Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

for

Reductive N-Alkylation of Primary and Secondary Amines Using Carboxylic Acids and Borazane under Mild Conditions

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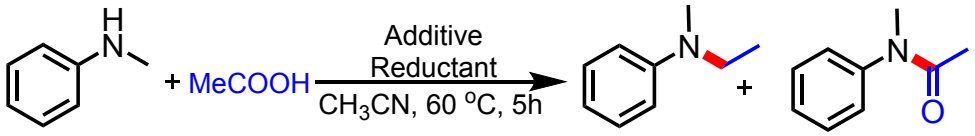
1. General information

All chemicals were purchased from Adamas Reagent, energy chemical company, J&K Scientific Ltd, Bide Pharmatech Ltd and Tansoole. The reagents and solvents were purchased from commercial suppliers and used without further purification. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III 500MHz NMR spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) as an internal reference. High resolution mass spectra were recorded using a Thermo Fisher Scientific LTQ FT Ultra or Waters Micromass GCT Premier instrument. Coupling constants (*J*) were reported in Hertz (Hz).

2. Screening of Conditions

Table S1 Optimization of the reaction with 1a and MeCOOH

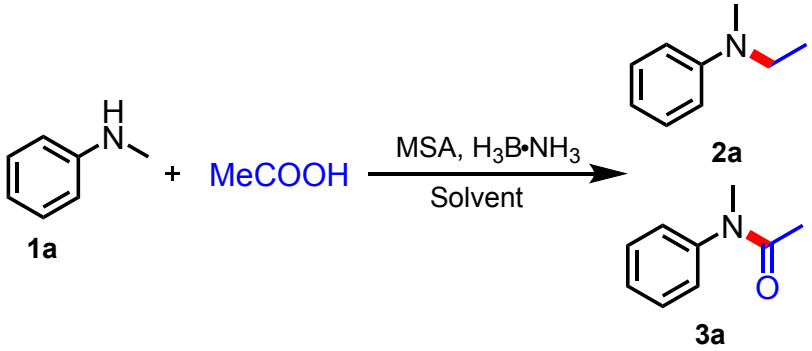


1a **2a** **3a**

Entry[a]	Reductant	Additive	Yield[b](%) 2a	3a
1	B_2pin_2	$[RuCl_2(p\text{-cymene})]_2$(3 %)	trace	0
2	$B_2(OH)_4$	$[RuCl_2(p\text{-cymene})]_2$(3 %)	21	0
3	$B_2(OH)_4$	$Pd(OAc)_2$(10 %)	14	0
4	$B_2(OH)_4$	$Fe(acac)_3$(10 %)	23	0
5	$B_2(OH)_4$	$CuSO_4$(10 %)	10	0
6	$H_3B{\bullet}NH_3$	$[RuCl_2(p\text{-cymene})]_2$(3 %)	42	0
7	$H_3B{\bullet}NH_3$	$CuSO_4$(10 %)	52	0
8	$H_3B{\bullet}NH_3$	$Cu(OAc)_2.H_2O$(10 %)	62	0
9	$H_3B{\bullet}NH_3$	Cs_2CO_3(100 %)	0	0
10	$H_3B{\bullet}NH_3$	DBU(100 %)	trace	0
11	$H_3B{\bullet}NH_3$	$HNTf_2$(100 %)	trace	0
12	$H_3B{\bullet}NH_3$	$BF_3{\bullet}Et_2O$(100 %)	59	trace
13	$H_3B{\bullet}NH_3$	HBF_4(100 %)	38	trace
14	$H_3B{\bullet}NH_3$	MSA(100 %)	66	trace
15	$H_3B{\bullet}NH_3$	MSA(200 %)	97(89[c])	0

[a]Reaction conditions: 1a(0.2 mmol), MeCOOH(3.0 equiv), Reductant(2.0 equiv), CH_3CN(1 mL), under N_2. [b]Determined by GC using n-dodecane as an internal standard. [c]Isolated yield.

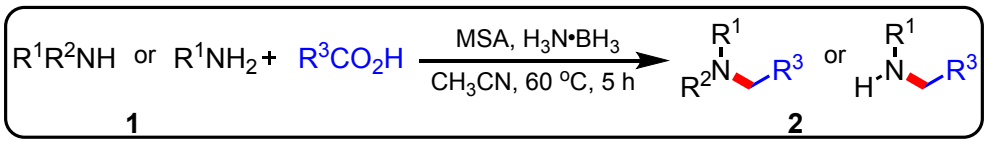
Table S2 Screening of solvent



Entry[a]	Solvent	Yield[b](%) 2a	3a
1	Acetone	trace	0
2	CH_3OH	n.r.	0
3	HFIP	n.r.	0
4	Hexane	48	0
5	THF	55	0
6	Toluene	45	0
7	1,4-dioxane	n.r.	0
8	n-Bu_2O	n.d.	0
9	CH_3CN	97	0
10[c]	CH_3CN	76	0
11[d]	CH_3CN	83	0
12[e]	CH_3CN	82	0
13[f]	CH_3CN	88	0
14[g]	CH_3CN	66	18

[a]Reaction conditions: 1a (0.2 mmol), MeCOOH (3.0 equiv), $H_3B{\bullet}NH_3$ (2.0 equiv), solvent (1 mL), 5 h, 50 °C, under N_2. [b]under air. [d]40 °C. [e]3 h. [f]MeCOOH (2.5 equiv). [g]MSA (1.0 equiv). n.r.=no reaction. n.d.= not detected.

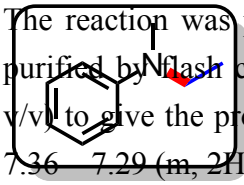
3. General process for the synthesis of 2



To a mixture of $H_3N{\bullet}BH_3$ (30.9 mg, 1 mmol, 2.0 equiv) and **1** (0.5 mmol, 1.0 equiv) in CH_3CN (2 mL) was added RCOOH (1.25 or 1.5 mmol, 2.5 or 3.0 equiv). Then the Schlenk tube was evacuated with N_2 three times and finally MSA (1 mmol, 2.0 equiv) was added. The resulting mixture was stirred at 60 °C for 5 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 50:1, v/v) to give the desired product **2**.

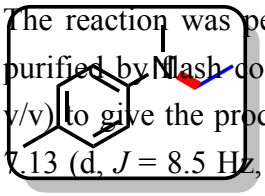
4. Characterization data for products

N-ethyl-N-methylaniline (2a) (CAS: No. 613-97-8)[1]



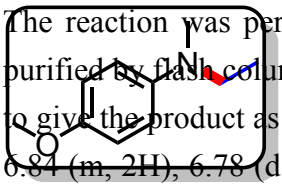
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (60.1 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 6.83 – 6.74 (m, 3H), 3.48 (q, J = 7.1 Hz, 2H), 2.98 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 129.2, 116.2, 112.5, 46.9, 37.5, 11.3.

N-ethyl-N,4-dimethylaniline (2b) (CAS: No. 35113-87-2)[3]



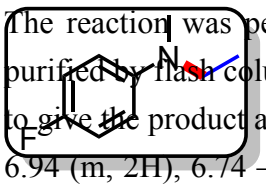
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (65.6 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.5 Hz, 2H), 6.77 – 6.73 (m, 2H), 3.44 (q, J = 7.1 Hz, 2H), 2.94 (s, 3H), 2.34 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 129.7, 125.6, 113.1, 47.2, 37.8, 20.3, 11.1.

N-ethyl-4-methoxy-N-methylaniline (2c) (CAS: No. 6114-15-4)[3]



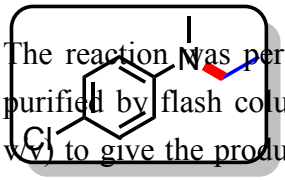
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (70.1 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 – 6.84 (m, 2H), 6.78 (d, J = 9.1 Hz, 2H), 3.79 (s, 3H), 3.34 (q, J = 7.1 Hz, 2H), 2.86 (s, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 144.0, 115.2, 114.8, 55.8, 48.2, 38.4, 11.1.

N-ethyl-4-fluoro-N-methylaniline (2d) (CAS: No. 67274-53-7)[3]



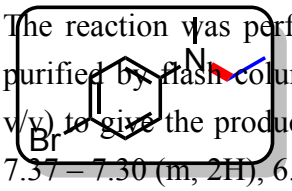
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 80:1, v/v) to give the product as yellow oil (63.5 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 – 6.94 (m, 2H), 6.74 – 6.67 (m, 2H), 3.38 (q, J = 7.1 Hz, 2H), 2.89 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.4 (d, J = 235.0 Hz), 145.9, 115.5 (d, J = 21.9 Hz), 114.0 (d, J = 6.9 Hz), 47.7, 38.1, 11.0.

4-chloro-N-ethyl-N-methylaniline (2e) (CAS: No. 13519-85-2)[3]



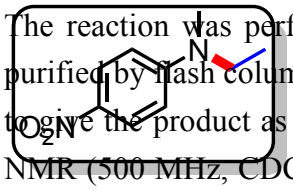
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (71.0 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 2H), 6.68 – 6.65 (m, 2H), 3.41 (q, *J* = 7.1 Hz, 2H), 2.92 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 128.9, 120.8, 113.5, 47.0, 37.6, 11.1.

4-bromo-N-ethyl-N-methylaniline (2f) (CAS: No. 67274-54-8)[3]



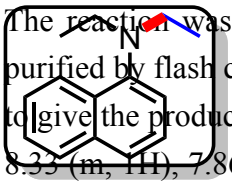
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (94.8 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 2H), 6.66 – 6.57 (m, 2H), 3.41 (q, *J* = 7.1 Hz, 2H), 2.92 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 131.8, 114.0, 107.9, 46.9, 37.6, 11.1.

N-ethyl-N-methyl-4-nitroaniline (2g) (CAS: No. 56269-48-8)[3]



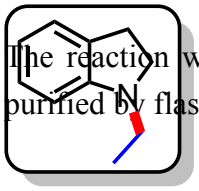
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a yellow solid (82.8 mg, 92%). M. P. 87 °C (Lit. 87-89 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 6.60 – 6.54 (m, 2H), 3.49 (q, *J* = 7.2 Hz, 2H), 3.04 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 136.4, 126.2, 110.1, 47.0, 37.8, 11.6.

N,N-diethylnaphthalen-1-amine (2h) (CAS: No. 84-95-7)[6]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (82.6 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 – 8.33 (m, 1H), 7.86 (dd, *J* = 6.6, 2.5 Hz, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.43 (m, 3H), 7.19 (d, *J* = 7.3 Hz, 1H), 3.25 (q, *J* = 7.0 Hz, 4H), 1.11 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 134.9, 131.3, 128.1, 125.6, 125.5, 125.1, 124.3, 123.3, 117.9, 47.7, 12.3.

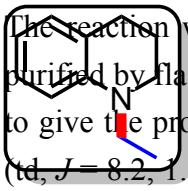
1-ethylindoline (2i) (CAS: No. 5876-09-5)[3]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v)

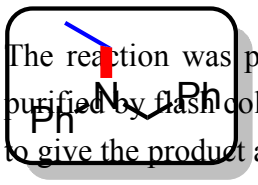
to give the product as yellow oil (63.2 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.74 (td, *J* = 7.5, 0.8 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 3.40 (t, *J* = 8.3 Hz, 2H), 3.22 (d, *J* = 7.2 Hz, 2H), 3.03 (t, *J* = 8.3 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3, 130.4, 127.3, 124.4, 117.6, 107.3, 52.4, 43.3, 28.6, 12.0.

1-ethyl-1,2,3,4-tetrahydroquinoline (2j) (CAS: No. 16768-69-7)[5]



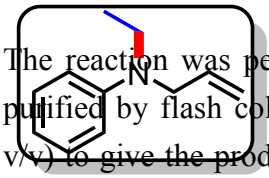
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (75.7 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (td, *J* = 8.2, 1.7 Hz, 1H), 7.06 (dd, *J* = 7.3, 0.7 Hz, 1H), 6.74 – 6.66 (m, 2H), 3.45 (t, *J* = 7.1 Hz, 2H), 3.38 – 3.35 (m, 2H), 2.87 (t, *J* = 6.4 Hz, 2H), 2.09 – 2.05 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 129.3, 127.2, 122.5, 115.5, 110.6, 48.5, 45.4, 28.3, 22.4, 10.9.

N-benzyl-N-ethylaniline (2k) (CAS: No. 92-59-1)[3]



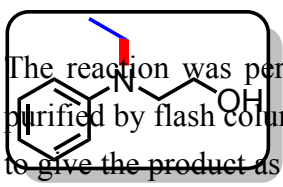
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as colorless oil (95.0 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 2H), 7.47 – 7.37 (m, 5H), 6.94 – 6.86 (m, 3H), 4.71 (s, 2H), 3.67 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 139.5, 129.4, 128.7, 126.9, 126.8, 116.3, 112.4, 54.1, 45.3, 12.3.

N-allyl-N-ethylaniline (2l) (CAS: No. 16078-91-4)[3]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (74.9 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 2H), 6.76 (dd, *J* = 19.3, 7.7 Hz, 3H), 5.94 (ddt, *J* = 17.1, 10.0, 4.9 Hz, 1H), 5.24 (ddq, *J* = 19.0, 10.3, 1.7 Hz, 2H), 3.97 (dt, *J* = 4.7, 1.7 Hz, 2H), 3.46 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.3, 134.5, 129.2, 115.9, 115.8, 112.1, 52.7, 44.8, 12.3.

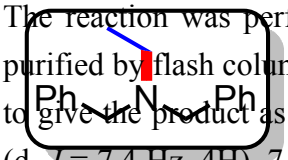
2-(ethyl(phenyl)amino)ethan-1-ol (2m) (CAS: No. 92-50-2)[1]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (73.4 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 3.80 (t, *J* = 5.9 Hz, 2H),

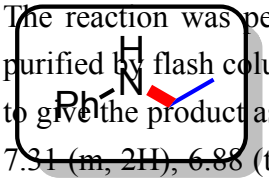
3.50 – 3.42 (m, 4H), 2.41 (s, 1H), 1.19 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 129.4, 116.9, 113.1, 60.1, 52.7, 45.8, 11.9.

N,N-dibenzylethanamine (2n) (CAS: No. 10479-25-1)[1]



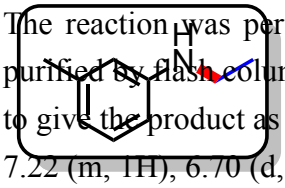
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (77.6 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 7.4 Hz, 4H), 7.35 (dd, J = 10.3, 4.7 Hz, 4H), 7.29 – 7.25 (m, 2H), 3.63 (s, 4H), 2.56 (q, J = 7.0 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 128.8, 128.8, 128.2, 126.8, 57.7, 47.1, 11.8.

N-ethylaniline (2o) (CAS: No. 103-69-5)[2]



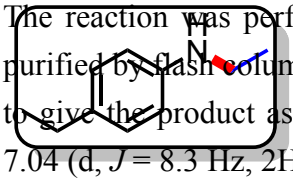
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (50.8 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 2H), 6.88 (tt, J = 7.3, 1.0 Hz, 1H), 6.79 – 6.72 (m, 2H), 3.63 (s, 1H), 3.29 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.4, 117.3, 112.9, 38.6, 15.0.

N-ethyl-3-methylaniline (2p) (CAS: No. 102-27-2)[1]



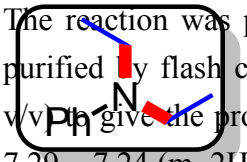
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (56.7 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 1H), 6.70 (d, J = 7.6 Hz, 1H), 6.58 (d, J = 6.5 Hz, 2H), 3.62 (s, 1H), 3.29 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 139.0, 129.2, 118.3, 113.7, 110.1, 38.6, 21.8, 15.1.

N,4-diethylaniline (2q) (CAS: No. 4960-26-3)[3]



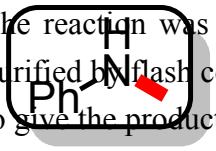
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (60.3 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, J = 8.3 Hz, 2H), 6.59 (d, J = 8.4 Hz, 2H), 3.17 (q, J = 7.1 Hz, 2H), 2.57 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 133.2, 128.5, 113.0, 38.8, 27.9, 16.0, 15.0.

N,N-diethylaniline (2r) (CAS: No. 91-66-7)[2]



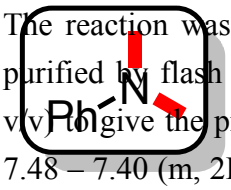
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (64.8 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 6.82 – 6.64 (m, 3H), 3.40 (d, *J* = 7.1 Hz, 4H), 1.21 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 129.3, 115.4, 111.9, 44.4, 12.6.

N-methylaniline (2s) (CAS: No. 100-61-8)[3]



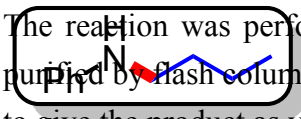
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (43.3 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 6.89 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.78 – 6.73 (m, 2H), 3.66 (s, 1H), 2.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.5, 129.4, 117.3, 112.6, 30.8.

N,N-dimethylaniline (2t) (CAS: No. 121-69-7)[3]



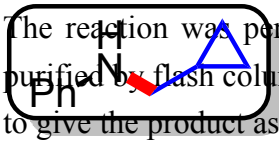
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (50.8 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 6.97 – 6.90 (m, 3H), 3.11 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 129.2, 116.8, 112.8, 40.7.

N-butylaniline (2u) (CAS: No. 1126-78-9)[1]



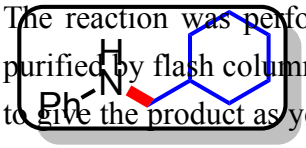
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (64.1 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 6.82 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.72 (dt, *J* = 8.9, 1.6 Hz, 2H), 3.24 – 3.19 (m, 2H), 1.71 (ddd, *J* = 12.6, 8.4, 6.4 Hz, 2H), 1.55 (dq, *J* = 14.5, 7.3 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.3, 117.1, 112.8, 43.8, 31.8, 20.4, 14.1.

N-(cyclopropylmethyl)aniline (2v) (CAS: No. 36178-60-6)[4]



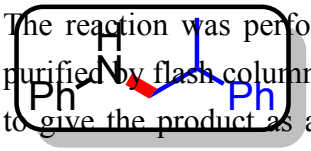
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (64.7 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 2H), 6.81 – 6.73 (m, 1H), 6.67 (dd, *J* = 8.6, 0.9 Hz, 2H), 3.84 (s, 1H), 3.01 (d, *J* = 6.9 Hz, 2H), 1.20 – 1.11 (m, 1H), 0.65 – 0.57 (m, 2H), 0.30 (dt, *J* = 9.6, 4.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.6, 129.3, 117.3, 112.8, 49.1, 11.0, 3.5.

N-(cyclohexylmethyl)aniline (2w) (CAS: No. 79952-92-4)[1]



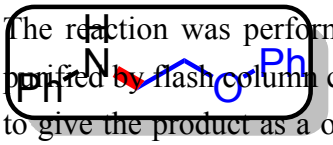
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (85.1 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.16 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.67 – 6.61 (m, 2H), 3.74 (s, 1H), 3.00 (d, *J* = 6.7 Hz, 2H), 1.90 – 1.83 (m, 2H), 1.76 (dddd, *J* = 6.3, 4.9, 4.2, 2.4 Hz, 3H), 1.67 – 1.59 (m, 1H), 1.34 – 1.22 (m, 3H), 1.03 (qd, *J* = 12.3, 3.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.2, 116.9, 112.6, 50.6, 37.6, 31.4, 26.6, 26.0.

N-(2-phenylpropyl)aniline (2x) (CAS: No. 56165-31-2)[11]



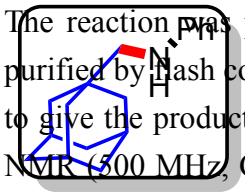
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (93.9 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 2H), 7.30 – 7.25 (m, 3H), 7.23 – 7.18 (m, 2H), 6.75 (dd, *J* = 11.5, 4.2 Hz, 1H), 6.67 – 6.60 (m, 2H), 3.38 (dd, *J* = 12.4, 6.2 Hz, 1H), 3.28 (dd, *J* = 12.4, 8.2 Hz, 1H), 3.10 (dq, *J* = 14.0, 6.9 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 144.5, 129.3, 128.7, 127.3, 126.7, 117.6, 113.2, 51.1, 39.2, 19.8.

N-(2-phenoxyethyl)aniline (2y) (CAS: No. 622-18-4)[1]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a orange solid (87.3 mg, 82%). M. P. 48 °C (Lit. 48-50 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.28 – 7.24 (m, 2H), 7.05 – 6.96 (m, 3H), 6.80 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.73 (dt, *J* = 8.8, 1.6 Hz, 2H), 4.22 (t, *J* = 5.3 Hz, 2H), 3.58 (t, *J* = 5.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 147.9, 129.6, 129.4, 121.1, 117.9, 114.6, 113.2, 66.4, 43.4.

N-(((3r,5r,7r)-adamantan-1-yl)methyl)aniline (2aa) (CAS: No. 802038-41-1)[8]

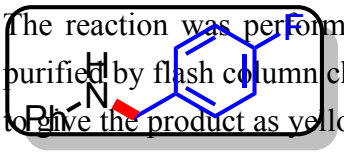


The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (102.4 mg, 85%). M. P. 49 °C (Lit. 49-51 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.72 (t, *J* = 7.3 Hz, 1H), 6.70 – 6.66 (m, 2H), 3.71 (s, 1H), 2.86 (s, 2H), 2.07 (s, 3H), 1.81 (d, *J* = 12.2 Hz, 3H), 1.73 (d, *J* = 11.4 Hz, 3H), 1.65 (d, *J* = 2.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 1493, 129.2, 116.8, 112.6, 56.3, 40.8, 37.2, 33.9, 28.4.

N-benzylaniline (2ab) (CAS: No. 103-32-2)[1]

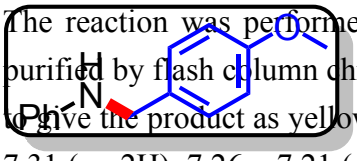
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a grey solid (76.9 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (dt, *J* = 15.0, 7.4 Hz, 4H), 7.37 (t, *J* = 6.9 Hz, 1H), 7.30 – 7.25 (m, 2H), 6.82 (td, *J* = 7.3, 0.6 Hz, 1H), 6.73 (d, *J* = 8.5 Hz, 2H), 4.41 (s, 2H), 4.10 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 139.5, 129.4, 128.7, 127.6, 127.3, 117.6, 112.9, 48.4.

N-(4-fluorobenzyl)aniline (2ac) (CAS: No. 83444-25-1)[4]



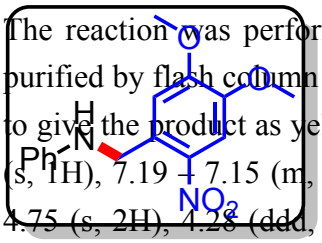
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (84.4 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.27 – 7.22 (m, 2H), 7.13 – 7.05 (m, 2H), 6.80 (tt, *J* = 7.4, 1.0 Hz, 1H), 6.69 (dt, *J* = 8.9, 1.6 Hz, 2H), 4.35 (s, 2H), 4.07 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 161.1, 148.0, 135.18 (d, *J* = 3.1 Hz), 129.4, 129.05 (d, *J* = 8.0 Hz), 117.8, 115.6, 115.4, 112.9, 47.6.

N-(4-methoxybenzyl)aniline (2ad) (CAS: No. 3526-43-0)[4]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as yellow oil (84.1 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.26 – 7.21 (m, 2H), 6.96 – 6.92 (m, 2H), 6.81 – 6.75 (m, 1H), 6.69 (dd, *J* = 8.6, 1.0 Hz, 2H), 4.30 (s, 2H), 4.00 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 148.3, 131.5, 129.3, 128.9, 117.5, 114.1, 112.9, 55.3, 47.8.

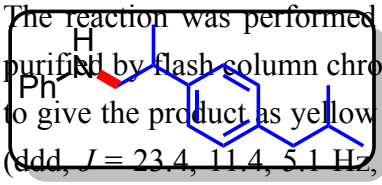
N-(4,5-dimethoxy-2-nitrobenzyl)aniline (2ae)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as yellow oil (118.1 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.19 – 7.15 (m, 3H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.60 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.75 (s, 2H), 4.28 (ddd, *J* = 28.6, 22.9, 13.5 Hz, 1H), 3.96 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.7, 147.6, 147.6, 140.1, 131.3, 129.3, 118.1, 113.1, 111.0, 108.5, 56.4, 56.4, 46.5.

HRMS (ESI, m/z) calcd for $C_{15}H_{17}N_2O_4[M+H]^+$: 289.1183; found: 289.1185.

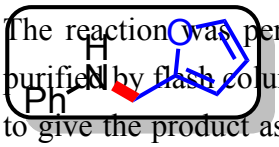
N-(2-(4-isobutylphenyl)propyl)aniline (2af) (CAS: No. 1553525-77-1)[2]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (117.5 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (ddd, *J* = 23.4, 11.4, 5.1 Hz, 6H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (dd, *J* = 8.5, 0.9 Hz,

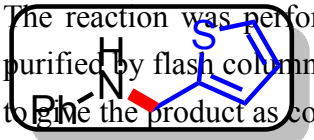
2H), 3.37 (dd, *J* = 12.3, 6.2 Hz, 1H), 3.27 (dd, *J* = 12.3, 8.2 Hz, 1H), 3.12 – 3.04 (m, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.91 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 141.7, 140.0, 129.4, 129.3, 127.0, 117.3, 113.0, 51.0, 45.1, 38.8, 30.3, 22.5, 19.8.

N-(furan-2-ylmethyl)aniline (2ag) (CAS: No. 4439-56-9)[13]



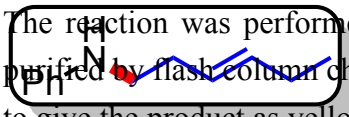
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (74.4 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 1.5 Hz, 1H), 7.24 – 7.20 (m, 2H), 6.77 (t, *J* = 7.3 Hz, 1H), 6.73 – 6.69 (m, 2H), 6.35 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 4.35 (s, 2H), 4.05 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 147.6, 141.9, 129.2, 118.0, 113.2, 110.3, 107.0, 41.5.

N-(thiophen-2-ylmethyl)aniline (2ah) (CAS: No. 40625-28-3)[4]



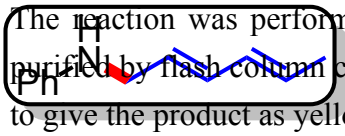
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as colorless oil (82.2 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (ddd, *J* = 8.5, 6.2, 1.6 Hz, 3H), 7.07 – 7.04 (m, 1H), 7.01 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.82 – 6.77 (m, 1H), 6.72 (dd, *J* = 8.5, 0.9 Hz, 2H), 4.55 (s, 2H), 4.08 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 143.0, 129.3, 126.9, 125.1, 124.6, 118.1, 113.2, 43.5.

N-(hex-3-en-1-yl)aniline (2ai) (CAS: No. 634181-56-9)[9]



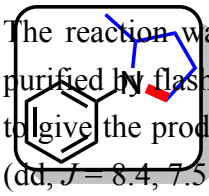
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (75.3 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.76 – 6.70 (m, 1H), 6.64 (dd, *J* = 8.6, 0.9 Hz, 2H), 5.63 (dtt, *J* = 13.8, 6.3, 1.2 Hz, 1H), 5.48 – 5.39 (m, 1H), 3.69 (s, 1H), 3.16 (t, *J* = 6.7 Hz, 2H), 2.35 (qd, *J* = 6.7, 1.0 Hz, 2H), 2.07 (pd, *J* = 7.4, 1.1 Hz, 2H), 1.03 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 135.0, 129.2, 125.9, 117.3, 112.9, 43.4, 32.4, 25.7, 13.9.

N-((2E,4E)-hexa-2,4-dien-1-yl)aniline (2aj) (CAS: No. 115477-06-0)[10]



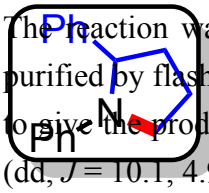
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (71.8 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.4 Hz, 2H), 6.76 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.33 – 6.20 (m, 1H), 6.17 – 6.03 (m, 1H), 5.72 (dd, *J* = 13.8, 7.7 Hz, 2H), 3.81 (d, *J* = 5.4 Hz, 2H), 3.47 (s, 1H), 1.79 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.1, 132.2, 130.9, 129.4, 129.2, 127.6, 117.6, 113.1, 46.0, 18.1.

2-methyl-1-phenylpyrrolidine (2ak) (CAS: No. 33342-99-3)[12]



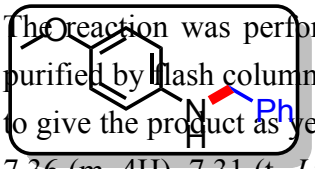
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as yellow oil (58.8 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.7 Hz, 2H), 3.93 – 3.78 (m, 1H), 3.17 (t, *J* = 6.9 Hz, 2H), 1.79 – 1.68 (m, 2H), 1.62 – 1.56 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 129.3, 117.4, 112.9, 67.9, 44.1, 36.8, 25.9, 23.7.

1,2-diphenylpyrrolidine (2al) (CAS: No. 72709-29-6)[12]



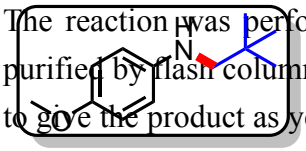
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as yellow oil (97.0 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 10.1, 4.9 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 3H), 7.17 (dd, *J* = 8.4, 7.4 Hz, 2H), 6.66 (t, *J* = 7.3 Hz, 1H), 6.52 (d, *J* = 8.2 Hz, 2H), 4.76 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.77 – 3.71 (m, 1H), 3.44 (td, *J* = 9.1, 6.9 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.08 – 1.94 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 144.6, 129.0, 128.5, 126.6, 125.9, 115.7, 112.3, 62.9, 49.1, 36.1, 23.1.

N-benzyl-4-methoxyaniline (2am) (CAS: No. 17377-95-6)[4]



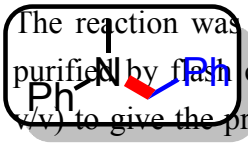
The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as yellow oil (78.8 mg, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 4H), 7.31 (t, *J* = 7.1 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.68 – 6.62 (m, 2H), 4.32 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 142.5, 139.7, 128.6, 127.6, 127.2, 114.9, 114.2, 55.8, 49.3.

4-methoxy-N-neopentylaniline (2an) (CAS: No. 65570-14-1)[4]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as yellow oil (83.0 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 – 6.79 (m, 2H), 6.65 – 6.60 (m, 2H), 3.78 (s, 3H), 3.40 (s, 1H), 2.88 (s, 2H), 1.02 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.8, 143.5, 114.9, 113.9, 57.1, 55.9, 31.8, 27.7.

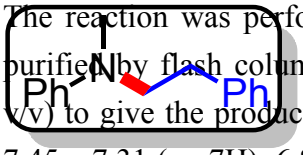
N-benzyl-N-methylaniline (2ao) (CAS: No. 614-30-2)[3]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (93.9 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.34 – 7.28 (m, 5H), 6.88 – 6.77 (m, 3H), 4.61 (s, 2H), 3.09 (s,

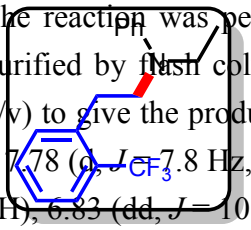
3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.8, 139.1, 129.2, 128.6, 126.9, 126.8, 116.6, 112.4, 56.7, 38.6.

N-methyl-N-phenethylaniline (2ap) (CAS: No. 28059-49-6)[7]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as yellow oil (97.1 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 7H), 6.86 (dd, *J* = 16.1, 7.9 Hz, 3H), 3.71 – 3.66 (m, 2H), 3.01 (s, 3H), 3.00 – 2.96 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 139.9, 129.4, 128.9, 128.6, 126.3, 116.3, 112.3, 54.9, 38.6, 33.0.

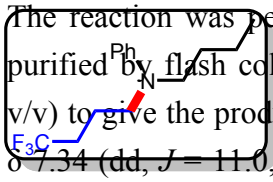
N-ethyl-N-(2-(trifluoromethyl)phenethyl)aniline (2aq)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 200:1, v/v) to give the product as a yellow oil (128.9 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.32 (m, 4H), 6.93 – 6.86 (m, 2H), 6.83 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.65 (dd, *J* = 9.9, 5.6 Hz, 2H), 3.45 (q, *J* = 7.0 Hz, 2H), 3.20 (t, *J* = 7.5 Hz, 2H), 1.27 (ddd, *J* = 7.1, 4.4, 1.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 138.4, 132.0 (d, *J* = 7.4 Hz), 129.5, 129.3, 128.9, 128.7, 126.4, 126.2 (q, *J* = 5.7 Hz), 116.0, 111.9, 52.2, 45.1, 30.9, 12.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -59.32 – -59.38 (m).

HRMS (ESI, m/z) calcd for $C_{17}H_{19}F_3N[M+H]^+$: 294.1464; found: 294.1467.

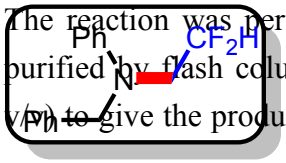
N-butyl-N-(4,4,4-trifluorobutyl)aniline (2ar)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 200:1, v/v) to give the product as a yellow oil (114.0 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 11.0, 4.4 Hz, 2H), 6.85 – 6.77 (m, 3H), 3.45 (t, *J* = 7.2 Hz, 2H), 3.37 (dd, *J* = 10.4, 4.8 Hz, 2H), 2.29 – 2.17 (m, 2H), 2.01 – 1.93 (m, 2H), 1.72 – 1.66 (m, 2H), 1.48 (dt, *J* = 15.0, 7.4 Hz, 2H), 1.11 – 1.06 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 129.4, 127.3 (q, *J* = 275.0 Hz), 116.2, 112.4, 51.1, 49.8, 31.4 (q, *J* = 28.8 Hz), 29.4, 20.4, 20.1 (d, *J* = 2.1 Hz), 14.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -65.93 (s).

HRMS (ESI, m/z) calcd for $C_{14}H_{21}F_3N[M+H]^+$: 260.1621; found: 260.1623.

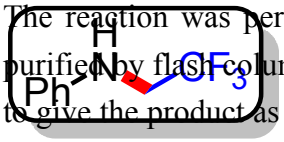
N-benzyl-N-(2,2-difluoroethyl)aniline (2as)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 200:1, v/v) to give the product as a yellow oil (105.0 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$)

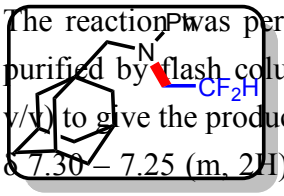
δ 7.49 – 7.31 (m, 7H), 6.90 (d, *J* = 6.7 Hz, 3H), 6.25 – 5.94 (m, 1H), 4.78 (s, 2H), 3.88 (td, *J* = 14.0, 4.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 137.9, 129.6, 128.8, 127.2, 126.7, 118.0, 114.9 (t, *J* = 242.5 Hz), 112.8, 55.1, 53.6 (t, *J* = 26.3 Hz). ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.27 (dd, *J* = 9.9, 5.2 Hz).
HRMS (ESI, m/z) calcd for $C_{15}H_{16}F_2N[M+H]^+$: 248.1245; found: 248.1245.

N-(2,2,2-trifluoroethyl)aniline (2at) (CAS: No. 351-61-1)[3]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as yellow oil (63.0 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 2H), 6.84 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 2H), 3.95 (s, 1H), 3.80 (qd, *J* = 8.9, 5.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 129.4, 125.1(q, *J* = 278.8 Hz), 119.1, 113.1, 46.0 (q, *J* = 33.8 Hz).

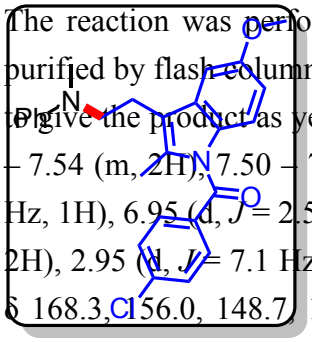
N-(((3r,5r,7r)-adamantan-1-yl)methyl)-N-(2,2-difluoroethyl)aniline (2au)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 200:1, v/v) to give the product as light green oil (122.1 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 6.90 (d, *J* = 8.2 Hz, 2H), 6.78 (t, *J* = 7.3 Hz, 1H), 5.96 (tt, *J* = 56.1, 4.3 Hz, 1H), 3.82 (td, *J* = 13.5, 4.3 Hz, 2H), 3.23 (s, 2H), 2.03 (s, 3H), 1.76 (d, *J* = 12.1 Hz, 3H), 1.69 (d, *J* = 11.4 Hz, 3H), 1.64 (d, *J* = 2.6 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 129.2, 117.0, 114.1(t, *J* = 243.8 Hz), 113.1, 62.9, 54.9(t, *J* = 26.3 Hz), 41.5, 37.3, 37.0, 28.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.39 (d, *J* = 3.5 Hz).

HRMS (ESI, m/z) calcd for $C_{19}H_{26}F_2N[M+H]^+$: 306.2028; found: 306.2029.

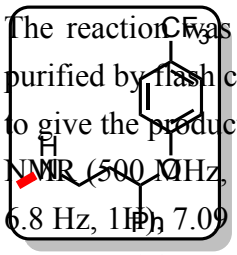
(4-chlorophenyl)(5-methoxy-2-methyl-3-(2-(methyl(phenyl)amino)ethyl)-1H-indol-1-yl)methanone (2av)



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 15:1, v/v) to give the product as yellow oil (175.0 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.50 – 7.44 (m, 2H), 7.26 (dd, *J* = 10.3, 5.6 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.78 – 6.70 (m, 4H), 3.84 (s, 3H), 3.65 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.93 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 156.0, 148.7, 139.0, 134.5, 134.2, 131.1, 131.0, 129.3, 129.1, 117.3, 116.1, 115.1, 111.8, 111.3, 101.0, 55.7, 52.1, 38.6, 21.6, 13.4.

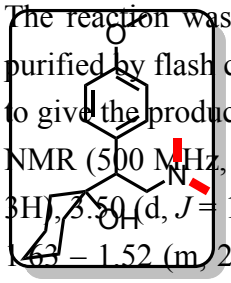
HRMS (ESI, m/z) calcd for $C_{26}H_{26}ClN_2O_2[M+H]^+$: 433.1677; found: 433.1679.

N-methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine (2aw) (CAS: No. 54910-89-3)[14]



The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (80.3 mg, 52%). M. P. 157 °C (Lit. 157-159 °C). ^{1}H NMR (500 MHz, DMSO) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.33 (m, 4H), 7.29 (t, *J* = 6.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 5.75 (s, 1H), 2.97 (s, 2H), 2.51 (s, 3H), 2.32 (dd, *J* = 13.5, 6.4 Hz, 1H), 2.20 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 160.6, 140.6, 129.2, 128.5, 128.1, 127.3 (d, *J* = 3.6 Hz), 126.4, 124.9(d, *J* = 270.0 Hz), 121.8(q, *J* = 32.5 Hz), 116.8, 77.0, 45.7, 34.8, 33.1. ^{19}F NMR (471 MHz, DMSO) δ -59.98 (s).

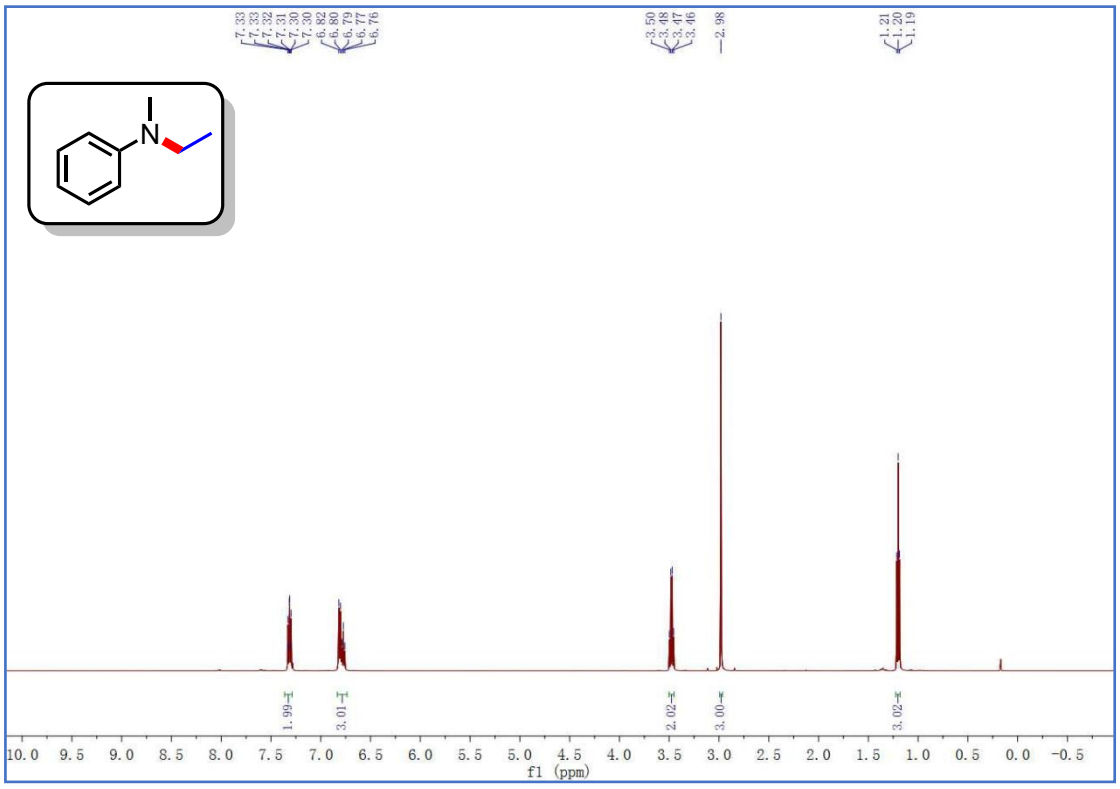
1-(2-(dimethylamino)-1-(4-methoxyphenyl)ethyl)cyclohexan-1-ol (2ax) (CAS: No. 93413-69-5)[15]

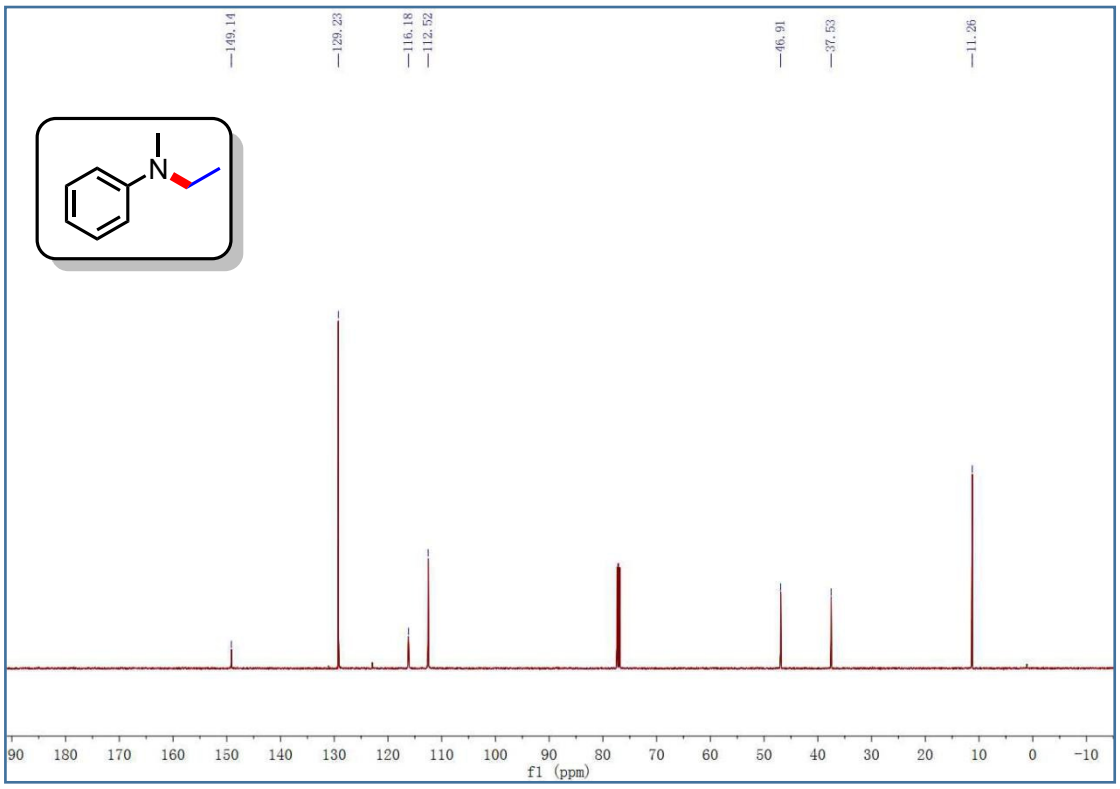


The reaction was performed by following the general procedure **3**. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a white solid (84.5 mg, 61%). M. P. 102 °C (Lit. 102-104 °C). ^{1}H NMR (500 MHz, DMSO) δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 3.50 (d, *J* = 10.3 Hz, 1H), 3.22 (s, 1H), 3.03 (dd, *J* = 8.4, 4.2 Hz, 1H), 2.50 (s, 6H), 1.63 – 1.52 (m, 2H), 1.49 – 1.24 (m, 5H), 1.18 – 1.02 (m, 2H), 0.95 (q, *J* = 11.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 158.5, 132.1, 131.0, 113.9, 72.6, 59.1, 55.4, 50.8, 44.0, 36.8, 33.5, 25.8, 21.8, 21.5.

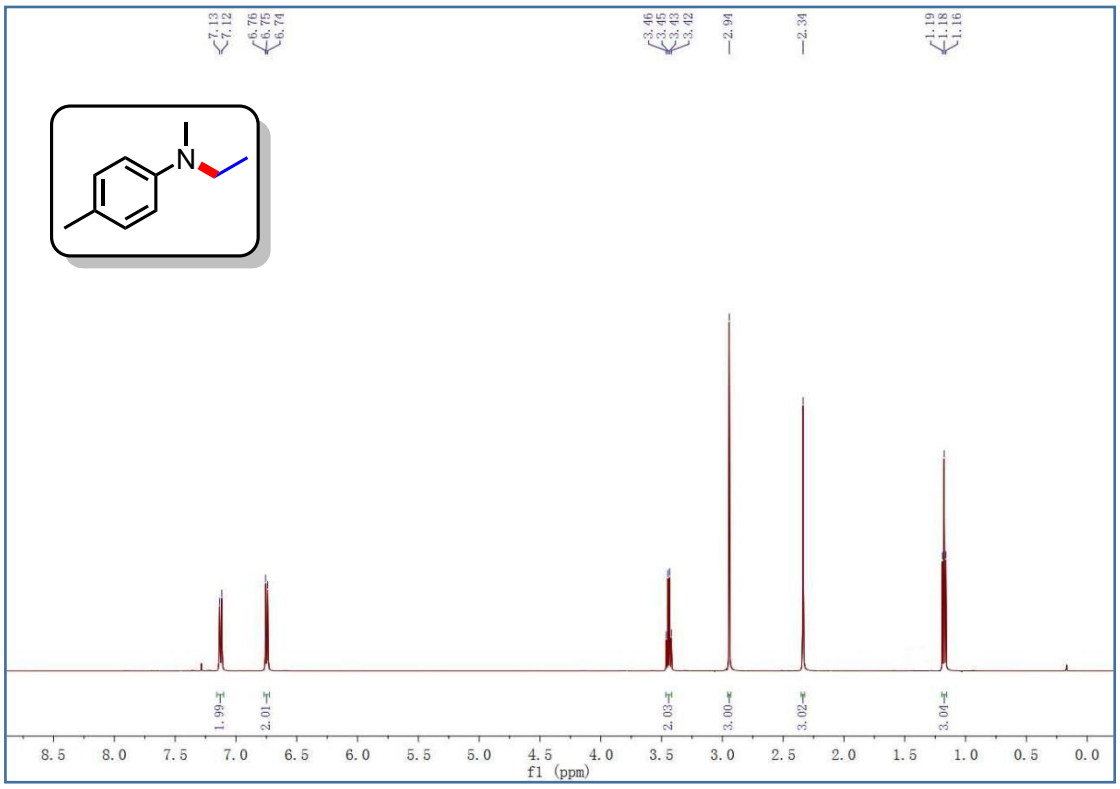
5. NMR spectroscopic data

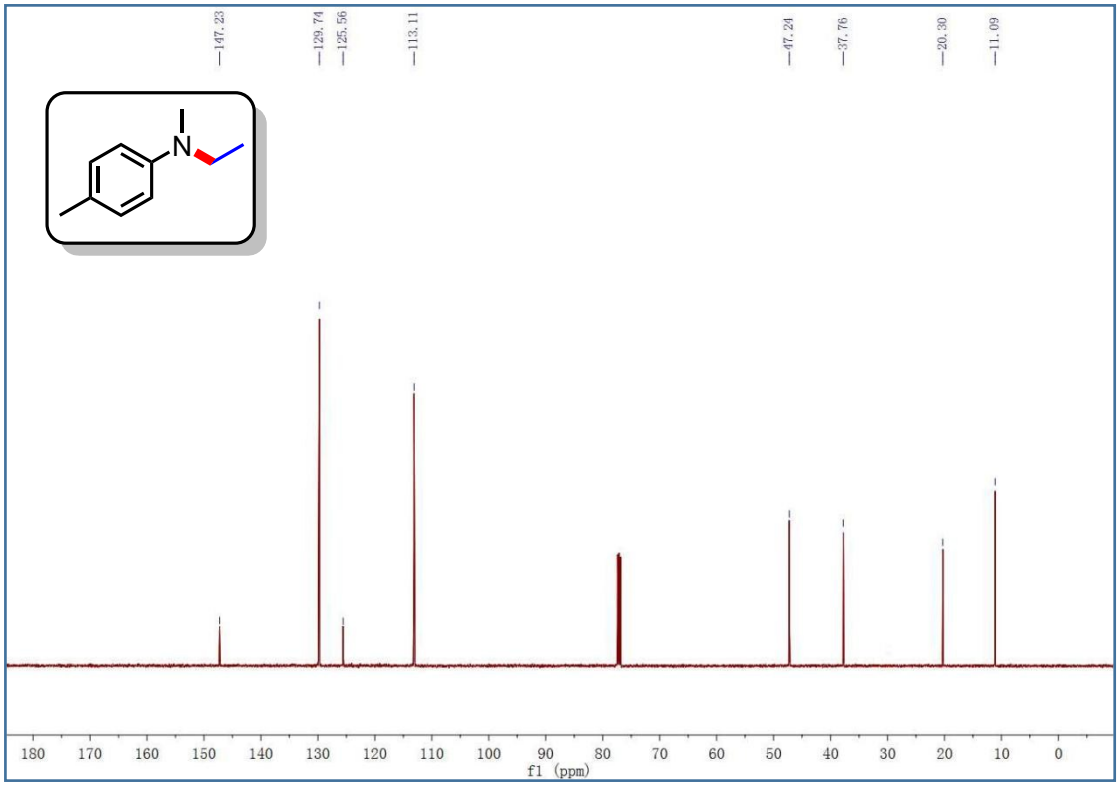
N-ethyl-N-methylaniline (2a)



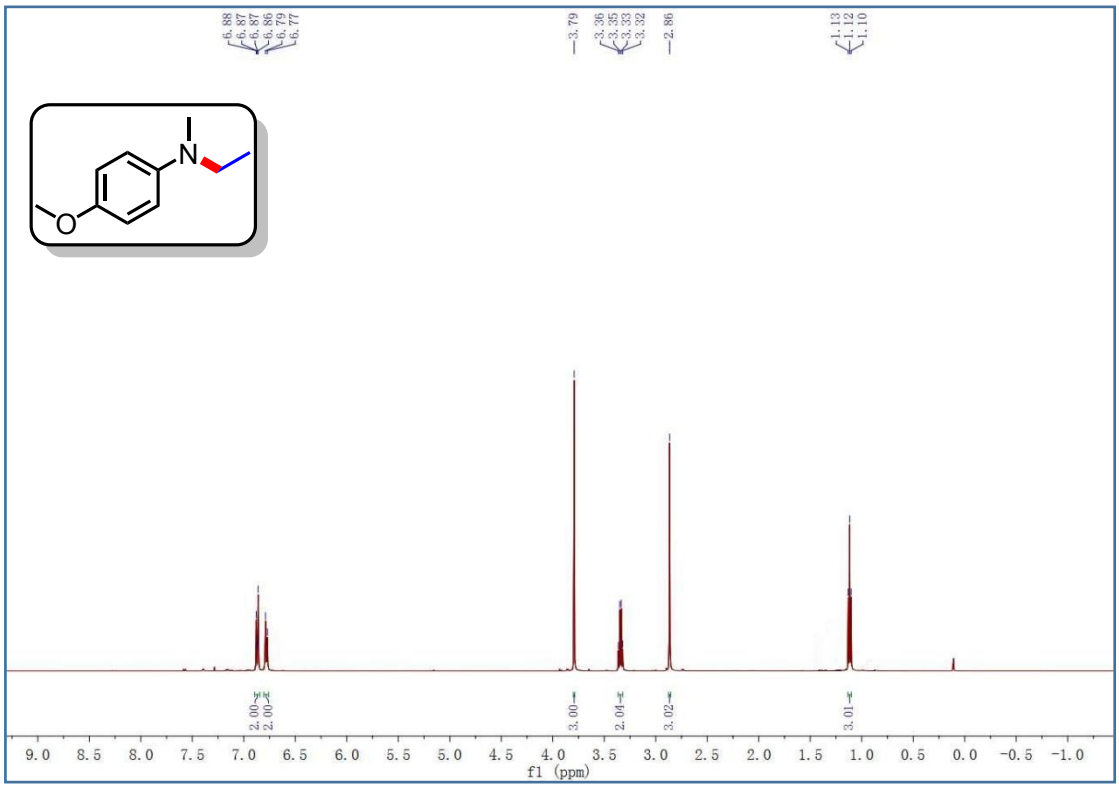


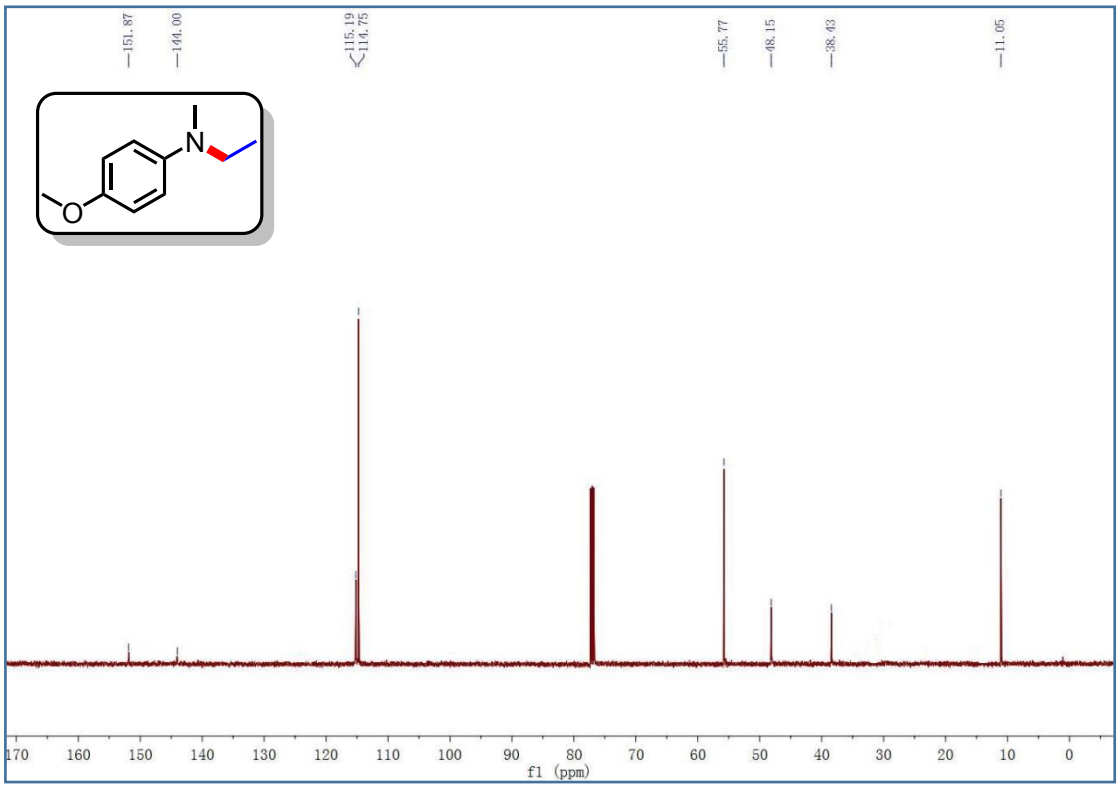
N-ethyl-N,4-dimethylaniline (2b)



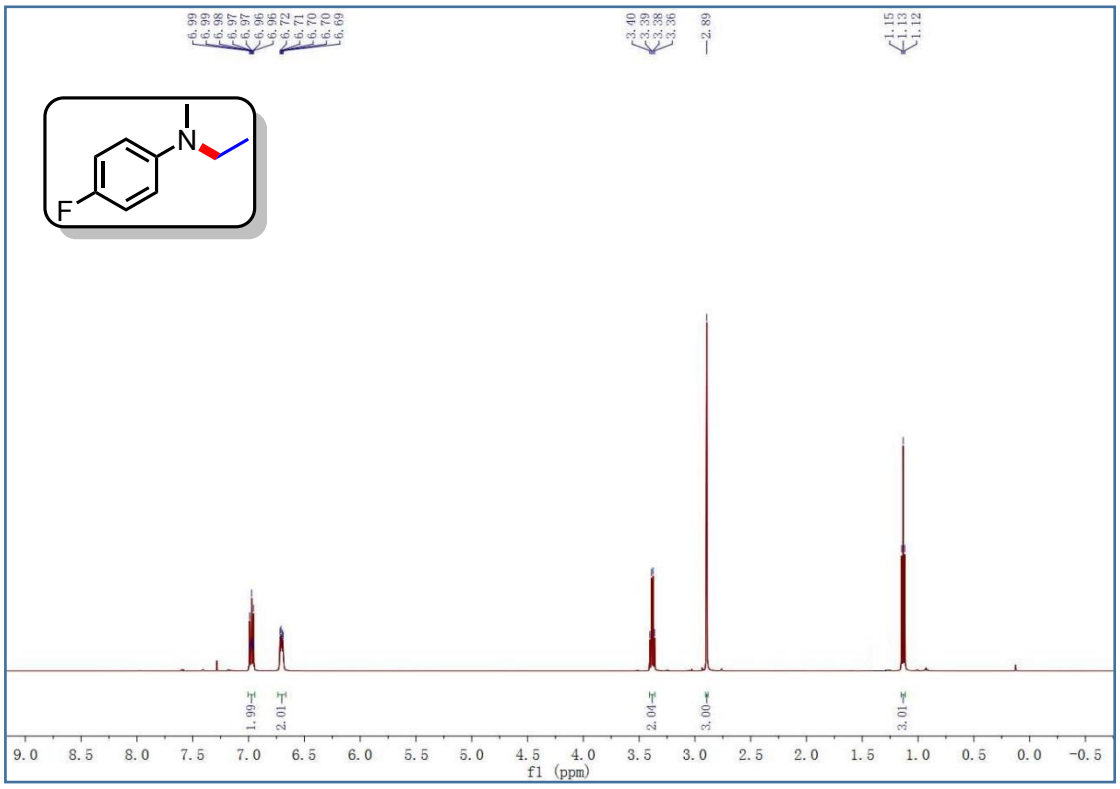


N-ethyl-4-methoxy-N-methylaniline (2c)





N-ethyl-4-fluoro-N-methylaniline (2d)


6.99
6.99
6.98
6.97
6.97
6.96
6.96
6.72
6.71
6.70
6.70
6.69
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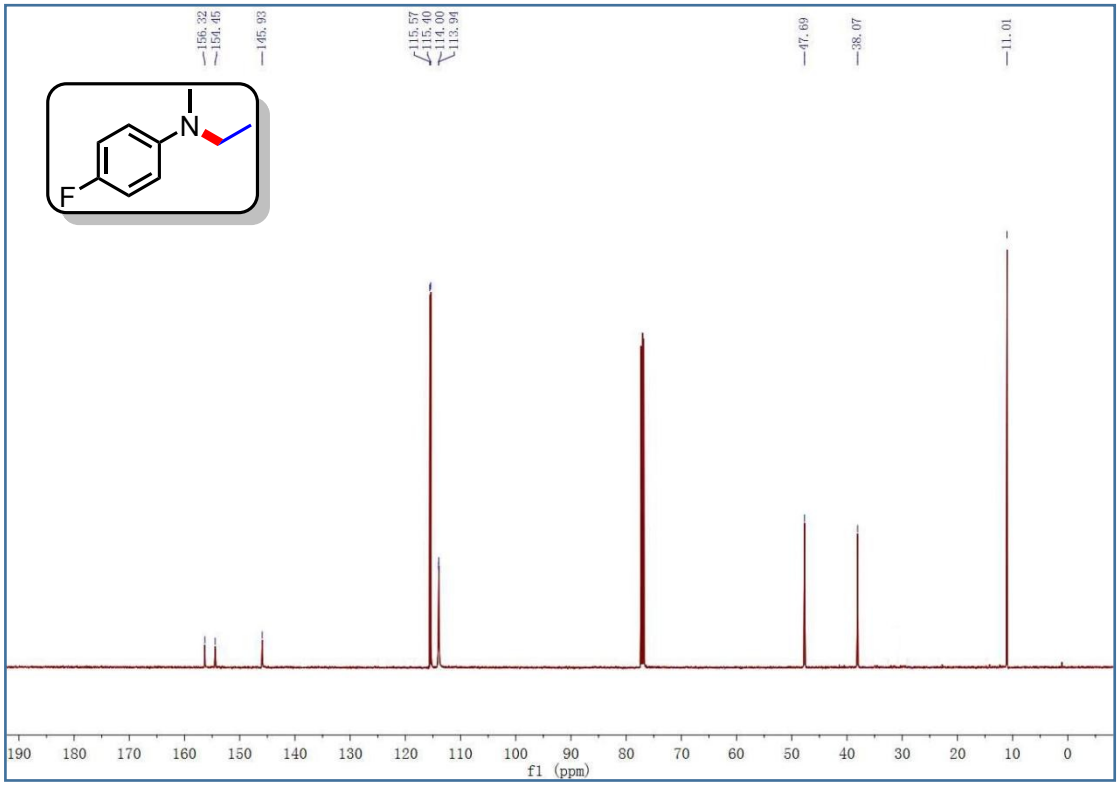
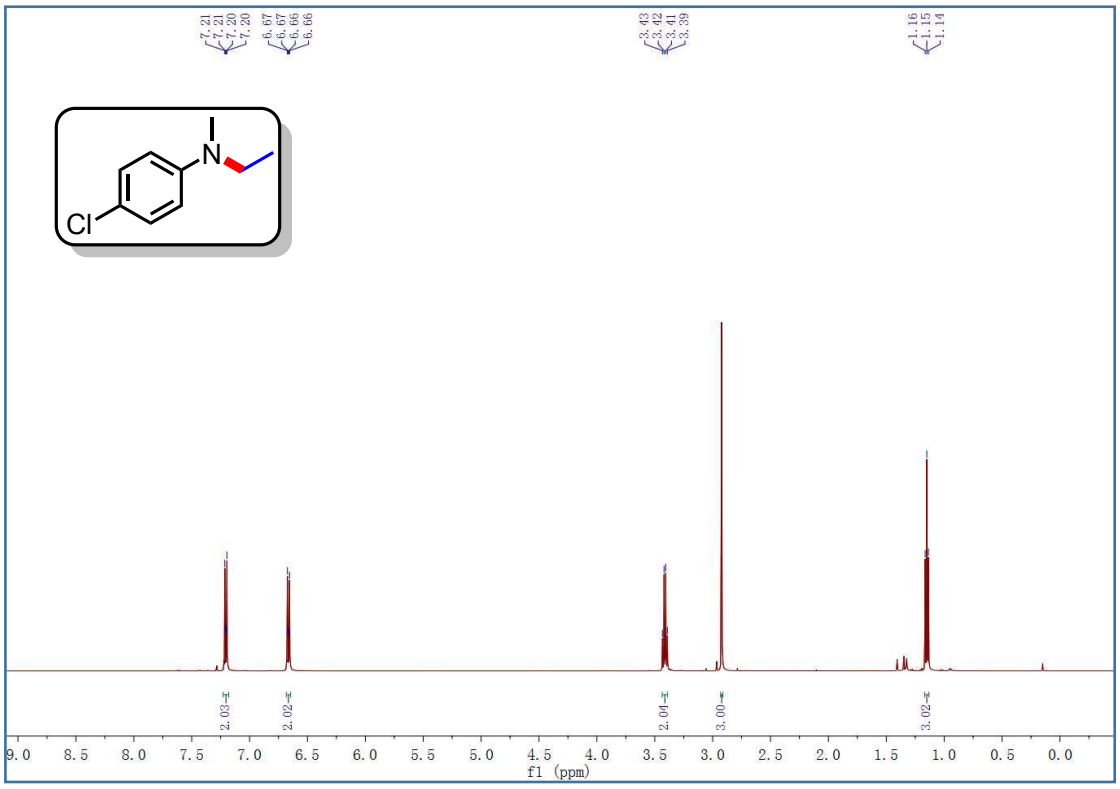
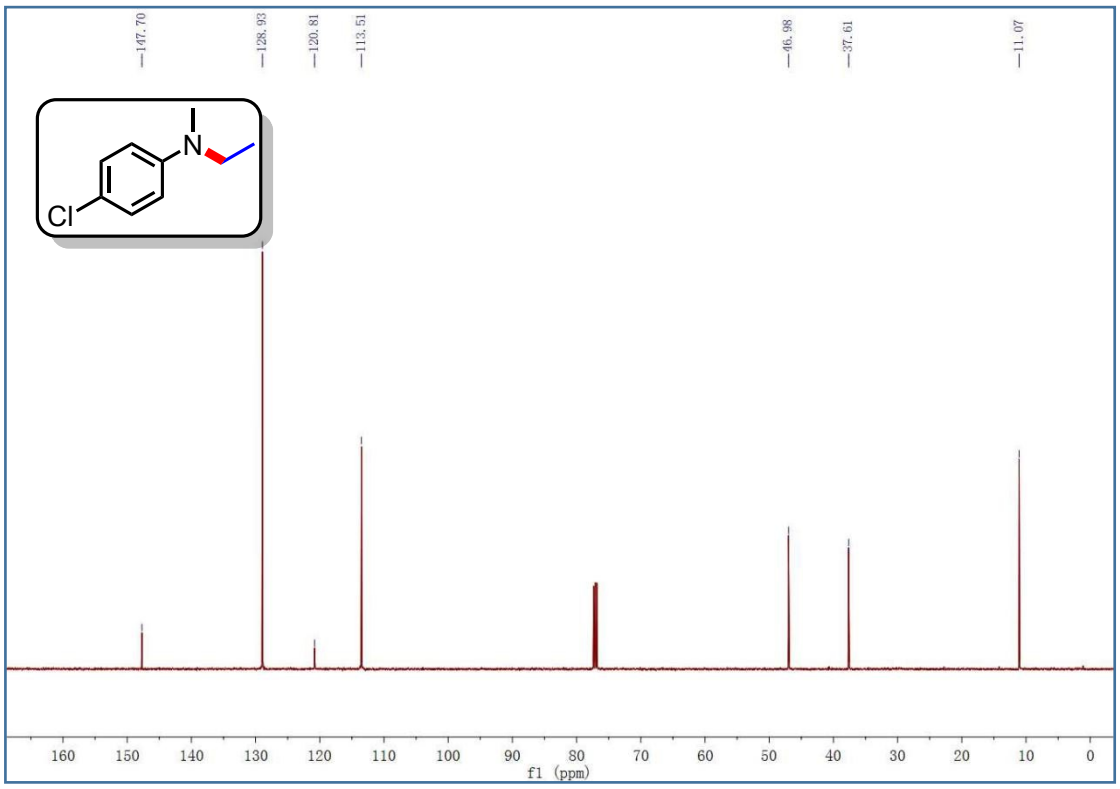
3.39
3.38
3.36
2.89
1.15
1.13
1.12
N
F
1.99
2.01
2.04
3.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

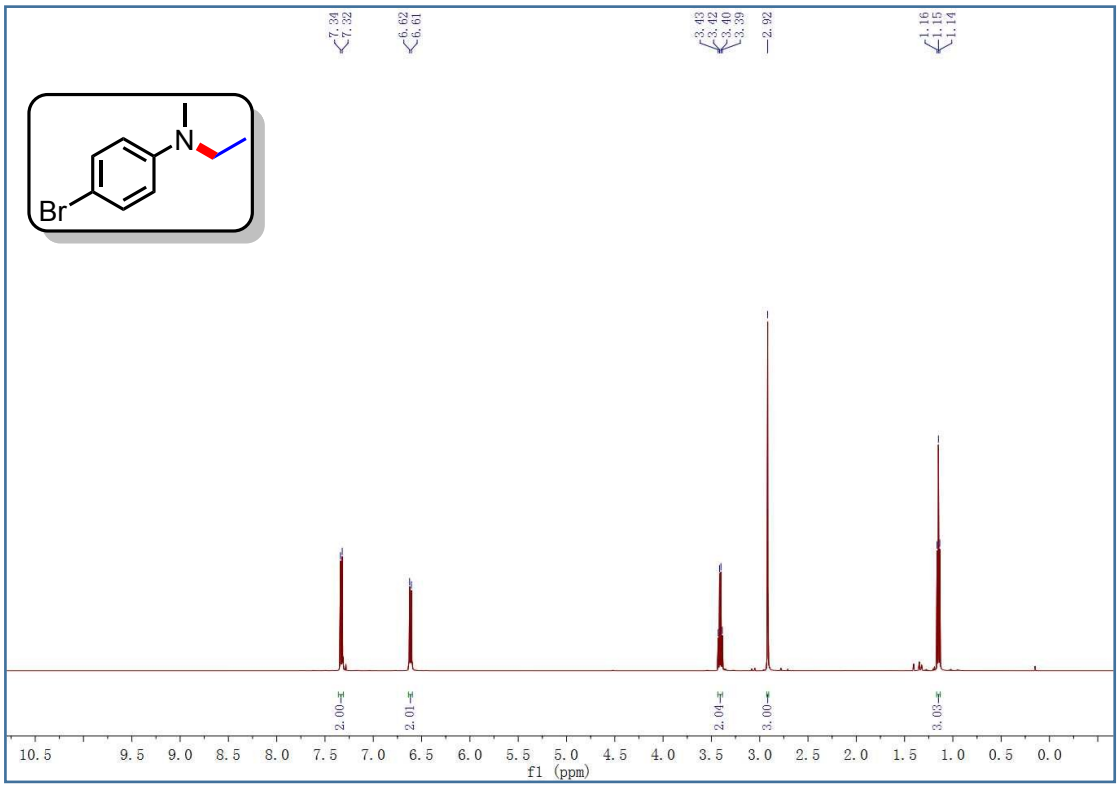

156.32
154.45
145.93
115.57
115.40
114.00
113.94
47.69
38.07
11.01
N
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

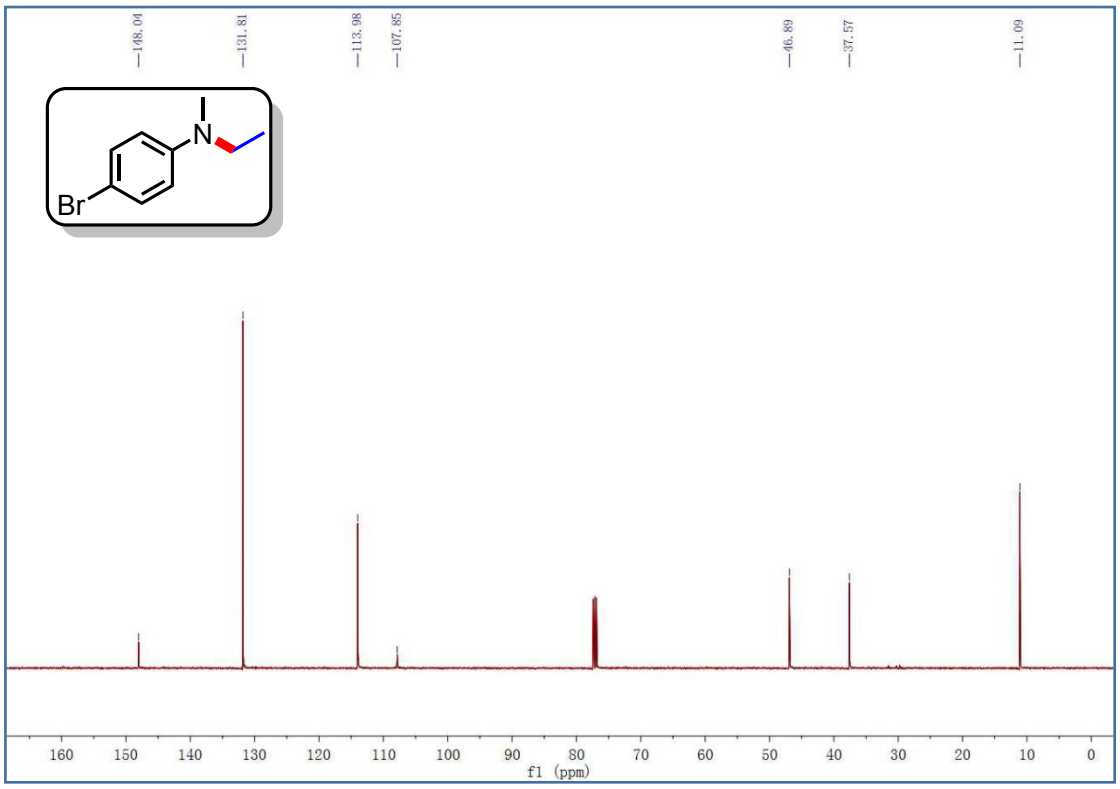
4-chloro-N-ethyl-N-methylaniline (2e)



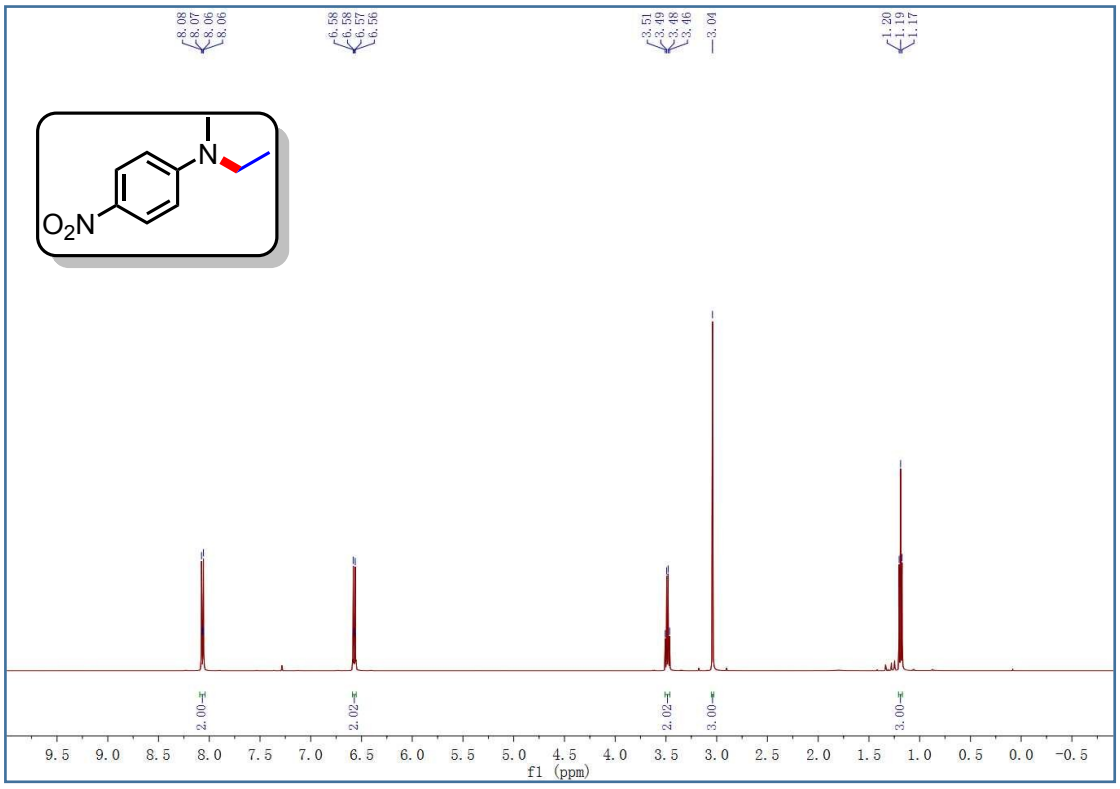


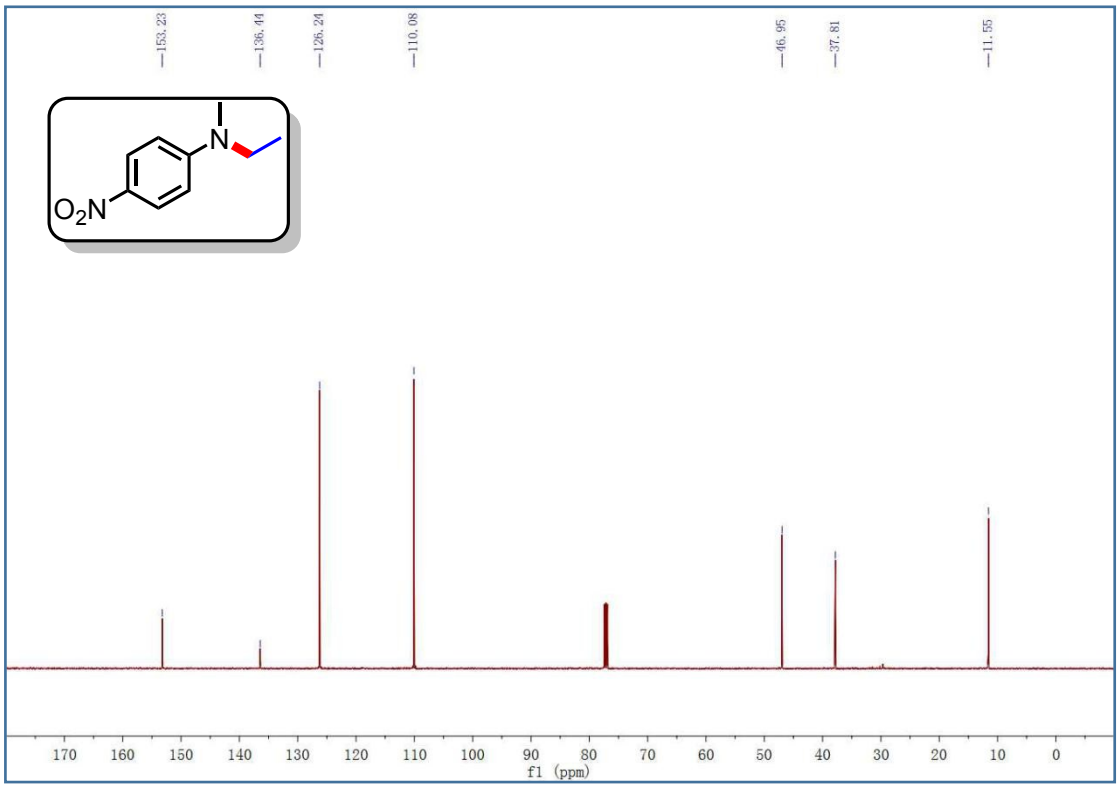
4-bromo-N-ethyl-N-methylaniline (2f)



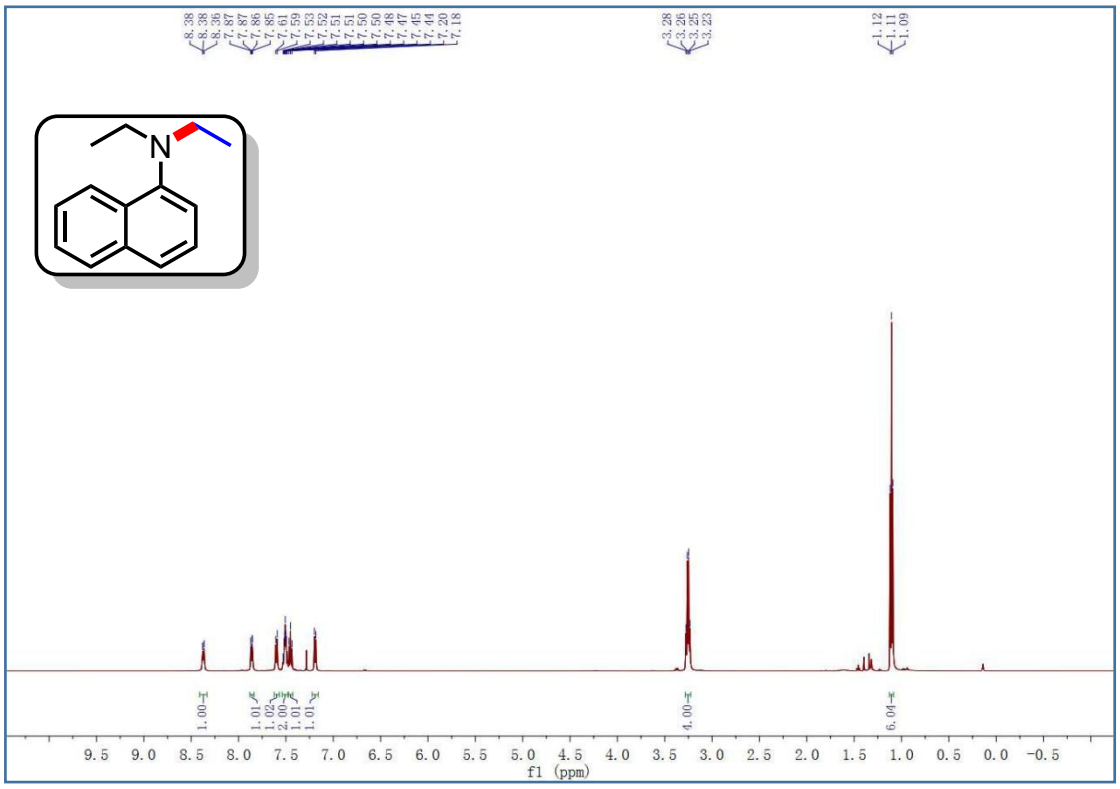


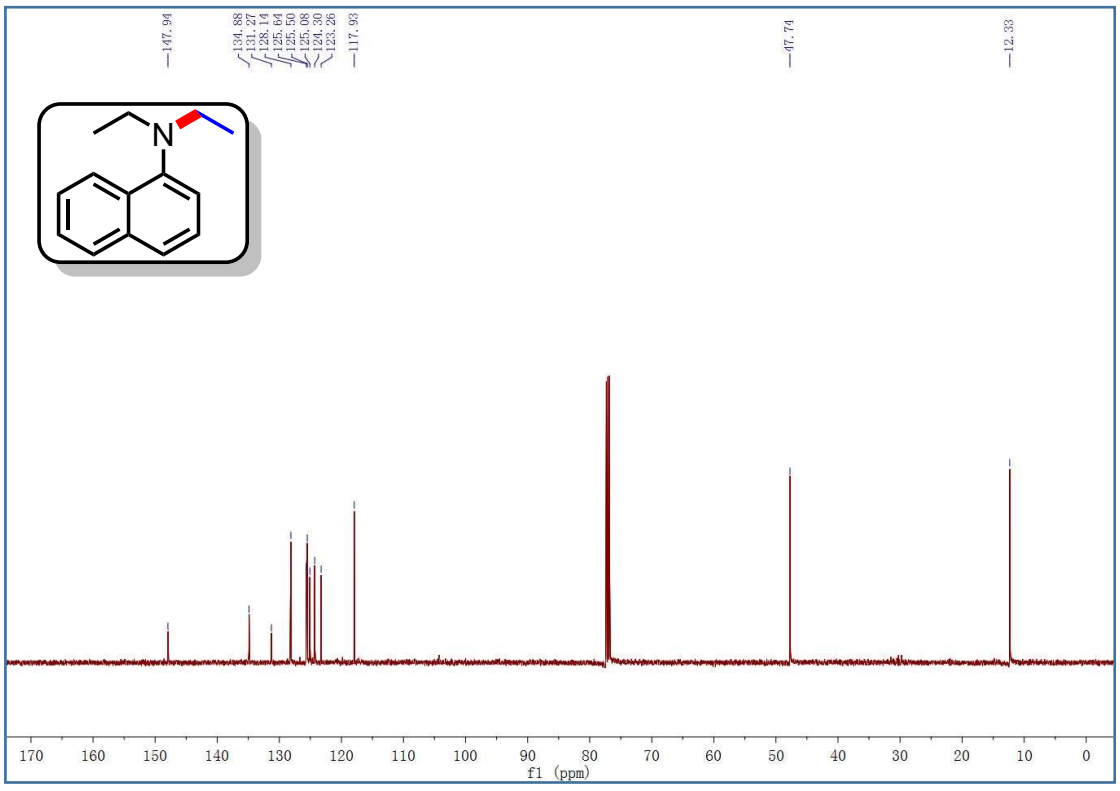
N-ethyl-N-methyl-4-nitroaniline (2g)



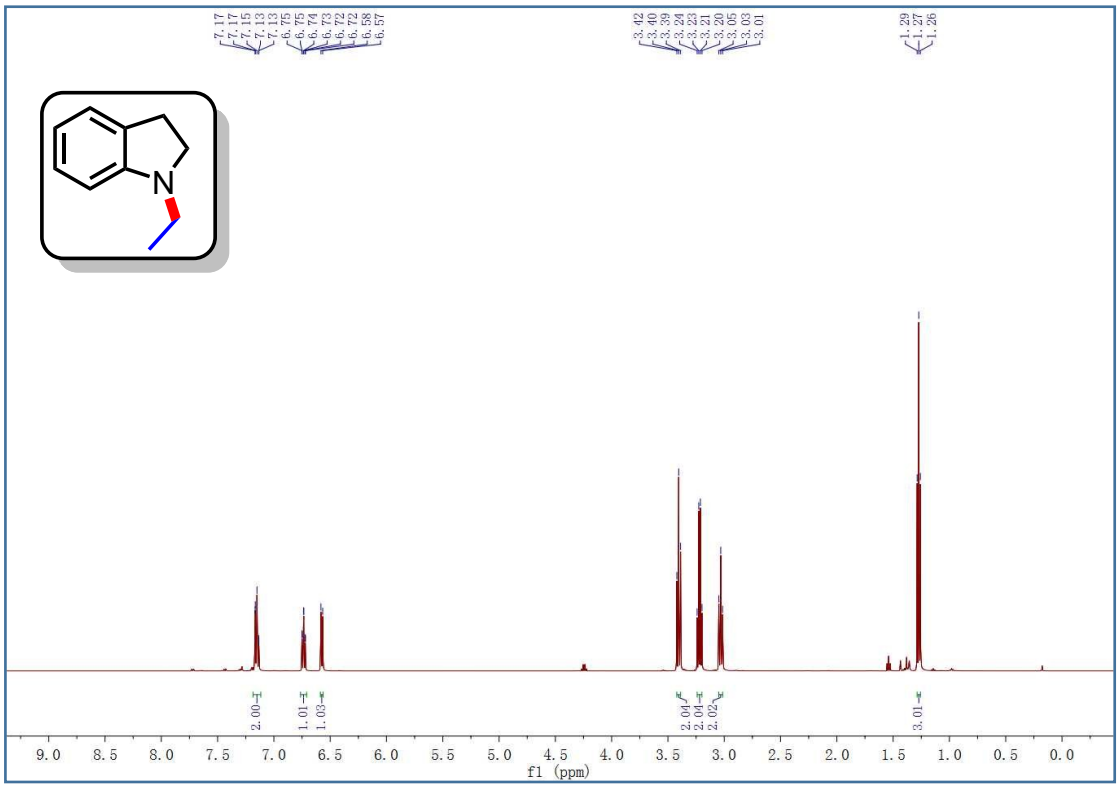


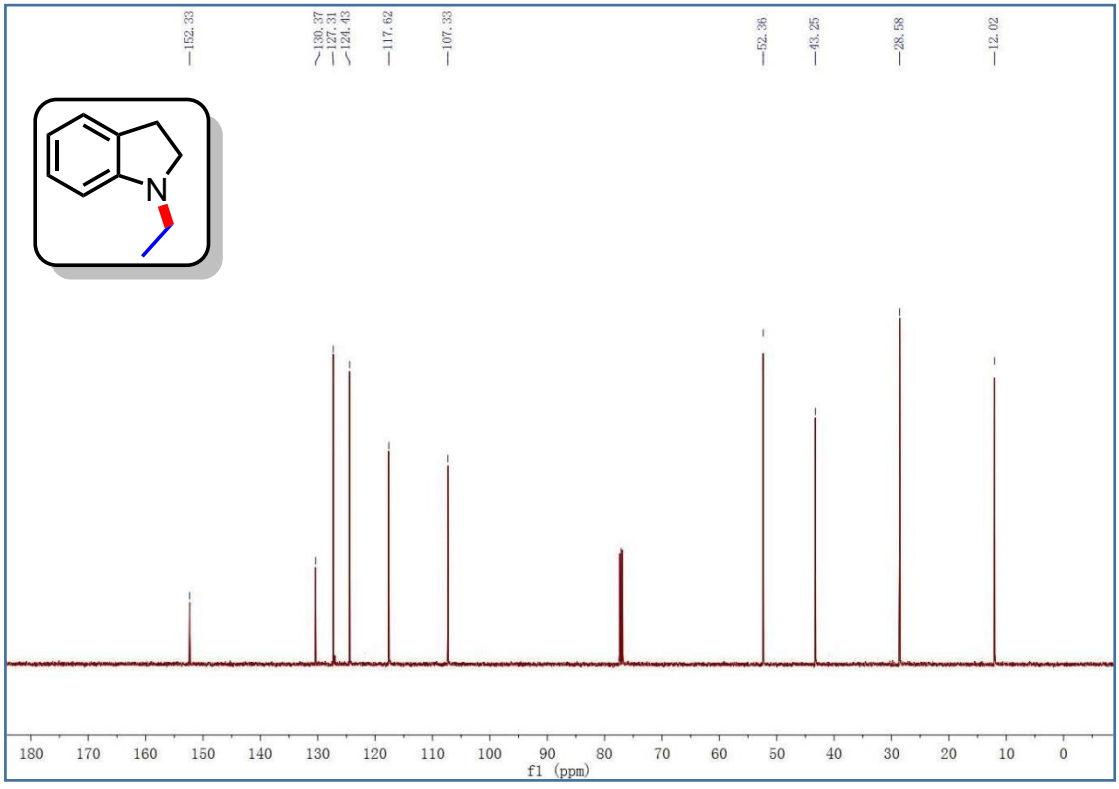
N,N-diethylnaphthalen-1-amine (2h)


8.38
8.38
8.36
7.87
7.87
7.86
7.85
7.61
7.59
7.53
7.52
7.51
7.51
7.50
7.50
7.48
7.47
7.45
7.44
7.20
7.18
3.28
3.26
3.25
3.23
1.12
1.11
1.09
1.00
1.01
1.02
2.00
1.01
1.01
4.00
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

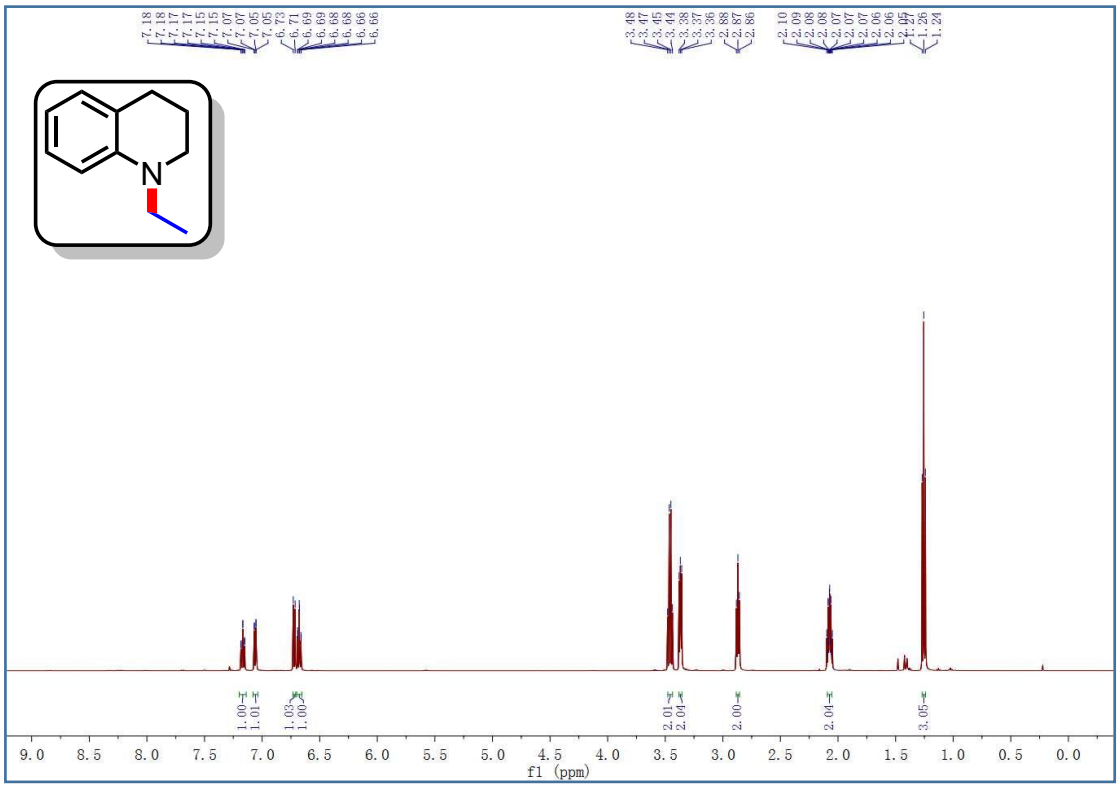

147.94
134.88
131.27
128.14
125.64
125.50
125.08
124.30
123.26
117.93
47.74
12.33
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

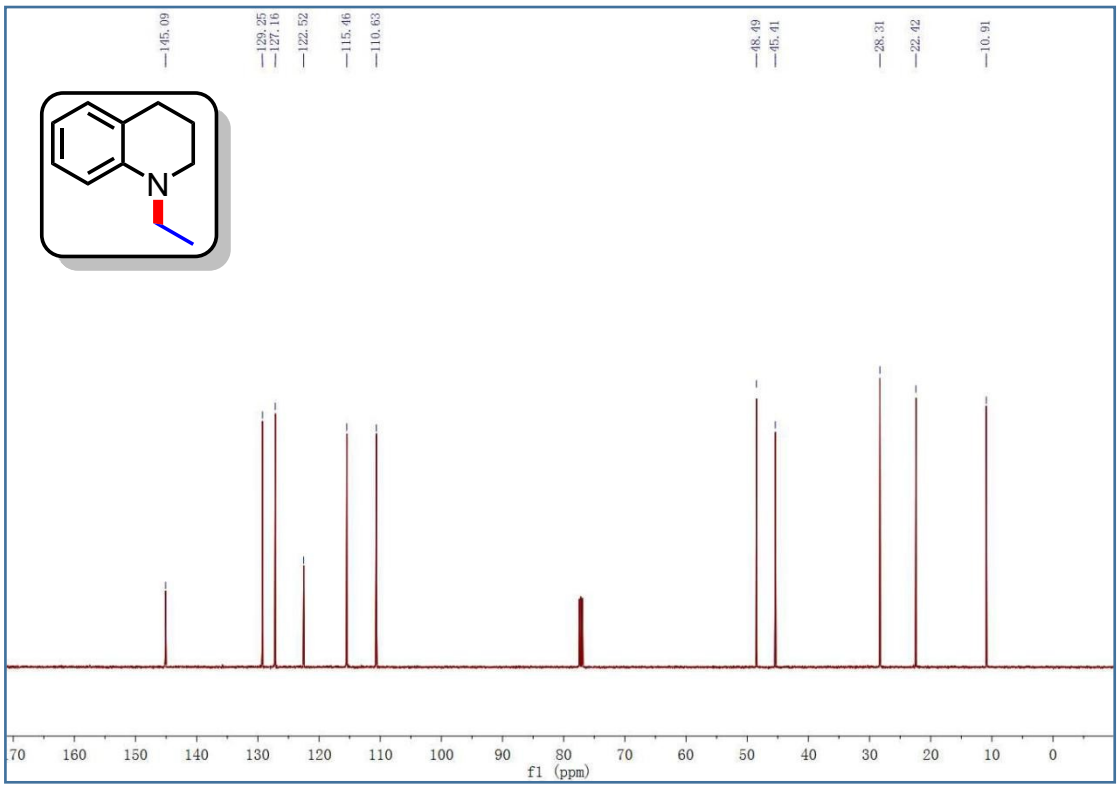
1-ethylindoline (2i)



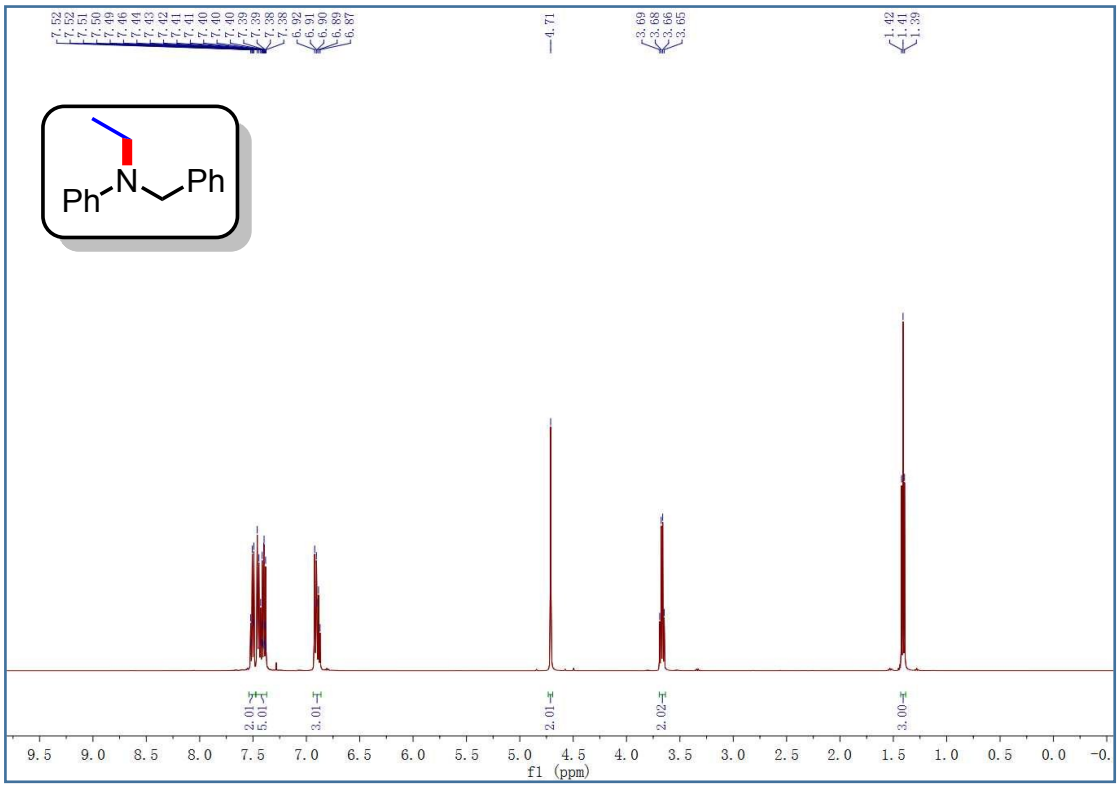


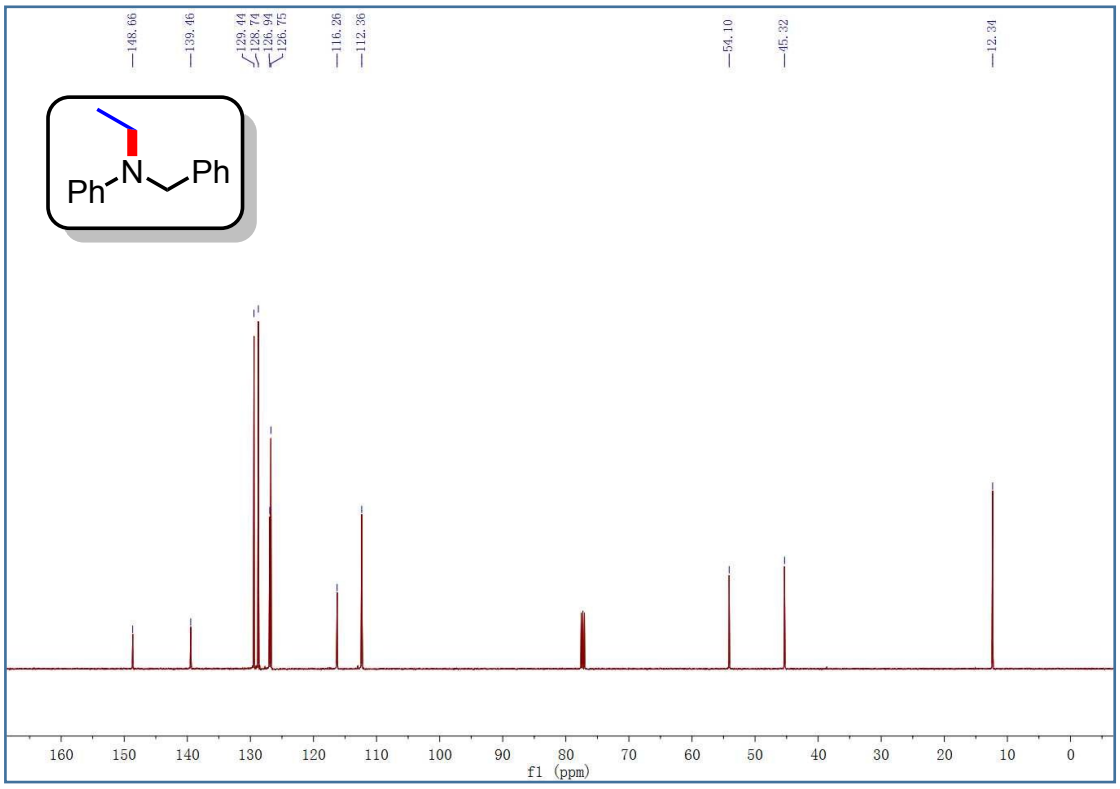
1-ethyl-1,2,3,4-tetrahydroquinoline (2j)



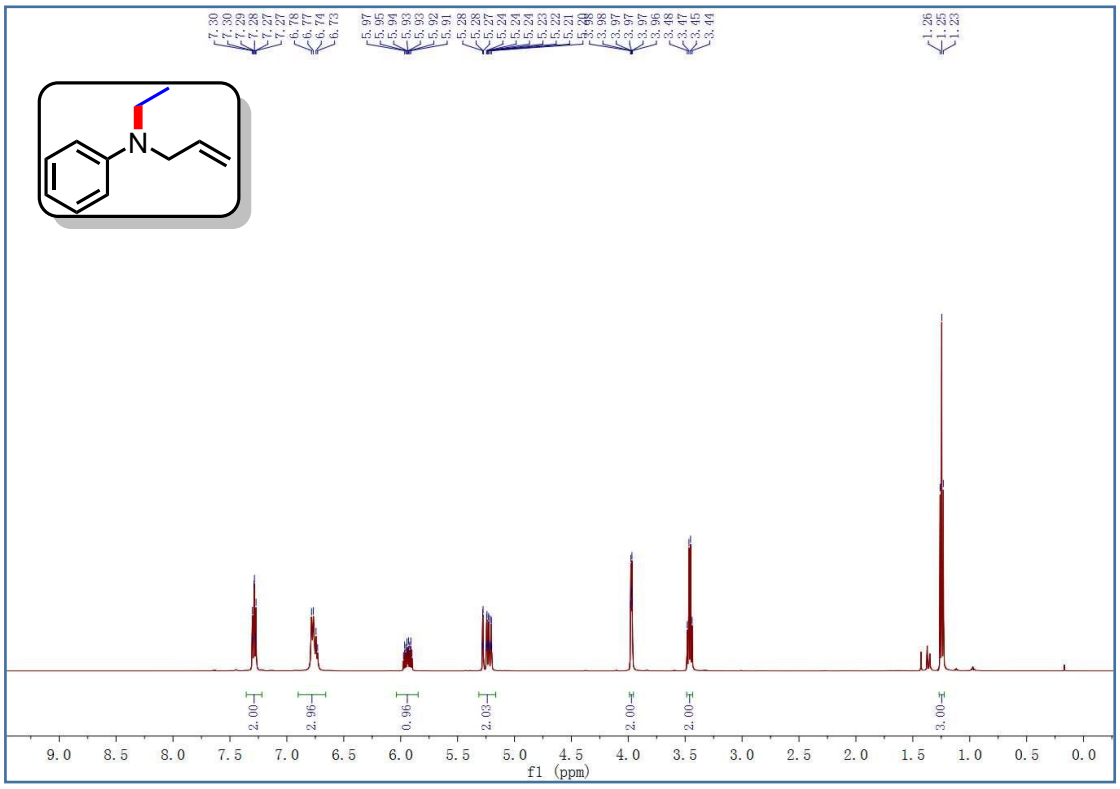


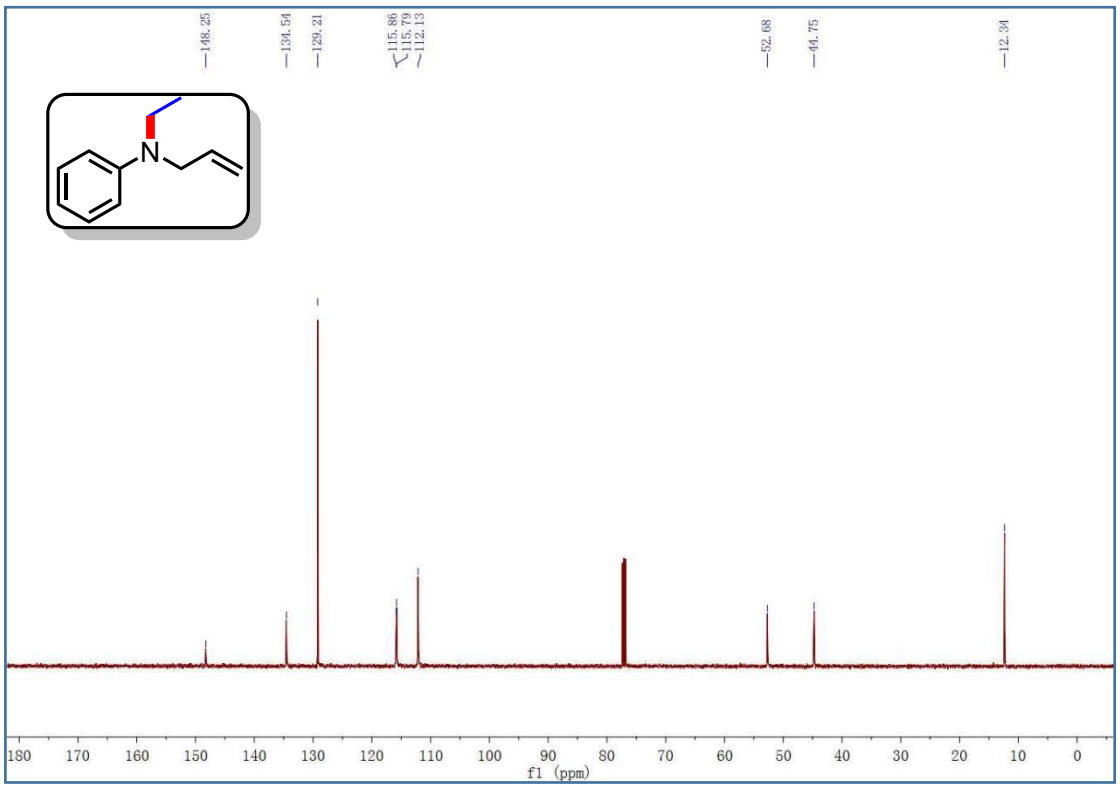
N-benzyl-N-ethylaniline (2k)



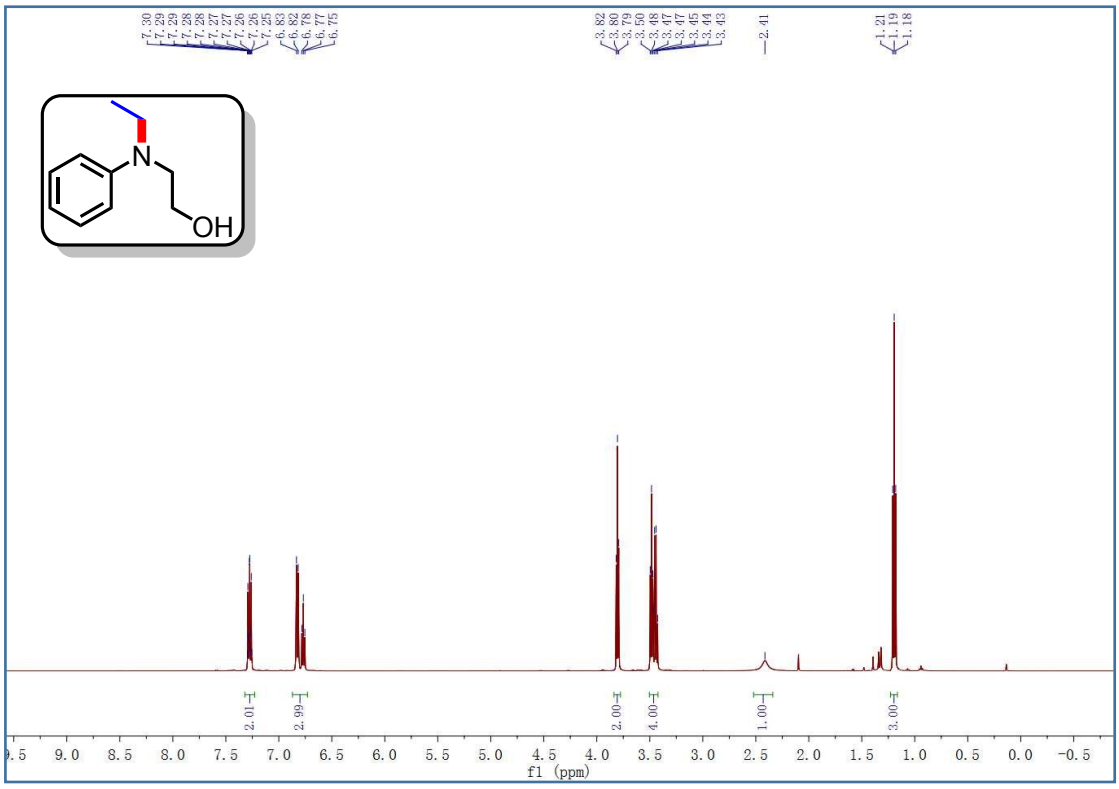


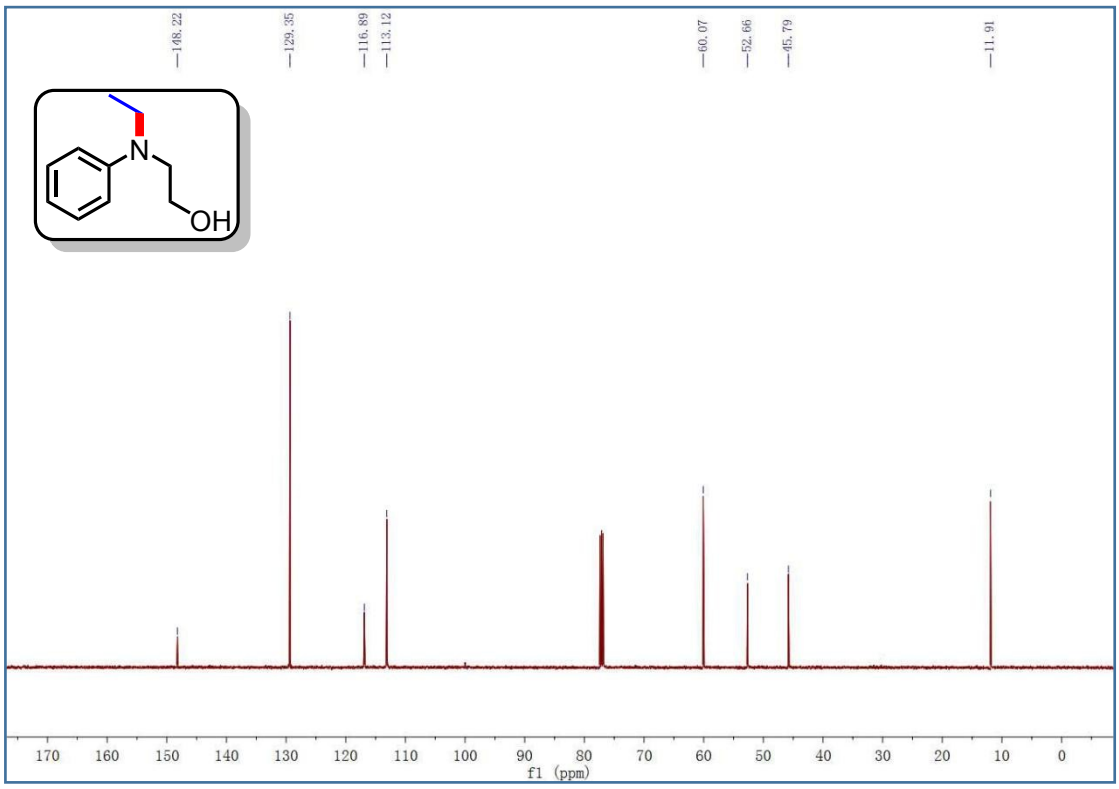
4-allyl-N-ethyl-N-methylaniline (2l)


7.30
7.30
7.29
7.28
7.27
7.27
6.78
6.77
6.74
6.73
5.97
5.95
5.94
5.93
5.93
5.92
5.91
5.28
5.27
5.24
5.24
5.23
5.22
5.21
3.98
3.97
3.97
3.96
3.48
3.47
3.45
3.44
1.26
1.25
1.23
N
2.00
2.96
0.96
2.03
2.00
2.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

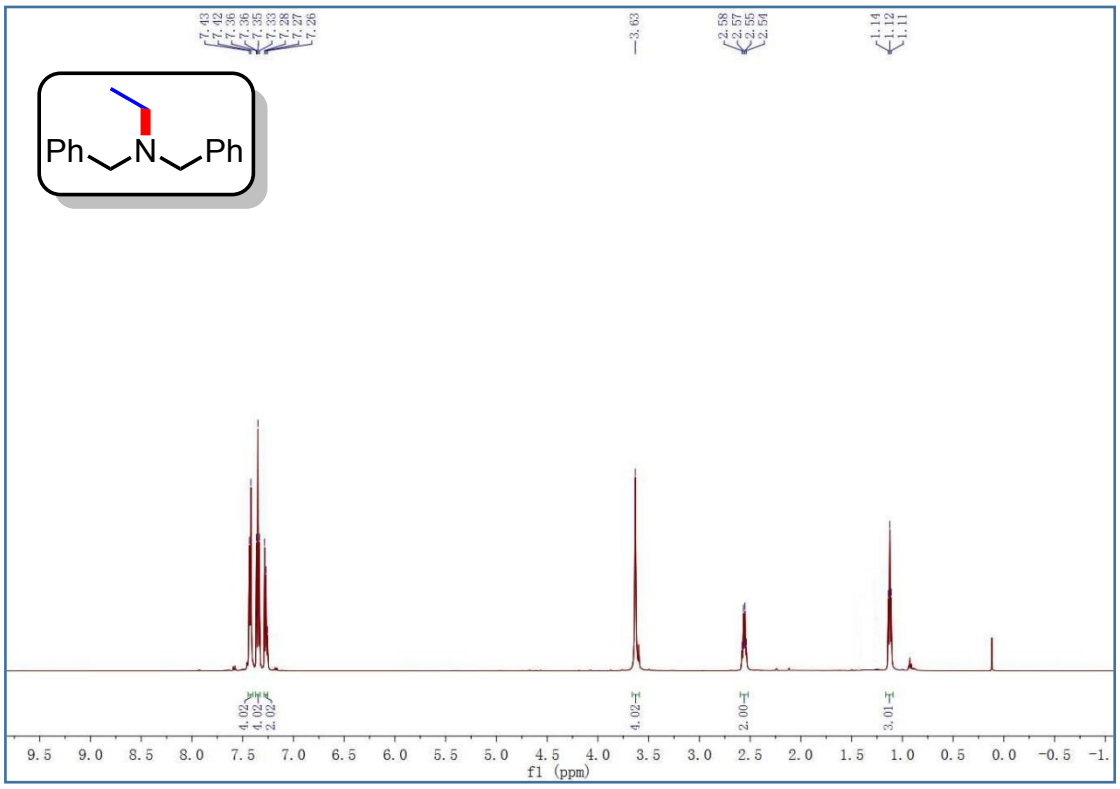

148.25
134.54
129.21
115.86
115.79
112.13
52.68
44.75
12.34
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

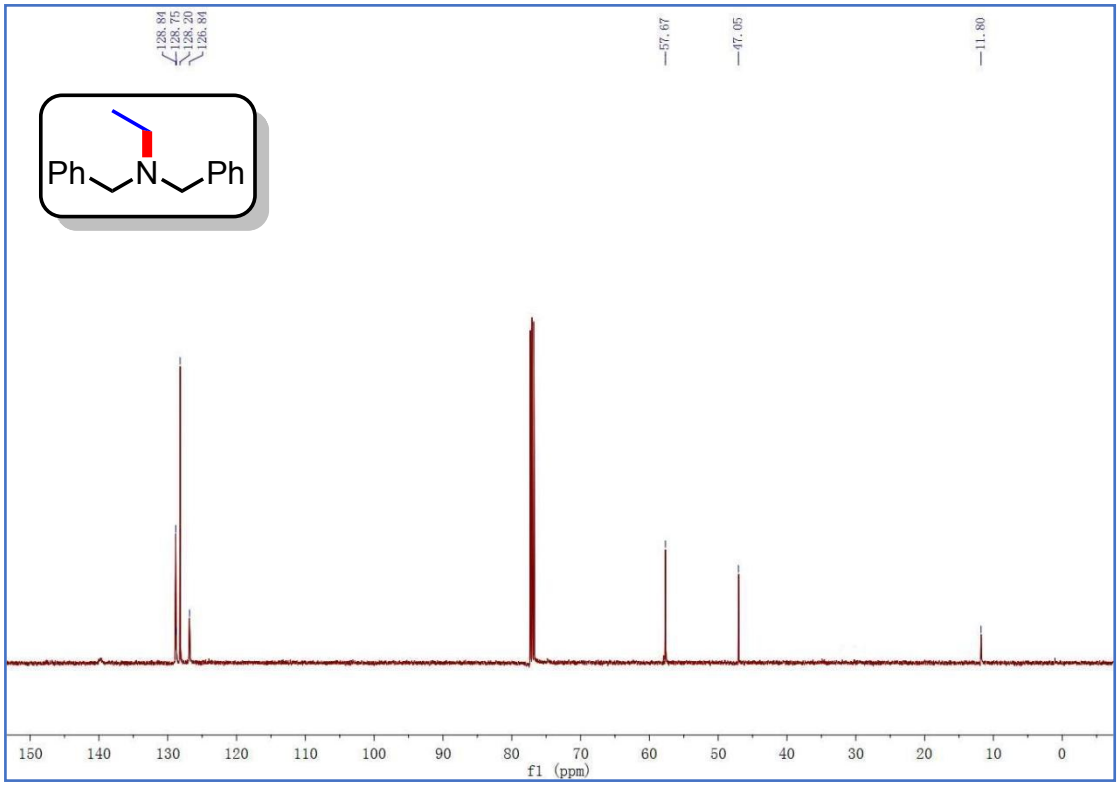
2-(4-(ethyl(methyl)amino)phenyl)ethan-1-ol (2m)



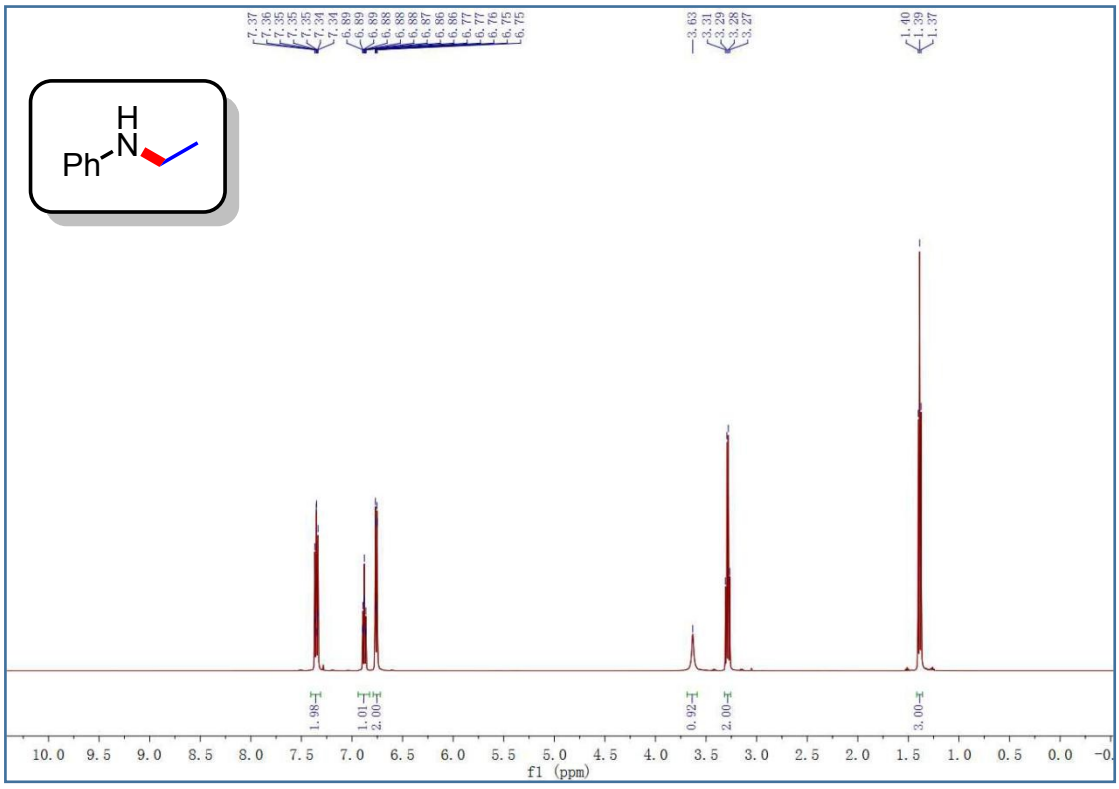


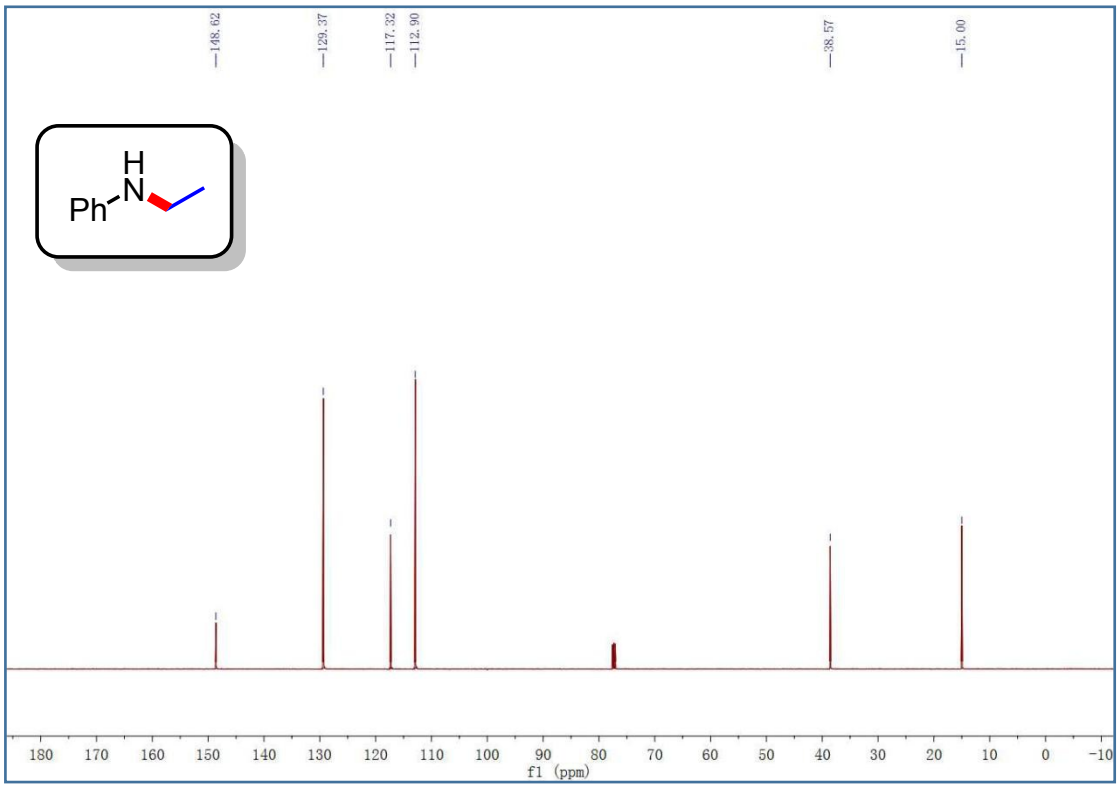
N,N-dibenzylethanamine (2n)



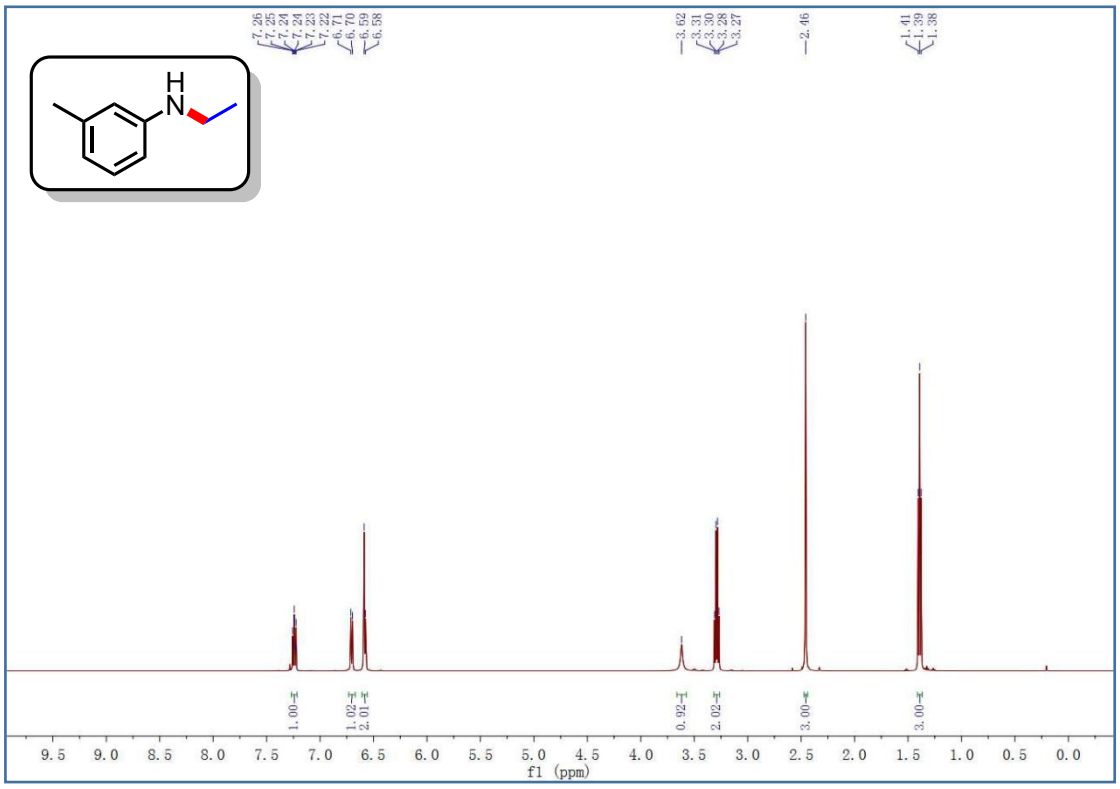


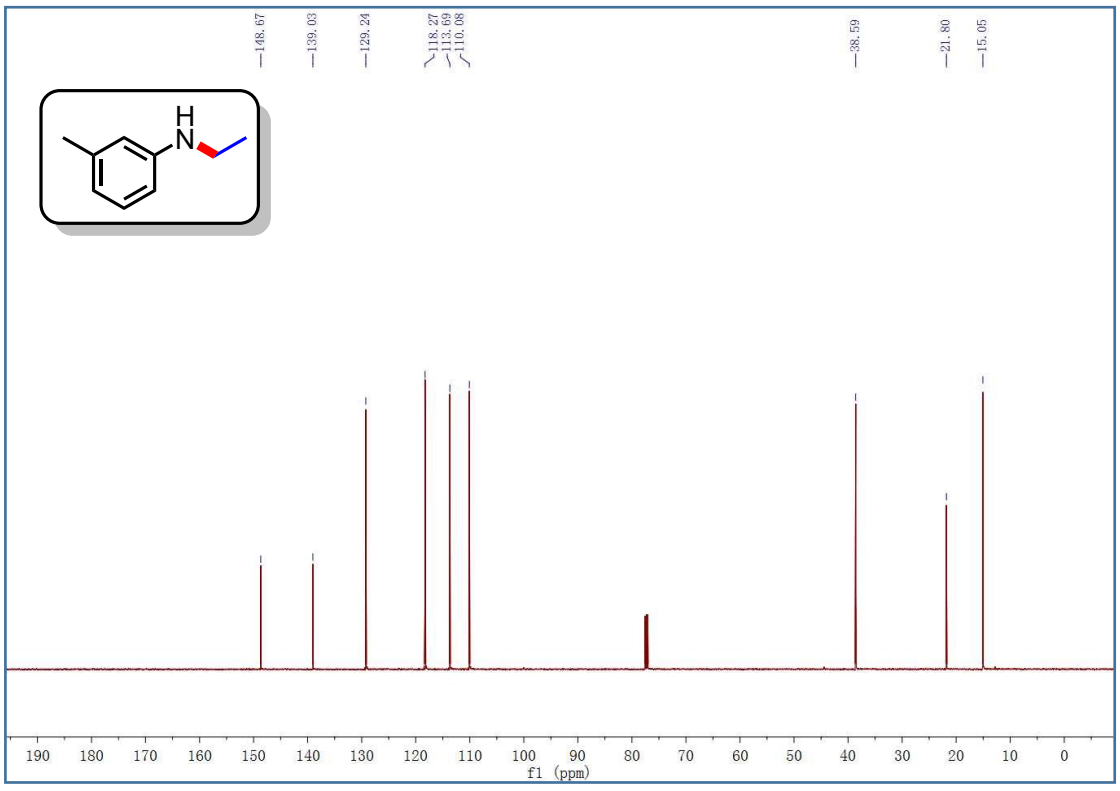
N-ethylaniline (2o)



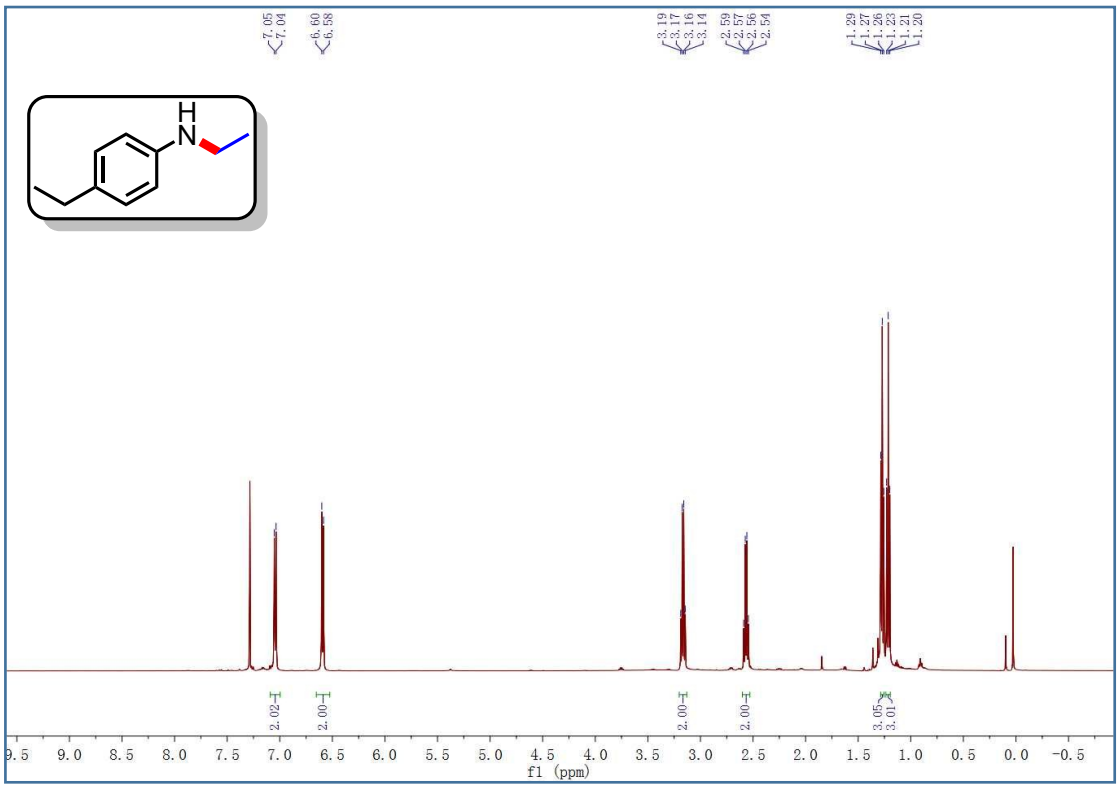


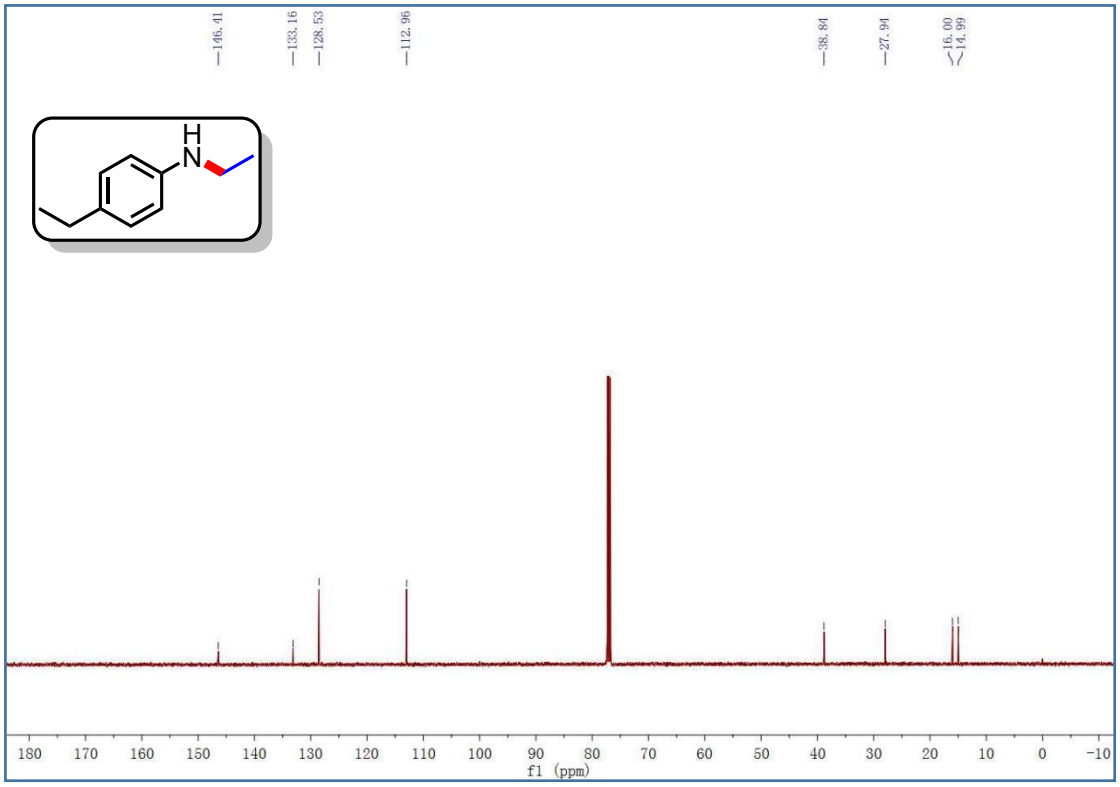
N-ethyl-3-methylaniline (2p)


7.26
7.25
7.24
7.24
7.23
7.22
6.71
6.59
6.58
3.62
3.31
3.30
3.28
3.27
2.46
1.41
1.39
1.38
1.00
1.02
2.01
0.92
2.02
3.00
3.00
f1 (ppm)

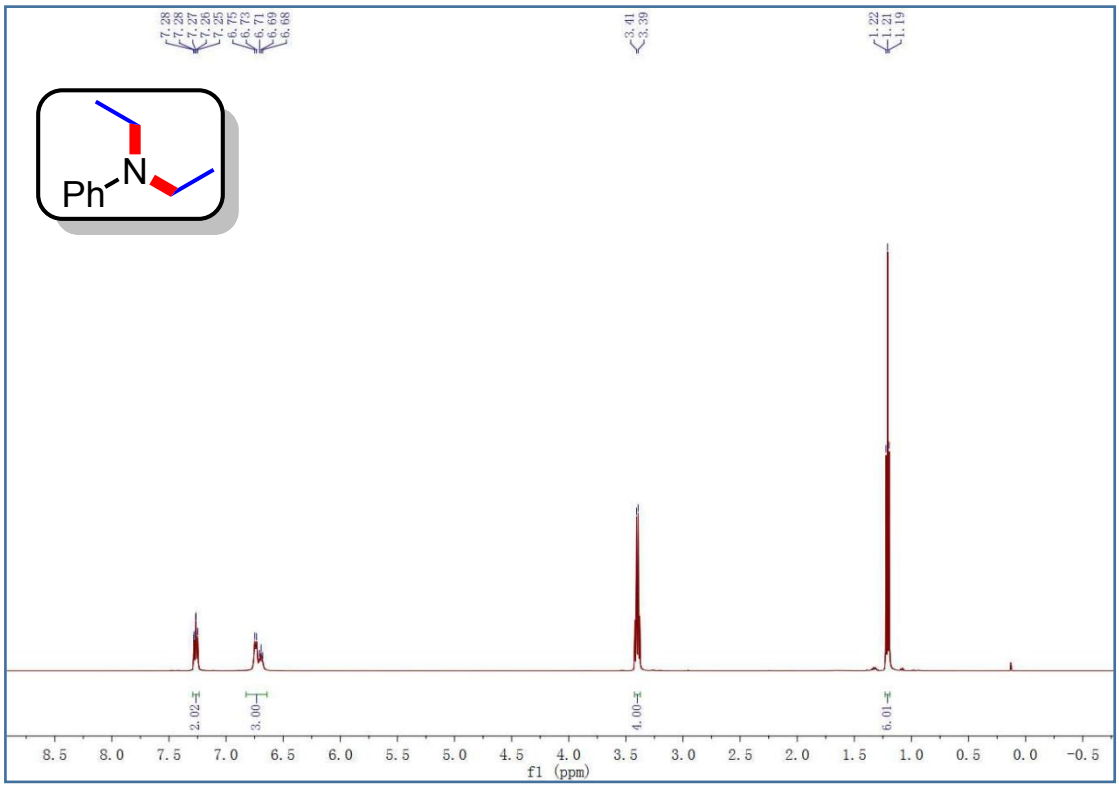

148.67
139.03
129.24
118.27
113.69
110.08
38.59
21.80
15.05
f1 (ppm)

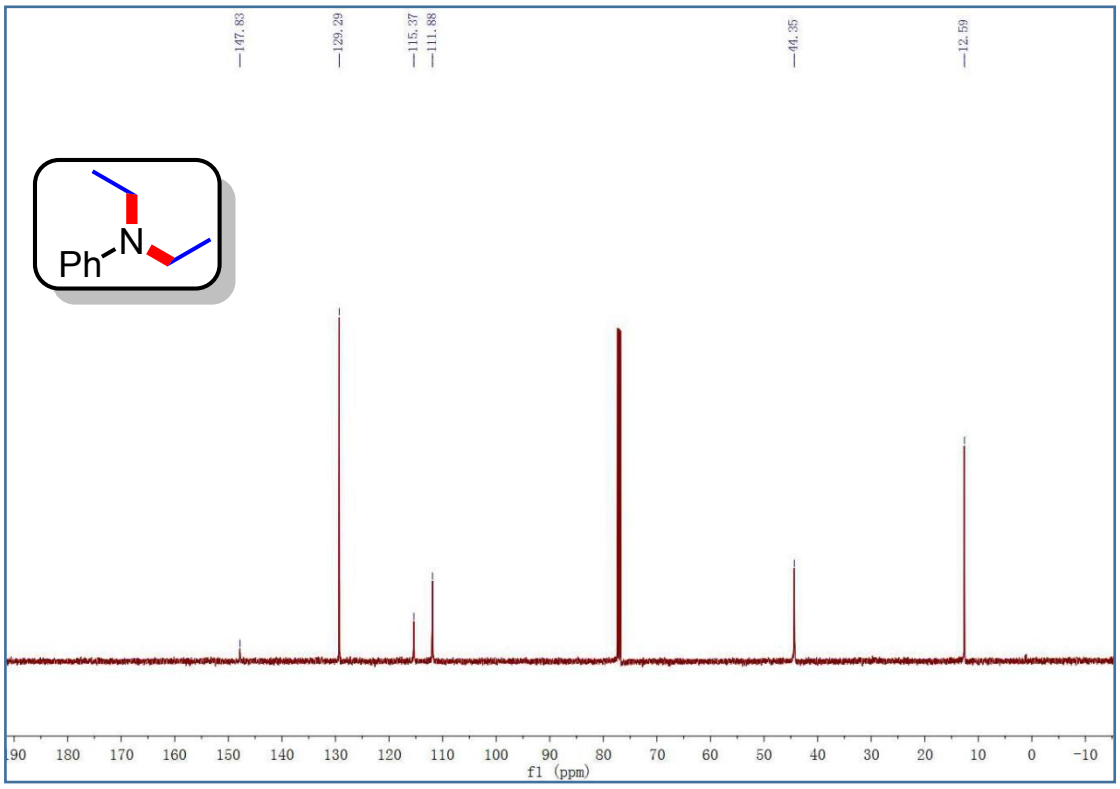
N,4-diethylaniline (2q)



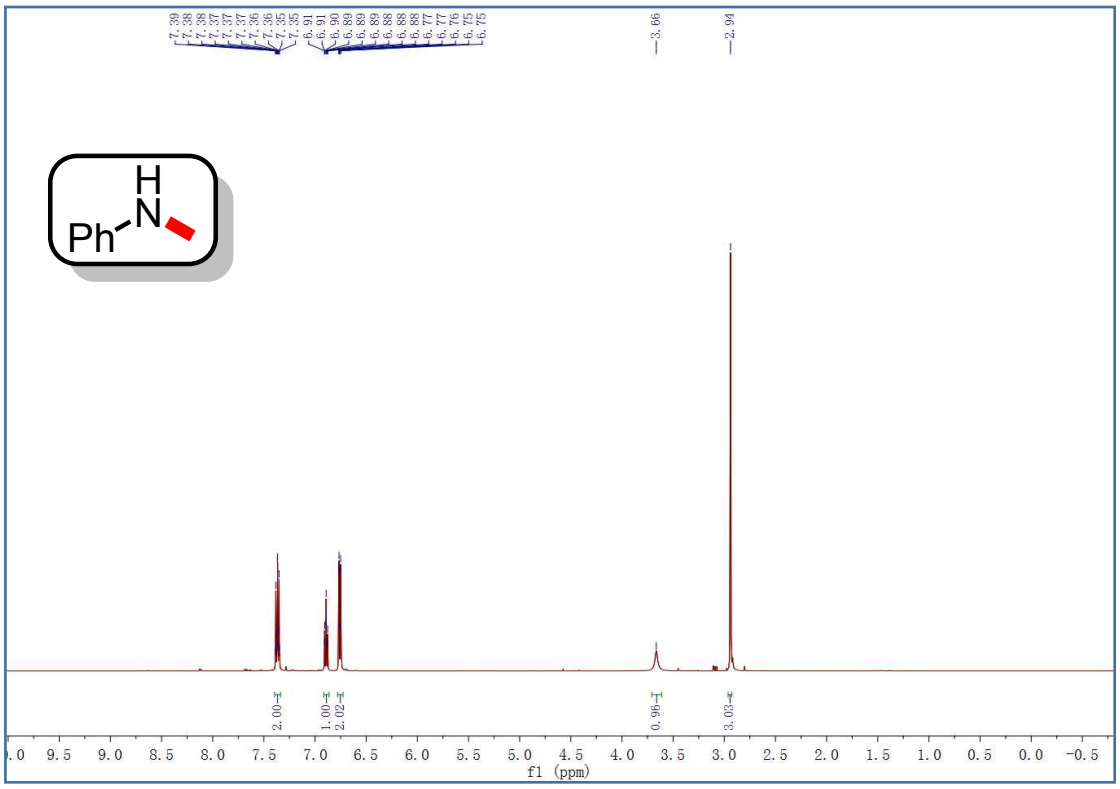


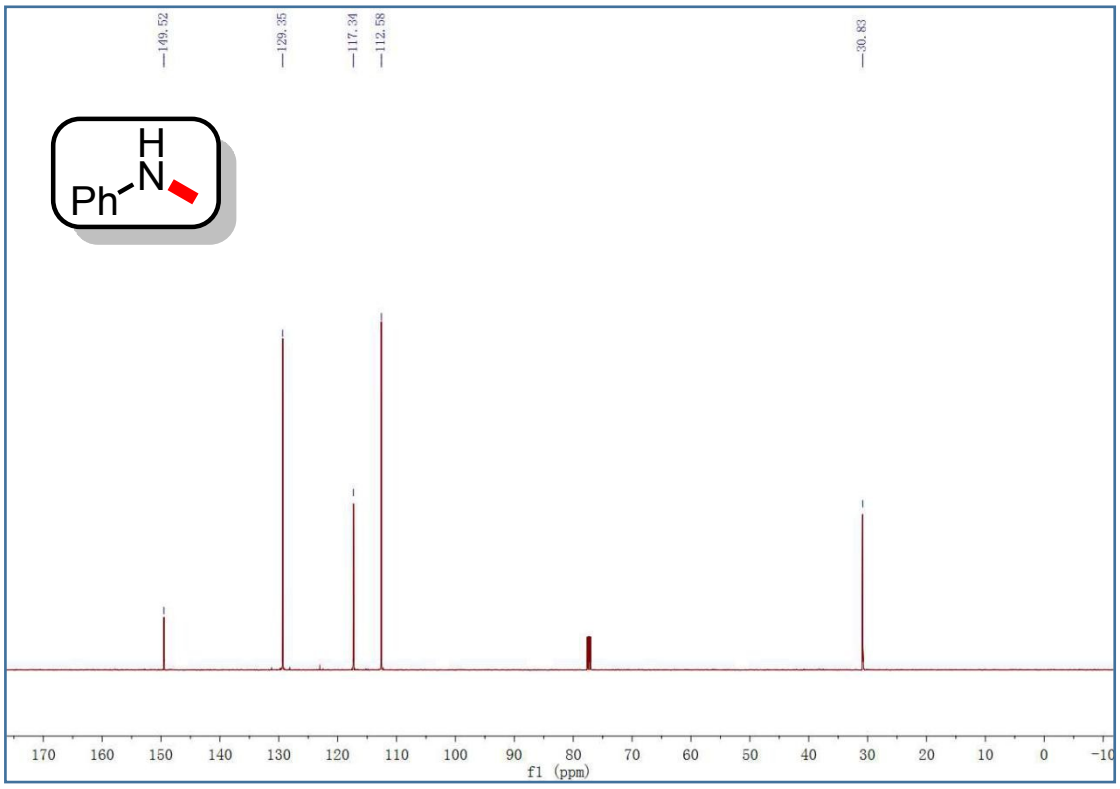
N,N-diethylaniline (2r)



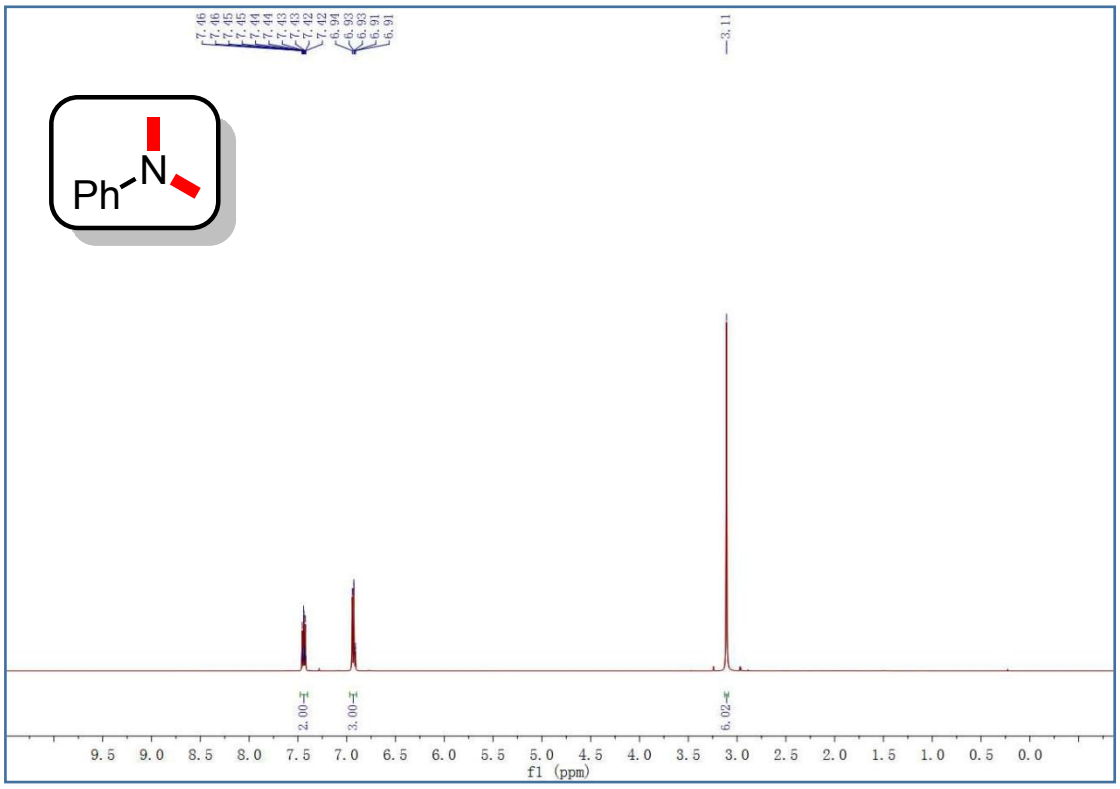


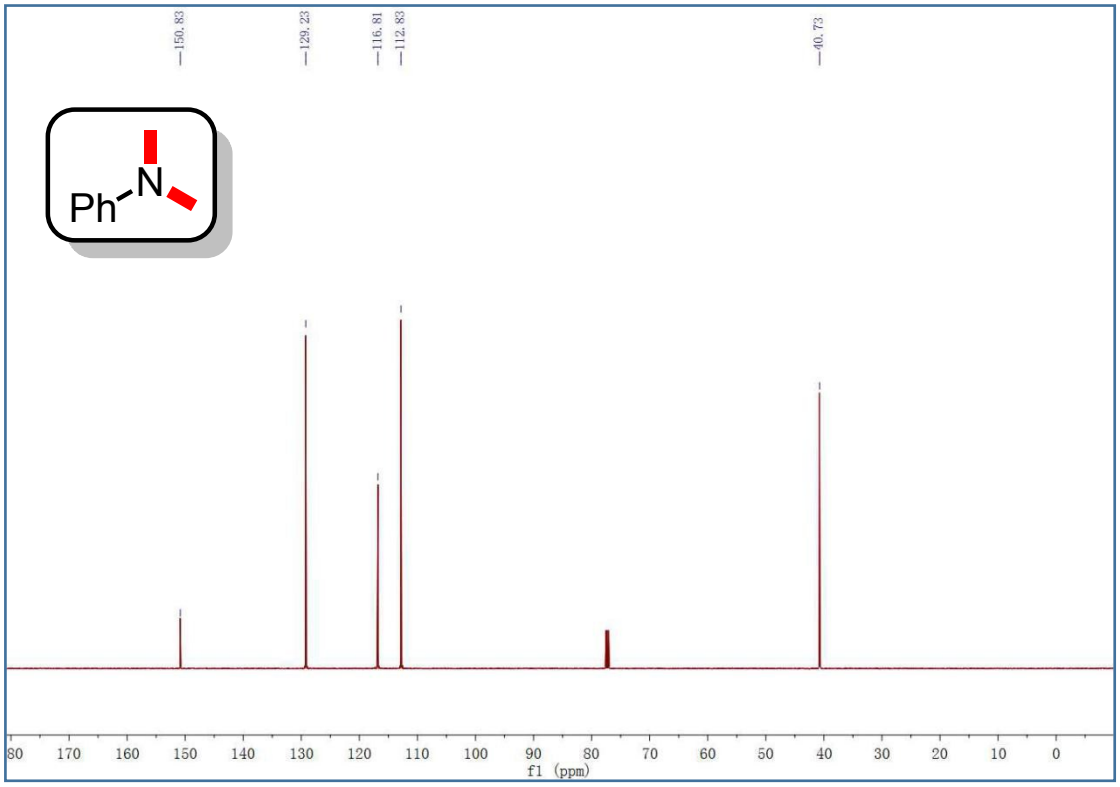
N-methylaniline (2s)



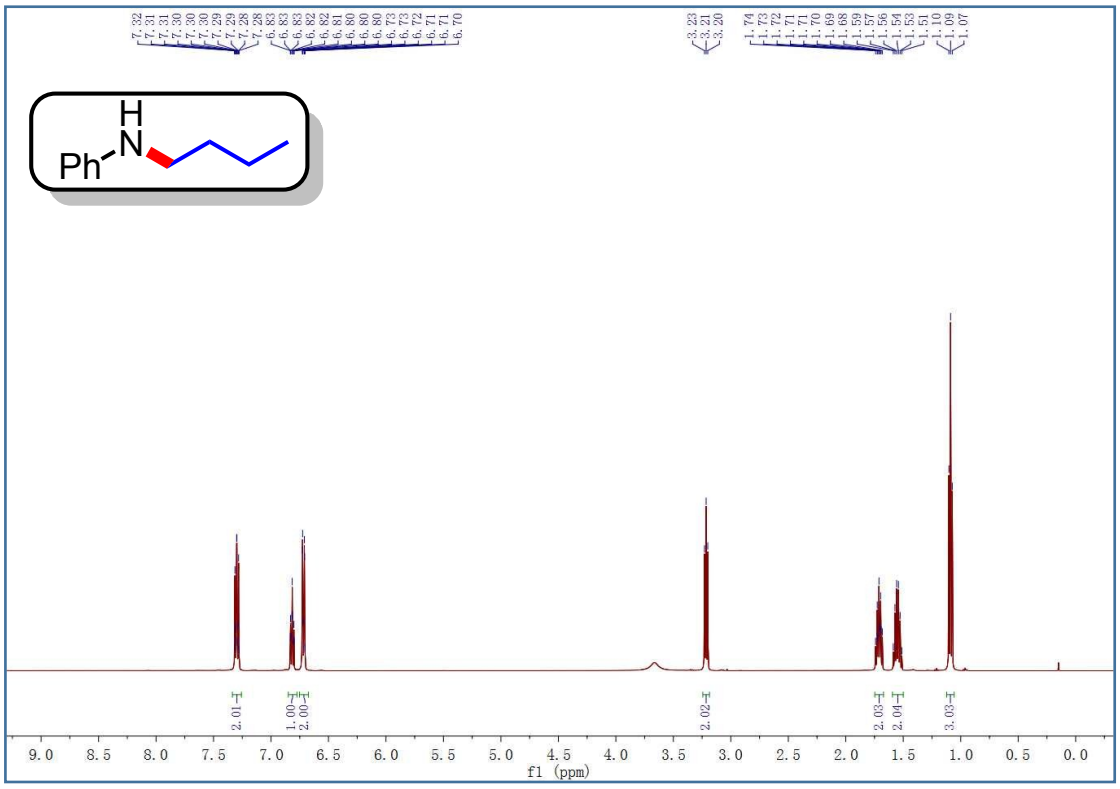


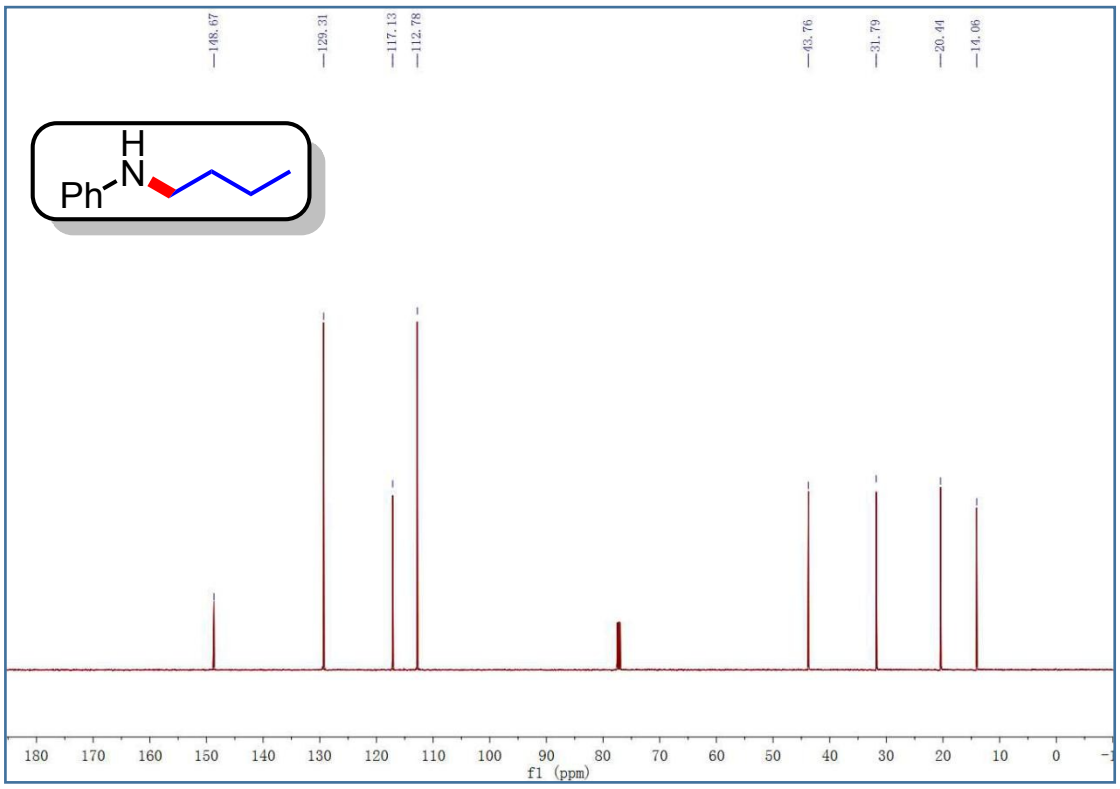
N,N-dimethylaniline (2t)


7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
6.94
6.93
6.91
6.91
3.11
Ph
N
2.00
3.00
6.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

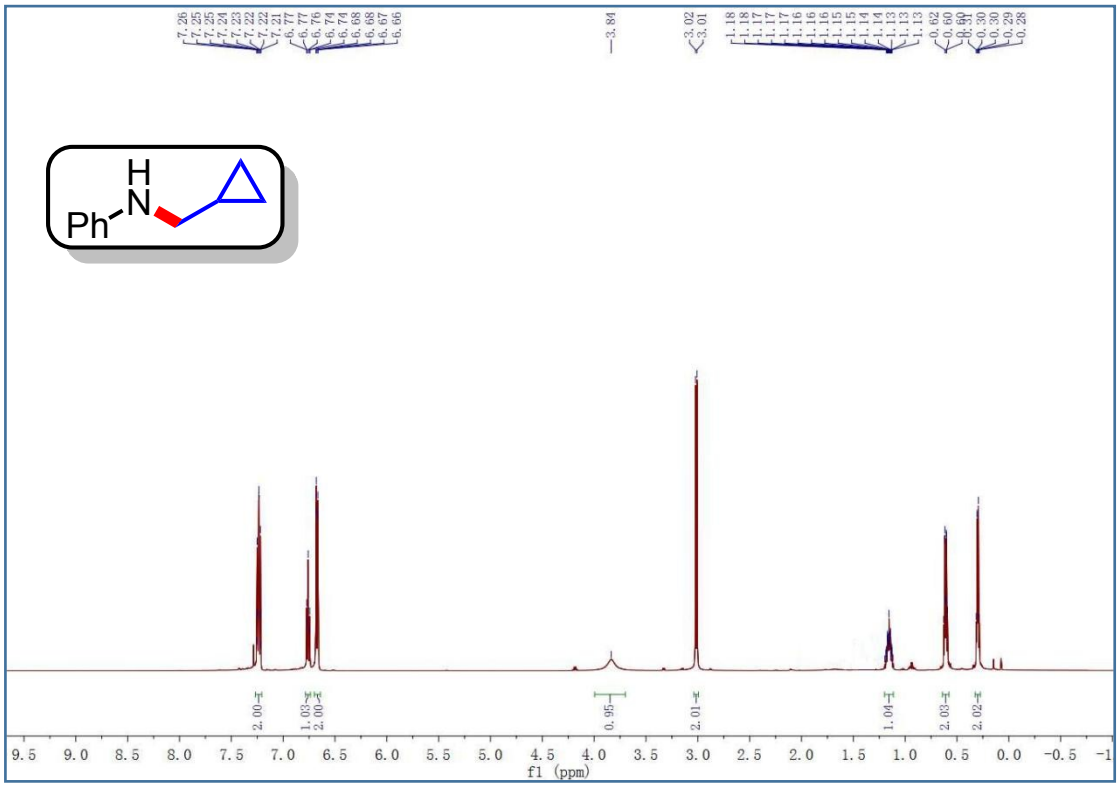

150.83
129.23
116.81
112.83
40.73
Ph
N
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

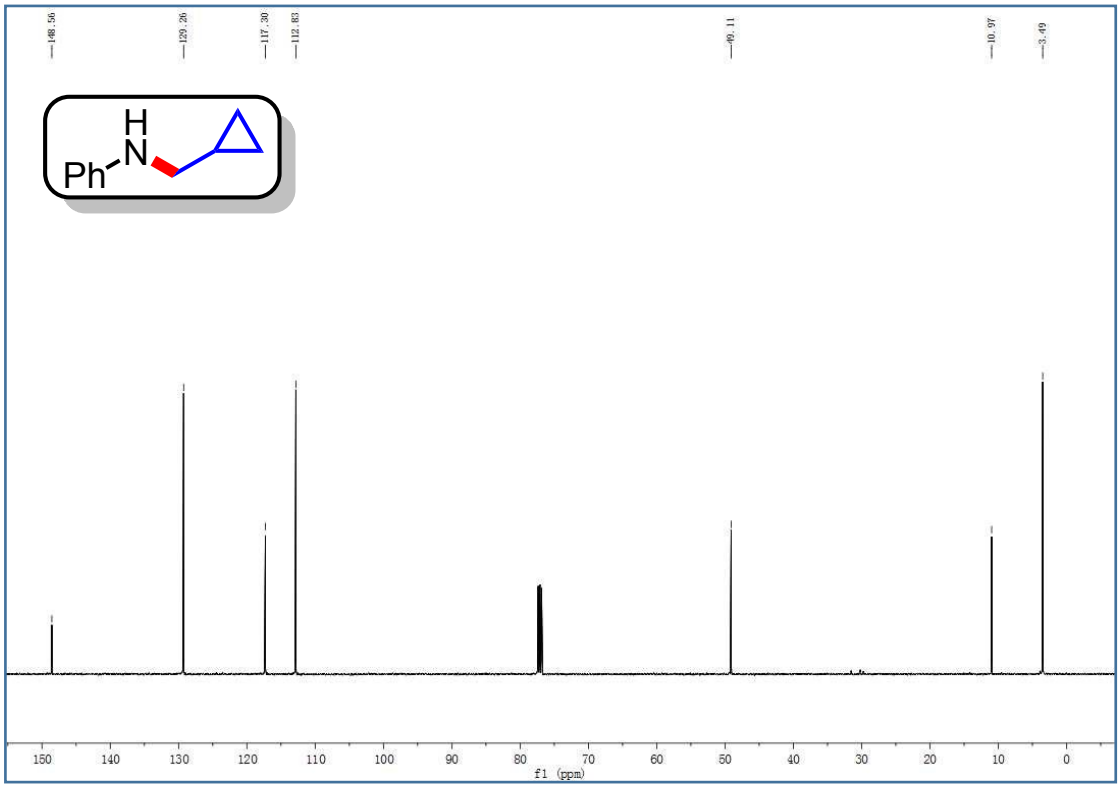
N-butylaniline (2u)



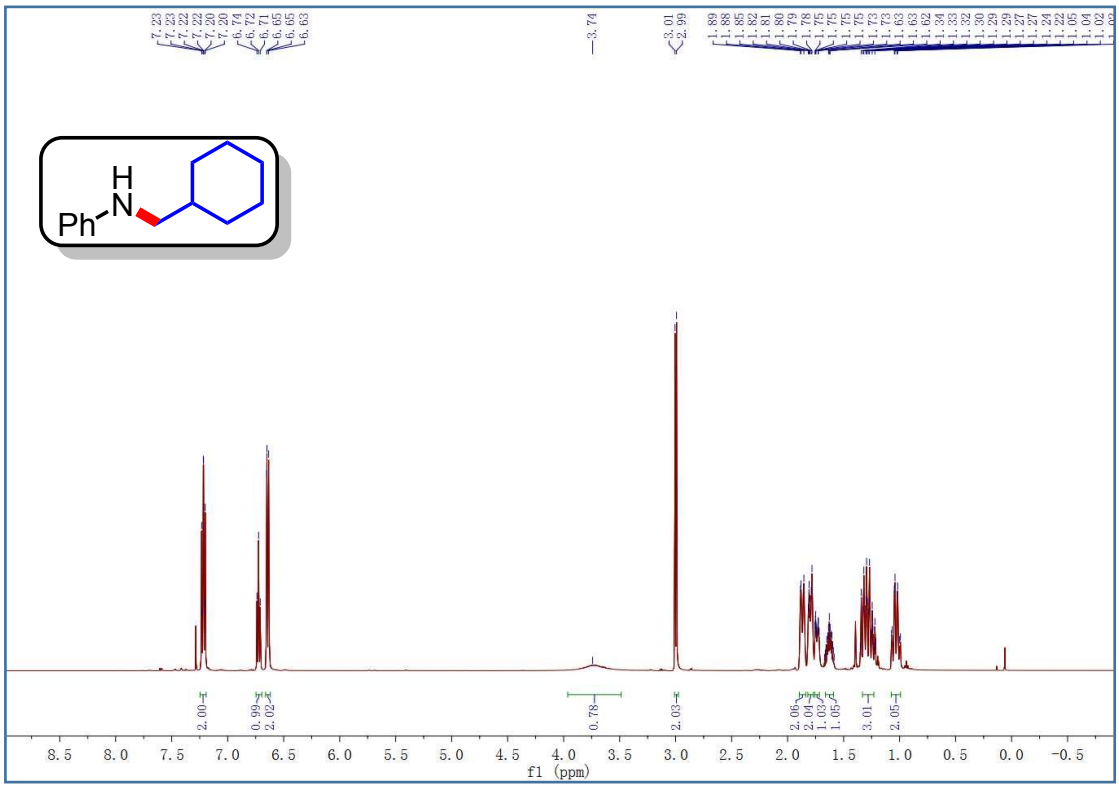


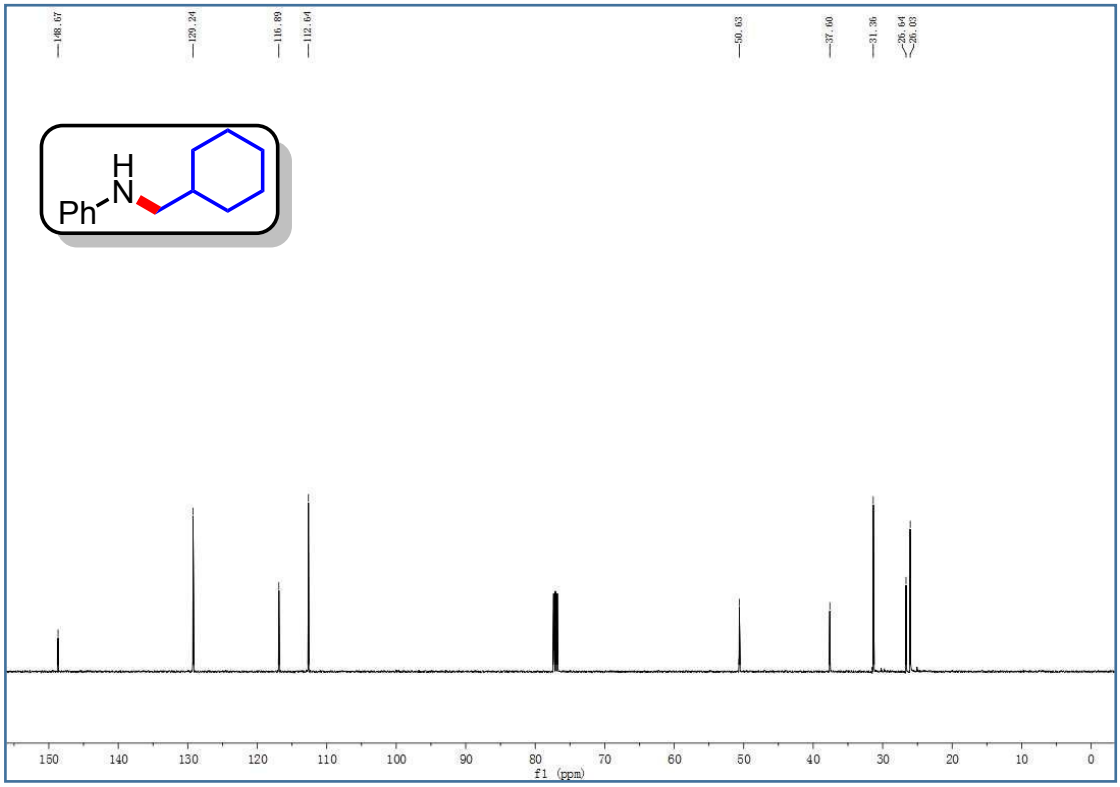
N-(cyclopropylmethyl)aniline (2v)



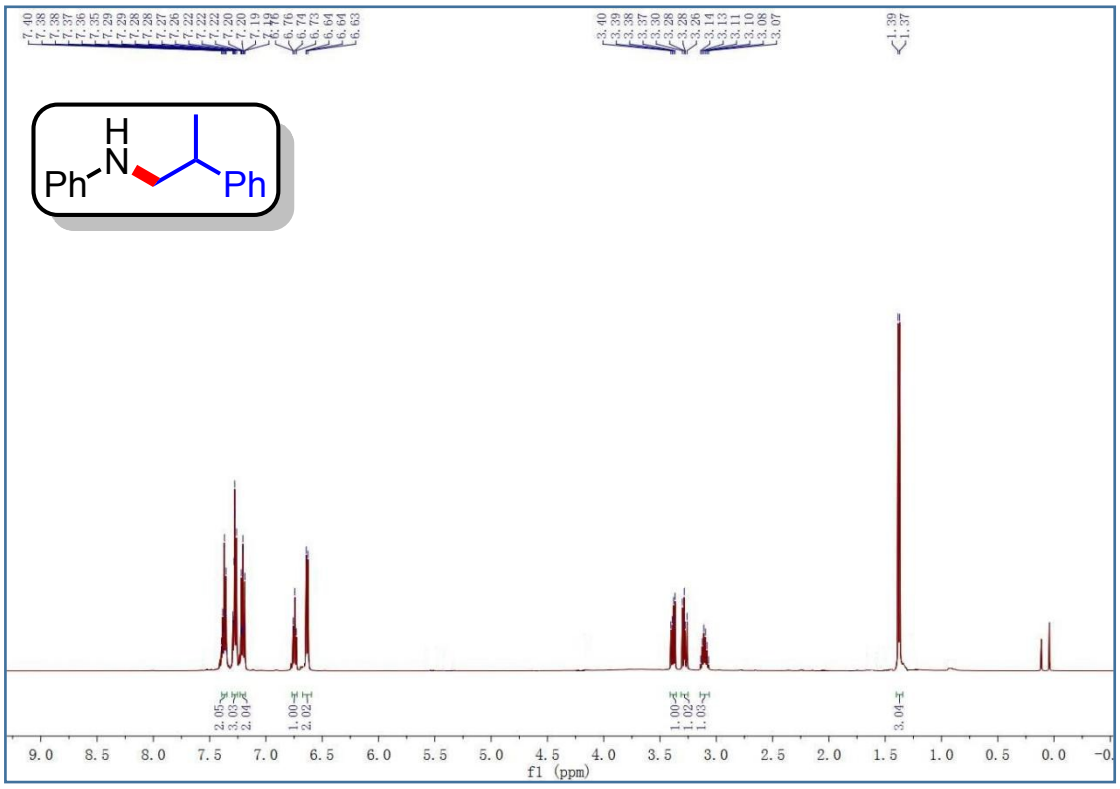


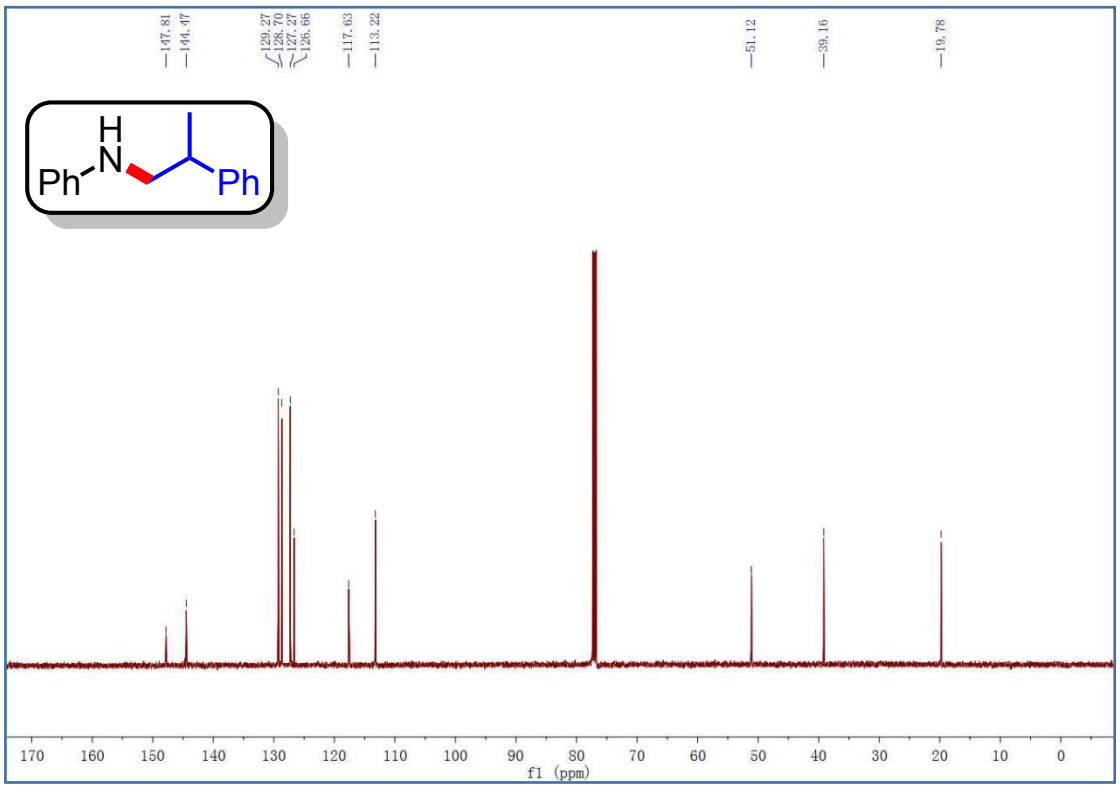
N-(cyclohexylmethyl)aniline (2w)



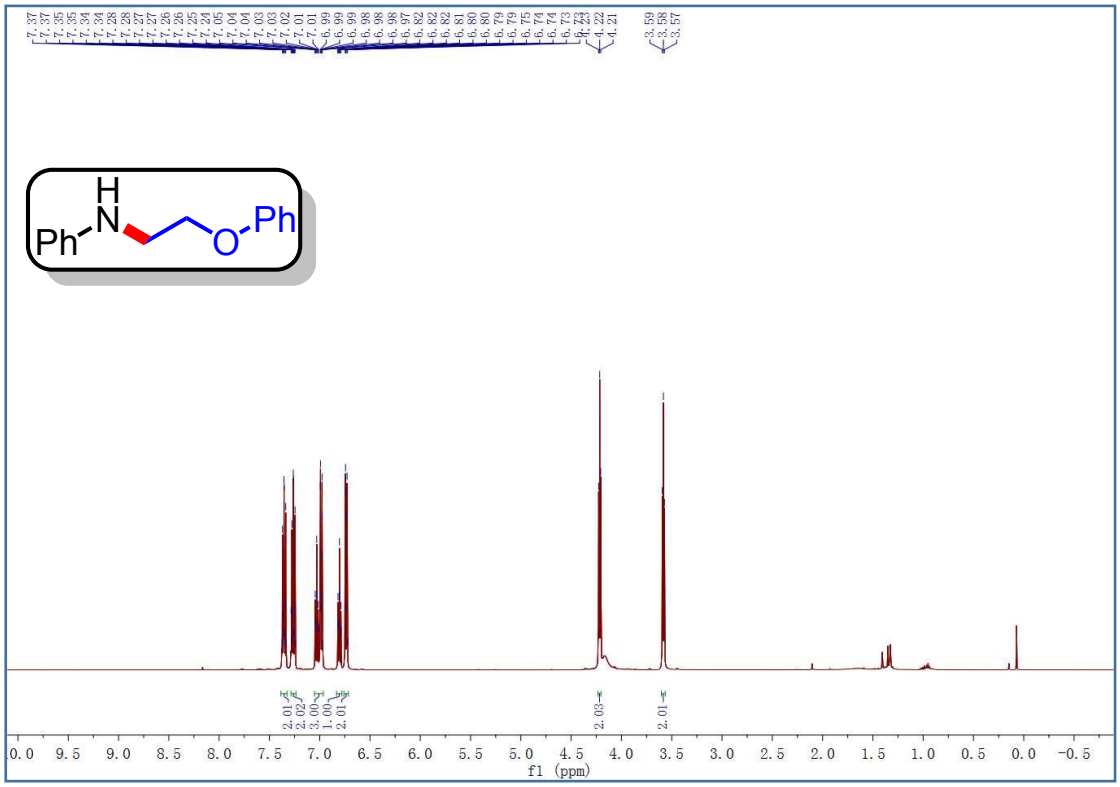


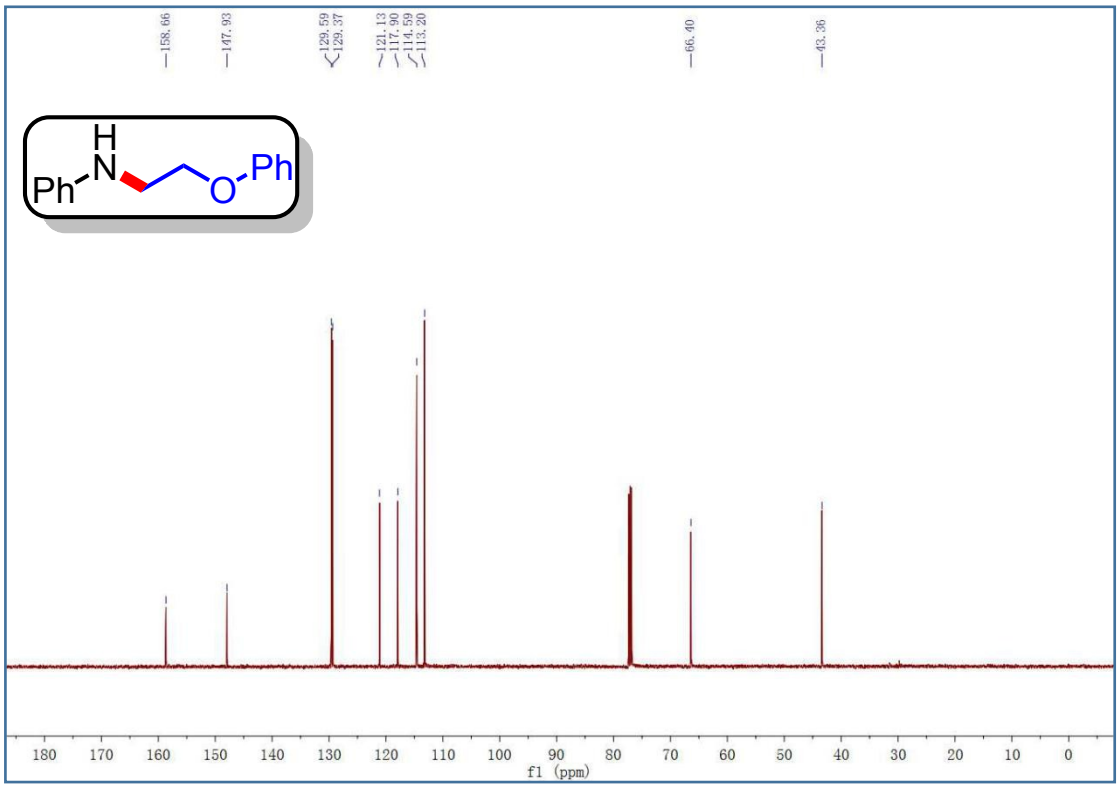
N-(2-phenylpropyl)aniline (2x)


Ph
H
N
Ph
f1 (ppm)

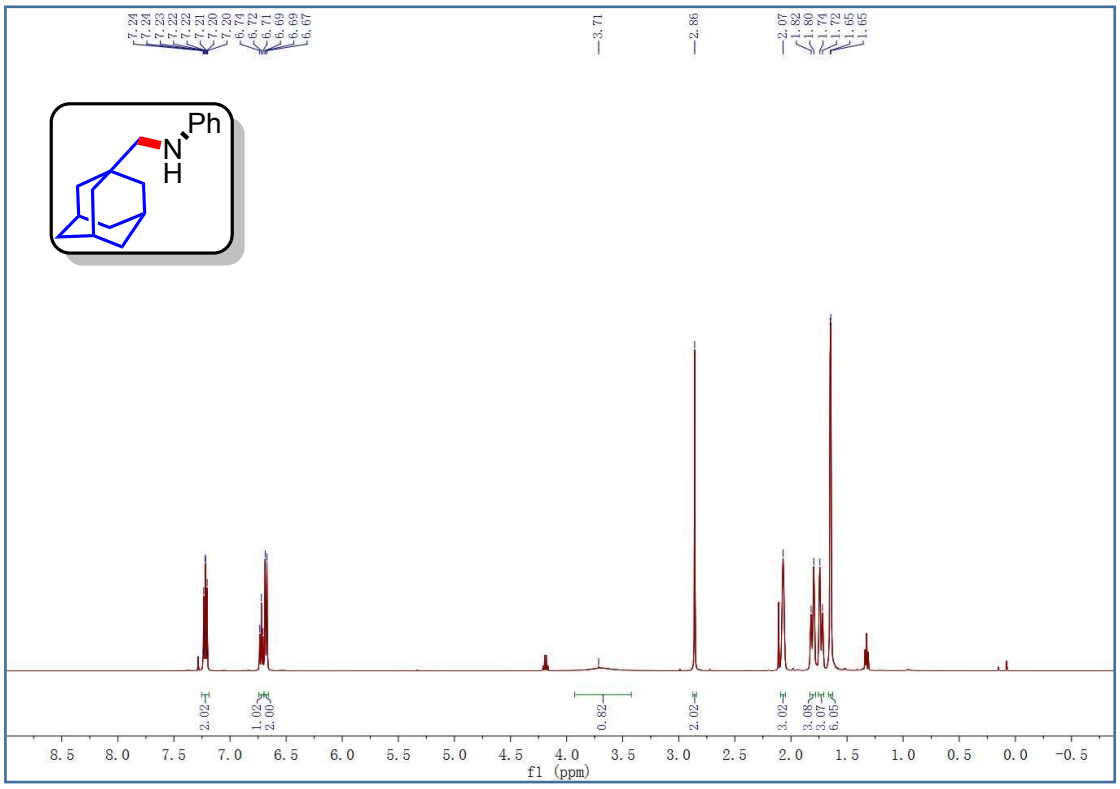

Ph
H
N
Ph
f1 (ppm)

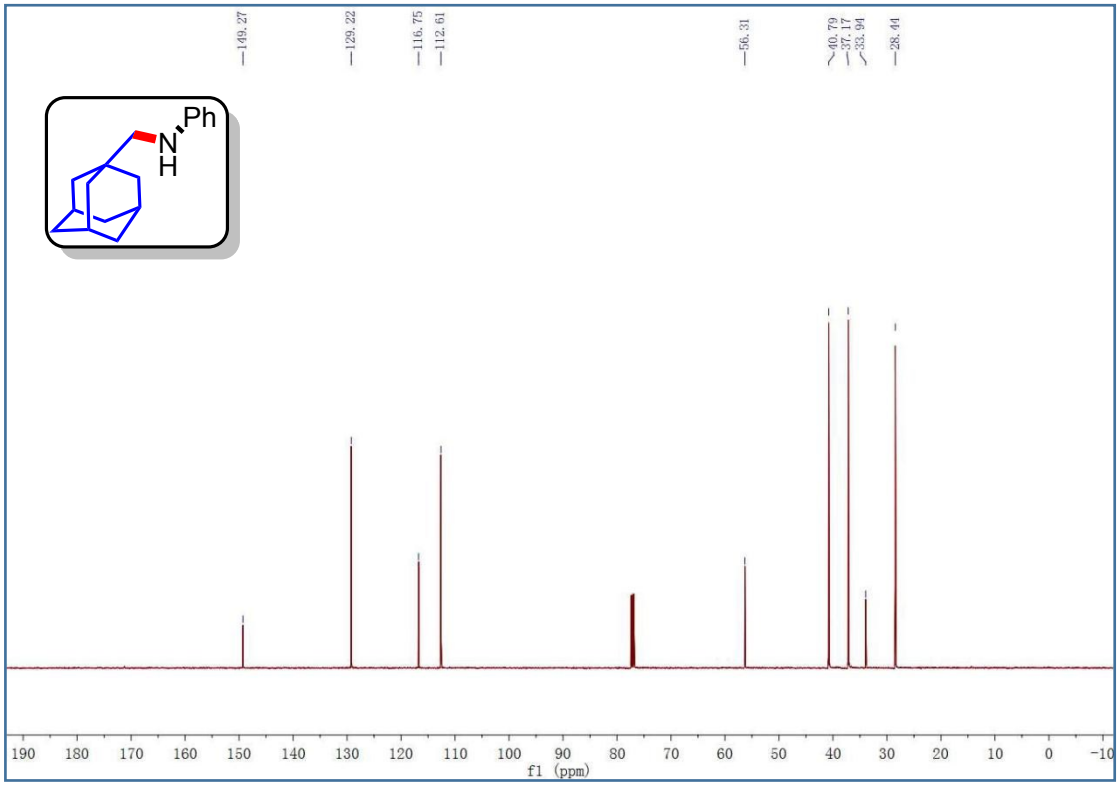
N-(2-phenoxyethyl)aniline (2y)



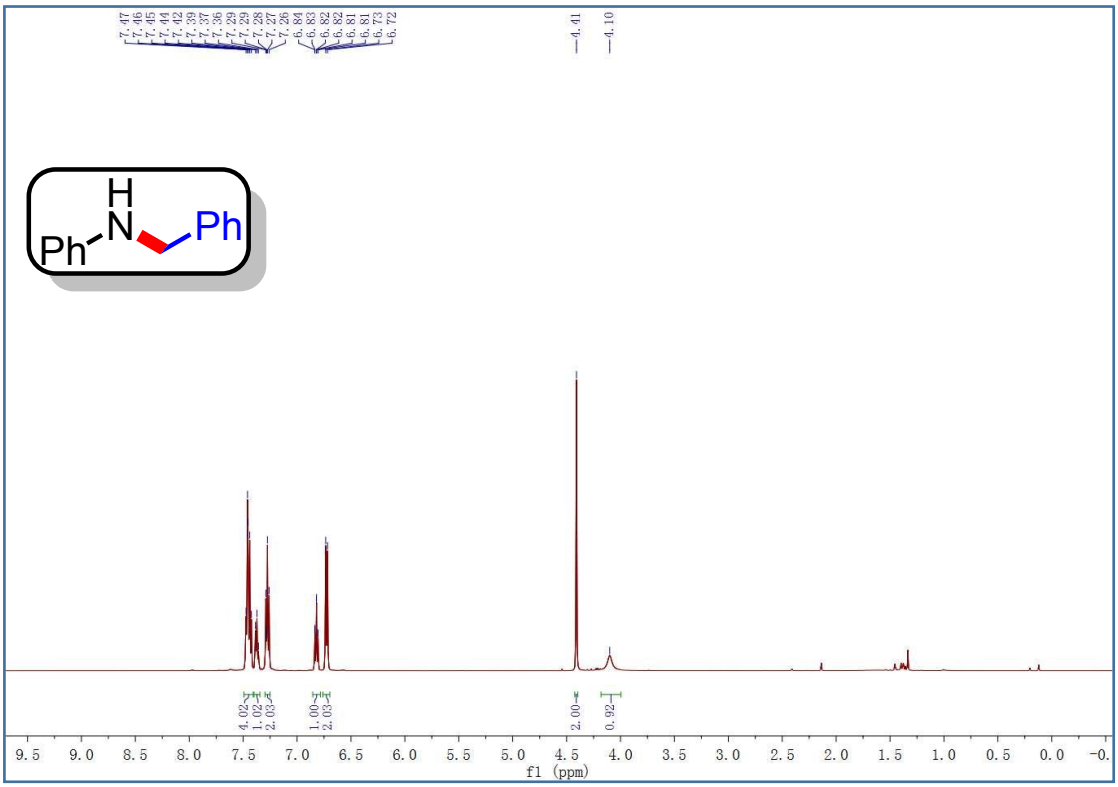


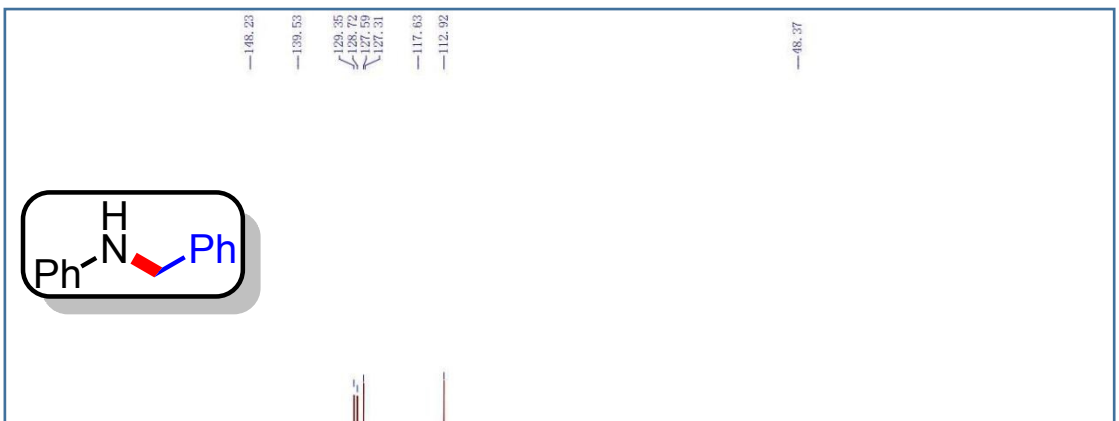
N-(((3r,5r,7r)-adamantan-1-yl)methyl)aniline (2aa)


Ph
N
H
f1 (ppm)

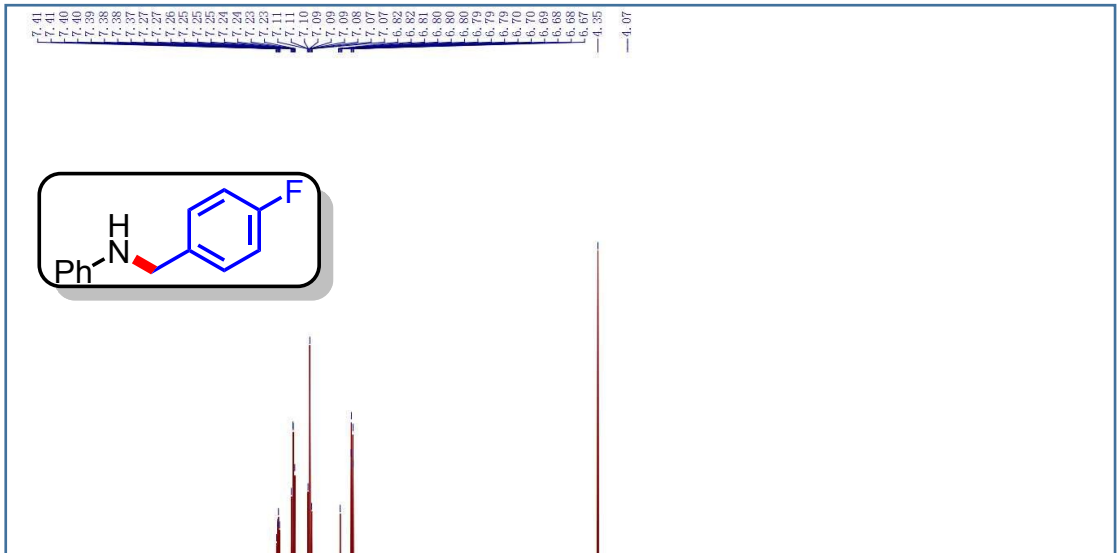

Ph
N
H
f1 (ppm)

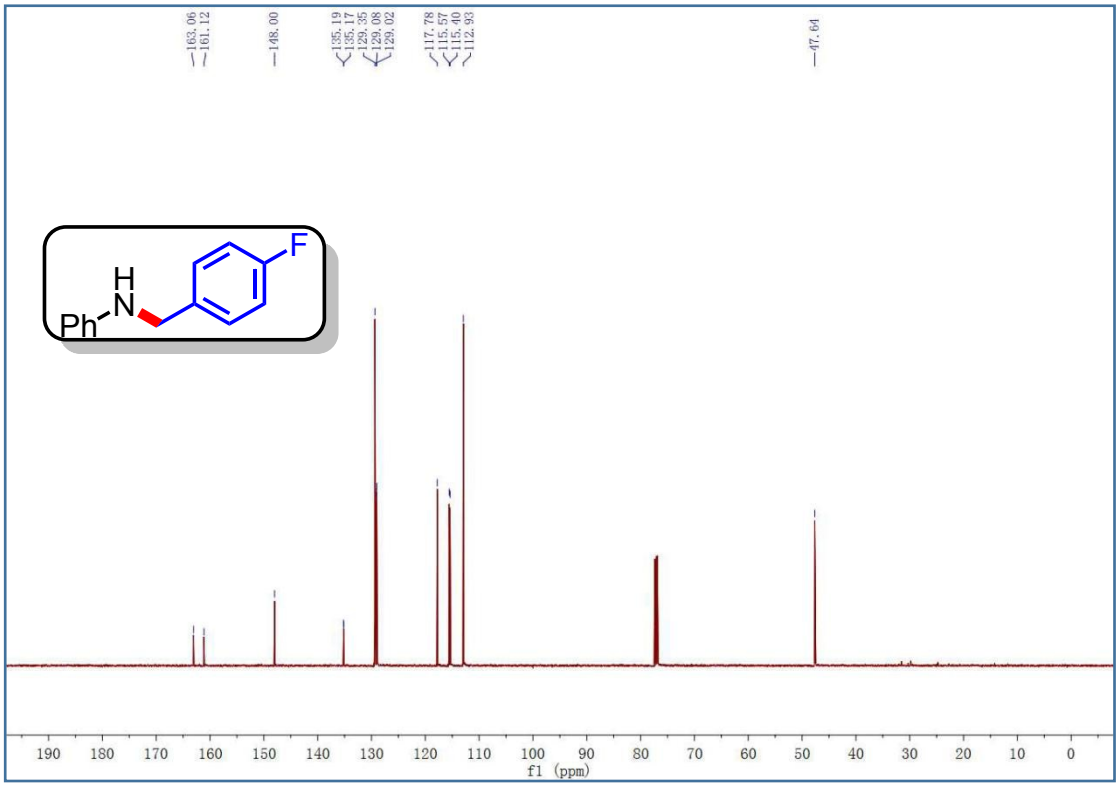
N-benzylaniline (2ab)



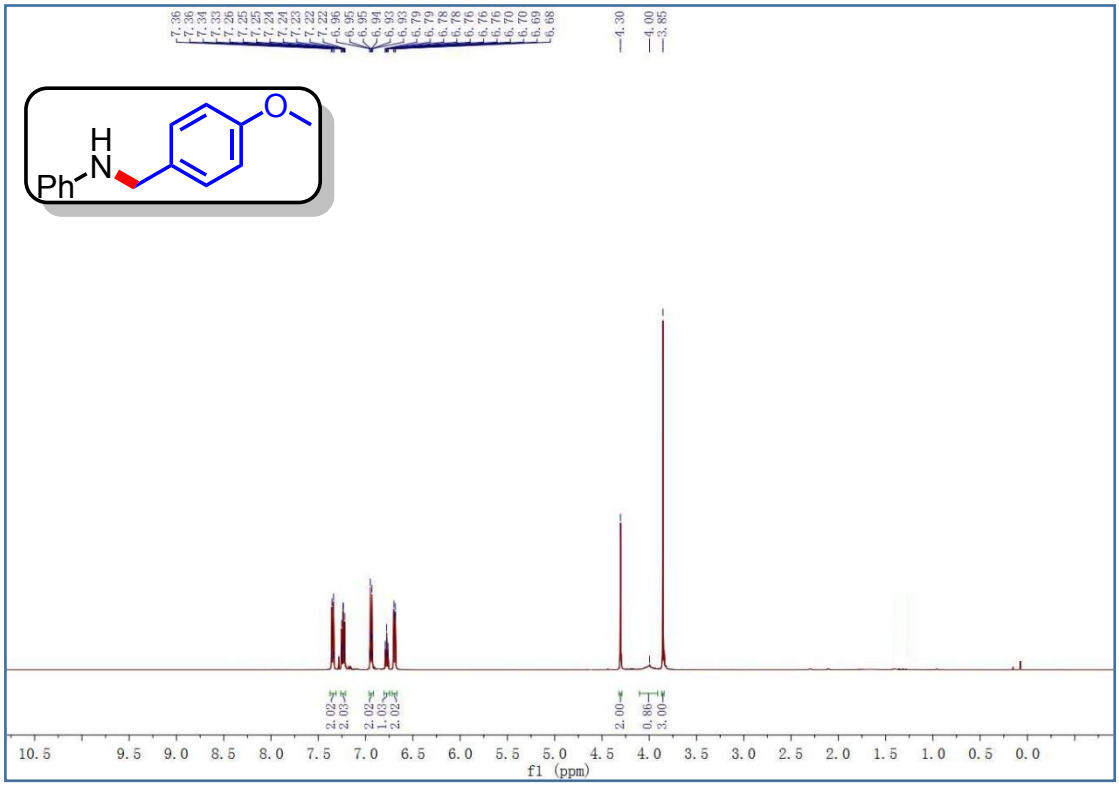


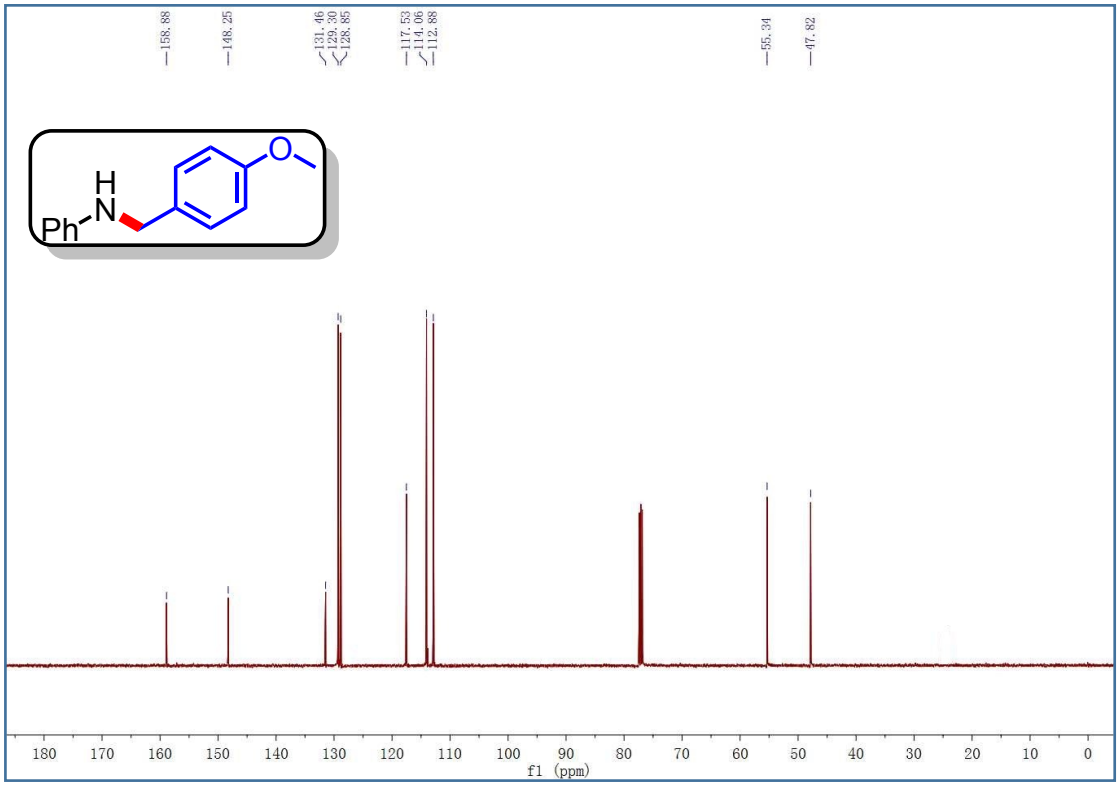
N-(4-fluorobenzyl)aniline (2ac)



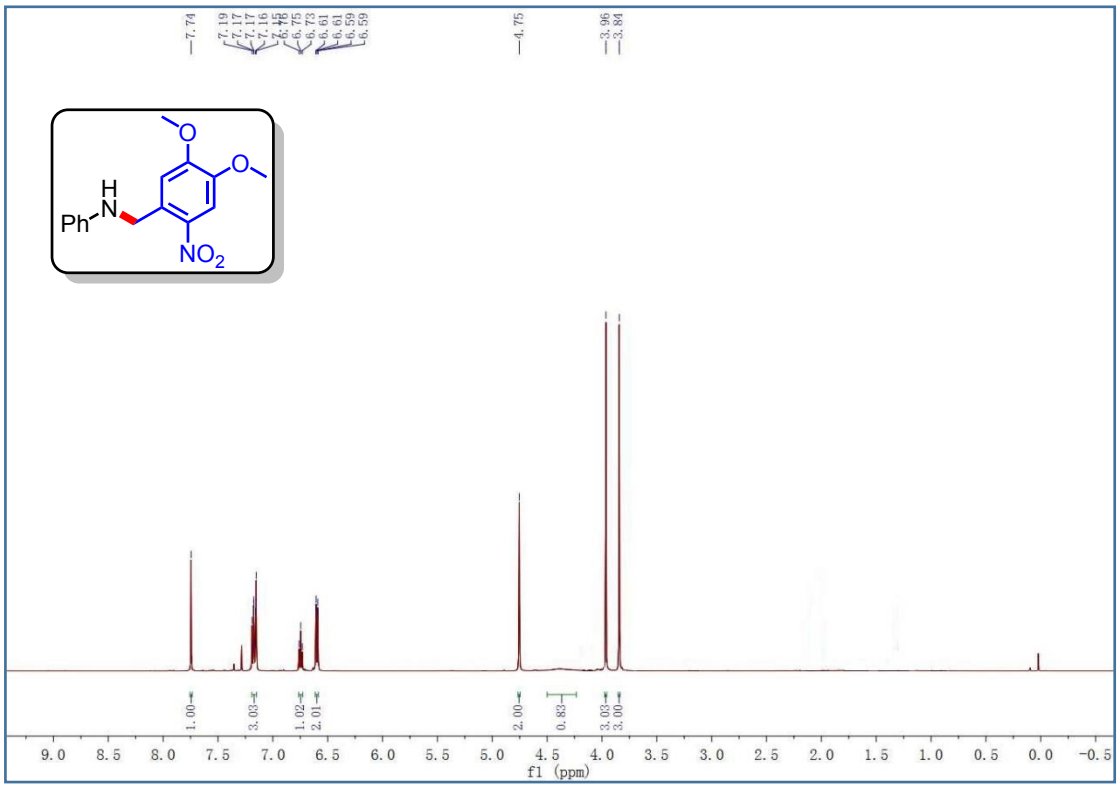

163.06
161.12
148.00
135.19
135.17
129.35
129.08
129.02
117.78
115.57
115.40
112.93
47.64
F
H
N
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

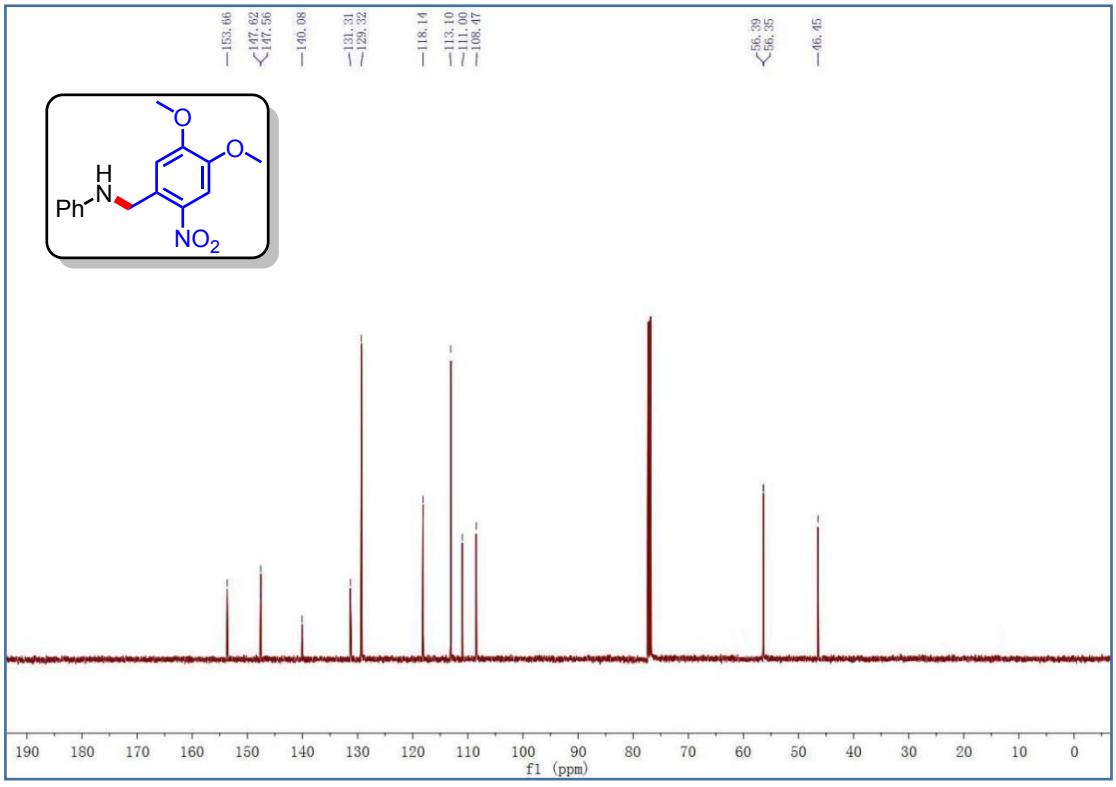
N-(4-methoxybenzyl)aniline (2ad)



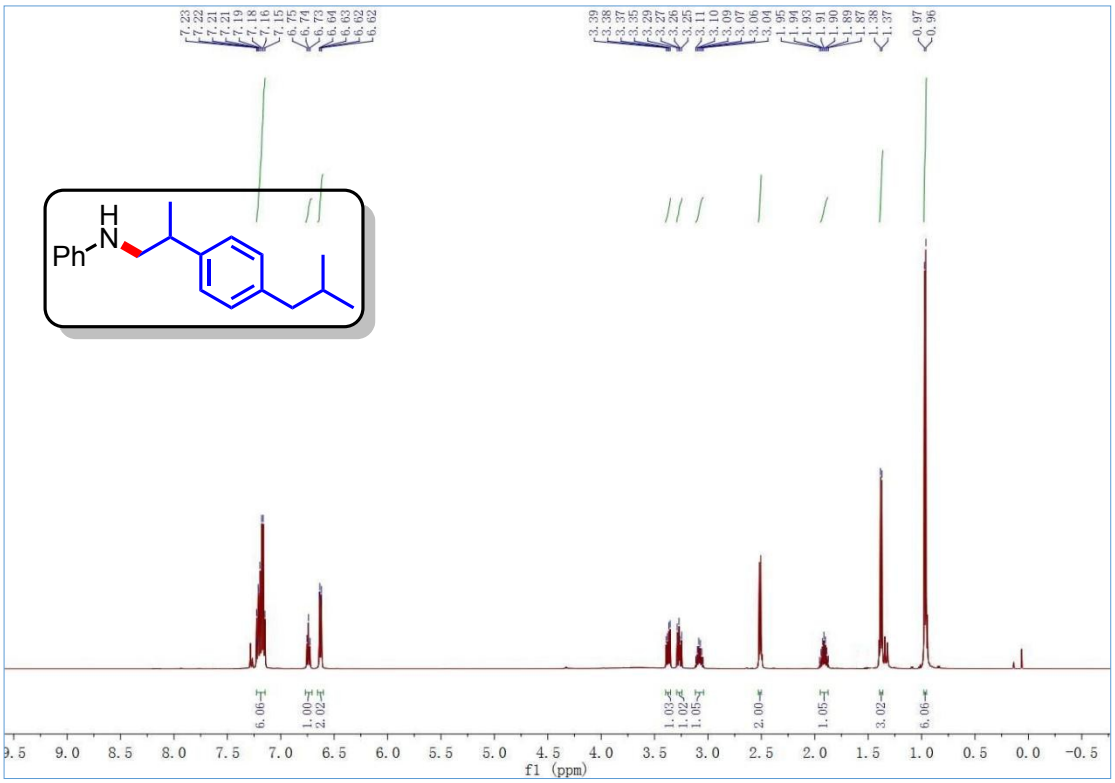


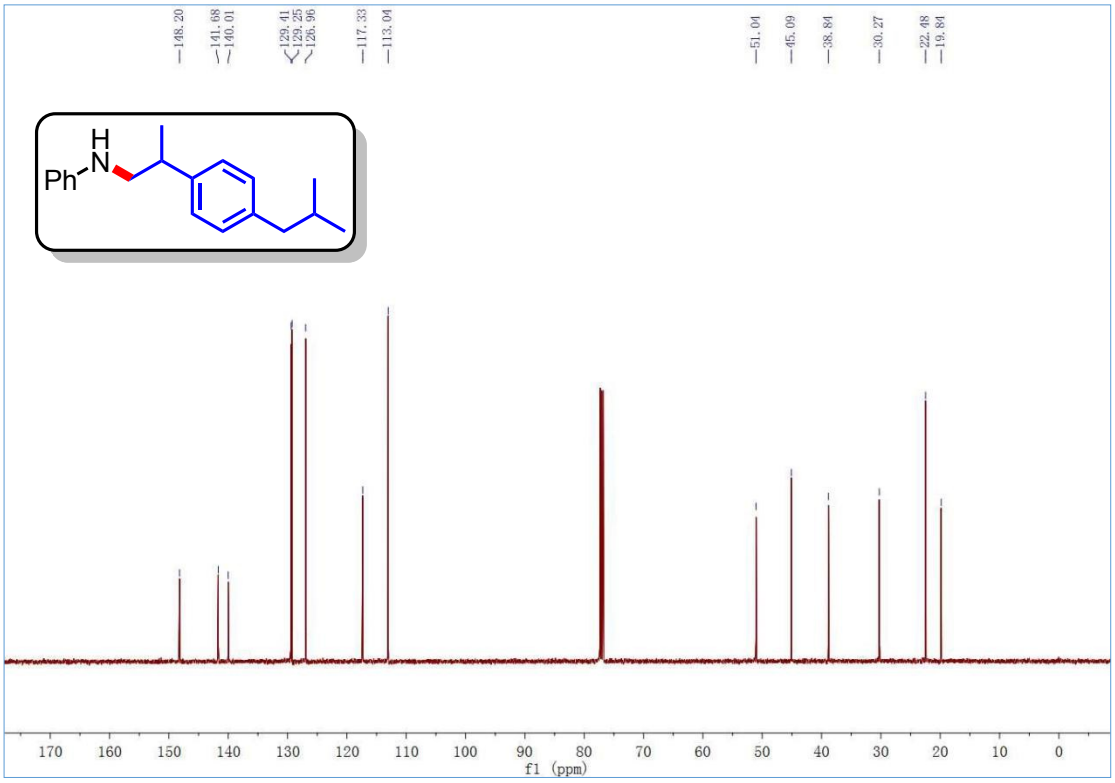
N-(4,5-dimethoxy-2-nitrobenzyl)aniline (2ae)


7.74
7.19
7.17
7.17
7.16
6.76
6.75
6.73
6.61
6.59
6.59
4.75
3.96
3.84
O
O
H
N
Ph
NO2
1.00
3.03
1.02
2.01
2.00
0.83
3.03
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

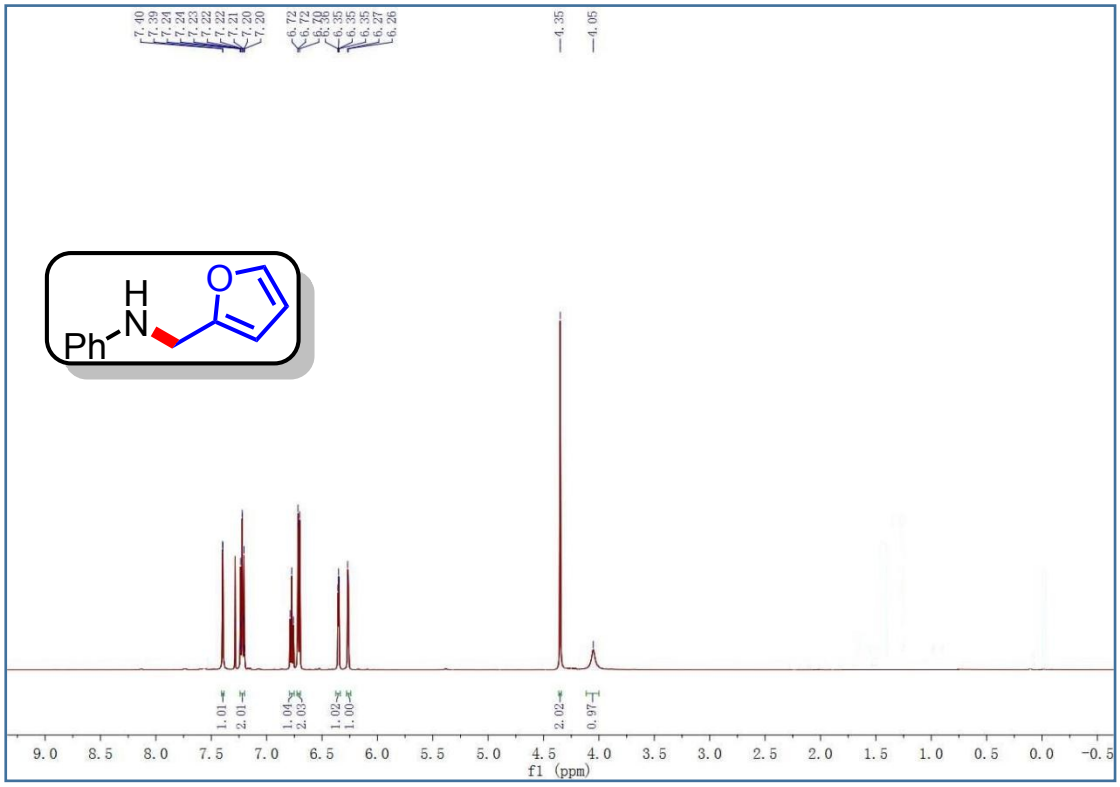

153.66
147.62
147.56
140.08
131.31
129.32
118.14
113.10
111.00
108.47
56.39
56.35
46.45
O
O
H
N
Ph
NO2
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

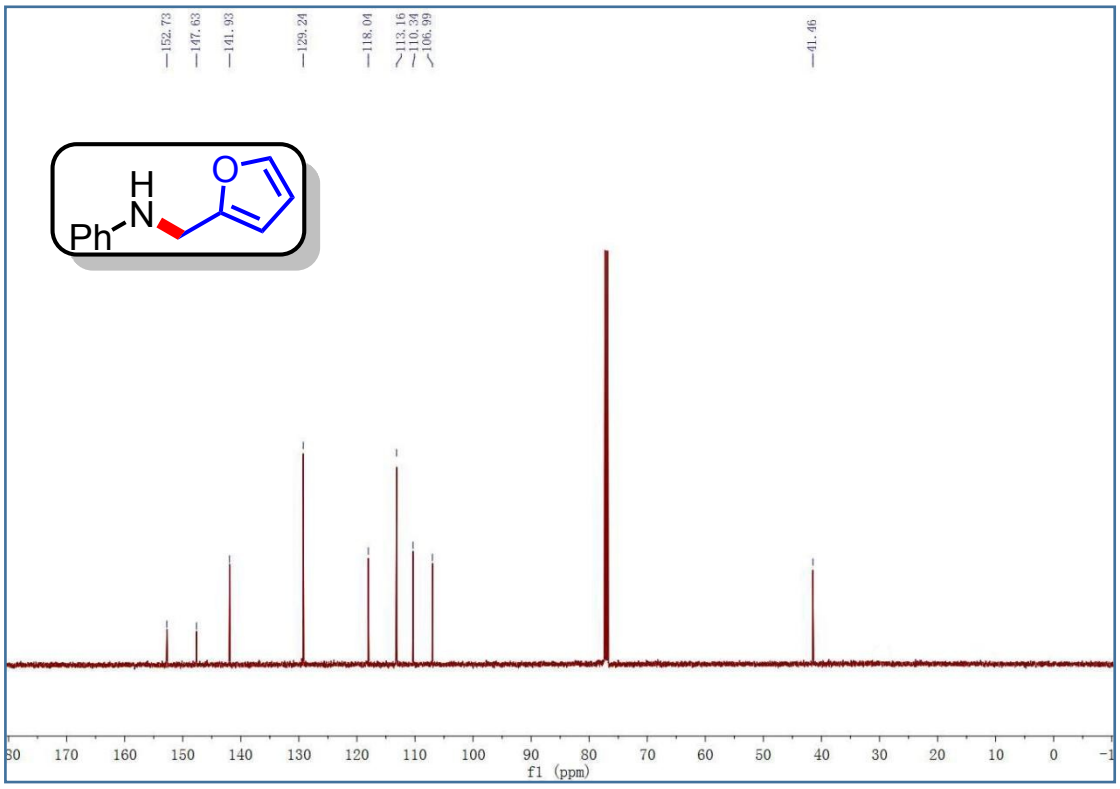
N-(2-(4-isobutylphenyl)propyl)aniline (2af)



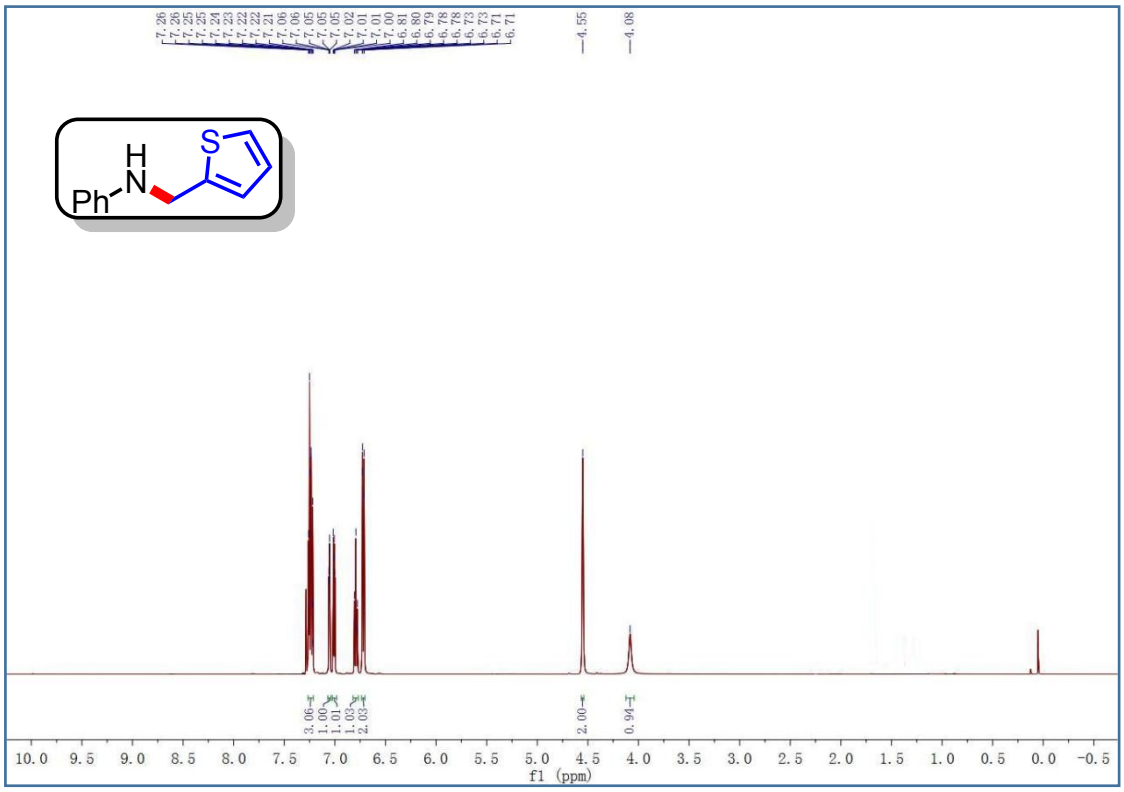


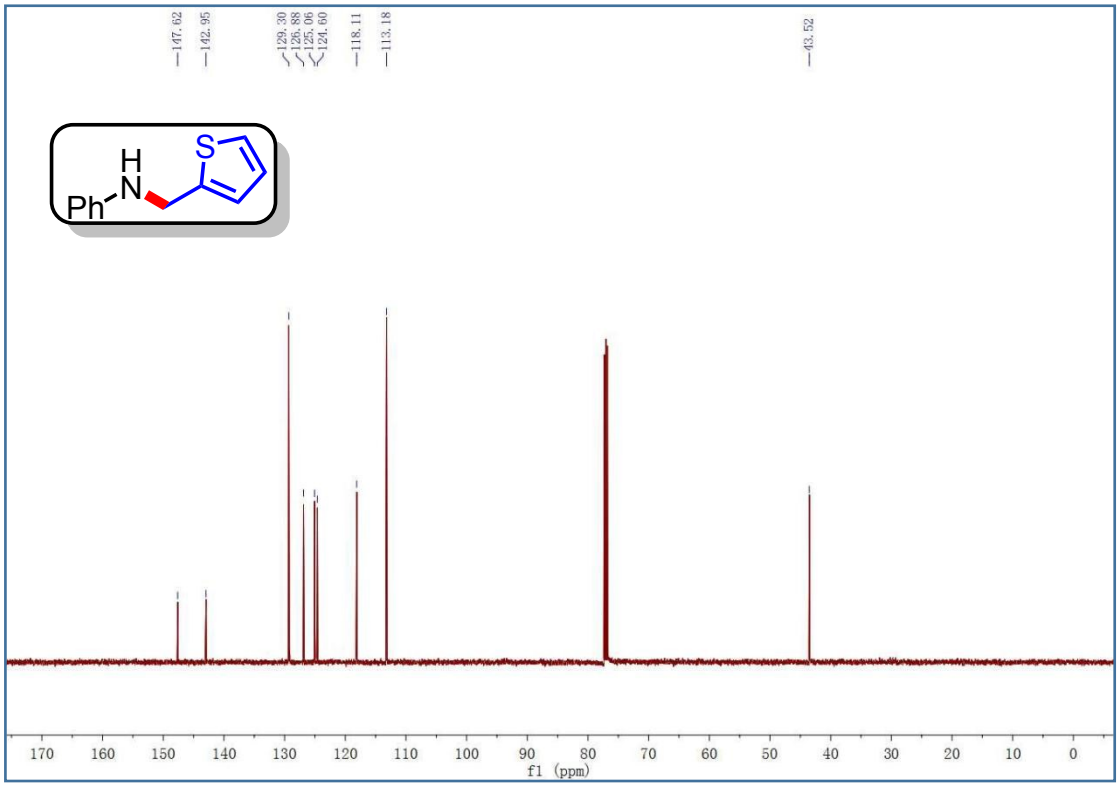
N-(furan-2-ylmethyl)aniline (2ag)



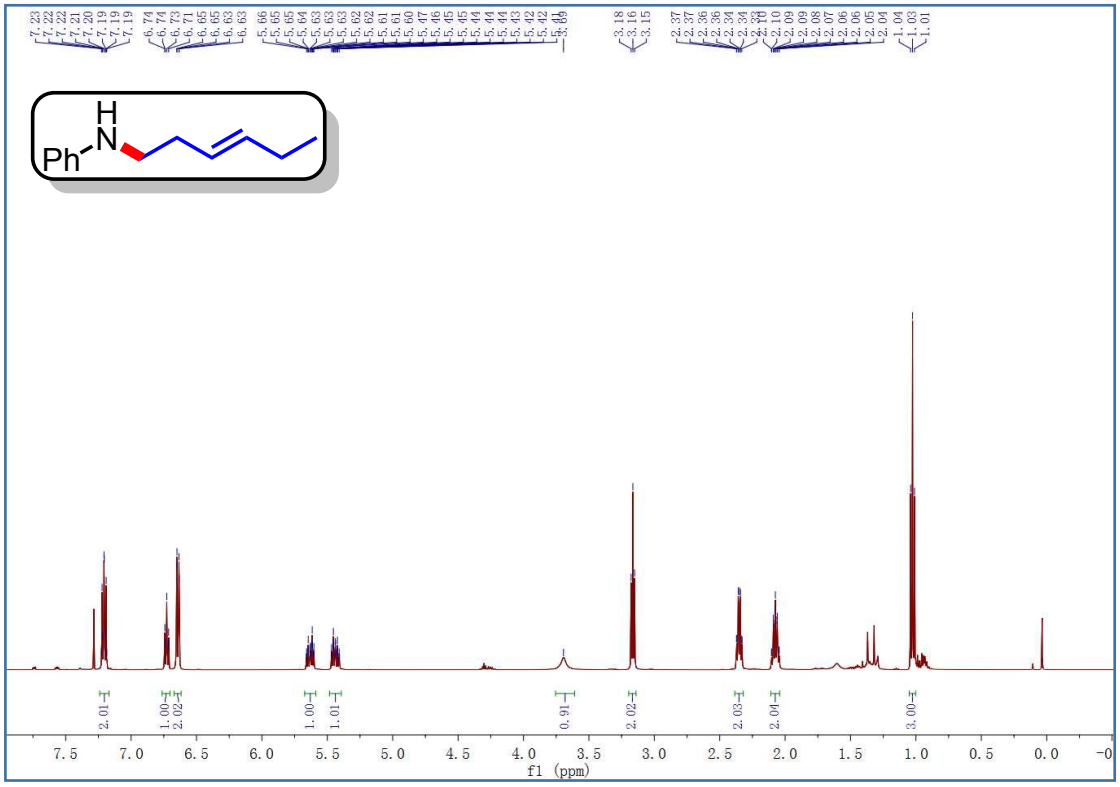


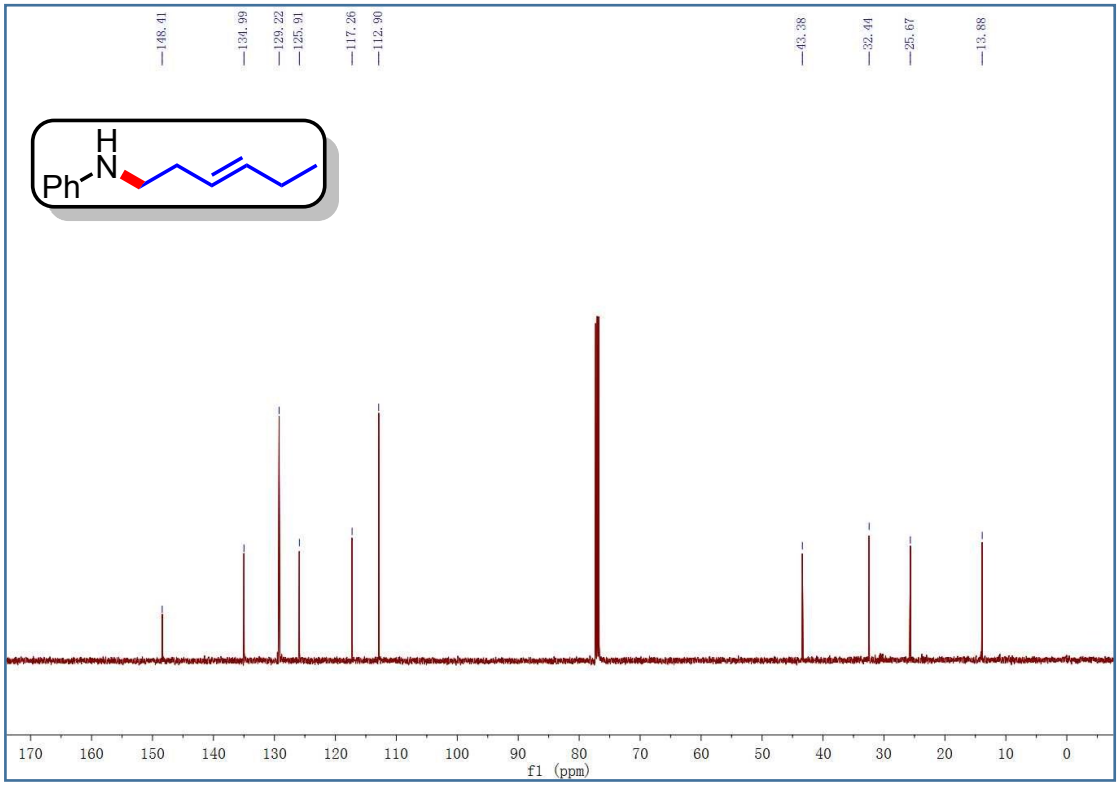
N-(thiophen-2-ylmethyl)aniline (2ah)


7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.06
7.05
7.05
7.05
7.02
7.01
7.01
7.00
6.81
6.80
6.79
6.78
6.78
6.73
6.73
6.71
6.71
4.55
4.08
H
N
Ph
S
3.06
1.00
1.01
1.03
2.03
2.00
0.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

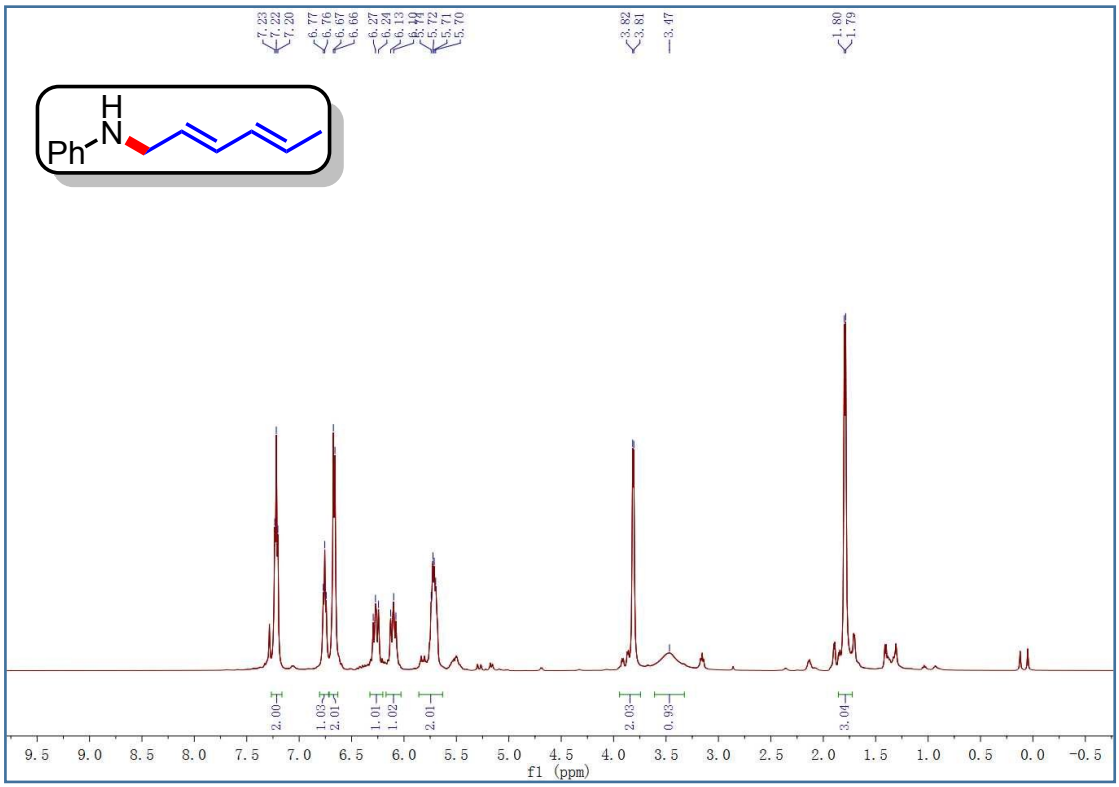

147.62
142.95
129.39
126.88
125.05
124.60
118.11
113.18
43.52
H
N
Ph
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

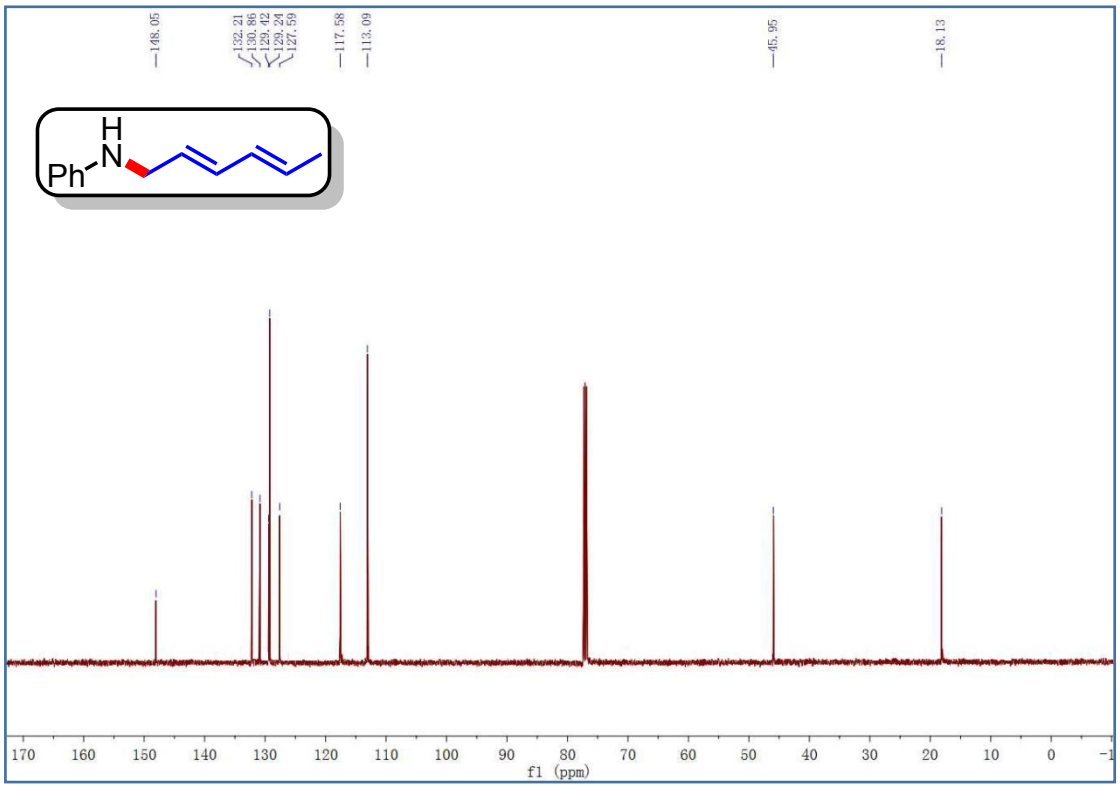
N-(hex-3-en-1-yl)aniline (2ai)



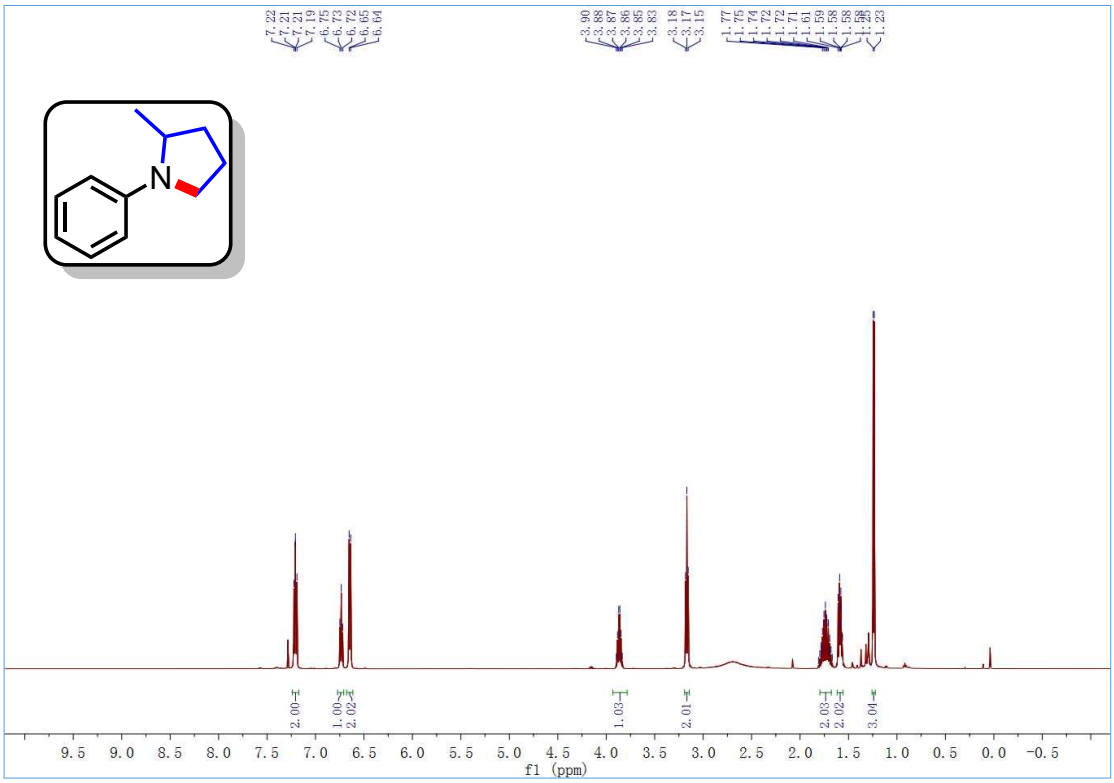


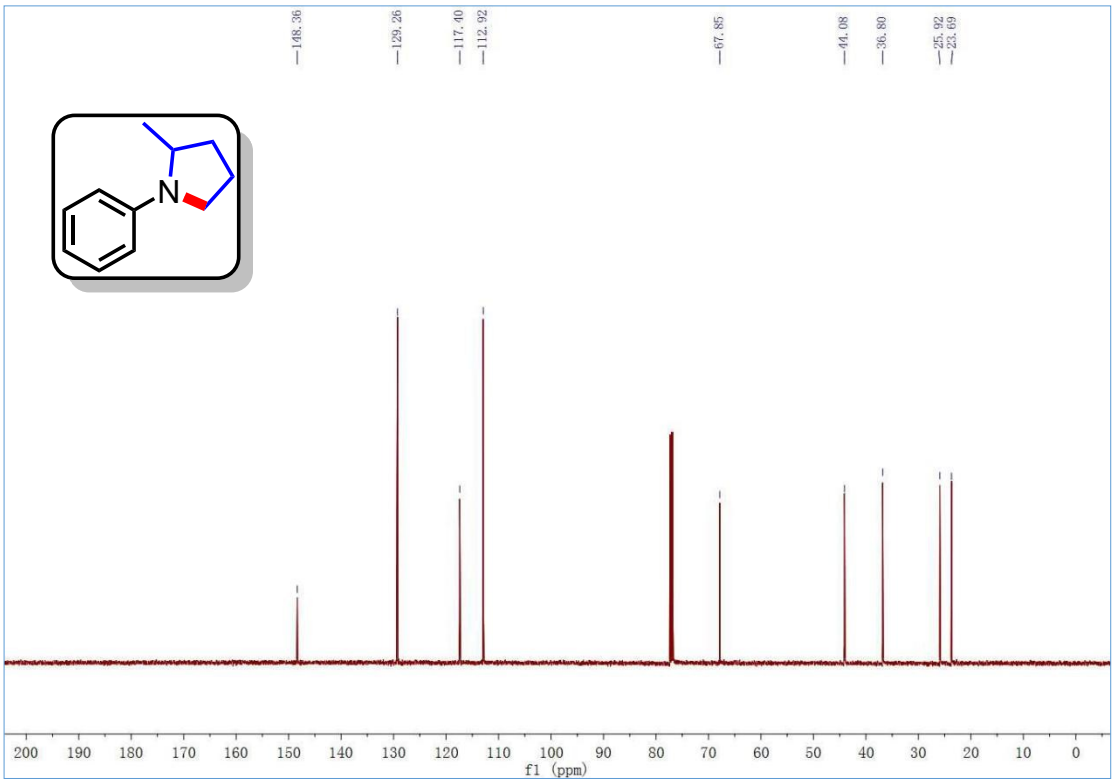
N-((2E,4E)-hexa-2,4-dien-1-yl)aniline (2aj)



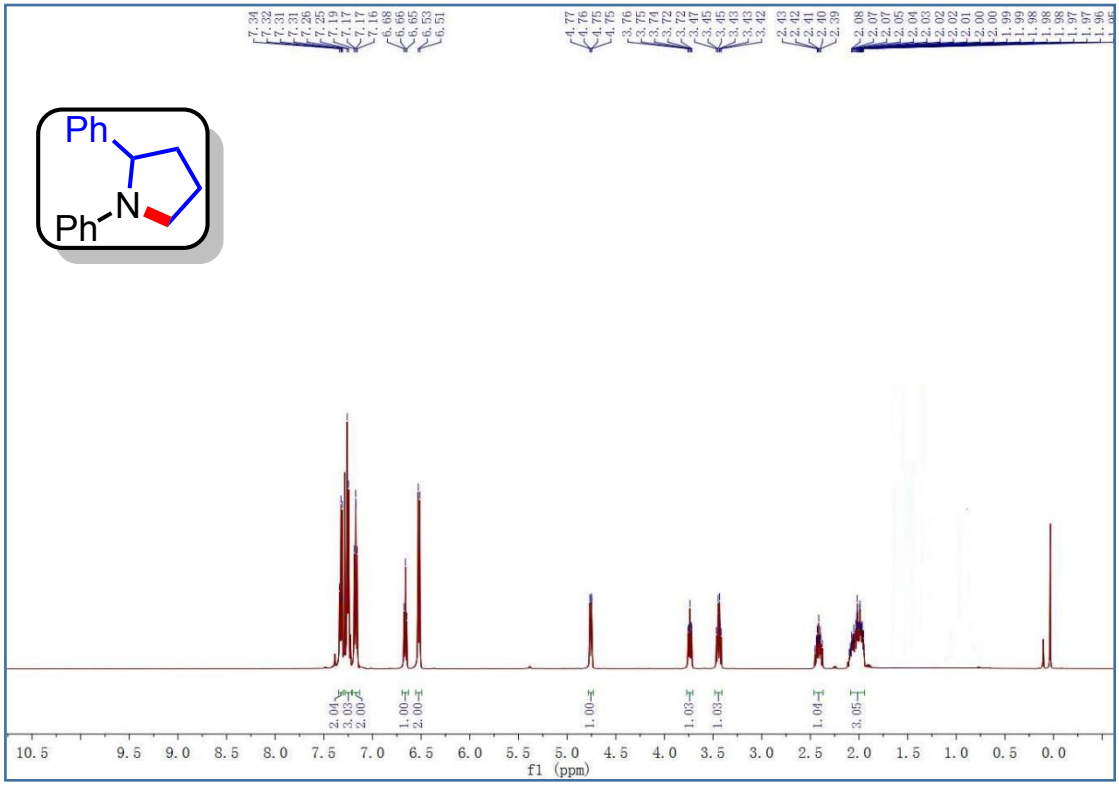


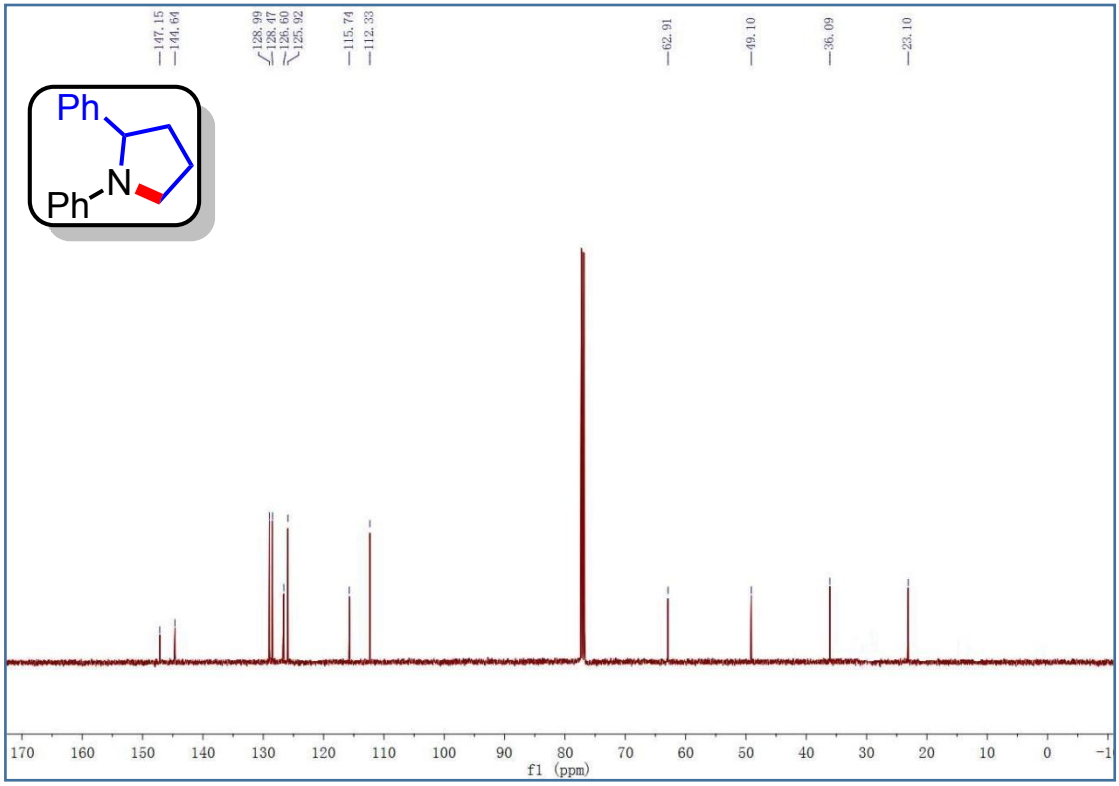
2-methyl-1-phenylpyrrolidine (2ak)


7.22
7.21
7.21
7.19
6.75
6.73
6.72
6.65
6.64
3.90
3.88
3.87
3.86
3.85
3.83
3.18
3.17
3.15
1.77
1.75
1.74
1.72
1.72
1.71
1.61
1.59
1.58
1.58
1.23
2.00
1.00
2.02
1.03
2.01
2.03
2.02
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

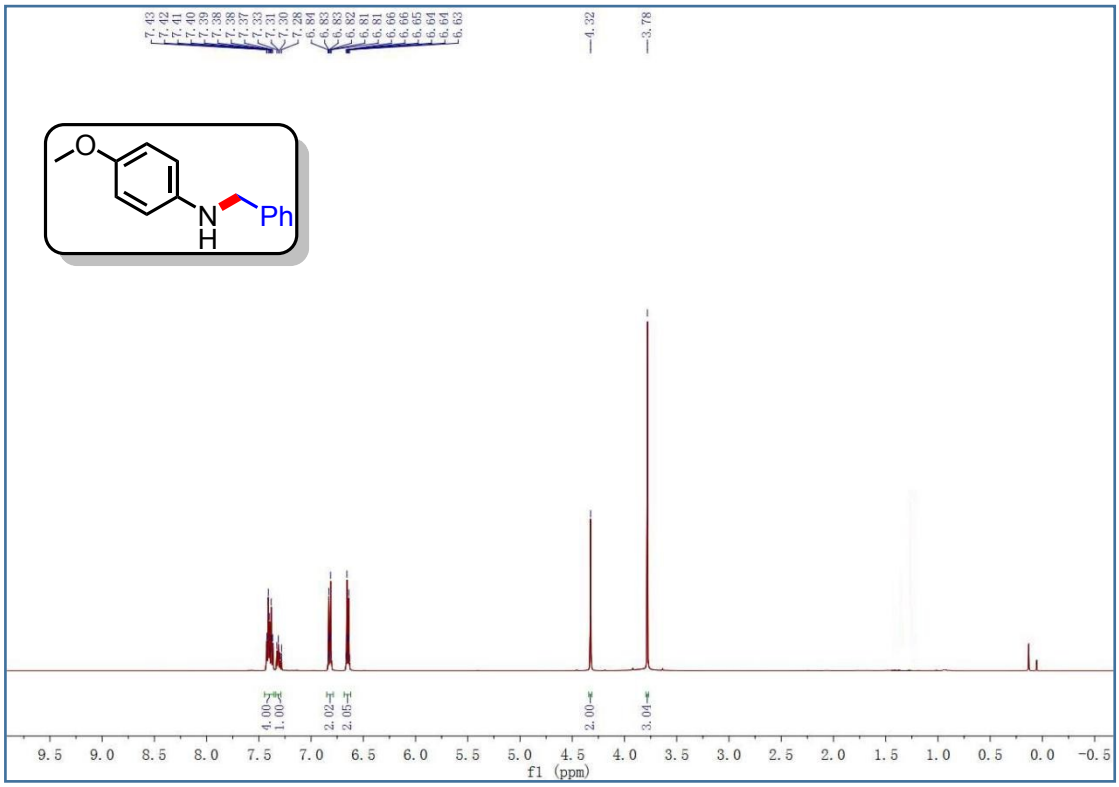

148.36
129.26
117.40
112.92
67.85
44.08
36.80
25.92
23.69
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

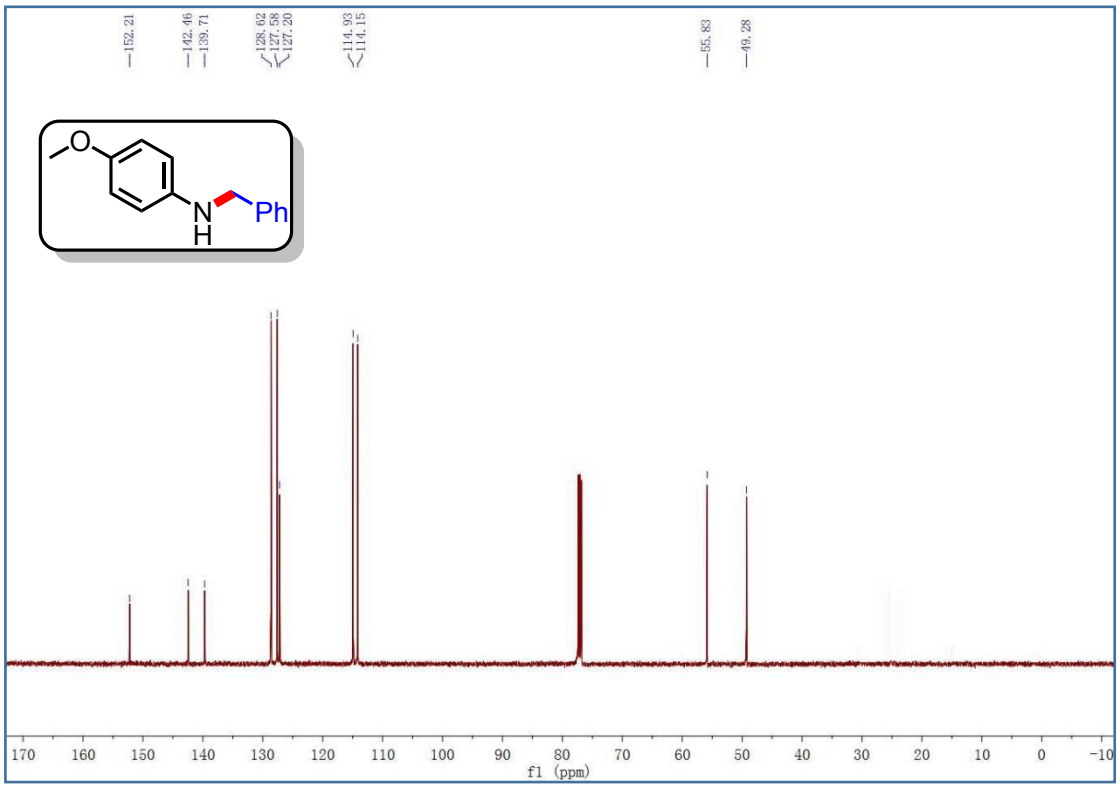
1,2-diphenylpyrrolidine (2al)



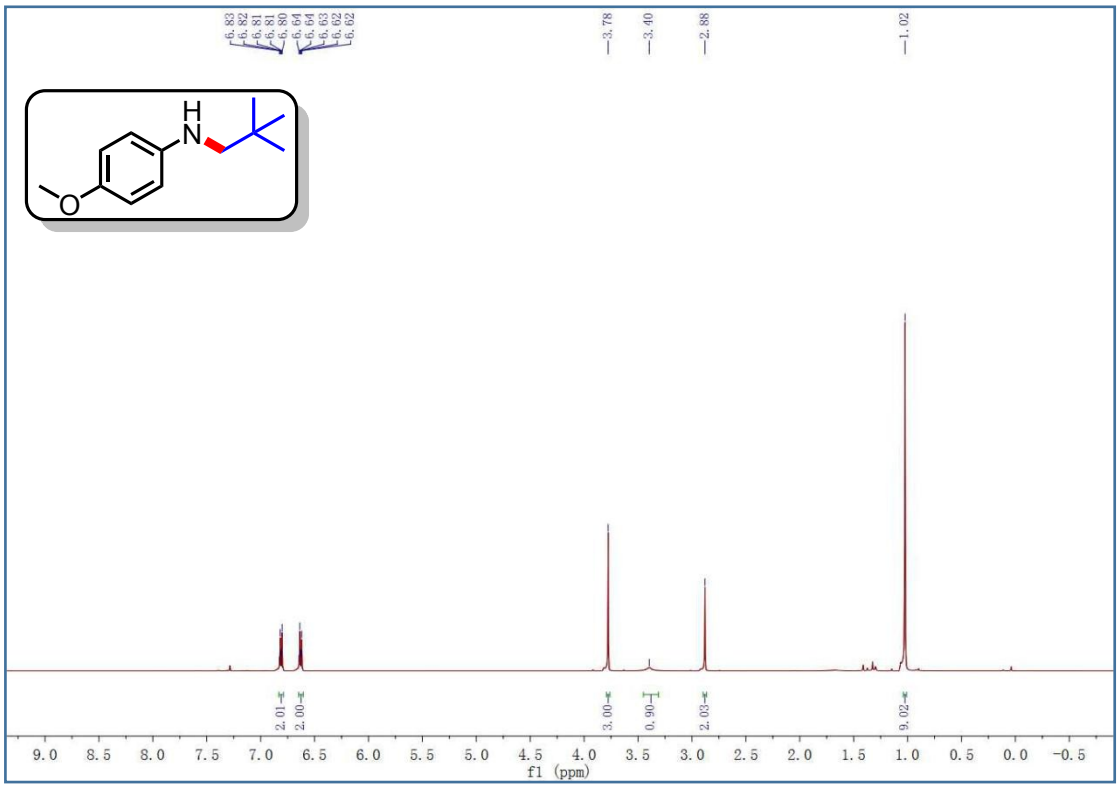


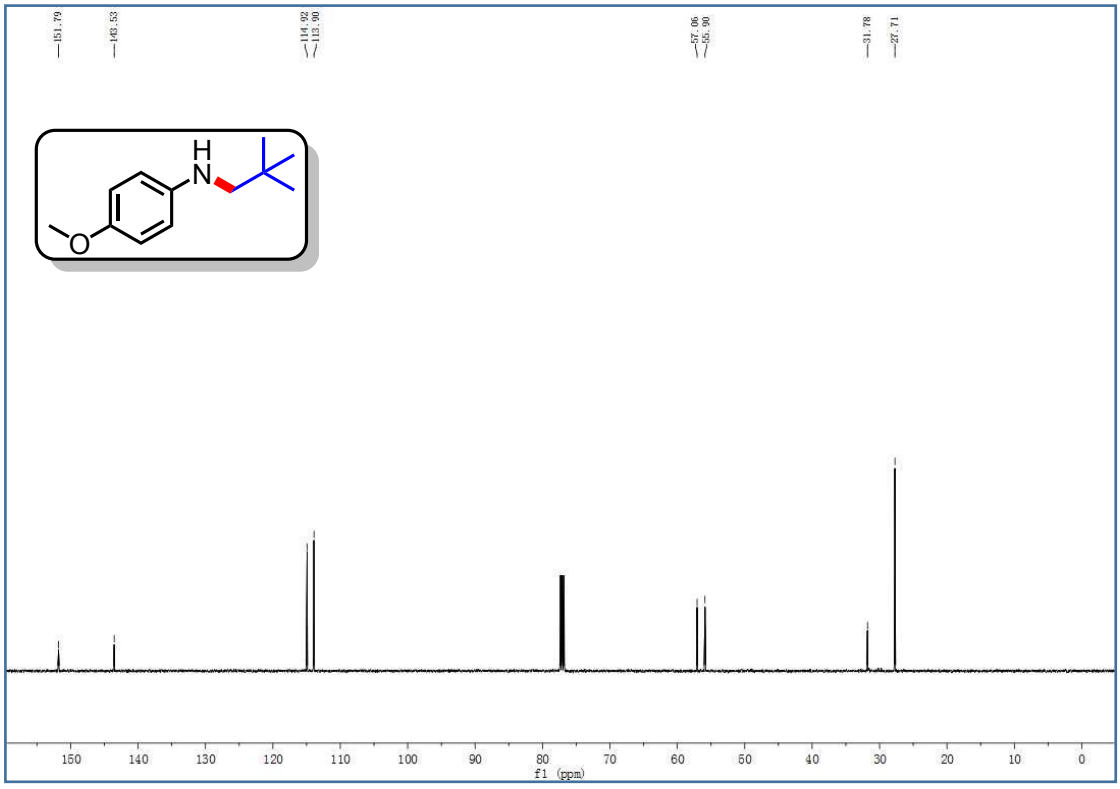
N-benzyl-4-methoxyaniline (2am)



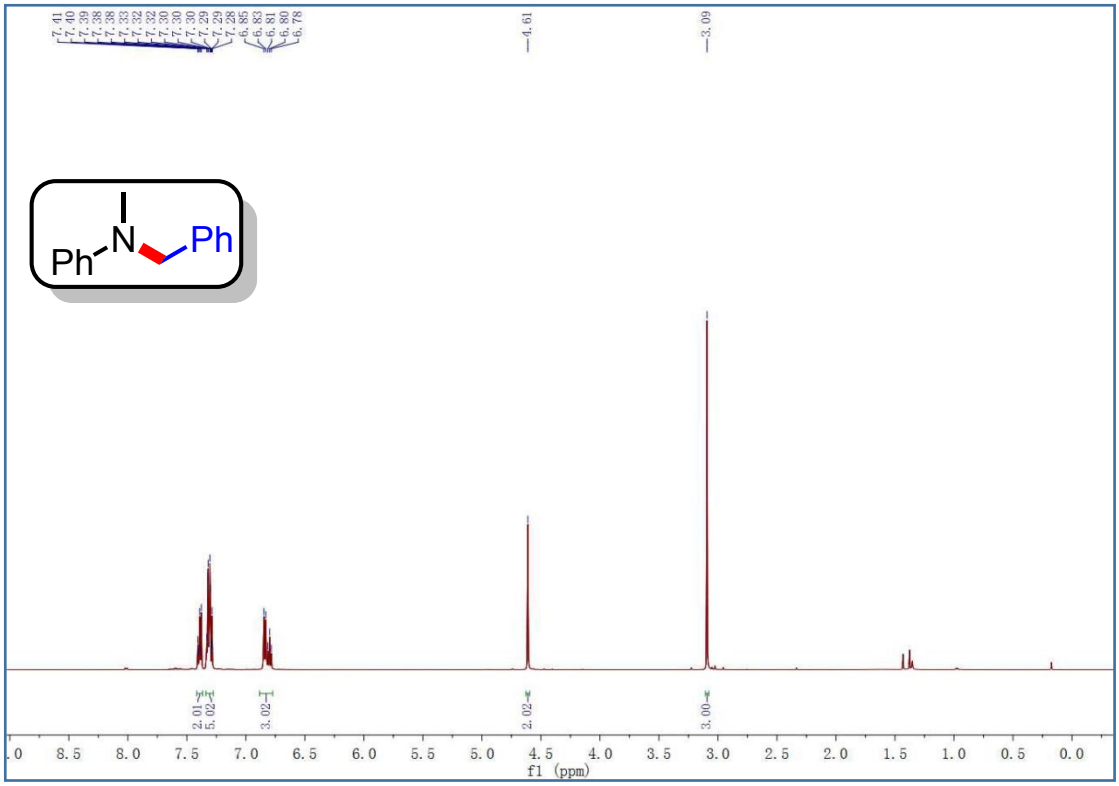


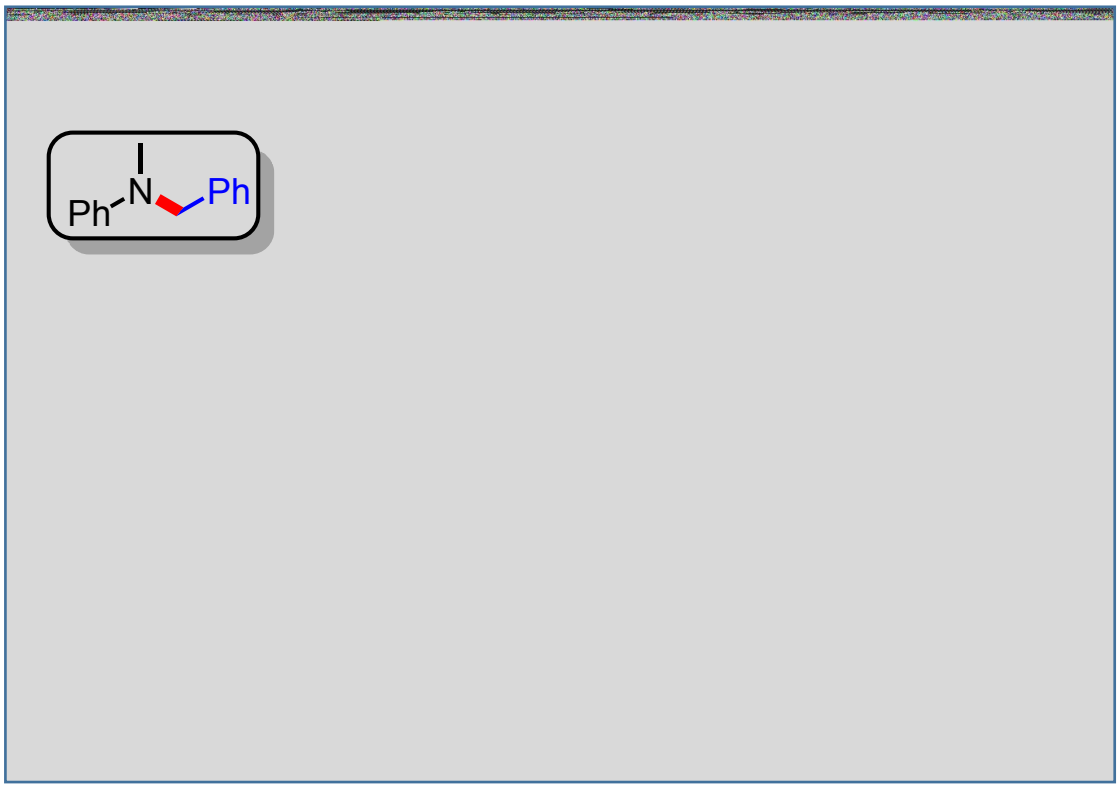
4-methoxy-N-neopentylaniline (2an)


6.83
6.82
6.81
6.80
6.64
6.63
6.62
6.62
3.78
3.40
2.88
1.02
H
N
O
2.01
2.00
3.00
0.90
2.03
9.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

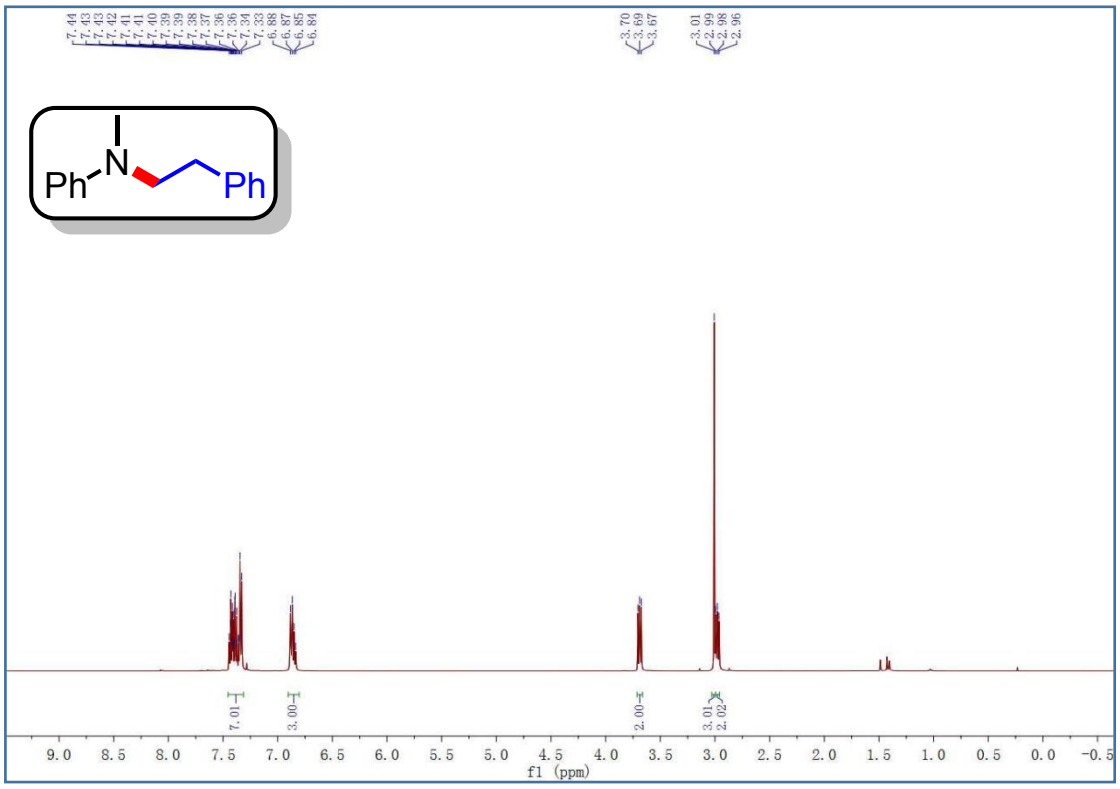

151.79
143.53
114.92
113.90
57.06
55.90
31.78
27.71
H
N
O
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

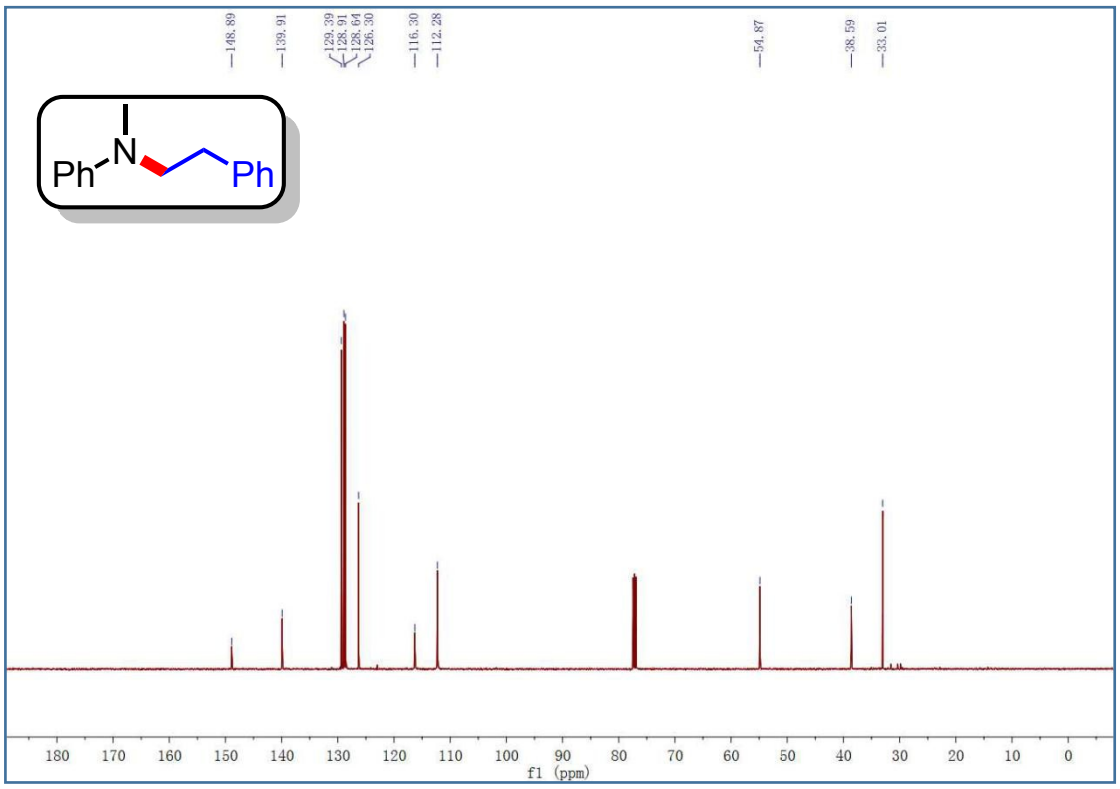
N-benzyl-N-methylaniline (2ao)



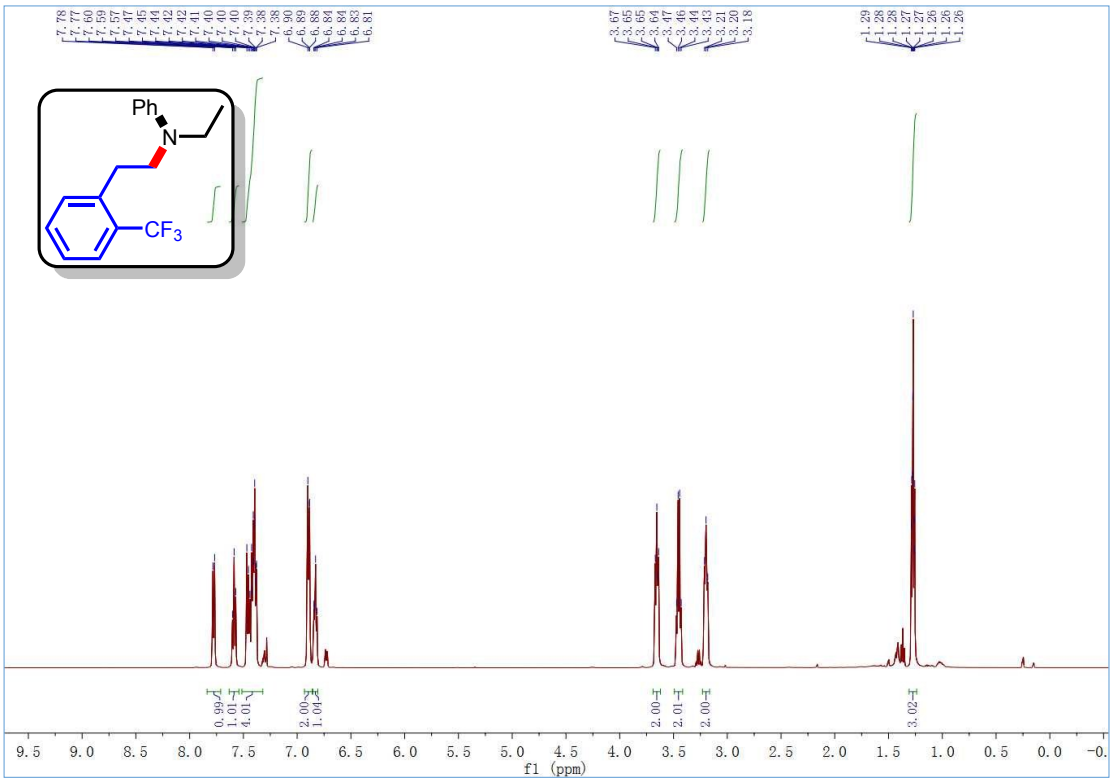


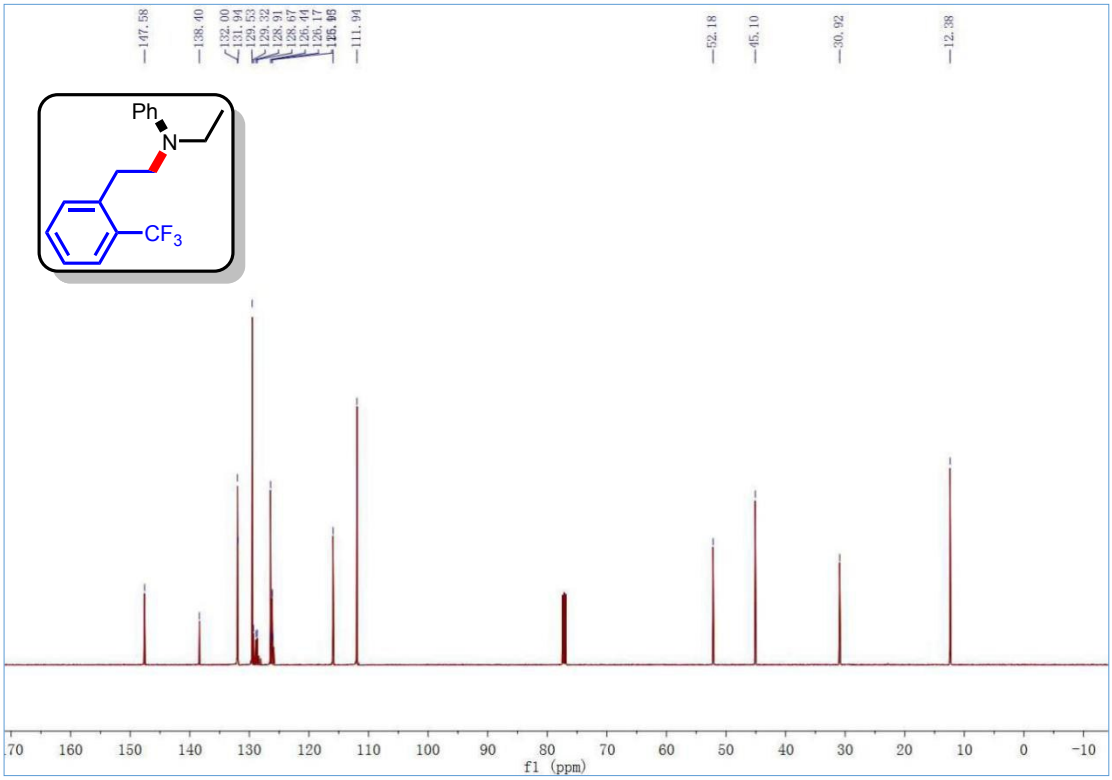
N-methyl-N-phenethylaniline (2ap)

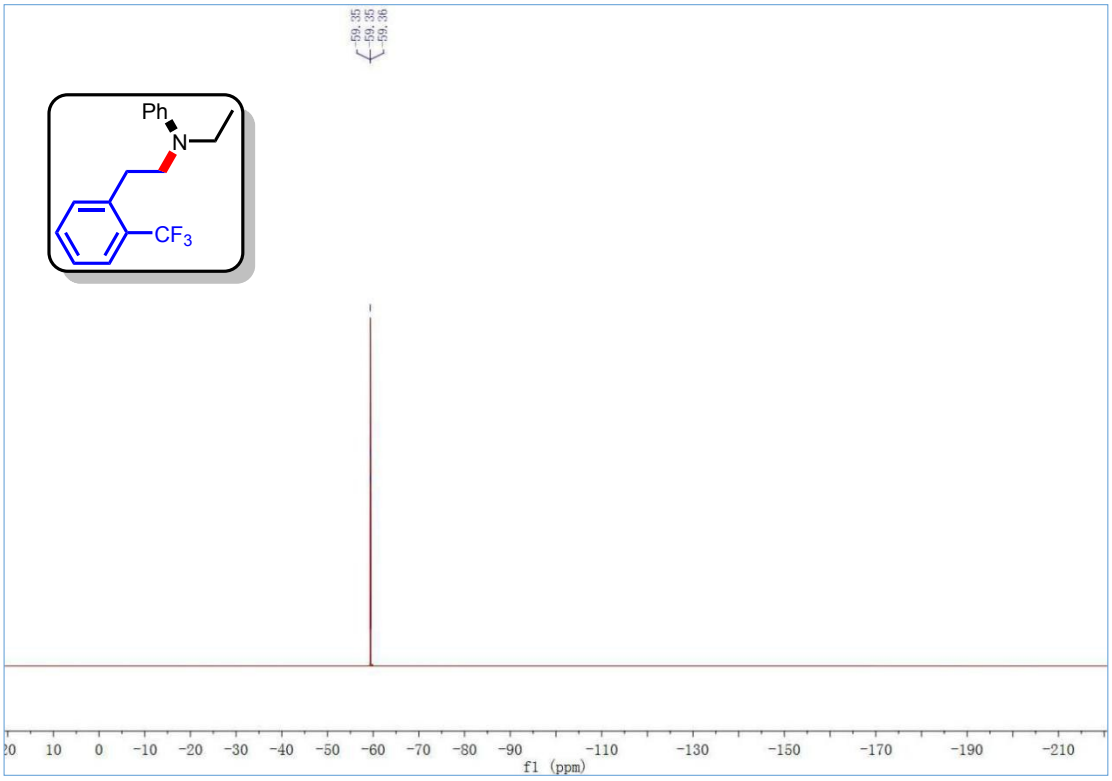

7.44
7.43
7.43
7.42
7.41
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.34
7.33
6.88
6.87
6.85
6.84
3.70
3.69
3.67
3.01
2.99
2.98
2.96
Ph
N
Ph
7.01
3.00
2.00
3.01
2.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


148.89
139.91
129.39
128.91
128.64
126.30
116.30
112.28
54.87
38.59
33.01
Ph
N
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

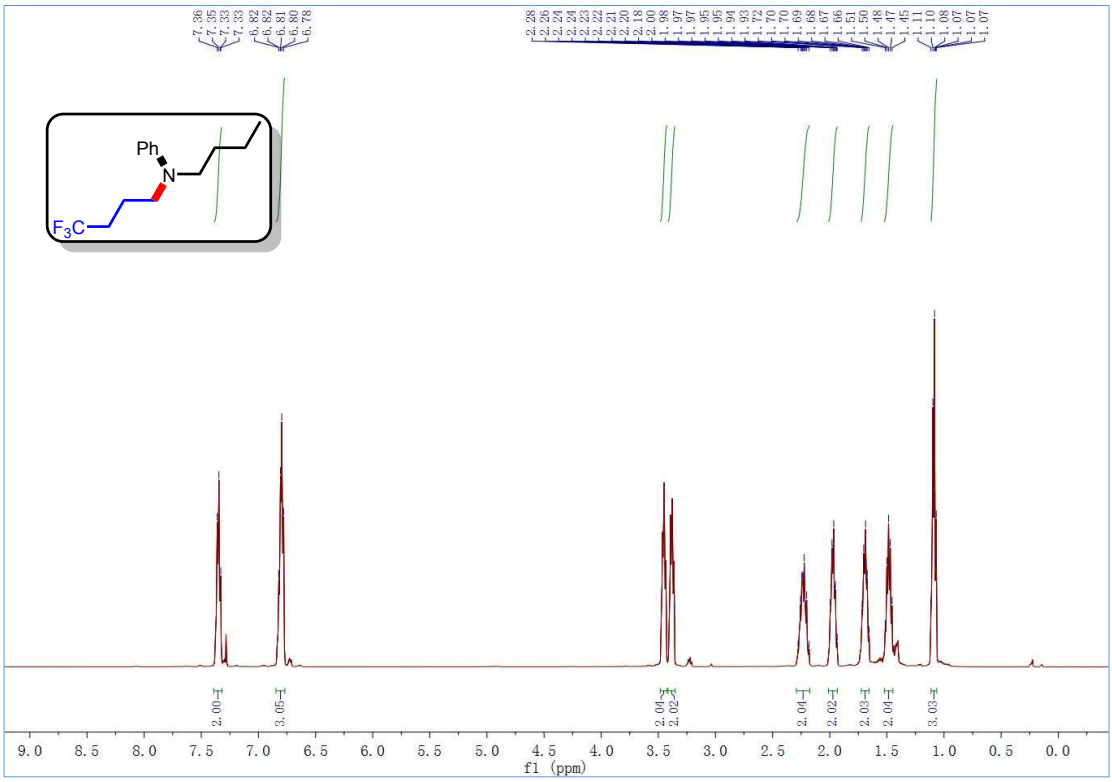
N-ethyl-N-(2-(trifluoromethyl)phenethyl)aniline (2aq)

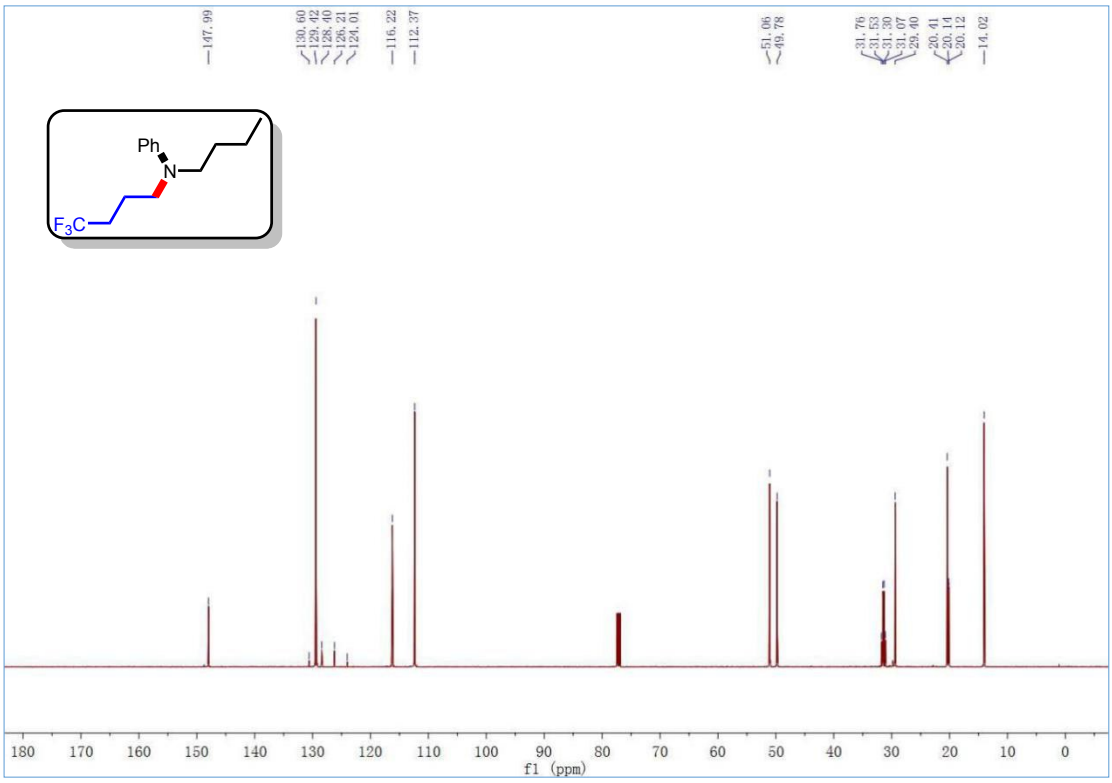


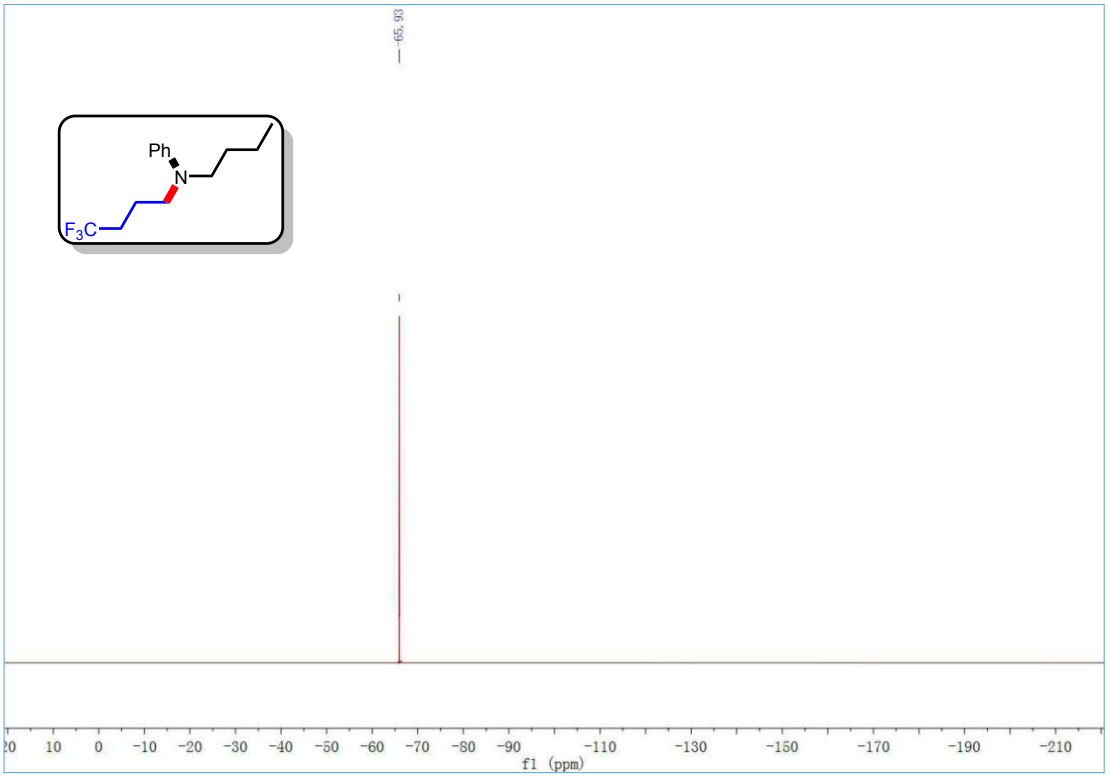



-59.35
-59.35
-59.36
Ph
N
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

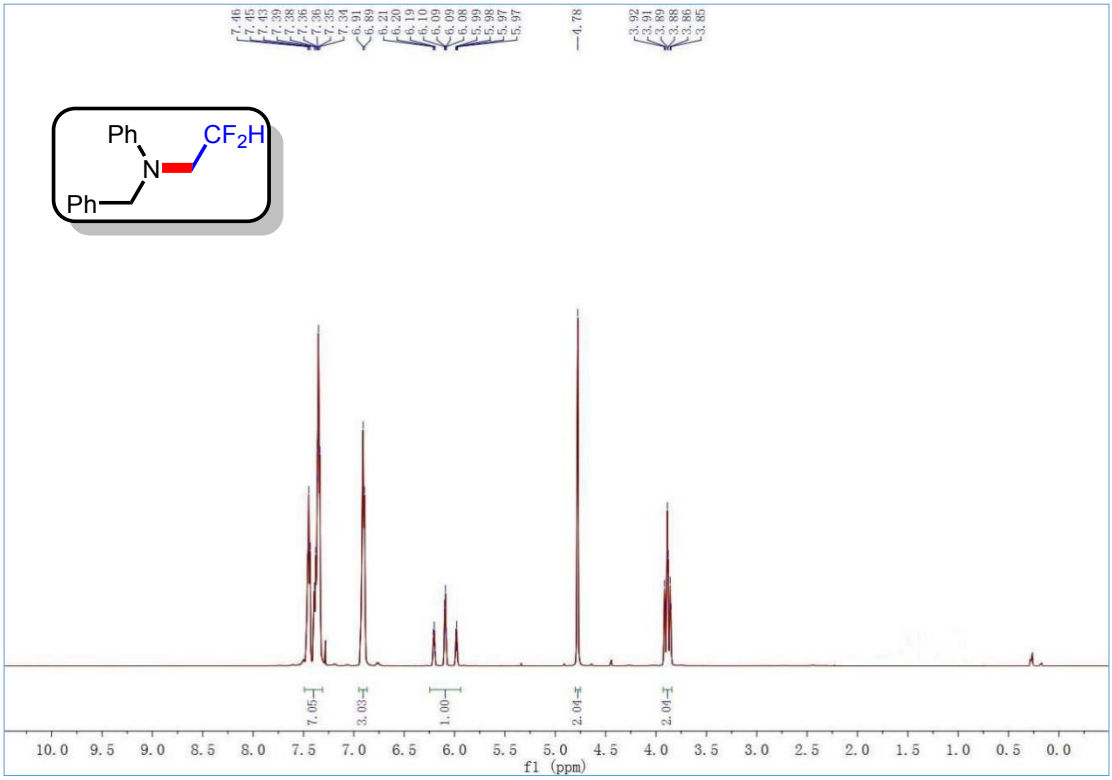
N-butyl-N-(4,4,4-trifluorobutyl)aniline (2ar)

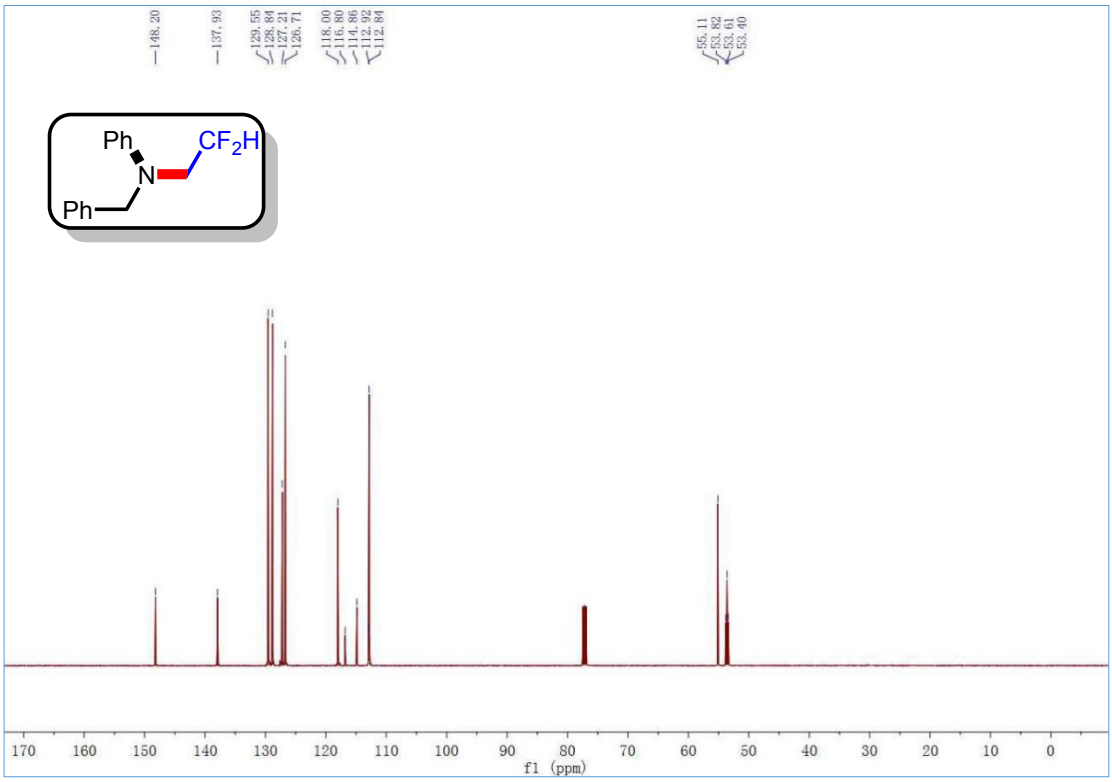

Ph
N
F3C
f1 (ppm)

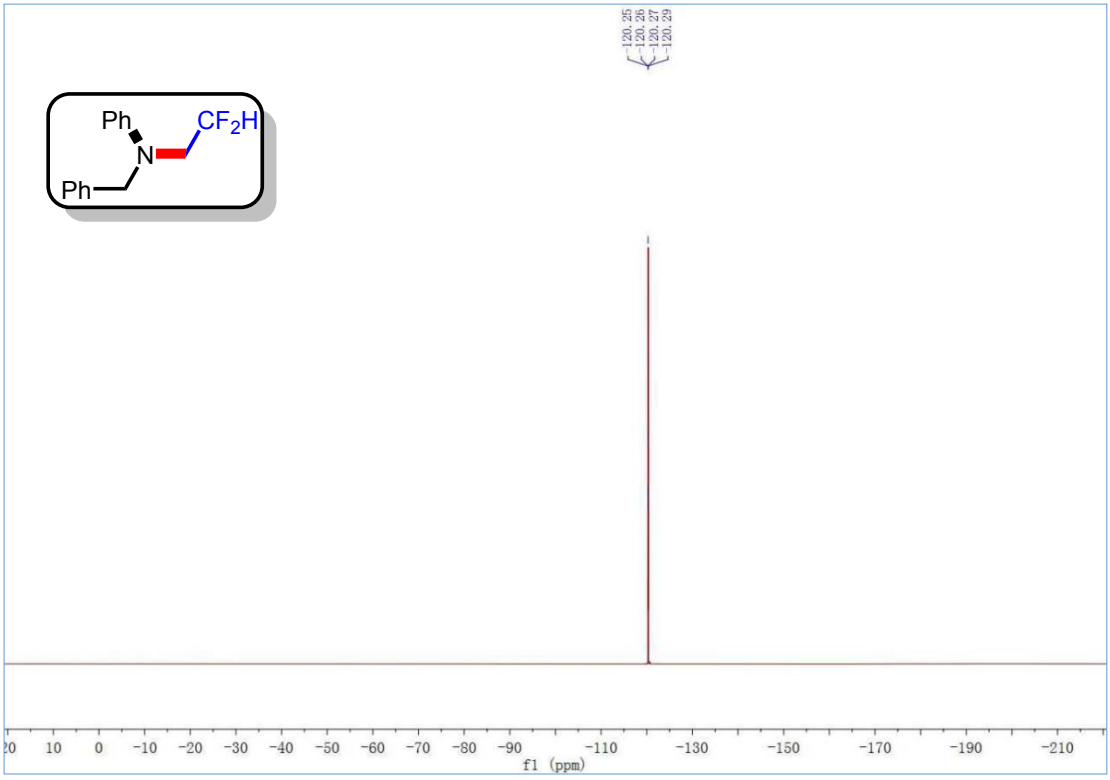

Ph
N
F3C
f1 (ppm)


-65.93
Ph
N
F3C
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

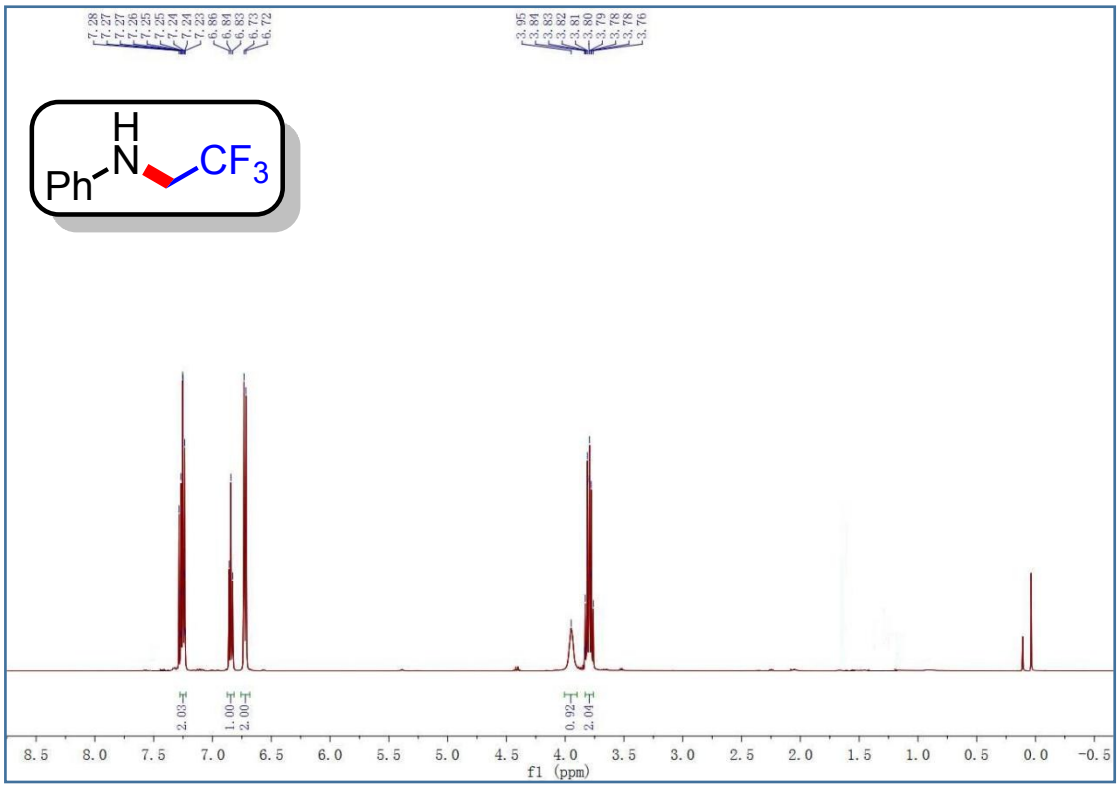
N-benzyl-N-(2,2-difluoroethyl)aniline (2as)

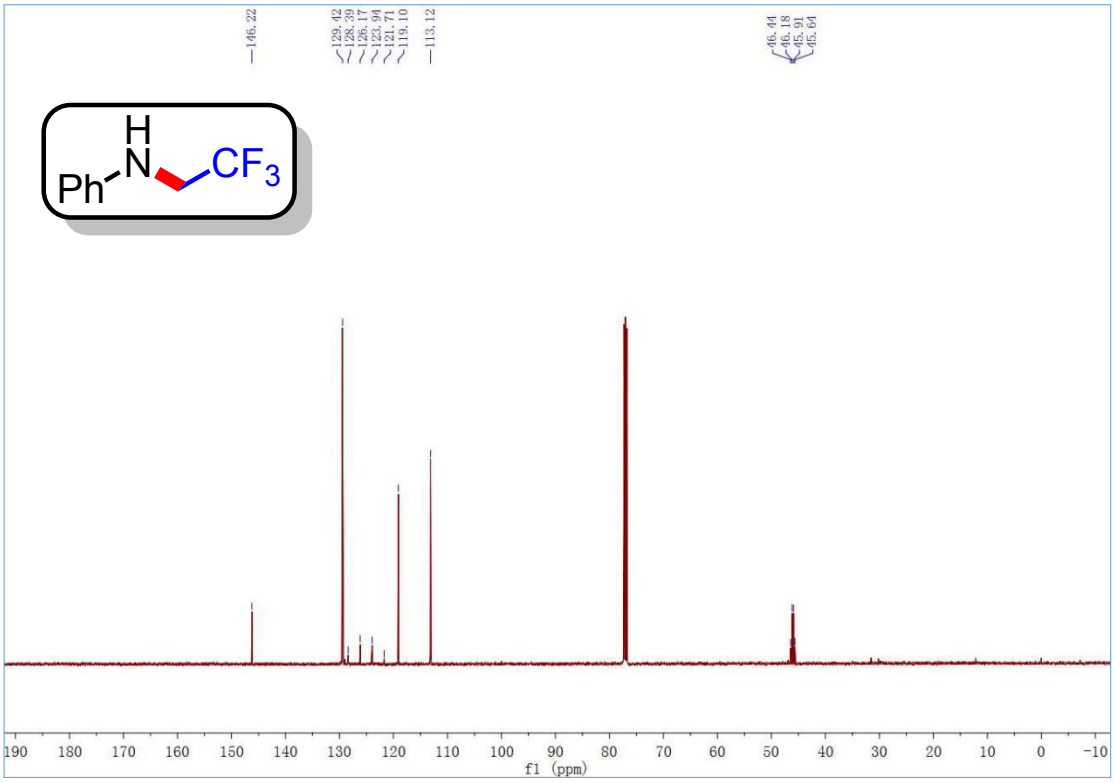



148.20
137.93
129.55
128.84
127.21
126.71
118.00
116.80
114.86
112.92
112.84
55.11
53.82
53.61
53.40
Ph
N
Ph
CF2H
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

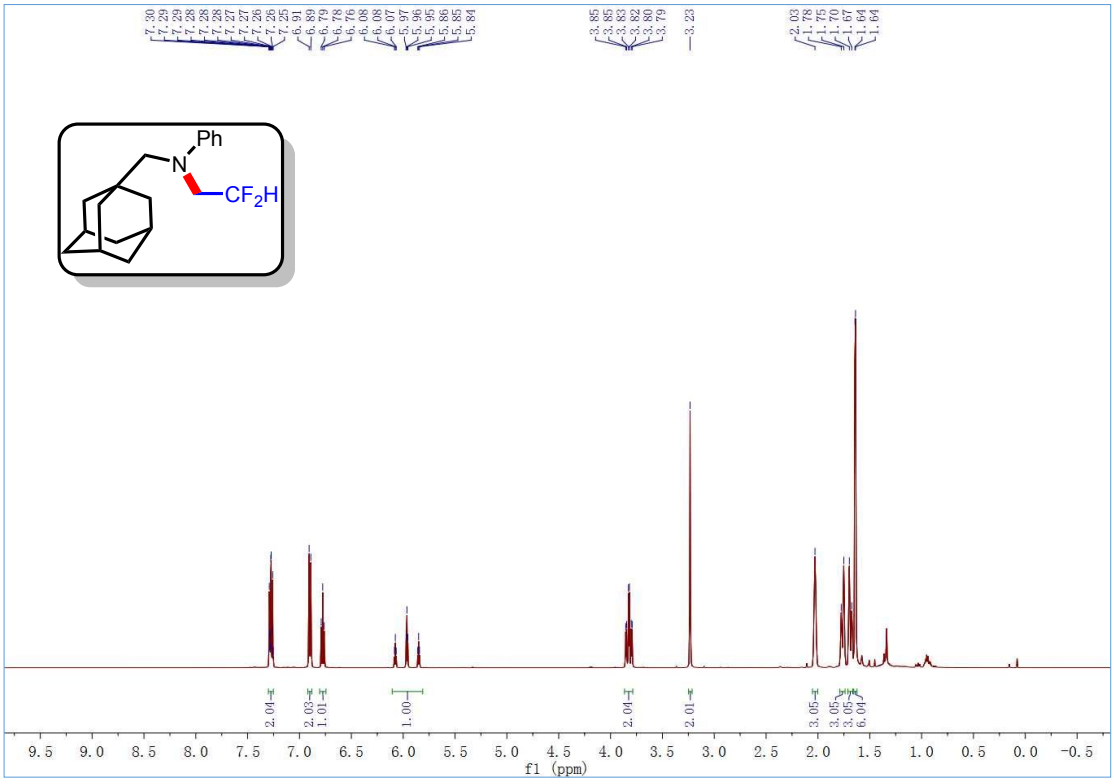

120.25
120.26
120.27
120.29
Ph
N
Ph
CF2H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

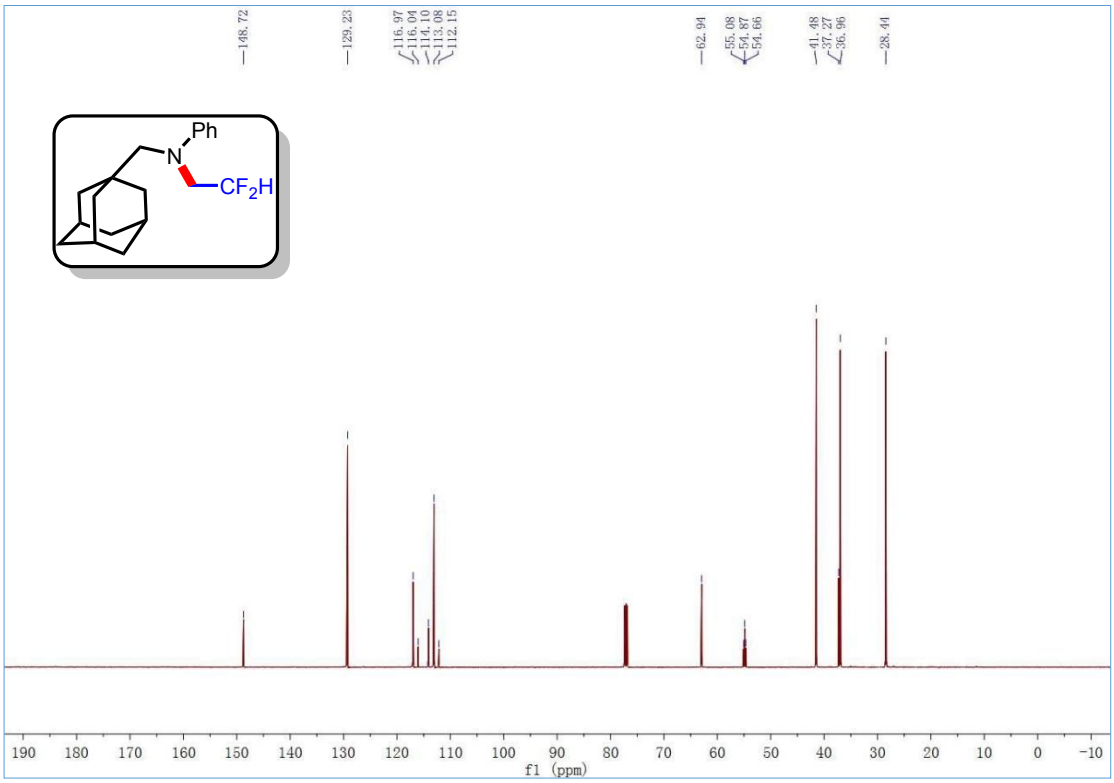
N-(2,2,2-trifluoroethyl)aniline (2at)

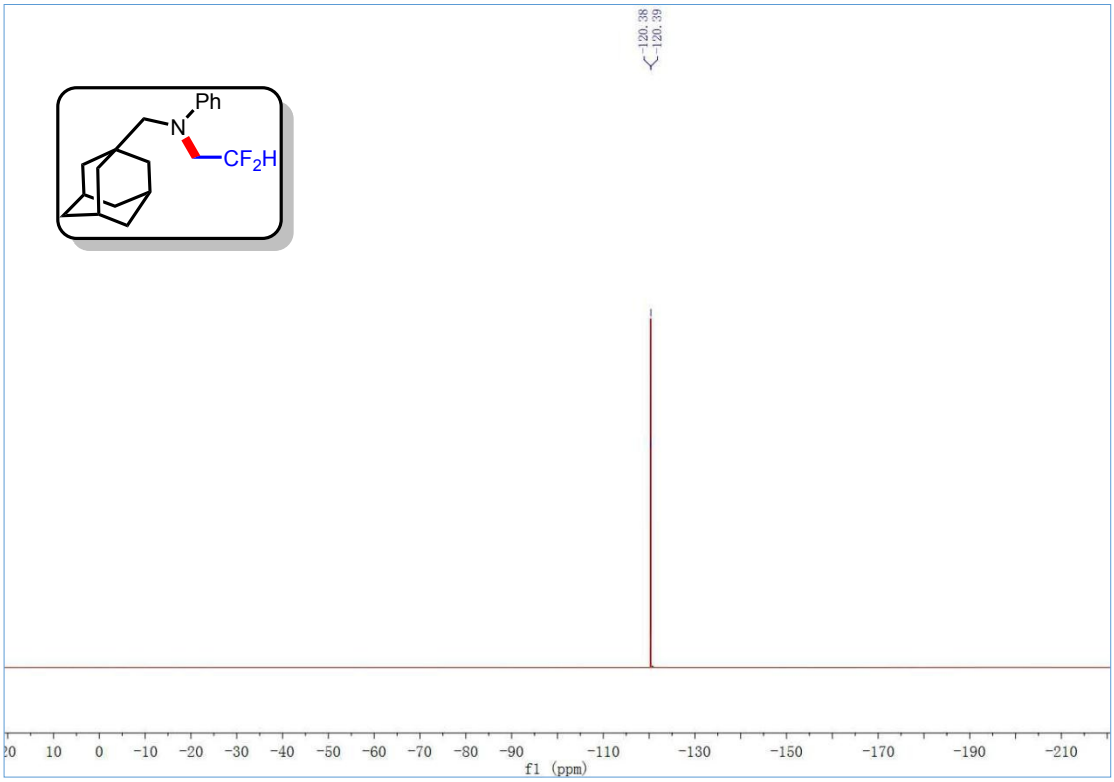




N-(((3r,5r,7r)-adamantan-1-yl)methyl)-N-(2,2-difluoroethyl)aniline (2au)

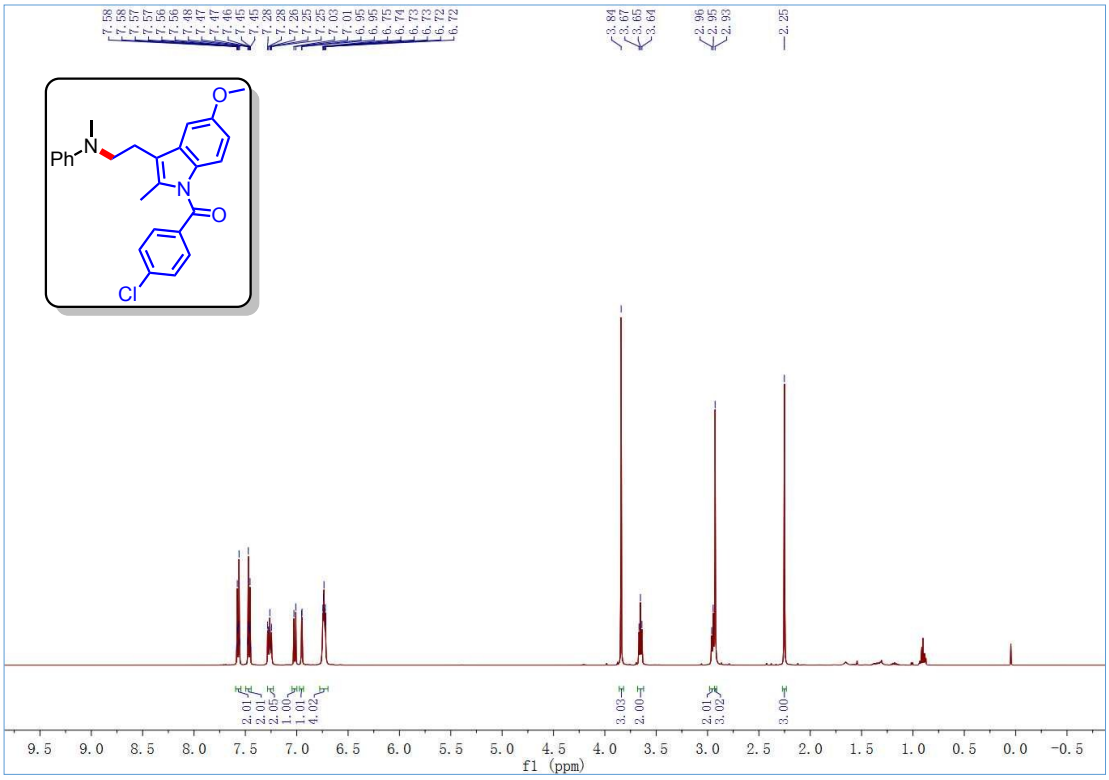


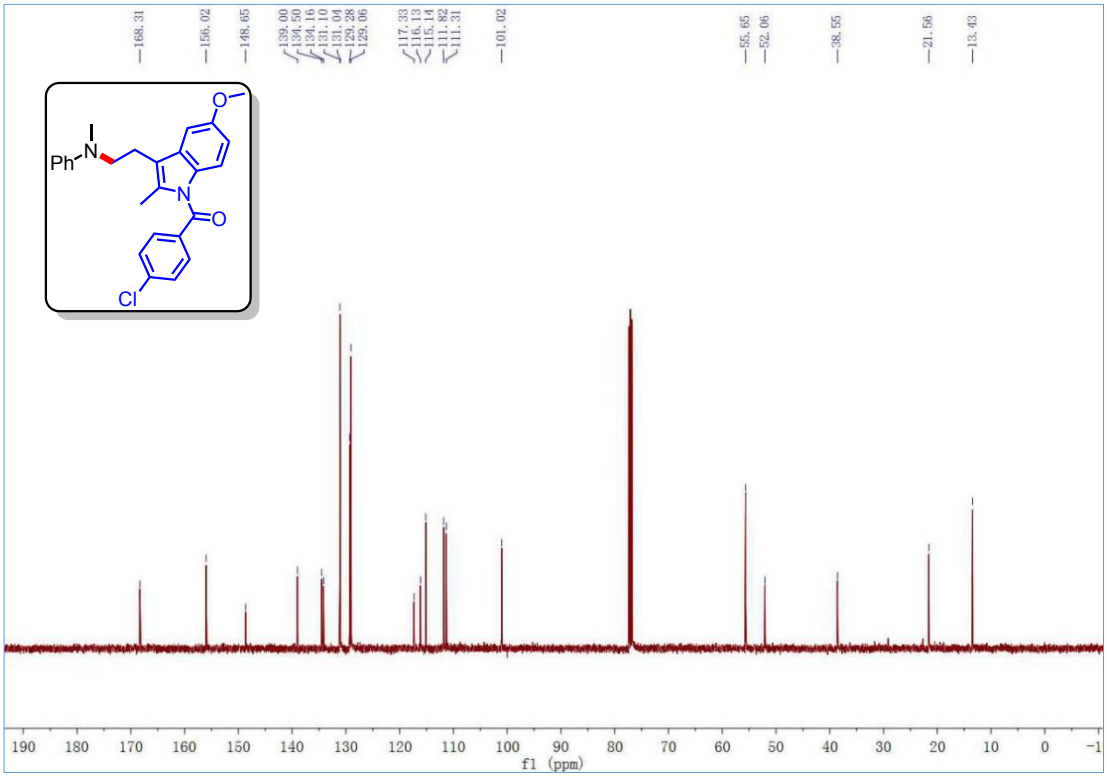

148.72
129.23
116.97
116.04
114.10
113.08
112.15
62.94
55.08
54.87
54.66
41.48
37.27
36.96
28.44
Ph
N
CF2H
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


120.38
120.39
Ph
N
CF2H
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

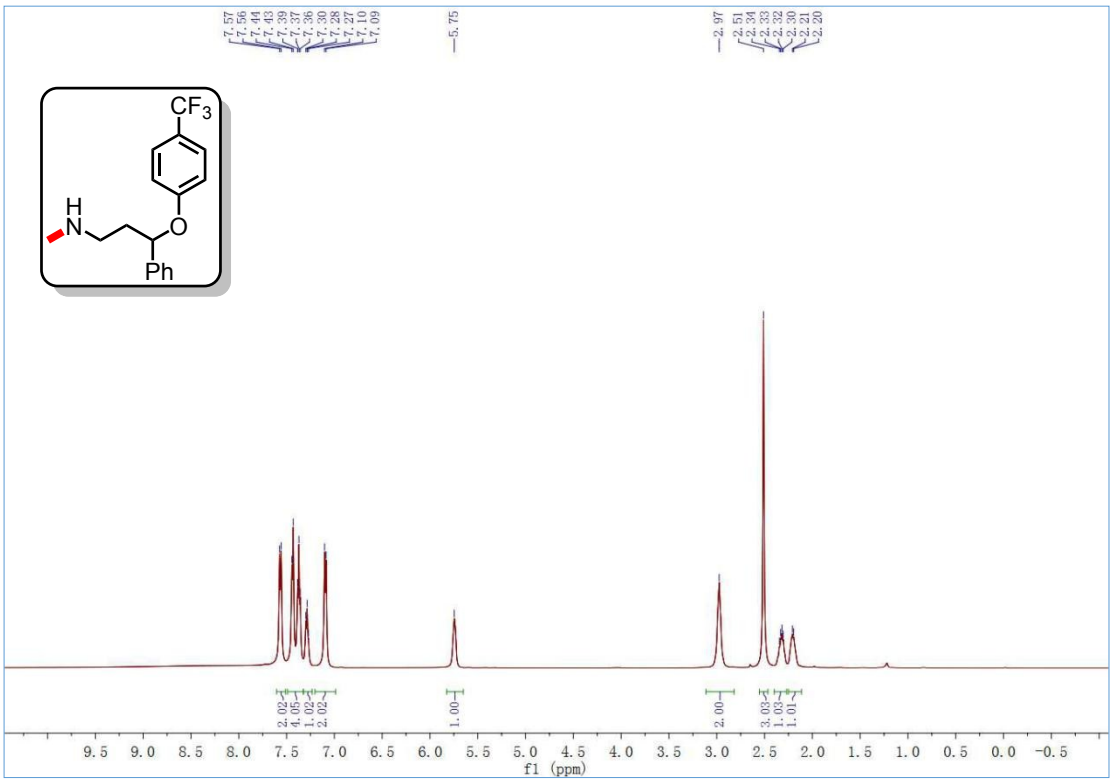
(4-chlorophenyl)(5-methoxy-2-methyl-3-(2-

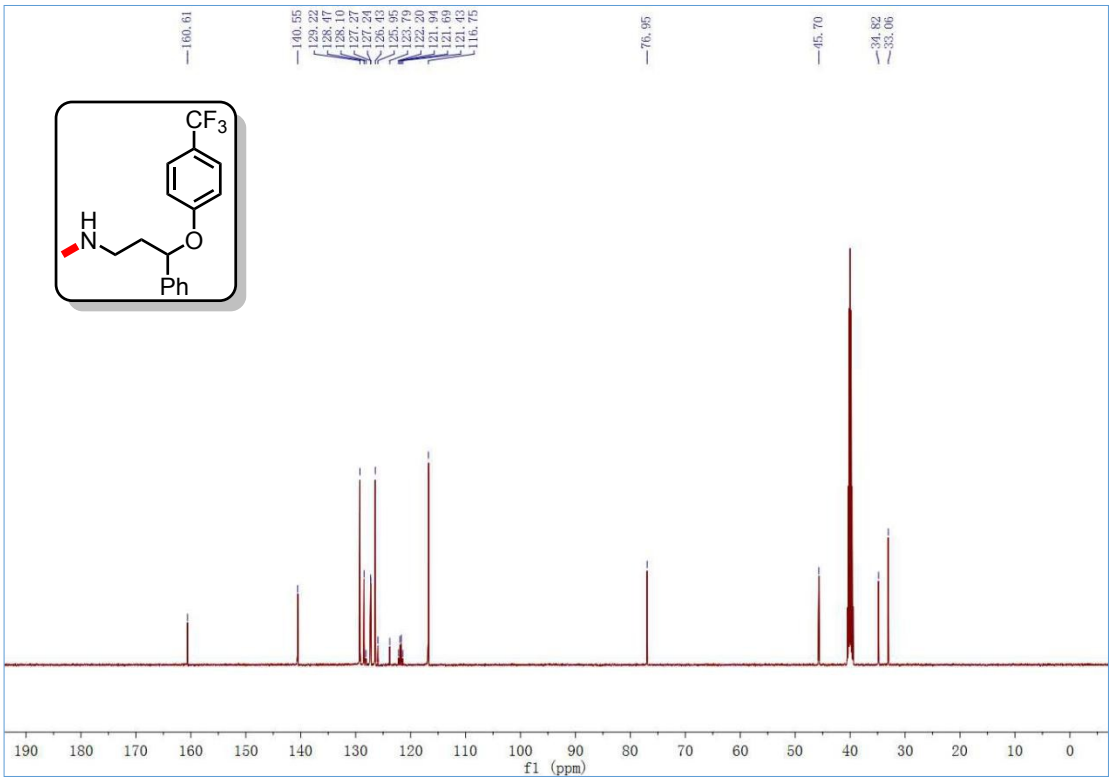
(methyl(phenyl)amino)ethyl)-1H-indol-1-yl)methanone (2av)

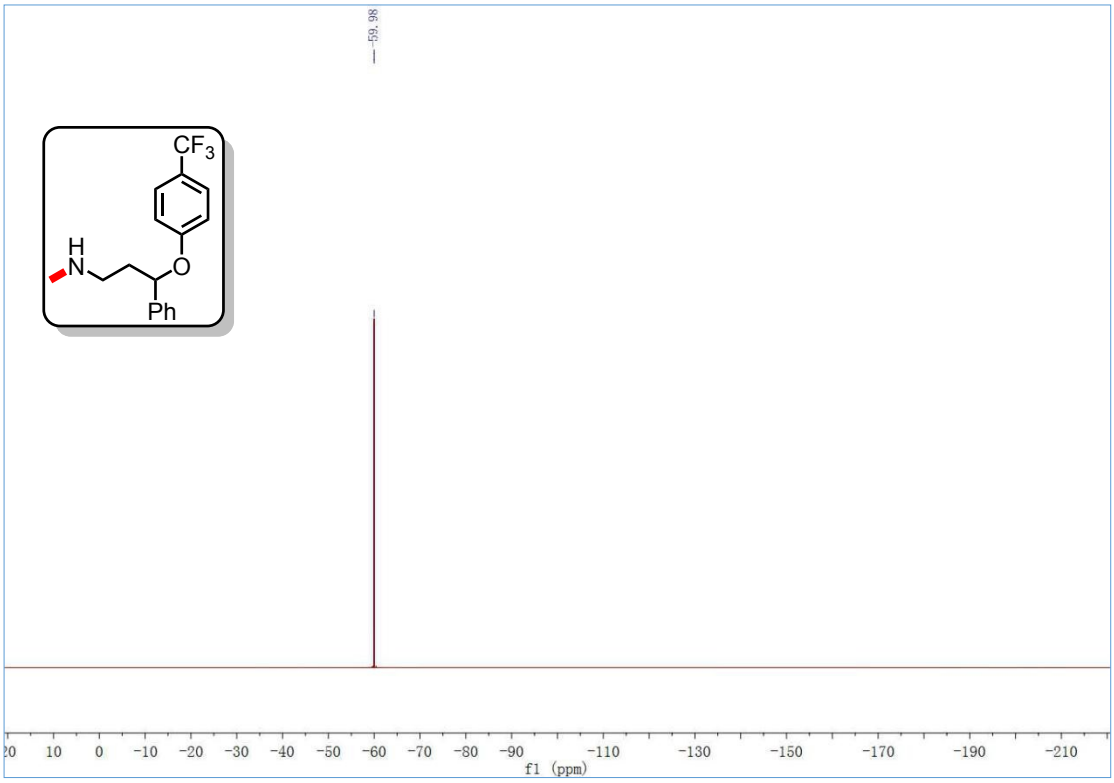




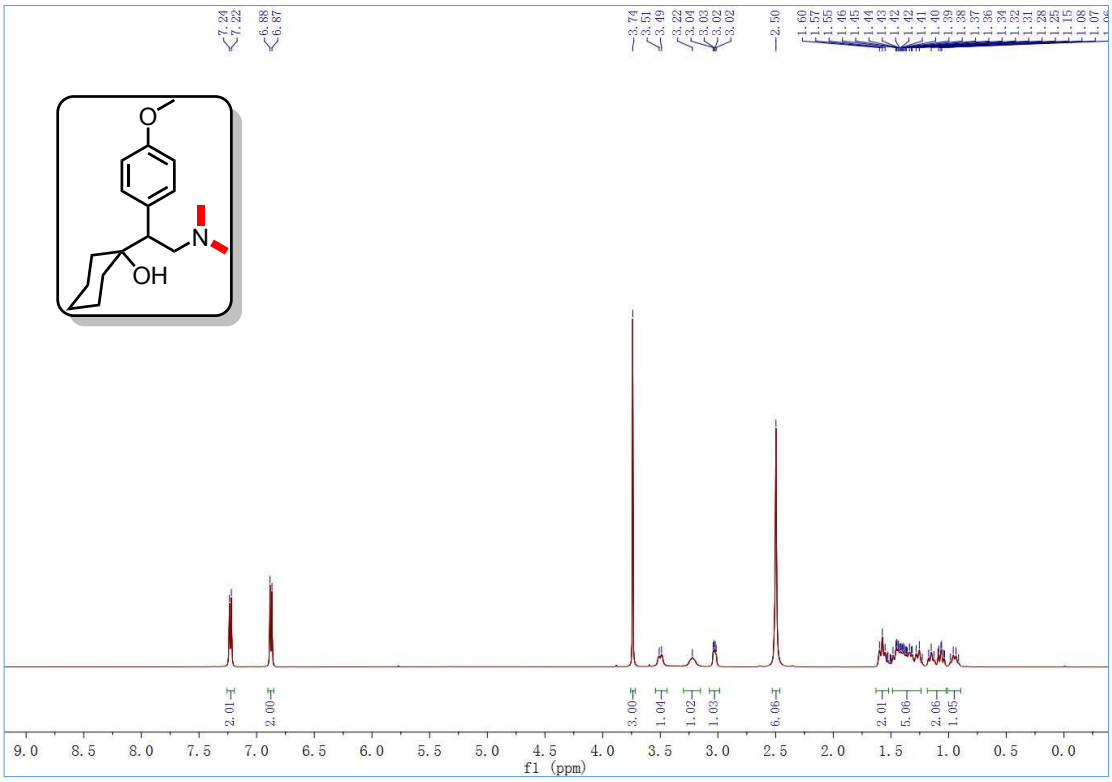
N-methyl-3-phenyl-3-(4-(trifluoromethyl)phenoxy)propan-1-amine (2aw)

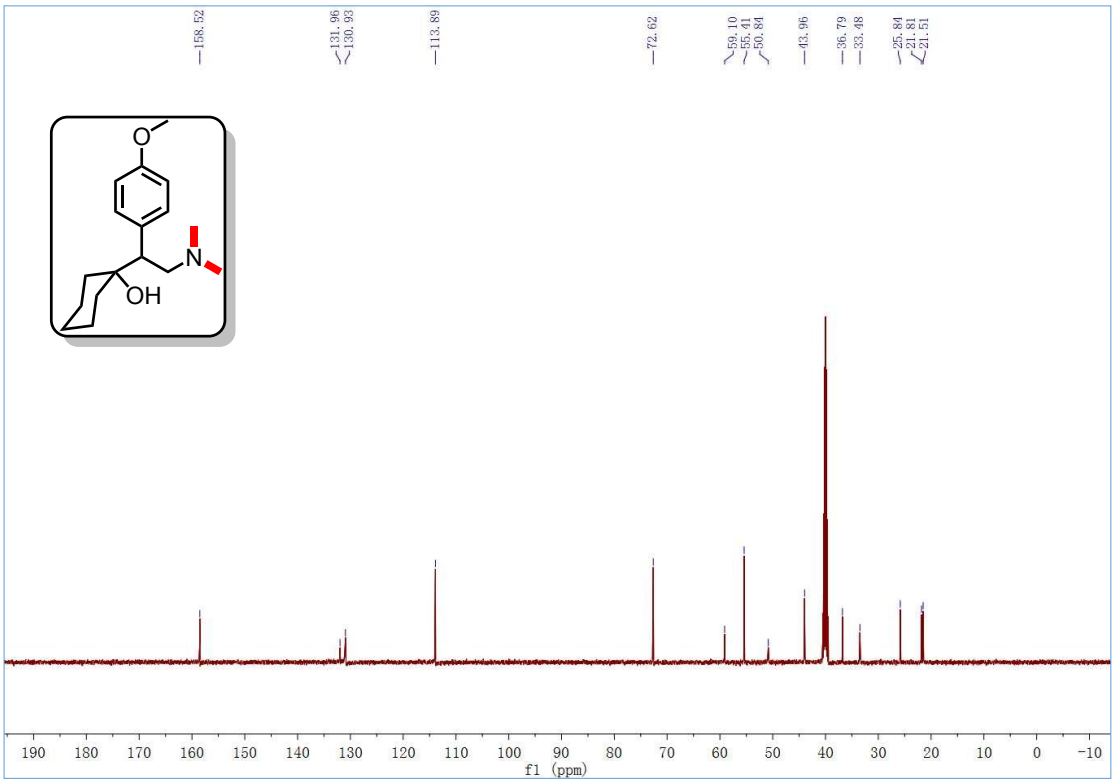



160.61
140.55
129.22
128.47
128.10
127.27
127.24
126.43
125.95
123.79
122.20
121.94
121.69
121.43
116.75
76.95
45.70
34.82
33.06
CF3
H
N
O
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-59.98
CF3
H
N
O
Ph
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190 -210
f1 (ppm)

1-(2-(dimethylamino)-1-(4-methoxyphenyl)ethyl)cyclohexan-1-ol (2ax)


7.24
7.22
6.88
6.87
3.74
3.51
3.49
3.22
3.04
3.03
3.02
3.02
2.50
1.60
1.57
1.55
1.46
1.45
1.44
1.43
1.42
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.34
1.32
1.31
1.28
1.25
1.15
1.08
1.07
O
N
OH
2.01
2.00
3.00
1.04
1.02
1.03
6.06
2.01
5.06
2.06
1.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.52
131.96
130.93
113.89
72.62
59.10
55.41
50.84
43.96
36.79
33.48
25.84
21.81
21.51
O
N
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

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