Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cp_2TiCl_2-catalyzed highly regioselective hydroamination of styrenes with hydroxylamines

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1. General Comments

All the reactions were carried out in oven-dried sealed tube with Teflon-lined septum under N_2 atmosphere. Unless indicated, all materials were obtained from commercial sources and used as received. Diethyl ether was dried by solvent processing system. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, s referred to multiplet, quartet, triplet, doublet, singlet. The reaction progress was monitored by GC-MS if applicable.

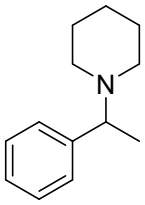
1-Methyl-2-vinylbenzene **1b**, 1-methyl-3-vinylbenzene **1c**, 1-methyl-4-vinylbenzene **1d**, 1-isobutyl-4-vinylbenzene **1e**, 1-methoxy-3-vinylbenzene **1g**, 1-methoxy-4-vinylbenzene **1h**, 1-methoxy-2-vinylbenzene **1i**, 1,4-divinylbenzene **1j**, 1,4-dimethyl-2-vinylbenzene **1k**, and 1,2-dimethyl-4-vinylbenzene **1l** were synthesized through the Wittig reaction with the corresponding aldehydes.

Piperidin-1-yl benzoate **2a**, morpholino benzoate **2b**, *O*-benzoyl-*N,N*-dibenzylhydroxylamine **2c**, *O*-benzoyl-*N*-cyclohexyl-*N*-methylhydroxylamine **2d**, *O*-benzoyl-*N*-butyl-*N*-methylhydroxylamine **2e**, *N,N*-diallyl-*O*-benzoylhydroxylamine **2f**, *O*-benzoyl-*N,N*-diisopropylhydroxylamine **2g**, 2,2,6,6-tetramethylpiperidin-1-yl benzoate **2h** and *O*-benzoyl-*N*-butylhydroxylamine **2i** were synthesized through the reaction of benzoyl peroxide with the corresponding amines.

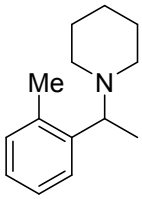
2. Experimental Section

General procedure

An oven-dried Schleck tube was charged with Cp_2TiCl_2 (6.2 mg, 0.025 mmol), which was degassed at 50 °C for 0.5 h, then degassed and refilled with N_2 for 5 times. Then dry diethyl ether (2 mL) was added into the mixture, and ^{i}PrMgCl (0.28 mL, 0.55 mmol, 2 M in diethyl ether) was added by drops. Subsequently, the alkenes **1a-1m** (0.5 mmol) were added *via* syringe. The resulting mixture was stirred at 30 °C for 24 h under N_2 protection. Then, the reaction mixture was cooled down to 0 °C, and amine benzoate (0.41 mmol) was added at the same temperature. The mixture was stirred at ambient temperature for 2 h. Quenching the reaction with sat. aq. $NaHCO_3$ and ethyl acetate (EA) was added. The aqueous layer was extracted with EA twice. The combined organic layer was then extracted with 1 M HCl twice. NaOH pellets were added until the solution is strong basicity. The aqueous layer was then extracted with EA three times, dried by Na_2SO_4, and concentrated in *vacuo* to give **3aa-3fg**, which were identified by ^{1}H and ^{13}C NMR.

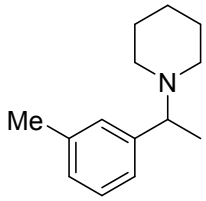


1-(1-Phenylethyl)piperidine (3aa)[1]: Pale yellow oil liquid, 64.3 mg (85% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, J = 4.3 Hz, 4H), 7.26 – 7.20 (m, 1H), 3.39 (q, J = 6.8 Hz, 1H), 2.45 – 2.29 (m, 4H), 1.55 (dt, J = 10.9, 5.6 Hz, 4H), 1.42-1.35 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.03, 128.13, 127.89, 126.77, 65.32, 51.63, 26.39, 24.74, 19.53. GC-MS m/z. 189.

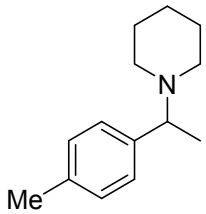


Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(*o*-Tolyl)ethyl)piperidine (3ba)**[2]: Pale yellow oil liquid, 50.1 mg (61% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.43 (d, J =

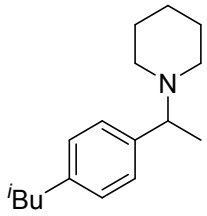
7.5 Hz, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.08 (m, 2H), 3.58 (q, *J* = 6.6 Hz, 1H), 2.47 (dd, *J* = 13.8, 8.6 Hz, 2H), 2.35 (s, 3H), 2.32 (d, *J* = 10.4 Hz, 2H), 1.57 – 1.48 (m, 4H), 1.43 – 1.37 (m, 2H), 1.29 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.20, 136.01, 130.37, 126.84, 126.26, 125.95, 60.81, 51.67, 26.28, 24.74, 19.69, 18.49. GC-MS m/z. 203.



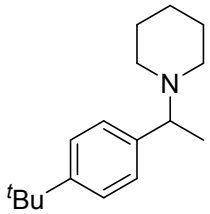
Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(*m*-Tolyl)ethyl)piperidine (3ca)**[2]: Isolated by column chromatography. Pale yellow oil liquid, 49.7 mg (60% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.18 (t, *J* = 7.5 Hz, 1H), 7.11 – 7.05 (m, 2H), 7.03 (d, *J* = 7.3 Hz, 1H), 3.33 (q, *J* = 6.7 Hz, 1H), 2.36 (d, *J* = 16.6 Hz, 7H), 1.54 (dt, *J* = 11.0, 5.5 Hz, 4H), 1.41 – 1.33 (m, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.00, 137.62, 128.54, 127.98, 127.52, 124.99, 65.40, 51.71, 26.36, 24.72, 21.61, 19.71. GC-MS m/z. 203.



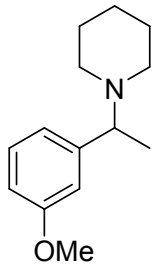
1-(1-(*p*-Tolyl)ethyl)piperidine (3da)[2]: Pale yellow oil liquid, 59.0 mg (72% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.17 (d, *J* = 7.9 Hz, 2H), 7.10 (d, *J* = 7.8 Hz, 2H), 3.36 (q, *J* = 6.8 Hz, 1H), 2.43 – 2.32 (m, 4H), 2.32 (s, 3H), 1.57-1.49 (m, 4H), 1.41-1.36 (m, 2H), 1.35 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.83, 136.23, 128.79, 127.81, 64.95, 51.56, 26.39, 24.73, 21.15, 19.56. GC-MS m/z. 203.



1-(1-(4-*iso*-Butylphenyl)ethyl)piperidine (3ea): Pale yellow oil liquid, 64.5 mg (65% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.21 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.41 (q, *J* = 6.8 Hz, 1H), 2.48 (d, *J* = 7.2 Hz, 2H), 2.36 (dt, *J* = 20.0, 10.7 Hz, 4H), 1.87 (td, *J* = 13.5, 6.7 Hz, 1H), 1.62 – 1.52 (m, 4H), 1.41 (dd, *J* = 12.0, 6.4 Hz, 5H), 0.93 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.91, 140.13, 128.82, 127.64, 77.48, 77.16, 76.84, 65.01, 51.56, 45.24, 30.34, 26.38, 24.74, 22.56, 19.41. GC-MS m/z. 245.

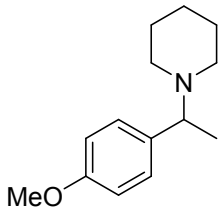


1-(1-(4-(*tert*-Butyl)phenyl)ethyl)piperidine (3fa)[2]: Pale yellow oil liquid, 71.6 mg (73% yield); ^{1}H NMR (400 MHz, CDCl3) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 3.38 (q, *J* = 6.8 Hz, 1H), 2.45 – 2.26 (m, 4H), 1.59 – 1.50 (m, 4H), 1.41 – 1.37 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.47, 140.74, 127.53, 124.93, 64.90, 51.58, 34.52, 31.56, 26.43, 24.77, 19.37. GC-MS m/z. 245.

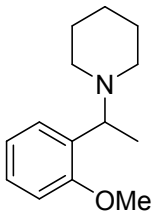


Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(3-Methoxyphenyl)ethyl)piperidine (3ga)**[2]: Pale yellow oil liquid, 60.4 mg (69% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.24 – 7.18 (m, 1H), 6.89 (dd, *J* = 4.3, 1.9 Hz, 2H), 6.79 – 6.75 (m, 1H), 3.80 (s, 3H),

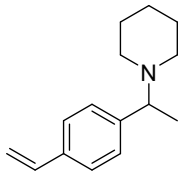
3.36 (q, *J* = 6.7 Hz, 1H), 2.47 – 2.26 (m, 4H), 1.58-1.51 (m, 4H), 1.43 – 1.37 (m, 2H), 1.35 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 159.56, 145.96, 129.00, 120.28, 113.52, 111.90, 65.29, 55.24, 51.64, 26.38, 24.72, 19.57. GC-MS m/z. 219.



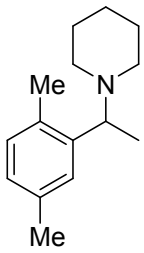
1-(1-(4-Methoxyphenyl)ethyl)piperidine (3ha)[2]: Pale yellow oil liquid, 54.3 mg (62% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.24 – 7.17 (m, 2H), 6.89 – 6.80 (m, 2H), 3.80 (s, 3H), 3.38 (q, *J* = 6.8 Hz, 1H), 2.47 – 2.25 (m, 4H), 1.59 – 1.51 (m, 4H), 1.41 – 1.37 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 158.46, 135.83, 128.88, 113.41, 64.50, 55.29, 51.46, 26.37, 24.73, 19.42. GC-MS m/z. 219.



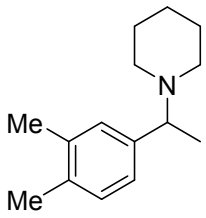
Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(2-Methoxyphenyl)ethyl)piperidine (3ia)**[2]: Isolated by column chromatography. Pale yellow oil liquid, 31.54 mg (18% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.42 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.19 (td, *J* = 8.2, 1.7 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.95 (q, *J* = 6.7 Hz, 1H), 3.81 (s, 3H), 2.37 (dd, *J* = 21.7, 15.7 Hz, 4H), 1.55 (dt, *J* = 11.0, 5.5 Hz, 4H), 1.38 (dd, *J* = 11.5, 6.0 Hz, 2H), 1.30 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 157.22, 132.58, 128.04, 127.33, 120.53, 110.65, 56.36, 55.57, 51.70, 26.44, 24.81, 19.87. GC-MS m/z. 219.



1-(1-(4-Vinylphenyl)ethyl)piperidine (3ja): Pale yellow oil liquid, 55.0 mg (64% yield, isolated by column chromatography on silica gel); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.35 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.22 (m, 2H), 6.70 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.72 (dd, *J* = 17.5, 0.7 Hz, 1H), 5.23 – 5.17 (m, 1H), 3.37 (q, *J* = 6.8 Hz, 1H), 2.43 – 2.27 (m, 4H), 1.54 (dt, *J* = 10.9, 5.6 Hz, 4H), 1.37 (dd, *J* = 10.4, 6.2 Hz, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.85, 136.79, 136.18, 128.07, 126.03, 113.33, 65.04, 51.64, 26.41, 24.74, 19.49. GC-MS m/z. 215.

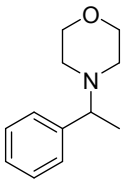


Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(2,5-Dimethylphenyl)ethyl)piperidine (3ka)**: Pale yellow oil liquid, 41.6 mg (48% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.25 (s, 1H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 7.6, 1.7 Hz, 1H), 3.51 (q, *J* = 6.7 Hz, 1H), 2.54 – 2.41 (m, 2H), 2.38 – 2.28 (m, 8H), 1.60 – 1.49 (m, 4H), 1.42 (dt, *J* = 11.3, 5.8 Hz, 2H), 1.28 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 143.37, 135.27, 132.83, 130.26, 127.42, 126.92, 77.48, 77.16, 76.84, 61.02, 51.94, 26.44, 24.86, 21.27, 19.27, 18.82. GC-MS m/z. 217.

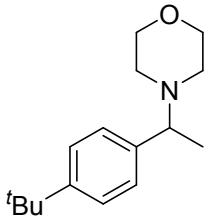


Do as the general procedure expect that LiBr (47.7 mg, 0.55 mmol) was added at the beginning as an additive. **1-(1-(3,4-Dimethylphenyl)ethyl)piperidine (3la)**: Pale yellow oil liquid, 53.8 mg (62% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ

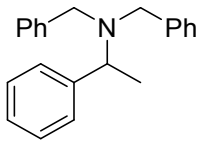
7.09 – 6.98 (m, 3H), 3.40 (q, *J* = 6.8 Hz, 1H), 2.39 (dd, *J* = 11.2, 5.8 Hz, 4H), 2.25 (d, *J* = 6.6 Hz, 6H), 1.57 (ddd, *J* = 8.9, 5.9, 3.3 Hz, 4H), 1.37 (t, *J* = 5.4 Hz, 5H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.42, 136.24, 135.18, 129.39, 129.34, 125.52, 77.48, 77.16, 76.84, 65.03, 51.44, 26.04, 24.52, 19.97, 19.50, 19.45. GC-MS m/z. 217.



4-(1-Phenylethyl)morpholine (3ab)[1]: Pale yellow oil liquid, 61.9 mg (81% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.30 (d, *J* = 4.3 Hz, 4H), 7.26 – 7.20 (m, 1H), 3.71 – 3.63 (m, 4H), 3.29 (q, *J* = 6.6 Hz, 1H), 2.55 – 2.42 (m, 2H), 2.40 – 2.31 (m, 2H), 1.34 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.03, 128.39, 127.72, 127.07, 67.32, 65.49, 51.41, 19.94. GC-MS m/z. 191.

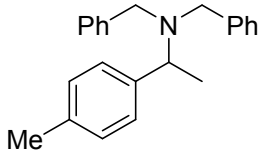


4-(1-(4-(*tert*-Butyl)phenyl)ethyl)morpholine (3fb): Pale yellow oil liquid, 65.2 mg (66% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 3.68 (t, *J* = 4.7 Hz, 4H), 3.29 (q, *J* = 6.7 Hz, 1H), 2.53 – 2.41 (m, 2H), 2.41 – 2.30 (m, 2H), 1.34 (d, *J* = 6.7 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.95, 140.48, 127.44, 125.23, 77.48, 77.16, 76.84, 67.34, 65.11, 51.35, 34.56, 31.54, 19.69. GC-MS m/z. 247.

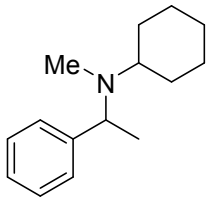


***N,N*-Dibenzyl-1-phenylethan-1-amine (3ac)**[1]: Pale yellow oil liquid, 78.2 mg (65% yield, isolated by column chromatography on silica gel); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (dd, *J* = 5.9, 2.0 Hz, 6H), 7.35 – 7.26 (m, 6H), 7.25 – 7.16 (m, 3H), 3.92 (q, *J* = 6.9 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 2H), 3.45 (d, *J* = 13.8 Hz, 2H),

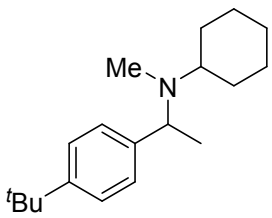
1.42 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 142.84, 140.56, 128.77, 128.31, 128.15, 128.08, 126.86, 56.27, 53.69, 13.88. GC-MS m/z. 301.



***N,N*-Dibenzyl-1-(p-tolyl)ethan-1-amine (3dc)**: Pale yellow oil liquid, 100.8 mg (80% yield, isolated by column chromatography on silica gel); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.38 (d, *J* = 7.6 Hz, 4H), 7.31 – 7.23 (m, 6H), 7.21 – 7.09 (m, 4H), 3.88 (q, *J* = 6.8 Hz, 1H), 3.59 (d, *J* = 13.8 Hz, 2H), 3.43 (d, *J* = 13.8 Hz, 2H), 2.31 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.65, 139.63, 136.28, 128.78, 128.75, 128.29, 128.08, 126.81, 56.00, 53.66, 21.20, 14.24. GC-MS m/z. 315.

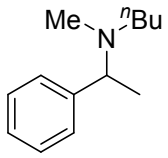


***N*-Methyl-*N*-(1-phenylethyl)cyclohexanamine (3ad)**: Pale yellow oil liquid, 59.0 mg (68% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.31 (ddd, *J* = 14.9, 10.8, 4.5 Hz, 4H), 7.20 (ddd, *J* = 8.2, 2.5, 1.2 Hz, 1H), 3.76 (q, *J* = 6.7 Hz, 1H), 2.50 (tt, *J* = 11.2, 3.1 Hz, 1H), 2.17 (s, 3H), 1.73 (dt, *J* = 20.0, 11.8 Hz, 4H), 1.59 – 1.52 (m, 1H), 1.33 (d, *J* = 6.7 Hz, 3H), 1.30 – 1.17 (m, 2H), 1.09 (dddd, *J* = 15.3, 12.6, 6.5, 3.2 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 146.17, 128.29, 127.44, 126.62, 77.48, 77.16, 76.84, 60.76, 58.71, 33.22, 29.54, 28.37, 26.54, 26.21, 26.16, 20.55. GC-MS m/z. 317.

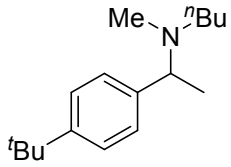


***N*-(1-(4-(*tert*-Butyl)phenyl)ethyl)-*N*-methylcyclohexanamine (3fd)**: Pale yellow oil liquid, 43.7 mg (40% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.28 (dd, *J* = 22.1, 8.2 Hz, 4H), 3.77 (q, *J* = 6.7 Hz, 1H), 2.52 (ddd, *J* = 11.3, 7.3, 2.9 Hz, 1H), 2.16

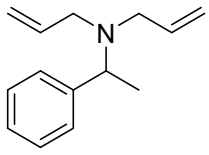
(s, 3H), 1.79 – 1.69 (m, 4H), 1.58 (d, *J* = 11.3 Hz, 1H), 1.34 – 1.25 (m, 14H), 1.20 – 0.87 (m, 4H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.33, 142.79, 127.10, 125.10, 77.48, 77.16, 76.84, 59.99, 58.81, 34.50, 33.17, 31.56, 29.51, 28.86, 26.56, 26.19, 26.16, 19.90. GC-MS m/z. 273.



***N*-Methyl-*N*-(1-phenylethyl)butan-1-amine (3ae)**: Pale yellow oil liquid, 45.1 mg (59% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.35 – 7.28 (m, 4H), 7.26 – 7.20 (m, 1H), 3.56 (q, *J* = 6.7 Hz, 1H), 2.42 (dt, *J* = 12.6, 7.7 Hz, 1H), 2.30 – 2.22 (m, 1H), 2.18 (s, 3H), 1.44 (dd, *J* = 14.8, 7.4 Hz, 2H), 1.36 (d, *J* = 6.7 Hz, 3H), 1.28 (ddd, *J* = 10.1, 7.3, 2.4 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.29, 128.15, 127.80, 126.75, 77.48, 77.16, 76.84, 63.48, 54.25, 38.61, 29.53, 20.72, 18.72, 14.19. GC-MS m/z. 191.

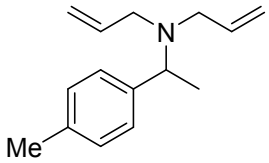


***N*-(1-(4-(*tert*-Butyl)phenyl)ethyl)-*N*-methylbutan-1-amine (3fe)**: Pale yellow oil liquid, 63.2 mg (64% yield); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 – 7.29 (m, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.57 (q, *J* = 6.8 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.31 – 2.23 (m, 1H), 2.17 (s, 3H), 1.47 – 1.41 (m, 2H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H), 1.29 – 1.24 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 149.59, 140.62, 127.54, 125.00, 77.48, 77.16, 76.84, 62.87, 54.19, 38.45, 34.54, 31.55, 29.54, 20.77, 18.25, 14.21. GC-MS m/z. 247.

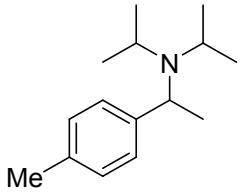


***N*-Allyl-*N*-(1-phenylethyl)prop-2-en-1-amine (3af)**[1]: Pale yellow oil liquid, 41.0 mg (51% yield, isolated by column chromatography on silica gel); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.34 – 7.25 (m, 4H), 7.19 (dd, *J* = 8.3, 6.0 Hz, 1H), 5.81 (ddt, *J* = 16.6, 10.2, 6.3 Hz, 2H), 5.13 (dd, *J* = 17.2, 1.4 Hz, 2H), 5.07 (dd, *J* = 10.3, 0.9 Hz,

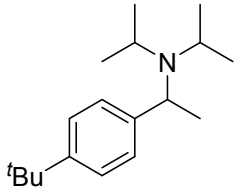
2H), 3.87 (q, *J* = 6.8 Hz, 1H), 3.11 (dd, *J* = 14.4, 6.3 Hz, 2H), 3.00 (dd, *J* = 14.4, 6.3 Hz, 2H), 1.32 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.14, 136.69, 128.17, 127.77, 126.75, 116.86, 58.41, 52.65, 17.18. GC-MS m/z. 201.



***N*-allyl-*N*-(1-(p-tolyl)ethyl)prop-2-en-1-amine (3df)**: Pale yellow oil liquid, 62.7 mg (73% yield,isolated by column chromatography on silica gel); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.27 (d, *J* = 6.9 Hz, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 5.95 – 5.79 (m, 2H), 5.15 (dd, *J* = 25.7, 13.7 Hz, 4H), 3.90 (q, *J* = 6.6 Hz, 1H), 3.17 (dd, *J* = 14.5, 5.9 Hz, 2H), 3.04 (dd, *J* = 14.4, 6.2 Hz, 2H), 2.35 (s, 3H), 1.36 (dd, *J* = 6.7, 1.5 Hz, 3H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 140.65, 139.63, 136.28, 128.78, 128.75, 128.29, 128.08, 126.81, 77.48, 77.16, 76.84, 56.00, 53.66, 21.20, 14.24. GC-MS m/z. 215.



***N-iso*-Propyl-*N*-(1-(p-tolyl)ethyl)propan-2-amine (3dg)**: Pale yellow oil liquid, 36.8 mg (42% yield, isolated by column chromatography on basicity aluminium oxide); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 4.07 (q, *J* = 6.8 Hz, 1H), 3.07 (dq, *J* = 13.3, 6.6 Hz, 2H), 2.30 (s, 3H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.6 Hz, 6H), 0.97 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 144.49, 135.27, 128.53, 127.65, 77.48, 77.16, 76.84, 51.78, 45.29, 23.39, 22.90, 21.10, 19.97. GC-MS m/z. 219.



***N*-(1-(4-(*tert*-Butyl)phenyl)ethyl)-*N-iso*-propylpropan-2-amine (3fg)**: Pale yellow oil liquid, 36.5 mg (35% yield, isolated by column chromatography on basicity

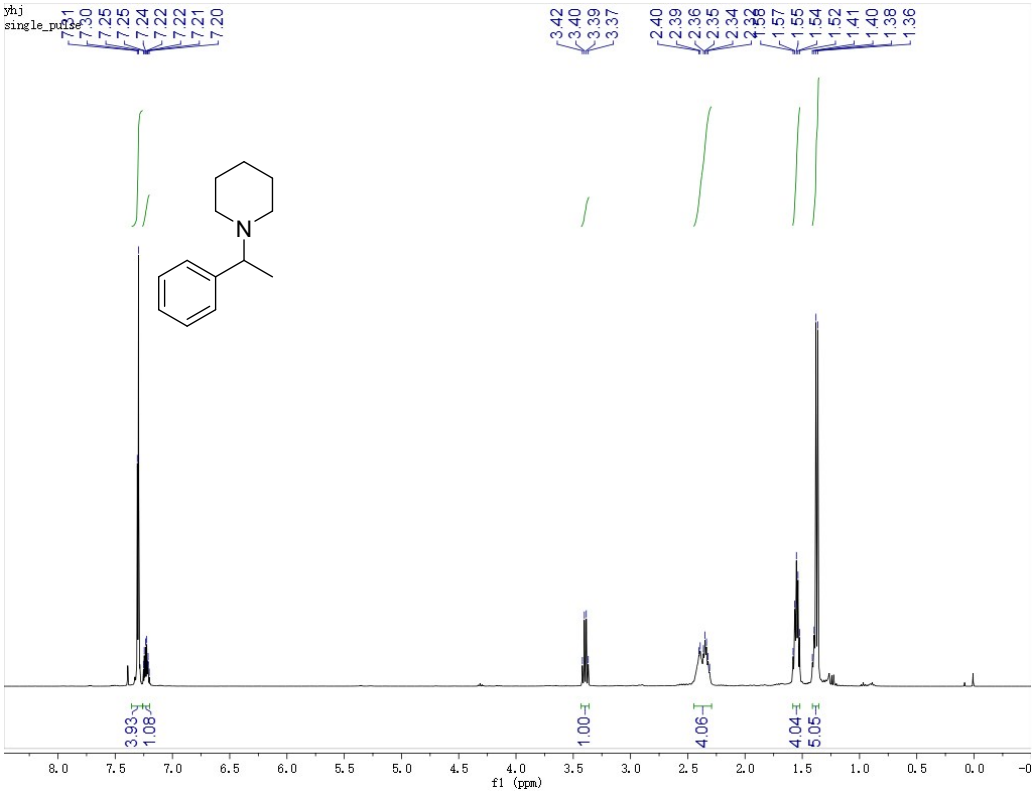
aluminium oxide); ^{1}H NMR (400 MHz, CHLOROFORM-D) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.25 (m, 2H), 4.10 (q, *J* = 6.8 Hz, 1H), 3.10 (dt, *J* = 13.3, 6.6 Hz, 2H), 1.44 (d, *J* = 6.8 Hz, 3H), 1.31 (s, 9H), 1.09 (d, *J* = 6.6 Hz, 6H), 1.00 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, CHLOROFORM-D) δ 148.57, 144.36, 127.38, 124.67, 51.61, 45.30, 34.44, 31.62, 23.50, 22.92, 19.83. GC-MS m/z. 261.

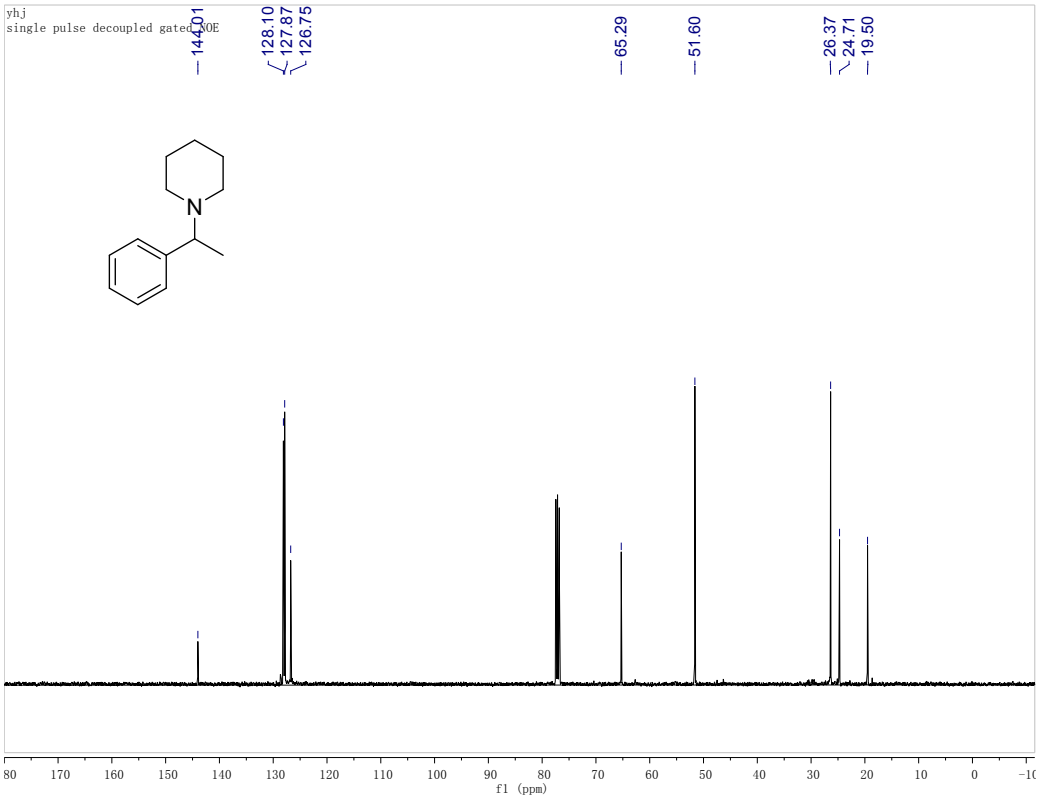
3. Reference

1. Y. Miki, K. Hirano, T. Satoh, and M. Miura, *Angew. Chem. Int. Ed.* **2013**, *52*, 10830 –10834.

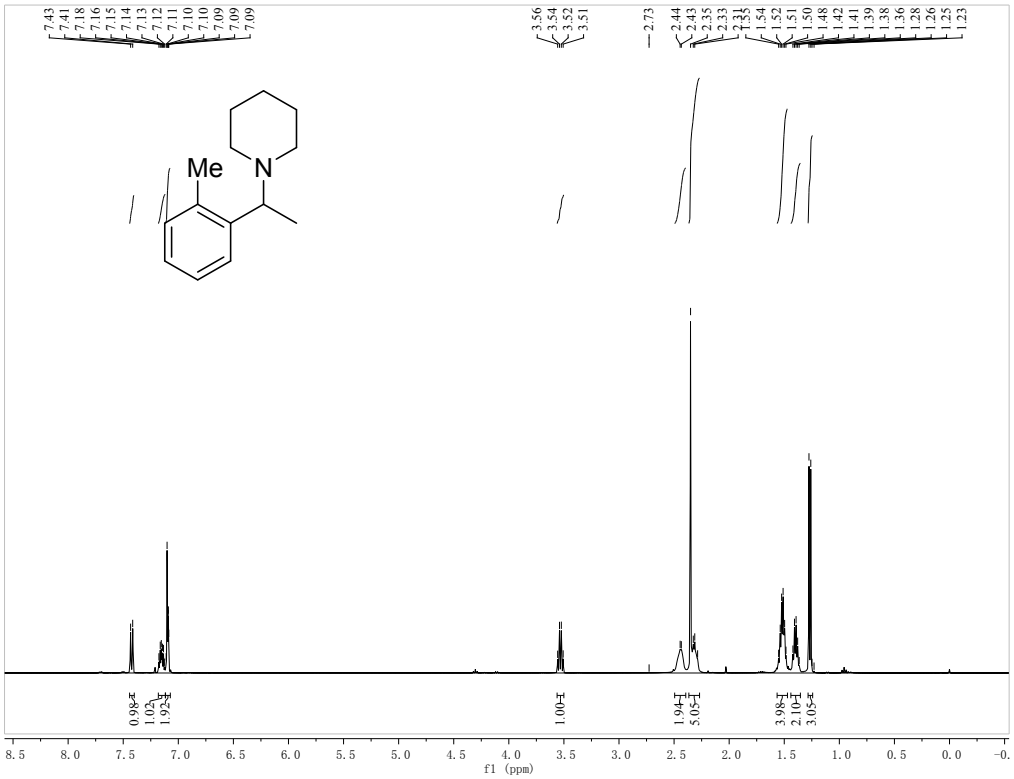
2. C. B. Huehls, A. Lin, and J. Yang, *Org. Lett.* **2014**, *16*, 3620−3623.

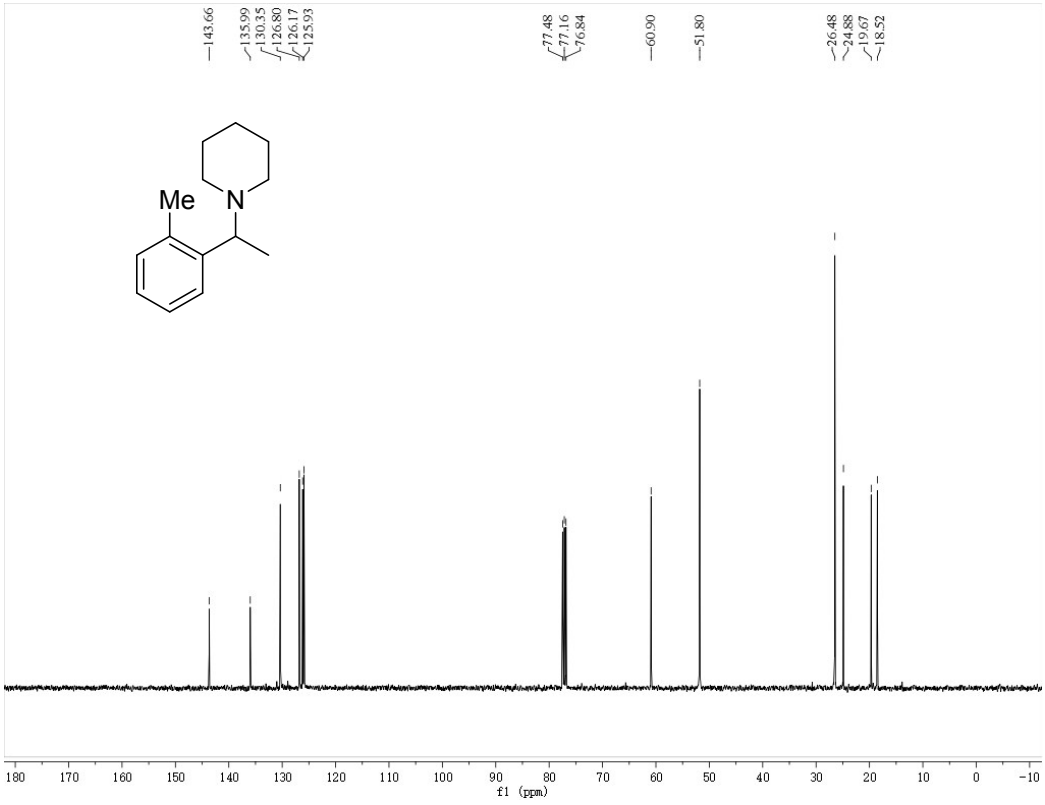
4. Copies of ^{1}H and ^{13}C NMR Spectra



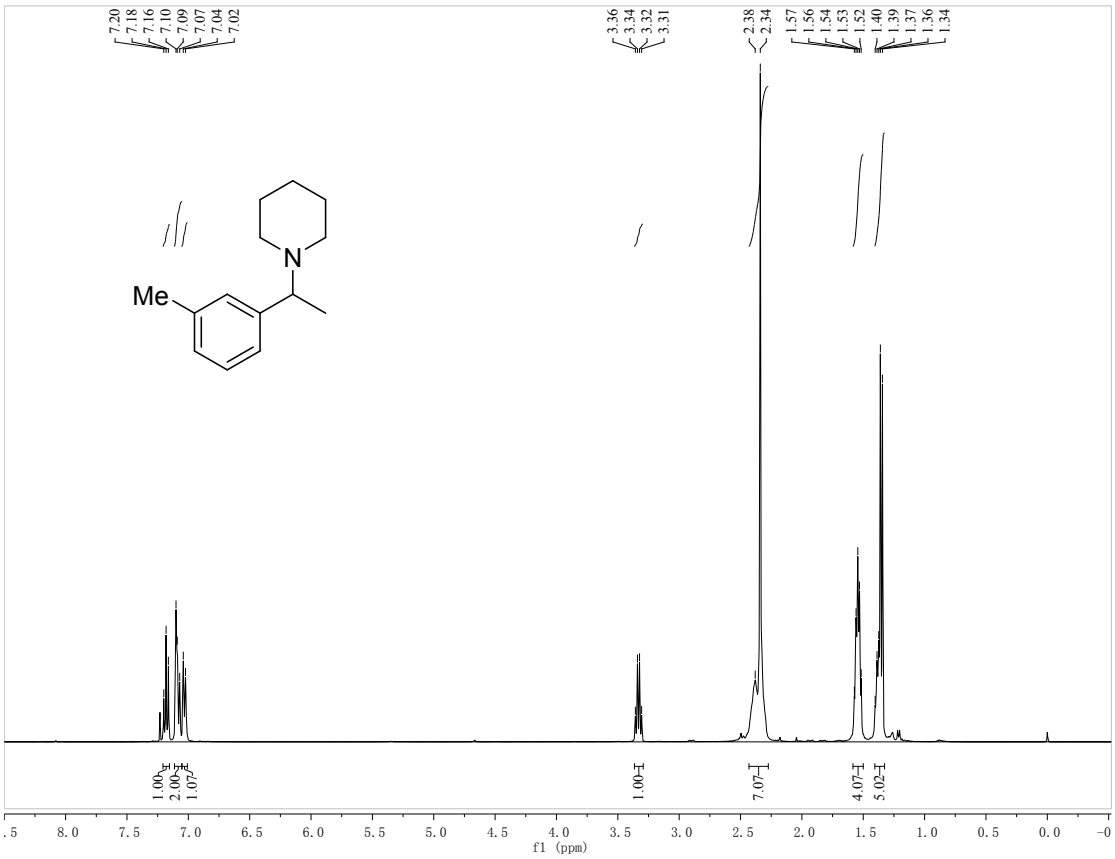


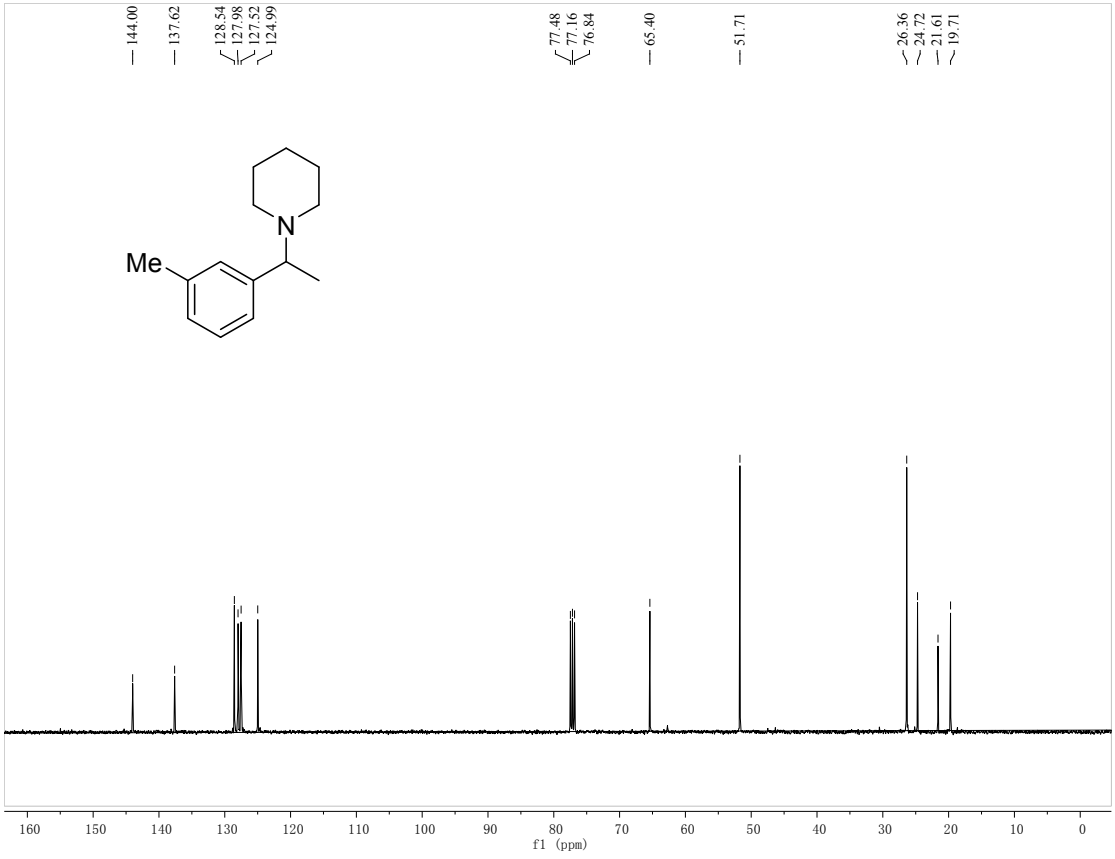
^{1}H NMR and ^{13}C NMR of **3aa**





^{1}H NMR and ^{13}C NMR of **3ba**





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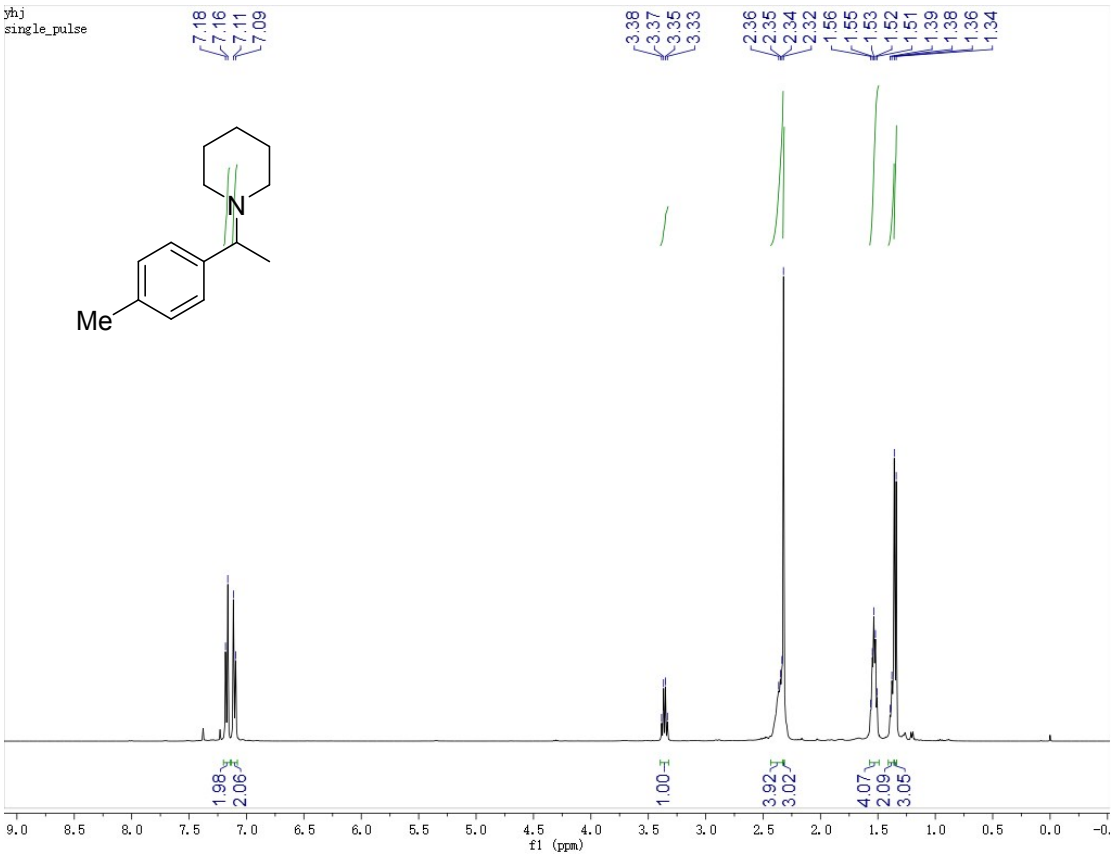
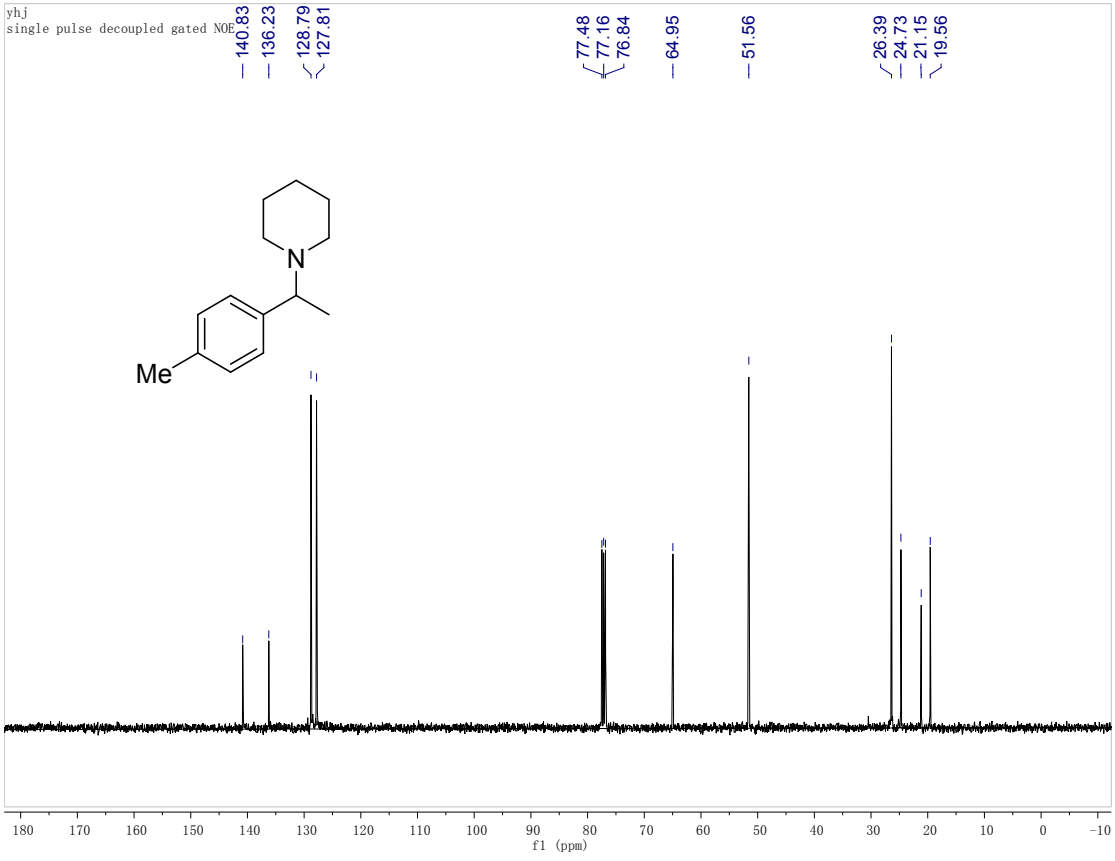
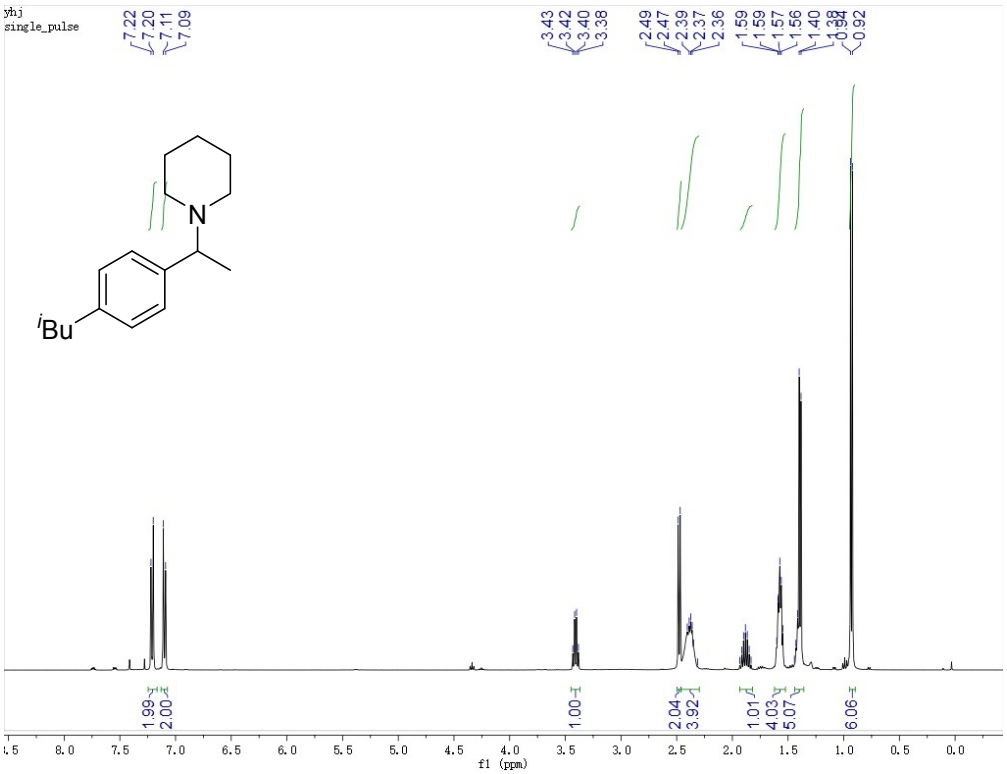
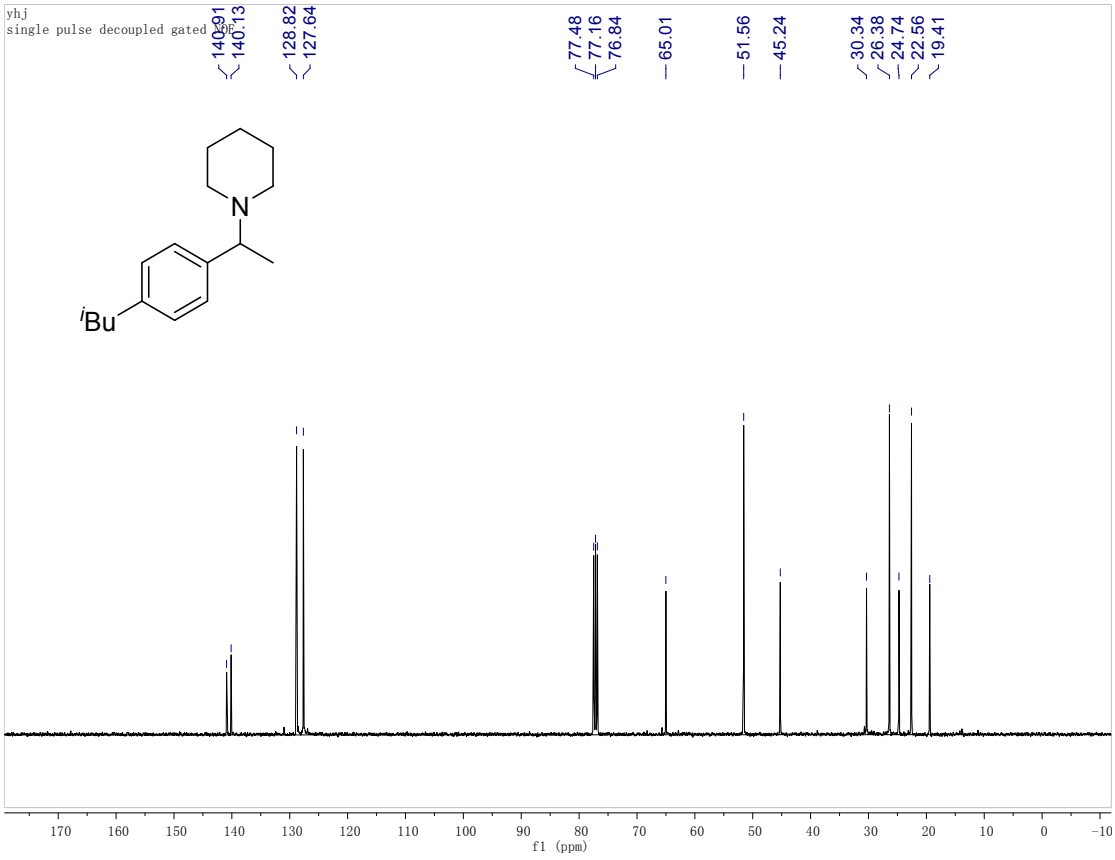


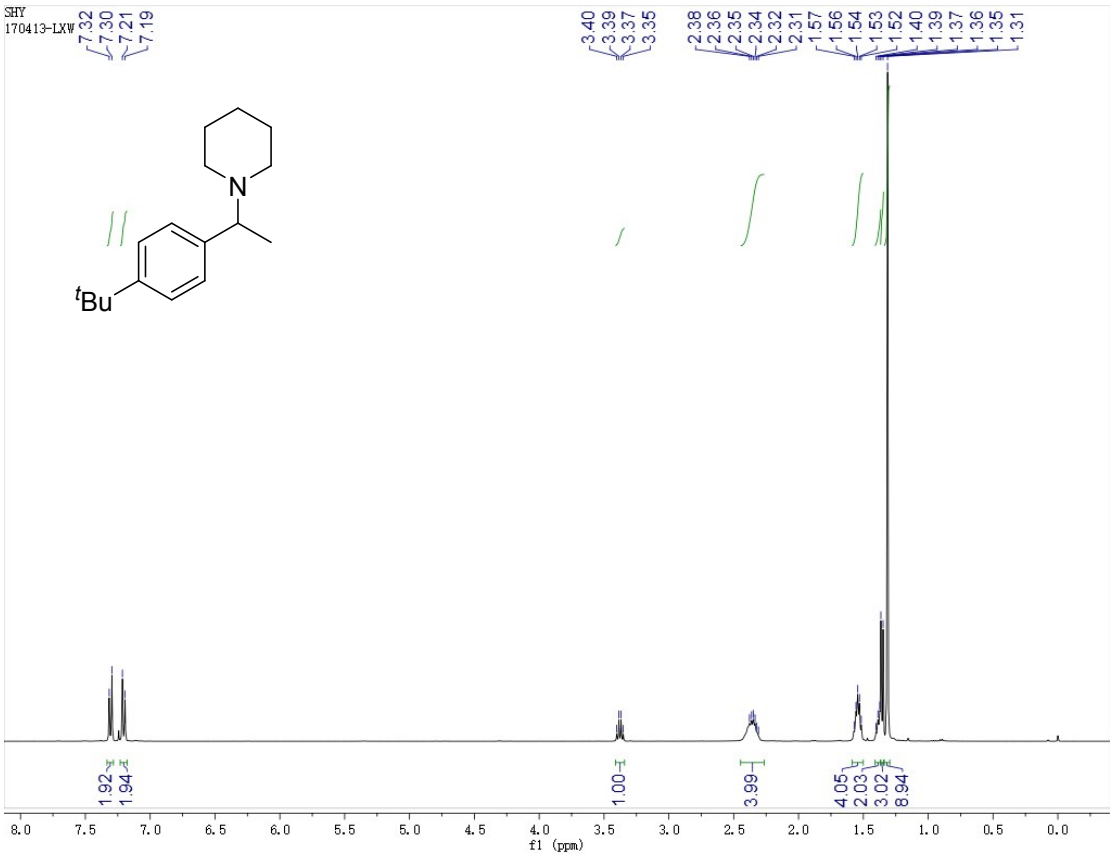


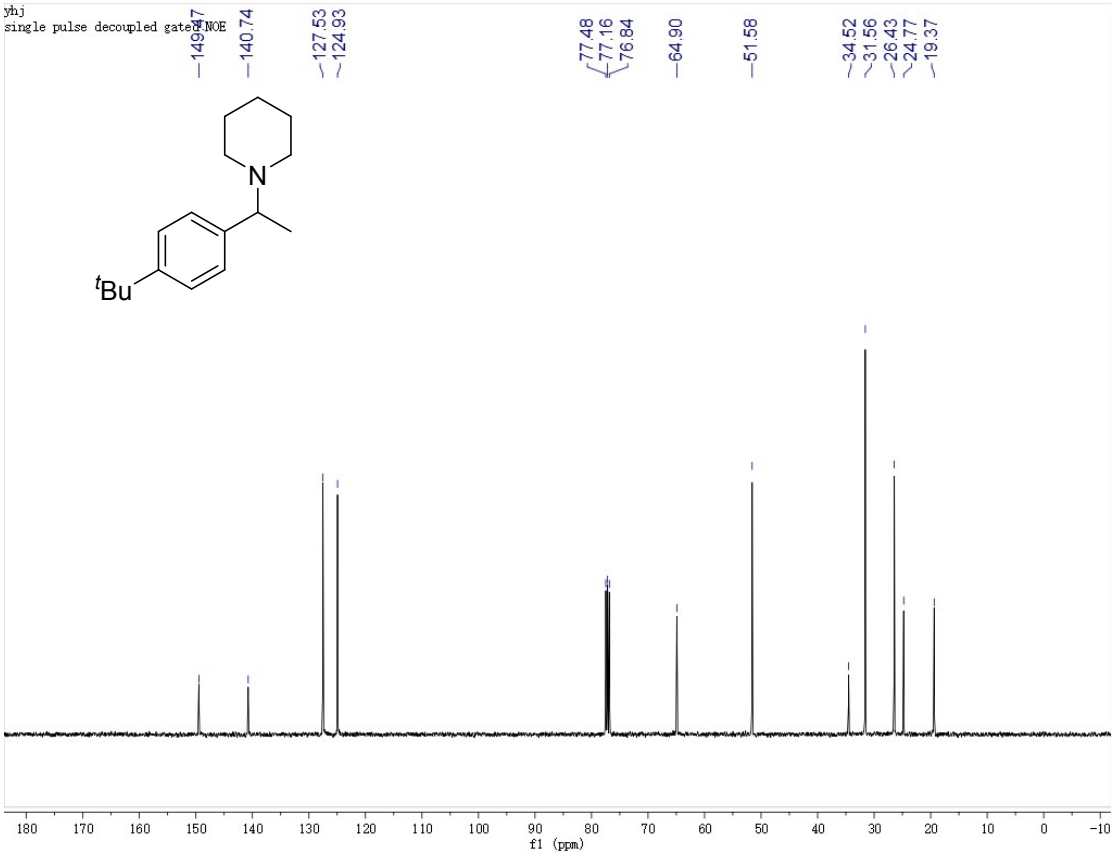
^{1}H NMR and ^{13}C NMR of **3da**



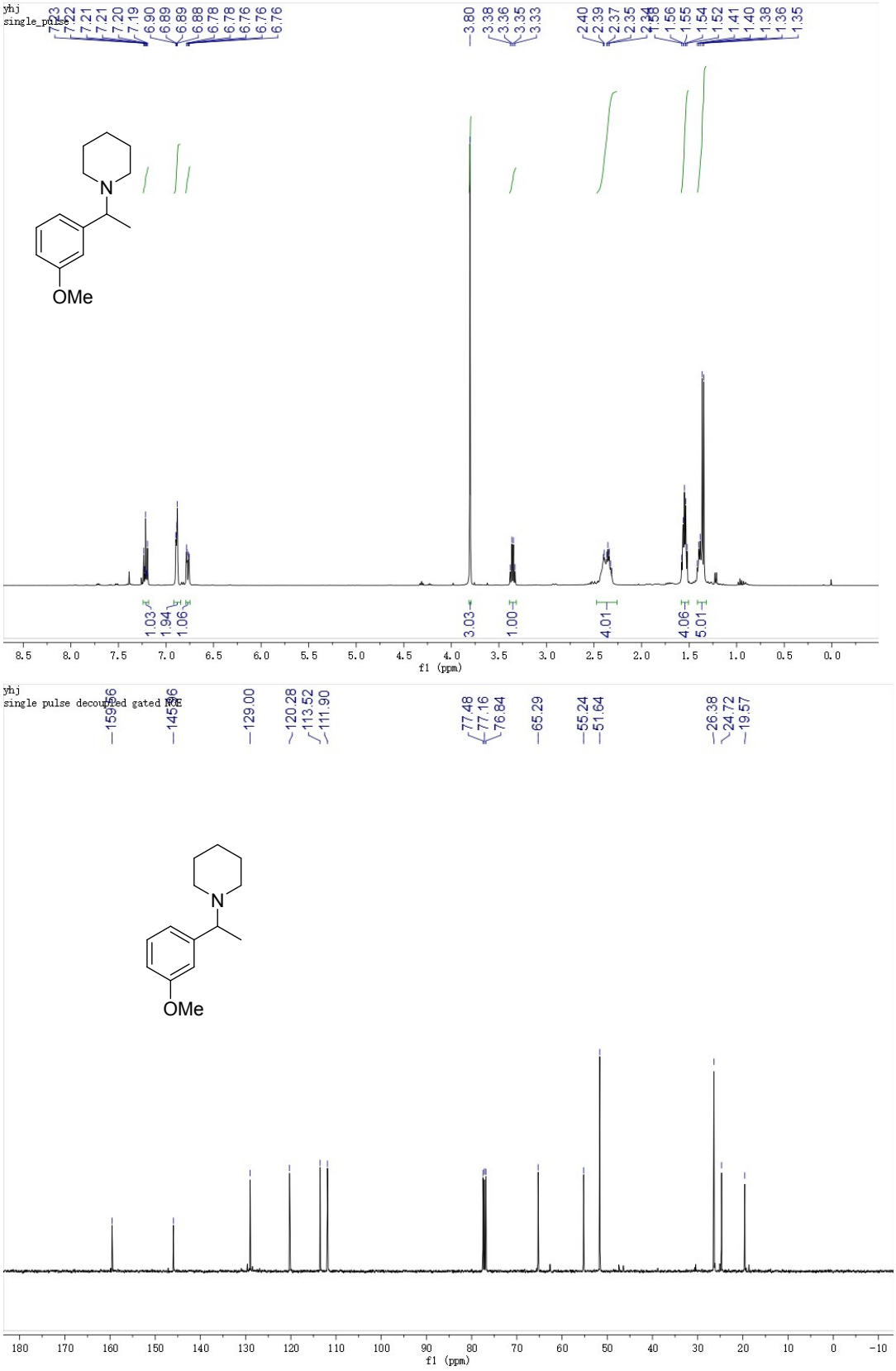


^{1}H NMR and ^{13}C NMR of **3ea**

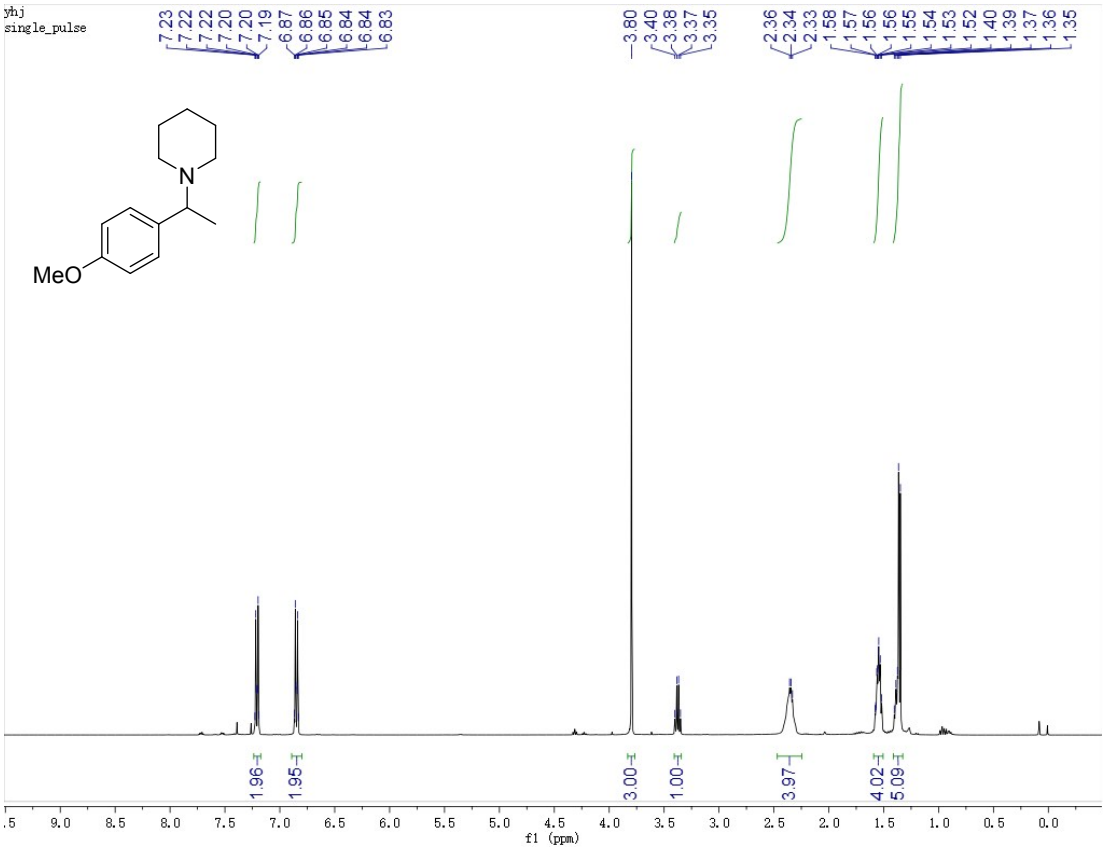


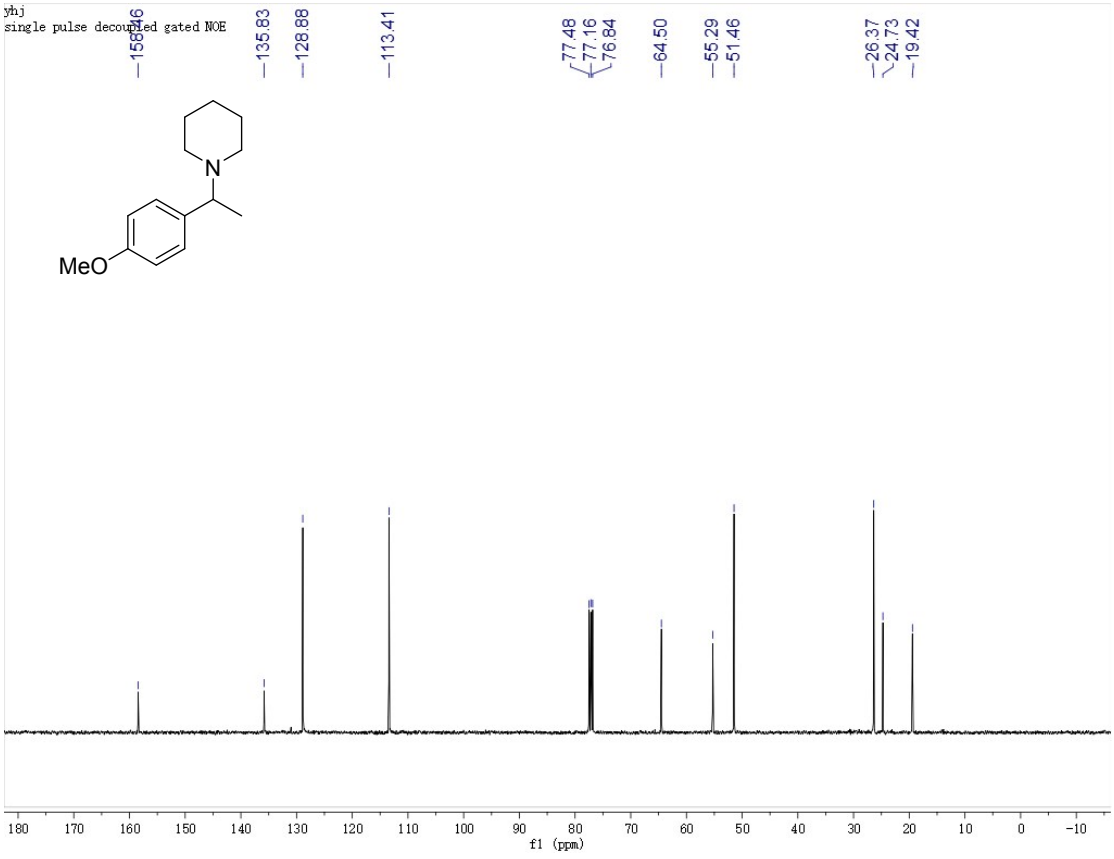


^{1}H NMR and^{13}C NMR of **3fa**

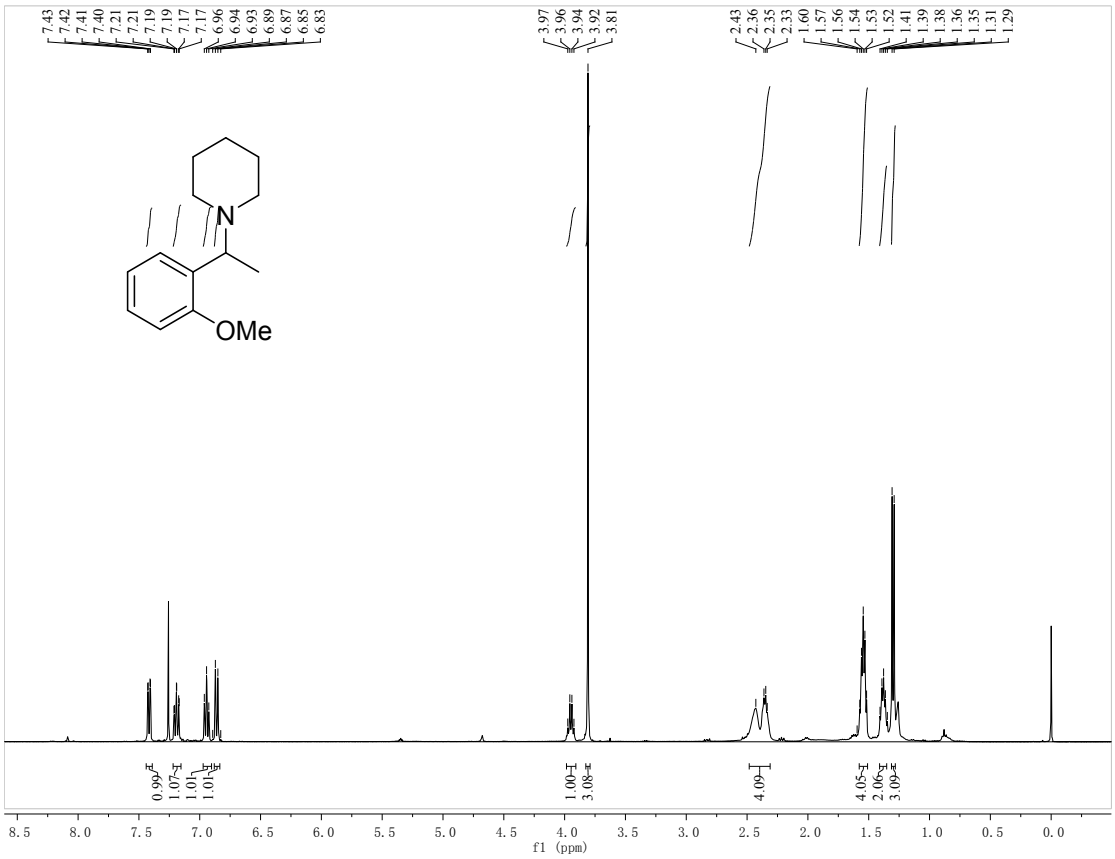


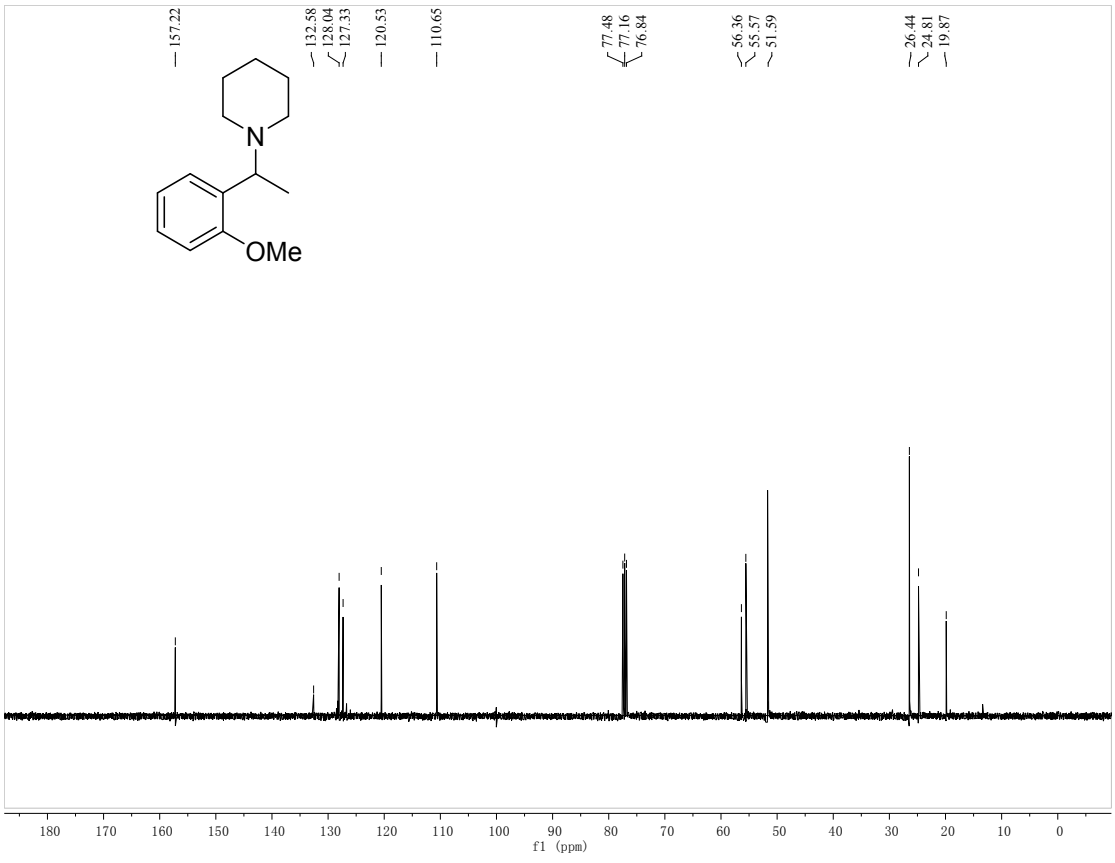
^{1}H NMR and ^{13}C NMR of **3ga**



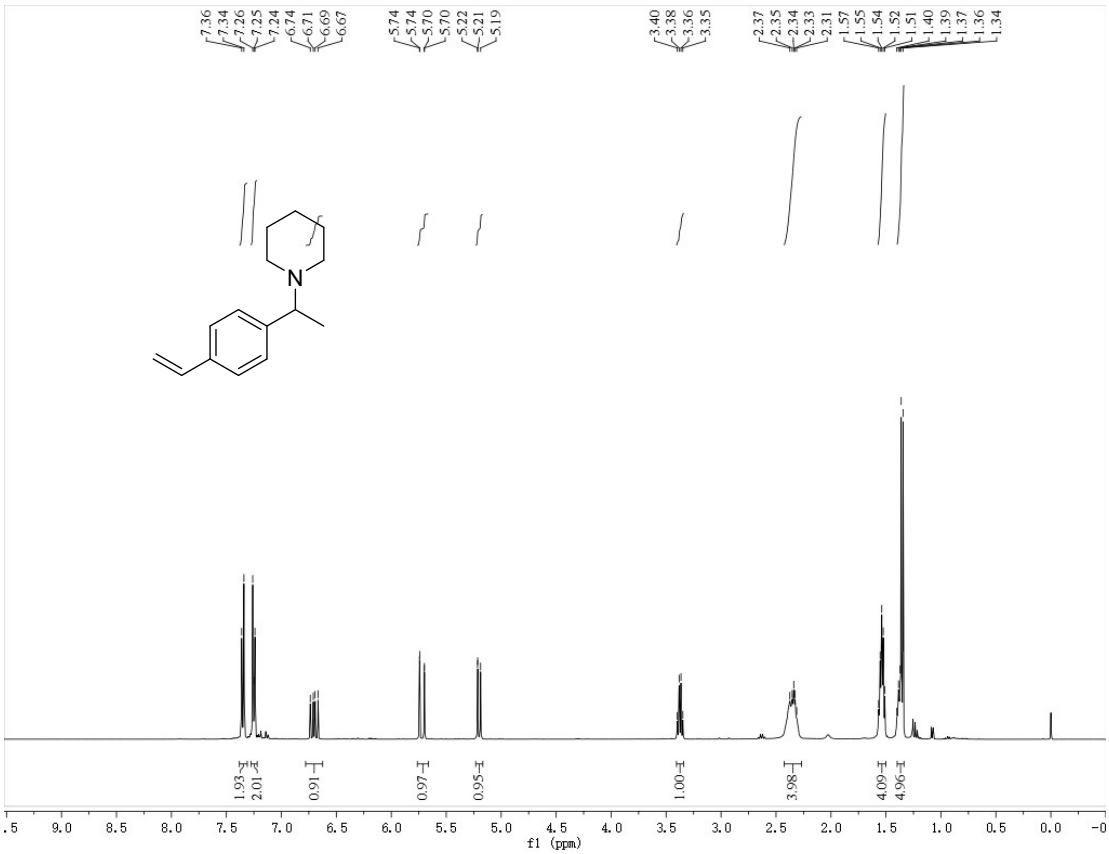


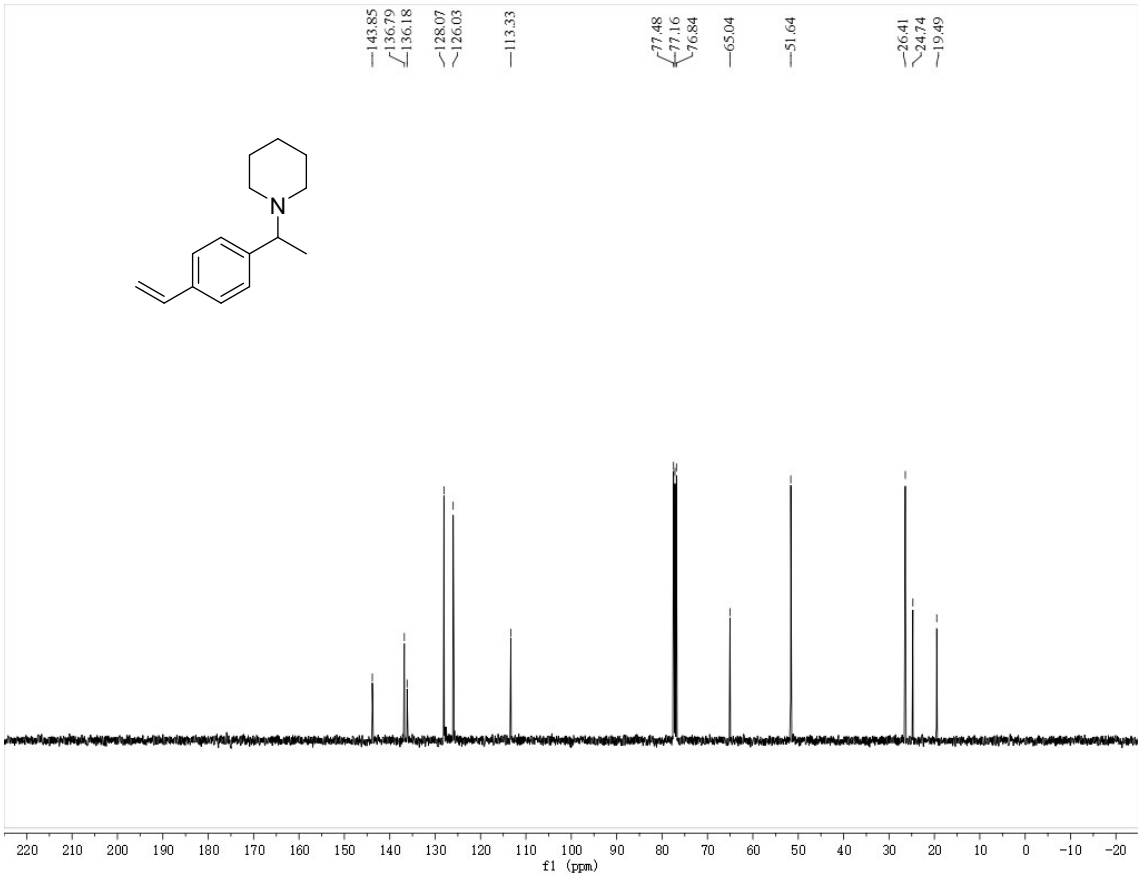
^{1}H NMR and ^{13}C NMR of **3ha**





^{1}H NMR and ^{13}C NMR of **3ia**





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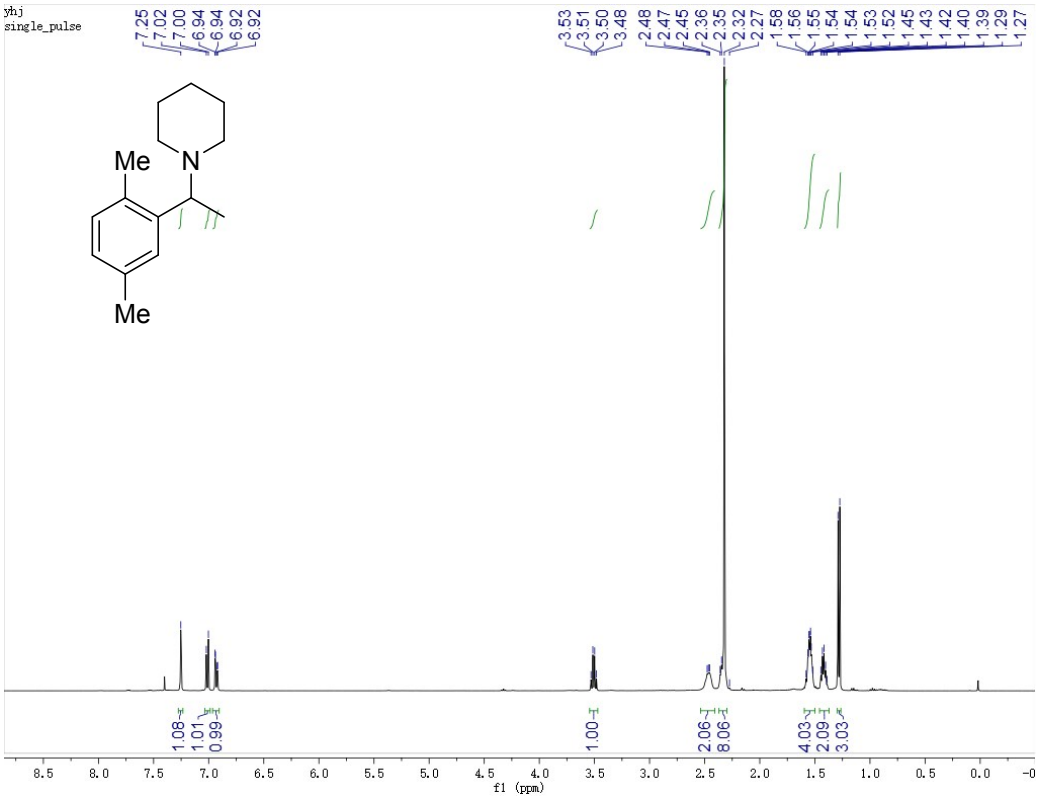
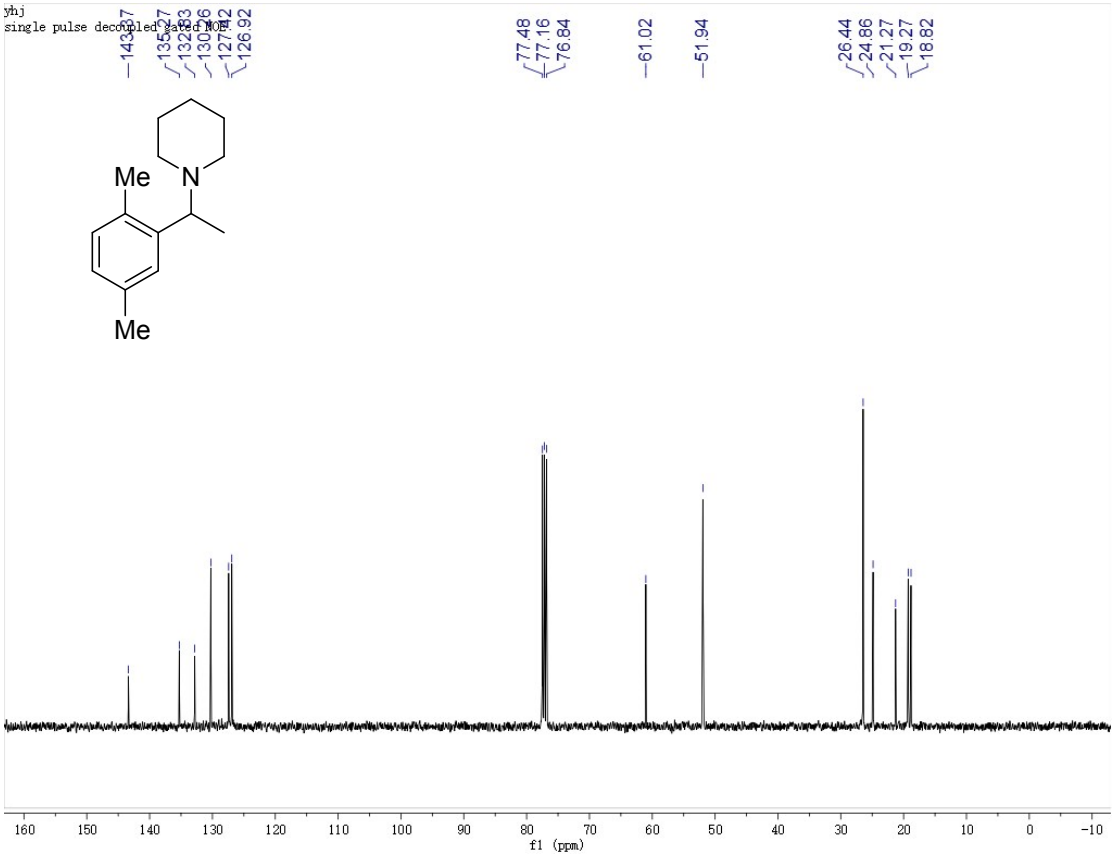
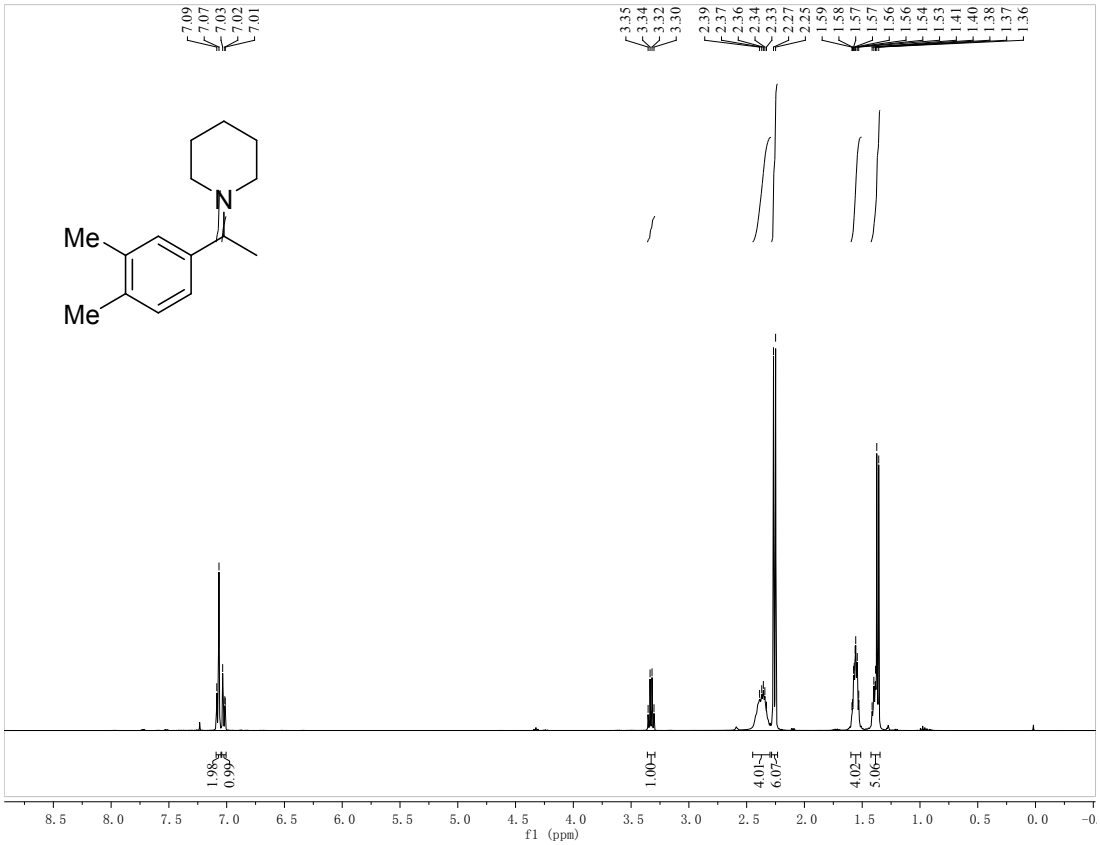
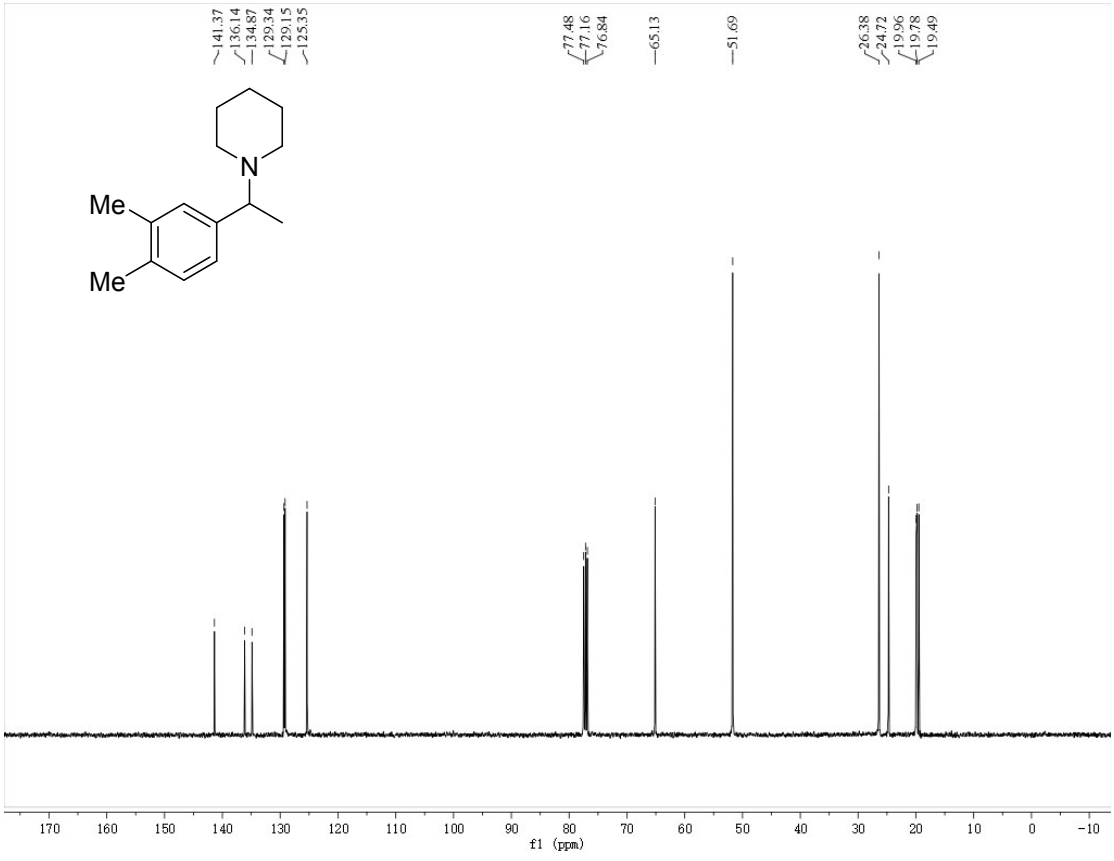


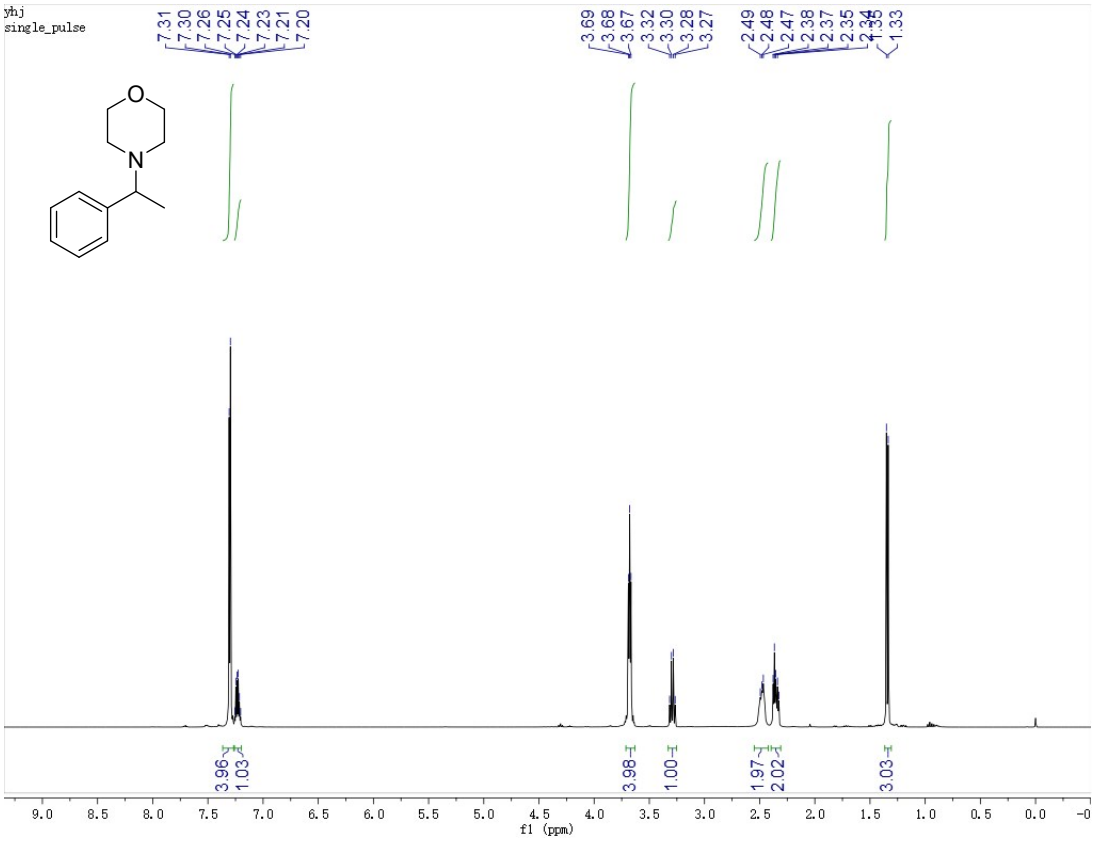


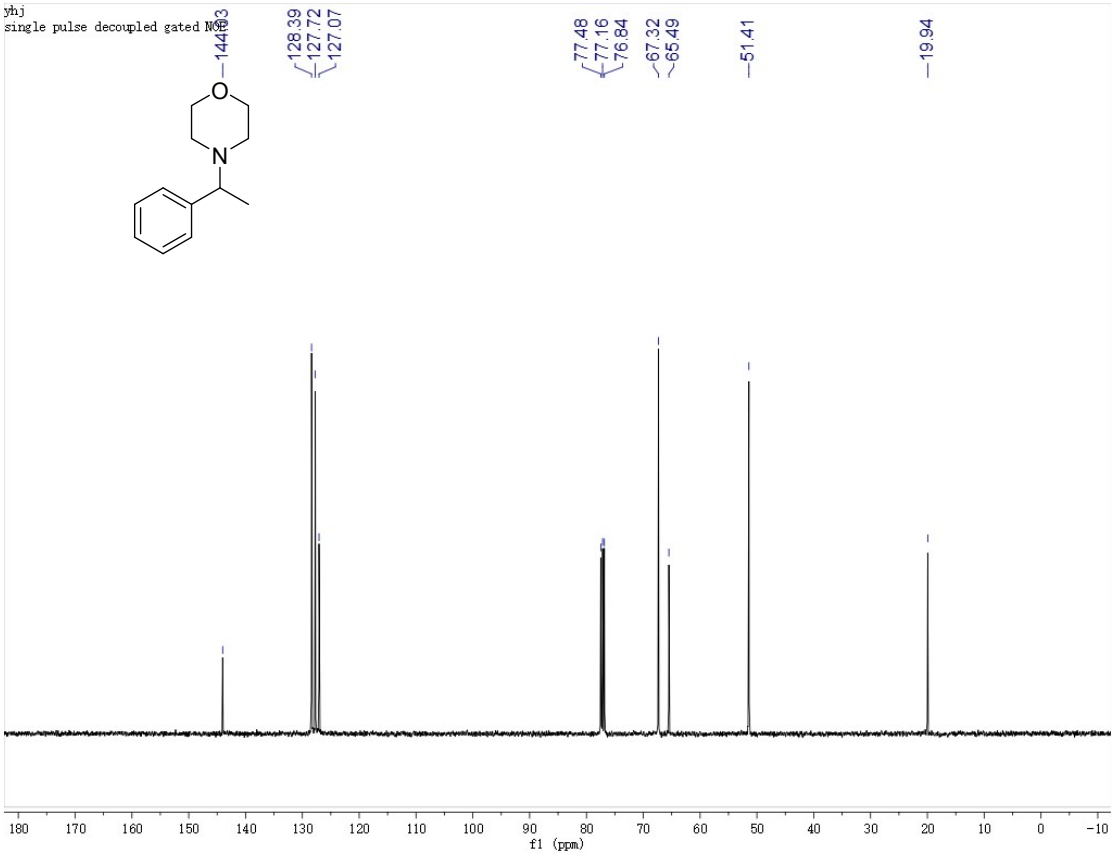
^{1}H NMR and ^{13}C NMR of **3ka**



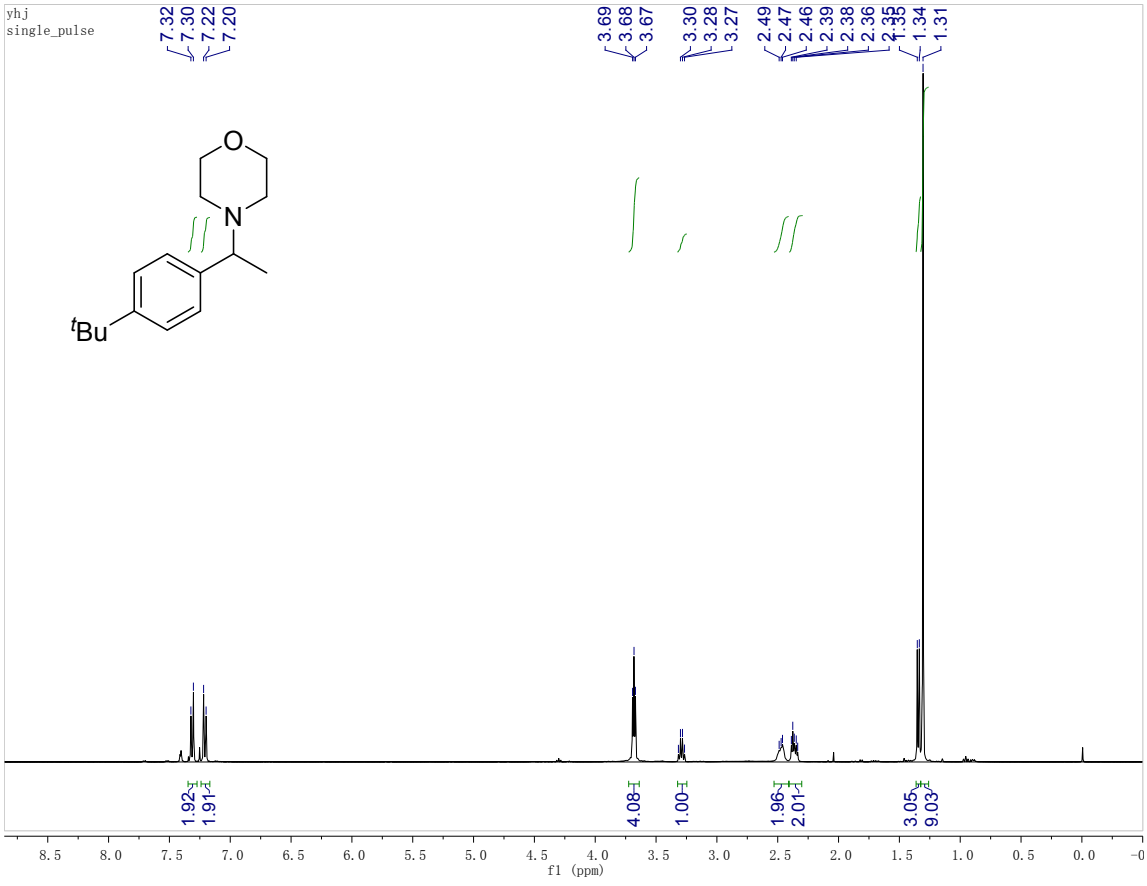


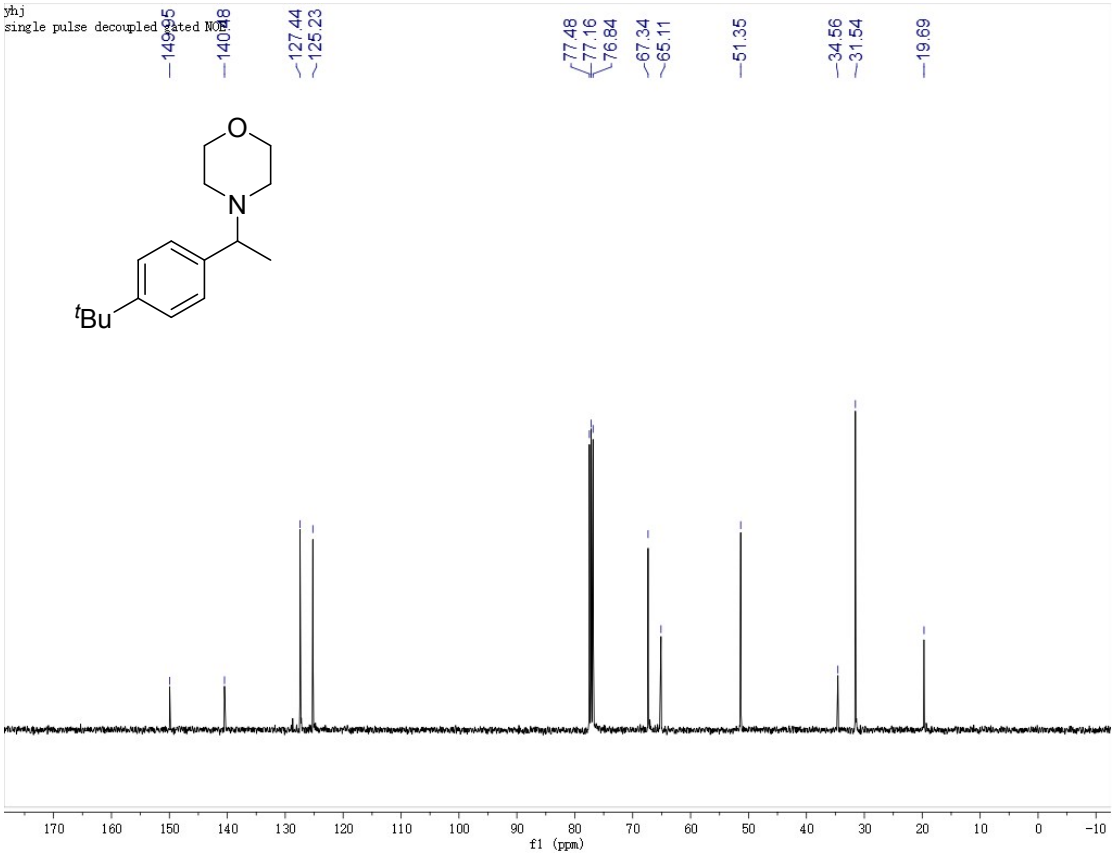
^{1}H NMR and ^{13}C NMR of **3la**



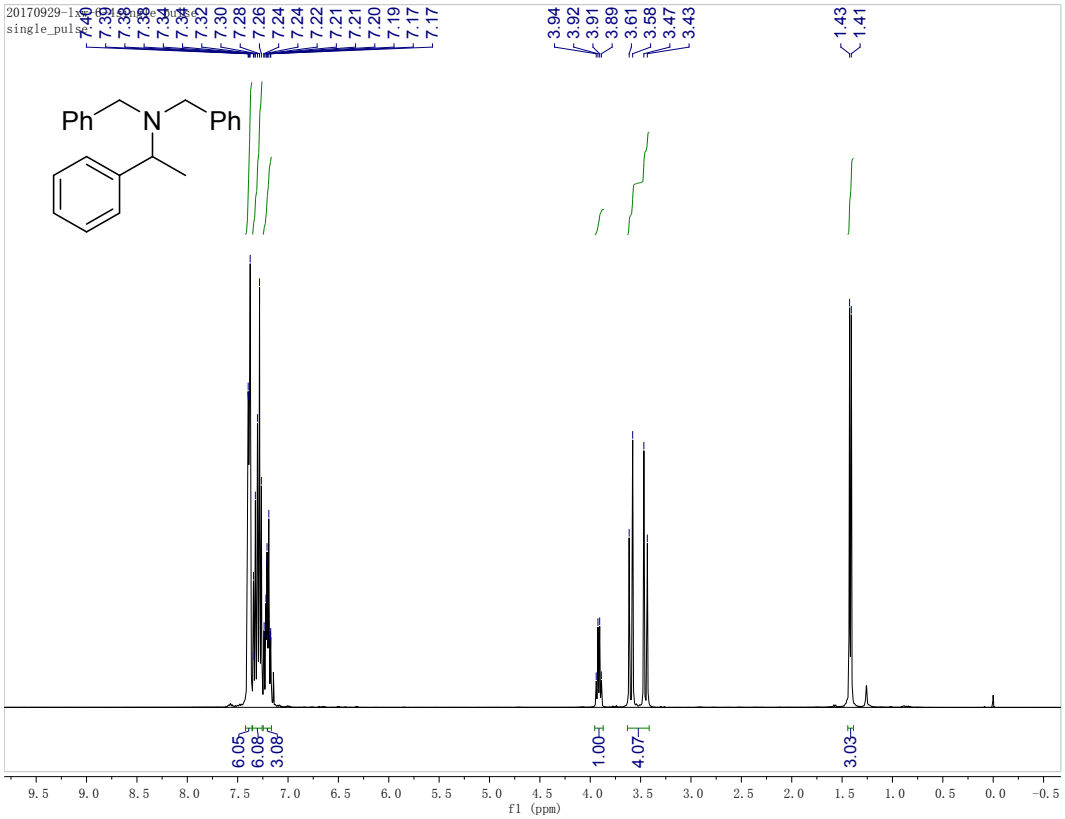


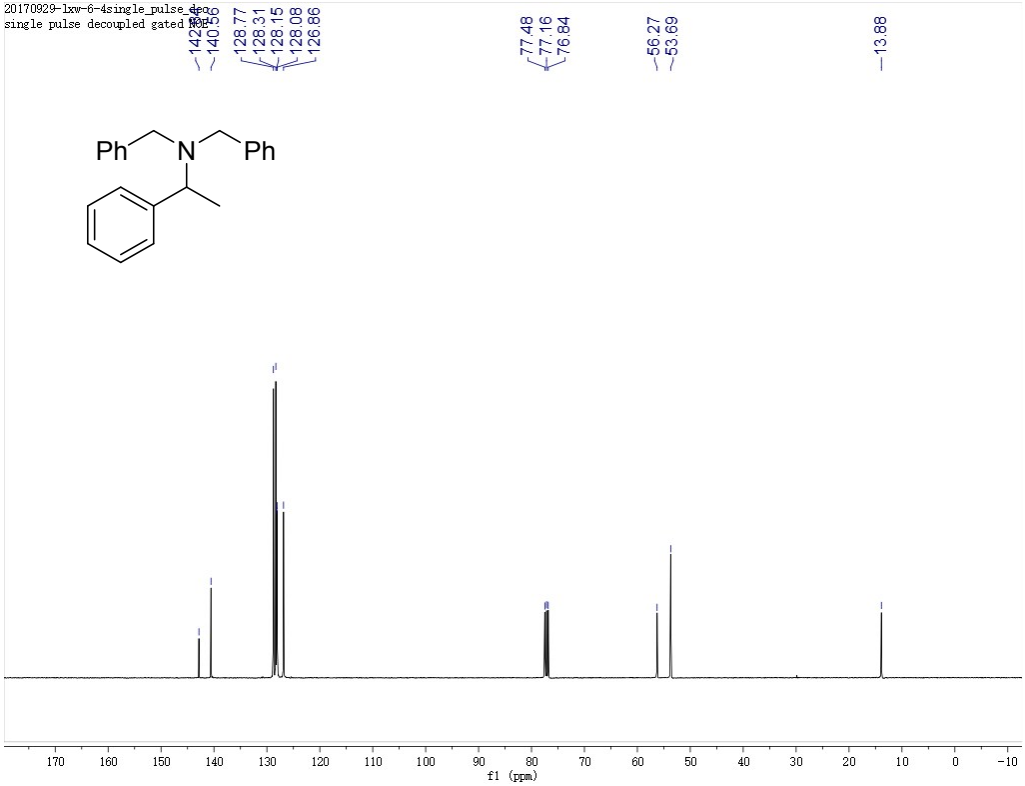
^{1}H NMR and ^{13}C NMR of **3ab**



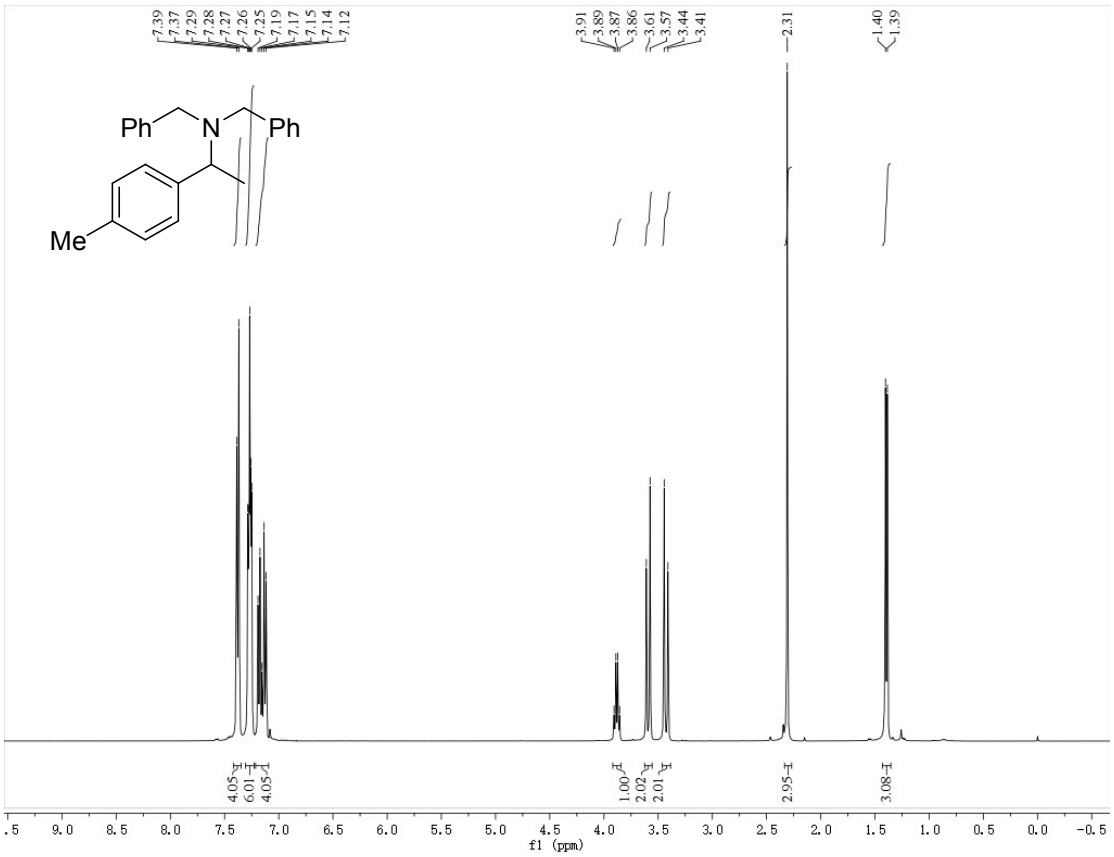


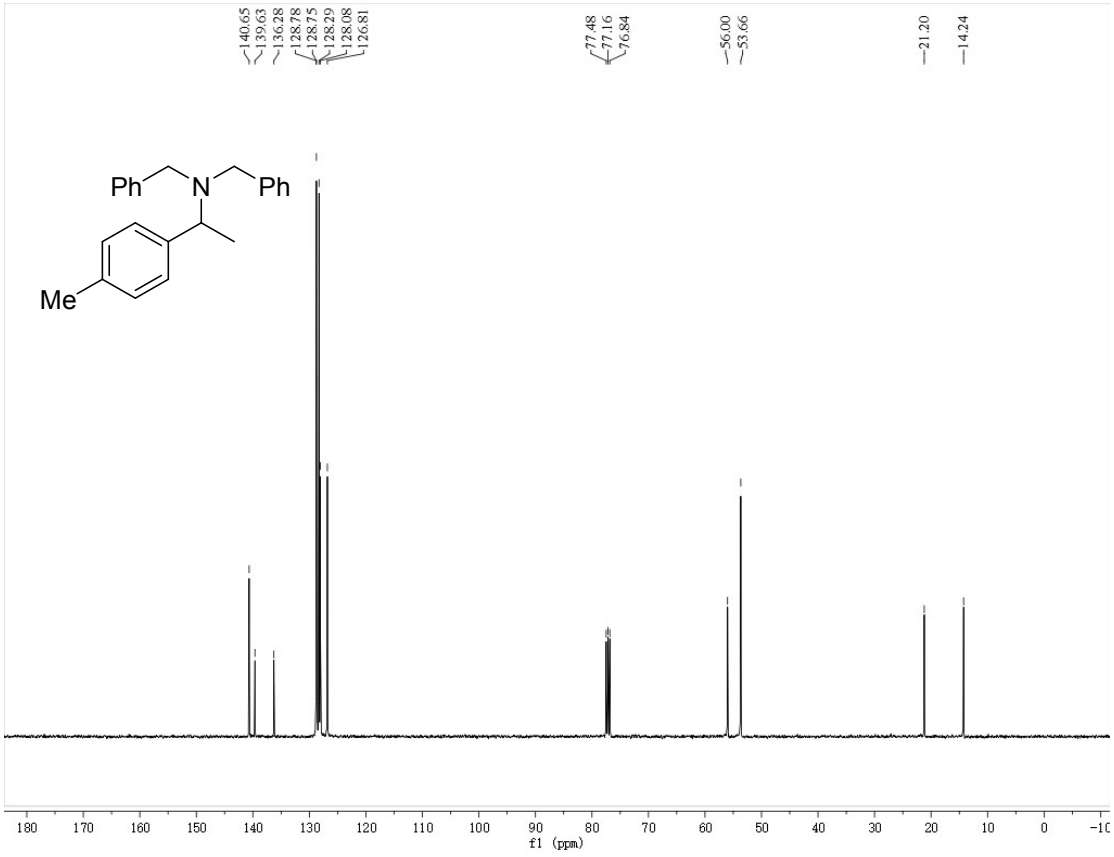
^{1}H NMR and ^{13}C NMR of **3fb**



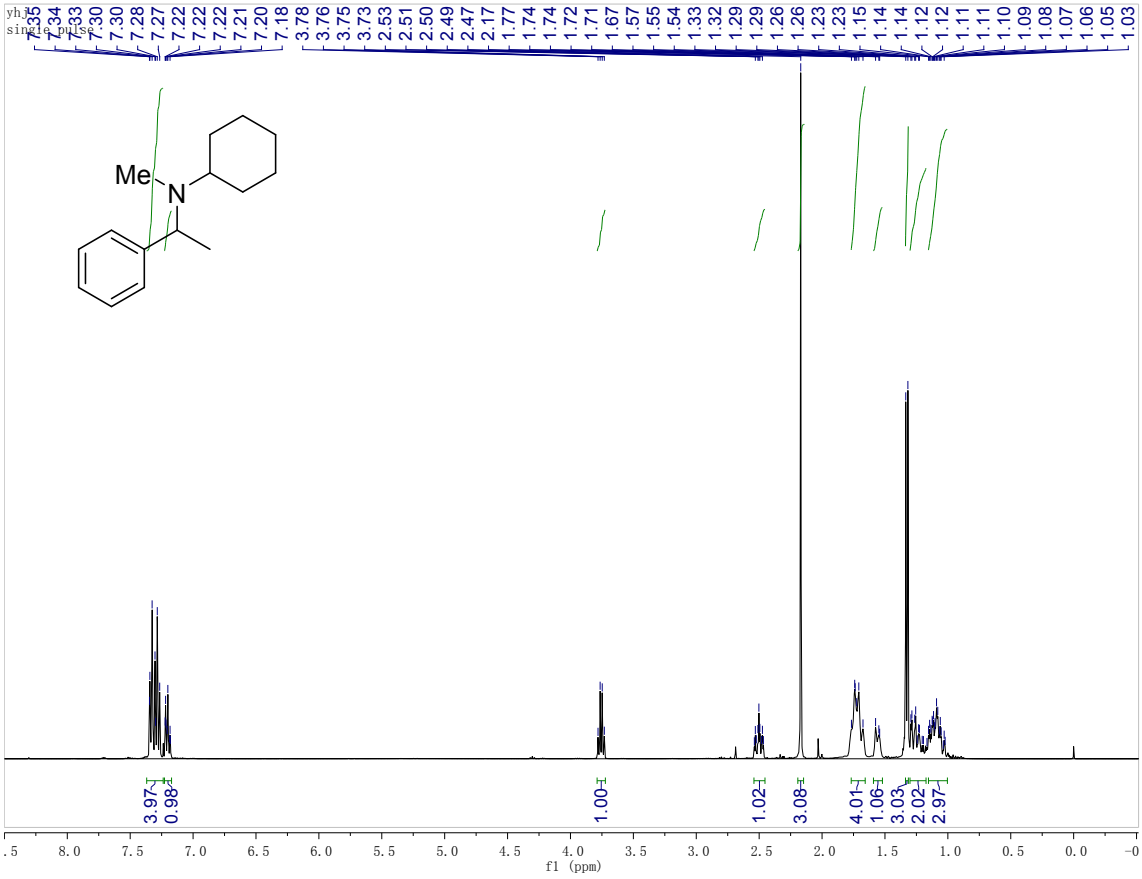


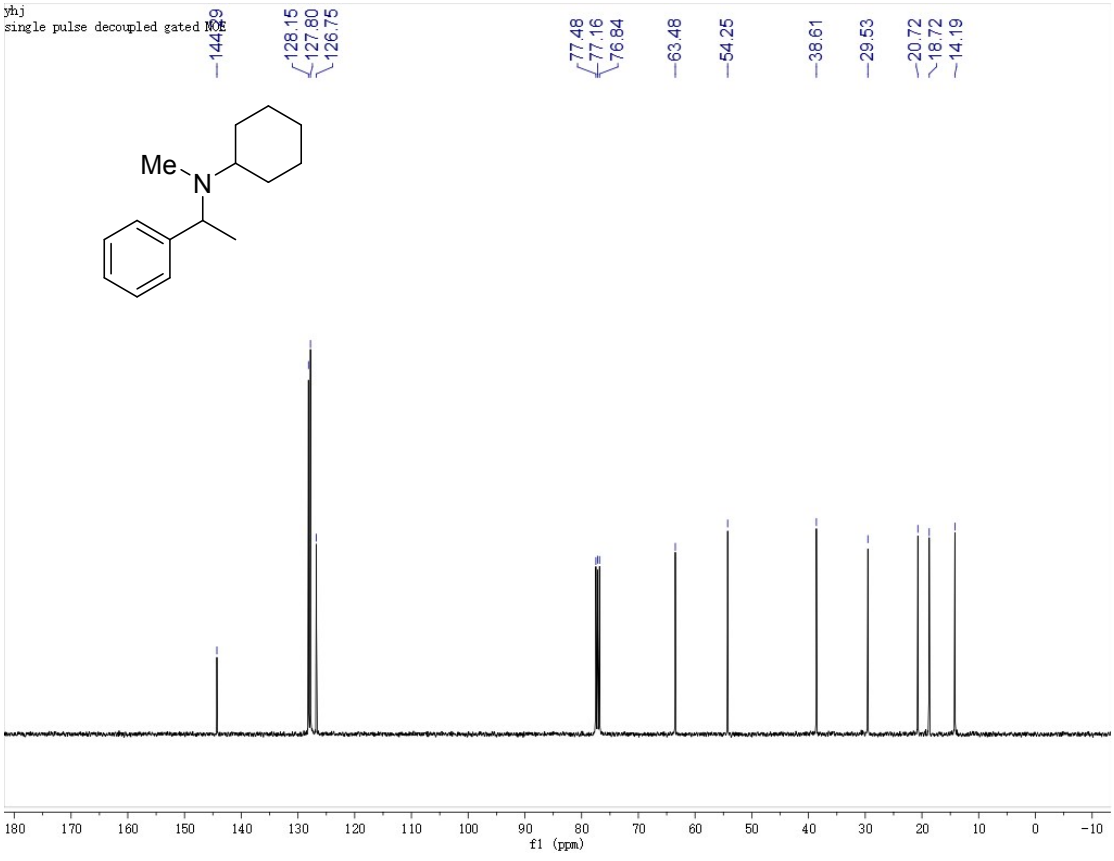
^{1}H NMR and ^{13}C NMR of **3ac**



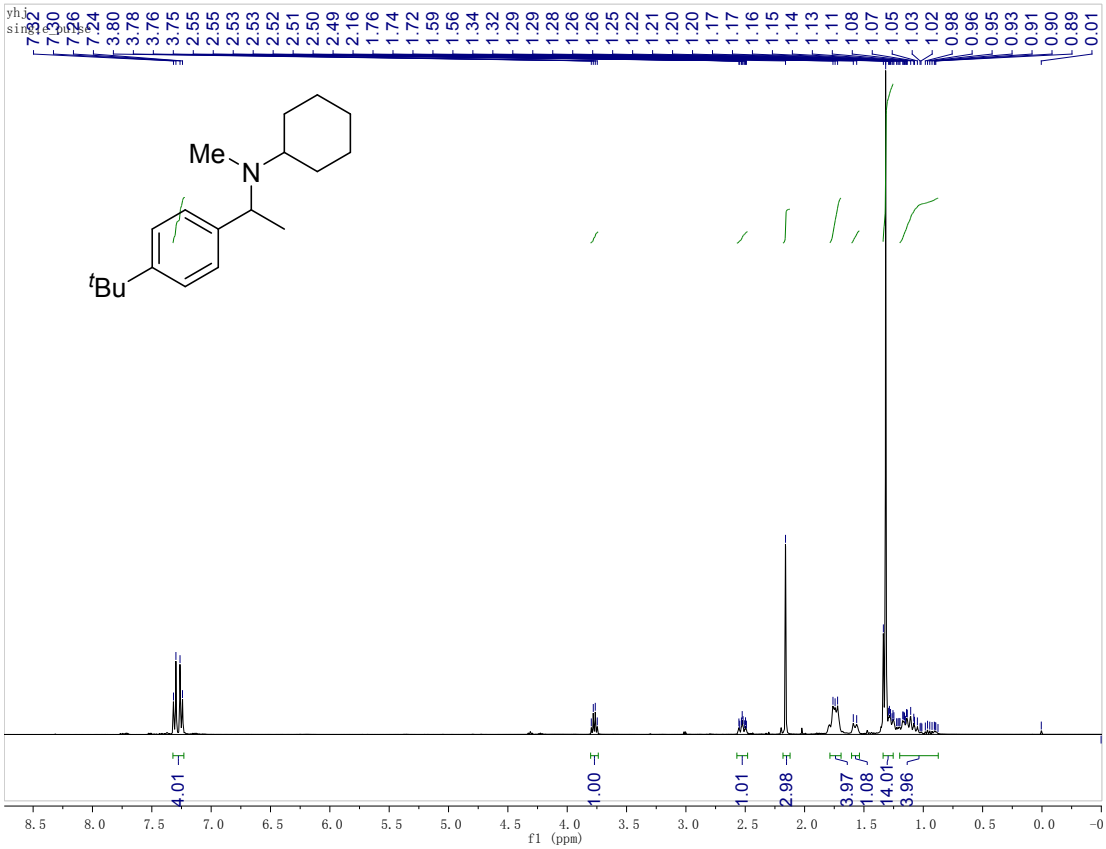


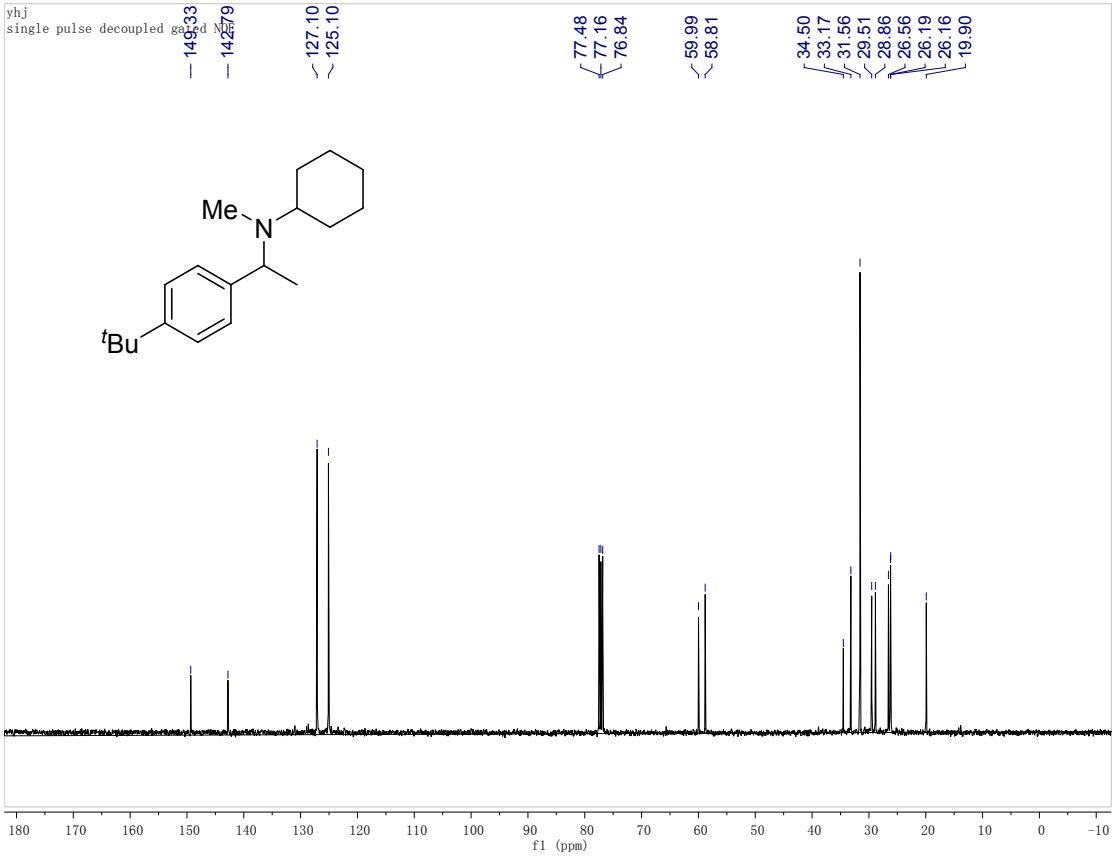
^{1}H NMR and ^{13}C NMR of **3dc**



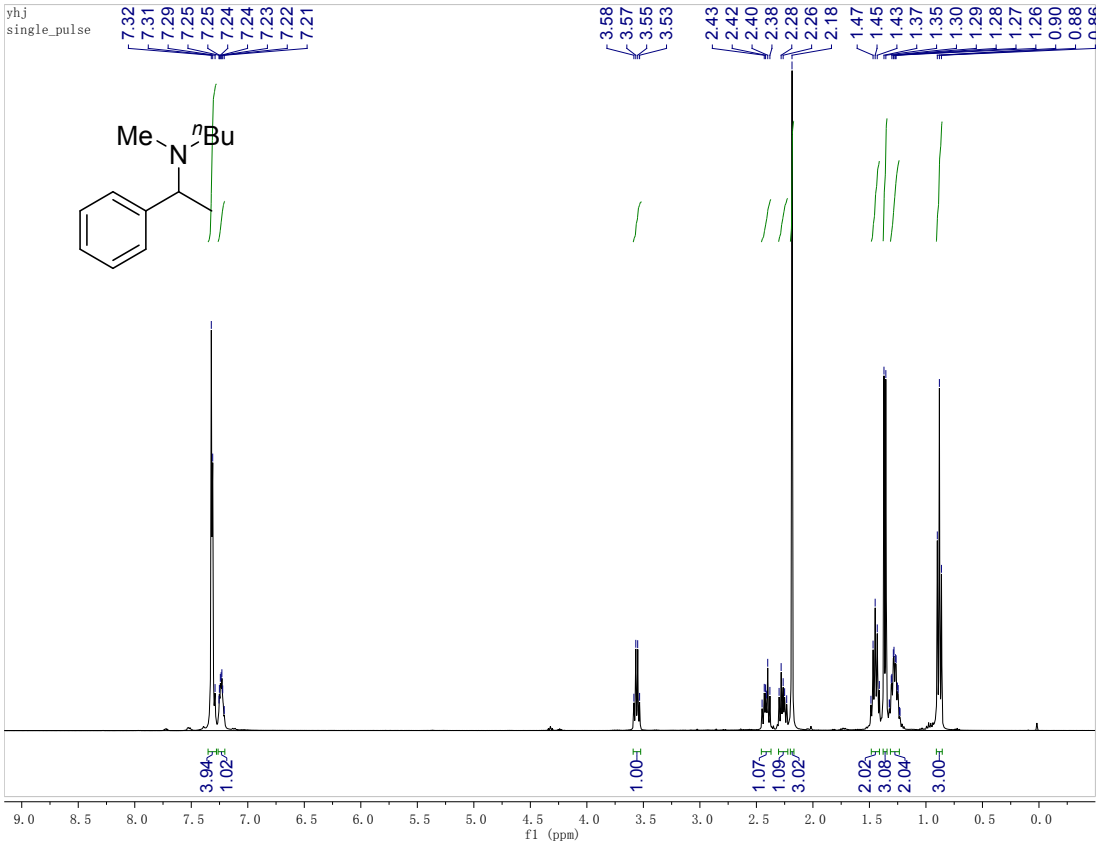


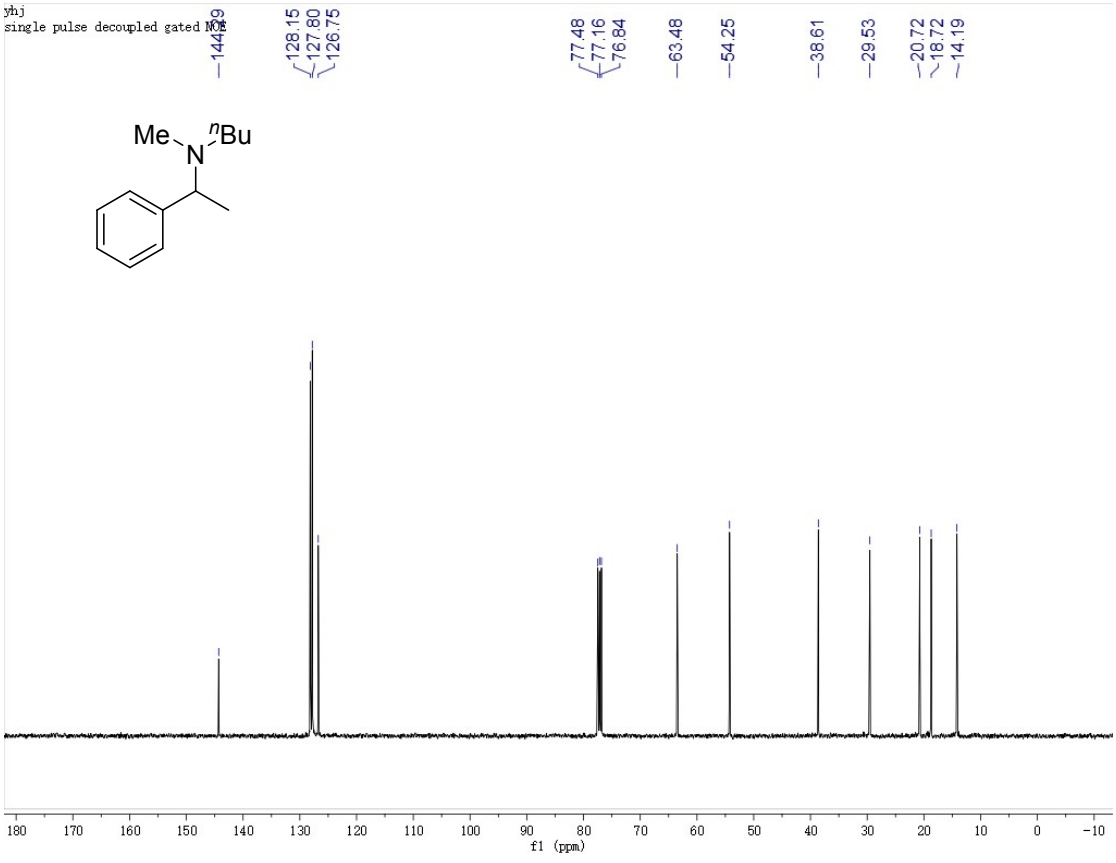
^{1}H NMR and ^{13}C NMR of **3ad**



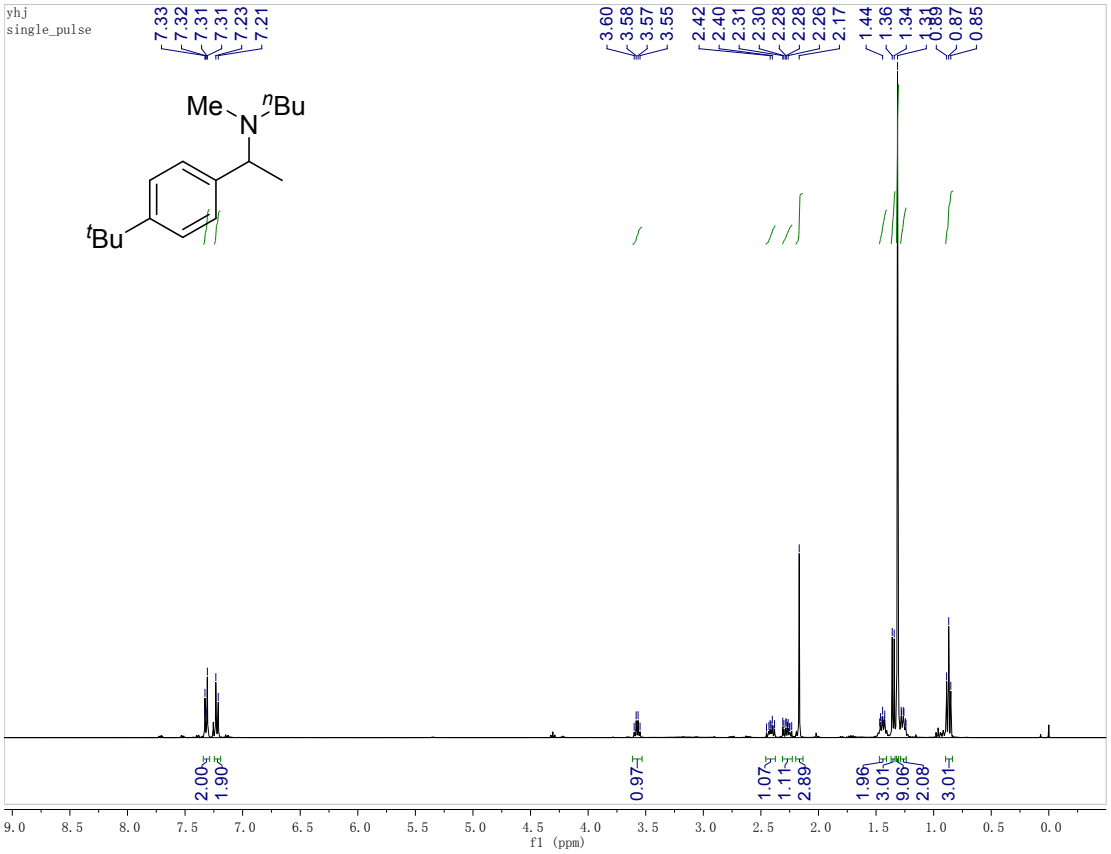


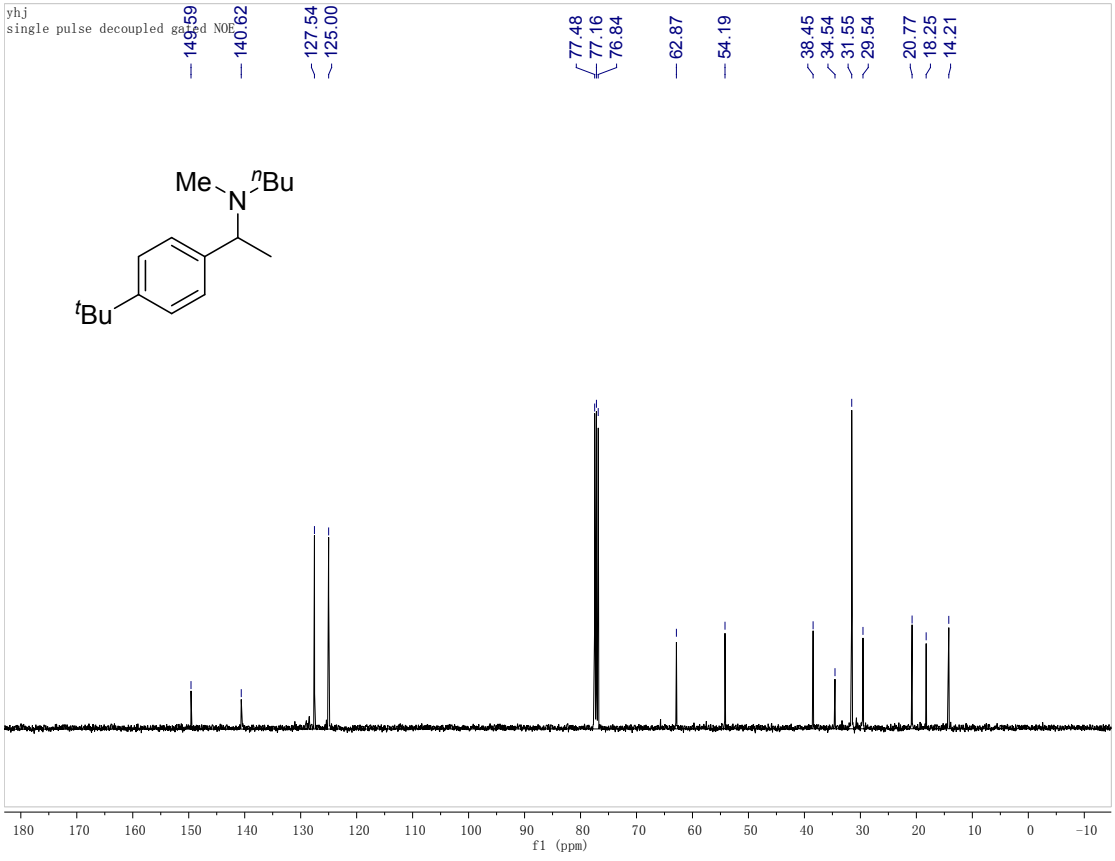
^{1}H NMR and ^{13}C NMR of **3fd**



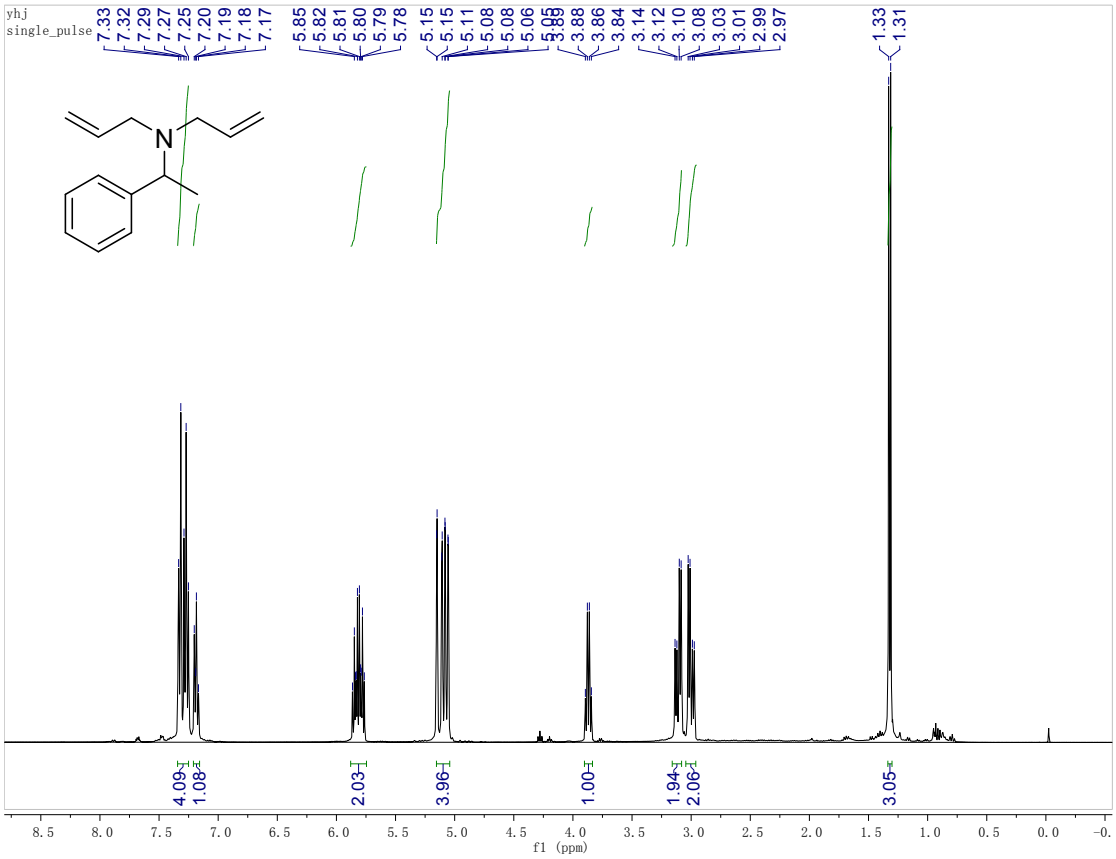


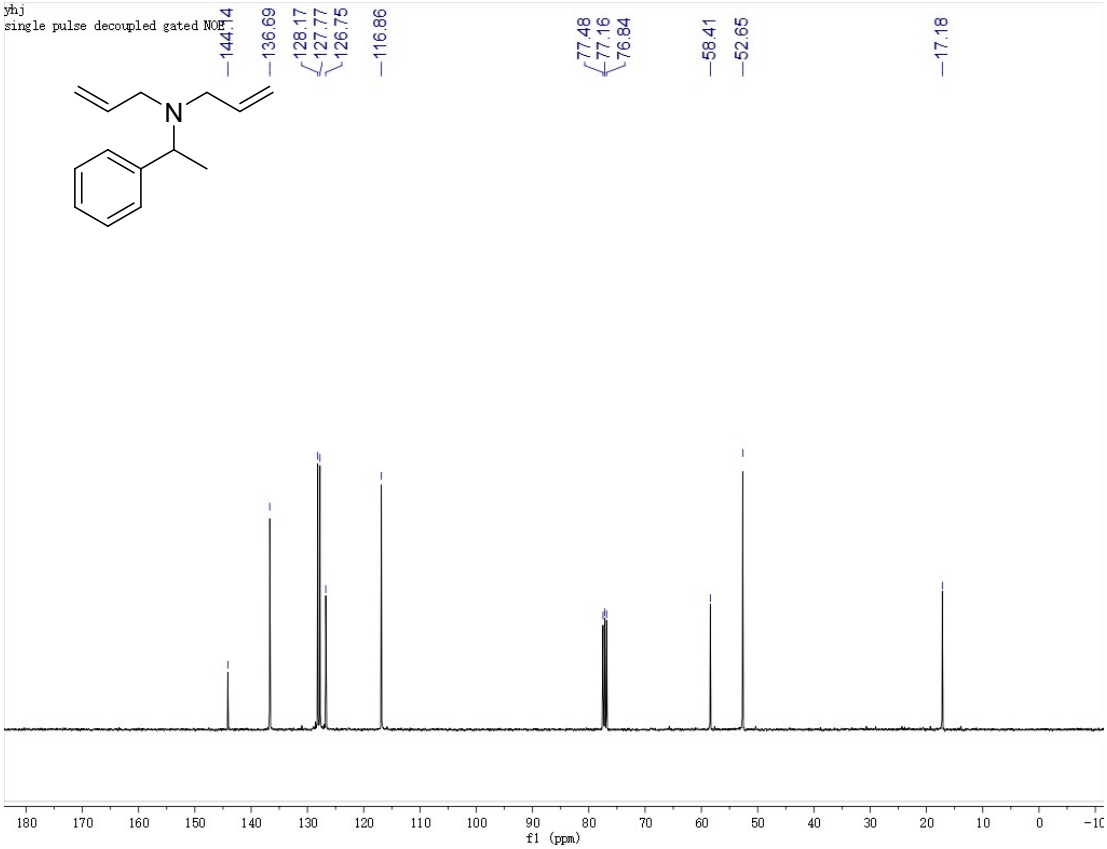
^{1}H NMR and ^{13}C NMR of **3ae**



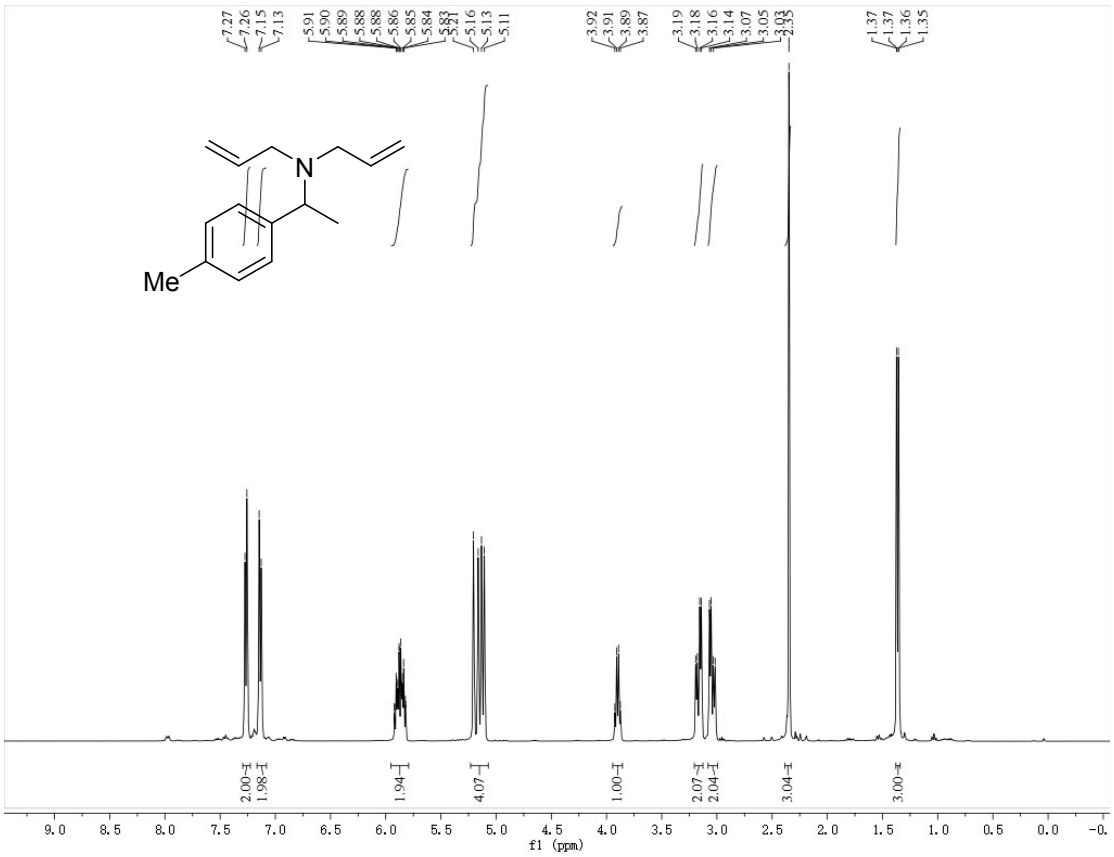


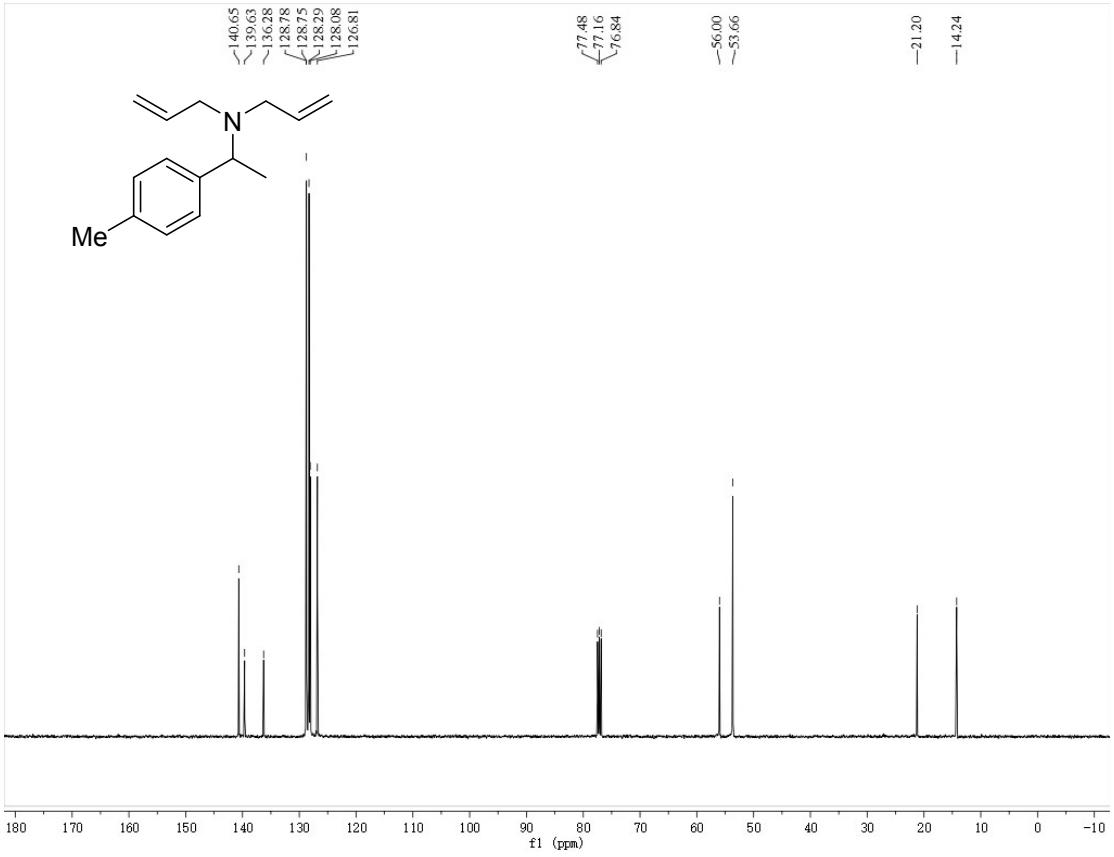
^{1}H NMR and ^{13}C NMR of **3fe**



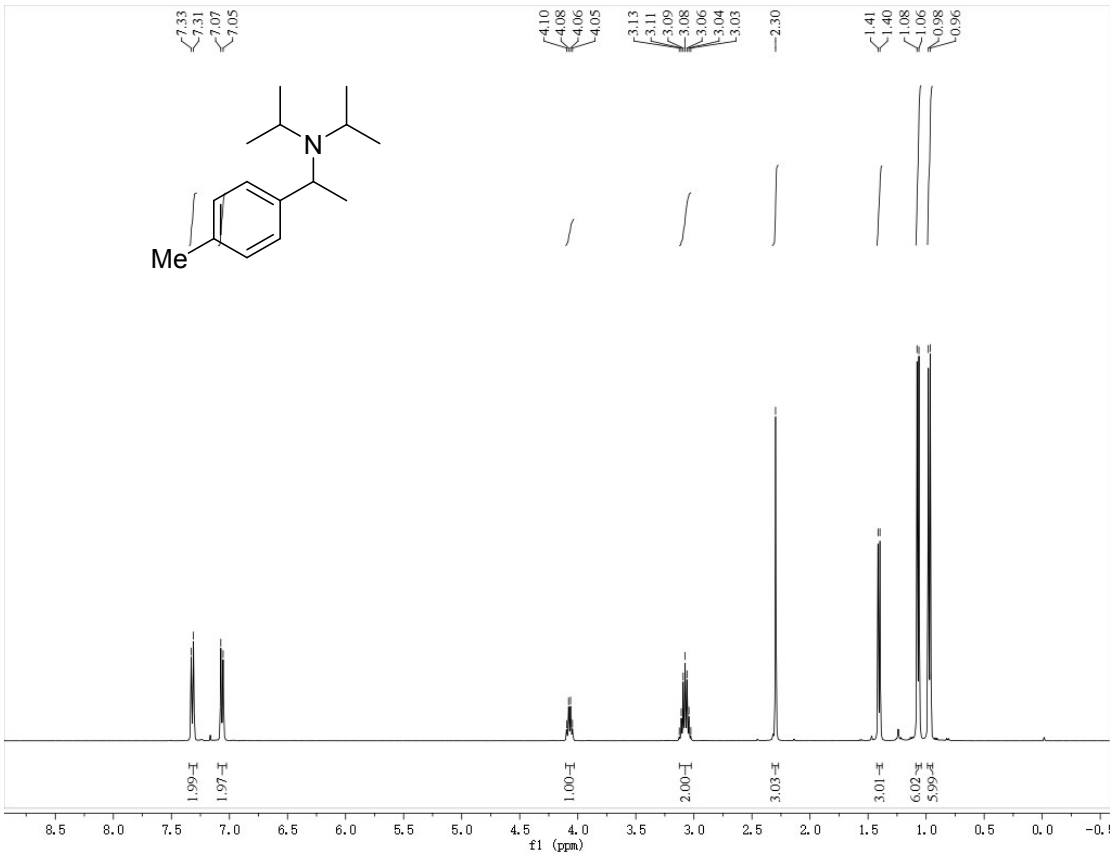


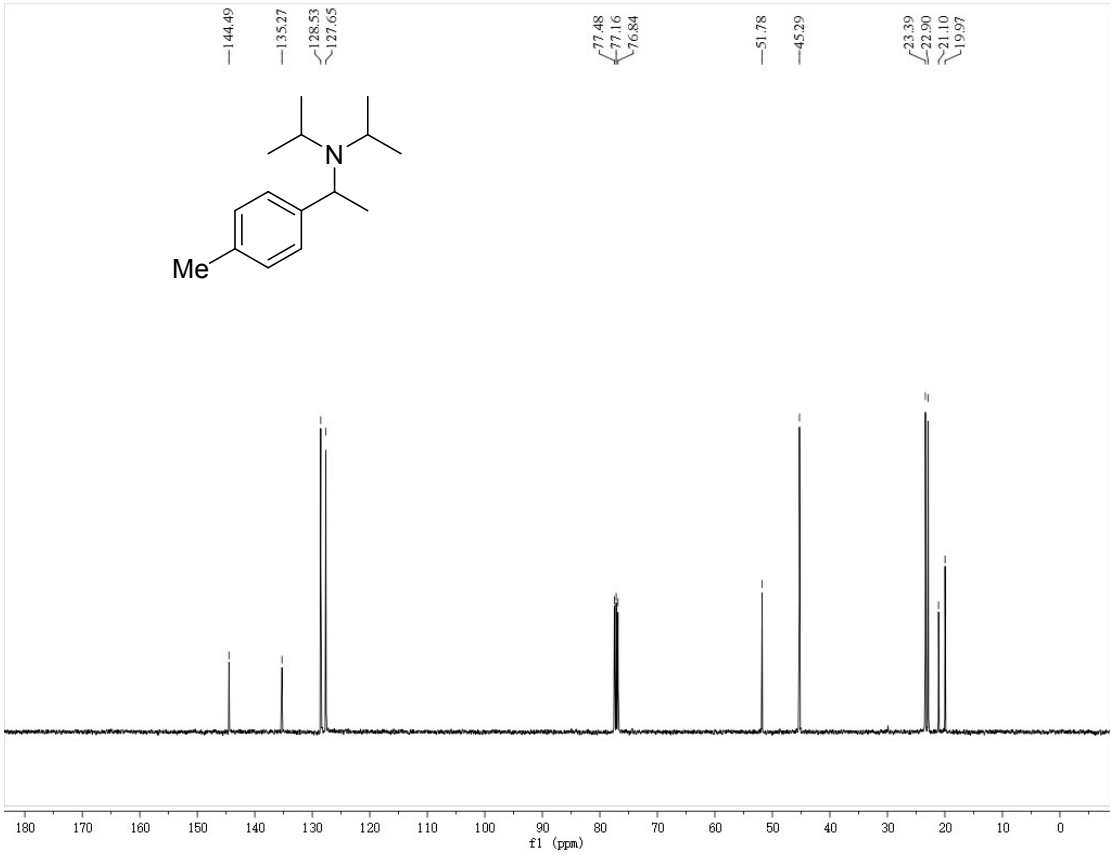
^{1}H NMR and ^{13}C NMR of **3af**



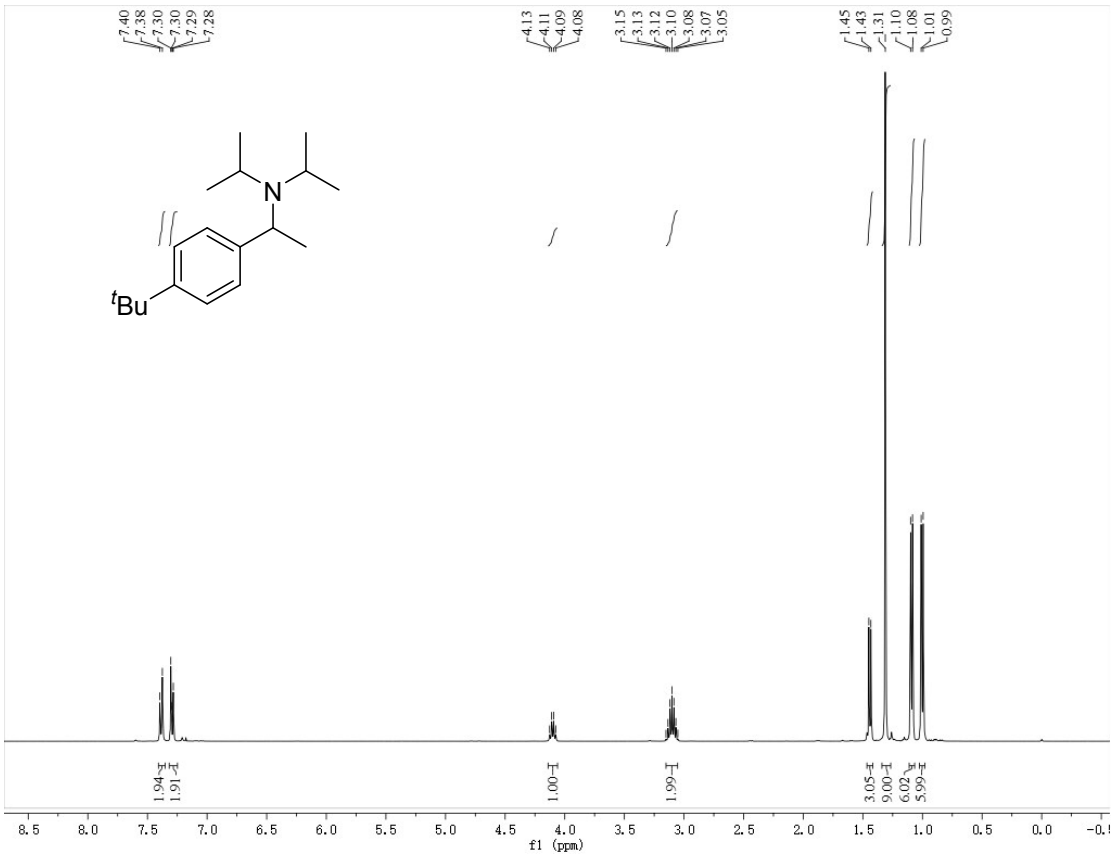


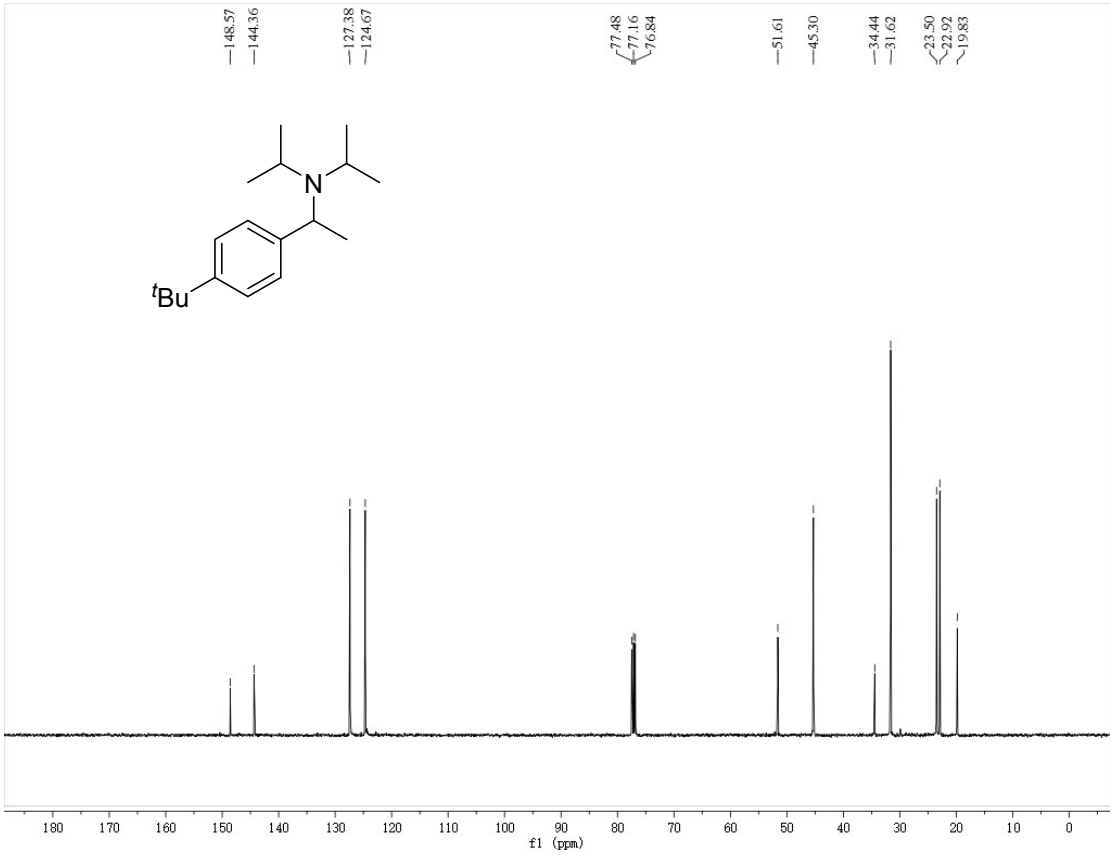
^{1}H NMR and ^{13}C NMR of **3df**





^{1}H NMR and ^{13}C NMR of **3dg**





^{1}H NMR and ^{13}C NMR of **3fg**