

Supporting Information for:

## N-alkylation of Amines with Phenols over Highly Active Heterogeneous Palladium Hydride Catalysts

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### Materials

Active carbon was purchased from TCI Chemicals Co. Ltd. Cerium(IV) oxide (CeO<sub>2</sub>), and zirconium(IV) oxide (ZrO<sub>2</sub>) were purchased from Aladdin Chemicals Co. Ltd. Chromic(III) nitrate (Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), magnesium(II) oxide (MgO), 1,4-dicarboxybenzene (C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>), sodium borohydride (NaBH<sub>4</sub>), Palladium(II) chloride (PdCl<sub>2</sub>), palladium(II) acetate (Pd(OAc)<sub>2</sub>), concentrated hydrochloric acid (35% HCl), phenol (C<sub>6</sub>H<sub>5</sub>OH), and paratoluidine (*p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>) were all purchased from Sinopharm Chemical Reagent Co., Ltd. All of the above chemicals were used without further purification.

### Catalyst preparation

*Preparation of the Pd/Al<sub>2</sub>O<sub>3</sub>*: 2.0 g of Al<sub>2</sub>O<sub>3</sub> was impregnated with the solution of Pd(OAc)<sub>2</sub> (0.228 g Pd(OAc)<sub>2</sub> was dissolved in 30 mL acetone) overnight. After impregnating, the solvent was removed under vacuum, and the catalyst precursors were dried at 373K for 8 hours. The dried powders were then reduced in H<sub>2</sub> flow at 473K (heating rate 10 K/min) for 2 hours. Cooling down to room temperature, 5% Pd/ Al<sub>2</sub>O<sub>3</sub> was got as black powder. 5%Pd/HZSM-5, 5%Pd/MIL-101(Cr), 5%Pd/MgO, 5%Pd/CeO<sub>2</sub>, 5%Pd/ZrO<sub>2</sub>, were all synthesized in this method.

*Preparation of the PdH<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>*: 0.178 g PdCl<sub>2</sub> was dispersed in 10 mL water, and 35% HCl solution was added into the suspension until PdCl<sub>2</sub> dissolved completely. 2.0 g of Al<sub>2</sub>O<sub>3</sub> was impregnated with the solution of PdCl<sub>2</sub>-HCl for more than 4 hours. Then, NaOH solution was dropped into the mixture until the pH value increased to 12. The alkaline solution was kept stirring for another 3 hours, and subsequently 0.380 g NaBH<sub>4</sub> (10 eq to PdCl<sub>2</sub>) was added into the system slowly to reduce gas releasing. Finishing the adding of NaBH<sub>4</sub>, the solution was kept stirring for more 3~4 hours to make sure that the Pd<sup>2+</sup> cations were totally reduced. The mixture was filtered and washed by deionized water three times. The wet powders were dried under vacuum at 353K over night. PdH<sub>x</sub>/C was synthesized in the same method.

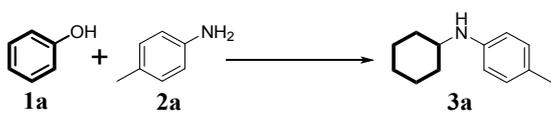
## Characterization

X-ray power diffraction (XRD) patterns of the catalysts were recorded on an X'pert (PANalytical) diffractometer at 40 kV and 40 mA. Transmission electron microscopy (TEM) microphotographs were acquired on a JEOL-2010 electron microscope. A Thermo Scientific Escalab 250-X-ray photoelectron spectrometer was employed for X-ray photoelectron spectra (XPS) analysis. Optima 7300 DV was employed for the inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. FT-IR analysis was recorded on Nicolet 8700 Fourier transform infrared spectroscopy. Bruker 400 MHz NMR was used for the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR characterizations of products.

## General reaction

The model reaction was N-alkylation of *p*-toluidine with phenol. Phenol (0.2 mmol, 18.8 mg) and *p*-toluidine (0.4 mmol, 42.8 mg) were added into the quartz tube with supported Pd catalysts (5% wt Pd, 40 mg), then solvent (2 mL) was injected into the mixtures. The solution was heated to the target temperature by oil bath under 1 atm  $\text{H}_2$  atmosphere ( $\text{H}_2$  balloon). The products were purified by TLC and identified by GC-MS and  $^1\text{H}$ ,  $^{13}\text{C}$ -NMR. The conversions and yields of products were determined by GC using *p*-tertbutyl benzene as internal standard.

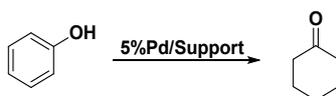
**Table S1.** Catalysts screening for the phenol reductive amination with *p*-toluidine<sup>a</sup>



Reaction scheme showing the reductive amination of phenol (1a) and *p*-toluidine (2a) to form N-(*p*-tolyl)cyclohexylamine (3a).

Entry	Catalyst	Conversion (%)	3a Yield (%)
1	5%Pd/HZSM-5	7.9	5.6
2	5%Pd/CeO <sub>2</sub>	8.0	3.5
3	5%Pd/ZrO <sub>2</sub>	7.4	4.8
4	5%Pd/MgO	15.1	7.3
5	5%Pd/MIL-101(Cr)	22.7	8.3
6	5%Pd/Al <sub>2</sub> O <sub>3</sub>	57.4	44.8
7 <sup>b</sup>	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	<5	--

<sup>a</sup>Reaction conditions: 0.2 mmol phenol and 0.4 mmol *p*-toluidine are added into 2 mL hexane with 40 mg catalyst under 1 atm  $\text{H}_2$  atmosphere, 50°C for 3 hours. The yield is confirmed by GC with *p*-tertbutylbenzene as internal standard. <sup>b</sup>Reaction is conducted under Ar atmosphere.

**Table S2.** Catalysts hydrogenation activity tests for phenols <sup>a</sup>

Catalyst	Conversion	Yield
Pd/HZSM-5	38.2%	32.2%
Pd/Al <sub>2</sub> O <sub>3</sub>	55.7%	50.4%
PdH <sub>x</sub> /C	41.3%	37.5%
PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	85.0%	82.1%

<sup>a</sup>Reaction conditions: 0.2 mmol phenol is added into 2 mL hexane with 40 mg catalyst under 1 atm H<sub>2</sub> atmosphere, 50°C for 3 hours. The yields are confirmed by GC with *p*-tertbutylbenzene as internal standard

**Table S3.** The influence of different solvents for reductive amination<sup>a</sup>

Entry	Catalyst	Solvent	Conversion (%)	<b>3a</b> Yield (%)
1	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	55.6	47.4
2	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	MeOH	4.3	2.5
3	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	EtOH	7.5	4.1
4	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	PhMe	58.4	30
5	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	GVL	0	0
6	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	CH <sub>3</sub> CN	0	0
7	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	DMF	0	0
8	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub>	1,4-dioxane	0	0

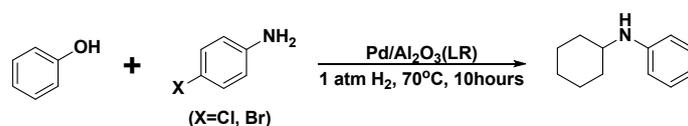
<sup>a</sup>Reaction conditions: 0.2 mmol phenol and 0.4 mmol *p*-toluidine are added into 2 mL solvent with 40 mg catalyst under 1 atm H<sub>2</sub> atmosphere, keeping in 50°C for 3 hours. The yield is confirmed by GC with *p*-tertbutylbenzene as internal standard.

In the Sheldon's hot filtration test, the catalysts were filtrated out and the reaction was detected after 1 hour reaction. 35% conversion and 29% yield of targeted products were confirmed via GC analysis. The filtrated reaction solvent was heated continuously and kept for 1 hour. After that, the results of the reaction were analyzed. However, the reaction completely stopped with the absence of Pd-catalyst, the conversion and yield did not increase any more. We also detected the leaching Pd in the filtrated solvent, 0.0025mg Pd was found in the solvent via ICP analysis.

**Table S4.** Sheldon's hot filtration test<sup>a</sup>

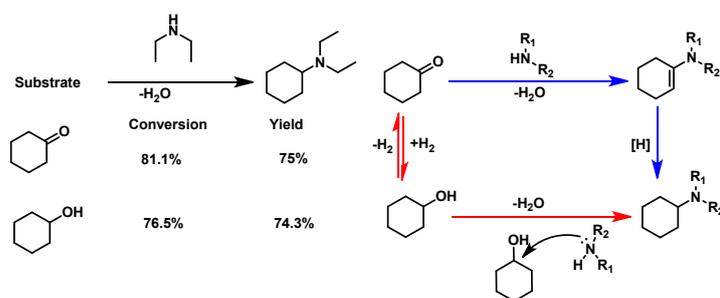
Entry	Catalyst	Conversion (%)	3a Yield (%)	Pd content in the solvent <sup>c</sup>
1 <sup>b</sup>	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> (40mg)	35	29	0mg
<b>After hot filtration</b>				
2 <sup>b</sup>	5%PdH <sub>x</sub> /Al <sub>2</sub> O <sub>3</sub> (0mg)	35	29	0.0025mg

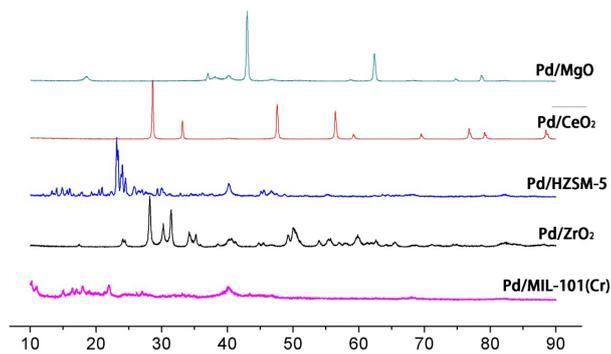
<sup>a</sup>Reaction conditions: 0.2 mmol phenol and 0.4 mmol *p*-toluidine are added into 2 mL solvent with 40 mg catalyst under 1 atm H<sub>2</sub> atmosphere, keeping in 50°C. <sup>b</sup>the reaction was conducted for 1 hour. <sup>c</sup>The content of Pd in the solvent was detected via ICP analysis.

**Scheme S1.** The reactions of halogen substituted anilines.

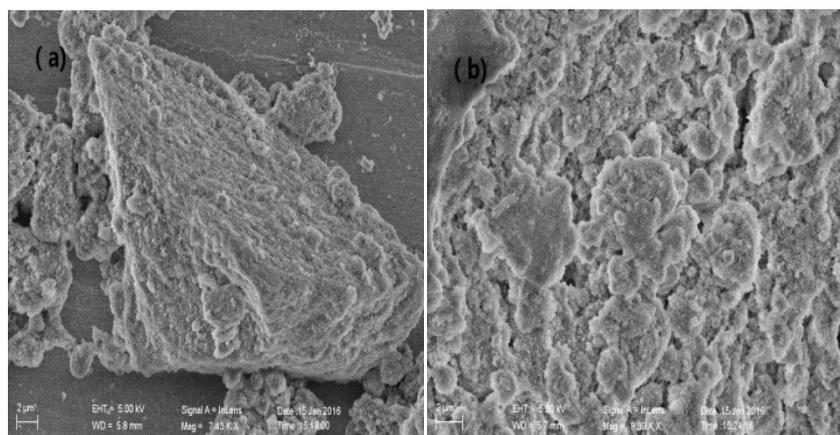
The products were separated from the mixture via TLC and identified by <sup>1</sup>H, <sup>13</sup>C-NMR. It was proved that halogen atoms were removed through C-X (X=Cl, Br) bond's cleavage in the reaction system.

Cyclohexanol and cyclohexanone were both used as substrates in the reductive aminations to explore the mechanism, and similar results were detected in both reaction. Two possible reaction pathways possibly existed in this conversion. One pathway was that cyclohexanone coupled with secondary amine and formed enamine first. And then the enamine was hydrogenated over PdH<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts under H<sub>2</sub> atmosphere. Another proposed pathway was that the hydroxyl in cyclohexanol was replaced by amino via S<sub>N</sub> reaction. The cyclohexanol were produced from cyclohexanone.

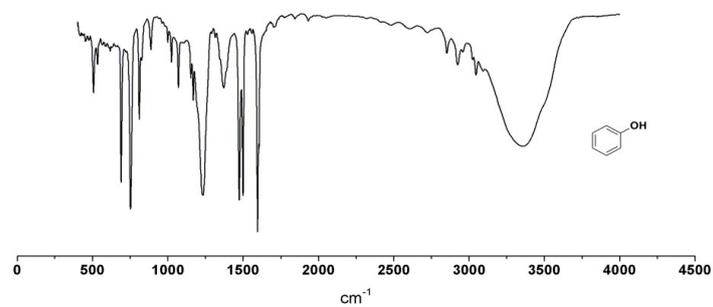
**Scheme S2.** The verification of secondary amines coupling mechanism.



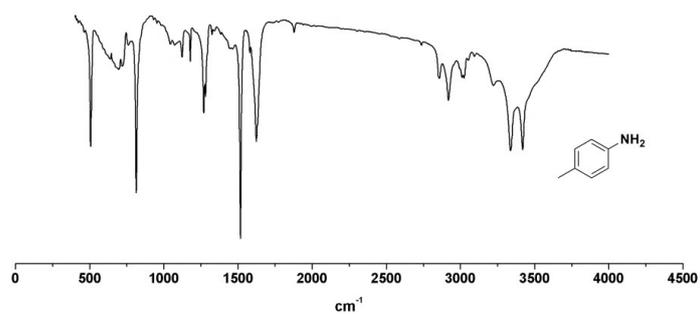
**Figure S1.** XRD patterns for catalysts in Table S1.



**Figure S2.** SEM images of (a) PdH<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>, (b) Pd/Al<sub>2</sub>O<sub>3</sub>.



**Figure S3.** FT-IR spectrum of phenol from 400 to 4000 cm<sup>-1</sup>



**Figure S4.** FT-IR spectrum of *p*-toluidine from 400 to 4000 cm<sup>-1</sup>

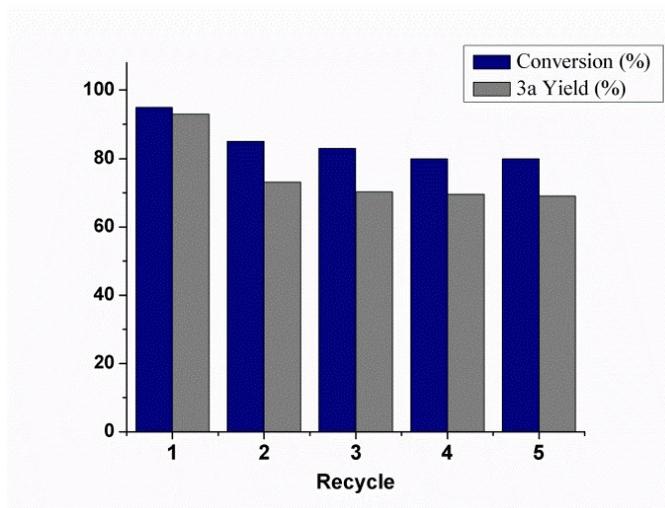


Figure S5. Recycle tests for PdH<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>

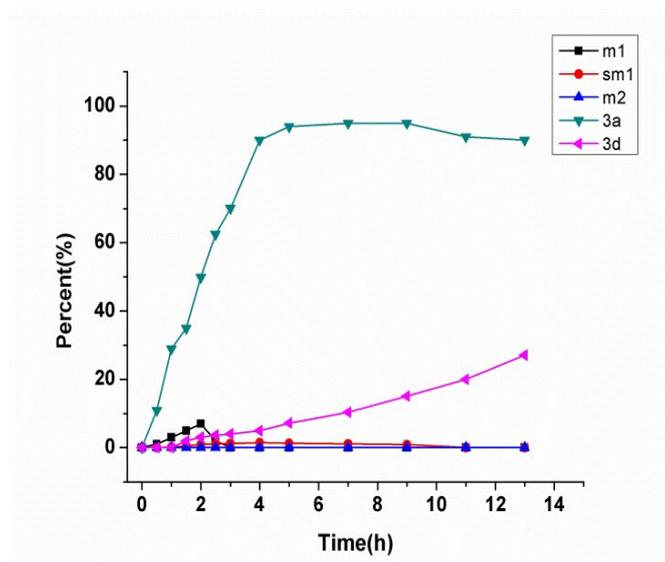


Figure S6. The kinetics test of reaction with PdH<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst

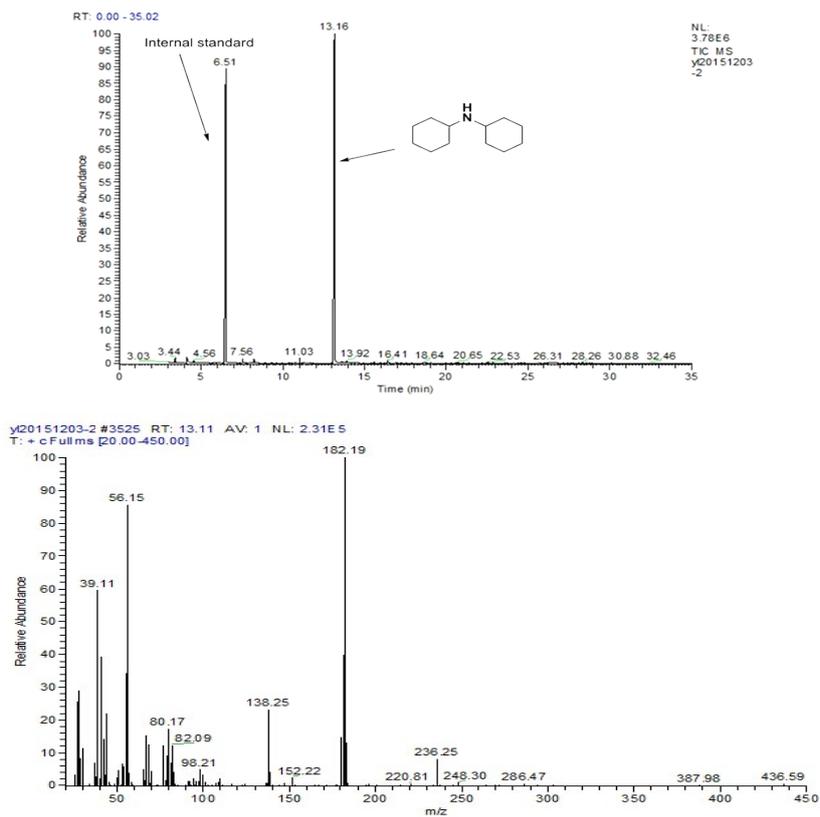


Figure S7. The GC-MS spectrum of 3t

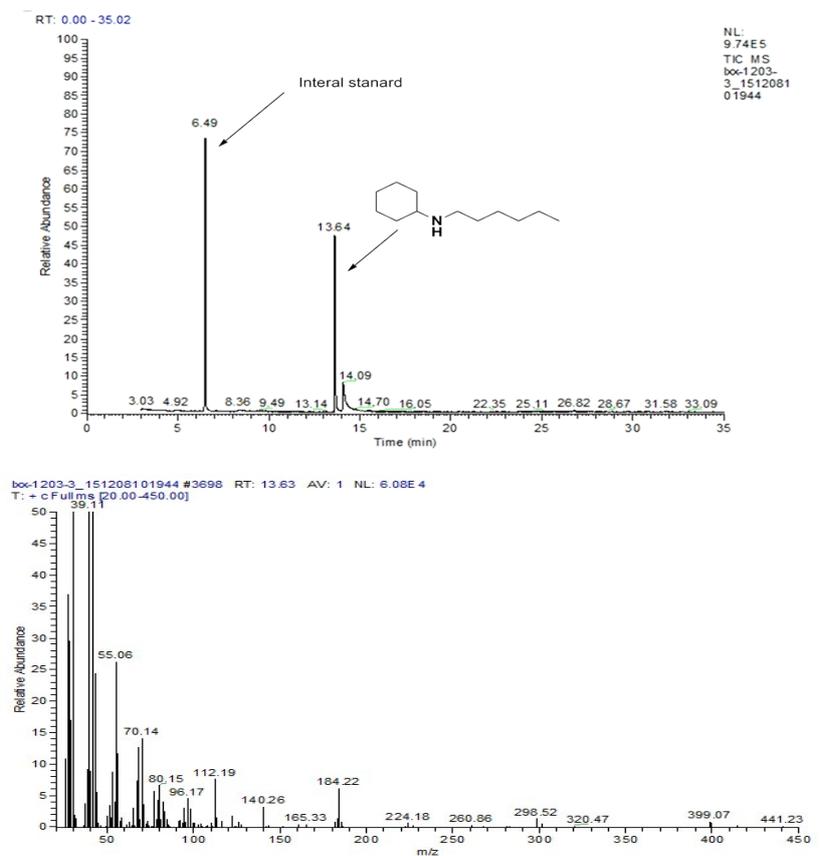


Figure S8. The GC-MS spectrum of 3u

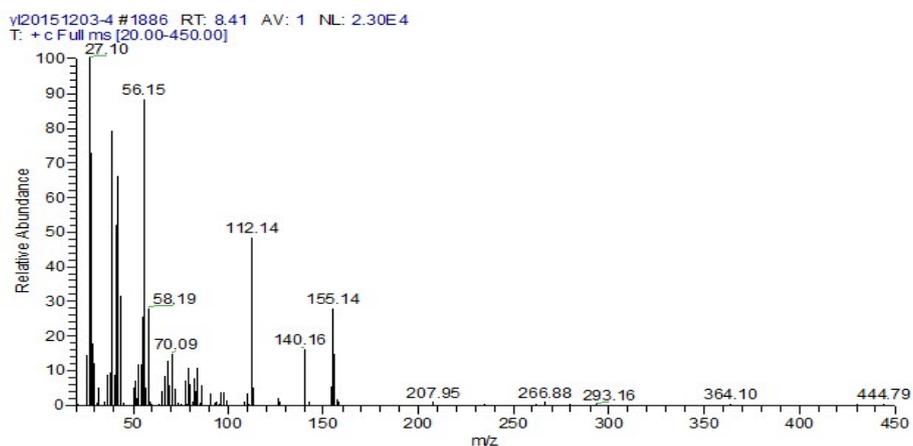
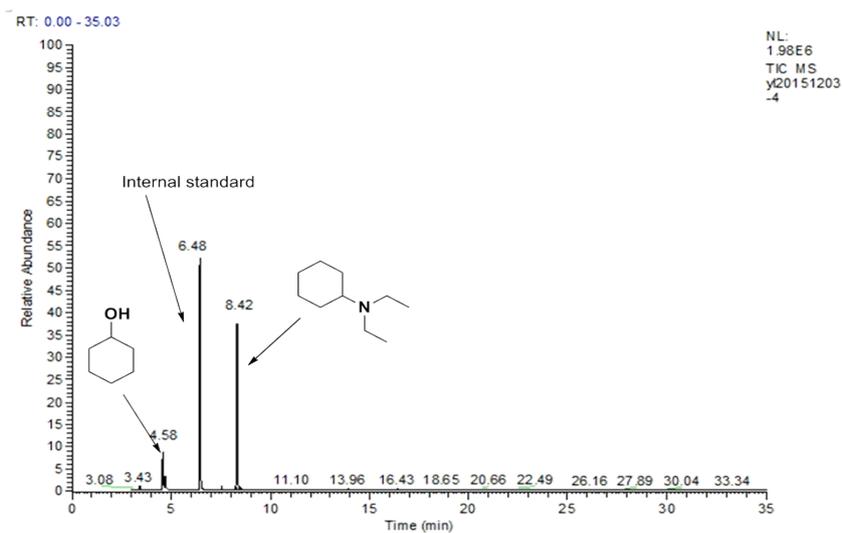
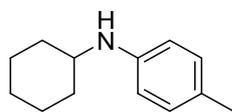


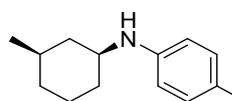
Figure S9. The GC-MS spectrum of **3v**

**NMR Data:**



**N-cyclohexyl-4-methylaniline (3a)**

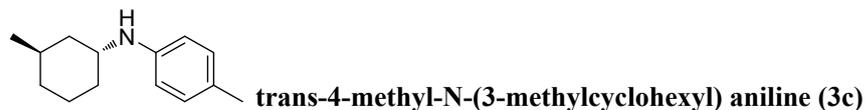
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.96 (d,  $J$  = 8.2 Hz, 2H), 6.52 (d,  $J$  = 8.3 Hz, 2H), 3.21 (t,  $J$  = 10.1 Hz, 1H), 2.22 (s, 3H), 2.04 (d,  $J$  = 12.8 Hz, 2H), 1.74 (d,  $J$  = 13.0 Hz, 2H), 1.64 (d,  $J$  = 12.6 Hz, 1H), 1.35 (dd,  $J$  = 24.9, 12.0 Hz, 2H), 1.27 – 1.21 (m, 1H), 1.16 – 1.07 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =144.73, 129.76, 126.50, 113.83, 52.39, 33.44, 25.97, 25.05, 20.38.



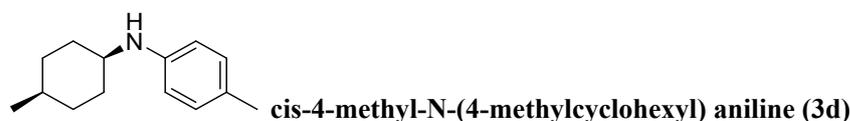
**cis-4-methyl-N-(3-methylcyclohexyl) aniline (3c)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.97 (d,  $J$  = 8.5 Hz, 2H), 6.55 (d,  $J$  = 6.6 Hz, 2H), 3.63 (t,  $J$  = 4.0 Hz,

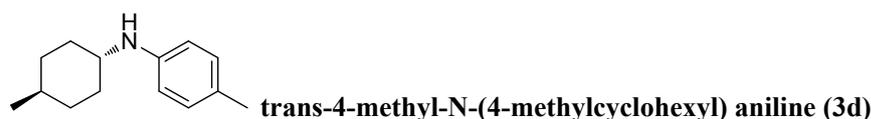
1H), 2.23 (s, 3H), 1.76-1.70 (m 2H), 1.69-1.63 (m, 2H), 1.59-1.48 (m, 3H), 1.37-1.30 (m, 1H), 1.08-1.00 (m, 1H), 0.91 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.78, 129.78, 126.37, 113.70, 48.26, 38.82, 33.95, 30.46, 27.16, 21.63, 20.54, 20.36$ .



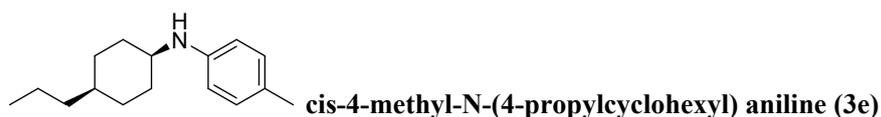
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.97$  (d,  $J = 8.5$  Hz, 2H), 6.55 (d,  $J = 8.4$  Hz, 2H), 3.20 (tt,  $J = 11.2, 3.8$  Hz, 1H), 2.23 (s, 3H), 2.11-2.05 (m, 2H), 1.81-1.74 (m, 1H), 1.67 (d,  $J = 13.0$  Hz, 1H), 1.54-1.43 (m, 1H), 1.40-1.29 (m, 1H), 1.01-0.94 (m, 1H), 0.91 (d,  $J = 6.6$  Hz, 3H), 0.89-0.79 (m, 1H), 0.76-0.69 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.62, 129.77, 126.72, 114.04, 77.35, 77.03, 76.71, 52.98, 42.43, 34.70, 33.31, 32.08, 25.07, 22.50, 20.38$ .



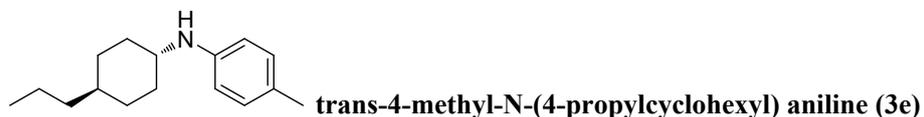
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.97$  (d,  $J = 8.0$  Hz, 2H), 6.56 (d,  $J = 8.4$  Hz, 2H), 3.55-3.45 (t,  $J = 4.1$  Hz, 1H), 2.23 (s, 3H), 1.77-1.71 (m, 2H), 1.66-1.58 (m, 2H), 1.57-1.50 (m, 3H), 1.29-1.21 (m, 2H), 0.93 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.48, 129.50, 126.13, 113.53, 48.70, 30.56, 29.55, 28.92, 20.98, 20.09$ .



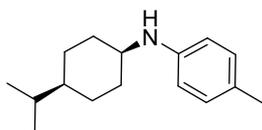
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.96$  (d,  $J = 8.0$  Hz, 2H), 6.54 (d,  $J = 8.4$  Hz, 2H), 3.14 (tt,  $J = 10.8, 3.7$  Hz, 1H), 2.22 (s, 3H), 2.13-2.06 (m, 2H), 1.76-1.69 (m, 2H), 1.43-1.31 (m, 1H), 1.15-0.99 (m, 4H), 0.91 (d,  $J = 6.5$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.77, 129.74, 126.60, 113.92, 52.87, 34.15, 33.52, 32.35, 22.23, 20.35$ .



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.97$  (d,  $J = 8.1$  Hz, 2H), 6.53 (d,  $J = 8.3$  Hz, 2H), 3.54-3.51 (m, 1H), 2.22 (s, 3H), 1.74-1.70 (m, 2H), 1.65-1.52 (m, 4H), 1.43-1.35 (m, 1H), 1.34-1.20 (m, 6H), 0.89 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.19, 129.11, 125.66, 113.09, 48.54, 37.24, 34.98, 28.66, 27.21, 19.70, 19.51, 13.68$ .

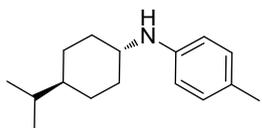


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 6.96$  (d,  $J = 8.1$  Hz, 2H), 6.51 (d,  $J = 8.2$  Hz, 2H), 3.17-3.11 (m, 1H), 2.22 (s, 3H), 2.11 (d,  $J = 11.7$  Hz, 2H), 1.79 (d,  $J = 12.4$  Hz, 2H), 1.36-1.27 (m, 2H), 1.25-1.15 (m, 3H), 1.12-1.05 (m, 4H), 0.88 (t,  $J = 7.2$  Hz, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 144.83, 129.74, 126.53, 113.87, 53.16, 39.29, 36.99, 33.56, 32.08, 20.36, 20.15, 14.35$ .



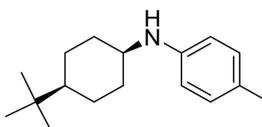
**cis-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.97 (d,  $J$  = 8.2 Hz, 2H), 6.54 (d,  $J$  = 8.3 Hz, 2H), 3.59-5.56 (m, 1H), 2.23 (s, 3H), 1.84-1.80 (m, 2H), 1.60-1.43 (m, 5H), 1.33-1.23 (m, 2H), 1.12-1.07 (m, 1H), 0.88 (d,  $J$  = 6.8 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =144.96, 129.76, 126.17, 113.63, 48.37, 43.22, 31.78, 29.73, 24.52, 20.35, 20.03.



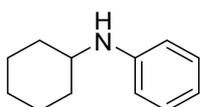
**trans-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.96 (d,  $J$  = 8.2 Hz, 2H), 6.52 (d,  $J$  = 8.4 Hz, 2H), 3.16-3.08 (m, 1H), 2.22 (s, 3H), 2.16-2.13 (m, 2H), 1.77-1.75 (m, 2H), 1.47-1.40 (m, 1H), 1.12-1.01 (m, 5H), 0.87 (d,  $J$  = 6.8 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =145.00, 129.75, 126.38, 113.74, 53.05, 43.69, 33.77, 32.65, 28.67, 20.36, 19.74.



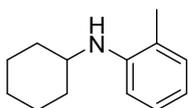
**cis-4-methyl-N-(4-tertbutylcyclohexyl) aniline (3g)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.97 (d,  $J$  = 8.2 Hz, 2H), 6.54 (d,  $J$  = 8.3 Hz, 2H), 3.64-3.62 (m, 1H), 2.23 (s, 3H), 1.98-1.96 (m, 2H), 1.59-1.54 (dd,  $J$  = 16.4, 3.3 Hz, 2H), 1.54-1.39 (m, 2H), 1.18 (ddd,  $J$  = 15.6, 10.8, 2.4 Hz, 2H), 1.06-0.98 (m, 1H), 0.86 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =145.02, 129.77, 126.03, 113.50, 77.38, 77.06, 76.74, 47.96, 47.11, 32.57, 30.30, 27.50, 21.48, 20.39.



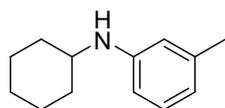
**N-cyclohexylaniline (3h)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.17-7.13 (m, 2H), 6.65 (t,  $J$  = 7.3 Hz, 1H), 6.58 (d,  $J$  = 7.6 Hz, 2H), 3.28-3.21 (m, 1H), 2.07-2.03 (m, 2H), 1.78-1.73 (m, 2H), 1.68-1.62 (m, 1H), 1.42-1.31 (m, 2H), 1.27-1.20 (m, 1H), 1.19-1.09 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =147.38, 129.26, 116.88, 113.21, 51.74, 33.49, 25.96, 25.03.



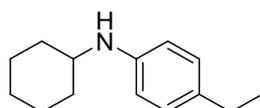
**N-cyclohexyl-2-methylaniline (3i)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.09 (t,  $J$  = 7.7 Hz, 1H), 7.03 (d,  $J$  = 7.2 Hz, 1H), 6.66-6.55 (m, 2H), 3.30 (tt,  $J$  = 10.0, 3.6 Hz, 1H), 2.11 (s, 3H), 2.10-2.02 (m, 2H), 1.82-1.72 (m, 2H), 1.69-1.61 (m, 1H), 1.39-1.28 (m, 2H), 1.29-1.15 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =145.33, 130.31, 127.10, 121.67, 116.34, 110.27, 51.57, 33.68, 26.07, 25.09, 17.60.



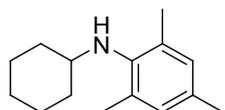
**N-cyclohexyl-3-methylaniline (3j)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.04 (t,  $J$  = 8.0 Hz, 1H), 6.49 (d,  $J$  = 7.6 Hz, 1H), 6.41 (d,  $J$  = 6.5 Hz, 2H), 3.24 (tt,  $J$  = 10.2, 3.7 Hz, 1H), 2.26 (s, 3H), 2.13-1.98 (m, 2H), 1.82-1.71 (m, 2H), 1.68-1.61 (m, 1H), 1.42-1.31 (m, 2H), 1.27-1.24 (m, 1H), 1.19-1.09 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =147.31, 139.03, 129.15, 117.89, 114.00, 110.37, 51.74, 33.52, 25.96, 25.05, 21.67.



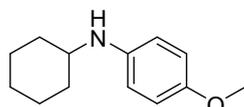
**N-cyclohexyl-4-ethylaniline (3k)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.99 (d,  $J$  = 8.4 Hz, 2H), 6.54 (d,  $J$  = 8.4 Hz, 2H), 3.21 (tt,  $J$  = 10.1, 3.7 Hz, 1H), 2.52 (q,  $J$  = 7.6 Hz, 2H), 2.16-1.96 (m, 2H), 1.83-1.68 (m, 2H), 1.68-1.55 (m, 1H), 1.42-1.29 (m, 2H), 1.25-1.07 (m, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =145.22, 132.94, 128.59, 113.55, 52.19, 33.58, 27.94, 26.01, 25.08, 15.97.



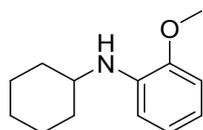
**N-cyclohexyl-2,4,6-trimethylaniline (3l)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.80 (s, 2H), 2.87 (tt,  $J$  = 10.4, 3.6 Hz, 1H), 2.23 (s, 6H), 2.22 (s, 3H), 1.95 (d,  $J$  = 10.5 Hz, 2H), 1.77-1.70 (m, 2H), 1.65-1.58 (m, 1H), 1.26-1.16 (m, 3H), 1.15-1.07 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =142.37, 130.50, 129.39, 129.30, 56.58, 34.91, 26.03, 25.64, 20.50, 18.87.



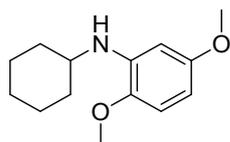
**N-cyclohexyl-4-methoxyaniline (3n)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.79-6.74 (m, 2H), 6.62-6.58 (m, 2H), 3.74 (s, 3H), 3.16 (tt,  $J$  = 10.2, 3.7 Hz, 1H), 3.10 (ds, 1H), 2.06-2.02 (m, 2H), 1.81-1.70 (m, 2H), 1.67-1.62 (m, 1H), 1.40-1.29 (m, 2H), 1.26-1.22 (m, 1H), 1.18-1.08 (m, 2H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =152.47, 140.55, 115.65, 114.93, 55.82, 53.53, 33.32, 25.91, 25.04.



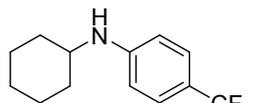
**N-cyclohexyl-2-methoxyaniline (3o)**

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.84 (td,  $J$  = 7.6, 1.3 Hz, 1H), 6.75 (dd,  $J$  = 8.2, 1.2 Hz, 1H), 6.63-6.59 (m, 2H), 3.82 (s, 3H), 3.24 (tt,  $J$  = 10.0, 3.7 Hz, 1H), 2.07-2.04 (m, 2H), 1.81-1.72 (m, 2H), 1.68-1.60 (m, 1H), 1.42-1.31 (m, 2H), 1.28-1.13 (m, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =146.79, 137.27, 121.28, 115.85, 110.32, 109.63, 55.40, 51.43, 33.46, 26.06, 25.11.



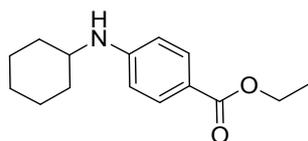
**N-cyclohexyl-2,5-dimethoxyaniline (3p)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =6.64 (d,  $J$  = 8.6 Hz, 1H), 6.23 (d,  $J$  = 2.8 Hz, 1H), 6.10 (dd,  $J$  = 8.6, 2.9 Hz, 1H), 4.25 (ds, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.20 (tt,  $J$  = 10.0, 3.6 Hz, 1H), 2.10-2.01 (m, 2H), 1.78-1.73 (m, 2H), 1.67-1.62 (m, 1H), 1.42-1.31 (m, 2H), 1.26-1.15 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =154.85, 141.56, 138.34, 110.00, 98.52, 97.92, 56.00, 55.53, 51.39, 33.32, 25.99, 25.06.



**N-cyclohexyl-4-(trifluoromethyl)aniline (3q)**

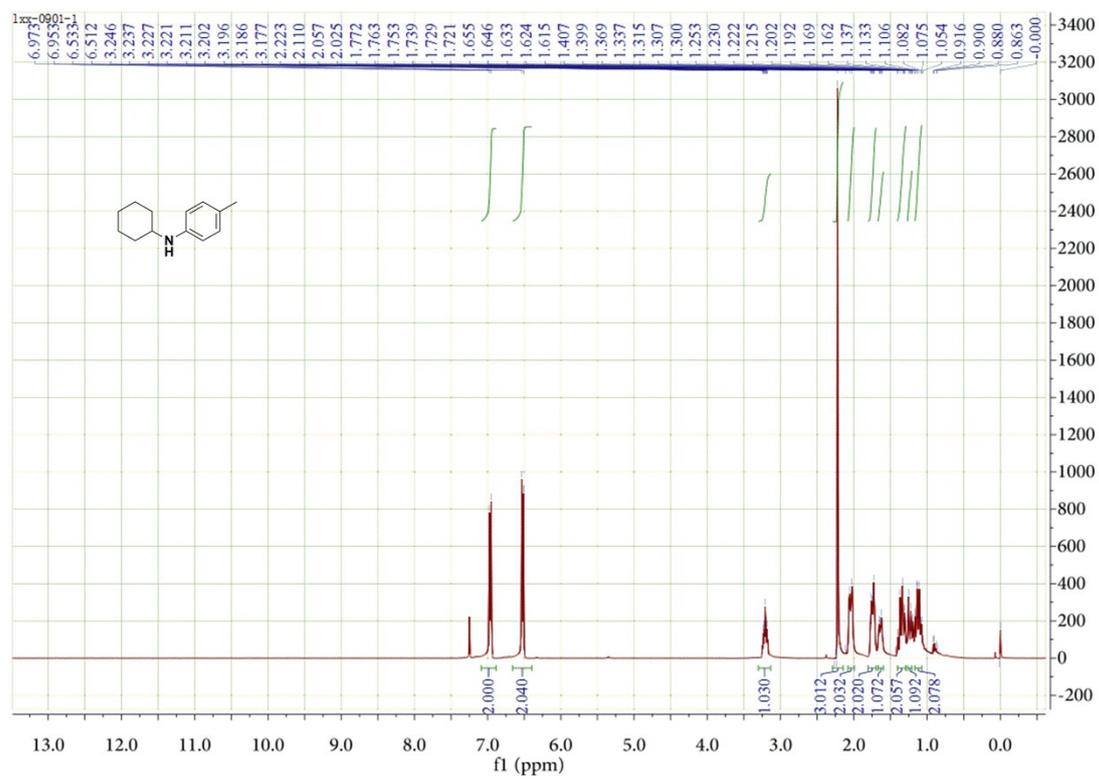
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$ =7.36 (d,  $J$  = 8.5 Hz, 2H), 6.55 (d,  $J$  = 8.6 Hz, 2H), 3.89 (s, 1H), 3.28 (tt,  $J$  = 10.1, 3.7 Hz, 1H), 2.07-1.99 (m, 2H), 1.80-1.72 (m, 2H), 1.69-1.62 (m, 1H), 1.43-1.32 (m, 2H), 1.28-1.11 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =149.83, 126.60, 123.76, 118.26, 117.94, 112.01, 51.37, 33.14, 25.78, 24.87.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$ = -60.91.



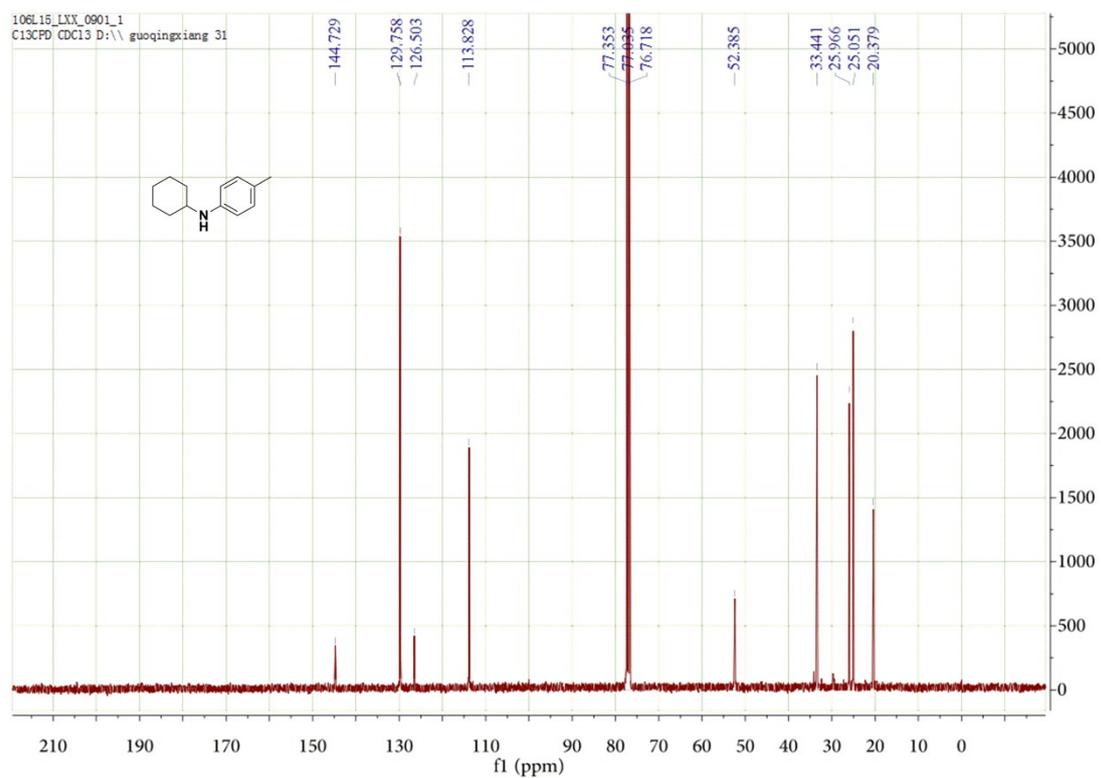
**Ethyl 4-(cyclohexylamino)benzoate (3r)**

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.86 (d,  $J$  = 8.9 Hz, 2H), 6.53 (d,  $J$  = 8.8 Hz, 2H), 4.32 (q,  $J$  = 7.1 Hz, 2H), 4.09 (ds, 1H), 3.33 (tt,  $J$  = 10.1, 3.7 Hz, 1H), 2.08-2.04 (m, 2H), 1.81-1.75 (m, 2H), 1.70-1.65 (m, 1H), 1.45-1.34 (m, 5H), 1.29-1.14 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$ =166.93, 151.06, 131.58, 118.08, 111.65, 60.12, 51.31, 33.15, 25.77, 24.88, 14.49.

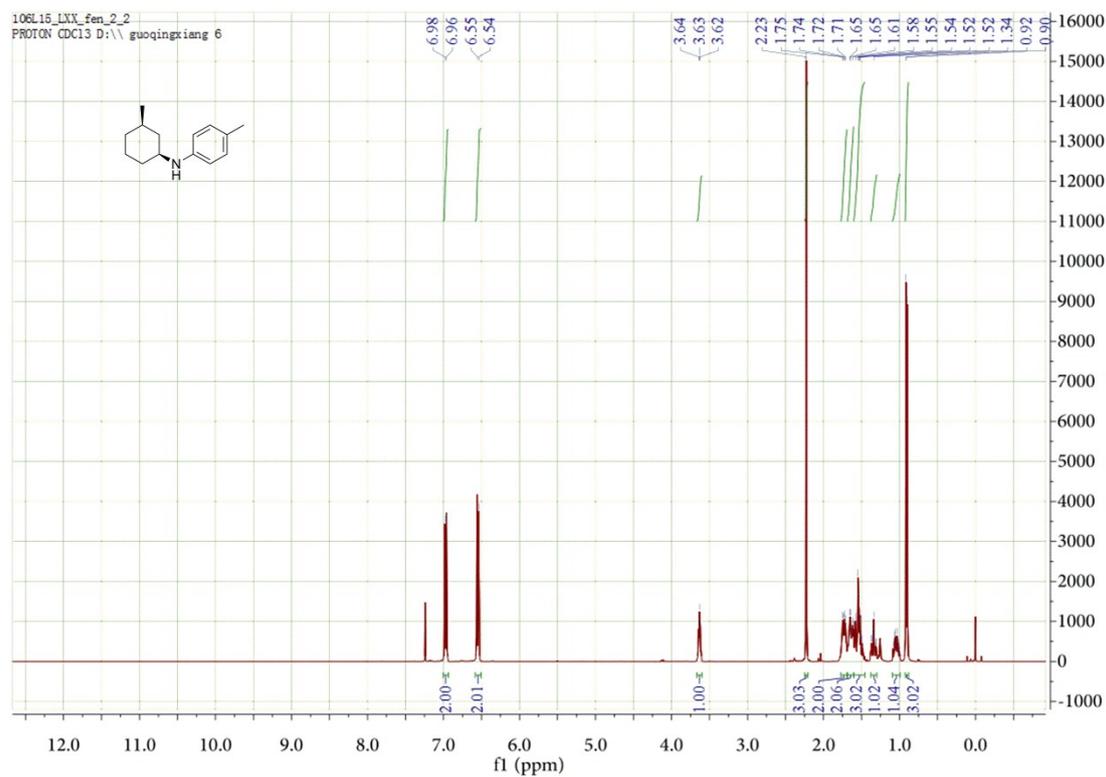
# N-cyclohexyl-4-methylaniline (3a) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



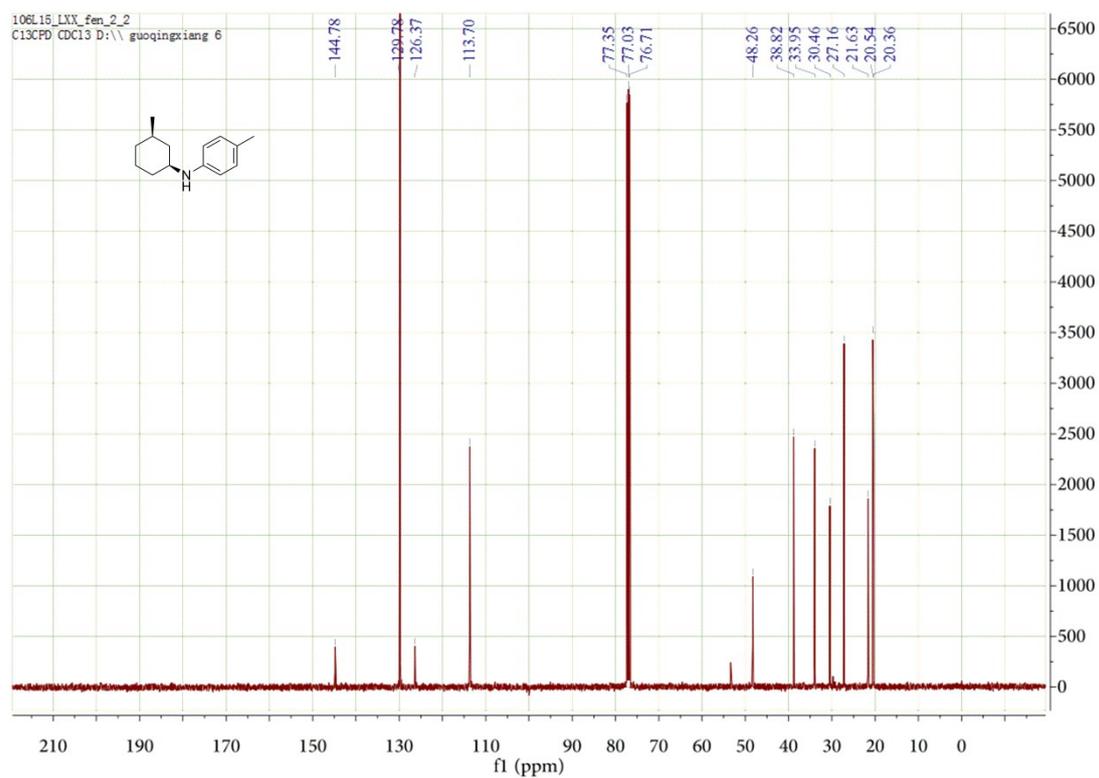
# N-cyclohexyl-4-methylaniline (3a) ( $^{13}\text{C}$ NMR, 101 MHz, $\text{CDCl}_3$ )



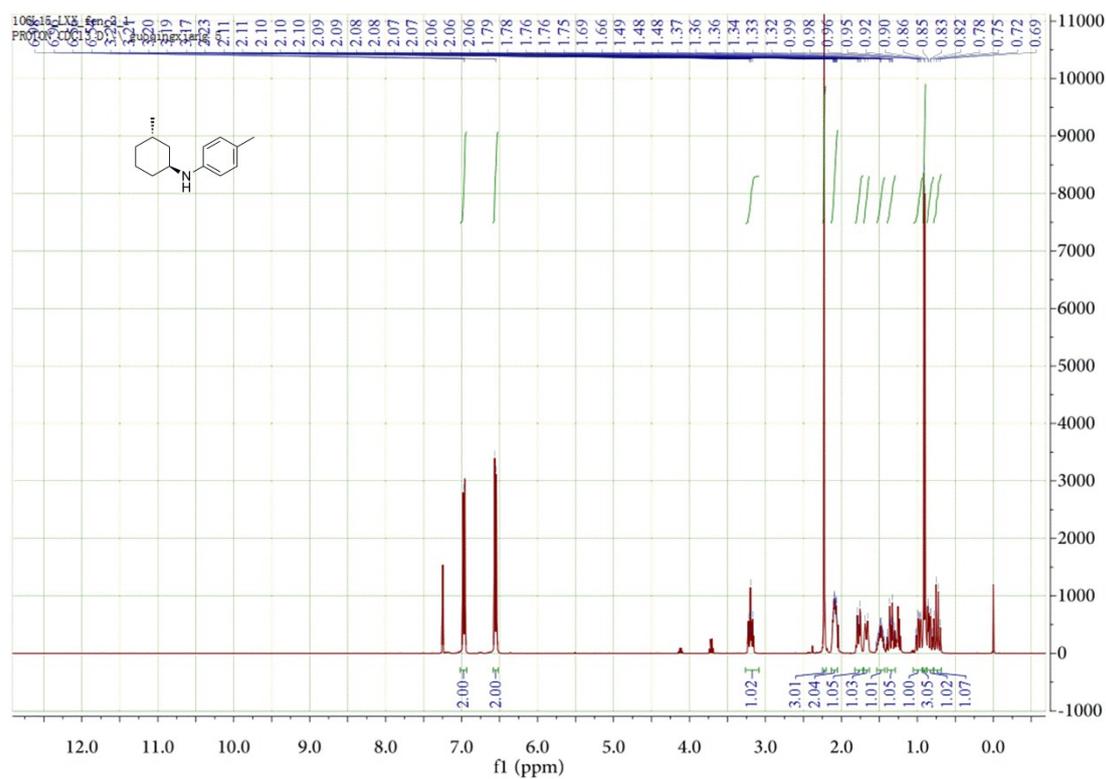
**cis-4-methyl-N-(3-methylcyclohexyl) aniline (3c) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



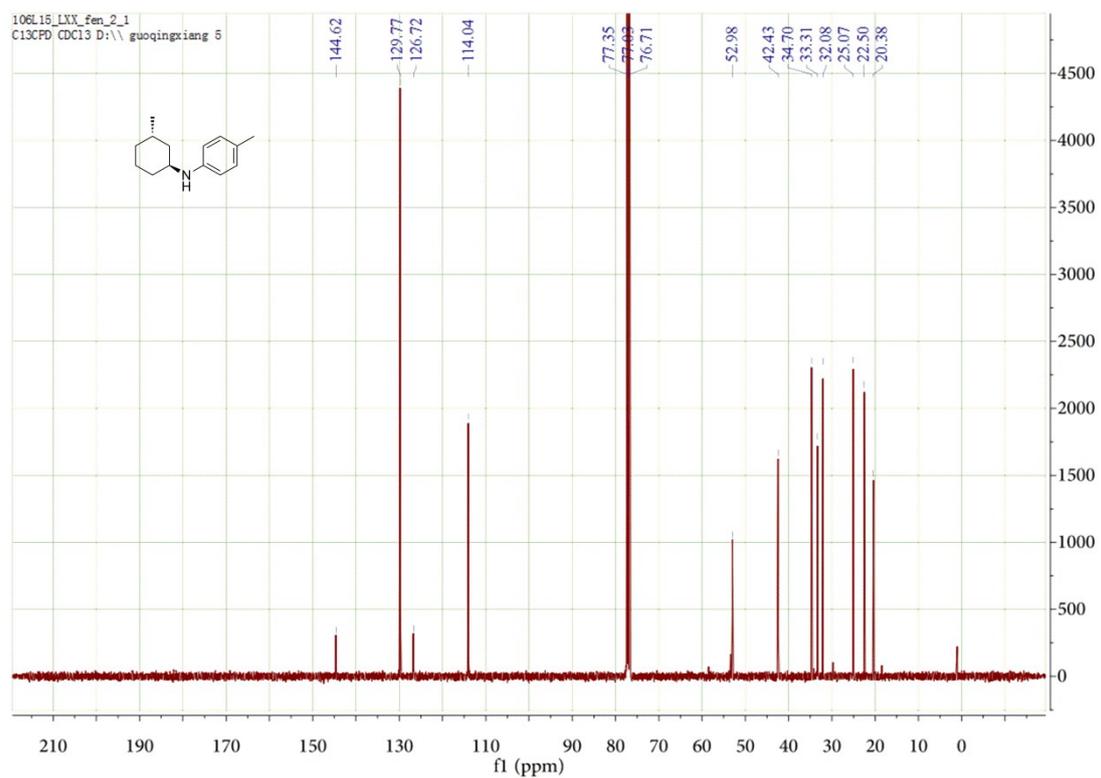
**cis-4-methyl-N-(3-methylcyclohexyl) aniline (3c) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**



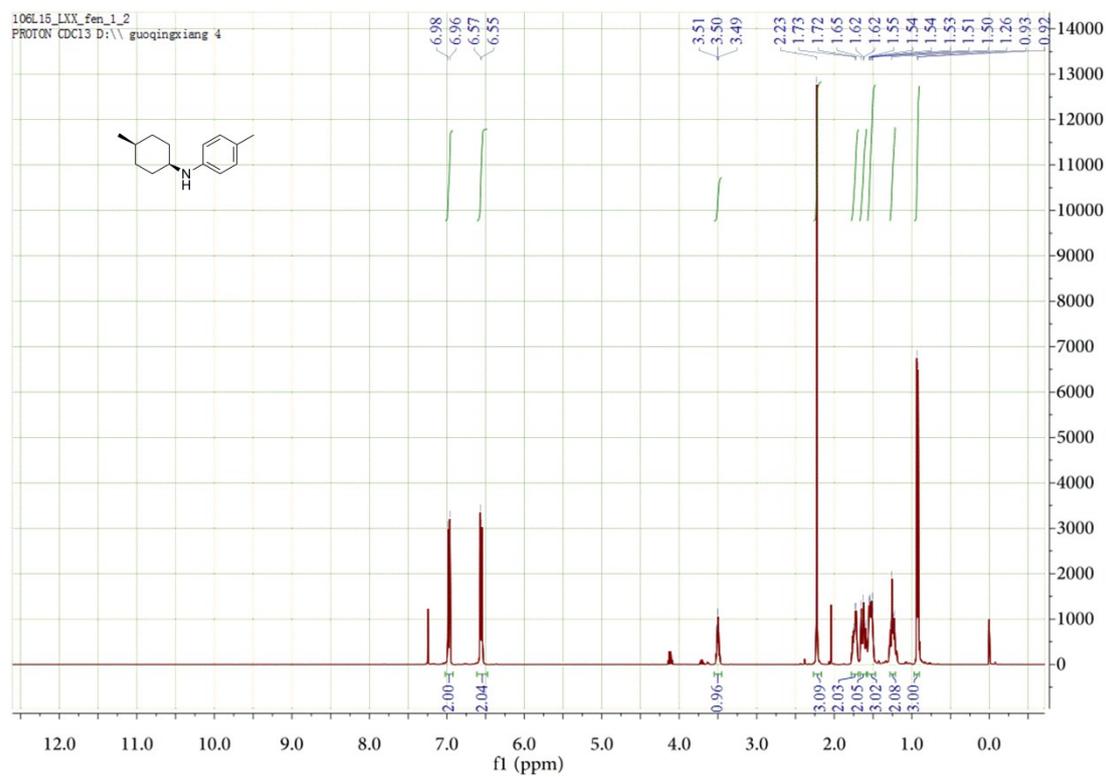
**trans-4-methyl-N-(3-methylcyclohexyl) aniline (3c) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



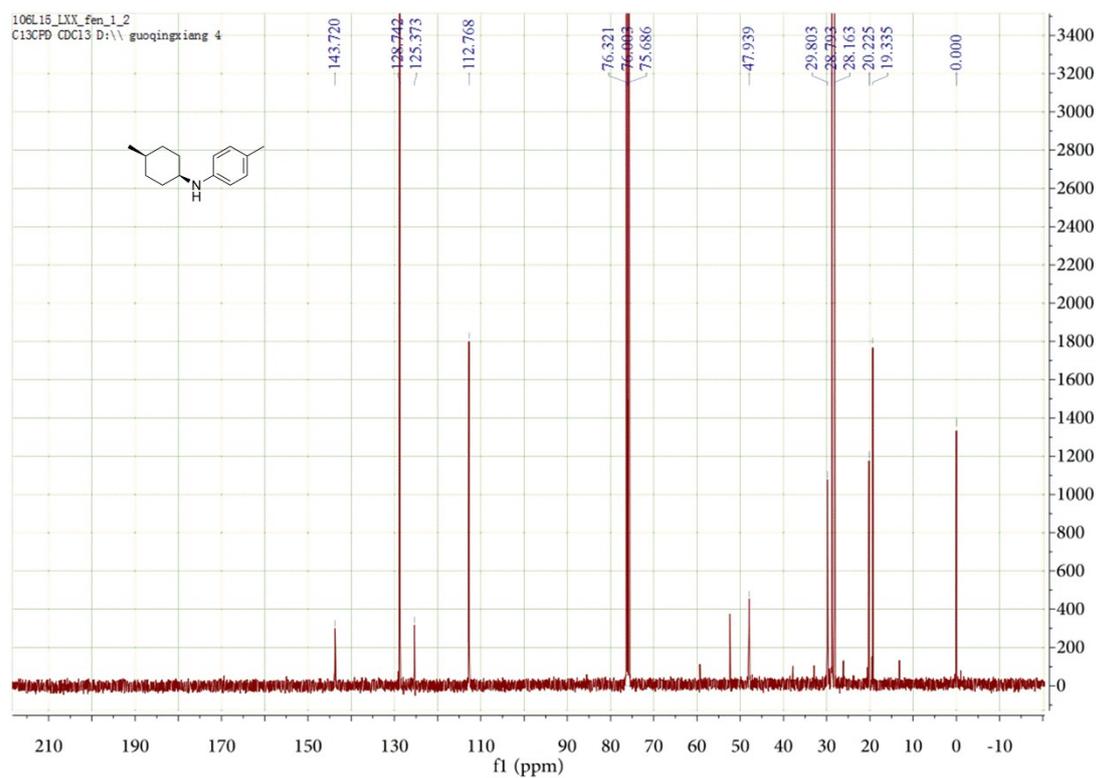
**trans-4-methyl-N-(3-methylcyclohexyl) aniline (3c) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**



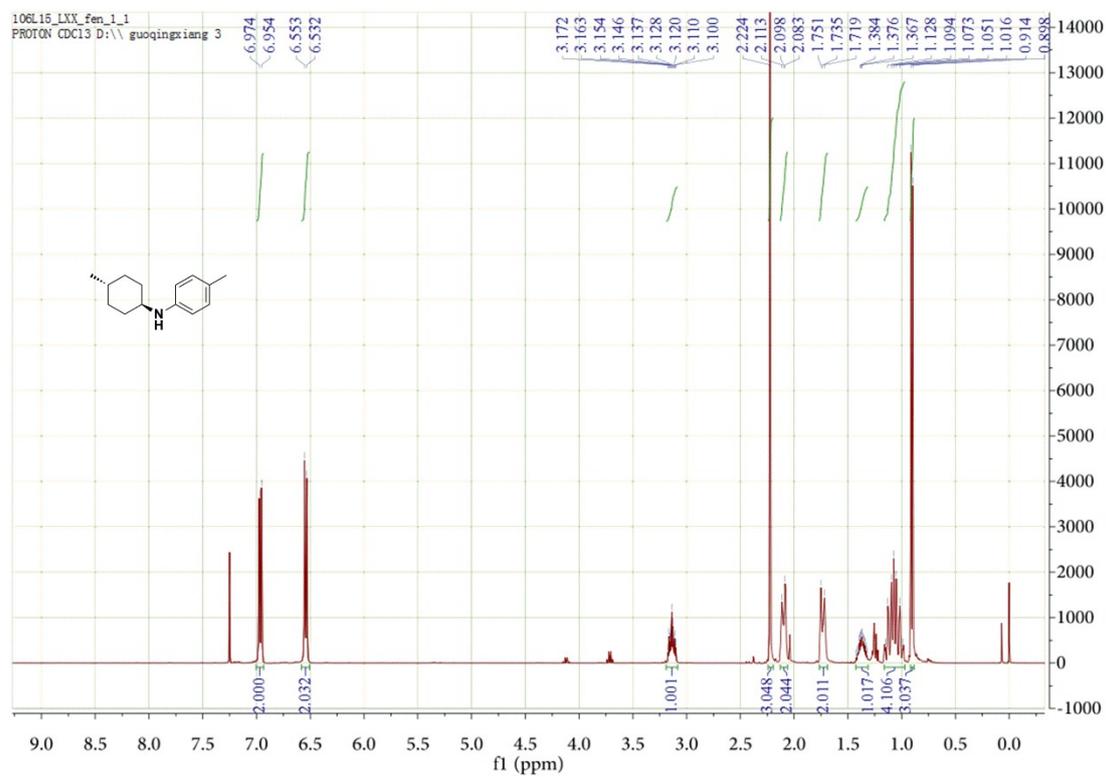
**cis-4-methyl-N-(4-methylcyclohexyl) aniline (3d) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



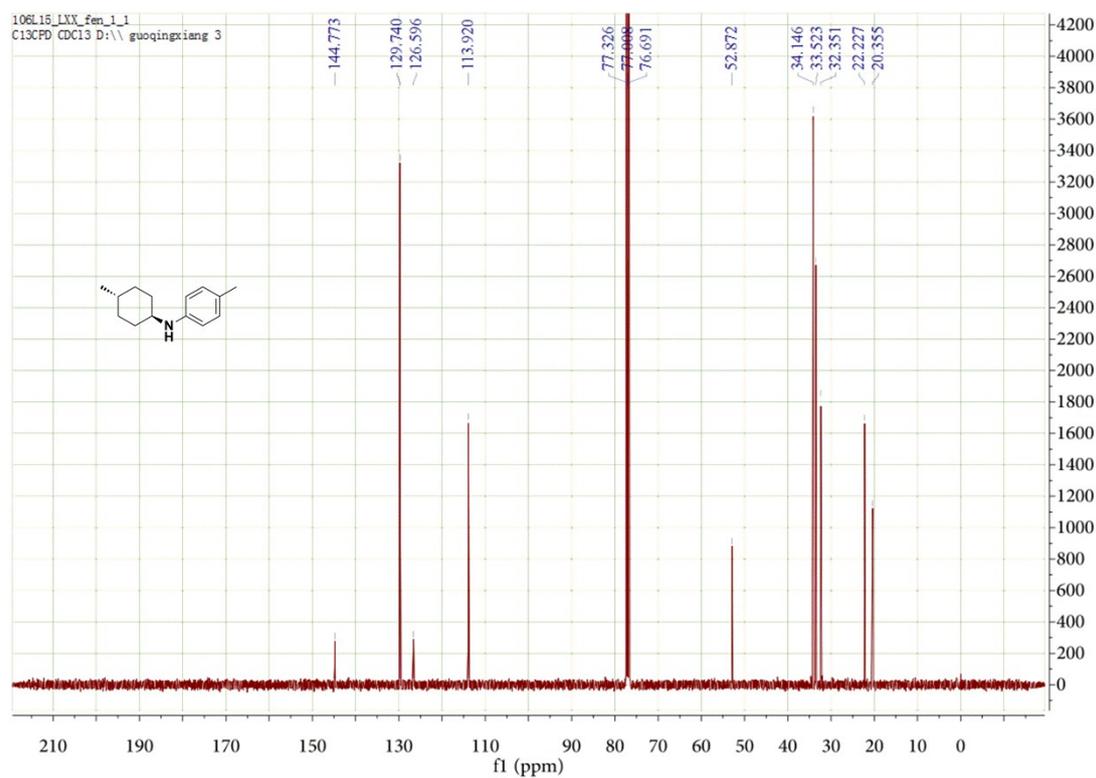
**cis-4-methyl-N-(4-methylcyclohexyl) aniline (3d) ( $^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$ )**



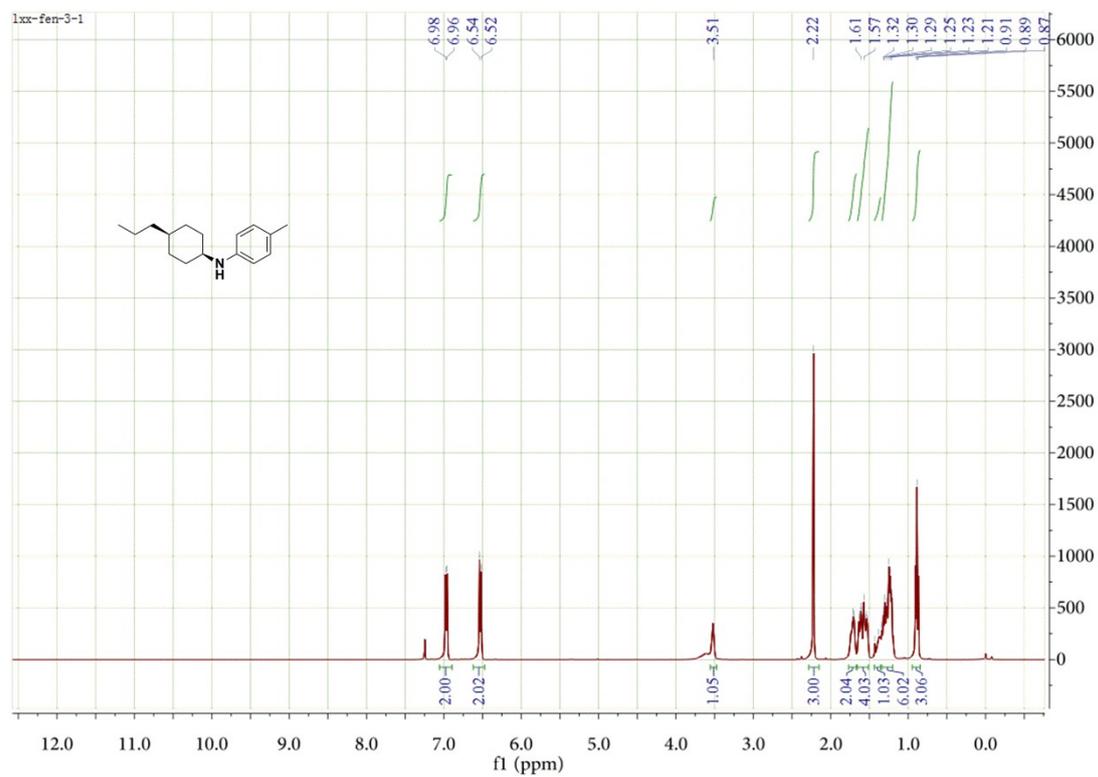
**trans-4-methyl-N-(4-methylcyclohexyl) aniline (3d) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



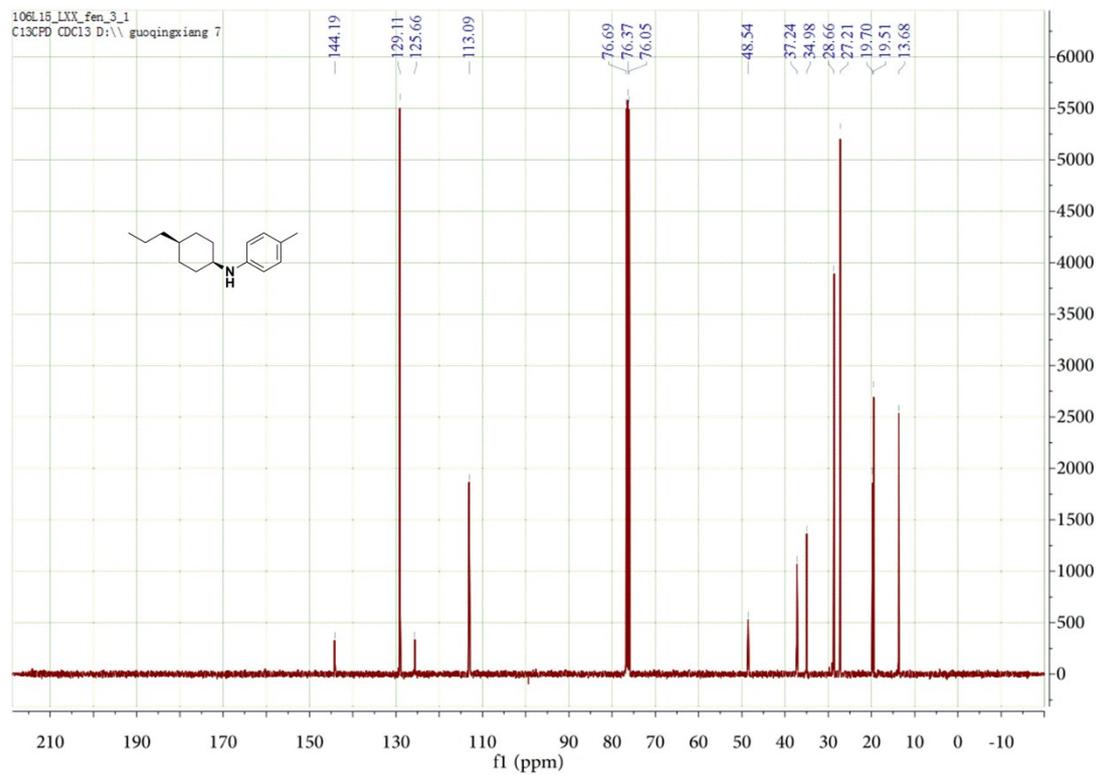
**trans-4-methyl-N-(4-methylcyclohexyl) aniline (3d) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**



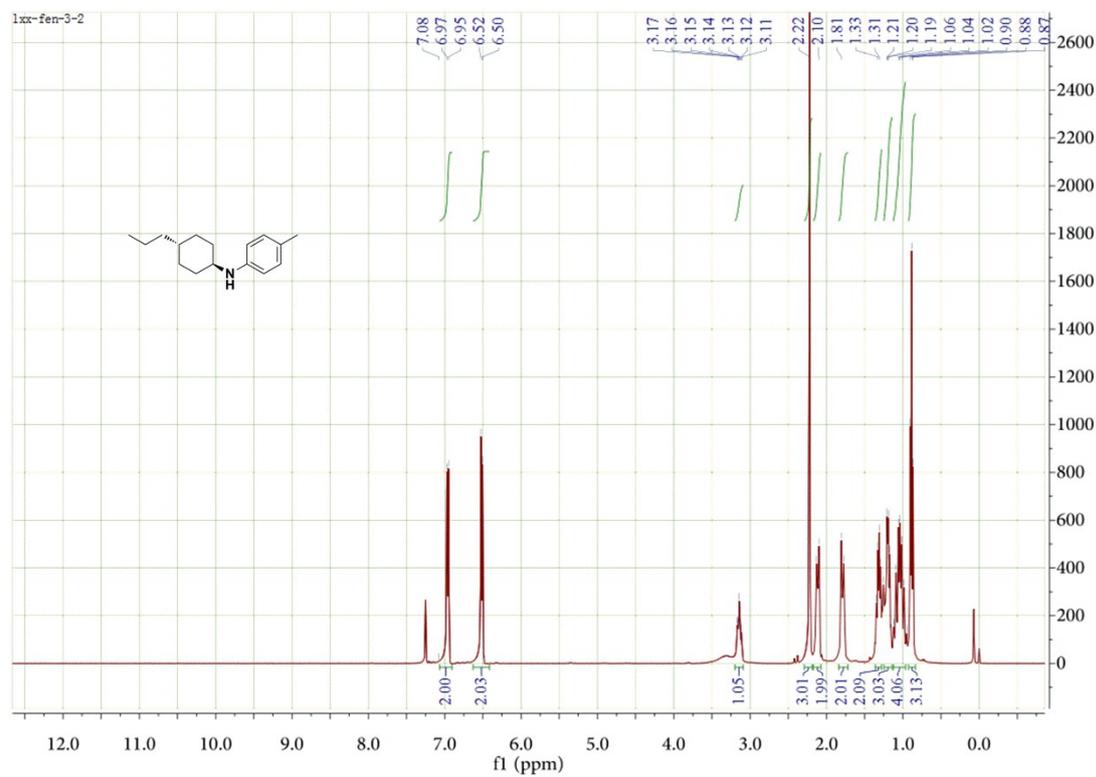
**cis-4-methyl-N-(4-propylcyclohexyl) aniline (3e) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



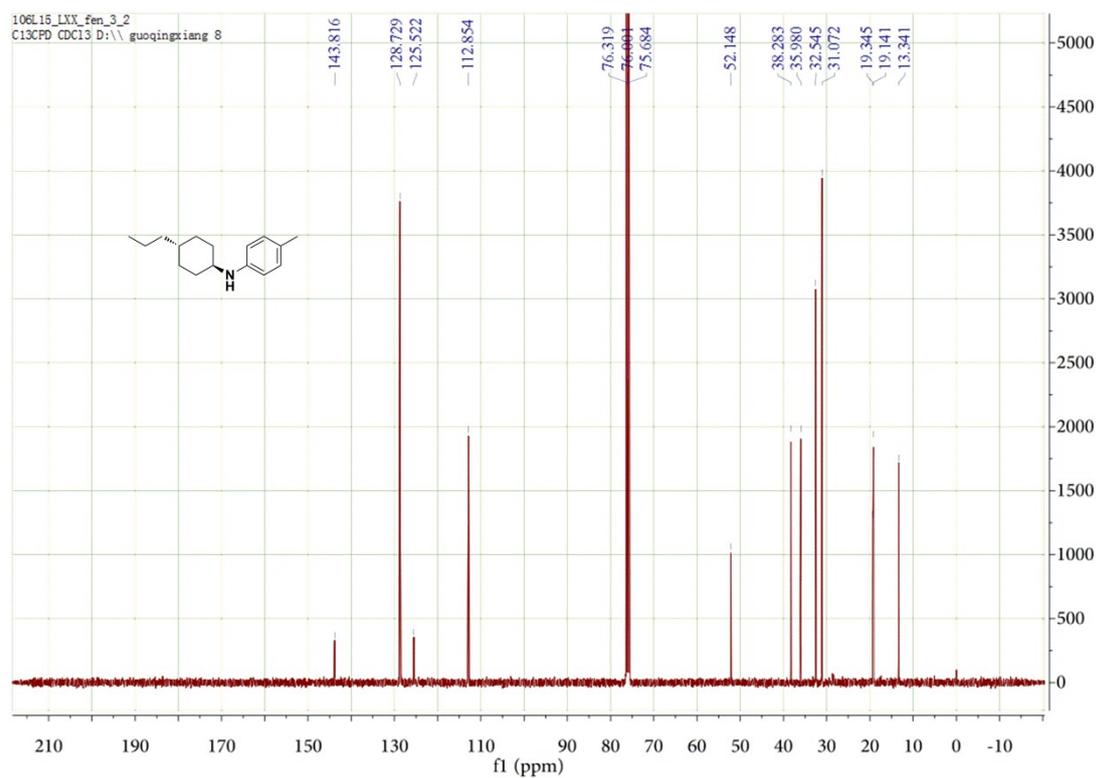
**cis-4-methyl-N-(4-propylcyclohexyl) aniline (3e) ( $^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$ )**



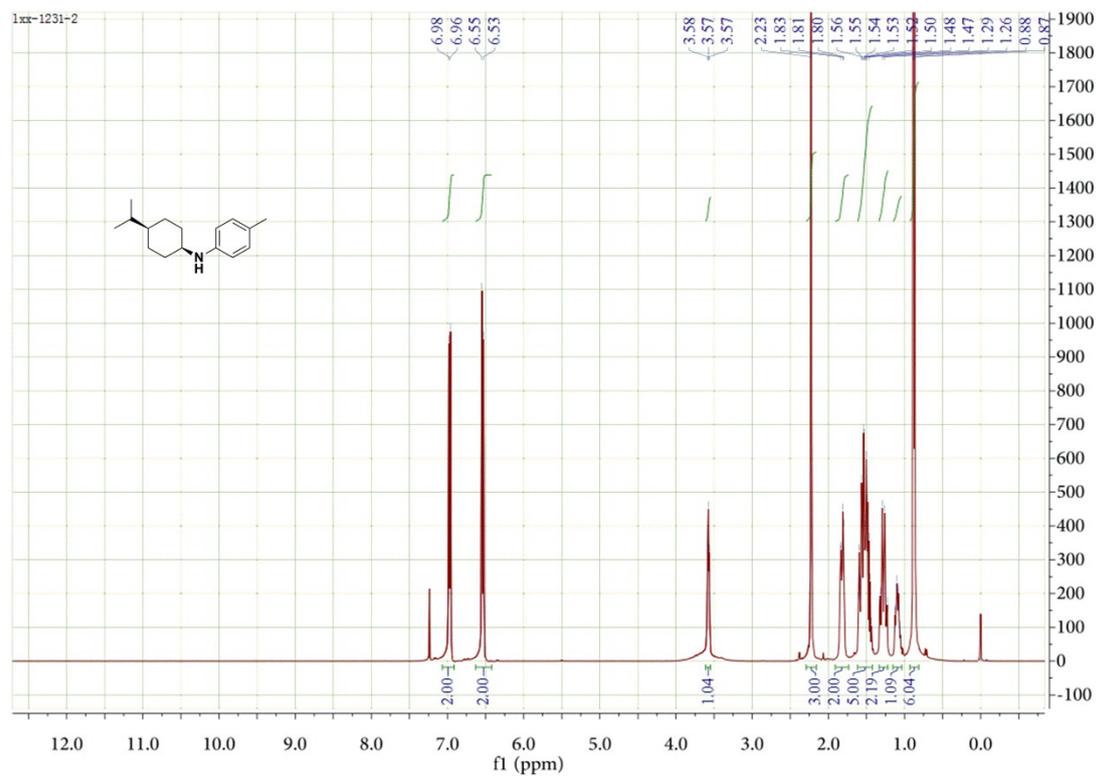
**trans-4-methyl-N-(4-propylcyclohexyl) aniline (3e) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



**trans-4-methyl-N-(4-propylcyclohexyl) aniline (3e) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**

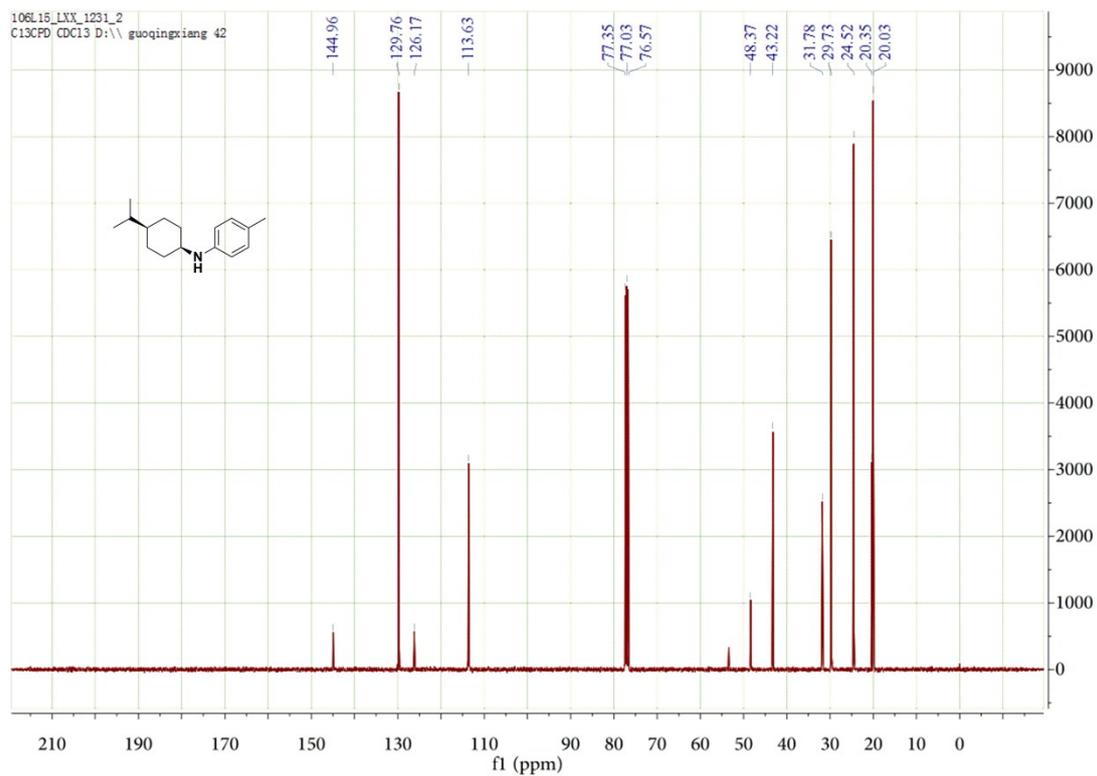


**cis-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f) ( $^1\text{H}$  NMR, 400 MHz,  $\text{CDCl}_3$ )**

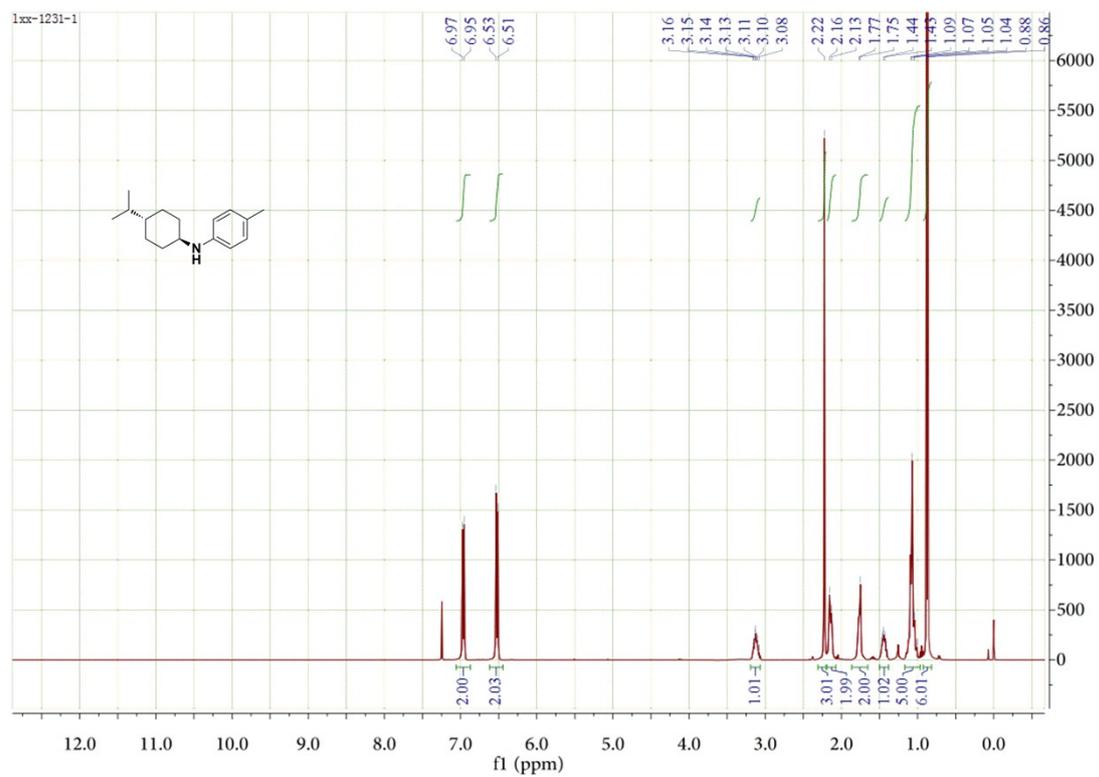


**cis-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**

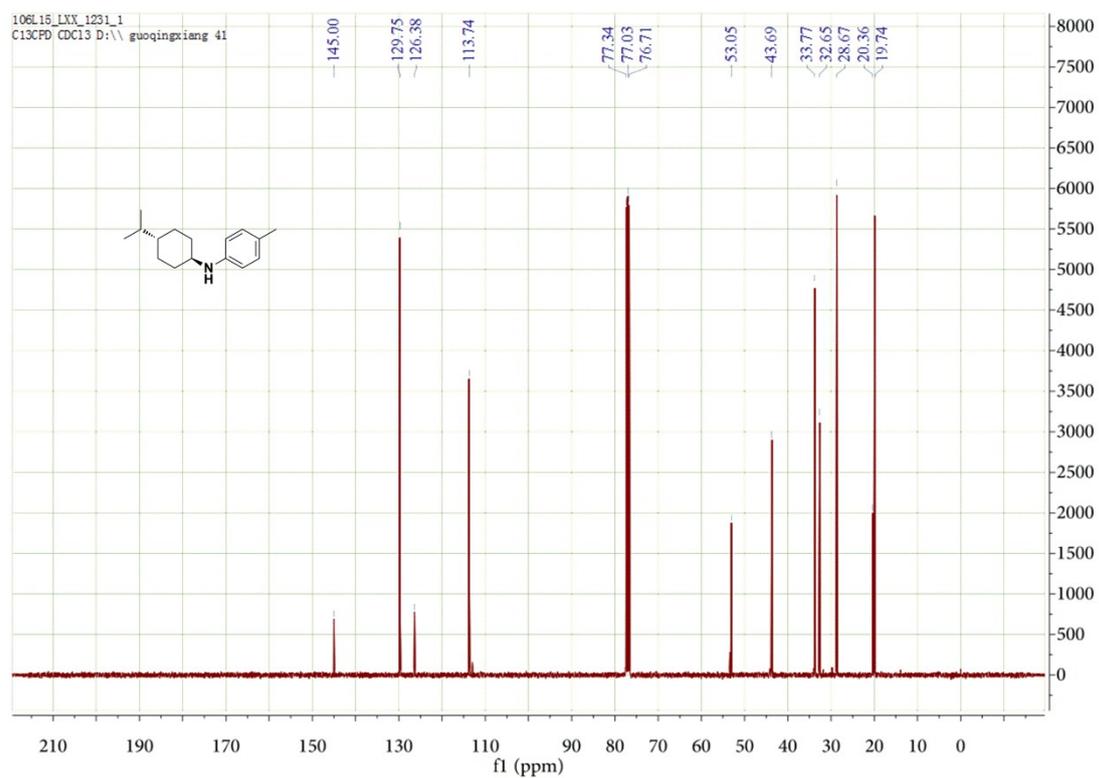
106L15\_LXX\_1231\_2  
C13CPD CDCl3 D:\ guoqingxiang 42



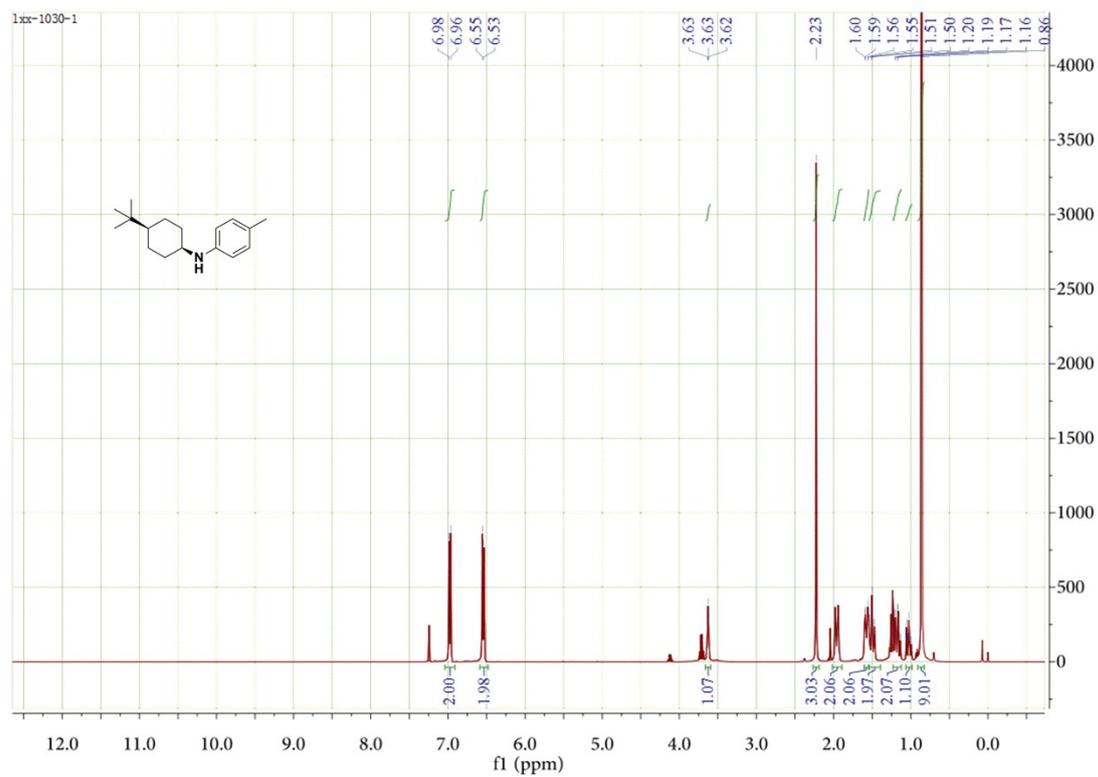
**trans-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



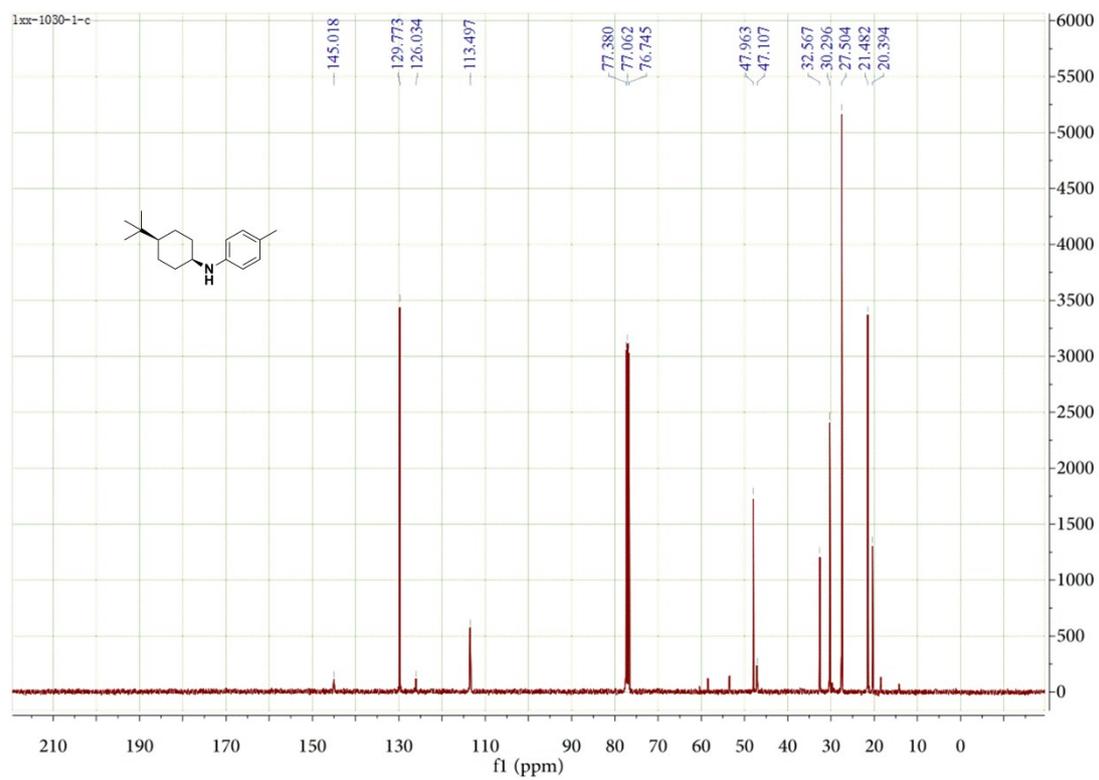
**trans-4-methyl-N-(4-isopropylcyclohexyl) aniline (3f) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**



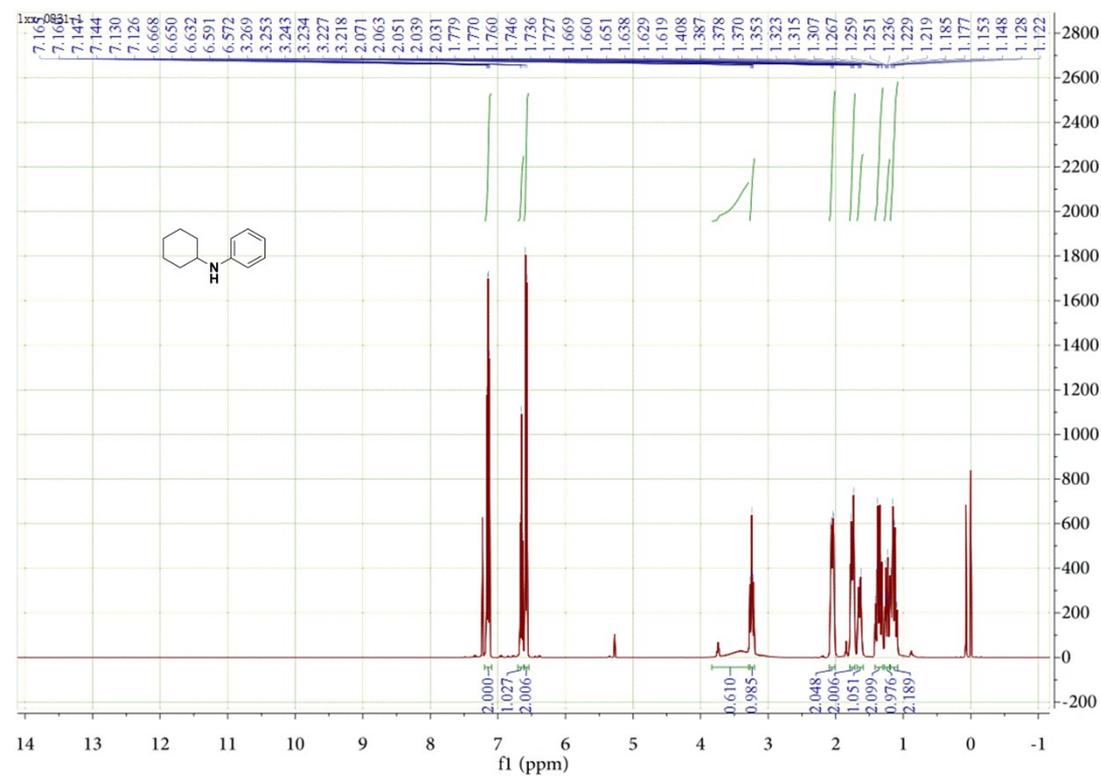
**cis-4-methyl-N-(4-tertbutylcyclohexyl) aniline (3g) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



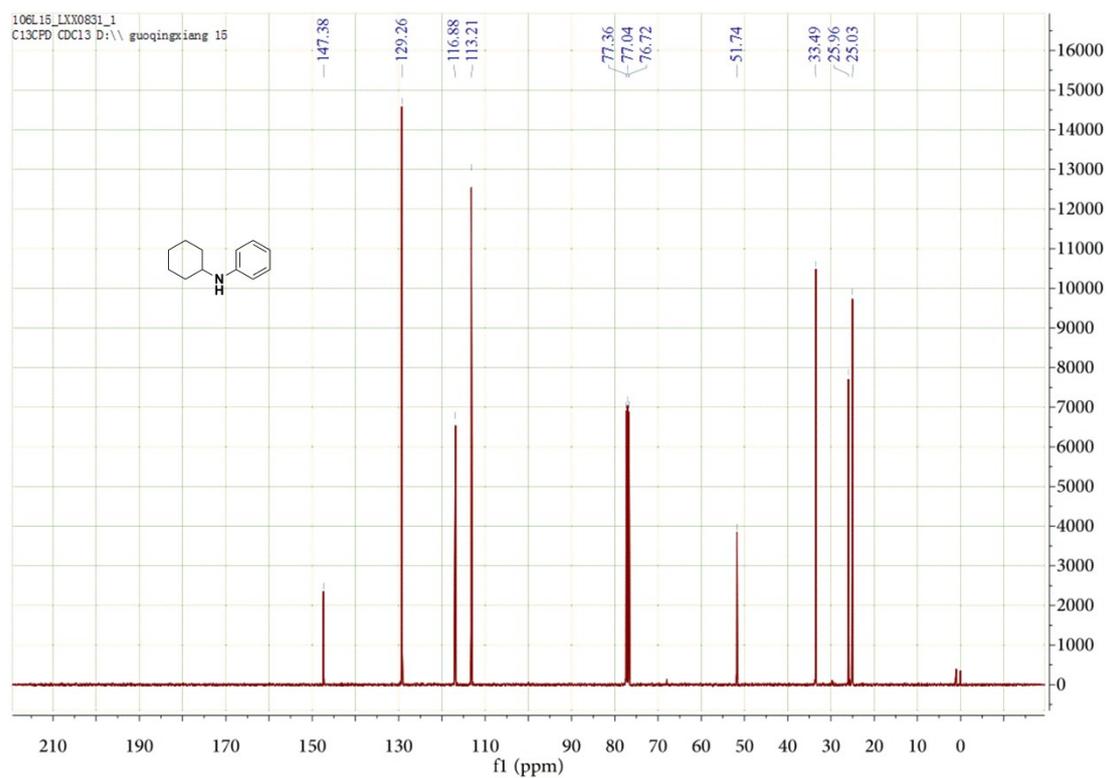
**cis-4-methyl-N-(4-tertbutylcyclohexyl) aniline (3g) ( $^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$ )**



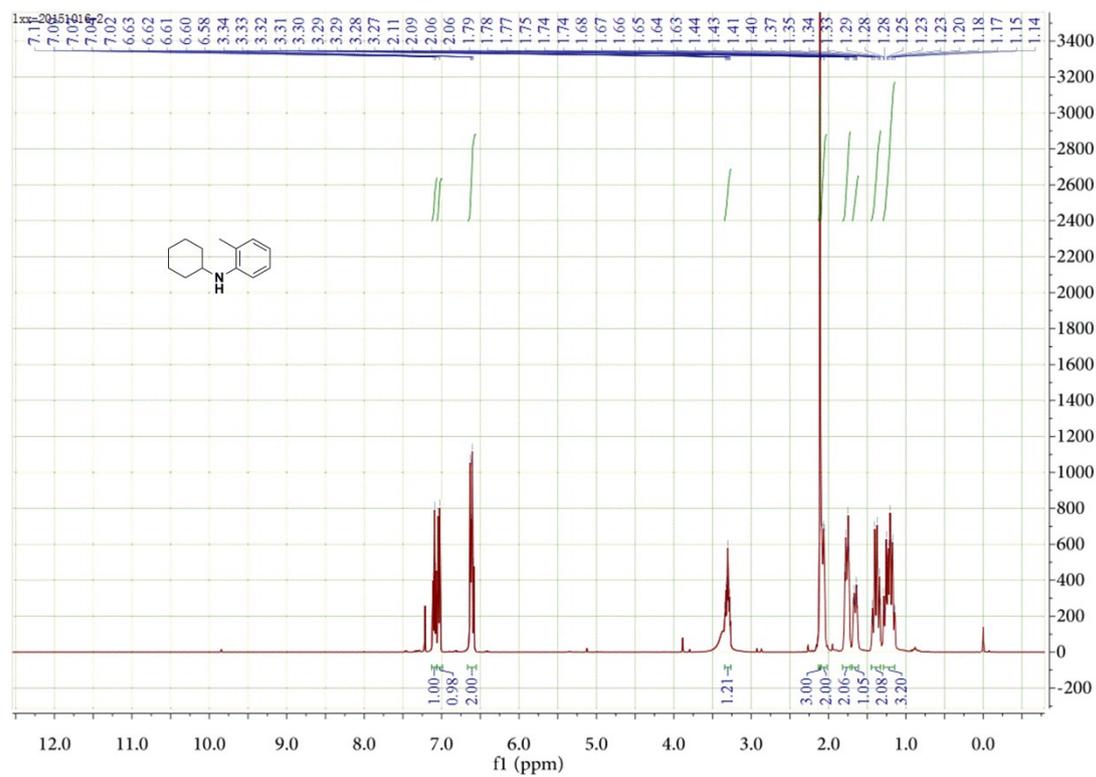
# N-cyclohexylaniline (3h) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



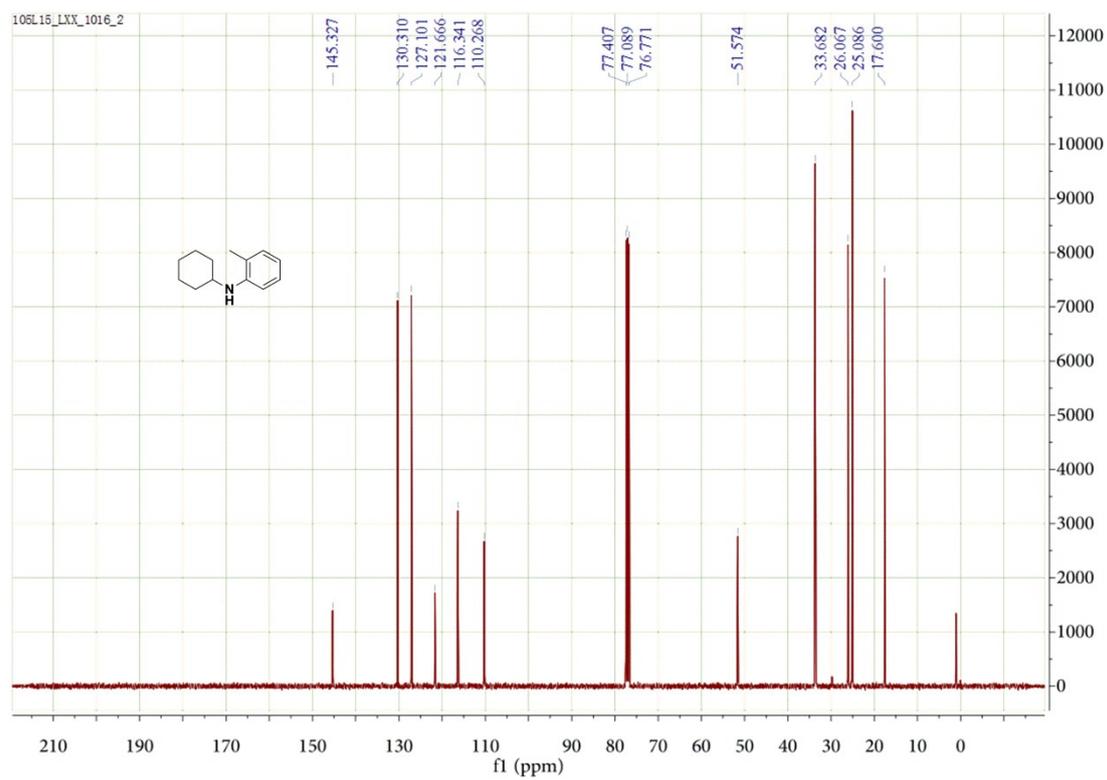
# N-cyclohexylaniline (3h) ( $^{13}\text{C}$ NMR, 101 MHz, $\text{CDCl}_3$ )



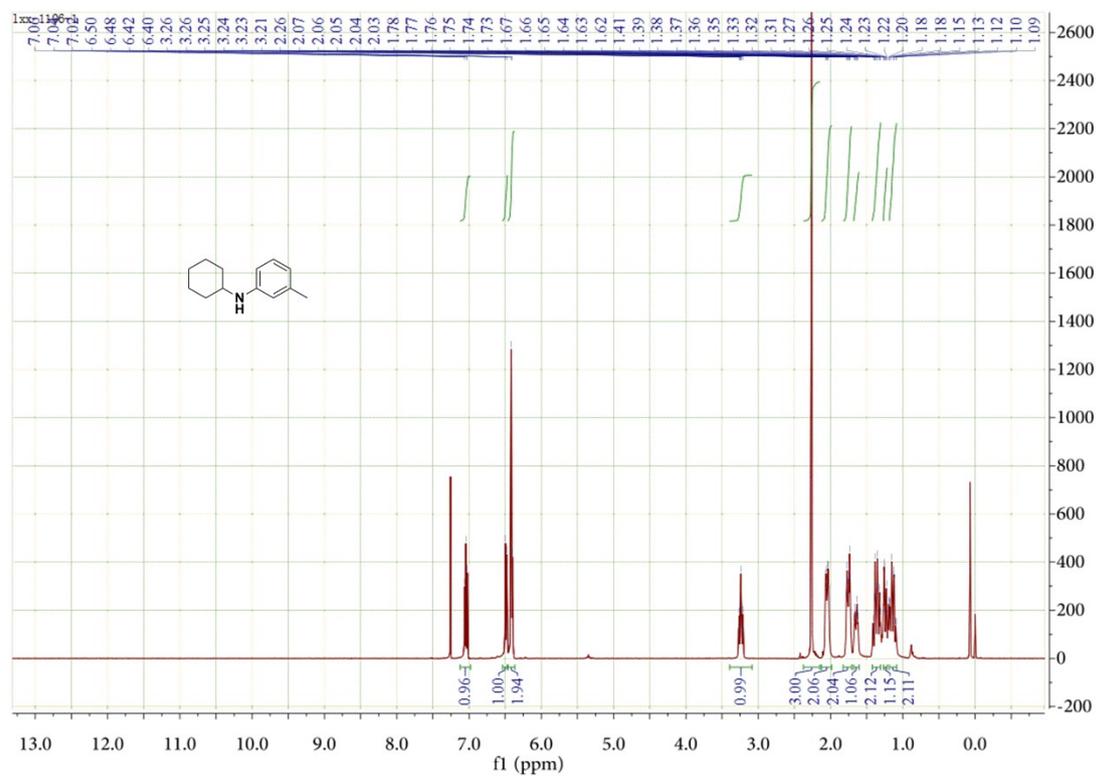
N-cyclohexyl-2-methylaniline (3i) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



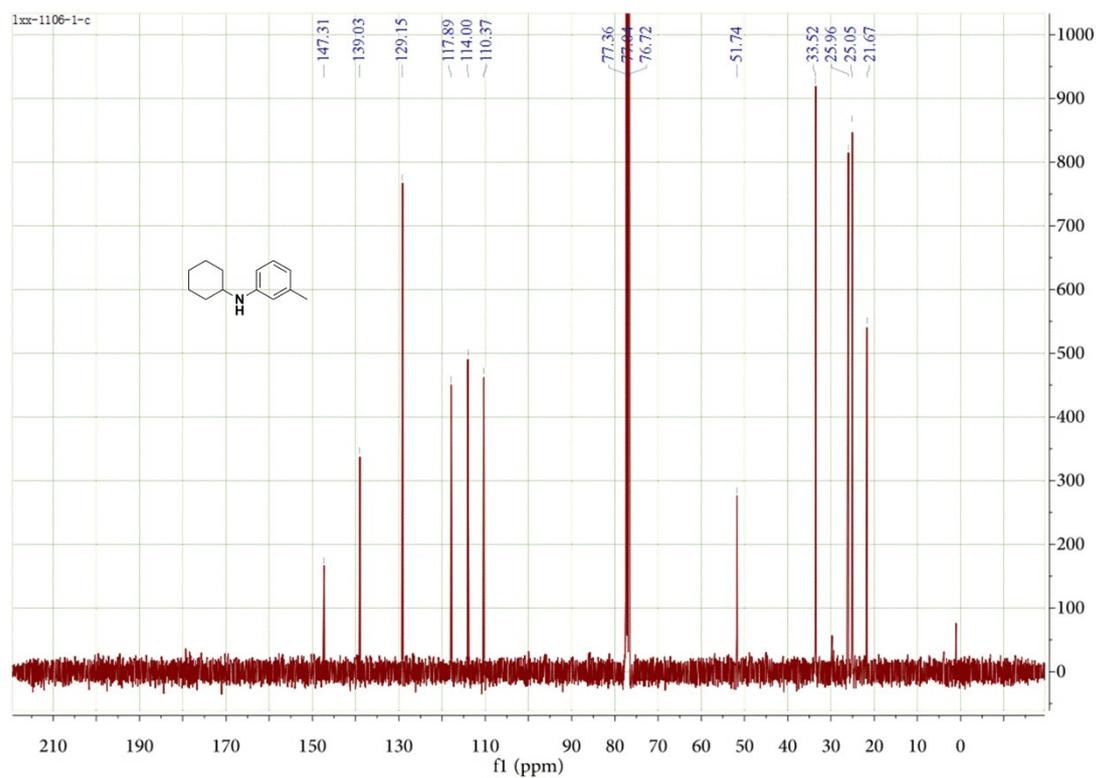
N-cyclohexyl-2-methylaniline (3i) ( $^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$ )



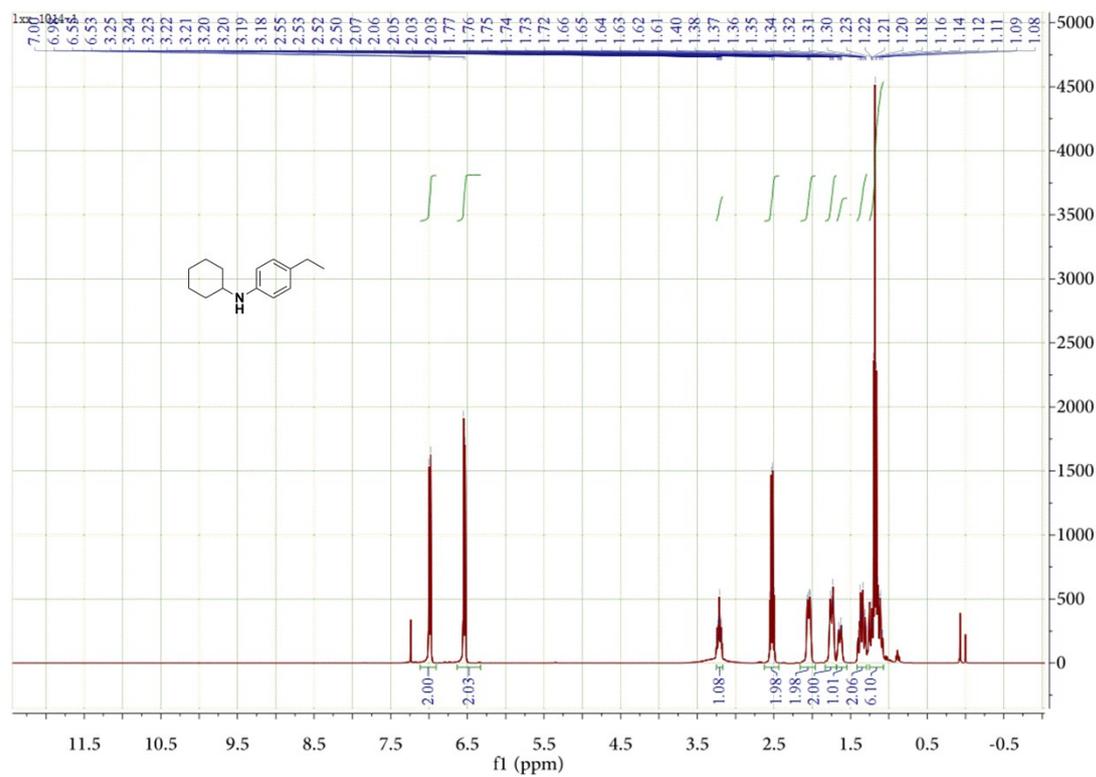
N-cyclohexyl-3-methylaniline (3j) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



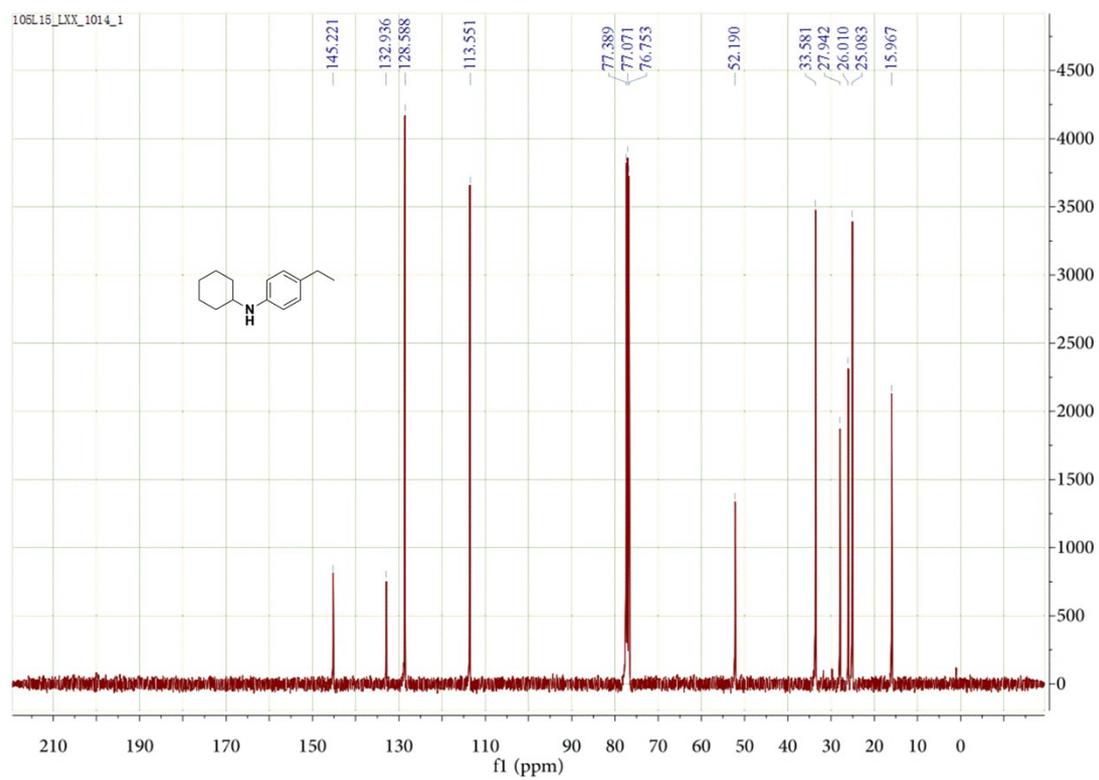
N-cyclohexyl-3-methylaniline (3j) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)



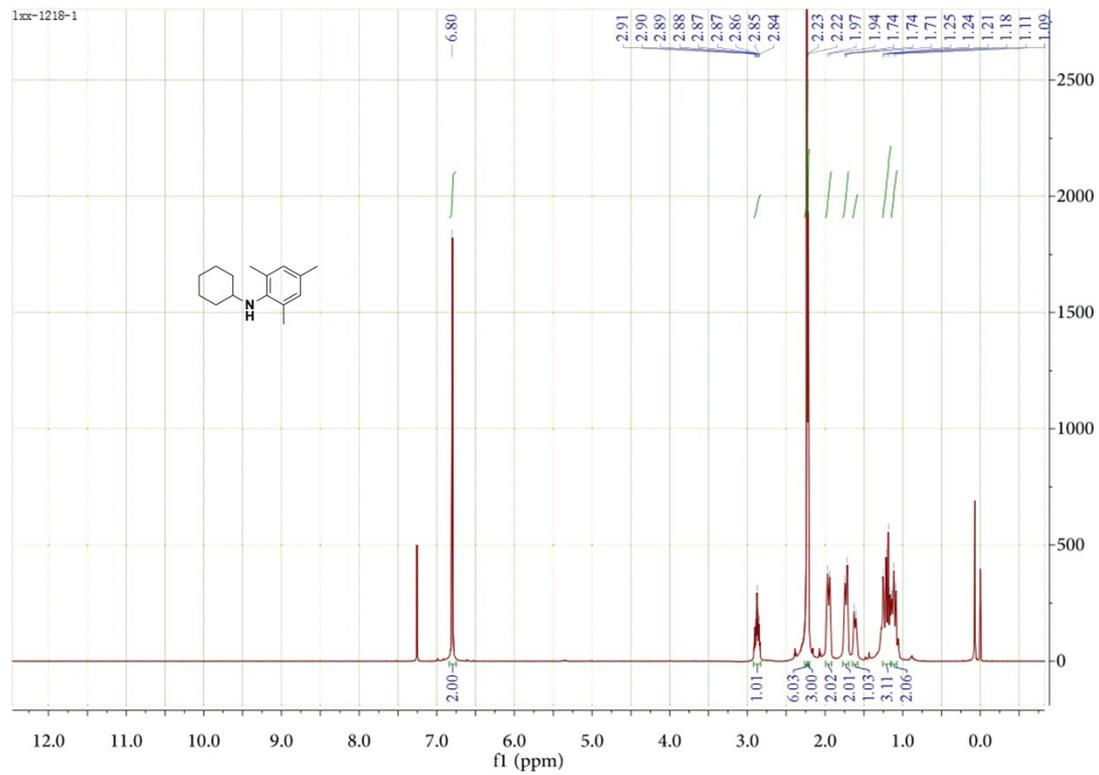
# N-cyclohexyl-4-ethylaniline (3k) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



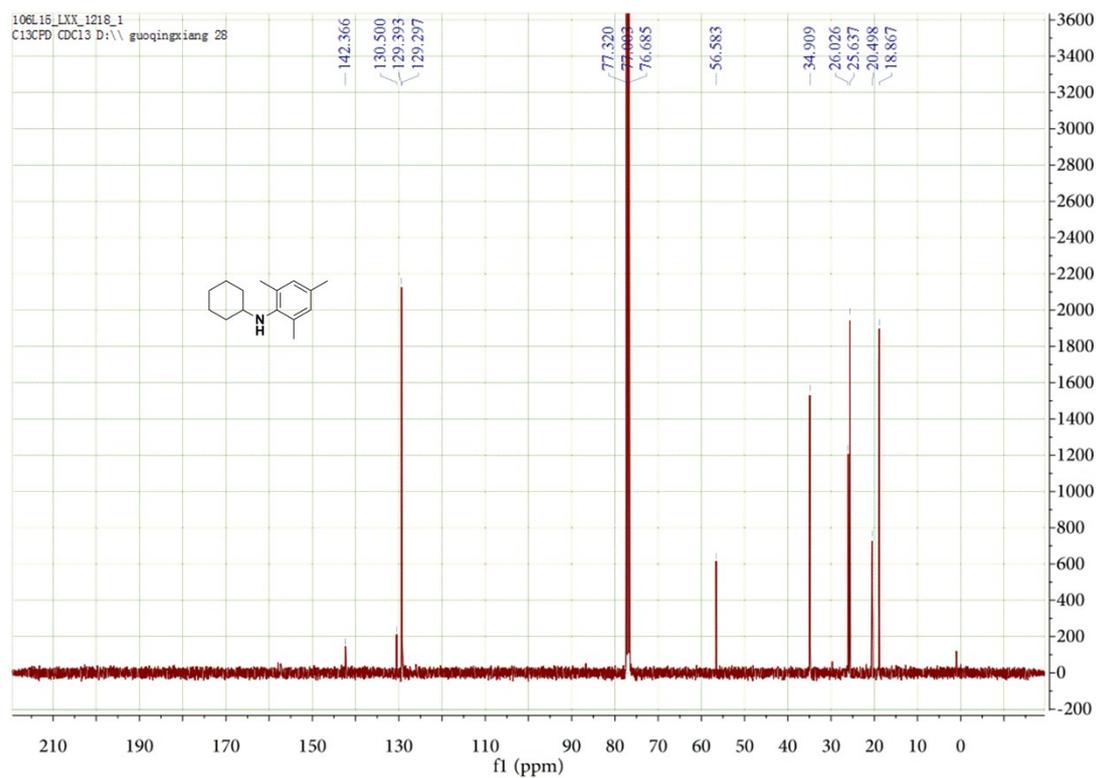
**N-cyclohexyl-4-ethylaniline (3k) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**



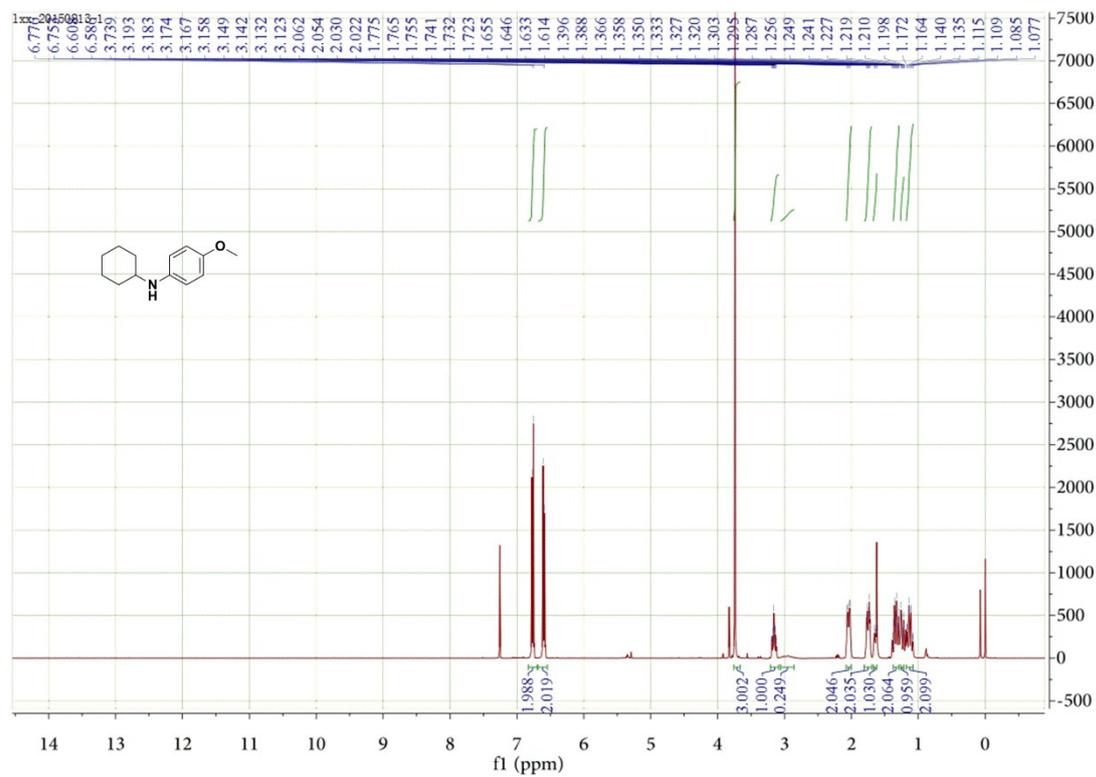
**N-cyclohexyl-2,4,6-trimethylaniline (3l) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)**



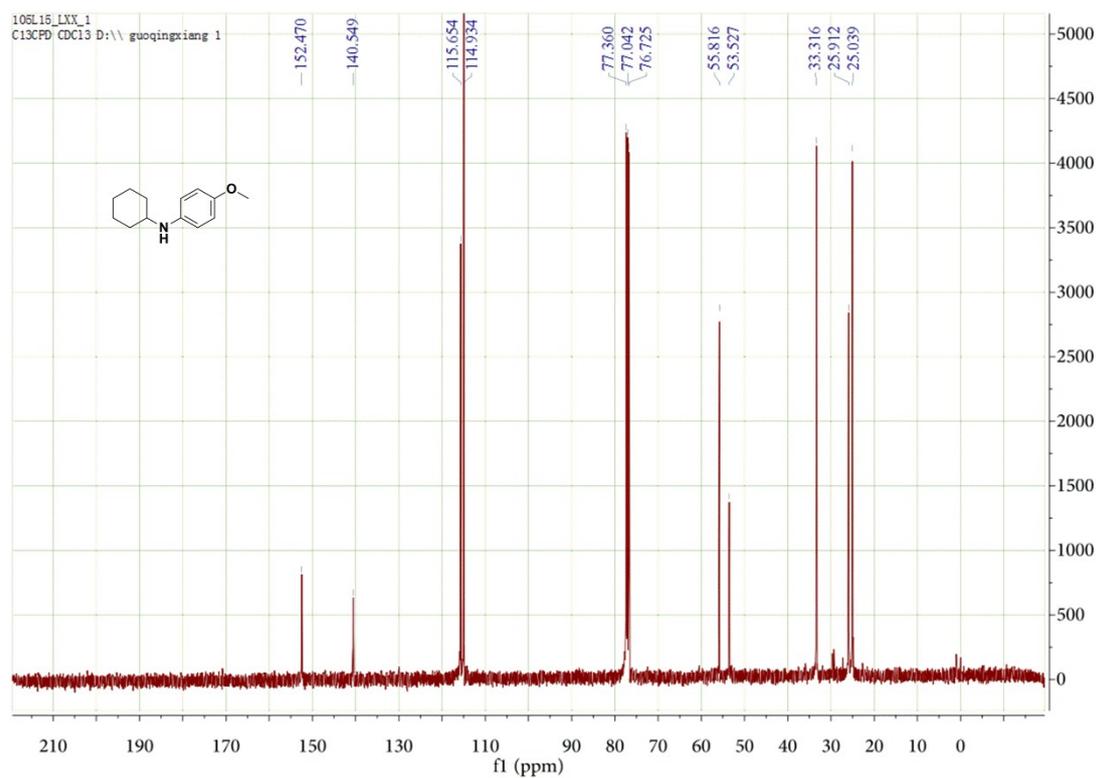
# N-cyclohexyl-2,4,6-trimethylaniline (3l) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)



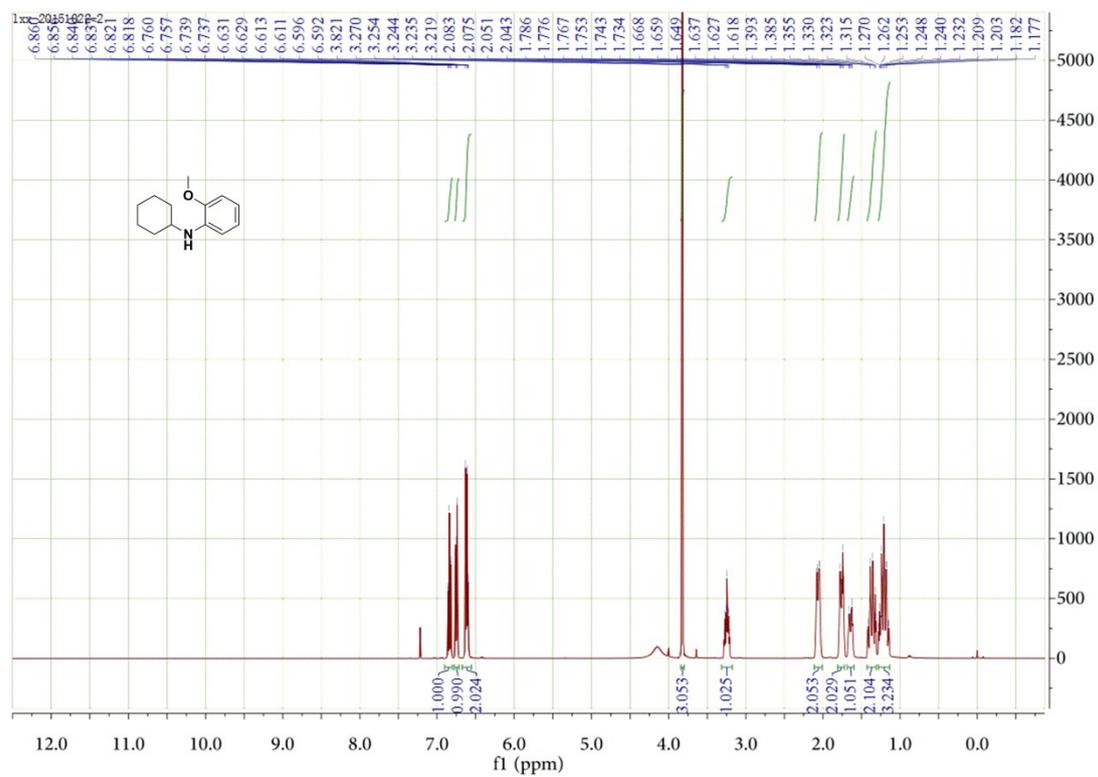
# N-cyclohexyl-4-methoxyaniline (3n) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



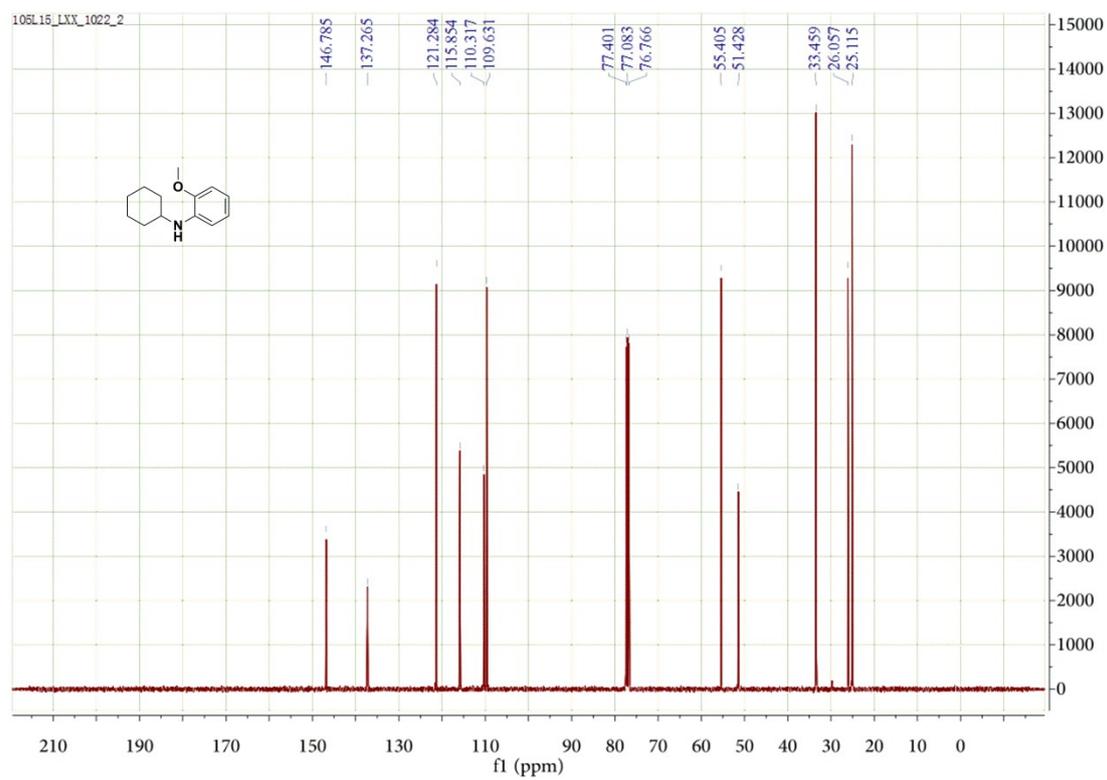
# N-cyclohexyl-4-methoxyaniline (3n) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)



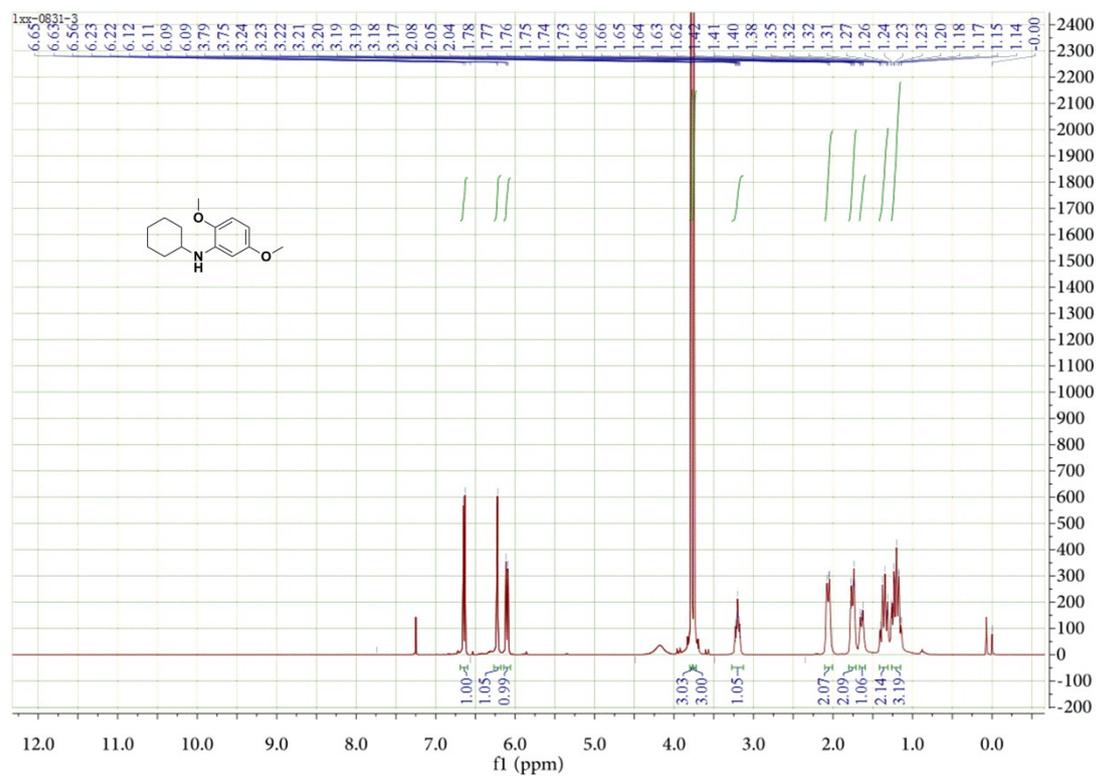
N-cyclohexyl-2-methoxyaniline (3o) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



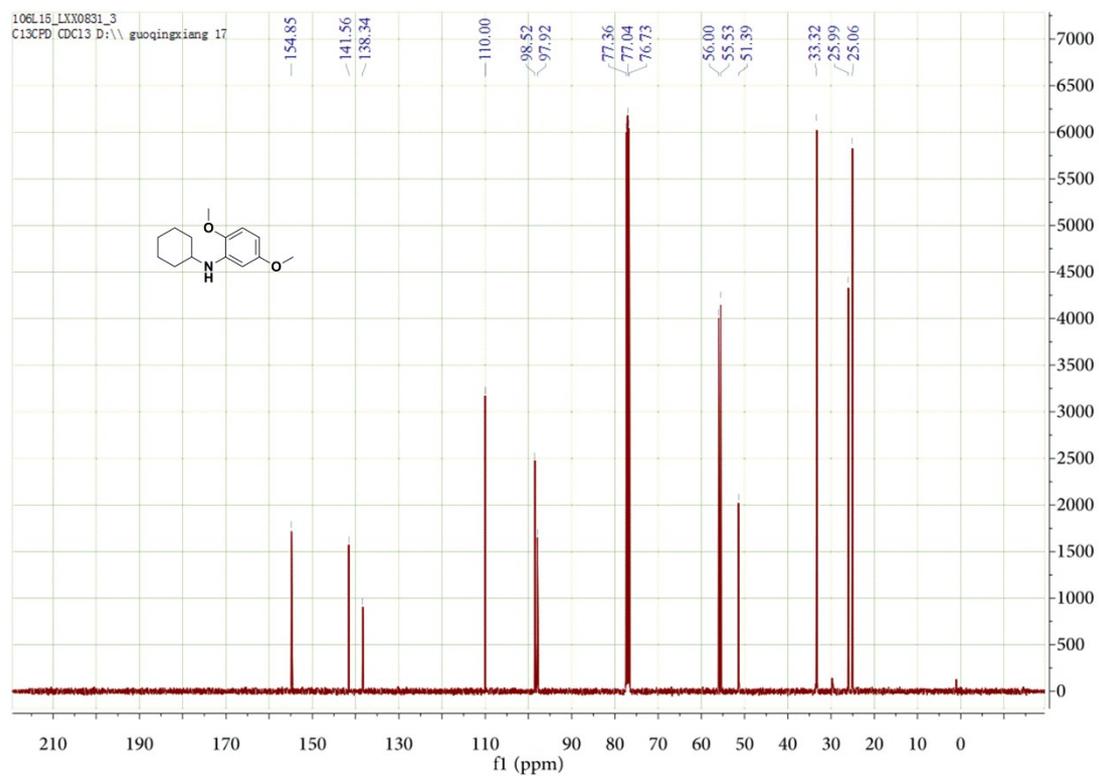
N-cyclohexyl-2-methoxyaniline (3o) ( $^{13}\text{C}$  NMR, 101 MHz,  $\text{CDCl}_3$ )



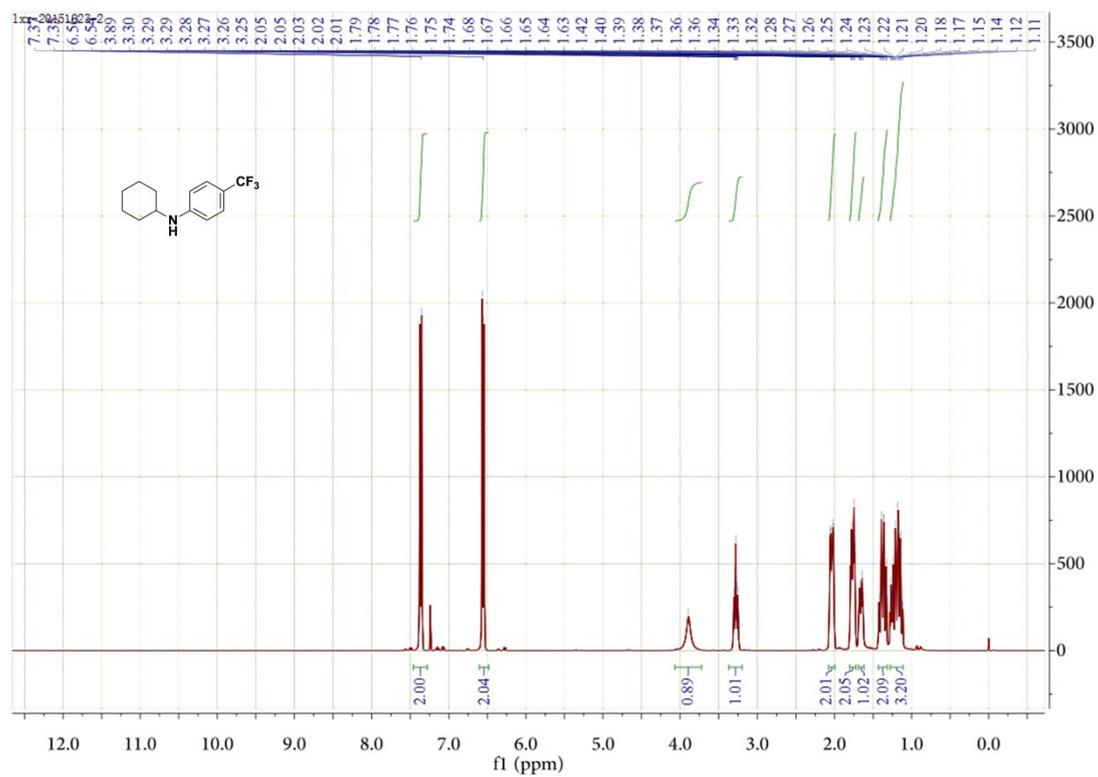
N-cyclohexyl-2,5-dimethoxyaniline (3p) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



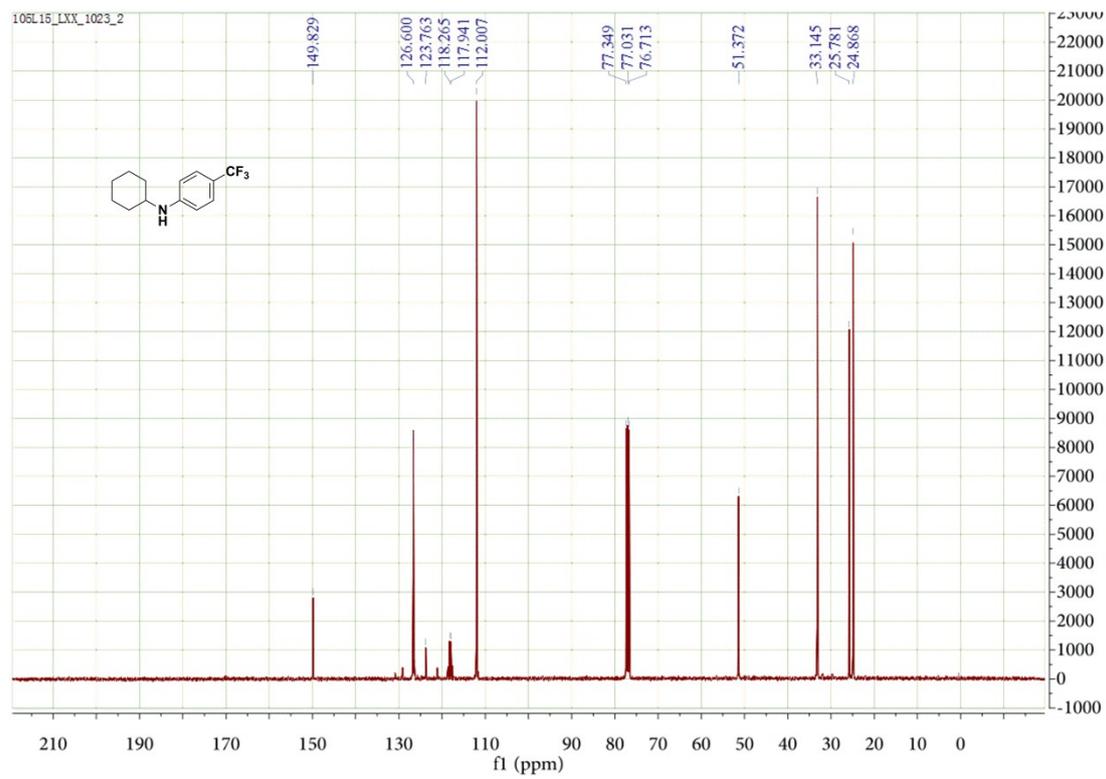
# N-cyclohexyl-2,5-dimethoxyaniline (3p) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)



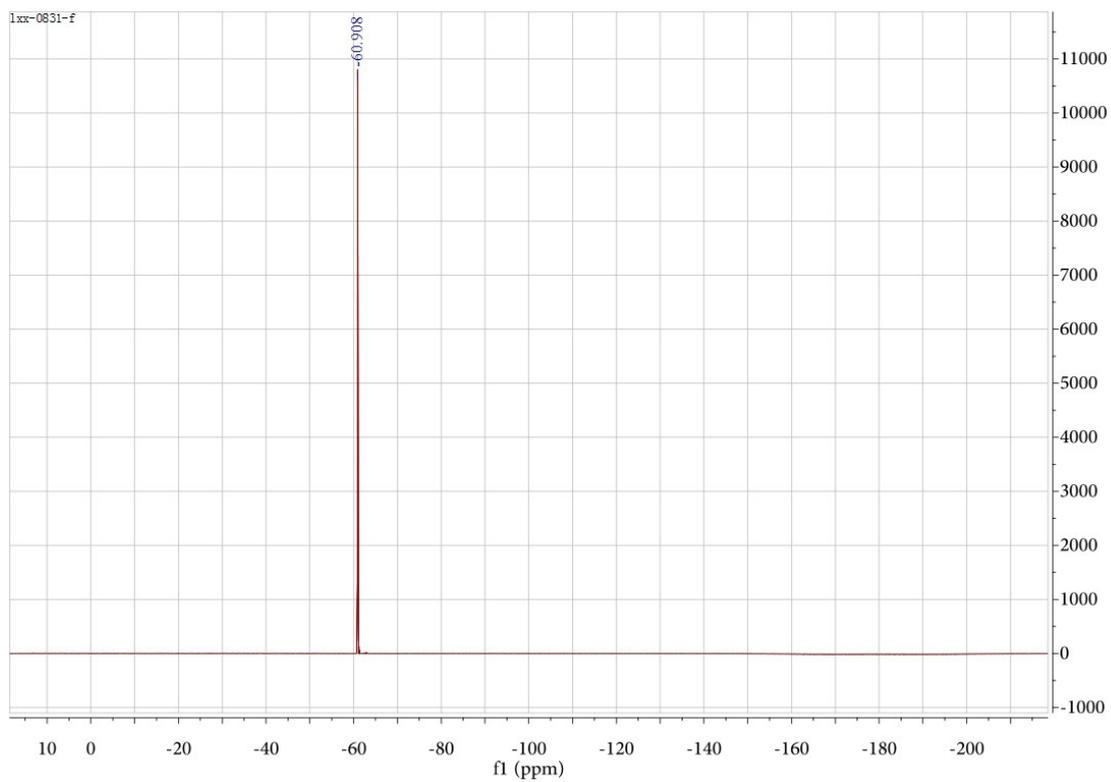
N-cyclohexyl-4-(trifluoromethyl)aniline (3q) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



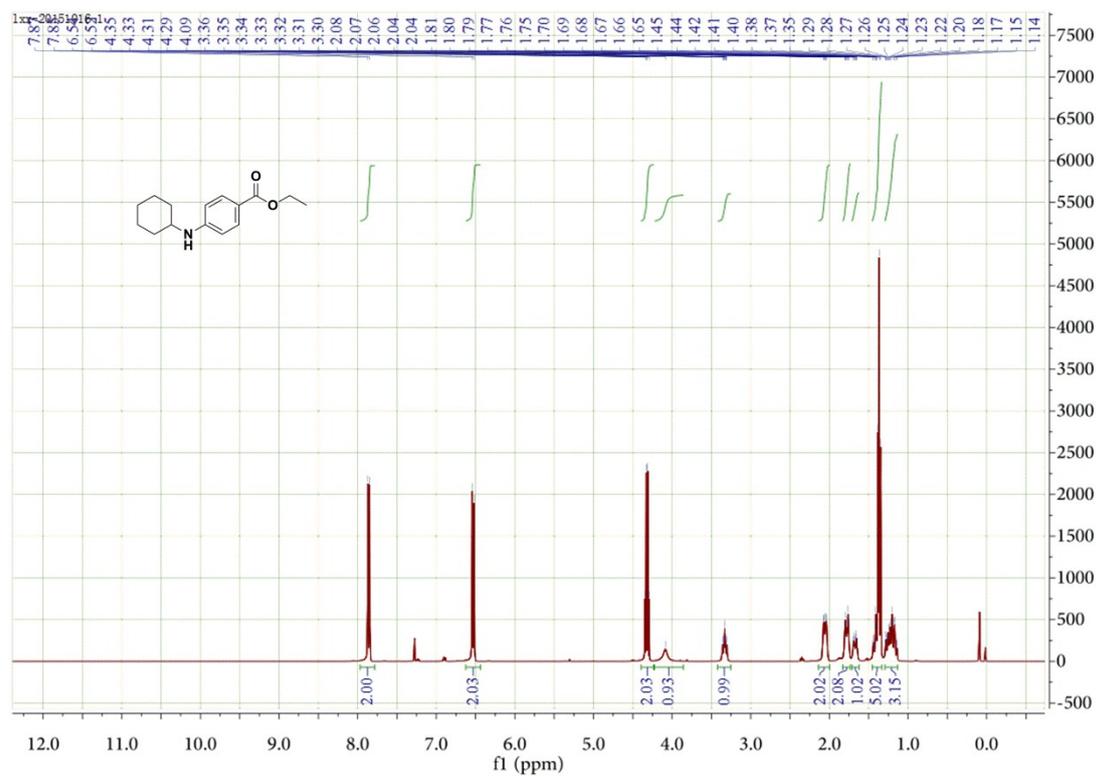
N-cyclohexyl-4-(trifluoromethyl)aniline (3q) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)



**N-cyclohexyl-4-(trifluoromethyl)aniline (3q) ( $^{19}\text{F}$  NMR, 376 MHz,  $\text{CDCl}_3$ )**



Ethyl-4-(cyclohexylamino)benzoate (3r) (<sup>1</sup>H NMR, 400 MHz, CDCl<sub>3</sub>)



**Ethyl-4-(cyclohexylamino)benzoate (3r) (<sup>13</sup>C NMR, 101 MHz, CDCl<sub>3</sub>)**

