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General Synthesis of Secondary Imines *via* Reductive Coupling of Carbonyl and Nitro Compounds Employing a Reusable Cobalt Catalyst

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Experimental Section

Materials

Pd/C (5 wt.%), Pt/C (5 wt.%), urea, chitosan and $Co(NO_3)_2 \cdot 6H_2O$ were purchase from Aladdin Chemicals Co. Ltd. (Beijing, China), and used as received. All aldehydes, nitro compounds and the chemical reagents were analytical grade and used directly without purification. All the solvents were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used directly without further purification.

Catalyst preparation

Typically, urea (8.0 g), chitosan (1.0 g) and $Co(NO_3)_2 \cdot 6H_2O$ (58 mg, 0.2 mmol) were homogeneously mixed by dry sanding method for 30 min. Then, the composite was placed on an alumina boat in a quartz tube furnace and heated from room temperature to the set temperature with a ramp of 3 °C/min under nitrogen atmosphere and then remained for 2 h. Finally, it was cooled down to 400 °C at 10 °C/min, and then to room temperature naturally in the air. The as-prepared catalysts were denoted as Co@NC-T, where T represents the pyrolysis temperature. For comparison, the Co@C-800 catalyst was also prepared by the same procedure as for the preparation of Co@NC-800 without the use of urea.

Catalyst characterization

The content of Co was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista-MPX). Transmission electron microscope (TEM) images of the samples were performed on a Talos F200X electron microscope at an acceleration voltage of 200 kV. X-ray powder diffraction (XRD) patterns of the catalysts were conducted on a Bruker advanced D8 powder diffractometer (Cu Kα). All XRD patterns were collected in the 2θ range of 10-80° with a scanning rate of 0.016 °/s. Surface area and pore size measurements were performed with N_2 adsorption/desorption isotherms at 77 K on a V-Sorb 2800P instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific K-Alpha spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV, and was provided technical support by Shiyanjia lab "www.shiyanjia.com". Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566).

General procedures

Synthesis of secondary imines from the reductive amination of aldehydes with NH_3. Typically, benzaldehyde (1.0 mmol), 26.5% aqueous $NH_3 \cdot H_2O$ (0.2 mL, 2.8 mmol), of methanol (10 mL), the Co@NC-800 catalyst (20 mg), and a magnetic stirring bar 50 mL were charged into an autoclave. After removal of the air in the autoclave by flushing H_2 for five times, the autoclave was charged with 10 bar H_2. Then the reaction was performed at 100 °C for a certain time. After the reaction, the autoclave was cooled with the ice-water, and the reaction solution was subjected to be quantified by GC (GC-FID, Agilent 7890A) with ethylbenzene as the internal standard. The conversion and yield were calculated from the following equations:

$$\text{Conversion}_{\text{Benzaldehyde}} = n'_{\text{Benzaldehyde}} / n_{\text{Benzaldehyde}} \times 100$$

$$\text{Yield}_{\text{Benzylamine}} = n_{\text{Produced benzylamine}} / n_{\text{Benzaldehyde}} \times 100$$

$$\text{Yield}_{N\text{-benzylidenebenzylamine}} = n_{\text{Produced } N\text{-benzylidenebenzylamine}}/n_{\text{Benzaldehyde}} \times 2 \times 100$$

$$\text{Yield}_{\text{Dibenzylamine}} = n_{\text{Produced dibenzylamine}}/n_{\text{Benzaldehyde}} \times 2 \times 100$$

Where $n_{\text{Benzaldehyde}}$, $n'_{\text{benzaldehyde}}$, $n_{\text{Produced benzylamine}}$, $n_{\text{Produced } N\text{-benzylidenebenzylamine}}$, and $n_{\text{Produced dibenzylamine}}$ represents the initial molar amount of benzaldehyde, the molar amount of benzaldehyde at a certain time, and the molar amount of benzylamine, *N*-benzylidenebenzylamine, and dibenzylamine at a certain time, respectively.

Synthesis of secondary imines from the reductive amination of aldehydes with nitro compounds. In a typical run, benzaldehyde (1.5 mmol), nitrobenzene (1.0 mmol), acetonitrile (10 mL), and the Co@NC-800 catalyst (20 mg) were used. The procedure was the same as above.

Analytic Methods

Agilent 7890A gas chromatography (GC) instrument with a cross-linked capillary HP-5 column (30 m × 0.32 mm × 0.4 mm) was used to analyze the products by a flame ionization detector. N_2 was used as the carrier gas with a flow rate at 40 mL/min. Standard analysis conditions were described as follows: injector temperature 300 °C, detector temperature 300 °C, column temperature program: from 50 °C (hold 1.5 min) to 300 °C (hold 3 min) at a heating rate of 15 °C/min. The molecular mass and structural formula of each product were determined according to gas-chromatography mass spectrometry (GC-MS, Thermo Scientific™ ISQ™ 7000 Single Quadrupole GC-MS).

Repeated experiment

The recycling experiments of the Co@CN-800 catalyst was studied using synthesis of N-benzylidenebenzylamine from the reductive amination of benzaldehyde with aqueous ammonia ($NH_3 \cdot H_2O$) at 100 °C under 1 MPa H_2 as the model reaction. After reaction, the Co@CN-800 was collected by centrifugation to prevent mass loss and then washed with methanol and water for several times. Any lost catalyst during the process was replenished with new catalyst for the next use.

Supplementary Figures

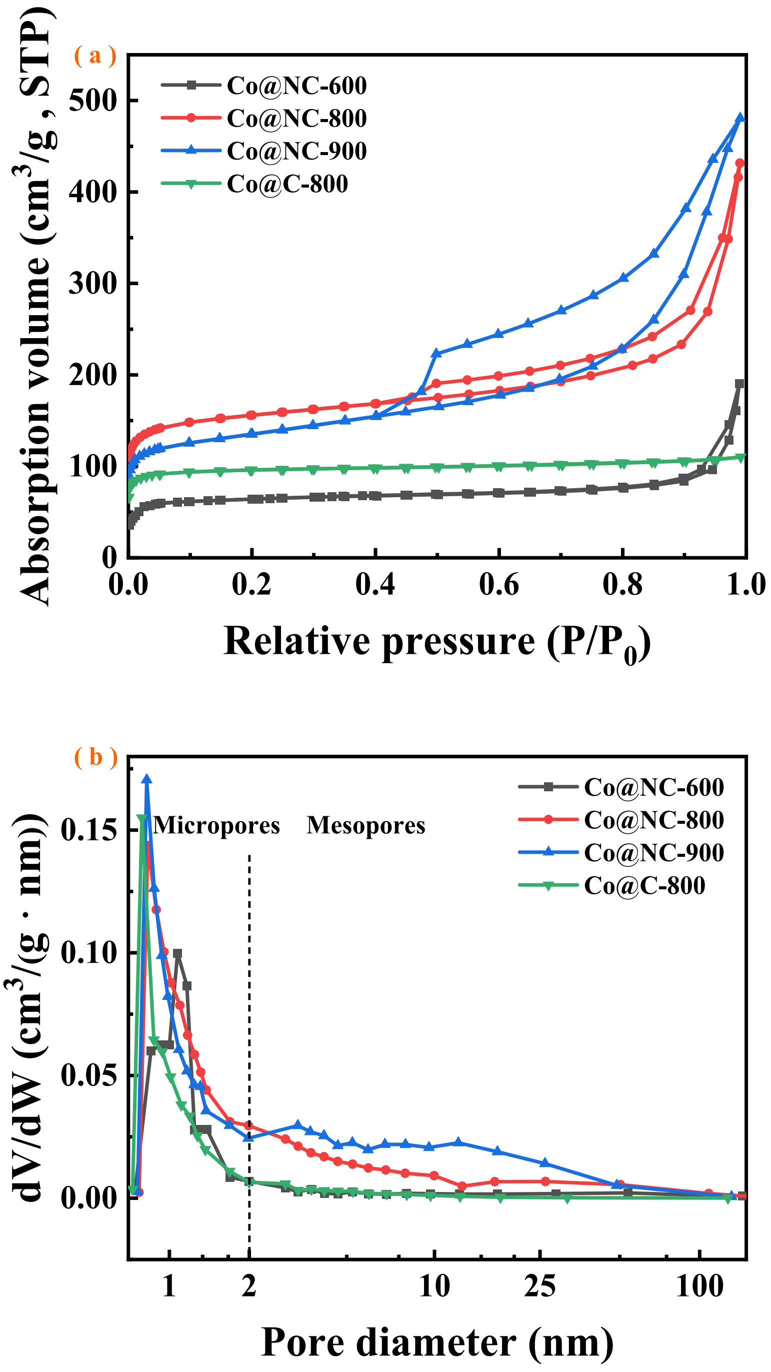


Figure S1. N_2 adsorption-desorption isotherms (a) and pore size distribution (b) of the Co@NC-T and Co@C-800 samples.

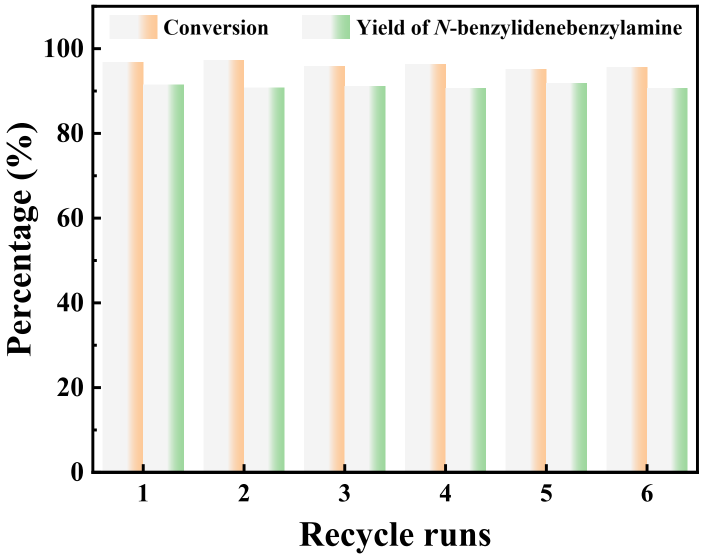


Figure S2. Recycling experiments of Co@NC-800 catalyst. Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (20 mg, the weight of catalyst corresponds to 1.2 mol%), 100 °C, MeOH (10 mL), H_2 (1 MPa), $NH_3{\cdot}H_2O$ (0.2 mL), and 8 h.

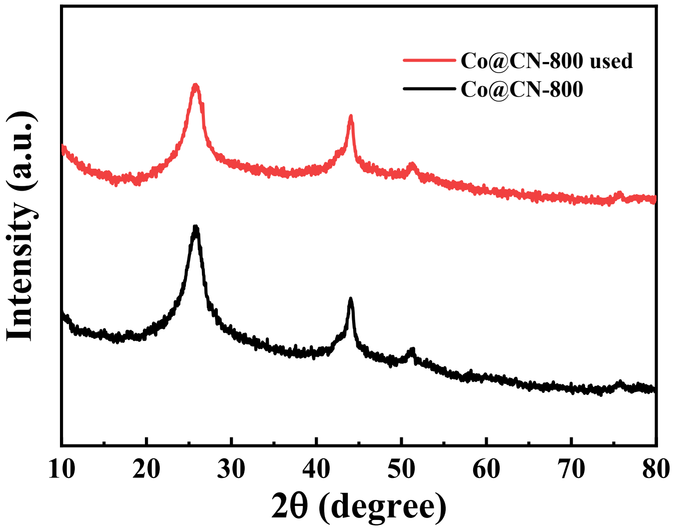


Figure S3. XRD pattern of catalyst after recovery experiment. Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (20 mg, the weight of catalyst corresponds to 1.2 mol%), 100 °C, MeOH (10 mL), H_2 (1 MPa), $NH_3{\cdot}H_2O$ (0.2 mL), and 8 h.

Supplementary Tables

Table S1. Textural parameters and the Co weight percentage of the Co@NC-T and Co@C-800 samples.

Catalyst	Co [a] (wt.%)	Surface area (m^2/g)		Pore size (nm)		Pore volume (cm^3/g)	
		Meso	Micro	Meso	Micro	Meso	Micro
Co@NC-600	2.1	255.8	51.1	13.7	1.1	0.206	0.099
Co@NC-800	3.6	593.1	349.9	7.8	0.9	0.475	0.240
Co@NC-900	6.8	561.0	194.8	6.3	0.8	0.613	0.208
Co@C-800	2.8	61.7	126.5	3.2	0.8	0.029	0.148

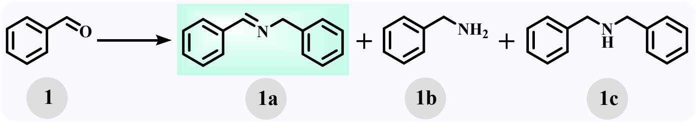
[a] Determined by ICP-AES

Table S2. The atomic percentage of the N species in the Co@NC-T and Co@C-800 samples.

Catalyst	Total N [a] (at.%)	Pyridinic N (at.%)	Pyrrolic N (at.%)	Graphitic N (at.%)
Co@NC-600	9.4	60.3	28.5	10.2
Co@NC-800	7.8	47.4	27.9	24.7
Co@NC-900	4.1	35.7	22.5	41.8
Co@C-800	3.5	24.8	40.0	35.2

[a] Determined by XPS

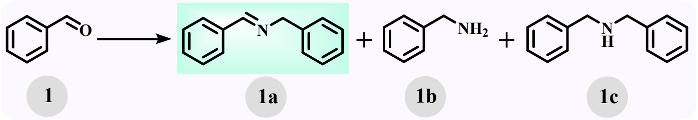
Table S3. Results of the reductive amination of benzaldehyde in different solvents.



Entry	Solvent	Conversion (%)	Yield (%)			
			1a	1b	1c	Other
1	MeOH	96.8	91.5	-	<1	4.3
2	EtOH	88.1	81.7	-	-	6.4
3	*iso*-Propanol	77.8	71.6	-	2.5	3.7
4	THF	81.6	76.8	-	4.8	-
5	Toluene	49.3	45.1	-	-	4.2
6	Hexane	31.2	25.0	2.5	-	3.7

Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (the weight of catalyst corresponds to 1.2 mol%), 100 °C, 10 mL of solvents, H_2 (1 MPa), $NH_3 \cdot H_2O$ (0.2 mL), and 8 h. Conversion (%) and Yield (%) were determined by GC using ethylbenzene (1.0 mmol) as the internal standard.

Table S4. Effect of the amount of ammonia on the reductive amination of benzaldehyde.

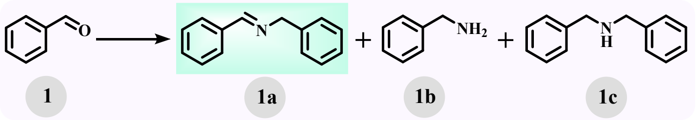


Entry	$NH_3 \cdot H_2O$ (mL)	Conversion (%)	Yield (%)			
			1a	1b	1c	Other
1	0.1	74.5	53.8	Trace	-	20.7
2	0.2	96.8	91.5	-	<1	4.3
3	0.3	98.4	93.1	2.0	<1	2.3
4	0.5	98.9	82.9	2.4	3.4	10.2
5	1.0	>99	62.5	5.5	9.7	22.3

Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (the weight of catalyst corresponds to 1.2 mol%), 100 °C, MeOH (10 mL), H_2 (1 MPa) and 8 h. Conversion

(%) and Yield (%) were determined by GC using ethylbenzene (1.0 mmol) as the internal standard.

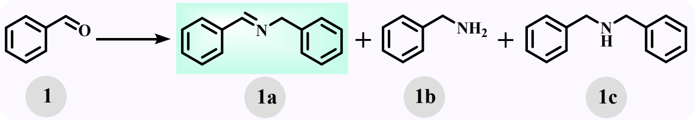
Table S5. Effect of the reaction temperature and H_2 pressure on the reductive amination of benzaldehyde.



Entry	Temperature (°C)	Conversion (%)	Yield (%)			
			1a	1b	1c	Other
1	60	78.2	61.7	2.1	-	14.4
2	80	81.2	74.3	<1	-	5.9
3	100	96.8	91.5	-	<1	4.3
4	120	97.6	73.9	<1	20.3	2.4
5 [a]	100	>99	84.1	1.9	12.7	1.3
6 [b]	100	>99	67.6	3.5	27.9	<1

Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (the weight of catalyst corresponds to 1.2 mol%), MeOH (10 mL), H_2 (1 MPa), $NH_3 \cdot H_2O$ (0.2 mL), and 8 h. Conversion (%) and Yield (%) were determined by GC using ethylbenzene (1.0 mmol) as the internal standard. [a] 100 °C and H_2 (2 MPa). [b] 100 °C and H_2 (3 MPa).

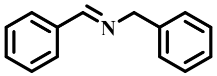
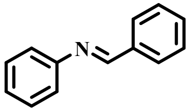
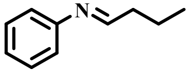
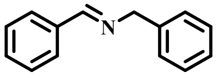
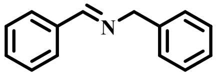
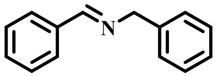
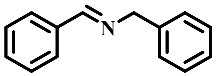
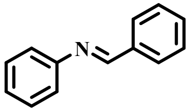
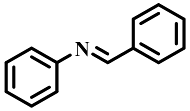
Table S6. Time course of the products distribution.



Entry	Time (h)	Conversion (%)	Yield (%)			
			1a	1b	1c	Other
1	1	23.5	14.2	-	-	9.3
2	2	43.7	34.9	-	-	8.8
3	4	71.6	62.7	-	-	8.9
4	6	87.1	80.7	-	<1	6.6
5	8	96.8	91.5	-	<1	4.3
6	10	>99	93.7	-	5.3	<1
7	14	>99	89.4	-	10.6	-

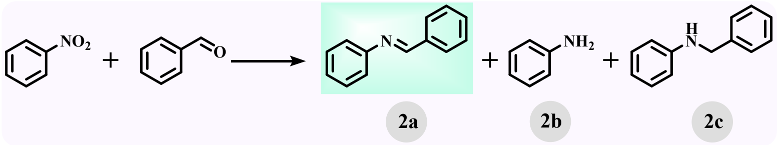
Reaction conditions: benzaldehyde (1.0 mmol), Co@NC-800 (the weight of catalyst corresponds to 1.2 mol%), 100 ℃, MeOH (10 mL), H_2 (1 MPa), $NH_3 \cdot H_2O$ (0.2 mL), and 8 h.

Table S8. Comparison of Co@NC-800 with state-of-the-art catalysts in the reductive coupling of carbonyl and nitro compounds for the synthesis secondary imines

Entry	**Catalyst**	**Conditions**	**Product**	**C/Y (%)**	***Ref***
1	Co@NC-800	100 °C, H_2 (1 MPa), 10 h, $NH_3{\cdot}H_2O$ (2.8 equiv.) 1.0 mmol carbonyl compounds		>99/94	This work
		100 °C, H_2 (1 MPa), 24 h, $NH_3{\cdot}H_2O$ (2.8 equiv.) 1.0 mmol carbonyl compounds		93/71	
2	Co@NC-800	100 °C, H_2 (1 MPa), 24 h, 1.0 mmol nitro and 1.5 mmol carbonyl compounds		>99/92	This work
		100 °C, H_2 (1 MPa), 36 h, 1.0 mmol nitro and 2.0 mmol carbonyl compounds		95/73	
3	Rh/COF	90 °C, H_2 (2 MPa), 15 h, $NH_3{\cdot}H_2O$ (0.9 equiv.) 7.2 mmol aromatic aldehydes		>99/95	8
4	Ni/Al_2O_3-400	80 °C, H_2 (2 MPa), 12 h, $NH_3{\cdot}H_2O$ (7.0 equiv.) 1.0 mmol aromatic aldehydes		>99/80	24
5	Fe_xO_y@HC_{180}	110 °C, H_2 (2 MPa), 4 h, $NH_3{\cdot}H_2O$ (70.0 equiv.) 0.5 mmol aromatic aldehydes		>99/92	25
6	Pt_1/$CoBO_x$	90 °C, H_2 (1 MPa), 10 h 1.0 benzonitrile (nitrogen loss)		>99/98	7
7	Pt/CoFe-LDH	70 °C, H_2 (1 MPa), 2 h, 1.0 mmol nitroarenes, 1.2 mmol aldehydes		>99/98	17
8	Co/SiN	110 °C, H_2 (5 MPa), 24 h, 1.5 mmol nitroarenes, 3.0 mmol aldehydes	 (Over-reduction)	>99/82	16

The "C" for conversion and "Y" for yield.

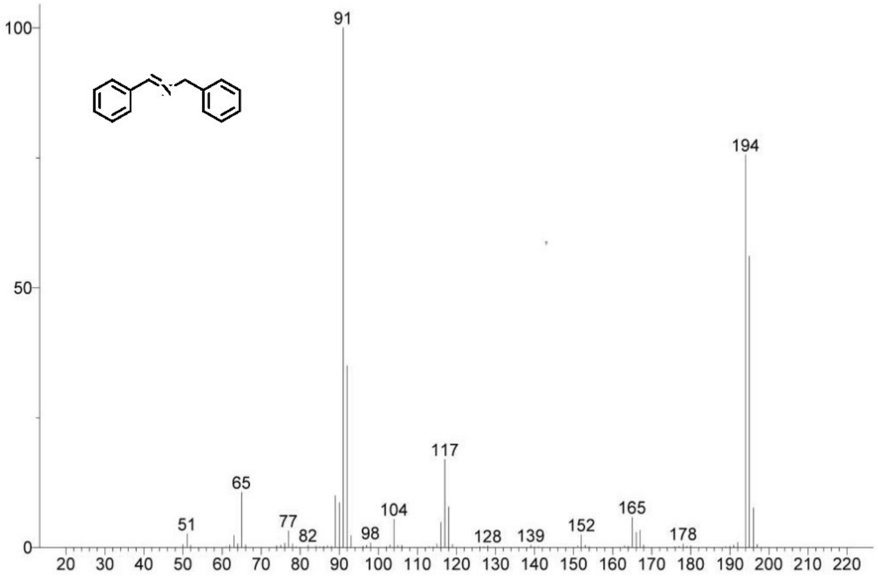
Table S7. Results of the reductive coupling of carbonyl and nitro compounds in different solvents.

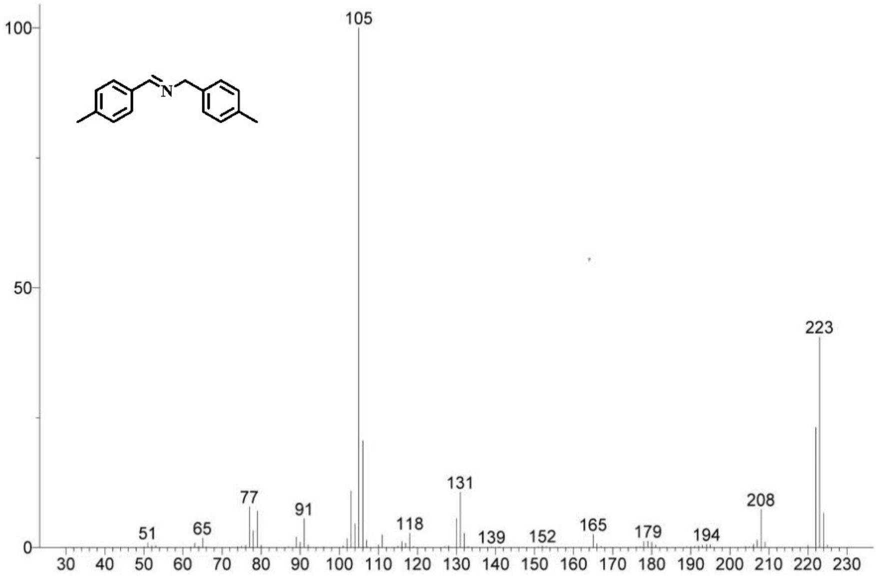


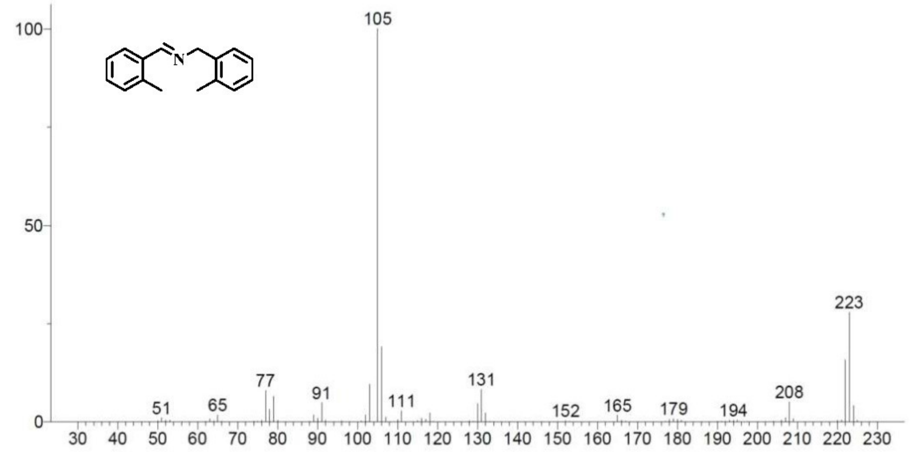
Entry	Solvent	Conversion (%)	Yield (%)		
			2a	2b	2c
1	MeOH	>99	18.4	43.9	37.7
2	EtOH	>99	14.3	51.5	34.2
3	*iso*-Propanol	>99	8.0	32.8	59.2
4	Acetonitrile	95.8	81.5	14.0	0.3
5	THF	83.7	66.4	14.8	2.5
6	Toluene	64.1	1.7	59.6	2.8
7	Hexane	49.7	-	42.4	7.3
8 [a]	Acetonitrile	>99	91.8	6.4	1.8

Reaction conditions: nitrobenzene (1.0 mol), benzaldehyde (1.5 mmol), Co@NC-800 (the weight of catalyst corresponds to 1.2 mol%), 100 °C, 10 mL of solvents, H_2 (1 MPa), and 20 h. Conversion (%) and Yield (%) were determined by GC using ethylbenzene (1.0 mmol) as the internal standard. [a] Same as “a”, and 24 h.

The mass spectra of products



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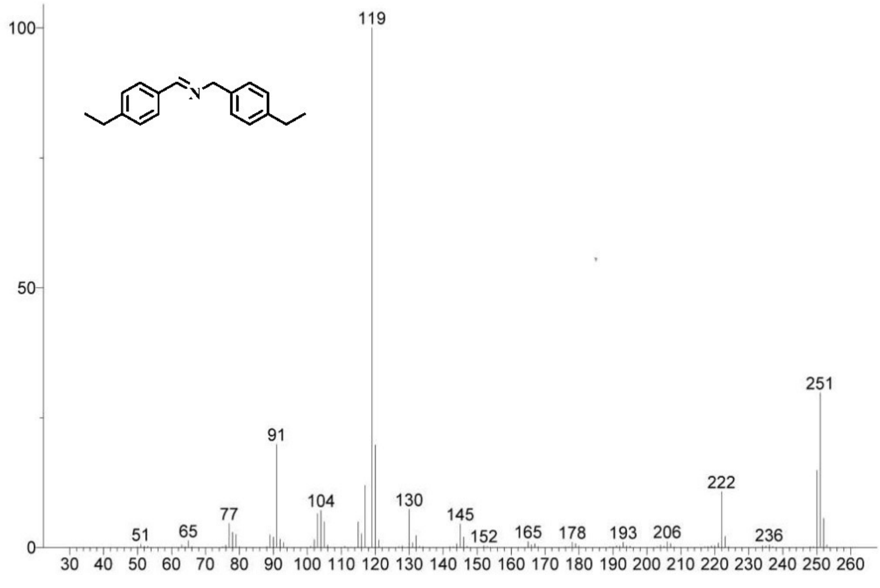
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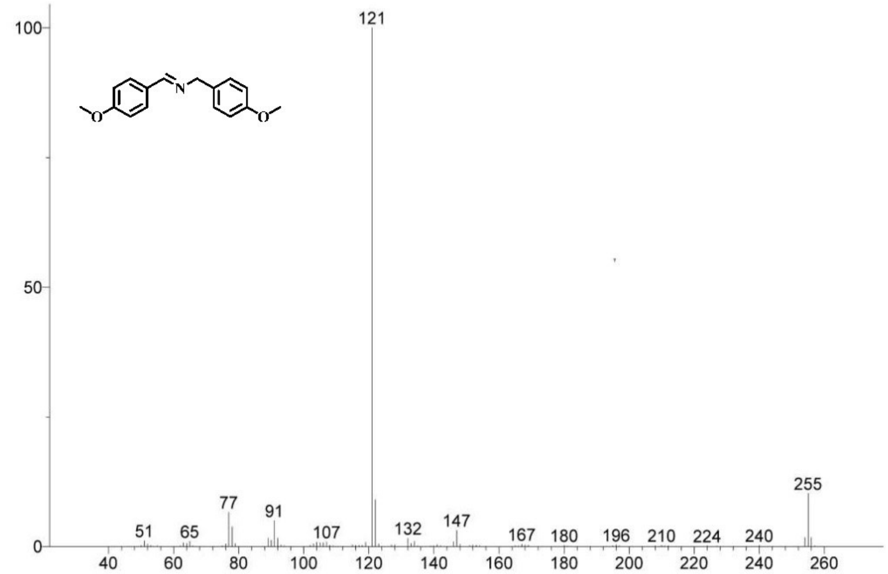
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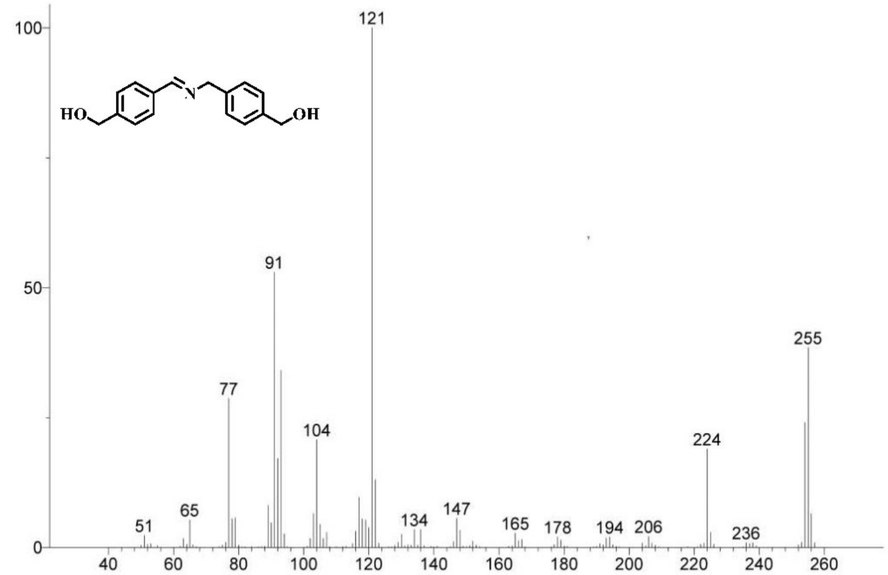
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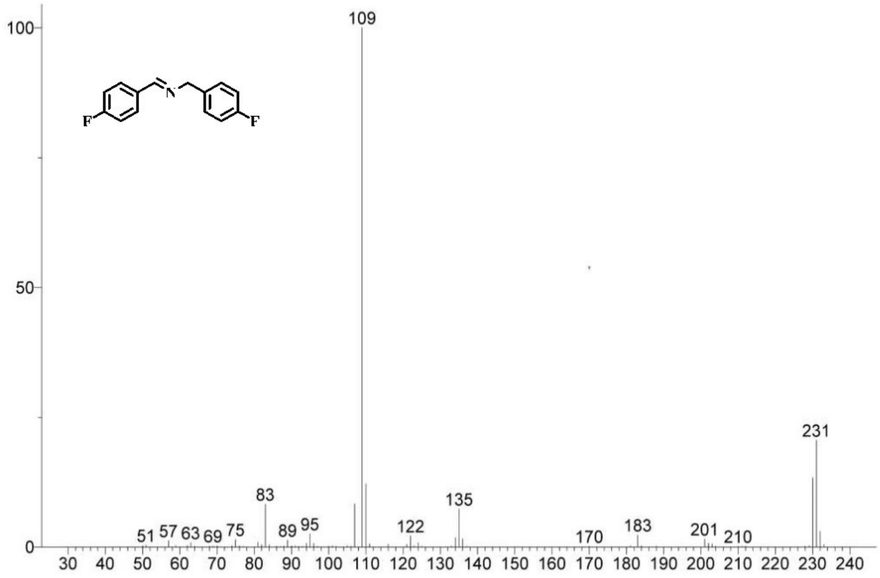
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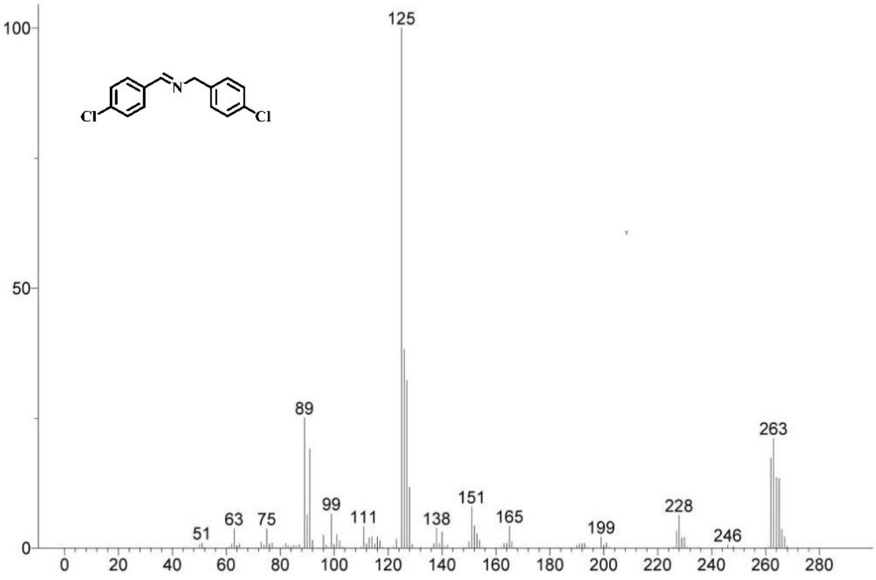
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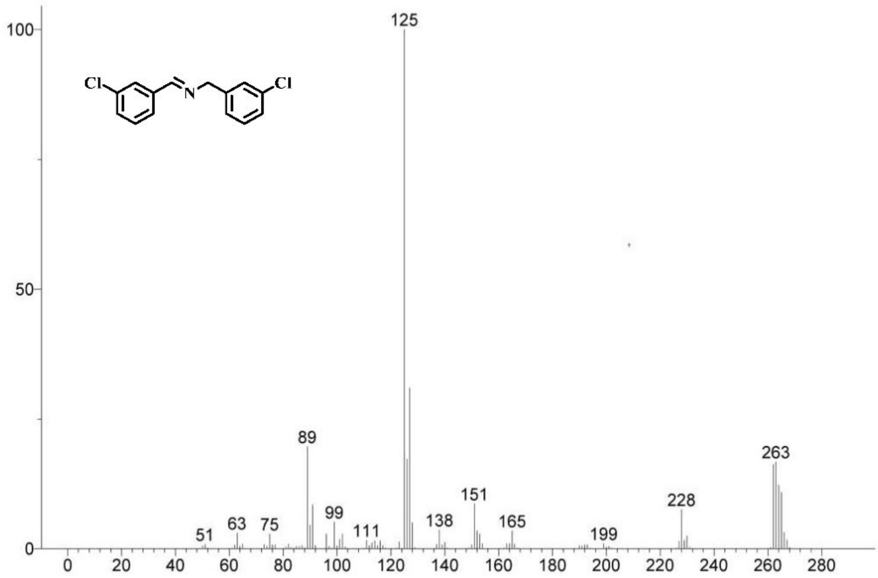
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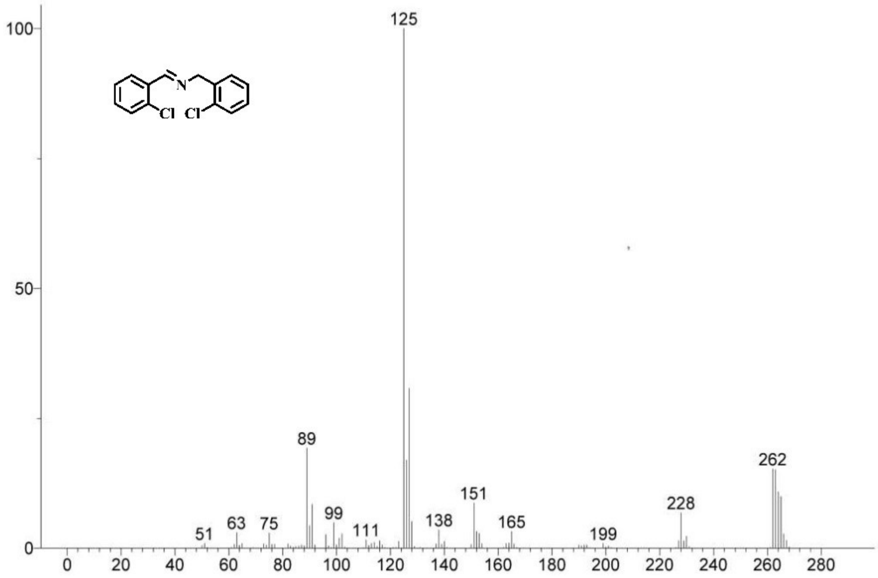
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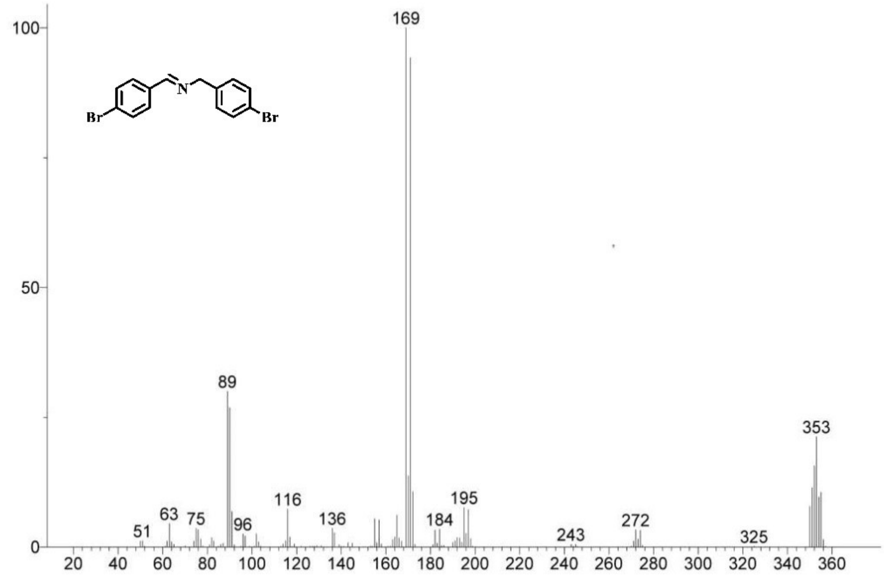
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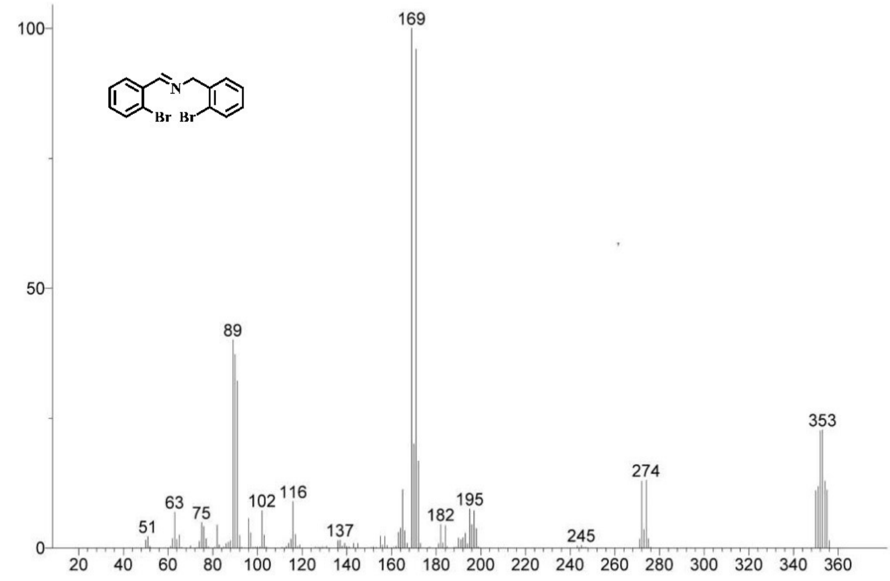
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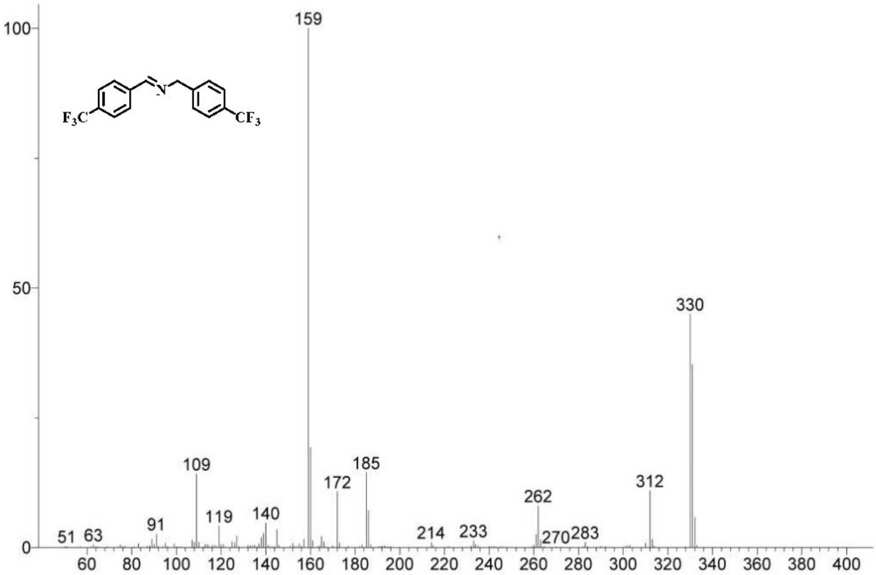
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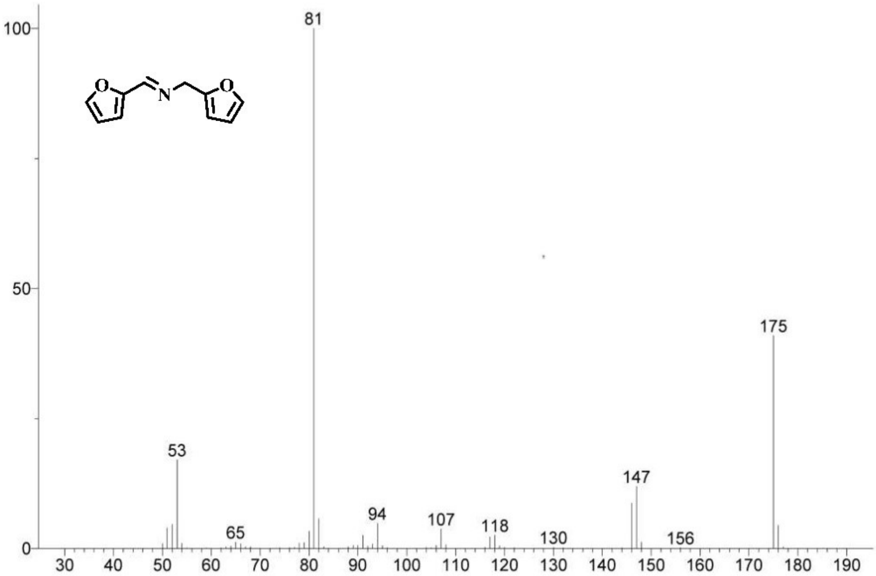
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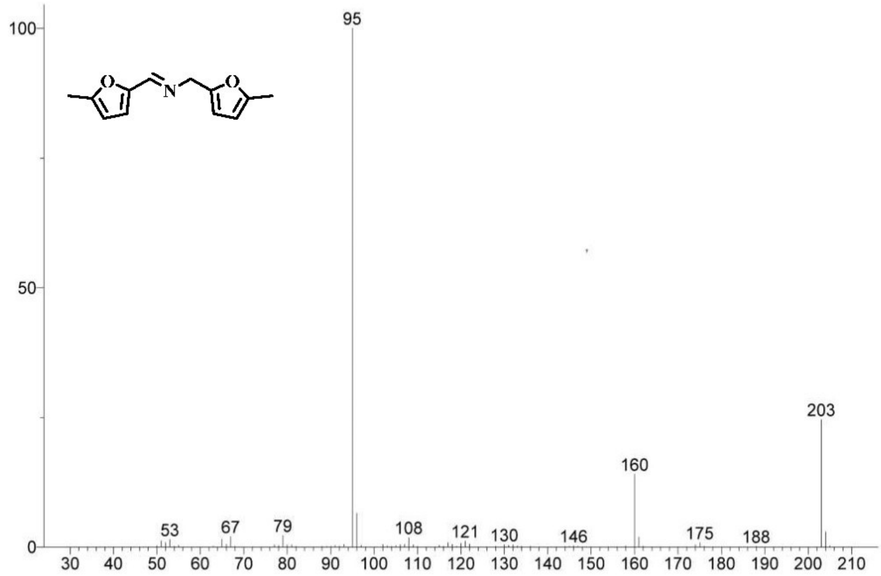
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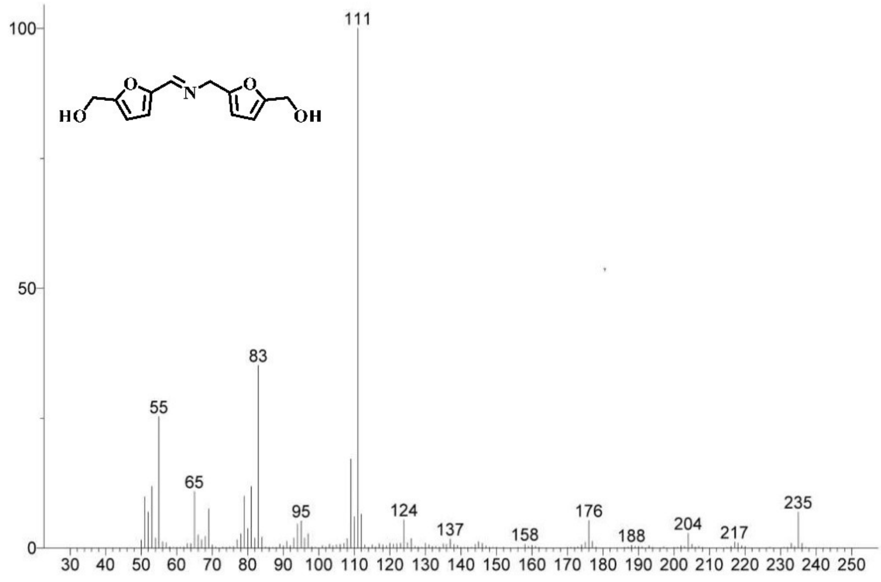
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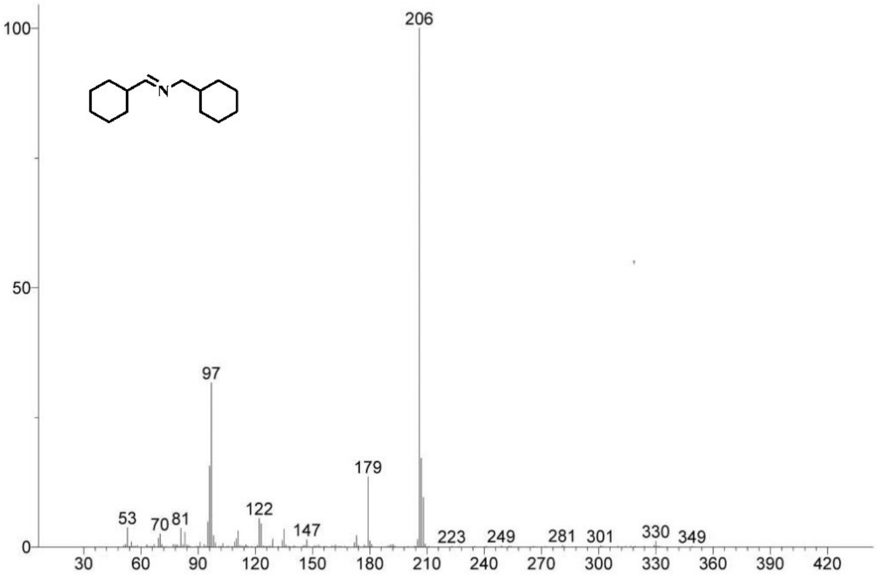
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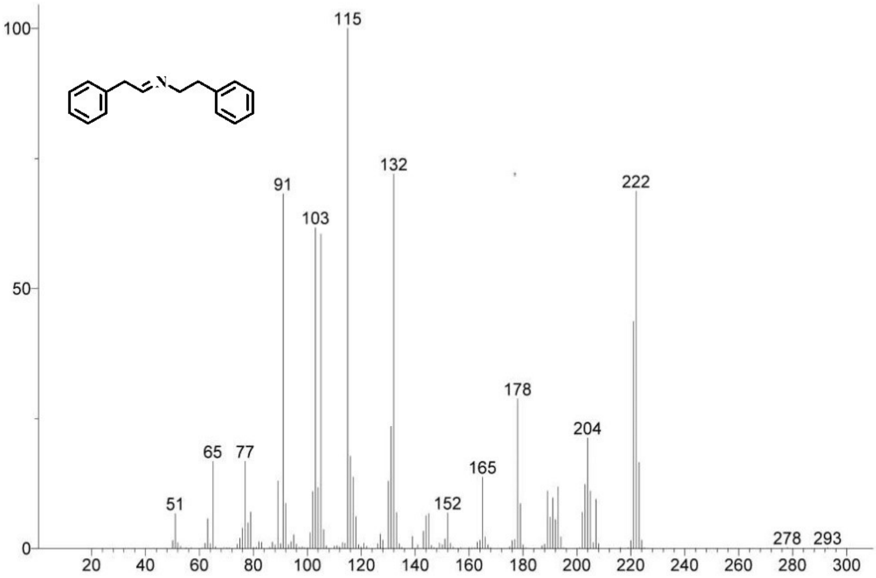
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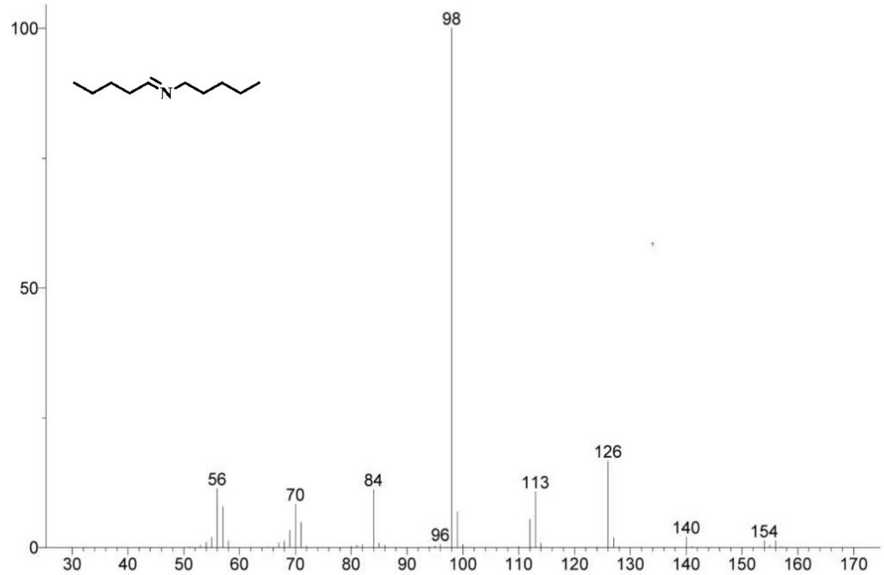
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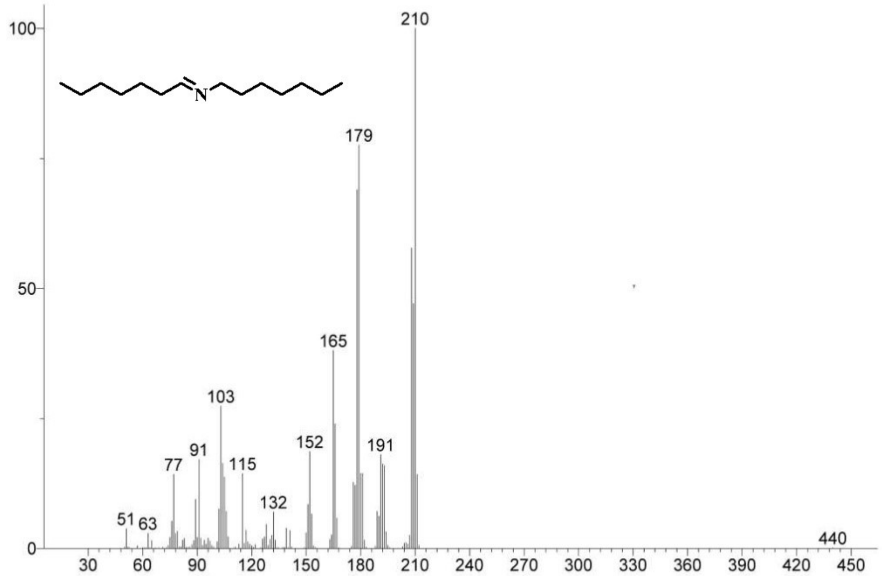
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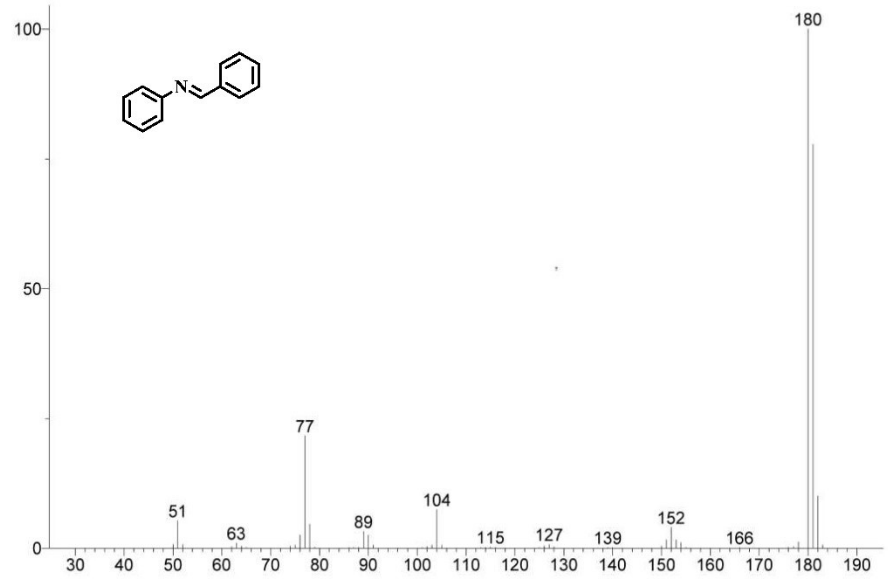
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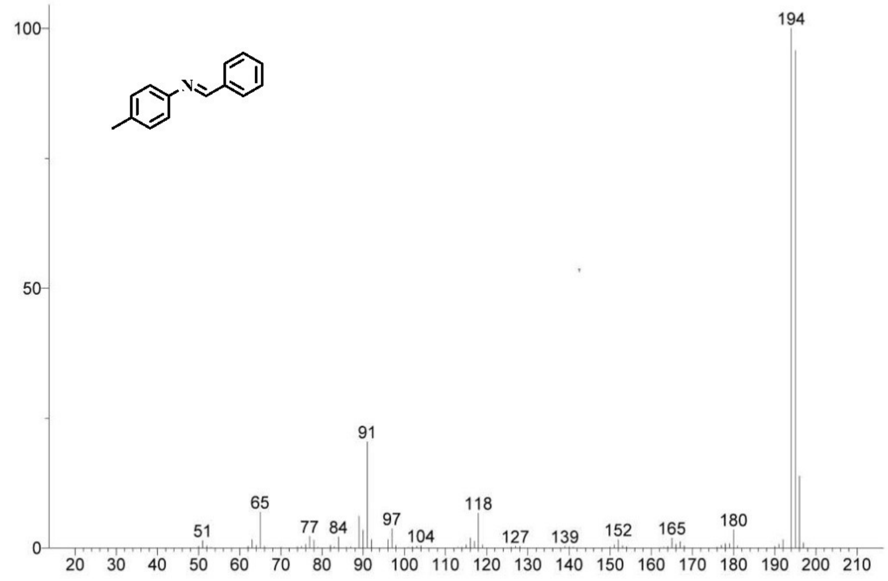
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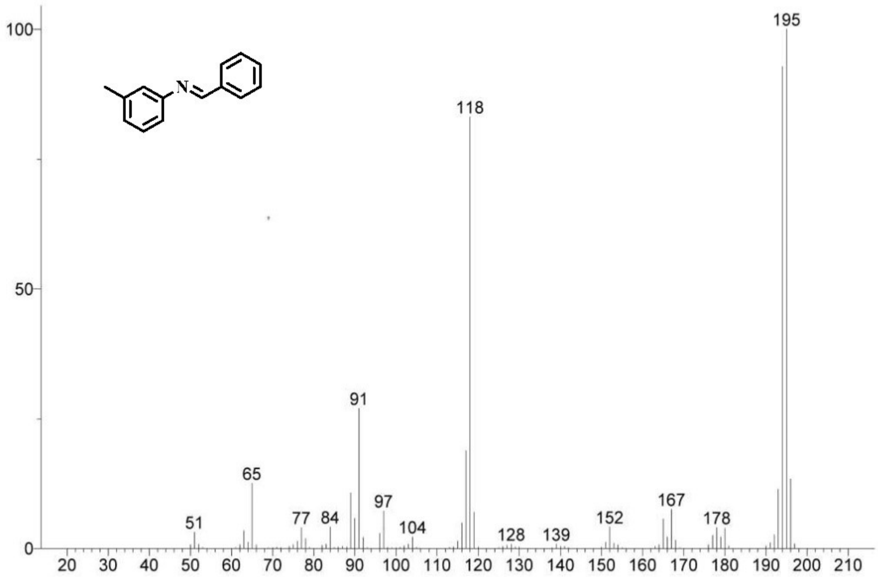

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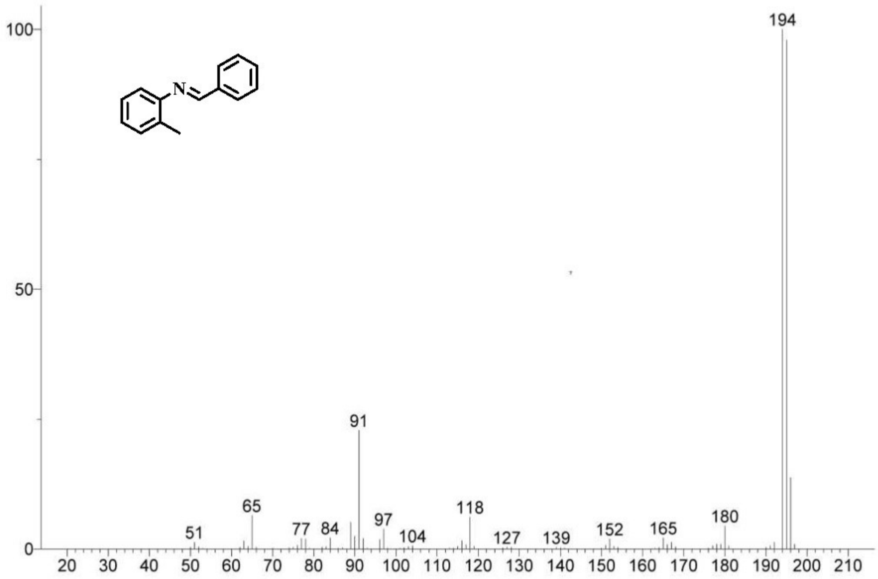

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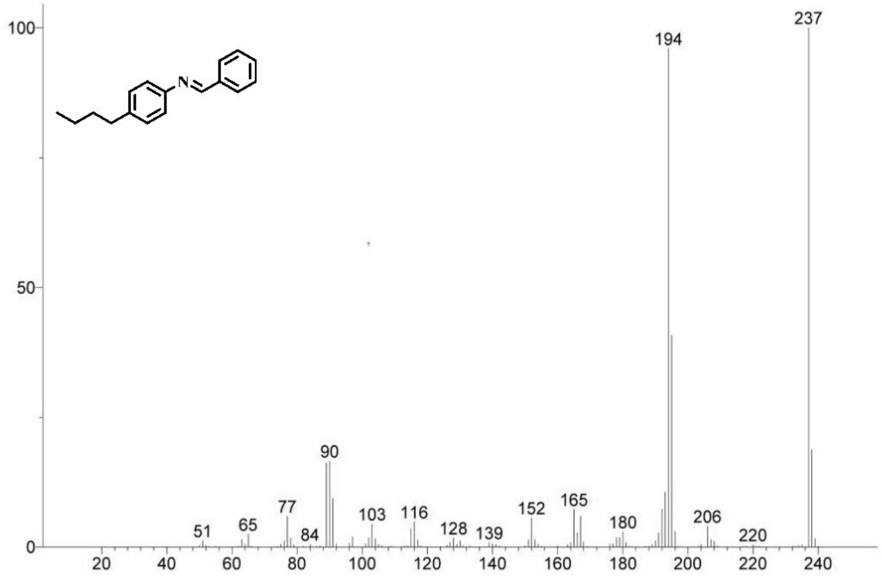
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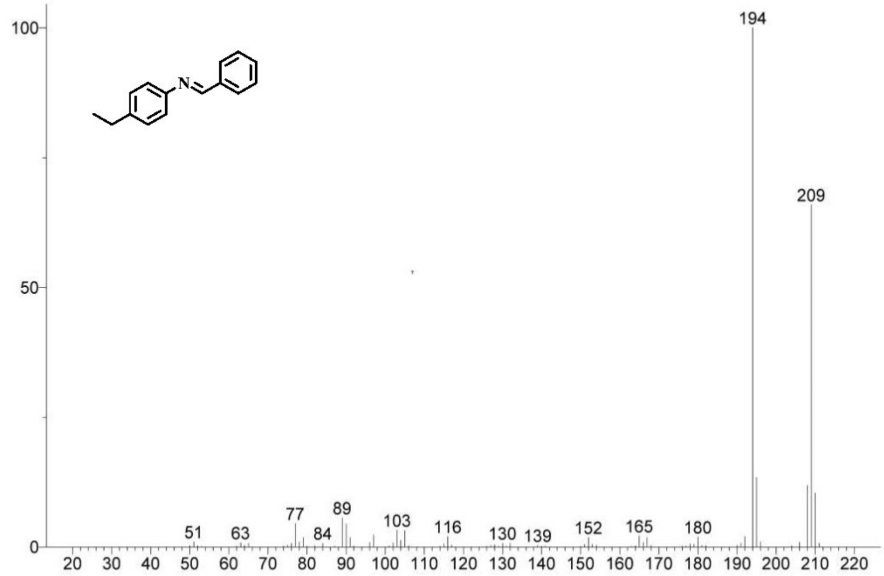
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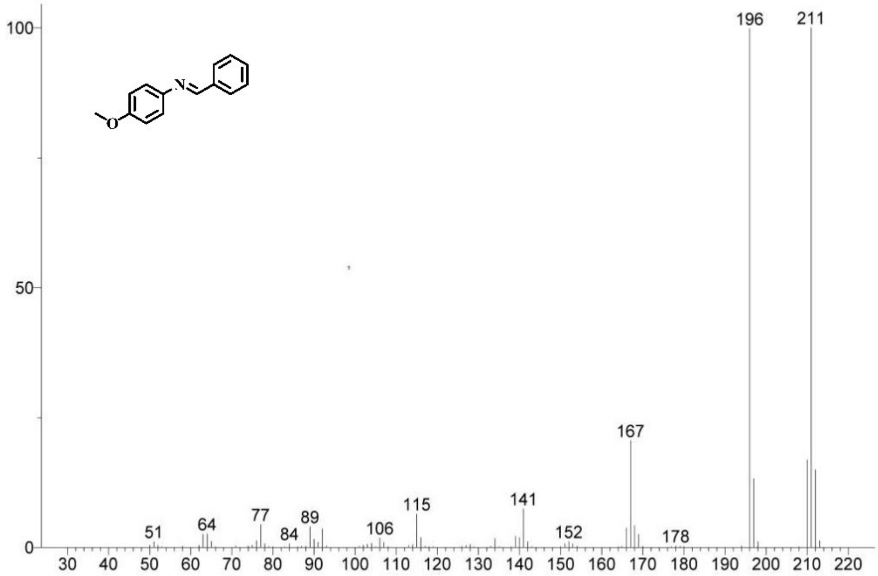
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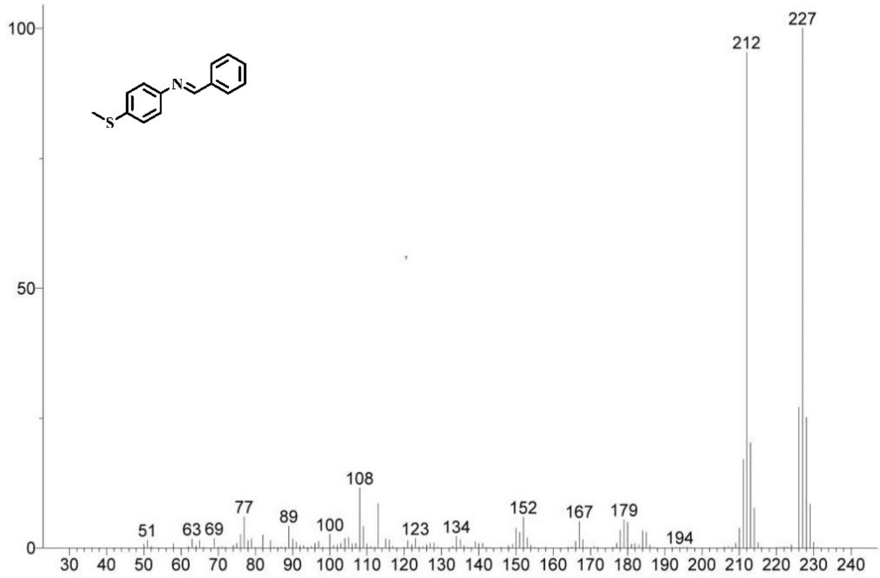
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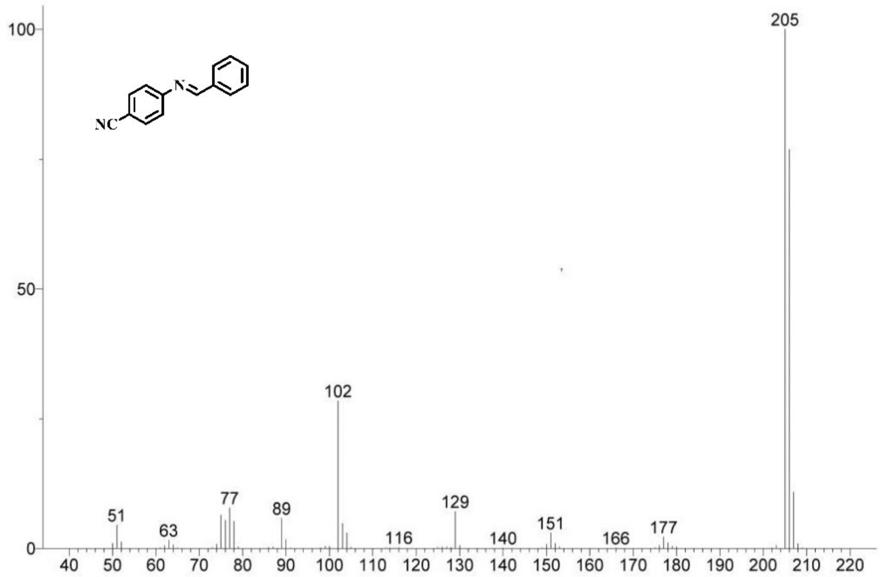
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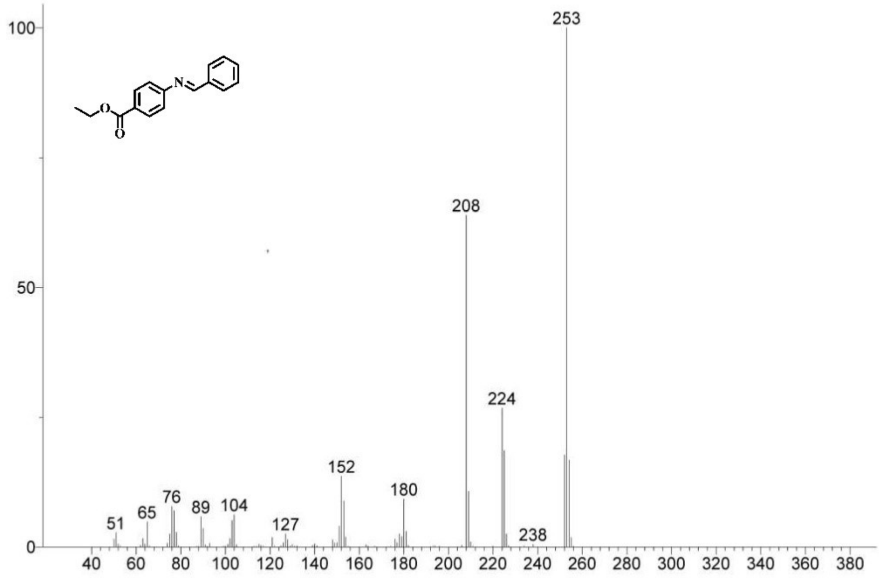
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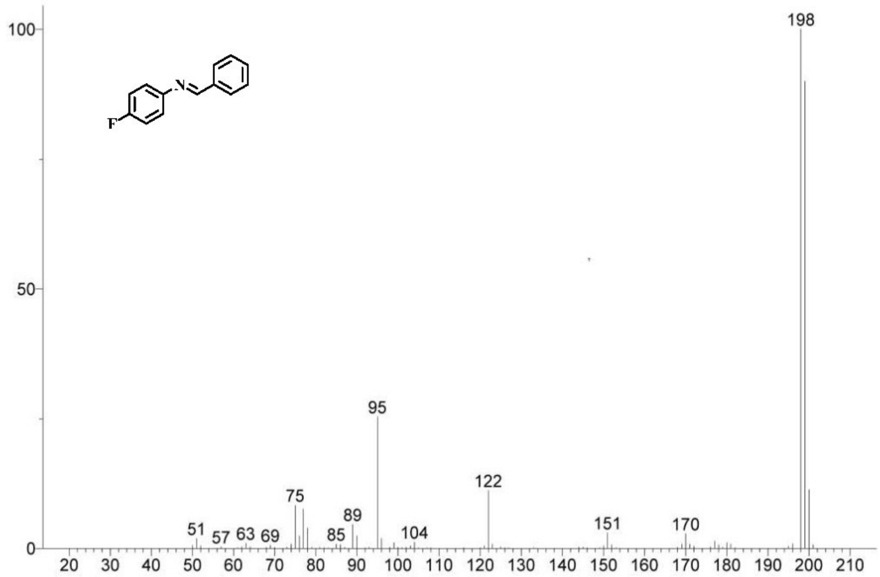
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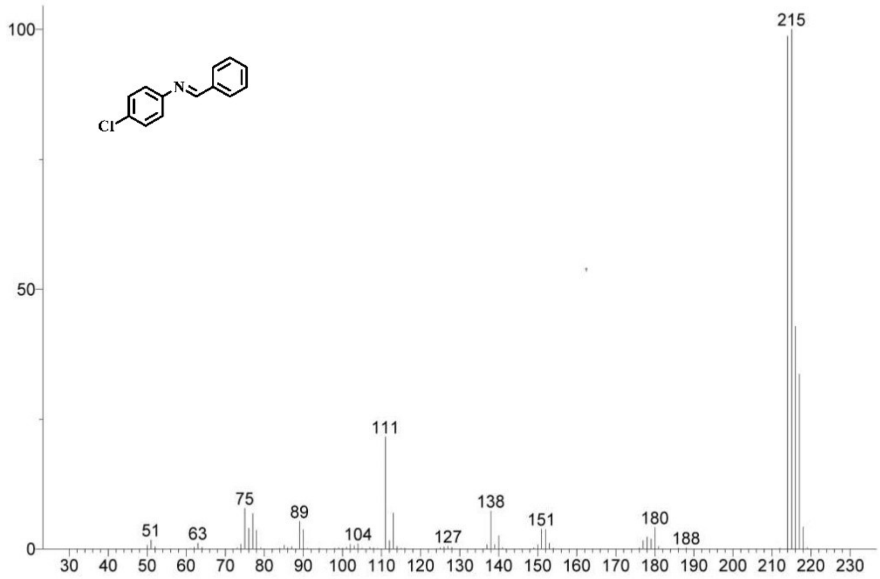
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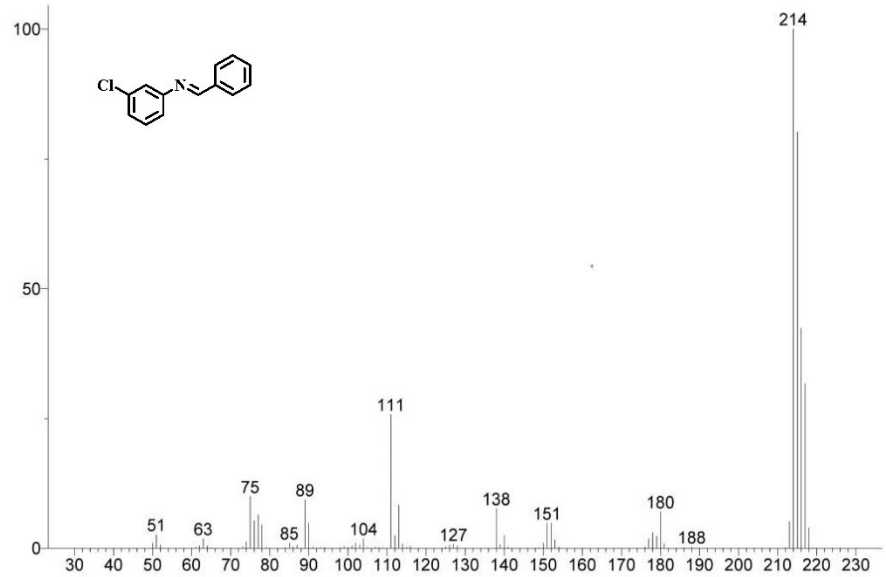
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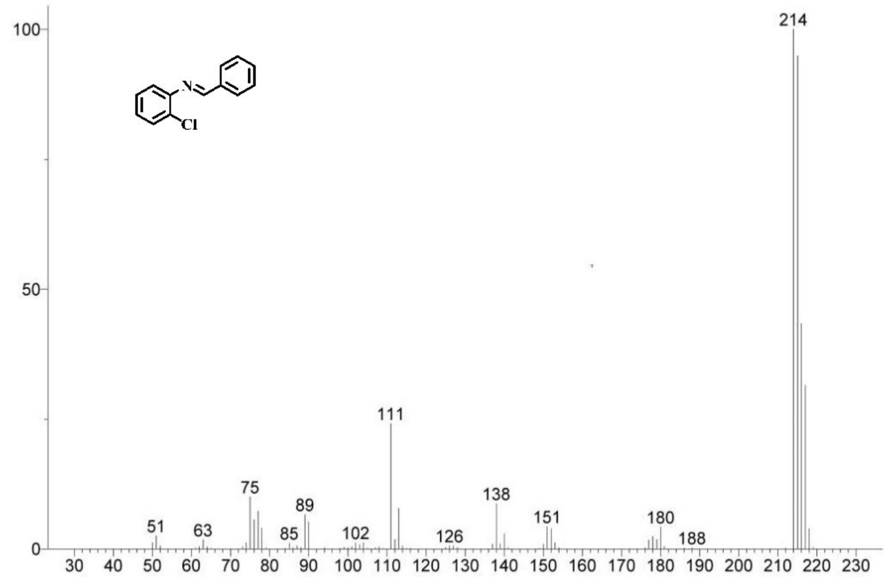
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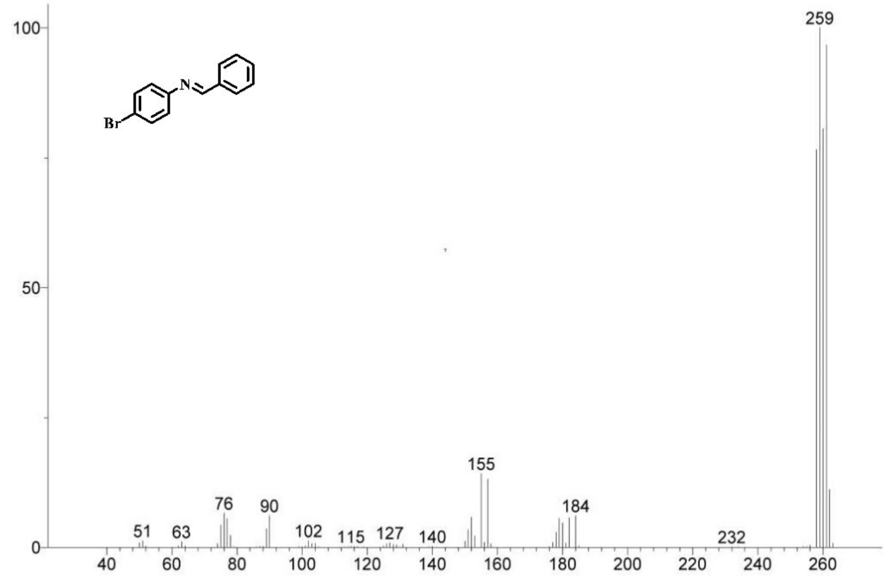
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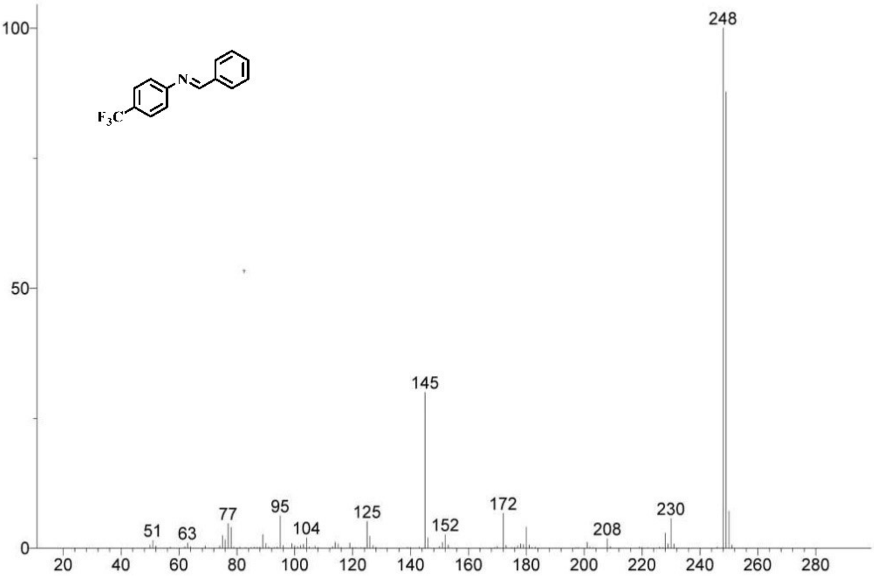
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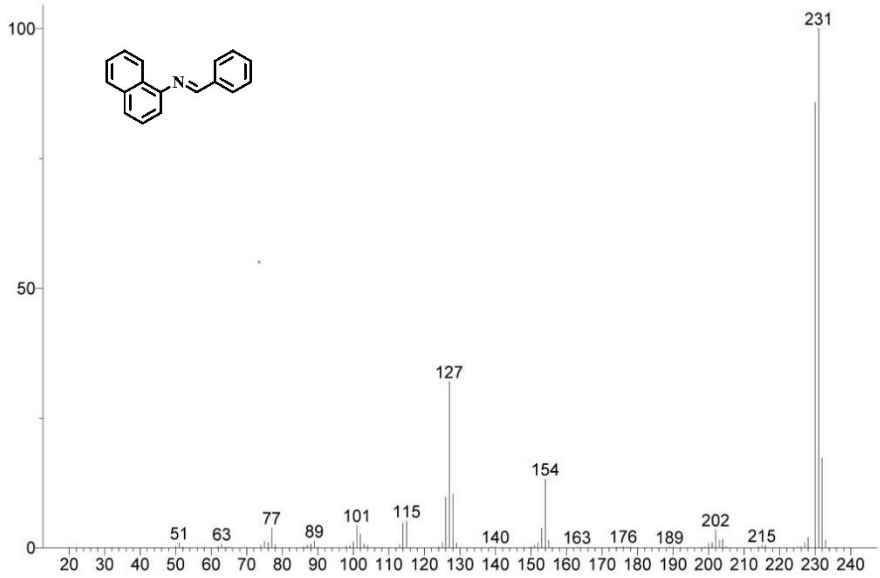
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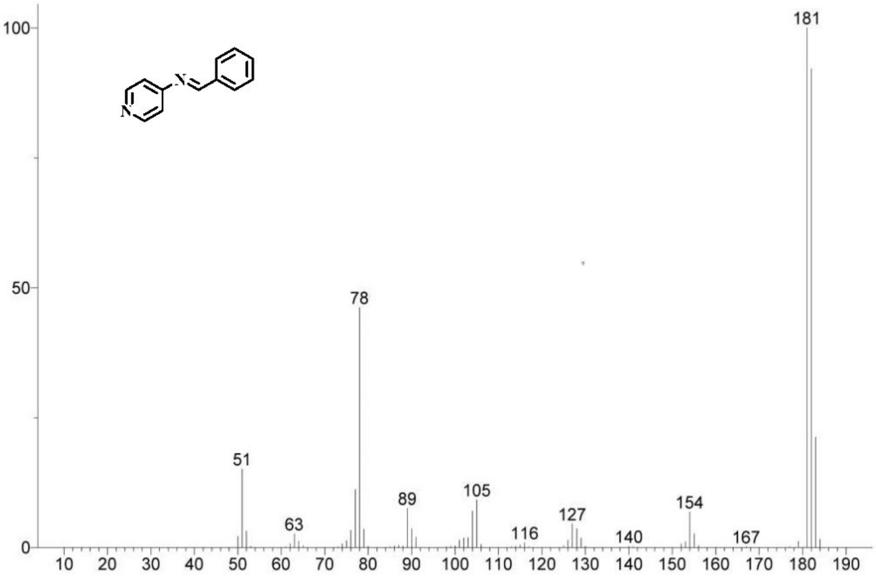
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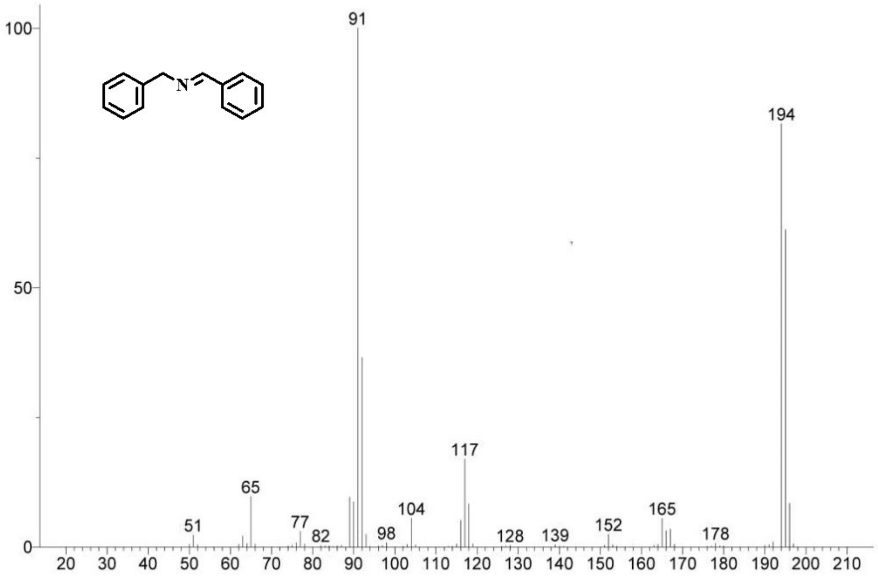

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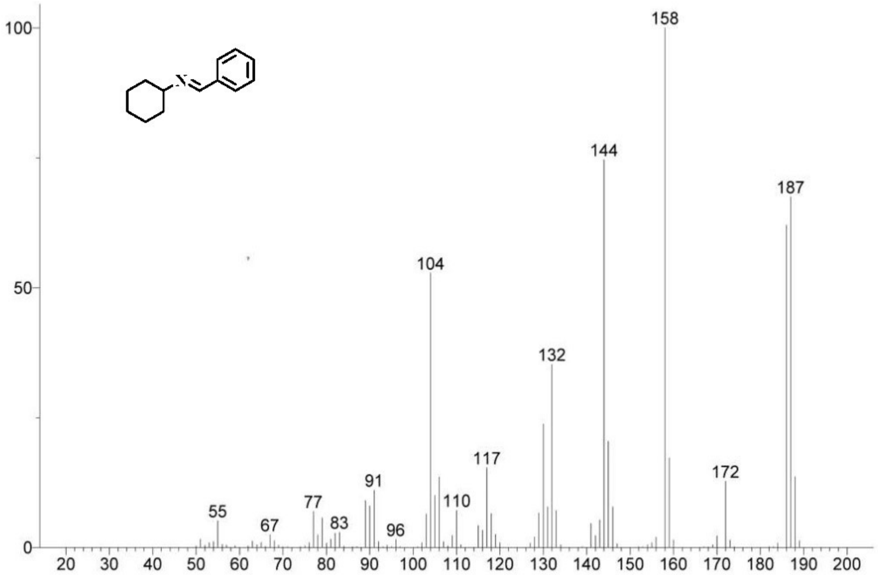

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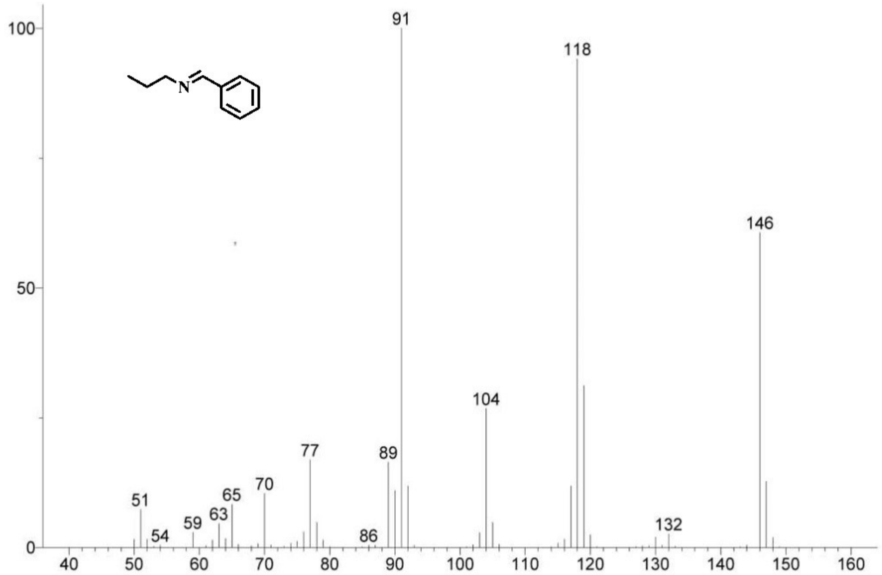
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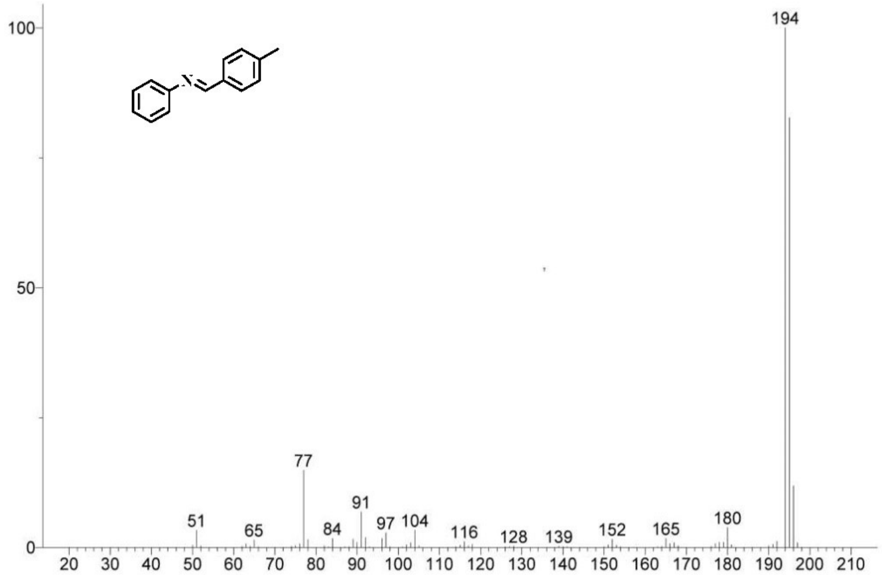
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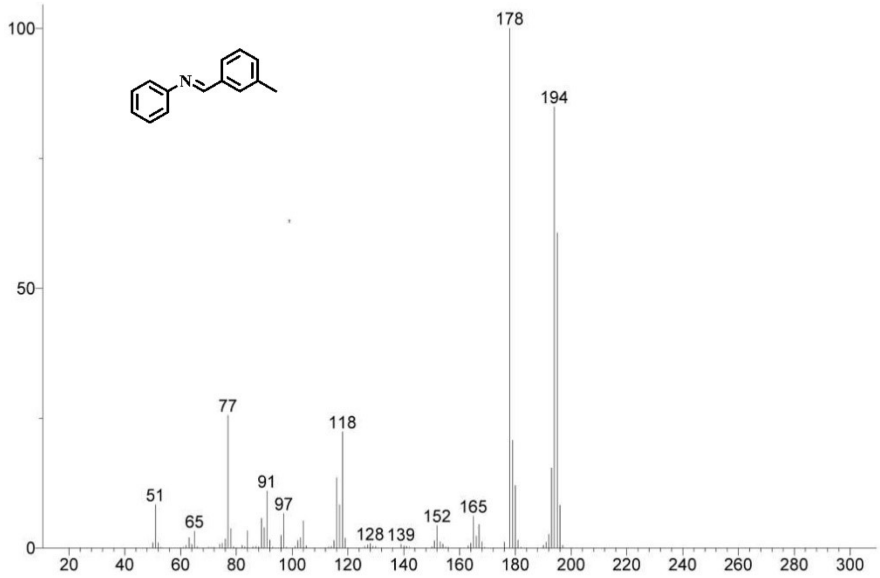
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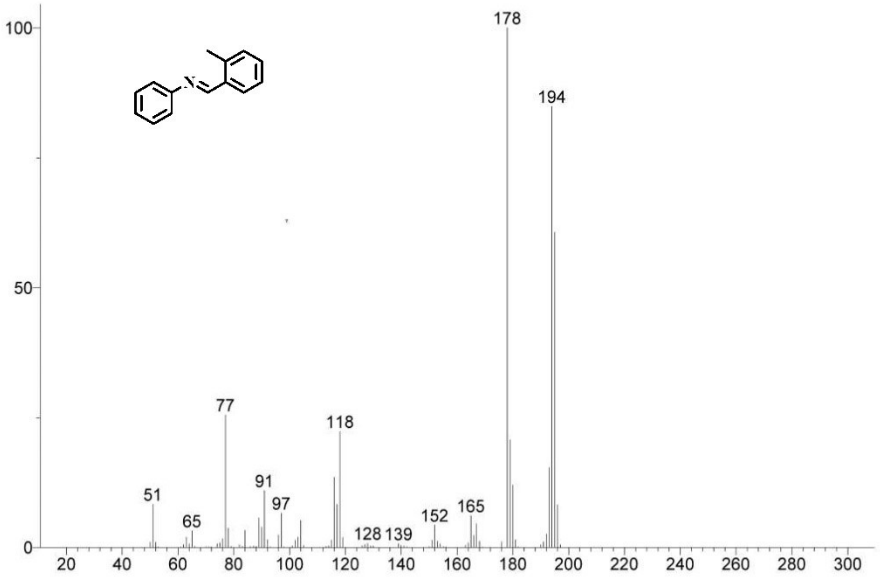
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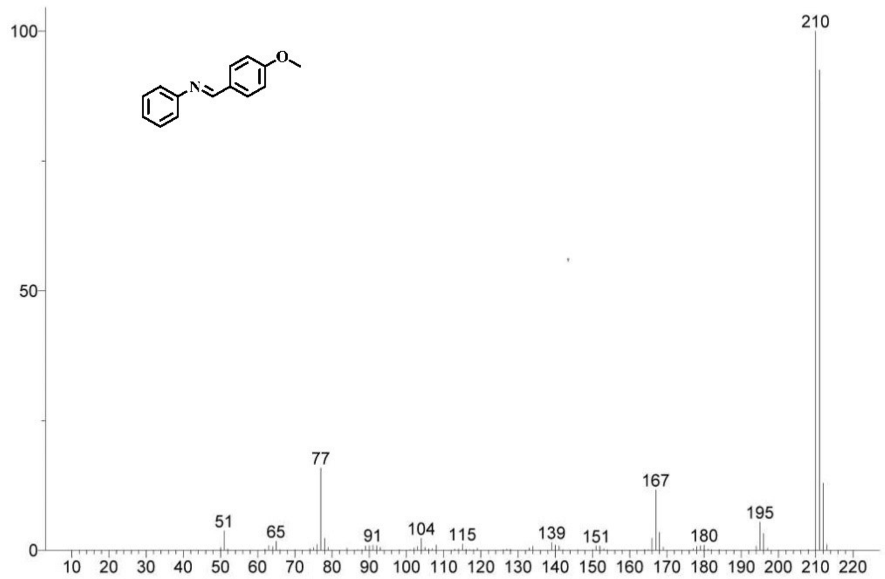
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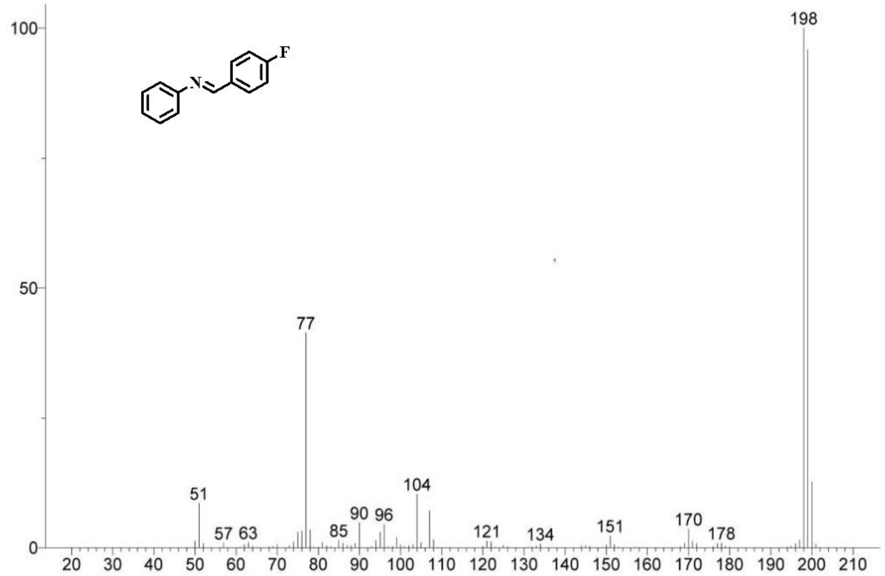
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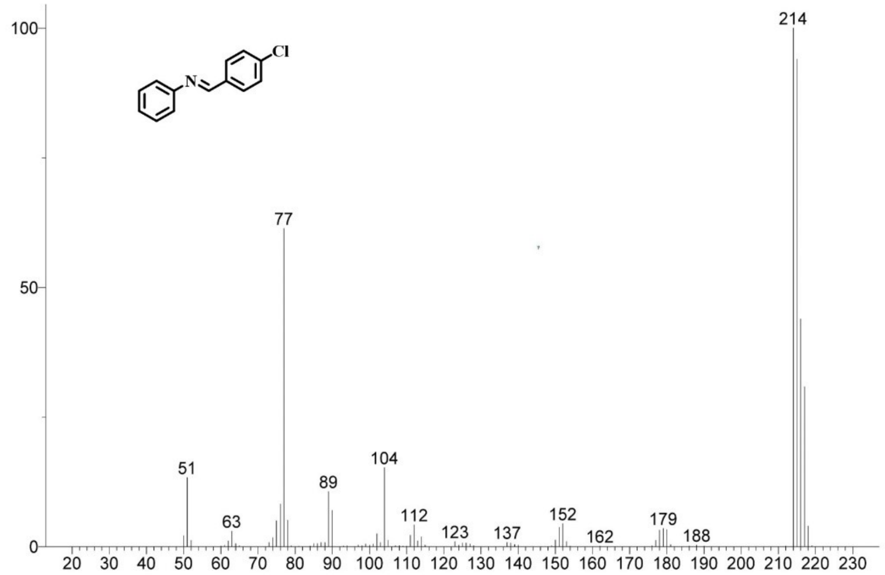
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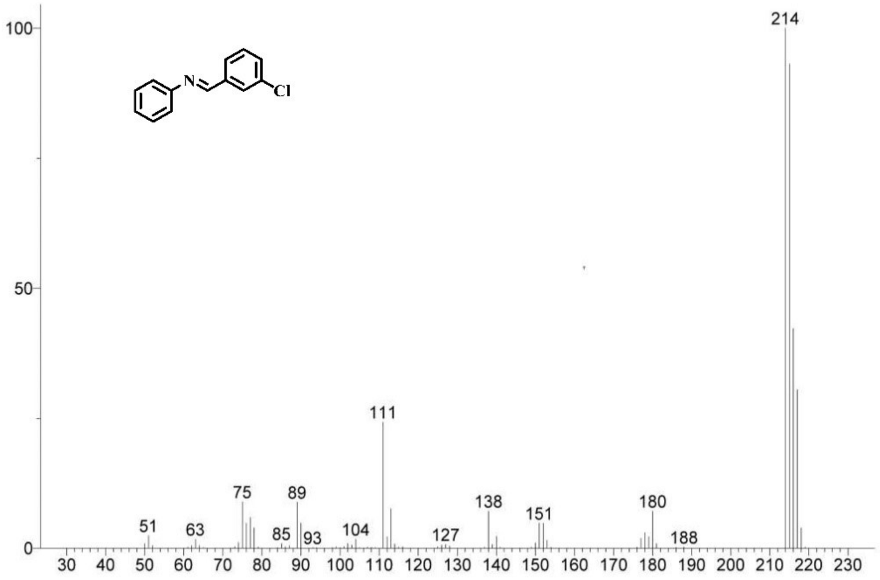
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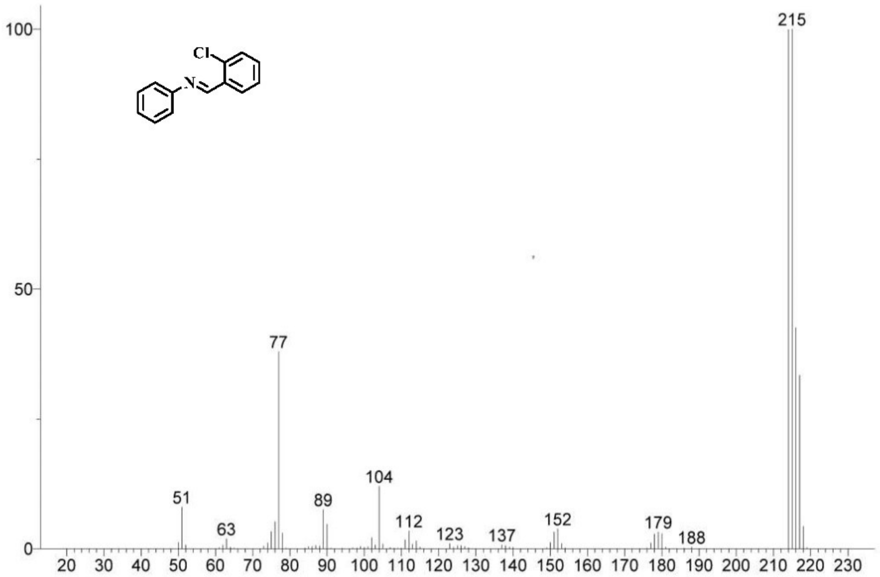
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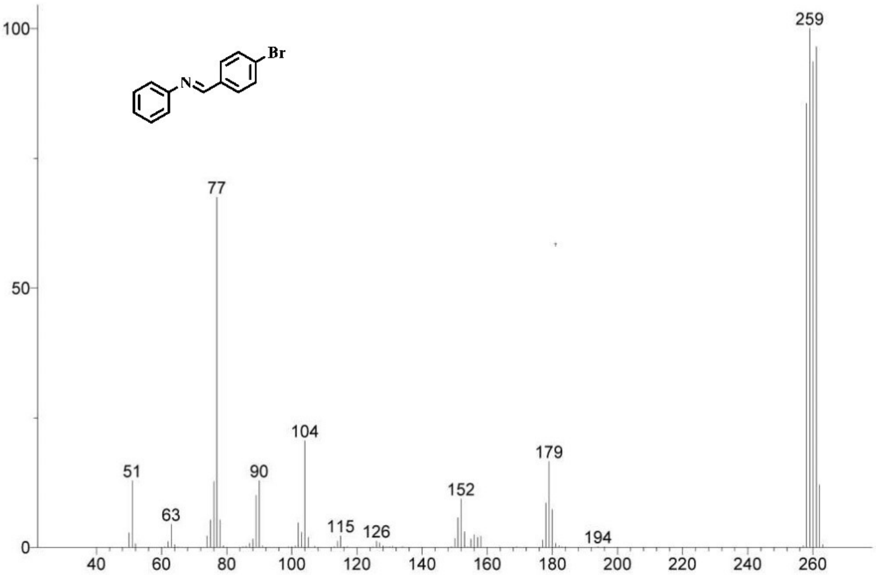
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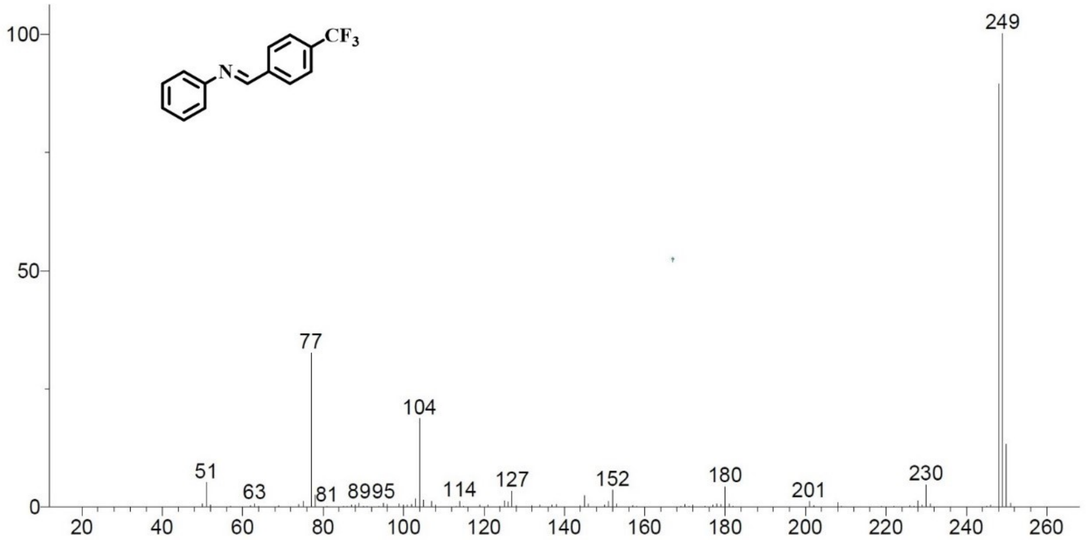
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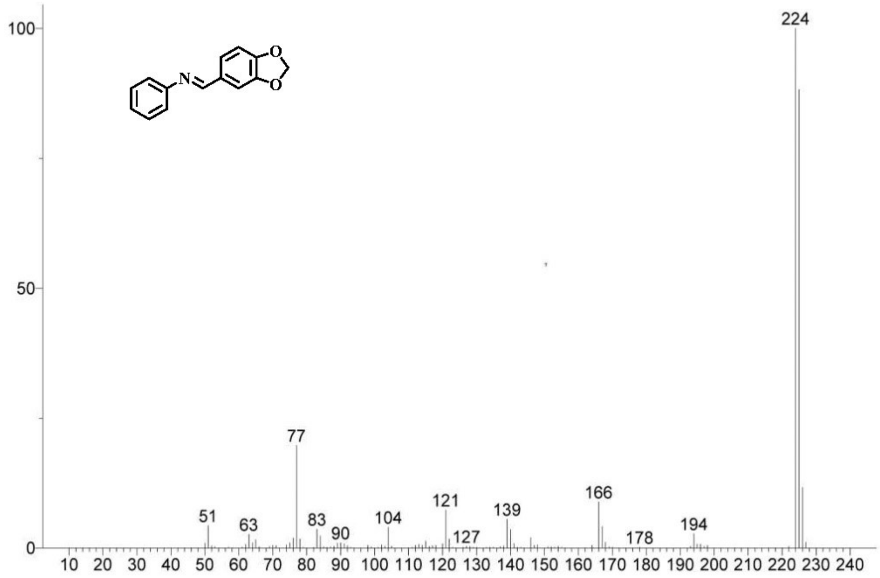
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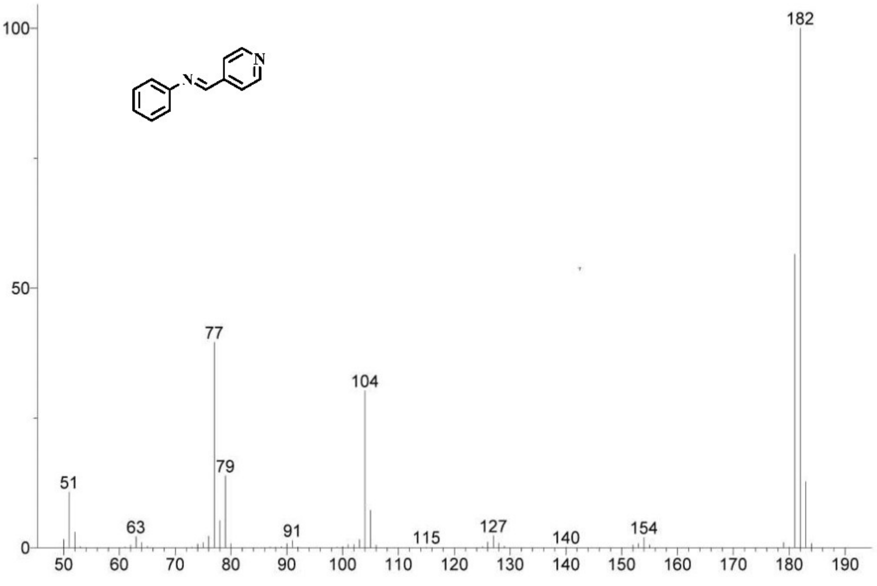
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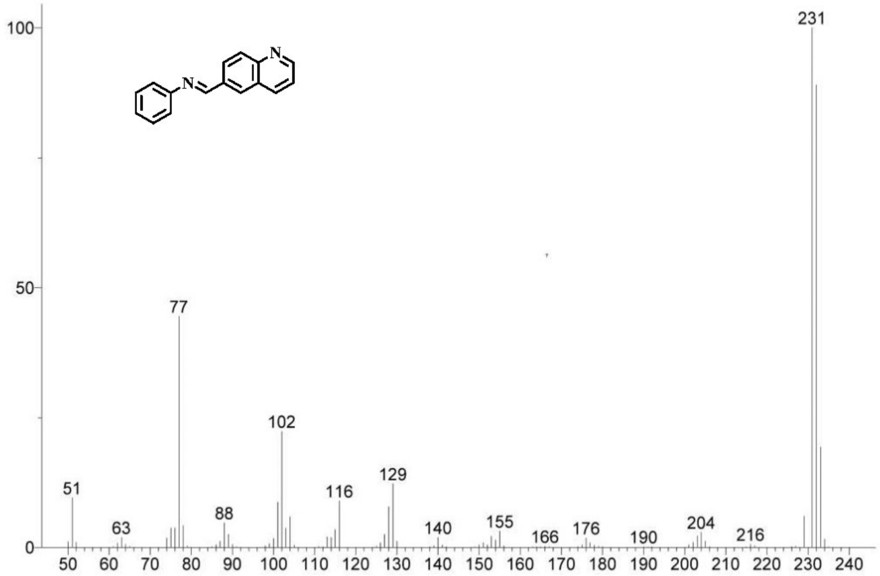

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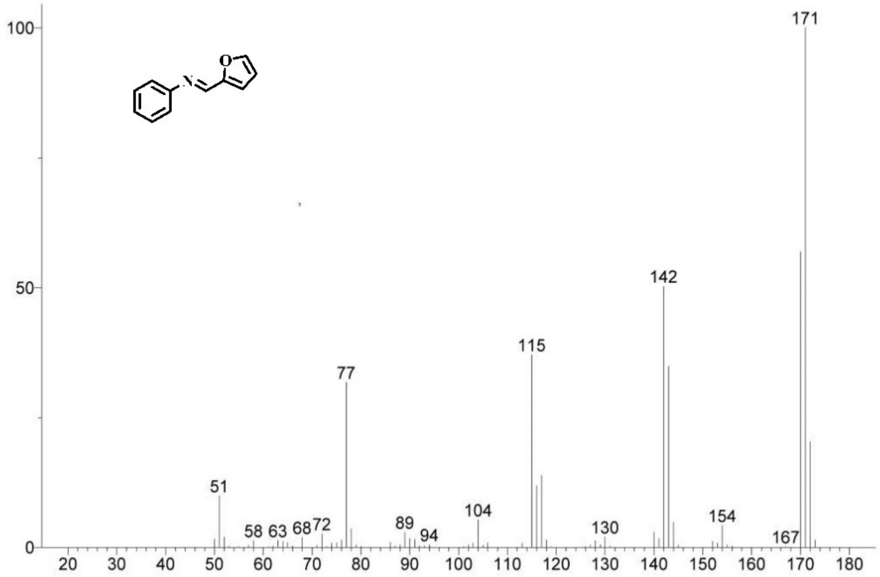

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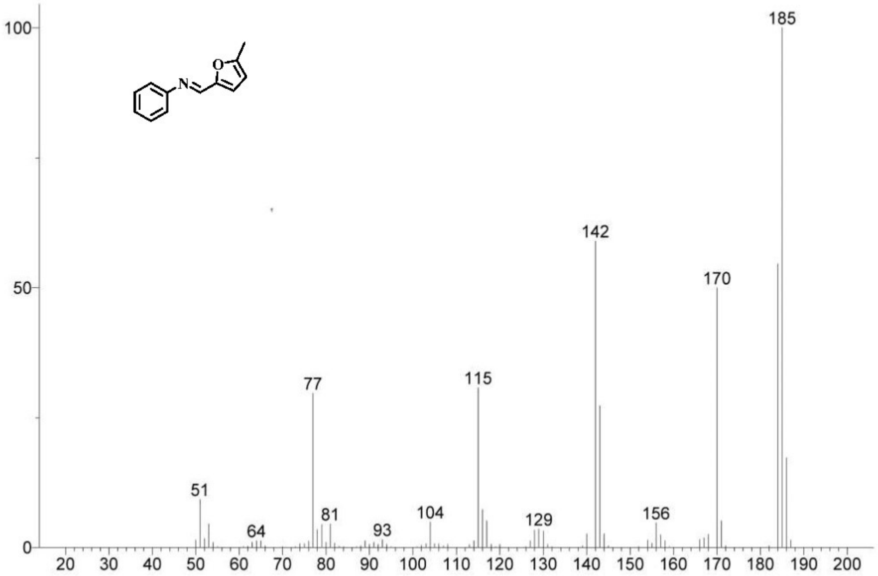

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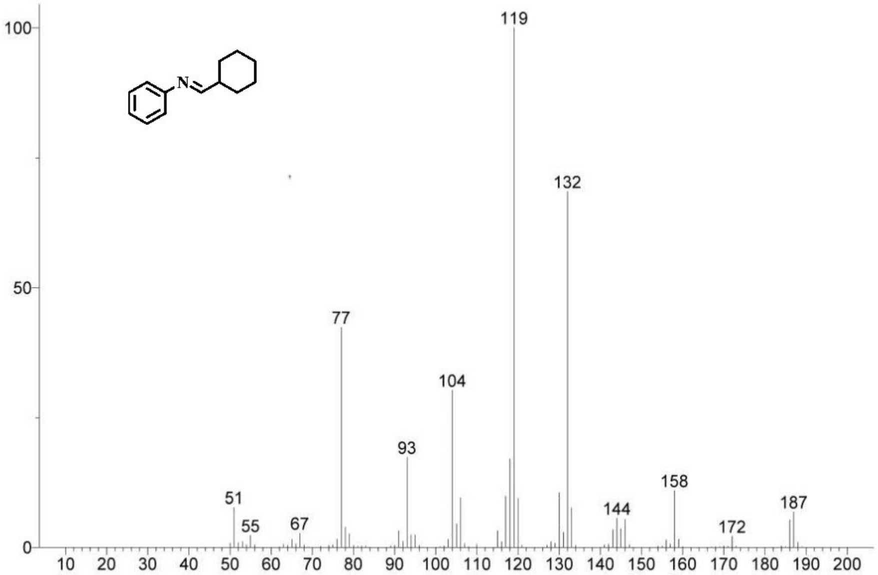

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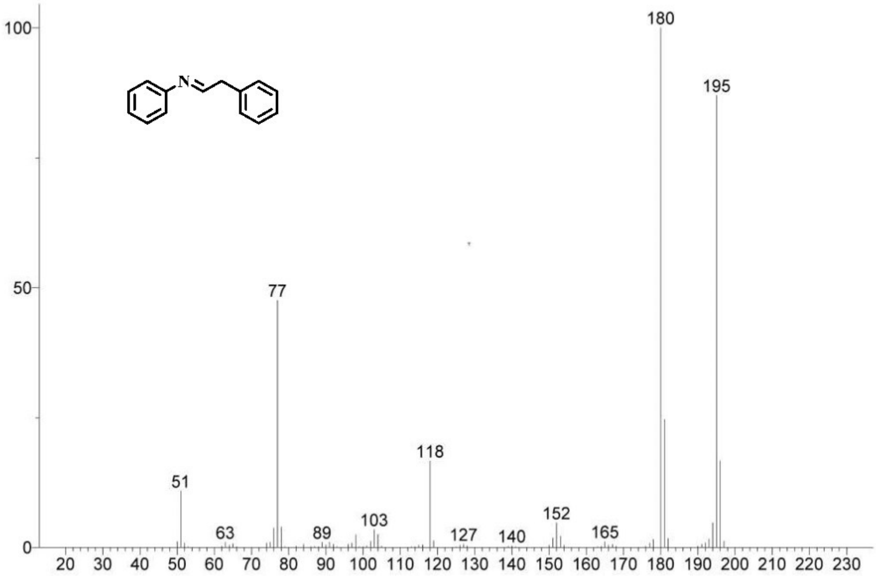
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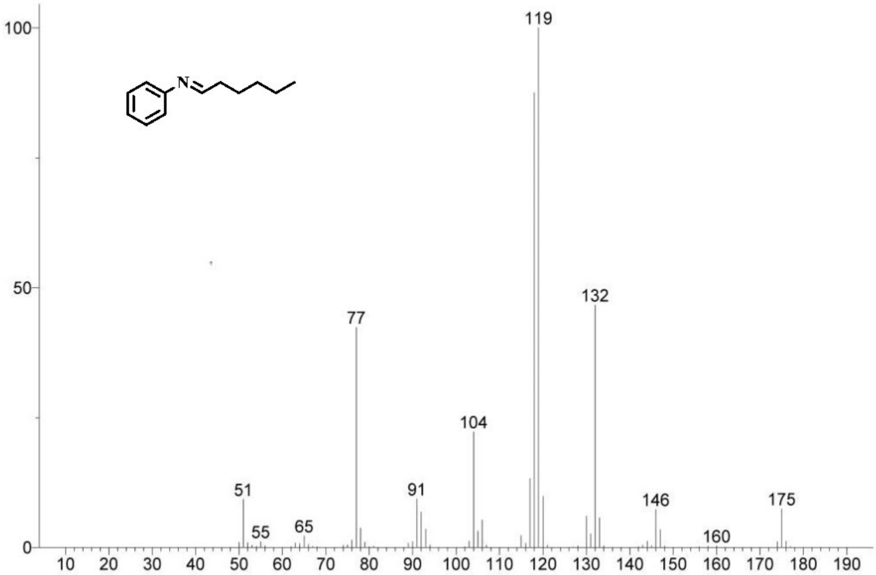
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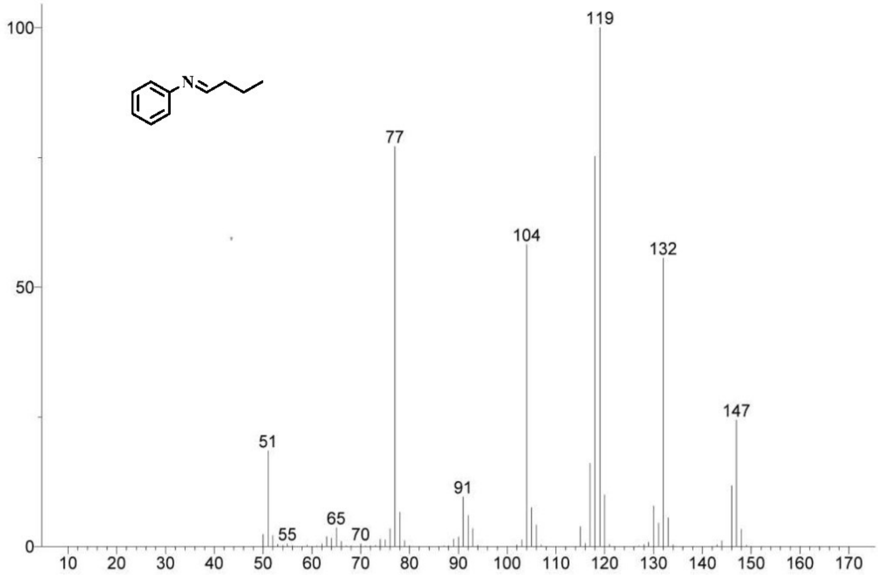
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