Supporting Information

Diastereo- and Enantioselective Synthesis of β-Hydroxy-α-Amino Acids: Application to the synthesis of a key intermediate for Lactacystin

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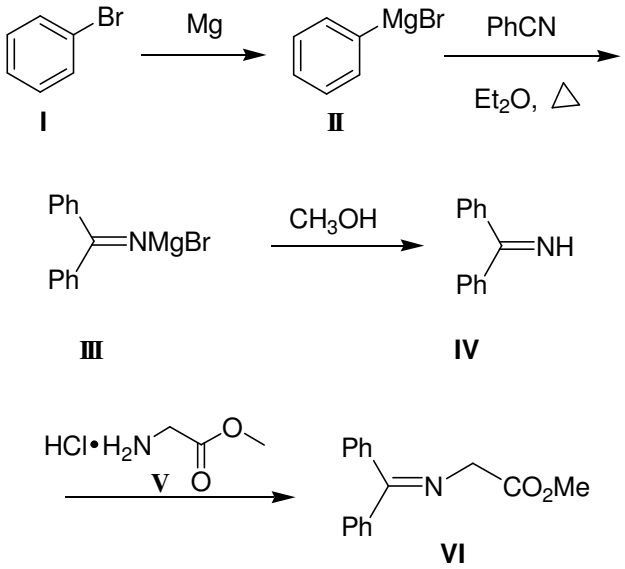
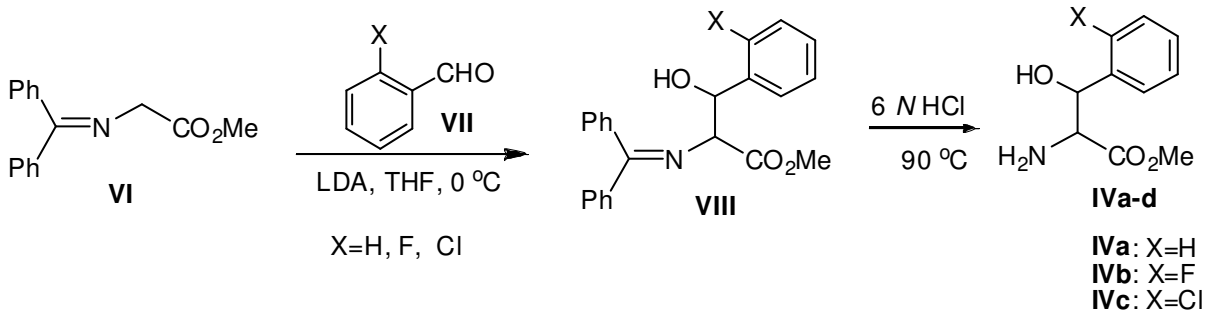
General Methods. All aldol reactions were conducted in flame-dried modified long-neck flasks fitted with rubber septa under an argon atmosphere. Solvents and reagents were dried prior to use as required. Diisopropylamine were distilled from calcium hydride immediately prior to use, THF was distilled from sodium benzophenone. *n*-butylithium in hexane (nominally 2.8 M) was purchased from Alfa and titrated before each use. Thin-layer chromatography plates visualized by exposure to ultraviolet light and/or immersion in a staining solution (phosphomolybdic acid) followed by heating on a hot plate. Flash chromatography was carried out utilizing silica gel 200-300 mesh. ^{1}H NMR spectra were recorded at 300 or 400 MHz, ^{13}C NMR spectra were recorded at 75 or 100 MHz. For ^{1}H NMR spectral, data are reported in *ppm* relative to chloroform (δ = 7.26 ppm) or deuterium oxide (δ = 4.80 ppm) as internal standard and ^{13}C NMR data are repoted in *ppm* relative to chloroform (δ = 77.0 ppm) as internal standard. High-resolution mass spectral analysis (HRMS) data were measures on the Bruker Spexll by means of the ESI technique. Optical rotation was recorded at 20 ^{o}C by the DekinEImer Model 341 Polarimeter. For chiral aldol adducts, diastereomeric ratios were determined by the integration of the ^{1}H NMR spectra (400 MHz). The ee value of the β-hydroxy-α-amino acids obtained from hydrolysis of the aldol adducts was determined by measuring the optical rotation or by HPLC analysis on a CR(+) column.

For detecting if aldol products have been epimerized in the course of hydrolysis, the racemic β-hydroxy-α-amino acids **IV** were prepared as shown in Scheme **1** and **2**. Using bromobenzene as the starting material, the Grignard reagent phenyl magnesium bromide **II** was gotten and reacted with benzonitrile to yield Grignard-nitrile complex **III**. Compound **III** was decomposed by cautious addition of anhydrous methanol to give diphenyl ketimine **IV**. Diphenyl ketimine **IV** reacted with the amino ester salt **V**, the imine **VI** could be accessed (Scheme 1).

Treatment of the imine **VI** with LDA and 2-halogenobenzaldehyde **VII** in THF at 0 °C delivered the desired aldol analogues **VIII**. The products of aldol reaction were hydrolyzed with 6 *N* HCl at 90 °C for three hours to afforded recemic β-hydroxy-α-amino acids (Scheme 2).



Scheme 1 Preparation of the achiral glycine equivalent



Scheme 2 Preparation of recemic β-hydroxy-α-amino acids.

With these racemic β-hydroxy-α-amino acids and our pure compounds in hand, HPLC was performed on WATERS HPLC systems consisting of the following: pump, PU-980; detector, UVIDEC-100-IV, measured at 254 nm; column, CR (+); mobile phase, aq. $HClO_4$ (PH = 1.5); flow rate, 0.8 mL/min. In contrast to the spectrogram of the racemic and pure compounds, the result displayed that the enantiomer can not be separated with this column but the diastereomer can be separated nicely. Even so, if the α-position of the carbonyl was racemized in the condition of hydrolyses, two diastereomer should be afforded. However, HPLC analyses results of the β-hydroxy-α-amino acids indicated another diastereomer was not been found. We can get the conclusion that there is not racemization in the course of hydrolysis of the aldol products.

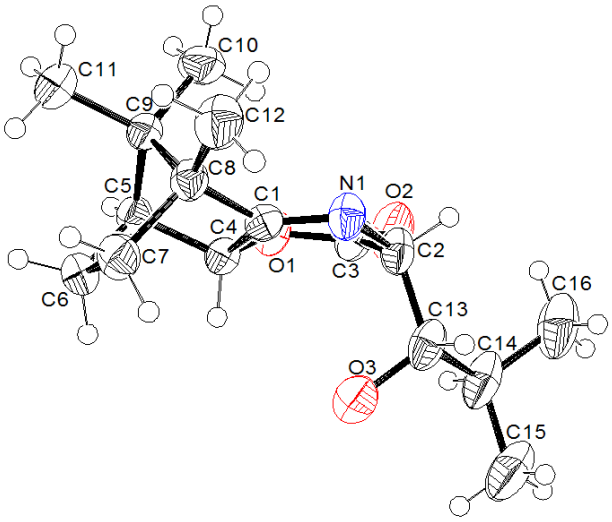


FIGURE 1. X-ray structures of Compound **2c'**

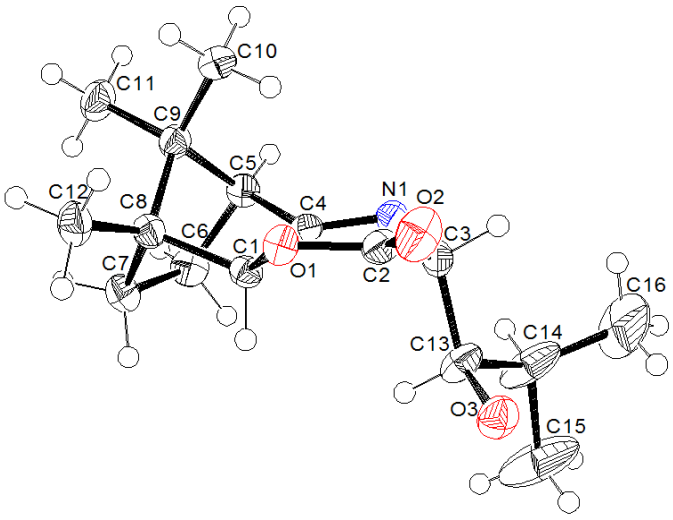


FIGURE 2. X-ray structures of Compound **3c'**

Spectral data of typical compounds

(1*S*,2*R*,5*S*,8*R*,1'*S*)-5-(1'-Hydroxybutyl)-8,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}]undec-6-en-4-one (2b'): White solid (334 mg, 80 %), $[\alpha]_D^{20}$ +37 (*c* 1.15, $CHCl_3$); m.p. 99–101°C; IR (KBr): 3438 (s), 2959 (m), 1740 (s), 1691(s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.82 (s, 1H), 4.46 (d, *J* = 4 Hz, 1H), 3.97 (m, 1H), 2.18 (d, *J* = 4.4 Hz, 1H), 2.09–2.00 (m, 1H), 1.79–1.35 (m, 7H), 1.07 (s, 3H), 0.96 (s, 3H), 0.96 (t, *J* = 7.2 Hz, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.7, 169.9, 80.2, 73.4, 67.0, 52.9, 48.3, 47.8, 37.5, 29.3, 25.9, 20.1, 19.5, 19.0, 13.7, 10.1; HRMS (ESI): calcd for $C_{16}H_{26}NO_3[M+H]^+$: 280.1907, found 280.1907.

(1*S*,2*R*,5*S*,8*R*,1'*S*)-5-(1'-Hydroxy*iso*butyl)-8,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}]undec-6-en-4-one (2c'): White solid (351 mg, 84 %), $[\alpha]_D^{20}$ +38 (*c* 1.17, $CHCl_3$); m.p. 102–104 °C; IR (KBr): 3422(s), 2962 (m), 1717 (S), 1693 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.80 (s, 1H), 4.67 (d, *J* = 4.4 Hz, 1H), 3.59 (m, 1H), 2.19 (d, *J* = 4.8 Hz, 1H), 2.11 (d, *J* =5.2 Hz, 1H), 2.07–2.00 (m, 2H), 1.80–1.73 (m, 1H), 1.64–1.59 (m, 1H), 1.41–1.35 (m, 1H), 1.09 (d, *J* = 6.8 Hz, 3H), 1.07 (s, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.6, 170.1, 80.1, 79.2, 64.8, 52.8, 48.3, 47.8, 31.7, 29.3, 25.9, 20.1, 19.6, 19.5, 17.9, 10.2; HRMS (ESI): calcd for $C_{16}H_{26}NO_3[M+H]^+$: 280.1907, found 280.1908 .

(1*S*,2*R*,5*S*,8*R*,1'*S*)-5-(1'-Hydroxy-1'-cyclohexylmethyl)-8,11,11-trimethyl-3-oxa-6-aza-tricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (2d'): White solid (392 mg, 82 %), $[\alpha]_D^{20}$ +33

(c 1.22, $CHCl_3$); m. p. 154–156 °C; IR (KBr): 3583 (s), 2927 (s), 1726 (s), 1699 (s), 1038 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.80 (s, 1H), 4.69 (d, *J* = 4.2 Hz, 1H), 3.62 (dd, *J* = 8.1 Hz, 3.9 Hz, 1H), 2.18 (d, *J* = 4.5 Hz, 1H), 2.08–1.71 (m, 4H), 1.70–1.56 (m, 6H), 1.41–1.11 (m, 5H), 1.08 (s, 3H), 0.93 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 182.9, 170.0, 80.2, 78.6, 64.2, 52.9, 48.4, 47.7, 40.9, 29.6, 29.3, 28.3, 26.2, 25.9, 25.7, 25.6, 20.1, 19.5, 10.2; HRMS (ESI): calcd for $C_{19}H_{30}NO_3[M+H]^+$: 320.2220, found 320.2223.

(1*S*,2*R*,5*S*,8*R*,1'*R*)-5-(1'-Hydroxybenzyl)-8,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}]undec-6-en-4-one (2e): White solid (375 mg, 80 %), $[\alpha]_D^{20}$ –3 (c 1.27, $CHCl_3$); m.p. 141–143 °C; IR (KBr): 3467 (s), 2960 (s), 1747 (s), 1624 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36–7.27 (m, 5H), 5.23 (t, *J* = 4.8 Hz, 1H), 4.85 (d, *J* = 4.0 Hz, 1H), 3.39 (s, 1H), 3.19 (d, *J* = 5.6 Hz, 1H), 2.00 (d, *J* = 4.8 Hz, 1H), 1.94–1.86 (m, 1H), 1.72–1.65 (m, 1H), 1.53–1.46 (m, 1H), 1.03 (s, 3H), 1.00–0,97(m, 1H), 0.96 (s, 3H), 0.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.3, 170.8, 139.6, 128.6, 128.5, 126.6, 79.6, 74.9, 67.4, 53.0, 48.2, 47.4, 29.1, 25.9, 20.0, 19.4, 10.1; HRMS(ESI): calcd for $C_{19}H_{24}NO_3[M+H]^+$: 314.1751, found 314.1754.

(1*S*,2*R*,5*S*,8*R*,1'*R*)-5-(1'-Hydroxy-*o*-chlorobenzyl)-8,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (2g): White solid (380 mg, 73 %), $[\alpha]_D^{20}$ –40 (*c* 1.19, $CHCl_3$); m.p. 176–178 °C; IR (KBr): 3375 (br), 2960 (s), 1743 (s), 1691 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48–7.45 (m, 1H), 7.34–7.24 (m, 3H), 5.75 (t, *J* = 3.2 Hz, 1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.53 (s, 1H), 3.15 (d, *J* = 2.8 Hz, 1H), 2.15 (d, *J* = 4.4 Hz, 1H), 2.04–2.02 (m, 1H), 1.75–1.72 (m, 1H), 1.68–1.64 (m, 1H), 1.34–1.23 (m, 1H), 0.97 (s, 3H), 0.93 (s, 3H), 0.74(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.6, 170.6, 137.3,

132.0, 129.4, 129.3, 128.4, 126.9, 80.0, 72.0, 65.9, 53.0, 48.1, 47.7, 29.3, 26.0, 20.0, 19.4, 10.0; HRMS(ESI): calcd for $C_{19}H_{23}ClNO_3[M+H]^+$ 348.1361, found 348.1371.

(1*S*,2*R*,5*S*,8*R*,1'*R*)-5-(1'-Hydroxy-*o*-methoxybenzyl)-8,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (2h): White solid (400 mg, 78 %), $[\alpha]_D^{20}$ –2 (*c* 1.15, $CHCl_3$); m. p. 138–140°C; IR (KBr): 3632 (s), 2960 (s), 1746 (s), 1693 (s), 1240 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.26 (m, 2H), 6.98–6.96 (m, 1H), 6.86 (d, *J* = 5.2 Hz, 1H), 5.42 (d, *J* = 5.6 Hz, 1H), 4.83 (d, *J* = 5.2 Hz, 1H), 4.29 (s, 1H), 3.81 (s, 3H), 2.11 (d, *J* = 4.4 Hz, 1H), 2.02–1.96 (m, 1H), 1.74–1.68 (m, 1H), 1.56–1.50 (m, 1H), 1.28–1.17 (m, 1H), 1.00 (s, 3H), 0.92 (s, 3H), 0.75(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 183.1, 170.2, 156.4, 129.3, 127.9, 127.4, 120.7, 110.5, 79.5, 72.3, 67.5, 55.1, 52.9, 48.1, 47.6, 29.4, 26.0, 20.0, 19.4, 10.1; HRMS (ESI) calcd for $C_{20}H_{26}NO_4[M+H]^+$: 344.1856, found 344.1861.

(1*R*,2*S*,5*R*,8*S*,1'*S*)-5-(1'-Hydroxyethyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}]undec-6-en-4-one (3a, minor): ^1H NMR (400 MHz, $CDCl_3$): δ 4.59 (s, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 4.16 (m, 1H), 2.43 (d, *J* = 4.4 Hz, 1H), 2.05–2.00 (m, 1H), 1.92–1.85 (m, 1H), 1.63–1.57 (m, 1H), 1.47 (d, *J* = 2.4 Hz, 3H), 1.46–1.37 (m, 1H), 1.05 (s, 3H), 0.97 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 169.5, 82.0, 69.3, 68.0, 53.9, 49.5, 48.2, 34.5, 21.8, 21.5, 20.0, 19.3, 9.7.

(1*R*,2*S*,5*R*,8*S*,1'*R*)-5-(1'-Hydroxybutyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}]undec-6-en-4-one (3b'): Colorless oil (334 mg, 80 %), $[\alpha]_D^{20}$ –3 (*c* 1.61, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ 4.60 (s, 1H), 4.43 (d, *J* = 4.0 Hz, 1H), 3.96 (s, 1H), 2.41 (d, *J* = 4.4 Hz, 1H), 2.05–1.36 (m, 8H), 1.05 (s, 3H), 1.00–0.95 (m, 6H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.1, 169.6, 82.1, 73.3, 66.9, 53.9, 49.5, 48.2, 37.4, 34.5,

21.5, 19.9, 19.2, 19.0, 13.8, 9.7; HRMS (ESI): calcd for $C_{16}H_{26}NO_3[M+H]^+$ 280.1907, found 280.1902.

(1*R*,2*S*,5*R*,8*S*,1'*R*)-5-(1'-Hydroxy-*iso*-butyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}] undec-6-en-4-one (3c'): White solid (359 mg, 86 %), $[\alpha]_D^{20}$ –40 (*c* 1.38, CH_2Cl_2); m.p. 178 °C (dec), IR (KBr): 3407 (s), 3471 (s), 2966 (m), 1746 (s), 1695(s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.59 (d, *J* = 3.2 Hz, 1H), 3.55 (s, 1H), 2.55 (s, 1H), 2.41 (d, *J* = 4.4 Hz, 1H), 2.05–1.96 (m, 2H), 1.91–1.84 (m, 1H), 1.61–1.54 (m, 1H), 1.41–1.35 (m, 1H),1.08 (d, *J* = 6.8 Hz, 3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.00 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.0, 169.8, 81.8, 78.7, 64.7, 53.9, 49.5, 48.2, 34.4, 31.5, 21.4, 19.9, 19.5, 19.2, 17.6, 9.7; HRMS (ESI): calcd for $C_{16}H_{26}NO_3[M+H]^+$ 280.1907, found 280.1900.

(1*R*,2*S*,5*R*,8*S*,1'*R*)-5-(1'-Hydroxy-*n*-heptyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo[6.2.1.0^{2,7}] undec-6-en-4-one (3d'): Colorless oil (399 mg, 83 %), $[\alpha]_D^{20}$ –8 (*c* 1.02, CH_2Cl_2); IR (KBr): 3260 (s), 2956 (s), 2928 (s), 1743 (s), 1701 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.62 (s, 1H), 4.43 (s, 1H), 3.94–3.90 (m, 1H), 2.42 (d, *J* = 4.4 Hz, 1H), 2.04–1.58 (m, 6H), 1.56–1.29 (m, 8H), 1.05 (s, 3H), 0.96 (s, 3H), 0.90–0.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.2, 169.6, 82.0, 73.5, 66.9, 53.9, 49.5, 48.2, 35.2, 34.5, 31.7, 28.9, 25.7, 22.5, 21.5, 20.0, 19.3, 14.0, 9.7; HRMS (ESI): calcd for $C_{19}H_{32}NO_3[M+H]^+$ 322.2377, found 322.2371.

(1*R*,2*S*,5*R*,8*S*,1'*R*)-5-(1'-Hydroxy-1'-*cyclo*-hexylmethyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (3e'): Colorless oil (397 mg, 82 %); $[\alpha]_D^{20}$ +1.5 (*c* 1.49, CH_2Cl_2); IR (KBr): 3414 (s), 2926 (s), 1741 (s), 1700 (s), 1075 (s) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.59 (d, *J* = 4.8Hz, 2H), 3.54 (dd, *J* = 7.5 Hz, 4.5 Hz, 1H), 2.38 (d,

J = 4.8 Hz, 1H), 2.01–1.82 (m, 4H), 1.78–1.55 (m, 6H), 1.36–1.04 (m, 5H), 1.01 (s, 3H), 0.93 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.2, 169.7, 81.8, 78.0, 64.2, 53.8, 49.4, 48.2, 40.8, 34.4, 29.6, 27.9, 26.2, 25.8, 25.6, 21.4, 19.9, 19.2, 9.7; HRMS (ESI): calcd for $C_{19}H_{30}NO_3[M+H]^+$ 320.2220, found 320.2216.

(1*R*,2*S*,5*R*,8*S*,1'*S*)-5-(1'-Hydroxy-*o*-fluorobenzyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (3g): White solid (406 mg, 82 %), $[\alpha]_D^{20}$ +64 (*c* 1.05, CH_2Cl_2); decomposed with blurry melt point; IR (KBr): 3179 (br), 2931 (m), 1745 (s), 1700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.40 (m, 1H), 7.39–7.27 (m, 1H), 7.18–7.14 (m, 1H) 7.06–7.00 (m, 1H), 5.65 (t, *J* = 4.4 Hz, 1H), 4.76 (d, *J* = 4.0 Hz, 1H), 4.32 (s, 1H), 3.05 (d, *J* = 4.8 Hz, 1H), 2.34 (d, *J* = 4.8 Hz, 1H), 2.04–1.94 (m, 1H), 1.89–181 (m, 1H), 1.60–1.53 (m, 1H), 1.32–1.23 (m, 1H), 1.03 (s, 3H), 0.93 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0, 170.3, 128.0, 127.9, 127.0, 124.3, 115.3, 82.8, 69.7, 66.3, 54.0, 49.4, 48.0, 34.6, 21.4, 19.9, 19.2, 9.7; HRMS (ESI): calcd for $C_{19}H_{23}FNO_3[M+H]^+$ 332.1656, found 332.1658.

(1*R*,2*S*,5*R*,8*S*,1'*S*)-5-(1'-Hydroxy-*o*-chlorobenzyl)-1,11,11-trimethyl-3-oxa-6-azatricyclo [6.2.1.0^{2,7}]undec-6-en-4-one (3h): White solid (416 mg, 80 %), $[\alpha]_D^{20}$ +32 (*c* 1.05, DMSO); decomposed with blurry melt point; IR (KBr): 3145 (b), 2960 (s), 1744 (s), 1700 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49–7.28 (m, 4H), 5.82 (t, *J* = 4.0 Hz, 1H), 4.90 (d, *J* = 4.0 Hz, 1H), 4.50 (s, 1H), 2.57 (d, *J* = 3.6Hz, 1H), 2.36 (d, *J* = 4.4Hz, 1H), 2.17–1.96 (m, 1H), 1.91–1.84 (m, 1H), 1.66–1.59 (m, 1H),1.40–1.24 (m, 1H), 1.05 (s, 3H), 0.94 (s, 3H), 0.80(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0, 170.4, 137.1, 131.7, 129.5, 128.2, 127.0, 82.0, 72.5, 65.2, 54.0, 49.4, 48.0, 34.7, 21.5, 19.9, 19.2, 9.7; HRMS (ESI): calcd for $C_{19}H_{23}ClNO_3)[M+H]^+$: 348.1361, found 348.1361.

(2*S*, 3*S*)-3-Hydroxyleucine (4c): White solid (153 mg, 87 %), $[\alpha]_D^{20}$ +20 (*c* 1.1, H_2O), lit[12g] $[\alpha]_D^{20}$ + 22 (*c* 1, H_2O); m.p. 224–226 °C; ^{1}H NMR (400 MHz, D_2O): δ 3.91 (s, 1H), 3.52 (dd, *J* = 9.2 Hz, 6 Hz, 1H), 1.94 (m, 1H), 0.97 (m, 6H). ^{13}C NMR (100 MHz, D_2O): δ 171.8, 76.1, 57.1, 30.3, 18.6, 18.5.

(2*S*, 3*S*)-2-Amino-3-*cyclo*-hexyl-3-hydroxypropanoic acid (4d): White solid (166 mg, 74 %), $[\alpha]_D^{20}$ +33 (*c* 1.1, 2*N* HCl); m.p. 208–210 °C; ^{1}H NMR (400 MHz, D_2O): δ 3.92 (d, *J* = 3.2 Hz, 1H), 3.61 (dd, *J* = 9.2 Hz, 6 Hz, 1H), 1.94–0.89 (m, 11H).

(2*S*, 3*R*)-2-Amino-3-hydroxy-3-phenylpropanoic acid (4e): White solid (141 mg, 65 %), $[\alpha]_D^{20}$ –30 (*c* 1.0, H_2O), lit[12d] $[\alpha]_D^{20}$ –32.8 (*c* 0.1, H_2O); m.p. 184–186 °C; ^{1}H NMR (400 MHz, D_2O): δ 7.43 (m, 5H), 5.3 (s, 1H), 3.91 (dd, *J* = 8 Hz, 4 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 172.1, 139.1, 128.9, 128.5, 125.8, 71.3, 60.8.

(2*S*, 3*R*)-2-Amino-3-hydroxy-3-(*o*-fluorophenyl)propanoic acid (4f): White solid (167 mg, 70 %), $[\alpha]_D^{20}$ –20 (*c* 1.0, H_2O), lit[12h] $[\alpha]_D^{20}$ –18.5 (*c* 0.8, H_2O); m.p. 204–206 °C; ^{1}H NMR (400 MHz, D_2O): δ 7.59–7.56 (m, 1H), 7.45–7.42 (m, 1H), 7.32–7.26 (m, 1H), 7.22–7.15 (m, 1H), 5.52 (dd, *J* = 7.2 Hz, 4.8 Hz, 1H), 4.0 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 171.7, 130.6, 130.5, 127.7, 124.8, 115.8, 115.5, 66.4, 59.4.

(2*S*, 3*R*)-2-Amino-3-hydroxy-3-(*o*-chlorophenyl)propanoic acid (4g): White solid (196 mg, 76 %), $[\alpha]_D^{20}$ –34 (*c* 1.0, H_2O); m.p. 206–208 °C; ^{1}H NMR (400 MHz, D_2O): δ 7.65 (d, *J* = 7.6 Hz, 1H), 7.51–7.36 (m, 3H), 5.68 (d, *J* = 3.2 Hz, 1H), 4.1 (t, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 171.9, 136.3, 131.5, 129.9, 129.8, 127.5, 127.4, 68.2, 58.1.

(2*R*, 3*R*)-2-Amino-3-hydroxynonanoic acid (5d): White solid (191 mg, 81 %), $[\alpha]_D^{20}$ –6.7 (*c* 1.0, 6*N* HCl); m.p. 207 °C (dec); ^{1}H NMR (400 MHz, D_2O): δ 4.12 (m, 1H), 3.84 (d, *J* = 4 Hz, 1H), 1.49–1.28 (m, 10H), 0.88–0.85 (m, 3H). ^{13}C NMR (100 MHz, D_2O): δ 171.9, 69.6, 59.3, 30.9, 30.7, 28.0, 25.2, 21.9, 13.3.

(2*R*, 3*R*)-2-Amino-3-*cyclo*-hexyl-3-hydroxypropanoic acid (5e): White solid (170 mg, 76 %), $[\alpha]_D^{20}$ –33 (*c* 1.0, H_2O); m.p. 208–210 °C; ^{1}H NMR (300 MHz, D_2O): δ 3.74 (d, *J* = 3.0 Hz, 1H), 3.43 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 1.76–0.74 (m, 11H). (deuterium oxide (δ = 4.68 ppm) as internal standard)

(2*R*, 3*S*)-2-Amino-3-hydroxy-3-phenylpropanoic acid (5f): White solid (173 mg, 80 %), $[\alpha]_D^{20}$ +31 (*c* 1.28, H_2O), lit[12d] $[\alpha]_D^{20}$ +30.6 (*c* 0.7, H_2O); m.p. 196–197 °C; ^{1}H NMR (400 MHz, D_2O): δ 7.507–7.408 (m, 5H), 5.31 (d, *J* = 4.4 Hz, 1H), 3.93 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 172.0, 139.1, 128.9, 128.5, 125.8, 71.2, 60.8.

(2*R*, 3*S*)-2-Amino-3-hydroxy-3-(*o*-fluorophenyl)propanoic acid (5g): White solid (198 mg, 83 %), $[\alpha]_D^{20}$ +21 (*c* 1.0, H_2O), lit[12] $[\alpha]_D^{20}$ +20.6 (*c* 0.32, H_2O); m.p. 204–206 °C (dec); ^{1}H NMR (400 MHz, D_2O): δ 7.57–7.55 (m, 1H), 7.55–7.40 (m, 1H), 7.30–7.20 (m, 1H), 7.20–7.15 (m, 1H), 5.51 (d, *J* = 4.4 Hz, 1H), 3.99 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 171.7, 130.5, 130.4, 127.5, 124.7, 115.6, 115.4, 66.3, 59.2.

(2*R*, 3*S*)-2-Amino-3-hydroxy-3-(*o*-chlorophenyl)propanoic acid (5h): White solid (209 mg, 81 %), $[\alpha]_D^{20}$ +34 (*c* 1.0, H_2O); m.p. 206–208 °C (dec); ^{1}H NMR (400 MHz, D_2O): δ 7.64 (d, *J* =7.2 Hz, 1H), 7.50–7.36 (m, 3H), 5.68 (d, *J* = 3.2 Hz, 1H), 4.10 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (100 MHz, D_2O): δ 171.9, 136.3, 131.5, 129.9, 129.8, 127.5, 127.4, 68.2, 58.1.

Methyl (2*R*, 3*R*)-2-benzotylamino-3-hydroxy-4-methyl pentanoate 8: Dry hydrogen chloride was passed rapidly into a stirred suspension of (2*R*, 3*R*)-3-hydroxyleucine **5c** (292 mg, 2 mmol) in methol until the solution was boiled. The introduction of HCl was terminated, and the solution was stirred at rt. for 24 h, concentrated. The crude material used for the next step without further purification. Methyl ester was dissolved in methol (10 mL) and treated with triethylamine (0.84 mL, 6 mmol). After stirring at rt. for 15 min, the solution was cooled to 0 °C. Then benzoyl chloride was added and stirred at 0 °C for another 2 h. The reaction mixture was quenched with H_2O (1 mL). Then methol was removed and aqueous was extracted with DCM (3×10 mL). The combined organic layer dried over Na_2SO_4, filtered and concentrated. Flash chromatography (4:1 petrol ether/EtOAc) afford **8** (405 mg 77 %) as colorless oil. $[\alpha]_D^{20}$ –38 (C 0.038, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00 (d, *J* = 6.8 Hz,3H), 1.02 (d, *J* = 6.8 Hz, 3H), 1.74–1.80 (m, 1H), 3.18 (d, *J* = 6.4 Hz, 1H), 3.59–3.60 (m, 1H), 3.76 (s, 3H), 4.95 (dd, *J* = 3.6, 7.6 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.40–7.44 (m, 2H), 7.49–7.52 (m, 1H), 7.80 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz,$CDCl_3$): δ 18.9, 19.0, 31.4, 52.5, 55.8, 78.7, 127.1, 128.5, 131.9, 133.3, 167.4, 171.4; HRMS (ESI): Calcd for $C_{14}H_{20}NO_4$ $[M+H]^+$: 266.1387, found 266.1388.

Methyl (4*R*, 5*R*)-5-Isopropyl-2-phenyl-4, 5-dihydrooxazole-4-carboxylate 10: Dry hydrogen chloride was passed rapidly into a stirred suspension of (2*R*, 3*R*)-3-hydroxyleucine **5c** (292 mg, 0.2 mmol) in methol until the solution was boiled. The introduction of HCl was terminated, and the solutuin was stirred at rt. for 24 h. It was then concentrated and methol was removed under high vacuum without any purification, methyl ester and p-TsOH.H_2O (38 mg, 0.2 mmol) in dimethoxyl ethane (5 mL) was

treated with trimethyl orthozoate (0.103 mL 0.6 mmol), heated at reflux for 4 h. the solution mixture was cooled to rt. and quenched with H_2O (2 mL), the aqueous layer was separated and extracted with ether (3×5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4, filtered and concentrated. Flash chromatography (8:1 petrol ether/EtOAc) afford **10** (402 mg 82 %) as colourless oil. $[\alpha]_D^{20}$ +74 (C 0.04, $CHCl_3$); IRυmax (film):2924, 1733, 1642, 1438, 1386; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.02 (d, *J* = 6.8 Hz, 3H), 1.07 (d, *J* = 6.4 Hz, 3H), 2.06–2.01 (m, 1H), 3.77 (s, 3H), 4.54 (dd, *J* = 8, 9.6 Hz, 1H), 4.95 (d, *J* = 9.6 Hz, 1H), 7.40–7.44 (m, 2H), 7.49–7.51 (m, 1H), 7.98–8.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.7, 19.6, 29.2, 52.0, 70.6, 87.6, 127.2, 128.3, 128.5, 131.8, 166.7, 170.5; HRMS (ESI): Calcd for $C_{14}H_{18}NO_3$ $[M+H]^+$: 248.1281, found 247.1287.

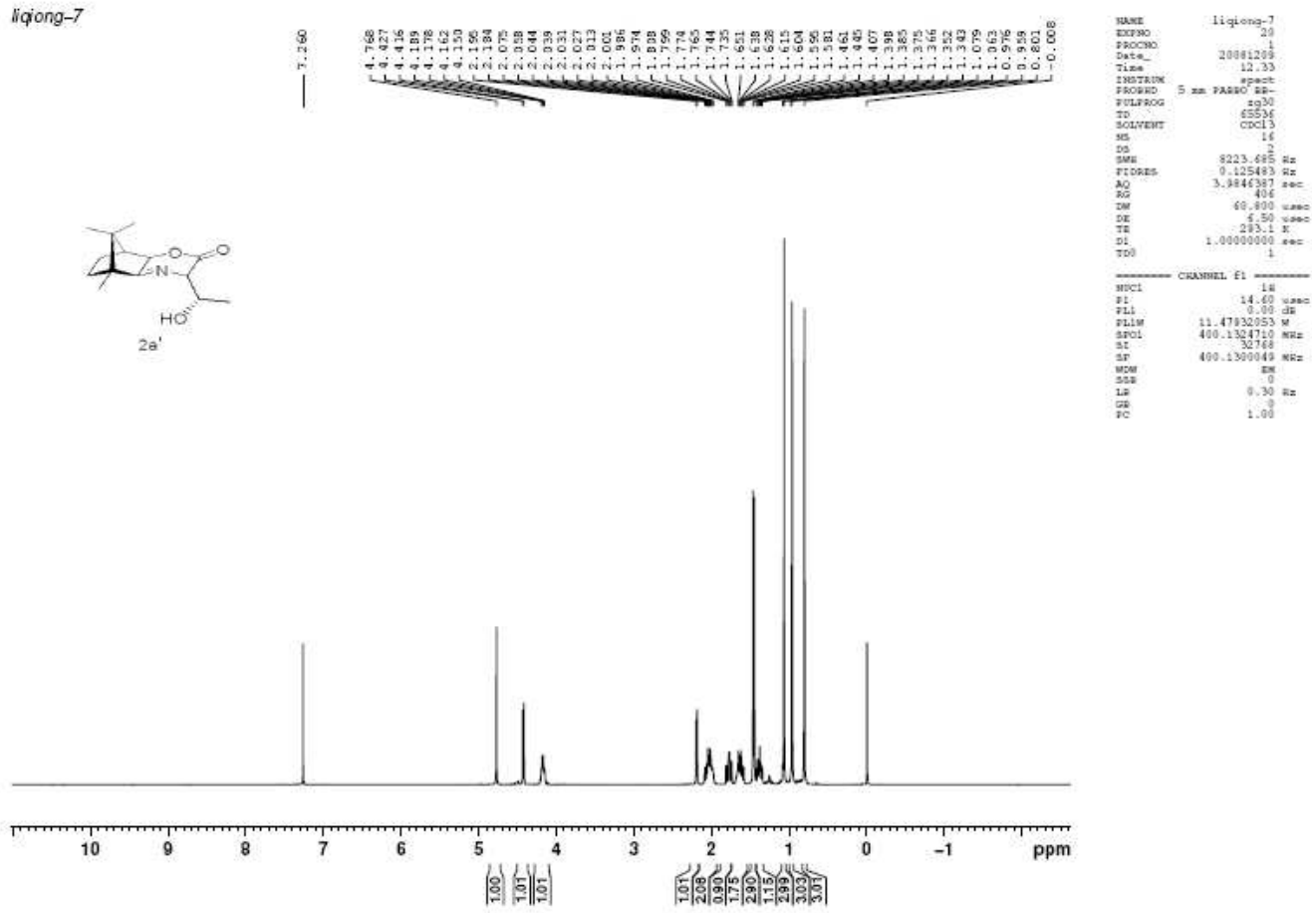
Methyl(4*S*,5*S*)-5-Isopropyl-2-phenyl-4,5-dihydrooxazole-4-carboxylate 11: Following the procedure described for **10**. only change (2*R*,3*R*) 3-hydroxyleucine **5c** into (2*S*, 3*S*) 3-hydroxyleucine **4c** .Colourless oil; $[\alpha]_D^{20}$-74 (C 0.04, $CHCl_3$); IRυmax (film): 2924, 1740, 1645, 1443, 1372; ^{1}H NMR (300 MHz,$CDCl_3$): δ 1.02 (d, *J* = 6.9 Hz, 3H), 1.06 (d, *J* = 6.3 Hz, 3H), 2.03–2.12 (m, 1H), 3.77 (s, 3H), 4.54 (dd, *J* = 8.4, 9.9 Hz, 1H), 4.95 (d *J* = 9.9 Hz, 1H), 7.42–7.45 (m, 2H), 7.49–7.54 (m, 1H), 7.98–8.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 18.7, 19.6, 29.2, 52.0, 70.6, 87.6, 127.2, 128.3, 128.5, 131.8, 166.7, 170.5; HRMS (ESI): Calcd for $C_{14}H_{18}NO_3[M+H]^+$: 248.1281, found 247.1284.

Methyl (2*S*,3*S*)-2-benzotylamino-3-hydroxy-4-methyl pentanoate 12: Following the procedure described for **8**. only change (2*R*,3*R*)-3-hydroxyleucine **5c** into (2*S*, 3*S*)-3-hydroxyleucine **4c**. Colourless oil; $[\alpha]_D^{20}$ +38 (C 0.038, $CHCl_3$); ^{1}H NMR (400

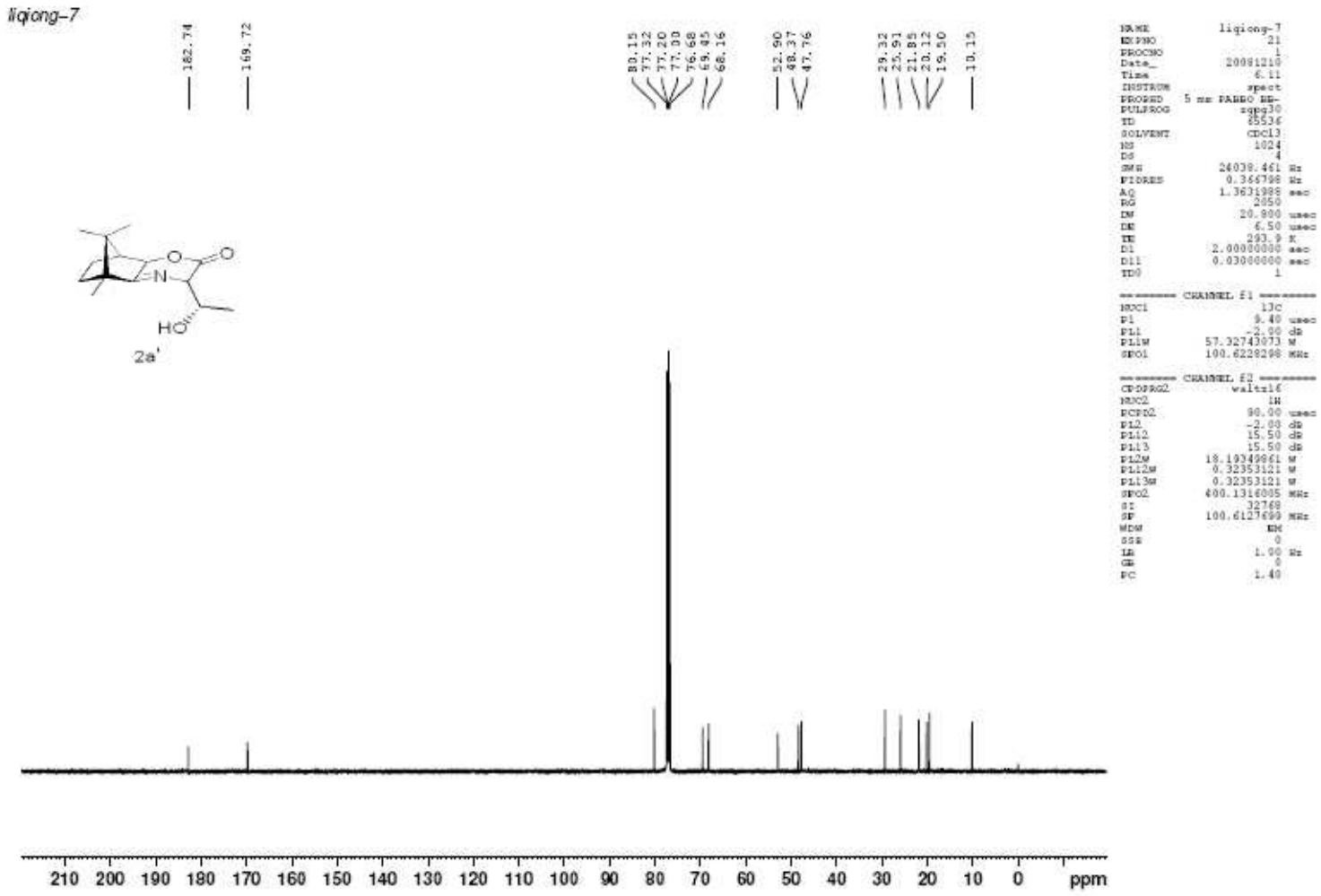
MHz,$CDCl_3$): δ 1.00 (d, *J* = 6.8 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H), 1.74–1.80 (m, 1H), 3.09 (d, *J* = 8 Hz, 1H), 3.59–3.62 (m, 1H), 3.80 (s, 3H), 4.96 (dd, *J* = 3.6, 7.6 Hz, 1H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.41–7.45 (m, 2H), 7.50–7.54 (m, 1H), 7.80–7.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 19.0, 31.5, 52.6, 55.9, 78.8, 127.2, 128.6, 132.0, 133.4, 167.4, 171.4; HRMS (ESI): Calcd for $C_{14}H_{20}NO_4[M+H]^+$: 266.1387, found 266.1393.

^{1}H NMR and ^{13}C NMR spectra of typical compounds

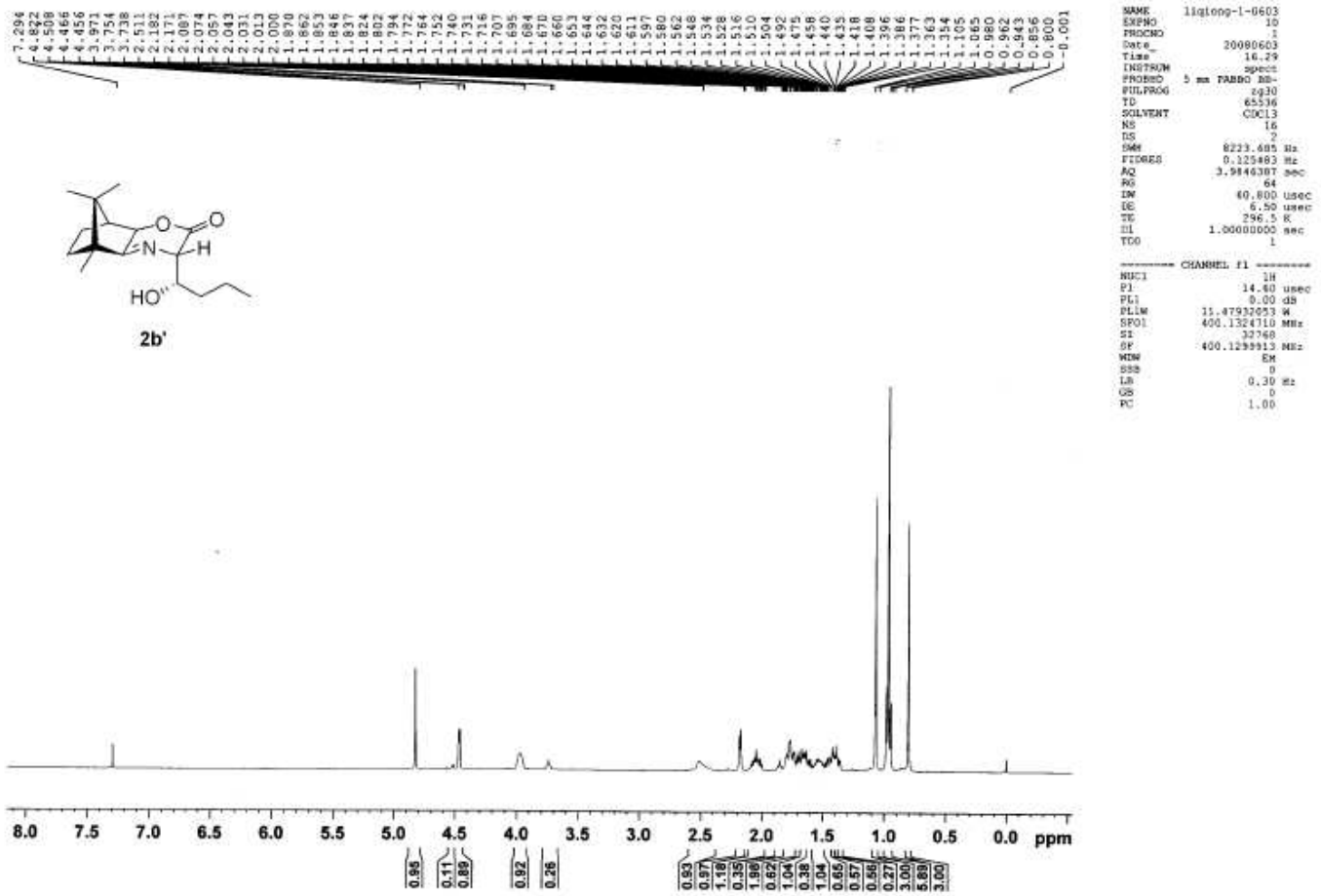
^{1}H NMR spectrum of compound **2a**' (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2a'** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2b'** (400 MHz, $CDCl_3$)

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RG                       64
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DE                   6.50 usec
TE                   296.5 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
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SFO1              400.1324710 MHz
SI                      32768
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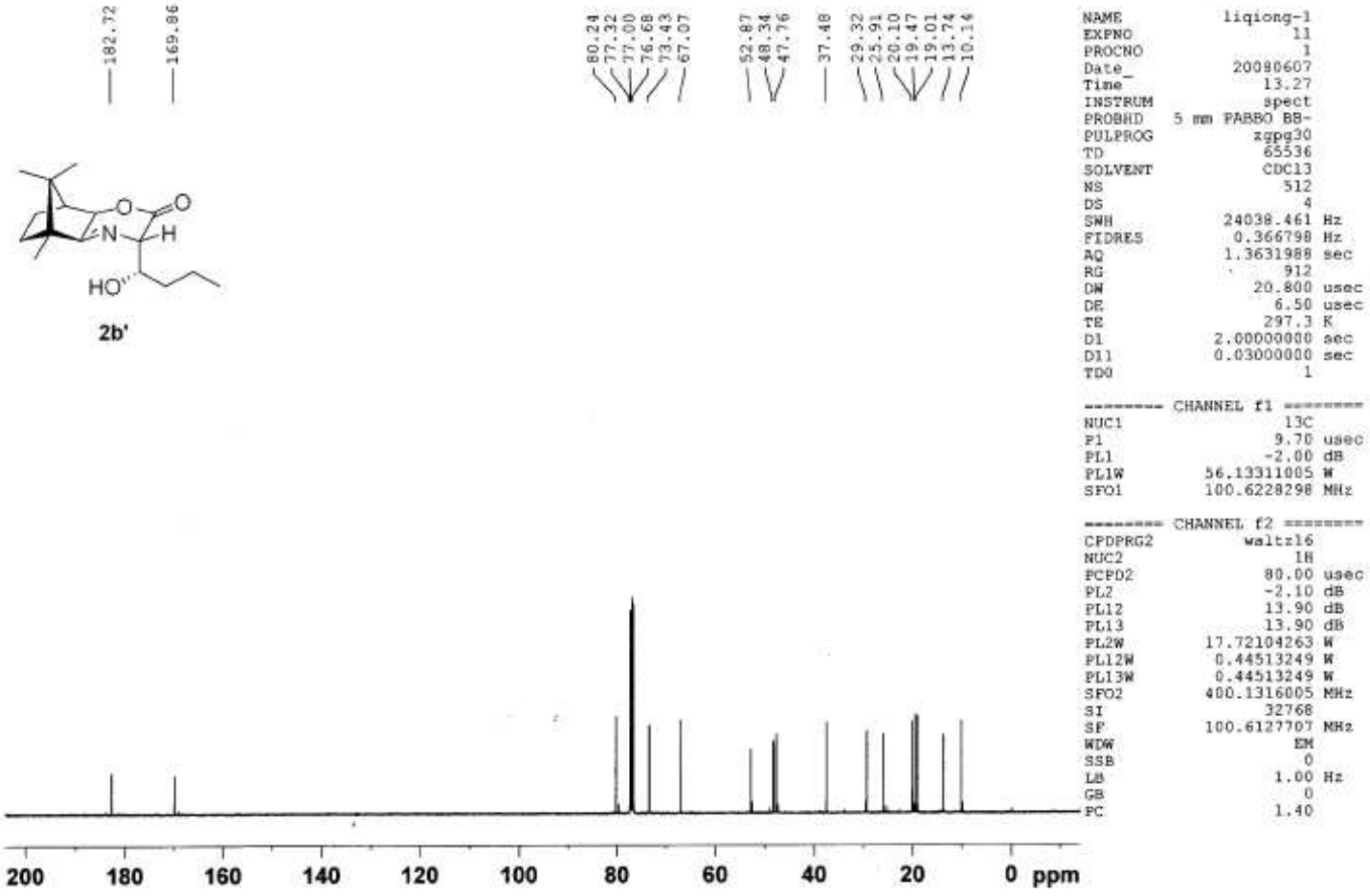
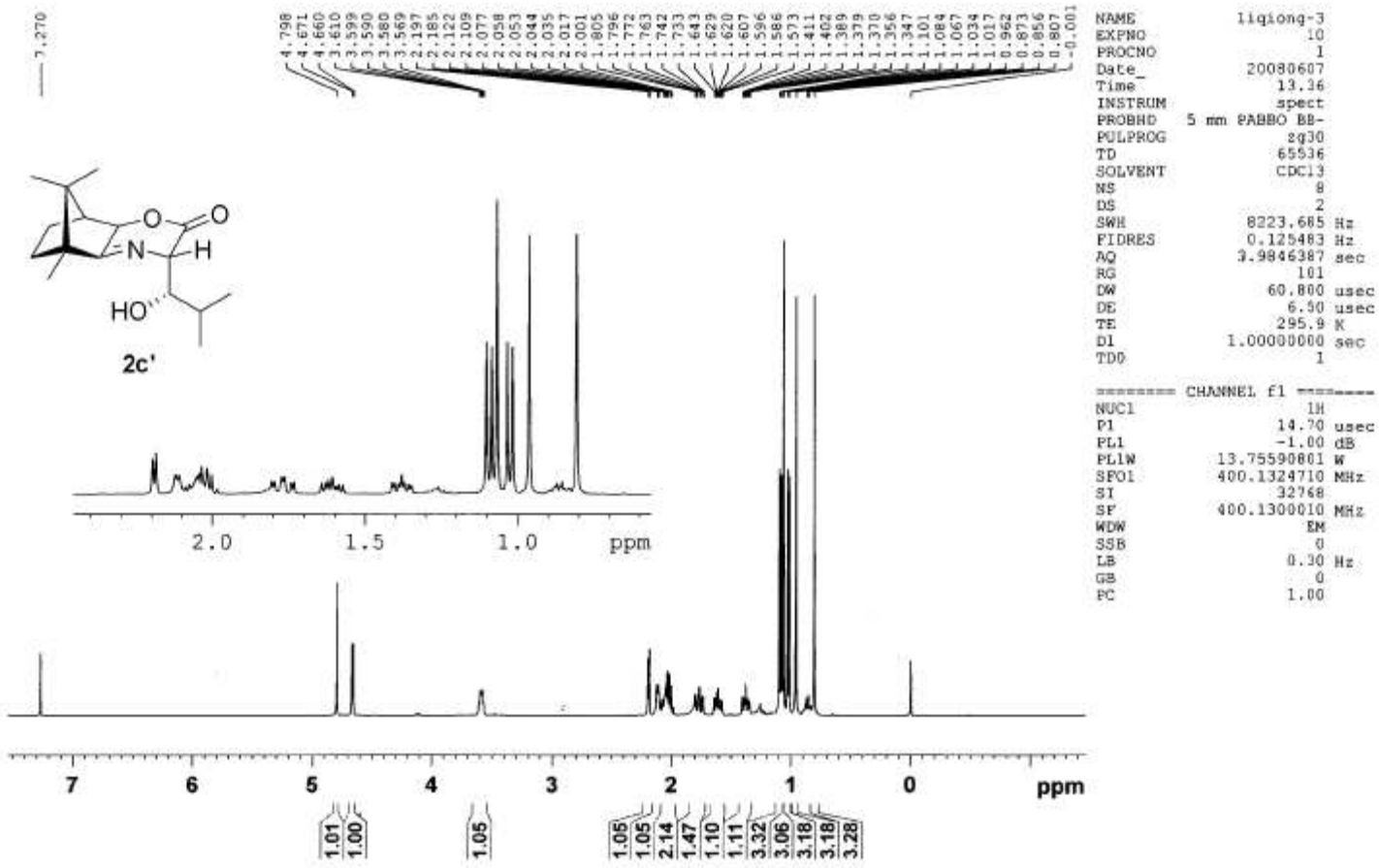
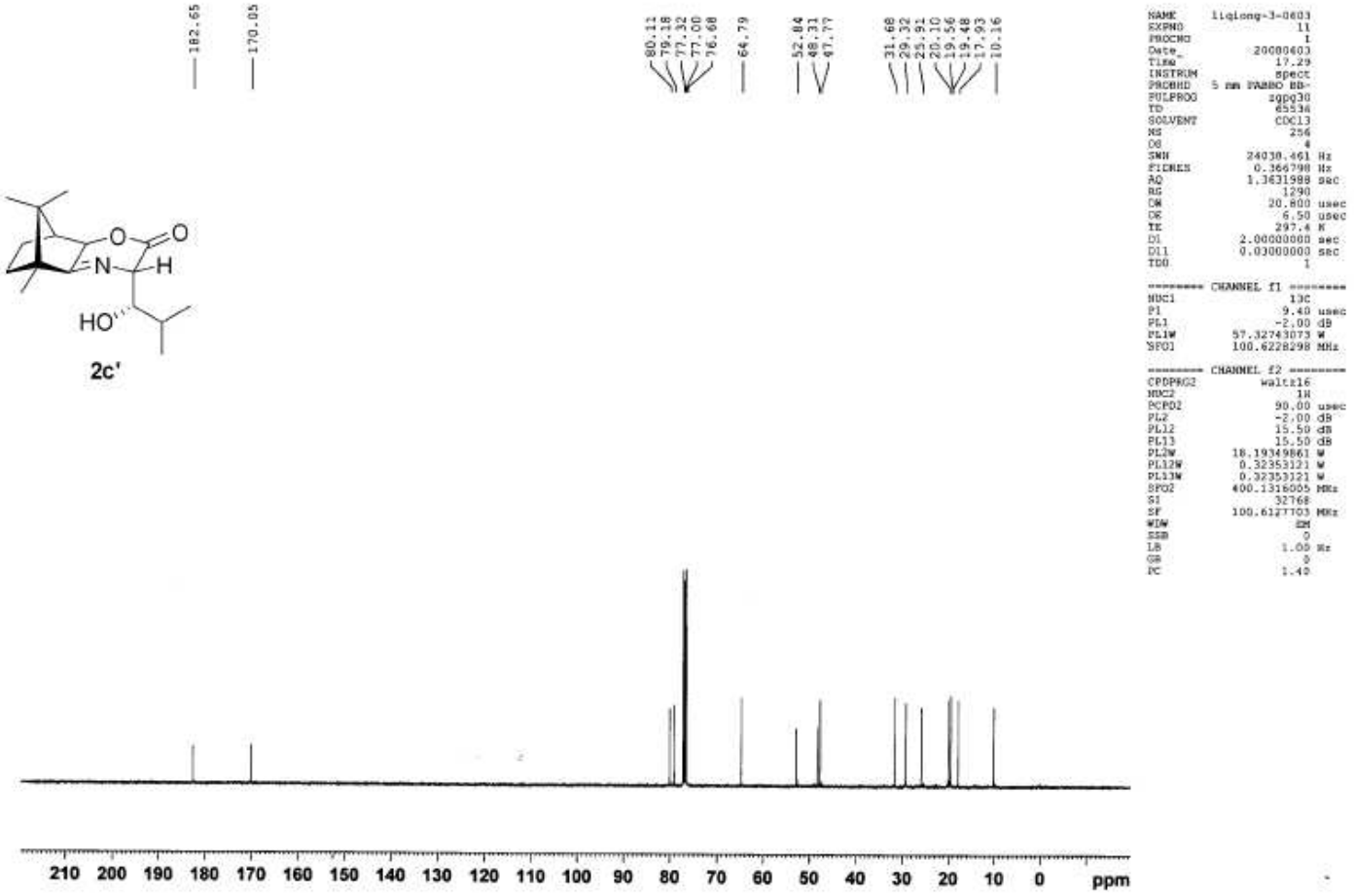
^{13}C NMR spectrum of compound **2b'** (100 MHz, $CDCl_3$)



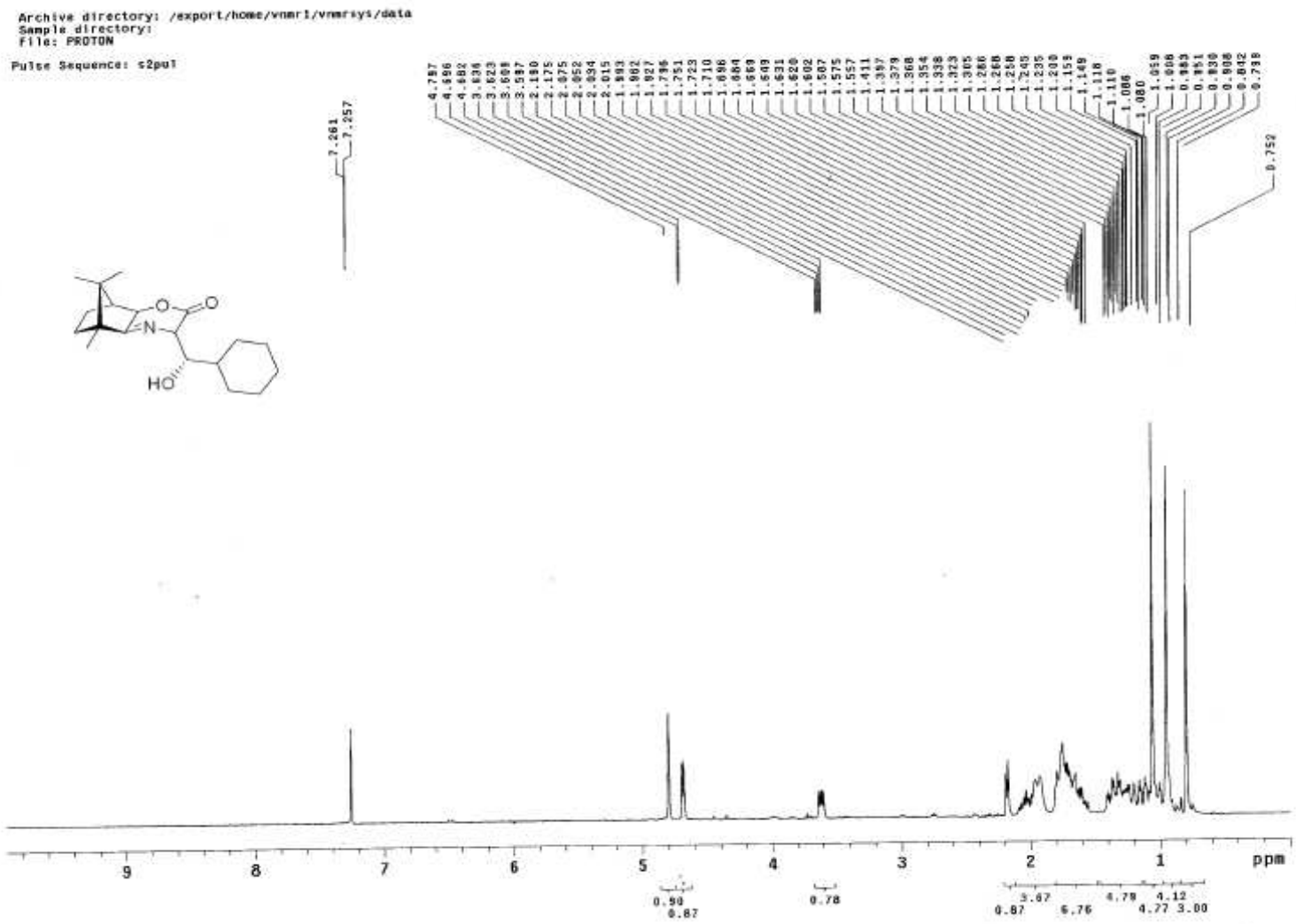
^{1}H NMR spectrum of compound **2c'** (400 MHz, $CDCl_3$)



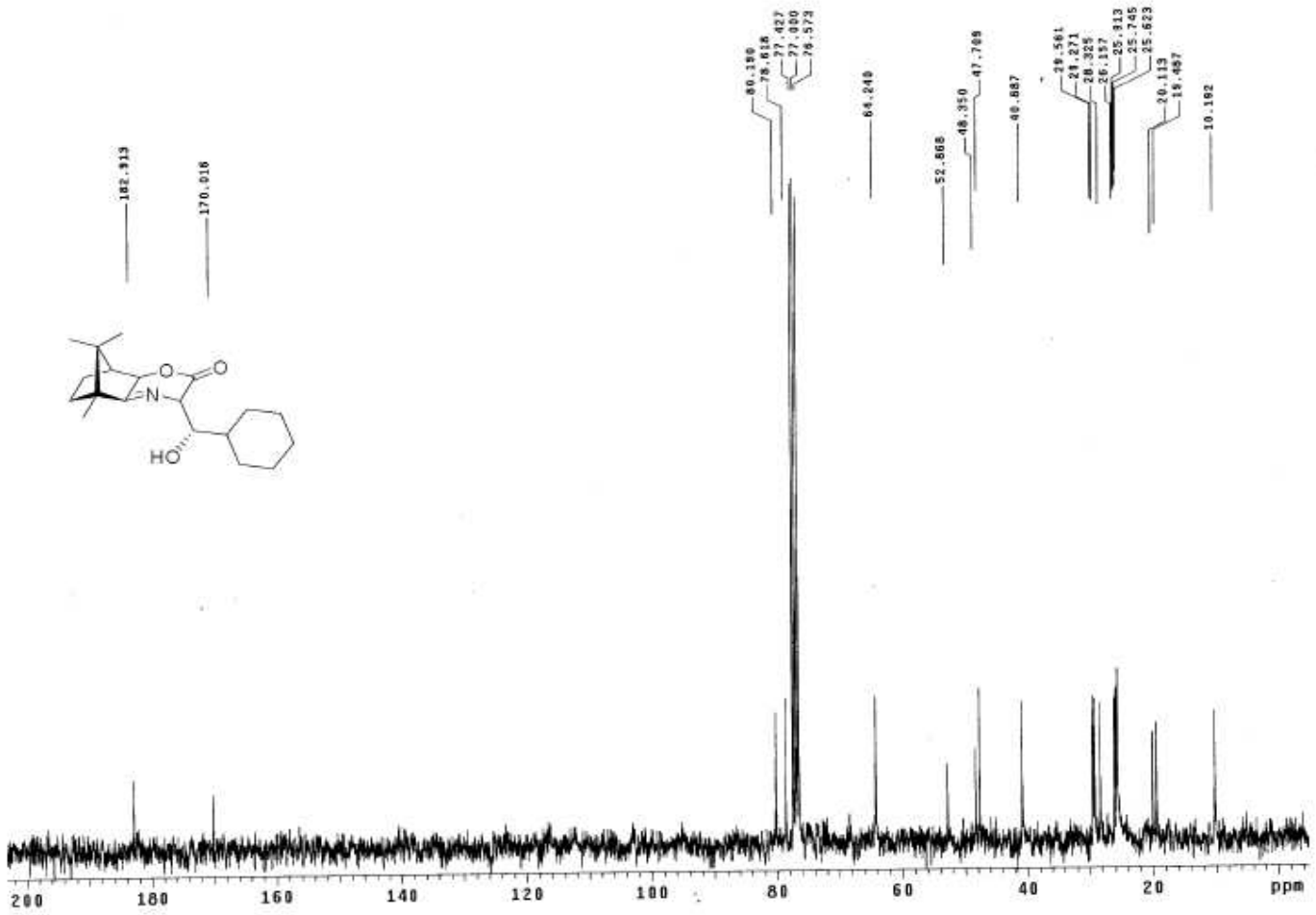
^{13}C NMR spectrum of compound **2c'** (100 MHz, $CDCl_3$)



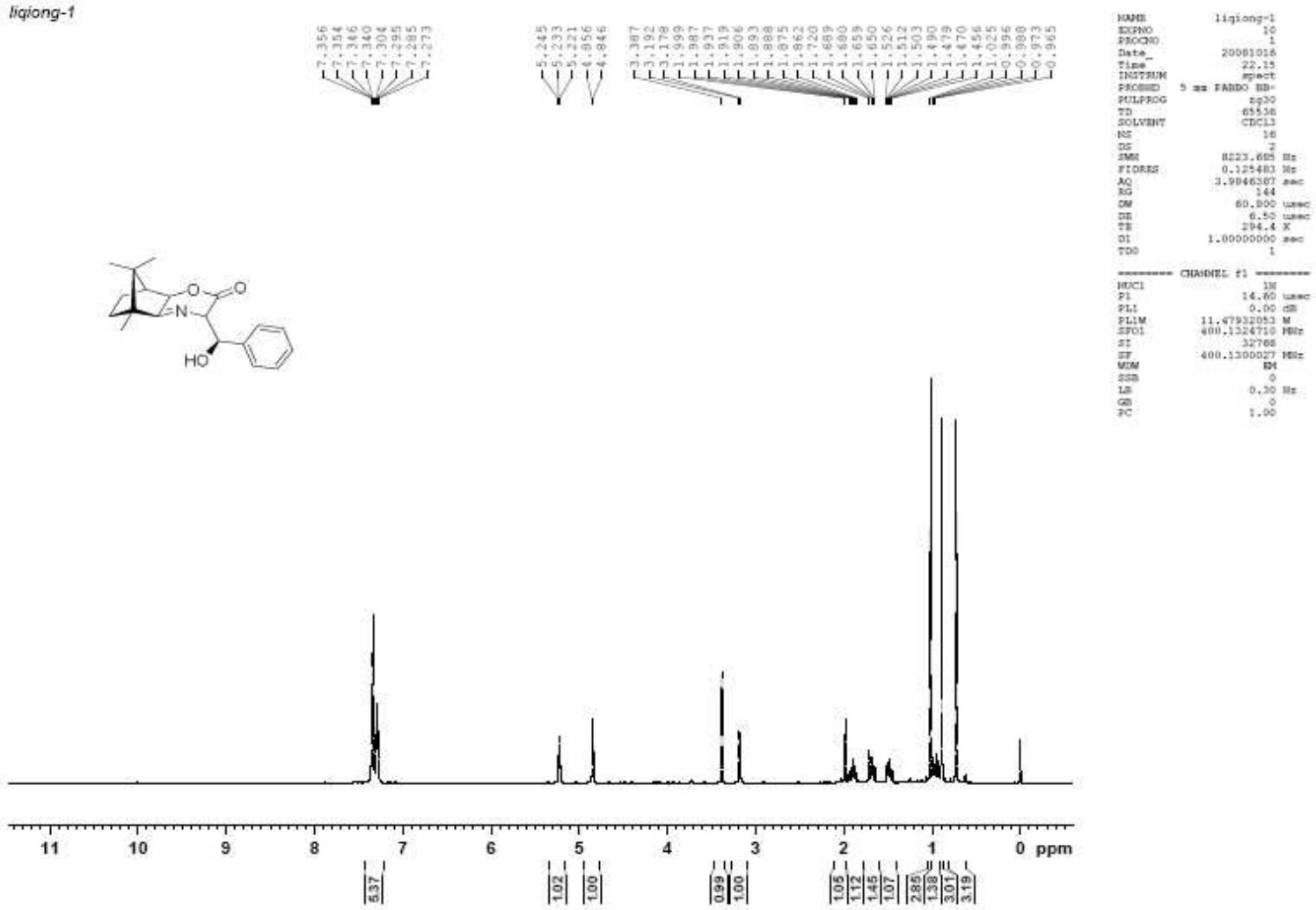
^{1}H NMR spectrum of compound **2d'** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2d'** (75 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2e** (400 MHz, $CDCl_3$)



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RG 144
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TE 294.4 K
D1 1.00000000 sec
TD0 1
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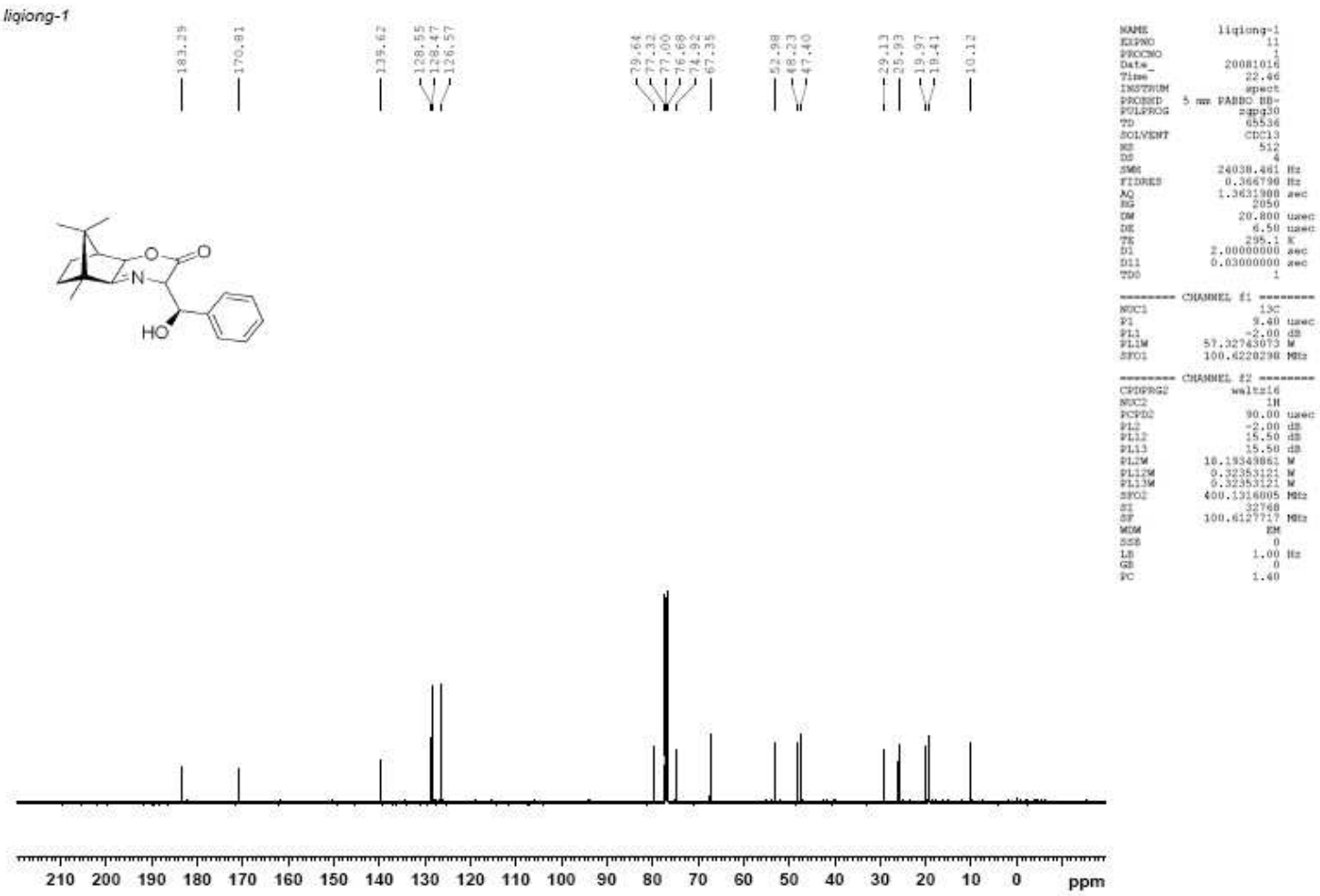
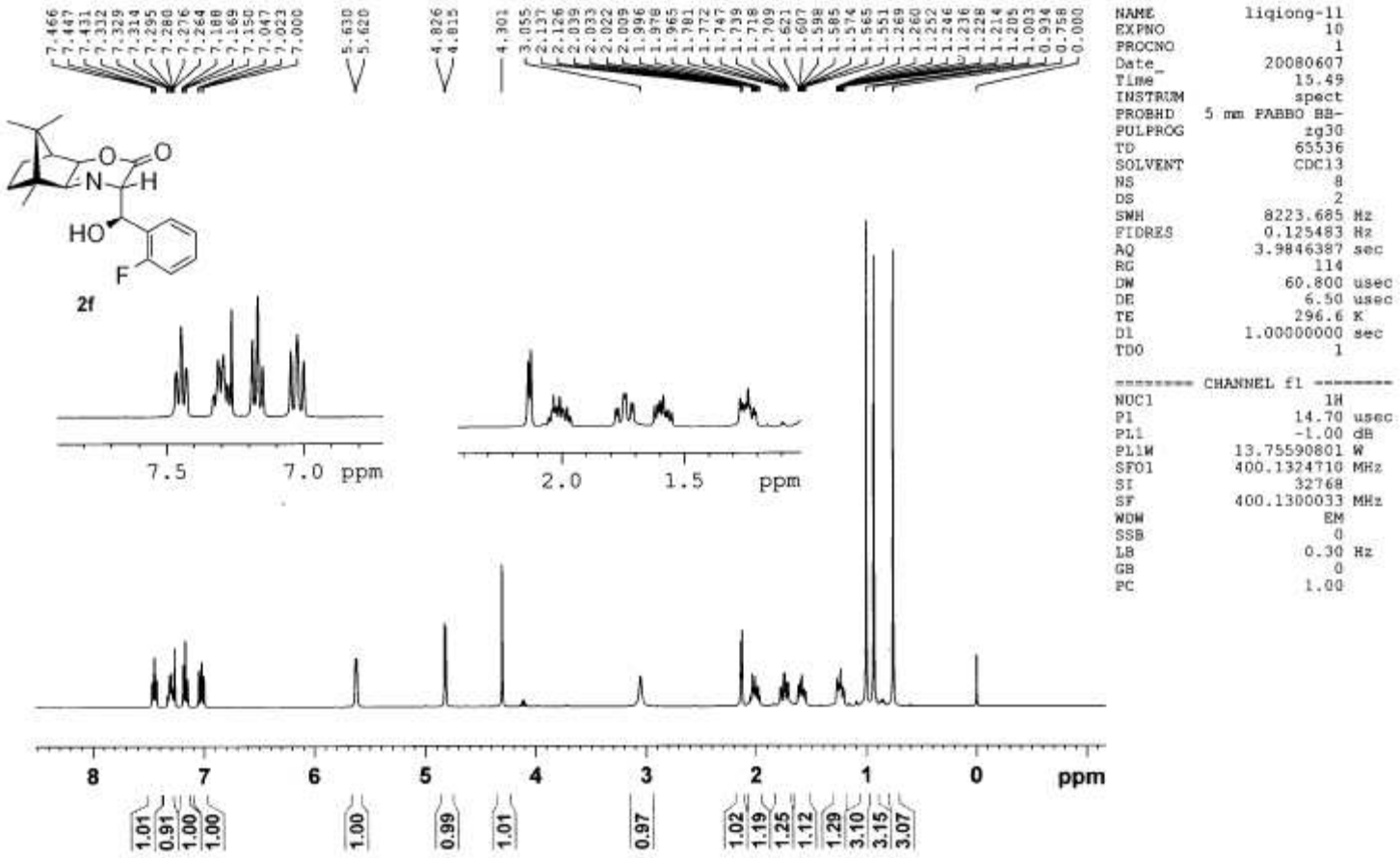
GB 0
PC 1.00

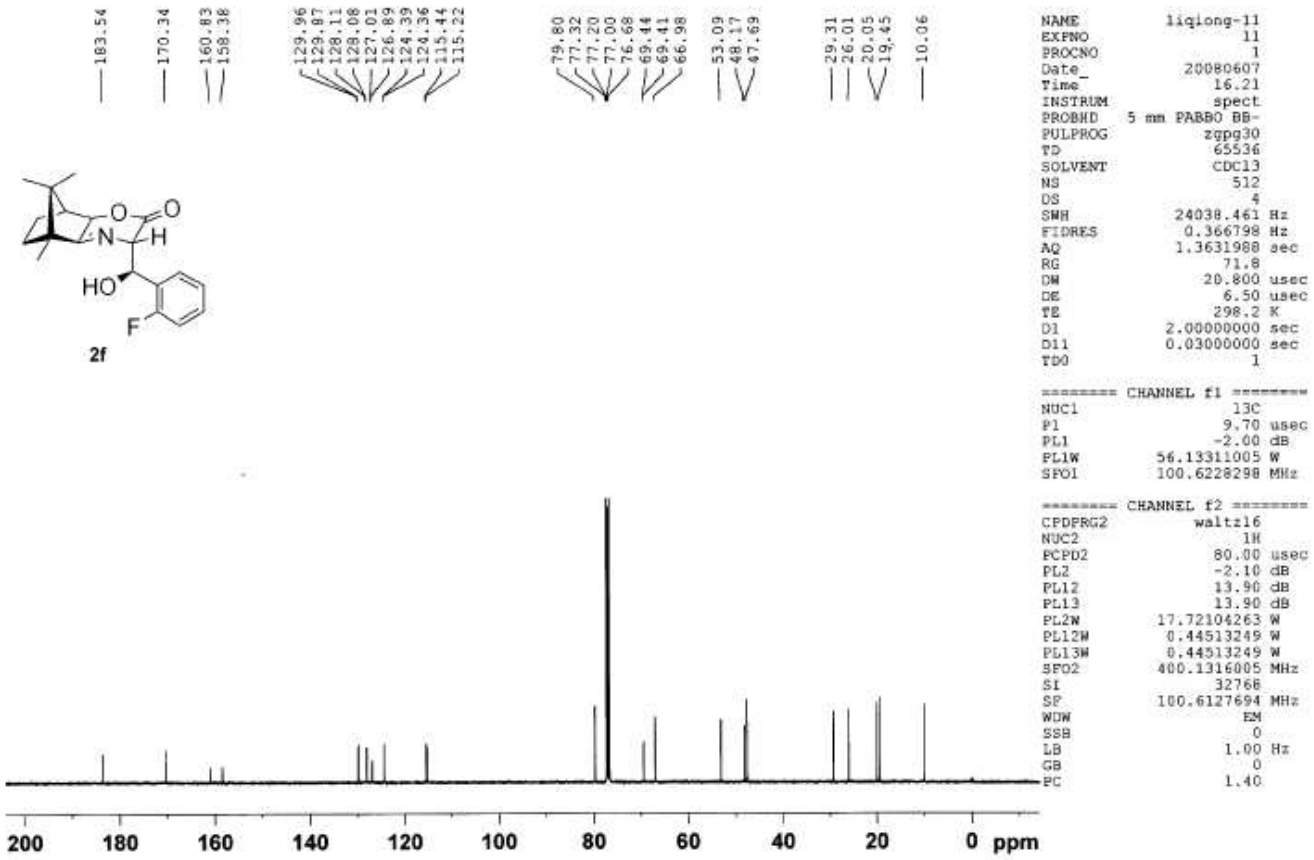
^{13}C NMR spectrum of compound **2e** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **2f** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2f** (100 MHz, $CDCl_3$)

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RG                     71.8
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DE                  6.50 usec
TE                  298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
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PL1                 -2.00 dB
PL1W          56.13311005 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
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NUC2                    1H
PCPD2               80.00 usec
PL2                 -2.10 dB
PL12                13.90 dB
PL13                13.90 dB
PL2W          17.72104263 W
PL12W          0.44513249 W
PL13W          0.44513249 W
SFO2         400.1316005 MHz
SI                   32768
SF           100.6127694 MHz
WDW                     EM
SSB                      0
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GB                       0
PC                    1.40
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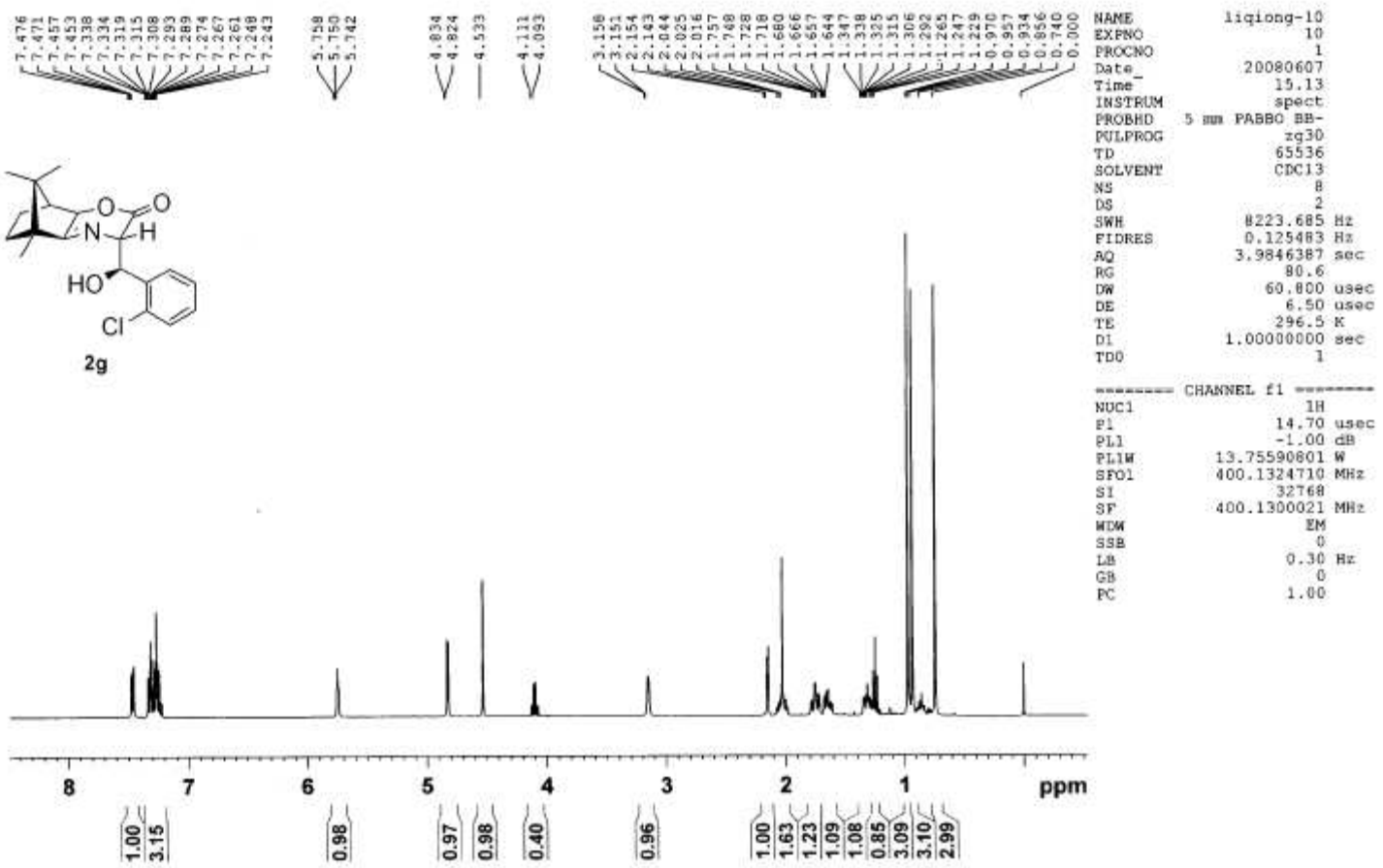
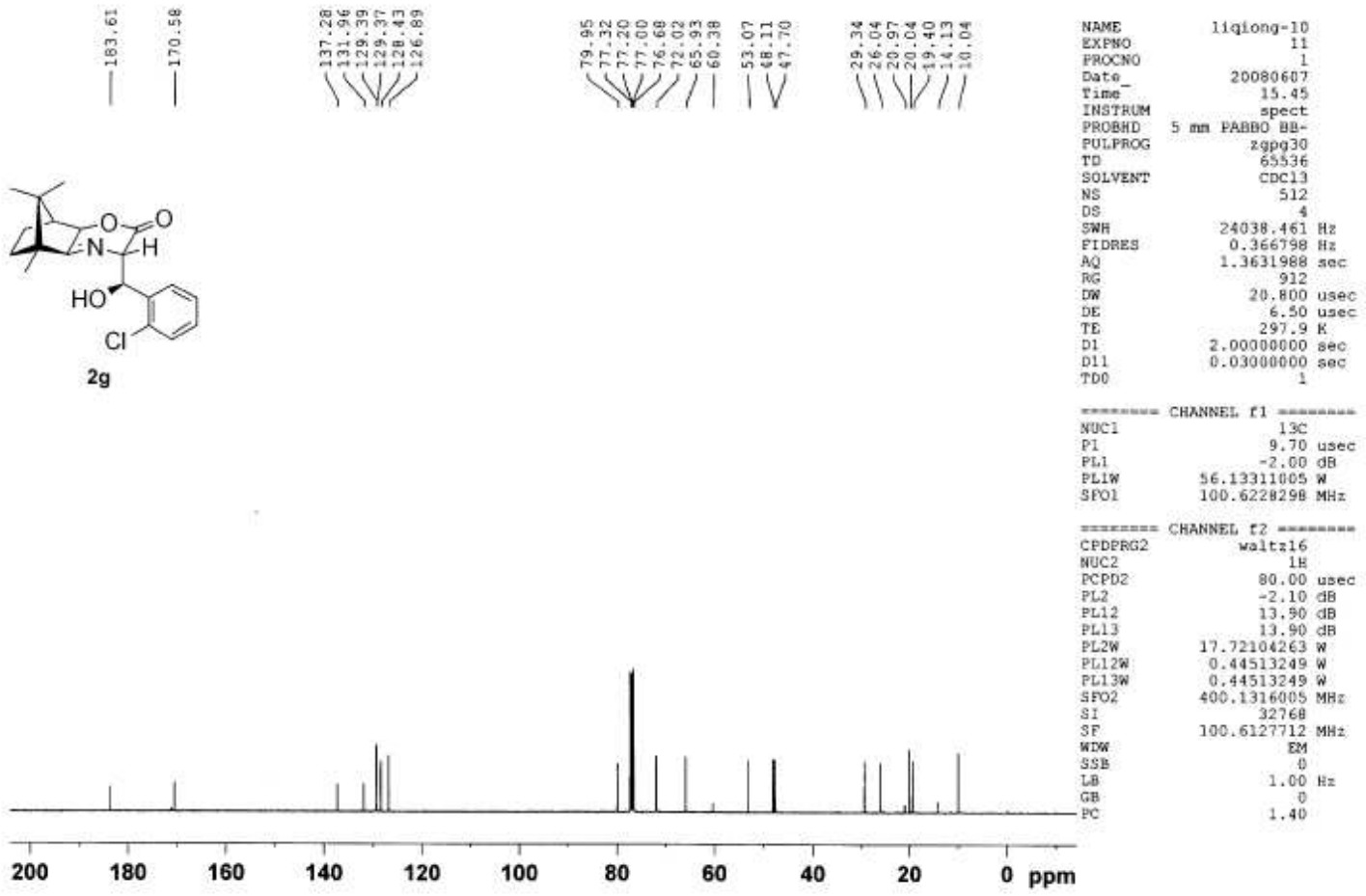
^{1}H NMR spectrum of compound **2g** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **2g** (100 MHz, $CDCl_3$)



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RG	912
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TE	297.9 K
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PL13	13.90 dB
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PL12W	0.44513249 W
PL13W	0.44513249 W
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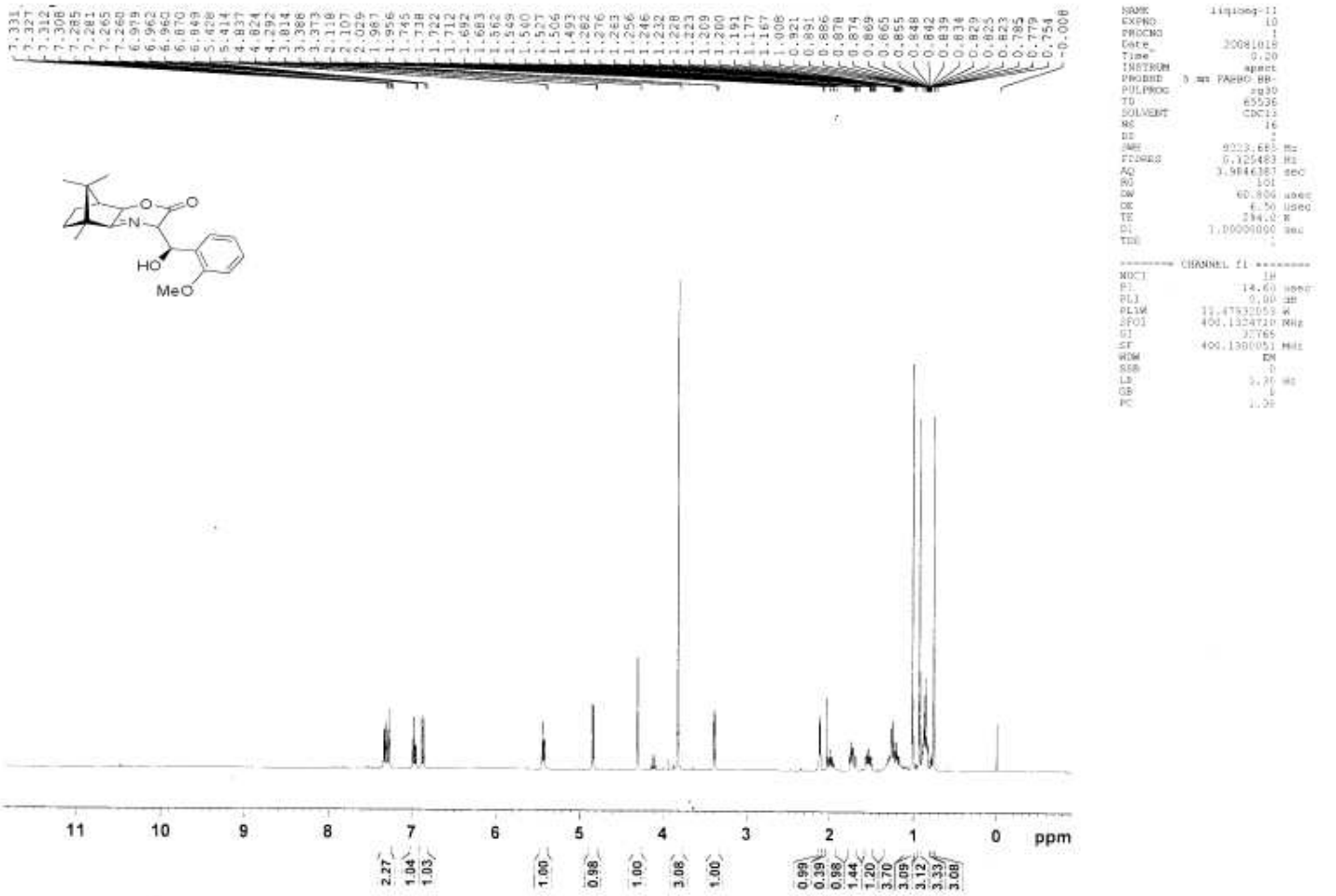
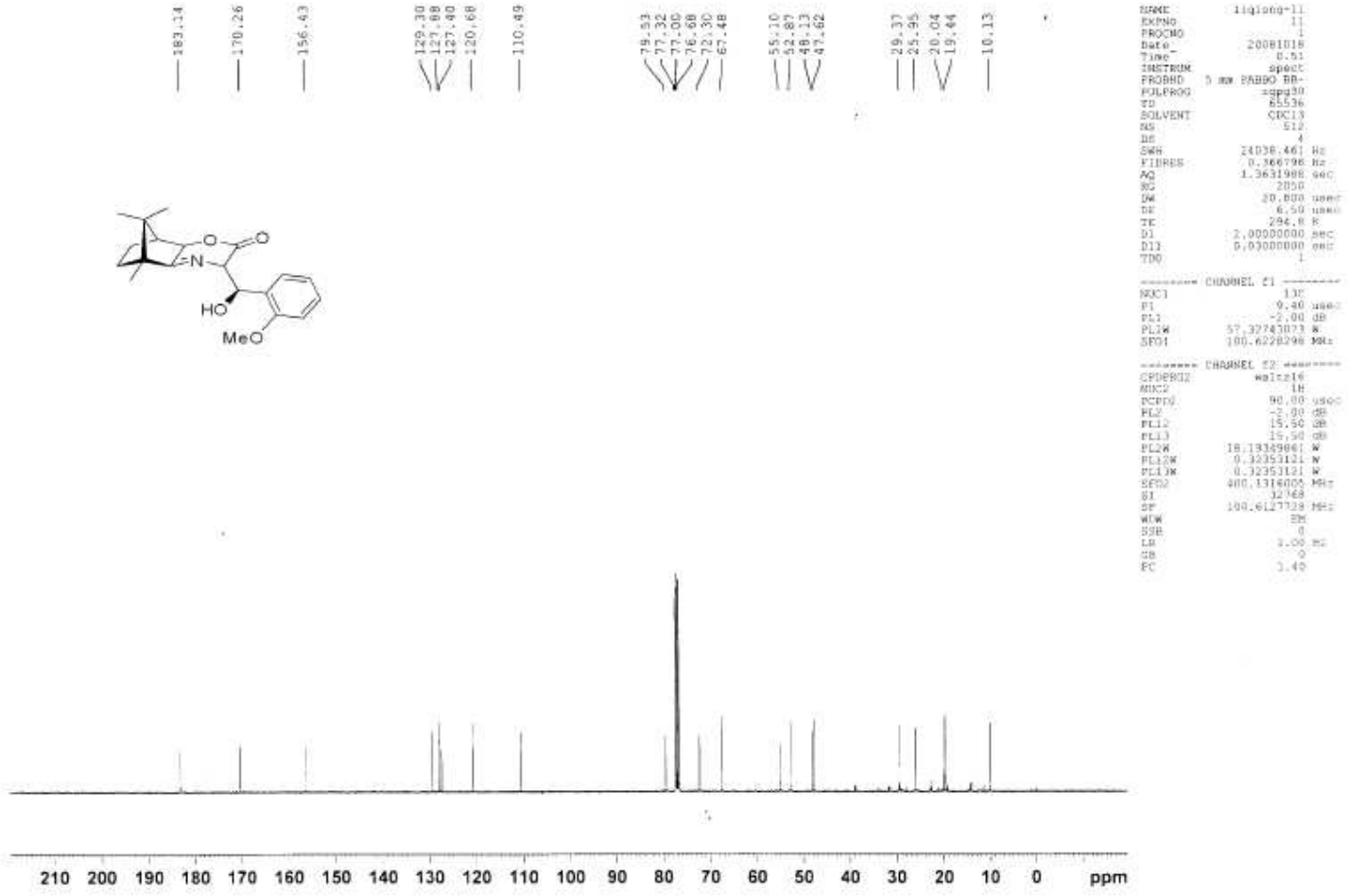
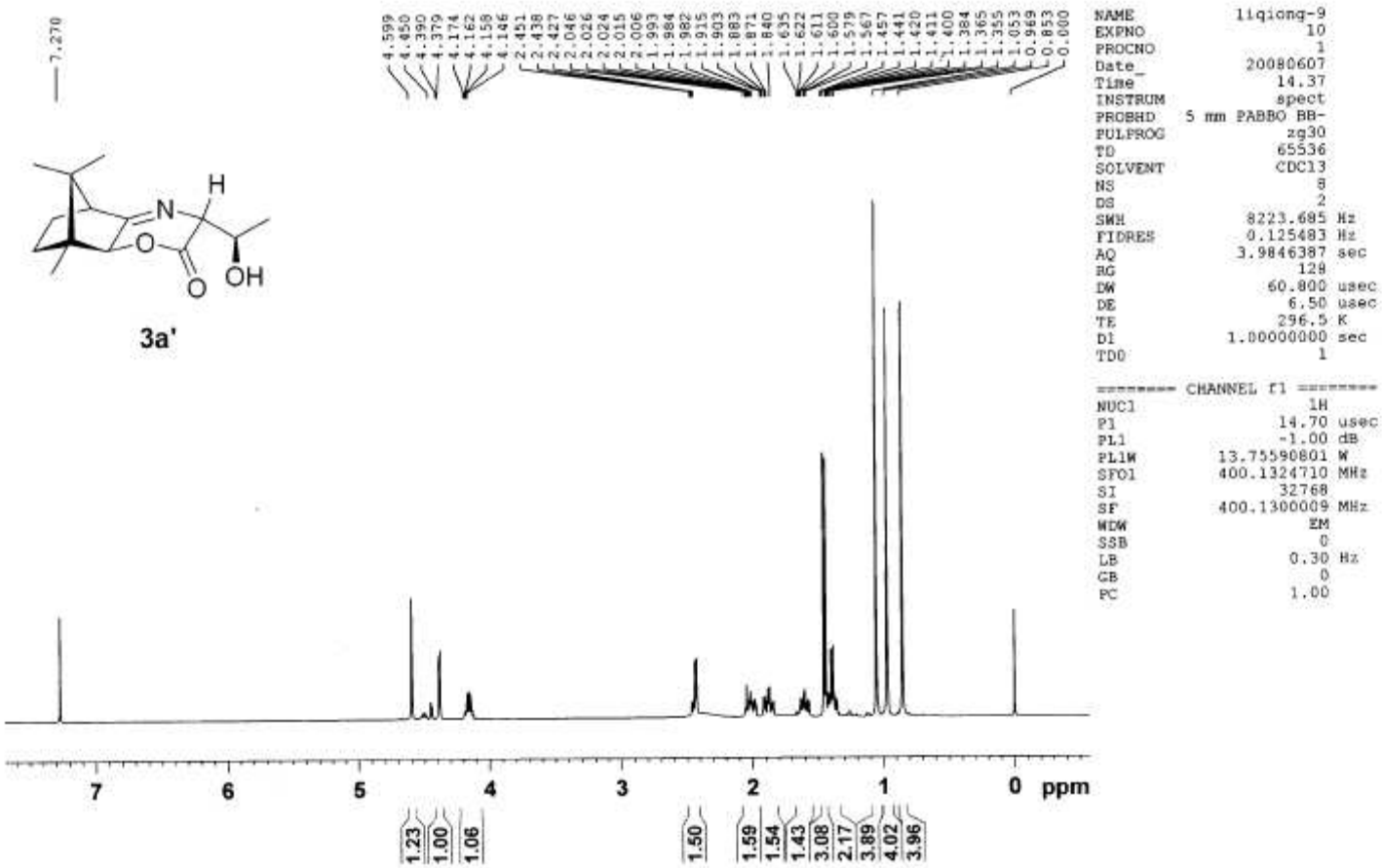
^{1}H NMR spectrum of compound **2h** (400 MHz, $CDCl_3$)



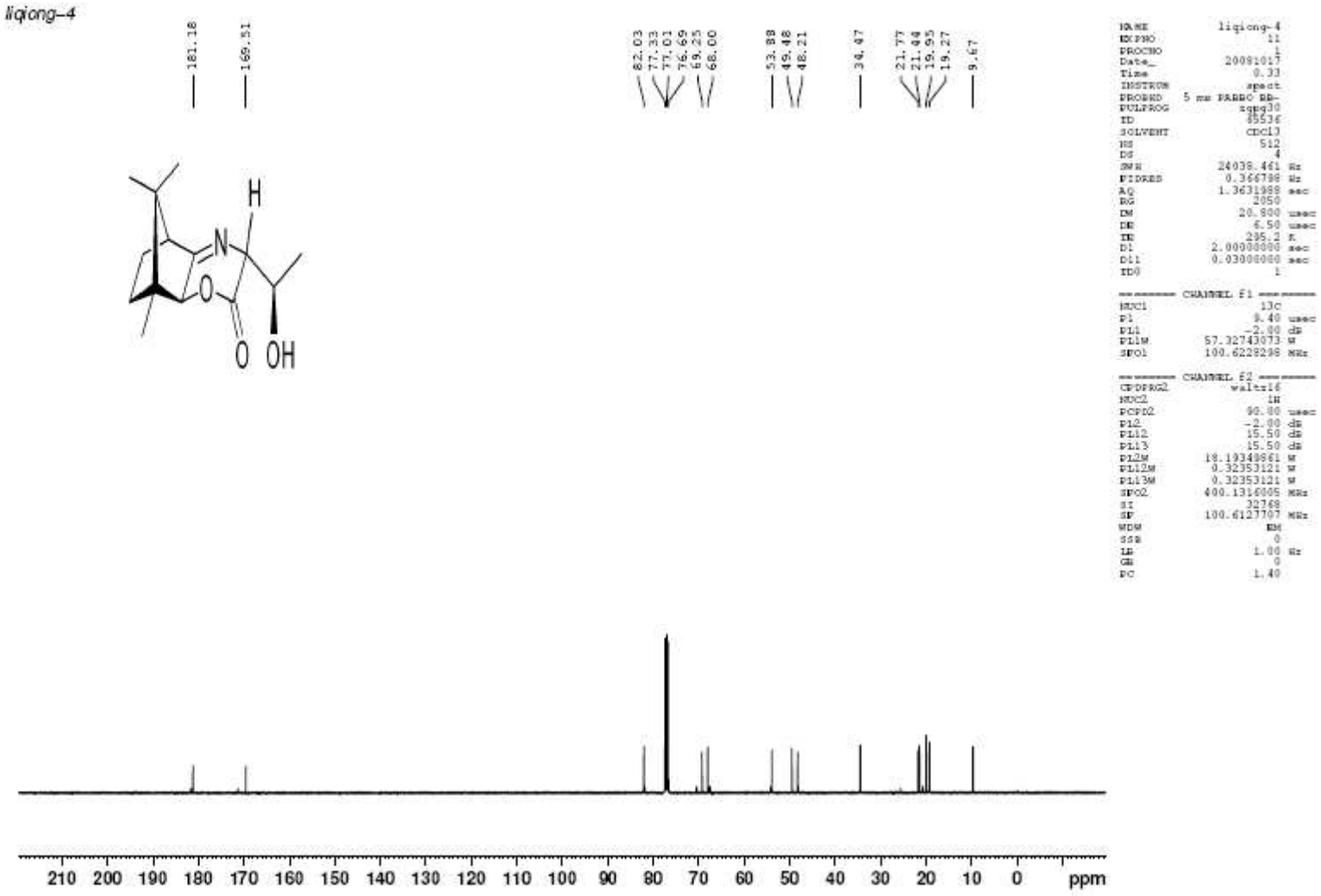
^{13}C NMR spectrum of compound **2h** (100 MHz, $CDCl_3$)



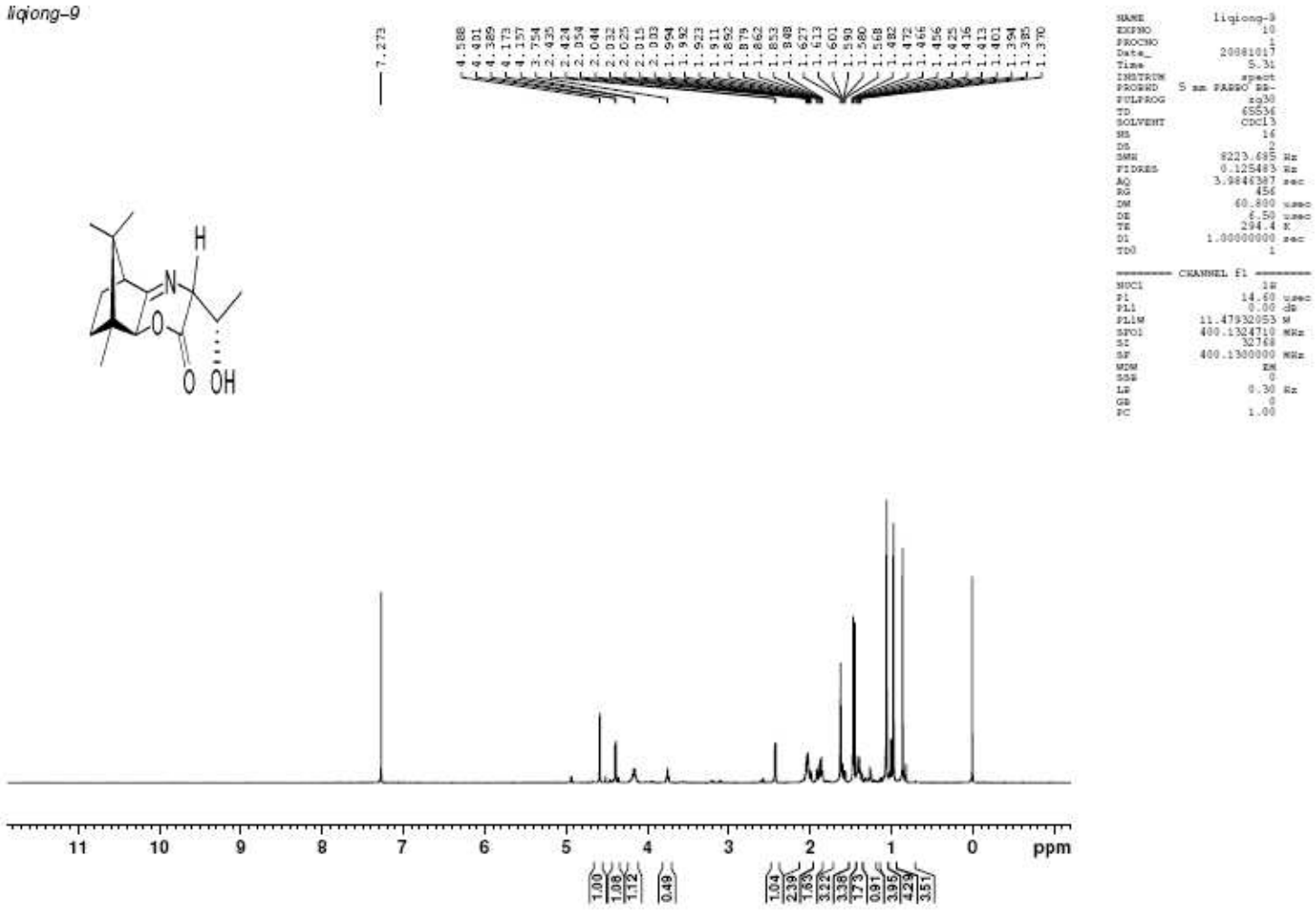
^{1}H NMR spectrum of compound **3a'** (400 MHz, $CDCl_3$)



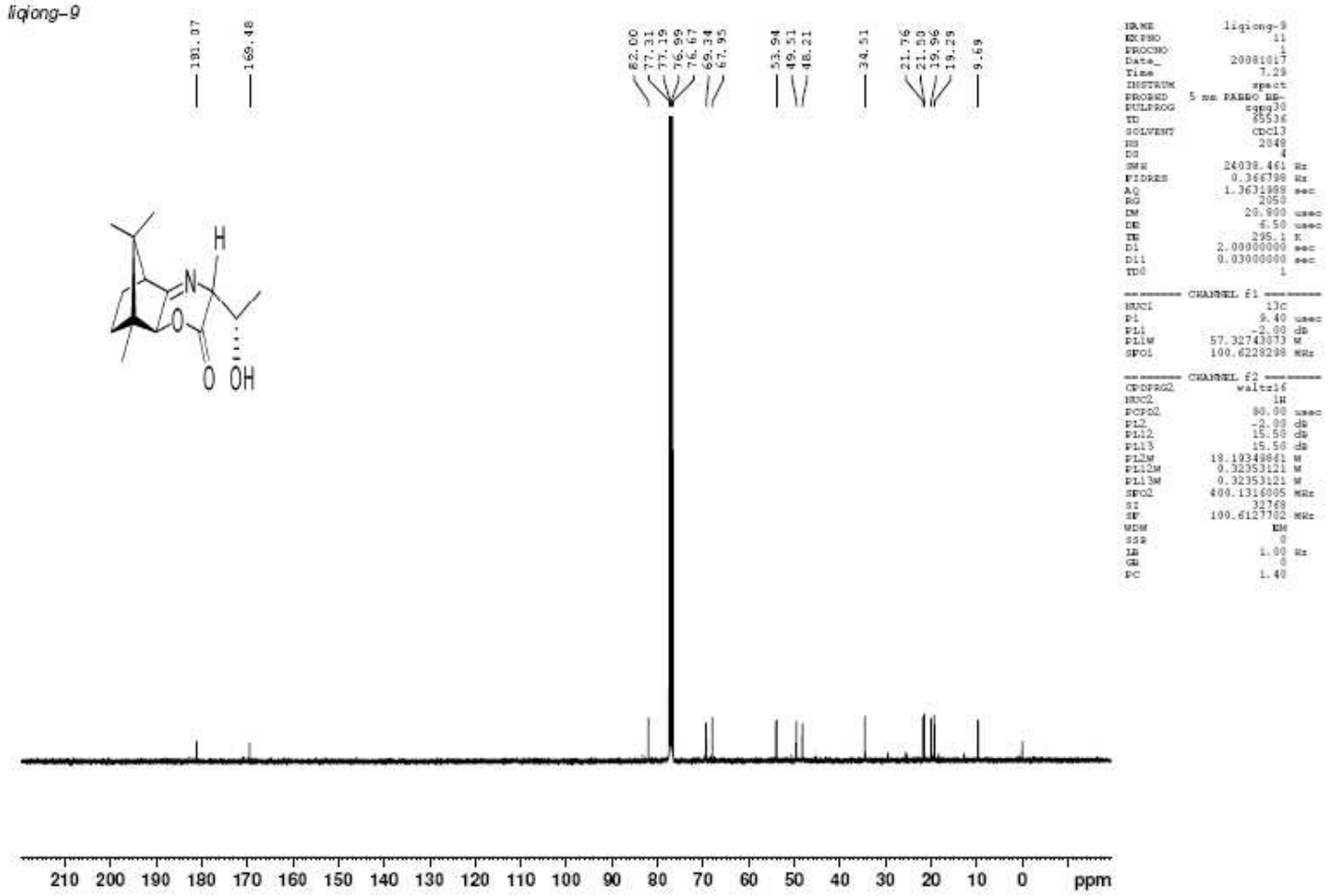
^{13}C NMR spectrum of compound **3a'** (100 MHz, $CDCl_3$)



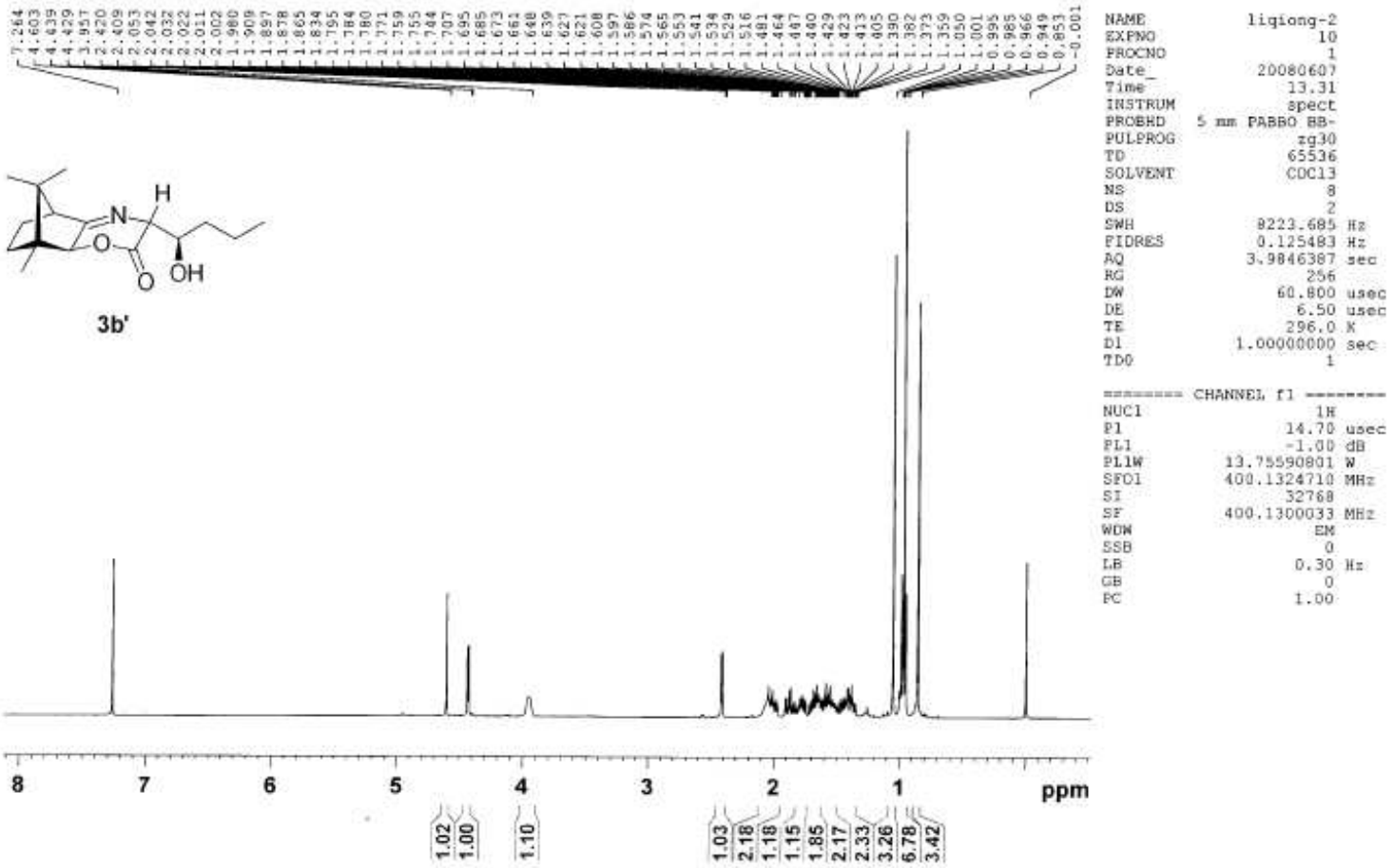
^{1}H NMR spectrum of compound **3a** (minor) (400 MHz, $CDCl_3$)



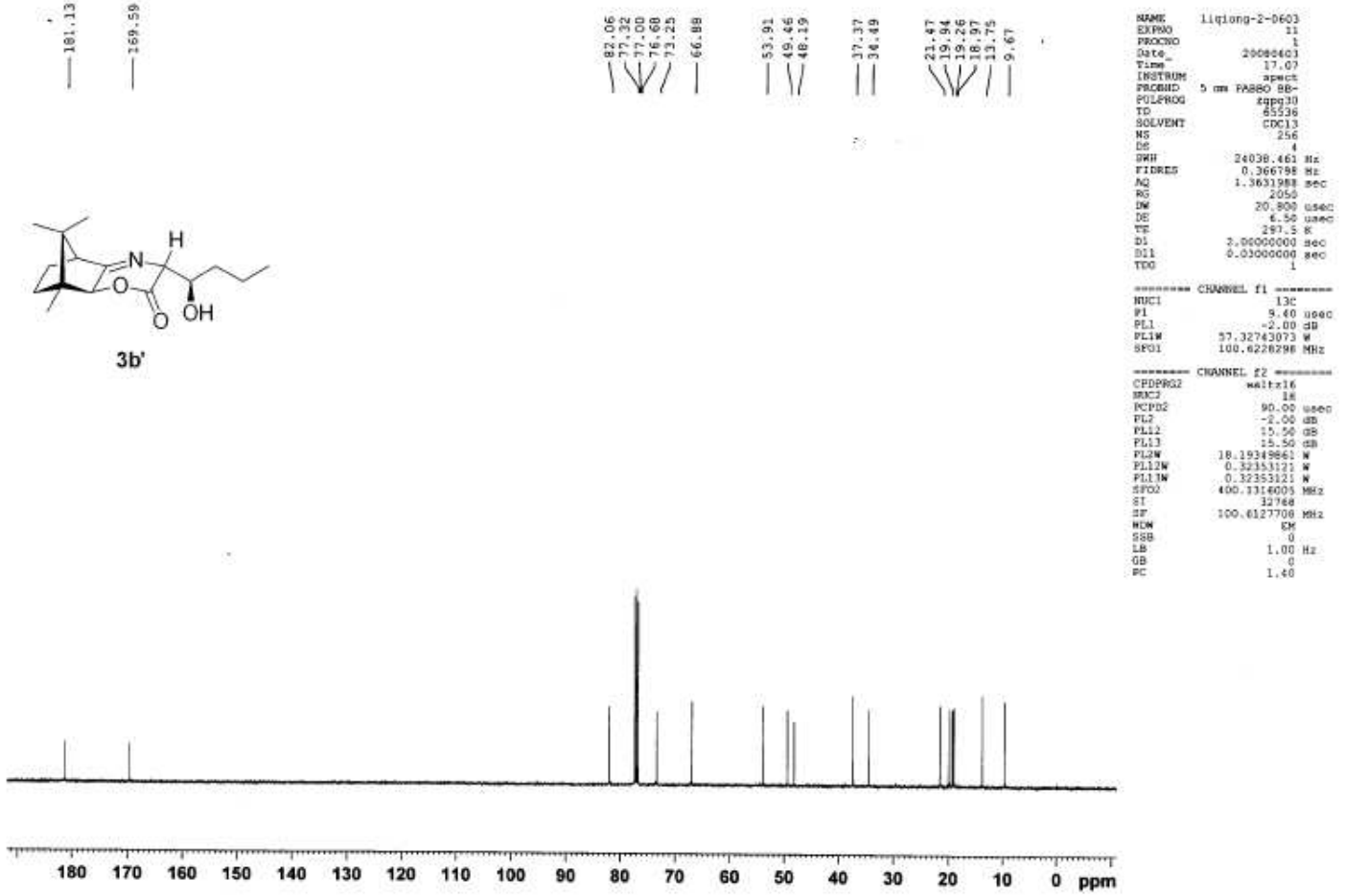
^{13}C NMR spectrum of compound **3a (minor)** (100 MHz, $CDCl_3$)



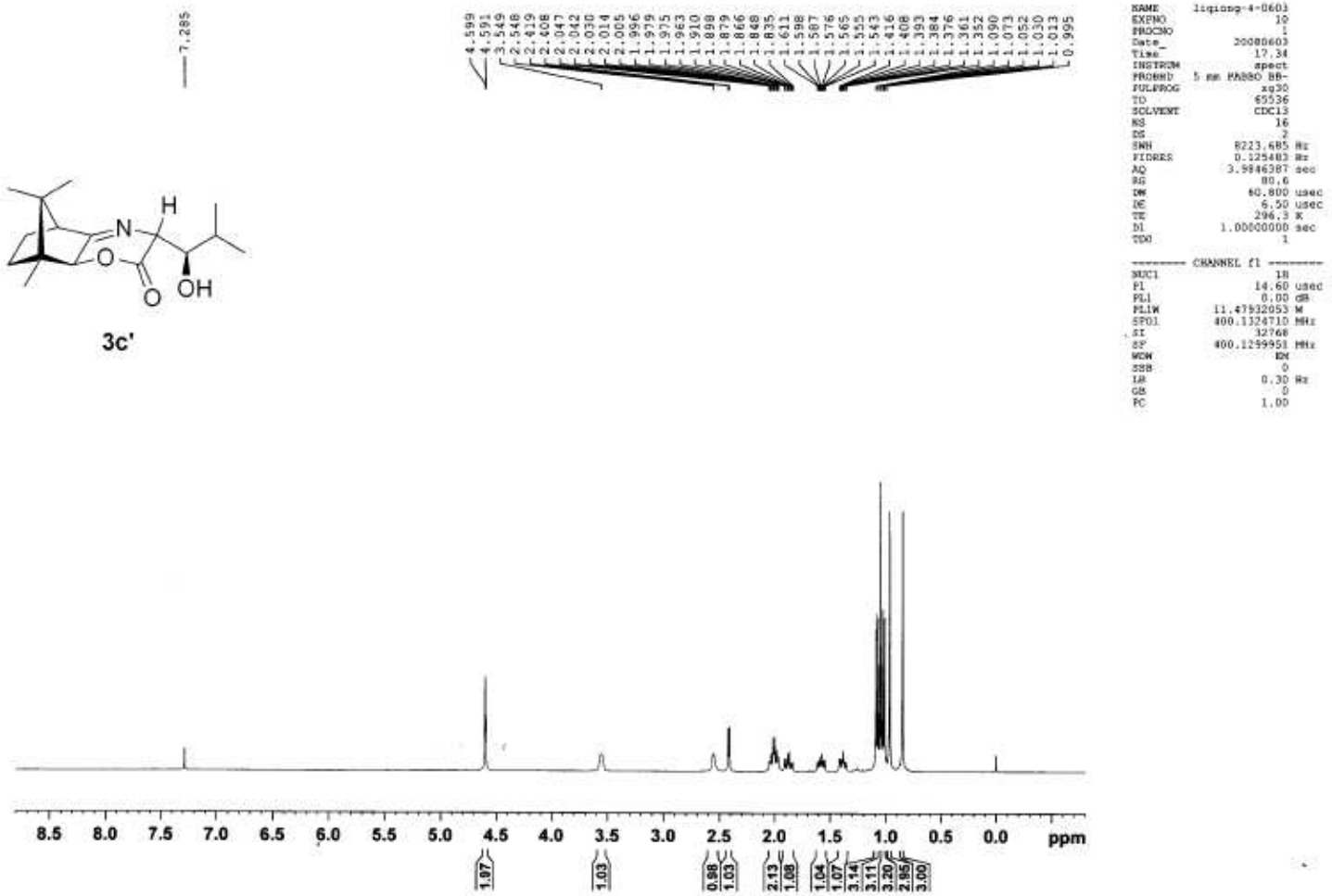
^{1}H NMR spectrum of compound **3b'** (400 MHz, $CDCl_3$)



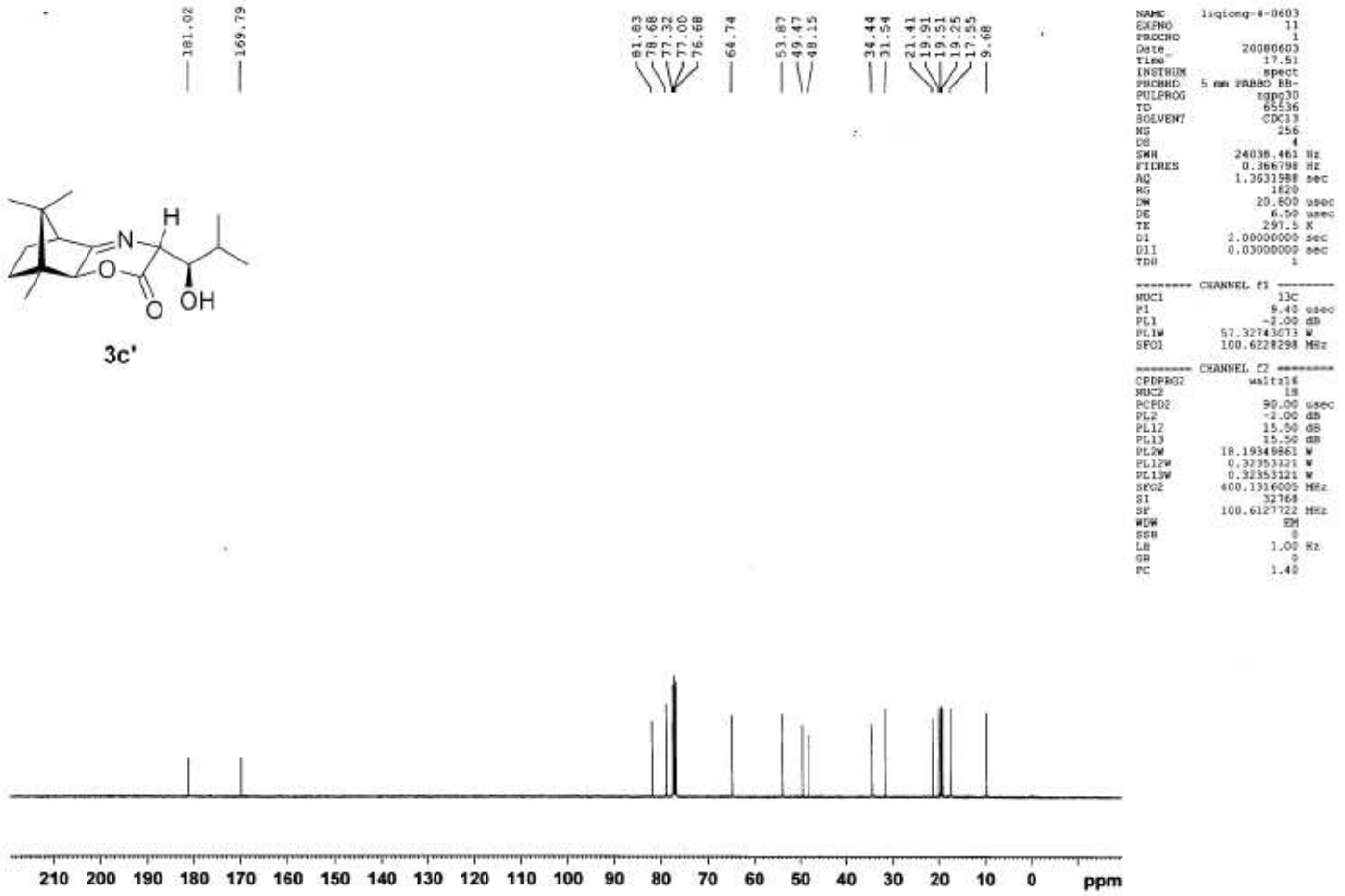
^{13}C NMR spectrum of compound **3b'** (100 MHz, $CDCl_3$)



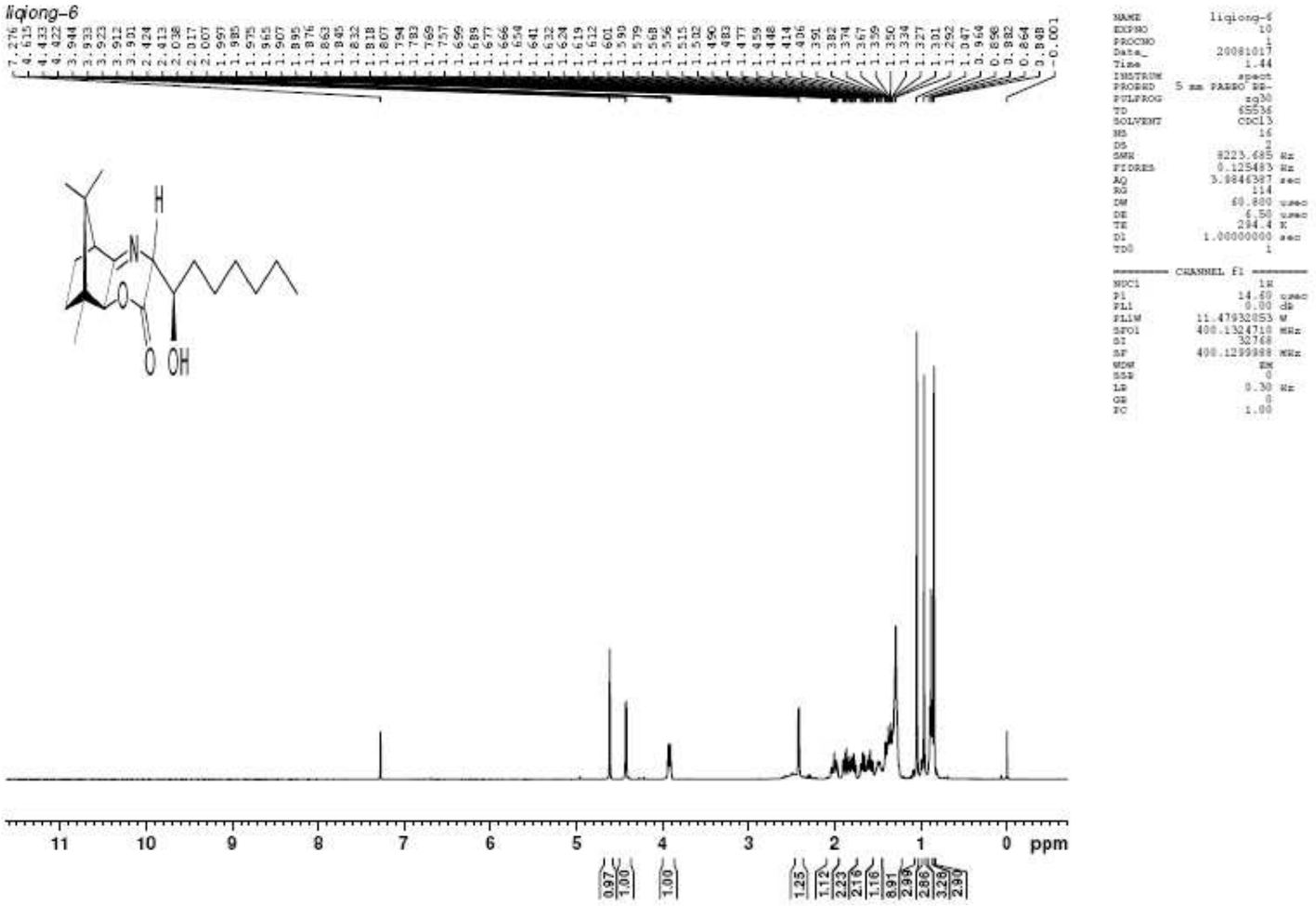
^{1}H NMR spectrum of compound **3c'** (400 MHz, $CDCl_3$)



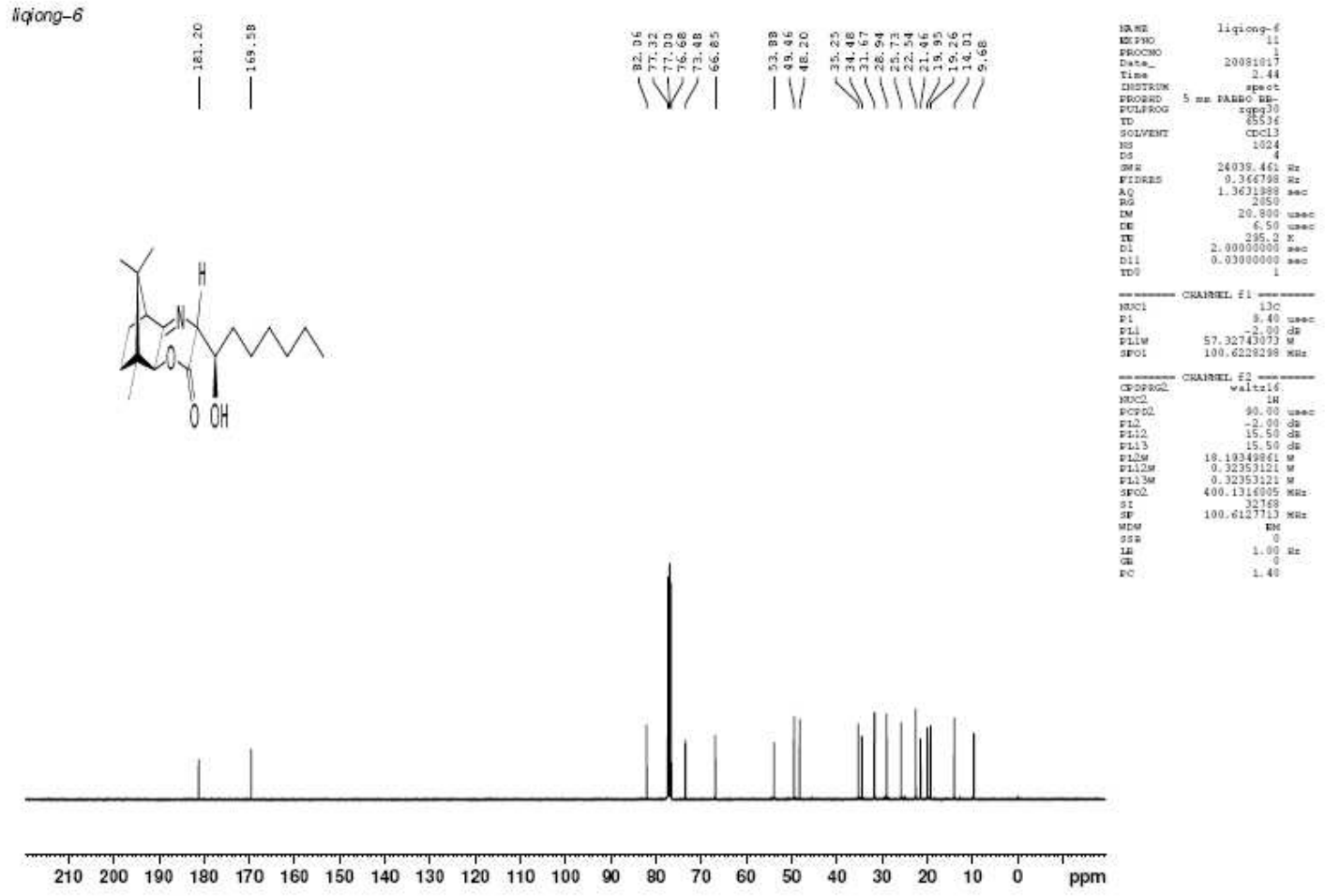
^{13}C NMR spectrum of compound **3c'** (100 MHz, $CDCl_3$)



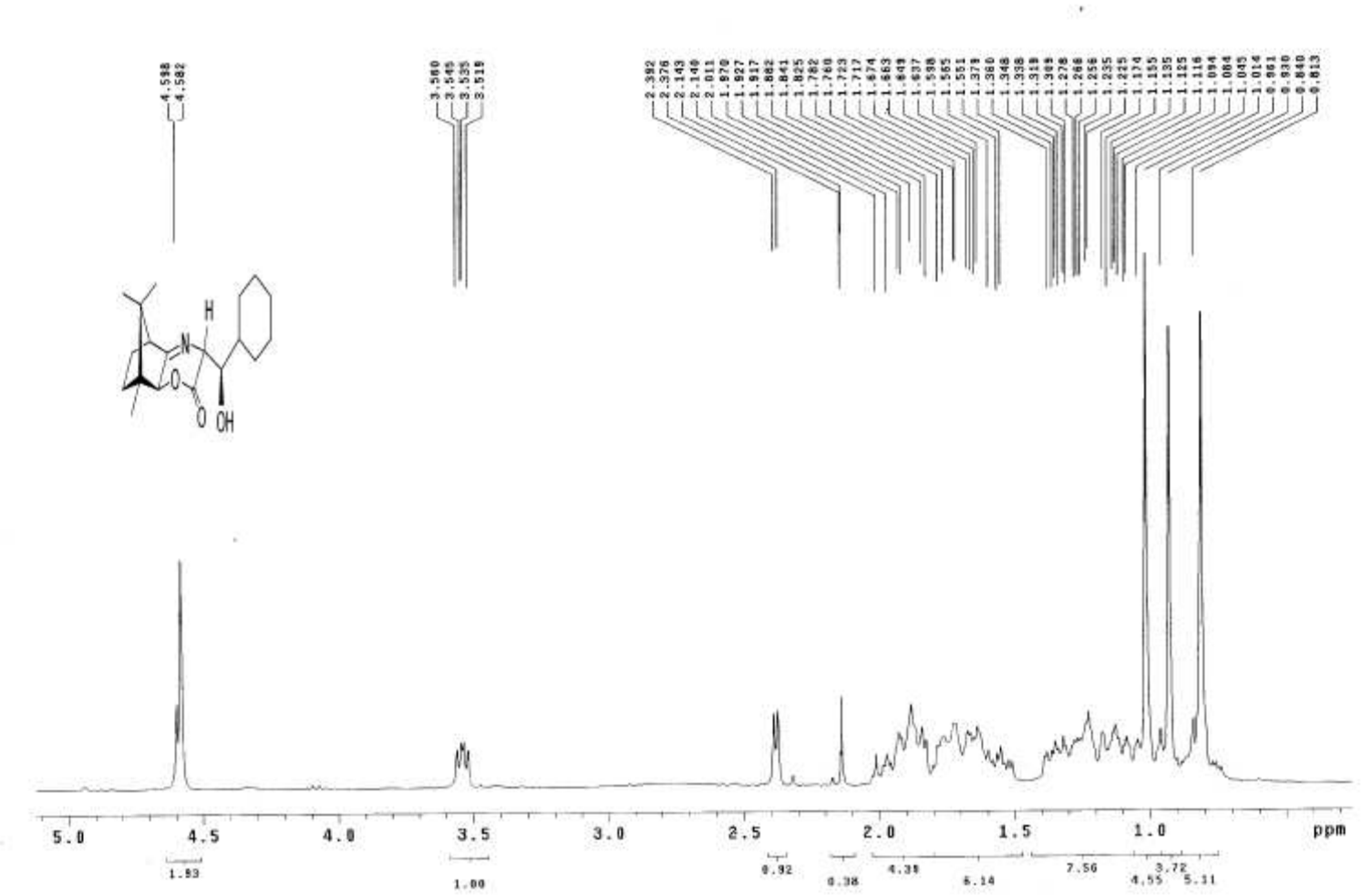
^{1}H NMR spectrum of compound **3d'** (400 MHz, $CDCl_3$)



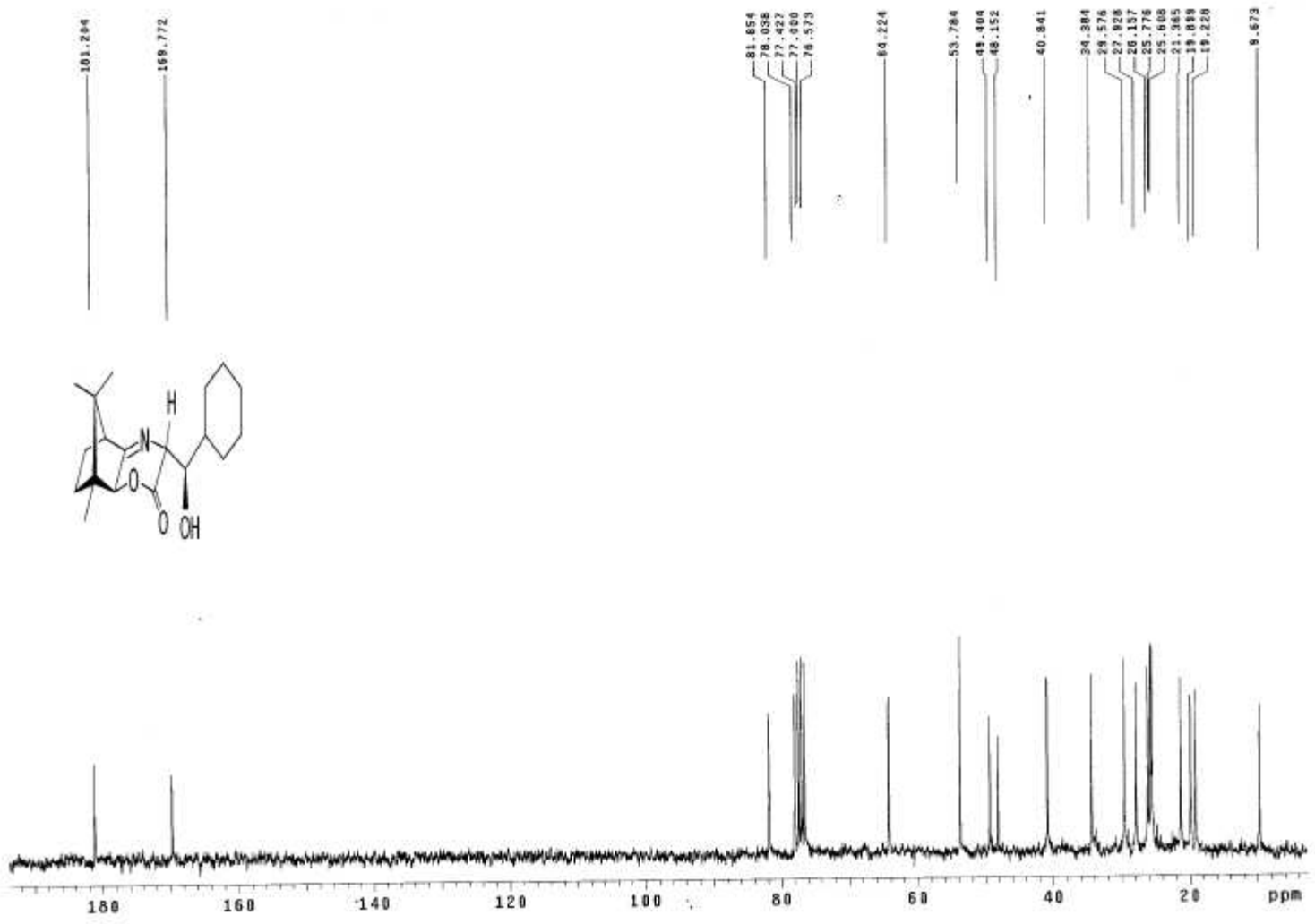
^{13}C NMR spectrum of compound **3d'** (100 MHz, $CDCl_3$)



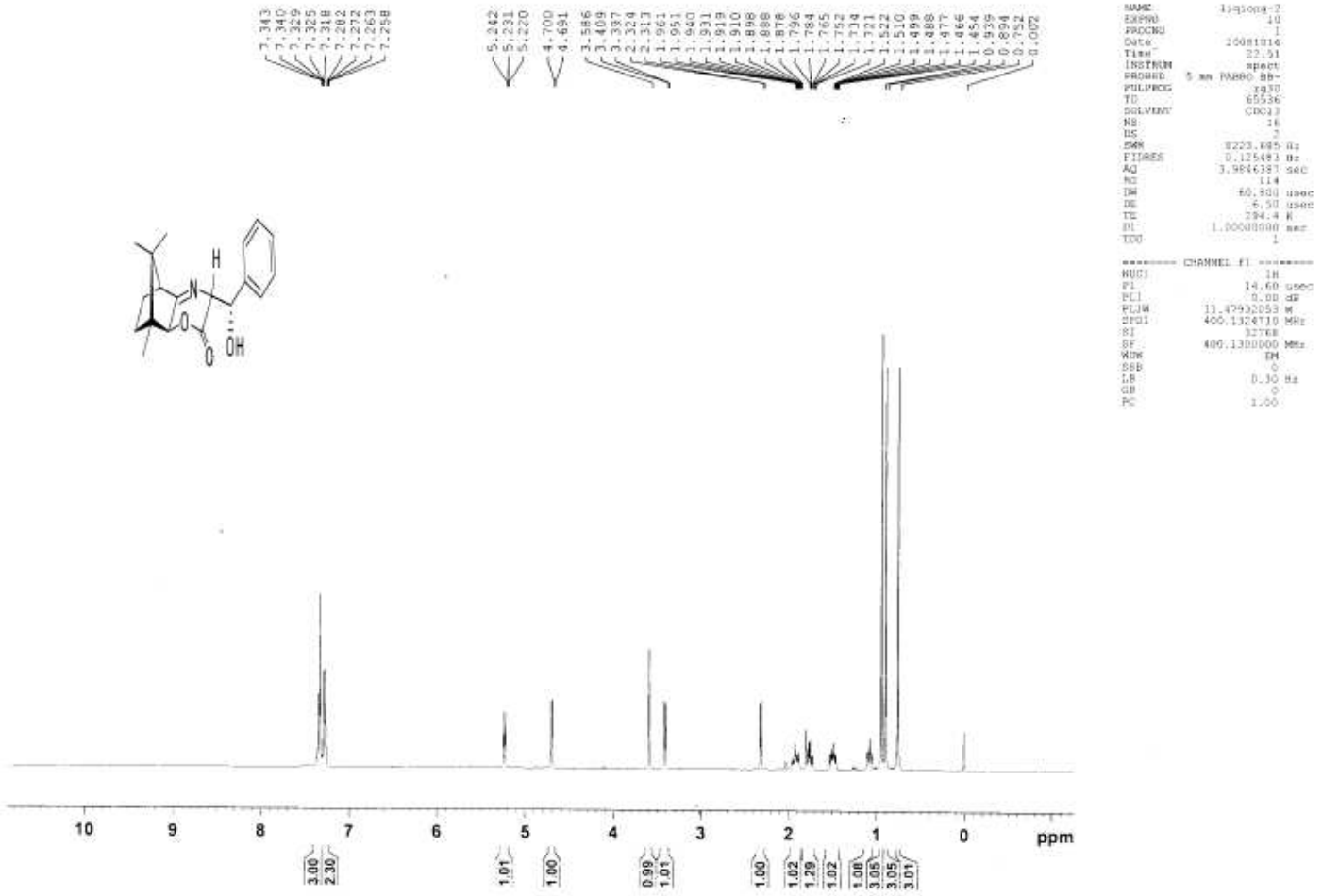
^{1}H NMR spectrum of compound **3e'** (300 MHz, $CDCl_3$)



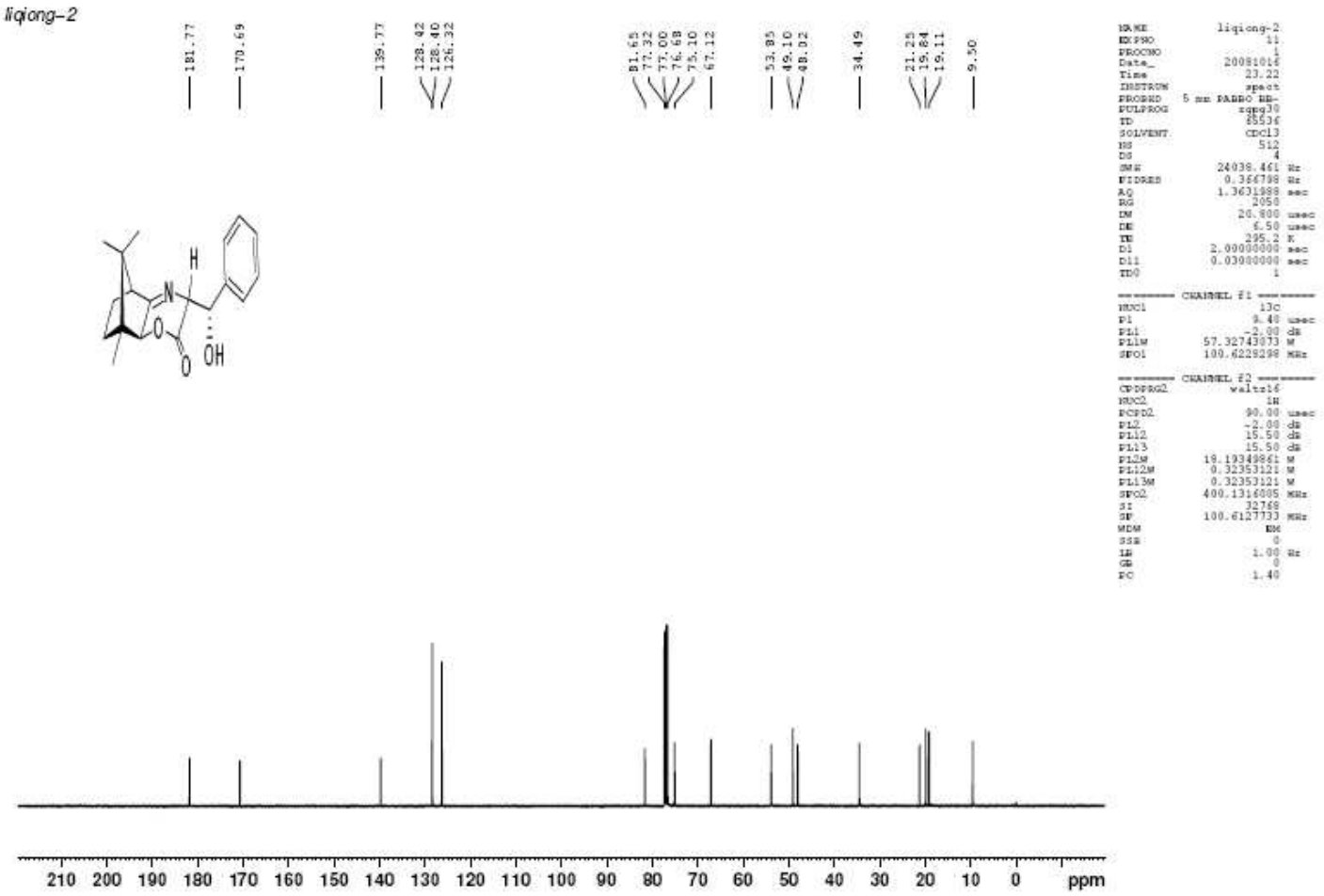
^{13}C NMR spectrum of compound **3e'** (75 MHz, $CDCl_3$)



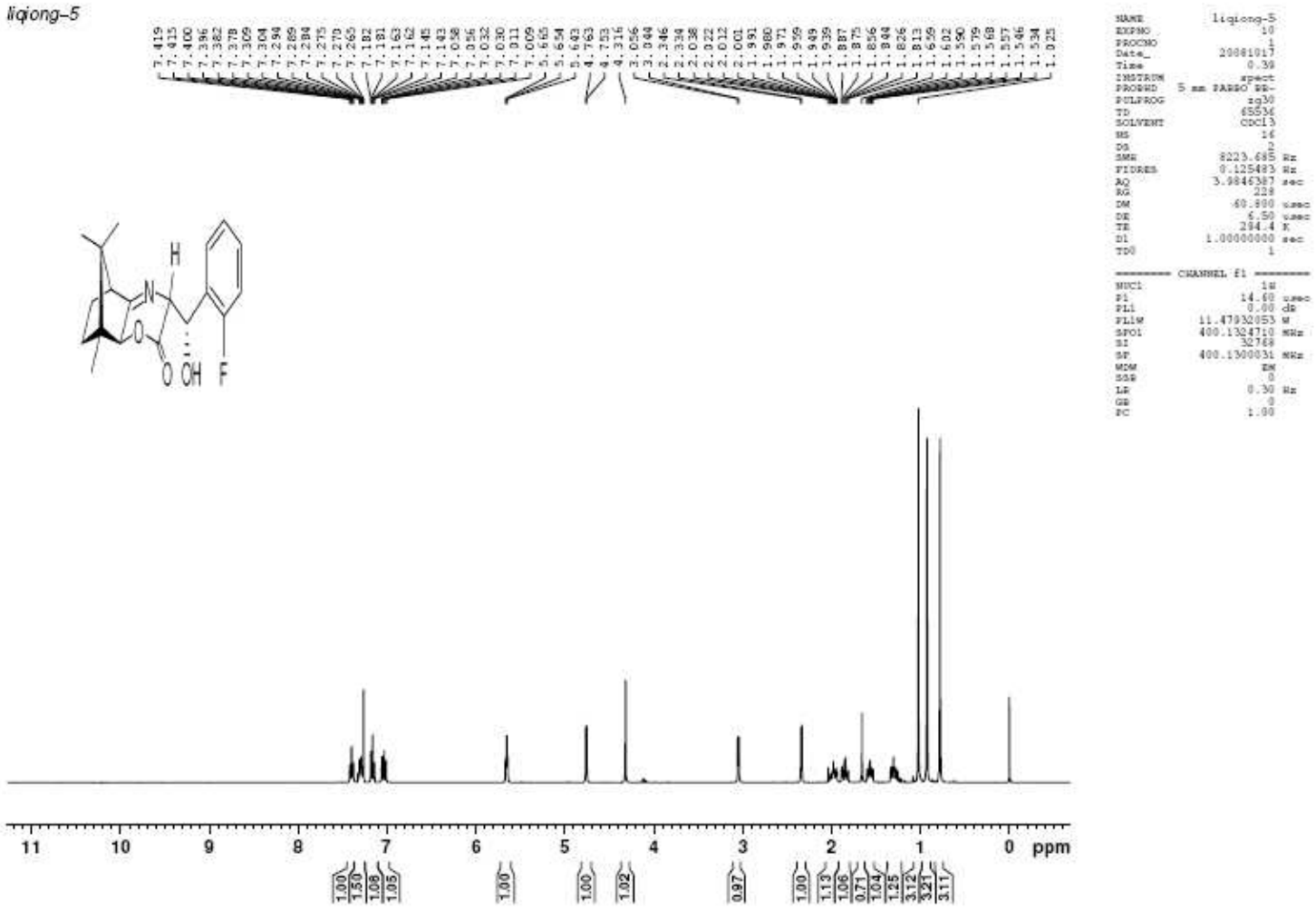
^{1}H NMR spectrum of compound **3f** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **3f** (100 MHz, $CDCl_3$)



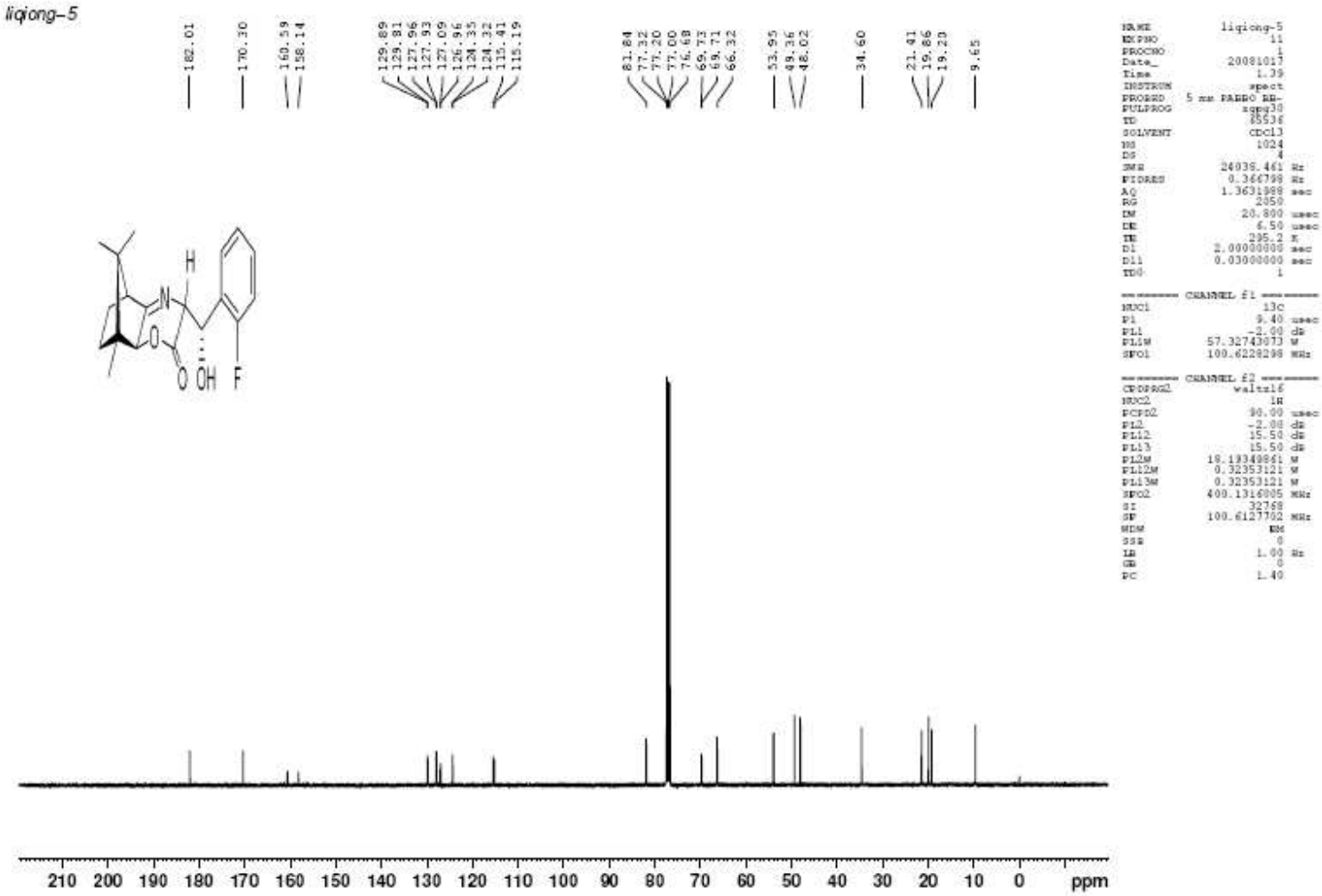
^{1}H NMR spectrum of compound **3g** (400 MHz, $CDCl_3$)



NAME liqiong-5
EXPNO 10
PROCNO 1
Date_ 20081017
Time 0.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 228
DW 60.800 usec
DE 6.50 usec
TE 294.4 K
D1 1.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 14.60 usec
PL1 0.00 dB
PLW1 11.47932053 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300031 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{13}C NMR spectrum of compound **3g** (100 MHz, $CDCl_3$)

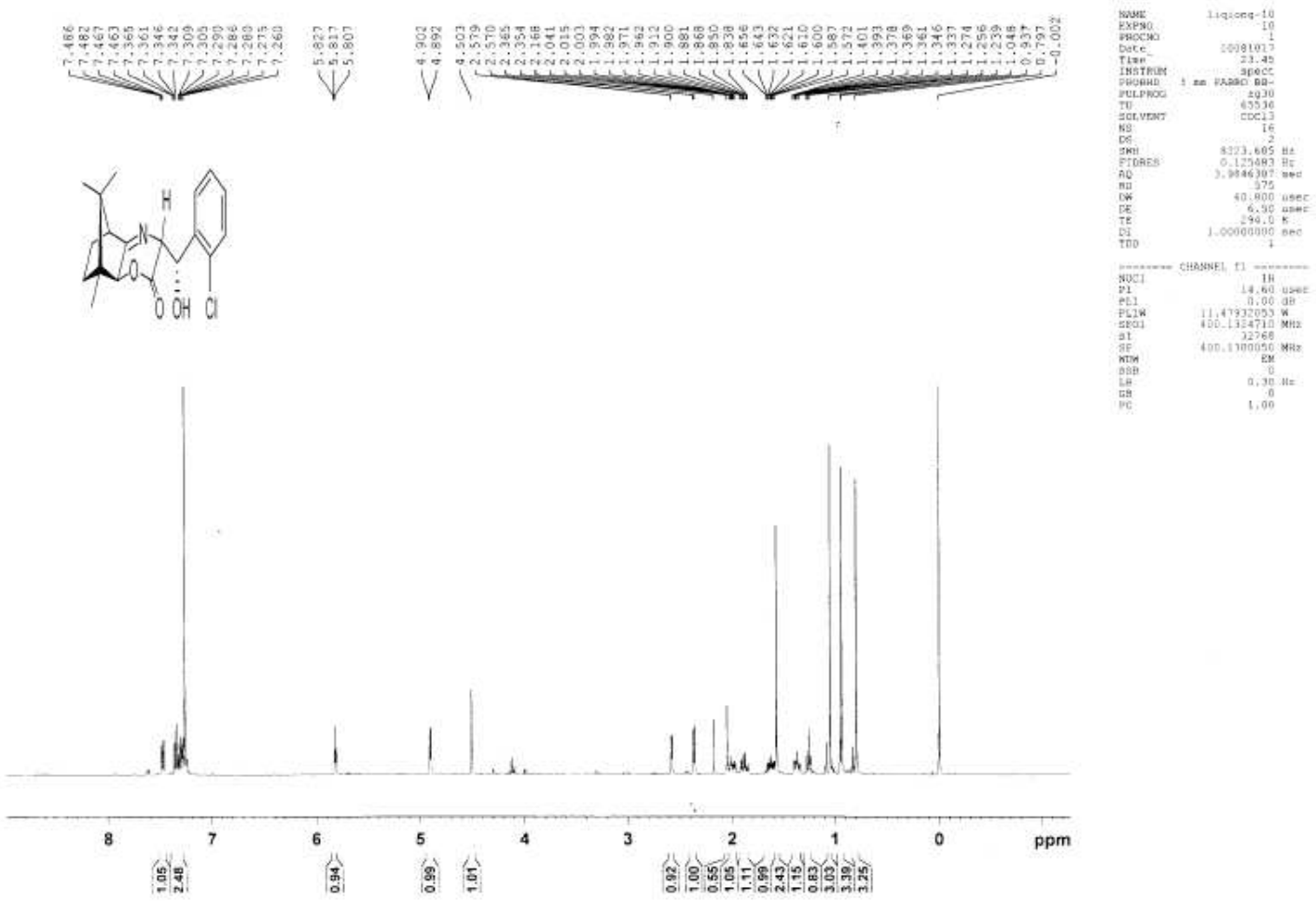


NAME liqiong-5
EXPNO 11
PROCNO 1
Date_ 20081017
Time 1.39
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 2050
DW 20.800 usec
DE 6.50 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

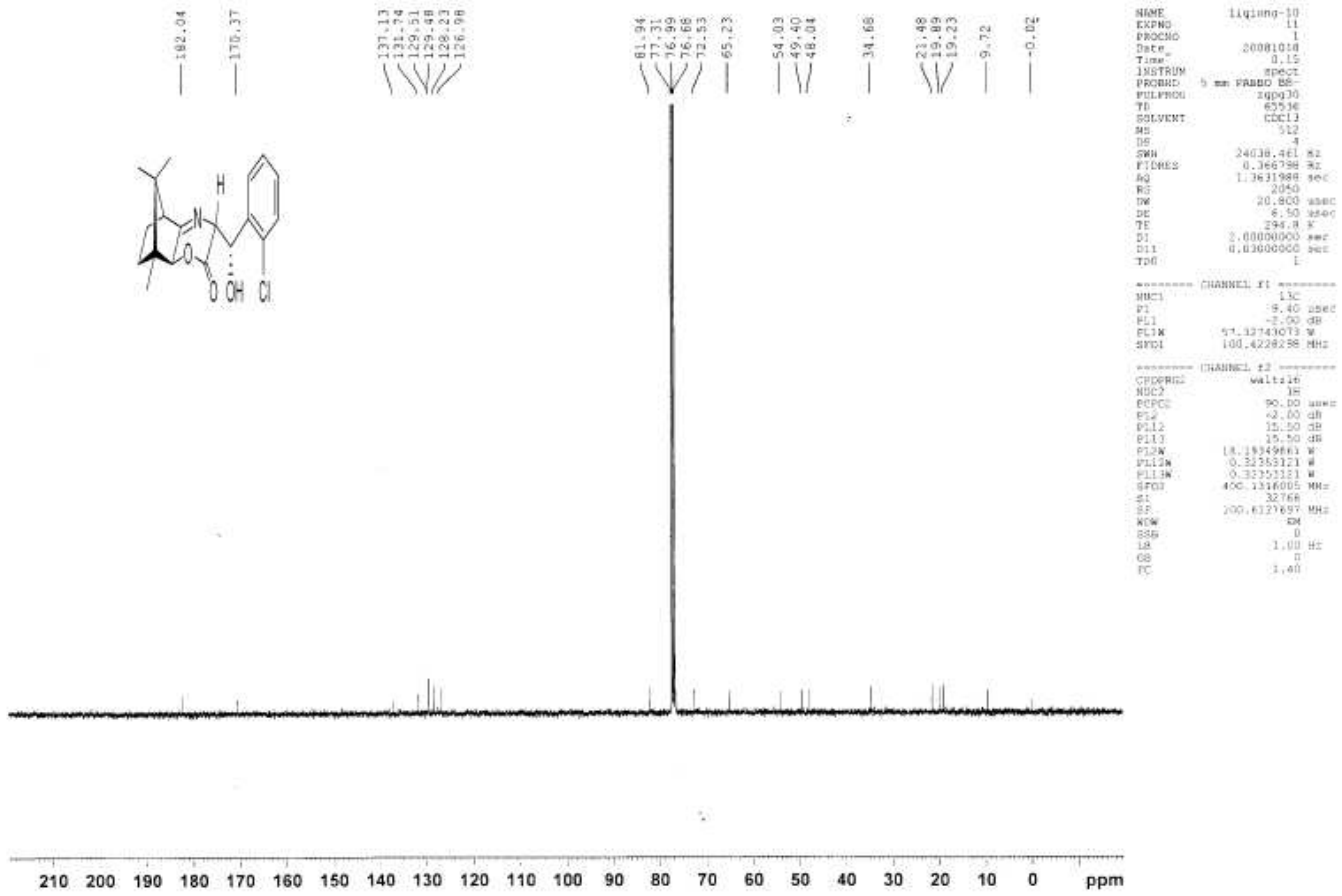
======== CHANNEL f1 ========
NUC1 13C
P1 9.40 usec
PL1 -2.00 dB
PL1W 57.32743073 W
SFO1 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 15.50 dB
PL13 15.50 dB
PL2W 18.19348841 W
PL12W 0.32353121 W
PL13W 0.32353121 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127702 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

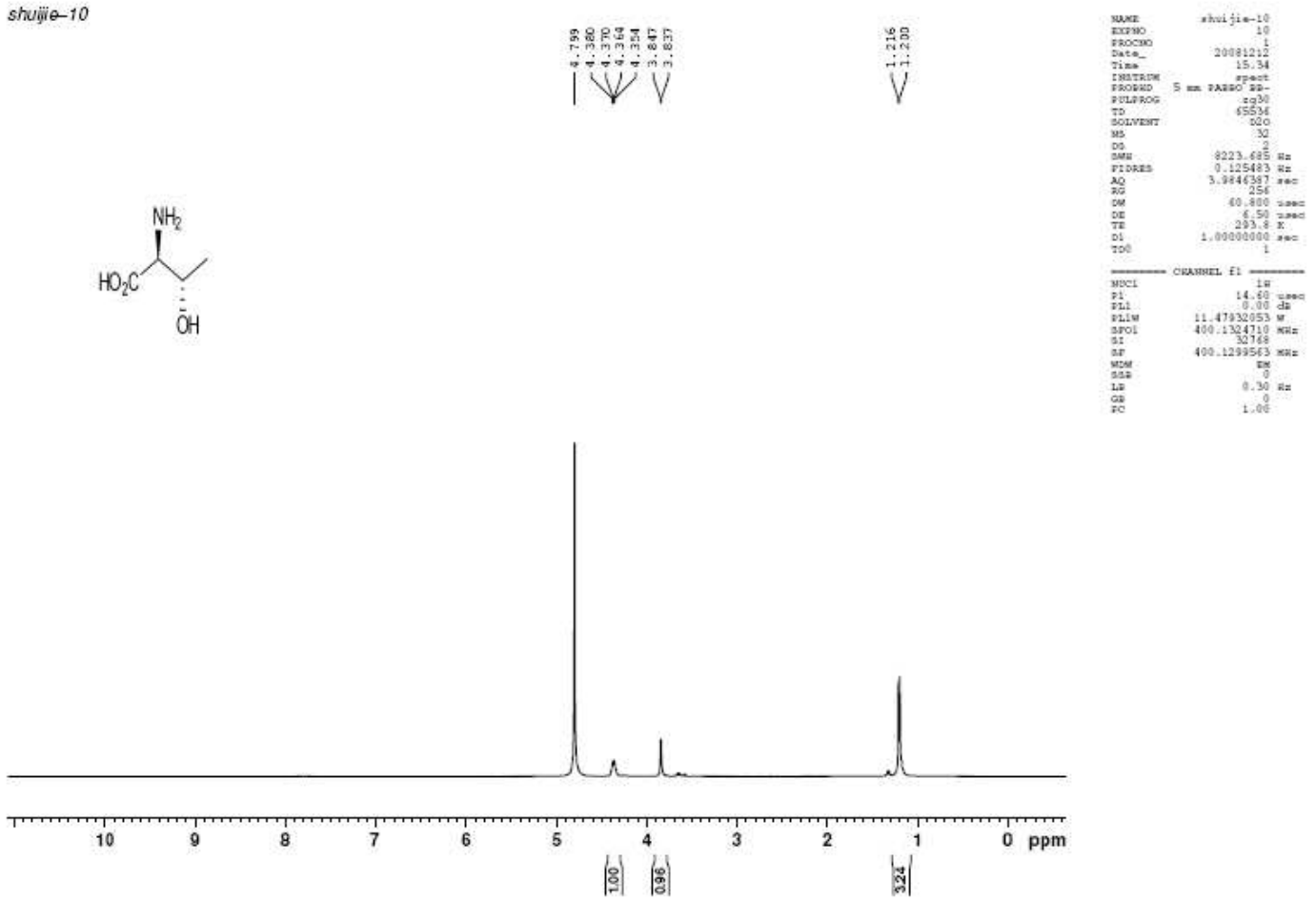
^{1}H NMR spectrum of compound **3h** (400 MHz, $CDCl_3$)



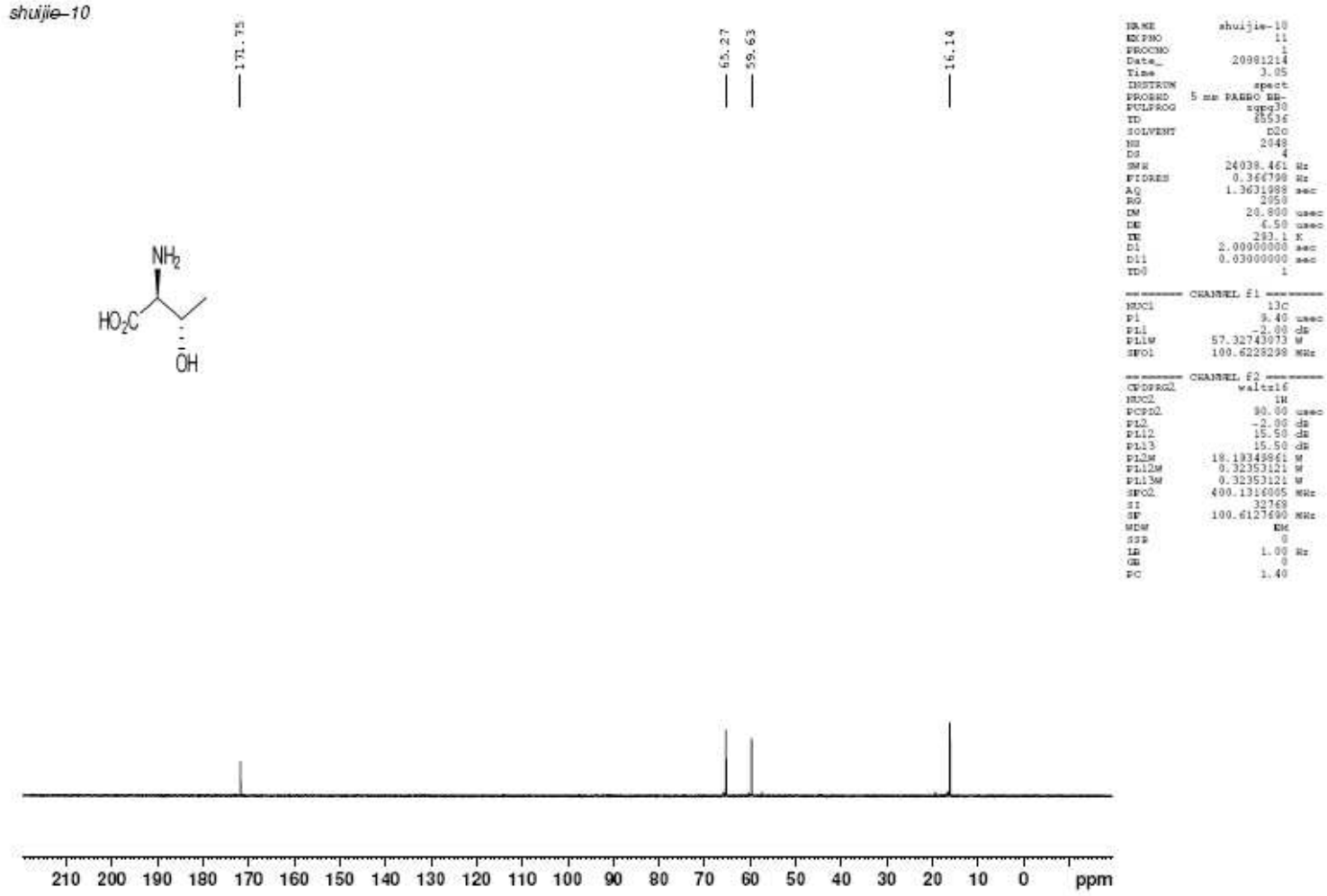
^{13}C NMR spectrum of compound **3h** (100 MHz, $CDCl_3$)



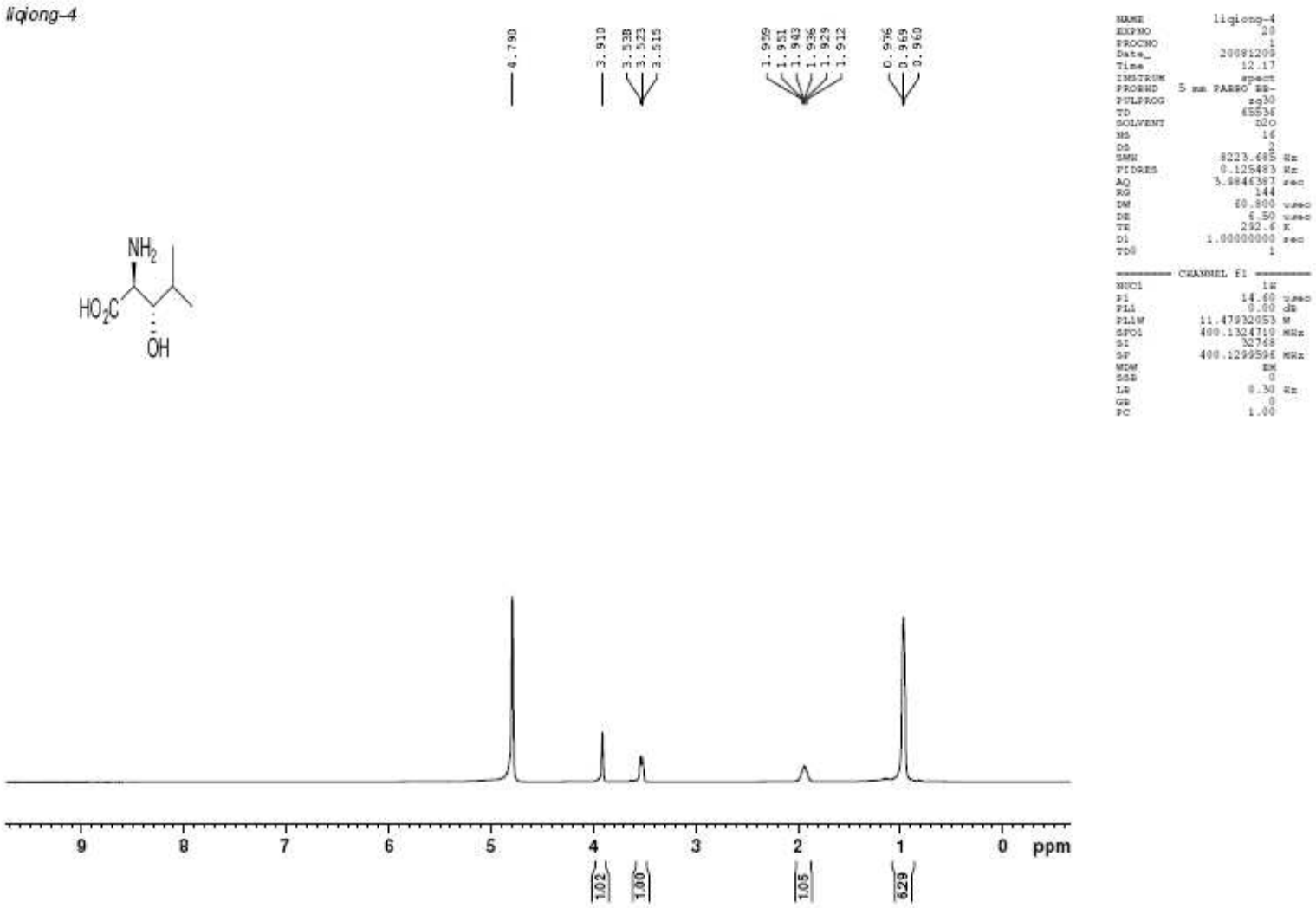
^{1}H NMR spectrum of compound **4a** (400 MHz, D_2O)



^{13}C NMR spectrum of compound **4a** (100 MHz, D_2O)

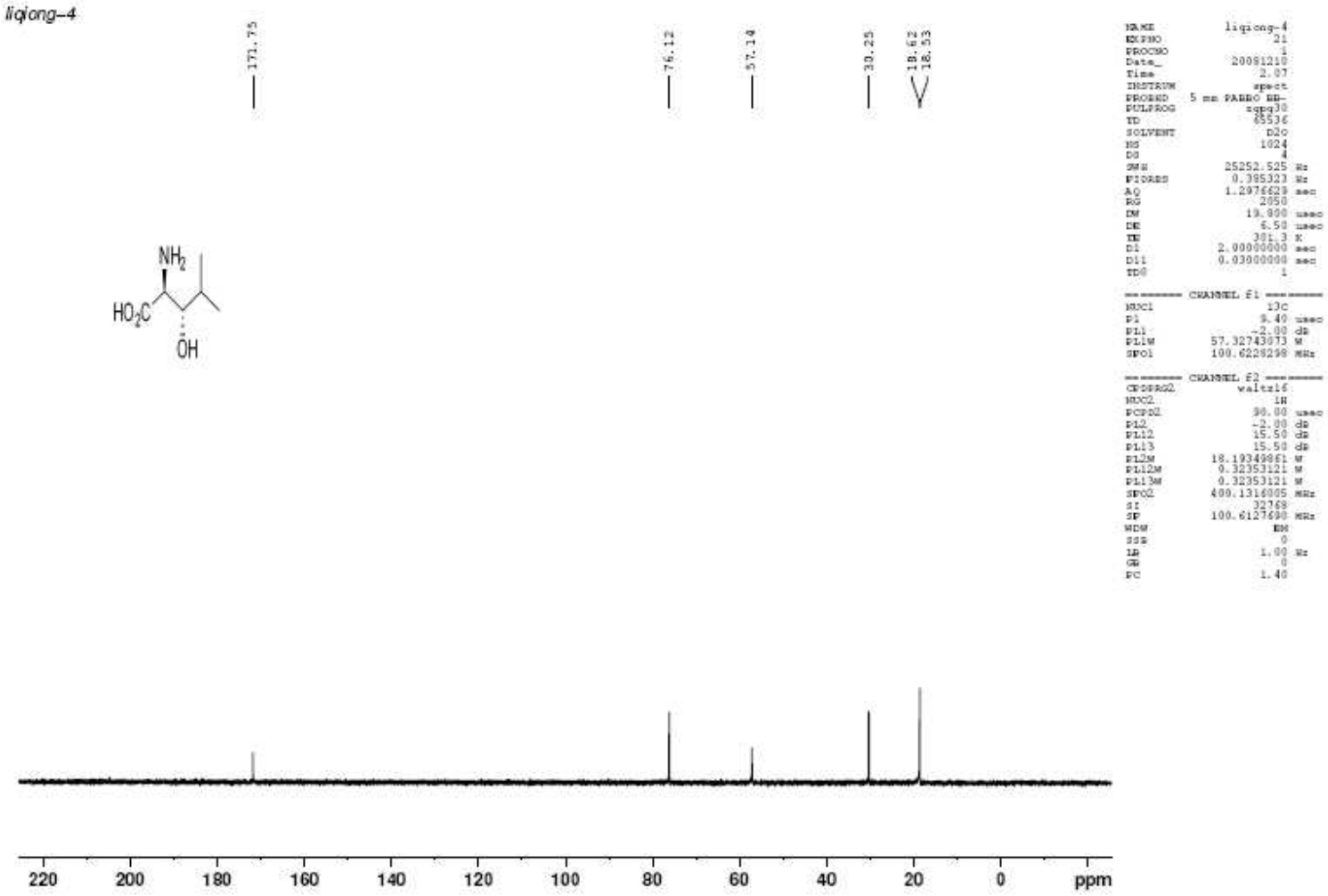


^{1}H NMR spectrum of compound **4c** (400 MHz, D_2O)

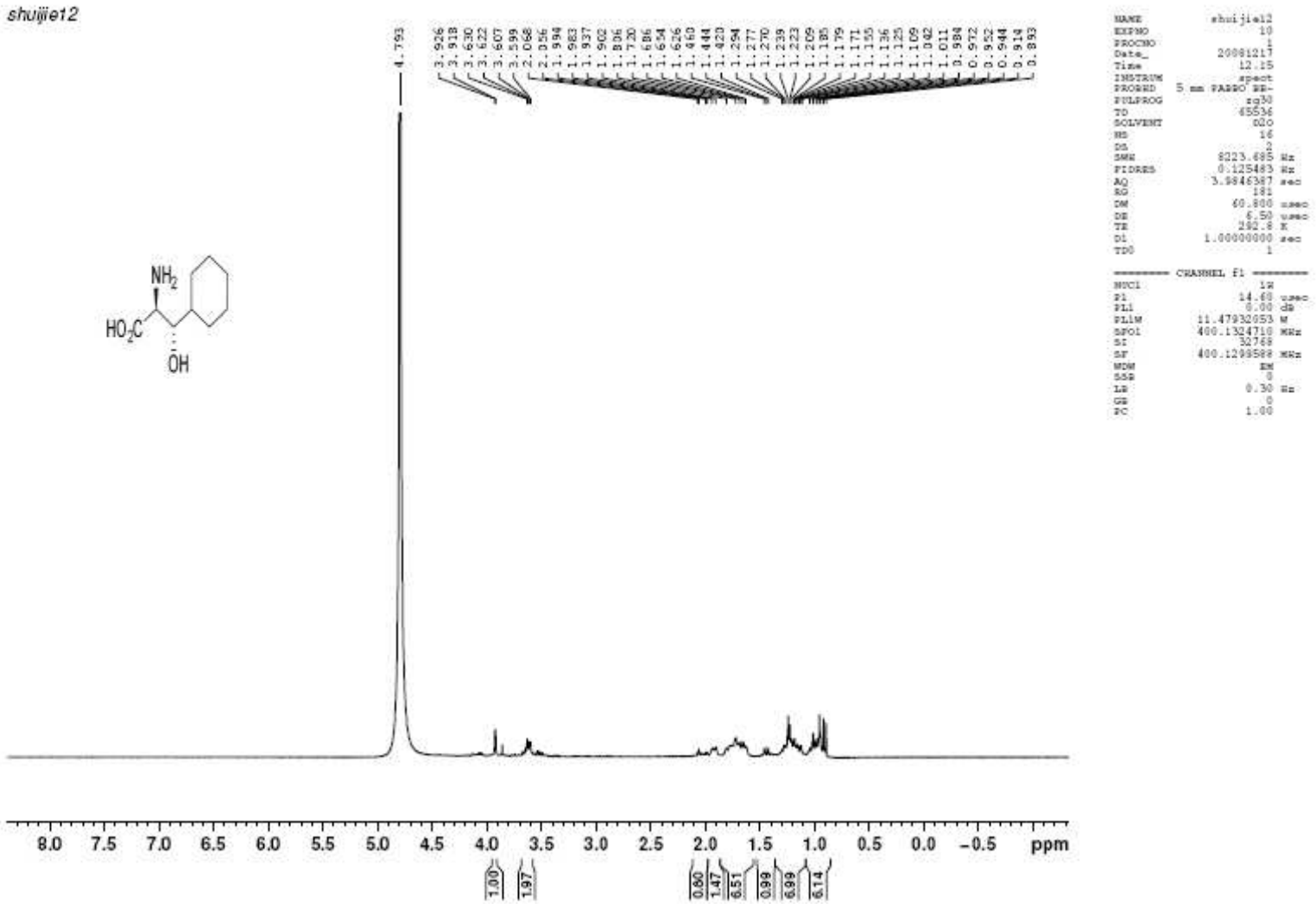


NAME liqiong-4
EXPNO 20
PROCNO 1
Date_ 20081205
Time 12.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT D2O
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9844387 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 292.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.60 usec
PL1 0.00 dB
PL1W 11.47932053 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299596 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

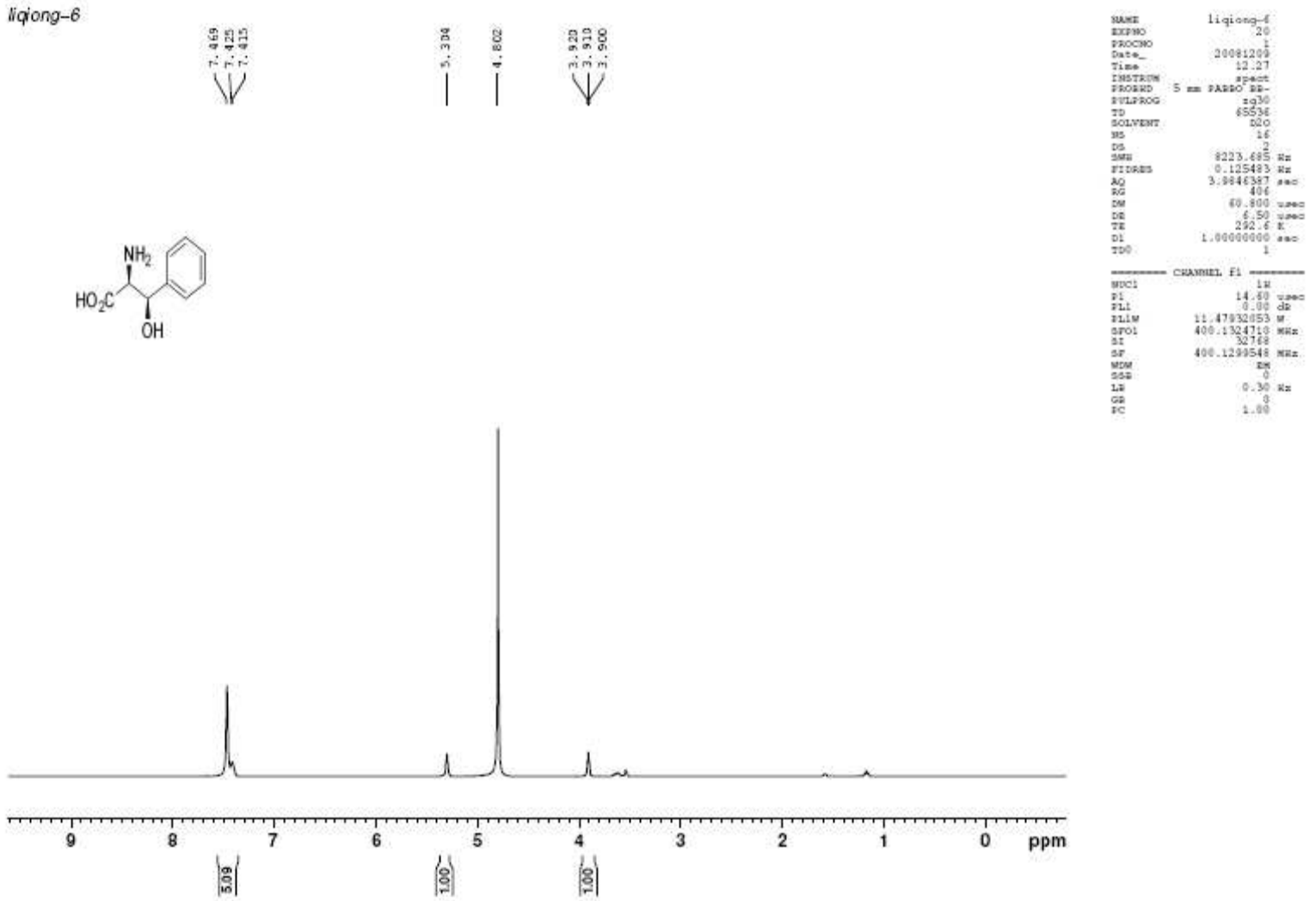
^{13}C NMR spectrum of compound **4c** (100 MHz, D_2O)



^{1}H NMR spectrum of compound **4d** (400 MHz, D_2O)



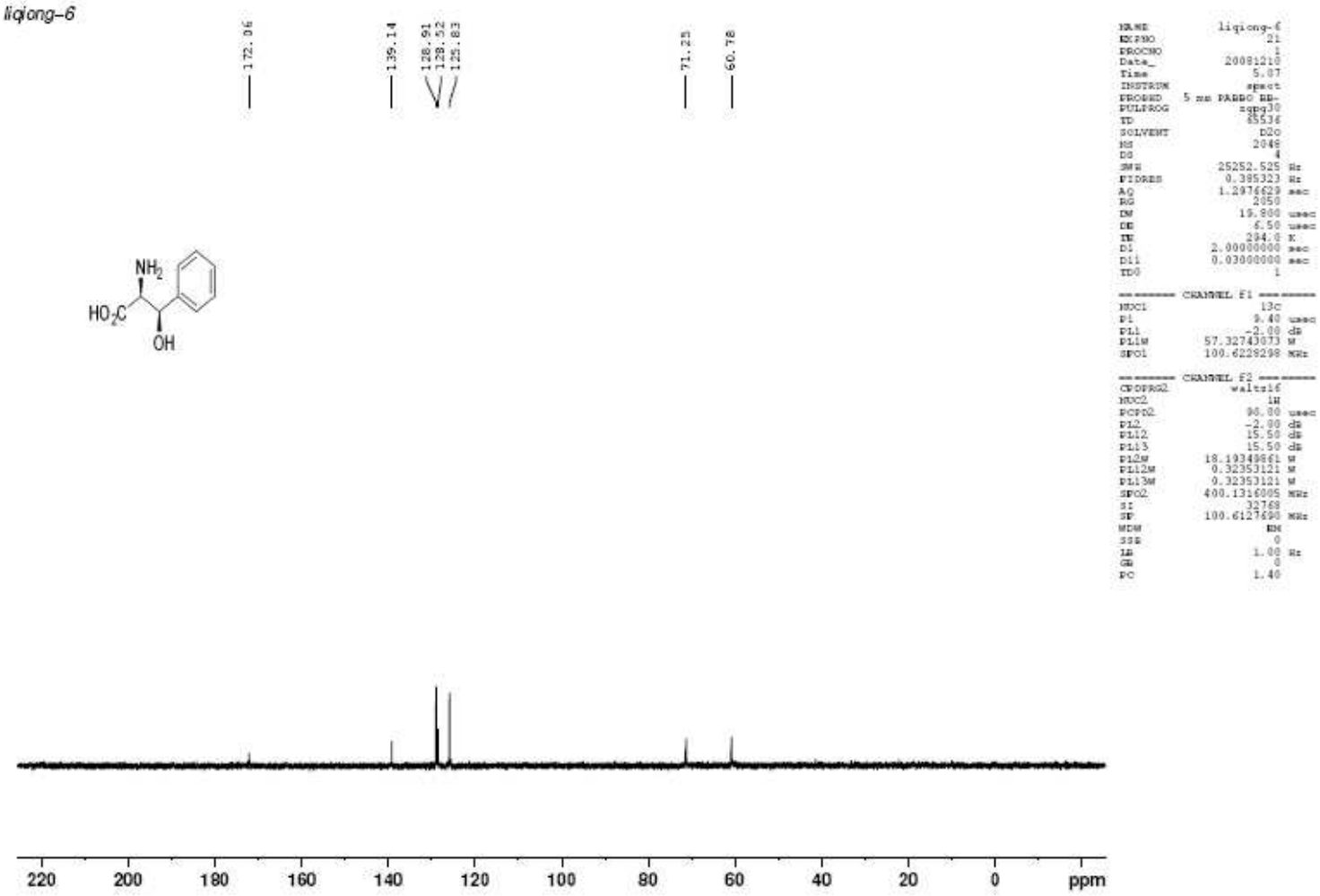
^{1}H NMR spectrum of compound **4e** (400 MHz, D_2O)



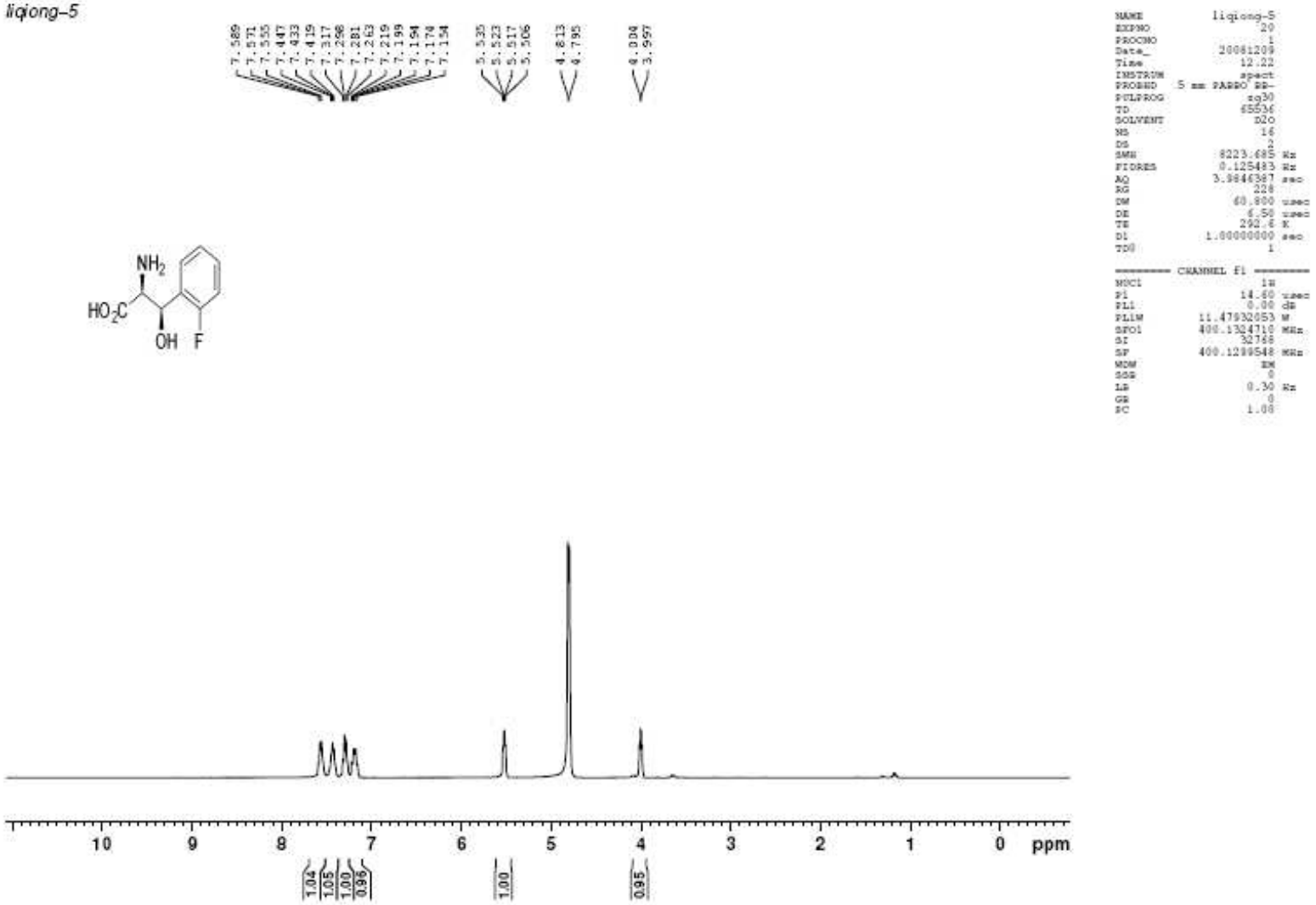

```
NAME                liqiong-6
EXPNO                      20
PROCNO                      1
Date_              20081209
Time                    12.27
INSTRUM                  spect
PROBHD   5 mm PABBO BB-
PULPROG                 zg30
TD                      65536
SOLVENT                   D2O
NS                         16
DS                          2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                        406
DW                     60.800 usec
DE                      6.50 usec
TE                     292.6 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                      14.60 usec
PL1                      0.00 dB
PLW1                11.47932053 W
SFO1                400.1324710 MHz
SI                        32768
SF                  400.1299548 MHz
WDW                        EM
SSB                         0
LB                       0.30 Hz
GB                          0
PC                       1.00
```

^{13}C NMR spectrum of compound **4e** (100 MHz, D_2O)

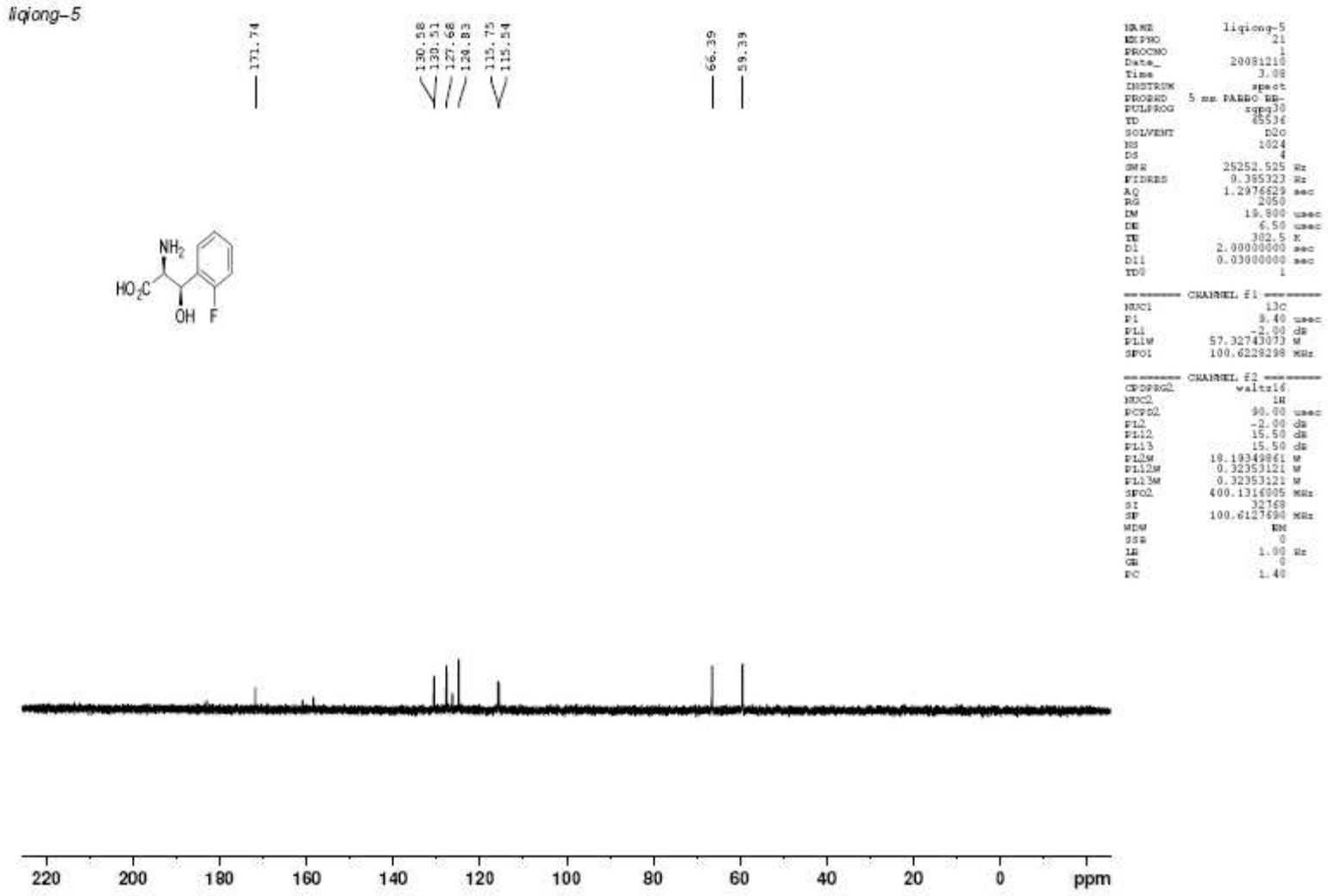


^{1}H NMR spectrum of compound **4f** (400 MHz, D_2O)

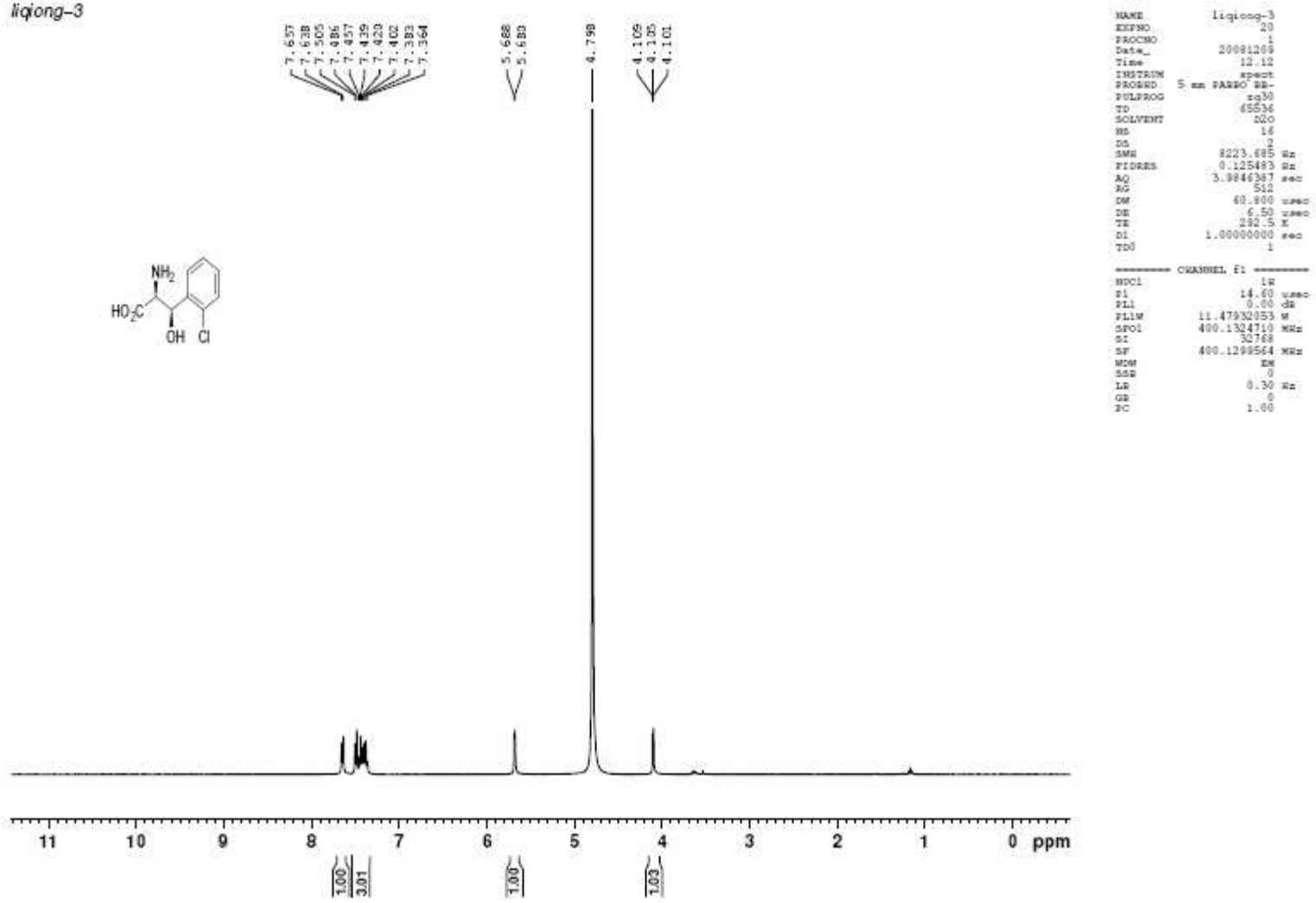


NAME	liqiong-5
EXPNO	20
PROCNO	1
Date_	20081209
Time	12.22
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	D2O
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	228
DW	60.800 usec
DE	6.50 usec
TE	292.6 K
D1	1.00000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	1H
P1	14.60 usec
PL1	0.00 dB
PLLW	11.47932053 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299548 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum of compound **4f** (100 MHz, D_2O)

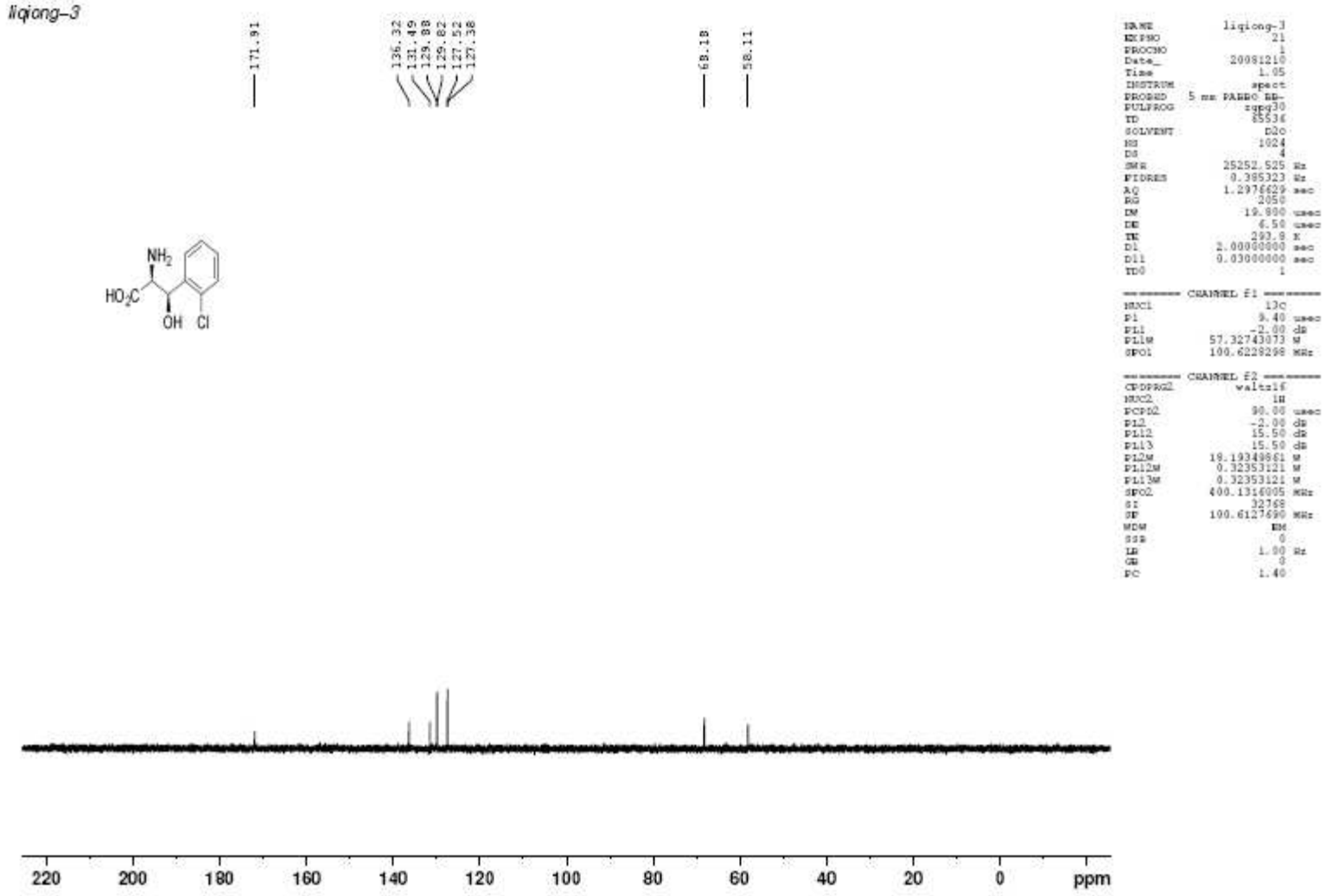


^{1}H NMR spectrum of compound **4g** (400 MHz, D_2O)



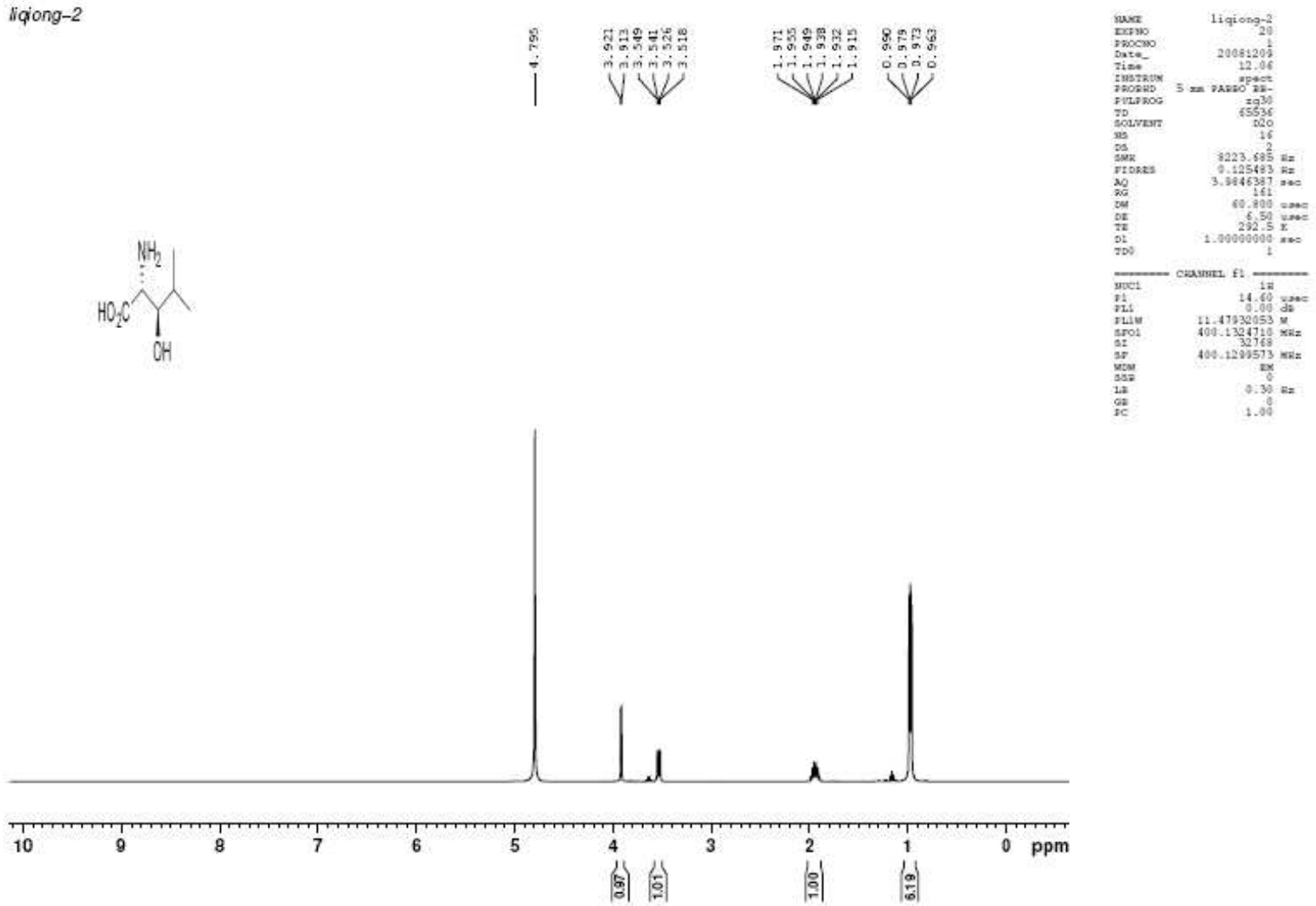
NAME	liqiong-3
EXPNO	20
PROCNO	1
Date_	20081209
Time	12.12
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	D2O
NS	16
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	512
DW	60.800 usec
DE	6.50 usec
TE	282.5 K
D1	1.00000000 sec
TD0	1
==========	CHANNEL f1 ==========
NUC1	1H
P1	14.60 usec
PL1	0.00 dB
PL1W	11.47932053 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299564 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

^{13}C NMR spectrum of compound **4g** (100 MHz, D_2O)

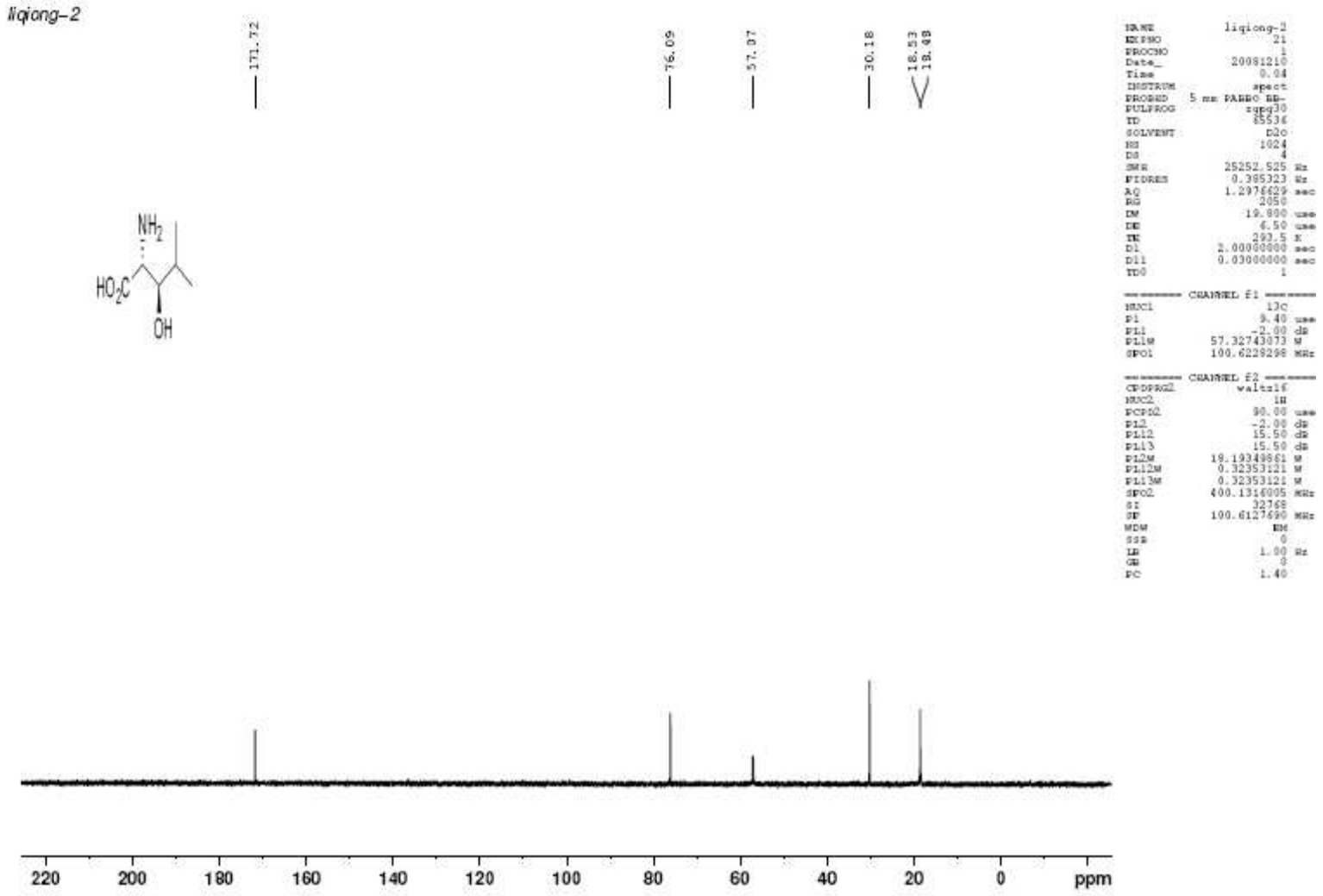


NAME	liqiong-3
EXPNO	21
PROCNO	1
Date_	20081210
Time	1.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	85536
SOLVENT	D2O
NS	1024
DS	4
SWH	25252.525 Hz
FIDRES	0.395323 Hz
AQ	1.2976629 sec
RG	2050
DW	19.800 usec
DE	6.50 usec
TE	293.8 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.40 usec
PL1	-2.00 dB
PL1W	57.32743073 W
SFO1	100.6228298 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	-2.00 dB
PL12	15.50 dB
PL13	15.50 dB
PL2W	18.19349861 W
PL12W	0.32353121 W
PL13W	0.32353121 W
SFO2	400.1316005 MHz
SI	32768
SF	100.6127690 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

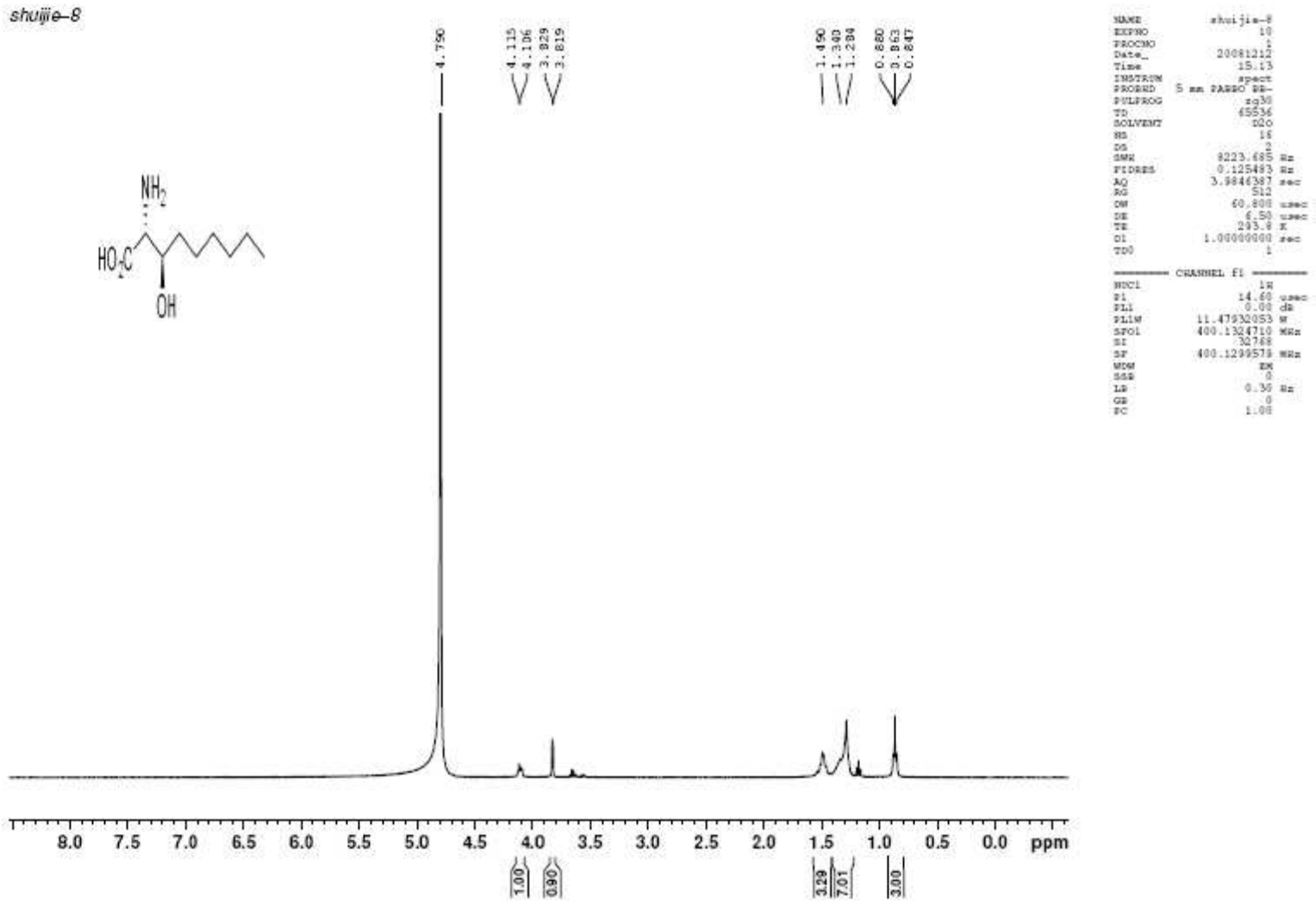
^{1}H NMR spectrum of compound **5c** (400 MHz, D_2O)



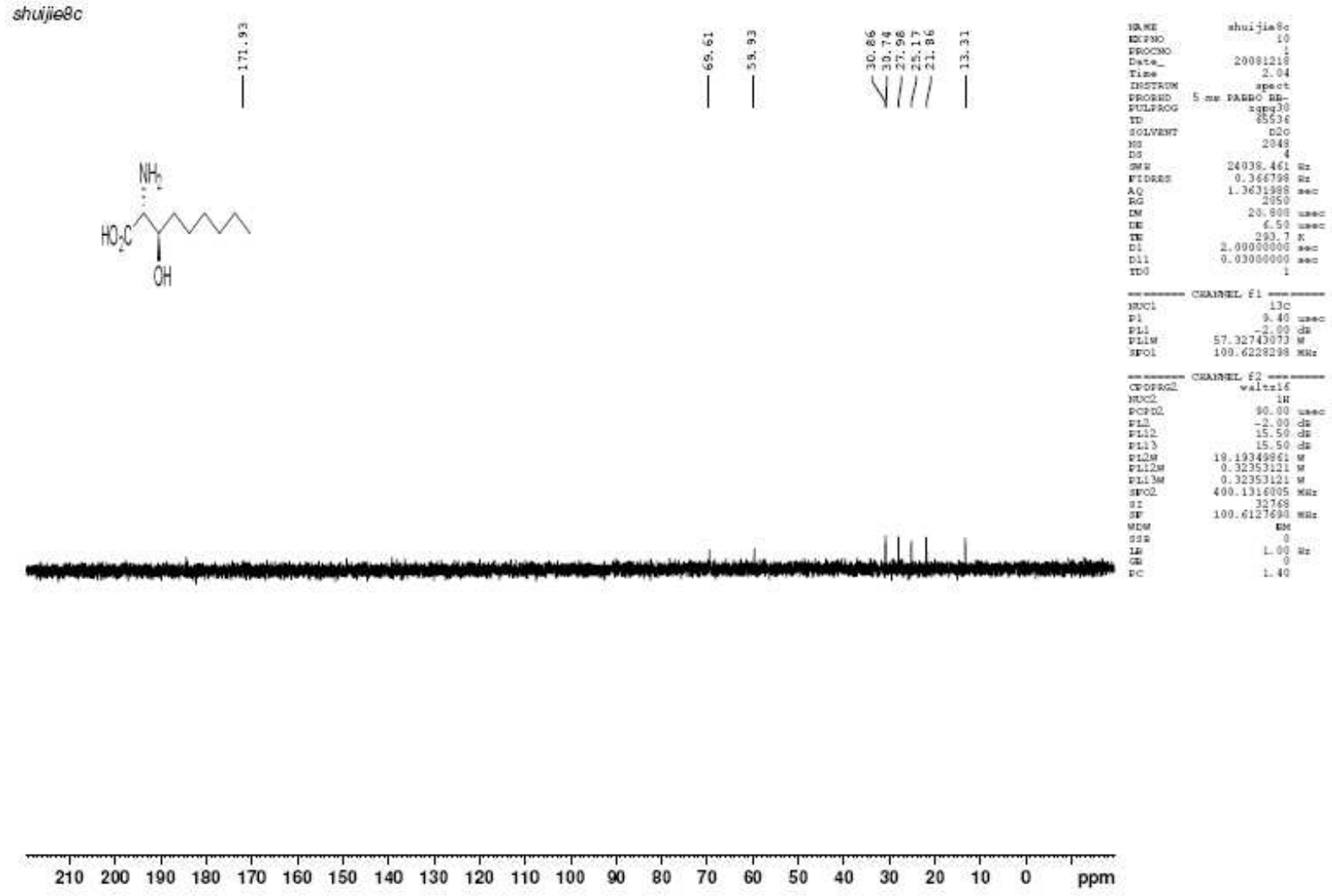
^{13}C NMR spectrum of compound **5c** (100 MHz, D_2O)



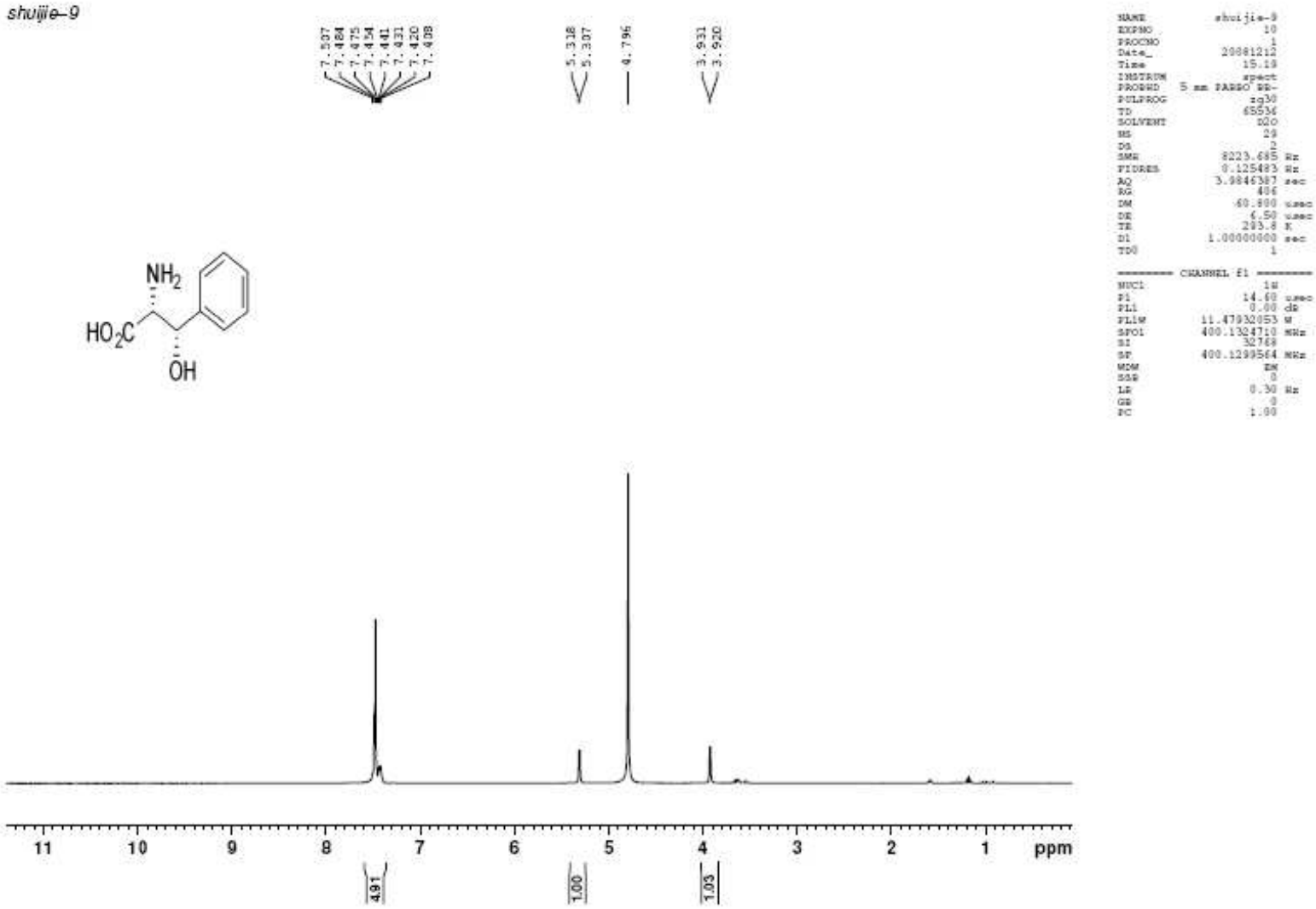
^{1}H NMR spectrum of compound **5d** (400 MHz, D_2O)



^{13}C NMR spectrum of compound **5d** (100 MHz, D_2O)

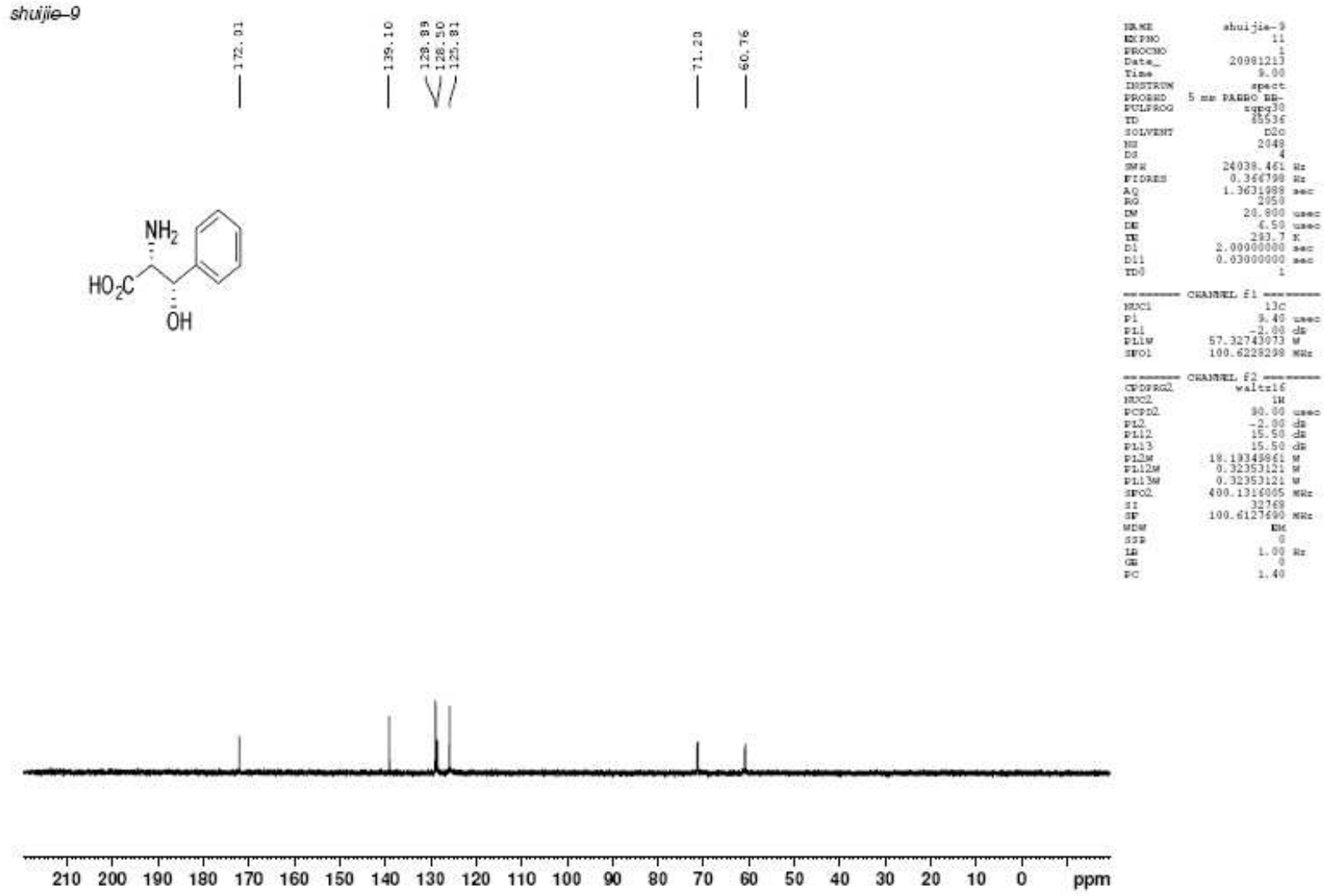


^{1}H NMR spectrum of compound **5f** (400 MHz, D_2O)

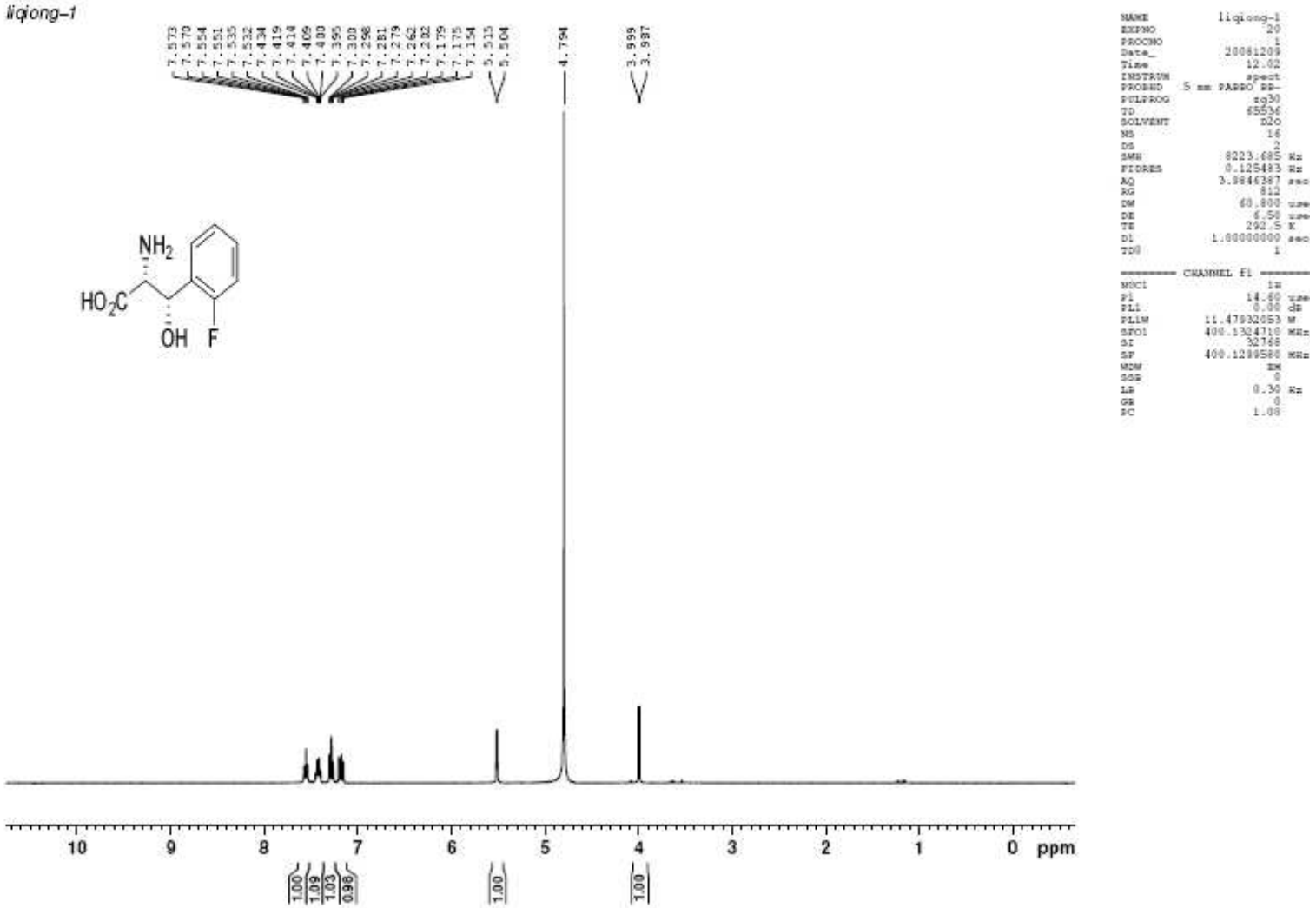


NAME	shuijie-9
EXPNO	10
PROCNO	1
Date_	20081212
Time	15.19
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zg30
TD	65536
SOLVENT	D2O
NS	24
DS	2
SWH	8223.685 Hz
FIDRES	0.125483 Hz
AQ	3.9846387 sec
RG	406
DW	60.800 usec
DE	6.50 usec
TE	293.8 K
D1	1.00000000 sec
TD0	1
---------- CHANNEL f1 ----------	
NUC1	1H
P1	14.60 usec
PL1	0.00 dB
PL1W	11.47932053 W
SFO1	400.1324710 MHz
SI	32768
SF	400.1299564 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

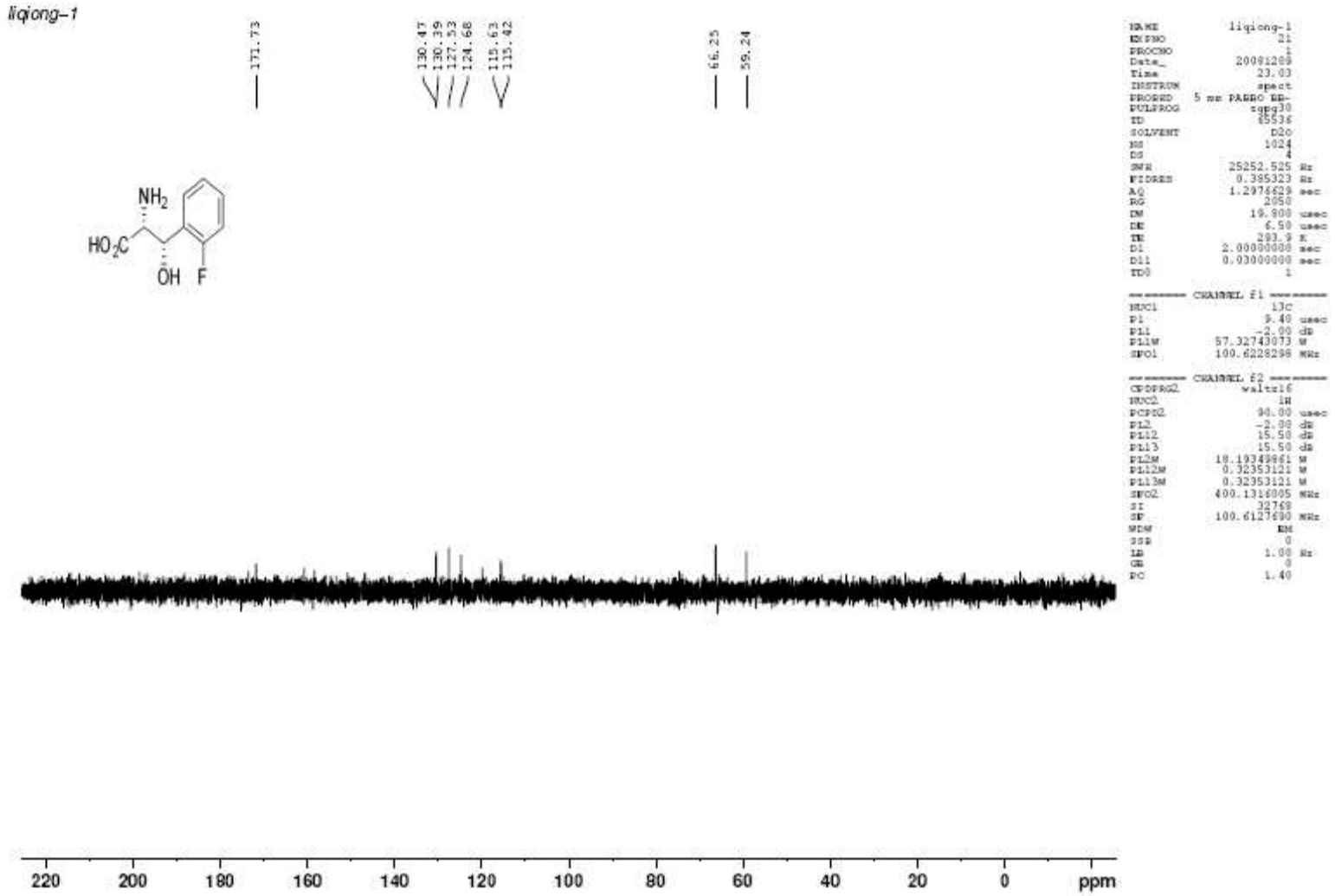
^{13}C NMR spectrum of compound **5f** (100 MHz, D_2O)



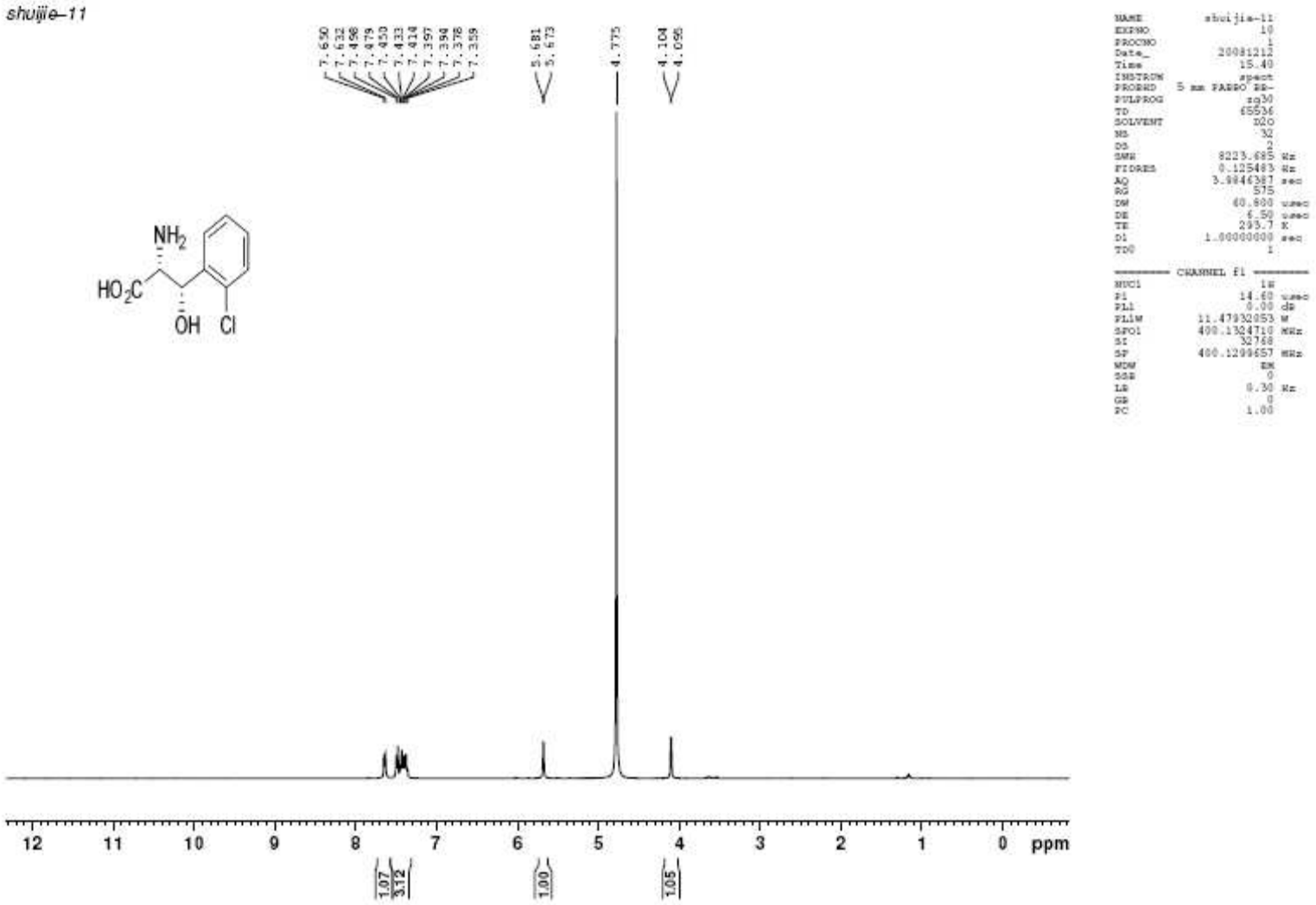
^{1}H NMR spectrum of compound **5g** (400 MHz, D_2O)



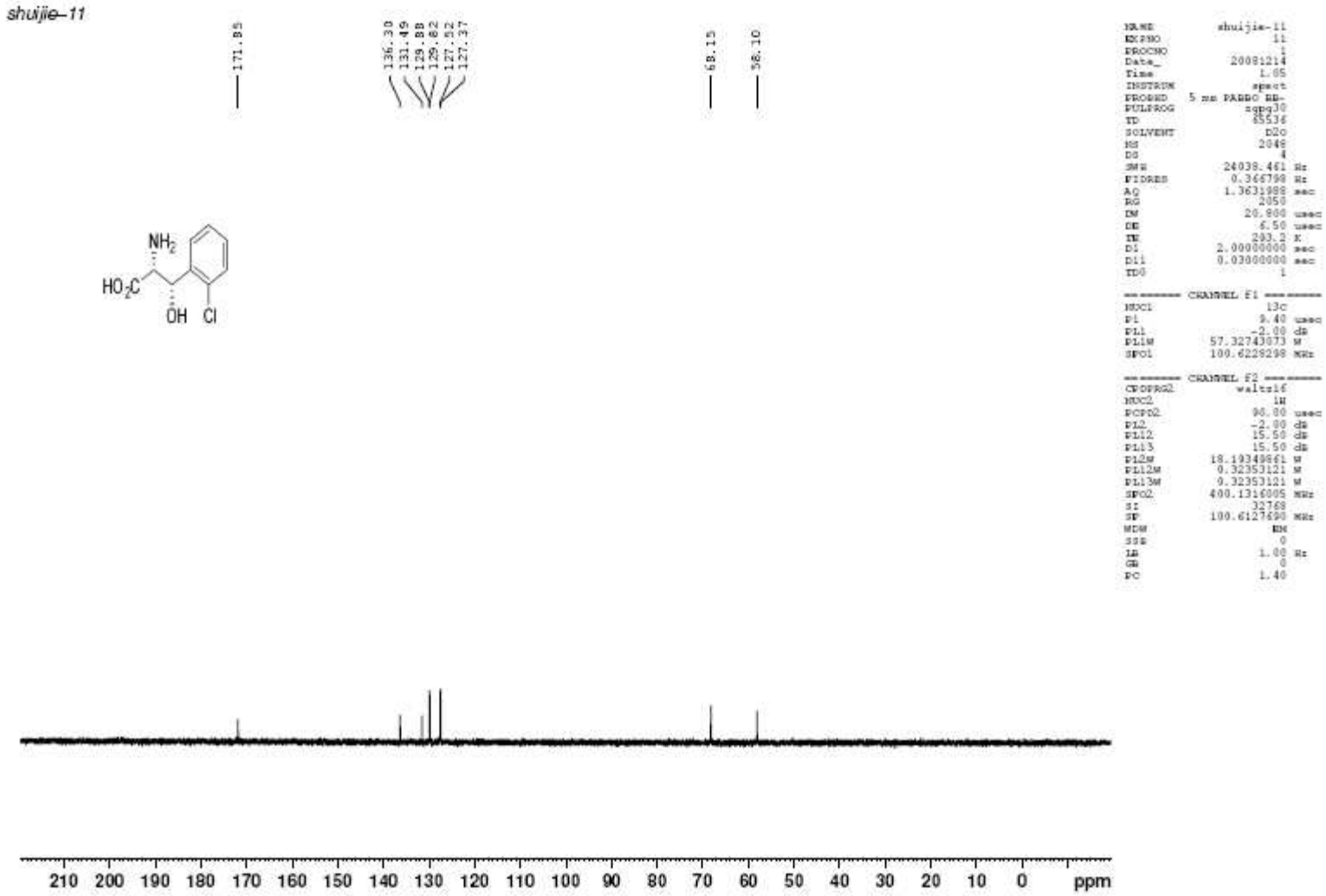
^{13}C NMR spectrum of compound **5g** (100 MHz, D_2O)



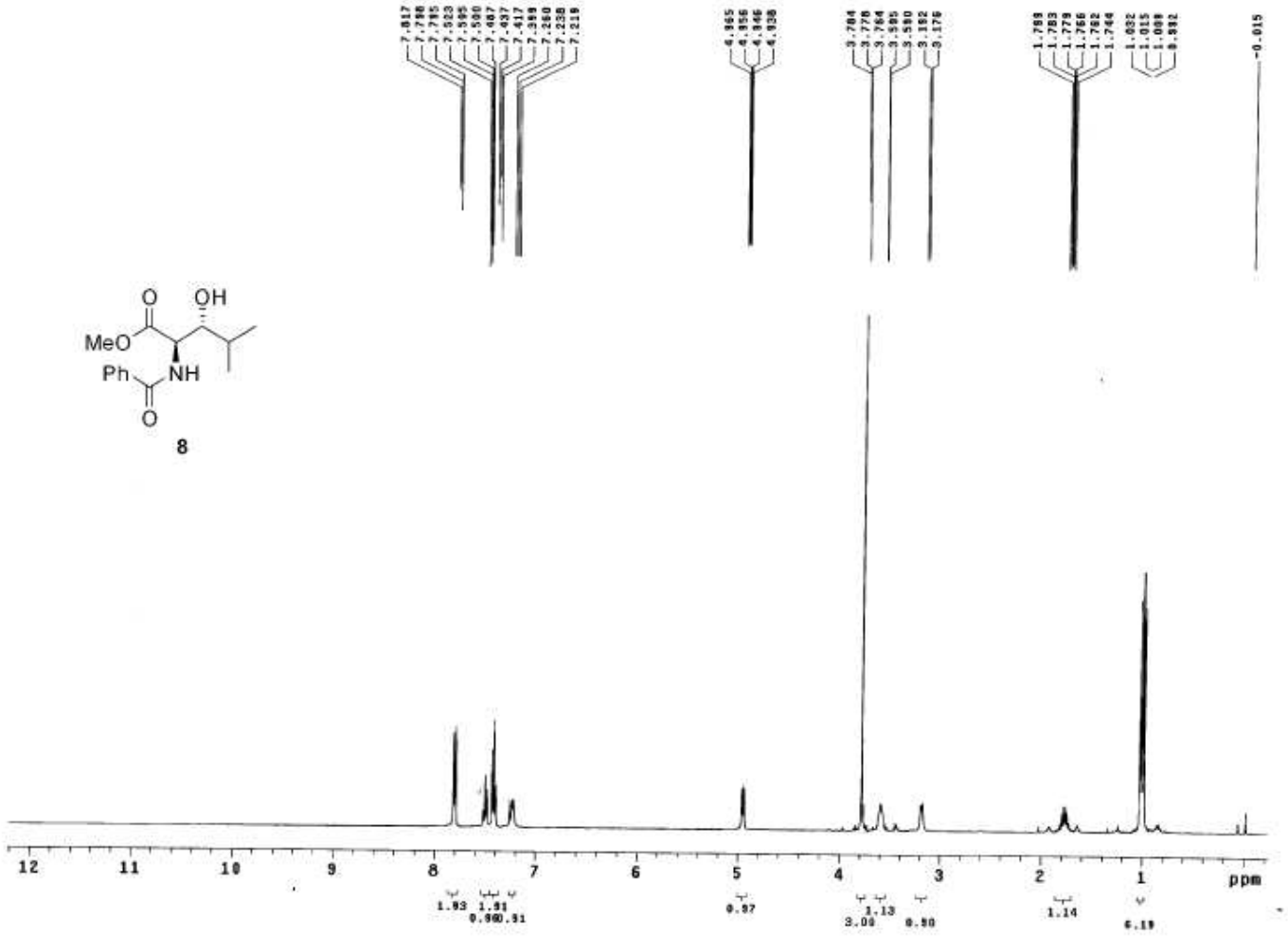
^{1}H NMR spectrum of compound **5h** (400 MHz, D_2O)



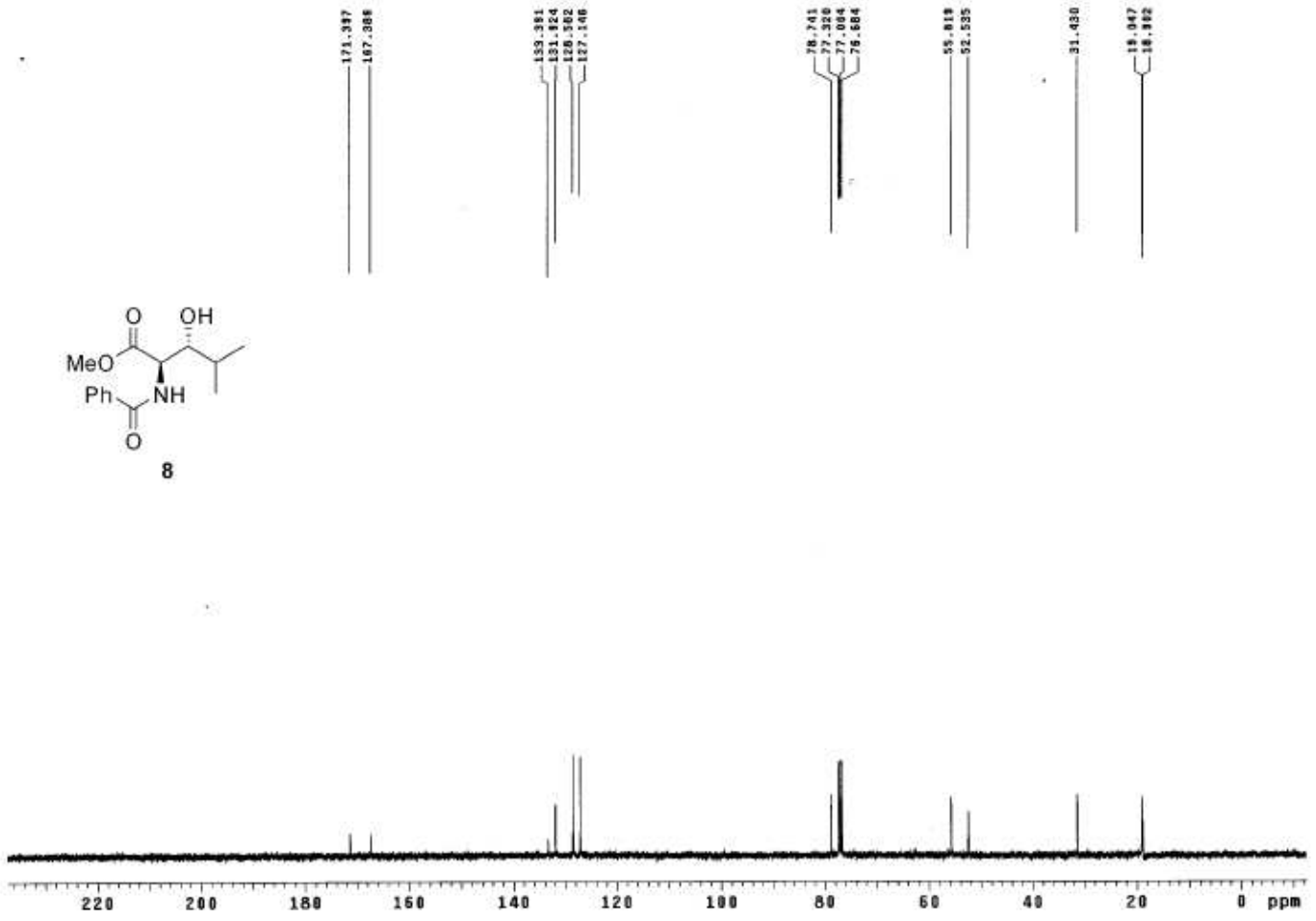
^{13}C NMR spectrum of compound **5h** (100 MHz, D_2O)



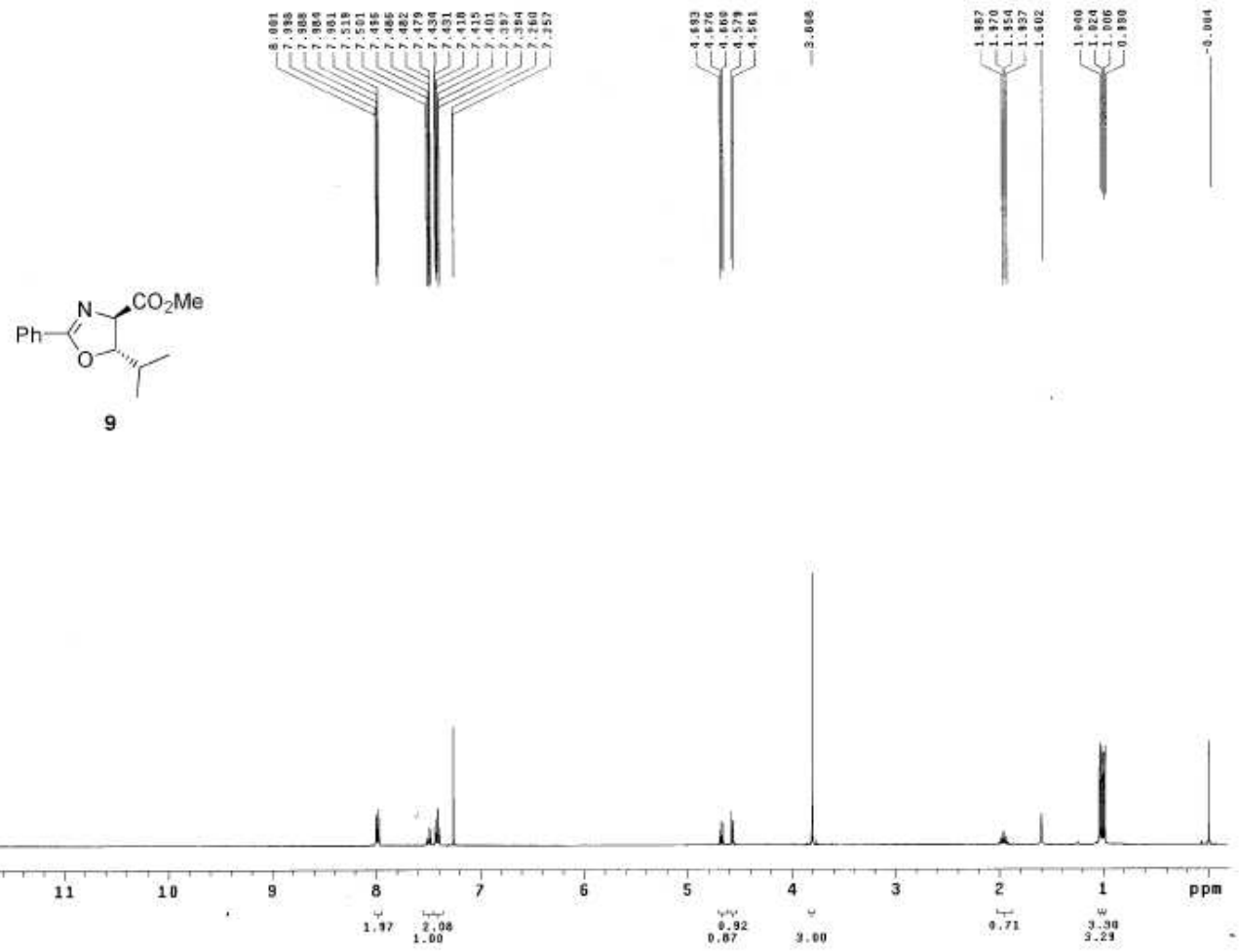
^{1}H NMR spectrum of compound **8** (400 MHz, $CDCl_3$)



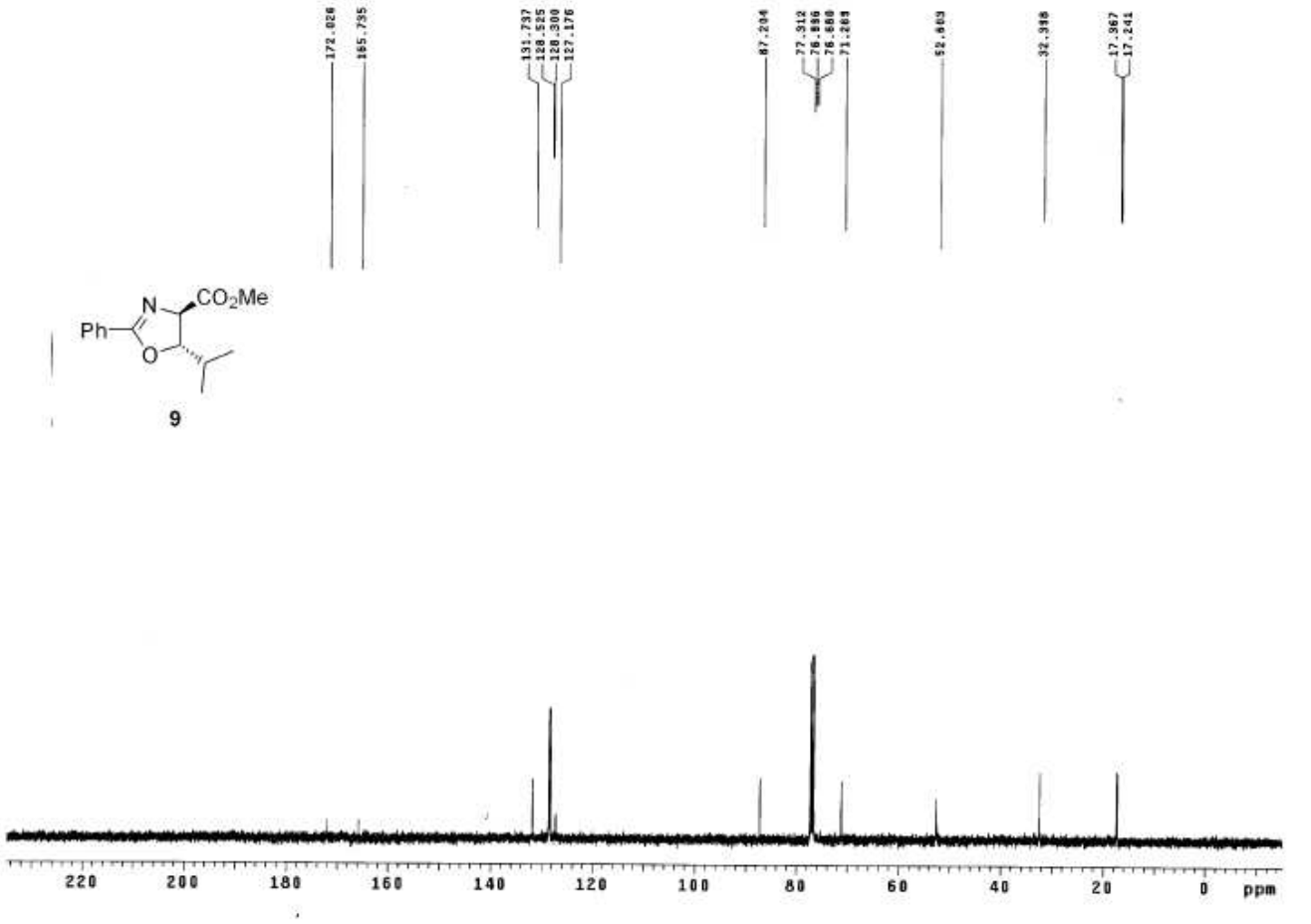
^{13}C NMR spectrum of compound **8** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$)



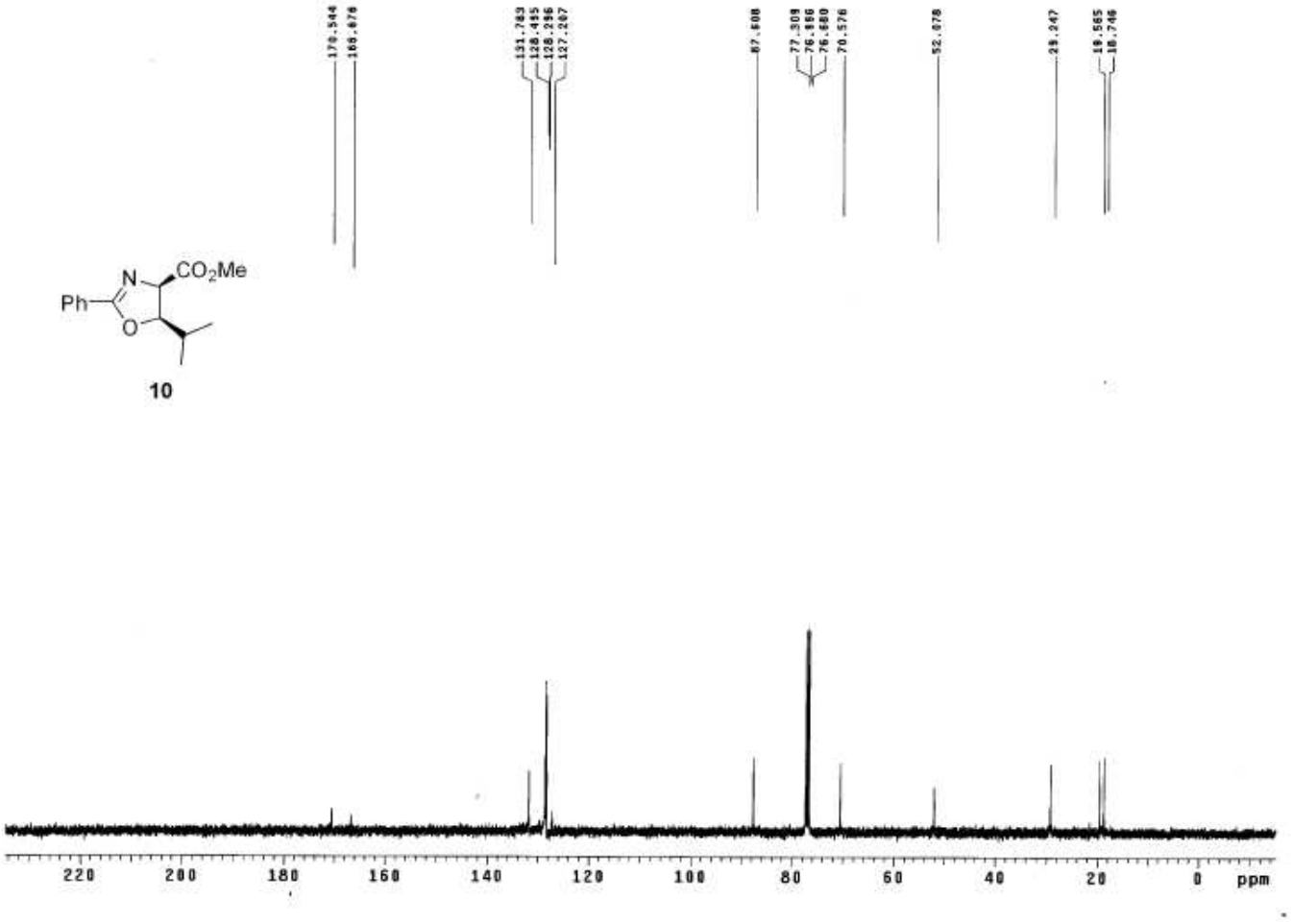
^{13}C NMR spectrum of compound **9** (100 MHz, $CDCl_3$)



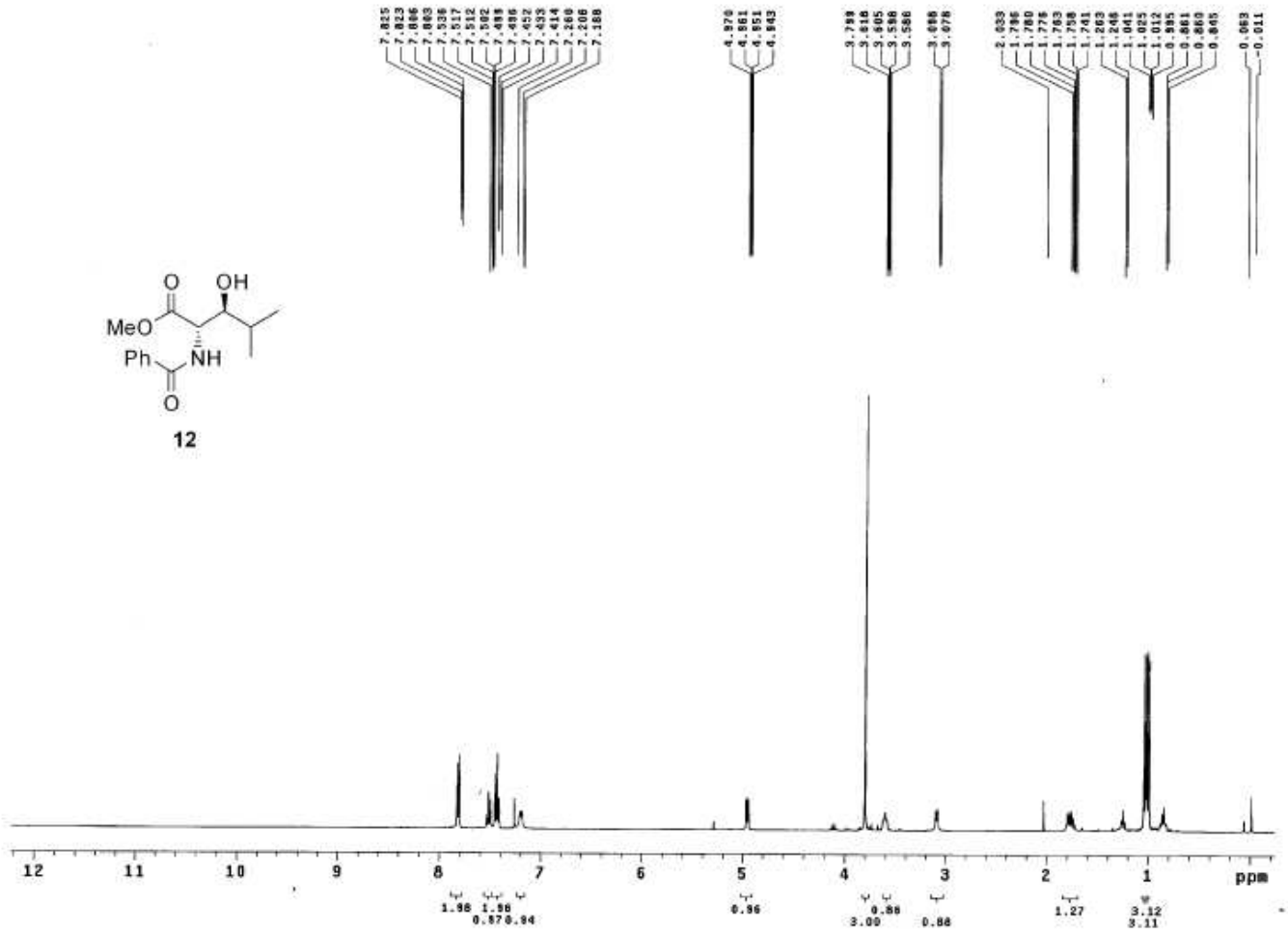
^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$)

10

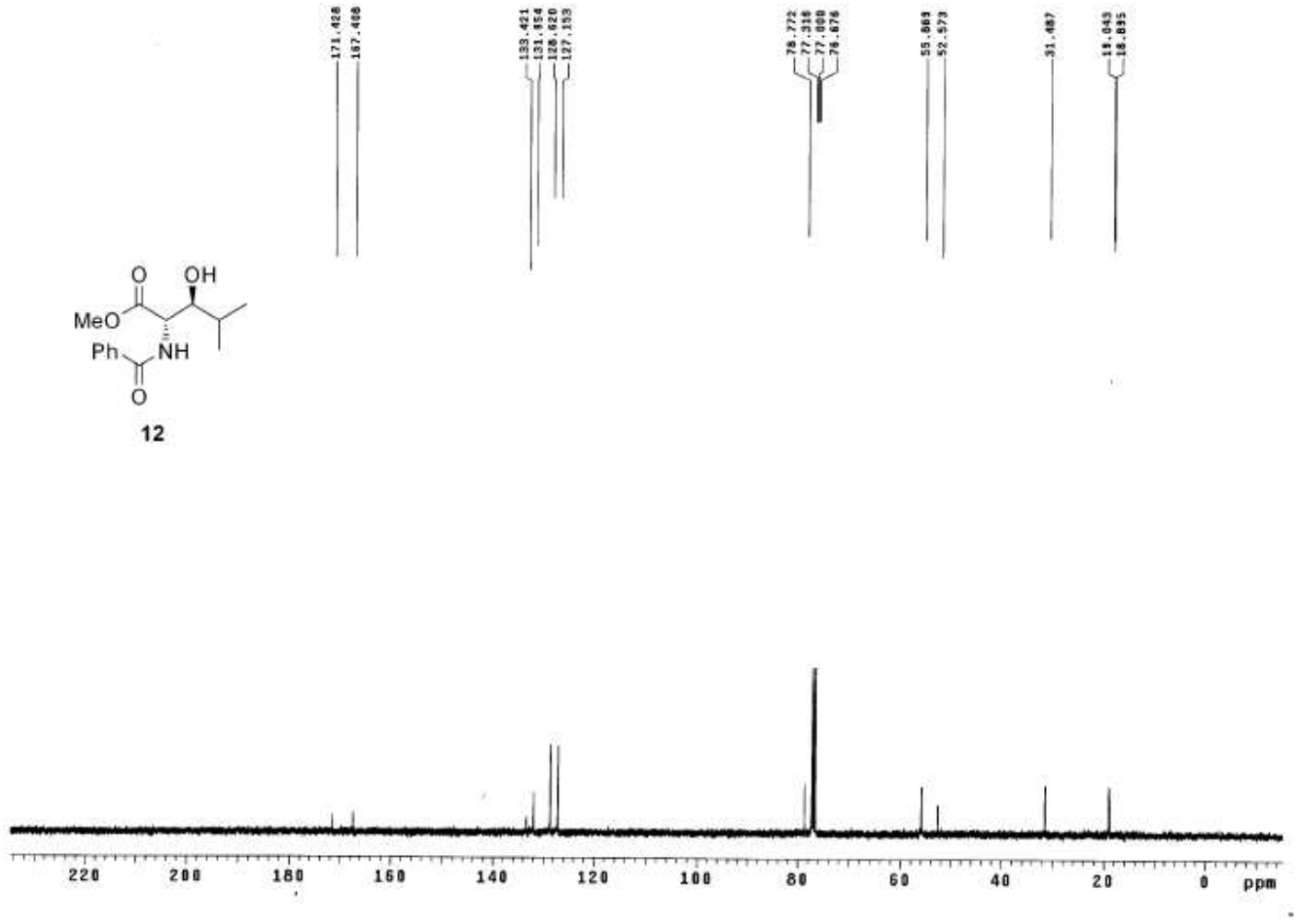
^{13}C NMR spectrum of compound **10** (100 MHz, $CDCl_3$)



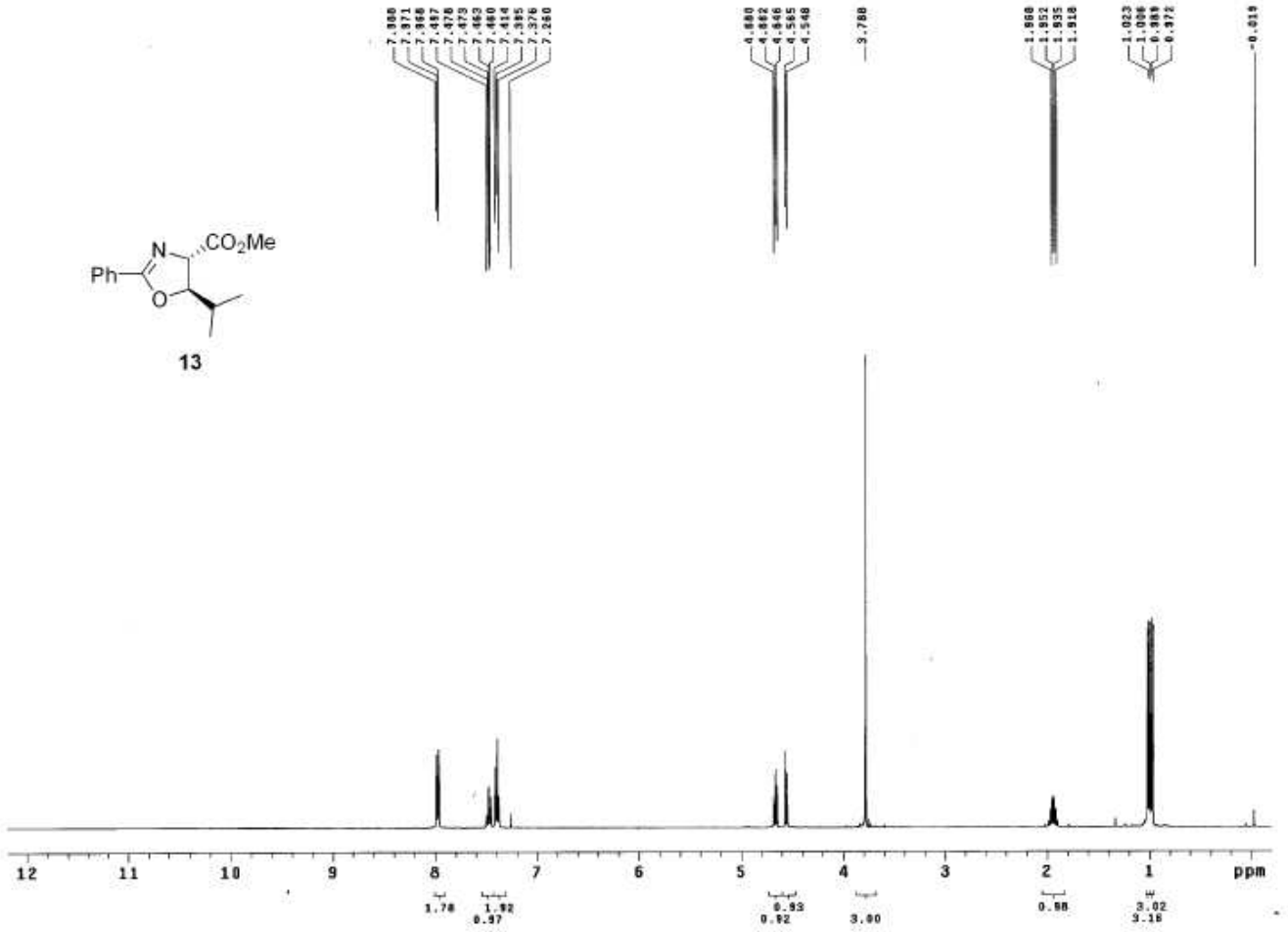
^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$)



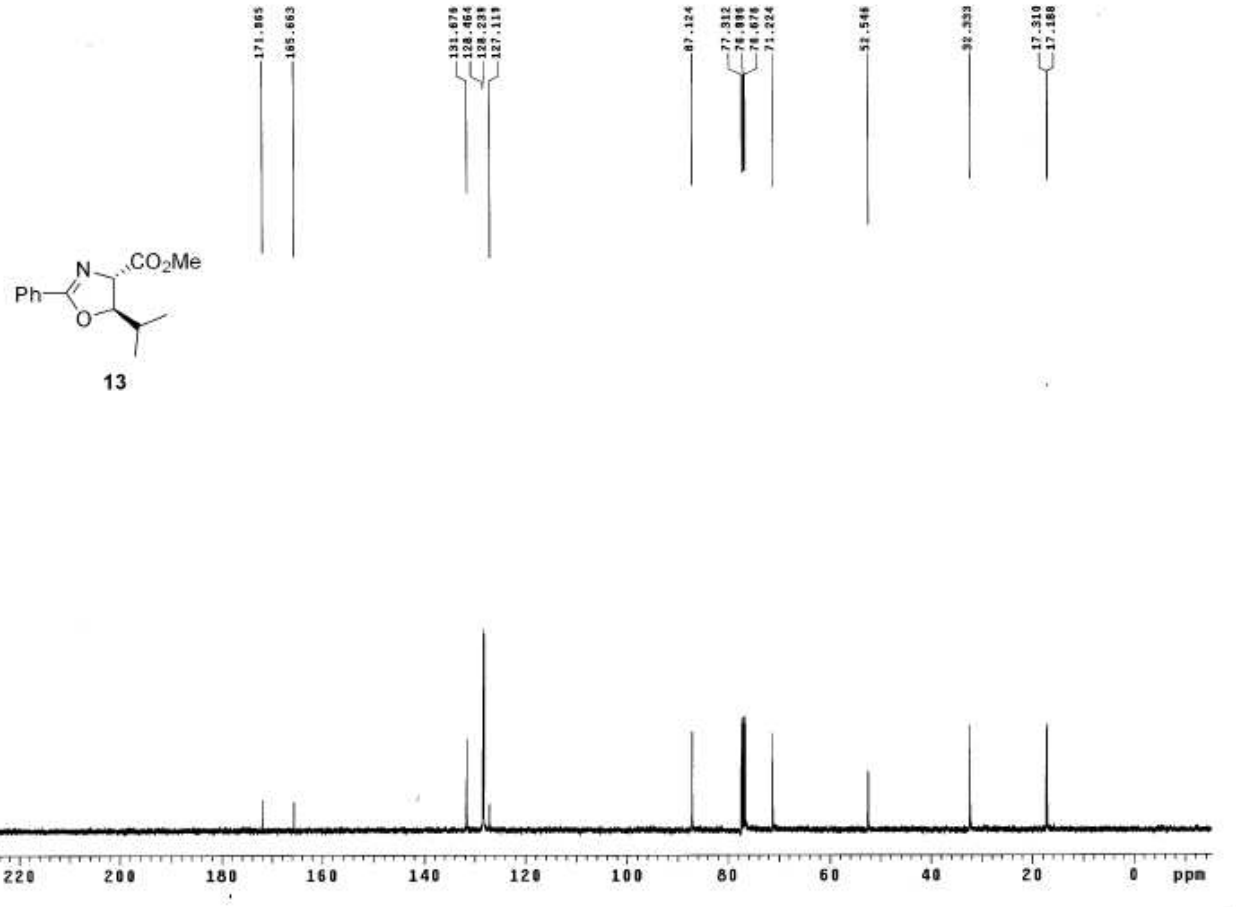
^{13}C NMR spectrum of compound **12** (100 MHz, $CDCl_3$)



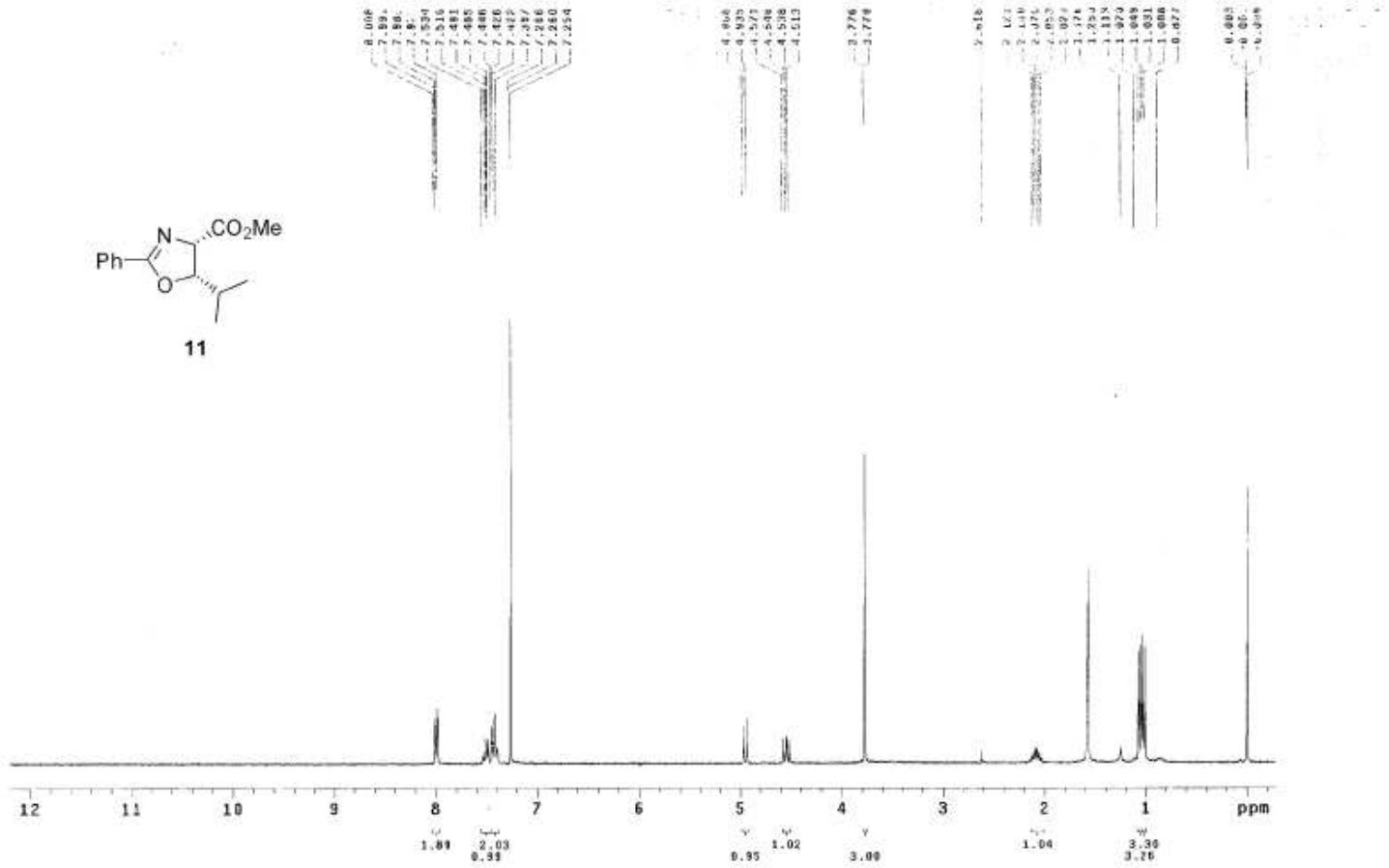
^{1}H NMR spectrum of compound **13** (400 MHz, $CDCl_3$)



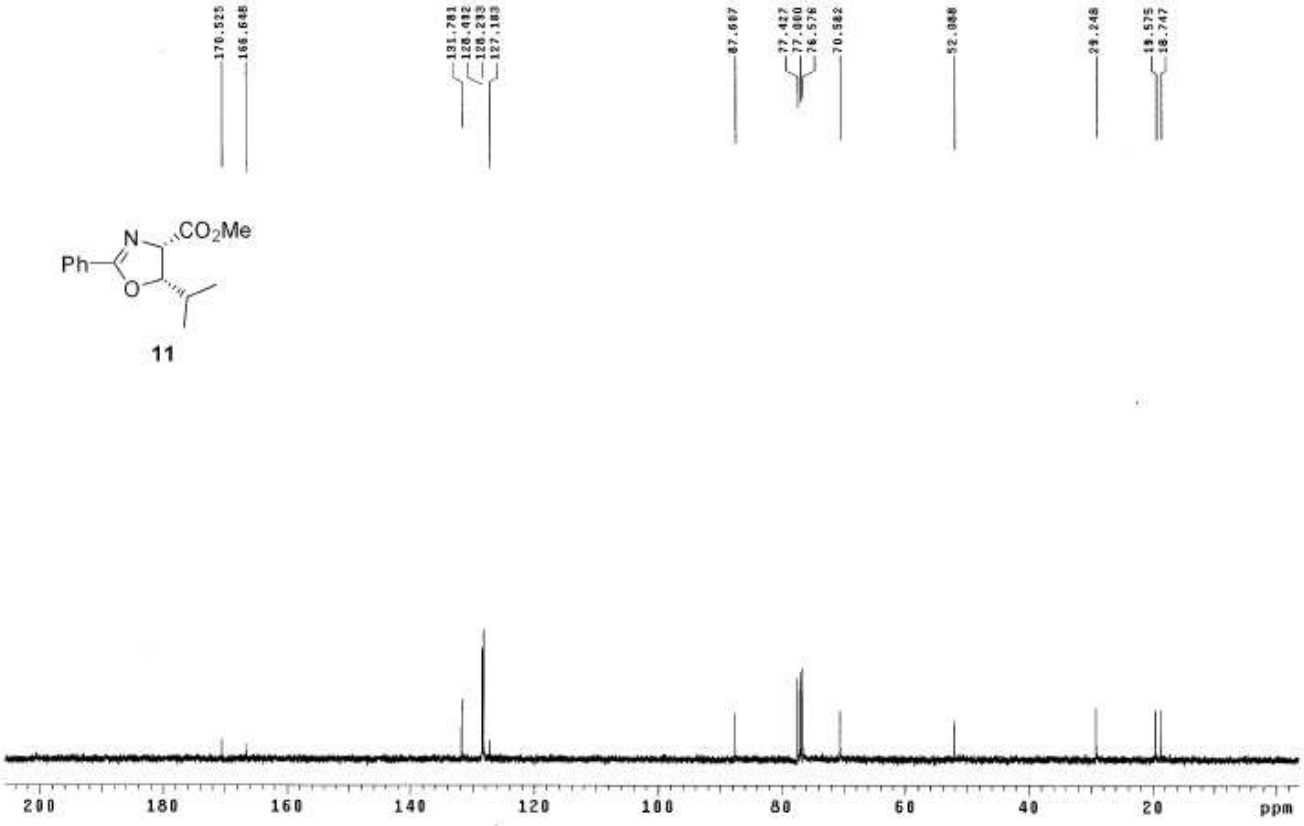
^{13}C NMR spectrum of compound **13** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of compound **11** (300 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **11** (75 MHz, $CDCl_3$)



HPLC spectrum of the compound **IVa**

Empower

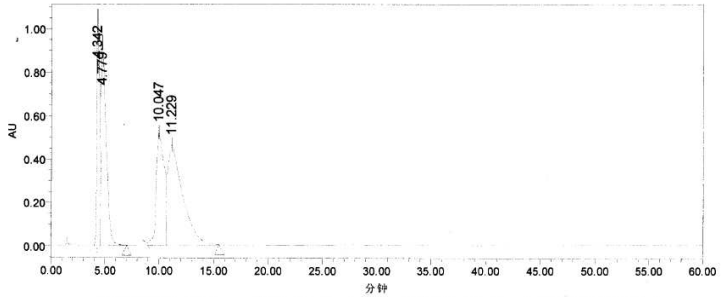
进样综合报告 报告

用户名称：System　　项目名称：Defaults

样品信息

样品名称:	ysb-Phe-xx	采集者:	System
样品类型:	未知	采集时间:	2007-6-22 16:17:44
瓶号:	1	采集方法组:	yangshb
进样次数:	1	处理日期:	2007-6-22 21:03:19
进样体积:	5.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 220.0 纳米

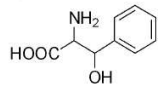
自动标尺色谱图



SampleName ysb-Phe-xx; Vial 1; Injection 1; Channel W2996 ; Date Acquired 2007-6-22 16:17:44

处理通道: PDA 220.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 220.0 纳米	4.342	19534863	16.07	1063571
2	PDA 220.0 纳米	4.779	31583731	25.98	935350
3	PDA 220.0 纳米	10.047	26712574	21.97	523419
4	PDA 220.0 纳米	11.229	43734517	35.98	463574



IV a

报告方法：进样综合报告　　打印 21:04:32　　2007-6-22　　页码：1 (共计 1)

HPLC spectrum of the compound **5f**

Empower

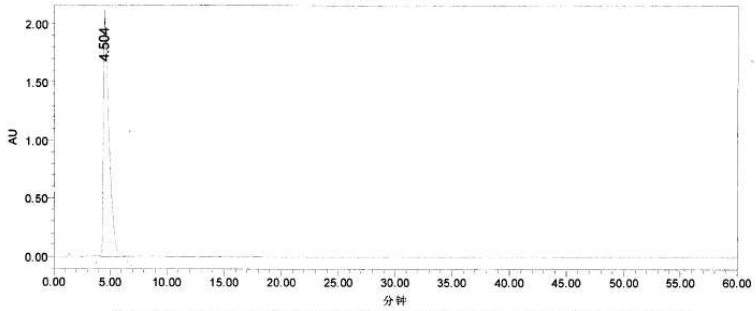
进样综合报告 报告

用户名称：System　　项目名称：Defaults

样品信息

样品名称:	ysb-Phe-ii	采集者:	System
样品类型:	未知	采集时间:	2007-6-22 19:57:56
瓶号:	1	采集方法组:	yangshb
进样次数:	1	处理日期:	2007-6-22 21:06:53
进样体积:	5.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 220.0 纳米

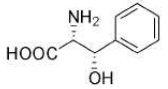
自动标尺色谱图



SampleName ysb-Phe-ii; Vial 1; Injection 1; Channel W2996 ; Date Acquired 2007-6-22 19:57:56

处理通道: PDA 220.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 220.0 纳米	4.504	70949671	100.00	2060226



5f

报告方法：进样综合报告　　打印 21:07:31　　2007-6-22　　页码：1 (共计 1)

HPLC spectrum of the compound **4e**

Empower

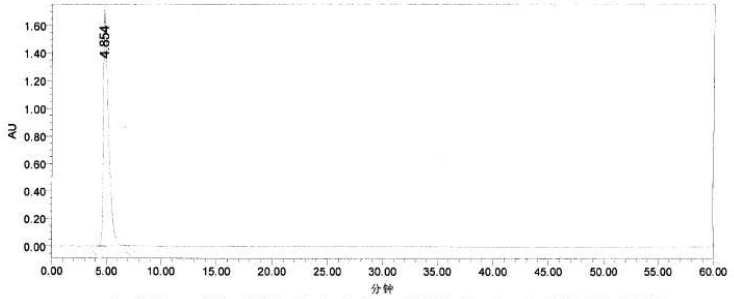
进样综合报告 报告

用户名称: System　　项目名称: Defaults

样品信息

样品名称:	ysb-Phe-i	采集者:	System
样品类型:	未知	采集时间:	2007-6-22 17:20:09
瓶号:	1	采集方法组:	yangshb
进样次数:	2	处理日期:	2007-6-22 21:04:45
进样体积:	5.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch1
样品组名称:		处理通道注释:	PDA 220.0 纳米

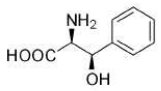
自动标尺色谱图



SampleName ysb-Phe-i; Vial 1; Injection 2; Channel W2996 ; Date Acquired 2007-6-22 17:20:09

处理通道: PDA 220.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 220.0 纳米	4.854	55511109	100.00	1674199



4e

报告方法: 进样综合报告　　打印 21:05:43　　2007-6-22　　页码: 1 (共计 1)

HPLC spectrum of the compound **IVb**

Empower

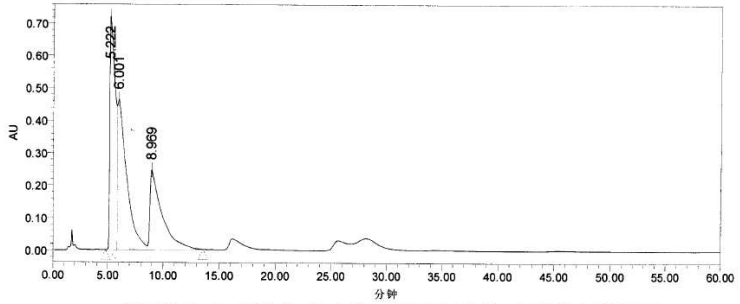
进样综合报告 报告

用户名称: System　　项目名称: liuxia

样品信息

样品名称:	y-f-x	采集者:	System
样品类型:	未知	采集时间:	2007-9-17 16:09:57
瓶号:	1	采集方法组:	yangshb
进样次数:	1	处理日期:	2007-9-17 19:29:41
进样体积:	10.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch20
样品组名称:		处理通道注释:	PDA 254.0 纳米

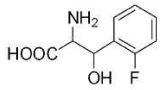
自动标尺色谱图



SampleName y-f-x; Vial 1; Injection 1; Channel W2996 ; Date Acquired 2007-9-17 16:09:57

处理通道: PDA 254.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	5.222	24838564	35.54	723637
2	PDA 254.0 纳米	6.001	26917813	38.51	463043
3	PDA 254.0 纳米	8.969	18138729	25.95	244832



IVb

报告方法: 进样综合报告　　打印 19:30:07　　2007-9-17　　页码: 1 (共计 1)

HPLC spectrum of the compound **4f**

Empower

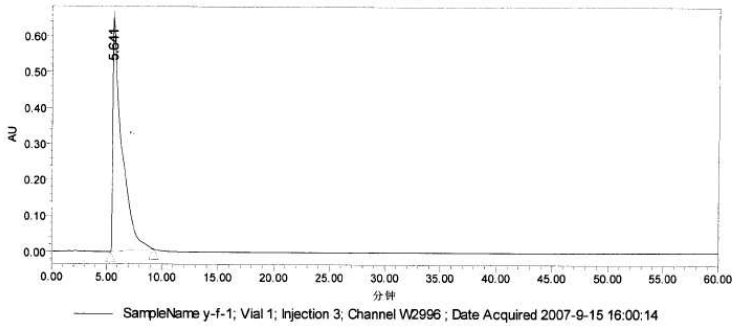
进样综合报告 报告

用户名称: System　　项目名称: liuxia

样品信息

样品名称:	y-f-1	采集者:	System
样品类型:	未知	采集时间:	2007-9-15 16:00:14
瓶号:	1	采集方法组:	yangshb
进样次数:	3	处理日期:	2007-9-17 19:11:18
进样体积:	10.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	WvIn Ch19
样品组名称:		处理通道注释:	PDA 254.0 纳米

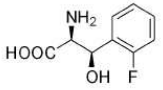
自动标尺色谱图



SampleName y-f-1; Vial 1; Injection 3; Channel W2996 ; Date Acquired 2007-9-15 16:00:14

处理通道: PDA 254.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	5.641	36467964	100.00	652906



4f

报告方法: 进样综合报告　　打印 19:11:33　　2007-9-17　　页码: 1 (共计 1)

HPLC spectrum of the compound **5g**

Empower

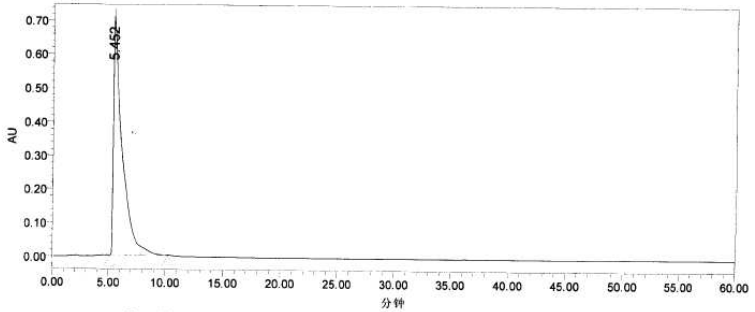
进样综合报告 报告

用户名称: System　　项目名称: liuxia

样品信息

样品名称:	y-f-2	采集者:	System
样品类型:	未知	采集时间:	2007-9-17 19:19:43
瓶号:	1	采集方法组:	yangshb
进样次数:	3	处理日期:	2007-9-17 20:25:26
进样体积:	10.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch21
样品组名称:		处理通道注释:	PDA 254.0 纳米

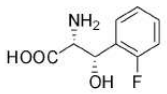
自动标尺色谱图



SampleName y-f-2; Vial 1; Injection 3; Channel W2996 ; Date Acquired 2007-9-17 19:19:43

处理通道: PDA 254.0 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	5.452	37763132	100.00	710510



5g

报告方法: 进样综合报告　　打印 20:25:46　　2007-9-17　　页码: 1 (共计 1)

HPLC spectrum of the compound **IVc**

Empower

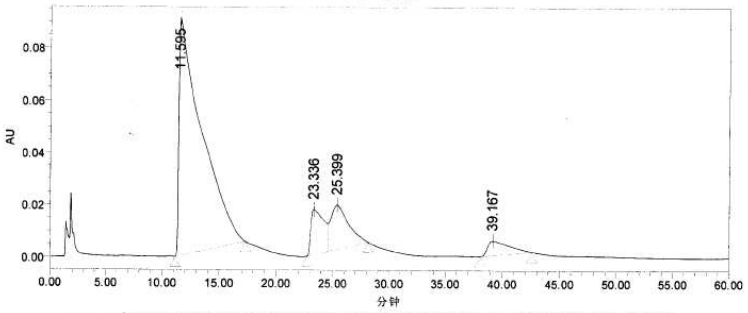
进样综合报告 报告

用户名称：System　　项目名称：liuxia

样品信息

样品名称：	y-cl-x	采集者：	System
样品类型：	未知	采集时间：	2007-9-17 17:50:04
瓶号：	1	采集方法组：	yangshb
进样次数：	2	处理日期：	2007-9-17 19:15:54
进样体积：	10.00 ul	处理方法：	20061123_1
运行时间：	60.0 Minutes	通道名称：	Wvln Ch10
样品组名称：		处理通道注释：	PDA 231.6 纳米

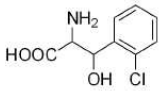
自动标尺色谱图



SampleName y-cl-x; Vial 1; Injection 2; Channel W2996 ; Date Acquired 2007-9-17 17:50:04

处理通道: **PDA 231.6** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 231.6 纳米	11.595	12527758	76.24	90801
2	PDA 231.6 纳米	23.336	1321283	8.04	17173
3	PDA 231.6 纳米	25.399	1884732	11.47	16921
4	PDA 231.6 纳米	39.167	699148	4.25	5464



IVc

报告方法：进样综合报告　　打印 19:16:11　2007-9-17　　页码：1 (共计 1)

HPLC spectrum of the compound **4g**

Empower

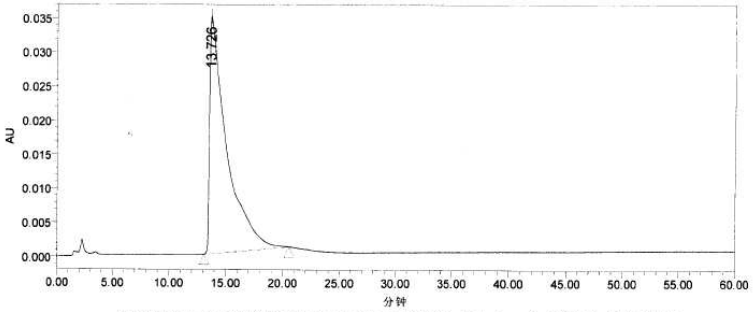
进样综合报告 报告

用户名称: System　　项目名称: liuxia

样品信息

样品名称:	y-cl-1	采集者:	System
样品类型:	未知	采集时间:	2007-9-15 10:40:57
瓶号:	1	采集方法组:	yangshb
进样次数:	1	处理日期:	2007-9-17 18:55:45
进样体积:	10.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wln Ch10
样品组名称:		处理通道注释:	PDA 254.0 纳米

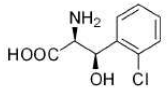
自动标尺色谱图



SampleName y-cl-1; Vial 1; Injection 1; Channel W2996 ; Date Acquired 2007-9-15 10:40:57

处理通道: **PDA 254.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	13.726	3602895	100.00	34850



4g

报告方法: 进样综合报告　　打印 18:56:26　　2007-9-17　　页码: 1 (共计 1)

HPLC spectrum of the compound **5h**

Empower

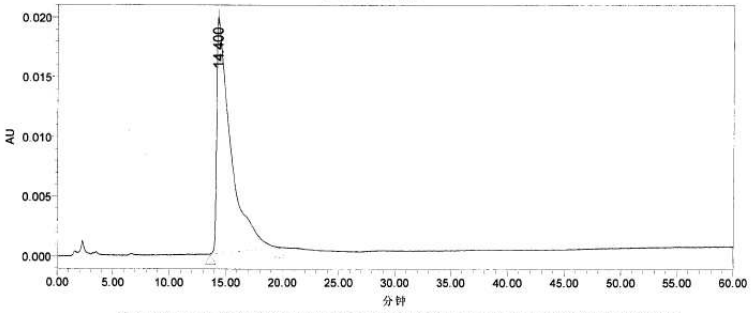
进样综合报告 报告

用户名称： System　　项目名称： liuxia

样品信息

样品名称:	y-cl-2	采集者:	System
样品类型:	未知	采集时间:	2007-9-15 11:43:35
瓶号:	1	采集方法组:	yangshb
进样次数:	2	处理日期:	2007-9-17 19:07:57
进样体积:	10.00 ul	处理方法:	20061123_1
运行时间:	60.0 Minutes	通道名称:	Wvln Ch15
样品组名称:		处理通道注释:	PDA 254.0 纳米

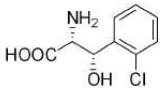
自动标尺色谱图



SampleName y-cl-2; Vial 1; Injection 2; Channel W2996 ; Date Acquired 2007-9-15 11:43:35

处理通道: **PDA 254.0** 纳米

	处理通道	保留时间 (分钟)	面积	% 面积	峰高
1	PDA 254.0 纳米	14.400	1700943	100.00	19755



5h

报告方法： 进样综合报告　　打印 19:09:04　　2007-9-17　　页码： 1 (共计 1)