Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

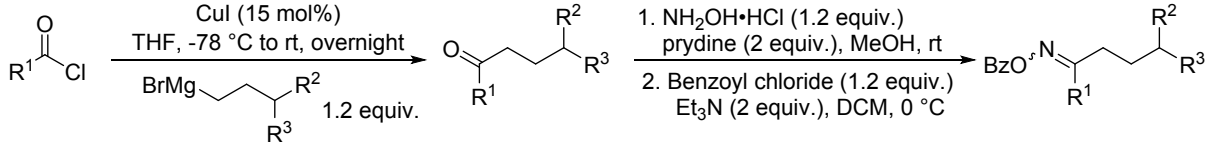
Contents

1. General comments

Chemicals were purchased from Sigma-Aldrich, Strem, Acros, TCI or Alfa Aesar and used as such unless stated otherwise. NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. All solvents and reagents were purchased from Sigma-Aldrich and used as received. Chemical shifts (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^1H NMR) and 77.00 ppm (^{13}C NMR). Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), dd (doublet of doublet), m (multiplet) and br.s (broad singlet). GC-yields were calculated using hexadecane as internal standard. All measurements were carried out at room temperature unless otherwise stated. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Gas chromatography analysis was performed on an Agilent HP-7890A instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d. 0.25 μm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

2. General procedures

2.1 General procedures for the synthesis of start materials.[1]



Step 1

To a 100 mL three-necked flask was charged with CuI (0.15 equiv), the flask was evacuated and backfilled with nitrogen (3 times). Dry THF (0.5 M) and the acid chloride (1.0 equiv) was added. The solution was cooled to –78 °C and grignard reagent (1.2 equiv) was added dropwise. Then the mixture was warmed to room temperature for 6 h. The reaction was quenched with an aqueous solution of saturated NH_4Cl. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried (Na_2SO_4). Then the solution was filtered, concentrated to give the crude ketones, which were used in the next step without further purification.

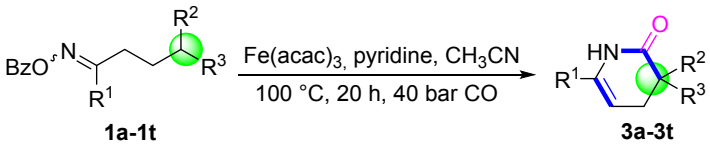
Step 2

A mixture of ketone (1.0 equiv), hydroxylamine hydrochloride (1.2 equiv) and pyridine (2.0 equiv) were dissolved in MeOH (0.5 M). The mixture stirred at room temperature for 3 h. Then MeOH was removed by concentration, the residue was diluted with 1M HCl aqueous solution and ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ solution, brine, dried (Na_2SO_4), and concentrated to give the crude ketone oximes, which were used in the next step without further purification.

To a mixture of ketone oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5 M) in a 100 mL three-necked flask was added benzoyl chloride (1.2 equiv) at 0 °C. After addition, the reaction mixture was stirred at same temperature for half hours. The reaction was quenched with an aqueous solution of saturated $NaHCO_3$. The

layers were separated and the aqueous layer was extracted with DCM. The combined organic layers were washed with brine, dried (Na_2SO_4). Then the solution was filtered, concentrated to give the crude oxime esters. Purification by column chromatography on silica gel (Pentane/ethyl acetate 10:1), gave the corresponding products.

2.2 General procedure for the cabonylation of tertiary carbon radicals

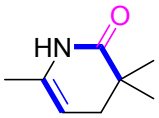


1a-1t **3a-3t**

To each screw-cap vial (4 ml) equipped with a septum, a small cannula, and a stirring bar was added oxime esters (0.20 mmol), $Fe(acac)_3$ (7.0 mg, 0.02 mmol) and CH_3CN (3 mL). The vials then were purged with argon three times before placed on an alloy plate and transferred into a 300 mL autoclave of the 4560 series from Parr instruments under air. After flushing the autoclave three times with CO, a pressure of 40 bar CO was set and the reaction was performed for 16 hours at 100 °C. Afterwards, the autoclave was cooled to room temperature and the pressure was released carefully. The solvent was removed under reduced pressure and the crude products were purified by column chromatography on silica gel (eluent: pentane/ethyl acetate = 5:1).

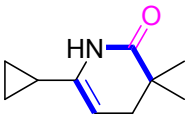
3. Spectroscopic Data of Products

3,3,6-Trimethyl-3,4-dihydropyridin-2(1*H*)-one



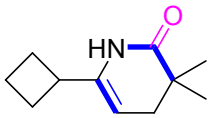
22.5 mg, white solid, yield: 81%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 – 7.77 (br.s, 1H), 4.76 (tt, *J* = 2.9, 1.5 Hz, 1H), 2.11 (dd, *J* = 4.2, 2.0 Hz, 2H), 1.80 (q, *J* = 1.7 Hz, 3H), 1.16 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.34, 132.03, 99.93, 36.41, 35.54, 24.60, 18.62.
GC-MS (EI, 70ev): m/z (%) = 139 (M^+, 47), 124 (27), 96 (32), 83 (16), 70 (100), 42 (27).
HRMS (ESI) Calc. for $C_{13}H_{13}NO$ ($M+H^+$): 140.1075; found: 140.1073.

6-Cyclopropyl-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



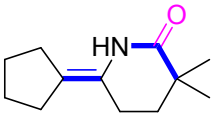
23.1 mg, white solid, yield: 70%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (br.s, 1H), 4.82 – 4.69 (m, 1H), 2.10 (dd, *J* = 4.5, 1.6 Hz, 2H), 1.41 – 1.28 (m, 1H), 1.14 (s, 6H), 0.75 – 0.63 (m, 2H), 0.56 – 0.45 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.07, 137.53, 98.14, 36.77, 35.38, 24.61, 12.75, 4.42.
GC-MS (EI, 70ev): m/z (%) = 165 (M^+, 67), 150 (100), 137 (37), 122 (51), 96 (97), 83 (44), 70 (51).
HRMS (ESI) Calc. for $C_{10}H_{15}NO$ ($M+H^+$): 166.1232; found: 166.1228.

6-Cyclobutyl-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



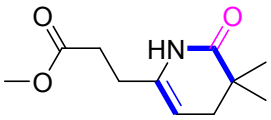
24.3 mg, white solid, yield: 68%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (br.s, 1H), 4.81 – 4.71 (m, 1H), 3.03 – 2.82 (m, 1H), 2.20 – 2.05 (m, 4H), 2.07 – 1.87 (m, 3H), 1.86 – 1.75 (m, 1H), 1.15 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.29, 139.29, 97.23, 36.86, 36.80, 35.39, 26.15, 24.64, 17.94.
GC-MS (EI, 70ev): m/z (%) = 179 (M^+, 81), 164 (16), 151 (100), 136 (65), 123 (42), 109 (45), 82 (46), 70 (35).
HRMS (ESI) Calc. for $C_{11}H_{17}NO$ ($M+H^+$): 180.1388; found: 180.1389.

6-Cyclopentylidene-3,3-dimethylpiperidin-2-one



20.8 mg, colorless oil, yield: 54%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (br.s, 1H), 2.49 – 2.34 (m, 2H), 2.25 – 2.06 (m, 4H), 1.76 – 1.61 (m, 6H), 1.24 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 175.61, 124.68, 117.08, 37.61, 34.07, 29.54, 27.87, 26.88, 26.75, 25.84, 22.23.
GC-MS (EI, 70ev): m/z (%) = 193 (M^+, 100), 178 (48), 165 (42), 152 (46), 122 (30), 96 (27), 41 (27).
HRMS (ESI) Calc. for $C_{12}H_{19}NO$ ($M+H^+$): 194.1545; found: 194.1553.

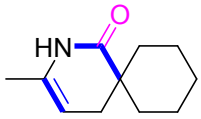
Methyl 3-(5,5-dimethyl-6-oxo-1,4,5,6-tetrahydropyridin-2-yl)propanoate



21.1 mg, white solid, yield: 50%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H), 4.83 – 4.75 (m, 1H), 3.70 (s, 3H), 2.54 (td, *J* = 7.1, 0.9 Hz, 2H), 2.40 (ddt, *J* = 8.2, 7.0, 1.1 Hz, 2H), 2.11 (d, *J* = 4.4 Hz, 2H), 1.14 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 177.27, 173.30, 135.12, 99.88, 51.89, 36.54, 35.44, 32.06, 27.83, 24.57.
GC-MS (EI, 70ev): m/z (%) = 211 (M^+, 85), 196 (59), 183 (21), 164 (41), 152 (85), 136 (33), 110 (100), 82 (56), 70 (54).

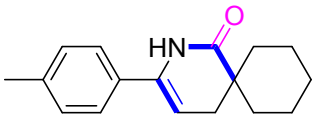
HRMS (ESI) Calc. for $C_{11}H_{17}NO_3$ (M+H$^+$): 212.1286; found: 212.1288.

3-Methyl-2-azaspiro[5.5]undec-3-en-1-one



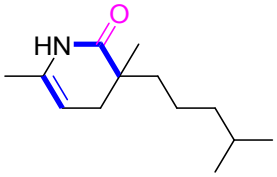
18.3 mg, white solid, yield: 51%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.66 (s, 1H), 4.73 (tt, *J* = 4.5, 1.5 Hz, 1H), 2.26 – 2.16 (m, 2H), 1.84–1.71 (m, 5H), 1.66 – 1.52 (m, 3H), 1.53 – 1.30 (m, 5H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.08, 131.78, 99.16, 39.59, 31.62, 29.84, 25.89, 21.31, 18.70.
GC-MS (EI, 70ev): m/z (%) = 179 (M$^+$, 97), 162 (37), 150 (70), 136 (72), 123 (100), 110 (35), 94 (37), 70 (61).
HRMS (ESI) Calc. for $C_{11}H_{17}NO_2$ (M+H$^+$): 180.1388; found: 180.1389.

3-(*p*-Tolyl)-2-azaspiro[5.5]undec-3-en-1-one



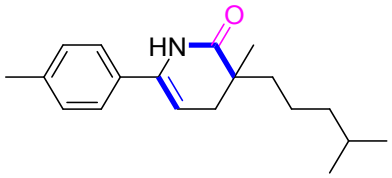
27.0 mg, white solid, yield: 53%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 2H), 7.23 – 7.13 (m, 2H), 6.96 (br.s, 1H), 5.33 (td, *J* = 4.9, 1.8 Hz, 1H), 2.42 (d, *J* = 4.8 Hz, 2H), 2.36 (s, 3H), 1.90 – 1.76 (m, 2H), 1.71 – 1.35 (m, 8H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.11, 138.59, 136.03, 132.15, 129.53, 124.52, 100.37, 39.85, 31.59, 30.35, 25.92, 21.41, 21.18.
GC-MS (EI, 70ev): m/z (%) = 255 (M$^+$, 57), 227 (100), 212 (29), 199 (37), 170 (17), 146 (45), 118 (22).

(*S*)-3,6-Dimethyl-3-(4-methylpentyl)-3,4-dihydropyridin-2(1*H*)-one



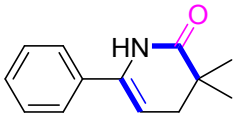
23.4 mg, colorless oil, yield: 56%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 6.68 (s, 1H), 4.72 (tp, *J* = 4.6, 1.4 Hz, 1H), 2.28 – 2.12 (m, 1H), 2.14 – 1.99 (m, 1H), 1.77 (q, *J* = 1.7 Hz, 3H), 1.60 – 1.41 (m, 3H), 1.32 – 1.22 (m, 2H), 1.21 – 1.08 (m, 5H), 0.86 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.69, 131.65, 99.54, 39.90, 39.49, 37.04, 33.13, 27.86, 22.64, 22.62, 22.60, 21.67, 18.77.
GC-MS (EI, 70ev): m/z (%) = 209 (M$^+$, 26), 166 (11), 125 (71), 97 (100), 70 (17), 41 (16).
HRMS (ESI) Calc. for $C_{13}H_{23}NO$ (M+H$^+$): 210.1858; found: 210.1855.

(*S*)-3-Methyl-3-(4-methylpentyl)-6-(p-tolyl)-3,4-dihydropyridin-2(1*H*)-one



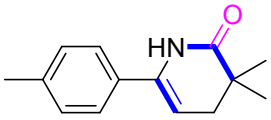
35.3 mg, white solid, yield: 62%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.18 (dt, *J* = 8.0, 0.7 Hz, 2H), 7.02 (s, 1H), 5.32 (ddd, *J* = 5.1, 4.4, 1.8 Hz, 1H), 2.46 – 2.22 (m, 5H), 1.65 – 1.45 (m, 3H), 1.36 – 1.25 (m, 2H), 1.20 (s, 3H), 1.18 – 1.06 (m, 2H), 0.85 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.68, 138.60, 135.97, 132.23, 129.55, 124.55, 100.77, 40.20, 39.46, 36.89, 33.55, 27.83, 22.65, 22.57, 22.42, 21.73, 21.17.
GC-MS (EI, 70ev): m/z (%) = 285 (M$^+$, 25), 242 (7), 201 (62), 186 (13), 173 (100), 146 (12), 118(11), 41 (8).

3,3-Dimethyl-6-phenyl-3,4-dihydropyridin-2(1*H*)-one [2]



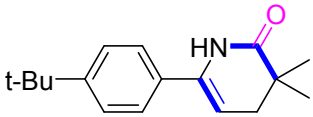
28.1 mg, white solid, yield: 70%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.31 (m, 5H), 7.32 – 7.21 (br.s, 1H), 5.39 (td, *J* = 4.7, 1.9 Hz, 1H), 2.34 (d, *J* = 4.7 Hz, 2H), 1.23 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.20, 136.31, 135.00, 128.87, 128.63, 124.74, 101.68, 36.83, 35.97, 24.55.
GC-MS (EI, 70ev): m/z (%) = 201 (M^+, 100), 186 (85), 173 (35), 158 (65), 132 (84), 104 (37), 77 (33).
HRMS (ESI) Calc. for $C_{13}H_{15}NO_2$ ($M+H^+$): 202.1232; found: 202.1230.

3,3-Dimethyl-6-(*p*-tolyl)-3,4-dihydropyridin-2(1*H*)-one



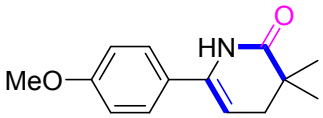
37.4 mg, white solid, yield: 87%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.13 (br.s, 1H), 5.35 (td, *J* = 4.7, 1.8 Hz, 1H), 2.36 (s, 3H), 2.33 (d, *J* = 4.7 Hz, 2H), 1.23 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.28, 138.66, 136.13, 132.17, 129.56, 124.57, 100.97, 36.88, 35.94, 24.54, 21.18.
GC-MS (EI, 70ev): m/z (%) = 215 (M^+, 96), 200 (100), 187 (32), 172 (66), 146 (67), 133 (18), 118 (33), 91 (20), 70 (16).

6-(4-(*tert*-Butyl)phenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



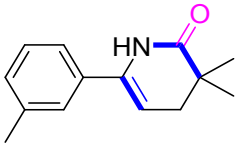
38.0 mg, white solid, yield: 74%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 2H), 7.00 (s, 1H), 5.37 (td, *J* = 4.7, 1.8 Hz, 1H), 2.33 (d, *J* = 4.7 Hz, 2H), 1.33 (s, 9H), 1.23 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.10, 151.91, 136.04, 132.12, 125.84, 124.35, 101.08, 36.90, 35.96, 34.67, 31.24, 24.53.
GC-MS (EI, 70ev): m/z (%) = 257(M^+, 81), 242 (100), 229 (37), 214 (56), 200 (38), 172 (24), 132 (27), 70 (7).

6-(4-Methoxyphenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



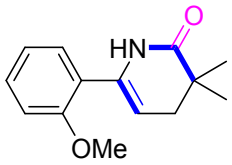
41.6 mg, white solid, yield: 90%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 2H), 7.25 (s, 1H), 6.96 – 6.84 (m, 2H), 5.27 (td, *J* = 4.7, 1.8 Hz, 1H), 3.82 (s, 3H), 2.31 (d, *J* = 4.7 Hz, 2H), 1.22 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.27, 159.89, 135.92, 127.63, 126.05, 114.19, 100.13, 55.36, 36.87, 35.92, 24.53.
GC-MS (EI, 70ev): m/z (%) = 231 (M^+, 94), 216 (100), 203 (27), 188 (67), 162 (36), 134 (35), 77 (14).
HRMS (ESI) Calc. for $C_{14}H_{17}NO_2$ ($M+H^+$): 232.1337; found: 232.1340.

3,3-Dimethyl-6-(*m*-tolyl)-3,4-dihydropyridin-2(1*H*)-one



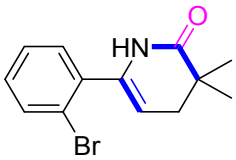
30.5 mg, white solid, yield: 71%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.07 (m, 5H), 5.38 (td, *J* = 4.7, 1.8 Hz, 1H), 2.37 (s, 3H), 2.33 (d, *J* = 4.7 Hz, 2H), 1.23 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.13, 138.63, 136.33, 134.97, 129.39, 128.79, 125.40, 121.85, 101.44, 36.86, 35.96, 24.54, 21.44.
GC-MS (EI, 70ev): m/z (%) = 215 (M^+, 96), 200 (100), 187 (32), 172 (66), 146 (67), 133 (18), 118 (33), 91 (20), 70 (16).

6-(2-Methoxyphenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



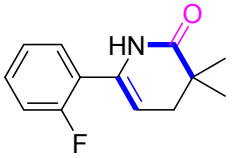
24.5 mg, white solid, yield: 53%.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 (br.s, 1H), 7.41 – 7.28 (m, 2H), 7.03 – 6.86 (m, 2H), 5.26 (td, *J* = 4.7, 1.8 Hz, 1H), 3.85 (s, 3H), 2.32 (d, *J* = 4.7 Hz, 2H), 1.23 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.38, 156.34, 135.78, 129.98, 129.48, 123.90, 121.08, 111.12, 103.72, 55.59, 36.51, 36.11, 24.56.
GC-MS (EI, 70ev): m/z (%) = 231 (M^+, 94), 216 (100), 203 (27), 188 (67), 162 (36), 134 (35), 77 (14).

6-(2-Bromophenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



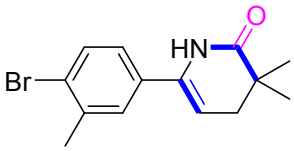
44.4 mg, white solid, yield: 79%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 7.9, 0.8 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.22 (dt, *J* = 7.9, 4.6 Hz, 1H), 6.81 (s, 1H), 5.12 (td, *J* = 4.5, 1.9 Hz, 1H), 2.33 (d, *J* = 4.5 Hz, 2H), 1.28 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 176.17, 136.54, 136.25, 133.36, 131.07, 130.27, 127.64, 122.26, 104.72, 36.57, 35.87, 24.53.
GC-MS (EI, 70ev): m/z (%) = 281 (M^+,^{81}Br, 98), 279 (M^+,^{79}Br, 100), 266 (70), 253 (51), 236 (54), 210 (41), 181 (27), 157 (29), 131 (68), 83 (67), 70 (62).
HRMS (ESI) Calc. for $C_{13}H_{14}NOBr$ ($M+H^+$): 280.0337; found: 280.0335.

6-(2-Fluorophenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



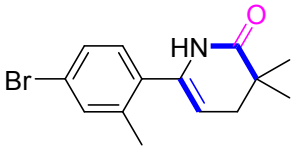
27.2 mg, white solid, yield: 62%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 2H), 7.20 – 7.07 (m, 2H), 7.03 (br.s, 1H), 5.38 (tdd, *J* = 4.7, 1.9, 0.8 Hz, 1H), 2.35 (d, *J* = 4.7 Hz, 2H), 1.25 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 176.47, 159.50 (d, *J* = 248 Hz), 131.91, 130.19 (d, *J* = 8 Hz), 128.61 (d, *J* = 3 Hz), 124.56 (d, *J* = 3 Hz), 122.92 (d, *J* = 12 Hz), 116.30 (d, *J* = 22 Hz), 105.17 (d, *J* = 3 Hz), 36.58, 36.02, 24.53.
GC-MS (EI, 70ev): m/z (%) = 219 (M^+, 100), 204 (72), 191 (27), 176 (70), 150 (87), 122 (24), 70 (29).
HRMS (ESI) Calc. for $C_{13}H_{14}NOF$ ($M+H^+$): 220.1137; found: 220.1141.

6-(4-Bromo-3-methylphenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



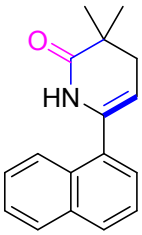
30.1 mg, white solid, yield: 51%.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.25 (br.s, 1H), 7.10 (ddd, *J* = 8.3, 2.4, 0.6 Hz, 1H), 5.38 (td, *J* = 4.7, 1.8 Hz, 1H), 2.41 (q, *J* = 0.5 Hz, 3H), 2.32 (d, *J* = 4.7 Hz, 2H), 1.22 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.12, 138.49, 135.56, 134.14, 132.76, 126.99, 125.01, 123.67, 101.99, 36.79, 35.93, 24.52, 22.97.
GC-MS (EI, 70ev): m/z (%) = 295 (M^+,^{81}Br, 98), 293 (M^+,^{79}Br, 100), 280 (85),265 (45), 250 (60), 224 (26), 198 (26), 145 (75), 130 (71), 115 (2), 83 (57), 70 (63).

6-(4-Bromo-2-methylphenyl)-3,3-dimethyl-3,4-dihydropyridin-2(1*H*)-one



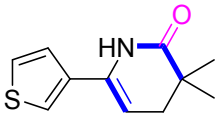
33.0 mg, white solid, yield: 56%.
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.43 – 7.33 (m, 2H), 7.08 (dd, *J* = 8.7, 0.7 Hz, 1H), 6.65 (br.s, 1H), 5.03 (td, *J* = 4.5, 1.8 Hz, 1H), 2.33 (d, *J* = 4.5 Hz, 2H), 2.30 (dt, *J* = 0.4 Hz, 3H), 1.27 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.30, 137.28, 135.31, 134.98, 132.27, 131.75, 131.69, 119.42, 104.06, 36.60, 35.90, 24.57, 19.38.
GC-MS (EI, 70ev): m/z (%) = 295 (M^+,^{81}Br, 98), 293 (M^+,^{79}Br, 100), 278 (60), 252 (34), 224 (26), 211 (38), 145 (55), 130 (71), 115 (31), 83 (50), 70 (57).

3,3-Dimethyl-6-(naphthalen-1-yl)-3,4-dihydropyridin-2(1*H*)-one



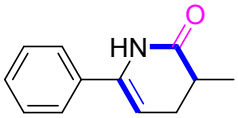
^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.11 – 8.01 (m, 1H), 7.92 – 7.81 (m, 2H), 7.57 – 7.44 (m, 4H), 6.91 (br.s, 1H), 5.25 (td, *J* = 4.5, 1.8 Hz, 1H), 2.43 (d, *J* = 4.5 Hz, 2H), 1.35 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.36, 135.69, 133.75, 133.47, 130.88, 129.29, 128.58, 126.71, 126.57, 126.20, 125.29, 124.85, 104.55, 36.74, 36.14, 24.71.
20.1 mg, white solid, yield: 40%.
GC-MS (EI, 70ev): m/z (%) = 251 (M^+, 100), 236 (26), 223 (10), 208 (13), 180 (71), 154 (25), 127 (27).

3,3-Dimethyl-6-(thiophen-3-yl)-3,4-dihydropyridin-2(1*H*)-one



29.4 mg, white solid, yield: 81%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (br.s, 1H), 7.34 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.29 (dd, *J* = 2.9, 1.4 Hz, 1H), 7.20 (dd, *J* = 5.0, 1.4 Hz, 1H), 5.42 (td, *J* = 4.7, 1.8 Hz, 1H), 2.32 (d, *J* = 4.7 Hz, 2H), 1.23 (s, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.14, 136.41, 132.03, 126.77, 124.72, 119.31, 101.02, 37.00, 35.76, 24.62.
GC-MS (EI, 70ev): m/z (%) = 207 (M^+, 100), 192 (80), 179 (36), 164 (52), 138(82), 125 (13), 110 (37), 83 (32), 70 (32).

3-Methyl-6-phenyl-3,4-dihydropyridin-2(1*H*)-one [3]



16.8 mg, white solid, yield: 45%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.49 (br.s, 1H), 7.45 – 7.30 (m, 5H), 5.44 (ddd, *J* = 5.5, 3.7, 1.7 Hz, 1H), 2.66 – 2.47 (m, 2H), 2.32 – 2.18 (m, 1H), 1.27 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.92, 136.87, 135.02, 128.85, 128.65, 124.84, 102.26, 34.64, 28.89, 15.33.
GC-MS (EI, 70ev): m/z (%) = 187 (M^+, 100), 172 (77), 158 (47), 144 (39), 132 (28), 116 (21), 104 (50), 77 (27).
HRMS (ESI) Calc. for $C_{12}H_{13}NO$ ($M+H^+$): 188.1075; found: 188.1075.

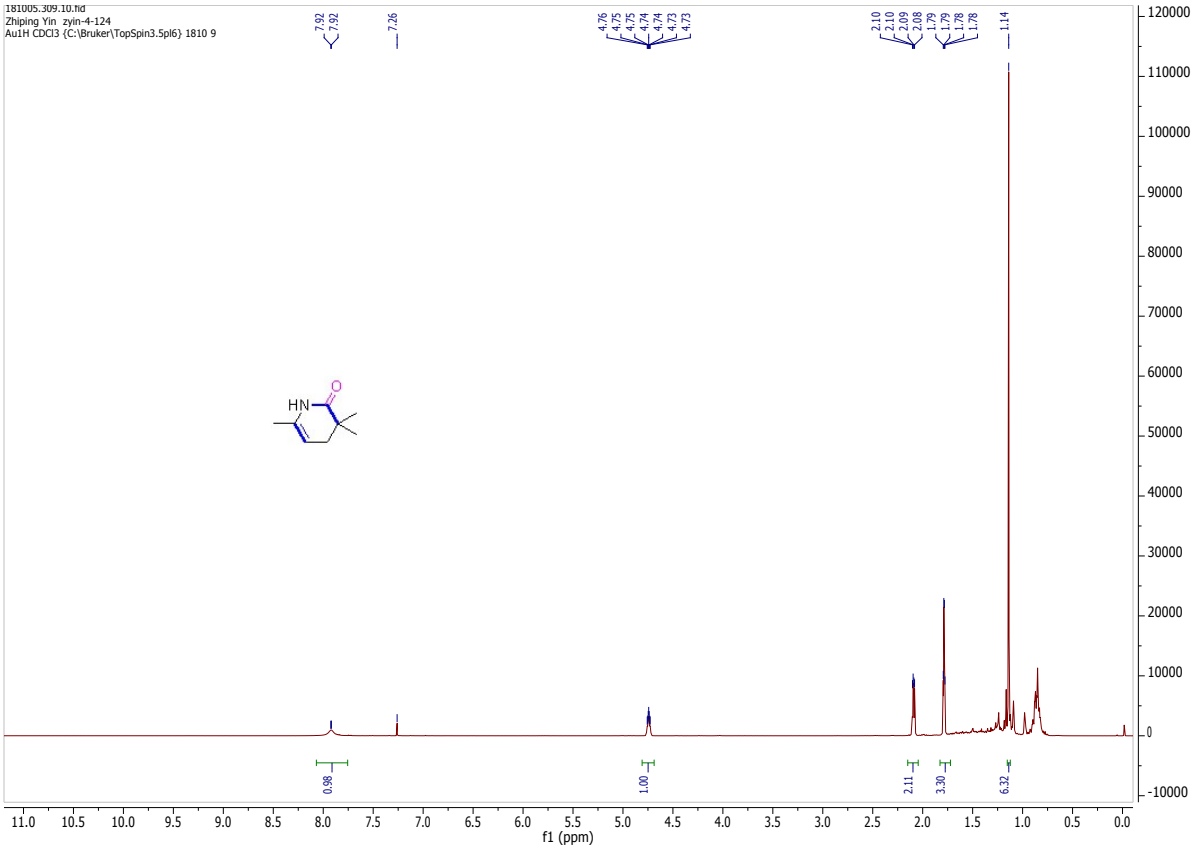
4. References

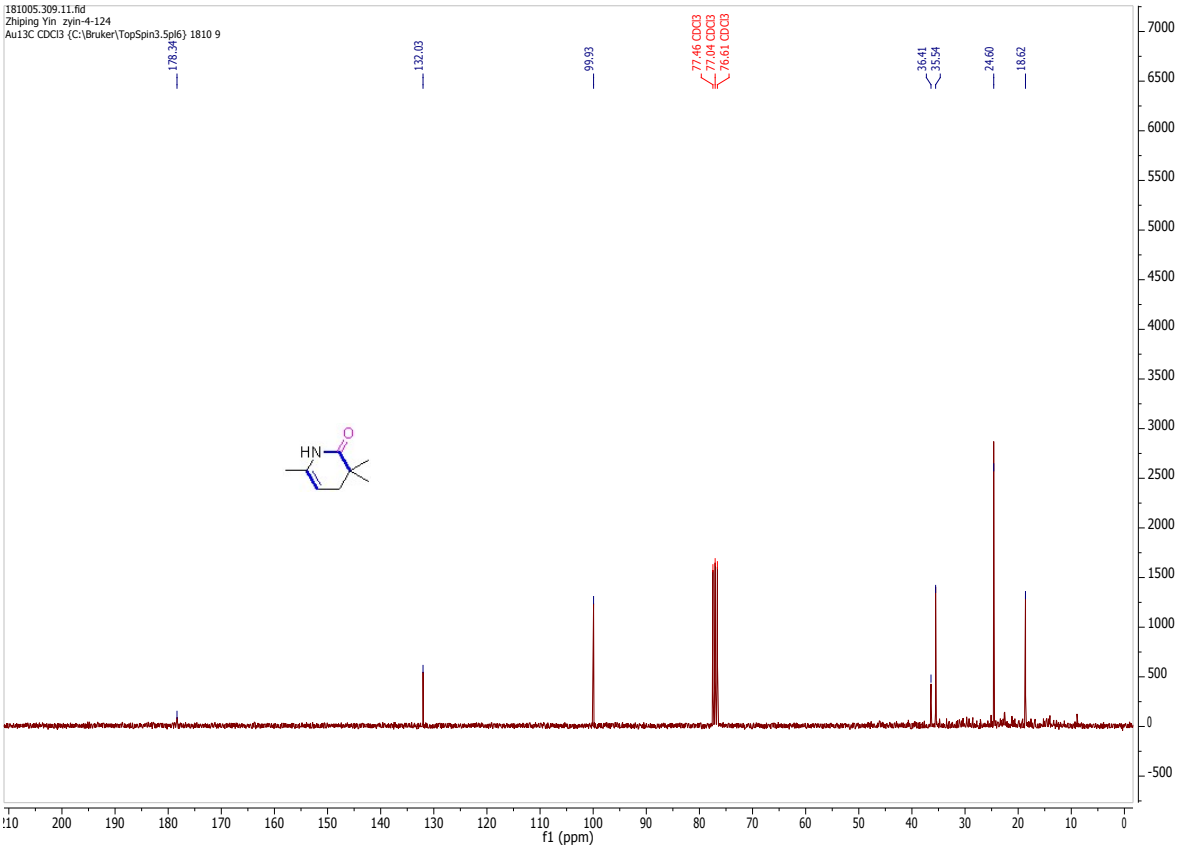
[1] a) Z. Y. Ma, L. N. Guo, Y. R. Gu, L. Chen, X. H. Duan, *Adv. Synth. Catal.* **2018**, 360, 4341-4347; b) W. Shu, C. Nevado, *Angew. Chem., Int. Ed.* **2017**, 56, 1881-1884; c) E. M. Dauncey, S. P. Morcillo, J. J. Douglas, N. S. Sheikh, D. Leonori, *Angew. Chem., Int. Ed.***2018**, 57, 744-748.

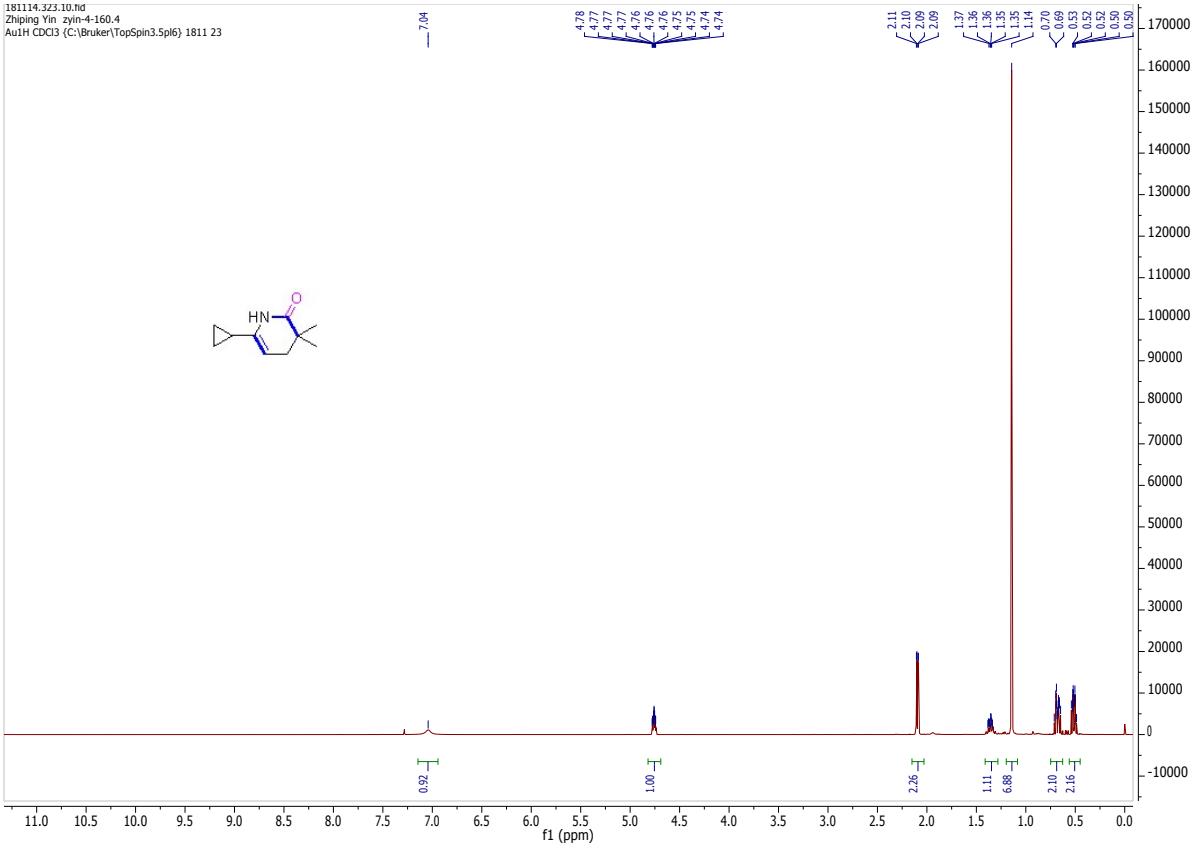
[2] M. Pawlowski, J. K. Maurin, A. Leniewski, *Heterocycles* **2005**, 65, 9-22.

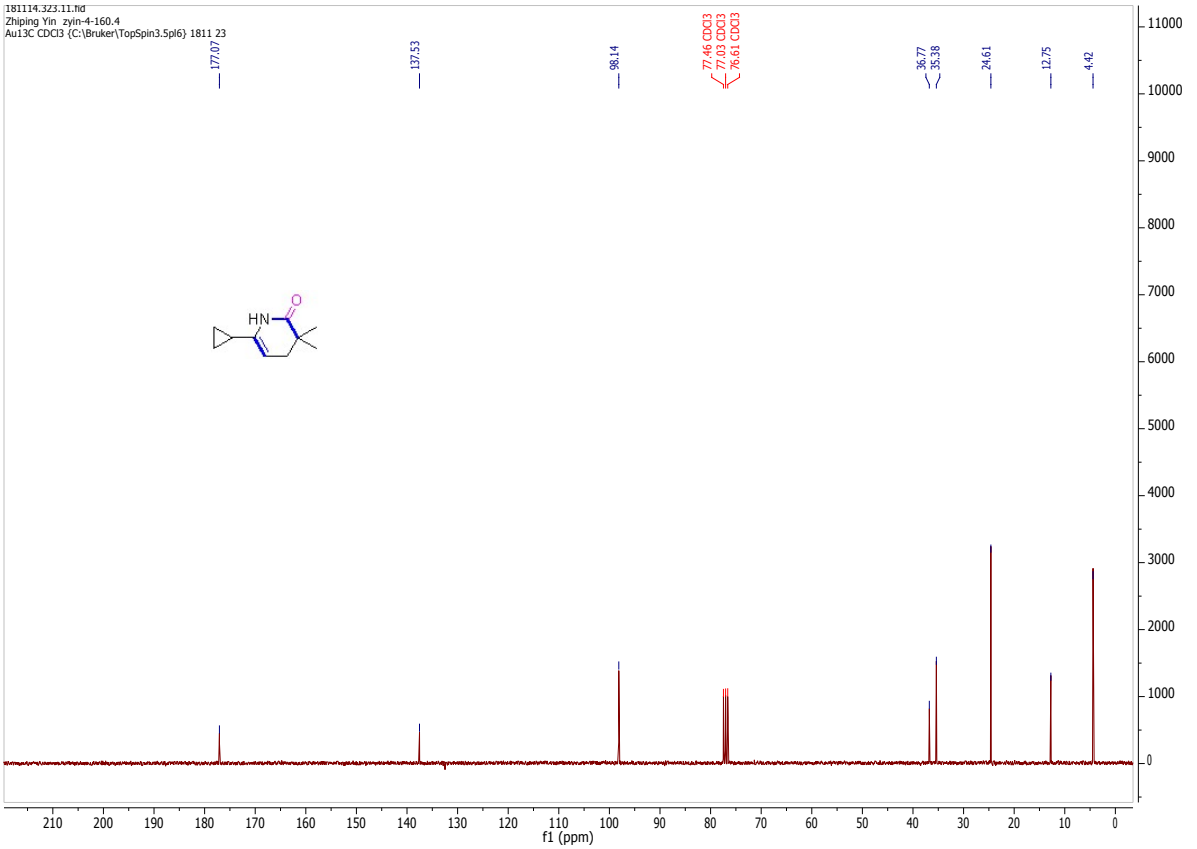
[3] C. Chuit, R. Corriu, R. Perz, C. Reye, *Tetrahedron* **1986**, 42, 2293-2301.

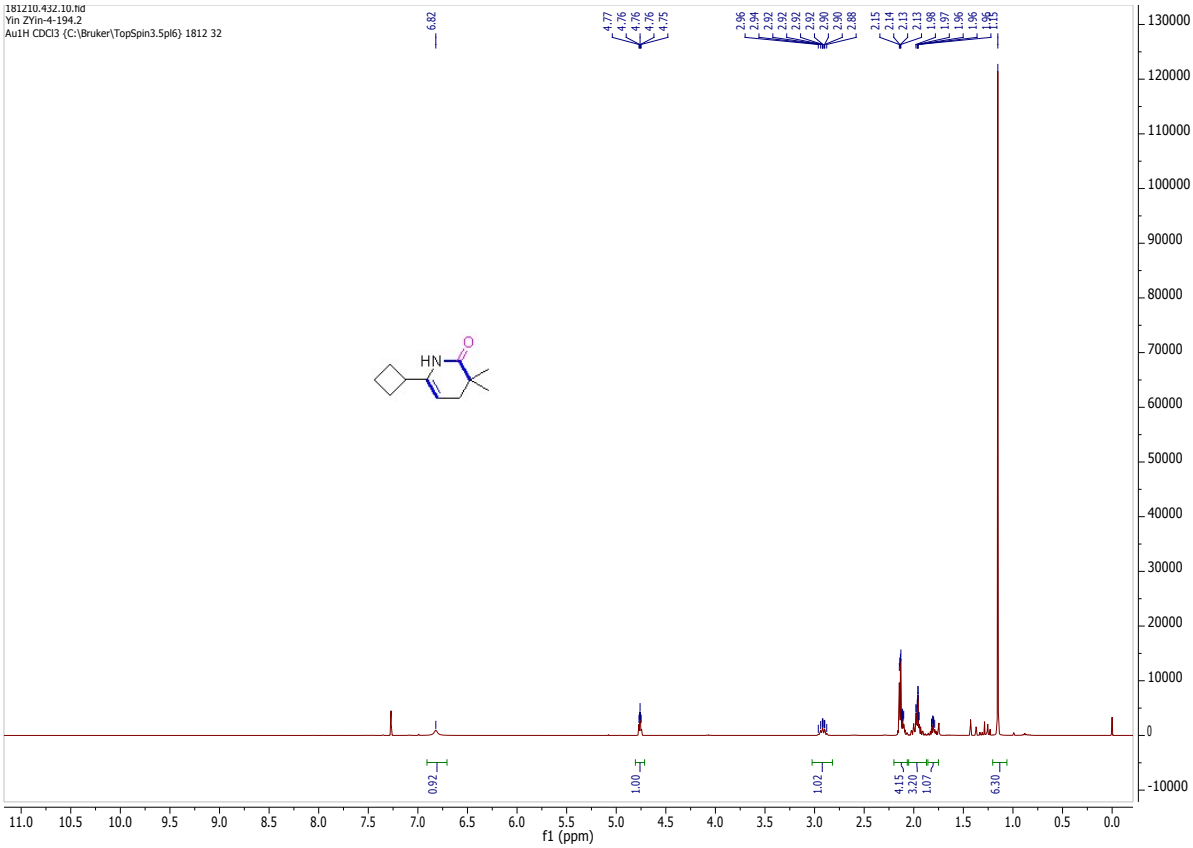
5. Copy of ^{1}H and ^{13}C NMR Spectra of Products

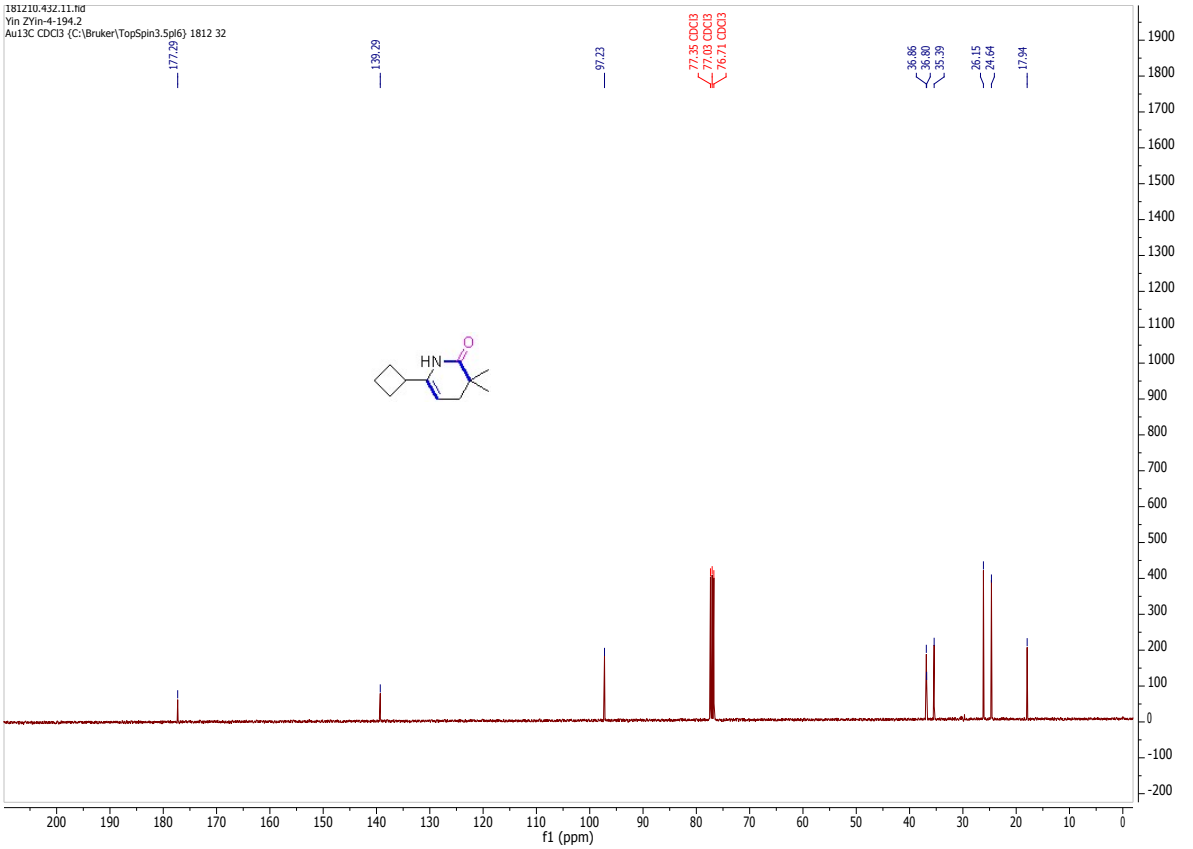


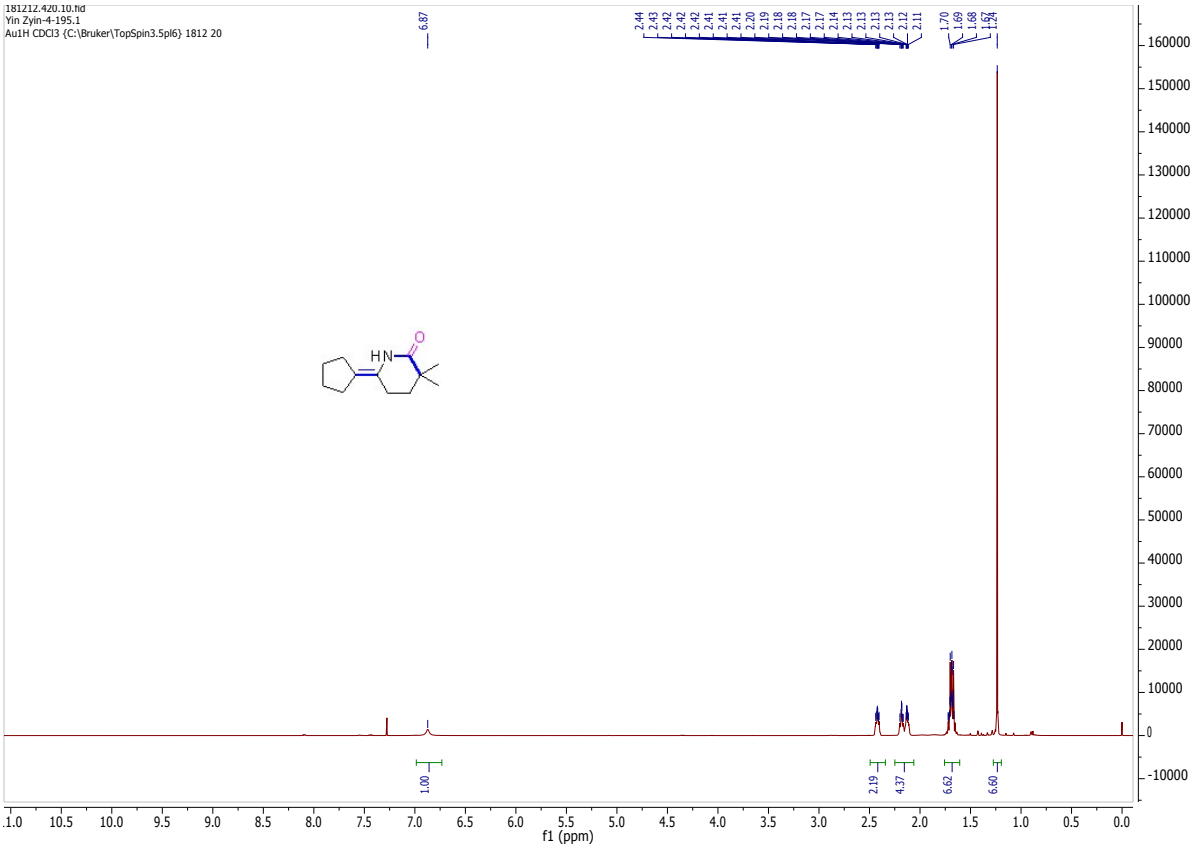


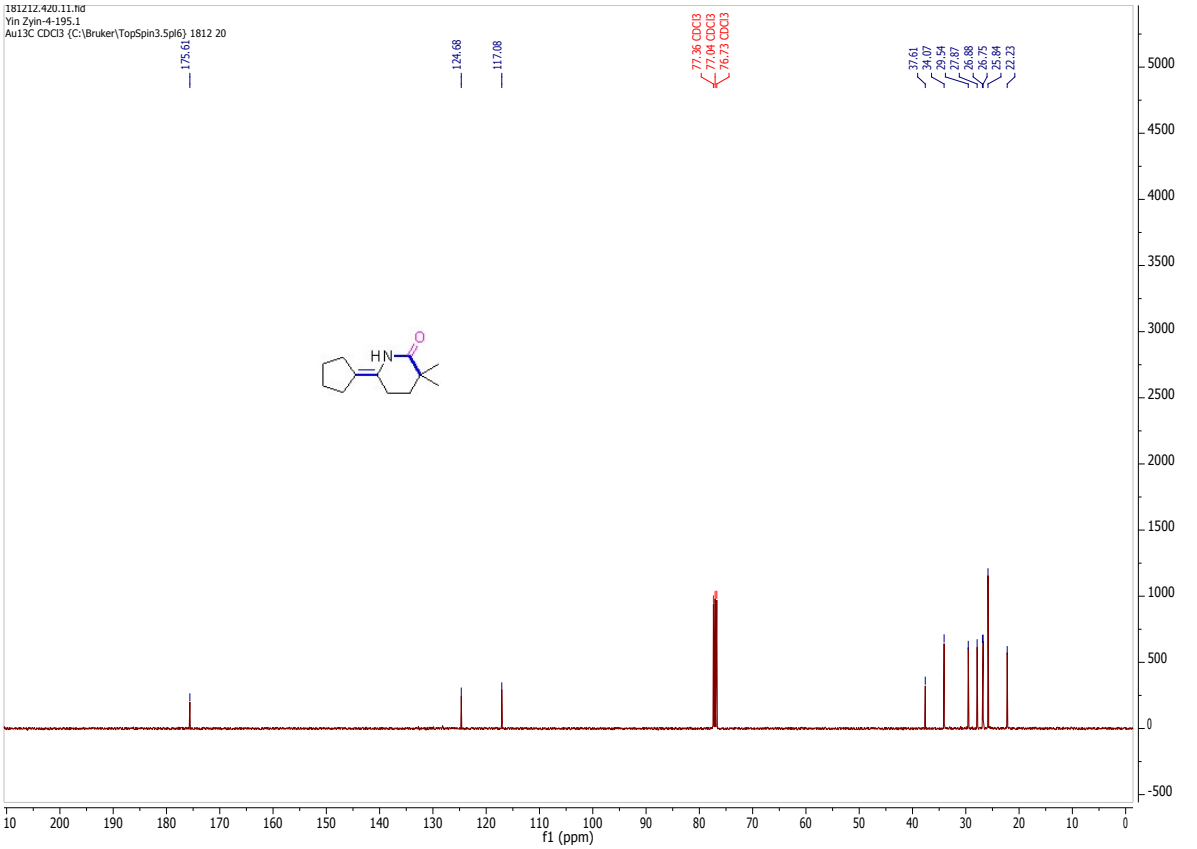

181114.323.10.fid
Zhiping Yin zyin-4-160.4
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 23
7.04
4.78
4.77
4.77
4.77
4.77
4.76
4.76
4.76
4.75
4.75
4.74
4.74
2.11
2.10
2.09
2.09
1.37
1.36
1.36
1.35
1.35
1.14
0.70
0.69
0.53
0.52
0.52
0.50
0.50
HN
O
0.92
1.00
2.26
1.11
6.88
2.10
2.16
f1 (ppm)

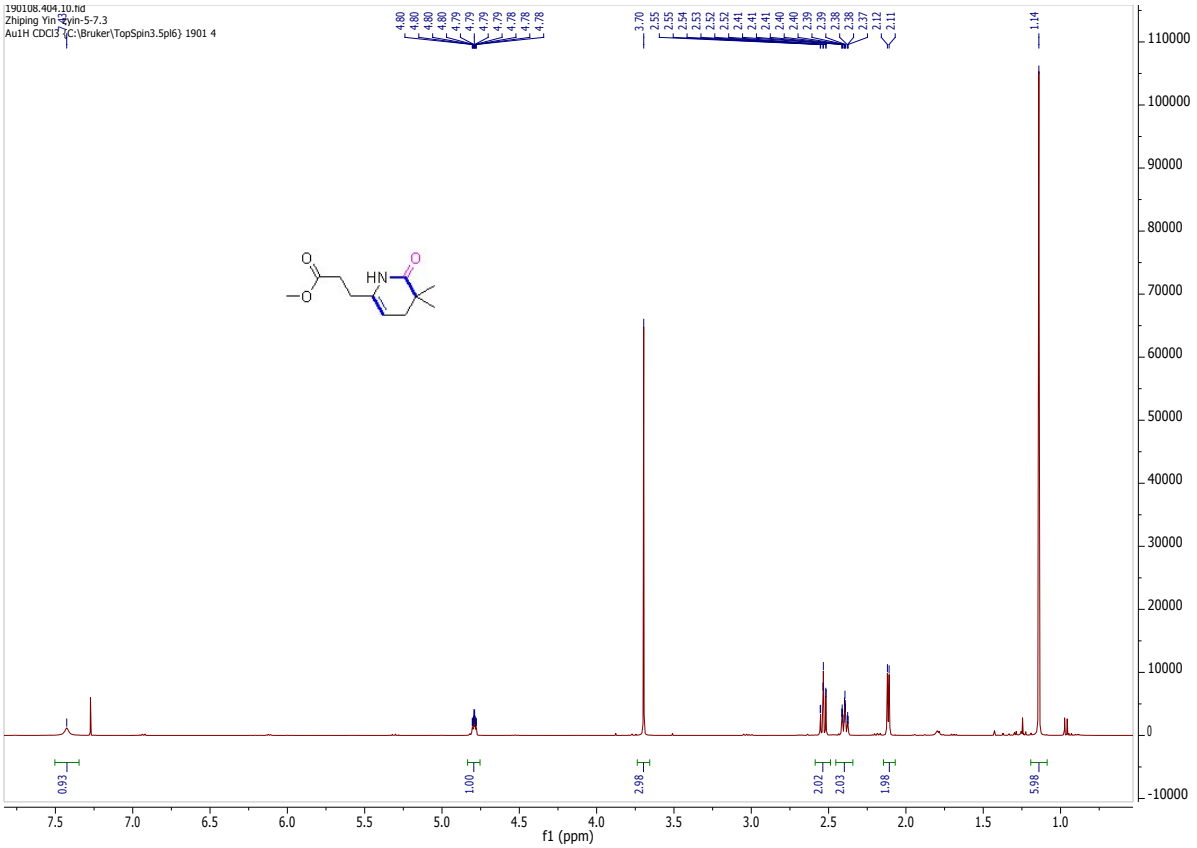

181114.323.11.fid
Zhiping Yin zyin-4-160.4
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 23
177.07
137.53
98.14
77.46 CDCl3
77.03 CDCl3
76.61 CDCl3
36.77
35.38
24.61
12.75
4.42
HN
O
f1 (ppm)

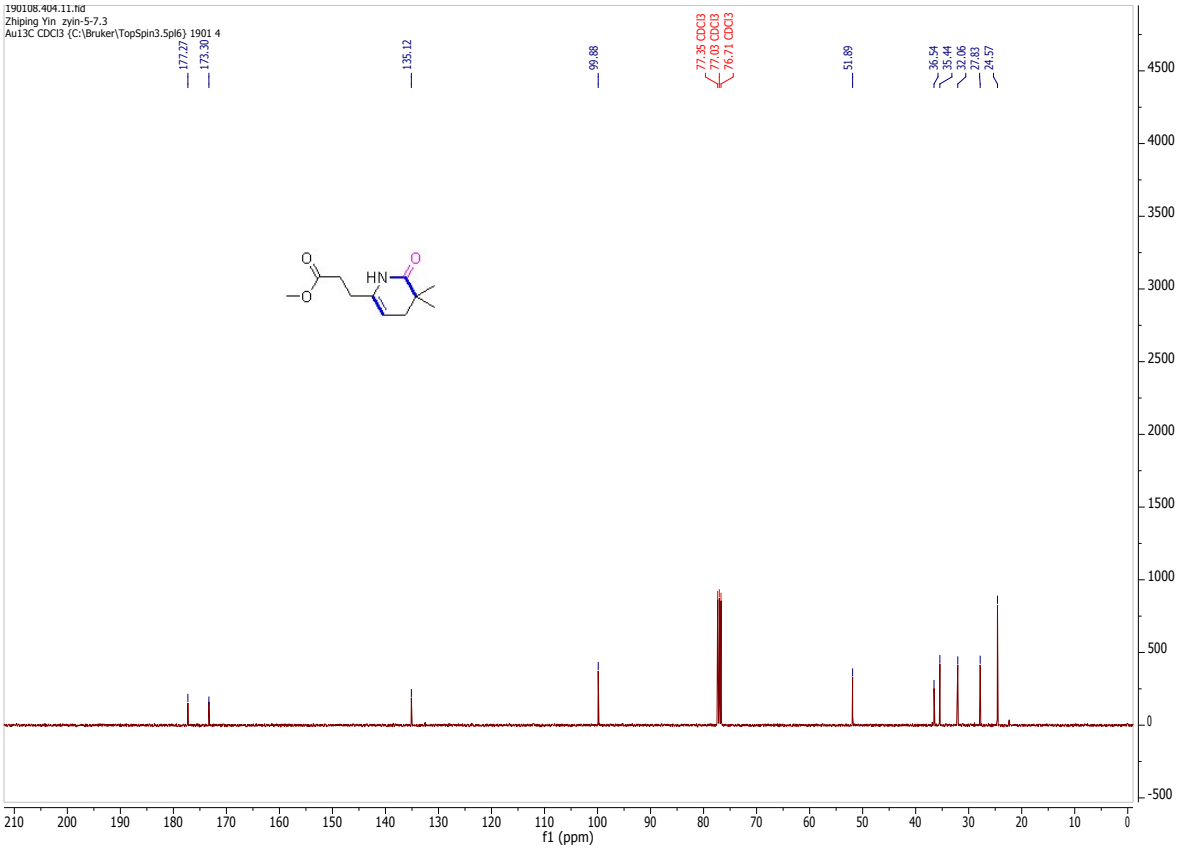

181210.432.10.fid
Yin ZYin-4-194.2
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 32
6.82
4.77
4.76
4.76
4.76
4.75
2.96
2.94
2.92
2.92
2.92
2.92
2.90
2.90
2.88
2.15
2.14
2.13
2.13
1.98
1.97
1.96
1.96
1.96
1.95
1.15
HN
O
0.92
1.00
1.02
4.15
3.20
1.07
6.30
f1 (ppm)

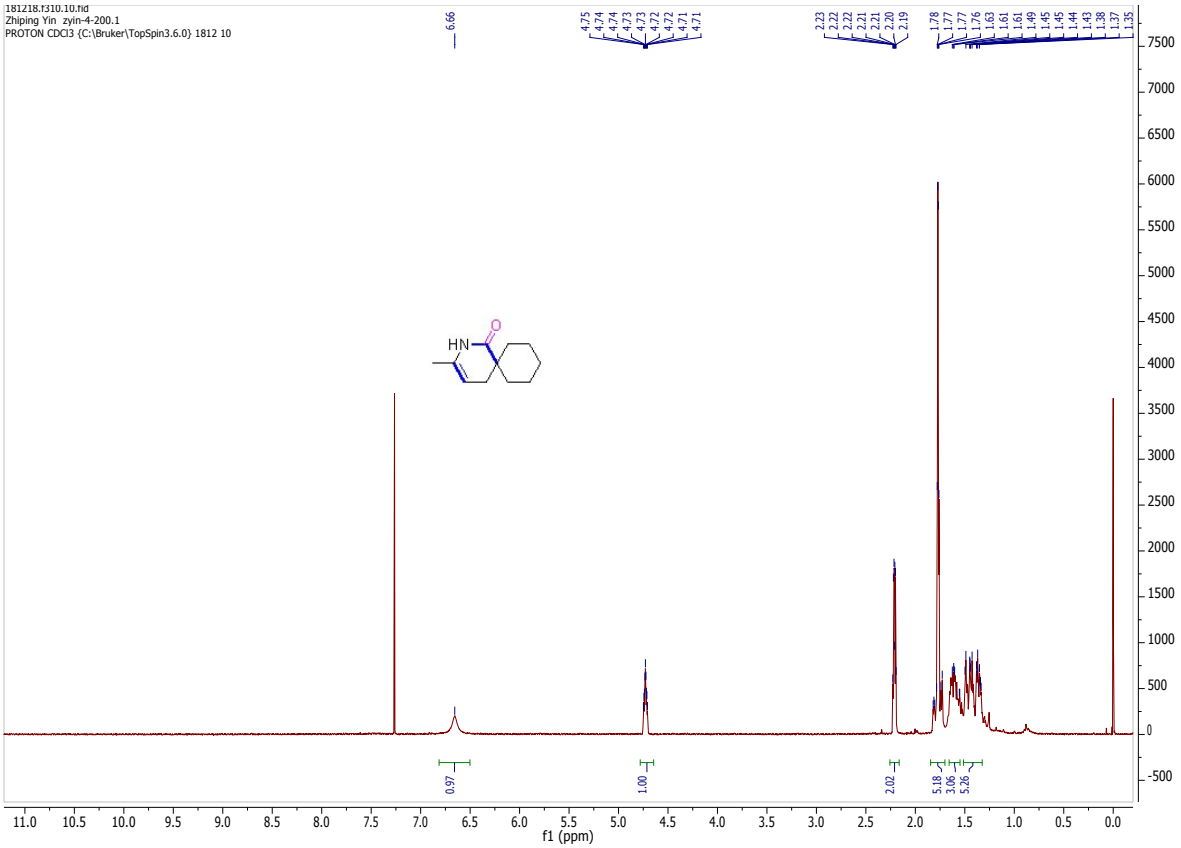

181210.432.11.fid
Yin ZYin-4-194.2
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 32
177.29
139.29
97.23
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
36.86
36.80
35.39
26.15
24.64
17.94
HN
O
f1 (ppm)

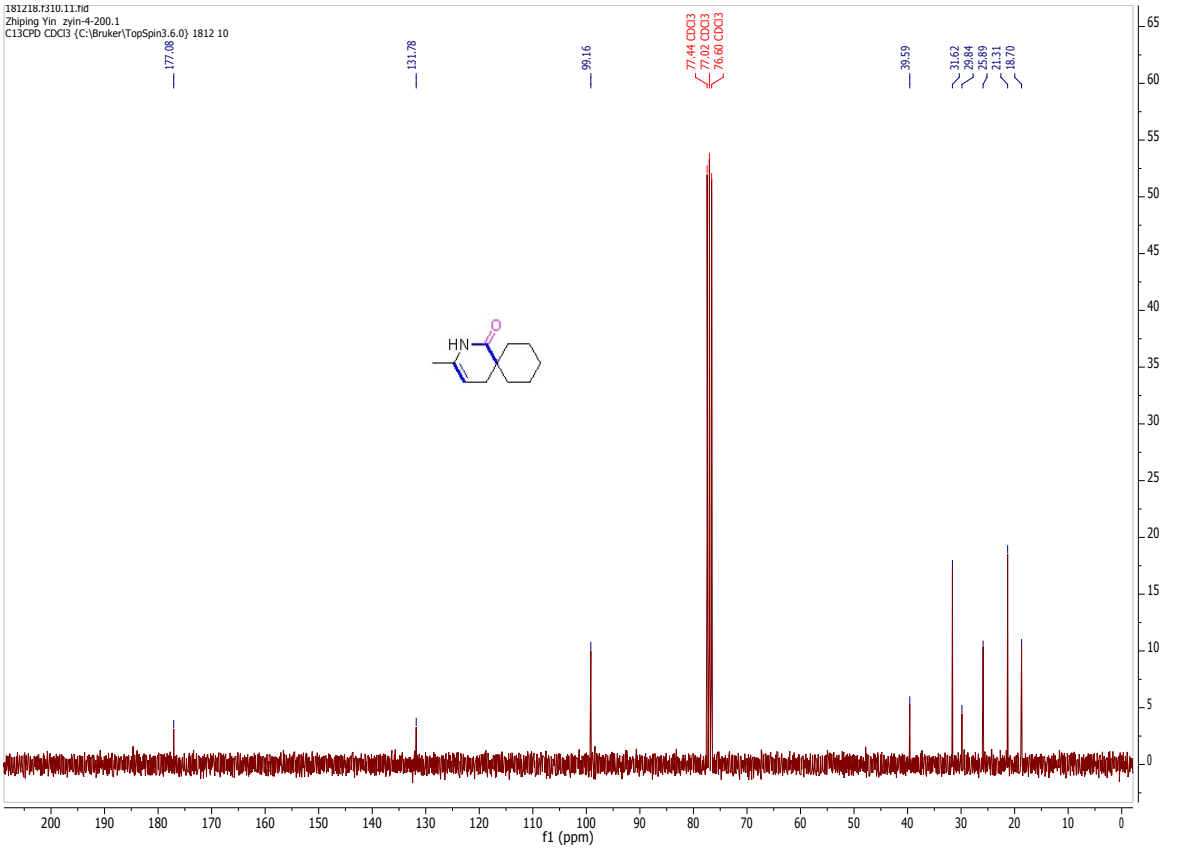

181212.420.10.fid
Yin Zyin-4-195.1
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 20
6.87
2.44
2.43
2.42
2.42
2.42
2.41
2.41
2.41
2.20
2.19
2.18
2.18
2.17
2.17
2.14
2.13
2.13
2.13
2.13
2.12
2.11
1.70
1.69
1.68
1.67
1.24
HN
O
1.00
2.19
4.37
6.62
6.60
f1 (ppm)

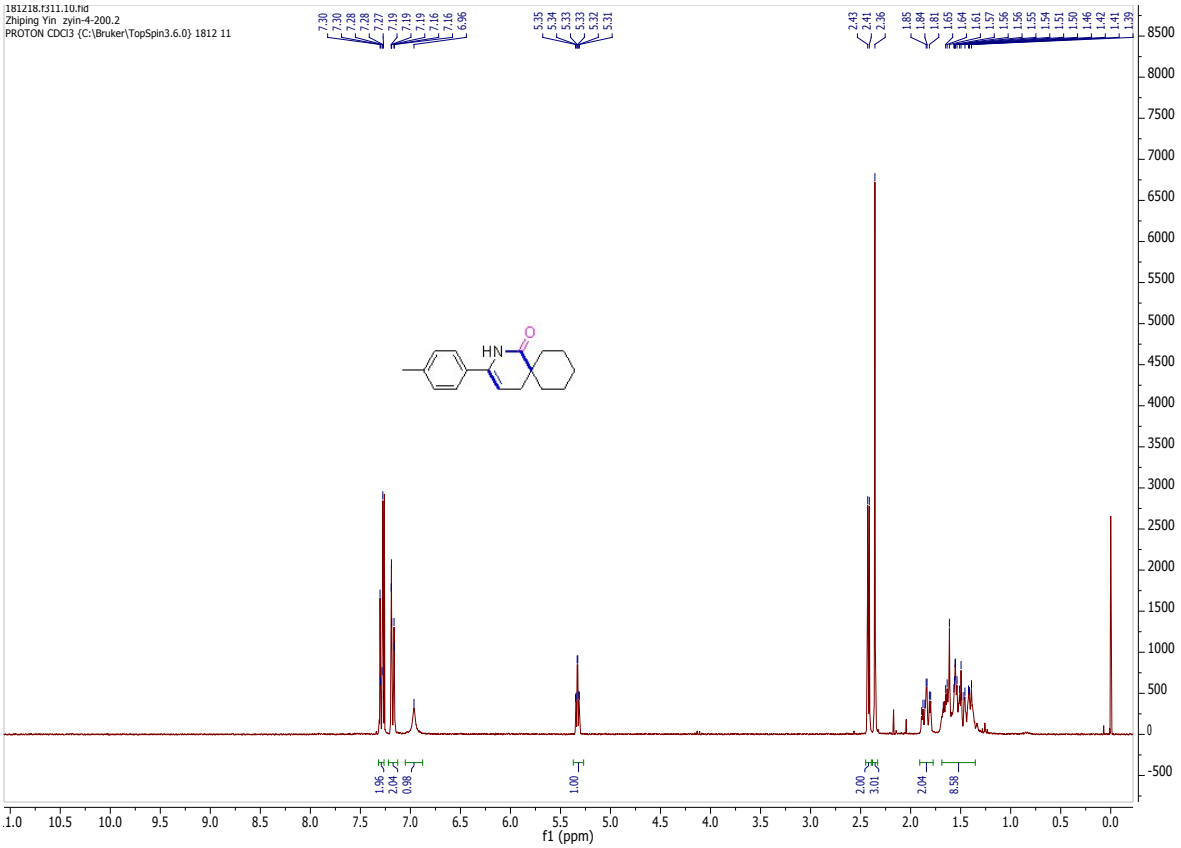

181212.420.11.fid
Yin Zyin-4-195.1
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 20
175.61
124.68
117.08
77.36 CDCl3
77.04 CDCl3
76.73 CDCl3
37.61
34.07
29.54
27.87
26.88
26.75
25.84
22.23
HN
O
f1 (ppm)

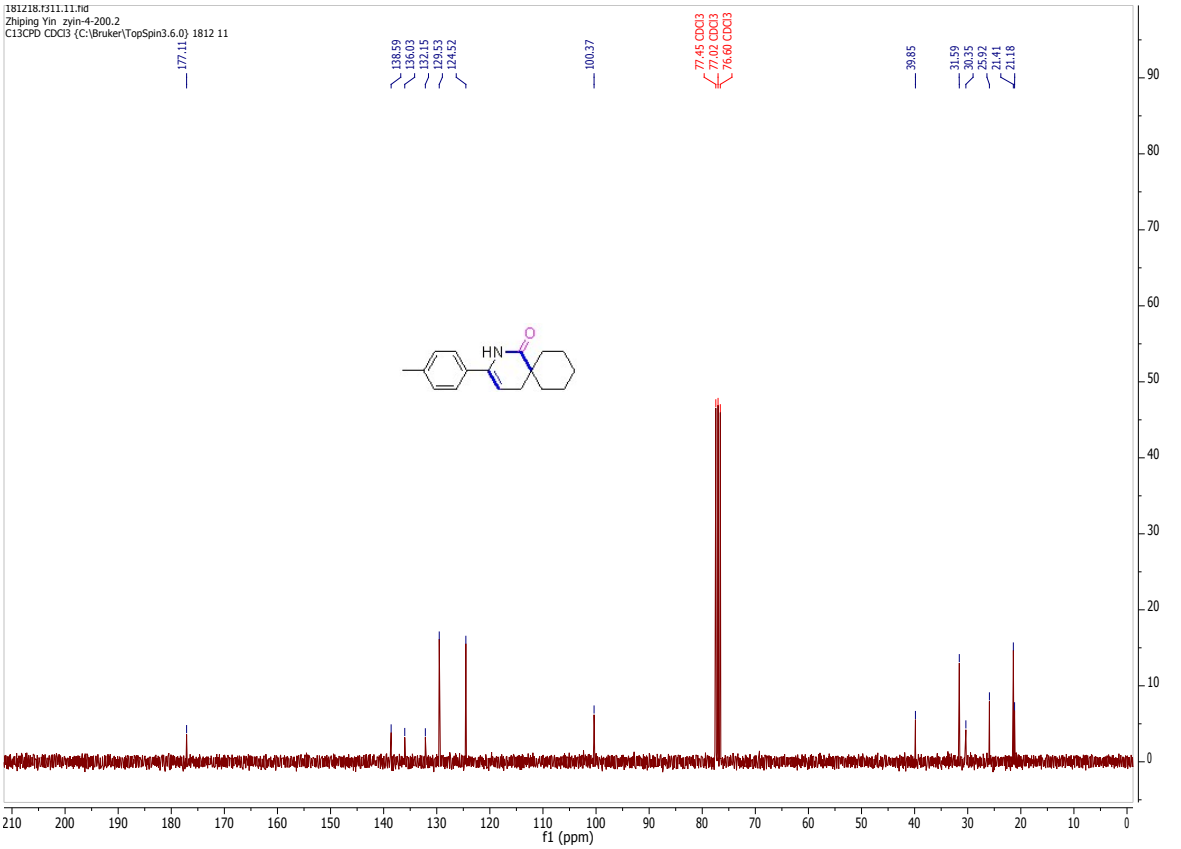

190108.404.10.fid
Zhiping Yin zyin-5-7.3
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 4
4.80
4.80
4.80
4.80
4.79
4.79
4.79
4.78
4.78
4.78
4.78
3.70
2.55
2.55
2.54
2.53
2.52
2.52
2.41
2.41
2.41
2.40
2.40
2.39
2.39
2.38
2.38
2.37
2.12
2.11
1.14
HN
O
O
O
0.93
1.00
2.98
2.02
2.03
1.98
5.98
f1 (ppm)

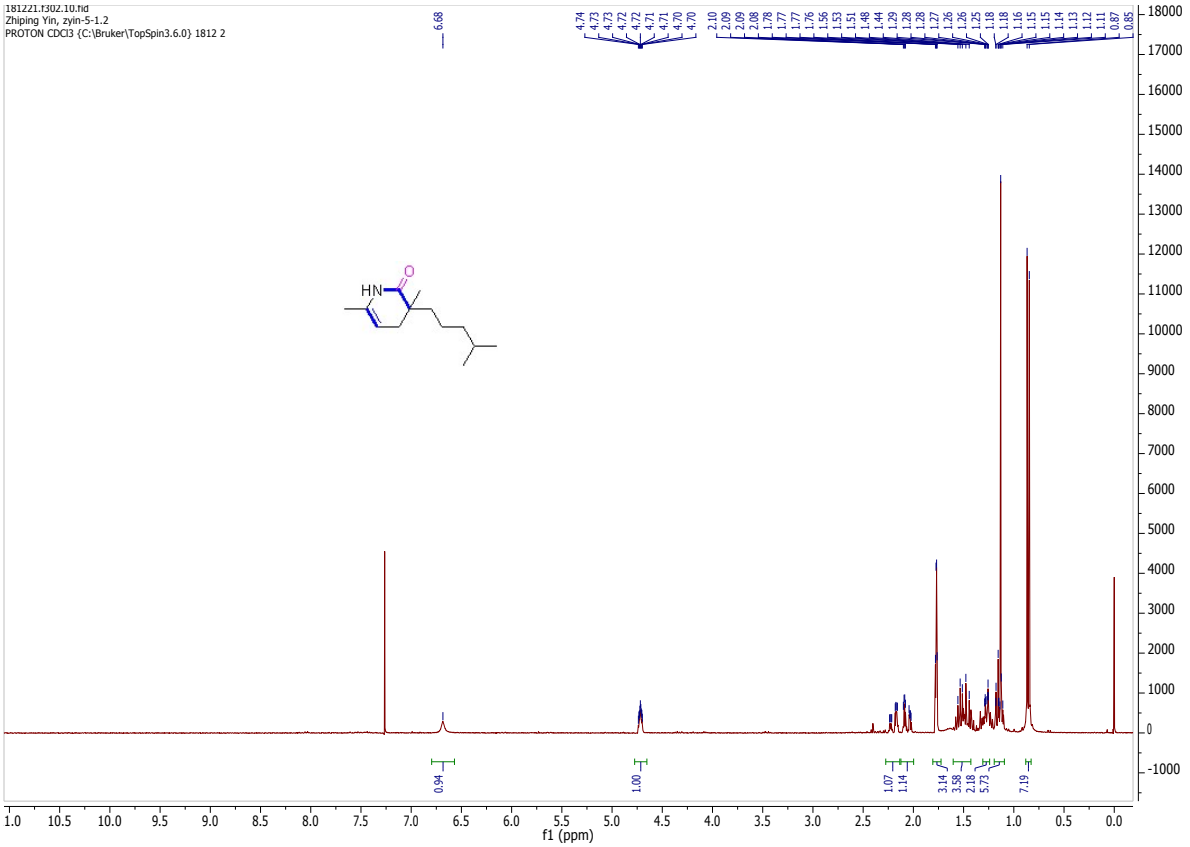

190108.404.11.fid
Zhiping Yin zyin-5-7.3
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 4
177.27
173.30
135.12
99.88
77.35 CDCl3
77.03 CDCl3
76.71 CDCl3
51.89
36.54
35.44
32.06
27.83
24.57
HN
O
O
O
f1 (ppm)

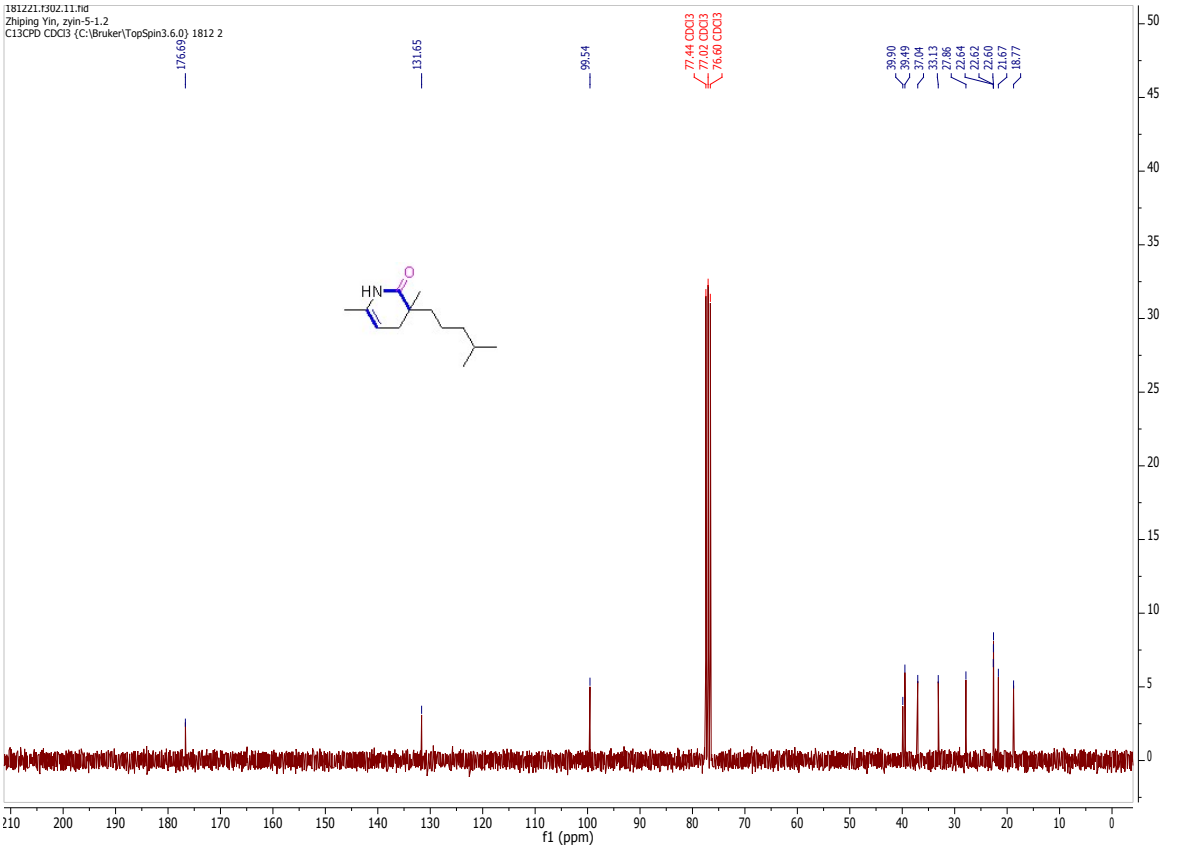

181218.t310.10.fid
Zhiping Yin zyin-4-200.1
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 10
6.66
4.75
4.74
4.74
4.73
4.73
4.72
4.72
4.71
4.71
2.23
2.22
2.22
2.21
2.21
2.20
2.19
1.78
1.77
1.77
1.76
1.63
1.61
1.61
1.49
1.45
1.45
1.44
1.43
1.38
1.37
1.35
HN
O
0.97
1.00
2.02
5.18
3.06
5.26
f1 (ppm)

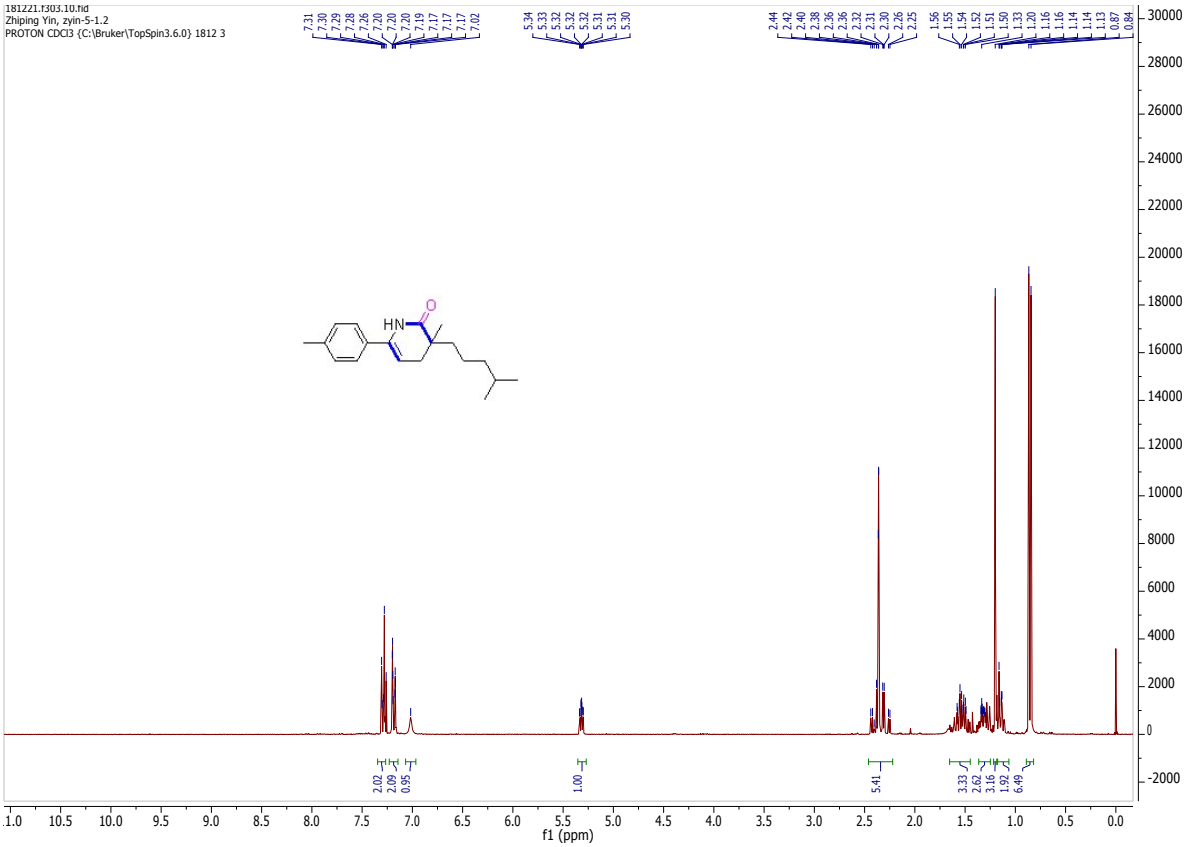

181218.t310.11.fid
Zhiping Yin zyin-4-200.1
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 10
177.08
131.78
99.16
77.44 CDCl3
77.02 CDCl3
76.60 CDCl3
39.59
31.62
29.84
25.89
21.31
18.70
HN
O
f1 (ppm)

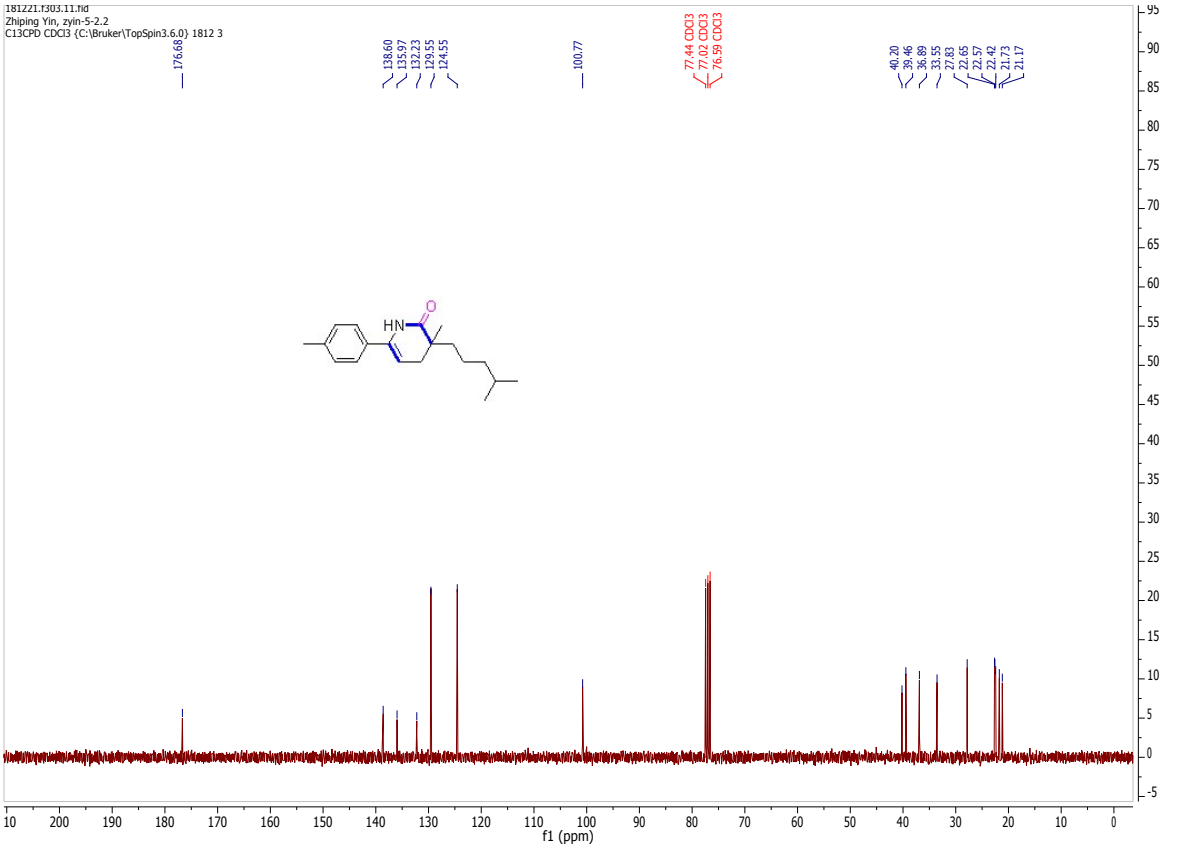

181218.f311.10.fid
Zhiping Yin zyin-4-200.2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 11
7.30
7.30
7.28
7.28
7.27
7.19
7.19
7.19
7.16
7.16
6.96
5.35
5.34
5.33
5.33
5.32
5.31
2.43
2.41
2.36
1.85
1.84
1.81
1.65
1.64
1.61
1.57
1.56
1.56
1.55
1.54
1.51
1.50
1.46
1.42
1.41
1.39
HN
O
1.96
2.04
0.98
1.00
2.00
3.01
2.04
8.58
f1 (ppm)

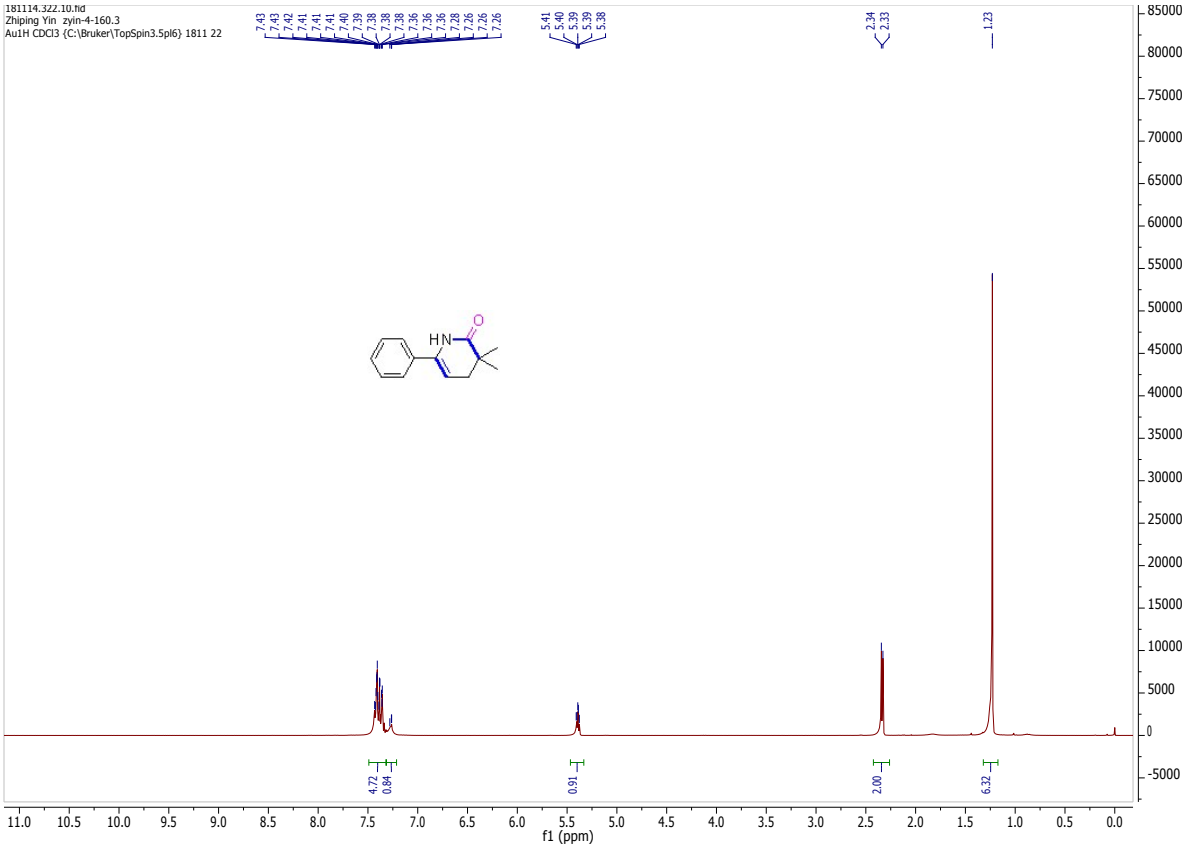

181218.f311.11.fid
Zhiping Yin zyin-4-200.2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 11
177.11
138.59
136.03
132.15
129.53
124.52
100.37
77.45 CDCl3
77.02 CDCl3
76.60 CDCl3
39.85
31.59
30.35
25.92
21.41
21.18
HN
O
f1 (ppm)

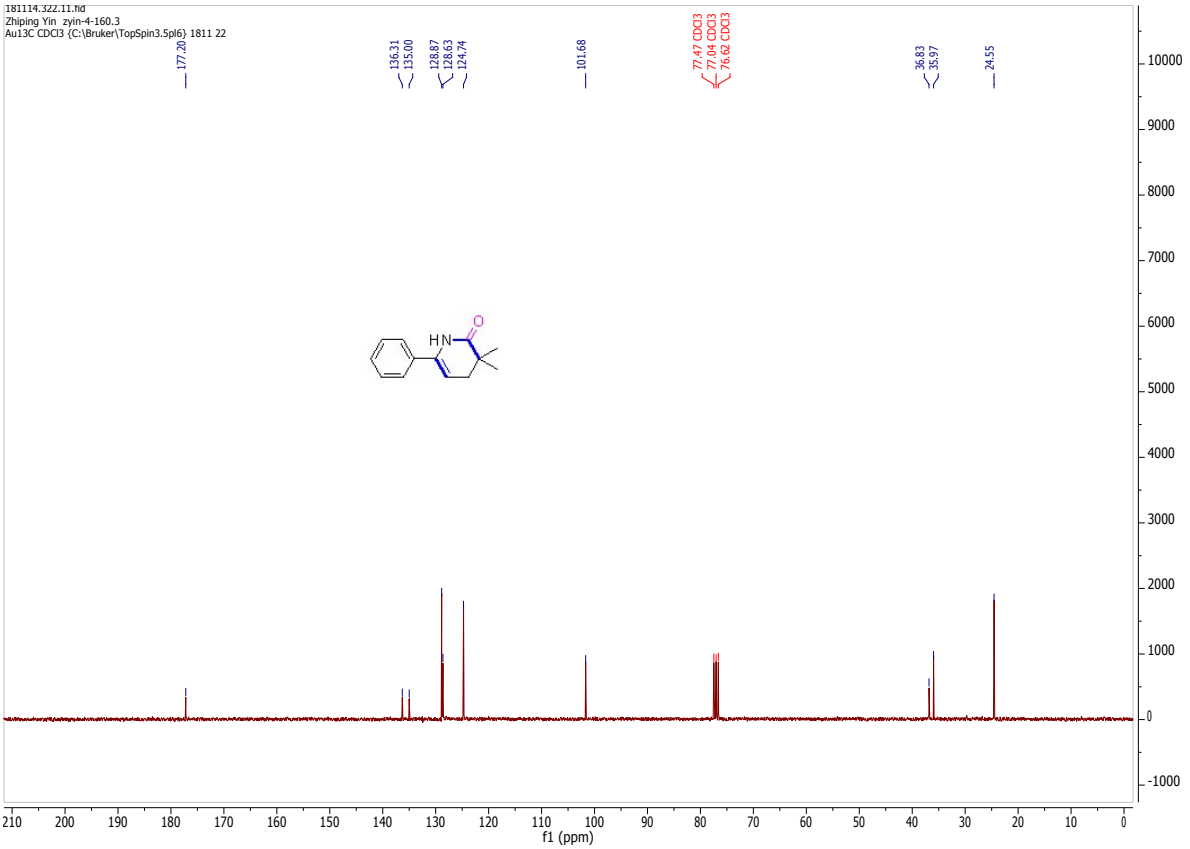

1812Z1.f30Z.10.fid
Zhiping Yin, zyin-5-1.2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 2
6.68
4.74
4.73
4.73
4.72
4.72
4.71
4.71
4.70
4.70
2.10
2.09
2.09
2.08
1.78
1.77
1.77
1.76
1.56
1.53
1.51
1.48
1.44
1.29
1.28
1.28
1.27
1.26
1.25
1.18
1.16
1.15
1.15
1.14
1.13
1.12
1.11
0.87
0.85
HN
O
0.94
1.00
1.07
1.14
3.14
3.38
2.18
5.73
7.19
f1 (ppm)

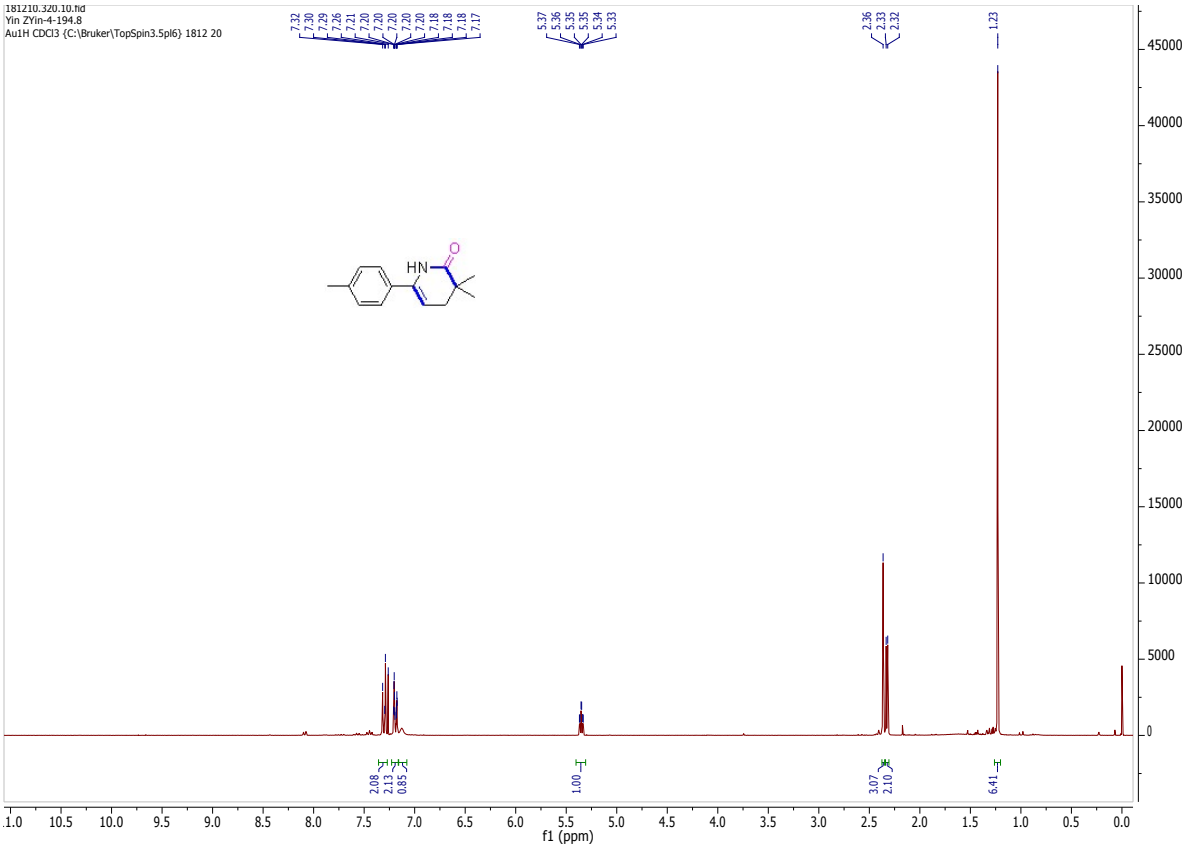

1812Z1.f30Z.11.fid
Zhiping Yin, zyin-5-1.2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 2
176.69
131.65
99.54
77.44 CDCl3
77.02 CDCl3
76.60 CDCl3
39.90
39.49
37.04
33.13
27.86
22.64
22.62
22.60
21.67
18.77
HN
O
f1 (ppm)

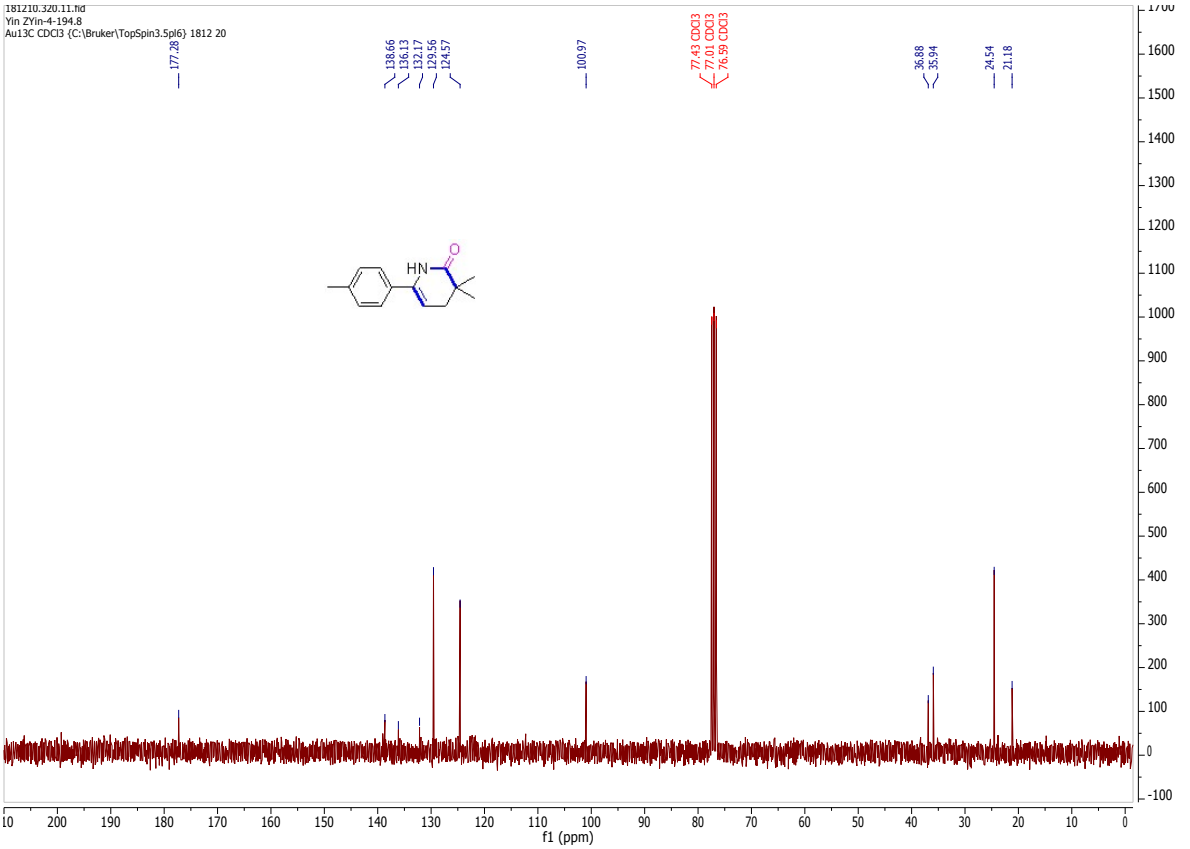

181221.f303.10.fid
Zhiping Yin, zyin-5-1.2
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 3
7.31 7.30 7.29 7.28 7.26 7.20 7.20 7.20 7.19 7.17 7.17 7.17 7.02
5.34 5.33 5.32 5.32 5.31 5.31 5.30
2.44 2.42 2.40 2.38 2.36 2.32 2.31 2.30 2.26 2.25
1.56 1.55 1.54 1.52 1.51 1.50 1.33 1.20 1.16 1.16 1.14 1.13 0.87 0.84
HN
O
2.02 2.09 0.95 1.00 5.41 3.33 2.02 3.16 1.92 6.49
f1 (ppm)

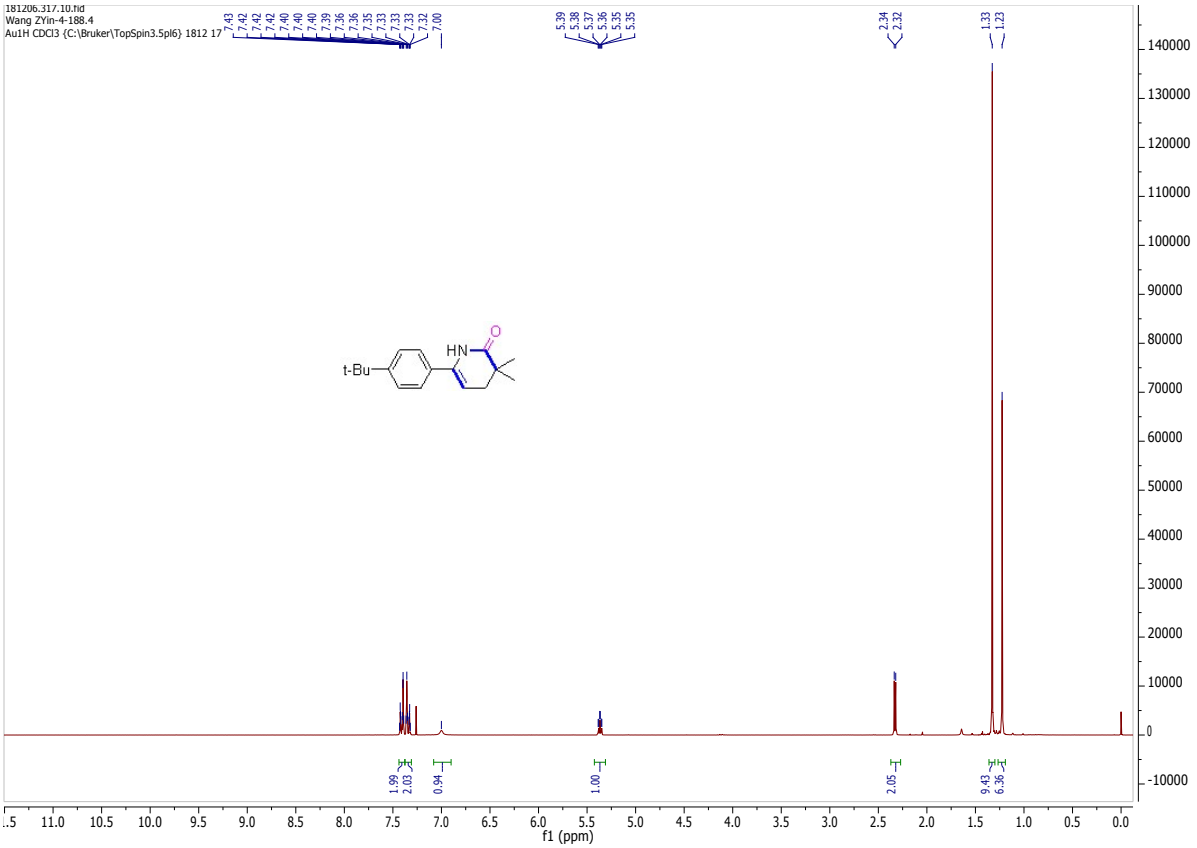

181221.f303.11.fid
Zhiping Yin, zyin-5-2.2
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 3
176.68
138.60 135.97 132.23 129.55 124.55
100.77
77.44 CDCl3
77.02 CDCl3
76.59 CDCl3
40.20 39.46 36.89 33.55 27.83 22.65 22.57 22.42 21.73 21.17
HN
O
f1 (ppm)

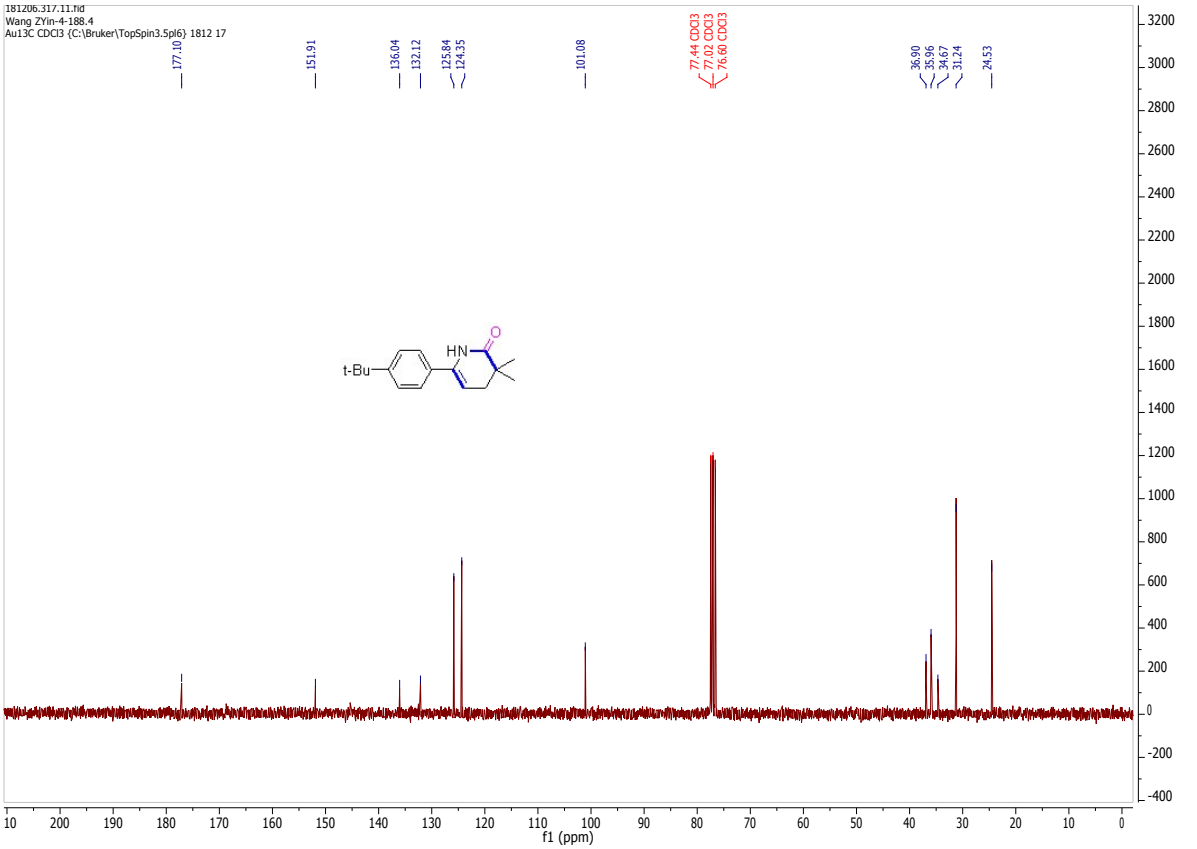

181114.3Z2.10.fid
Zhiping Yin zyin-4-160.3
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 22
7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.39 7.38 7.38 7.38 7.36 7.36 7.36 7.28 7.26 7.26 7.26
5.41 5.40 5.39 5.39 5.38
2.34 2.33
1.23
HN
O
4.72 0.84 0.91 2.00 6.32
f1 (ppm)

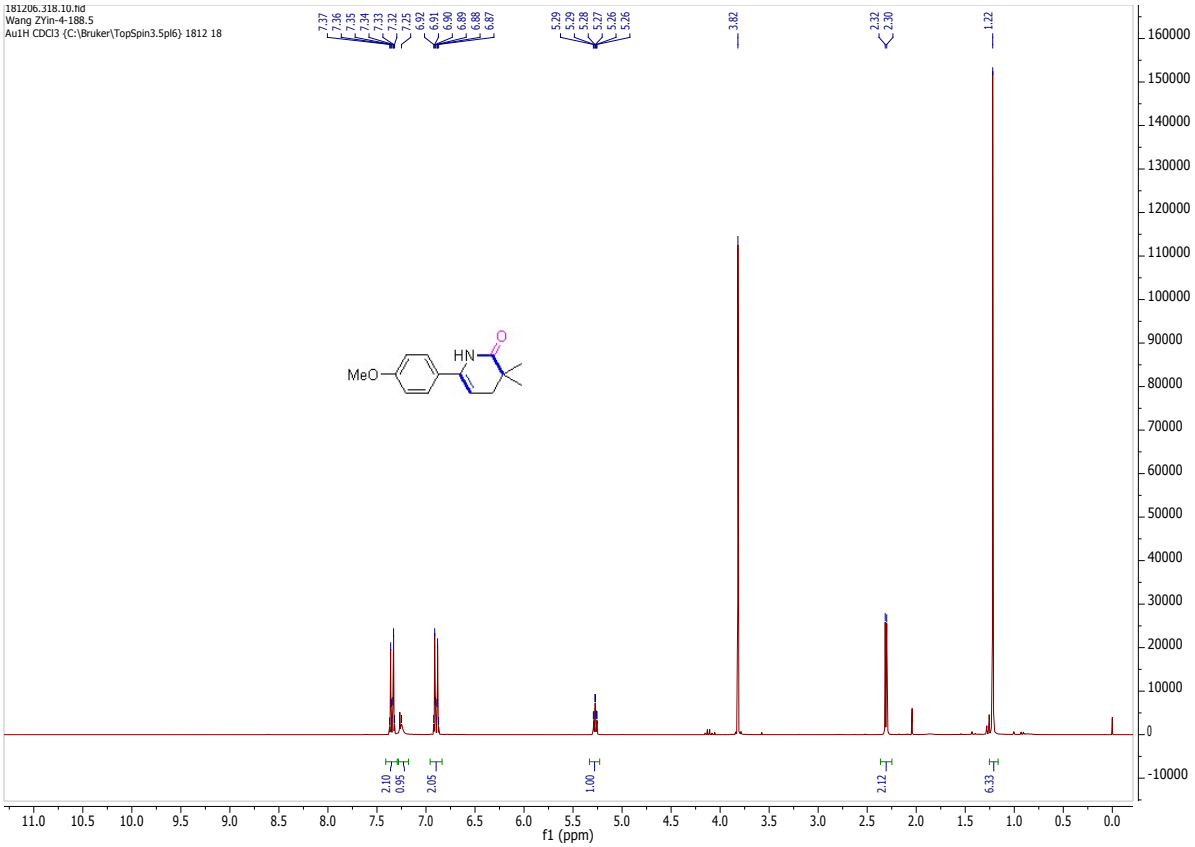

181114.3Z2.11.fid
Zhiping Yin zyin-4-160.3
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 22
177.20
136.31 135.00 128.87 128.63 124.74
101.68
77.47 CDCl3 77.04 CDCl3 76.62 CDCl3
36.83 35.97
24.55
HN
O
f1 (ppm)

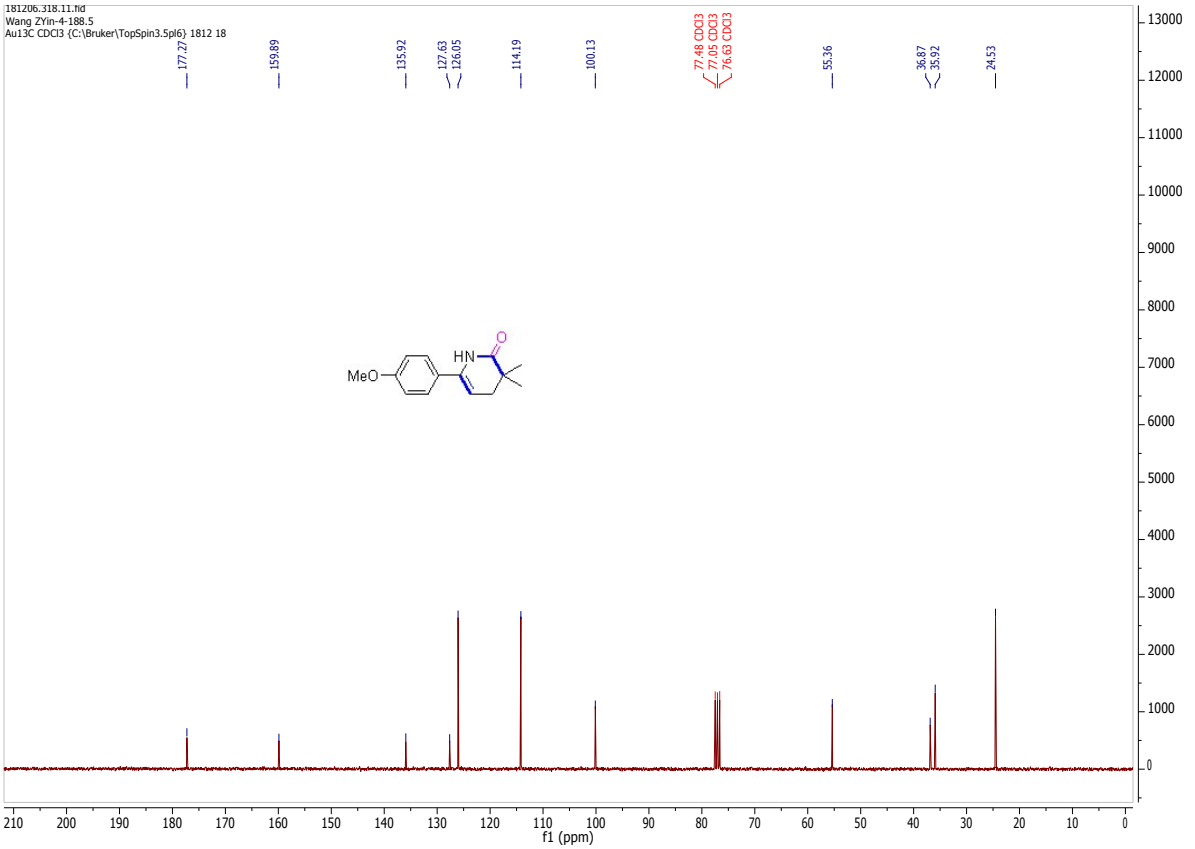

181210.320.10.fid
Yin ZYin-4-194.8
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 20
7.32
7.30
7.29
7.26
7.21
7.20
7.20
7.20
7.20
7.20
7.18
7.18
7.17
5.37
5.36
5.35
5.35
5.34
5.33
2.36
2.33
2.32
1.23
HN
O
2.08
2.13
0.85
1.00
3.07
2.10
6.41
f1 (ppm)

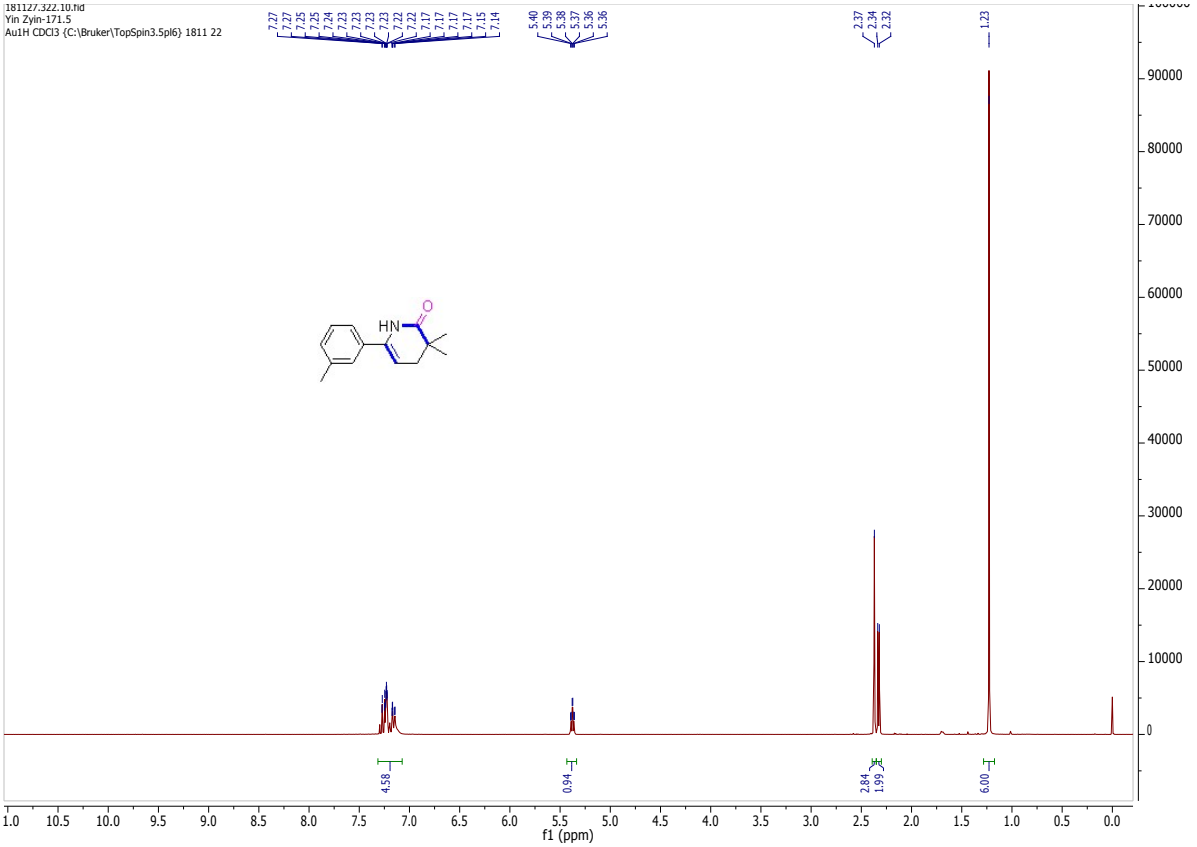

181210.320.11.fid
Yin ZYin-4-194.8
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 20
177.28
138.66
136.13
132.17
129.56
124.57
100.97
77.43 CDCl3
77.01 CDCl3
76.59 CDCl3
36.88
35.94
24.54
21.18
HN
O
f1 (ppm)

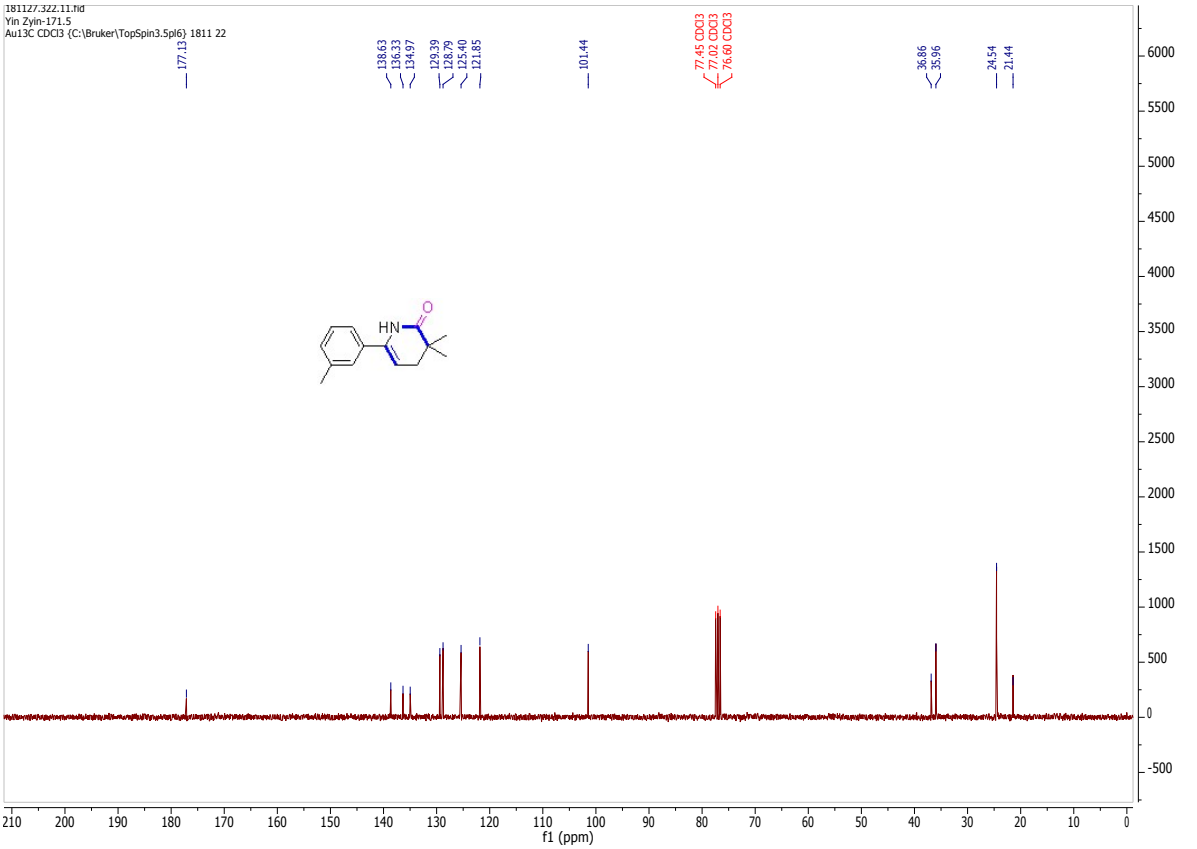

181206.317.10.fid
Wang ZYin-4-188.4
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 17
7.43 7.42 7.42 7.42 7.40 7.40 7.40 7.39 7.36 7.36 7.35 7.33 7.33 7.33 7.32 7.00
5.39 5.38 5.37 5.36 5.35 5.35
2.34 2.32
1.33 1.23
HN
O
t-Bu
1.99 2.03 0.94 1.00 2.05 9.43 6.36
f1 (ppm)

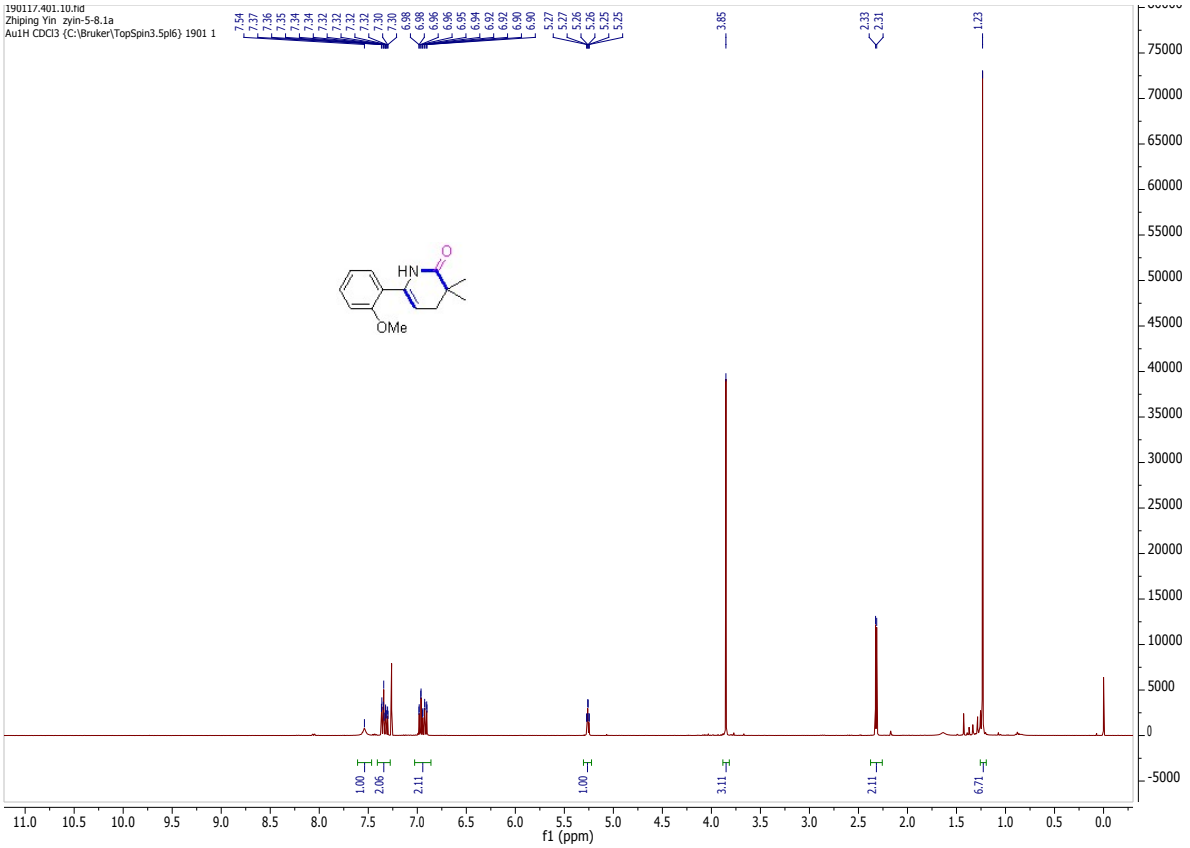

181206.317.11.fid
Wang ZYin-4-188.4
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 17
177.10 151.91 136.04 132.12 125.84 124.35 101.08
77.44 CDCl3
77.02 CDCl3
76.60 CDCl3
36.90 35.96 34.67 31.24 24.53
HN
O
t-Bu
f1 (ppm)

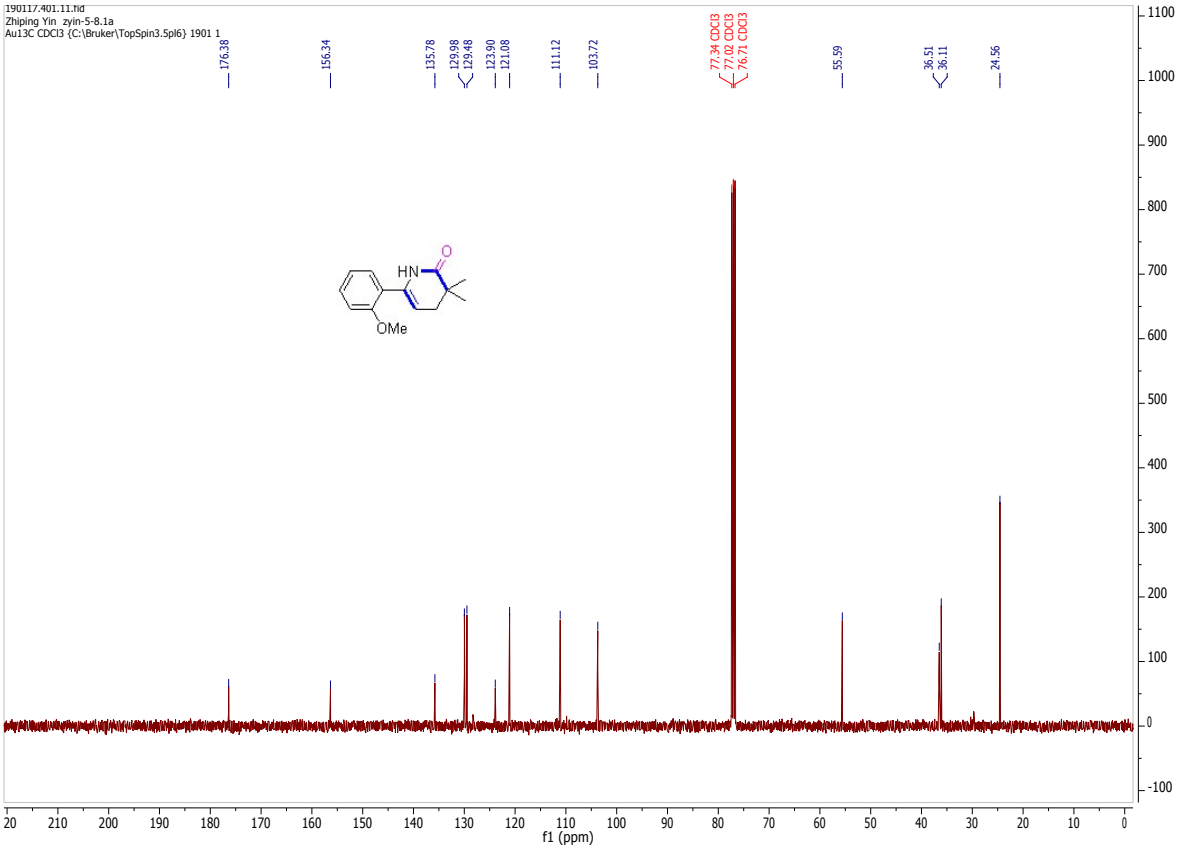

181206.318.10.fid
Wang ZYin-4-188.5
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 18
7.37
7.36
7.35
7.34
7.33
7.32
7.25
6.92
6.91
6.90
6.89
6.88
6.87
5.29
5.29
5.28
5.27
5.26
5.26
3.82
2.32
2.30
1.22
MeO
HN
O
2.10
0.95
2.05
1.00
2.12
6.33
f1 (ppm)

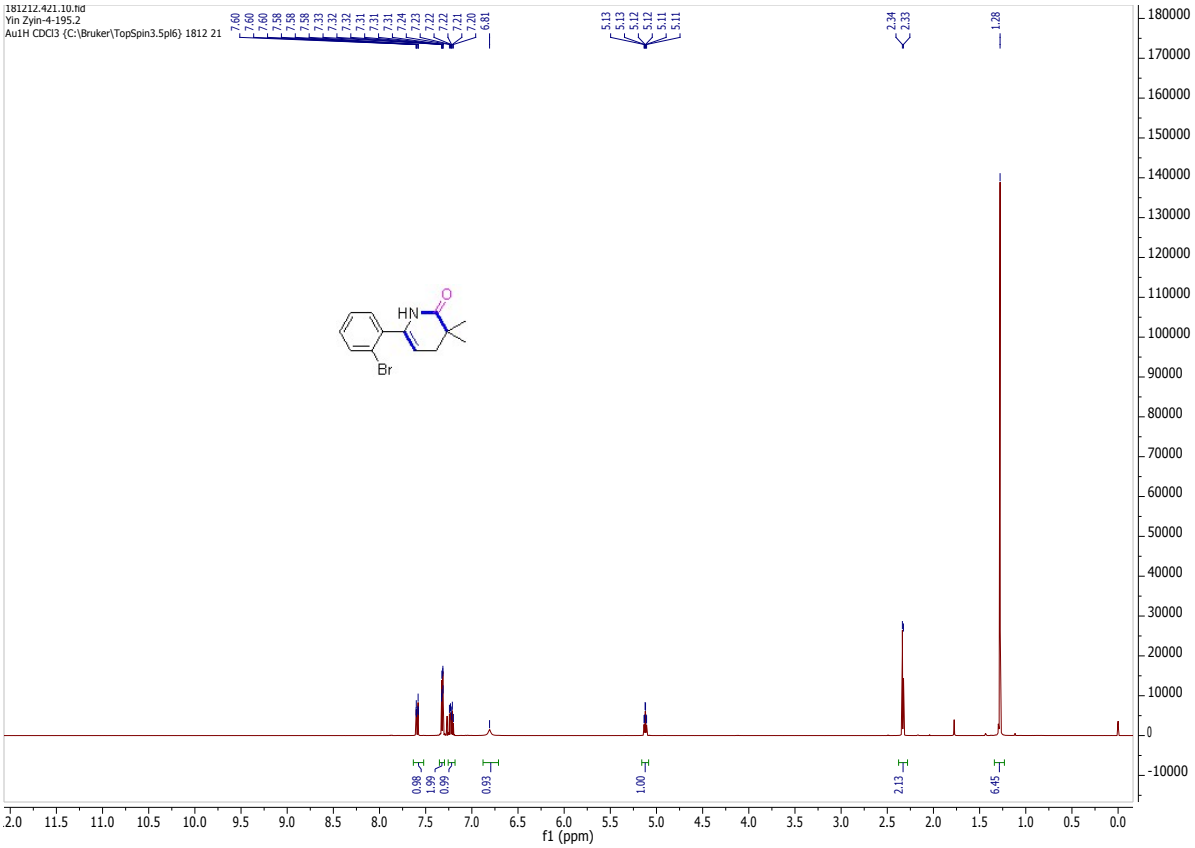

181206.318.11.fid
Wang ZYin-4-188.5
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 18
177.27
159.89
135.92
127.63
126.05
114.19
100.13
77.48 CDCl3
77.05 CDCl3
76.63 CDCl3
55.36
36.87
35.92
24.53
MeO
HN
O
f1 (ppm)

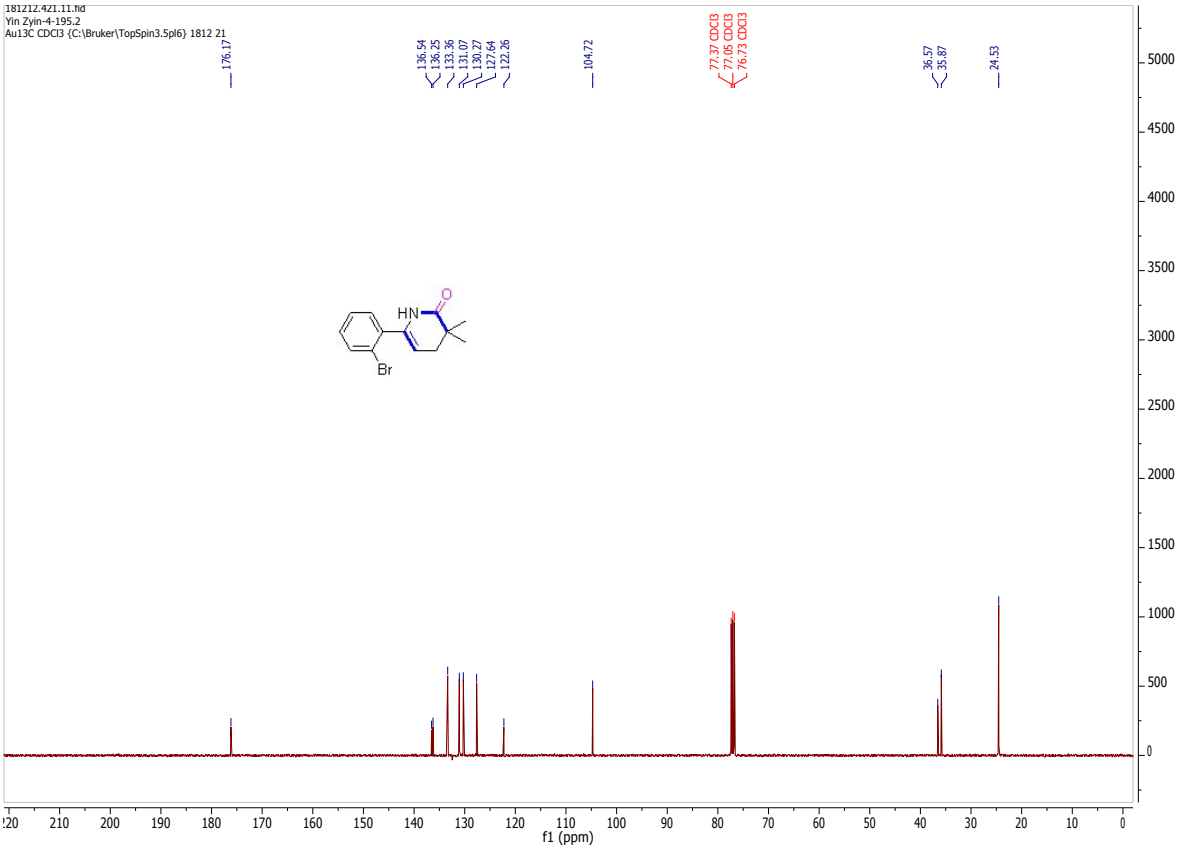

181127.322.10.fid
Yin Zyin-171.5
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 22
7.27
7.27
7.25
7.25
7.24
7.23
7.23
7.23
7.23
7.22
7.22
7.17
7.17
7.17
7.17
7.15
7.14
5.40
5.39
5.38
5.37
5.36
5.36
2.37
2.34
2.32
1.23
HN
O
4.58
0.94
2.84
1.99
6.00
f1 (ppm)

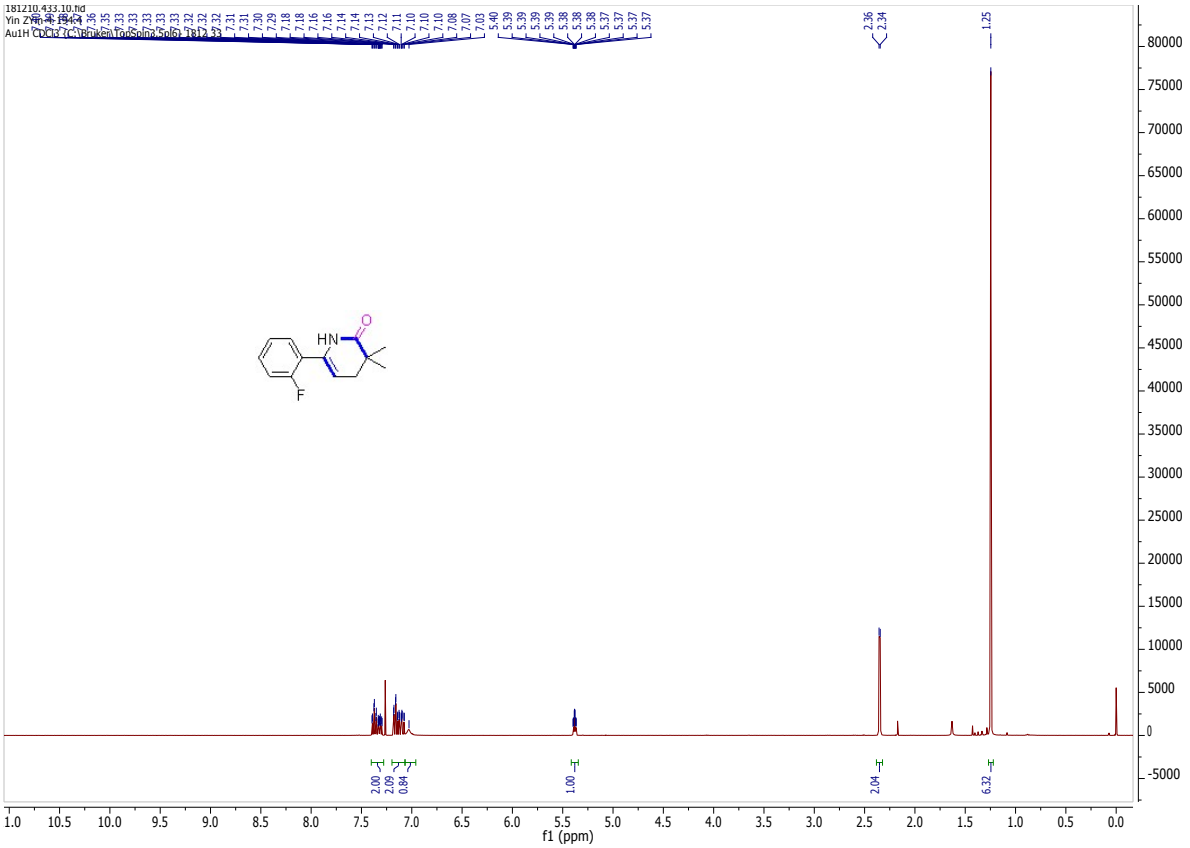

181127.322.11.fid
Yin Zyin-171.5
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 22
177.13
138.63
136.33
134.97
129.39
128.79
125.40
121.85
101.44
77.45 CDCl3
77.02 CDCl3
76.60 CDCl3
36.86
35.96
24.54
21.44
HN
O
f1 (ppm)

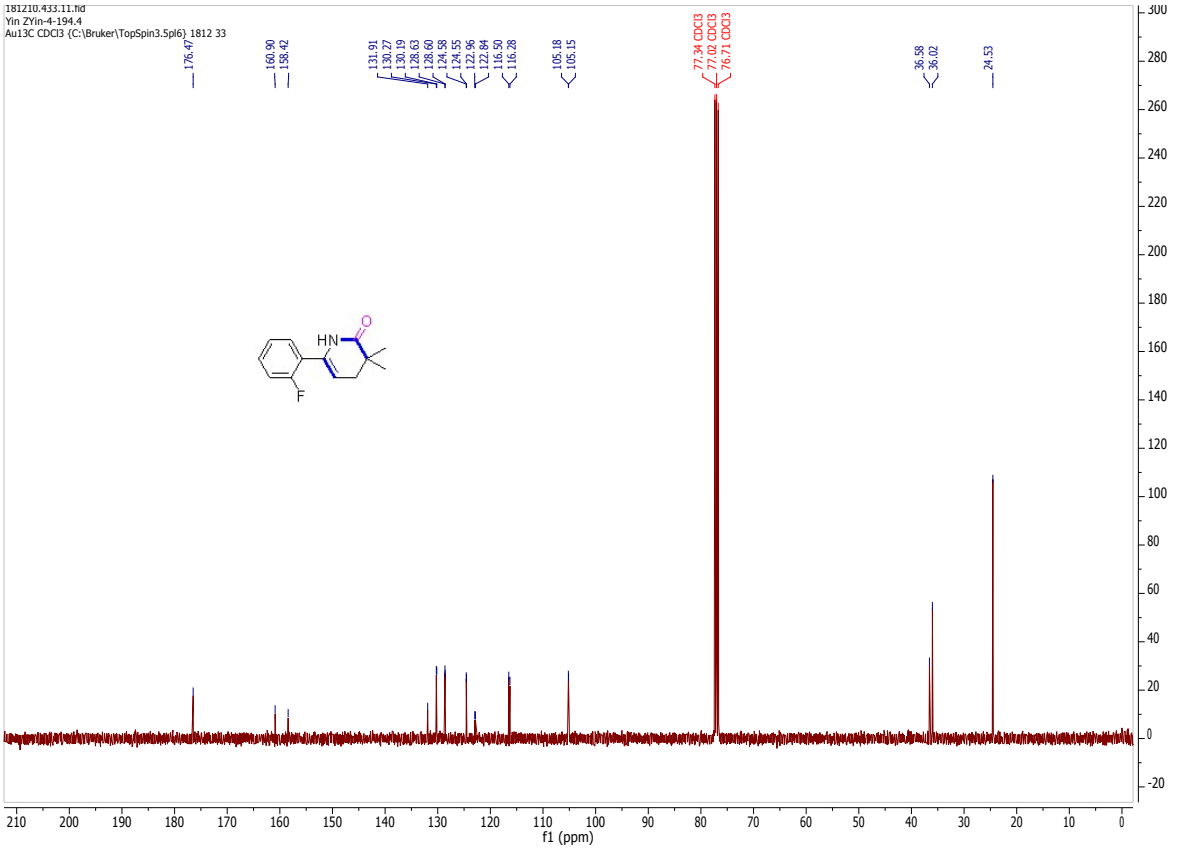

190117.401.10.fid
Zhiping Yin zyin-5-8.1a
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 1
7.54
7.37
7.36
7.35
7.34
7.34
7.32
7.32
7.32
7.32
7.30
7.30
6.98
6.96
6.96
6.95
6.94
6.92
6.92
6.90
6.90
5.27
5.27
5.26
5.26
5.25
5.25
3.85
2.33
2.31
1.23
HN
O
OMe
1.00
2.06
2.11
1.00
3.11
2.11
6.71
f1 (ppm)

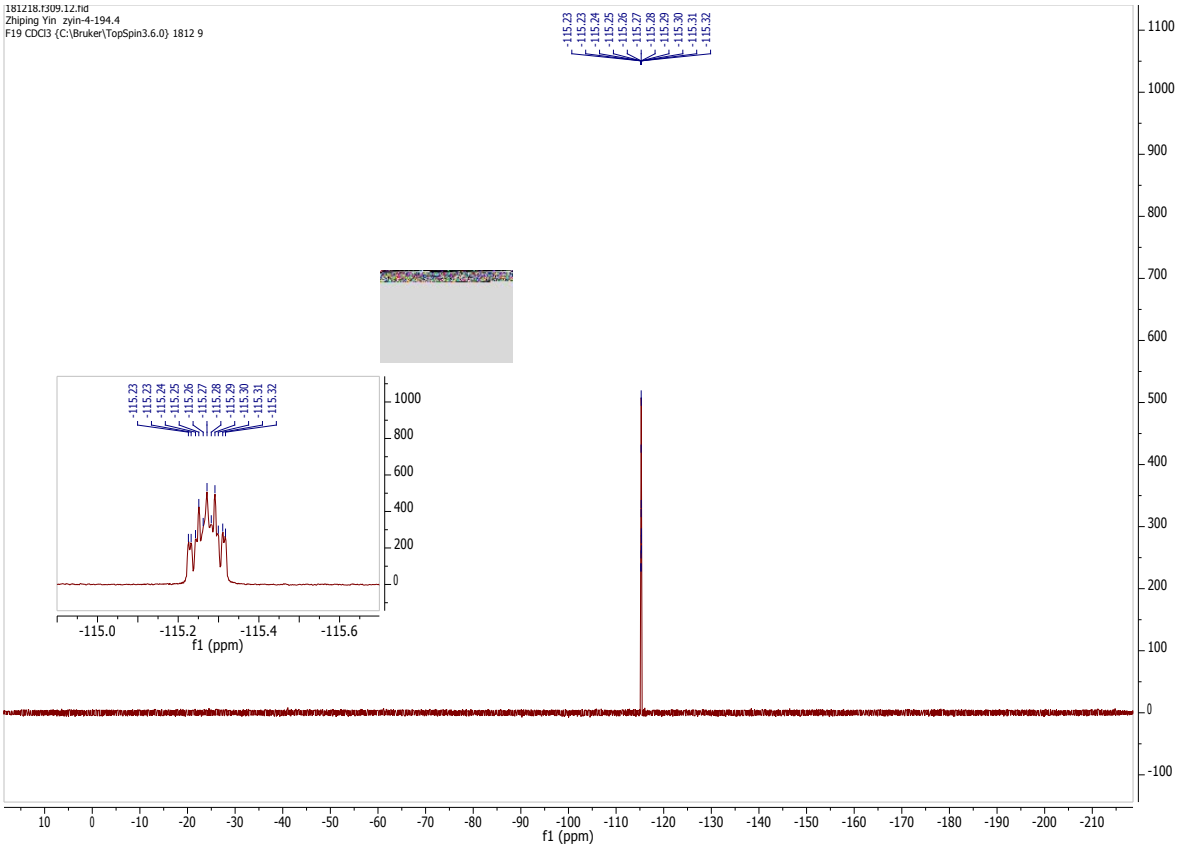

190117.401.11.fid
Zhiping Yin zyin-5-8.1a
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 1
176.38
156.34
135.78
129.98
129.48
123.90
121.08
111.12
103.72
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
55.59
36.51
36.11
24.56
HN
O
OMe
f1 (ppm)

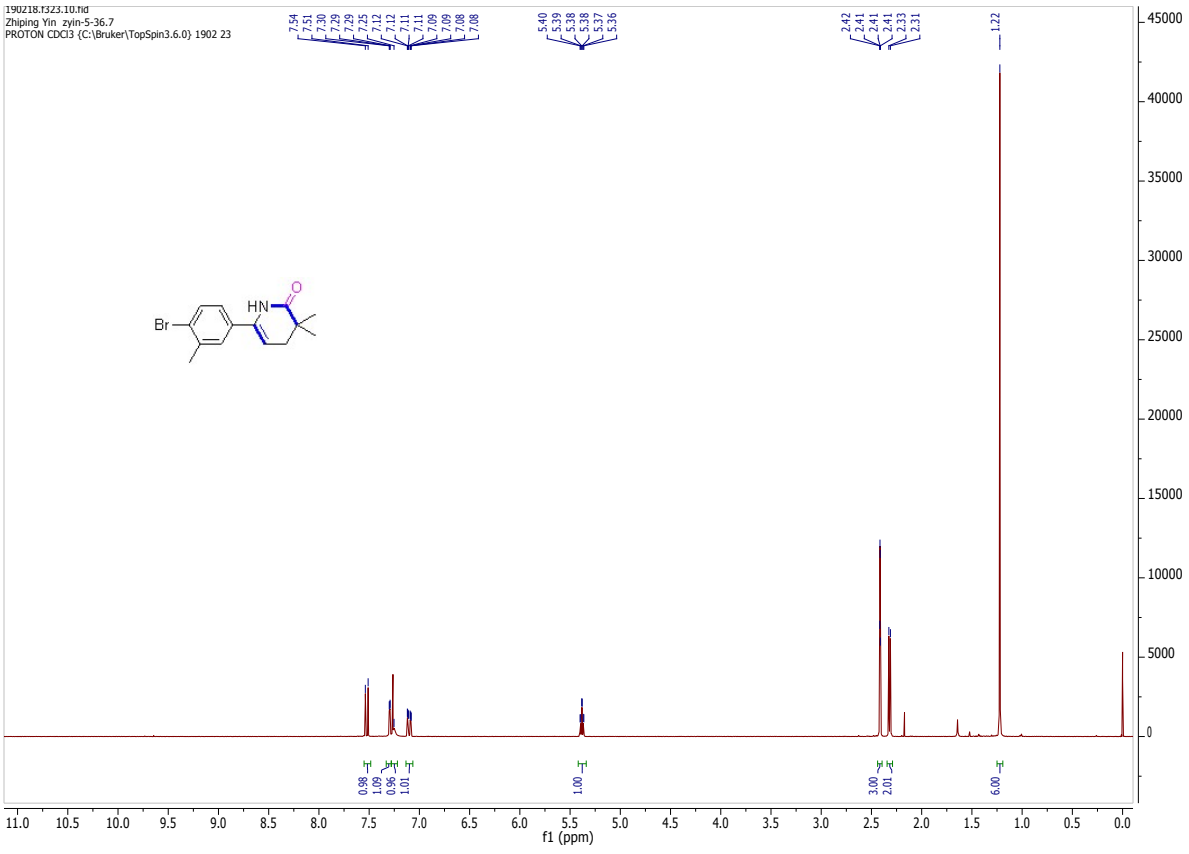

181212.421.10.fid
Yin Zyin-4-195.2
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 21
7.60
7.60
7.60
7.58
7.58
7.58
7.33
7.32
7.31
7.31
7.31
7.24
7.23
7.22
7.22
7.21
7.20
6.81
5.13
5.13
5.12
5.12
5.11
5.11
2.34
2.33
1.28
HN
O
Br
0.98
1.99
0.99
0.93
1.00
2.13
6.45
f1 (ppm)

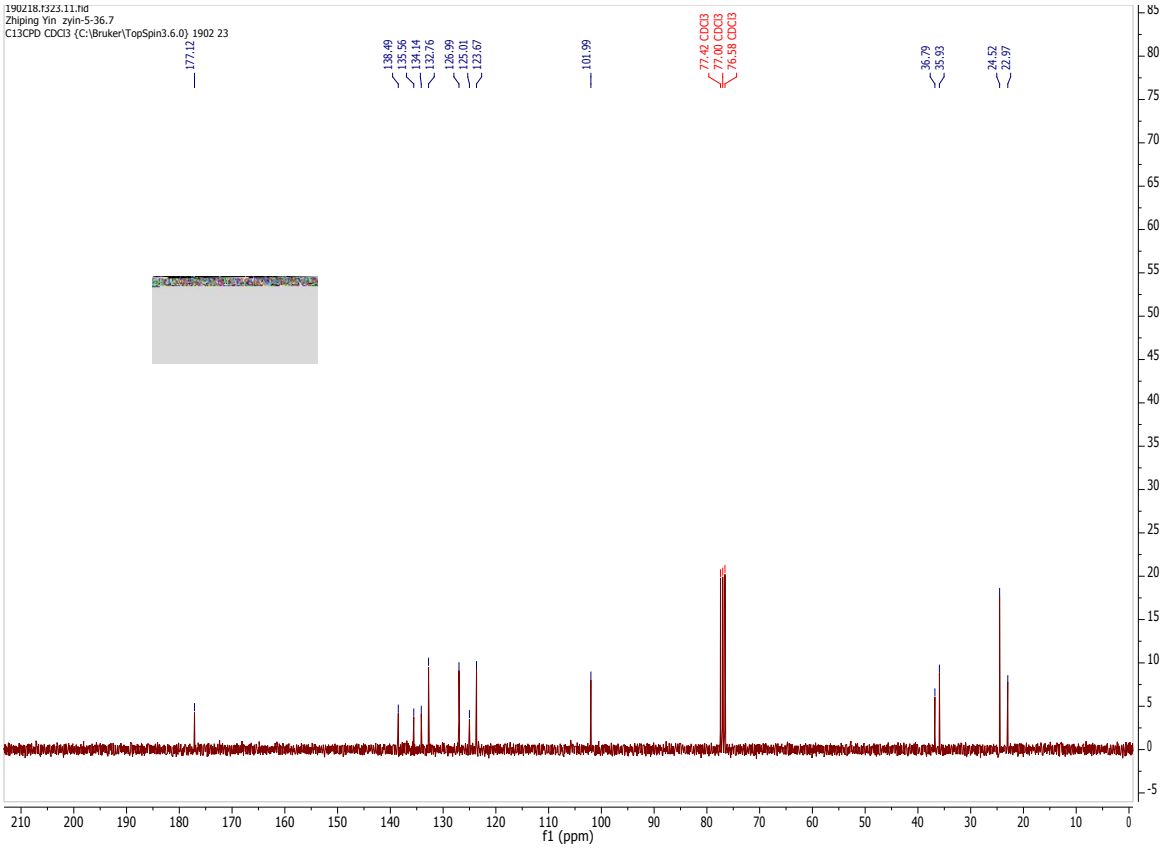

181212.421.11.fid
Yin Zyin-4-195.2
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 21
176.17
136.54
136.25
133.36
131.07
130.27
127.64
122.26
104.72
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
36.57
35.87
24.53
HN
O
Br
f1 (ppm)

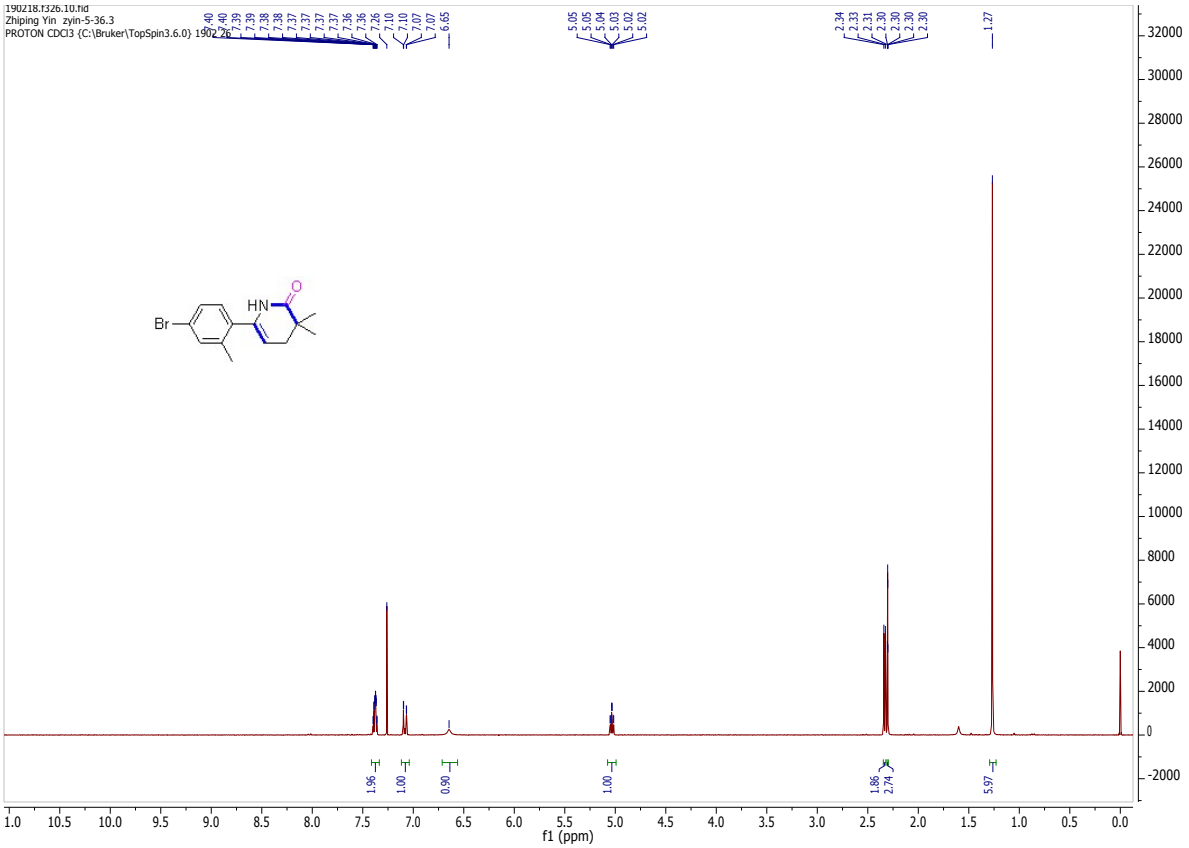

181210.433.10.fid
Yin ZYin-4-194.4
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 33
2.36
2.34
1.25
HN
O
F
2.00
2.09
0.84
1.00
2.04
6.32
f1 (ppm)

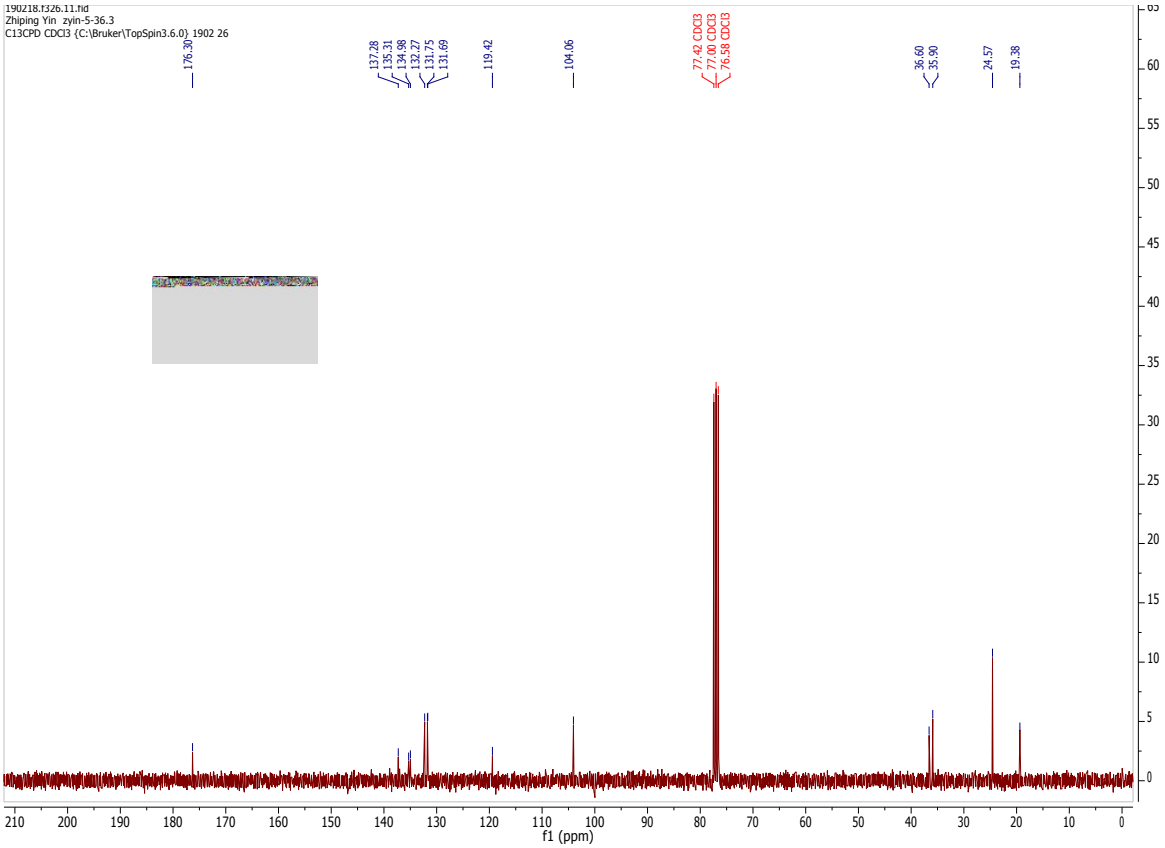

181210.433.11.fid
Yin ZYin-4-194.4
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1812 33
176.47
160.90
158.42
131.91
130.27
130.19
128.63
128.60
124.58
124.55
122.96
122.84
116.50
116.28
105.18
105.15
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
36.58
36.02
24.53
HN
O
F
f1 (ppm)

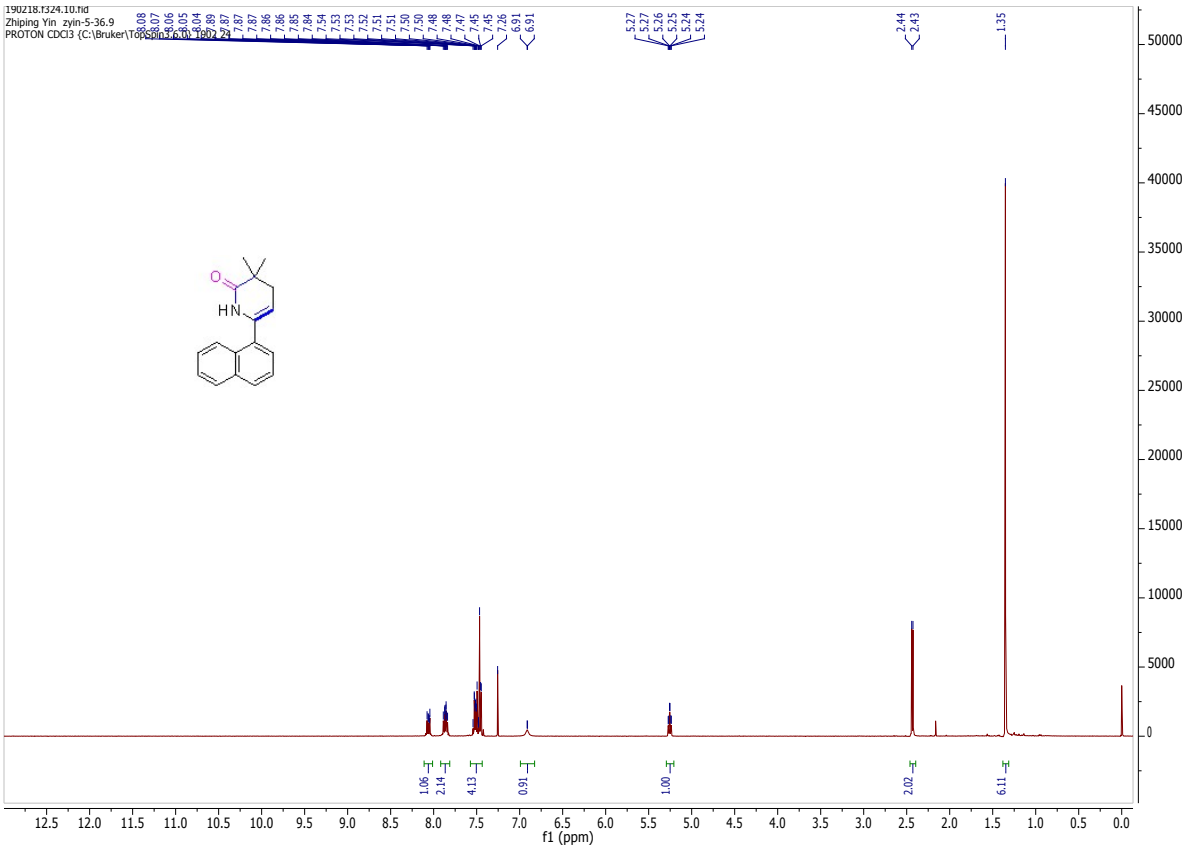

181218.t309.12.fid
Zhiping Yin zyin-4-194.4
F19 CDCl3 {C:\Bruker\TopSpin3.6.0} 1812 9
-115.23
-115.23
-115.24
-115.25
-115.26
-115.27
-115.28
-115.29
-115.30
-115.31
-115.32
f1 (ppm)

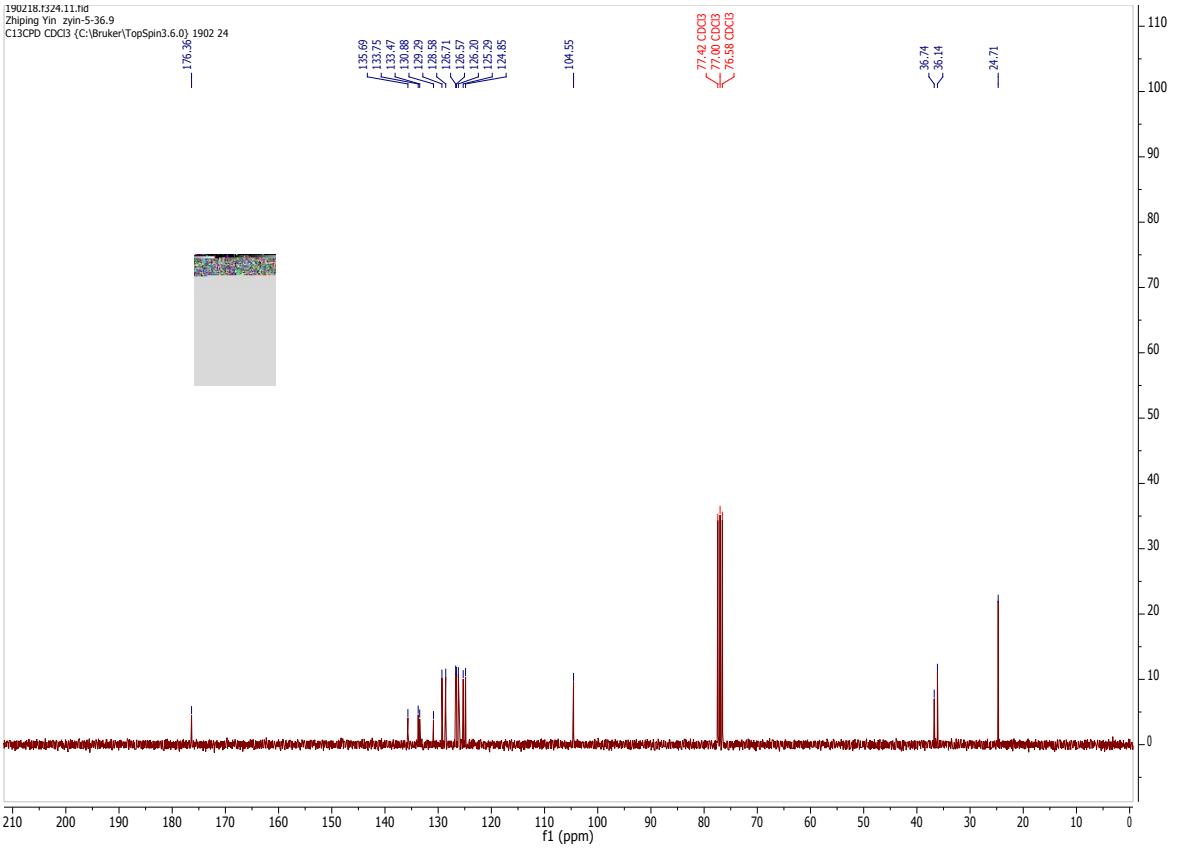

190218.t323.10.fid
Zhiping Yin zyin-5-36.7
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 23
7.54
7.51
7.30
7.29
7.29
7.25
7.12
7.12
7.11
7.11
7.09
7.09
7.08
7.08
5.40
5.39
5.38
5.38
5.37
5.36
2.42
2.41
2.41
2.41
2.33
2.31
1.22
Br
HN
O
0.98
1.09
0.96
1.01
1.00
3.00
2.01
6.00
f1 (ppm)

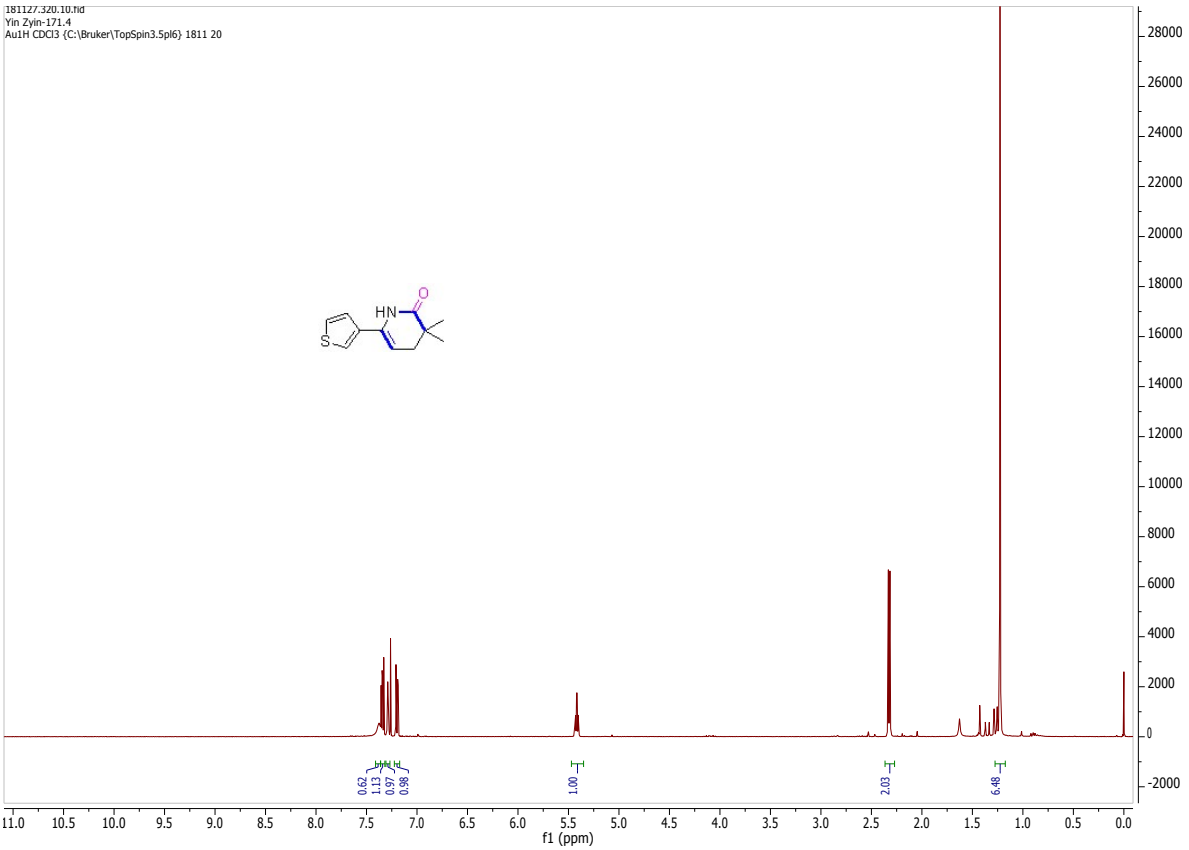

190218.t323.11.fid
Zhiping Yin zyin-5-36.7
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 23
177.12
138.49
135.56
134.14
132.76
126.99
125.01
123.67
101.99
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
36.79
35.93
24.52
22.97
f1 (ppm)

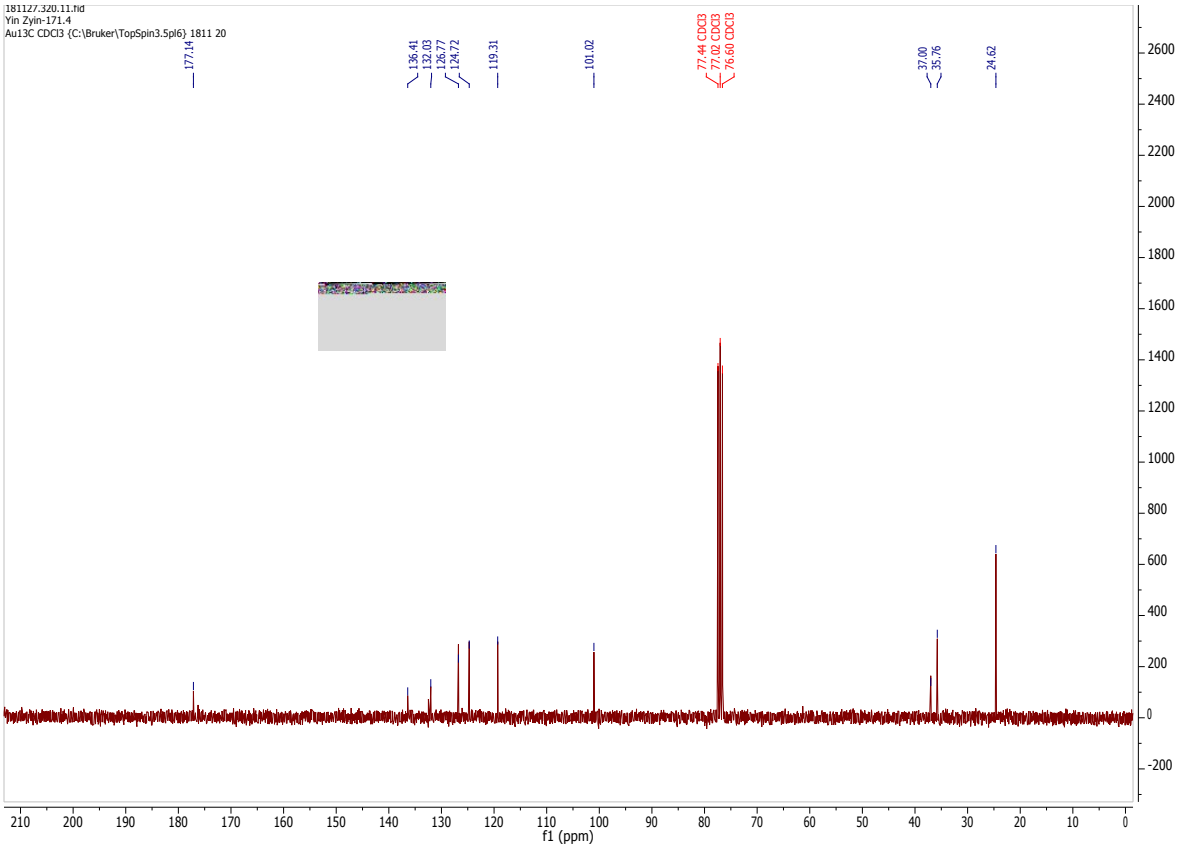

190218.t326.10.fid
Zhiping Yin zyin-5-36.3
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 26
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.37
7.37
7.37
7.36
7.36
7.26
7.10
7.10
7.07
7.07
6.65
5.05
5.05
5.04
5.03
5.02
5.02
2.34
2.33
2.31
2.30
2.30
2.30
2.30
1.27
Br
HN
O
1.96
1.00
0.90
1.00
1.86
2.74
5.97
f1 (ppm)

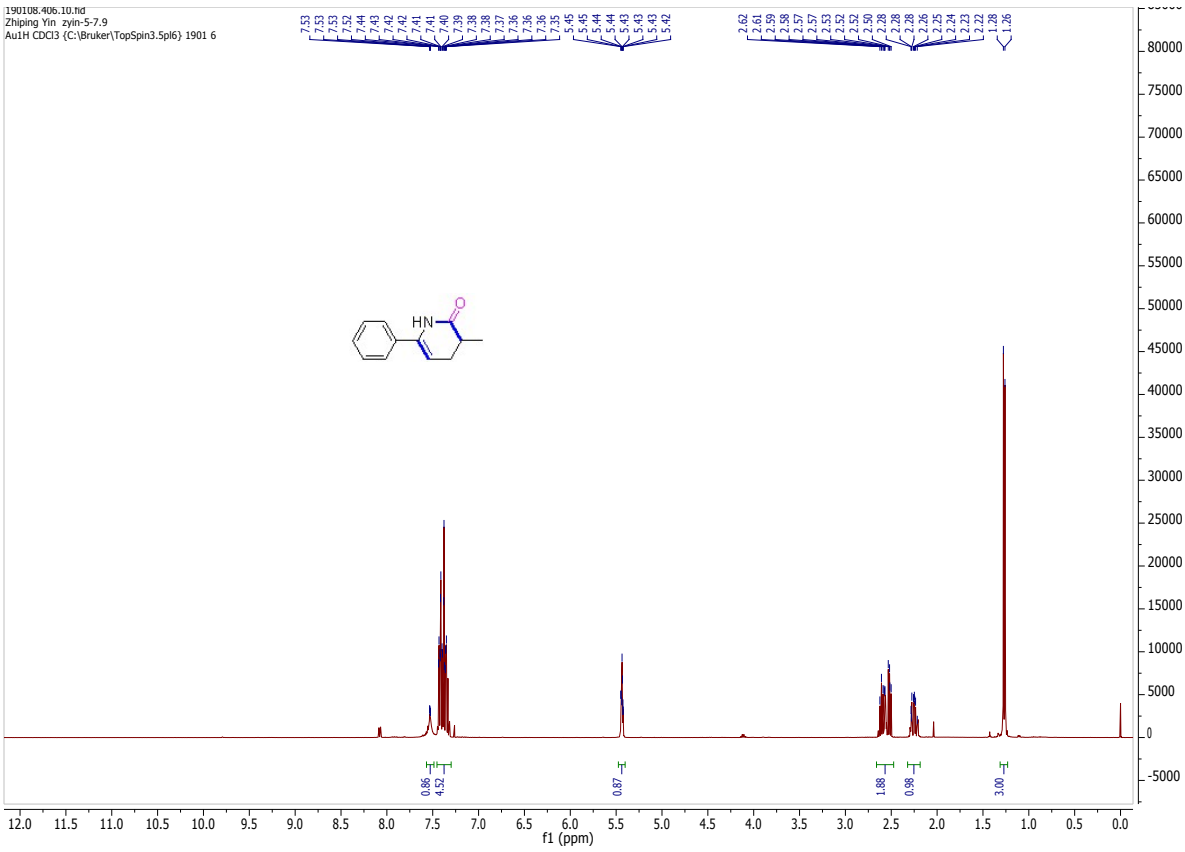

190218.t326.11.fid
Zhiping Yin zyin-5-36.3
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 26
176.30
137.28
135.31
134.98
132.27
131.75
131.69
119.42
104.06
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
36.60
35.90
24.57
19.38
f1 (ppm)

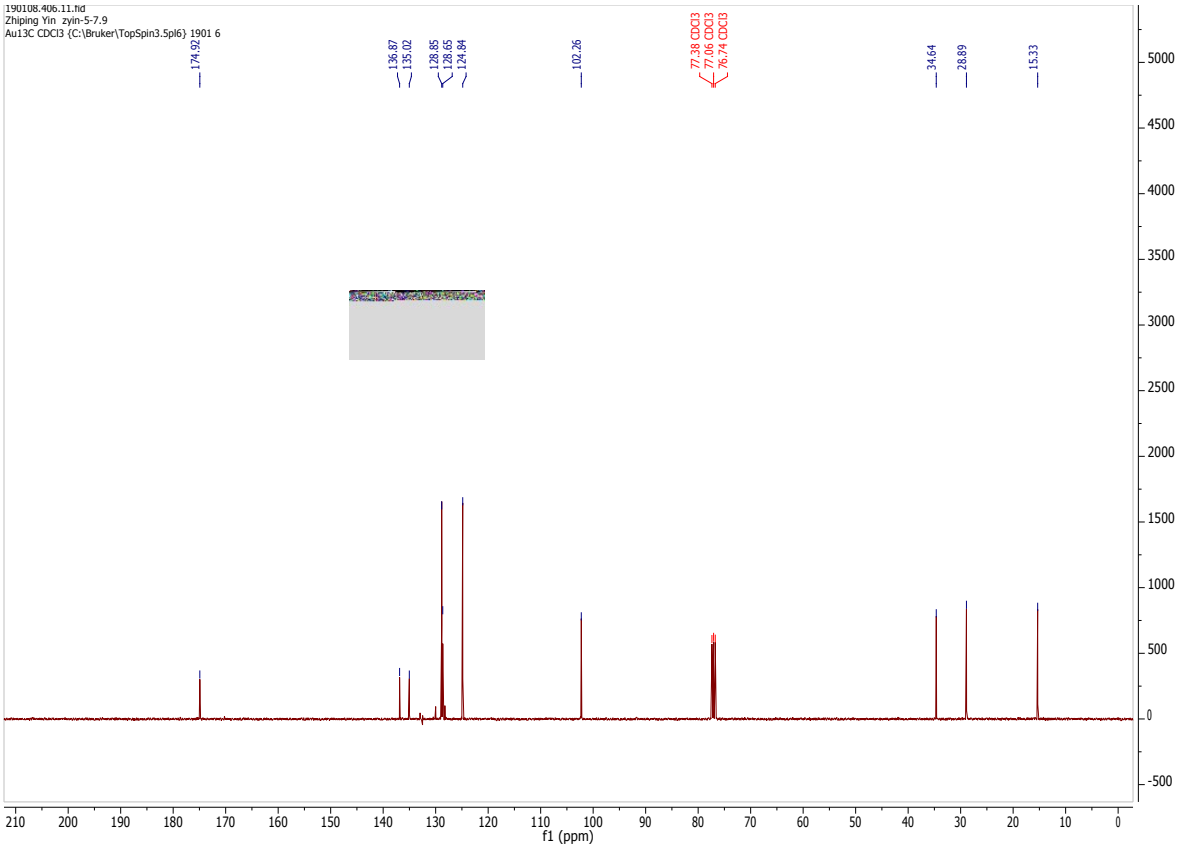

190218.t324.10.fid
Zhiping Yin zyin-5-36.9
PROTON CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 24
8.08
8.07
8.06
8.05
8.04
7.89
7.87
7.87
7.87
7.86
7.86
7.85
7.84
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.48
7.48
7.47
7.45
7.45
7.26
6.91
6.91
5.27
5.27
5.26
5.25
5.24
5.24
2.44
2.43
1.35
O
HN
1.06
2.14
4.13
0.91
1.00
2.02
6.11
f1 (ppm)


190218.t324.11.fid
Zhiping Yin zyin-5-36.9
C13CPD CDCl3 {C:\Bruker\TopSpin3.6.0} 1902 24
176.36
135.69
133.75
133.47
130.88
129.29
128.58
126.71
126.57
126.20
125.29
124.85
104.55
77.42 CDCl3
77.00 CDCl3
76.58 CDCl3
36.74
36.14
24.71
f1 (ppm)


181127.320.10.fid
Yin Zyin-171.4
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 20
HN
O
S
0.62
1.13
0.97
0.98
1.00
2.03
6.48
f1 (ppm)


181127.320.11.fid
Yin Zyin-171.4
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1811 20
177.14
136.41
132.03
126.77
124.72
119.31
101.02
77.44 CDCl3
77.02 CDCl3
76.60 CDCl3
37.00
35.76
24.62
f1 (ppm)


190108.406.10.fid
Zhiping Yin zyin-5-7.9
Au1H CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 6
HN
O
0.86
4.52
0.87
1.88
0.98
3.00
f1 (ppm)


190108.406.11.fid
Zhiping Yin zyin-5-7.9
Au13C CDCl3 {C:\Bruker\TopSpin3.5pl6} 1901 6
174.92
136.87
135.02
128.85
128.65
124.84
102.26
77.38 CDCl3
77.06 CDCl3
76.74 CDCl3
34.64
28.89
15.33
f1 (ppm)