

Supporting information

Aluminum-Catalyzed Anti-Markovnikov Hydroamination of Aromatic Alkenes with Aromatic Amines

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Contents

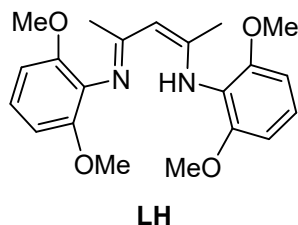
1. General Information	S2
2. Synthesis of Ligand and New Catalyst.....	S3
3. Optimization of Reaction Conditions	S6
4. Typical Procedures for Alkene Hydroamination	S10
5. Transformations of Hydroamination Products and Gram-scale Synthesis	S11
6. Analytical Data of Compounds.....	S14
7. Copies of NMR Spectra	S24
8. References	S57

1. General Information

Unless otherwise noted, all manipulations were carried out using standard Schlenk and glovebox techniques. AlMe_3 (1.0 M in hexane) was purchased from Energy Chemical and used as received. Anhydrous solvents were purified and dried following standard procedures.¹ All commercially available reagents were used as received. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Column chromatography was performed on silica gel (200-300 mesh). Melting points (abbreviated as m.p.) were measured on a YRT-3 apparatus and uncorrected. The NMR spectra were recorded on a Bruker Ascend 400M or a Bruker Ascend 500 M spectrometer. Chemical shifts were reported in ppm downfield from internal tetramethylsilane (^1H NMR: 0 ppm) and CDCl_3 (^{13}C NMR: 77.16 ppm). Abbreviations are used in the description of NMR data as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (J , Hz). The LC-MS was performed on Agilent Q-TOF 6520 instruments.

2. Synthesis of Ligand and New Catalyst

(1) Synthesis of Ligand **LH**



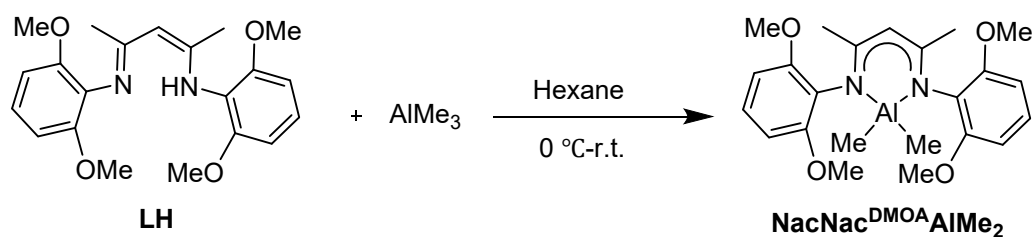
The title compound **LH** ($L = \text{HC}(\text{CCH}_3\text{NAr})_2$, $\text{Ar} = 2,6\text{-(OMe)}_2\text{C}_6\text{H}_3$) was prepared according to a literature procedure with a slight modification.² To an oven-dried 500 mL round-bottom flask equipped with a magnetic stir bar was added 2,6-dimethoxyaniline (20.220 g, 132 mmol), acetylacetone (6.007 g, 60 mmol) and toluene (150 mL). The solution was added 4-methylbenzenesulfonic acid (10.332 g, 60 mmol). The reaction vessel was equipped with a Dean-Stark apparatus and allowed to reflux for 30 h. The solution was then cooled to room temperature and a gray precipitate was collected by vacuum filtration and washed with excess toluene. The solid was then dissolved into 160 mL of an 80:80 mL mixture of dichloromethane and saturated sodium bicarbonate in water. The mixture was then stirred vigorously for 2 h followed by separation using a separatory funnel. The aqueous layer was then washed with dichloromethane (2×100 mL). All organic phases were then combined, dried over sodium sulfate, filtered, and concentrated under vacuum to give a gray solid. The solid was washed with cold ethanol until the solid became a light yellow solid which was dried under high vacuum.

18.576 g, 84% yield, m.p. 167-170 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 12.00 (s, 1H), 7.00 (t, $J = 8.3$ Hz, 2H), 6.57 (d, $J = 8.3$ Hz, 4H), 4.93 (s, 1H), 3.78 (s, 12H), 1.81 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 162.28, 153.81, 124.59, 124.29, 105.19, 95.46, 56.18, 20.82.

(2) Synthesis of New Catalyst **NacNac^{DMOA}AlMe₂**

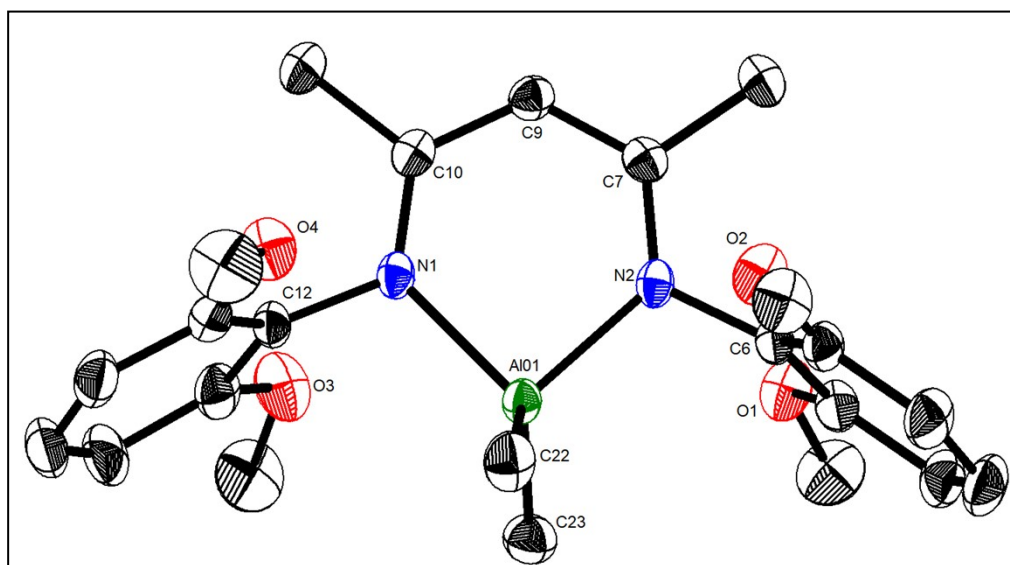


A solution of **LH** (1.852 g, 5 mmol) in hexane (10 mL) was added dropwise AlMe_3 (6 mL, 6 mmol, 1.0 M in hexane) at ice bath under nitrogen atmosphere, and the reaction mixture was allowed to warm up to room temperature and stirred for 18 h. After the reaction, a yellow solid was generated. The yellow solid was filtered and washed with hexane (3×10 mL), and the residue was dried under high vacuum to afford a white solid. Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization in a saturated hexane solution of **NacNac^{DMOA}AlMe₂**.

1.735 g, 81% yield, m.p. $104\text{--}107\text{ }^\circ\text{C}$.

¹H NMR (400 MHz, Benzene-*d*₆) δ 6.77 (t, $J = 8.3$ Hz, 2H), 6.23 (d, $J = 8.3$ Hz, 4H), 4.99 (s, 1H), 3.27 (s, 12H), 1.72 (s, 6H), -0.65 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 168.02, 153.87, 124.59, 123.37, 104.19, 96.48, 55.16, 54.85, 21.64.

Table S1. Crystal data and structure refinement for **NacNac^{DMOA}AlMe₂**

CCDC	2401637
Empirical formula	C ₂₃ H ₃₁ AlN ₂ O ₄
Formula weight	426.48
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Aea2
a/Å	14.4662(5)
b/Å	21.9361(7)
c/Å	15.0299(5)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	4769.5(3)
Z	8
ρ _{calc} /cm ³	1.188
μ/mm ⁻¹	0.114
F(000)	1824
Crystal size/mm ³	0.36 × 0.25 × 0.24
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	6.522 to 61.88
Index ranges	-13 ≤ h ≤ 20, -30 ≤ k ≤ 23, -18 ≤ l ≤ 18
Reflections collected	14189
Independent reflections	5505 [R _{int} = 0.0294, R _{sigma} = 0.0372]
Data/restraints/parameters	5505/1/279
Goodness-of-fit on F ²	1.067
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0410, wR ₂ = 0.1017
Final R indexes [all data]	R ₁ = 0.0519, wR ₂ = 0.1054
Largest diff. peak/hole / e Å ⁻³	0.28/-0.22
Flack parameter	0.05(9)

3. Optimization of Reaction Conditions

Table S2. Evaluation of bases^[a]

Entry	Base	Loading (mol%)	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	<i>t</i> BuOK	200	76	93:7
2	KOH	200	n.d.	n.d.
3	K ₂ CO ₃	200	n.d.	n.d.
4	KPF ₆	200	n.d.	n.d.
5	<i>t</i> BuONa	200	n.d.	n.d.
6	NaOH	200	n.d.	n.d.
7	NaH	200	n.d.	n.d.
8	NaNH ₂	200	n.d.	n.d.
9	MeONa	200	n.d.	n.d.
10	Cs ₂ CO ₃	200	n.d.	n.d.
11	CaH ₂	200	n.d.	n.d.
12	DBU	200	n.d.	n.d.
13	Et ₃ N	200	n.d.	n.d.
14	NMM	200	n.d.	n.d.
15	<i>t</i> BuOK	50	59	95:5
16	<i>t</i> BuOK	100	43	95:5
17	<i>t</i> BuOK	150	47	92:8
18	<i>t</i> BuOK	220	43	96:4
19	<i>t</i> BuOK	250	46	94:6
20	<i>t</i> BuOK	300	45	93:7
21	<i>t</i> BuOK	320	45	93:7

^[a] General conditions: aniline (0.25 mmol), styrene (1.2 equiv.), base, and **NacNac**^{DMOAA}**I**Me₂ (10 mol%) were stirred in 1 mL THF at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard. n.d. = not detected.

Table S3. Evaluation of solvents^[a]

Entry	Solvent	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	THF	76	93:7
2	Dioxane	30	100:0
3	MTBE	28	100:0
4	PhCl	13	100:0
5	DMF	n.d.	n.d.
6	DMSO	5	85:15
7	Hexane	8	87:13
8	MeCN	n.d.	n.d.
9	<i>p</i> -Xylene	5	100:0
10	Toluene	6	86:14

^[a] General conditions: aniline (0.25 mmol), styrene (1.2 equiv.), ^tBuOK (2 equiv.) and **NacNac^{DMOAA}AI Me₂** (10 mol%) were stirred in 1 mL solvent at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard. n.d. = not detected.

Table S4. Evaluation of Substrate ratio^[a]

Entry	Aniline (equiv.)	Styrene (equiv.)	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	1	5	80	84:16
2	1	3	61	94:6
3	1	1.5	47	95:5
4	1	1.2	76	93:7
5	1	1	45	96:4
6	1.2	1	39	96:4
7	2	1	55	97:3
8 ^[c]	1	1.2	30	100:0
9 ^[c]	1	2	57	97:3
10 ^[c]	1	3	57	97:3
11 ^[c]	1	5	84	94:6

^[a] General conditions: 1 equiv. = 0.25 mmol, aniline, styrene, ^tBuOK (2 equiv.) and **NacNac^{DMOAA}AI Me₂** (10 mol%) were stirred in 1 mL THF at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard. n.d. = not detected. ^[c] Dioxane instead of THF.

Table S5. Evaluation of catalysts and catalyst loadings ^[a]

Entry	Catalyst	Loading (mol%)	Solvent	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	AlMe₃	10	THF	39	93:7
2	AlⁱBu₂H	10	THF	19	100:0
3	AlClEt₂	10	THF	25	93:7
4	NacNac^{DMOA}AlMe₂	10	THF	80	84:16
5	NacNac^{DMOA}AlMe₂	10	Dioxane	84	94:6
6	NacNac^{DMOA}AlMe₂	15	Dioxane	63	66:34
7	NacNac^{DMOA}AlMe₂	5	Dioxane	70	95:5
8	NacNac^{DMOA}AlMe₂	1	Dioxane	18	100:0

^[a] General conditions: aniline (0.25 mmol), styrene (5 equiv.), ^tBuOK (2 equiv.), and catalyst were stirred in 1 mL solvent at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard.

Table S6. Evaluation of amounts of solvent ^[a]

Entry	Dioxane (mL)	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	1.5	61	97:3
2	1.0	84	94:6
3	0.5	84	88:12
4	0.1	73	75:25

^[a] General conditions: aniline (0.25 mmol), styrene (5 equiv.), ^tBuOK (2 equiv.) and **NacNac^{DMOA}AlMe₂** (10 mol%) were stirred in Dioxane at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard.

Table S7. Evaluation of amounts of solvent ^[a]

Entry	Temperature (°C)	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]

1	90	78	80:20
2	60	84	94:6
3	r.t.	18	100:0

^[a] General conditions: aniline (0.25 mmol), styrene (5 equiv.), ^tBuOK (2 equiv.) and **NacNac^{DMOA}AlMe₂** (10 mol%) were stirred in Dioxane at different temperature for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard.

Table S8. Evaluation of time ^[a]

Entry	Time (h)	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1	4	84	92:8
2	5	84	90:10
3	6	83	87:13
4	8	83	85:15
5	24	78	80:20

^[a] General conditions: aniline (0.25 mmol), styrene (5 equiv.), ^tBuOK (2 equiv.) and **NacNac^{DMOA}AlMe₂** (10 mol%) were stirred in 1 mL Dioxane at 90 °C for different time under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard.

Table S9. Other control experiments ^[a]

Entry	Variables	Yield of 3a (%) ^[b]	Ratio (3a/4a) ^[b]
1 ^[c]	without NacNac^{DMOA}AlMe₂	5	100:0
2 ^[d]	without ^t BuOK	n.d.	n.d.
3 ^[d]	without THF	23	89:11
4 ^[d]	THF: Dioxane = 0.5:0.5 mL	41	97:3
5	THF: Dioxane = 0.5:0.5 mL	86	87:13
6 ^[e]	THF: Dioxane = 0.5:0.5 mL	90	91:9
7 ^[f]	THF: Dioxane = 0.5:0.5 mL	84	92:8
8 ^[g]	THF: Dioxane = 0.5:0.5 mL	83	92:8
9	LH instead of NacNac^{DMOA}AlMe₂	73	95:5
10	none	80	84:16
11 ^[c]	none	84	94:6

^[a] General conditions: aniline (0.25 mmol), styrene (5 equiv.), ^tBuOK (2 equiv.) and

NacNac^{DMOA}**AlMe₂** (10 mol%) were stirred in THF at 60 °C for 24 h under a N₂ atmosphere. ^[b] The yield of **3a** and ratio were determined by ¹H NMR using toluene as an internal standard. n.d. = not detected. ^[c] Dioxane instead of THF. ^[d] Styrene (1.2 equiv.). ^[e] 21 h. ^[f] 18 h. ^[g] 15 h.

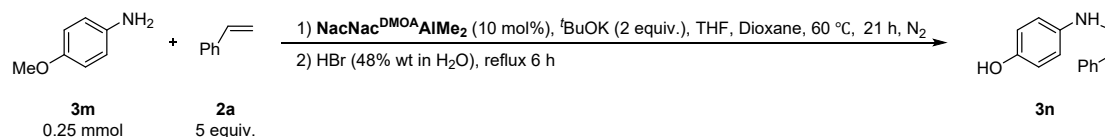
4. Typical Procedures for Alkene Hydroamination

General procedure: In a nitrogen-filled glovebox, a 10 mL Schlenk flask was charged with **NacNac**^{DMOA}**AlMe₂** (0.025 mmol, 10 mol %) and ^tBuOK (0.5 mmol, 2 equiv.), then amine (0.25 mmol), alkene (0.3-1.25 mmol, 1.2-5 equiv.) and solvent was added by sequence. The flask was removed from the glovebox and the reaction mixture was stirred for indicated time at specified temperature. After indicated time, the reaction mixture was filtered through a short pad of silica gel (Hexane: EA = 5:1), the filtrate was dried under high vacuum and analyzed by ¹H NMR using toluene as an internal standard after which was purified by flash column chromatography (Hexane: EA = 10:1-10:2 with 1% Et₃N) to afford the desired product.

5. Transformations of Hydroamination Products and Gram-scale Synthesis

5.1 Transformations of Hydroamination Products

(1) Synthesis of 4-(phenethylamino)phenol (3n)



In a nitrogen-filled glovebox, a 10 mL Schlenk flask was charged with $\text{NacNac}^{\text{DMOA}}\text{AlMe}_2$ (0.025 mmol, 10 mol %) and $t\text{BuOK}$ (0.5 mmol, 2 equiv.), then 4-methoxyaniline (0.25 mmol), styrene (1.25 mmol, 5 equiv.) and 1 mL of an equal volume mixture of THF and Dioxane was added by sequence. The flask was removed from the glovebox and the reaction mixture was stirred for 21 hours at 60 °C. After the completion of the reaction, the mixture was purified by flash column chromatography (Hexane: EA = 10:1 with 1% Et_3N) to afford 4-methoxy-*N*-phenethylaniline (**3m**). To start, **3m** and 10 mL of HBr (48 wt% in H_2O) were added to a round-bottom flask. The mixture was refluxed at 120 °C for 6 hours. Once the reaction was completed, the mixture was allowed to cool to room temperature. Next, the pH was adjusted to 8 using ammonia. The solution was then extracted with DCM: 3×20 mL, and the organic phases were combined and dried over Na_2SO_4 . The target reddish brown powder **5n** was gained by column chromatography (hexane: EA = 10:5) after filtration and drying by rotary evaporation.

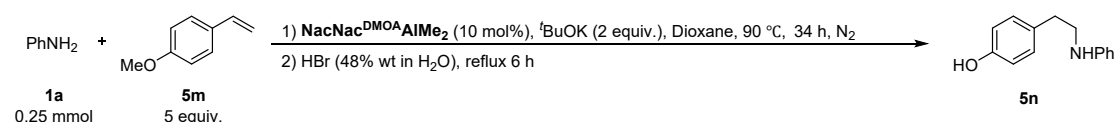
Reddish brown solid, 43 mg, 81% Yield.

$^1\text{H NMR}$ (500 MHz, Chloroform- d) δ 7.26 – 7.08 (m, 5H), 6.64 – 6.39 (m, 4H), 4.25 (s, 2H), 3.25 (t, J = 7.0 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform- d) δ 147.30, 140.63, 138.25, 127.78, 127.58, 125.39, 115.29, 114.15, 45.36, 34.41.

MS (ESI-TOF, $[\text{M}+\text{H}]^+$) m/z calcd. for $\text{C}_{14}\text{H}_{15}\text{NOH}^+$ $[\text{M}+\text{H}]^+$: 214.1226; found: 214.1260.

(2) Synthesis of 4-(2-(phenylamino)ethyl)phenol (**5n**)



In a nitrogen-filled glovebox, a 10 mL Schlenk flask was charged with **NacNac**^{DMOAAI}**OMe**₂ (0.025 mmol, 10 mol %) and ^tBuOK (0.5 mmol, 2 equiv.), then aniline (0.25 mmol), 1-methoxy-4-vinylbenzene (1.25 mmol, 5 equiv.) and 1 mL of Dioxane was added by sequence. The flask was removed from the glovebox and the reaction mixture was stirred for 34 hours at 90 °C. After the completion of the reaction, the mixture was purified by flash column chromatography (Hexane: EA = 10:1 with 1% Et₃N) to afford *N*-(4-methoxyphenethyl)aniline (**5m**). To start, **5m** and 10 mL of HBr (48 wt% in H₂O) were added to a round-bottom flask. The mixture was refluxed at 120 °C for 6 hours. Once the reaction was completed, the mixture was allowed to cool to room temperature. Next, the pH was adjusted to 8 using ammonia. The solution was then extracted with DCM: 3×20 mL, and the organic phases were combined and dried over Na₂SO₄. The target white powder **5n** was gained by column chromatography (hexane: EA = 10:5) after filtration and drying by rotary evaporation.

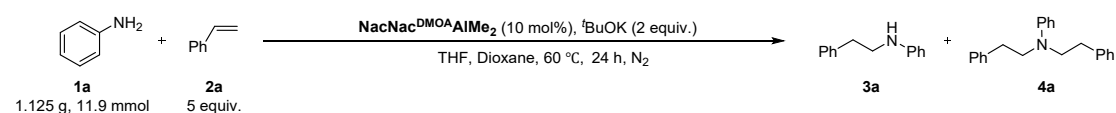
White solid, 49 mg, 92% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 6.95 (m, 4H), 6.73 – 6.50 (m, 5H), 4.23 (s, 2H), 3.28 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 154.13, 148.01, 131.39, 129.94, 129.32, 117.64, 115.47, 113.18, 45.29, 34.56.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₄H₁₅NOH⁺ [M+H]⁺: 214.1226; found: 214.1240.

5.2 Gram-scale Synthesis



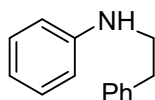
In a nitrogen-filled glovebox, a 50 mL Schlenk flask was charged with **NacNac**^{DMOAAI}**OMe**₂ (1.19 mmol, 10 mol %) and ^tBuOK (23.8 mmol, 2 equiv.), then aniline (11.9 mmol, 1.125 g), styrene (59.5 mmol, 5 equiv.) and 24 mL of an equal volume mixture of THF and Dioxane was added by sequence. The flask was removed

from the glovebox and the reaction mixture was stirred for 24 h at 60 °C. After indicated time, the reaction mixture was purified by flash column chromatography (Hexane: EA = 10:1 with 1% Et₃N) to afford the **3a** 1.640 g, 70% yield, 87:13 ratio.

6. Analytical Data of Compounds

6.1 Analytical Data of Hydroboration Products: Amine Scope

N-phenethylaniline (3a)

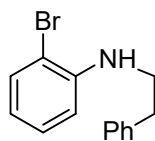


Yellow oil, 44 mg, 89% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 6.89 (m, 7H), 6.60 – 6.45 (m, 1H), 6.42 – 6.29 (m, 2H), 3.37 (s, 1H), 3.11 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.1 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.42, 139.79, 129.68, 129.18, 128.97, 126.78, 117.76, 113.35, 45.36, 35.84.

2-bromo-*N*-phenethylaniline (3b)



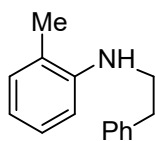
Yellow oil, 26 mg, 37% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.00 (m, 6H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 2H), 3.61 (s, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 143.70, 137.94, 131.41, 127.76, 127.63, 127.45, 125.51, 116.71, 110.30, 108.85, 44.03, 34.34.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₄H₁₄BrNH⁺ [M+H]⁺: 276.0382; found: 276.0396.

2-methyl-*N*-phenethylaniline (3c)

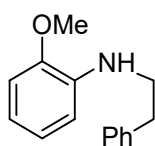


Yellow oil, 40 mg, 70% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.00 (m, 6H), 6.94 (d, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 3.42 (s, 1H), 3.34 (t, *J* = 7.0 Hz, 2H), 2.86 (t, *J* = 6.9 Hz, 2H), 1.92 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.92, 138.34, 129.08, 129.07, 127.76, 127.74, 127.58, 127.57, 126.11, 125.41, 121.04, 115.98, 115.97, 108.85, 108.83, 43.92, 34.45, 16.25.

2-methoxy-*N*-phenethylaniline (3d)

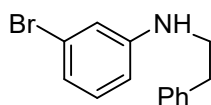


Orange oil, 47 mg, 83% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.03 (m, 5H), 6.79 (t, *J* = 7.6 Hz, 1H), 6.74 – 6.47 (m, 3H), 4.21 (s, 1H), 3.70 (s, 3H), 3.30 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 145.87, 138.49, 136.99, 127.72, 127.46, 125.26, 120.30, 115.44, 108.92, 108.54, 54.37, 43.99, 34.65.

3-bromo-*N*-phenethylaniline (3e)

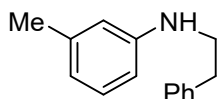


Rose-red oil, 30 mg, 43% Yield.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 (td, *J* = 8.0, 7.6, 1.9 Hz, 2H), 7.26 – 7.20 (m, 1H), 7.22 – 7.17 (m, 2H), 6.98 (td, *J* = 8.0, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.9, 2.0 Hz, 1H), 6.71 (t, *J* = 2.0 Hz, 1H), 6.47 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.70 (s, 1H), 3.34 (t, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 149.34, 138.99, 130.56, 128.81, 128.73, 126.62, 123.38, 120.17, 115.44, 111.72, 44.79, 35.34.

3-methyl-*N*-phenethylaniline (3f)

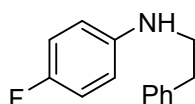


Yellow oil, 36 mg, 68% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.06 (m, 5H), 6.98 (dd, J = 8.9, 7.4 Hz, 1H), 6.45 (d, J = 7.4 Hz, 1H), 6.32 – 6.34 (m, 2H), 3.51 (s, 1H), 3.29 (t, J = 7.0 Hz, 2H), 2.81 (t, J = 7.0 Hz, 2H), 2.18 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.04, 138.34, 137.98, 128.11, 127.74, 127.55, 125.35, 117.38, 112.75, 109.12, 44.03, 34.54, 20.59.

4-fluoro-*N*-phenethylaniline (3g)



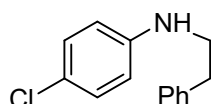
Pale yellow oil, 41 mg, 76% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.09 (m, 5H), 6.80 (t, J = 8.7 Hz, 2H), 6.54 – 6.36 (m, 2H), 3.45 (s, 1H), 3.27 (t, J = 7.0 Hz, 2H), 2.81 (t, J = 6.9 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 156.01, 153.67, 143.35, 143.33, 138.16, 127.67 (d, J = 13.2 Hz), 125.45, 114.65 (d, J = 22.2 Hz), 112.79 (d, J = 7.4 Hz), 44.65, 34.44.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -127.98.

4-chloro-*N*-phenethylaniline (3h)

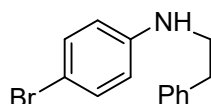


Yellow oil, 41 mg, 71% Yield.

¹H NMR (500 MHz, Chloroform-*d*) δ 7.31 – 6.99 (m, 7H), 6.50 – 6.39 (m, 2H), 3.60 (s, 1H), 3.29 (t, J = 7.0 Hz, 2H), 2.83 (t, J = 7.0 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 145.52, 138.00, 128.06, 127.73, 127.63, 125.50, 120.94, 112.99, 44.05, 34.29.

4-bromo-*N*-phenethylaniline (3i)

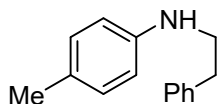


Claybank gum, 52 mg, 71% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.04 (m, 7H), 6.43 – 6.29 (m, 2H), 3.58 (s, 1H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 145.95, 137.98, 130.91, 127.71, 127.62, 125.49, 113.48, 107.91, 43.93, 34.26.

4-methyl-*N*-phenethylaniline (3j)

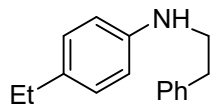


Yellow oil, 37 mg, 70% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.09 (m, 5H), 6.90 (d, *J* = 8.1 Hz, 2H), 6.54 – 6.40 (m, 2H), 3.54 – 3.34 (m, 1H), 3.29 (t, *J* = 7.0 Hz, 2H), 2.81 (t, *J* = 7.0 Hz, 2H), 2.15 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.71, 138.38, 128.73, 127.75, 127.53, 125.64, 125.33, 112.19, 44.39, 34.51, 19.35.

4-ethyl-*N*-phenethylaniline (3k)



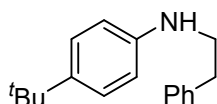
Yellow oil, 38 mg, 68% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.09 (m, 5H), 6.97 – 6.90 (m, 2H), 6.51 – 6.45 (m, 2H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.46 (q, *J* = 7.6 Hz, 2H), 1.11 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.96, 138.40, 132.34, 127.76, 127.56, 127.54, 125.34, 112.15, 44.37, 34.59, 26.90, 14.91.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₆H₁₉NH⁺ [M+H]⁺: 226.1590; found: 226.1603.

4-(*tert*-butyl)-*N*-phenethylaniline (3l)

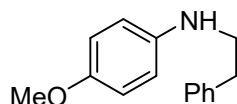


Yellow solid, 38 mg, 60% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.10 (m, 7H), 6.57 – 6.43 (m, 2H), 3.49 (s, 1H), 3.32 (t, *J* = 7.0 Hz, 2H), 2.84 (t, *J* = 7.0 Hz, 2H), 1.21 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 144.67, 139.26, 138.41, 127.76, 127.55, 125.35, 125.01, 111.72, 44.30, 34.68, 32.83, 30.53.

4-methoxy-*N*-phenethylaniline (3m)

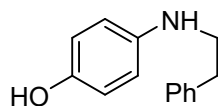


Orange oil, 46 mg, 81% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.26 – 7.17 (m, 2H), 7.17 – 7.09 (m, 3H), 6.73 – 6.65 (m, 2H), 6.54 – 6.40 (m, 2H), 3.74 (s, 1H), 3.64 (s, 3H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 151.15, 141.20, 138.38, 127.75, 127.54, 125.34, 113.89, 113.34, 54.75, 45.00, 34.55.

4-(phenethylamino)phenol (3n)



Reddish brown solid, 43 mg, 81% Yield.

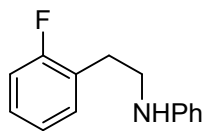
¹H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.08 (m, 5H), 6.64 – 6.39 (m, 4H), 4.25 (s, 2H), 3.25 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.30, 140.63, 138.25, 127.78, 127.58, 125.39, 115.29, 114.15, 45.36, 34.41.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₄H₁₅NOH⁺ [M+H]⁺: 214.1226; found: 214.1260.

6.2 Analytical Data of Hydroboration Products: Alkene Scope

N-(2-fluorophenethyl)aniline (5b)



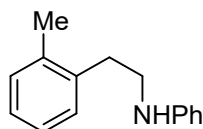
Yellow oil, 38 mg, 71% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 6.89 (m, 6H), 6.67 – 6.59 (m, 1H), 6.58 – 6.52 (m, 2H), 3.65 (s, 1H), 3.33 (t, *J* = 7.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 161.55, 146.89, 130.04 (d, *J* = 5.0 Hz), 128.27, 127.17 (d, *J* = 8.1 Hz), 125.23 (d, *J* = 16.1 Hz), 123.11 (d, *J* = 3.6 Hz), 116.45, 114.38 (d, *J* = 22.2 Hz), 111.88, 42.86, 28.17.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -118.42.

N-(2-methylphenethyl)aniline (5c)

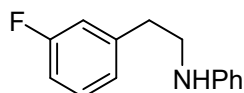


Yellow oil, 41 mg, 78% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.14 – 7.06 (m, 6H), 6.63 (t, *J* = 7.3 Hz, 1H), 6.54 (d, *J* = 7.9 Hz, 2H), 3.61 (s, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 2.26 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.04, 136.39, 135.29, 129.41, 128.27, 128.24, 125.52, 125.09, 116.42, 111.90, 42.85, 31.93, 18.37.

N-(3-fluorophenethyl)aniline (5d)



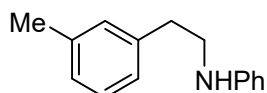
Yellow oil, 33 mg, 62% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 6.49 (m, 9H), 3.57 (s, 1H), 3.33 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.22, 146.79, 140.89 (d, J = 7.3 Hz), 128.99 (d, J = 8.3 Hz), 128.31, 123.40 (d, J = 2.9 Hz), 116.62, 114.60 (d, J = 20.9 Hz), 112.31 (d, J = 21.0 Hz), 111.98, 43.76, 34.28.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -113.25.

***N*-(3-methylphenethyl)aniline (5e)**

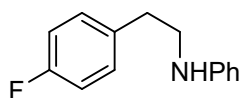


Pale yellow oil, 36 mg, 78% Yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 6.86 (m, 6H), 6.67 – 6.47 (m, 3H), 3.56 (s, 1H), 3.29 (t, J = 7.0 Hz, 2H), 2.78 (t, J = 7.0 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.05, 138.20, 137.16, 128.53, 128.23, 127.45, 126.14, 124.76, 116.40, 111.98, 44.02, 34.44, 20.35.

***N*-(4-fluorophenethyl)aniline (5f)**



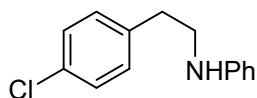
Yellow oil, 16 mg, 30% Yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 6.83 (m, 6H), 6.68 – 6.43 (m, 3H), 3.54 (s, 1H), 3.29 (t, J = 7.0 Hz, 2H), 2.79 (t, J = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.83, 159.40, 146.87, 133.93 (d, J = 3.2 Hz), 129.17, 129.09, 128.29, 116.56, 114.34 (d, J = 21.2 Hz), 111.97, 44.07, 33.68.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.74.

***N*-(4-chlorophenethyl)aniline (5g)**

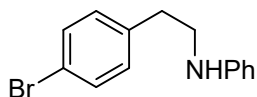


Yellow oil, 32 mg, 56% Yield.

^1H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 6.95 (m, 6H), 6.76 – 6.36 (m, 3H), 3.54 (s, 1H), 3.30 (t, J = 7.0 Hz, 2H), 2.80 (t, J = 6.9 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.77, 136.75, 131.20, 129.10, 128.30, 127.67, 116.60, 111.96, 43.85, 33.82.

***N*-(4-bromophenethyl)aniline (5h)**

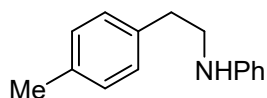


Yellow oil, 28 mg, 40% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 6.90 (m, 6H), 6.69 – 6.42 (m, 3H), 3.55 (s, 1H), 3.30 (t, *J* = 7.0 Hz, 2H), 2.79 (t, *J* = 6.9 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.75, 137.28, 130.63, 129.50, 128.30, 119.23, 116.61, 111.97, 43.79, 33.89.

***N*-(4-methylphenethyl)aniline (5j)**

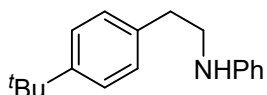


Pale yellow oil, 43 mg, 82% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.15 – 6.87 (m, 6H), 6.70 – 6.44 (m, 3H), 3.55 (s, 1H), 3.27 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.24 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 147.06, 135.15, 134.92, 128.26, 128.24, 127.64, 116.41, 111.98, 44.10, 34.05, 19.99.

***N*-(4-(*tert*-butyl)phenethyl)aniline (5k)**



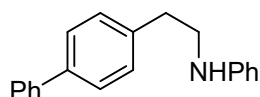
Yellow oil, 51 mg, 80% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.00 (m, 6H), 6.70 – 6.46 (m, 3H), 3.61 (s, 1H), 3.32 (t, *J* = 7.0 Hz, 2H), 2.82 (t, *J* = 7.0 Hz, 2H), 1.25 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 148.26, 147.08, 135.17, 128.24, 127.42, 124.47, 116.40, 111.98, 44.01, 33.97, 33.40, 30.37.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₈H₂₃NH⁺ [M+H]⁺: 254.1903; found: 254.1927.

***N*-(2-([1,1'-biphenyl]-4-yl)ethyl)aniline (5l)**



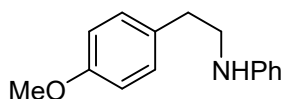
White solid, 55 mg, 81% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 6.23 (m, 13H), 3.43 (t, *J* = 7.7 Hz, 2H), 2.78 (t, *J* = 7.7 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.32, 139.90, 138.19, 137.73, 128.46, 128.15, 127.70, 126.21, 126.08, 125.96, 115.05, 111.03, 52.19, 32.25.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₂₀H₁₉NH⁺ [M+H]⁺: 274.1590; found: 274.1597.

***N*-(4-methoxyphenethyl)aniline (5m)**

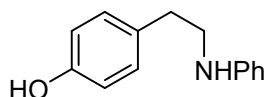


Yellow oil, 51 mg, 89% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.16 – 6.42 (m, 9H), 3.69 (s, 3H), 3.55 (s, 1H), 3.26 (t, *J* = 7.0 Hz, 2H), 2.76 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 157.23, 147.07, 130.27, 128.67, 128.23, 116.38, 113.02, 111.97, 54.23, 44.18, 33.56.

4-(2-(phenylamino)ethyl)phenol (5n)



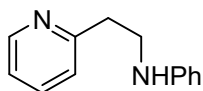
White solid, 49 mg, 92% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 6.95 (m, 4H), 6.73 – 6.50 (m, 5H), 4.23 (s, 2H), 3.28 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 154.13, 148.01, 131.39, 129.94, 129.32, 117.64, 115.47, 113.18, 45.29, 34.56.

MS (ESI-TOF, [M+H]⁺) *m/z* calcd. for C₁₄H₁₅NOH⁺ [M+H]⁺: 214.1226; found: 214.1240.

***N*-(2-(pyridin-2-yl)ethyl)aniline (5o)**

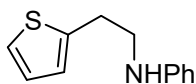


Yellow oil, 22 mg, 89% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 4.9 Hz, 1H), 7.58 – 6.39 (m, 8H), 3.91 (s, 1H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.99 (t, *J* = 6.6 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 158.78, 148.35, 147.17, 135.45, 128.19, 122.28, 120.42, 116.26, 111.91, 42.51, 36.45.

***N*-(2-(thiophen-2-yl)ethyl)aniline (5p)**

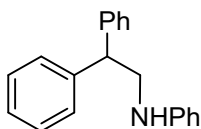


Brown oil, 38 mg, 75% Yield.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.21 – 6.40 (m, 8H), 3.68 (s, 1H), 3.35 (t, *J* = 6.8 Hz, 2H), 3.04 (t, *J* = 6.8 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.73, 140.73, 128.28, 125.94, 124.25, 122.83, 116.62, 112.05, 44.19, 28.72.

***N*-(2,2-diphenylethyl)aniline (5q)**



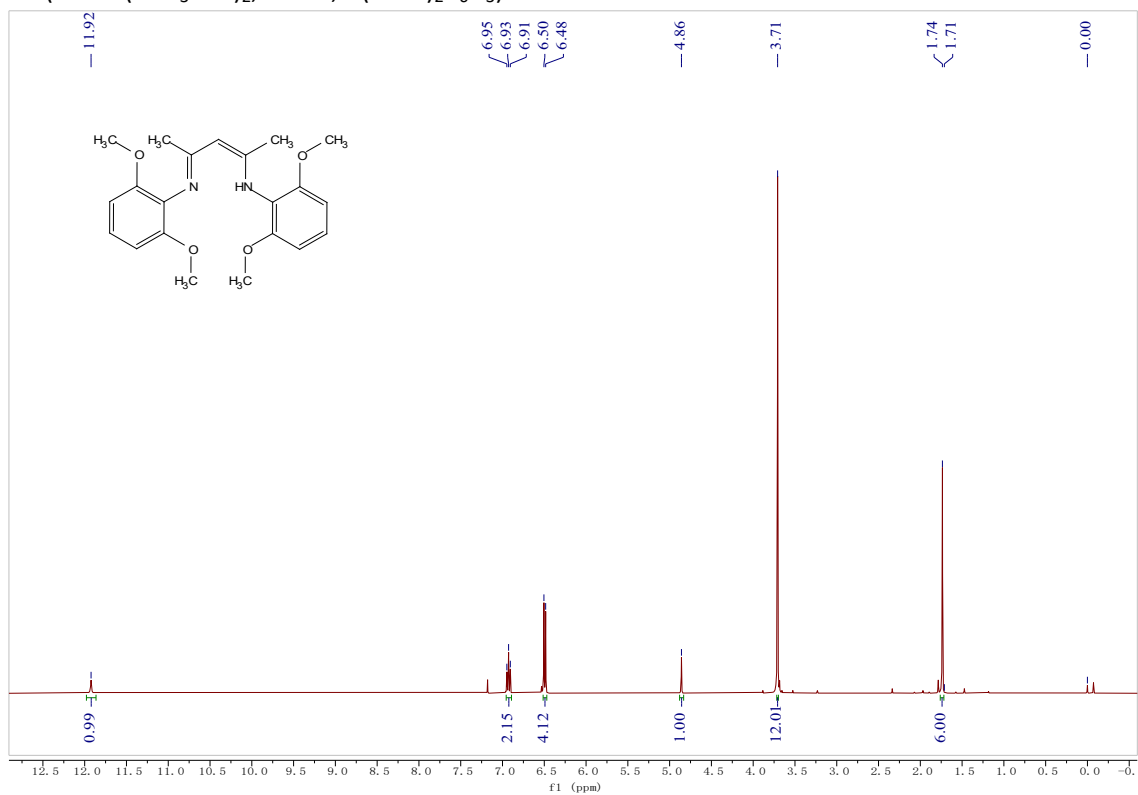
Pale yellow oil, 40 mg, 59% Yield.

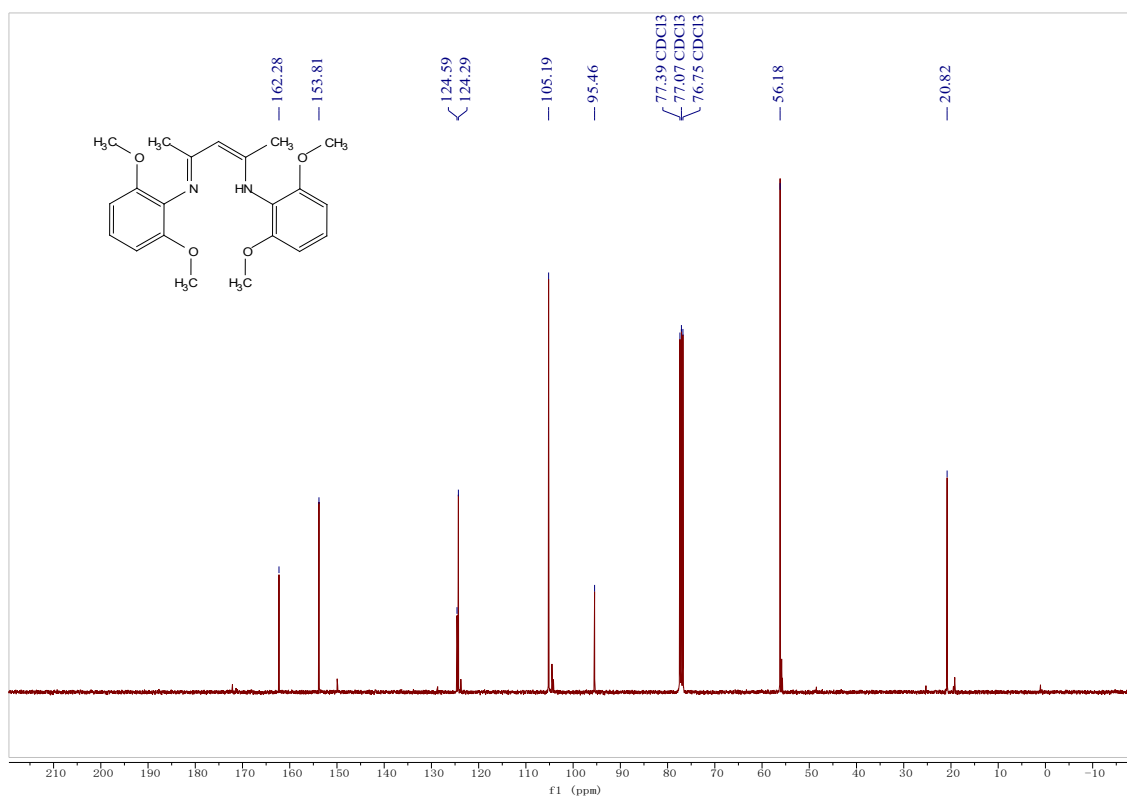
¹H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.05 (m, 12H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 7.9 Hz, 2H), 4.22 (t, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 7.7 Hz, 2H), 3.56 (s, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 146.81, 141.27, 128.27, 127.71, 127.14, 125.77, 116.65, 112.15, 49.27, 47.54.

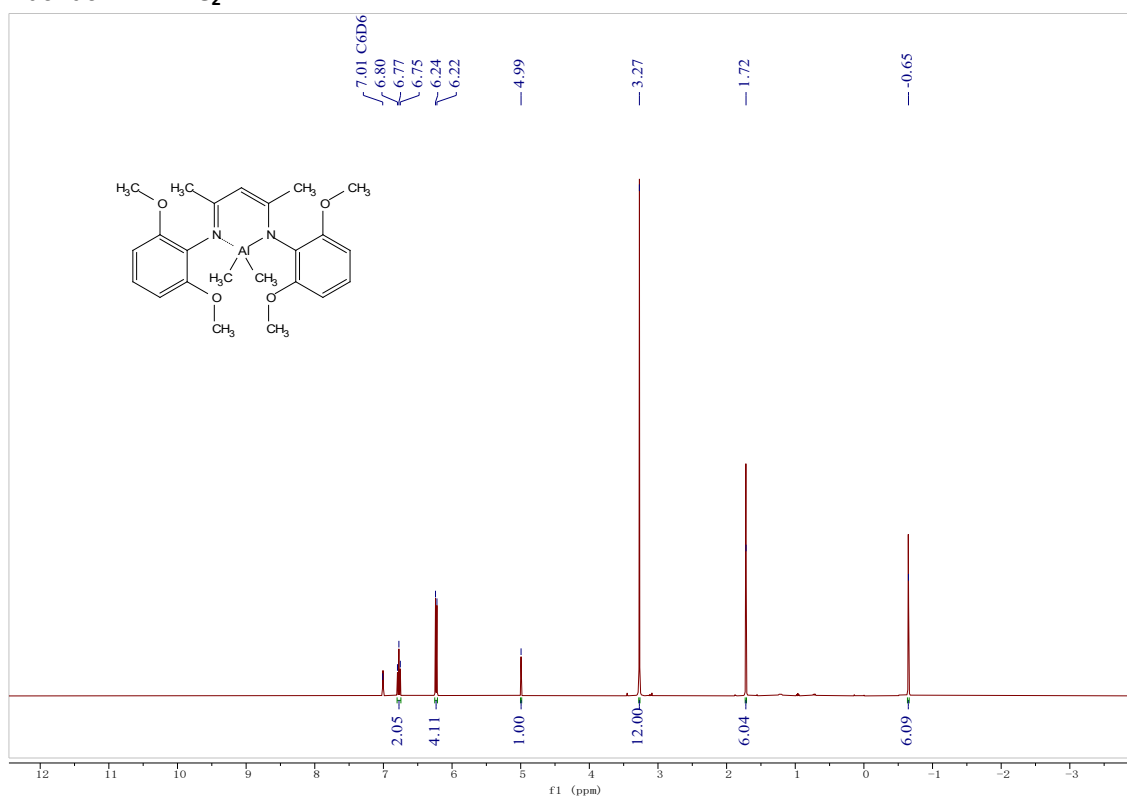
7.Copies of NMR Spectra

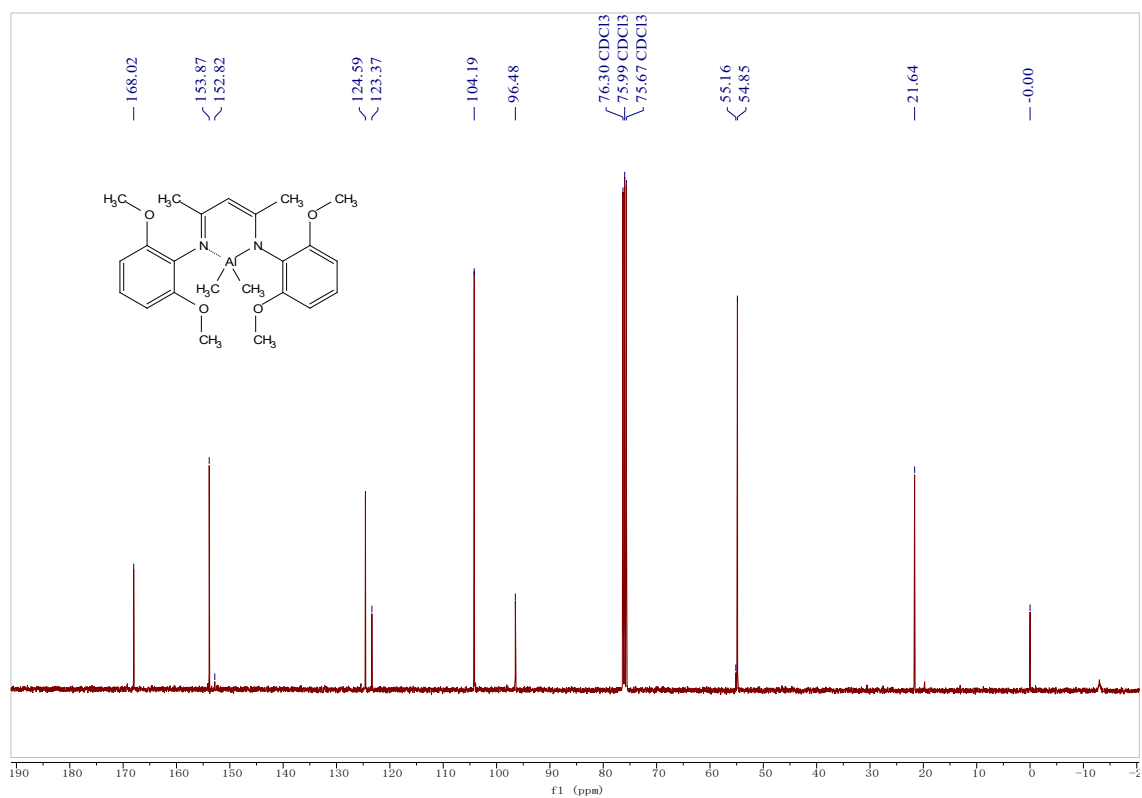
LH (L = HC(CCH₃NAr)₂, Ar = 2,6-(OMe)₂C₆H₃)



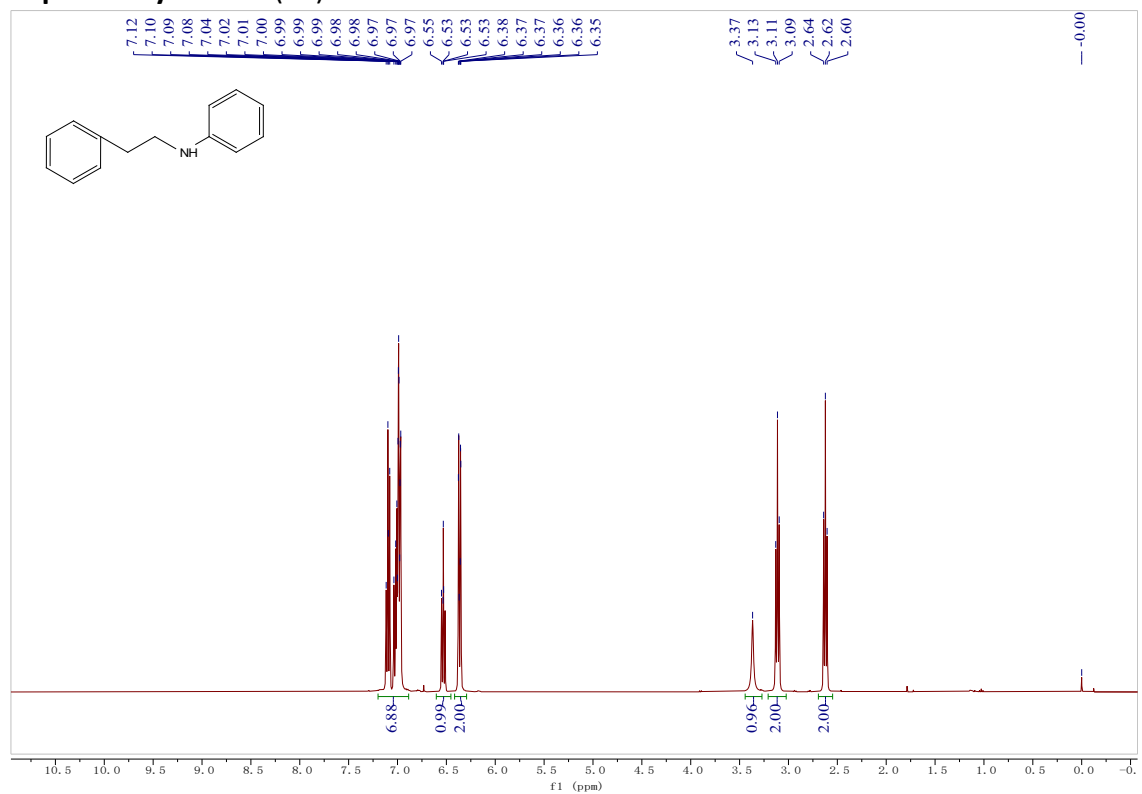


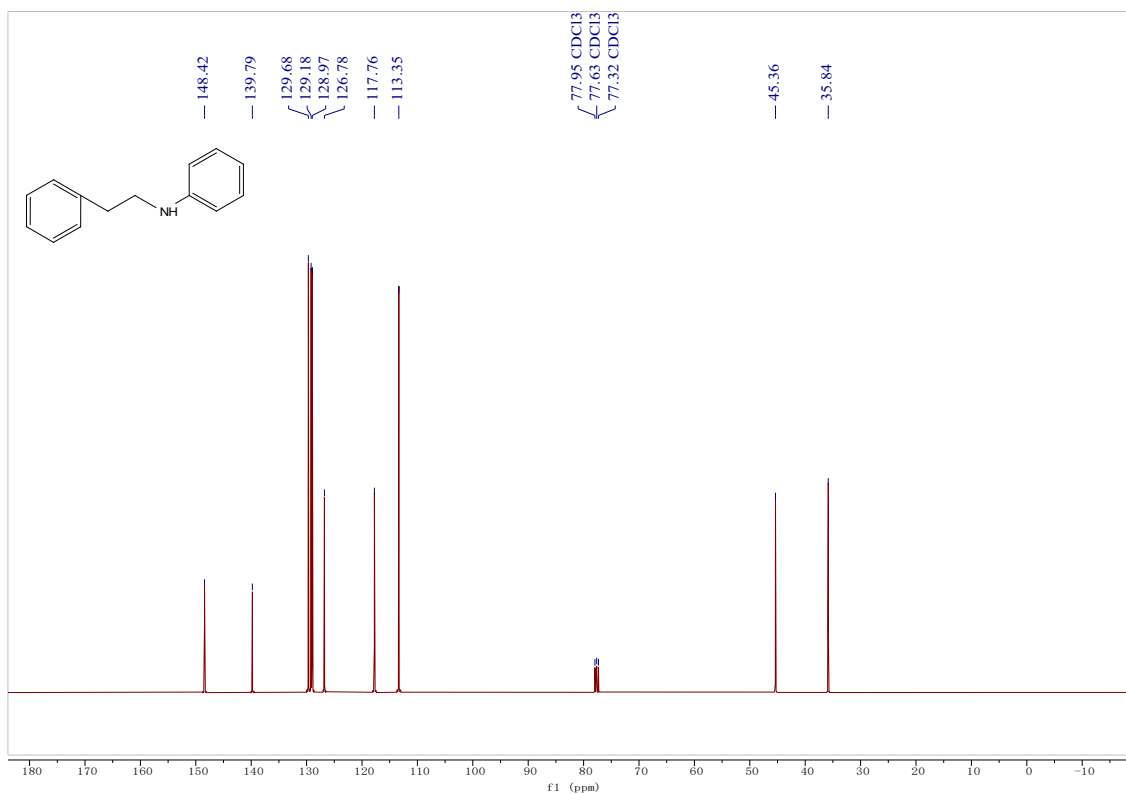
NacNac^{DMOA}AlMe₂



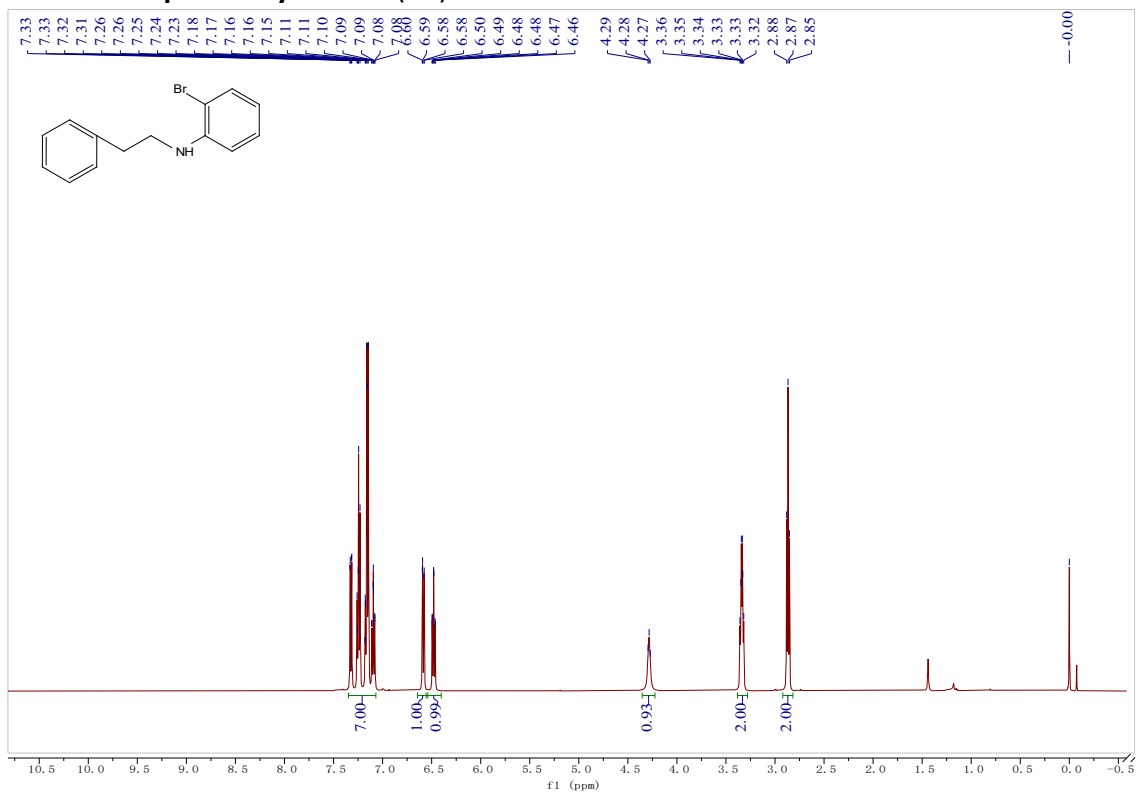


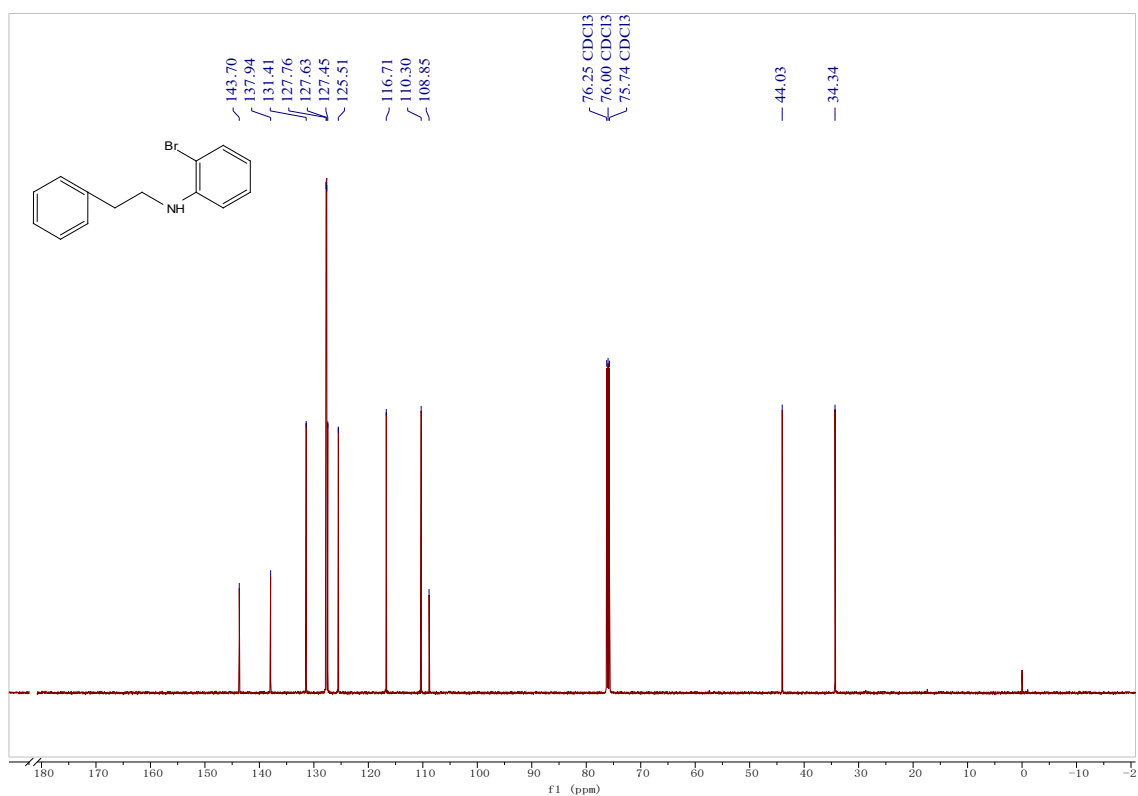
N-phenethylaniline (3a)



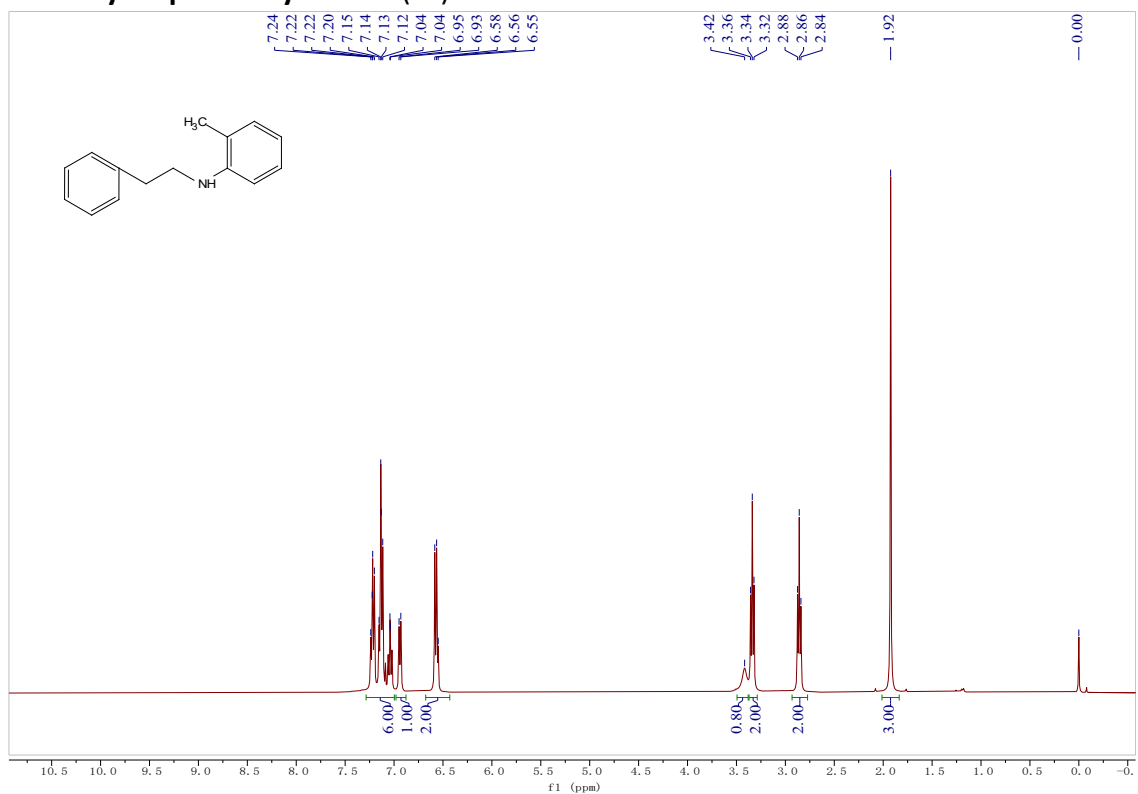


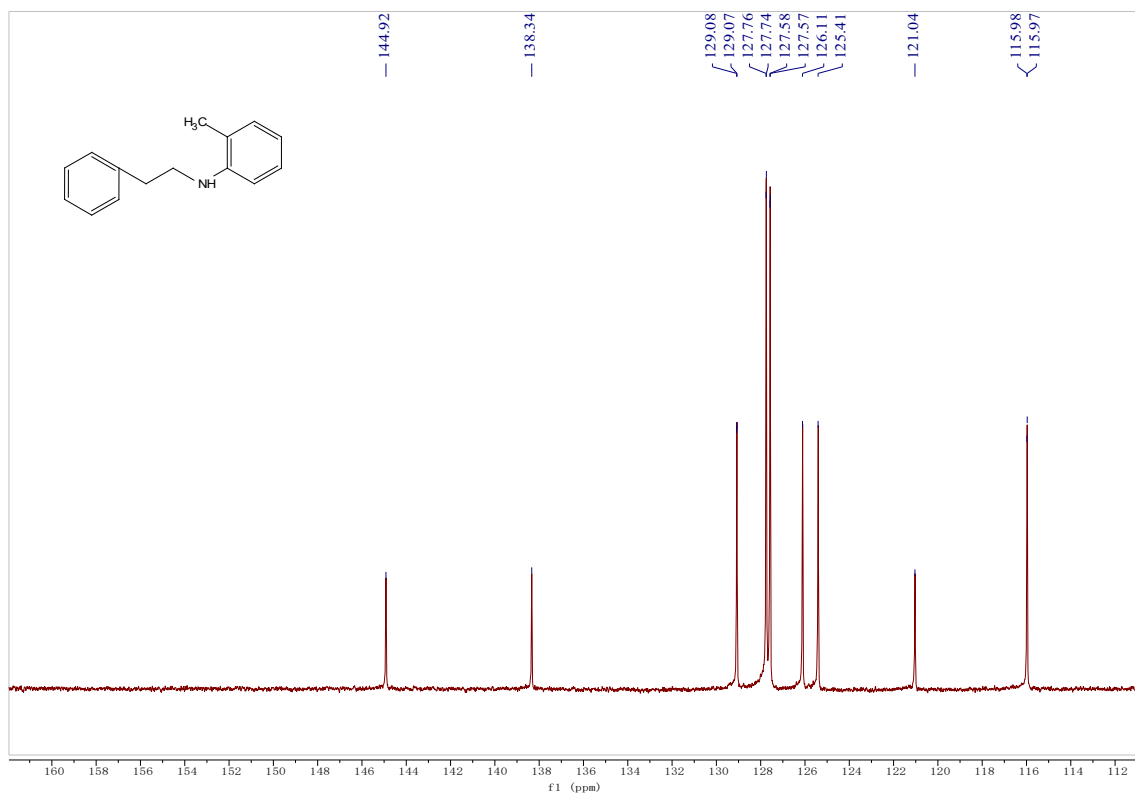
2-bromo-N-phenethylamine (3b)



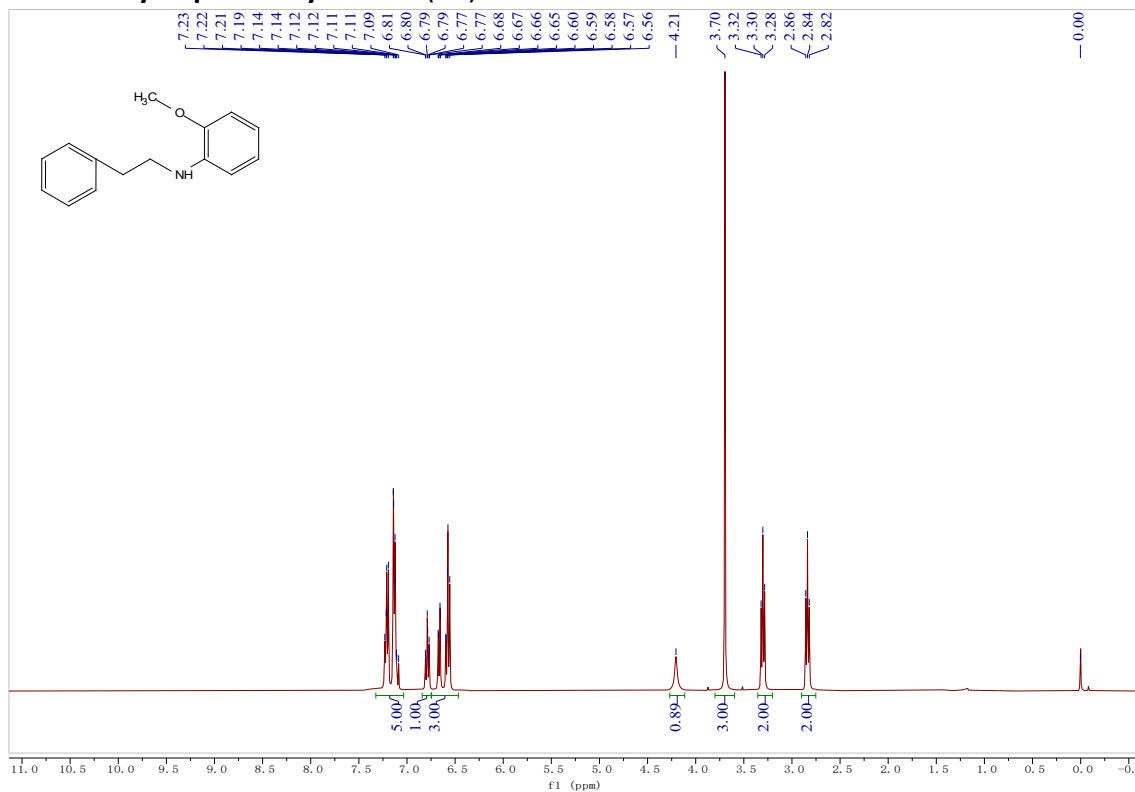


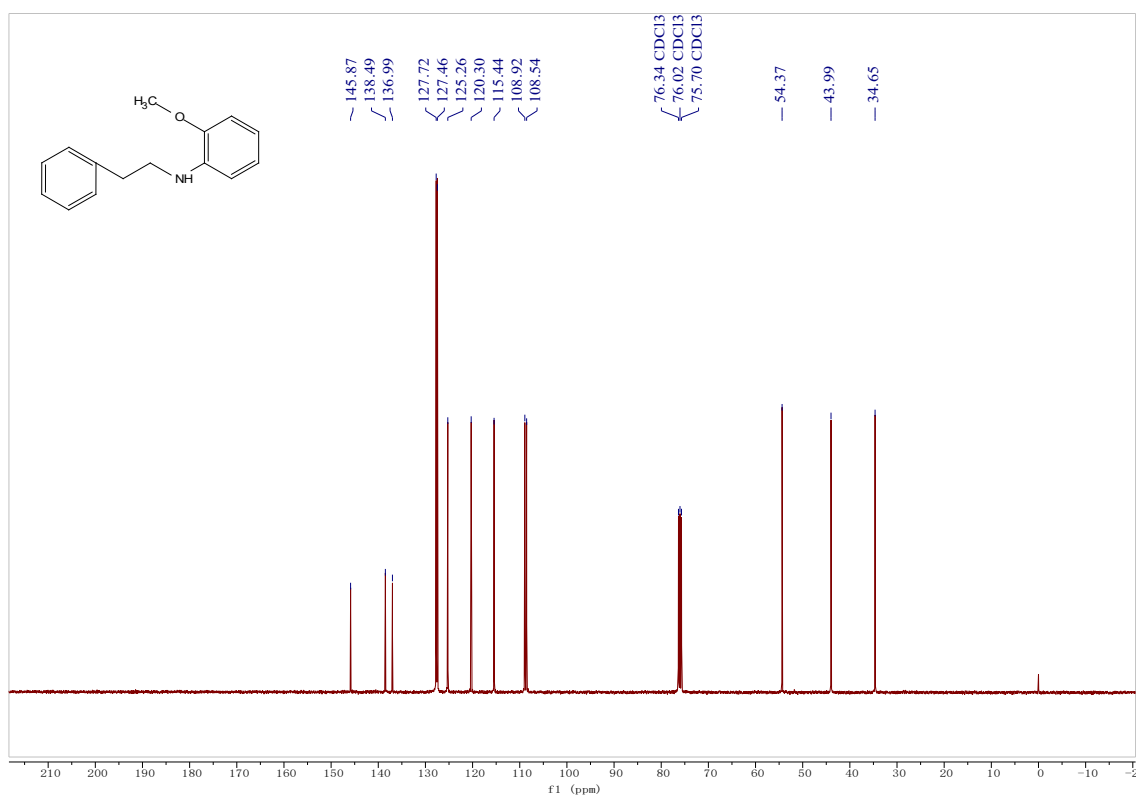
2-methyl-N-phenethylaniline (3c)



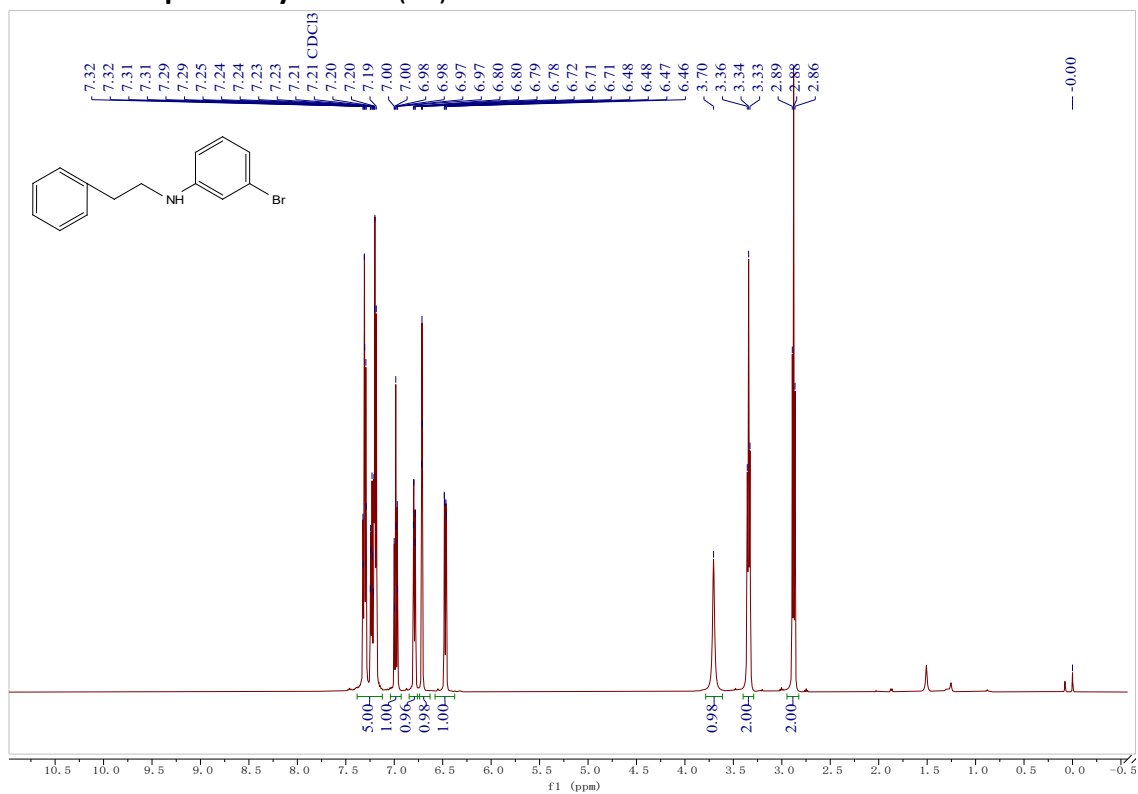


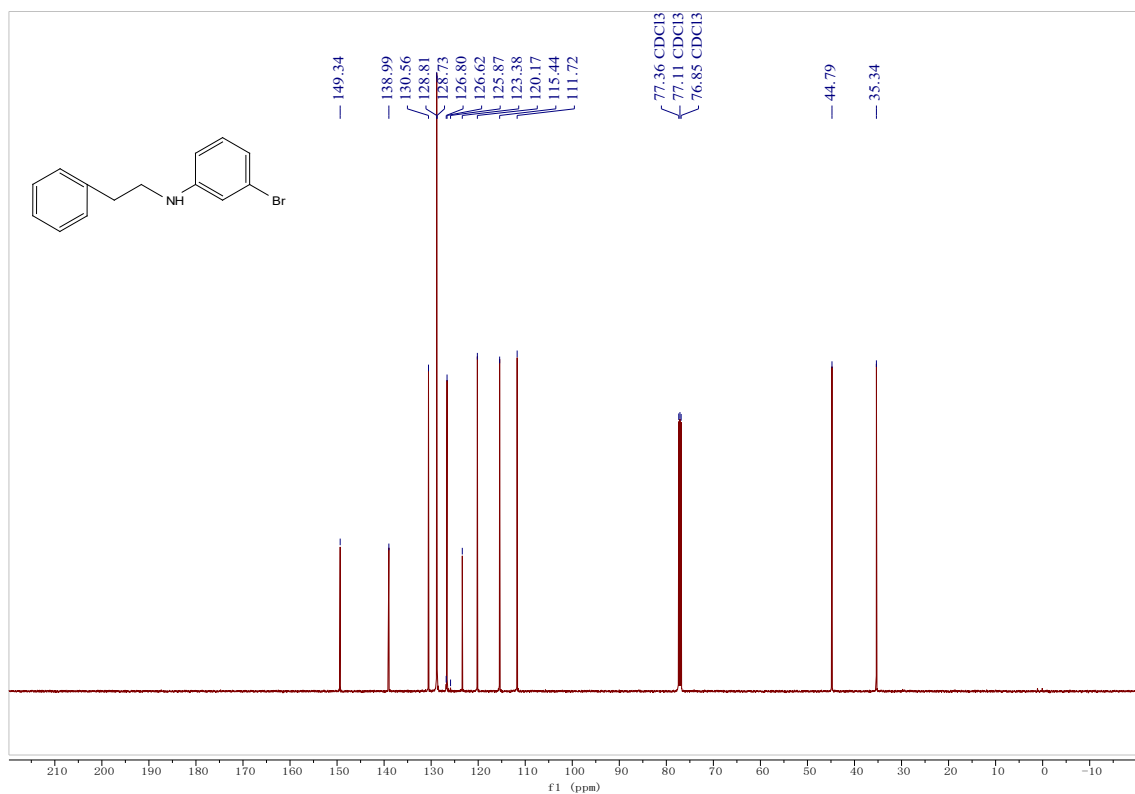
2-methoxy-*N*-phenethylaniline (3d)



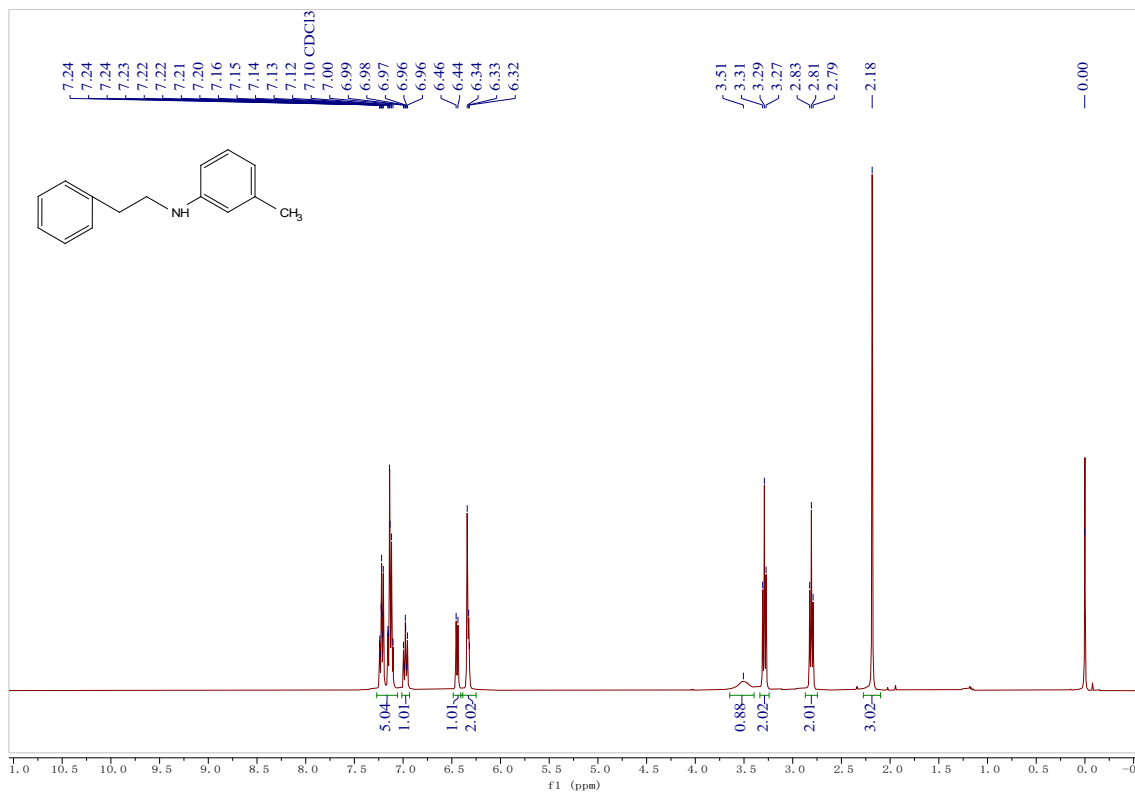


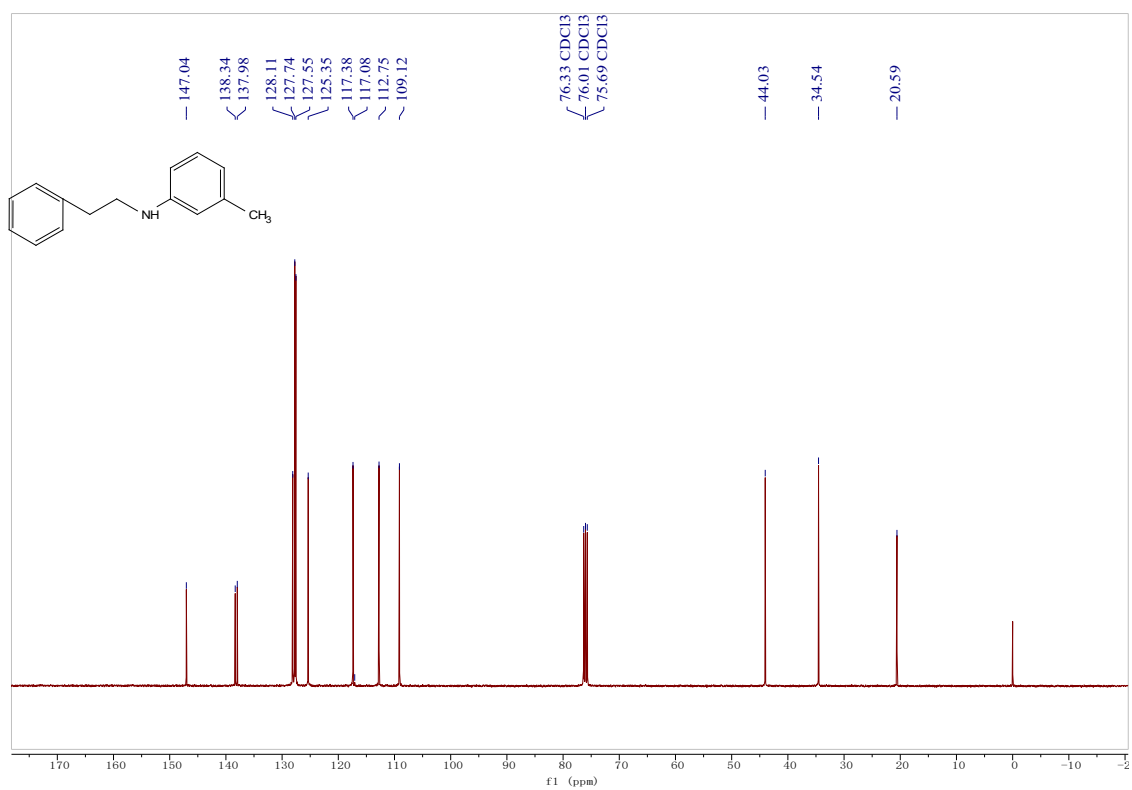
3-bromo-*N*-phenethylaniline (3e)



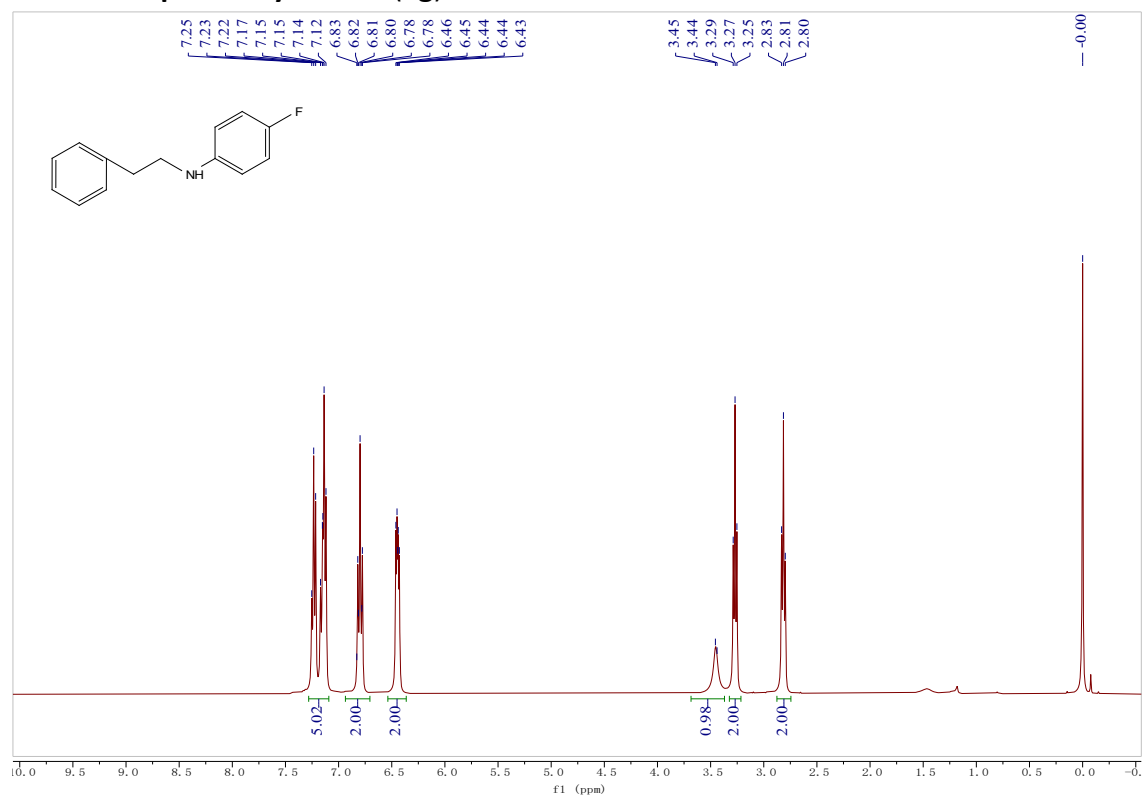


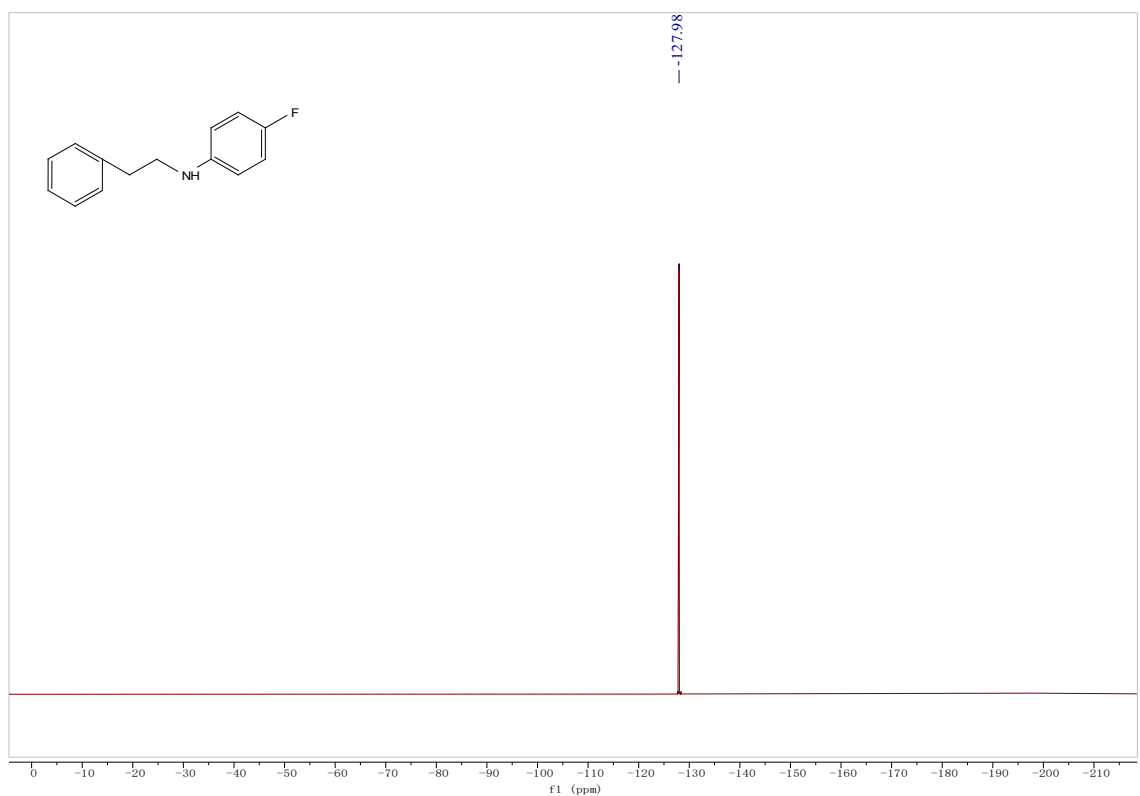
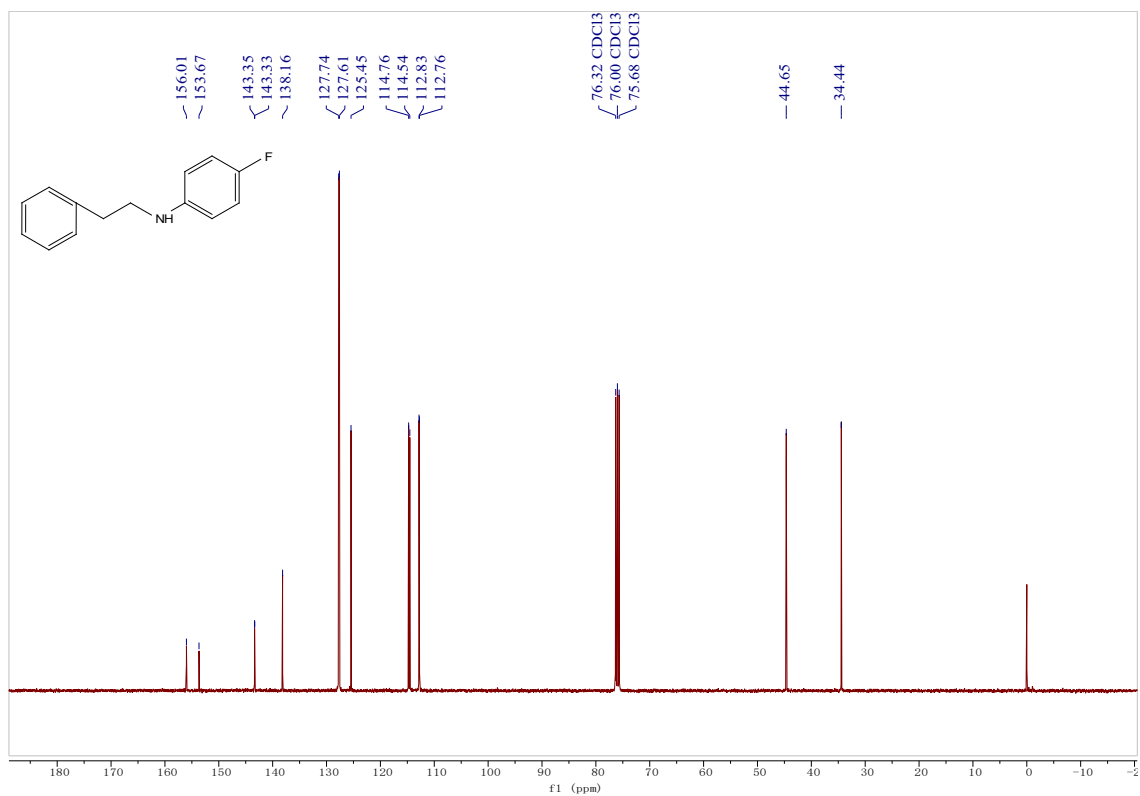
3-methyl-N-phenethylaniline (3f)



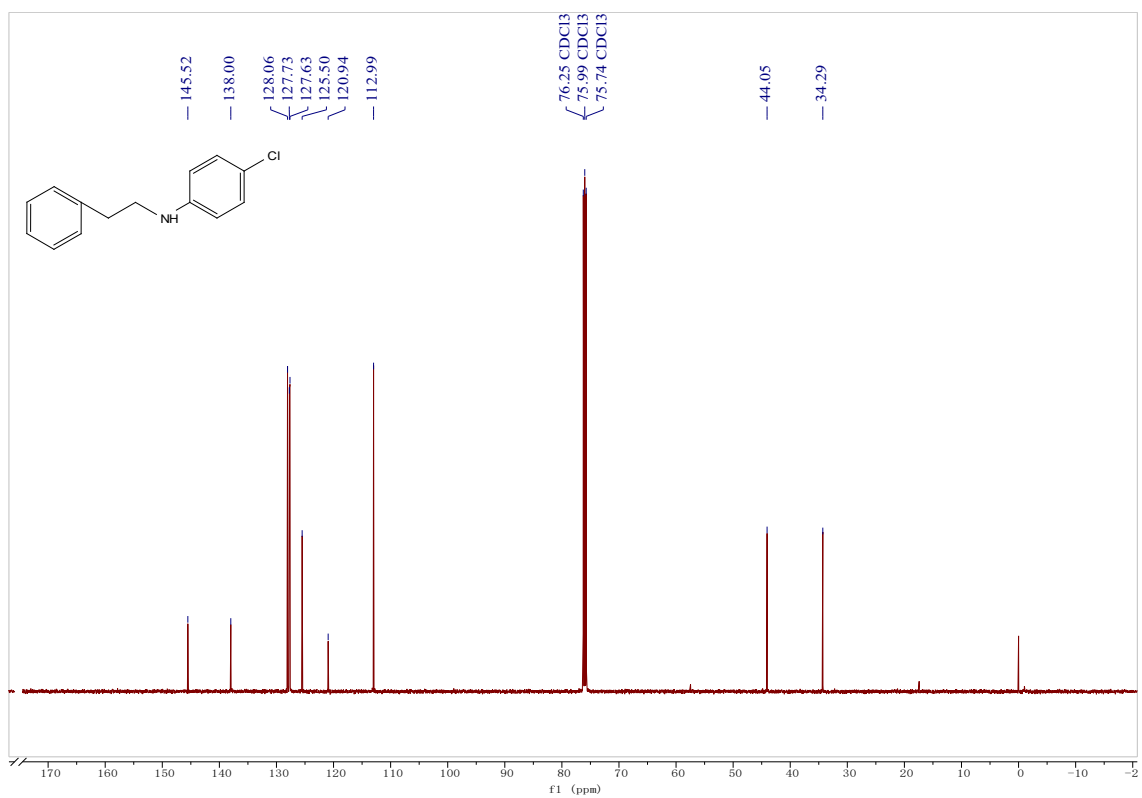
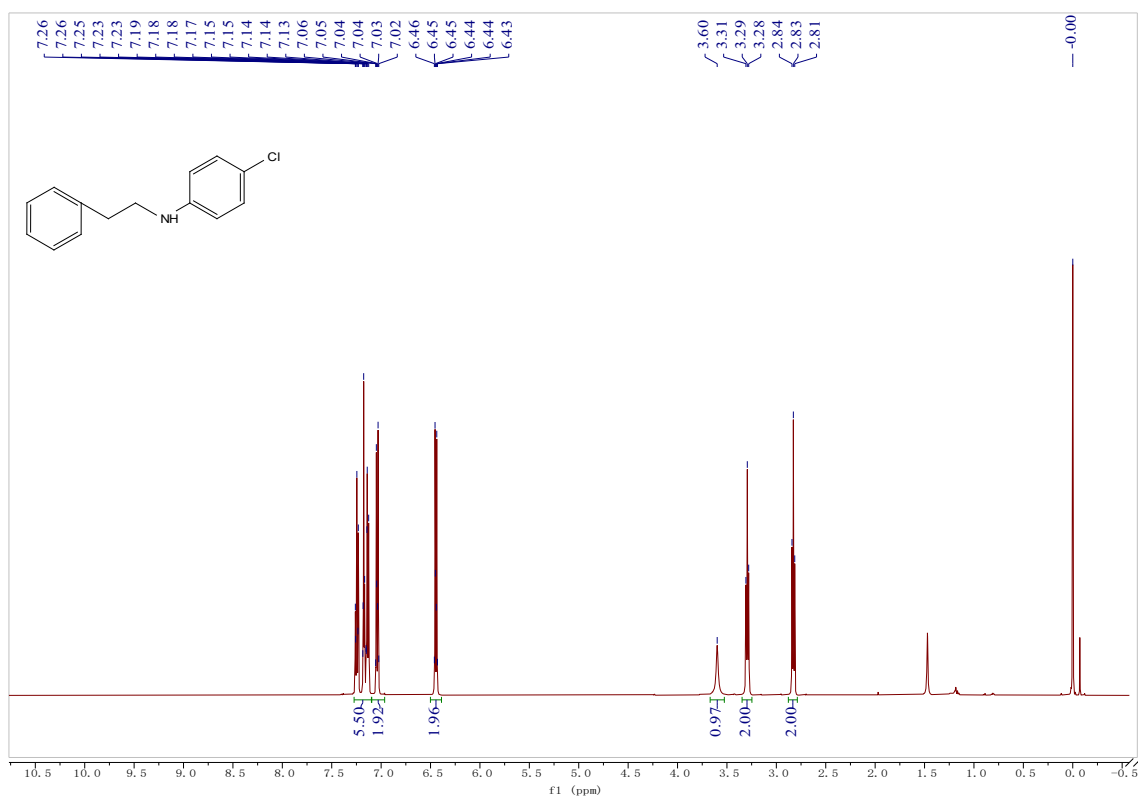


4-fluoro-N-phenethylaniline (3g)

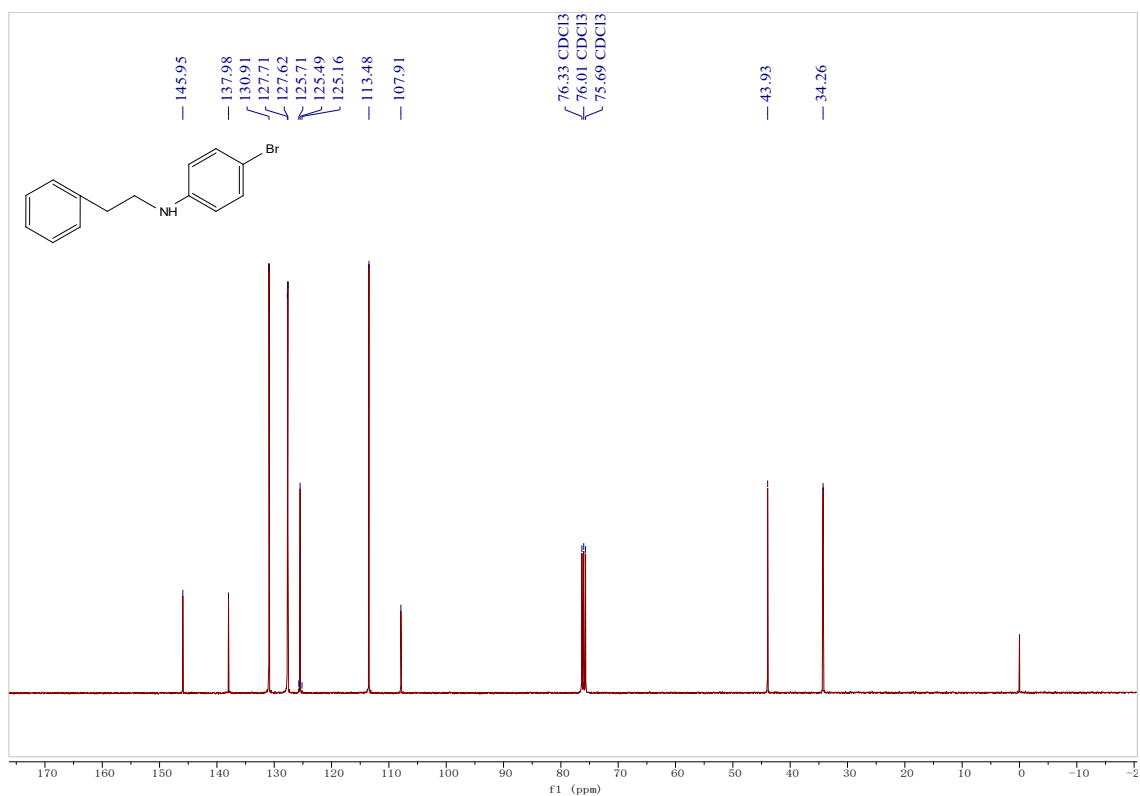
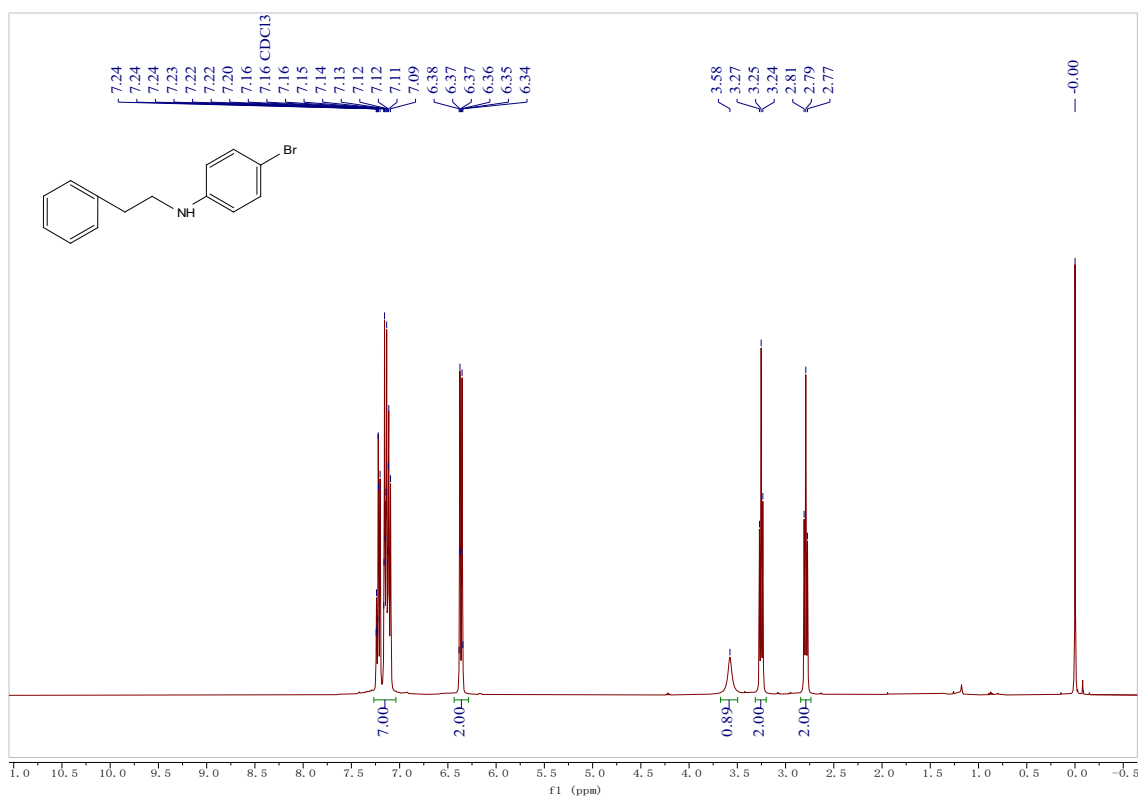




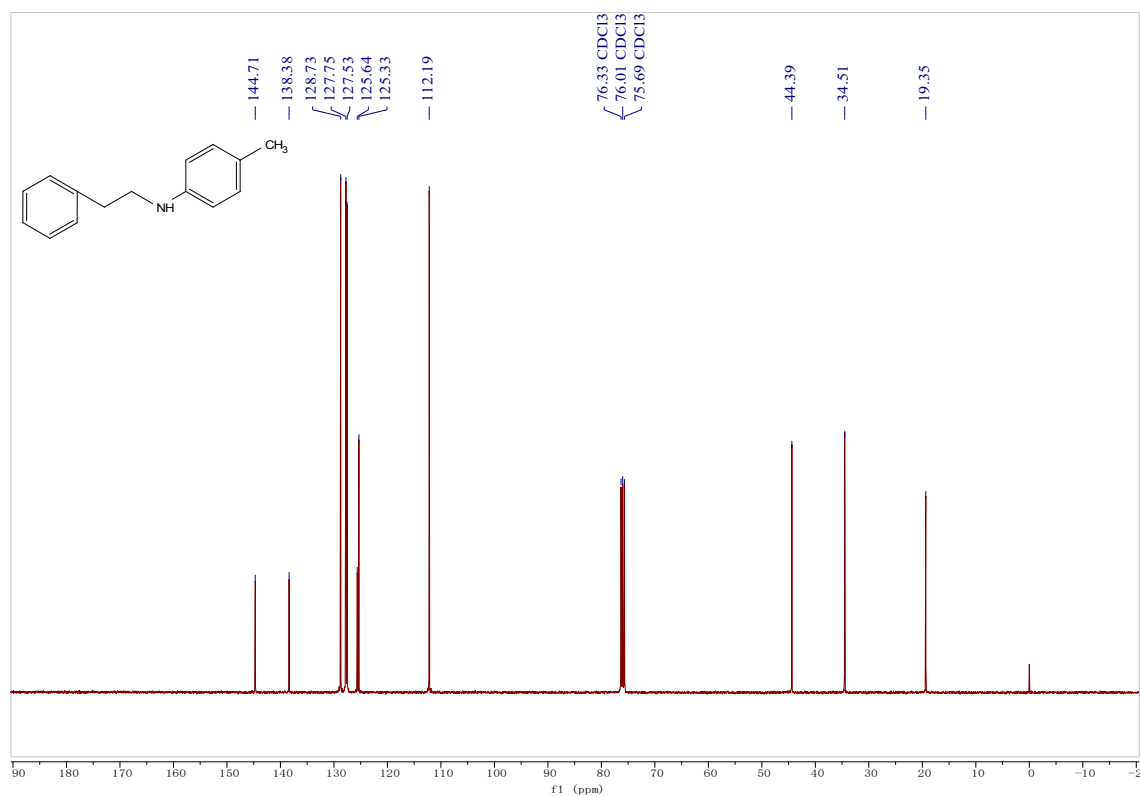
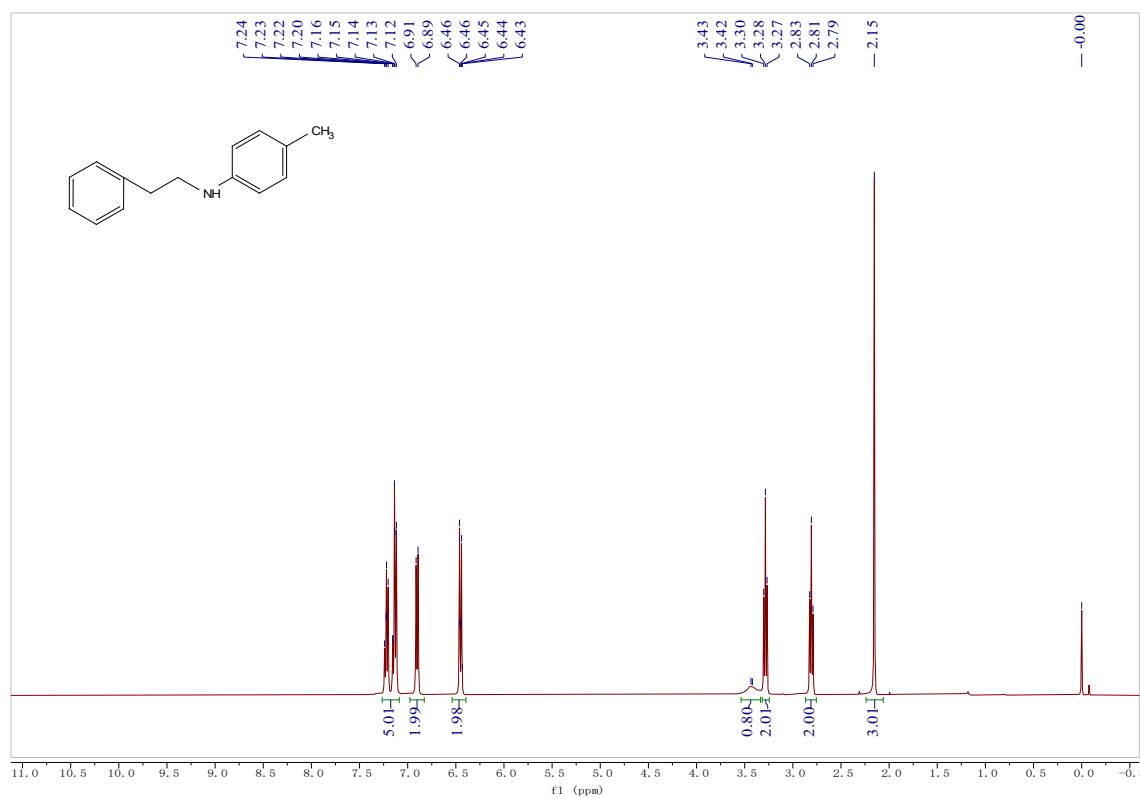
4-chloro-*N*-phenethylaniline (3h)



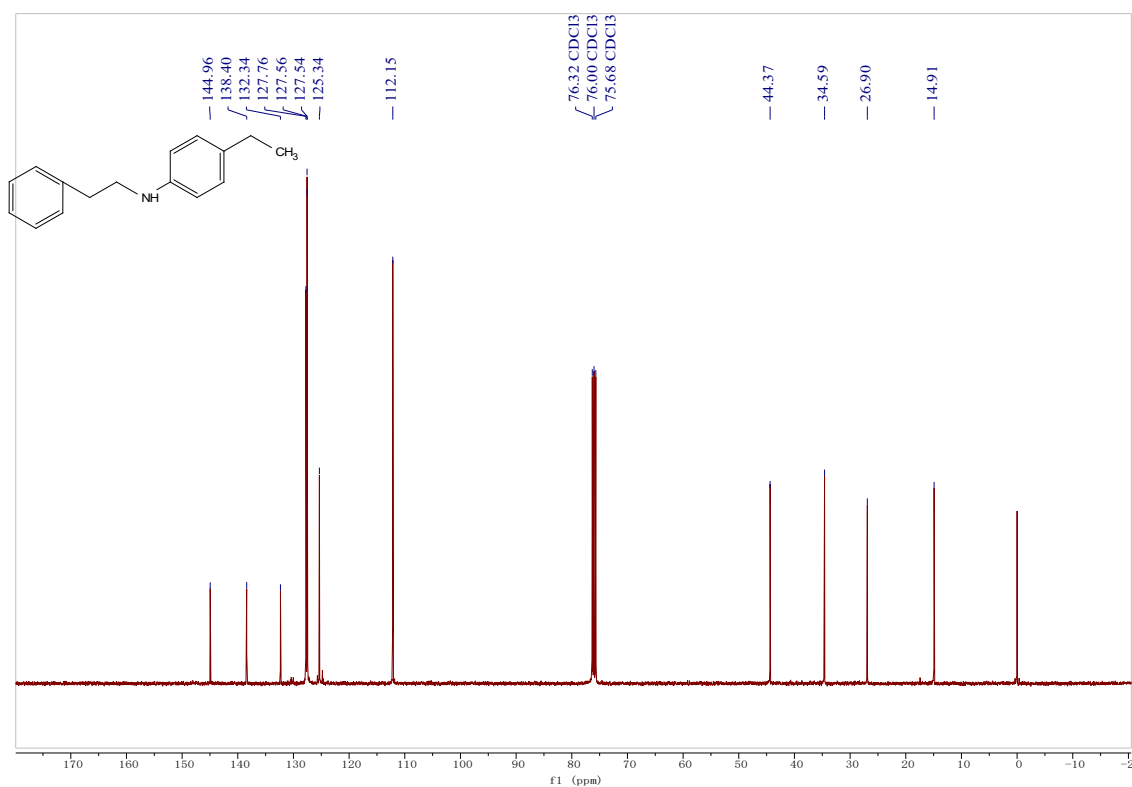
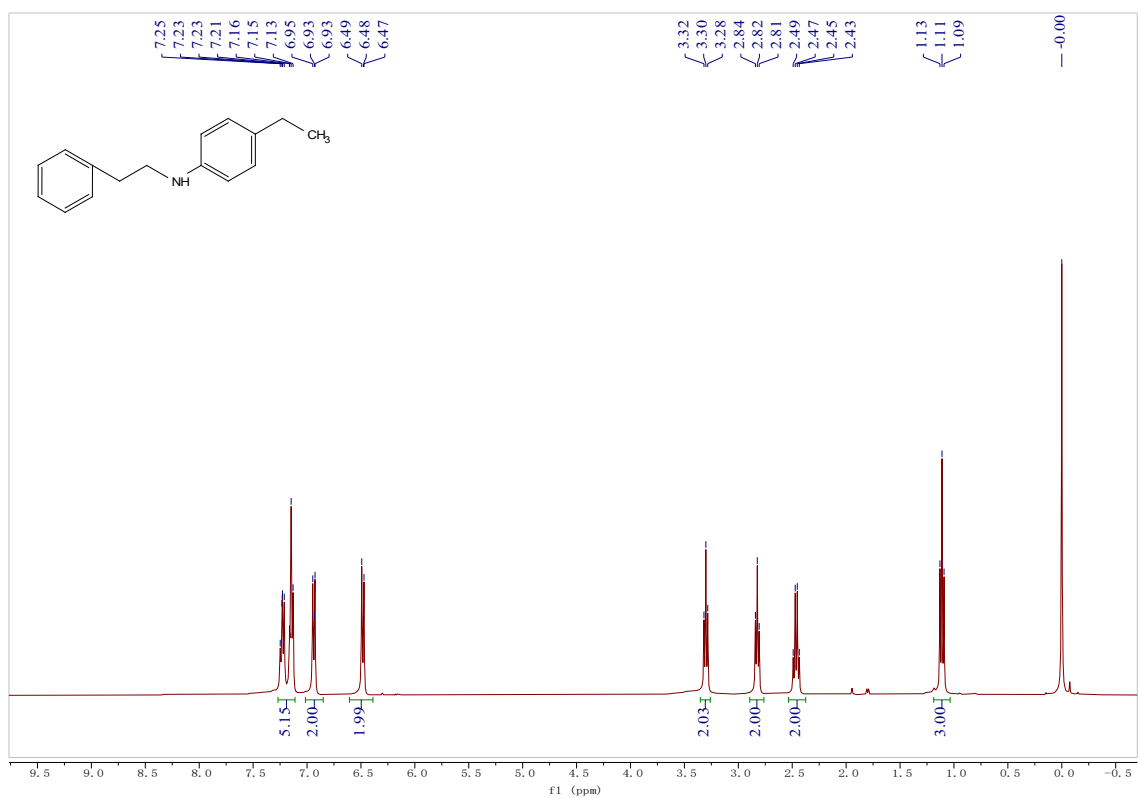
4-bromo-*N*-phenethylaniline (3i)



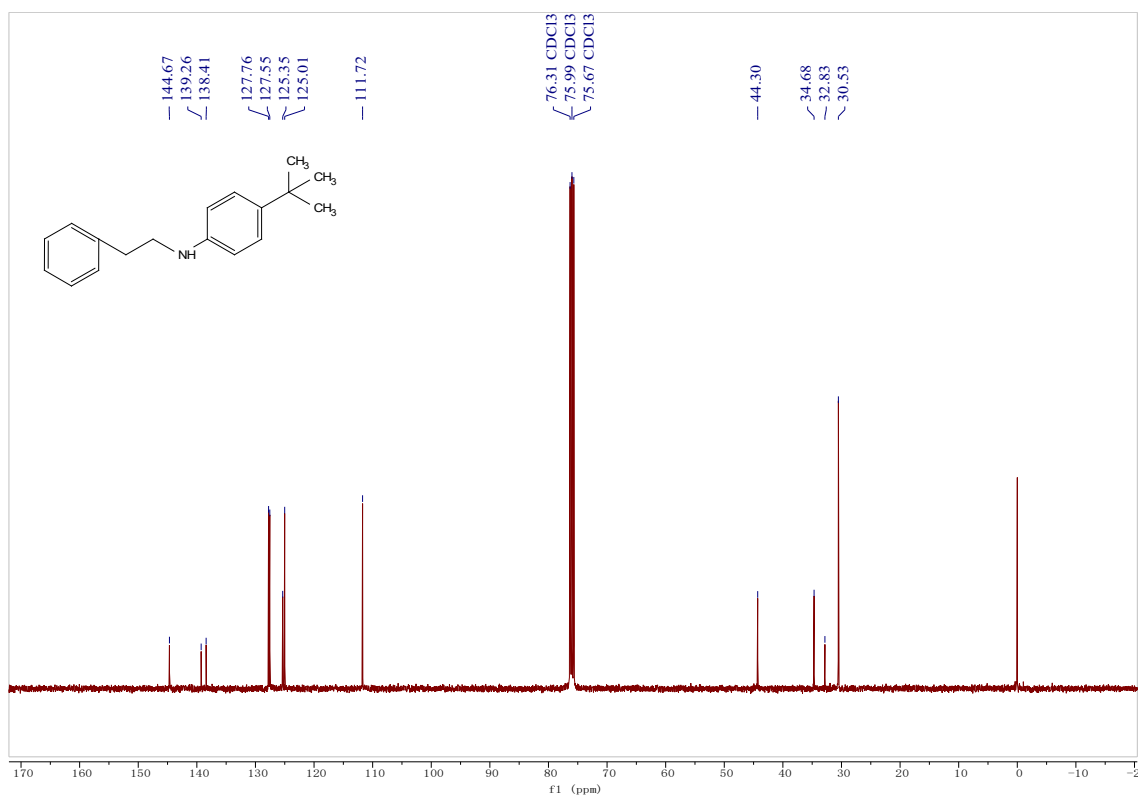
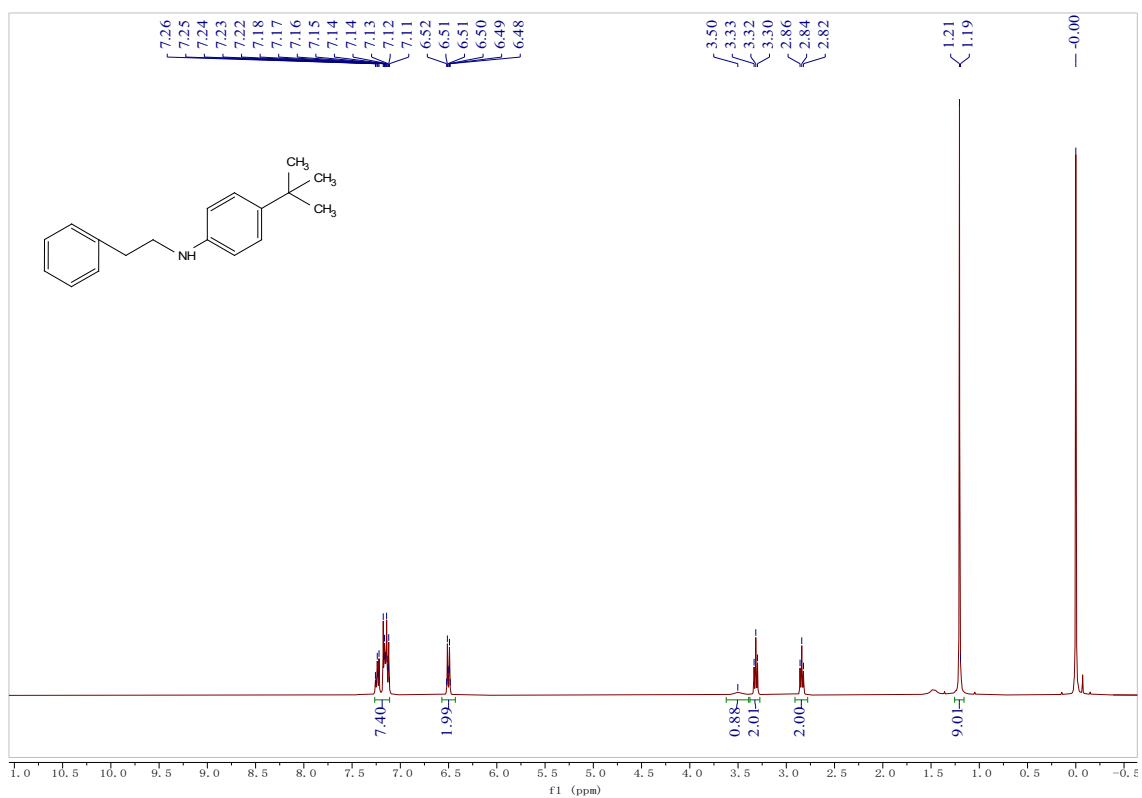
4-methyl-N-phenethylaniline (3j)



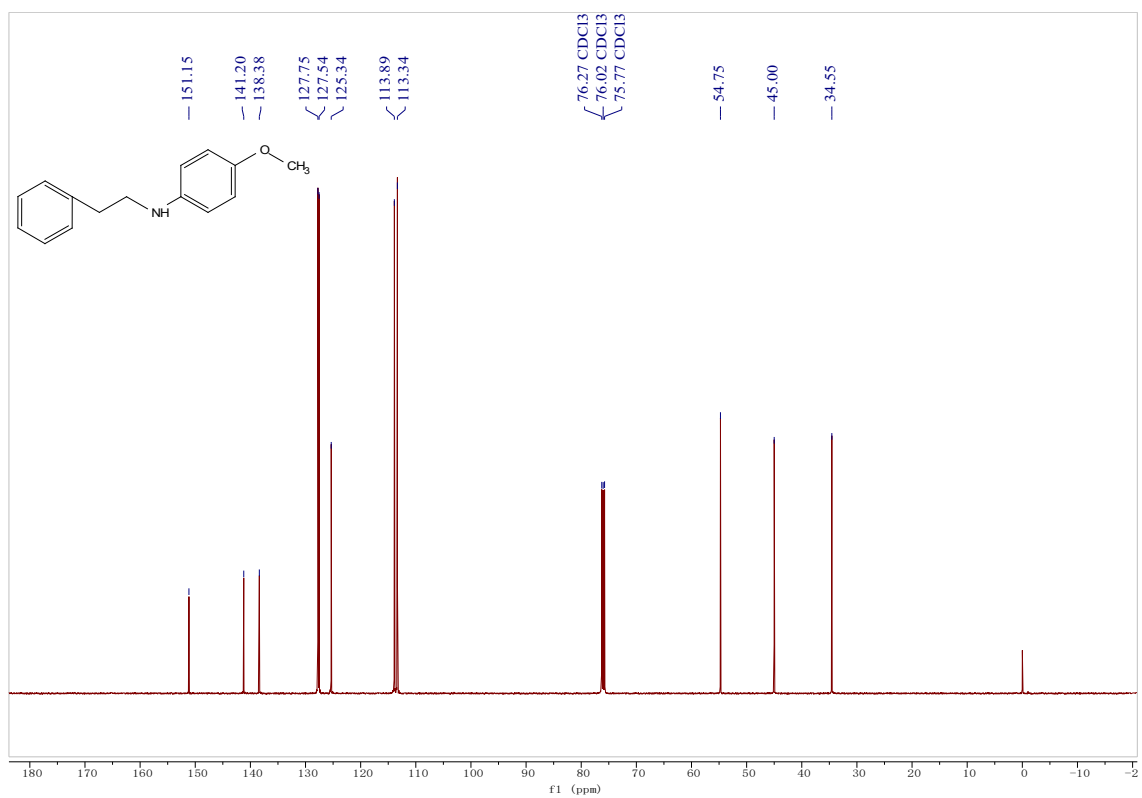
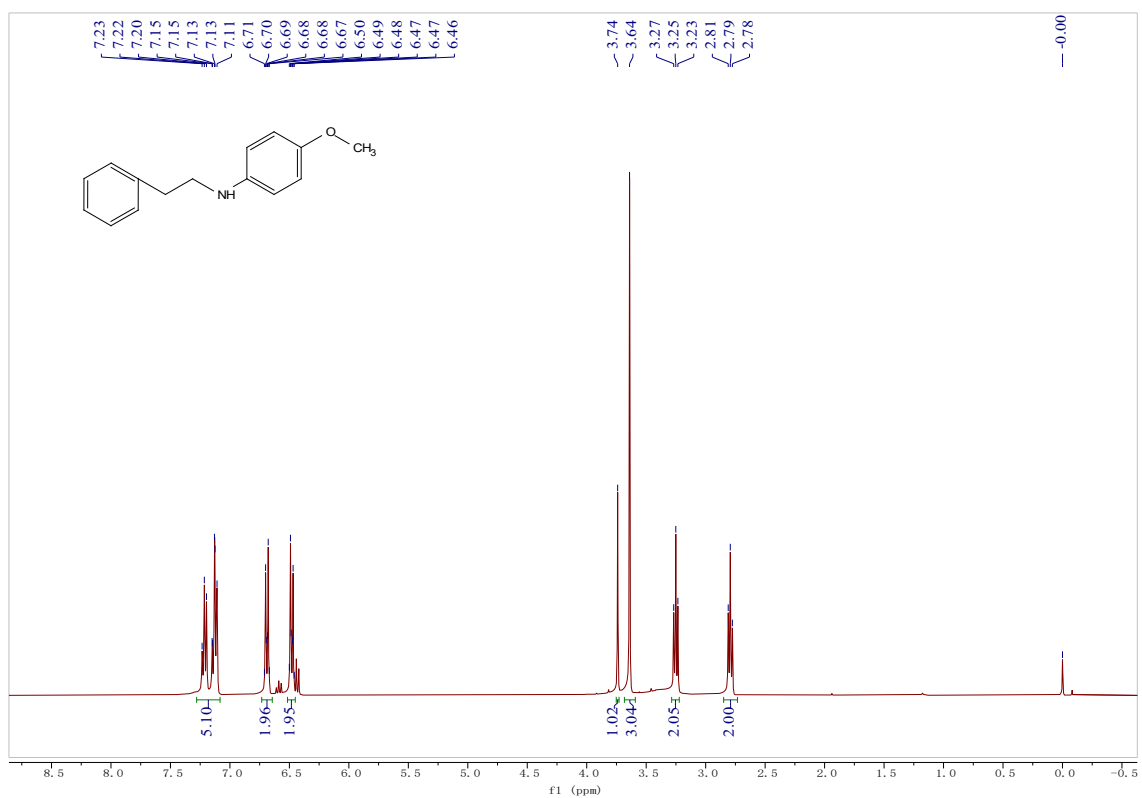
4-ethyl-*N*-phenethylaniline (3k)



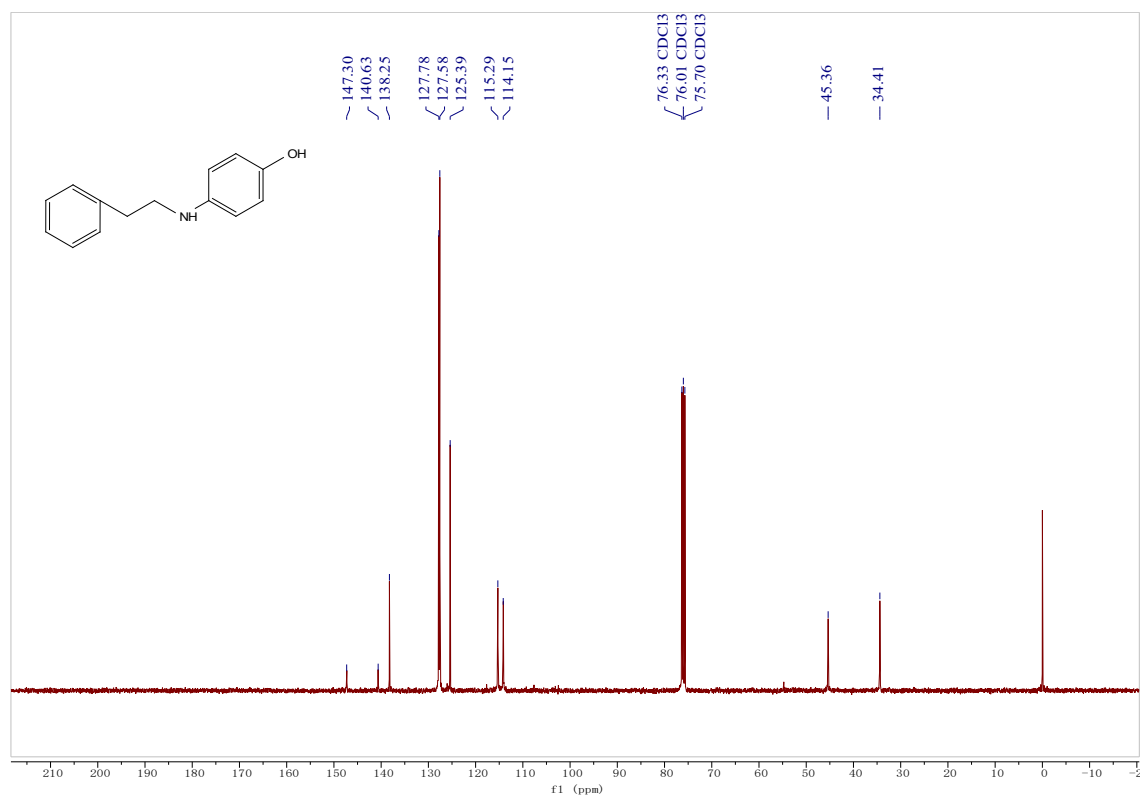
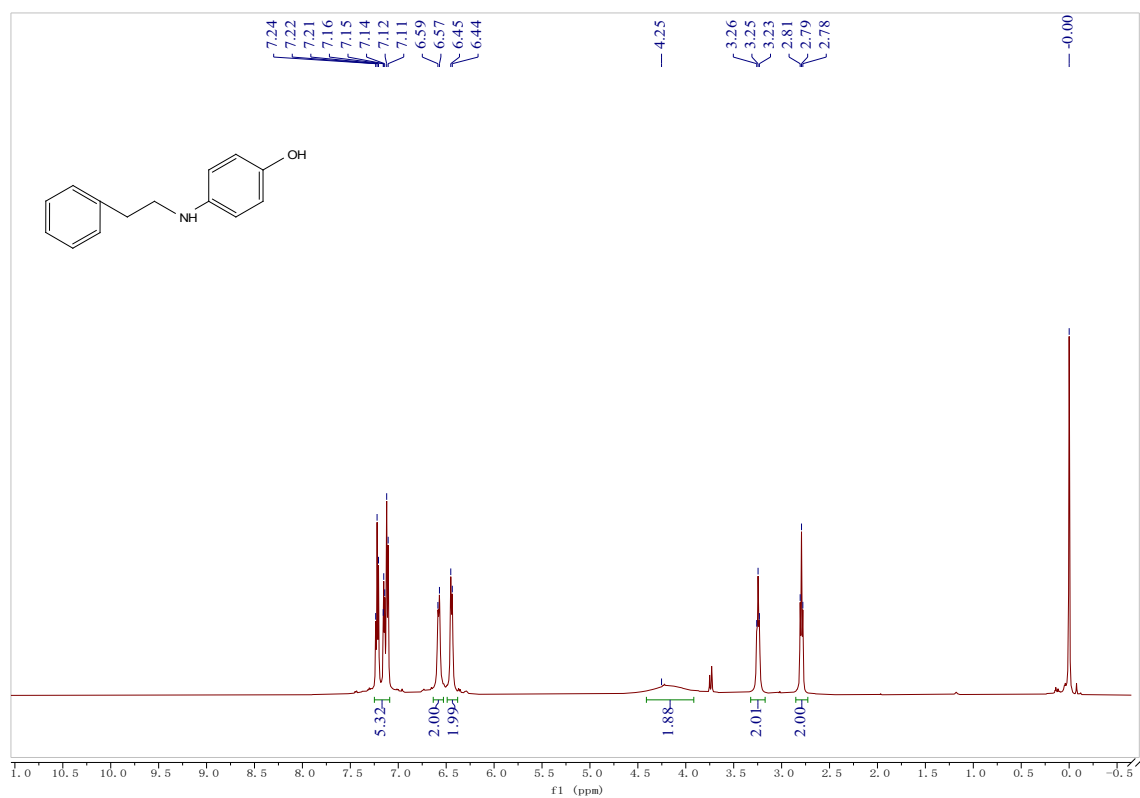
4-(*tert*-butyl)-*N*-phenethylamine (3I)



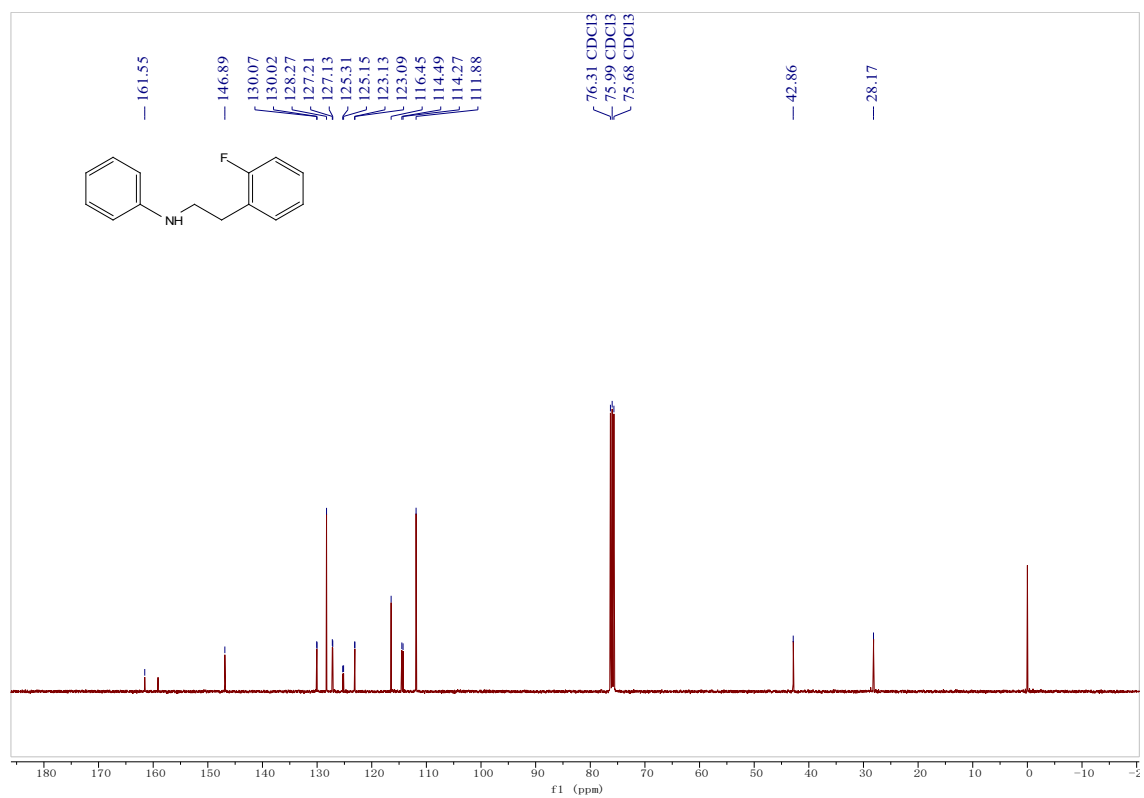
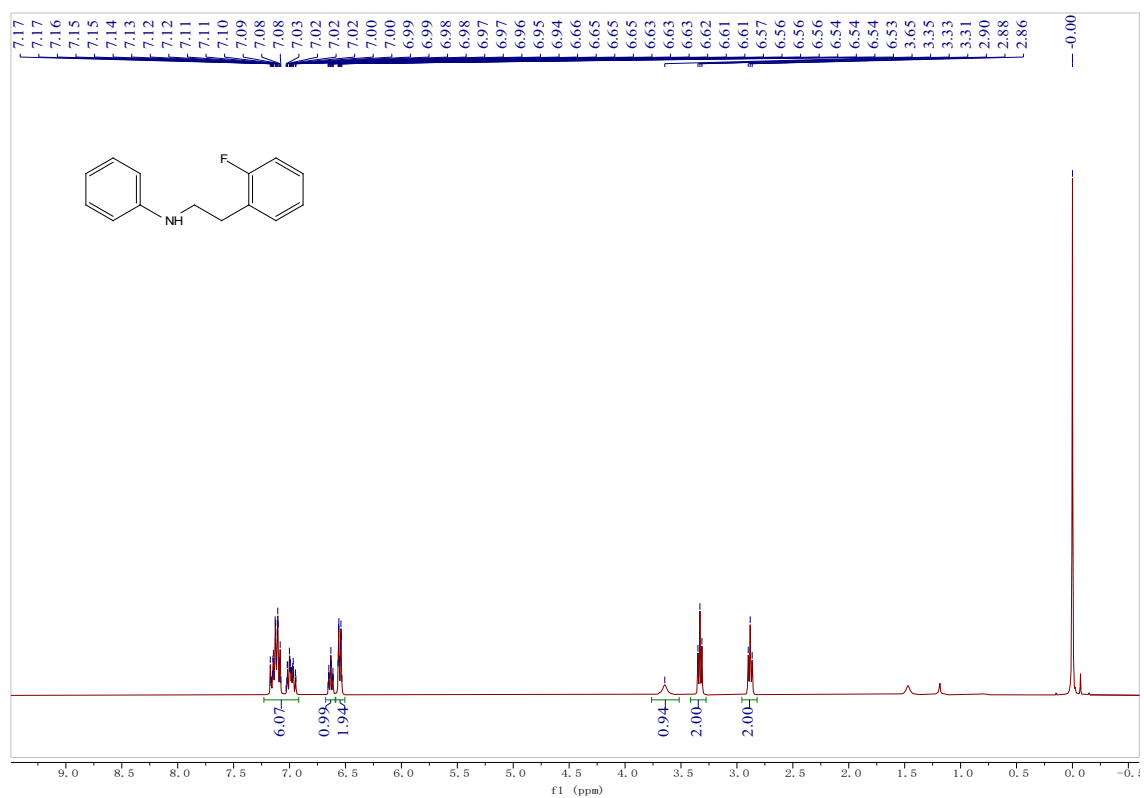
4-methoxy-*N*-phenethylaniline (3m)



4-(phenethylamino)phenol (3n)

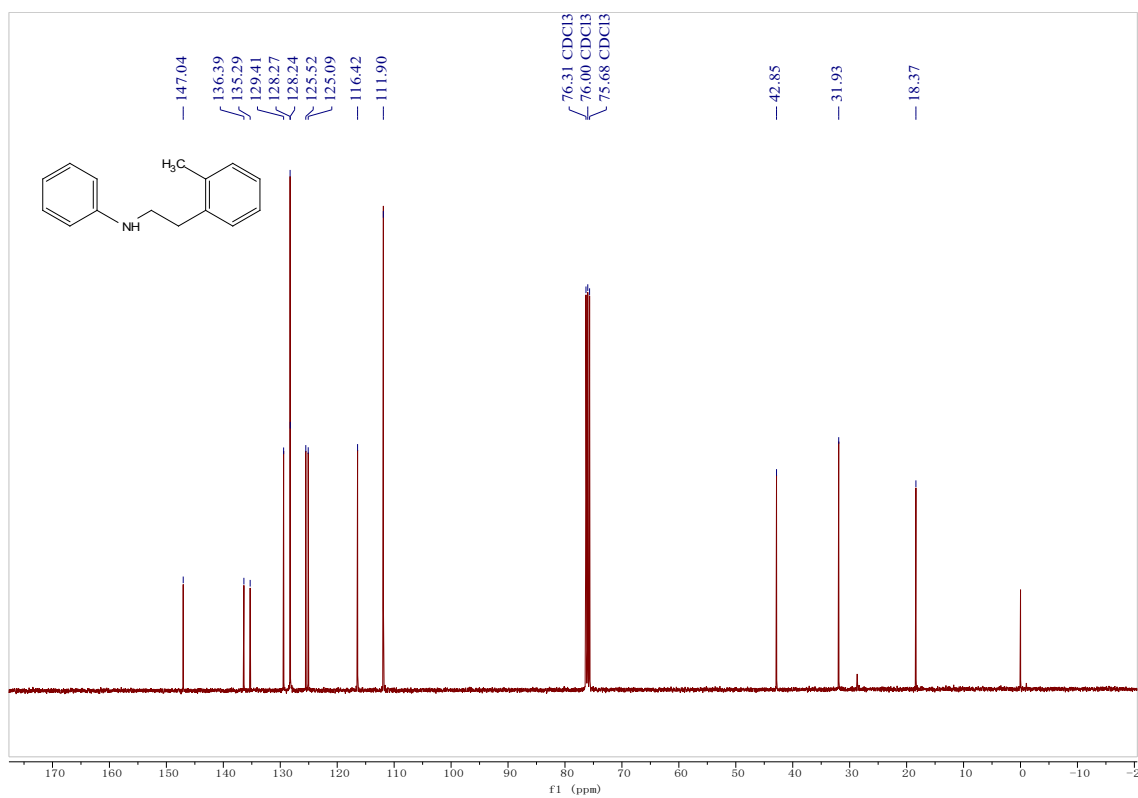
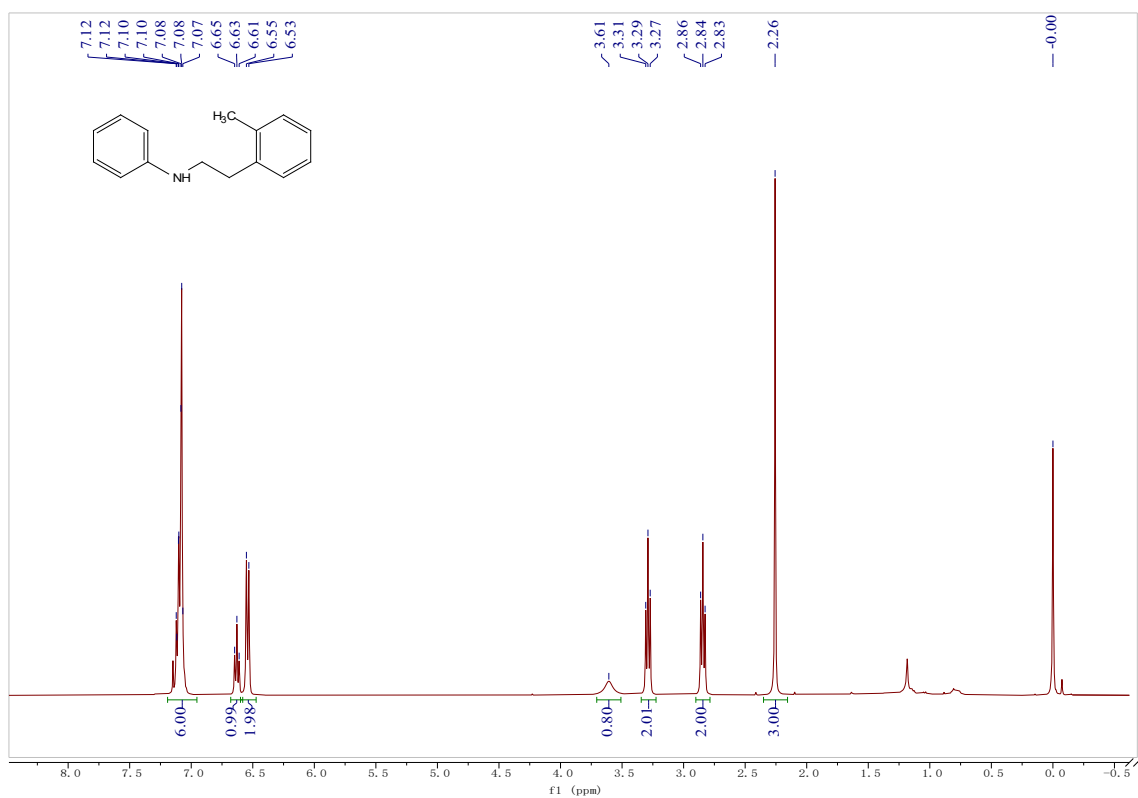


***N*-(2-fluorophenethyl)aniline (5b)**

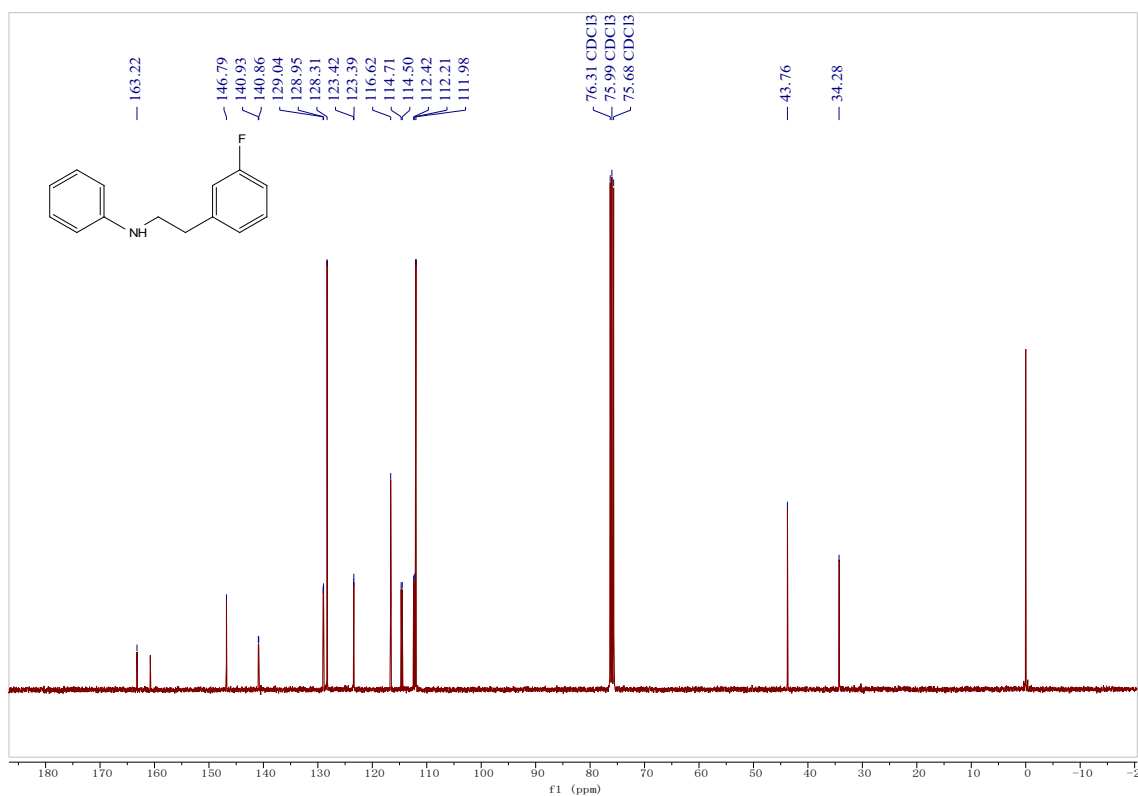
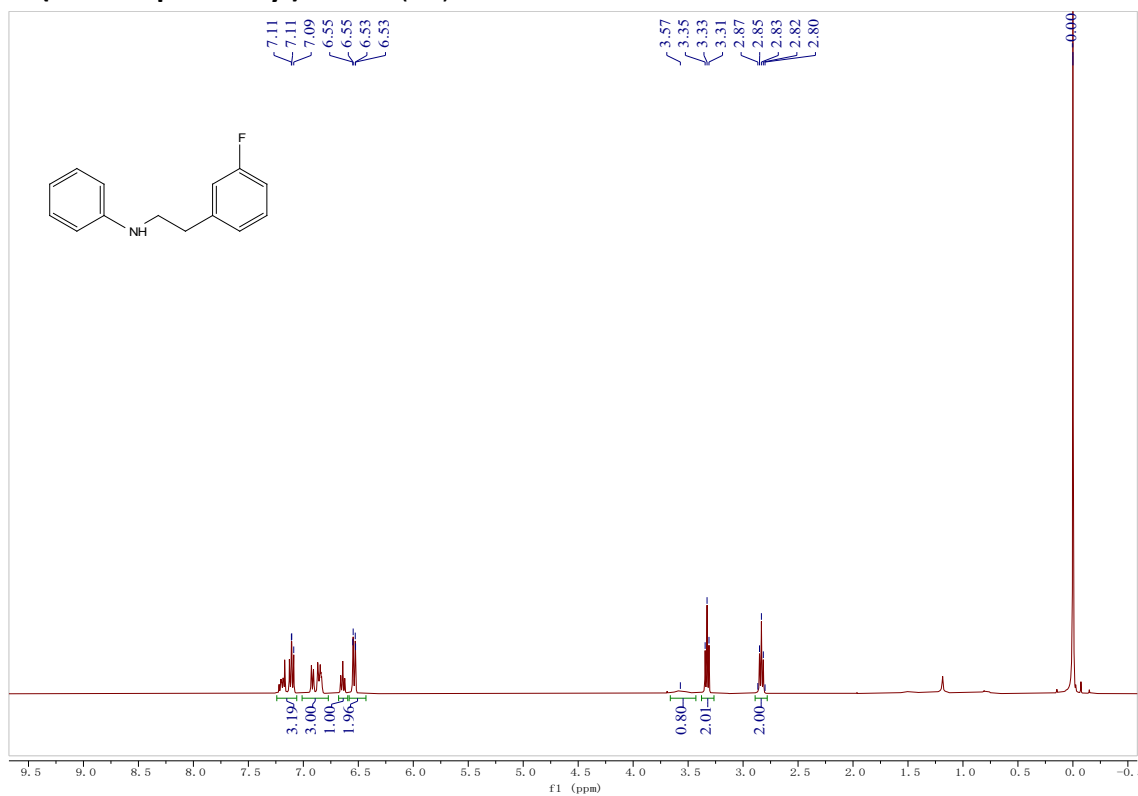




***N*-(2-methylphenethyl)aniline (5c)**

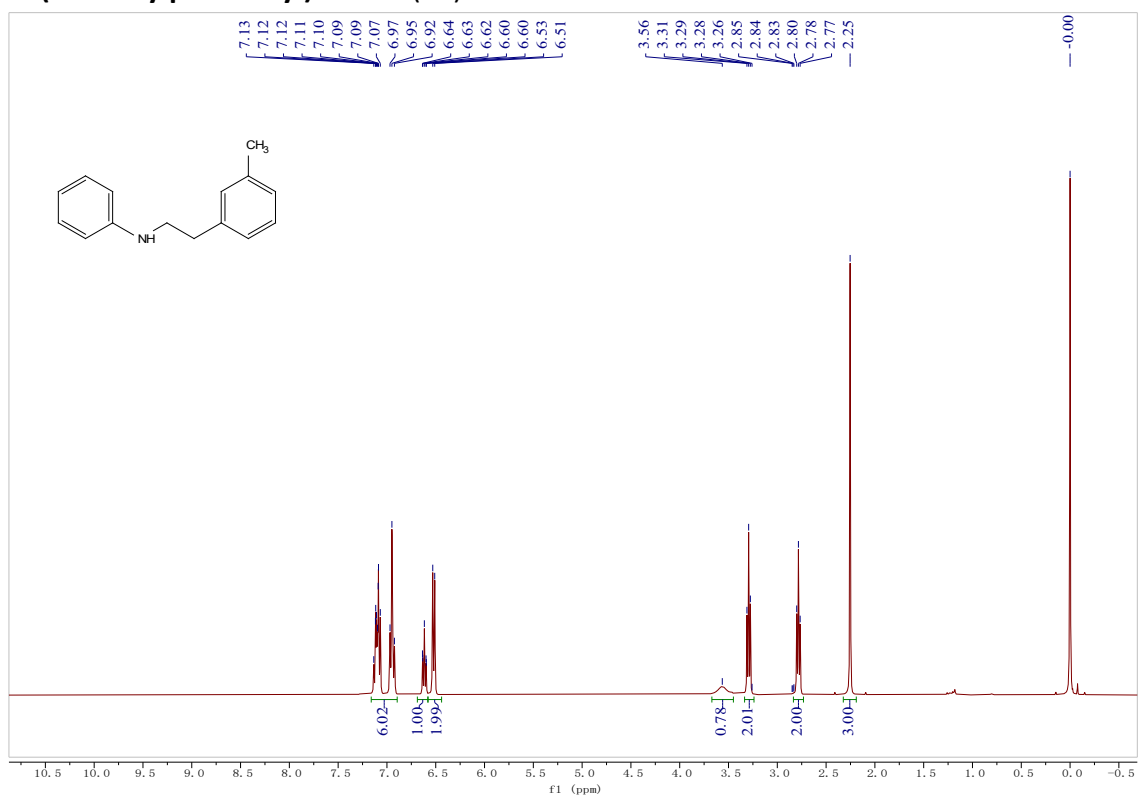


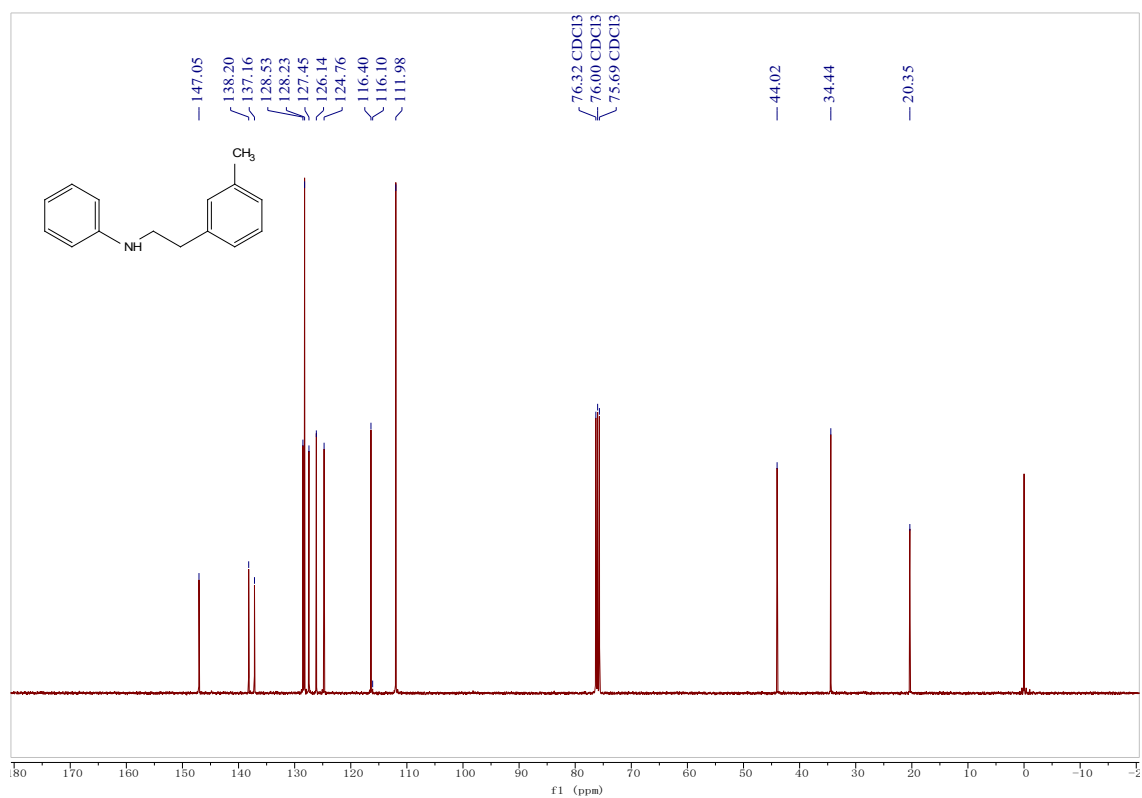
***N*-(3-fluorophenethyl)aniline (5d)**



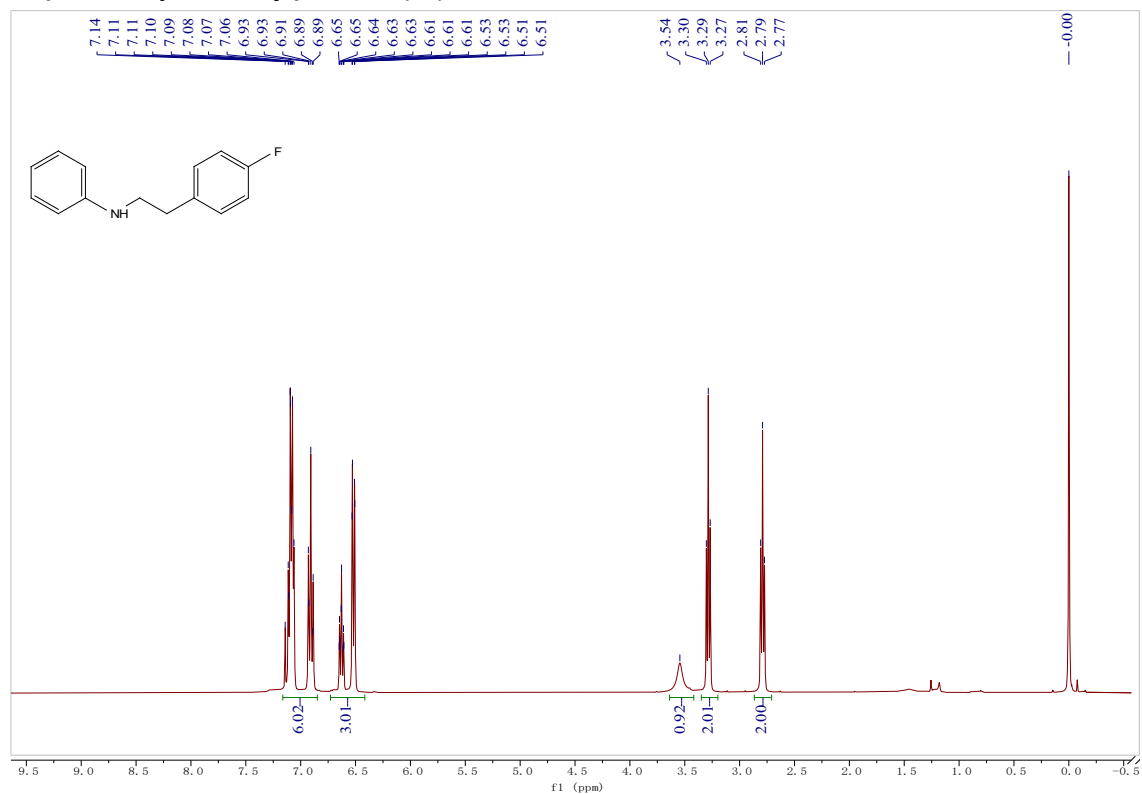


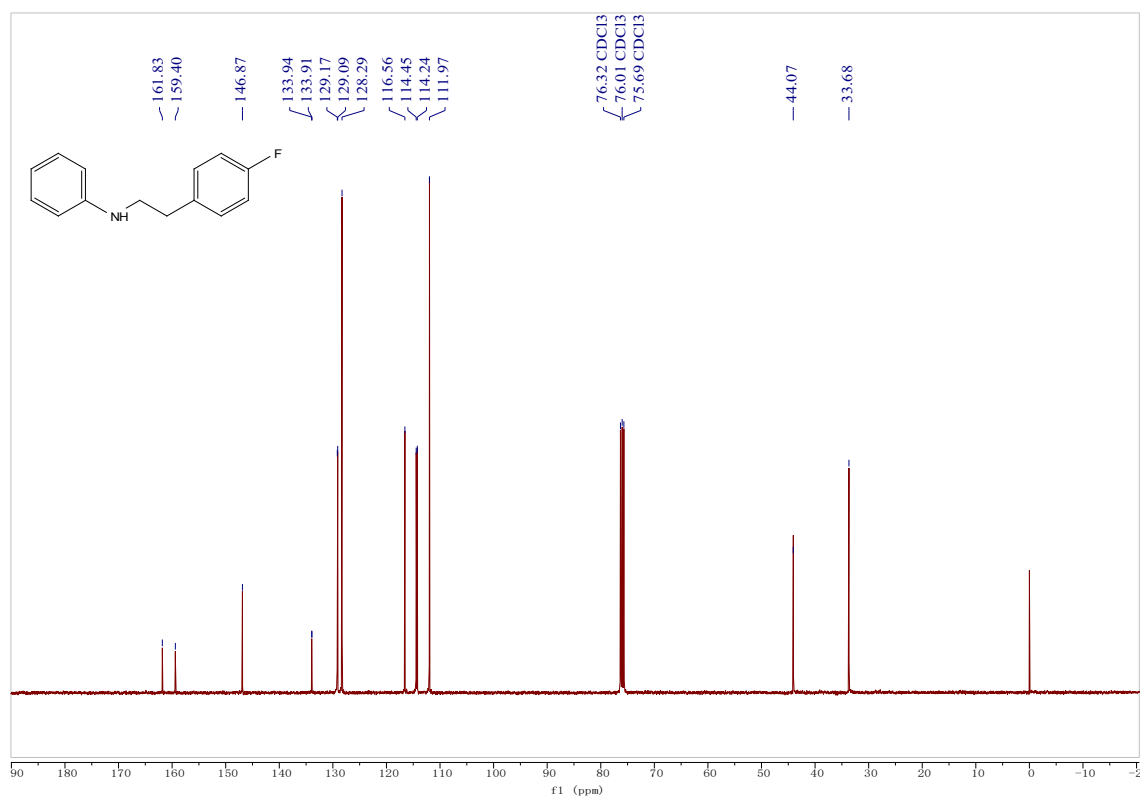
***N*-(3-methylphenethyl)aniline (5e)**

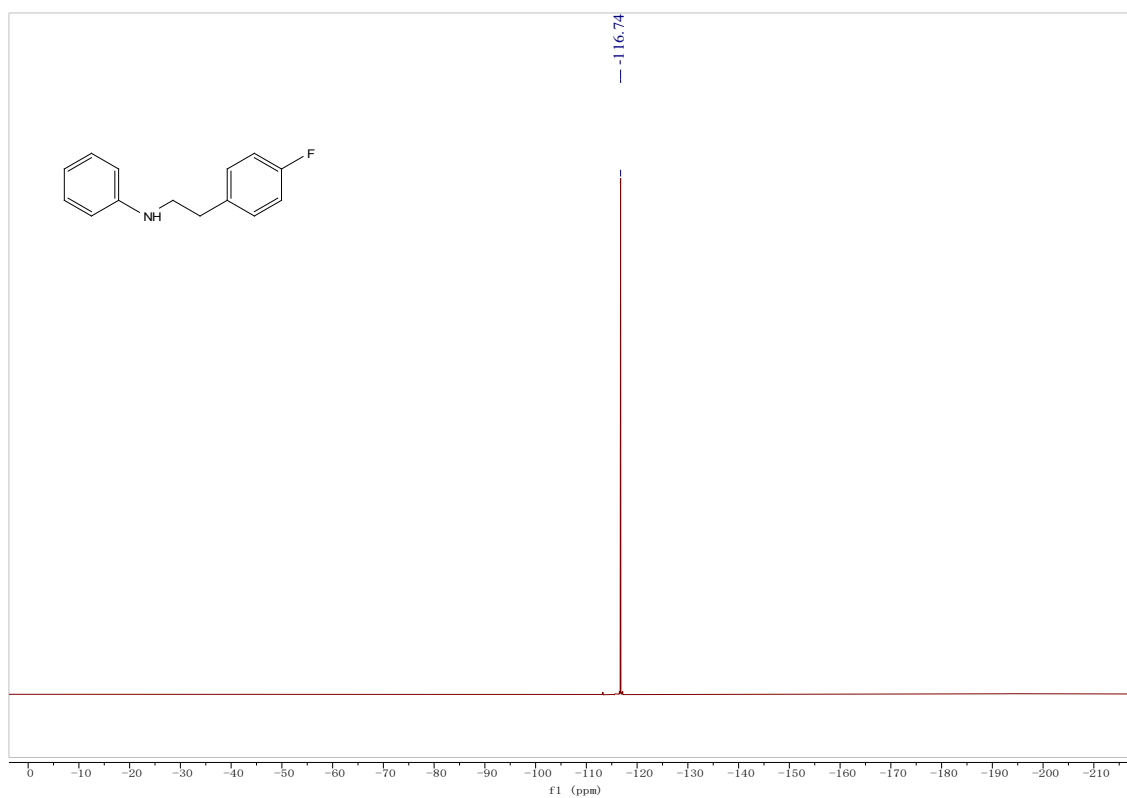




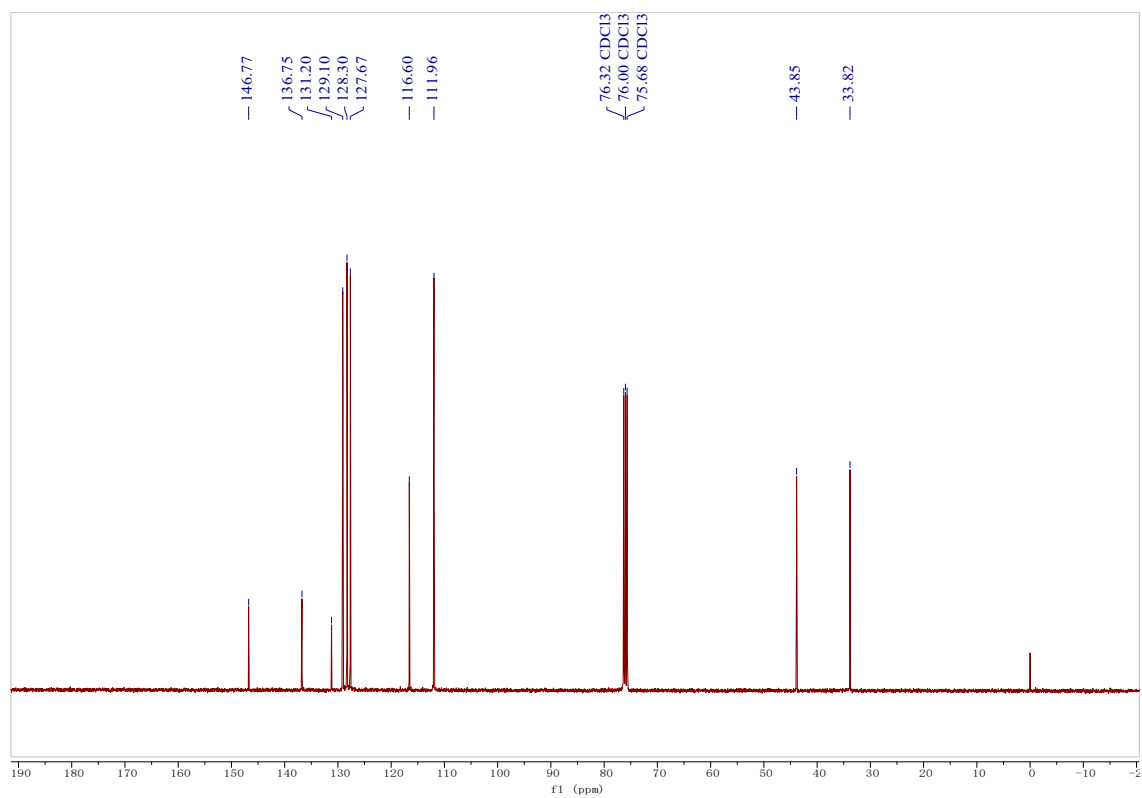
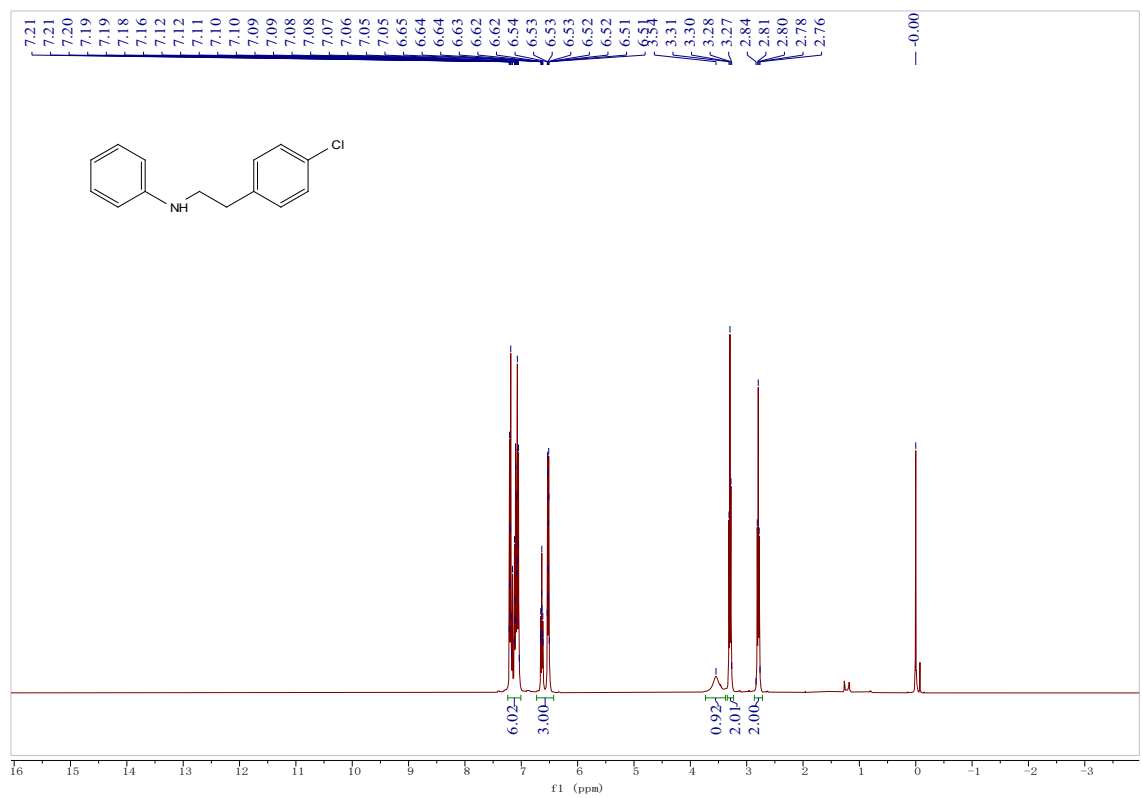
***N*-(4-fluorophenethyl)aniline (5f)**



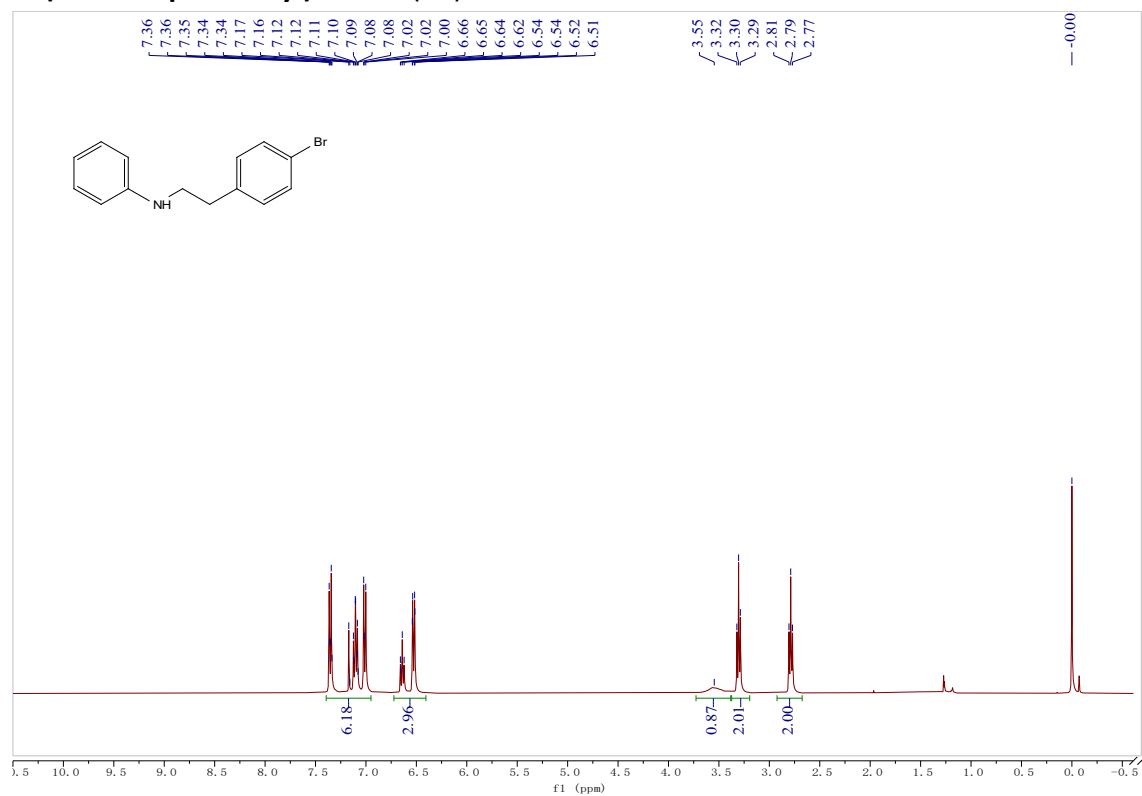


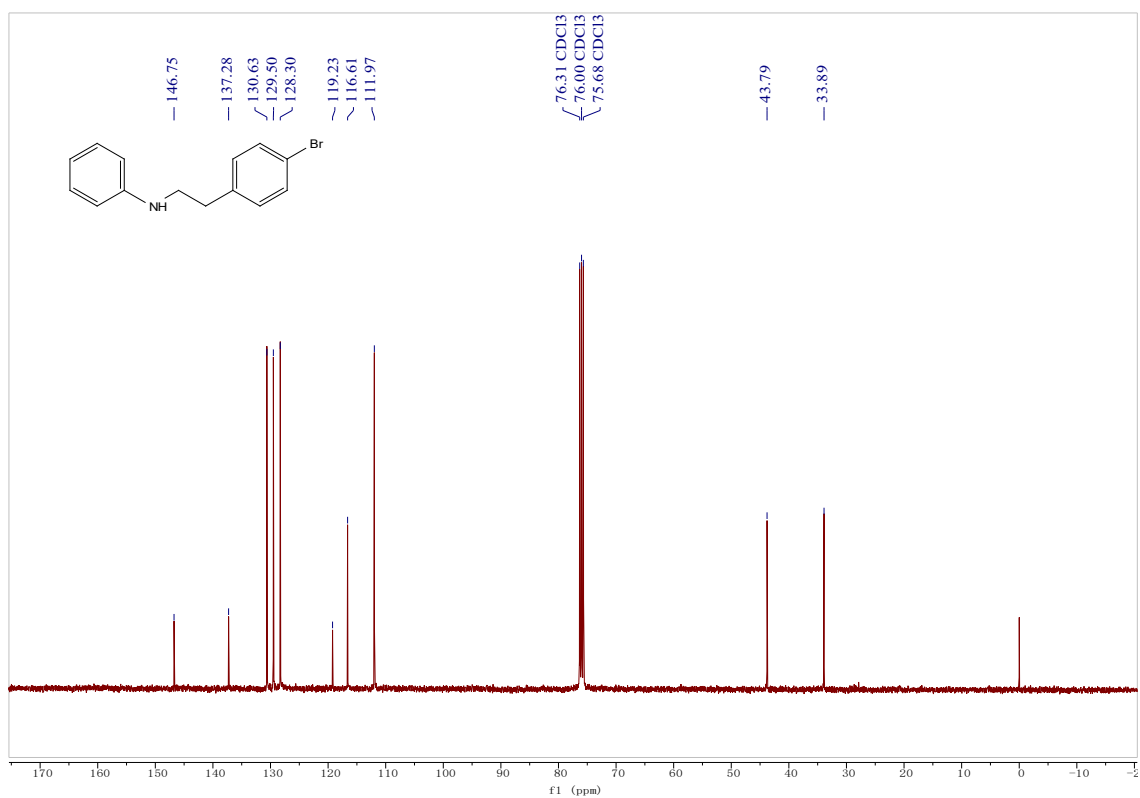


***N*-(4-chlorophenethyl)aniline (5g)**

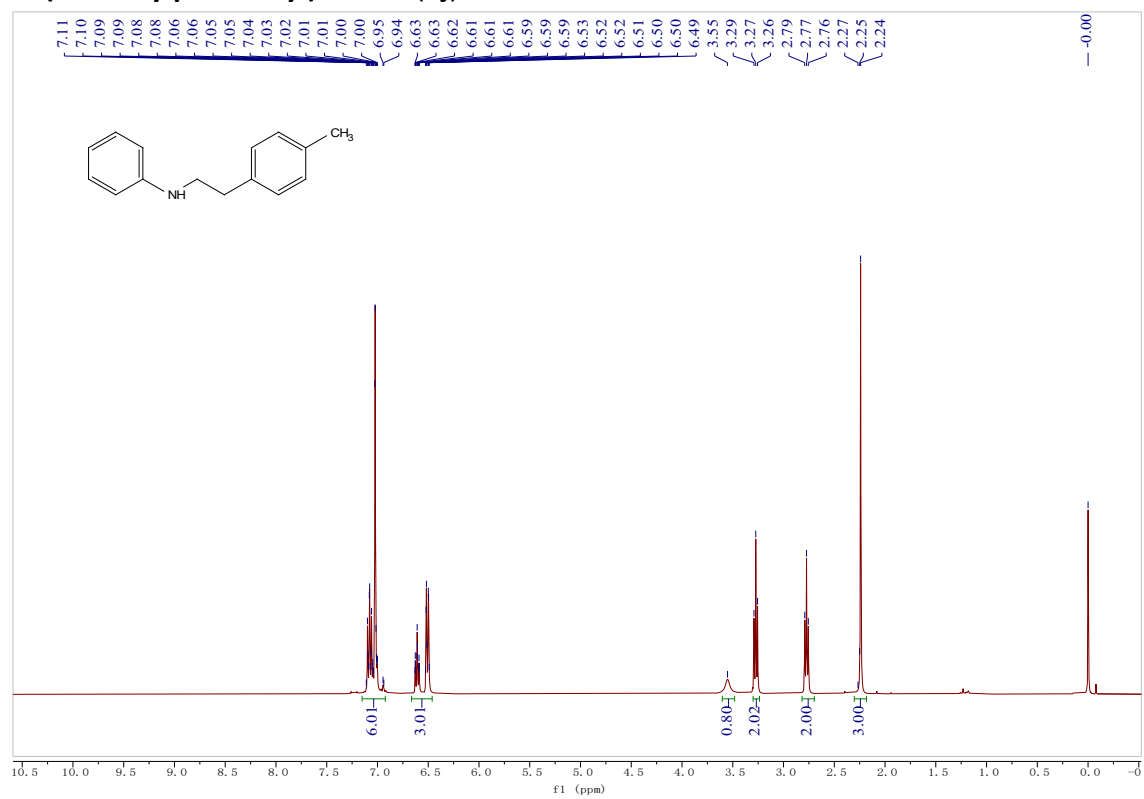


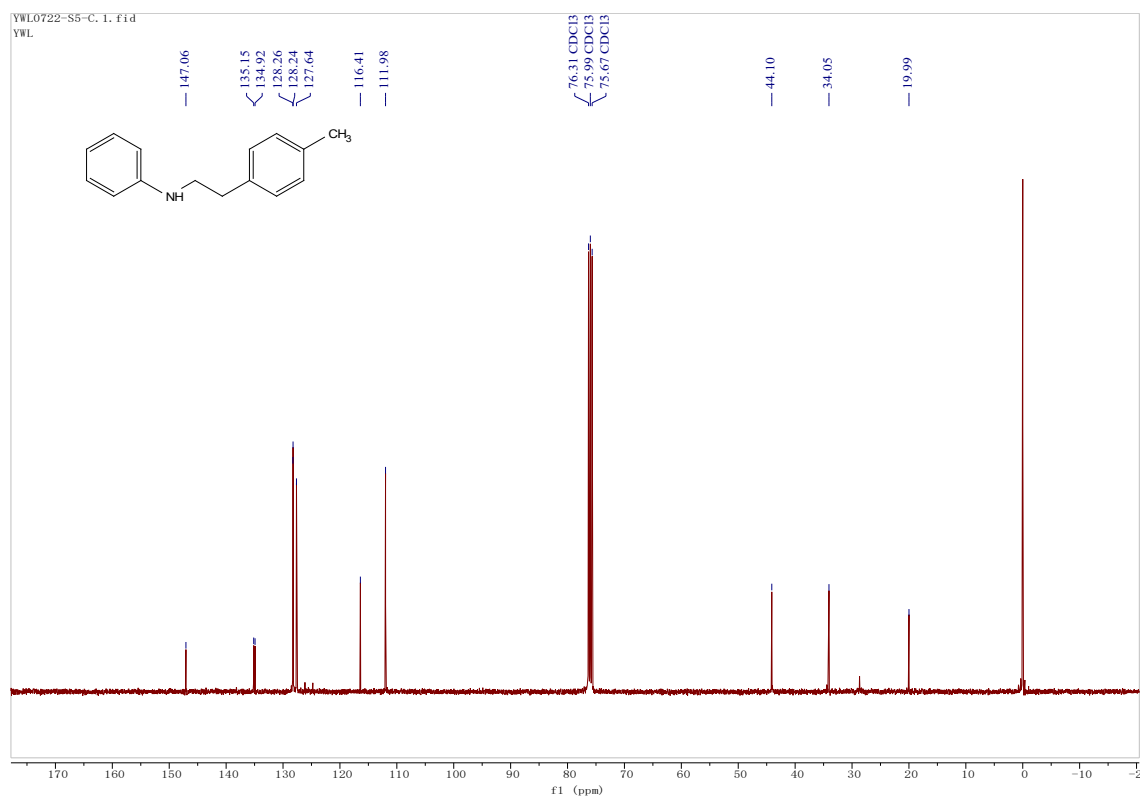
***N*-(4-bromophenethyl)aniline (5h)**



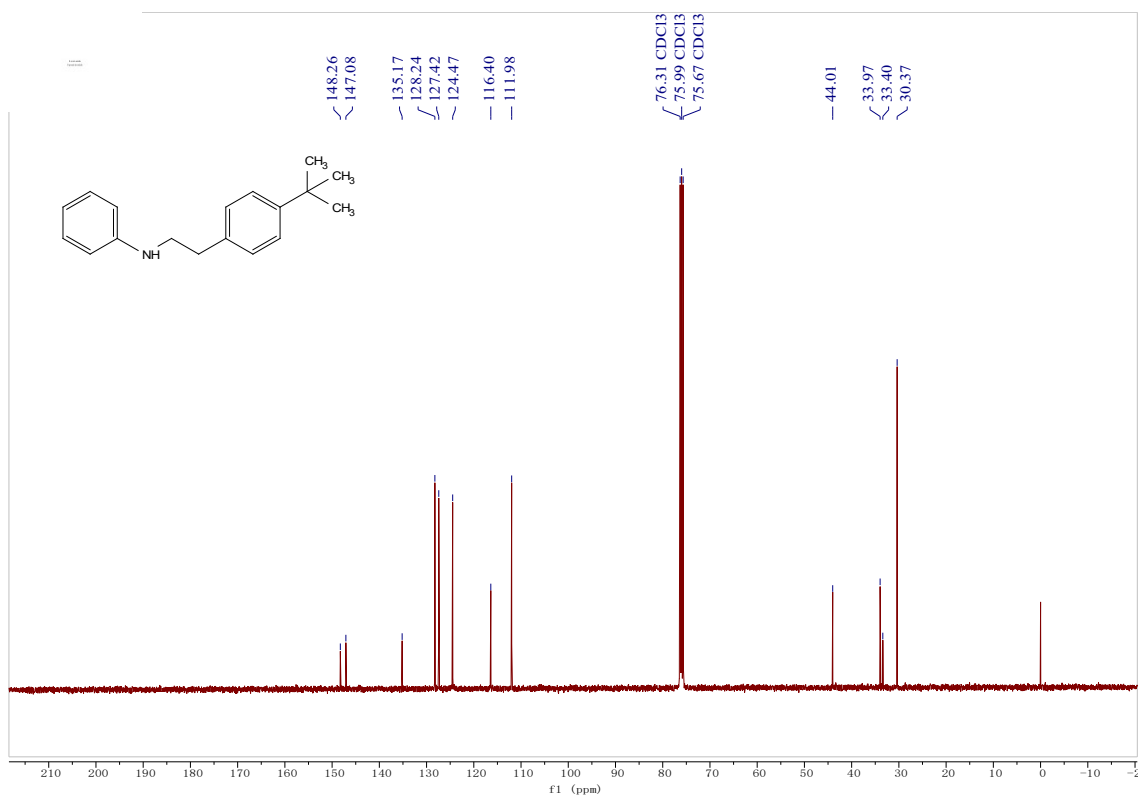
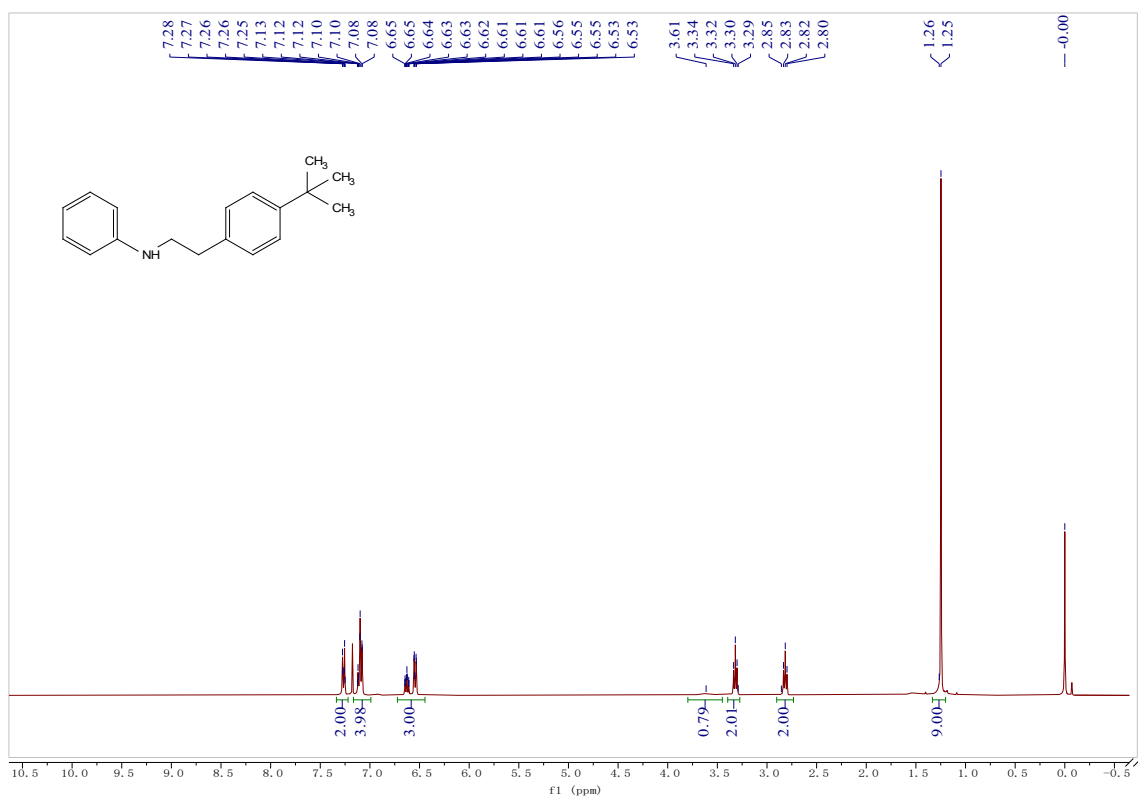


***N*-(4-methylphenethyl)aniline (5j)**

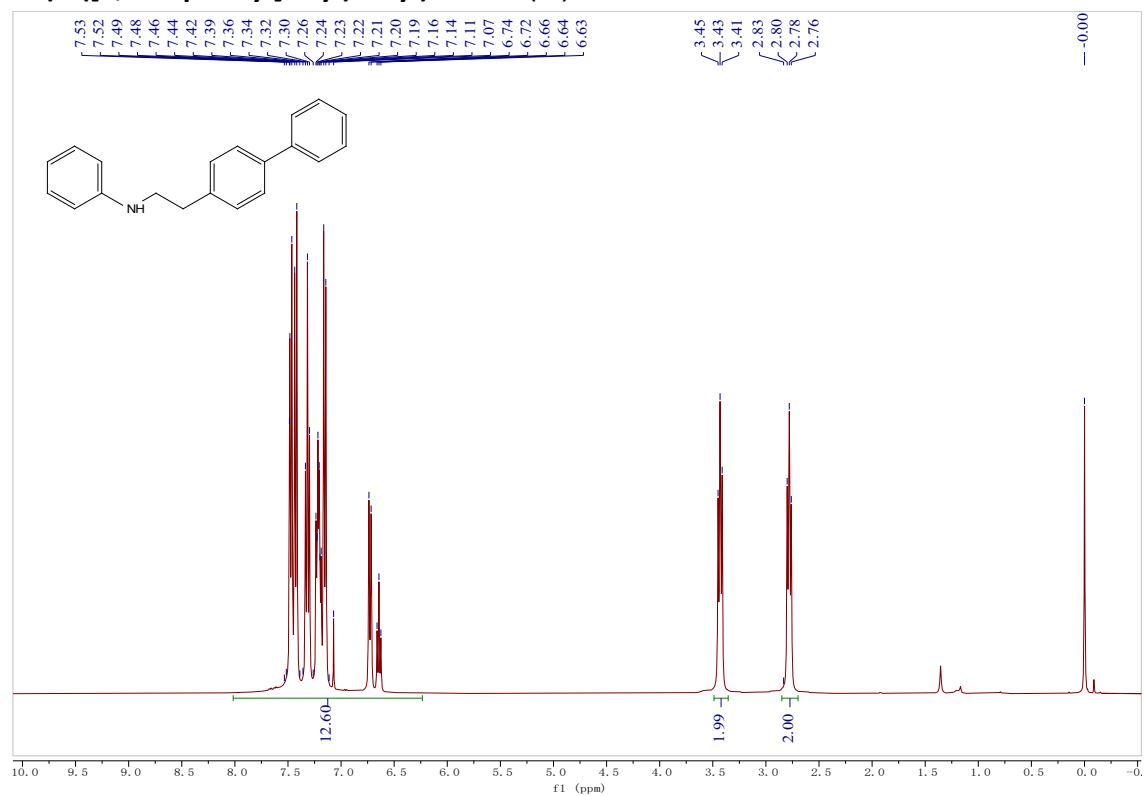


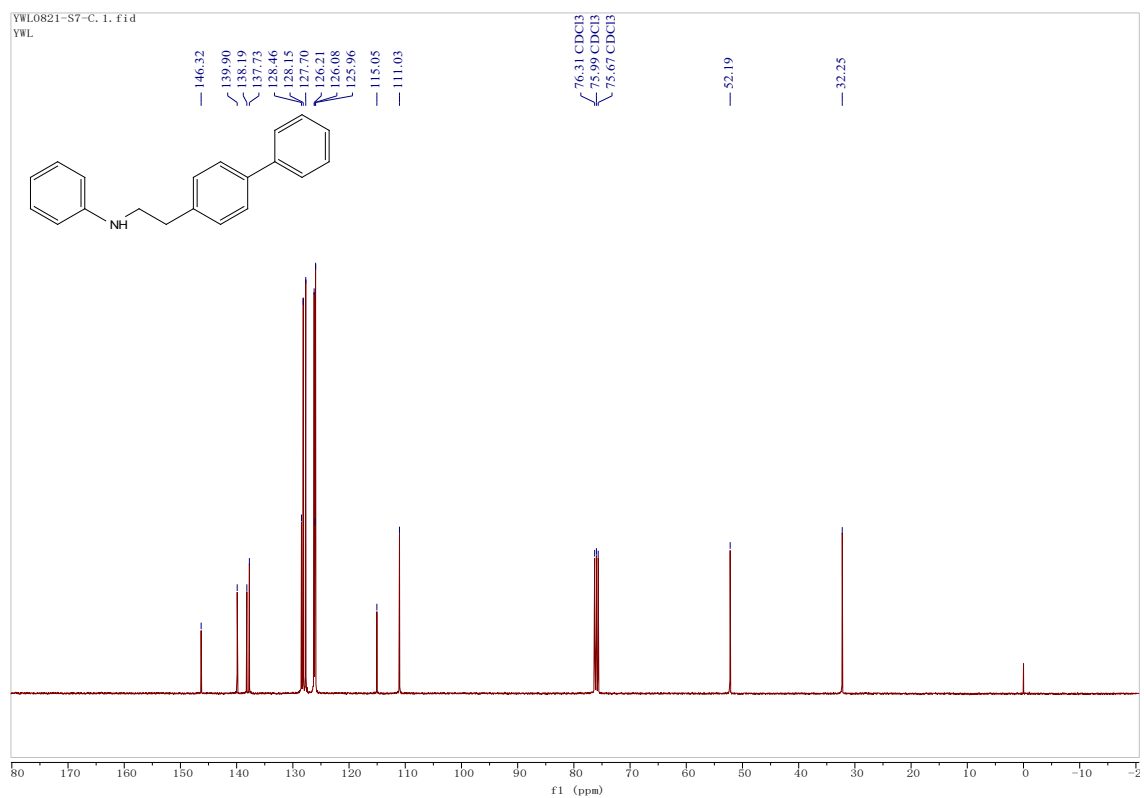


***N*-(4-(*tert*-butyl)phenethyl)aniline (5k)**

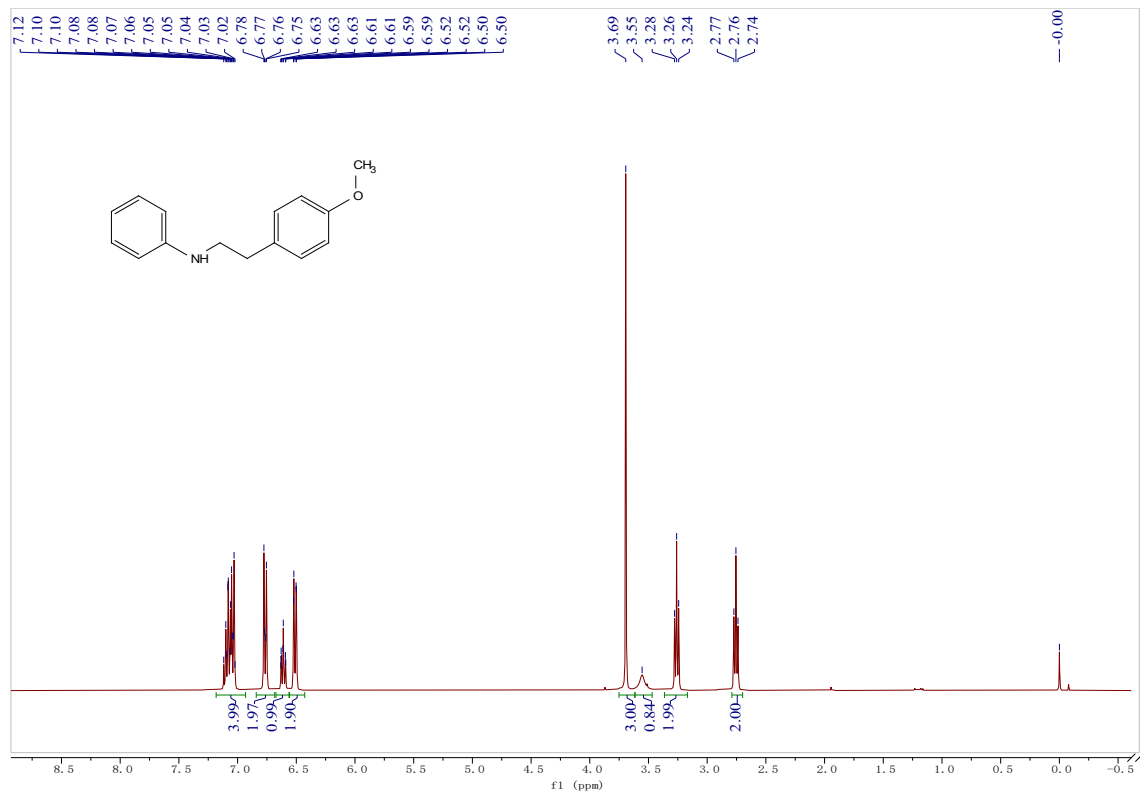


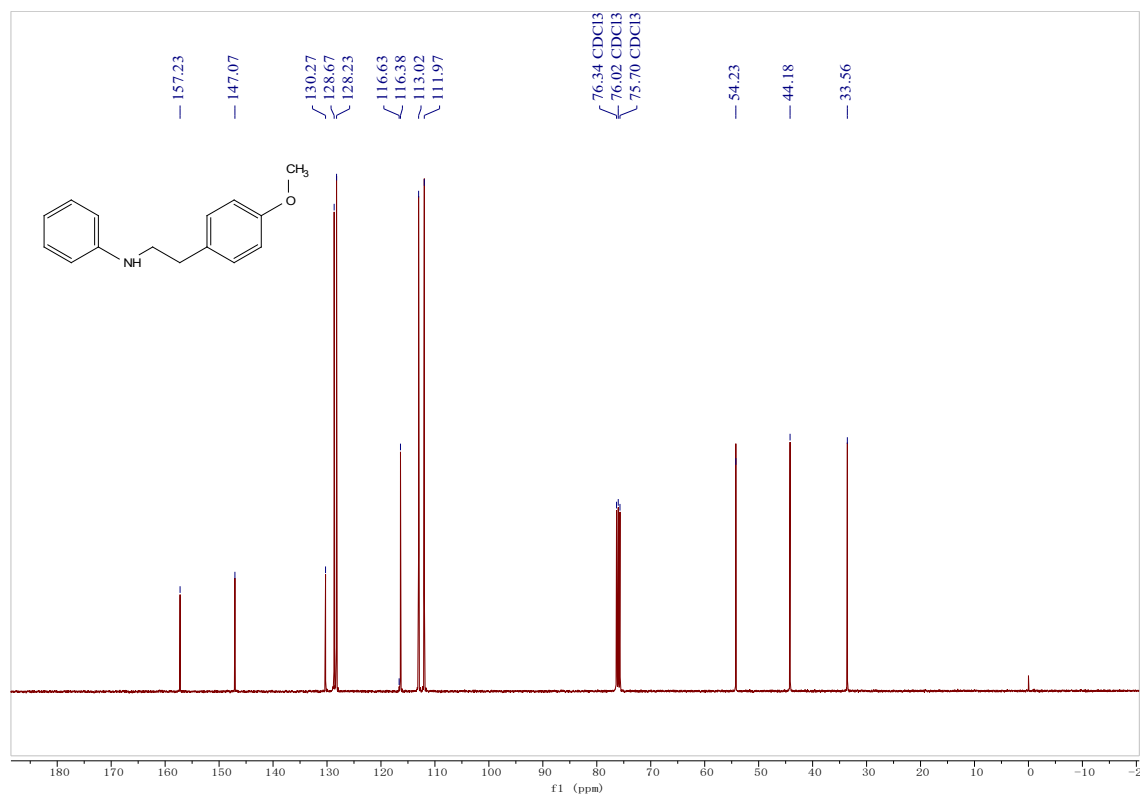
***N*-(2-([1,1'-biphenyl]-4-yl)ethyl)aniline (5l)**



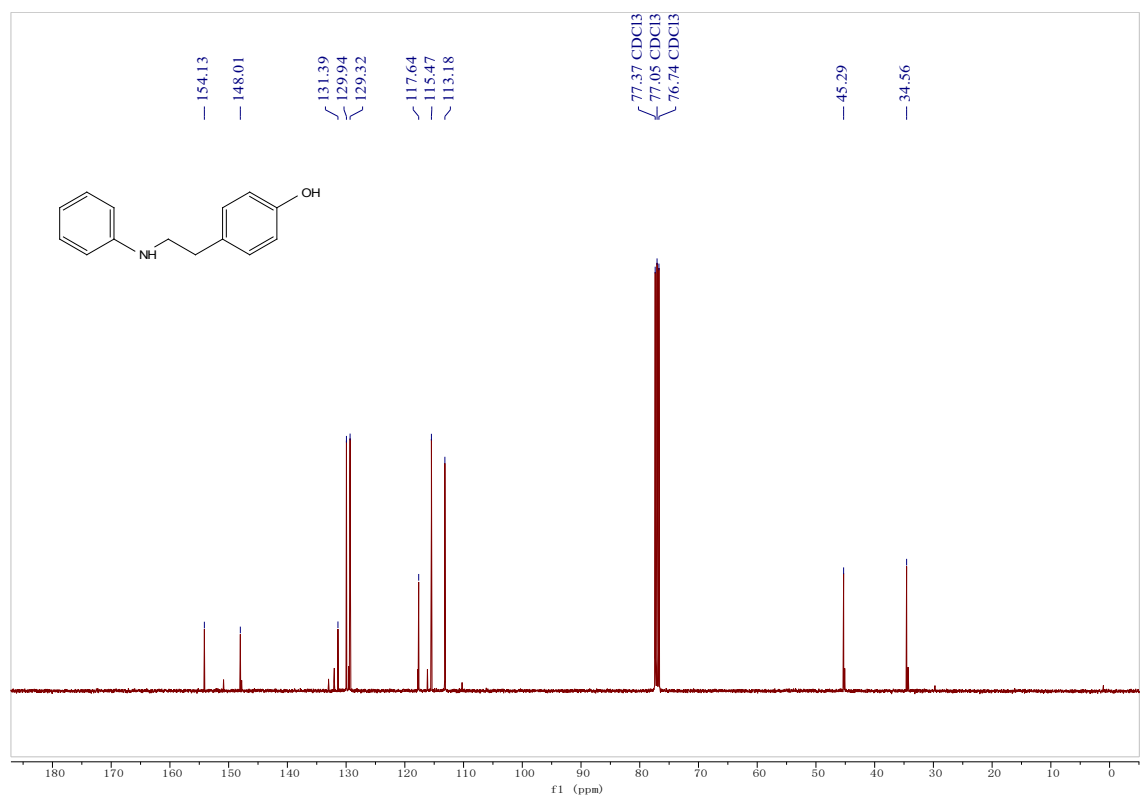
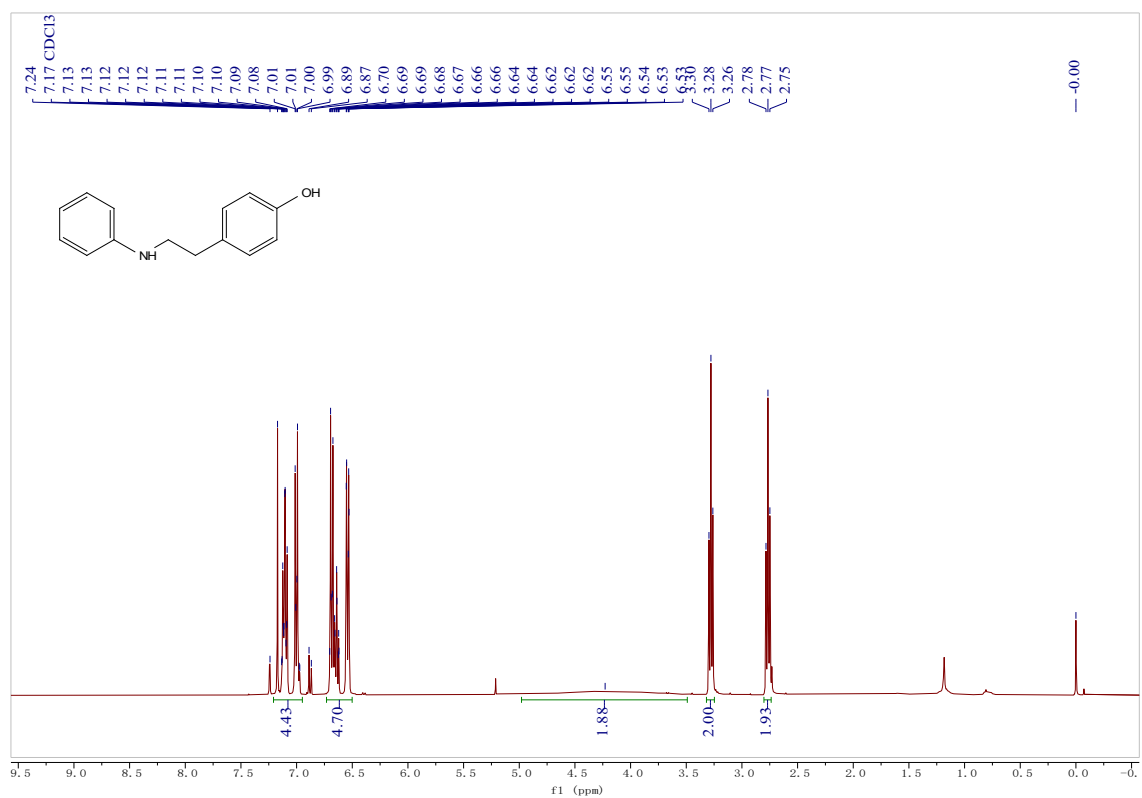


***N*-(4-methoxyphenethyl)aniline (5m)**

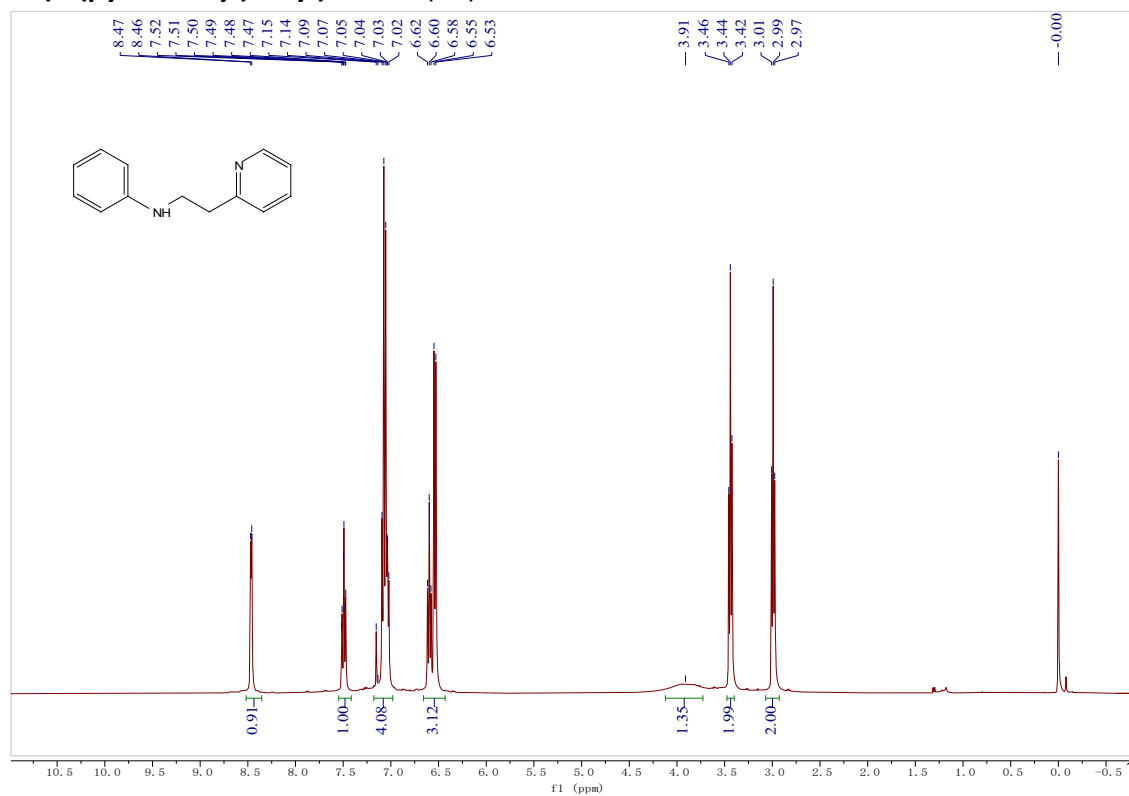


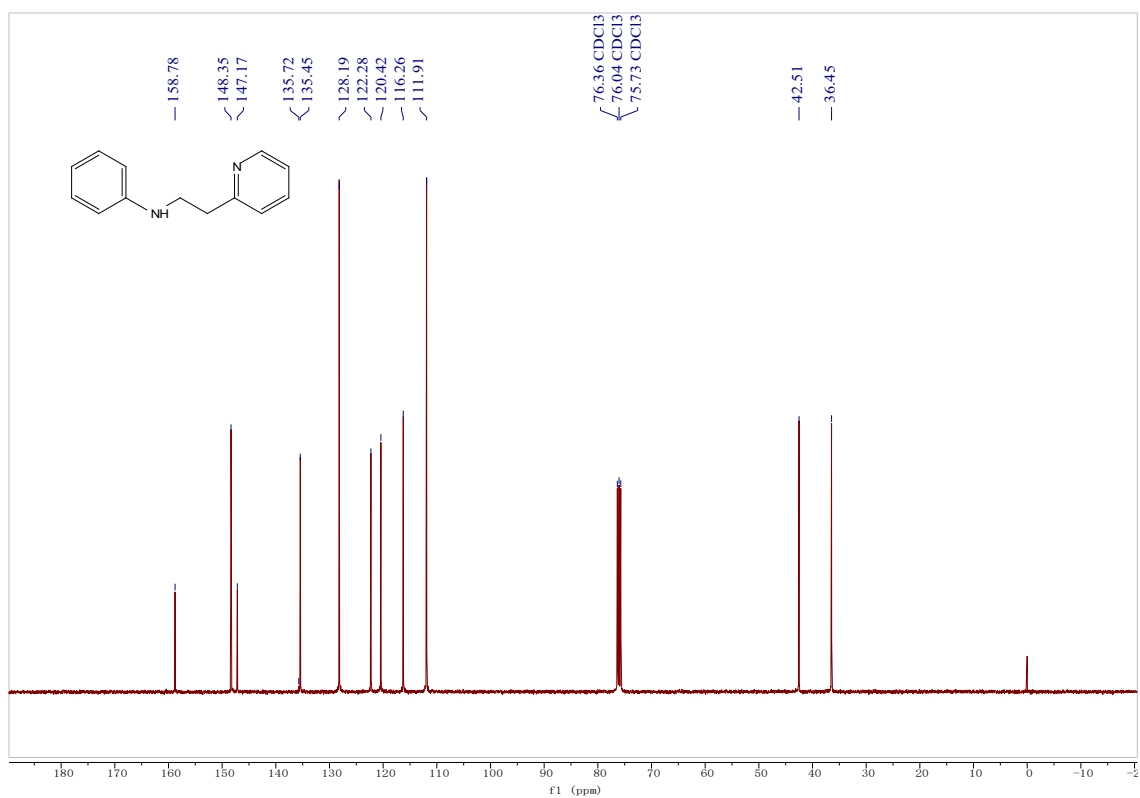


4-(2-(phenylamino)ethyl)phenol (5n)

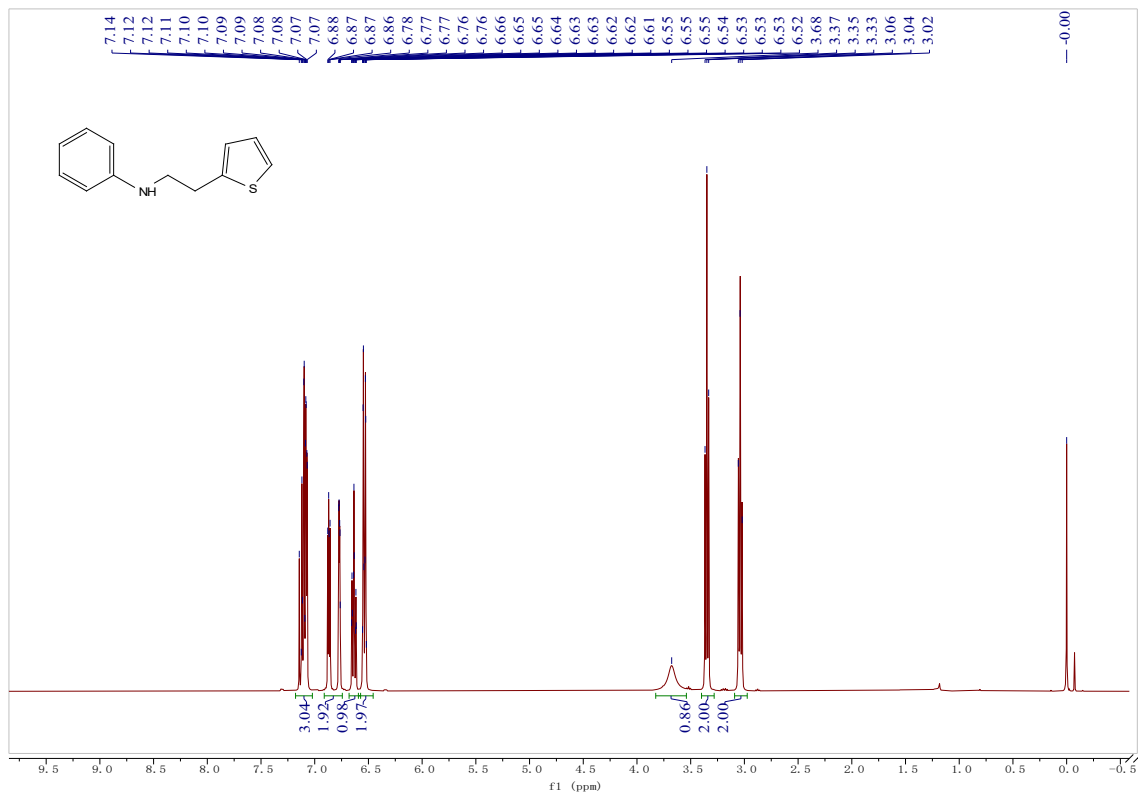


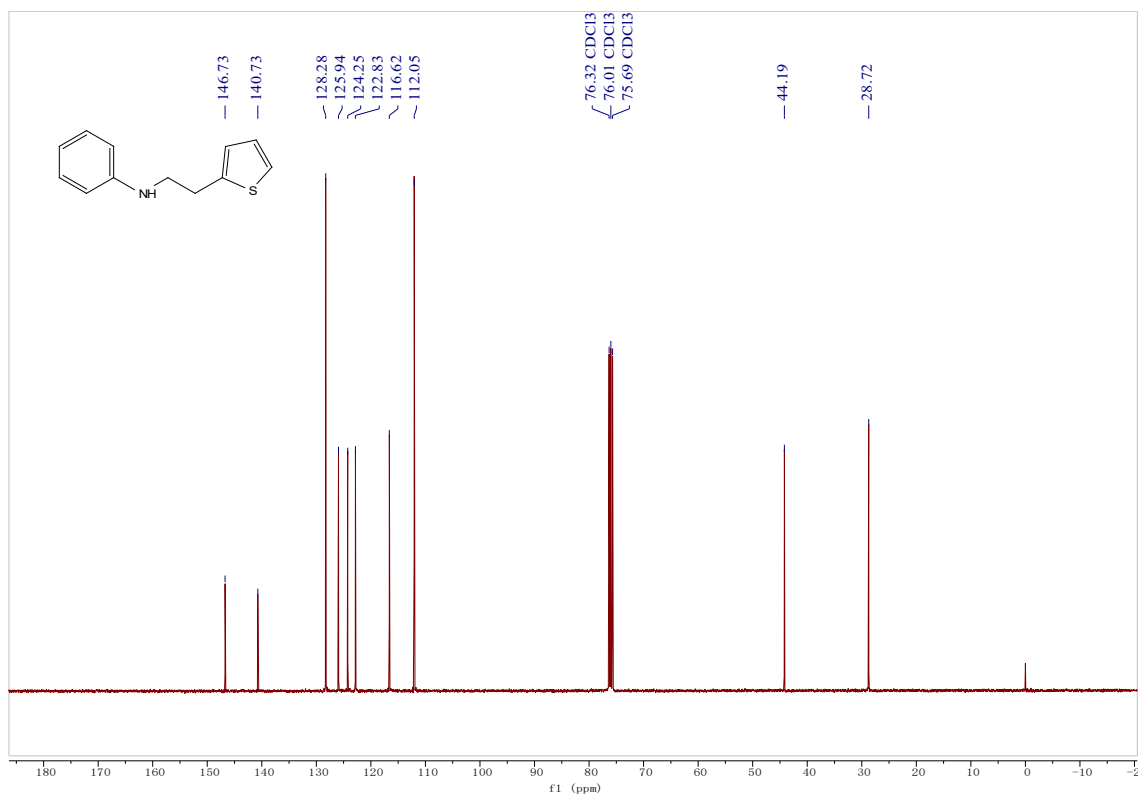
***N*-(2-(pyridin-2-yl)ethyl)aniline (5o)**



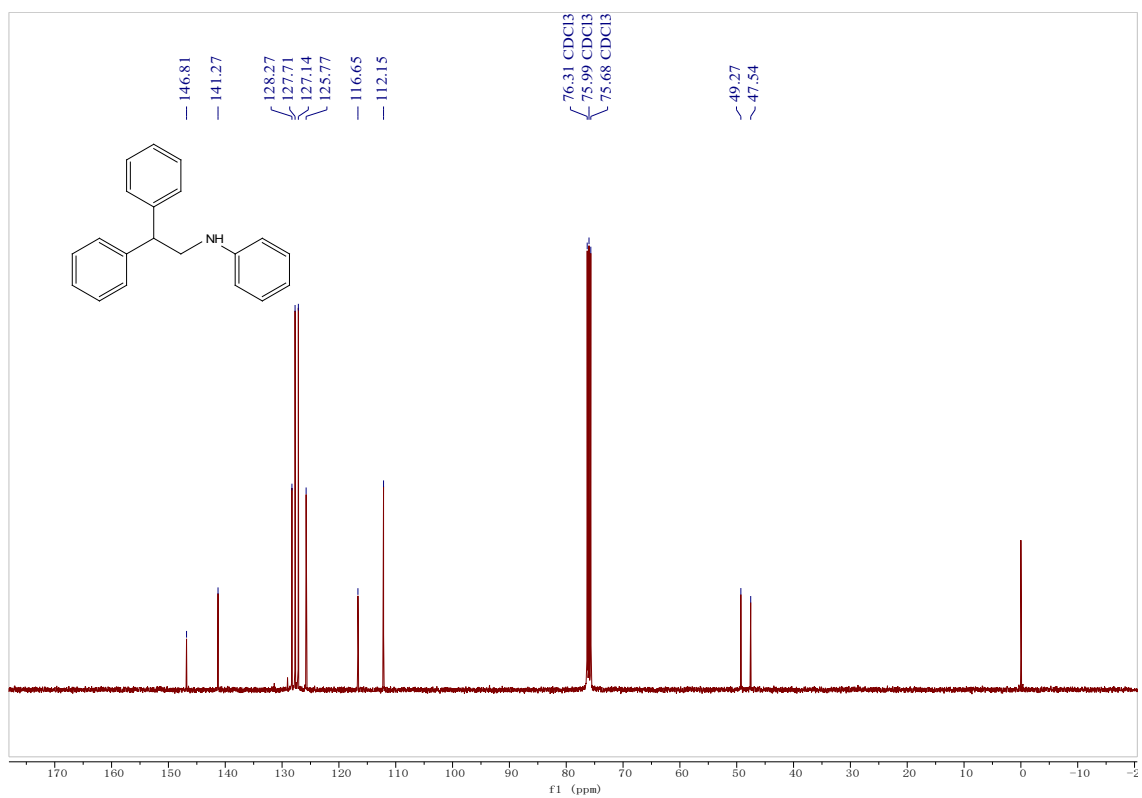
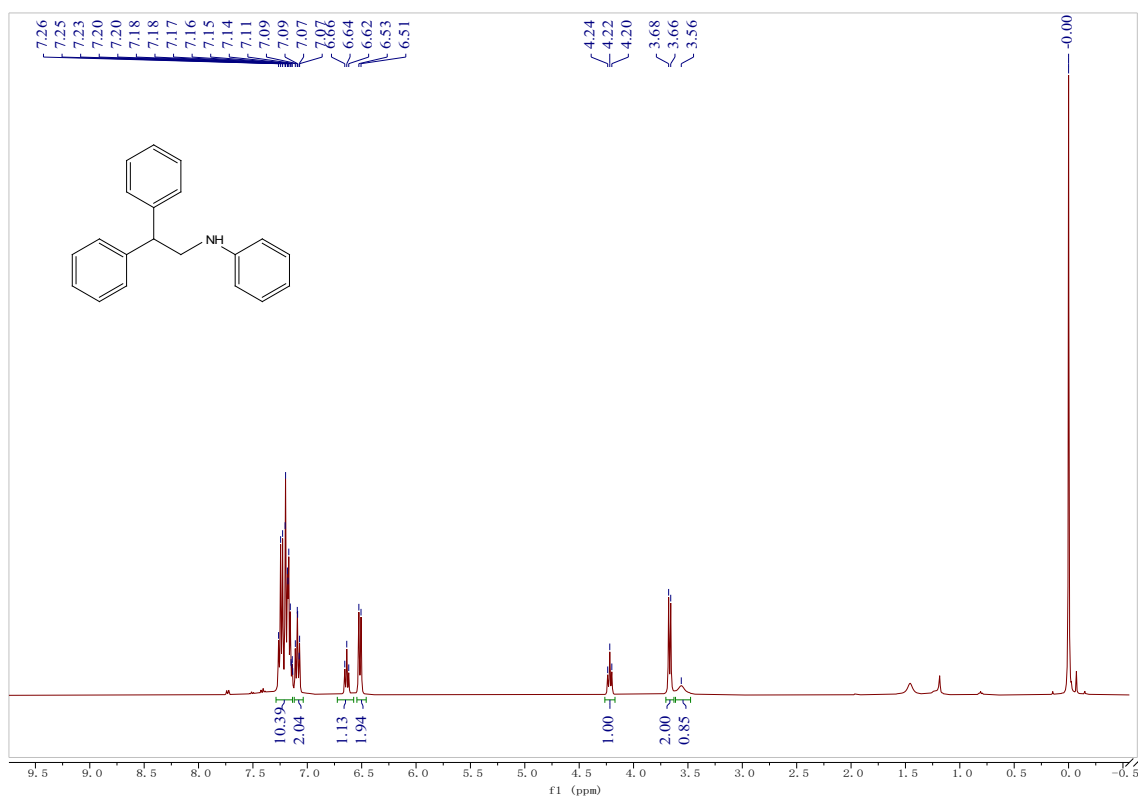


***N*-(2-(thiophen-2-yl)ethyl)aniline (5p)**





***N*-(2,2-diphenylethyl)aniline (5q)**



8. References

- 1 W. L. F. Armarego, *Purification of Laboratory Chemicals*, The Australian National University, Canberra, 2017.
- 2 T. K. Salvador, C. H. Arnett, S. Kundu, N. G. Sapiezynski, J. A. Bertke, M. Raghbi Boroujeni and T. H. Warren, *J. Am. Chem. Soc.*, 2016, **138**, 16580–16583.