Selective mono-*N*-methylation of amines using methanol as the methylated reagent over heterogeneous Ni catalysts

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Experimental Section

1.1 Materials

Methanol solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). $Ni(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, urea, and amines were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). All of the chemicals used in this study are analytical grade and they were used without further purification.

1.2 Catalysts preparation

1.2.1 Synthesis of the NiZnAl-LDH

The NiZnAl-layered double hydroxide (LDH) was prepared by a precipitation method. In a typical synthesis, 30 mmol of $Ni(NO_3)_2 \cdot 6H_2O$, 10 mmol of $Zn(NO_3)_2 \cdot 6H_2O$, 20 mmol of $Al(NO_3)_3 \cdot 9H_2O$, and 150 mmol of urea were dissolved in 200 mL distilled water with a magnetic stirring at a rate of 1000 RPM. Then, the transparent solution was transferred into an autoclave, and heated at 100 °C for 24 h. The as-obtained LDH was centrifuged, washed with distilled water to remove the impurity, and dried at 70 °C for 12 h in the air, which named as NiZnAl-LDH. The ZnAl-LDH was prepared without the addition of $Ni(NO_3)_2 \cdot 6H_2O$ and the rest of the steps were the same as for NiZnAl-LDH. The preparation procedure of NiAl-LDH was the same as that of NiZnAl-LDH, and the molar ratio of (Ni+Zn):Al=2:1 was maintained during the process, and without the addition of $Zn(NO_3)_2 \cdot 6H_2O$.

1.2.2 Synthesis of the Ni/ZnAlO$_x$-T

Then, the NiZnAl-LDH were calcined at 600 °C for 2 h with a ramping rate of 5 °C/min to obtain the NiZnAl-MMO mixed oxides. Finally, the NiZnAl-MMO were reduced at the 600 °C by H_2 (10 vol.%)/Ar atmosphere for 2 h, and a heating rate of 3 °C/min. Afterwards, the sample was allowed to cool to room temperature and was treated in a flow of O_2 (1 vol.%)/N_2 atmosphere for 2 h at room temperature. The as-prepared catalysts were labelled as the Ni/ZnAlO$_x$-600 catalysts. For Ni/ZnAlO$_x$-T (where T represented the reduction temperature) catalysts with different reduction temperatures, the NiZnAl-MMO were reduced at the set temperature by H_2 (10 vol.%)/Ar atmosphere for 2 h, and other steps are the same as before. The ZnAlO$_x$ and Ni/AlO$_x$-600 were reduced using the same procedure as described above.

1.3 Catalyst characterization

The content of Ni was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES, Varian Vista-MPX). Transmission electron microscope (TEM) was performed on an FEI Tecnai G^2-20 instrument. X-ray powder diffraction (XRD) measurements were conducted on a Bruker advanced D8 powder diffractometer (Cu Kα), operating with 2θ range of 10–80° at a scanning rate of 0.016 °/s. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV. Nitrogen physisorption measurements were conducted at 77 K

on a quantachrome Autosorb-1-C-MS instrument. Surface area was determined by the standard BET method based on the relative pressure between 0.05 and 0.20. The pore size distribution was calculated using the non-local density functional theory method.

1.4 General procedure of the *N*-methylation of amines

In a typical run, Aniline (1.0 mmol), the Ni/$ZnAlO_x$-600 catalyst (40 mg) and methanol (10 mL) were added into a 50 mL autoclave, which was equipped with a magnetic stirrer and a temperature controller. Initially, the air in the autoclave was removed by the flush of nitrogen for five times, and then the autoclave was charged with 1 MPa N_2 at room temperature The experiment was performed at 160 °C under magnetic stirring of 1000 rpm. After cooling to room temperature, the reaction mixture was analyzed by GC-MS and GC with ethylbenzene as an internal standard. The selectivity was calculated from the following equations:

$$Con._{aniline} = (n_{aniline} - n'_{aniline}) / n_{aniline} \times 100\%$$

$$Yield_{N\text{-methylaniline}} = n_{Produced\ N\text{-methylaniline}} / n_{aniline} \times 100\%$$

Where:

$n_{aniline}$: the molar amount of aniline added in the reaction system;

$n'_{aniline}$: the molar amount of aniline in the reaction system after the reaction;

$n_{Produced\ N\text{-methylaniline}}$: the molar amount of *N*-methylaniline in the reaction system after the reaction.

1.5 Analytic method

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 ℃, detector temperature 300 ℃, column temperature program: from 50 ℃ (hold 1.5 min) to 300 ℃ (hold 3 min) at a heating rate of 15 ℃/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). The peaks were identified by comparison of the retention times of the unknown compounds with those of standard compounds and quantified based on the internal standard method using ethylbenzene as the internal standard.

1.6 Recycling experiments

After reaction, the Ni/$ZnAlO_x$-600 catalyst could be easily removed from the reaction mixture with an assist of the external magnet. After washing with methanol and water for three times, the spent catalyst was dried in a vacuum oven at 50 ℃, and the spent catalyst was used directly for the next run under the same conditions.

Supplementary Figures

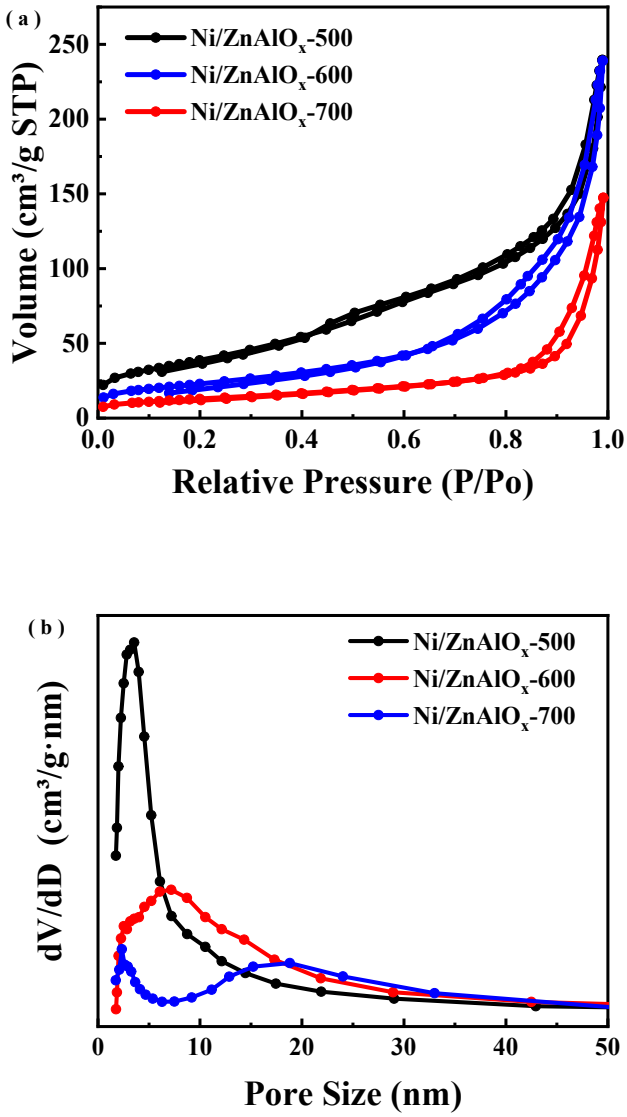


Figure S1. N_2-sorption isotherm curves (a) and pore size distributions (b) of the Ni/ZnAlO$_x$-T catalysts, respectively.

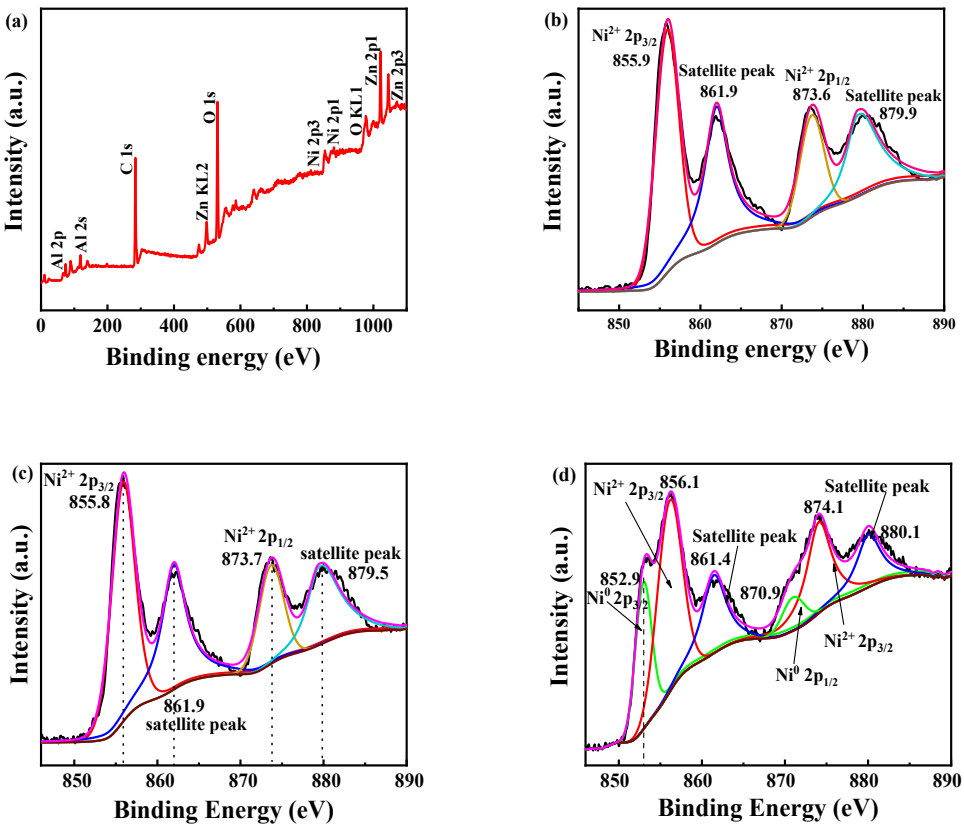


Figure S2. The full XPS survey spectrum of the representative Ni/ZnAlO$_x$-600 (a), and the XPS of the Ni 2p in the NiZnAl-MMO (b), Ni/ZnAlO$_x$-500 (c) and Ni/ZnAlO$_x$-700 (d) catalysts, respectively.

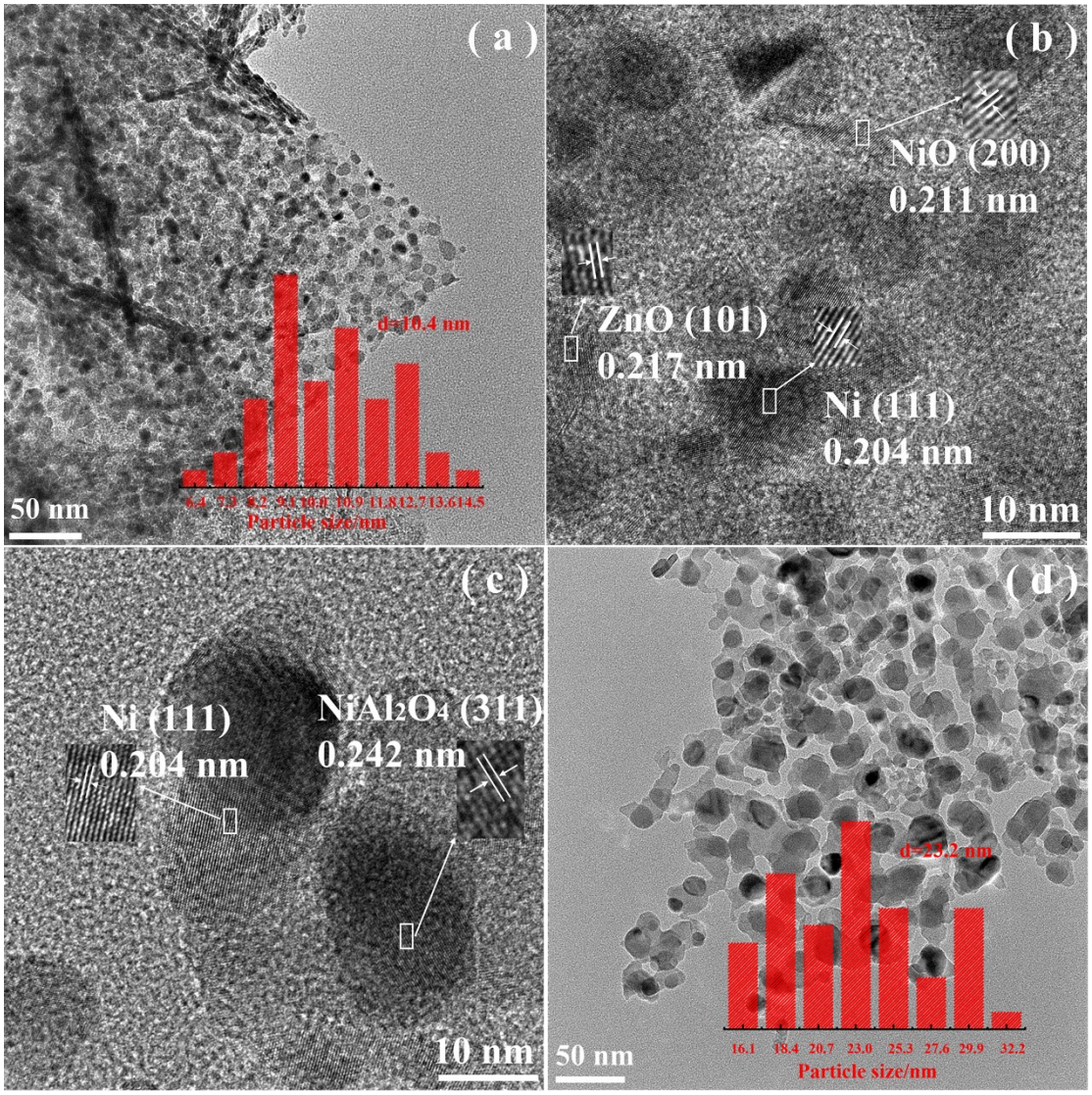


Figure S3. The TEM (a, d), HR-TEM (b, c) images of Ni/ZnAlO$_x$-500 and Ni/ZnAlO$_x$-700 catalysts, respectively.

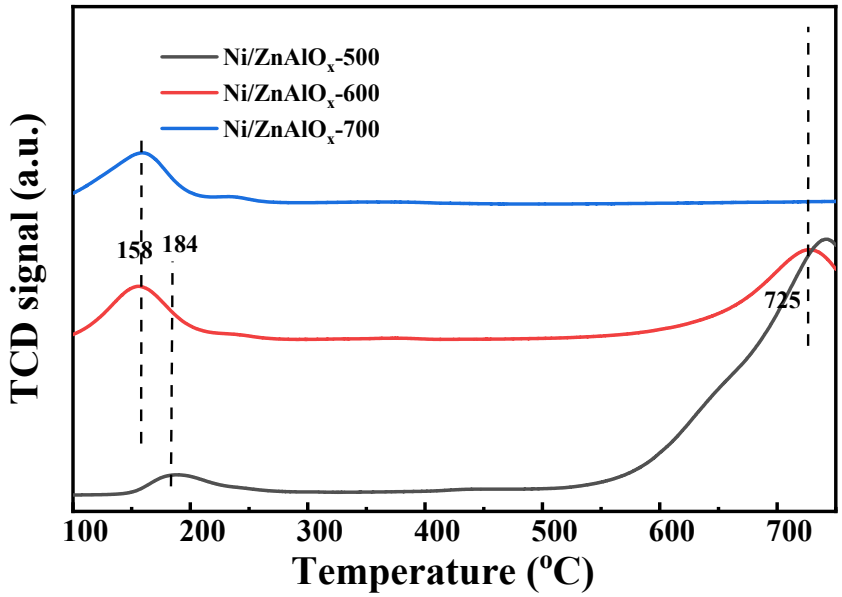


Figure S4. H_2-TPR profiles of Ni/ZnAlO$_x$-T catalysts.

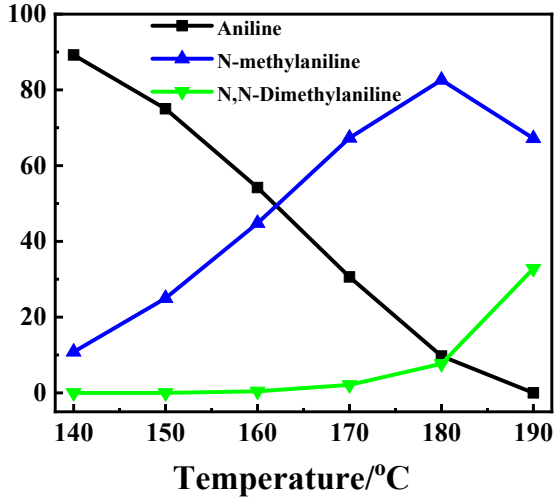


Figure S5. The effect of reaction temperature on the *N*-methylation of aniline with methanol. Reaction conditions: aniline (1.0 mmol), methanol (10 mL), Ni/ZnAlO$_x$-600 (40 mg), 10 bar N_2, 4 h.

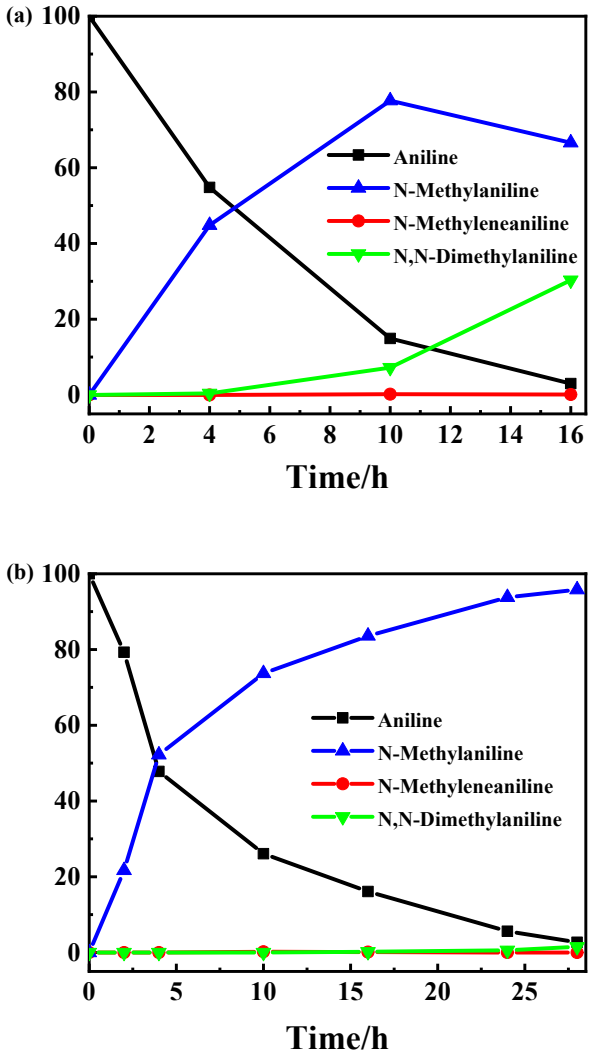


Figure S6. Time course of *N*-methylation product distribution of aniline with methanol in the absence (a) or presence (b) of base (NaOH, 0.25 equiv.). Reaction conditions: aniline (1 mmol), methanol (10 mL), Ni/$ZnAlO_x$-600 (40 mg), 160 °C, 10 bar N_2.

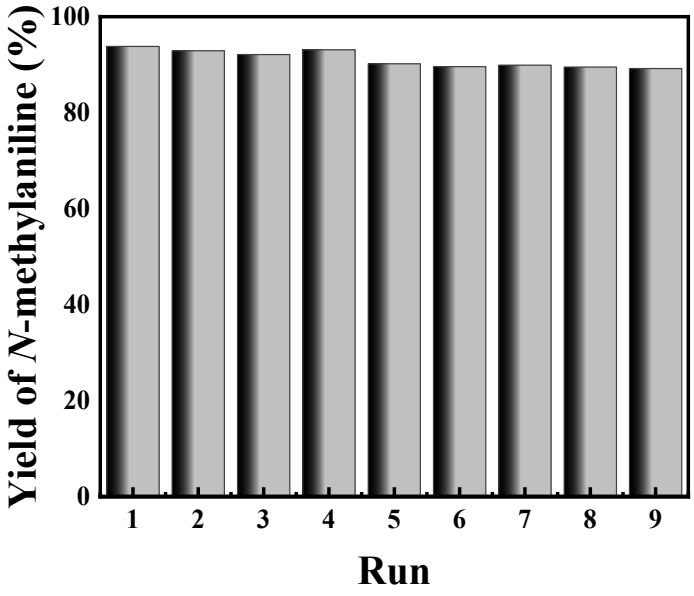


Figure S7. Results of the recycling of the Ni/$ZnAlO_x$-600 catalyst. Reaction conditions: aniline (1 mmol), methanol (10 mL), Ni/$ZnAlO_x$-600 (40 mg), 160 °C, NaOH (0.25 equiv.), 10 bar N_2, and 24 h.

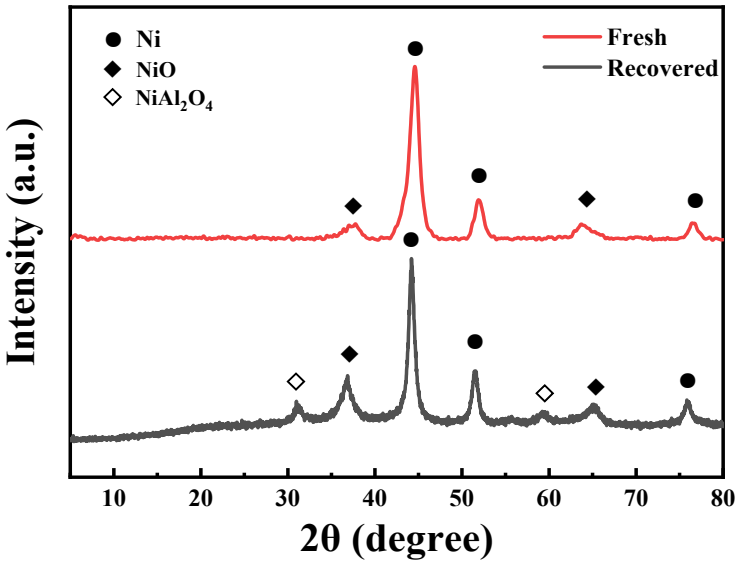


Figure S8. The XRD patterns of fresh and recovered Ni/ZnAlO$_x$-600 catalyst.

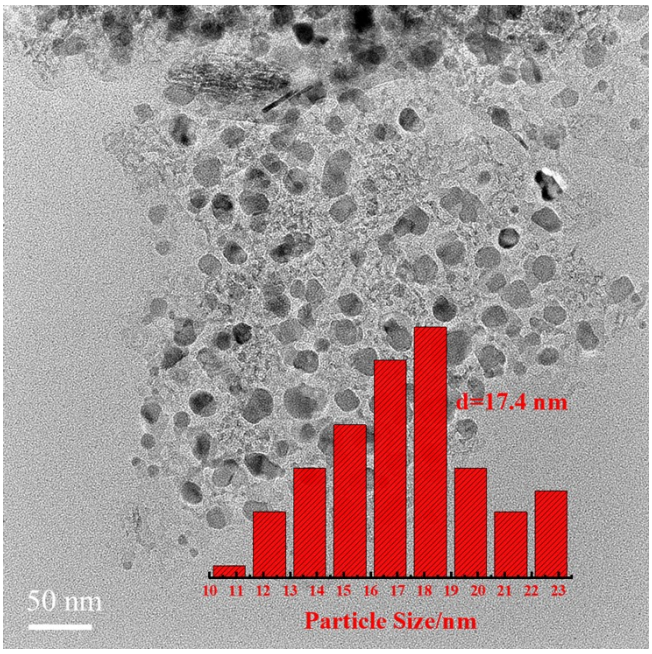


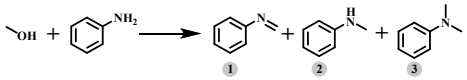
Figure S9. The TEM image of recovered Ni/ZnAlO$_x$-600 catalyst.

Supplementary Tables

Table S1. The textural parameters of the Ni/$ZnAlO_x$-T catalysts

Catalyst	Surface area (m^2/g)	Pore size (nm)	Pore volume (cm^3/g)
Ni/$ZnAlO_x$-500	143.4	8.9	0.366
Ni/$ZnAlO_x$-600	82.2	15.1	0.348
Ni/$ZnAlO_x$-700	45.8	20.1	0.224

Table S2. The results of the *N*-methylation of aniline over various catalysts.



Entry	Additive	Con. (%)	Yield (%)		
			1	2	3
1	-	97	0.1	66.6	30.3
2	NaOH (0.25 equiv.)	83.9	0	83.6	0.2
3	NaOH (0.50 equiv.)	55.9	0	55.8	0
4 [b]	-	93.8	0.2	80.9	13.7
5 [c]	-	72.6	0.2	72.4	0
6 [d]	Pyridine	73.8	0.3	64.9	8.6
7 [d]	Pyrrole	33.5	2.1	28.2	3.2

[a] **Reaction conditions:** aniline (1 mmol), methanol (10 mL), Ni/$ZnAlO_x$-600 (40 mg), 160 °C, 1 MPa N_2, 16 h. Yields were determined by GC using ethylbenzene as the internal standard. [b] Same as "a" but use H_2 to remove air followed by N_2 to remove it one time, and flush in N_2 1 MPa. [c] Same as "a" but the H_2 (1 bar)/N_2 (9 bar). [d] Same as "a" but before the reaction, 2.0 equiv. of pyridine or pyrrole was injected into the reaction system

Table S3. Comparison of previous non-noble metal catalytic reactions for the synthesis of mono-*N*-methylaniline.

Ent	Catalyst	T/°C	Time/h	Base	Y/%	conditions	Ref.
1	$Ni/ZnAlO_x$	160	24	NaOH (1 equiv.)	93	1.0 mmol anilines, Cat. (40 mg, 26.5 mol%)	***This work***
2	Fe-Catalyzed BH	150	24	K_2CO_3 (2 equiv.)	64	1.0 mmol amines, Me_3NO (4 mol %), Cat. (2 mol %).	21
3	Mn-PNP	100	24	t-BuOK (1 equiv.)	86	1.0 mmol amines, Cat. (3 mol%),	23
4	Co-NPs@NC	160	24	t-BuOK (1 mmol)	67	0.5 mmol amines, Cat. (60 mg, 3.5 mol%)	29

Ent for Entry, T for Temperature, Y for Yield and Ref for Reference.

NMR and GC-MS data of products

1. N-methylaniline, CAS:100-61-8, 107.15, MS (EI, m/z):107 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.11 (t, *J* = 7.7 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 3H), 2.75 (s, 3H).

2. N-methyl-4-methylaniline, CAS:623-08-5, 121.18, MS (EI, m/z):120 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 6.93 (d, *J* = 8.1 Hz, 2H), 6.55 (d, *J* = 8.4 Hz, 2H), 2.71 (s, 3H), 2.19 (s, 3H).

3. 3-(methylamino)toluene, CAS:696-44-6, 121.18, MS (EI, m/z):120 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.09 (dd, *J* = 9.0, 7.3 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 6.5 Hz, 2H), 2.83 (s, 3H), 2.30 (s, 3H).

4. 4-ethyl-N-methylaniline, CAS:37846-06-3, 135.21, MS (EI, m/z):135 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 6.98 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 2.74 (s, 3H), 2.51 (q, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.6 Hz, 3H).

5. 4-isopropyl-N-methylaniline, CAS: 6950-79-4, 149.23, MS (EI, m/z):149 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.09 (d, J = 8.4 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 2.84 (s, 4H), 1.23 (d, J = 6.9 Hz, 6H).

6. (4-tertbutylphenyl)-methylamine, CAS:5279-59-4, 163.26, MS (EI, m/z):163 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.17 (d, J = 8.5 Hz, 2H), 6.60 (d, J = 8.5 Hz, 2H), 2.74 (s, 3H), 1.26 (s, 9H).

7. 4-butyl-N-methylaniline, CAS:137273-36-0, 163.26, MS (EI, m/z):163 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 6.95 (d, J = 8.3 Hz, 2H), 6.58 (d, J = 8.3 Hz, 2H), 2.73 (s, 3H), 2.47 (t, J = 7.6 Hz, 2H), 1.53 (p, J = 7.5 Hz, 2H), 1.33 (dt, J = 14.9, 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

8. 2-Aminofluorene, CAS: 63019-68-1, 195.26, MS (EI, m/z):195 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.35 – 7.27 (m, 2H), 7.08 (dt, J = 14.6, 7.6 Hz, 2H), 6.97 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 9.1 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 4.20 (s, 1H), 2.87 (s, 3H).

9. N-methyl-4-(phenylmethyl)benzenamine, CAS:6851-78-1, 197.28, MS (EI, m/z):197 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.32 – 7.25 (m, 2H), 7.20 (d, J = 7.2 Hz, 3H), 7.03 (d, J

= 8.4 Hz, 2H), 6.58 (d, J = 8.4 Hz, 2H), 3.90 (s, 2H), 2.83 (s, 3H)

10. N-methylnaphthalen-1-amine, CAS: 2216-68-4, 157.21, MS (EI, m/z):157 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.83 – 7.76 (m, 2H), 7.50 – 7.41 (m, 3H), 7.38 (t, J = 7.8 Hz, 1H), 7.24 (d, J = 7.6 Hz, 2H), 6.61 (d, J = 7.5 Hz, 1H), 4.67 (s, 1H), 3.00 (d, J = 16.3 Hz, 4H).

11. 4-fluoro-N-methylaniline, CAS:459-59-6, 125.14, MS (EI, m/z):124 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 6.89 – 6.79 (m, 2H), 6.62 – 6.55 (m, 2H), 2.72 (s, 3H).

12. N-methyl-4-(trifluoromethoxy)aniline, CAS:41419-59-4, 191.15, MS (EI, m/z):191 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.00 (d, J = 8.8 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 2.75 (s, 3H).

13. 4-chloro-N-methyl-anilin, CAS:932-96-7, 141.6, MS (EI, m/z):140 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.06 (d, J = 8.8 Hz, 2H), 6.55 (d, J = 8.8 Hz, 2H), 2.72 (s, 3H).

14. 3-chloro-N-methylaniline, CAS:7006-52-2, 141.6, MS (EI, m/z):140 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.03 (t, J = 8.3 Hz, 1H), 6.59 – 6.51 (m, 2H), 6.48 (d, J = 8.2 Hz, 1H), 2.72 (s, 3H).

15. 4-methoxy-N-methylaniline, CAS:5961-59-1, 137.18, MS (EI, m/z):137 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 6.80 (s, 2H), 6.58 (s, 2H), 3.75 (s, 3H), 2.80 (s, 3H).

16. 4-ethoxy-N-methylaniline, CAS:3154-18-5, 151.21, MS (EI, m/z):151 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 6.80 (d, J = 8.9 Hz, 2H), 6.59 (d, J = 8.9 Hz, 2H), 3.97 (q, J = 7.0 Hz, 2H), 2.81 (s, 3H), 1.38 (t, J = 7.0 Hz, 3H).

17. N-methyl-2-phenoxyaniline, CAS: 640766-50-3, 199.25, MS (EI, m/z):199 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.35 – 7.27 (m, 2H), 7.08 (dt, J = 14.6, 7.6 Hz, 2H), 6.97 (d, J = 7.8 Hz, 2H), 6.86 (d, J = 9.1 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 6.67 (t, J = 7.6 Hz, 1H), 4.20 (s, 1H), 2.87 (s, 3H).

18. 3-chloro-4-fluoro-N-methylaniline, CAS: 77898-24-9,159.59, MS (EI, m/z):158 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 6.95 (t, J = 8.9 Hz, 1H), 6.59 (d, J = 2.8 Hz, 1H), 6.45 – 6.38 (m, 1H), 2.79 (s, 3H).

19. 4-chloro-N,2-dimethylaniline, CAS 30273-07-5, 155.62, MS (EI, m/z):155 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.10 (dd, J = 8.6, 2.5 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 2.87 (s, 3H), 2.10 (s, 3H).

20.5-methyl-2-(methylamino)phenol, CAS:425375-95-7, 137.18, MS (EI, m/z):137 $[M]^+$

21. N-methyl-4-(piperidin-1-yl)aniline, CAS:173186-18-0, 190.29, MS (EI, m/z):190 $[M]^+$

22. 4-fluoro-N,2-dimethylaniline, CAS: 35114-07-9, 139.17, MS (EI, m/z):139 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 6.90 – 6.79 (m, 2H), 6.51 (dd, J = 8.6, 4.8 Hz, 1H), 2.87 (s, 3H), 2.13 (s, 3H).

23. N-methyl-4-pyridinamine, CAS:1121-58-0, 108.14, MS (EI, m/z):107 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.97 (d, *J* = 6.3 Hz, 2H), 6.50 (d, *J* = 6.4 Hz, 2H), 2.79 (s, 3H).

24. N-methylquinolin-6-amine, CAS: 83407-38-9, 158.2, MS (EI, m/z):158 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 8.61 (d, *J* = 4.1 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.09 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 2.95 (s, 3H).

25. N-methylcyclohexanamine, CAS:100-60-7, 113.2, MS (EI, m/z):113 $[M]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 2.35 (s, 3H), 1.93 (d, *J* = 11.2 Hz, 2H), 1.81 – 1.72 (m, 2H), 1.66 (dd, *J* = 15.4, 3.0 Hz, 1H), 1.36 – 0.99 (m, 6H).

26. N-methylbenzylamine, CAS:103-67-3, 121.18, MS (EI, m/z):120 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.32 (d, *J* = 6.0 Hz, 5H), 3.75 (s, 2H), 2.46 (s, 3H)

27. 4-fluoro-N-methylbenzylamine, CAS:405-66-3,139.17, MS (EI, m/z):139 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.31 – 7.25 (m, 2H), 7.01 (d, J = 17.3 Hz, 2H), 3.71 (s, 2H), 2.44 (s, 3H)

28. 4-chloro-N-methylbenzylamine, CAS:104-11-0, 155.62, MS (EI, m/z):154 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.28 (q, *J* = 8.3 Hz, 4H), 3.73 (s, 2H), 2.45 (s, 3H).

29. N-(4-methoxybenzyl)-N-methylamine, CAS:702-24-9, 151.21, MS (EI, m/z):150 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.68 (s, 2H), 2.43 (s, 3H).

30. N,N-dimethylbenzylamine, CAS:103-83-3, 135.21, MS (EI, m/z):135 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.10 (dd, J = 8.6, 2.5 Hz, 1H), 7.02 (d, J = 2.5 Hz, 1H), 6.50 (d, J = 8.5 Hz, 1H), 2.87 (s, 3H), 2.10 (s, 3H).

31. N,N-dimethylaniline, CAS:121-69-7, 121.18, MS (EI, m/z):120 $[M-1]^+$

^{1}H NMR (400 MHz, CD_3OD) δ 7.17 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 2.89 (s, 6H).

32. 1-methyl-1,2,3,4-tetrahydroquinoline, CAS, 491-34-9, 147.22, MS (EI, m/z):146 $[M-1]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 7.11 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 2H), 3.25 (t, *J* = 5.7 Hz, 2H), 2.92 (s, 3H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.02 (s, 2H).

33. 4-methylmorpholine, CAS:109-02-4, 101.15, MS (EI, m/z):101 $[M]^+$

^{1}H NMR (400 MHz, CCl_3D) δ 3.69 (t, *J* = 4.7 Hz, 4H), 2.48 – 2.30 (m, 4H), 2.27 (s, 3H).

34. Fluoxetine, CAS:54910-89-3, 309.33, MS (EI, m/z):309 $[M]^+$

^{1}H NMR (600 MHz, CCl_3D) δ 7.43 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 3.5 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.48 (dd, *J* = 8.3, 4.3 Hz, 1H), 3.14 (tdd, *J* = 15.6, 7.6, 4.6 Hz, 2H), 2.64 (s, 3H), 2.56 – 2.49 (m, 1H), 2.48 – 2.42 (m, 1H).

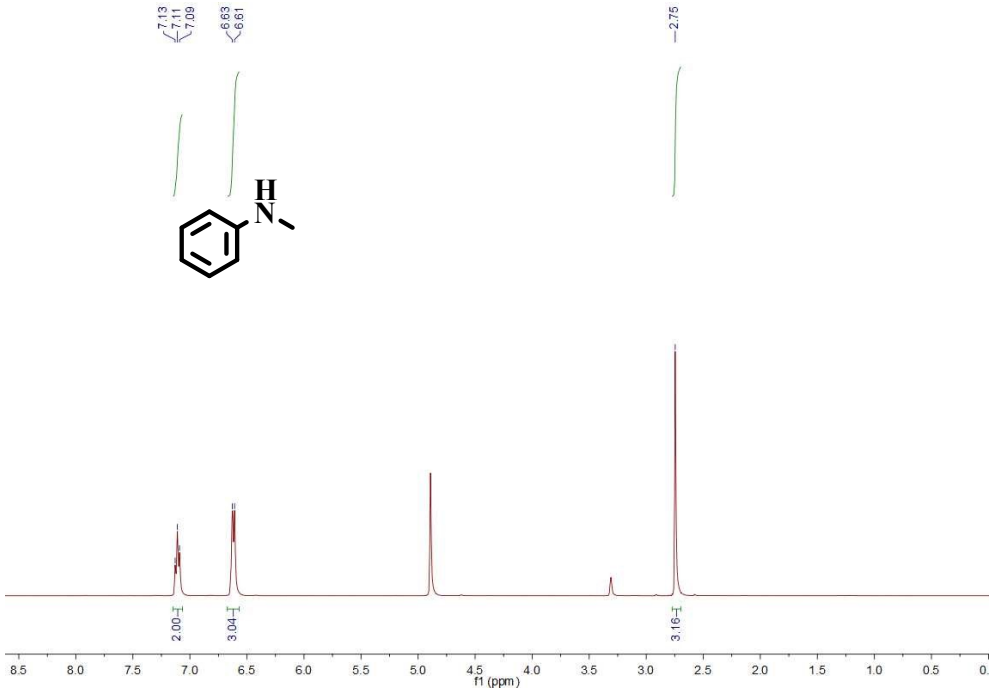


Figure S10. ^{1}H NMR spectrum of N-methylaniline (1)

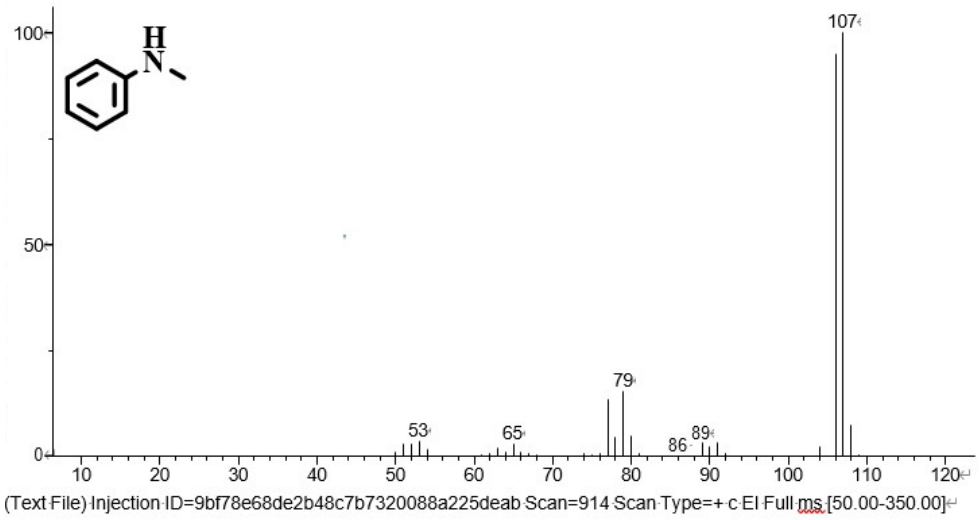


Figure S11. GC-MS spectra of the N-methylaniline (1)

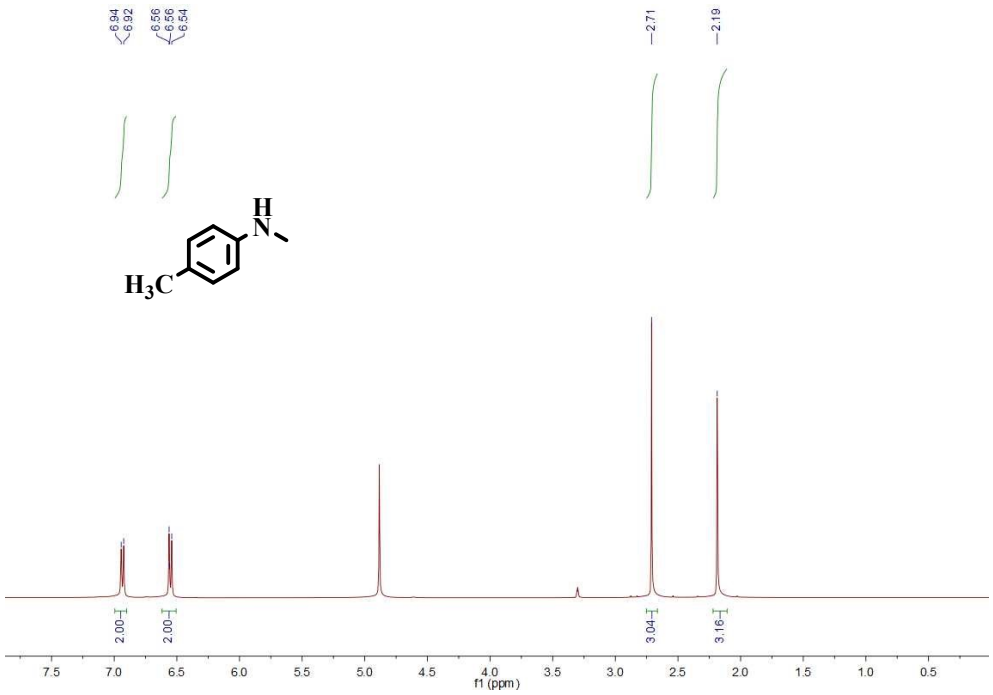


Figure S12. ^{1}H NMR spectrum of N-methyl-4-methylaniline (2)

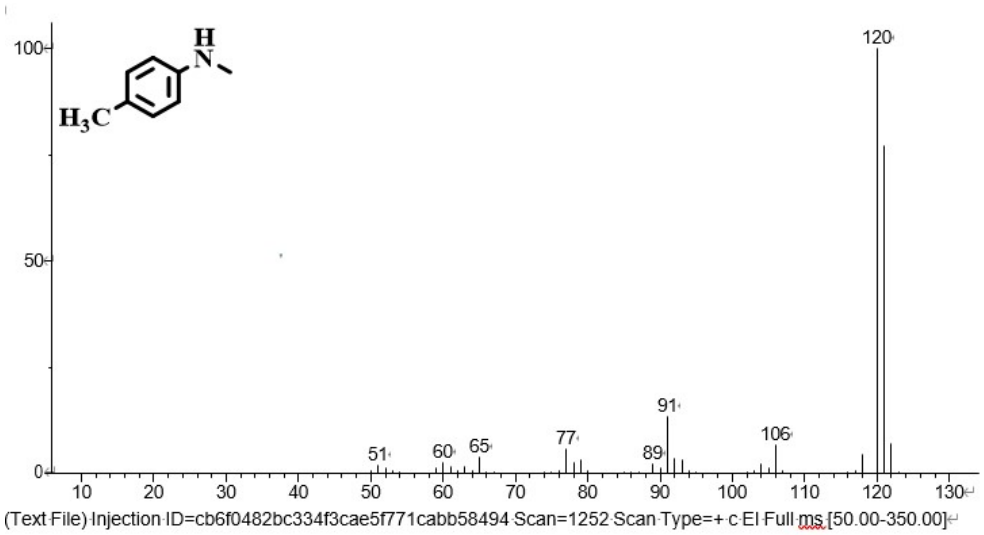


Figure S13. GC-MS spectra of the N-methyl-4-methylaniline (2)

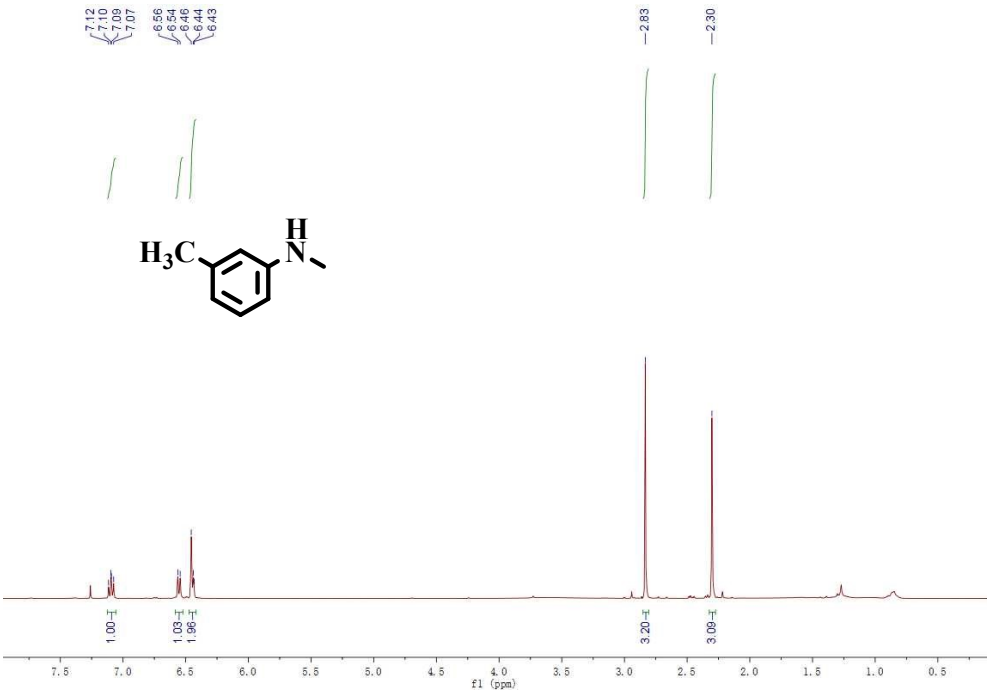


Figure S14. ^{1}H NMR spectrum of 3-(methylamino)toluene (3)

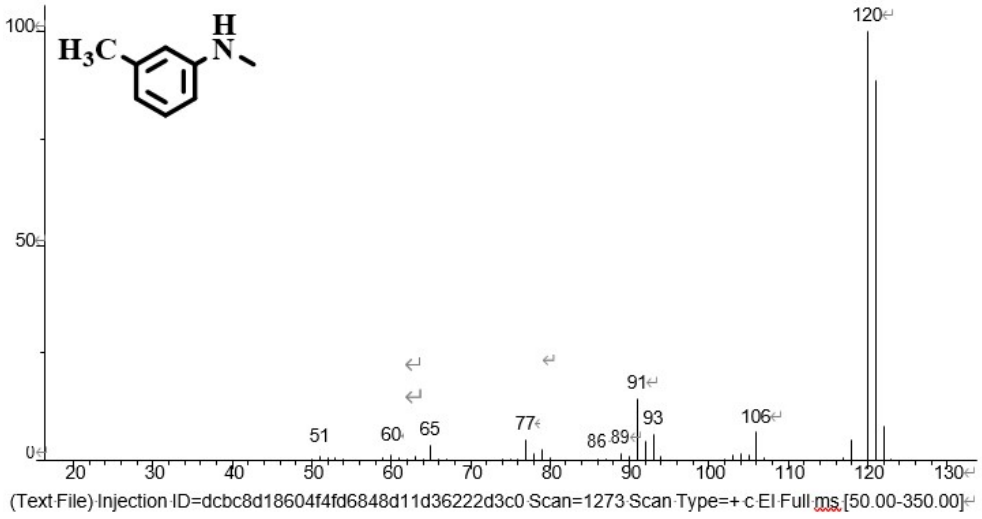


Figure S15. GC-MS spectra of the 3-(methylamino)toluene (3)

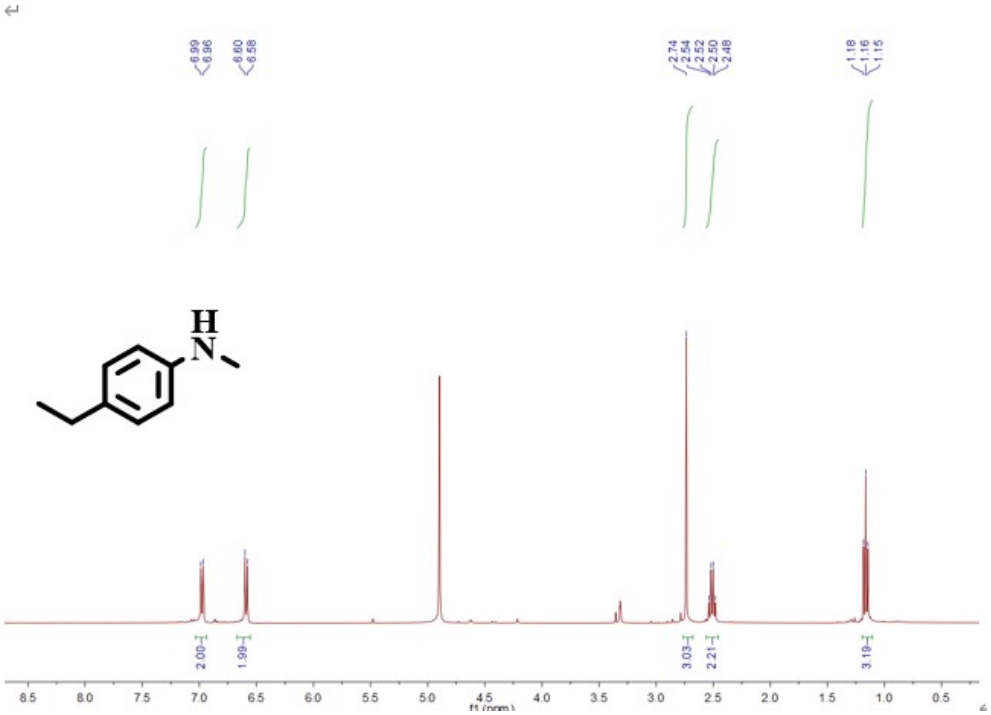


Figure S16. ^{1}H NMR spectrum of 4-ethyl-N-methylaniline (4)

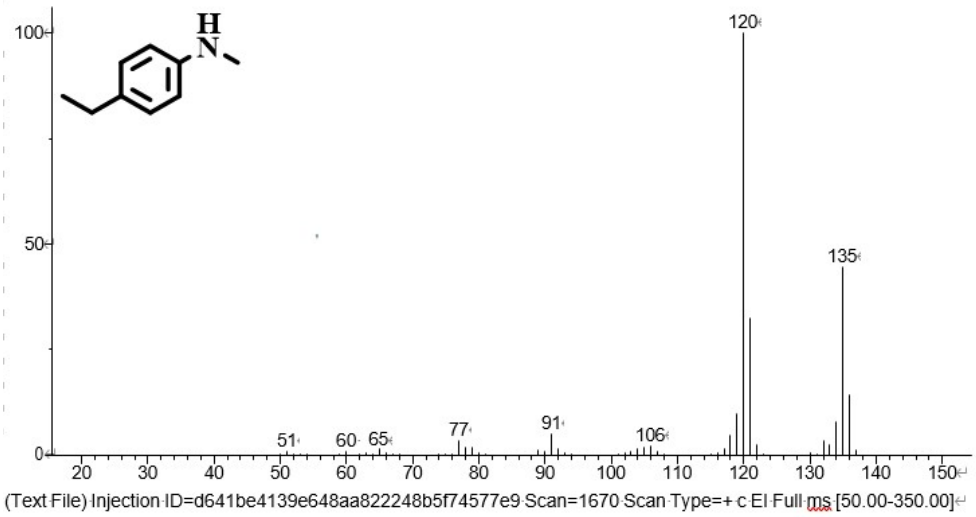


Figure S17. GC-MS spectra of the 4-ethyl-N-methylaniline (4)

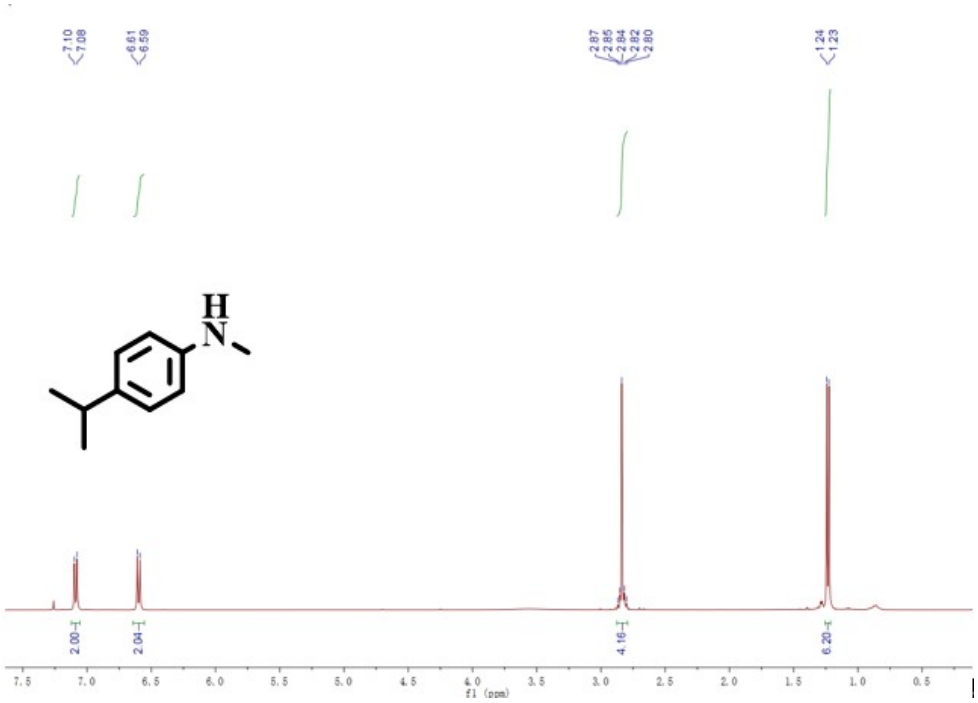


Figure S18. ^{1}H NMR spectrum of 4-isopropyl-N-methylaniline (5)

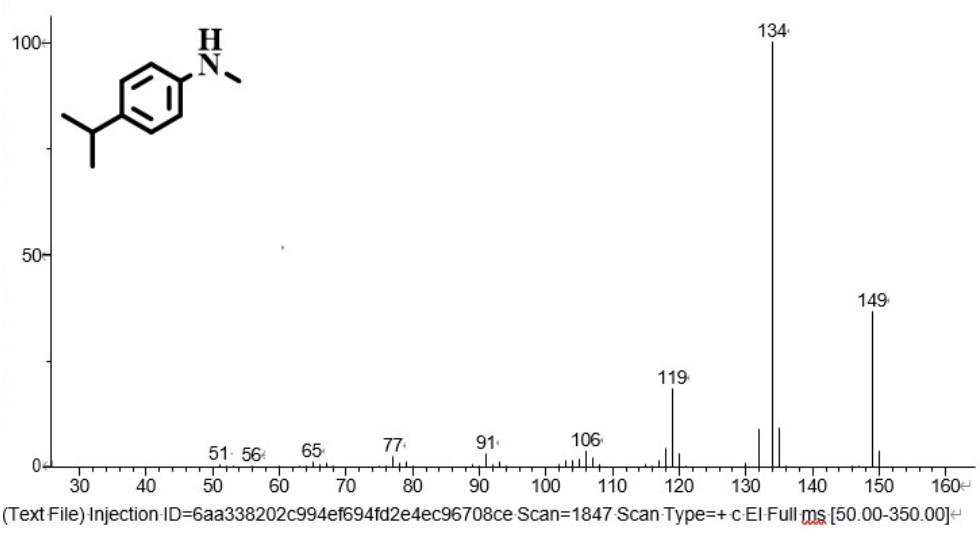


Figure S19. GC-MS spectra of the 4-isopropyl-N-methylaniline (5)

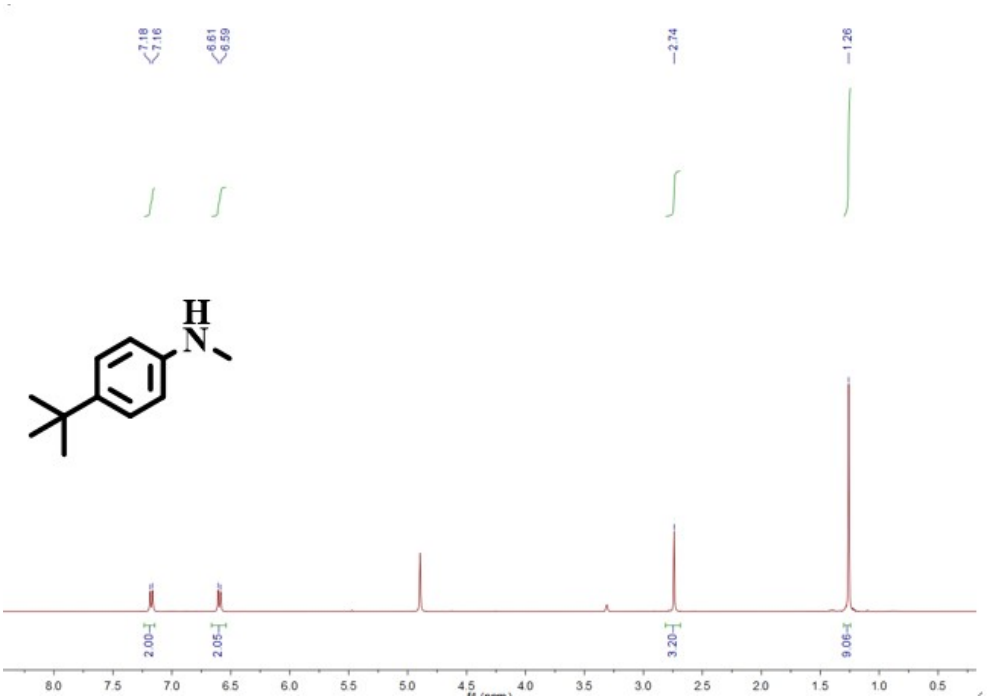


Figure S20. ^{1}H NMR spectrum of (4-tertbutylphenyl)-methylamine (6)

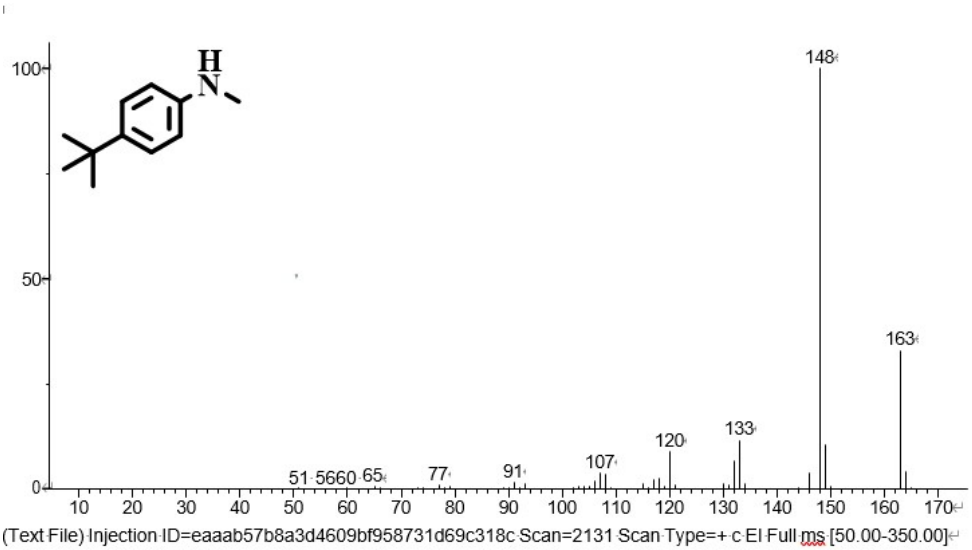


Figure S21. GC-MS spectra of the (4-tertbutylphenyl)-methylamine (6)

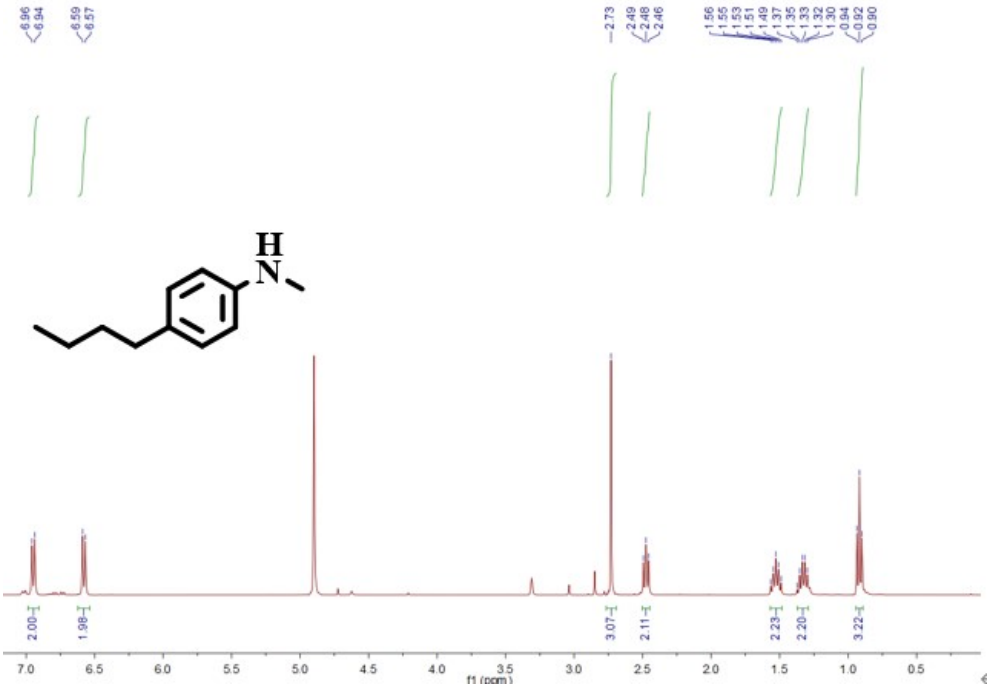


Figure S22. [1]H NMR spectrum of 4-butyl-N-methylaniline (7)

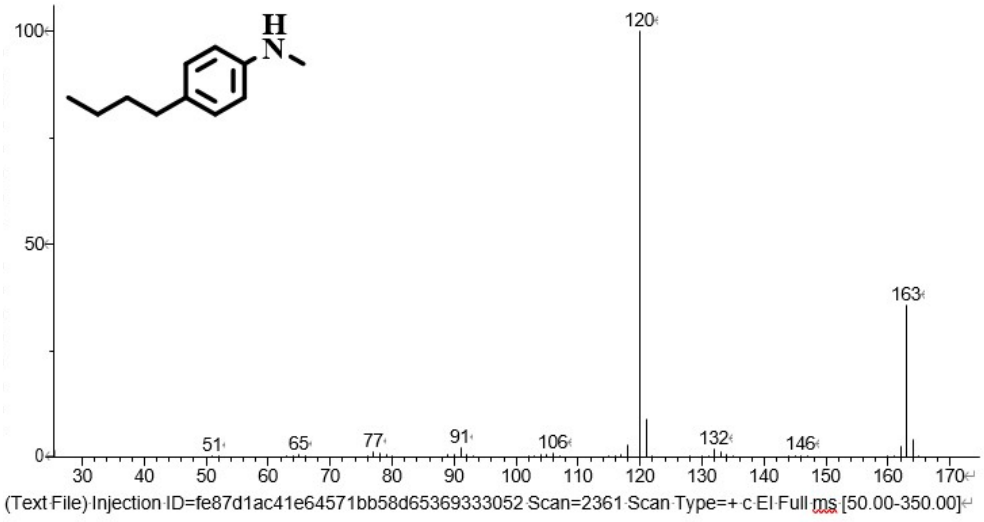


Figure S23. GC-MS spectra of the 4-butyl-N-methylaniline (7)

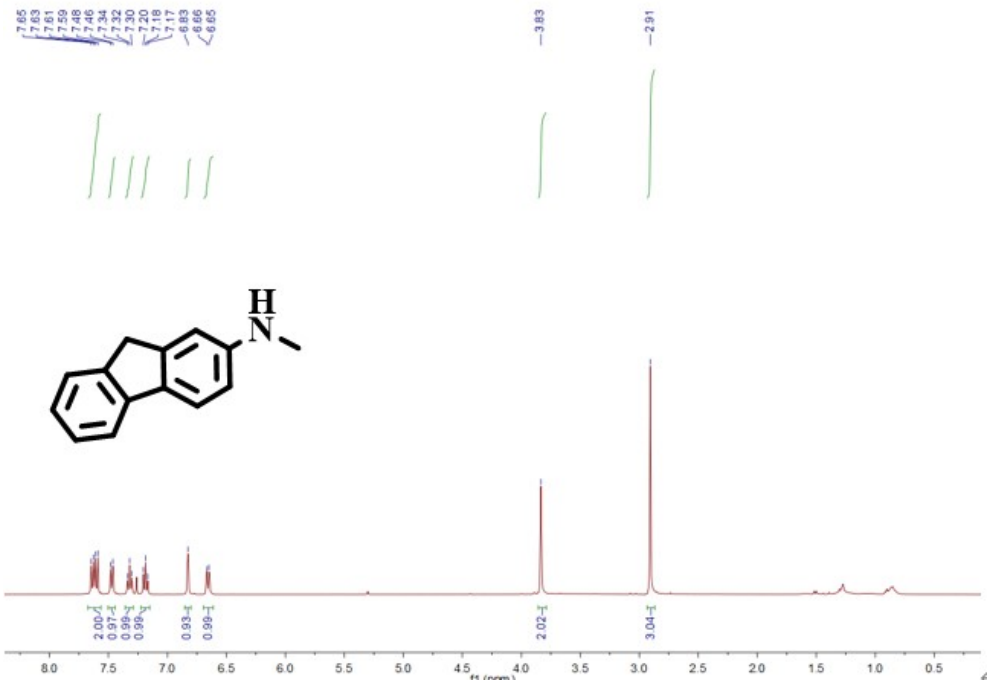


Figure S24. [1]H NMR spectrum of 2-Aminofluorene (8)

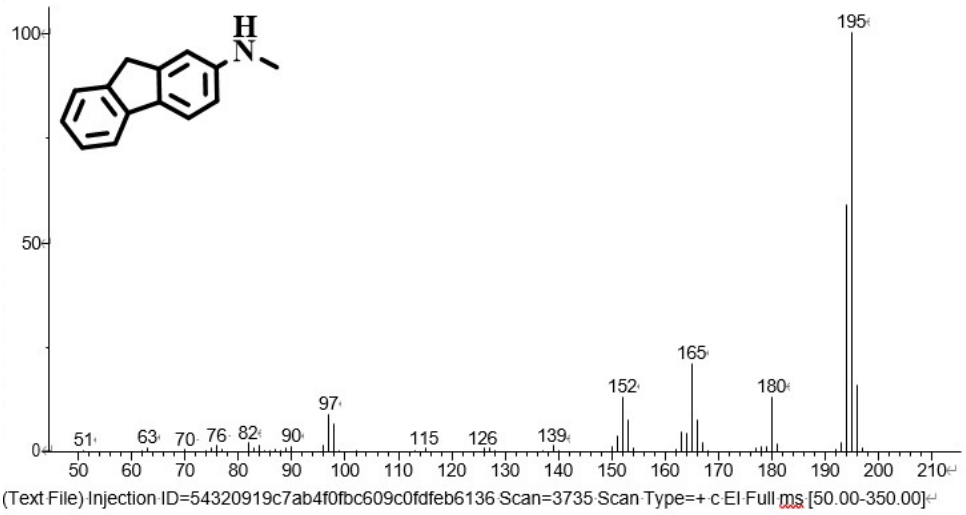


Figure S25. GC-MS spectra of the 2-Aminofluorene (8)

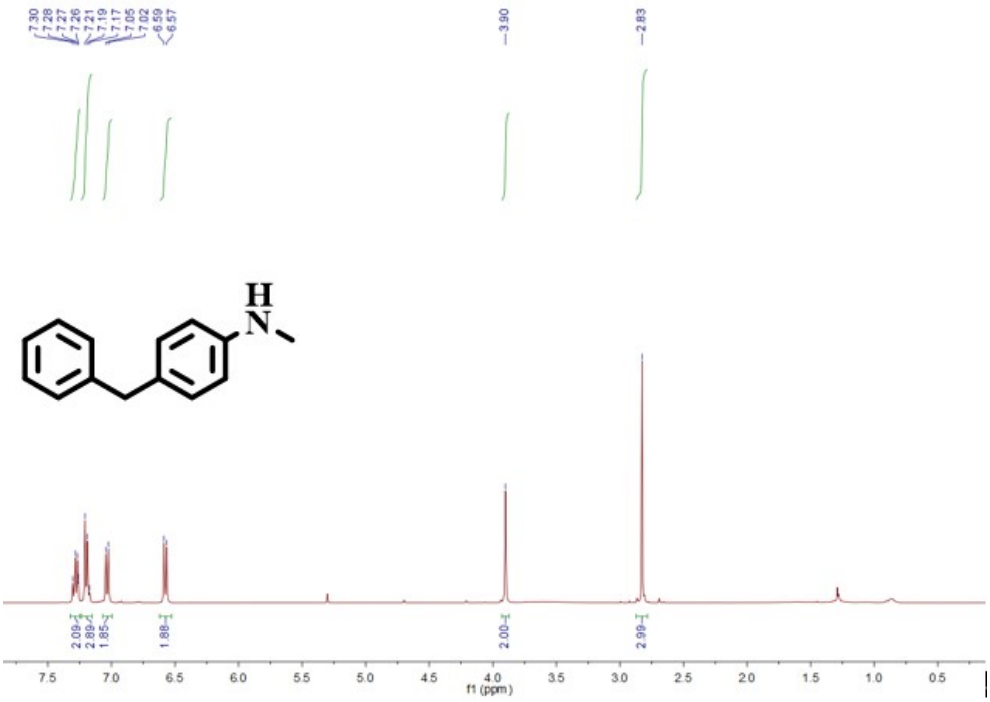


Figure S26. ^{1}H NMR spectrum of N-methyl-4-(phenylmethyl)benzenamine(9)

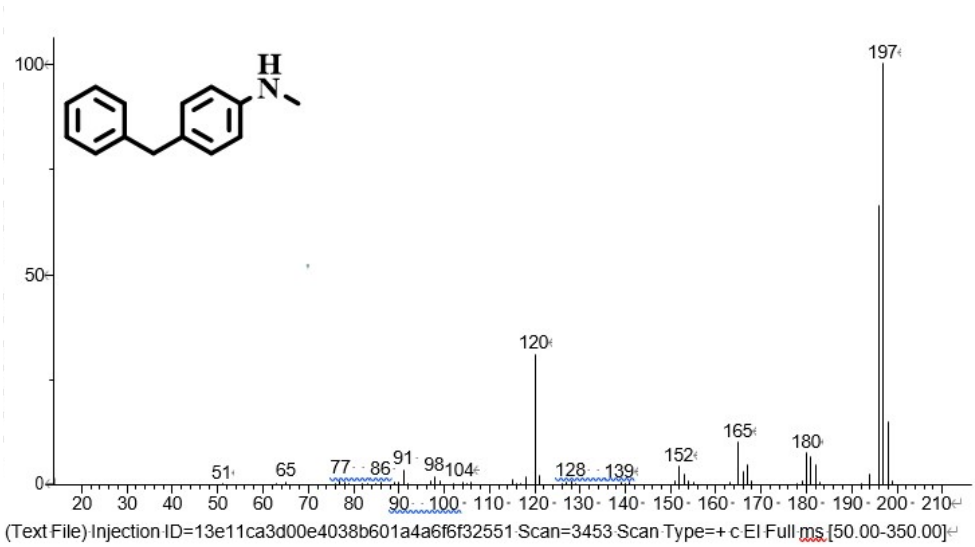


Figure S27. GC-MS spectra of the N-methyl-4-(phenylmethyl)benzenamine (9)

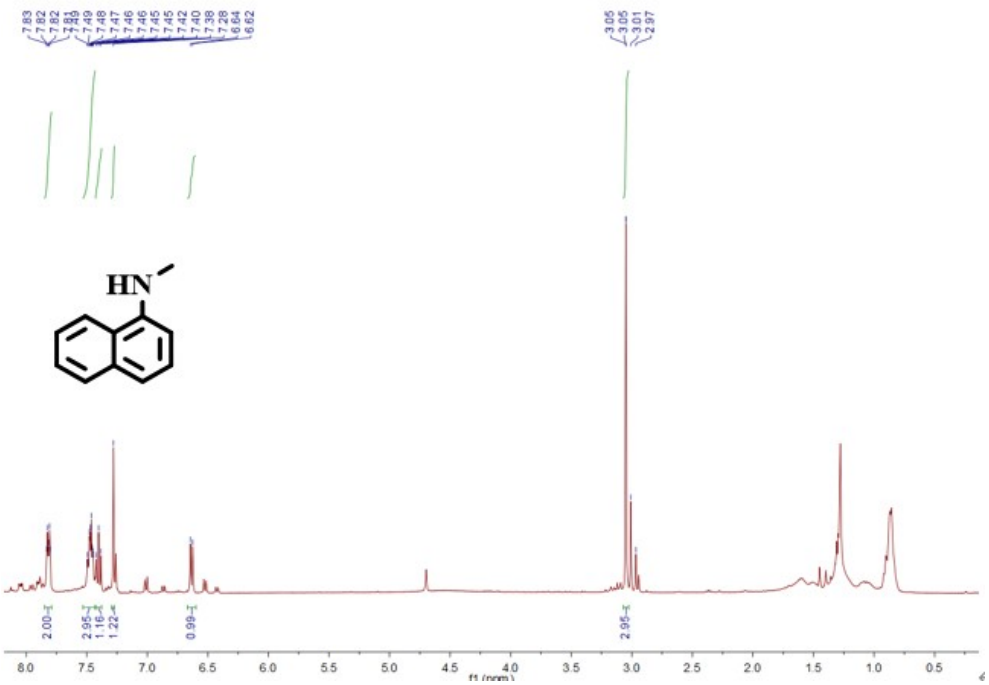


Figure S28. ^{1}H NMR spectrum of N-methylnaphthalen-1-amine (10)

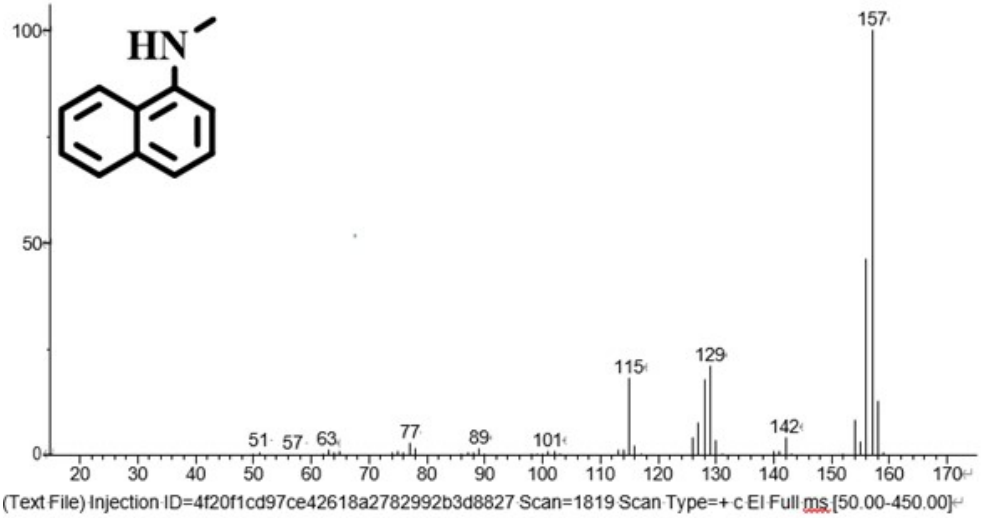


Figure S29. GC-MS spectra of the N-methylnaphthalen-1-amine (10)

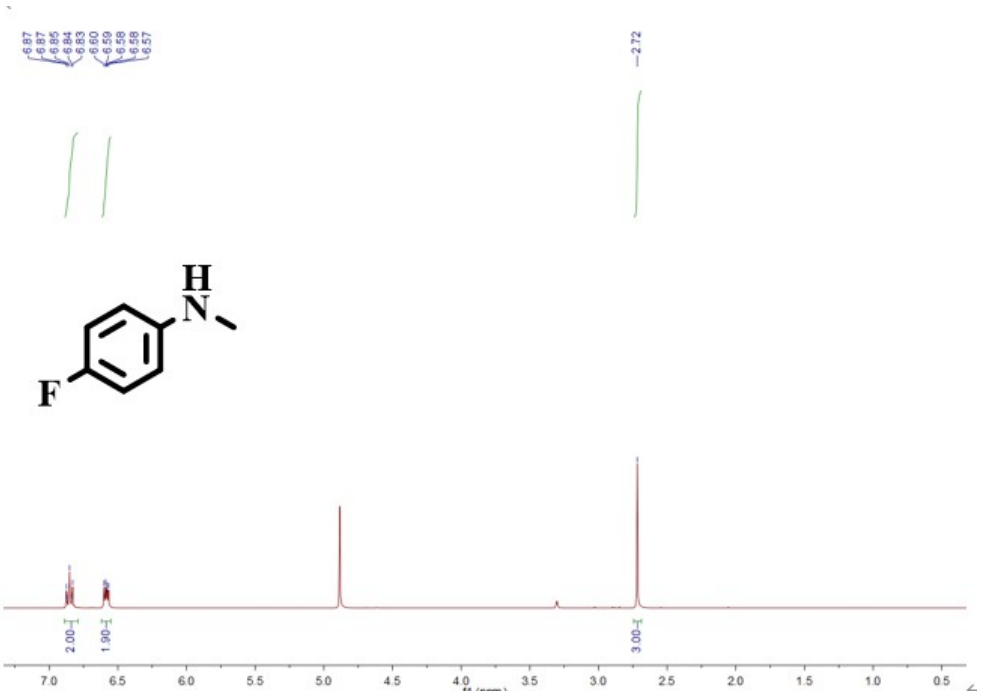


Figure S30. ^{1}H NMR spectrum of 4-fluoro-N-methylaniline (11)

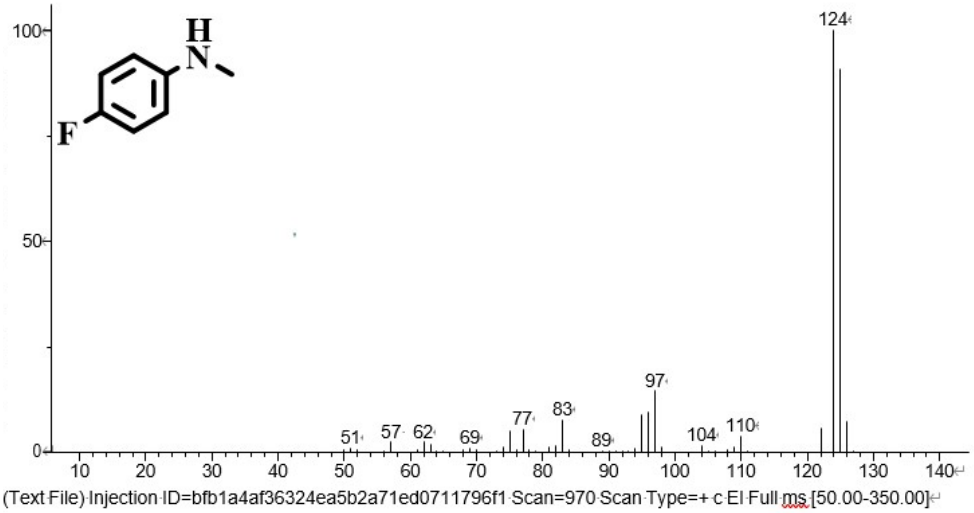


Figure S31. GC-MS spectra of the 4-fluoro-N-methylaniline (11)

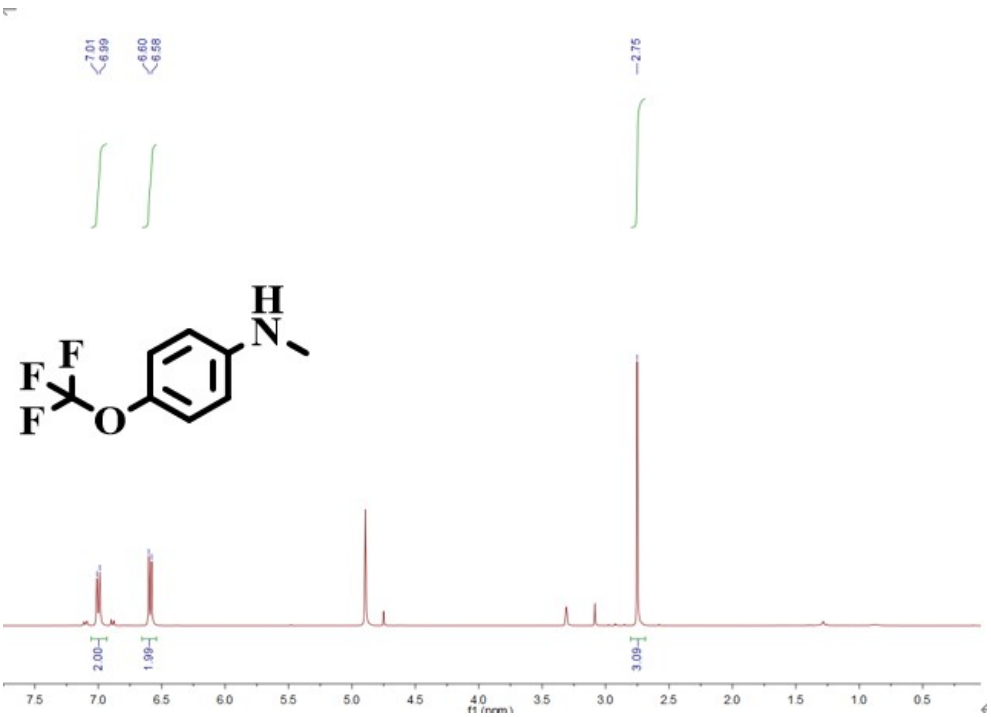


Figure S32. ^{1}H NMR spectrum of N-methyl-4-(trifluoromethoxy)aniline (12)

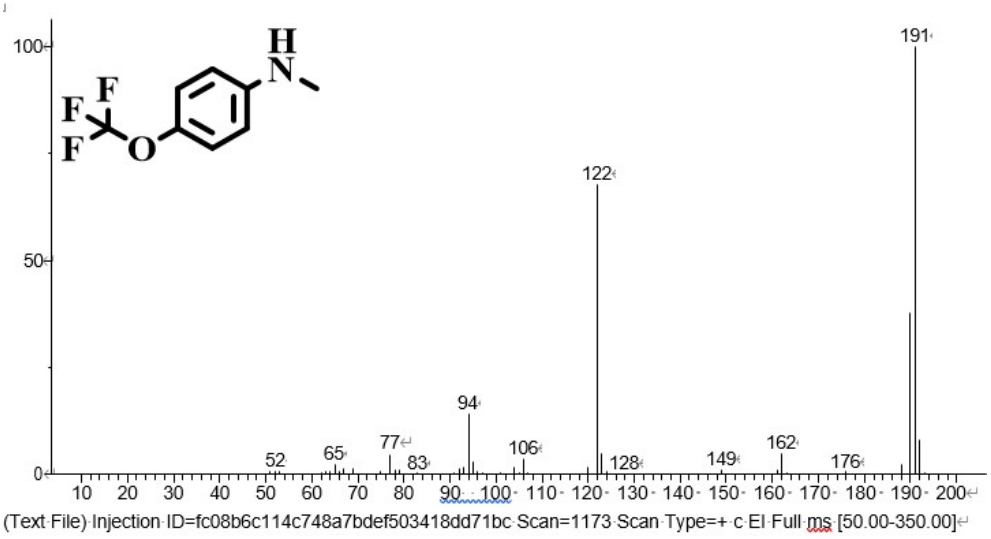


Figure S33. GC-MS spectra of the N-methyl-4-(trifluoromethoxy)aniline (12)

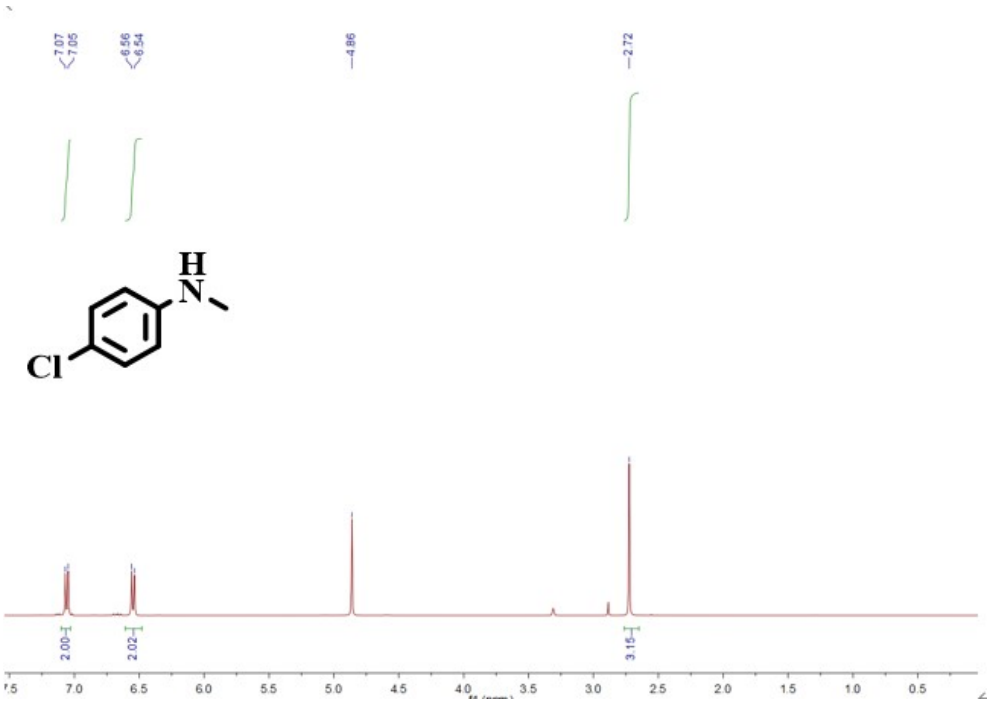


Figure S34. [1]H NMR spectrum of 4-chloro-N-methyl-anilin (13)

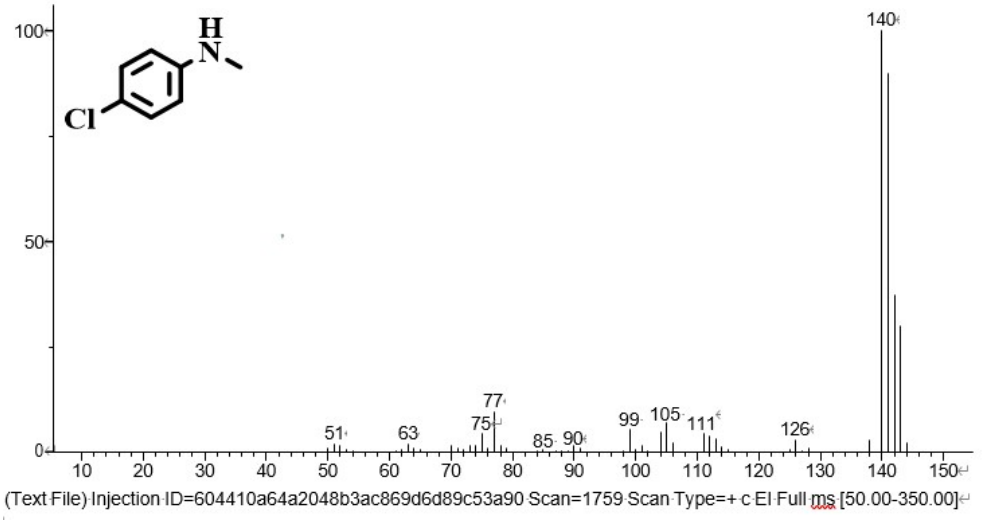


Figure S35. GC-MS spectra of the 4-chloro-N-methyl-anilin (13)

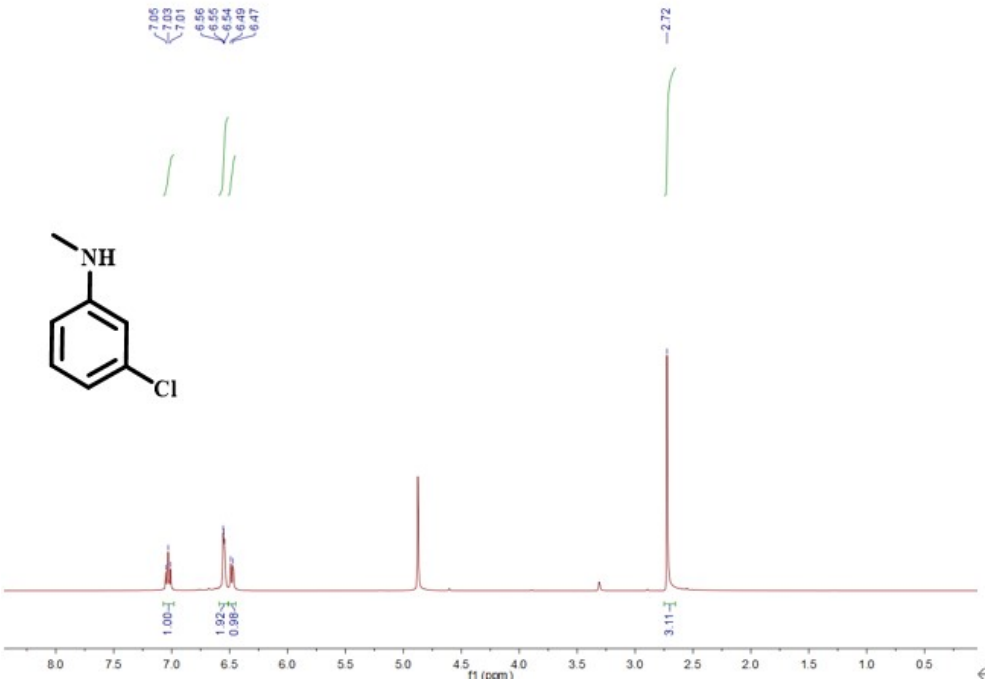


Figure S36. ^{1}H NMR spectrum of 3-chloro-N-methylaniline (14)

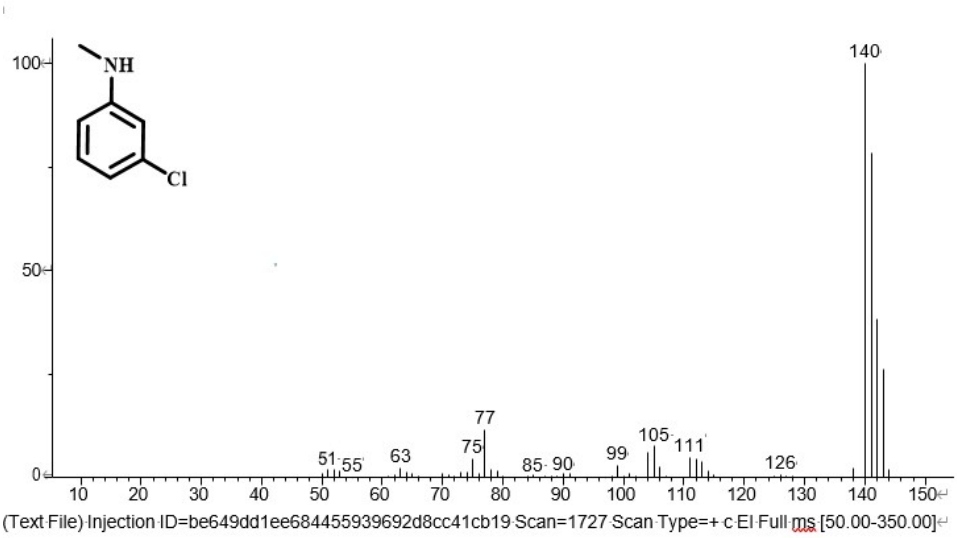


Figure S37. GC-MS spectra of the 3-chloro-N-methylaniline (14)

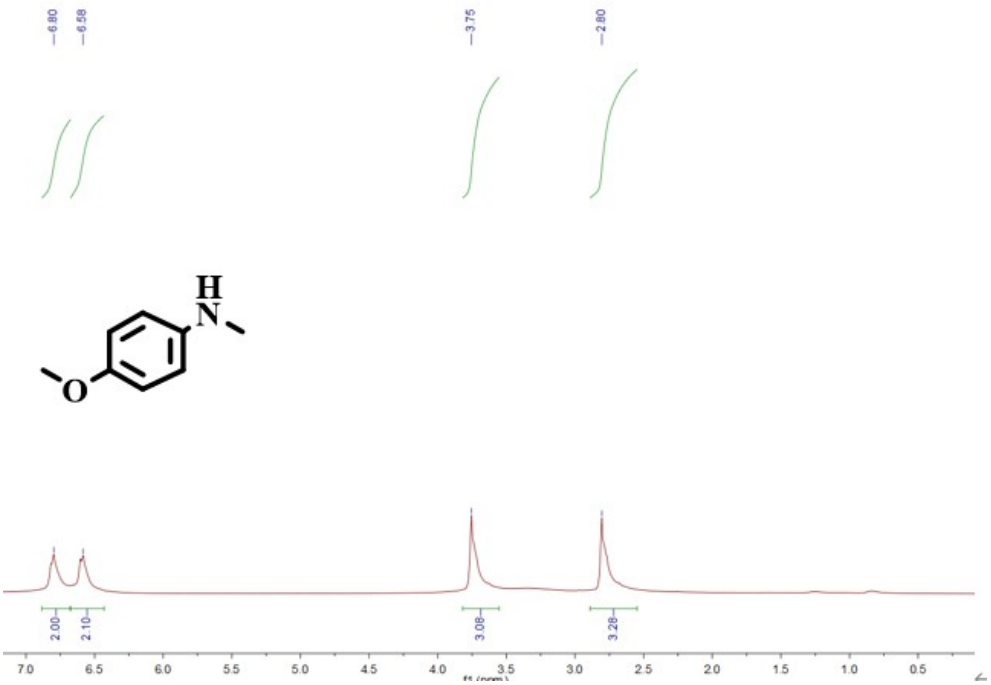


Figure S38. [1]H NMR spectrum of 4-methoxy-N-methylaniline (15)

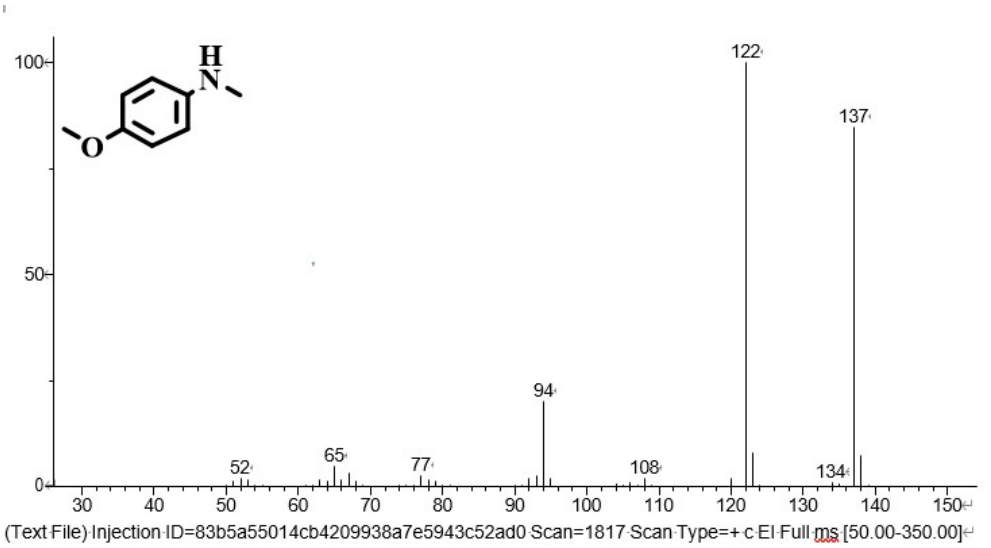


Figure S39. GC-MS spectra of the 4-methoxy-N-methylaniline (15)

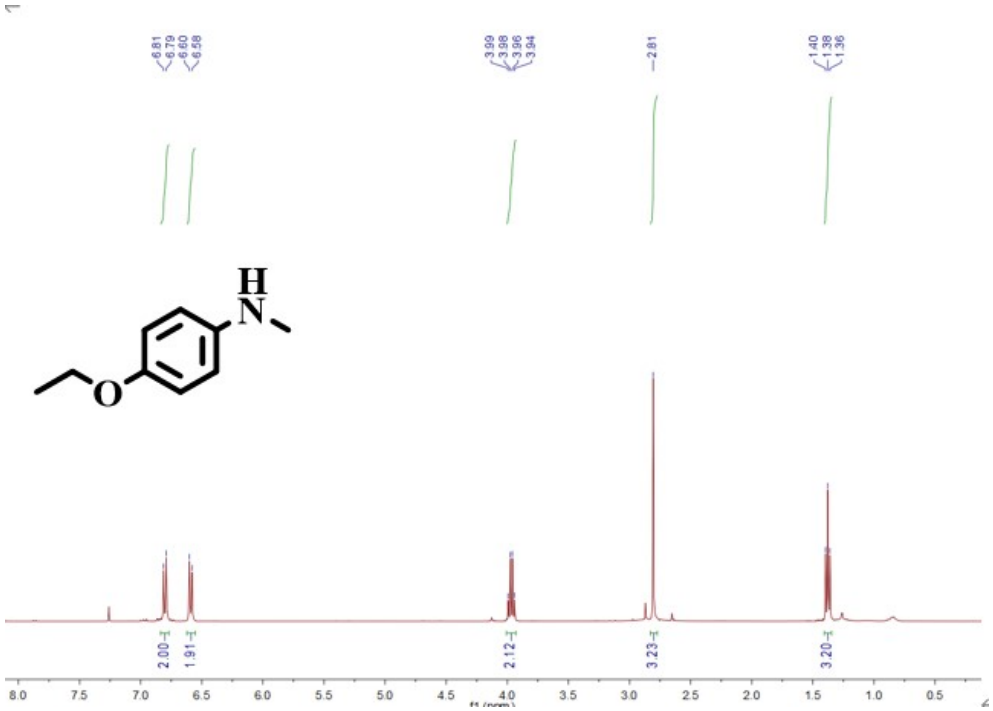


Figure S40. [1]H NMR spectrum of 4-ethoxy-N-methylaniline (16)

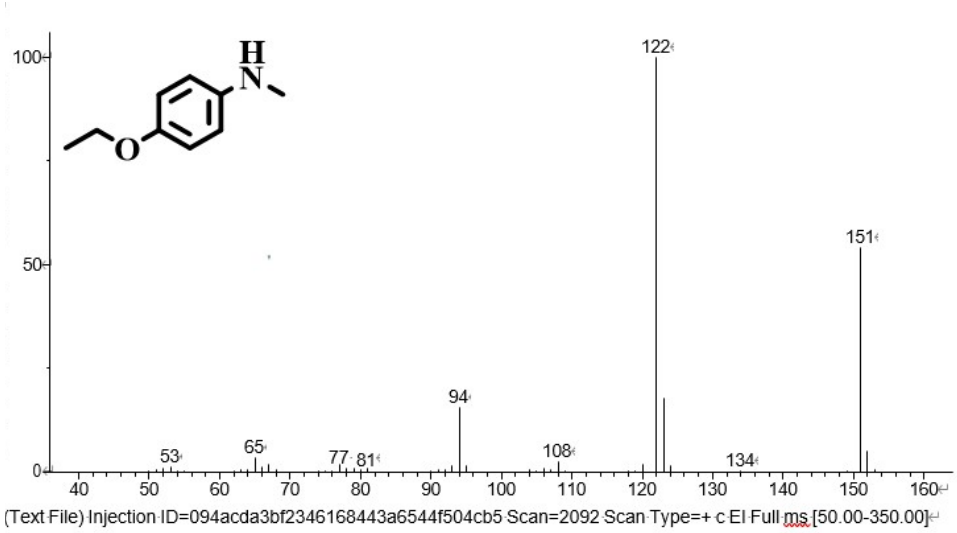


Figure S41. GC-MS spectra of the 4-ethoxy-N-methylaniline (16)

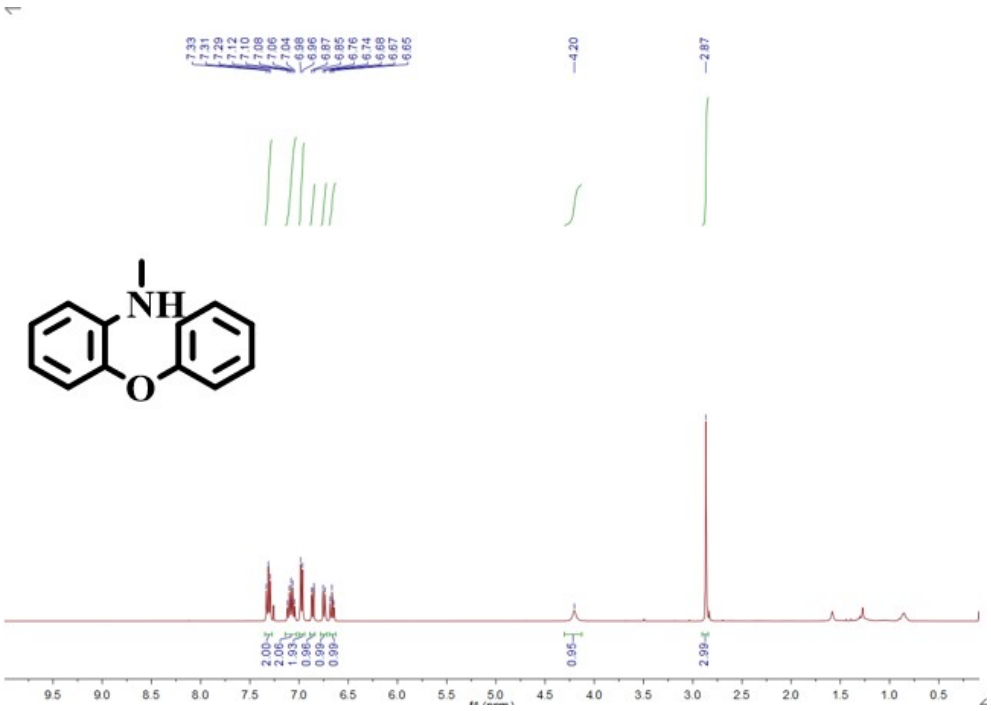


Figure S42. ^{1}H NMR spectrum of N-methyl-2-phenoxyaniline (17)

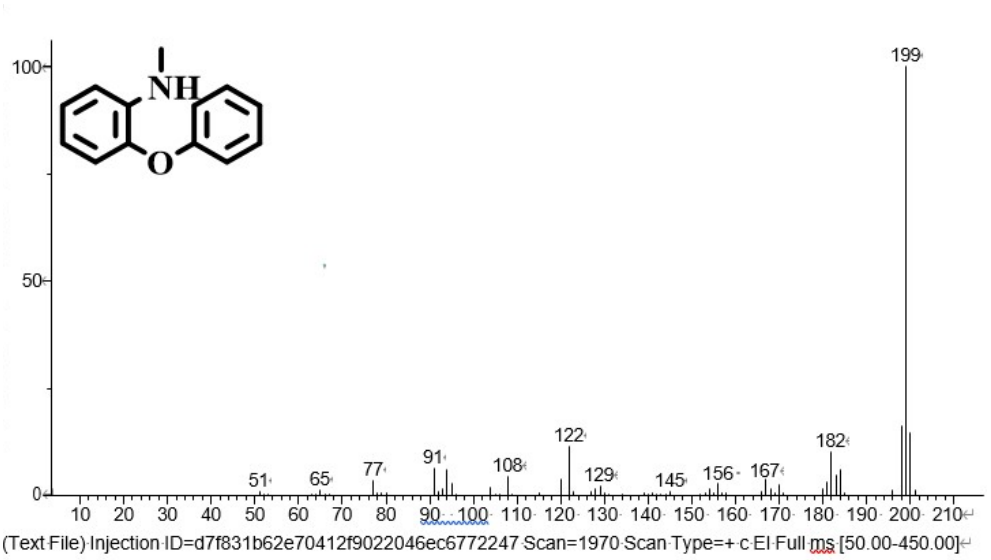


Figure S43. GC-MS spectra of the N-methyl-2-phenoxyaniline (17)

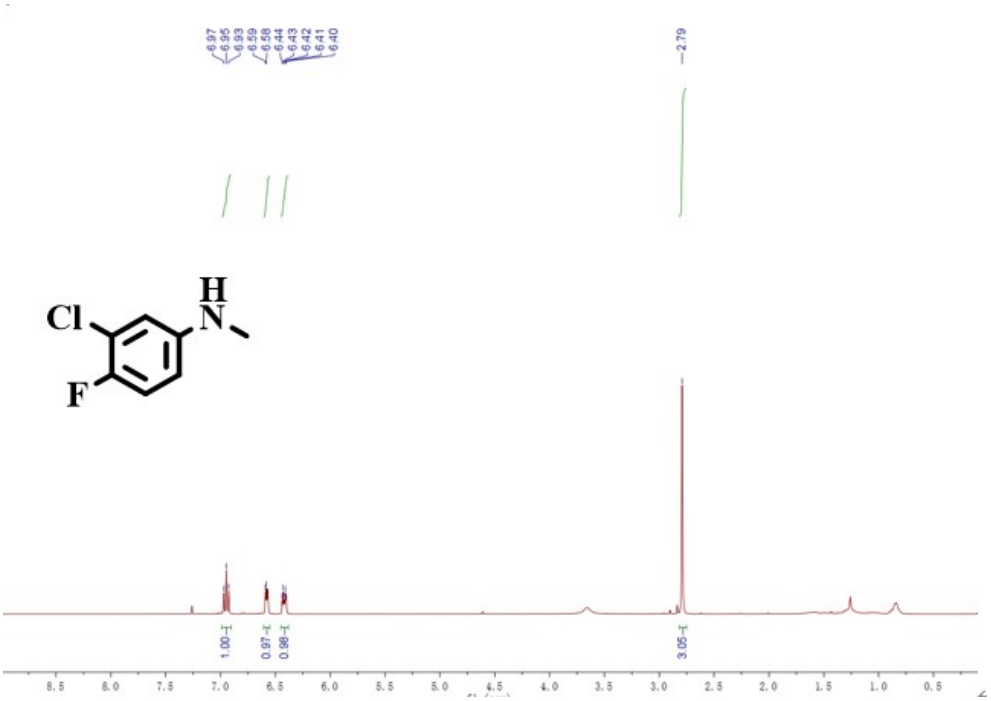


Figure S44. [1]H NMR spectrum of 3-chloro-4-fluoro-N-methylaniline (18)

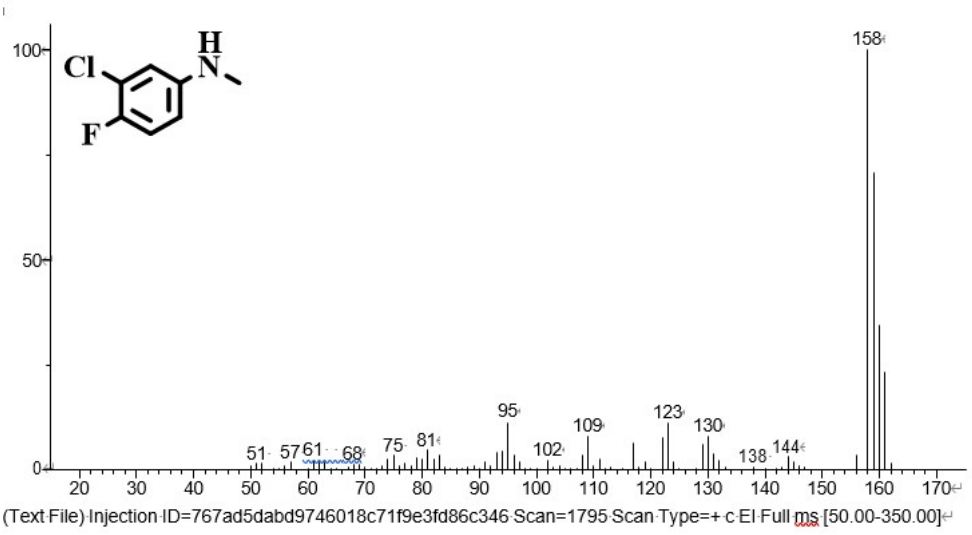


Figure S45. GC-MS spectra of the 3-chloro-4-fluoro-N-methylaniline (18)

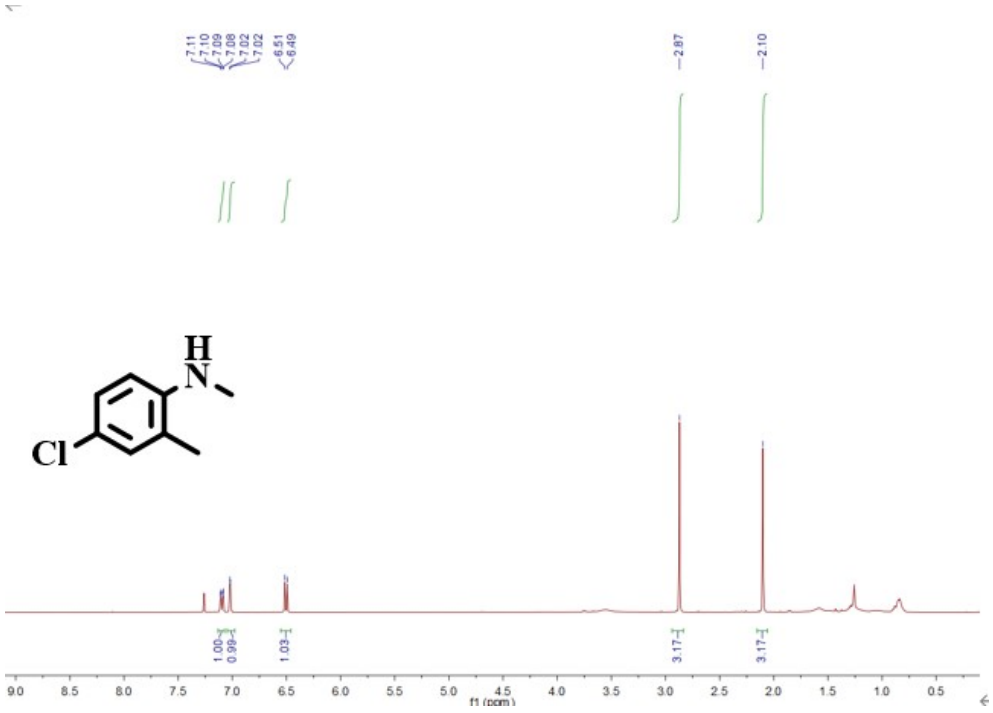


Figure S46. [1]H NMR spectrum of 4-chloro-N,2-dimethylaniline (19)

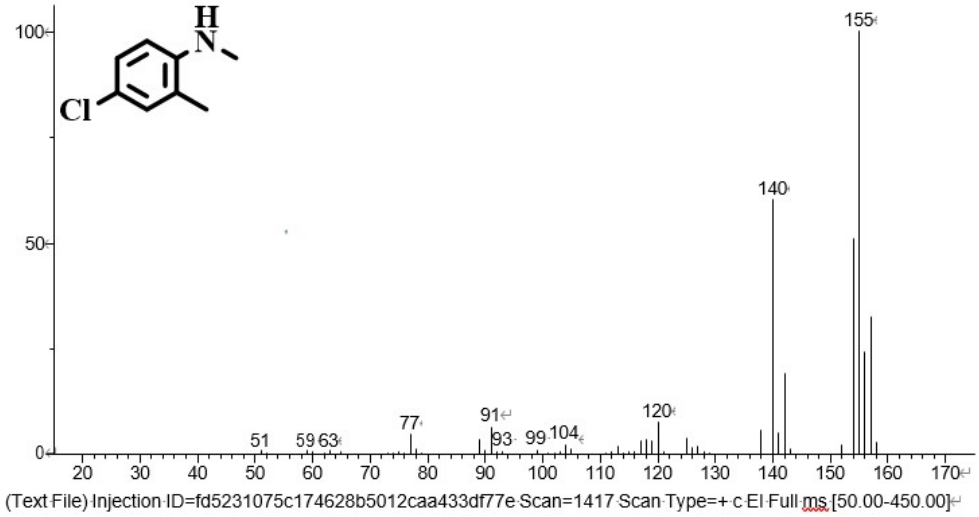


Figure S47. GC-MS spectra of the 4-chloro-N,2-dimethylaniline (19)

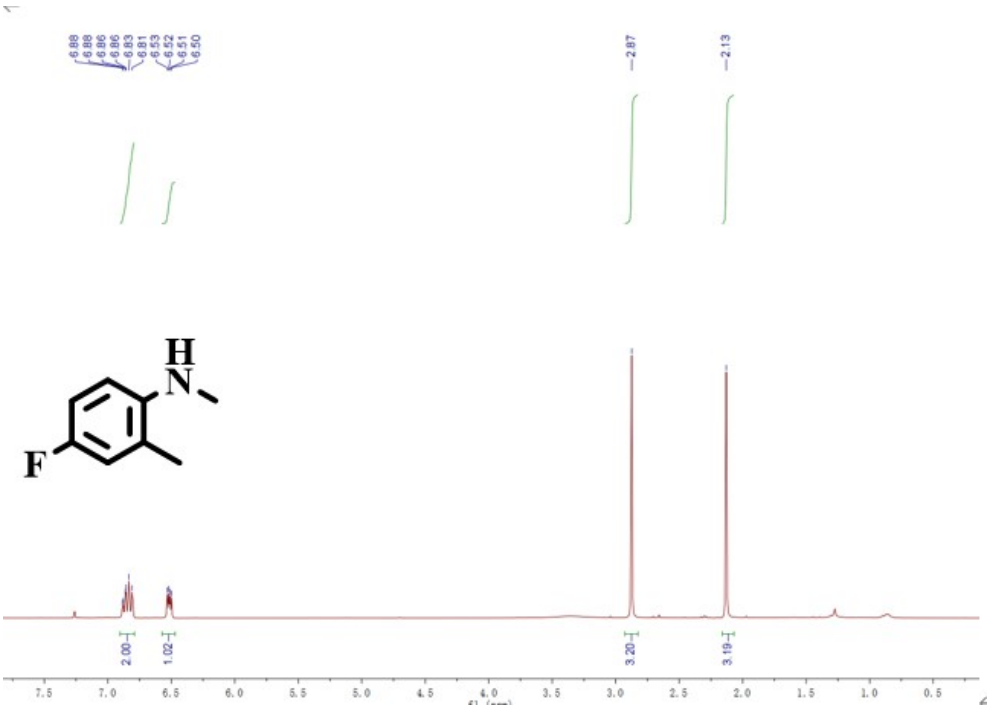


Figure S48. [1]H NMR spectrum of 4-fluoro-N,2-dimethylaniline (20)

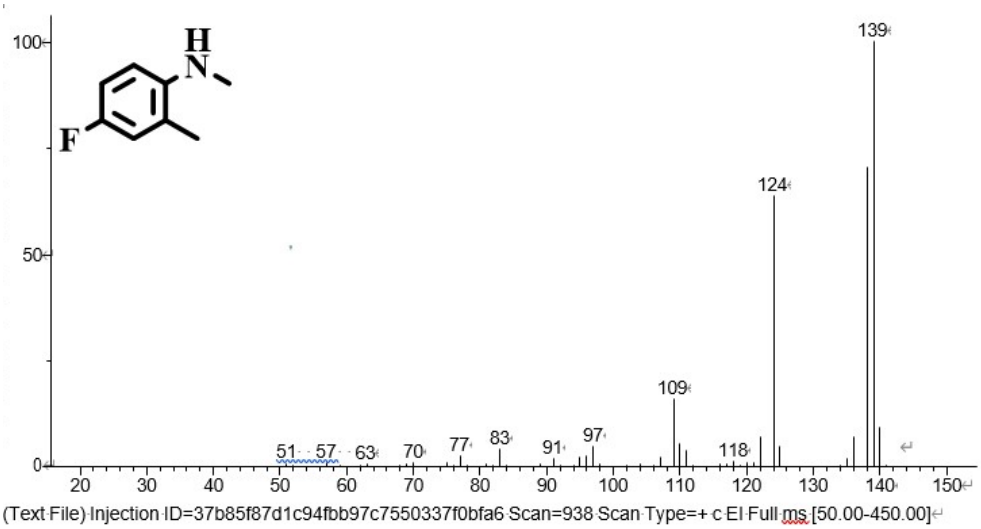


Figure S49. GC-MS spectra of the 4-fluoro-N,2-dimethylaniline (20)

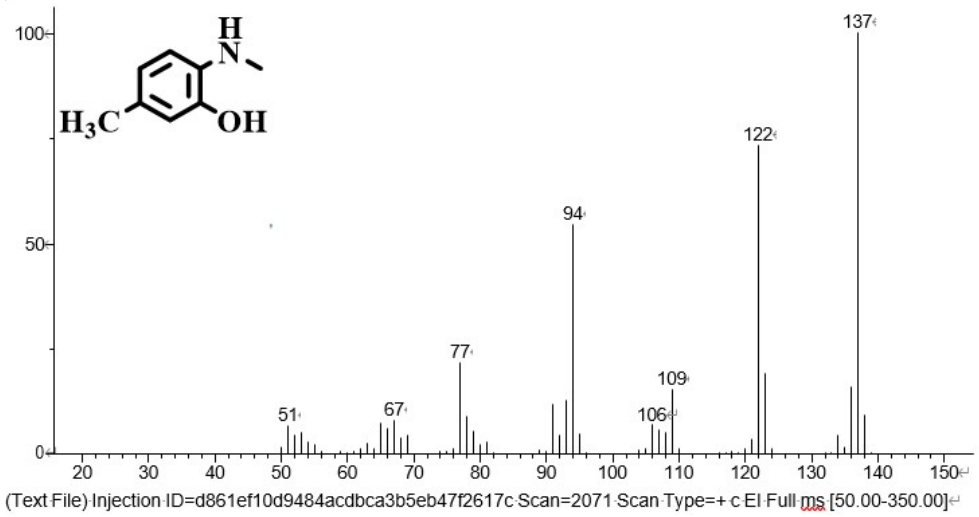


Figure S50. GC-MS spectra of the 5-methyl-2-(methylamino)phenol (21)

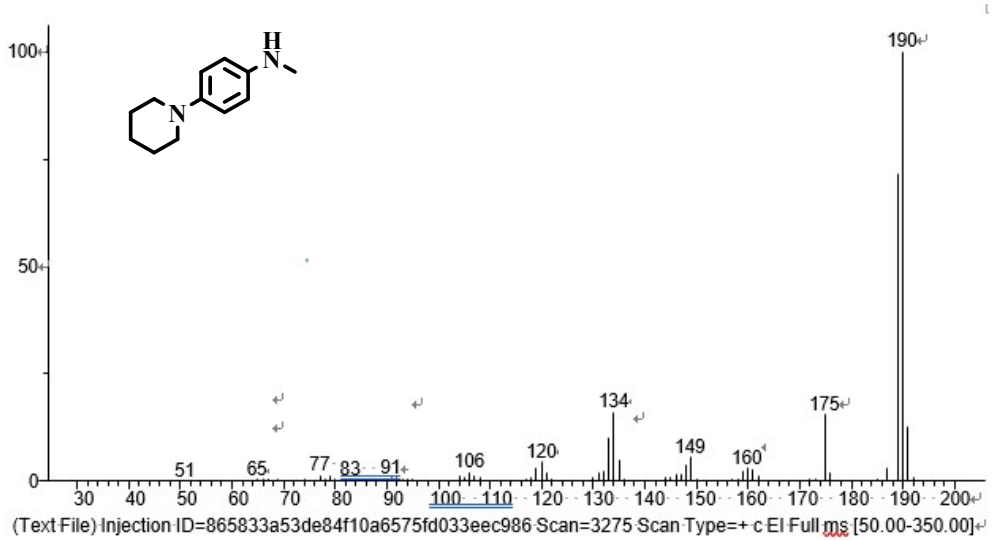


Figure S51. GC-MS spectra of the N-methyl-4-(piperidin-1-yl)aniline (22)

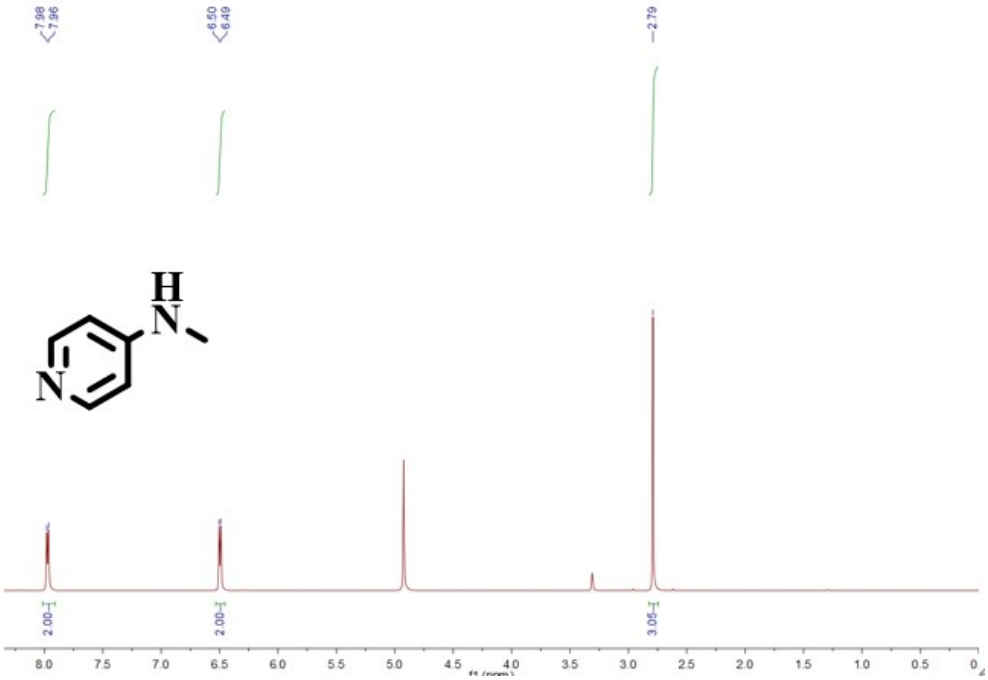


Figure S52. ^{1}H NMR spectrum of N-methyl-4-pyridinamine (23)

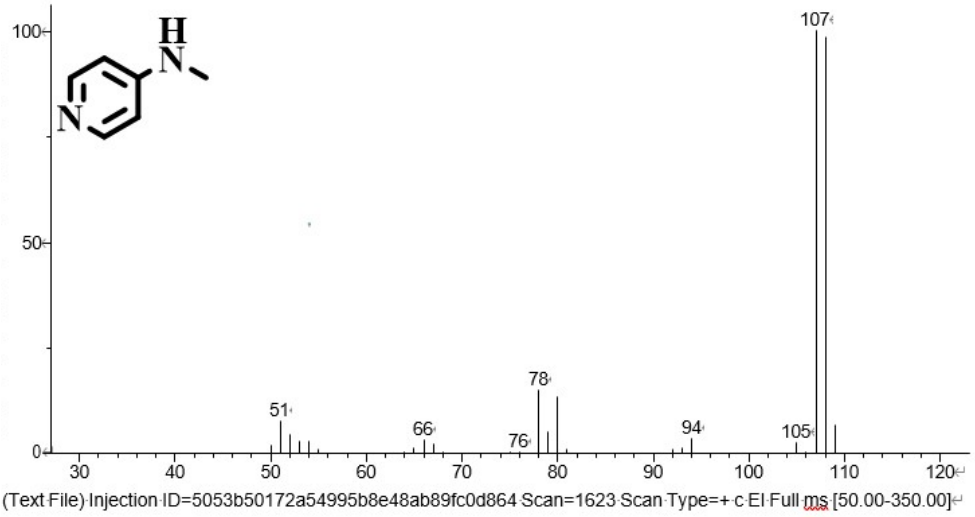


Figure S53. GC-MS spectra of the N-methyl-4-pyridinamine (23)

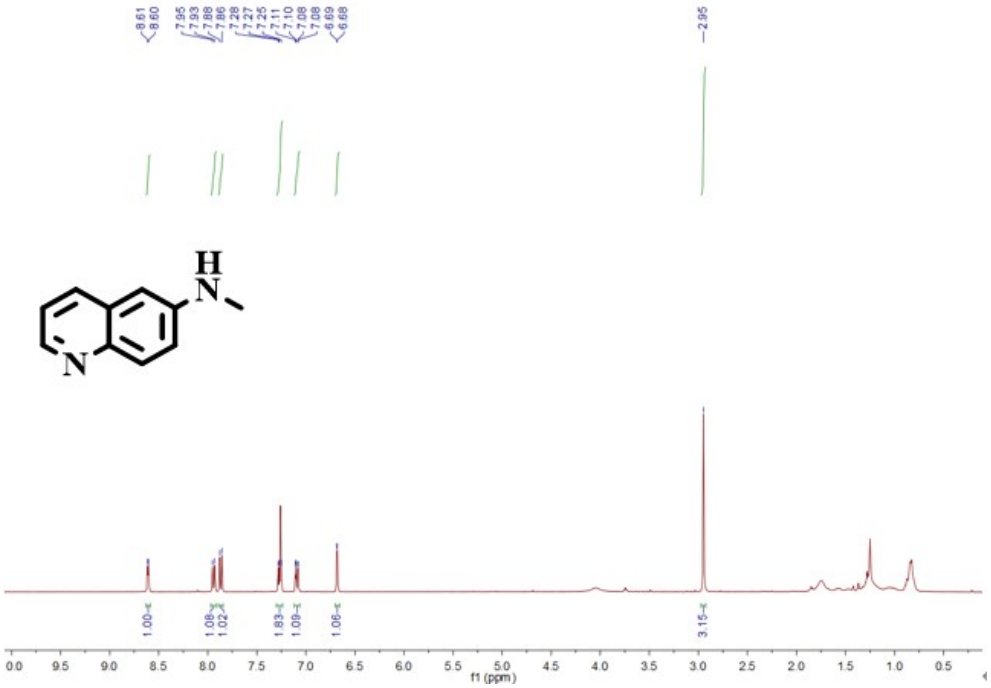


Figure S54. [1]H NMR spectrum of N-methylquinolin-6-amine (24)

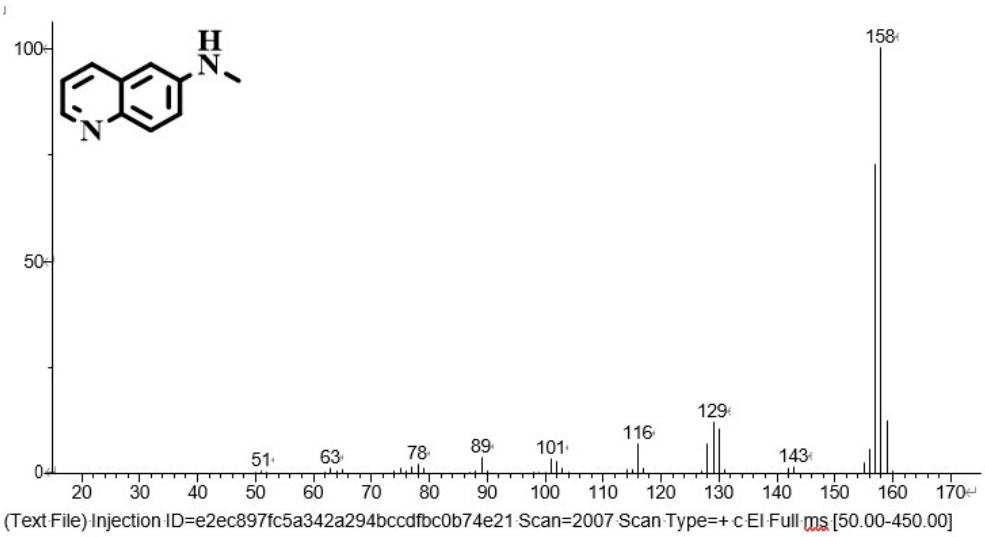


Figure S55. GC-MS spectra of the N-methylquinolin-6-amine (24)

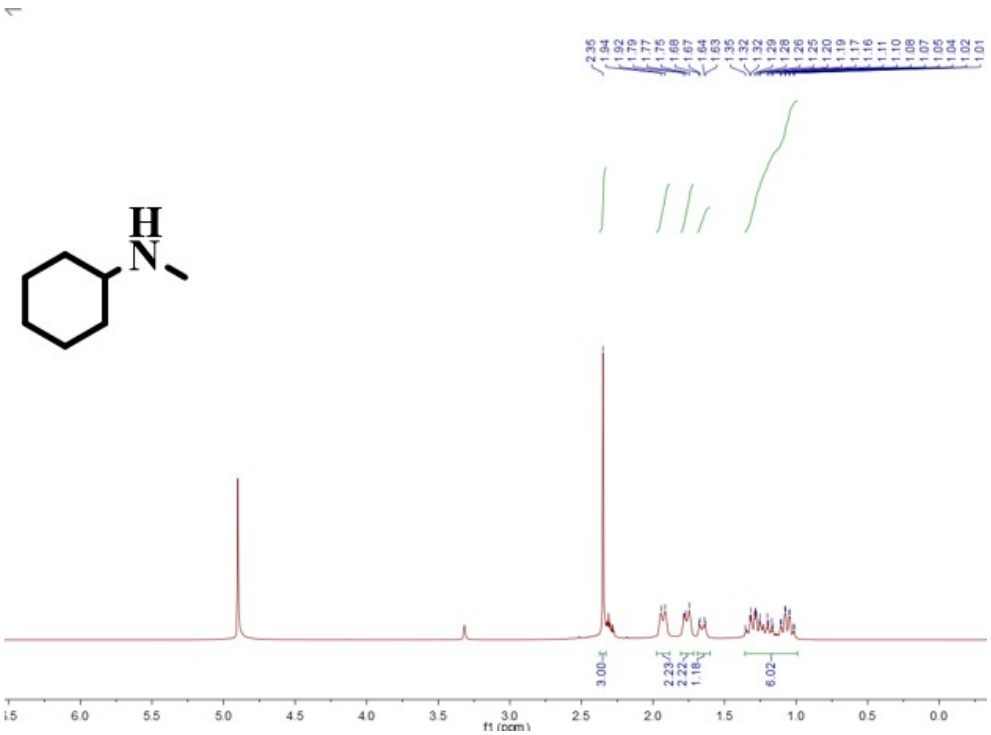


Figure S56. ^{1}H NMR spectrum of N-methylcyclohexanamine (25)

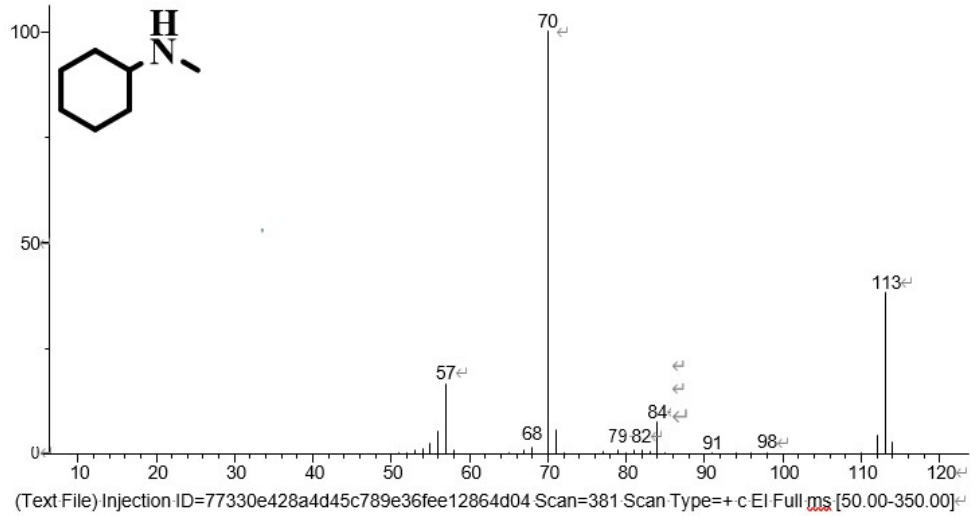


Figure S57. GC-MS spectra of the N-methylcyclohexanamine (25)

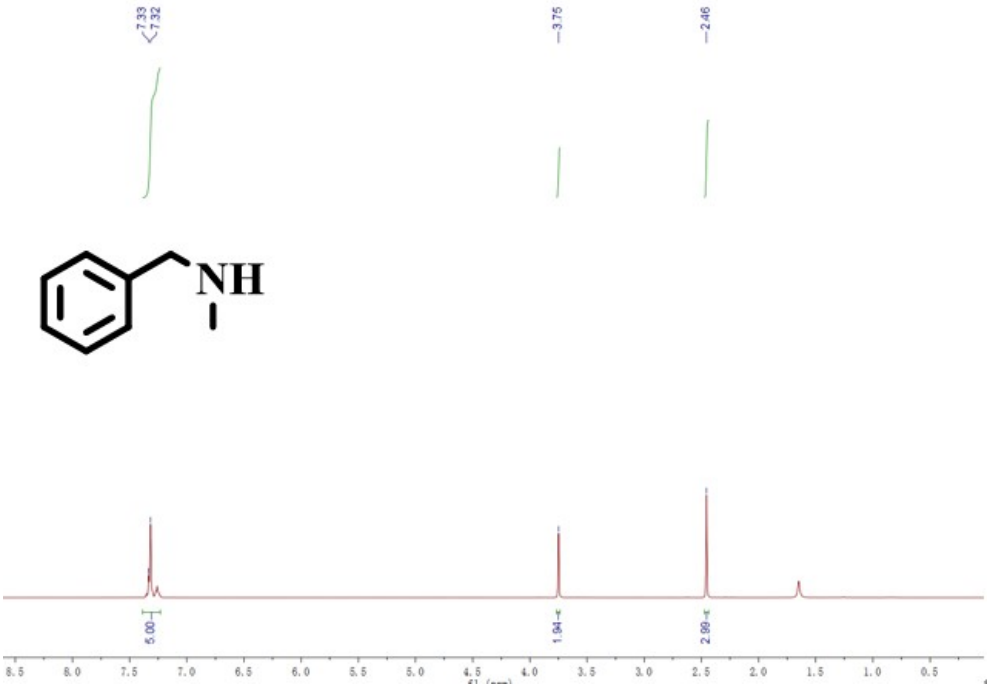


Figure S58. ^{1}H NMR spectrum of N-methylbenzylamine (26)

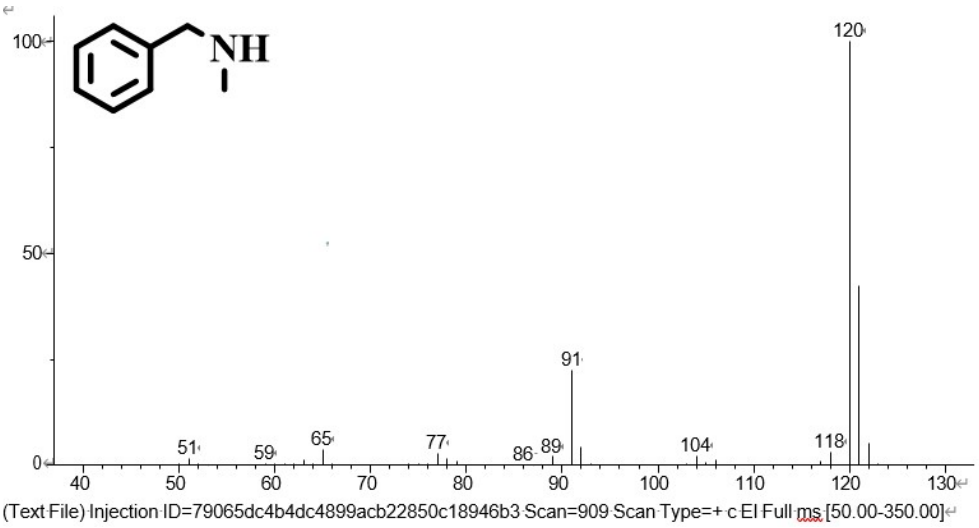


Figure S59. GC-MS spectra of the N-methylbenzylamine (26)

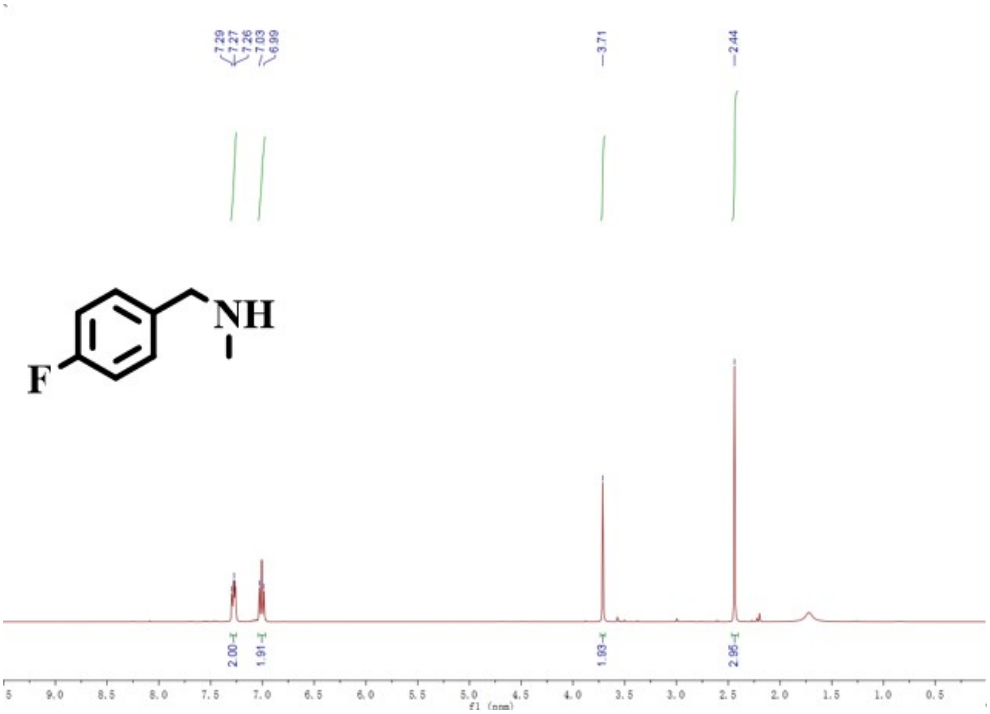


Figure S60 ^{1}H NMR spectrum of 4-fluoro-N-methylbenzylamine (27)

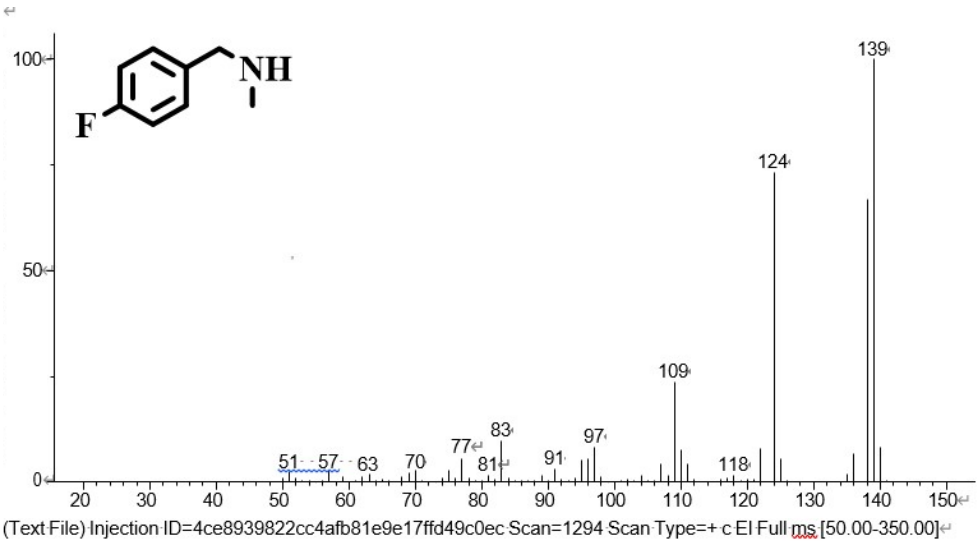


Figure S61. GC-MS spectra of the 4-fluoro-N-methylbenzylamine (27)

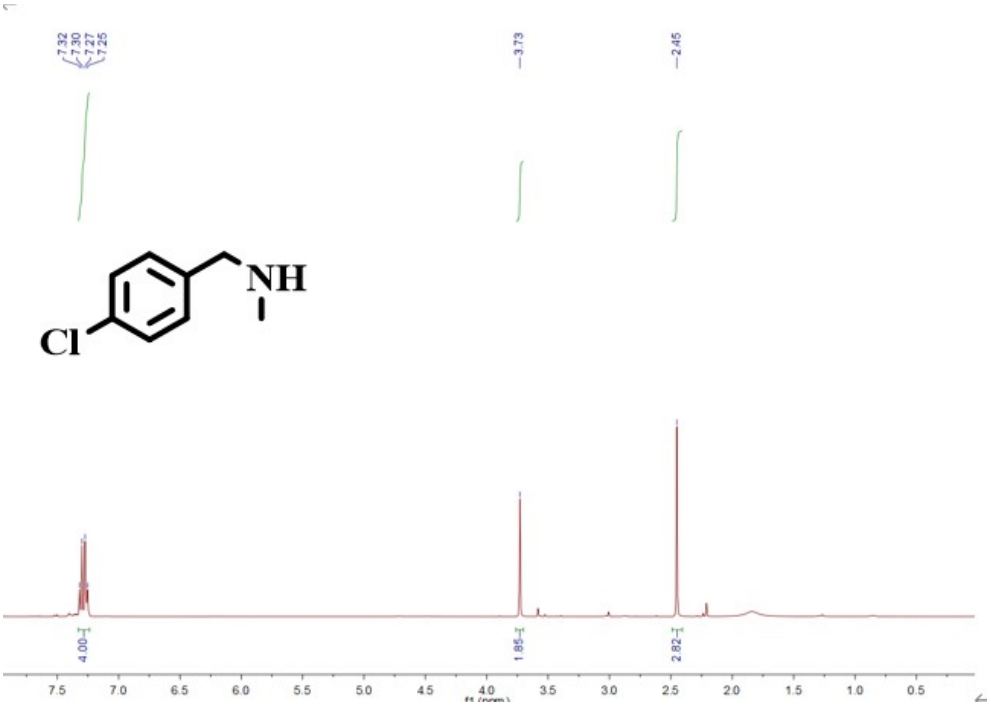


Figure S62. [1]H NMR spectrum of 4-chloro-N-methylbenzylamine (28)

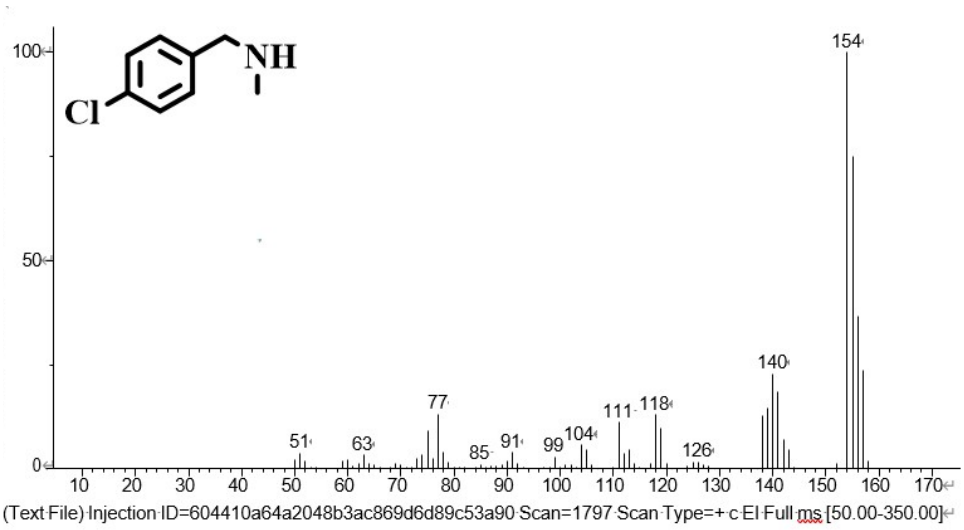


Figure S63. GC-MS spectra of the 4-chloro-N-methylbenzylamine (28)

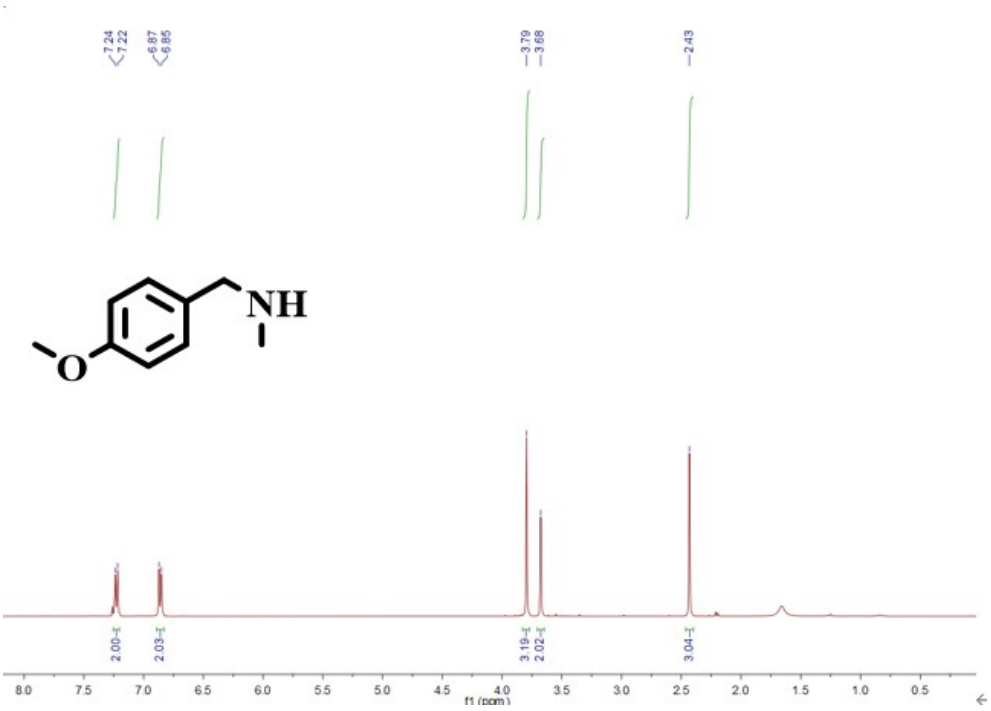


Figure S64. [1]H NMR spectrum of N-(4-methoxybenzyl)-N-methylamine (29)

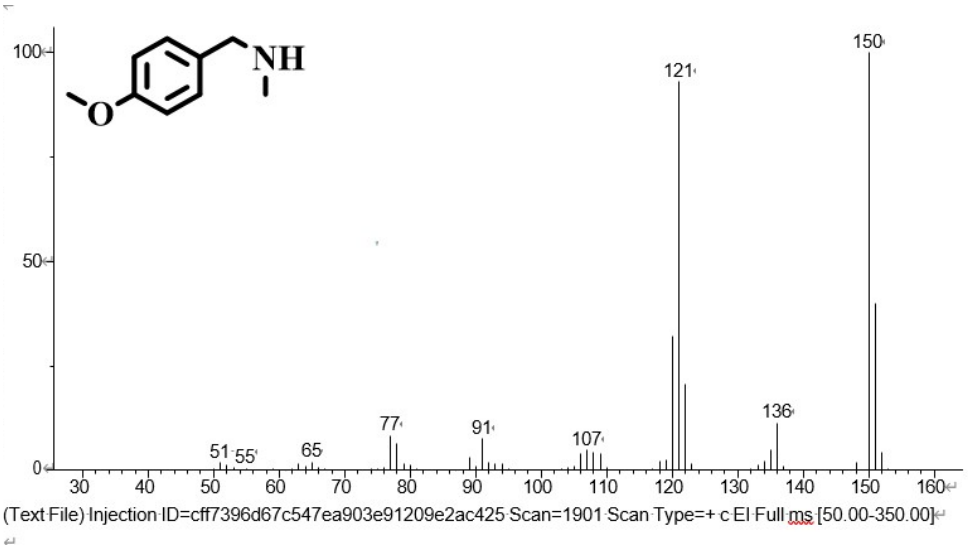


Figure S65. GC-MS spectra of the N-(4-methoxybenzyl)-N-methylamine (29)

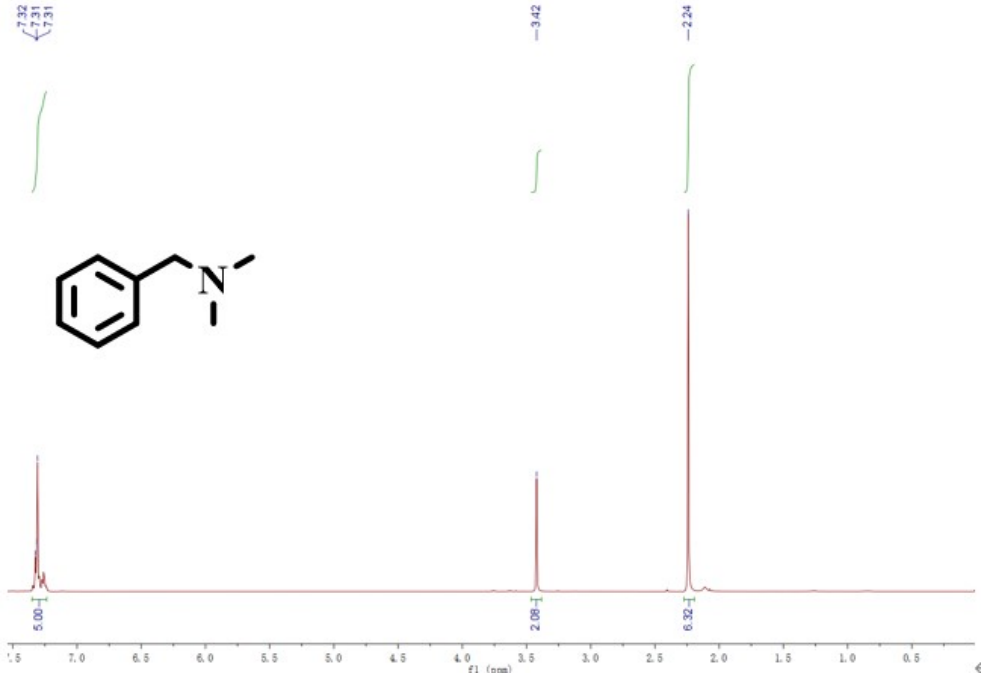
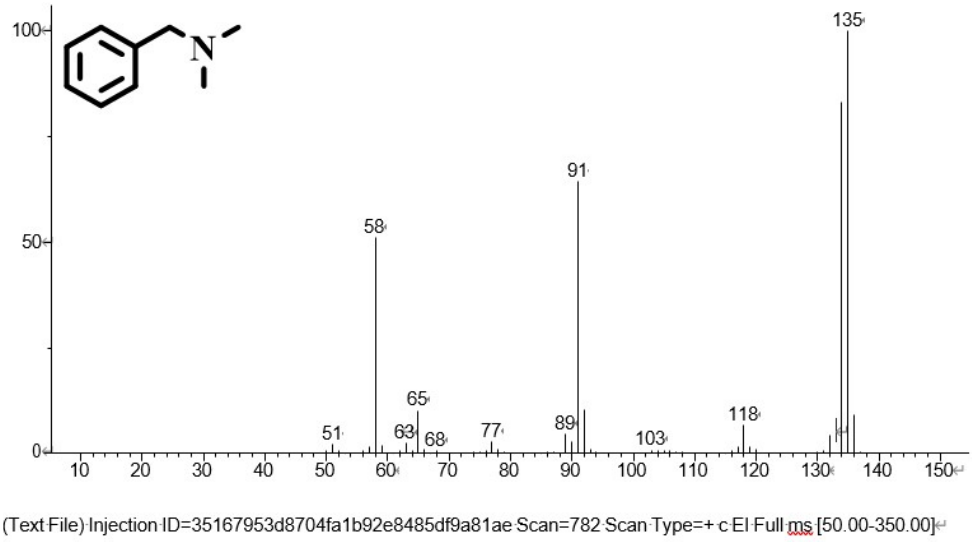


Figure S66. ^{1}H NMR spectrum of N,N-dimethylbenzylamine (30)



(Text File) Injection ID=35167953d8704fa1b92e8485df9a81ae Scan=782 Scan Type=+ c EI Full ms [50.00-350.00]

Figure S67. GC-MS spectra of the N,N-dimethylbenzylamine (30)

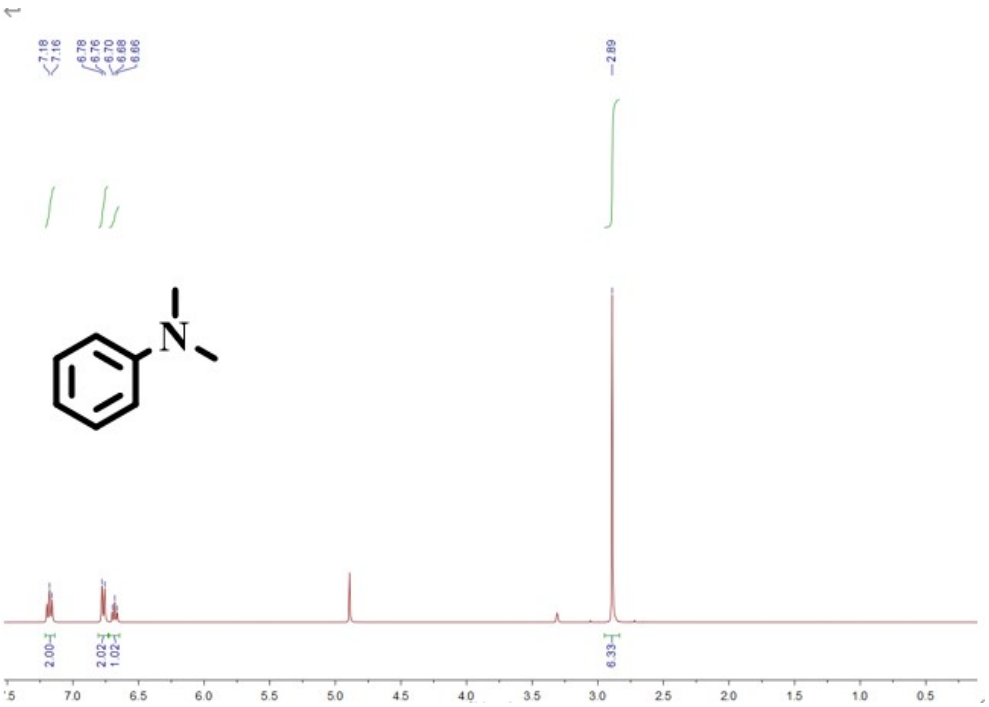


Figure S68. ^{1}H NMR spectrum of N, N-dimethylaniline (31)

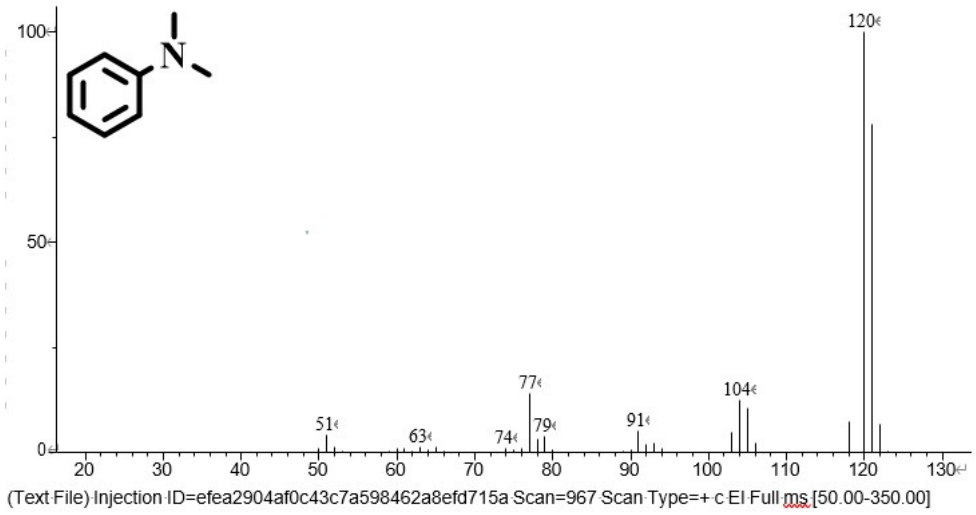


Figure S69. GC-MS spectra of the N, N-dimethylaniline (31)

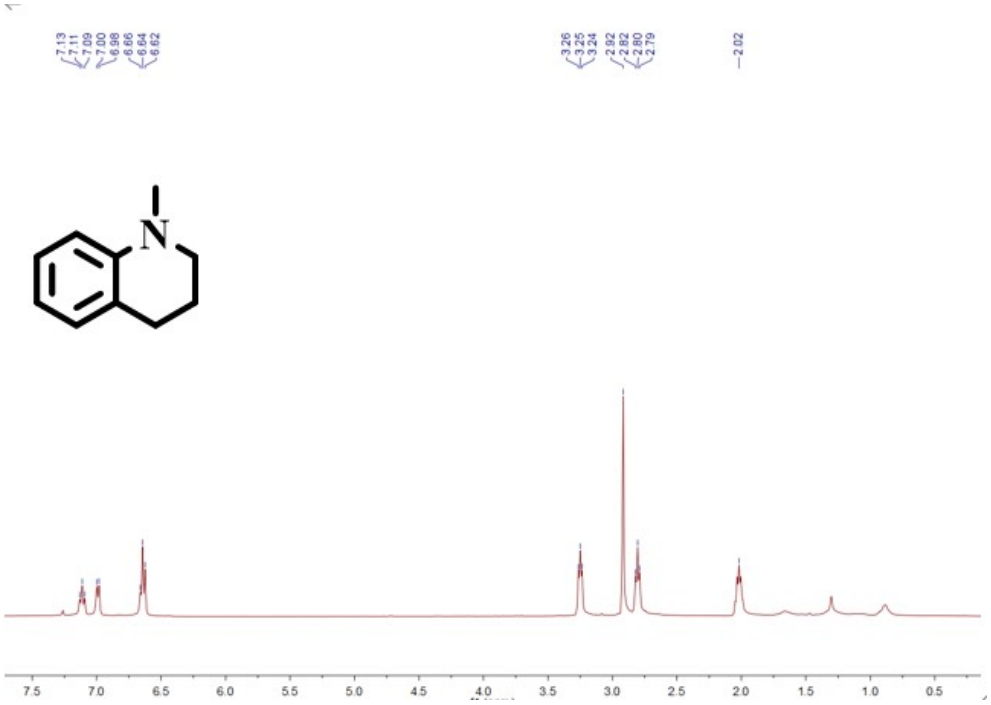


Figure S70. [1]H NMR spectrum of 1-methyl-1,2,3,4-tetrahydroquinoline (32)

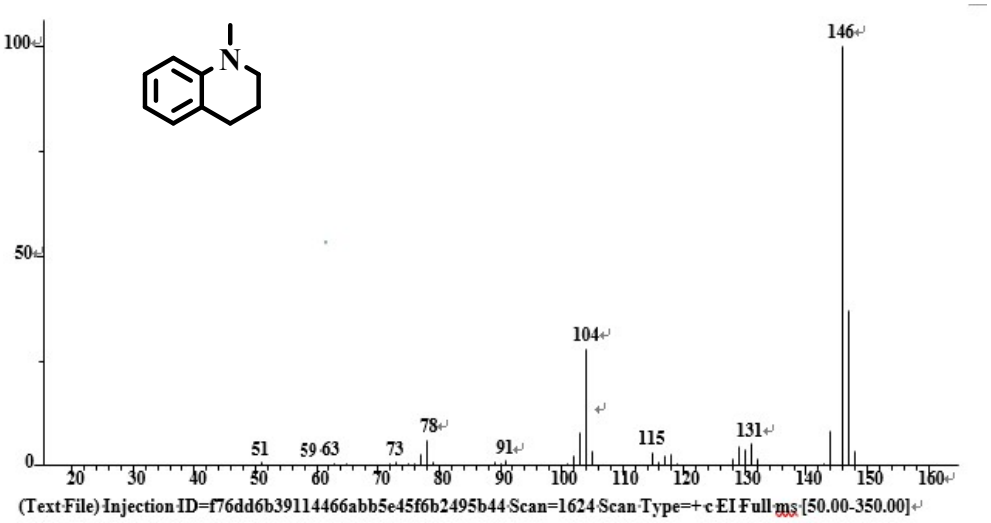


Figure S71. GC-MS spectra of the 1-methyl-1,2,3,4-tetrahydroquinoline (32)

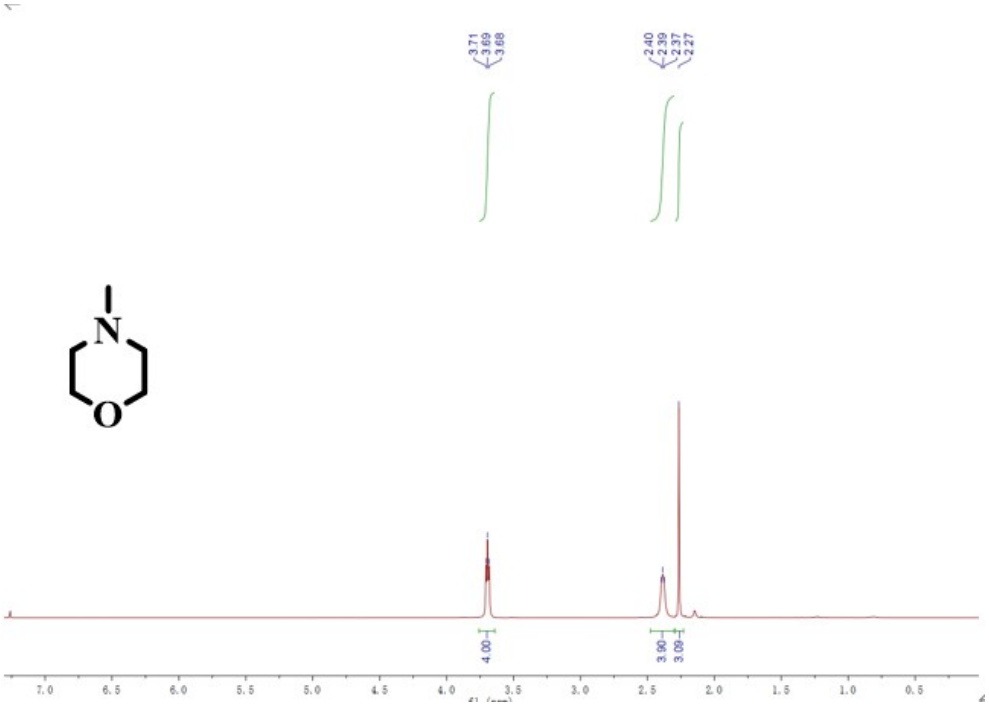


Figure S72. ^{1}H NMR spectrum of 4-methylmorpholine (33)

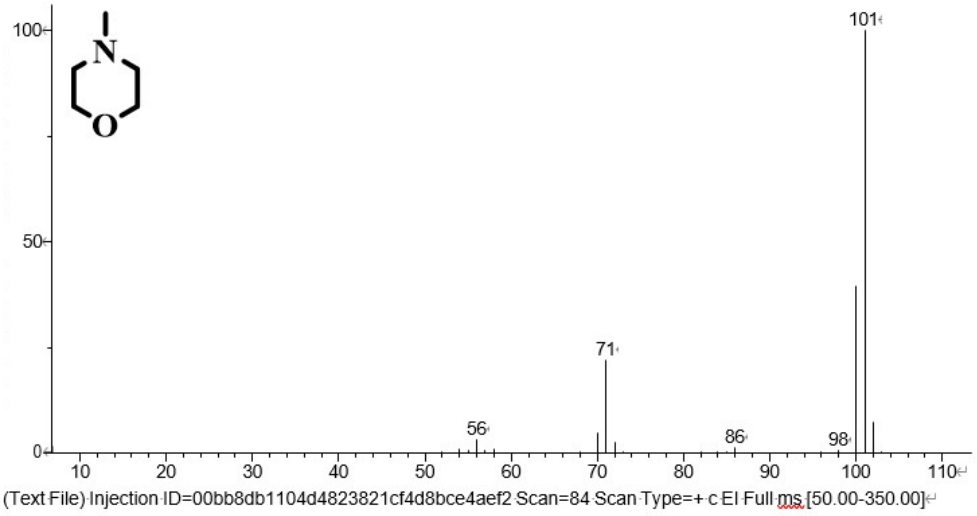


Figure S73. GC-MS spectra of the 4-methylmorpholine (33)

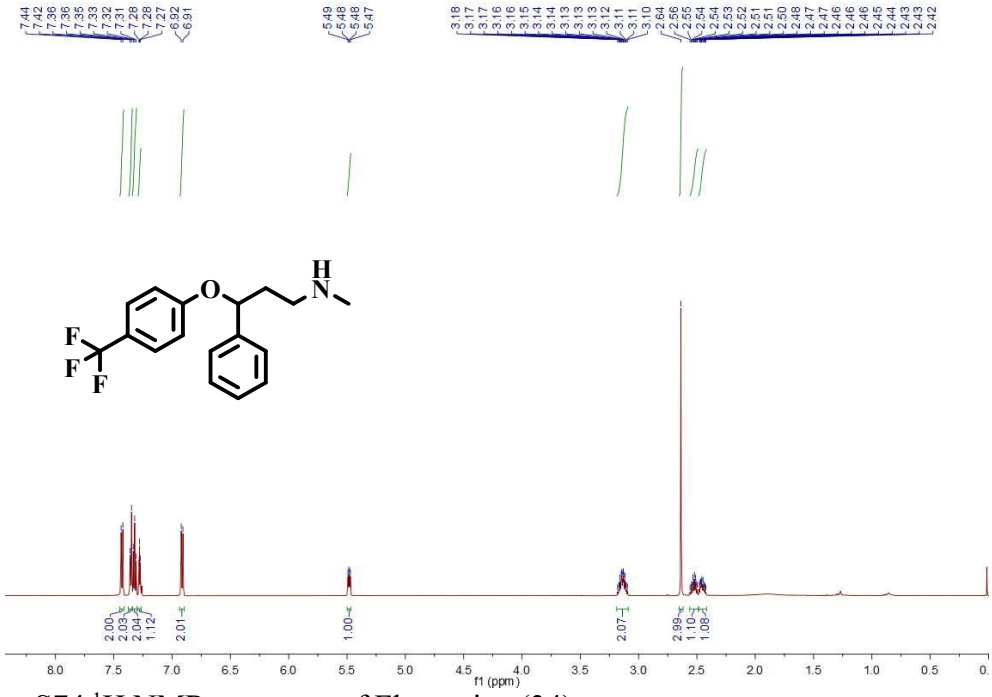


Figure S74.[1]H NMR spectrum of Fluoxetine (34)

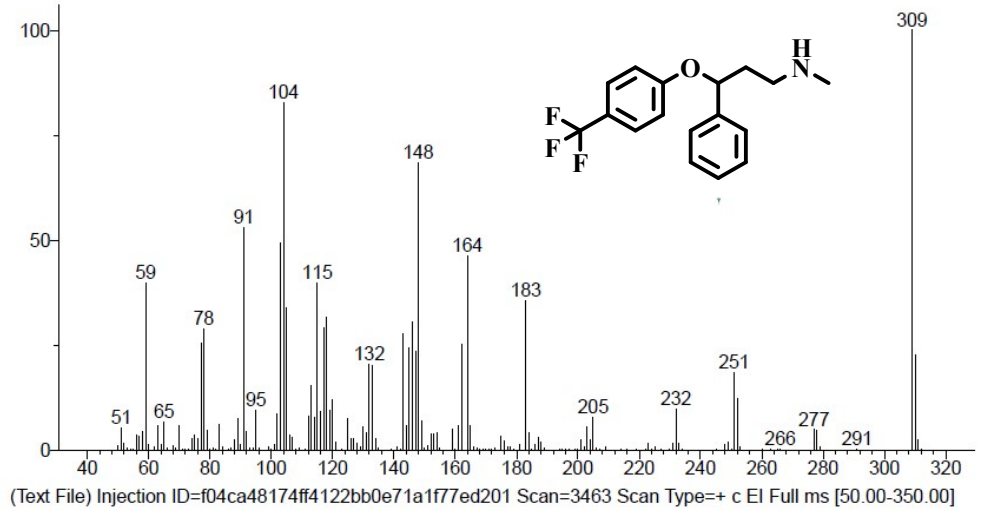


Figure S75. GC-MS spectra of the Fluoxetine (34)