

Supplementary Information

1. Reagents and analysis

The chemical reagents were purchased from Shanghai Aladdin Chemical Reagent Co. Ltd. and Alfa Aesar China, which were used as received. All the solvents were dried and distilled before use. The ^1H and ^{13}C NMR spectra were recorded on a Bruker ARX 500 spectrometer at ambient temperature. Gas chromatography (GC) analysis was performed on a SHIMADZU-2014 equipped with a DM-Wax capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). The analysis conditions were as follows: Injector temperature $250\text{ }^\circ\text{C}$; Detector temperature $250\text{ }^\circ\text{C}$; Initial column temperature at $60\text{ }^\circ\text{C}$ with retention time of 1 min and then rising up to $240\text{ }^\circ\text{C}$ with a temperature ramp of $10\text{ }^\circ\text{C min}^{-1}$; Final column temperature $240\text{ }^\circ\text{C}$ with retention time of 10 min. GC-mass spectrometry (GC-MS) which equipped with a DB-Wax capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) was recorded on an Agilent 6890 instrument equipped with an Agilent 5973 mass selective detector. The analysis conditions were as follows: Injector temperature $250\text{ }^\circ\text{C}$; Detector temperature $250\text{ }^\circ\text{C}$; Initial oven temperature at $40\text{ }^\circ\text{C}$ with retention time of 3 min and then rising up to $250\text{ }^\circ\text{C}$ with a temperature ramp of $10\text{ }^\circ\text{C min}^{-1}$; Final column temperature $250\text{ }^\circ\text{C}$ with retention time of 3 min. FT-IR spectra were recorded on a Nicolet NEXUS 670 spectrometer. TG/DTG analysis was performed on a Thermo Gravimetric Analyzer (TGA/SDTA/SF/1100/851e). The amount of Ir and P in the sample was quantified by using an inductively coupled plasma optical emission spectrometer (ICP-OES) on an Optima 8300 instrument (PE Corporation).

2. Synthesis

L1–L6 were prepared according to the procedures reported by our group previously^{1–4}.

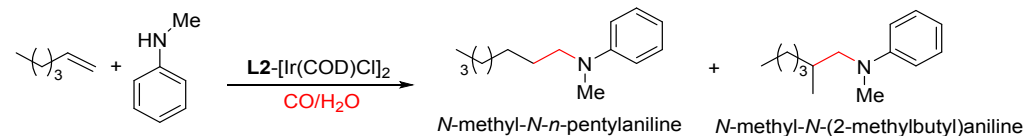
3. General procedures for hydroaminomethylation of olefins

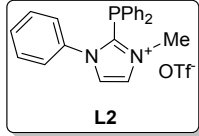
In a typical experiment, $[\text{Ir}(\text{COD})\text{Cl}]_2$ 0.025 mmol (Ir 1.0 mol %), mono-phosphine 0.05 mmol, diphosphine 0.025 mmol (**L5** and **L6**), were mixed with 1-hexene 5.0 mmol, *N*-methylaniline 8.0 mmol, water 0.35 mL and *N*-methyl pyrrolidone (NMP) 2 mL (solvent). The mixture was added in a 50 mL sealed Teflon-lined stainless steel autoclave which was purged with CO (0.5 MPa) for three times and then pressured by CO to 4.0 MPa. Then the reaction mixture was stirred vigorously at appointed temperature for some time. Upon completion, the autoclave was cooled down to room temperature and slowly depressurized. The solution was analyzed by GC to determine the conversions (*n*-dodecane as internal standard) and the selectivities (normalization method). To isolate the selected compound, the mixture was extracted with diethyl ether and NMP was removed by washing with water. After drying and removal of the solvent, the crude product is purified by column chromatography on silica gel ((gradient elution, *n*-pentane /ethyl acetate= 9:1 with 0.5% Et_3N). The products were further identified by GC-mass spectrometry and $^1\text{H}/^{13}\text{C}$ NMR spectroscopy.

As an ionic ligand with high polarity, **L6**-base Ir-catalyst could be recycled after extracting the reaction solution by *n*-hexane. Upon reaction completion, *n*-hexane (45 mL) was added to the yellow reaction solution. Then the upper colorless and transparent phase was decanted from the obtained biphasic mixture. The lower phase containing NMP and the catalyst was further washed with *n*-hexane ($3\text{ mL} \times 3$) to completely extract the reactants and products. The combined *n*-hexane phase was analyzed by GC and ICP-AES. The remaining phase was reused for the next run.

4. Selected screening data

S. Table 1 Hydroaminomethylation of 1-hexene with *N*-methylaniline in the presence of CO and H₂O catalyzed by Ir-catalyst under different conditions^a





L2

Entry	[Ir(COD)Cl] ₂ (mol%)	Ir/P	Temp (°C)	Time (h)	Sol.	Conv. of 1- hexene(%) ^b	Sel. (%) ^b		hexane	Yield (%)	L/B ^b
							Amine	Isomer.			
1	1.0	1/1	120	20	NMP	50	>99	-	<1	50	90:10
2	1.0	1/1	130	20	NMP	80	>99	-	<1	80	85:15
3	1.0	1/1	140	20	NMP	86	>99	-	<1	86	84:16
4	0.5	1/1	140	20	NMP	75	>99	-	<1	75	83:17
5	1.0	2/1	140	20	NMP	79	>99	-	<1	78	82:18
6	1.0	1/2	140	20	NMP	33	>99	-	<1	33	84:16
7	1.0	1/1	140	20	Toluene	36	>99	-	<1	67	75:25
8	1.0	1/1	140	20	MeCN	43	>99	-	<1	62	82:18
9	1.0	1/1	140	20	Diglyme	45	>99	-	<1	52	78:22
10	1.0	1/1	140	20	THF	69	>99	-	<1	75	80:20
11	1.0	1/1	140	11	NMP	59	>99	-	<1	58	83:17
12	1.0	1/1	140	22	NMP	80	>99	-	<1	79	83:17
13	1.0	1/1	140	24	NMP	86	>99	-	<1	85	84:16

^a [Ir(COD)Cl]₂ 0.025 mmol (Ir 1.0 mol %), ligand **L2** 0.05 mmol, P/Ir = 1 (molar ratio), 1-hexene 5.0 mmol, *N*-methylaniline 8.0 mmol, H₂O 0.3 mL, *N*-methyl pyrrolidone (NMP) 2 mL, CO 4.0 MPa, time 22 h; ^b Determined by GC and GC-Mass.

5. The scope of hydroaminomethylation catalysed by L6-based Ir-catalyst

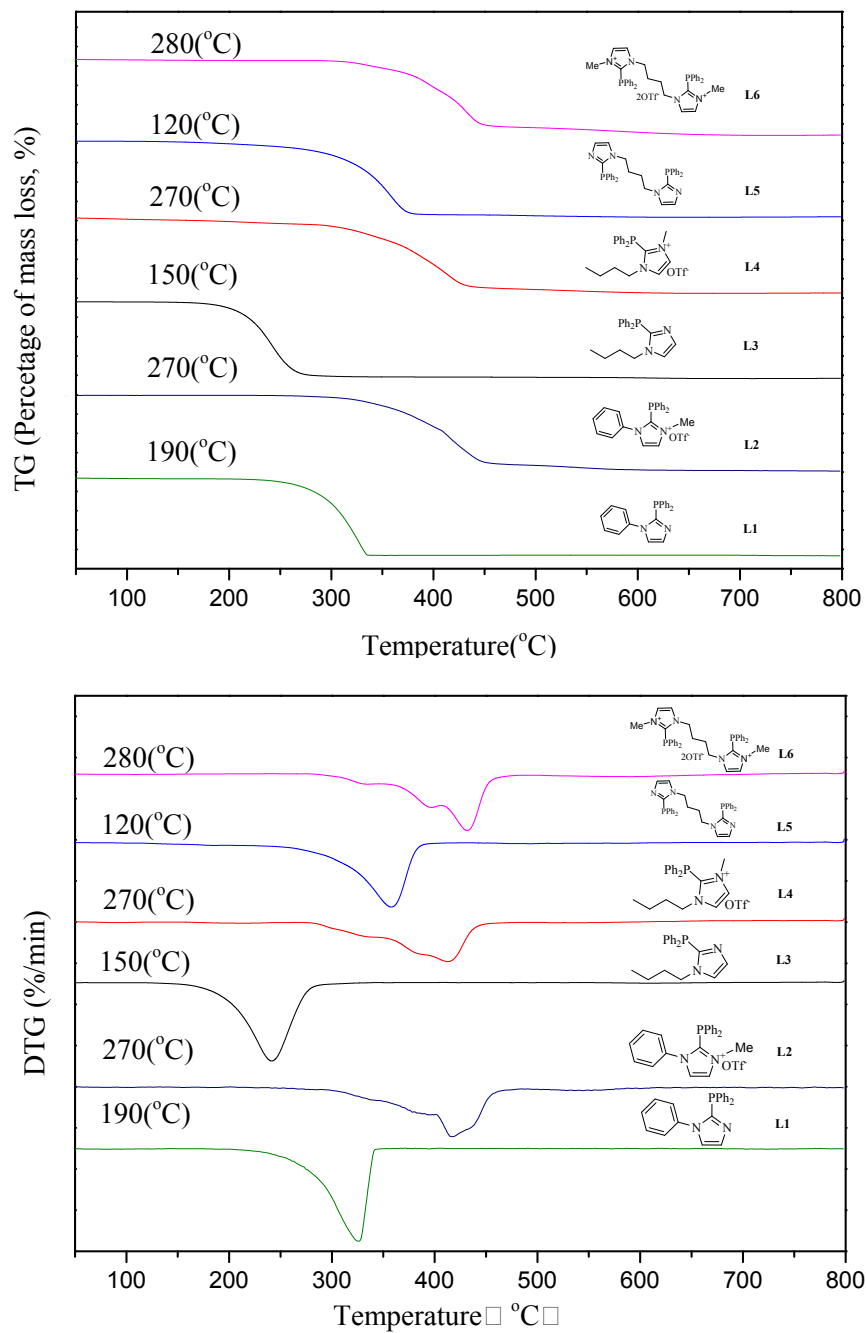
S. Table 2 Generality of **L6**-based Ir-catalyst for hydroaminomethylation of olefins with amines^a

Entry	Olefin	Amine	Major product	Conv. (%) ^b	Yield (%) ^b	L/B ^b
1				94	93	84:16
2				92	86	83:17
3				94	83	81:19
4				90	80	81:19
5				89	82	83:17
6				82	48	22:78
7				13	12	-
8 ^c				81	80	50:50
9 ^c				59	58	44:56
10 ^c				71	70	47:53
11 ^c				66	65	26:74
12 ^c				91	90	38:62
13 ^c				92	91	23:77
14 ^d				90	53	83:17
15				16	15	90:10

^a [Ir(COD)Cl]₂ 0.025 mmol (Ir 1 mol%), **L6** 0.025 mmol, P/Ir = 1 (molar ratio), olefin 5.0 mmol, amine 8.0 mmol, H₂O 0.3 mL, NMP 2 mL, CO 4.0 MPa, time 22 h, temperature 140 °C; ^b The yield of amine was determined by GC (the ¹H/¹³C NMR spectra of the corresponding products were provided in ESI); ^c time 48 h; ^d 36% yield of imine was obtained.

6. TG/DTG analysis

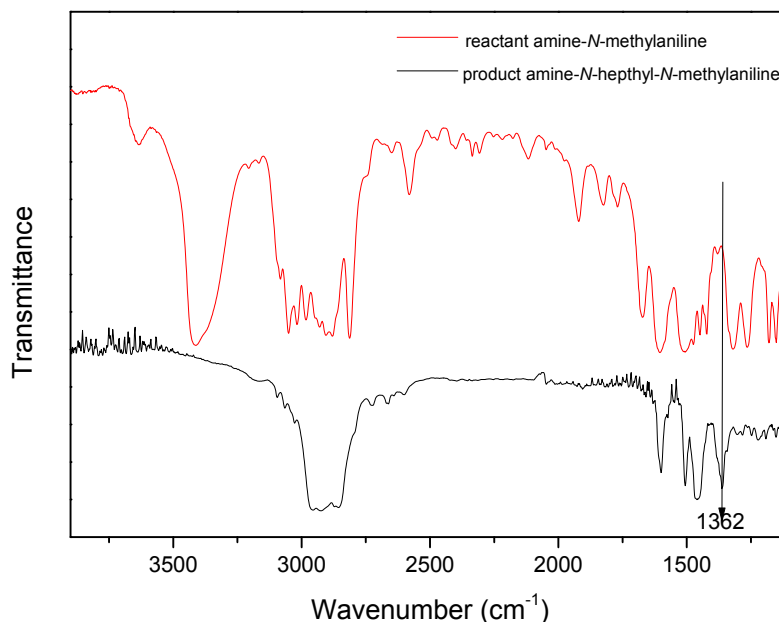
S. Fig. 1 TG/DTG analyses of the phosphine ligands of L1-L6 in air flow.



7. FT-IR spectral characterization

FT-IR analysis

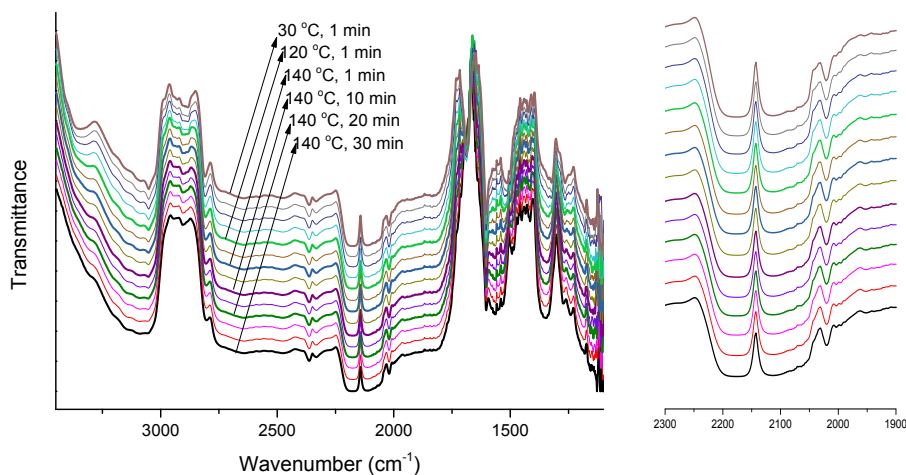
S. Fig. 2 The FT-IR spectra of *N*-methylaniline and *N*-heptyl-*N*-methylaniline (CaF₂ pellet) recorded at room temperature in air atmosphere.



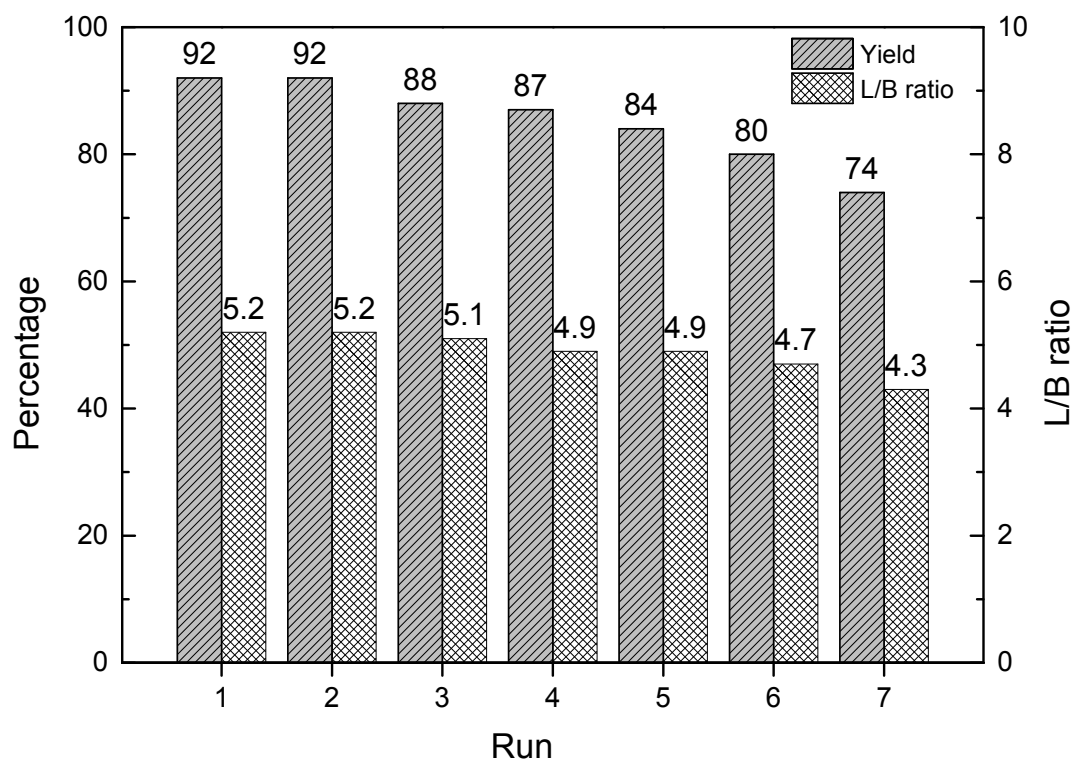
High-pressure *in situ* FT-IR analysis

The hydroaminomethylation of 1-hexene catalyzed by **L6**-base Ir-catalyst was *in situ* recorded by a Nicolet NEXUS 670 spectrometer, which was combined with a specially designed *in situ* high-pressure IR cell. The mixture compositions including **L6**, [Ir(COD)Cl]₂, 1-hexene, *N*-methylaniline, and syngas or CO (with water) were completely the same as those for the real reaction in Table 1 (Entry 6), except for the much high concentration of **L6** and [Ir(COD)Cl]₂ required for IR spectral detection and relatively lower syngas pressure (2.0 MPa; $v_{\text{CO}}/v_{\text{H}_2} = 3/1$) or CO pressure (0.5 MPa instead of 4.0 MPa in the real hydroaminomethylation) due to the limited pressure endurance capability of the designed IR cell. For comparison, the mixtures containing **L5**, [Ir(COD)Cl]₂, 1-hexene, and CO, water were recorded in parallel.

S. Fig. 3 The *in situ* high-pressure FT-IR spectra recorded from 30 to 140 °C after mixing [IrCl(COD)]₂, **L5**, 1-hexene, *N*-methylaniline, H₂O and NMP in CO (0.5 MPa).



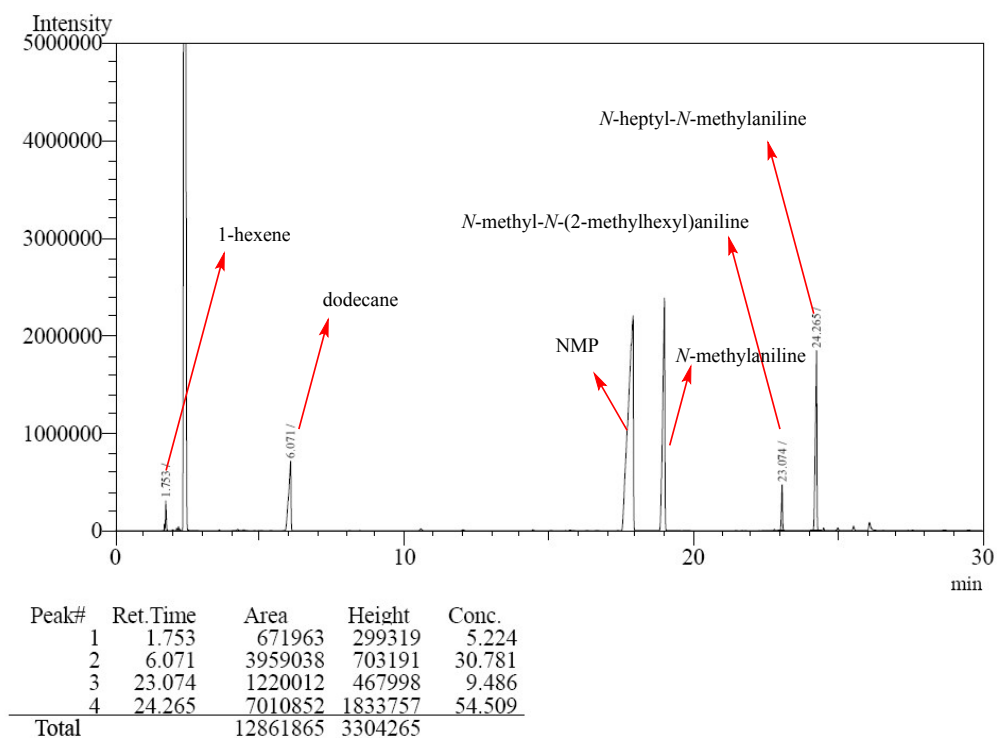
8. The recycling uses of L6-based Ir-catalyst for hydroaminomethylation



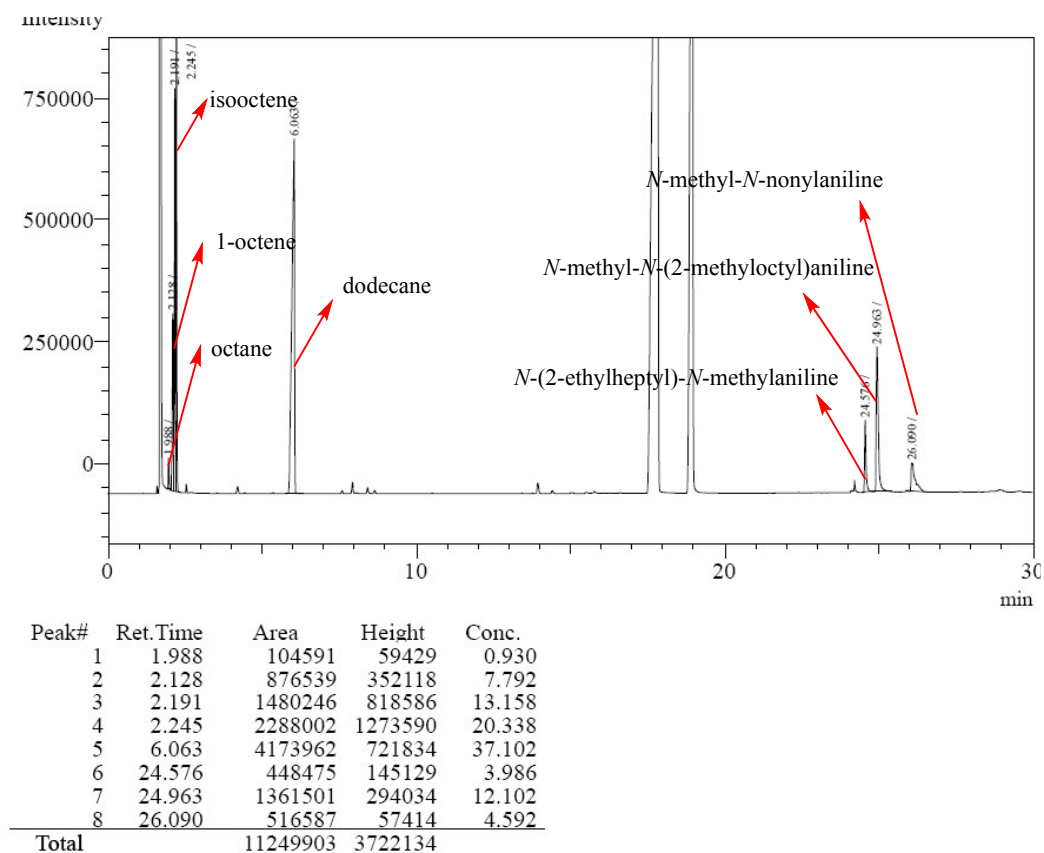
S. Fig. 4 The recycling uses of **L6**-based Ir-catalyst for hydroaminomethylation of 1-hexene with *N*-methylaniline in CO/H₂O

9. Gas-chromatographic data

The standard GC data of 1-hexene



The standard GC data of 2-octene

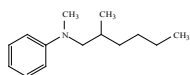
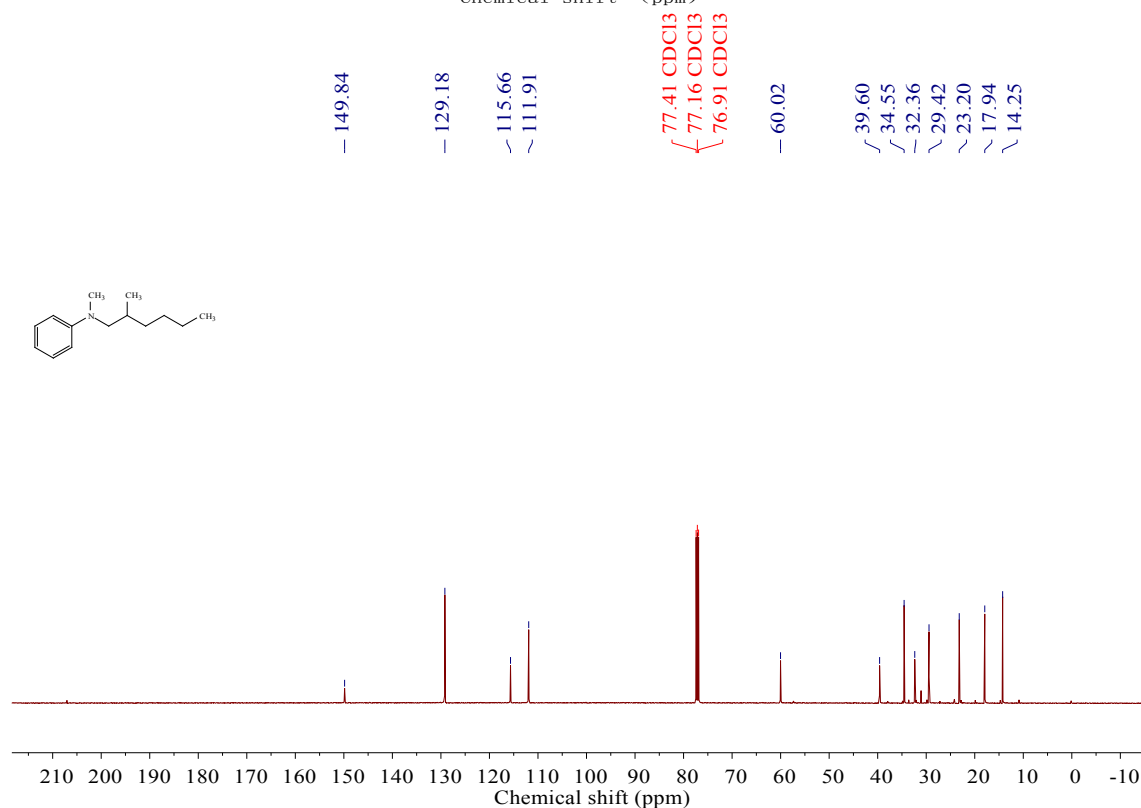
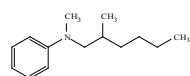
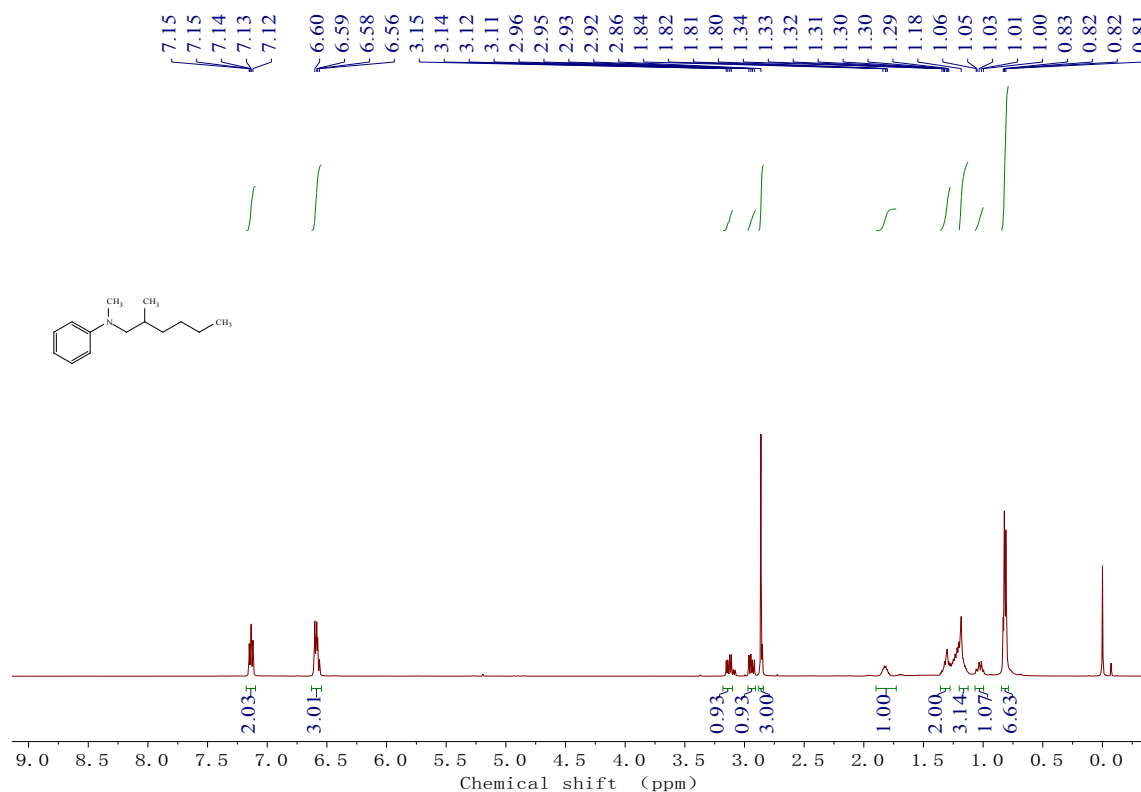


10. $^1\text{H}/^{13}\text{C}$ NMR spectra for the products in S. Table 2

1-1-*N*-methyl-*N*-(2-methylhexyl)aniline

^1H NMR (500 MHz, CDCl_3): δ = 7.15-7.12 (m, 2H, C_6H_2), 6.60-6.39 (m, 3H, C_6H_3), 3.15-3.11 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 2.96-2.92 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 2.86 (m, 3H, PhNCH_3), 1.85-1.80 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CH}$), 1.35-1.29 (m, 2H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2$), 1.22-1.18 (m, 3H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}$), 1.06-1.00 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}$), 0.83-0.81 (m, 6H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

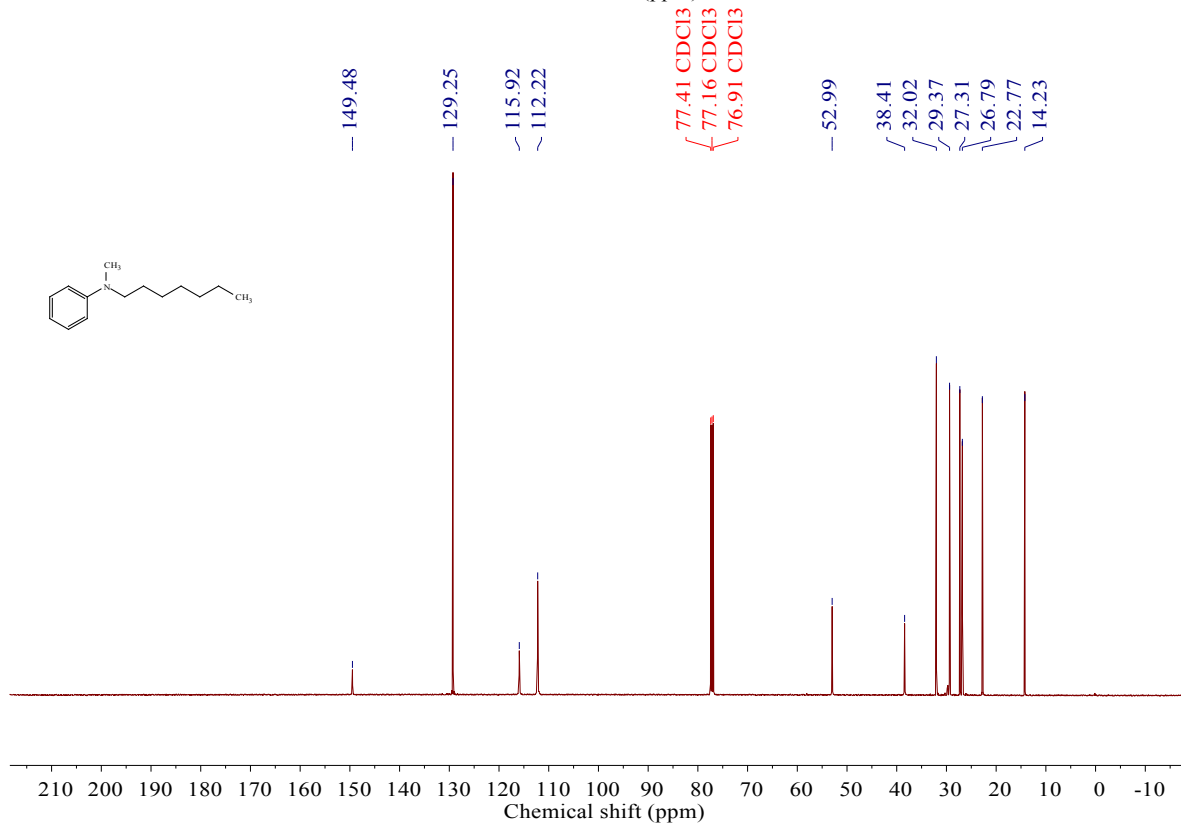
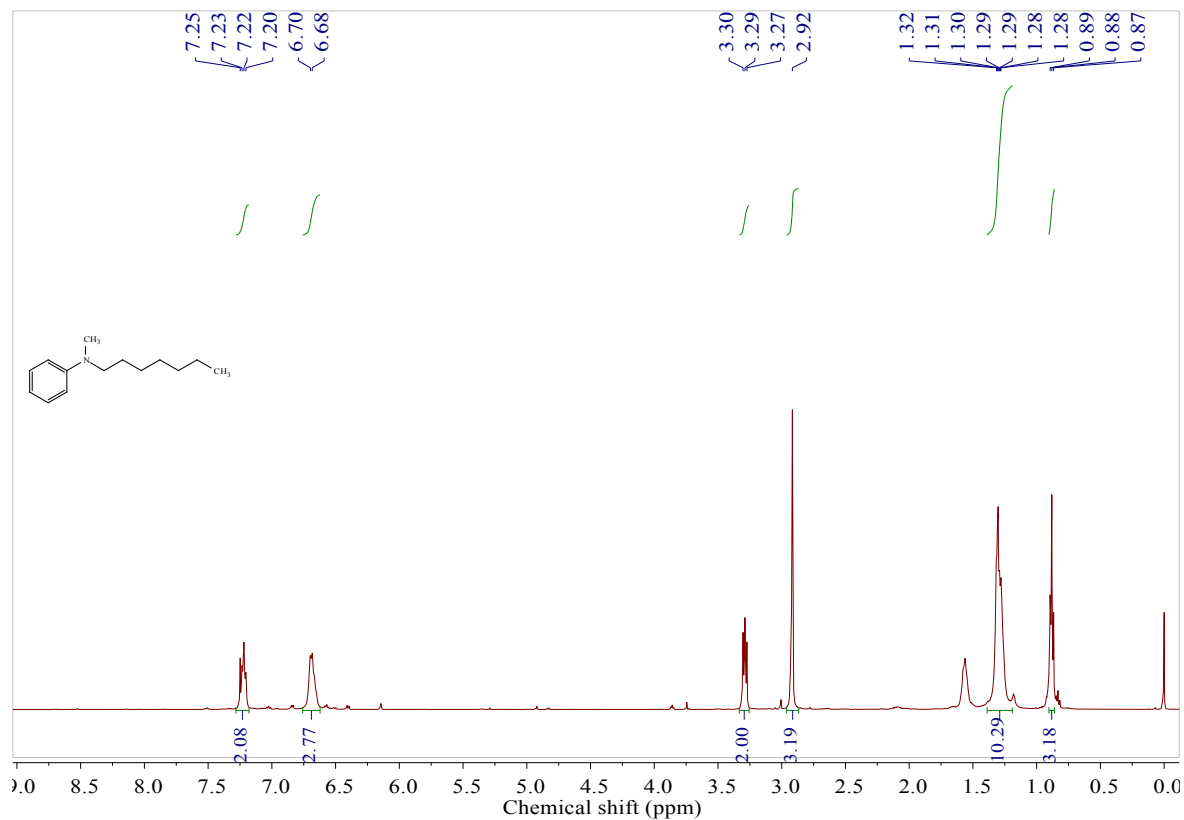
^{13}C NMR (126 MHz, CDCl_3) δ = 149.84, 129.18, 115.66, 111.91, 60.02, 39.60, 34.55, 32.36, 29.42, 23.20, 17.94, 14.25.



1-2. *N*-heptyl-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3): δ = 7.25-7.20 (m, 2H, C_6H_2), 6.70-6.68 (m, 3H, C_6H_3), 3.30-3.27 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.86 (m, 3H, PhNCH_3), 1.30-1.28 (m, 10H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89-0.87 (t, 3H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

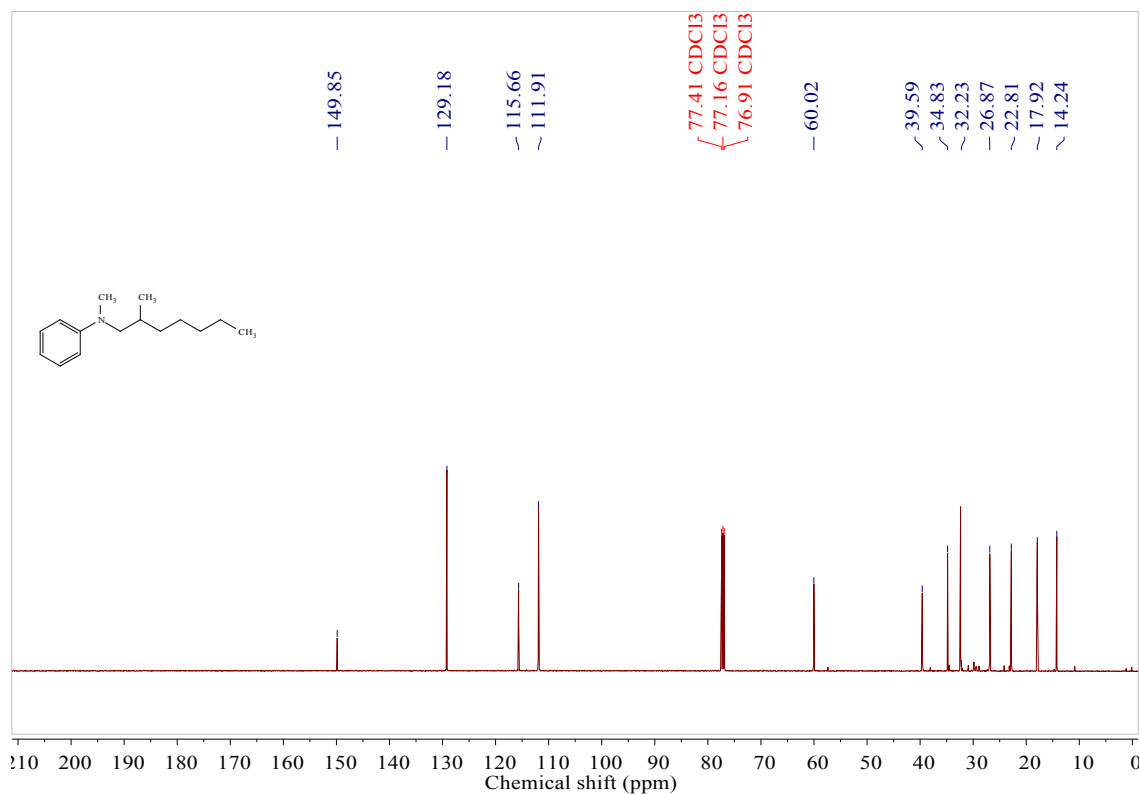
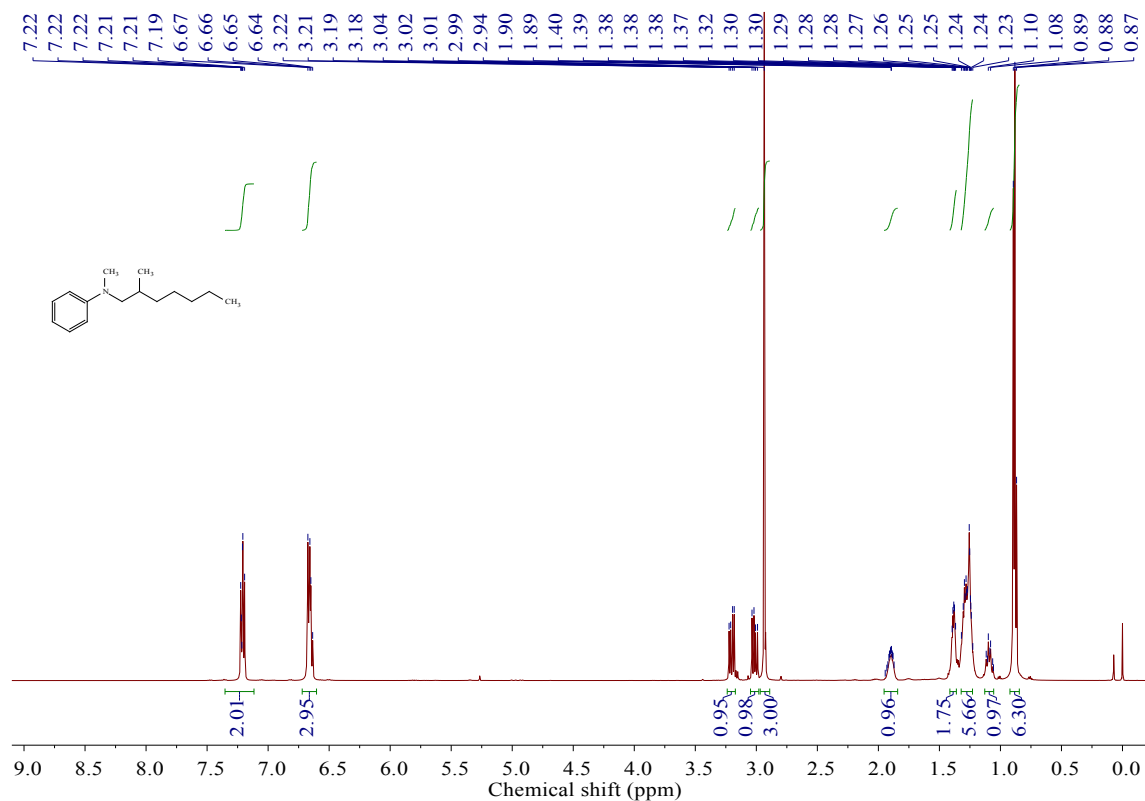
^{13}C NMR (126 MHz, CDCl_3) δ = 149.48, 129.25, 115.92, 112.22, 52.99, 38.41, 32.02, 29.37, 27.31, 26.79, 22.77, 14.23.



2-1. *N*-methyl-*N*-(2-methylheptyl)aniline

^1H NMR (500 MHz, CDCl_3): δ = 7.22-7.19 (m, 2H, C_6H_2), 6.67-6.64 (m, 3H, C_6H_3), 3.22-3.18 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 3.04-2.99 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 2.94 (m, 3H, PhNCH_3), 1.91-1.87 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CH}$), 1.40-1.37 (m, 2H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2$), 1.28-1.26 (m, 5H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$), 1.12-1.06 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}$), 0.89-0.87 (t, 6H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

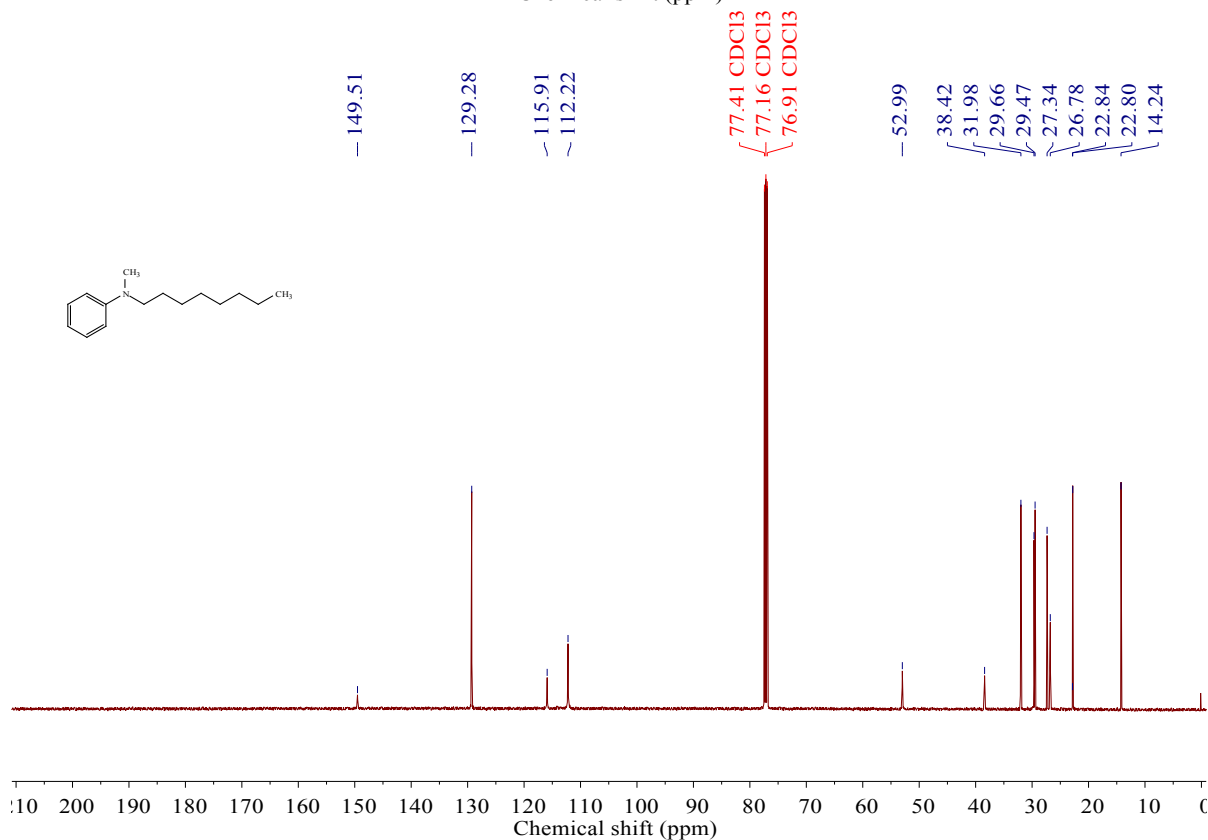
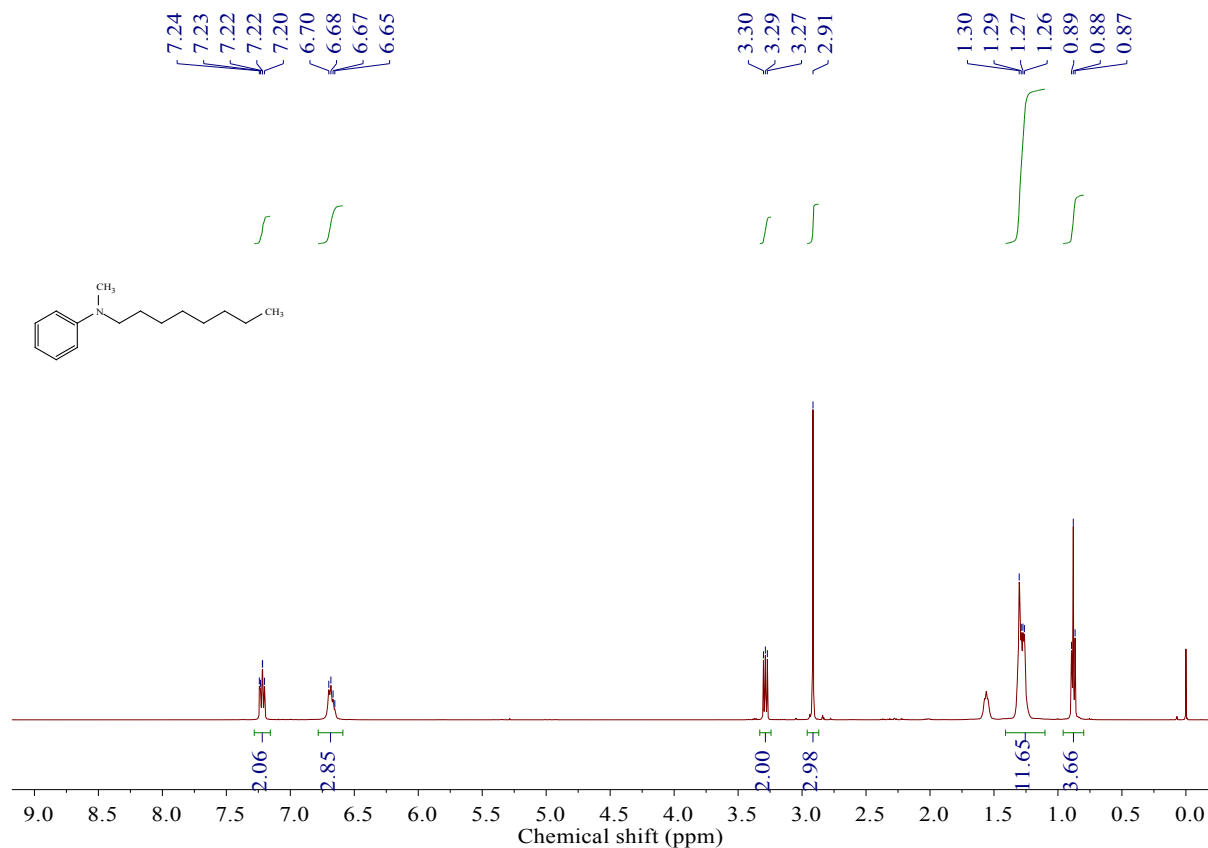
^{13}C NMR (126 MHz, CDCl_3) δ = 149.85, 129.18, 115.66, 111.91, 60.02, 39.59, 34.83, 32.23, 26.87, 22.81, 17.92, 14.24.



2-2. *N*-methyl-*N*-octylaniline

^1H NMR (500 MHz, CDCl_3): δ = 7.24-7.20 (m, 2H, C_6H_2), 6.70-6.65 (m, 3H, C_6H_3), 3.30-3.27 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.91 (m, 3H, PhNCH_3), 1.30-1.26 (m, 12H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.89-0.87 (t, 3H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

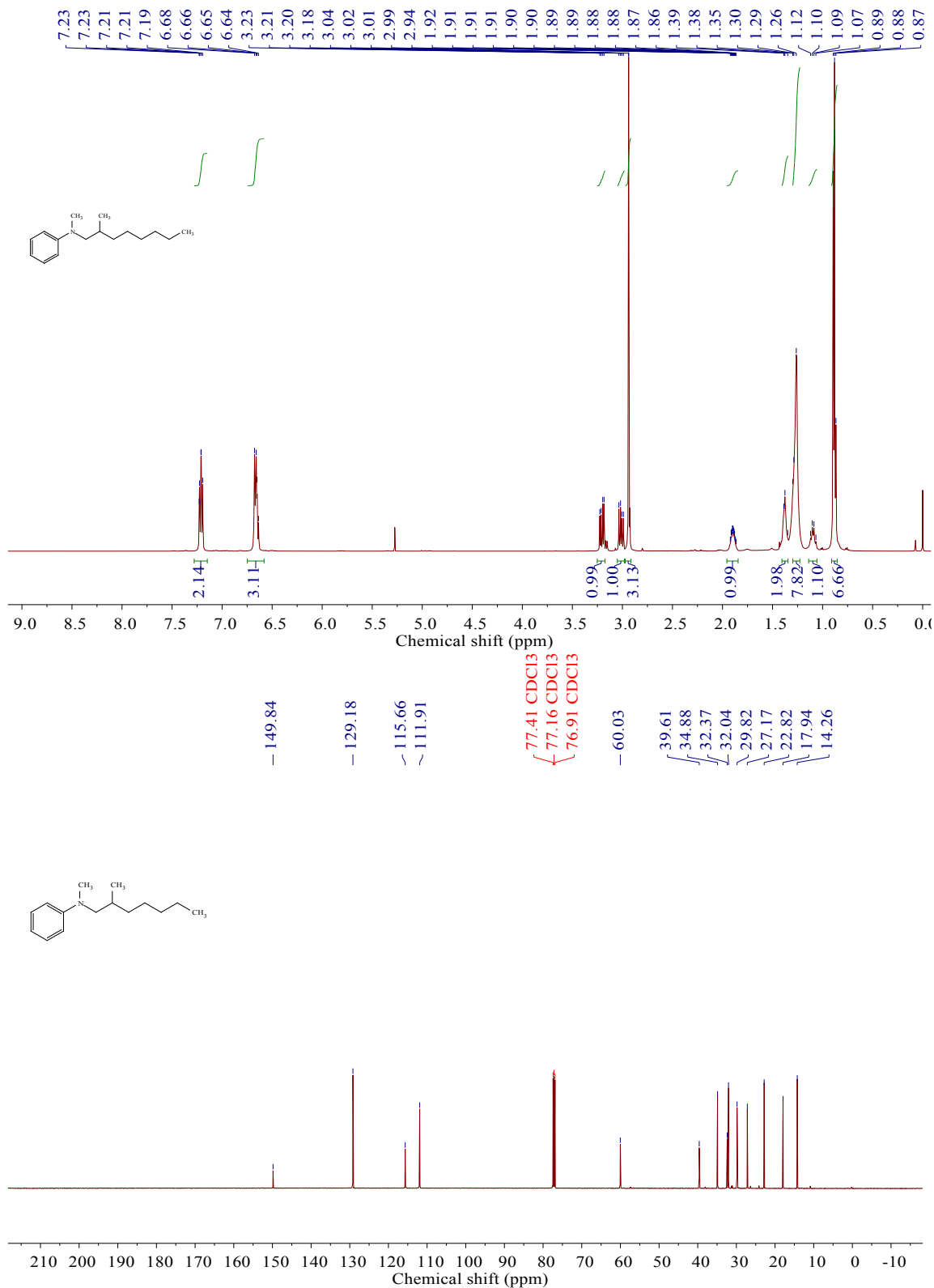
^{13}C NMR (126 MHz, CDCl_3) δ = 149.51, 129.28, 115.91, 112.22, 52.99, 38.42, 31.98, 29.66, 29.47, 27.34, 26.78, 22.84, 22.80, 14.24.



3-1. *N*-methyl-*N*-(2-methyloctyl)aniline

^1H NMR (500 MHz, CDCl_3): δ = 7.23-7.19 (m, 2H, C_6H_2), 6.68-6.64 (m, 3H, C_6H_3), 3.23-3.18 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 3.04-2.99 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 2.94 (m, 3H, PhNCH_3), 1.92-1.85 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CH}$), 1.39-1.35 (m, 2H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2$), 1.30-1.26 (m, 7H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$), 1.12-1.07 (m, 1H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$), 0.89-0.87 (t, 6H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

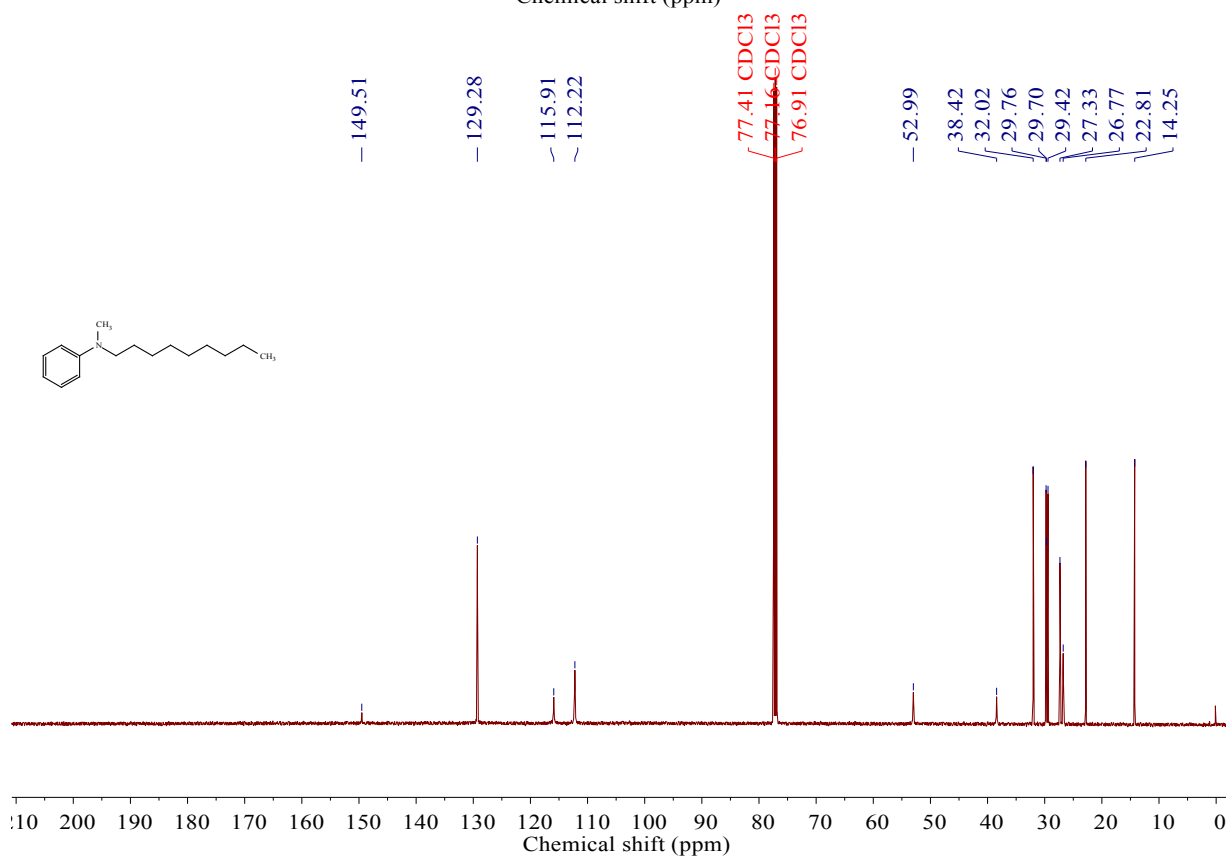
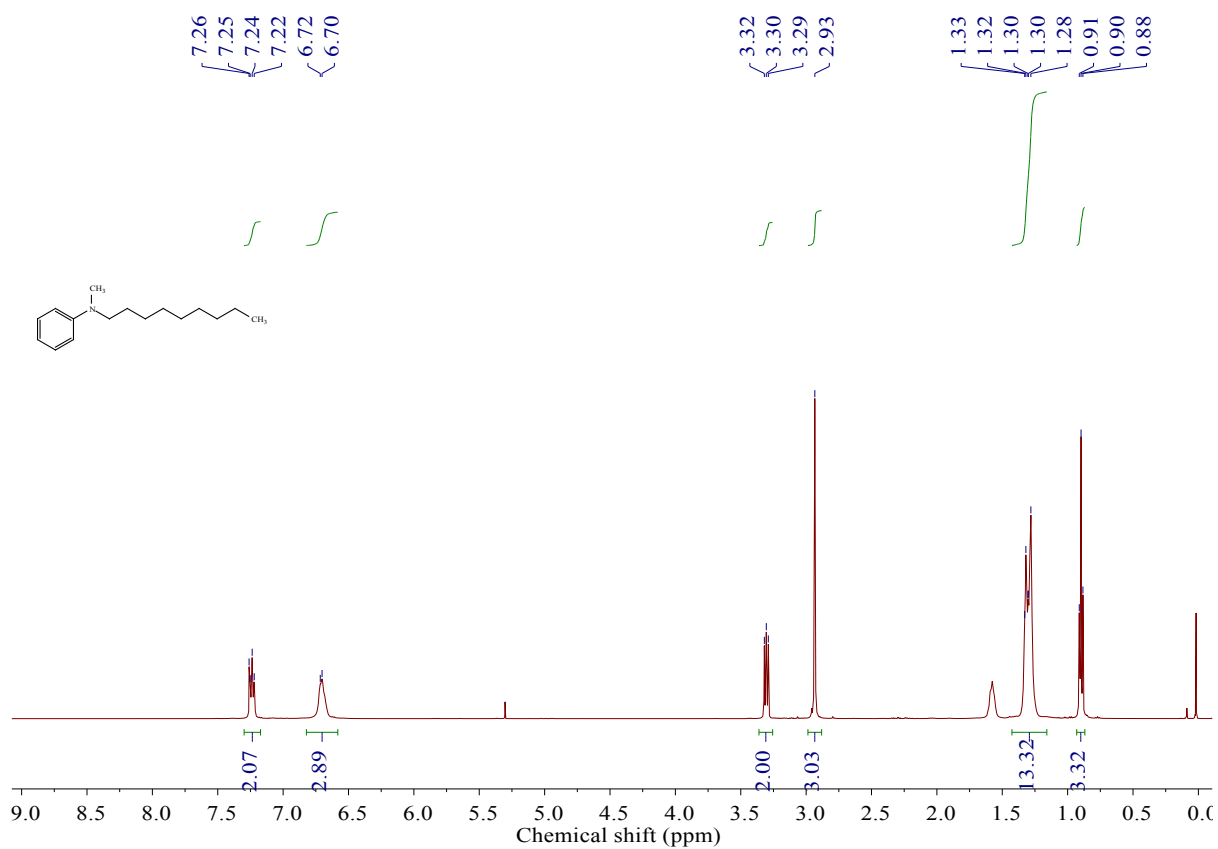
^{13}C NMR (126 MHz, CDCl_3) δ = 149.84, 129.18, 115.66, 111.91, 60.03, 39.61, 34.88, 32.37, 32.04, 29.82, 27.17, 22.82, 17.94, 14.26.



3-2. *N*-methyl-*N*-nonylaniline

^1H NMR (500 MHz, CDCl_3): δ = 7.25-7.22 (t, 2H, C_6H_2), 6.72-6.70 (d, 3H, C_6H_3), 3.32-3.29 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.93 (m, 3H, PhNCH_3), 1.33-1.28 (m, 14H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.91-0.88 (t, 3H, $\text{PhNCH}_2\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

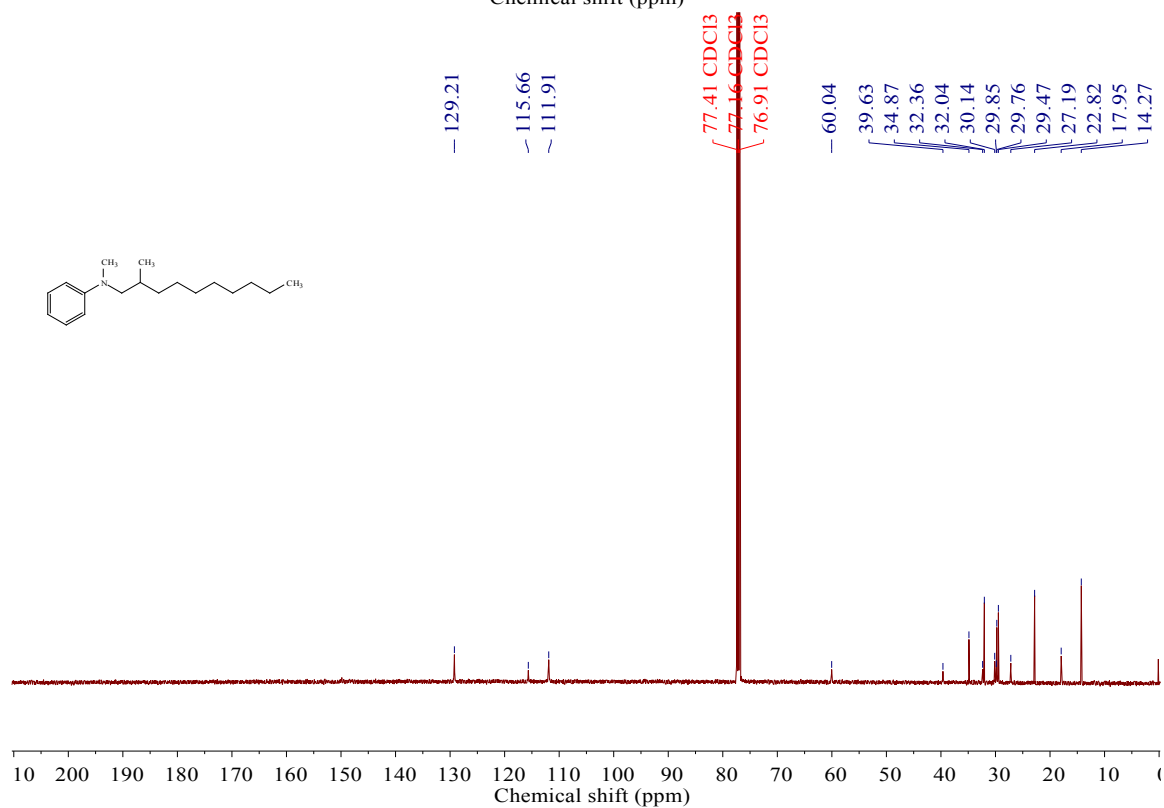
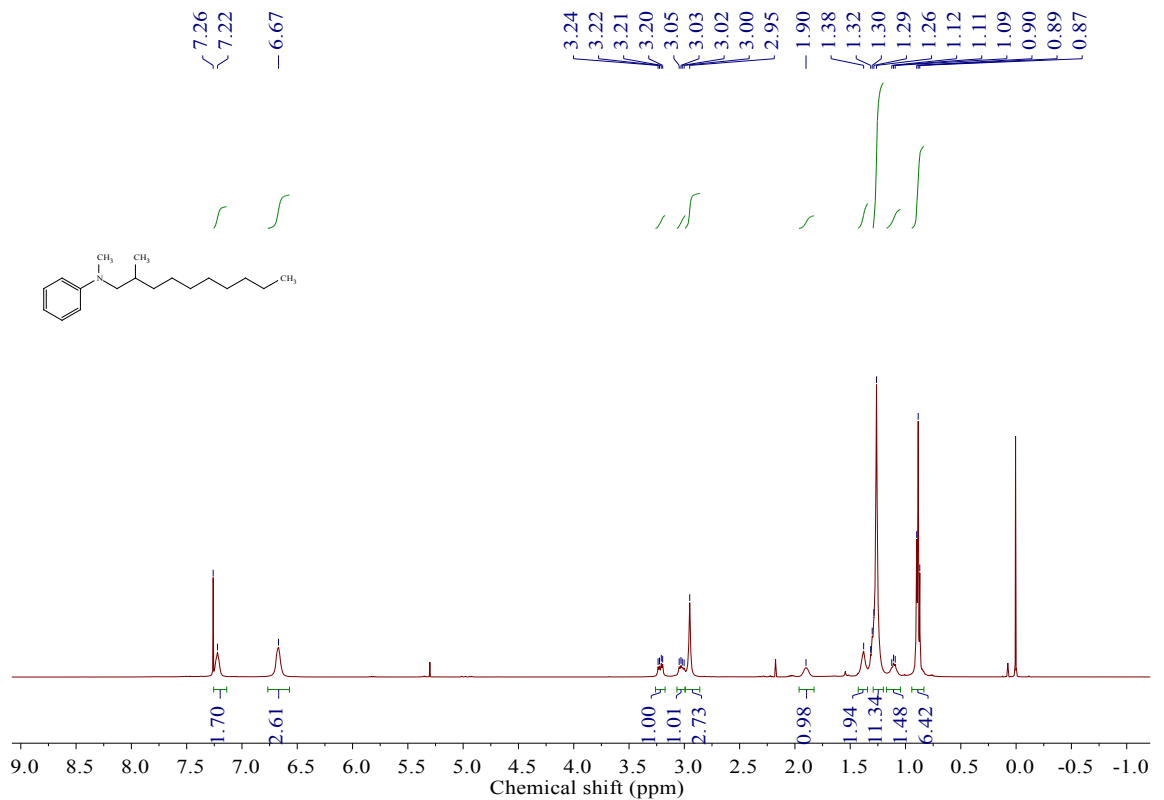
^{13}C NMR (126 MHz, CDCl_3) δ = 149.51, 129.28, 115.91, 112.22, 52.99, 38.42, 32.02, 29.76, 29.70, 29.42, 27.33, 26.77, 22.81, 14.25.



4-1. *N*-methyl-*N*-(2-methyldecyl)aniline

^1H NMR (500 MHz, CDCl_3): δ = 7.22 (s, 2H, C_6H_2), 6.67 (s, 3H, C_6H_3), 3.24-3.20 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 3.05-3.00 (q, 1H, J = 5.0 Hz, PhNCHCH_3), 2.95 (m, 3H, PhNCH_3), 1.90 (s, 1H, $\text{PhNCH}_2\text{CH}_3\text{CH}$), 1.38 (s, 2H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2$), 1.32-1.26 (q, 11H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$), 1.12-1.09 (t, 1H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}$), 0.90-0.87 (t, 6H, $\text{PhNCH}_2\text{CH}_3\text{CHCH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$).

^{13}C NMR (126 MHz, CDCl_3) δ = 129.21, 115.66, 111.91, 77.41, 77.16, 76.91, 60.04, 39.63, 34.87, 32.36, 32.04, 30.15, 29.85, 29.76, 29.47, 27.19, 22.83, 17.95, 14.27.



[illegible]

Chemical structure of 1-phenylundecane: CCCCCCCCCCC[C@H](C)c1ccccc1

¹H NMR spectrum (400 MHz, CDCl₃) showing peaks from 0.8 to 7.3 ppm. The spectrum includes integration values and chemical shift labels.

Chemical shift (ppm): 7.26, 7.23, 6.69, 3.31, 3.30, 3.28, 2.93, 1.57, 1.31, 1.30, 1.29, 1.27, 0.90, 0.89, 0.87.

Integration values: 2.02, 2.86, 2.00, 3.00, 1.99, 17.94, 3.32.



[illegible]

The figure displays the ^1H and ^{13}C NMR spectra of N-methyl-N-undecylbenzylamine, with the chemical structure shown in the top left corner.

^1H NMR Spectrum (Top):

- Chemical Shift (ppm):** 9.0 to 0.0.
- Integration:** 2.11, 2.96, 2.06, 3.00, 21.52, 3.27.
- Peak Labels:** 7.26, 7.24, 7.23, 7.21, 6.71, 6.69, 6.68, 6.66, 3.31, 3.30, 3.28, 2.93, 1.31, 1.30, 1.30, 1.27, 0.91, 0.89, 0.88.

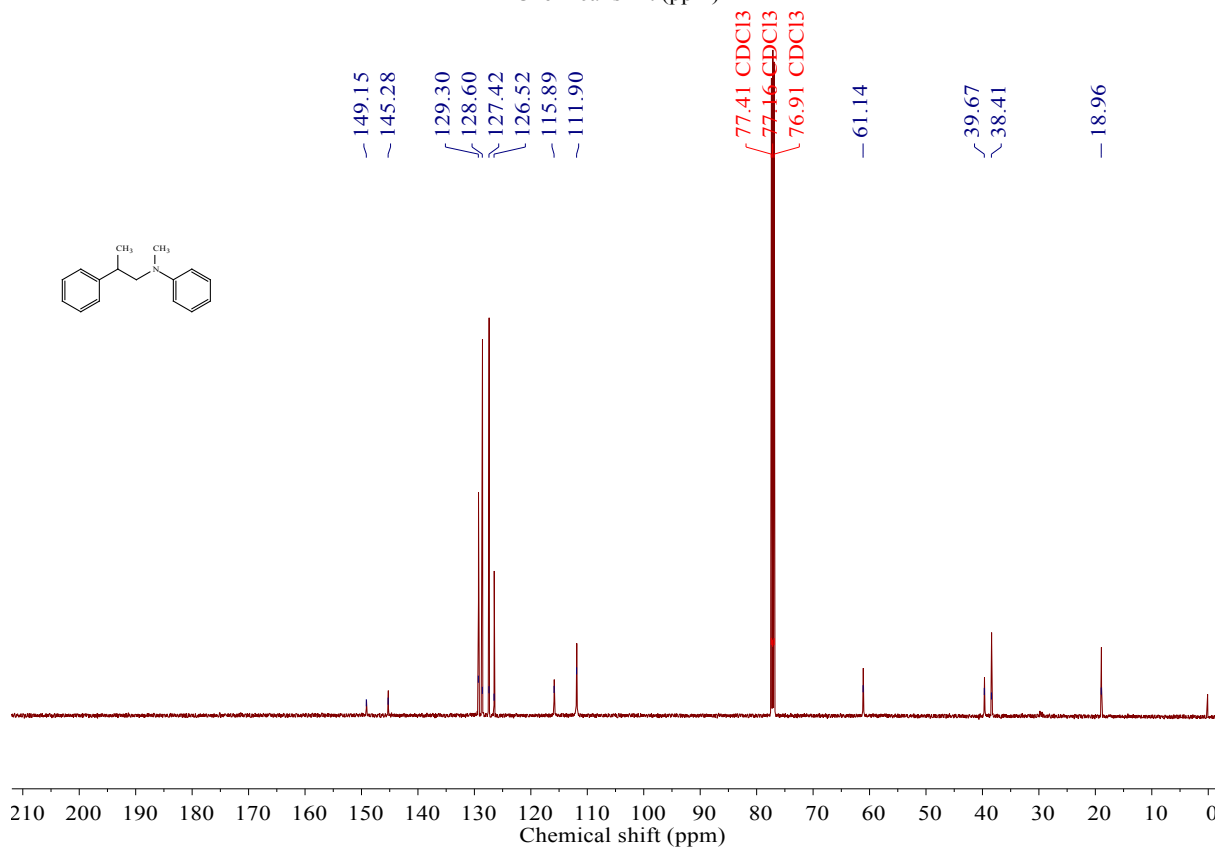
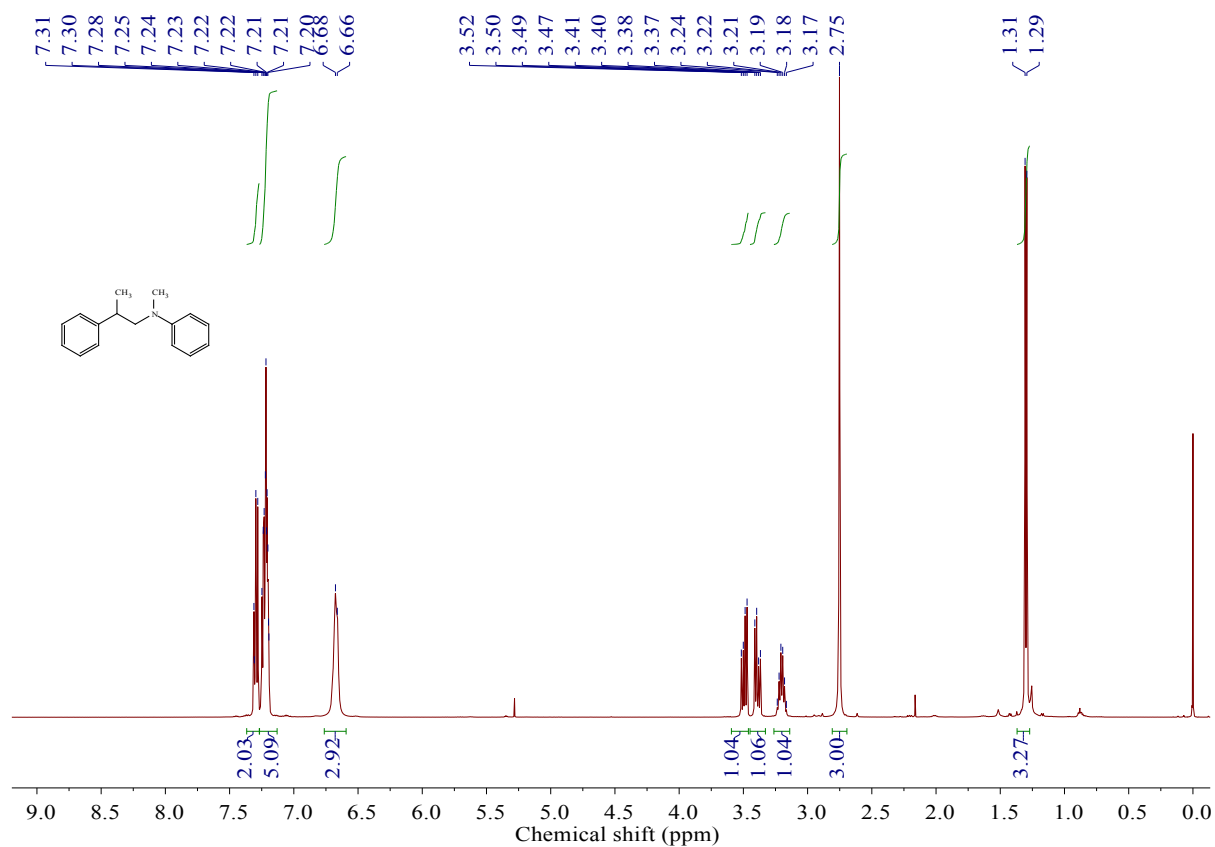
^{13}C NMR Spectrum (Bottom):

- Chemical Shift (ppm):** 210 to 0.
- Peak Labels:** 149.52, 129.26, 115.90, 112.21, 77.41 CDCl₃, 77.16 CDCl₃, 76.90 CDCl₃, 52.98, 38.40, 32.07, 29.82, 29.80, 29.76, 29.71, 29.51, 27.34, 26.79, 22.84, 14.27.

6-1. *N*-methyl-*N*-(2-phenylpropyl)aniline

^1H NMR (500 MHz, CDCl_3) δ = 7.31-7.28 (m, 2H, C_6H_2), 7.25-7.19 (m, 5H, C_6H_5), 6.68-6.66 (m, 3H, C_6H_3), 3.52-3.47 (dd, 1H, PhNCHCH_3), 3.41-3.37 (dd, 1H, PhNCHCH_3), 3.24-3.17 (m, 1H, PhCHCH_3), 2.75 (s, 3H, PhNCHCH_3), 1.31-1.29 (d, 3H, PhCHCH_3).

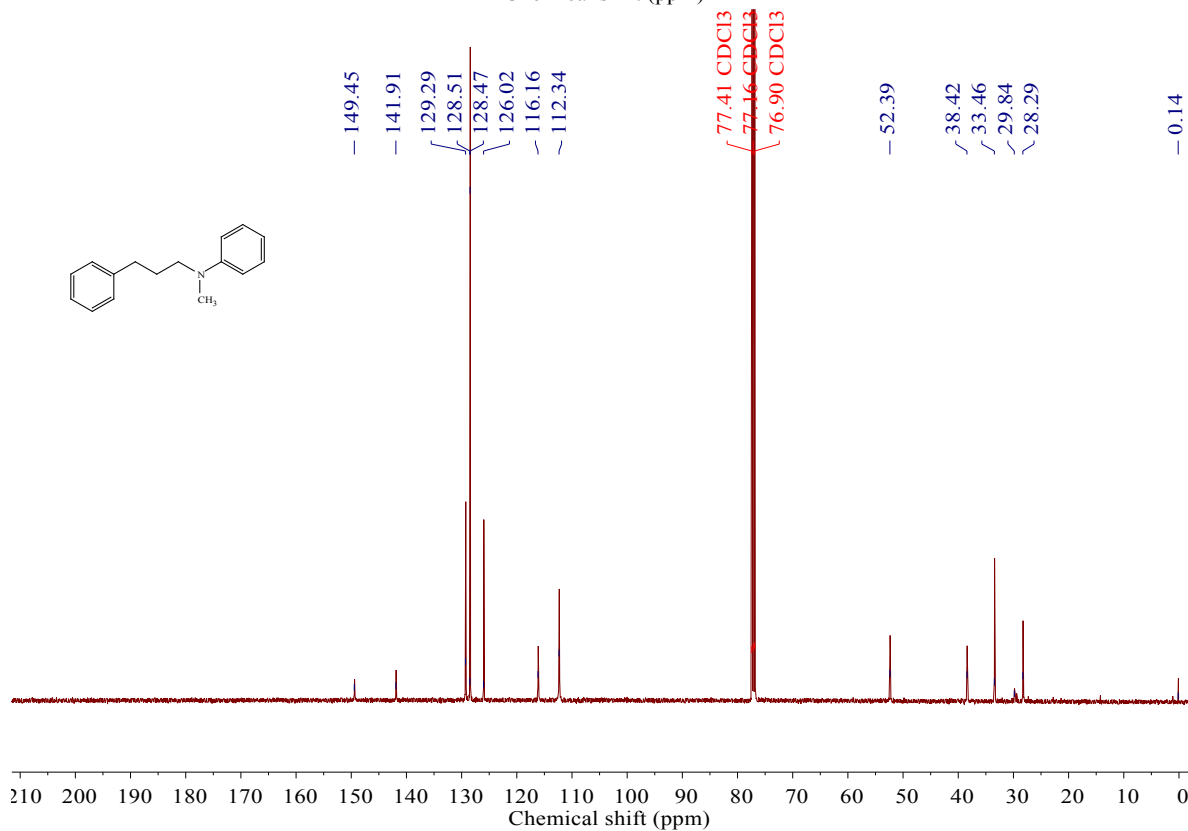
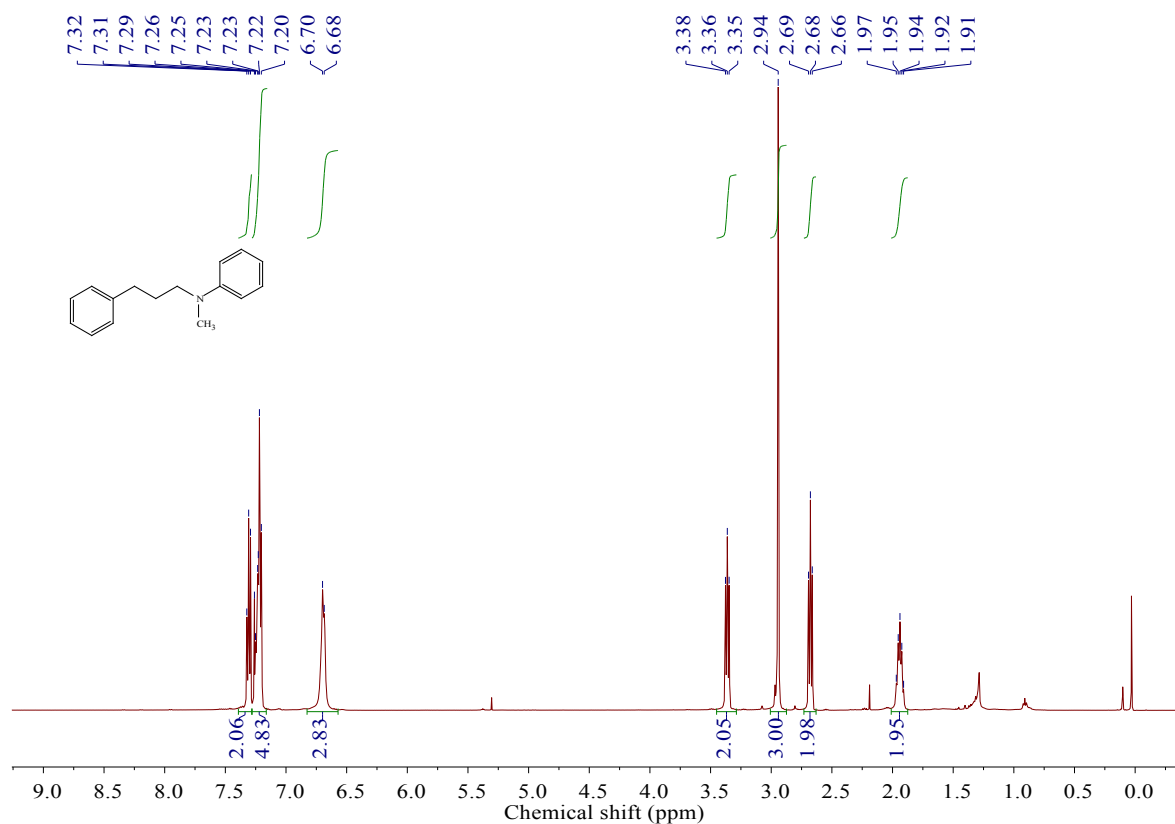
^{13}C NMR (126 MHz, CDCl_3) δ = 149.15, 145.28, 129.30, 128.60, 127.42, 126.52, 115.89, 111.90, 61.14, 39.67, 38.41, 18.96.



6-2. *N*-methyl-*N*-(3-phenylpropyl)aniline

^1H NMR (500 MHz, CDCl_3) δ = 7.32-7.29 (m, 2H, C_6H_2), 7.26-7.20 (m, 5H, C_6H_5), 6.70-6.68 (m, 3H, C_6H_3), 3.38-3.35 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.94 (s, 3H, PhNCHCH_3), 2.69-2.66 (t, 2H, PhCH_2), 1.97-1.91 (m, 2H, PhCH_2CH_2).

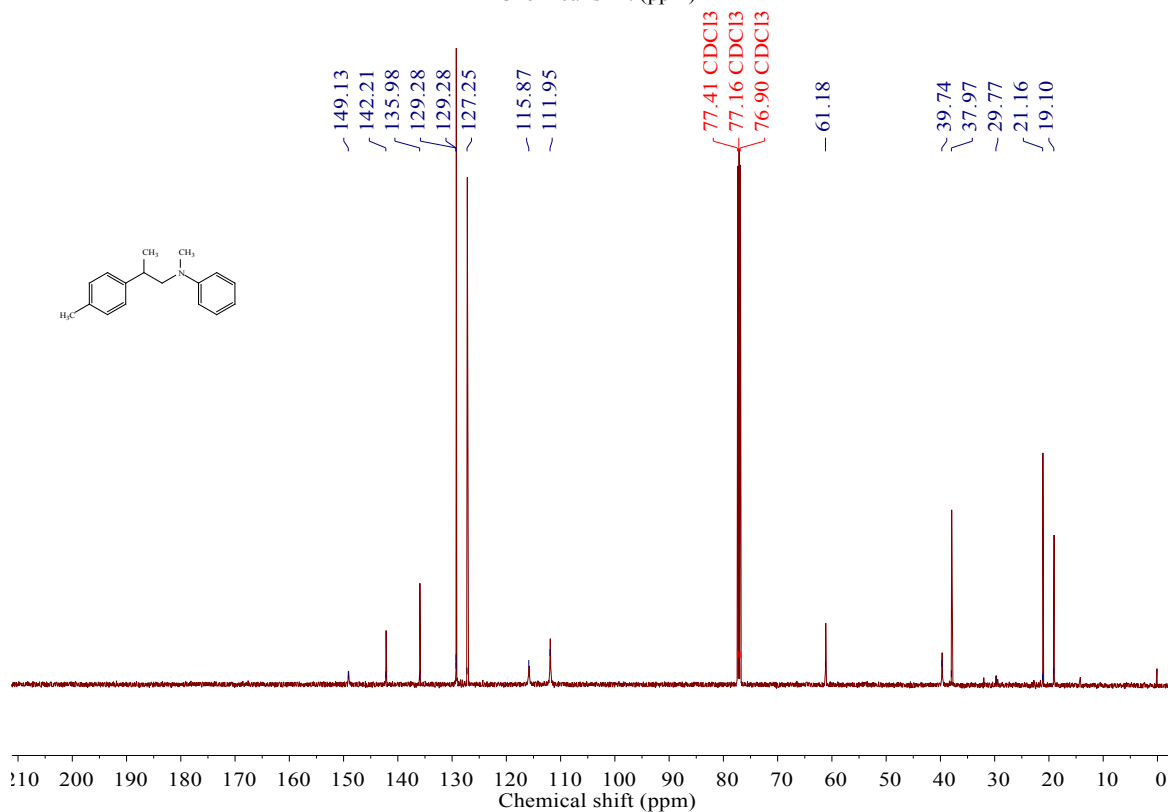
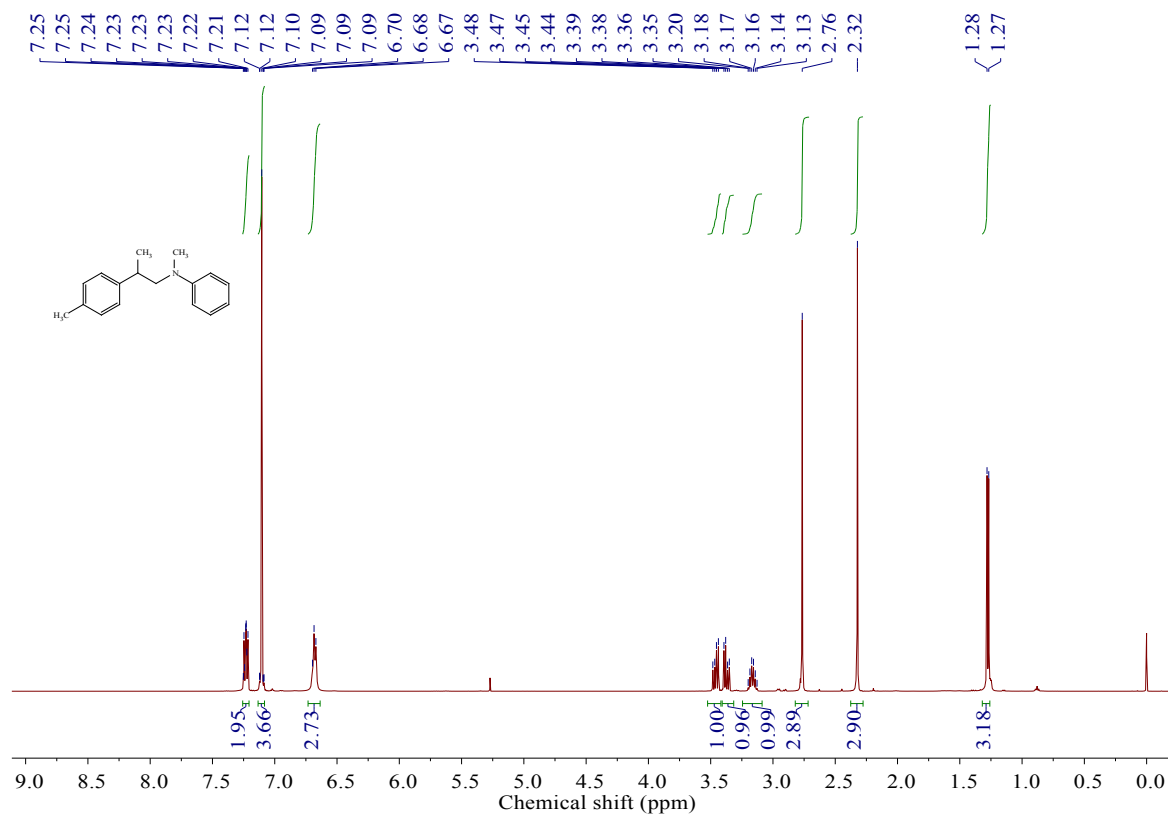
^{13}C NMR (126 MHz, CDCl_3) δ = 149.45, 141.91, 129.29, 128.51, 128.47, 126.02, 116.16, 112.34, 52.39, 38.42, 33.46, 29.84, 28.29, 0.14.



7-1. *N*-methyl-*N*-(2-(*p*-tolyl)propyl)aniline

^1H NMR (500 MHz, CDCl_3) δ = 7.25-7.21 (m, 2H, C_6H_2), 7.12-7.09 (m, 4H, C_6H_4), 6.70-6.67 (m, 3H, C_6H_3), 3.48-3.44 (dd, 1H, PhNCHCH_3), 3.39-3.35 (dd, 1H, PhNCHCH_3), 3.20-3.14 (m, 1H, $p\text{-CH}_3\text{PhCHCH}_3$), 2.76 (s, 3H, PhNCHCH_3), 1.28-1.27 (d, 3H, $p\text{-CH}_3\text{PhCHCH}_3$).

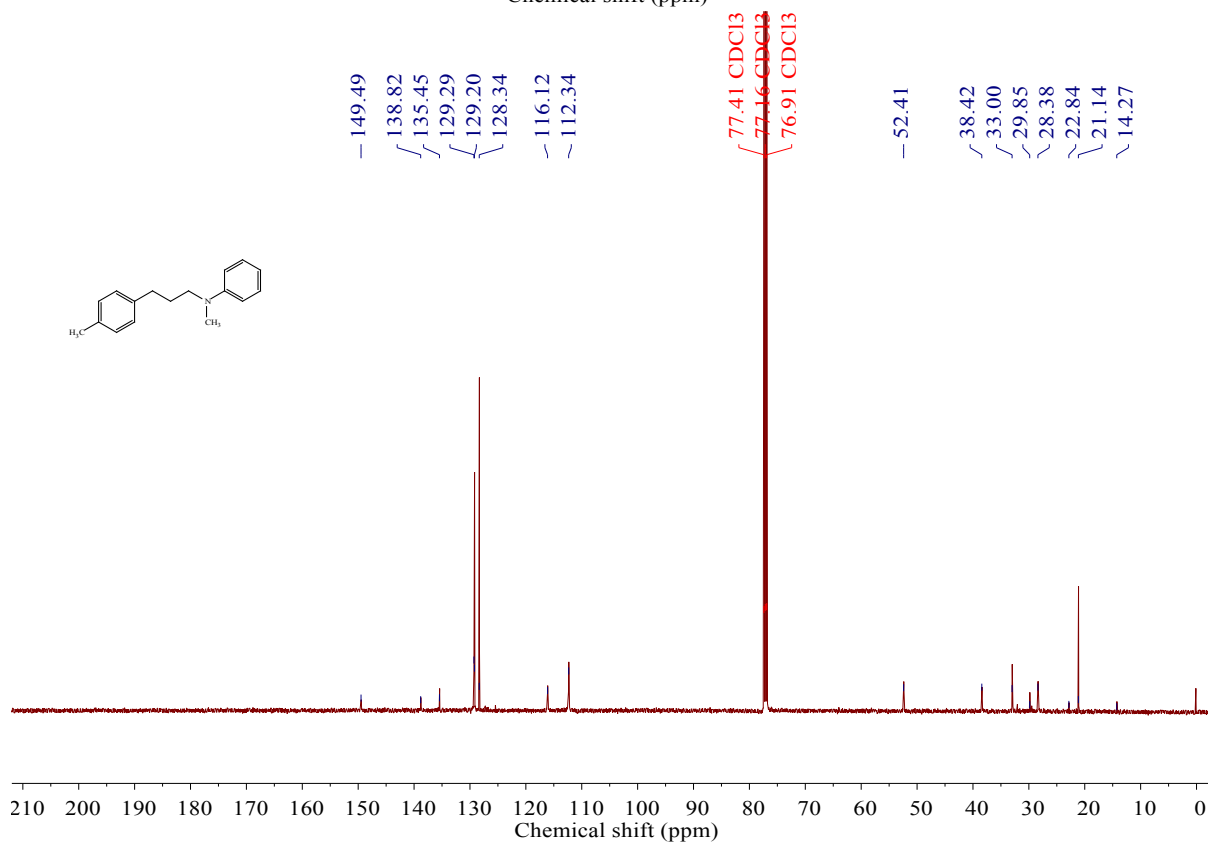
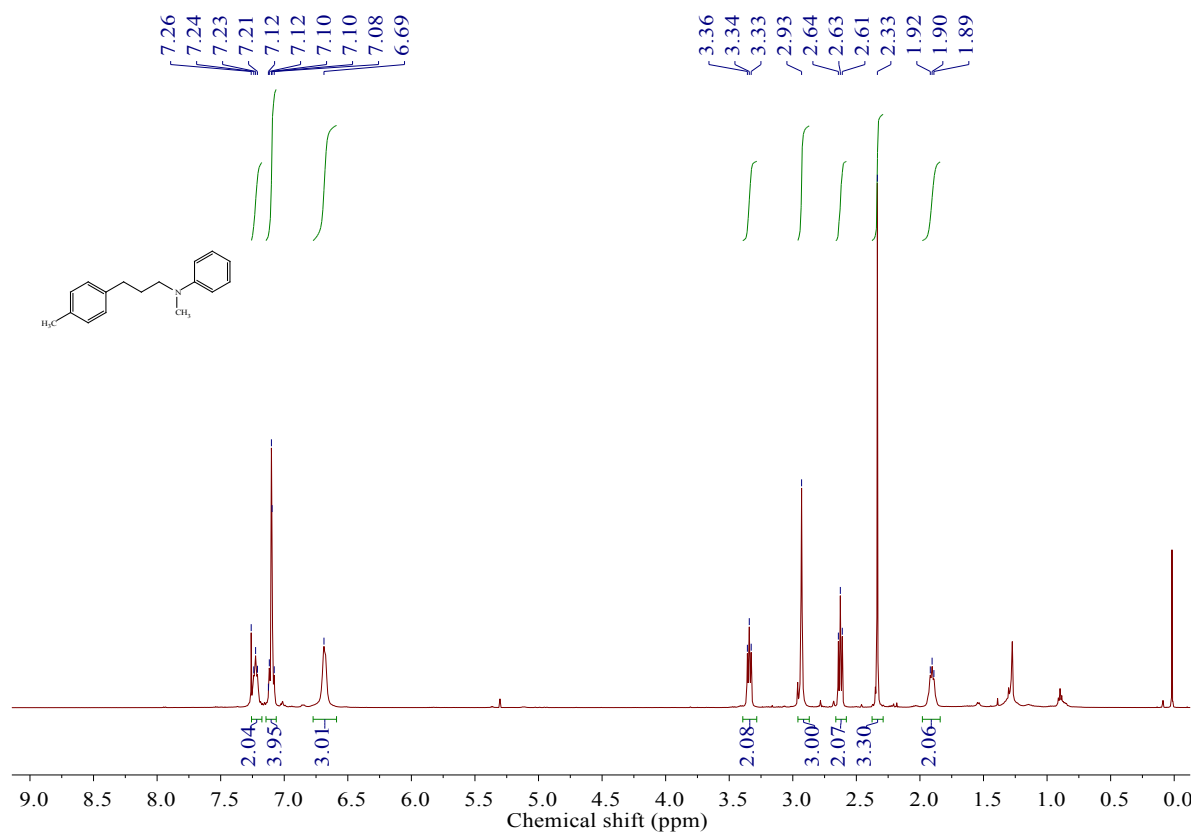
^{13}C NMR (126 MHz, CDCl_3) δ = 149.13, 142.21, 135.98, 129.28, 129.28, 127.25, 115.87, 111.95, 61.18, 39.74, 37.97, 29.77, 21.16, 19.10.



7-2. *N*-methyl-*N*-(3-(*p*-tolyl)propyl)aniline

^1H NMR (500 MHz, CDCl_3) δ = 7.24-7.21 (m, 2H, C_6H_2), 7.12-7.08 (m, 4H, C_6H_4), 6.69 (m, 3H, C_6H_3), 3.36-3.33 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.93 (s, 3H, PhNCHCH_3), 2.64-2.61 (t, 2H, $p\text{-CH}_3\text{PhCH}_2$), 2.33 (s, 3H, $p\text{-CH}_3\text{Ph}$), 1.92-1.89 (m, 2H, $p\text{-CH}_3\text{PhCH}_2\text{CH}_2$).

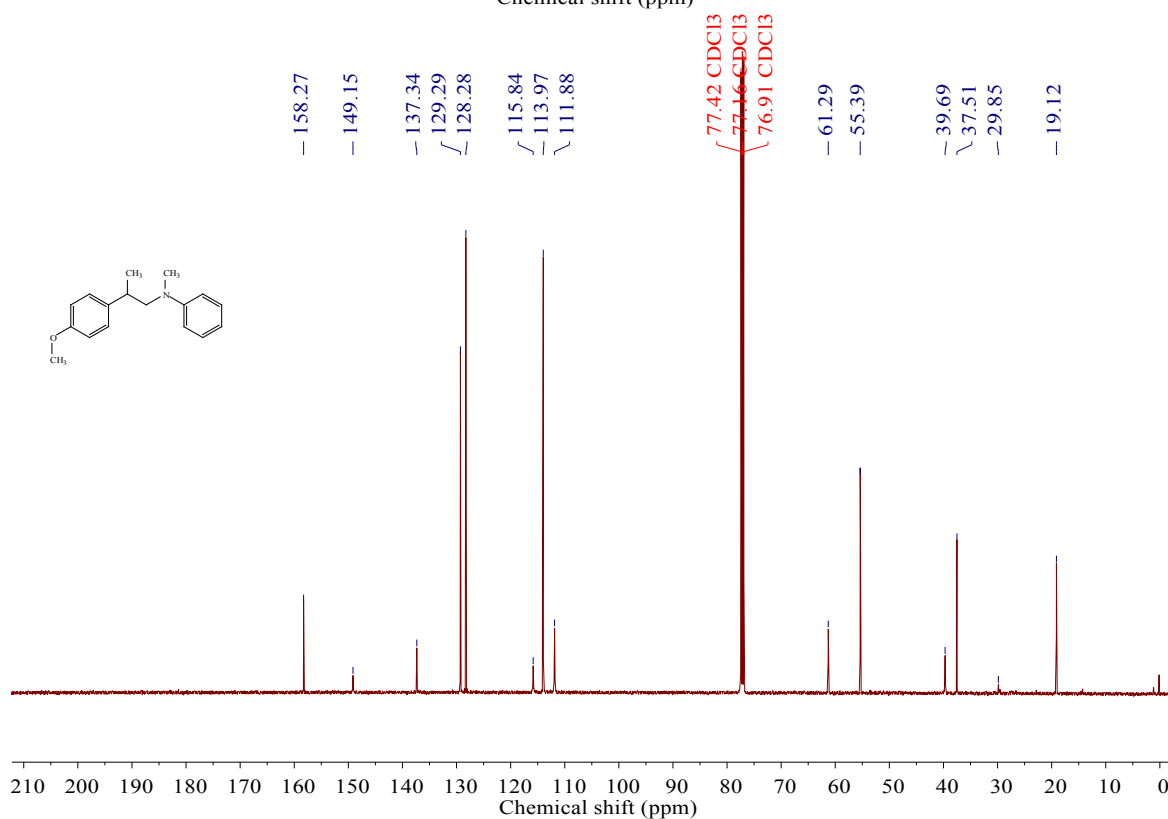
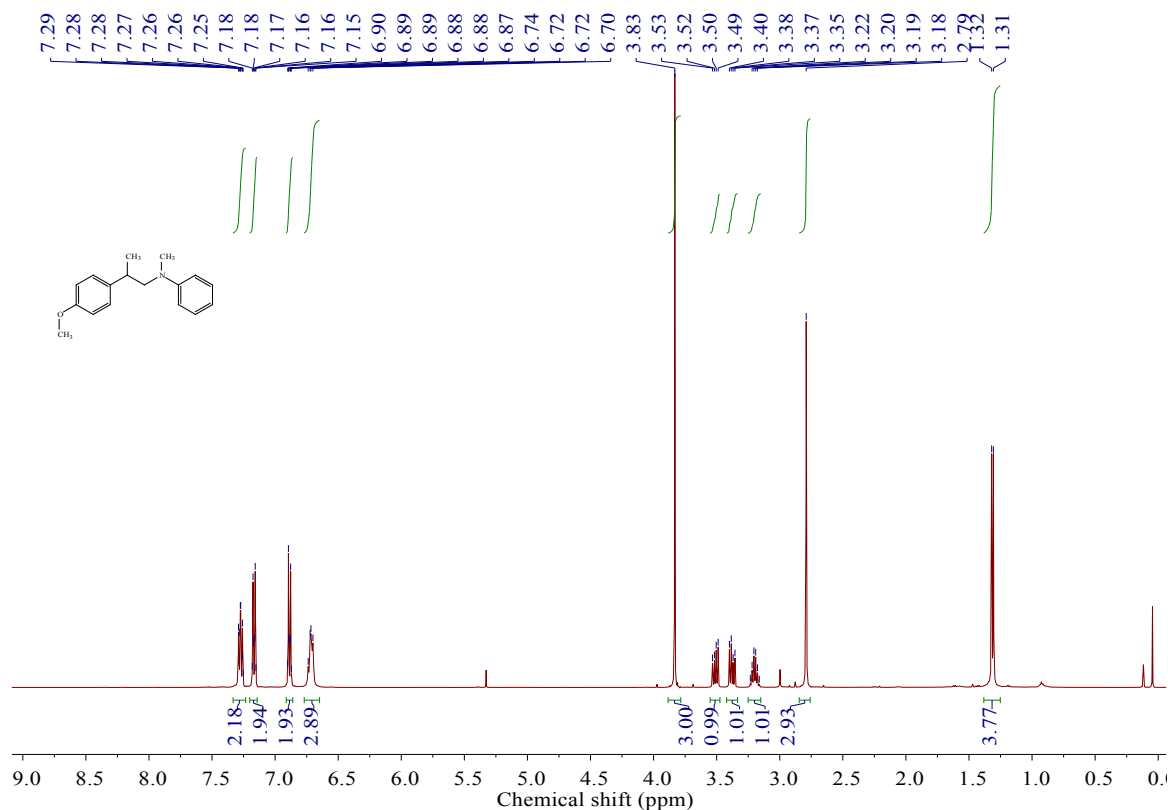
^{13}C NMR (126 MHz, CDCl_3) δ = 149.49, 138.82, 135.45, 129.29, 129.20, 128.34, 116.12, 112.34, 52.41, 38.42, 33.00, 29.85, 28.38, 22.84, 21.14, 14.27.



8-1. *N*-(2-(4-methoxyphenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.29-7.25 (m, 2H, C_6H_2), 7.18-7.15 (m, 2H, C_6H_2), 6.90-6.87 (m, 2H, C_6H_2), 6.74-6.70 (m, 3H, C_6H_3), 3.83 (s, 3H, $p\text{-CH}_3\text{OPh}$), 3.53-3.49 (dd, 1H, PhNCHCH_3), 3.40-3.35 (dd, 1H, PhNCHCH_3), 3.23-3.16 (m, 1H, $p\text{-CH}_3\text{OPhCHCH}_3$), 2.79 (s, 3H, PhNCHCH_3), 1.32-1.31 (d, 3H, $p\text{-CH}_3\text{OPhCHCH}_3$).

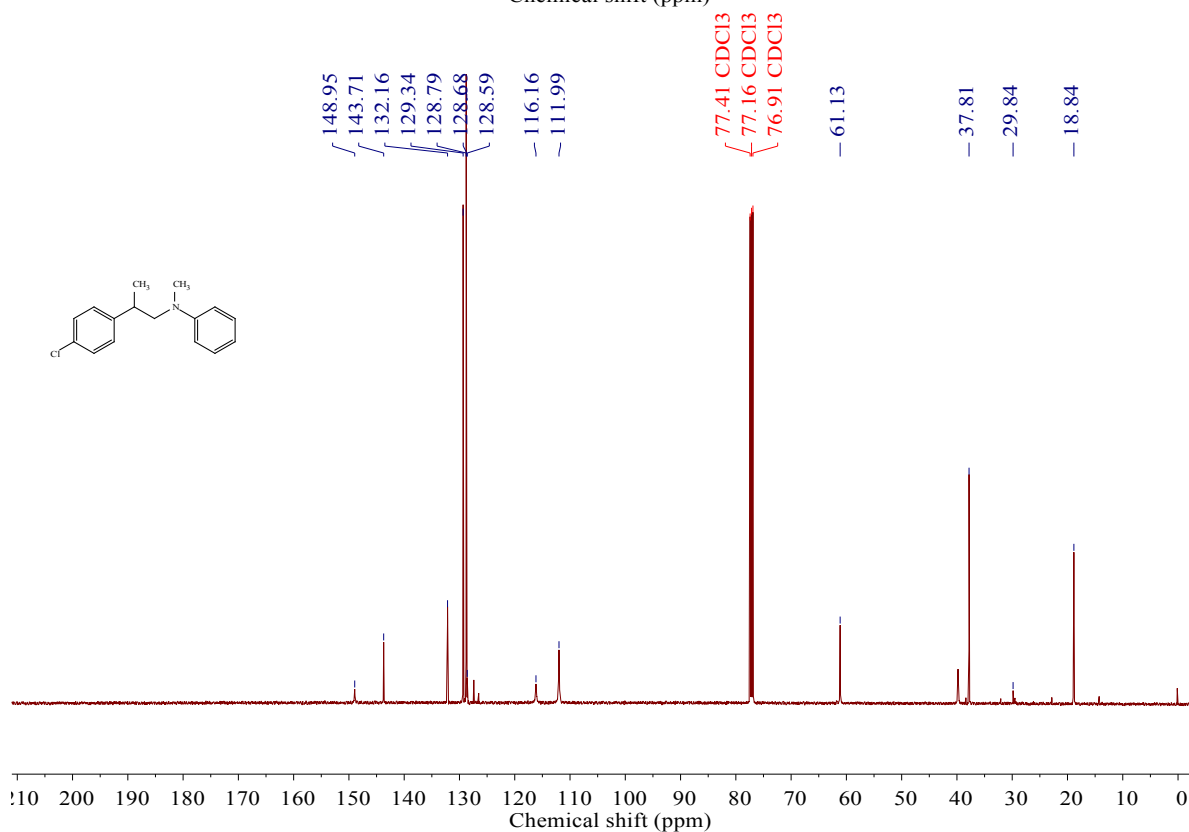
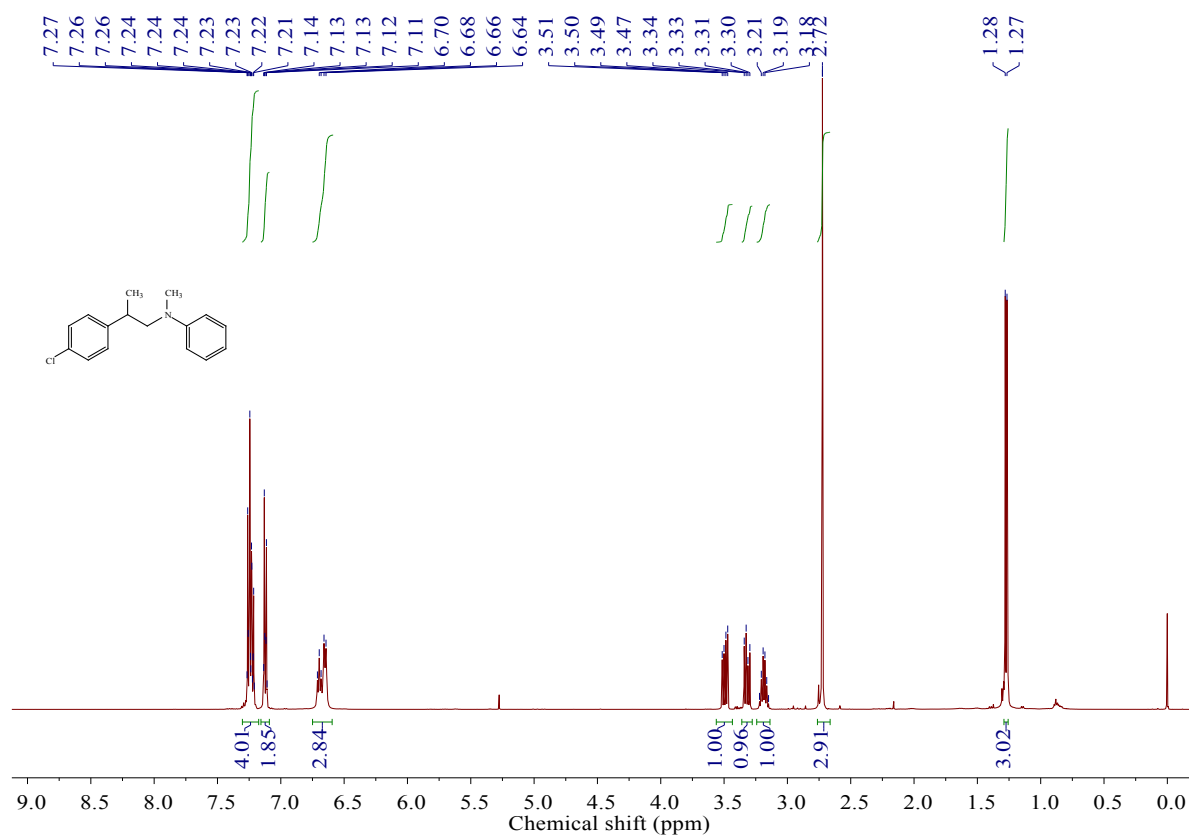
^{13}C NMR (126 MHz, CDCl_3) δ = 158.27, 149.15, 137.34, 129.29, 128.28, 115.84, 113.97, 111.88, 61.29, 55.39, 39.69, 37.51, 29.85, 19.12.



9-1. *N*-(2-(4-chlorophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.27-7.21 (m, 4H, C_6H_4), 7.14-7.11 (m, 2H, C_6H_2), 6.71-6.64 (m, 3H, C_6H_3), 6.74-6.70 (m, 3H, C_6H_3), 3.51-3.47 (dd, 1H, PhNCHCH_3), 3.34-3.30 (dd, 1H, PhNCHCH_3), 3.22-3.15 (m, 1H, $p\text{-ClPhCHCH}_3$), 2.72 (s, 3H, PhNCHCH_3), 1.28-1.27 (d, 3H, $p\text{-ClPhCHCH}_3$).

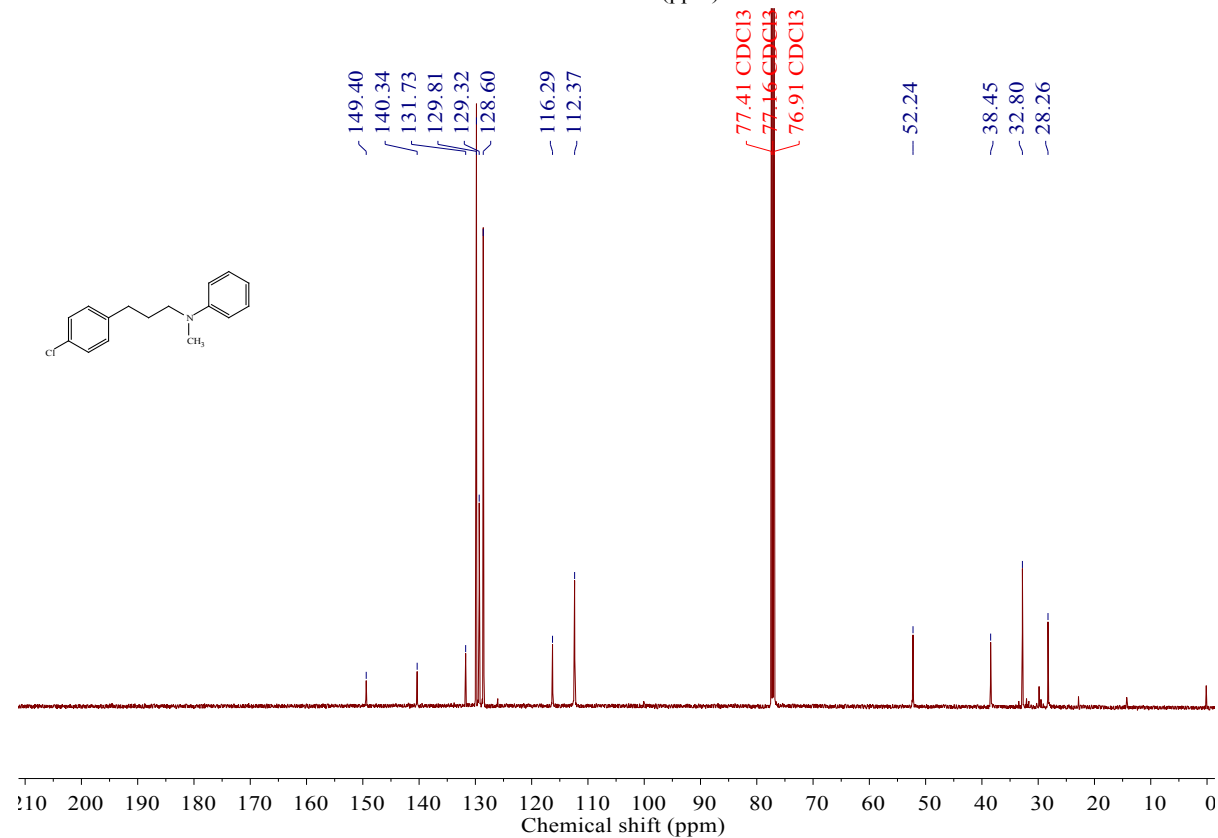
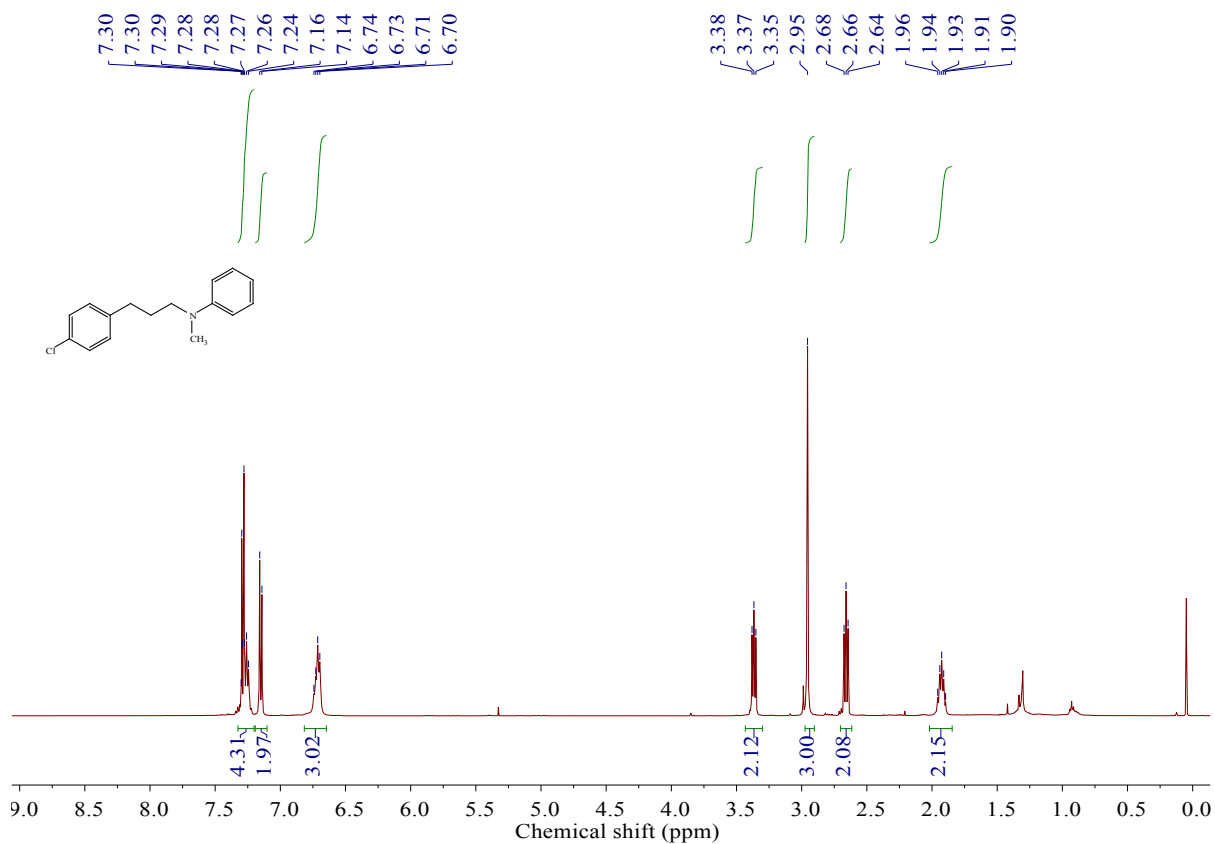
^{13}C NMR (126 MHz, CDCl_3) δ = 148.95, 143.71, 132.16, 129.34, 128.79, 128.68, 128.59, 116.16, 111.99, 61.13, 37.81, 29.84, 18.84.



9-2. *N*-(3-(4-chlorophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.30-7.24 (m, 4H, C_6H_4), 7.16-7.14 (m, 2H, C_6H_2), 6.74-6.70 (m, 3H, C_6H_3), 3.38-3.35 (t, 2H, $\text{PhNCH}_2\text{CH}_2$), 2.95 (s, 3H, PhNCHCH_3), 2.68-2.64 (t, 2H, $p\text{-ClPhCH}_2$), 1.96-1.90 (m, 2H, $p\text{-ClPhCH}_2\text{CH}_2$).

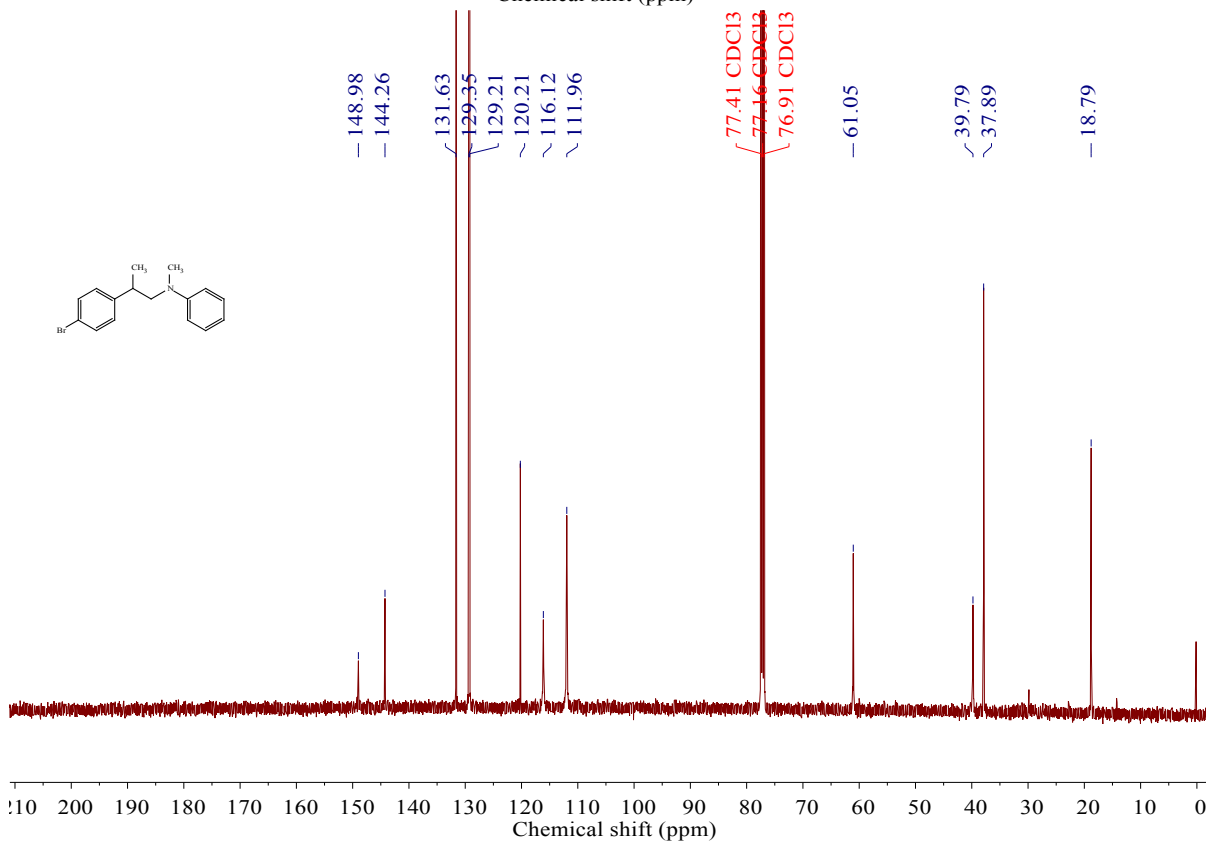
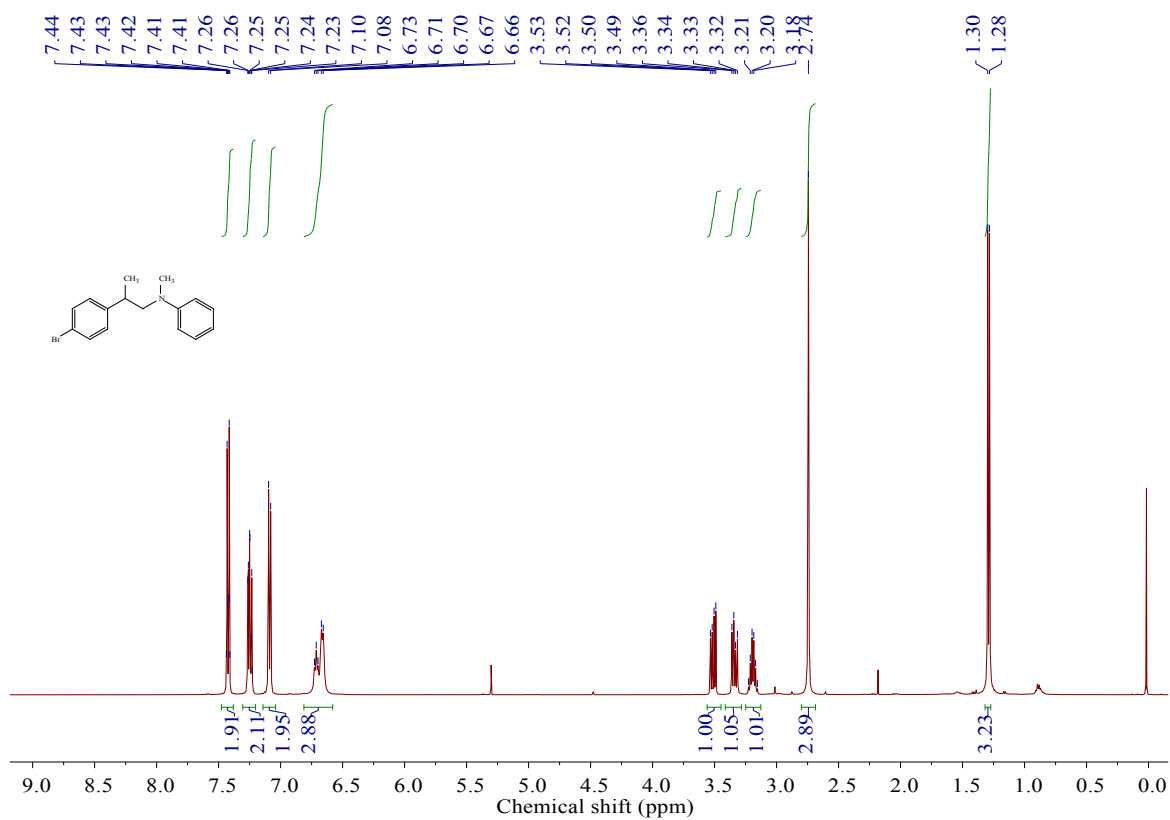
^{13}C NMR (126 MHz, CDCl_3) δ = 149.40, 140.34, 131.73, 129.81, 129.32, 128.60, 116.29, 112.37, 52.24, 38.45, 32.80, 28.26.



10-1. *N*-(2-(4-bromophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.44-7.41 (m, 2H, C_6H_2), 7.26-7.23 (m, 2H, C_6H_2), 7.11-7.08 (d, 2H, C_6H_2), 6.73-6.66 (m, 3H, C_6H_3), 6.74-6.70 (m, 3H, C_6H_3), 3.53-3.49 (dd, 1H, PhNCHCH_3), 3.36-3.32 (dd, 1H, PhNCHCH_3), 3.23-3.16 (m, 1H, *p*-BrPhCHCH $_3$), 2.74 (s, 3H, PhNCHCH_3), 1.30-1.28 (d, 3H, *p*-BrPhCHCH $_3$).

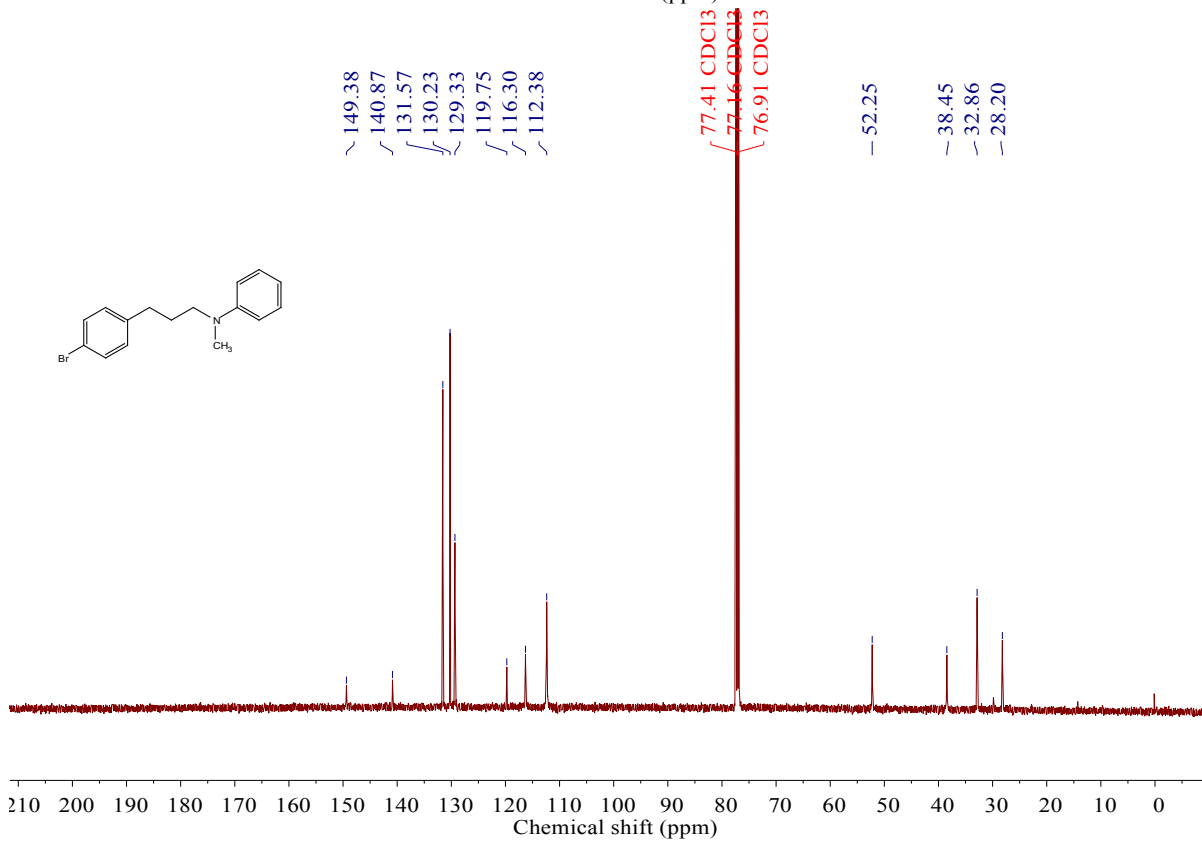
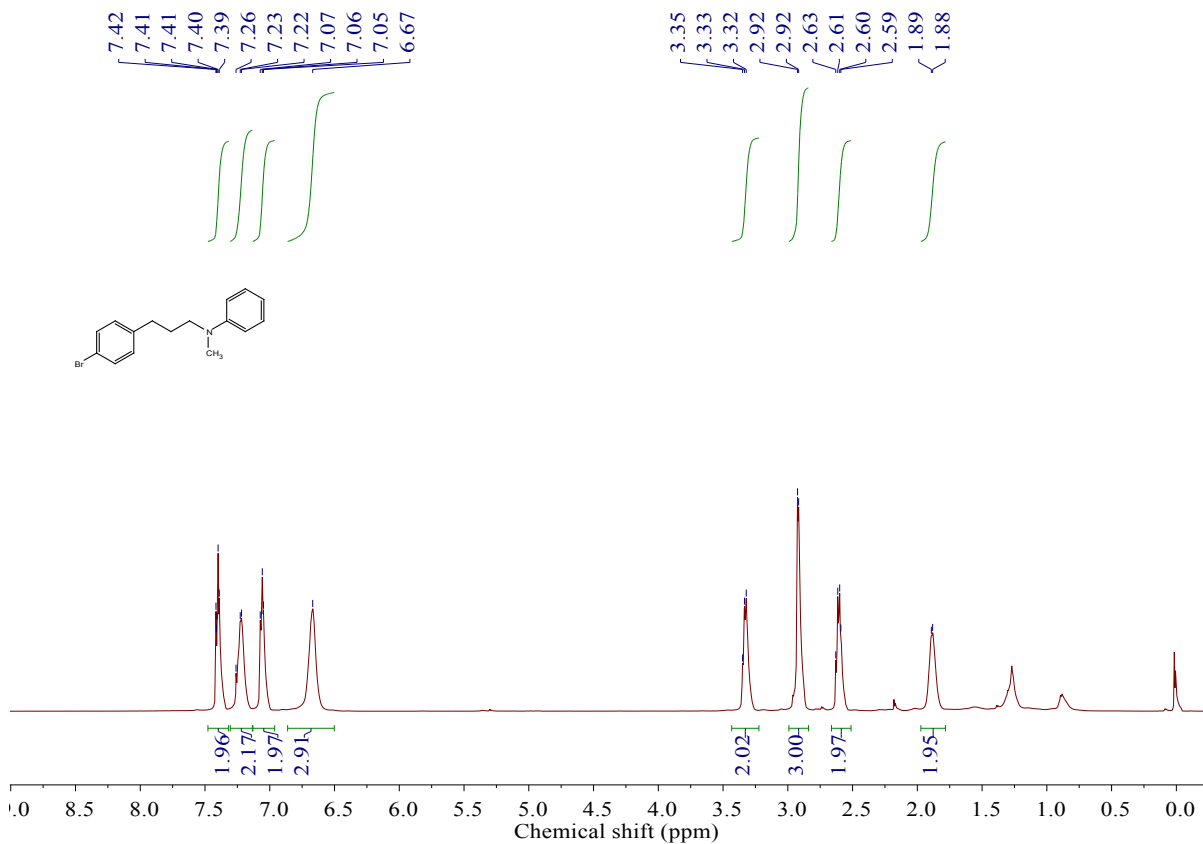
^{13}C NMR (126 MHz, CDCl_3) δ = 148.98, 144.26, 131.63, 129.35, 129.21, 120.21, 116.12, 111.96, 61.05, 39.79, 37.89, 18.79.



10-2. *N*-(3-(4-bromophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.42-7.39 (m, 2H, C_6H_2), 7.26-7.22 (m, 2H, C_6H_2), 7.07-7.05 (m, 2H, C_6H_2), 6.67 (s, 3H, C_6H_3), 3.35-3.32 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.92 (d, 3H, PhNCHCH_3), 2.63-2.64 (q, 2H, $p\text{-BrPhCH}_2$), 1.89-1.88 (d, 2H, $p\text{-BrPhCH}_2\text{CH}_2$).

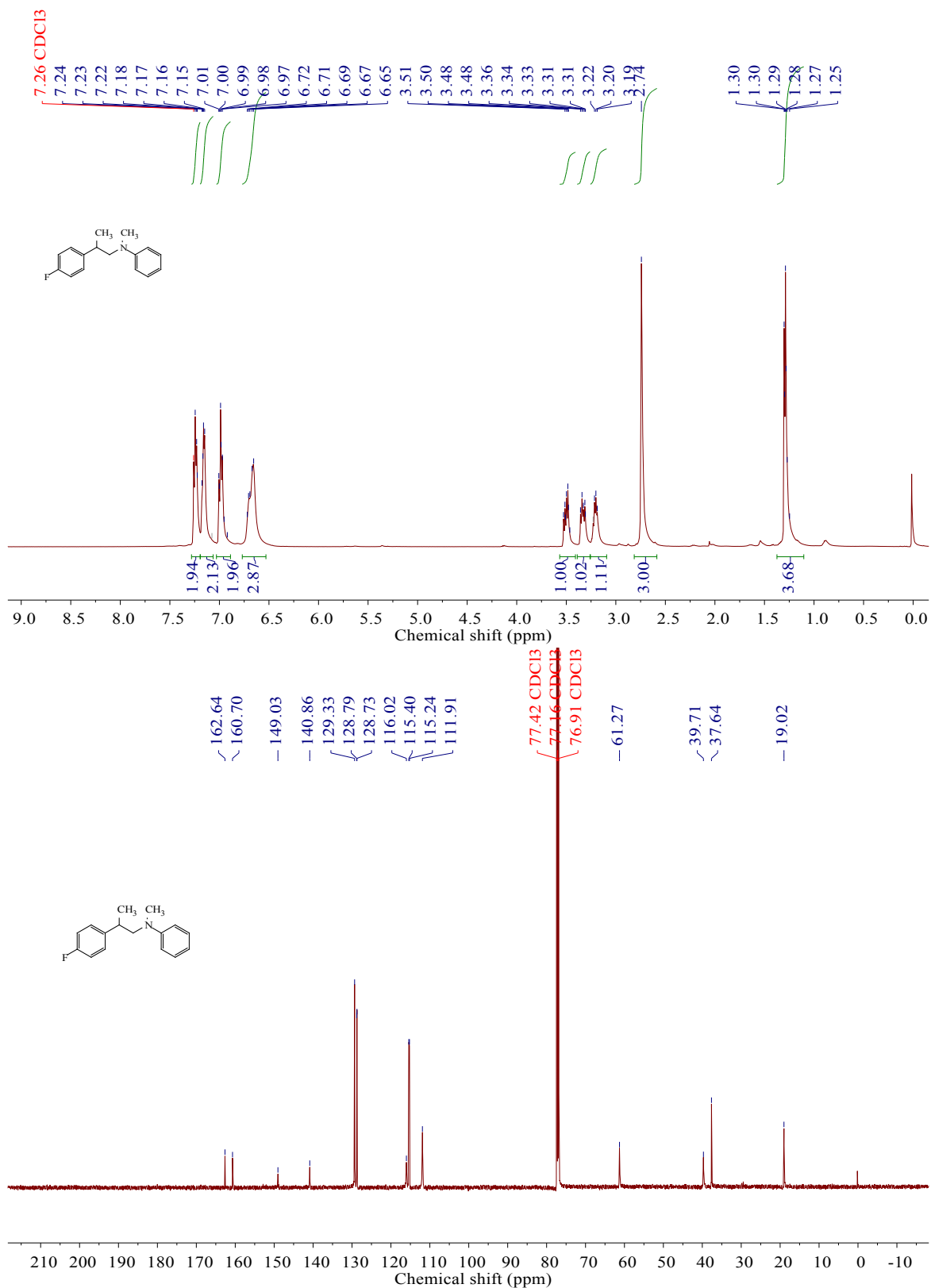
^{13}C NMR (126 MHz, CDCl_3) δ = 149.38, 140.87, 131.57, 130.23, 129.33, 119.75, 116.30, 112.38, 52.25, 38.45, 32.86, 28.20.



11-1 *N*-(2-(4-fluorophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.24-7.22 (m, 2H, C_6H_2), 7.18-7.15 (m, 2H, C_6H_2), 7.01-6.92 (m, 2H, C_6H_2), 6.72-6.65 (m, 3H, C_6H_3), 6.74-6.70 (m, 3H, C_6H_3), 3.53-3.46 (m, 1H, PhNCHCH_3), 3.36-3.31 (m, 1H, PhNCHCH_3), 3.23-3.19 (m, 1H, *p*-BrPhCHCH $_3$), 2.74 (s, 3H, PhNCHCH_3), 1.30-1.25 (m, 3H, *p*-BrPhCHCH $_3$).

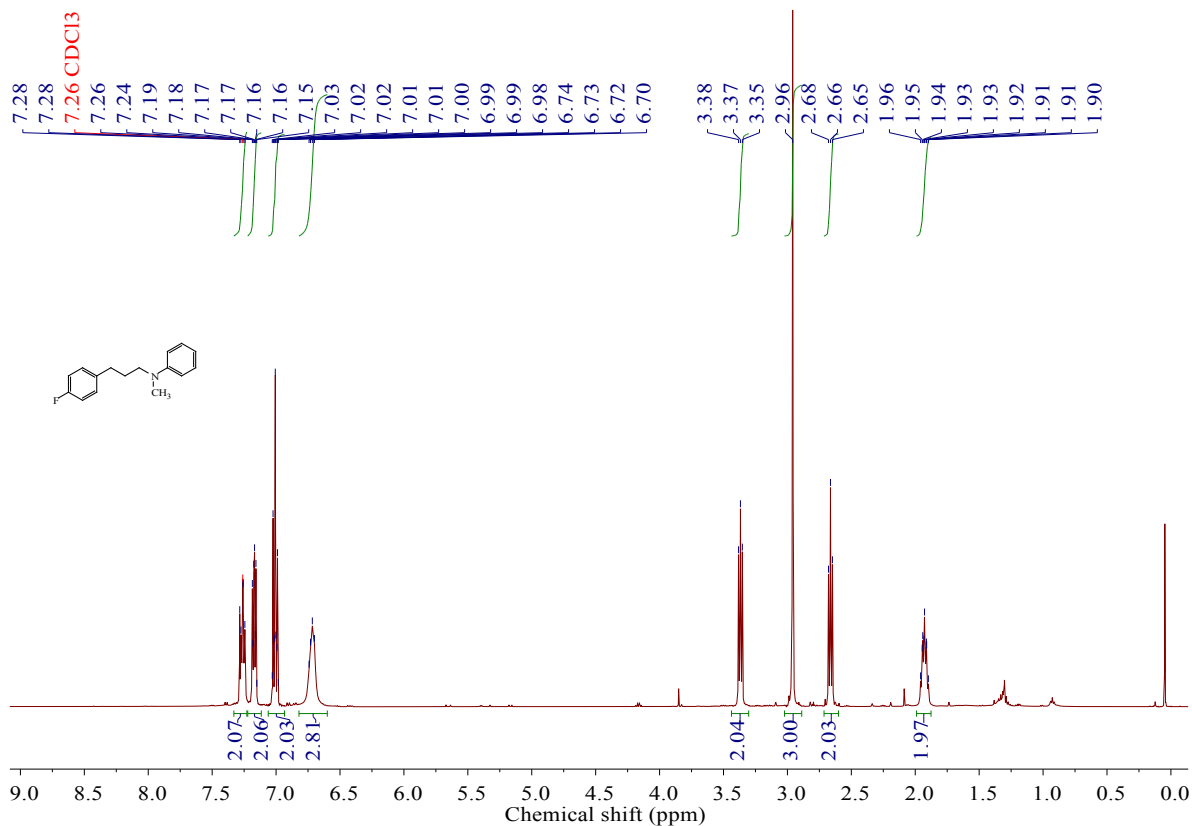
^{13}C NMR (126 MHz, CDCl_3) δ = 162.64, 160.70, 149.03, 140.86, 129.33, 128.79, 128.73, 128.73, 116.02, 115.40, 115.24, 111.91, 61.27, 39.71, 37.64, 19.02.



11-2 *N*-(3-(4-fluorophenyl)propyl)-*N*-methylaniline

^1H NMR (500 MHz, CDCl_3) δ = 7.28-7.24 (m, 2H, C_6H_2), 7.19-7.15 (m, 2H, C_6H_2), 7.03-6.98 (m, 2H, C_6H_2), 6.74-6.70 (m, 3H, C_6H_3), 3.38-3.35 (t, 2H, $\text{PhNCH}_2\text{CH}_3$), 2.96 (d, 3H, PhNCHCH_3), 2.68-2.65 (m, 2H, $p\text{-BrPhCH}_2$), 1.96-1.90 (m, 2H, $p\text{-BrPhCH}_2\text{CH}_2$).

^{13}C NMR (126 MHz, CDCl_3) δ = 162.38, 160.44, 149.39, 137.47, 129.79, 129.73, 129.32, 116.25, 115.31, 115.15, 112.37, 52.27, 38.45, 32.63, 28.44.



11. Notes and references

- 1 H. Liu, D.-L. Wang, X. Chen, Y. Lu, X.-L. Zhao and Y. Liu, *Green Chem.*, 2017, **19**, 1109–1116.
- 2 P. Wang, D.-L. Wang, H. Liu, X.-L. Zhao, Y. Lu and Y. Liu, *Organometallics*, 2017, **36**, 2404–2411.
- 3 H. Zhang, Y.-Q. Li, P. Wang, Y. Lu, X.-L. Zhao and Y. Liu, *J. Mol. Catal. Chem.*, 2016, **411**, 337–343.
- 4 S.-J. Chen, Y.-Q. Li, Y.-Y. Wang, X.-L. Zhao and Y. Liu, *J. Mol. Catal. Chem.*, 2015, **396**, 68–76.