Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Supporting Information

## Synthesis of Chiral Piperazin-2-ones through Palladium-Catalyzed Asymmetric Hydrogenation of Pyrazin-2-ols

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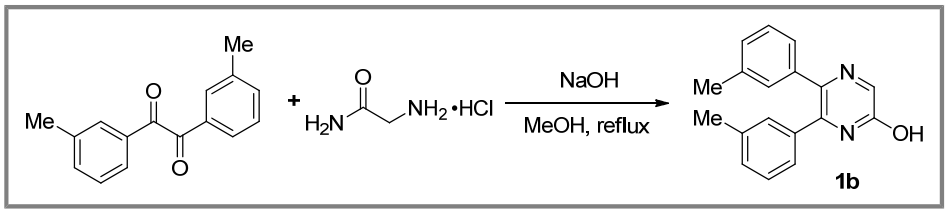
## 1. General and Materials

**General:** All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. $^{1}H$ NMR, $^{13}C$ NMR spectra were recorded at room temperature in $CDCl_3$ or DMSO-$d_6$ on 400 MHz instrument with TMS as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). The heat source for all heating reactions is the oil bath. High-resolution mass spectrometry (HRMS) was measured on an electrospray ionization (ESI) apparatus using the time-of-flight (TOF) mass spectrometry. All reactions were monitored by TLC analysis.

**Materials:** Commercially available reagents and solvents were used throughout without further purification.

## 2. Synthesis of Pyrazin-2-ol Derivatives

The pyrazin-2-ol derivatives **1** could be synthesized in two methods. One is from commercially available dichloropyrazine through 2,3-diarylpyrazines intermediate **S1** according to the literature procedure.[1] Subsequently, pyrazin-2-ol derivatives could be prepared from the intermediate **S1** through oxidation and rearrangement according to the literature procedure with slight modification.[2] The pyrazin-2-ol derivatives **1a**,[3a] **1c**,[3b] **1e**,[3c] **1j**,[3d] **1n**[3e] and **1o**[3f] are the known compounds. The other is from readily available 1,2-diketone and glycinamide hydrochloride according to the literature procedure,[3b] 5,6-di-*m*-tolylpyrazin-2-ol **1b** could be conveniently prepared.




**Typical procedure**: Under the nitrogen atmosphere, 1,2-di-*m*-tolylethane-1,2-dione (1.195 g, 5.0 mmol), glycinamide hydrochloride (0.663 g, 6.0 mmol), sodium hydroxide (0.480 g, 12.0 mmol) and methanol (10 mL) were added to a dry flask. This mixture was heated under reflux for 3 hours. Then, the temperature of the flask was cooled to room temperature, concentrated hydrochloric acid (1.0 mL) was added to this mixture, and stirring was performed for 30 minutes. Subsequently, the mixture pH was adjusted to 7 with the saturated potassium bicarbonate solution. Filtration was performed to give a solid, and washed with water and cool methanol. The crude product was recrystallized with toluene to give pale yellow solid.

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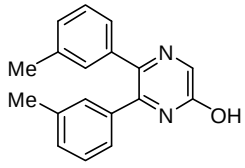
**5,6-Di-*m*-tolylpyrazin-2-ol (1b):** 0.845 g, 68% yield, pale yellow solid, new compound, mp: 178-179 $^{o}C$, $R_f$ = 0.49 (ethyl acetate). $^{1}H$ NMR (400 MHz, DMSO-$d_6$) δ 12.17 (s, 1H), 8.12 (s, 1H), 7.24-7.16 (m, 4H), 7.09-7.02 (m, 3H), 6.91 (d, *J* = 7.2 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 157.3, 138.3, 137.9, 137.4, 130.6, 130.2, 130.0, 128.5, 128.3, 128.0, 127.2, 126.8, 21.5, 21.4. HRMS Calcu- lated for $C_{18}H_{17}N_2O$ $[M+H]^+$ 277.1335, found 277.1332.

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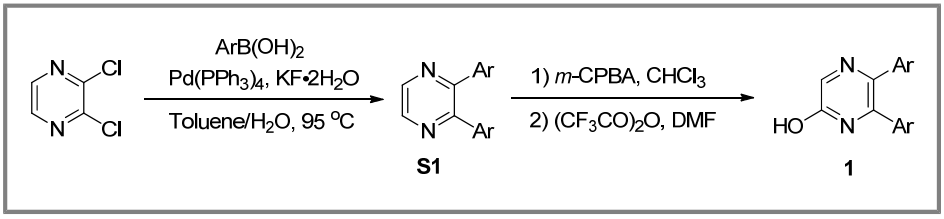


**General procedure**: Under nitrogen atmosphere, aryl boronic acid (22.0 mmol) was added to a mixture of 2,3-dichloropyrazine (1.490 g, 10.0 mmol), $Pd(PPh_3)_4$ (116 mg, 0.10 mmol, 1.0%), toluene (20 mL) and water (20 mL). The resulting solution was heated at 95 °C for 10 min. Then, the mixture was cooled down to room temperature. Next, potassium fluoride dihydrate (2.071 g, 22.0 mmol) was added in one portion. The mixture was stirred and heated at 95 °C until the starting material was consumed. After cooling to room temperature, organic phase was separated. The aqueous phase was extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexanes/ethyl acetate as eluent to give the **S1**.

Subsequently, *m*-CPBA (1.908 g, 9.4 mmol, 85% wt) was added to a solution of **S1** (7.2 mmol) in chloroform (15 mL) at 0 °C. After stirring for 1 h, TLC indicated that the reaction finished. Sodium thiosulfate solution (8.0 mL) was added to the reaction mixture. The organic phases were separated. The aqueous phase was extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered and concentrated. This crude product was immediately used for the next step without further purification.

Next, trifluoroacetic anhydride (6.049 g, 28.8 mmol) was added to the solution of the above crude product in anhydrous DMF (3.0 mL) at 0 ºC. The reaction mixture was stirred at 25 ºC for 12 h. Then the mixture pH adjusted to 7 with saturated sodium bicarbonate solution and stirred for 2 h. Filtration was performed to give a solid. The solid was dissolved in dichloromethane and the solution was dried over anhydrous sodium sulfate, filtered and concentrated under the reduced pressure. The residue was purified by flash column chromatography using hexanes/ethyl acetate as eluent to give the desired products **1**.

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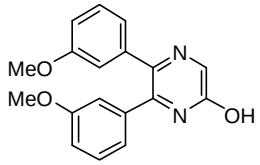
**5,6-Bis(3-methoxyphenyl)pyrazin-2-ol (1d):**

0.978 g, 32% yield (three steps), pale yellow solid, new compound, mp: 197-198 °C, $R_f$ = 0.72 (ethyl acetate). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.20 (s, 1H), 8.10 (s, 1H), 7.22 (t, *J* = 8.4 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 6.92-6.91 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 6.4 Hz, 3H), 3.64 (s, 3H), 3.57 (s, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 158.9, 158.7, 156.8, 142.4, 139.2, 136.4, 129.3, 128.8, 121.8, 121.5, 114.9, 114.8, 114.5, 113.1, 55.0, 54.8. HRMS Calculated for $C_{18}H_{17}N_2O_3$ $[M+H]^+$ 309.1234, found 309.1231.

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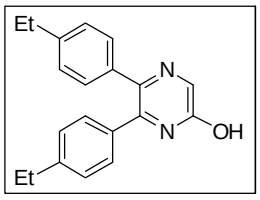
**5,6-Bis(4-ethylphenyl)pyrazin-2-ol (1f):**

1.055 g, 44% yield (three steps), pale yellow solid, new compound, mp: 185-186 °C, $R_f$ = 0. 62 (ethyl acetate). $^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.09 (s, 1H), 8.07 (s, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.15-7.11 (m, 4H), 7.03 (d, *J* = 7.8 Hz, 2H), 2.61-2.55 (m, 2H), 2.54-2.50 (m, 2H), 1.15 (d, *J*



= 7.8 Hz, 3H), 1.11 (d, *J* = 7.8 Hz, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 156.7, 144.6, 142.6, 141.8, 139.2, 136.6, 135.5, 132.7, 129.5, 129.1, 127.5, 127.2, 27.8, 27.7, 15.1, 15.0. HRMS Calculated for $C_{20}H_{21}N_2O$ $[M+H]^+$ 305.1648, found 305.1649.

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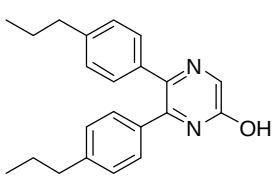
**5,6-Bis(4-propylphenyl)pyrazin-2-ol (1g):**

0.983 g, 30% yield (three steps), pale yellow solid, new compound, mp: 178-179 °C, $R_f$ = 0.65 (ethyl acetate). 

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.05 (s, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.12-7.09 (m, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 2.52 (t, *J* = 7.6 Hz, 2H), 2.47 (d, *J* = 7.4 Hz, 2H), 1.60-1.54 (m, 2H), 1.54-1.48 (m, 2H), 0.86-0.84 (m, 3H), 0.83-0.80 (m, 3H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 156.9, 142.9, 142.1, 141.0, 138.9, 136.8, 135.6, 132.9, 129.4, 129.0, 128.0, 127.7, 36.9, 36.8, 23.7, 23.6, 13.4, 13.3. HRMS Calculated for $C_{22}H_{25}N_2O$ $[M+H]^+$ 333.1961, found 333.1966.

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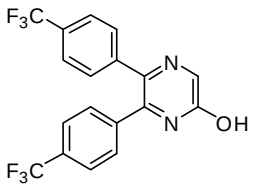
**5,6-Bis(4-(trifluoromethyl)phenyl)pyrazin-2-ol (1h):**

1.441 g, 37% yield (three steps), pale yellow solid, new compound, mp: 219-220 °C, $R_f$ = 0.60 (ethyl acetate). 

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.38 (s, 1H), 8.21 (s, 1H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.58 (dd, *J* = 12.6, 8.4 Hz, 4H), 7.44 (d, *J* = 7.8 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ157.5, 143.2, 142.1, 141.8, 139.6, 130.6, 130.4, 129.3 (q, *J* = 31.5 Hz), 127.9 (q, *J* = 31.5 Hz), 125.2, 124.9, 124.1 (q, *J* = 271.8 Hz), 123.9 (q, *J* = 271.8 Hz), 123.0. $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -60.99, -61.15. HRMS Calculated for $C_{18}H_{11}N_2O_1F_6$ $[M+H]^+$ 385.0770, found 385.0771.

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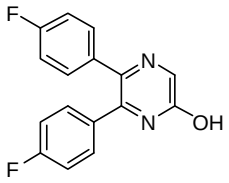
**5,6-Bis(4-fluorophenyl)pyrazin-2-ol (1i):**

1.216 g, 43% yield (three steps), pale yellow solid, new compound, mp: 207-208 °C, $R_f$ = 0.68 (ethyl acetate). 

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.22 (s, 1H), 8.10 (s, 1H), 7.35 (dd, *J* = 8.4, 5.8 Hz, 2H), 7.23 (dd, *J* = 8.2, 5.8 Hz, 2H), 7.15 (t, *J* = 8.8 Hz, 2H), 7.05 (t, *J* = 8.8 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 163.1 (d, *J* = 245 Hz), 160.6 (d, *J* = 243 Hz), 157.0, 141.8, 138.8, 136.5, 134.3, 131.9 (d, *J* = 8.5 Hz), 131.2 (d, *J* = 8.0 Hz), 115.3 (d, *J* = 21.8 Hz), 114.8 (d, *J* = 21.5 Hz). $^{19}$F NMR (376 MHz, DMSO-$d_6$) δ -112.16, -114.69. HRMS Calculated for $C_{16}H_{11}N_2OF_2$ $[M+H]^+$ 285.0834, found 285.0832.

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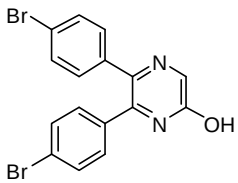
**5,6-Bis(4-bromophenyl)pyrazin-2-ol (1k):**

0.567 g, 28% yield (three steps), pale yellow solid, new compound, mp: 245-246 °C, $R_f$ = 0.50 (ethyl acetate). 

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 12.27 (s, 1H), 8.14 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 157.2, 137.1, 134.6, 132.1, 131.7, 131.4, 131.4, 131.3, 131.1, 131.0, 122.6, 120.9. HRMS Calculated for $C_{16}H_{11}N_2OBr_2$ $[M+H]^+$ 404.9233 ($^{79}$Br and $^{79}$Br), found 404.9230 ($^{79}$Br and $^{79}$Br), 406.9211 ($^{79}$Br and $^{81}$Br), 408.9202 ($^{81}$Br and $^{81}$Br)

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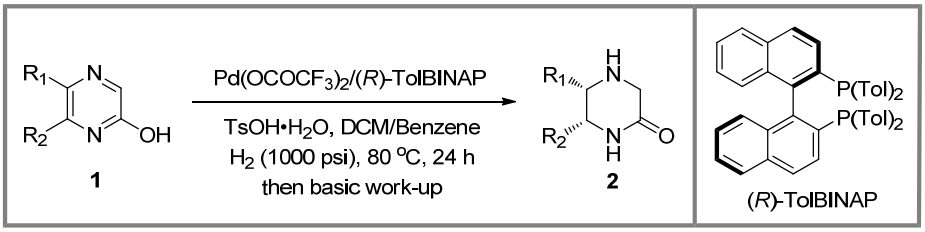
**5,6-Di(naphthalen-2-yl)pyrazin-2-ol (1l):**

1.117 g, 32%, yield (three steps), pale yellow solid, new compound, mp: 224-225 $^{o}$C, $R_f$ = 0.59 (ethyl acetate). $^{1}$H NMR (400 MHz, DMSO-$d_6$) δ 12.21 (s, 1H), 8.23 (s, 1H), 8.05 (s, 1H), 7.91 (s, 1H), 7.84-7.78 (m, 2H), 7.77-7.72 (m, 2H), 7.69-7.62 (m, 2H), 7.51-7.46 (m, 2H), 7.44-7.37 (m, 2H), 7.35-7.28 (m, 2H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 157.0, 142.5, 139.6, 139.3, 137.3, 135.5, 132.9, 132.7, 132.7, 132.6, 132.5, 132.0, 129.4, 128.3, 128.2, 127.9, 127.5, 127.4, 127.2, 127.1, 127.0, 126.9, 126.5, 126.2. HRMS Calculated for $C_{24}H_{17}N_2O$ $[M+H]^+$ 349.1335, found 349.1338.

**5-(4-Methoxyphenyl)-6-phenylpyrazin-2-ol (1m):**

0.545 g, 14% yield (four steps), yellow solid, new compound, mp: 255-256 $^{o}$C, $R_f$ = 0.20 (hexanes/ethyl acetate). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 11.99 (s, 1H), 8.21 (s, 1H), 7.47-7.30 (m, 5H), 7.19 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 159.1, 157.0, 146.2, 135.4, 133.7, 132.7, 130.6, 130.0, 129.3, 129.2, 129.0, 113.7, 55.2. HRMS Calculated for $C_{17}H_{15}N_2O_2$ $[M+H]^+$ 279.1128, found 279.1124.

## 3. Palladium-Catalyzed Asymmetric Hydrogenation of Pyrazin-2-ols 1




**General procedure**: Palladium trifluoroacetate (3.0 mg, 0.009 mmol, 3.0 mol%) and ligand (*R*)-Tol-BINAP (6.6 mg, 0.0099 mmol, 3.3 mol%) were placed in a dried Schlenk tube under nitrogen atmosphere. Then degassed anhydrous acetone (1.0 mL) was added to the mixture. The mixture was stirred at room temperature for 30 min, then the solvent was removed under vacuum to give the catalyst. In a glovebox, pyrazin-2-ol **1** (0.2 mmol or 0.3 mmol) and $TsOH{\cdot}H_2O$ (1 equiv.) were stirred in benzene (1.5 mL) at room temperature for 5 min. Subsequently, a solution of the above palladium catalyst in dichloromethane (1.5 mL) was added to the reaction mixture. The hydrogenation was performed at 80 °C under hydrogen gas (1000 psi) in a stainless steel autoclave for 24-48 h. The mixture was cooled to room temperature. After carefully releasing the hydrogen gas, saturated aqueous sodium bicarbonate (3.0 mL) was added into the mixture and stirred for 10-15 min. The mixture was extracted with dichloromethane three times and the combined organic extract was dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated under the reduced pressure, and further purification was performed by a silica gel column eluted with ethyl acetate/methanol to give the desired hydrogenation products **2**. The enantiomeric excesses were determined by chiral HPLC for the corresponding protected products with *p*-toluenesulfonyl chloride.

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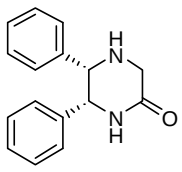
**(*5S*,*6R*)-5,6-Diphenylpiperazin-2-one (2a):**

46 mg, 92% yield, yellow oil, the known compound,[4] 90% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +283.20 (*c* 0.90, $CHCl_3$), $R_f$ = 0.40 (ethyl acetate/methanol = 80/1). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 4.6 Hz, 1H), 7.18-7.09 (m, 5H), 6.90-6.78 (m, 5H), 4.64 (s, 1H), 4.51 (s, 1H), 3.90-3.78 (m, 2H), 2.00 (s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.0, 138.5, 137.0, 128.3, 128.1, 127.8, 127.7, 127.5, 127.0, 61.4, 61.1, 50.4. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 80/20, detector: 230 nm, flow rate: 0.80 mL/min, 30 °C), $t_1$ = 14.6 min, $t_2$ = 22.0 min (major).

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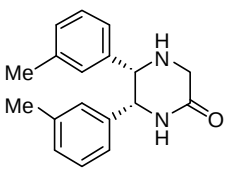
**(5*S*,6*R*)-5,6-Di-*m*-tolylpiperazin-2-one (2b):**

80 mg, 95% yield, yellow oil, new compound, 84% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +251.20 (*c* 0.90, $CHCl_3$), $R_f$ = 0.30 (ethyl acetate/methanol = 80/1). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.05-6.97 (m, 4H), 6.87 (s, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.58-6.55 (m, 3H), 4.58 (t, *J* = 3.8 Hz, 1H), 4.42 (d, *J* = 3.8 Hz, 1H), 3.81 (q, *J* = 17.8 Hz, 2H), 2.18 (s, 3H), 2.17 (s, 3H), 1.95 (s, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 170.1, 138.4, 137.6, 137.1, 136.9, 129.0, 128.5, 128.3, 127.8, 127.3, 125.4, 124.1, 61.3, 61.1, 50.4, 21.3, 21.2. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-



PrOH = 80/20, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), $t_1$ = 11.0 min, $t_2$ = 13.5 min (major). HRMS Calculated for $C_{18}H_{21}N_2O$ $[M+H]^+$ 281.1648, found 281.1646.

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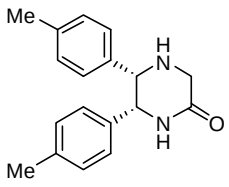
**(5*S*,6*R*)-5,6-Di-*p*-tolylpiperazin-2-one (2c)**:



79 mg, 94% yield, pale oil, new compound, 90% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +313.88 (*c* 1.0, $CHCl_3$), $R_f$ = 0.29 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.93 (dd, *J* = 11.4, 8.0 Hz, 4H), 6.68 (dd, *J* = 15.0, 7.8 Hz, 4H), 4.56 (t, *J* = 3.4 Hz, 1H), 4.39 (d, *J* = 3.6 Hz, 1H), 3.77 (q, *J* = 17.8 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 1.95 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.2, 137.3, 137.1, 135.6, 134.1, 128.7, 128.2, 128.2, 126.9, 61.0, 60.8, 50.4, 21.1, 21.1. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 80/20, detector: 254 nm, flow rate: 0.80 mL/min, 30 °C), $t_1$ = 15.8 min, $t_2$ = 22.6 min (major). HRMS Calculated for $C_{18}H_{21}N_2O_1$ $[M+H]^+$ 281.1648, found 281.1649.

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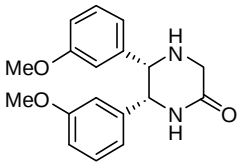
**(5*S*,6*R*)-5,6-Bis(3-methoxyphenyl)piperazin-2-one (2d):**



90 mg, 96% yield, yellow oil, new compound, 85% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +250.40 (*c* 0.24, $CHCl_3$), $R_f$ = 0.62 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.12-7.05 (m, 2H), 6.88-6.84 (m, 1H), 6.74-6.71 (m, 2H), 6.55 (d, *J* = 7.6 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 1H), 6.33 (d, *J* = 1.8 Hz, 1H), 6.31-6.26 (m, 1H), 4.61 (t, *J* = 3.8 Hz, 1H), 4.46 (t, *J* = 3.8 Hz, 1H), 3.89-3.76 (m, 2H), 3.59 (s, 3H), 3.57 (s, 3H), 1.94 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.9, 159.4, 158.9, 140.1, 138.7, 129.1, 128.6, 120.6, 119.5, 113.8, 113.7, 112.2, 61.3, 61.0, 55.1, 55.1, 50.4. Enantiomeric excess was determined by chiral HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 °C), $t_1$ = 14.8 min, $t_2$ = 18.3 min (major). HRMS Calculated for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1555.

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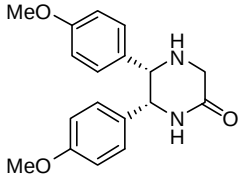
**(5*S*,6*R*)-5,6-Bis(4-methoxyphenyl)piperazin-2-one (2e) :**



89 mg, 95% yield, yellow oil, new compound, 90% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +330.24 (*c* 0.76, $CHCl_3$), $R_f$ = 0.60 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.8 Hz, 4H), 6.71-6.67 (m, 4H), 6.35 (d, *J* = 2.2 Hz, 1H), 4.56 (t, *J* = 3.8 Hz, 1H), 4.43 (d, *J* = 3.8 Hz, 1H), 3.86 (q, *J* = 17.6 Hz, 2H), 3.75 (s, 3H), 3.75 (s, 3H), 1.72 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.7, 159.2, 159.0, 130.7, 129.4, 129.1, 128.2, 113.4, 113.0, 61.1, 60.9, 55.2, 55.2, 50.7. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 °C), $t_1$ = 18.5 min, $t_2$ = 35.4 min (major). HRMS Calculated for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1553.

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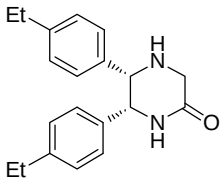
**(5*S*,6*R*)-5,6-Bis(4-ethylphenyl)piperazin-2-one (2f):**

87 mg, 94% yield, pale yellow solid, mp: 167-168 °C, new compound, 84% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +292.89 (*c* 0.86, $CHCl_3$), $R_f$ = 0.60 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ

6.96 (t, *J* = 8.6 Hz, 4H), 6.86 (s, 1H), 6.73-6.68 (m, 4H), 4.60 (t, *J* = 3.8 Hz, 1H), 4.43 (d, *J* = 3.8 Hz, 1H), 3.81 (q, *J* = 17.6 Hz, 2H), 2.59-2.57 (m, 2H), 2.54-2.53 (m, 2H), 1.91 (s, 1H), 1.19-1.17 (m, 3H), 1.16-1.14 (m, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.1, 143.8, 143.7, 135.8, 134.3, 128.2, 127.5, 127.1, 127.0, 61.2, 61.0, 50.5, 28.5, 28.4, 15.6, 15.6. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/ min, 30 $^{o}$C), $t_1$ = 10.0 min (minor), $t_2$ = 14.2 min (major). HRMS Calculated for $C_{20}H_{25}N_2O_1$ $[M+H]^+$ 309.1961, found 309.1960.



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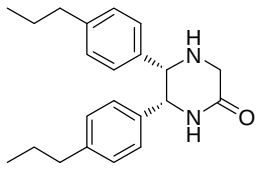
**(5*S*,6*R*)-5,6-Bis(4-propylphenyl)piperazin-2-one (2g):**

90 mg, 89% yield, pale yellow solid, mp: 115-116 $^{o}$C, new compound, 87% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +299.18 (*c* 1.12, $CHCl_3$), $R_f$ = 0.50 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.08-7.02 (m, 1H), 6.93-6.89 (m, 4H), 6.71-6.65 (m, 4H), 4.57 (t, *J* = 3.8 Hz, 1H), 4.41 (d, *J* = 38 Hz, 1H), 3.78 (q, *J* = 17.6 Hz, 2H), 2.51-2.47 (m, 4H), 2.12 (s, 1H), 1.61-1.50 (m, 4H), 0.86 (t, *J* = 7.4Hz, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.2, 142.1, 141.9, 135.8, 134.3, 128.1, 127.6, 126.8, 61.1, 60.8, 50.4, 37.5, 37.5, 24.4, 13.6, 13.5. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 $^{o}$C), $t_1$ = 8.0 min, $t_2$ = 10.5 min (major). HRMS Calculated for $C_{22}H_{29}N_2O_1$ $[M+H]^+$ 337.2274, found 337.2271.



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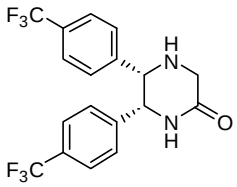
**(5*S*,6*R*)-5,6-Bis(4-(trifluoromethyl)phenyl)piperazin-2-one (2h):**

105 mg, 91% yield, yellowi oil, new compound, 85% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +210.34 (*c* 0.56, $CHCl_3$), $R_f$ = 0.55 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 12.4, 8.2 Hz, 4H), 7.07 (s, 1H), 6.98 (dd, *J* = 16.0, 8.2 Hz, 4H), 4.70 (t, *J* = 3.8 Hz, 1H), 4.62 (d, *J* = 3.8 Hz, 1H), 3.96-3.83 (m, 2H), 1.76 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.5, 142.1, 140.8, 130.4 (q, *J* = 32.0 Hz), 130.3 (q, *J* = 32.0 Hz), 128.8, 127.4, 126.48 (q, *J* = 270.0 Hz), 126.59 (q, *J* = 270.0 Hz), 125.25 (q, *J* = 3.8 Hz), 124.52 (q, *J* = 3.8 Hz), 61.0, 60.9, 50.4. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -62.6, -62.7. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 $^{o}$C), $t_1$ = 7.9 min, $t_2$ = 11.6 min (major). HRMS Calculated for $C_{18}H_{15}F_6N_2O_1$ $[M+H]^+$ 389.1083, found 389.1084.



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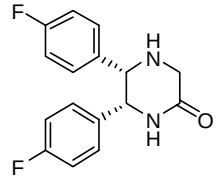
**(5*S*,6*R*)-5,6-Bis(4-fluorophenyl)piperazin-2-one (2i):**

78 mg, 91% yield, yellow oil, new compound, 89% ee, >20:1 d.r., $[\alpha]^{20}_D$ = +223.27 (*c* 0.64, $CHCl_3$), $R_f$ = 0.65 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 1H), 6.88-6.78 (m, 8H), 4.56 (d, *J* = 3.6 Hz, 1H), 4.47 (d, *J* = 3.8 Hz, 1H), 3.85 (q, *J* = 17.4 Hz, 2H), 1.83 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.1, 162.0 (d, *J* = 247.0 Hz), 161.7 (d, *J* = 247.0 Hz), 133.8, 132.3, 129.5 (d, *J* = 8.0 Hz), 128.1 (d, *J* = 8.0 Hz), 114.6 (d, *J* = 21.6 Hz), 114.0 (d, *J* = 21.6 Hz), 60.3, 60.2, 50.1. $^{19}$F NMR (376 MHz, $CDCl_3$) δ -113.9, -114.2. Enantiomeric excess was determined by HPLC for the corresponding 4-tosyl piperazin-2-one (Chiralcel



AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 $^{o}$C), $t_1$ = 11.4 min (minor), $t_2$ = 15.1 min (major). HRMS Calculated for $C_{16}H_{15}F_2N_2O_1$ $[M+H]^+$ 289.1147, found 289.1152.

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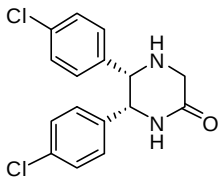
**(5*S*,6*R*)-5,6-Bis(4-chlorophenyl)piperazin-2-one (2j):**

83 mg, 86% yield, pale yellow solid, mp: 239-240 $^{o}$C, new compound, 88% ee, >20:1 d.r., $[\alpha]^{20}_{D}$ = +388.81 (*c* 0.86, $CHCl_3$), $R_f$ = 0.55 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.15-7.10 (m, 4H), 7.04 (s, 1H), 6.78 (dd, *J* = 12.2, 8.4 Hz, 4H), 4.55 (t, *J* = 3.8 Hz, 1H), 4.46 (d, *J* = 4.0 Hz, 1H), 3.83 (q, *J* = 17.4 Hz, 2H), 1.81 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.6, 136.8, 135.4, 133.9, 133.7, 129.7, 128.5, 128.3, 127.8, 60.7, 60.7, 50.5. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/ min, 30 $^{o}$C), $t_1$ = 13.4 min (minor), $t_2$ = 17.5 min (major). HRMS Calculated for $C_{16}H_{15}Cl_2N_2O$ $[M+H]^+$ 321.0556 ($^{35}$Cl and $^{35}$Cl), found 321.0562 ($^{35}$Cl and $^{35}$Cl), 323.0532 ($^{35}$Cl and $^{37}$Cl), 325.0503 ($^{37}$Cl and $^{37}$Cl).



Exact Mass: 320.0483

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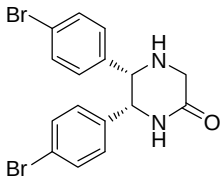
**(5*S*,6*R*)-5,6-Bis(4-bromophenyl)piperazin-2-one (2k):**

113 mg, 92% yield, pale oil, new compound, 87% ee, >20:1 d.r., $[\alpha]^{20}_{D}$ = +332.81 (*c* 1.06, $CHCl_3$), $R_f$ = 0.45 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31-7.27 (m, 4H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.73 (dd, *J* = 12.6, 8.4 Hz, 4H), 4.54 (t, *J* = 3.8 Hz, 1H), 4.45 (d, *J* = 3.8 Hz, 1H), 3.84 (q, *J* = 17.4 Hz, 2H), 1.75 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.5, 137.3, 135.9, 131.4, 130.8, 130.1, 128.7, 122.2, 121.9, 60.7, 60.7, 50.5. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 $^{o}$C), $t_1$ = 15.5 min, $t_2$ = 21.1 min (major); HRMS Calculated for $C_{16}H_{15}Br_2N_2O$ $[M+H]^+$ 408.9546 ($^{79}$Br and $^{79}$Br), found 408.9546 ($^{79}$Br and $^{79}$Br), 410.9522 ($^{79}$Br and $^{81}$Br), 412.9513 ($^{81}$Br and $^{81}$Br).

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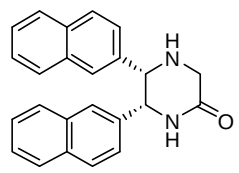
**(5*S*,6*R*)-5,6-Di(naphthalen-2-yl)piperazin-2-one (2l):**

101 mg, 95% yield, yellow oil, new compound, 88% ee, >20:1 d.r., $[\alpha]^{20}_{D}$ = +440.87 (*c* 1.44, $CHCl_3$), $R_f$ = 0.56 (ethyl acetate/methanol = 80/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.67-7.63 (m, 2H), 7.57-7.52 (m, 2H), 7.44-7.35 (m, 6H), 7.31 (s, 1H), 6.97 (s, 1H), 6.92 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.64 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.88 (t, *J* = 3.8 Hz, 1H), 4.70 (d, *J* = 3.8 Hz, 1H), 4.02-3.86 (m, 2H), 1.97 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.2, 135.8, 134.7, 132.9, 132.8, 132.8, 132.6, 128.0, 127.9, 127.8, 127.6, 127.5, 127.2, 127.0, 126.4, 126.1, 126.1, 126.0, 124.9, 61.4, 61.3, 50.6. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 70/30, detector: 230 nm, flow rate: 0.70 mL/min, 30 $^{o}$C), $t_1$ = 21.8 min, $t_2$ = 23.1 min (major). HRMS Calculated for $C_{24}H_{21}N_2O$ $[M+H]^+$ 353.1648, found 353.1648.

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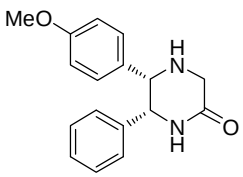
**(5*S*,6*R*)-5-(4-Methoxyphenyl)-6-phenylpiperazin-2-one (2m):**

52 mg, 92% yield, yellow solid, new compound, 85% ee, >20:1 d.r., $[\alpha]^{20}_{D}$ = +259.56 (*c* 0.94, $CHCl_3$), $R_f$ = 0.25 (ethyl acetate/methanol = 50/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.23-7.11 (m, 3H), 6.82 (d, *J* = 7.1 Hz, 2H), 6.77-6.63 (m, 5H), 4.59 (t, *J* = 3.7 Hz, 1H), 4.45 (d, *J* = 3.9 Hz, 1H), 3.96-3.78 (m, 2H), 3.73 (s, 3H), 1.90 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 169.9, 159.0, 137.1, 130.6, 128.4, 128.1, 127.8, 127.6, 113.4, 61.5, 60.7, 55.2, 50.6. Enantiomeric excess was determined by HPLC analysis for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 80/20, detector: 220 nm, flow rate: 0.80 mL/min, 30 $^o$C), $t_1$ = 21.8 min, $t_2$ = 28.4 min (major). HRMS Calculated for $C_{17}H_{19}N_2O_2$ $[M+H]^+$ 283.1441, found 283.1435.

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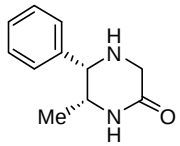
**(5*S*,6*R*)-6-Methyl-5-phenylpiperazin-2-one (2n):**

30 mg, 79% yield, yellow solid, new compound, 71% ee, 9.5:1 d.r., $[\alpha]^{20}_{D}$ = +155.95 (*c* 0.52, $CHCl_3$), $R_f$ = 0.45 (ethyl acetate/methanol = 20/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 7.16 (s, 1H), 4.27 (d, *J* = 3.8 Hz, 1H), 3.75-3.63 (m, 3H), 2.43 (s, 1H), 0.95 (d, *J* = 6.5 Hz, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 170.10, 139.36, 128.60, 127.67, 126.60, 59.51, 52.13, 50.09, 16.67. Enantiomeric excess was determined by HPLC for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/ *i*-PrOH = 90/10, detector: 220 nm, flow rate: 0.80 mL/min, 30 $^o$C), $t_1$ = 31.0 min (major), $t_2$ = 33.8 min. HRMS Calculated for $C_{11}H_{15}N_2O$ $[M+H]^+$ 191.1179, found 191.1179.

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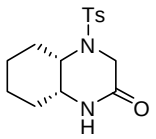
**(4*aS*,8*aR*)-4-Tosyloctahydroquinoxalin-2(1H)-one (2o):**

44 mg, 71% yield, white solid, new compound, 8% ee, >20:1 d.r., $[\alpha]^{20}_{D}$ = +15.50 (*c* 0.20, $CHCl_3$), $R_f$ = 0.35 (dichloromethane/ethyl acetate = 10/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.02 (s, 1H), 4.12 (d, *J* = 17.7 Hz, 1H), 4.05-3.97 (m, 1H), 3.70-3.65 (m, 1H), 3.60 (d, *J* = 17.7 Hz, 1H), 2.41 (s, 3H), 1.86-1.66 (m, 3H), 1.64-1.56 (m, 1H), 1.49-1.41 (m, 2H), 1.31-1.22 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.7, 144.0, 136.4, 130.0, 127.1, 52.4, 50.8, 44.0, 30.3, 24.3, 23.0, 21.6, 18.4. Enantiomeric excess was determined by HPLC for the corresponding 4-tosyl piperazin-2-one (Chiralcel AD-H column, Hexanes/*i*-PrOH = 80/20, detector: 220 nm, flow rate: 0.80 mL/ min, 30 $^o$C), $t_1$ = 14.1 min, $t_2$ = 17.5 min (major). HRMS Calculated for $C_{15}H_{21}N_2O_3S$ $[M+H]^+$ 309.1267, found 309.1268.

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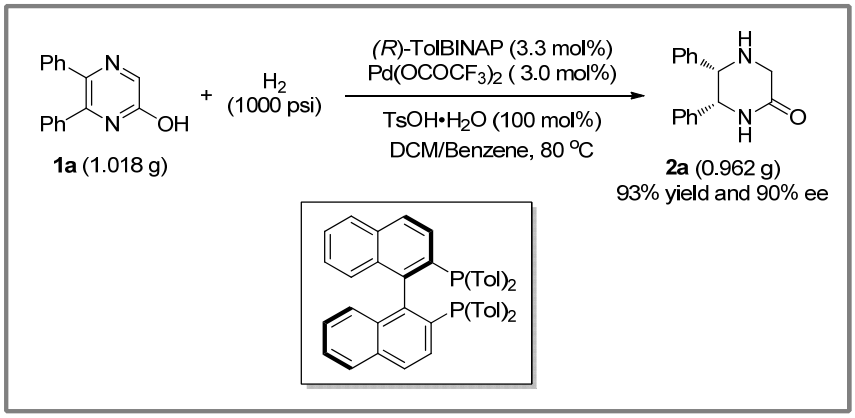
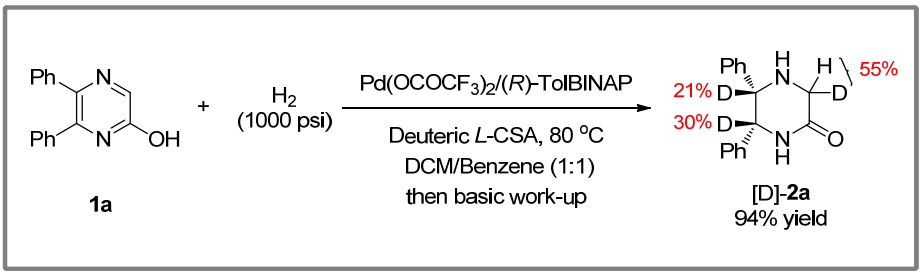
## 4. Asymmetric Hydrogenation at Gram Scale




Palladium trifluoroacetate (40.9 mg, 0.123 mmol, 3.0 mol%) and (*R*)-Tol-BINAP (90.8 mg, 0.135 mmol, 3.3 mol%) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at room temperature for 30 min. Then, the solvent was removed under vacuum to give the catalyst. In a glovebox, the substrate **1a** (1.018 g, 4.1 mmol) and $TsOH \cdot H_2O$ (780 mg, 4.1 mmol, 100 mol%) were stirred in benzene (8.0 mL) at room temperature for 5 min. Subsequently, the aboved catalyst in dichloromethane (8.0 mL) was added to the reaction mixture. The hydrogenation reaction was performed at 80 $^{o}$C under hydrogen (1000 psi) in a stainless steel autoclave for 36 h. The mixture was cooled to room temperature. After carefully releasing the hydrogen gas, saturated aqueous sodium bicarbonate (10 mL) was added to the mixture and stirred for 10-15 min. The mixture was extracted with dichloromethane three times, and the combined organic extracts dried over anhydrous sodium sulfate. After filtration, the filtrate was concentrated under the reduce pressure, and further purification was performed by flash chromatography on silica gel eluted with ethyl acetate/methanol to give the hydrogenation product **2a** (0.962 g in 93% yield and 90% ee).

## 5. Mechanistic Investigation

**Asymmetric Hydrogenation of 5,6-Diphenylpyrazin-2-ol (1a) with Deuteric *L*-CSA:** 5,6-Diphenylpyrazin-2-ol **1a** was hydrogenated with the $Pd(OCOCF_3)_2$/(*R*)-Tol-BINAP/Deuteric *L*-CSA/DCM:Benzene (1:1) condition.




Deuteric *L*-CSA was obtained *in situ* by stirring $CD_3OD$ (0.5 mL) and *L*-CSA (46 mg, 0.20 mmol) at room temperature in glove box for 0.5 h and then the solvent was removed in vacuum. Repeat this procedure twice for sufficient Hydrogen/Deuterium exchange. Subsequently, the prepared catalyst (3.0 mol %) and **1a** (50 mg, 0.20 mmol) were transferred to the above preformed deuteric *L*-CSA by dichloromethane/benzene (1.5 mL/1.5 mL) and the hydrogenation was carried out under the optimal conditions for 24 h. $^1$H NMR analysis of the crude hydrogenated product showed that deuterium atoms were incorporated to the 3,5,6-position (with 55%, 21%, 30% incorporation) of hydrogenation product 5,6-diphenylpiperazin-2-one [D]-**2a** (**Figure S1**).

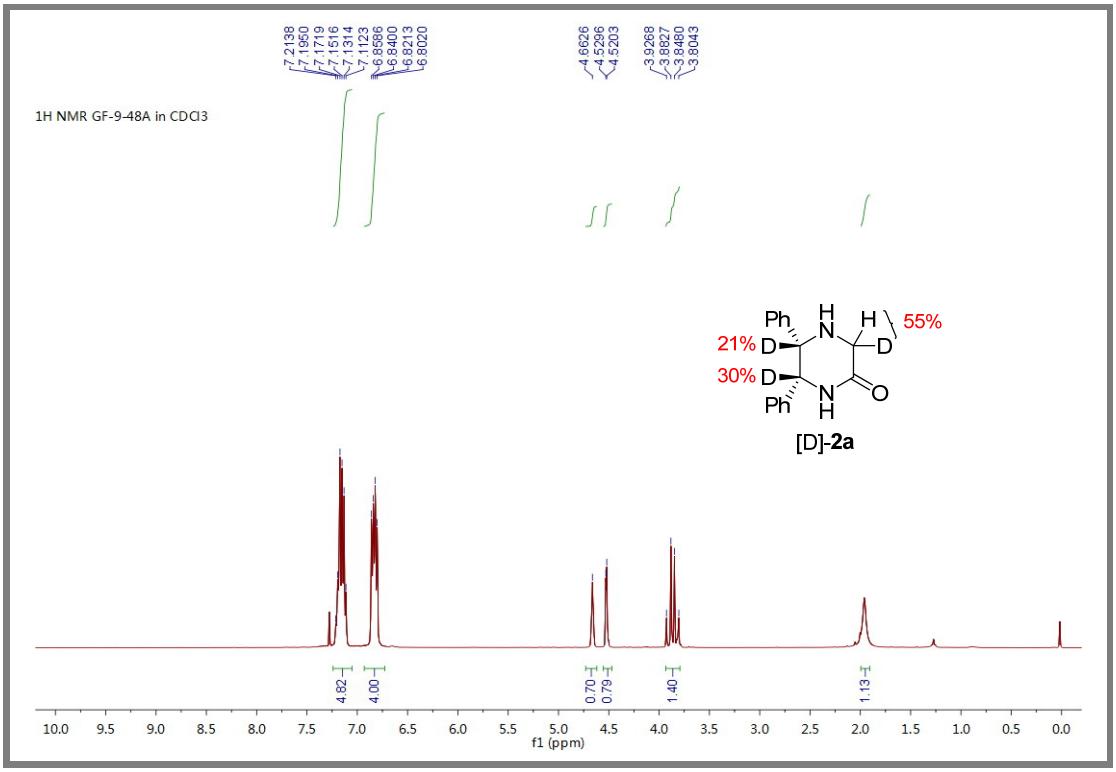
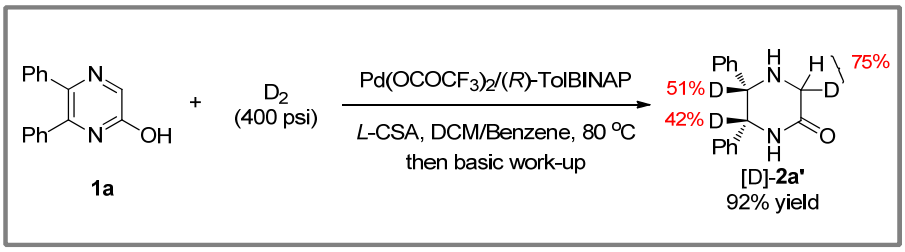



**Figure S1.** $^1$H NMR of [D]-**2a**

**Asymmetric Hydrogenation with $D_2$**: 5,6-Diphenylpyrazin-2-ol **1a** was hydrogenated in $D_2$ (400 psi) with the $Pd(OCOCF_3)_2$/(*R*)-Tol-BINAP/*L*-CSA/DCM:Benzene (1:1) condition.




$^1$H NMR analysis of the crude hydrogenation product showed that deuterium atoms were incorporated to the 3,5,6-position (with 75%, 51%, 42% incorporation) of product 5,6-diphenyl-piperazin-2-one [D]-**2a'** (**Figure S2**).

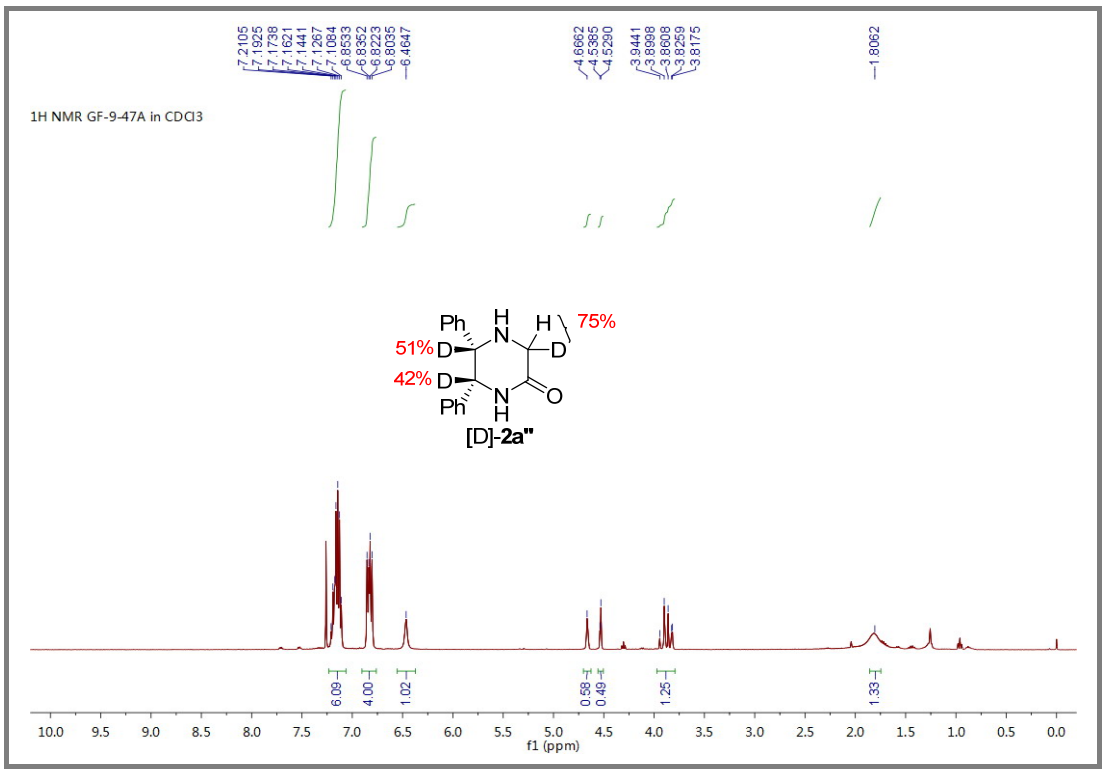
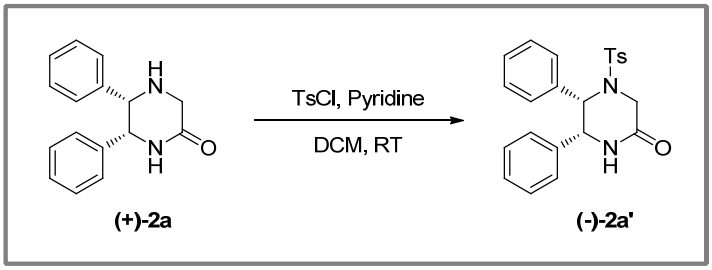



**Figure S2**. $^1$H NMR of [D]-**2a'**

## 6. The Determination of Structure of (+)-2a and 1m

### 6.1. The Determination of Absolute Configuration of Hydrogenation Product (+)-2a

The hydrogenation product **(+)-2a** was not directly suitable for X-ray diffraction experiment. In order to determine the absolute configuration, **(+)-2a** was protected with tosyl chloride.




A solution of **(+)-2a** (81 mg, 0.32 mmol) and pyridine (25 mg, 0.32 mmol) in dichloromethane, tosyl chloride (61 mg, 0.32 mmol) was added. The mixture was stirred at room temperature. When TLC indicated that the reaction was finished, water (10 mL) was added. The mixture was extracted with ethyl acetate and the combined organic layer was washed with HCl and brine. After dried over anhydrous sodium sulfate, the mixture was concentrated and further purification was performed by a silica gel column to achieve the product **(-)-2a'** (0.114 g, 88% yield).

---

**(5*S*,6*R*)-(-)-5,6-Diphenyl-4-tosylpiperazin-2-one (2a'):**

0.114 g, 88% yield, white solid, new compound, mp 228-229 $^{o}$C, >99% ee, $[\alpha]^{20}_{D}$ = -108.44 (*c* 1.22, $CHCl_3$), $R_f$ = 0.15 (hexanes/ethyl acetate = 4:1). $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.22-7.09 (m, 4H), 7.02-6.95 (m, 4H), 6.88-6.86 (m, 2H), 6.65 (d, *J* = 7.6 Hz, 2H), 6.54 (s, 1H), 5.26 (d, *J* = 4.4 Hz, 1H), 5.17 (d, *J* = 4.2 Hz, 1H), 4.42 (d, *J* = 17.6 Hz, 1H), 3.93 (d, *J* = 17.6 Hz, 1H), 2.31 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 167.6, 143.7, 135.4, 134.2, 134.1, 129.3, 128.8, 128.7, 128.6, 128.0, 128.0, 127.4, 127.0, 61.0, 60.2, 46.4, 21.4. Enantiomeric excess was deter- mined by HPLC (AD-H column, Hexanes/*i*-PrOH = 80/20, detector: 230 nm, flow rate: 0.80 mL/min, 30 $^{o}$C), $t_1$ = 14.3 min, $t_2$ = 21.4 min (major). HRMS Calculated for $C_{23}H_{23}N_2O_3S$ $[M+H]^+$ 407.1424, found 407.1424.

---

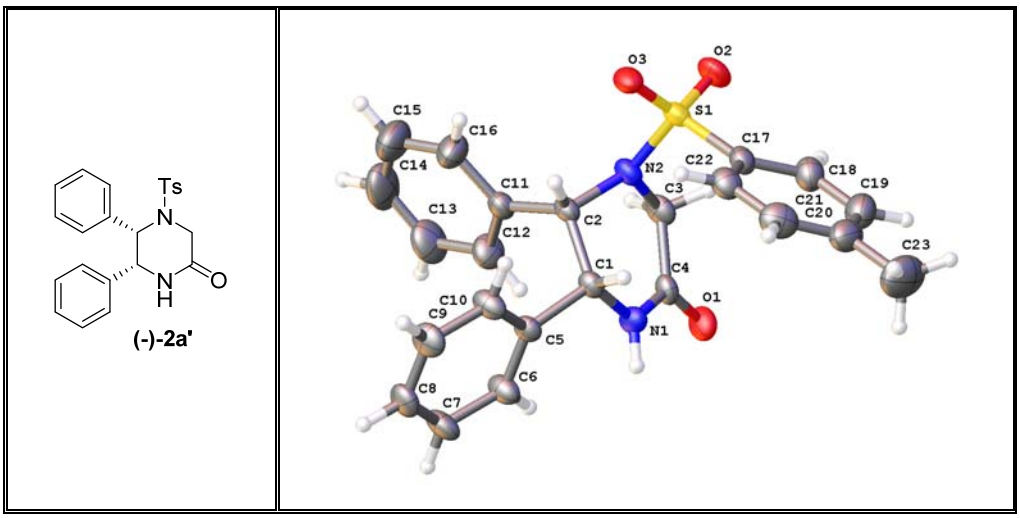



**Figure S3**. X-ray Crystallographic Analysis of Compound (-)-**2a'**

After recrystallizing in dichloromethane and *n*-hexane, optically pure product could be obtained. Then, a crystal of was grown from dichloromethane and *n*-hexane, which is suitable for X-ray diffraction analysis. The structure in **Figure S3** shows that the absolute configuration of **(-)-2a'** is (5*S*,6*R*), CCDC number is 1846833. Hence, the absolute configuration of hydrogenation product **(+)-2a** could be deduced from this structure. The absolute configuration of **(+)-2a** is (5*S*,6*R*). These details can be obtained free of charge *via* www.ccdc. com.ac.uk/data_request/cif from the Cambridge Crystallographic Data Centre.

## Crystal Data and Structure Refinement for mjr18056 for (-)-(5*S*,6*R*)-2a'

| | | |
|---|---|---|
| Identification code | mjr18056 | |
| Empirical formula | C23H22N2O3S | |
| Formula weight | 406.48 | |
| Temperature | 304.8 K | |
| Wavelength | 1.34139 Å | |
| Crystal system | Tetragonal | |
| Space group | $P4_3$ | |
| Unit cell dimensions | a = 14.1925(3) Å | α = 90° |
| | b = 14.1925(3) Å | β = 90° |
| | c = 10.5312(2) Å | γ = 90° |
| Volume | 2121.27(10) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.273 $Mg/m^3$ | |
| Absorption coefficient | 1.016 $mm^{-1}$ | |
| F(000) | 856 | |
| Crystal size | 0.15 x 0.03 x 0.01 $mm^3$ | |
| Theta range for data collection | 3.832 to 54.904°. | |
| Index ranges | -17<=h<=17, -17<=k<=17, -9<=l<=12 | |
| Reflections collected | 23362 | |
| Independent reflections | 3691 [R(int) = 0.0693] | |
| Completeness to theta = 53.594° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7508 and 0.6158 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3691 / 1 / 264 | |
| Goodness-of-fit on $F^2$ | 1.044 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0372, wR2 = 0.0739 | |
| R indices (all data) | R1 = 0.0605, wR2 = 0.0842 | |
| Absolute structure parameter | 0.014(12) | |
| Extinction coefficient | 0.0027(4) | |
| Largest diff. peak and hole | 0.145 and -0.151 e.$Å^{-3}$ | |

### 6.2. The Determination of Structure of Substrate 1m

The substrstate **1m** was recrystallized twice in dichloromethane and *n*-hexane. Then, a crystal of was grown from dichloromethane, methanol and *n*-hexane, which is suitable for X-ray diffraction analysis. The chemical structure was showed in **Figure S4**, CCDC number is 2023354. These aboved data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc. com.ac.uk/data_request/cif.

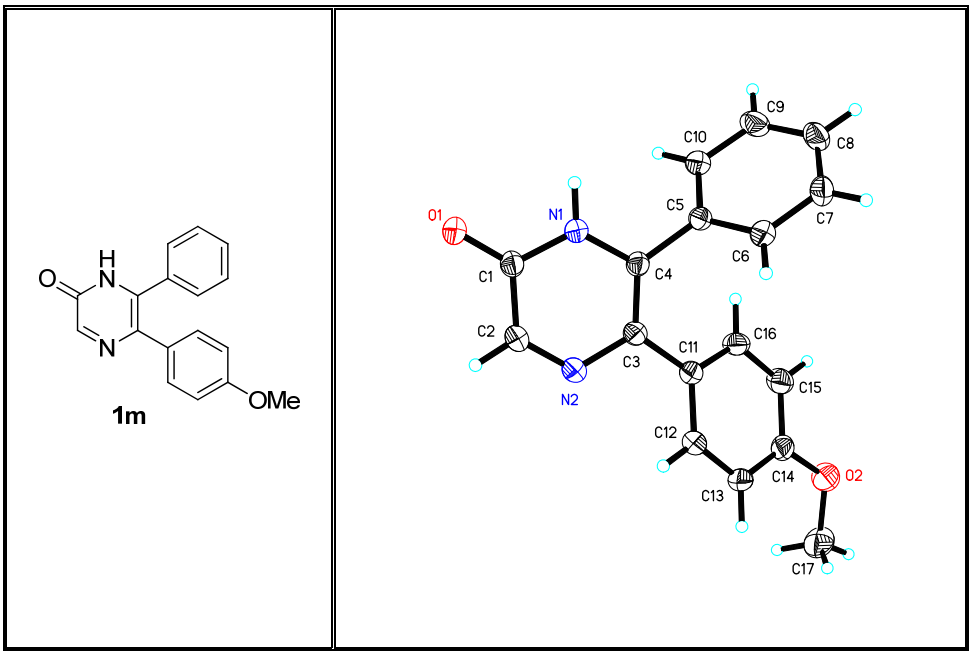
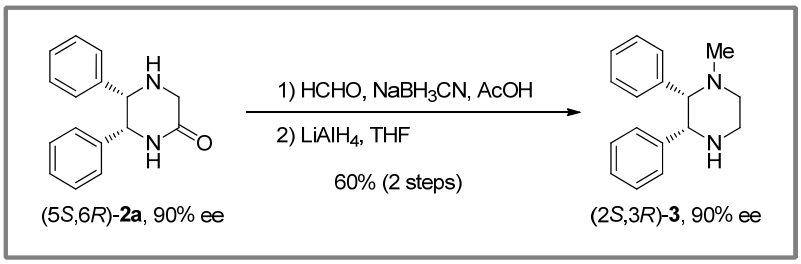



**Figure S4**. X-ray Crystallographic Analysis of Substrate **1m**

## Crystal Data and Structure Refinement for mo_d8v20299_0m for 1m

| | | |
|---|---|---|
| Identification code | mo_d8v20299_0m | |
| Empirical formula | C17H14N2O2 | |
| Formula weight | 278.30 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | a = 6.1923(2) Å | α = 106.2360(10)° |
| | b = 9.0465(3) Å | β = 98.2550(10)° |
| | c = 13.1134(4) Å | γ = 94.1460(10)° |
| Volume | 693.09(4) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.334 $Mg/m^3$ | |
| Absorption coefficient | 0.089 $mm^{-1}$ | |
| F(000) | 292 | |
| Crystal size | 0.200 x 0.120 x 0.060 $mm^3$ | |
| Theta range for data collection | 2.361 to 25.994°. | |
| Index ranges | -7<=h<=7, -11<=k<=11, -16<=l<=16 | |
| Reflections collected | 17265 | |
| Independent reflections | 2704 [R(int) = 0.0518] | |
| Completeness to theta = 25.242° | 99.5 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.7456 and 0.6086 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2704 / 0 / 196 | |
| Goodness-of-fit on $F^2$ | 1.073 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0444, wR2 = 0.1191 | |
| R indices (all data) | R1 = 0.0556, wR2 = 0.1310 | |
| Extinction coefficient | 0.088(17) | |
| Largest diff. peak and hole | 0.187 and -0.158 $e.Å^{-3}$ | |

## 7. Product Elaboration




The product (5*S*,6*R*)-**2a** could be conveniently converted into piperazine derivative according to the known literature procedure.[5]

A mixture of (5*S*,6*R*)-**2a** (101 mg, 0.40 mmol, 90% ee), acetic acid (0.1 mL), formaldehyde (HCHO, 37-40% in water) (486 mg, 11.2 mmol), $NaBH_3CN$ (113 mg, 1.80 mmol) and acetonitrile (4.0 mL) in a 25 mL round-bottomed flask was stirred at room temperature overnight. The mixture was diluted with 15 mL of ethyl acetate and washed with 10 mL of saturated aqueous solution of sodium chloride. The organic layer was dried over anhydrous sodium sulfate and filtered. The solvent was evaporated under reduced pressure to give the crude product. This crude product was used for the next step without further purification.

The aboved crude product was dissolved in tetrahydrofuran (5.0 mL). The lithium aluminum hydride (91 mg, 2.4 mmol) was added to the mixture at 0 °C. The reaction mixture was reflux for 12 h, and then cooled to room temperature. The reaction was quenched with water, and 20% aqueous sodium hydroxide (5 mL) was added. After being stirred for 15 minutes, the mixture was diluted with ethyl acetate, filtered through Celite, and concentrated under the reduced presssure to give the crude product. The residue was purified by silica gel chromatography using dichloromethane/methanol (20:1) as eluent to give the desirable product (2*S*,3*R*)-**3** as pale oil.

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**(2*S*,3*R*)-1-Methyl-2,3-diphenylpiperazine (3):**

61 mg, 60% yield (two steps), 90% ee, pale oil, known compound, $[\alpha]^{20}_D$ = -99.99 (*c* 0.12, $CHCl_3$), [Lit:[1a] $[\alpha]^{20}_D$ = +92.4 (*c* 1.0, $CHCl_3$) for 94 % ee], $R_f$ = 0.15 (dichloromethane/methanol = 20/1). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 2H), 7.26-7.23 (m, 2H), 7.14-7.04 (m, 6H), 4.44 (d, *J* = 3.8 Hz, 1H), 3.87 (d, *J* = 3.8 Hz, 1H), 3.43-3.38 (m, 1H), 3.27-3.21 (m, 1H), 3.10-3.04 (m, 1H), 2.64-2.60 (m, 2H), 2.17 (s, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 141.0, 136.0, 131.2, 127.8 127.3, 127.1, 126.8, 70.2, 64.2, 49.7, 45.3, 43.5. Enantiomeric excess was determined by HPLC for the corresponding benzamide (IA, elute: Hexanes/*i*-PrOH = 70/30, detector: 220 nm, flow rate: 0.8 mL/min, 30 $^o$C), $t_1$ = 7.0 min, $t_2$ = 10.6 min (major).

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## 8. References


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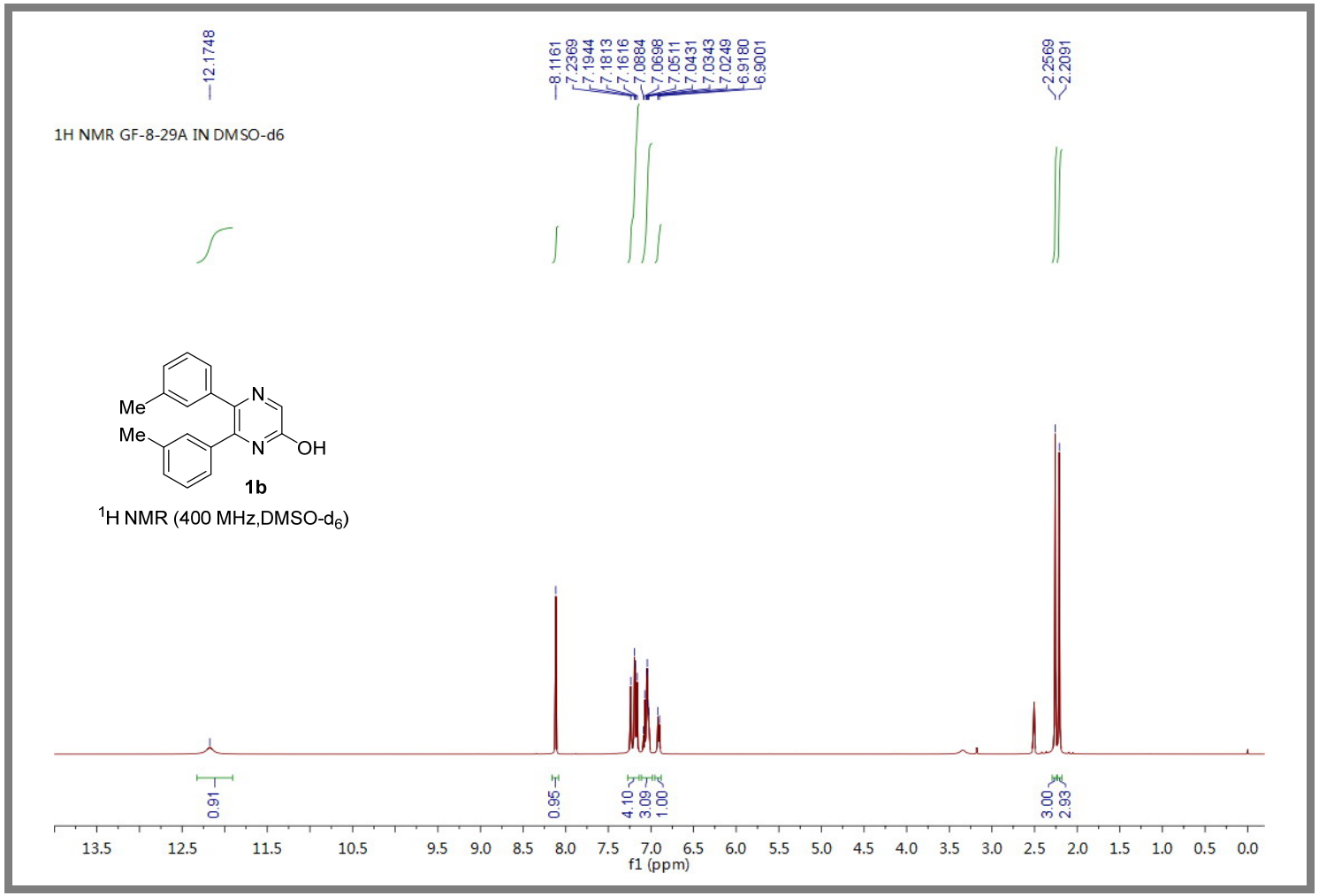
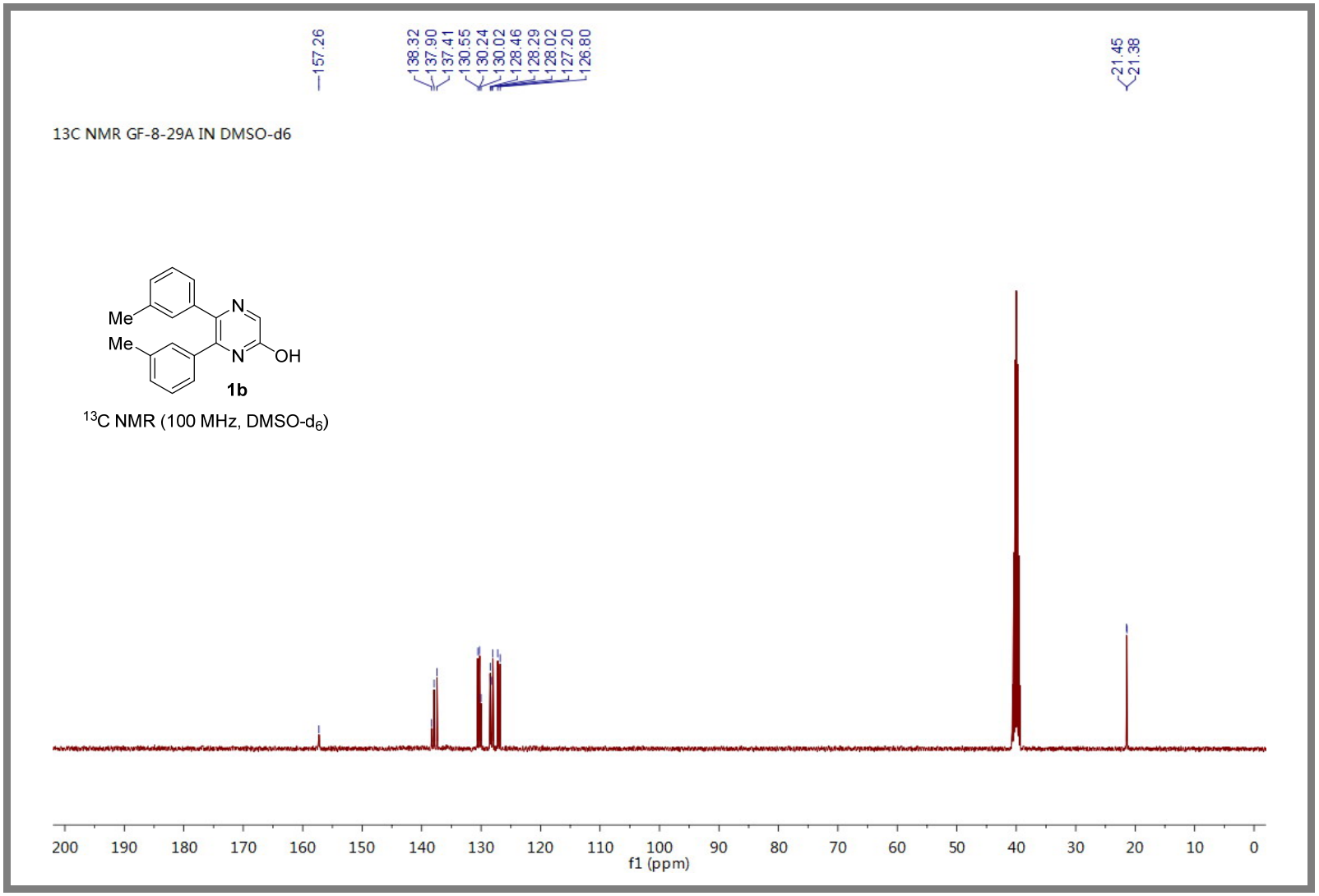
2. (a) Ohta, A.; Masano, S.; Iwakura, S.; Tamura, A.; Watahiki, H.; Tsutsui, M.; Akita, Y.; Watanabe, T. Syntheses and Reaction of Some 2,3-Disubstitued Pyrazine Monoxides. *J. Heterocyclic Chem*. **1982**, *19*, 465-473; (b) Mandal, D.; Yamaguchi, A. D.; Yamaguchi, J.; Itami, K. Synthesis of Dragmacidin D *via* Direct C-H Couplings. *J. Am. Chem. Soc*. **2011**, *133*, 19660-19663.
3. (a) Kaftory, M.; Shteiman, V.; Lavy, T.; Scheffer, J. R.; Yang, J.; Enkelmann, V. Discrimination in the Solid-State Photodimerization of 1-Methyl-5,6-diphenylpyrazin-2-one. *Eur. J. Org. Chem*. **2005**, 847-853; (b) Inoue, H.; Kubota, T.; Kanamoto, M. Synthesis Method of Organometallic Complex, Synthesis Method of Pyrazine Derivative, 5,6-Diaryl-2-Pyrazyl Triflate, Light-Emitting Element, Light-Emitting Device, Electronic Device, and Lighting Device. US2015147840, **2015** A1. (c) Matsuda, T.; Aoki, T.; Ohgiya, T.; Koshi, T.; Ohkuchi, M.; Shigyo, H. Synthesis and Bioactivities of Novel Pyridazine Derivatives: Inhibitors of Interleukin-1 Beta (IL-1β) production. *Bioorg. Med. Chem. Lett*. **2001**, *11*, 2369-2372. (d) Yuan, J.; Guo, Q.; Zhao, H.; Hu, S.; Whitehouse, D. L.; Pringle, W.C.; Mao, J.; Maynard, G. D.; Hammer, J. D.; Wustrow, D. J.; Li, H. Substituted heteroaryl CB1 antagonists. US2007-078135, **2007** A1. (e) Alvernhe, G.; Laurent, A.; Masroue, A. Addition of α-Aminoesters or α-Hydroxy-esters to Azirines. *Tetrahedron Lett*. **1983**, *24*, 1153-1156; (f) Shibayama, K.; Kuwahara, R.; Sato, M.; Nishimura, S.; Shiinoki, Y.; Yokoyama, M.; Kitamura, J. Nitrogenated Heterocyclic Compound and Agricultural or Horticultural Fungicide. US2014073792, **2014** A1.
4. Darko, L.; Karliner, J. Lactam Formation from the Condensation of Stilbenediamine with Glyoxal. *J. Org. Chem*. **1971**, *36*, 3810-3812.
5. (a) Chen, M.-W.; Yang, Q.; Deng, Z.; Zhou, Y.; Ding, Q.; Peng, Y. Organocatalytic Asymmetric Reduction of Fluorinated Alkynyl Ketimines. *J. Org. Chem*. **2018**, *83*, 8688-8694; (b) Chardon, A.; Morisset, E.; Rouden, J.; Blanchet, J. Recent Advances in Amide Reductions. *Synthesis* **2018**, *50*, 984-997.

## 9. Copy of NMR and HPLC

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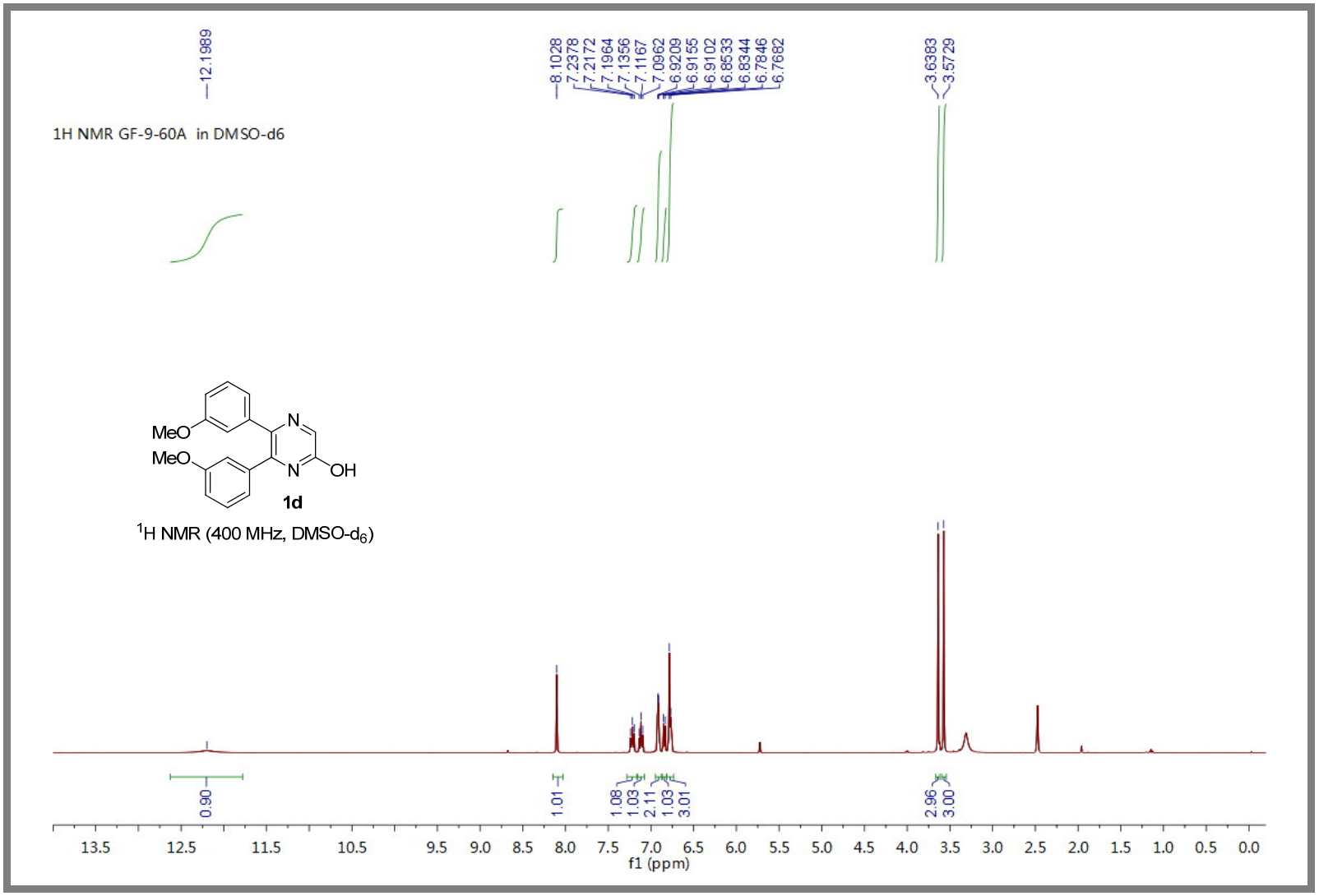
138.32
137.90
137.41
130.55
130.24
130.02
128.46
128.29
128.02
127.20
126.80
21.45
21.38
13C NMR GF-8-29A IN DMSO-d6
Me
Me
N
N
OH
1b
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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8.1028
7.2378
7.2172
7.1964
7.1356
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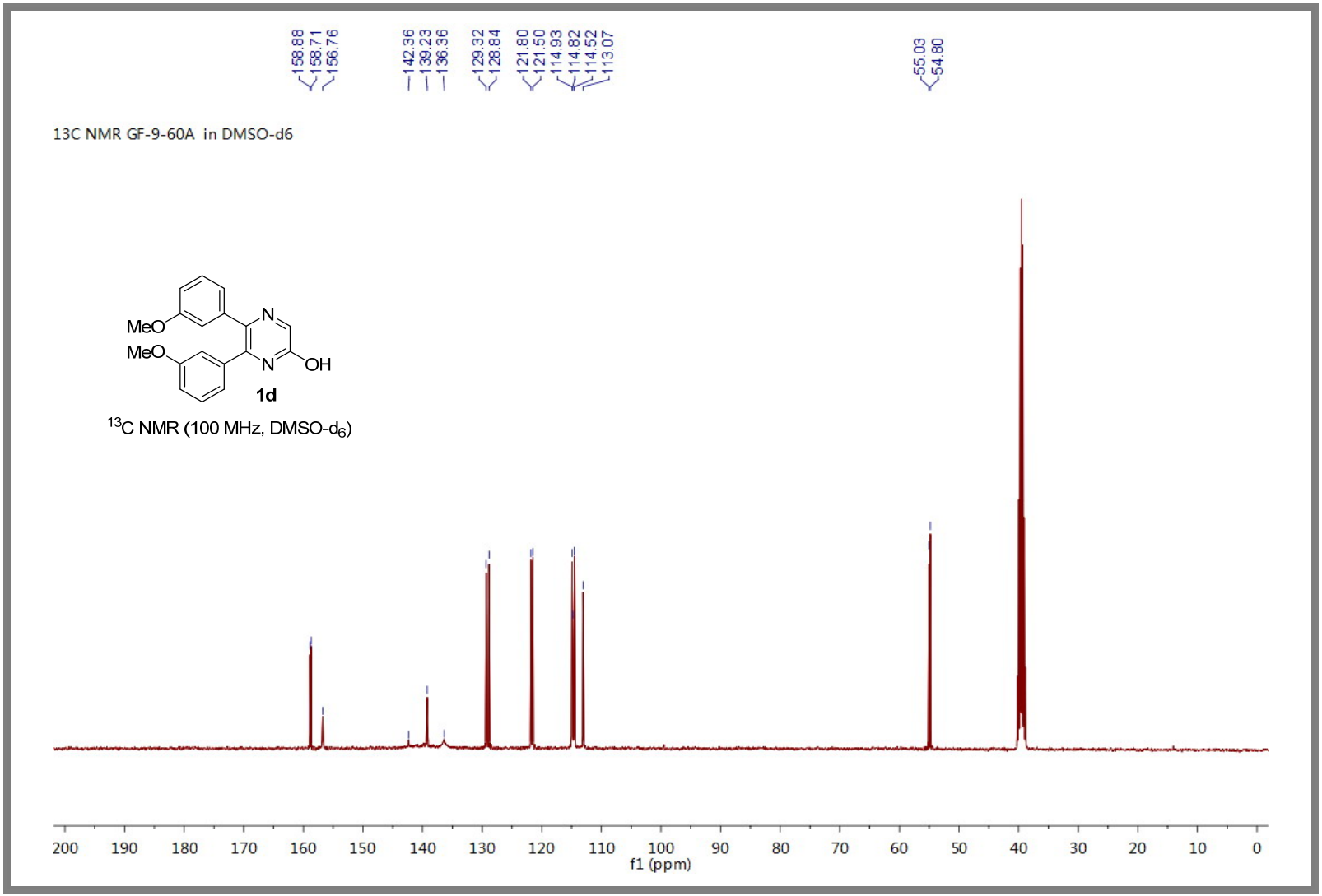
7.0962
6.9209
6.9155
6.9102
6.8533
6.8344
6.7846
6.7682
3.6383
3.5729
1H NMR GF-9-60A in DMSO-d6
MeO
MeO
N
N
OH
1d
1H NMR (400 MHz, DMSO-d6)
0.90
1.01
1.08
1.03
2.11
1.03
3.01
2.96
3.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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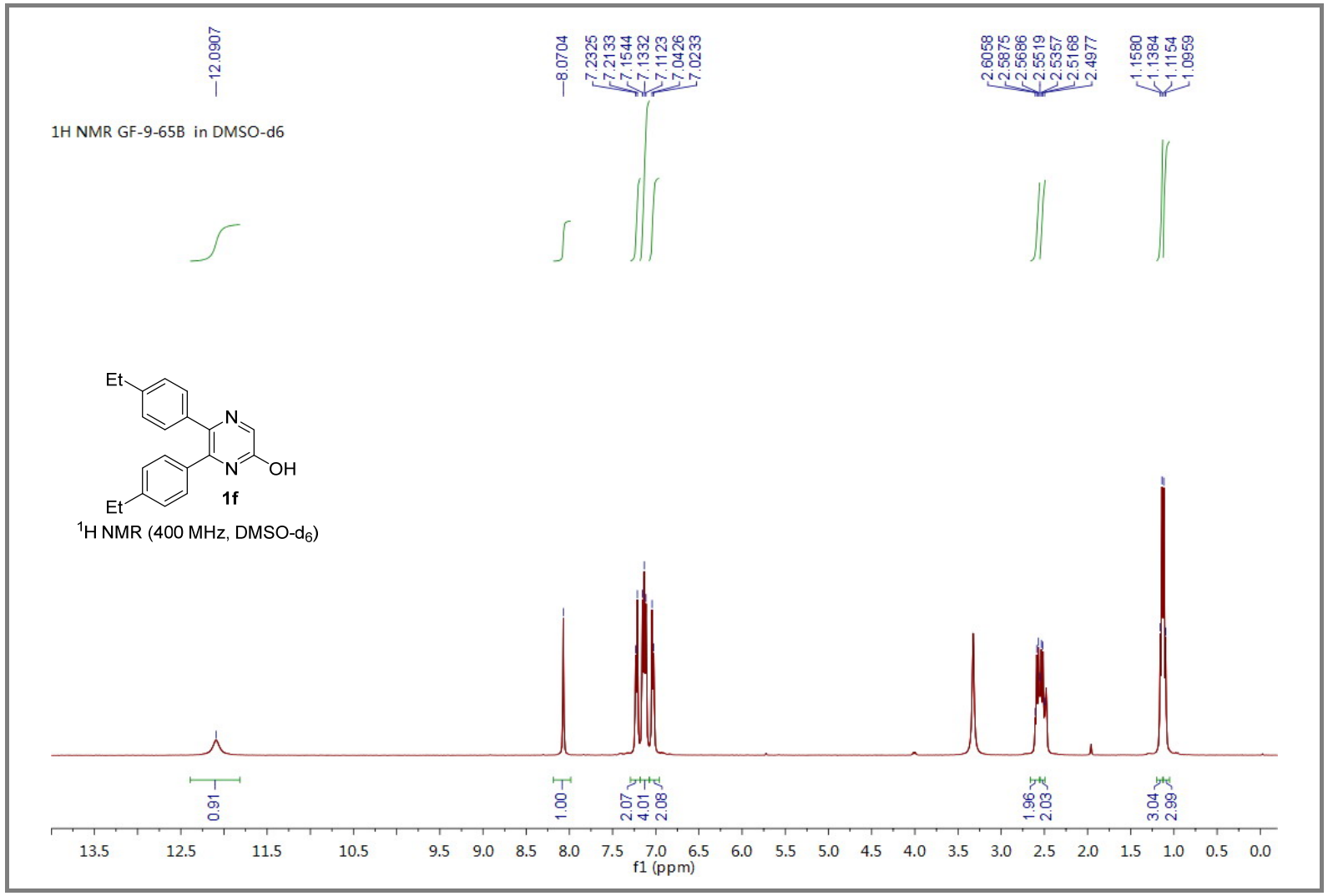
158.71
156.76
142.36
139.23
136.36
129.32
128.84
121.80
121.50
114.93
114.82
114.52
113.07
55.03
54.80
13C NMR GF-9-60A in DMSO-d6
MeO
MeO
N
N
OH
1d
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.2133
7.1544
7.1332
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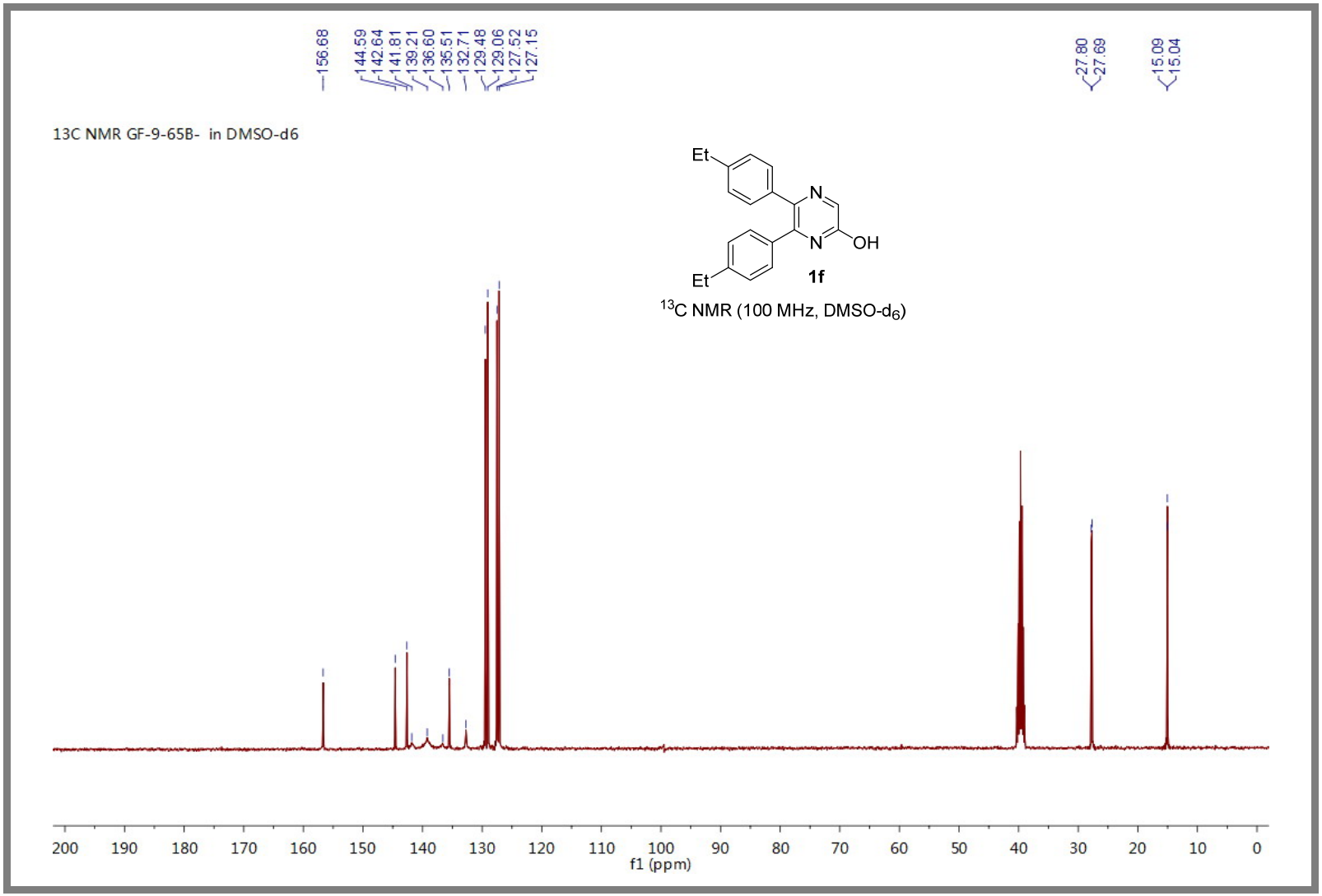
7.0233
2.6058
2.5875
2.5686
2.5519
2.5357
2.5168
2.4977
1.1580
1.1384
1.1154
1.0959
1H NMR GF-9-65B in DMSO-d6
Et
N
N
OH
Et
1f
1H NMR (400 MHz, DMSO-d6)
0.91
1.00
2.07
4.01
2.08
1.96
2.03
3.04
2.99
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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144.59
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141.81
139.21
136.60
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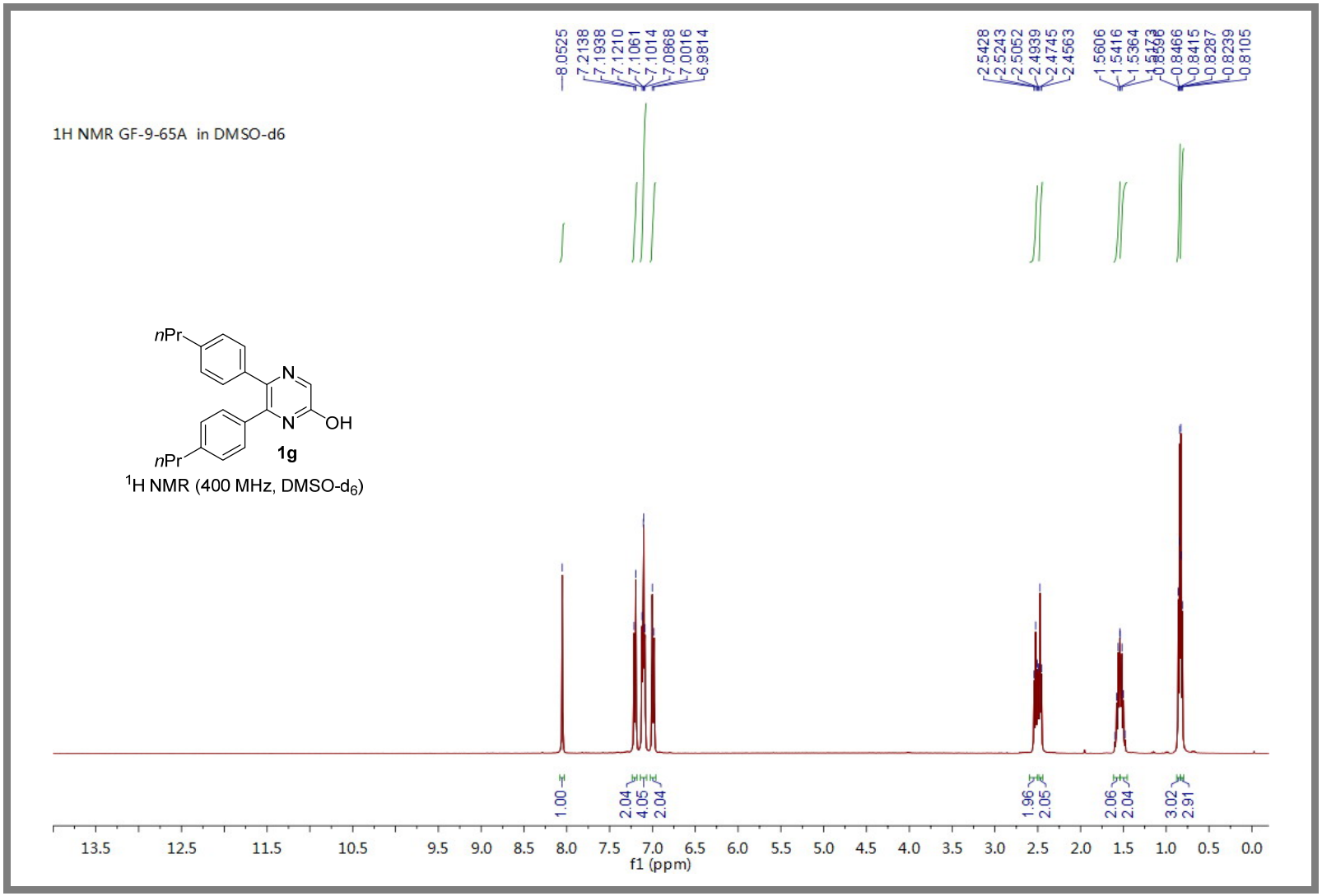
132.71
129.48
129.06
127.52
127.15
27.80
27.69
15.09
15.04
13C NMR GF-9-65B- in DMSO-d6
Et
N
N
OH
Et
1f
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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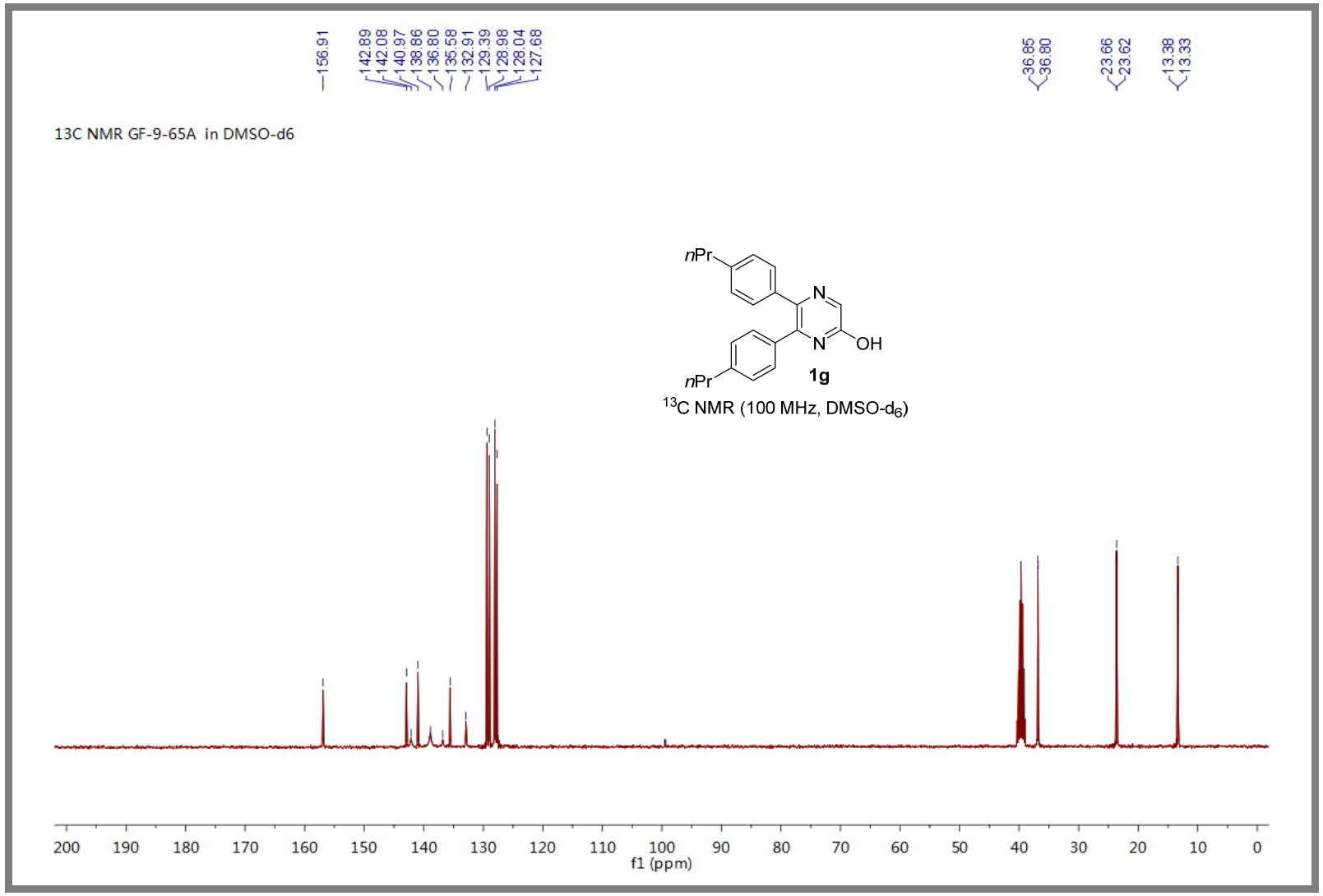
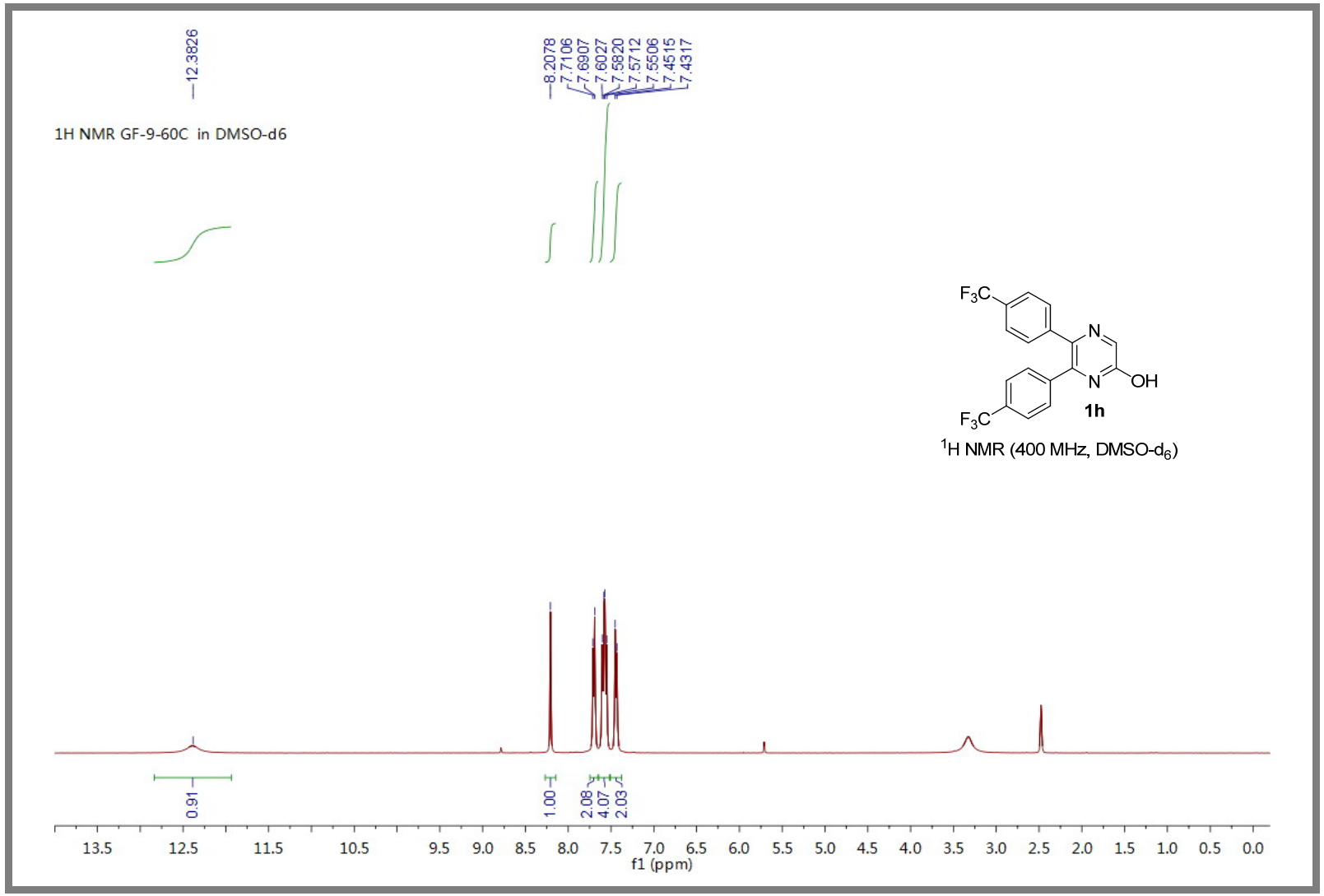
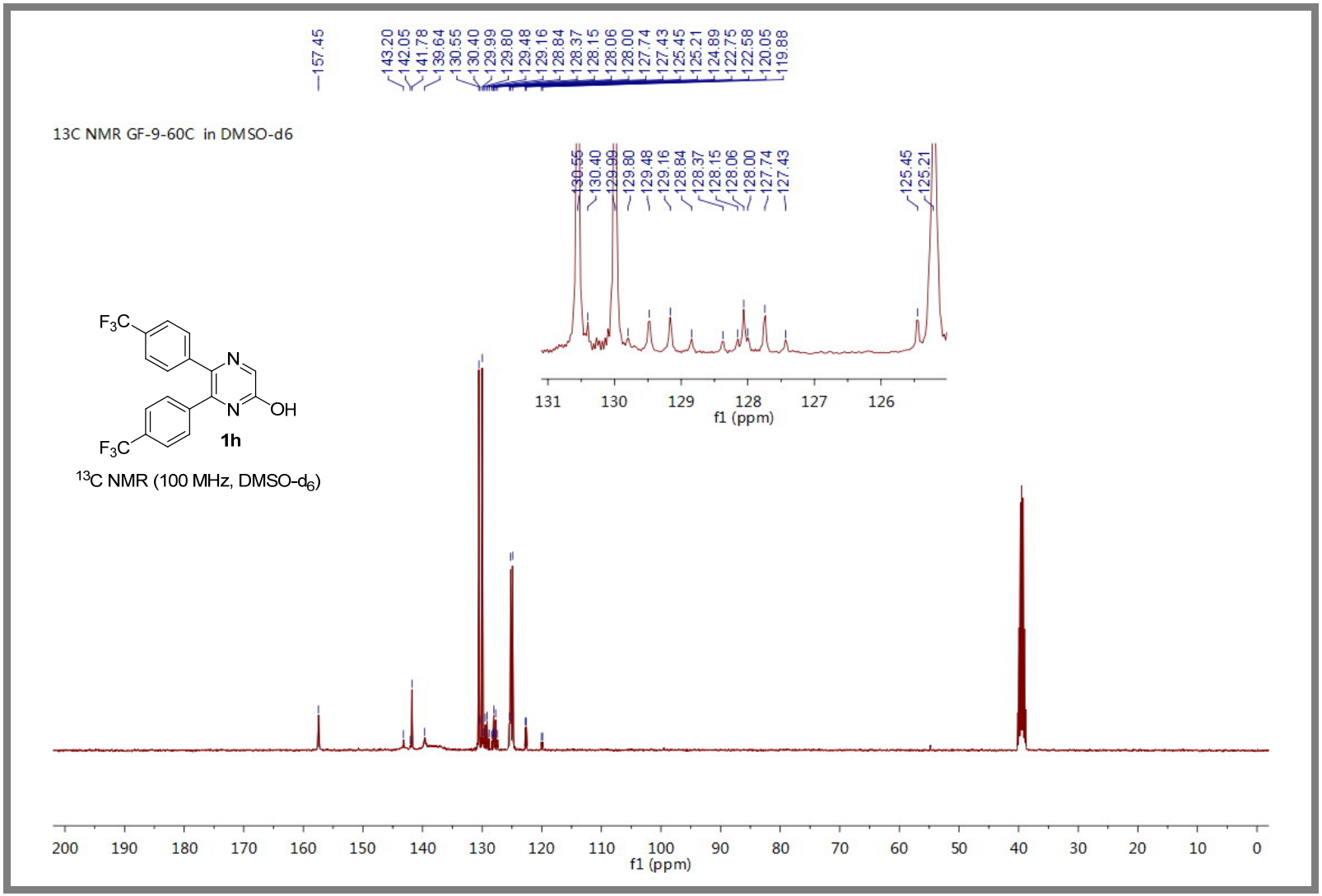
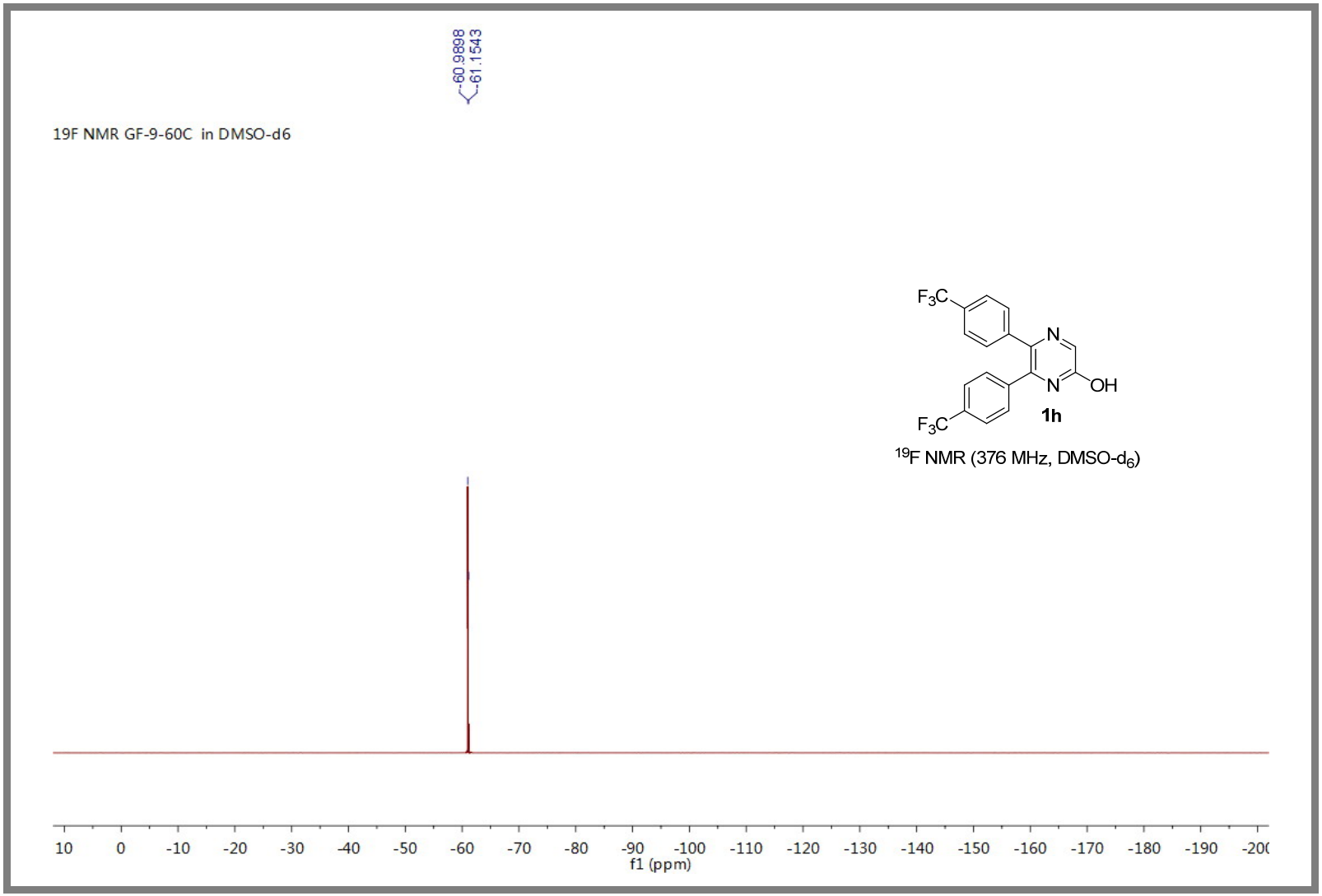
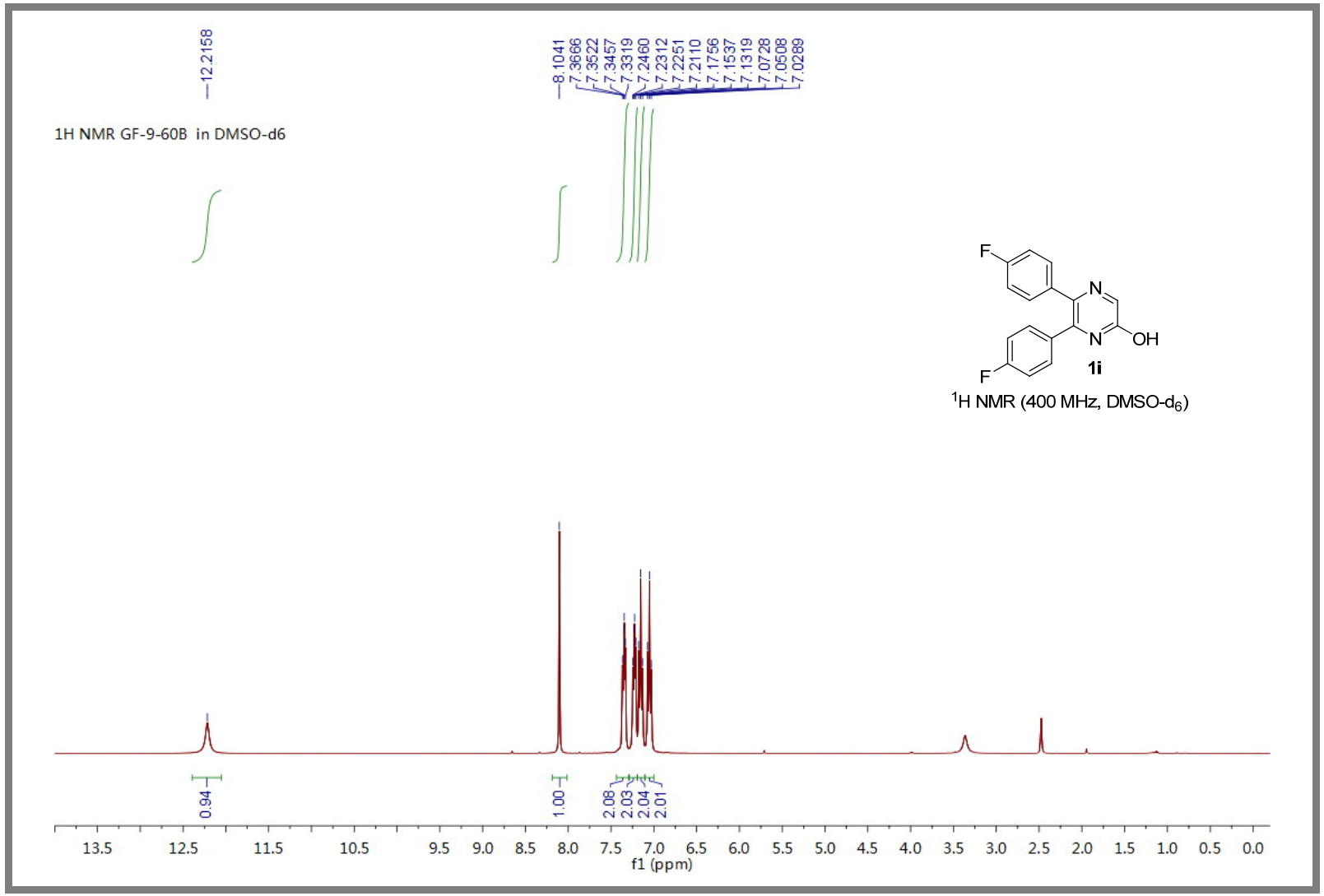
2.5428
2.5243
2.5052
2.4939
2.4745
2.4563
1.5606
1.5416
1.5364
0.8466
0.8415
0.8287
0.8239
0.8105
nPr
N
N
OH
nPr
1g
1H NMR (400 MHz, DMSO-d6)
1.00
2.04
4.05
2.04
1.96
2.05
2.06
2.04
3.02
2.91
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

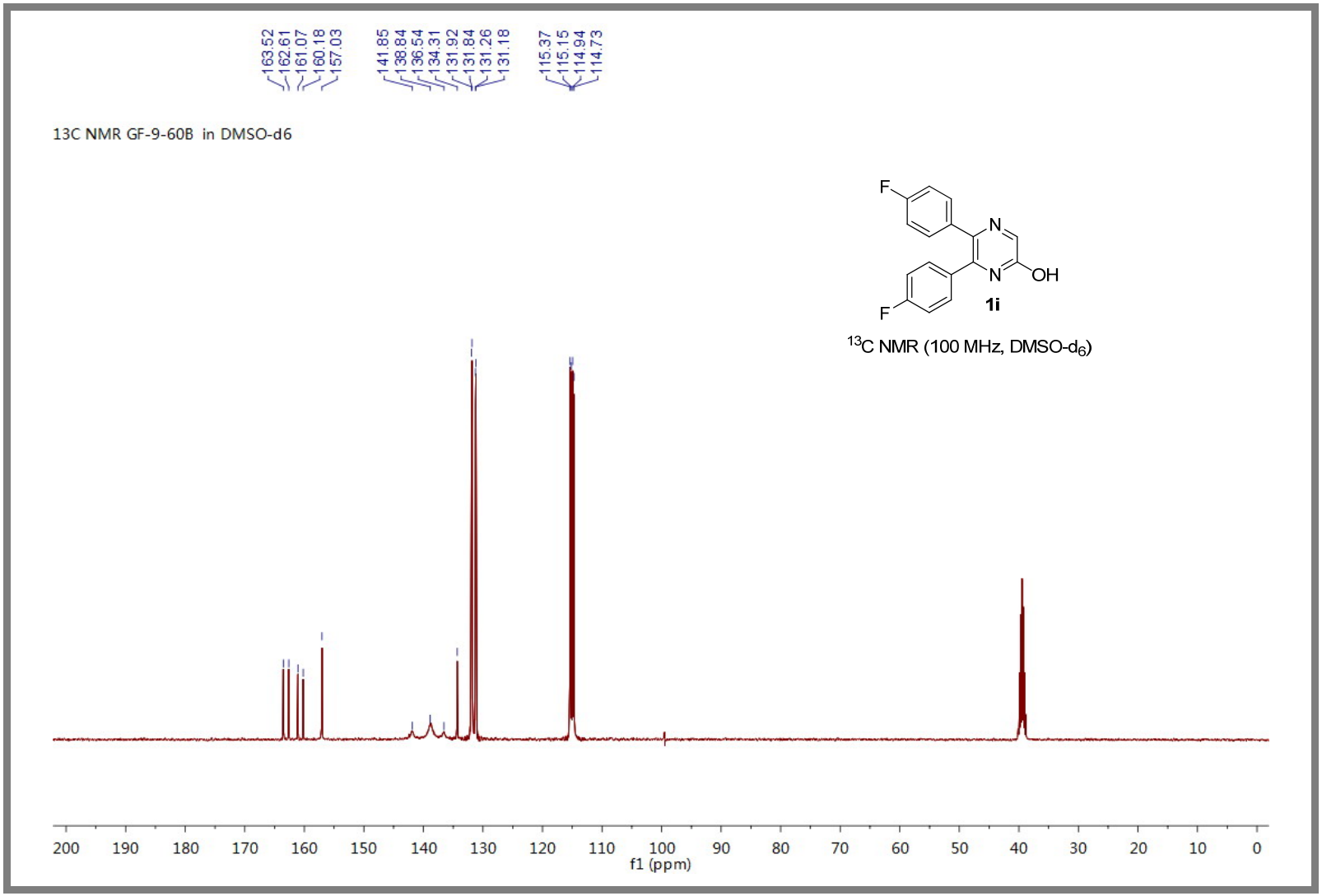

156.91
142.89
142.08
140.97
138.86
136.80
135.58
132.91
129.39
128.98
128.04
127.68
36.85
36.80
23.66
23.62
13.38
13.33
13C NMR GF-9-65A in DMSO-d6
nPr
N
N
OH
nPr
1g
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

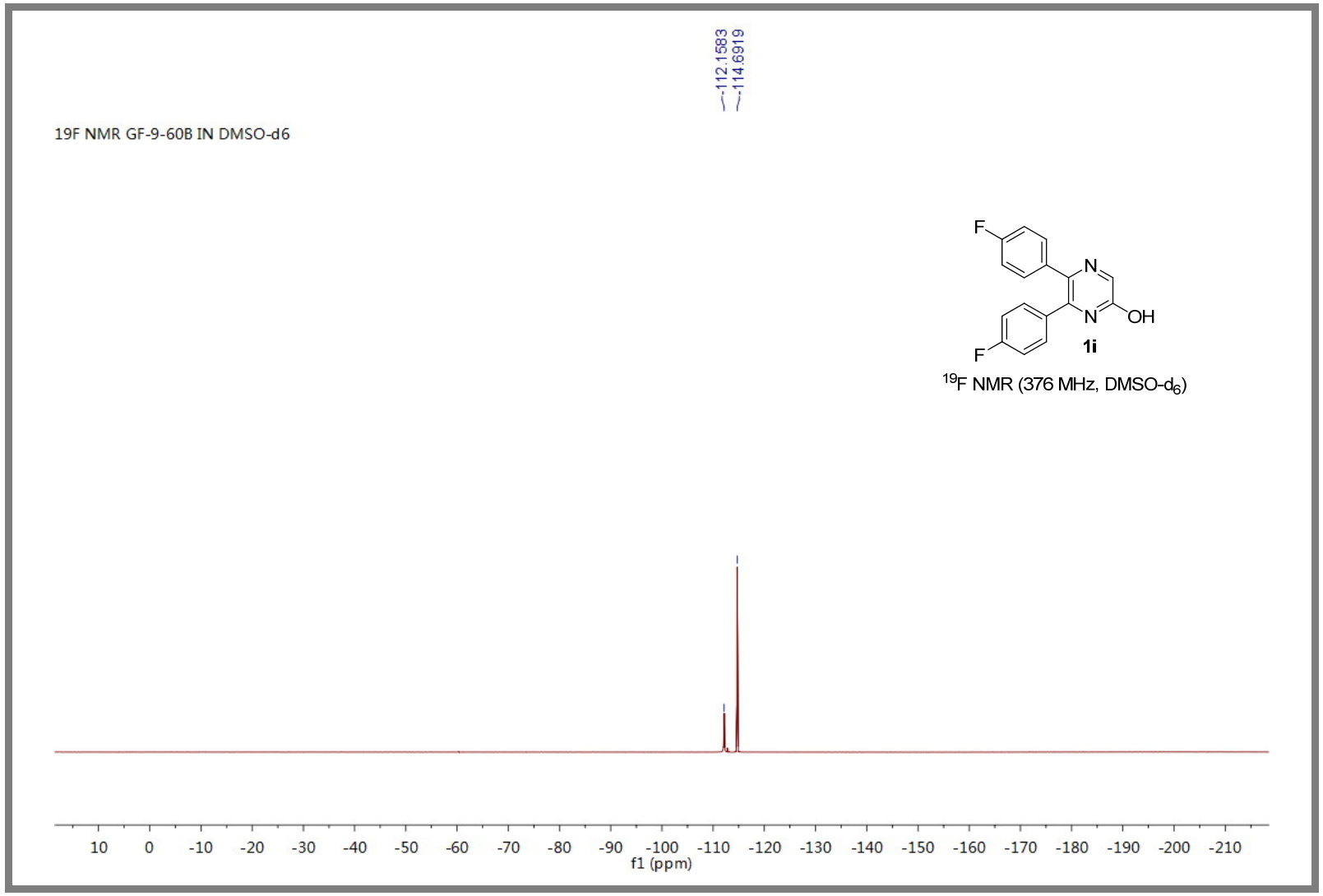

12.3826
8.2078
7.7106
7.6907
7.6027
7.5820
7.5712
7.5506
7.4515
7.4317
1H NMR GF-9-60C in DMSO-d6
F3C
N
N
OH
F3C
1h
1H NMR (400 MHz, DMSO-d6)
0.91
1.00
2.08
4.07
2.03
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

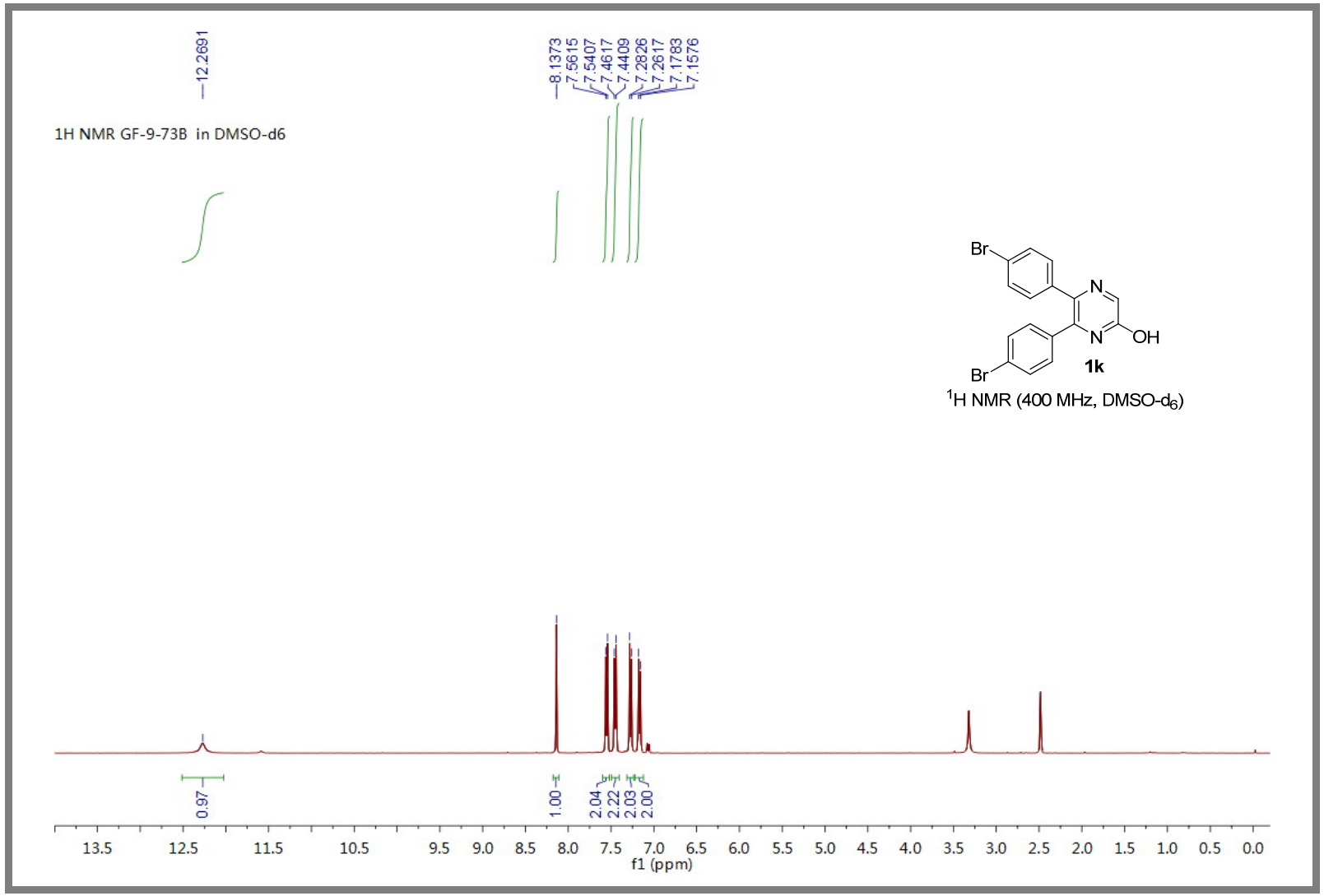

157.45
143.20
142.05
141.78
139.64
130.55
130.40
129.99
129.80
129.48
129.16
128.84
128.37
128.15
128.06
128.00
127.74
127.43
125.45
125.21
124.89
122.75
122.58
120.05
119.88
13C NMR GF-9-60C in DMSO-d6
F3C
N
N
OH
F3C
1h
13C NMR (100 MHz, DMSO-d6)
131
130
129
128
127
126
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

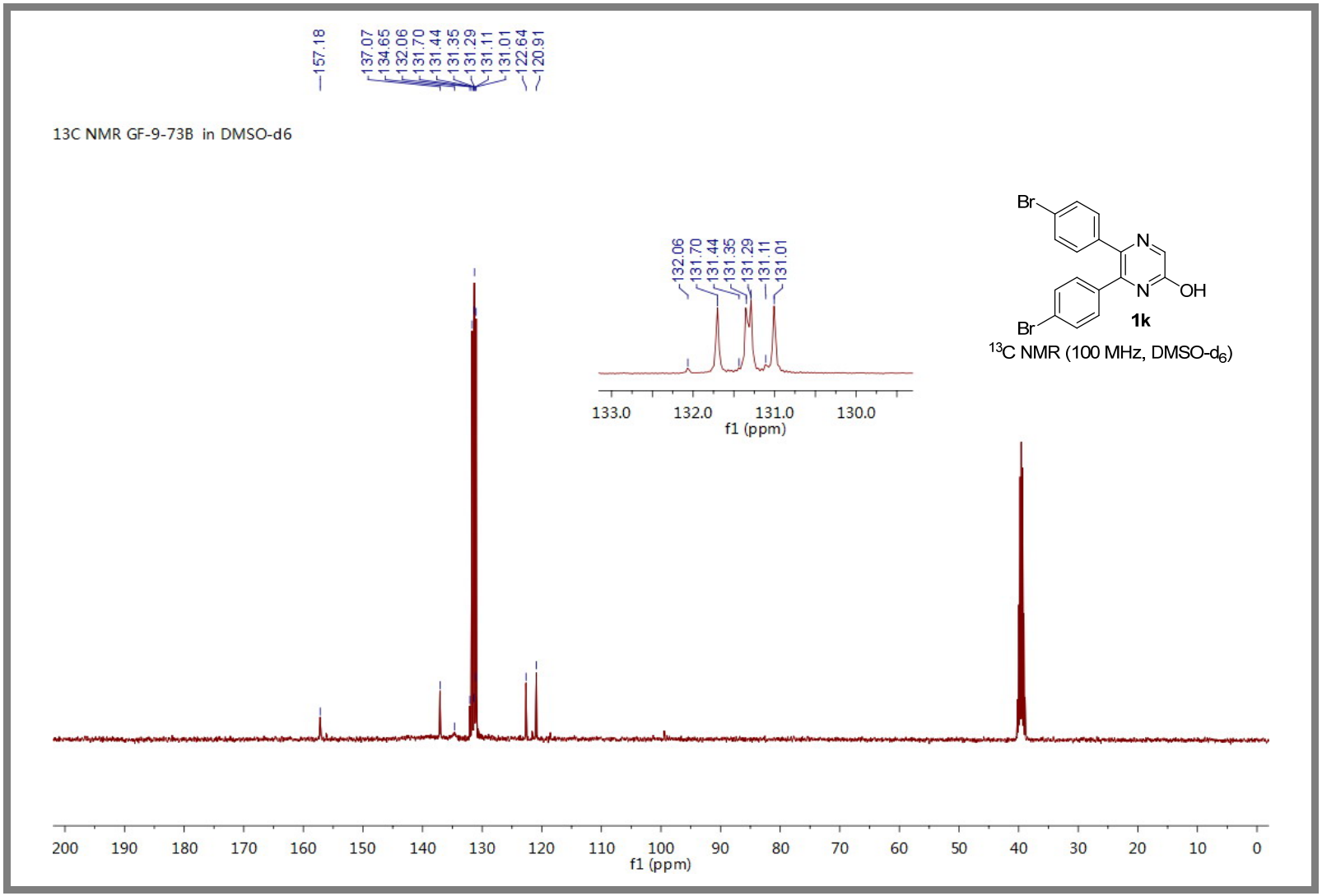

-60.9898
-61.1543
19F NMR GF-9-60C in DMSO-d6
F3C
N
N
OH
F3C
1h
19F NMR (376 MHz, DMSO-d6)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

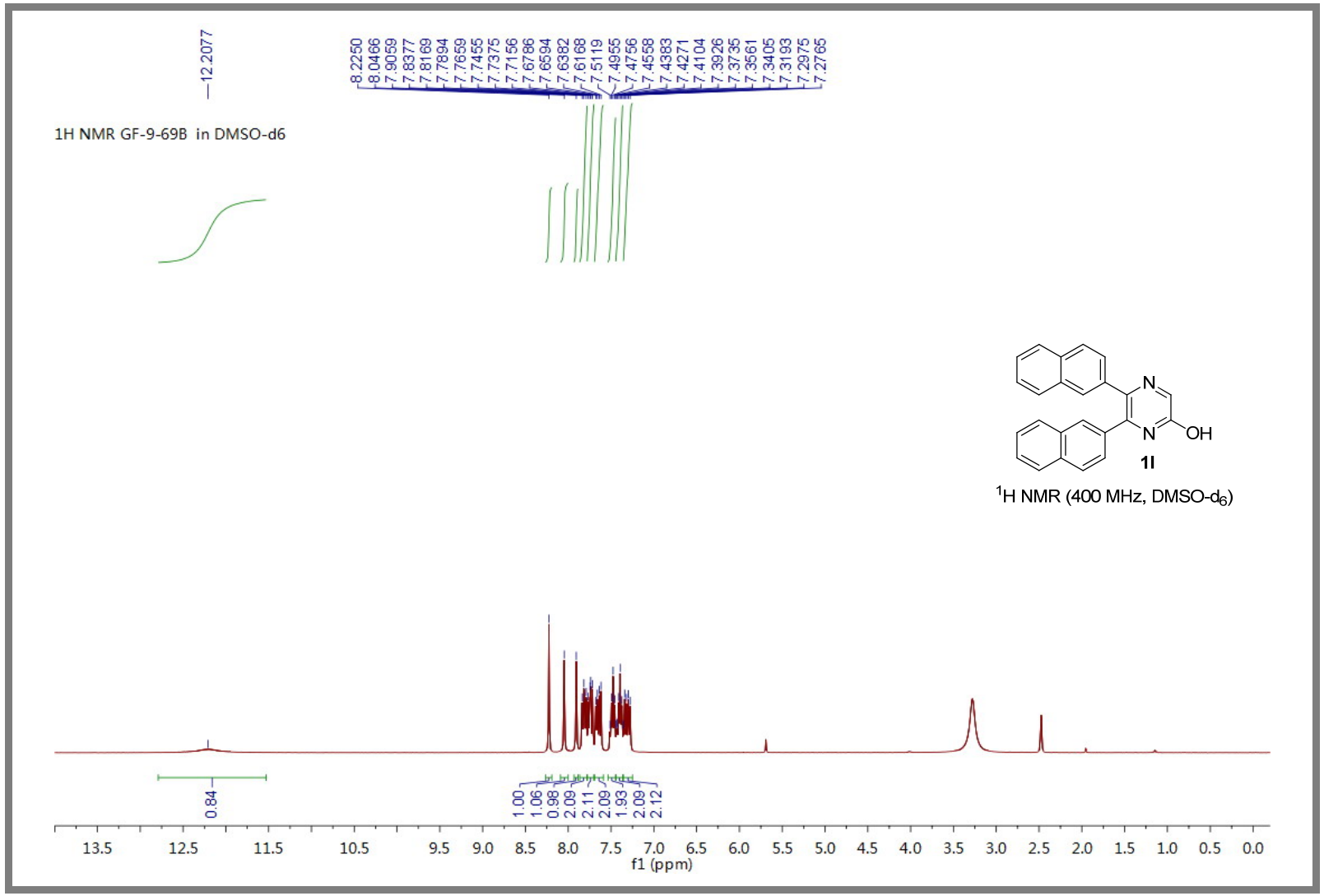

12.2158
8.1041
7.3666
7.3522
7.3457
7.3319
7.2460
7.2312
7.2251
7.2110
7.1756
7.1537
7.1319
7.0728
7.0508
7.0289
1H NMR GF-9-60B in DMSO-d6
F
N
N
OH
F
1i
1H NMR (400 MHz, DMSO-d6)
0.94
1.00
2.08
2.03
2.04
2.01
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

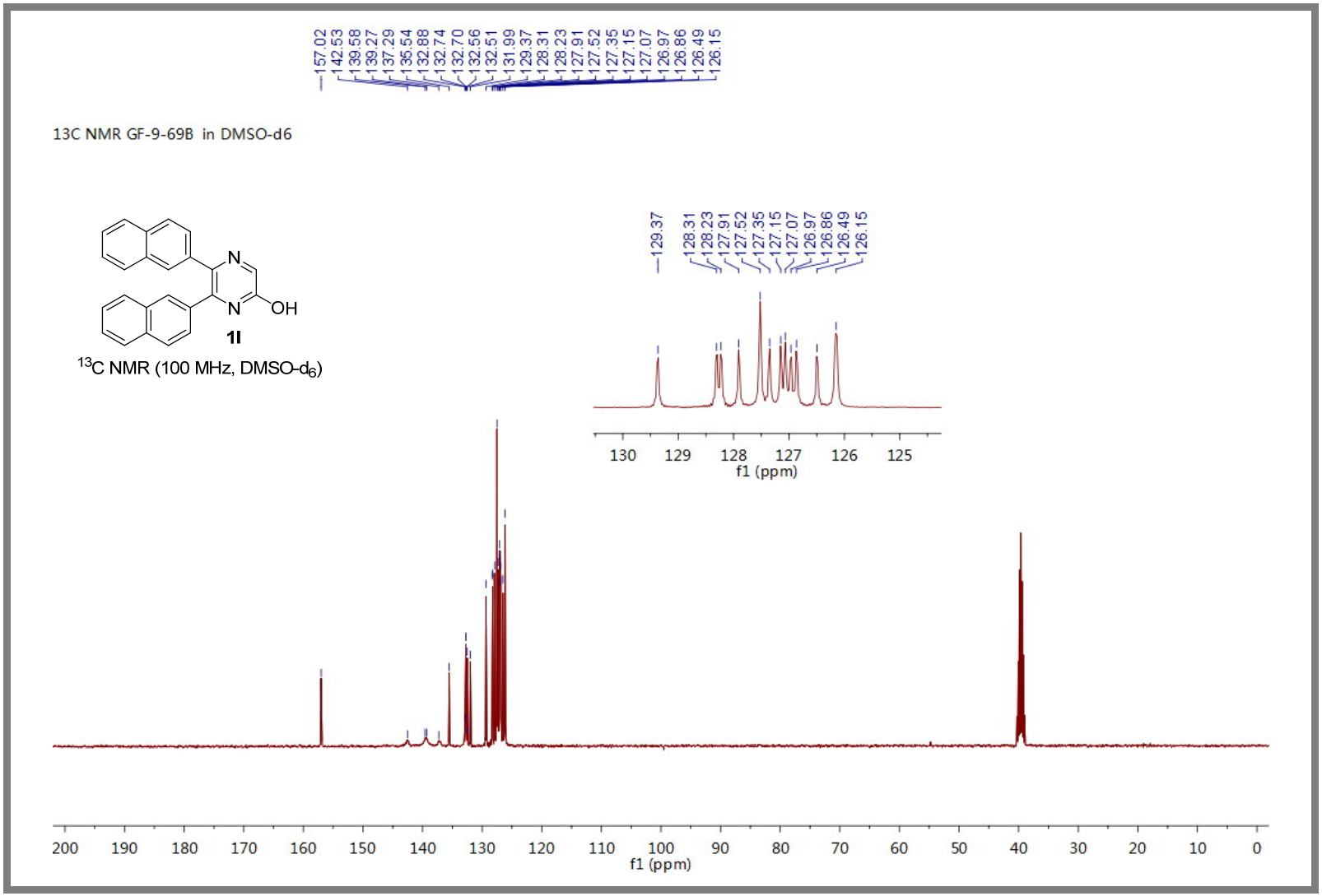

163.52
162.61
161.07
160.18
157.03
141.85
138.84
136.54
134.31
131.92
131.84
131.26
131.18
115.37
115.15
114.94
114.73
13C NMR GF-9-60B in DMSO-d6
F
N
N
OH
F
1i
13C NMR (100 MHz, DMSO-d6)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

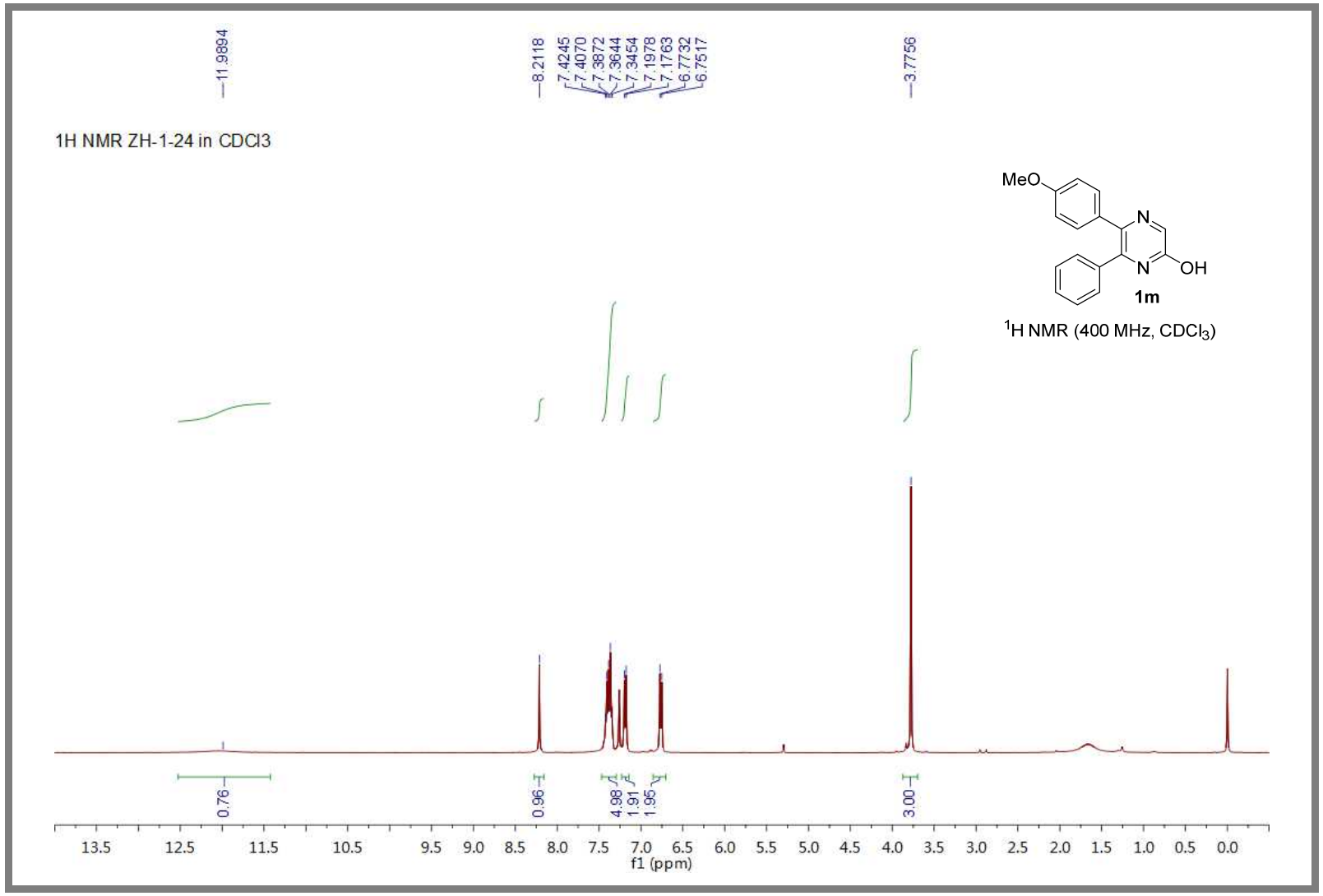

-112.1583
-114.6919
19F NMR GF-9-60B IN DMSO-d6
F
N
N
OH
F
1i
19F NMR (376 MHz, DMSO-d6)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

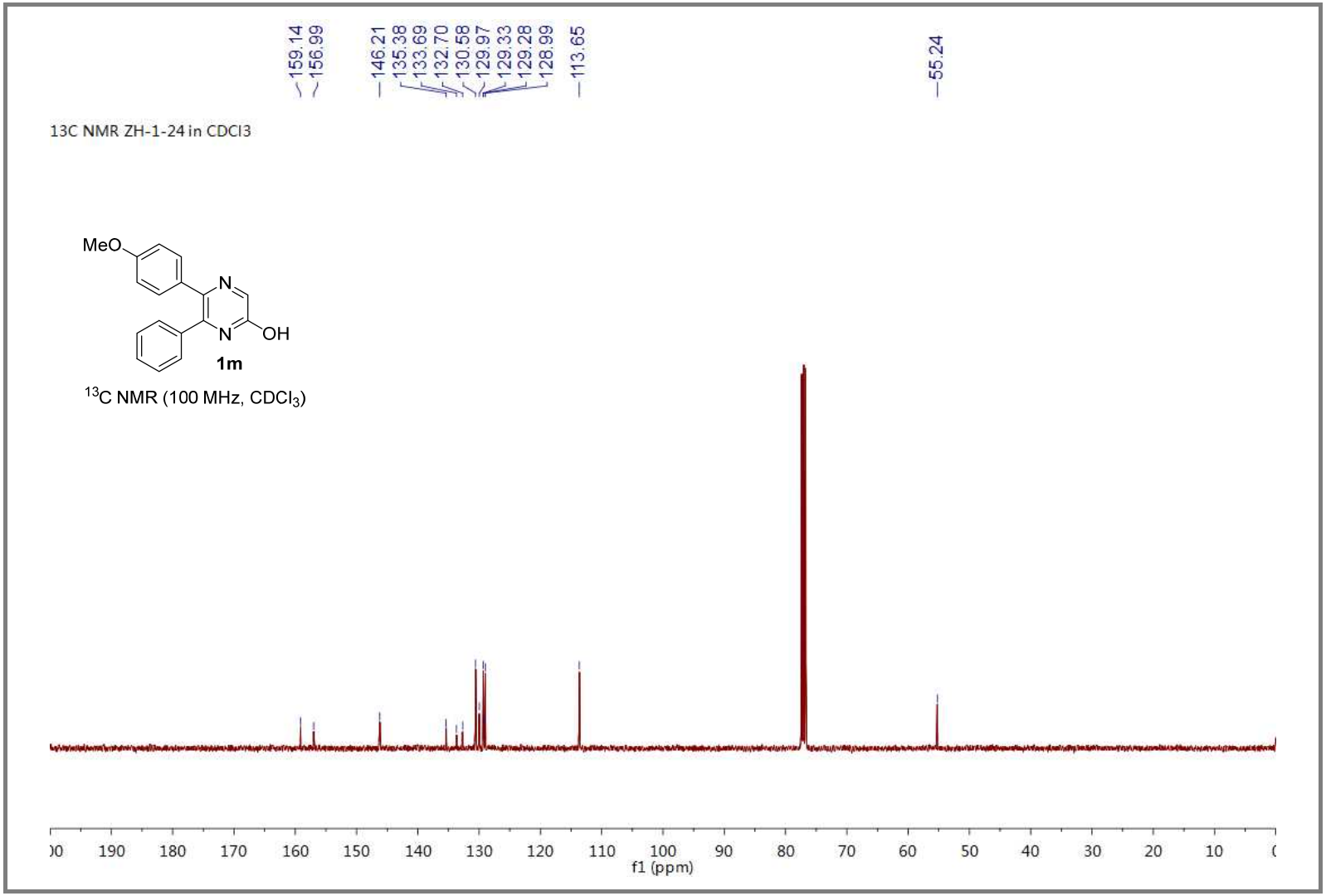

12.2691
8.1373
7.5615
7.5407
7.4617
7.4409
7.2826
7.2617
7.1783
7.1576
1H NMR GF-9-73B in DMSO-d6
Br
N
N
OH
Br
1k
1H NMR (400 MHz, DMSO-d6)
0.97
1.00
2.04
2.22
2.03
2.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

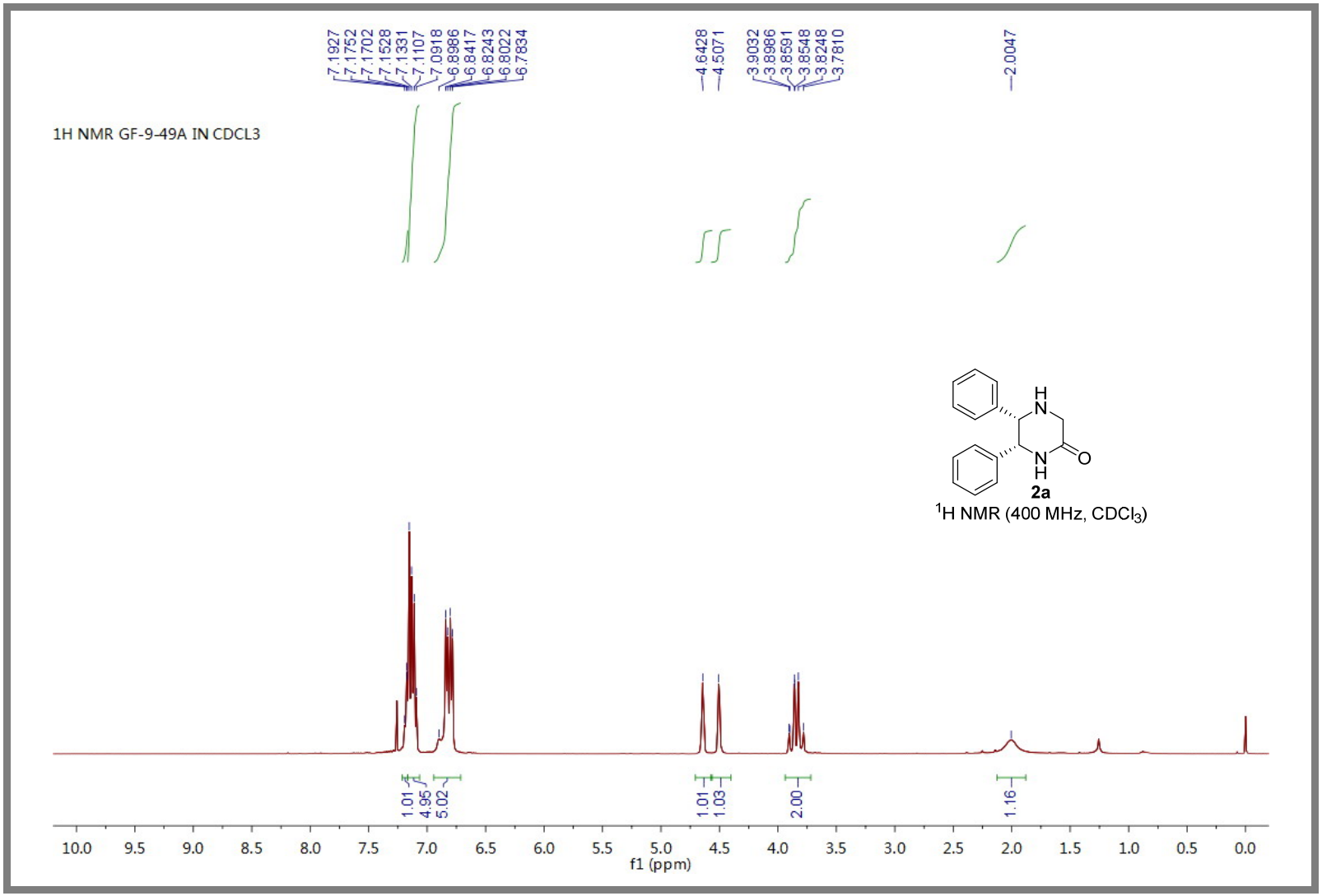

157.18
137.07
134.65
132.06
131.70
131.44
131.35
131.29
131.11
131.01
122.64
120.91
13C NMR GF-9-73B in DMSO-d6
Br
N
N
OH
Br
1k
13C NMR (100 MHz, DMSO-d6)
f1 (ppm)
f1 (ppm)

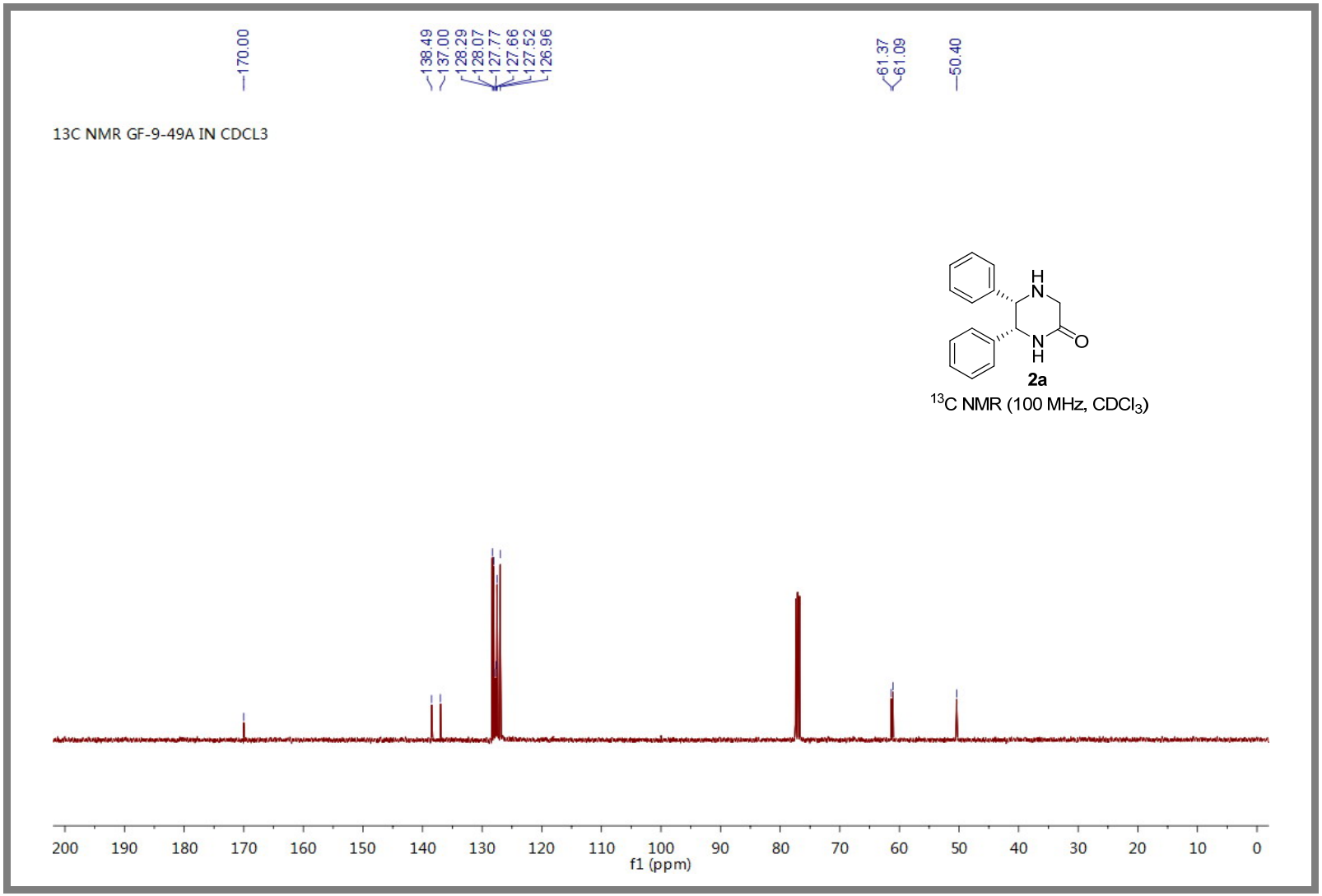

12.2077
8.2250
8.0466
7.9059
7.8377
7.8169
7.7894
7.7659
7.7455
7.7375
7.7156
7.6786
7.6594
7.6382
7.6168
7.5119
7.4955
7.4756
7.4558
7.4383
7.4271
7.4104
7.3926
7.3735
7.3561
7.3405
7.3193
7.2975
7.2765
1H NMR GF-9-69B in DMSO-d6
N
N
OH
1l
1H NMR (400 MHz, DMSO-d6)
0.84
1.00
1.06
0.98
2.09
2.11
2.09
1.93
2.09
2.12
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

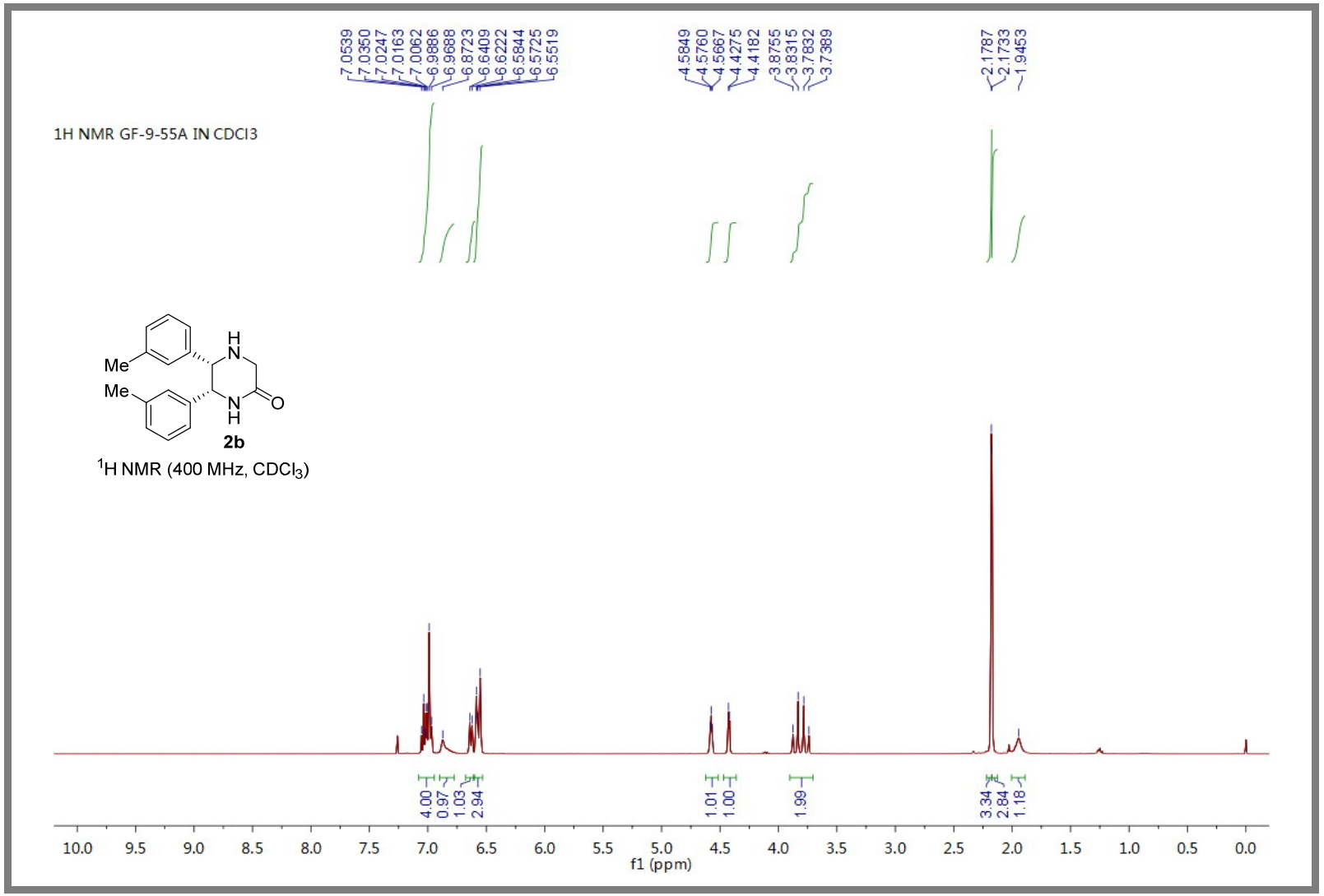

157.02
142.53
139.58
139.27
137.29
135.54
132.88
132.74
132.70
132.56
132.51
131.99
129.37
128.31
128.23
127.91
127.52
127.35
127.15
127.07
126.97
126.86
126.49
126.15
13C NMR GF-9-69B in DMSO-d6
N
N
OH
1l
13C NMR (100 MHz, DMSO-d6)
129.37
128.31
128.23
127.91
127.52
127.35
127.15
127.07
126.97
126.86
126.49
126.15
130
129
128
127
126
125
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

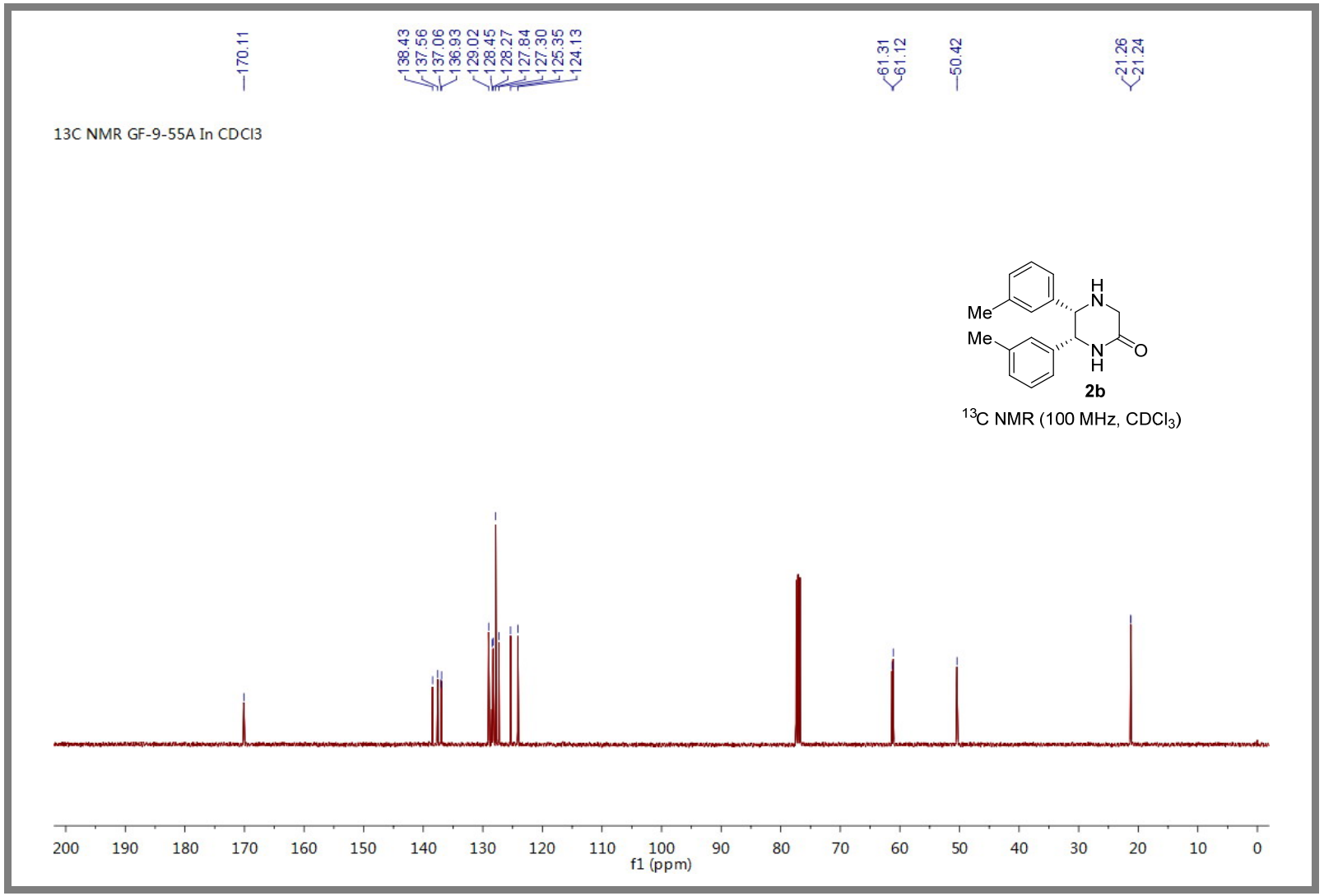

11.9894
8.2118
7.4245
7.4070
7.3872
7.3644
7.3454
7.1978
7.1763
6.7732
6.7517
3.7756
1H NMR ZH-1-24 in CDCl3
MeO
N
N
OH
1m
1H NMR (400 MHz, CDCl3)
0.76
0.96
4.98
1.91
1.95
3.00
13.5 12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

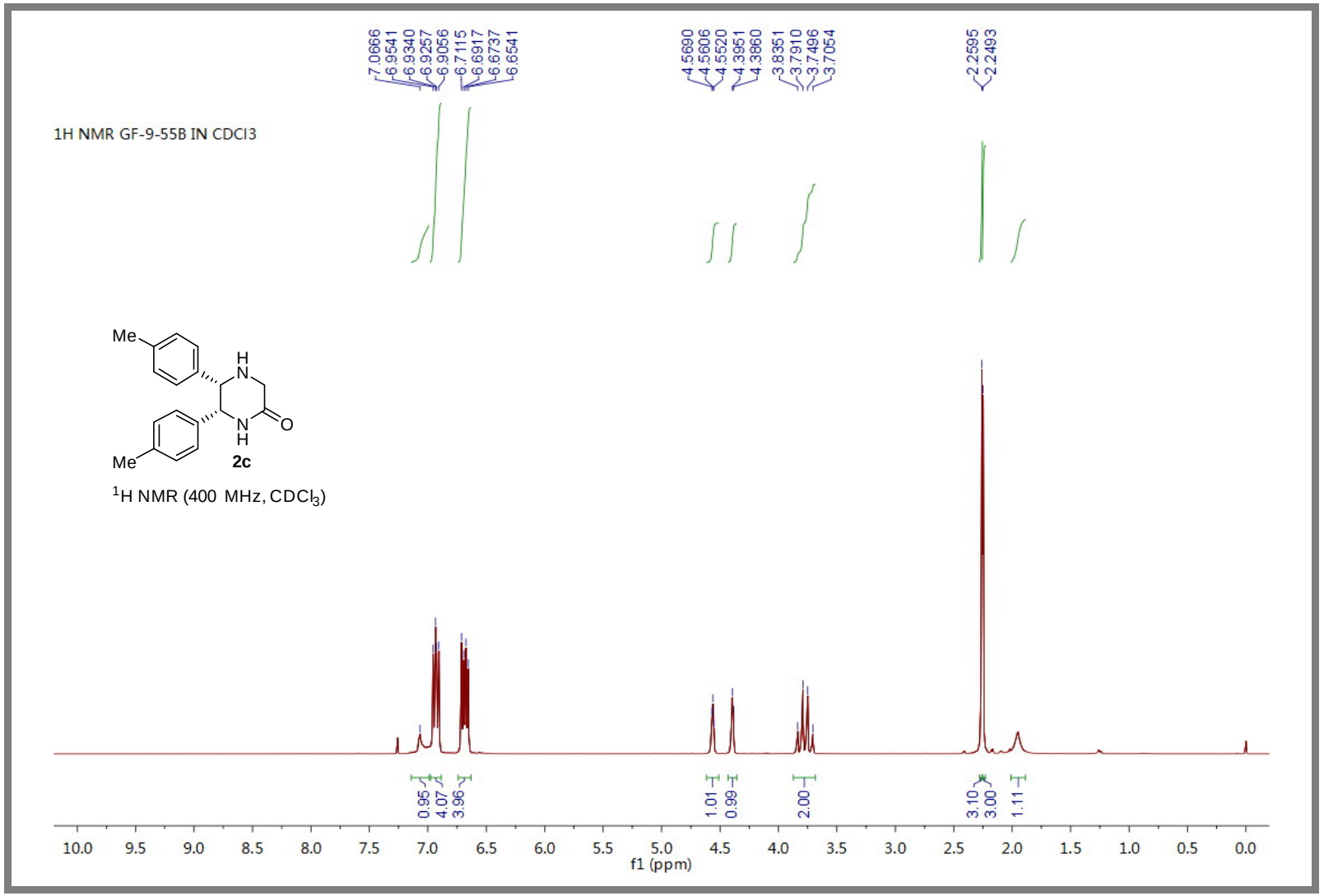

159.14
156.99
146.21
135.38
133.69
132.70
130.58
129.97
129.33
129.28
128.99
113.65
55.24
13C NMR ZH-1-24 in CDCl3
MeO
N
N
OH
1m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

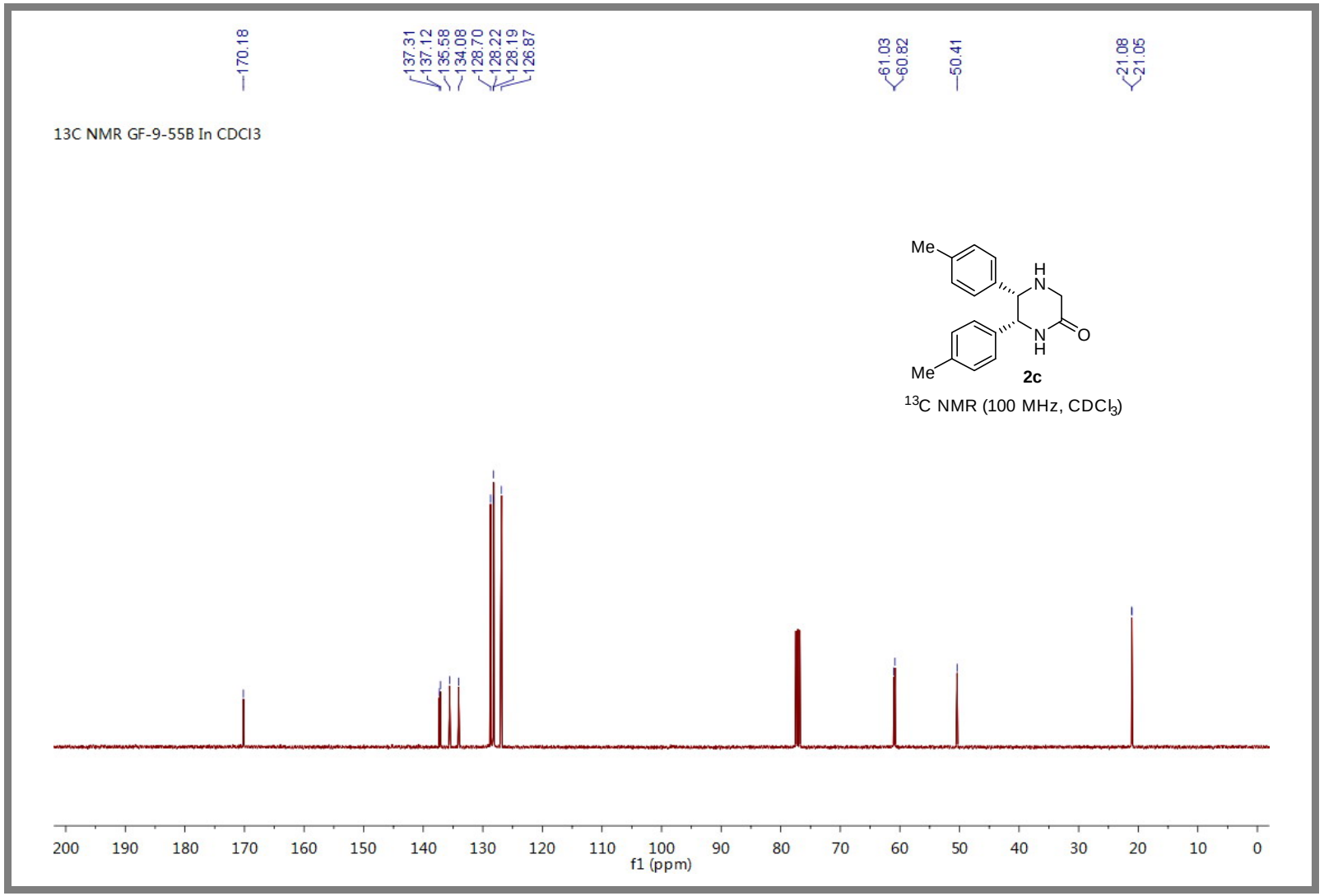

1H NMR GF-9-49A IN CDCL3
7.1927
7.1752
7.1702
7.1528
7.1331
7.1107
7.0918
6.8986
6.8417
6.8243
6.8022
6.7834
4.6428
4.5071
3.9032
3.8986
3.8591
3.8548
3.8248
3.7810
2.0047
H
N
N
H
O
2a
1H NMR (400 MHz, CDCl3)
1.01
4.95
5.02
1.01
1.03
2.00
1.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

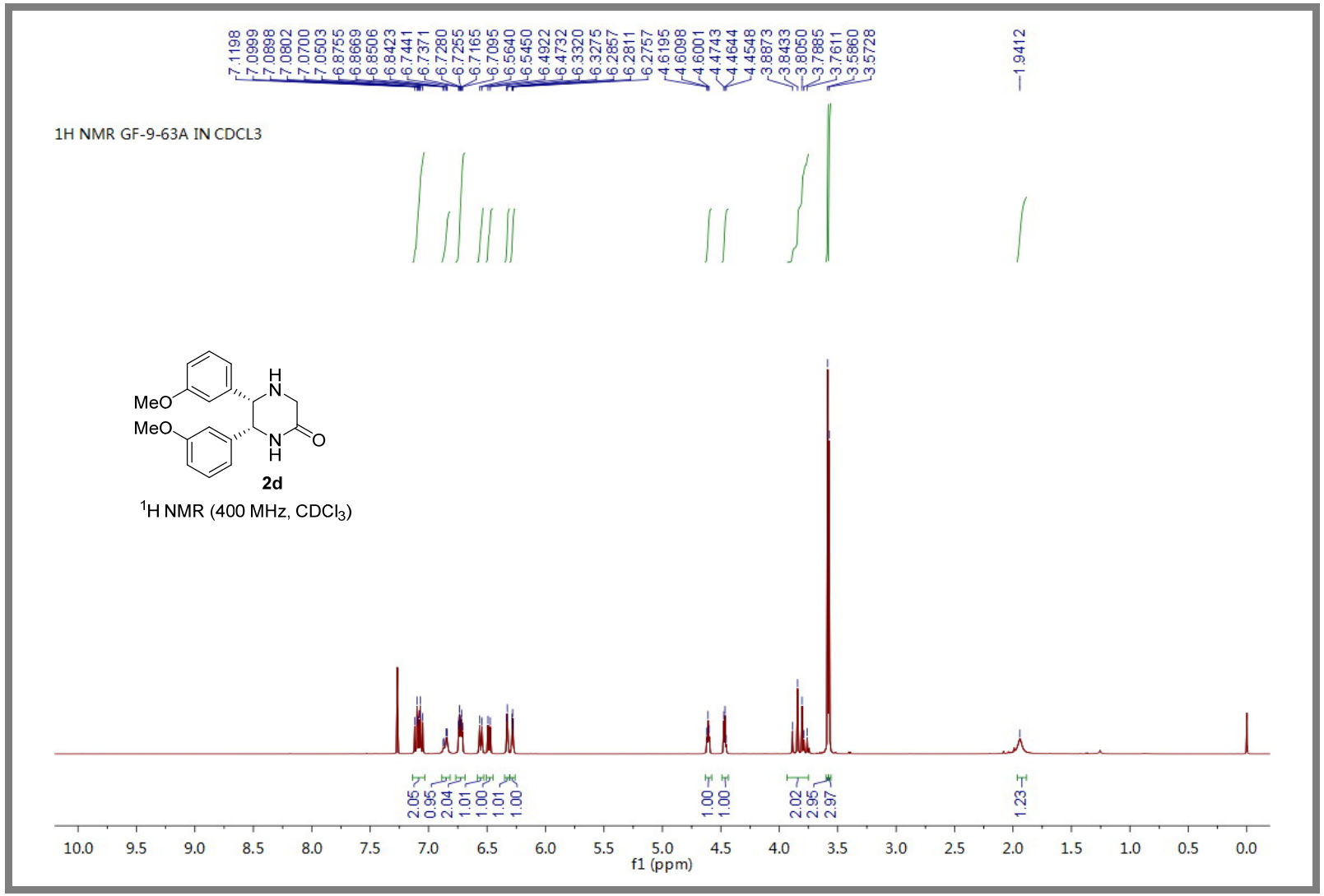

170.00
138.49
137.00
128.29
128.07
127.77
127.66
127.52
126.96
61.37
61.09
50.40
13C NMR GF-9-49A IN CDCL3
H
N
N
H
O
2a
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

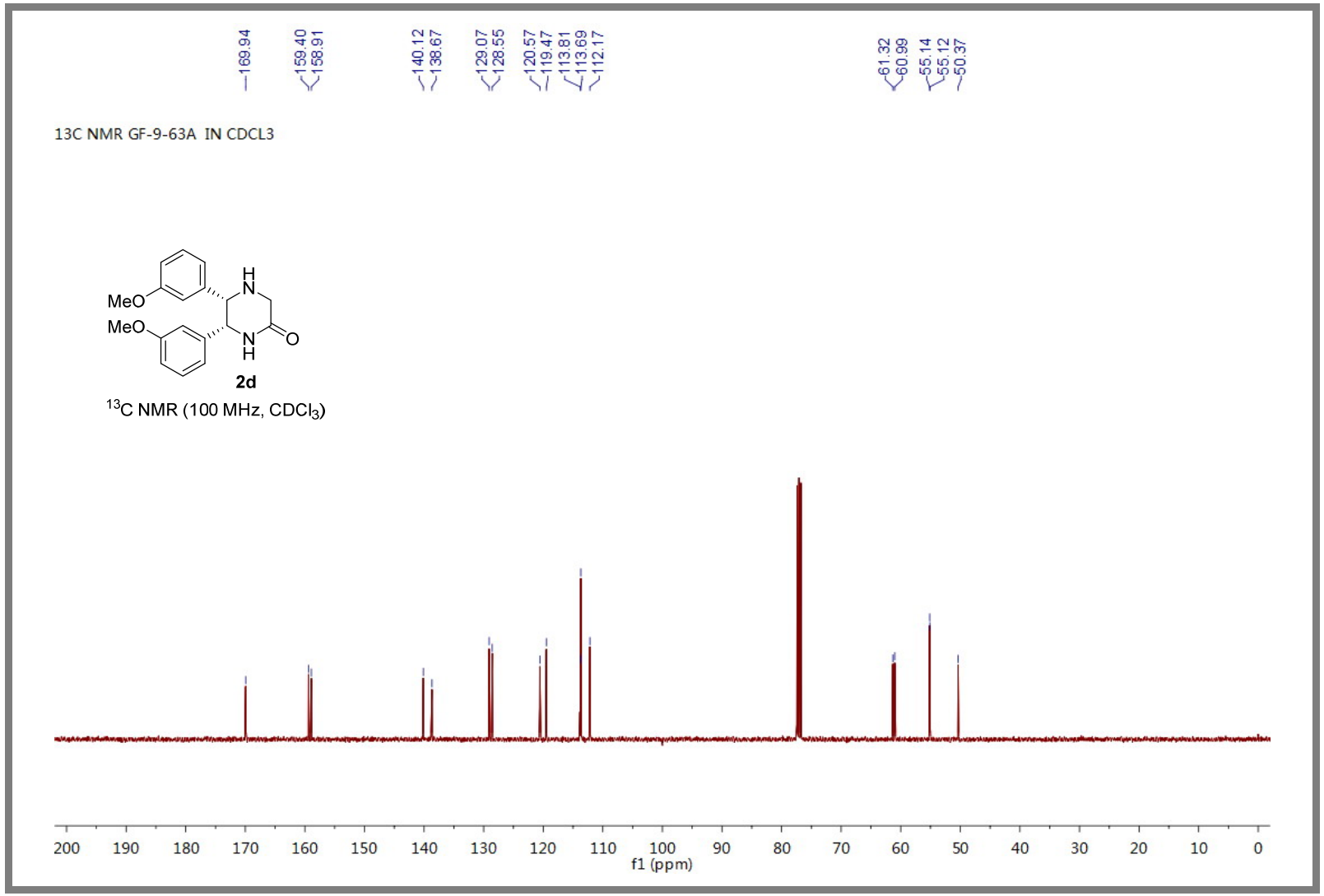

7.0539
7.0350
7.0247
7.0163
7.0062
6.9886
6.9688
6.8723
6.6409
6.6222
6.5844
6.5725
6.5519
4.5849
4.5760
4.5667
4.4275
4.4182
3.8755
3.8315
3.7832
3.7389
2.1787
2.1733
1.9453
1H NMR GF-9-55A IN CDCl3
Me
Me
H
N
N
H
O
2b
1H NMR (400 MHz, CDCl3)
4.00
0.97
1.03
2.94
1.01
1.00
1.99
3.34
2.84
1.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

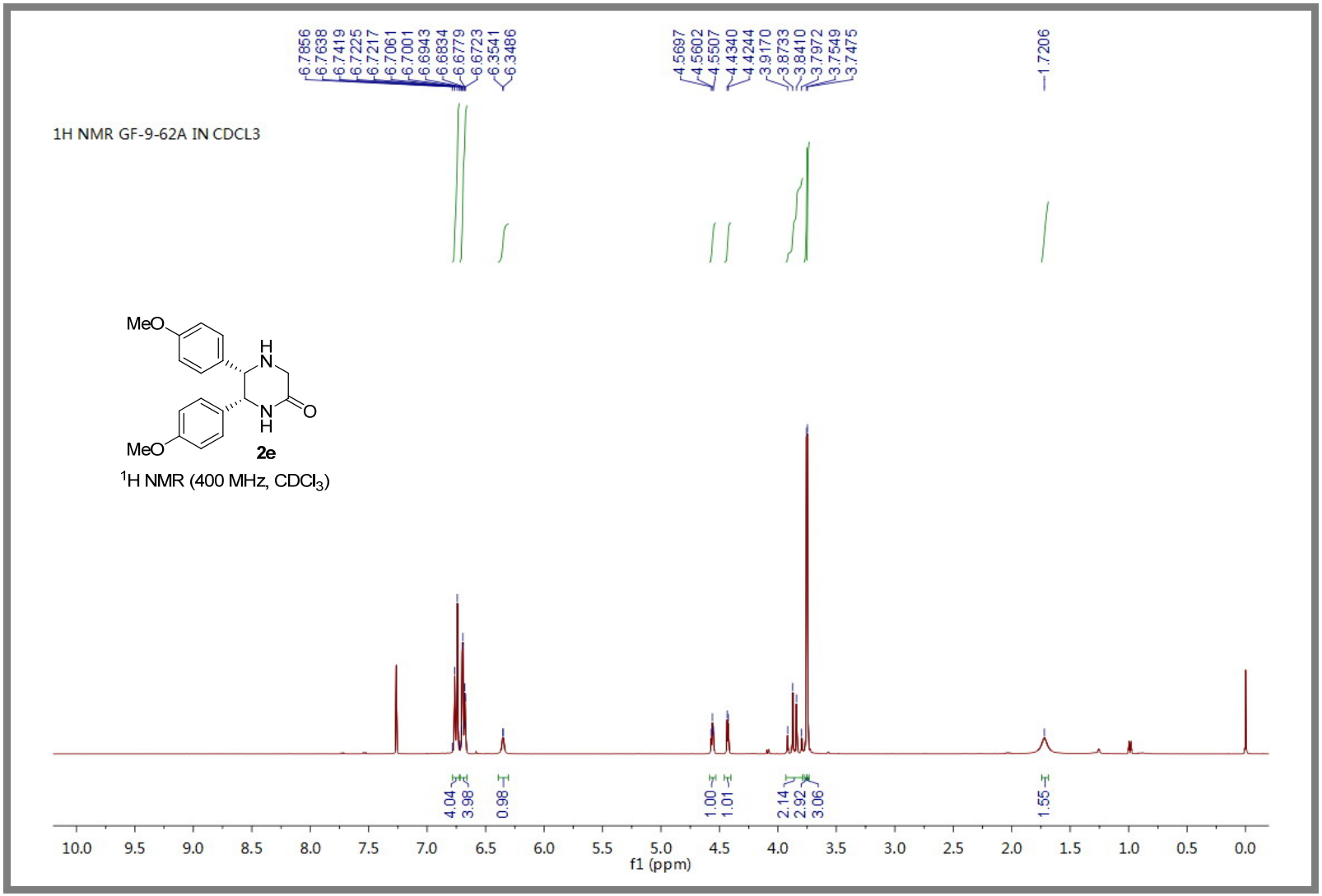

170.11
138.43
137.56
137.06
136.93
129.02
128.45
128.27
127.84
127.30
125.35
124.13
61.31
61.12
50.42
21.26
21.24
13C NMR GF-9-55A In CDCl3
Me
Me
H
N
N
H
O
2b
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

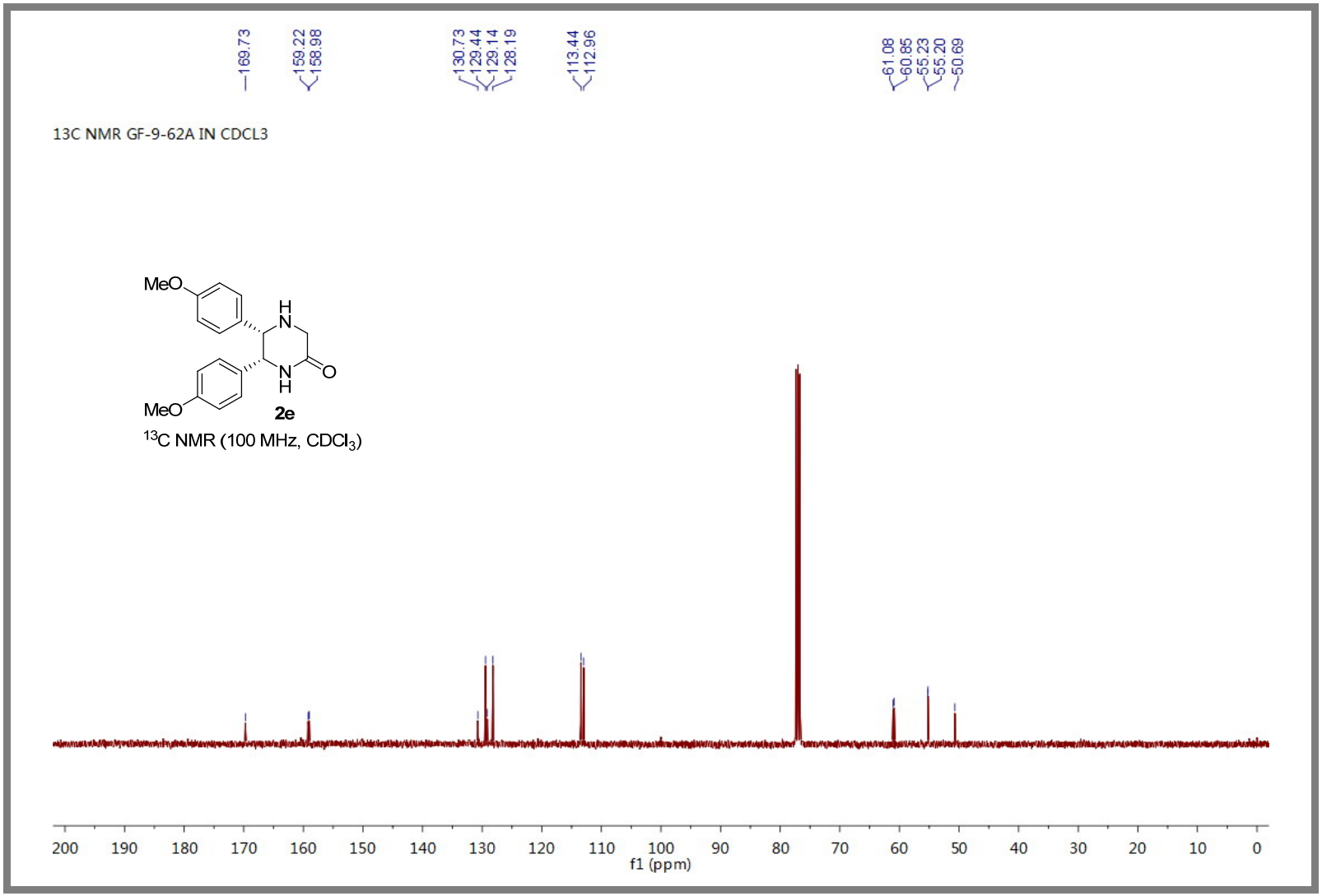

1H NMR GF-9-55B IN CDCl3
7.0666
6.9541
6.9340
6.9257
6.9056
6.7115
6.6917
6.6737
6.6541
4.5690
4.5606
4.5520
4.3951
4.3860
3.8351
3.7910
3.7496
3.7054
2.2595
2.2493
Me
H
N
N
H
O
Me
2c
1H NMR (400 MHz, CDCl3)
0.95
4.07
3.96
1.01
0.99
2.00
3.10
3.00
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

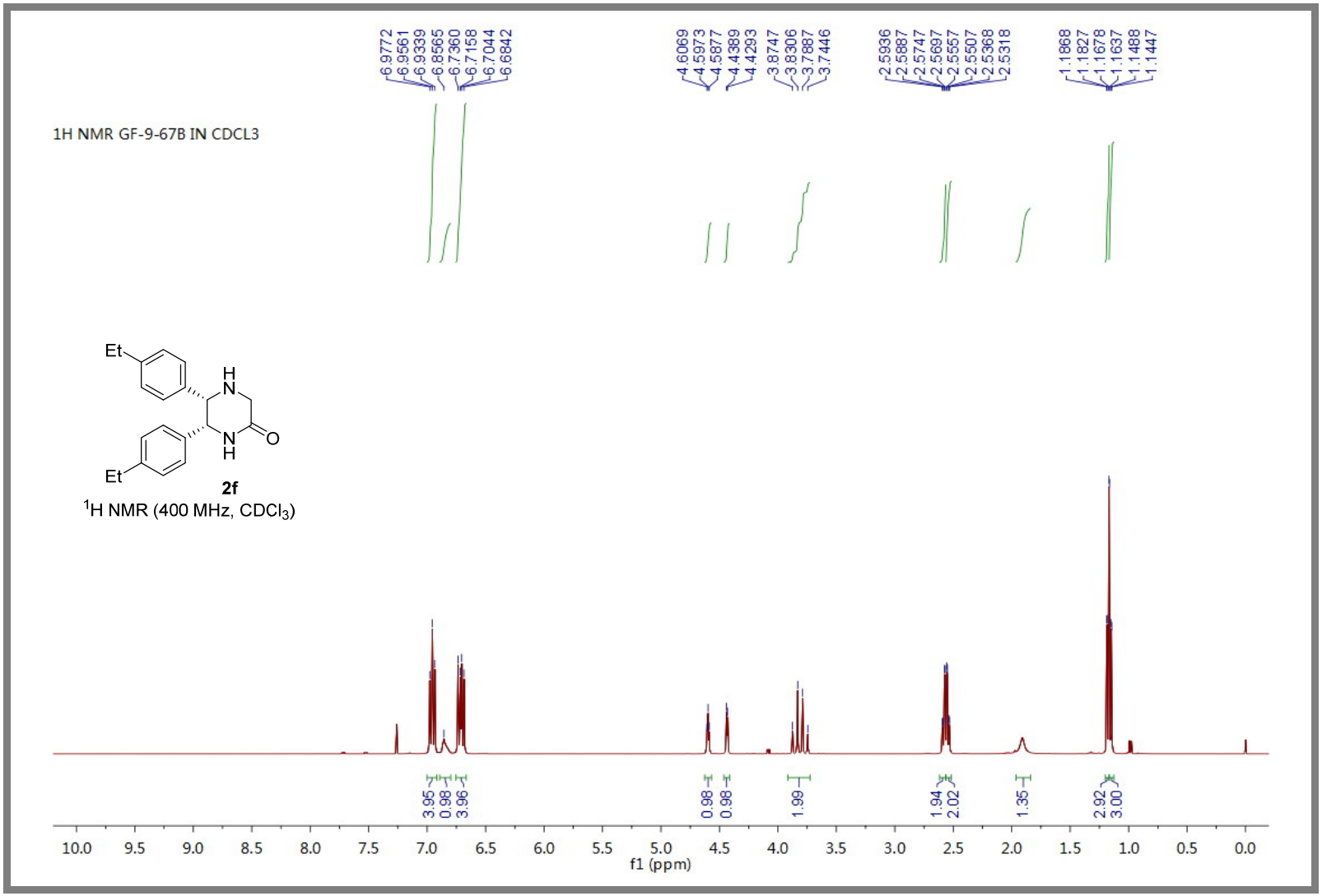

170.18
137.31
137.12
135.58
134.08
128.70
128.22
128.19
126.87
61.03
60.82
50.41
21.08
21.05
13C NMR GF-9-55B In CDCl3
Me
H
N
N
H
O
Me
2c
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

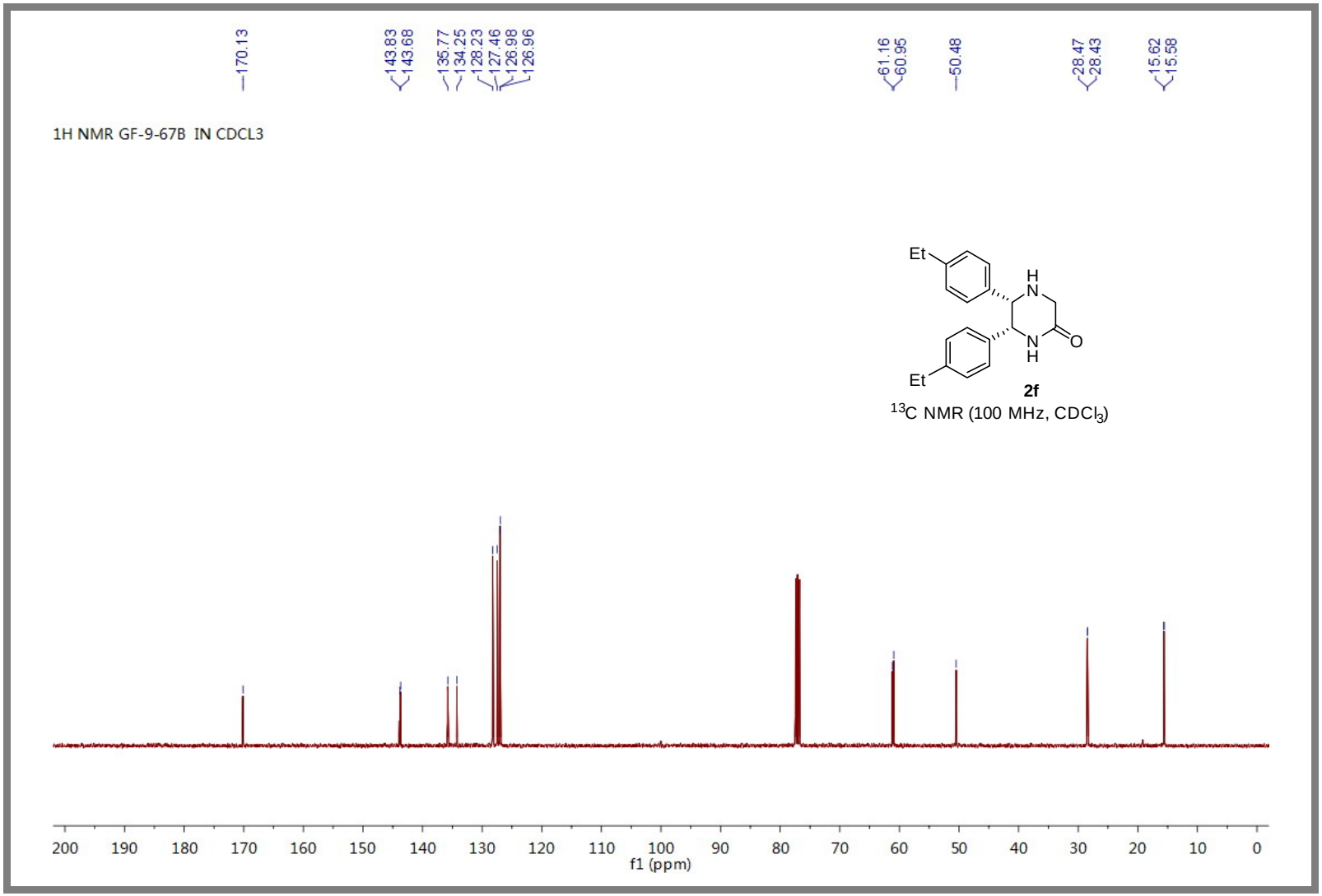

7.1198
7.0999
7.0898
7.0802
7.0700
7.0503
6.8755
6.8669
6.8506
6.8423
6.7441
6.7371
6.7280
6.7255
6.7165
6.7095
6.5640
6.5450
6.4922
6.4732
6.3320
6.3275
6.2857
6.2811
6.2757
4.6195
4.6098
4.6001
4.4743
4.4644
4.4548
3.8873
3.8433
3.8050
3.7885
3.7611
3.5860
3.5728
1.9412
1H NMR GF-9-63A IN CDCL3
MeO
MeO
H
N
N
H
O
2d
1H NMR (400 MHz, CDCl3)
2.05
0.95
2.04
1.01
1.00
1.01
1.00
1.00
1.00
2.02
2.95
2.97
1.23
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

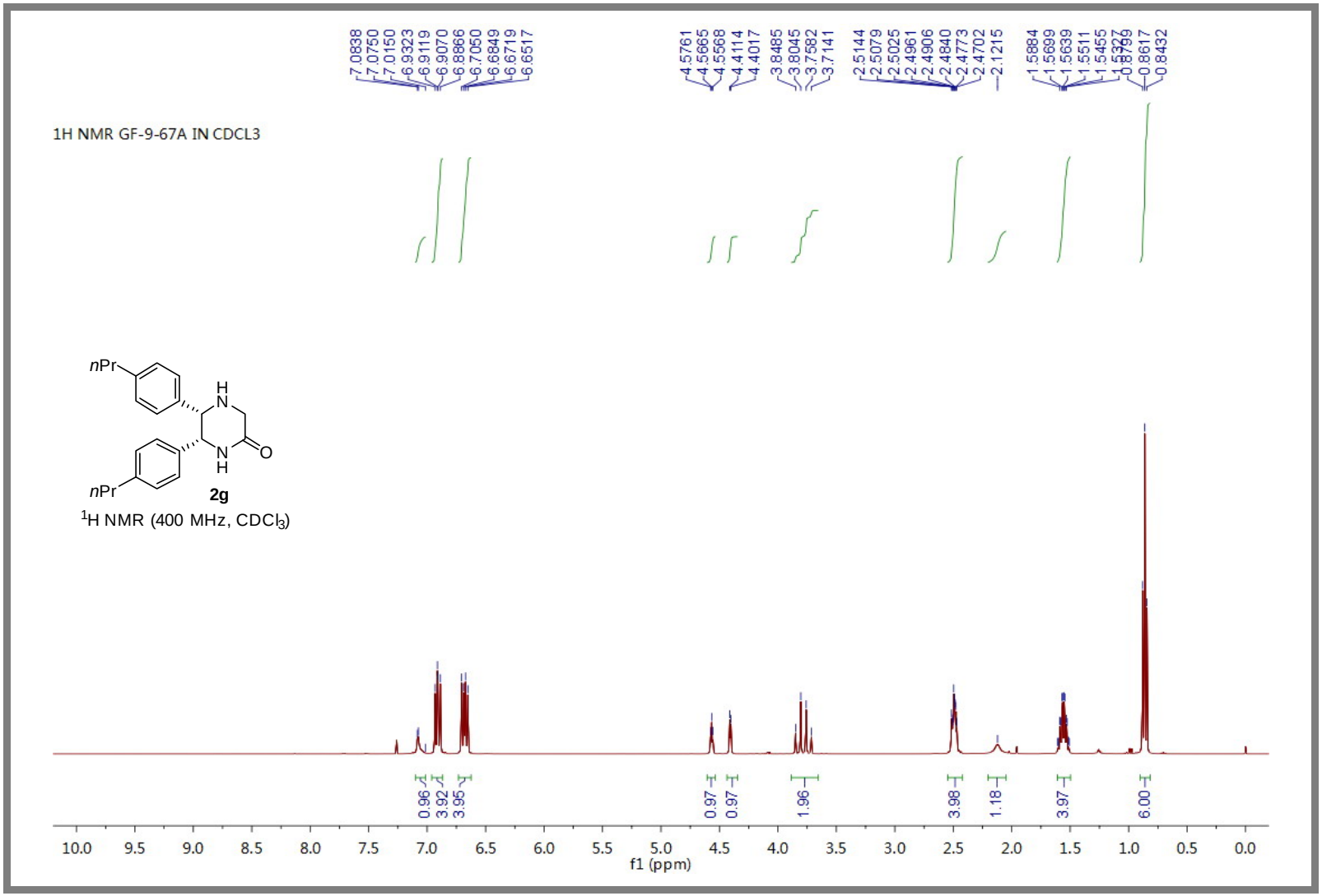

169.94
159.40
158.91
140.12
138.67
129.07
128.55
120.57
119.47
113.81
113.69
112.17
61.32
60.99
55.14
55.12
50.37
13C NMR GF-9-63A IN CDCL3
MeO
MeO
H
N
N
H
O
2d
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

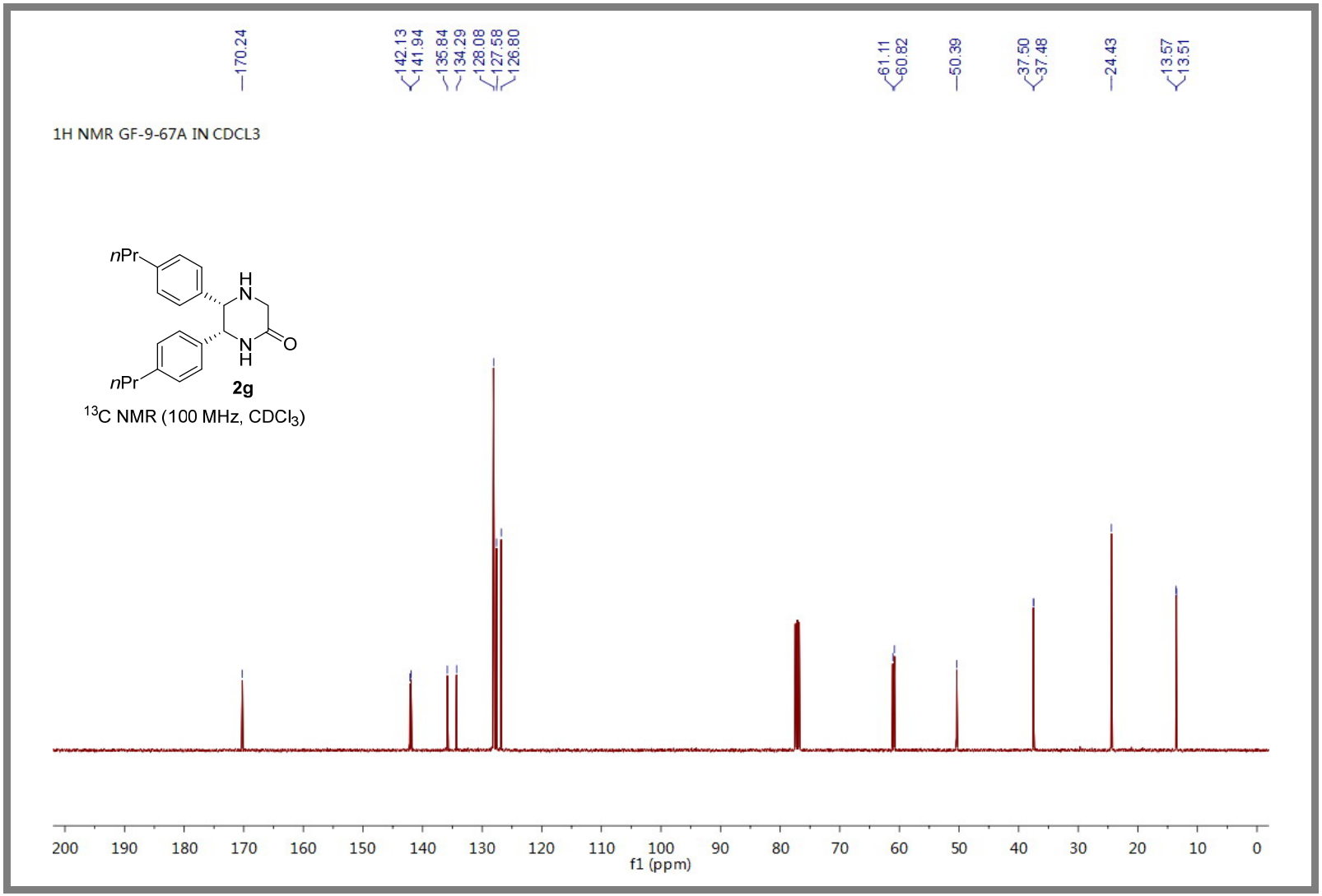

1H NMR GF-9-62A IN CDCL3
6.7856
6.7638
6.7419
6.7225
6.7217
6.7061
6.7001
6.6943
6.6834
6.6779
6.6723
6.3541
6.3486
4.5697
4.5602
4.5507
4.4340
4.4244
3.9170
3.8733
3.8410
3.7972
3.7549
3.7475
1.7206
MeO
MeO
H
N
N
H
O
2e
1H NMR (400 MHz, CDCl3)
4.04
3.98
0.98
1.00
1.01
2.14
2.92
3.06
1.55
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

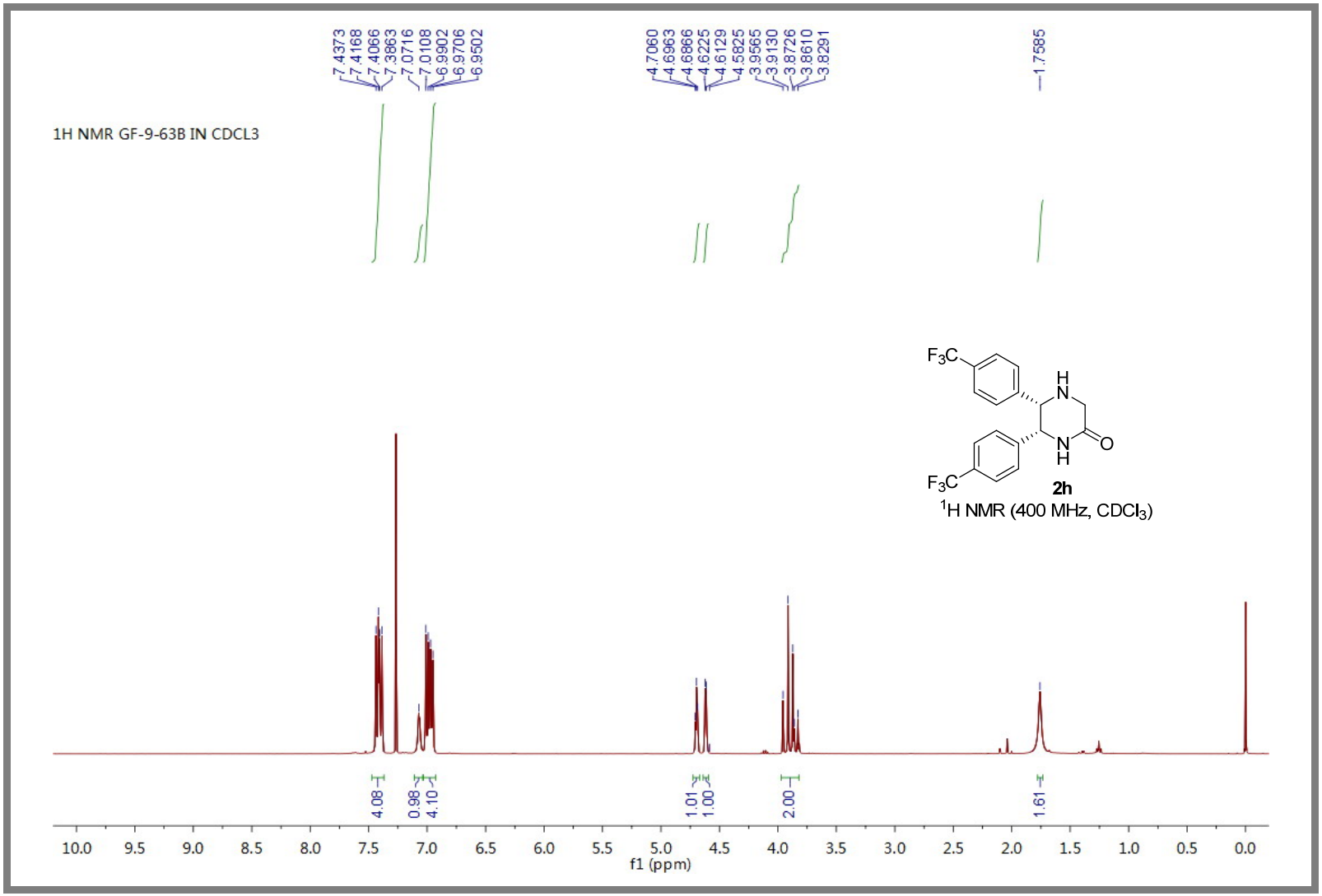

169.73
159.22
158.98
130.73
129.44
129.14
128.19
113.44
112.96
61.08
60.85
55.23
55.20
50.69
13C NMR GF-9-62A IN CDCL3
MeO
H
N
N
H
O
MeO
2e
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

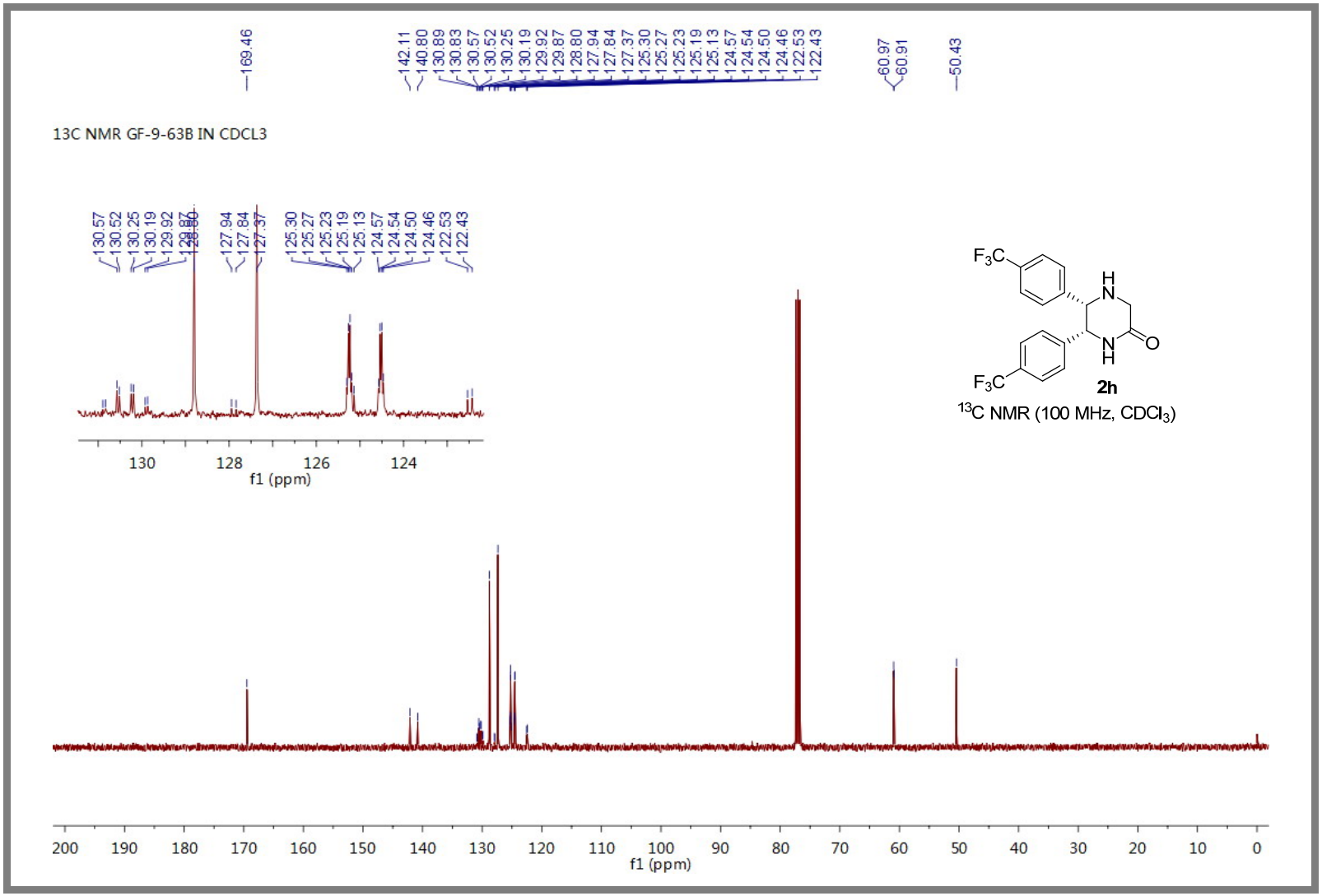

1H NMR GF-9-67B IN CDCL3
6.9772
6.9561
6.9339
6.8565
6.7360
6.7158
6.7044
6.6842
4.6069
4.5973
4.5877
4.4389
4.4293
3.8747
3.8306
3.7887
3.7446
2.5936
2.5887
2.5747
2.5697
2.5557
2.5507
2.5368
2.5318
1.1868
1.1827
1.1678
1.1637
1.1488
1.1447
Et
H
N
N
H
O
Et
2f
1H NMR (400 MHz, CDCl3)
3.95
0.98
3.96
0.98
0.98
1.99
1.94
2.02
1.35
2.92
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

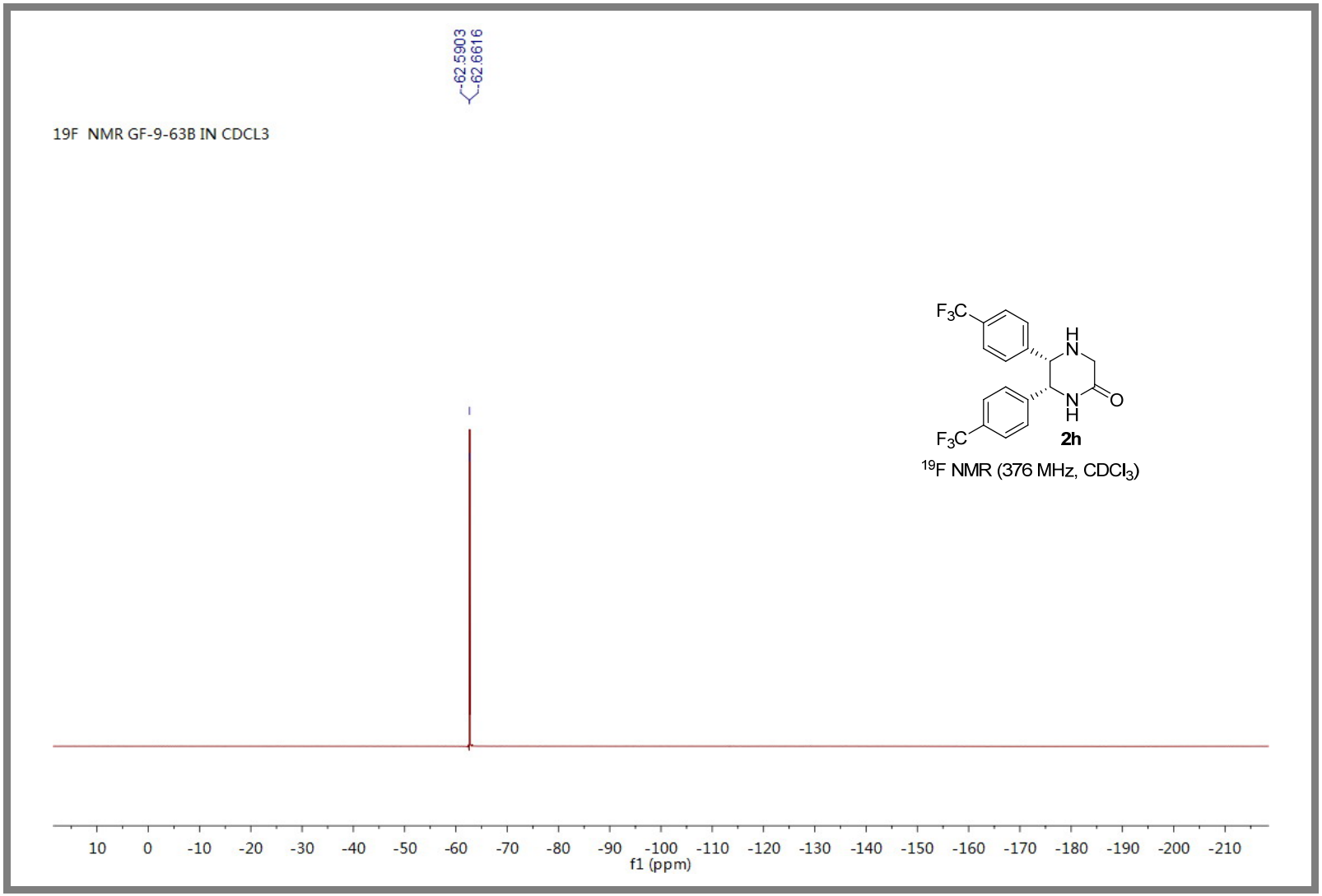

170.13
143.83
143.68
135.77
134.25
128.23
127.46
126.98
126.96
61.16
60.95
50.48
28.47
28.43
15.62
15.58
1H NMR GF-9-67B IN CDCL3
Et
H
N
N
H
O
Et
2f
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

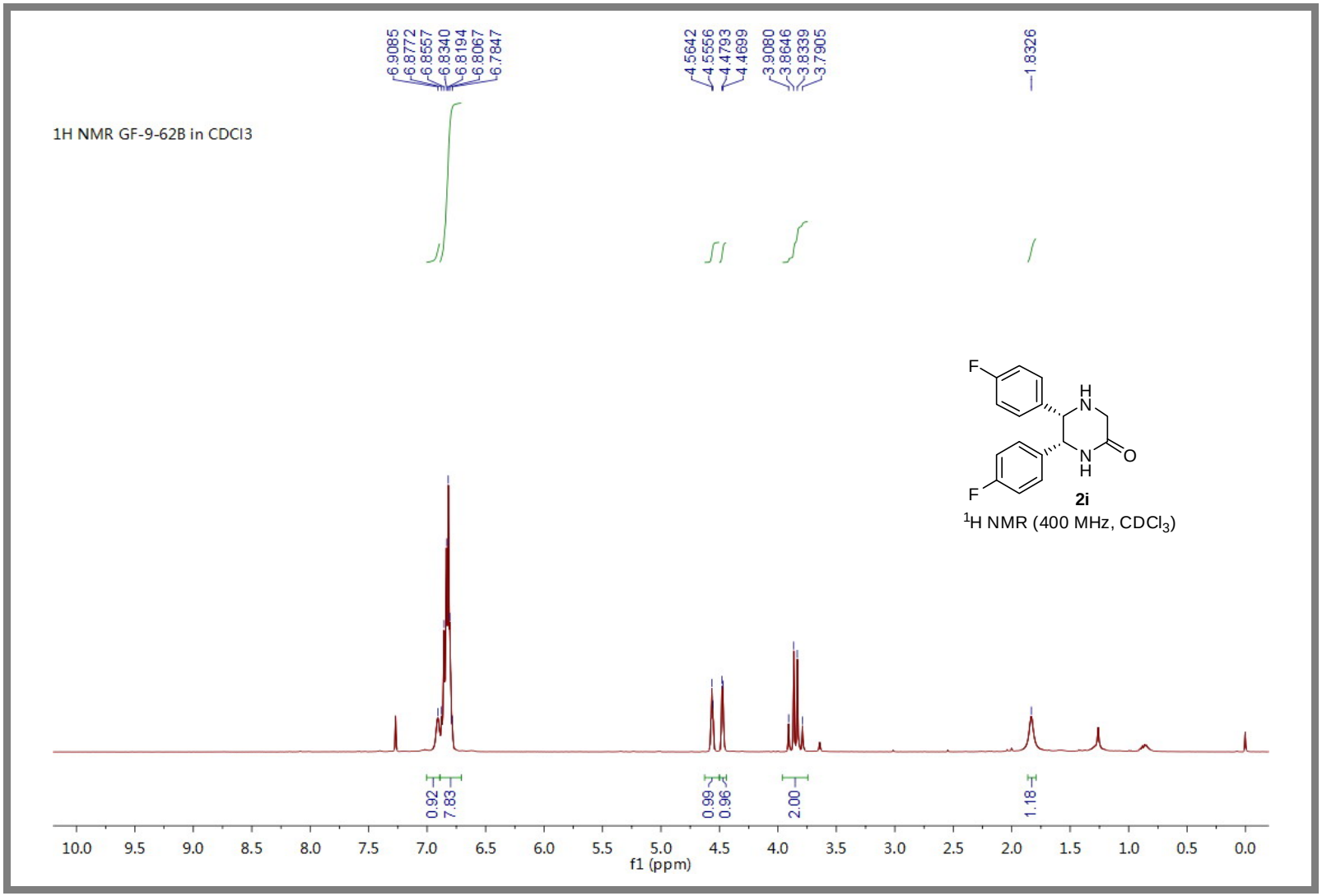

1H NMR GF-9-67A IN CDCL3
nPr
H
N
N
H
O
nPr
2g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

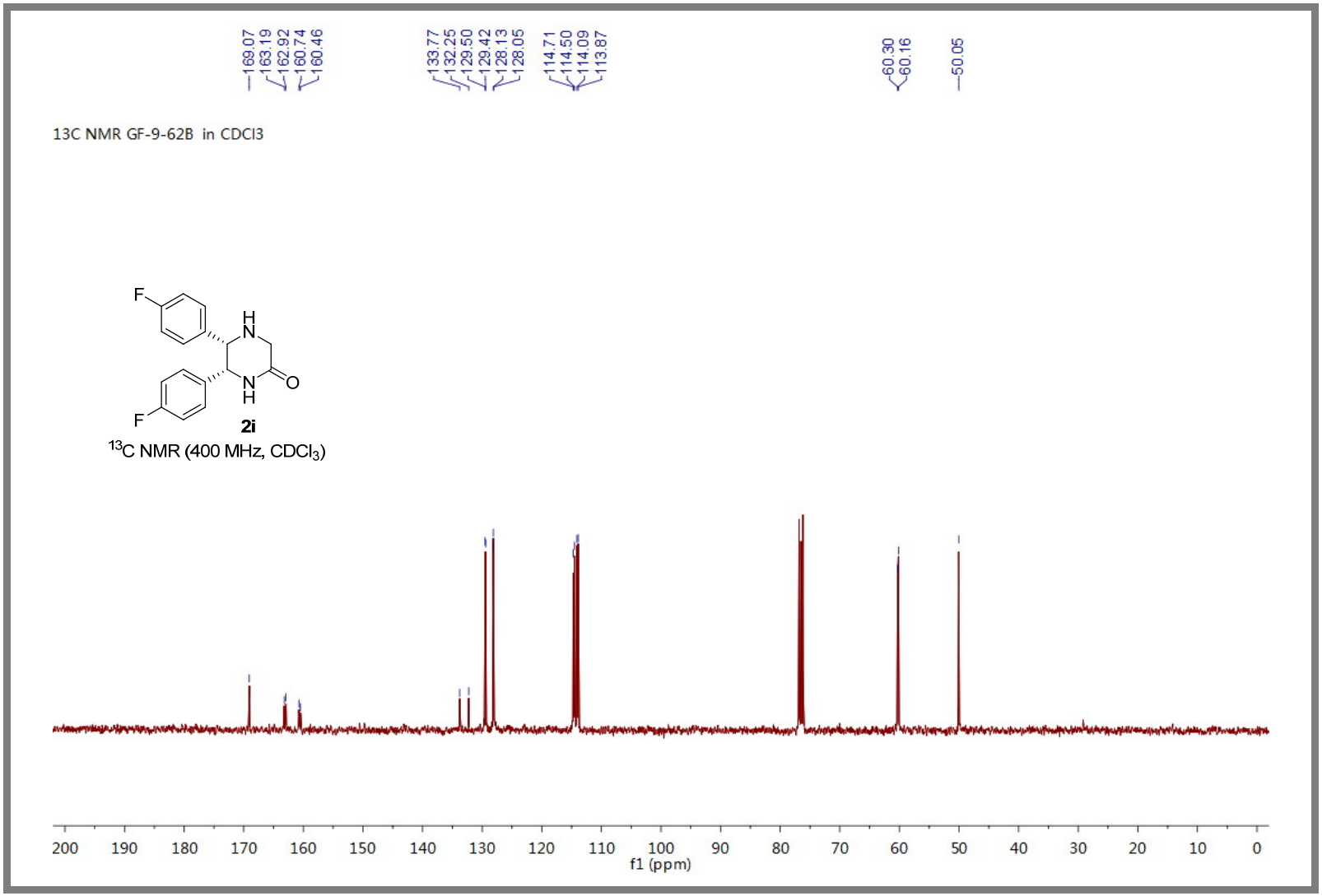

170.24
142.13
141.94
135.84
134.29
128.08
127.58
126.80
61.11
60.82
50.39
37.50
37.48
24.43
13.57
13.51
1H NMR GF-9-67A IN CDCL3
nPr
nPr
H
N
N
H
O
2g
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

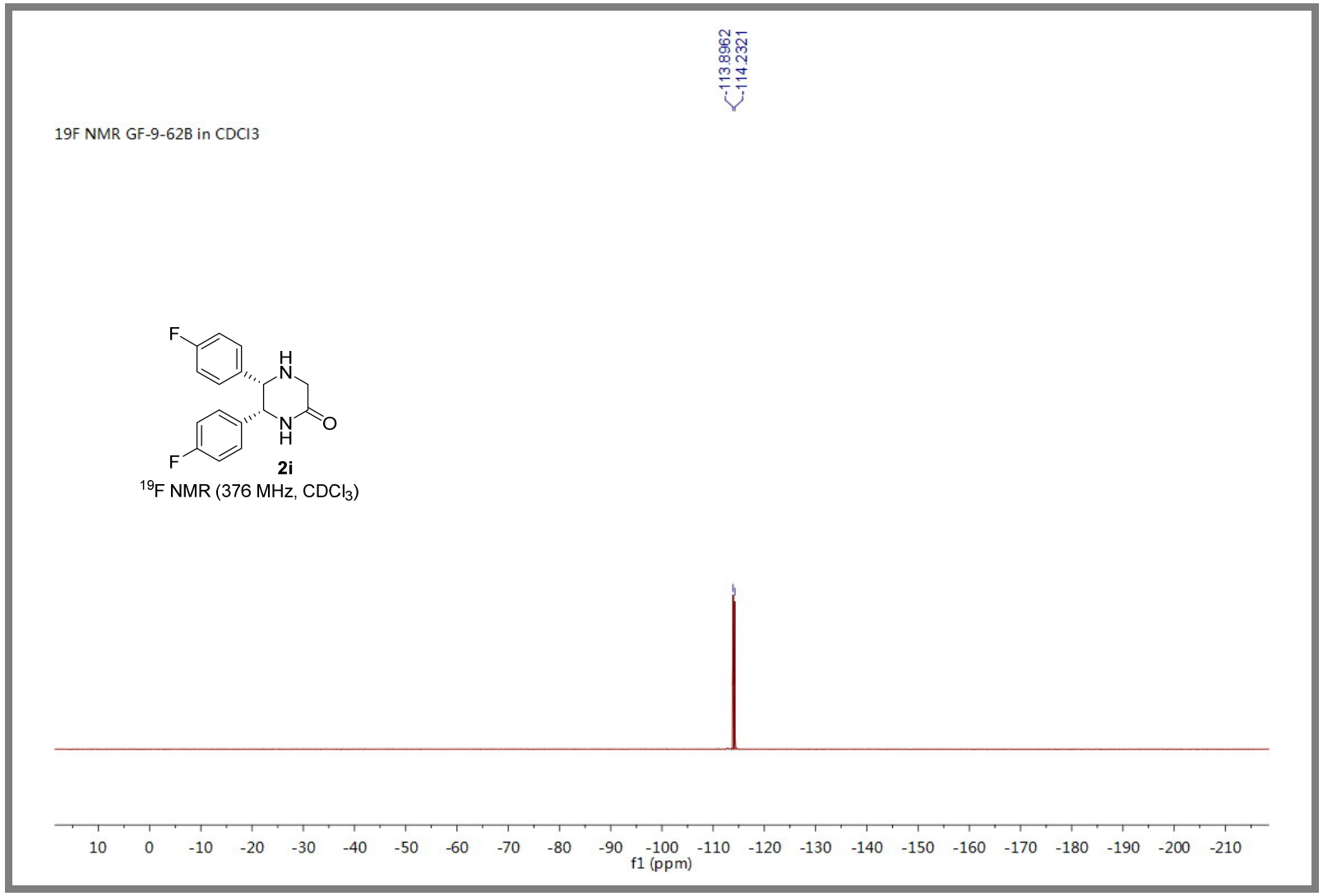

1H NMR GF-9-63B IN CDCL3
7.4373
7.4168
7.4066
7.3863
7.0716
7.0108
6.9902
6.9706
6.9502
4.7060
4.6963
4.6866
4.6225
4.6129
4.5825
3.9565
3.9130
3.8726
3.8610
3.8291
1.7585
F3C
H
N
N
H
O
F3C
2h
1H NMR (400 MHz, CDCl3)
4.08
0.98
4.10
1.01
1.00
2.00
1.61
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

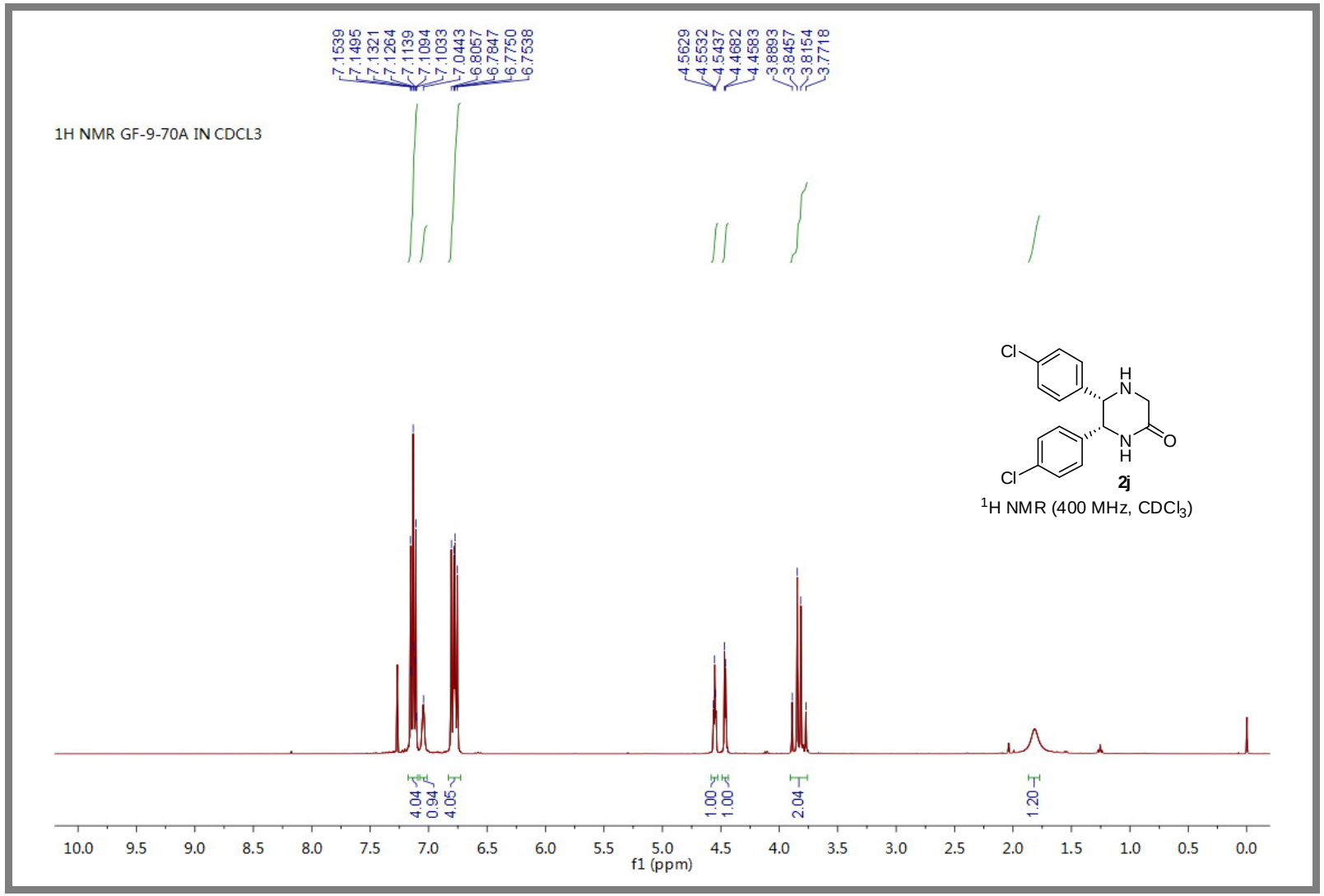

169.46
142.11
140.80
130.89
130.83
130.57
130.52
130.25
130.19
129.92
129.87
128.80
127.94
127.84
127.37
125.30
125.27
125.23
125.19
125.13
124.57
124.54
124.50
124.46
122.53
122.43
60.97
60.91
50.43
13C NMR GF-9-63B IN CDCL3
f1 (ppm)
F3C
H
N
N
H
O
F3C
2h
13C NMR (100 MHz, CDCl3)

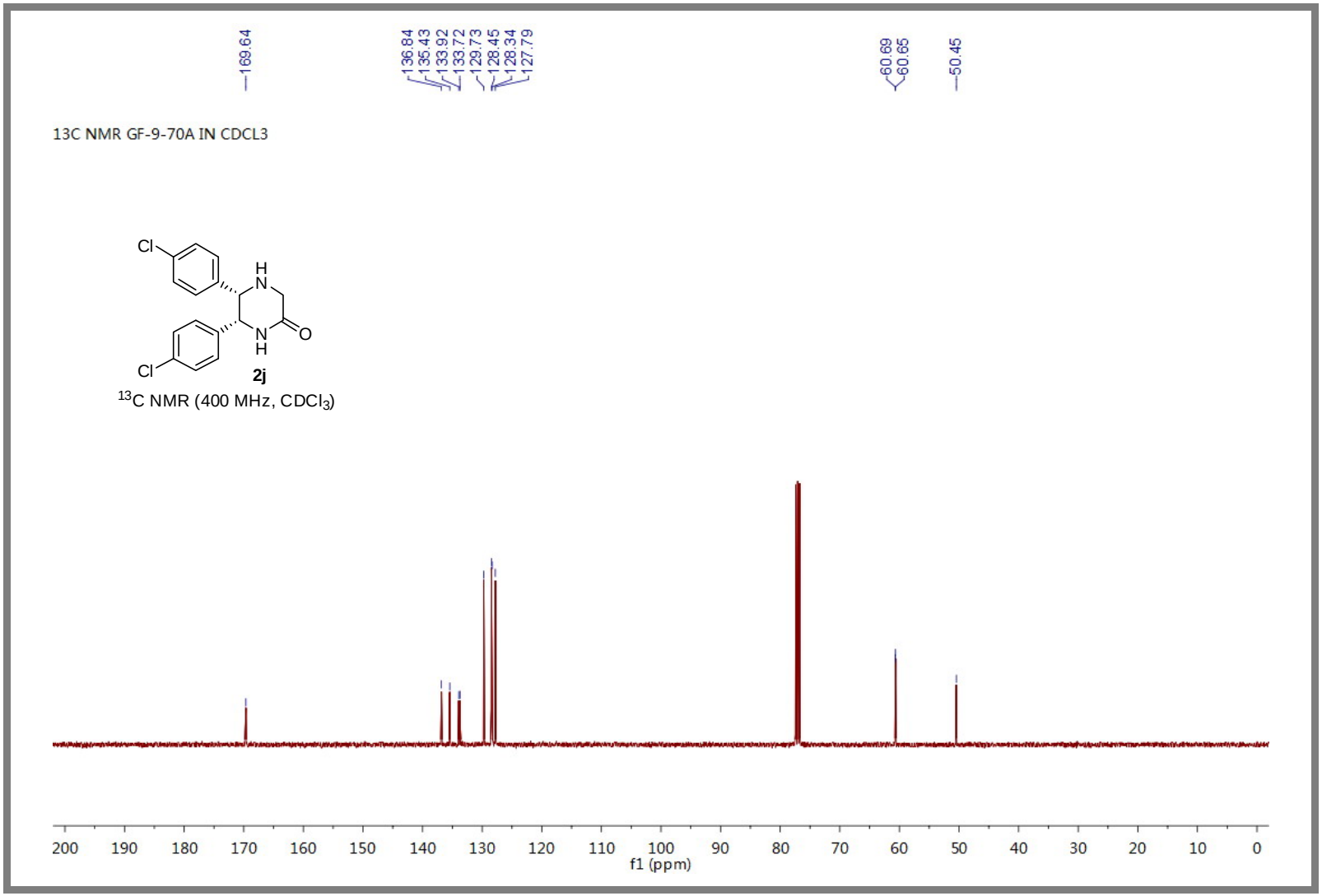

-62.5903
-62.6616
19F NMR GF-9-63B IN CDCL3
F3C
H
N
N
H
O
F3C
2h
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

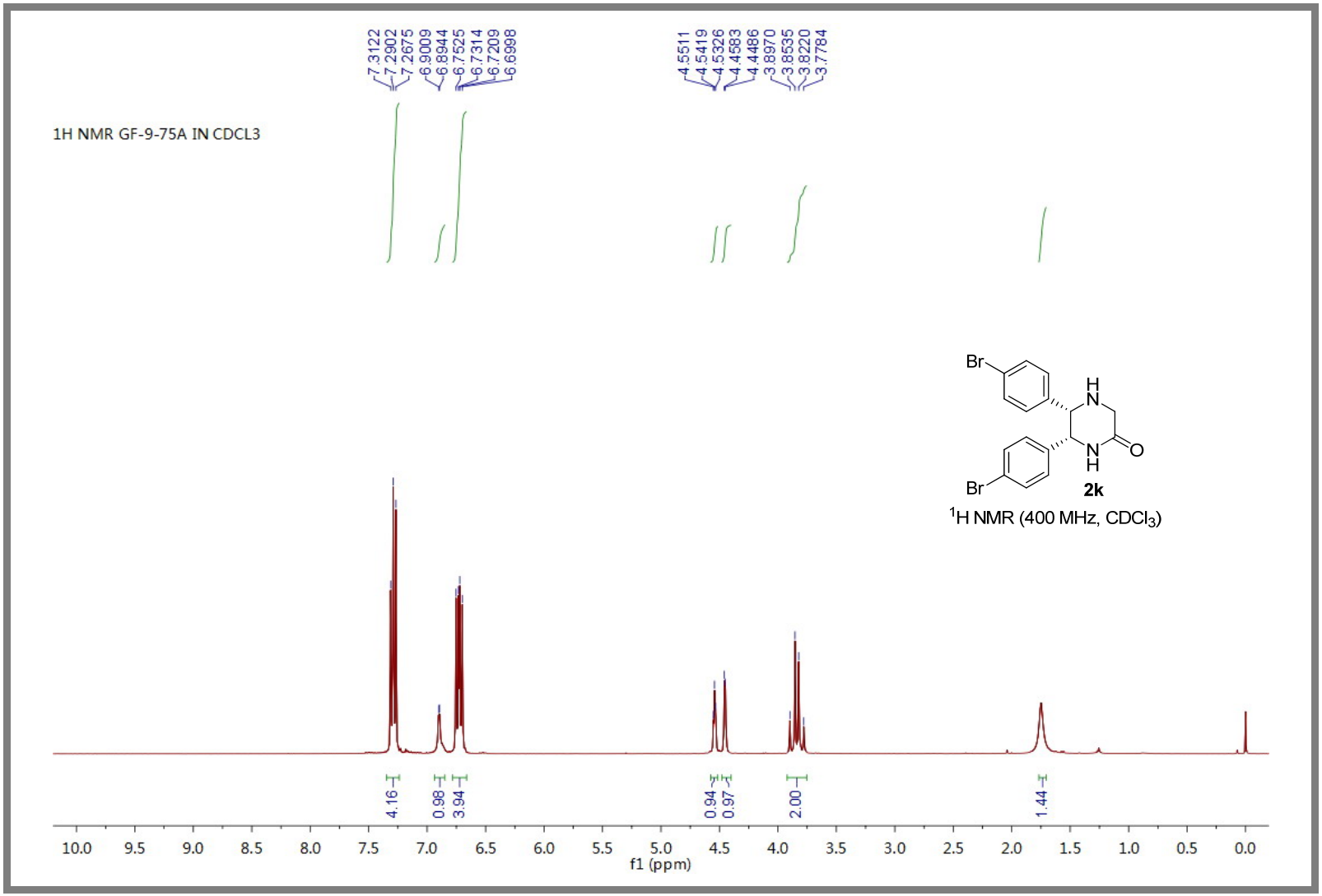

1H NMR GF-9-62B in CDCl3
6.9085
6.8772
6.8557
6.8340
6.8194
6.8067
6.7847
4.5642
4.5556
4.4793
4.4699
3.9080
3.8646
3.8339
3.7905
1.8326
F
H
N
N
H
O
F
2i
1H NMR (400 MHz, CDCl3)
0.92
7.83
0.99
0.96
2.00
1.18
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

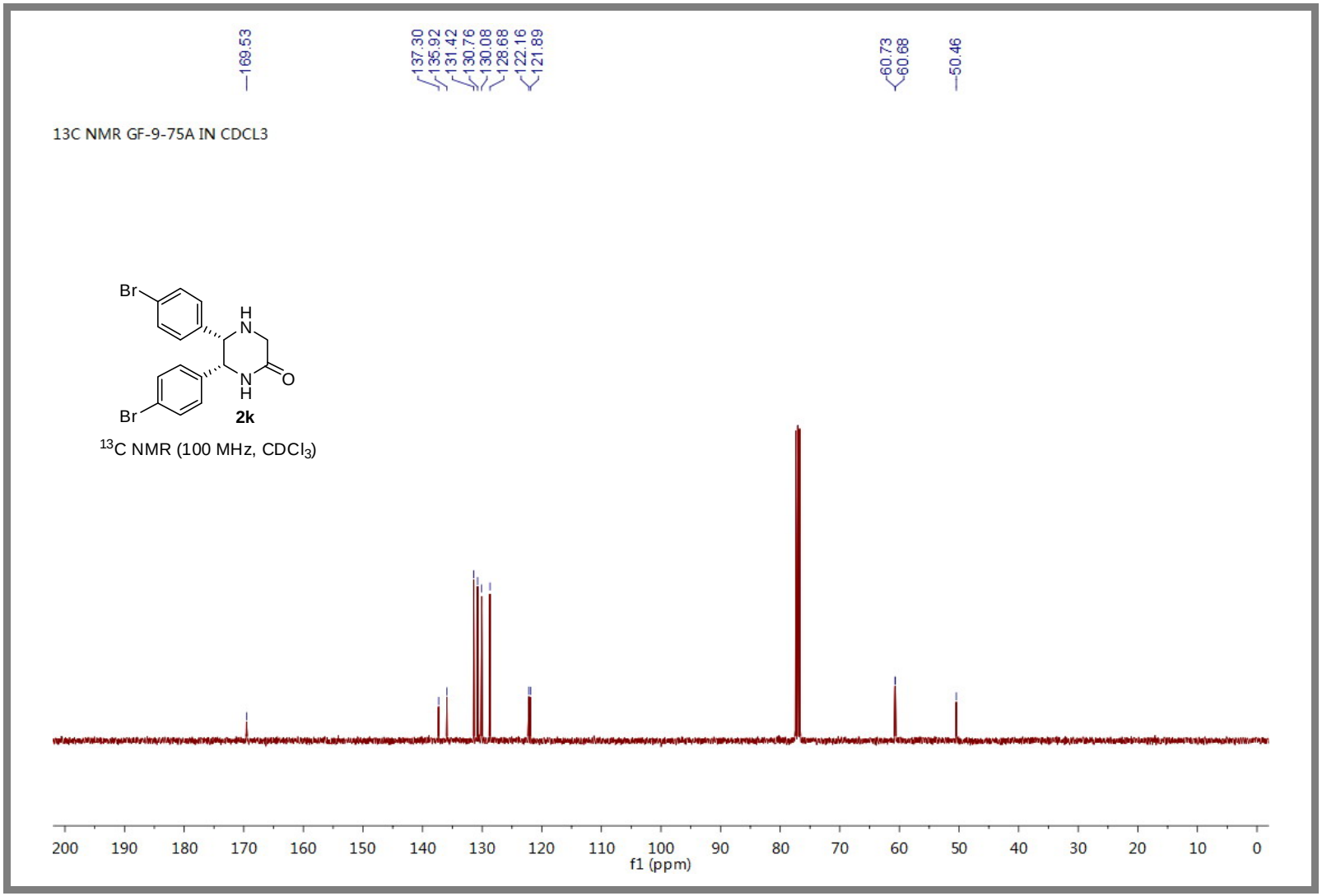

169.07
163.19
162.92
160.74
160.46
133.77
132.25
129.50
129.42
128.13
128.05
114.71
114.50
114.09
113.87
60.30
60.16
50.05
13C NMR GF-9-62B in CDCl3
F
H
N
N
H
O
F
2i
13C NMR (400 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

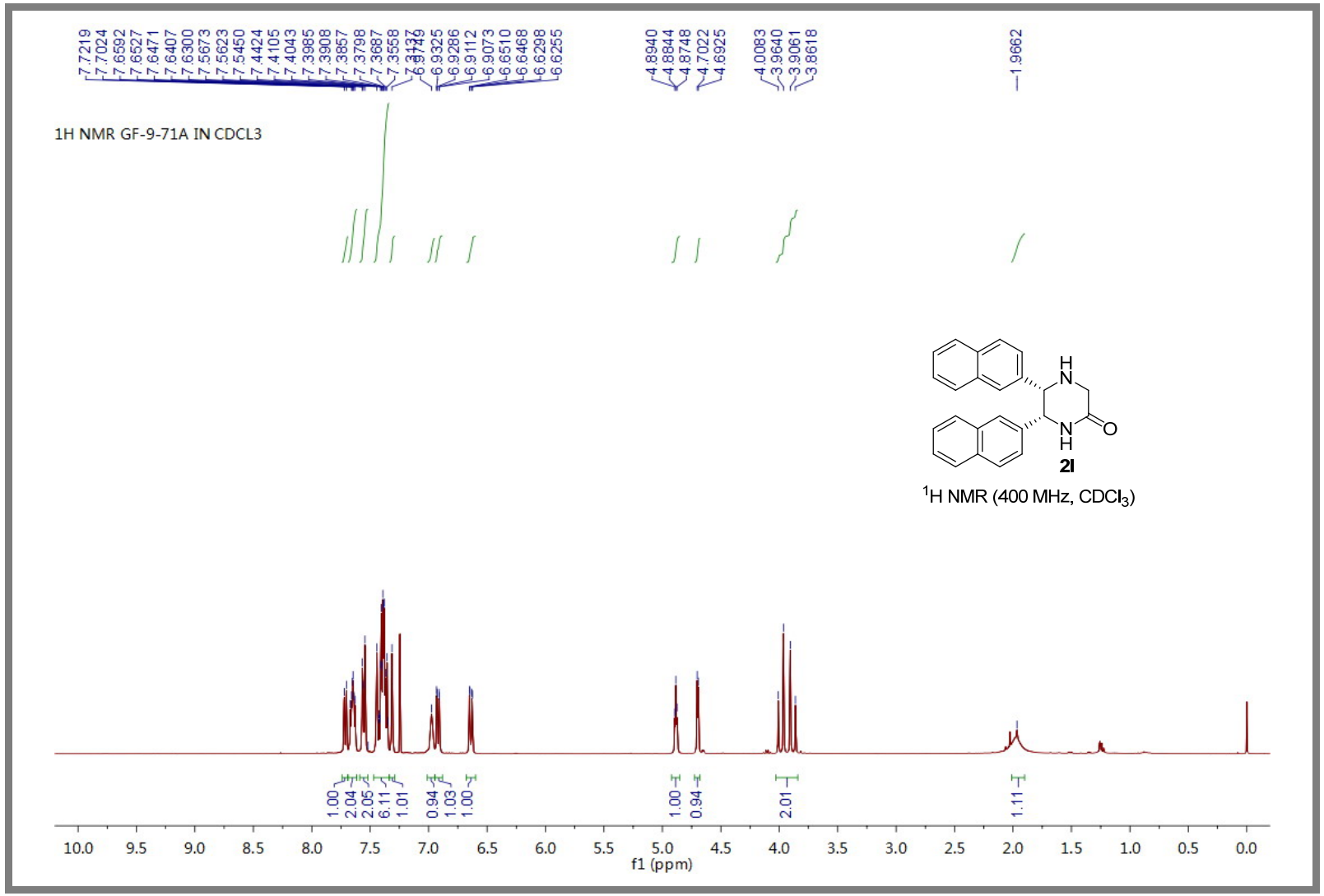

-113.8962
-114.2321
19F NMR GF-9-62B in CDCl3
F
H
N
N
H
O
F
2i
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

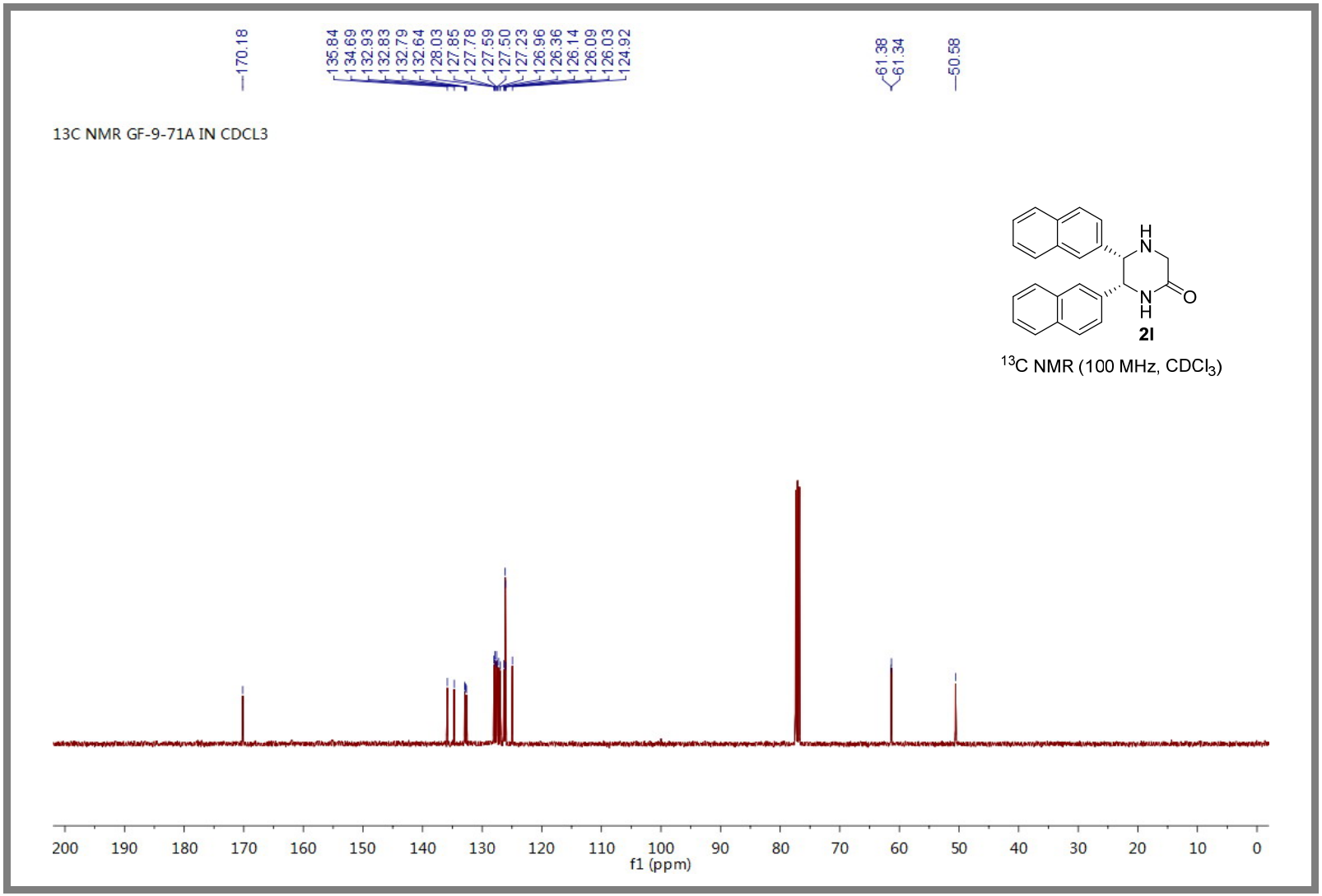

7.1539
7.1495
7.1321
7.1264
7.1139
7.1094
7.1033
7.0443
6.8057
6.7847
6.7750
6.7538
4.5629
4.5532
4.5437
4.4682
4.4583
3.8893
3.8457
3.8154
3.7718
1H NMR GF-9-70A IN CDCL3
Cl
H
N
N
H
O
Cl
2j
1H NMR (400 MHz, CDCl3)
4.04
0.94
4.05
1.00
1.00
2.04
1.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

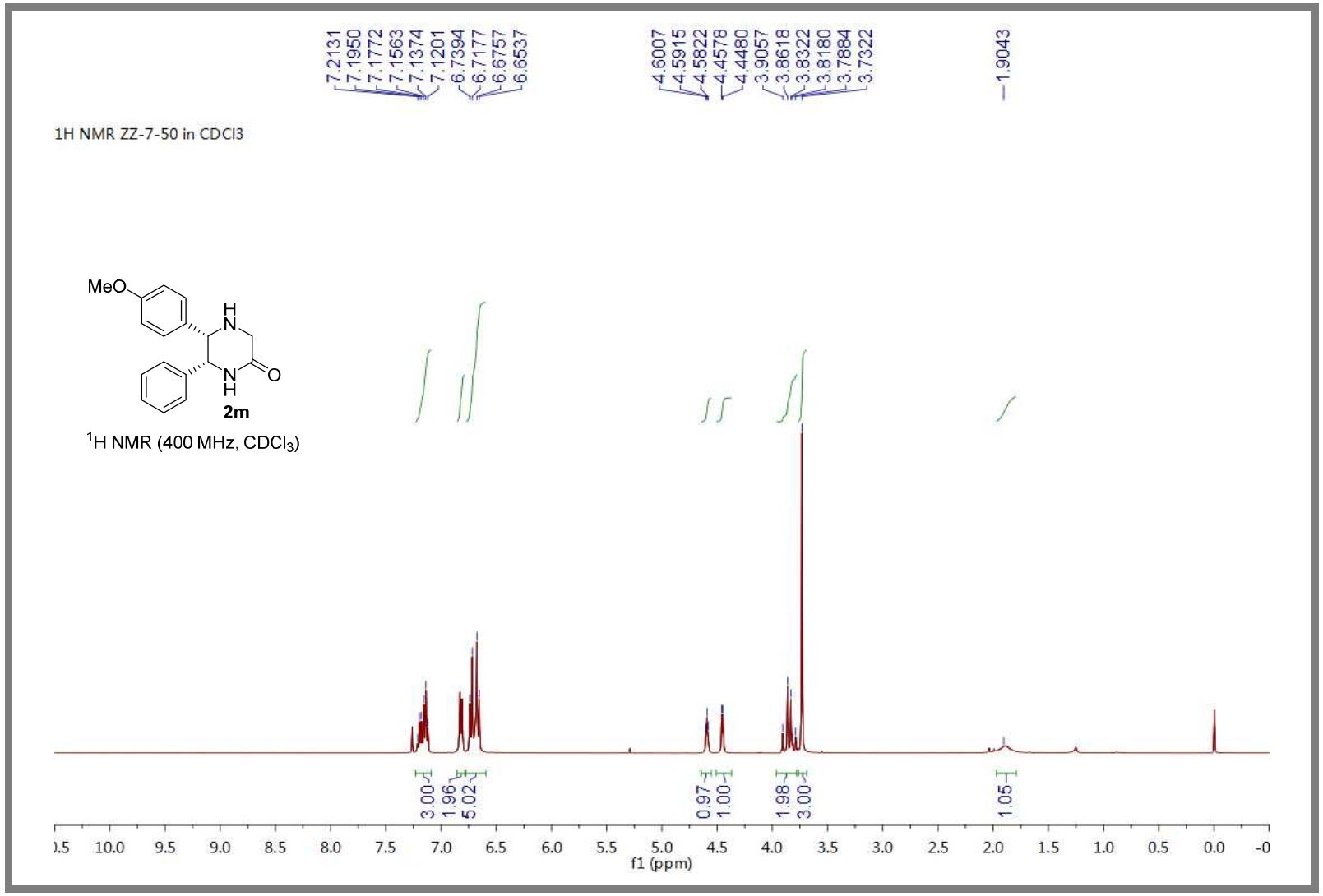

169.64
136.84
135.43
133.92
133.72
129.73
128.45
128.34
127.79
60.69
60.65
50.45
13C NMR GF-9-70A IN CDCL3
Cl
H
N
N
H
O
Cl
2j
13C NMR (400 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

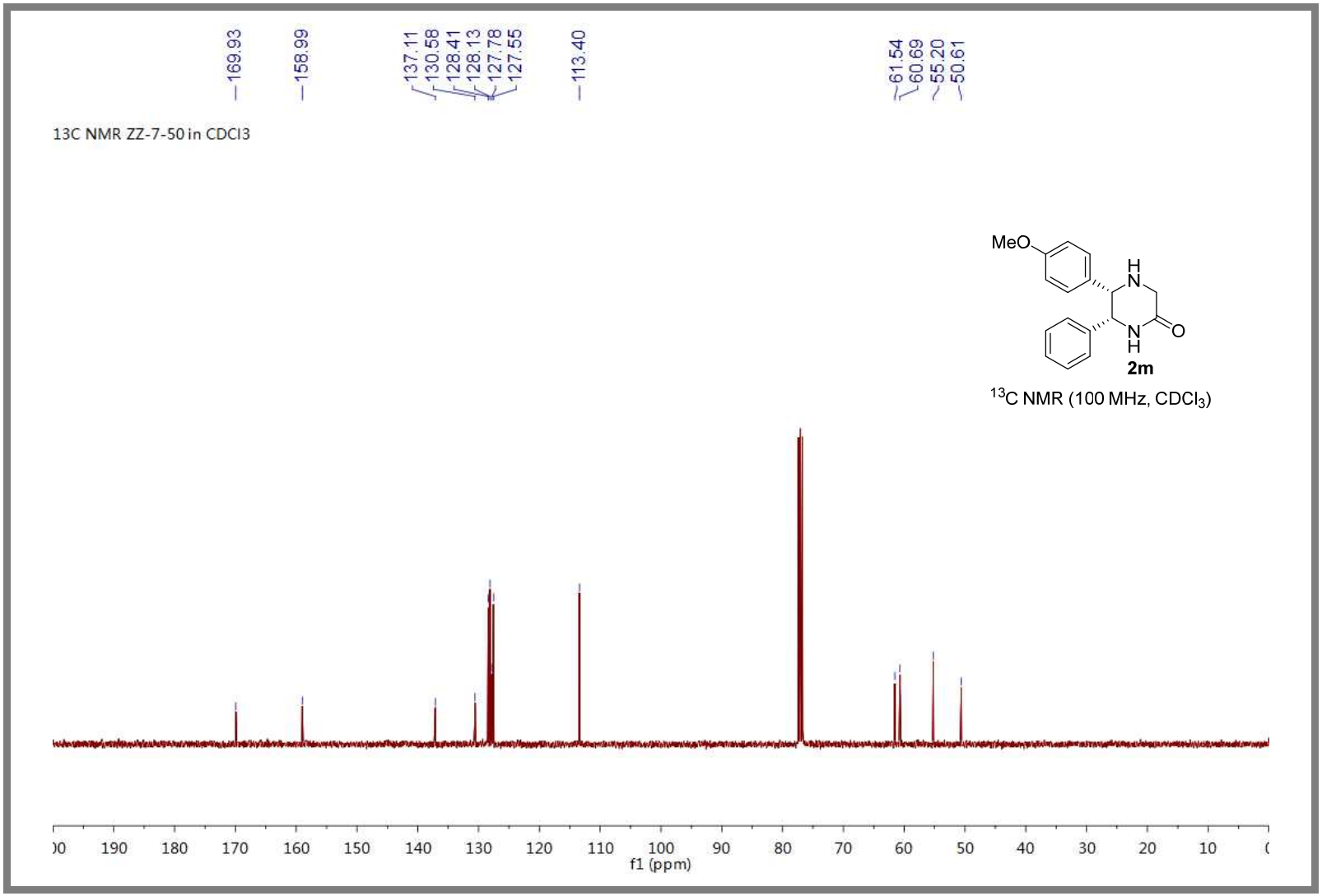

1H NMR GF-9-75A IN CDCL3
7.3122
7.2902
7.2675
6.9009
6.8944
6.7525
6.7314
6.7209
6.6998
4.5511
4.5419
4.5326
4.4583
4.4486
3.8970
3.8535
3.8220
3.7784
Br
H
N
N
H
O
Br
2k
1H NMR (400 MHz, CDCl3)
4.16
0.98
3.94
0.94
0.97
2.00
1.44
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

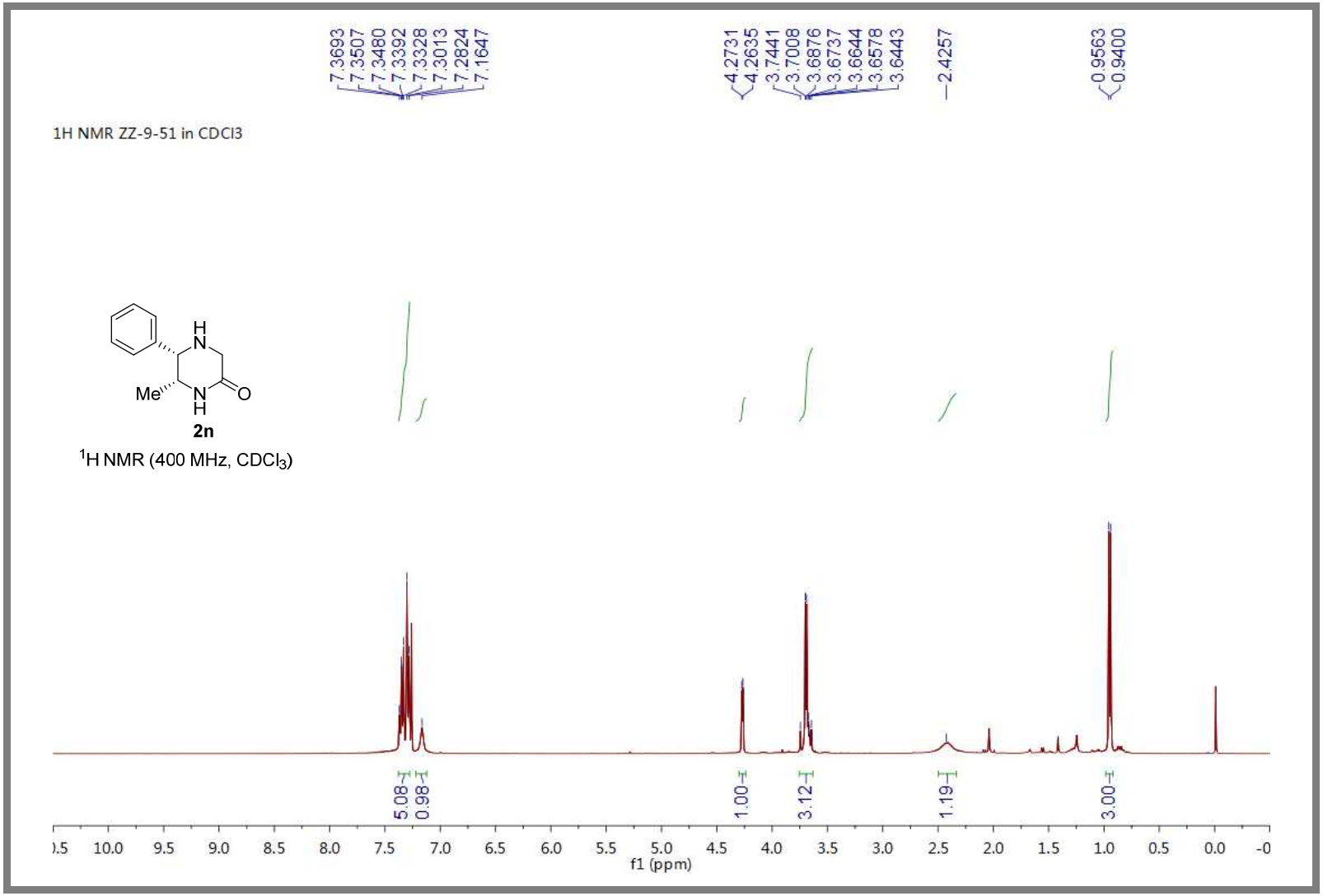

169.53
137.30
135.92
131.42
130.76
130.08
128.68
122.16
121.89
60.73
60.68
50.46
13C NMR GF-9-75A IN CDCL3
Br
H
N
N
H
O
Br
2k
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

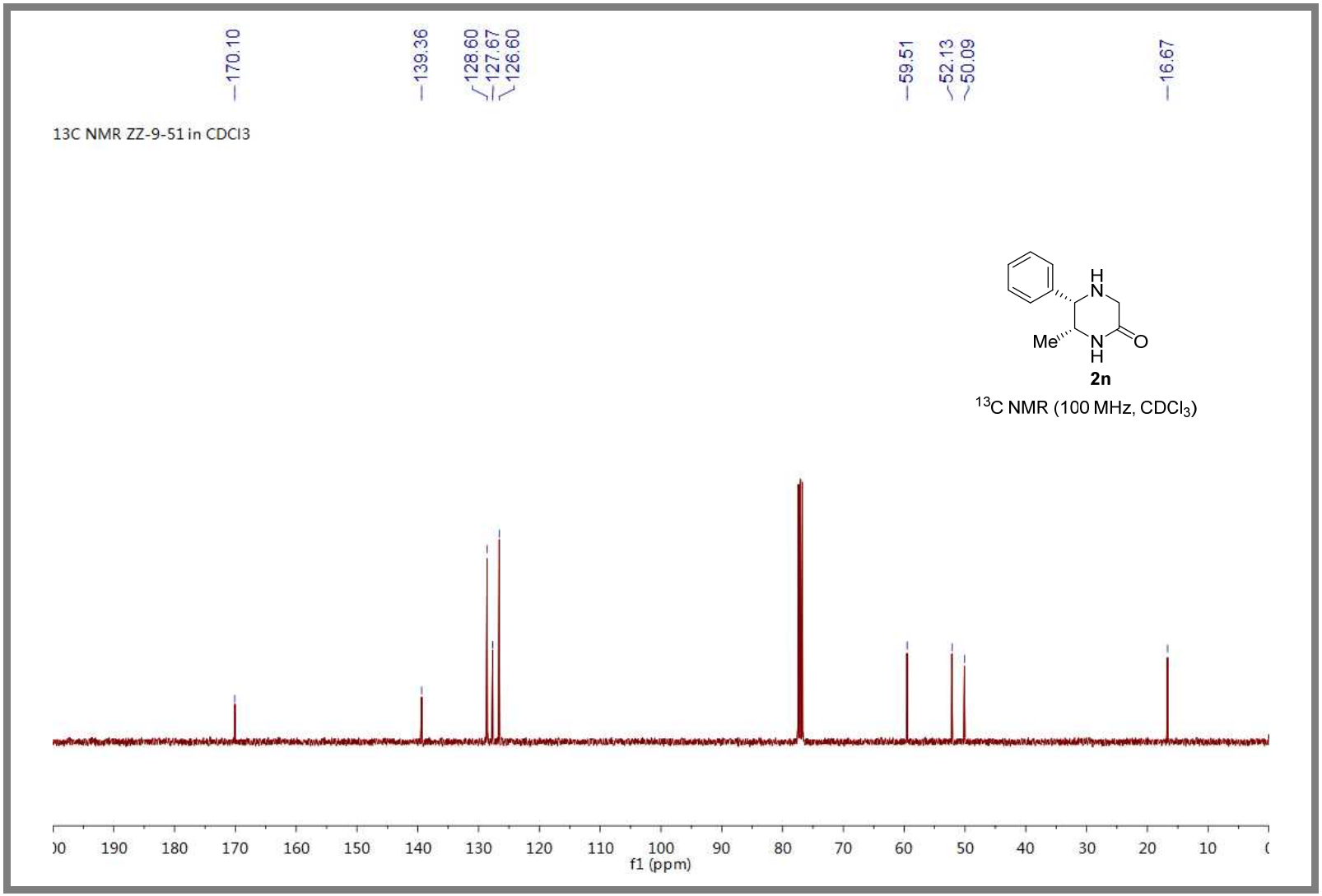

7.7219
7.7024
7.6592
7.6527
7.6471
7.6407
7.6300
7.5673
7.5623
7.5450
7.4424
7.4105
7.4043
7.3985
7.3908
7.3857
7.3798
7.3687
7.3558
6.9325
6.9286
6.9112
6.9073
6.6510
6.6468
6.6298
6.6255
4.8940
4.8844
4.8748
4.7022
4.6925
4.0083
3.9640
3.9061
3.8618
1.9662
1H NMR GF-9-71A IN CDCL3
2I
1H NMR (400 MHz, CDCl3)
1.00
2.04
2.05
6.11
1.01
0.94
1.03
1.00
1.00
0.94
2.01
1.11
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

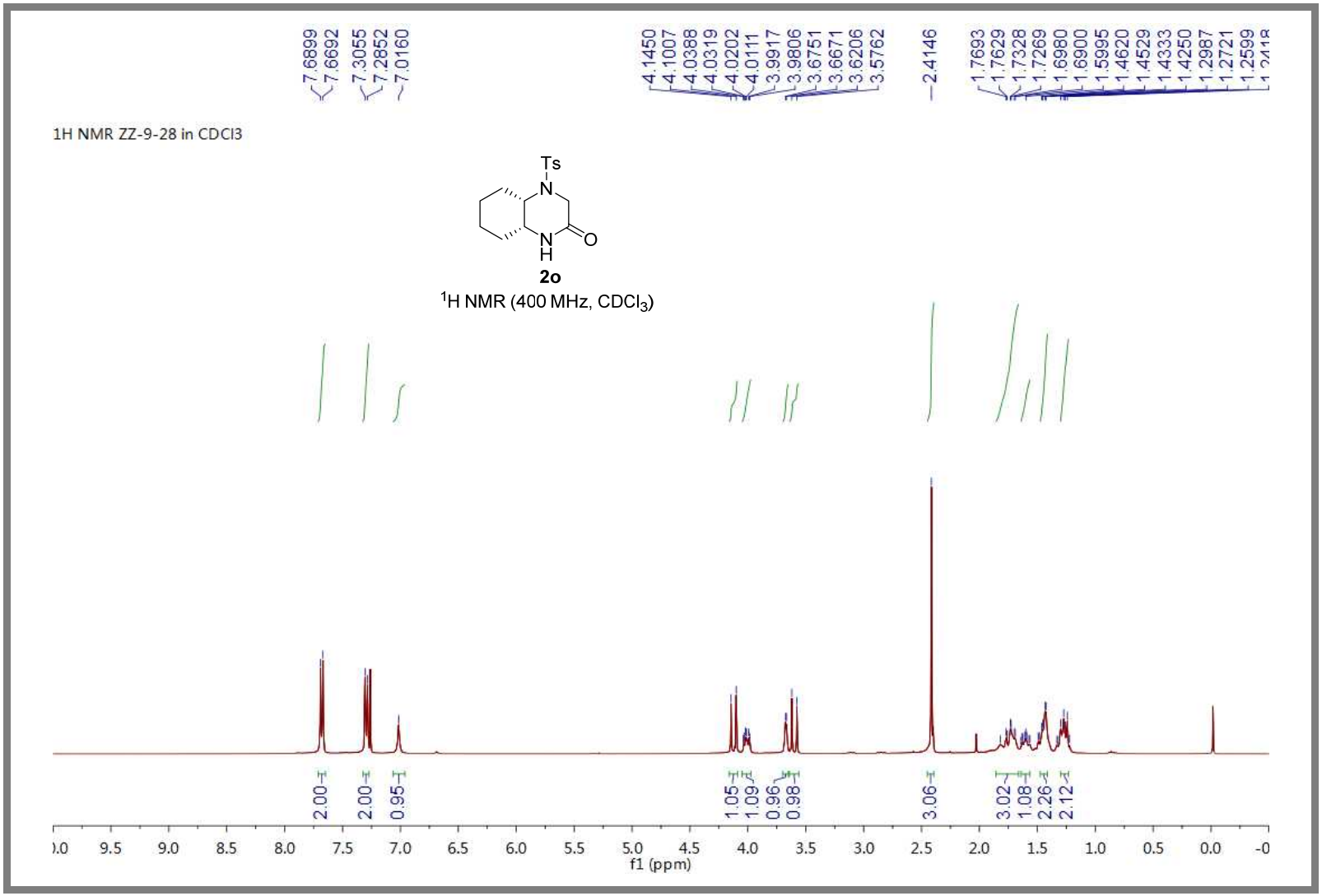

170.18
135.84
134.69
132.93
132.83
132.79
132.64
128.03
127.85
127.78
127.59
127.50
127.23
126.96
126.36
126.14
126.09
126.03
124.92
61.38
61.34
50.58
13C NMR GF-9-71A IN CDCL3
H
N
N
H
O
2l
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

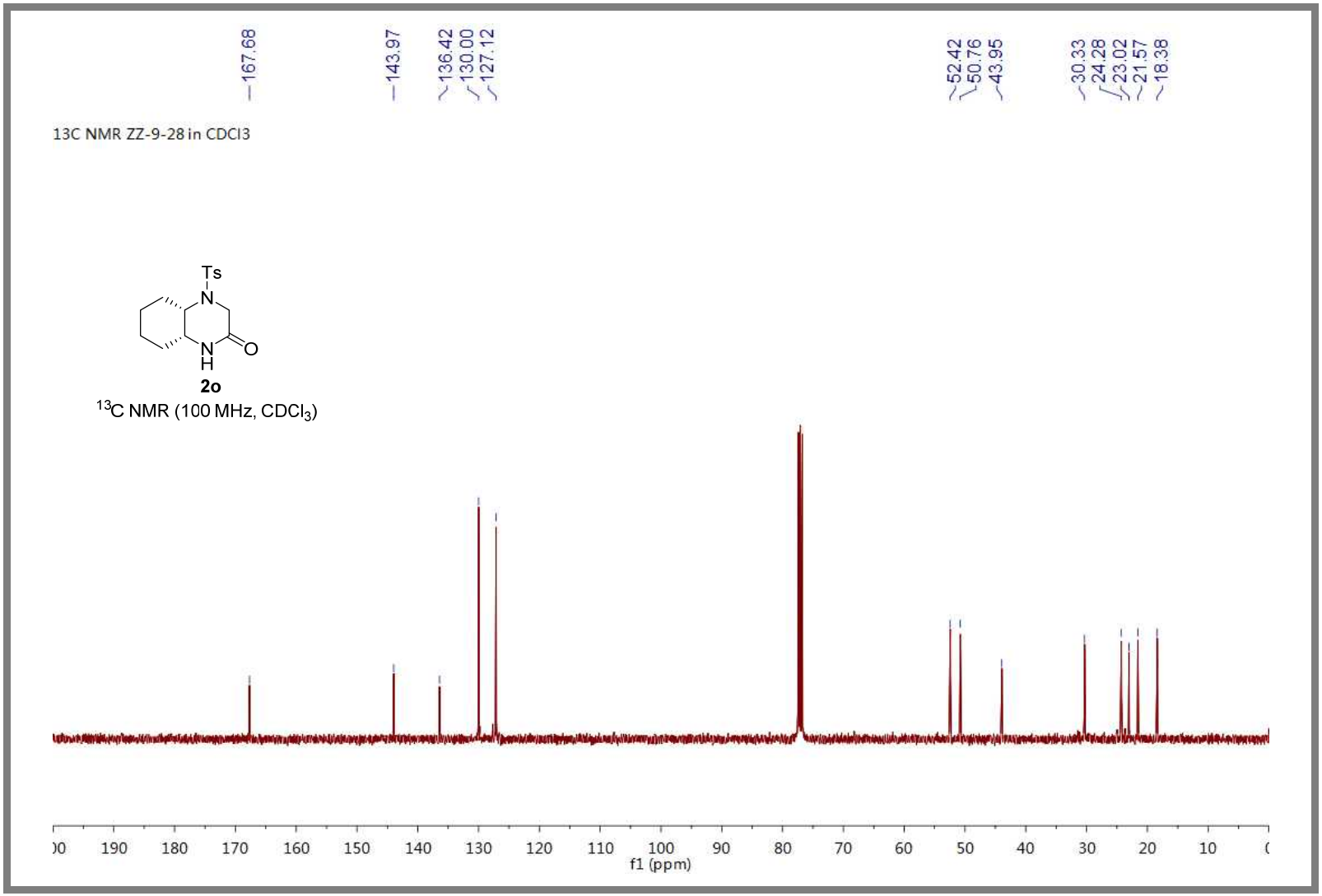

7.2131
7.1950
7.1772
7.1563
7.1374
7.1201
6.7394
6.7177
6.6757
6.6537
4.6007
4.5915
4.5822
4.4578
4.4480
3.9057
3.8618
3.8322
3.8180
3.7884
3.7322
1.9043
1H NMR ZZ-7-50 in CDCl3
MeO
H
N
N
H
O
2m
1H NMR (400 MHz, CDCl3)
3.00
1.96
5.02
0.97
1.00
1.98
3.00
1.05
f1 (ppm)

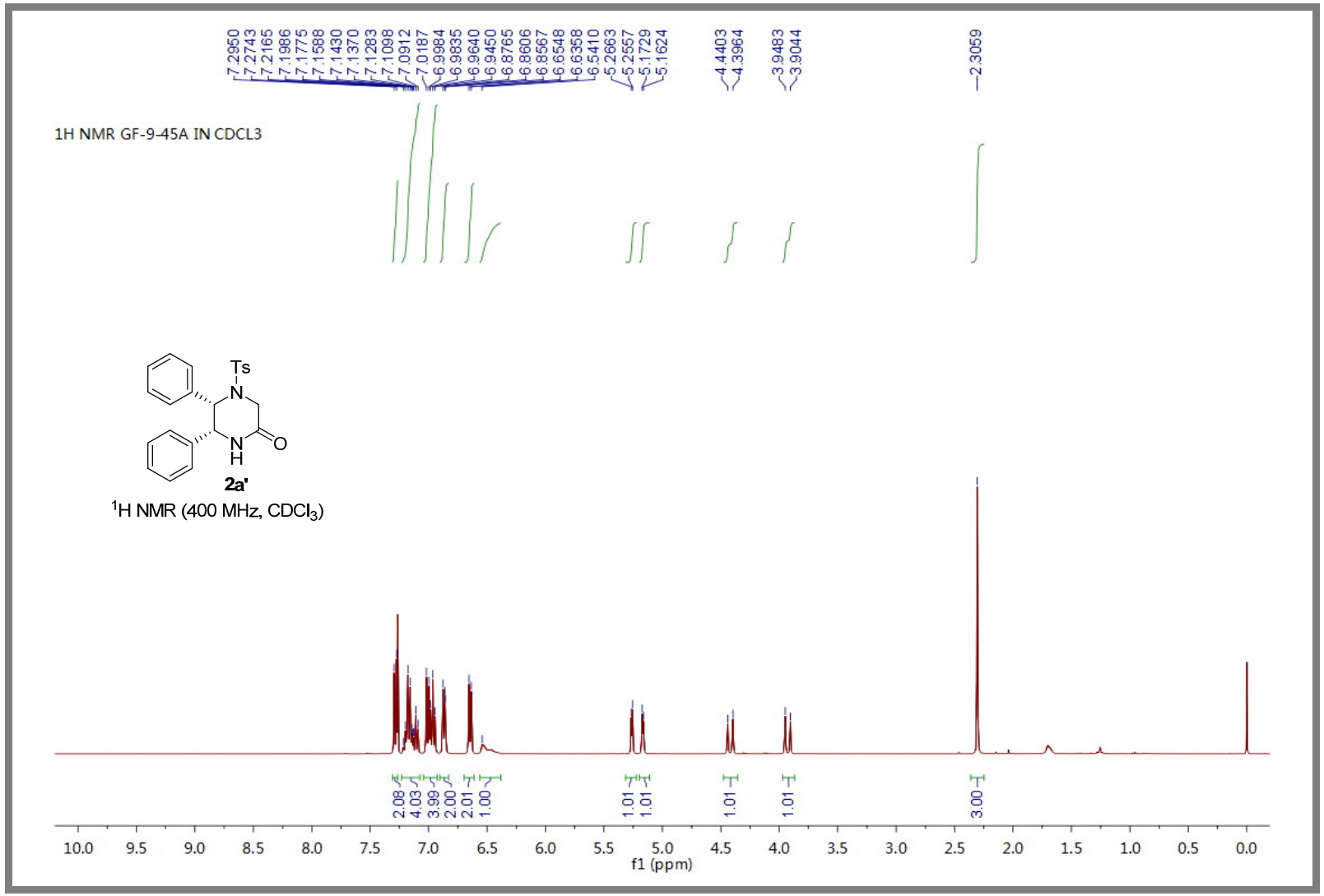

169.93
158.99
137.11
130.58
128.41
128.13
127.78
127.55
113.40
61.54
60.69
55.20
50.61
13C NMR ZZ-7-50 in CDCl3
MeO
H
N
N
H
O
2m
13C NMR (100 MHz, CDCl3)
f1 (ppm)

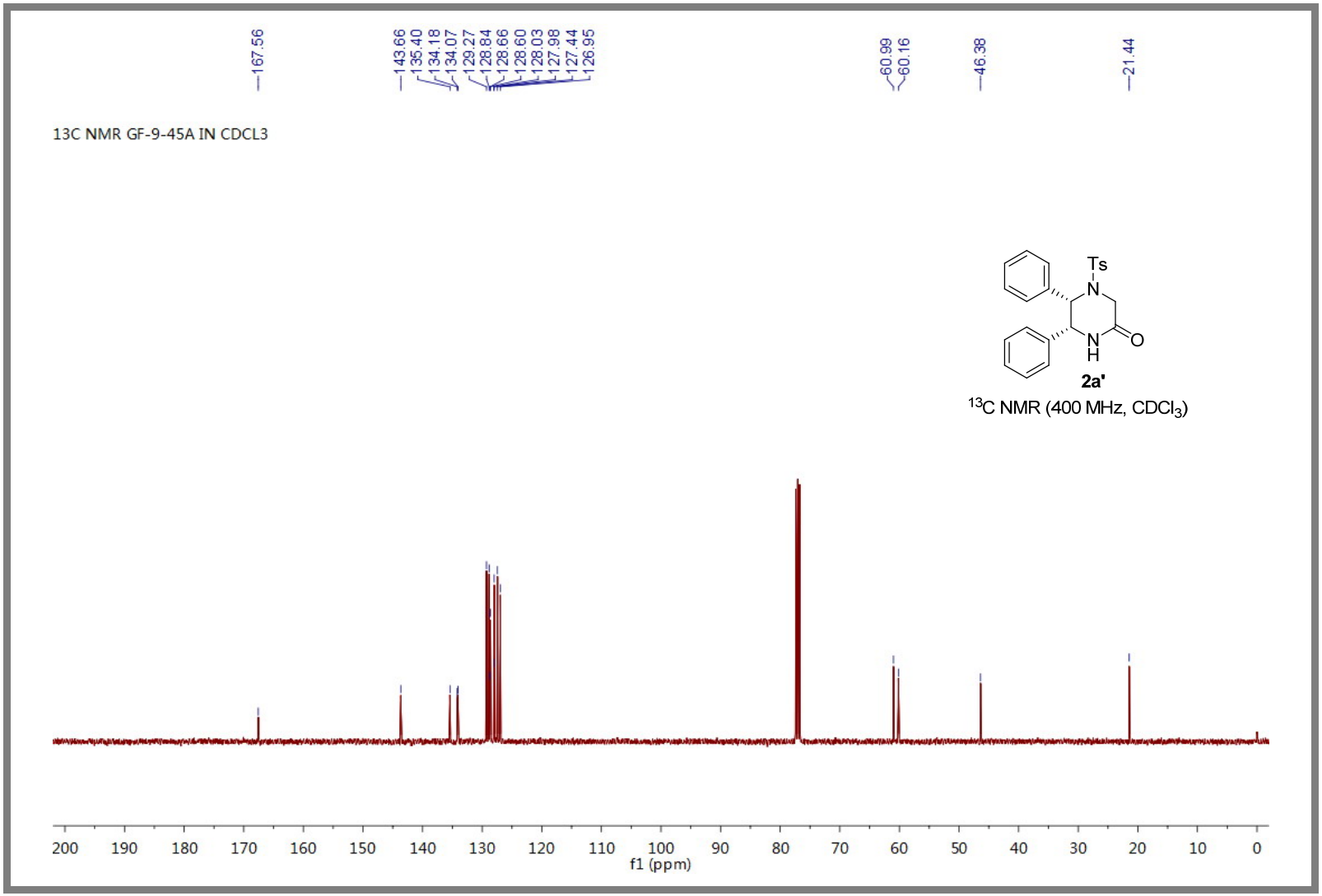

7.3693
7.3507
7.3480
7.3392
7.3328
7.3013
7.2824
7.1647
4.2731
4.2635
3.7441
3.7008
3.6876
3.6737
3.6644
3.6578
3.6443
2.4257
0.9563
0.9400
1H NMR ZZ-9-51 in CDCl3
Me
H
N
N
H
O
2n
1H NMR (400 MHz, CDCl3)
5.08
0.98
1.00
3.12
1.19
3.00
f1 (ppm)

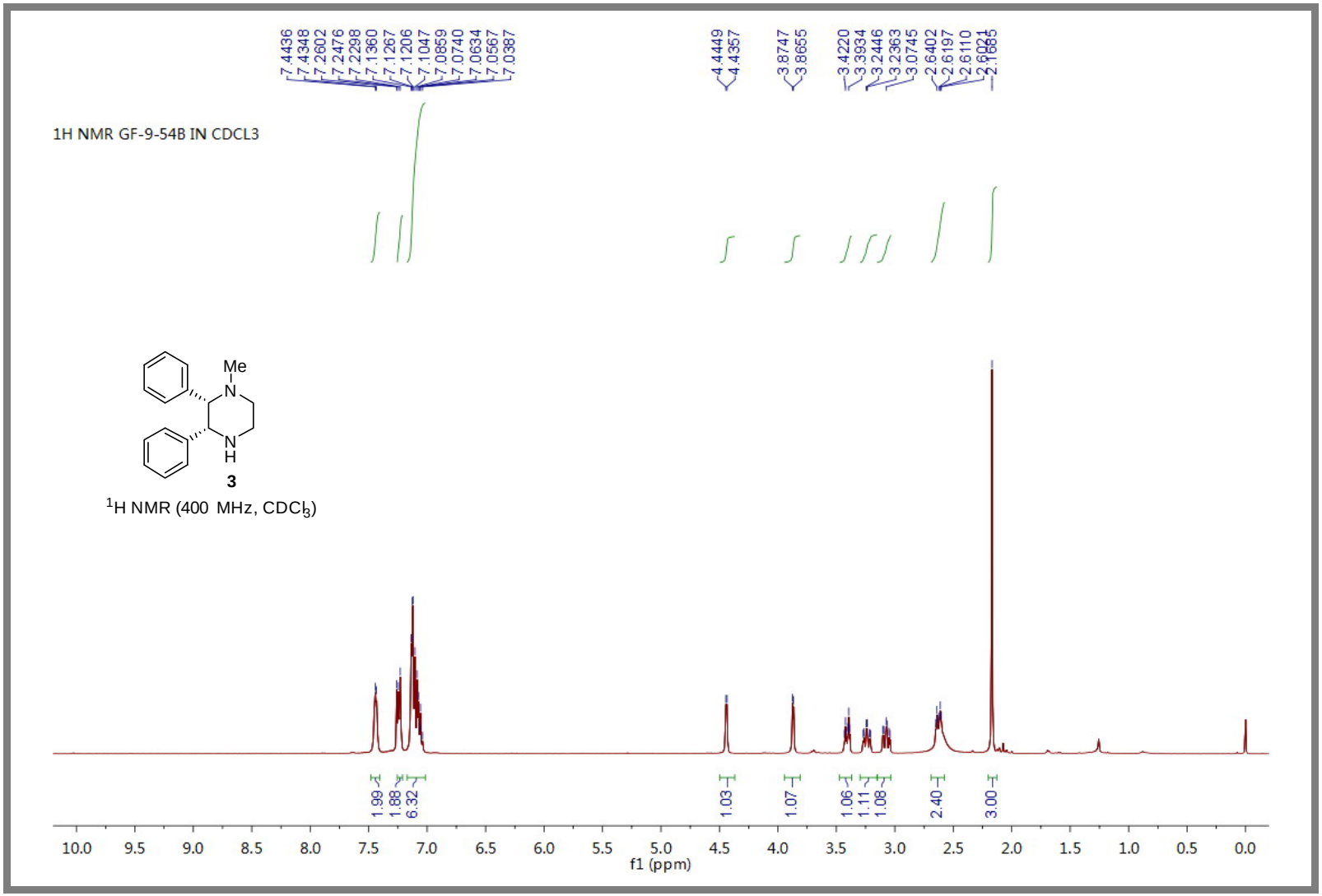

170.10
139.36
128.60
127.67
126.60
59.51
52.13
50.09
16.67
13C NMR ZZ-9-51 in CDCl3
H
N
Me
N
H
O
2n
13C NMR (100 MHz, CDCl3)
f1 (ppm)

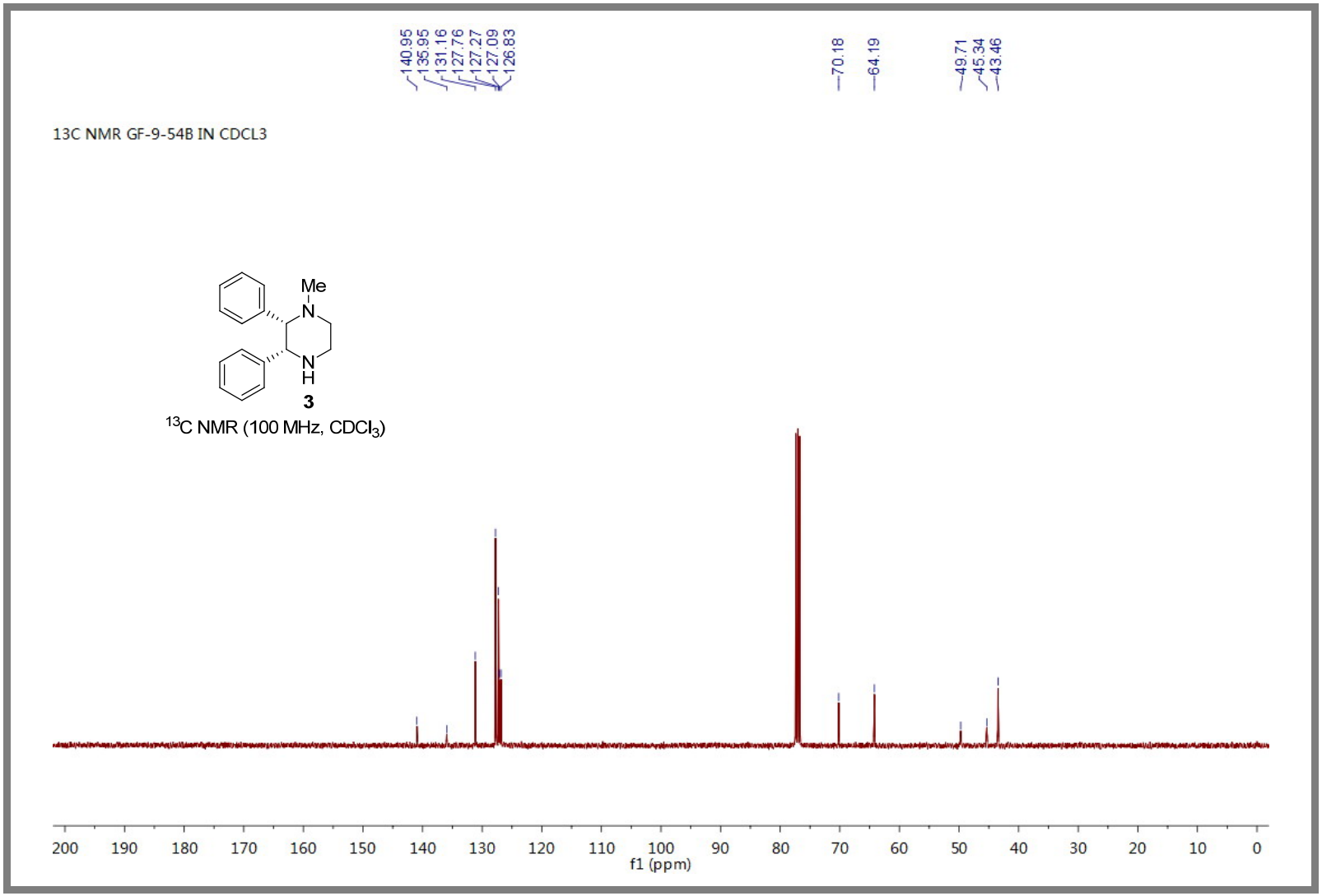

7.6899
7.6692
7.3055
7.2852
7.0160
4.1450
4.1007
4.0388
4.0319
4.0202
4.0111
3.9917
3.9806
3.6751
3.6671
3.6206
3.5762
2.4146
1.7693
1.7629
1.7328
1.7269
1.6980
1.6900
1.5995
1.4620
1.4529
1.4333
1.4250
1.2987
1.2721
1.2599
1H NMR ZZ-9-28 in CDCl3
Ts
N
N
H
O
2o
1H NMR (400 MHz, CDCl3)
2.00
2.00
0.95
1.05
1.09
0.96
0.98
3.06
3.02
1.08
2.26
2.12
f1 (ppm)


167.68
143.97
136.42
130.00
127.12
52.42
50.76
43.95
30.33
24.28
23.02
21.57
18.38
13C NMR ZZ-9-28 in CDCl3
Ts
N
N
H
O
2o
13C NMR (100 MHz, CDCl3)
f1 (ppm)


1H NMR GF-9-45A IN CDCL3
7.2950
7.2743
7.2165
7.1986
7.1775
7.1588
7.1430
7.1370
7.1283
7.1098
7.0912
7.0187
6.9984
6.9835
6.9640
6.9450
6.8765
6.8606
6.8567
6.6548
6.6358
6.5410
5.2663
5.2557
5.1729
5.1624
4.4403
4.3964
3.9483
3.9044
2.3059
Ts
N
N
H
O
2a'
1H NMR (400 MHz, CDCl3)
2.08
4.03
3.99
2.00
2.01
1.00
1.01
1.01
1.01
1.01
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

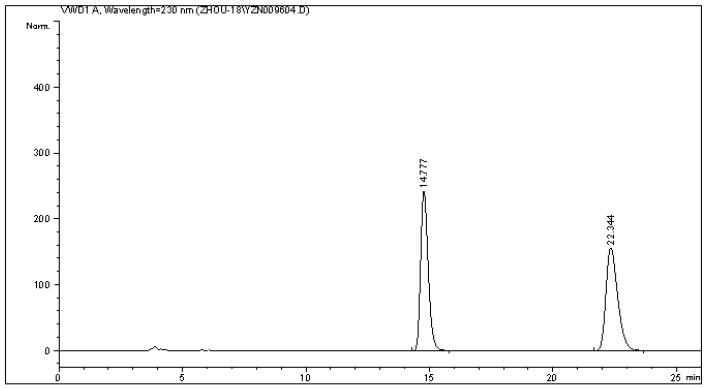

167.56
143.66
135.40
134.18
134.07
129.27
128.84
128.66
128.60
128.03
127.98
127.44
126.95
60.99
60.16
46.38
21.44
13C NMR GF-9-45A IN CDCL3
Ts
N
N
H
O
2a'
13C NMR (400 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR GF-9-54B IN CDCL3
7.4436
7.4348
7.2602
7.2476
7.2298
7.1360
7.1267
7.1206
7.1047
7.0859
7.0740
7.0634
7.0567
7.0387
4.4449
4.4357
3.8747
3.8655
3.4220
3.3934
3.2446
3.2363
3.0745
2.6402
2.6197
2.6110
2.6021
2.1685
Me
N
N
H
3
1H NMR (400 MHz, CDCl3)
1.99
1.88
6.32
1.03
1.07
1.06
1.11
1.08
2.40
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

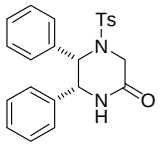

140.95
135.95
131.16
127.76
127.27
127.09
126.83
70.18
64.19
49.71
45.34
43.46
13C NMR GF-9-54B IN CDCL3
Me
N
N
H
3
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009604.D
Sample Name: GF-9-49A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 8/3/2018 6:57:02 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/3/2018 6:39:35 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/3/2018 8:18:30 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 80/20, 0.8 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.777 BB    0.3265 5153.16699  242.53030  50.0744
   2  22.344 BB    0.5071 5137.85547  156.38524  49.9256

Totals :                  1.02910e4   398.91554

                          *** End of Report ***
```

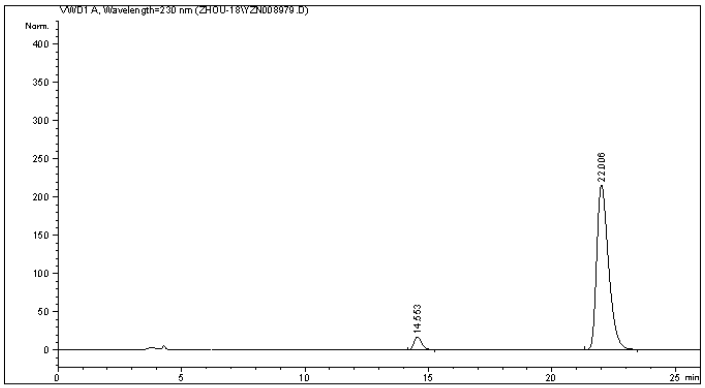



**(+/-)-2a'**

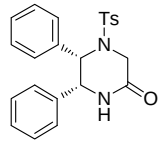


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN008979.D
Sample Name: GF-9-49A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/16/2018 12:02:09 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/16/2018 11:33:33 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:12:45 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 230 nm
```



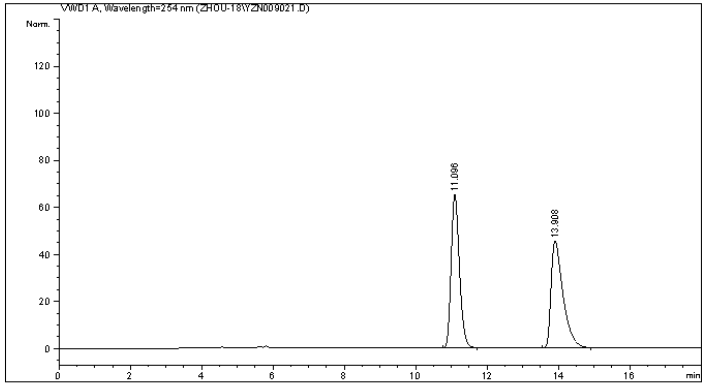

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.553 BB    0.3259  359.52924   16.96055   4.7862
   2  22.006 BB    0.5078 7152.20752  215.66374  95.2138

Totals :                  7511.73676  232.62429

                          *** End of Report ***
```



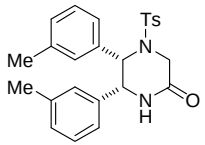

**(+)-2a'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009021.D
Sample Name: GF-9-55A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/20/2018 9:09:48 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/20/2018 8:34:07 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:15:42 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  11.096 BB    0.2480 1051.00183   65.10173  49.8744
   2  13.908 BB    0.3486 1056.29358   45.40697  50.1256

Totals :                  2107.29541  110.50870
```



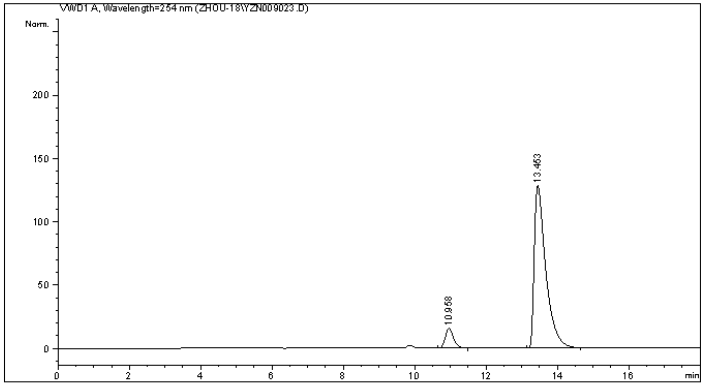

**(+/-)-2b'**

```
                          *** End of Report ***
```

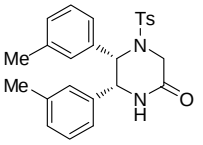


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009023.D
Sample Name: GF-9-55A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/20/2018 11:57:55 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/20/2018 11:42:28 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:17:14 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  10.958 BB    0.2441  249.25523   15.64439   7.9567
   2  13.453 BB    0.3337 2883.37769  128.22861  92.0433

Totals :                  3132.63292  143.87300
```

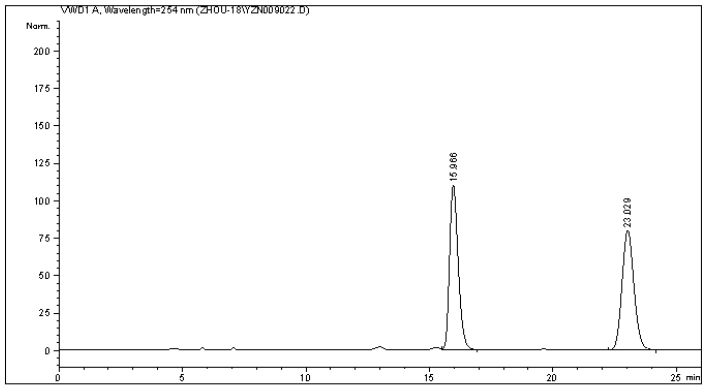



**(+)-2b'**

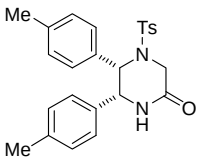
```
                          *** End of Report ***
```

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009022.D
Sample Name: GF-9-55B(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/20/2018 9:45:14 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/20/2018 9:43:15 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:21:51 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  15.966 VB    0.3737 2677.59009  110.21766  49.9601
   2  23.029 BB    0.5182 2681.87183   79.91466  50.0399

Totals :                  5359.46191  190.13232

                          *** End of Report ***
```

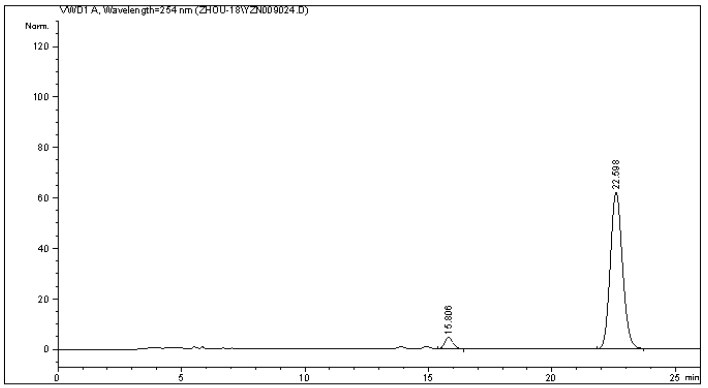



**(+/-)-2c'**

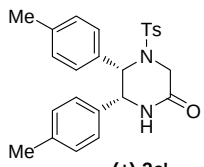
Instrument 1 8/1/2018 12:21:56 PM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009024.D
Sample Name: GF-9-55B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 6/21/2018 12:22:55 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 6/21/2018 12:22:03 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:20:38 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 254 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  15.806 VB    0.3735  109.31574    4.57281   4.8818
   2  22.598 BB    0.5327 2129.95044   62.08694  95.1182

Totals :                  2239.26618   66.65975

                          *** End of Report ***
```

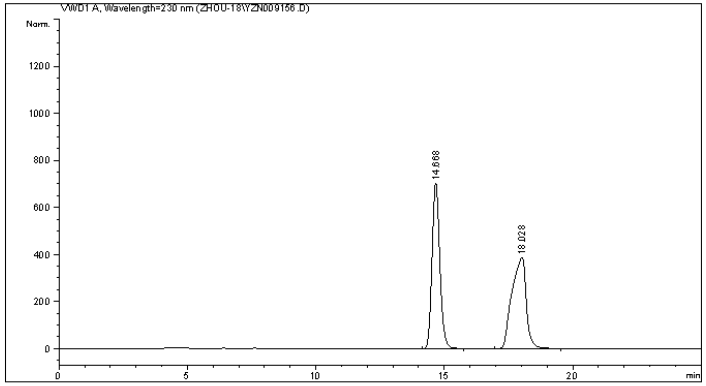



**(+)-2c'**

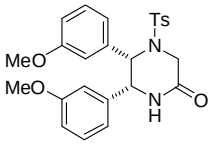
Instrument 1 8/1/2018 12:20:42 PM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009156.D
Sample Name: GF-9-63A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/3/2018 1:24:04 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/3/2018 1:02:32 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:25:15 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.668 BB    0.3244 1.48374e4   704.44238  49.8423
   2  18.028 BB    0.6630 1.49313e4   387.96564  50.1577

Totals :                  2.97687e4  1092.40802

                          *** End of Report ***
```

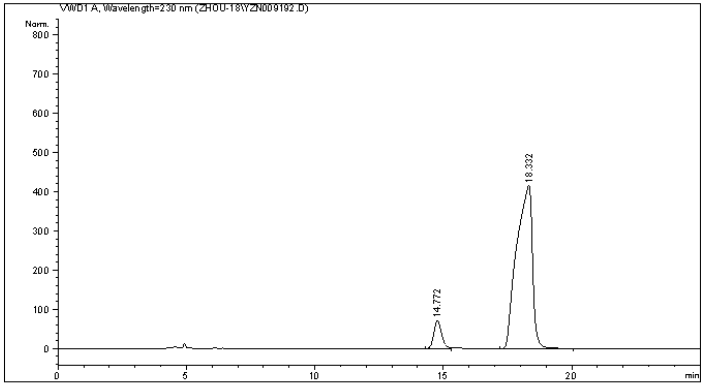



**(+/-)-2d'**

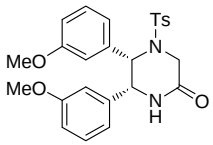


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009192.D
Sample Name: GF-9-63A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/6/2018 9:30:56 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/6/2018 9:14:09 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:23:50 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



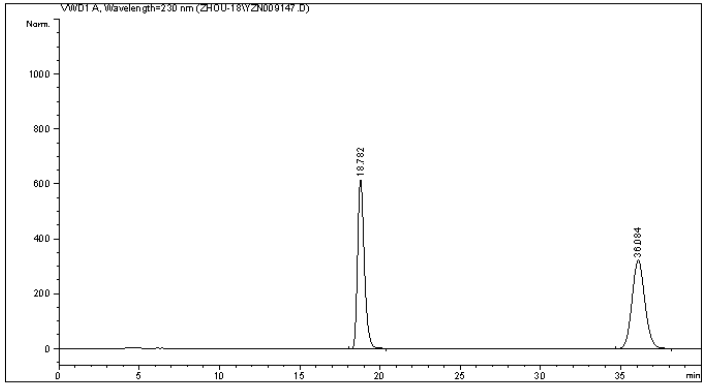

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  14.772 BV    0.3246 1492.76868   70.79812   7.7369
   2  18.332 BB    0.7576 1.78013e4   415.41751  92.2631

Totals :                  1.92940e4   486.21563

                          *** End of Report ***
```



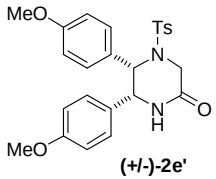

**(+)-2d'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009147.D
Sample Name: GF-9-62A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/2/2018 8:54:25 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/2/2018 8:32:01 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:29:02 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|------|---------|---------|-------|
   1  18.782 VB    0.4467 1.78816e4   615.44922  49.9695
   2  36.084 BB    0.8613 1.79034e4   321.99438  50.0305

Totals :                  3.57849e4   937.44360

                          *** End of Report ***
```

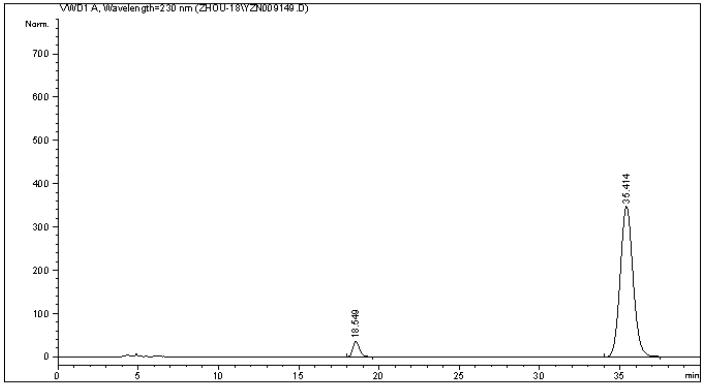



**(+/-)-2e'**

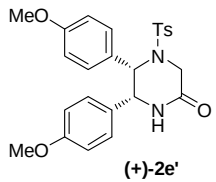


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009149.D
Sample Name: GF-9-62A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/2/2018 11:45:50 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/2/2018 11:39:23 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:27:25 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7mL/min, 30 oC, 230 nm
```



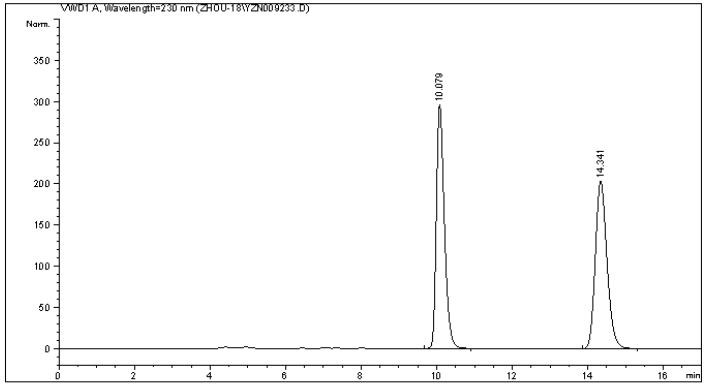

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s    [mAU   ]      %
----|-------|----|------|---------|---------|-------|
   1  18.549 BB    0.4421 1029.21985   35.59795   5.0900
   2  35.414 BB    0.8503 1.91911e4   347.90341  94.9100

Totals :                  2.02203e4   383.50136

                          *** End of Report ***
```



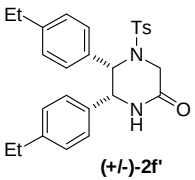

**(+)-2e'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009233.D
Sample Name: GF-9-67B(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/8/2018 2:28:29 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/8/2018 2:27:12 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:32:03 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  10.079 BB    0.2261 4369.80908  296.00070  50.0354
   2  14.341 BB    0.3288 4363.62158  203.48685  49.9646

Totals :                  8733.43066  499.48755

                          *** End of Report ***
```

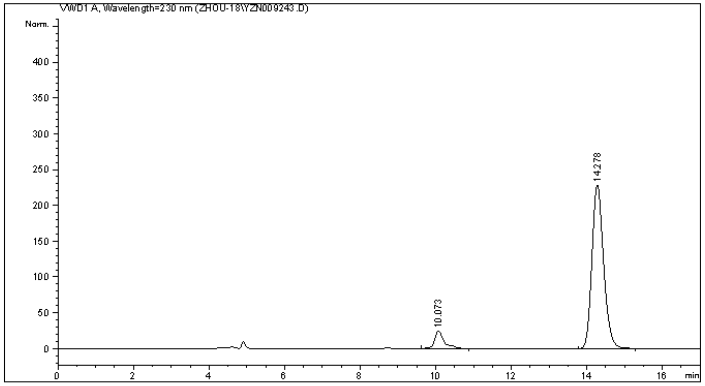



**(+/-)-2f'**

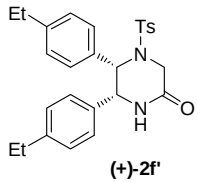


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009243.D
Sample Name: GF-9-67B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/8/2018 9:37:46 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/8/2018 9:36:51 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:30:51 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



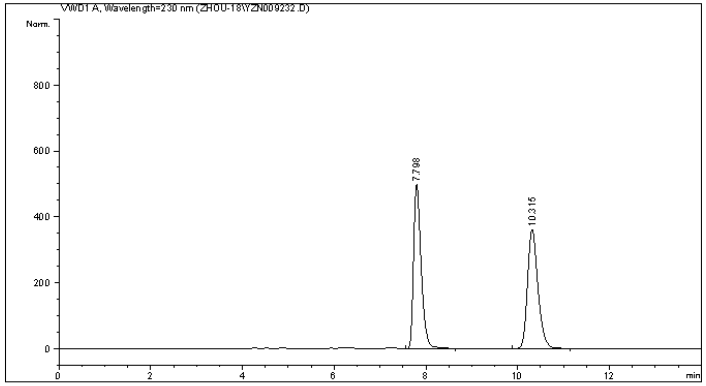

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  10.073 BB    0.2592  433.99991   24.48208   8.1255
   2  14.278 BB    0.3288 4907.23975  228.88188  91.8745

Totals :                  5341.23965  253.36396

                          *** End of Report ***
```



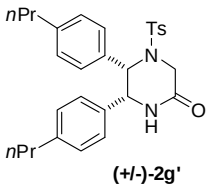

**(+)-2f'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009232.D
Sample Name: GF-9-67A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/8/2018 2:06:35 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/8/2018 2:05:59 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:36:41 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1   7.798 VB    0.1745 5703.43555  497.70593  50.0338
   2  10.315 BB    0.2402 5695.72217  362.28497  49.9662

Totals :                  1.13992e4   859.99091

                          *** End of Report ***
```

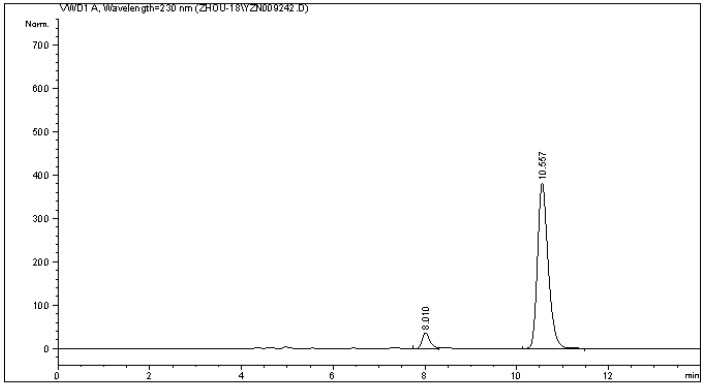



**(+/-)-2g'**

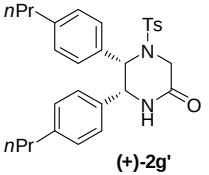


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009242.D
Sample Name: GF-9-67A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/8/2018 9:22:34 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/8/2018 9:20:51 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:33:52 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



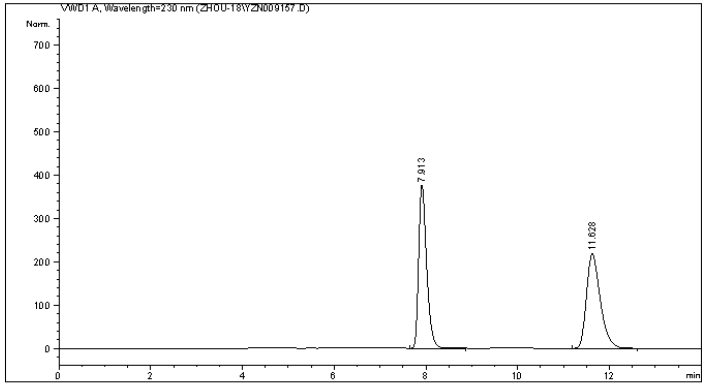

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1   8.010 VV    0.1752  417.72684   36.25928   6.3692
   2  10.557 VB    0.2445 6140.86768  381.71692  93.6308

Totals :                  6558.59451  417.97620

                          *** End of Report ***
```



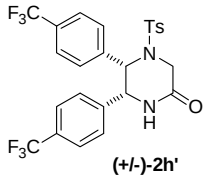

**(+)-2g'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009157.D
Sample Name: GF-9-63B(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/3/2018 1:50:20 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/3/2018 1:49:00 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:40:06 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.913 VB    0.1849 4569.60254  377.51147  50.0427
   2  11.628 BB    0.3178 4561.81055  218.50819  49.9573

Totals :                  9131.41309  596.01967

                          *** End of Report ***
```

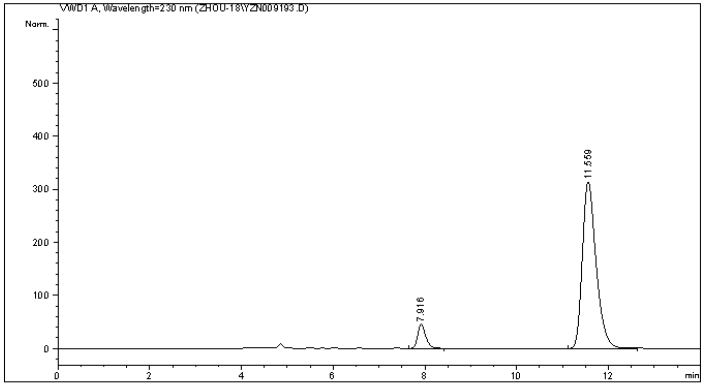



**(+/-)-2h'**

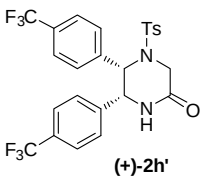


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009193.D
Sample Name: GF-9-63B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/6/2018 10:11:41 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/6/2018 9:57:57 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:41:27 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



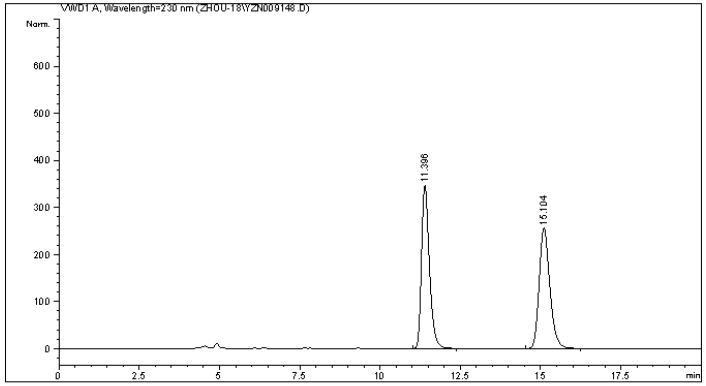

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1   7.916 VB    0.1827  544.47845   45.22761   7.7061
   2  11.559 BB    0.3166 6521.10693  313.87607  92.2939

Totals :                  7065.58539  359.10368

                          *** End of Report ***
```



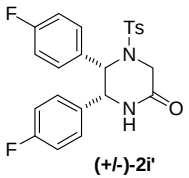

**(+)-2h'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009148.D
Sample Name: GF-9-62B(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/2/2018 11:12:48 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/2/2018 10:52:27 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:44:49 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  11.396 BB    0.2608 5931.07715  346.55286  50.0121
   2  15.104 BB    0.3531 5928.19629  256.05997  49.9879

Totals :                 1.18593e4   602.61282

                          *** End of Report ***
```

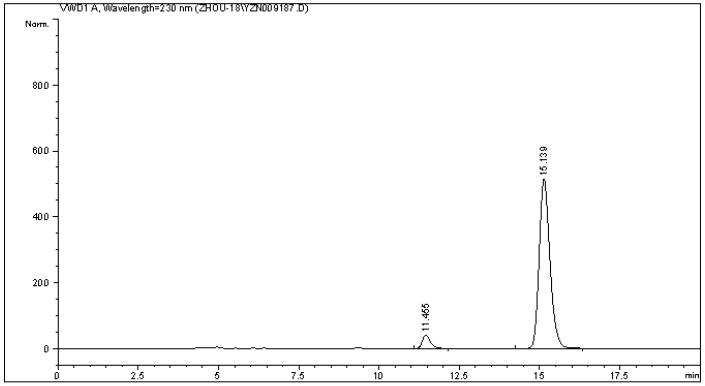



**(+/-)-2i'**

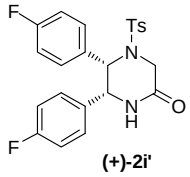


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009187.D
Sample Name: GF-9-62B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/5/2018 1:13:37 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/5/2018 12:29:11 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:43:28 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



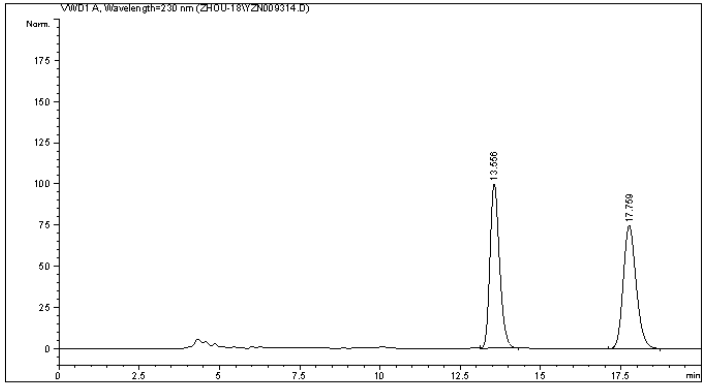

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #  [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  11.455 BB    0.2647  714.33740   40.94229   5.6237
   2  15.139 BB    0.3559 1.19879e4   515.31512  94.3763

Totals :                 1.27023e4   556.25741

                          *** End of Report ***
```



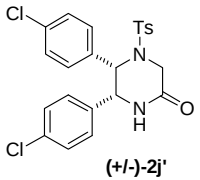

**(+)-2i'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009314.D
Sample Name: GF-9-70A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/13/2018 8:06:56 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/13/2018 8:06:05 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:47:57 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  13.556 VB    0.3165 2063.22876   99.94914  49.6625
   2  17.759 BB    0.4290 2091.27441   74.93134  50.3375

Totals :                  4154.50317  174.88048

                          *** End of Report ***
```

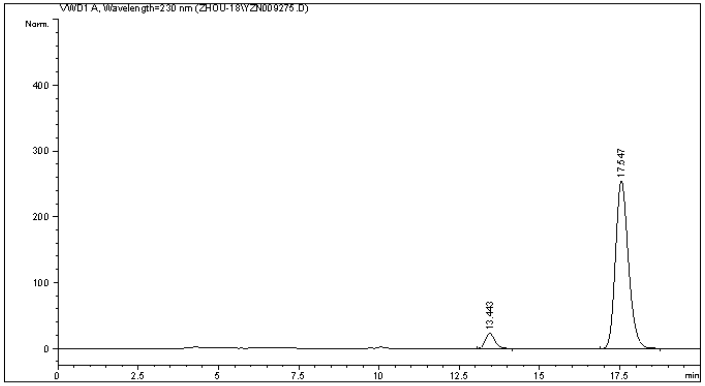



**(+/-)-2j'**

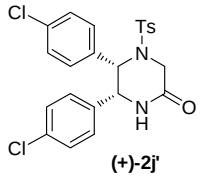


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009275.D
Sample Name: GF-9-70A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location : Vial 1
Injection Date  : 7/11/2018 11:08:16 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/11/2018 11:07:05 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:46:35 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```



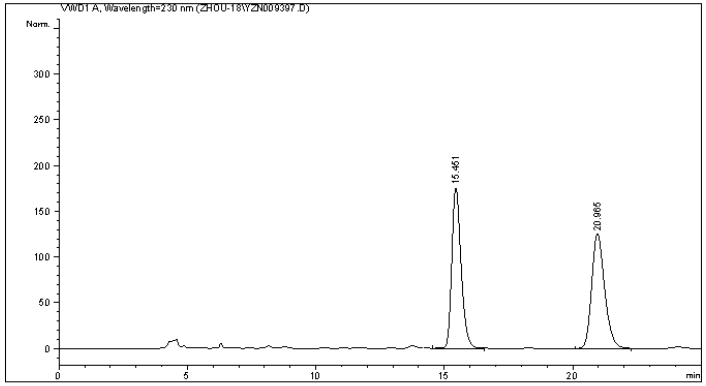

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  13.443 BB    0.3162  474.76199   23.03591   6.2539
   2  17.547 BB    0.4288 7116.74805  255.14998  93.7461

Totals :                  7591.51004  278.18589

                          *** End of Report ***
```



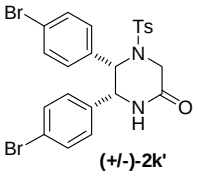

**(+)-2j'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009397.D
Sample Name: GF-9-75A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/20/2018 9:04:01 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/20/2018 9:02:30 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:51:27 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  15.451 VB    0.3849 4416.99365  175.77422  50.0641
   2  20.965 BB    0.5378 4405.68750  125.47818  49.9359

Totals :                  8822.68115  301.25240

                          *** End of Report ***
```

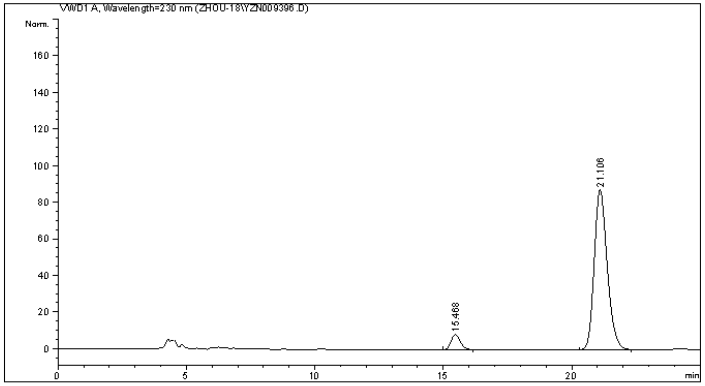



(+/-)-2k'

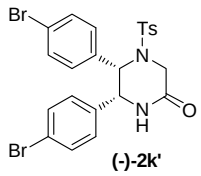
Instrument 1 8/1/2018 12:51:30 PM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009396.D
Sample Name: GF-9-75A

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/20/2018 8:21:31 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/20/2018 7:56:08 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2018 12:53:41 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  15.468 BB    0.3787  207.07285    8.29150   6.2985
   2  21.106 BB    0.5408 3080.58862   87.40034  93.7015

Totals :                  3287.66147   95.69185

                          *** End of Report ***
```

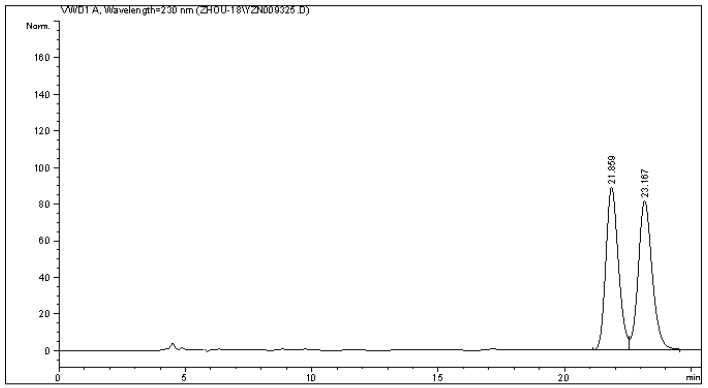



(-)-2k'

Instrument 1 8/1/2018 12:53:45 PM Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009325.D
Sample Name: GF-9-71A(+-)

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 7/14/2018 4:00:34 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 7/14/2018 3:50:58 PM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 8/1/2018 12:55:44 PM
(modified after loading)
Sample Info : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm

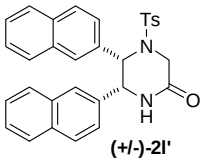



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.859 | BV | 0.5308 | 3057.47412 | 88.90438 | 49.7090 |
| 2 | 23.167 | VB | 0.5820 | 3093.26538 | 81.34102 | 50.2910 |
| Totals : | | | | 6150.73950 | 170.24540 | |



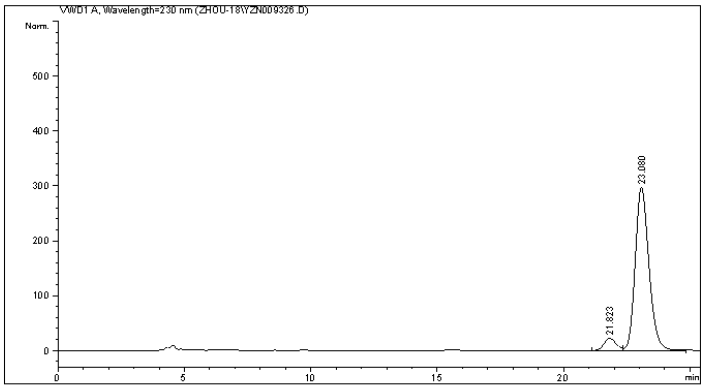

**(+/-)-2l'**

*** End of Report ***



Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009326.D
Sample Name: GF-9-71A

Acq. Operator :
Acq. Instrument : Instrument 1 Location : Vial 1
Injection Date : 7/14/2018 4:28:19 PM
Acq. Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 7/14/2018 4:25:57 PM
(modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed : 8/1/2018 12:57:30 PM
(modified after loading)
Sample Info : AD-H, Hexane/i-PrOH =70/30, 0.7 mL/min, 30 oC, 230 nm

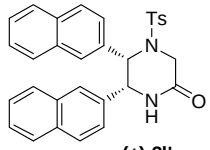



Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=230 nm

| Peak # | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.823 | BV | 0.5204 | 735.73389 | 21.88438 | 6.1847 |
| 2 | 23.080 | VB | 0.5782 | 1.11603e4 | 296.99338 | 93.8153 |
| Totals : | | | | 1.18960e4 | 318.87776 | |

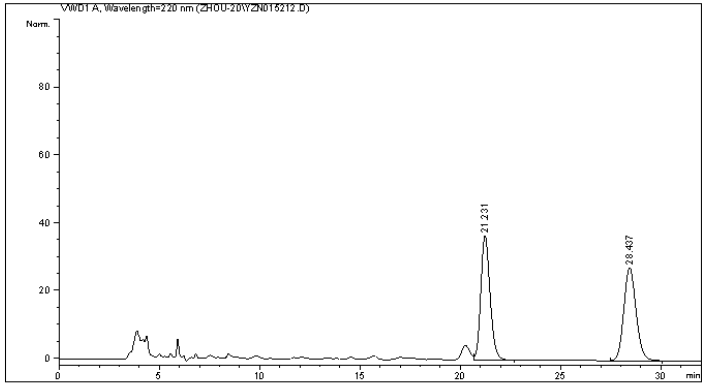



**(+)-2l'**

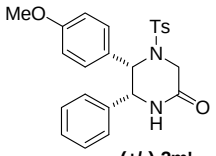
*** End of Report ***

Data File C:\CHEM32\1\DATA\ZHOU-20\YZN015212.D
Sample Name: zz-7-50(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/4/2020 6:13:31 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/4/2020 5:54:26 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:02:59 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 80/20, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  21.231 VB    0.5013 1197.82666   36.87651  50.5904
   2  28.437 BB    0.6582 1169.86731   27.56517  49.4096

Totals :                  2367.69397   64.44169


                          *** End of Report ***
```

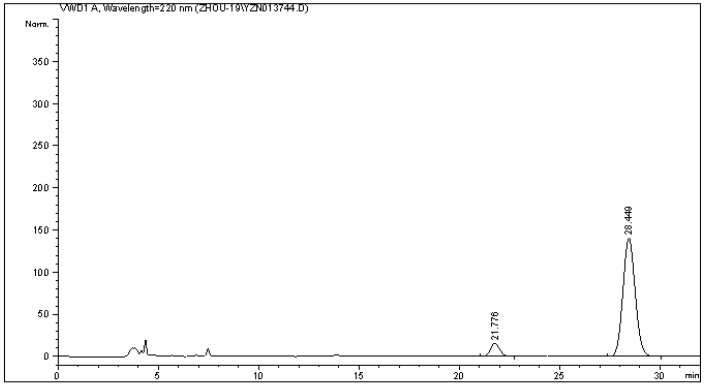



**(+/-)-2m'**

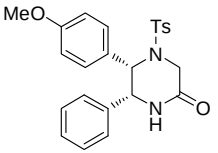


Data File C:\CHEM32\1\DATA\ZHOU-19\YZN013744.D
Sample Name: zz-7-50

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 10/26/2019 10:11:39 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 10/26/2019 9:59:12 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:05:28 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH =80/20, 0.8 mL/min, 30 oC, 220 nm
```



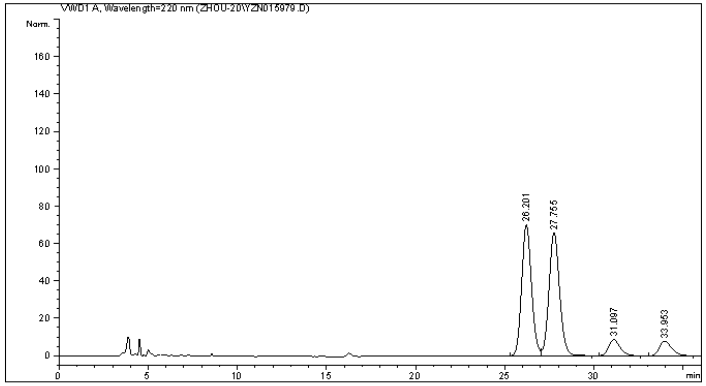

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  21.776 VB    0.4957  496.30634   15.50778   7.6922
   2  28.449 BB    0.6606 5955.76709  140.49104  92.3078

Totals :                  6452.07343  155.99882


                          *** End of Report ***
```



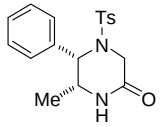

**(+)-2m'**

Data File C:\CHEM32\1\DATA\ZHOU-20\YZN015979.D
Sample Name: zz-9-51(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 9/9/2020 6:18:51 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/9/2020 6:13:29 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:12:51 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  26.201 BV    0.5912 2677.90918   70.11043  43.3892
   2  27.755 VB    0.6347 2715.11230   65.93609  43.9920
   3  31.097 BB    0.6877  394.36530    8.72116   6.3898
   4  33.953 BB    0.7566  384.44772    7.82516   6.2291

Totals :                  6171.83450  152.59283

                          *** End of Report ***
```

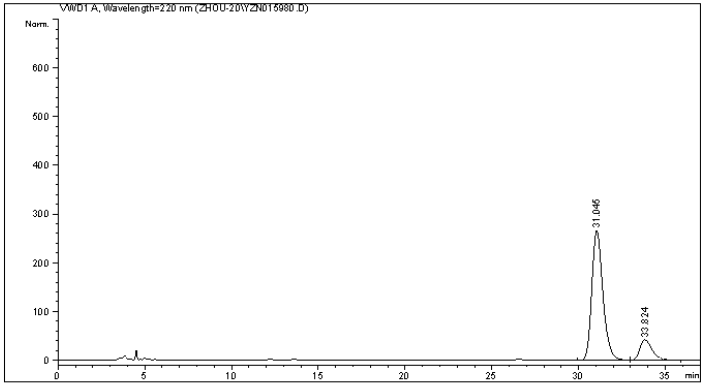



**(+/-)-2n'**

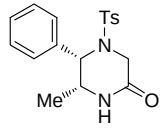


Data File C:\CHEM32\1\DATA\ZHOU-20\YZN015980.D
Sample Name: zz-9-51

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 9/9/2020 6:56:56 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/9/2020 6:56:03 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:14:53 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 90/10, 0.8 mL/min, 30 oC, 220 nm
```



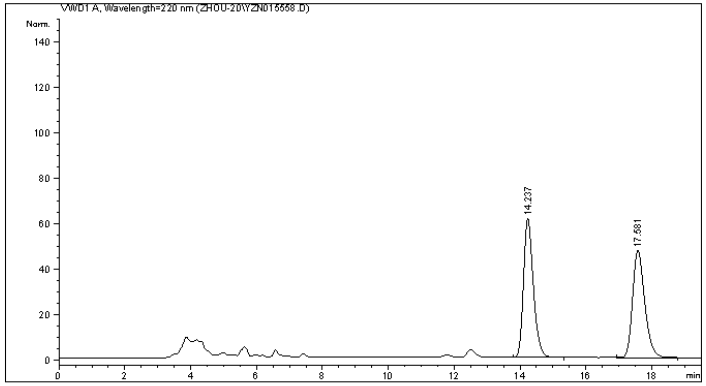

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|-------|
   1  31.045 VV    0.6818 1.18238e4   265.93173  85.2533
   2  33.824 VB    0.7504 2045.23425   41.66250  14.7467

Totals :                  1.38691e4   307.59423

                          *** End of Report ***
```



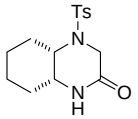

**(+)-2n'**

Data File C:\CHEM32\1\DATA\ZHOU-20\YZN015558.D
Sample Name: zz-9-28(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 8/1/2020 8:12:14 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2020 8:09:58 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:08:56 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 80/20, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  14.237 BB    0.3185 1271.00842   61.08355  51.2672
   2  17.581 VB    0.3922 1208.17456   47.13610  48.7328

Totals :                  2479.18298  108.21965
```



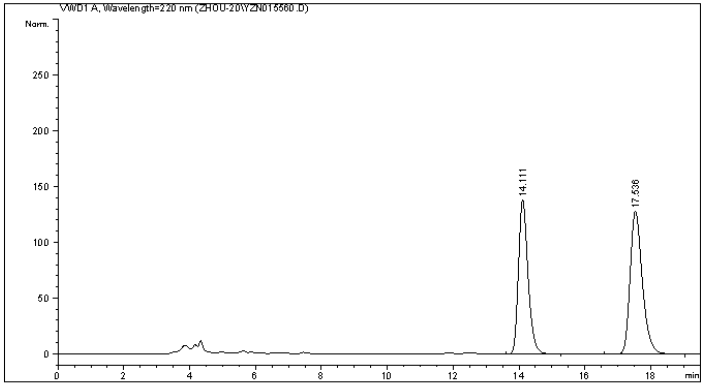

**(+/-)-2o**

```
                          *** End of Report ***
```

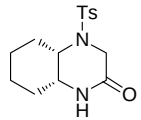
Instrument 1 9/19/2020 9:09:00 AM  Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-20\YZN015560.D
Sample Name: zz-9-28

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 8/1/2020 9:41:07 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/1/2020 9:04:45 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 9/19/2020 9:10:17 AM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 80/20, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|------|----------|----------|-------|
   1  14.111 VB    0.3082 2790.82935  138.32959  45.7786
   2  17.536 BB    0.3941 3305.53149  128.16830  54.2214

Totals :                  6096.36084  266.49789
```



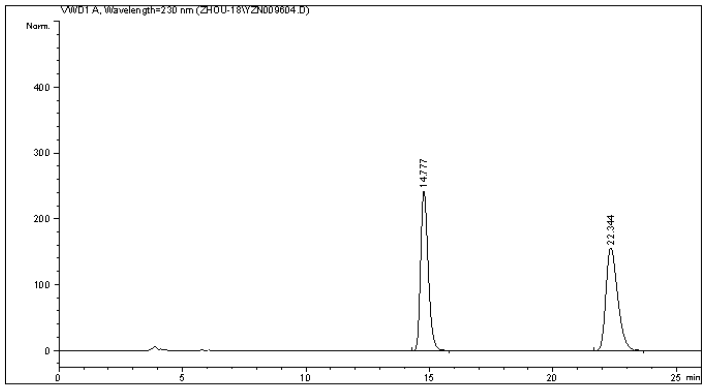

**(+)-2o**

```
                          *** End of Report ***
```

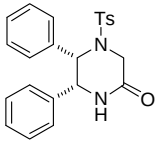
Instrument 1 9/19/2020 9:10:29 AM  Page 1 of 1

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009604.D
Sample Name: GF-9-49A(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 8/3/2018 6:57:02 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/3/2018 6:39:35 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 8/3/2018 8:18:30 PM
                  (modified after loading)
Sample Info     : AD-H, Hexane/i-PrOH = 80/20, 0.8 mL/min, 30 oC, 230 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|----------|----------|--------|
   1  14.777 BB    0.3265 5153.16699  242.53030  50.0744
   2  22.344 BB    0.5071 5137.85547  156.38524  49.9256

Totals :                  1.02910e4   398.91554

                          *** End of Report ***
```

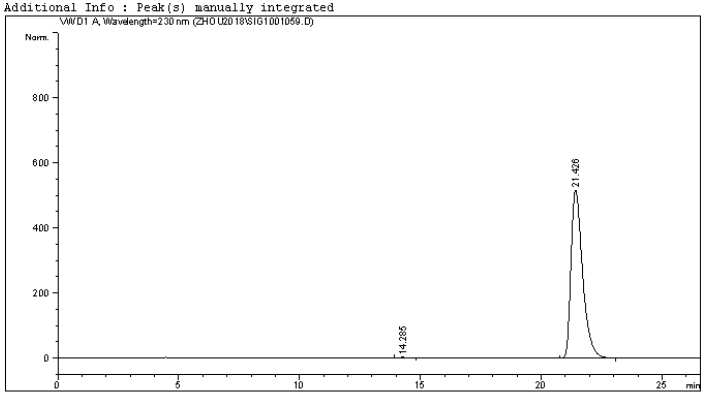



**(+/-)-2a'**

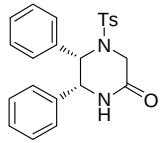


Data File C:\CHEM32\1\DATA\ZHOU2018\SIG1001059.D
Sample Name: GF-9-45A

```
Acq. Operator   : m
                                                  Location : Vial 91
Injection Date  : 5/24/18 16:58:25
Acq. Method     : FM-4-4_LC.M
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/27/18 1:51:59
                  (modified after loading)
Sample Info     : AD-H, n-hexane / i-PrOH = 80/20 , 0.8 mL/min, 30 oC, 23
                  0 nm

Additional Info : Peak(s) manually integrated
```



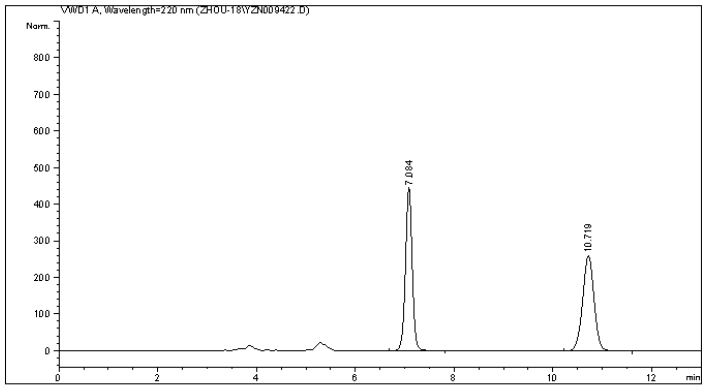

```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=230 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  14.285 BB    0.3246   39.19082    1.83894   0.2282
   2  21.426 BB    0.5074 1.71340e4   515.94037  99.7718

Totals :                  1.71732e4   517.77931
```



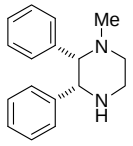

**(-)-2a'**

Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009422.D
Sample Name: GF-9-54B(+-)

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/21/2018 6:21:24 PM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC.M
Last changed    : 7/21/2018 6:04:14 PM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/31/2018 12:41:06 AM
                  (modified after loading)
Sample Info     : IA, Hexane/iPrOH = 70/30, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|-------|
   1   7.084 VB    0.1459 4243.03857  446.23868  50.2315
   2  10.719 BB    0.2478 4203.92725  260.74030  49.7685

Totals :                 8446.96582  706.97897

                          *** End of Report ***
```

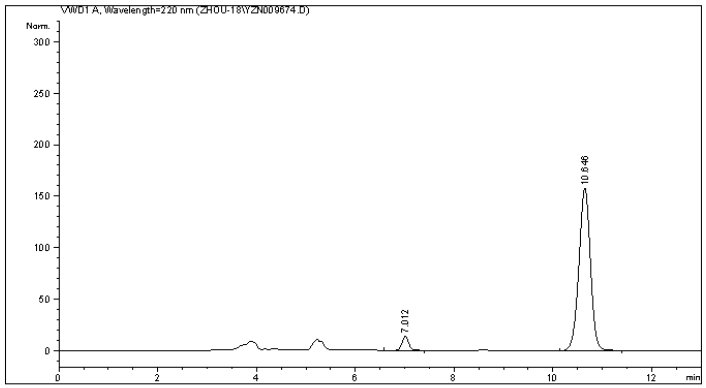



**(+/-)-3**

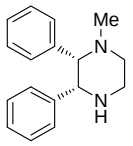


Data File C:\CHEM32\1\DATA\ZHOU-18\YZN009674.D
Sample Name: GF-9-54B

```
Acq. Operator   :
Acq. Instrument : Instrument 1                    Location :   -
Injection Date  : 7/31/2018 12:25:43 AM
Acq. Method     : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/31/2018 12:24:27 AM
                  (modified after loading)
Analysis Method : C:\CHEM32\1\METHODS\DEF_LC11.M
Last changed    : 7/31/2018 12:42:11 AM
                  (modified after loading)
Sample Info     : IA, Hexane/i-PrOH = 70/30, 0.8 mL/min, 30 oC, 220 nm
```




```
                          Area Percent Report

Sorted By             :      Signal
Multiplier:                   :      1.0000
Dilution:                     :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: VWD1 A, Wavelength=220 nm

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]  mAU   *s   [mAU   ]      %
----|-------|----|-------|---------|----------|-------|
   1   7.012 VB    0.1437  129.28876   13.86694   4.8098
   2  10.646 BB    0.2499 2558.75830  158.16457  95.1902

Totals :                 2688.04706  172.03151

                          *** End of Report ***
```

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