Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Formic acid as hydrogen source for the iridium-catalyzed reductive amination of levulinic acid and 2-formylbenzoic acid

Shengdong Wang,[a] Haiyun Huang,[a] Christian Bruneau,[a] CédricFischmeister*[a]

General remarks

Levulinic acid (98%), formic acid, formyl benzoic acid and 2,2'-dipyridylamine (98%) were purchased from Sigma-Aldrich. Amines were purchased from commercial sources and used as received. Solvents (water) were HPLC grade and used as received. **Ir1, Ir2, Ir3, Ir4** were synthesized according to reported procedures from our group.[1, 3] NMR spectra were recorded on a Bruker Avance I 300 MHz or Avance III 400 MHz spectrometers. Chemical shifts are given as ppm vs TMS by reference to the residual solvent signal.

General procedure for the reductive amination of LA

Levulinic acid (2 mmol, 0.23 g), formic acid (4 mmol, 0,18 g), amine (2.2 mmol), catalyst (0.01-0.05 mol %) and 2 mL of water were added to a heavy walled Schlenk tube* equipped with a Teflon screw cap. The mixture was stirred at the appropriate temperature for the desired time. Volatile compounds were removed under vacuum. The crude mixtures were analysed by ^{1}H NMR and purified by column chromatography using petroleum ether and ethyl acetate with 1% triethylamine as eluent.

General procedure for the reductive amination of 2-formylbenzoic acid

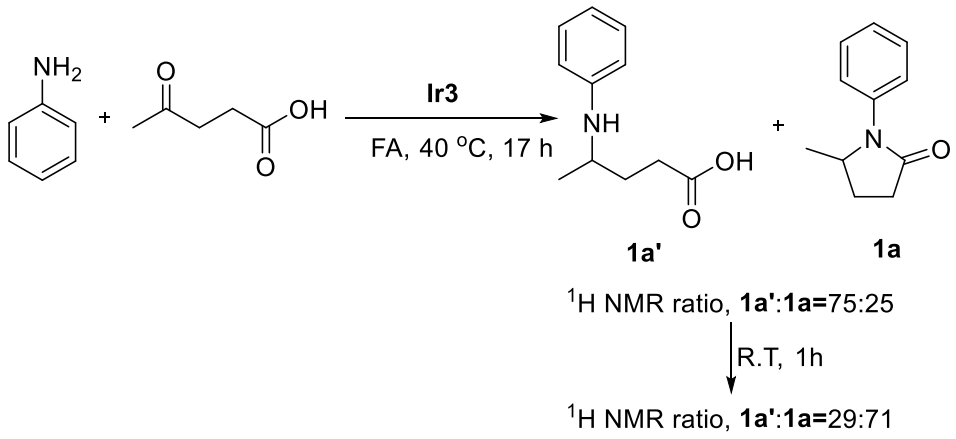
2-formylbenzoic acid (2 mmol, 0.30 g), formic acid (4 mmol, 0.18 g), amine (2.2 mmol), **Ir1** (0.05mol%) and 2 mL of water were added to heavy walled Schlenk tube* equipped with a Teflon screw cap. The mixture was stirred at the appropriate temperature for desired time. Volatile compounds were removed under vacuum. The crude mixtures were analysed by ^{1}H NMR. Then the crude product was purified by column chromatography using petroleum ether and ethyl acetate with 1% triethylamine as eluent.

⚠ * For safety reasons, the reactions were conducted in thick wall Schlenk tubes of small size as the internal pressure increases due to formic acid dehydrogenation. Tube size: H = 11 cm, i.d. = 1.5 cm, glass thickness = 2.7 mm.

General procedure for the sequential dehydration/reductive amination sequence:

Glucose (0.45 g, 2.5 mmol, 1 equiv.) was loaded into a 20 mL autoclave, and H_2SO_4 (2.5 mL, 0.5 m) was added. The autoclave was quickly heated to 170°C, and vigorously stirred for 2 h at the same temperature. The reaction mixture was allowed to cool to room temperature. Insoluble by-products were removed by filtration. The filtrate was transferred into a 20 mL reactor containing the desired amount of catalyst **Ir1** (0.05 mol% vs glucose) and aniline (1.1 equiv.). The reactor was heated in an oil bath at 60 °C for 16 h and allowed to cool to r. t. The reaction medium was extracted with dichloromethane (3x5 mL). The combined organic phases were evaporated to dryness and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (3:1 v/v) as eluent.

Intermediate compounds



LA (2 mmol), aniline (2 mmol), FA (4 mmol), **Ir3** (0.05 mol%) and 2 mL water were added to a heavy walled Schlenk tube equipped with a Teflon screw cap and stirred for 17 h at 40 °C. Water was evaporated under vacuum and the crude mixture was analysed by ^{1}H NMR. As shown in Figure 1, the ratio of the desired product and secondary amine was 25:75. Further stirring this neat mixture for one hour at r.t resulted in a reversed ratio of 71:29 as shown in figure 2.

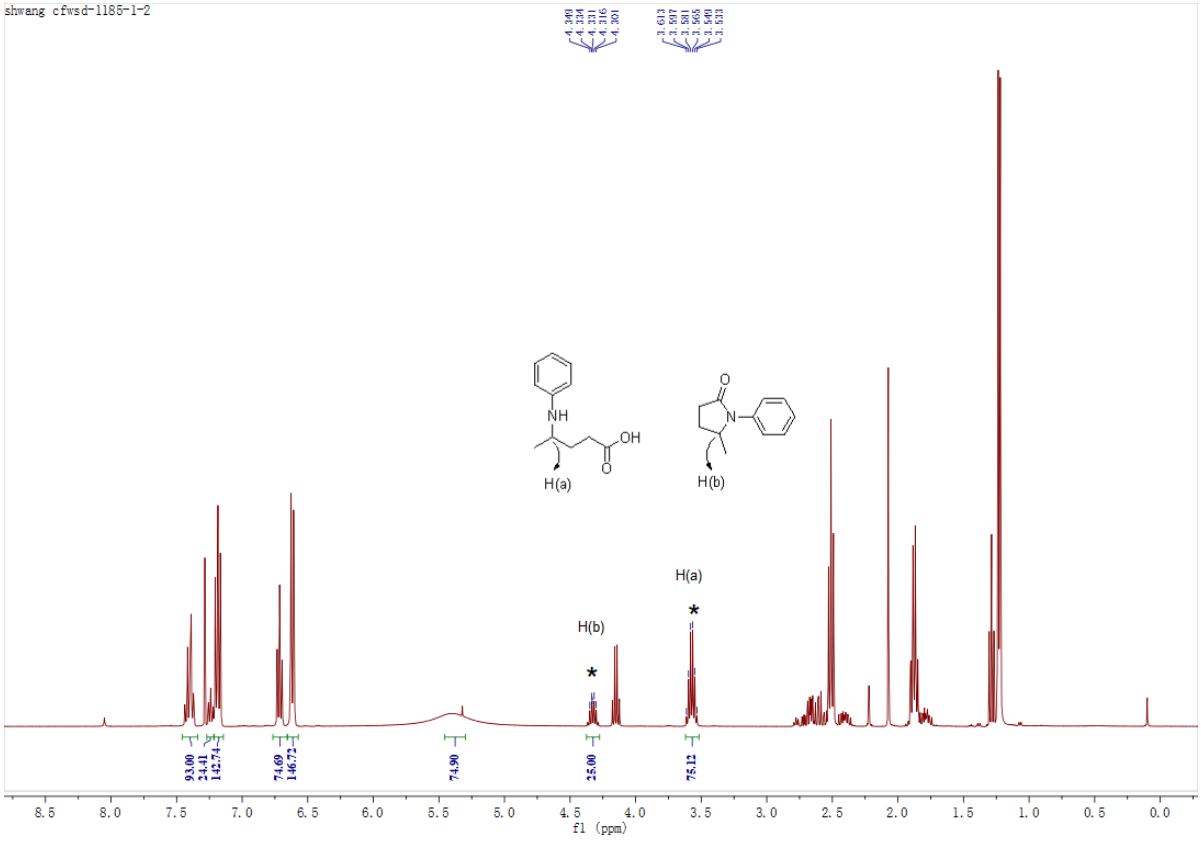


Figure 1. ^{1}H NMR of crude mixture after the reaction.

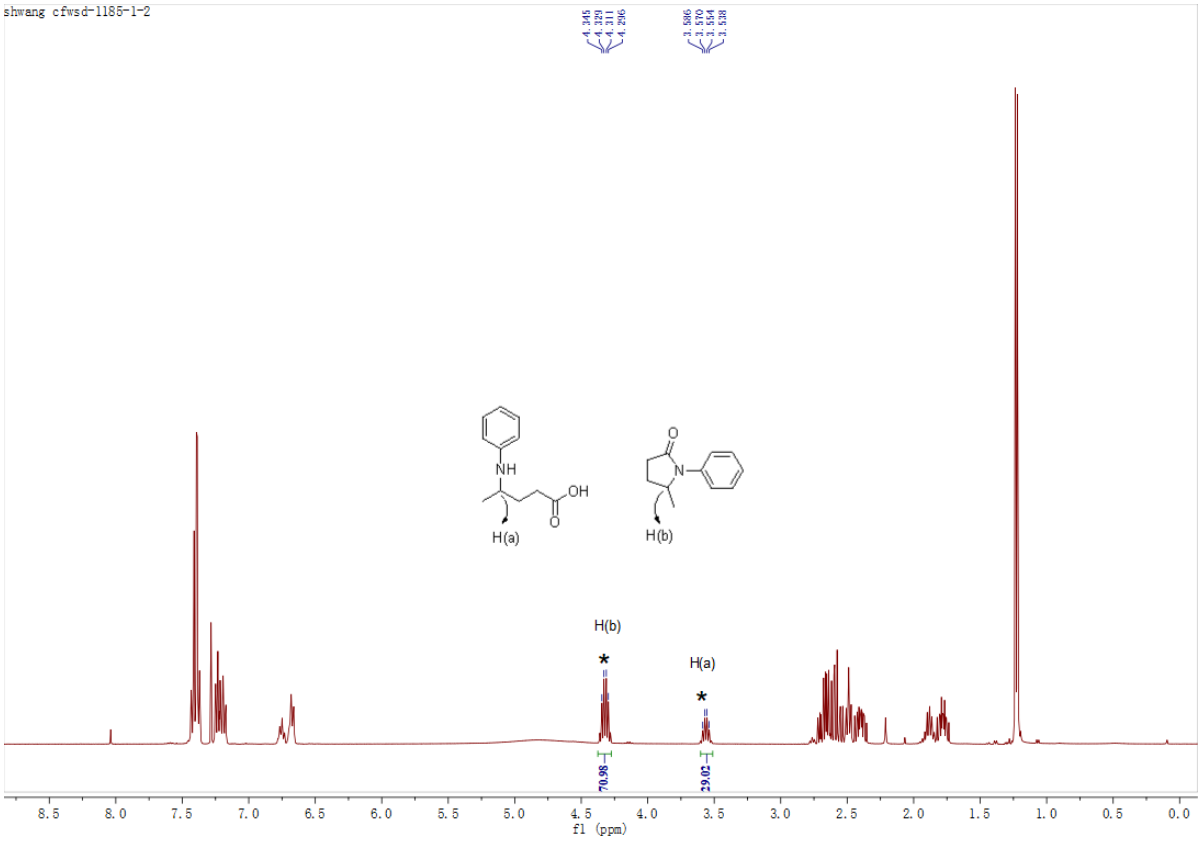
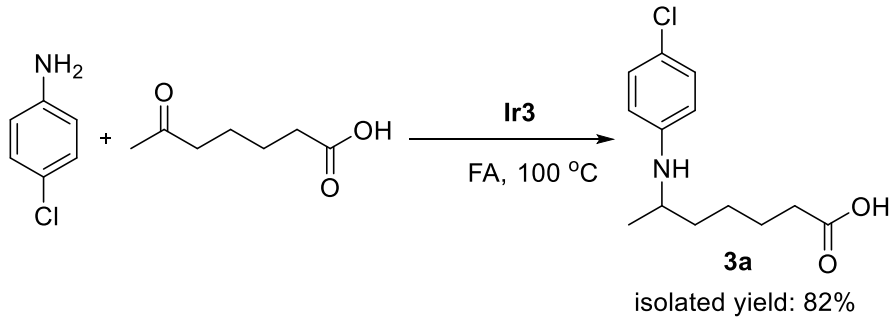


Figure 2. ^{1}H NMR of crude mixture keep for 1h.



6-Oxoheptanoic acid (2 mmol), 4-chloroaniline (2 mmol), FA (4 mmol), **Ir3** (0.05 mol%) and 2 mL water were added to a heavy walled Schlenk tube equipped with a Teflon screw cap and stirred for 17 h at 100 °C. After removal of the solvent, the crude was purified by column chromatography using petroleum ether and ethyl acetate with 1% triethylamine as eluent. **3a** was isolated in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 11.6 Hz, 2H), 6.48 (d, J = 11.6 Hz, 2H), 5.98 (br, 1H), 3.44-3.38 (m, 1H), 2.36 (t, J = 10.0 Hz, 2H), 1.67-1.40 (m, 6H), 1.15 (d, J = 8.4 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 146.0, 129.0, 121.5, 114.3, 48.6, 36.6, 33.8, 25.5, 24.6, 20.6.

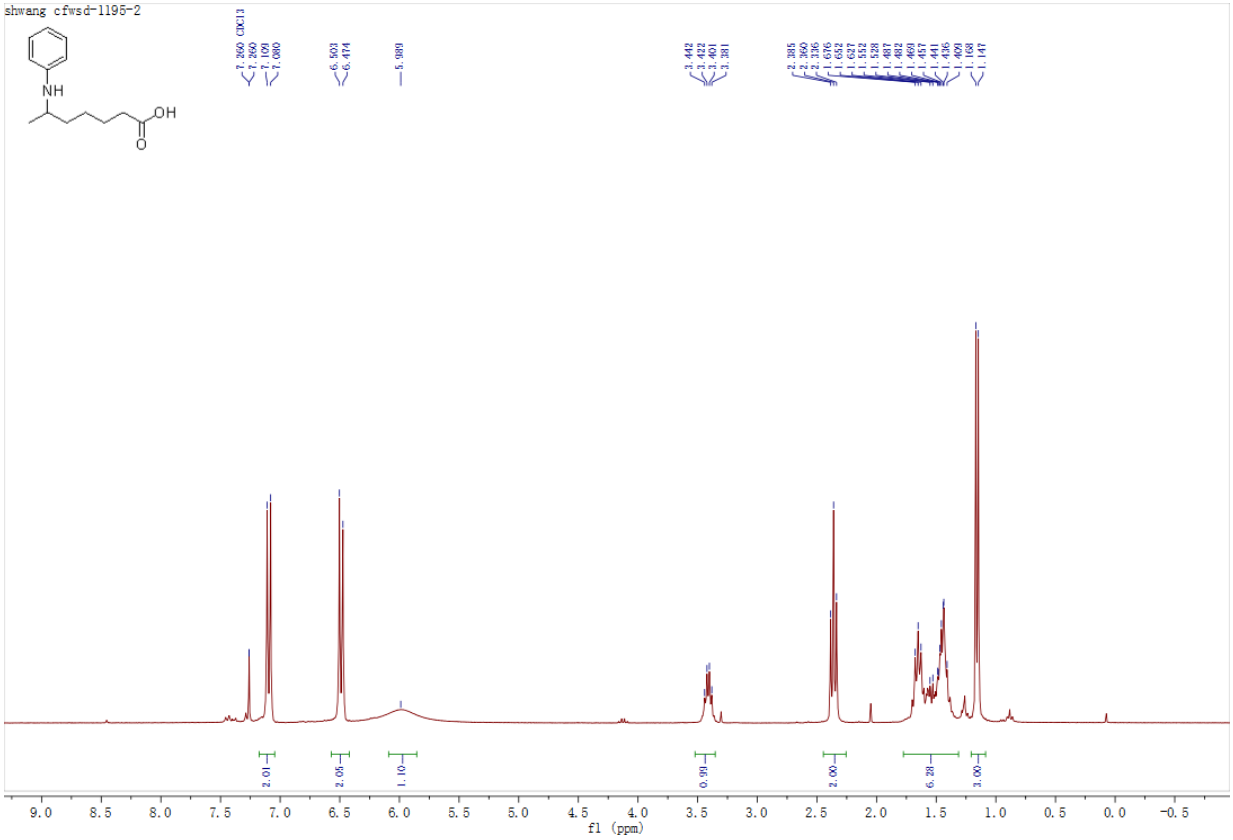


Figure 3. ^{1}H NMR of **3a**.

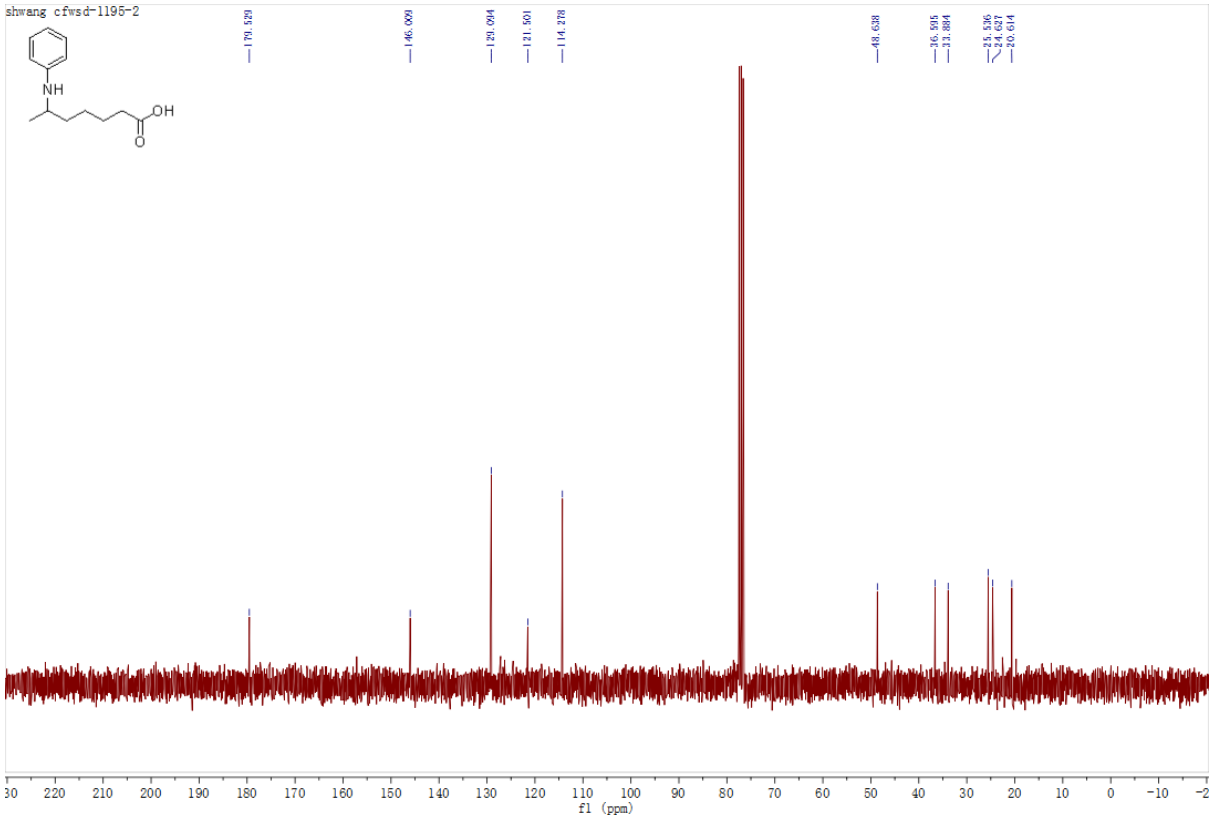
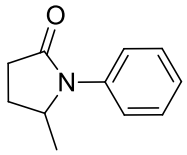


Figure 4. ^{13}C NMR of **3a**

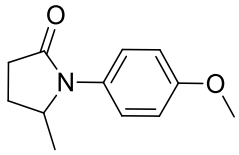
Synthesis of pyrrolidinone derivatives

1-phenyl-5-Methylpyrrolidin-2-one **1a**[2]



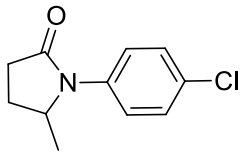
97% yield; white solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.33 (m, 4H, CH), 7.19-7.15 (m, 1H, CH), 4.30-4.22 (m, 1H, CH), 2.63-2.45 (m, 2H, CH_2), 2.35-2.31 (m, 1H, CH), 1.74-1.70 (m, 1H, CH), 1.17 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ174.2, 137.5, 128.9, 125.7, 124.0, 55.6, 31.3, 26.7, 20.1.

1-(4-methoxyphenyl)-5-methylpyrrolidin-2-one **1b**[2]



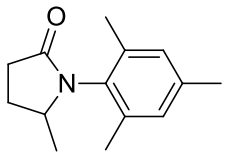
92% yield; yellow solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, $^{3}J_{H-H}$=8.8 Hz, 2H, CH), 6.90 (d, $^{3}J_{H-H}$=8.8 Hz, 2H, CH), 4.19-4.13 (m, 1H, CH), 3.78 (s, 3H, CH_3), 2.59-2.46 (m, 2H, CH_2), 2.37-2.32 (m, 1H, CH_2), 1.77-1.63 (m, 1H, CH_2), 1.16 (d, $^{3}J_{H-H}$=6.0 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 157.8, 130.4, 126.2, 114.4, 56.2, 55.5, 31.2, 26.9, 20.3.

1-(4-chlorophenyl)-5-methylpyrrolidin-2-one **1c**[2]



85% yield; yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.23 (m, 4H, CH), 4.22-4.14 (m, 1H, CH), 2.57-2.49 (m, 1H, CH_2), 2.46-2.38 (m, 1H, CH_2), 2.31-2.23 (m, 1H, CH_2), 1.69-1.60 (m, 1H, CH_2), 1.10 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ174.0, 136.0, 130.5, 128.7, 124.7, 55.2, 31.0, 26.3, 19.7.

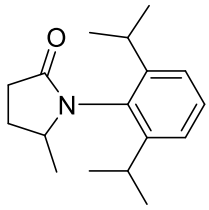
1-mesityl-5-methylpyrrolidin-2-one **1d**[2]



88% yield; colorless oil;

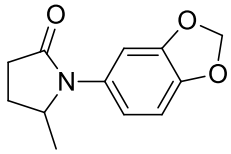
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H, CH), 6.87 (s, 1H, CH), 4.04-3.96 (m, 1H, CH), 2.67-2.46 (m, 2H, CH_2), 2.42-2.34 (m, 1H, CH_2), 2.24 (s, 3H, CH_3), 2.15 (s, 3H), 2.11 (s, 3H, CH_3), 1.81-1.76 (m, 1H, CH), 1.06 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 137.4, 136.9, 135.0, 131.9, 129.3, 129.2, 56.1, 30.6, 28.2, 20.8, 19.5, 18.5, 18.0.

1-(2,6-diisopropylphenyl)-5-methylpyrrolidin-2-one **1e**[2]



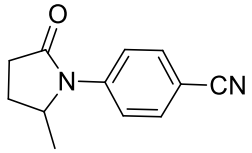
75% yield; white solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.29 (m, 1H, CH), 7.21-7.16 (m, 2H, CH), 3.97-3.89 (m, 1H, CH), 2.99-2.96 (m, 1H, CH), 2.80-2.76 (m, 1H, CH), 2.63-2.57 (m, 2H, CH_2), 2.43-2.41 (m, 1H, CH), 1.85-1.80 (m, 1H, CH), 1.23-1.17 (m, 12H, CH_3), 1.09 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ175.3, 148.1, 146.5, 131.7, 128.8, 124.2, 124.1, 57.9, 30.9, 29.0, 28.9, 28.5, 25.4, 24.8, 24.2, 23.5, 19.8.

1-(benzo[d][1,3]dioxol-5-yl)-5-methylpyrrolidin-2-**one 1f**[2]



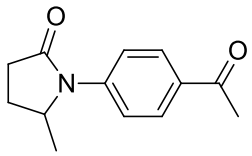
91% yield; yellow solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (d, $^{3}J_{H-H}$=2 .0 Hz, 1H, CH), 6.78 (d, $^{3}J_{H-H}$=8.0 Hz, 1H, CH), 6.70-6.67 (dd, $^{4}J_{H-H}$=2.0 Hz, $^{3}J_{H-H}$=8.0 Hz 1H, CH), 5.94 (s, 2H, CH_2), 4.16-4.07 (m, 1H, CH), 2.61-2.45 (m, 2H, CH_2), 2.37-2.28 (m, 1H, CH), 1.75-1.66 (m, 1H, CH), 1.15 (d, $^{3}J_{H-H}$ =6.0 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ174.4, 148.0, 145.9, 131.5, 118.2, 108.3, 106.8, 101.5, 56.5, 31.2, 26.8, 20.3.

4-(2-methyl-5-oxopyrrolidin-1-yl)benzonitrile **1g**[2]



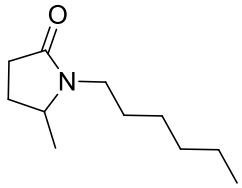
83% yield; white solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.63 (m, 4H, CH), 4.37-4.29 (m, 1H, CH), 2.64-2.56 (m, 1H, CH), 2.50-2.41 (m, 1H, CH), 2.35-2.25 (m, 1H, CH), 1.75-1.67 (m, 1H, CH), 1.18 (d, $^{3}J_{H-H}$= 6.0 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 141.7, 132.7, 122.0, 118.5, 107.4, 54.6, 31.2, 26.0, 19.4.

1-(4-acetylphenyl)-5-methylpyrrolidin-2-**one 1h**[2]



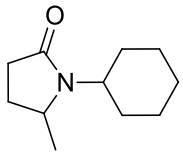
77% yield; colorless oil;
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, $^{3}J_{H-H}$=8.8 Hz, 2H), 7.56 (d, $^{3}J_{H-H}$=8.8 Hz, 2H), 4.46-4.36 (m, 1H, CH), 2.64-2.63 (m, 1H, CH,), 2.56 (s, 3H, CH_3), 2.55-2.47 (m, 1H, CH), 2.42-2.32 (m, 1H, CH), 1.80-1.73 (m, 1H, CH), 1.24 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3);
^{13}C NMR (75 MHz, $CDCl_3$) δ 197.1, 174.5, 142.1, 133.6, 129.4, 122.1, 55.1, 31.5, 26.6, 26.5, 19.9.

1-hexyl-5-methylpyrrolidin-2-one (**1i**)[2]



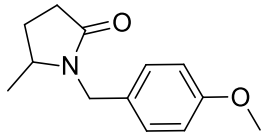
82% yield; yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.56-3.53 (m, 1H, CH), 3.47-3.38 (m, 1H, CH), 2.78-2.73 (m, 1H, CH), 2.24-2.16 (m, 2H, CH_2), 2.06-2.00 (m, 1H, CH), 1.42-1.29 (m, 3H, CH), 1.13-1.01 (m, 9H, CH), 0.73-072 (m, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 53.1, 39.8, 31.3, 30.1, 27.2, 26.6, 26.4, 22.3, 19.6, 13.8.

1-cyclohexyl-5-methylpyrrolidin-2-one **1j**[2]



76% yield; colourless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76-3.72 (m, 1H, CH), 3.69-3.61 (m, 1H, CH), 2.44-2.35 (m, 1H, CH), 2.23-2.16 (m, 1H, CH), 2.12-2.02 (m, 1H, CH), 1.77-1.68 (m, 3H, CH), 1.63-1.43 (m, 5H, CH), 1.30-1.23 (m, 2H, CH), 1.18 (d, $^{3}J_{H-H}$= 6.4 Hz, 3H, CH_3), 1.11-1.05 (m, 1H, CH);
^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 52.9, 52.6, 31.8, 30.2, 30.4, 27.5, 26.0, 25.9, 25.6, 22.4.

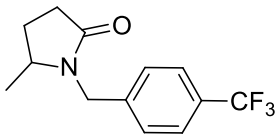
1-(4-Methoxybenzyl)-5-methylpyrrolidin-2-one **1k**[2]



83% yield; yellow oil;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, $^{3}J_{H-H}$= 7.6 Hz 2H, CH), 6.91-6.79 (d, $^{3}J_{H-H}$=7.6 Hz, 2H, CH), 4.81 (d, $^{2}J_{H-H}$=14.8 Hz, 1H, CH), 3.84 (d, $^{2}J_{H-H}$= 14.8 Hz, 1H, CH), 3.69 (s, 3H), 3.40-3.45 (m, 1H, CH), 2.39-2.28 (m, 2H, CH_2), 2.07-2.03 (m, 1H, CH), 1.50-1.48 (m, 1H, CH), 1.07 (d, $^{3}J_{H-H}$=6.4 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ174.7, 158.8, 129.1, 128.7, 113.8, 55.1, 52.6, 43.1, 30.2, 26.5, 19.5.

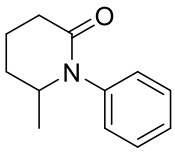
1-(4-trifluoromethyl)-5-methylpyrrolidin-2-one **1l**[2]



80% yield; yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, $^{3}J_{H-H}$=6.8 Hz, 2H, CH), 7.30 (d, $^{3}J_{H-H}$=6.8 Hz, 2H, CH), 4.84 (d, $^{2}J_{H-H}$=15.2 Hz, 1H, CH), 4.15 (d, $^{2}J_{H-H}$= 15.2 Hz, 1H, CH), 3.51-3.48 (m, 1H, CH), 2.45-2.34 (m, 2H, CH_2), 2.14-2.12 (m, 1H, CH), 1.57-1.55 (m, 1H, CH), 1.10 (d, $^{3}J_{H-H}$=6.0 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 141.6, 129.7 (q, $^{2}J_{C-F}$=32.1 Hz), 128.0, 125.4 (q, $^{3}J_{C-F}$= 3.8 Hz), 124.7 (q, $^{1}J_{C-F}$=270.1 Hz), 53.6, 43.5, 30.0, 26.6, 19.5.

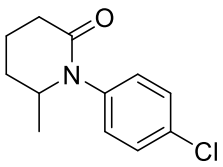
Synthesis of piperidinones derivatives

6-methyl-1-phenylpiperidin-2-one **1m**[4]



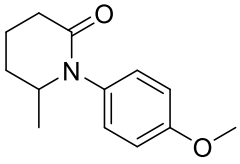
91% yield, yellow oil;
^{1} H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.28-7.23 (tt, $^{3}J_{H-H}$=7.6 Hz, $^{4}J_{H-H}$=1.2 Hz 1H), 7.15-7.12 (m, 2H), 3.93-3.85 (m, 1H), 2.53-2.49 (m, 2H), 2.14-2.05 (m, 1H), 2.02-1.92 (m, 1H), 1.86-1.77 (m, 1H), 1.74-1.66 (m, 1H), 1.05 (d, $^{3}J_{H-H}$=6.4 Hz, 3H) ppm.
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.5, 129.1, 128.1, 127.1, 55.7, 32.7, 30.8, 20.8, 18.3.

1-(4-chlorophenyl)-6-methylpiperidin-2-one **1n** [4]



83%, yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, $^{3}J_{H-H}$=8.4 Hz, 2H), 7.06 (d, $^{3}J_{H-H}$=8.4 Hz, 2H), 3.88 - 3.80 (m, 1H), 2.47 (t, $^{3}J_{H-H}$= 6.8 Hz, 2H), 2.06-2.02 (m, 1H), 1.94-1.90 (m, 1H), 1.80-1.77 (m, 1H), 1.69-1.65 (m, 1H), 1.01 (d, $^{3}J_{H-H}$=6.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 139.8, 132.5, 129.3,129.1, 55.6, 32.6, 30.6, 20.7, 18.1.

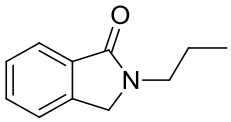
1-(4-methoxyphenyl)-6-methylpiperidin-2-one **1o** [4]



93% yield, brown oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, $^{3}J_{H-H}$=9.2 Hz, 2H, CH), 6.90 (d, $^{3}J_{H-H}$=8.8 Hz, 2H, CH), 3.87-3.82 (m, 1H, CH), 3.80 (s, 3H, CH_3), 2.52 (t, $^{3}J_{H-H}$=6.4, 2H, CH_2), 2.12-2.09 (m, 1H, CH), 2.03-1.92 (m, 1H, CH), 1.87-1.78 (m, 1H, CH), 1.75-1.67 (m, 1H, CH), 1.07 (d, $^{3}J_{H-H}$=6.4 Hz, 3H, CH_3).
^{13}C NMR (100 MHz, $CDCl_3$) δ170.5, 158.1, 134.1, 128.8, 114.2, 55.7, 55.2, 32.5, 30.6, 20.6, 18.1.

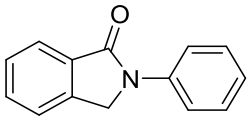
Synthesis of isoindolinone derivatives

2-propylisoindolin-1-one (**2a**)[2]



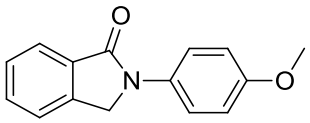
93% yield; colorless oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, $^{3}J_{H-H}$= 6.8 Hz, 1H, CH), 7.47-7.43 (m, 1H, CH), 7.39-7.26 (m, 2H, CH), 4.30 (s, 2H, CH_2), 3.52 (t, $^{3}J_{H-H}$= 7.2 Hz, 2H, CH_2), 1.66-1.58 (m, 2H, CH_2), 0.90 (t, $^{3}J_{H-H}$= 7.2 Hz, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 141.1, 132.9, 131.1, 127.8, 123.5, 122.6, 49.8, 43.9, 21.7, 11.2.

2-phenylisoindolin-1-one **2b**[2]



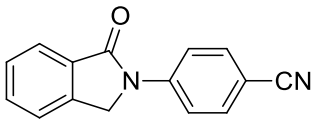
96% yield; yellow solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ7.93 (d, $^{3}J_{H-H}$= 7.2 Hz, 1H, CH), 7.88-7.86 (m, 2H, CH), 7.62-7.60 (m, 1H, CH), 7.53-7.49 (m, 2H, CH), 7.45-7.41 (m, 2H, CH), 7.20-7.16 (m, 1H, CH), 4.86 (s, 2H, CH_2);
^{13}C NMR (100 MHz, $CDCl_3$) δ167.6, 140.2, 139.6, 133.4, 132.2, 129.3, 128.5, 124.6, 124.3, 122.7, 119.6, 50.9.

2-(4-methoxyphenyl)isoindolin-1-one (**2c**)[2]



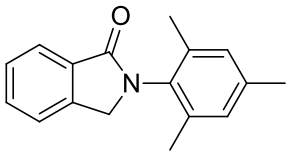
90% yield; brown solid;
^{1}H NMR (400 MHz, $CDCl_3$) δ7.92 (d, $^{3}J_{H-H}$= 8.0 Hz, 1H, CH), 7.73 (d, $^{3}J_{H-H}$= 9.2 Hz, 2H, CH), 7.60-7.57 (m, 1H, CH), 7.52-7.48 (m, 2H, CH), 6.98-6.95 (m, 2H, CH), 4.82 (s, 2H, CH_2), 3.83 (s, 3H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ167.6, 157.2, 141.0, 133.8, 133.4, 132.3, 128.7, 124.1, 123.3, 121.9, 114.7, 56.0, 51.7.

4-(1-oxoisoindolin-2-yl)benzonitrile **2d**[2]



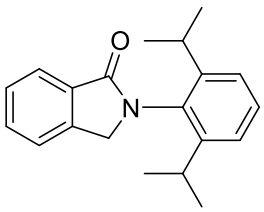
88% yield; brown solid
^{1}H NMR (400 MHz, $CDCl_3$) δ8.00 (d, $^{3}J_{H-H}$=8.8 Hz, 2H, CH), 7.86 (d, $^{3}J_{H-H}$=7.6 Hz, 1H, CH), 7.65-7.60 (m, 3H, CH), 7.52-7.48 (m, 2H, CH), 4.82 (s, 2H, CH_2);
^{13}C NMR (100 MHz, $CDCl_3$) δ167.9, 143.3, 139.8, 133.3, 133.0, 132.4, 128.8, 124.5, 122.9, 118.9, 118.5, 107.0, 50.3.

2-mesitylisoindolin-1-one (2e)[2]



91% yield; yellow solid
^{1}H NMR (400 MHz, $CDCl_3$) δ7.98-7.96 (m, 1H, CH), 7.61-7.59 (m, 1H, CH), 7.52-7.50 (m, 2H, CH), 6.98 (s, 2H, CH), 4.59 (s, 2H, CH_2), 2.32 (s, 3H, CH_3), 2.15 (s, 6H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ168.0, 141.8, 138.3, 136.5, 132.9, 132.5, 131.7, 129.4, 128.2, 124.4, 123.0, 51.4, 21.1, 17.9.

2-(2,6-diisopropylphenyl)isoindolin-1-one (**2f**)[2]

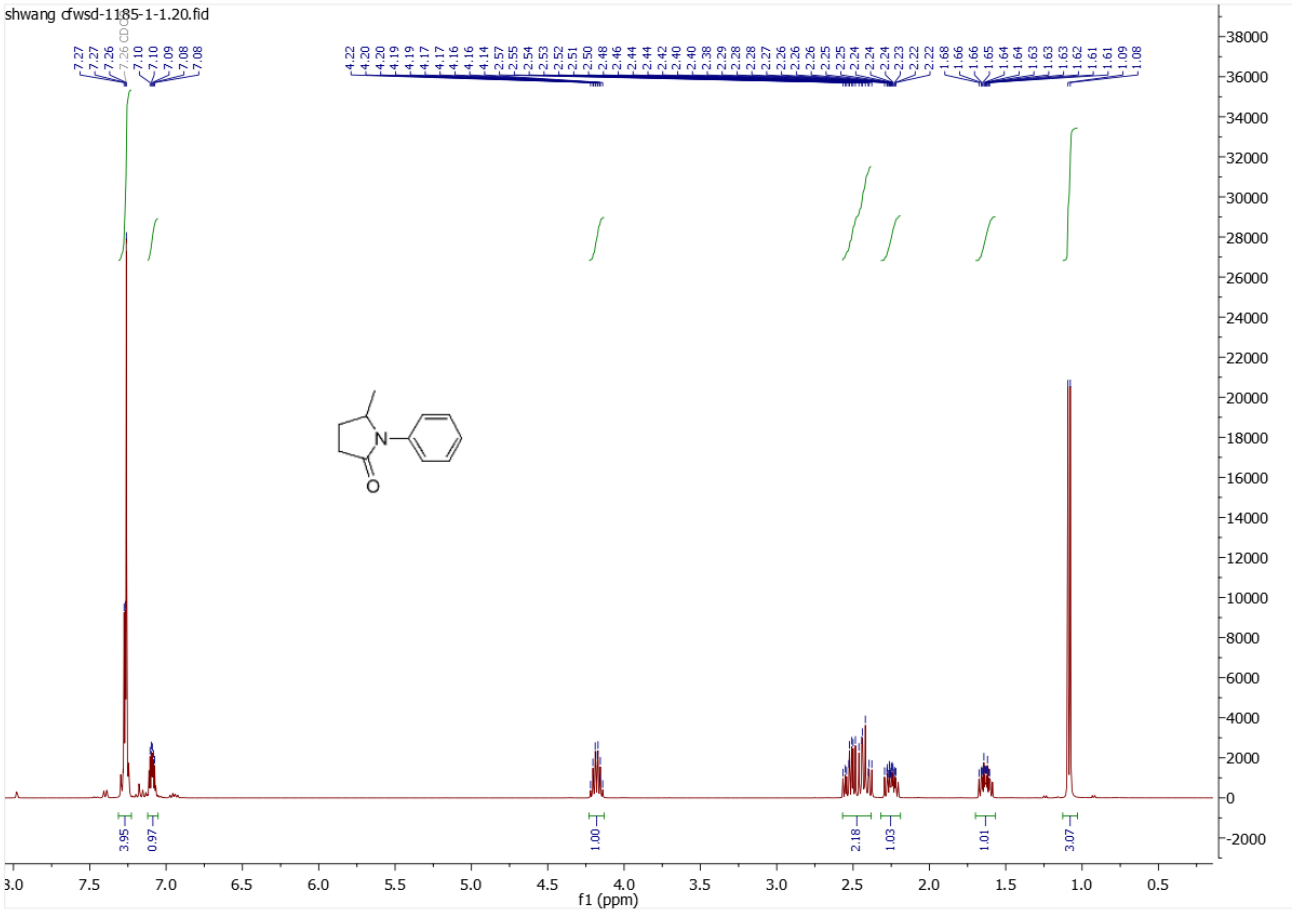


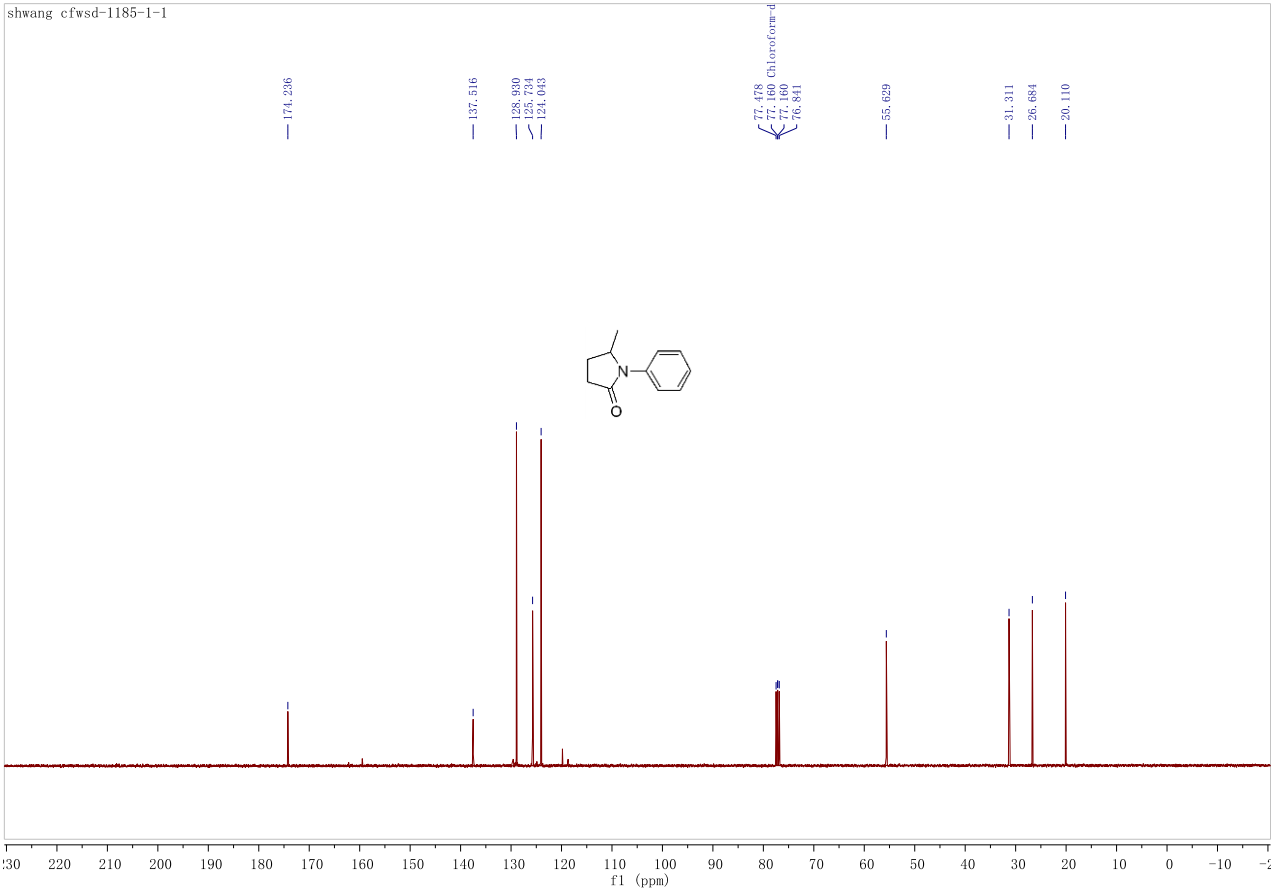
84% yield; yellow solid

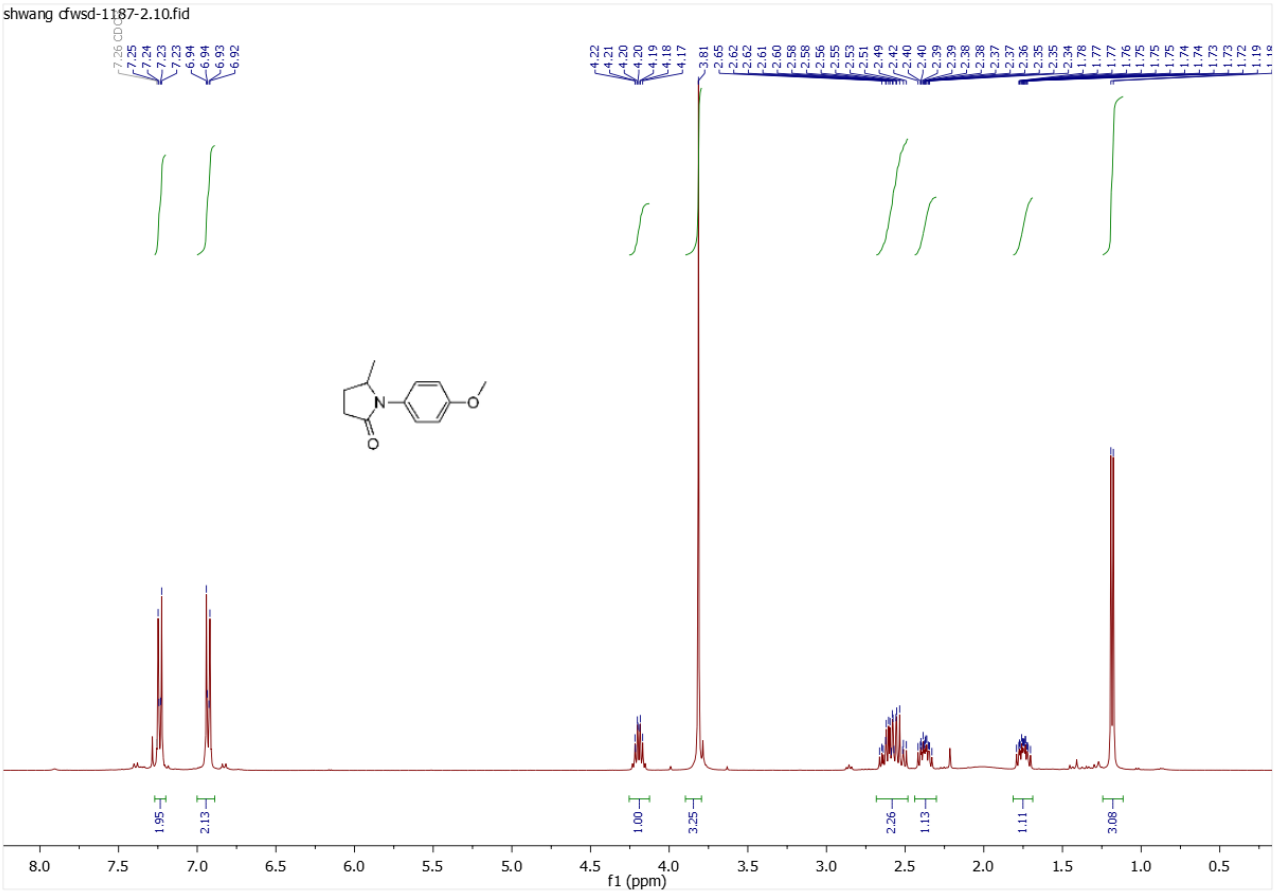
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, $^{3}J_{H-H}$=7.2 Hz, 1H), 7.67-7.63 (m, 1H, CH), 7.59-7.54 (m, 2H, CH), 7.45-7.41 (m, 1H, CH), 7.28 (d, $^{3}J_{H-H}$=7.6 Hz, 2H, CH), 4.60 (s, 2H, CH_2), 2.84-2.77 (m, 2H, CH), 1.24 (d, $^{3}J_{H-H}$= 6.8 Hz, 12H, CH_3);
^{13}C NMR (100 MHz, $CDCl_3$) δ168.7, 147.7, 141.5, 132.8, 132.5, 131.8, 129.4, 128.4, 124.6, 124.2, 123.0, 53.9, 28.9, 24.7, 24.4.

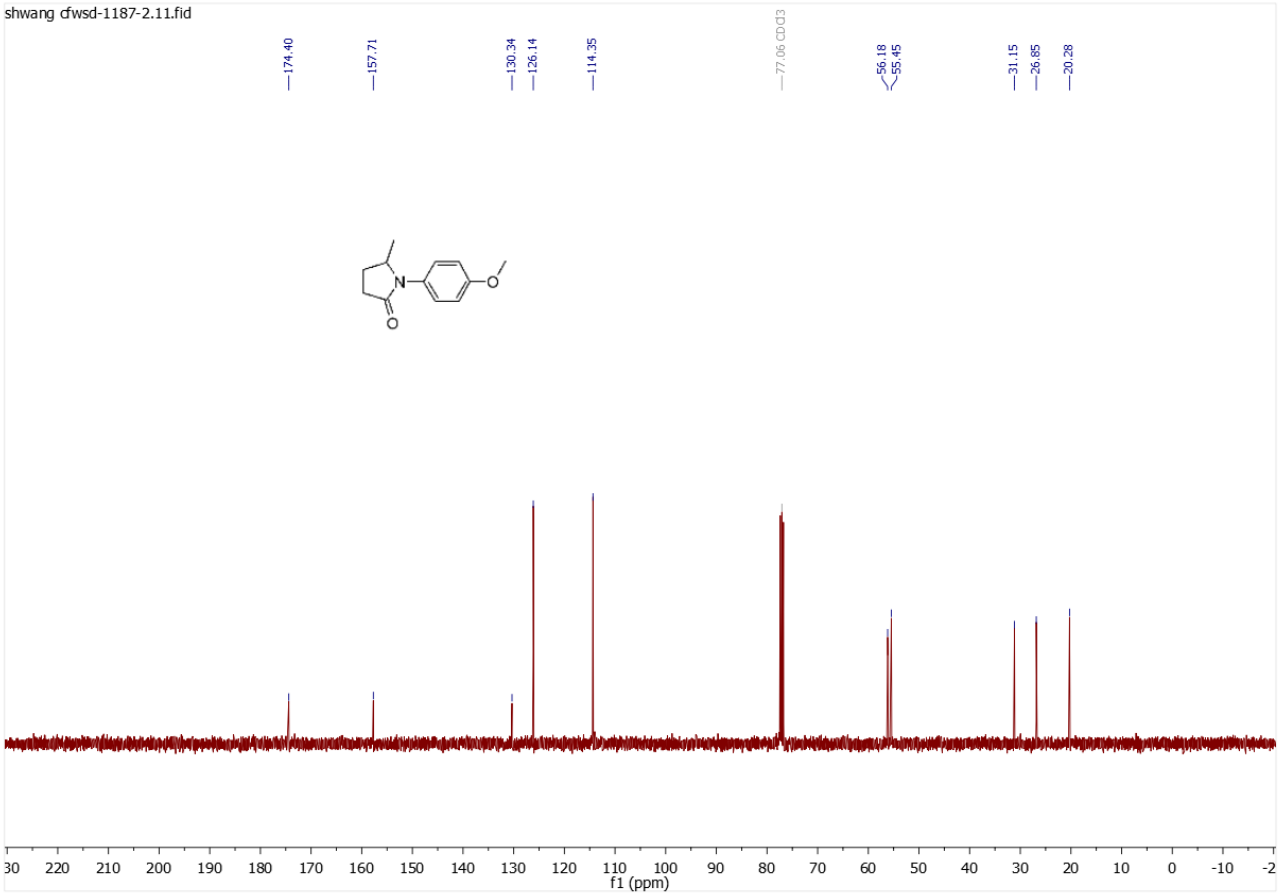
References

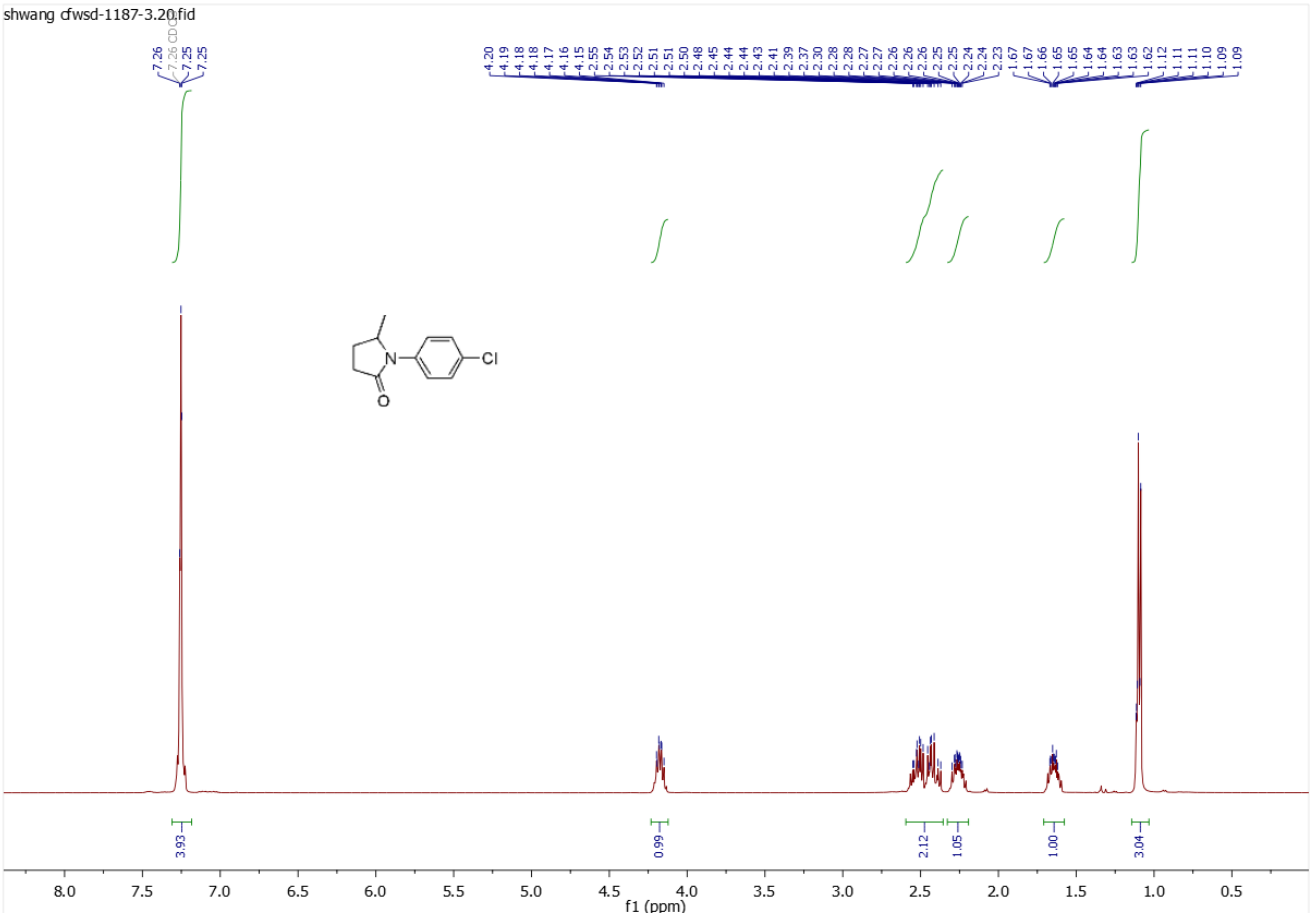
[1] S. Wang, H. Huang, V. Dorcet, T. Roisnel, C. Bruneau, C. Fischmeister, *Organometallics* **2017**, *36*, 3152-3162.
[2] S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem* **2017**, *10*, 4150-4154.
[3] S. Wang, H. Huang, T. Roisnel, C. Bruneau, C. Fischmeister, *ChemSusChem* **2019**, *12,* 179-184.
[4] C. Wu, H. Zhang, B. Yu, Y. Chen, Z. Ke, S. Guo, Z. Liu, *ACS Catal.* **2017**, *7*, 7772-7776.

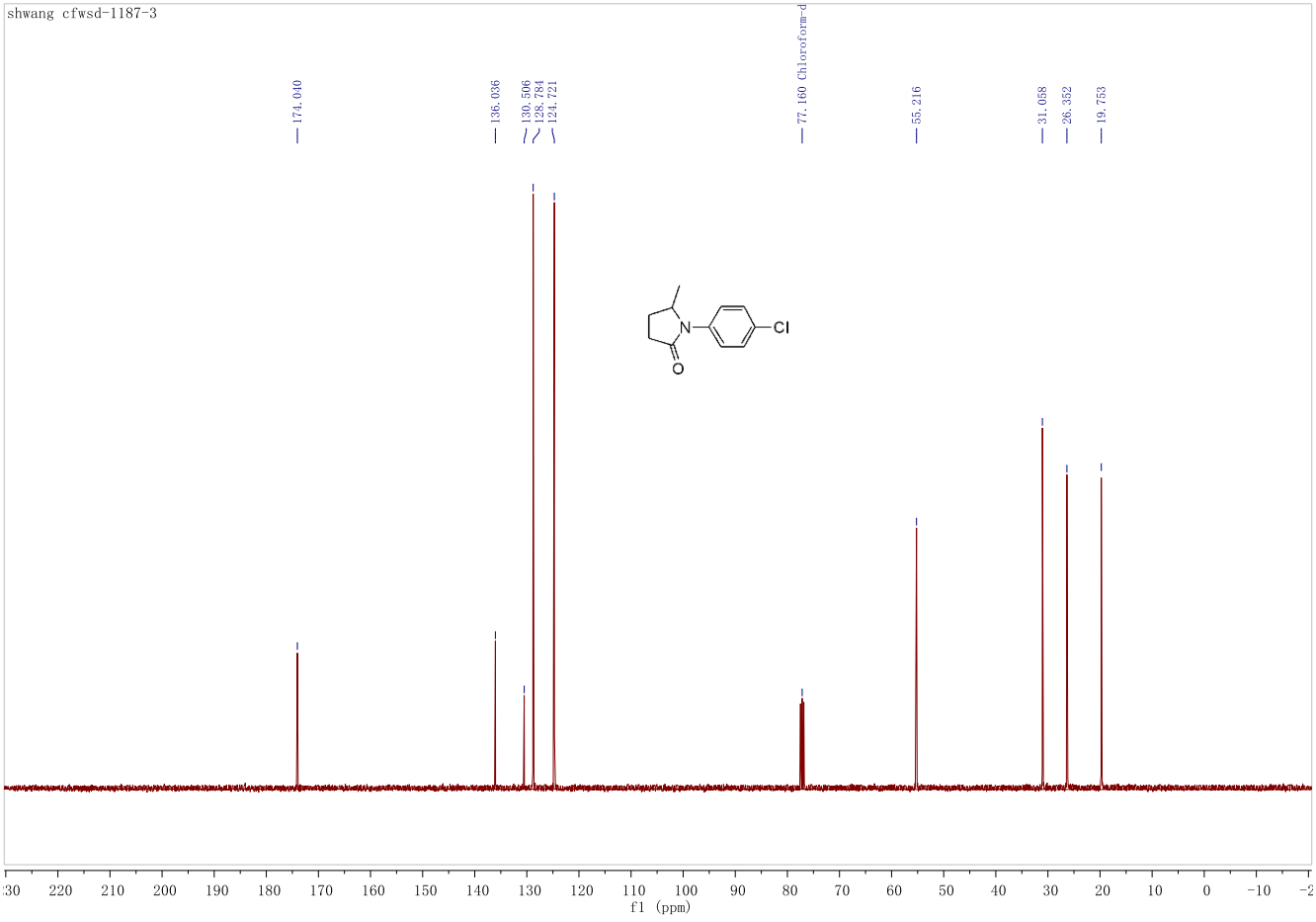

shwang cfwsd-1185-1-1.20.fid
f1 (ppm)

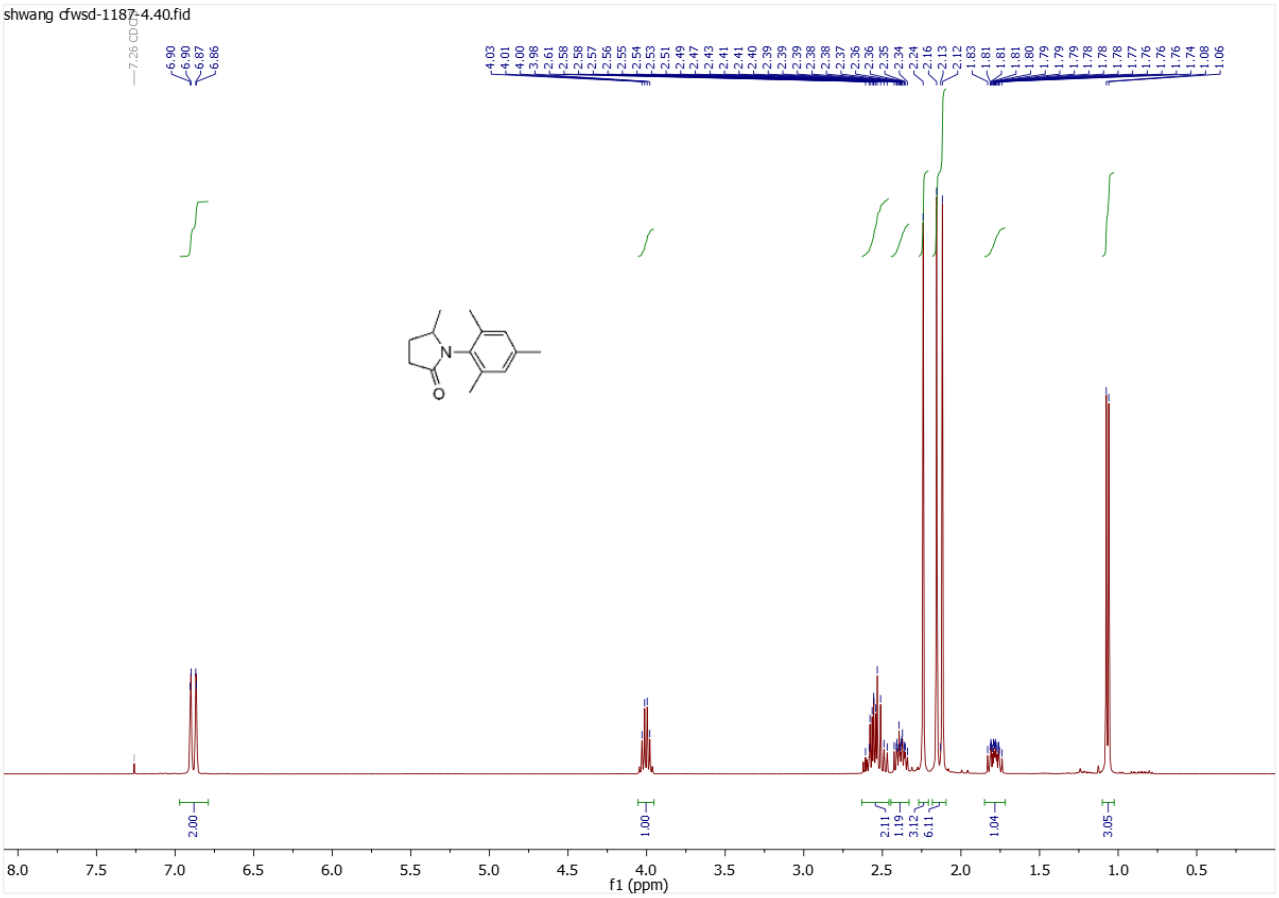

shwang cfwsd-1185-1-1
f1 (ppm)

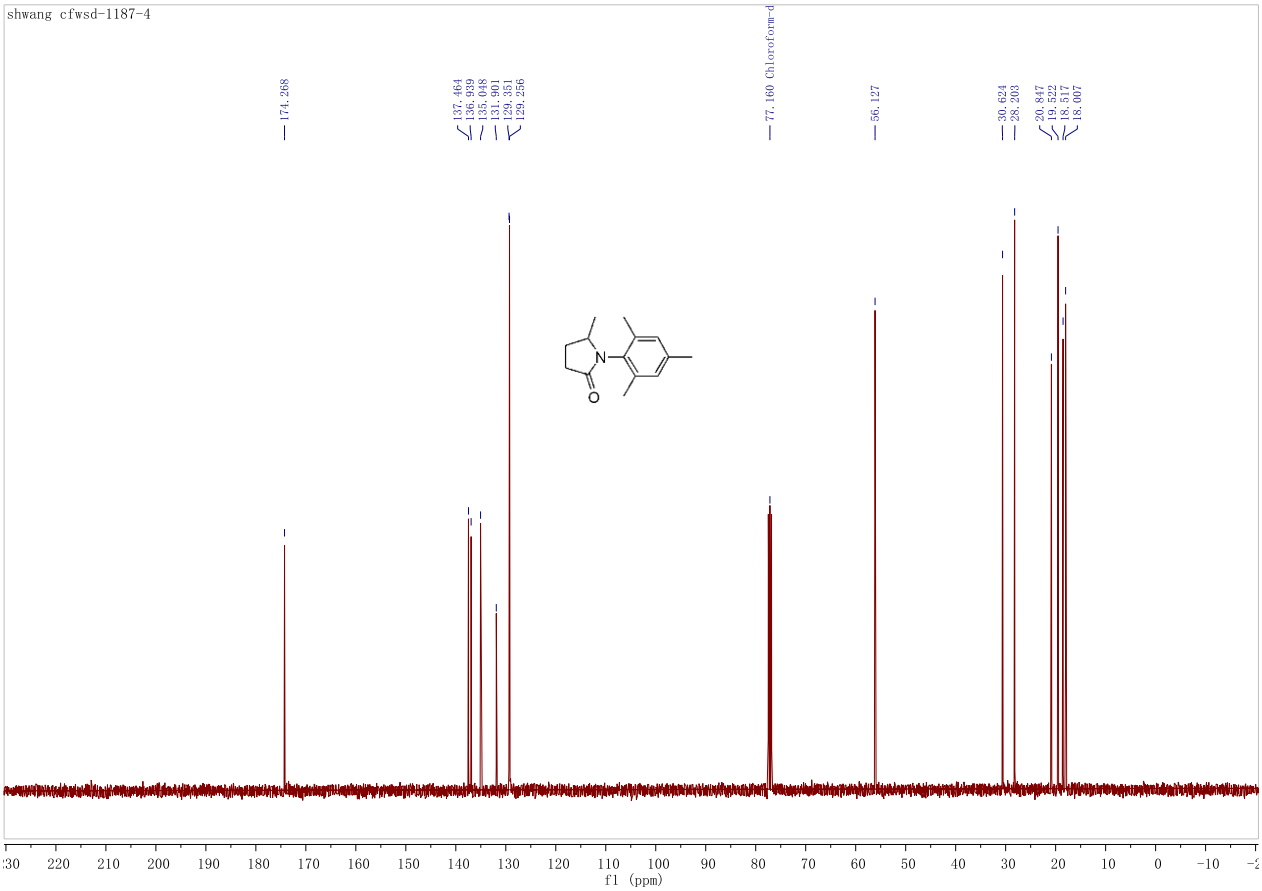

shwang cfwsd-1187-2.10.fid
f1 (ppm)

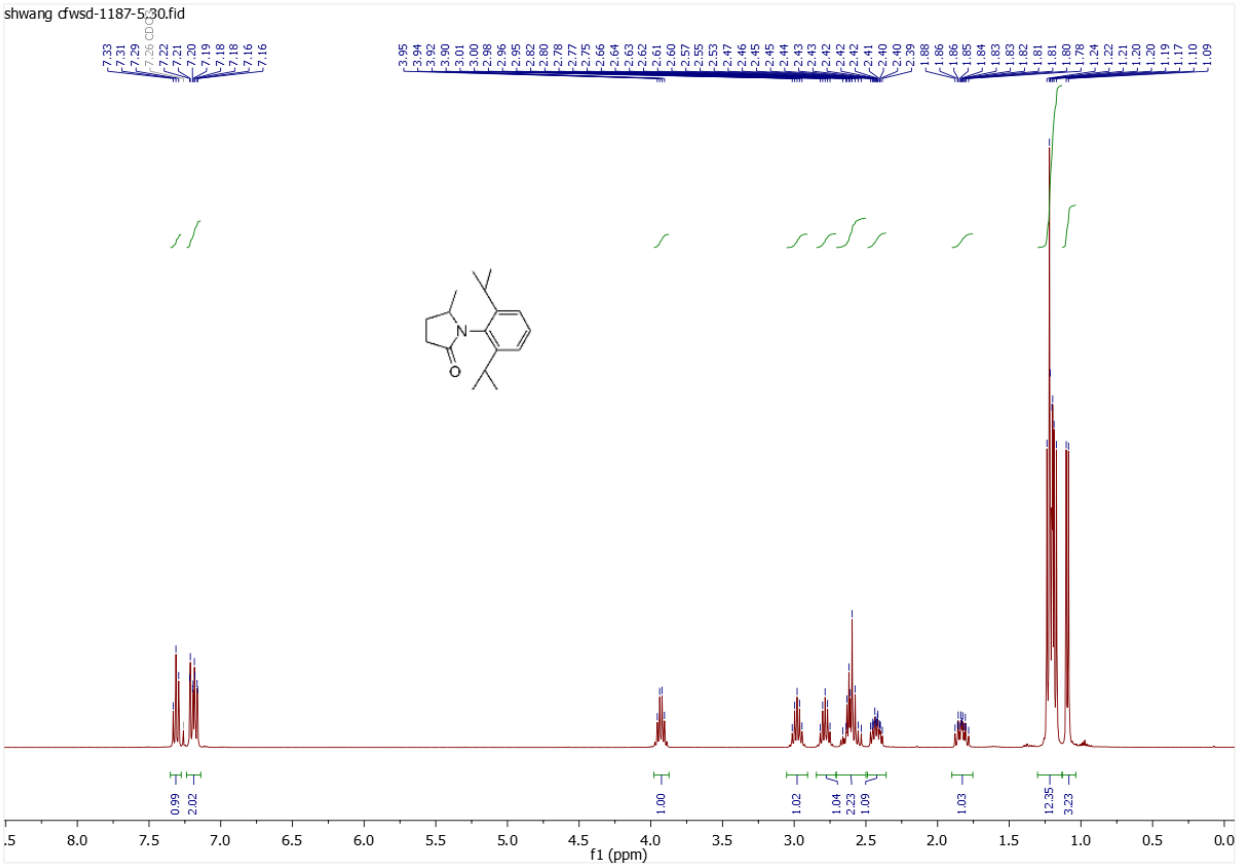

shwang cfwsd-1187-2.11.fid
f1 (ppm)

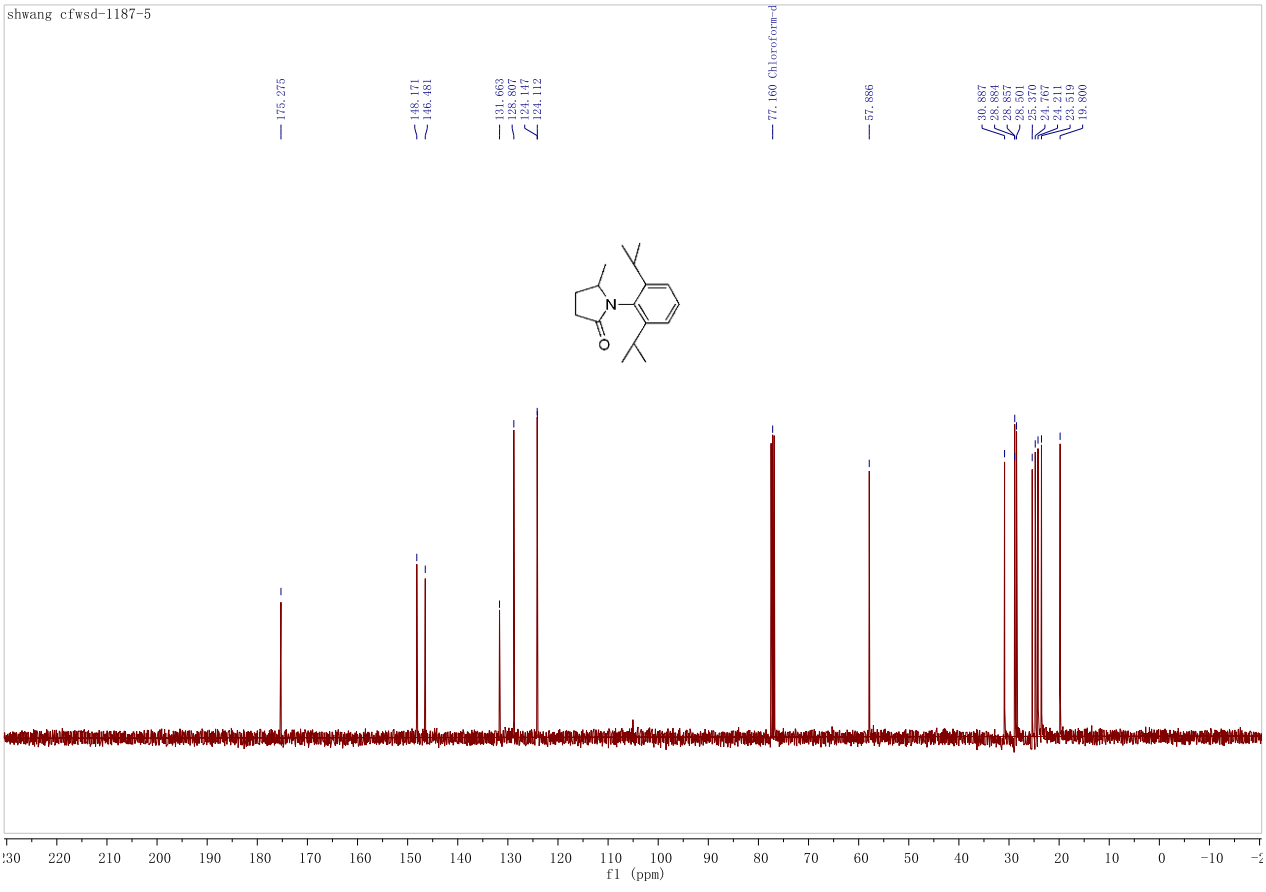

shwang cfwsd-1187-3.20.fid
7.26
7.25
4.20
4.19
4.18
4.17
4.16
4.15
2.55
2.54
2.53
2.52
2.51
2.50
2.48
2.45
2.44
2.43
2.41
2.39
2.37
2.30
2.28
2.27
2.26
2.25
2.24
2.23
1.67
1.66
1.65
1.64
1.63
1.62
1.12
1.11
1.10
1.09
N
Cl
O
3.93
0.99
2.12
1.05
1.00
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

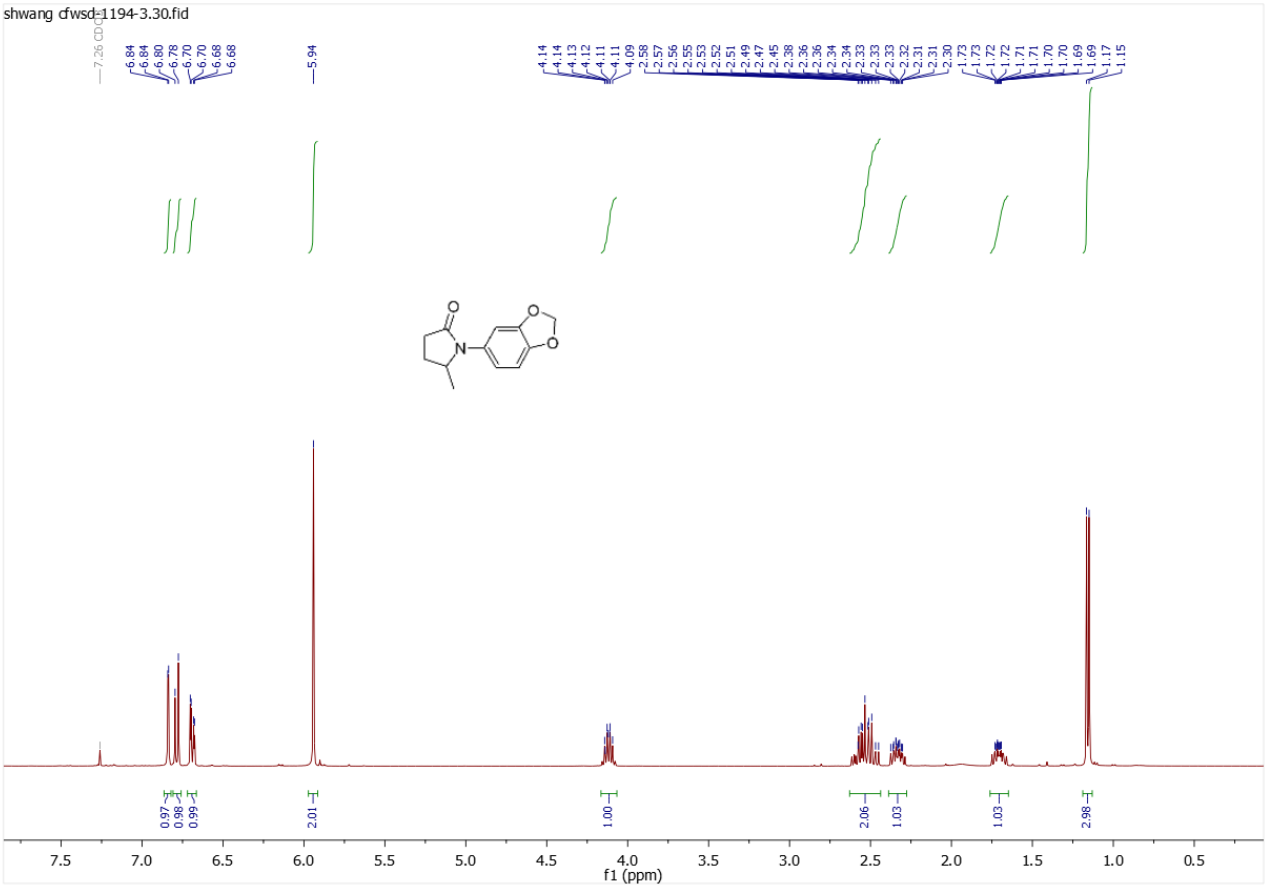

shwang cfwsd-1187-3
174.040
136.036
130.506
128.784
124.721
77.160 Chloroform-d
55.216
31.658
26.352
19.753
N
Cl
O
f1 (ppm)

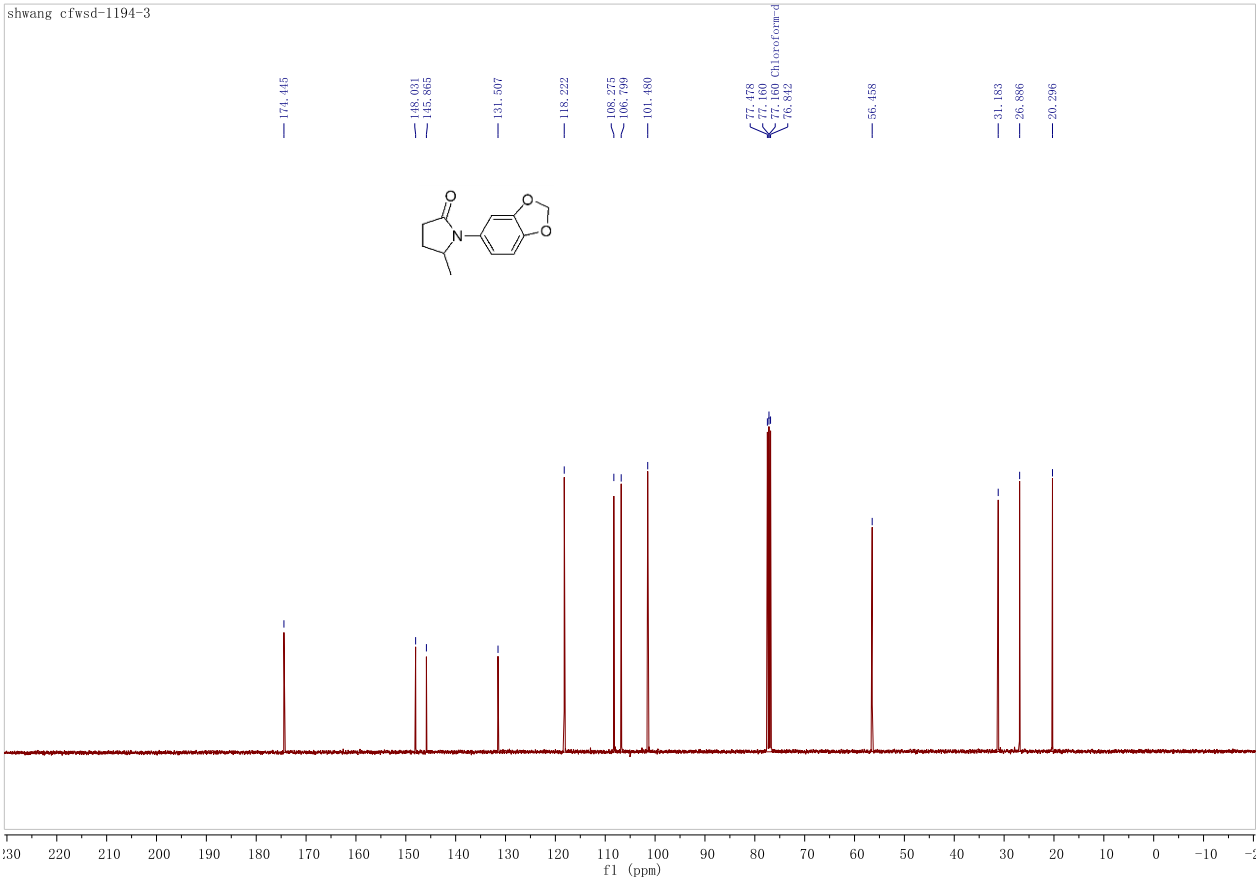

shwang cfwsd-1187-4.40.fid
f1 (ppm)

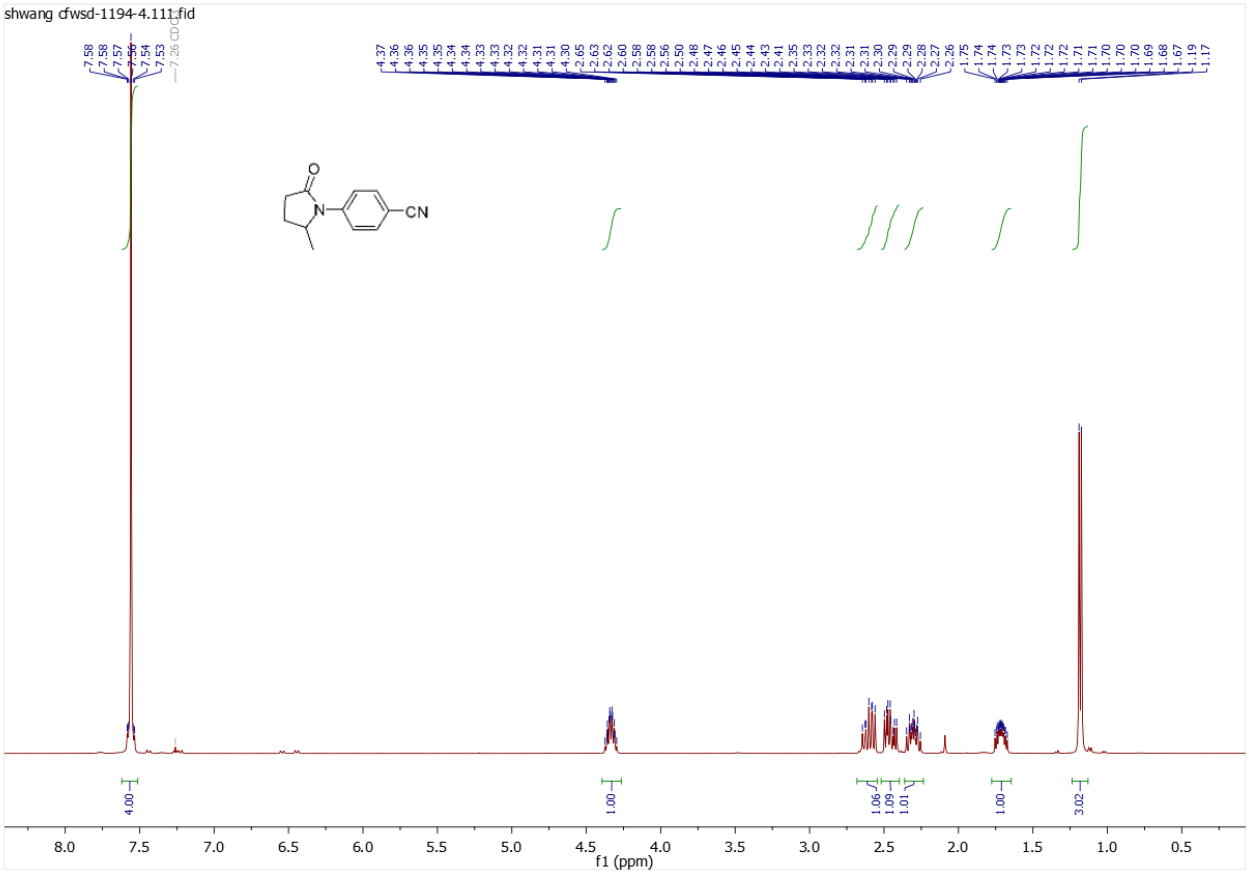

shwang cfwsd-1187-4
f1 (ppm)

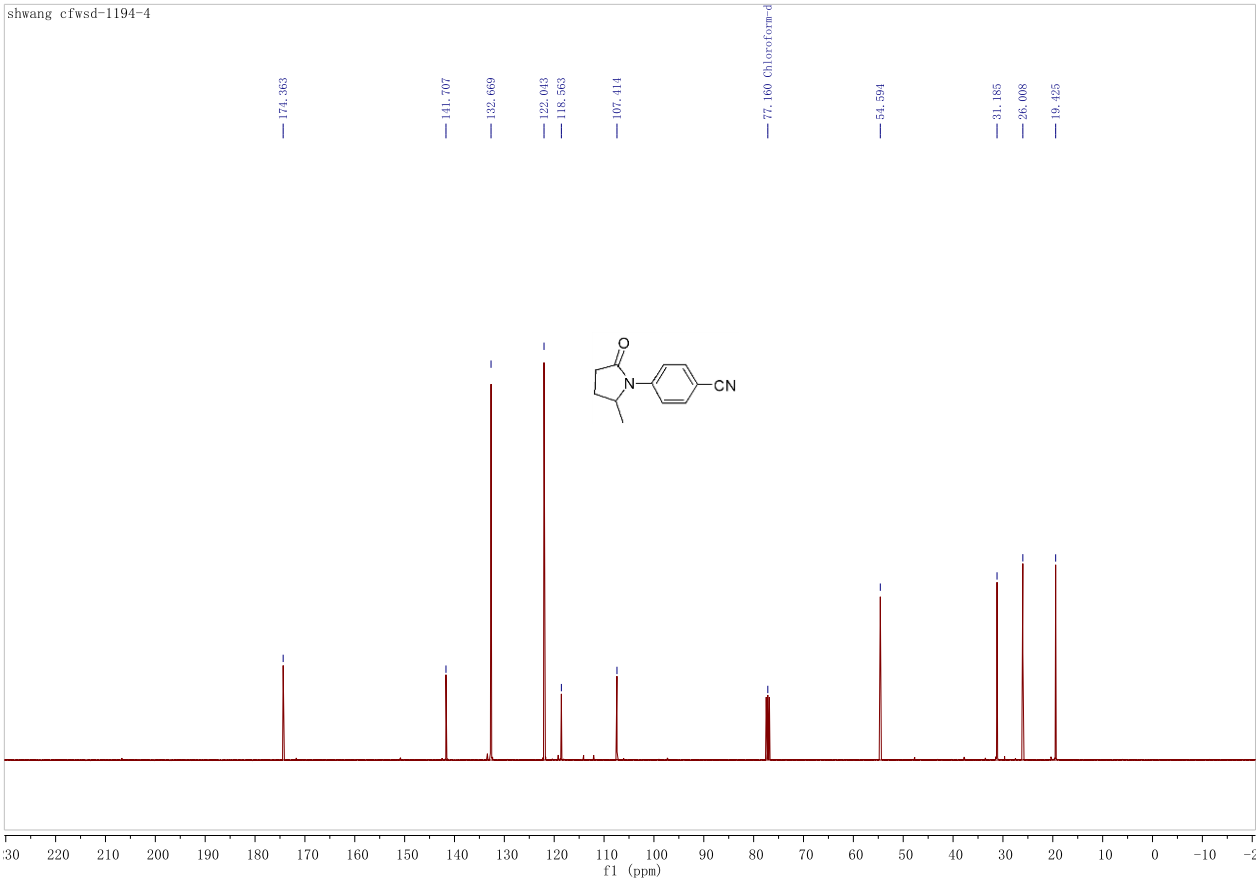

shwang cfwsd-1187-5-30.fid
f1 (ppm)

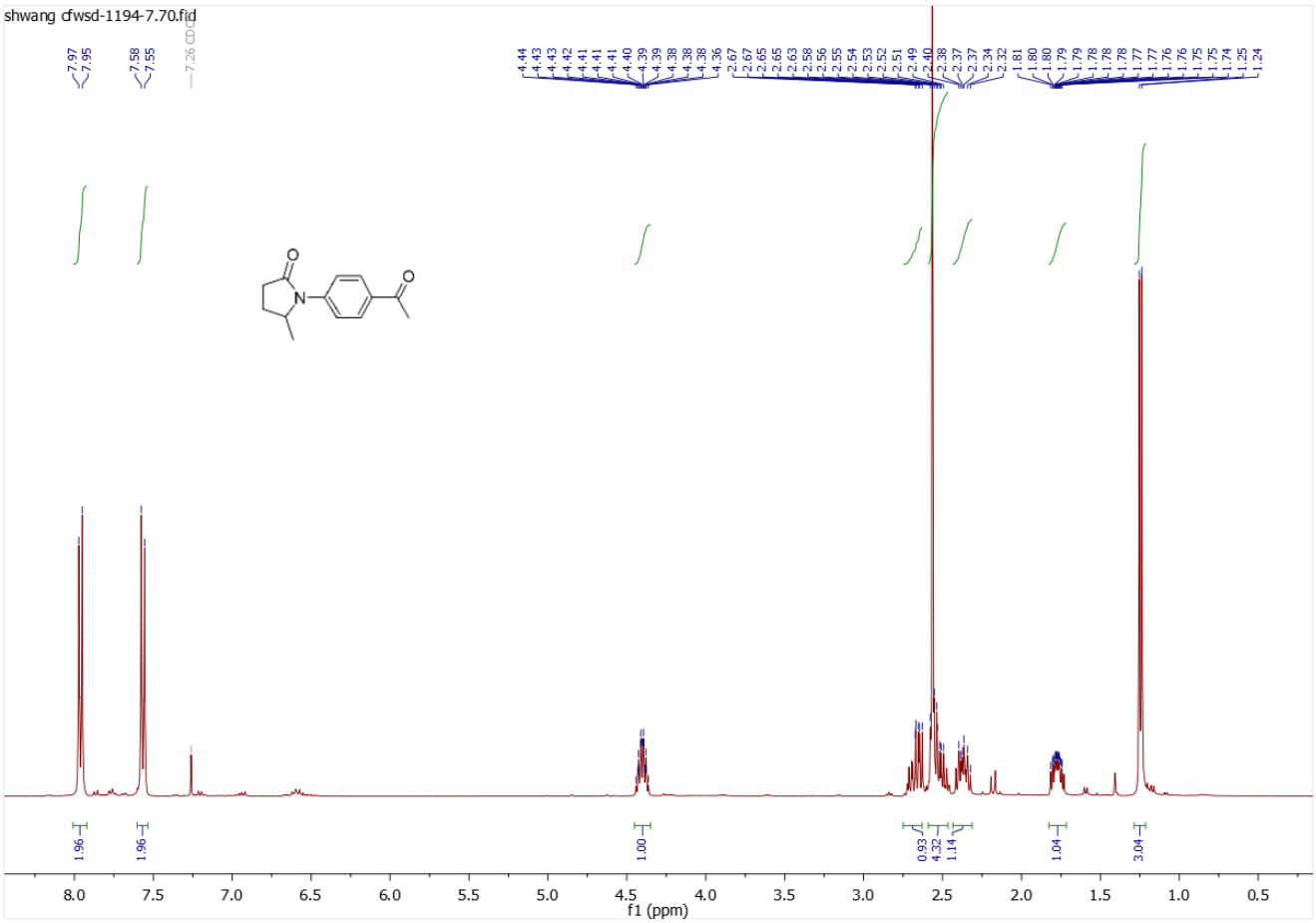

shwang cfwsd-1187-5
f1 (ppm)

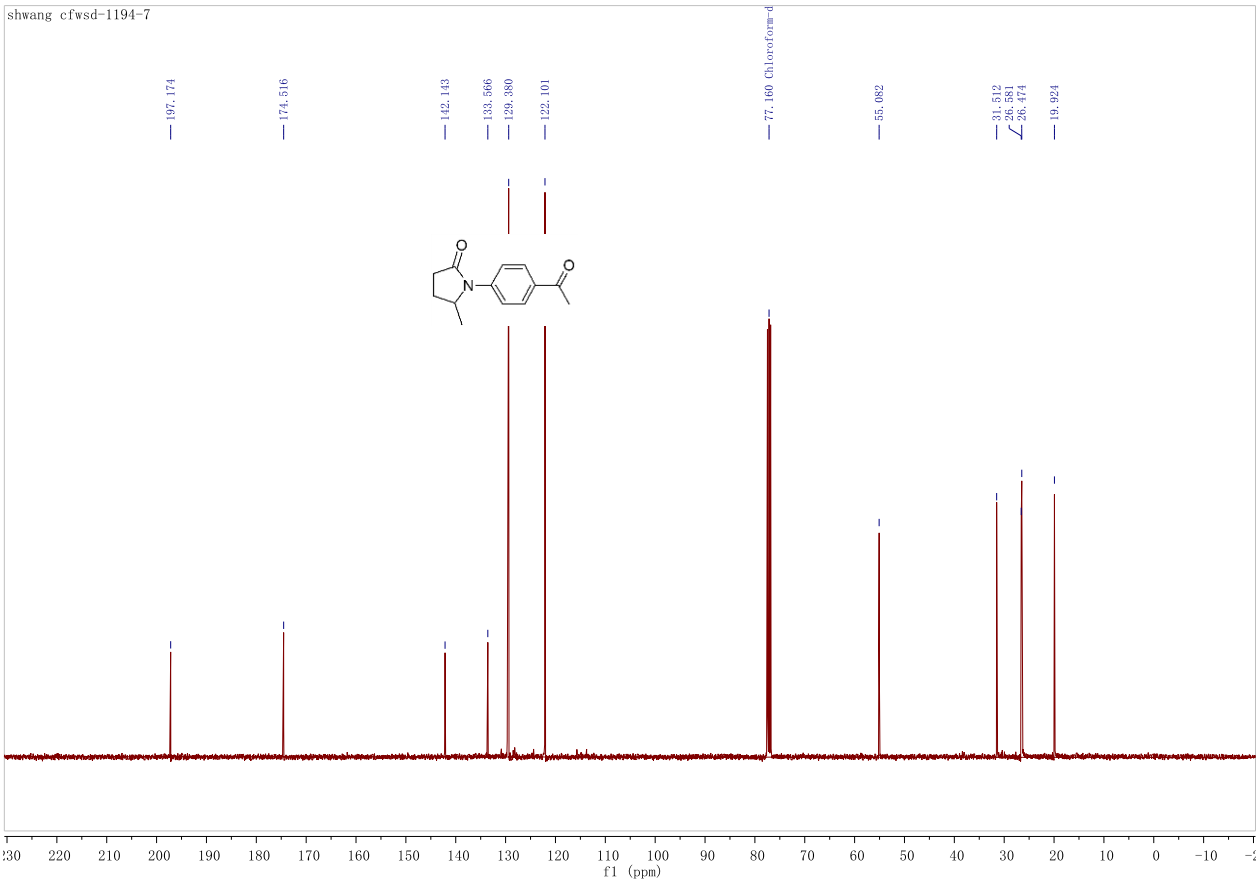

shwang cfwsd-1194-3.30.fid
7.26 CDCl3
6.84
6.84
6.80
6.78
6.70
6.70
6.68
6.68
5.94
4.14
4.14
4.13
4.12
4.11
4.11
4.09
2.58
2.57
2.56
2.55
2.53
2.52
2.51
2.49
2.47
2.45
2.38
2.36
2.36
2.34
2.34
2.33
2.33
2.33
2.32
2.31
2.31
2.30
1.73
1.73
1.72
1.72
1.71
1.71
1.70
1.70
1.69
1.69
1.17
1.15
0.97
0.98
0.99
2.01
1.00
2.06
1.03
1.03
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

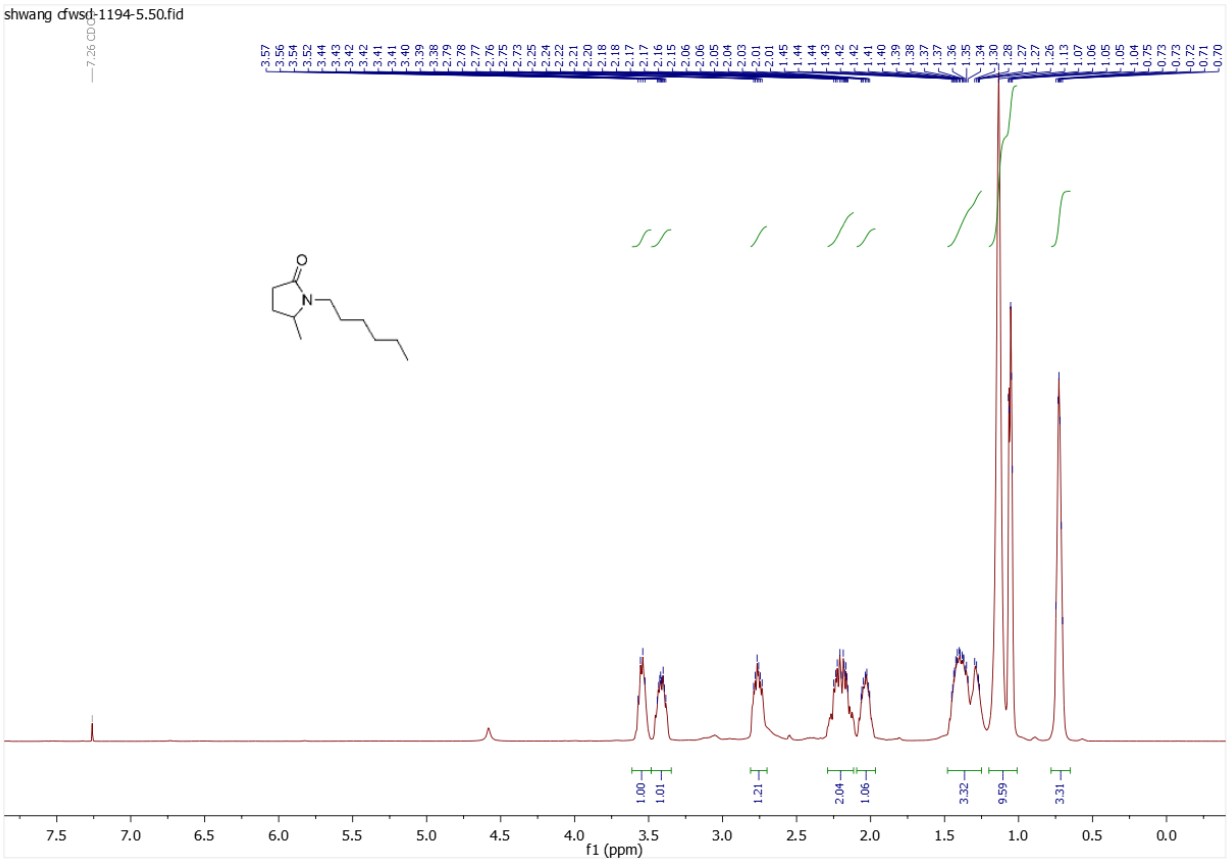

shwang cfwsd-1194-3
174.445
148.031
145.865
131.507
118.222
108.275
106.799
101.480
77.478
77.160
77.160 Chloroform-d
76.842
56.458
31.183
26.886
20.296
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

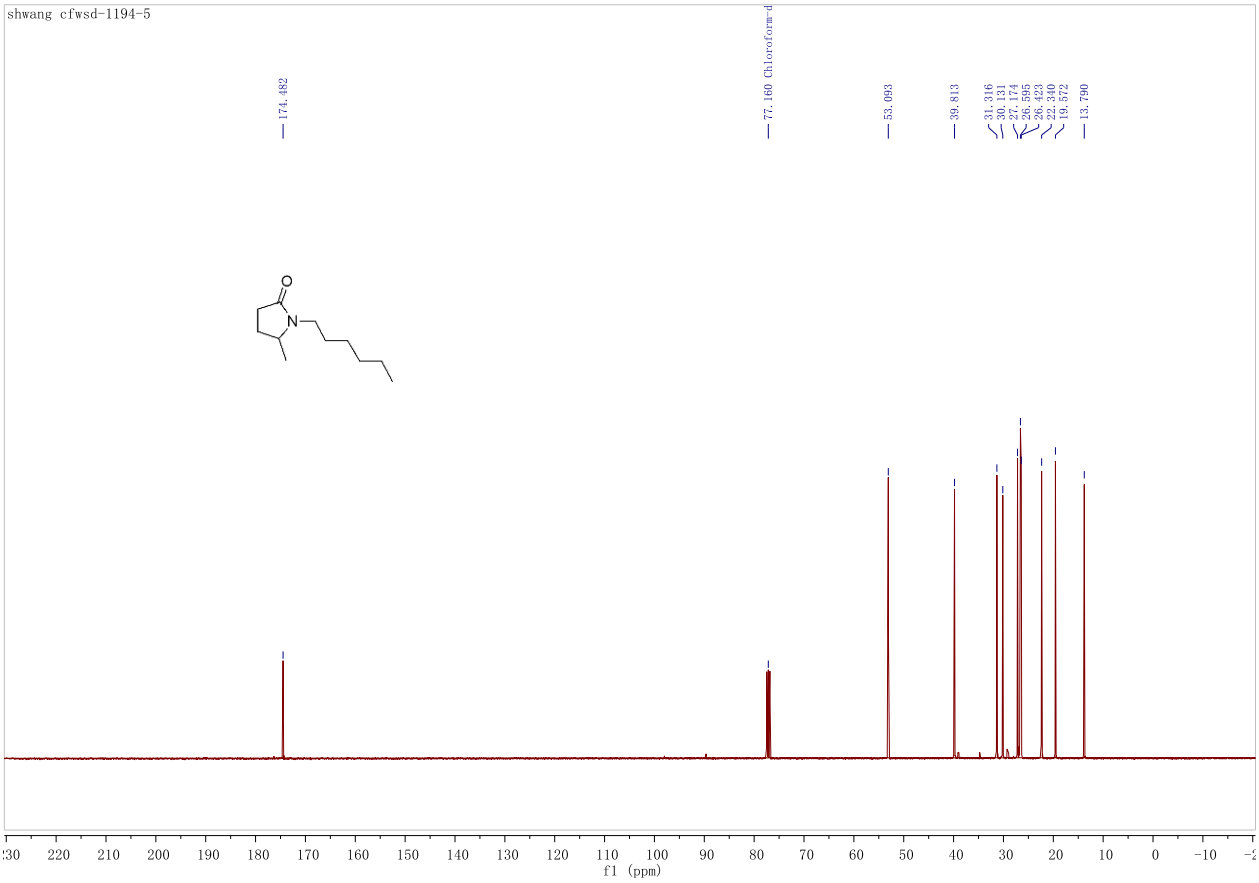

shwang cfwsd-1194-4.11.fid
CN
f1 (ppm)

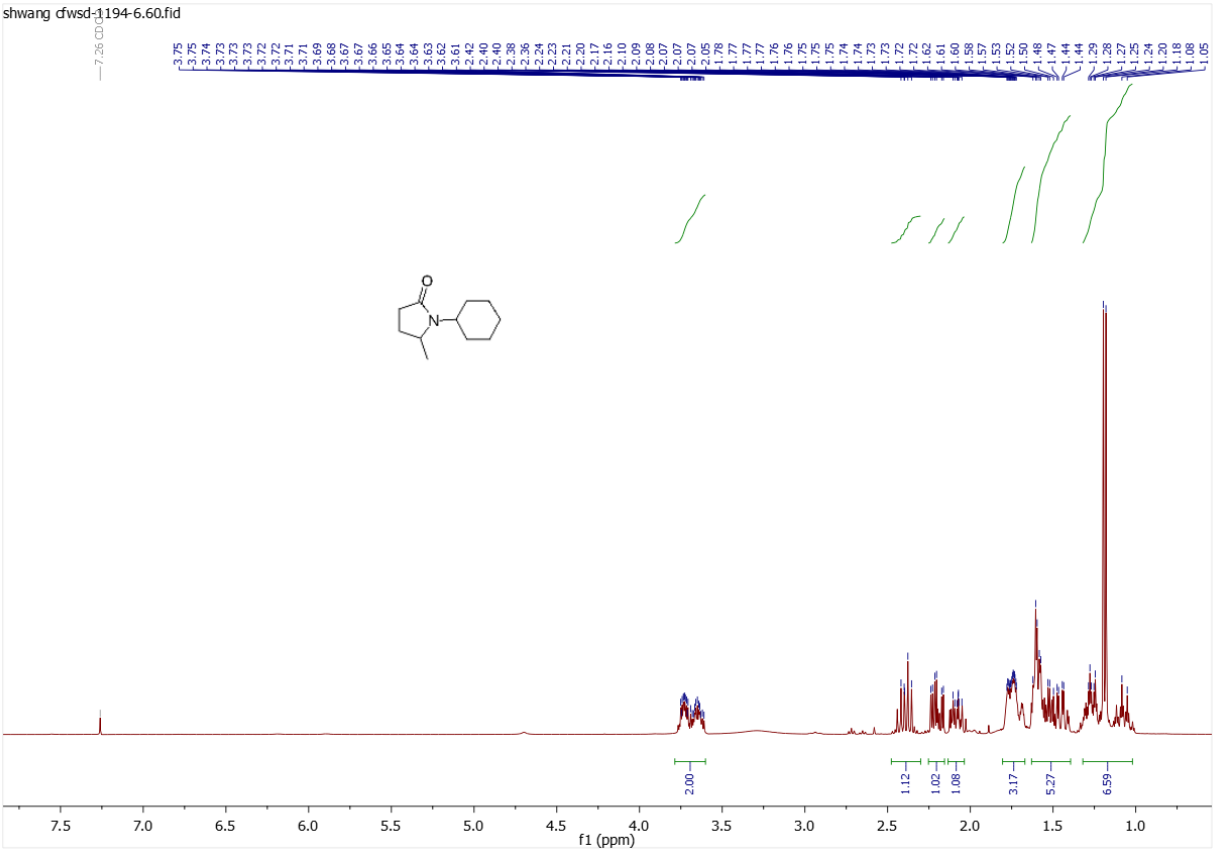

shwang cfwsd-1194-4
174.363
141.707
132.669
122.043
118.563
107.414
77.160 Chloroform-d
54.594
31.185
26.008
19.425
CN
f1 (ppm)

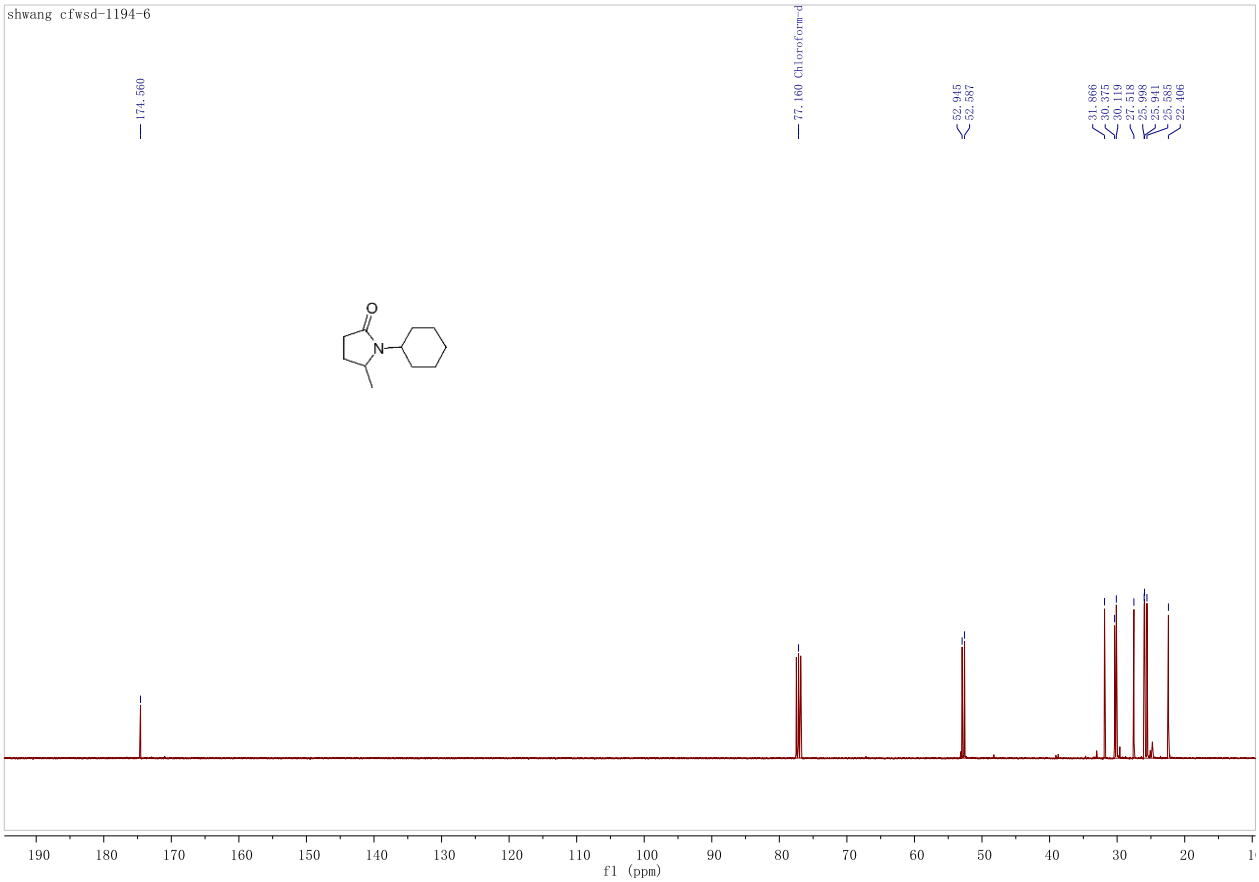

shwang cfwsd-1194-7.70.fid
7.97
7.95
7.58
7.55
7.26 CDCl3
1.96
1.96
1.00
0.93
4.32
1.14
1.04
3.04
f1 (ppm)

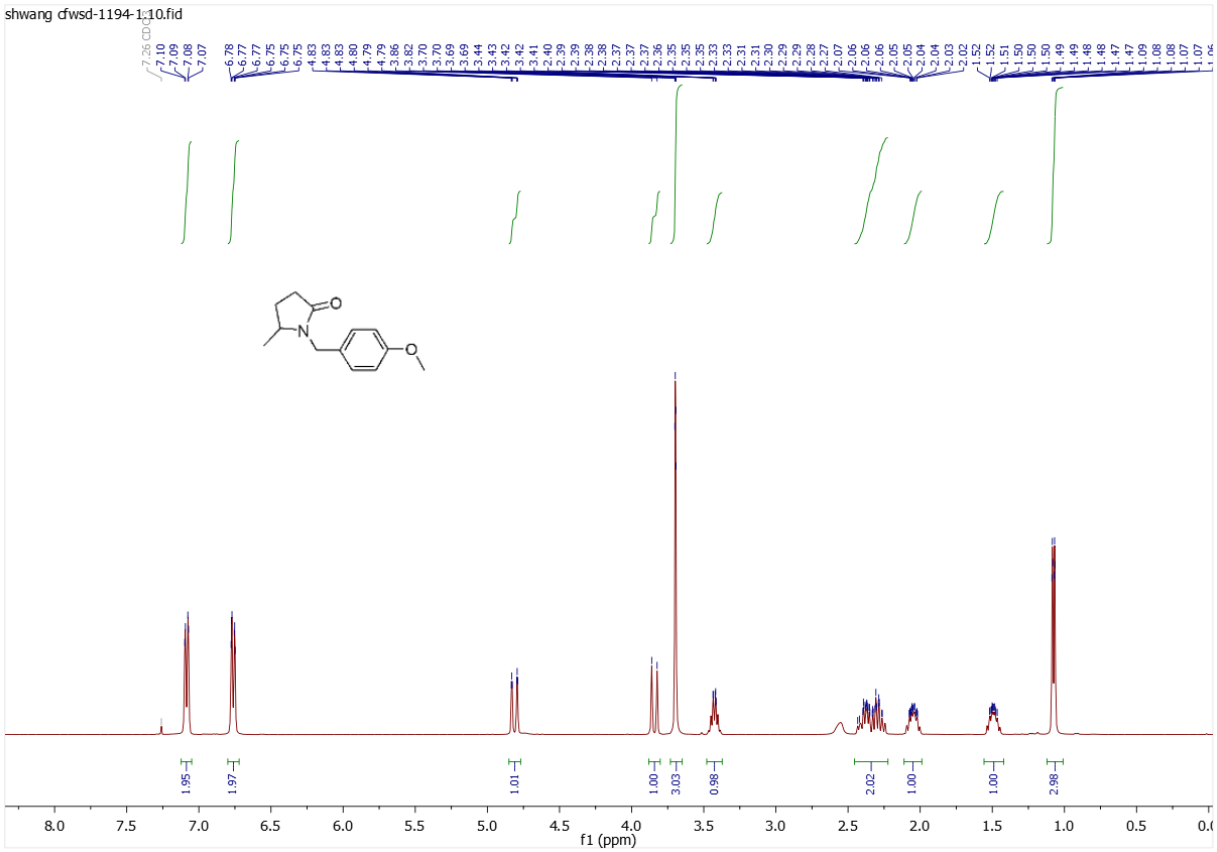

shwang cfwsd-1194-7
197.174
174.516
142.143
133.566
129.380
122.101
77.160 Chloroform-d
55.082
31.512
26.581
26.474
19.924
f1 (ppm)

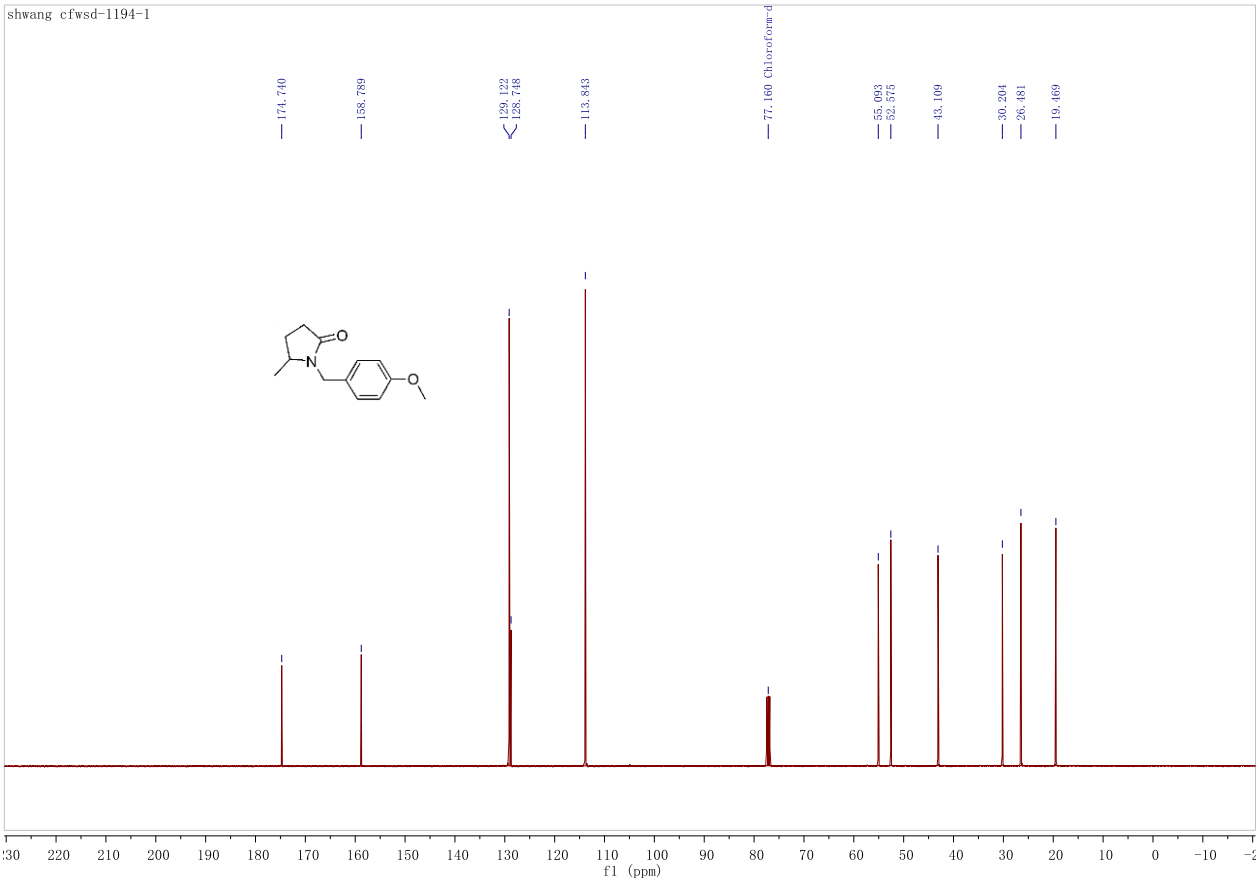

shwang cfwsd-1194-5.50.fid
7.26 CDCl3
3.57 3.56 3.54 3.52 3.44 3.43 3.42 3.41 3.40 3.39 3.38 2.79 2.78 2.77 2.76 2.75 2.73 2.25 2.24 2.22 2.21 2.20 2.18 2.18 2.17 2.17 2.16 2.15 2.06 2.06 2.05 2.04 2.03 2.01 2.01 1.45 1.44 1.43 1.42 1.42 1.41 1.40 1.39 1.38 1.37 1.37 1.36 1.35 1.34 1.30 1.28 1.27 1.27 1.26 1.13 1.07 1.06 1.05 1.05 1.04 0.75 0.73 0.73 0.72 0.71 0.70
1.00 1.01 1.21 2.04 1.06 3.32 9.59 3.31
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

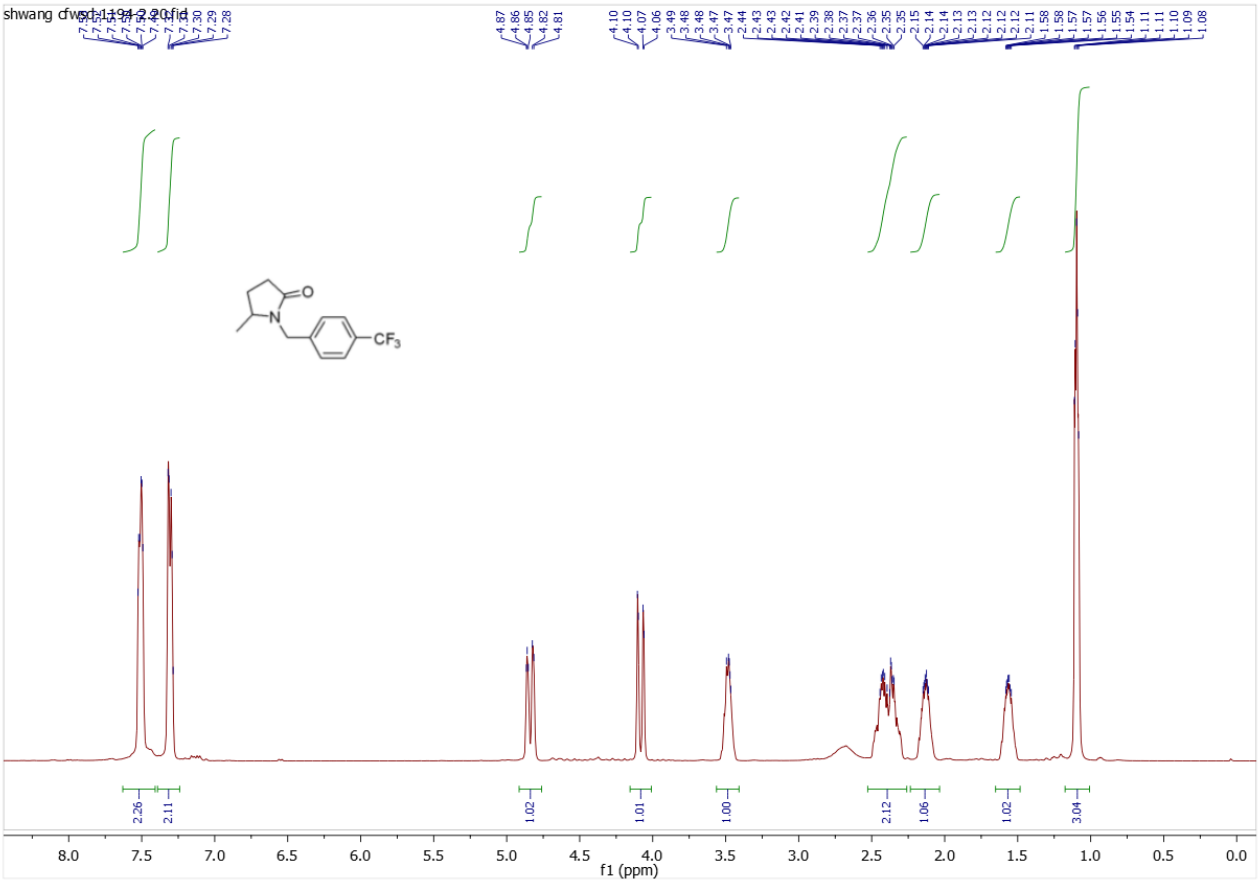

shwang cfwsd-1194-5
174.482
77.160 Chloroform-d
53.093
39.813
31.316
30.131
27.174
26.996
26.323
23.340
19.572
13.790
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

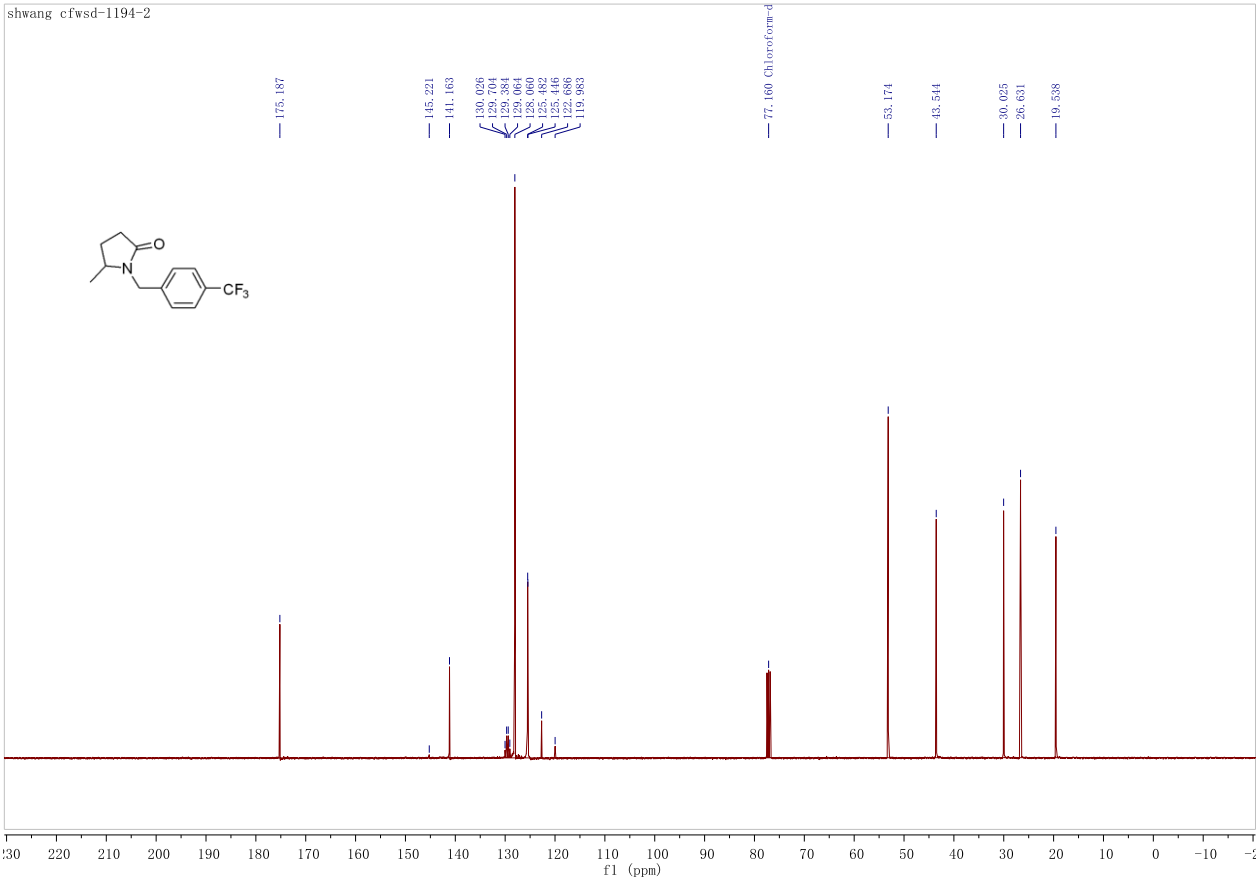

shwang cfwsd-1194-6.60.fid
f1 (ppm)

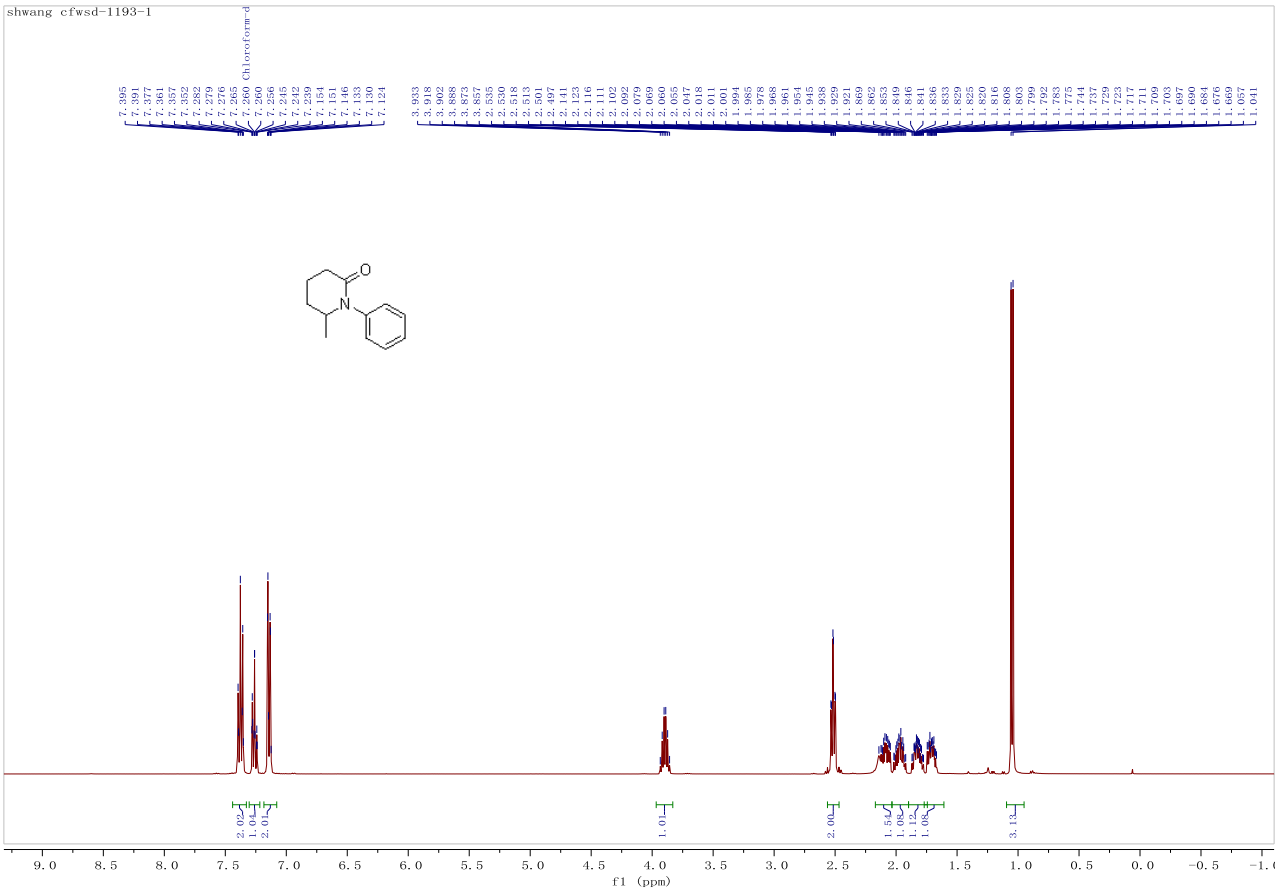

shwang cfwsd-1194-6
f1 (ppm)

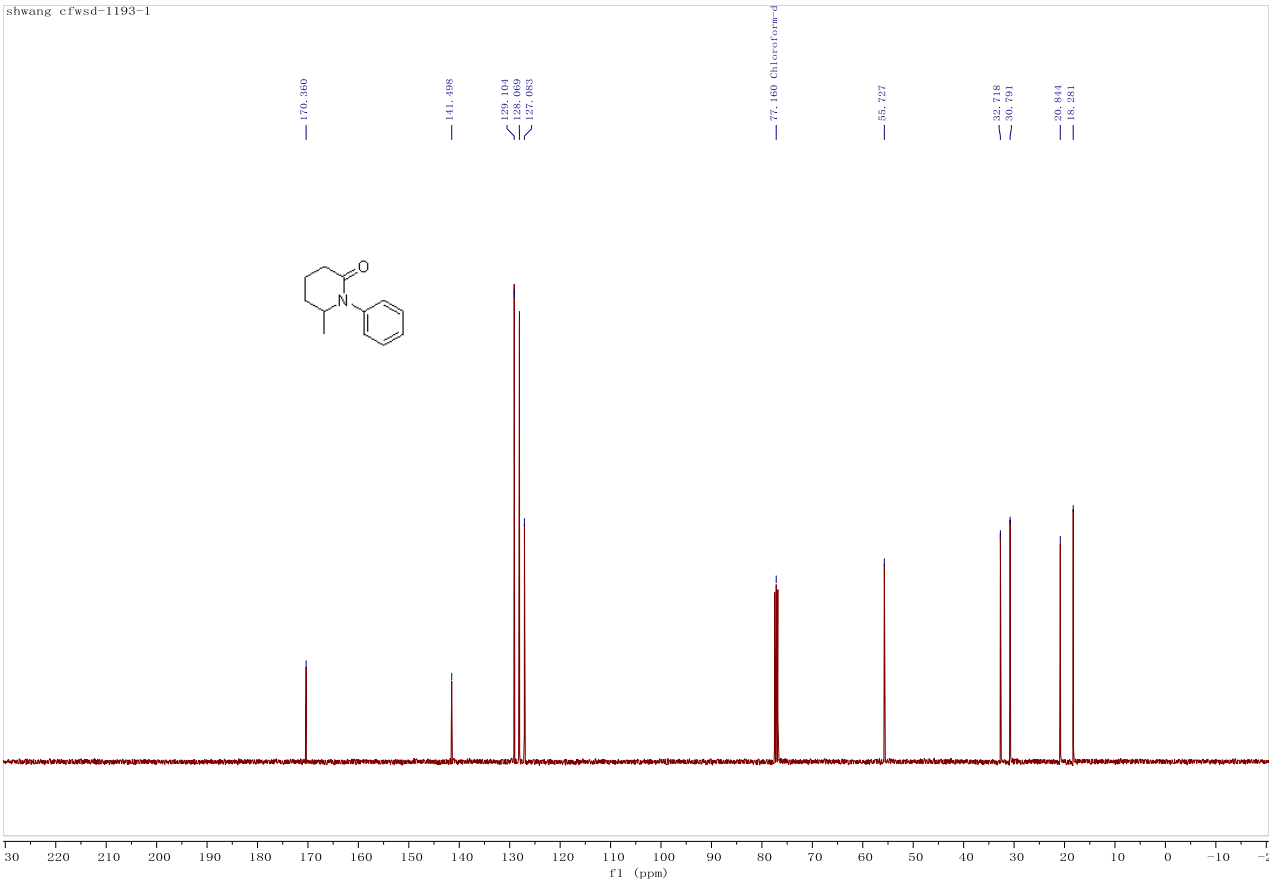

shwang cfwsd-1194-1-10.fid
f1 (ppm)

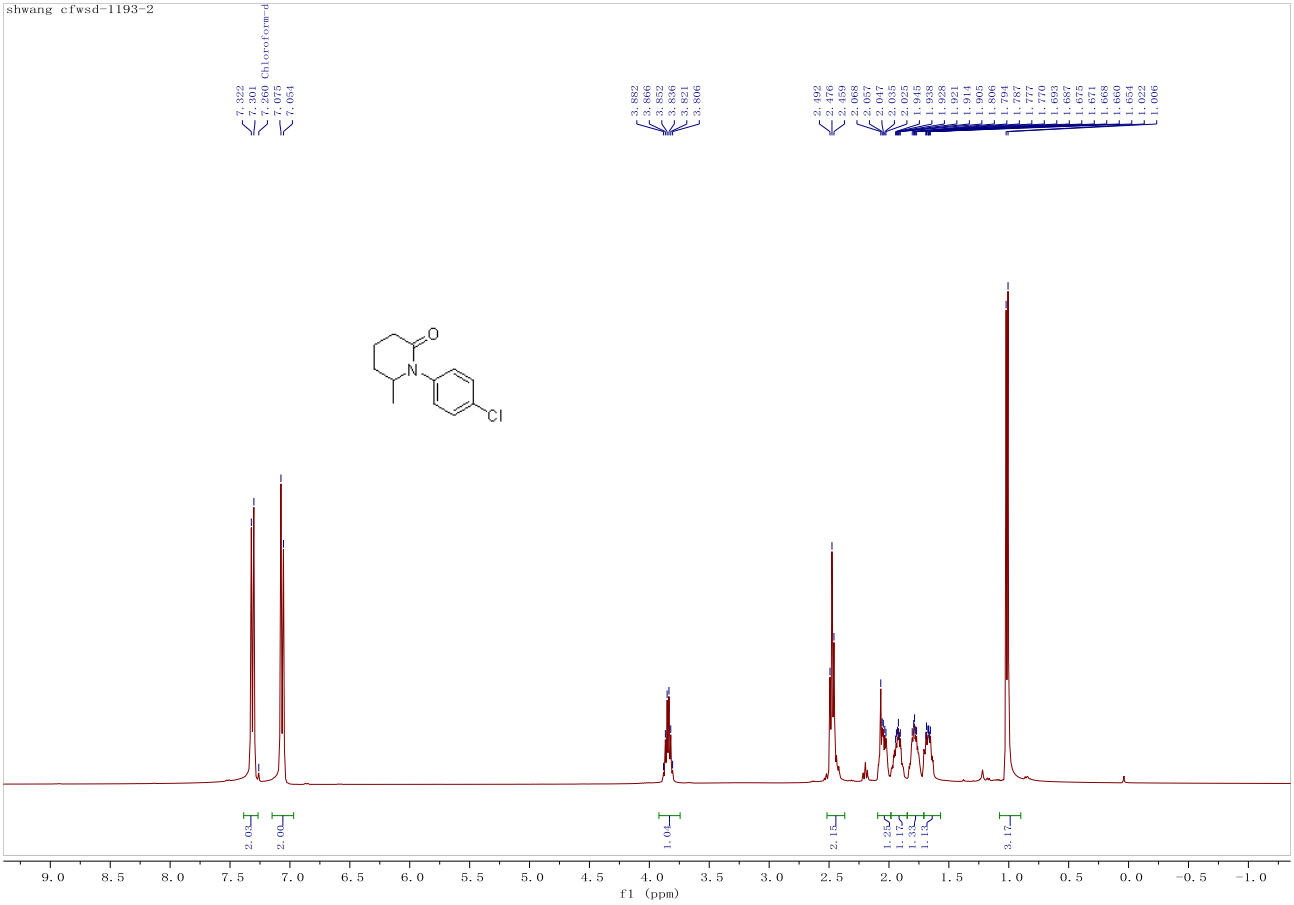

shwang cfwsd-1194-1
174.740
158.789
129.122
128.748
113.843
77.160 Chloroform-d
55.093
52.575
43.109
30.204
26.481
19.469
f1 (ppm)

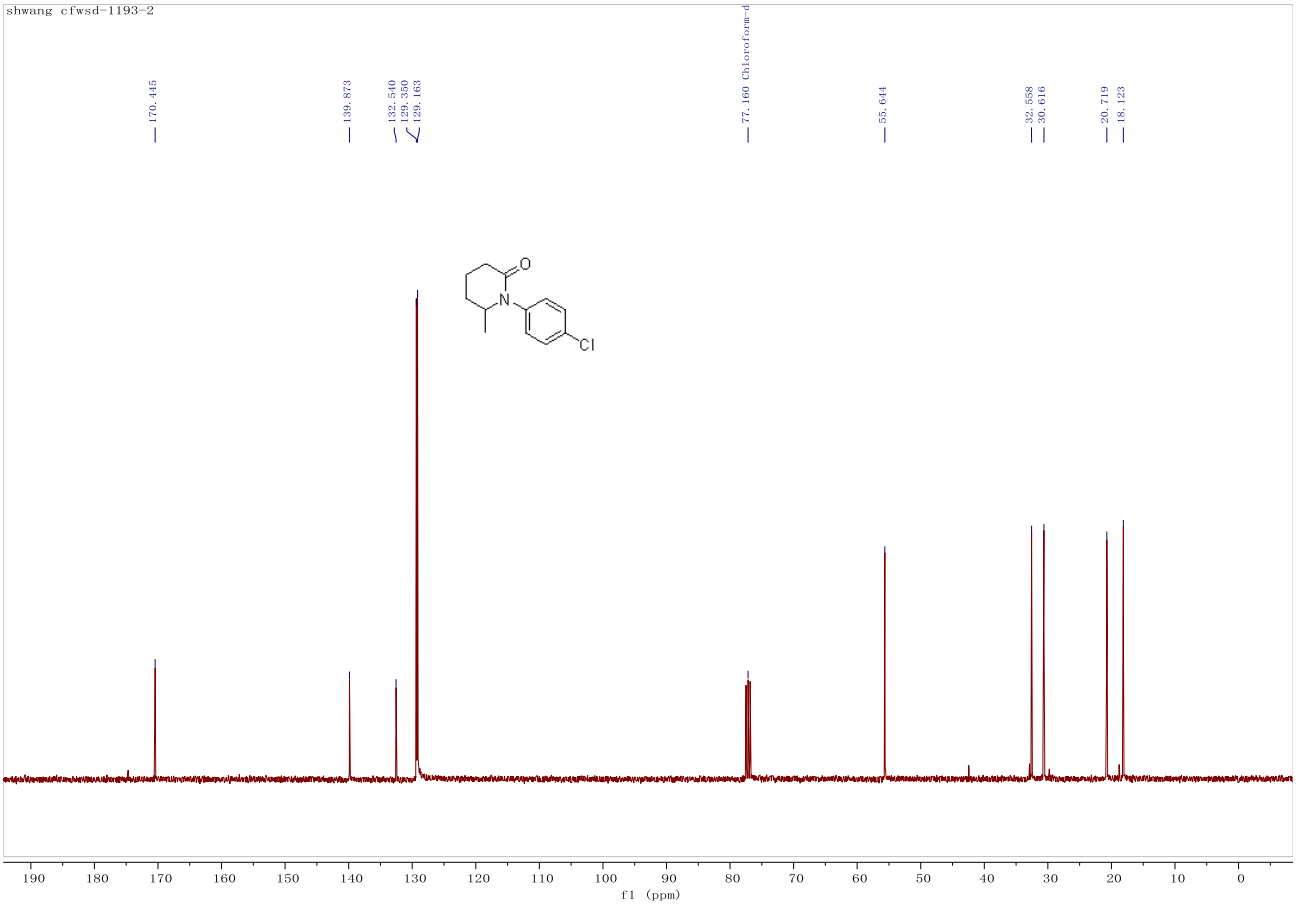

shwang cfwsd-1194-2.20.fid
f1 (ppm)

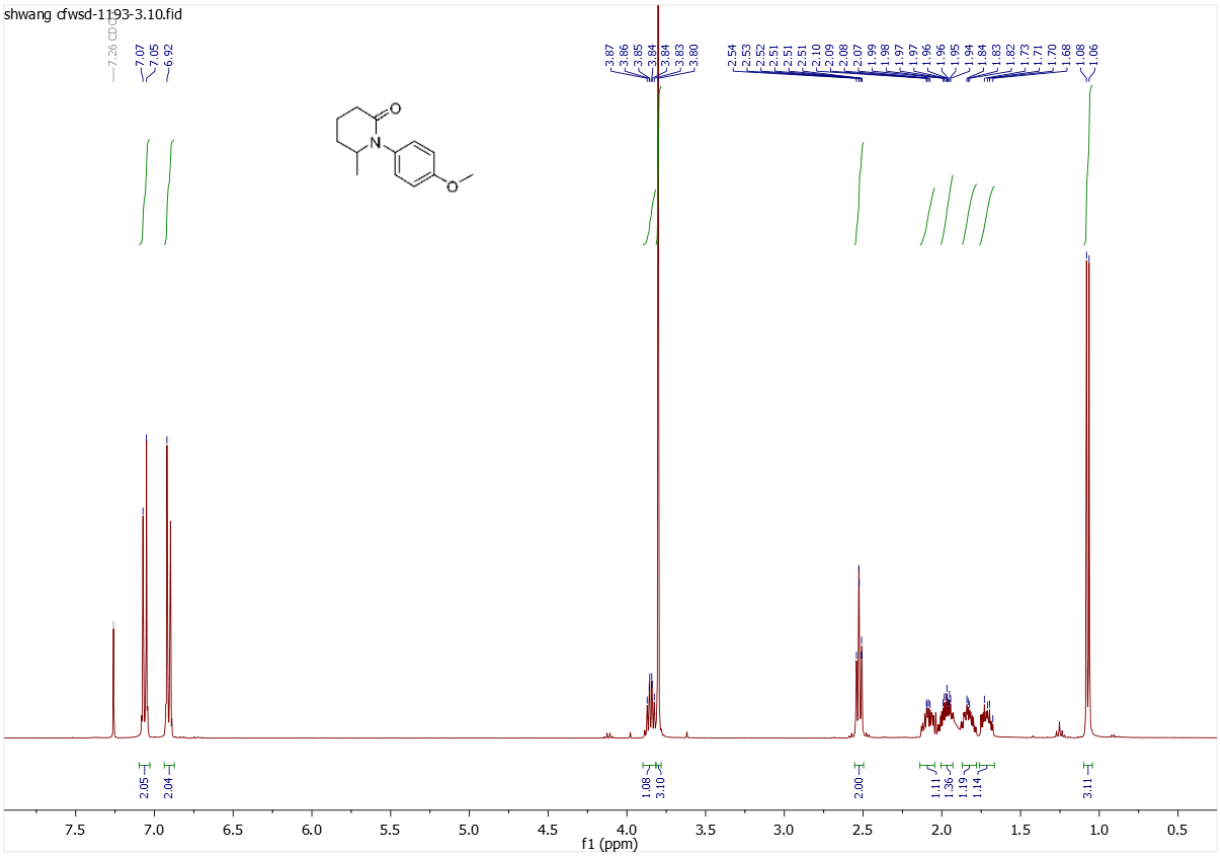

shwang cfwsd-1194-2
f1 (ppm)

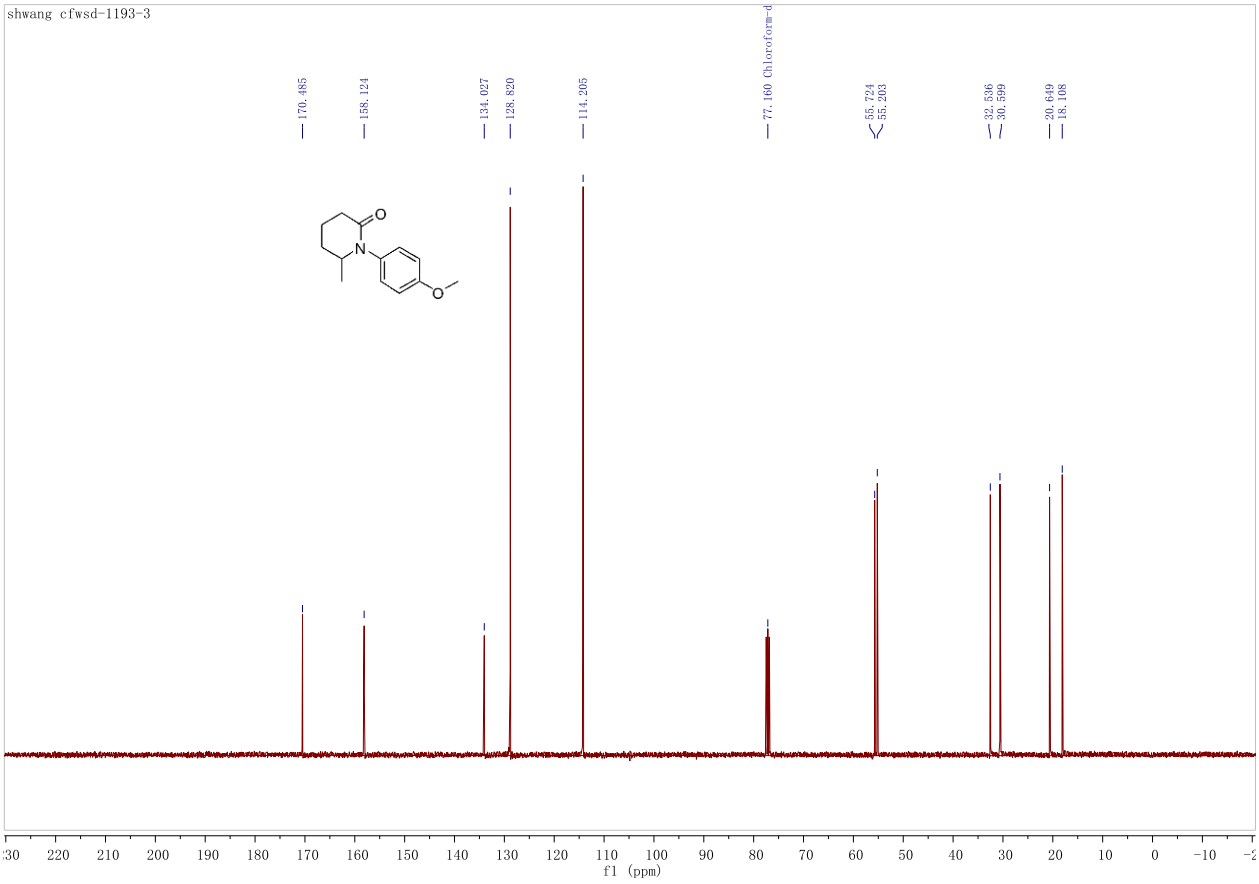

shwang cfwsd-1193-1
Chloroform-d
f1 (ppm)

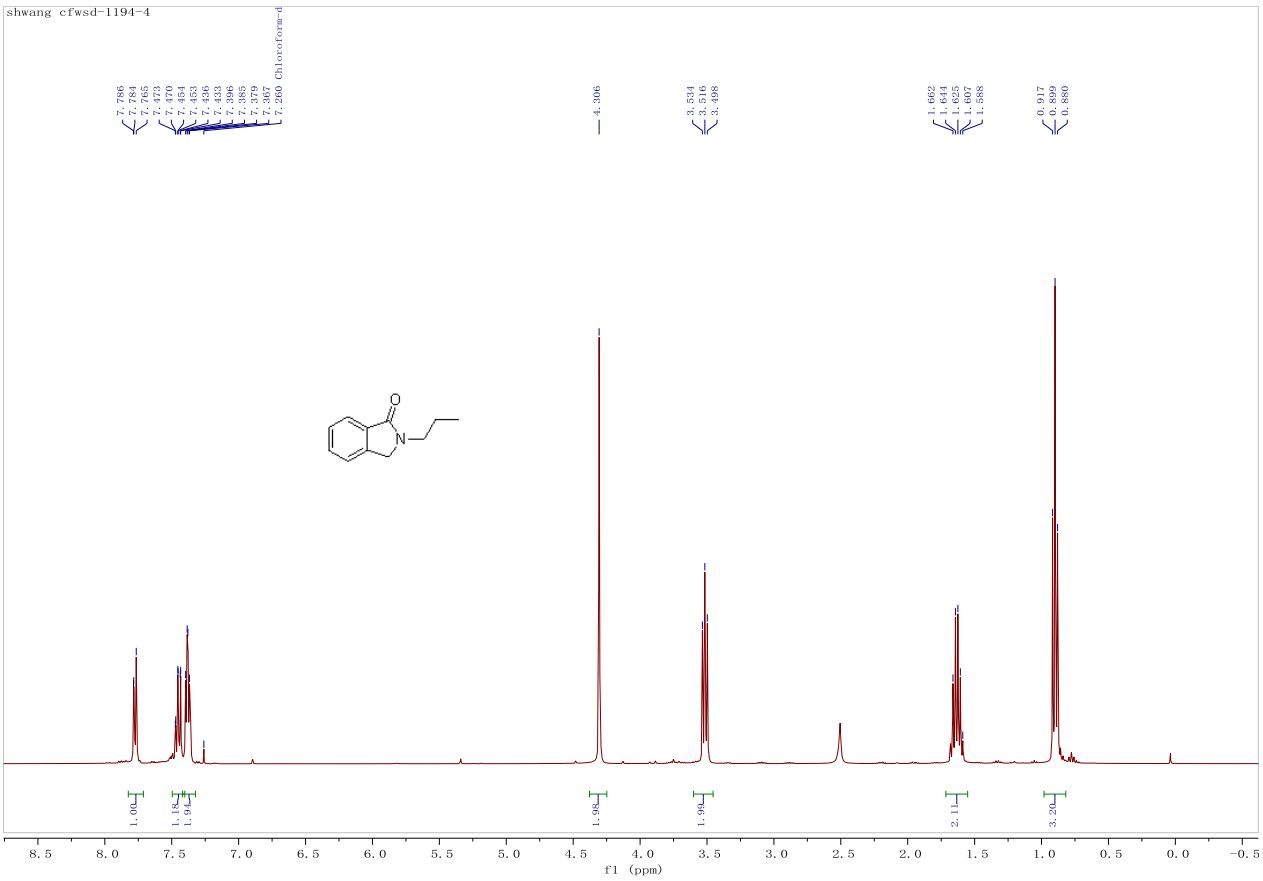

shwang cfwsd-1193-1
170.360
141.498
129.104
128.069
127.083
77.160 Chloroform-d
55.727
32.718
30.791
20.844
18.281
f1 (ppm)

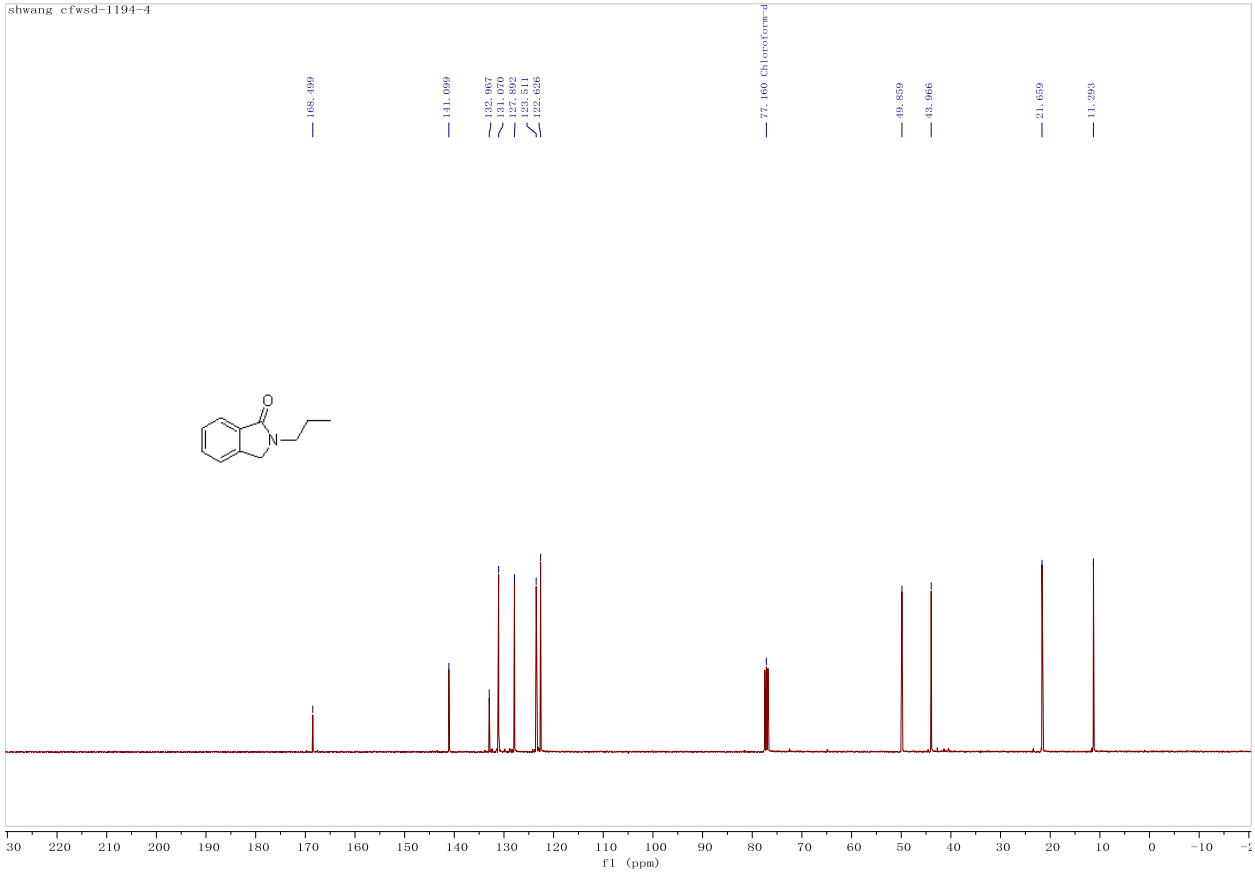

shwang cfwsd-1193-2
7.322
7.301
7.260 Chloroform-d
7.075
7.054
3.882
3.866
3.852
3.836
3.821
3.806
2.492
2.476
2.459
2.068
2.057
2.047
2.035
2.025
1.945
1.938
1.928
1.921
1.914
1.905
1.806
1.794
1.787
1.777
1.770
1.693
1.687
1.675
1.671
1.668
1.660
1.654
1.022
1.006
O
N
Cl
2.03
2.00
1.04
2.15
1.25
1.17
1.33
1.13
3.17
f1 (ppm)

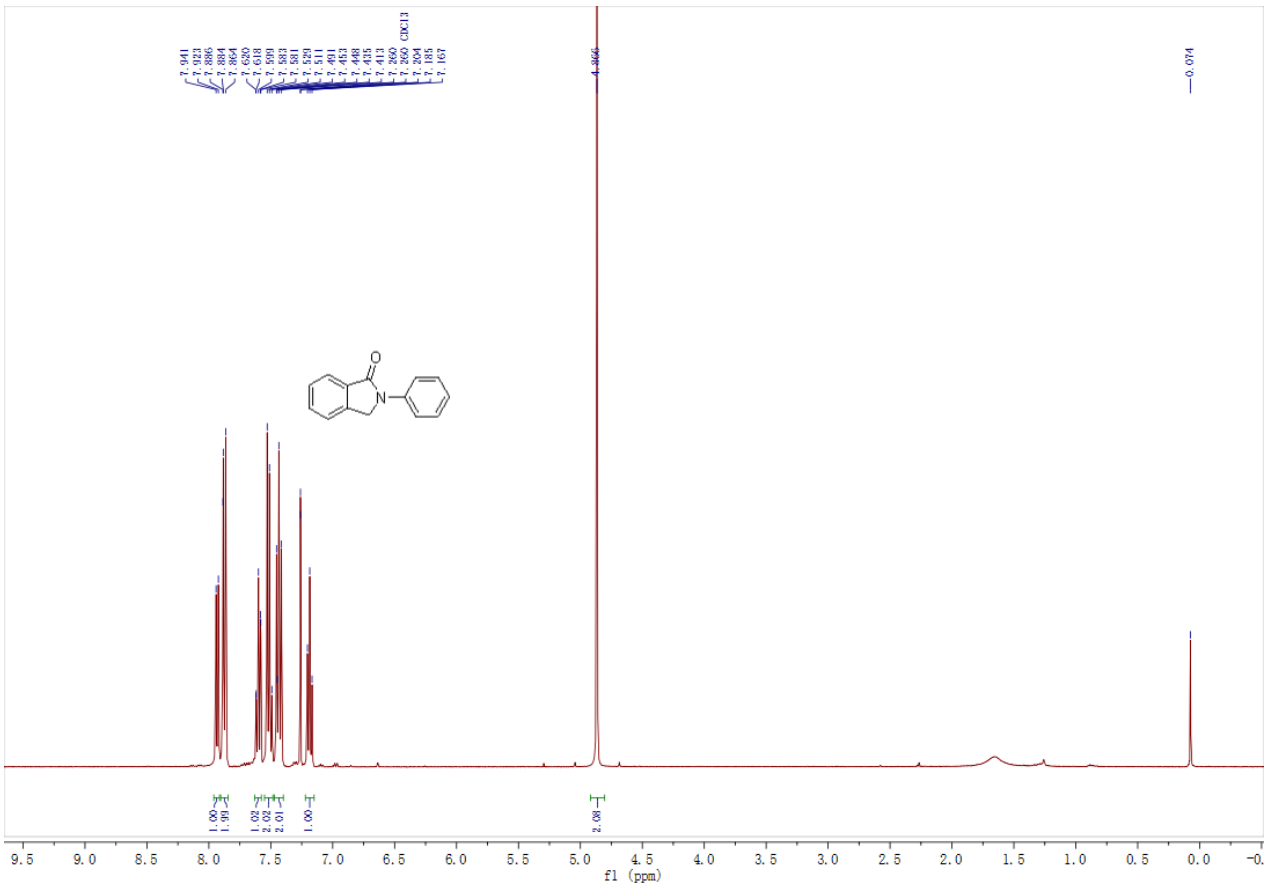

shwang cfwsd-1193-2
170.445
139.873
132.540
129.350
129.163
77.160 Chloroform-d
55.644
32.558
30.616
20.719
18.123
O
N
Cl
f1 (ppm)

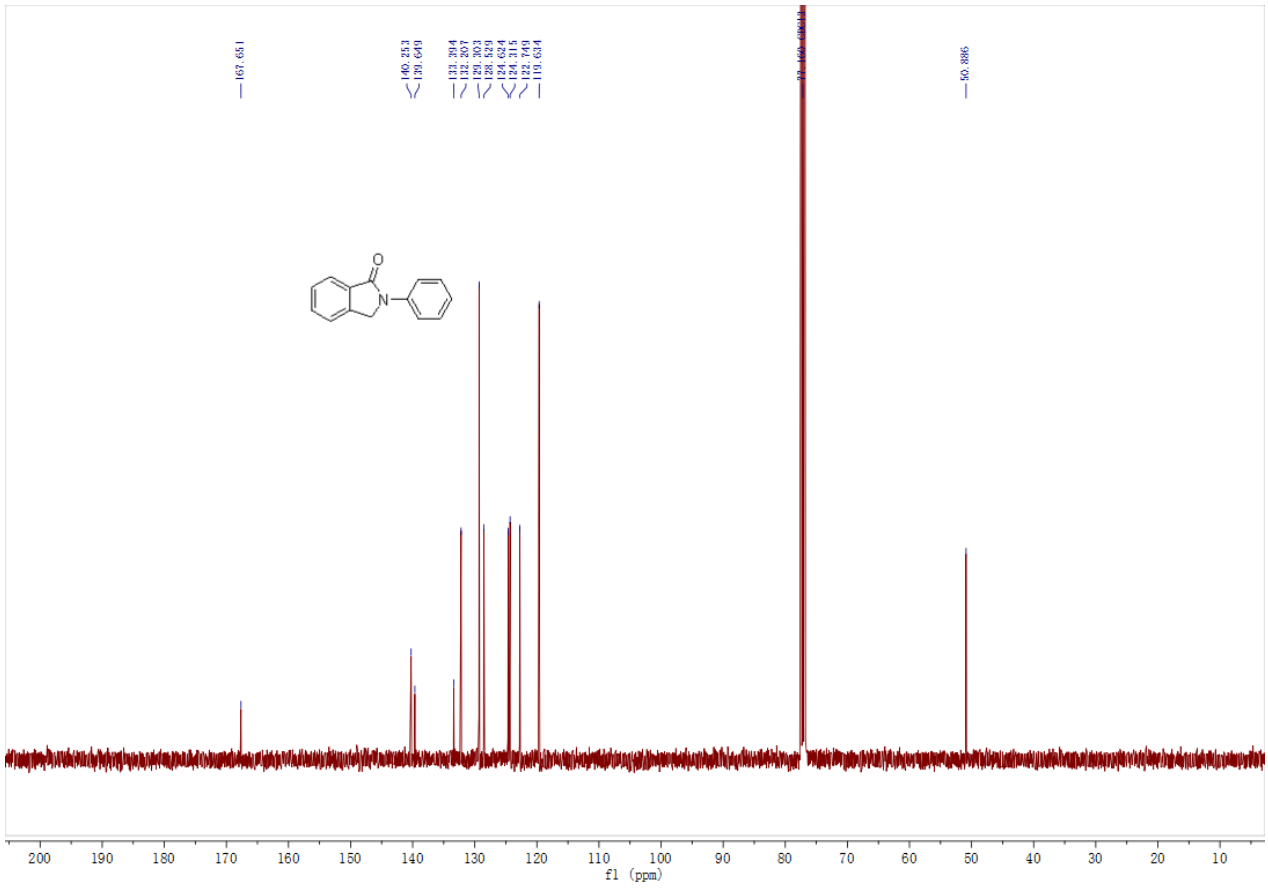

shwang cfwsd-1193-3.10.fid
f1 (ppm)

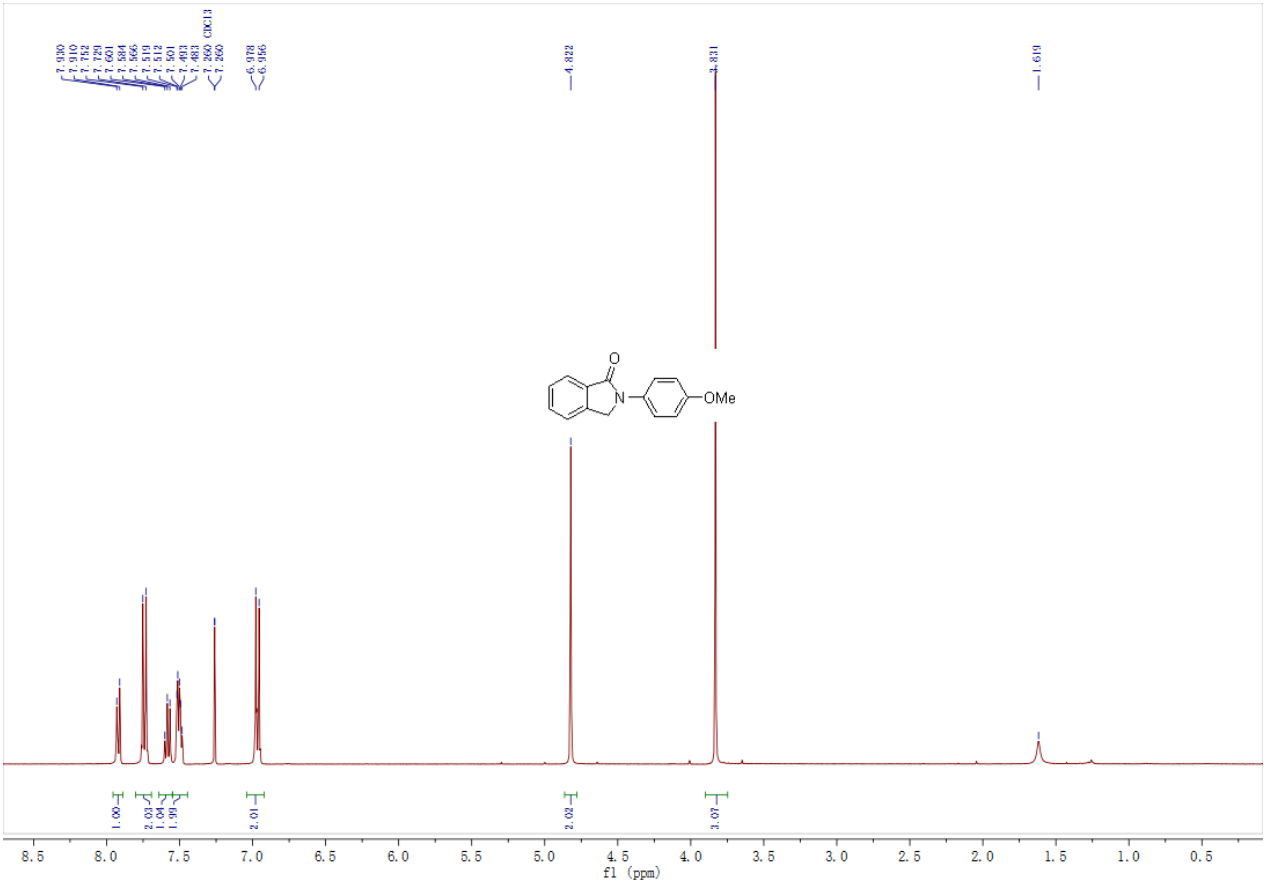

shwang cfwsd-1193-3
f1 (ppm)

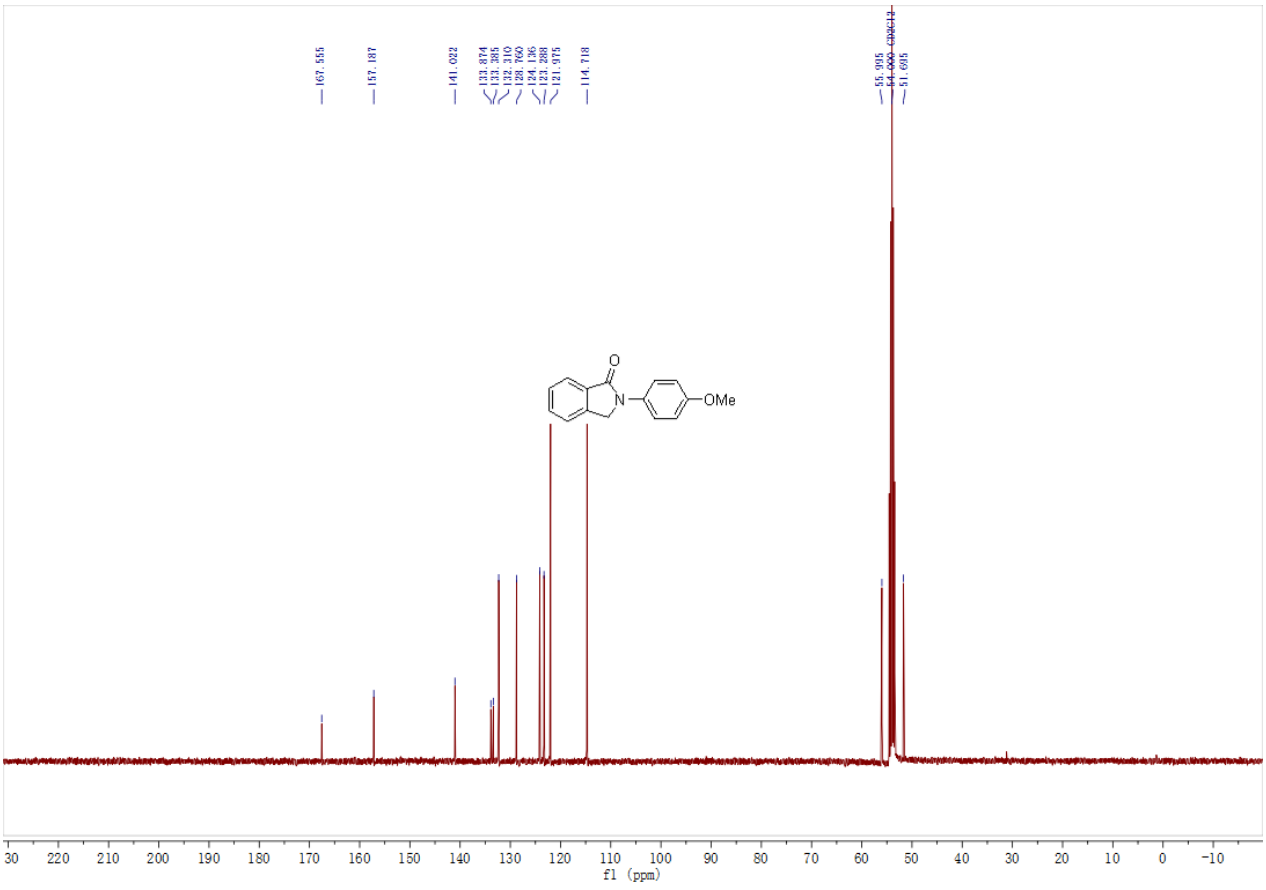

shwang cfwsd-1194-4
7.786
7.784
7.765
7.763
7.470
7.454
7.453
7.436
7.433
7.396
7.395
7.379
7.367
7.260 Chloroform-d
4.306
3.534
3.516
3.498
1.662
1.644
1.625
1.607
1.588
0.917
0.899
0.880
1.00
1.18
1.94
1.98
1.99
2.11
3.20
f1 (ppm)

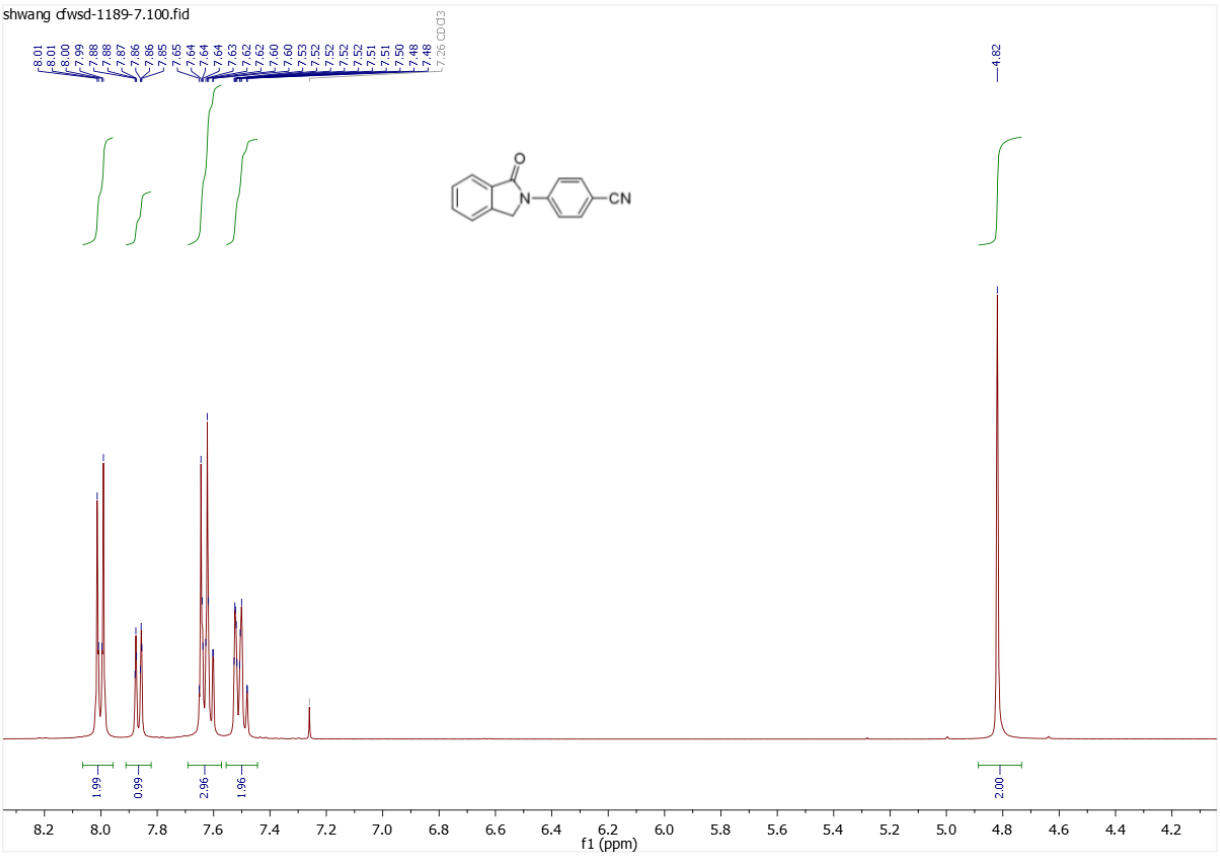

shwang cfwsd-1194-4
168.499
141.099
132.967
131.070
127.892
123.511
122.626
77.160 Chloroform-d
49.859
43.966
21.659
11.293
f1 (ppm)

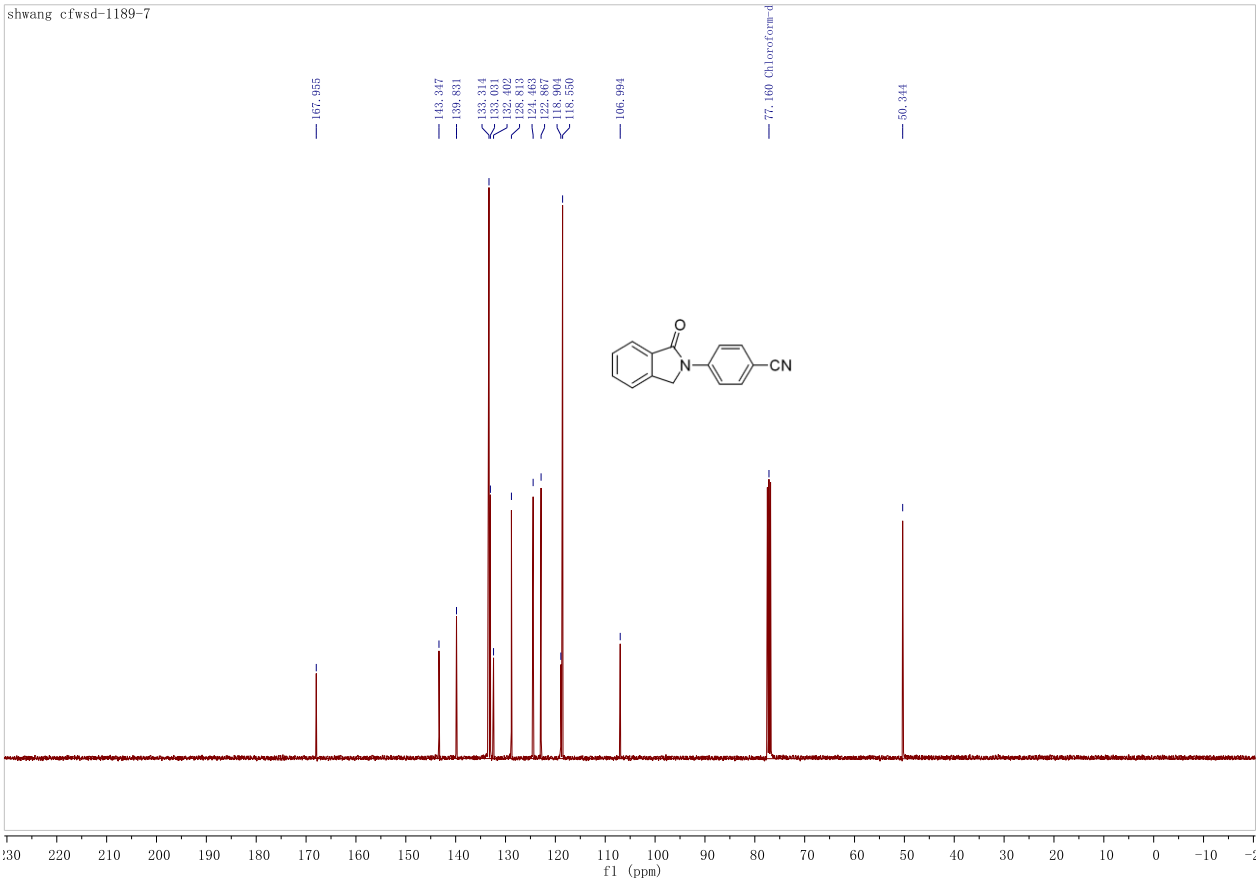

7.941
7.923
7.886
7.884
7.864
7.630
7.618
7.599
7.583
7.581
7.529
7.511
7.491
7.453
7.448
7.435
7.413
7.260 CDCl3
7.204
7.185
7.167
4.866
0.074
1.00
1.99
1.02
2.02
2.01
1.00
2.08
f1 (ppm)

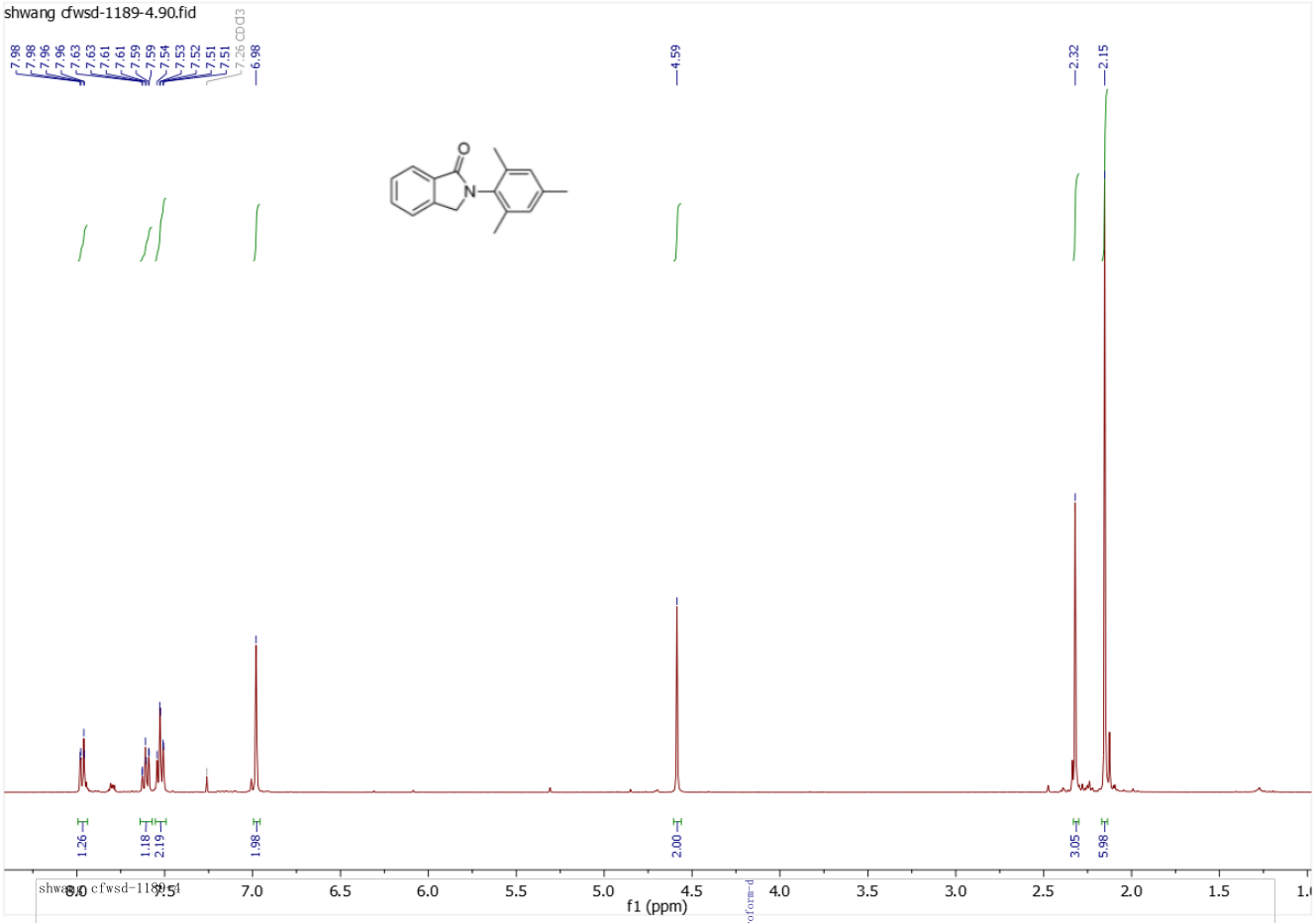

167.651
140.253
139.649
133.394
132.207
129.303
128.529
124.624
124.315
122.769
119.634
50.886
f1 (ppm)

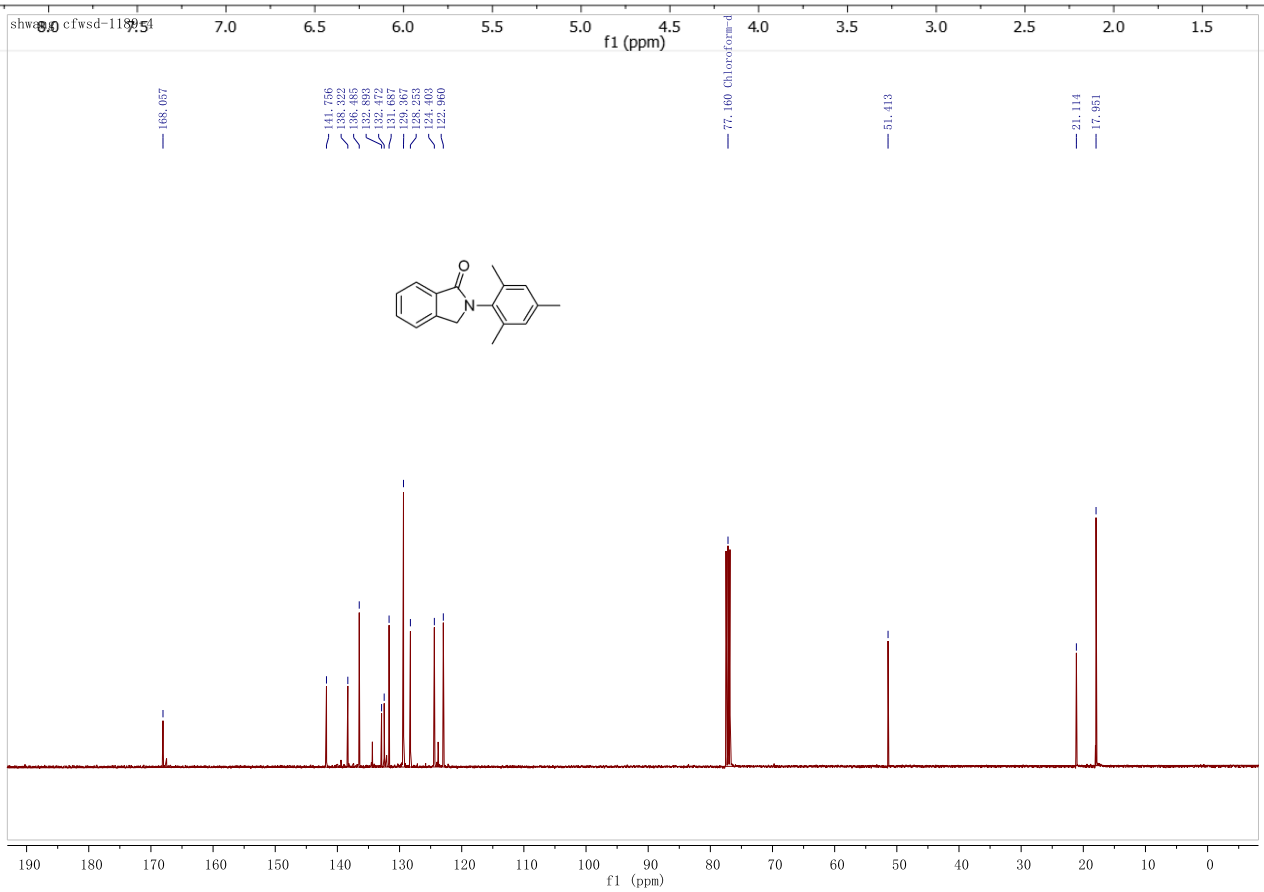

7.930
7.910
7.752
7.729
7.601
7.584
7.566
7.519
7.512
7.503
7.493
7.483
7.266 CDCl3
7.260
6.978
6.956
4.822
3.831
1.619
O
N
OMe
1.00
2.03
1.04
1.99
2.01
2.02
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

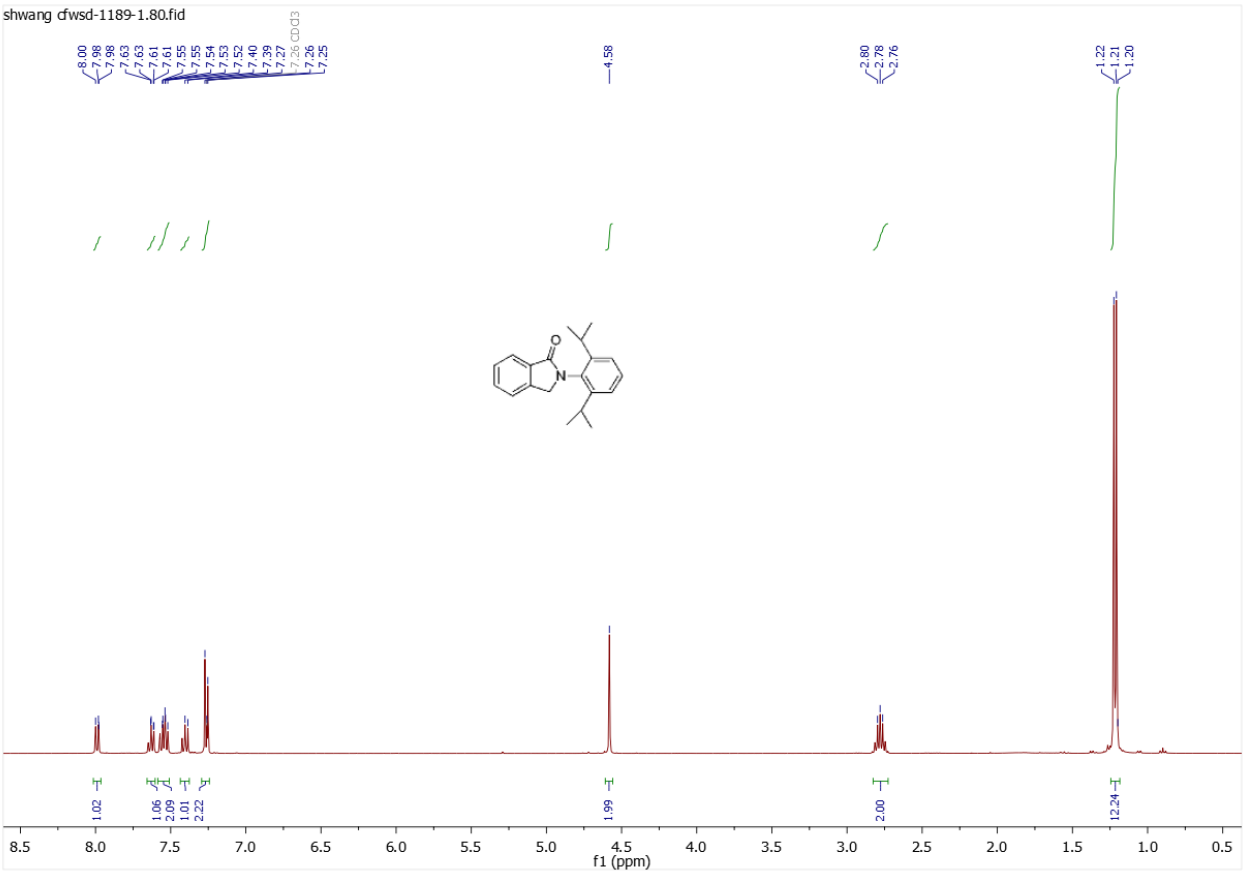

167.555
157.187
141.022
133.874
132.385
132.310
128.760
124.136
123.288
121.975
114.718
55.995
51.695
O
N
OMe
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

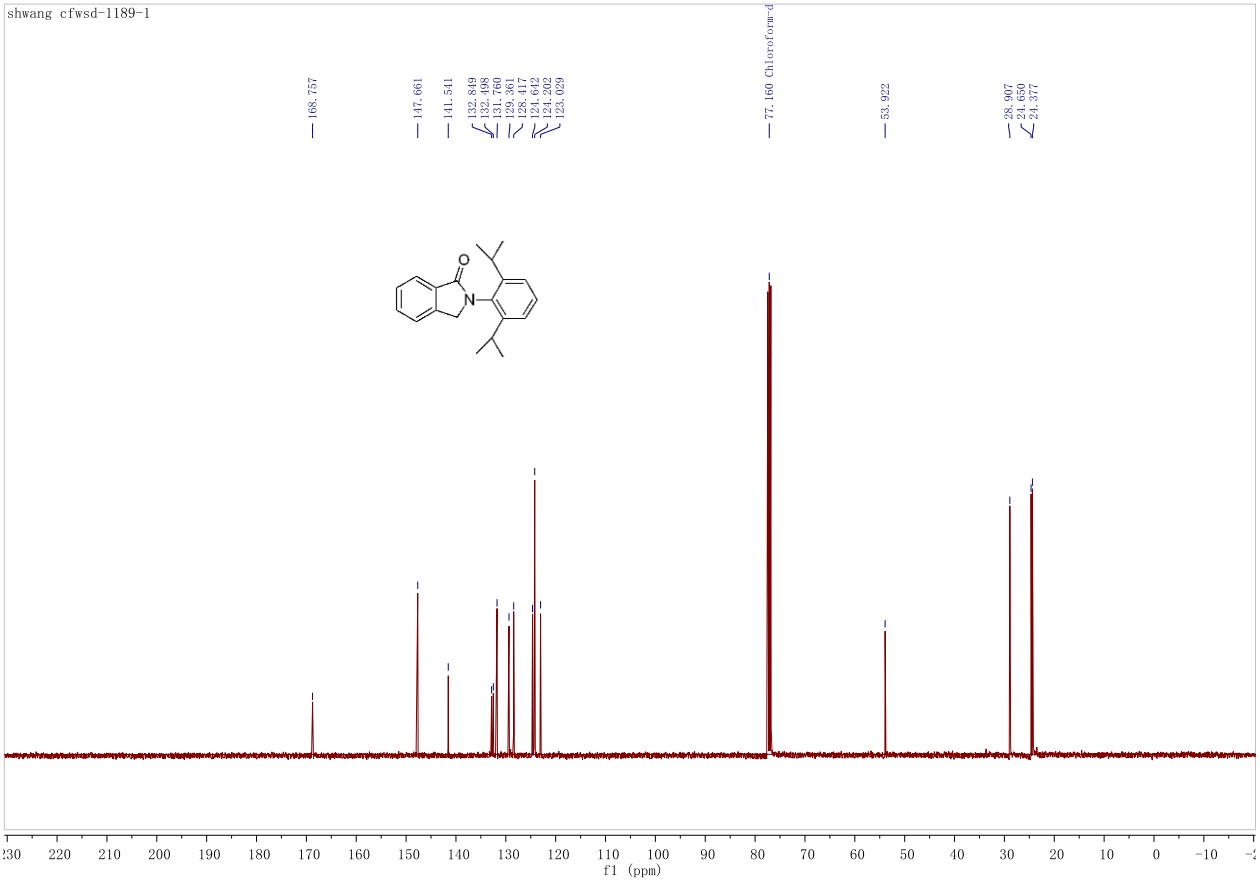

shwang cfwsd-1189-7.100.fid
8.01
8.01
8.00
7.99
7.88
7.88
7.87
7.86
7.86
7.85
7.65
7.64
7.64
7.64
7.63
7.62
7.62
7.62
7.60
7.60
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.50
7.48
7.48
7.36 CDCl3
4.82
O
N
CN
1.99
0.99
2.96
1.96
2.00
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
f1 (ppm)


shwang cfwsd-1189-7
167.955
143.347
139.831
133.314
133.031
132.802
129.813
124.463
122.867
118.904
118.550
106.994
77.160 Chloroform-d
50.344
O
N
CN
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


shwang cfwsd-1189-4.90.fid
7.98
7.98
7.96
7.96
7.63
7.63
7.61
7.61
7.59
7.59
7.54
7.53
7.52
7.51
7.51
7.26 CDCl3
6.98
4.59
2.32
2.15
1.26
1.18
2.19
1.98
2.00
3.05
5.98
f1 (ppm)


168.057
141.756
138.322
136.485
132.893
132.472
131.687
129.367
128.253
124.403
122.960
77.160 Chloroform-d
51.413
21.114
17.951
f1 (ppm)


shwang cfwsd-1189-1.80.fid
8.00
7.98
7.98
7.63
7.63
7.61
7.61
7.55
7.55
7.54
7.53
7.52
7.40
7.39
7.27
7.26 CDCl3
7.25
4.58
2.80
2.78
2.76
1.22
1.21
1.20
1.02
1.06
2.09
1.01
2.22
1.99
2.00
12.24
f1 (ppm)


shwang cfwsd-1189-1
168.757
147.661
141.541
132.849
132.498
131.760
129.361
128.417
124.642
124.202
123.029
77.160 Chloroform-d
53.922
28.907
24.650
24.377
f1 (ppm)