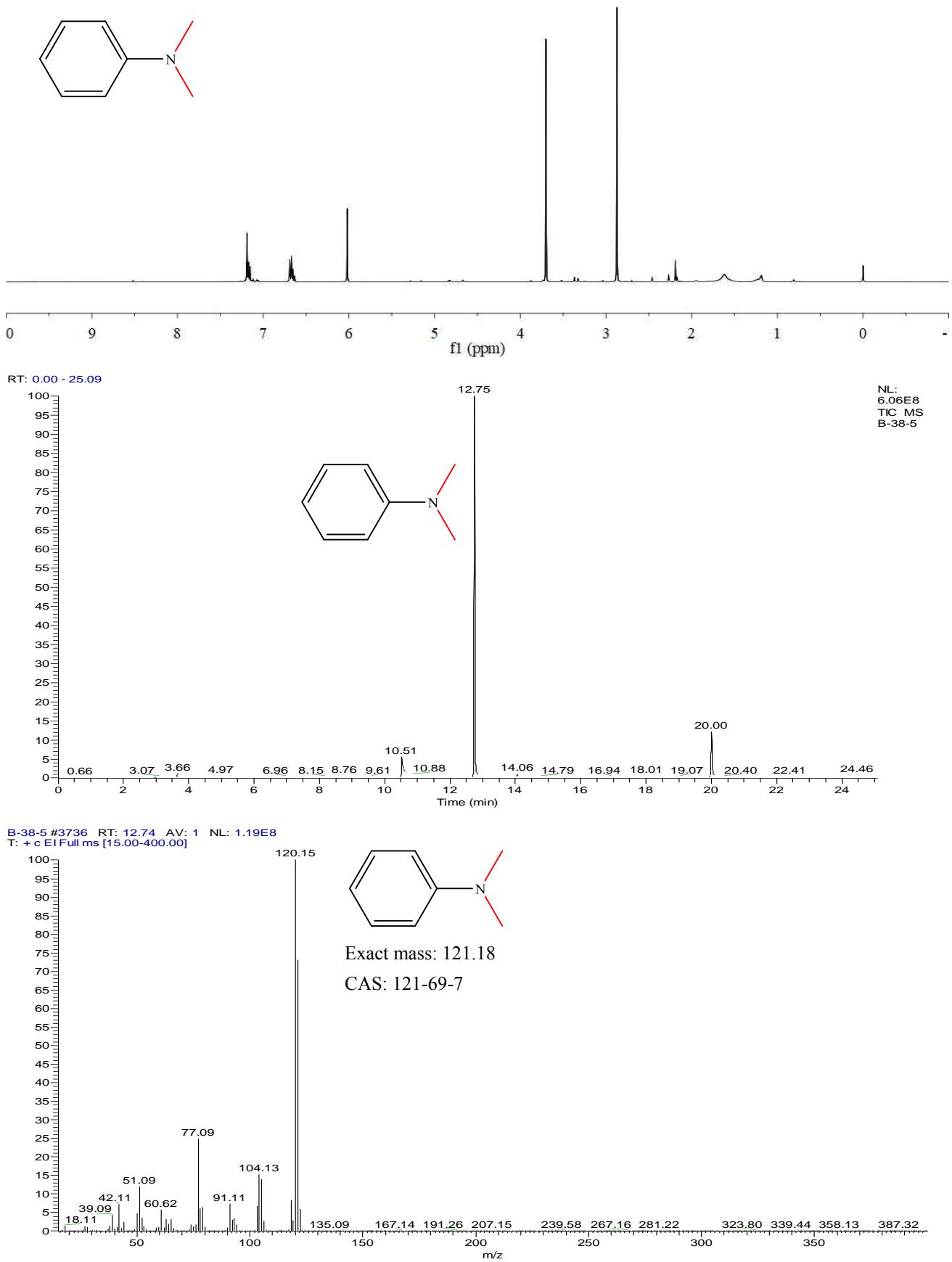


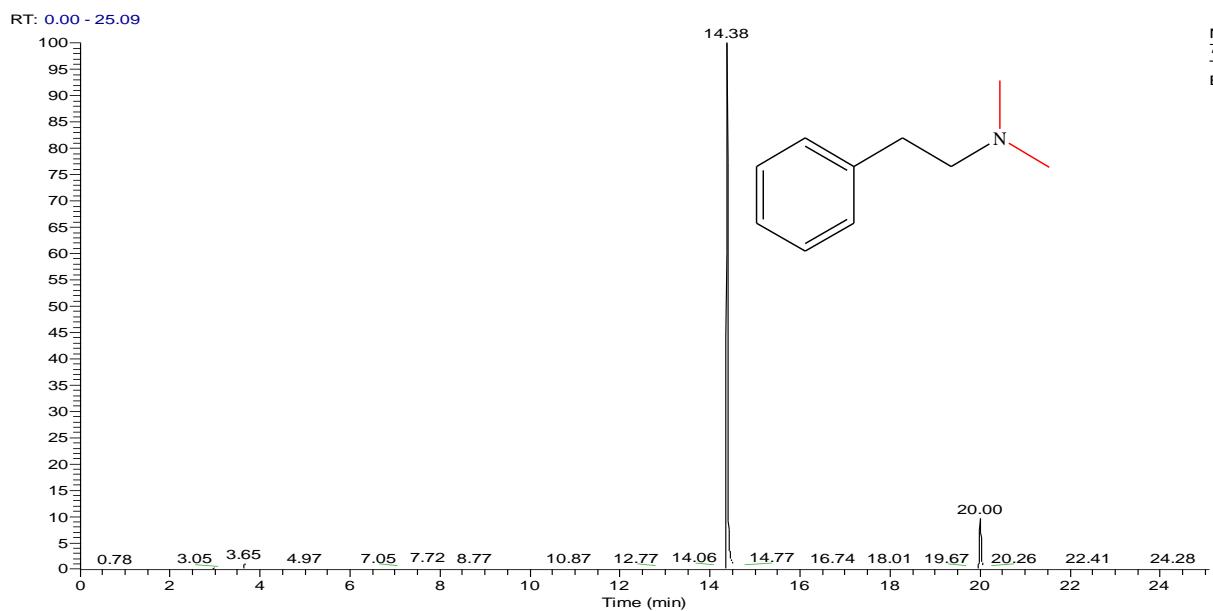
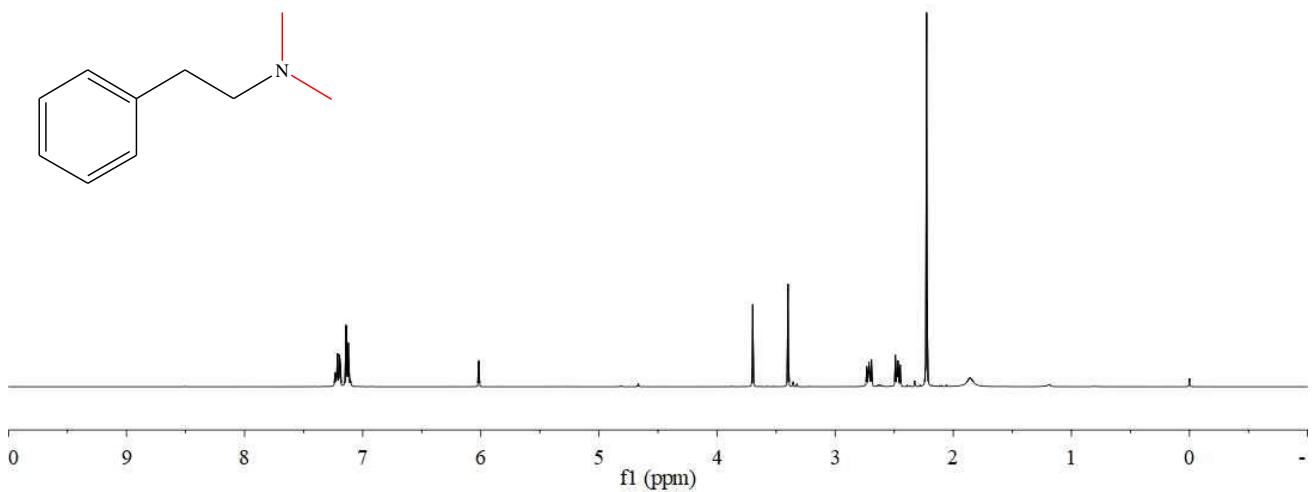
B-37-2 #5080 RT: 17.31 AV: 1 NL: 3.17E8
T: + c EIF Full ms [15.00-400.00]



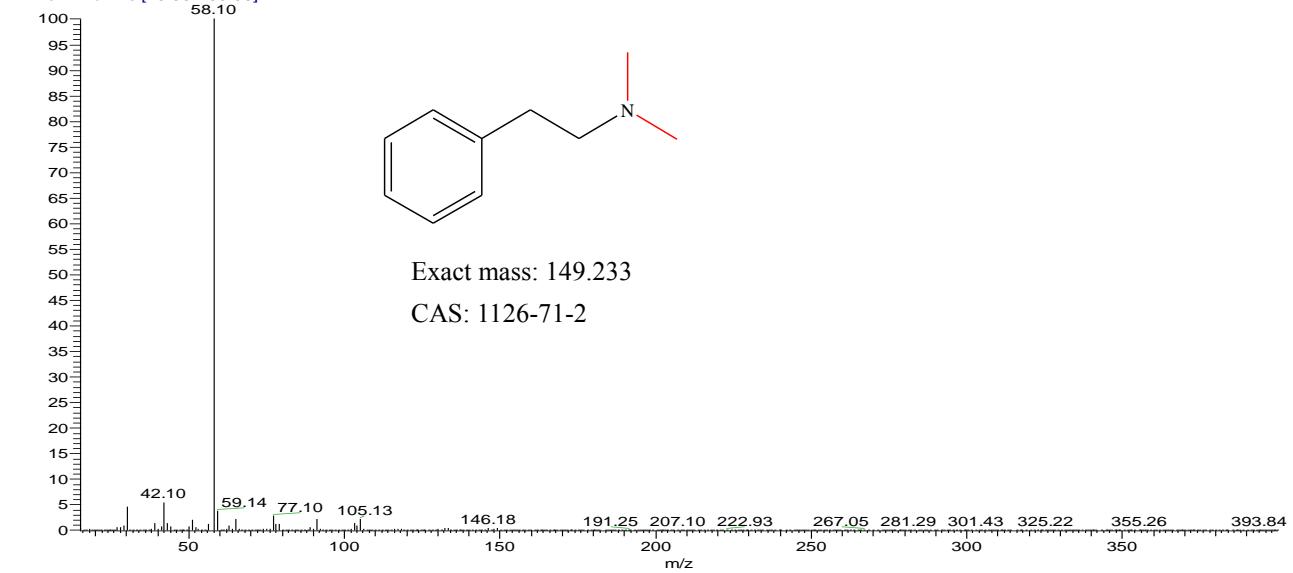


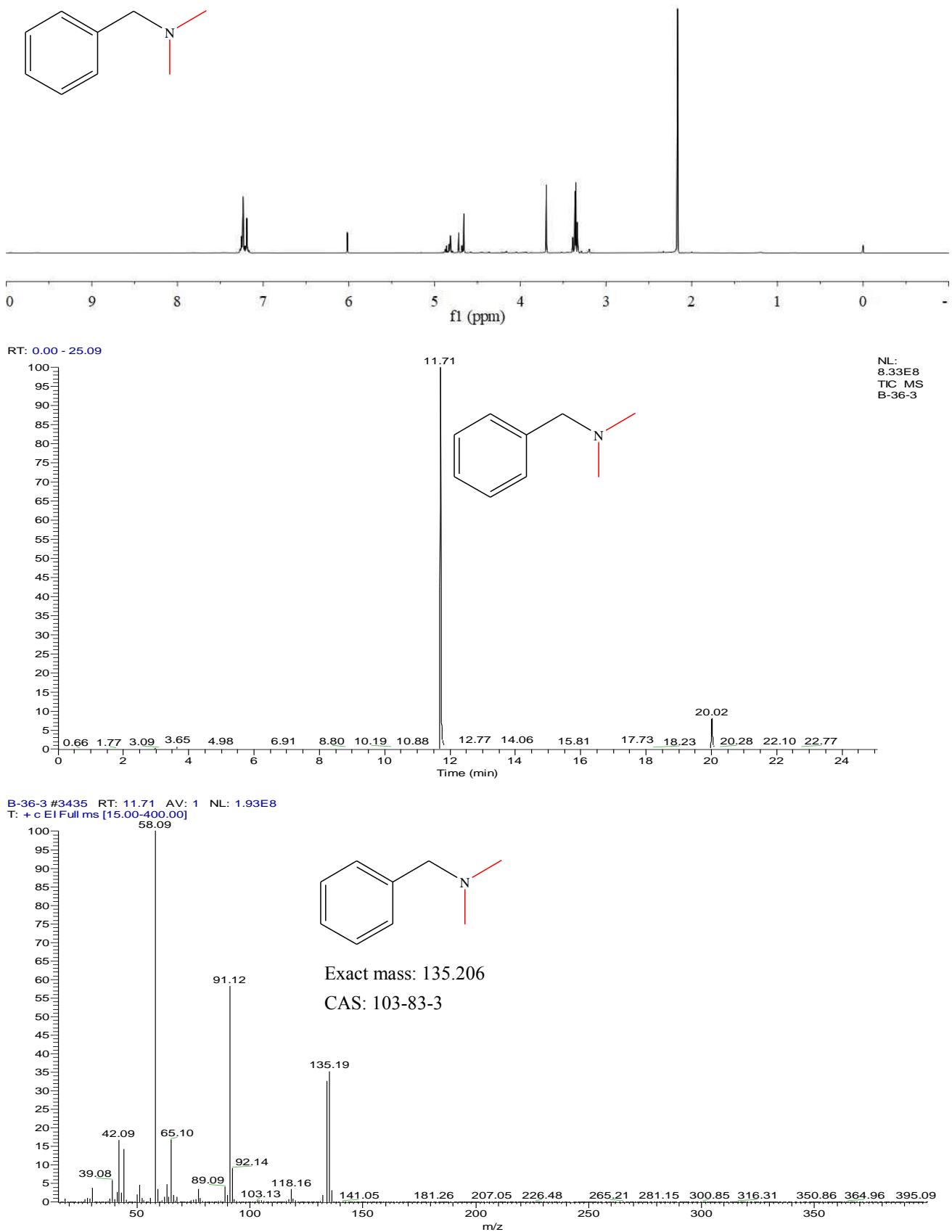


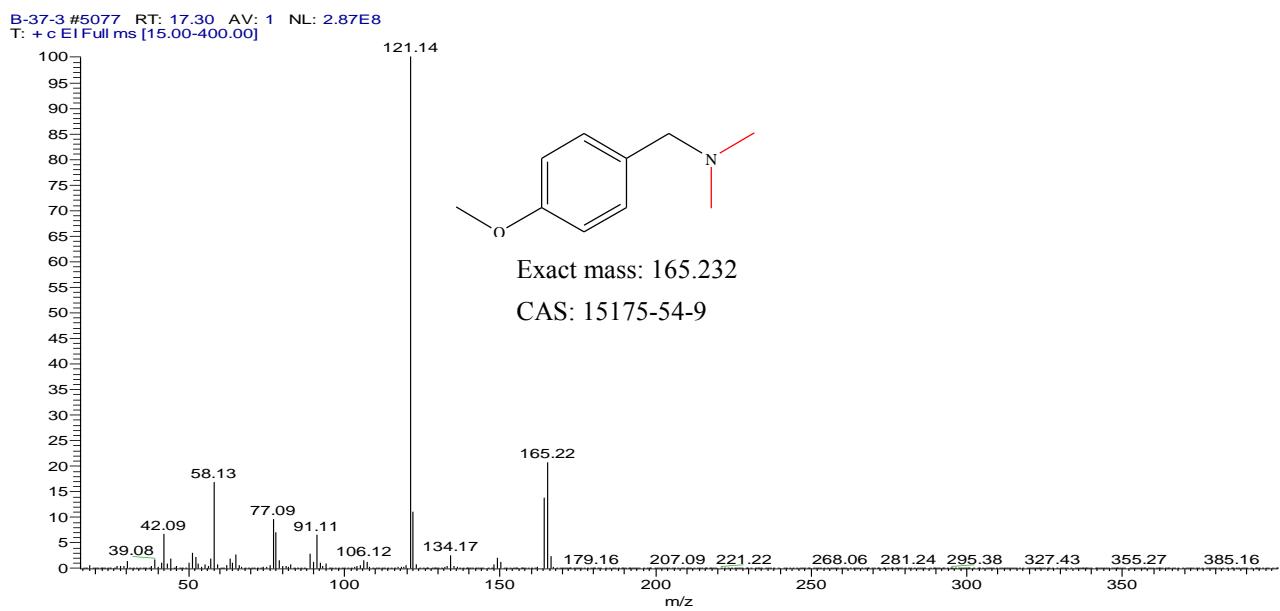
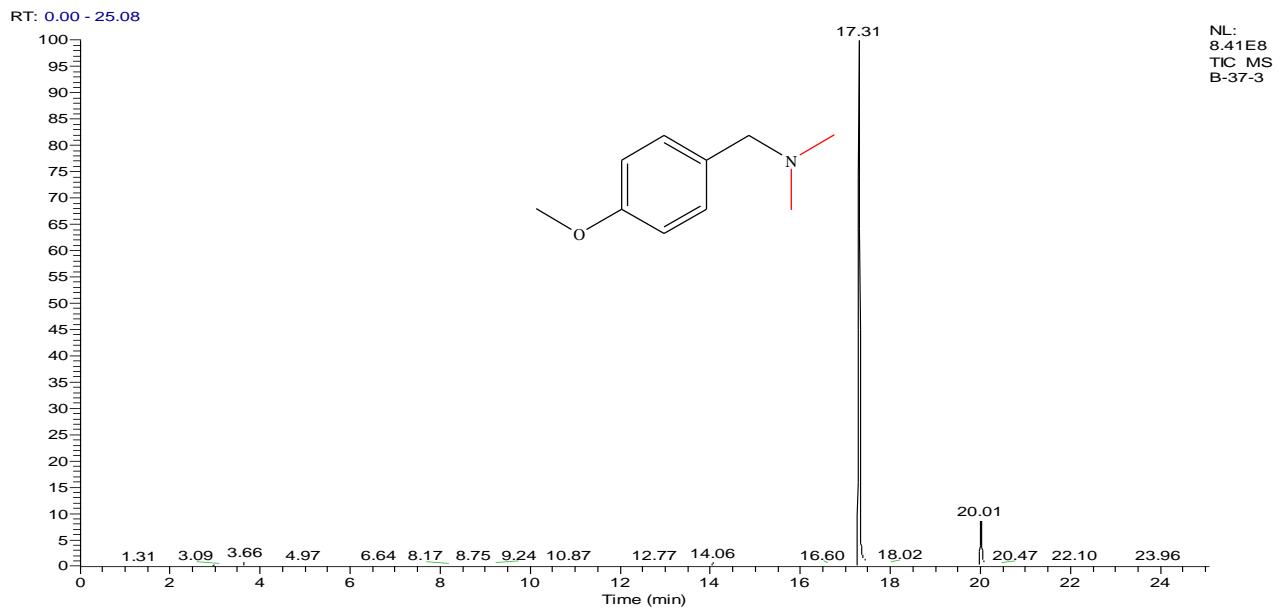
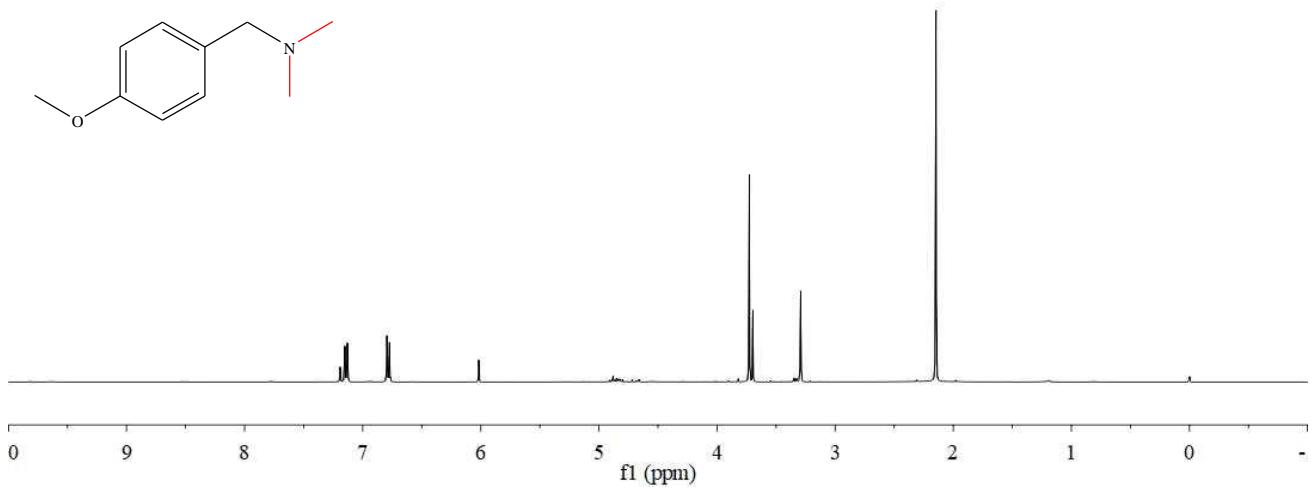


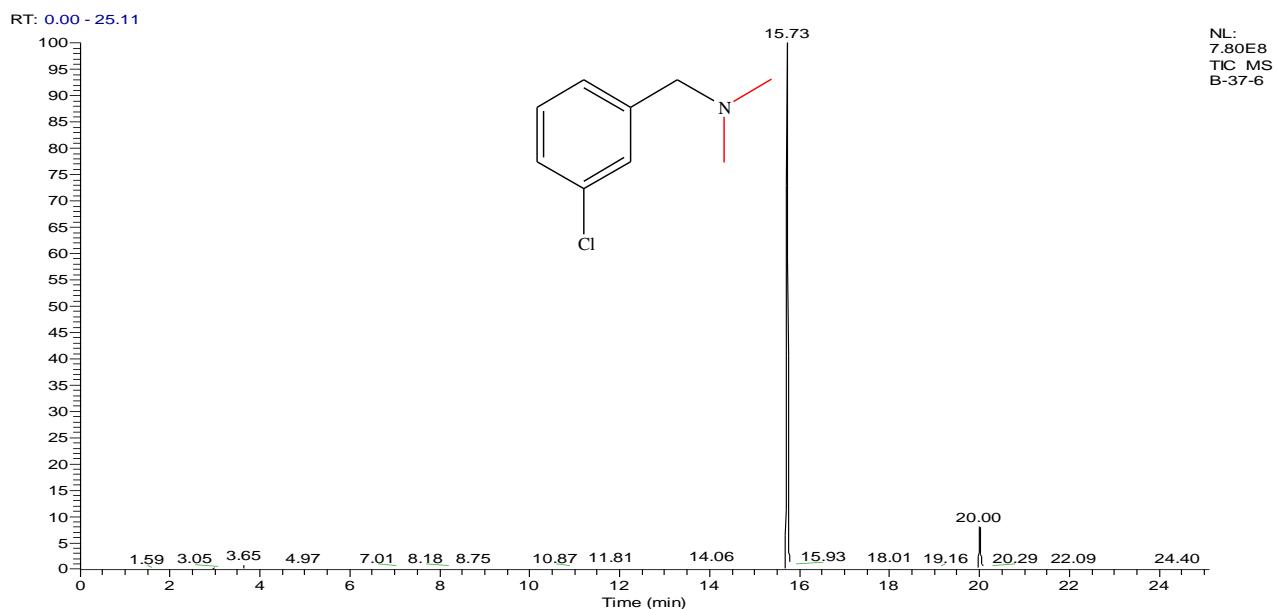
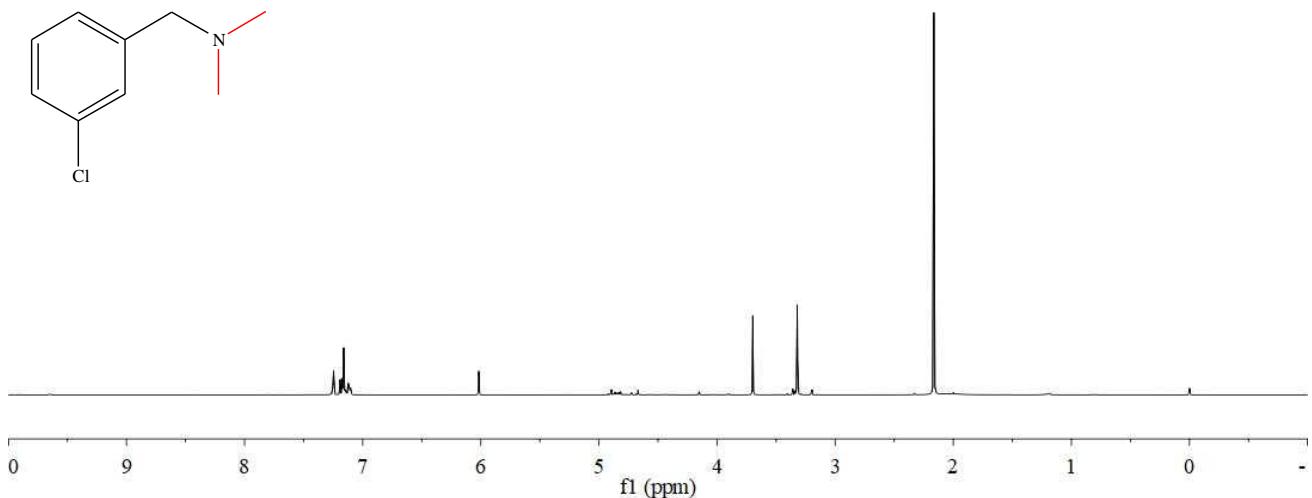


B-39-2 #4218 RT: 14.38 AV: 1 NL: 5.28E8
T: + c EI Full ms [15.00-400.00]

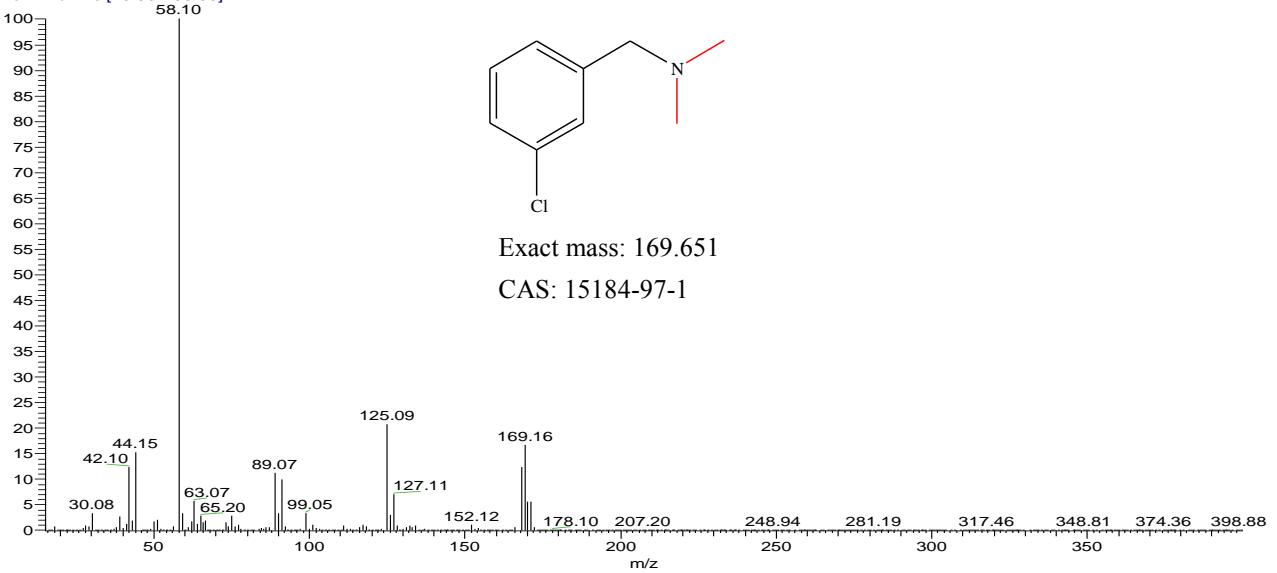


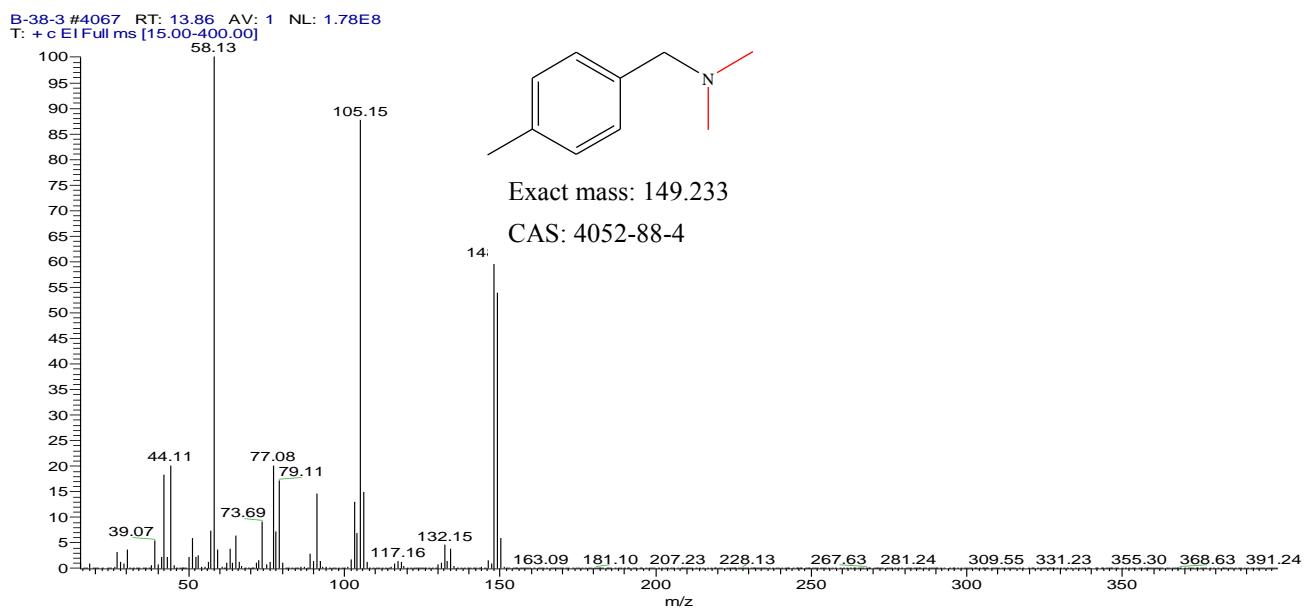
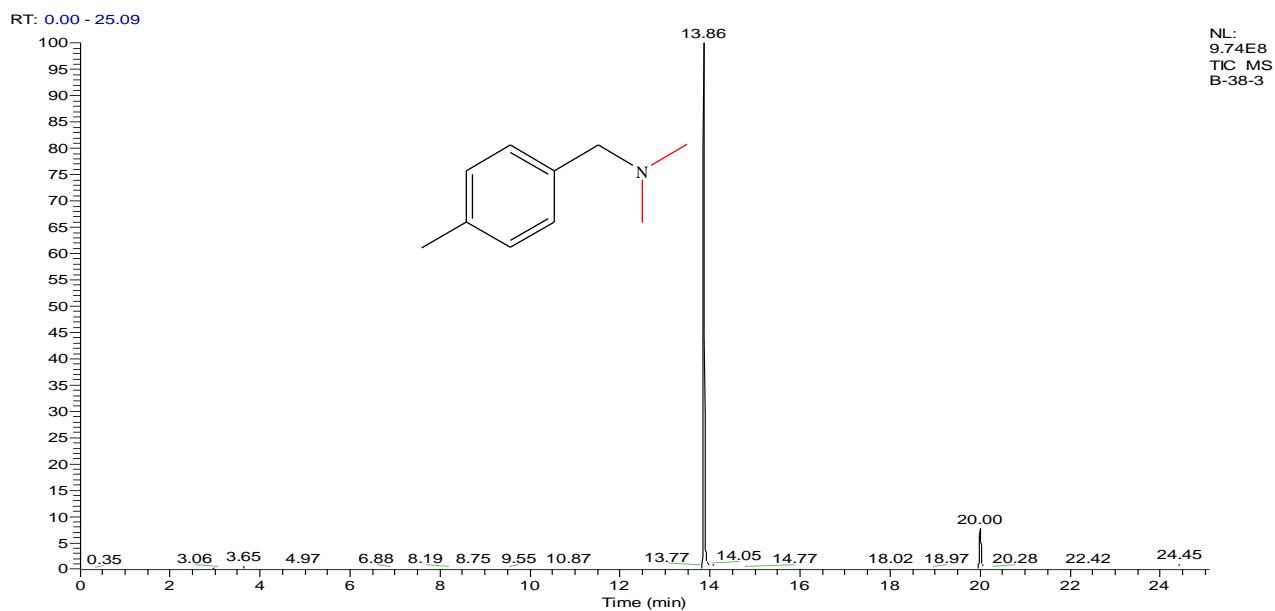
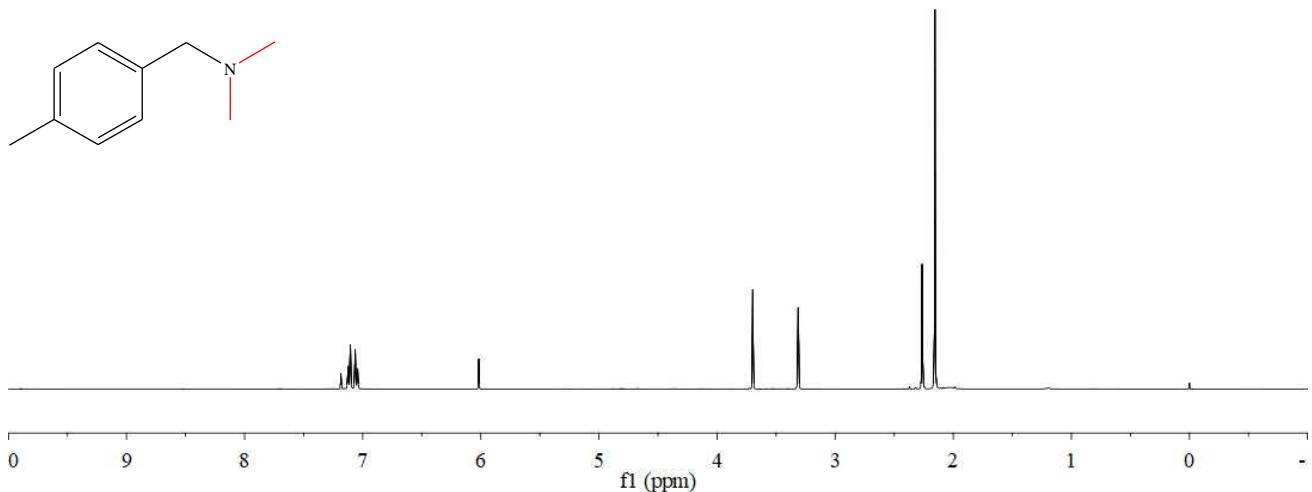


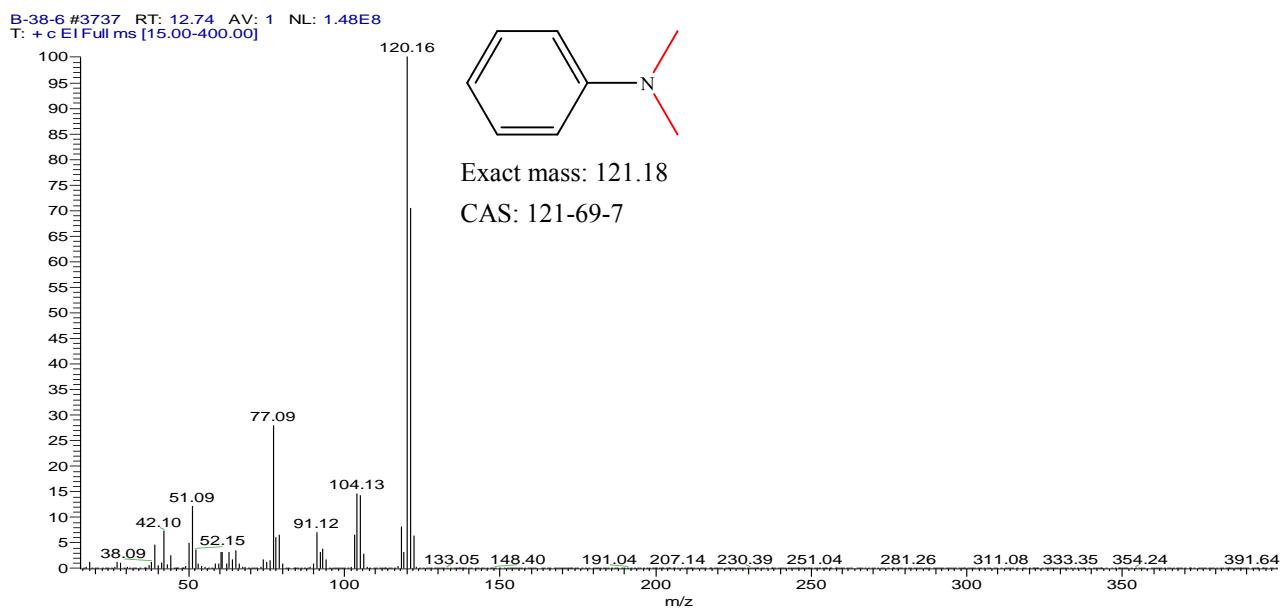
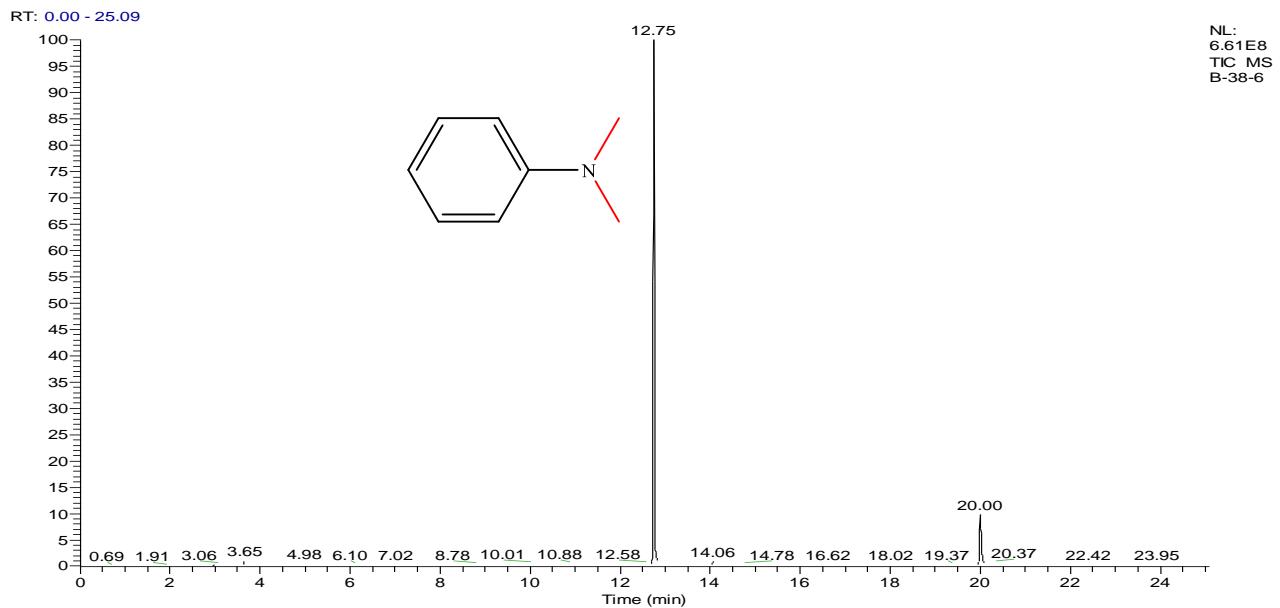
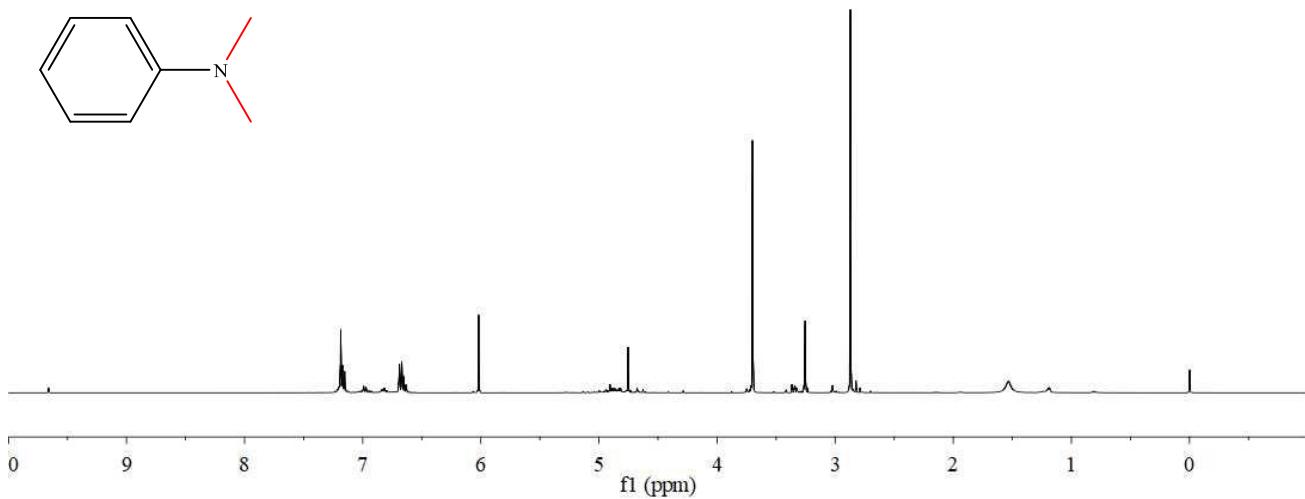


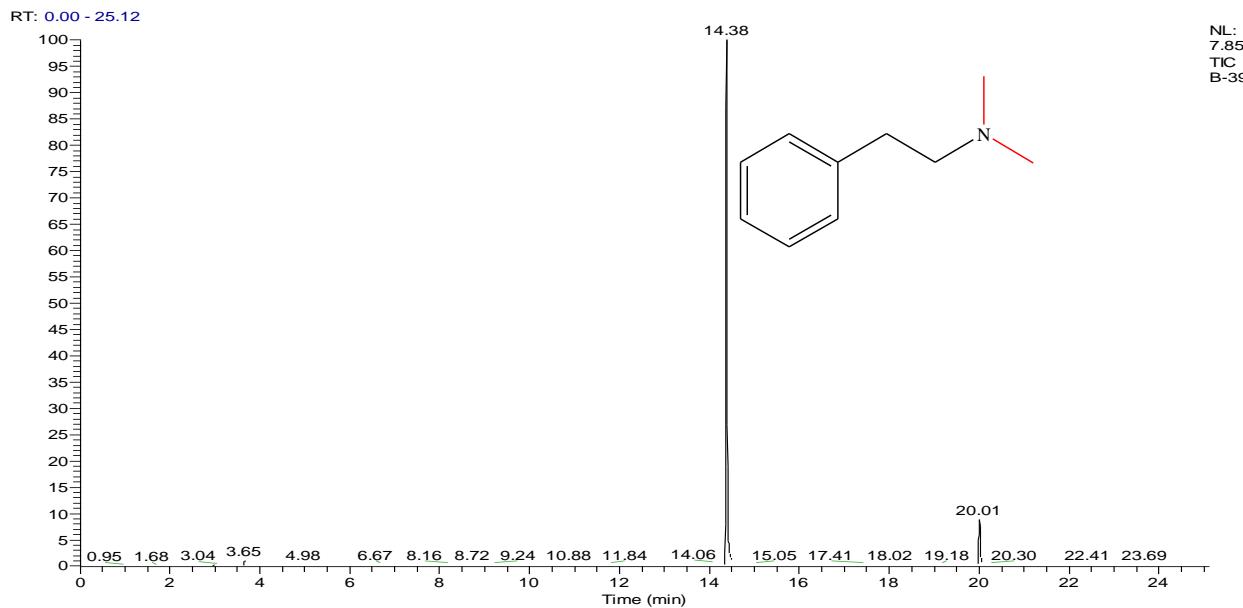
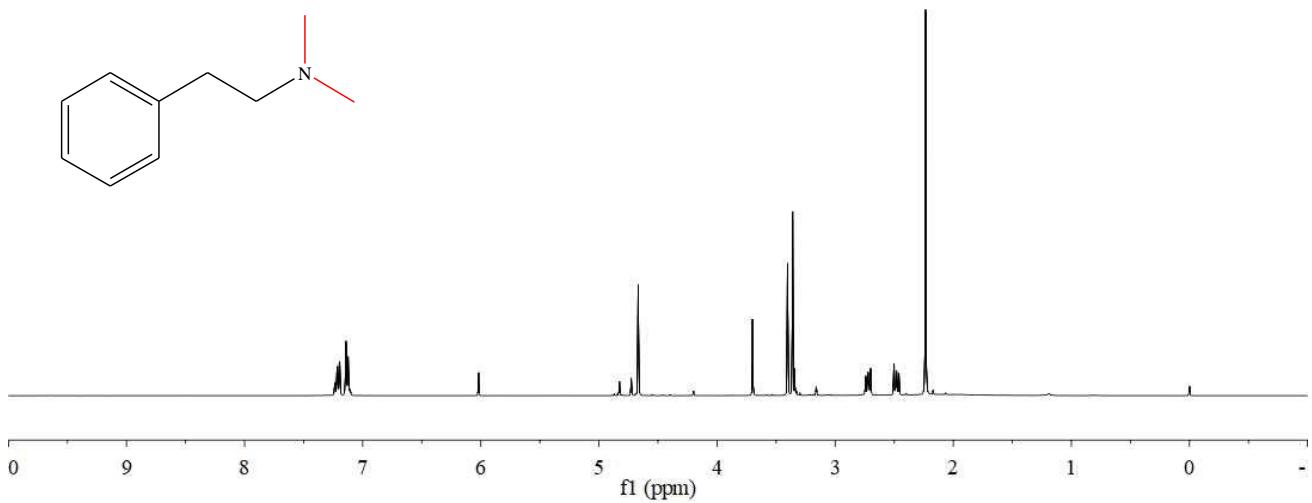


B-37-6 #4616 RT: 15.73 AV: 1 NL: 2.63E8
T: + c EI Full ms [15.00-400.00]

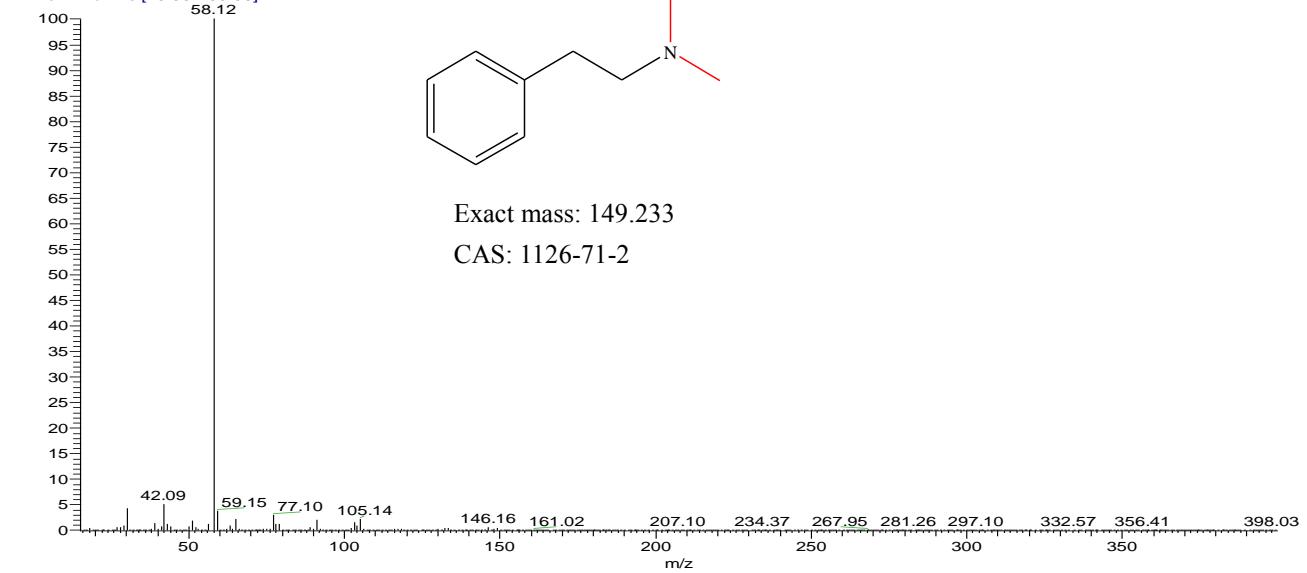


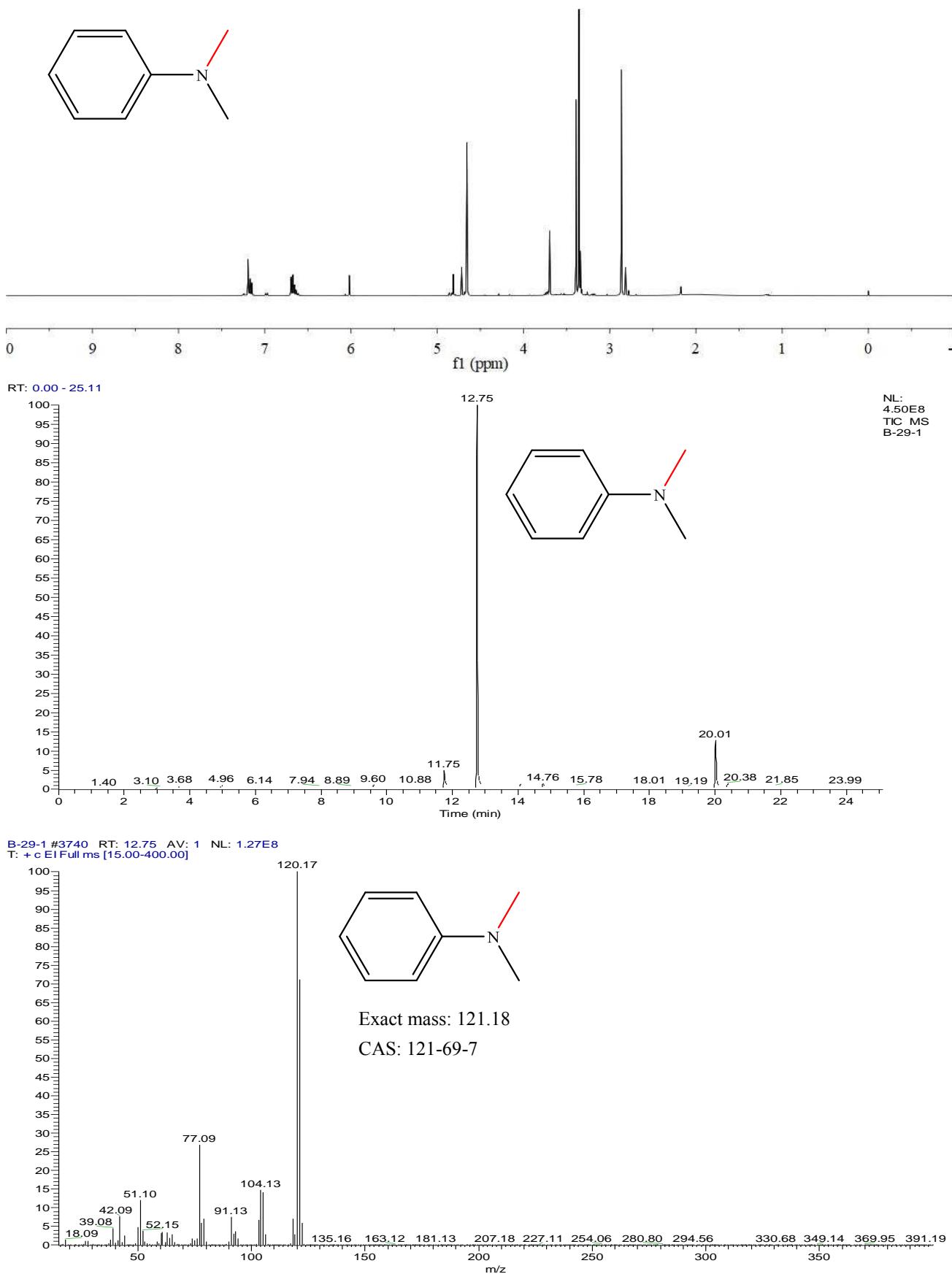


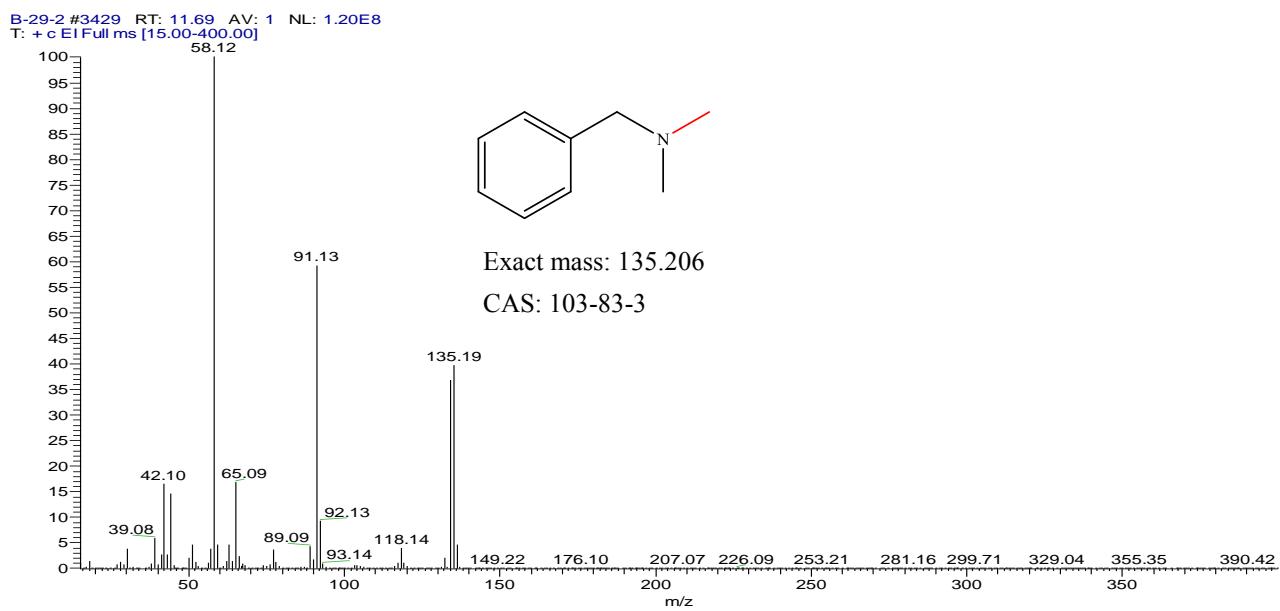
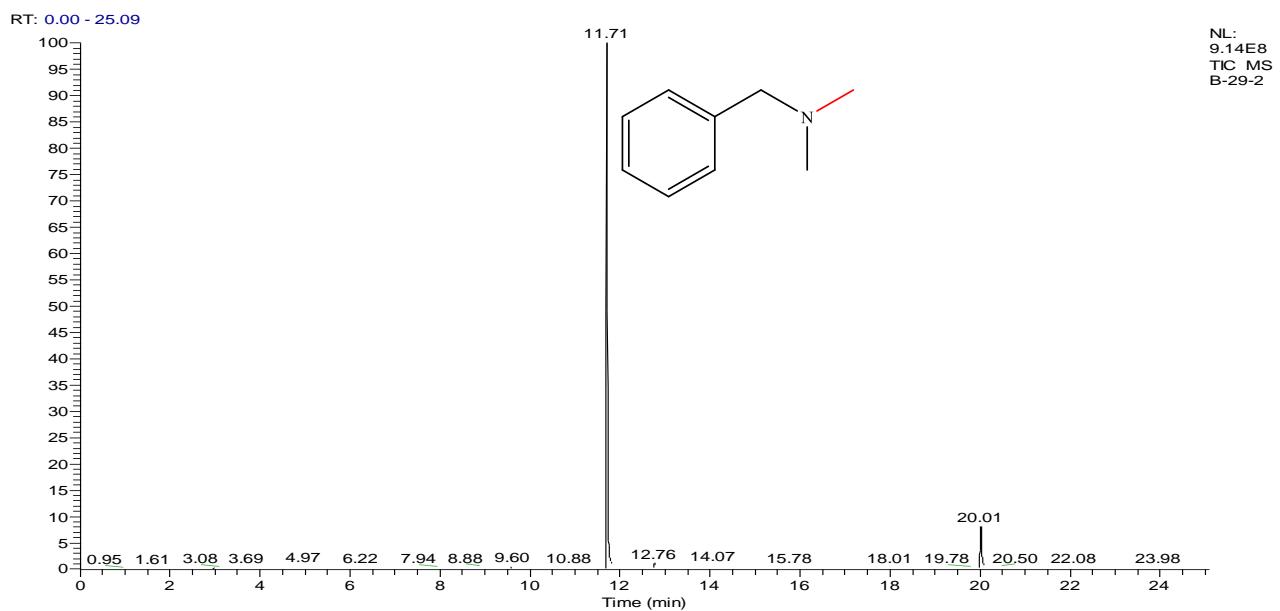
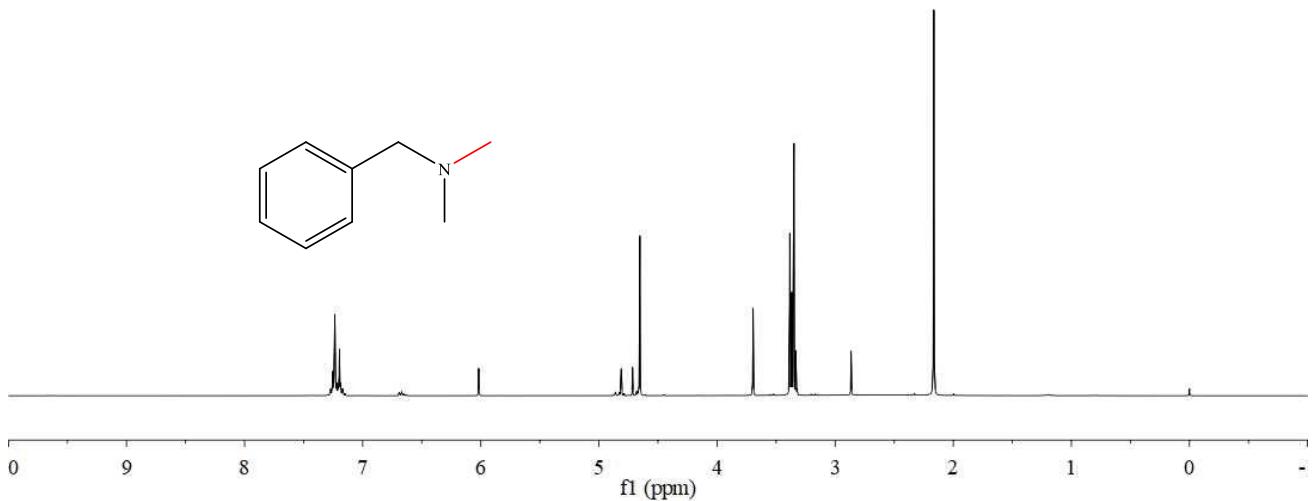


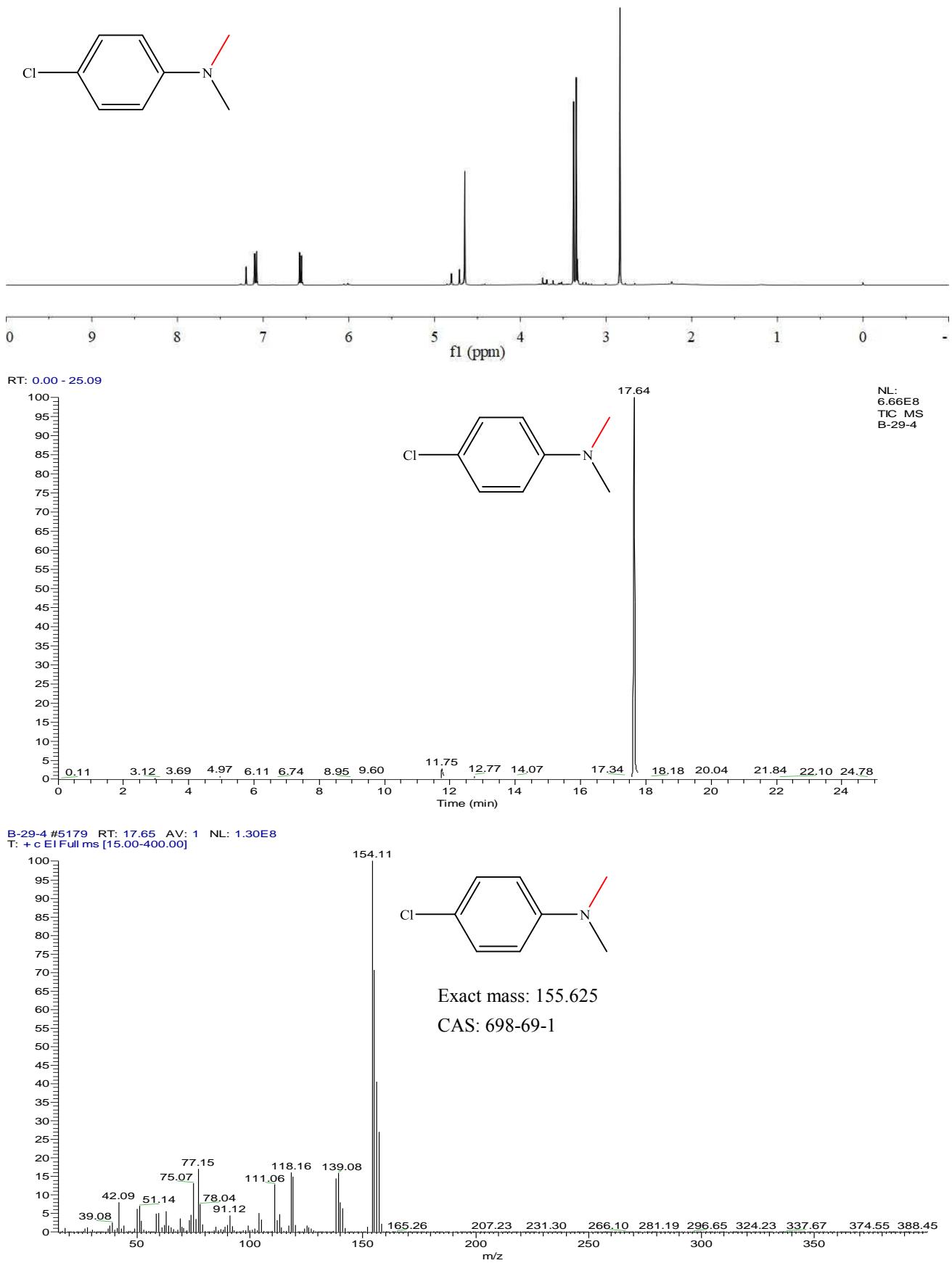


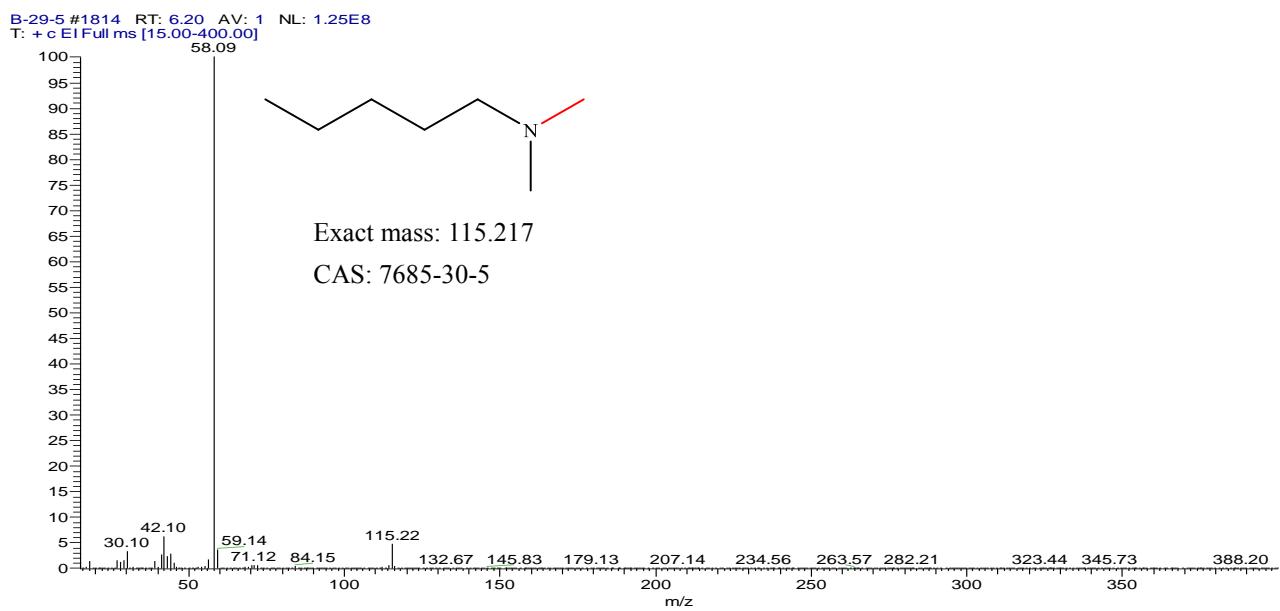
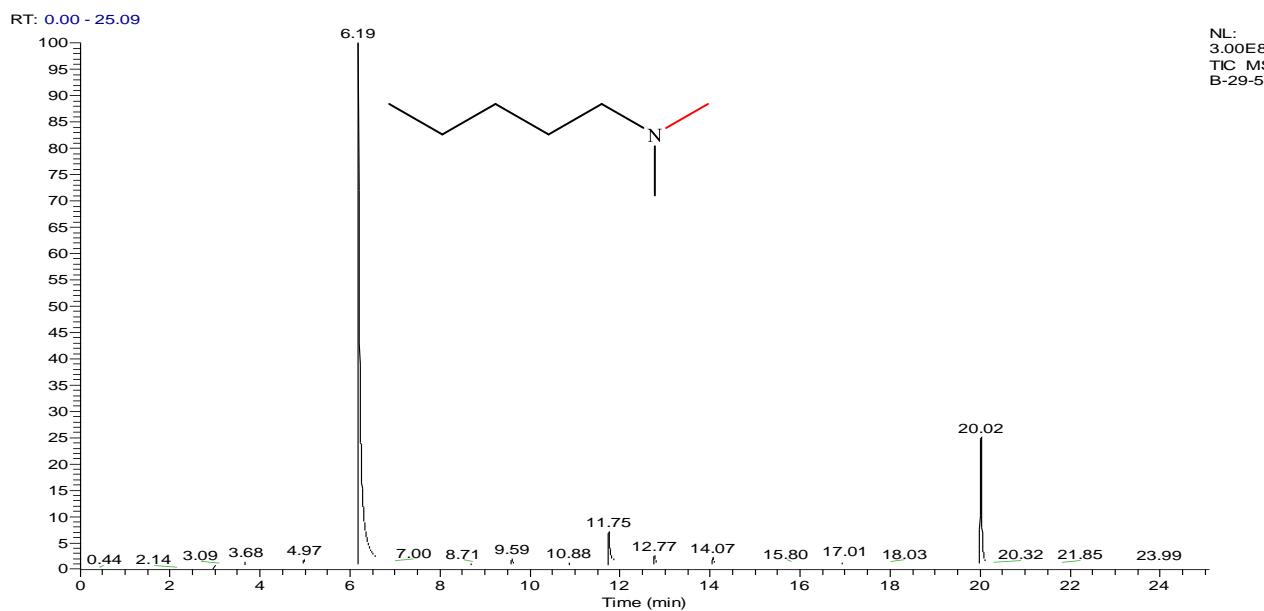
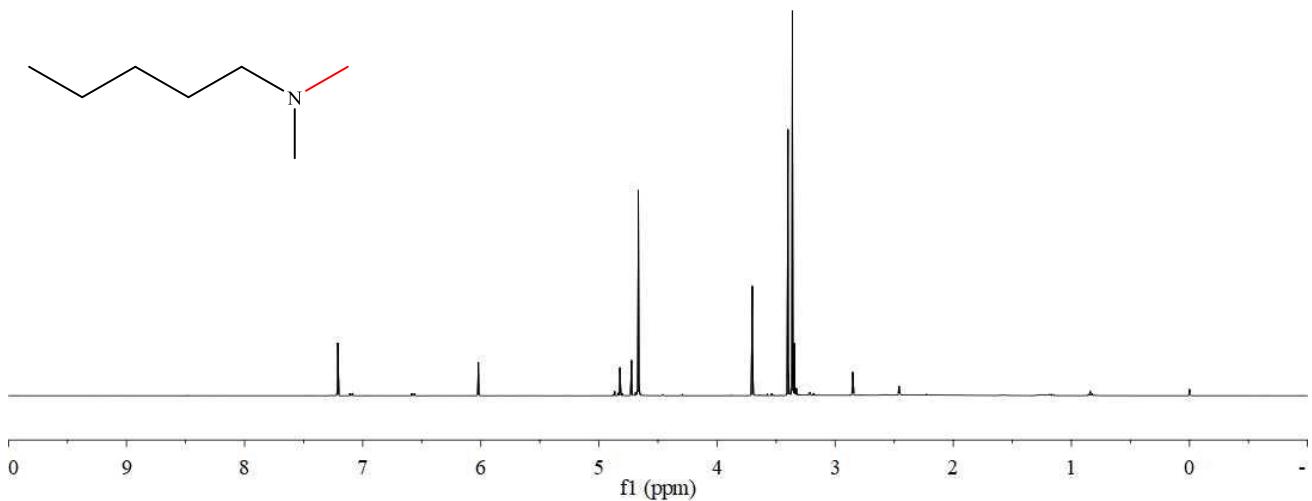
B-39-3 #4216 RT: 14.37 AV: 1 NL: 4.17E8
T: + c EI Full ms [15.00-400.00]

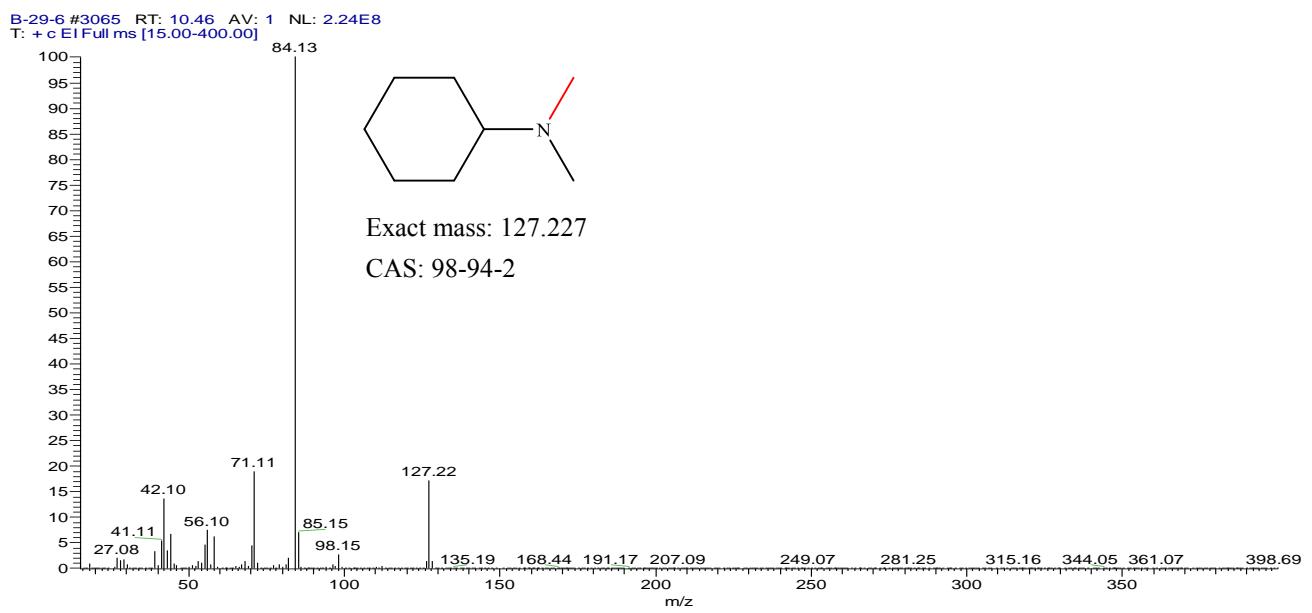
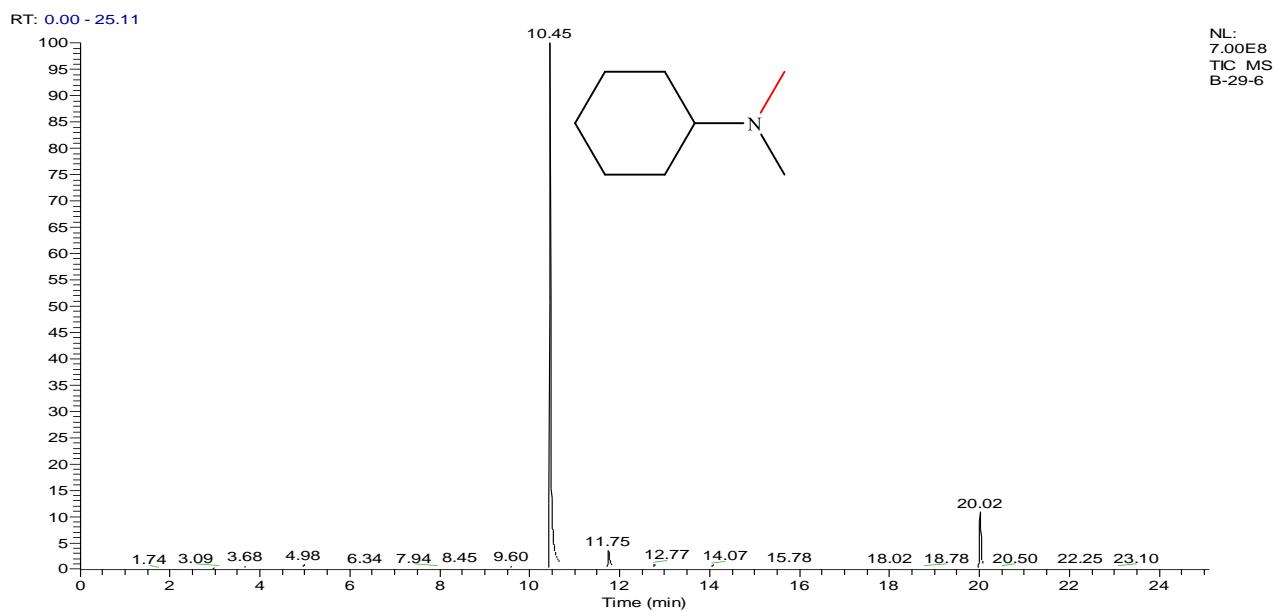
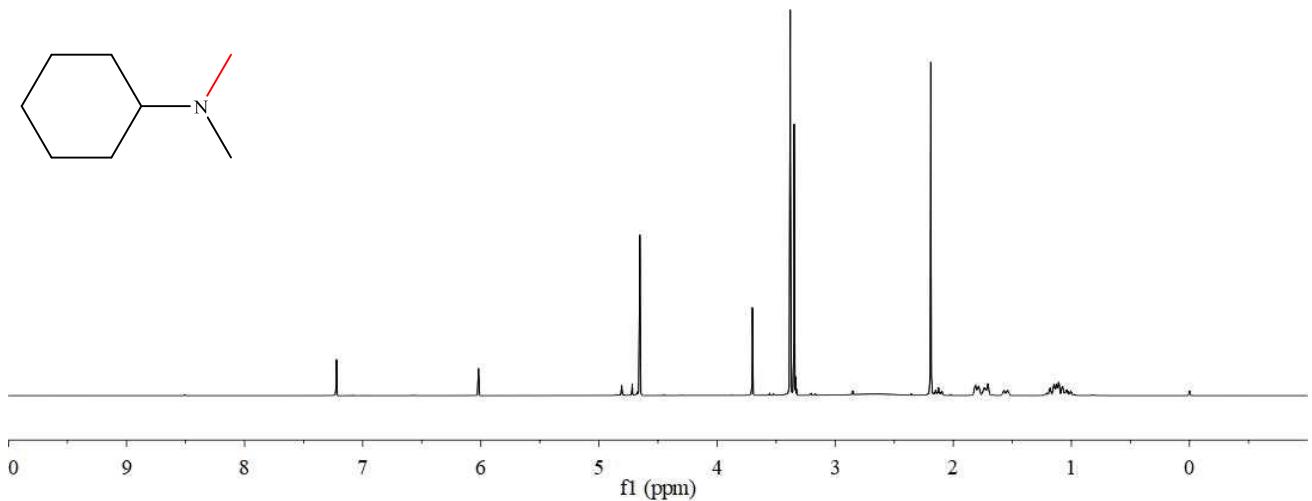


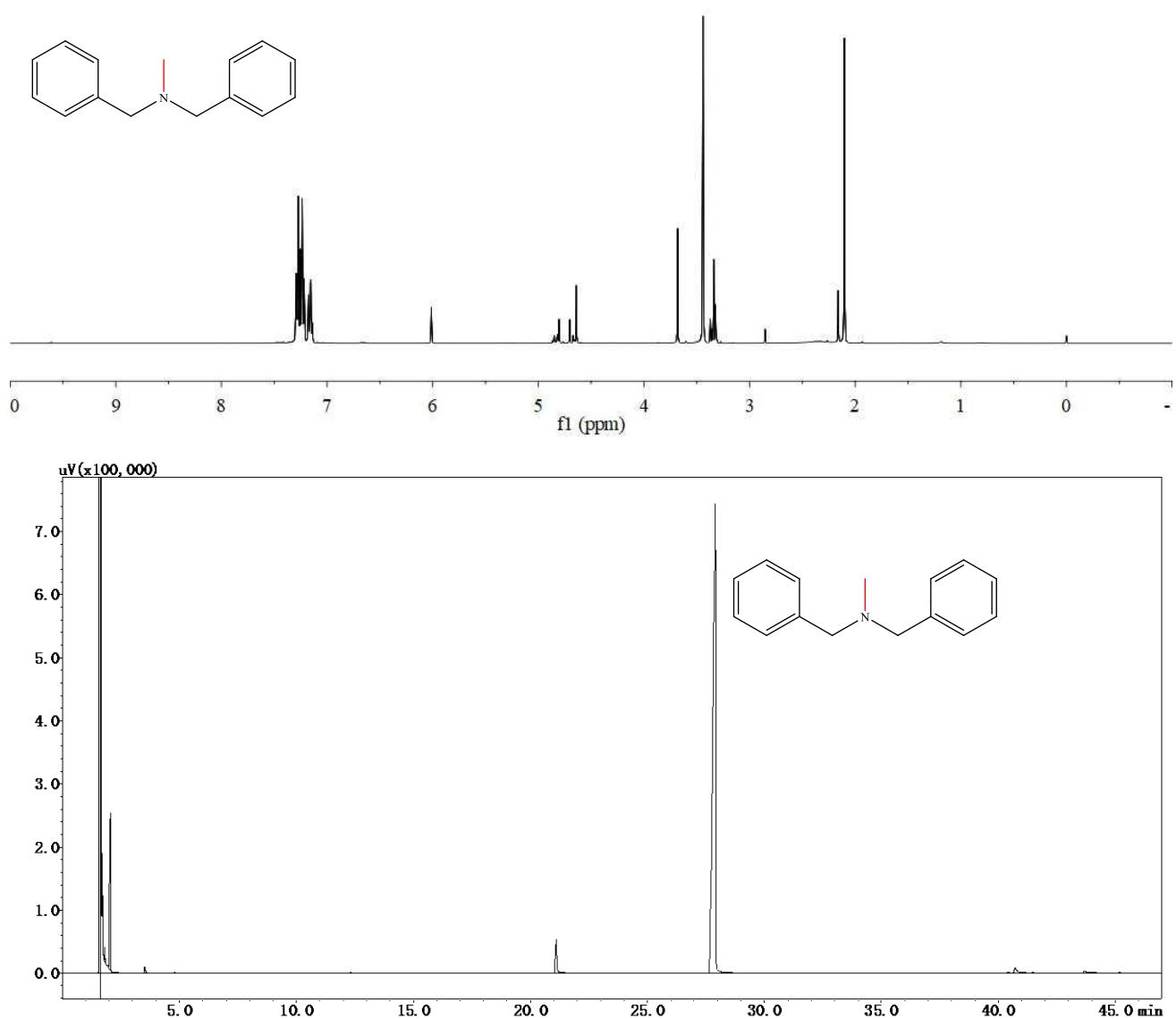


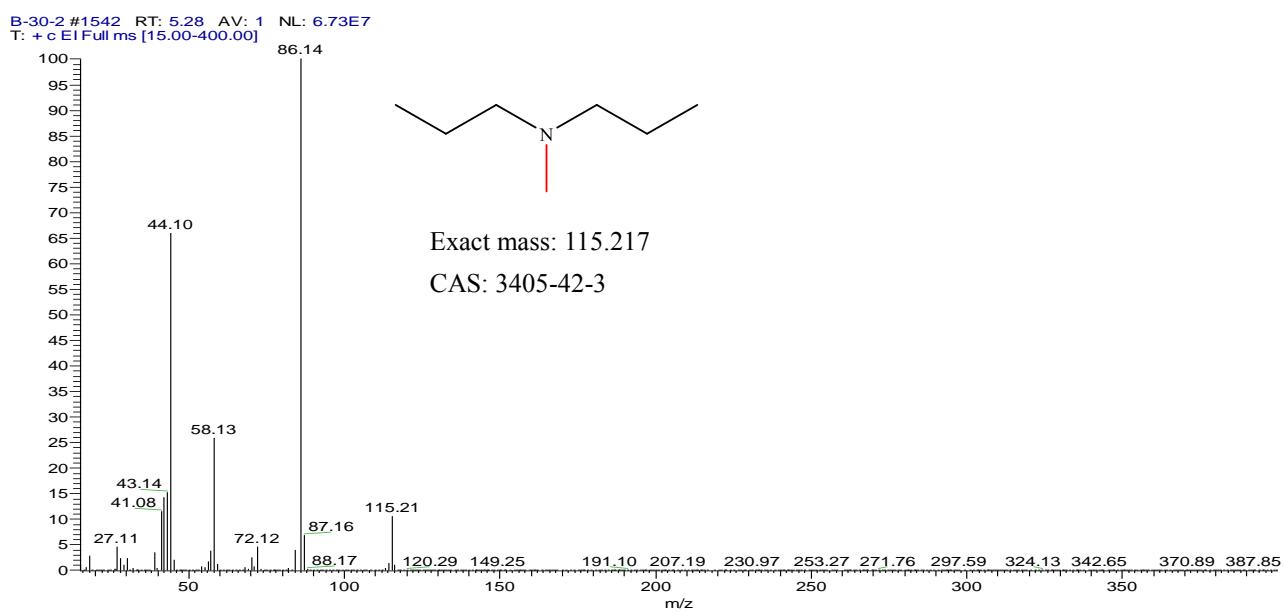
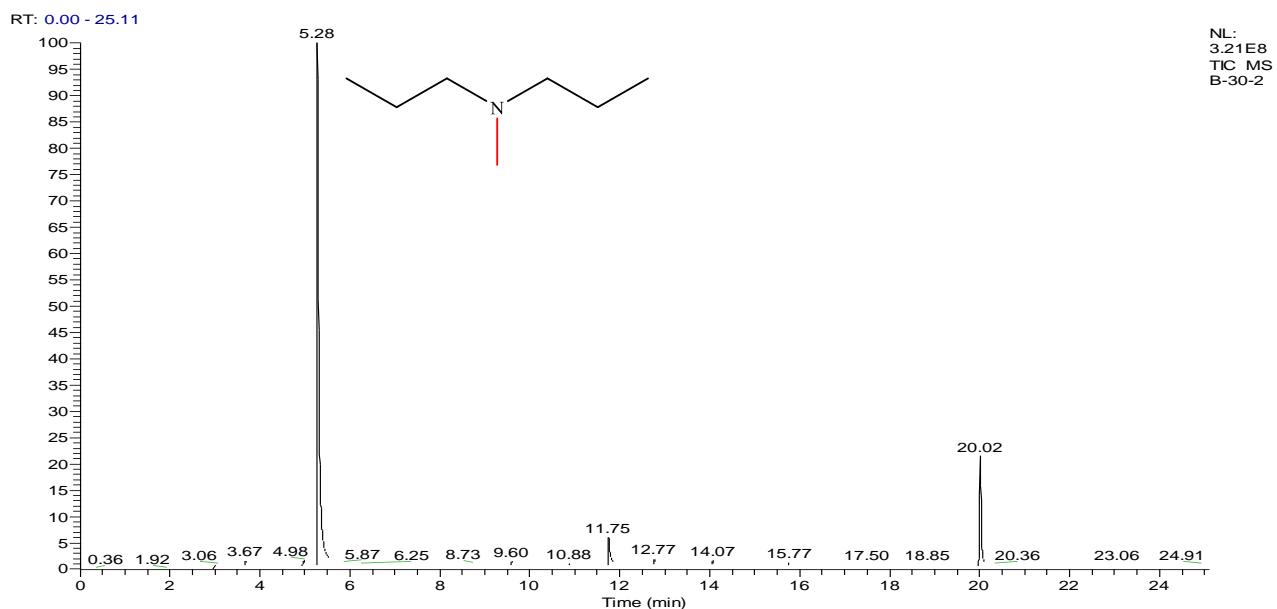
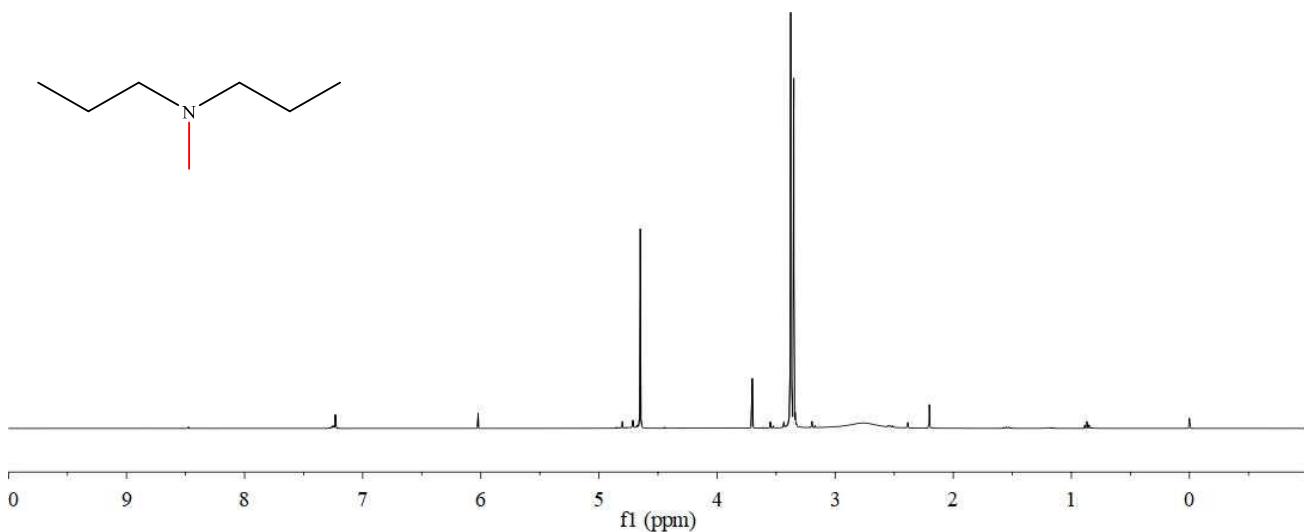


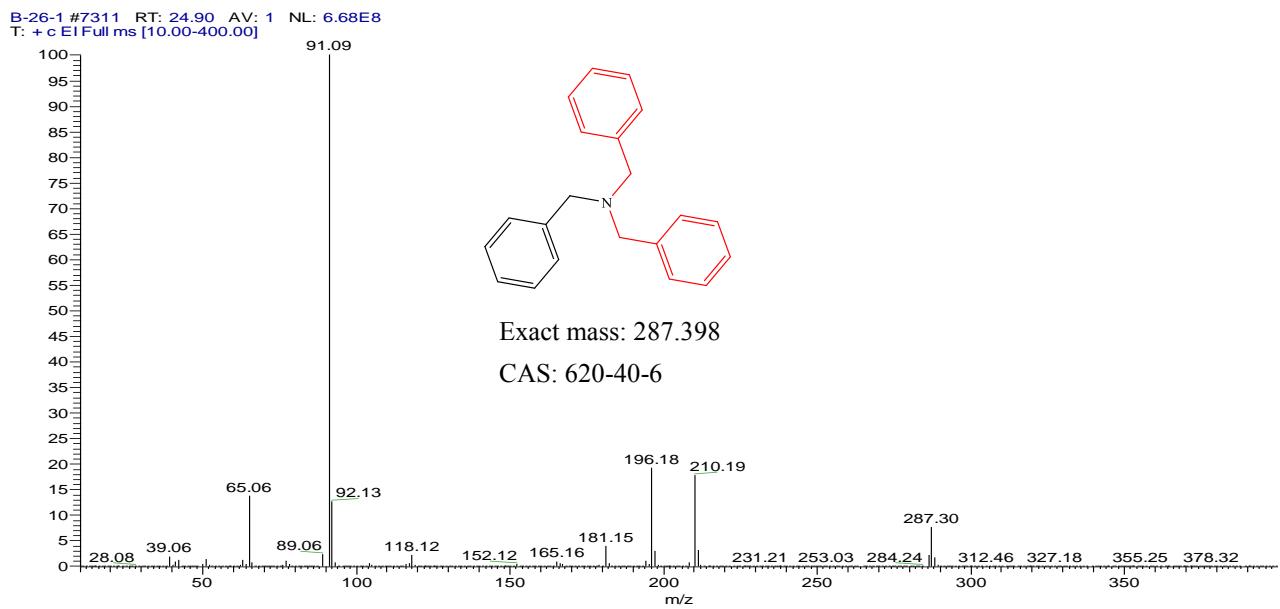
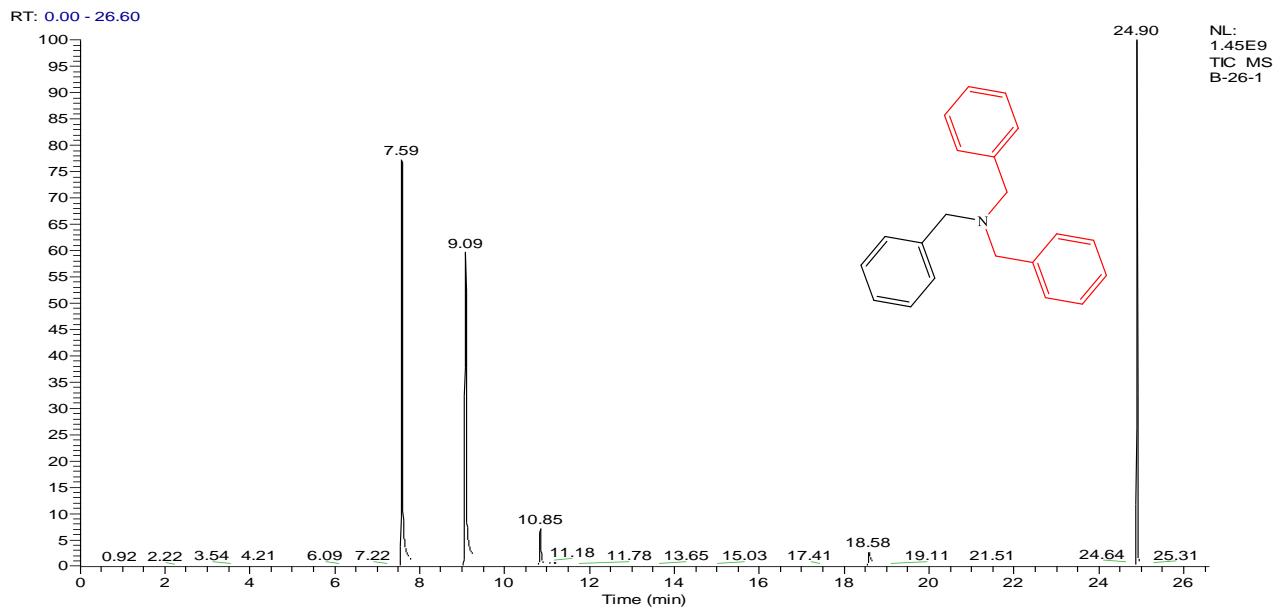
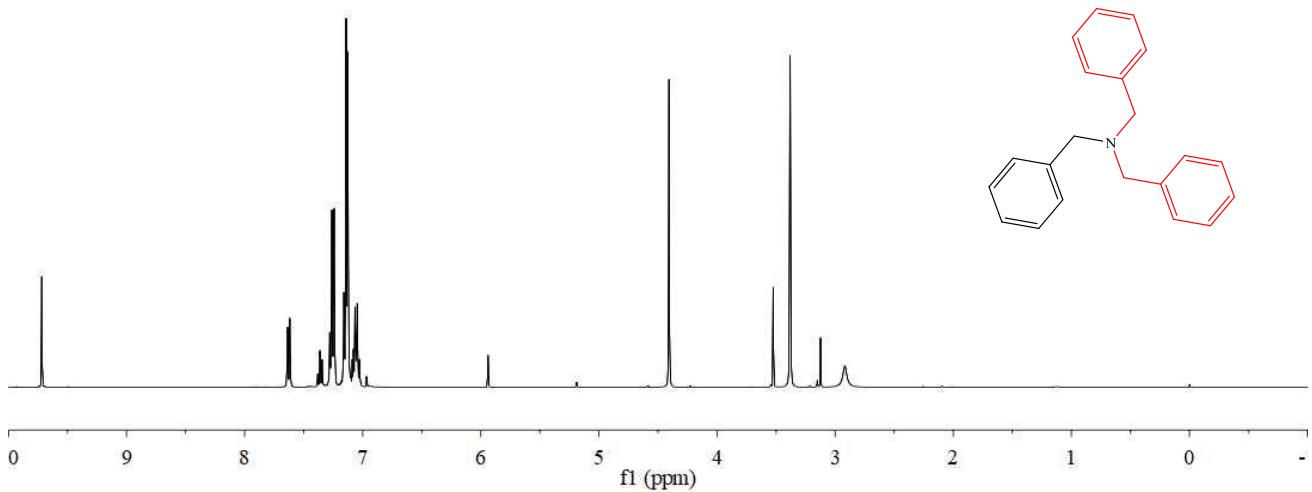


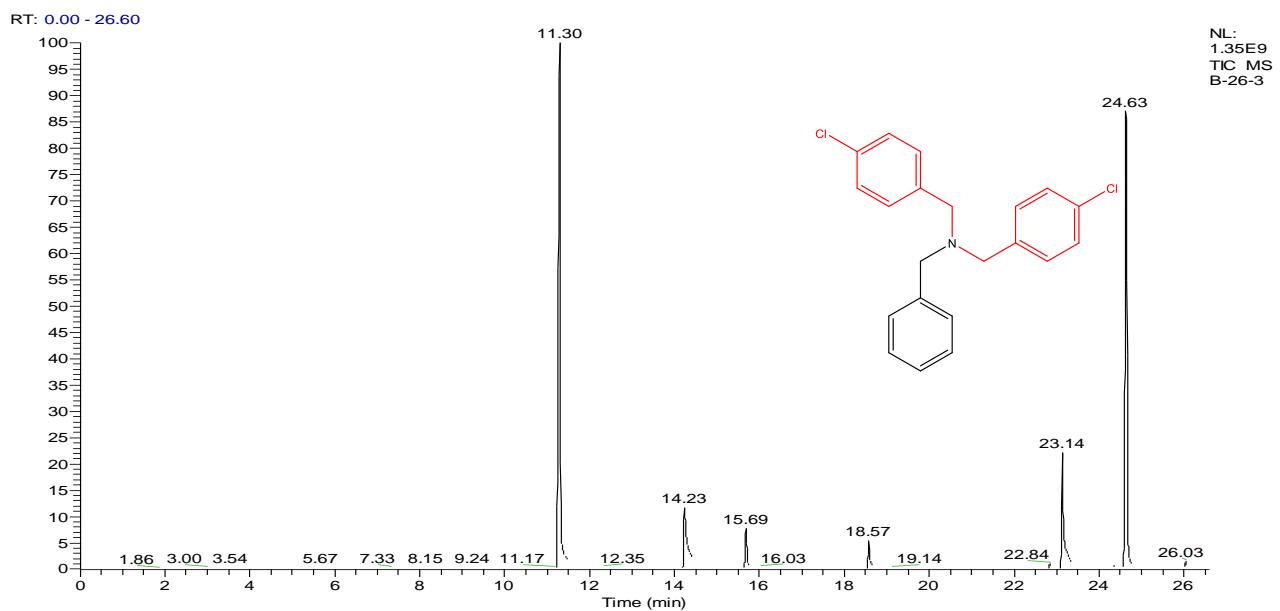
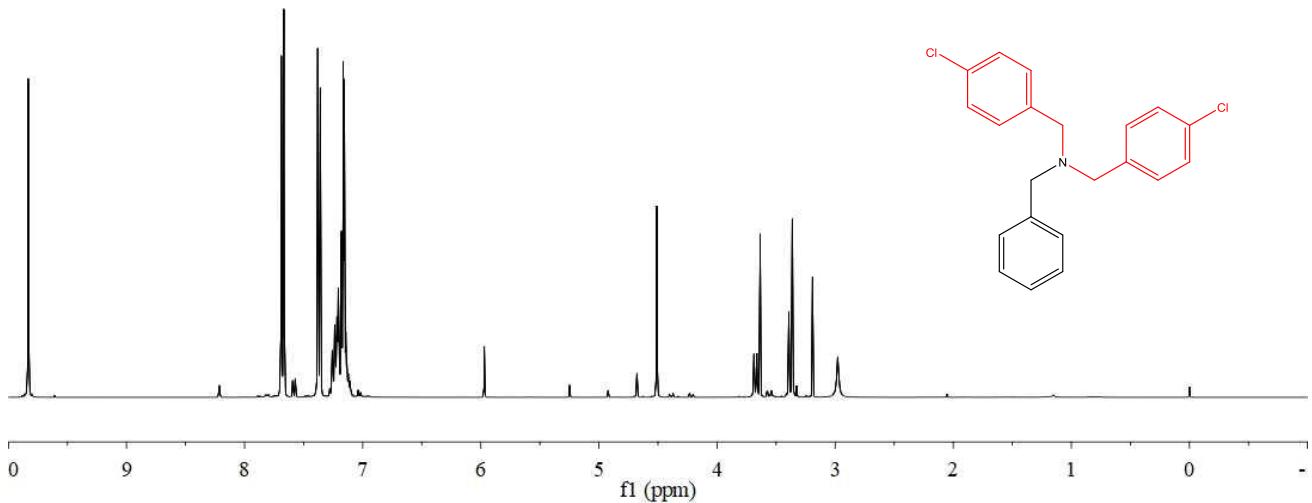




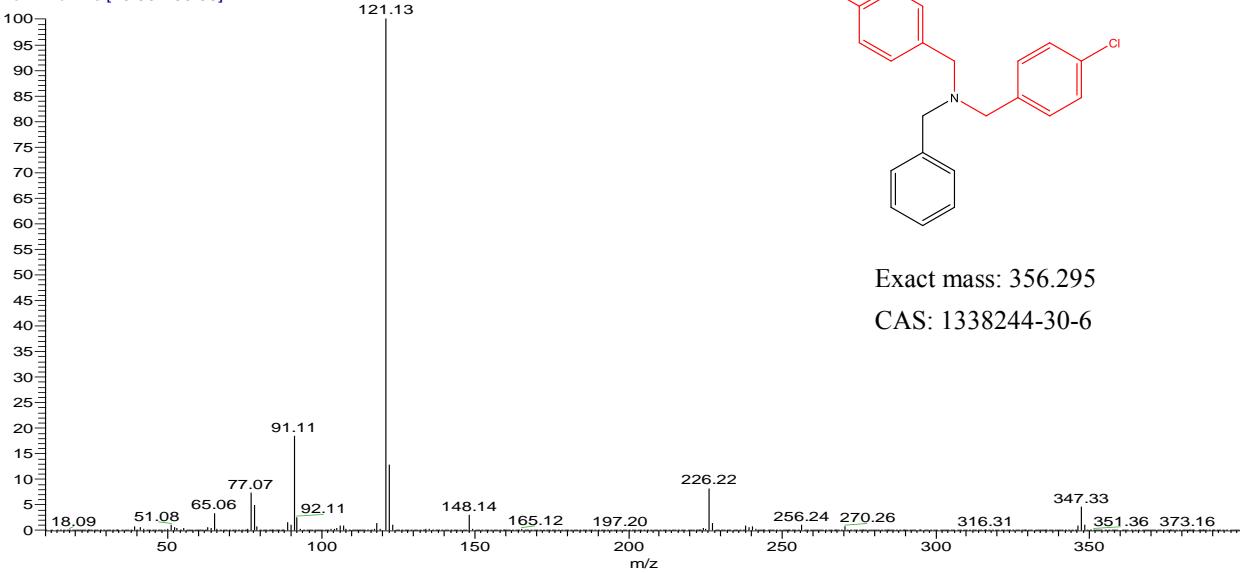


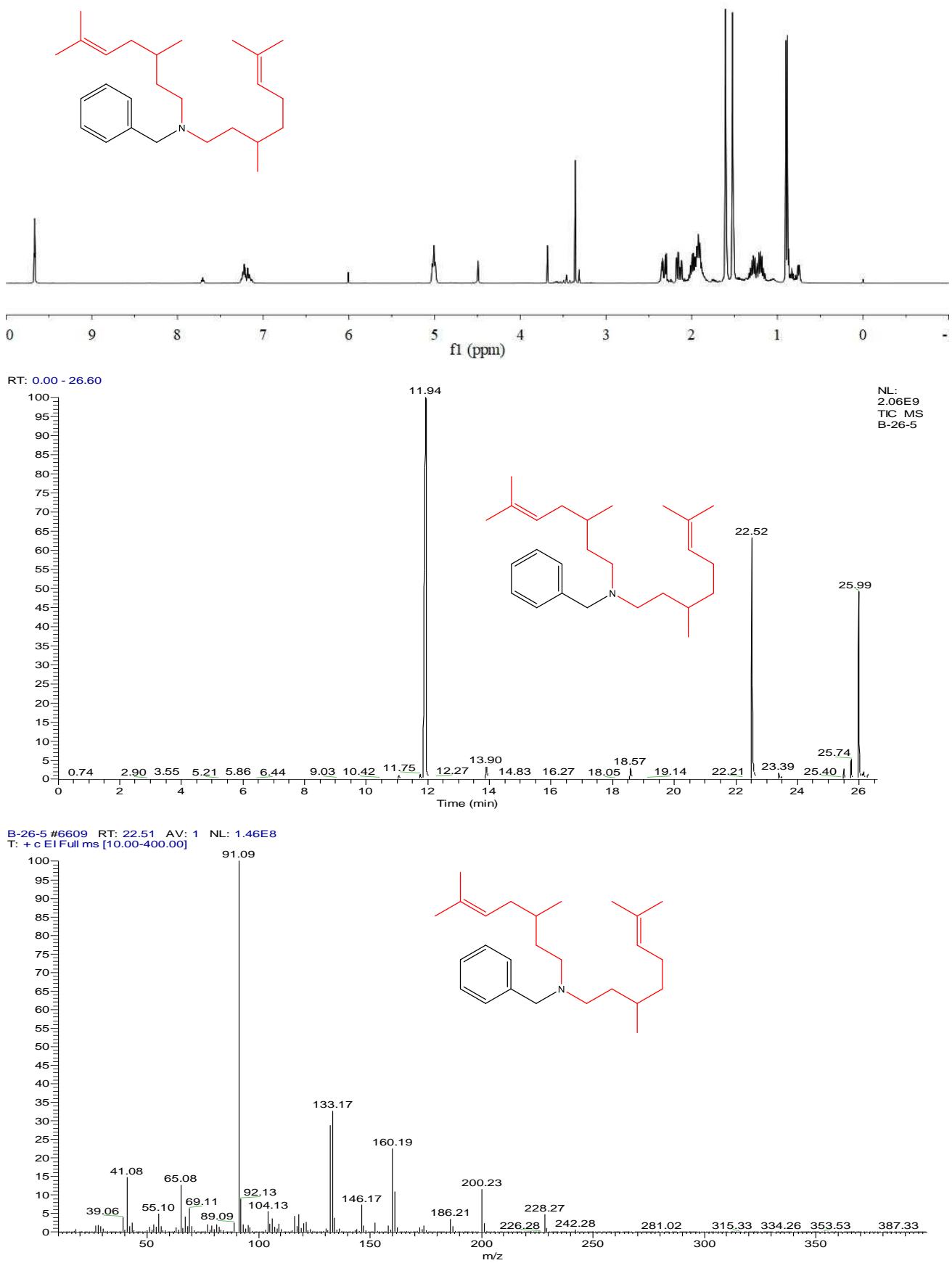


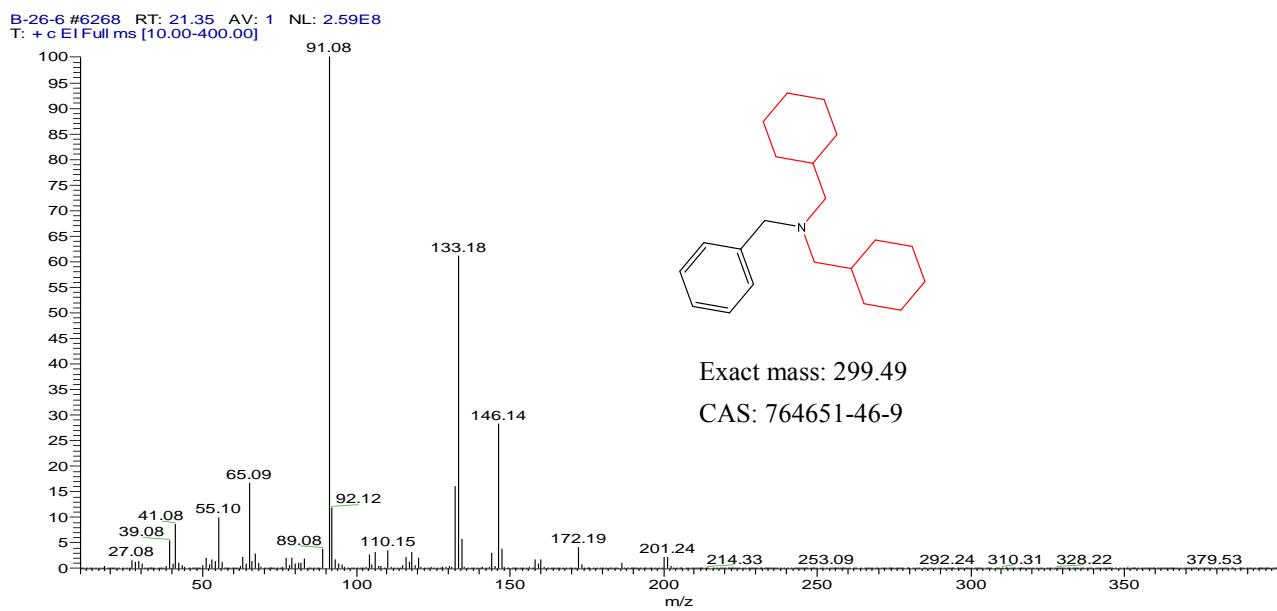
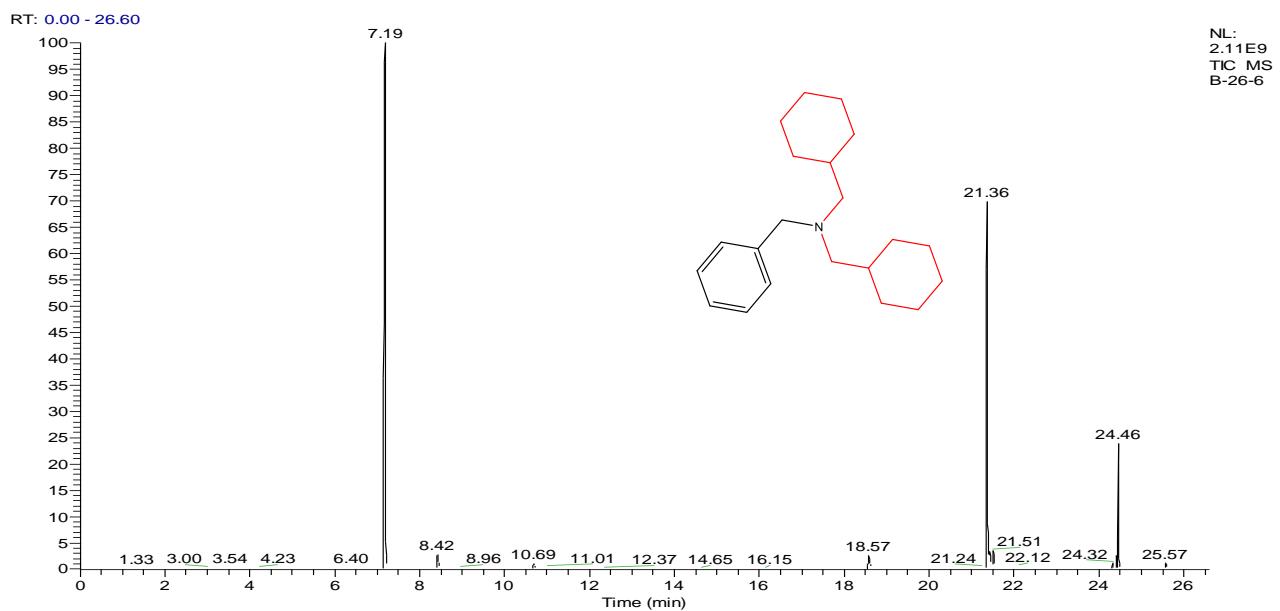
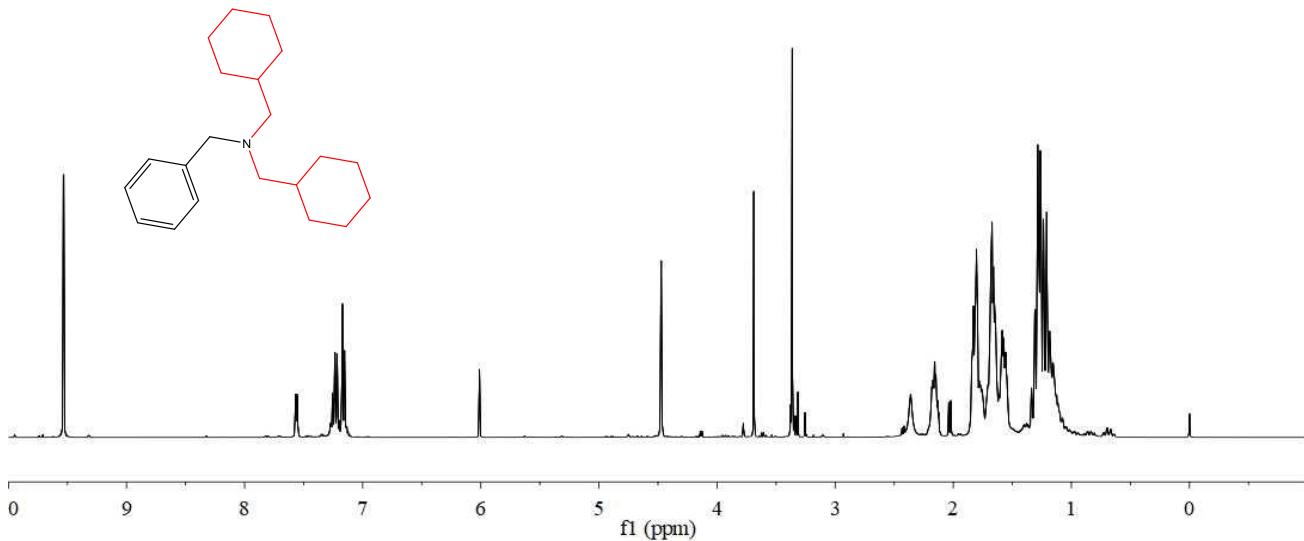


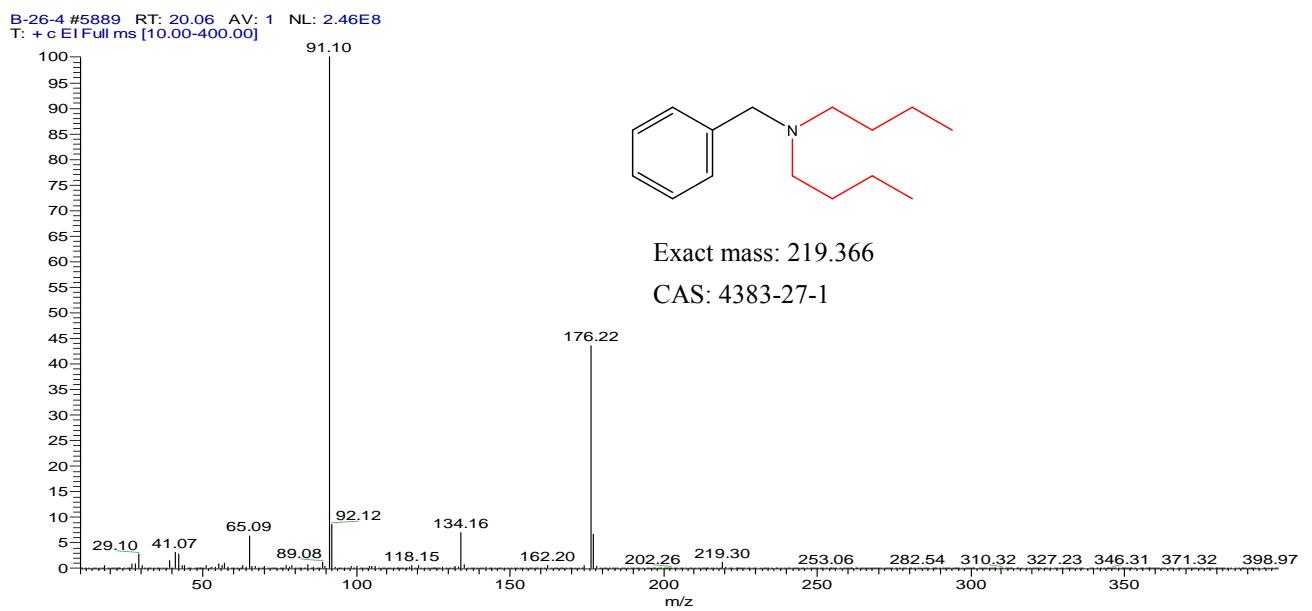
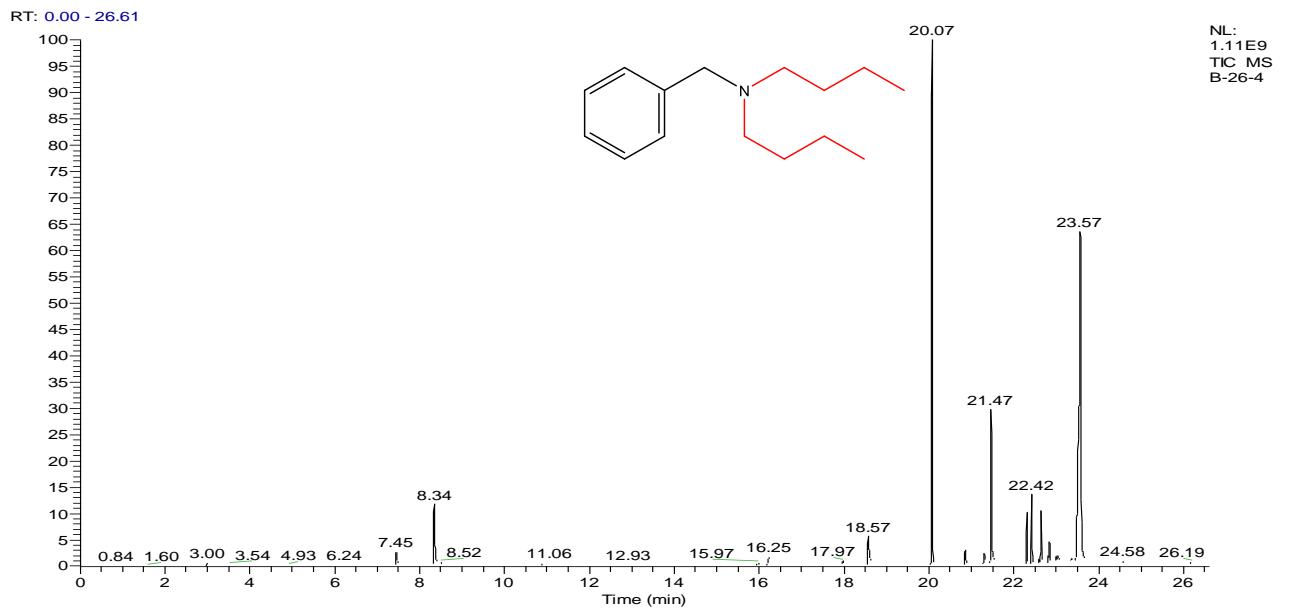
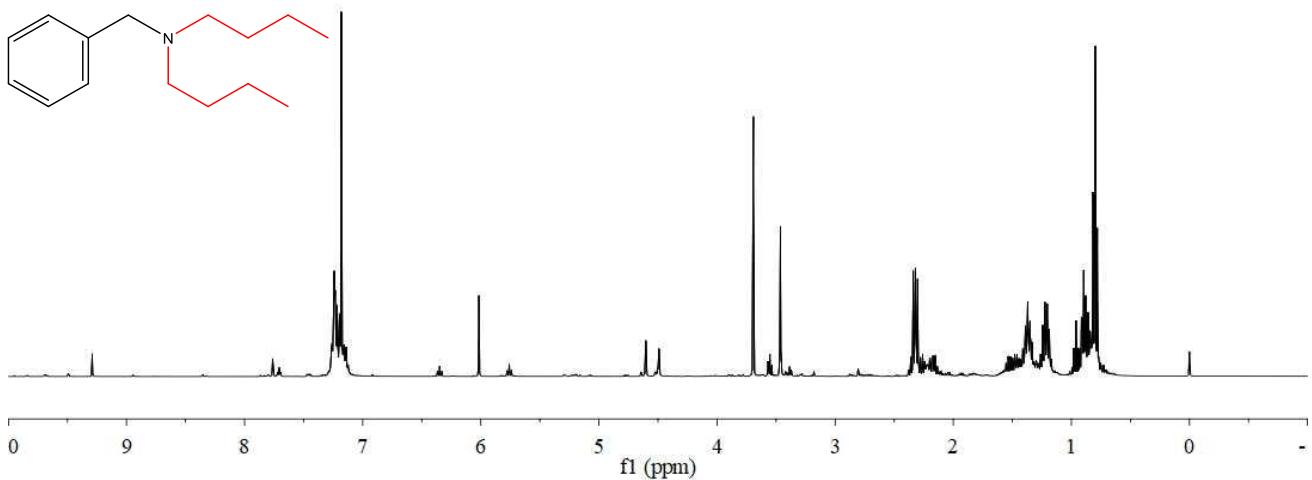


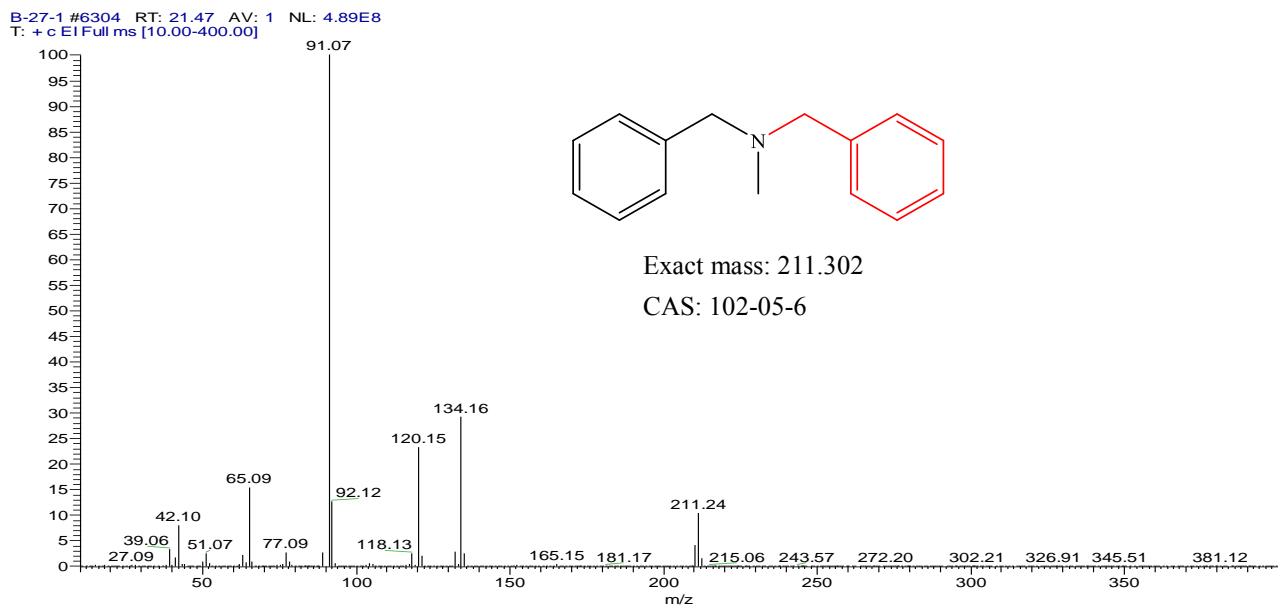
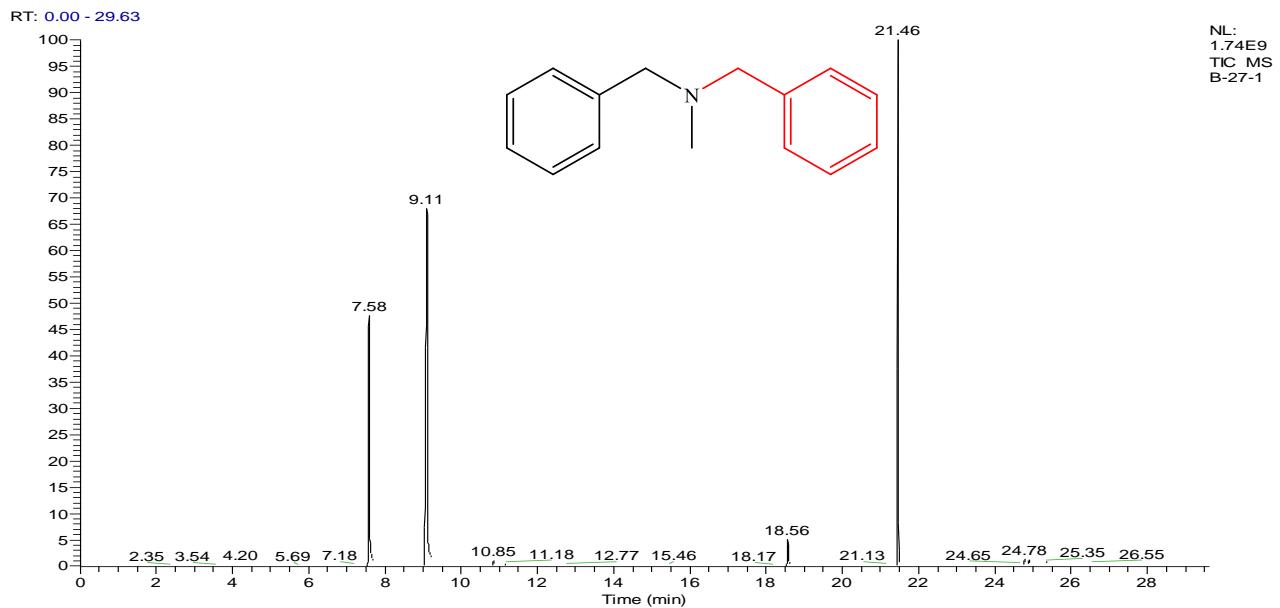
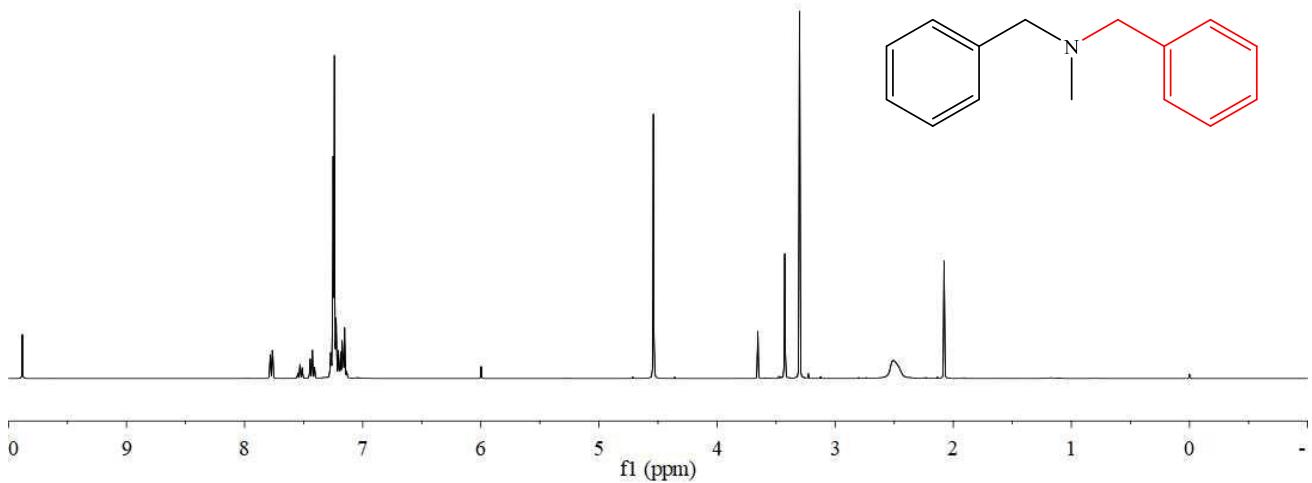
B-26-3 #7233 RT: 24.63 AV: 1 NL: 5.80E8
T: + c EI Full ms [10.00-400.00]

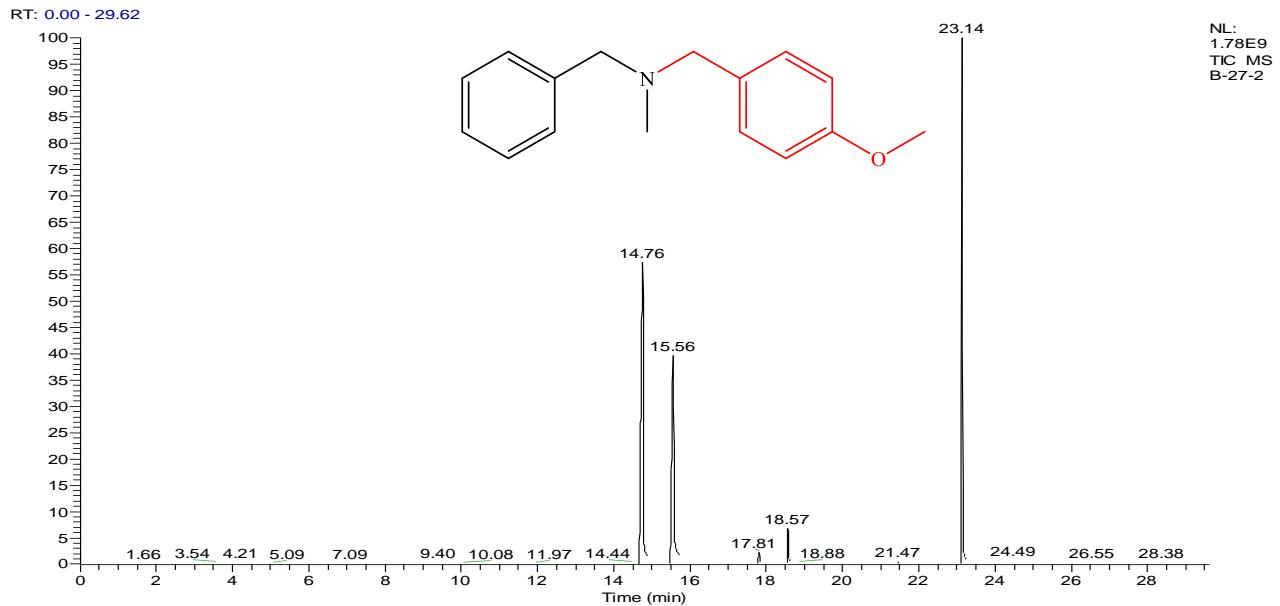
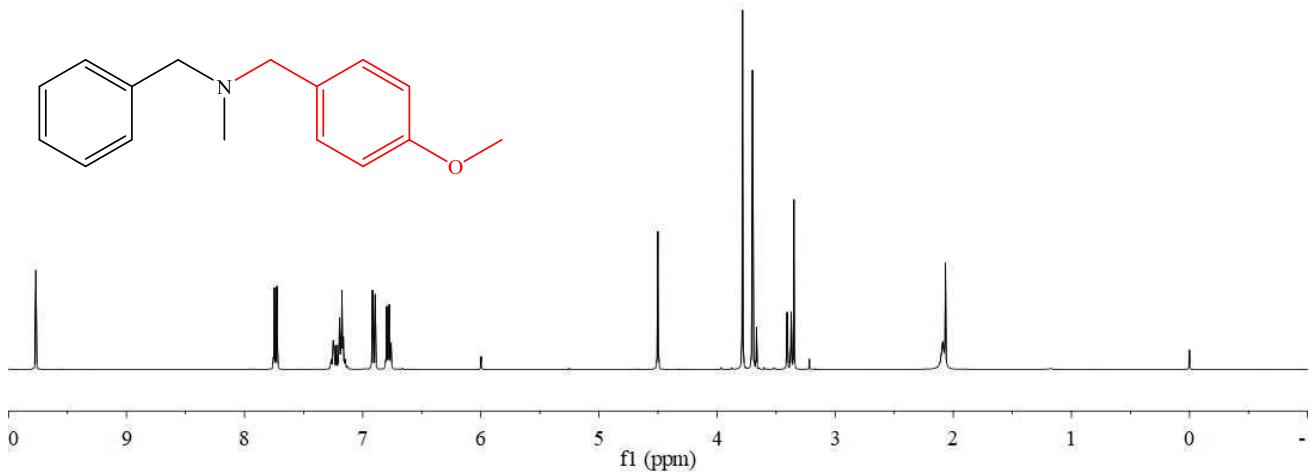




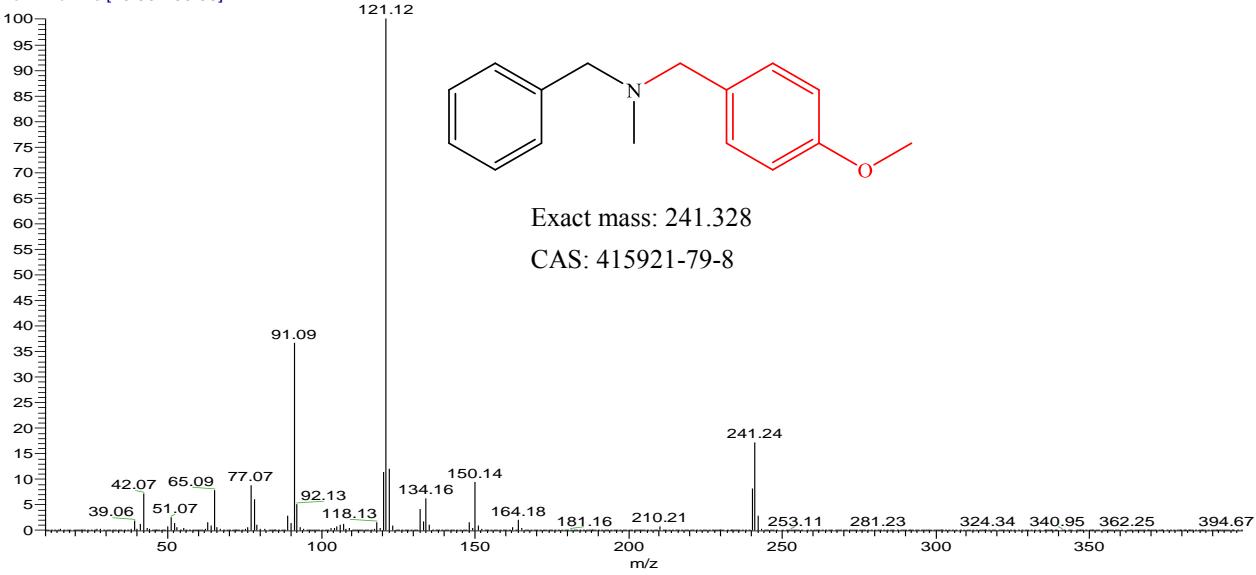


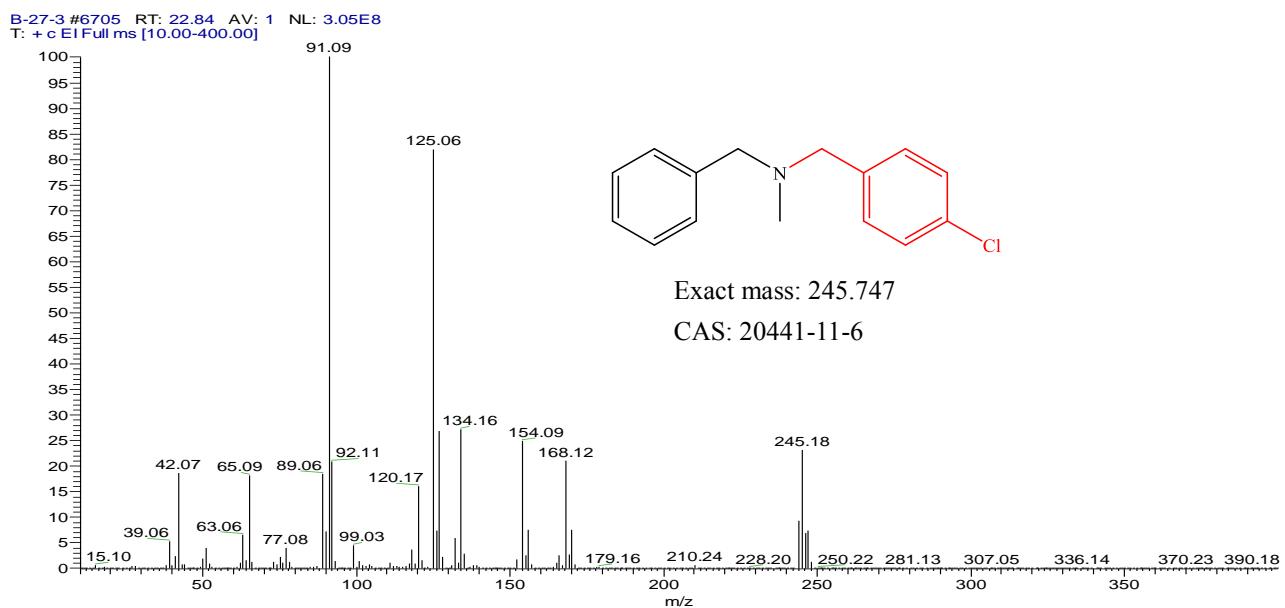
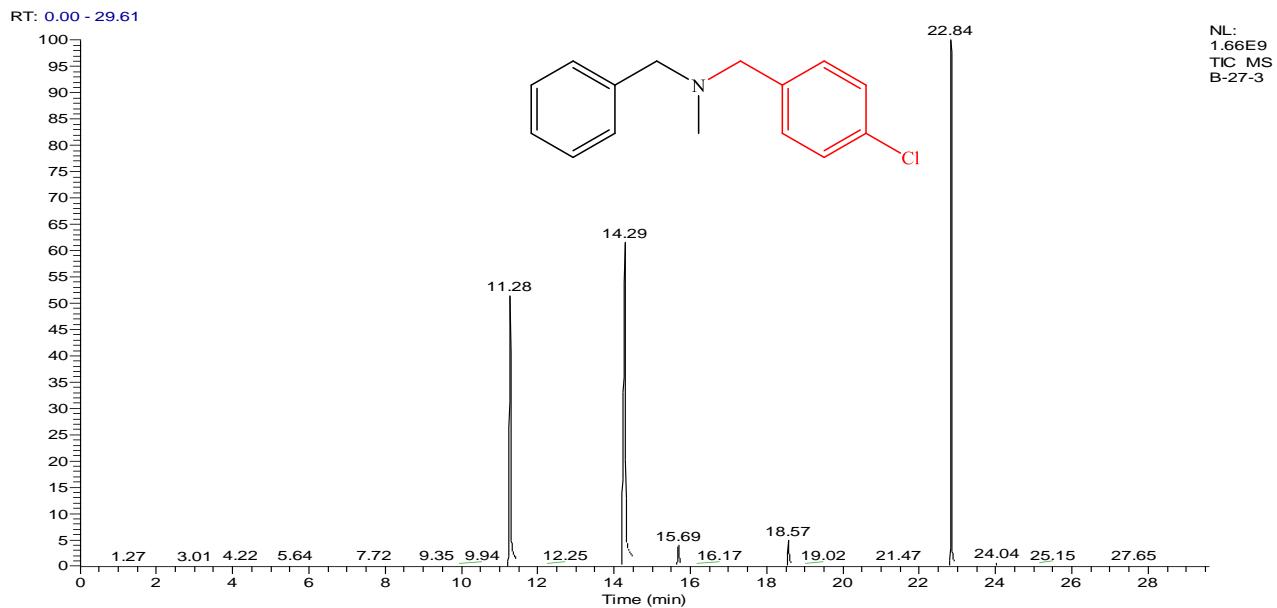
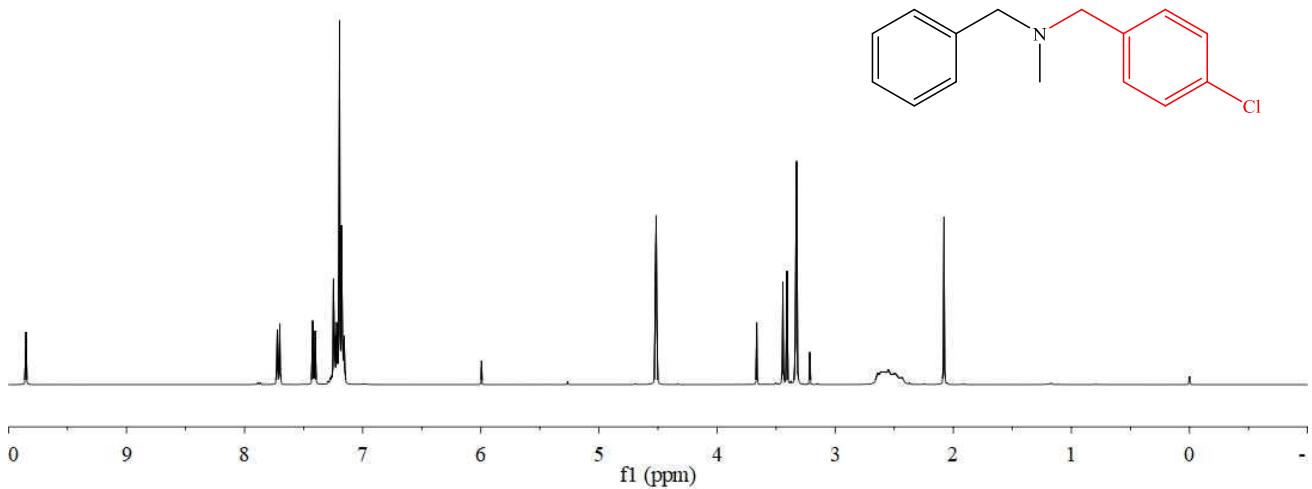




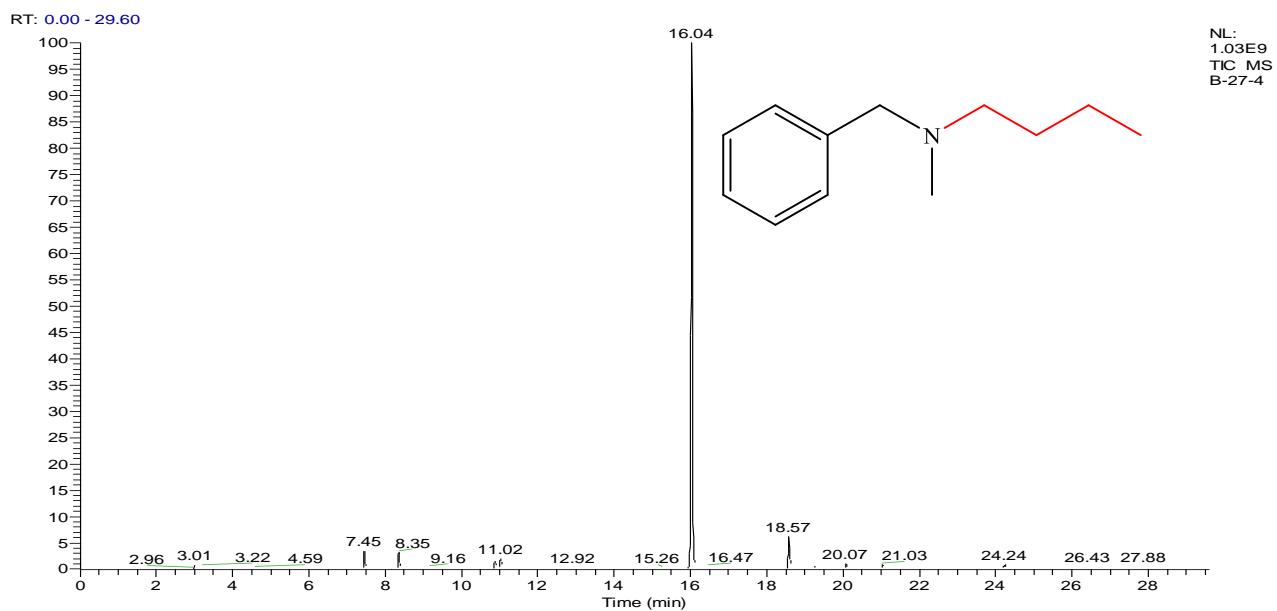
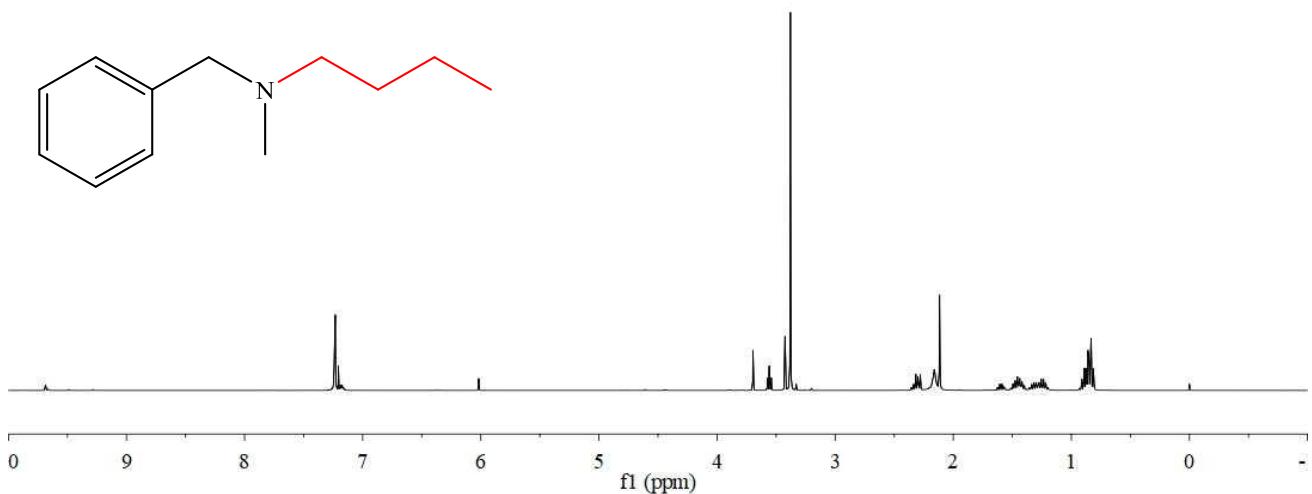


B-27-2 #6794 RT: 23.14 AV: 1 NL: 6.25E8
T: + c EI Full ms [10.00-400.00]

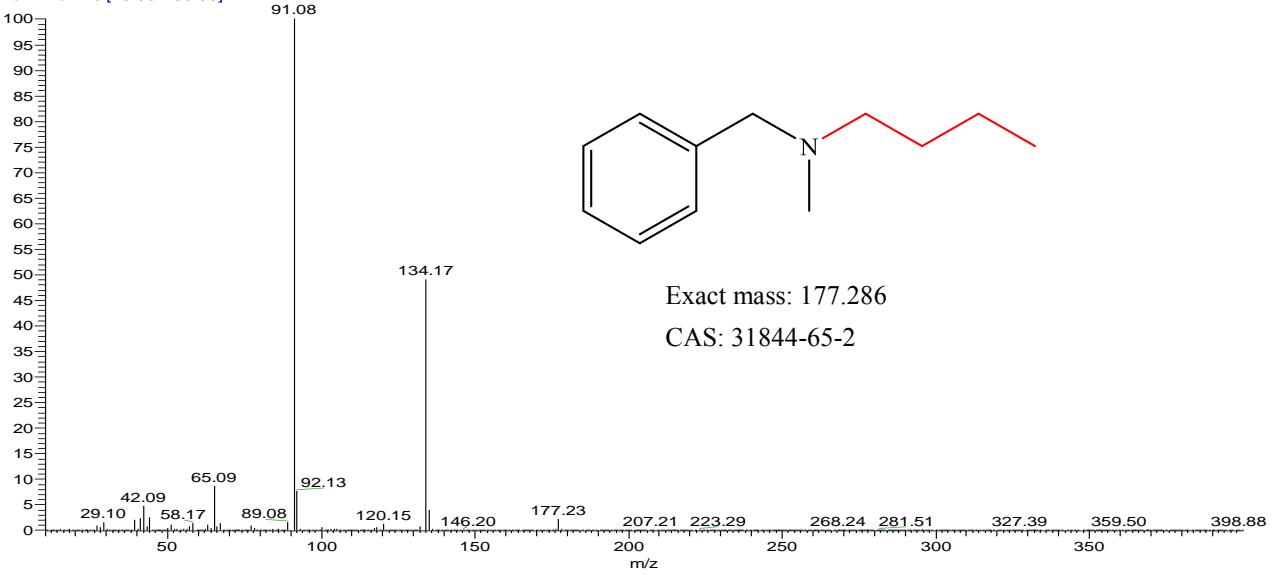


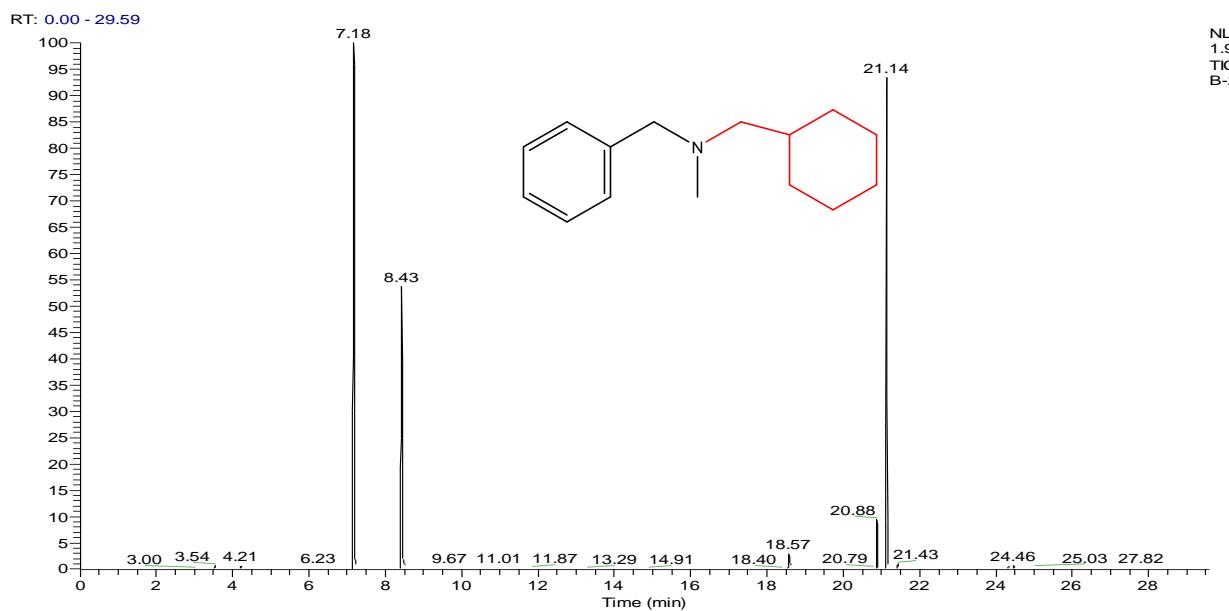
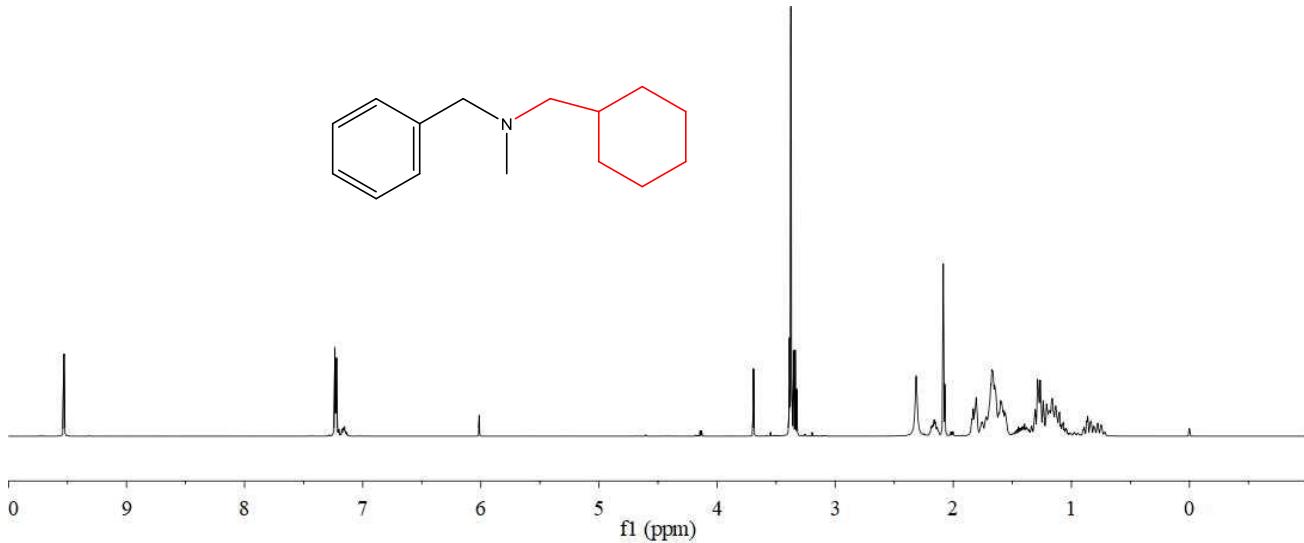


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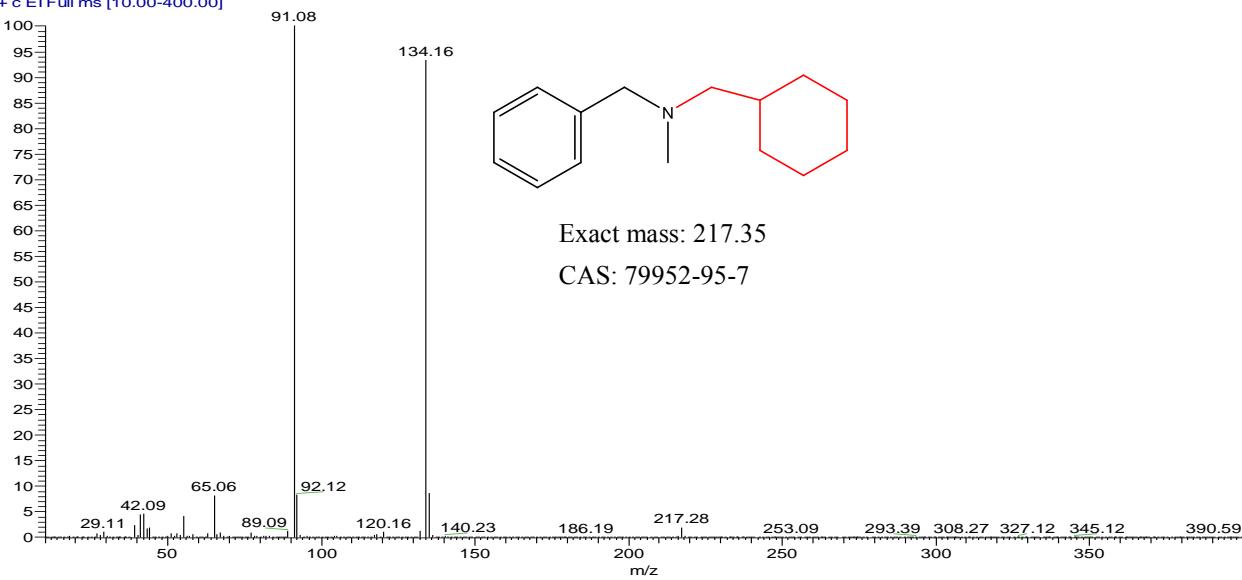


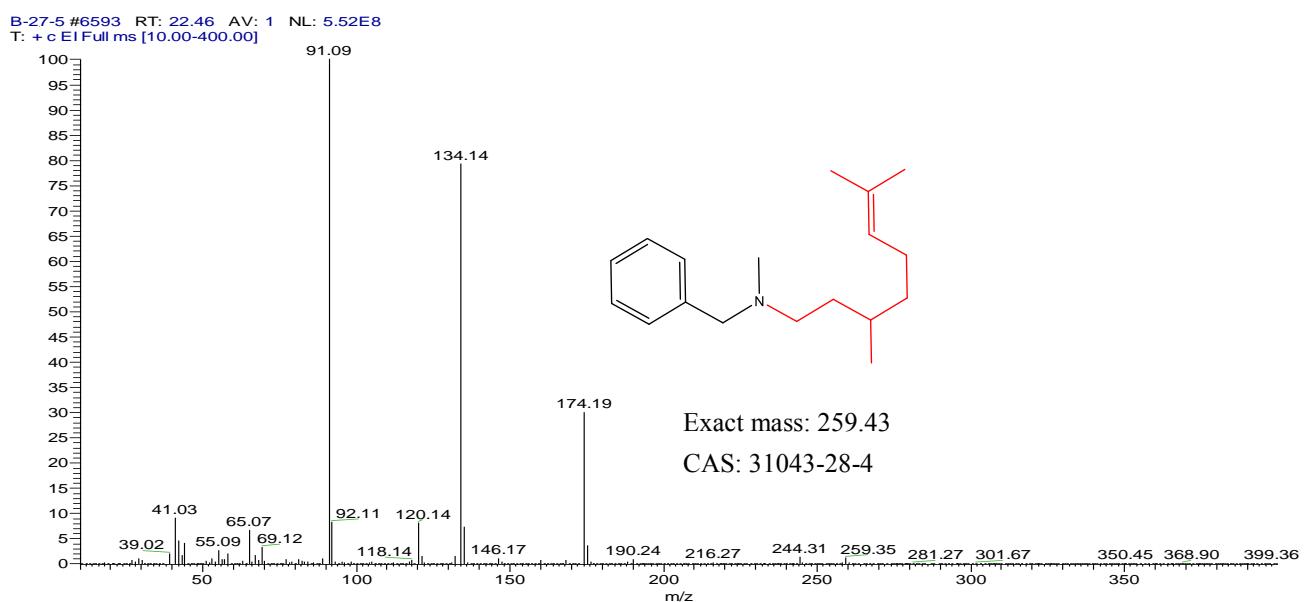
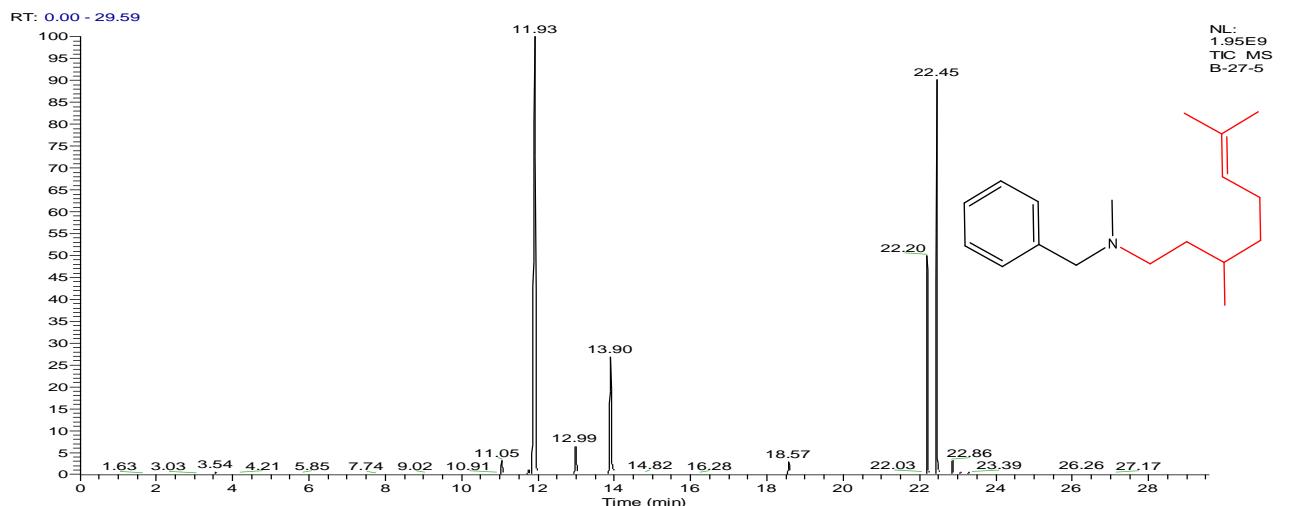
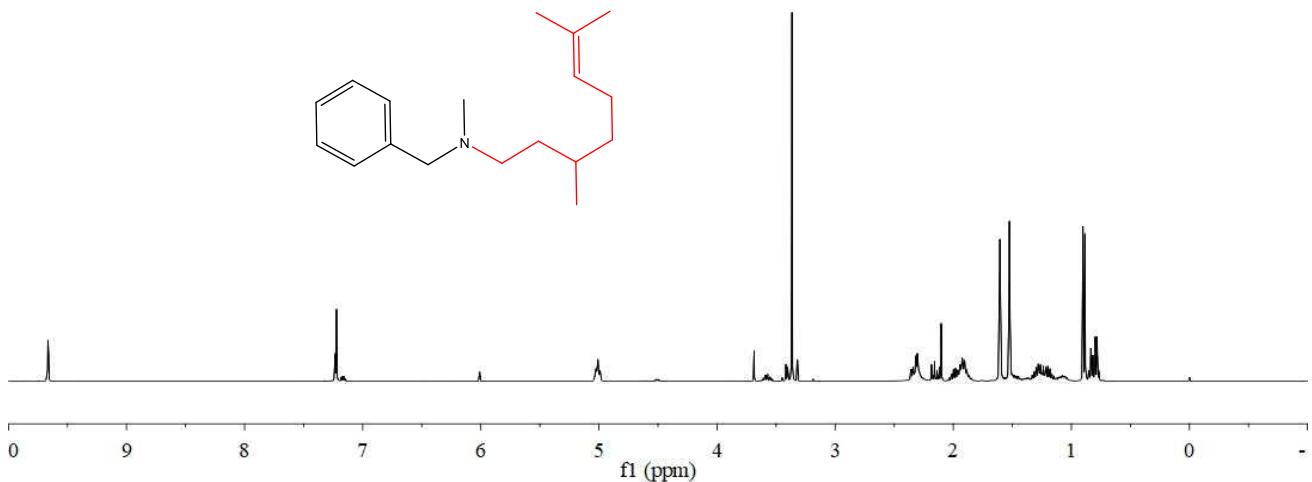
B-27-4 #4706 RT: 16.04 AV: 1 NL: 4.99E8
T: + c EI Full ms [10.00-400.00]



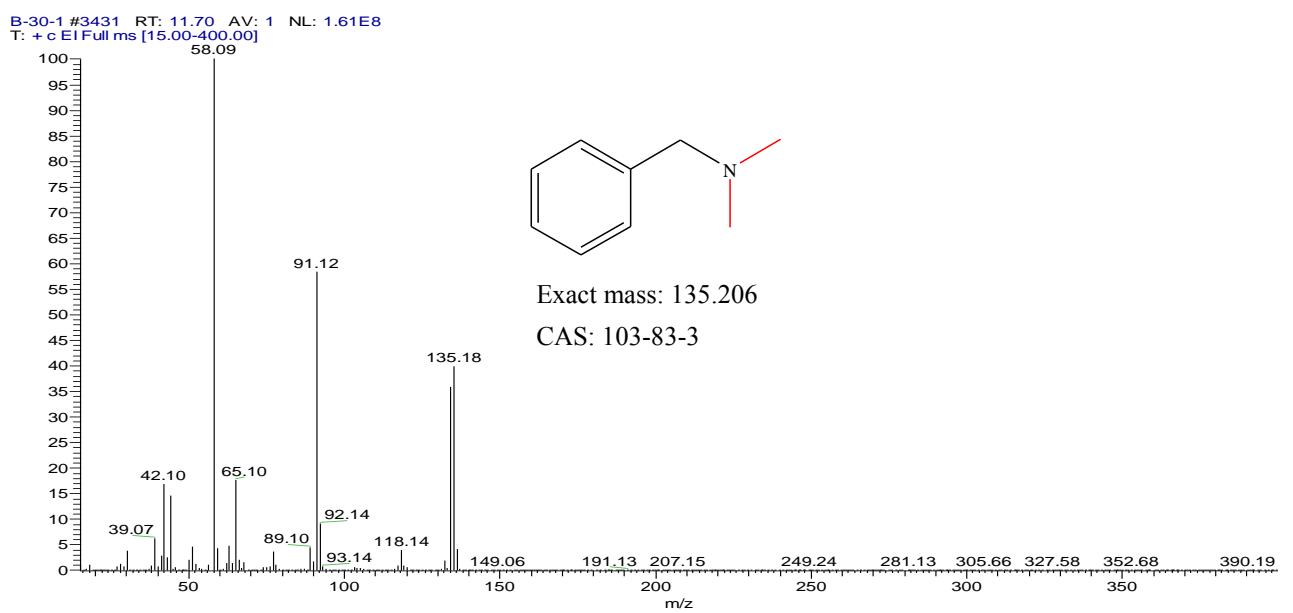
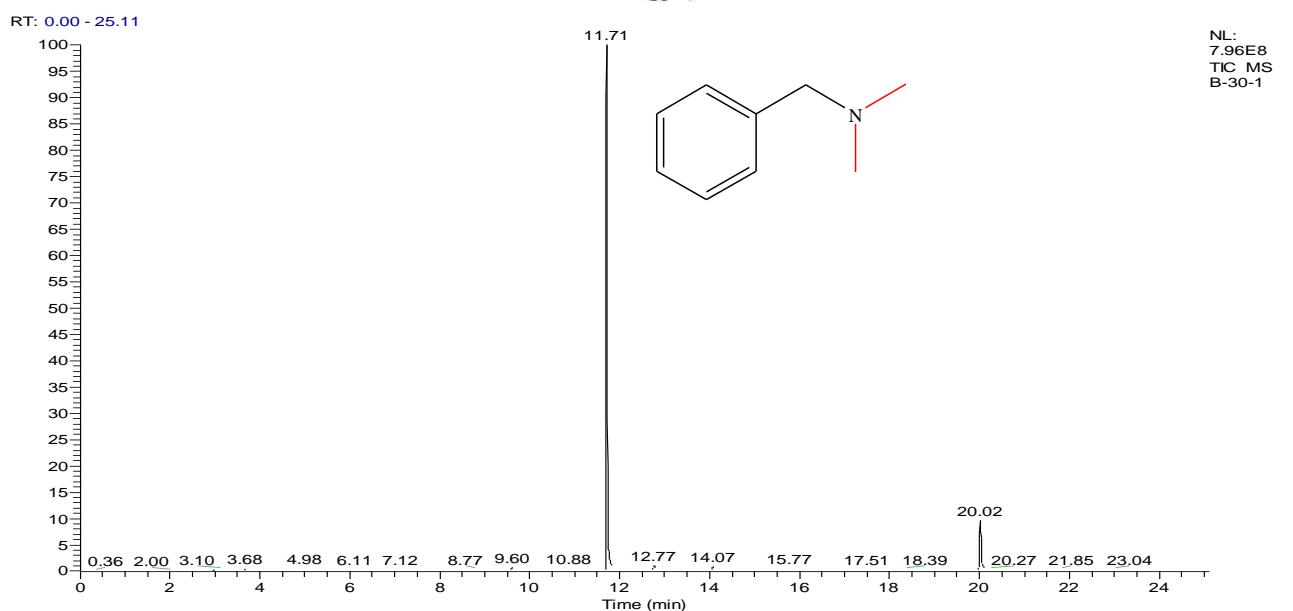
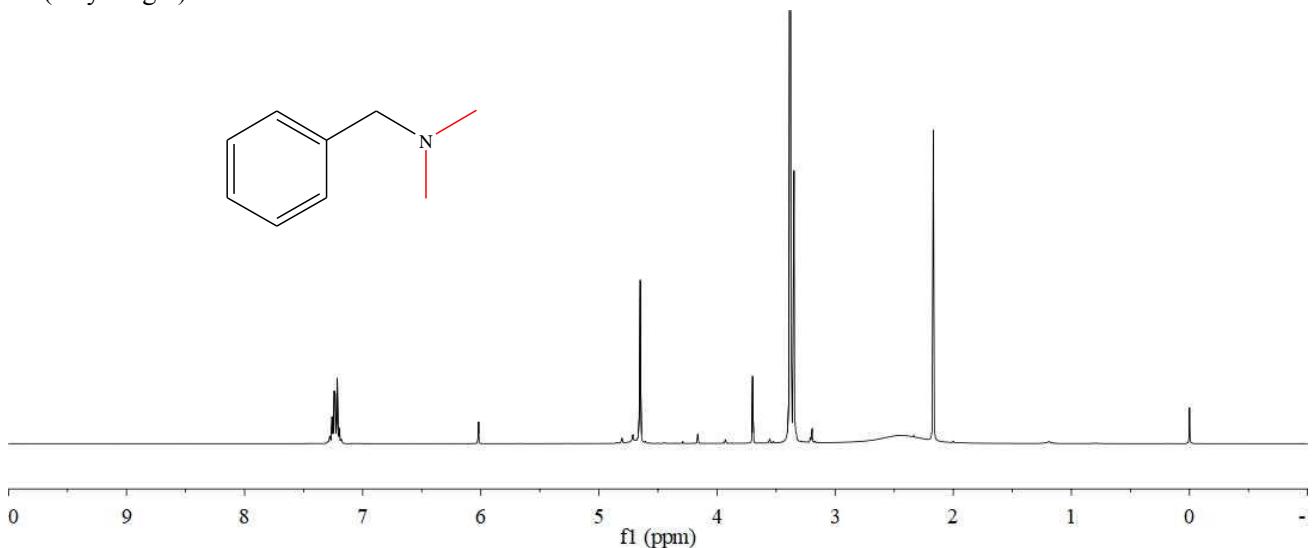


B-27-6 #6203 RT: 21.13 AV: 1 NL: 4.52E8
T: + c EI Full ms [10.00-400.00]

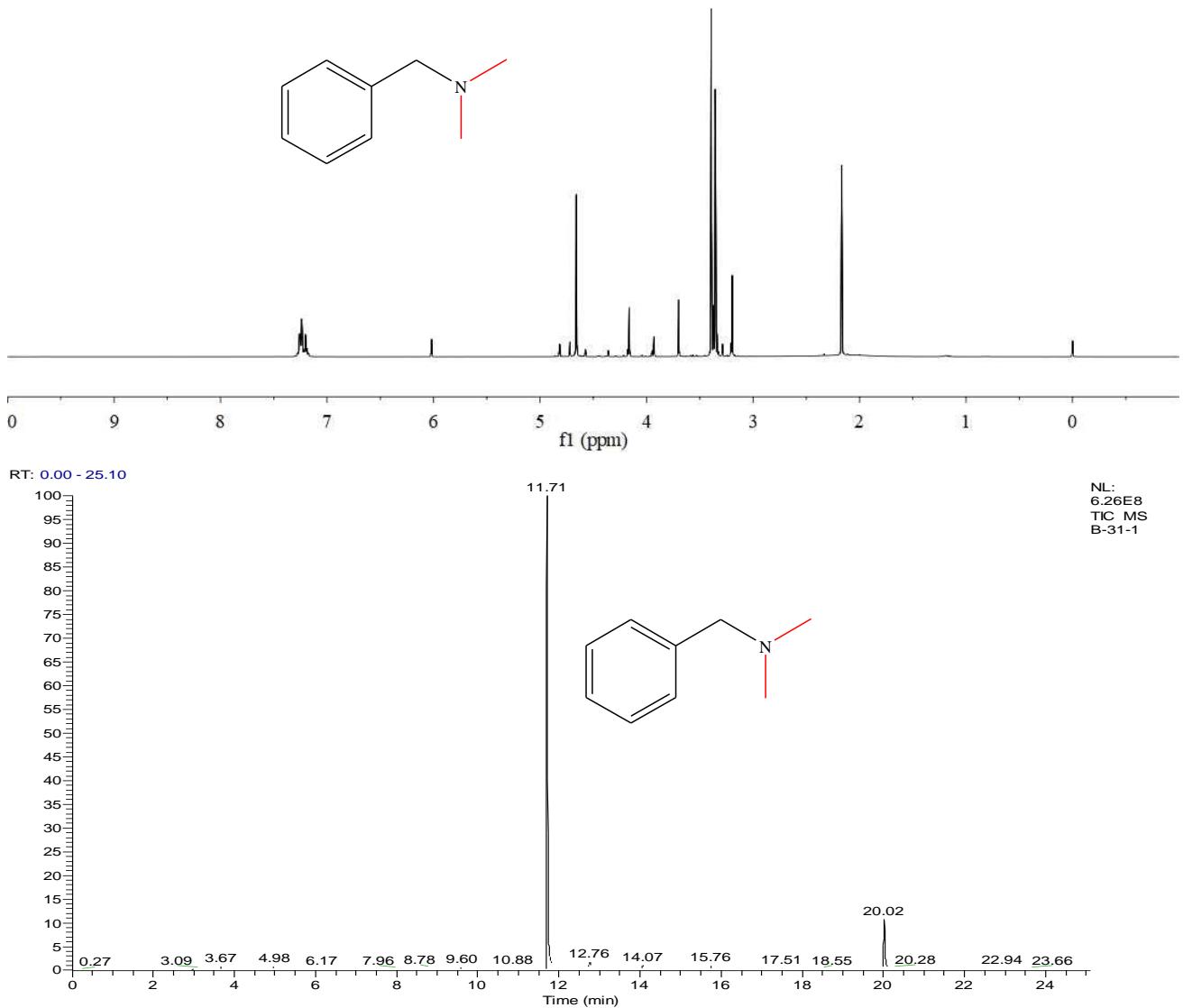




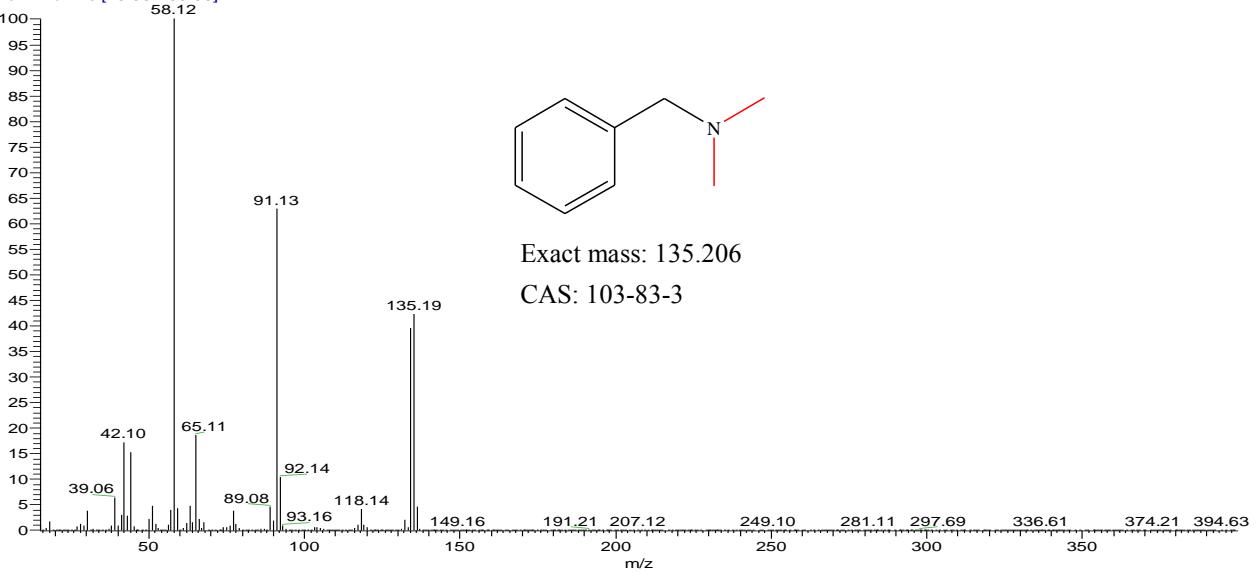
52 (recycling 1)



53 (recycling 2)



B-31-1 #3430 RT: 11.70 AV: 1 NL: 9.22E7
T: + c EIF Full ms [15.00-400.00]



54 (recycling 3)

