Coupling of C(sp^3)—H Bonds with C(sp^2)—O Electrophiles: Mild, General and Selective

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Supporting Information

General Considerations

All reactions were set up with glovebox and carried out under nitrogen atmosphere in Schlenk tubes. Reaction temperatures are reported as the temperature of the heat transfer medium surrounding the vessel unless otherwise stated. Anhydrous solvents were purchased from Acros Organics and used as received. Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Alfa Aesar, ABCR and TCI and used as received unless otherwise stated.

^{1}H and ^{13}C NMR spectra were recorded on a Brüker Advance 400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS. The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm; CD_3OD: δH = 3.31 ppm, δC = 49.00 ppm; $(CD_3)_2SO$: δH = 2.50 ppm, δC = 39.52 ppm).

GC-MS was obtained using electron ionization (SHIMADZU GCMS-QP 2010 SE). TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. Exact ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS were obtained on a Thermo LTQ mass spectrometer.

Synthesis of Substrates

2.1 General procedure for alkenyl tosylates 2 synthesis:

According to a procedure by Reeves et al[1a] **without further optimization**, in a 200 mL round-bottomed flask under magnetic stirring and nitrogen atmosphere was added appropriate ketones (19.02 mmol) in THF (47.6 mL) to give a pale yellow solution. The reaction mixture was cooled to -20 ^{o}C. Sodium tert-butoxide (2.01 g, 20.93 mmol) was added in one portion. The solution was stirred at -5 ^{o}C for 1 h then at room temperature for 30 min. The solution was cooled to -15^{o}C. p-Toluenesulfonic anhydride (6.83 g, 20.93 mmol) was added in one portion. The resulting solution was stirred at -15 to -5 ^{o}C for 1.5 h, quenched with aq. $NaHCO_3$ (20 mL). MTBE was added (100 mL) and the organic phase was washed with water (4 x 100 mL), dried on $MgSO_4$ and concentrated, and purified by flash column chromatography.

3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2a) The reaction of 3,4-dihydronaphthalen-2(1H)-one (2.78 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.86 g, 50%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.80 (m, 2H), 7.38 – 7.31 (m, 2H), 7.15 – 7.09 (m, 2H), 7.09 – 7.05 (m, 1H), 6.91 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.10 (s, 1H), 2.91 – 2.85 (m, 2H), 2.42 (dd, *J* = 8.1, 1.3 Hz, 5H).

6-phenyl-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2b) The reaction of 6-phenyl-3,4-dihydronaphthalen-2(1H)-one (4.20 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.15 g, 58%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.3 Hz, 2H), 7.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.38 – 7.28 (m, 5H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 1.4 Hz, 1H), 2.95 (t, *J* = 8.3 Hz, 2H), 2.59 – 2.33 (m, 5H).

6-fluoro-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2c) The reaction of 6-fluoro-3,4-dihydronaphthalen-2(1H)-one (3.17 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.98 g, 49 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.75 (m, 2H), 7.43 – 7.31 (m, 2H), 6.92 – 6.82 (m, 1H), 6.86 – 6.75 (m, 2H), 6.09 (d, *J* = 1.2 Hz, 1H), 2.93 – 2.81 (m, 2H), 2.47 (s, 3H), 2.41 (tt, *J* = 8.1, 1.0 Hz, 2H).

6-bromo-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2d) The reaction of 6-bromo-3,4-dihydronaphthalen-2(1H)-one (4.28 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.59 g, 64%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.41 – 7.31 (m, 2H), 7.26 – 7.20 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.08 (d, *J* = 1.4 Hz, 1H), 2.85 (t, *J* = 8.4 Hz, 2H), 2.46 (s, 3H), 2.40 (ddd, *J* = 9.4, 8.0, 1.3 Hz, 2H).

6-methoxy-3,4-dihydronaphthalen-2-yl 4-methylbenzenesulfonate (2e) The 6-methoxy-3,4-dihydronaphthalen-2(1H)-one (3.36 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (4.56 g, 72%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 2H), 7.31 – 7.23 (m, 2H), 6.80 – 6.73 (m, 1H), 6.61 – 6.54 (m, 2H), 5.97 (t, *J* = 1.2 Hz, 1H), 3.70 (s, 3H), 2.78 (t, *J* = 8.3 Hz, 2H), 2.41 – 2.28 (m, 5H).

3,4-dihydronaphthalene-2,6-diyl bis(4-methylbenzenesulfonate) (2f) The reaction of 6-hydroxy-3,4-dihydronaphthalen-2(1H)-one (3.09 g, 19.02 mmol) with p-Toluenesulfonic anhydride (2.2 eq.) as outlined in the general procedure provided the title compound (5.00 g, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 2H), 7.70 – 7.57 (m, 2H), 7.27 (dd, *J* = 13.5, 8.1 Hz, 4H), 6.73 (d, *J* = 8.3 Hz, 2H), 6.57 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.02 (d, *J* = 1.4 Hz, 1H), 2.75 (t, *J* = 8.4 Hz, 2H), 2.39 (d, *J* = 3.5 Hz, 5H), 2.32 (td, *J* = 8.4, 1.3 Hz, 2H).

cyclohex-1-en-1-yl 4-methylbenzenesulfonate (2g)[1b] The reaction of cyclohexanone (1.86 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.85 g, 59%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.75 (m, 2H), 7.36 – 7.30 (m, 2H), 5.35 (tt, *J* = 4.0, 1.5 Hz, 1H), 2.45 (s, 3H), 2.04 (dtdd, *J* = 21.6, 6.2, 3.9, 2.2 Hz, 4H), 1.67 – 1.60 (m, 2H), 1.48 (pd, *J* = 6.2, 3.0 Hz, 2H).

cyclohept-1-en-1-yl 4-methylbenzenesulfonate (2h)[1b] The reaction of cycloheptanone (2.13 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.20 g, 63%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.36 – 7.30 (m, 2H), 5.41 (t, J = 6.5 Hz, 1H), 2.45 (s, 3H), 2.37 – 2.27 (m, 2H), 2.03 – 1.93 (m, 2H), 1.64 (qd, J = 5.8, 5.0, 2.1 Hz, 2H), 1.56 – 1.47 (m, 4H). 6.5 Hz, 1H), 2.45 (s, 3H), 2.37 – 2.27 (m, 2H), 2.03 – 1.93 (m, 2H), 1.64 (qd, J = 5.8, 5.0, 2.1 Hz, 2H), 1.56 – 1.47 (m, 4H).

(E)-cyclooct-1-en-1-yl 4-methylbenzenesulfonate (2i)[1b] The reaction of cyclooctanone (2.40 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (2.51 g, 47%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.38 – 7.29 (m, 2H), 5.41 (t, *J* = 6.5 Hz, 1H), 2.45 (s, 3H), 2.35 – 2.30 (m, 2H), 2.02 – 1.94 (m, 2H), 1.64 (qd, *J* = 5.8, 5.0, 2.1 Hz, 2H), 1.55 – 1.46 (m, 4H).

4-methylcyclohex-1-en-1-yl 4-methylbenzenesulfonate (2j)[1b] The reaction of 4-methylcyclohexan-1-one (2.13 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (1.4 g, 18%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.30 (q, *J* = 2.5 Hz, 1H), 2.45 (s, 3H), 2.17 – 1.92 (m, 3H), 1.72 – 1.54 (m, 3H), 1.28 (dtd, *J* = 12.4, 9.9, 6.0 Hz, 1H), 0.91 (d, *J* = 6.2 Hz, 3H).

1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl 4-methylbenzenesulfonate (2k)[1b] The reaction of 4-Phenylcyclohexanonee (3.3 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.0 g, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.15 (m, 3H), 5.47 – 5.43 (m, 1H), 2.46 (s, 3H), 2.38 – 2.12 (m, 5H), 1.99 – 1.90 (m, 1H), 1.88 – 1.79 (m, 1H).

ethyl 4-(tosyloxy)cyclohex-3-enecarboxylate (2l)[1b] The reaction of ethyl 4-oxocyclohexanecarboxylate (3.23 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.32 (s, 2H), 5.32 (dd, *J* = 8.0, 3.4 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.53 – 2.39 (m, 4H), 2.28 (dt, *J* = 6.9, 3.1 Hz, 2H), 2.22 – 2.10 (m, 2H), 2.05 – 1.95 (m, 1H), 1.83 – 1.65 (m, 1H), 1.24 (td, *J* = 7.1, 1.1 Hz, 3H).

3,6-dihydro-2H-pyran-4-yl 4-methylbenzenesulfonate (2m) The reaction of dihydro-2H-pyran-4(3H)-one (1.90 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.45 – 7.29 (m, 2H), 5.41 (dt, *J* = 2.8, 1.4 Hz, 1H), 4.12 (q, *J* = 2.8 Hz, 2H), 3.76 (t, *J* = 5.5 Hz, 2H), 2.46 (s, 3H), 2.21 (dtd, *J* = 5.5, 2.7, 1.4 Hz, 2H).

tert-butyl 4-(tosyloxy)-5,6-dihydropyridine-1(2H)-carboxylate (2n) [1a] The reaction of tert-butyl 4-oxopiperidine-1-carboxylate (3.79 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.64 (m, 2H), 7.39 – 7.20 (m, 2H), 5.29 (s, 1H), 3.81 (q, *J* = 3.0 Hz, 2H), 3.42 (t, *J* = 5.8 Hz, 2H), 2.39 (s, 3H), 2.13 (s, 2H), 1.38 (s, 9H).

(*E*)-styryl 4-methylbenzenesulfonate (*E*:*Z* = 2.2 : 1) (2s)[1a] The reaction of 2-phenylacetaldehyde (2.28 g, 19.02 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (3.2 g, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$, the major isomer) δ 7.79 – 7.68 (m, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.25 – 7.09 (m, 5H), 7.00 (d, *J* = 12.3 Hz, 1H), 6.23 (d, *J* = 12.3 Hz, 1H), 2.37 (s, 3H),

2.2 General procedure for the synthesis of vinyl 4-methylbenzene sulfonate (2r)

According to a procedure by Skrydstrup *et al* [2], In a 500 mL round-bottomed flask under magnetic stirring and nitrogen atmosphere was added appropriate n-BuLi (100 mmol) in THF (150 mL) to give a pale yellow solution. The reaction mixture was stirred at 35 ^oC for 4h. Sodium tert-butoxide (15.25 g, 80 mmol, in 40 mL

anhydrous THF) was added dropwise in 30 min, then stirred for another 1h. The solution was poured into water, EtOAc was added (100 mL) and the organic phase was washed with brine (4 x 100 mL), dried on $MgSO_4$ and concentrated, and purified by flash column chromatography to get the desired product as colorless oil (6.9 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.39 – 7.33 (m, 2H), 6.60 (dd, *J* = 13.5, 5.9 Hz, 1H), 4.89 (dd, *J* = 13.5, 2.5 Hz, 1H), 4.68 (dd, *J* = 5.9, 2.5 Hz, 1H), 2.46 (s, 3H).

2.3 General procedure for alkenyl triflates 2 synthesis: 2v as an example

According to a procedure by Occhiato *et al*[3], to a solution of tert-butyl 2-oxopiperidine-1-carboxylate (2.0 g, 10.1 mmol), HMPA (2.62 mL) in THF (20 mL), cooled at -78℃ and under nitrogen atmosphere, was added a solution of LiHMDS (18 mL of a 1 M solution in toluene, 18 mmol) in THF (20 mL), and the resulting mixture was stirred at -78℃for 1.5 h. Afterward, a solution of $PhNTf_2$ (3.88 g, 10.9 mmol) in THF (5 mL) was quickly added, leaving under stirring for 2 h at -78℃. before allowing the temperature to rise to 0 ℃. Then, a 10% NaOH solution (20 mL) was added, the mixture was extracted with Et_2O (2*100 mL), and dried (K_2CO_3). After filtration and evaporation of the solvent, crude vinyl triflate **2v** was obtained as a yellowish oil and purified by flash chromatography (petroleum ether, 1.33g, 40%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.22 (t, J = 3.9 Hz, 1H), 3.56 – 3.49 (m, 2H), 2.19 (m, 2H), 1.73 – 1.64 (m, 2H), 1.42 (s, 9H). **GCMS:** calculated m/z for $C_{18}H_{19}N$: 331, found: 331.

(*1S,4R*)-bicyclo[2.2.1]hept-2-en-2-yl trifluoromethanesulfonate (2o) [4] The reaction of (*1S,4R*)-bicyclo[2.2.1]heptan-2-one (2.09 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl)sulfonyl)methanesulfonamide as outlined in the general procedure provided the title compound (4.05 g, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) ^{1}H δ 6.24 – 5.12 (m, 1H), 2.98 (dh, *J* = 4.8, 1.6 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.66 (dp, *J* = 8.5, 2.2 Hz, 1H), 1.49 – 1.34 (m, 1H), 1.30 – 1.07 (m, 2H).

(*1R,5S*)-8-methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl trifluoromethanesulfonate (2p) [4] The reaction of (1 (*1R,5S*)-8-methyl-8-azabicyclo [3.2.1]octan-3- one (3.96 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl) sulfonyl) methane sulfonamide as outlined in the general procedure provided the title compound (4.05 g, 57%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.84 (dt, *J* = 5.6, 1.4 Hz, 1H), 3.67 – 3.33 (m, 2H), 2.92 – 2.72 (m, 1H), 2.41 (s, 3H), 2.27 – 2.14 (m, 1H), 2.07 (tt, *J* = 11.6, 6.0 Hz, 1H), 1.98 – 1.88 (m, 2H), 1.69 – 1.58 (m, 1H).

(*1R,5S*)-9-methyl-9-azabicyclo[3.3.1]non-2-en-3-yl trifluoromethanesulfonate (2q) [4] The reaction of (*1R,5S*)-9-methyl-9-azabicyclo[3.3.1]nonan-3-one (2.91 g, 19.02

mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl)sulfonyl)methane sulfonamide as outlined in the general procedure provided the title compound (2.90 g, 27 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.69 (dt, *J* = 5.4, 1.7 Hz, 1H), 3.47 (ddd, *J* = 5.6, 4.0, 2.2 Hz, 1H), 3.20 (ddd, *J* = 7.0, 4.6, 2.1 Hz, 1H), 2.74 (dd, *J* = 18.2, 7.2 Hz, 1H), 2.38 (s, 3H), 2.00 (dd, *J* = 18.2, 1.4 Hz, 1H), 1.86 (tdd, *J* = 14.4, 13.2, 7.2, 4.0 Hz, 2H), 1.67 – 1.47 (m, 4H).

1H-isochromen-3-yl trifluoromethanesulfonate (2t)[5] The reaction of isochroman-3-one (2.81 g, 19.02 mmol) with 1,1,1-trifluoro-N-phenyl-N-((trifluoromethyl) sulfonyl)methanesulfonamide as outlined in the general procedure provided the title compound (2.60 g, 50 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.2 (m, 4H), 5.81 (s, 1H), 5.37 (s, 2H).

(1H-isochromen-3-yl)diphenylphosphine oxide (2u) The synthesis of 2u was as the same as the synthesis of alkenlyl triflates except adding diphenylphosphinic chloride instead of $PhNTf_2$. The reaction of isochroman-3-one (2.81 g, 19.02 mmol) with diphenylphosphinic chloride as outlined in the general procedure provided the title compound (2.40 g, 38 %). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42 – 7.31 (m, 2H), 7.29–7.14 (m, 8H), 7.00–6.89 (m, 3H), 6.87–6.78 (m, 2H), 5.35 (s, 2H). **GCMS:** calculated m/z for $C_{21}H_{17}O_3P$: 348, found: 348.

2.4 General procedure for aryl tosylates 4 synthesis

According to a procedure by Goo ßen *et al*[6], a solution of tosyl chloride (11.5 g, 120.0 mmol) in CH_2Cl_2 (100.0 mL) was added dropwise to a solution of appropriate phenol (100.0 mmol) and DABCO (22.4 g, 200.0 mmol) in anhydrous CH_2Cl_2 (200 mL) at 0 ℃. After complete addition, the mixture was warmed to room temperature and allowed to stir until completion following the reaction by TLC. The mixture was then diluted with Et_2O (200 mL), quenched with 10 % aq. HCl and washed successively with aqueous solution of $NaHCO_3$ and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure to give a solid. Recrystallization from chloroform-hexane gave the corresponding aryl tosylates.

4-acetylphenyl 4-methylbenzenesulfonate (4a) The reaction of 1-(4-hydroxyphenyl)ethanone (13.6 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.3 g, 94%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.68 – 7.61 (m, 2H), 7.29 – 7.21 (m, 2H), 7.05 – 6.98 (m, 2H), 2.50 (s, 3H), 2.38 (s, 3H).

4-(trifluoromethyl)phenyl 4-methylbenzenesulfonate (4b) The reaction of 4-(trifluoromethyl)phenol (16.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (16.4 g, 52%). **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.68 (m, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.17 – 7.08 (m, 2H), 2.46 (s, 3H).

4-(methylsulfonyl)phenyl 4-methylbenzenesulfonate (4c) The reaction of 4-(methylsulfonyl)phenol (17.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.1 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 2H), 7.77 – 7.70 (m, 2H), 7.39 – 7.32 (m, 2H), 7.25 – 7.18 (m, 2H), 3.05 (s, 3H), 2.47 (s, 3H).

4-cyanophenyl 4-methylbenzenesulfonate (4d) The reaction of 4-4-hydroxybenzonitrile (17.2 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.1 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.58 – 7.50 (m, 2H), 7.31 – 7.23 (m, 2H), 7.10 – 7.02 (m, 2H), 2.39 (s, 3H).

ethyl 4-(tosyloxy)benzoate (4e) The reaction of ethyl 4-hydroxybenzoate (16.6 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.8 g, 87%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.66 – 7.59 (m, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.94 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 2.37 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

4-benzoylphenyl 4-methylbenzenesulfonate (4f) The reaction of (4-hydroxyphenyl)(phenyl)methanone (19.8 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (24.3 g, 70%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 6H), 7.57 – 7.48 (m, 1H), 7.45 – 7.36 (m, 2H), 7.30 – 7.22 (m, 2H), 7.08 – 7.00 (m, 2H), 2.38 (s, 3H).

3-methoxyphenyl 4-methylbenzenesulfonate (4g) The reaction of 3-methoxyphenol (12.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (22.1 g, 79%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 – 7.61 (m, 2H), 7.27 – 7.20 (m, 2H), 7.13 – 7.03 (m, 1H), 6.71 (ddd, *J* = 8.4, 2.4, 1.1 Hz, 1H), 6.52 – 6.43 (m, 2H), 3.65 (s, 3H), 2.37 (s, 3H).

naphthalen-2-yl 4-methylbenzenesulfonate (4k) The reaction of naphthalen-2-ol (14.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (26.2 g, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 1H), 7.78 – 7.69 (m, 4H), 7.52 – 7.45 (m, 3H), 7.33 – 7.27 (m, 2H), 7.09 (dd, *J* = 8.9, 2.4 Hz, 1H), 2.44 (s, 3H).

naphthalen-1-yl 4-methylbenzenesulfonate (4l) The reaction of naphthalen-1-ol (14.4 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (27.3 g, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.90 (ddd, *J* = 8.1, 1.7, 0.8 Hz, 1H), 7.84 – 7.69 (m, 4H), 7.51 – 7.39 (m, 2H), 7.39 – 7.31 (m, 1H), 7.31 – 7.24 (m, 2H), 7.20 (dd, *J* = 7.6, 1.1 Hz, 1H), 2.41 (s, 3H).

quinolin-8-yl 4-methylbenzenesulfonate (4m) The reaction of quinolin-8-ol (14.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (24.5 g, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.06 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.86 – 7.76 (m, 2H), 7.67 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.51 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.32 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.22 – 7.16 (m, 2H), 2.34 (s, 3H).

pyridin-2-yl 4-methylbenzenesulfonate (4n) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (ddd, J = 4.9, 2.1, 0.8 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.78 – 7.64 (m, 1H), 7.30 – 7.23 (m, 2H), 7.14 (ddd, J = 7.3, 4.9, 1.0 Hz, 1H), 7.04 (dt, J = 8.1, 0.9 Hz, 1H), 2.37 (s, 3H).

pyridin-3-yl 4-methylbenzenesulfonate (4o) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%).

pyridin-4-yl 4-methylbenzenesulfonate (4p) The reaction of pyridin-2-ol (9.5 g, 100.0 mmol) with p-Toluenesulfonic anhydride as outlined in the general procedure provided the title compound (20.2 g, 81%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 – 8.54 (m, 2H), 7.79 – 7.71 (m, 2H), 7.38 – 7.31 (m, 2H), 7.06 – 6.99 (m, 2H), 2.46 (s, 3H).

2.5 General procedure for aryl triflates 4 synthesis

According to a procedure by Goossen *et al.* [7], a flame-dried flask was successively charged with appropriate phenol (10.6 mmol, 1.00 equiv), CH_2Cl_2 (10 mL), and pyridine (1.80 mL, 1.68 g, 21.3 mmol, 2.00 equiv) at 0 ℃. After dropwise addition of a solution of triflic anhydride (2.15 mL, 3.61 g, 12.8mmol, 1.20 equiv) in CH_2Cl_2 (5 mL), the reaction mixture was stirred at room temperature for 1.5 h and quenched with the addition of Et_2O (15 mL) and aqueous HCl (10%, 5 mL). The reaction mixture was washed successively with aqueous saturated $NaHCO_3$ (10 mL) and brine (10 mL). Drying over $MgSO_4$, evaporation of the solvents under reduced pressure and purification by flash column chromatography afforded the desired product.

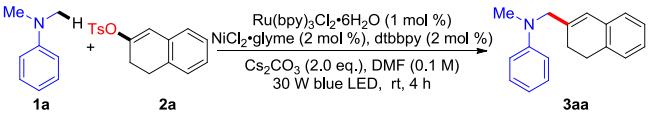
4-fluorophenyl trifluoromethanesulfonate (4h) The reaction of 4-fluorophenol (1.19 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (1.60 g, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.23 – 7.15 (m, 2H).

[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (4i) The reaction of [1,1'-biphenyl]-4-ol (1.80 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (1.57 g, 49%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.58 – 7.53 (m, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.32 (m, 3H).

phenyl trifluoromethanesulfonate (4j) The reaction of phenol (1.00 g, 10.6 mmol) with triflic anhydride as outlined in the general procedure provided the title compound as colorless oil (0.73 g, 30%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.41 – 7.36 (m, 1H), 7.32 – 7.24 (m, 2H).

Screening reaction conditions and Characterization of Products.

Table SI1 Screening reaction conditions

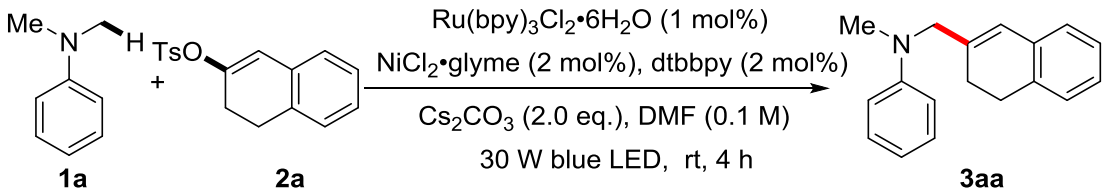


1a 2a 3aa

entry	variation from the standard conditions	yield (%)[b]
1	none	88
2	$Ru(bpy)_3Cl_2$ as photocatalyst	83
3	$Ru(bpy)_3(PF_6)_2$ as photocatalyst	87
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)(PF_6)$ as photocatalyst	trace
5	$Ni(cod)_2$ as Ni catalyst	87
6	no light	N.D.
7	no photocatalyst	N.D.
8	no Ni catalyst	N.D.
9	no base	trace

[a] 1a (0.9 mmol), 2a (0.3 mmol). [b] Isolated yield. bpy = 2,2'-bipyridine, dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyrididyl, cod = 1,5-cyclooctadiene, LED = light-emitting diode. N.D. = Not detected.

General procedure for the synthesis of 3

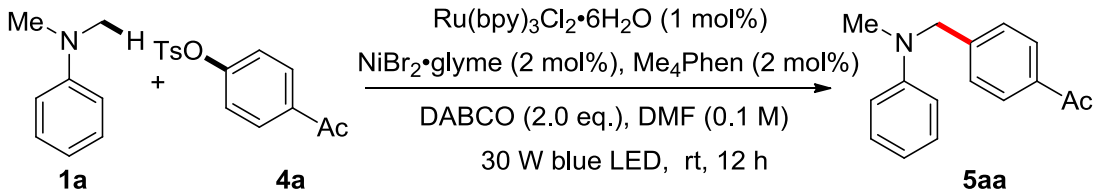


1a 2a 3aa

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ru(bpy)_3Cl_2$ $6H_2O$ (0.003 mmol), **2a** (0.3 mmol) and dtbbpy (0.006 mmol). The tube was evacuated and filled N_2 for three times before being transferred into a glovebox. $NiCl_2$ glyme (0.006 mmol) and Cs_2CO_3 (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at

room temperature for 4 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 500:1 to 300:1) to provide the pure product **3aa** as a pale yellow oil in 88% yield (65.7 mg, 0.264 mmol).

General procedure for the synthesis of 5



To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ru(bpy)_3Cl_2$ $6H_2O$ (0.003 mmol), **4a** (0.3 mmol). The tube was evacuated and filled N_2 for three times before being transferred into a glovebox. $NiBr_2$ glyme (0.006 mmol), Me_4Phen (0.006 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product **5aa** as a pale white solid in 78% yield (56.2 mg, 0.235 mmol).

General procedure for the synthesis of 5ma

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ir[dF(CF_3)ppy]_2(dtbbpy)(PF_6)$ (0.003 mmol, 0.01 equiv.), **4a** (0.3 mmol, 1.0 equiv.). The tube was evacuated and filled N_2 for three times before being transferred into a glovebox. $NiBr_2$ glyme (0.015 mmol, 0.05 equiv.), Me_4Phen (0.015 mmol, 0.05 equiv.) was added to the tube before transferring out of the glovebox and placing

under an atmosphere of N_2. Dry DMSO (3.0 mL) were added to the tube, followed by **3m** (0.9 mmol, 3.0 equiv.) and 3-acetoxyquinuclidine (0.33 mmol, 1.1 equiv.). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 24 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 20:1 to 10:1) to provide the pure product **5aa** as a pale white solid in 72% yield (62.3 mg, 0.215 mmol).

General procedure for the synthesis of 5na

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ir[dF(CF_3)ppy]_2(dtbbpy)(PF_6)$ (0.003 mmol, 0.01 equiv.), **4a** (0.3 mmol, 1.0 equiv.). The tube was evacuated and filled N_2 for three times before being transferred into a glovebox. $NiBr_2$·glyme (0.015 mmol, 0.05 equiv.), Me_4Phen (0.015 mmol, 0.05 equiv.) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMSO (3.0 mL) were added to the tube, followed by **3n** (3.0 mmol, 10.0 equiv.) and 3-acetoxyquinuclidine (0.33 mmol, 1.1 equiv.). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 36 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 20:1 to 15:1) to provide the pure product **5aa** as a pale white solid in 59% yield (33.5 mg, 0.176 mmol).

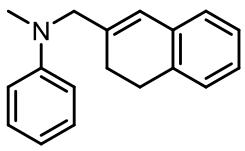
Tips:

1, Get rid of heat with fans.

2, Avoid other light source irradiation.

3, For the reaction of **2n**, **4a** in gram scale, the reaction mixture was degassed by purging nitrogen (30 min).

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3aa)



65.7 mg, 0.264 mmol, 88 %;

Yellow oil;

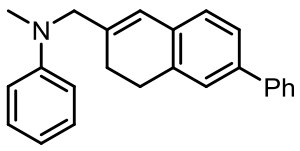
R$_f$ (PE:EA=50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.8, 7.3 Hz, 2H), 7.08 – 6.96 (m, 3H), 6.88 (d, *J* = 6.4 Hz, 1H), 6.76 – 6.47 (m, 3H), 6.21 (s, 1H), 3.89 (s, 2H), 2.90 (s, 3H), 2.75 (t, *J* = 8.2 Hz, 2 H), 2.15 (t, *J* = 8.2 Hz, 2 H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.90, 137.92, 134.79, 134.27, 129.12, 127.27, 126.58, 126.49, 125.84, 122.72, 116.39, 112.27, 58.27, 38.21, 27.93, 25.16;

ESI-MS: calculated m/z for $[C_{18}H_{20}N]^+$: 250.1, found: 250.1.

N-methyl-N-((6-phenyl-3,4-dihydronaphthalen-2-yl)methyl)aniline (3ab)



80.9 mg, 0.249 mmol, 83%;

Colorless oil;

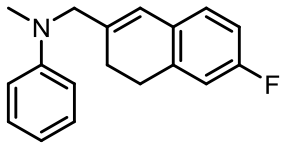
R$_f$ (PE:EA=50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 2H), 7.37 (m, 5H), 7.27 – 7.20 (m, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.82 – 6.67 (m, 3H), 6.35 (t, *J* = 1.8 Hz, 1H), 4.02 (s, 2H), 3.01 (s, 3H), 2.97 – 2.87 (t, *J* = 8.1 Hz, 2H), 2.37 – 2.20 (t, *J* = 8.1 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.80, 140.07, 138.36, 137.12, 134.17, 132.39, 128.08, 127.65, 125.97, 125.83, 125.16, 125.08, 124.16, 121.26, 115.34, 111.19, 57.24, 37.20, 27.07, 24.17;

Exact Mass ESI-MS: calculated m/z for $[C_{24}H_{23}N+H]^+$: 326.1903, found: 326.1909.

N-((6-fluoro-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ac)



63.1 mg, 0.236 mmol, 79%;

Yellow oil;

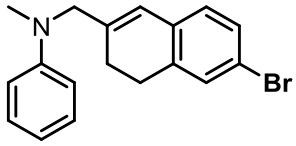
R$_f$ (PE:EA=50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.05 (m, 2H), 6.81 (m, 1H), 6.77 – 6.52 (m, 5H), 6.17 (t, *J* = 1.7 Hz, 1H), 3.88 (s, 2H), 2.89 (s, 3H), 2.72 (t, *J* = 8.1 Hz, 2H), 2.21 – 2.03 (t, *J* = 8.1 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.44 (d, *J* = 245.2 Hz), 148.74 , 136.01 (d, *J* = 7.5 Hz), 135.86 (d, *J* = 2.5 Hz), 129.32 (d, *J* = 3.0 Hz), 128.07 , 125.89 (d, *J* = 8.1 Hz), 120.58 , 115.36 , 113.37 (d, *J* = 21.7 Hz), 111.76 (d, *J* = 21.3 Hz), 111.15 , 57.06 , 37.16 , 27.03 (d, *J* = 1.8 Hz), 23.61;

ESI-MS: calculated m/z for $[C_{18}H_{18}FN+H]^+$: 268.15, found: 268.10.

N-((6-bromo-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ad)



69.9 mg, 0.213 mmol, 71%;

White solid;

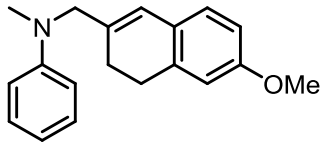
R$_f$ (PE:EA=50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (m, 4H), 6.76 – 6.56 (m, 4H), 6.15 (t, *J* = 1.7 Hz, , 1H), 3.86 (s, 2H), 2.89 (s, 3H), 2.70 (t, *J* = 8.1 Hz, 2H), 2.11 (t, *J* = 8.2 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.72, 137.58, 135.84, 132.14, 129.14, 128.35, 128.11, 126.16, 120.70, 118.74, 115.47, 111.19, 57.18, 37.27, 26.66, 23.82;

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{18}BrN+H]^+$: 328.0695 (100 %), 330.0675 (98 %), found: 328.0625.

N-((6-methoxy-3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ae)



60.9 mg, 0.219 mmol, 73%;

colorless oil;

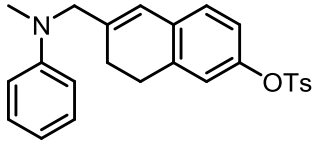
R$_f$ (PE:EA=50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (m, 2H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.82 – 6.61 (m, 5H), 6.25 (t, *J* = 1.6 Hz, 1H), 3.97 (d, *J* = 1.6 Hz, 2H), 3.78 (s, 3H), 2.98 (s, 3H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.21 (t, *J* = 8.1 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.45, 149.96, 136.52, 135.09, 129.12, 127.46, 126.77, 122.20, 116.31, 113.65, 112.28, 111.10, 58.23, 55.31, 38.14, 28.44, 24.99;

Exact Mass ESI-MS: calculated m/z for $[C_{19}H_{21}NO+H]^+$: 280.1696, found: 280.1701.

6-((methyl(phenyl)amino)methyl)-7,8-dihydronaphthalen-2-yl 4-methylbenzene sulfonate (3af)



71.7 mg, 0.171 mmol, 57 %;

White solid;

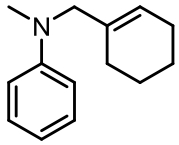
$\mathbf{R}_f$ (PE:EA=10:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 2H), 7.33 – 7.16 (m, 4H), 6.88 – 6.78 (m, 2H), 6.77 – 6.66 (m, 3H), 6.60 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.22 (t, *J* = 1.7 Hz, 1H), 3.96 (s, 2H), 2.97 (s, 3H), 2.76 (t, *J* = 8.2 Hz, 2H), 2.43 (s, 3H), 2.20 (t, *J* = 8.2 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.70, 147.86, 145.25, 138.78, 136.53, 133.27, 132.58, 129.73, 129.16, 128.53, 126.47, 121.45, 121.42, 119.96, 116.48, 112.17, 58.14, 38.37, 27.83, 24.68, 21.75;

Exact Mass ESI-MS: calculated m/z for $[C_{25}H_{25}NO_3S+Na]^+$: 442.1447, found: 442.1452.

N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (3ag)



51.3 mg, 0.255 mmol, 85 %;

Colorless oil;

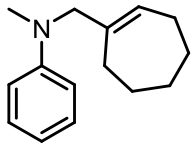
$\mathbf{R}_f$ (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 2H), 6.80 – 6.24 (m, 3H), 5.43 (t, *J* = 3.5, 1H), 3.65 (s, 2H), 2.82 (s, 3H), 2.05 – 1.66 (m, 4H), 1.52 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.06, 134.01, 129.02, 122.20, 115.89, 112.07 , 58.98, 37.98, 26.44, 25.01, 22.73, 22.68;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{19}N+H]^+$: 202.1590, found: 202.1596.

N-(cyclohept-1-en-1-ylmethyl)-N-methylaniline (3ah)



46.0 mg, 0.213 mmol, 71 %;

Colorless oil;

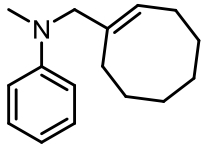
$\mathbf{R}_f$ (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 6.68 (m, 3H), 5.61 (t, *J* = 6.3 Hz, 1H), 3.74 (s, 2H), 2.90 (s, 3H), 2.08 (m, 4H), 1.78 – 1.70 (m, 2H), 1.48 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.92, 138.73, 127.95, 125.64, 114.85, 110.98, 58.86, 36.62, 31.45, 29.43, 27.07, 26.21, 25.58;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{21}N+H]^+$: 216.1747, found: 216.1752.

(E)-N-(cyclooct-1-en-1-ylmethyl)-N-methylaniline (3ai)



48.8 mg, 0.213 mmol, 71 %;

Colorless oil;

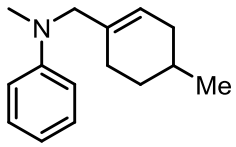
R$_f$ (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.10 (m, 2H), 6.60 (m, 3H), 5.33 (t, *J* = 8.2 Hz, 1H), 3.72 (s, 2H), 2.84 (s, 3H), 2.13 – 1.98 (m, 4H), 1.49 – 1.36 (m, 8H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.92, 136.43, 129.04, 124.36, 115.78, 111.81, 58.17, 38.00, 29.81, 28.77, 27.13, 26.52, 26.49, 25.9;

ESI-MS: calculated m/z for $[C_{16}H_{23}N+H]^+$: 230.19, found: 230.12.

N-methyl-N-((4-methylcyclohex-1-en-1-yl)methyl)aniline (3aj)



47.1 mg, 0.219 mmol, 73%;

Colorless oil;

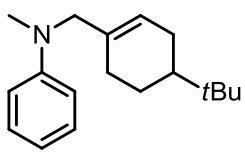
Rf (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.06 (m, 2H), 6.79 – 6.49 (m, 3H), 5.47 (m, 1H), 3.74 (s, 2H), 2.89 (s, 3H), 2.20 – 1.86 (m, 3H), 1.78 – 1.56 (m, 3H), 1.36 – 1.12 (m, 1H), 0.94 (d, *J* = 6.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.01, 133.66, 129.00, 121.81, 115.85, 112.03, 58.71, 37.96, 33.57, 30.92, 28.64, 26.48, 21.76;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{21}N+H]^+$: 216.1747, found: 216.1752.

N-((4-(tert-butyl)cyclohex-1-en-1-yl)methyl)-N-methylaniline (3ak)



53.5 mg, 0.207 mmol, 69%;

colorless oil;

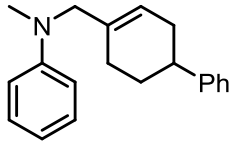
$\mathbf{R}_f$ (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.03 (m, 2H), 6.84 – 6.59 (m, 3H), 5.51 (m, 1H), 3.93 – 3.60 (m, 2H), 2.90 (s, 3H), 2.08 – 1.90 (m, 3H), 1.88 – 1.67 (m, 2H), 1.32 – 1.09 (m, 2H), 0.86 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.00, 133.80, 129.00, 122.44, 115.83, 112.02, 77.36, 58.52, 44.32, 37.97, 32.25, 27.88, 27.27, 26.56, 24.00.

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{27}N+H]^+$:258.2216; found:258.2218.

N-methyl-N-((1,2,3,6-tetrahydro-[1,1'-biphenyl]-4-yl)methyl)aniline (3al)



61.6 mg, 0.222 mmol, 74%;

Colorless oil;

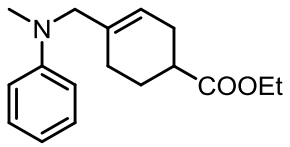
Rf (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.07 (m, 7H), 6.74 – 6.54 (m, 3H), 5.52 (dt, *J* = 5.2, 1.8 Hz, 1H), 3.71 (d, *J* = 2.2 Hz, 2H), 2.85 (s, 3H), 2.77 – 2.61 (m, 1H), 2.32 – 2.17 (m, 1H), 2.14 – 1.94 (m, 3H), 1.89 (m, 1H), 1.78 – 1.62 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.94, 147.04, 134.05, 129.11, 128.43, 126.97, 126.08, 121.79, 116.04, 112.10, 58.67, 40.31, 38.21, 33.21, 29.85, 27.03;

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{23}N+H]^+$: 278.1903, found: 278.1909.

ethyl 4-((methyl(phenyl)amino)methyl)cyclohex-3-enecarboxylate (3am)



63.9 mg, 0.234 mmol, 78%;

colorless oil;

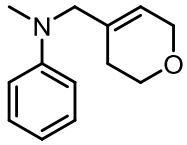
Rf (PE:EA=20:1): 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.08 (m, 2H), 6.71 – 6.51 (m, 3H), 5.44 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.75 – 3.59 (m, 2H), 2.82 (s, 3H), 2.51 – 2.36 (m, 1H), 2.18 (m, 2H), 2.05 – 1.81 (m, 3H), 1.73 – 1.54 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.76, 148.80, 132.80, 127.97, 119.29, 115.04, 111.04, 59.24, 57.49, 38.45, 36.95, 26.33, 24.59, 24.15, 13.21;

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{23}NO_2+H]^+$: 274.1802, found: 274.1807.

N-((3,6-dihydro-2H-pyran-4-yl)methyl)-N-methylaniline (3an)



51.1 mg, 0.252 mmol, 84%;

Colorless oil;

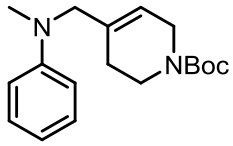
R$_f$ (PE:EA=10:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.12 (m, 2H), 6.83 – 6.59 (m, 3H), 5.52 (dt, *J* = 2.9, 1.3 Hz, 1H), 4.12 (q, *J* = 2.5 Hz, 2H), 3.99 – 3.70 (m, 4H), 2.93 (s, 3H), 2.03 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.62, 130.99, 128.03, 119.62, 115.23, 111.01, 64.32, 63.07, 57.01, 37.17, 25.48;

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{17}NO+H]^+$: 204.1383, found: 204.1383.

tert-butyl 4-((methyl(phenyl)amino) methyl)-5,6- dihydro pyridine-1(2H)-carboxylate (3ao)



81.5 mg, 0.270 mmol, 90%;

Colorless oil;

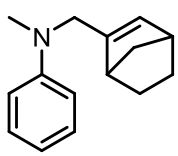
R$_f$ (PE:EA=10:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 8.9, 7.1 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 3H), 5.46 (s, 1H), 4.03 – 3.66 (m, 4H), 3.50 (t, *J* = 5.8 Hz, 2H), 2.92 (s, 3H), 2.03 (d, *J* = 6.4 Hz, 2H), 1.46 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.95, 149.67, 133.04, 129.11, 118.48, 116.33, 112.09, 79.56, 58.12, 42.86, 39.66, 38.24, 28.51, 26.38;

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{26}N_2O_2+H]^+$: 303.2067, found: 303.2073.

N-(bicyclo[2.2.1]hept-2-en-2-ylmethyl)-N-methylaniline (3ap)



47.9 mg, 0.225 mmol, 75 %;

colorless oil;

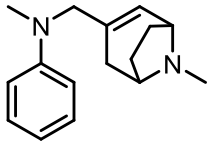
R$_f$ (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (m, 2H), 6.66 – 6.55 (m, 3H), 5.57 (s, 1H), 3.95 (dd, *J* = 17.1, 1.9 Hz, 1H), 3.76 (dd, *J* = 17.1, 1.6 Hz, 1H), 2.83 (s, 3H), 2.72 (m, 1H), 2.63 (s, 1H), 1.55 (m, 2H), 1.32 (m, 1H), 1.09 – 0.87 (m, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.78, 144.73, 129.22, 127.92, 114.94, 111.09, 50.86, 47.27, 42.31, 41.15, 37.03, 25.51, 23.40;

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{19}N+H]^+$: 214.1590, found: 214.1580.

N-methyl-N-((8-methyl-8-azabicyclo[3.2.1]oct-2-en-3-yl)methyl)aniline (3aq)



47.2 mg, 0.195 mmol, 65 %;

Colorless oil;

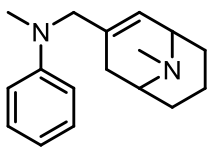
R$_f$ (EA:methol=0.3): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 2H), 6.77 – 6.60 (m, 3H), 5.65 (m, 1H), 3.78 – 3.68 (m, 2H), 3.36 – 3.21 (m, 2H), 2.91 (s, 3H), 2.46 (dd, *J* = 17.5, 4.4 Hz, 1H), 2.36 (s, 3H), 2.16 (m, 1H), 2.04 (m, 1H), 1.81 (m, 1H), 1.61 – 1.44 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.64, 129.94, 127.99, 124.53, 115.17, 111.08, 57.97, 56.74, 56.61, 37.21, 35.58, 32.54, 31.89, 28.45;

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{22}N_2+H]^+$: 243.1856, found: 243.1861.

N-methyl-N-((9-methyl-9-azabicyclo[3.3.1]non-3-en-3-yl)methyl)aniline (3ar)



47.6 mg, 0.186 mmol, 62 %;

colorless oil;

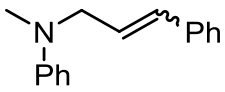
R$_f$ (EA:methol=0.3): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.15 (m, 2H), 6.71 (m, 3H), 5.45 (t, *J* = 5.2, 1H), 3.98 – 3.74 (m, 2H), 3.40 (d, J = 4.9 Hz, 1H), 3.21 (t, *J* = 5.9 Hz, 1H), 2.97 (s, 3H), 2.46 (s, 3H), 2.45 – 2.37 (m, 1H), 2.14 – 1.92 (m, 2H), 1.83 – 1.66 (m, 1H), 1.61 – 1.41 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.55, 135.11, 129.13, 120.05, 116.48, 112.13, 58.05, 55.11, 52.89, 41.08, 38.47, 31.95, 27.64, 26.69, 14.81;

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{25}N_2]^+$: 257.2012, found: 257.2002.

N-methyl-N-(3-phenylallyl)aniline (3as)



64.2 mg, 0.288 mmol, 96 %, (*E* : *Z* = 2.2 : 1);

colorless oil;

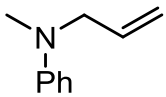
R$_f$ (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$, the major isomer) δ 7.45 – 6.80 (m, 7H), 6.75 – 6.56 (m, 3H), 6.56 – 5.54 (m, 2H), 4.06 (2H), 2.86 (3H);

^{13}C NMR (101 MHz, $CDCl_3$, the major isomer) δ 148.54, 135.87, 130.23, 128.14, 127.89, 127.48, 126.35, 125.27, 115.56, 111.60, 53.87, 36.98.

ESI-MS: calculated m/z for $[C_{16}H_{17}N]^+$: 224.14, found: 224.10.

N-allyl-N-methylaniline (3at)



21.6 mg, 0.147 mmol, 49 %;

colorless oil;

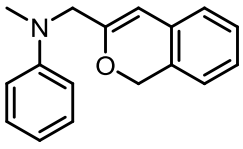
R$_f$ (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (m, 2H), 6.76 – 6.63 (m, 3H), 5.89 – 5.76 (m, 1H), 5.20 – 5.08 (m, 2H), 3.89 (dt, *J* = 5.4, 1.8 Hz, 2H), 2.91 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.55, 133.88, 129.15, 116.47, 116.18, 112.51, 55.32, 38.04;

Exact Mass ESI-MS: calculated m/z for $[C_{10}H_{13}N+H]^+$: 148.1121, found: 148.1126.

N-((1H-isochromen-3-yl)methyl)-N-methylaniline(3au)



30.6 mg, 0.122 mmol, 61 % (**2u**), (0.2 mmol scale);

37.7 mg, 0.100 mmol, 50 % (**2v**);

White solid;

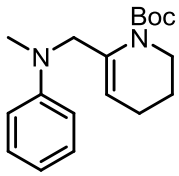
R$_f$ (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.20 (m, 2H), 7.14 (m, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.89 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.83 – 6.65 (m, 3H), 5.74 (d, *J* = 1.3 Hz, 1H), 5.08 (s, 2H), 3.98 (s, 2H), 3.04 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.41, 149.36, 131.28, 129.13, 128.17, 127.48, 126.20, 123.73, 122.91, 116.79, 112.45, 101.42, 68.88, 54.61, 38.69;

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{17}NO+H]^+$: 252.1383, found: 252.1388.

tert-butyl 6-((methyl(phenyl)amino)methyl)-3,4-dihydropyridine-1(2H) -carboxylate (3aw)



40.8 mg, 0.135 mmol, 45 % ;

Colorless oil;

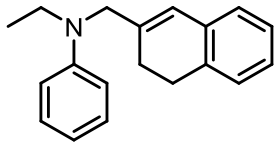
R$_f$ (PE:EA=10:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.89 – 6.51 (m, 3H), 5.08 (tt, *J* = 3.8, 1.5 Hz, 1H), 4.23 (m, 2H), 3.62 – 3.39 (m, 2H), 2.97 (s, 3H), 2.15 – 1.97 (m, 2H), 1.86 – 1.68 (m, 2H), 1.50 (s, 9H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.83, 148.30, 134.61, 127.94, 114.96, 110.96, 110.79, 79.70, 55.33, 43.73, 37.52, 27.37, 22.37, 21.72;

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{26}N_2O_2+H]^+$: 303.2067, found: 303.2073.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-ethylaniline (3ba)



59.1 mg, 0.225 mmol, 75%;

colorless oil;

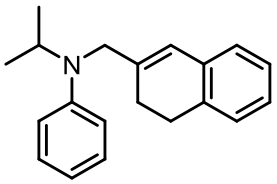
R$_f$ (PE:EA=100:1): 0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (td, *J* = 7.2, 1.9 Hz, 2H), 7.14 – 7.05 (m, 3H), 6.95 (dt, *J* = 6.5, 1.6 Hz, 1H), 6.76 – 6.61 (m, 3H), 6.29 (m, *J* = 1.6 Hz, 1H), 3.95 (s, 2H), 3.44 (q, *J* = 7.1 Hz, 2H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.25 (t, *J* = 8.2 Hz, 2H), 1.19 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.61, 137.94, 134.79, 134.38, 129.21, 127.28, 126.53, 126.51,125.87, 122.36, 115.92, 112.11, 55.53, 44.78, 28.01, 25.21, 12.04;

Exact Mass ESI-MS: calculated m/z for $[C_{19}H_{21}N+H]^+$: 264.1747, found: 264.1752.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-isopropylaniline (3ca)



62.3 mg, 0.225 mmol, 75%;

colorless oil;

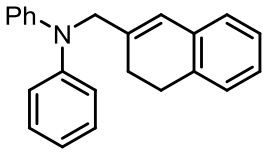
R$_f$ (PE:EA=100:1): 0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 6.95 (m, 5H), 6.93 – 6.80 (m, 1H), 6.72 – 6.56 (m, 3H), 6.29 (t, 1H), 4.12 (p, *J* = 6.6 Hz,1H), 3.73 (s, 2H), 2.79 (t, *J* = 8.1 Hz, 2H), 2.20 (t, *J* = 8.2 Hz, 2H), 1.13 (d, *J* = 6.6 Hz, 6H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.39 , 138.25 , 133.61, 128.03 , 126.16 , 125.43 , 125.27 , 124.71 , 121.03 , 115.20 , 111.99 , 49.09 , 46.80 , 27.04 , 24.21 , 18.64;

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{23}N+H]^+$: 278.1903, found: 278.1890.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-phenylaniline (3da)



60.7 mg, 0.195 mmol, 85 %;

colorless oil;

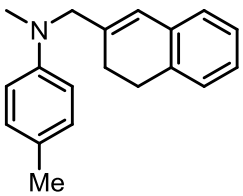
R$_f$ (PE:EA=100:1): 0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.21 (m, 5H), 7.10 – 7.03 (m, 6H), 6.94 (td, *J* = 7.3, 1.0 Hz, 3H), 6.45 (m, 1H), 4.45 (s, 2H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.28 (t, *J* = 8.1 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.14 , 137.82 , 134.70 ,134.26 , 129.35, 129.22 , 129.18, 127.22 , 126.56 , 126.45 , 125.90 , 123.03 , 121.31 , 120.67 , 57.75 , 27.89 , 25.20;

Exact Mass ESI-MS: calculated m/z for $[C_{23}H_{21}N+H]^+$: 312.1747, found: 312.1752.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N,4-dimethylaniline (3ea)



68.6 mg, 0.261 mmol, 87%;

colorless oil;

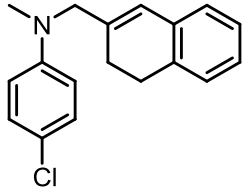
R_f (PE:EA=100:1): 0.4;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 6.86 (m, 6H), 6.60 (d, *J* = 8.6 Hz, 2H), 6.23 (t, *J* = 1.6 Hz, 1H), 3.86 (s, 2H), 2.87 (s, 3H), 2.75 (t, *J* = 8.2 Hz, 2H), 2.24 – 2.08 (m, 5H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.89, 137.20, 133.75, 133.26, 128.57, 126.20, 125.47, 125.41, 124.76, 124.55, 121.71, 111.52, 57.59, 37.27, 26.88, 24.11, 19.20;

Exact Mass ESI-MS: calculated m/z for $[C_{19}H_{21}N+H]^+$: 264.1747, found: 264.1752.

4-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3fa)



72.4 mg, 0.255 mmol, 85%;

colorless oil;

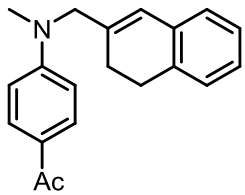
R_f (PE:EA=20:1): 0.8;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.04 (m, 5H), 7.02 – 6.91 (m, 1H), 6.57 (d, *J* = 9 Hz, 2H), 6.25 (t, *J* = 1.6 Hz, 1H), 3.96 (s, 2H), 2.98 (s, 3H), 2.83 (t, *J* = 8.2 Hz, 2H), 2.14(t, *J* = 8.2 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.33, 137.23,134.72, 134.07, 128.87, 127.31, 126.73, 126.54, 125.89, 122.88, 121.16, 113.33, 58.29, 38.56, 27.86, 25.13;

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{18}ClN+H]^+$: 284.1206, found: 284.1205.

1-(4-(((3,4-dihydronaphthalen-2-yl)methyl)(methyl)amino)phenyl)ethanone (3ga)



72.0 mg, 0.246 mmol, 82%;

White solid;

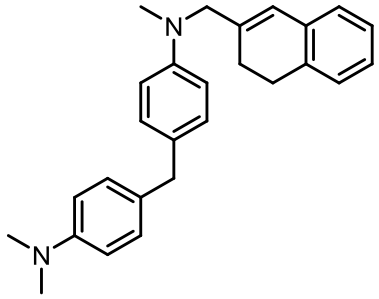
R_f (PE:EA=10:1): 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.76 (m, 2H), 7.21 – 7.05 (m, 3H), 6.95 (d, *J* = 4.6 Hz, 1H), 6.66 – 6.59 (m, 2H), 6.21 (t, *J* = 1.6 Hz, 1H), 4.09 (q, *J* = 1.3 Hz, 2H), 3.10 (s, 3H), 2.85 (t, *J* = 8.1 Hz, 2H), 2.50 (s, 3H), 2.23 (m, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.32, 152.94, 136.11, 134.62, 133.84, 130.61, 127.33, 126.89, 126.57, 125.97, 125.67, 122.98, 110.74, 57.44, 38.47, 27.79, 26.01, 25.09;

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{21}NO+H]^+$: 292.1696, found: 292.1692.

N-((3,4-dihydronaphthalen-2-yl)methyl)-4-(4-(dimethylamino)benzyl)-N-methylaniline (3ha)



73.2 mg, 0.192 mmol, 63%;

colorless oil;

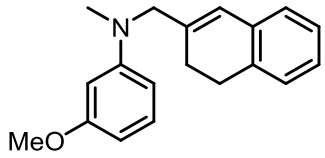
Rf (PE:EA=5:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 6.92 (m, 7H), 6.89 (dd, *J* = 6.6, 1.6 Hz, 1H), 6.65 – 6.57 (m, 4H), 6.22 (t, *J* = 1.6 Hz, 1H), 3.86 (s, 2H), 3.72 (s, 2H), 2.86 (s, 3H), 2.81 (s, 6H), 2.75 (t, *J* = 8.2 Hz, 2H), 2.15 (t, J = 8.2 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.08, 148.29,138.29 , 134.85 , 134.35, 130.42 , 130.03, 129.45, 127.28, 126.56, 126.49, 125.86 , 122.82, 113.12, 112.54, 58.60, 40.99, 39.93, 38.30 , 27.97, 25.19;

ESI-MS: calculated m/z for $[C_{27}H_{30}N_2+H]^+$: 383.2, found: 383.1.

N-((3,4-dihydronaphthalen-2-yl)methyl)-3-methoxy-N-methylaniline (3ia)



68.6 mg, 0.246 mmol, 82 %;

colorless oil;

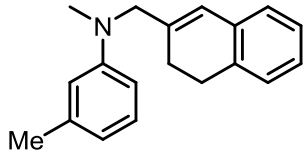
Rf (PE): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 6.99 (m, 4H), 6.90 (d, *J* = 6.4 Hz, 1H), 6.33 – 6.16 (m, 4H), 3.91 (s, 2H), 3.71 (s, 3H), 2.91 (s, 3H), 2.76 (t, *J* = 8.1 Hz, 2H), 2.16 (t, *J* = 7.8 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.72, 151.26, 137.82, 134.79, 134.26, 129.80, 127.28, 126.60, 126.50, 125.86, 122.71, 105.46, 101.04, 98.83, 58.19, 55.13, 38.33, 27.93, 25.13;

Exact Mass ESI-MS: calculated m/z for $[C_{19}H_{21}NO+H]^+$: 280.1696, found: 280.1701.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N,3-dimethylaniline (3ja)



63.2 mg, 0.240 mmol, 80%;

colorless oil;

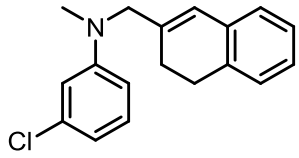
$\mathbf{R}_f$ (PE:EA=100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.05 (m, 4H), 6.97 (d, *J* = 6.4 Hz, 1H), 6.61 – 6.49 (m, 3H), 6.30 (t, *J* = 1.6 Hz, 1H), 3.96 (s, 2H), 2.96 (s, 3H), 2.83 (t, *J* = 8.1 Hz, 2H), 2.30 (s, 3H), 2.24 (t, *J* = 8.1 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.08, 138.81, 138.11, 134.84, 134.35, 129.02, 127.30, 126.59, 126.51, 125.88, 122.72, 117.44, 113.05, 109.61, 58.33, 38.18, 27.98, 25.21, 21.99;

Exact Mass ESI-MS: calculated m/z for $[C_{19}H_{21}N+H]^+$: 264.1747, found: 264.1752.

3-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ka)



67.2 mg, 0.237 mmol, 79%;

colorless oil;

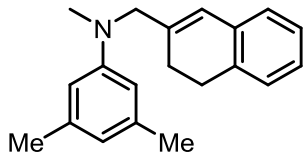
Rf (PE): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.04 (m, 4H), 7.01 – 6.92 (m, 1H), 6.72 – 6.62 (m, 2H), 6.58 (m, 1H), 6.24 (t, *J* = 1.6 Hz, 1H), 3.96 (s, 2H), 2.98 (s, 3H), 2.83 (t, *J* = 8.2 Hz, 2H), 2.21 (t, *J* = 8.7 Hz, 2H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.83 , 137.03 , 135.06 , 134.75 , 134.09 , 130.05 , 127.34 , 126.76 , 126.57 , 125.95 , 122.89 , 116.18 , 111.96 , 110.36 , 57.94 , 38.33 , 27.89 , 25.14;

ESI-MS: calculated m/z for $[C_{18}H_{17}NCl+H]^+$: 284.1, found: 284.0.

N-((3,4-dihydronaphthalen-2-yl)methyl)-N,3,5-trimethylaniline (3la)



69.8 mg, 0.252 mmol, 84%;

colorless oil;

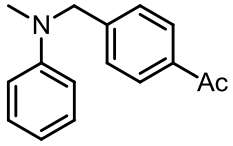
Rf (PE:EA=100:1): 0.6;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 – 6.98 (m, 3H), 6.90 (d, *J* = 6.8 Hz, 1H), 6.32 (s, 3H), 6.24 (t, *J* = 1.6 Hz, 1H), 3.87 (s, 2H), 2.87 (s, 3H), 2.77 (t, *J* = 8.2 Hz, 2H), 2.19 – 2.10 (m, 8H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.18, 137.62, 137.19, 133.79, 133.33, 126.21, 125.47, 125.43, 124.79, 121.55, 117.51, 109.26, 57.26, 37.04, 26.91, 24.14, 20.77;

Exact Mass ESI-MS: calculated m/z for $[C_{20}H_{23}N+H]^+$: 278.1903, found: 278.1909.

1-(4-((methyl(phenyl)amino)methyl)phenyl)ethanone (5aa)



56.2 mg, 0.235 mmol, 78%;

White solid;

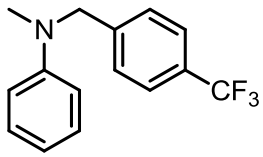
R$_f$ (PE:EA = 20:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.41 – 7.29 (m, 2H), 7.29 – 7.14 (m, 2H), 6.72 (dt, *J* = 7.7, 1.0 Hz, 3H), 4.58 (s, 2H), 3.04 (s, 3H), 2.58 (s, 3H).

^{13}C NMR (101 MHz,) δ 197.76, 149.42, 144.93, 136.06, 129.27, 128.76, 126.83, 116.94, 112.40, 56.65, 38.79, 26.63.

Exact Mass ESI-MS: calculated m/z for $[C_{16}H_{17}NO+H]^+$: 240.1388, found: 240.1376.

N-methyl-N-(4-(trifluoromethyl)benzyl)aniline (5ab)



64.5 mg, 0.243 mmol, 81%;

Yellow solid;

R$_f$ (PE): 0.5;

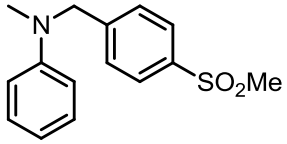
^{1}H NMR (400 MHz, $CHCl_3$) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.18 (m, 2H), 6.78 – 6.66 (m, 3H), 4.58 (s, 2H), 3.03 (s, 3H).

^{13}C NMR (101 MHz, $CHCl_3$) δ 149.40, 143.37, 129.29, 129.26 (q, *J* = 32.3 Hz), 126.94, 125.55 (q, *J* = 3.8 Hz), 124.24(q, *J* = 272.2 Hz), 117.02, 112.41, 56.49, 38.72.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.35.

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{15}F_3N]^+$:266.1151, found:266.1153.

N-methyl-N-(4-(methylsulfonyl)benzyl)aniline (5ac)



77.5 mg, 0.281 mmol, 94%;

Colorless oil;

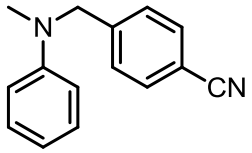
$\mathbf{R}_f$ (PE:EA = 1:1): 0.8;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 2H), 7.43 – 7.30 (m, 2H), 7.24 – 7.08 (m, 2H), 6.78 – 6.53 (m, 3H), 4.53 (s, 2H), 2.98 (s, 3H), 2.96 (s, 3H).

^{13}C NMR (101 MHz,) δ 148.15, 144.96, 138.11, 128.28, 126.72, 126.50, 116.16, 111.37, 55.50, 43.50, 37.85.

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{17}NO_2S+H]^+$: 276.1058, found: 276.1056.

4-((methyl(phenyl)amino)methyl)benzonitrile (5ad)



57.9 mg, 0.261 mmol, 87%;

Yellow oil;

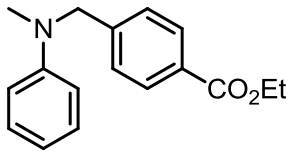
$\mathbf{R}_f$ (PE:EA=20:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.35– 7.20 m, 4H), 6.80 – 6.65 (m, 3H), 4.57 (s, 2H), 3.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.21, 145.02, 132.49, 129.35, 127.37, 118.93, 117.25, 112.43, 110.82, 56.67, 38.88.

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{14}N_2+H]^+$: 223.1235, found: 223.1229.

ethyl 4-((methyl(phenyl)amino)methyl)benzoate (5ae)



70.7 mg, 0.264 mmol, 88%;

Yellow oil;

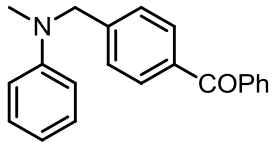
$\mathbf{R}_f$ (PE:EA=20:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.92 (m, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.25 – 7.19 (m, 2H), 6.77 – 6.68 (m, 3H), 4.57 (s, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.03 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.51, 149.48, 144.53, 129.91, 129.27, 129.25, 126.61, 116.89, 112.42, 60.89, 56.68, 38.73, 14.36.

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{19}NO_2+H]^+$: 270.1494, found: 270.1481.

(4-((methyl(phenyl)amino)methyl)phenyl)(phenyl)methanone (5af)



63.2 mg, 0.210 mmol, 70%;

Pale yellow oil;

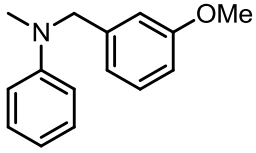
$\mathbf{R}_f$ (PE:EA = 20:1): 0.1;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (td, *J* = 8.2, 1.6 Hz, 4H), 7.56 – 7.44 (m, 1H), 7.45 – 7.32 (m, 2H), 7.26 (m, 2H), 7.20 – 7.06 (m, 2H), 6.77 – 6.54 (m, 3H), 4.52 (s, 2H), 2.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.28, 148.38, 143.21, 136.64, 135.27, 131.28, 129.50, 128.93, 128.21, 127.20, 125.49, 115.84, 111.34, 55.58, 37.73.

Exact Mass ESI-MS: calculated m/z for $[C_{21}H_{19}NO+H]^+$: 302.1545, found: 302.1545.

N-(3-methoxybenzyl)-N-methylaniline (5ag)



36.1 mg, 0.159 mmol, 53%;

Colorless oil;

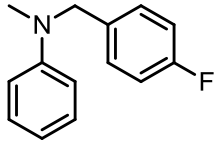
$\mathbf{R}_f$ (PE:EA = 100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.14 (m, 3H), 6.89 – 6.61 (m, 6H), 4.49 (s, 2H), 3.75 (s, 3H), 3.00 (s, 3H).

^{13}C NMR (101 MHz,) δ 159.96, 149.81, 140.93, 129.61, 129.18, 119.05, 116.60, 112.43, 112.40, 112.12, 56.72, 55.19, 38.57.

Exact Mass ESI-MS: calculated m/z for $[C_{15}H_{17}NO+H]^+$: 228.1388, found: 228.1374.

N-(4-fluorobenzyl)-N-methylaniline (5ah)



31.0 mg, 0.144 mmol, 48%;

Yellow oil;

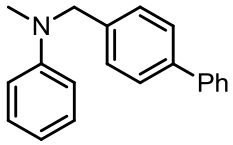
$\mathbf{R}_f$ (PE:EA = 100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.13 (m, 4H), 7.04 – 6.94 (m, 2H), 6.73 (m, 3H), 4.48 (d, *J* = 1.1 Hz, 2H), 2.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.90 (*J* = 152 Hz), 149.63, 134.61, 129.23, 128.27 (*J* = 5 Hz), 116.80, 115.39 (*J* = 13 Hz), 112.51, 56.09, 38.47.

LRMS: calculated m/z for $[C_{14}H_{14}FN+H]^+$: 216.12, found: 216.15.

N-([1,1'-biphenyl]-4-ylmethyl)-N-methylaniline (5ai)



41.4 mg, 0.151 mmol, 75%;

White solid;

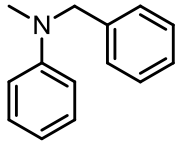
R$_f$ (PE:EA = 20:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 4H), 7.49 – 7.40 (m, 2H), 7.38 – 7.21 (m, 5H), 6.88 – 6.64 (m, 3H), 4.59 (d, *J* = 6.5 Hz, 2H), 3.13 – 3.00 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.76, 140.95, 139.90, 138.15, 129.25, 128.78, 127.35, 127.20, 127.07, 121.66, 116.61, 112.42, 56.42, 38.60.

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{17}N+H]^+$: 248.1439, found: 248.1432.

N-benzyl-N-methylaniline (5aj)



39.6 mg, 0.202 mmol, 67 %;

Yellow oil;

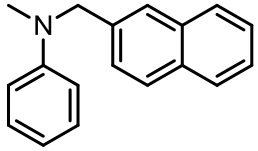
R$_f$ (PE:EA): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (m, 2H), 7.27 – 7.15 (m, 5H), 6.81 – 6.66 (m, 3H), 4.53 (s, 2H), 3.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.82, 139.10, 129.26, 128.63, 126.93, 126.82, 116.62, 112.45, 56.71, 38.58.

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{15}N+H]^+$: 198.1283, found: 198.1279.

N-methyl-N-(naphthalen-2-ylmethyl)aniline (5ak)



60.0 mg, 0.243 mmol, 81%;

Yellow solid;

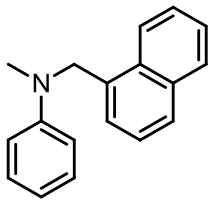
R$_f$ (PE): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.74 (m, 3H), 7.67 (s, 1H), 7.49 – 7.34 (m, 3H), 7.26 – 7.20 (m, 2H), 6.86 – 6.69 (m, 3H), 4.68 (s, 2H), 3.06 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.90, 136.62, 133.53, 132.70, 129.24, 128.36, 127.73, 127.70, 126.10, 125.56, 125.21, 125.13, 116.67, 112.49, 57.01, 38.54.

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{17}N+H]^+$: 248.1439, found: 248.1432.

N-methyl-N-(naphthalen-1-ylmethyl)aniline (5al)



48.8 mg, 0.198 mmol, 66%;

Pale yellow oil;

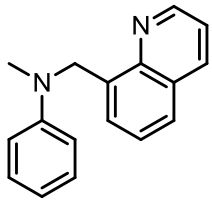
R$_f$ (PE:EA = 50:1): 0.8;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 1H), 7.92 – 7.86 (m, 1H), 7.79 – 7.73 (m, 1H), 7.57 – 7.47 (m, 2H), 7.38 (dd, *J* = 8.1, 7.1 Hz, 1H), 7.30 (dq, *J* = 7.0, 1.2 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.82 – 6.75 (m, 3H) 4.96 (s, 2H), 3.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.77, 133.90, 133.25, 131.23, 129.27, 128.93, 127.48, 126.10, 125.72, 125.67, 123.95, 122.75, 116.52, 112.20, 54.60, 38.49.

Exact Mass ESI-MS: calculated m/z for $[C_{18}H_{17}N+H]^+$: 248.1439, found: 248.1426.

N-methyl-N-(quinolin-8-ylmethyl)aniline (5am)



35.4 mg, 0.144 mmol, 48%;

Pale yellow oil;

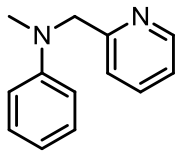
R$_f$ (PE:EA = 50:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.52 – 7.39 (m, 3H), 7.26 – 7.14 (m, 2H), 6.74 (dt, *J* = 7.8, 1.1 Hz, 2H), 6.72 – 6.64 (m, 1H), 5.27 (s, 2H), 3.18 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.53, 148.16, 145.37, 135.30, 135.04, 128.10, 127.34, 125.49, 125.42, 125.40, 119.98, 114.93, 110.77, 52.34, 37.93.

Exact Mass ESI-MS: calculated m/z for $[C_{17}H_{16}N_2+H]^+$: 249.1392, found: 249.1387.

N-methyl-N-(pyridin-2-ylmethyl)aniline (5an)



28.4 mg, 0.144 mmol, 48%;

Pale yellow oil;

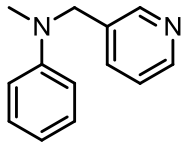
$\mathbf{R}_f$ (PE:EA = 100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (m, 1H), 7.59 (td, *J* = 7.7, 1.8 Hz, 1H), 7.39 – 7.03 (m, 4H), 6.84 – 6.60 (m, 3H), 4.65 (s, 2H), 3.12 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 149.55, 149.24, 136.75, 129.22, 121.90, 120.75, 116.71, 112.21, 58.88, 39.08.

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{14}N_2+H]^+$: 199.1235, found: 199.1232.

N-methyl-N-(pyridin-3-ylmethyl)aniline (5ao)



29.0mg, 0.147 mmol, 49%;

Pale yellow oil;

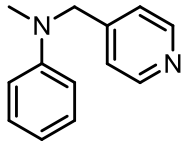
$\mathbf{R}_f$ (PE:EA = 100:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.73 – 7.43 (m, 1H), 7.33 – 7.13 (m, 3H), 6.89 – 6.56 (m, 3H), 4.54 (s, 2H), 3.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.36, 147.71, 147.41, 133.57, 128.25, 122.52, 116.19, 111.67, 53.47, 37.58.

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{14}N_2+H]^+$: 199.1235, found: 199.1230.

N-methyl-N-(pyridin-4-ylmethyl)aniline (5ap)



40.2mg, 0.204 mmol, 68%;

Pale yellow oil;

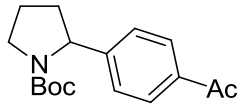
$\mathbf{R}_f$ (PE:EA = 50:1): 0.8;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.28 – 7.11 (m, 4H), 6.74 (tt, *J* = 7.2, 1.1 Hz, 1H), 6.69 (dt, *J* = 7.2, 1.1 Hz, 2H), 4.51 (s, 2H), 3.05 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.88, 148.13, 147.52, 128.26, 120.90, 116.10, 111.29, 54.92, 37.86.

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{14}N_2+H]^+$: 199.1235, found: 199.1233.

tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (5ma)



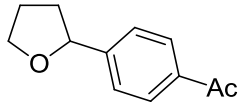
62.3 mg, 0.215 mmol, 72%;

Colorless oil;

$\mathbf{R}_f$ (PE:EA = 5:1): 0.3;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.77 (m, 2H), 7.41 – 7.01 (m, 2H), 5.08 – 4.71 (m, 1H), 3.65 (t, *J* = 6.8 Hz, 2H), 2.59 (d, *J* = 8.6 Hz, 3H), 2.36 (dt, *J* = 14.2, 7.9 Hz, 1H), 2.00 – 1.72 (m, 3H), 1.46 (s, 3H), 1.18 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.81, 154.43, 150.81, 135.72, 128.64, 128.44, 125.64, 79.54, 61.17, 60.67, 47.40, 47.15, 35.90, 34.75, 28.49, 28.16, 26.62, 23.66, 23.26. **GCMS:** calculated m/z for $C_{17}H_{23}NO_3$: 289.2, found: 289.2.

1-(4-(tetrahydrofuran-2-yl)phenyl)ethanone (5na)



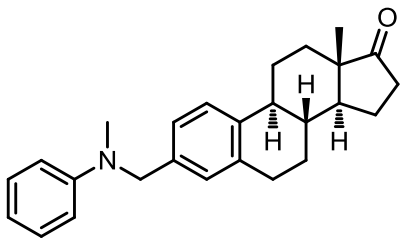
33.5 mg, 0.176 mmol, 59%;

Colorless oil;

$\mathbf{R}_f$ (PE:EA = 10:1): 0.2;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.16 – 3.95 (m, 1H), 3.95 – 3.82 (m, 1H), 2.52 (s, 3H), 2.30 (dd, *J* = 12.5, 6.4 Hz, 1H), 2.07 – 1.88 (m, 2H), 1.78 – 1.62 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.82, 148.17, 135.04, 127.44, 124.57, 79.11, 67.85, 33.68, 25.60, 24.94. **GCMS:** calculated m/z for $C_{12}H_{14}O_2$: 190.1, found: 190.1.

(*8R,9S,13S,14S*)-13-methyl-3-((methyl(phenyl)amino)methyl)-7,8,9,11,12,13,15, 16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (5aq)



76.0 mg, 0.204 mmol, 68 %;

White solid;

$\mathbf{R}_f$ (PE:EA=20:1): 0.2;

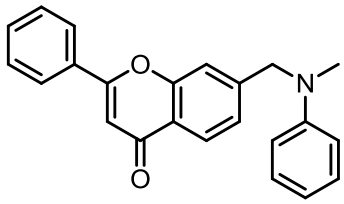
^{1}H NMR (400 MHz, $CDCl_3$)δ 7.22 – 7.08 (m, 3H), 6.97 – 6.86 (m, 2H), 6.72 – 6.57 (m, 3H), 4.39 (s, 2H), 2.92 (s, 3H), 2.80 (dd, *J* = 8.7, 4.0 Hz, 2H), 2.49 – 2.27 (m, 2H), 2.21 (td, *J* = 10.7, 4.2 Hz, 1H), 2.12 – 1.84 (m, 4H),

1.62 – 1.29 (m, 6H), 0.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 220.89, 149.87, 138.36, 136.74, 136.54, 129.16, 127.27, 125.56, 124.22, 116.43, 112.30, 56.35, 50.54, 48.01, 44.38, 38.48, 38.21, 35.88, 31.63, 29.50, 26.54, 25.76, 21.61, 13.87.

Exact Mass ESI-MS: calculated m/z for $[C_{26}H_{31}NO+H]^+$: 374.2484, found: 374.2493

7-((methyl(phenyl)amino)methyl)-2-phenyl-4H-chromen-4-one (5ar)



65.9 mg, 0.193 mmol, 64 %;

White solid;

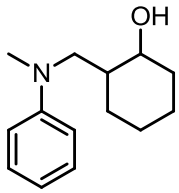
R_f (PE:EA=1:1): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.86 – 7.77 (m, 2H), 7.43 (ddd,*J* = 5.3, 4.2, 2.3 Hz, 3H), 7.36 (d, *J* = 1.4 Hz, 1H), 7.23 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.21 – 7.12 (m, 2H), 6.73 (s, 1H), 6.72 – 6.62 (m, 3H), 4.57 (s, 2H), 3.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.23, 162.29, 155.74, 148.26, 145.61, 130.69, 130.52, 128.30, 127.97, 125.27, 125.06, 122.75, 121.87, 116.14, 114.54, 111.35, 106.56, 55.79, 37.87.

LRMS: calculated m/z for $[C_{23}H_{19}NO_2+H]^+$: 342.15, found: 342.20

2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)



60.0 mg, 0.272 mmol, 68 %;

Yellow oil;

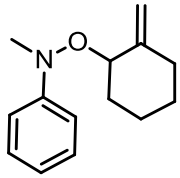
R_f (PE:EA): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 6.98 – 6.81 (m, 3H), 4.13 (s, 1H), 3.58 – 3.38 (m, 2H), 3.01 (dd, *J* = 14.0, 5.4 Hz, 1H), 2.89 (s, 3H), 2.04 – 1.94 (m, 1H), 1.78 – 1.63 (m, 4H), 1.32 – 1.15 (m, 3H), 1.01 – 0.90 (m, 1H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.00, 129.17, 119.24, 115.84, 76.14, 61.36, 42.29, 40.38, 35.07, 29.12, 25.42, 24.41;

Exact Mass ESI-MS: calculated m/z for $[C_{14}H_{22}NO]^+$: 220.1696, found: 220.1704.

N-methyl-O-(2-methylenecyclohexyl)-N-phenylhydroxylamine. (8ag)



30.4 mg, 0.140 mmol, 70 %;

Yellow oil;

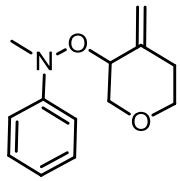
$\mathbf{R}_f$ (PE): 0.5;

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.25 – 7.15 (m, 2H), 7.04 – 6.93 (m, 2H), 6.87 (tt, J = 7.3, 1.1 Hz, 1H), 4.92 – 4.86 (m, 1H), 4.76 (dt, J = 2.2, 1.1 Hz, 1H), 4.13 – 4.05 (m, 1H), 3.00 (s, 3H), 2.33 (m, 1H), 2.05 (m, 1H), 1.80 (m, 2H), 1.78 – 1.65 (m, 1H), 1.60 – 1.42 (m, 1H), 1.47 – 1.35 (m, 1H), 1.19 (m, 1H);

^{13}C NMR (101 MHz, $CHCl_3$) δ152.37, 146.94, 127.72, 120.61, 114.96, 107.81, 80.86, 44.85, 32.13, 31.77, 26.80, 21.56;

ESI-MS: calculated m/z for $[C_{14}H_{20}NO]^+$: 218.15, found: 218.10.

N-methyl-O-(4-methylenetetrahydro-2H-pyran-3-yl)-N-phenylhydroxylamine (8an)



35.5 mg, 0.162 mmol, 81%;

Yellow oil;

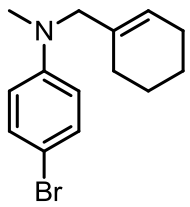
$\mathbf{R}_f$ (PE): 0.5;

^{1}H NMR (400 MHz, $CHCl_3$) δ 7.26 – 7.15 (m, 2H), 7.10 – 6.97 (m, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 5.02 (s, 1H), 4.90 (s, 1H), 4.04 (d, *J* = 3.4 Hz, 1H), 3.95 (dd, *J* = 11.7, 4.1 Hz, 1H), 3.81 (dt, *J* = 9.9, 4.7 Hz, 1H), 3.65 (dd, *J* = 11.7, 2.8 Hz, 1H), 3.50 (ddd, *J* = 10.8, 9.2, 3.4 Hz, 1H), 3.02 (s, 3H), 2.57 (ddd, *J* = 13.8, 9.2, 4.7 Hz, 1H), 2.15 (dt, *J* = 13.7, 4.0 Hz, 1H);

^{13}C NMR (101 MHz, $CHCl_3$) δ 153.02, 142.68, 128.82, 122.02, 116.13, 111.67, 79.84, 70.90, 69.13, 45.73, 33.21;

Exact Mass ESI-MS: calculated m/z for $[C_{13}H_{18}NO_2]^+$: 220.1332, found: 220.1341.

4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (9ag)



54.0 mg, 0.193 mmol, 97%;

Yellow oil;

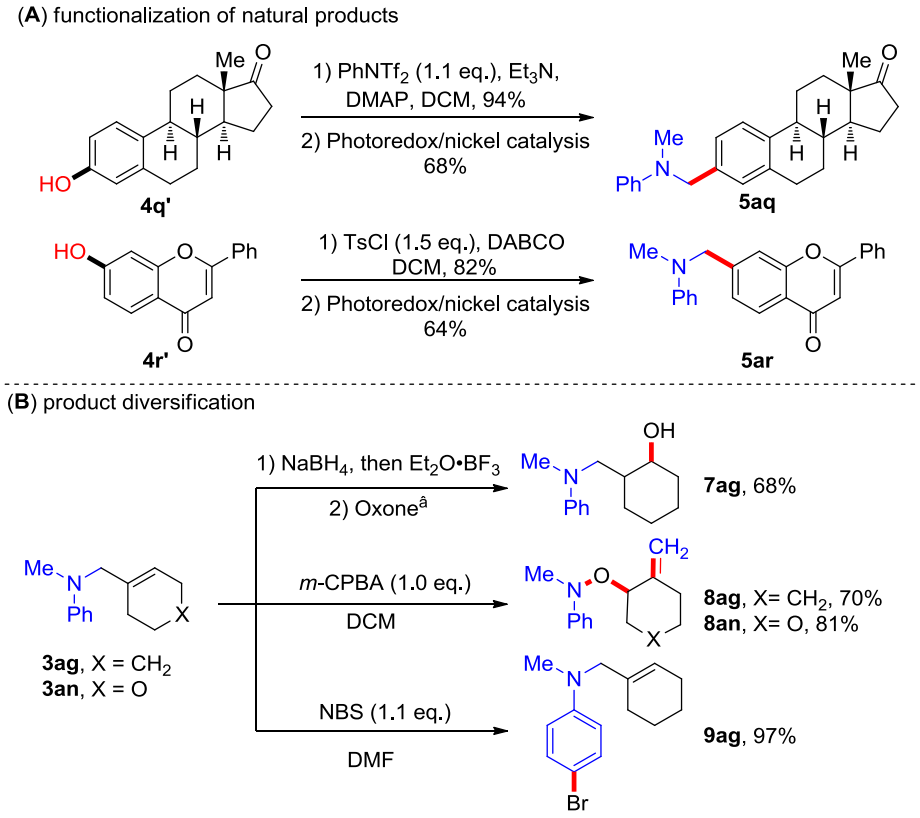
$\mathbf{R}_f$ (PE): 0.5;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23– 7.14 (m, 2H), 6.51– 6.43 (m, 2H), 5.39 (m, *J* = 5.3, 3.6, 1.7 Hz, 1H), 3.64 (s, 2H), 2.82 (s, 3H), 1.97 – 1.87 (m, 2H), 1.79 (t, 2H), 1.58 – 1.47 (m, 4H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.82, 132.36, 130.56, 121.34, 112.55, 106.59, 57.83, 37.20, 25.32, 23.88, 21.57, 21.52;

Exact Mass ESI MS: calculated m/z for $[C_{14}H_{19}BrN]^+$: 282.0675, found:282.0665.

The Application of the Reaction



Synthesis of 5aq

A 100 mL round-bottom flask containing a magnetic stir bar was charged with **4q'** (0.61 g, 2.26 mmol), and DMAP (30 mg, 0.25 mmol). Under a positive flow of nitrogen, CH_2Cl_2 (10 mL) and Et_3N (6.0 mL, 43 mmol) were each introduced via syringe, and the clear solution was cooled on a water/ice bath. N-phenyl bis(trifluoromethylsulfon)imide (0.93 g, 2.6 mmol) dissolved in CH_2Cl_2 (5 mL) was added via cannula and the reaction was allowed to stir at rt for 22 h. The mixture was diluted with Et_2O, washed once with water, twice with saturated aqueous ammonium chloride, twice with saturated aqueous sodium bicarbonate, and once with brine. The solution obtained was dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The oily residue was purified by flash chromatography eluting with 10/90 ethyl acetate/petroleum ether to afford the triflate as a white solid (0.86 g, 94%).

(*8R,9S,13S,14S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclo penta[a]phenanthren-3-yltrifluoro methanesulfonate. **^{1}H NMR** (400 MHz, $CDCl_3$)

δ 7.34 (dd, *J* = 8.7, 1.1 Hz, 1H), 7.08 – 6.97 (m, 2H), 2.95 (dd, *J* = 8.8, 4.1 Hz, 2H), 2.58 – 2.46 (m, 1H), 2.46 – 2.36 (m, 1H), 2.30 (td, *J* = 10.6, 4.4 Hz, 1H), 2.25 – 2.10 (m, 1H), 2.10 – 2.02 (m, 2H), 2.02 – 1.92 (m, 1H), 1.72 – 1.39 (m, 6H), 0.92 (s, 3H). All spectroscopic data is in agreement with those previously reported.[8]

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ir[dF(CF_3)ppy]_2(dtbbpy)(PF_6)$ (0.0075 mmol), the above solid (0.3 mmol). The tube was triple evacuated/N_2 filled before being transferred into a glovebox. $Ni(cod)_2$ (0.03 mmol), Me_4Phen (0.03 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product **5aq** as a pale white solid in 68% yield (76.0 mg, 0.204mmol).

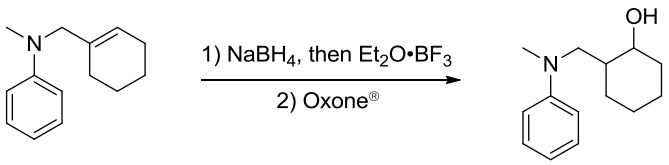
Synthesis of 5ar

To a solution of tosyl chloride (1.8 g, 6.3 mmol) in CH_2Cl_2 (10.0 mL) was added dropwise to a solution of **4r'** (1.5 g, 9.5 mmol) and DABCO (2.1 g, 18.9 mmol) in anhydrous CH_2Cl_2 (20 mL) at 0 ℃. After complete addition, the mixture was warmed to room temperature and allowed to stir until completion following the reaction by TLC. The mixture was then diluted with Et_2O (20 mL), quenched with 10 % aq. HCl and washed successively with aqueous solution of $NaHCO_3$ and brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure to give the tosylate as a white solid (2.03 g, 82%). **4-oxo-2-phenyl-4H-chromen-7-yl 4-methylbenzenesulfonate ^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.79 (m, 2H), 7.73 – 7.65 (m, 2H), 7.54 – 7.42 (m, 3H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.32 – 7.24 (m, 2H), 6.85 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.74 (s, 1H), 2.39 (s, 3H). All

spectroscopic data is in agreement with those previously reported.[9]

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ru(bpy)_3Cl_2$ $6H_2O$ (0.003 mmol), the above solid (0.3 mmol). The tube was triple evacuated/N_2 filled before being transferred into a glovebox. $NiBr_2$·glyme (0.006 mmol), Me_4Phen (0.006 mmol) and DABCO (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 50:1 to 30:1) to provide the pure product **5aa** as a pale white solid in 64% yield (65.9 mg, 0.193 mmol).

Synthesis of 2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)[10]



To a solution of alkene N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (0.4 mmol 80.4 mg) in THF (2 mL) was added $NaBH_4$ (0.8 mmol, 30.4 mg) at room temperature under N_2. The slurry was cooled to 0 ℃, and $BF_3.OEt_2$ (120 μL) in THF (1 mL) was slowly added. The addition was kept slow enough to keep the temperature of the reaction mixture below 0 ℃. After the addition the reaction mixture was stirred at 0 ℃ for 1 h and at room temperature for 1.5 h. The reaction was re-cooled to 0 ℃ and water (1 mL) was added slowly to destroy the excess borane. The reaction was stirred at rt for 2 h, followed by the addition of Oxone® (0.8 g) in water (1 mL) at 0 ℃. The reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by adding $NaHSO_3$ (solid) until all excess oxidant was

destroyed (KI/starch test paper). The pH of the reaction mixture was 1 - 2. The reaction mixture was extracted with ethyl acetate (2 mL), and the aqueous layer was adjusted to pH 12 with 6 N NaOH and extracted with ethyl acetate (4* 2 mL). The organic layer was washed with brine, dried over $NaSO_4$, and concentrated in vacuo. The residue obtained is pure alcohol (60.0 mg, 68%).

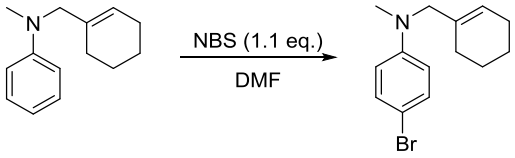
Synthesis of N-methyl-O-(4-methylenetetrahydro-2H-pyran-3-yl)-N-Phenylhydroxylamine (8an)

To a mixture of N-((3,6-dihydro-2H-pyran-4-yl)methyl)-N-methylaniline (0.2 mmol, 40.6 mg) in methylenechloride (2 mL) and 0.5 M aqueous sodium hydrogencarbonate (0.3 mmol, 1.5 eq.,) was added 70% m-chlorperbenzoic acid (0.2 mmol, 49.3 mg, 1.0 eq.) with stiring. After stirring at rt for 3 h. The organic layer was washed with 1N sodium solution, water, brine, dried over Na_2SO_4, and concentrated in vacuo. The residue obtained is pure (35.5mg, 81 %).

Synthesis of N-methyl-O-(2-methylenecyclohexyl)-N-phenylhydroxylamine (8ag)

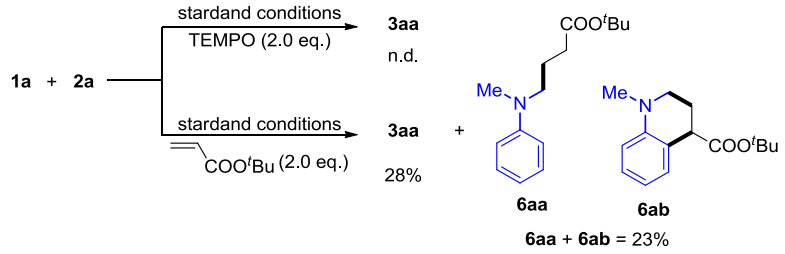
The procedure is the same to the Synthesis of **8an**.

Synthesis of 4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline (9ag)[11]



A mixture of 40.2 mg (0.200 mmol, 1.0 eq.) of N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline and 38.9 mg (0.220 mmol, 1.1 eq.) of NBS was dissolved in 3 mL of DMF. The reaction mixture was stirred for overnight at room temperature and the resulting solvent was concentrated in vacuo. The residue was purified by silica gel flash chromatography (pure petroleum) to give the pure desired product 4-bromo-N-(cyclohex-1-en-1.-ylmethyl)-N-methylaniline 54.0 mg (yield, 97%).

Mechanistic studies



Scheme SI-1 Trapping of free radical

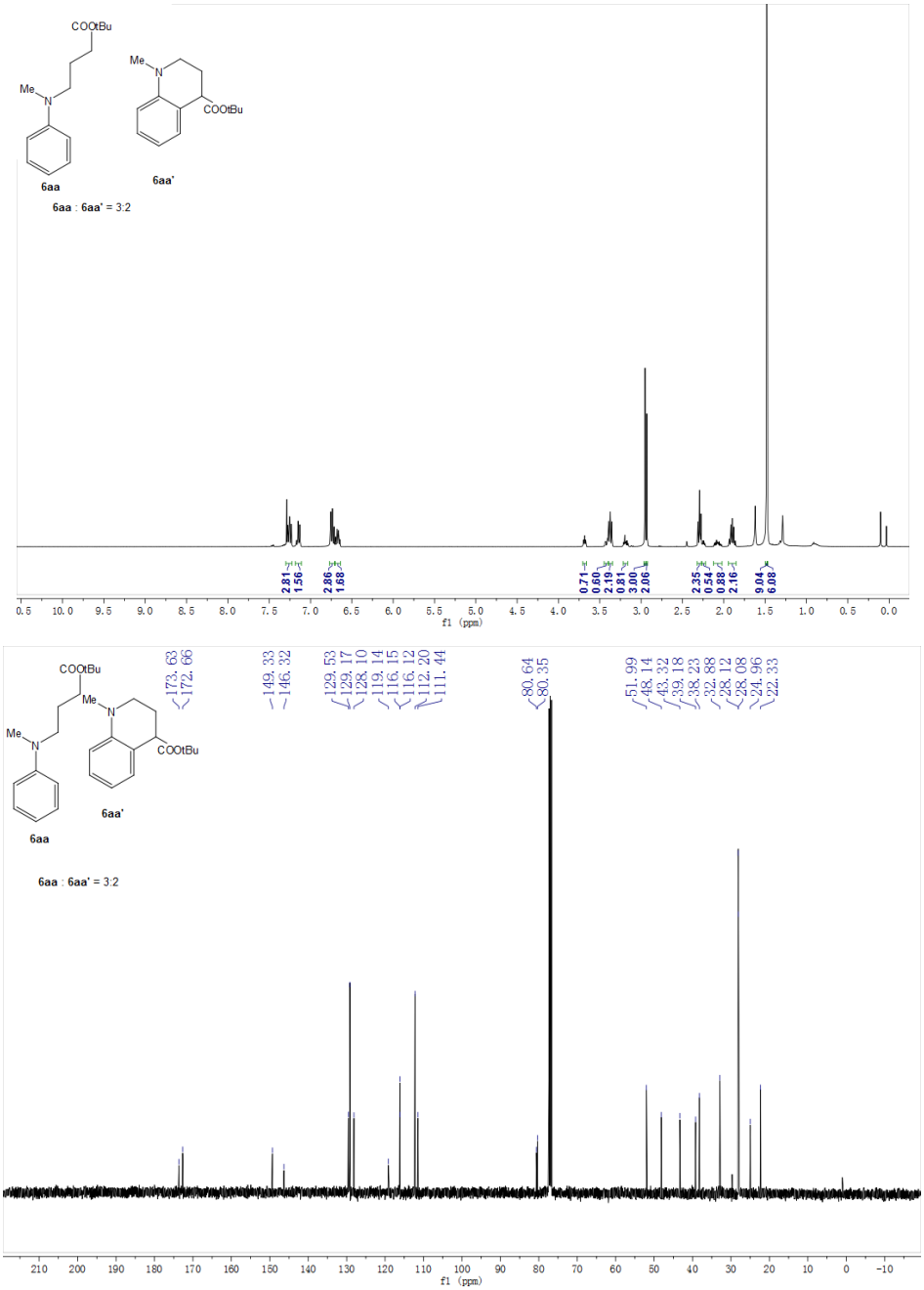
(1) **Trapping of free radical with TEMPO**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ru(bpy)_3Cl_2$ $6H_2O$ (0.003 mmol), **2a** (0.3 mmol) and dtbbpy (0.006 mmol), 2,2,6,6-tetramethylpiperding-1-oxyl (TEMPO, 0.6 mmol). The tube was evacuated and refilled with N_2 3 times before being transferred into a glovebox. $NiCl_2$ glyme (0.006 mmol) and Cs_2CO_3 (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from a 30 W blue LED and stirred at room temperature for 4 h. No desired product **3aa** was detected by TLC plate or GCMS.

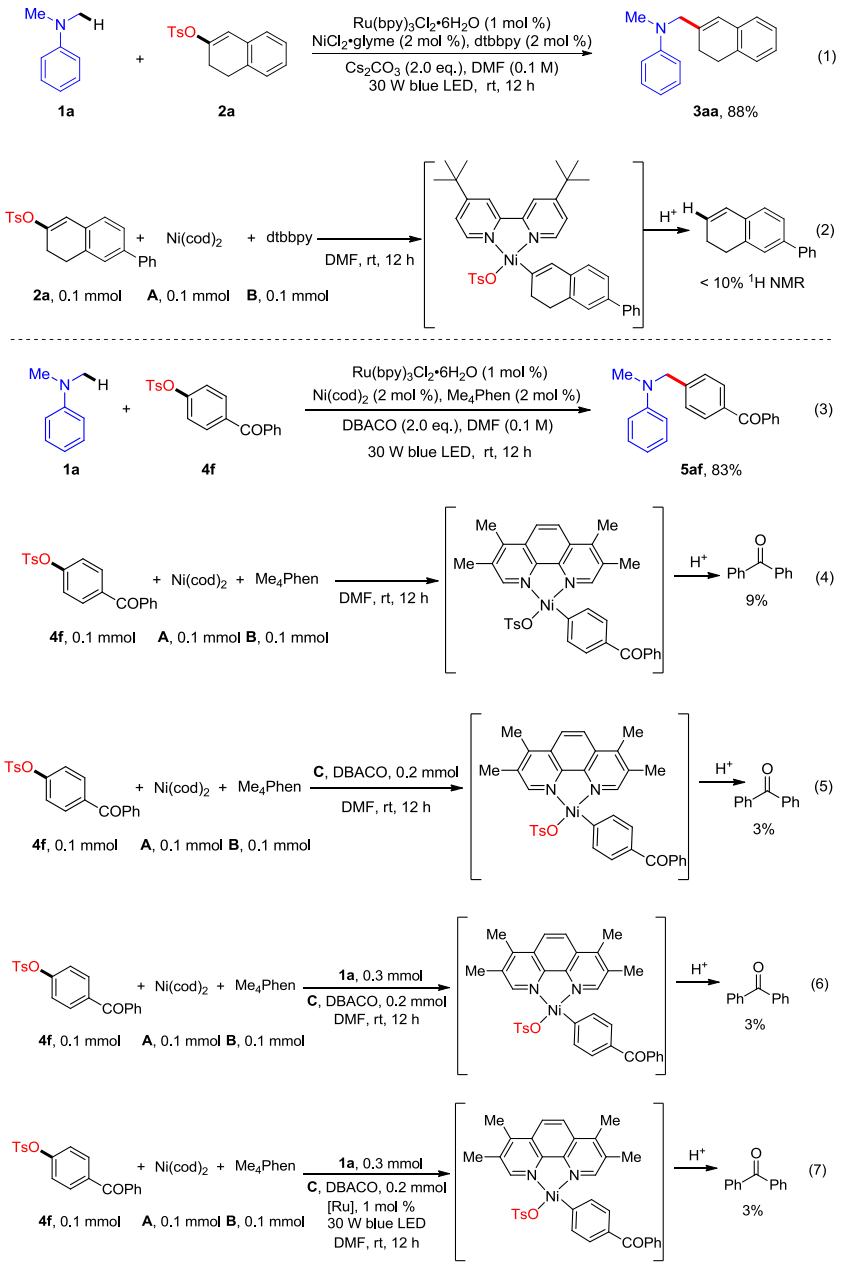
(2) **Trapping of free radical with tert-butyl acrylate**

To a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added $Ru(bpy)_3Cl_2$ $6H_2O$ (0.003 mmol), **2a** (0.3 mmol) and dtbbpy (0.006 mmol). The tube was evacuated and refilled with N_2 3 times before being transferred into a glovebox. $NiCl_2$ glyme (0.006 mmol) and Cs_2CO_3 (0.6 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (3.0 mL) were added to the tube, followed by **1a** (0.9 mmol) and *tert*-butyl acrylate (0.6 mmol). The resulting mixture was degassed by using a "freeze–pump–thaw" procedure (3 times). Afterwards, the solution was placed at a distance of 3~5 cm from

a 30 W blue LED and stirred at room temperature for 4 h. Then, the solvent was removed in vacuum and the crude product was purified by flash chromatography on silica gel (silica: 200–300 mm; eluent: petroleum ether/ethyl acetate 500:1 to 300:1 to 100:1) to provide the pure product **3aa** as a pale white solid in 28% yield (with 67% of **2a** recovered), **6aa and 6ab** as colorless oil in 23% yield (the ratio of **6aa**:**6ab** is 3:2, which are inseparable from each other).



(3) Stoichiometric reactions of Ni(0) complex with alkenyl/aryl tosylates



Scheme SI-2 Mechanistic studies on stoichiometric reactions

In order to get more insights to this reaction, stoichiometric reactions of Ni(0) complex with alkenyl/aryl tosylates were carried out (**Scheme SI-2**). The procedure for **Scheme S2** ia as following: to a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was added **2** (0.1 mmol) and dtbbpy (0.1 mmol). $Ni(cod)_2$ (0.1 mmol) and Cs_2CO_3 (0.2 mmol) was added to the tube before transferring out of the glovebox and placing under an atmosphere of N_2. Dry DMF (1.0 mL) were added to the tube, and then stirred at room temperature for 12 h. Afterwards, 1N HCl solution(2 mL) was added and stirred for 1h. The reaction mixture was extracted with EtOAc, dried

with $MgSO_4$. Then, the solvent was removed in vacuum. The yield of deoxyprotonation product was determined by ^1H NMR and/or GC.

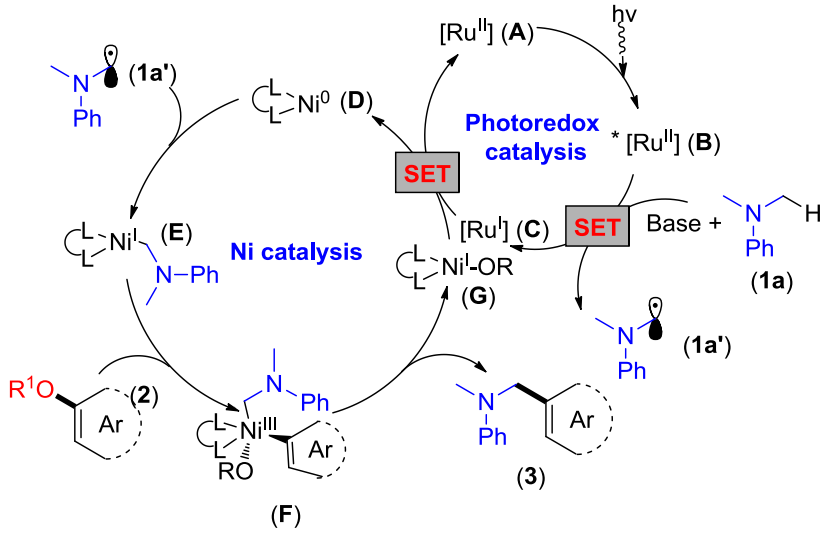


Figure SI-1 Proposed catalytic cycle I

All of such reactions showed low conversion and gave less than 10% of deoxyprotonation byproducts arising from C—O activation[12] and further protonation (**Scheme SI-2 Eqs 1-6**). Compared to the high efficiency of the catalytic reaction (83%, **Scheme SI-2 Eq 1,3**), these low yields indicated the direct oxidative addition to Ni(0) was inefficient and less favored in this reaction. Base on the above information and previous seminar works [13], we then proposed a possible pathway for the coupling of **1a** with **2** (Figure SI-1). Firstly, Ru-photocatalyst **A** is excited to generate **B**, which undergoes single-electron oxidation with **1a** to give Ru-photocatalyst **C** and, after deprotonation of the intermediate *N*-centered radical cation with the carbonate base, carbon-centered radical **1a'**. Combination of **1a'** with Ni(0) complex **D** might form the highly electron-rich Ni(I) complex **E**, which could undergo oxidative addition into the $C(sp^2)$—O bond of **2** at room temperature to generate the highly reactive Ni(III) species **F**. The following reductive elimination would give the desired product **3** and the Ni(I) complex **G**. Lastly, both **A** and **D** are regenerated to complete the dual catalytic cycle through reduction of **G** by the reduced form of Ru-photocatalyst **C**.

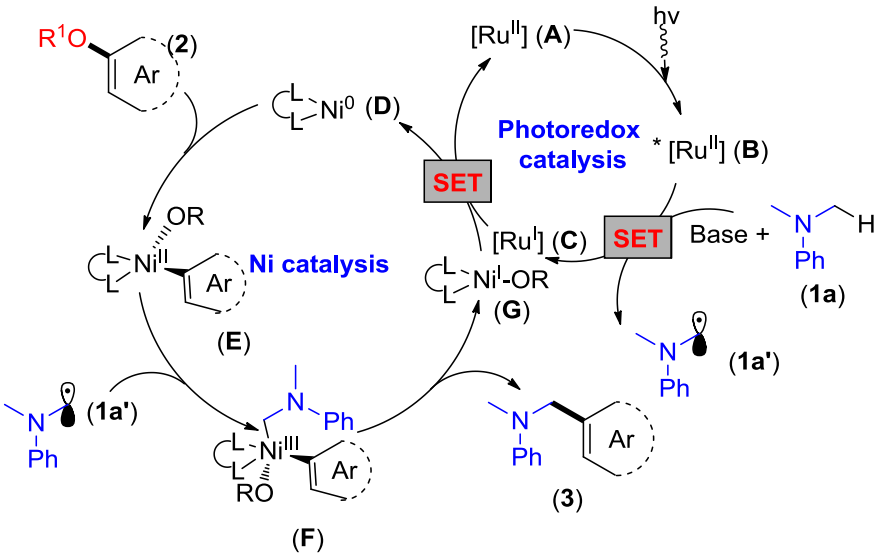


Figure SI-2 Proposed catalytic cycle II

However, at present stage, we cannot rule out the other catalytic cycle present in **Figure SI-2**[13]. Firstly, Ru-photocatalyst **A** is excited to generate **B**, which undergoes single-electron oxidation with **1a** to give Ru-photocatalyst **C** and, after deprotonation of the intermediate *N*-centered radical cation with the carbonate base, carbon-centered radical **1a'**. Concurrent with this photoredox mechanism, Ni(0) complex **D** could undergo oxidative addition into the C(sp^2)─O bond of **2** at room temperature to generate the Ni(II) species **E**. Interception of radical **1a'** by **E** would then generate organometallic Ni(III) adduct **F**. The following reductive elimination would give the desired product **3** and the Ni(I) complex **G**. Lastly, both **A** and **D** are regenerated to complete the dual catalytic cycle through reduction of **G** by the reduced form of Ru-photocatalyst **C**.

(4) Proposed catalytic cycle for coupling of aryl tosylate 4a with 1m and 1n

Firstly, Ir-photocatalyst **A** is excited to generate **B**, which undergoes single-electron oxidation with **4a** to give Ir -photocatalyst **C** and *N*-centered radical cation **4b**, Hydrogen atom transfer (HAT) between **4b** and **1** gived a carbon-centered radical **1'**. Concurrent with this photoredox mechanism, Ni(0) complex **D** could undergo oxidative addition into the C(sp^2)─O bond of **2** at room temperature to generate the Ni(II) species **E**. Interception of radical **1'** by **E** would

then generate organometallic Ni(III) adduct **F** (Interception of radical **1'** with Ni(0) to form Ni(I) and subsequent oxidation to C(sp^2)─O bond of **2** to form Ni(III) adduct **F** is also possible). The following reductive elimination would give the desired product **3** and the Ni(I) complex **G**. Lastly, both **A** and **D** are regenerated to complete the dual catalytic cycle through reduction of **G** by the reduced form of Ir-photocatalyst **C**.

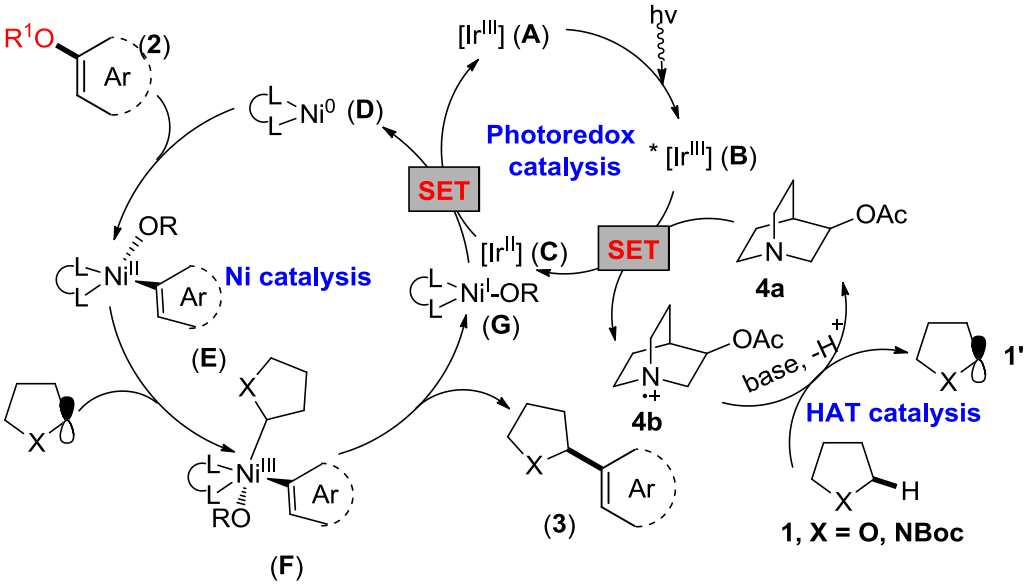


Figure SI-3 Proposed catalytic cycle III

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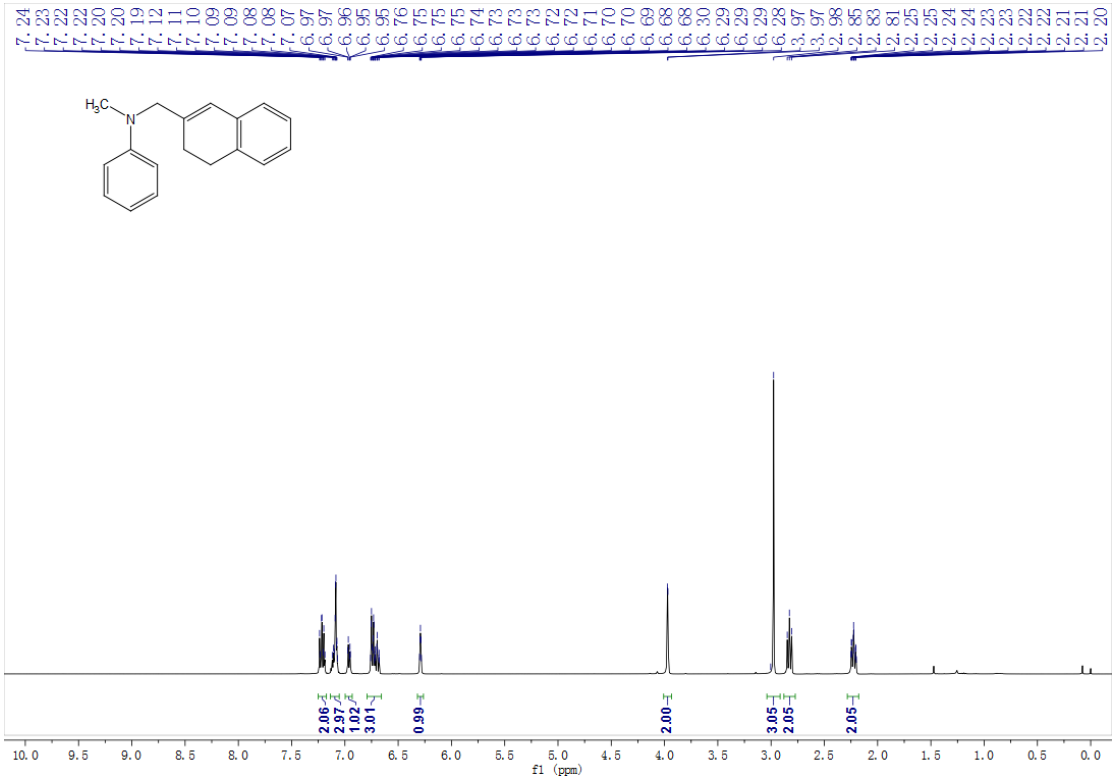
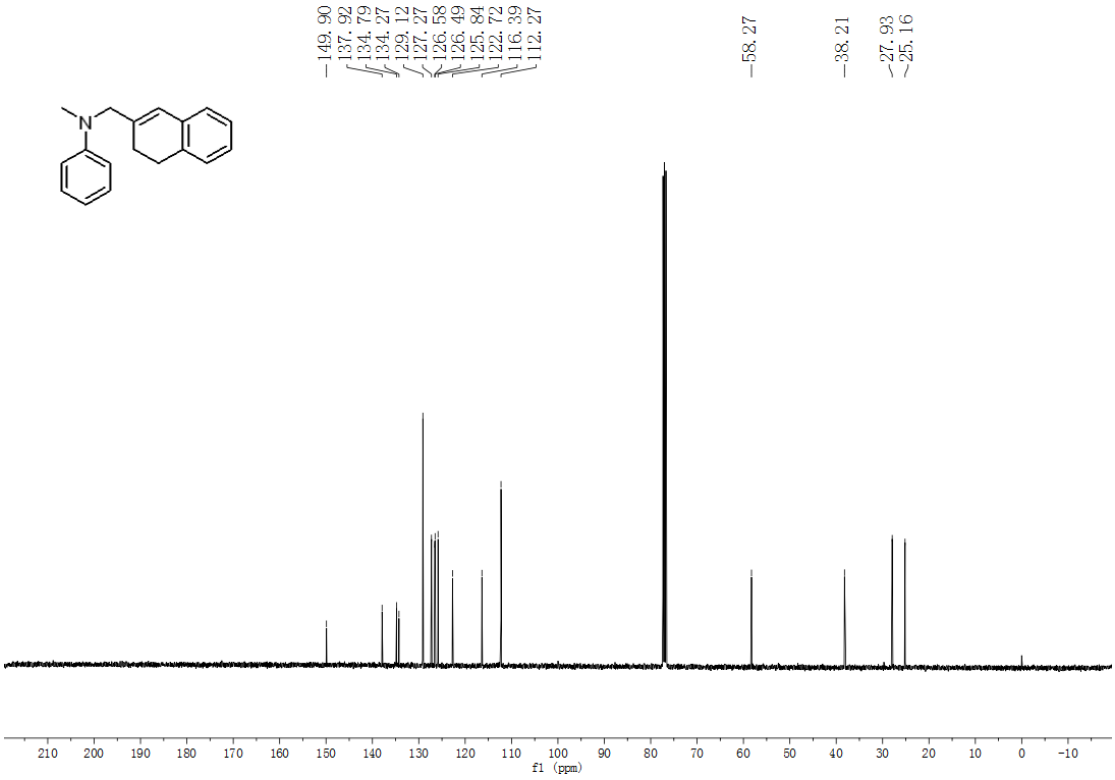
Copies of NMR spectra

N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3aa)





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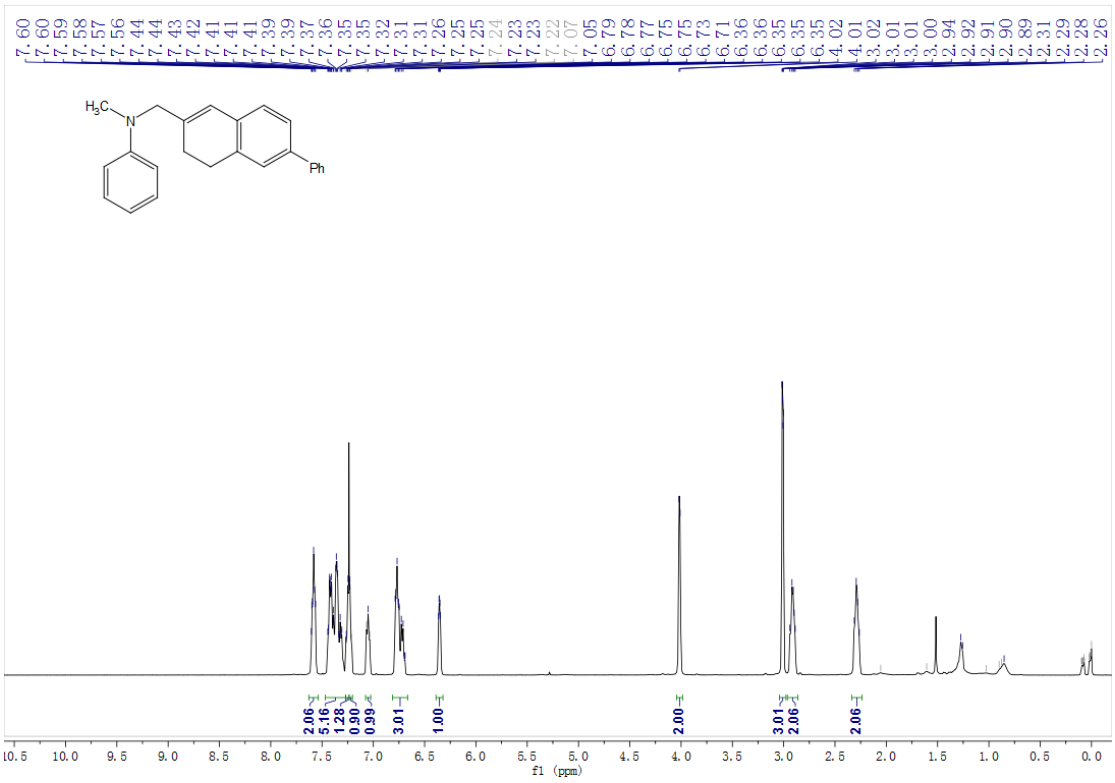

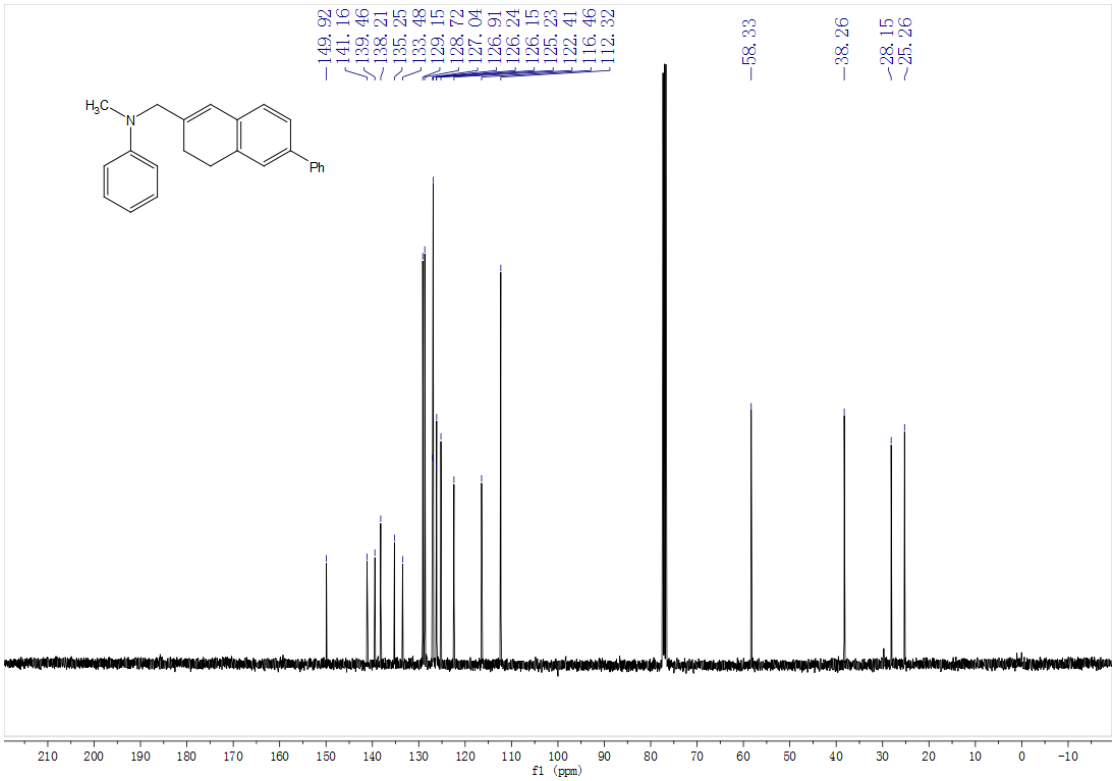

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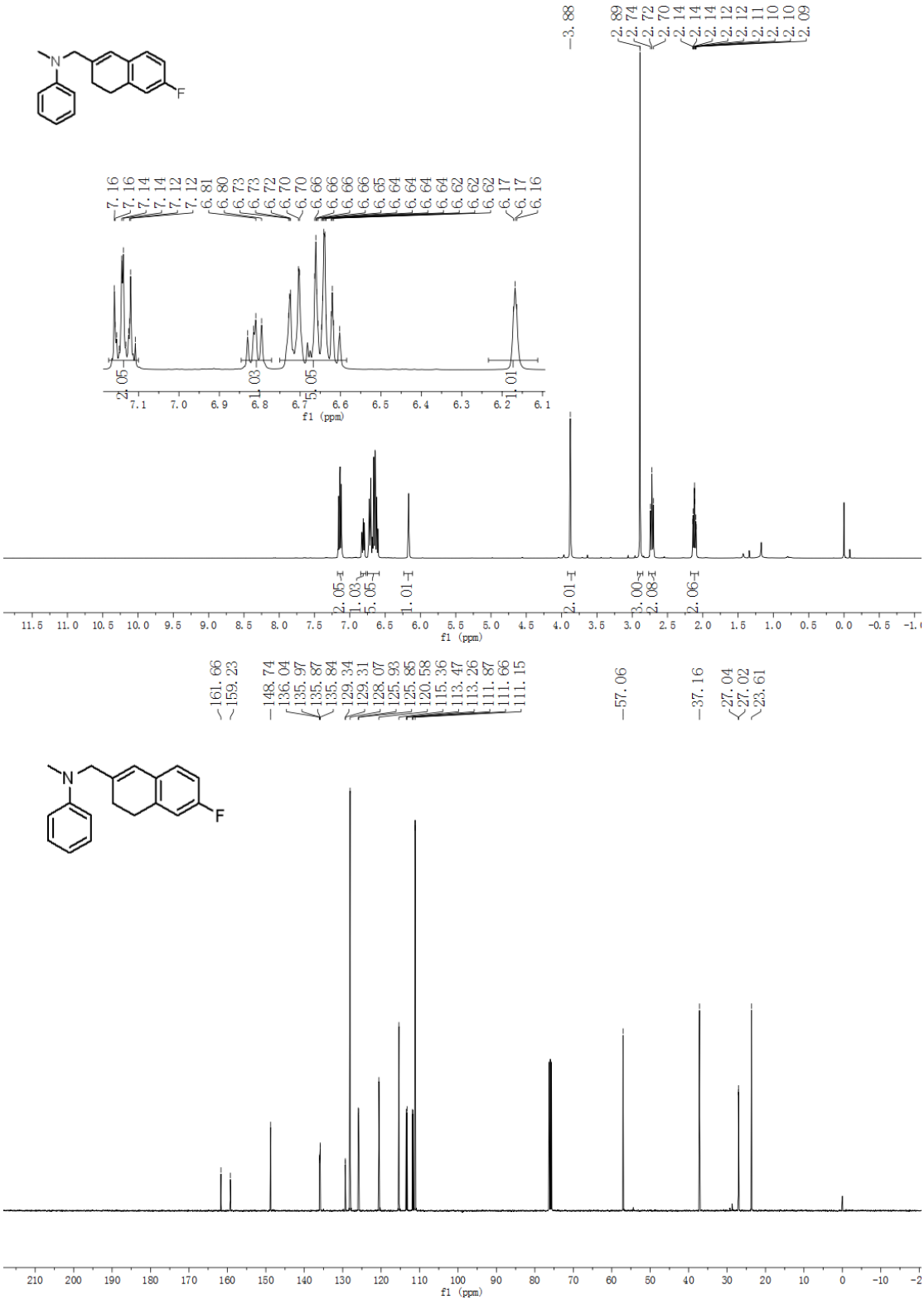

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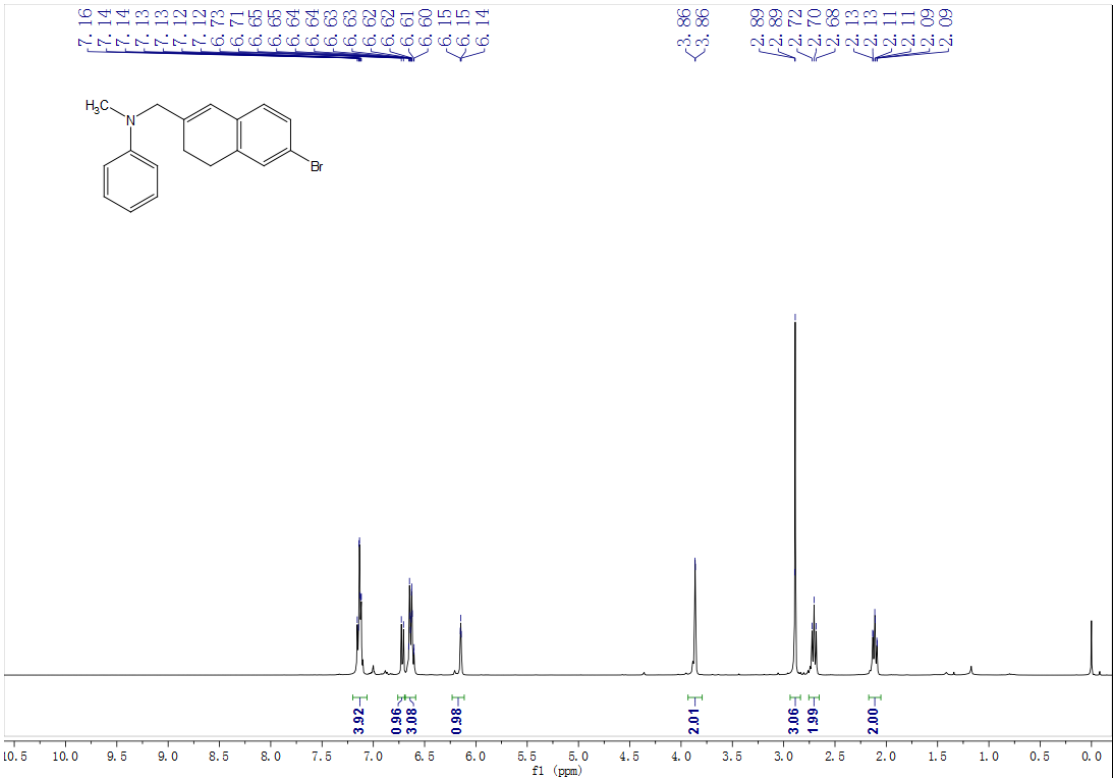

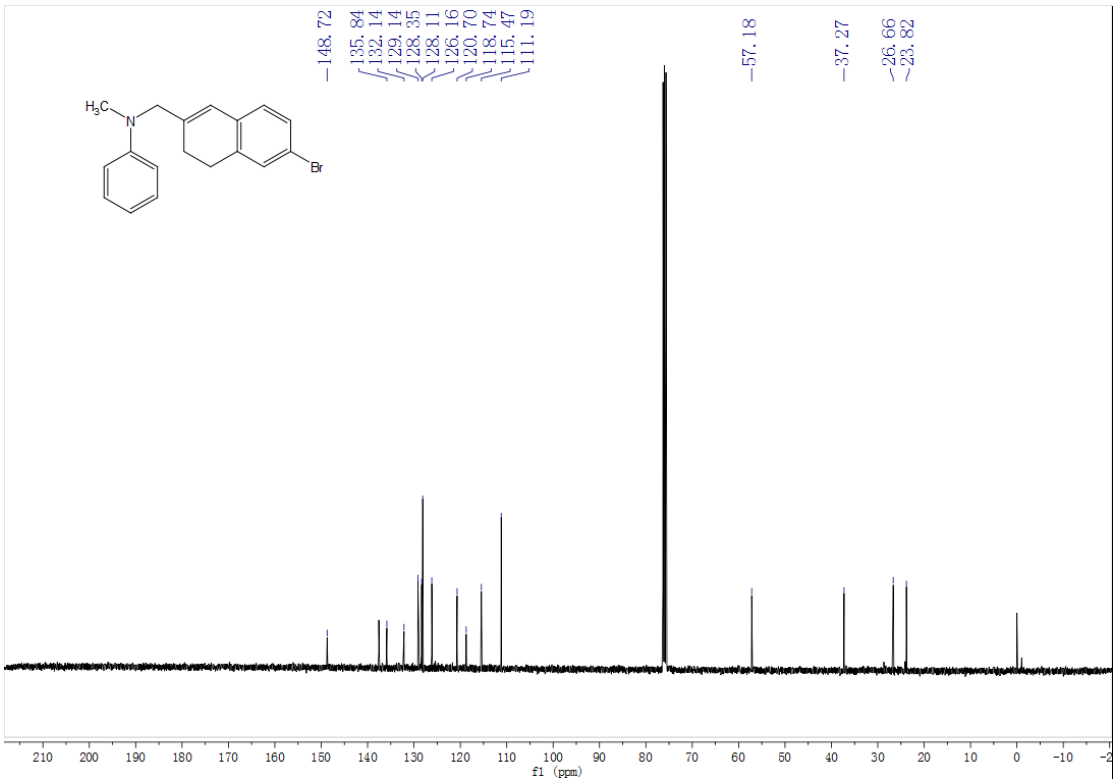

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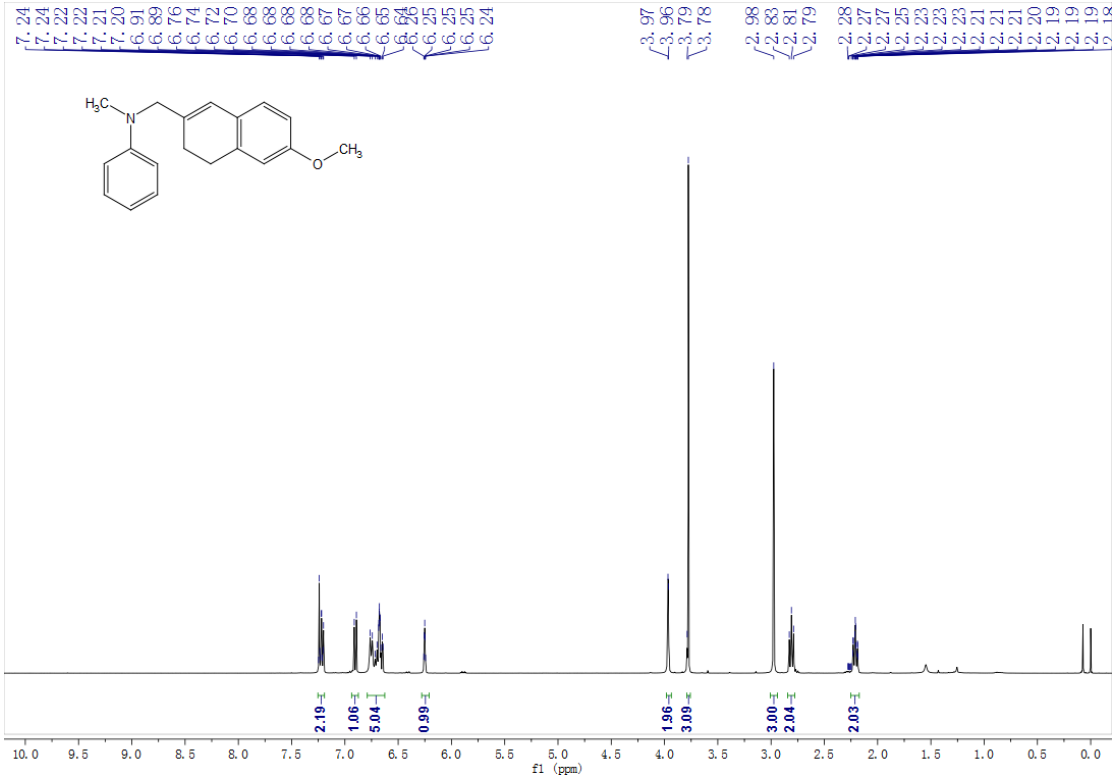

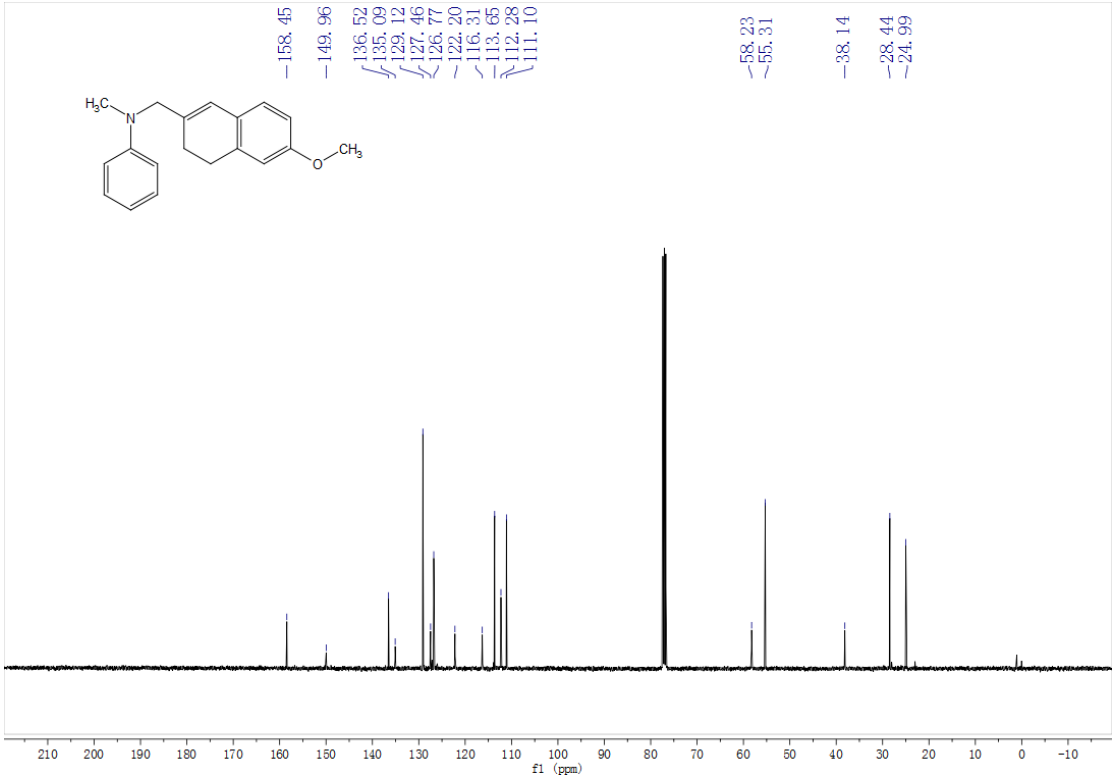

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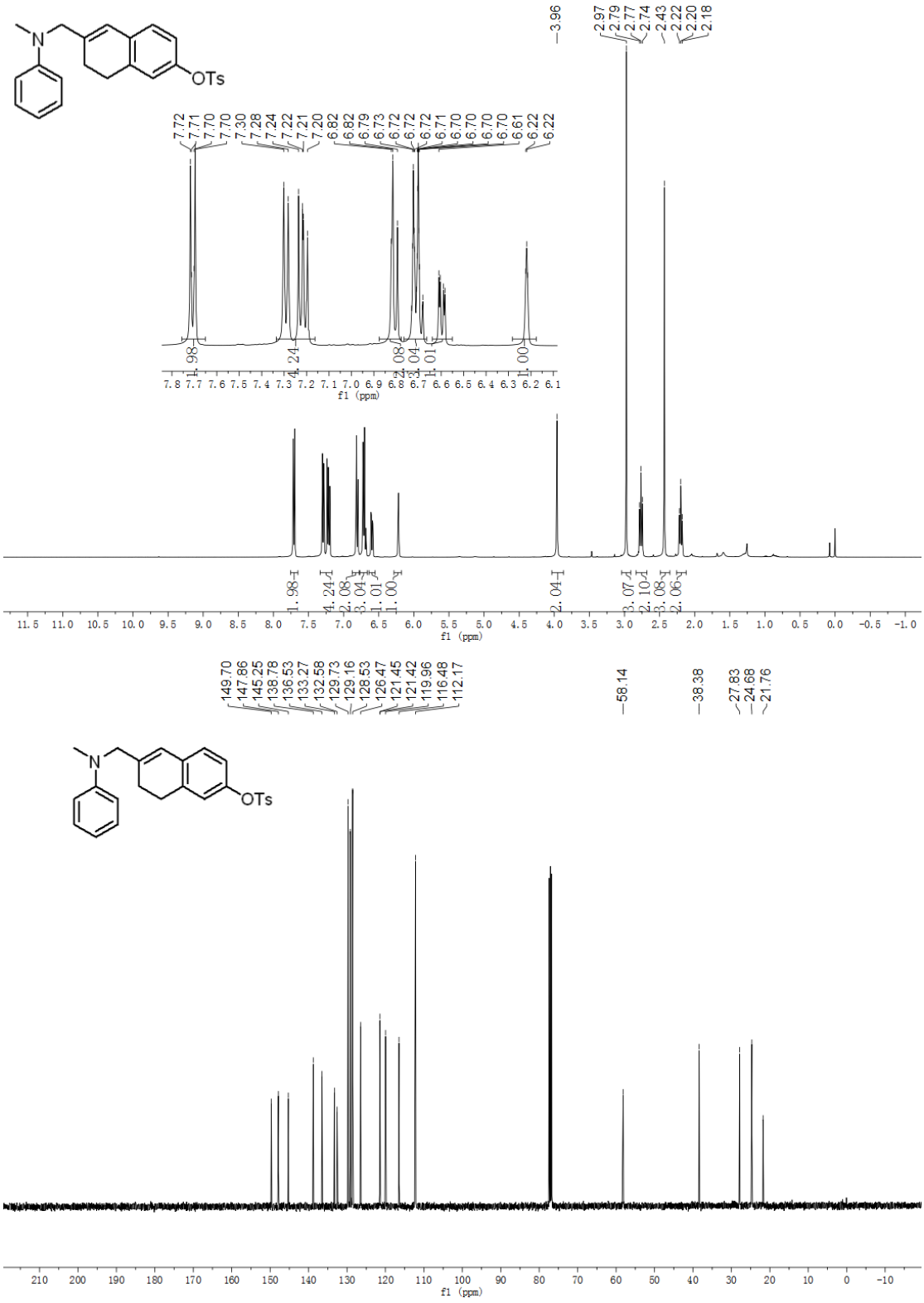

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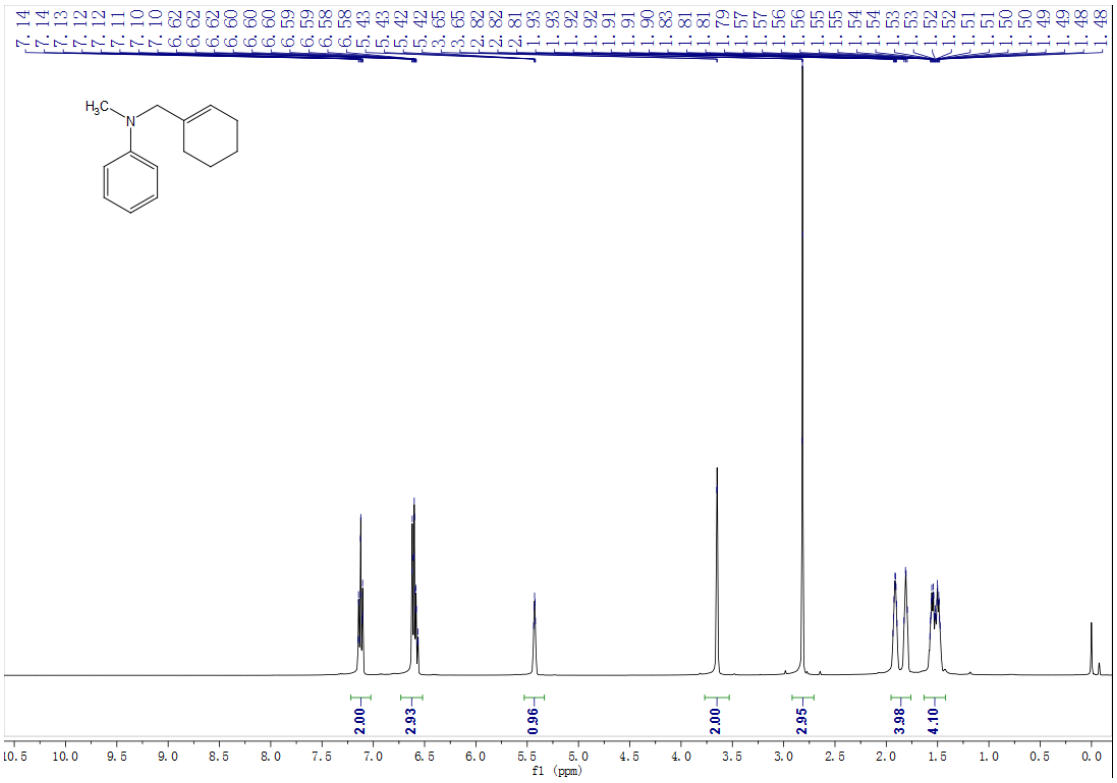

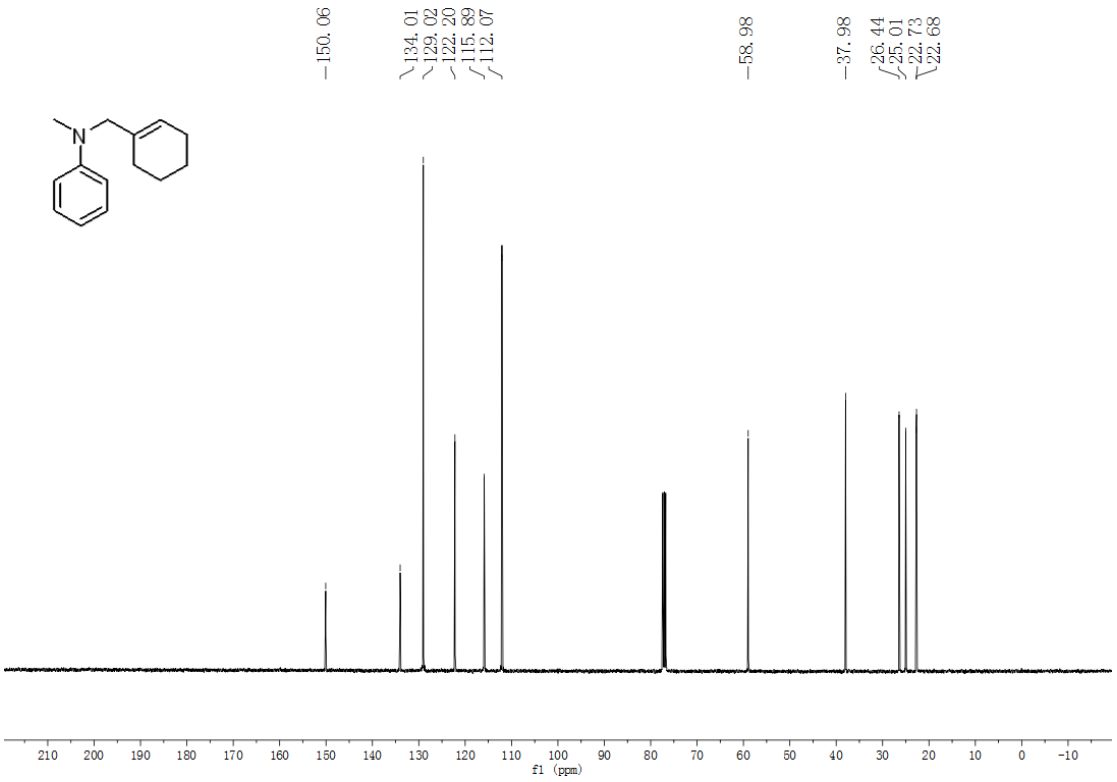

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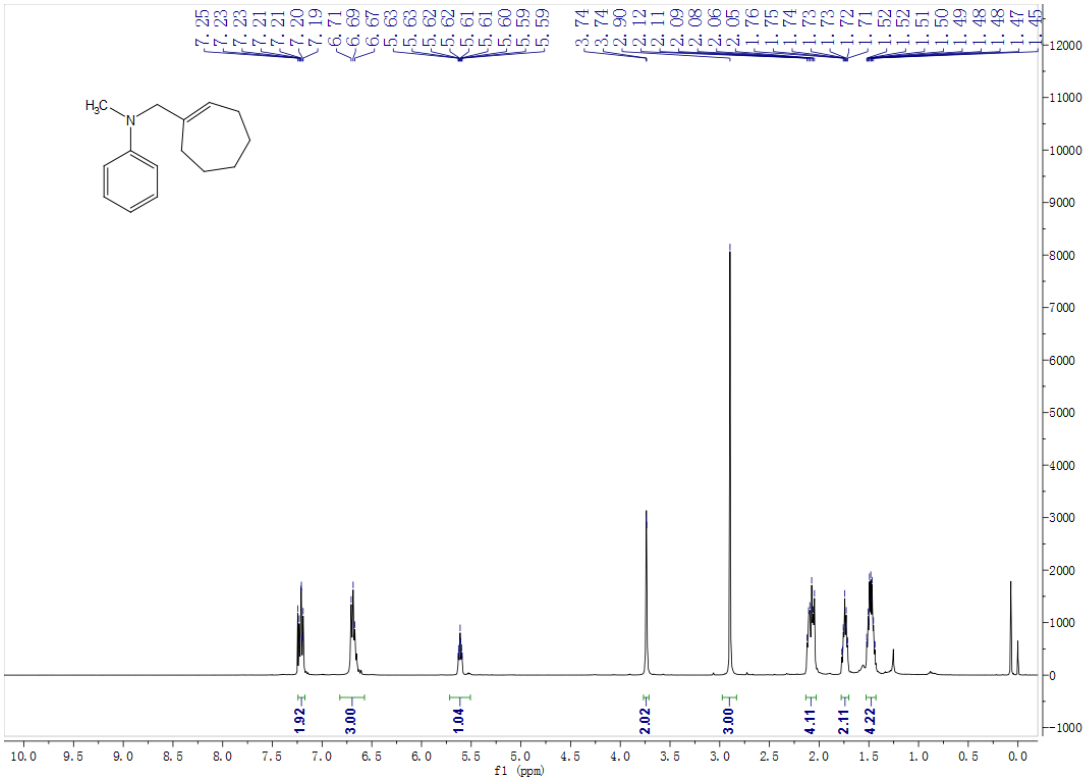

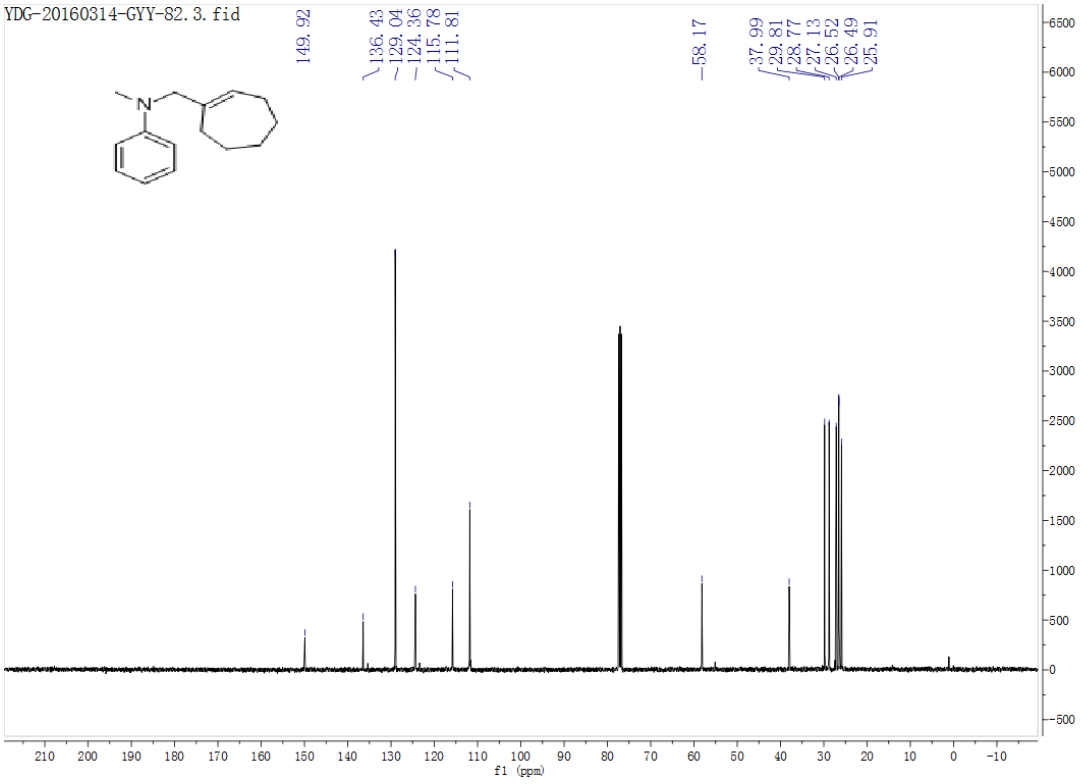

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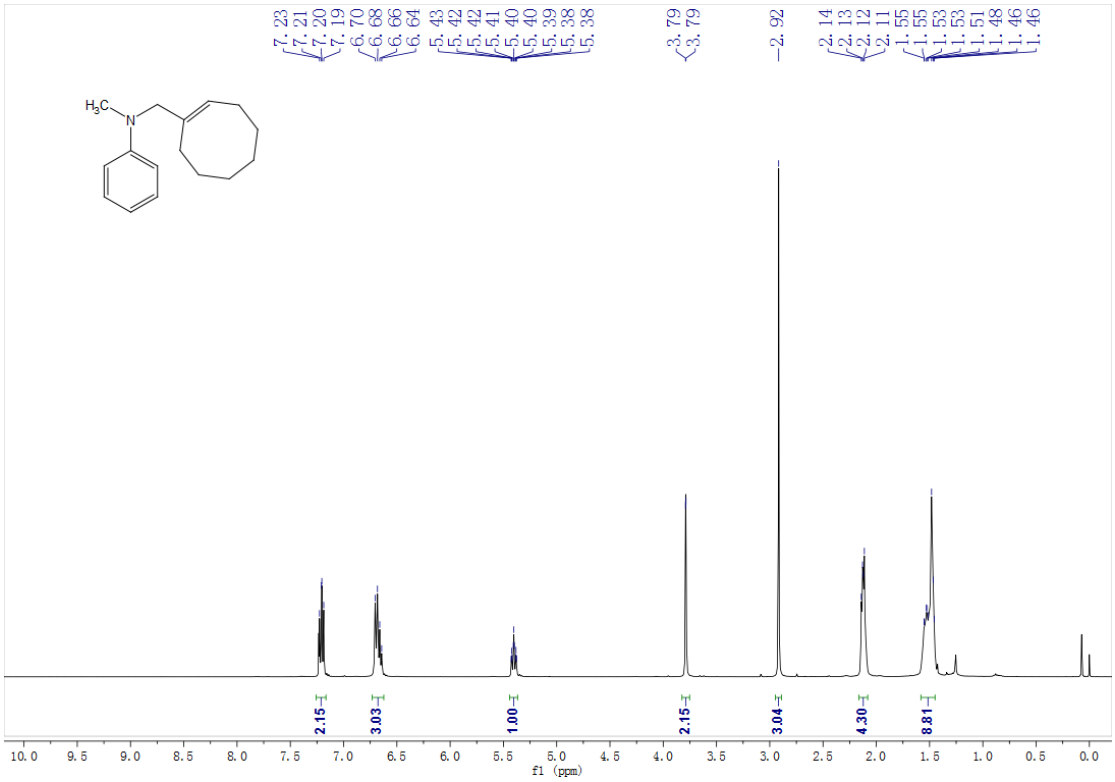

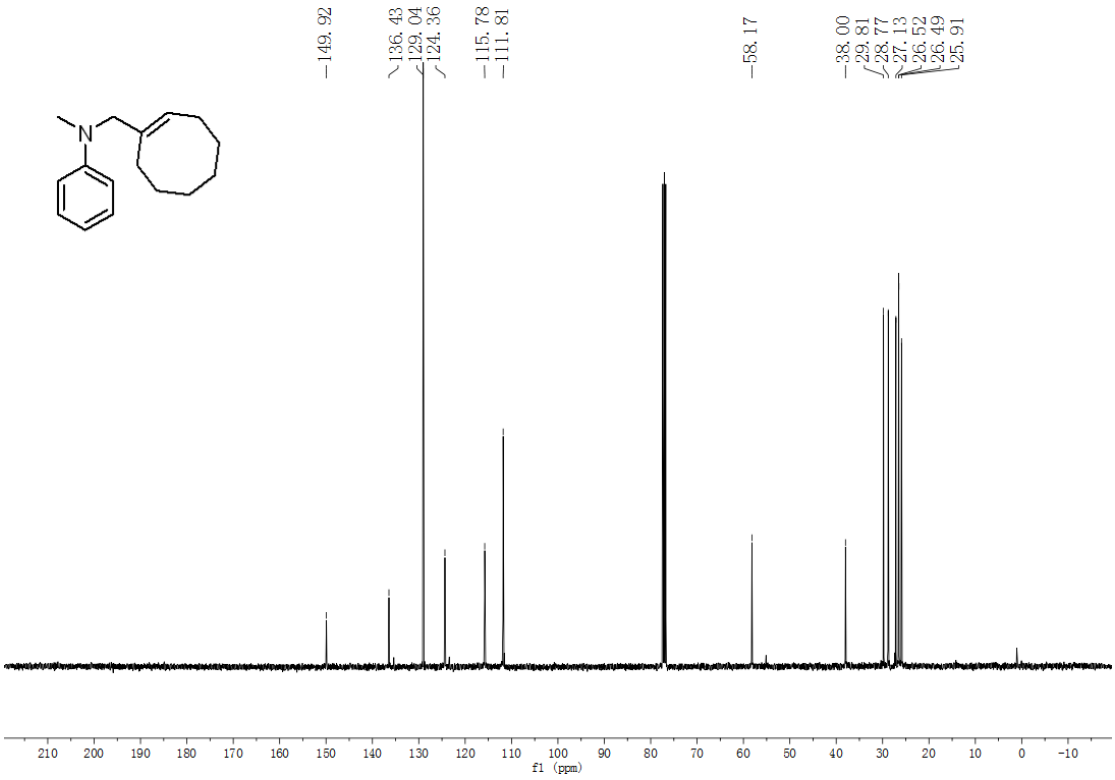

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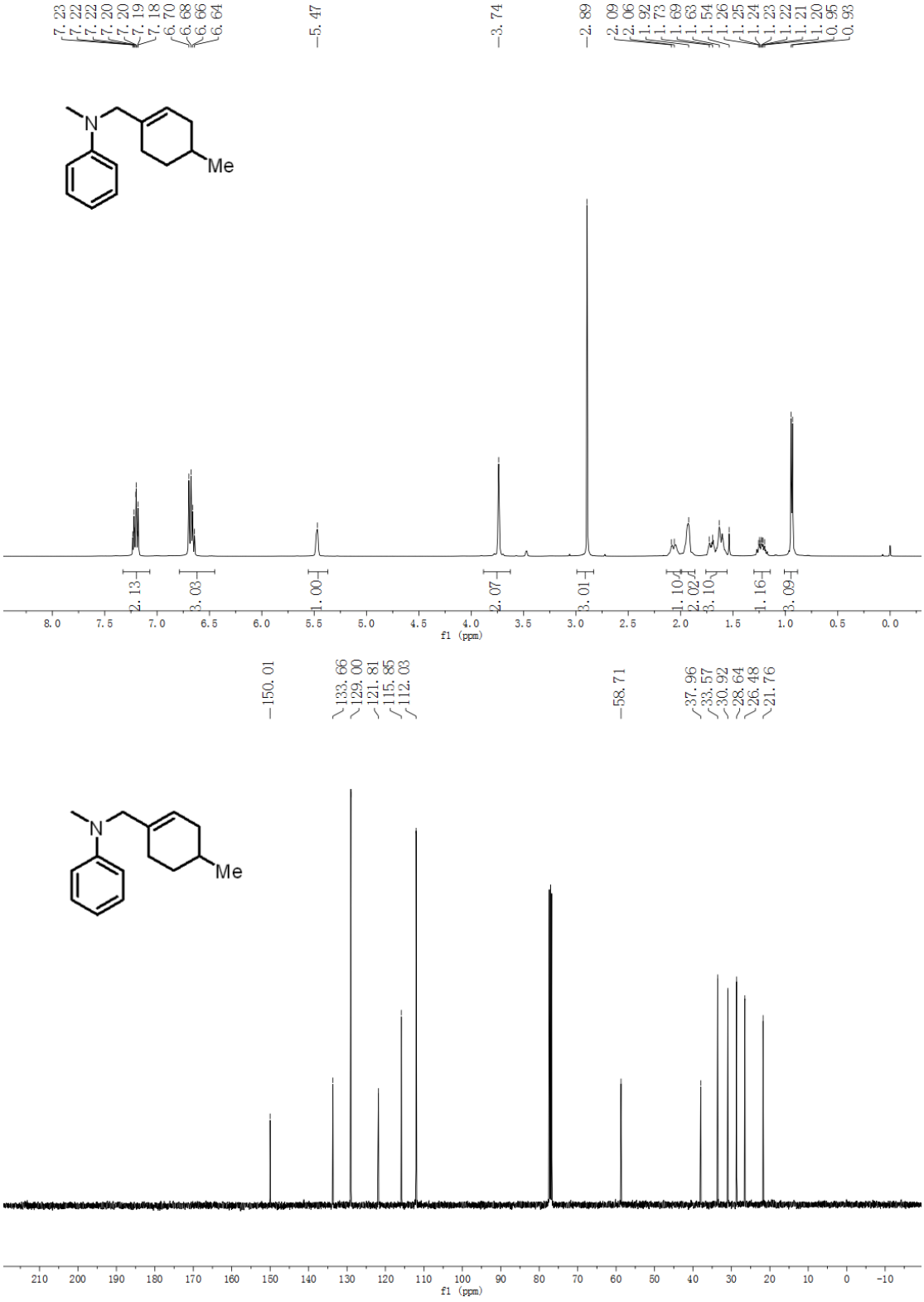

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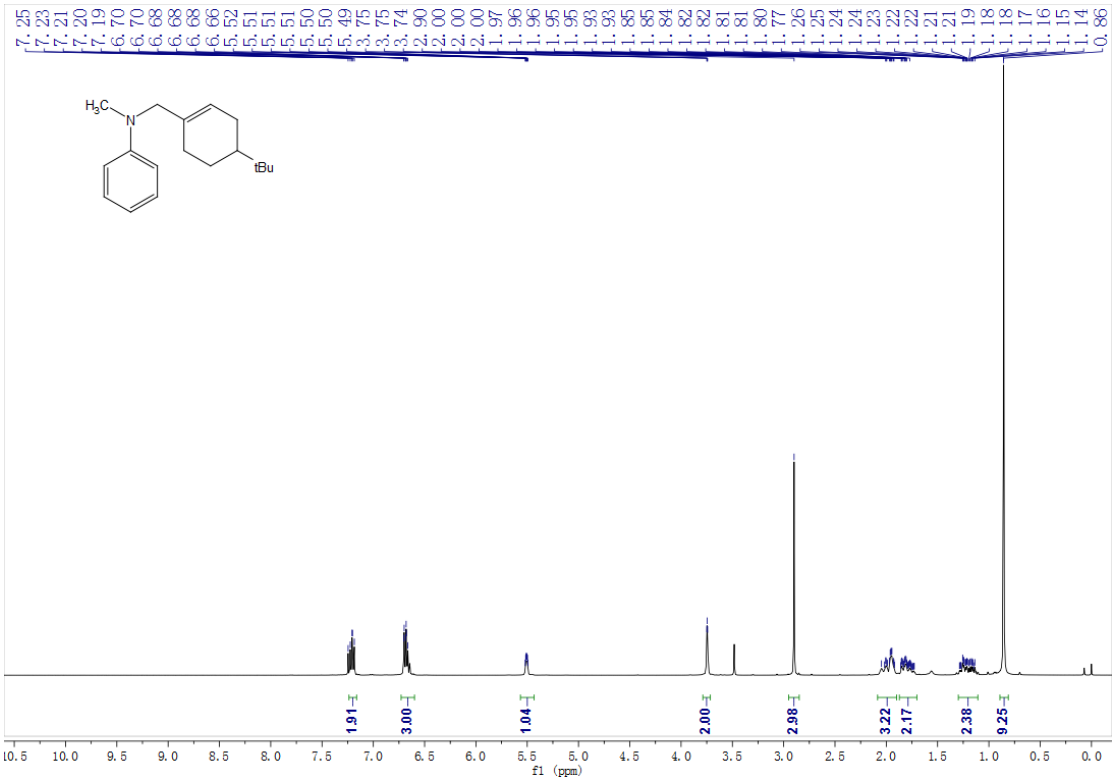

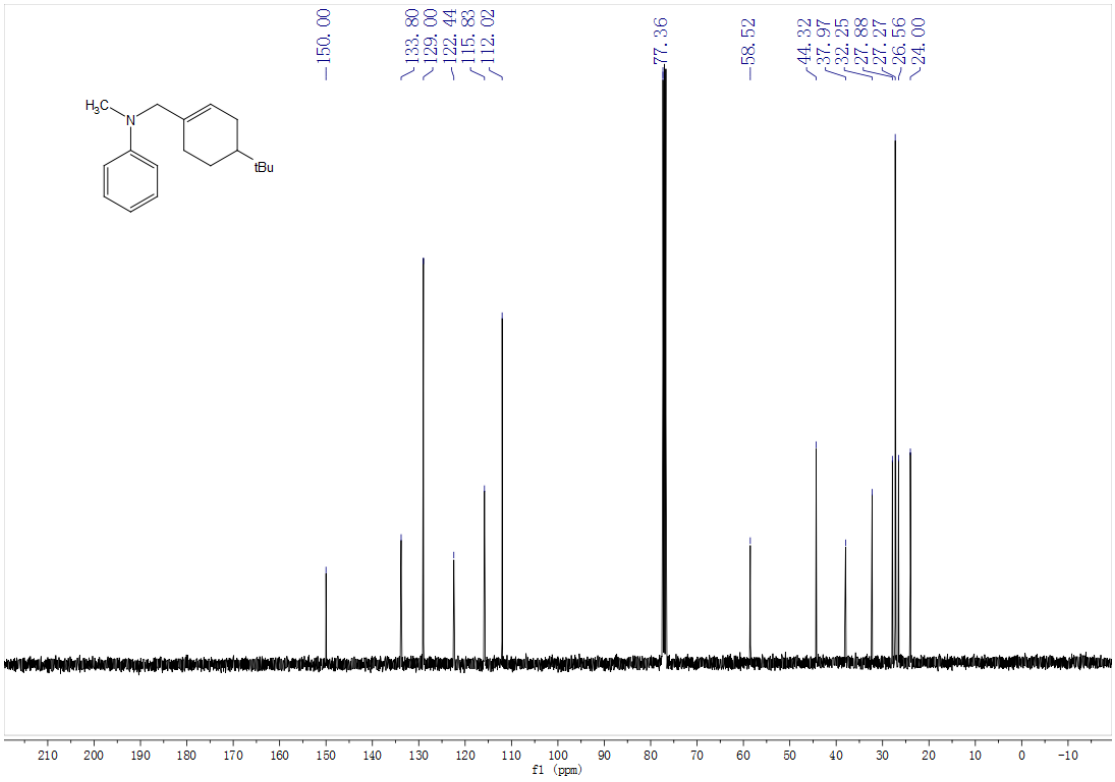

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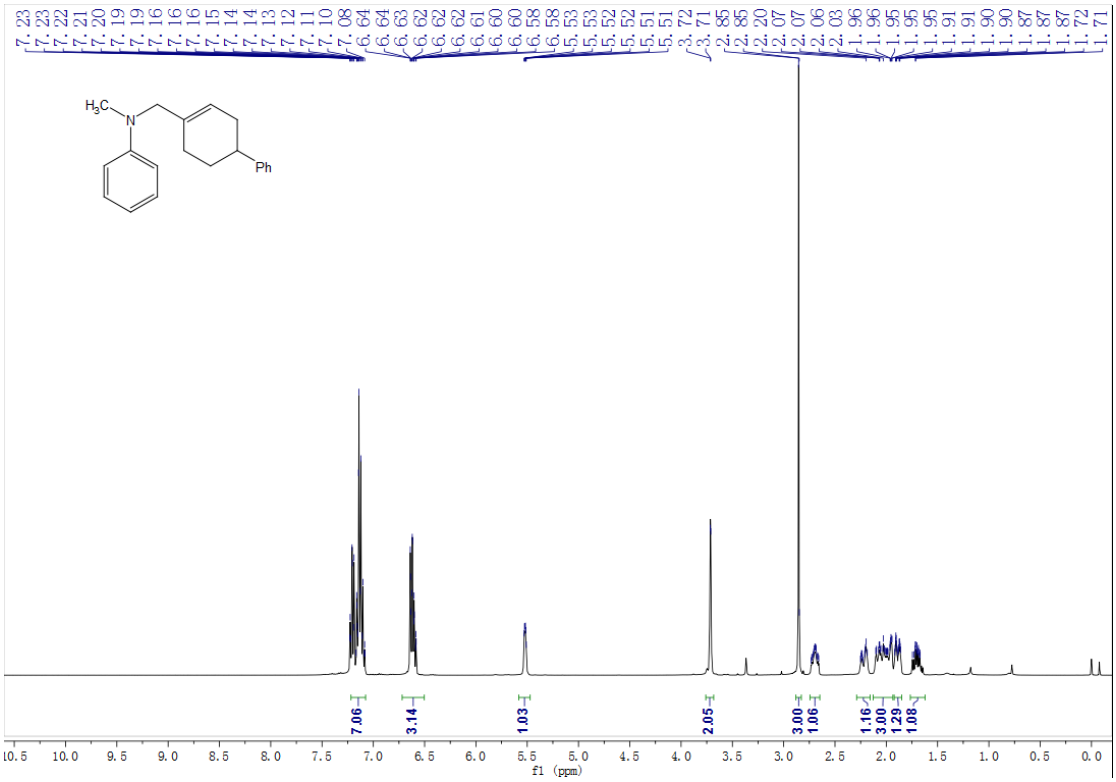

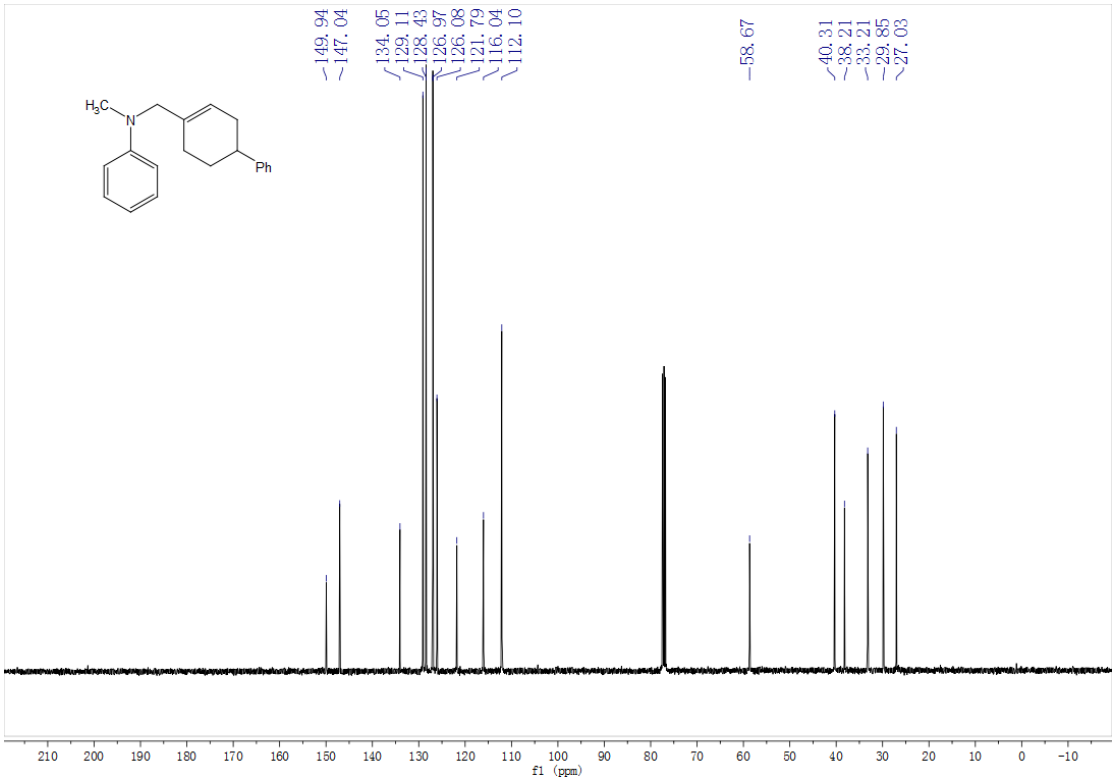

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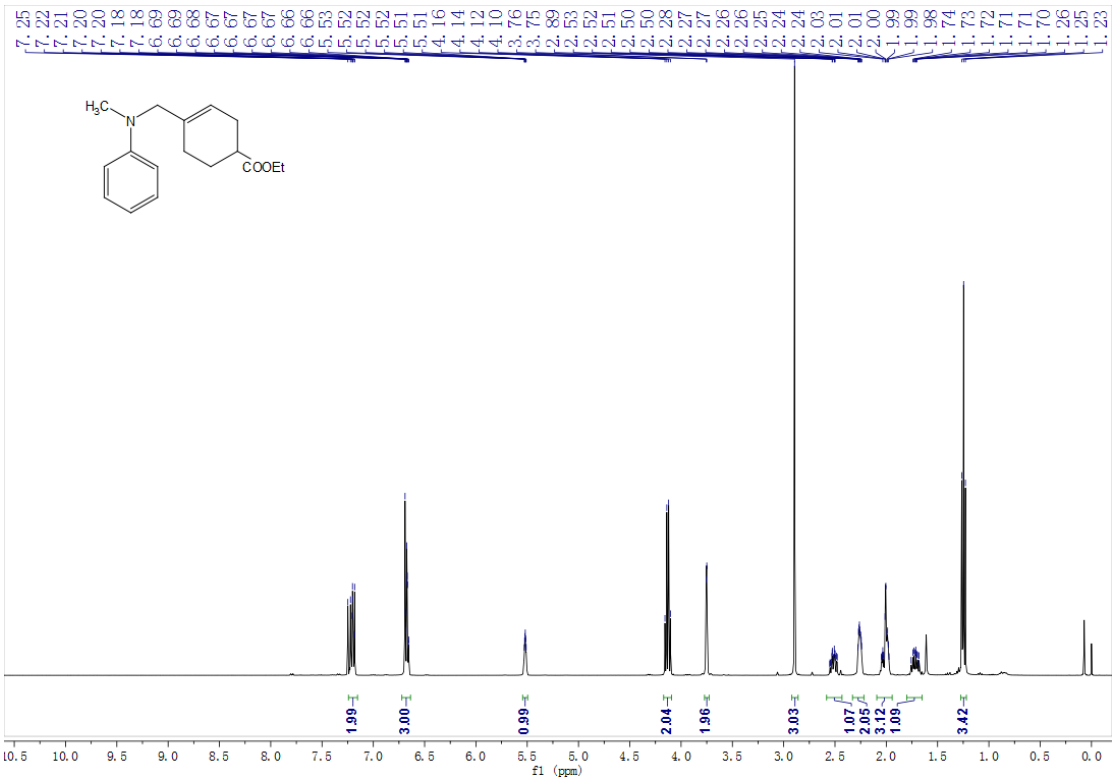

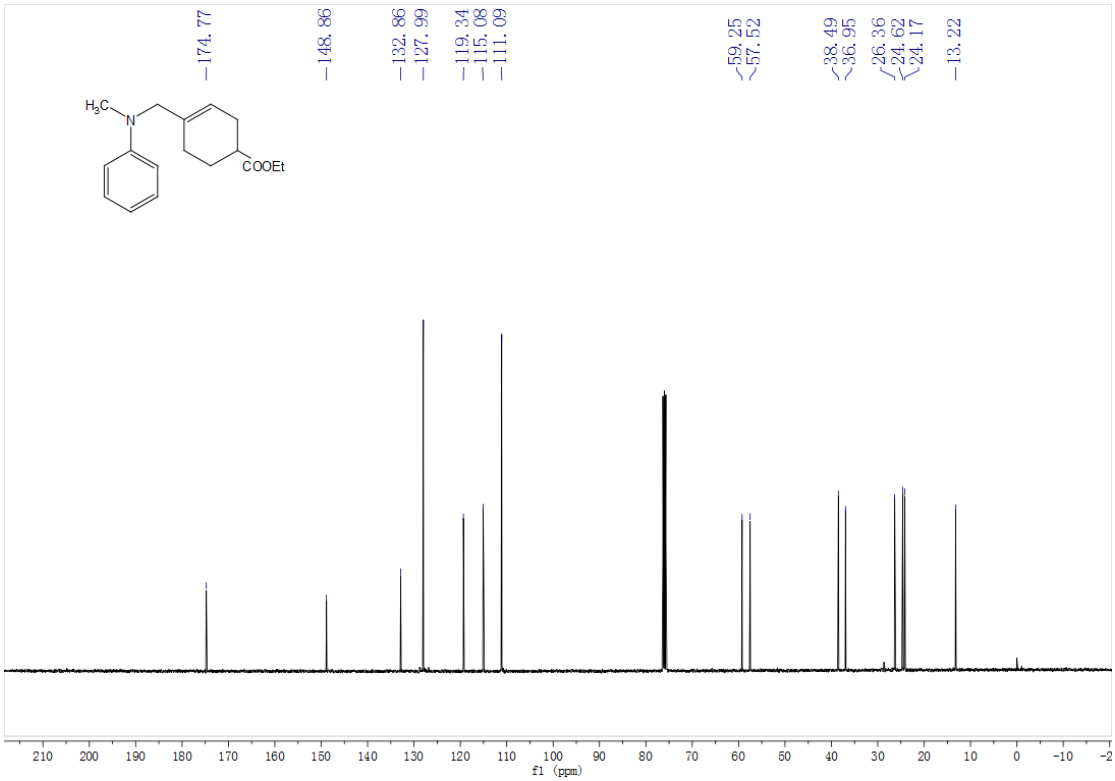

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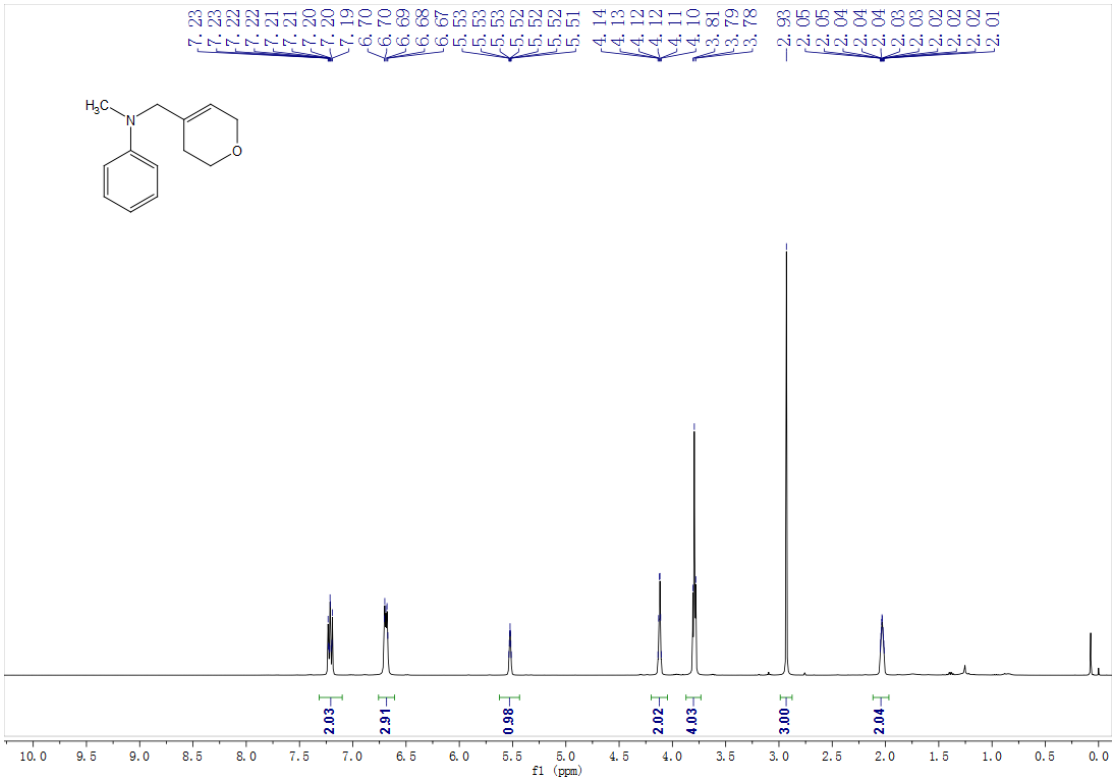

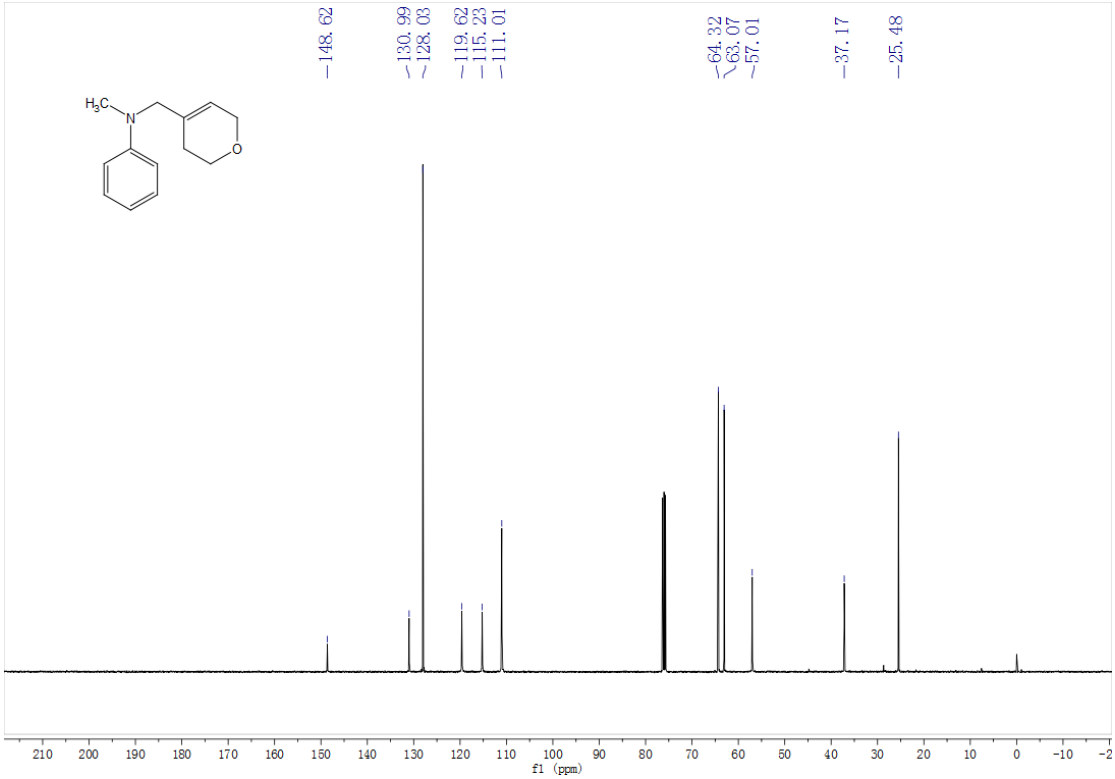

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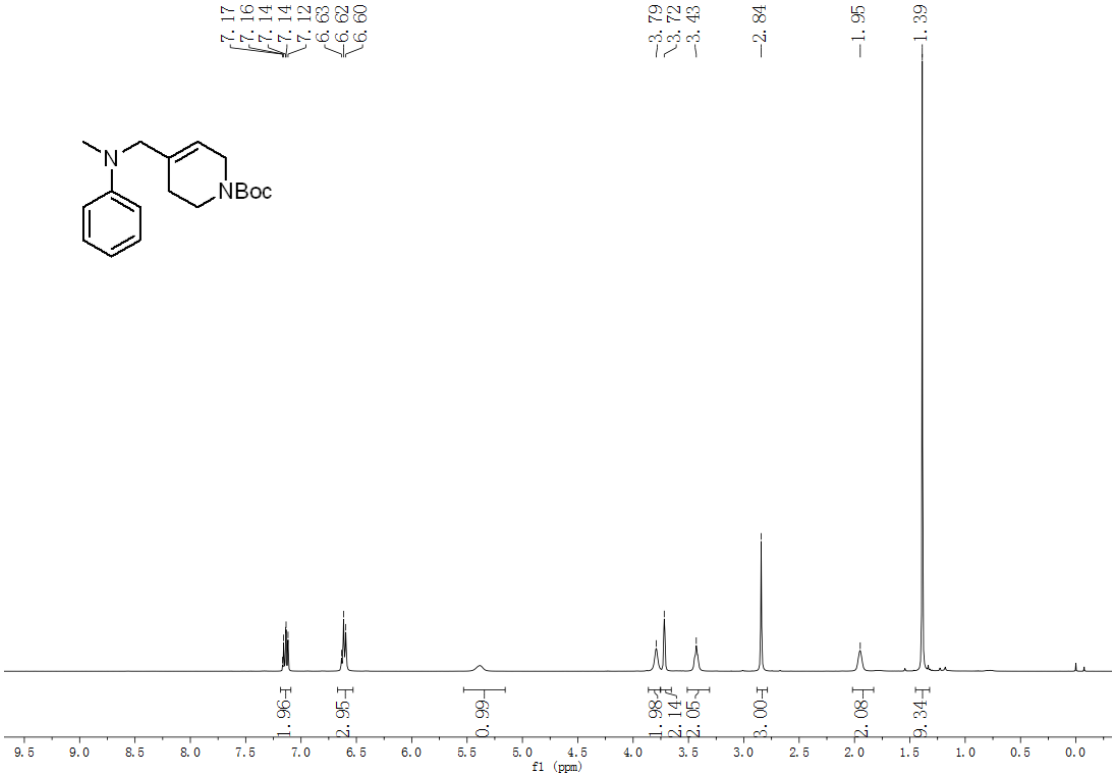

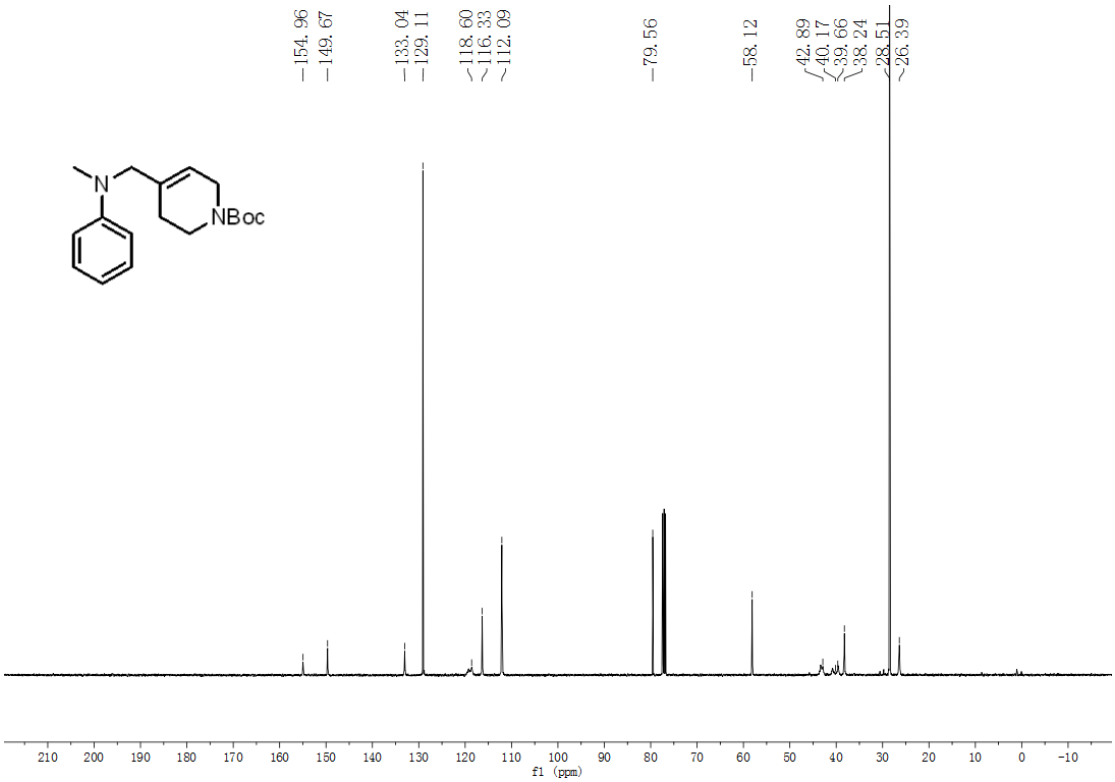

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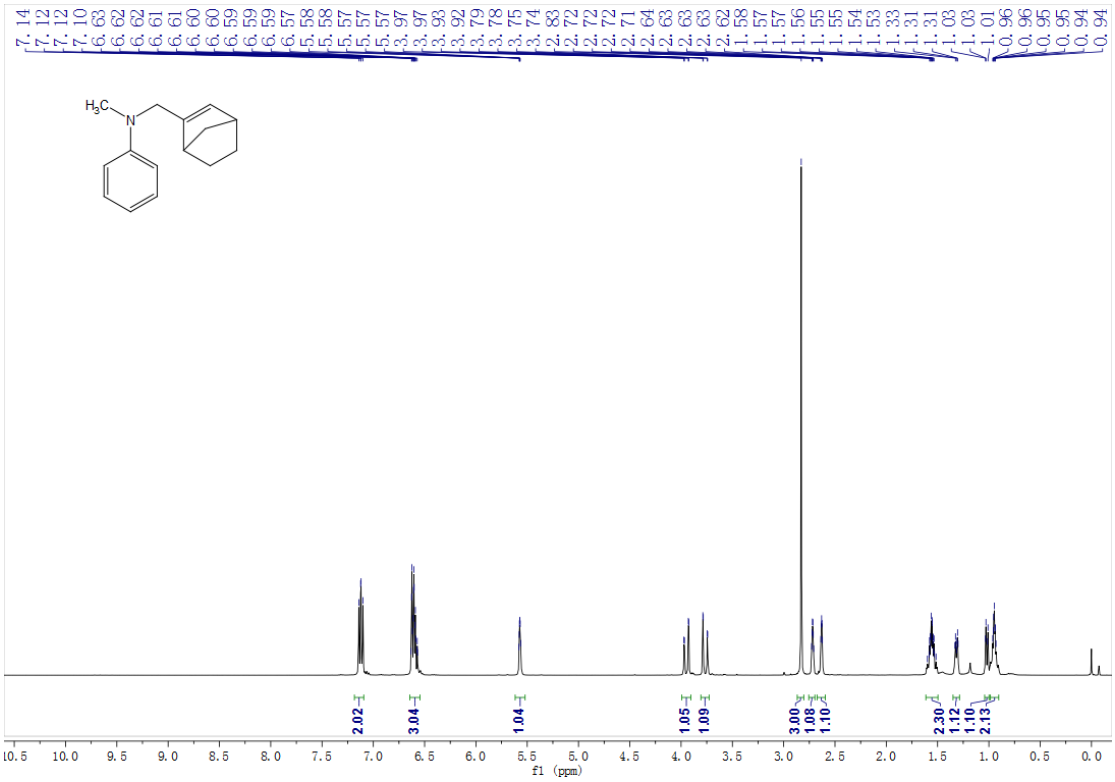

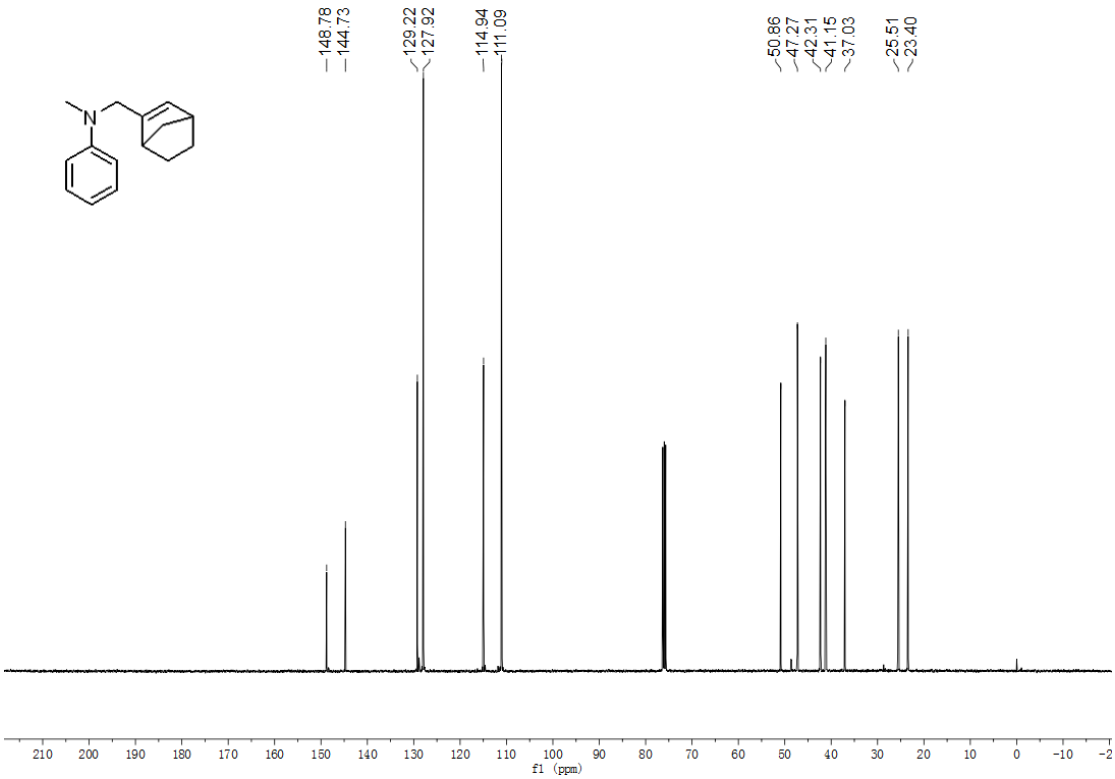

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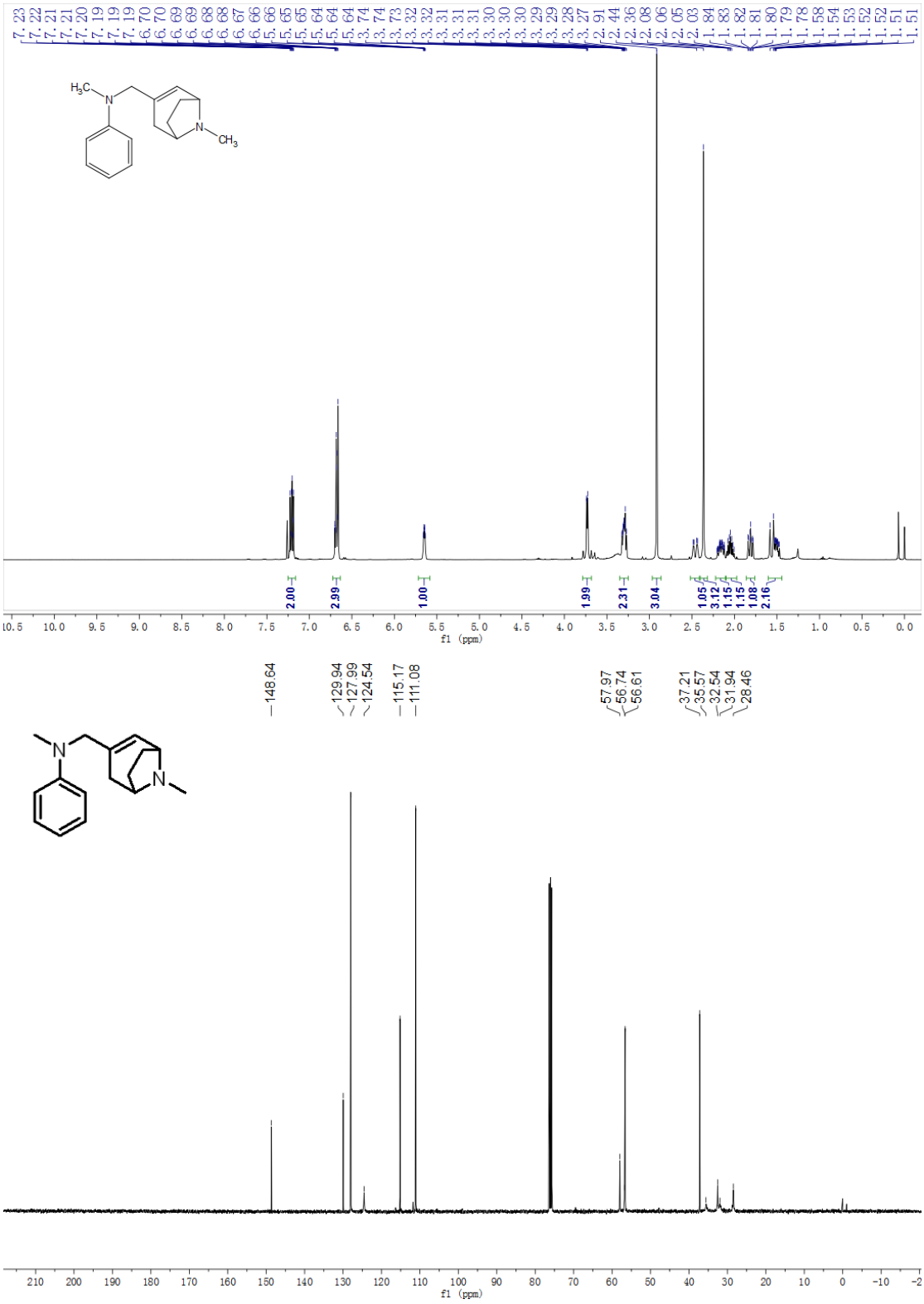
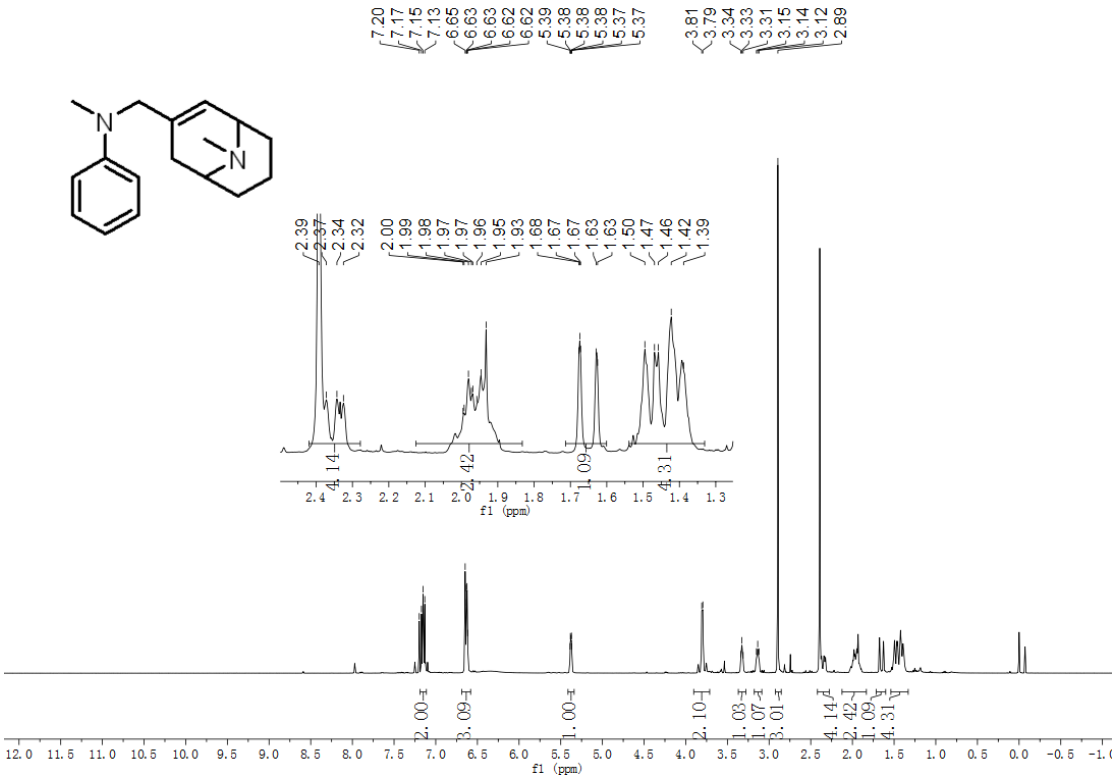
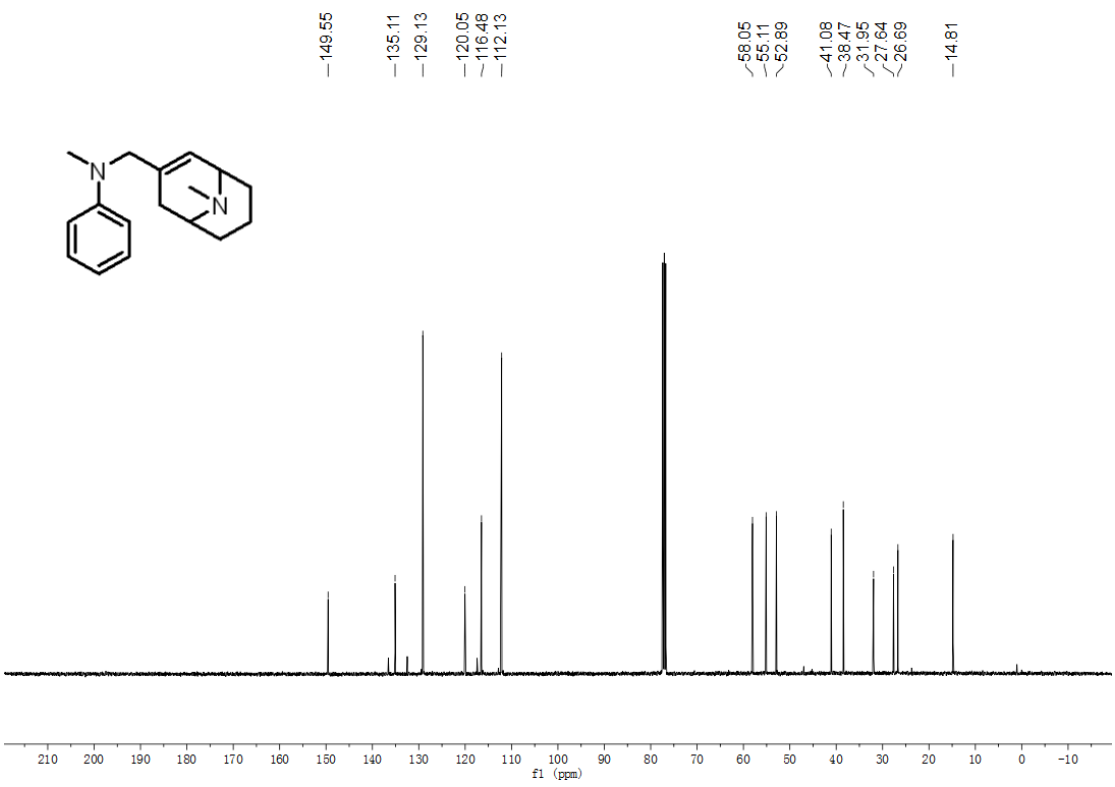
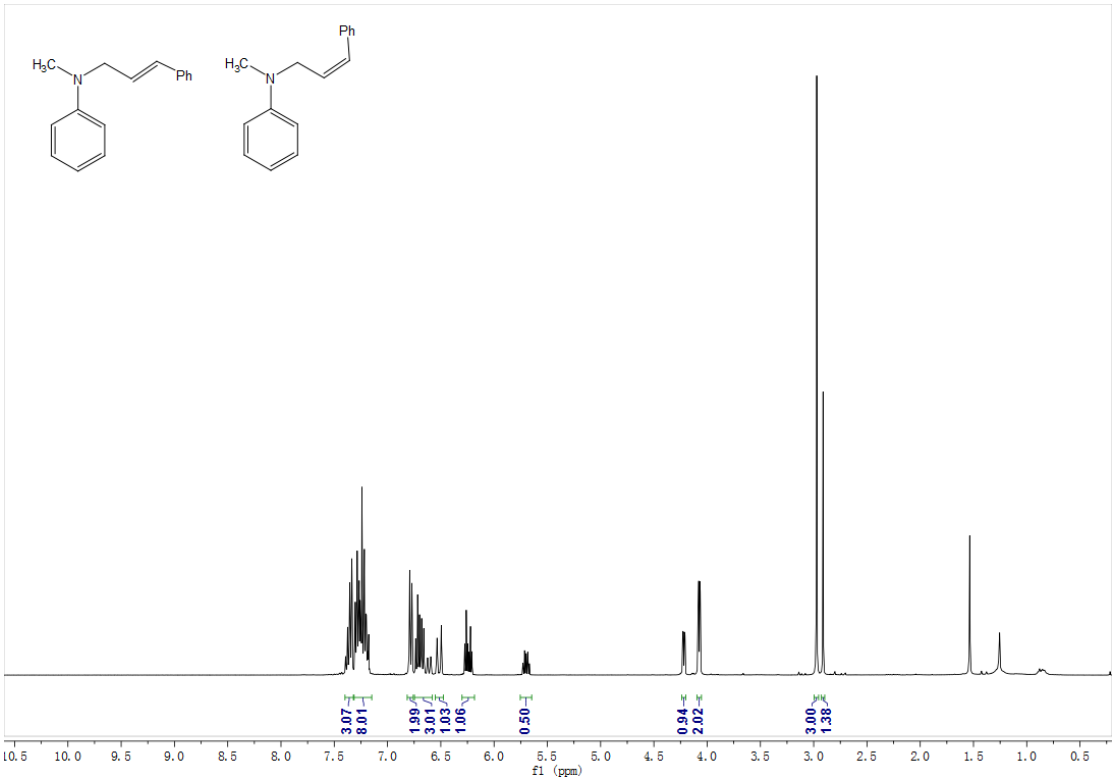


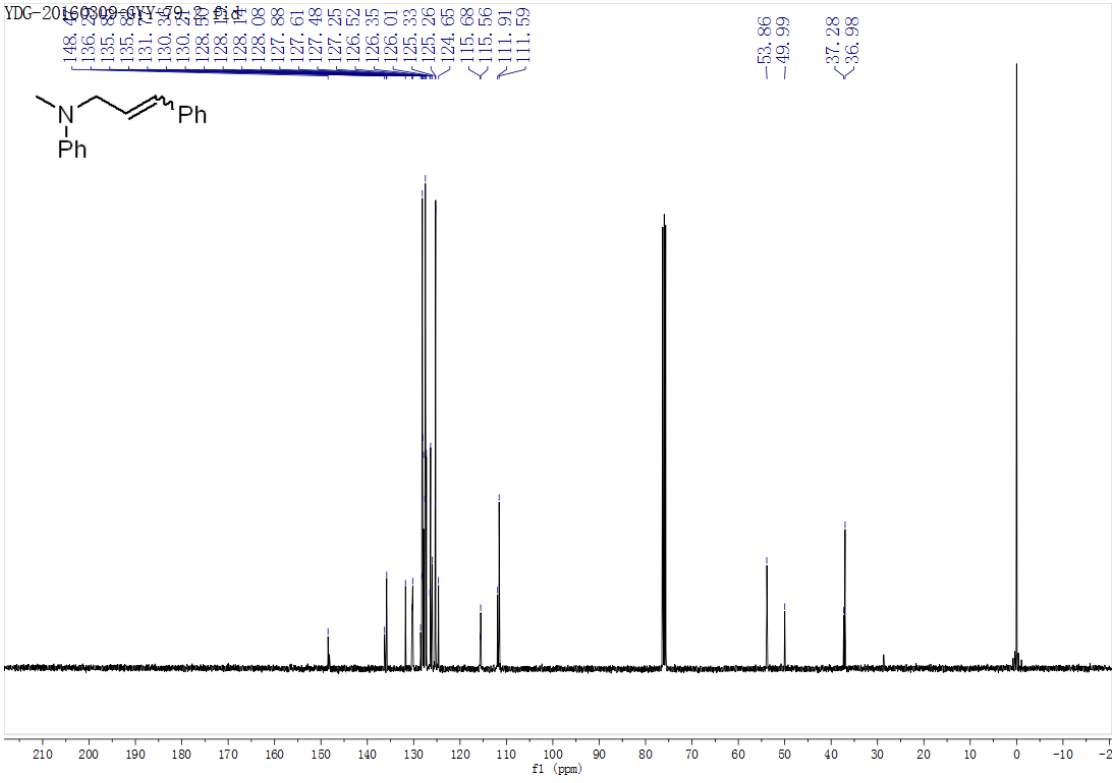
N-methyl-N-((9-methyl-9-azabicyclo[3.3.1]non-3-en-3-yl)methyl)aniline (3ar)



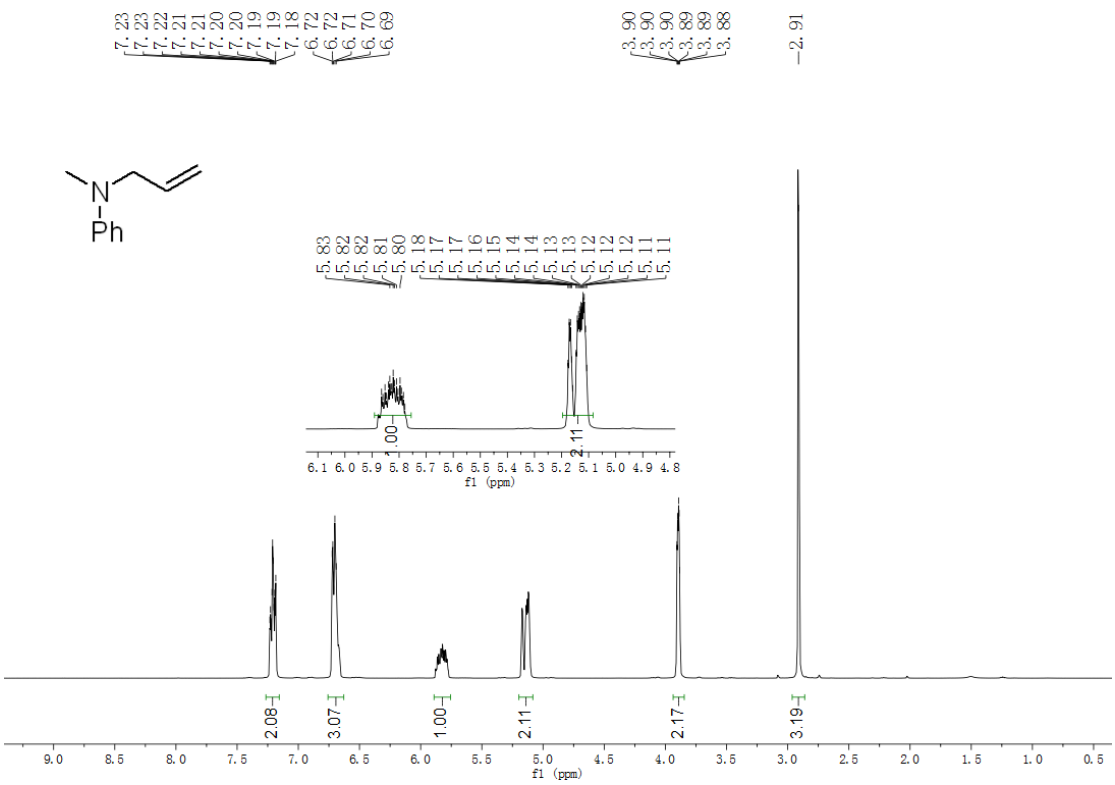


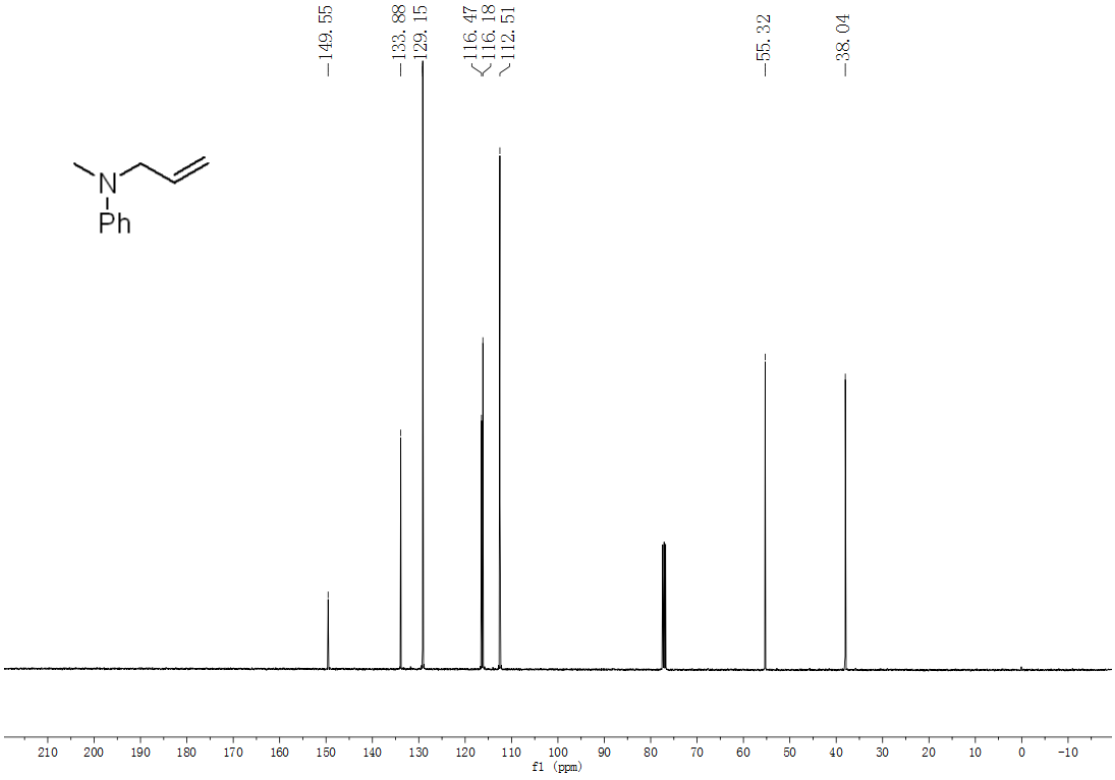
N-methyl-N-(3-phenylallyl)aniline (3as)



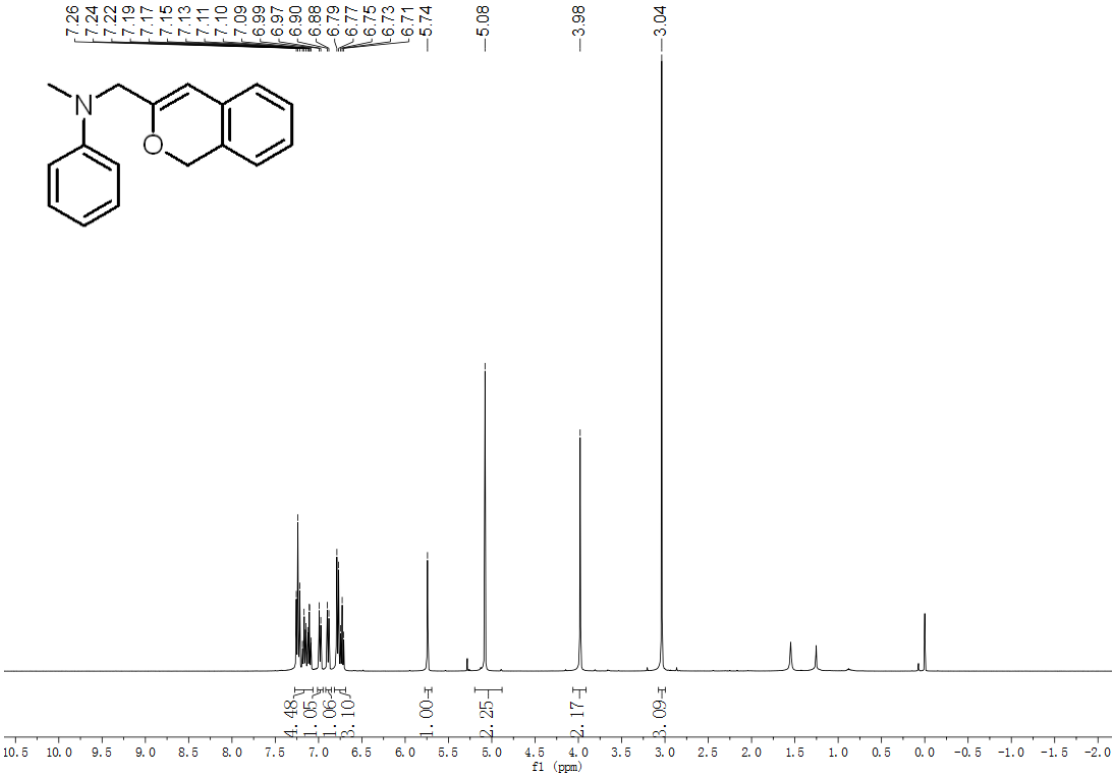


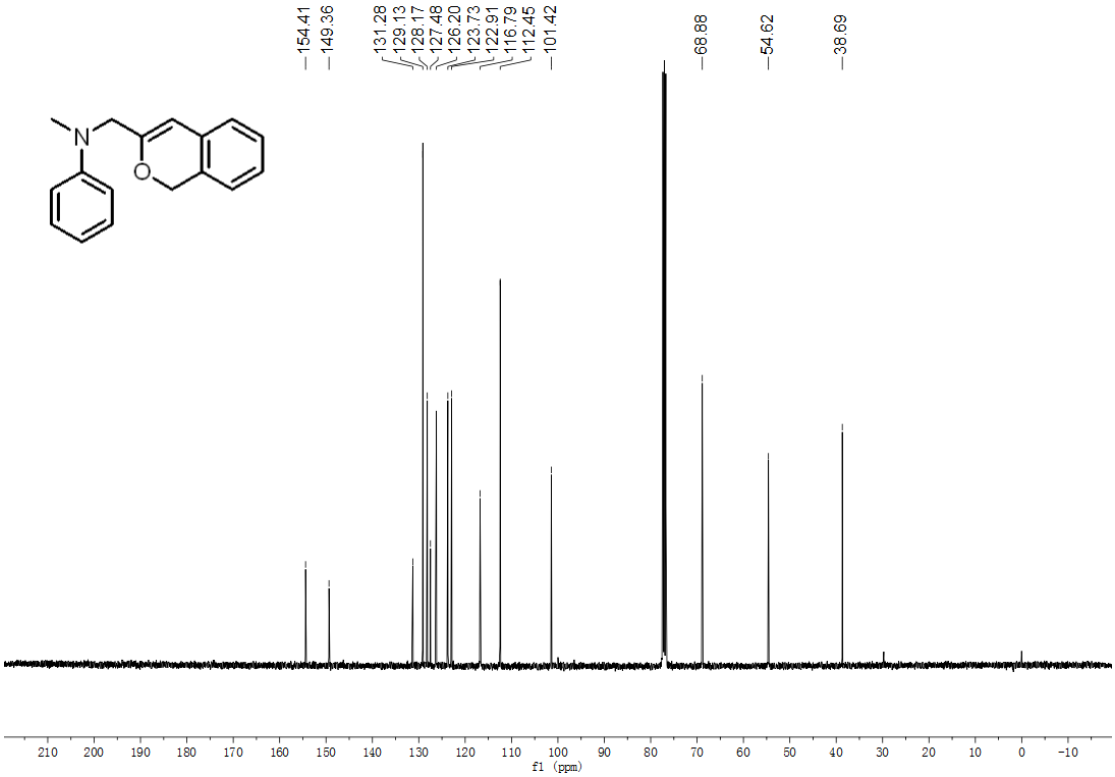
N-allyl-N-methylaniline (3at)





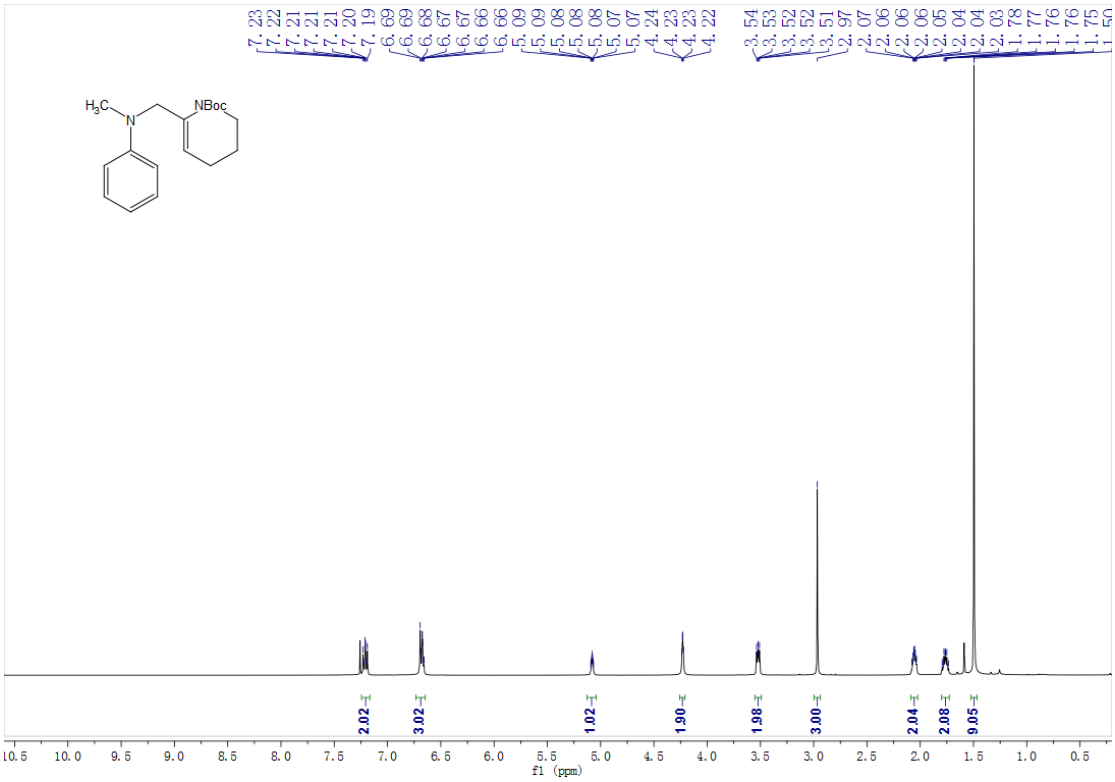
N-((1H-isochromen-3-yl)methyl)-N-methylaniline(3au)

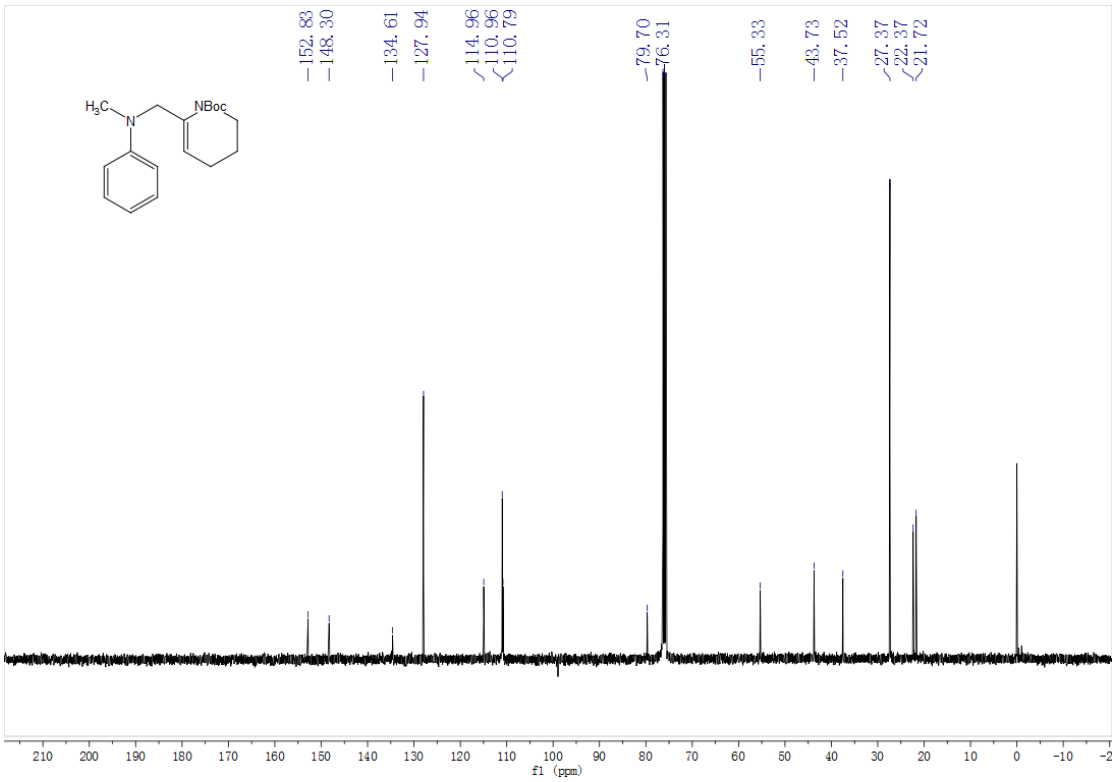




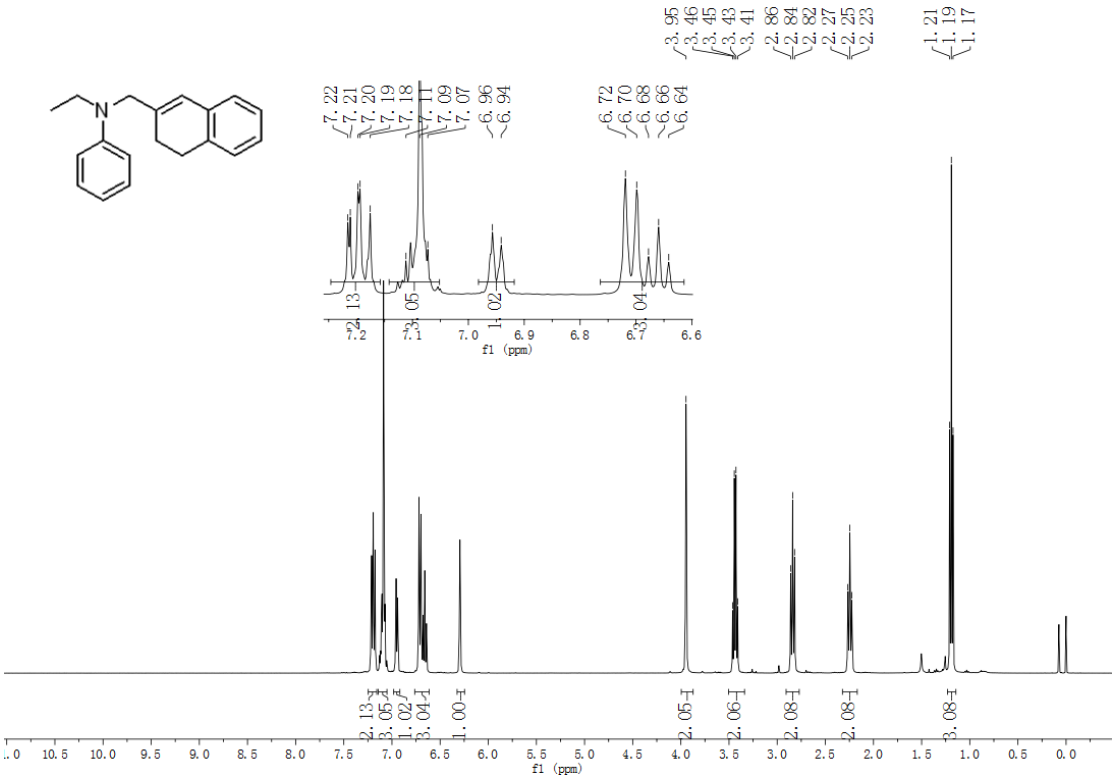
tert-butyl 6-((methyl(phenyl)amino)methyl)-3,4-dihydropyridine-1(2H)

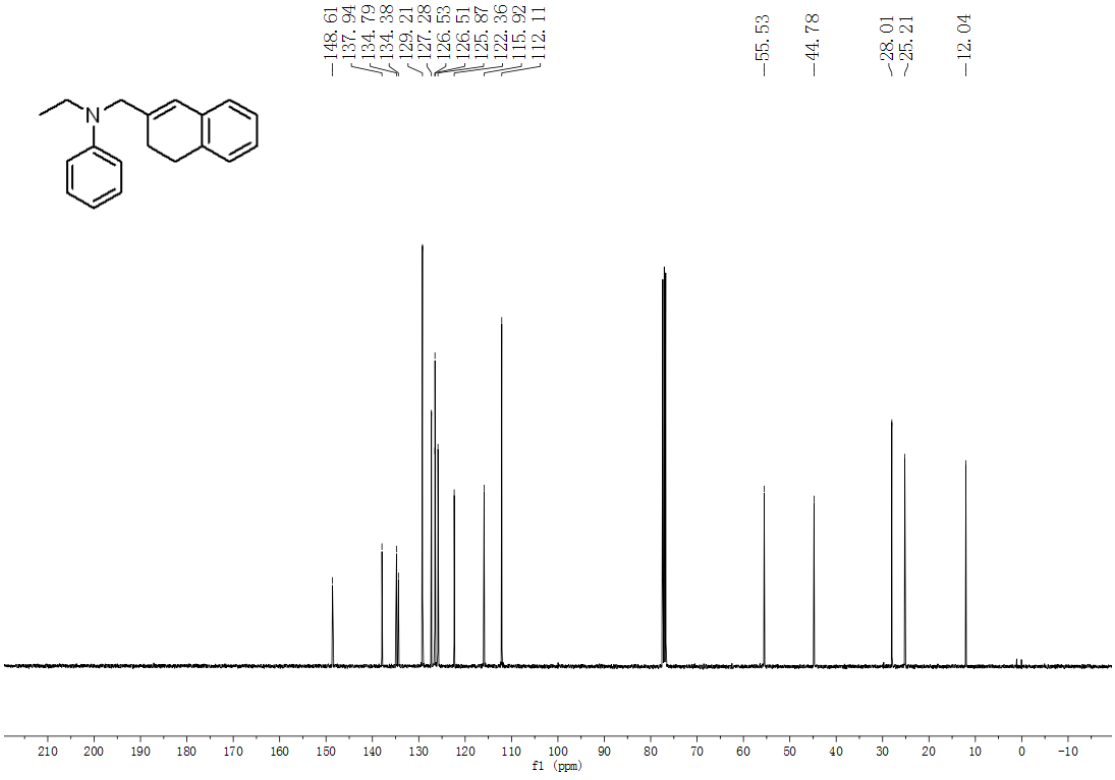
-carboxylate (3aw)



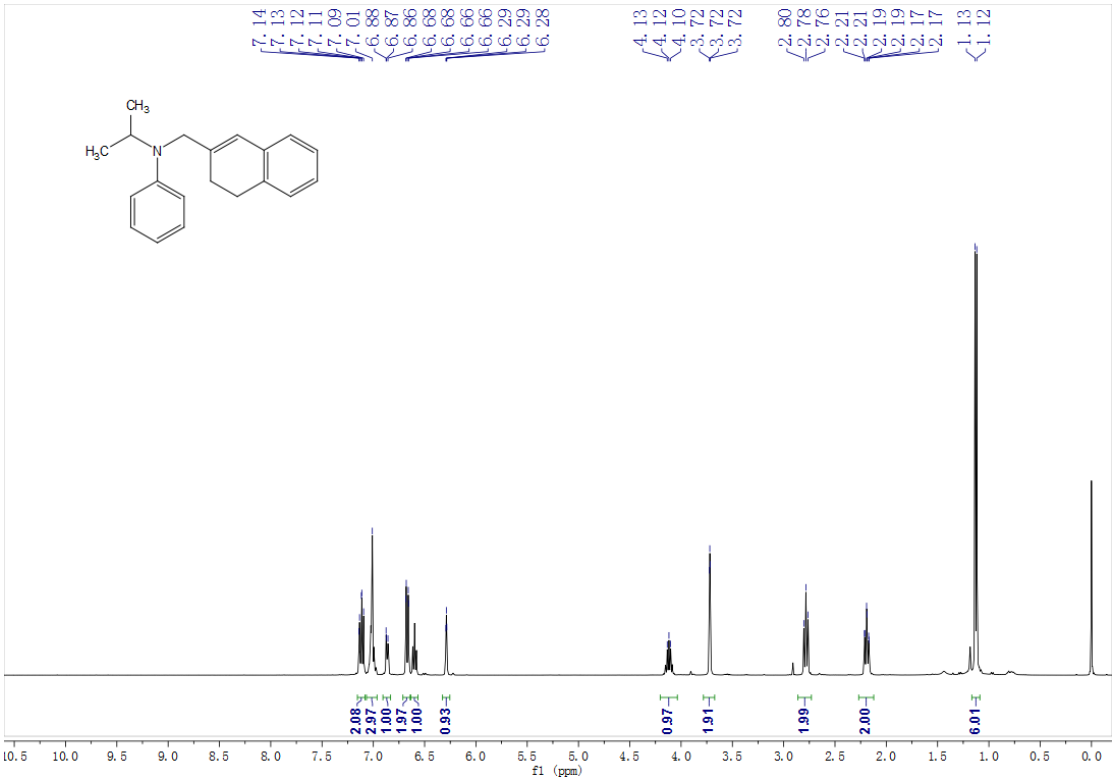


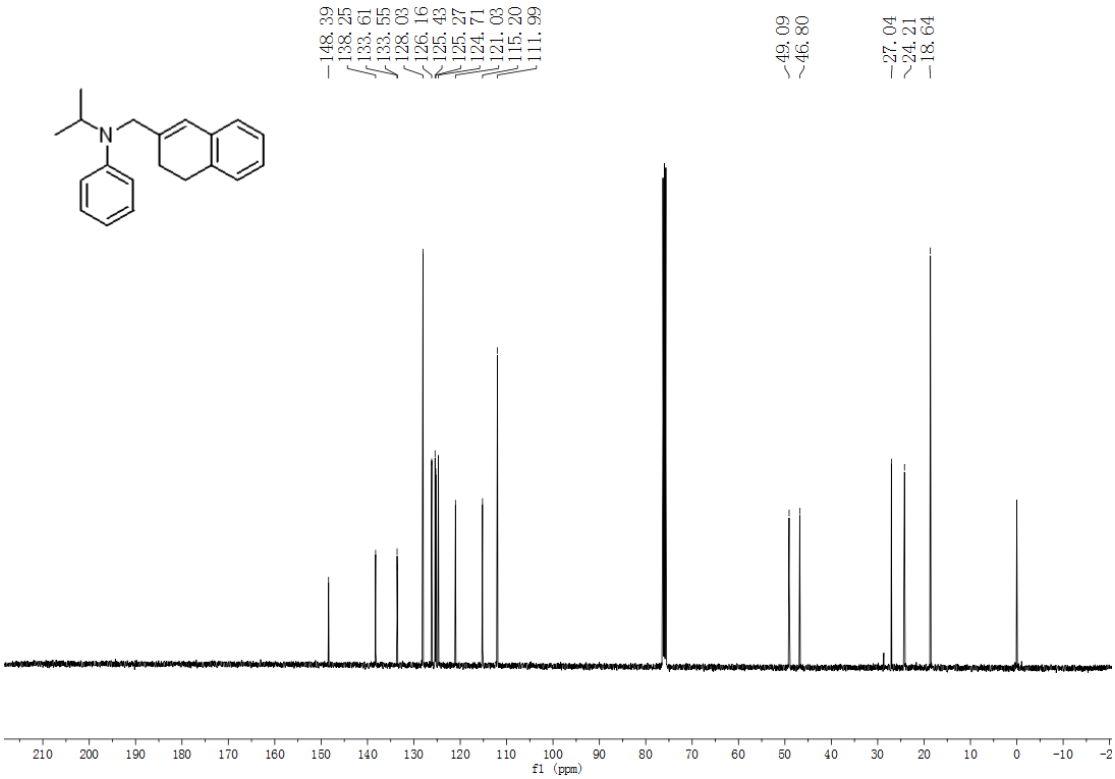
N-((3,4-dihydronaphthalen-2-yl)methyl)-N-ethylaniline (3ba)



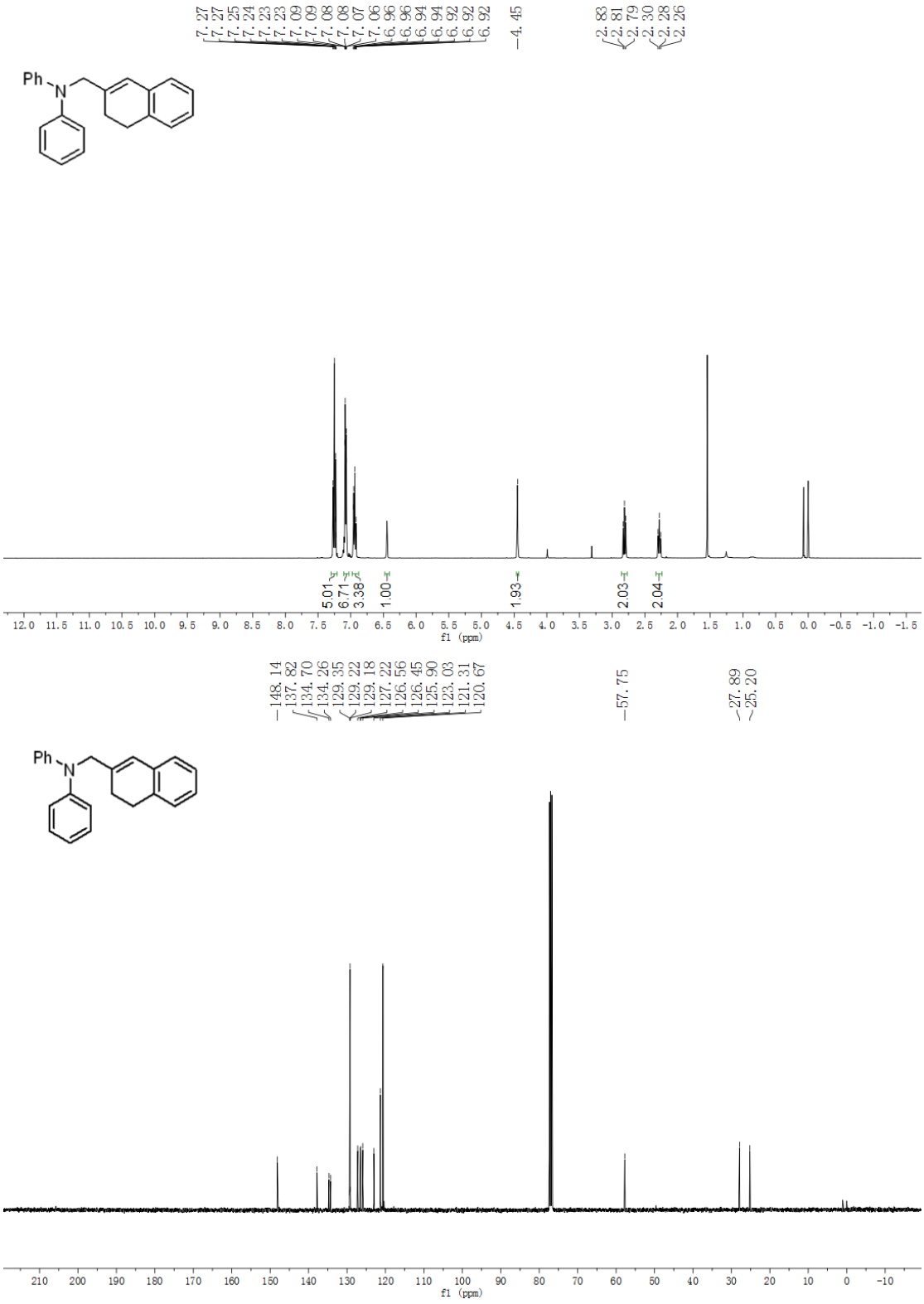


N-((3,4-dihydronaphthalen-2-yl)methyl)-N-isopropylaniline (3ca)

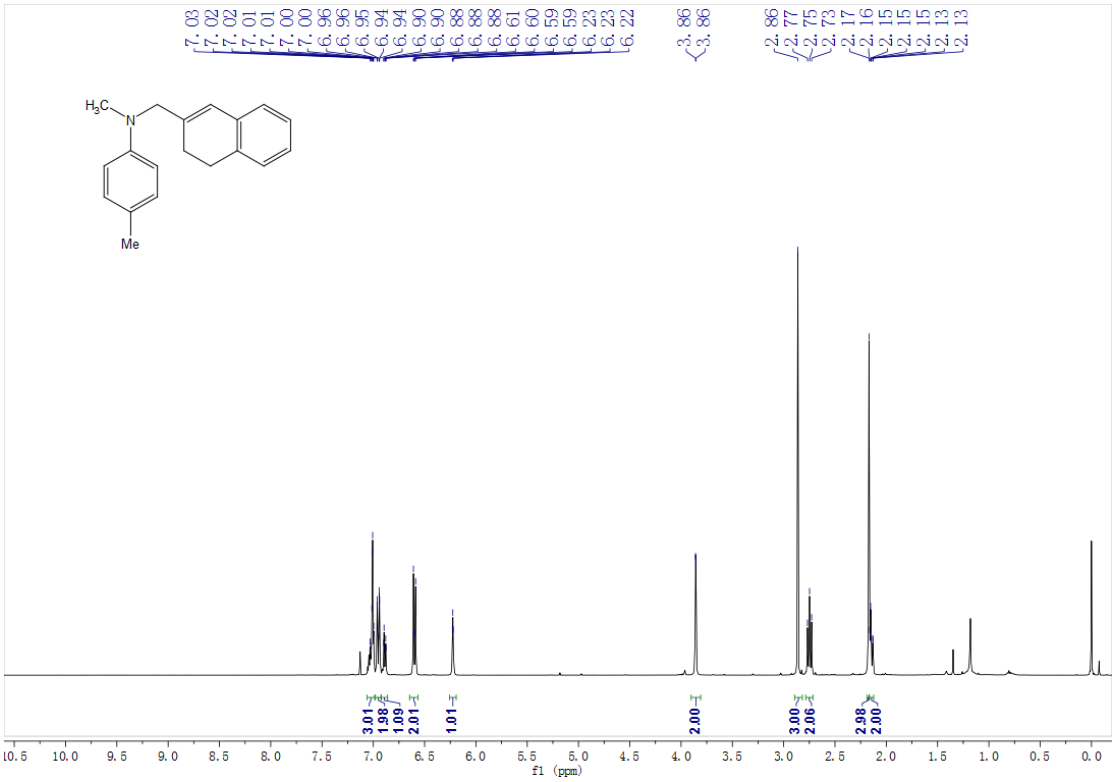


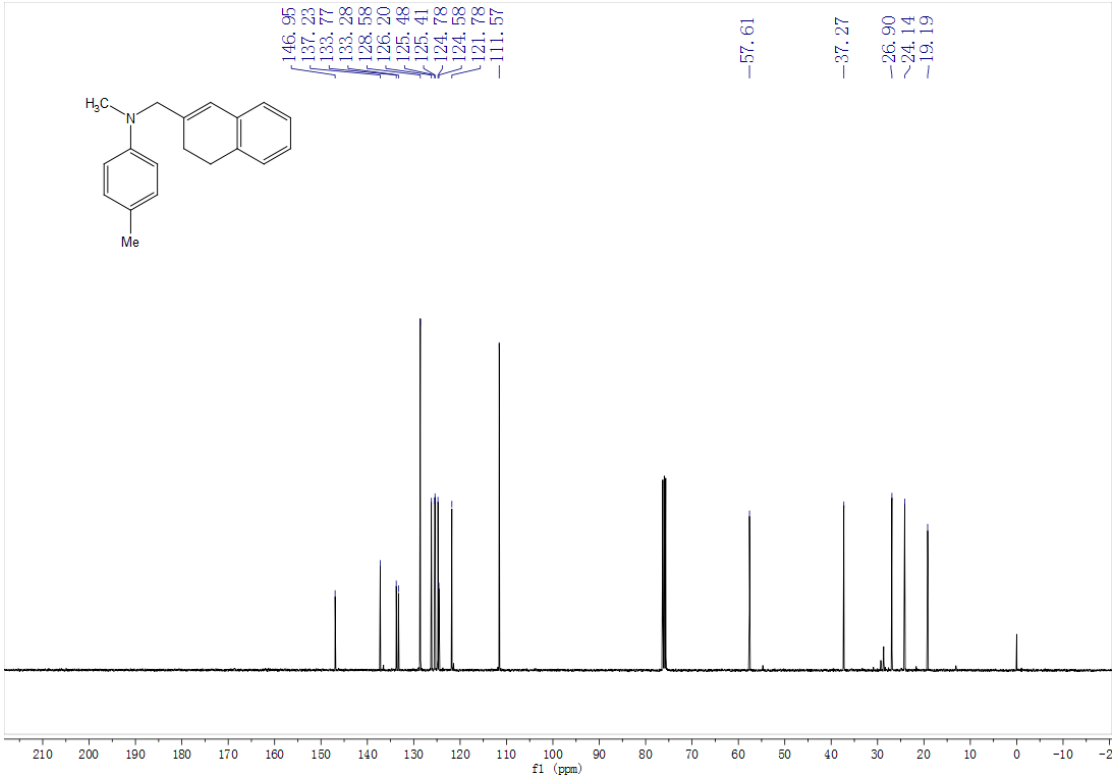


N-((3,4-dihydronaphthalen-2-yl)methyl)-N-phenylaniline (3da)

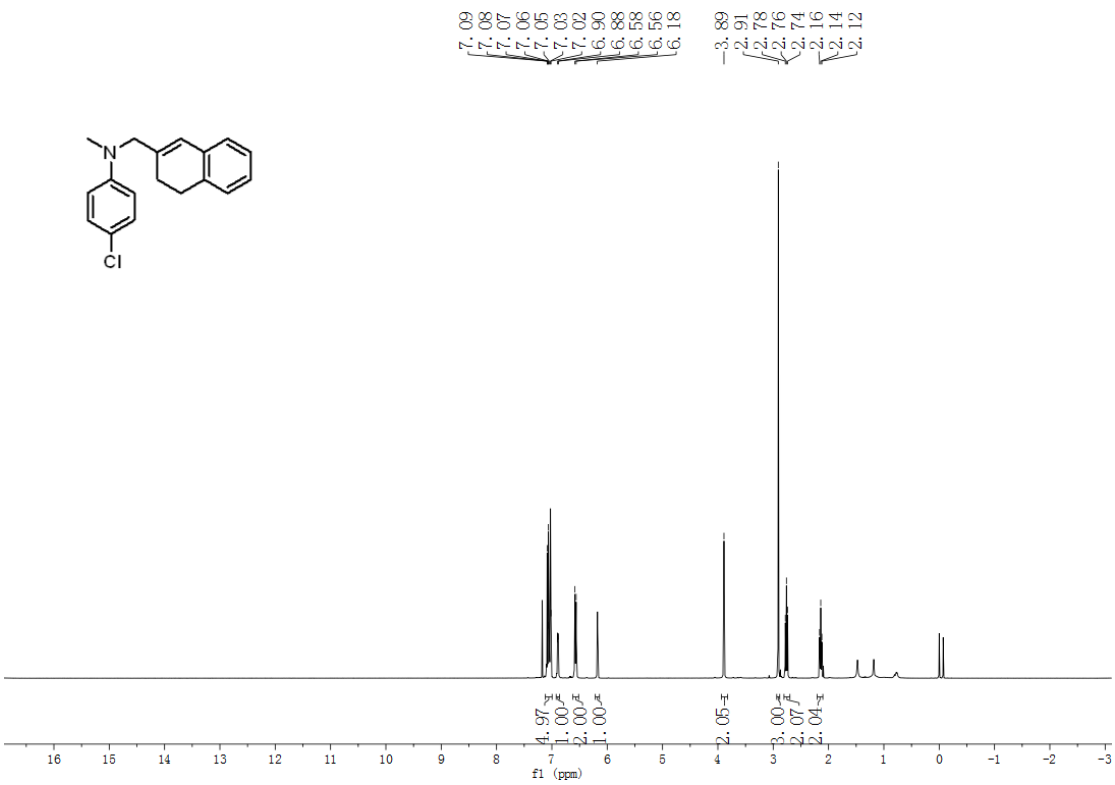


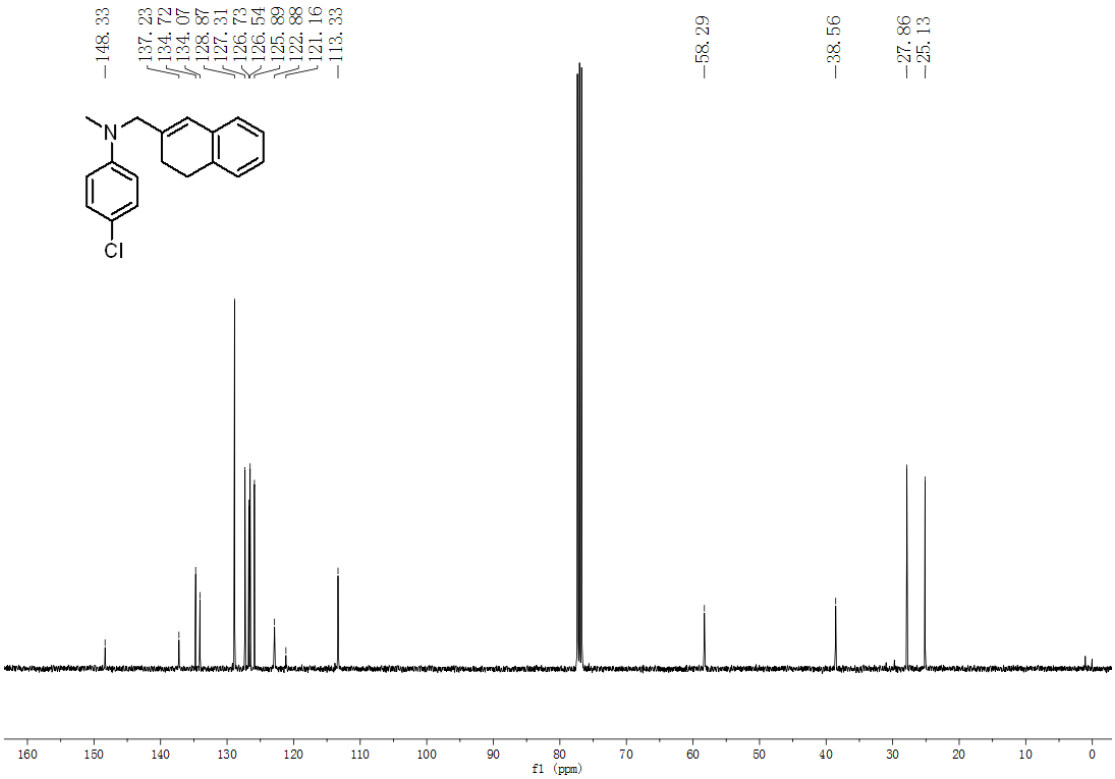
N-((3,4-dihydronaphthalen-2-yl)methyl)-N,4-dimethylaniline (3ea)



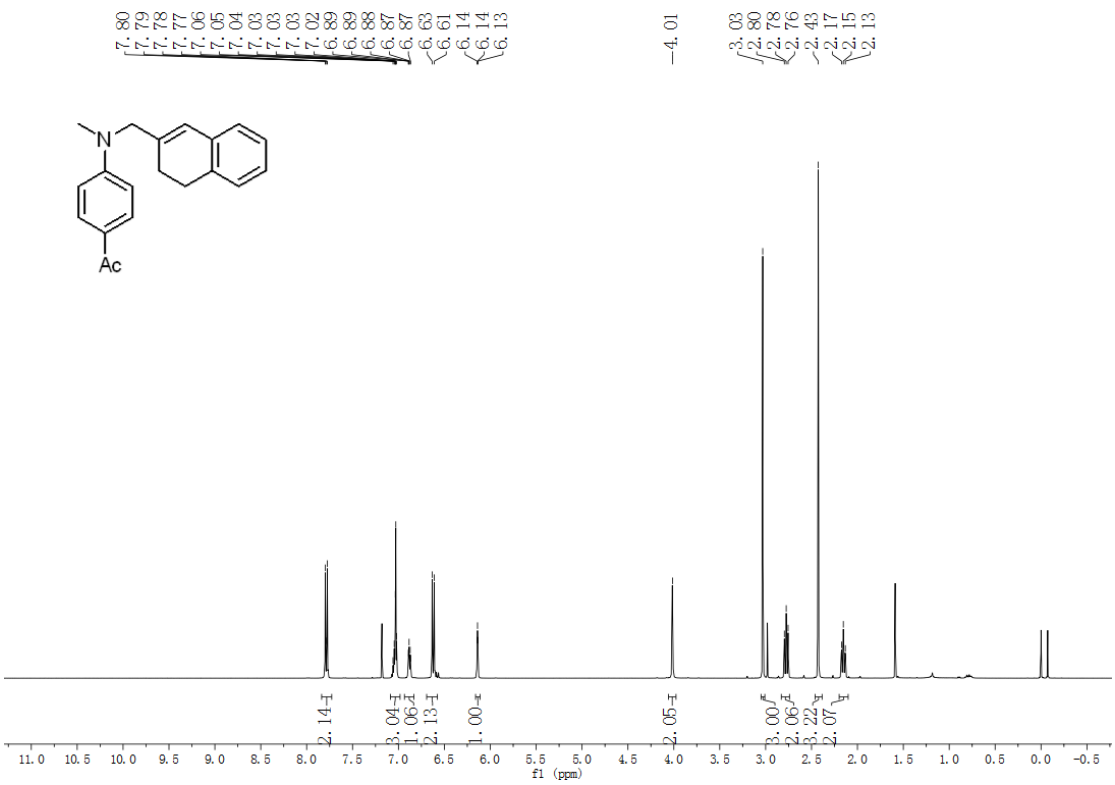


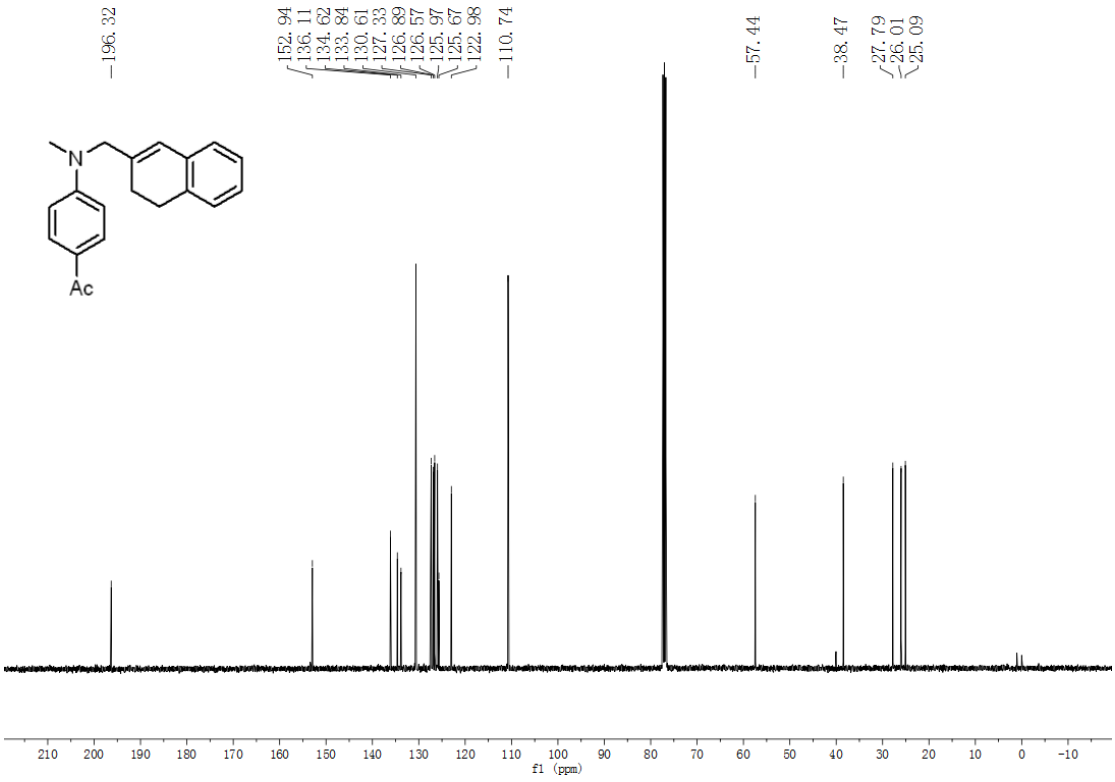
4-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3fa)



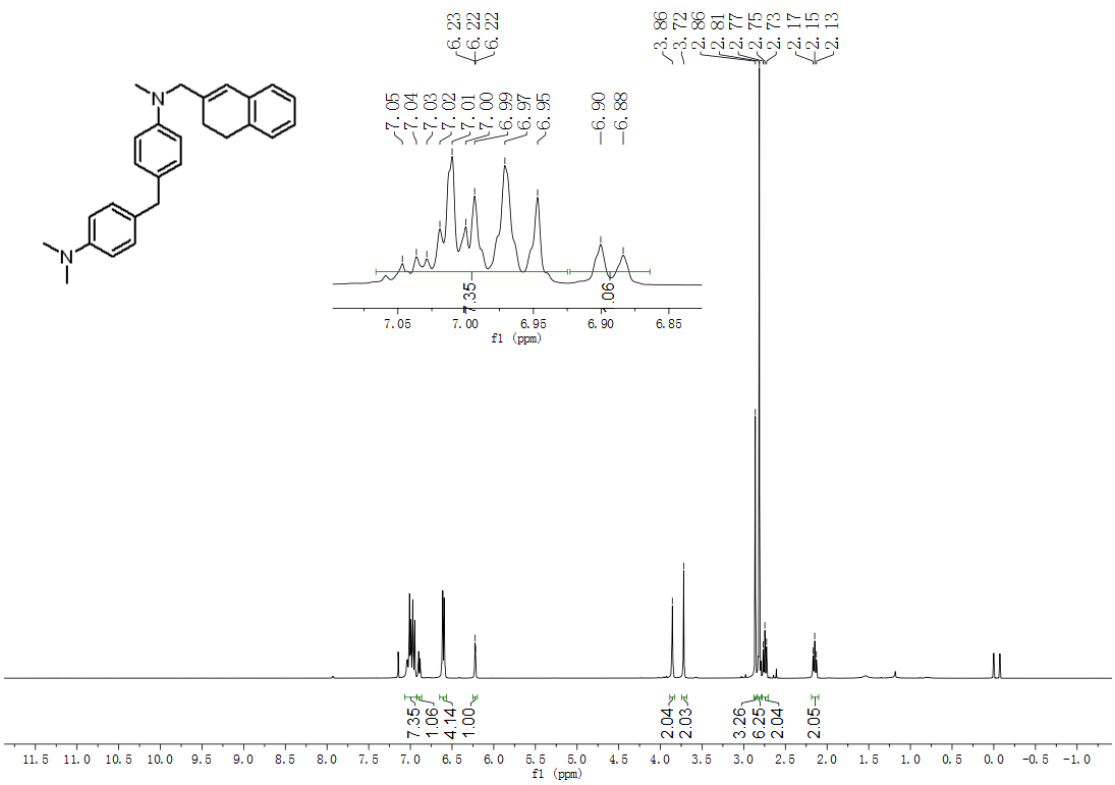


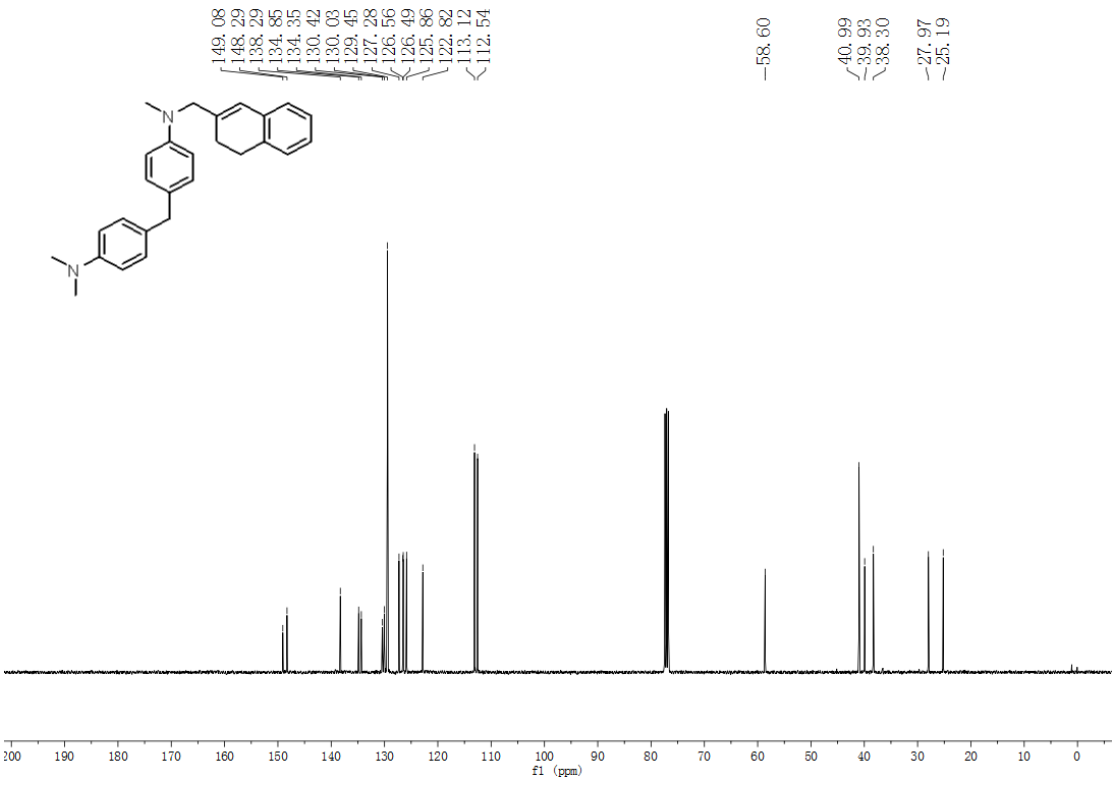
1-(4-(((3,4-dihydronaphthalen-2-yl)methyl)(methyl)amino)phenyl)ethanone (3ga)



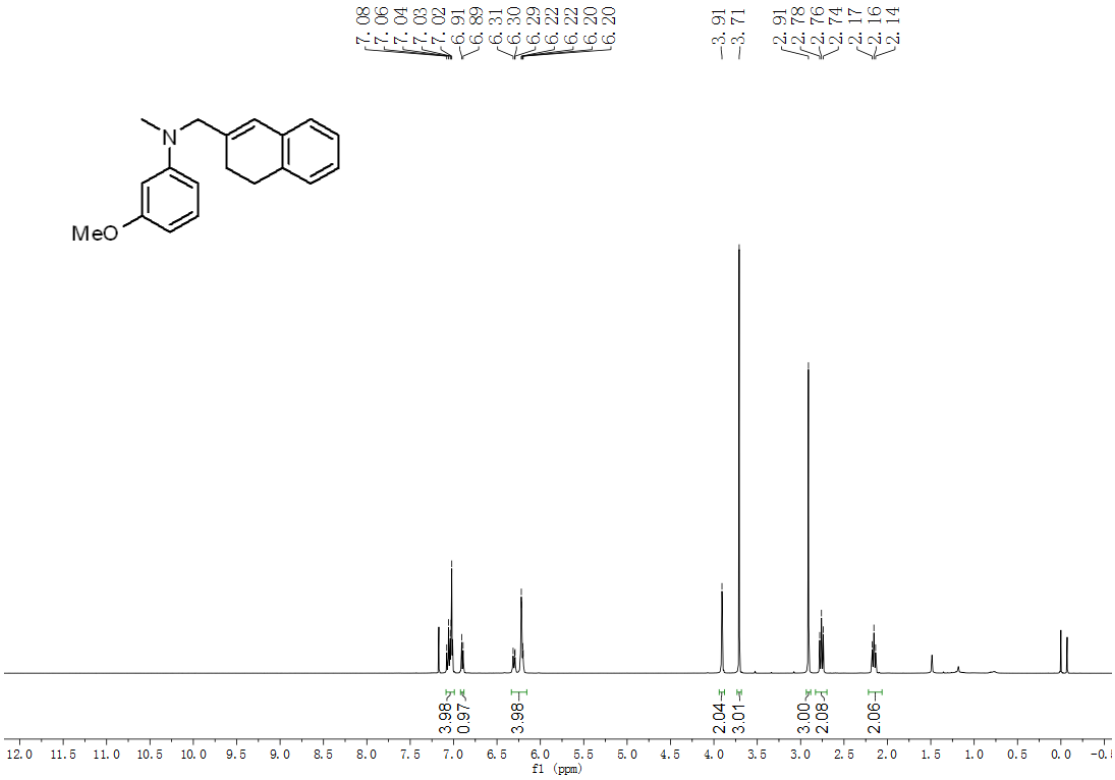


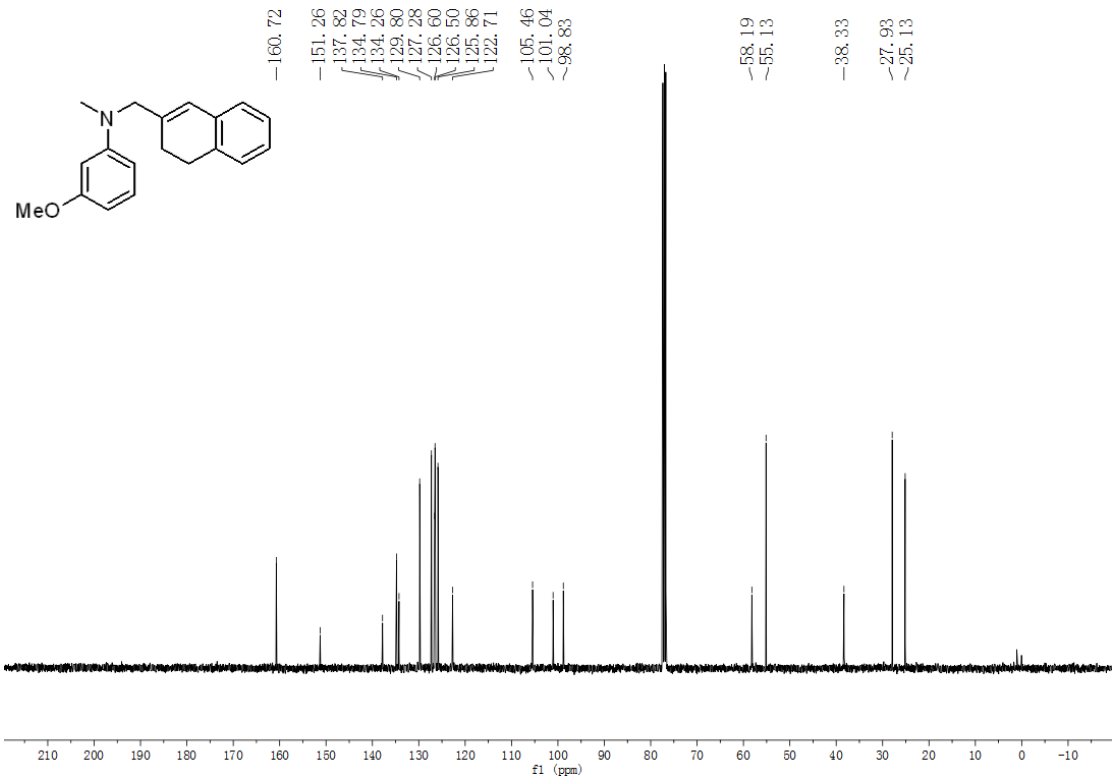
N-((3,4-dihydronaphthalen-2-yl)methyl)-4-(4-(dimethylamino)benzyl)-N-methylaniline (3ha)



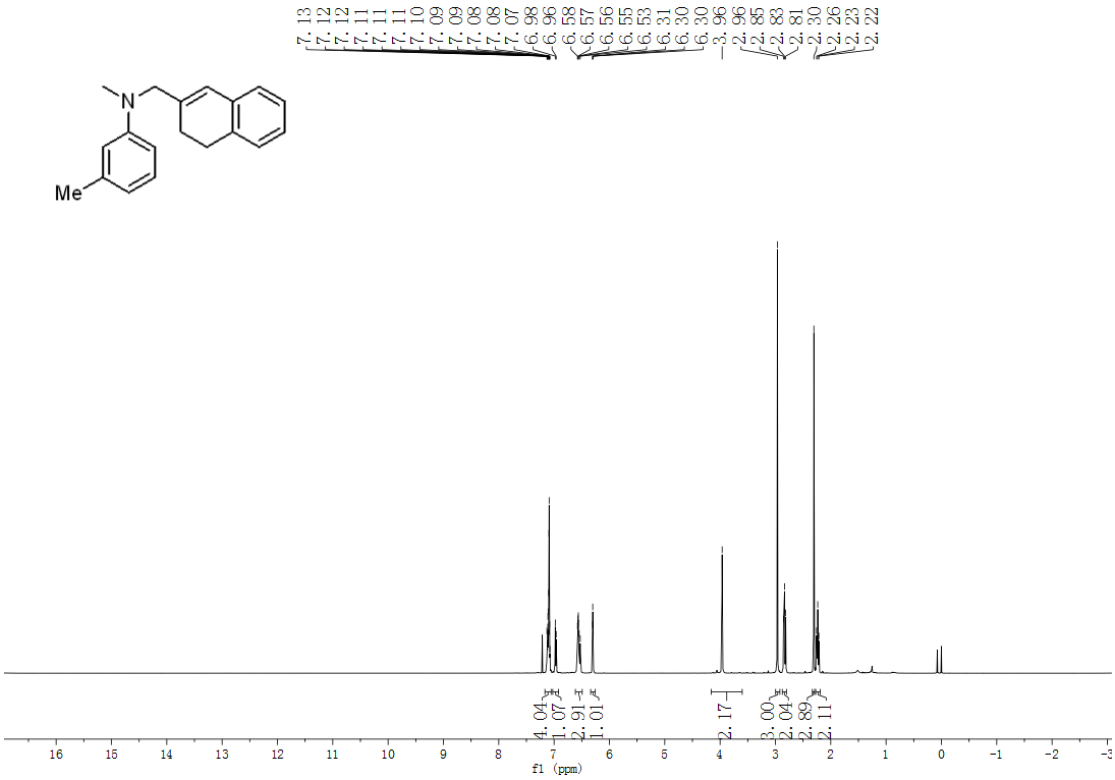


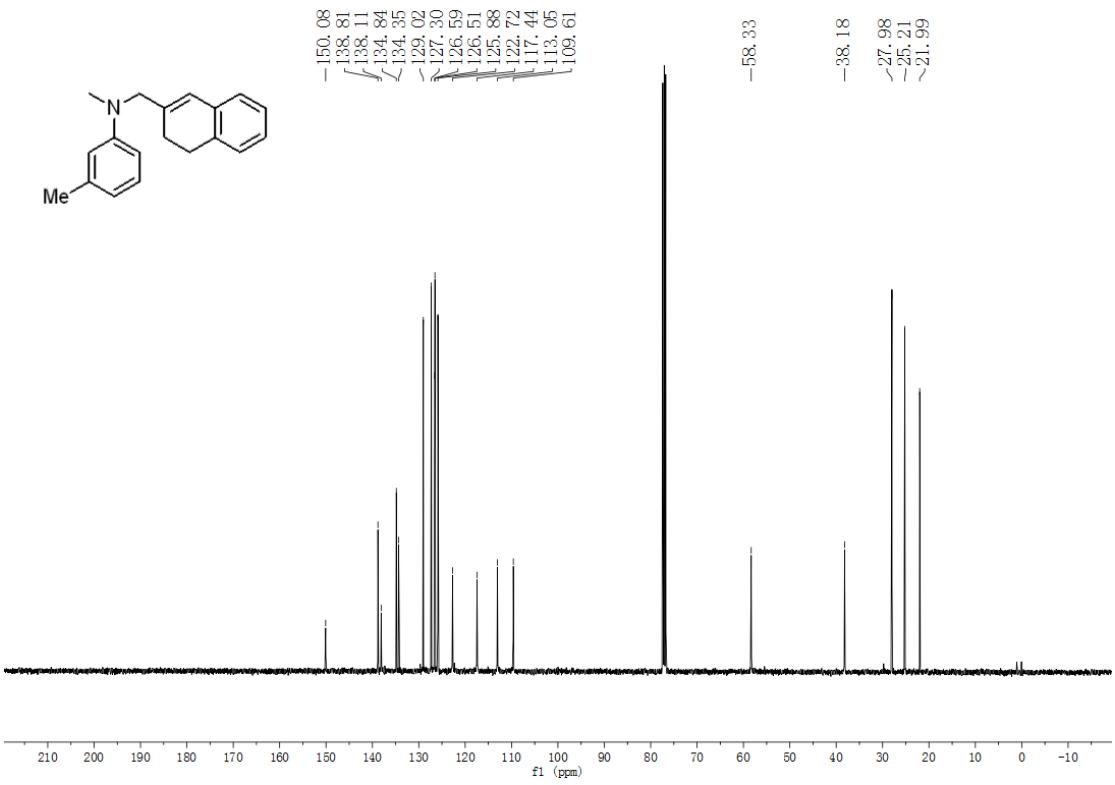
N-((3,4-dihydronaphthalen-2-yl)methyl)-3-methoxy-N-methylaniline (3ia)



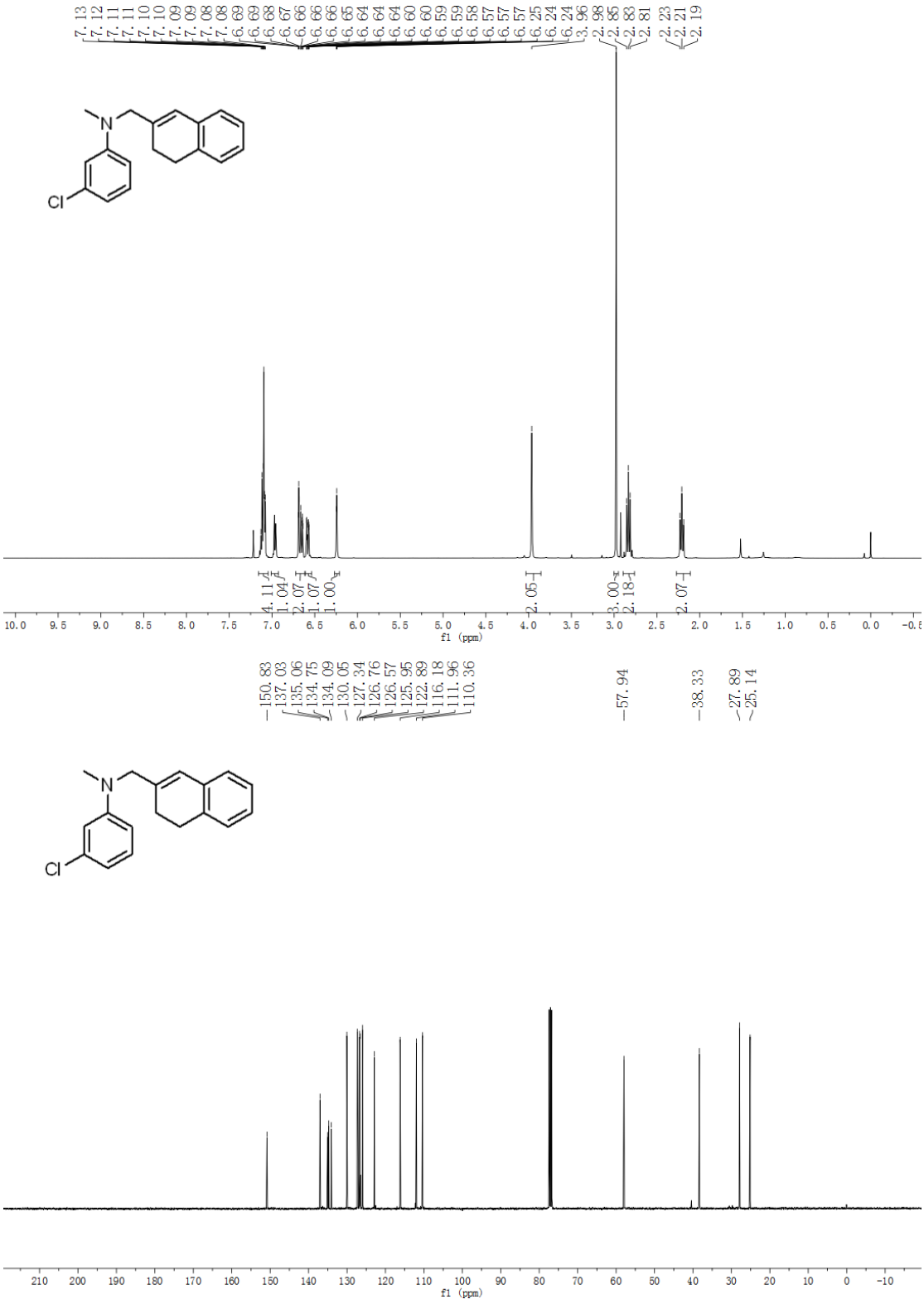


3-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ja)

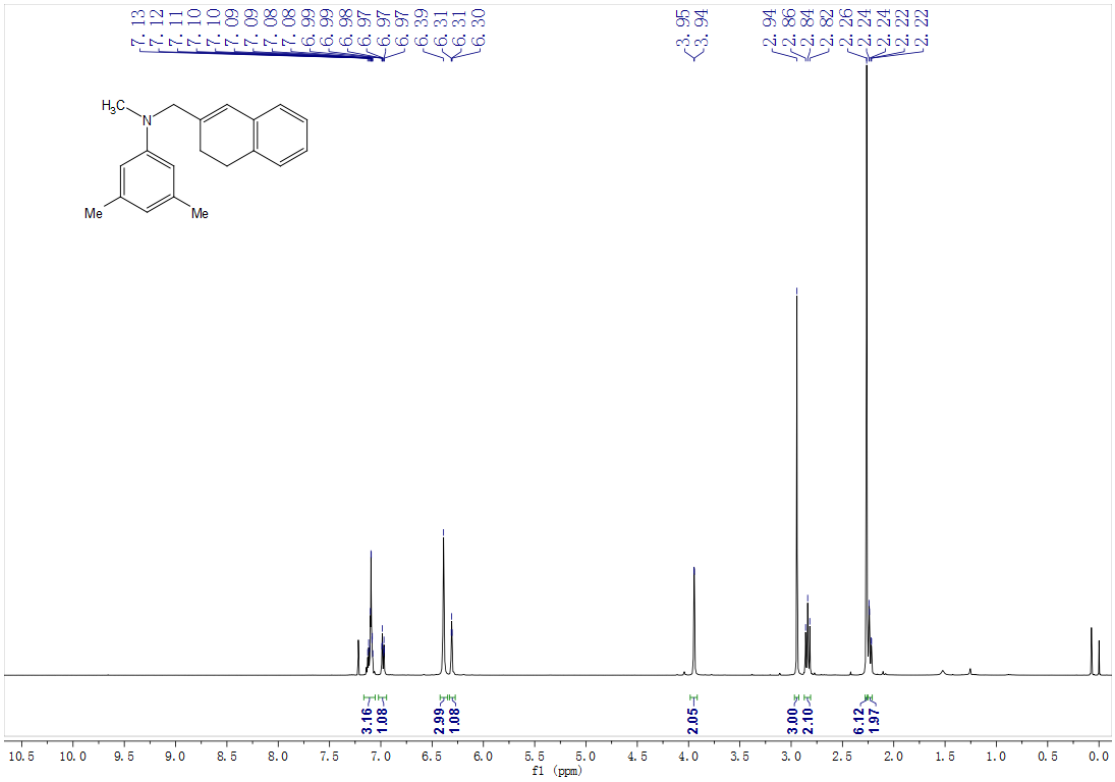


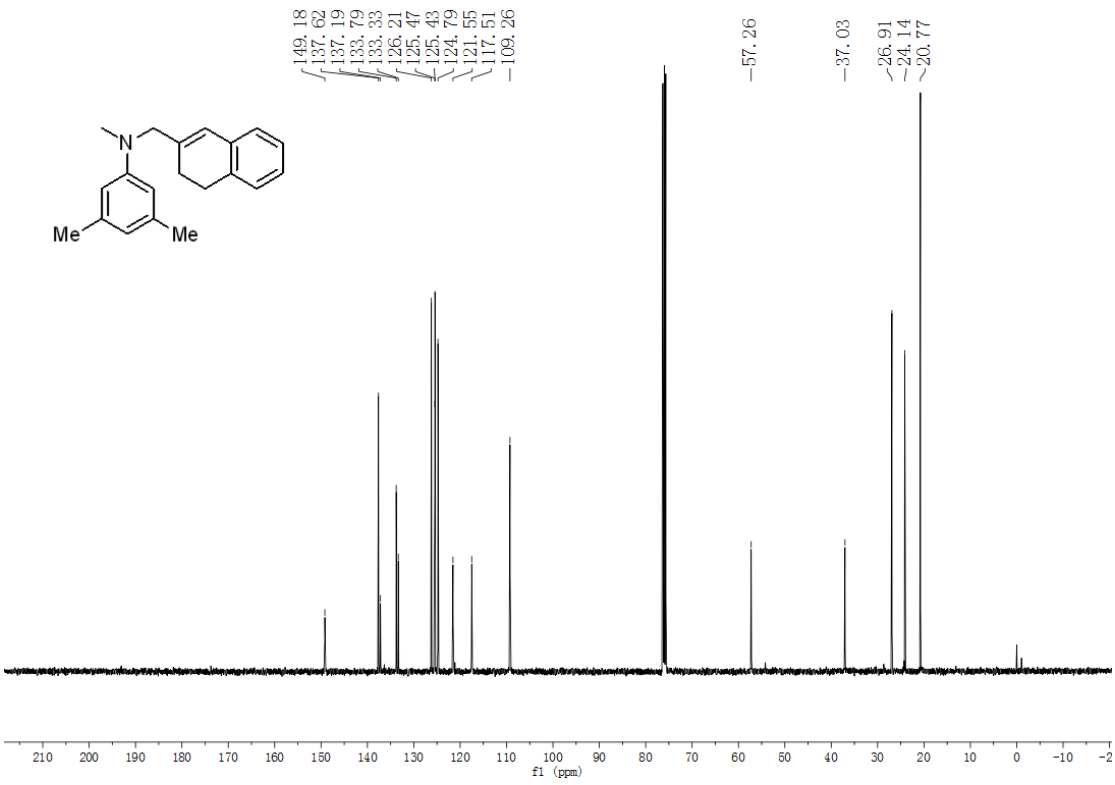


3-chloro-N-((3,4-dihydronaphthalen-2-yl)methyl)-N-methylaniline (3ka)

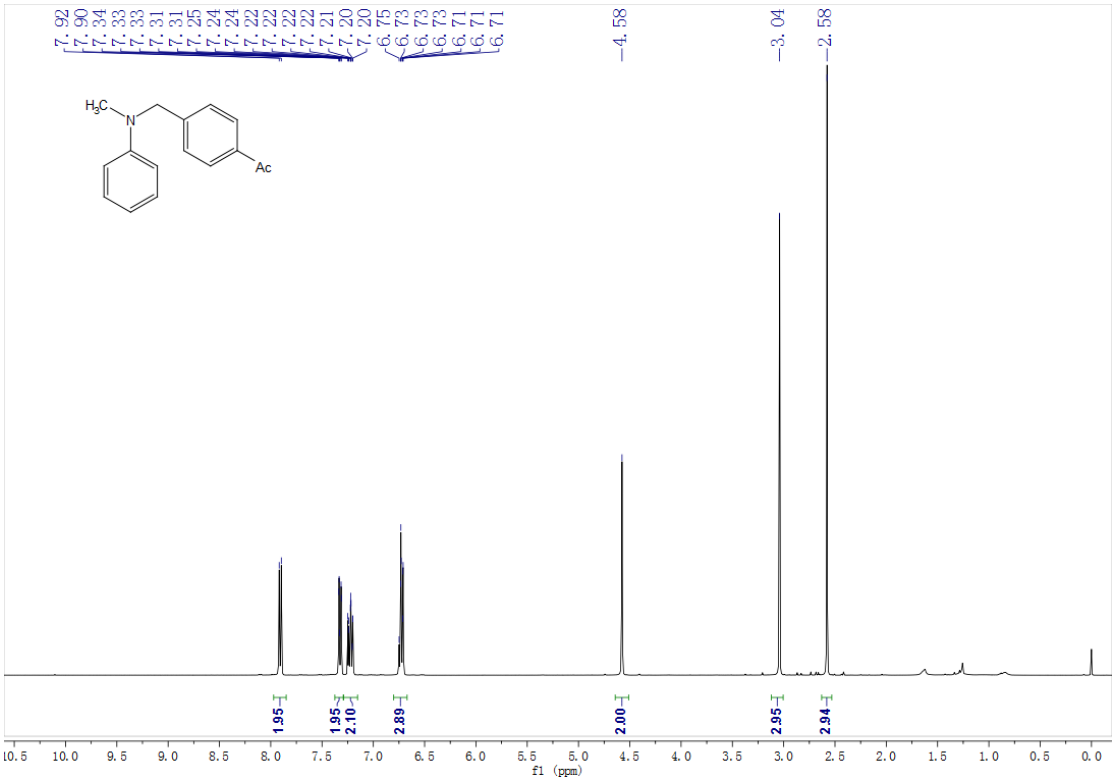


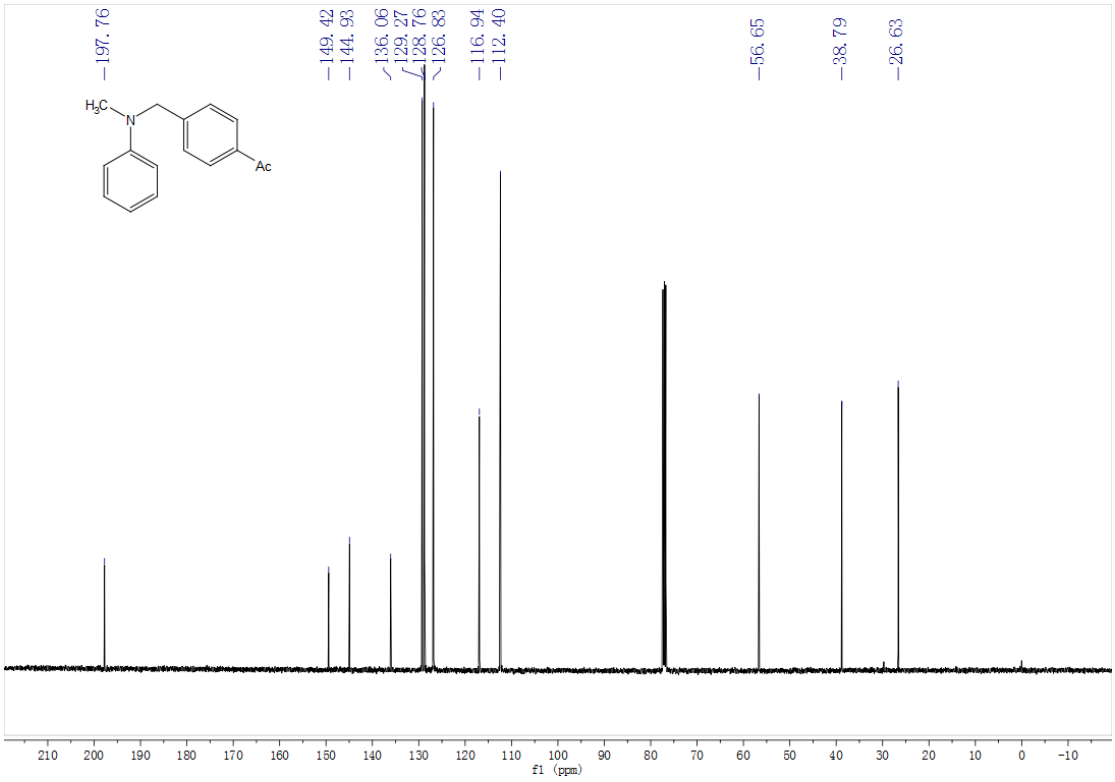
N-((3,4-dihydronaphthalen-2-yl)methyl)-N,3,5-trimethylaniline (3la)



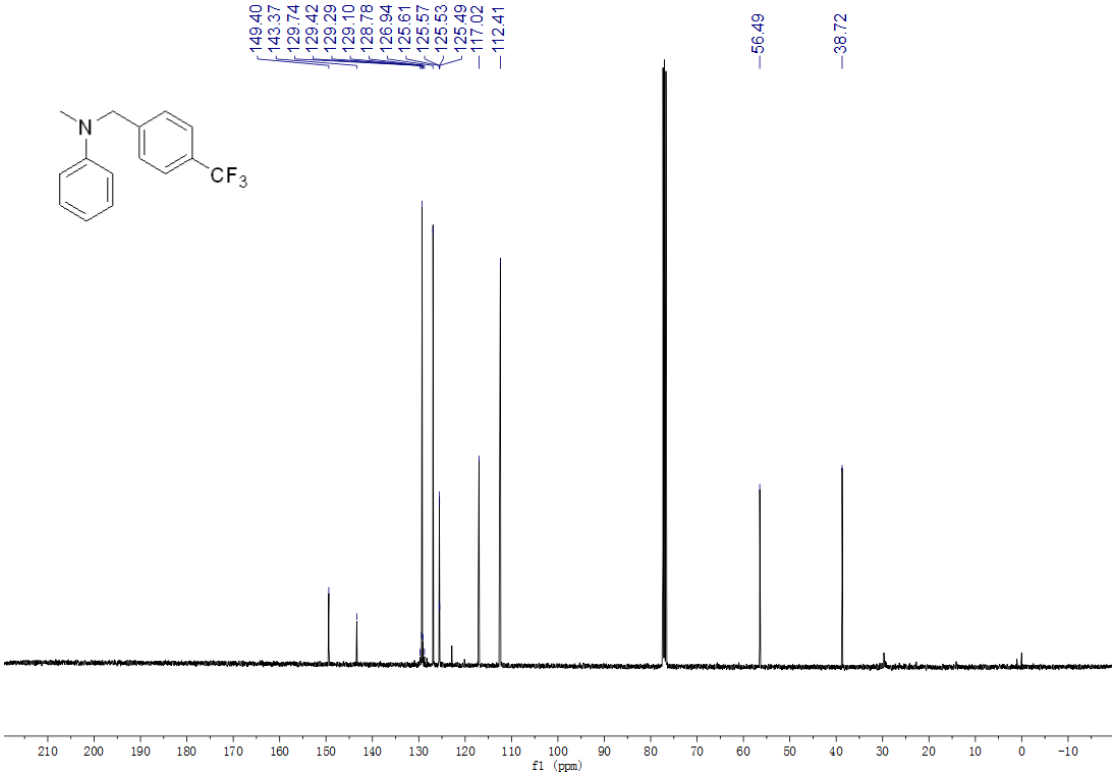


1-(4-((methyl(phenyl)amino)methyl)phenyl)ethanone (5aa)

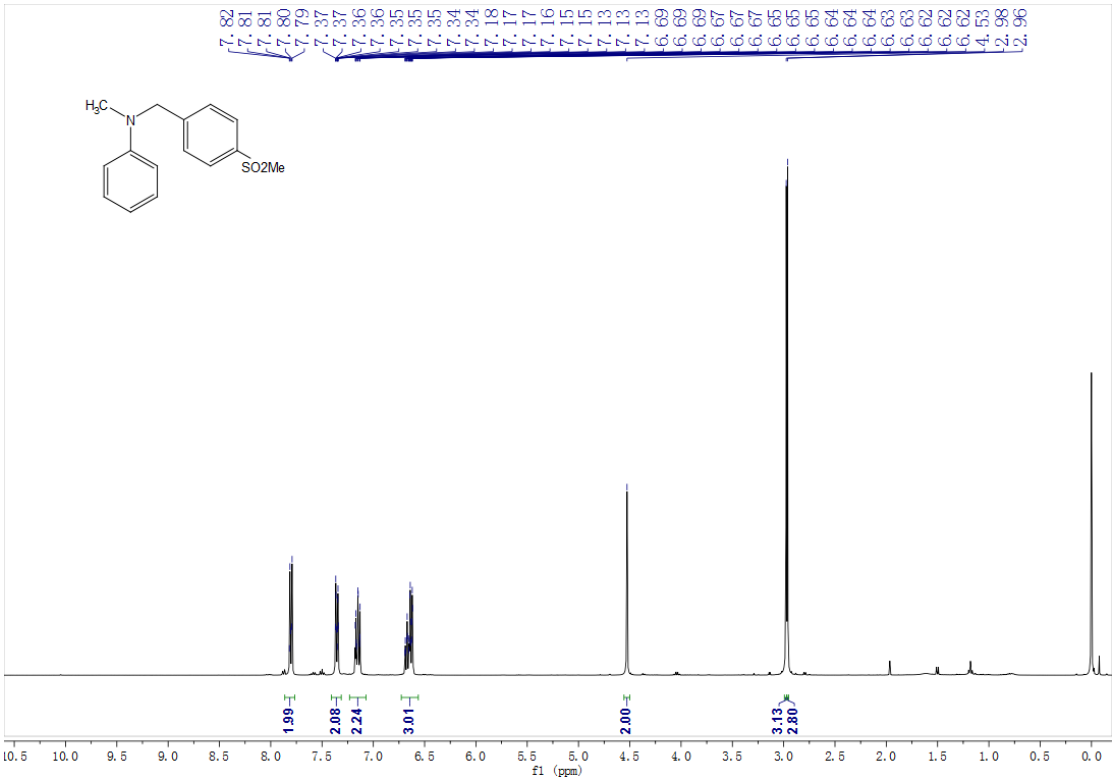


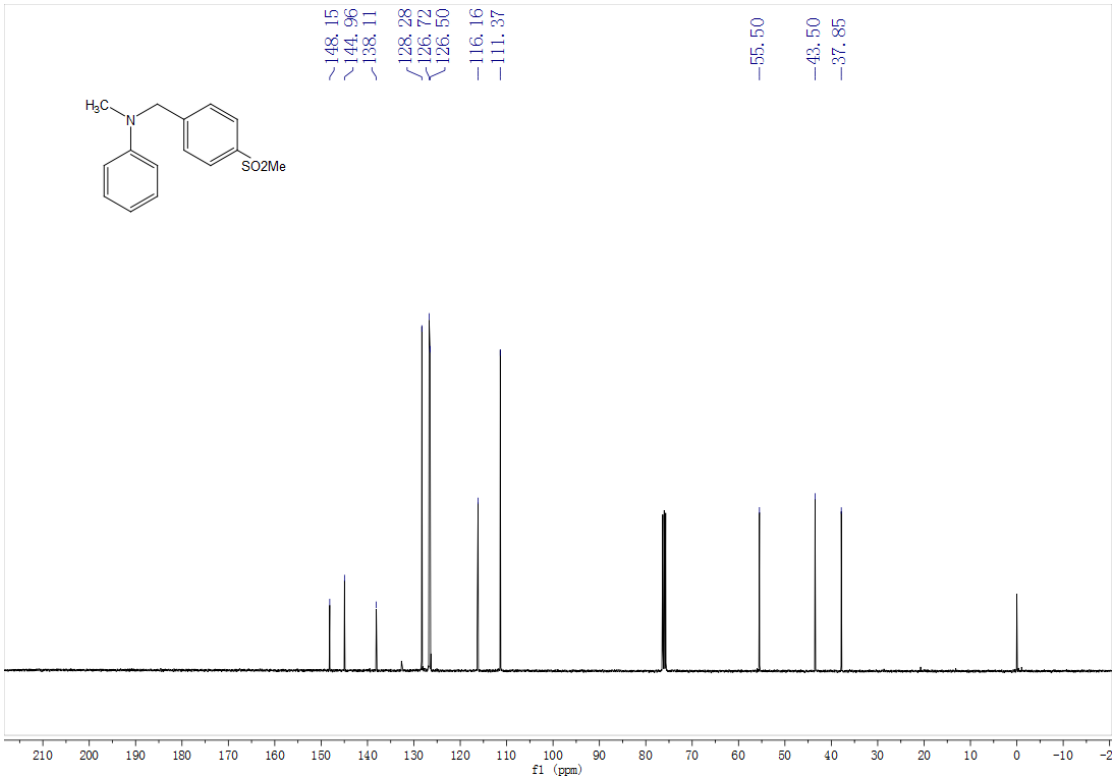


N-methyl-N-(4-(trifluoromethyl)benzyl)aniline （5ab）

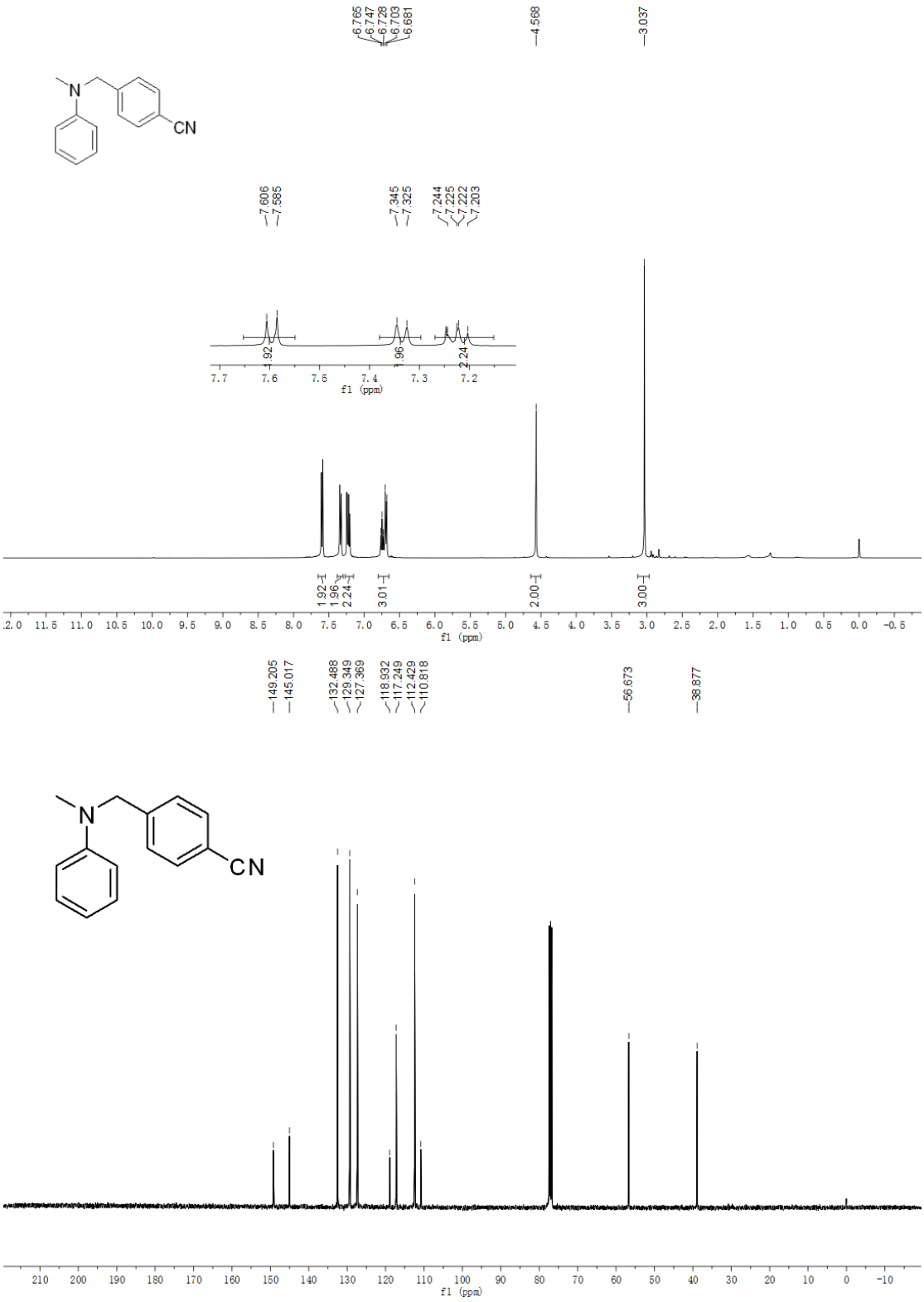


N-methyl-N-(4-(methylsulfonyl)benzyl)aniline (5ac)

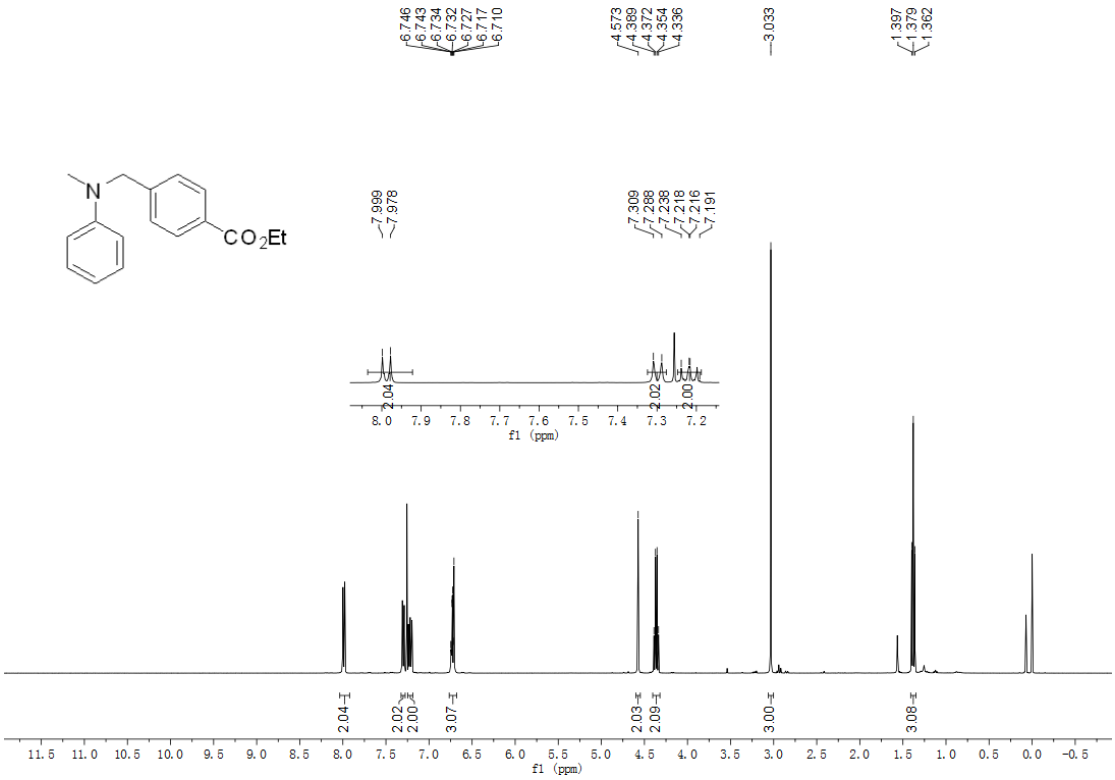


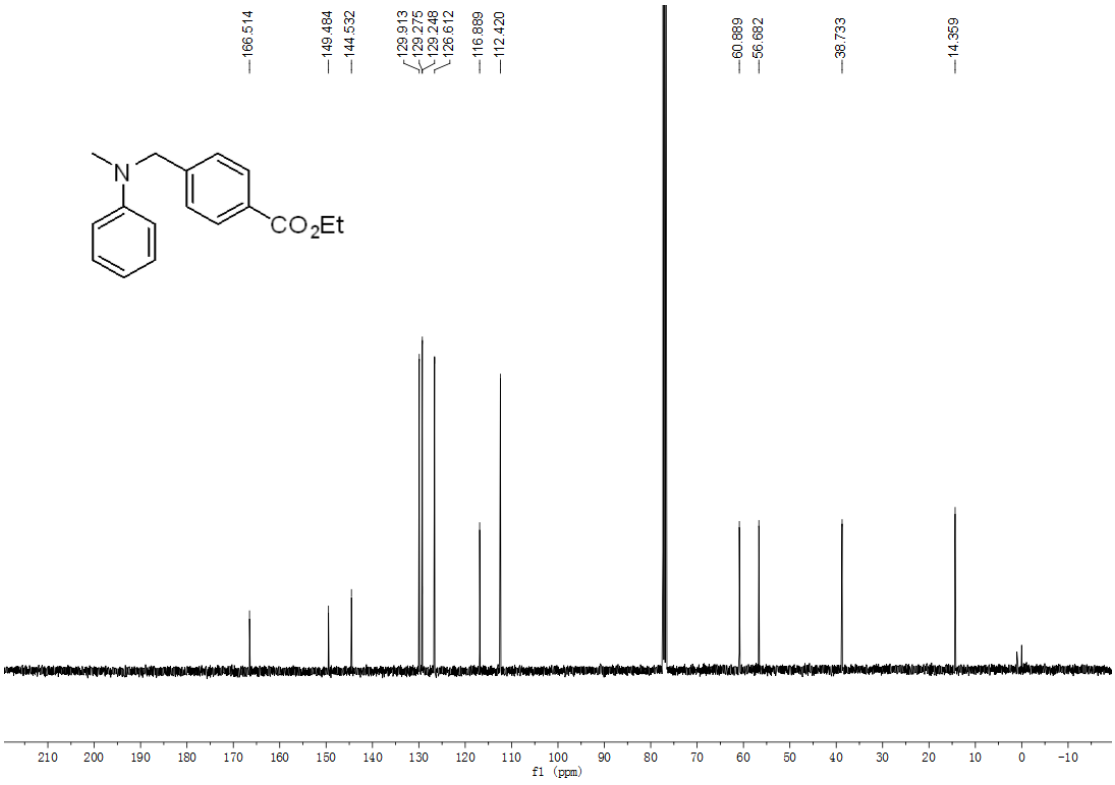


4-((methyl(phenyl)amino)methyl)benzonitrile （5ad）

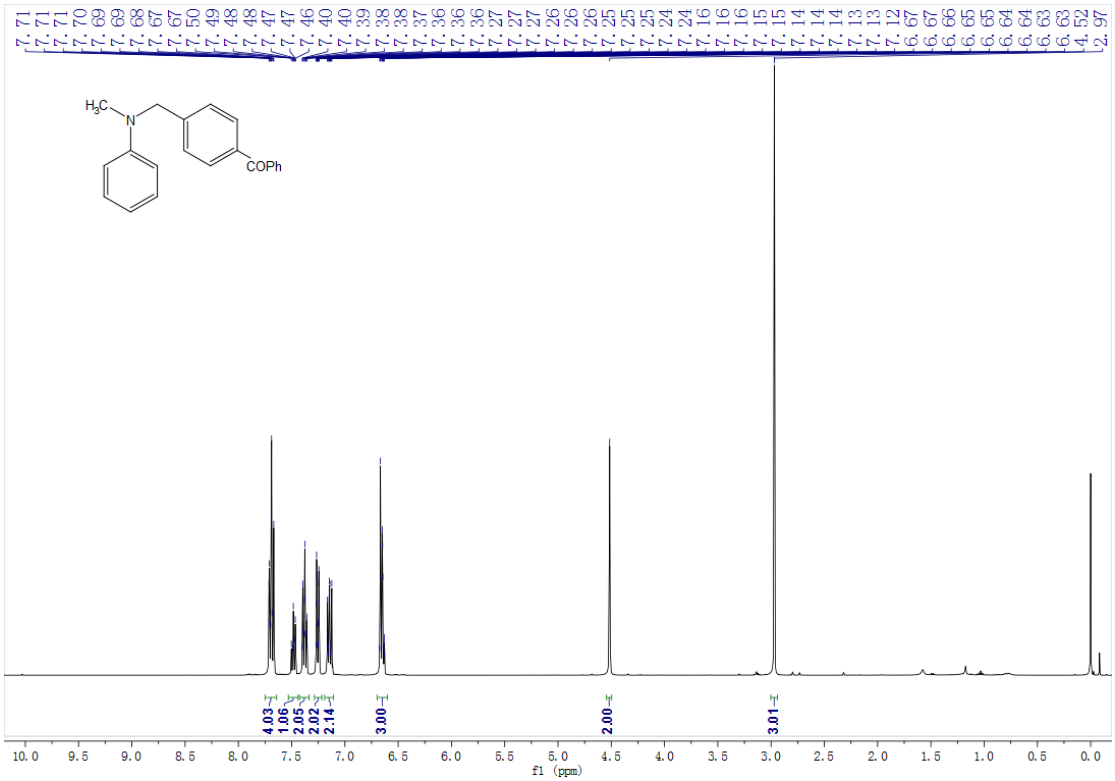


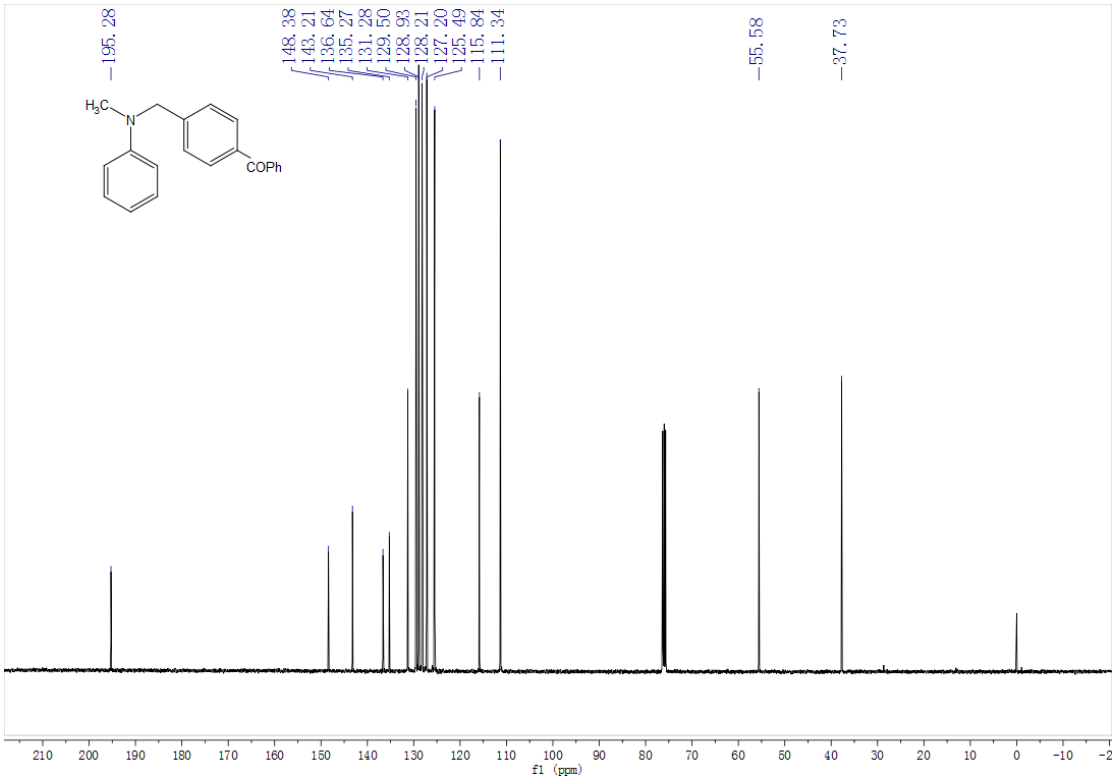
ethyl 4-((methyl(phenyl)amino)methyl)benzoate （5ae）



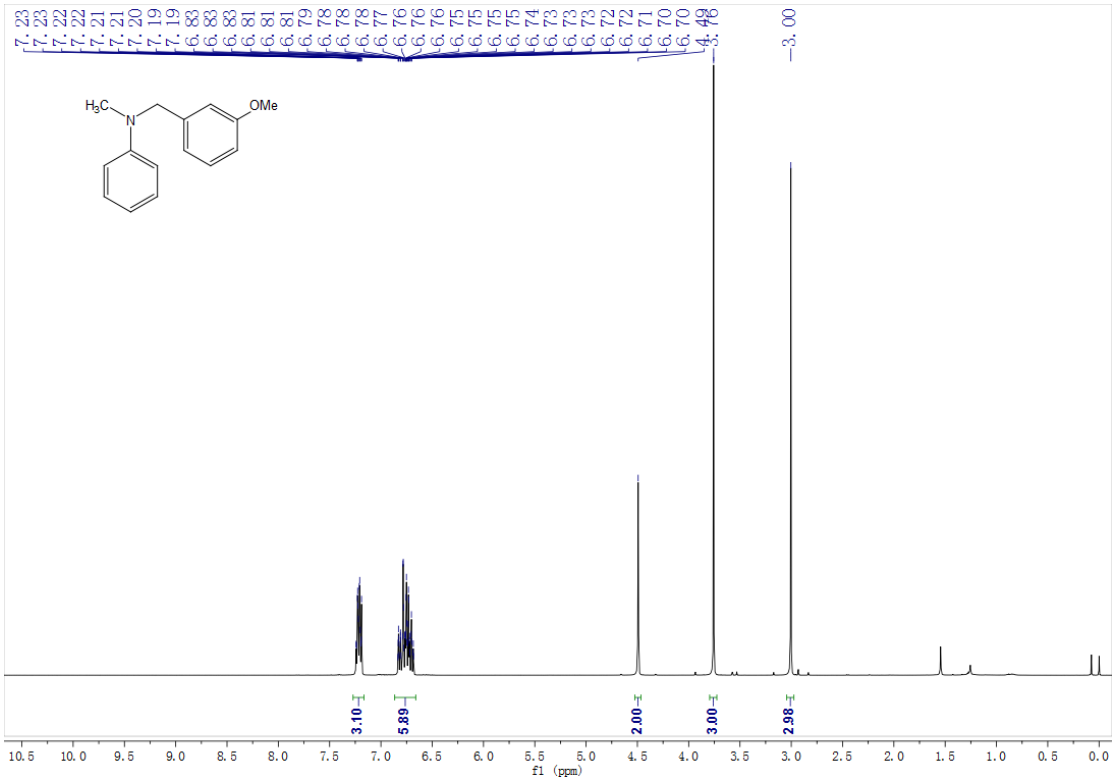


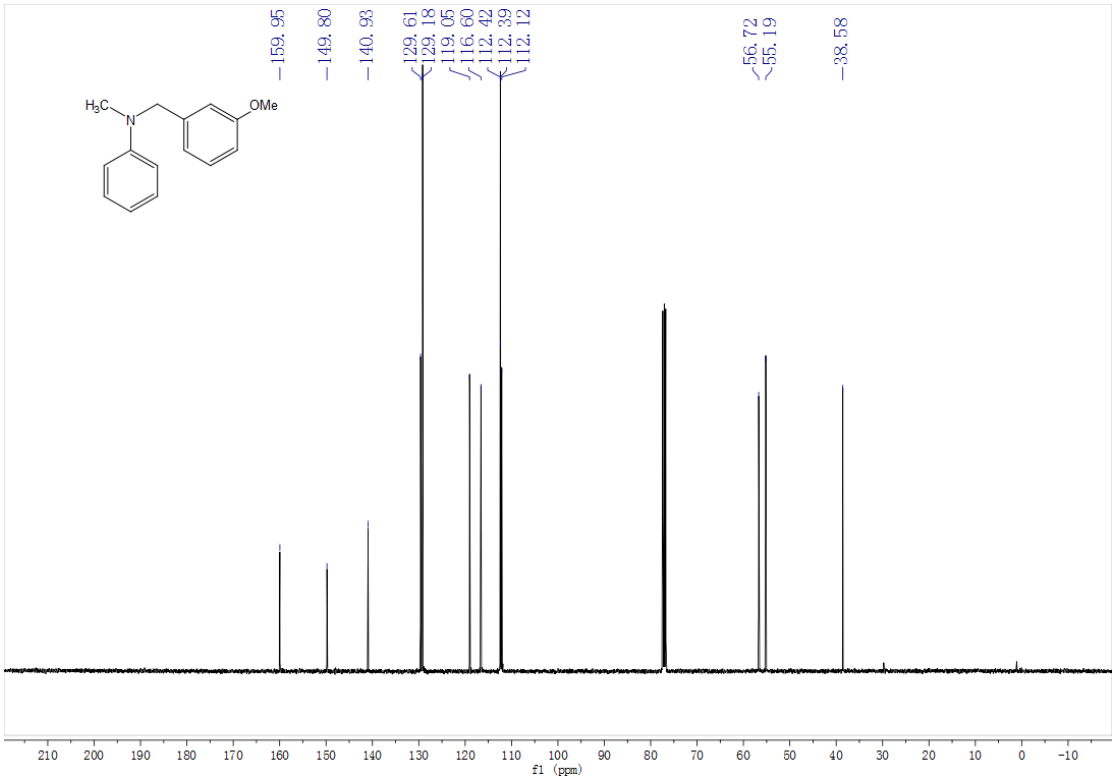
(4-((methyl(phenyl)amino)methyl)phenyl)(phenyl)methanone （5af）



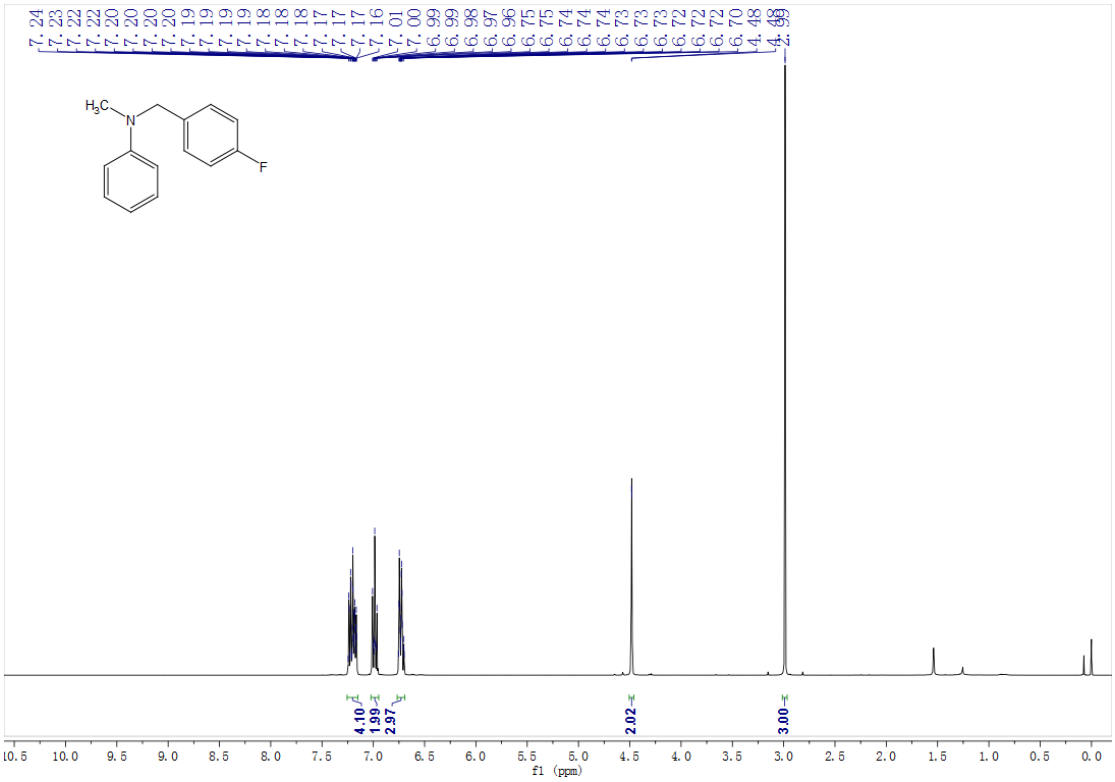


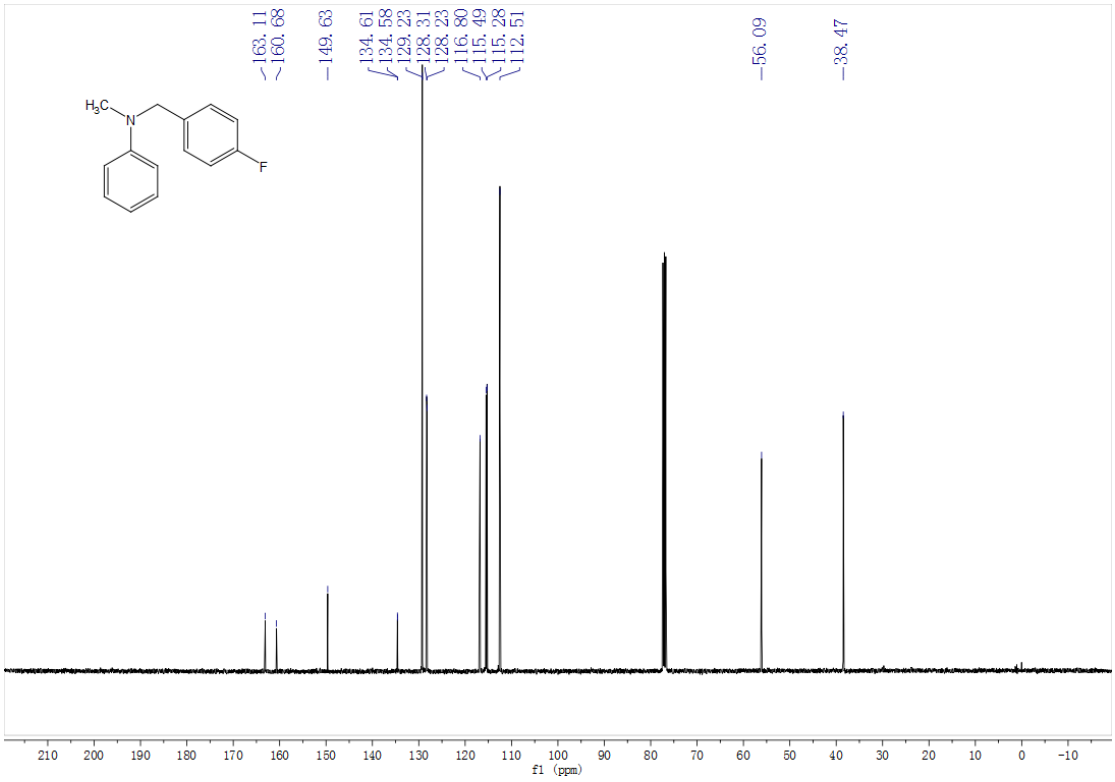
N-(3-methoxybenzyl)-N-methylaniline (5ag)



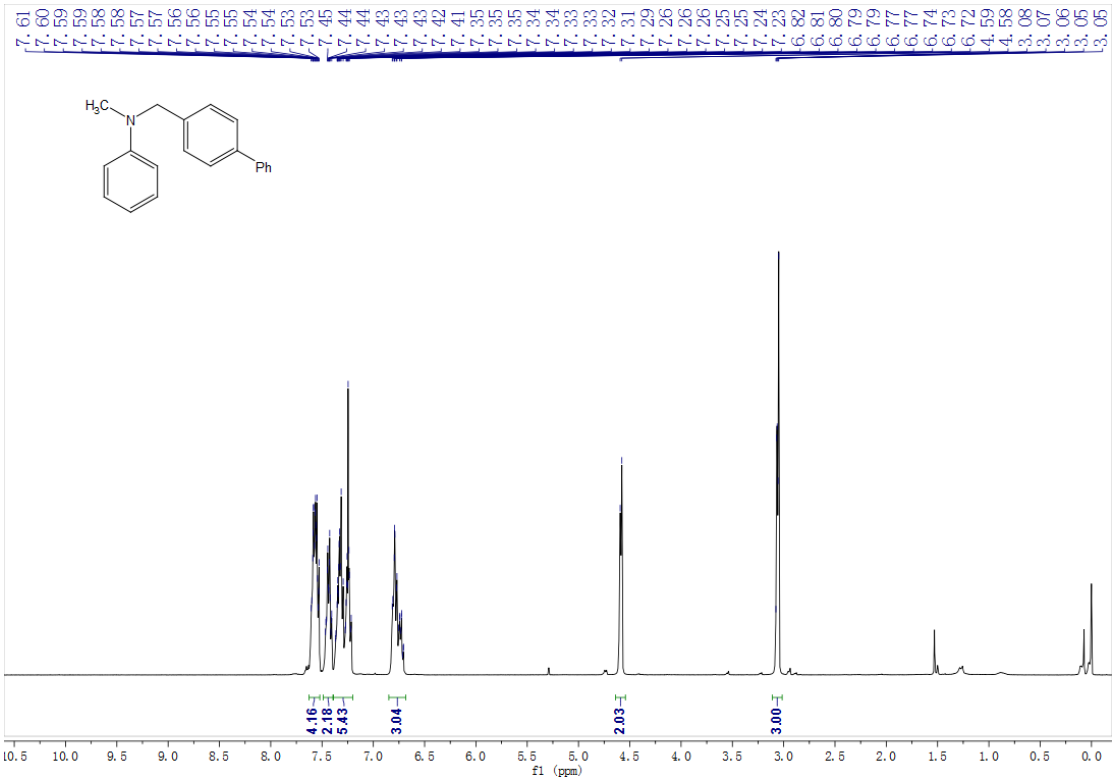


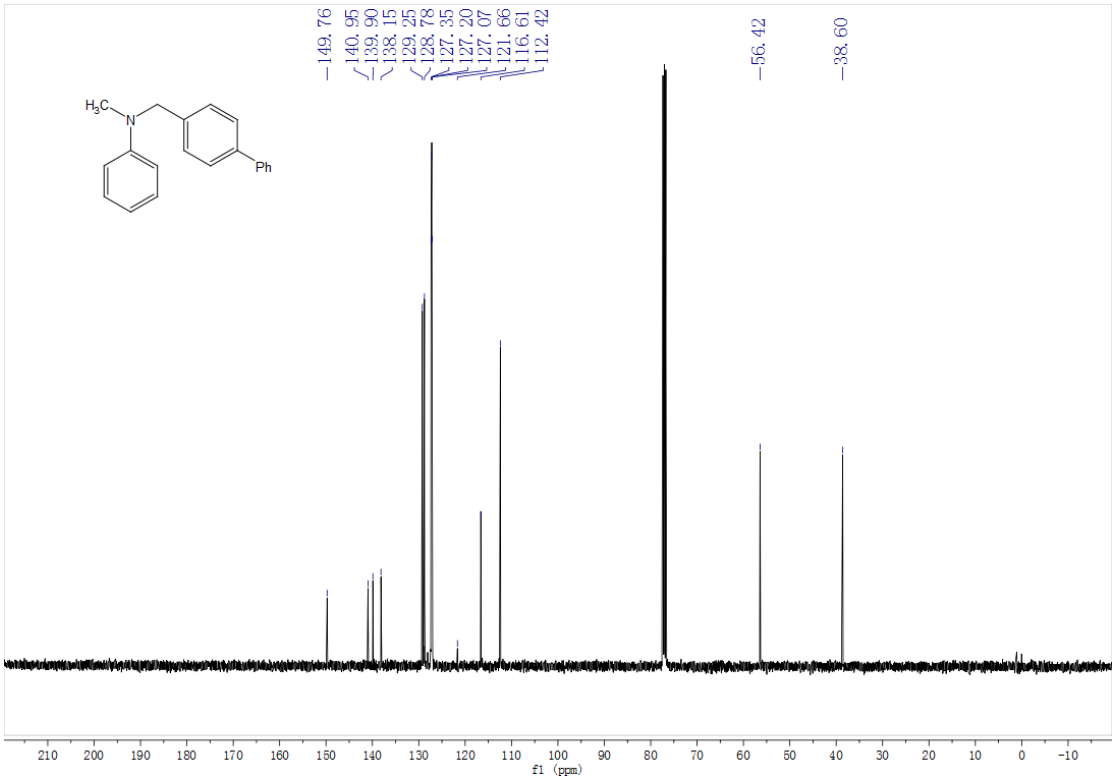
N-(4-fluorobenzyl)-N-methylaniline （5ah）



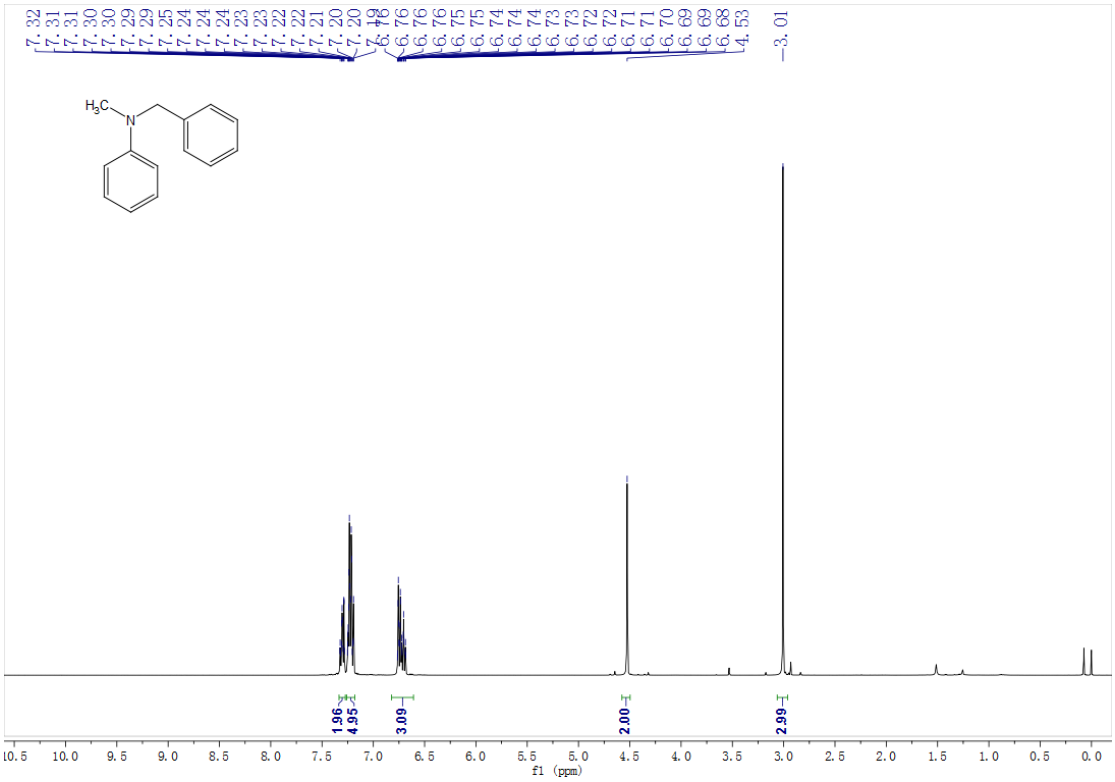


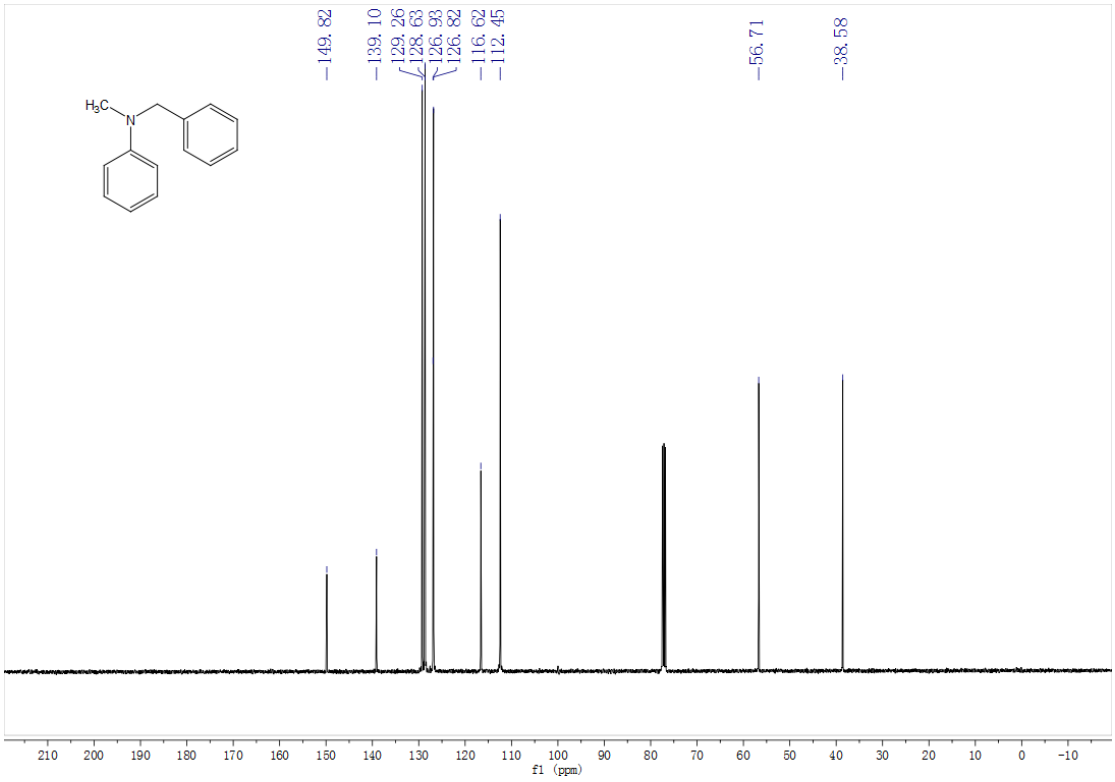
N-([1,1'-biphenyl]-4-ylmethyl)-N-methylaniline (5ai)



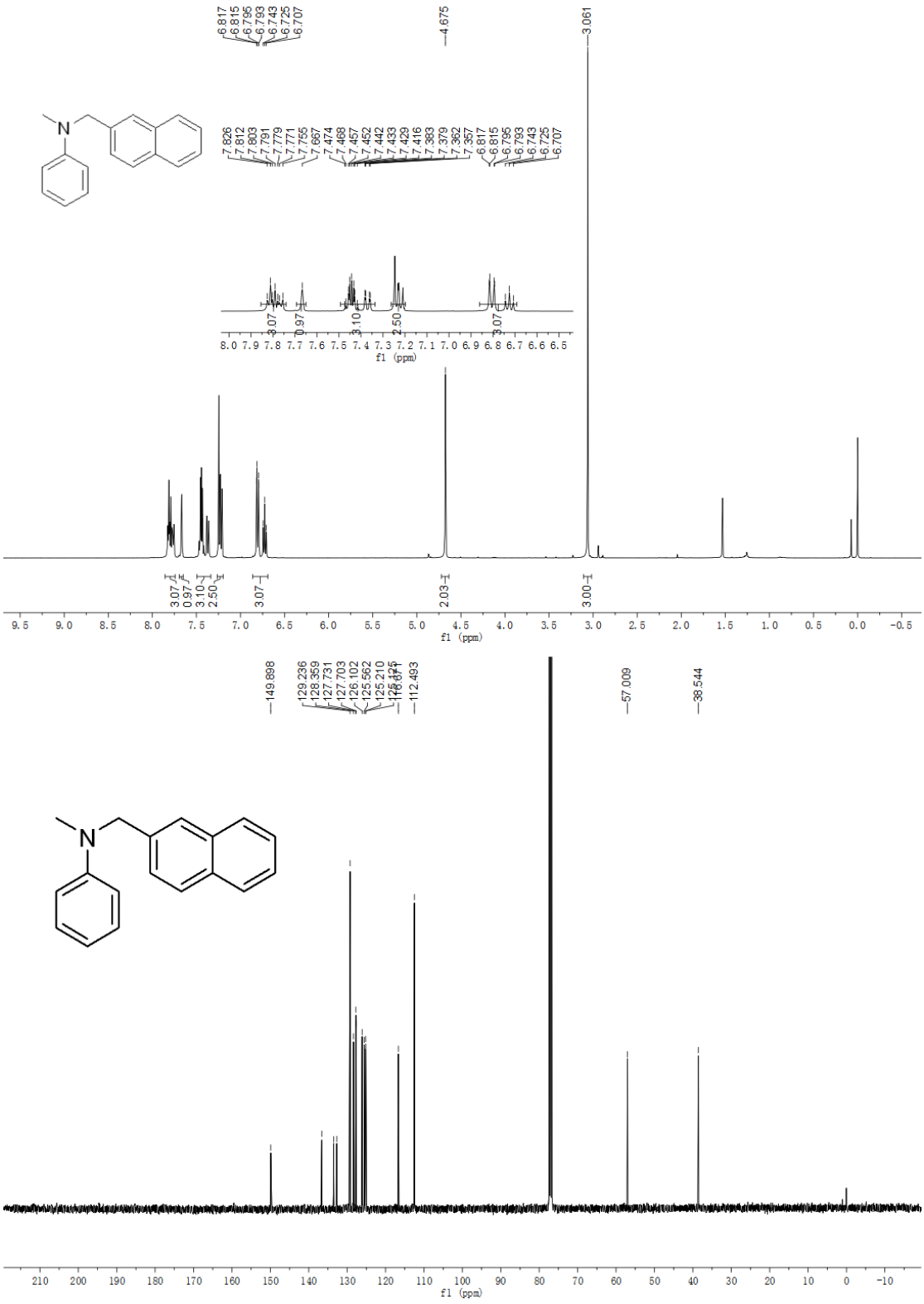


N-benzyl-N-methylaniline （5aj）

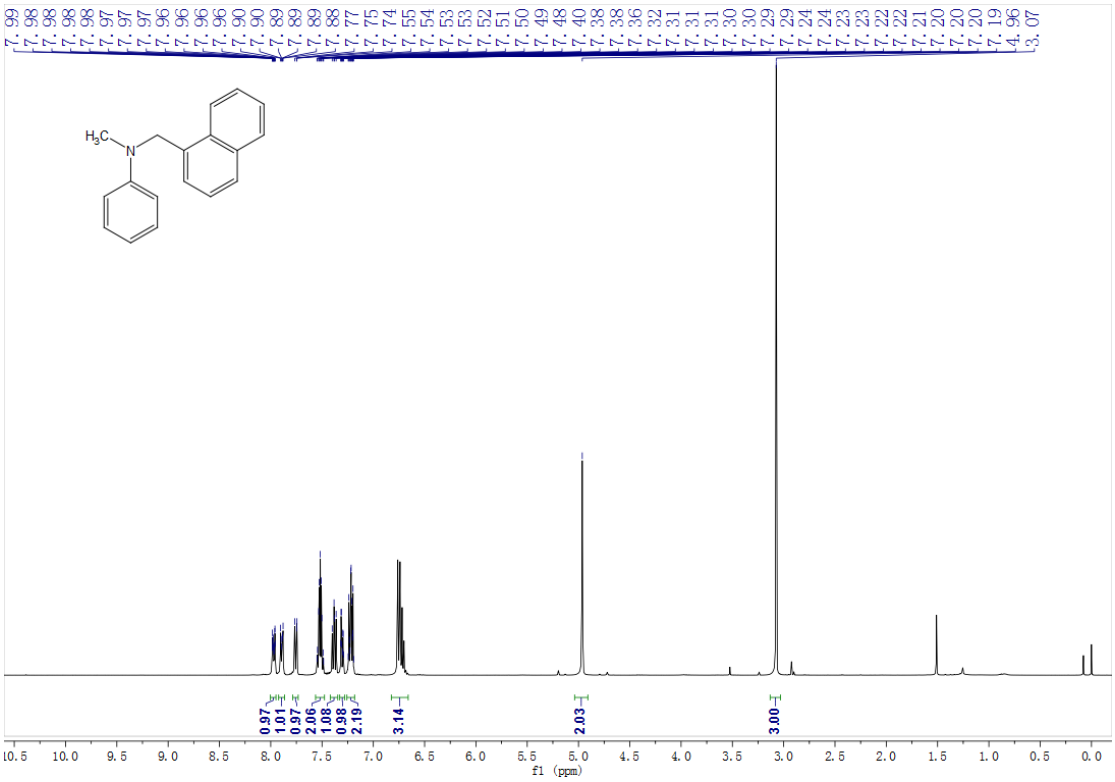


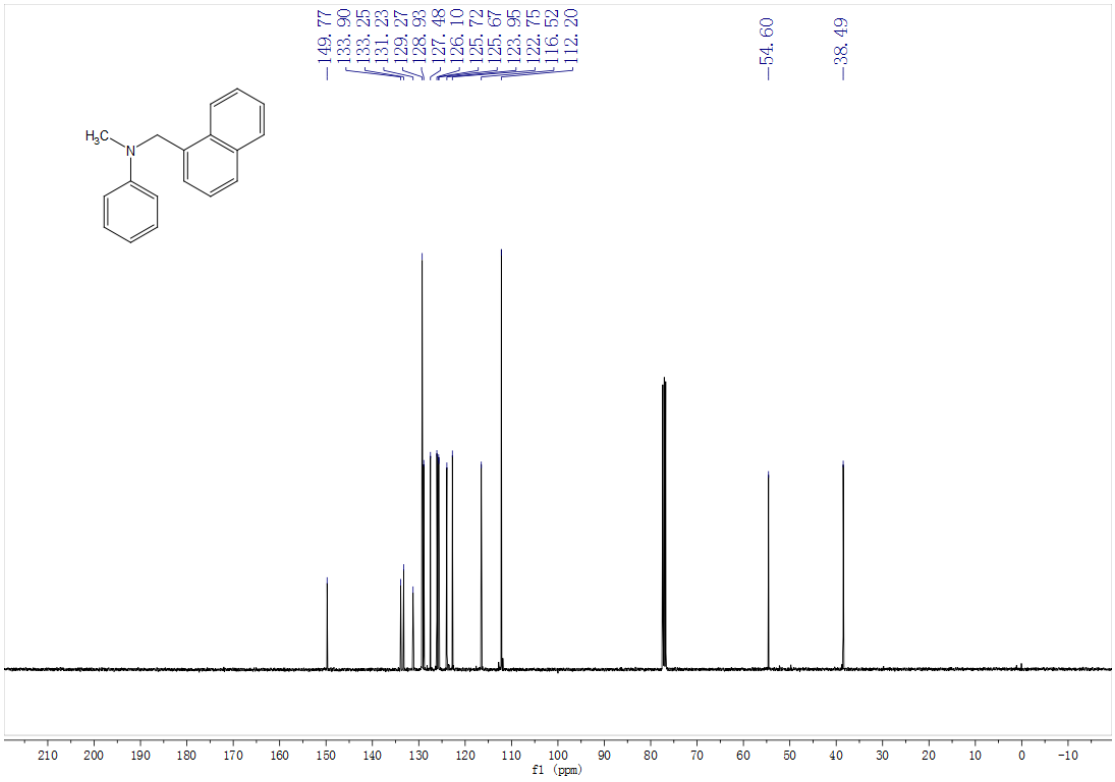


N-methyl-N-(naphthalen-2-ylmethyl)aniline （5ak）

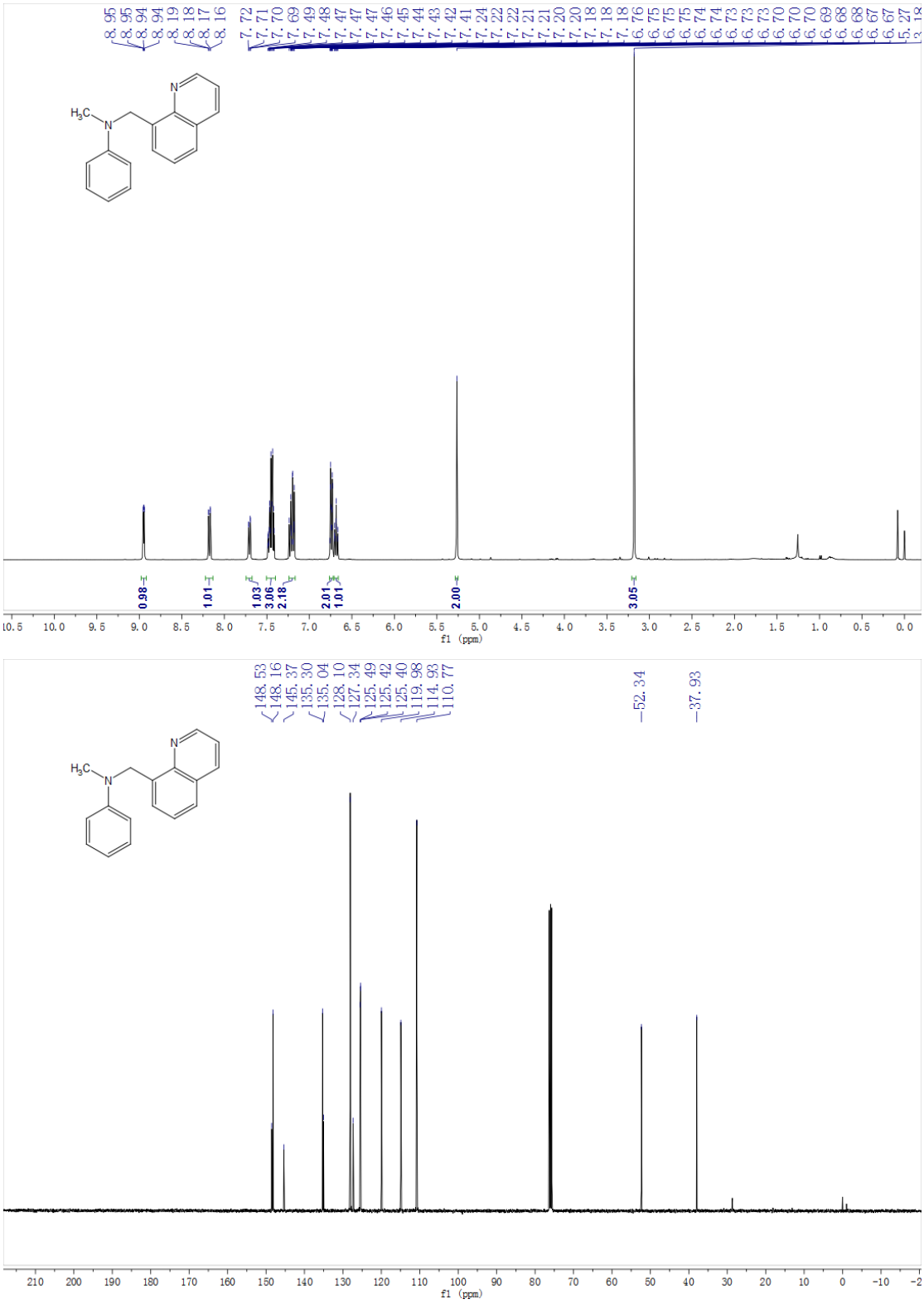


N-methyl-N-(naphthalen-1-ylmethyl)aniline (5al)

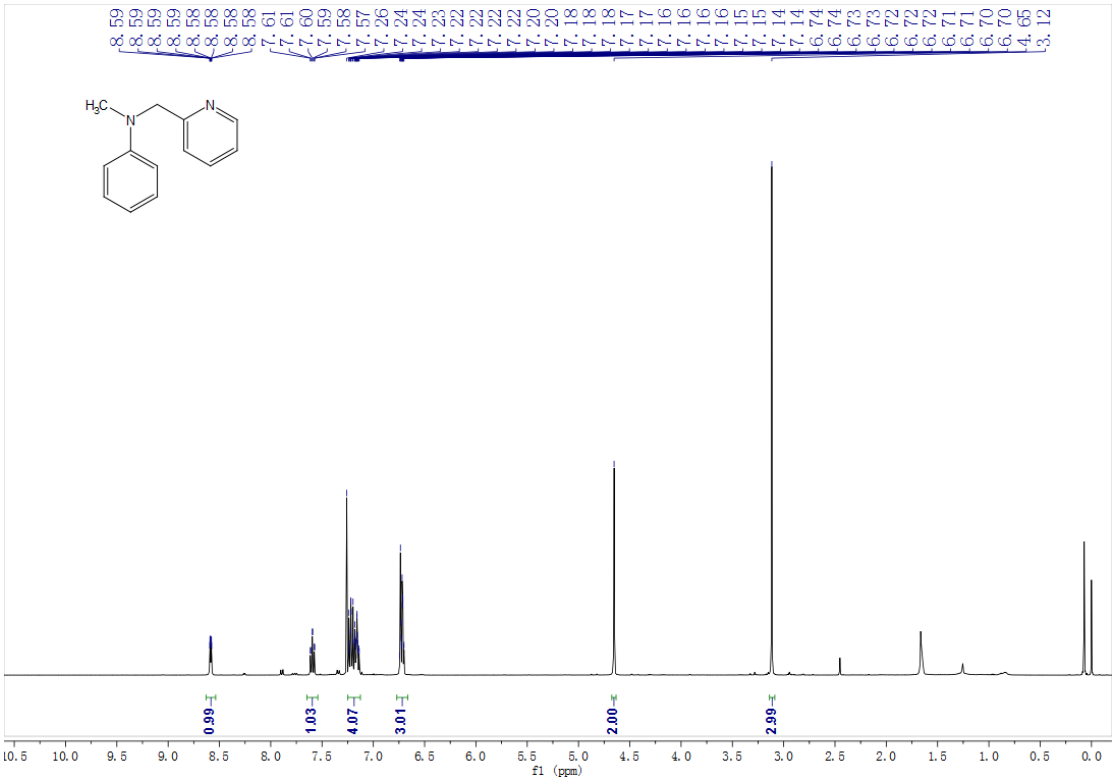


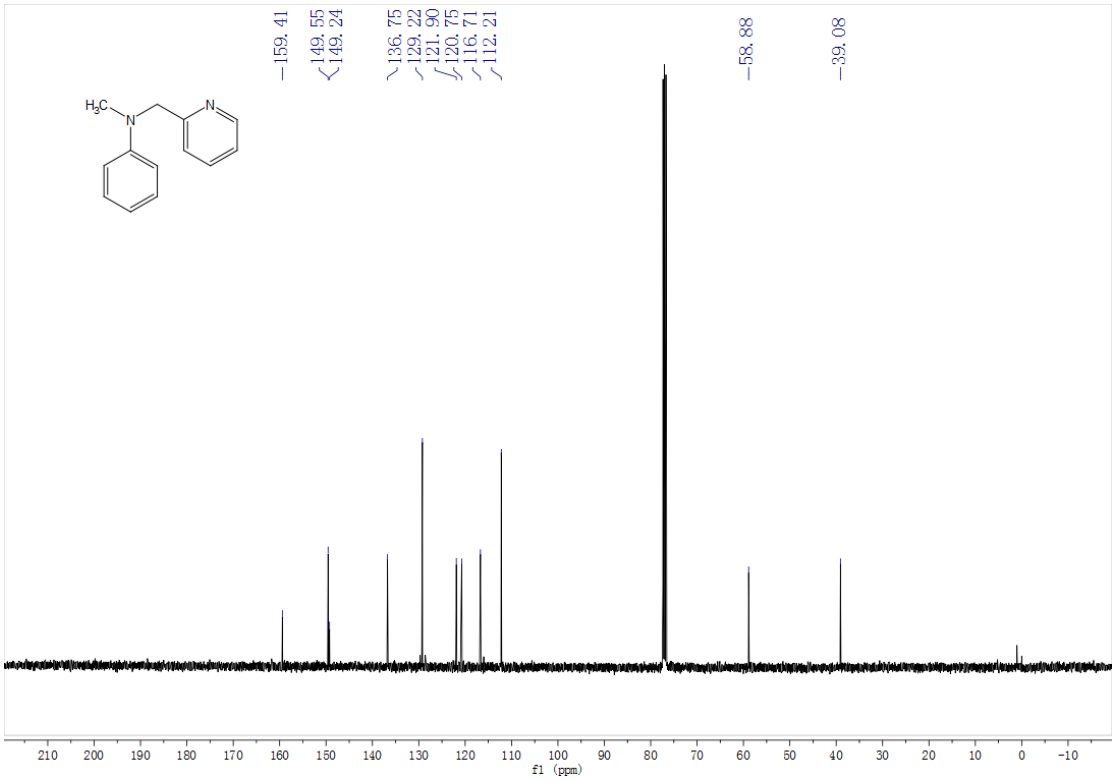


N-methyl-N-(quinolin-8-ylmethyl)aniline （5am）

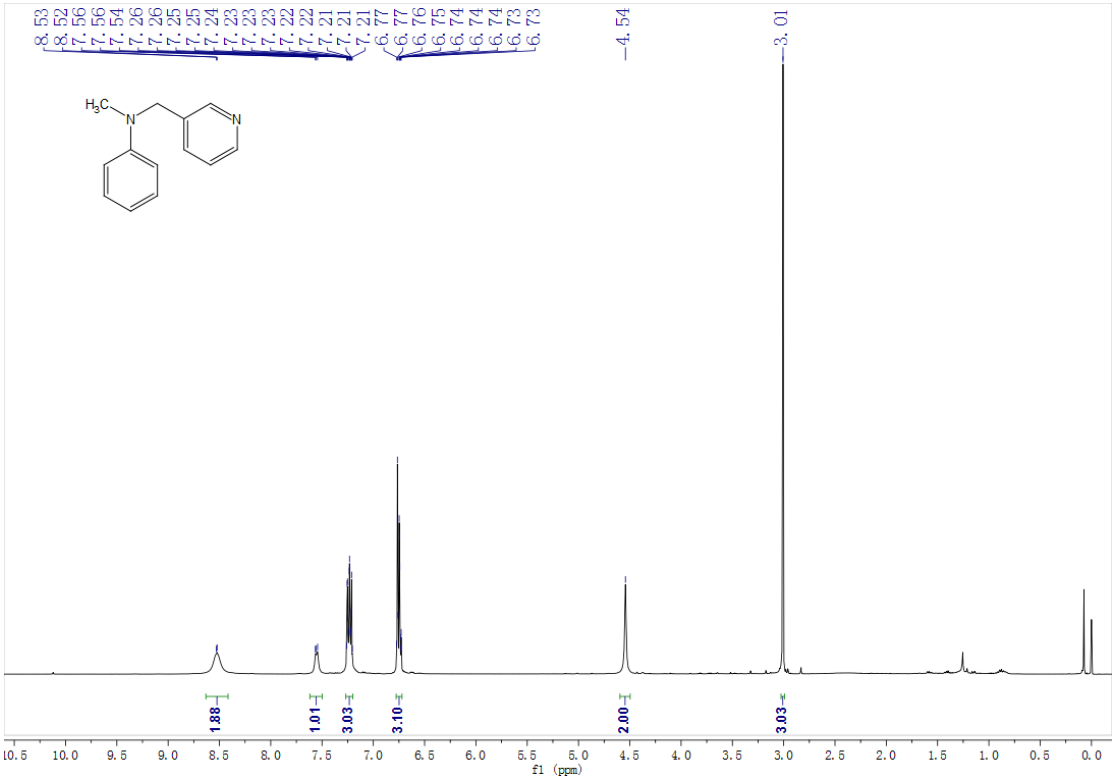


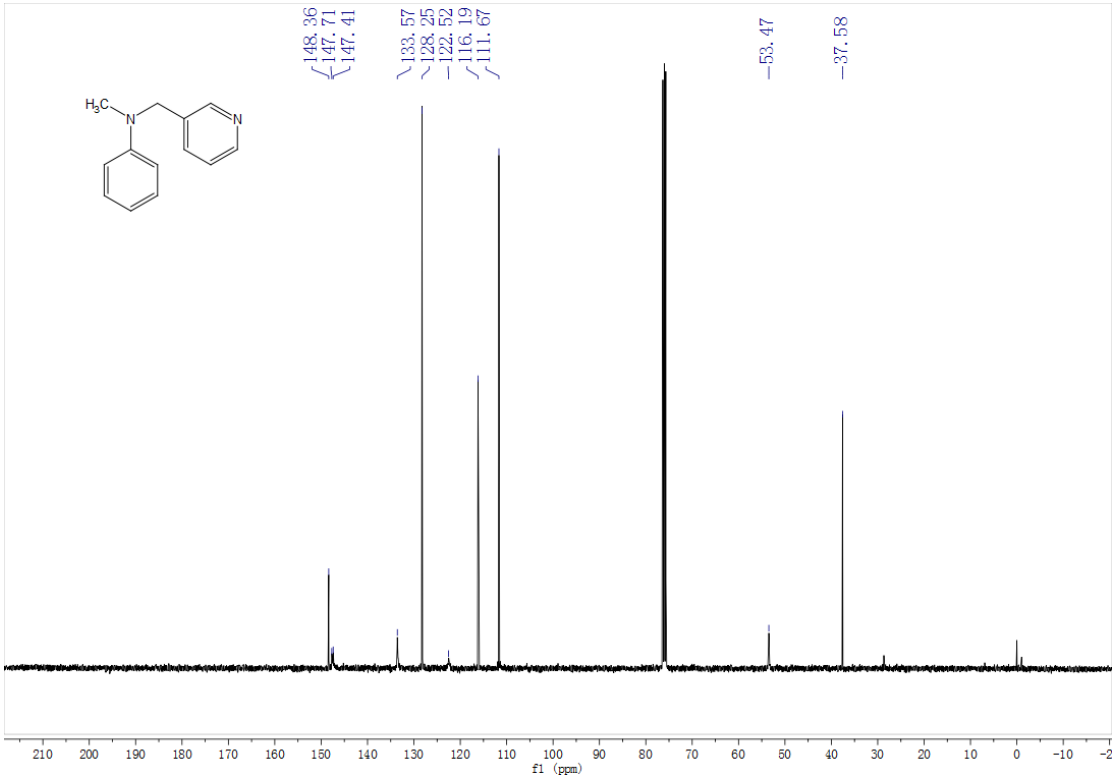
N-methyl-N-(pyridin-2-ylmethyl)aniline (5an)



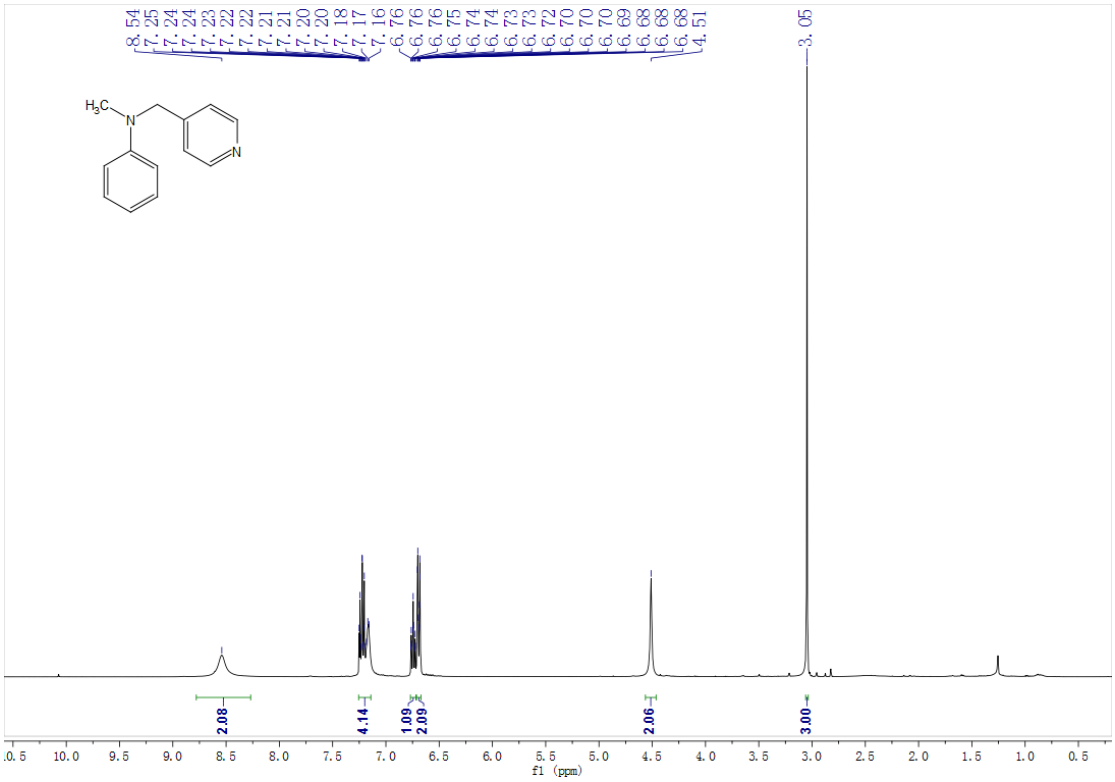


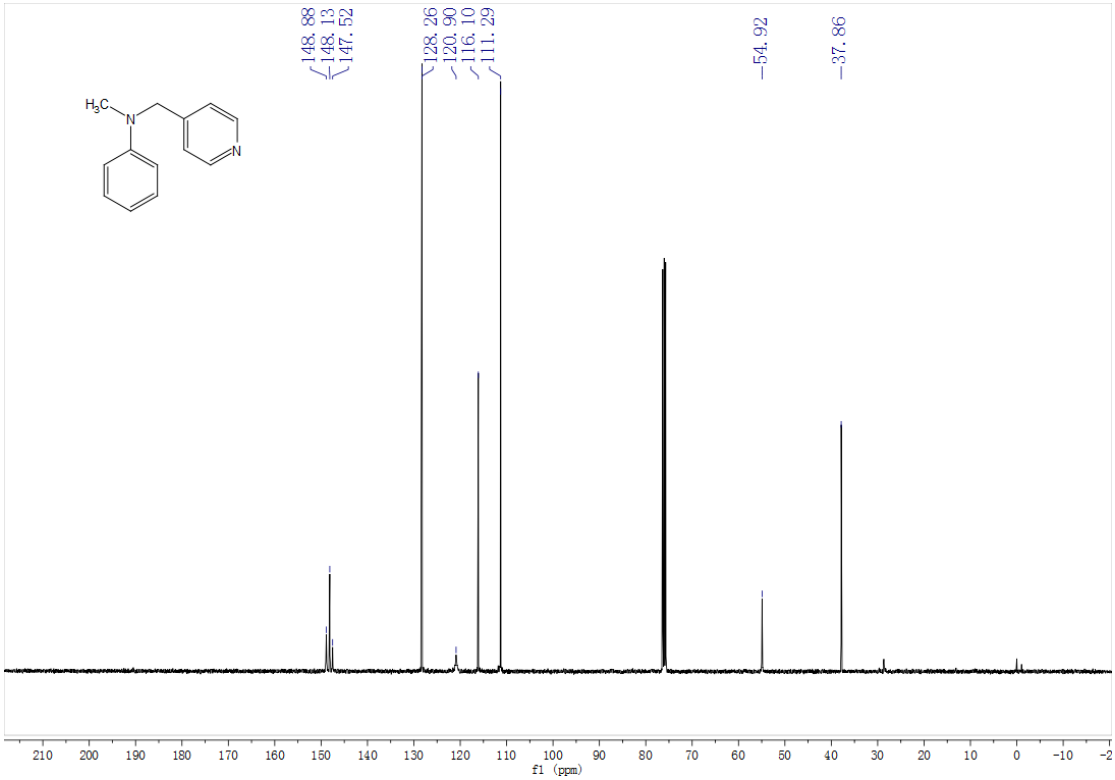
N-methyl-N-(pyridin-3-ylmethyl)aniline (5ao)



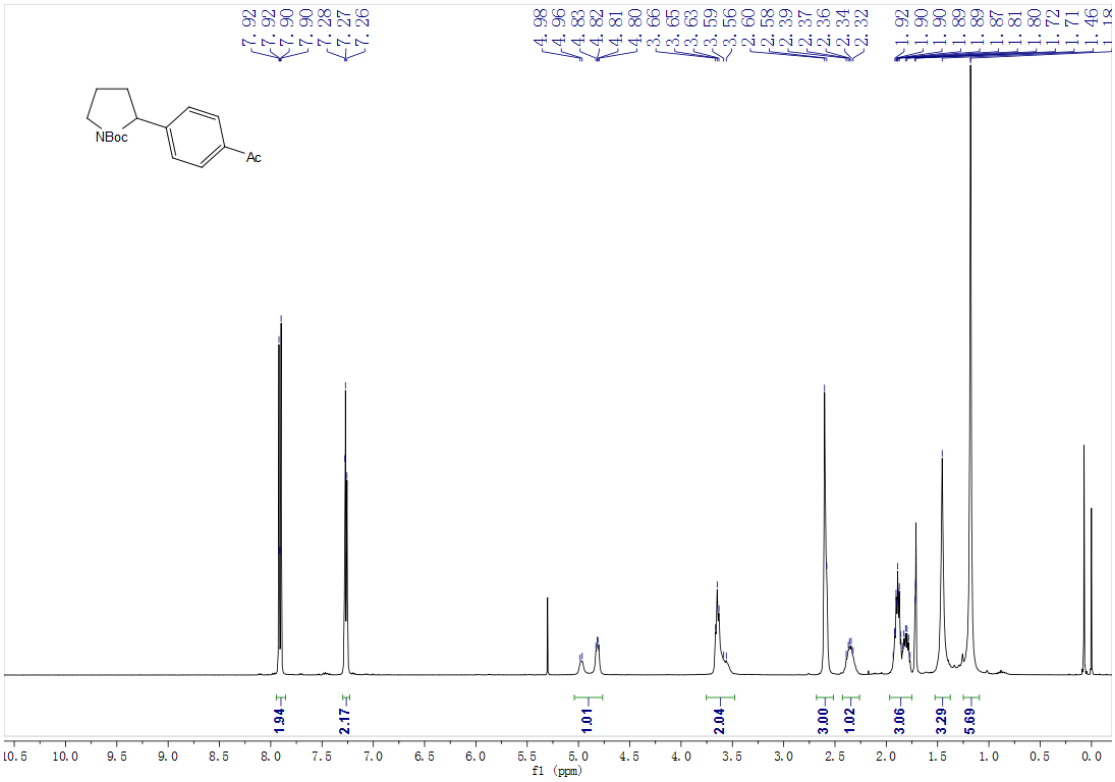


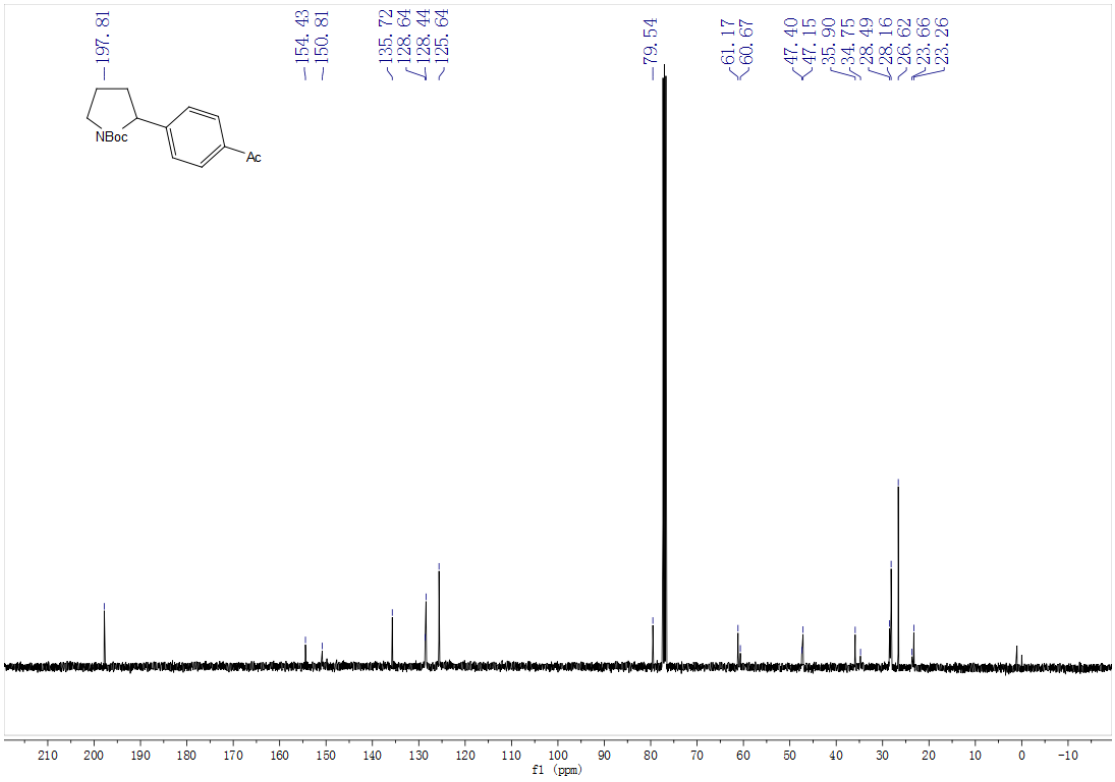
N-methyl-N-(pyridin-4-ylmethyl)aniline (5ap)



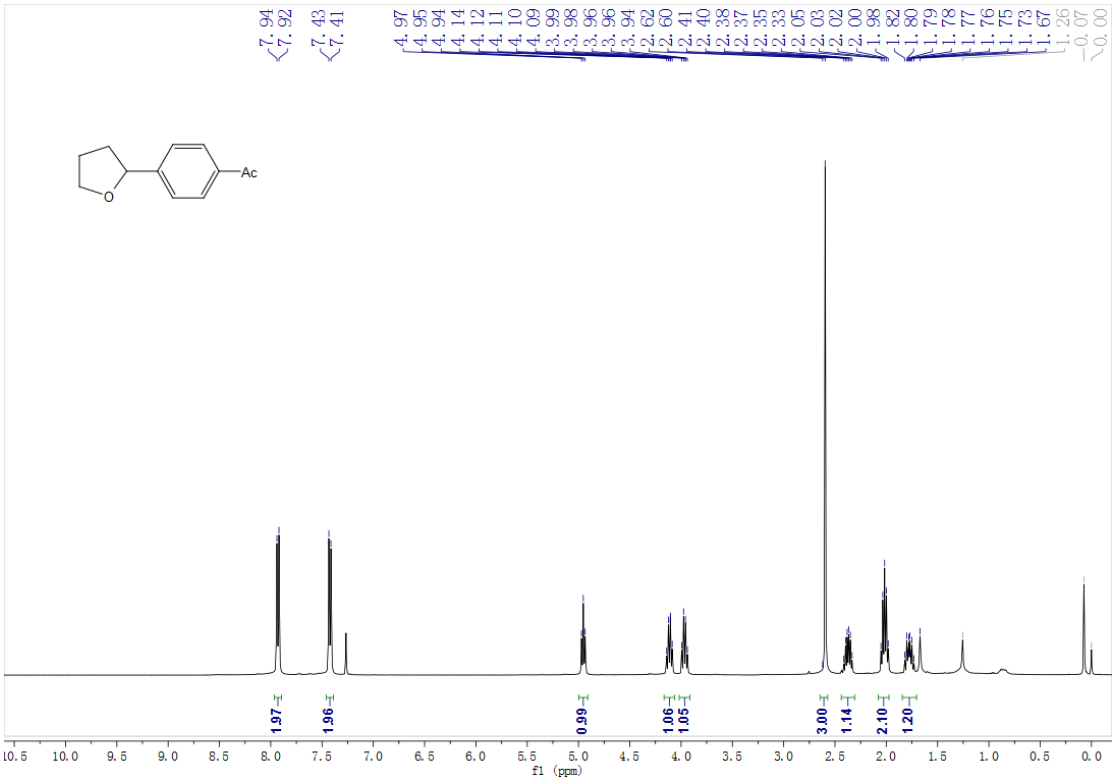


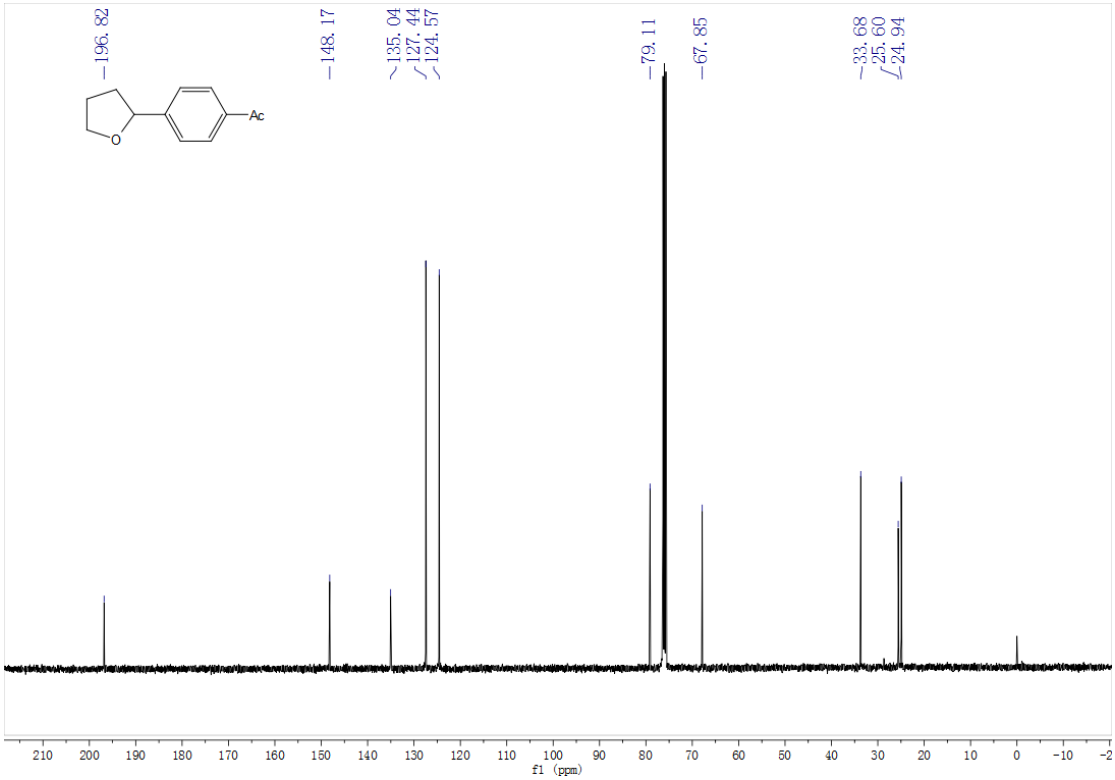
tert-butyl 2-(4-acetylphenyl)pyrrolidine-1-carboxylate (5ma)



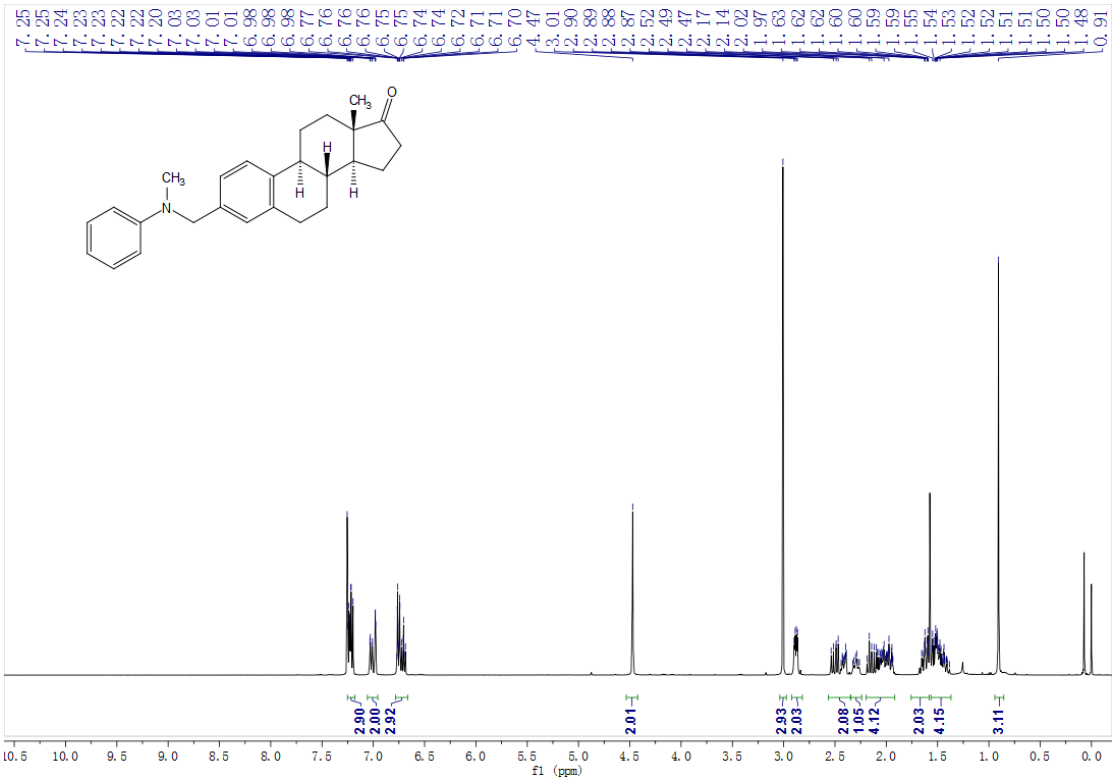


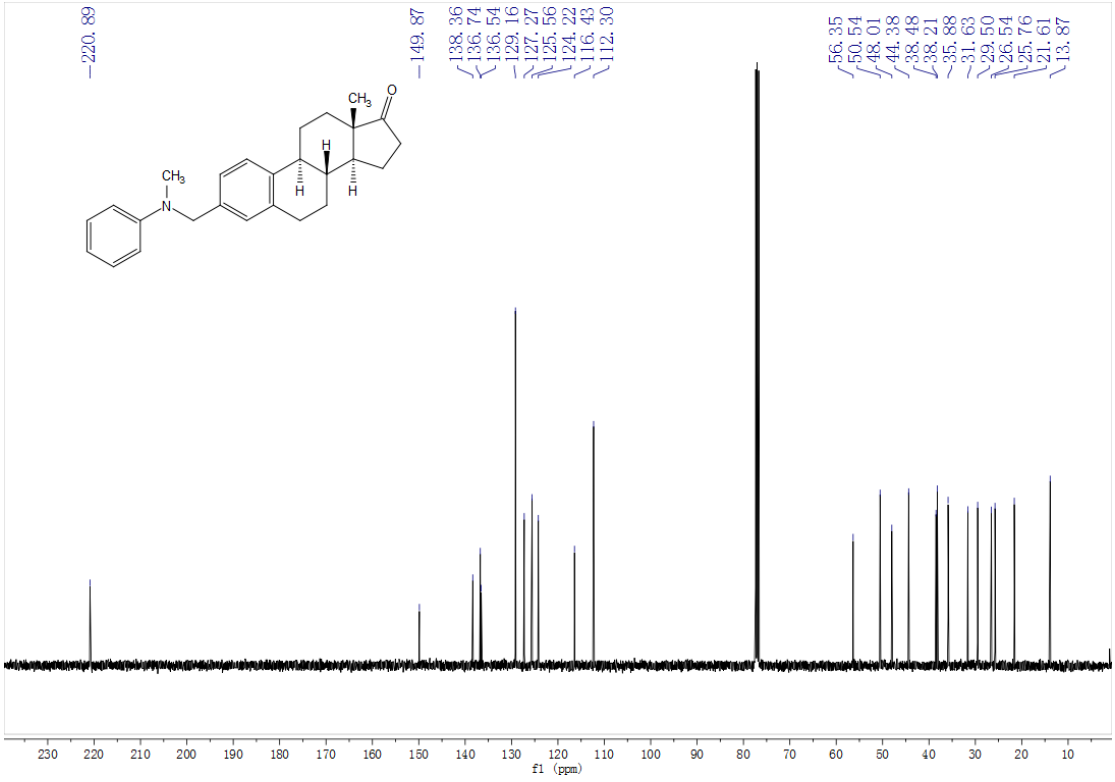
1-(4-(tetrahydrofuran-2-yl)phenyl)ethanone (5na)



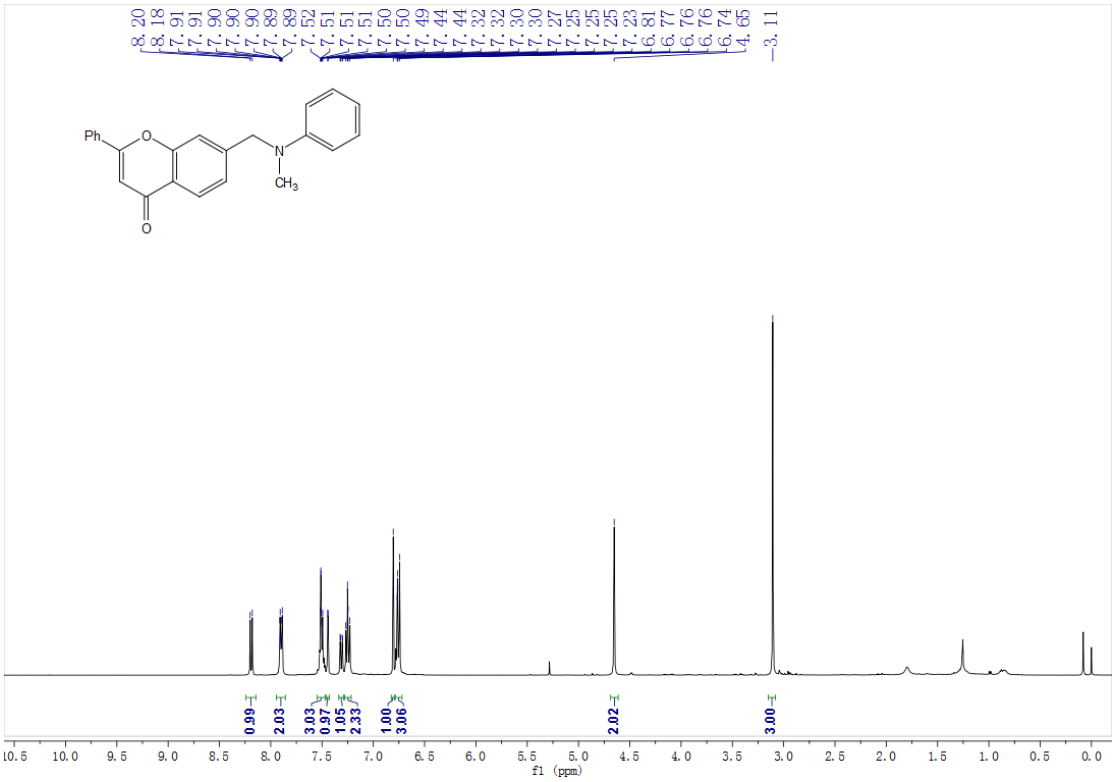


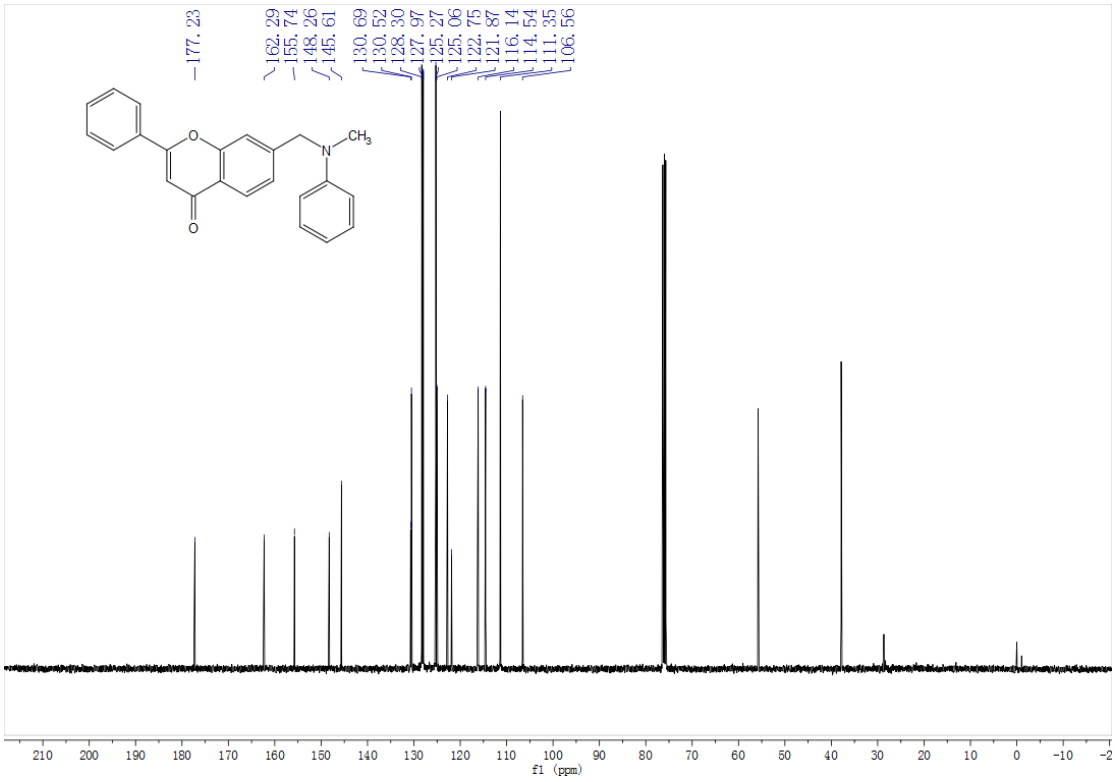
(*8R,9S,13S,14S*)-13-methyl-3-((methyl(phenyl)amino)methyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[a]phenanthren-17(14H)-one (5aq)



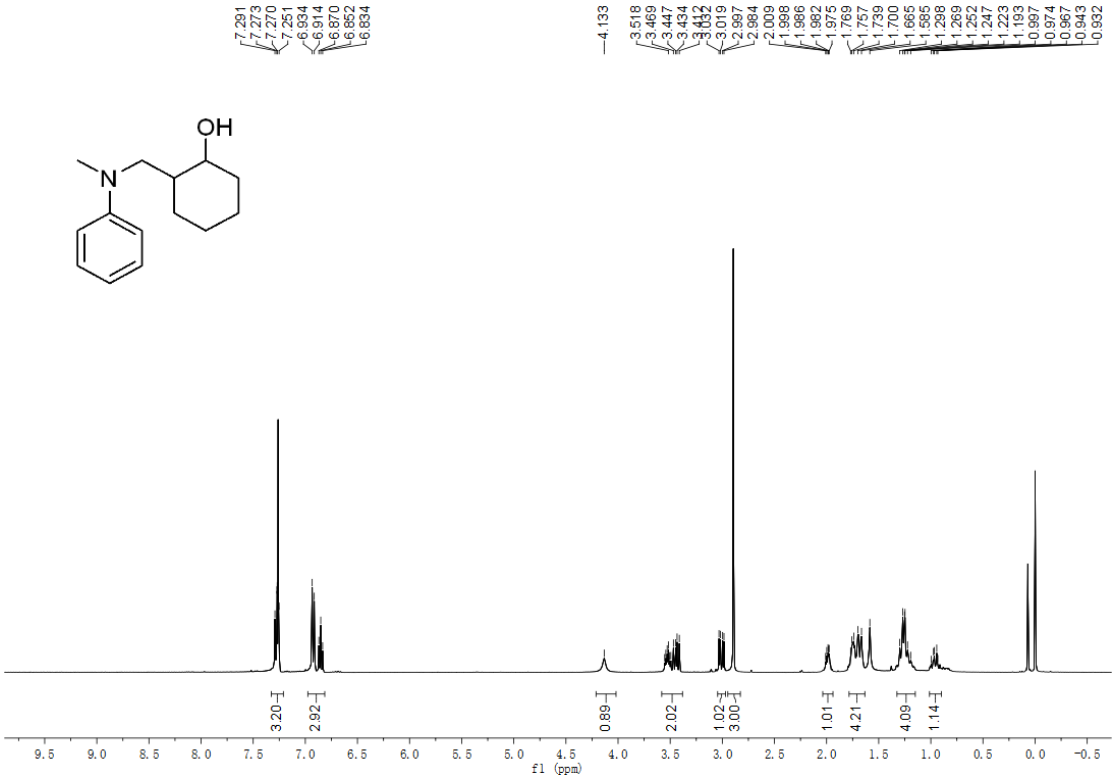


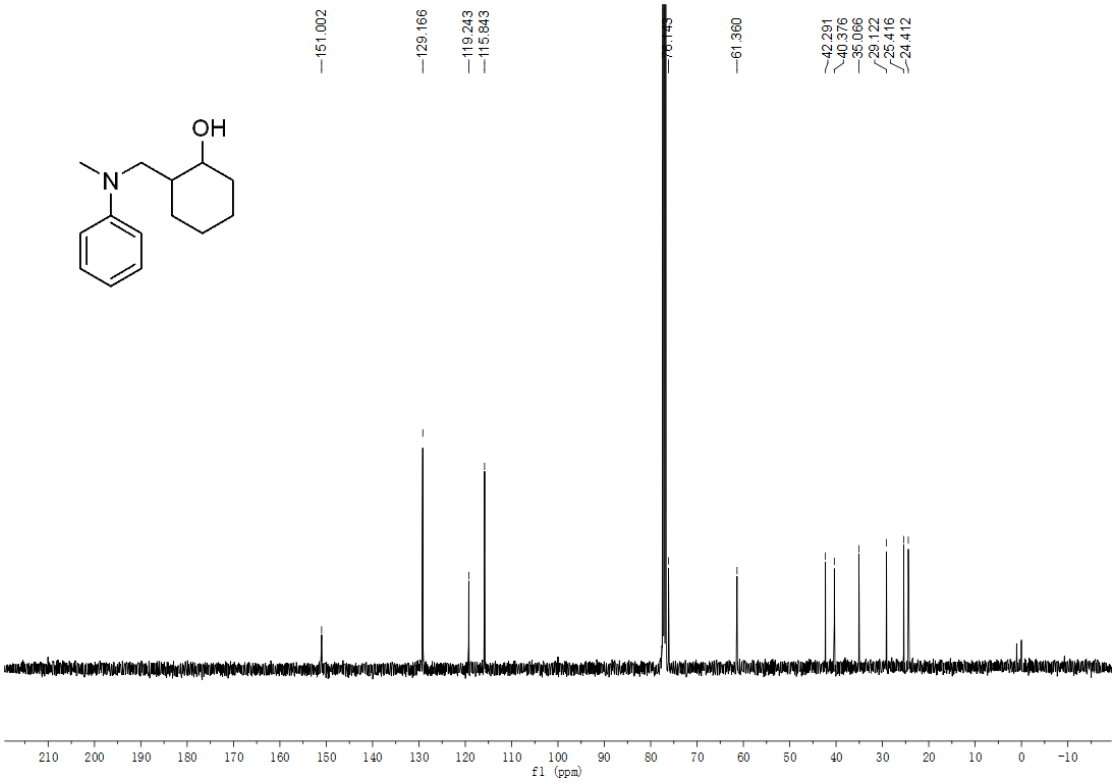
7-((methyl(phenyl)amino)methyl)-2-phenyl-4H-chromen-4-one (5ar)



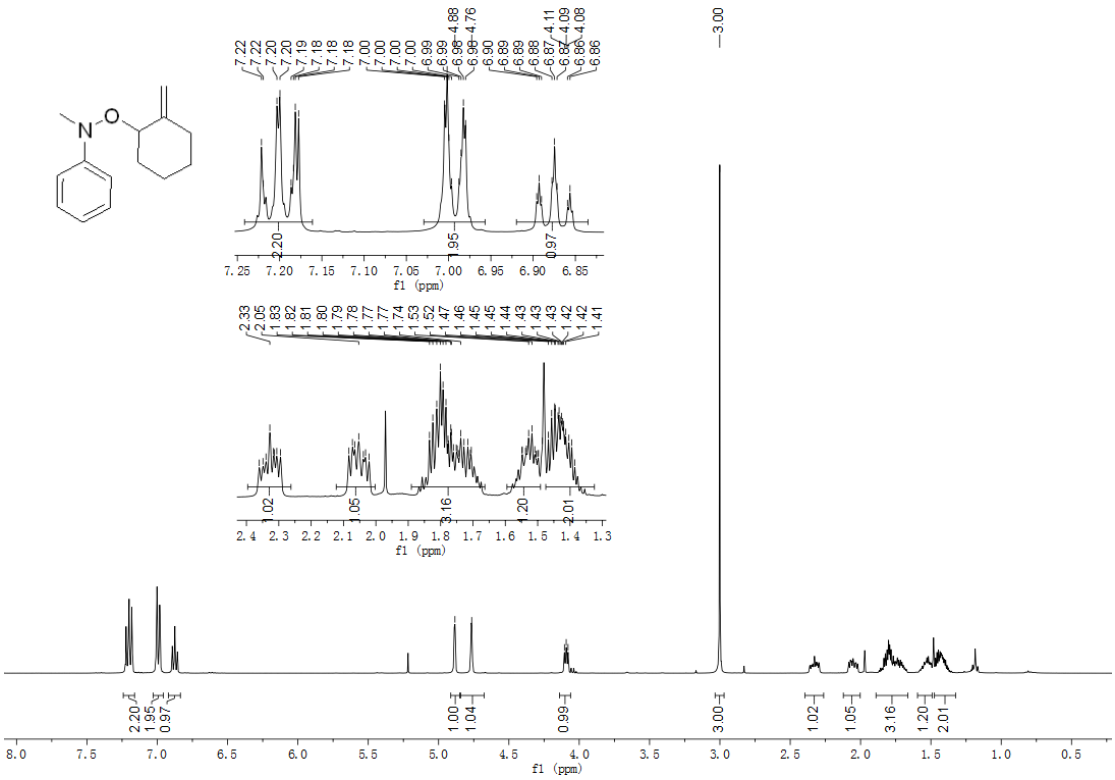


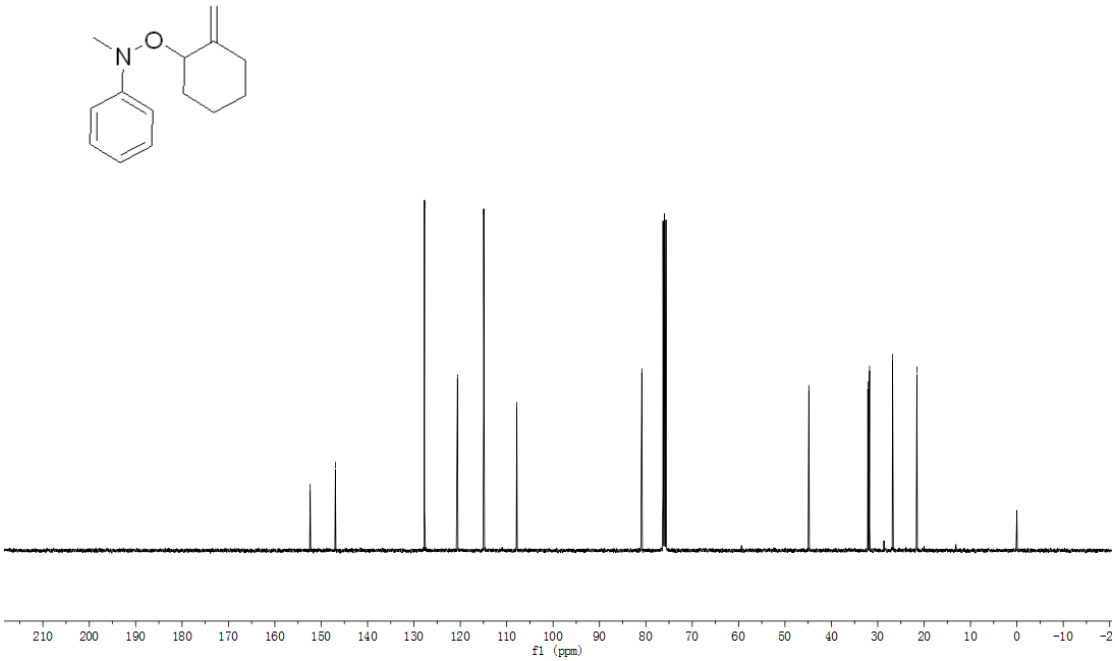
2-((methyl(phenyl)amino)methyl)cyclohexan-1-ol (7ag)



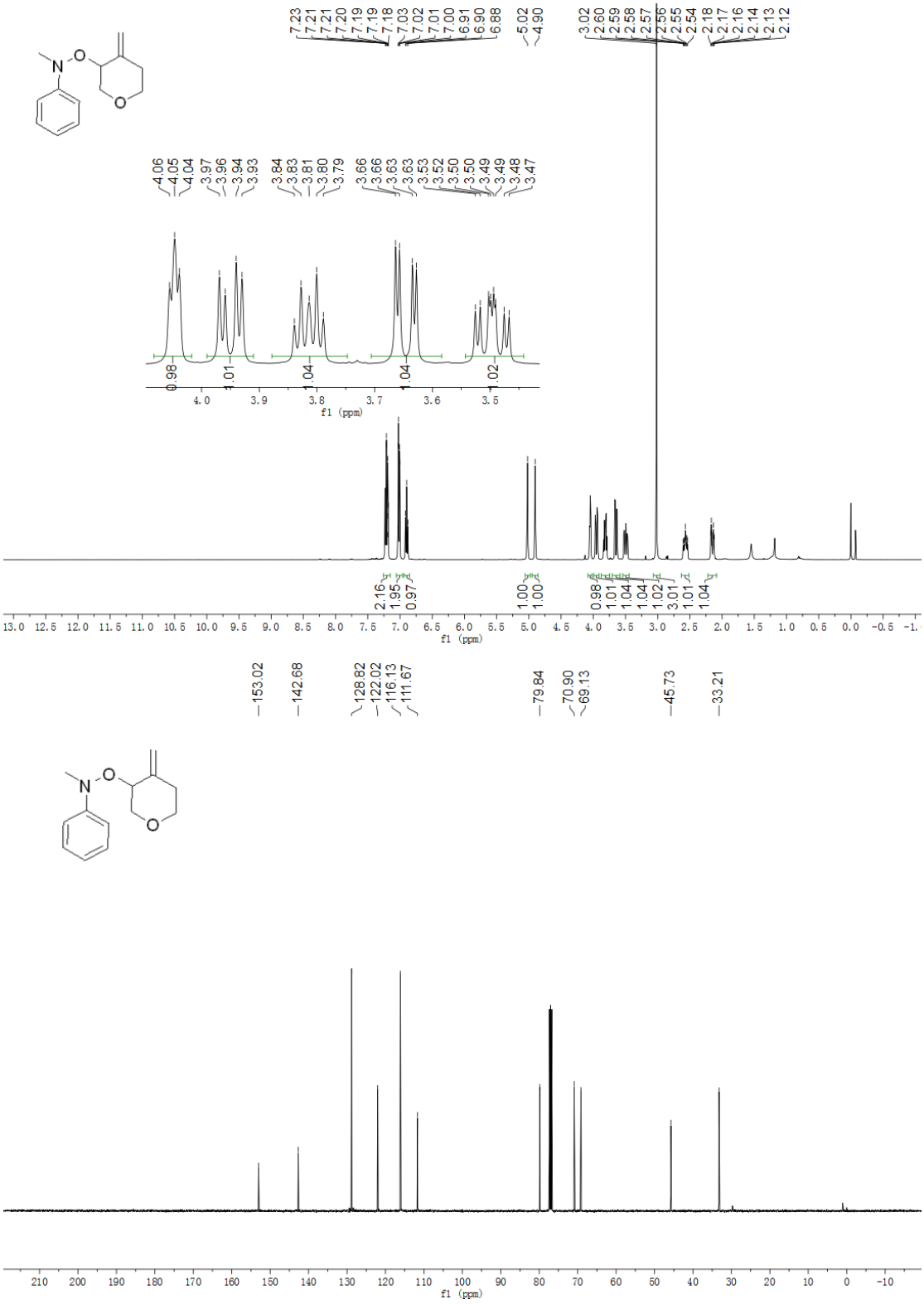


N-methyl-O-(2-methylenecyclohexyl)-N-phenylhydroxylamine(8ag)





N-methyl-O-(4-methylenetetrahydro-2H-pyran-3-yl)-N-phenylhydroxylamine (8an)



4-bromo-N-(cyclohex-1-en-1-ylmethyl)-N-methylaniline(9ag)