

Support information

Alternative reaction pathway triggered by oxygen vacancies for boosting selective hydrodeoxygenation reactions

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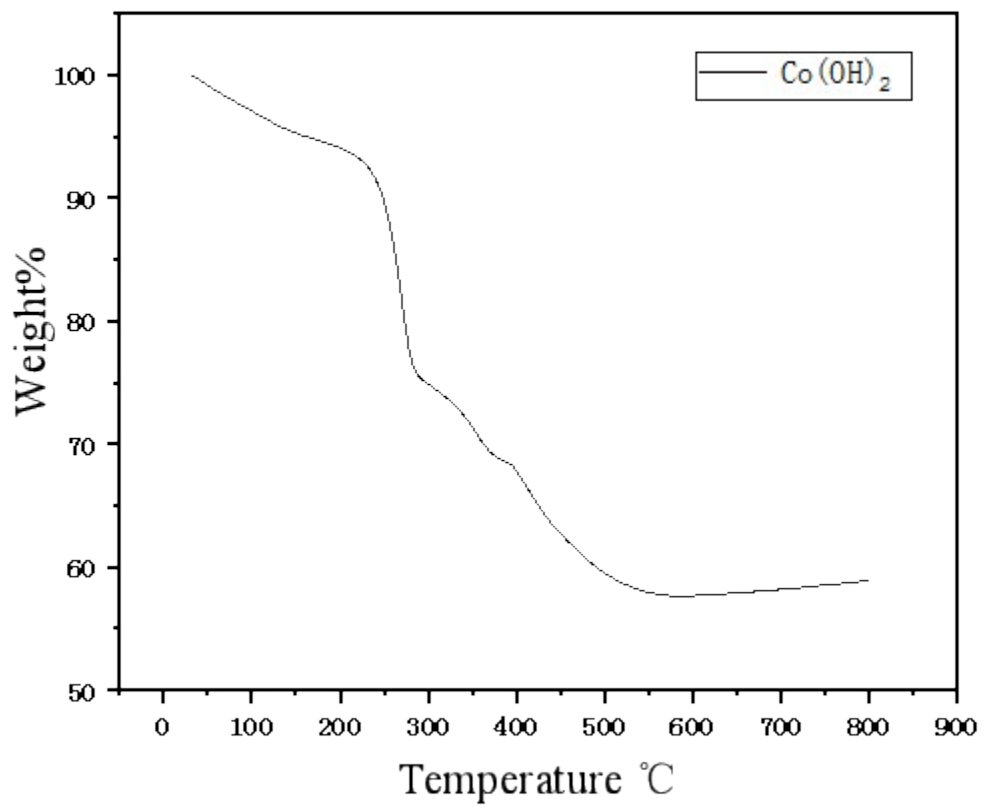


Fig.S1. TG curves of $\text{Co}(\text{OH})_2$ precursor in the flowing N_2 , $5\text{ }^\circ\text{C min}^{-1}$.

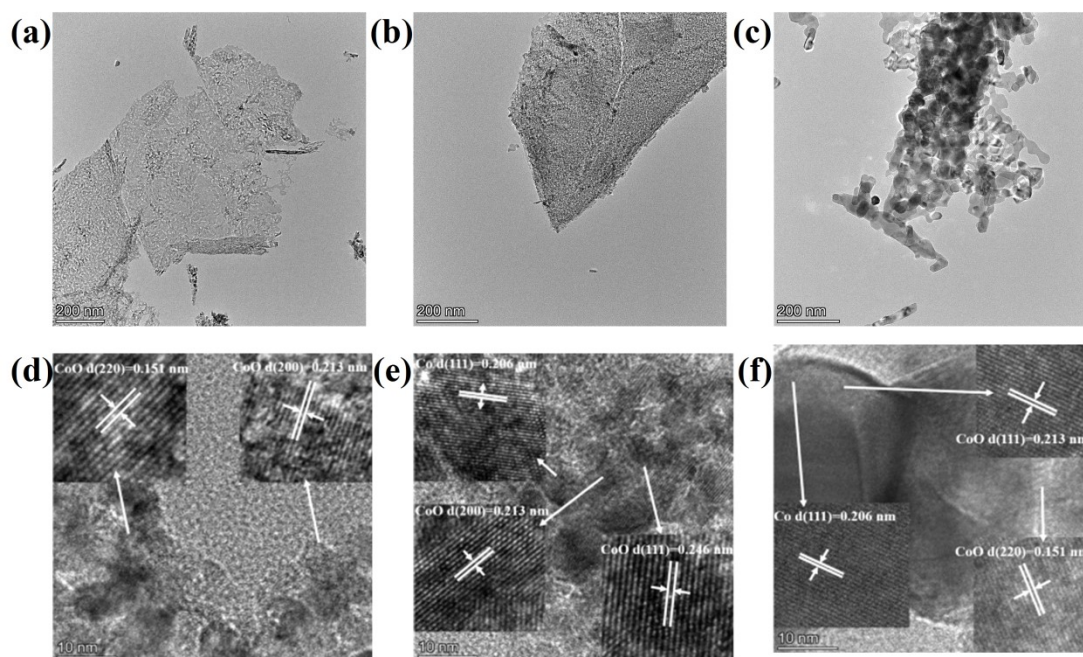


Fig. S2. Electron micrograph of *as*-prepared Co/CoO_x-V-T catalysts. (a-c) TEM images of CoO_x-V-300, Co/CoO_x-V-400 and Co/CoO_x-V-500, respectively; (d-f) HR-TEM images of CoO_x-V-300, Co/CoO_x-V-400 and Co/CoO_x-V-500, respectively.

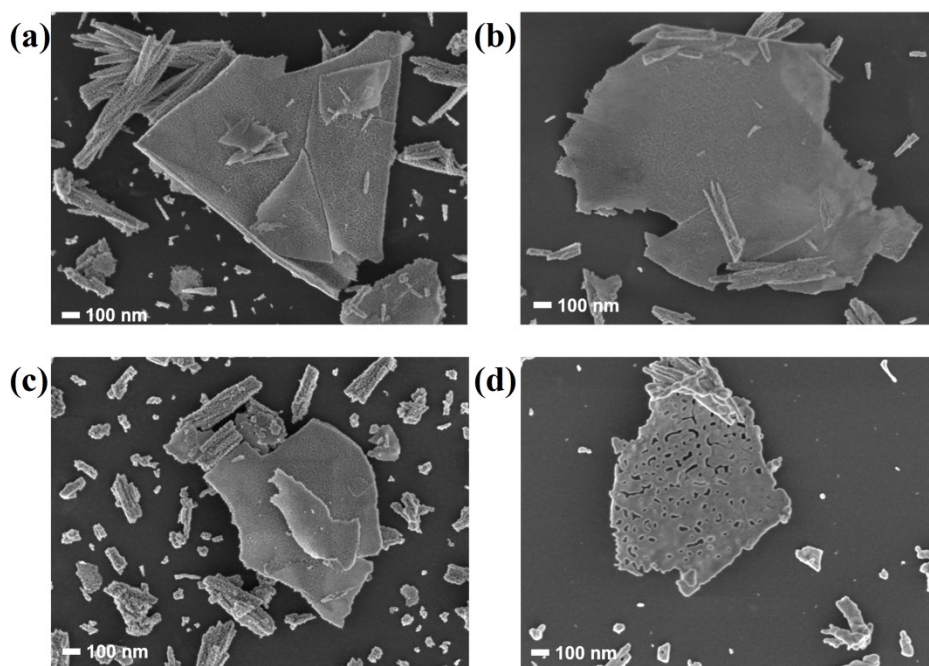


Fig. S3. SEM images of *as*-prepared Co/CoO_x-V-T catalysts. (a) CoO_x-V-300; (b) Co/CoO_x-V-350; (c) Co/CoO_x-V-400; and (d) Co/CoO_x-V-500.

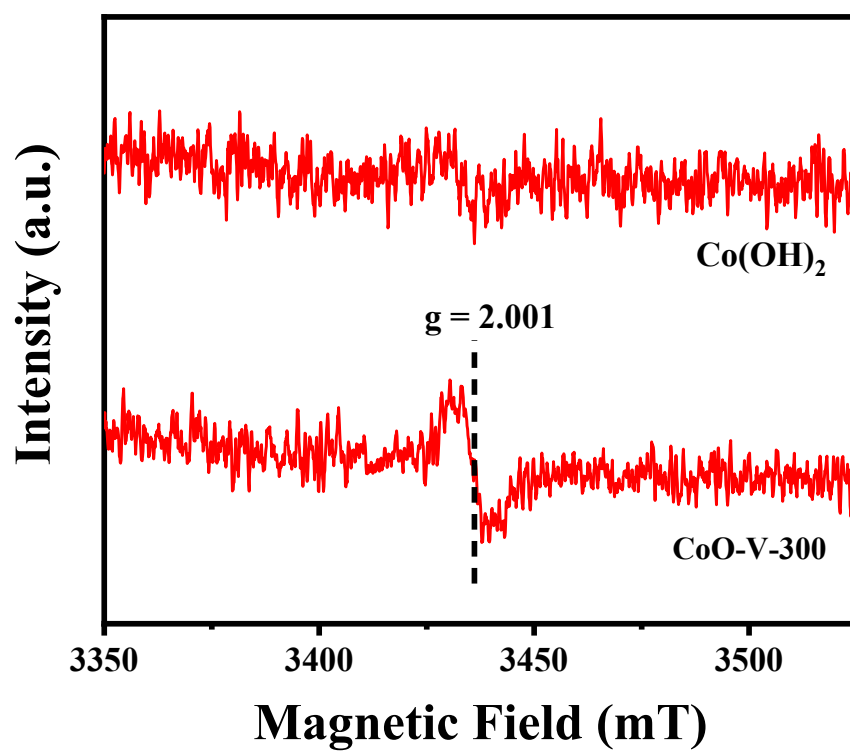


Fig. S4. EPR spectra of Co(OH)₂ and CoO_x-V-300.

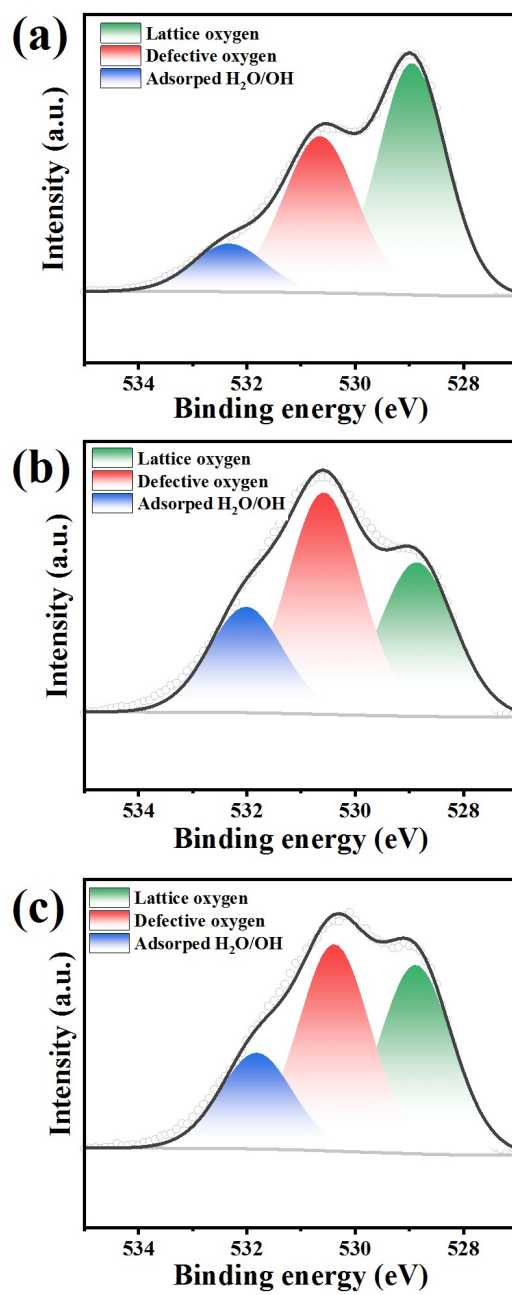


Fig. S5. O 1s XPS spectra of the *as*-prepared catalysts. (a) CoO_x-V-300; (b) Co/CoO_x-V-400; (c) Co/CoO_x-V-500.

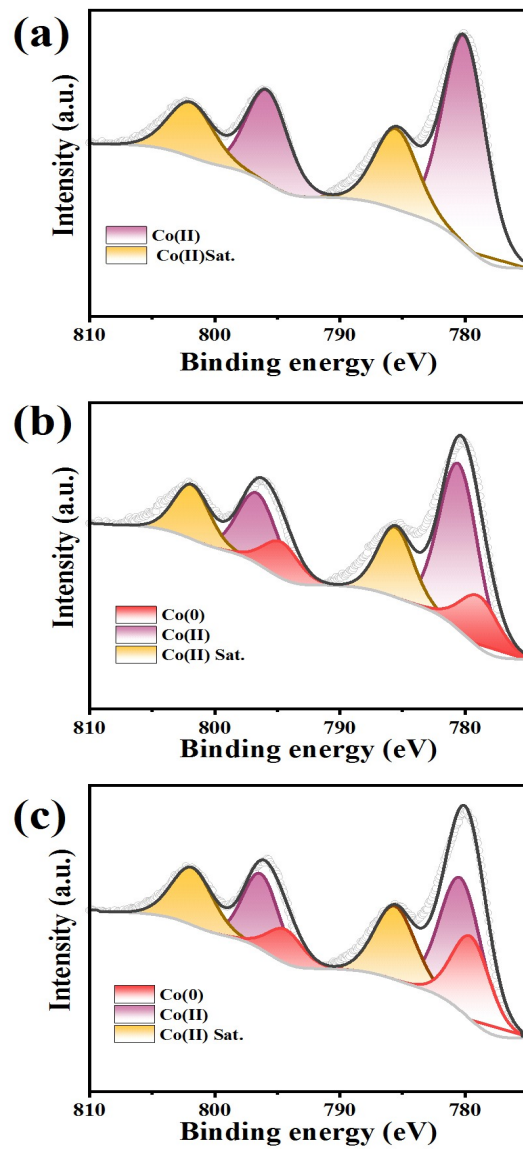


Fig. S6. Co 2p XPS spectra of the as-prepared samples. (a) CoO_x-V-300; (b) Co/CoO_x-V-400; (c) Co/CoO_x-V-500.

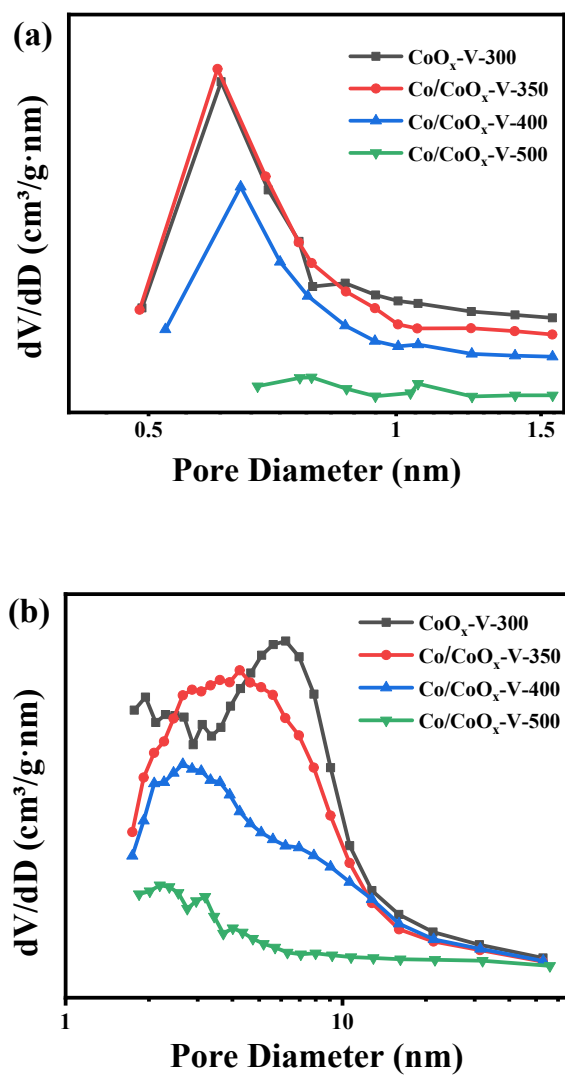


Fig. S7. (a) micropore and (b) mesoporous pore size distribution of the *as*-prepared catalysts.

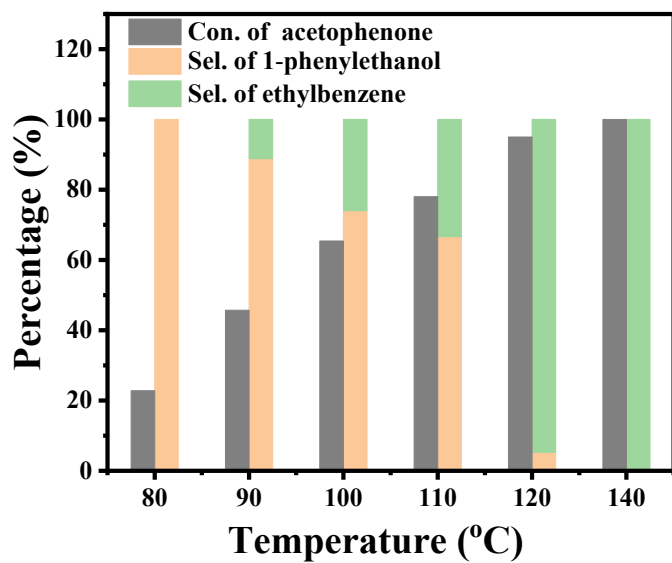


Fig. S8. The effect of reaction temperature on the hydrodeoxygenation of acetophenone. Reaction conditions: acetophenone (0.5 mmol), toluene (5 mL), Co/CoO-V-350 (20 mg), H₂ (10 bar), 4 h.

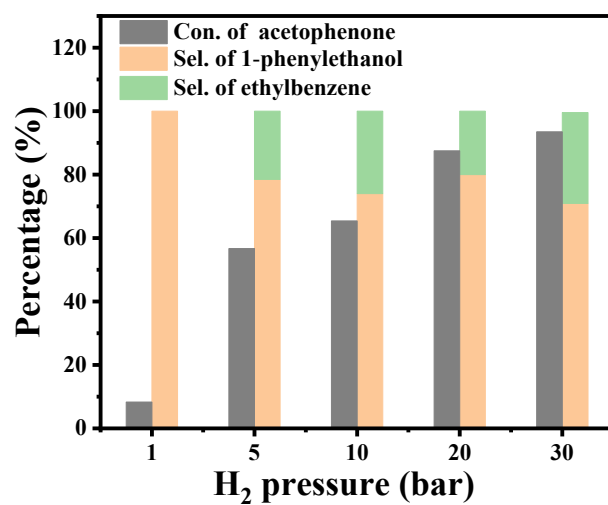


Fig. S9. The effect of H₂ pressure on the hydrodeoxygenation of acetophenone. Reaction conditions: acetophenone (0.5 mmol), toluene (5 mL), Co/CoO-V-350 (20 mg), 100 °C and 4 h.

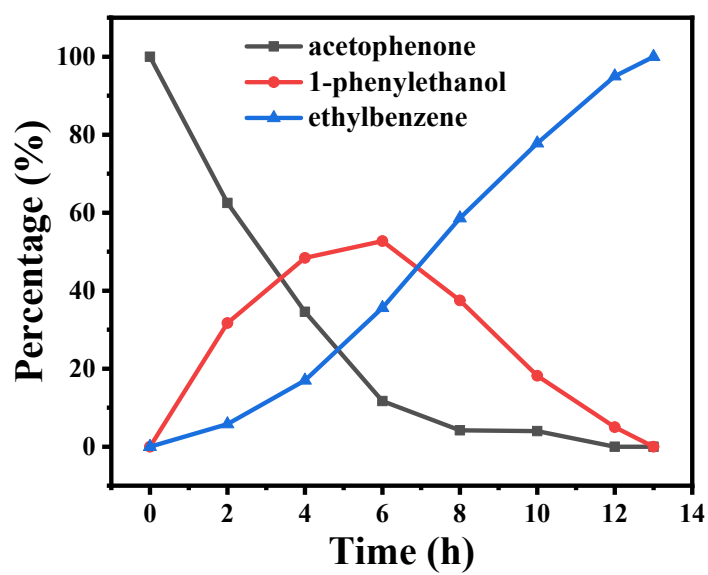


Fig. S10. Time distribution curve of the hydrodeoxygenation of acetophenone. Reaction conditions: acetophenone (0.5 mmol), 5 mL toluene, 20 mg catalyst, 10 bar H_2 , 100°C.

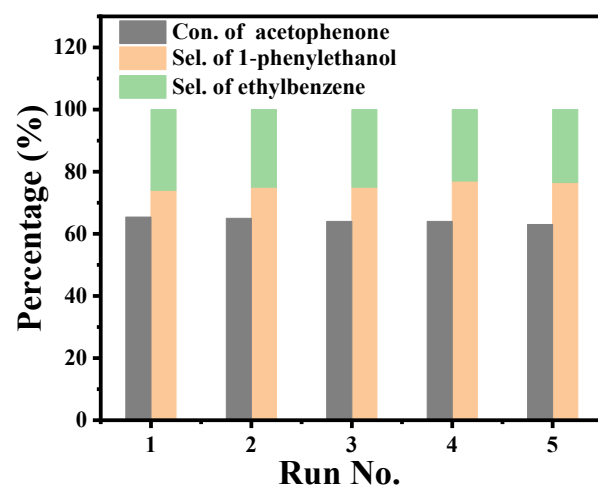


Fig. S11. Catalyst recycling experiments of the Co/CoO-V-350 catalyst. Reaction conditions: acetophenone (0.5 mmol), 5 mL toluene, 20 mg catalyst, 10 bar H₂, 100°C and 4 h.

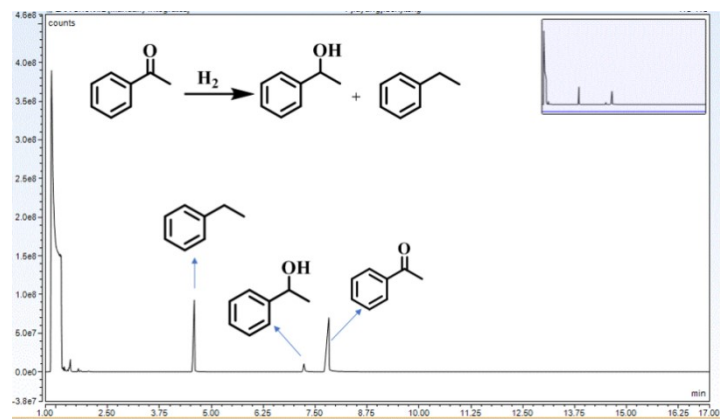


Fig. S12. GC-Mass spectra of the result of hydrodeoxygenation of acetophenone. Reaction conditions: acetophenone (0.5 mmol), 5 mL toluene, 20 mg catalyst, 10 bar H₂, 100 °C and 4 h.

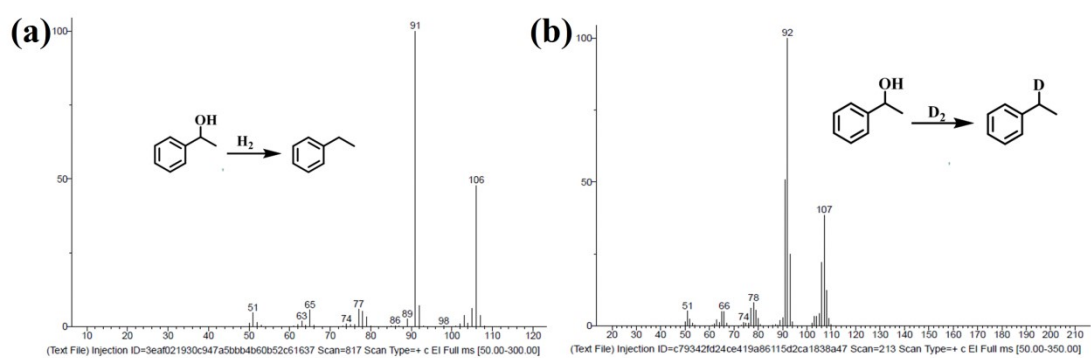


Fig. S13. Mass spectra of the product from isotope labeling experiments. Reaction conditions: 1-phenylethanol (0.5 mmol), 5 mL toluene, 20 mg catalyst, 120 °C and 12 h. (a) 10 bar H₂; (b) 3 bar D₂.

Table S1. The Co particles size calculated by Scherrer equation

Catalyst	Co particles size(nm)
Co/CoO-V-350	15.6
Co/CoO-V-400	22.0
Co/CoO-V-500	26.2
CoO-V-300-H ₂	28.9

Table S2. The binding energy and relative peak area percentage of different types of oxygen.

Catalyst	Lattice oxygen		Defective oxygen		Adsorbed H ₂ O/OH	
	B.E. (eV)	Percentage (%)	B.E. (eV)	Percentage (%)	B.E. (eV)	Percentage (%)
CoO-V-300	529.8	46.4	531.4	30.7	532.4	22.9
Co/CoO-V-350	529.7	24.6	531.6	56.7	532.4	18.7
Co/CoO-V-400	529.7	17.5	531.6	44.4	532.4	38.1
Co/CoO-V-500	529.8	18.9	531.2	42.9	532.4	38.2

Table S3. The peak area ratio of metallic Co and Co²⁺ in the catalysts

Catalyst	Co⁰ (%)	Co²⁺ (%)	Peak area ratio of Co⁰ to Co²⁺
CoO-V-300	0	100	0
Co/CoO-V-350	6.7	93.3	0.07
Co/CoO-V-400	13.5	86.5	0.16
Co/CoO-V-500	15.5	84.5	0.18

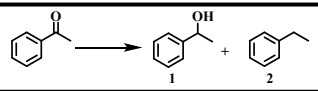
Table S4. The textural parameters of the cobalt catalysts.

Catalyst	Surface Area (m ² /g)			Pore Volume (mL/g)		
	Meso	Micro	Total surface area	Meso	Micro	Total pore volume
CoO-V-300	81.0	13.2	94.2	0.18	0.03	0.21
Co/CoO-V-350	72.1	6.2	78.3	0.15	0.001	0.15
Co/CoO-V-400	50.5	5.1	55.6	0.13	0.001	0.13
Co/CoO-V-500	13.7	4.6	18.3	0.04	0.003	0.04

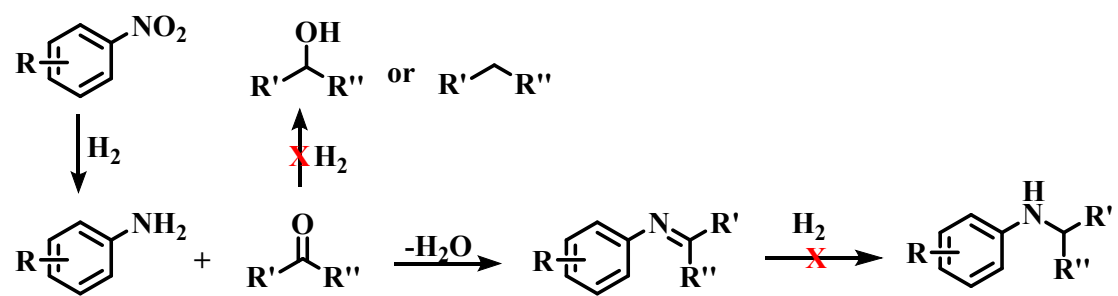
Table S5. The binding energy and relative peak area percentage of different types of oxygen in the treated catalysts.

Sample	Lattice oxygen		Defective oxygen		Adsorbed H ₂ O/OH	
	B.E. (eV)	Percentage (%)	B.E. (eV)	Percentage (%)	B.E. (eV)	Percentage (%)
Co/CoO-V-350	529.7	24.6	531.6	56.7	532.4	18.7
Treated by acetophenone	529.8	28.9	531.4	46.8	532.4	24.1
Treated by 1-phenylethanol	529.8	31.2	531.3	34.5	529.8	34.2

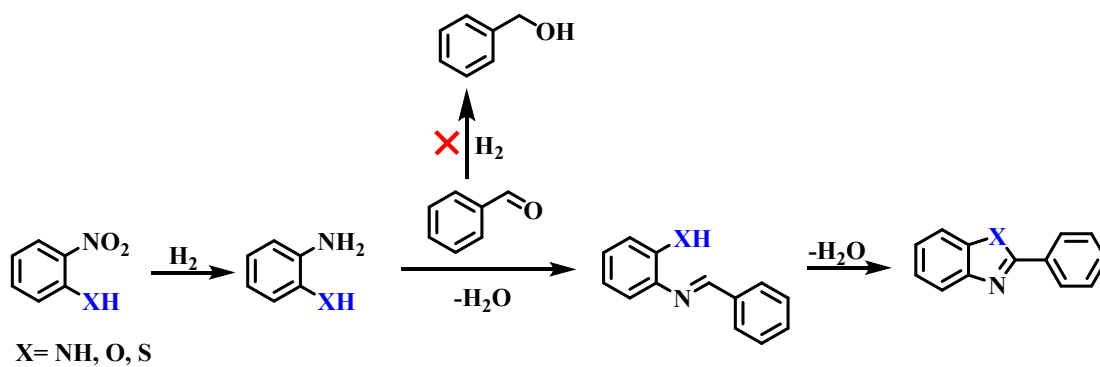
Table S6. The effect of the reaction solvents on the hydrodeoxygenation of acetophenone.

			
Solvents	Con. (%)	Sel. of 1 (%)	Sel. of 2 (%)
Toluene	95.0	5.3	94.7
<i>n</i> -Hexane	94.6	61.8	38.2
Acetonitrile	10.3	100	-
Tetrahydrofuran	45.2	93.4	6.6
MeOH	5.5	100	-
1,4-Dioxane	3.2	100	-
Ethyl acetate	2.3	100	-

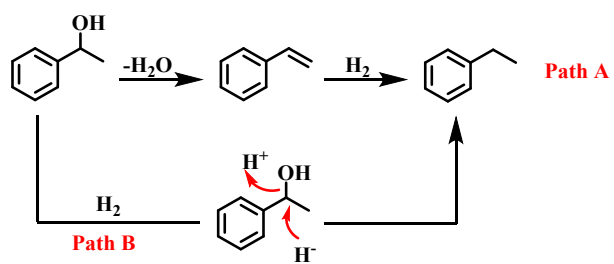
Reaction conditions: acetophenone (0.5 mmol), solvent (5 mL), Co/CoO-V-350 (20 mg), H₂ (10 bar), 4 h.



Scheme S1. Reaction pathways of the reductive coupling of nitro compounds with carbonyl compounds.



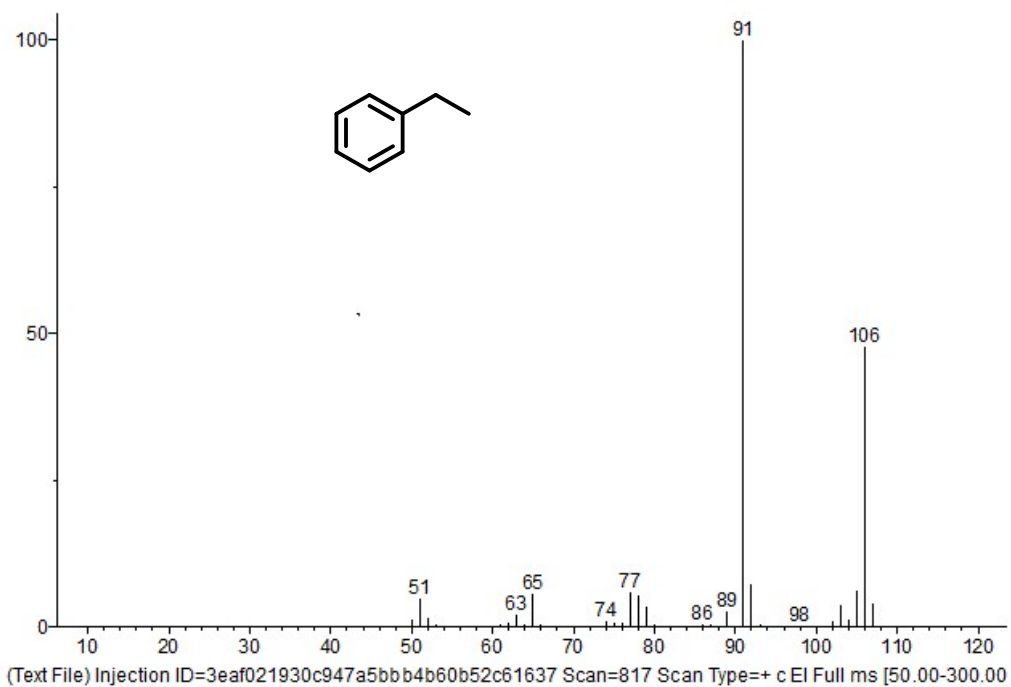
Scheme S2. Reaction pathways of the synthesis of benzazoles.



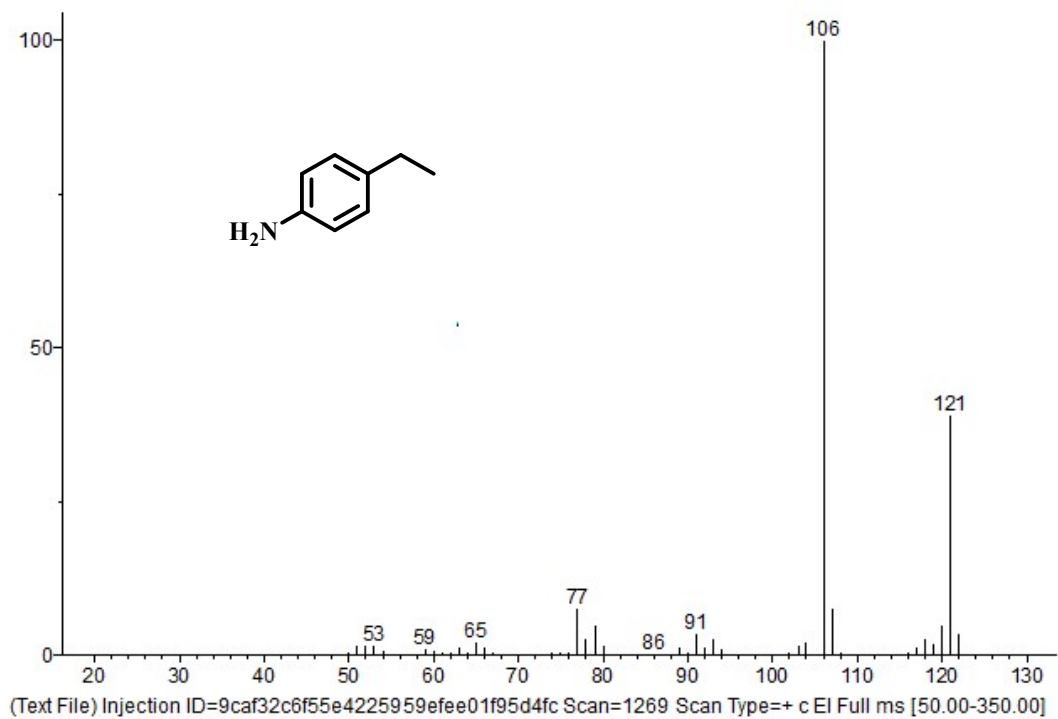
Scheme S3. The possible pathways the hydrodeoxygenation of 1-phenylethanol into ethylbenzene.

GC-MS data

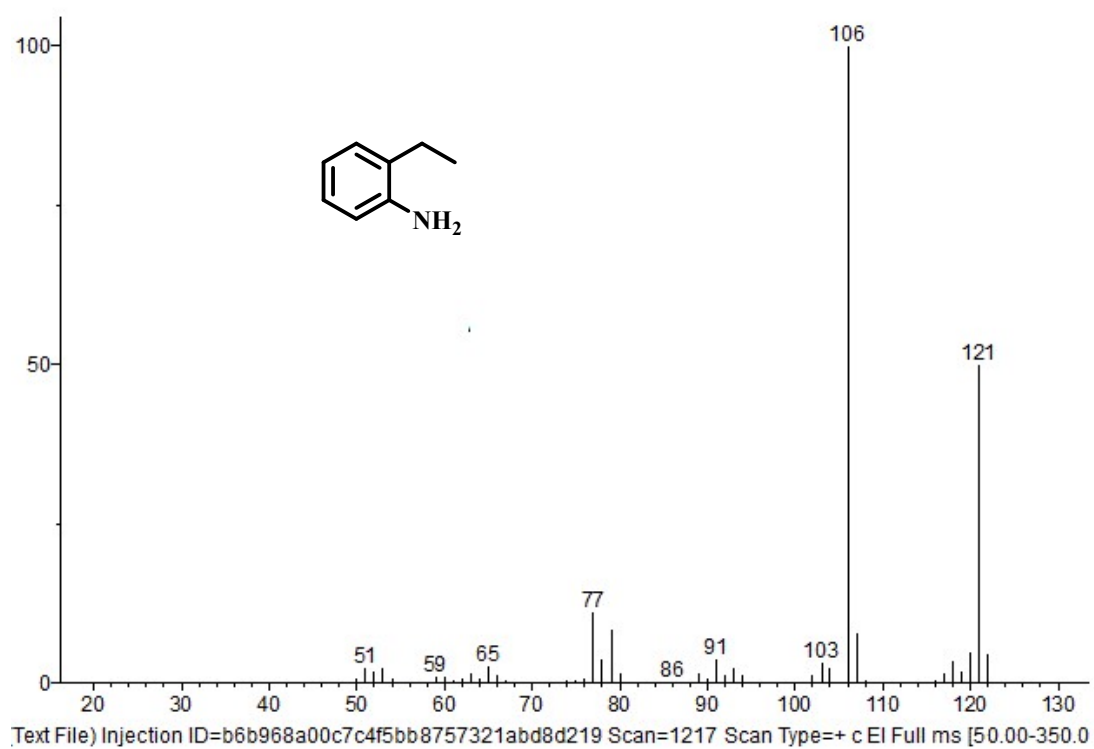
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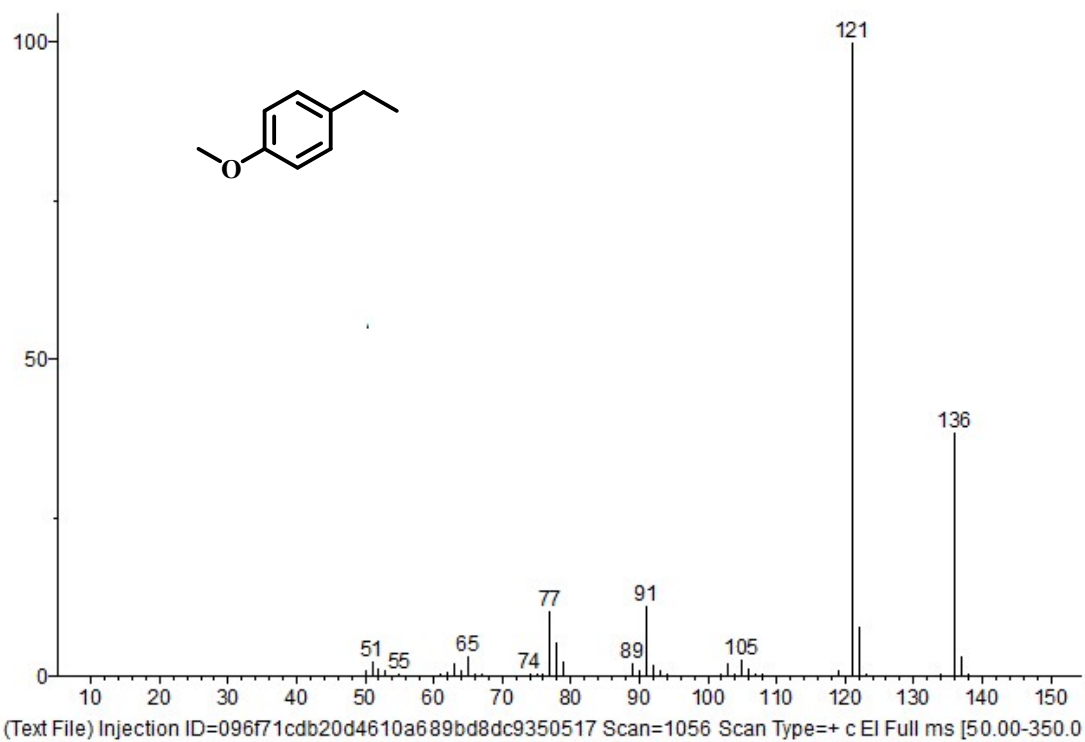
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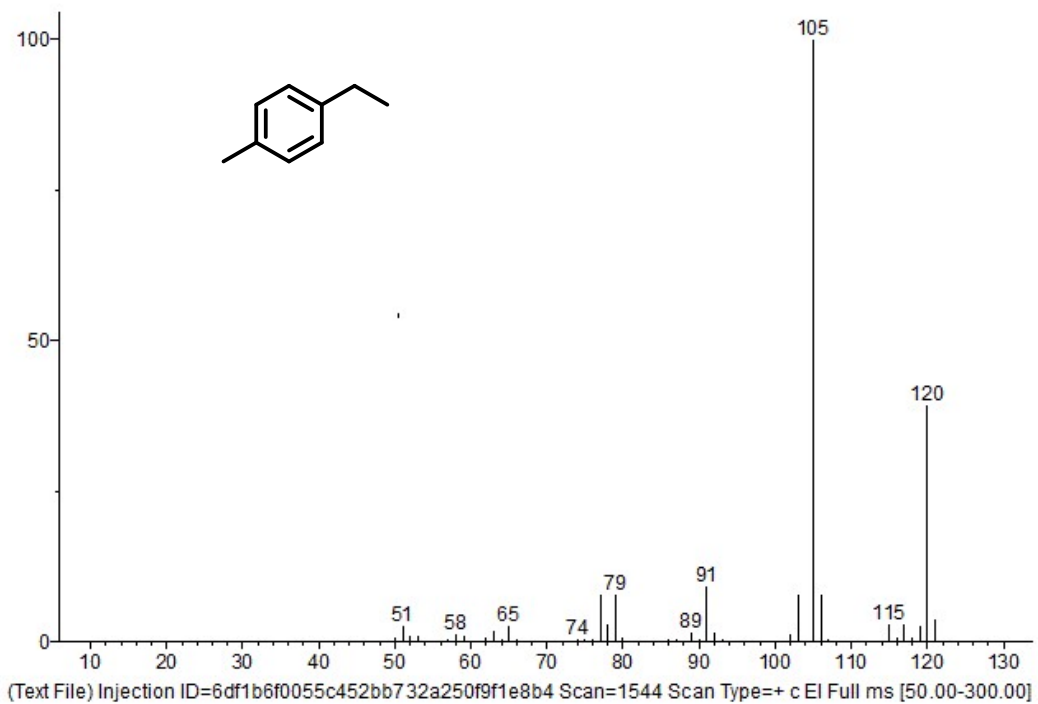
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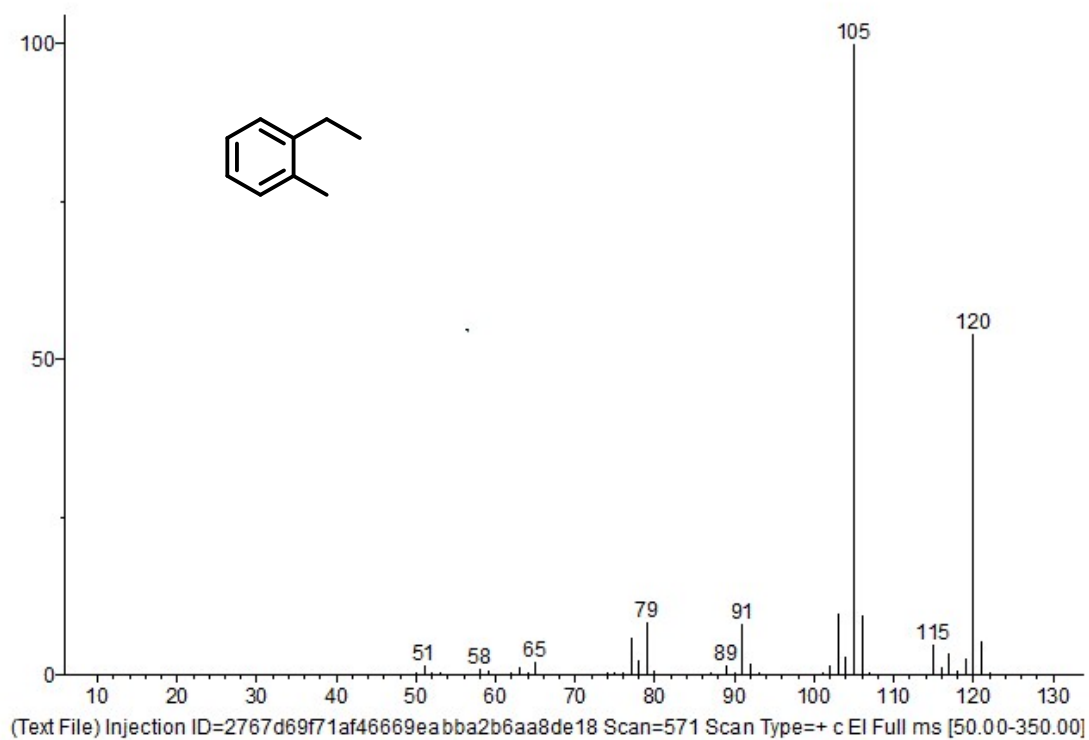
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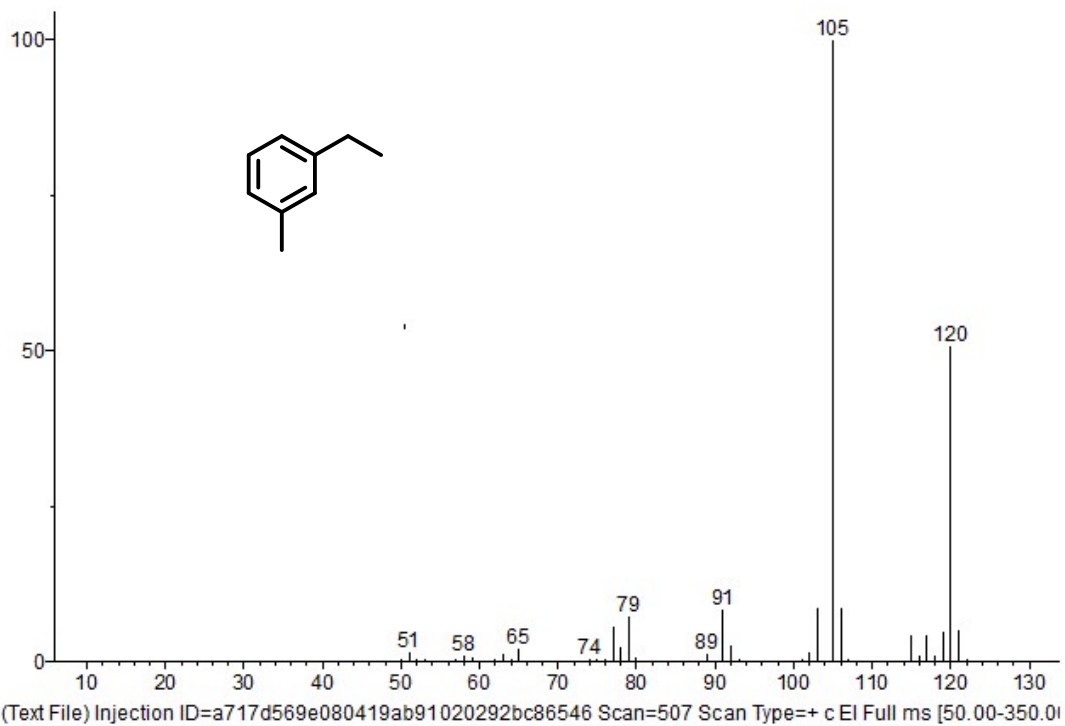
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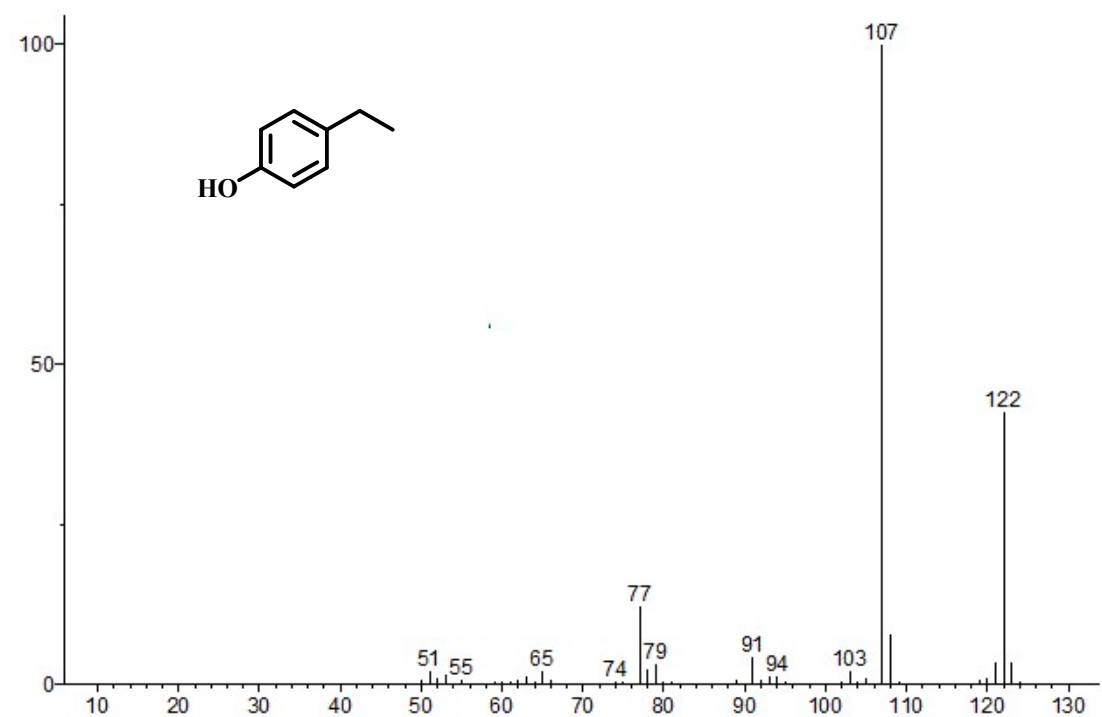
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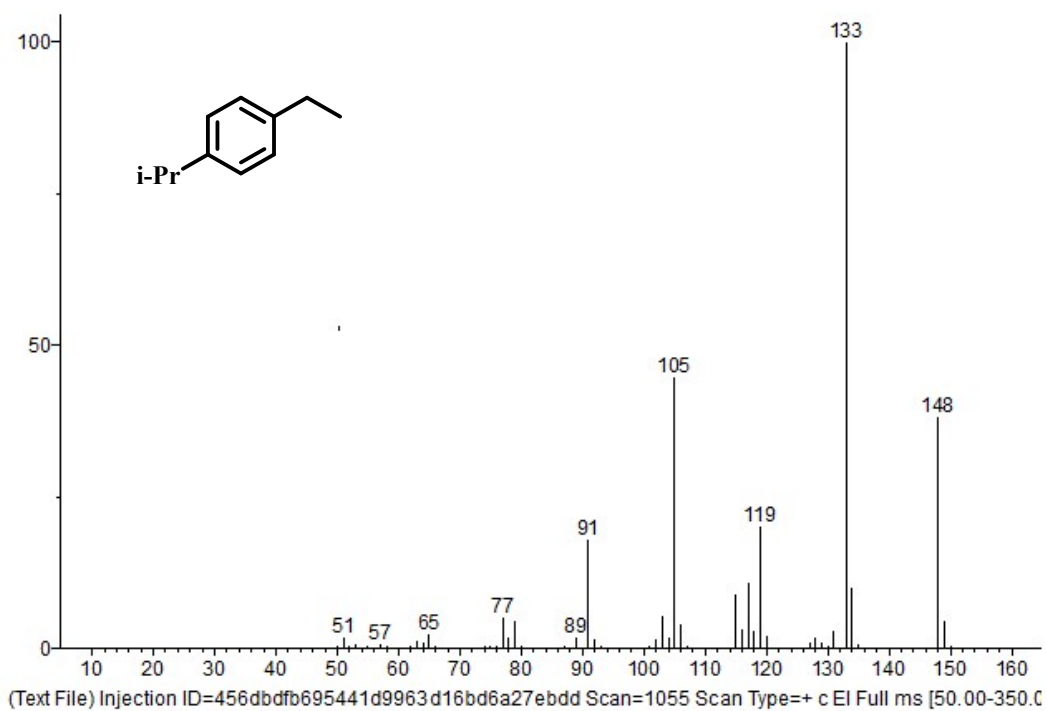


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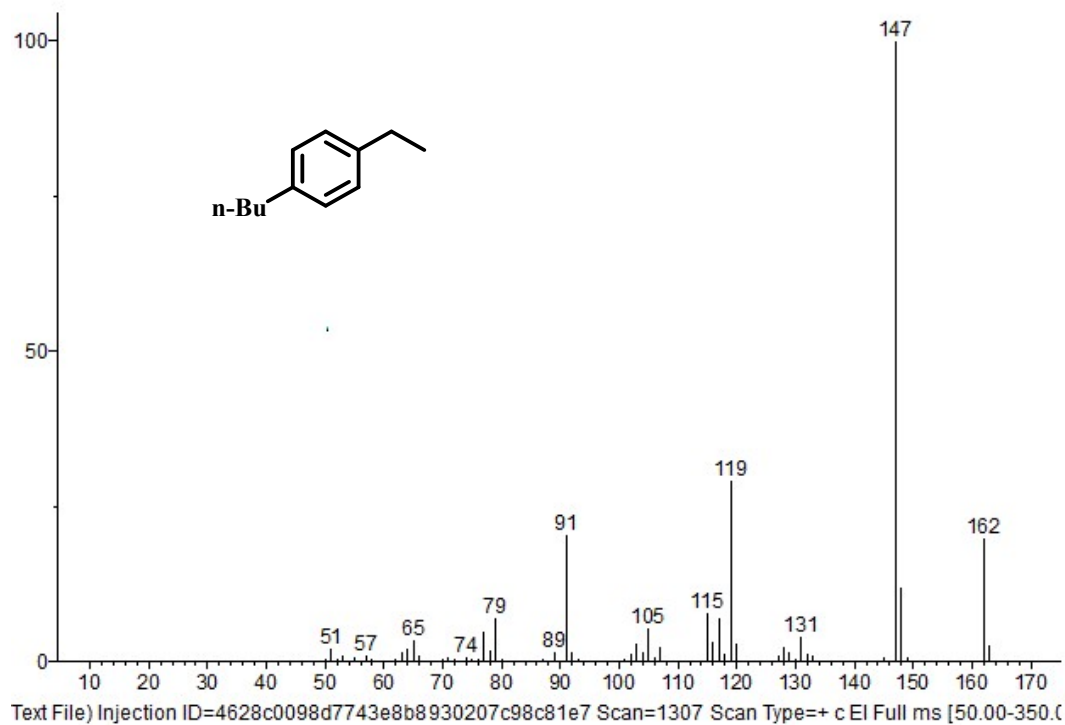


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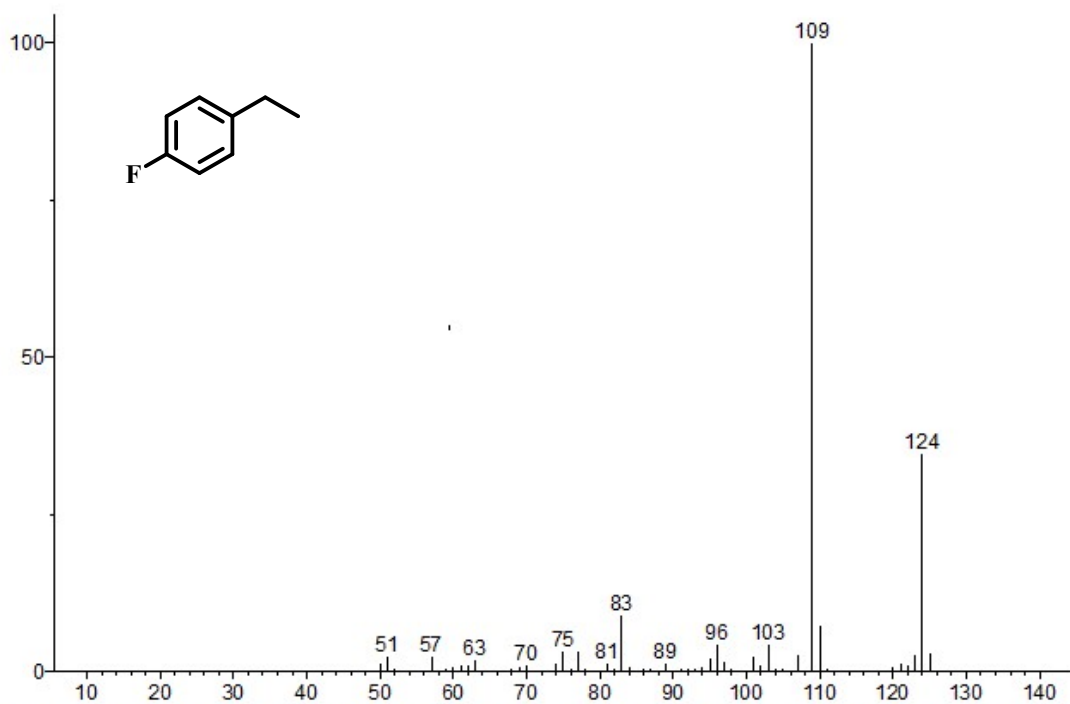
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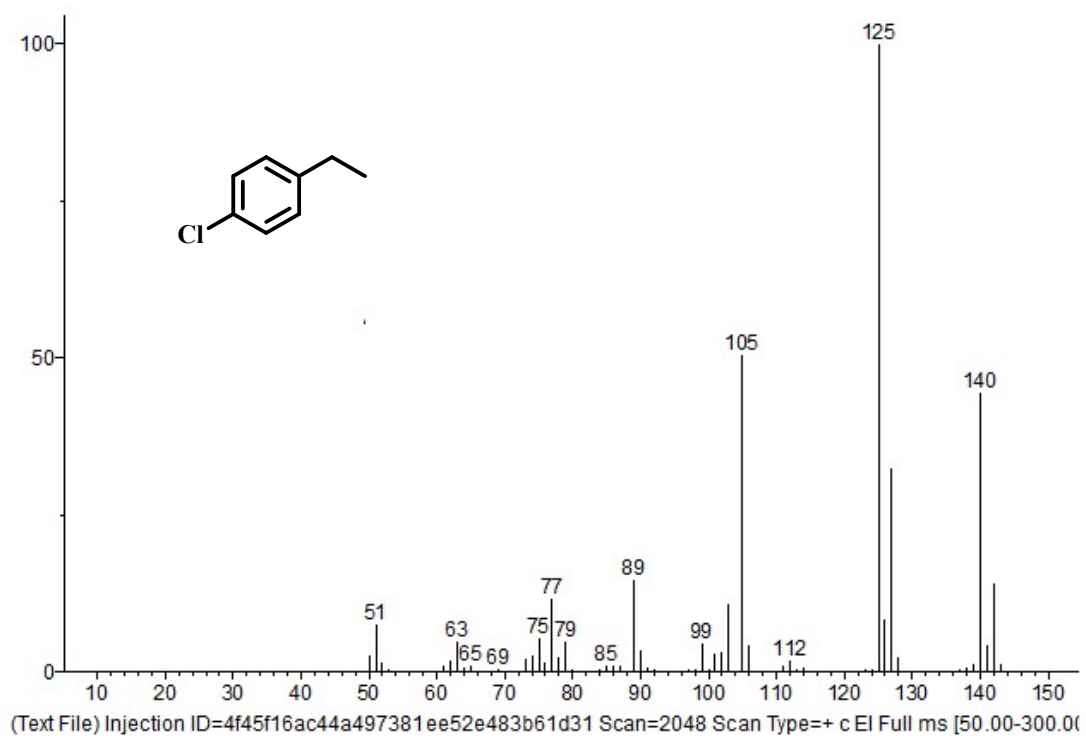


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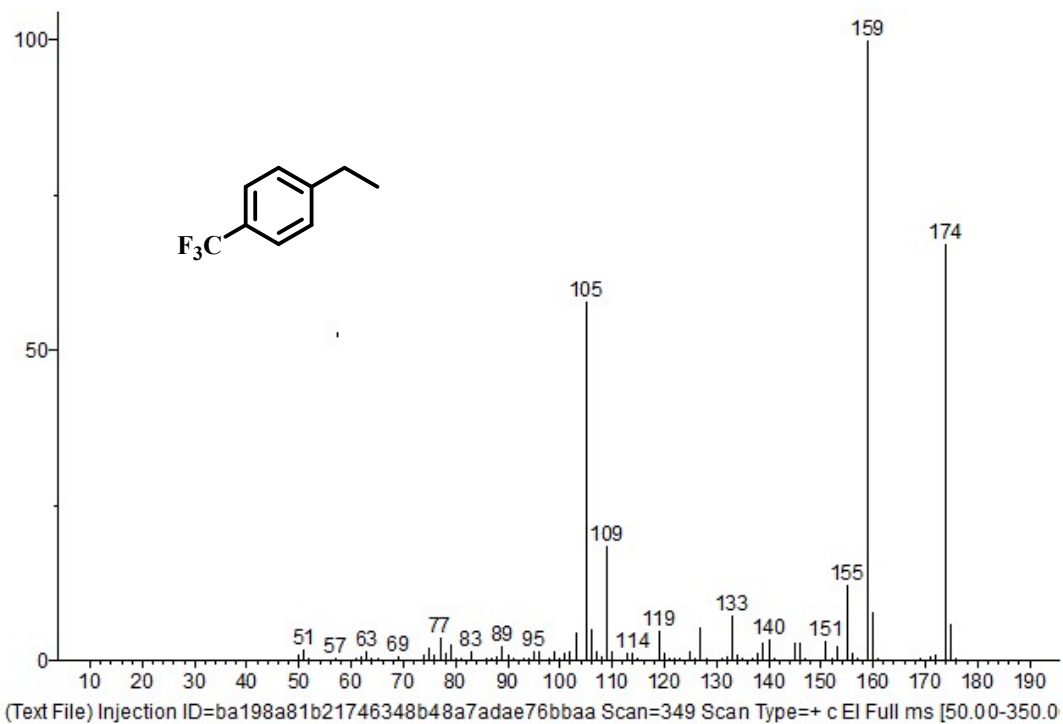


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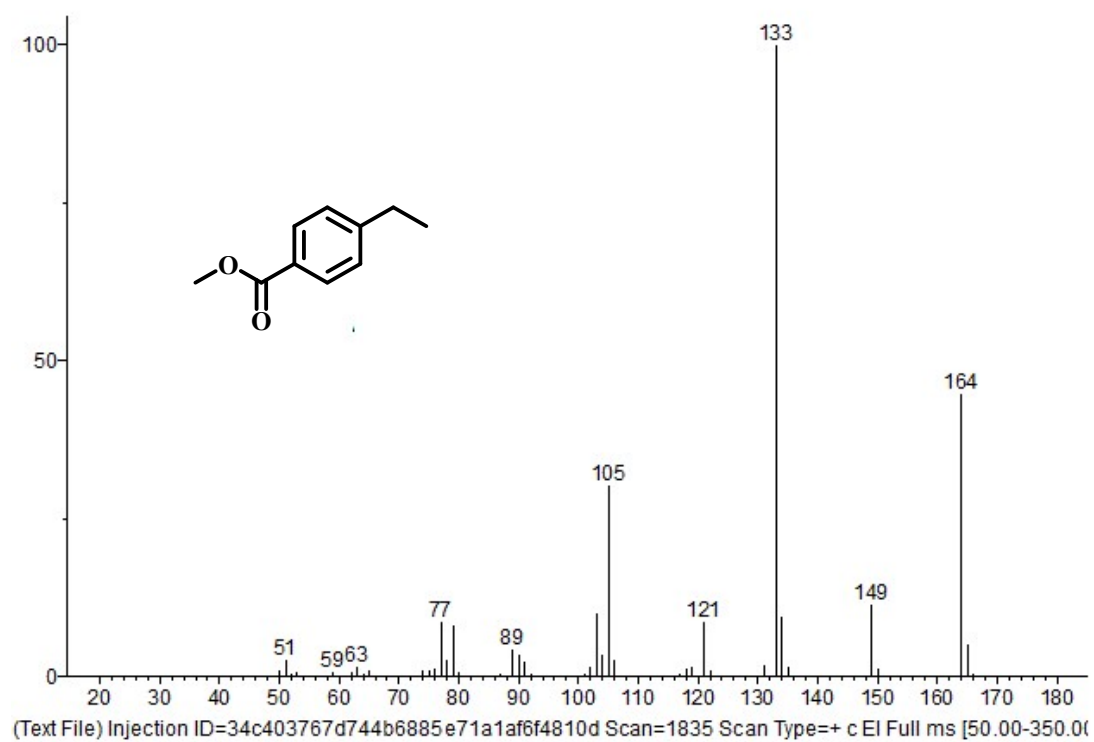
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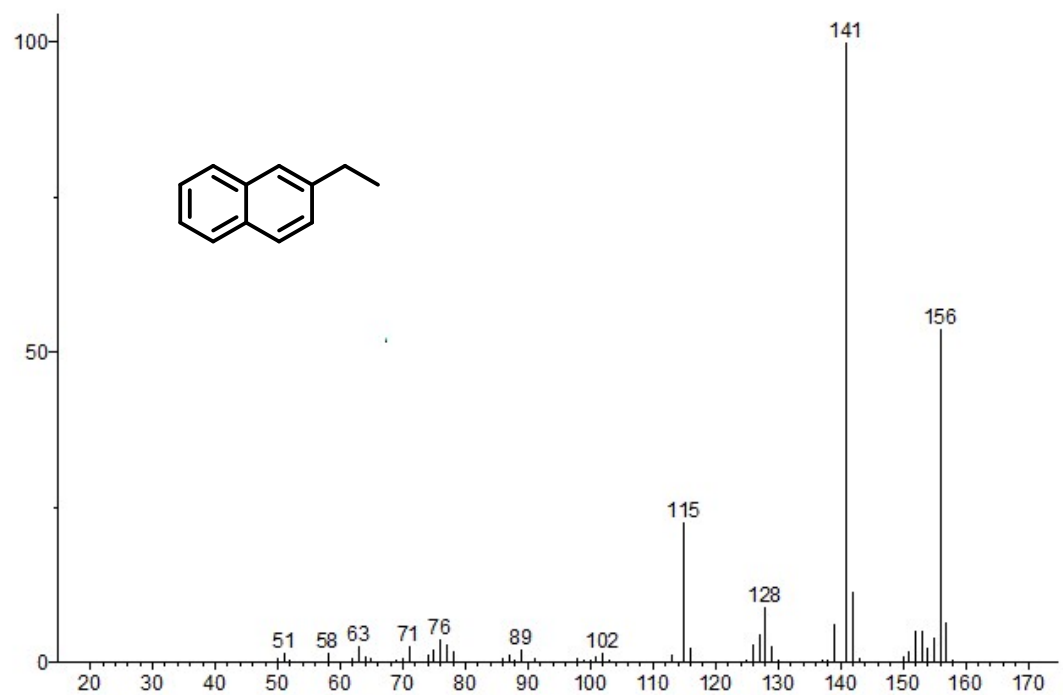
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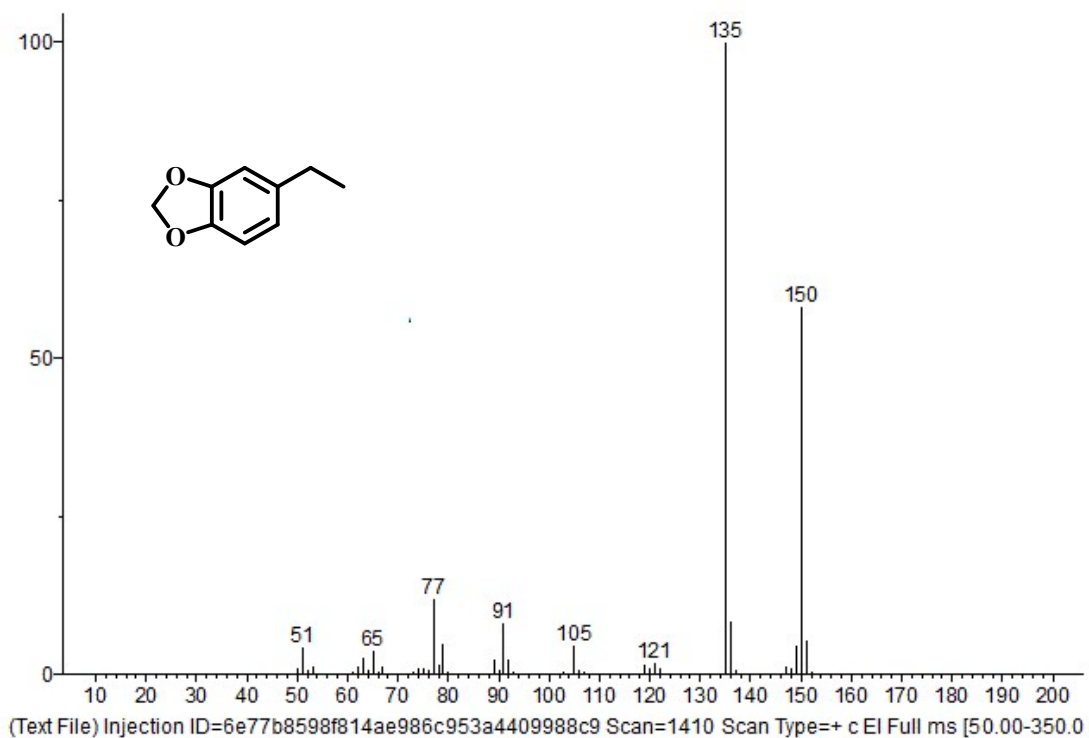


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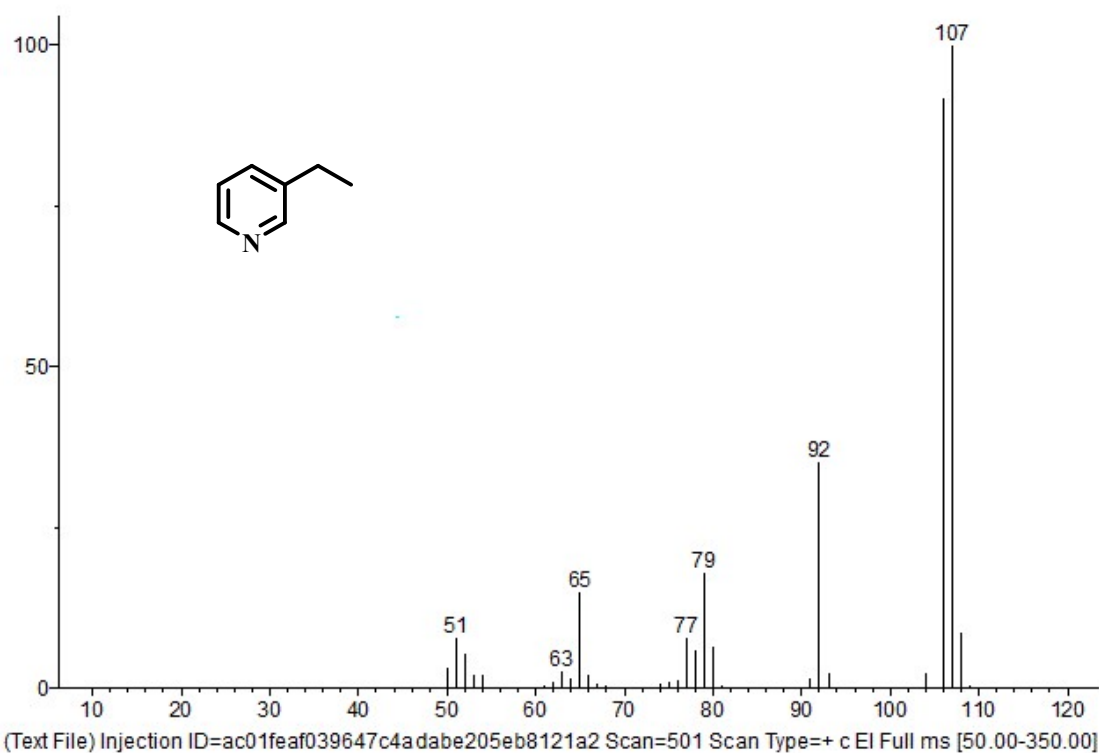


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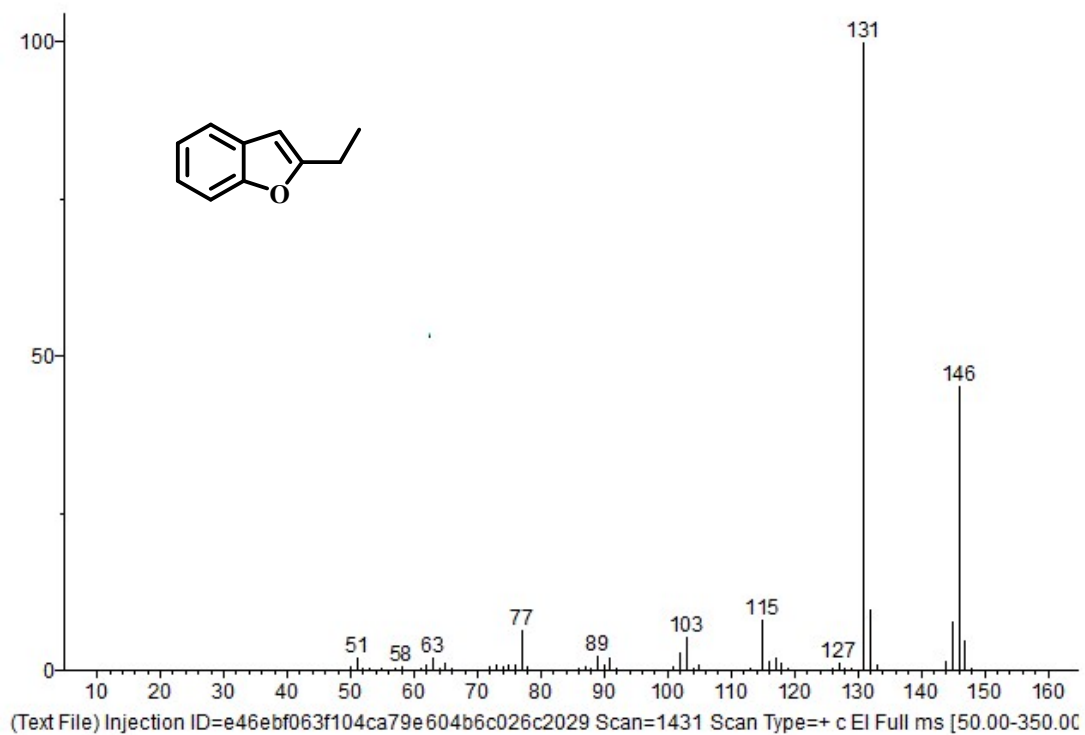
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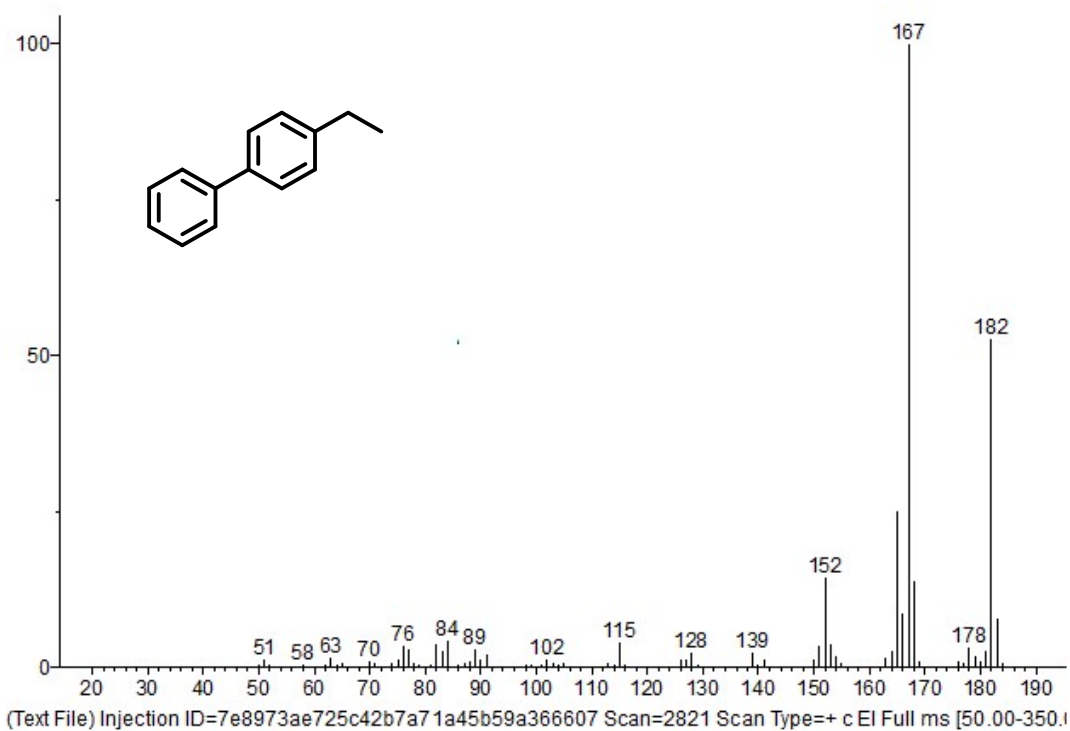
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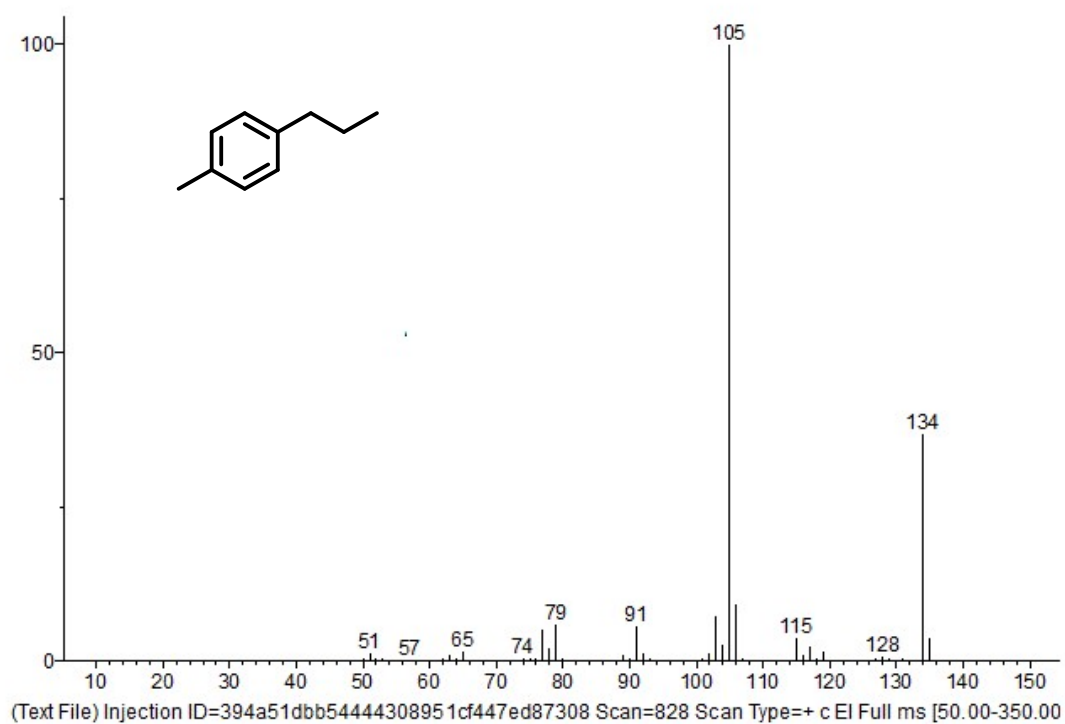
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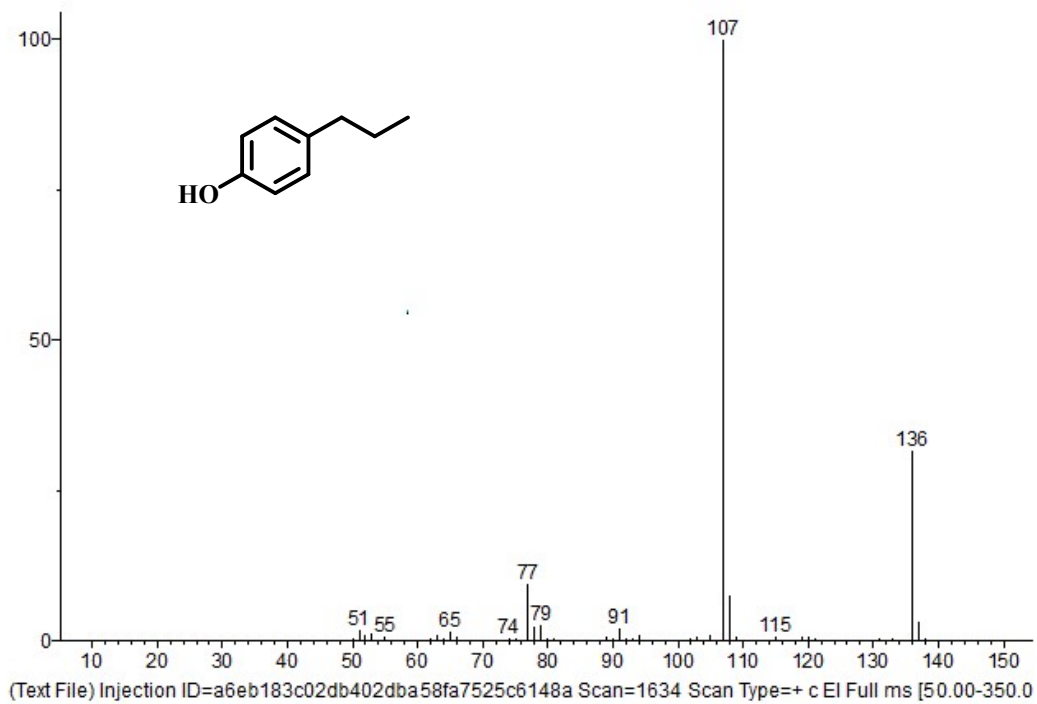
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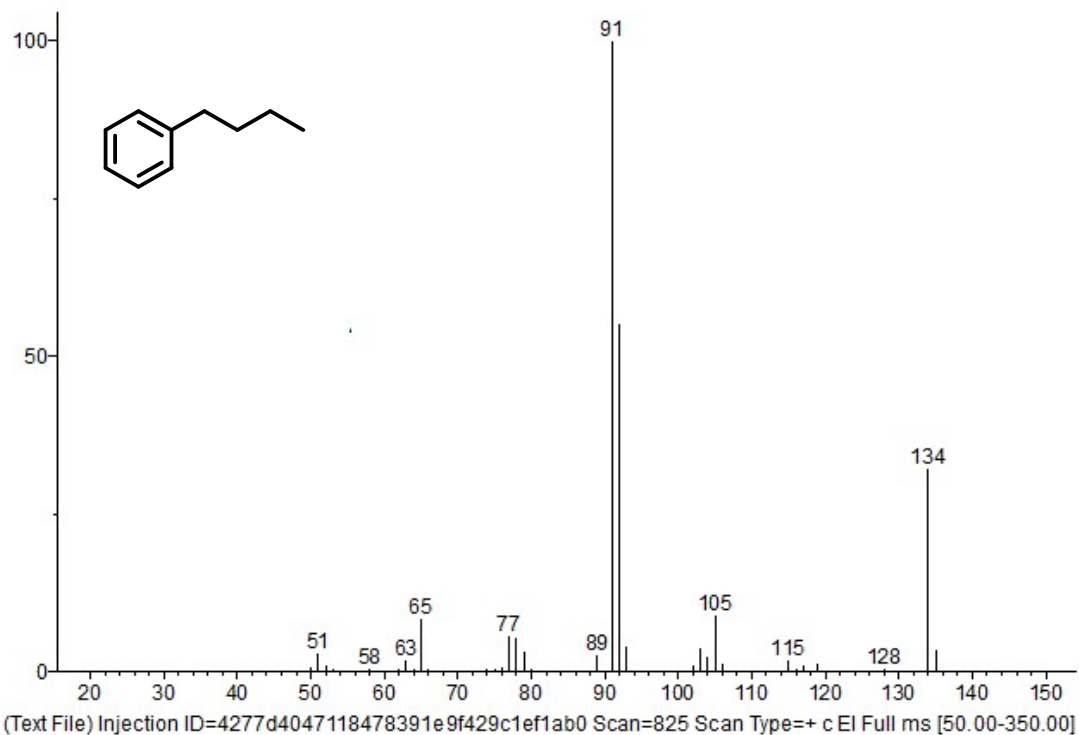
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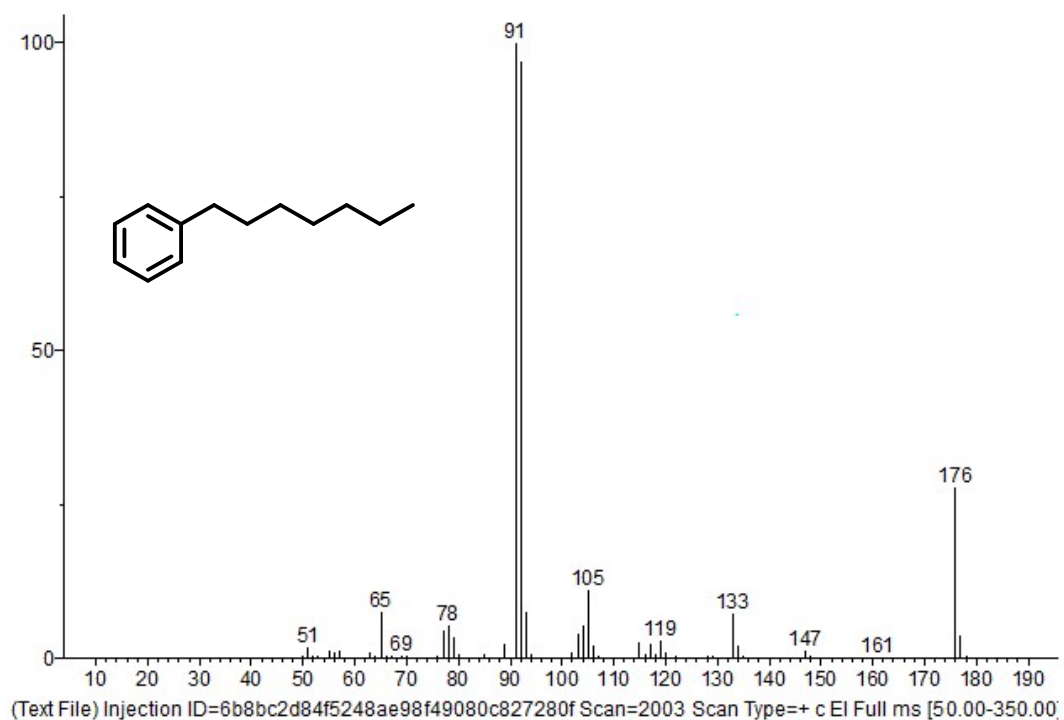
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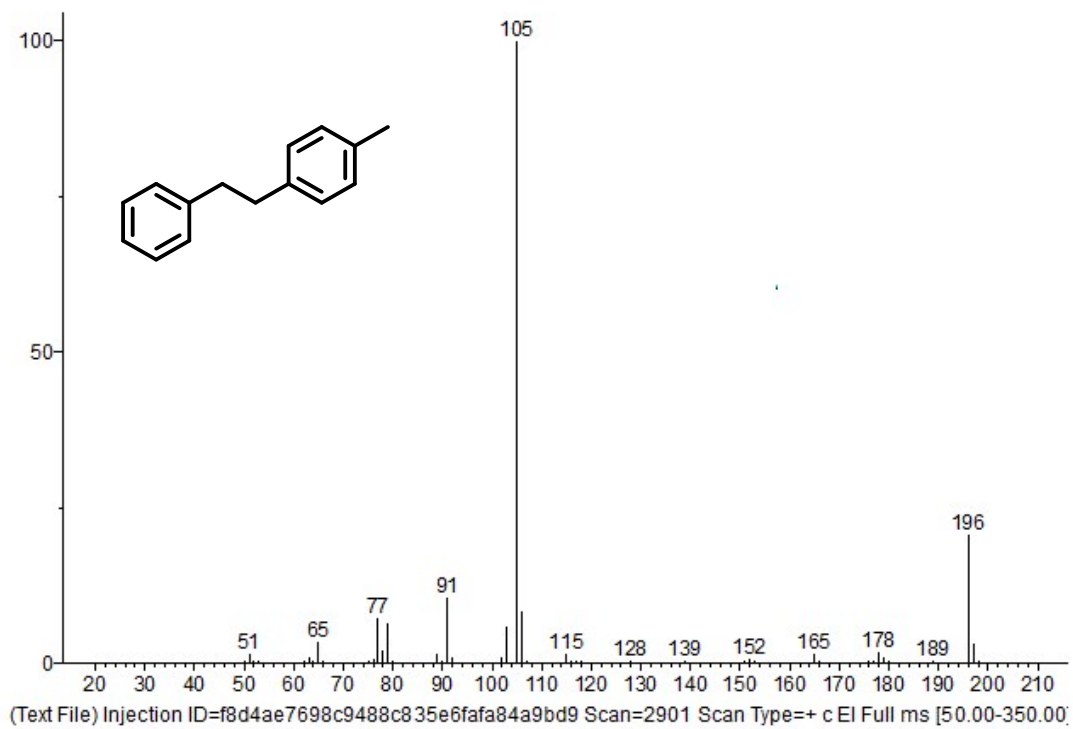
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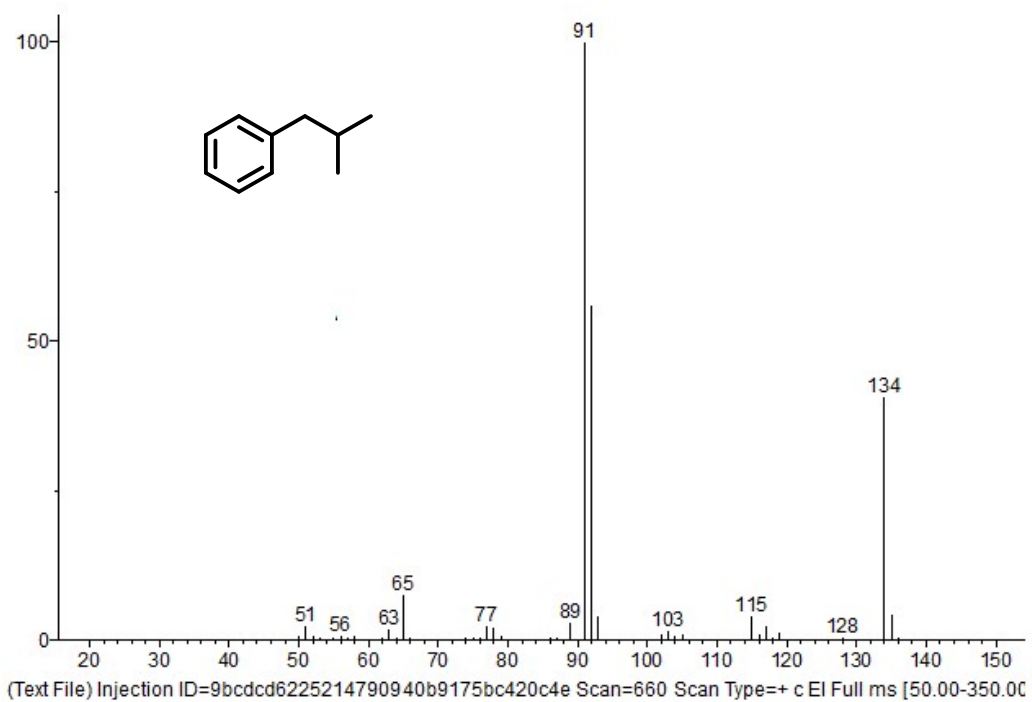
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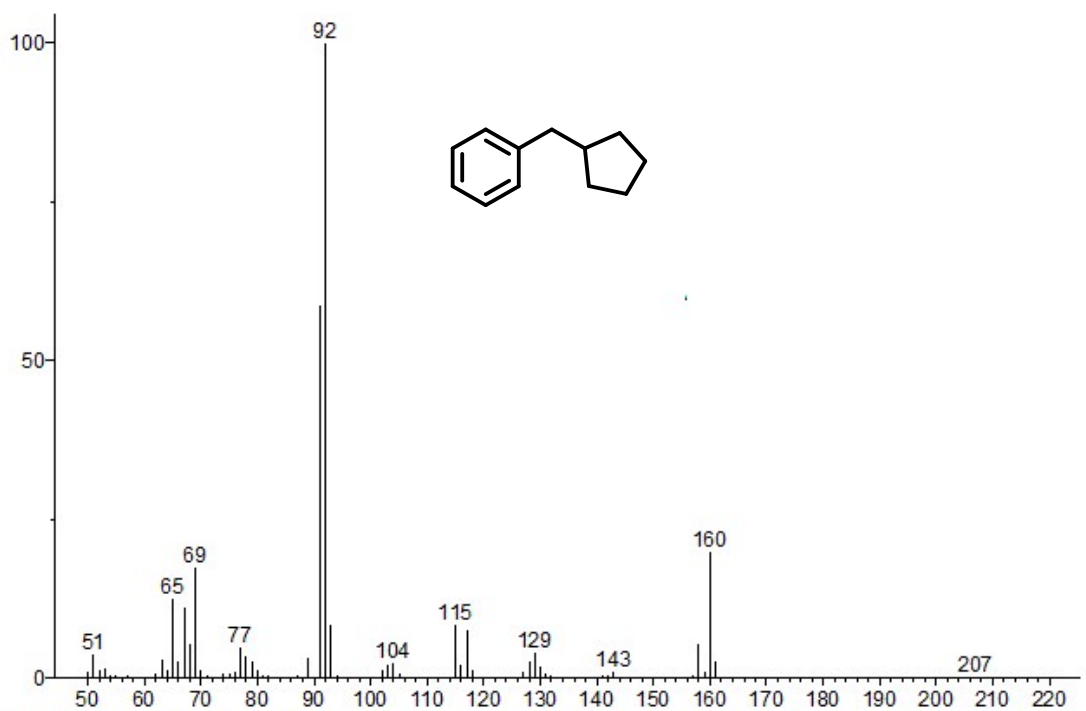
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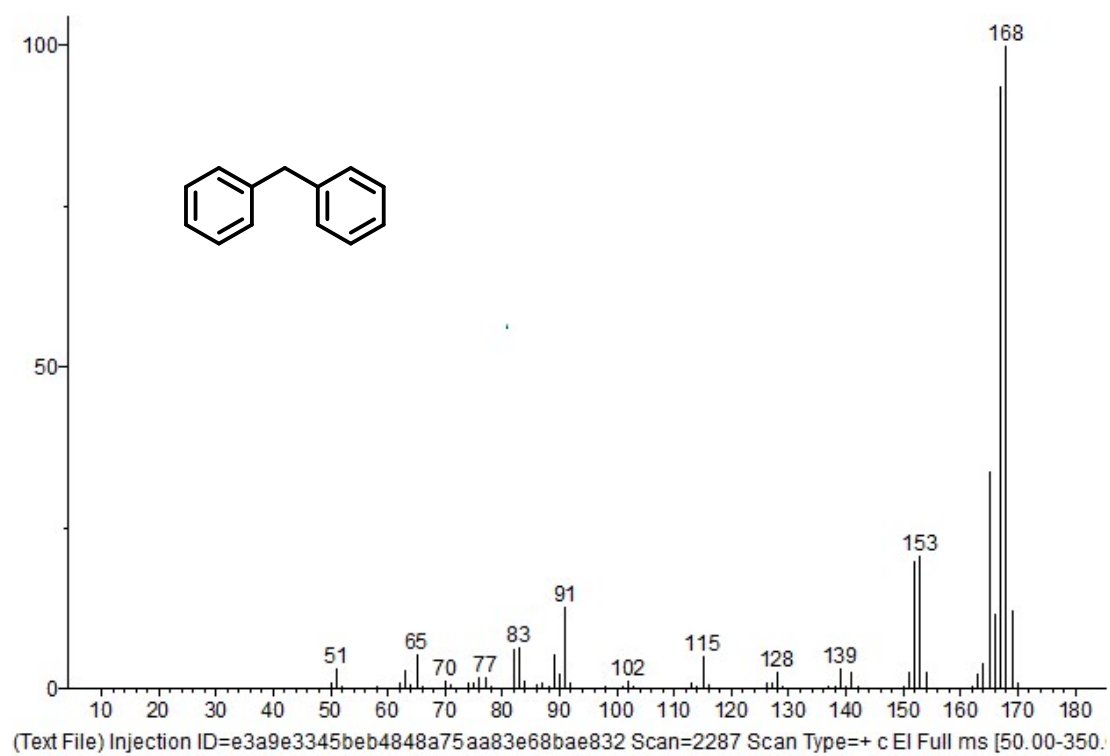


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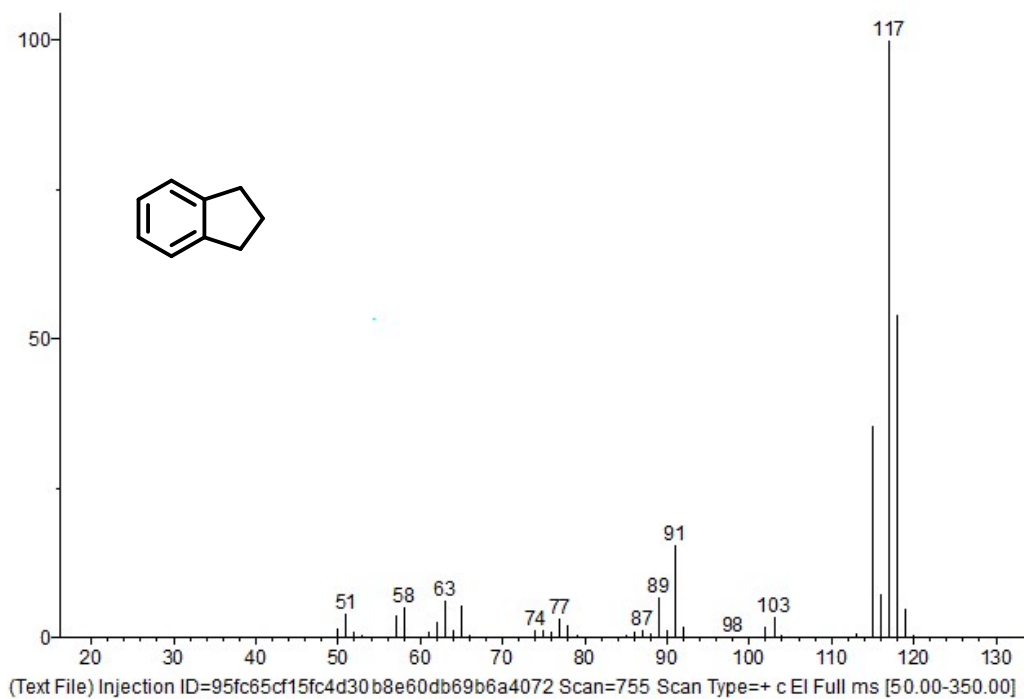


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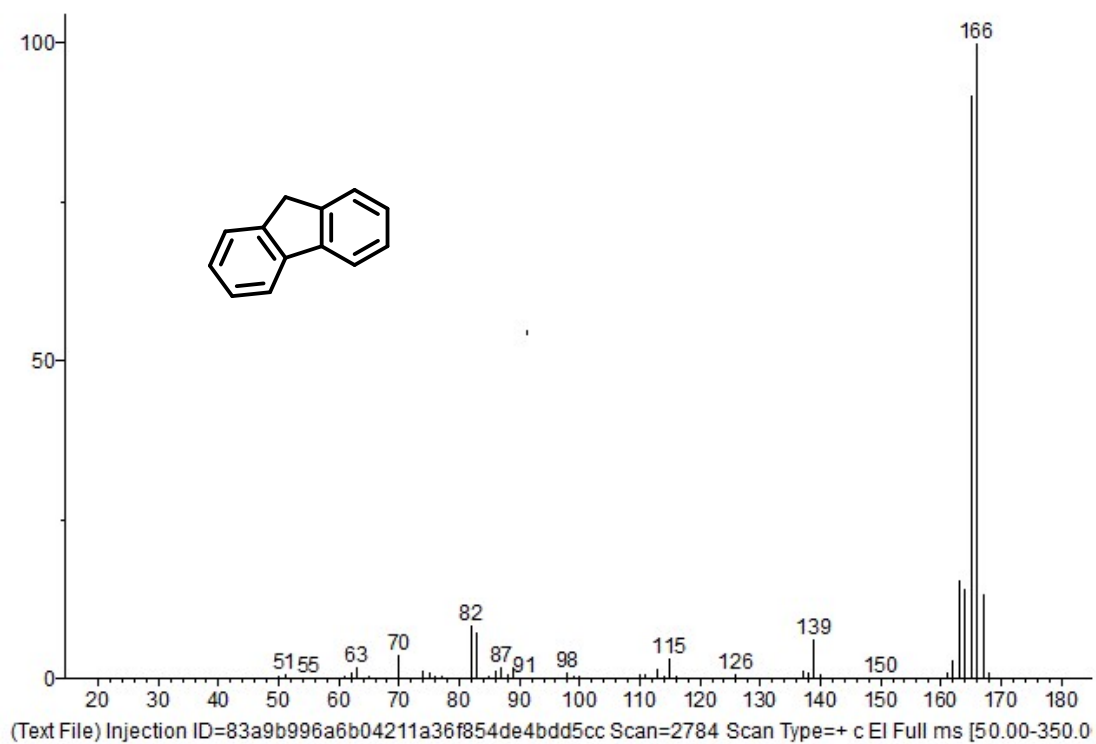
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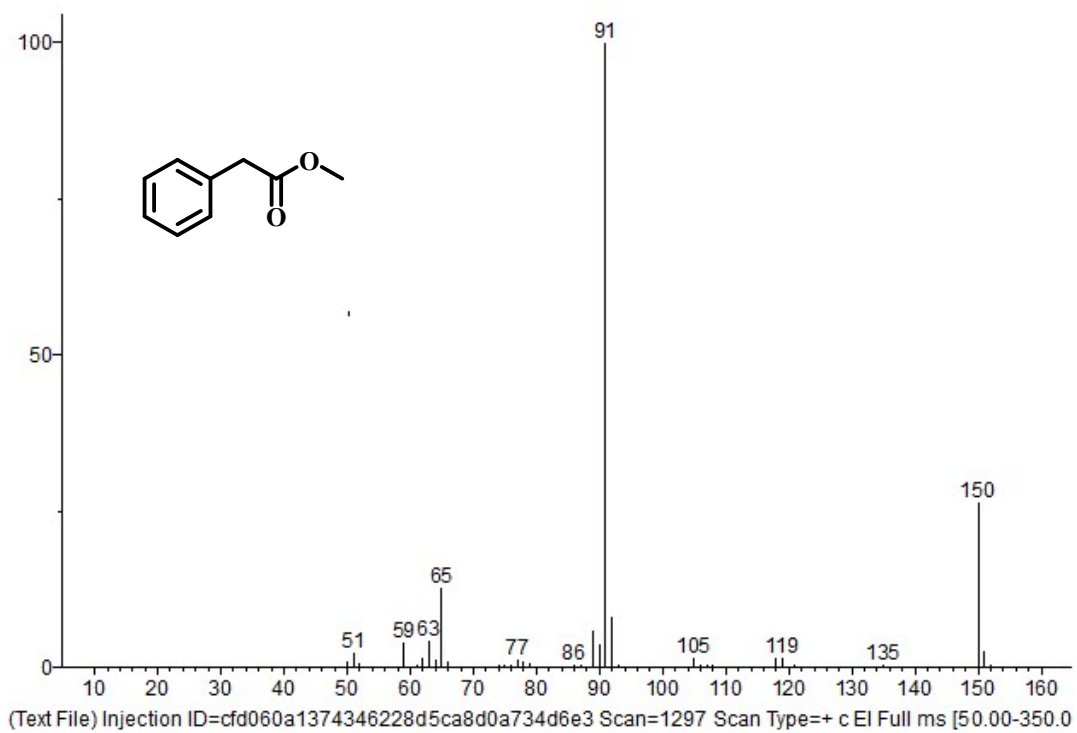
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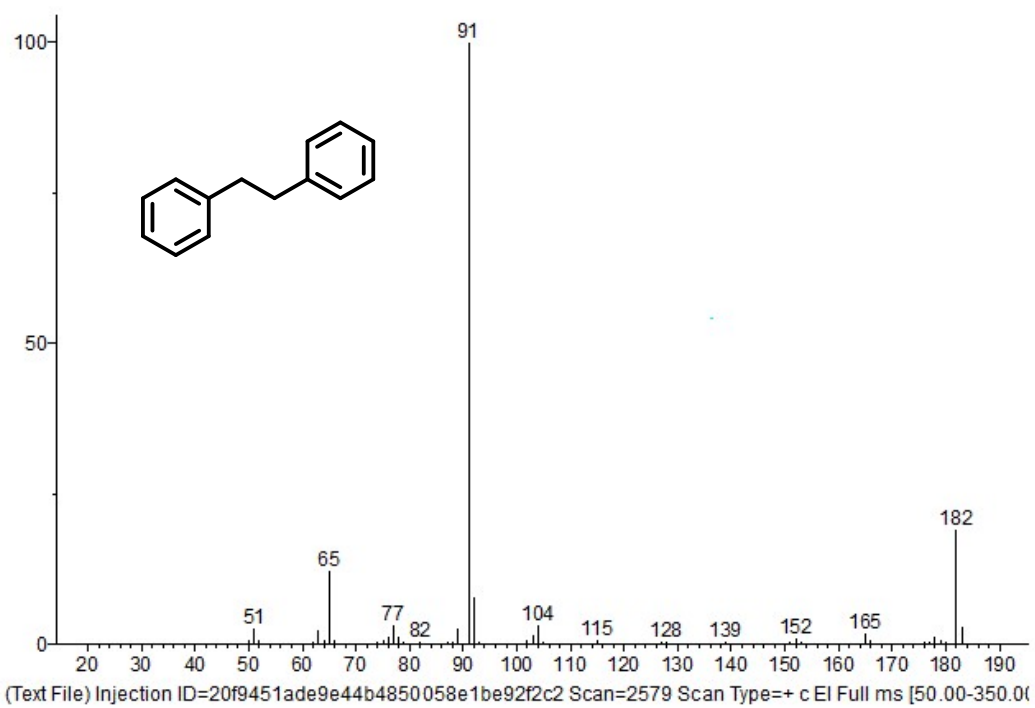
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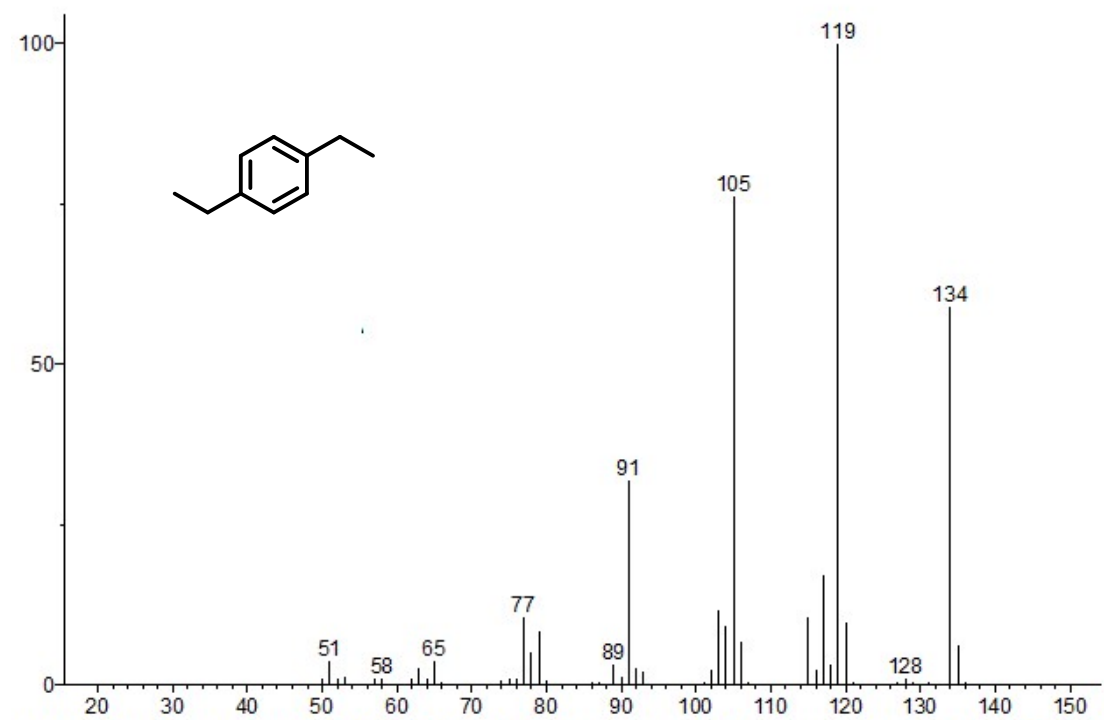
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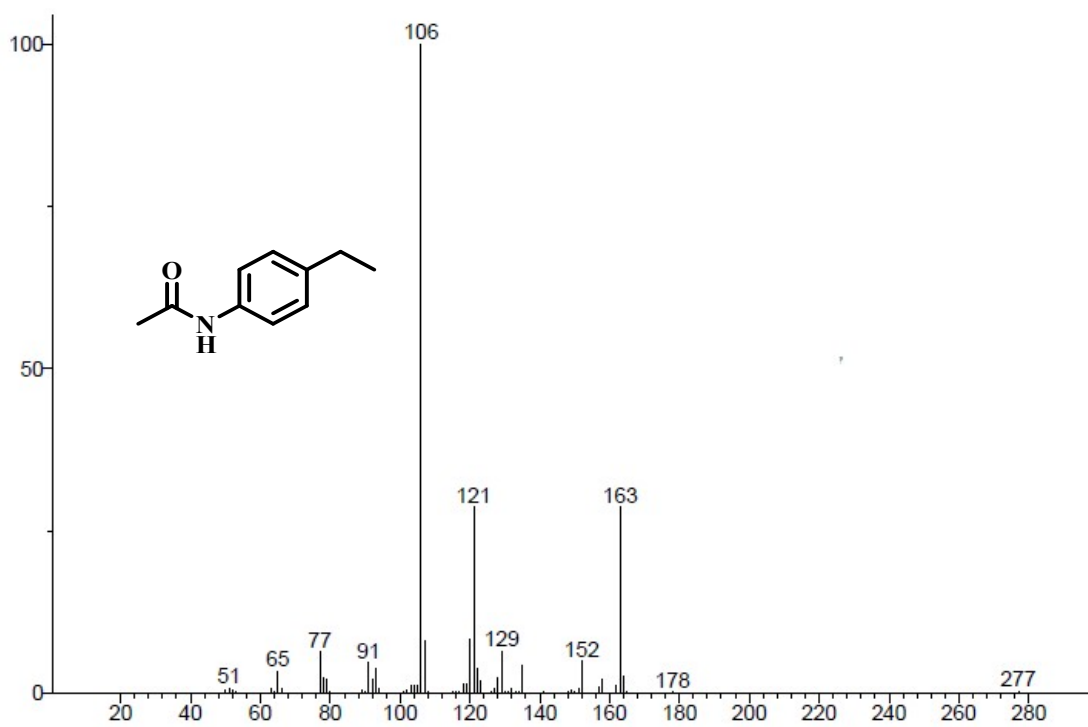


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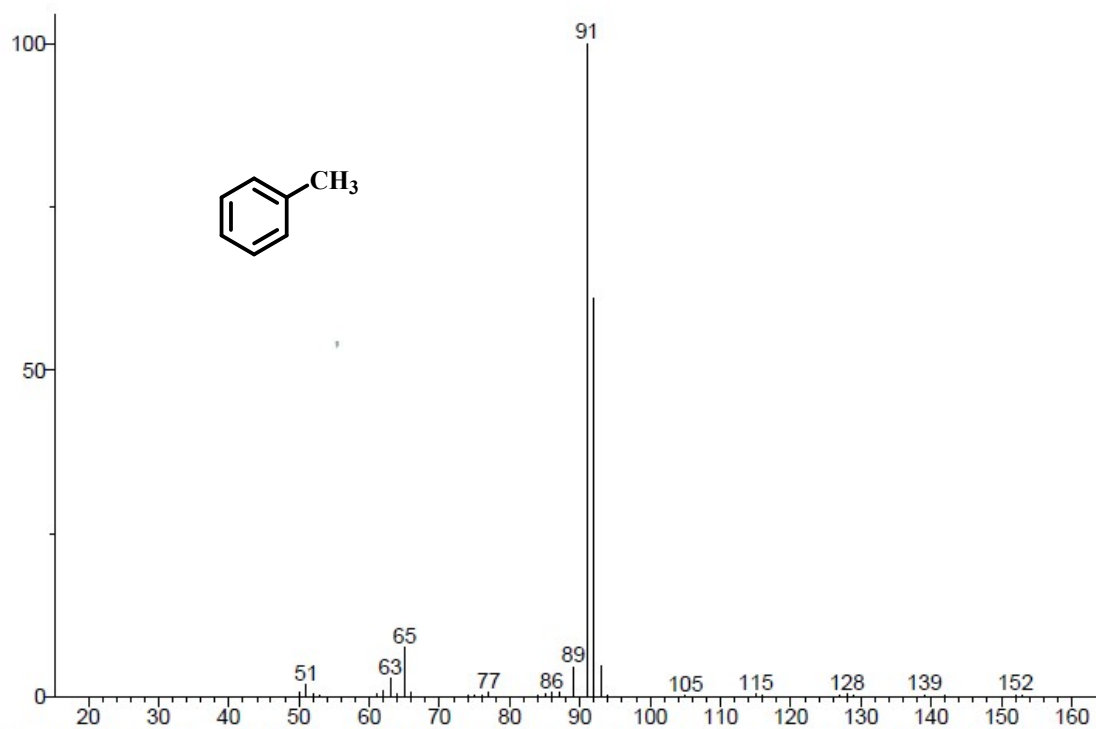
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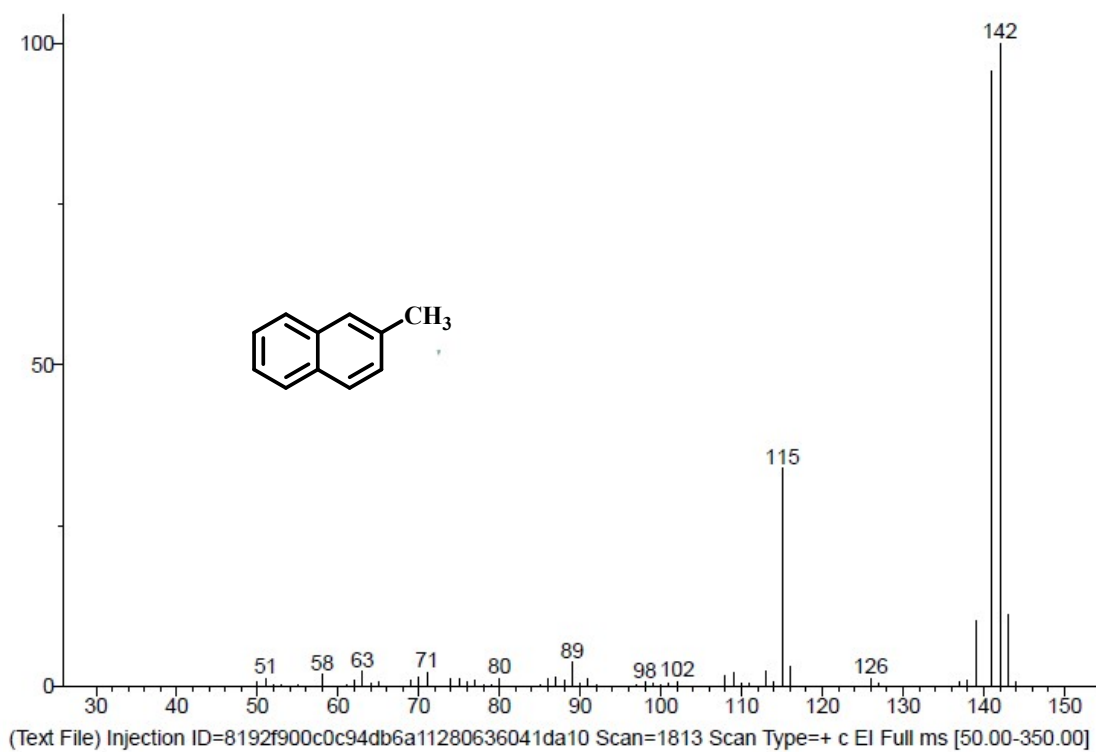
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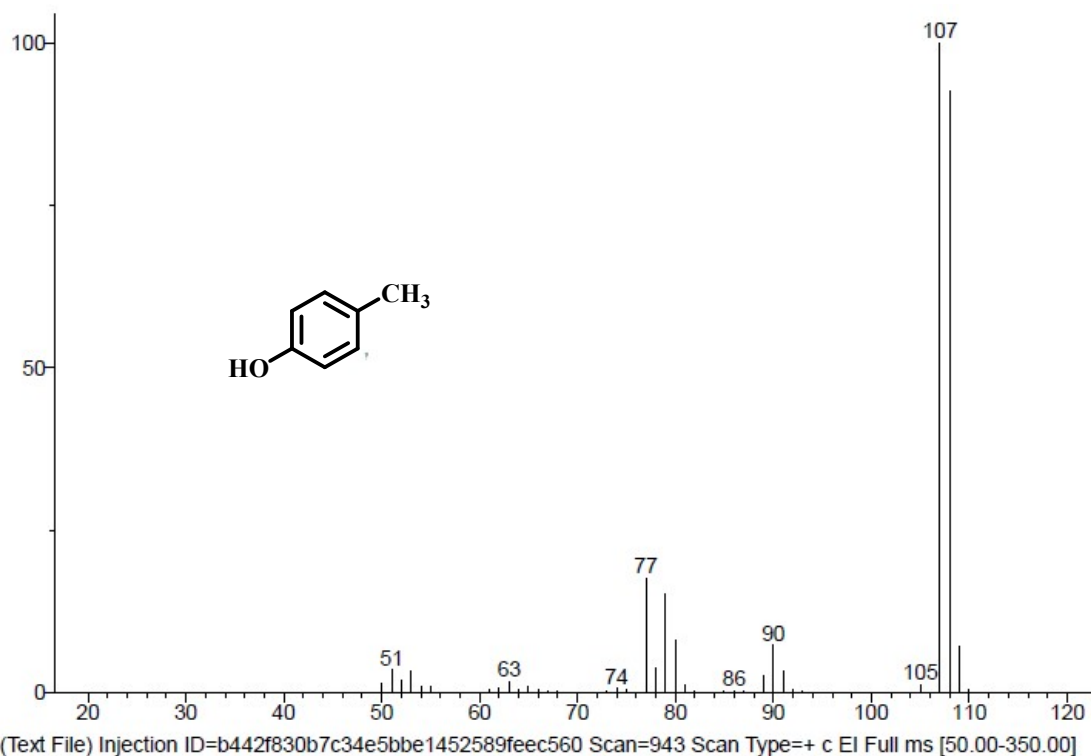


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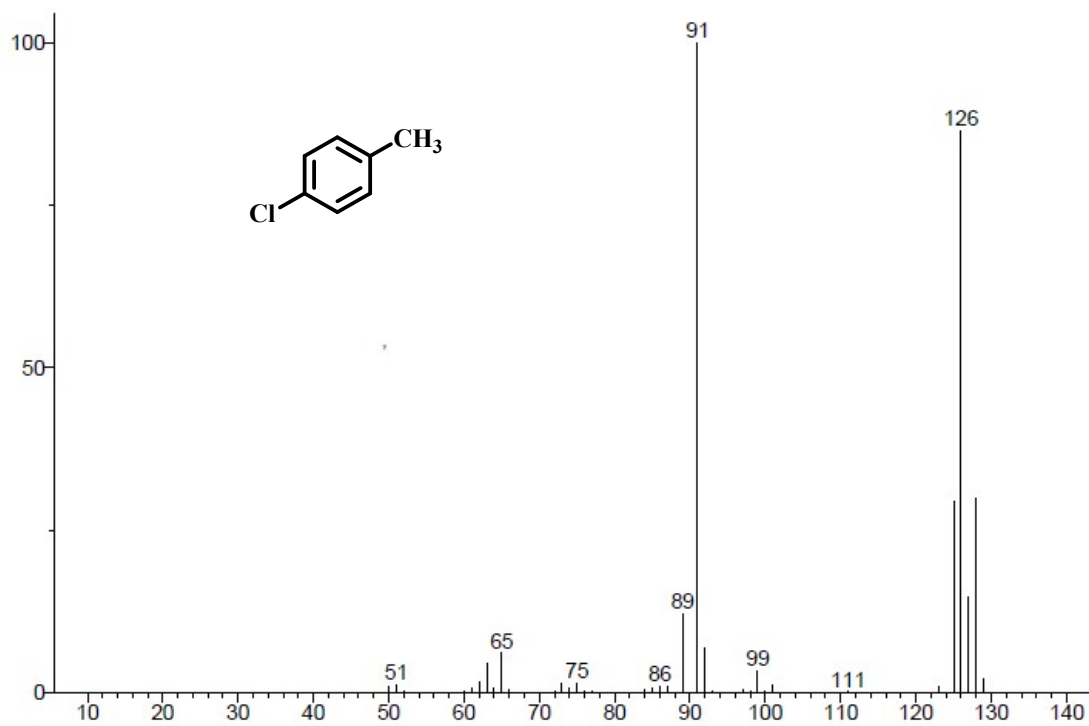
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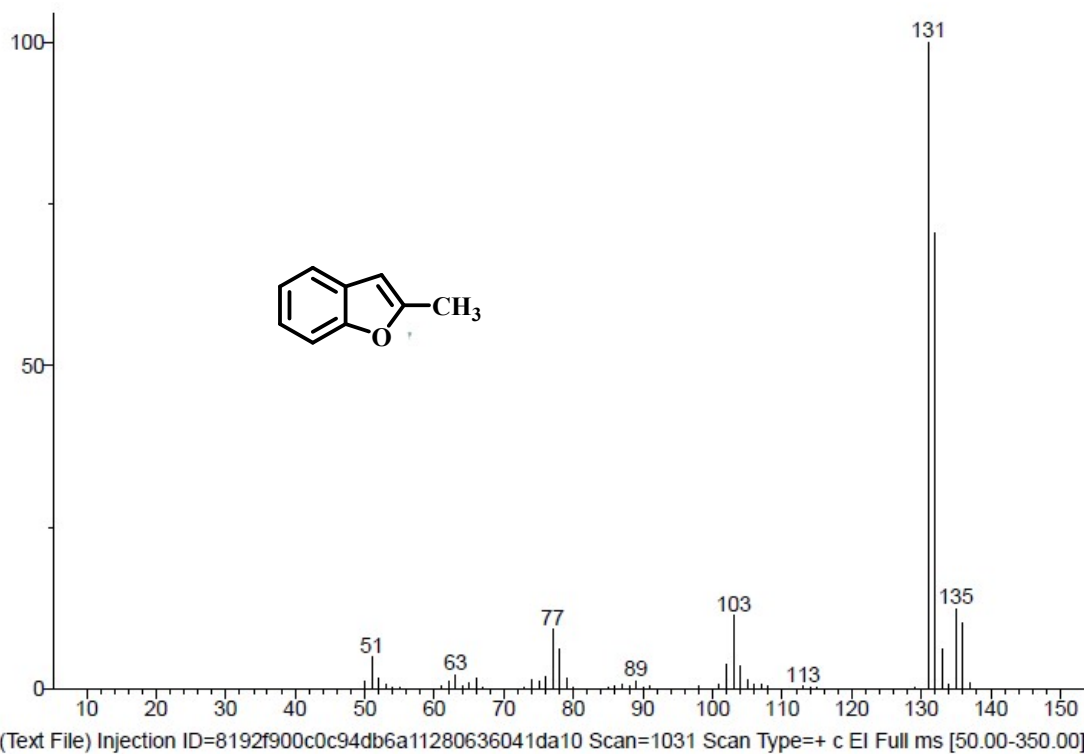


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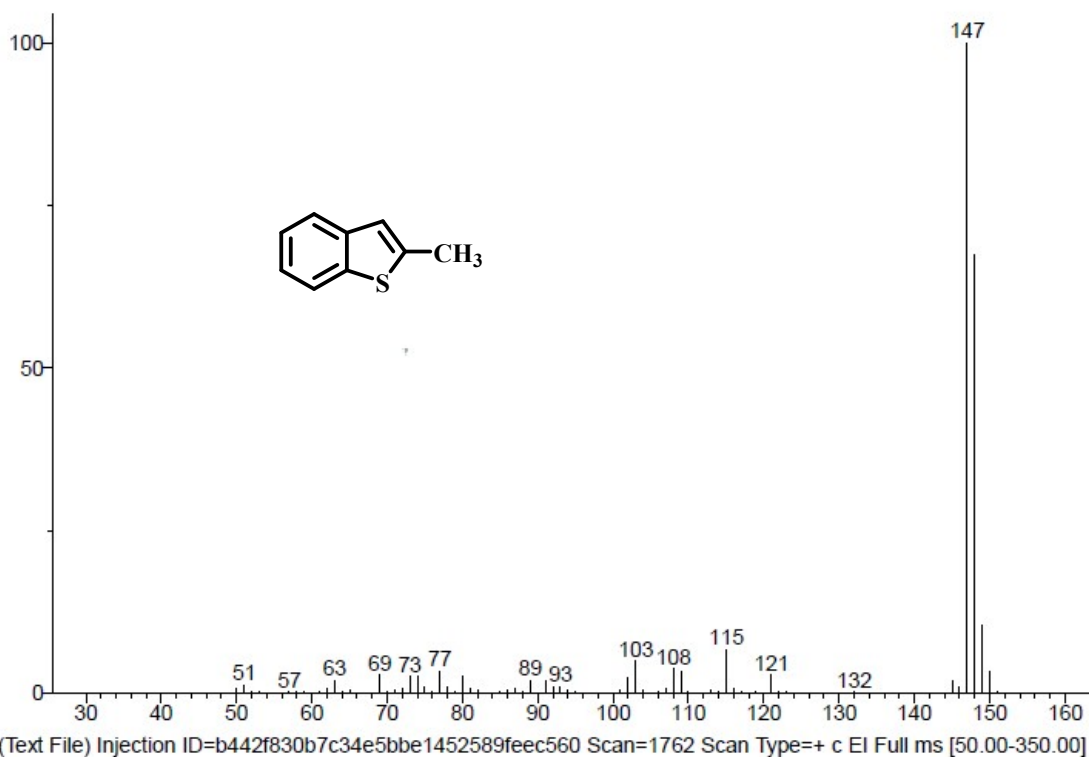


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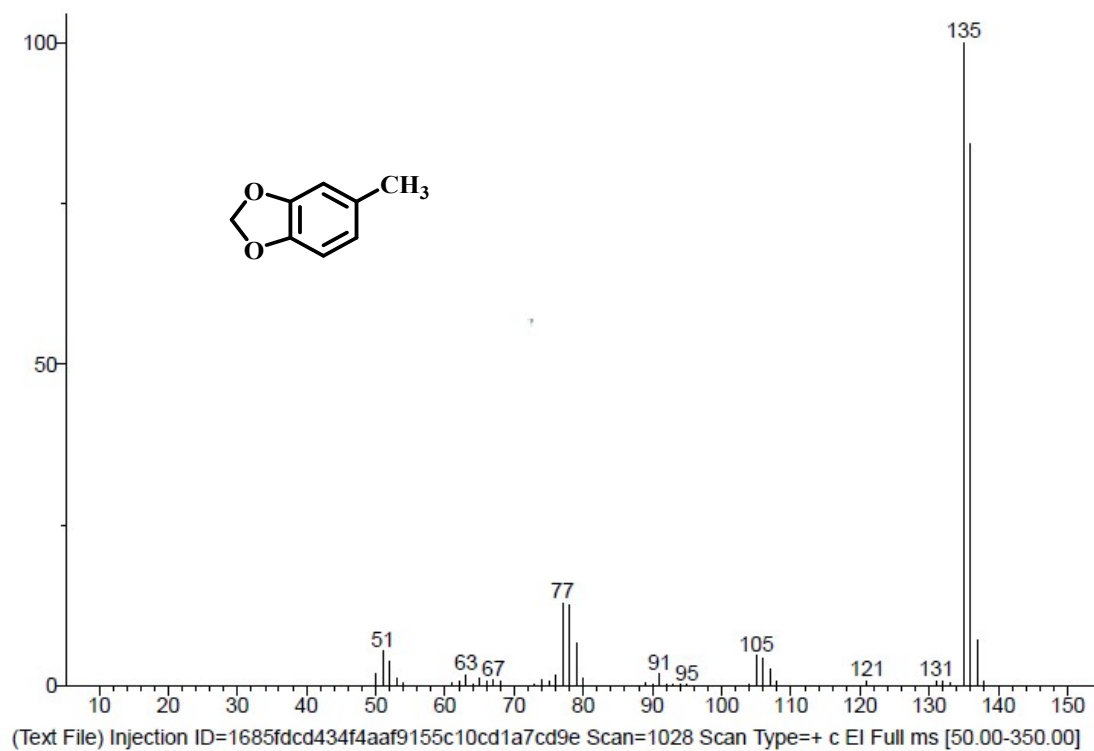
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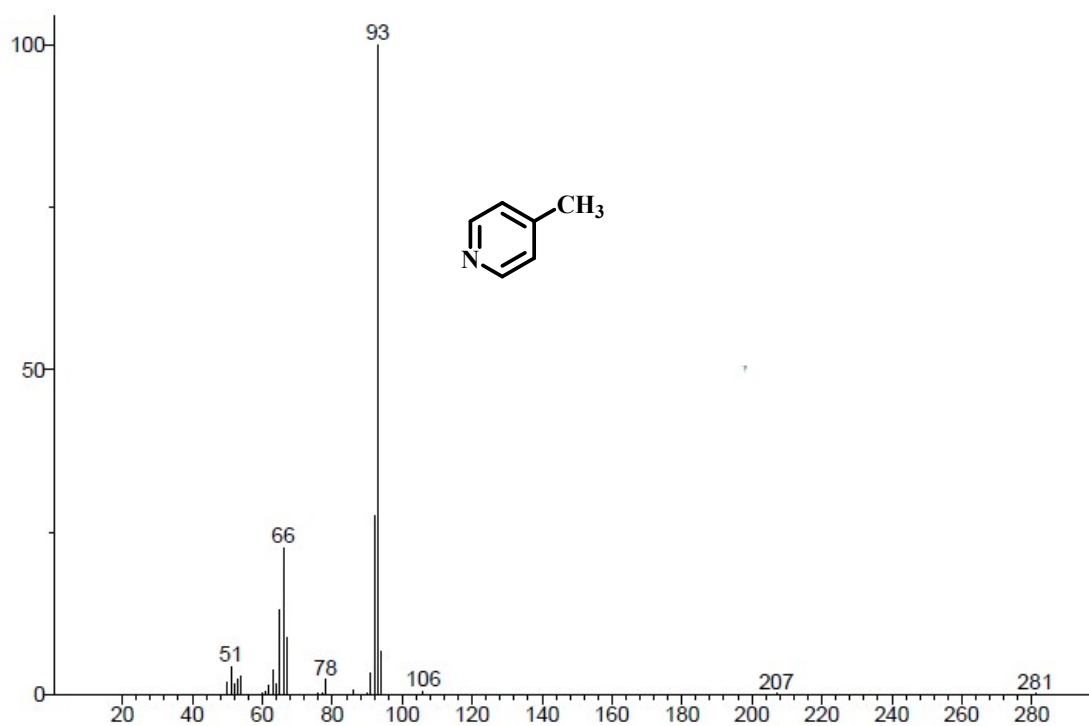
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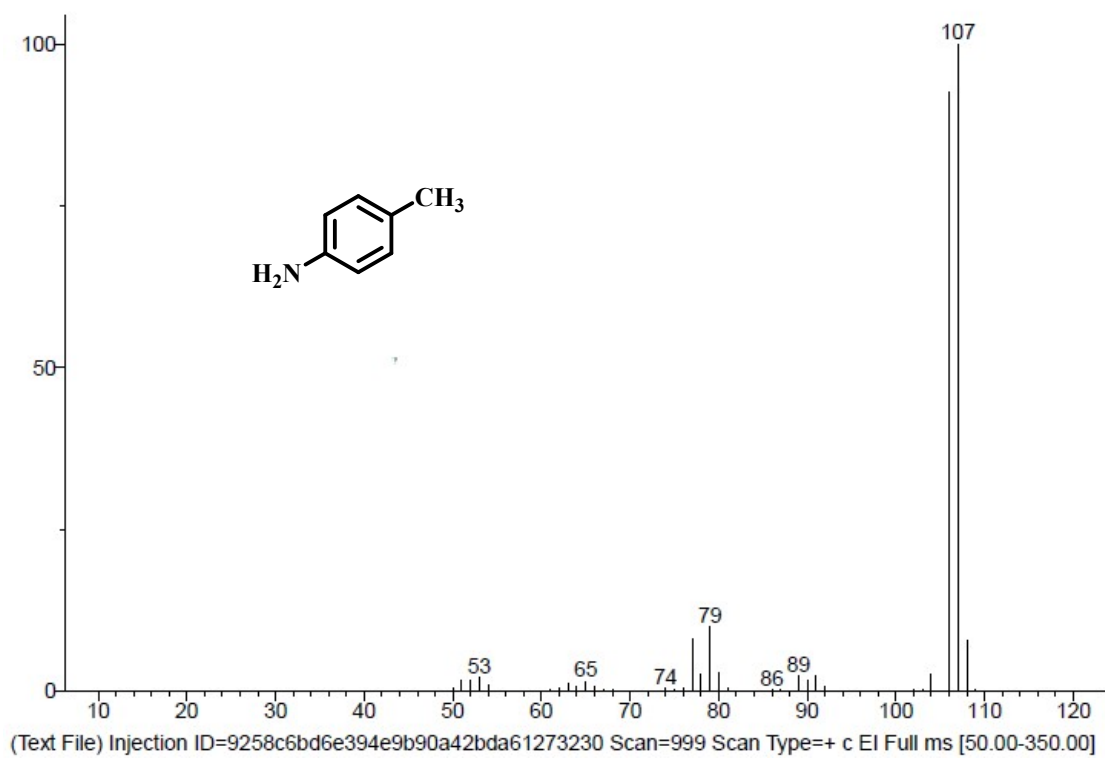


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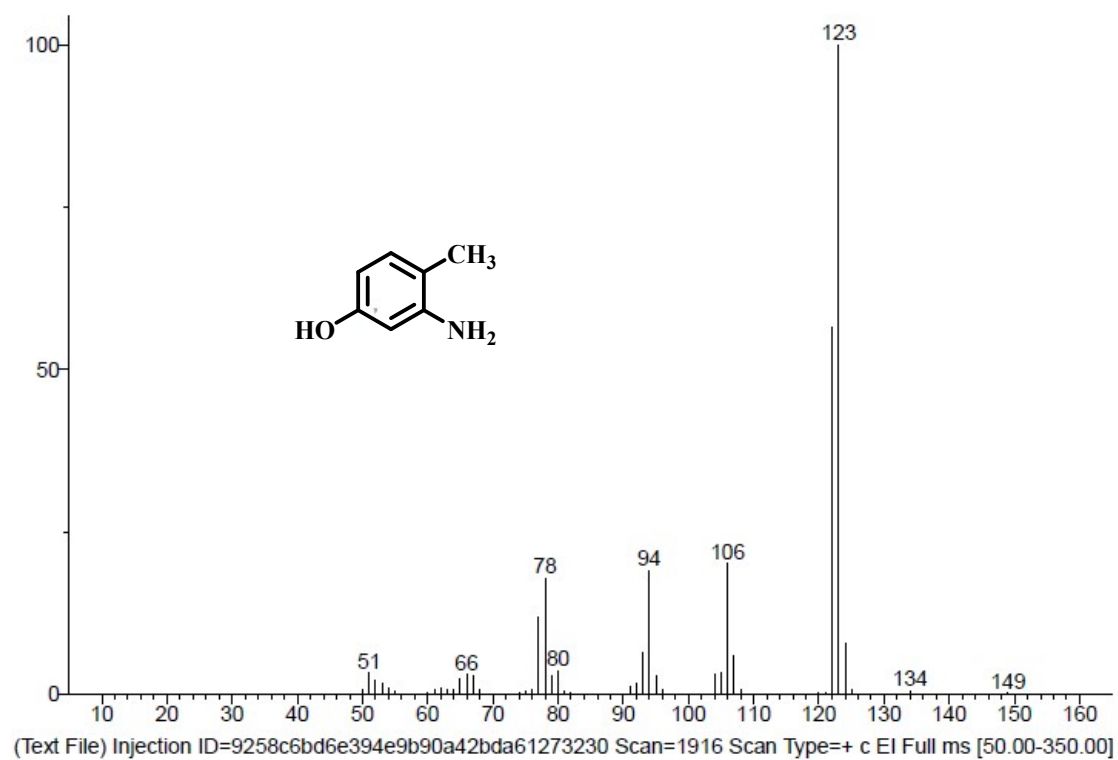


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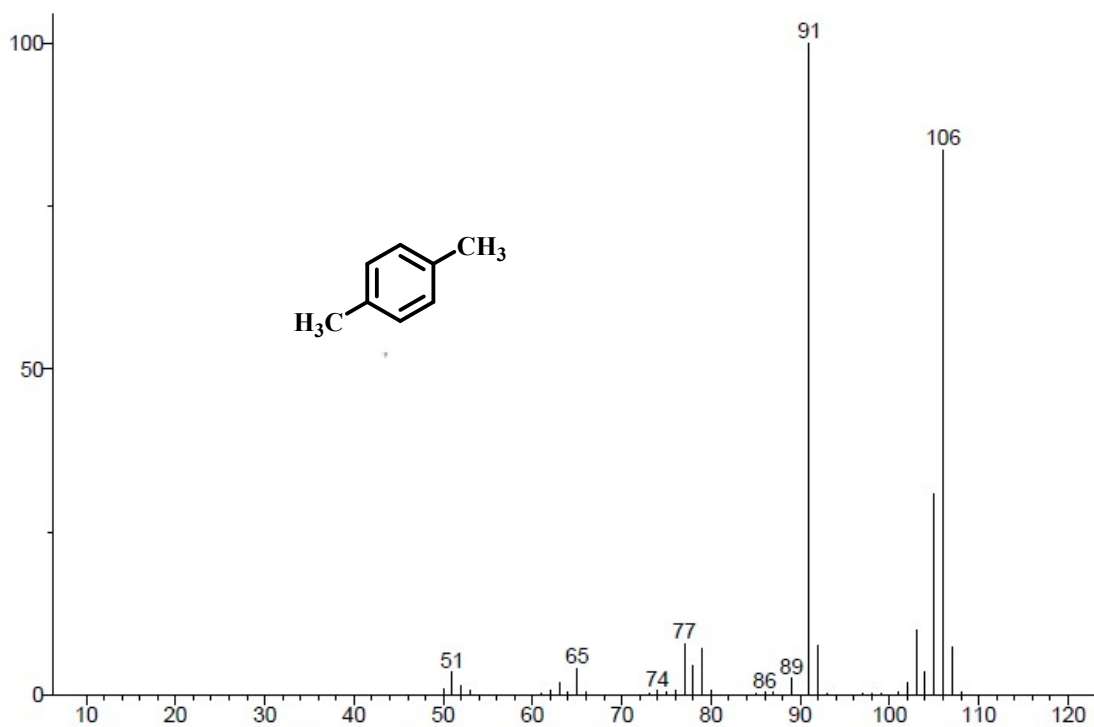
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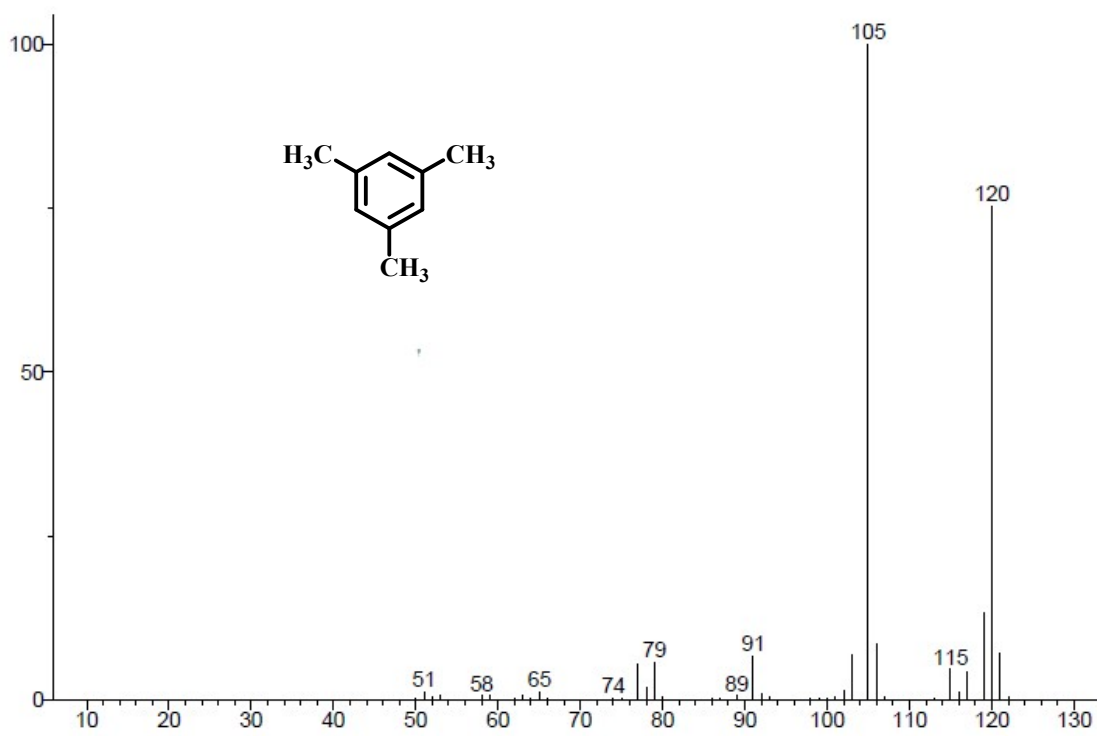


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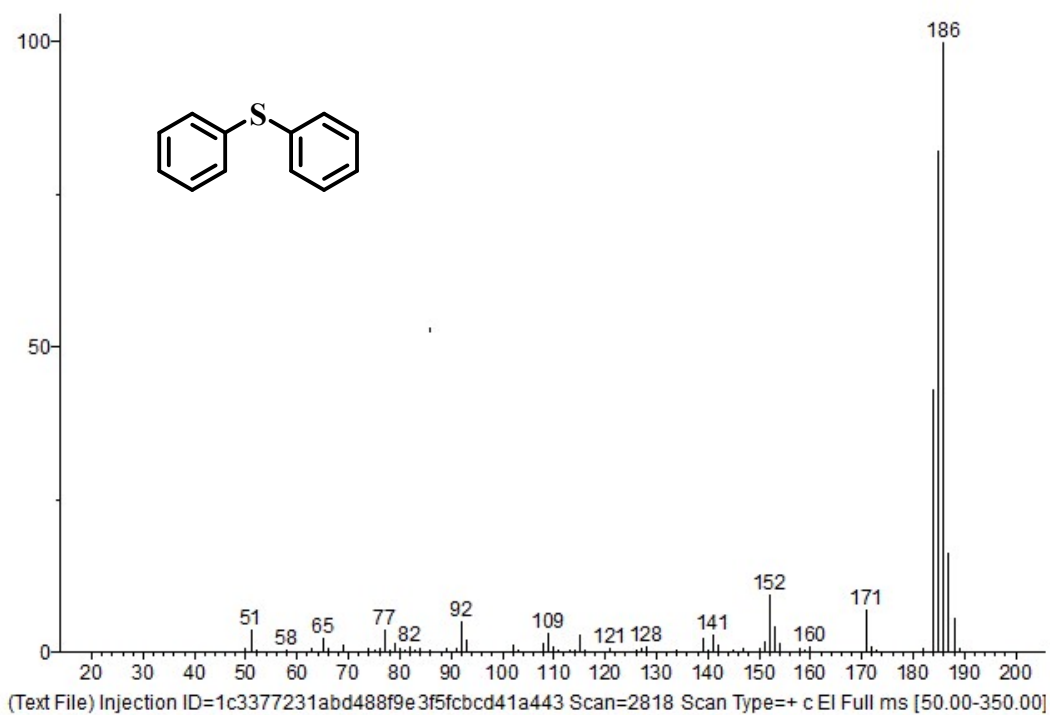
(Text File) Injection ID=9ee1d1b5f1bc4b2da3a3bee7bd768035 Scan=352 Scan Type=+ c EI Full ms [50.00-350.00]

(a45)

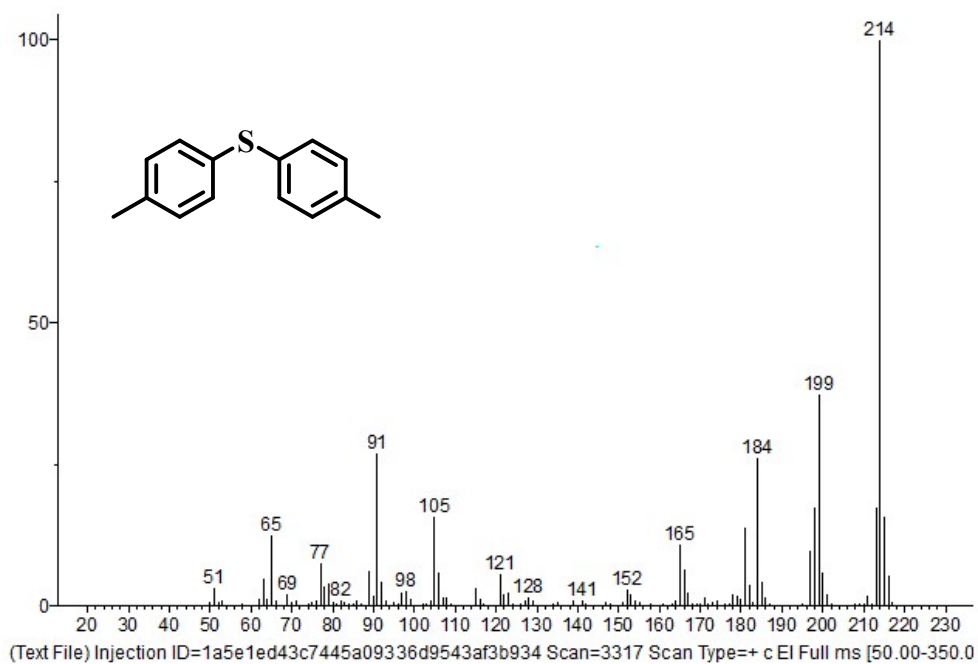


(Text File) Injection ID=9ee1d1b5f1bc4b2da3a3bee7bd768035 Scan=579 Scan Type=+ c EI Full ms [50.00-350.00]

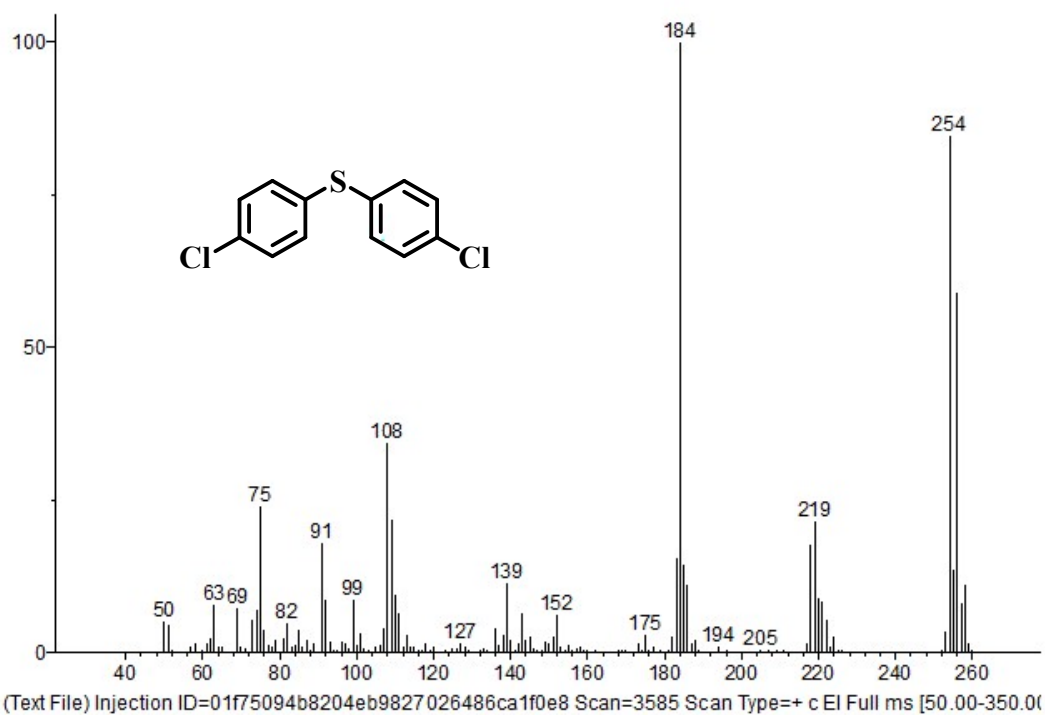
(b1)



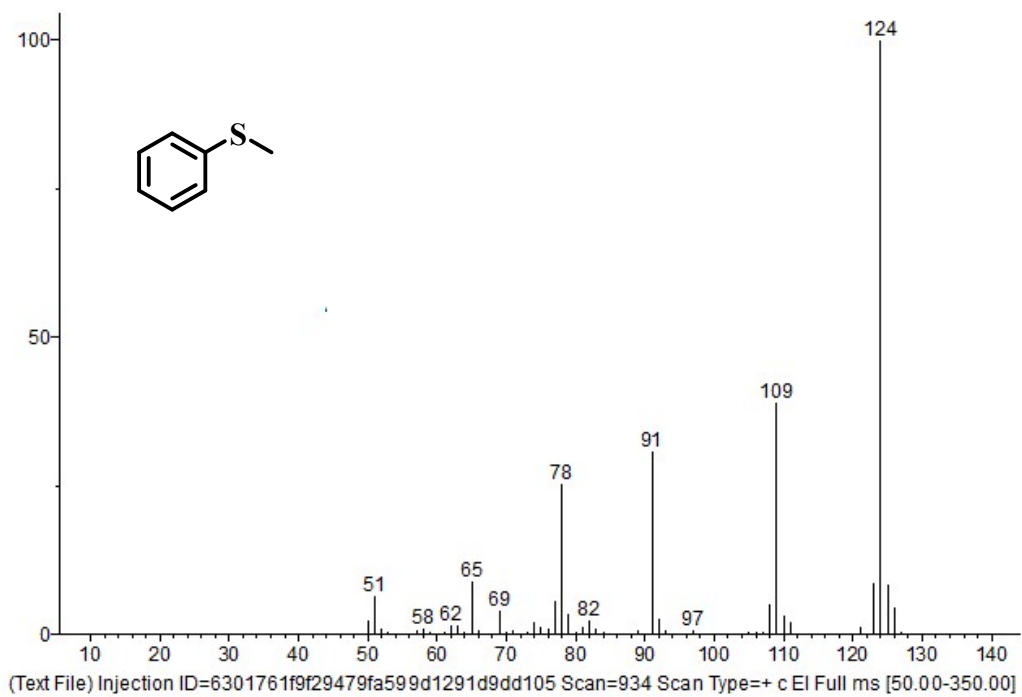
(b2)



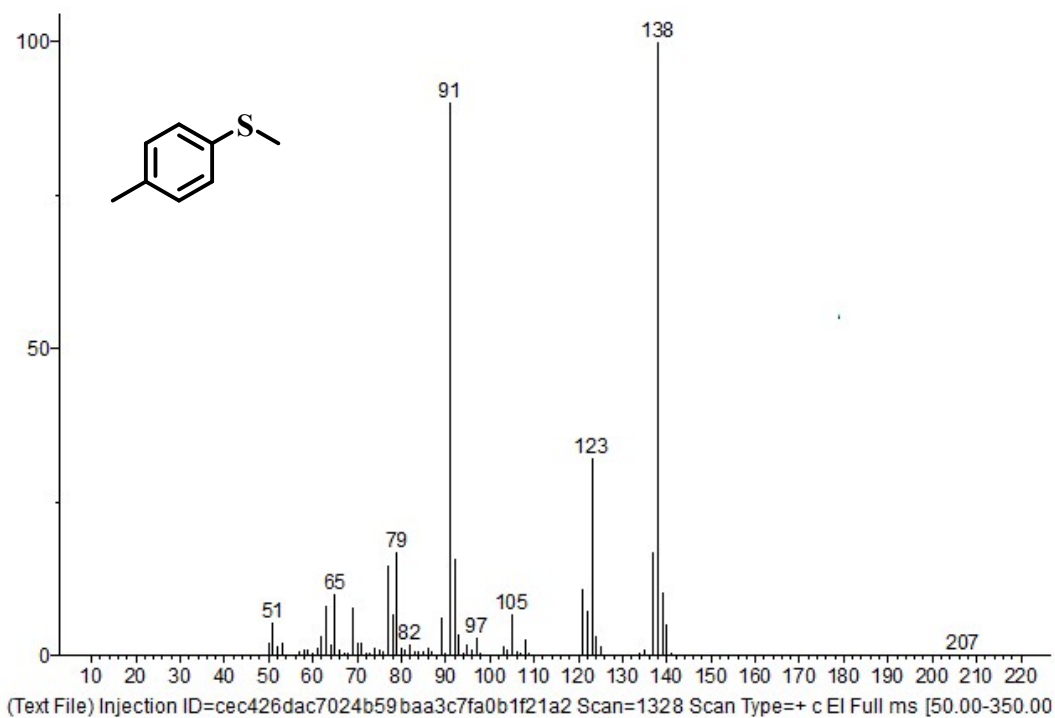
(b3)



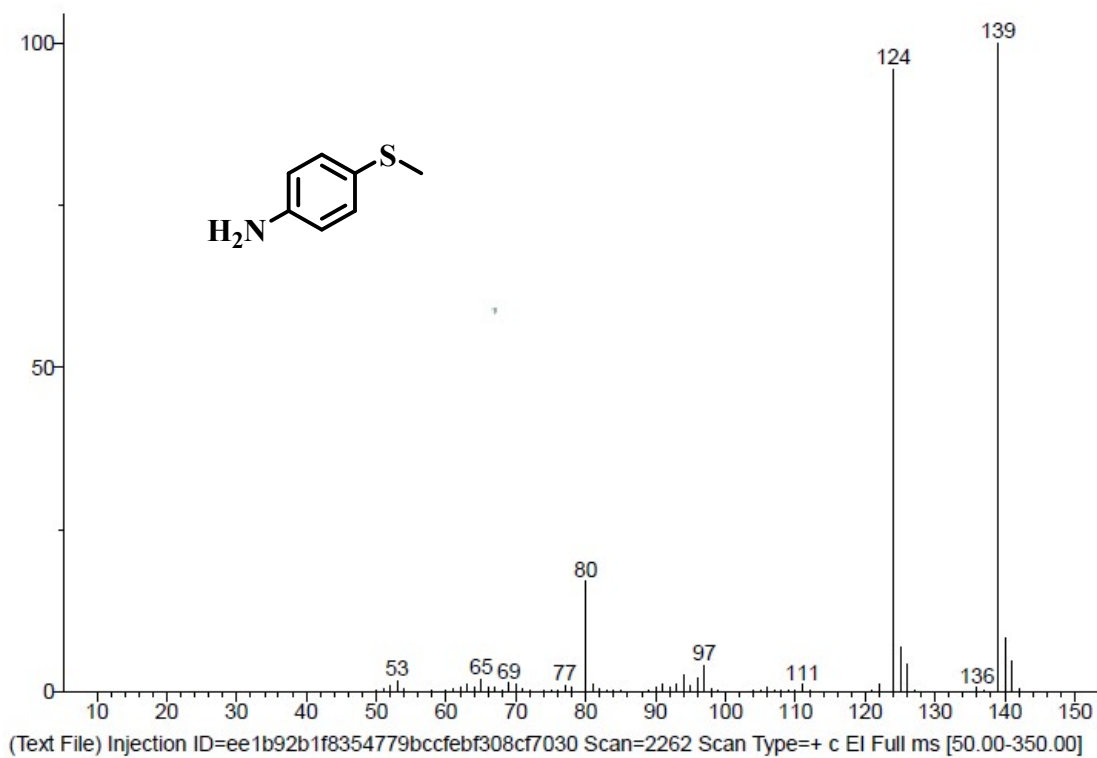
(b4)



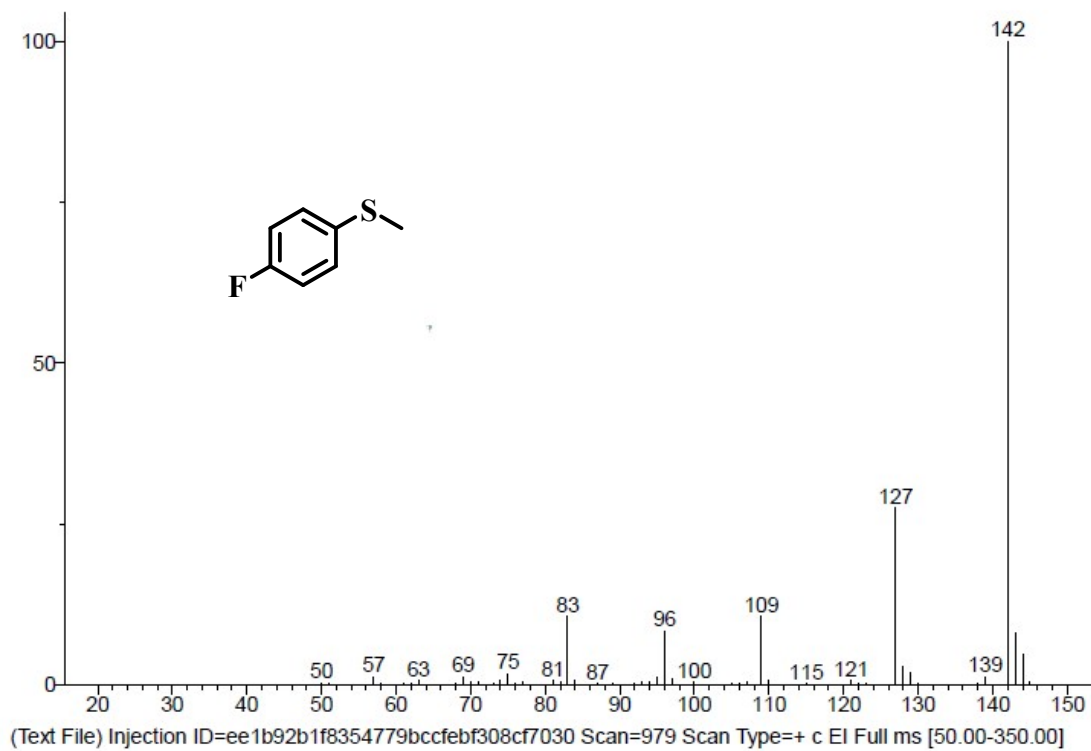
(b5)



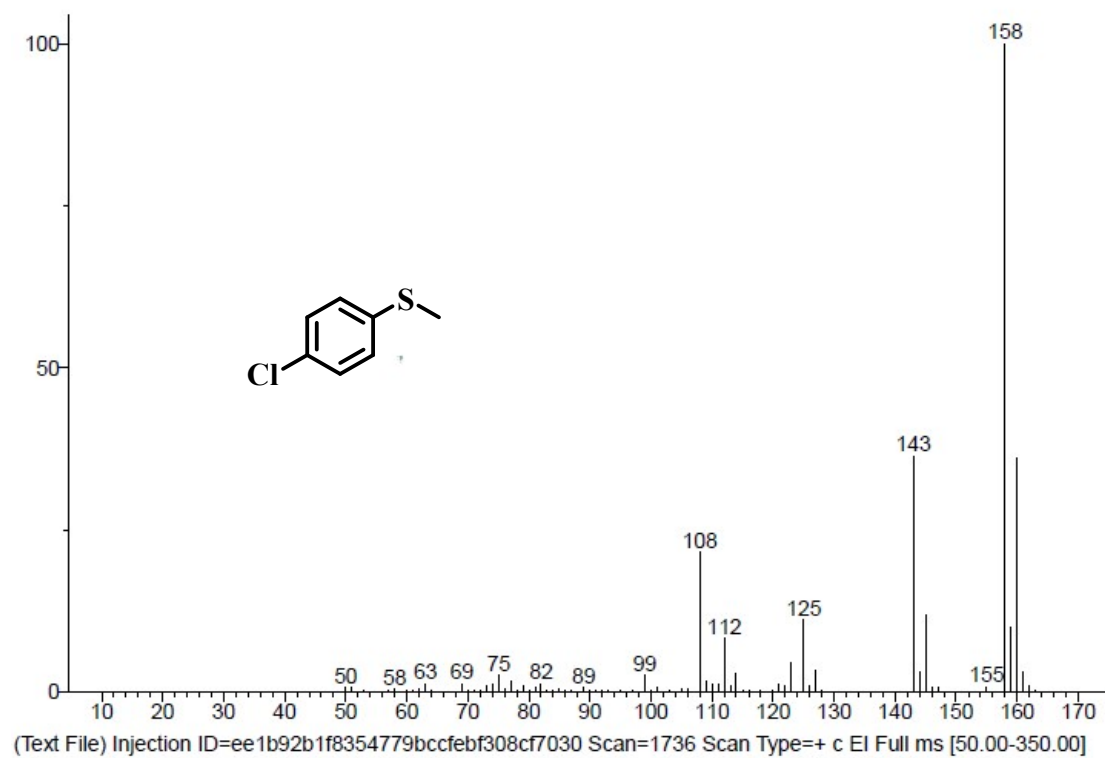
(b6)



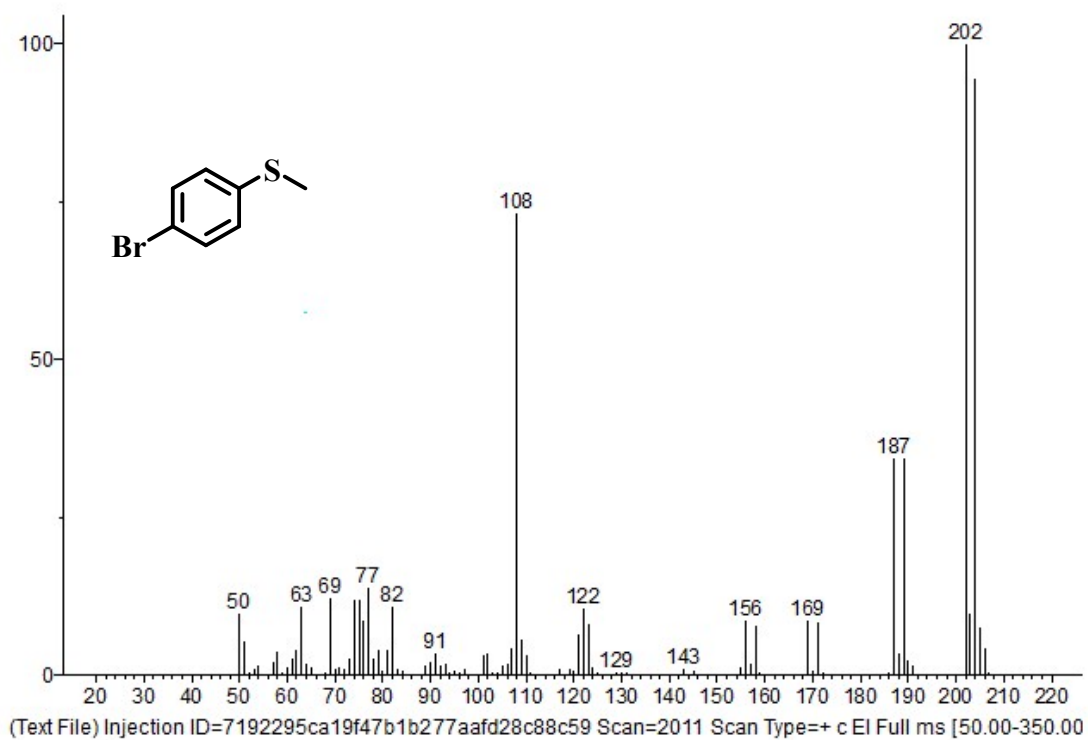
(b7)



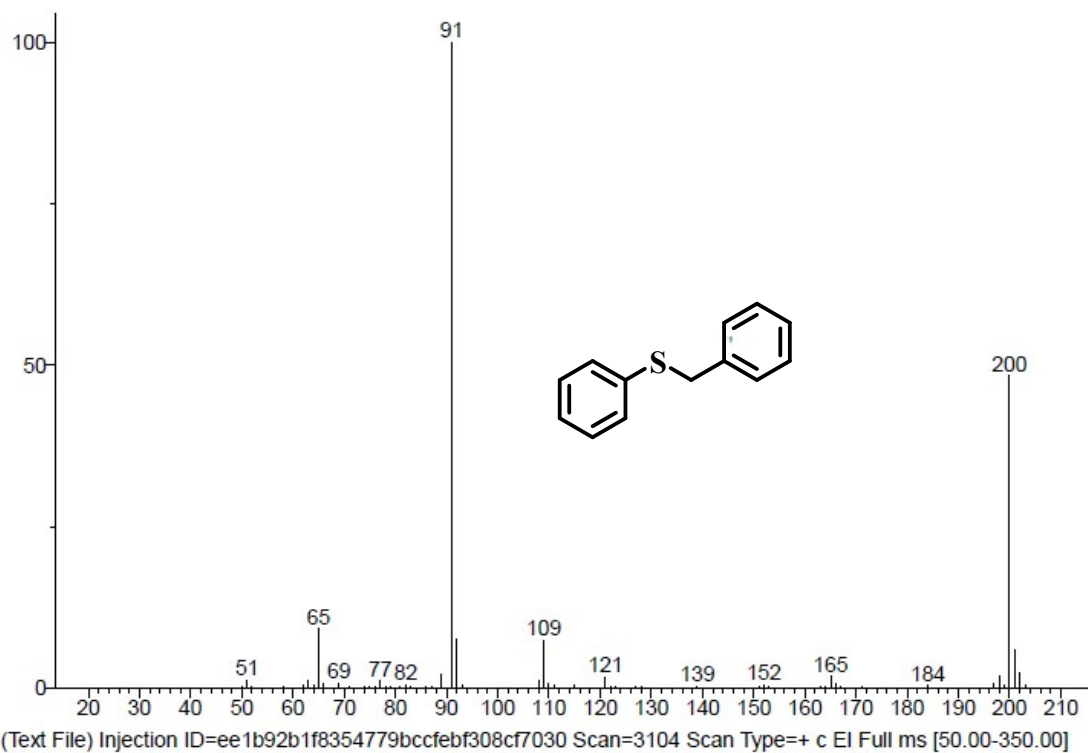
(b8)



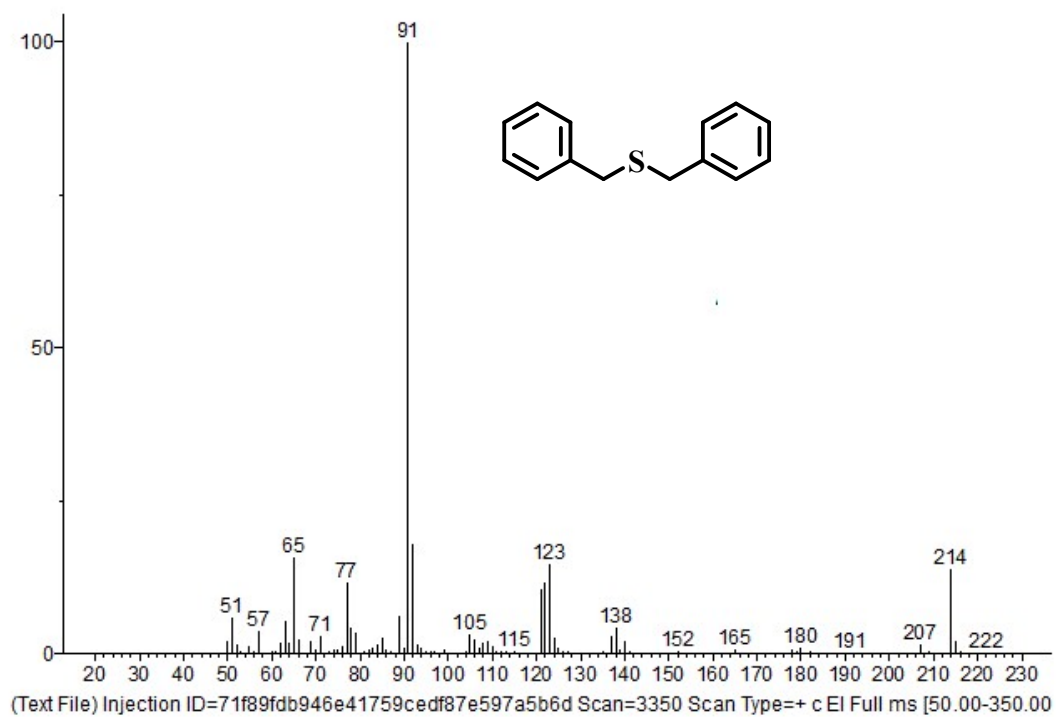
(b9)



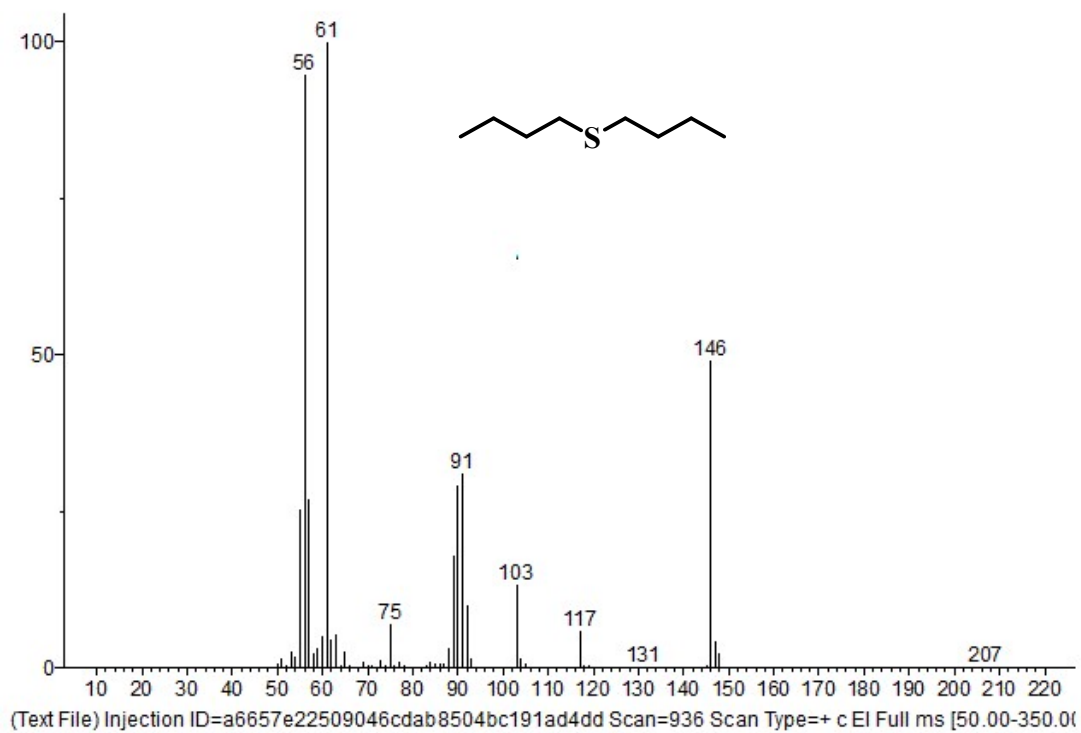
(b10)



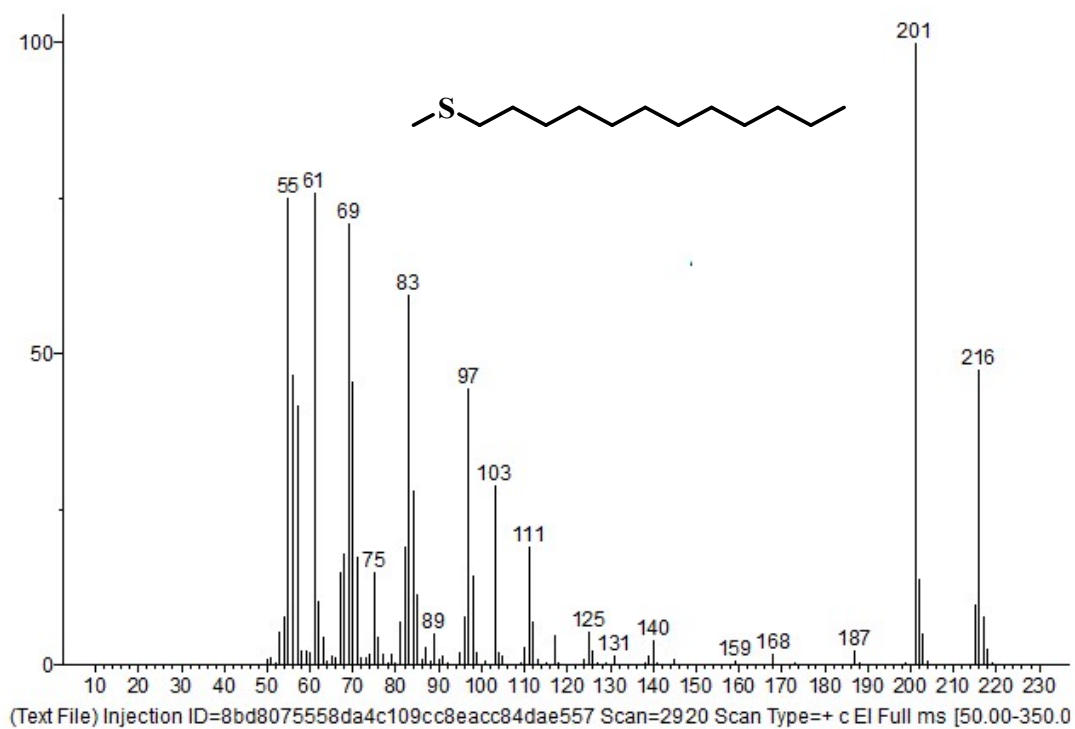
(b12)



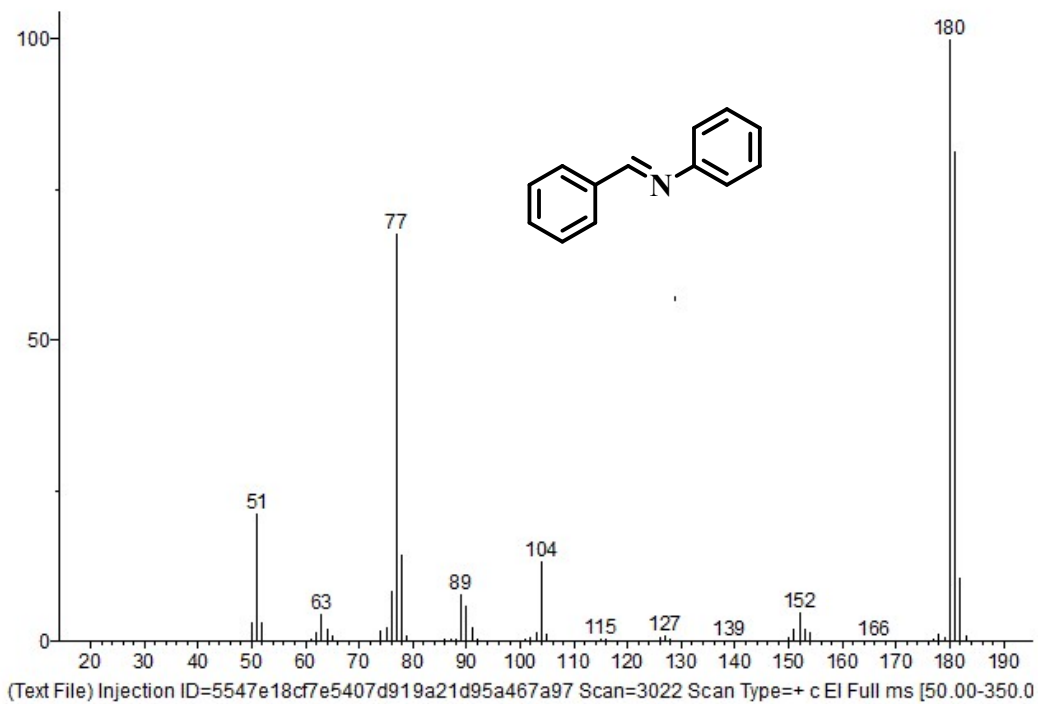
(b13)



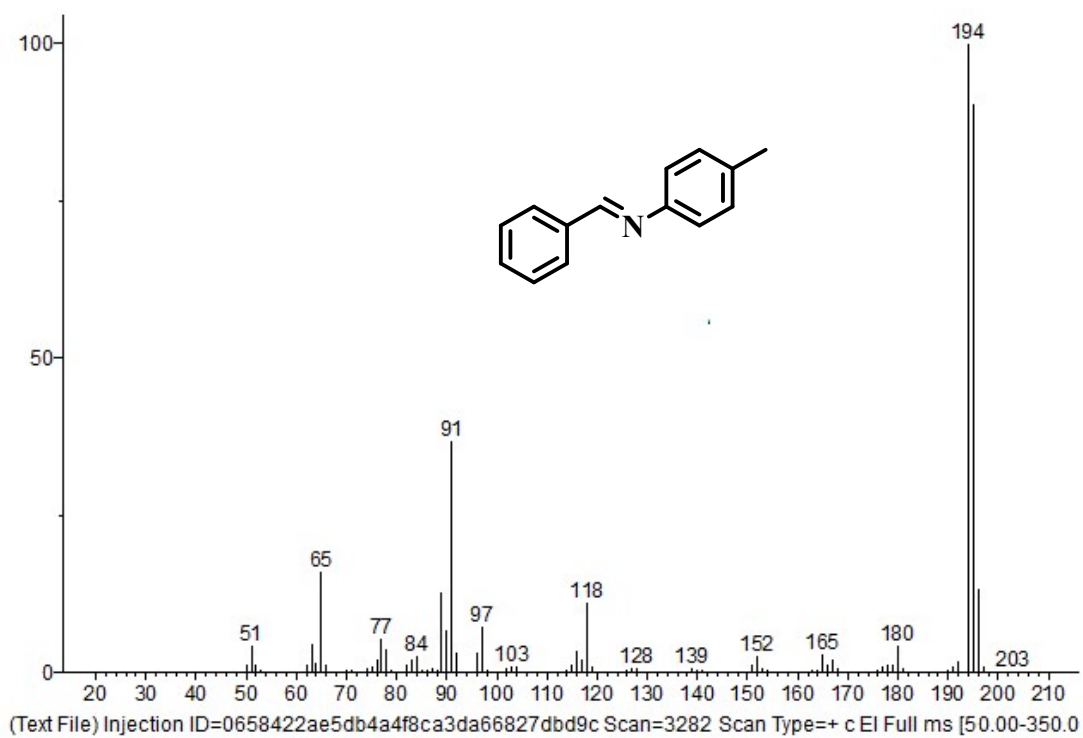
(b14)



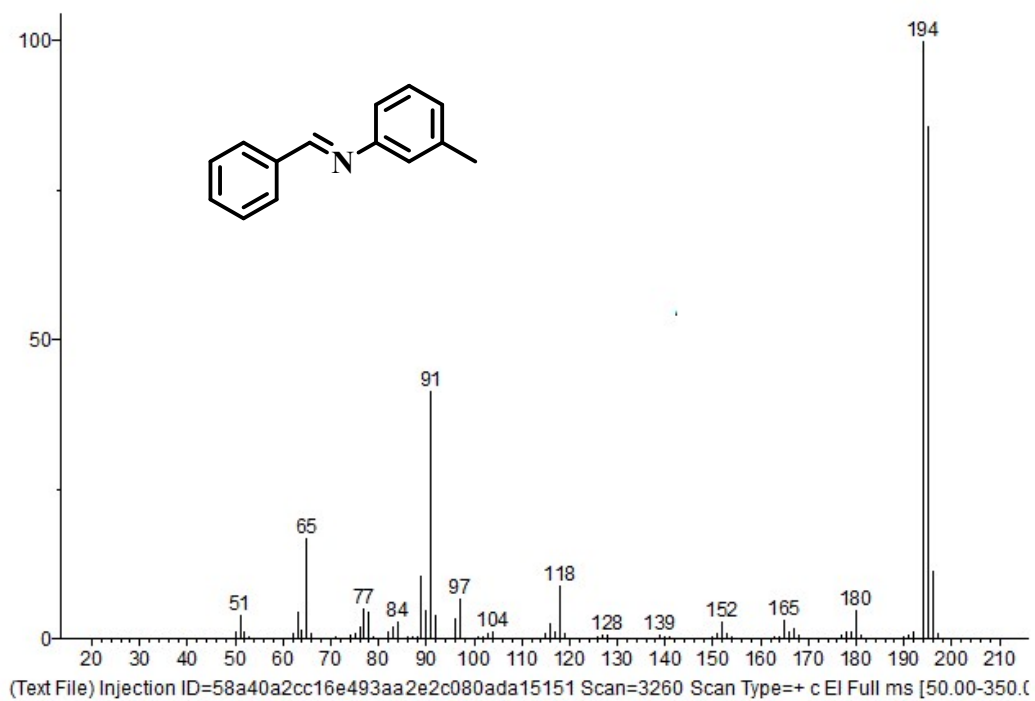
(c1)



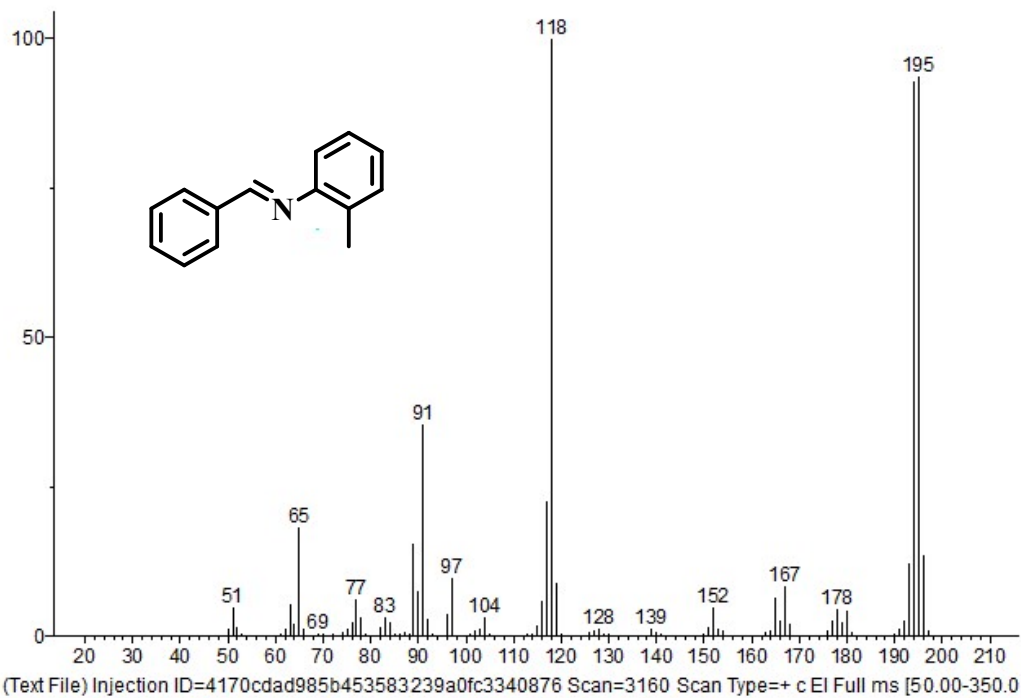
(c2)



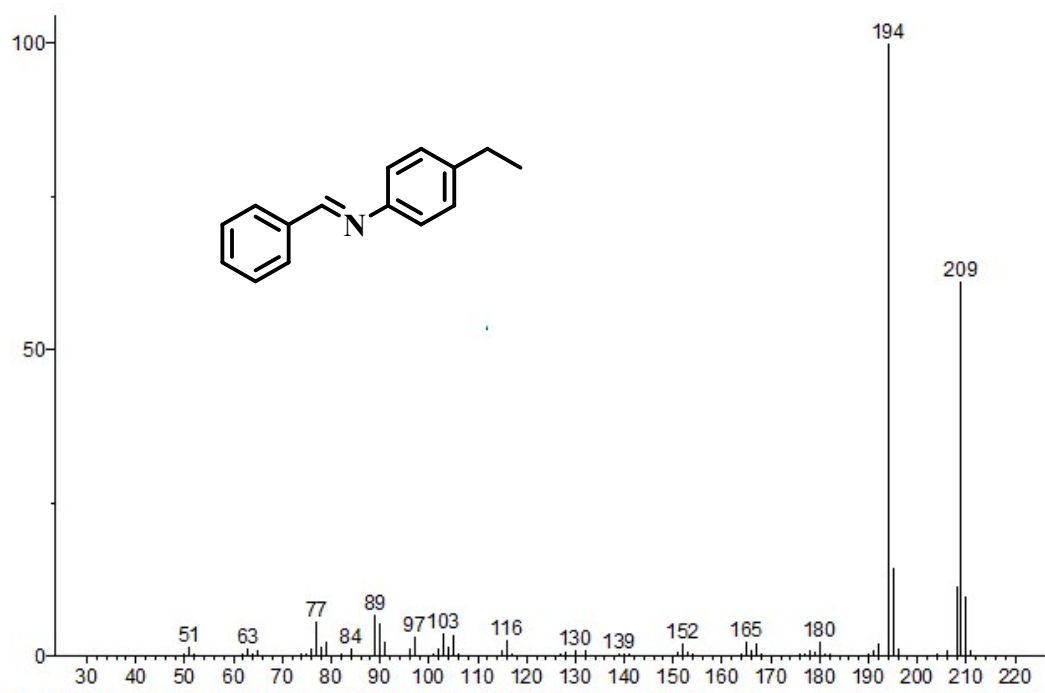
(c3)



(c4)

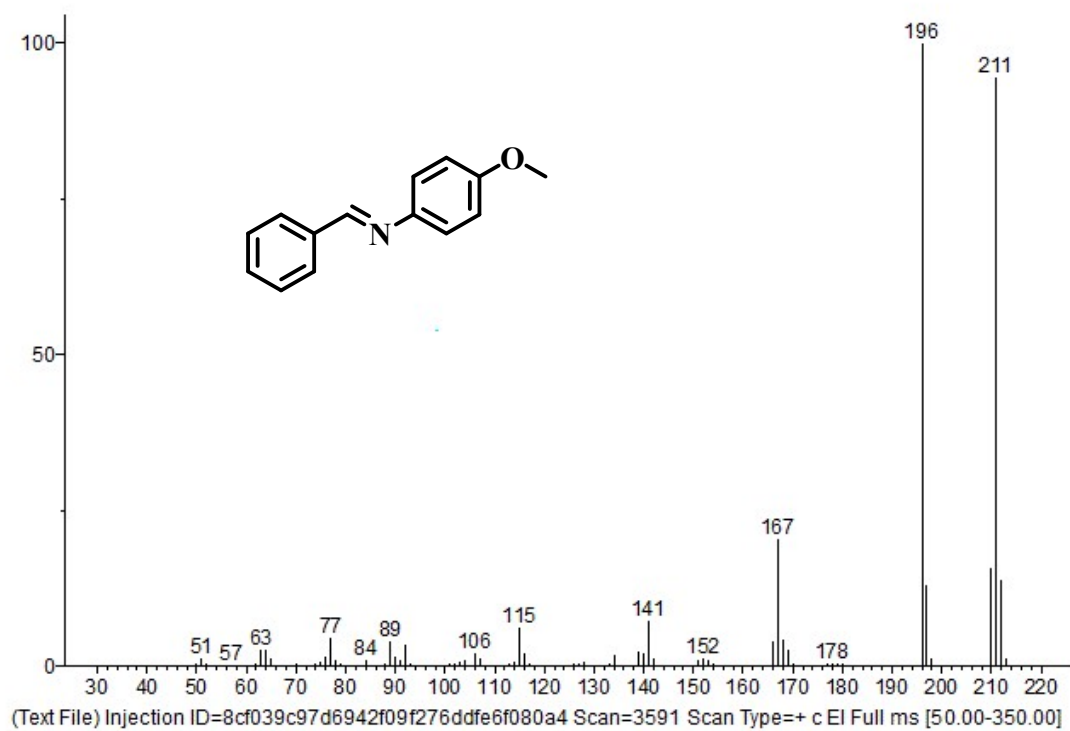


(c5)

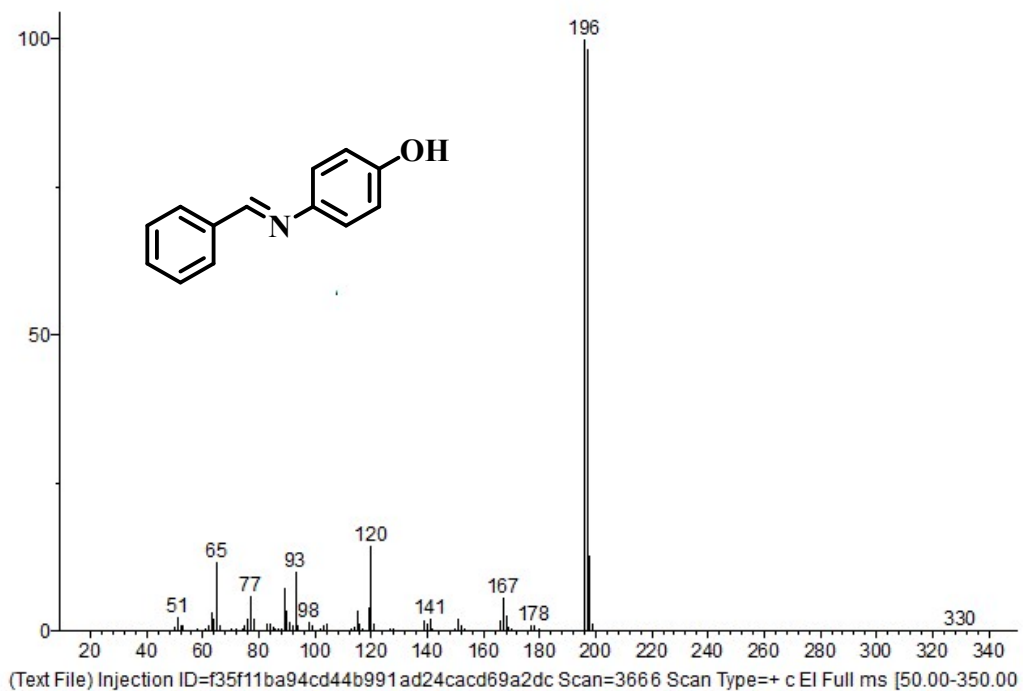


(Text File) Injection ID=376c7b00ed724378af7ad278c67d7493 Scan=3473 Scan Type=+ c EI Full ms [50.00-350.0

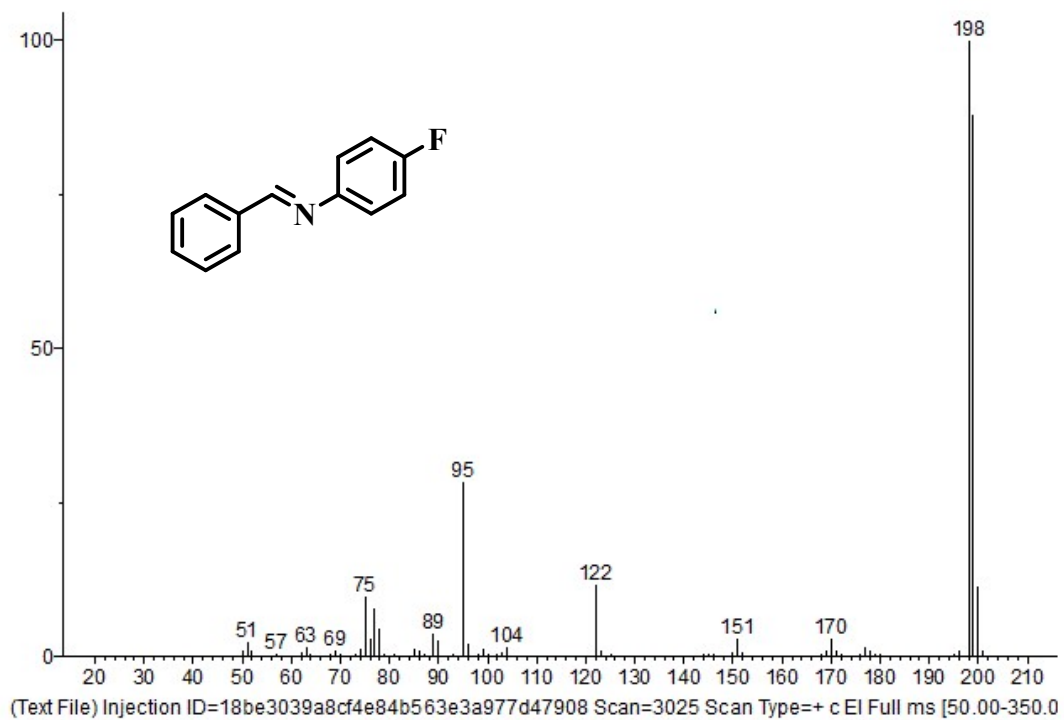
(b6)



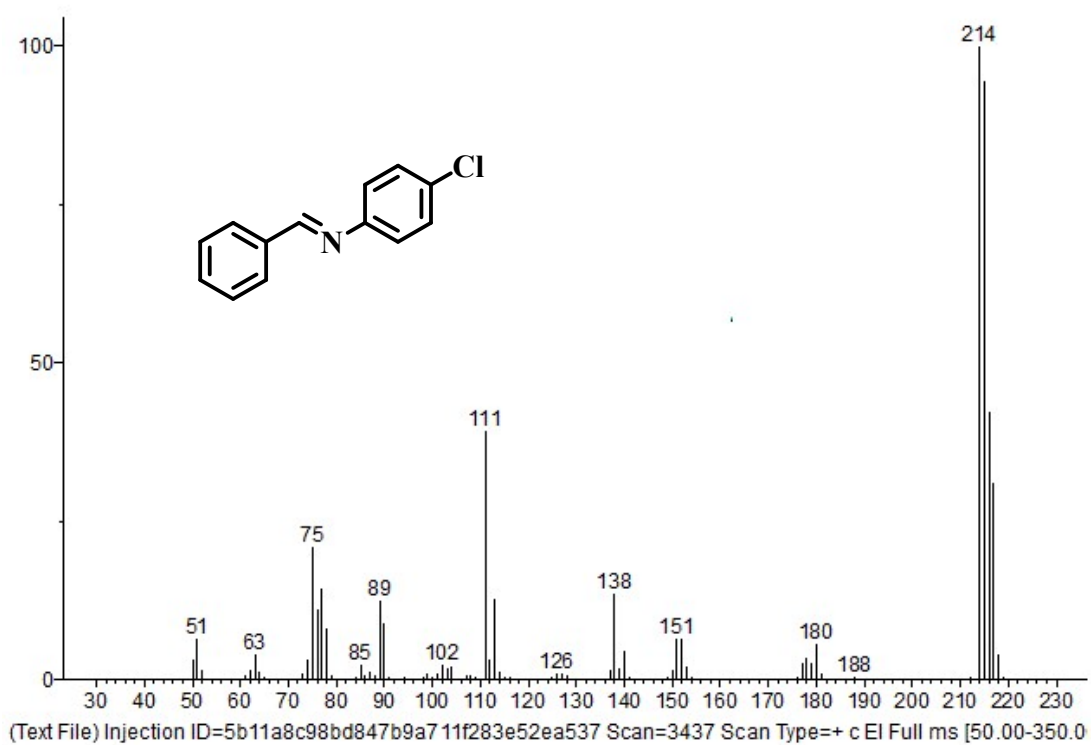
(b7)



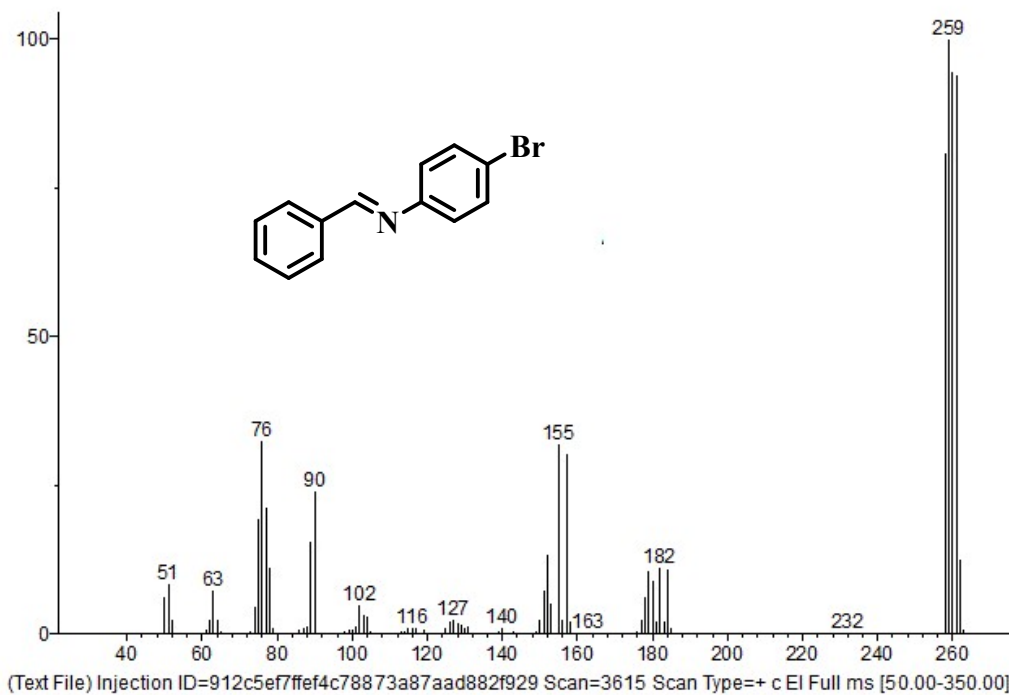
(b8)



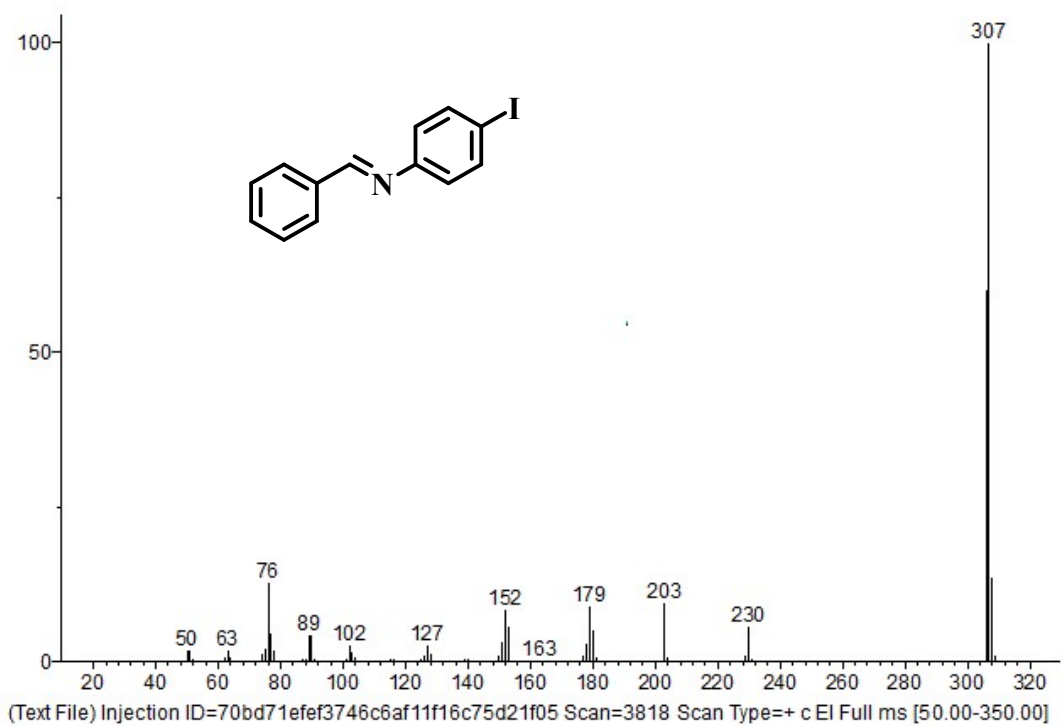
(c9)



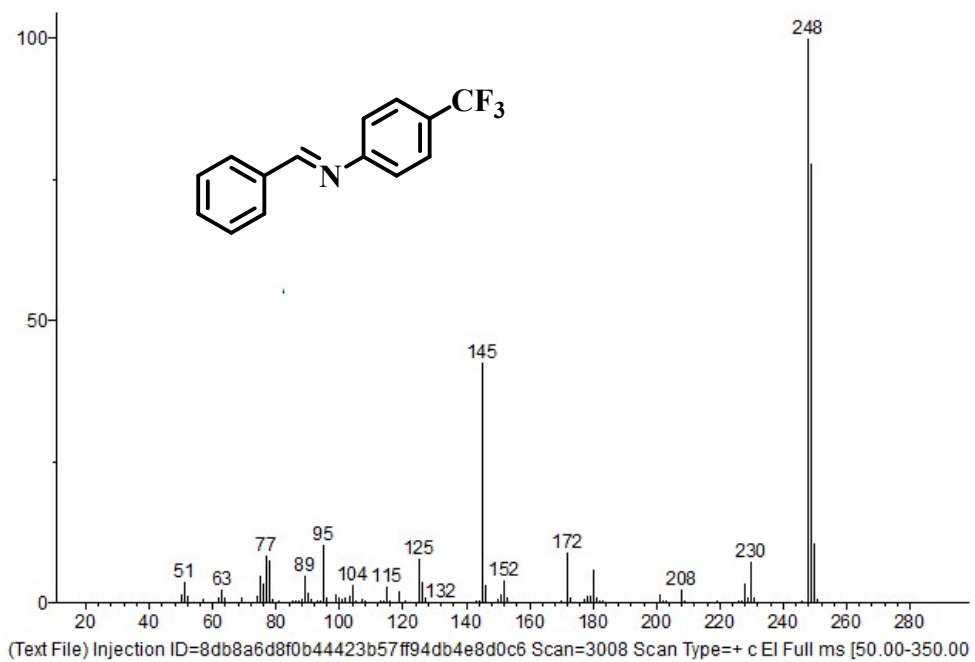
(c10)



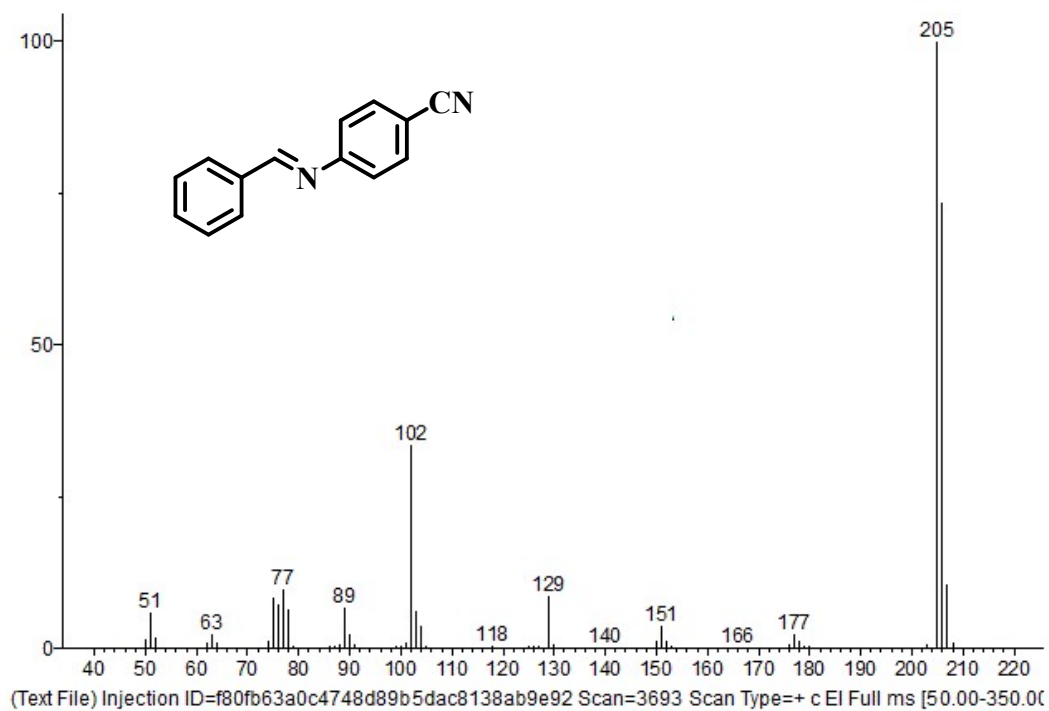
(c11)



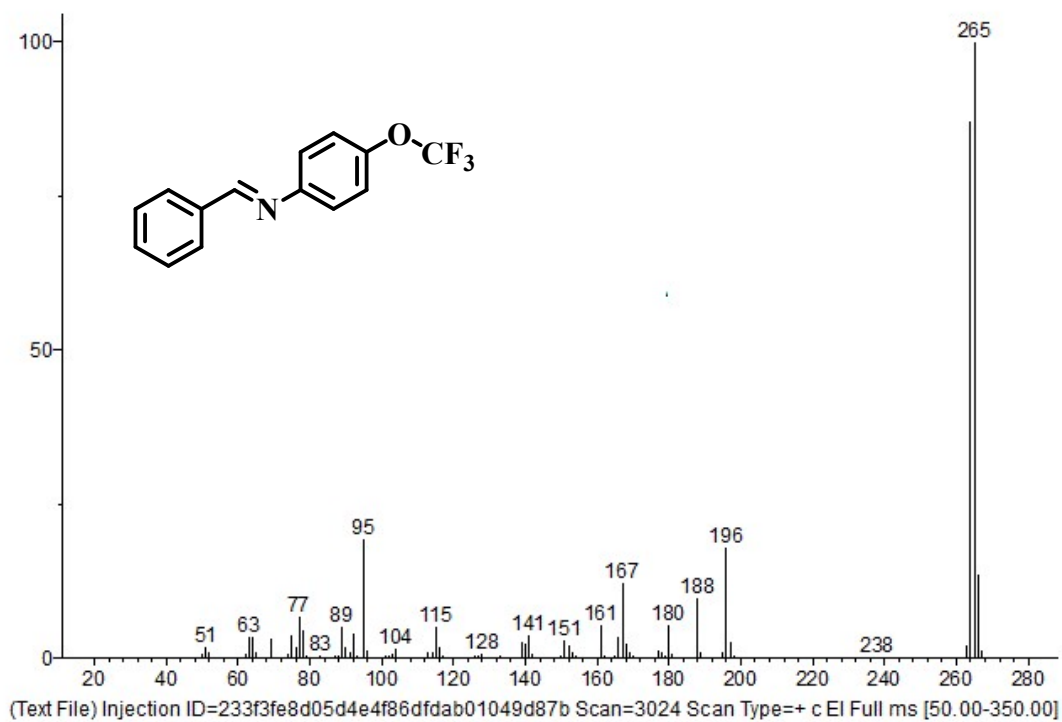
(c12)



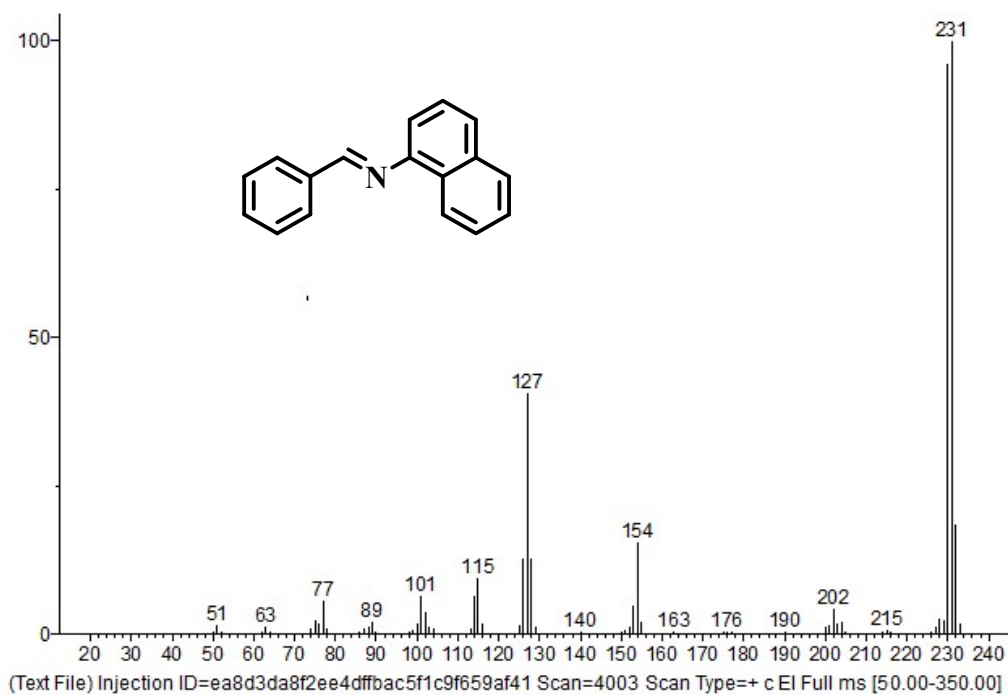
(c13)



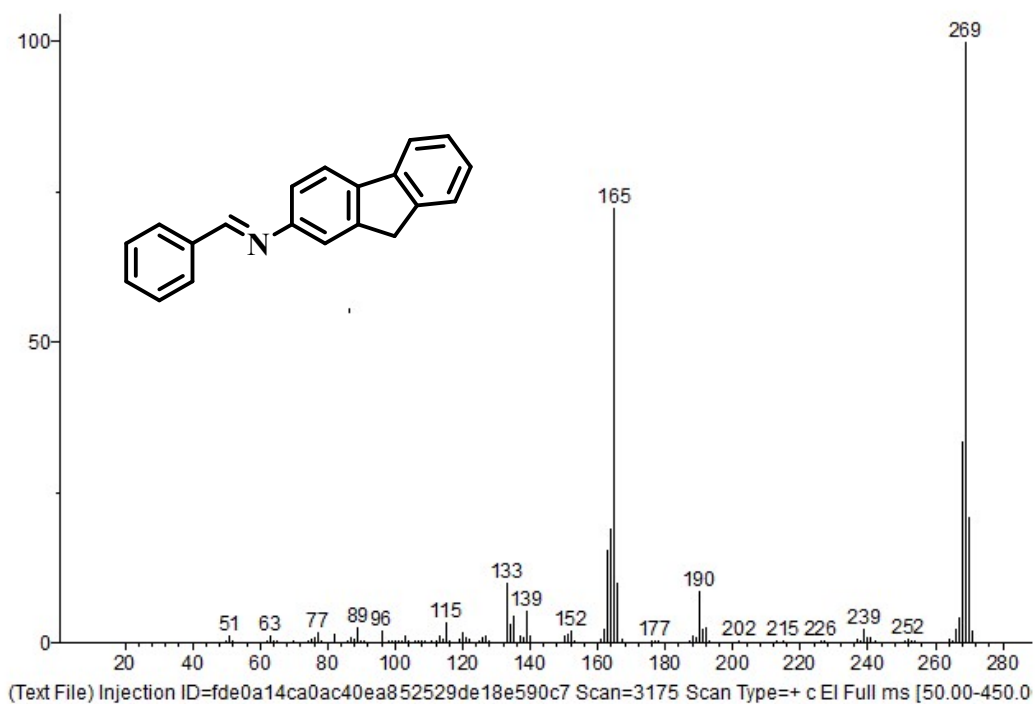
(c14)



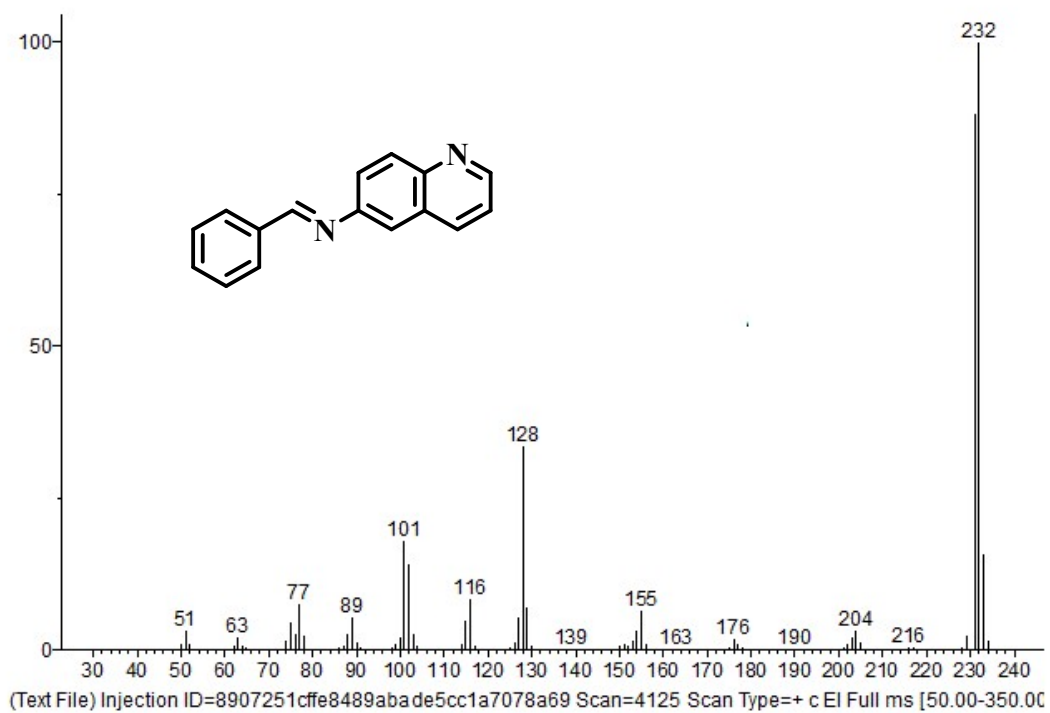
(c15)



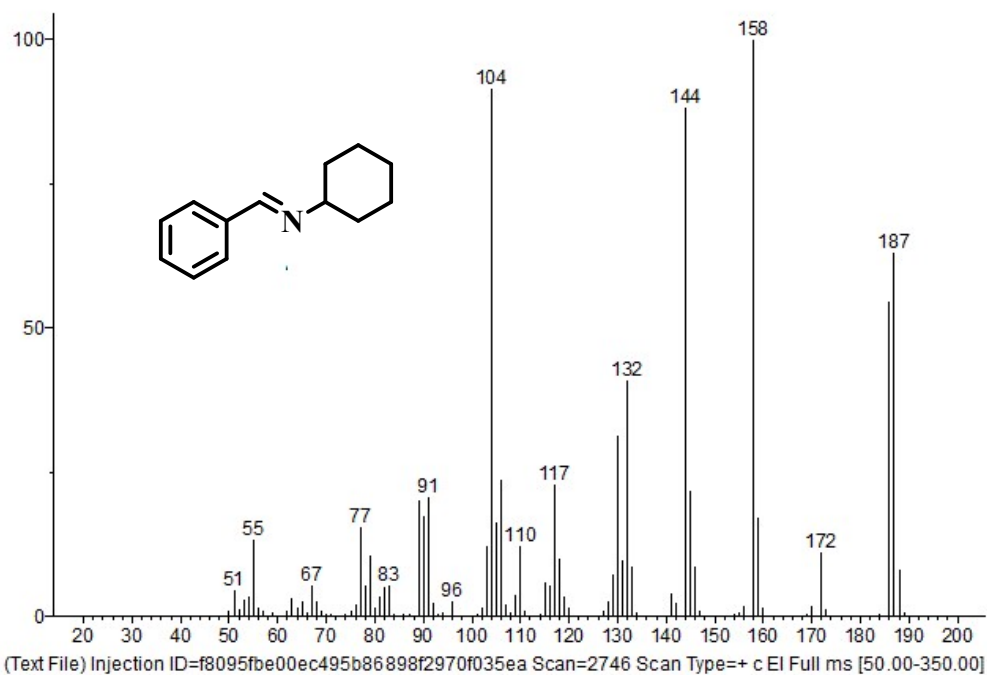
(c16)



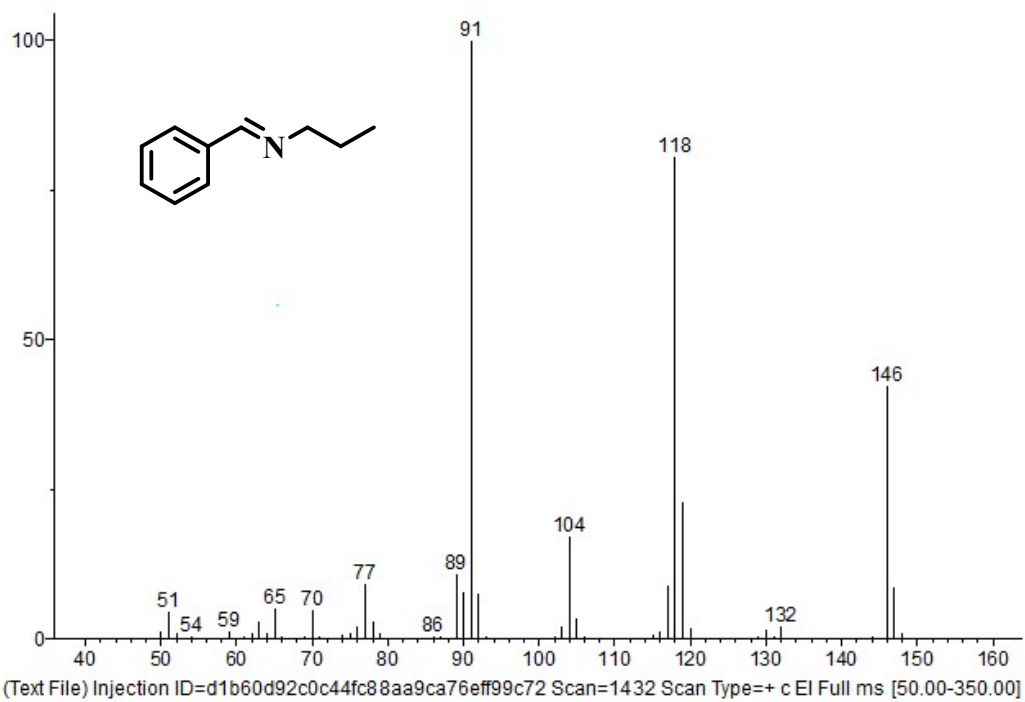
(c17)



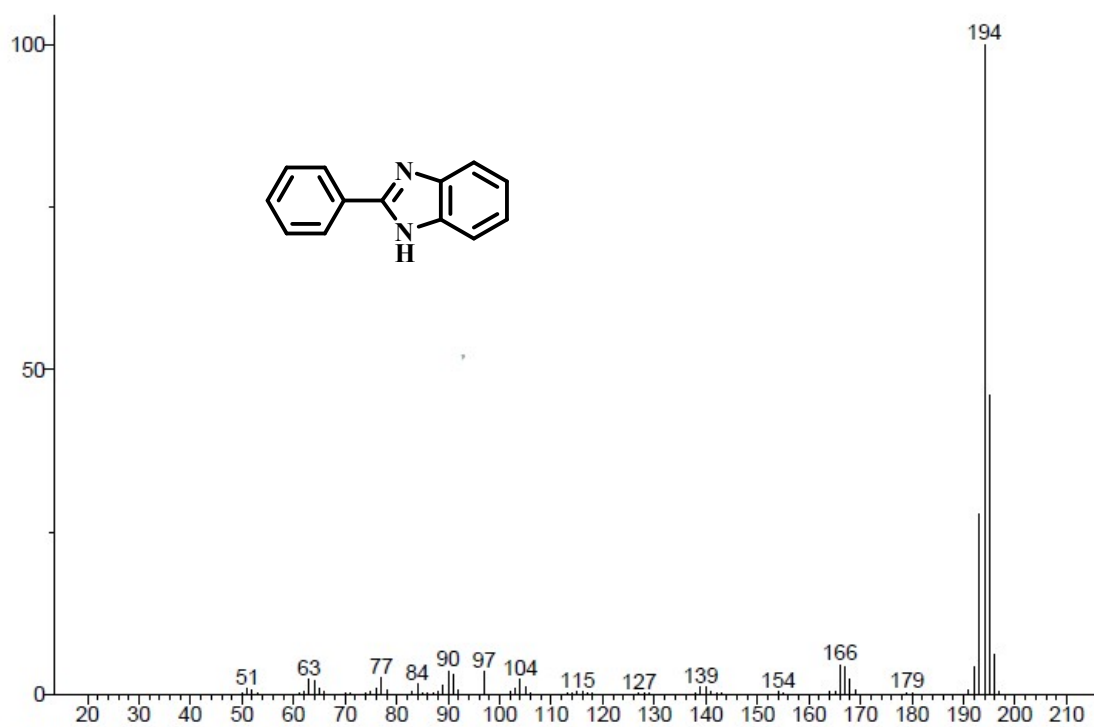
(c18)



(c19)

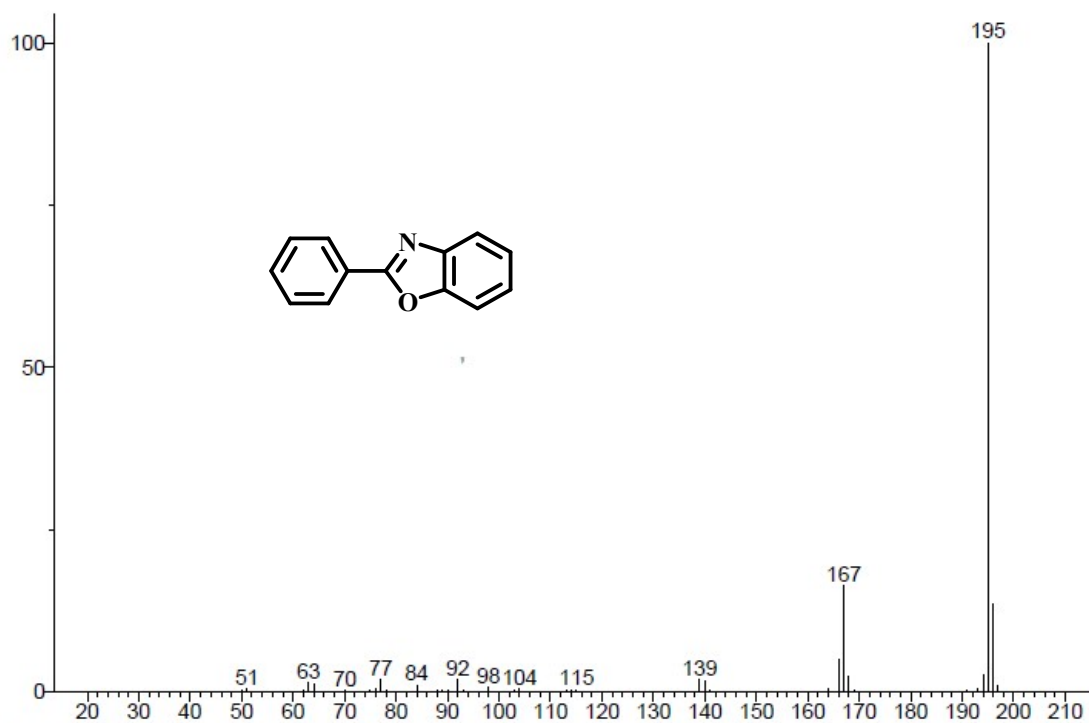


(c20)



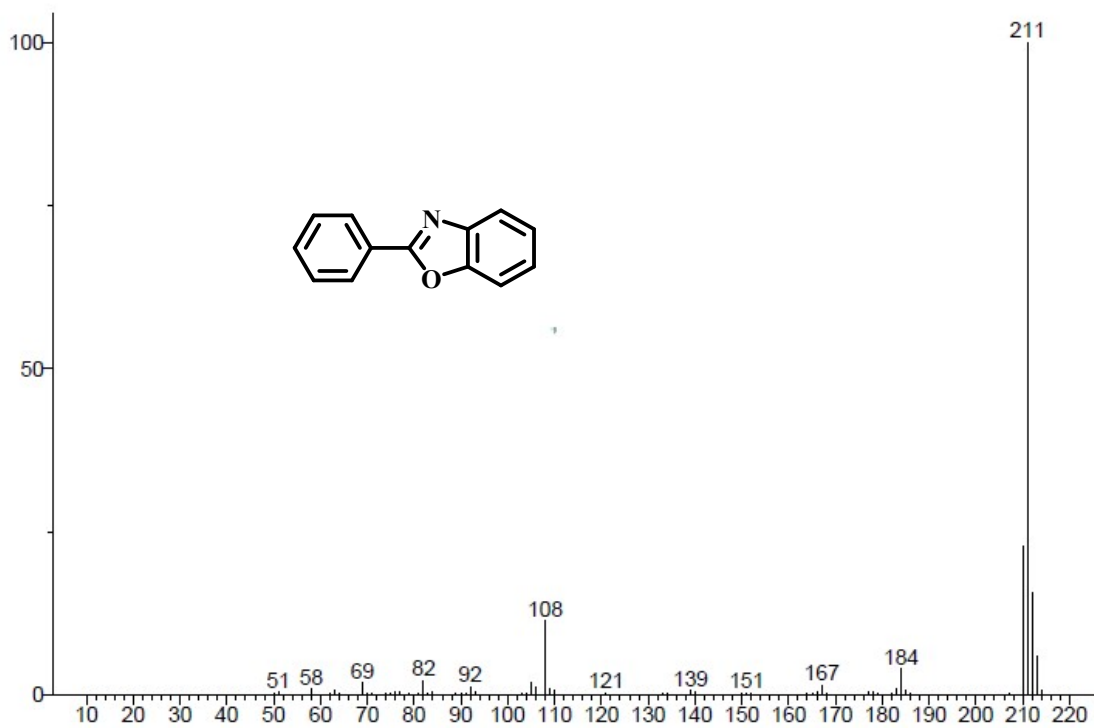
(Text File) Injection ID=3336a207186c42cdb186138c207830b4 Scan=2859 Scan Type=+ c EI Full ms [50.00-450.00]

(c21)



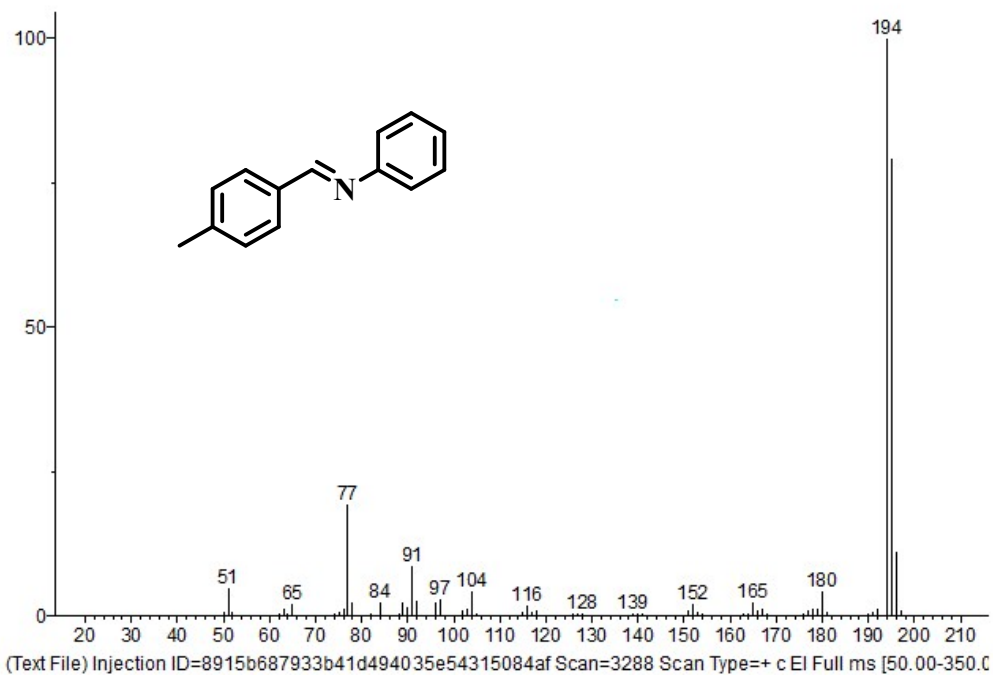
(Text File) Injection ID=62cd49b8c1b64861a2536fb30e10b7ab Scan=3052 Scan Type=+ c EI Full ms [50.00-400.00]

(c22)

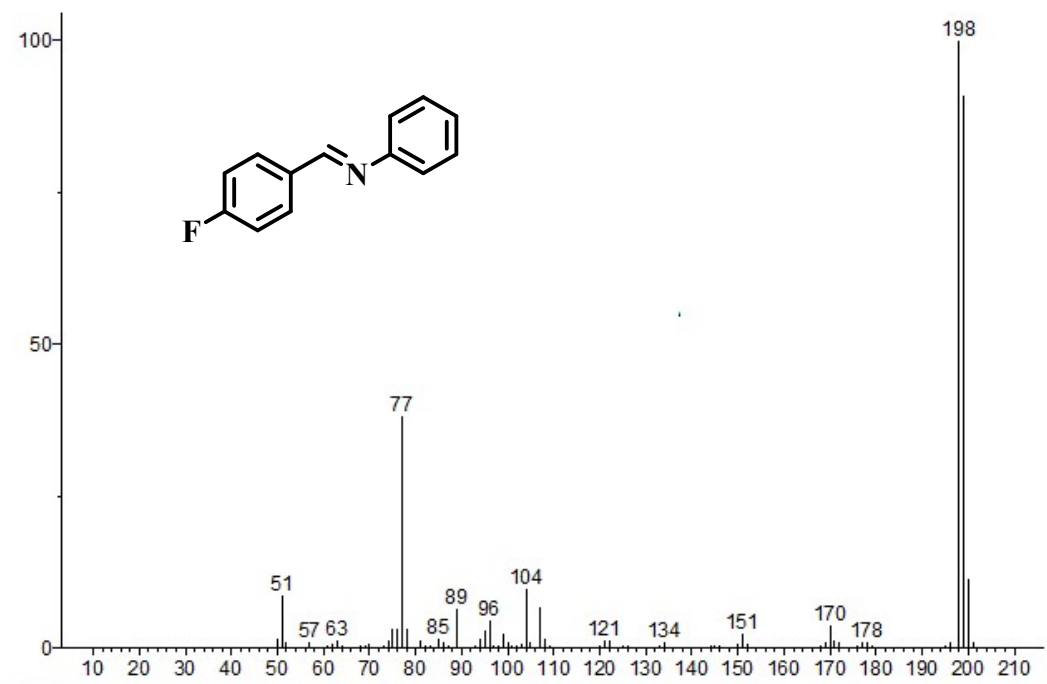


(Text File) Injection ID=db7c2f327ed44b05a0a7c4f76e2b9391 Scan=3434 Scan Type=+ c EI Full ms [50.00-400.00]

(c23)

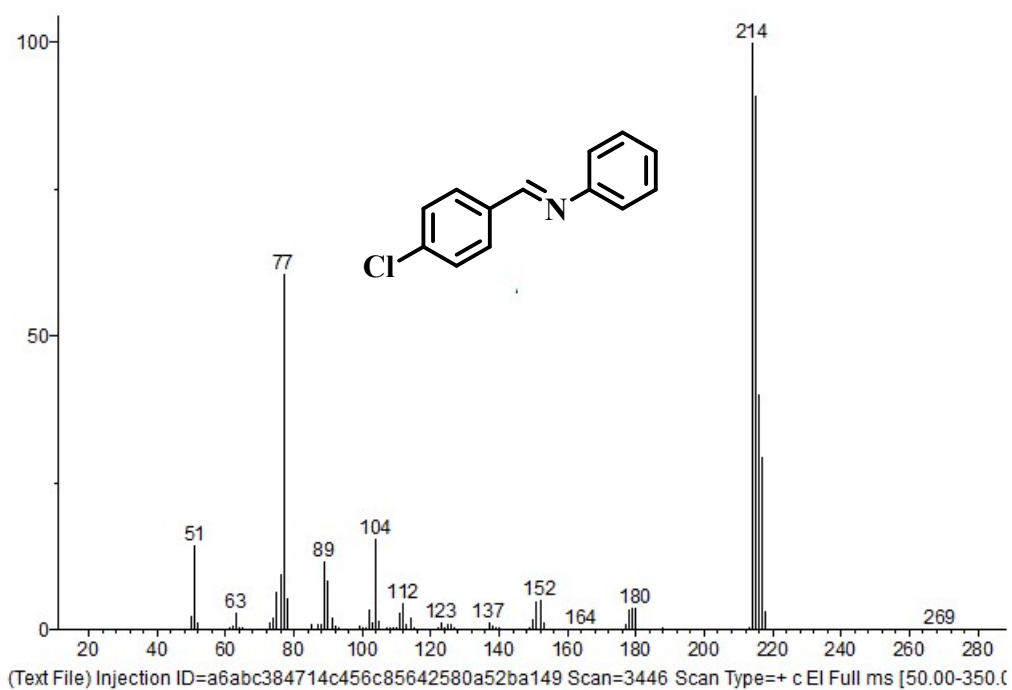


(c24)

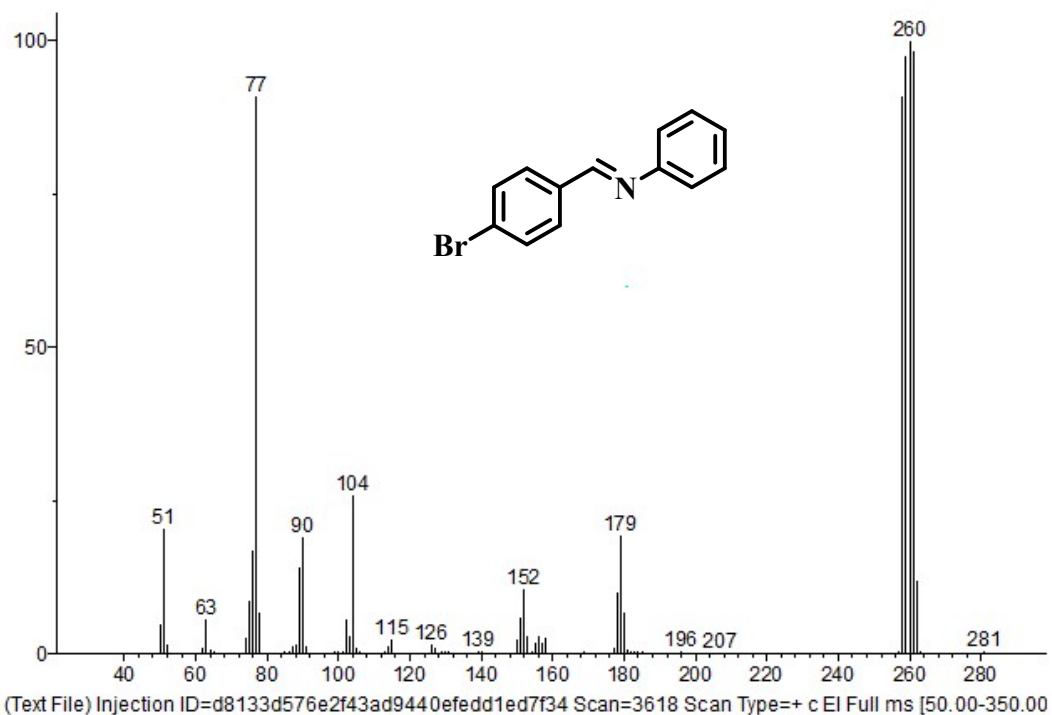


(Text File) Injection ID=69237bc63ce7445ca74f7b88baf65e2d Scan=2988 Scan Type=+ c EI Full ms [50.00-350.00]

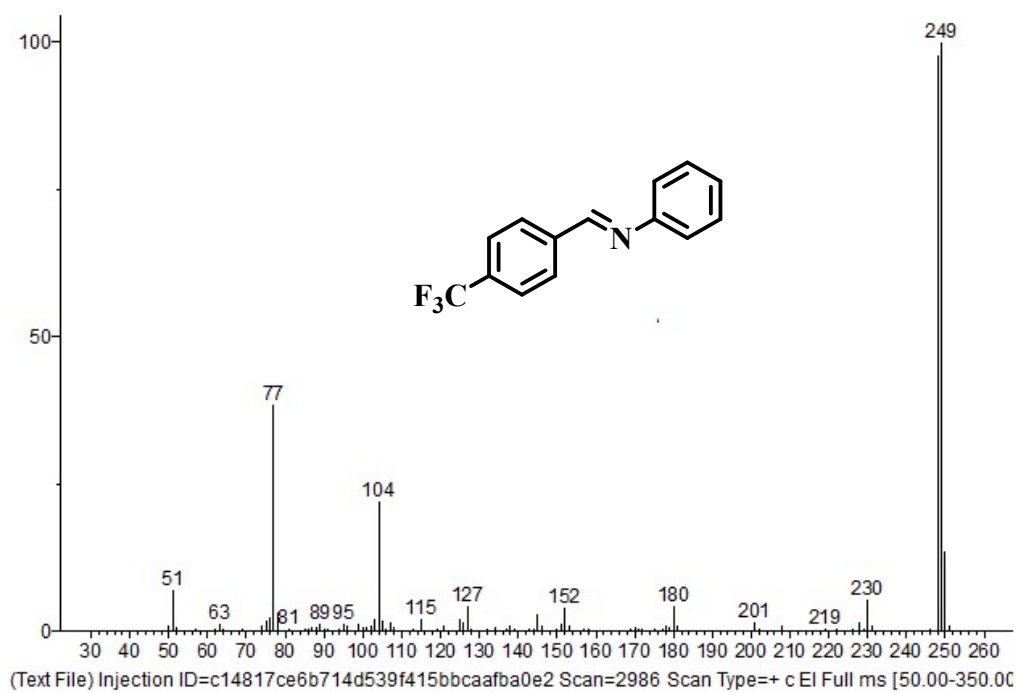
(c25)



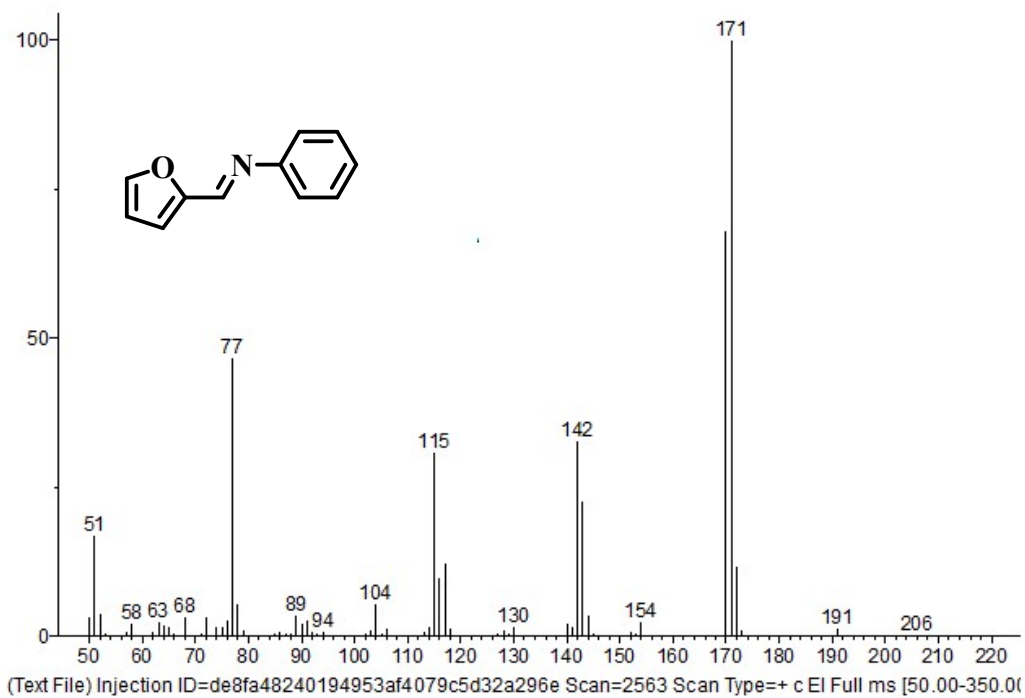
(c26)



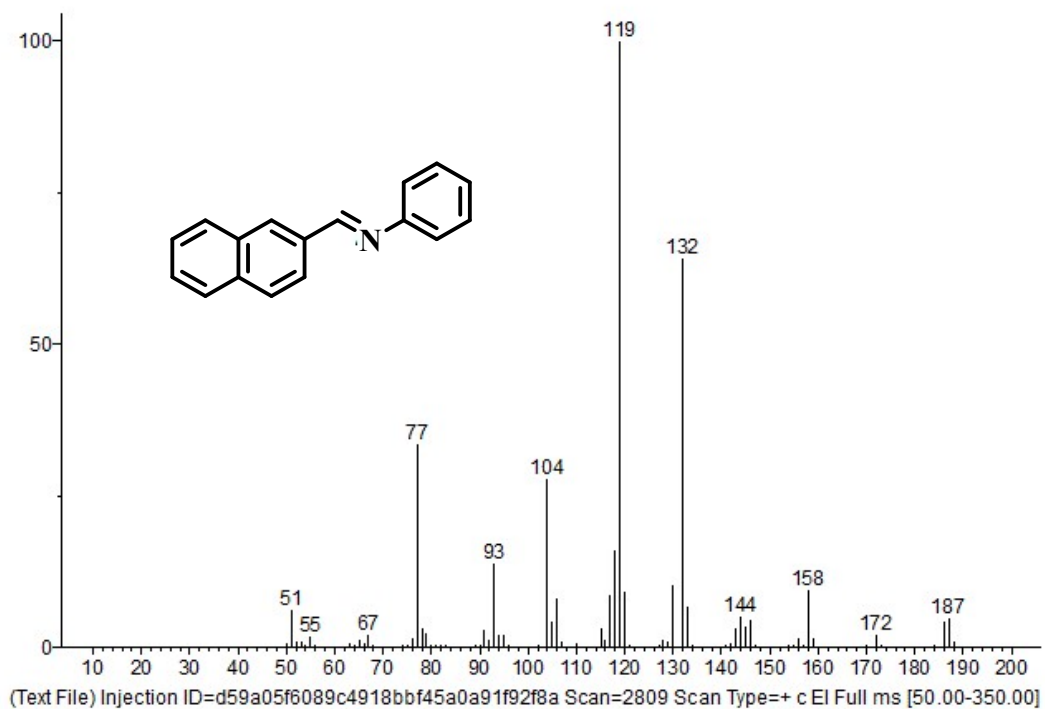
(c27)



(c28)



(c29)



(c30)

