Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Methylation of Aromatic Amines and Imines Using Formic Acid over Heterogeneous Pt/C Catalyst

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Supporting Information

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1. General Information

A. Materials:

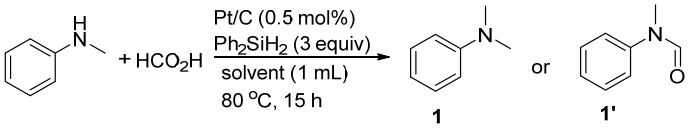
All reactions were conducted in oven-dried Schlenk tubes under argon atmosphere (purity≥99.99%) unless otherwise mentioned. Reagents were commercially supplied and used as received. ^{13}C-HCOOH (99%-^{13}C, purchased from Cambridge Isotope Laboratories, Inc.). Pt/C (5 wt %, 50 wt % of water) was bought from Alfa. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator.

B. Analytical Methods:

Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for ^{1}H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Optimization of reaction conditions

Table S1: Screening of different solvents[a,b]

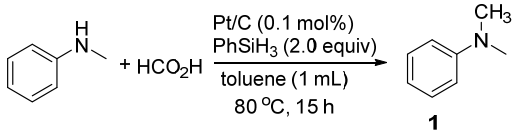


Entry	Solvent	Yield (%)	
		1	**1'**
1	THF	55	21
2	Dioxane	49	46
3	CH_3OH	2	40
4	Toluene	60	6
5	Cyclohexane	57	8
6	CH_2Cl_2	39	6
7	CH_3CN	14	81
8	DMF	49	34

[a] Reaction conditions: N-Methylaniline (0.3 mmol), Ph_2SiH_2 (3.0 equiv), Pt/C (0.5 mol%), HCO_2H (2.0 equiv), solvent (1.0 mL), 80 °C, 15 h.

[b] Determined by GC using n-dodecane as internal standard.

Table S2: Catalyst recycling experiment



Entry	Recycling number	Yield (%)
1	0	97
2	1	85
3	2	73

Recycling results of Pt/C catalysts under the following reaction conditions: N-Methylaniline (0.3 mmol), $PhSiH_3$ (2.5 equiv), Pt/C (0.1 mol%), HCO_2H (2.0 equiv), toluene (1.0 mL), 80 °C, 15 h. The yield was determined by GC using n-dodecane as internal standard.

3. Experimental procedures and Analytic data

General Procedure A (methylation of amines)

For the methylation reaction of primary amines: A 10 mL Schlenk tube containing a stirring bar was charged with Pt/C (0.3 mol%). The tube was then evacuated and back-filled with argon three times. Toluene (1.0 mL),substrate (0.3 mmol), HCO_2H (3.0 equiv) and $PhSiH_3$ (5.0 equiv) were added subsequently.

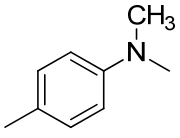
For the methylation reaction of secondary amines: A 10 mL Schlenk tube containing a stirring bar was charged with Pt/C (0.1 mol%). The tube was then evacuated and back-filled with argon three times. Toluene (1.0 mL), substrate (0.3 mmol), HCO_2H (2.0 equiv) and $PhSiH_3$ (2.5 equiv) were added subsequently.

The reaction mixture was heated to 80 ^oC (oil bath). After stirring for 15 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate (3 mL), quenched with aqueous NaOH (3 M solution; 3 mL) carefully. The yields were analyzed by GC using n-dodecane as internal standard. To determine the isolated yield of the methylated amines, the mixture was extracted with ethyl acetate (three times) and the combined organic layers were dried over Na_2SO_4. The organic phase was filtered, concentrated, and purified by silica gel column chromatography to give the corresponding methylated amines.

General Procedure B (methylation of imines)

A 10 mL Schlenk tube containing a stirring bar was charged with Pt/C (0.3 mol%). The tube was then evacuated and back-filled with argon three times. Toluene (1.0 mL) was added subsequently, then substrate (0.3 mmol), HCO_2H (2.0 equiv) and $PhSiH_3$ (3.0 equiv) were added. The reaction mixture was heated to 80 ^oC (oil bath). After stirring for 15 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate (3 mL), quenched with aqueous NaOH (3 M solution; 3 mL) carefully. The yields were analyzed by GC using n-dodecane as internal standard. To determine the isolated yield of the methylated amines, the mixture was extracted with ethyl acetate (three times) and the combined organic layers were dried over Na_2SO_4. The organic phase was filtered, concentrated, and purified by silica gel column chromatography to give the corresponding products.

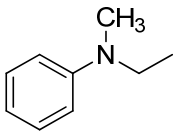
Spectral Data



***N,N*,4-trimethylaniline (2):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 80% yield as a yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2013**, *52*, 12156).

^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.6 Hz, 2H), 6.70 (d, J = 8.5 Hz, 2H), 2.90 (s, 6H), 2.26 (s, 3H).

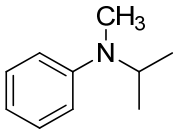
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.74, 129.61, 126.32, 113.33, 41.18, 20.28.



***N*-ethyl-*N*-methylaniline (3):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 76% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Am. Chem. Soc.* **2013**, *135*, 1549).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 8.0 Hz, 2H), 6.91 – 6.51 (m, 3H), 3.39 (q, *J* = 7.1 Hz, 2H), 2.89 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).

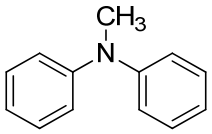
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.06, 129.21, 116.19, 112.52, 46.92, 37.55, 11.22.



***N*-isopropyl-*N*-methylaniline (4):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL cyclohexane, obtained in 64% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2015**, *54*, 15207).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.15 (m, 2H), 6.84 – 6.76 (m, 2H), 6.74 – 6.62 (m, 1H), 4.09 (dt, *J* = 13.2, 6.6 Hz, 1H), 2.73 (s, 3H), 1.16 (d, *J* = 6.6 Hz, 6H).

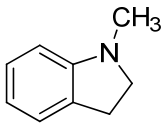
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.14, 129.08, 116.38, 113.29, 48.88, 29.75, 19.28.



***N*-methyl-*N*-phenylaniline (5):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 72% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Organometallics,* **2014**, *33*, 1587).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, *J* = 8.0 Hz, 4H), 7.13 – 7.04 (m, 4H), 6.99 (t, *J* = 7.3 Hz, 2H), 3.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.98, 129.15, 121.23, 120.40, 40.21.

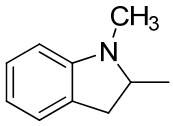


1-methylindoline (6): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL cyclohexane, obtained in 80% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2014**, *53*, 12876).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.03 (m, 2H), 6.72 – 6.64 (m, 1H), 6.53 – 6.45 (m, 1H), 3.28 (t, *J*

= 8.1 Hz, 2H), 2.94 (t, *J* = 8.1 Hz, 2H), 2.75 (s, 3H).

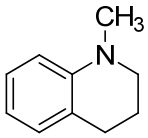
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 130.37, 127.35, 124.30, 117.91, 107.36, 56.19, 36.38, 28.75.



1,2-dimethylindoline (7): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 78% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2014**, *53*, 10476).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 17.1, 7.8 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 3.46 – 3.31 (m, 1H), 3.13 – 3.01 (m, 1H), 2.70 (s, 3H), 2.65 – 2.53 (m, 1H), 1.32 (d, *J* = 6.1 Hz, 3H).

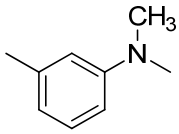
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.48, 129.22, 127.32, 123.97, 117.81, 107.18, 62.83, 37.34, 33.77, 18.75.



1-methyl-1,2,3,4-tetrahydroquinoline (8): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL cyclohexane, obtained in 85% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Chem. Eur. J.* **2014**, *20*, 7878).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (t, *J* = 6.9 Hz, 1H), 6.88 (d, *J* = 6.8 Hz, 1H), 6.61 – 6.48 (m, 2H), 3.14 (t, 2H), 2.81 (s, 3H), 2.69 (t, *J* = 6.4 Hz, 2H), 1.91 (dt, *J* = 12.9, 6.3 Hz, 2H).

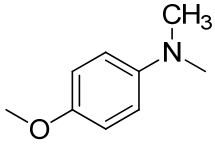
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.75, 128.85, 127.08, 122.91, 116.26, 111.02, 51.31, 39.18, 27.81, 22.47.



***N,N*,3-trimethylaniline(9):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 69% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J.Am. Chem. Soc*, **2016**, *138*, 766).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 6.77 (m, 1H), 6.70 – 6.43 (m, 3H), 2.93 (s, 6H), 2.32 (s, 3H).

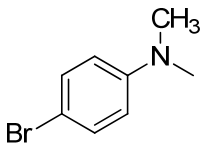
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.66, 138.71, 128.91, 117.72, 113.52, 109.97, 40.73, 21.87.



4-methoxy-*N,N*-dimethylaniline (10): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 74% yield as a white solid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Am. Chem. Soc.* **2013**, *135*, 1549).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.82 (m, 2H), 6.78 – 6.73 (m, 2H), 3.76 (s, 3H), 2.86 (s, 6H).

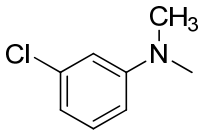
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.98, 145.70, 114.92, 114.59, 55.72, 41.83.



4-bromo-*N,N*-dimethylaniline (11): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 79% yield as a white solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2011**, *50*, 523).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 9.1 Hz, 2H), 6.58 (d, J = 9.0 Hz, 2H), 2.92 (s, 6H).

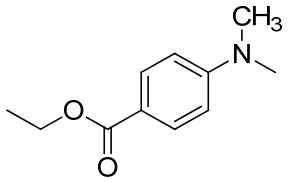
^{13}C NMR (101 MHz, $CDCl_3$) δ 149.44, 131.65, 114.09, 108.51, 40.57.



3-chloro-*N,N*-dimethylaniline (12): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 93% yield as as yellow liquid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2015**, *54*, 9042).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 8.3 Hz, 1H), 6.82 – 6.64 (m, 2H), 6.60 (d, J = 8.2 Hz, 1H), 2.95 (s, 6H).

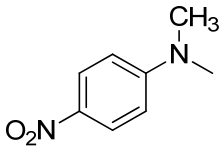
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.43, 133.93, 128.91, 115.14, 111.16, 109.44, 39.35.



ethyl 4-(dimethylamino)benzoate (13): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 91% yield as white solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Chem. Eur. J.* **2014**, *20*, 7878).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 9.1 Hz, 2H), 6.62 (d, J = 9.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 2H), 3.01 (s, 6H), 1.36 (t, J = 7.1 Hz, 3H).

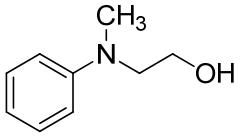
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.05, 153.24, 131.20, 117.29, 110.67, 60.12, 40.05, 14.51.



***N,N*-dimethyl-4-nitroaniline (14):** Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 61% yield as yellow solid (Eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2013**, *52*, 12156).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.4 Hz, 2H), 6.61 (d, *J* = 9.4 Hz, 2H), 3.12 (s, 6H).

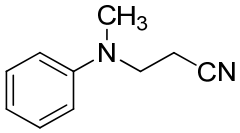
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.14, 137.06, 126.13, 110.34, 40.35.



2-(methyl(phenyl)amino)ethanol (15): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 86% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2013**, *52*, 12156).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.17 (m, 2H), 6.84 – 6.70 (m, 3H), 3.77 (t, *J* = 5.7 Hz, 2H), 3.43 (t, *J* = 5.7 Hz, 2H), 2.93 (s, 3H), 2.03 (br, 1H).

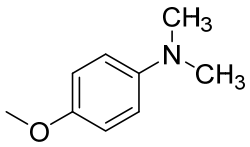
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.03, 129.20, 117.25, 113.08, 60.02, 55.44, 38.75.



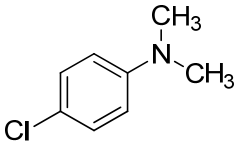
3-(methyl(phenyl)amino)propanenitrile (16): Following the general procedure, using 0.1 mol% Pt/C, 2.0 equiv. HCO_2H, 2.5 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 55% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Chem. Eur. J.* **2014**, *20*, 7878).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 2H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 8.2 Hz, 2H), 3.70 (t, *J* = 6.9 Hz, 2H), 3.02 (s, 3H), 2.56 (t, *J* = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.51, 129.48, 118.41, 117.70, 112.54, 48.95, 38.63, 15.15.



4-methoxy-*N,N*-dimethylaniline (17): Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 95% yield as a white solid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was identical with compound **10**.



4-chloro-*N*,*N*-dimethylaniline (18): Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 96% yield as white solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2013**, *52*, 9568).

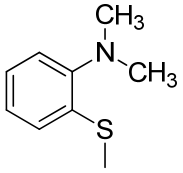
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 9.1 Hz, 2H), 6.63 (d, *J* = 9.0 Hz, 2H), 2.92 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.12, 128.78, 121.47, 113.65, 40.67.

***N*,*N*,2,4,6-pentamethylaniline (19):** Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 36% yield as white solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2015**, *54*, 9042).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 2.79 (s, 6H), 2.25 (s, 6H), 2.23 (s, 3H).

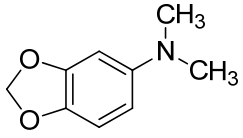
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.07, 136.95, 134.16, 129.42, 42.56, 20.67, 19.00.



***N*,*N*-dimethyl-2-(methylthio)aniline (20):** Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 96% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2015**, *54*, 9042).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 6.81 (m, 4H), 2.76 (s, 6H), 2.44 (s, 3H).

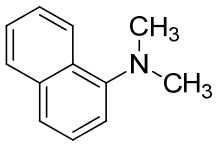
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.88, 134.28, 124.82, 124.55, 123.89, 119.05, 44.27, 14.71.



***N*,*N*-dimethylbenzo[*d*][1,3]dioxol-5-amine (21):** Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 55% yield as light yellow solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Org. Lett.* **2015**, *17*, 6270).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (d, *J* = 8.5 Hz, 1H), 6.42 (d, *J* = 2.5 Hz, 1H), 6.17 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.86 (s, 2H), 2.85 (s, 6H).

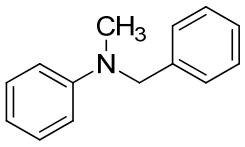
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.26, 147.19, 139.36, 108.27, 105.17, 100.56, 96.46, 41.82.



***N,N*-dimethylnaphthalen-1-amine (22):** Following the general procedure, using 0.3 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 46% yield as as light yellow solid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *Org. Lett.* **2015**, *17*, 6270).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.22 (m, 1H), 7.88 – 7.81 (m, 1H), 7.57 – 7.45 (m, 3H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 2.92 (s, 6H).

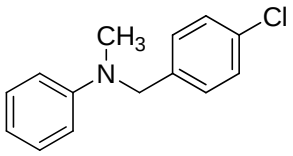
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.78, 134.76, 128.74, 128.30, 125.72, 125.66, 125.10, 124.09, 122.85, 113.87, 45.19.



***N*-benzyl-*N*-methylaniline (23):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 93% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *Angew. Chem. Int. Ed.* **2013**, *52*, 12156).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (m, 7H), 6.78 – 6.31 (m, 3H), 4.44 (s, 2H), 2.93 (s, 3H).

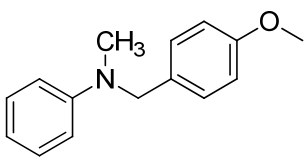
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.65, 137.95, 128.13, 127.51, 125.82, 125.70, 115.51, 111.33, 55.60, 37.48.



***N*-(4-chlorobenzyl)-*N*-methylaniline (24):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 91% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **2015**, *80*, 5912).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.12 (m, 7H), 6.72 (d, *J* = 7.5 Hz, 2H), 4.46 (s, 2H), 2.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.55, 137.57, 132.60, 129.28, 128.75, 128.18, 116.94, 112.54, 56.22, 38.61.

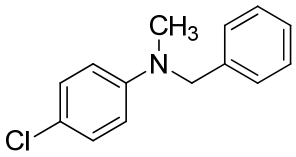


***N*-(4-methoxybenzyl)-*N*-methylaniline (25):** Following the general procedure, using 0.3 mol%

Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 92% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 50/1). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **2015**, *80*, 5912).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.79 – 6.67 (m, 3H), 4.45 (s, 2H), 3.77 (s, 3H), 2.97 (s, 3H).

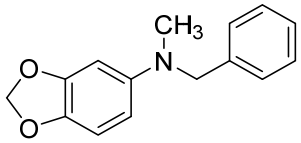
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.57, 149.76, 130.84, 129.13, 127.96, 116.51, 113.92, 112.50, 56.04, 55.23, 38.28.



***N*-benzyl-4-chloro-*N*-methylaniline (26):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 90% yield as light white solid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Org. Chem.* **1973**, *38*, 1136).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.27 – 7.17 (m, 3H), 7.13 (d, *J* = 9.0 Hz, 2H), 6.64 (d, *J* = 9.0 Hz, 2H), 4.50 (s, 2H), 3.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.24, 138.45, 128.96, 128.67, 127.06, 126.68, 121.39, 113.53, 56.74, 38.84.

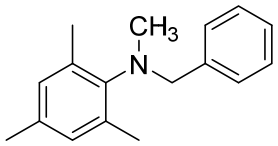


***N*-benzyl-*N*-methylbenzo[*d*][1,3]dioxol-5-amine (27):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 72% yield as white solid (Eluent: petroleum ether/ethyl acetate = 100/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.08 (m, 5H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.42 (s, 1H), 6.17 (d, *J* = 10.8 Hz, 1H), 5.84 (s, 2H), 4.41 (s, 2H), 2.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.42, 146.28, 128.61, 128.54, 127.01, 126.93, 126.83, 108.45, 105.02, 100.62, 96.30, 58.07, 39.39.

HRMS (ESI) calcd for $C_{15}H_{16}NO_2$ $[M+H]^+$: 242.1176, found 242.1158.



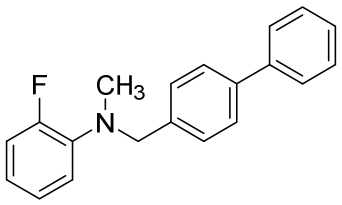
***N*-benzyl-*N*,2,4,6-tetramethylaniline (28):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 91% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 5H), 6.84 (s, 2H), 4.14 (s, 2H), 2.65 (s, 3H), 2.34 (s, 6H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.38, 140.56, 136.91, 134.47, 129.65, 128.49, 128.17, 126.71, 60.06,

39.31, 20.67, 19.51.

HRMS (ESI) calcd for $C_{17}H_{22}N$ $[M+H]^+$: 240.1747, found 240.1740.

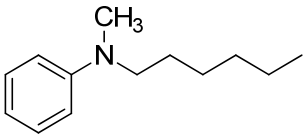


***N*-([1,1'-biphenyl]-4-ylmethyl)-2-fluoro-*N*-methylaniline (29):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 3.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 89% yield as white solid (Eluent: petroleum ether/ethyl acetate = 100/1).

^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.30 (m, 9H), 7.10 – 6.98 (m, 2H), 6.94 – 6.84 (m, 2H), 4.31 (s, 2H), 2.76 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.30 (d, J = 244.7 Hz), 141.00, 140.14 (d, J = 32.5 Hz), 140.10, 137.61, 128.81, 128.75, 127.24, 127.12, 127.11, 124.41 (d, J = 3.5 Hz), 121.23 (d, J = 7.5 Hz), 119.33 (d, J = 2.5 Hz), 116.26 (d, J = 20.9 Hz).

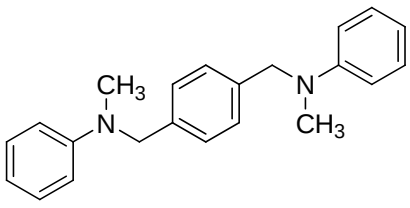
HRMS (ESI) calcd for $C_{20}H_{19}FN$ $[M+H]^+$: 292.1496, found 292.1385.



***N*-hexyl-*N*-methylaniline (30):** Following the general procedure, using 0.3 mol% Pt/C, 2.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 46% yield as light yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Am. Chem. Soc.* **2015**, *137*, 13768).

^1H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.09 (m, 2H), 6.93 – 6.44 (m, 3H), 3.67 – 3.22 (m, 2H), 2.91 (s, 3H), 1.73 – 1.44 (m, 2H), 1.44 – 1.21 (m, 6H), 0.89 (t, J = 6.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.33, 129.13, 115.76, 112.06, 52.84, 38.28, 31.76, 26.86, 26.59, 22.69, 14.06.



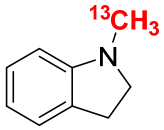
***N,N'*-(1,4-phenylenebis(methylene))bis(*N*-methylaniline) (31):** Following the general procedure, using 0.5 mol% Pt/C, 3.0 equiv. HCO_2H, 5.0 equiv. $PhSiH_3$, 1.0 mL toluene, obtained in 41% yield as white solid (Eluent: petroleum ether/ethyl acetate = 100/1). The compound data was in agreement with the literature (Ref. *J. Med. Chem.* **2007**, *50*, 5655).

^1H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.11 (m, 8H), 6.79 – 6.61 (m, 6H), 4.49 (s, 4H), 2.99 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.73, 137.70, 129.24, 127.05, 116.58, 112.41, 56.44, 38.59.

4. ^{13}C-Labeling Experiments

General Procedure C: A 10 mL Schlenk tube containing a stirring bar was charged with Pt/C (0.1 mol%). The tube was then evacuated and back-filled with argon three times. Toluene (1.0 mL) was added subsequently, then substrate (0.3 mmol), H^{13}CO$_2$H (2.0 equiv, >99% ^{13}C)) and PhSiH$_3$ (2.5 equiv) were added. The reaction mixture was heated to 80 ^{o}C (oil bath). After stirring for 15 h, the reaction mixture was cooled to room temperature, and diluted with ethyl acetate (3 mL), quenched with aqueous NaOH (3 M solution; 3 mL) carefully. The yields were analyzed by GC using n-dodecane as internal standard. To determine the isolated yield of the methylated amines, the mixture was extracted with ethyl acetate (three times) and the combined organic layers were dried over Na_2SO_4. The organic phase was filtered, concentrated, and purified by silica gel column chromatography to give the corresponding methylated amines.

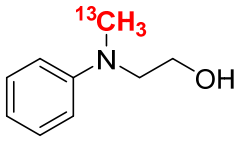


1-methylindoline (32): Following the general procedure C, using 0.1 mol% Pt/C, 2.0 equiv. H^{13}CO$_2$H, 2.5 equiv. PhSiH$_3$, 1.0 mL cyclohexane, obtained in 78% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 100/1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.01 (m, 2H), 6.81 – 6.62 (m, 1H), 6.65 – 6.41 (m, 1H), 3.31 (t, *J* = 8.2 Hz, 2H), 3.10 – 2.75 (m, 3.5H), 2.61 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.31, 130.33, 127.30, 124.26, 117.83, 107.30, 56.15, 36.31, 28.73.

HRMS (ESI) calcd for $C_8{}^{13}CH_{12}N$ $[M+H]^+$: 135.0998, found 135.1004.



2-(methyl(phenyl)amino)ethanol (33): Following the general procedure C, using 0.1 mol% Pt/C, 1.5 equiv. H^{13}CO$_2$H, 2.5 equiv. PhSiH$_3$, 1.0 mL toluene, obtained in 75% yield as yellow liquid (Eluent: petroleum ether/ethyl acetate = 10/1).

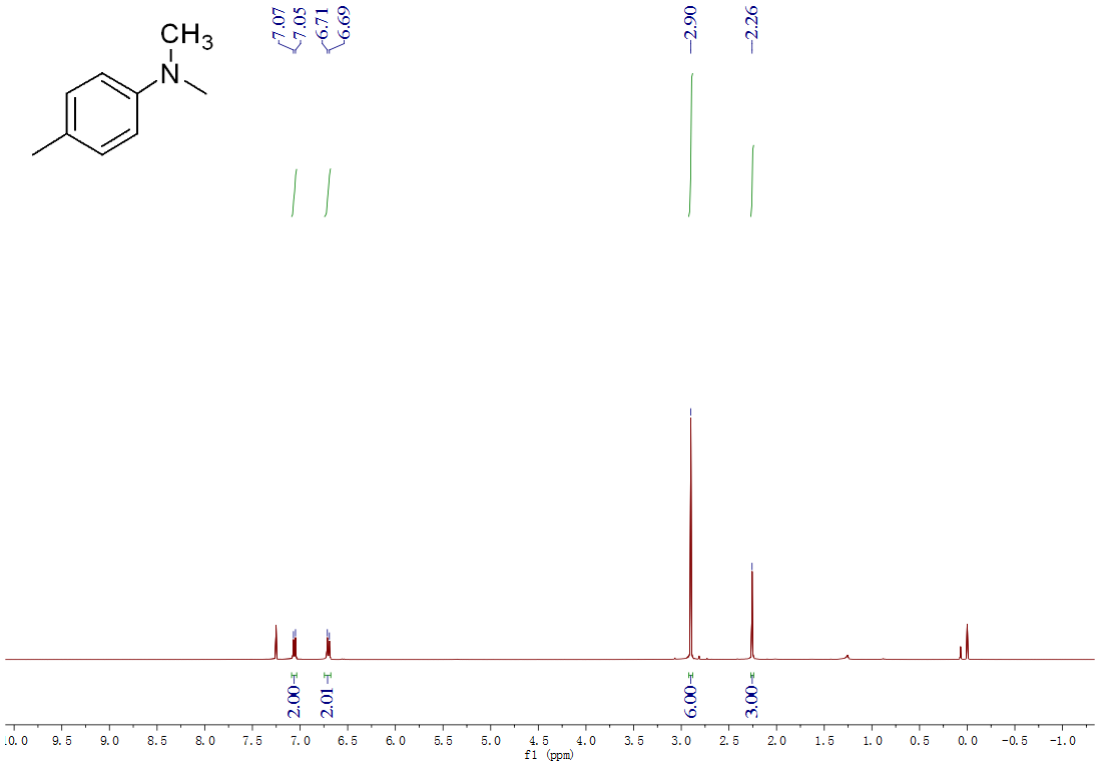
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.09 (m, 2H), 6.90 – 6.65 (m, 3H), 3.78 (t, *J* = 5.7 Hz, 2H), 3.44 (dd, *J* = 10.7, 5.5 Hz, 2H), 2.94 (d, *J* = 135.4 Hz, 3H), 2.02 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.02, 129.20, 117.24, 113.08, 60.01, 55.45, 38.77.

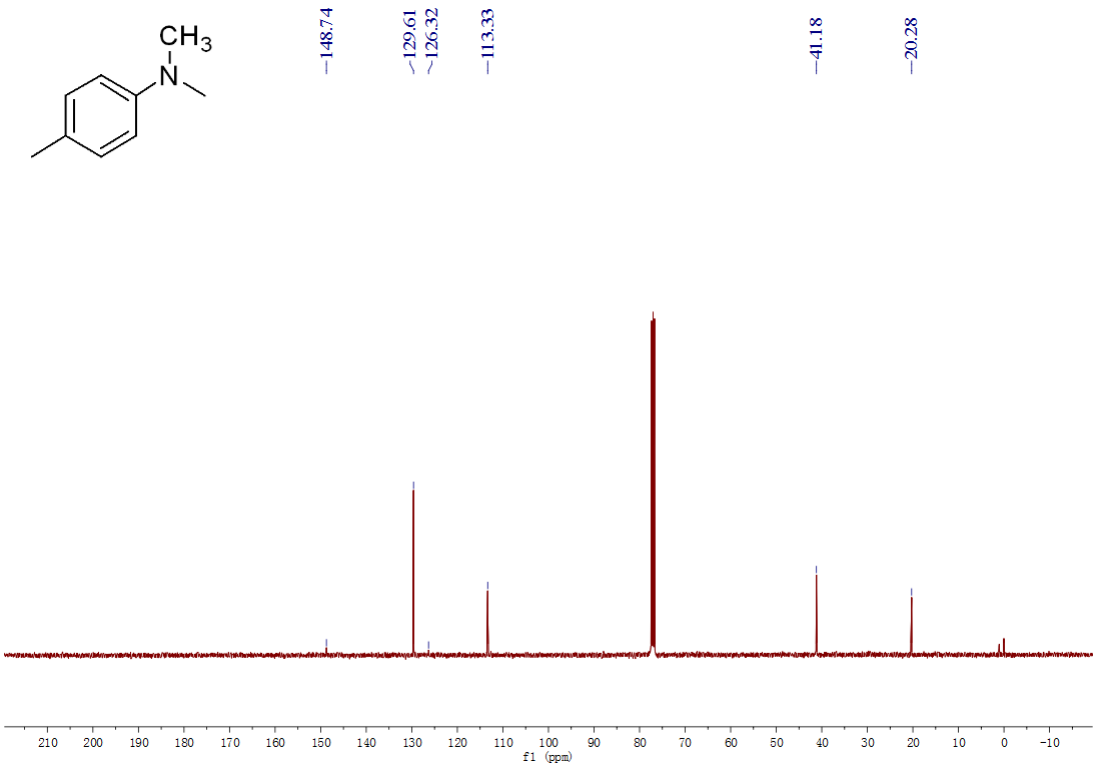
HRMS (ESI) calcd for $C_8{}^{13}CH_{14}NO$ $[M+H]^+$: 153.1103, found 153.1098.

5. ^{1}H and ^{13}C NMR spectra

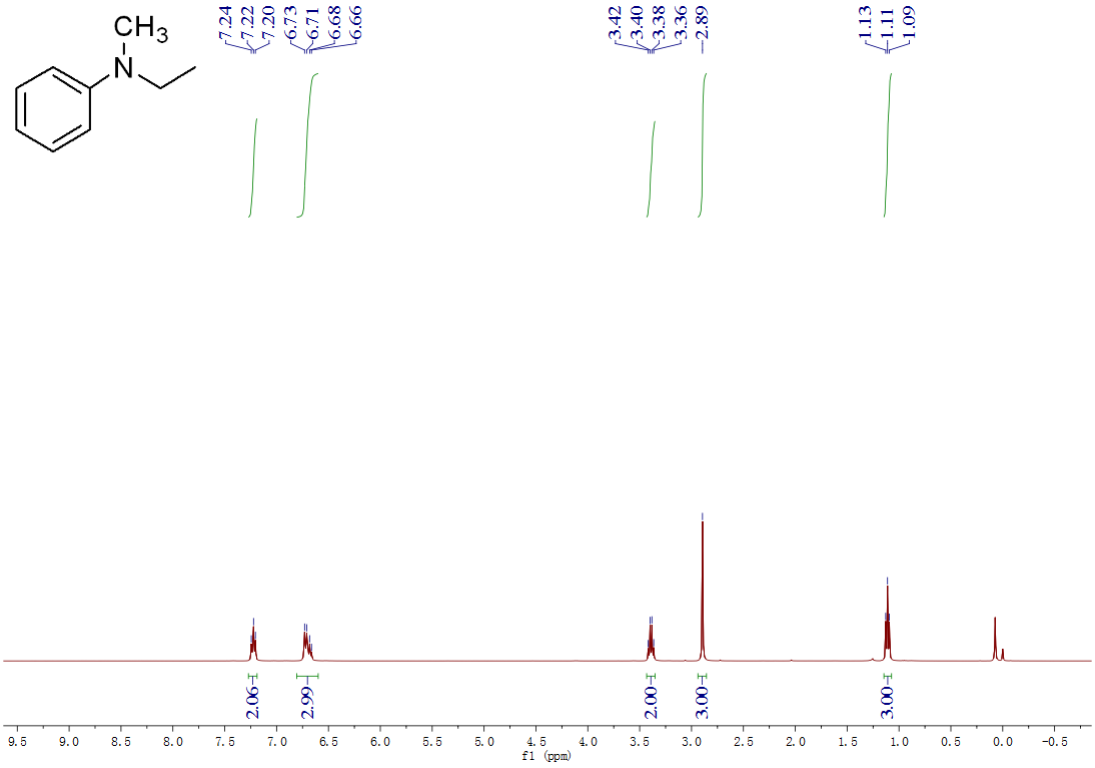
^{1}H NMR spectrum of ***N,N,*4-trimethylaniline (2)**



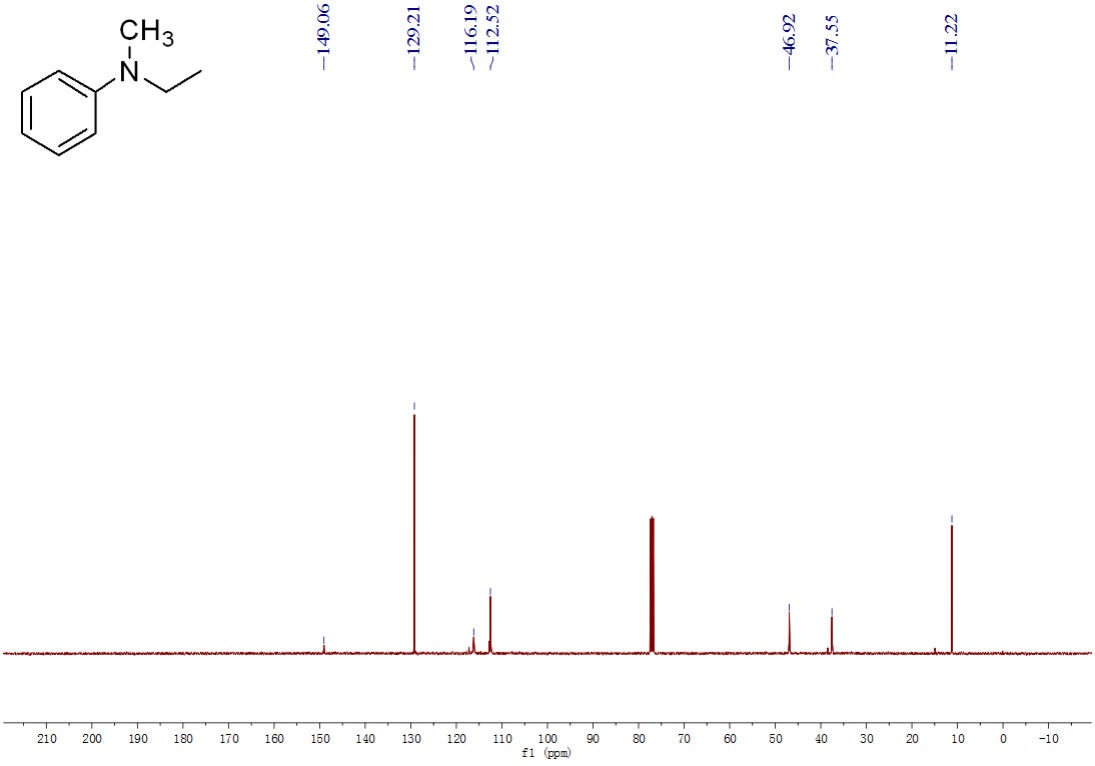
^{13}C NMR spectrum of ***N,N,*4-trimethylaniline (2)**



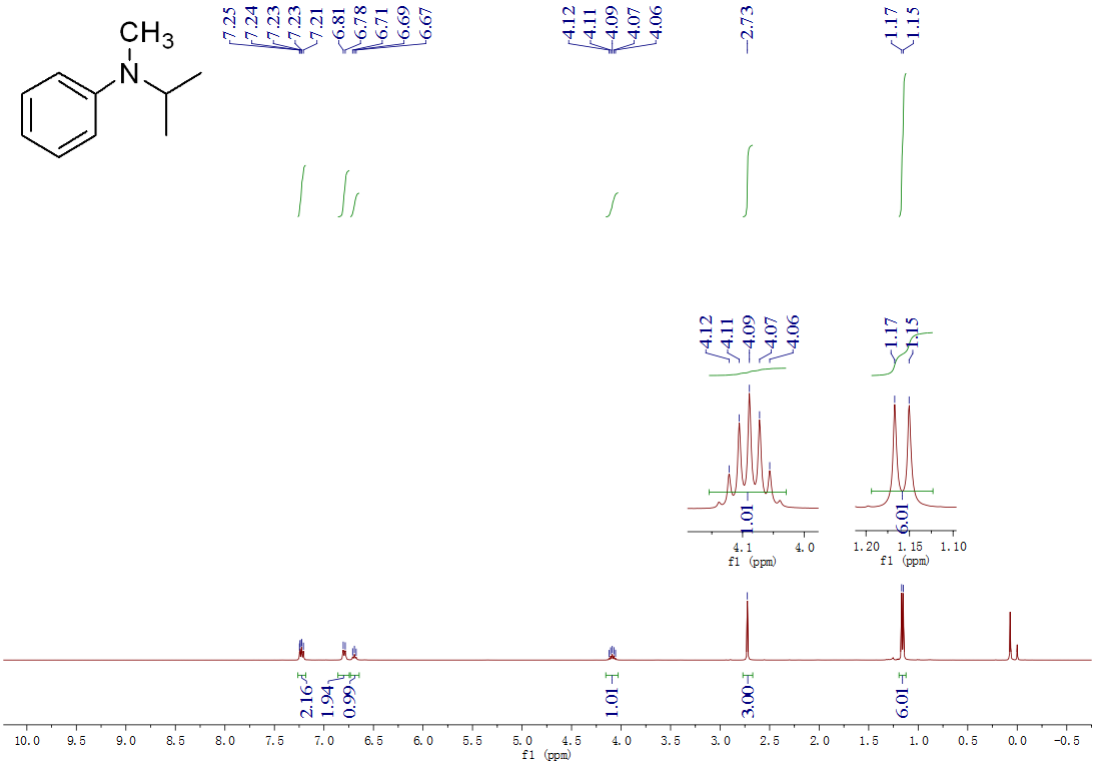
^{1}H NMR spectrum of ***N*-ethyl-*N*-methylaniline (3)**



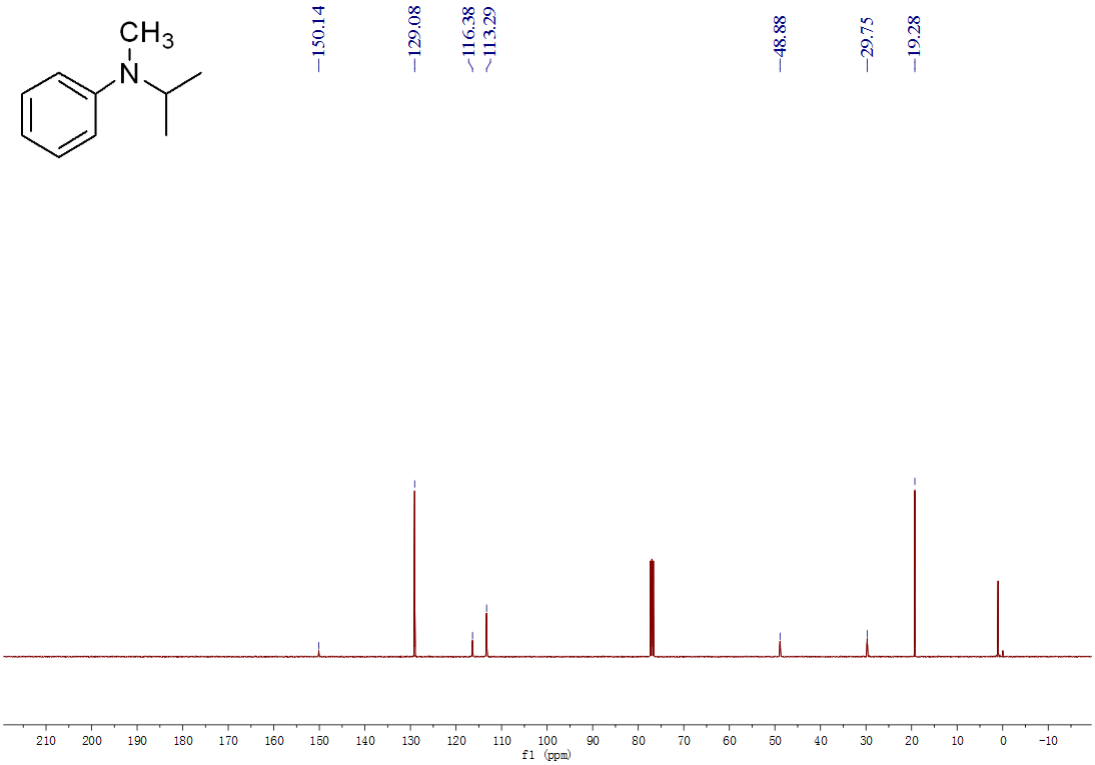
^{13}C NMR spectrum of ***N*-ethyl-*N*-methylaniline (3)**



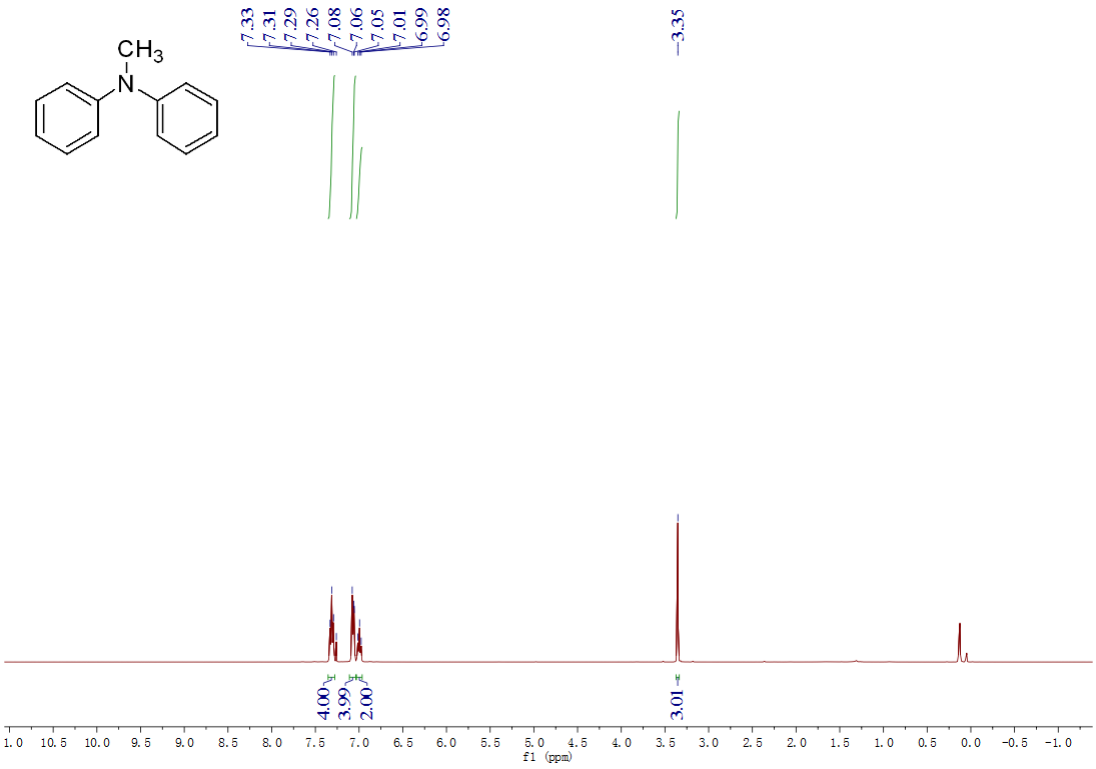
^{1}H NMR spectrum of ***N*-isopropyl-*N*-methylaniline (4)**



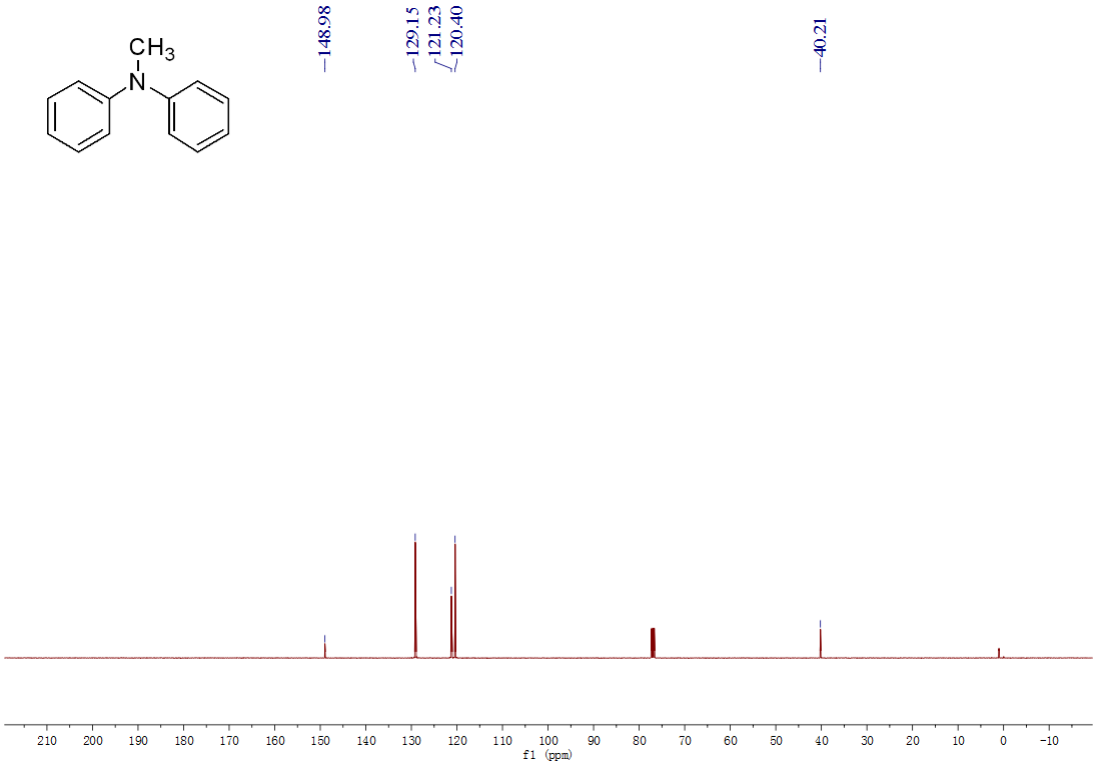
^{13}C NMR spectrum of ***N*-isopropyl-*N*-methylaniline (4)**



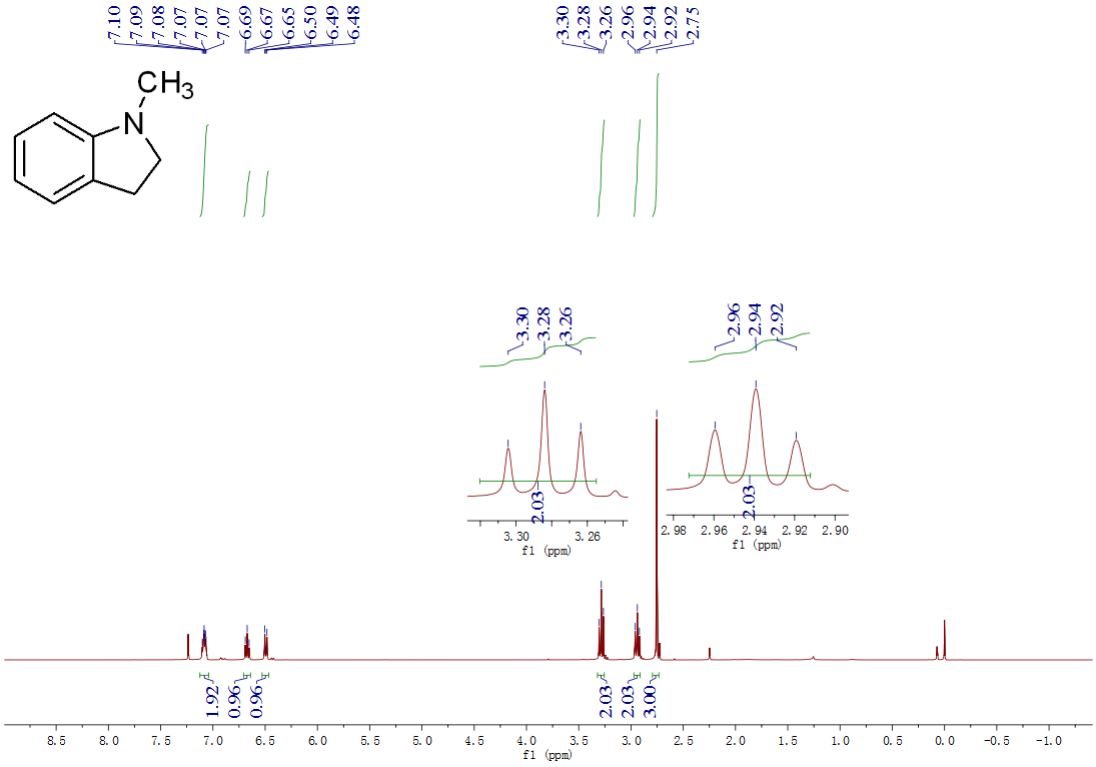
^{1}H NMR spectrum of ***N*-methyl-*N*-phenylaniline (5)**



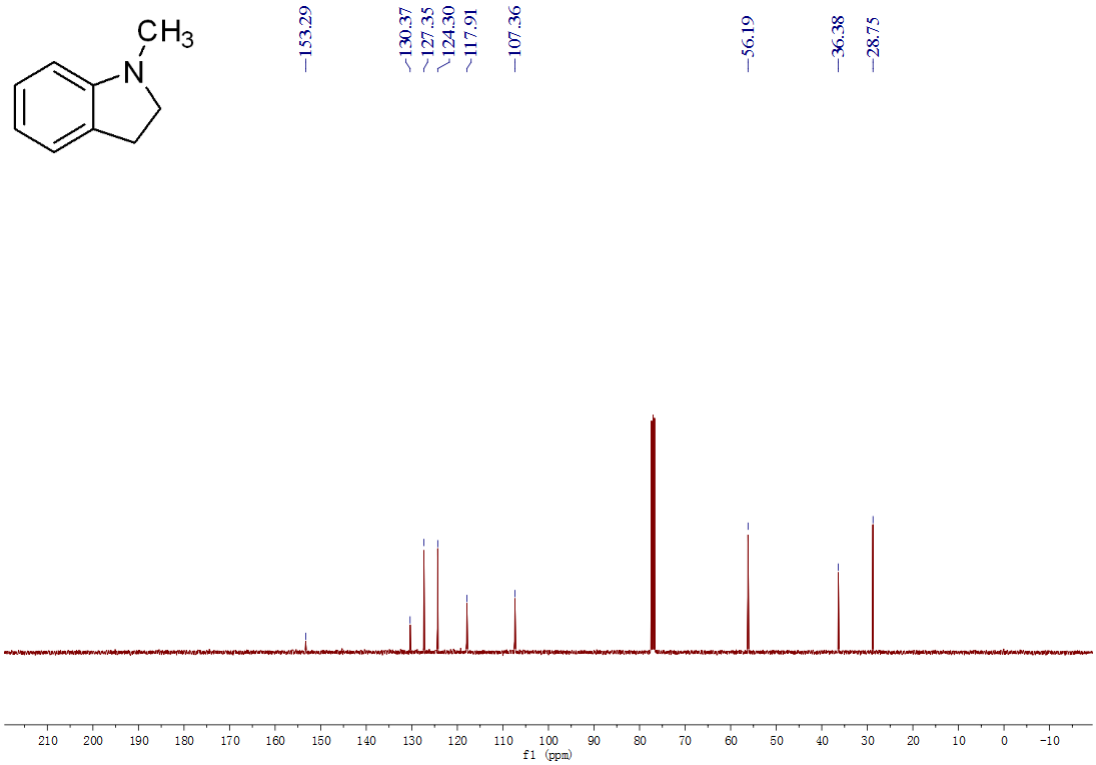
^{13}C NMR spectrum of ***N*-methyl-*N*-phenylaniline (5)**



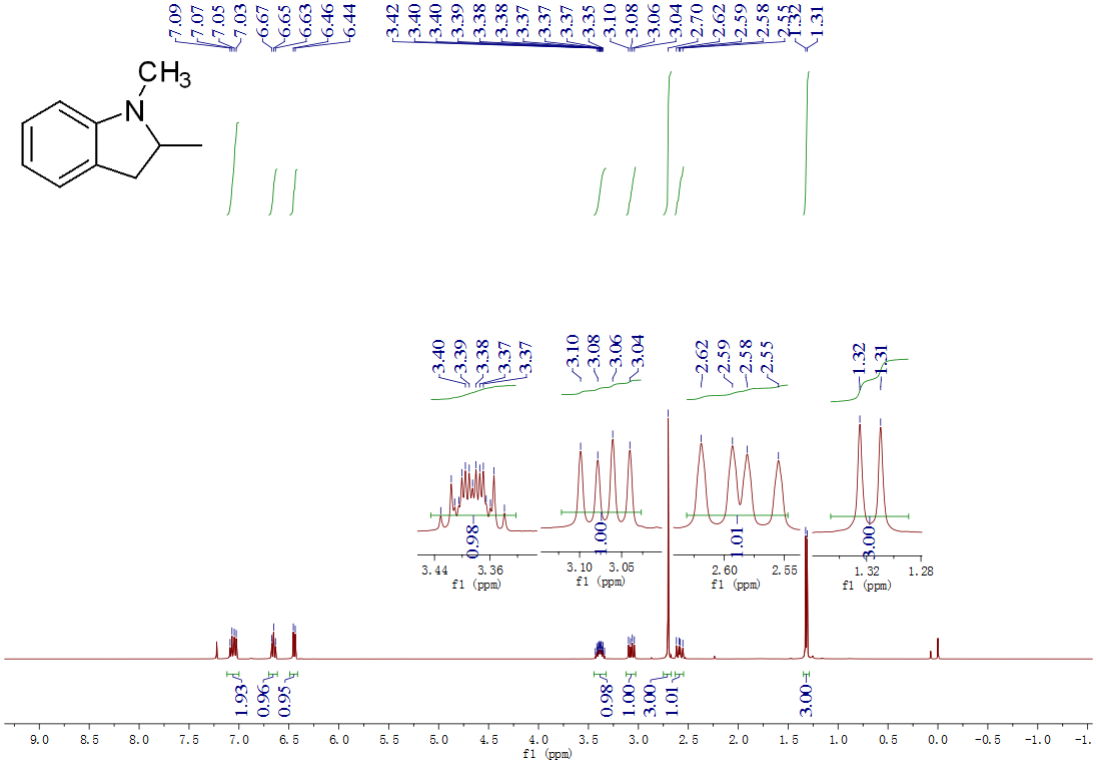
^{1}H NMR spectrum of **1-methylindoline (6)**



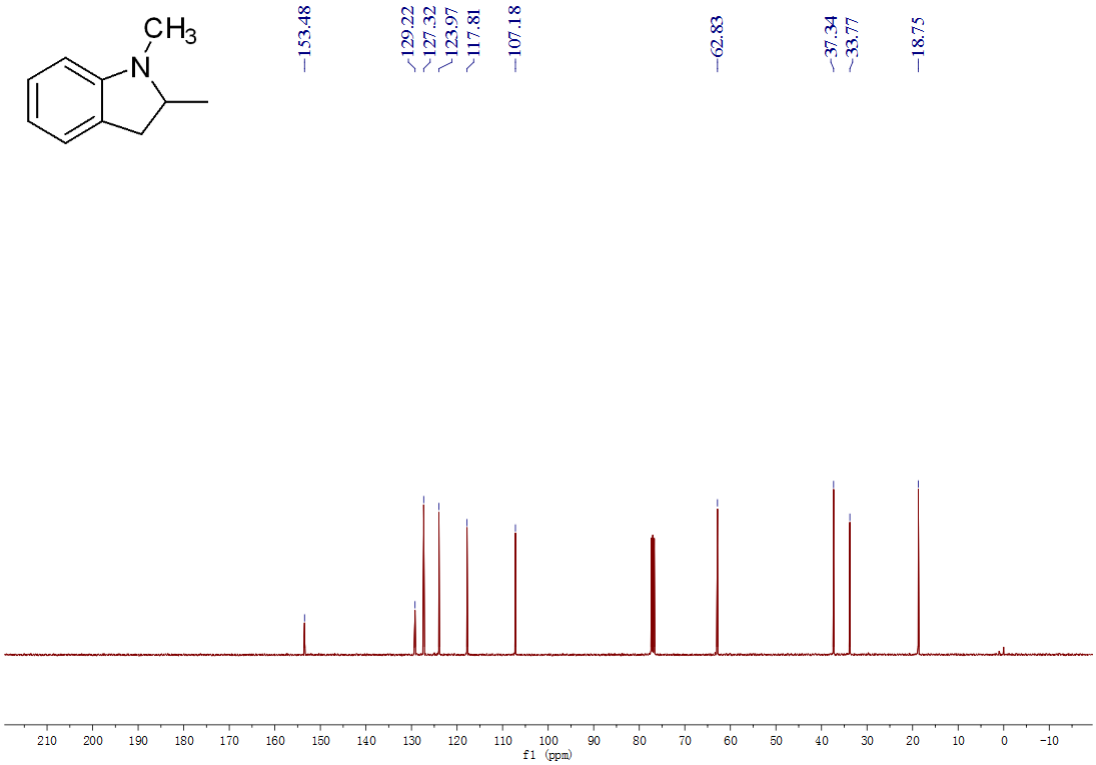
^{13}C NMR spectrum of **1-methylindoline (6)**



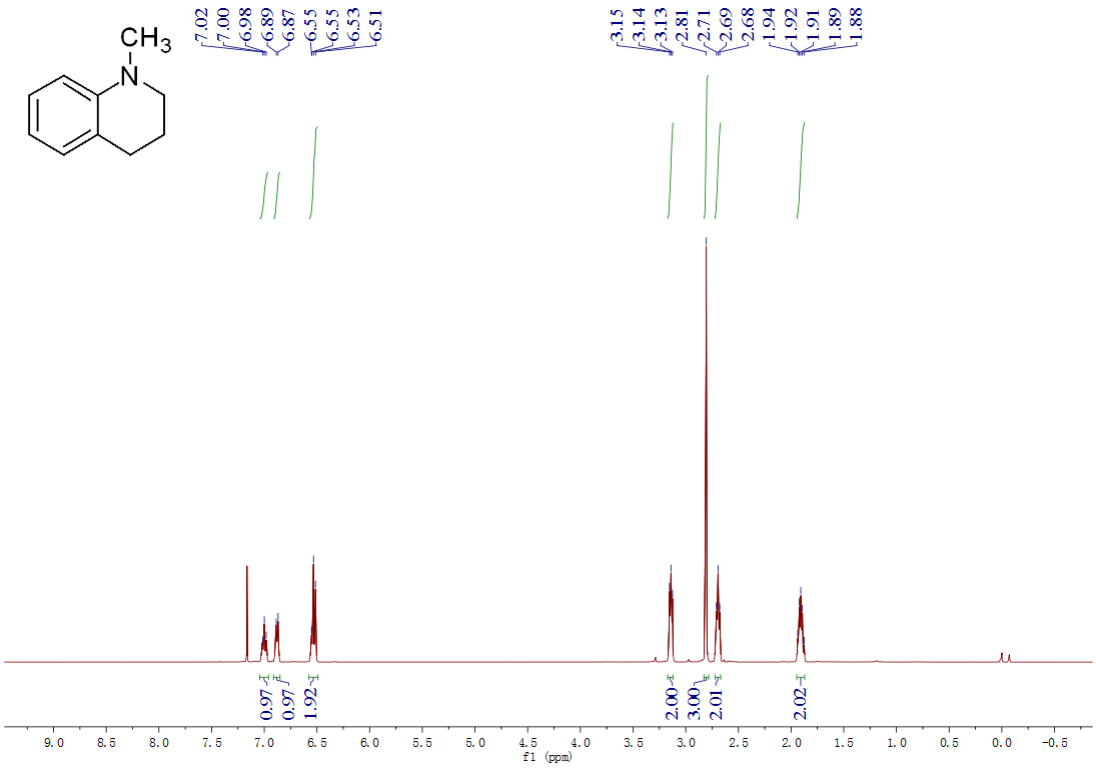
^{1}H NMR spectrum of **1,2-dimethylindoline (7)**



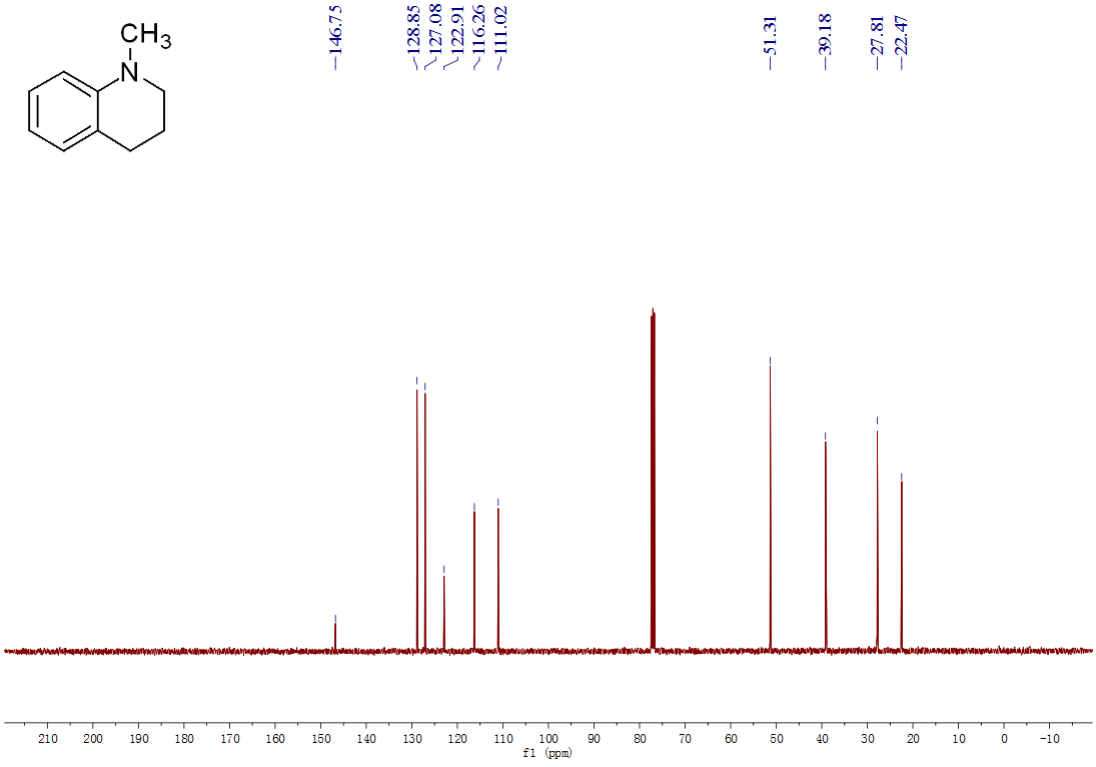
^{13}C NMR spectrum of **1,2-dimethylindoline (7)**



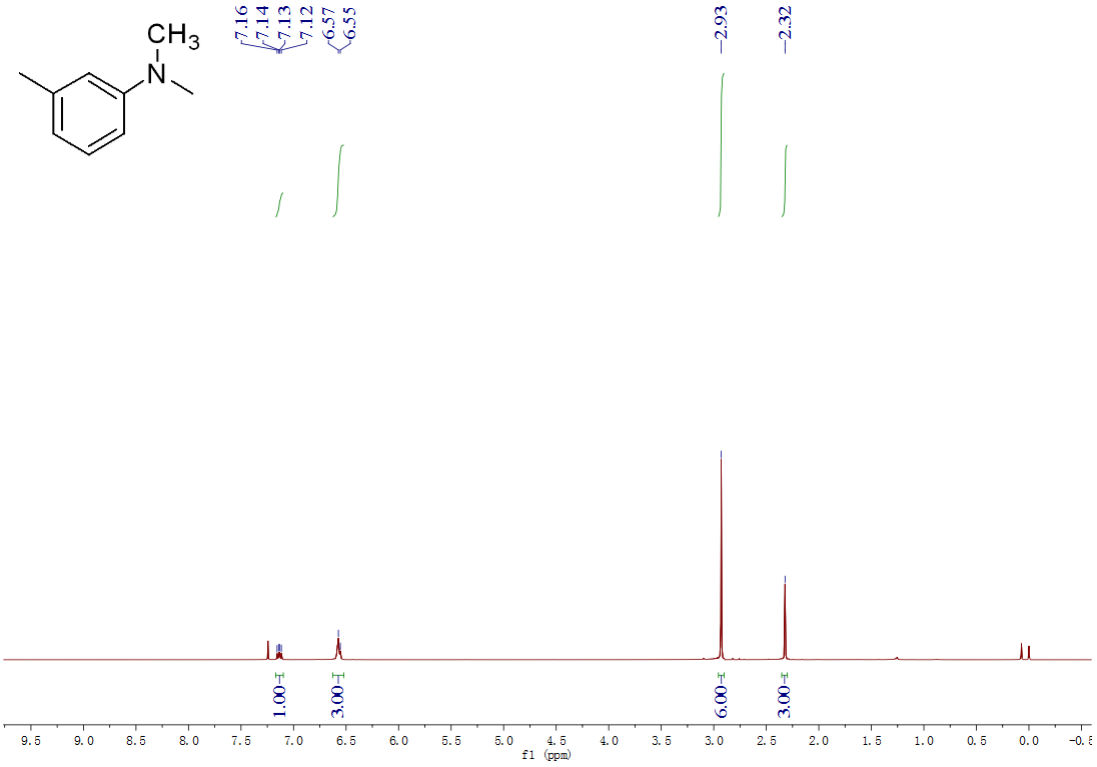
^{1}H NMR spectrum of **1-methyl-1,2,3,4-tetrahydroquinoline (8)**



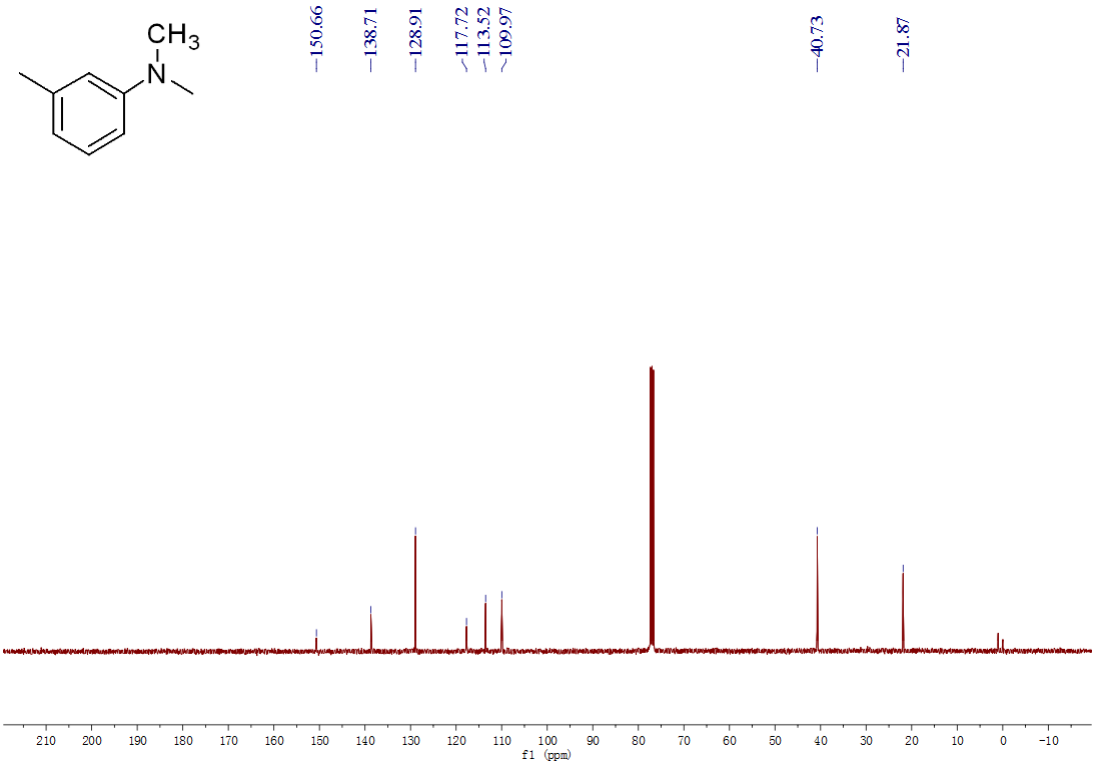
^{13}C NMR spectrum of **1-methyl-1,2,3,4-tetrahydroquinoline (8)**



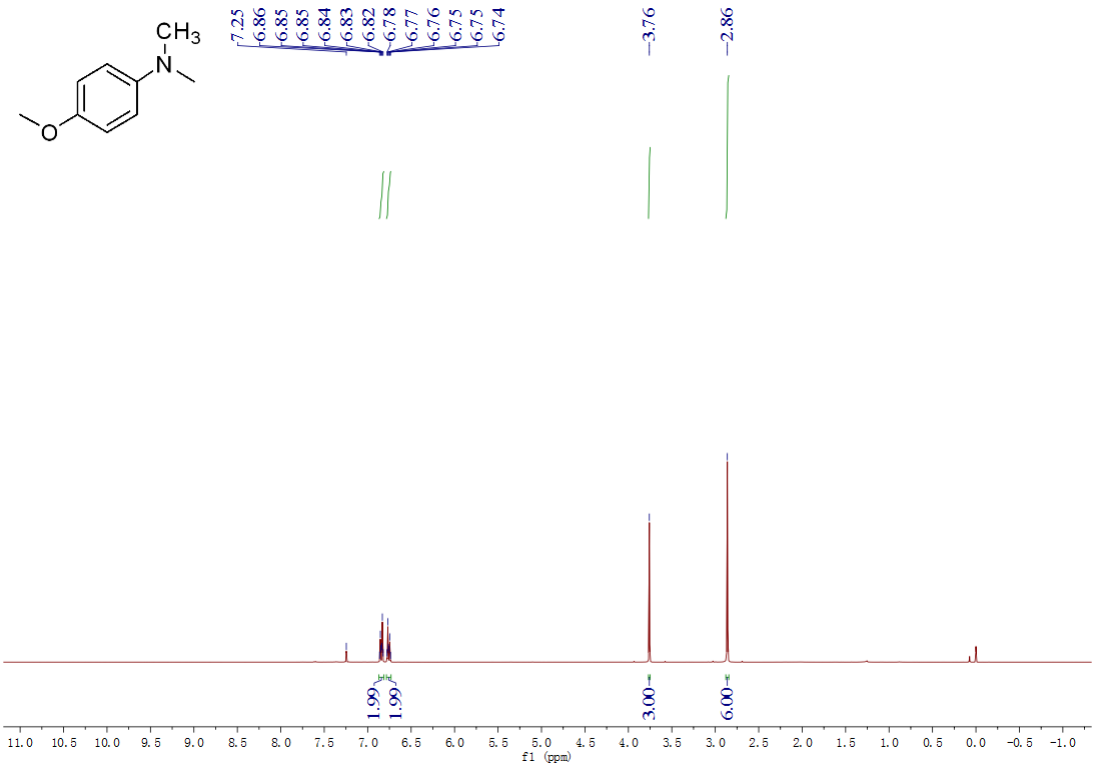
^{1}H NMR spectrum of ***N,N*,3-trimethylaniline(9)**



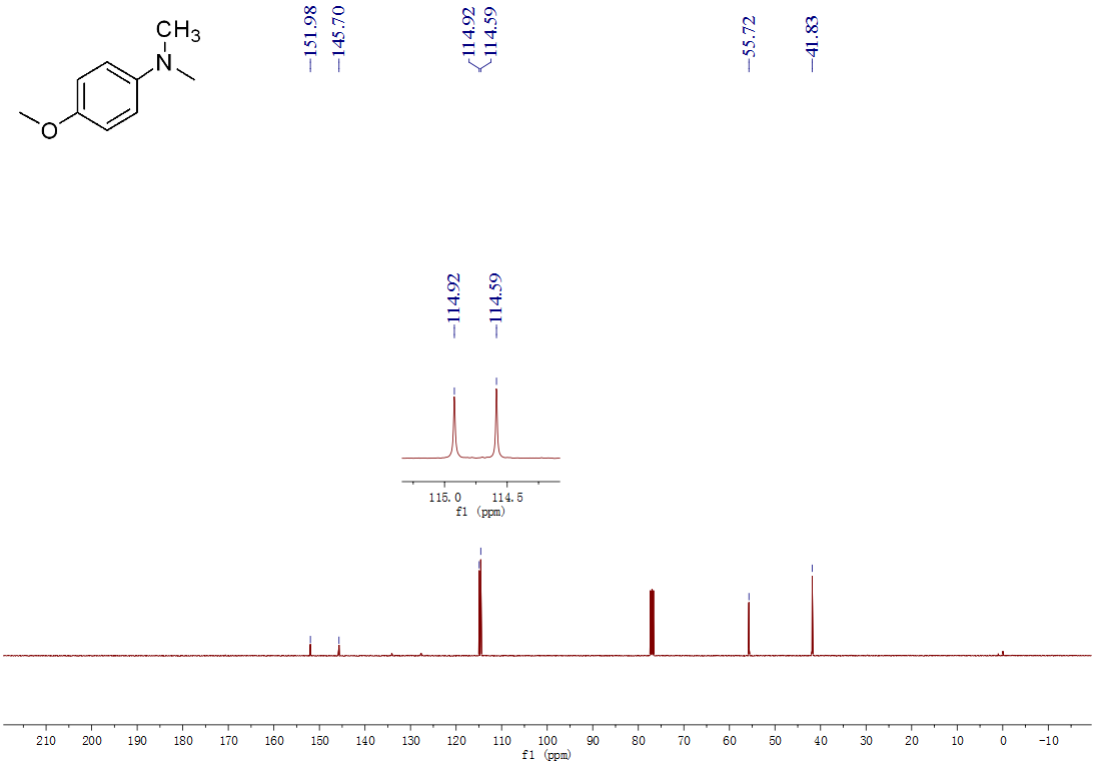
^{13}C NMR spectrum of ***N,N*,3-trimethylaniline(9)**



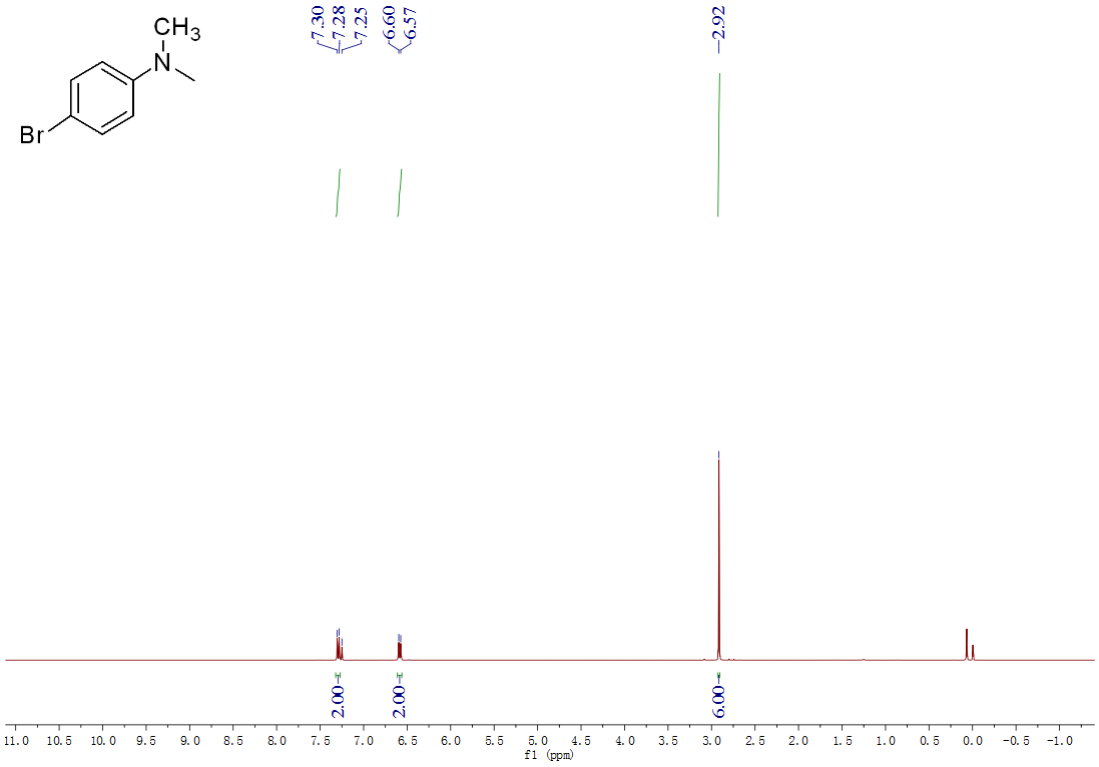
^{1}H NMR spectrum of **4-methoxy-*N*,*N*-dimethylaniline (10, 17)**



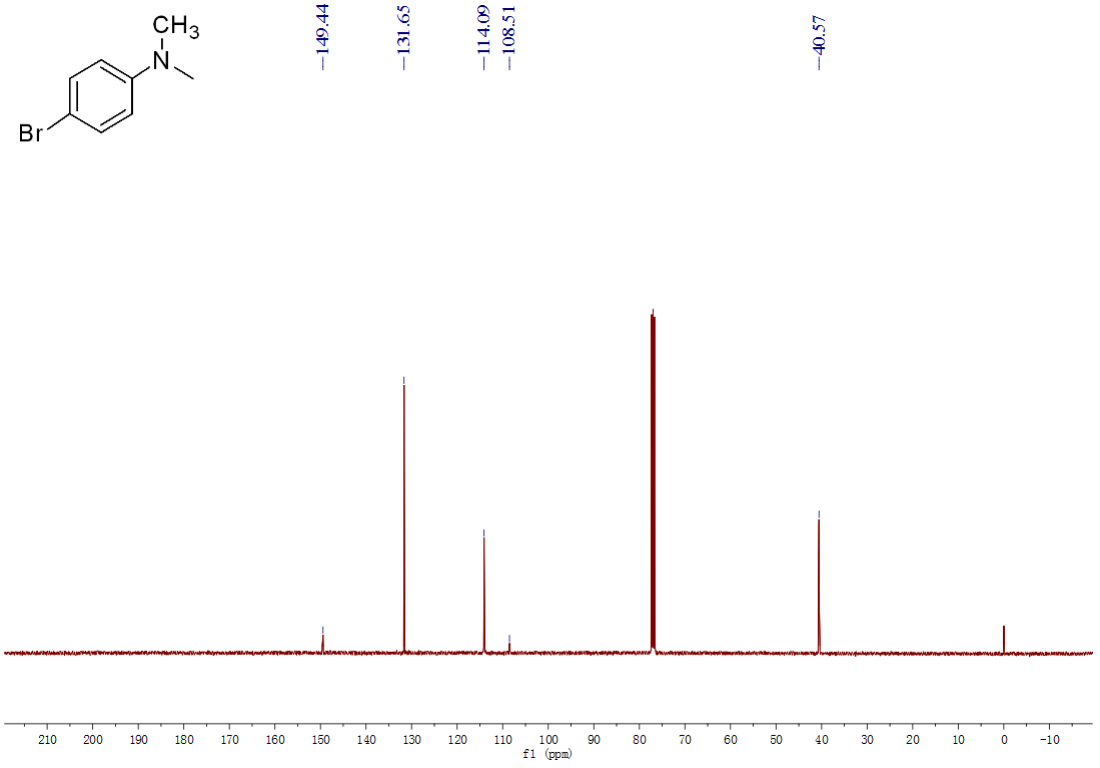
^{13}C NMR spectrum of **4-methoxy-*N*,*N*-dimethylaniline (10, 17)**



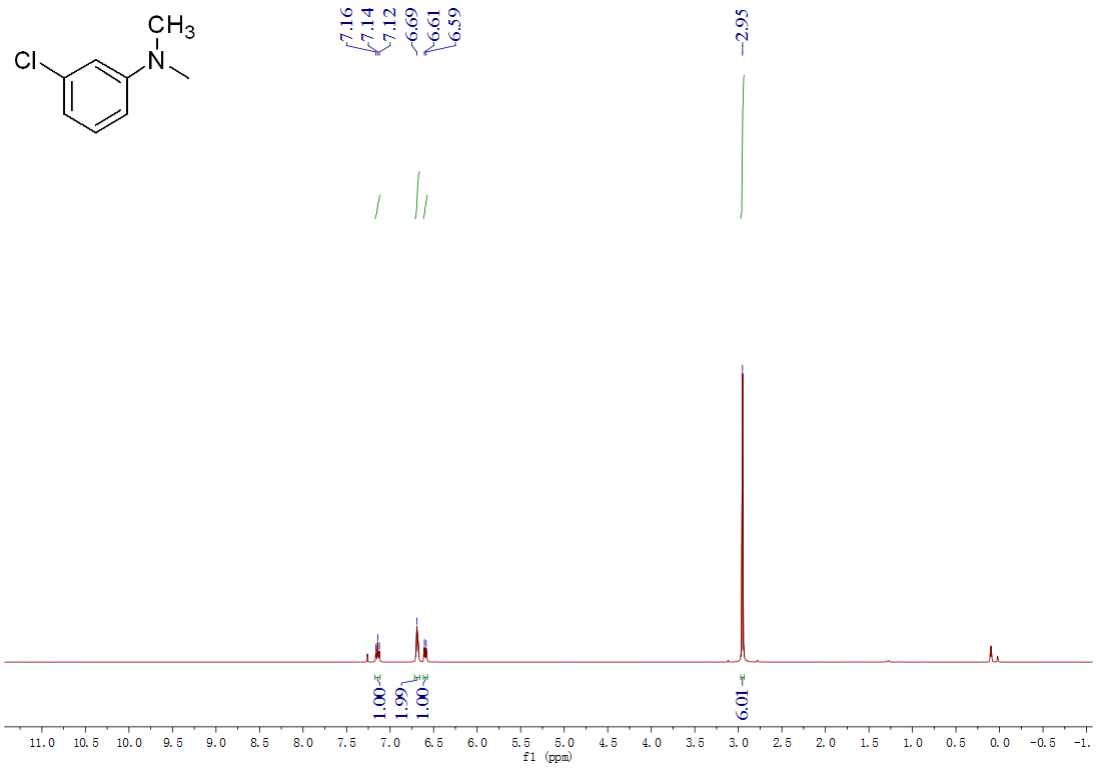
^{1}H NMR spectrum of **4-bromo-*N*,*N*-dimethylaniline (11)**



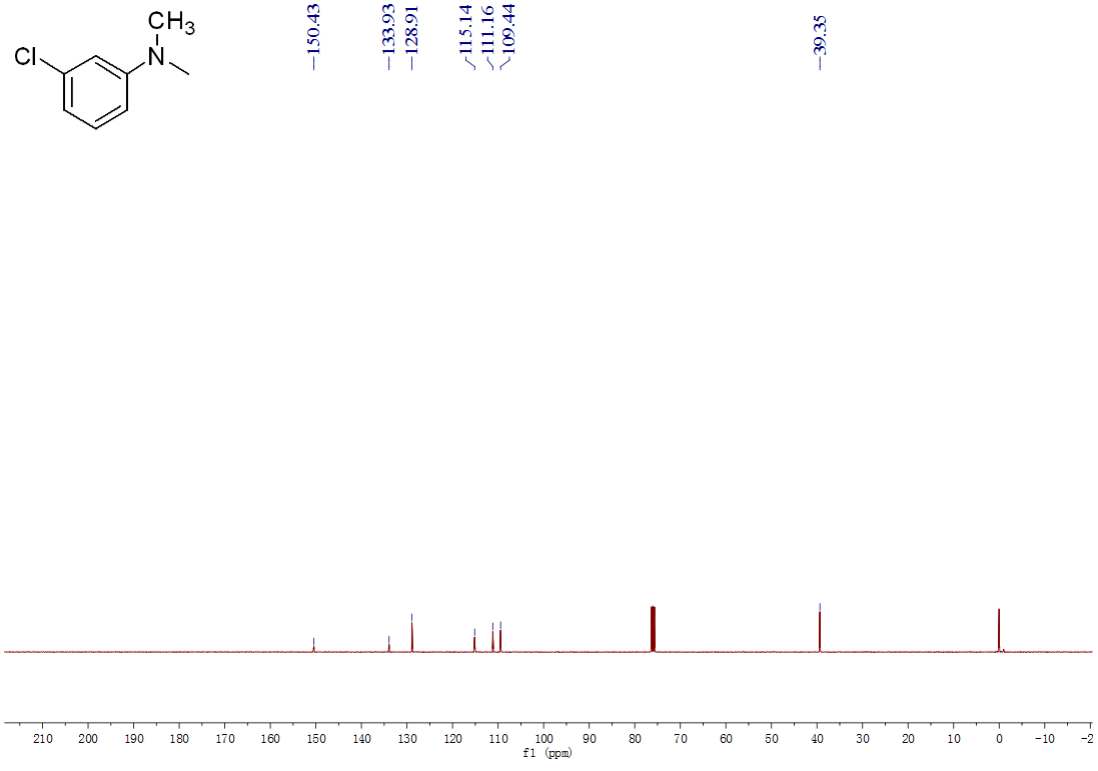
^{13}C NMR spectrum of **4-bromo-*N*,*N*-dimethylaniline (11)**



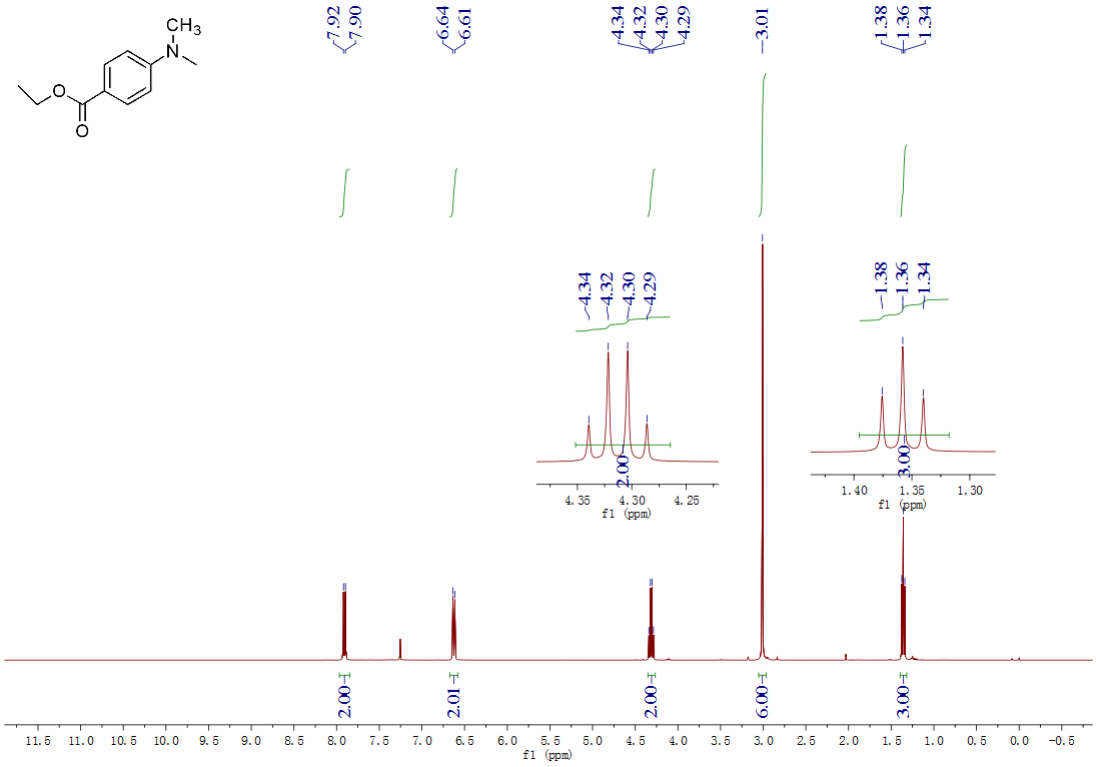
^{1}H NMR spectrum of **3-chloro-*N*,*N*-dimethylaniline (12)**



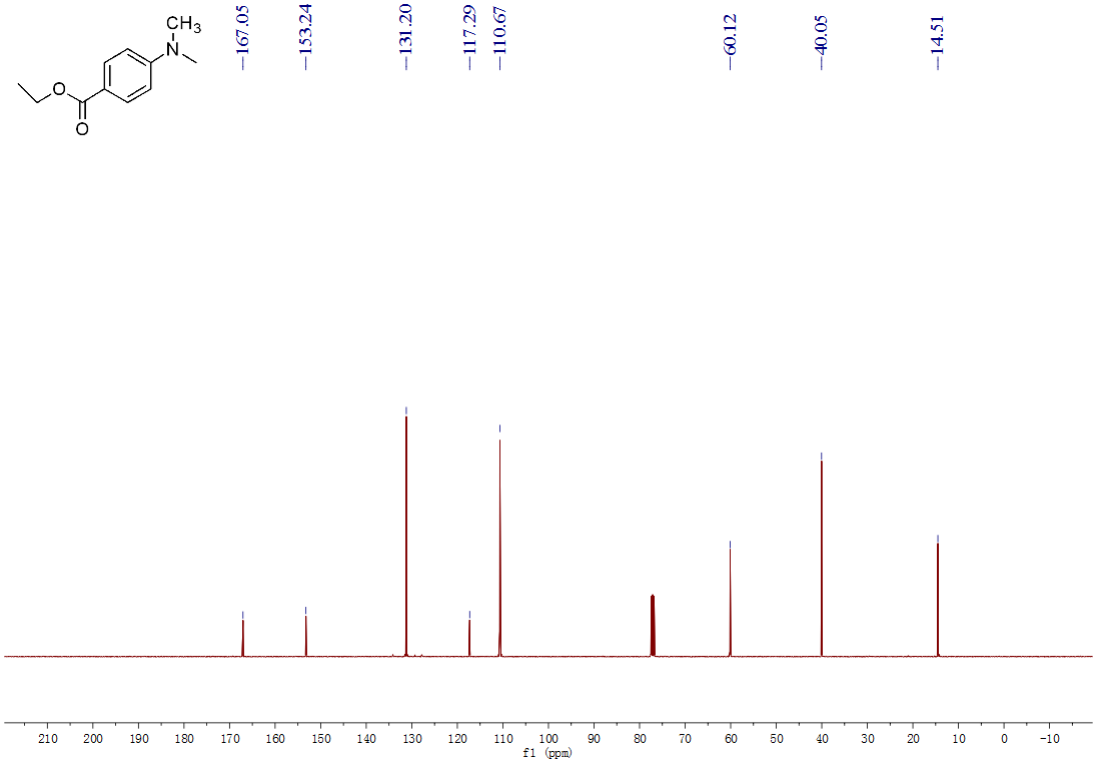
^{13}C NMR spectrum of **3-chloro-*N*,*N*-dimethylaniline (12)**



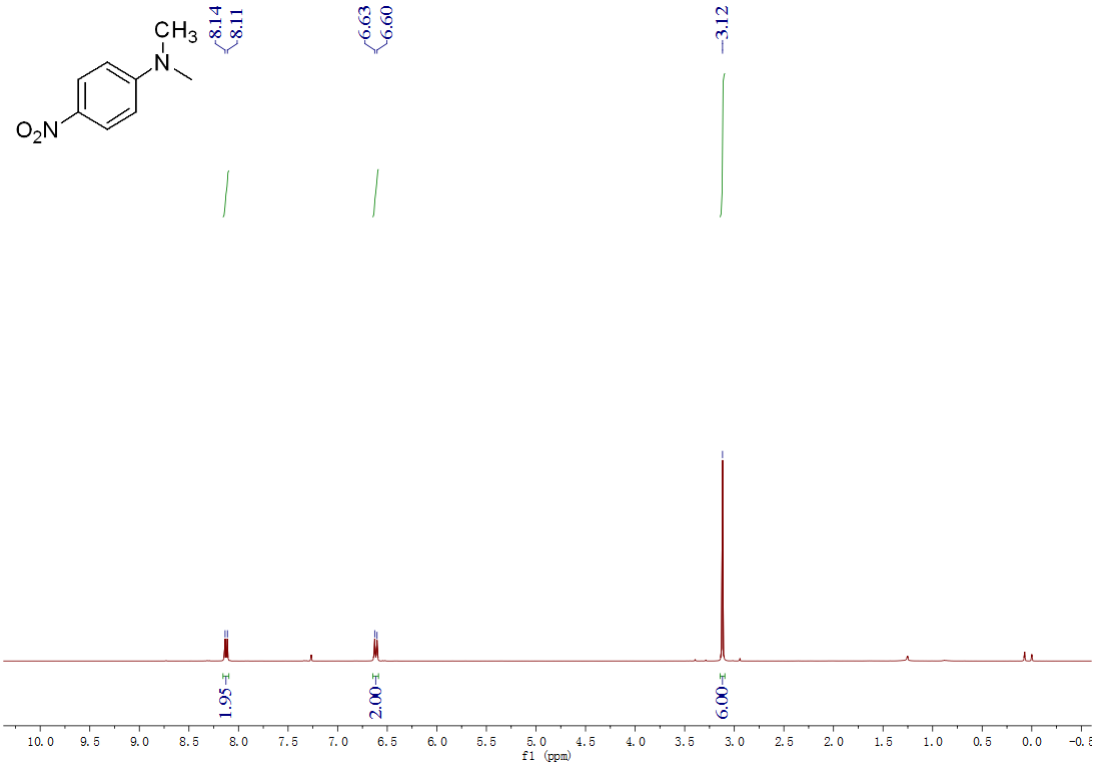
^{1}H NMR spectrum of **ethyl 4-(dimethylamino)benzoate (13)**



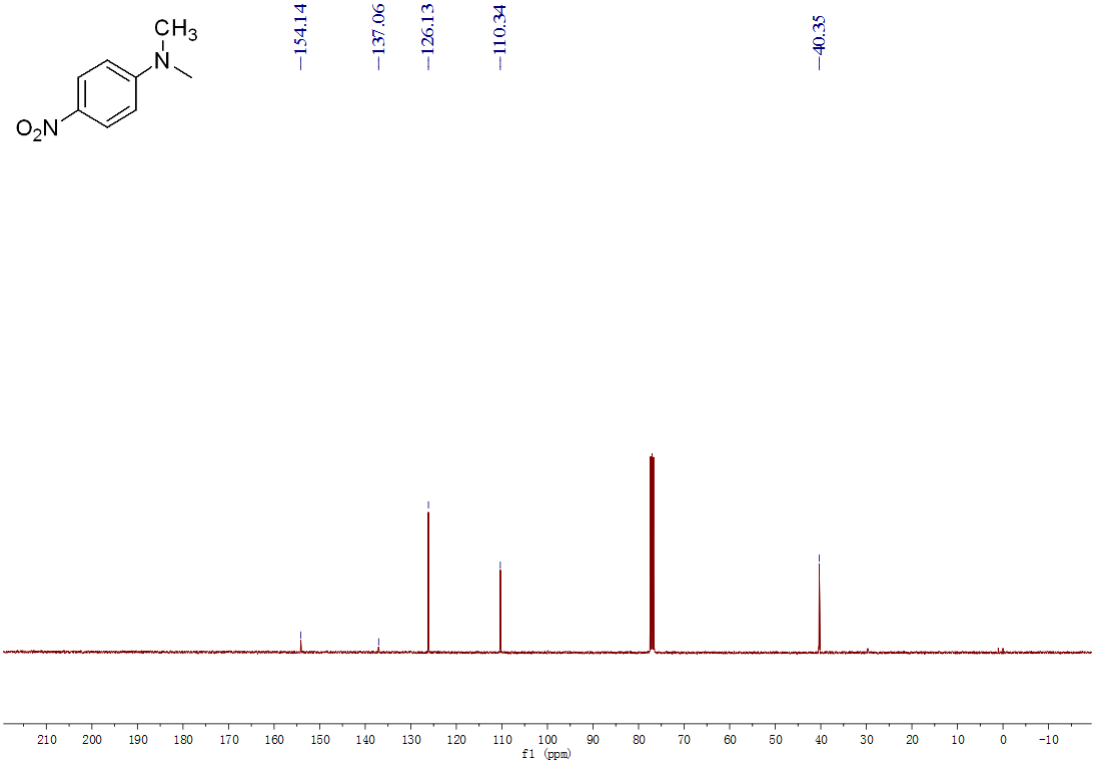
^{13}C NMR spectrum of **ethyl 4-(dimethylamino)benzoate (13)**



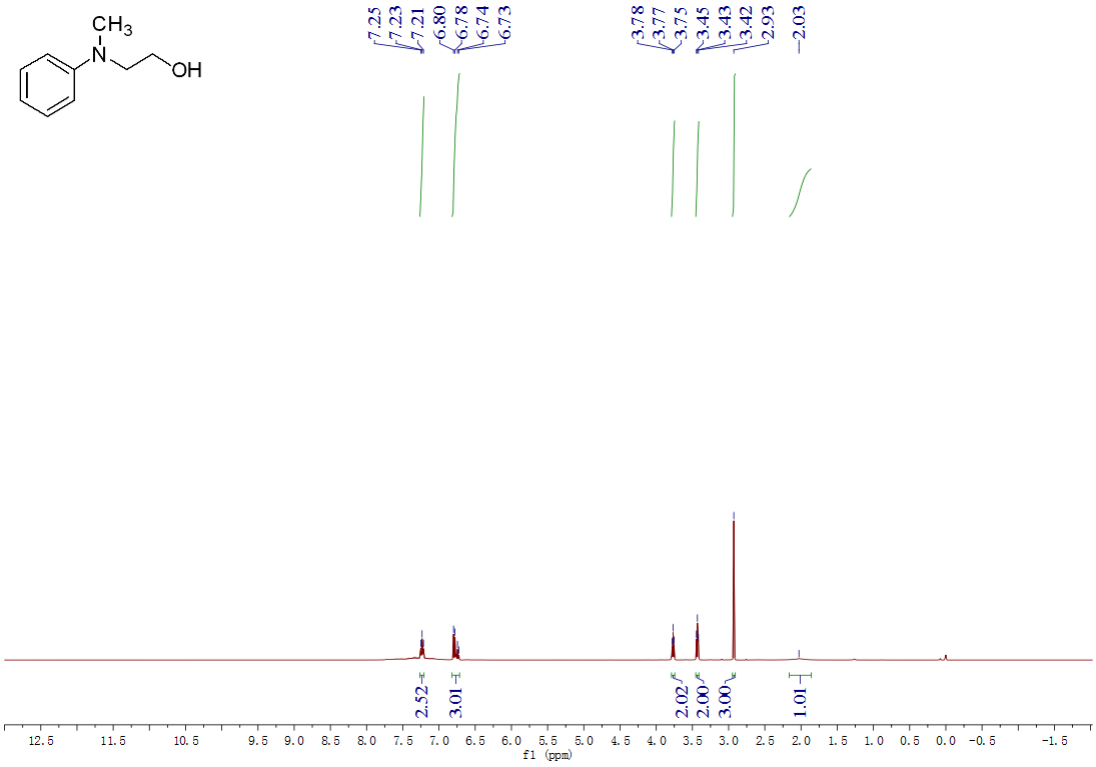
^{1}H NMR spectrum of ***N,N*-dimethyl-4-nitroaniline (14)**



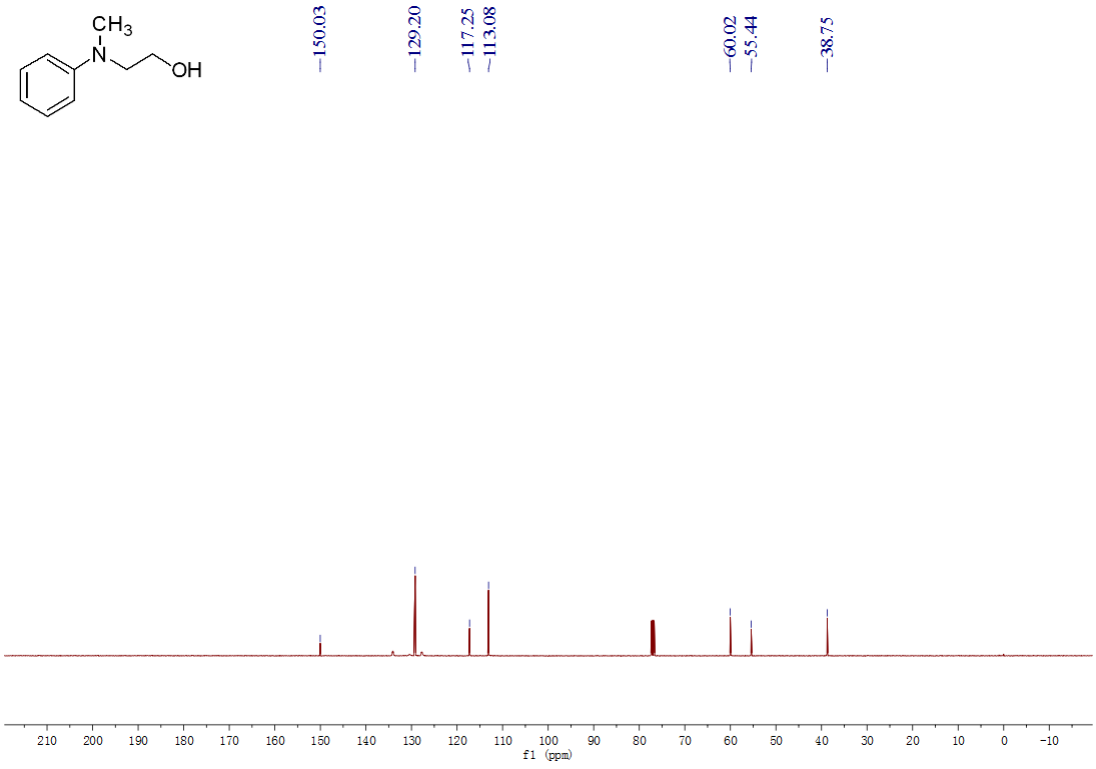
^{13}C NMR spectrum of ***N,N*-dimethyl-4-nitroaniline (14)**



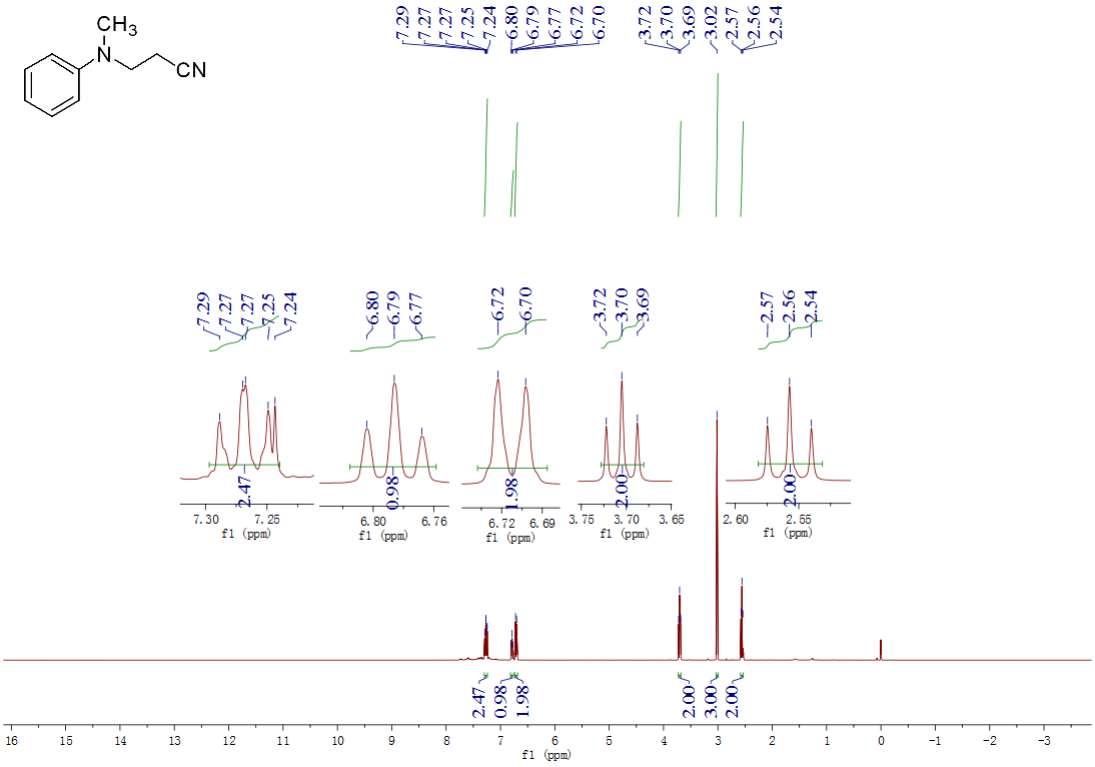
^{1}H NMR spectrum of **2-(methyl(phenyl)amino)ethanol (15)**



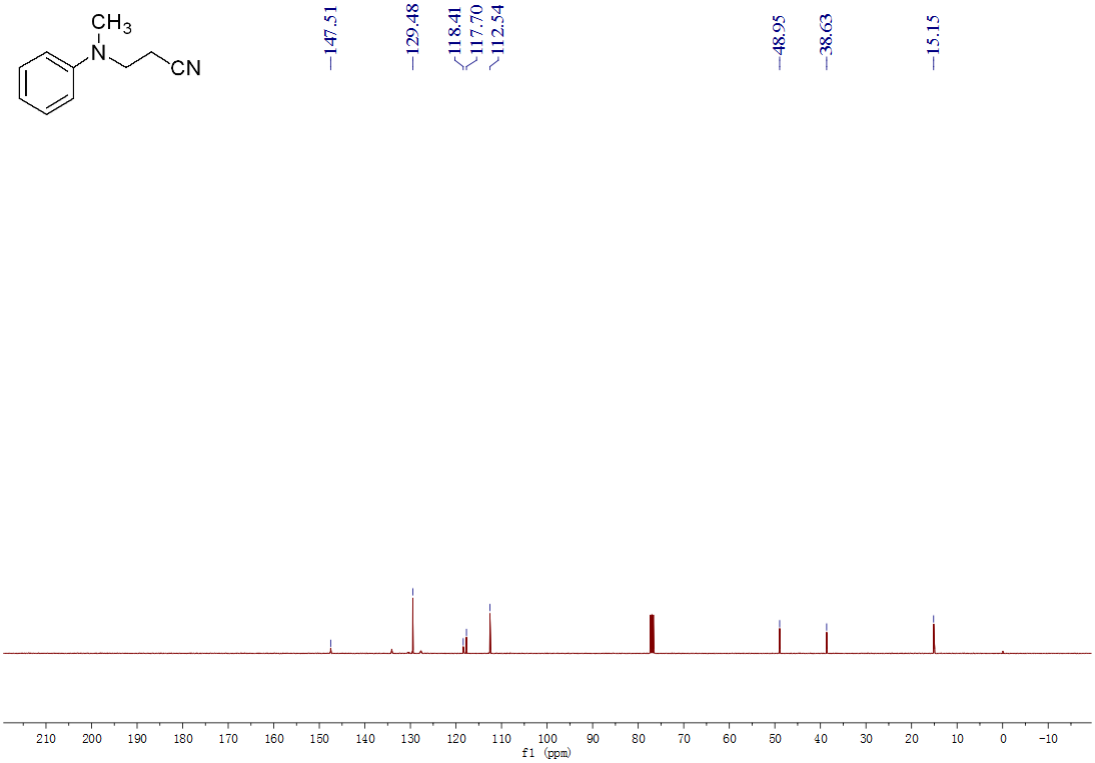
^{13}C NMR spectrum of **2-(methyl(phenyl)amino)ethanol (15)**



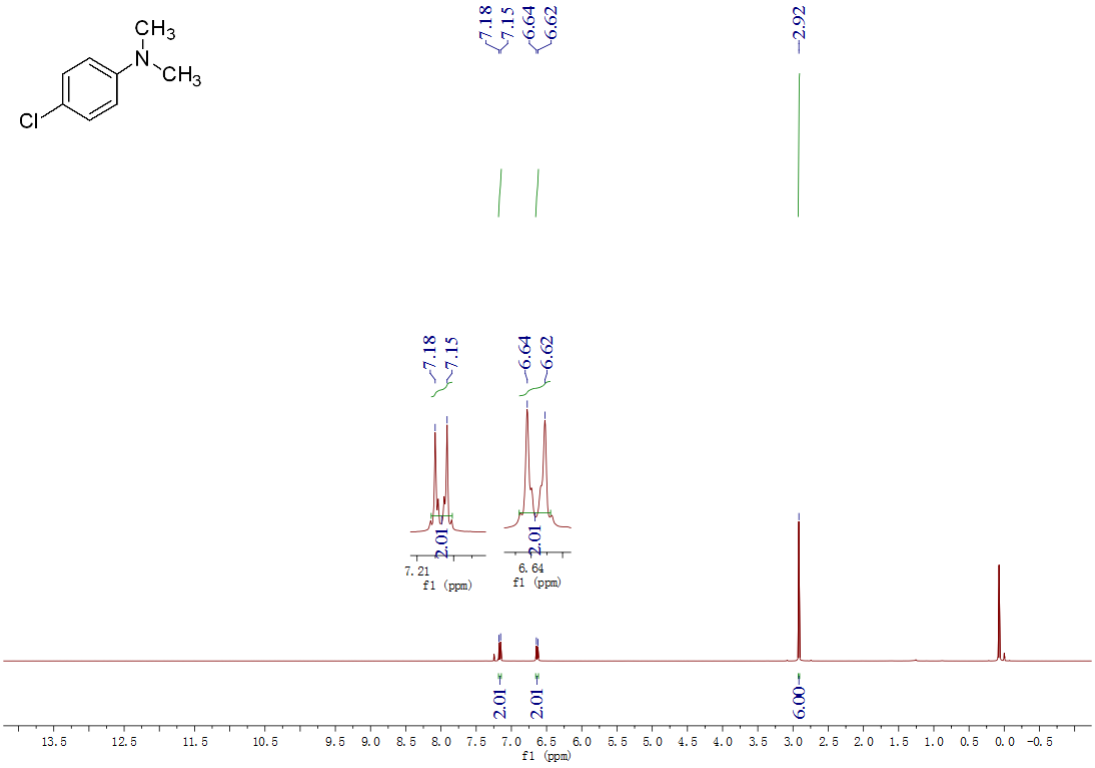
^{1}H NMR spectrum of **3-(methyl(phenyl)amino)propanenitrile (16)**



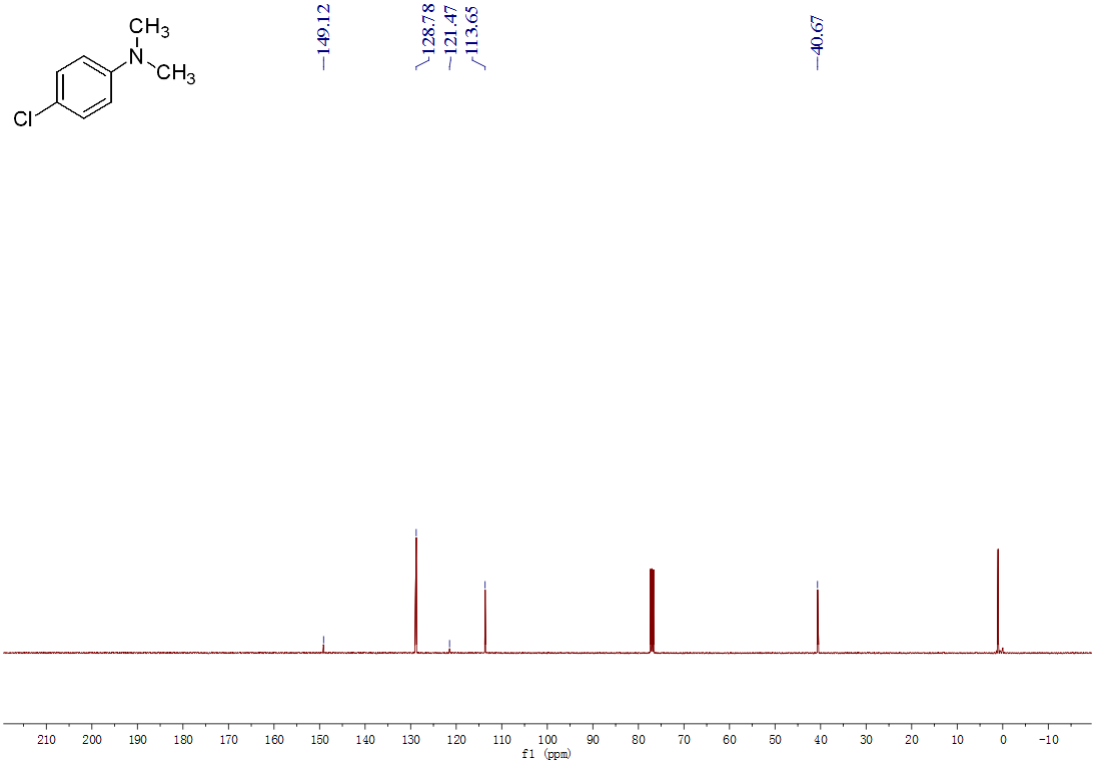
^{13}C NMR spectrum of **3-(methyl(phenyl)amino)propanenitrile (16)**



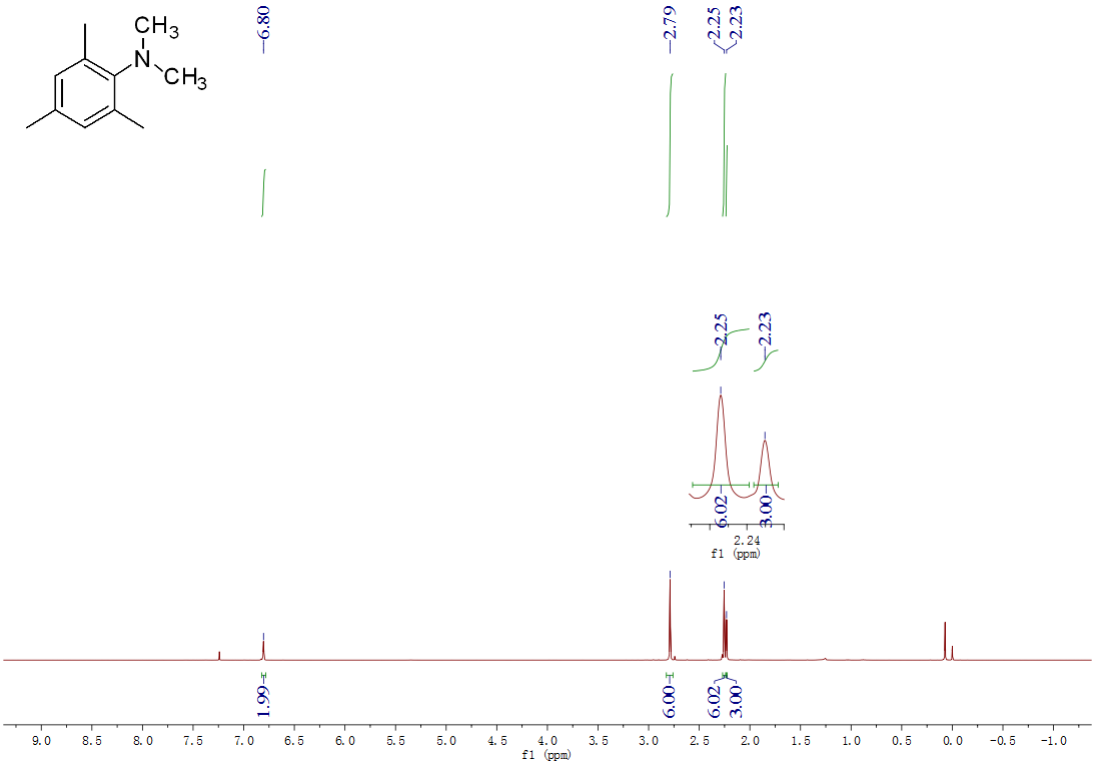
^{1}H NMR spectrum of **4-chloro-*N*,*N*-dimethylaniline (18)**



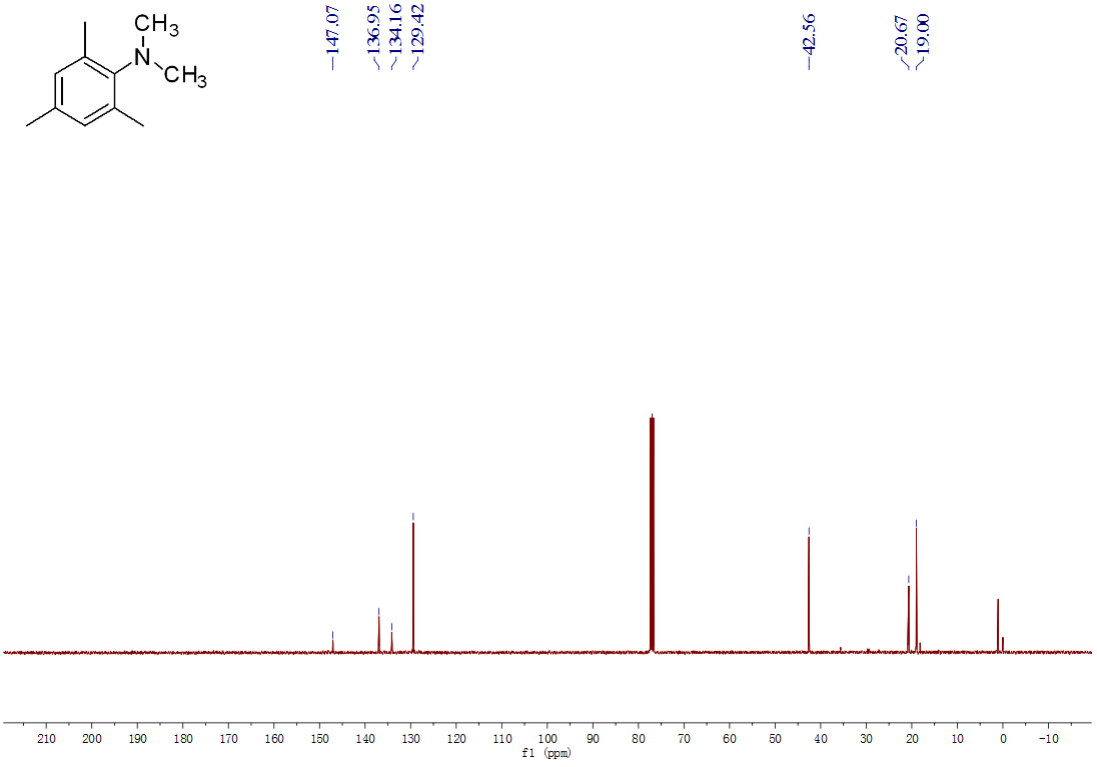
^{13}C NMR spectrum of **4-chloro-*N*,*N*-dimethylaniline (18)**



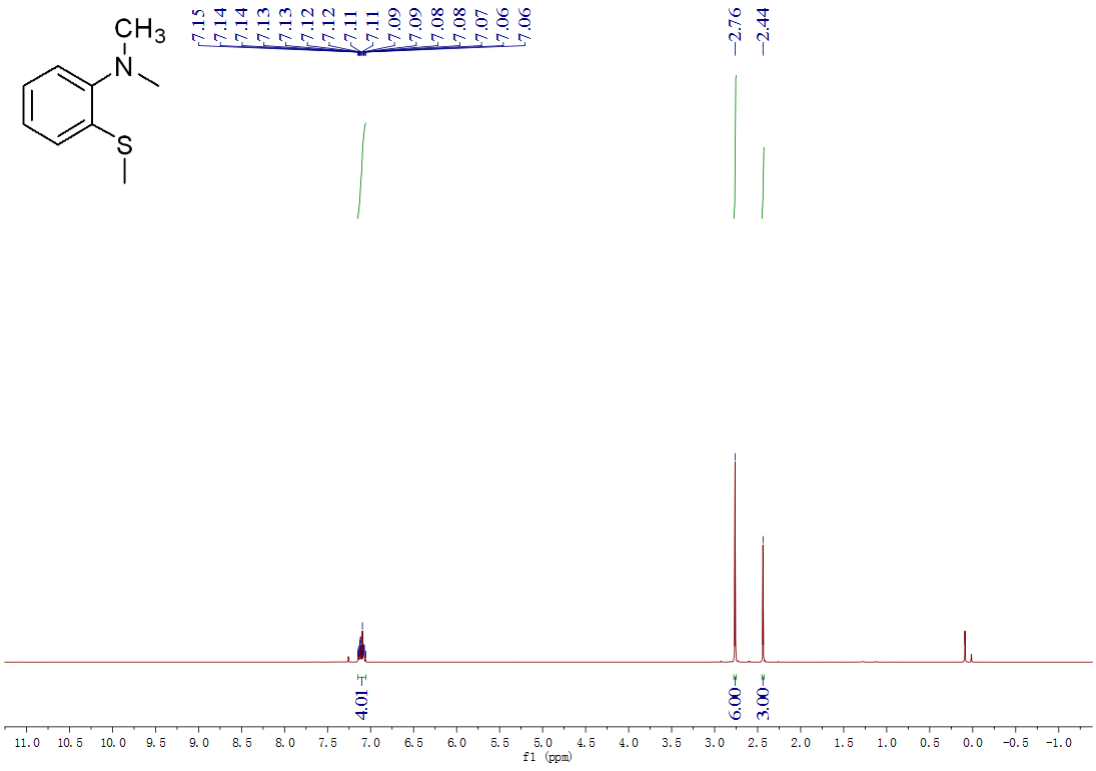
^{1}H NMR spectrum of ***N,N*,2,4,6-pentamethylaniline (19)**



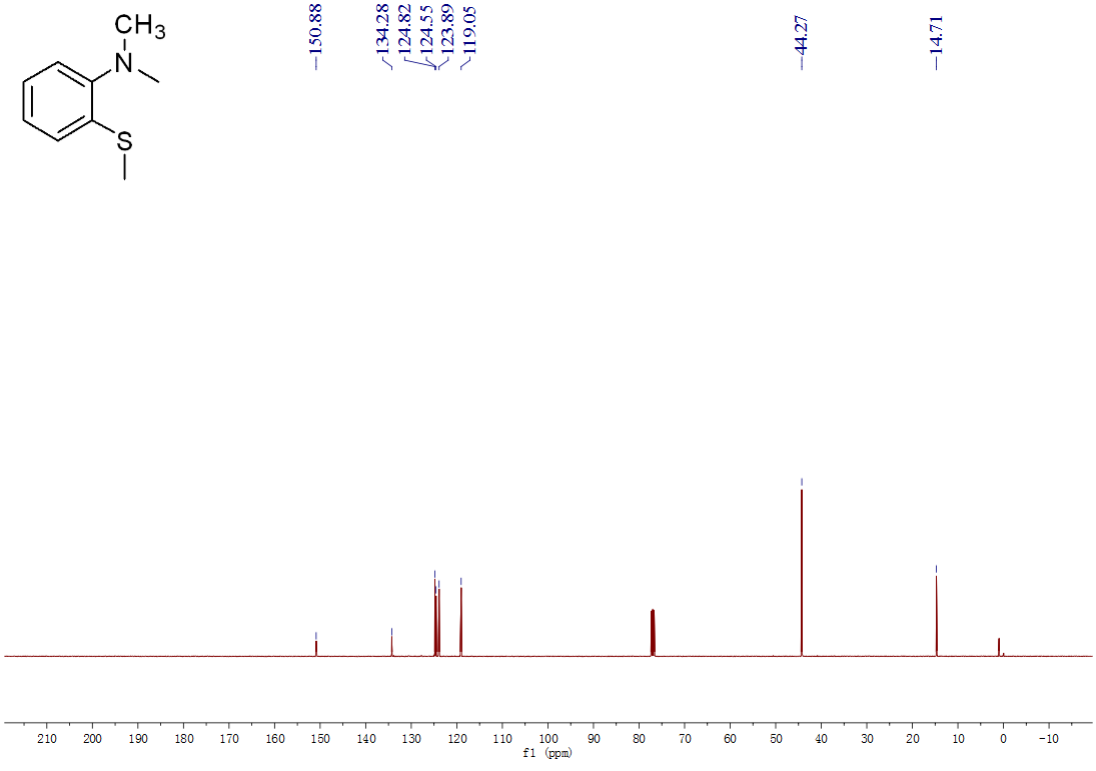
^{13}C NMR spectrum of ***N,N*,2,4,6-pentamethylaniline (19)**



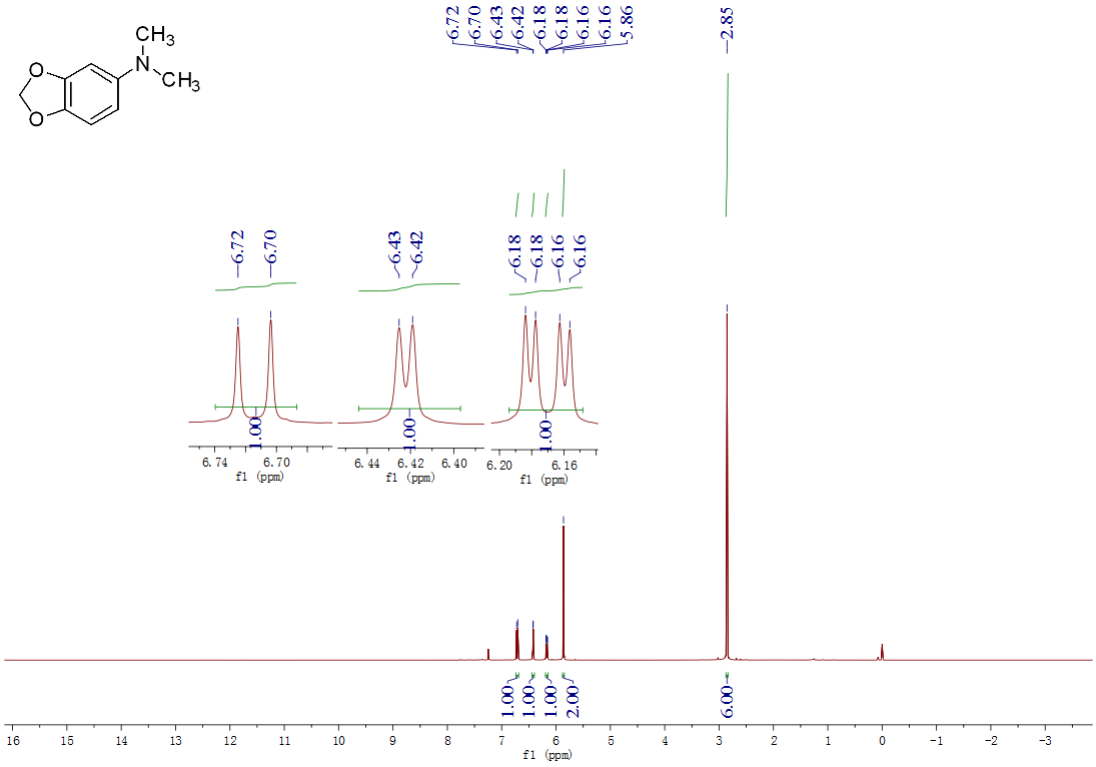
^{1}H NMR spectrum of ***N,N*-dimethyl-2-(methylthio)aniline (20)**



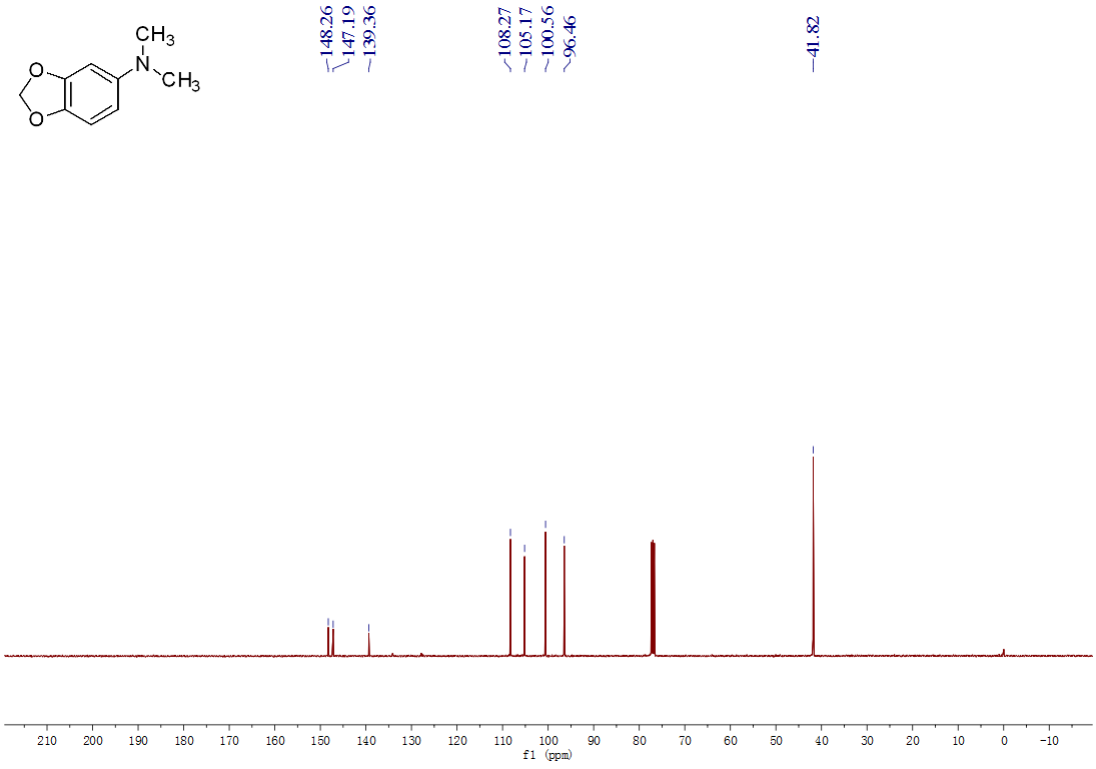
^{13}C NMR spectrum of ***N,N*-dimethyl-2-(methylthio)aniline (20)**



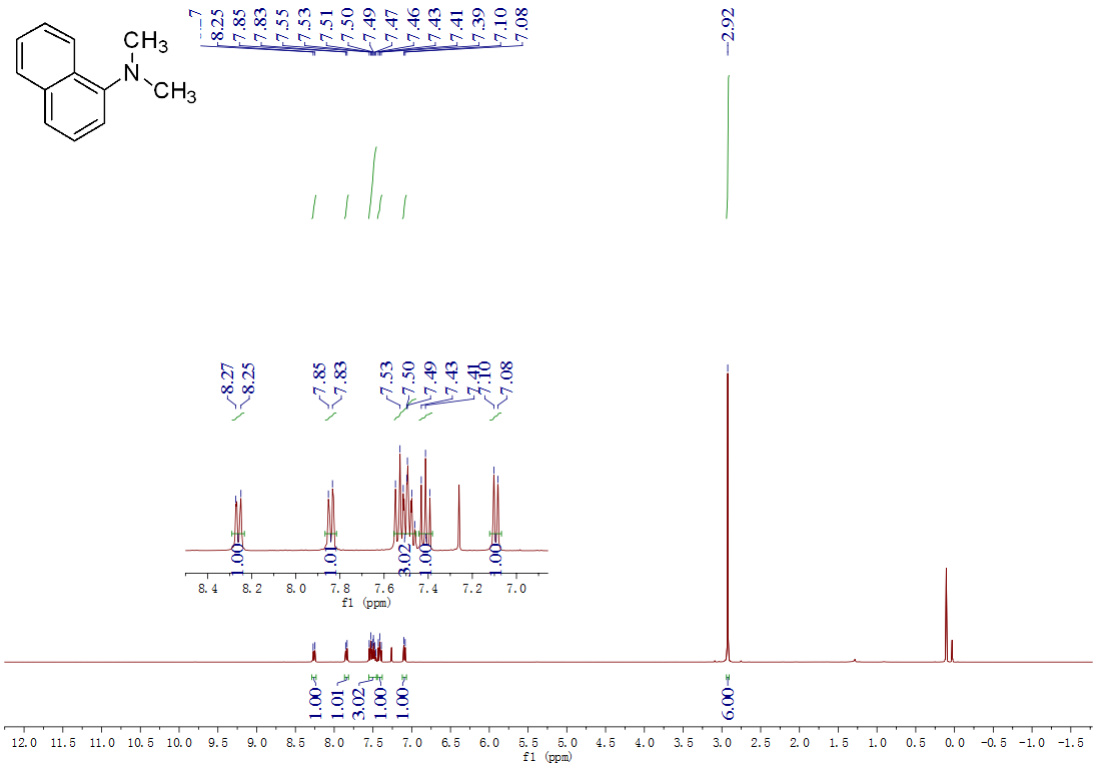
^{1}H NMR spectrum of ***N,N*-dimethylbenzo[*d*][1,3]dioxol-5-amine (21)**



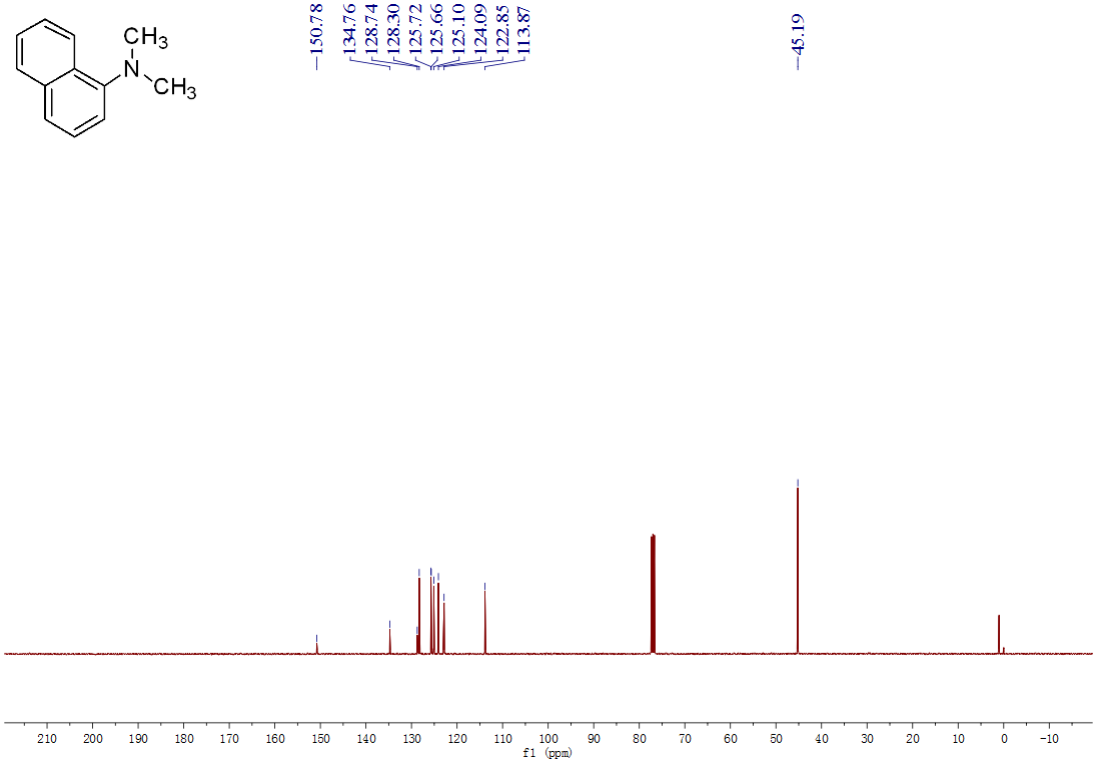
^{13}C NMR spectrum of ***N,N*-dimethylbenzo[*d*][1,3]dioxol-5-amine (21)**



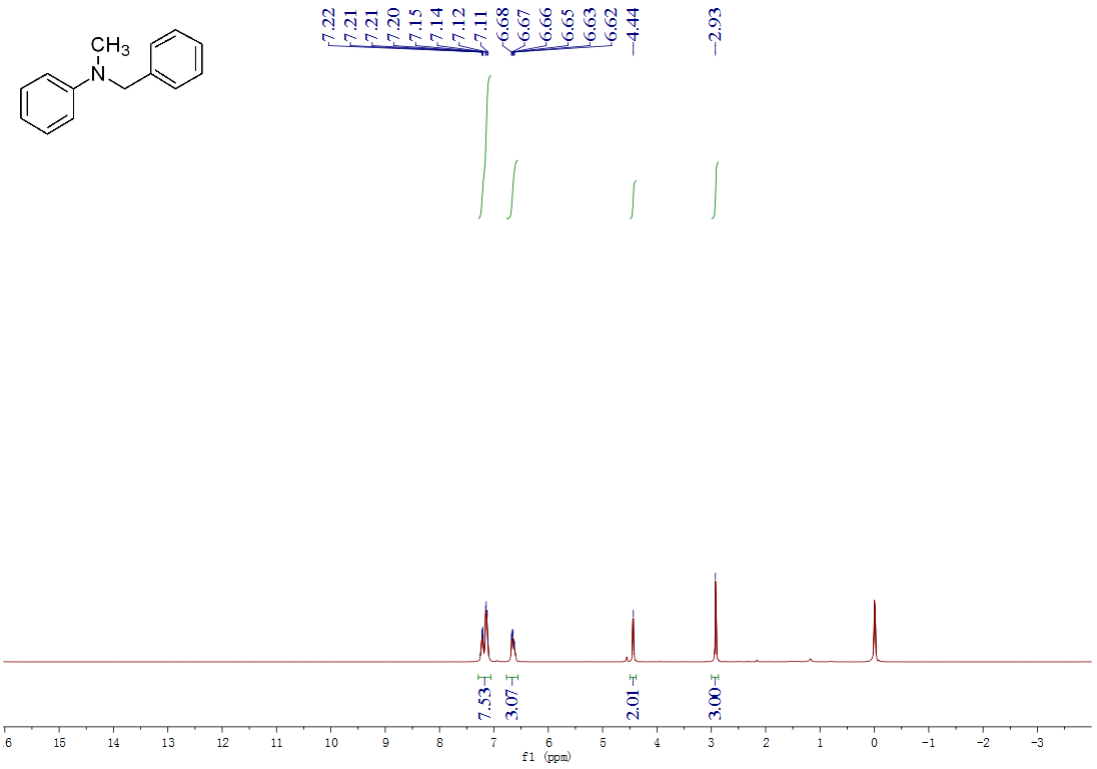
^{1}H NMR spectrum of ***N,N*-dimethylnaphthalen-1-amine (22)**



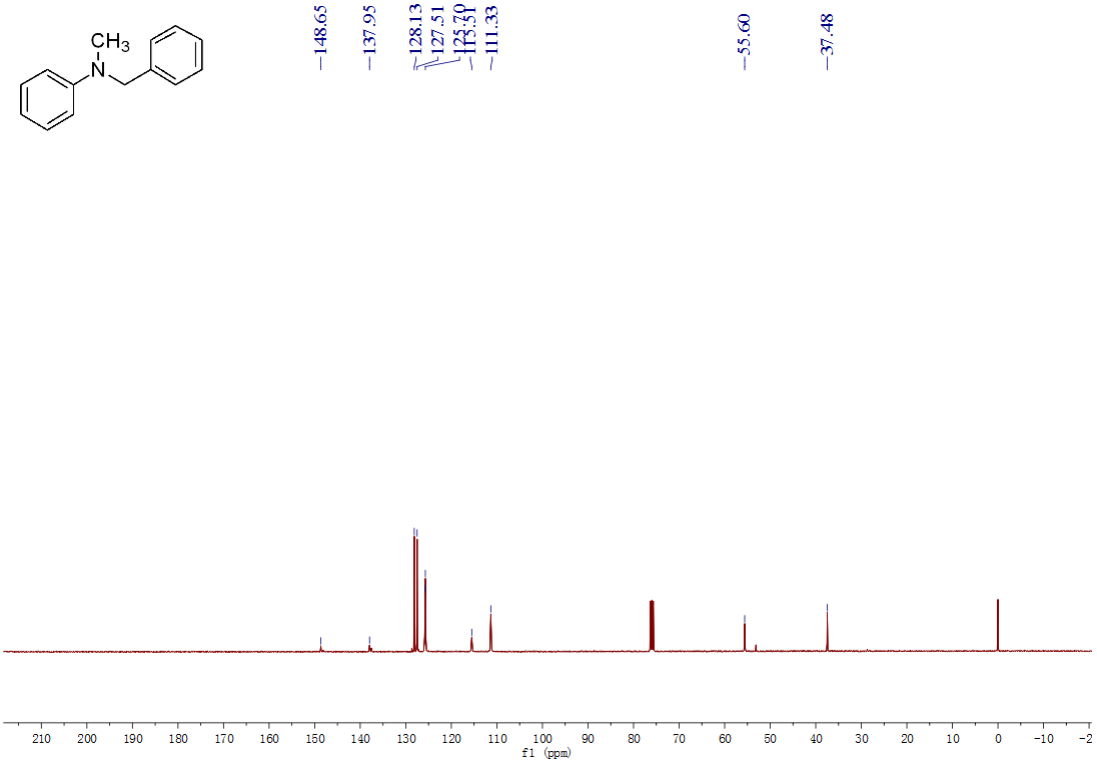
^{13}C NMR spectrum of ***N,N*-dimethylnaphthalen-1-amine (22)**



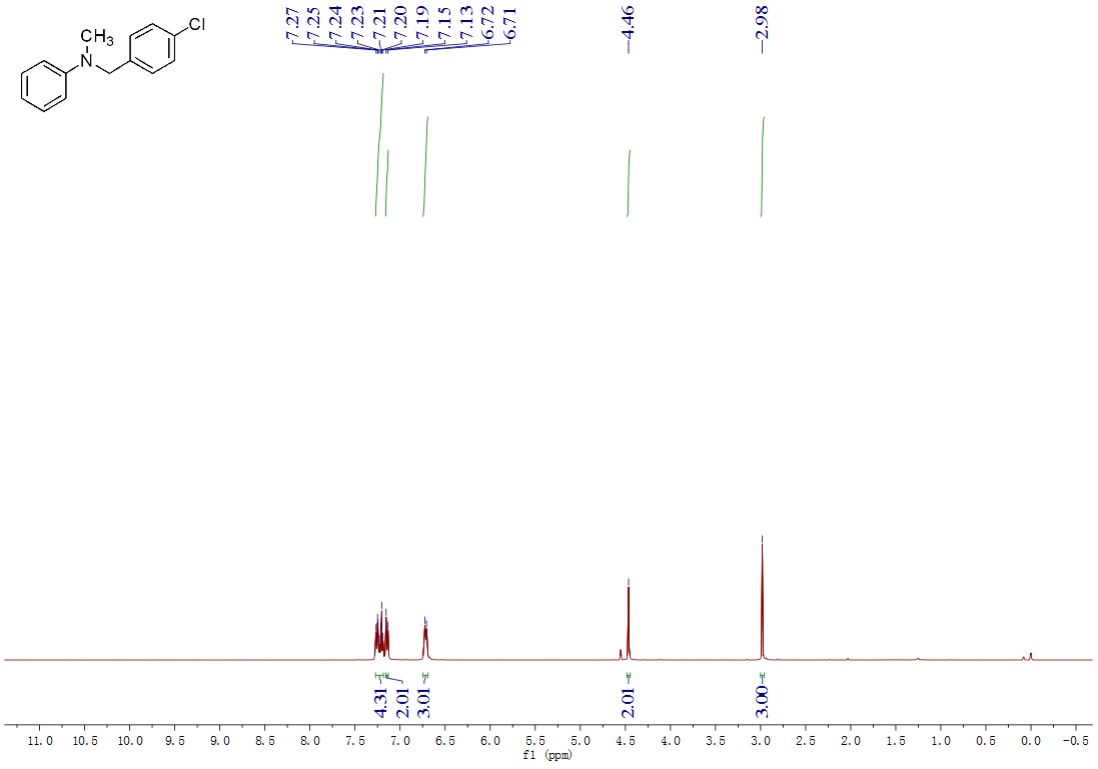
^{1}H NMR spectrum of ***N*-benzyl-*N*-methylaniline (23)**



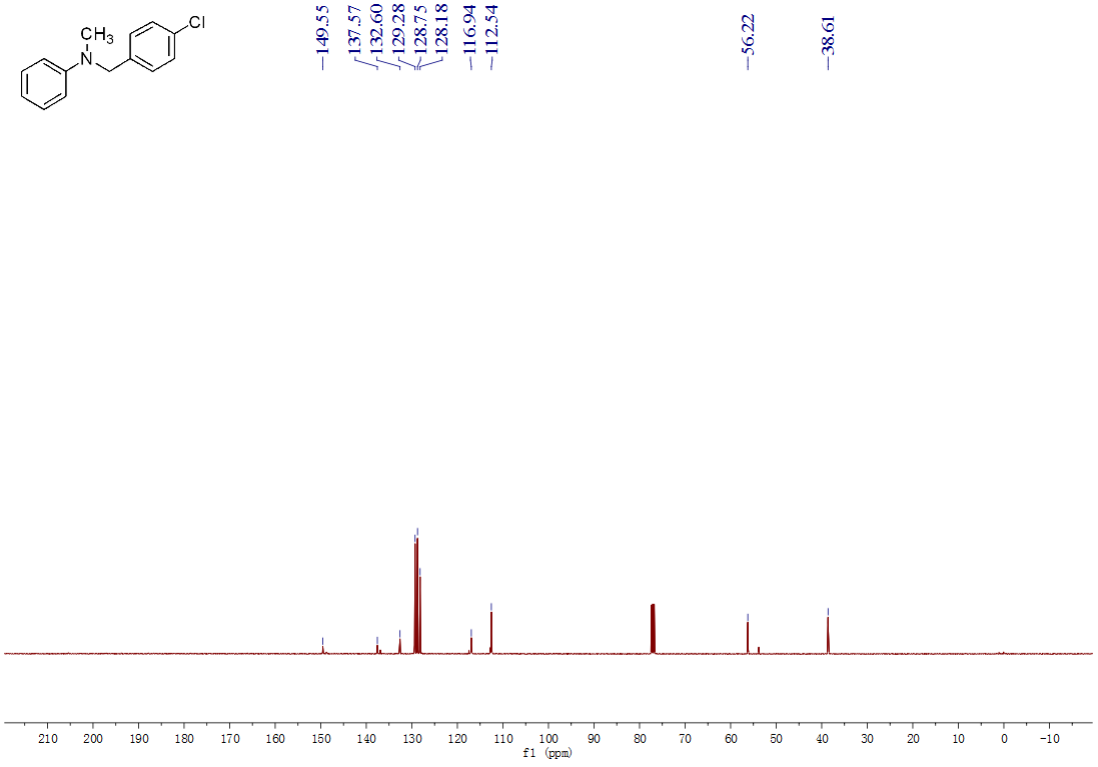
^{13}C NMR spectrum of ***N*-benzyl-*N*-methylaniline (23)**



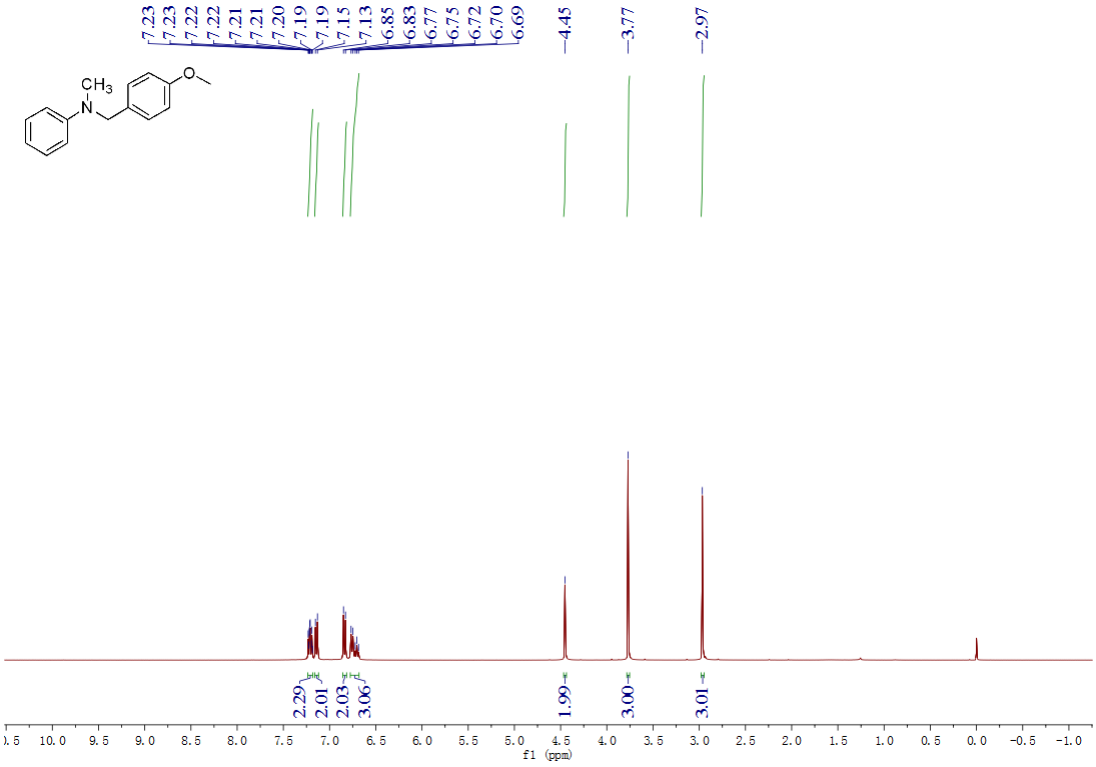
^{1}H NMR spectrum of ***N*-(4-chlorobenzyl)-*N*-methylaniline (24)**



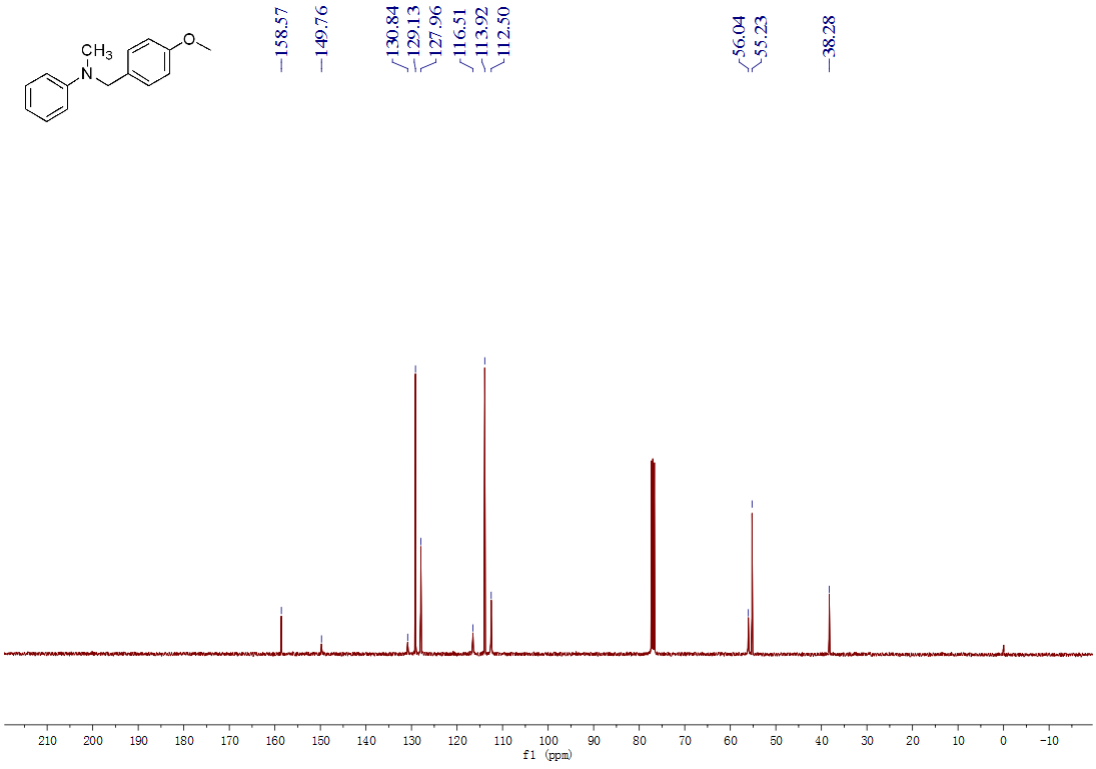
^{13}C NMR spectrum of ***N*-(4-chlorobenzyl)-*N*-methylaniline (24)**



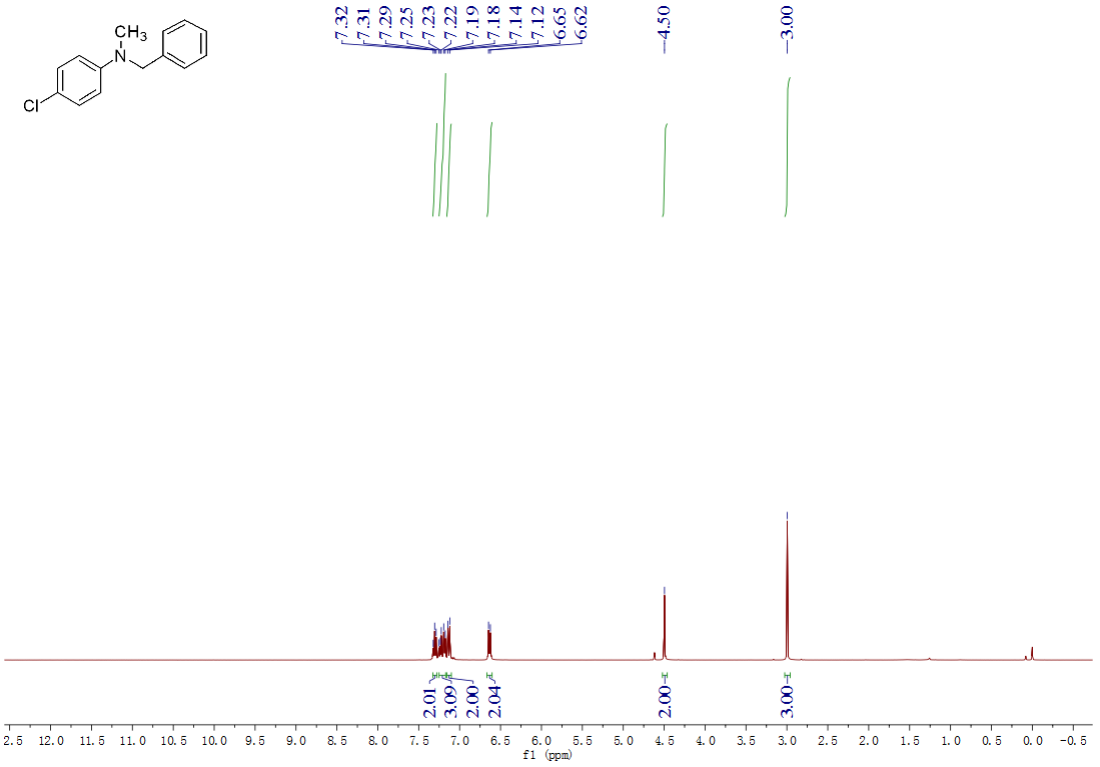
^{1}H NMR spectrum of ***N*-(4-methoxybenzyl)-*N*-methylaniline (25)**



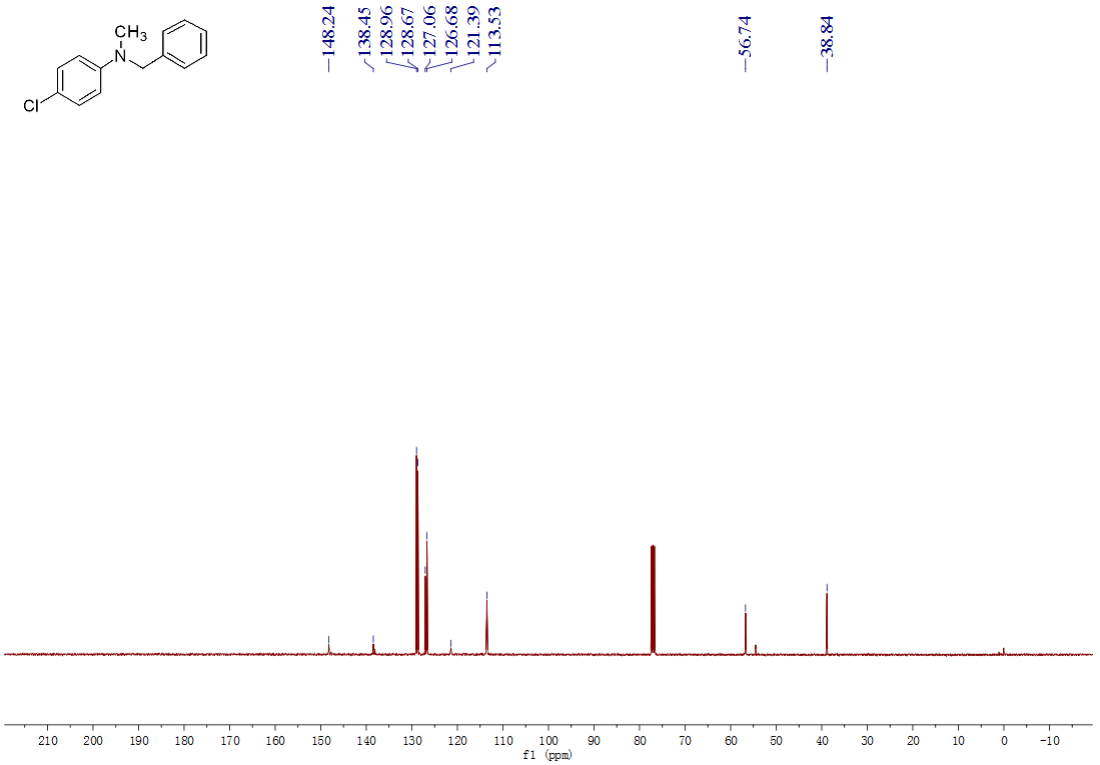
^{13}C NMR spectrum of ***N*-(4-methoxybenzyl)-*N*-methylaniline (25)**



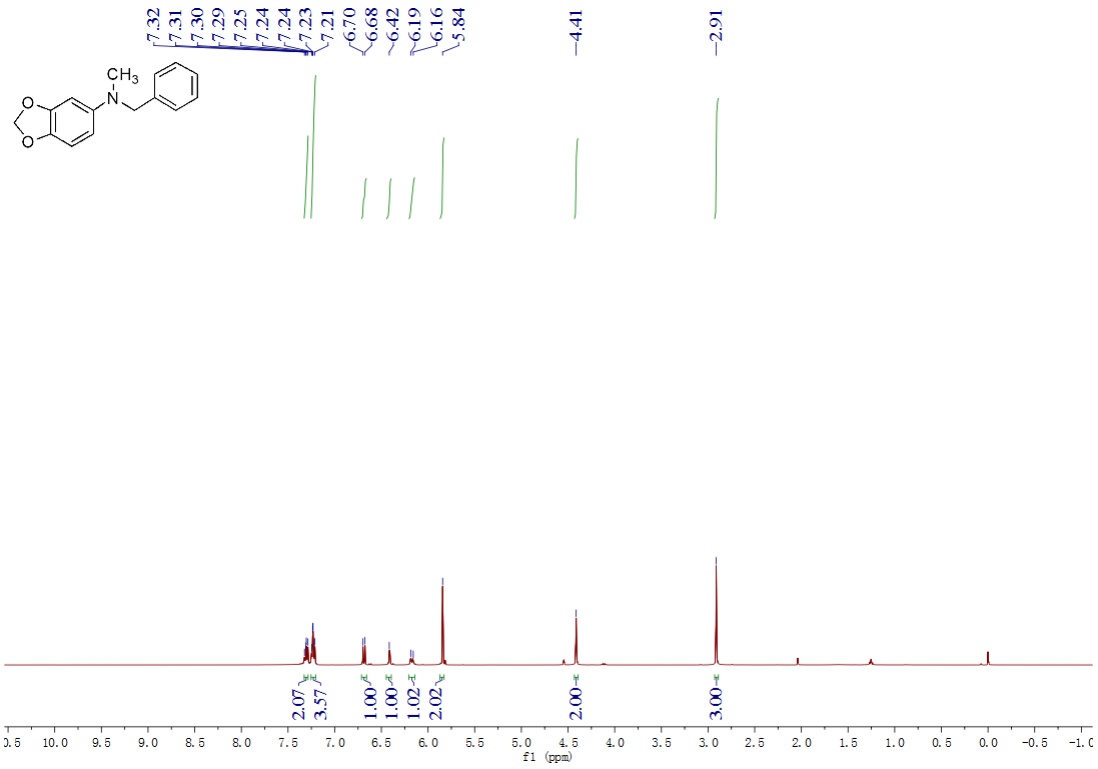
^{1}H NMR spectrum of ***N*-benzyl-4-chloro-*N*-methylaniline (26)**



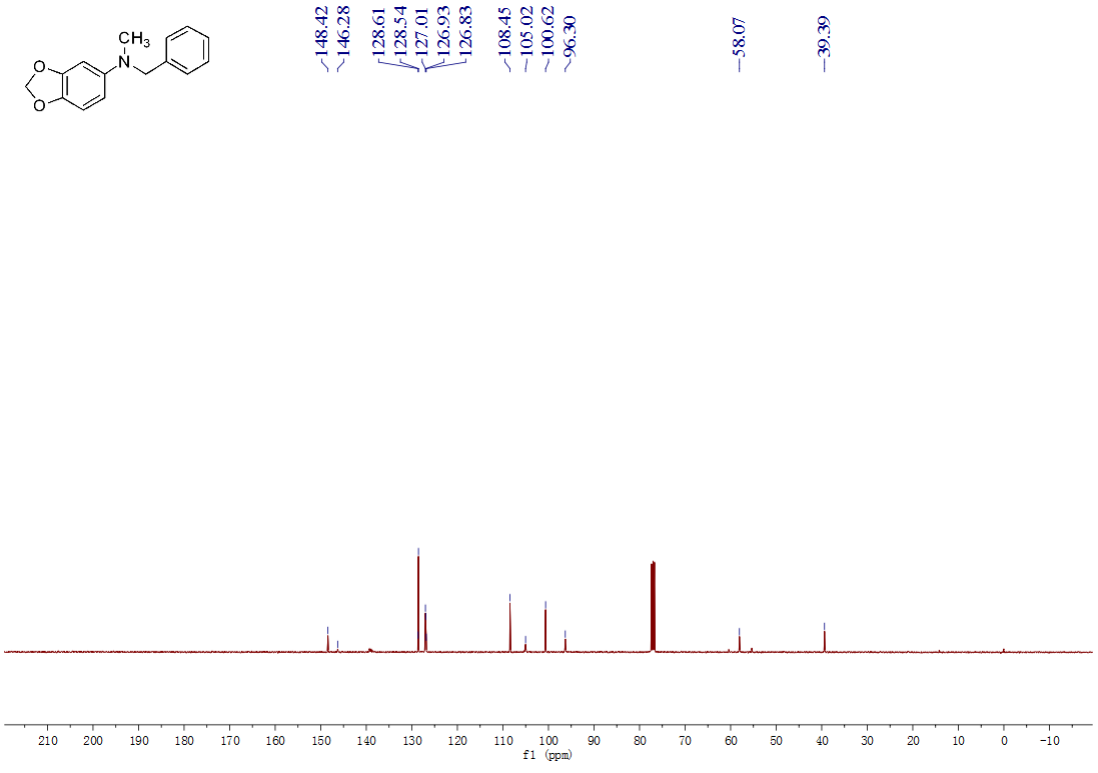
^{13}C NMR spectrum of ***N*-benzyl-4-chloro-*N*-methylaniline (26)**



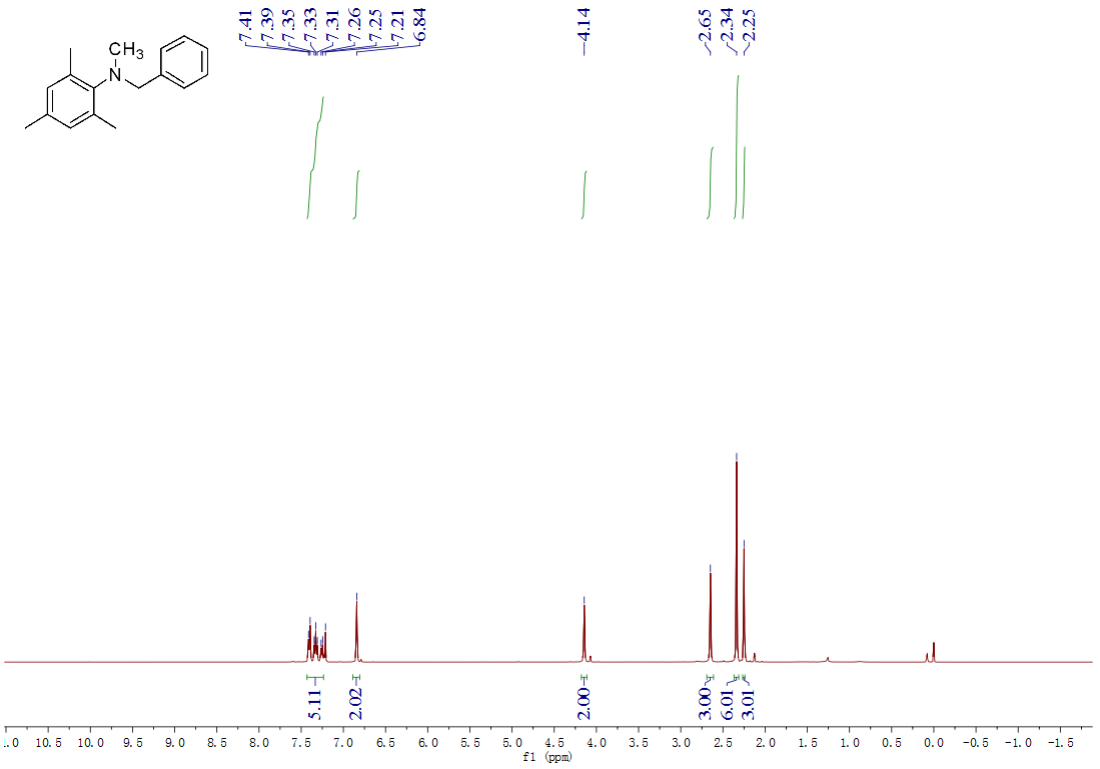
^{1}H NMR spectrum of ***N*-benzyl-*N*-methylbenzo[*d*][1,3]dioxol-5-amine (27)**



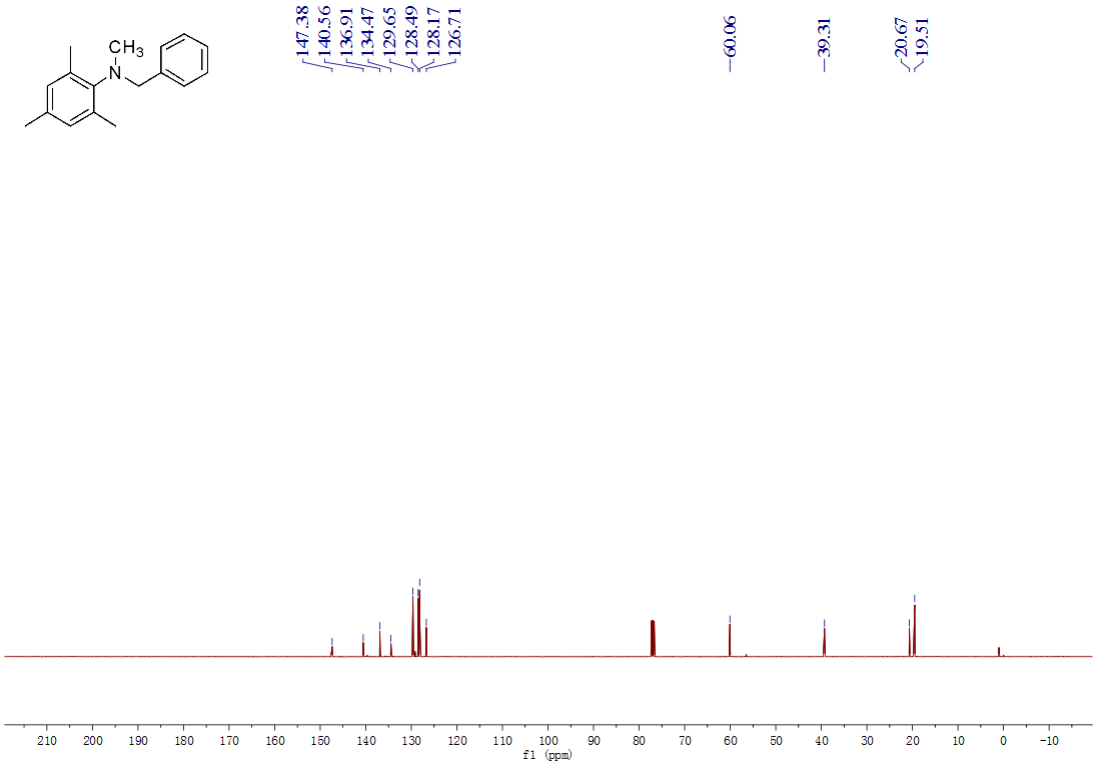
^{13}C NMR spectrum of ***N*-benzyl-*N*-methylbenzo[*d*][1,3]dioxol-5-amine (27)**



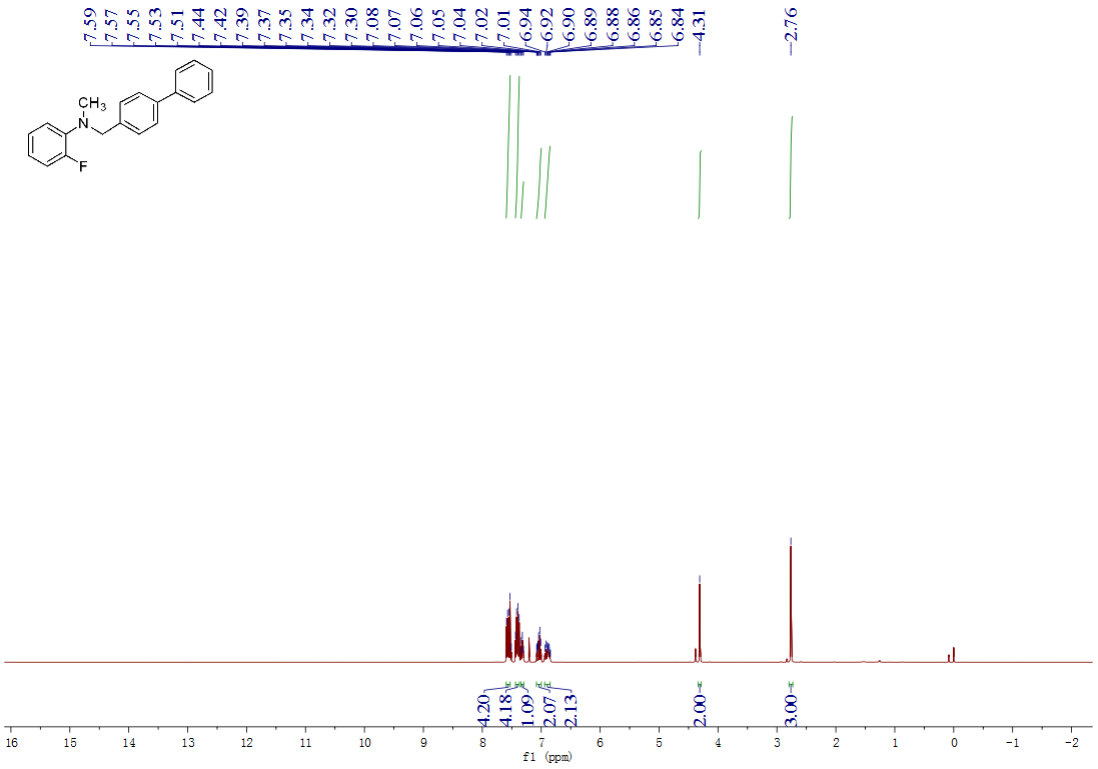
^{1}H NMR spectrum of ***N*-benzyl-*N*,2,4,6-tetramethylaniline (28)**



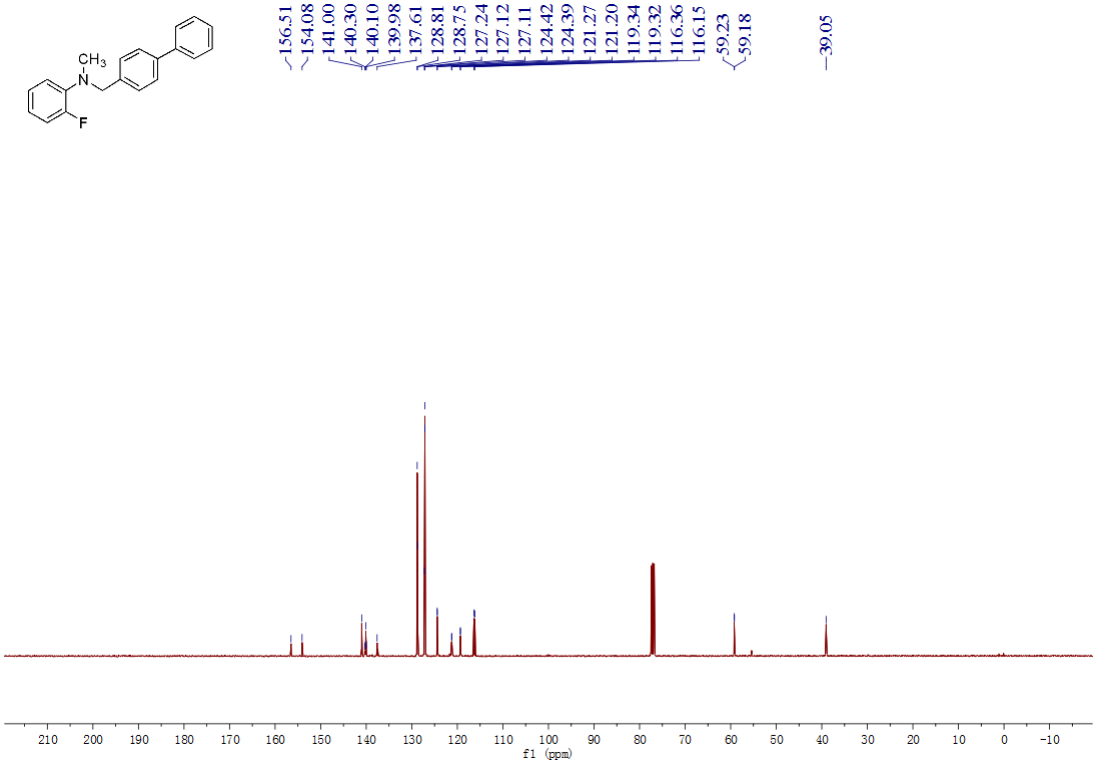
^{13}C NMR spectrum of ***N*-benzyl-*N*,2,4,6-tetramethylaniline (28)**



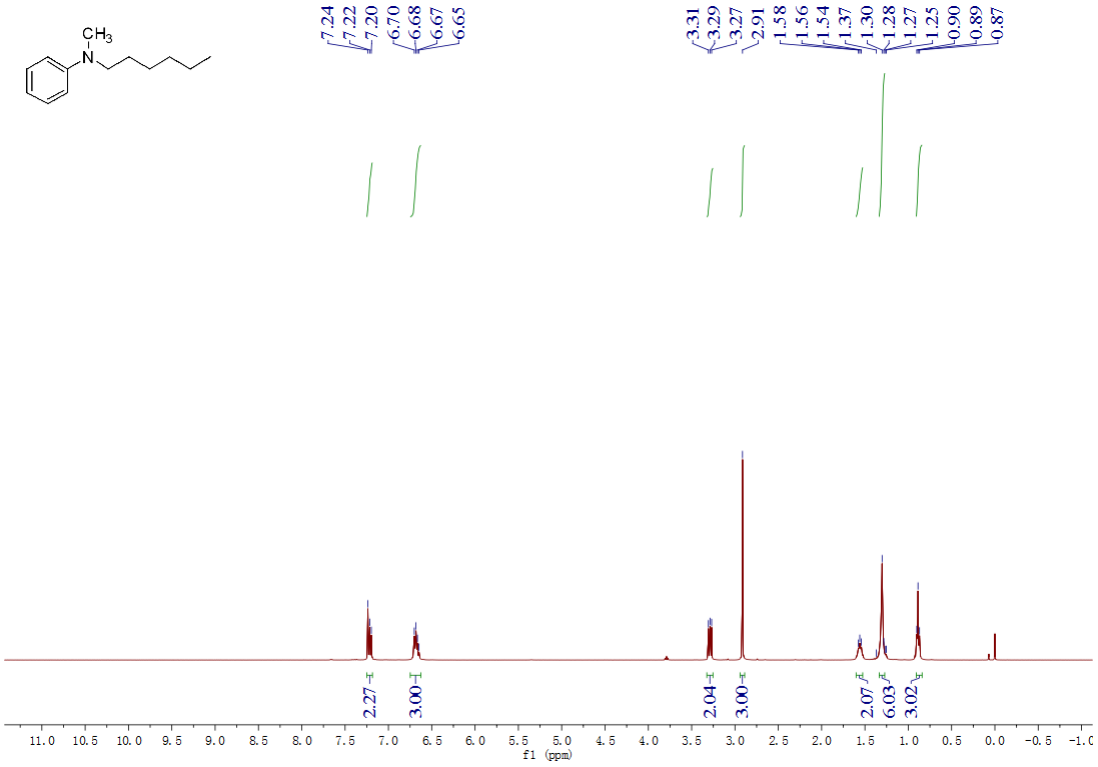
^{1}H NMR spectrum of ***N*-([1,1'-biphenyl]-4-ylmethyl)-2-fluoro-*N*-methylaniline (29)**



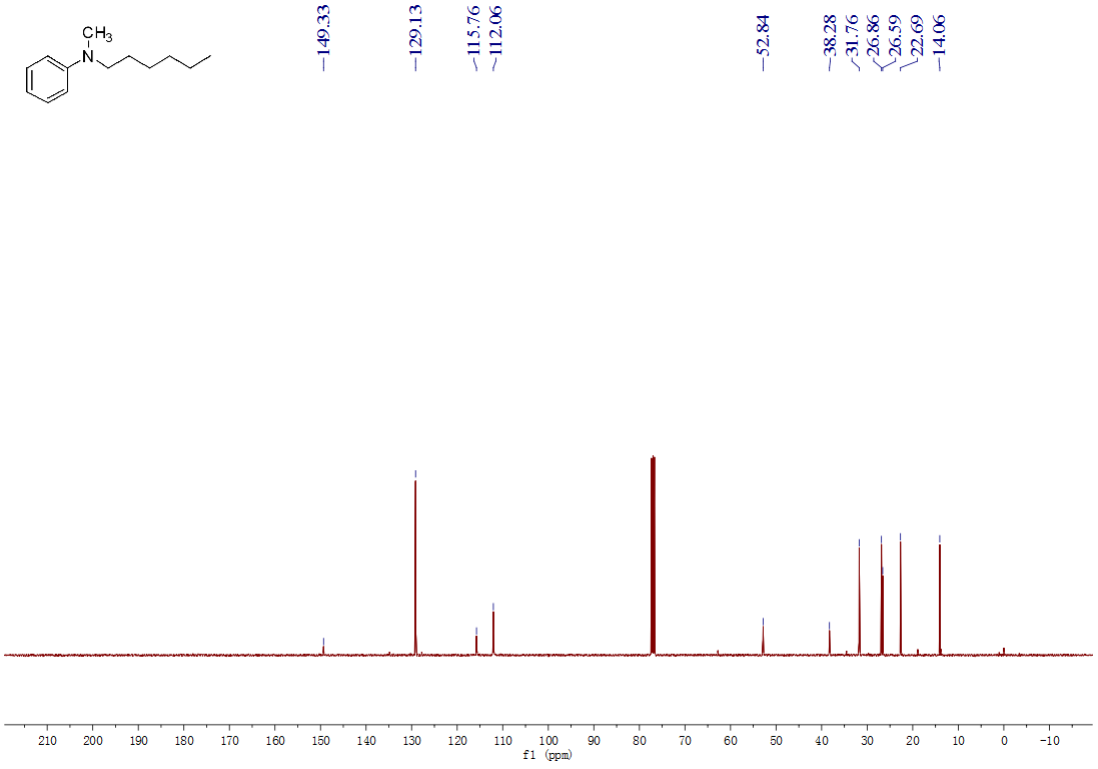
^{13}C NMR spectrum of ***N*-([1,1'-biphenyl]-4-ylmethyl)-2-fluoro-*N*-methylaniline (29)**



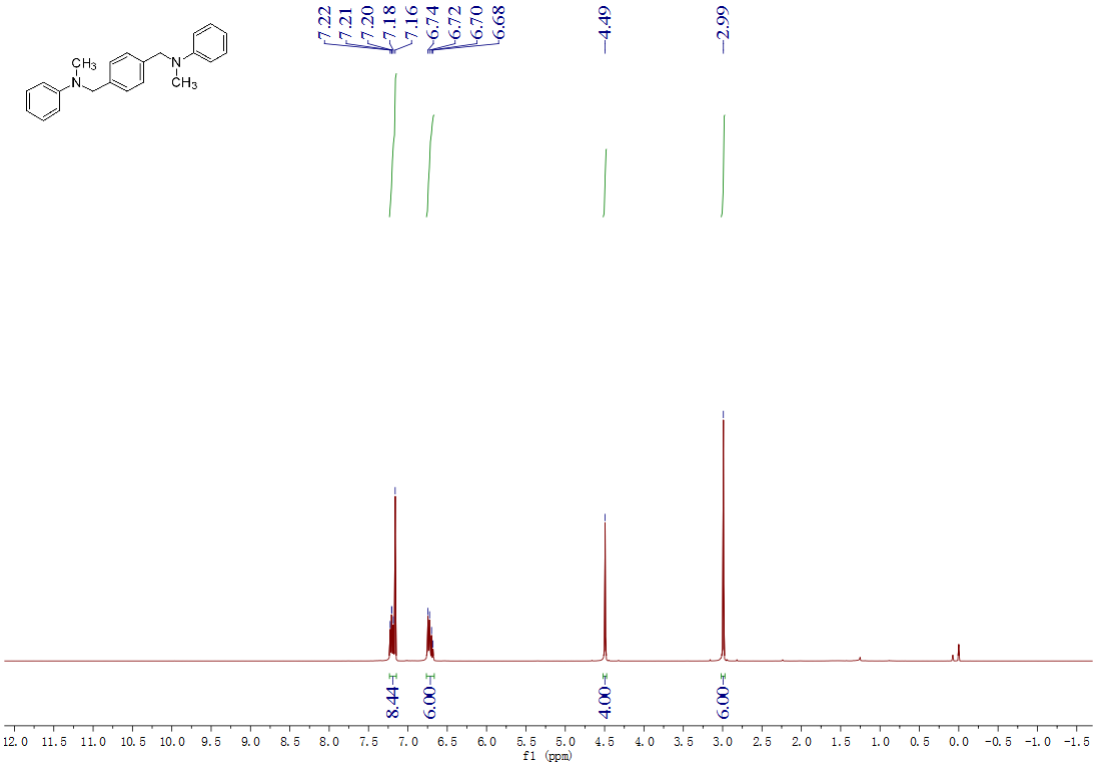
^{1}H NMR spectrum of ***N*-hexyl-*N*-methylaniline (30)**



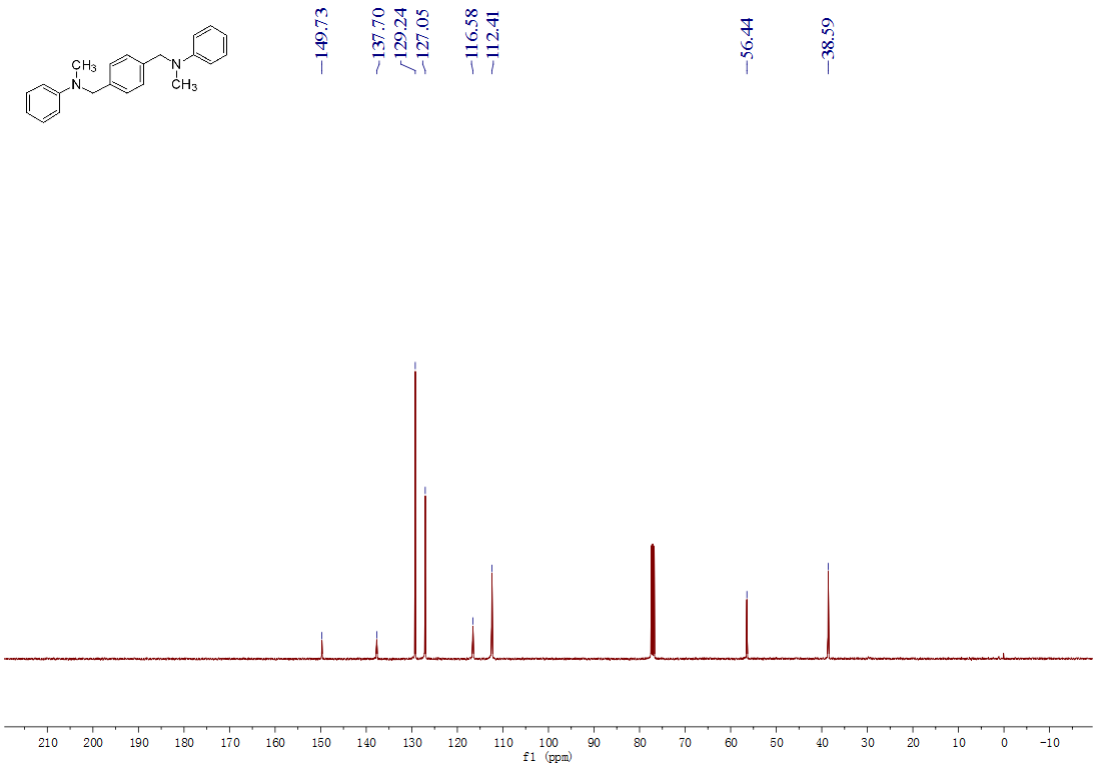
^{13}C NMR spectrum of ***N*-hexyl-*N*-methylaniline (30)**



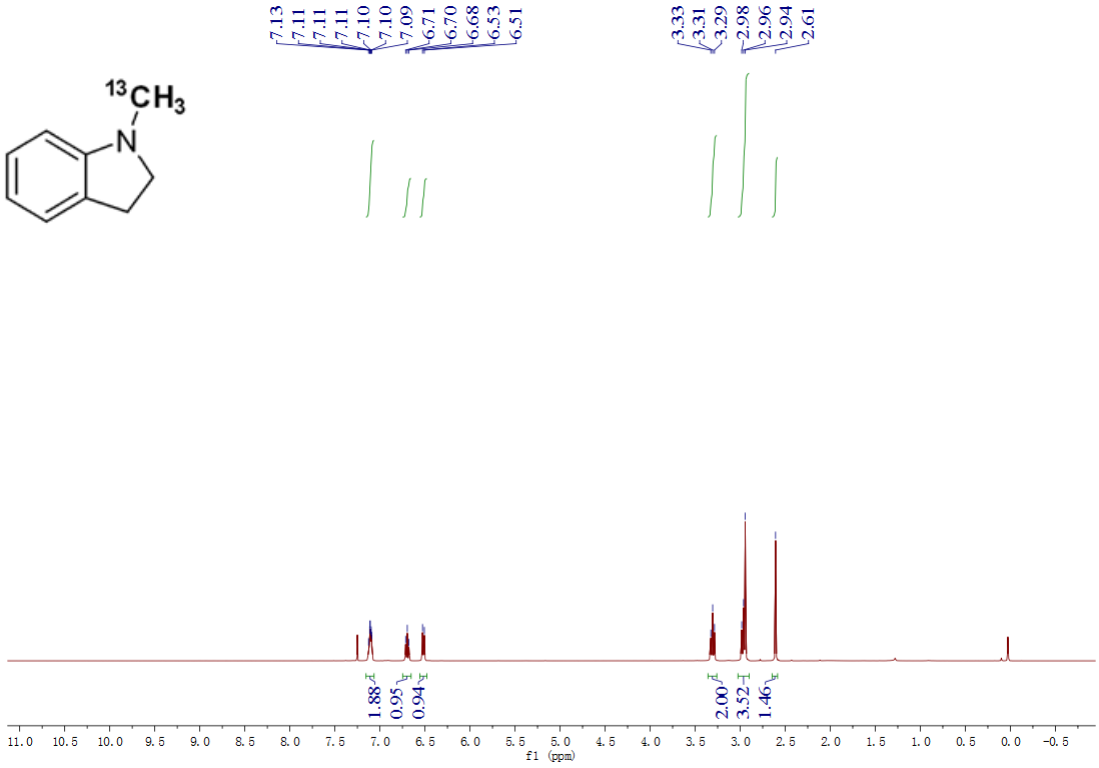
^{1}H NMR spectrum of ***N,N′*-(1,4-phenylenebis(methylene))bis(*N*-methylaniline) (31)**



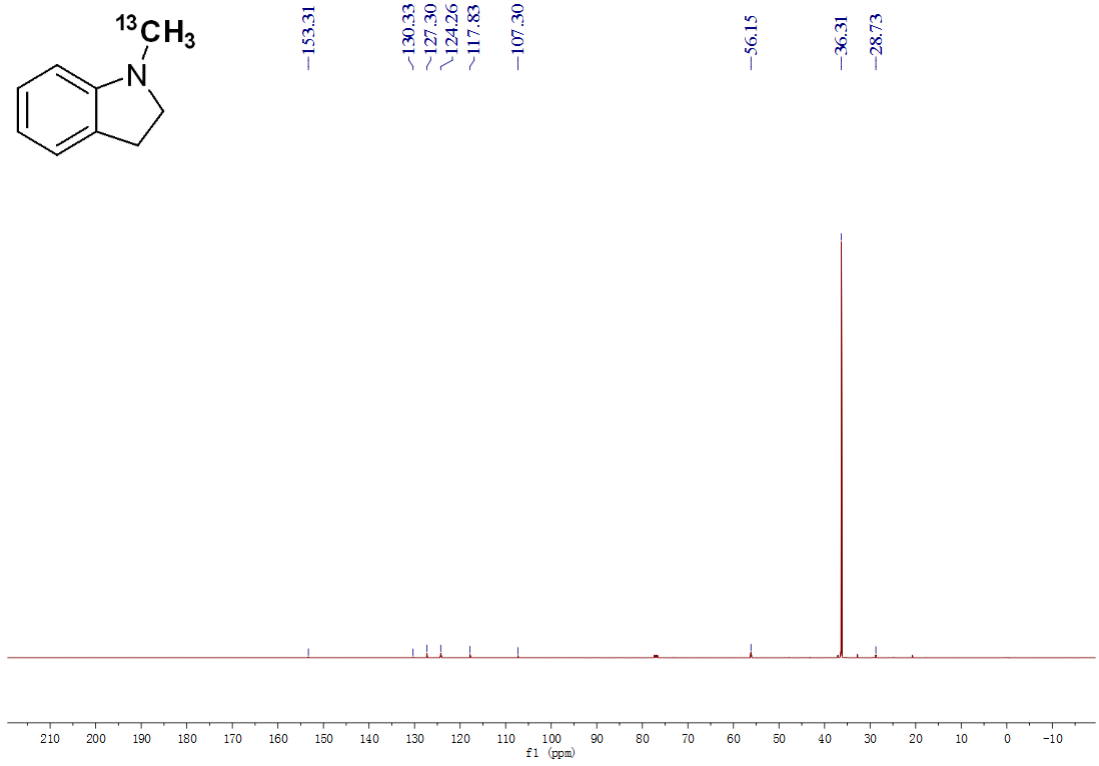
^{13}C NMR spectrum of ***N,N′*-(1,4-phenylenebis(methylene))bis(*N*-methylaniline) (31)**



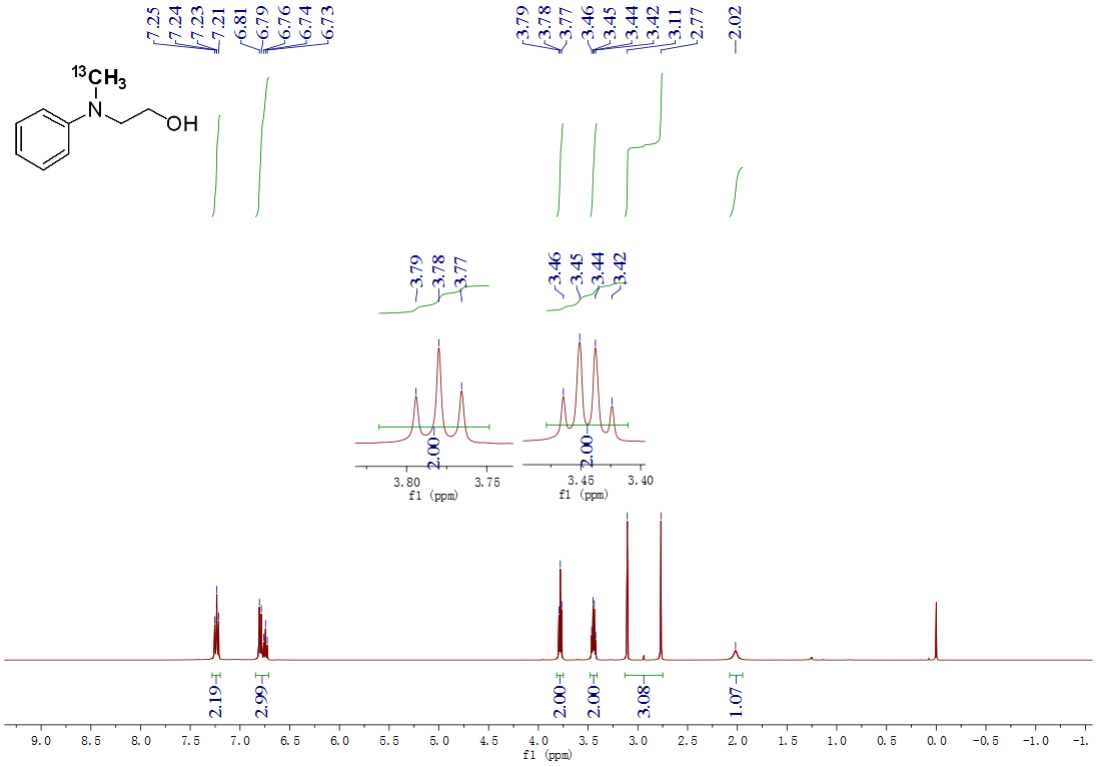
^{1}H NMR spectrum of **1-methylindoline (32)**



^{13}C NMR spectrum of **1-methylindoline (32)**



^{1}H NMR spectrum of **2-(methyl(phenyl)amino)ethanol (33)**



^{13}C NMR spectrum of **2-(methyl(phenyl)amino)ethanol (33)**