Supporting Information

Unified Enantioselective Total Syntheses of (-)-Scholarisine G, (+)-Melodinine E, (-)-Leuconoxine and (-)-Mersicarpine

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1 . General Experimental Details

The solvents used were dried by distillation over the drying agents indicated in parentheses and were transferred under argon: THF (Na-benzophenone), diethyl ether (Na-benzophenone), dichloromethane (CaH_2). Anhydrous DMF was purchased from Acros Organics and stored under argon. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

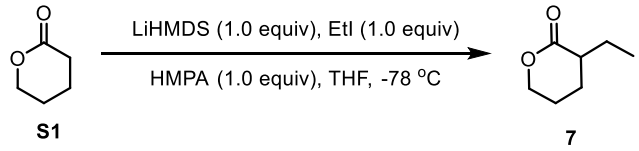
Proton (^1H), and Carbon NMR (^{13}C) were recorded at 400 MHz and 100 MHz NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} and G/UV_{365} plates. Visualization was accomplished with short wave UV light (254 nm and/or 365 mm) and/or phosphomolybdic acid or p-anisaldehyde stain or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

High-resolution mass spectra (HRMS) were recorded on Shimadzu LCMS-IT-TOF mass spectrometer. Enantiomeric excesses of compounds were determined by High performance liquid chromatography (HPLC) using a Daicel CHIRALPAK IG column (0.46 cm ×25 cm). Optical rotations were recorded on a Rudolph Autopol I polarimeter .

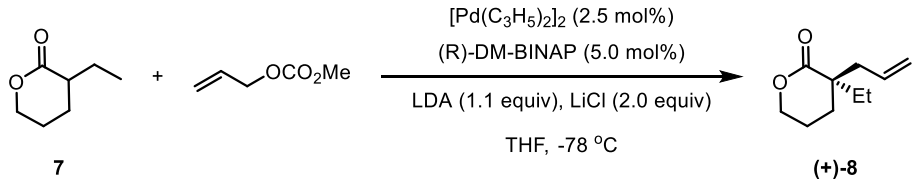
2 . Experimental Procedures

3-ethyltetrahydro-2H-pyran-2-one (7)[1]



To a solution of **LiHMDS** (1.3 M in THF, 17.0 mL, 22.1 mmol, 1.0 equiv) in THF (20 mL) was added **delta-Valerolactone (S1)** (2.0 mL, 22.1 mmol, 1.0 equiv) dropwise under argon at -78 °C. After stirring for 30 min, **HMPA** (3.8 mL, 22.1 mmol, 1.0 equiv) and **Iodoethane** (1.7 mL, 22.1 mmol, 1.0 equiv) were added and the mixture was stirred for an additional 3 h at same temperature. Then quenched by sat. aq NH_4Cl at -78 °C. The reaction was moved to room temperature, and the layers were separated. The aqueous layer was extracted with ether (3 x 20 mL) and the organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure no more than 35 °C. The resulting residue was purified via flash chromatography [PE (boiling range 30-60 °C)/TBME = 10/1) to afford **lactone (7)** (1.7 g, 63% yield) as a clear oil: R_f = 0.5 (PE/EA = 4/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.36 – 4.23 (m, 2H), 2.44 – 2.36 (m, 1H), 2.14 – 2.04 (m, 1H), 1.98 – 1.81 (m, 3H), 1.58 – 1.49 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 68.4, 41.0, 24.3, 24.2, 22.1, 11.3.

(*R*)-3-allyl-3-ethyltetrahydro-2H-pyran-2-one [(+)-8][1]

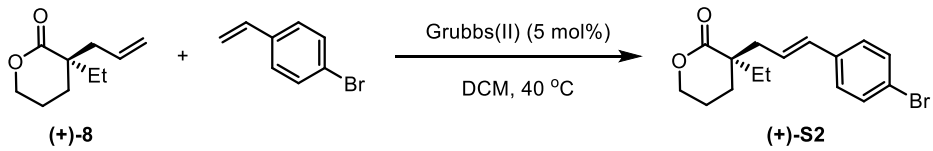


3-ethyltetrahydro-2H-pyran-2-one (**7**) (128 mg, 1.0 mmol, 1.0 equiv), **LiCl** (84 mg, 2.0 mmol, 2.0 equiv), and THF (5.0 mL) were added to a dry Schlenk tube under argon atmosphere. **LDA** (2.0 M in THF, 0.9 mL, 1.1 mmol, 1.1 equiv) was then added dropwise and the contents were stirred for 0.5 h at –78 ℃. In a separate flask, **$[Pd(C_3H_5)Cl]_2$** (9 mg, 0.025 mmol, 2.5 mol%) and ligand **(*R*)-DM-BINAP** (36.7 mg, 0.05 mmol, 5.0 mol%) were dissolved in THF (3.0 mL) under argon atmosphere and

stirred at room temperature for 0.5 h, which was then added to the above enolate solution at –78 ℃, followed by the addition of respective **allyl methyl carbonate** (0.2 mL, 1.75 mmol, 1.1 equiv). The resulting mixture was stirred at –78 ℃. After completion (monitored by TLC, 2 h), the reaction mixture was quenched by sat. aq NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried (Na_2SO_4) and the solvent was removed under reduced pressure. The residue was purified via column chromatography (PE/EA = 15/1) to afford the desired chiral lactone **(+)-8** (120 mg, 72 %,) as a pale yellow oil: R_f = 0.56 (PE/EA = 4/1); $[\alpha]_D$ +7.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CDCl3) δ 5.84 – 5.69 (m, 1H), 5.16 – 5.09 (m, 2H), 4.31 – 4.28 (m, 2H), 2.54 (dd, J = 13.6, 6.7 Hz, 1H), 2.20 (dd, J = 13.6, 8.1 Hz, 1H), 1.89 – 1.73 (m, 5H), 1.63 – 1.49 (m, 1H), 0.93 (t, J = 7.5 Hz, 3H); 13C NMR (100 MHz, CDCl3) δ 175.5, 133.6, 118.9, 70.1, 46.3, 43.6, 32.2, 28.6, 21.3, 8.8; HRMS–ESI (m/z) calcd for $C_{10}H_{16}O_2$ $[M+H]^+$: 169.1223, found 169.1221.

For determination of ee.

(*R*,*E*)-3-(3-(4-bromophenyl)allyl)-3-ethyltetrahydro-2H-pyran-2-one [(+)-S2]



(+)-8 (+)-S2

Grubbs catalyst II (13 mg, 0.015 mmol, 5 mol%) was added to a dry Schlenk tube under argon atmosphere. DCM (5 mL), **1-bromo-4-vinylbenzene** (108 mg, 0.6 mmol, 2.0 equiv) and **(+)-8** (50 mg, 0.3 mmol, 1.0 equiv) were then added sequentially and the contents were heating at 45 ℃. After 20 h, the solvent was evaporated under reduced pressure. Purification of the residual product by silica gel chromatography (PE/EA = 10:1) afforded **(+)-S2** (60 mg, 63%, with 89% ee) as a pale yellow oil: The enantiomeric excess of **S2** was determined by HPLC (DAICEL-CHIRALCEL-IG-H, hexane-*i*-PrOH = 90:10, flow rate = 0.5 mL/min, t+ = 17.7 min, t– = 19.3 min); R_f = 0.23 (PE/EA = 8/1); $[\alpha]_D$ +13.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.15 (dt, *J* = 15.5, 7.5 Hz, 1H), 4.33 – 4.23 (m, 2H), 2.68 (dd, *J* = 13.6, 6.7 Hz, 1H), 2.32 (dd, *J* = 13.8, 8.2 Hz, 1H), 1.89 – 1.78 (m, 5H), 1.65 – 1.56 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 136.0, 132.6, 131.6 (2C), 127.7 (2C), 126.1, 121.0,

70.1, 46.7, 42.8, 32.4, 28.9, 21.3, 8.8; HRMS–ESI (m/z) calcd for $C_{16}H_{19}O_2Br$ [M +Na]$^+$: 345.0461, found 345.0460.

HPLC for Measuring Enatiomeric Excess

The enantiomeric excess of **S2** was determined by HPLC (DAICEL-CHIRALCEL-IG-H, hexane-*i*-PrOH = 90:10, flow rate = 0.5 mL/min, t+ = 17.7 min, t– = 19.3 min)

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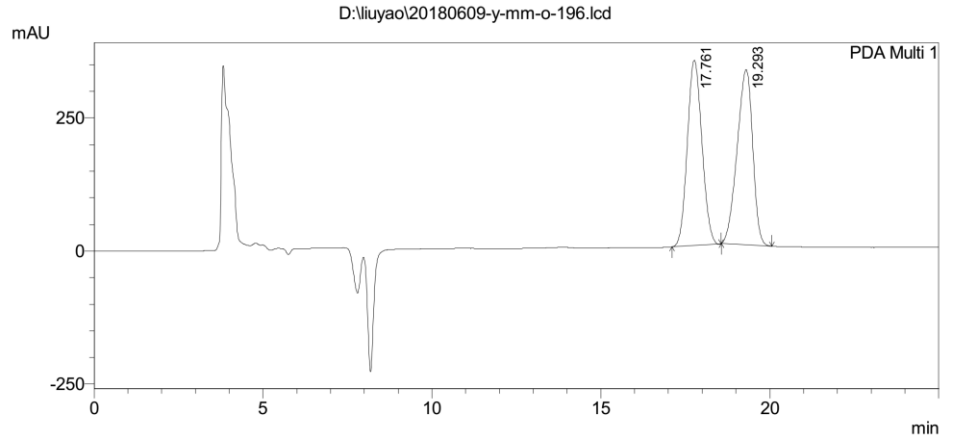

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PDA Ch1 214nm 4nm

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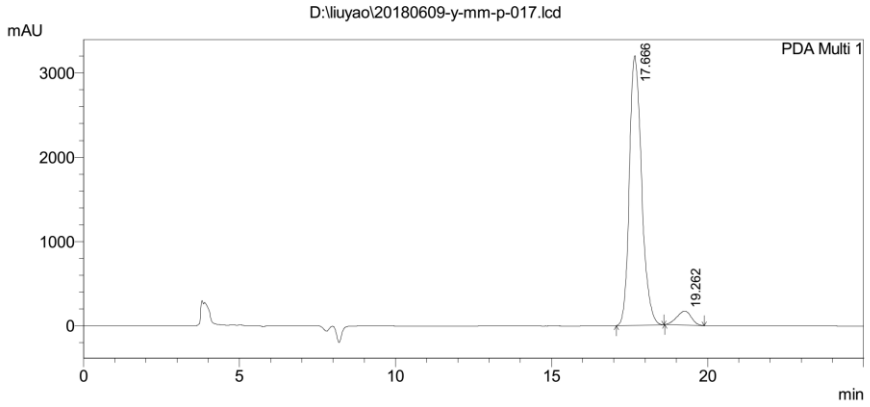

PeakTable

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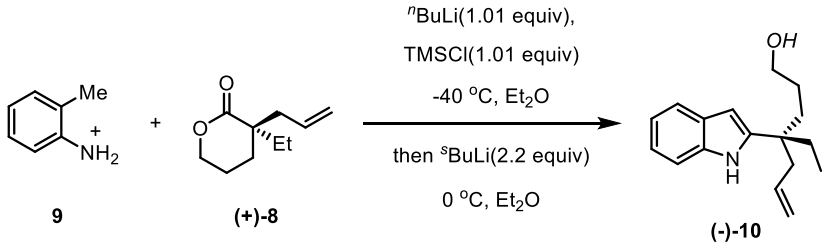
(*R*)-4-ethyl-4-(1H-indol-2-yl)hept-6-en-1-ol [(-)-10][2,3]

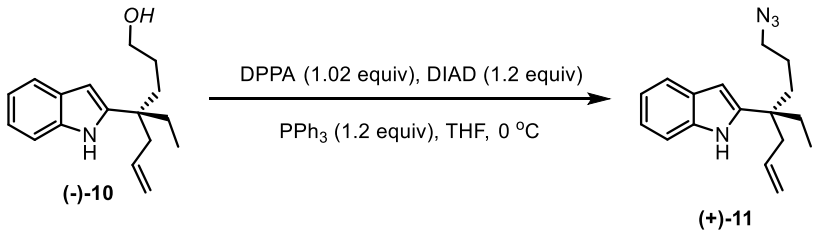


9 **(+)-8** **(-)-10**

To a solution of **o-toluidine (9)** (0.5 mL, 4.69 mmol, 1.0 equiv) in ether (5 mL) was added ***n*-butyllithium** (2.5 M in hexanes, 1.9 mL, 4.74 mmol, 1.01 equiv) dropwise under argon at -40 °C and stirred for 30 min. **Chlorotrimethylsilane (TMSCl)** (0.6 mL, 4.74 mmol, 1.01 equiv) was added and then warmed to 0 ℃ over 30 min. The resulting off-white slurry was treated with ***s*-butyllithium** (1.3 M in cyclohexane, 7.6 mL, 9.85 mmol, 2.1 equiv). After stirring for 30 min, the pale yellow suspension was treated with a solution of **lactone (+)-10** (336 mg, 2.0 mmol, 0.42 equiv.) in freshly distilled ether (3 mL) via syringe and stirred for 10 min. Then quenching with saturated ammonium chloride (50 mL) and stirred for 30 min., the mixture was extracted with EA (3×100 mL). The combined organic extract was washed with brine (100 mL), dried over Na_2SO_4 and concentrated in vacuo to a yellow oily residue. Flash column

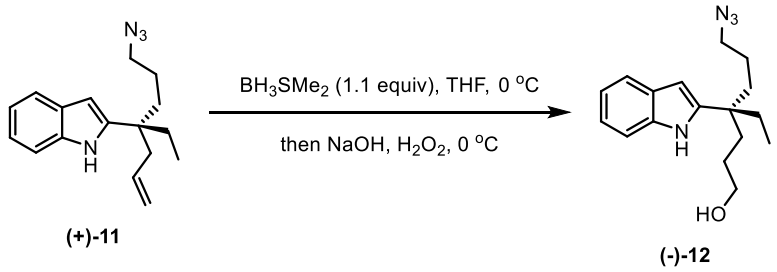
chromatography (PE/EA 4:1) afforded **(-)-26** (430 mg, 85 %) as a pale yellow oil: R_f = 0.23 (PE/EA = 4/1); $[\alpha]_D$ -18.5 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.4 Hz, 1H), 6.30 (s, 1H), 5.79 – 5.60 (m, 1H), 5.19 – 4.98 (m, 2H), 3.55 (t, J = 6.3 Hz, 2H), 2.50 – 2.48 (m, 2H), 1.74 – 1.71 (m, 4H), 1.61 (s, 1H), 1.48 – 1.33 (m, 2H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 135.8, 134.1, 128.3, 121.0, 119.8, 119.4, 117.7, 110.4, 100.3, 63.1, 41.3, 40.2, 33.0, 29.6, 26.9, 7.9; HRMS–ESI (m/z) calcd for $C_{17}H_{23}NO$ $[M-H]^-$: 256.1707, found 256.1709.

(*R*)-2-(7-azido-4-ethylhept-1-en-4-yl)-1H-indole [(+)-11]



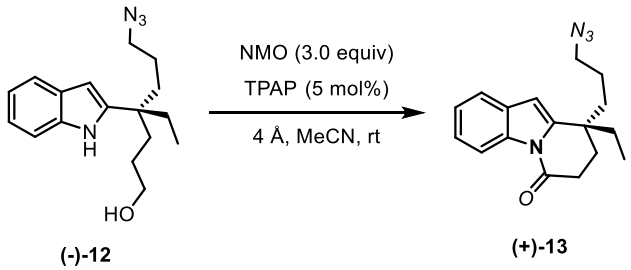
Diisopropyl azodicarboxylate (DIAD) (714 μL, 3.63 mmol, 1.2 equiv) was added under argon atmosphere to a stirred and cooled (0 ℃) solution of **(-)-10** (778 mg, 3.02 mmol, 1.0 equiv) and **triphenylphosphine** (951 mg,3.63 mmol, 1.2 equiv) in anhydrous THF (15 mL). The resulting solution was stirred for 10 minutes and before **diphenylphosphoryl azide (DPPA)** (849 mg, 3.08 mmol, 1.02 equiv) was added. The resulting solution was stirred another 6 h at 0 ℃. The reaction was concentrated directly under vacuum to afford a yellow oil, which was purified with silica gel chromatography (PE/EA = 30/1) to give **(+)-11** as a pale yellow oil (836 mg, 98%): R_f = 0.35 (PE/EA = 16/1); $[\alpha]_D$ +14.2 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.15 (t, *J* = 7.1 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.31 (s, 1H), 5.79 – 5.57 (m, 1H), 5.24 – 5.00 (m, 2H), 3.22 (t, *J* = 6.6 Hz, 2H), 2.49 (d, *J* = 7.1 Hz, 3H), 1.79 – 1.69 (m, 4H), 1.52 – 1.40 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 135.8, 133.8, 128.3, 121.2, 119.9, 119.6, 118.0, 110.4, 100.5, 51.9, 41.3, 40.2, 34.1, 29.6, 23.3, 7.9; HRMS–ESI (m/z) calcd for $C_{17}H_{22}N_4$ $[M+HCOO]^-$: 327.1826, found 327.1824.

(*R*)-7-azido-4-ethyl-4-(1H-indol-2-yl)heptan-1-ol [(-)-12]



To a solution of **(+)-11** (500 mg, 1.77 mmol, 1.0 eq.) in anhydrous THF (16 mL) was added dropwise **BH_3·SMe_2** (2.0 M in THF, 1.0 mL, 1.95 mmol, 1.1 equiv.) at 0 ℃ under argon atmosphere. The mixture was stirred for 2 h at 0 ℃ before a mixture of aqueous solution of **NaOH** (3 N, 1.8 mL, 5.31 mmol, 3.0 equiv) and **H_2O_2** (30% , 0.6 mL, 5.31 mmol, 3.0 equiv) was added. After it was stirred for another 30 min, the mixture was extracted with EA, washed with brine, and dried, and the solvents were removed in vacuo and the crude product was purified with column chromatography (PE/EA = 4/1→2/1) to give **(-)-12** as a colorless oil (377 mg, 71%): R_f = 0.40 (PE/EA = 2/1); $[\alpha]_D$ -21.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.13 (td, *J* = 8.0, 7.6, 1.4 Hz, 1H), 7.08 (td, *J* = 7.4, 1.2 Hz, 1H), 6.29 (d, *J* = 2.1 Hz, 1H), 3.57 (t, *J* = 6.3 Hz, 2H), 3.23 (t, *J* = 6.6 Hz, 2H), 1.77 – 1.71 (m, 7H), 1.47 – 1.33 (m, 5H), 0.79 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 135.8, 128.3, 121.1, 119.9, 119.5, 110.5, 100.4, 63.0, 51.9, 41.0, 33.7, 32.5, 28.8, 26.8, 23.3, 7.8; HRMS–ESI (m/z) calcd for $C_{17}H_{24}N_4O$ $[M-H]^-$: 299.1877, found 299.1875.

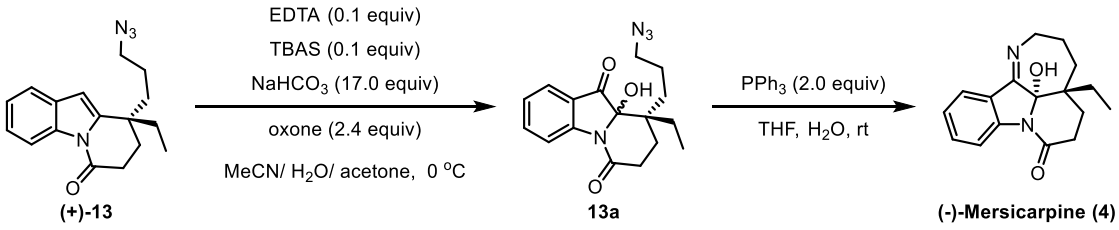
(*R*)-9-(3-azidopropyl)-9-ethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one [(+)-13][4]



To a solution of the enriched mixture containing **alcohol (-)-12** (400 mg, 1.33 mmol, 1.0 equiv), **4-methylmorpholine N-oxide (NMO)** (468 mg, 4.0 mmol, 3.0 equiv)

and activated powdered 4Å molecular sieves (800 mg) in anhydrous acetonitrile (30 mL) were added **tetrapropylammonium perruthenate (TPAP)** (23 mg, 0.07 mmol, 5 mol%) at room temperature until consumption of the **substrate (-)-12** (monitored by TLC, 8 h). The filtrate was concentrated under reduced pressure and the residue was purified by flash column chromatography (PE/EA = 50/1→20/1) to afford **(+)-13** as a colorless oil (268 mg, 68 %): R_f = 0.37 (PE/EA = 8/1); $[\alpha]_D$ +19.2 (c 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.33 – 7.23 (m, 2H), 6.32 (s, 1H), 3.29 (qt, *J* = 12.4, 6.5 Hz, 2H), 2.87 (t, *J* = 6.7 Hz, 2H), 1.99 (t, *J* = 6.7 Hz, 2H), 1.87 – 1.69 (m, 4H), 1.68 – 1.51 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.1, 144.0, 135.2, 129.5, 124.2, 123.9, 119.8, 116.5, 105.1, 63.1, 37.4, 32.9, 30.3, 30.0, 29.9, 26.9, 8.0; HRMS–ESI (m/z) calcd for $C_{17}H_{20}N_4O$ $[M+H]^+$: 297.1710, found 297.1707.

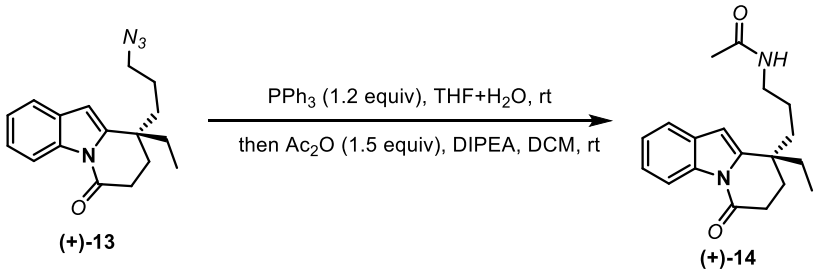
(-)-Mersicarpine (4)



Compound (+)-13 (30 mg, 0.1 mmol, 1.0 equiv) was dissolved in a mixture of acetonitrile (2 mL), water (1 mL) and acetone (2 mL). **Tetrabutylammonium hydrogen sulfate (TBAS)** (3.0 mg, 0.009 mmol, 0.09 equiv), **sodium bicarbonate** (139 mg, 1.7 mmol, 17.0 equiv) and **disodium ethylenediaminetetraacetic acid (EDTA)** (3.0 mg, 0.009 mmol, 0.09 equiv) were then added and the mixture was cooled to 0 ℃. A solution of **oxone** (150 mg, 0.243 mmol, 2.4 equiv) in water (2 mL) was added dropwise over 15 min with vigorous stirring. After 24 hours at same temperature, the reaction mixture was diluted with EA, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude **13a** as a brown solid, which was used directly in the next step without purification. To a solution of crude **13a** in THF (3.0 mL) and water (0.2 mL), **triphenylphosphine** (106 mg, 0.405 mmol, 2.0 equiv) was added at room temperature about string for 2 h. The reaction was concentrated directly under vacuum to afford a yellow oil, which was purified with silica gel

chromatography (PE/EA = 3/1) to give **(-)-Mersicarpine** as a white solid (18 mg, 64%): R_f = 0.35 (PE/EA = 2/1); $[\alpha]_D$ -18.5 (*c* 0.32, $CHCl_3$), lit.[5] $[\alpha]_D$ -18 (*c* 0.28, $CHCl_3$), lit.[6] $[\alpha]_D$ -18.3 (*c* 0.710, $CHCl_3$), lit.[7] $[\alpha]_D$ -20.4 (*c* 1.0, $CHCl_3$), lit.[8] $[\alpha]_D$ -22.0 (*c* 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 3.93 – 3.78 (m, 2H), 2.59 (ddd, *J* = 18.4, 9.6, 3.3 Hz, 1H), 2.44 – 2.35 (m, 1H), 2.10 – 2.02 (m, 1H), 1.96 – 1.85 (m, 1H), 1.77 – 1.72 (m, 1H), 1.70 – 1.62 (m, 3H), 1.34 – 1.28 (m, 1H), 1.16 – 1.07 (m, 1H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 169.0, 146.7, 133.5, 124.5, 124.4, 122.4, 116.9, 94.0, 50.6, 39.4, 34.5, 29.8, 29.3, 25.6, 23.1, 21.3, 7.0; HRMS–ESI (m/z) calcd for $C_{17}H_{20}N_2O_2$ $[M+H]^+$: 285.1598, found 285.1597.

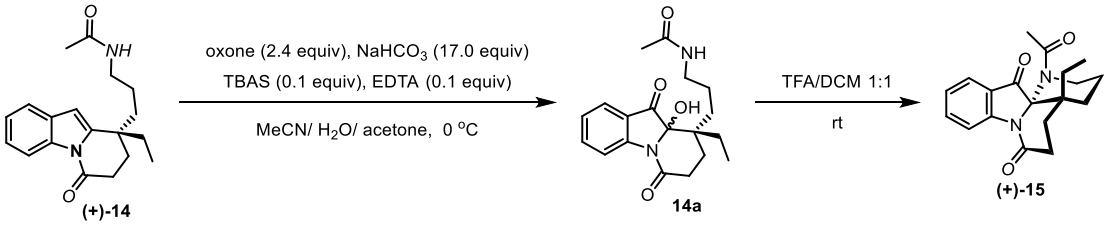
(*R*)-N-(3-(9-ethyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indol-9-yl)propyl)acetamide [(+)-14]



Triphenylphosphine (335 mg, 1.27 mmol, 1.2 equiv) was added to a solution of **(+)-13** (315 mg, 1.06 mmol, 1.0 equiv) in THF (5.0 mL) and water (0.5 mL) at room temperature. After completion (monitored by TLC), the reaction mixture was concentrated directly under vacuum to afford a crude amine. Then, to a solution of the crude amine in 4 mL DCM, Acetic anhydride (0.15 mL, 1.59 mmol, 1.5 equiv) and **N,N-Diisopropylethylamine (DIPEA)** (0.53 mL, 3.19 mmol, 3.0 equiv) were added and the mixture was stirred for 2 h at room temperature. The reaction was concentrated directly under vacuum to afford a yellow oil, which was purified with silica gel chromatography (PE/EA 1/1 to EA) to give **(+)-14** as a pale yellow oil (292 mg, 88%): R_f = 0.32 (PE/EA = 1/3); $[\alpha]_D$ +30.5 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.6 Hz, 1H), 7.48 (dd, *J* = 6.7, 1.8 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.29 (s, 1H), 5.54 (s, 1H), 3.28 – 3.15 (m, 2H), 2.84 (t, *J* = 6.7 Hz, 2H), 1.96 (t, *J* = 7.0 Hz, 2H), 1.93 (s, 3H), 1.82 – 1.67 (m, 4H), 1.63 – 1.49 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C

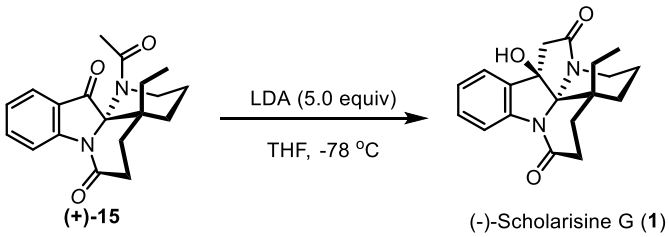
NMR (101 MHz, $CDCl_3$) δ 170.1, 169.0, 143.8, 135.2, 129.4, 124.3, 124.0, 119.8, 116.5, 105.1, 39.9, 37.4, 34.0, 30.3, 23.0, 24.2, 23.3, 8.0; HRMS–ESI (m/z) calcd for $C_{19}H_{24}N_2O_3$ [M +Na]$^+$: 335.1730, found 335.1724.

(4a*R*,13a*R*)-1-acetyl-4a-ethyl-2,3,4,4a,5,6-hexahydro-13H-indolo[1,2-i][1,8]naphthyridine-7,13(1H)-dione [(+)-14]



Compound (+)-14 (164 mg, 0.502 mmol, 1.0 equiv) was dissolved in a mixture of acetonitrile (8 mL), water (5 mL) and acetone (8 mL). **Tetrabutylammonium hydrogen sulfate (TBAS)** (17 mg, 0.05 mmol, 0.1 equiv), **sodium bicarbonate** (717 mg, 8.54 mmol, 17.0 equiv) and **disodium ethylenediaminetetraacetic acid (EDTA)** (17 mg, 0.05 mmol, 0.1 equiv) were then added and the mixture was cooled to 0 ℃. A solution of **oxone** (741 mg, 1.206 mmol, 2.4 equiv) in water (3 mL) was added dropwise over 15 min with vigorous stirring. After 24 hours at same temperature, the reaction mixture was diluted with EA, washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated to afford the crude **14a** as a brown solid, which was used directly in the next step without purification. To a stirred solution of the crude **14a** in CH_2Cl_2 (10 mL) was added TFA (10 mL) dropwise at room temperature. The reaction mixture was stirred at room temperature overnight. Solvent was removed under reduced pressure. The crude product was purified with silica gel chromatography (PE/EA = 3/2) to give **(+)-15** as a a white powder (106 mg, 65%); R_f = 0.24 (PE/EA = 2:1); $[\alpha]_D$ +70.5 (*c* 1.05, $CHCl_3$), lit.[7] $[\alpha]_D$ +75.1 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 8.5 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 3.85 – 3.74 (m, 1H), 3.63 (ddd, *J* = 13.2, 9.0, 4.1 Hz, 1H), 2.79 (ddd, *J* = 15.8, 10.6, 9.3 Hz, 1H), 2.50 (ddd, *J* = 15.8, 7.1, 3.2 Hz, 1H), 2.16 – 2.06 (m, 1H), 2.03 (s, 3H), 2.02 – 1.88 (m, 4H), 1.78 – 1.71 (m, 1H), 1.20 – 1.04 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 171.5, 169.0, 152.1, 136.8, 124.1, 123.8, 122.8, 117.1, 81.2, 43.9, 40.8, 30.9, 29.1, 28.2, 26.6, 24.1, 20.3, 7.1; HRMS–ESI (m/z) calcd for $C_{19}H_{22}N_2O_3$ [M +Na]$^+$: 349.1523, found 349.1526.

(-)-Scholarisine G (1)



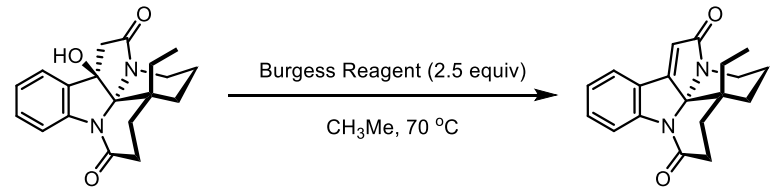
To a solution of **(+)-15** (130 mg, 0.4 mmol, 1.0 equiv) in THF (20 mL) was added **LDA** (2.0 M in THF, 1.0 mL, 2.0 mmol, 5.0 equiv) dropwise under argon at -78 °C. After completion (monitored by TLC), the reaction mixture was quenched by sat. aq NH_4Cl and extracted with EA and the organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography (PE/EA 4:1 to 3:2) to give **(-)-Scholarisine G (1)** (100 mg, 77%) as a white powder. Data for **(-)-Scholarisine G (1)**: R_f = 0.26 (PE/EA = 2:1); $[\alpha]_D$ -65.5 (*c* 0.95, $CHCl_3$), lit.[7] $[\alpha]_D$ -55.3 (*c* 1.0, $CHCl_3$), lit.[9] $[\alpha]_D$ -106.3 (*c* 1.0, $CHCl_3$), lit.[10] $[\alpha]_D$ -48 (*c* 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.56 (s, 1H), 2.90 (d, *J* = 16.6 Hz, 1H), 2.83 (d, *J* = 16.6 Hz, 1H), 2.67 – 2.56 (m, 2H), 2.26 (dd, *J* = 19.0, 6.0 Hz, 1H), 2.20 – 2.07 (m, 2H), 1.89 (td, *J* = 13.7, 4.0 Hz, 1H), 1.76 – 1.67 (m, 1H), 1.64 – 1.55 (m, 3H), 1.50 – 1.45 (m, 1H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 169.9, 141.5, 137.3, 129.8, 125.9, 123.0, 121.0, 90.7, 82.1, 42.3, 39.3, 37.0, 29.5, 27.4, 25.8, 22.7, 20.2, 7.1; HRMS–ESI (m/z) calcd for $C_{19}H_{22}N_2O_3$ $[M+Na]^+$: 349.1523, found 349.1519.

(-)-Scholarisine G ^{1}H NMR Wang (400 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Isolated (400 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Zhu (400 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Dai (800 MHz, $CDCl_3$)
7.72 (d, *J* = 7.9 Hz, 1H)	7.76 (d, *J* = 7.6 Hz, 1H)	7.72 (d, *J* = 7.6 Hz, 1H)	7.61 (d, *J* = 7.9 Hz, 1H)
7.32 (t, *J* = 7.7 Hz, 1H)	7.34 (t, *J* = 7.6 Hz, 1H)	7.32 (t, *J* = 7.6 Hz, 1H)	7.39 (d, *J* = 7.5 Hz, 1H)
7.28 (d, *J* = 7.5 Hz, 1H)	7.31 (d, *J* = 7.6 Hz, 1H)	7.27 (d, *J* = 7.6 Hz, 1H)	7.29 (t, *J* = 7.6 Hz, 1H)
7.15 (t, *J* = 7.2 Hz,	7.17 (t, *J* = 7.6 Hz,	7.14 (t, *J* = 7.6 Hz,	7.21 (t, *J* = 7.4 Hz,

1H)	1H)	1H)	1H)
3.89 – 3.83 (m, 1H)	3.92 (br s, 1H)	3.87 – 3.83 (m, 1H)	3.91 – 3.89 (m, 1H)
3.56 (s, 1H)	3.28 (br s, 1H, OH)	3.47 (br s, 1H, OH)	4.78 (brs, 1H)
2.90 (d, *J* = 16.6 Hz, 1H)	2.97 (d, *J* = 17 Hz, 1H)	2.88 (d, *J* = 16.8 Hz, 1H),	2.99 (d, *J* = 16.7 Hz, 1H)
2.83 (d, *J* = 16.6 Hz, 1H)	2.89 (d, *J* = 17 Hz, 1H)	2.81 (d, *J* = 16.8 Hz, 1H)	2.89 (d, *J* = 16.7 Hz, 1H),
2.67 – 2.56 (m, 2H)	2.73 (ddd, *J* = 19, 13, 6 Hz, 1H)	2.68 – 2.57 (m, 2H)	
	2.63 (td, *J* = 13, 3, 4 Hz, 1H)		2.53 (td, *J* = 12.7, 3.1 Hz, 1H)
2.26 (dd, *J* = 19.0, 6.0 Hz, 1H)	2.45 (dd, *J* = 19, 6 Hz, 1H)	2.34 (dd, *J* = 6.4, 18.8 Hz, 1H)	-
2.20 – 2.05 (m, 2H)	2.18 (m, 1H) 2.15 (m, 1H)	2.19 – 2.05 (m, 2H),	2.26 – 2.06 (m, 2H),
1.89 (td, *J* = 13.7, 4.0 Hz, 1H)	1.90 (dt, *J* = 13, 3.4 Hz, 1H)	1.90 (dt, *J* = 3.6, 13.6 Hz, 1H)	1.96 – 1.92 (m, 1H)
1.76 – 1.67 (m, 1H) 1.64 – 1.55 (m, 3H)	1.77 (dt, *J* = 14, 7.3 Hz, 1H)	1.76 – 1.54 (m, 4H)	1.79 (td, *J* = 13.6, 3.7 Hz, 1H)
	1.68 (m, 2H) 1.63 (m, 1H)		1.74 (dq, *J* = 14.7, 7.4 Hz, 1H) 1.62 – 1.56 (m, 2H),
1.50 – 1.45 (m, 1H)	1.50 (m, 1H)	1.49 – 1.46 (m, 1H)	1.44 – 1.42 (m, 1H)
			1.35 (dd, *J* = 14.1, 6.4 Hz, 1H),
0.89 (t, *J* = 7.4 Hz, 3H)	0.91 (t, *J* = 7.3 Hz, 3H)	0.90 (t, *J* = 7.2 Hz, 3H)	0.88 (t, *J* = 7.4 Hz, 3H),

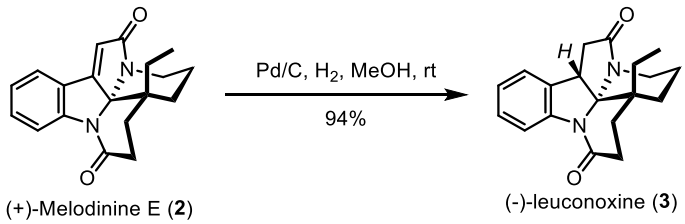
(-)-Scholarisine G ^{13}C NMR Wang (100 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Isolated (100 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Zhu (100 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Dai (100 MHz, $CDCl_3$)
173.6	173.6	173.6	174.4
169.9	170.0	170.0	170.0
141.5	141.3	141.5	141.0
137.3	137.4	137.3	138.4
129.8	129.4	129.9	129.3
125.9	125.6	125.9	126.4
123.0	122.9	123.0	123.5
121.0	120.7	120.9	122.0
90.7	90.4	90.7	91.0
82.1	81.9	82.1	82.2
42.3	42.2	42.3	42.3
39.3	39.1	39.3	39.3
-	-	-	
37.0	36.8	37.0	37.1
29.5	29.5	29.6	28.2
27.4	27.2	27.4	27.6
25.8	25.5	25.7	26.1
22.7	22.4	22.7	22.6
20.2	20.0	20.2	20.1
7.1.	6.9	7.1.	7.1

(+)-Melodinine E (2)



To a solution of **(-)-Scholarisine G (1)** (60 mg, 0.18 mmol, 1.0 equiv) in anhydrous acetonitrile (12 mL) was added **(methoxycarbonylsulfamoyl) triethylammonium hydroxide** (**Burgess reagent**, 107 mg, 0.45 mmol, 2.5 equiv). The reaction mixture was stirred 8 h at 70 ℃, before it was poured into EA (150 mL). The organic layer was washed with water, brine (20 mL), dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (PE/EA = 5:1) to give **(+)-Melodinine E (2)** (54 mg, 96%) as a white powder: R_f = 0.32 (PE/EA = 4:1); $[\alpha]_D$ +245.0 (*c* 0.45, $CHCl_3$), lit.[7, 12] $[\alpha]_D$ +250.8 (*c* 1.0, $CHCl_3$), lit.[11] $[\alpha]_D$ +304.0 (*c* 0.19, $CHCl_3$), lit.[7] $[\alpha]_D$ +250.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, CDCl3) δ 8.15 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.21 (s, 1H), 4.45 (ddd, *J* = 15.3, 11.7, 3.8 Hz, 1H), 3.21 (ddd, *J* = 15.4, 9.6, 6.2 Hz, 1H), 3.08 (td, *J* = 15.7, 6.2 Hz, 1H), 2.62 (ddd, *J* = 16.3, 5.3, 2.2 Hz, 1H), 2.13 – 1.98 (m, 2H), 1.84 – 1.61 (m, 3H), 1.44 (tt, *J* = 12.6, 6.4 Hz, 1H), 1.34 (dt, *J* = 14.4, 7.4 Hz, 1H), 1.09 (td, *J* = 13.5, 6.8 Hz, 1H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 173.6, 164.4, 148.8, 131.7, 124.5, 123.7, 121.7, 118.3, 116.1, 93.8, 44.7, 37.1, 34.3, 33.3, 30.6, 26.2, 16.9, 8.4; HRMS–ESI (m/z) calcd for $C_{19}H_{20}N_2O_3$ $[M+H]^+$: 309.1598, found 309.1593.

(-)-leuconoxine (3)



To a solution of **(+)-Melodinine E (2)** (20 mg, 0.065mmol) in MeOH (2.5 mL) was added Pd/C (7 mg, 0.007 mmol). The reaction mixture was stirred under an atmosphere of H2 (H2 balloon) for 2 h. The reaction mixture was filtered through a pad of celite, and washed with MeOH (20 mL). The filtrate was concentrated and the residue was purified by column chromatography (EtOAc) to give **(-)-leuconoxine (3)**

(18.5 mg) as a white solid in 92% yield: R_f = 0.40 (PE/EA = 2:1); $[\alpha]_D$ -87.0 (*c* 0.18, $CHCl_3$), lit.[7] $[\alpha]_D$ -81.1 (*c* 1.0, $CHCl_3$), lit.[12] $[\alpha]_D$ -87.7 (*c* 1.2, $CHCl_3$), lit.[13] $[\alpha]_D$ -88.0 (*c* 1.2, $CHCl_3$), lit.[14] $[\alpha]_D$ -80.0 (*c* 0.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 2H), 3.95 (d, *J* = 11.4 Hz, 1H), 3.82 (d, *J* = 7.3 Hz, 1H), 2.81 (dddd, *J* = 26.9, 19.9, 15.2, 6.7 Hz, 3H), 2.68 (d, *J* = 16.9 Hz, 1H), 2.49 (dd, *J* = 19.2, 5.8 Hz, 1H), 1.98 (td, *J* = 15.6, 8.6 Hz, 1H), 1.82 (ddt, *J* = 28.8, 14.1, 7.1 Hz, 2H), 1.69 – 1.56 (m, 4H), 1.44 – 1.30 (m, 1H), 0.92 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 171.0, 142.1, 135.2, 128.1, 125.7, 124.0, 120.3, 92.7, 42.1, 38.2, 37.73, 37.0, 29.6, 27.1, 26.7, 26.4, 20.2, 7.5; HRMS–ESI (m/z) calcd for $C_{19}H_{22}N_2O_2$ $[M+Na]^+$: 333.1573, found 333.1574.

3. References

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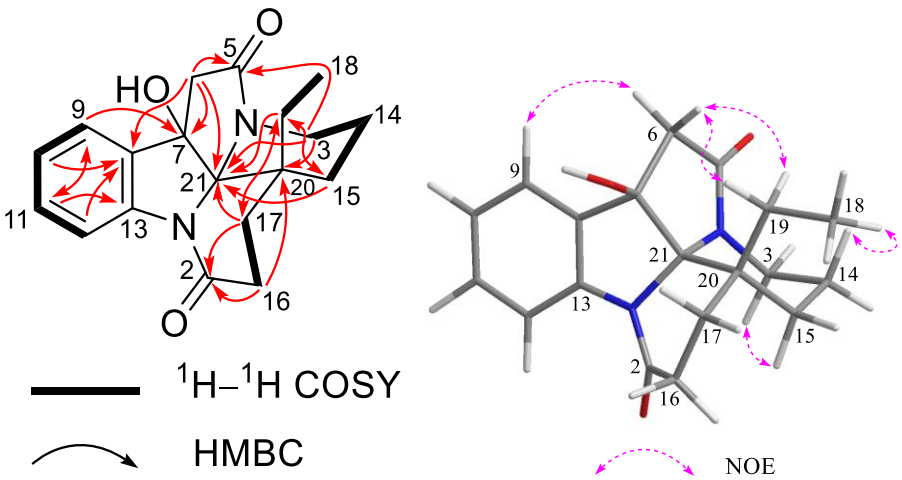
4. Discussion on the NMR Differences of Our Synthetic (-)-Scholarisine G with Other Samples

The NMR spectra of our synthetic sample matches well with that synthesized by Zhu (J. Am. Chem. Soc., 2013, 135, 19127, X-way provided), and is largely identical to those isolated by Kam (natural source, see: J. Nat. Prod., 2013, 76, 957, X-ray provided) and Luo (natural source, Planta Med., 2009, 75, 1537), but differs to some extent to those from the synthetic samples from Dai (Org. Lett., 2014, 16, 6216) and Tokuyama (Org. Lett., 2014, 16, 2526) and Liang (Org. Chem. Front., 2015, 2, 236). To further confirm the structure, some experiments were conducted and the discussion is provided below.

1) 2-D NMR analysis of our synthetic (-)Scholarisine G.

^{1}H-^{1}H COSY and HMBC demonstrated the right connection of the each atom. And NOE studies confirmed the right relative configuration of this compound.



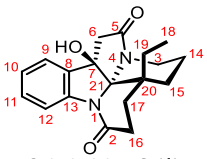
The numbering used is the biogenetic one proposed by LeMen and Taylor (Experientia 1965, 21, 508-510)

2) Comparison of our ^{1}H NMR, ^{13}C NMR with the ones from natural source (Kam's sample).

Kam conducted detailed NMR studies and also obtained the x-ray structure of Scholarisine G. Our above experiments allowed us to assign the individual signal to the corresponding carbon or hydrogen. The comparison of our spectra with Kam's showed that there is minor difference.

The maximum difference on ^{13}C NMR chemical shift is no more than 0.6 ppm (highlighted in red). The ^{1}H NMR also matches well with both the chemical shifts and coupling constants. The major difference is the shift of C-H on C16 (sensitive to acidity of NMR solvent), with a 0.25 ppm difference but similar coupling constant.

Chemical Shifts of ^{1}H NMR, ^{13}C NMR for Natural and Our Synthetic (-)-Scholarisine G



	our synthetic (600 MHz, $CDCl_3$)		isolated by Kam (400 MHz, $CDCl_3$)	
No*	δ_C	δ_H	δ_C	δ_H
2	173.5 (CO)	-	173.6 (C)	-
3	37.0 (CH2)	β 3.92 (m)	36.8 (CH2)	3.92 (br s)
		α 2.60 (m)		2.63 (td, *J* = 13, 3, 4 Hz)
5	169.8 (CO)	-	170.0 (C)	-
6	42.3 (CH2)	a 2.98 (d, *J* = 16.6 Hz)	42.2 (CH2)	2.97 (d, *J* = 17 Hz)
		b 2.90 (d, *J* = 16.6 Hz)		2.89 (d, *J* = 17 Hz)

7	82.2 (C)	-	81.9 (C)	-
8	137.3 (C)	-	137.4 (C)	-
9	123.0 (CH)	7.33 (d, *J* = 7.6 Hz)	122.9 (CH)	7.31 (d, *J* = 7.6 Hz)
10	126.0 (CH)	7.18 (t, *J* = 7.6 Hz)	125.6 (CH)	7.17 (t, *J* = 7.6 Hz)
11	130.0 (CH)	7.34 (t, *J* = 7.6 Hz)	129.4 (CH)	7.34 (t, *J* = 7.6 Hz)
12	121.1 (CH)	7.75 (d, *J* = 7.6 Hz)	120.7 (CH)	7.76 (d, *J* = 7.6 Hz)
13	141.4 (C)	-	141.3 (C)	-
14	20.1 (CH2)	β 1.61 (m)	20.0 (CH2)	1.63 (m)
		α 1.49 (m)		1.50 (m)
15	27.4 (CH2)	1.92 (td, *J* = 14.0, 3.3 Hz)	27.2 (CH2)	1.94 (dt, *J* = 13, 3.4 Hz)
		1.67 (m)		1.68 (m)
16	29.5 (CH2)	2.66 (ddd, *J* = 19.4, 13.2, 6.5 Hz)	29.5 (CH2)	2.73 (ddd, *J* = 19, 13, 6 Hz)
		2.20 (dd, *J* = 19.4, 6.5 Hz)		2.45 (dd, *J* = 19, 6 Hz)
17	25.9 (CH2)	2.14 (m)	25.5 (CH2)	2.18 (m)
		1.64 (m)		1.68 (m)
18	7.1 (CH3)	0.90 (t, *J* = 7.3 Hz)	6.9 (CH3)	0.91 (t, *J* = 7.3 Hz)
19	22.7 (CH2)	2.17 (m)	22.4 (CH2)	2.15 (m)
		1.78 (dt, *J* = 13.6, 7.1 Hz)		1.77 (dt, *J* = 14, 7.3 Hz)
20	39.3 (C)	-	39.1 (C)	-
21	90.7 (C)	-	90.4 (C)	-
OH		3.09 (br s)		3.28 (br s)

A detailed summary of the reported NMR spectrums were given below, including our sample, the isolated samples by Kam and Luo, the synthetic samples from Zhu, us, Liang, Tokuyama and Dai. From the table below, we can see there are indeed some discrepancies.

(-)-Scholarisine G ^{1}H NMR **Our's work** (600 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Isolated by Kam (400 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Isolated by Luo (400 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{1}H NMR Zhu (400 MHz, $CDCl_3$)	**Scholarisine G** ^{1}H NMR Liang (400 MHz, $CDCl_3$)	**Scholarisine G** ^{1}H NMR Dai (800 MHz, $CDCl_3$)	**Scholarisine G** ^{1}H NMR Tokuyama (600 MHz, $CDCl_3$)
7.75 (d, *J* = 7.6 Hz)	7.76 (d, *J* = 7.6 Hz, 1H)	7.82 (d, *J* = 7.6 Hz, 1H)	7.72 (d, *J* = 7.6 Hz, 1H)	7.60 (d, *J* = 7.6 Hz, 1 H)	7.61 (d, *J* = 7.9 Hz, 1H)	7.61 (d, *J* = 7.8 Hz, 1H)
7.34 (t, *J* = 7.6 Hz)	7.34 (t, *J* = 7.6 Hz, 1H)	7.40 (t, *J* = 7.6 Hz, 1H)	7.32 (t, *J* = 7.6 Hz, 1H)	7.39 (d, *J* = 7.2 Hz, 1 H)	7.39 (d, *J* = 7.5 Hz, 1H)	7.39 (d, *J* = 7.8 Hz1H)
7.33 (d, *J* = 7.6 Hz)	7.31 (d, *J* = 7.6 Hz, 1H)	7.37 (d, *J* = 7.6 Hz, 1H)	7.27 (d, *J* = 7.6 Hz, 1H)	7.27 (t, *J* = 8.0 Hz, 1 H)	7.29 (t, *J* = 7.6 Hz, 1H)	7.29 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H)
7.18 (t, *J* = 7.6 Hz)	7.17 (t, *J* = 7.6 Hz, 1H)	7.22 (t, *J* = 7.6 Hz, 1H)	7.14 (t, *J* = 7.6 Hz, 1H)	7.20 (t, *J* = 7.4 Hz, 1 H)	7.21 (t, *J* = 7.4 Hz, 1H)	7.21 (dd, *J* = 7.8, 7.8 Hz, 1H)
3.98 – 3.89 (m, 1H)	3.92 (br s, 1H)	3.98 (ddd, *J* = 13.6, 4.0, 2.4 Hz, 1H)	3.87 – 3.83 (m, 1H)	3.89 (d, *J* = 13.2 Hz, 1 H)	3.91 – 3.89 (m, 1H)	3.90 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H)
3.09 (br s, OH, 1H)	3.28 (br s, 1H, OH)	2.82 (s, 1H, OH)	3.47 (br s, 1H, OH)	4.81 (s, H, OH)	4.78 (brs, 1H, OH)	4.87 (br s, 1H, OH)
2.98 (d, *J* = 16.6 Hz, 1H)	2.97 (d, *J* = 17 Hz, 1H)	2.99 (d, *J* = 16.4 Hz, 1H)	2.88 (d, *J* = 16.8 Hz, 1H),	2.97 (d, *J* = 16.8 Hz, 1H)	2.99 (d, *J* = 16.7 Hz, 1H)	2.99 (d, *J* = 16.8 Hz, 1H)
2.90 (d, *J* = 16.6 Hz, 1H)	2.89 (d, *J* = 17 Hz, 1H)	2.96 (d, *J* = 16.4 Hz, 1H)	2.81 (d, *J* = 16.8 Hz, 1H)	2.87 (d, *J* = 16.4 Hz, 1 H)	2.89 (d, *J* = 16.7 Hz, 1H),	2.89 (d, *J* = 16.8 Hz, 1H)
2.70 – 2.57 (m, 2H),	2.73 (ddd, *J* = 19, 13, 6 Hz, 1H)	2.78 (m, 1H)	2.68-2.57 (m, 2H)	-	-	-

	2.63 (td, *J* = 13, 3, 4 Hz, 1H)	2.69 (m, 1H)		2.52 (t, *J* = 12.2 Hz, 1 H)	2.53 (td, *J* = 12.7, 3.1 Hz, 1H)	2.53 (ddd, *J* = 15.6, 6.3, 3.0 Hz, 1H), ,
2.23-2.09 (m, 3H),	2.45 (dd, *J* = 19, 6 Hz, 1H)	2.52 (dd, *J* = 18.8, 5.6 Hz, 1H)	2.34 (dd, *J* = 6.4, 18.8 Hz, 1H)	-	-	-
	2.18 (m, 1H) 2.15 (m, 1H)	2.22 (m, 1H) 2.16 (m, 1H)	2.19 – 2.11 (m, 2H)	2.29-2.13 (m, 2H)	2.26 – 2.17 (m, 2H),	2.25–2.18 (m, 2H)
1.97 – 1.87 (m, 1H),	1.94 (dt, *J* = 13, 3.4 Hz, 1H)	1.98 (m, 1H)	1.90 (dt, *J* = 3.6, 13.6 Hz, 1H)	1.95-1.87 (m, 1 H)	1.96 – 1.92 (m, 1H)	1.94 (dd, J = 13.8, 5.4 Hz, 1H)
1.78 (dt, *J* = 13.6, 7.1 Hz, 1H) 1.66-1.62 (m, 3H)	1.77 (dt, *J* = 14, 7.3 Hz, 1H) 1.68 (m, 2H) 1.63 (m, 1H)	1.83 (m, 1H) 1.76 (m, 1H) 1.73 (m, 1H) 1.69 (m, 1H)	1.76 – 1.54 (m, 4H)	1.82-1.71 (m, 2 H) 1.61-1.51 (m, 4 H)	1.79 (td, *J* = 13.6, 3.7 Hz, 1H) 1.74 (dq, *J* = 14.7, 7.4 Hz, 1H) 1.62 – 1.56 (m, 2H),	1.81–1.72 (m, 2H) 1.62–1.55 (m, 2H)
1.51-1.48 (m, 1H)	1.50 (m, 1H)	1.56 (m, 1H)	1.49 – 1.46 (m, 1H)	1.47-1.41 (m, 1 H)	1.44 – 1.42 (m, 1H)	1.45–1.42 (m, 1H)
	-	-	-	-	1.35 (dd, *J* = 14.1, 6.4 Hz, 1H)	1.35 (dd, J = 13.8, 5.4 Hz, 1H)
0.90 (t, *J* = 7.3 Hz)	0.91 (t, *J* = 7.3 Hz, 3H)	0.96 (t, *J* = 7.2 Hz, 3H);	0.90 (t, *J* = 7.2 Hz, 3H)	0.87 (t, *J* = 7.4, 3 H)	0.88 (t, *J* = 7.4 Hz, 3H),	0.88 (t, J = 7.8 Hz, 3H)
	-	-		-	-	0.79 (dd, J = 18.6, 3.0 Hz, 1H)

(-)-Scholarisine G ^{13}C NMR Our's work (126 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Isolated by kam (100 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Isolated by Lou (100 MHz, $CDCl_3$)	**(-)-Scholarisine G** ^{13}C NMR Zhu (100 MHz, $CDCl_3$)	**Scholarisine G** ^{13}C NMR Liang (100 MHz, $CDCl_3$)	**Scholarisine G** ^{13}C NMR Dai (100 MHz, $CDCl_3$)	**Scholarisine G** ^{13}C NMR Tokuyama (150 MHz, $CDCl_3$)
173.5	173.6	173.2	173.6	174.2	174.4	173.9
169.8	170.0	169.6	170.0	169.9	170.0	169.8
141.4	141.3	141.3	141.5	140.9	141.0	141.0
137.3	137.4	136.9	137.3	138.3	138.4	137.9
130.0	129.4	129.9	129.9	129.2	129.3	129.4
126.0	125.6	125.8	125.9	126.2	126.4	126.2
123.0	122.9	122.7	123.0	123.3	123.5	123.1
121.1	120.7	120.8	120.9	121.9	122.0	121.6
90.7	90.4	90.5	90.7	90.9	91.0	90.8
82.2	81.9	82.0	82.1	82.1	82.2	82.1
42.3	42.2	42.1	42.3	42.1	42.3	42.2
39.3	39.1	39.1	39.3	39.1	39.3	39.2
37.0	36.8	36.8	37.0	37.0	37.1	36.9
29.5	29.5	29.5	29.6	28.1	28.2	28.5
27.4	27.2	27.2	27.4	27.5	27.6	27.5

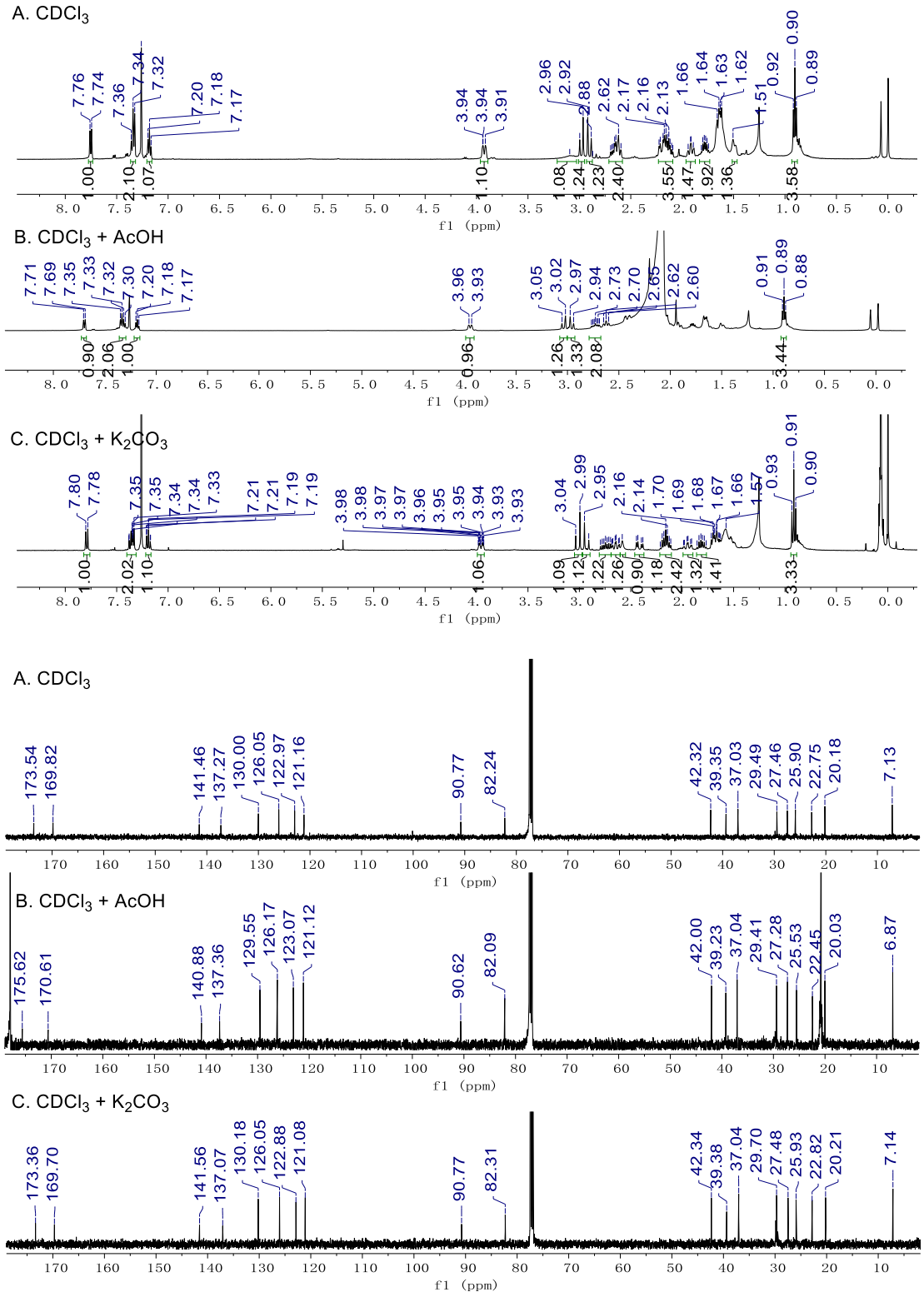
25.9	25.5	25.6	25.7	25.9	26.1	25.9
22.7	22.4	22.5	22.7	22.5	22.6	22.6
20.1	20.0	20.0	20.2	20.0	20.1	20.0
7.1	6.9	6.9	7.1.	6.9	7.1	6.9

3) Explanation on the NMR difference from different sources.

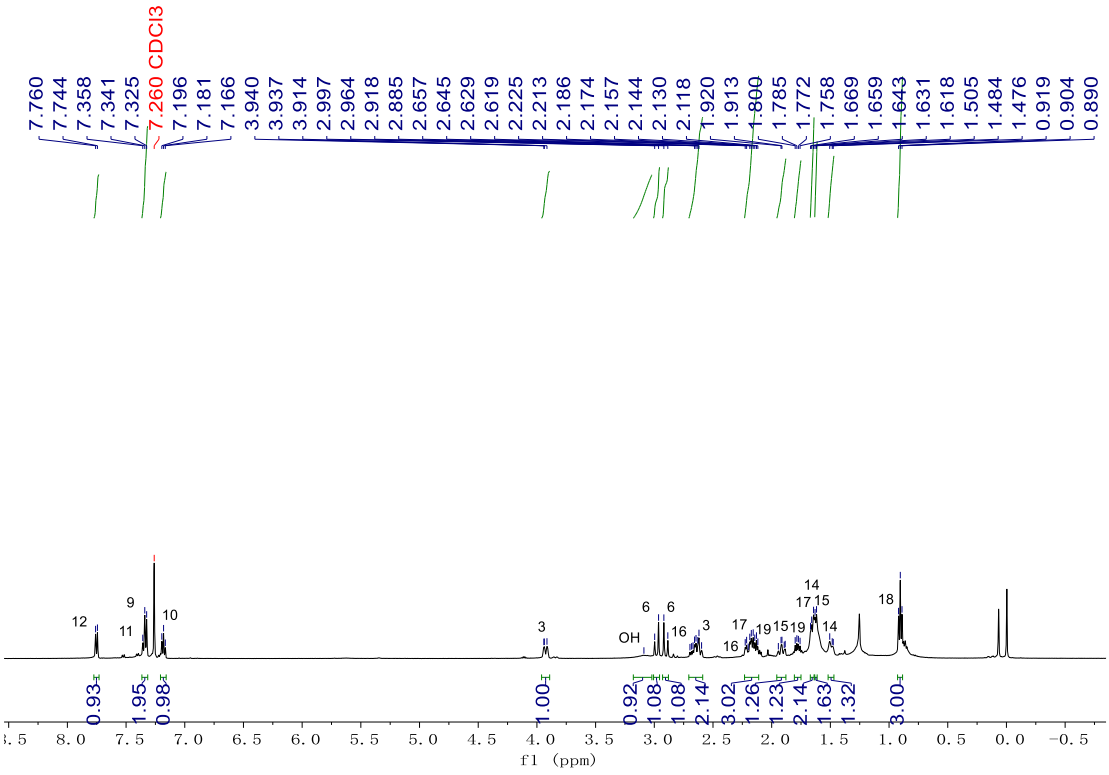
- The same X-ray structure (but different NMR spectra) for Scholarisine G has been obtained individually from Kam, Zhu and Dai. Moreover, the synthetic Scholarisine G from Zhu, Dai, Liang and us was derived from the same intermediate via a similar or same synthetic operation. We thus conclude the same molecule was obtained by each of us. Zhu previously attributed the minor NMR difference to the presence varying amount of H_2O residue. Another possibility is that the different quality, therefore different acidity of the $CDCl_3$ solvent used for NMR may cause the difference. We noticed a similar phenomenon was observed by Kerr and coworkers when synthesizing alkaloid Mersicarpine (OL, 2008, 10, 1437). Indeed, they found significant variation of 1H NMR resonances with added acid.
- To verify our hypothesis, ^{1}H NMR and ^{13}C NMR were recorded by adding AcOH or K_2CO_3 to the NMR tube. We did observe significant chemical shift when AcOH was added. The use of K_2CO_3 has also an obvious impact on the 1H NMR shift between the region of 3.0-1.5 ppm.
- Attempt to obtain a spectrum resemble the one from Dai is difficult considering the varying amount proton (and also counterion), H_2O.

^{13}C NMR (126 MHz, $CDCl_3$ + AcOH)	^{13}C NMR (126 MHz, $CDCl_3$)	^{13}C NMR (126 MHz, $CDCl_3$ + K_2CO_3)
175.8	173.5	173.4
170.7	169.8	169.7
141.0	141.5	141.6
137.5	137.3	137.1
129.7	130.0	130.2
126.3	126.1	126.0
123.2	123.0	122.9
121.3	121.2	121.1
90.8	90.8	90.8
82.2	82.2	82.3
42.1	42.3	42.3
39.4	39.4	39.4
37.2	37.0	37.0
29.5	29.5	29.7
27.4	27.5	27.5
25.7	25.9	25.9

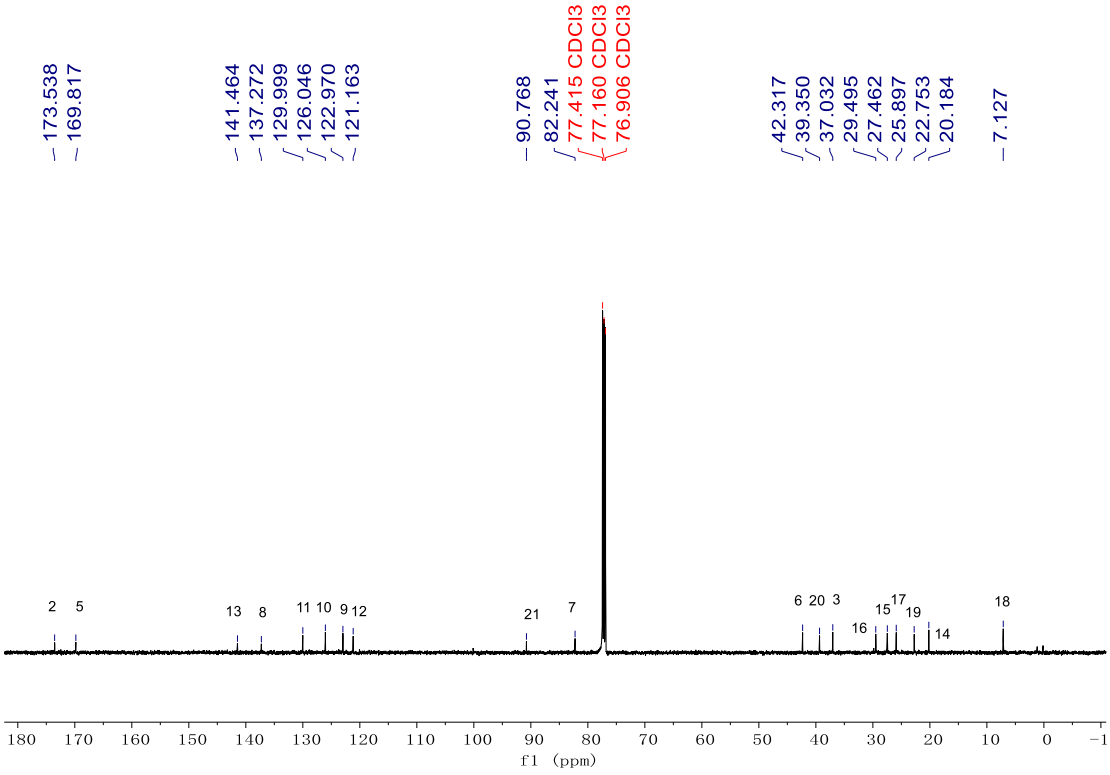
22.6	22.8	22.8
20.2	20.2	20.2
7.0	7.1	7.1



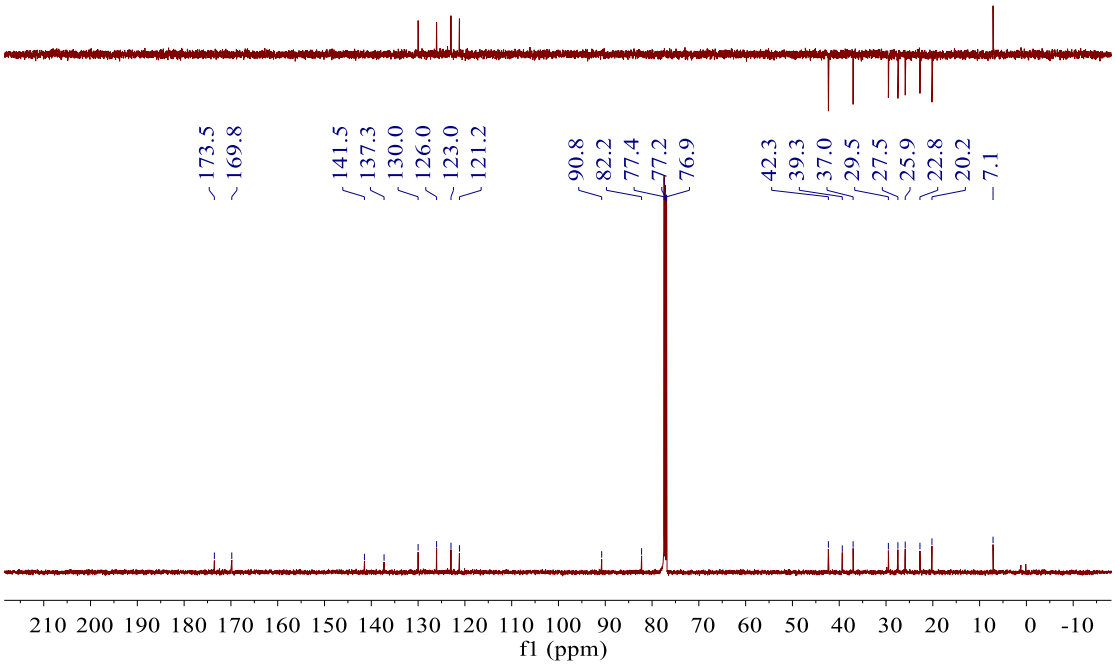
4) Copies of NMR spectra



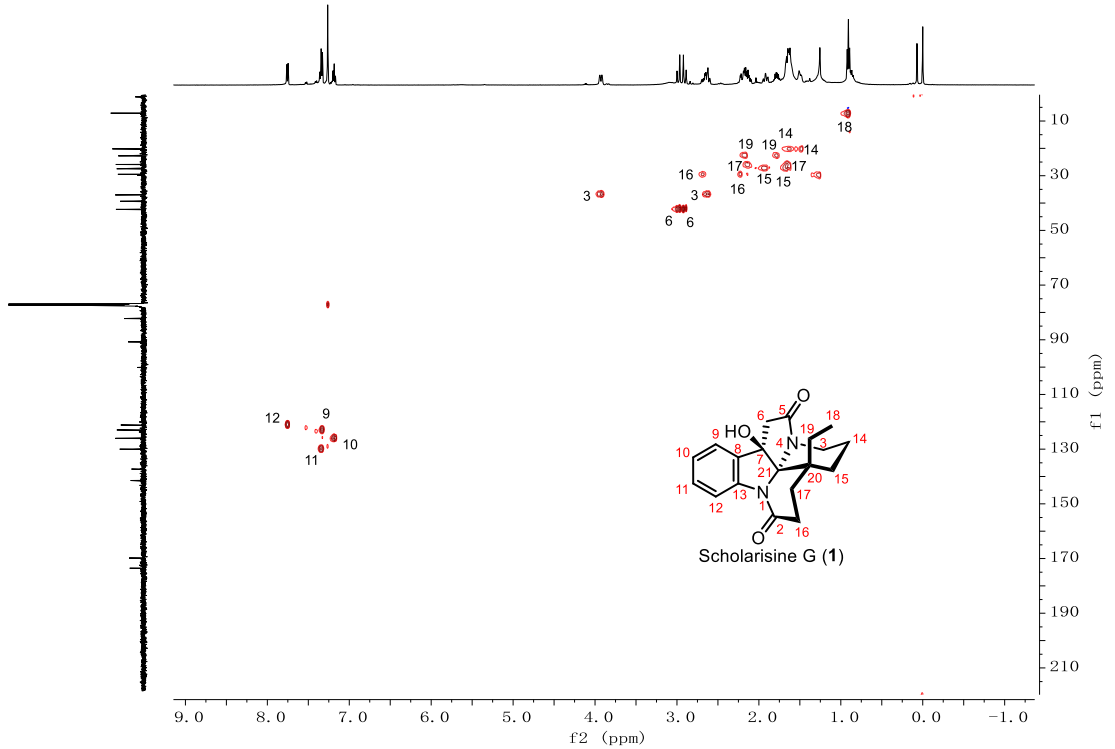
The ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**



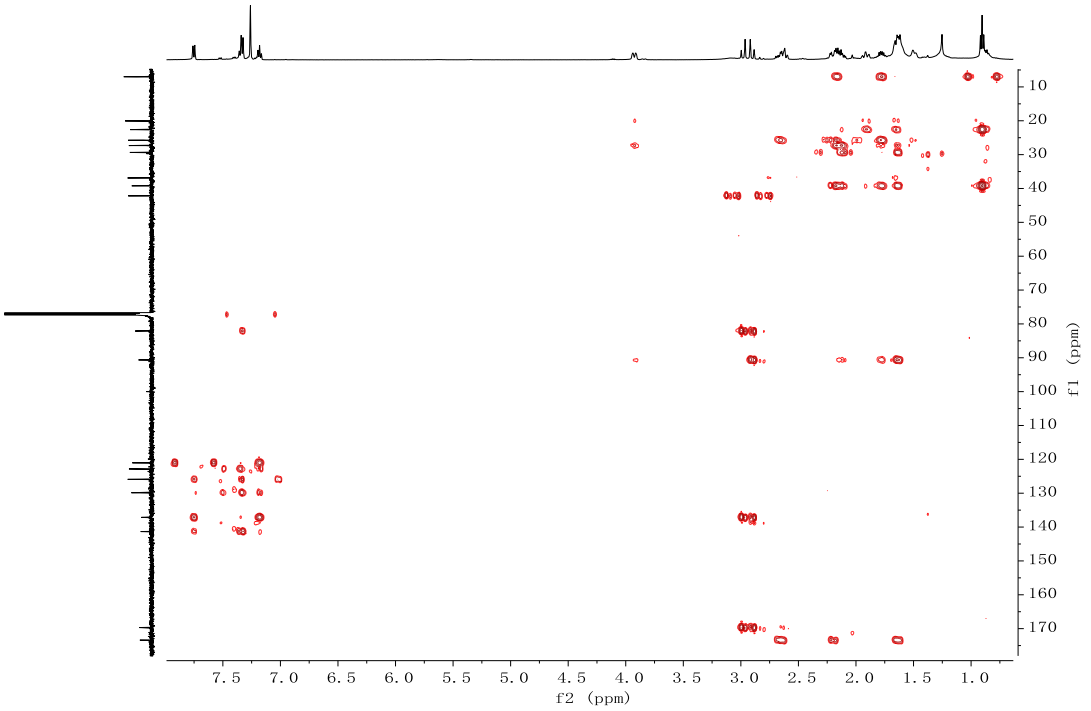
The ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **Scholarisine G**



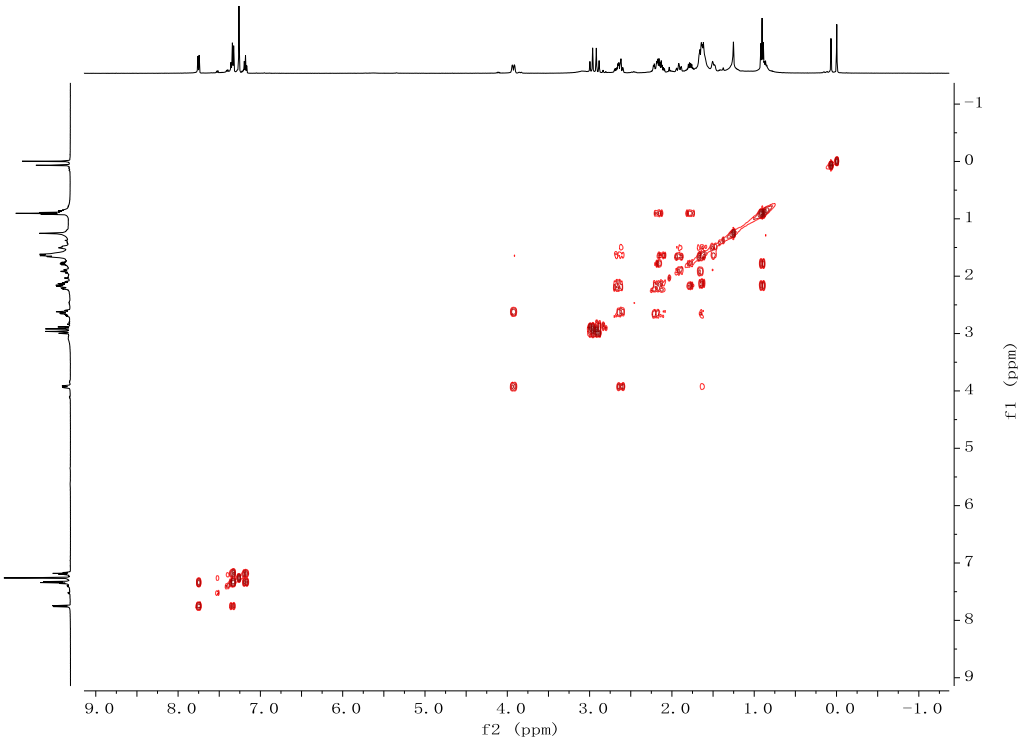
The DEP-135^o (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**



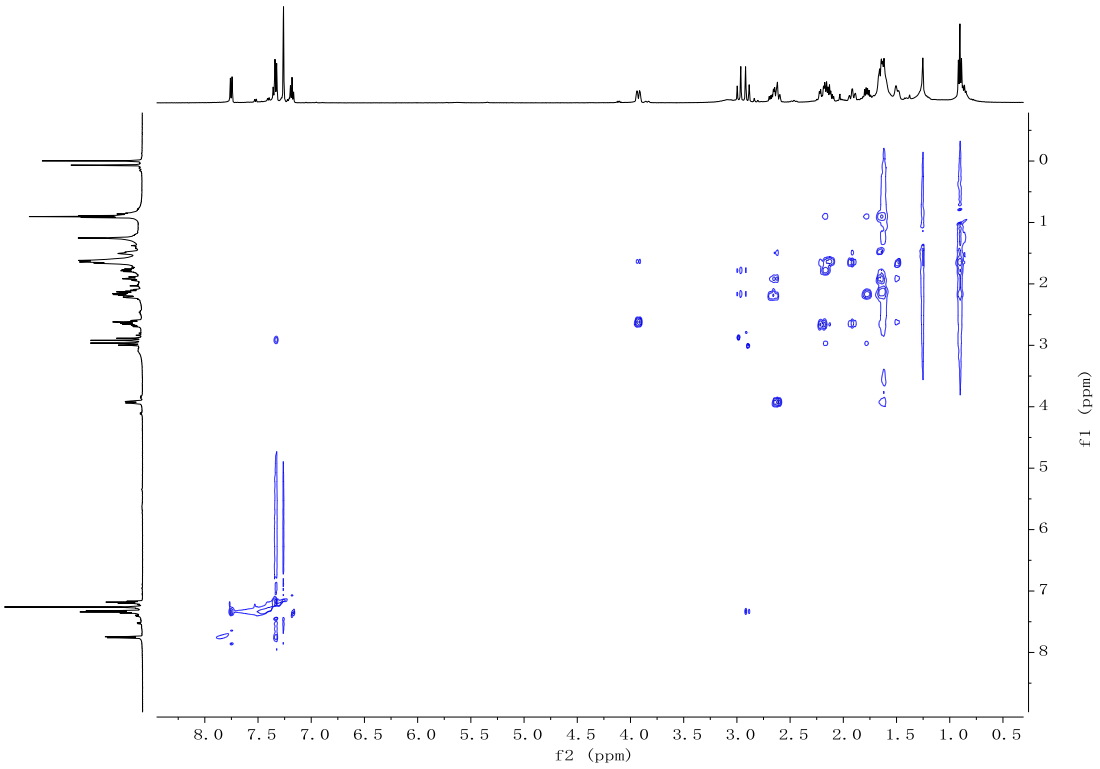
The HSQC (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**



The HMBC (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**



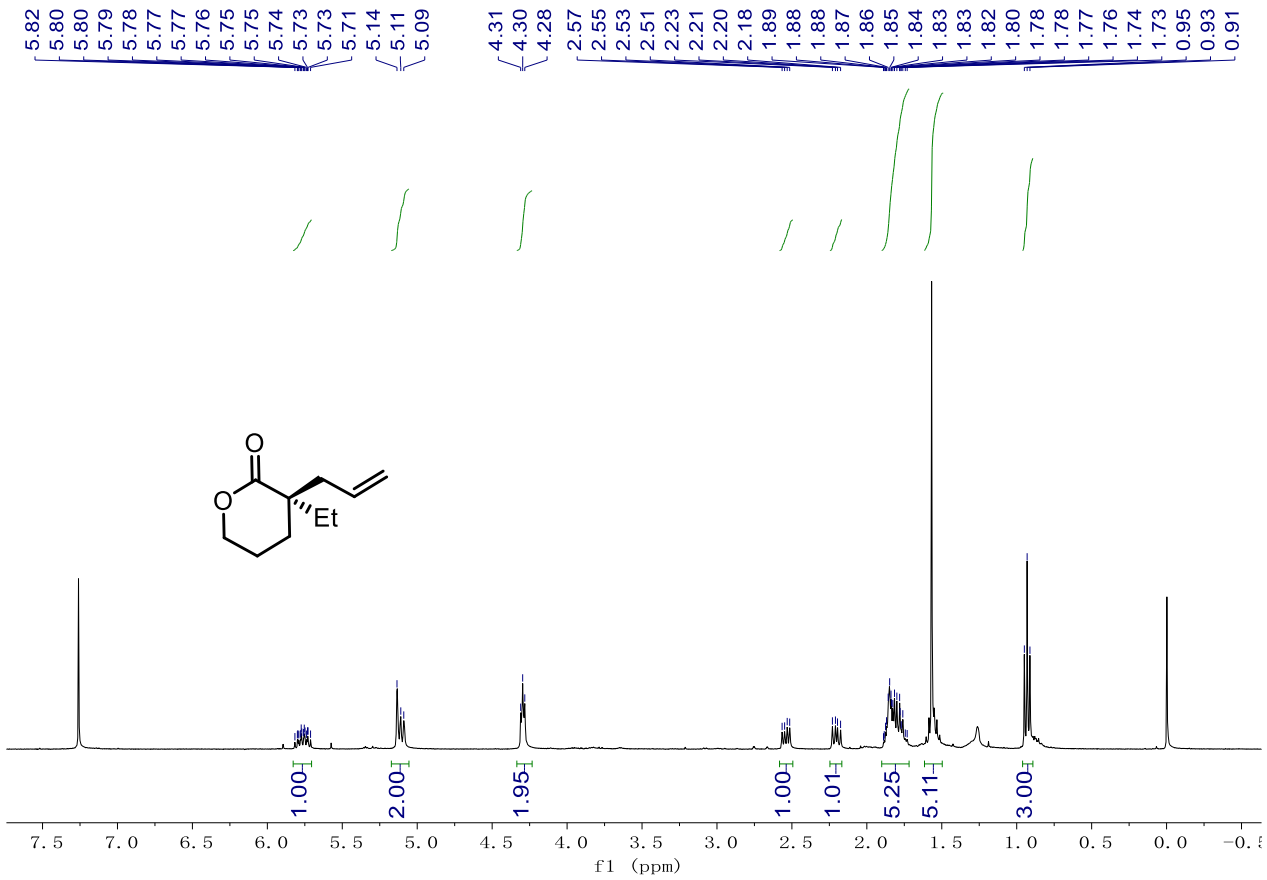
The ^1H-^1H COSY (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**



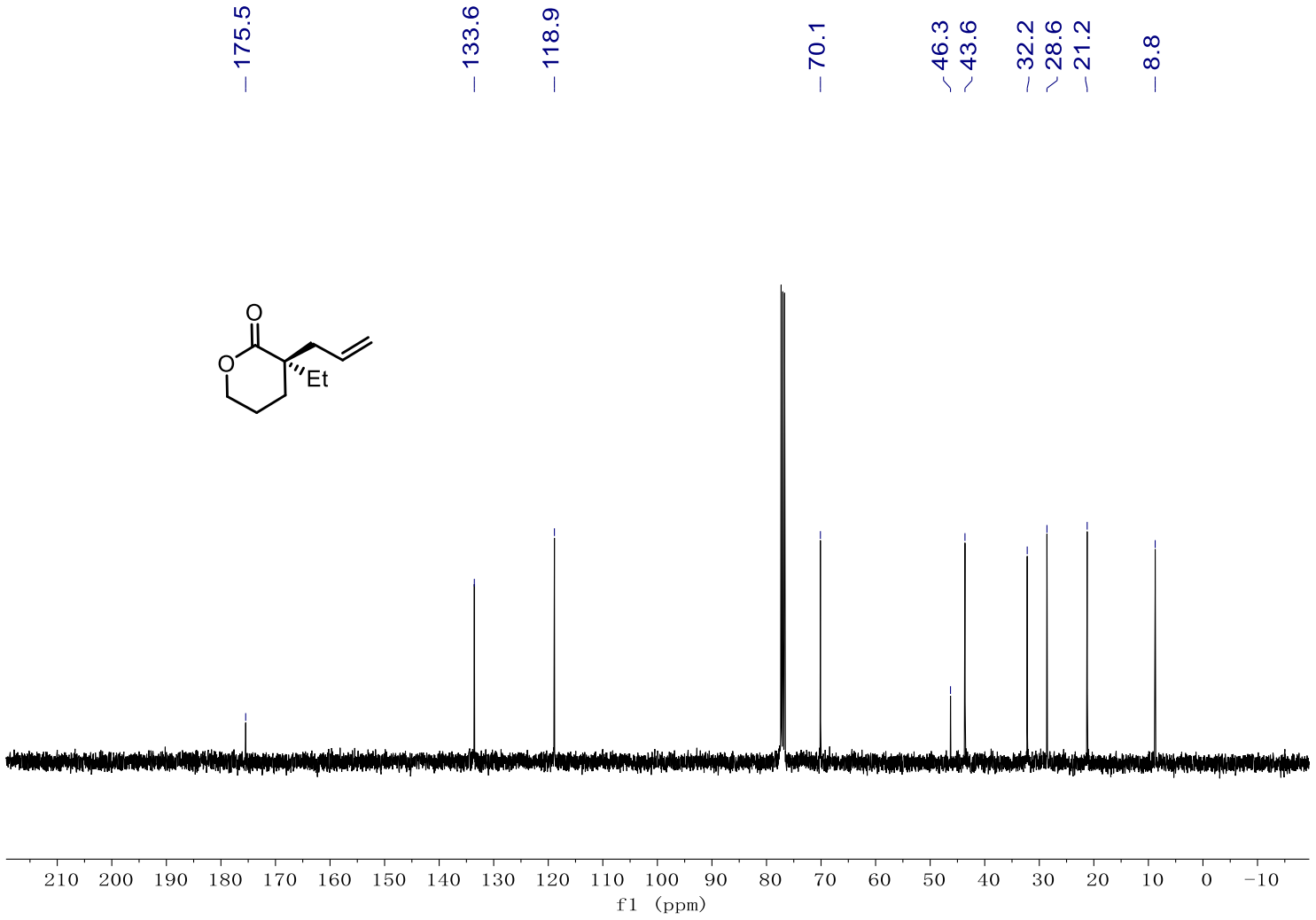
The ^{1}H-^{1}H NOE (600 MHz, $CDCl_3$) spectrum of **Scholarisine G**

5. NMR Spectra of Products

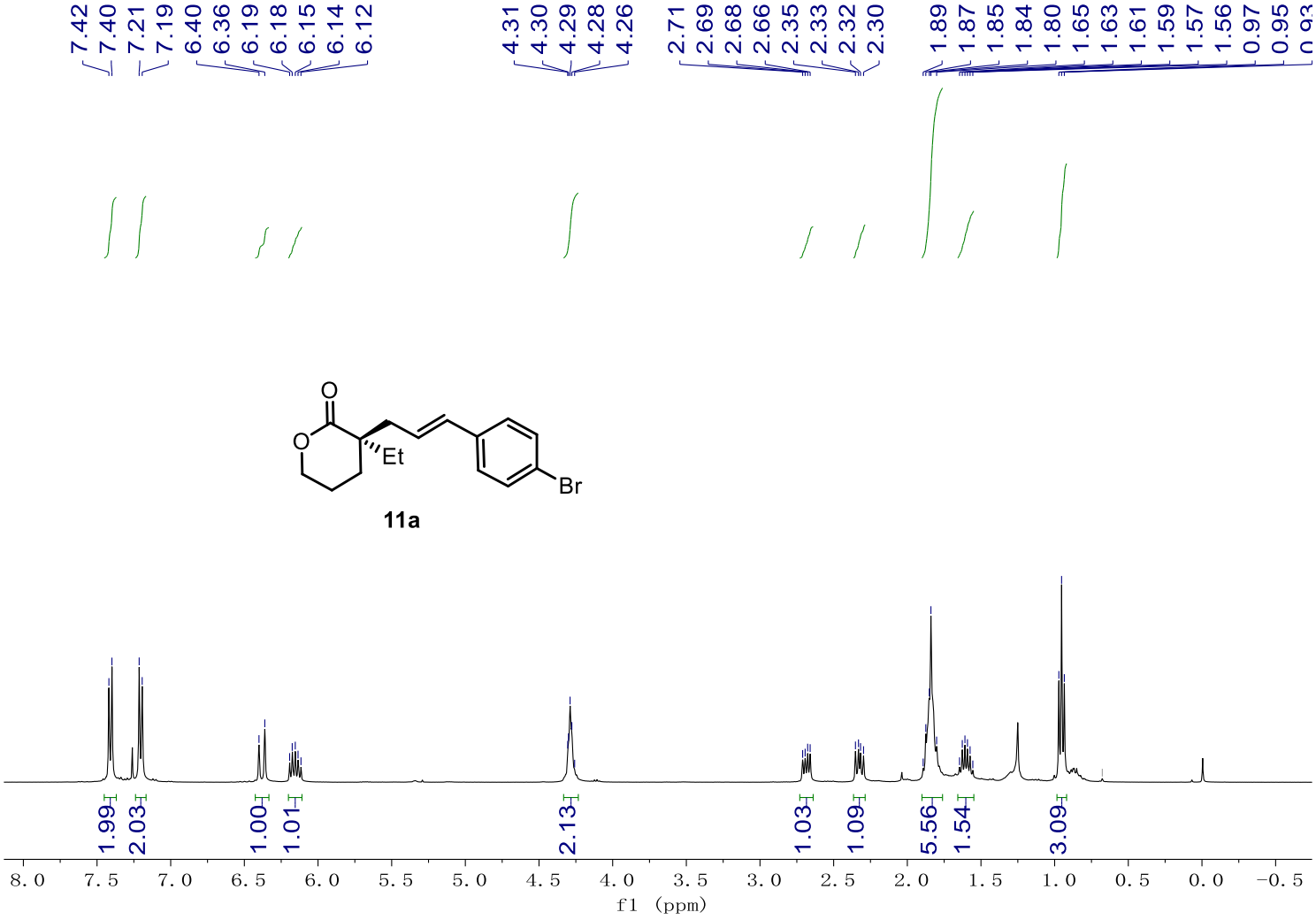
^{1}H NMR of Compound 17 ($CDCl_3$, 400Hz)



^{13}C NMR of Compound 17 ($CDCl_3$, 100Hz)

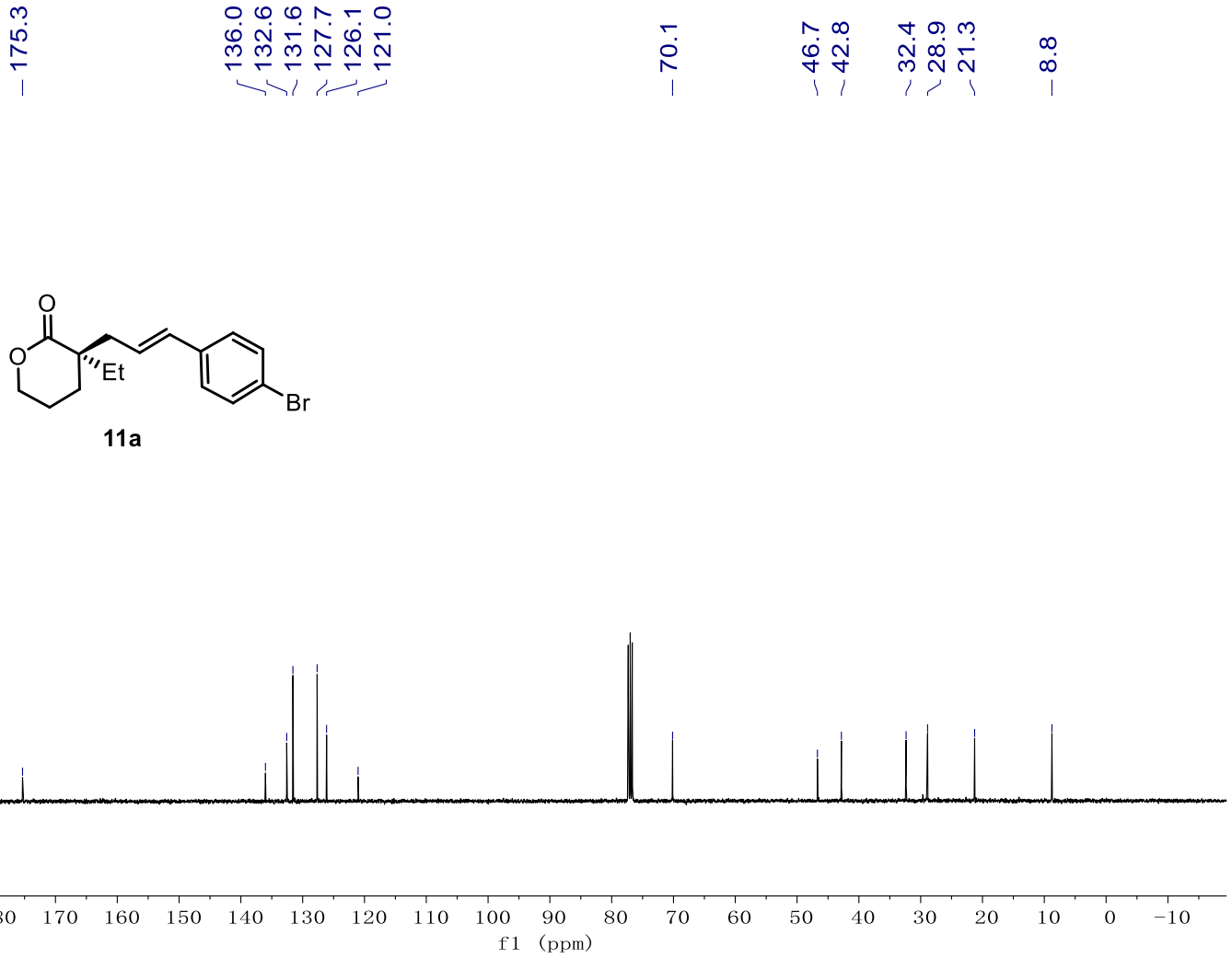


^{1}H NMR of Compound S2 ($CDCl_3$, 400Hz)



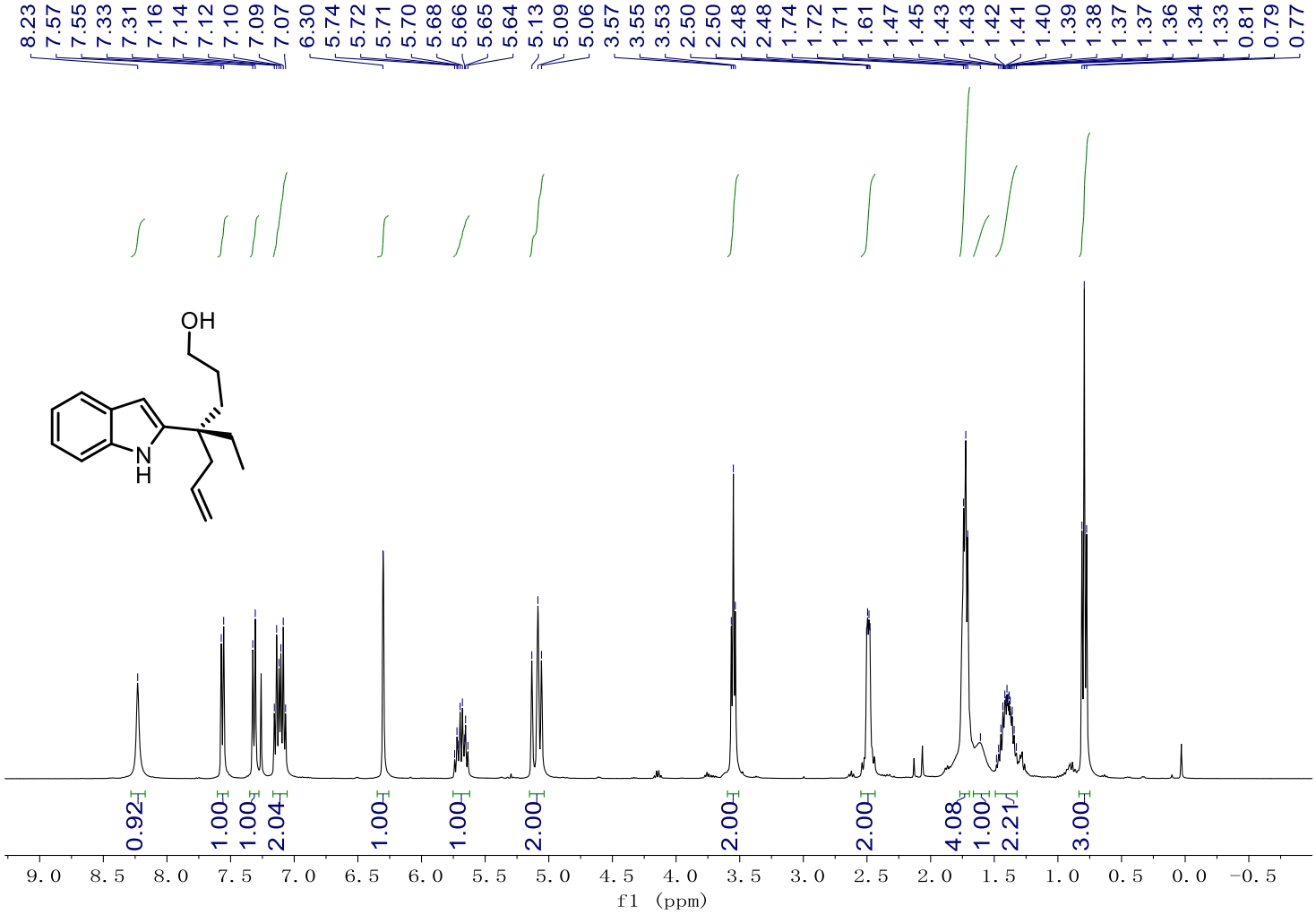
11a

^{13}C NMR of Compound S2 ($CDCl_3$, 100Hz)

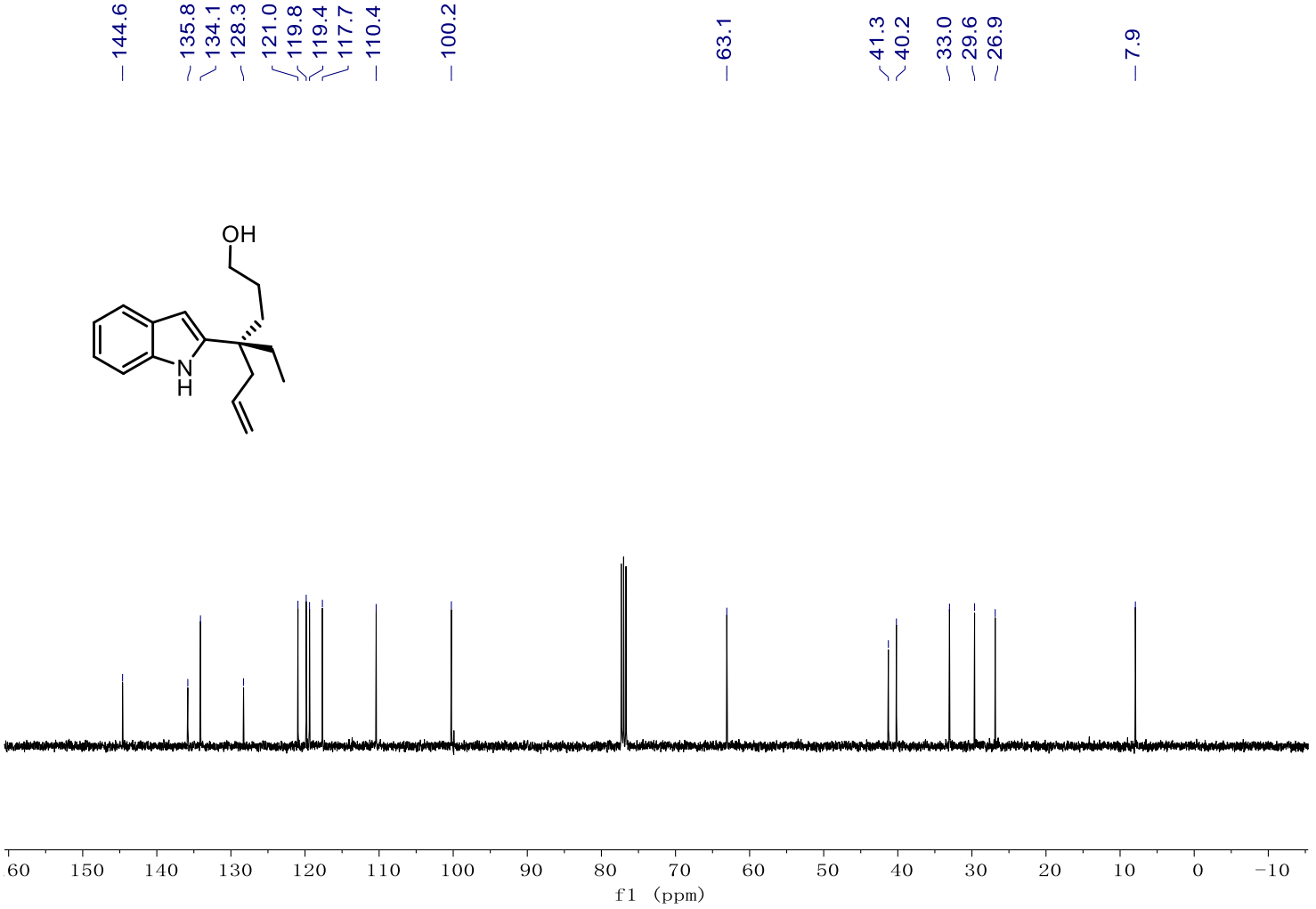


11a

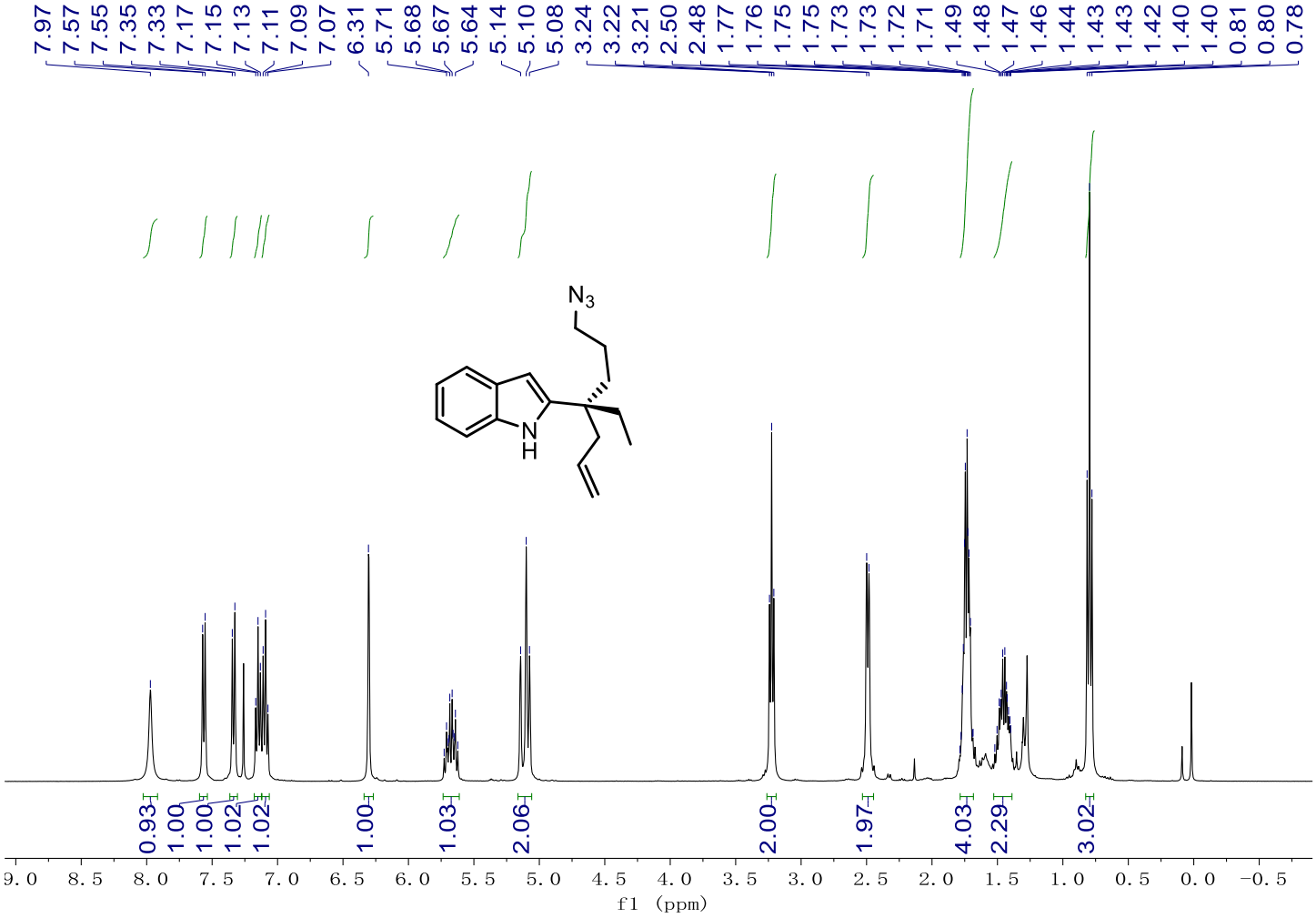
^{1}H NMR of Compound 26 ($CDCl_3$, 400Hz)



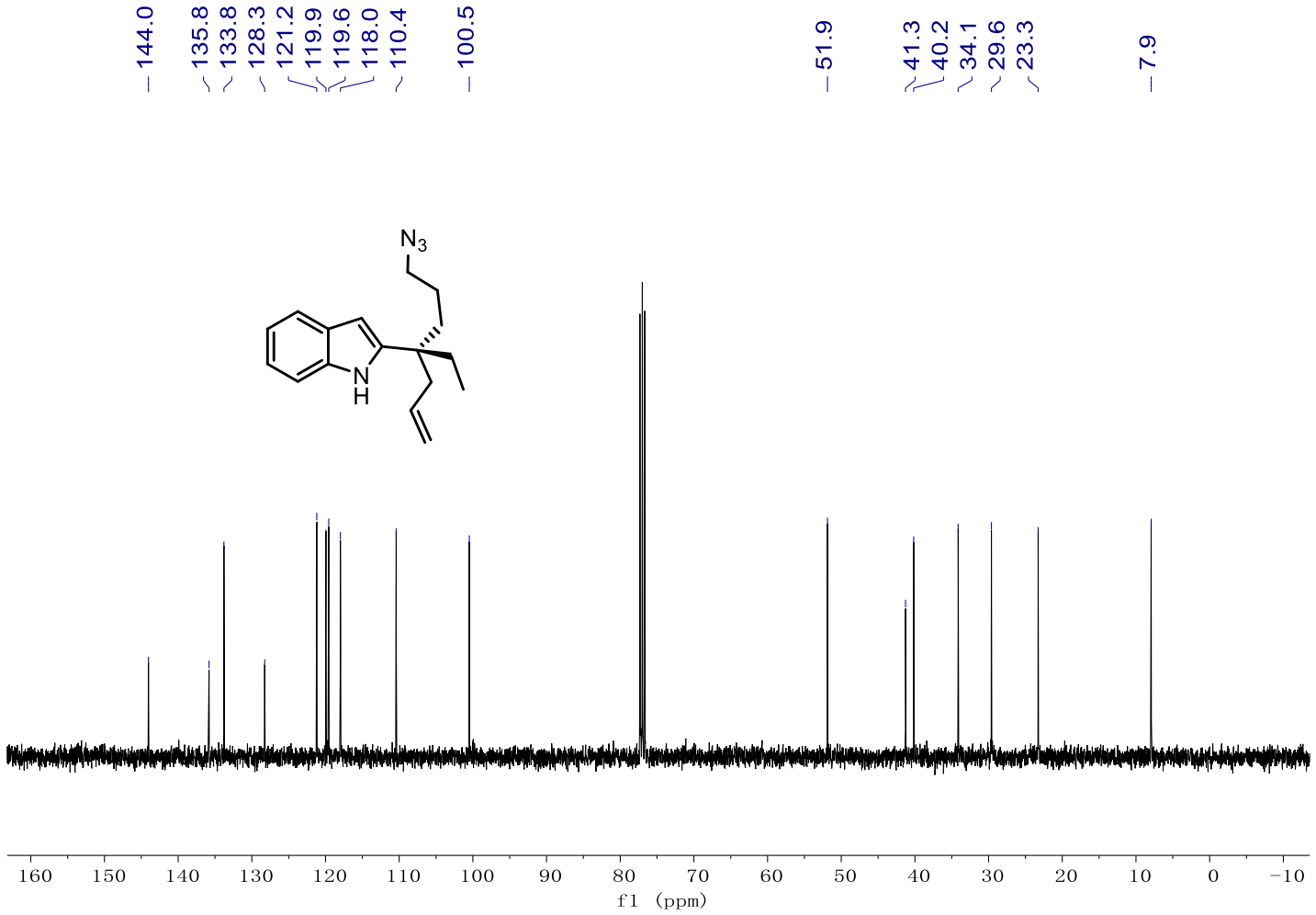
^{13}C NMR of Compound 26 ($CDCl_3$, 100Hz)



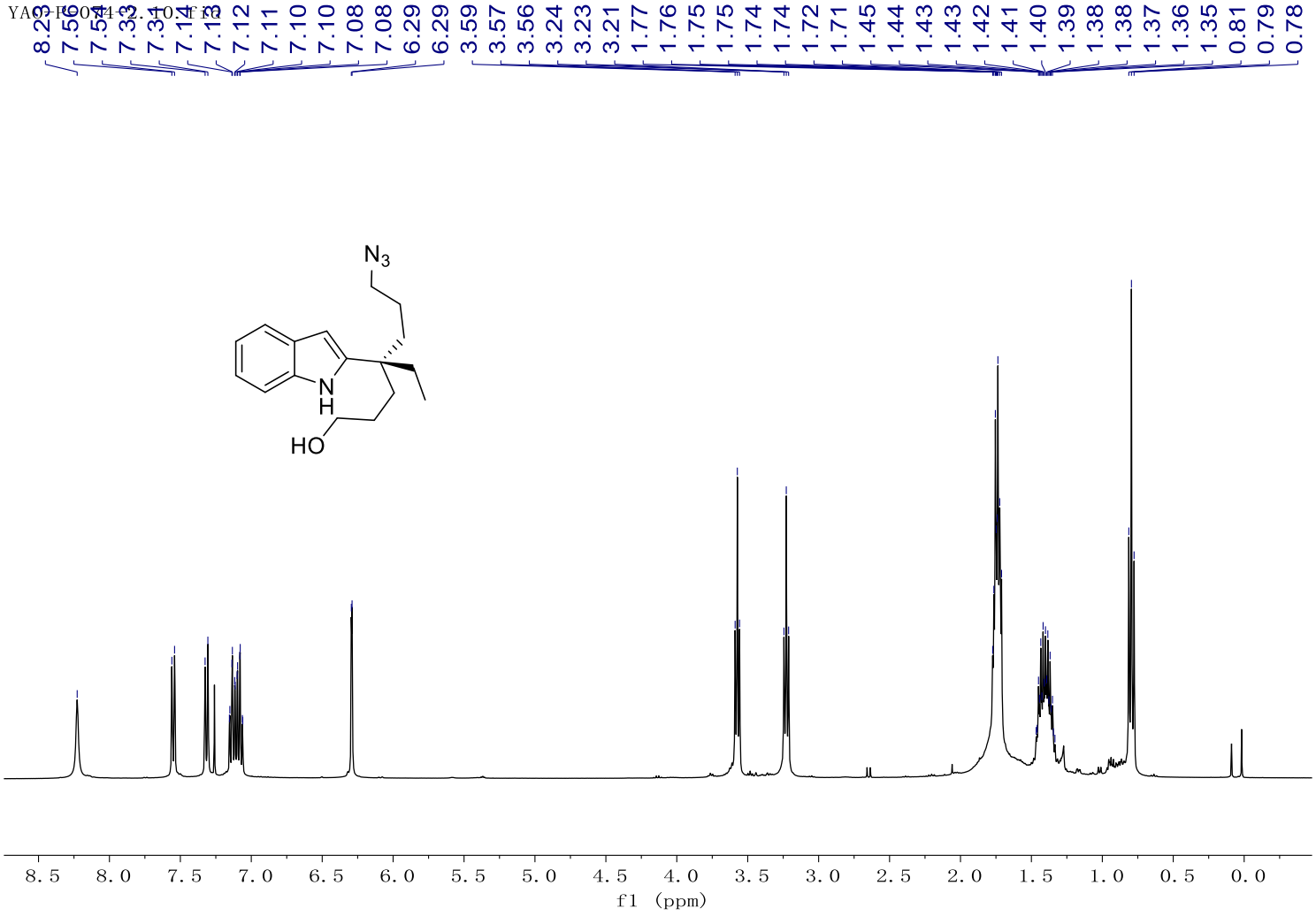
^{1}H NMR of Compound 26a ($CDCl_3$, 400Hz)



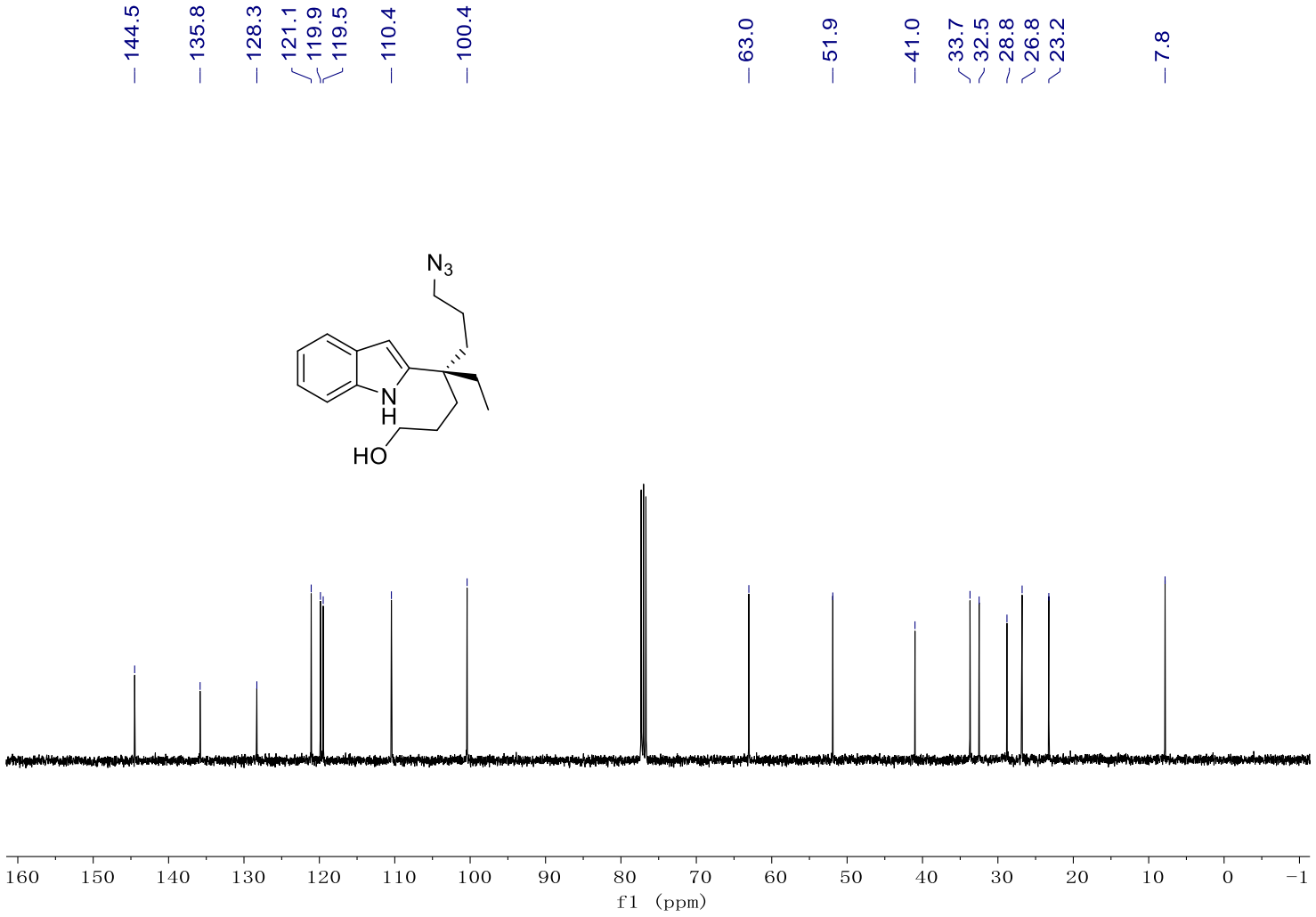
^{13}C NMR of Compound 26a ($CDCl_3$, 100Hz)



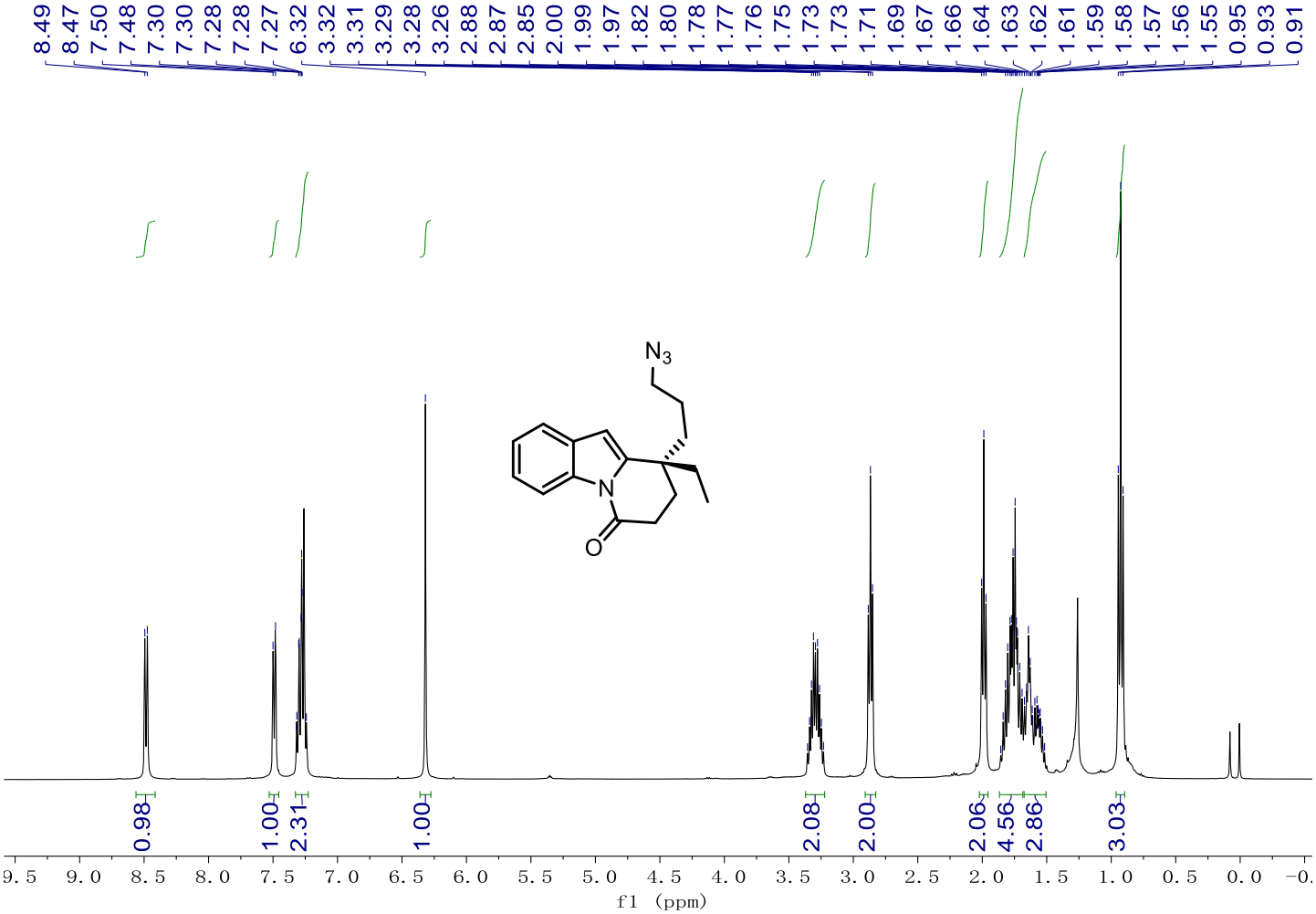
^{1}H NMR of Compound 26b ($CDCl_3$, 400Hz)



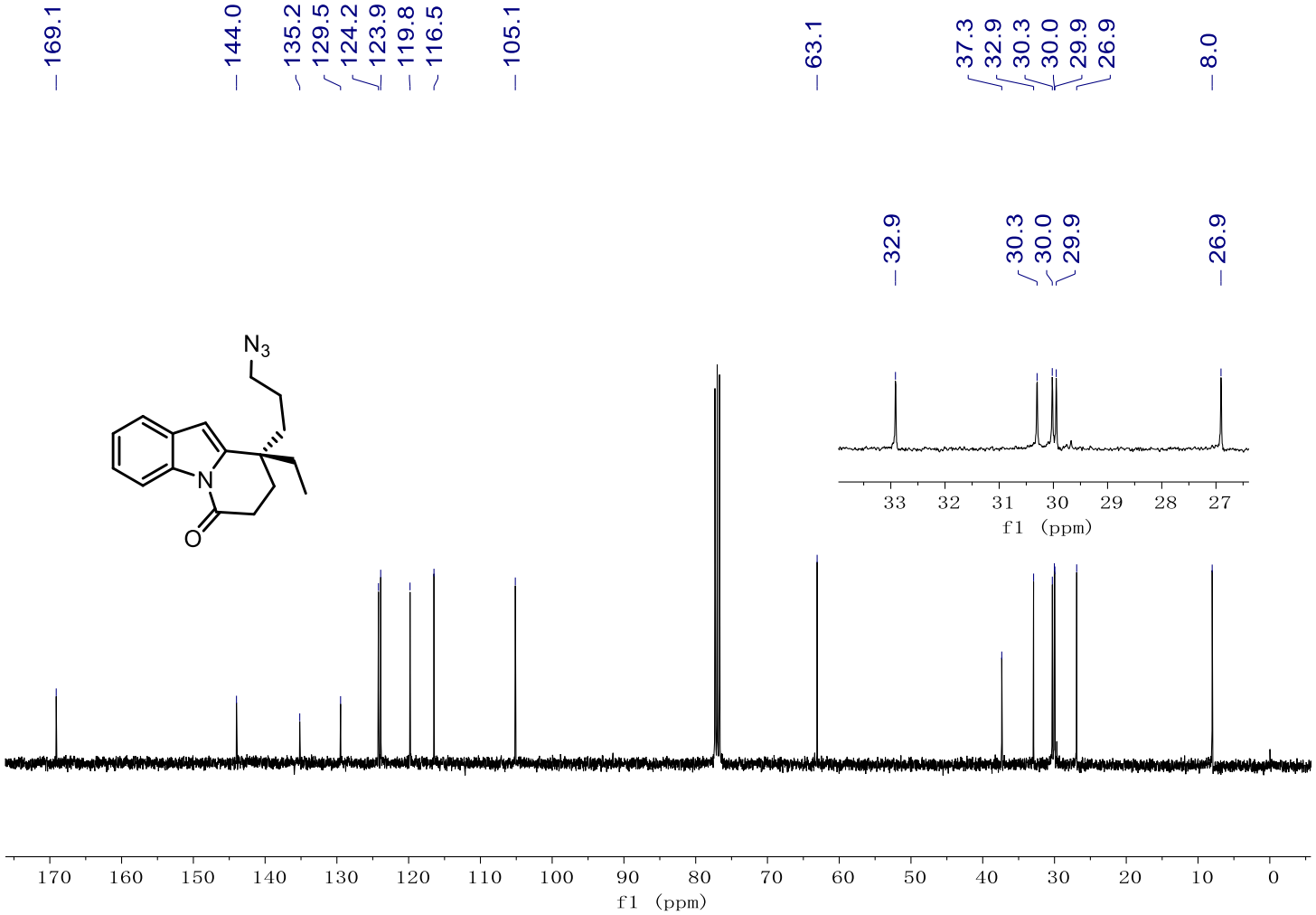
^{13}C NMR of Compound 26b ($CDCl_3$, 100Hz)



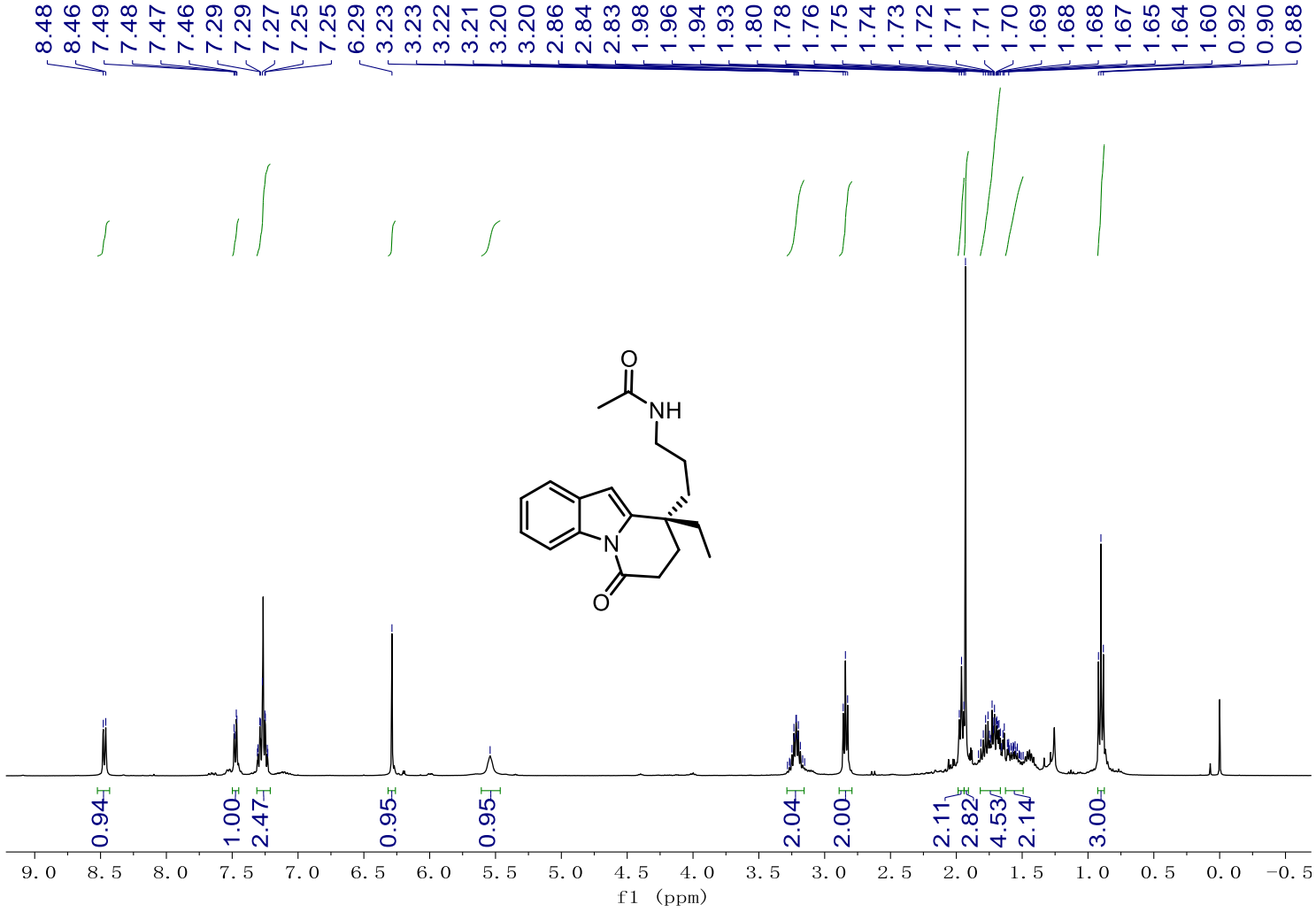
^{1}H NMR of Compound 27 ($CDCl_3$, 400Hz)



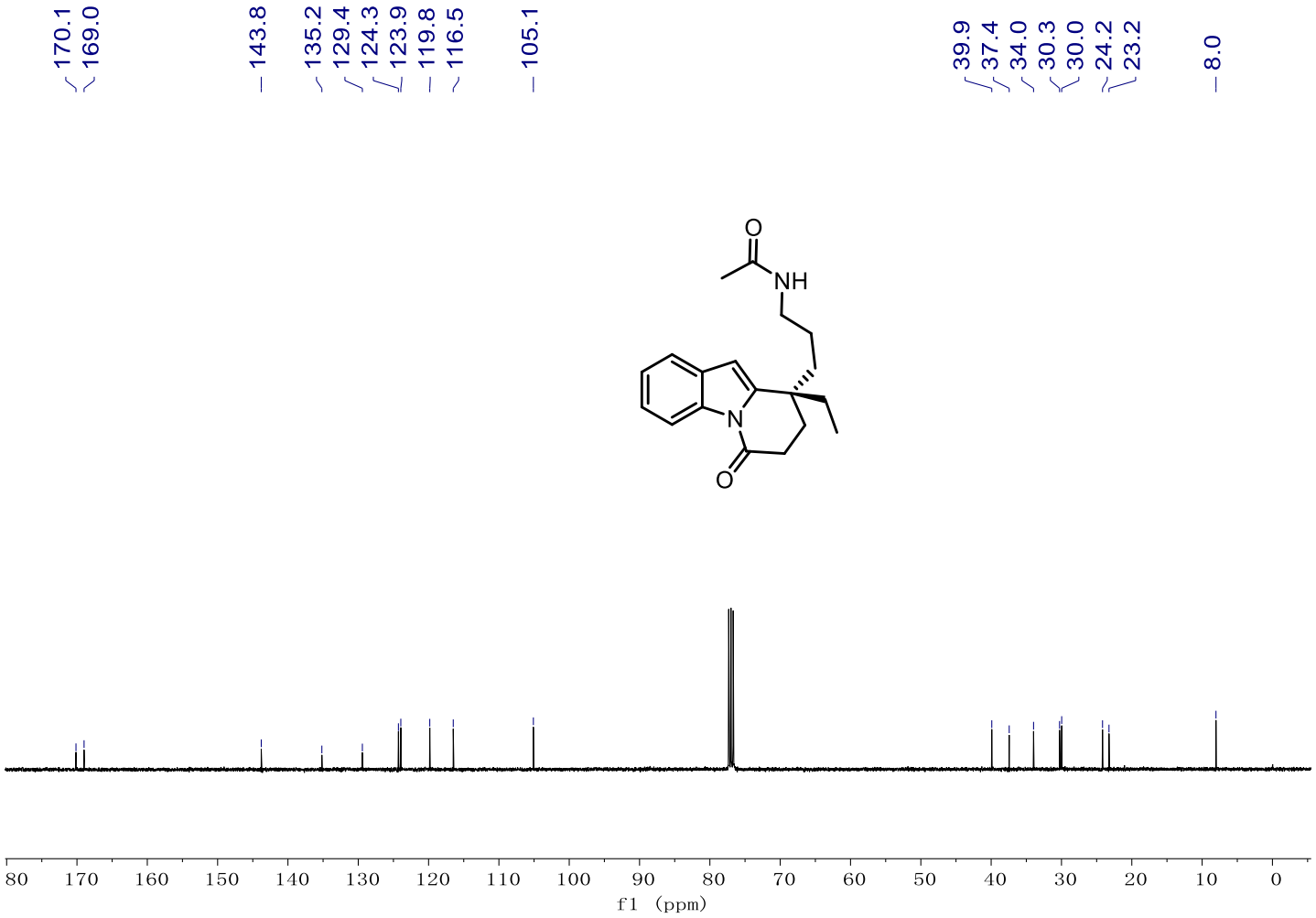
^{13}C NMR of Compound 27 ($CDCl_3$, 100Hz)



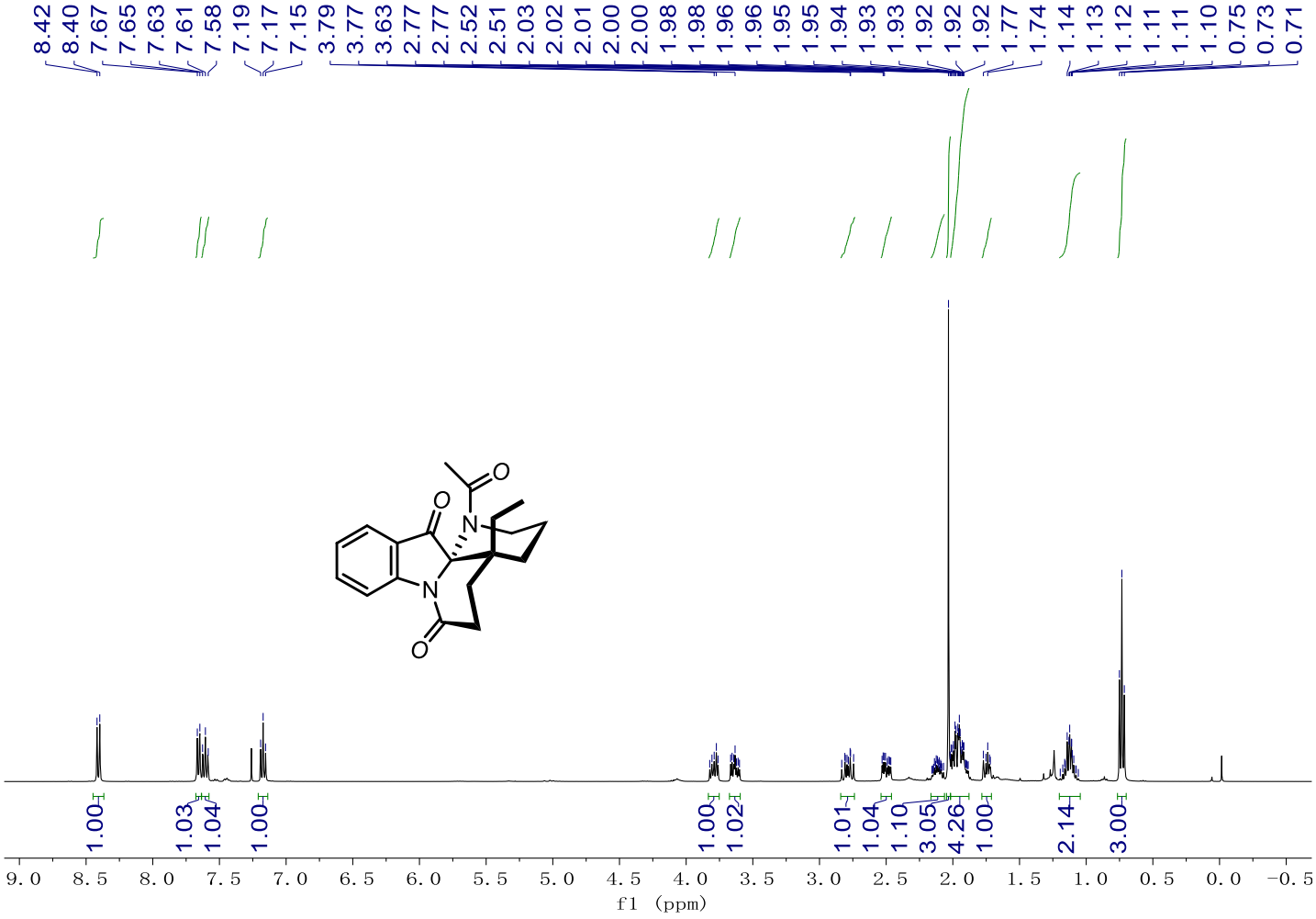
^{1}H NMR of Compound 28 ($CDCl_3$, 400Hz)



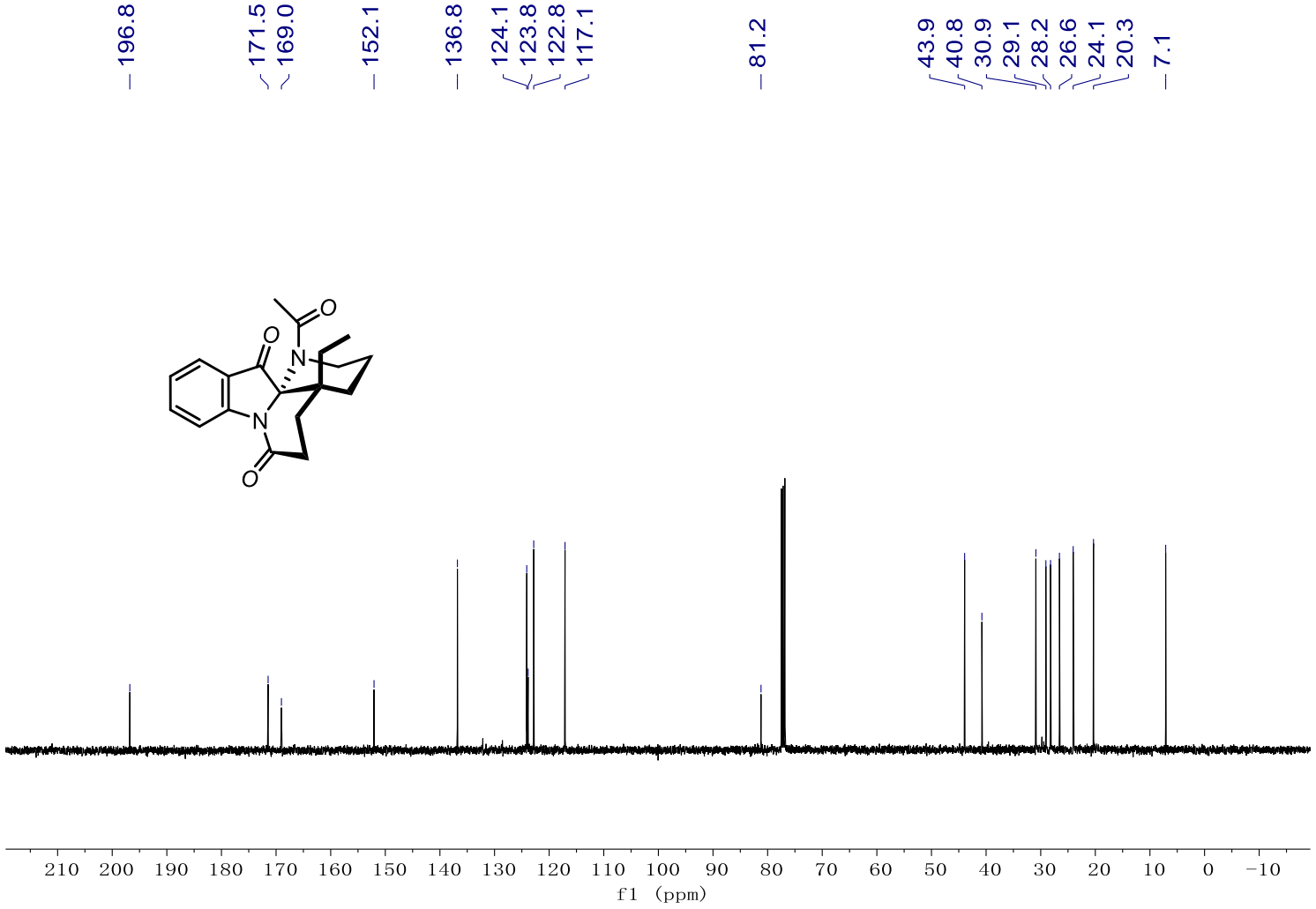
^{13}C NMR of Compound 28 ($CDCl_3$, 100Hz)



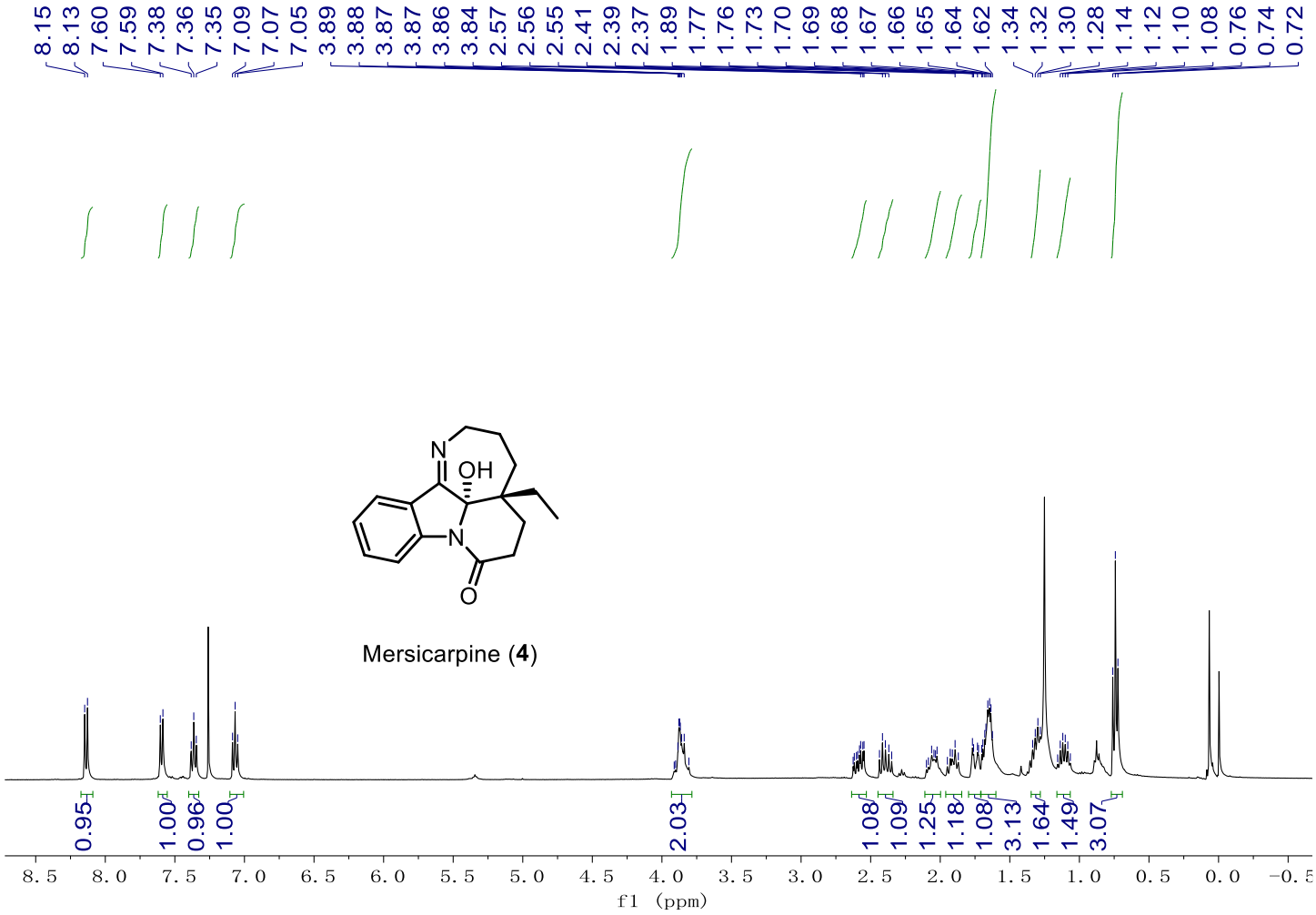
^{1}H NMR of Compound 27b ($CDCl_3$, 400Hz)



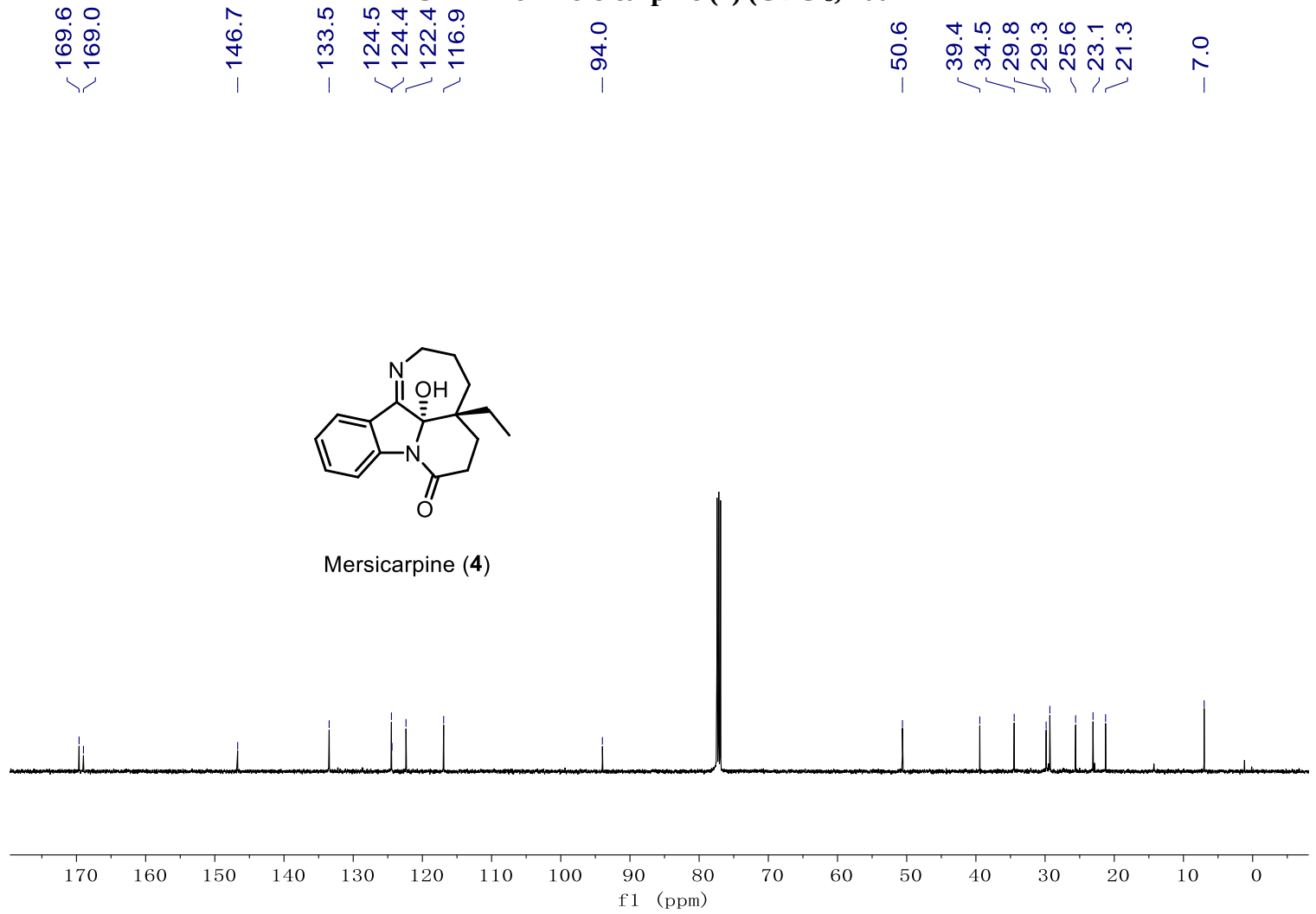
^{13}C NMR of Compound 27b ($CDCl_3$, 100Hz)



^{1}H NMR of Mersicarpine (4) ($CDCl_3$, 400Hz)

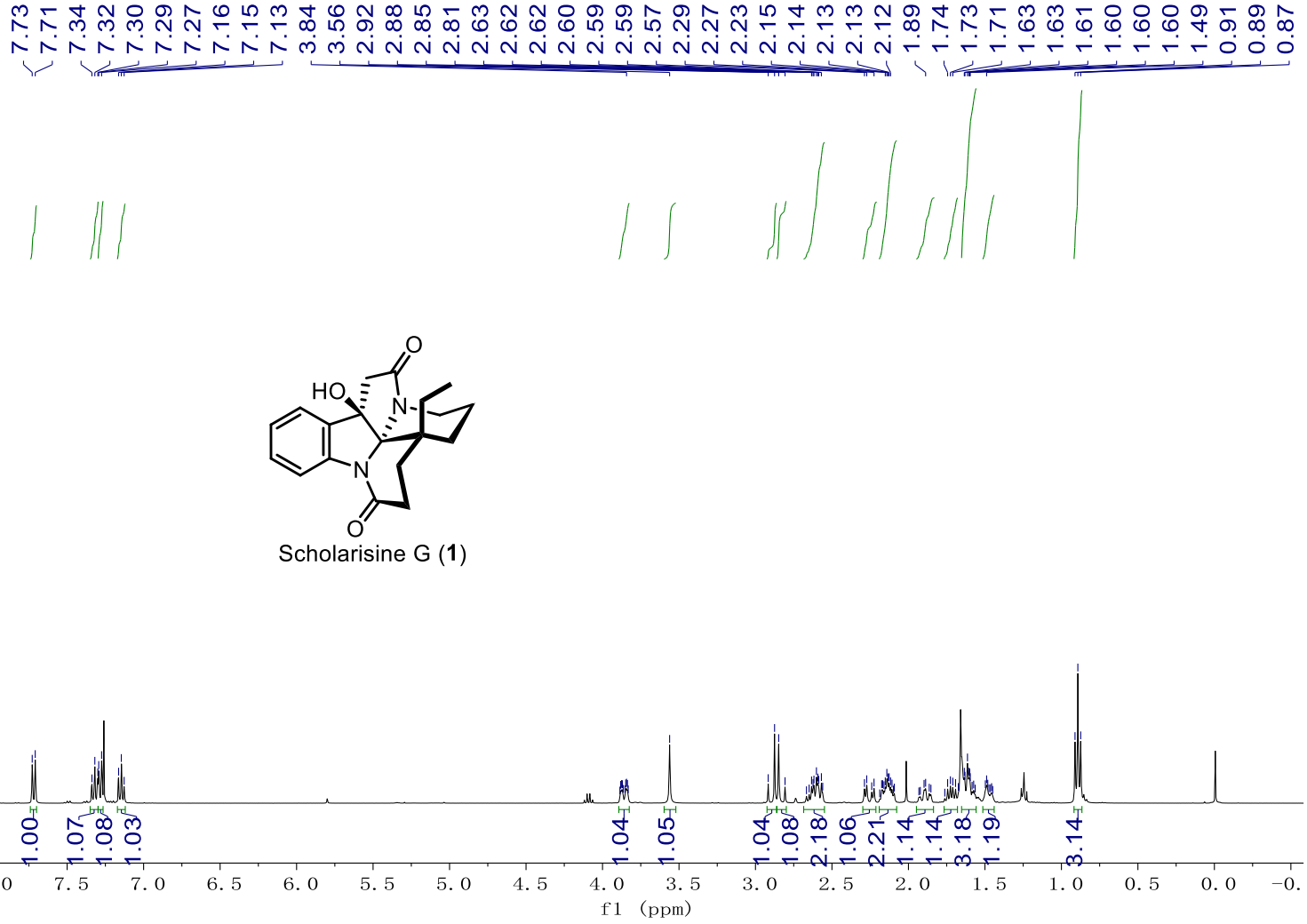


^{13}C NMR of Mersicarpine (4) ($CDCl_3$, 100Hz



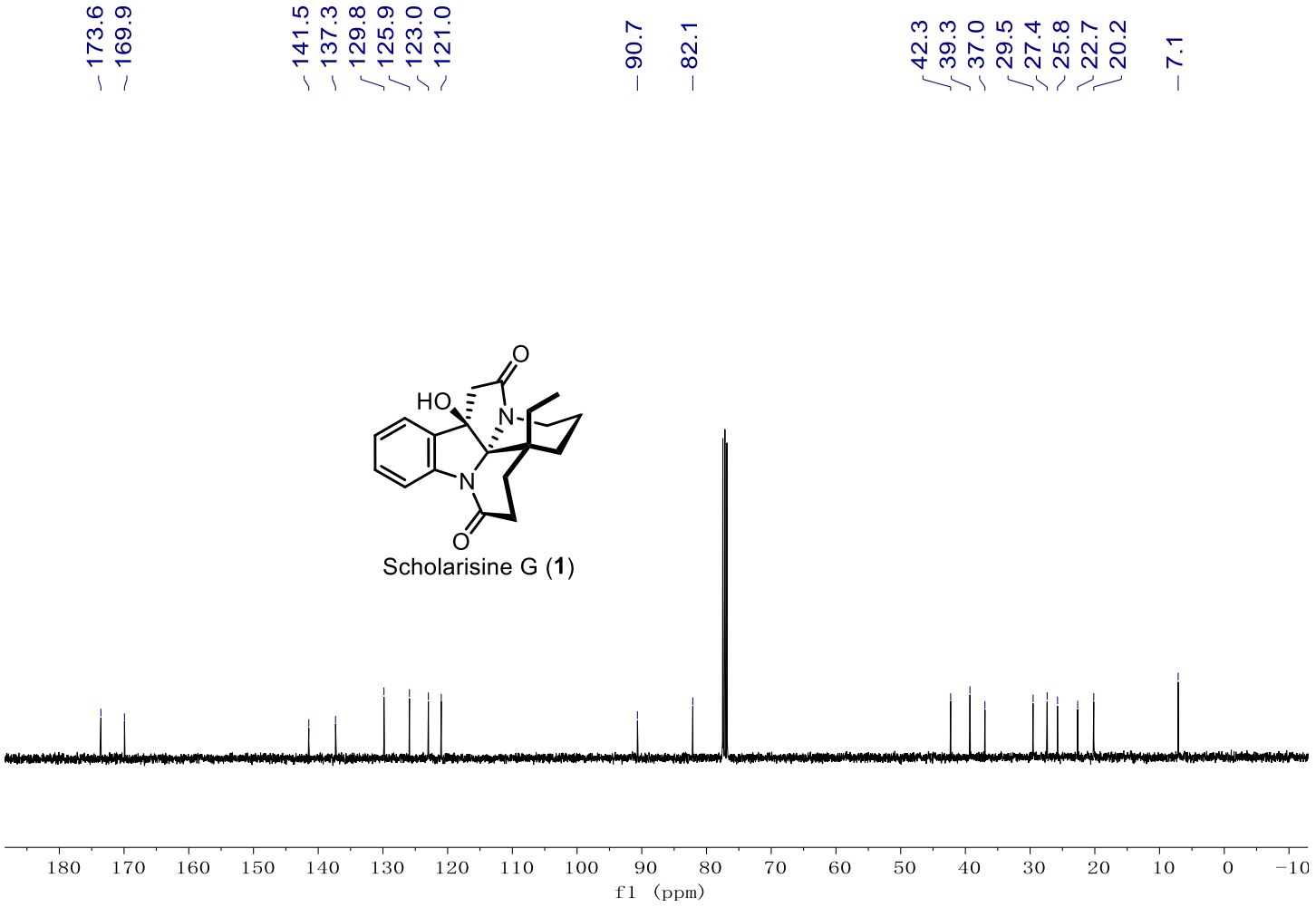
Mersicarpine (**4**)

^{1}H NMR of Scholarisine G (1) (CDCl3, 400Hz)

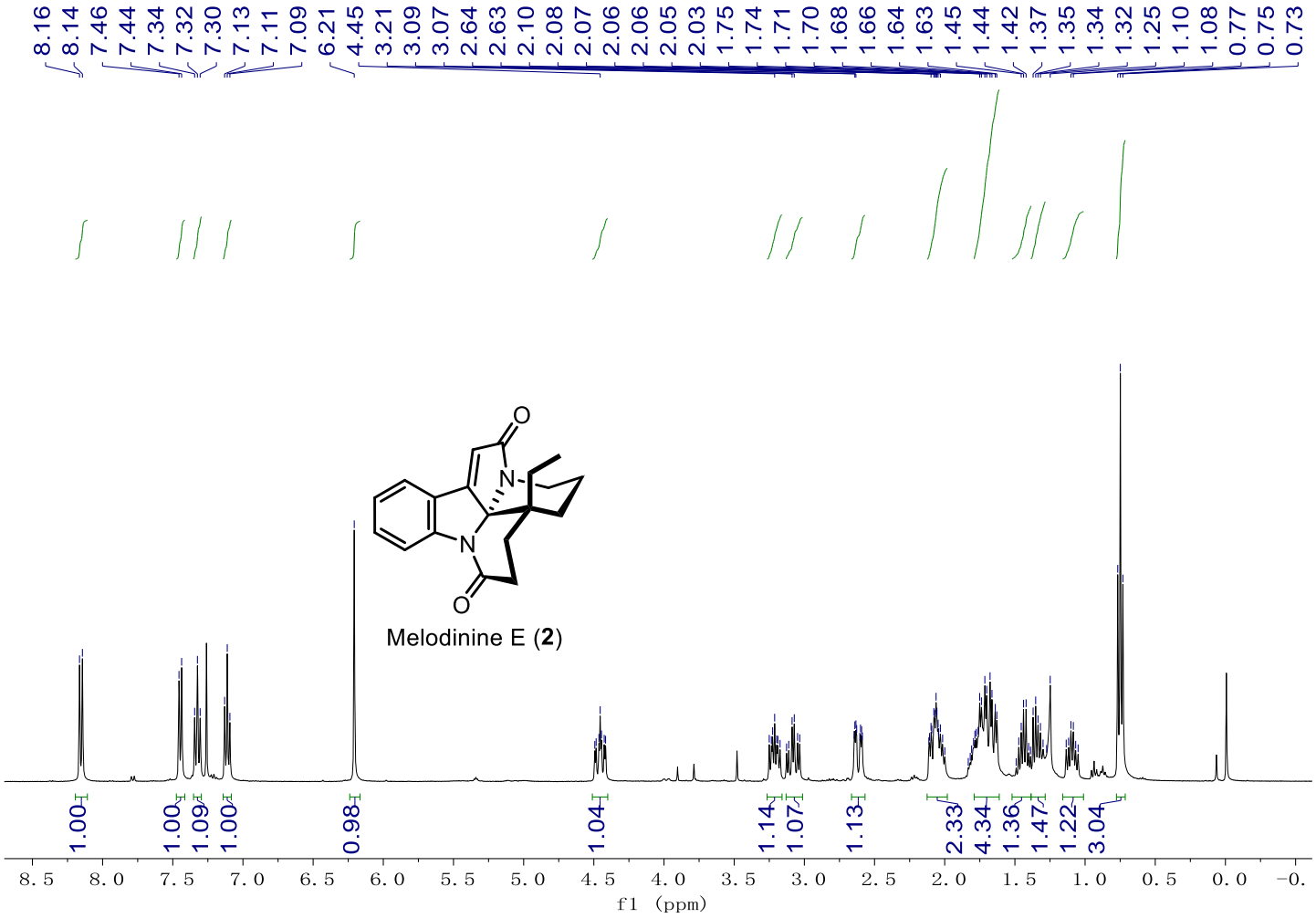


Scholarisine G (**1**)

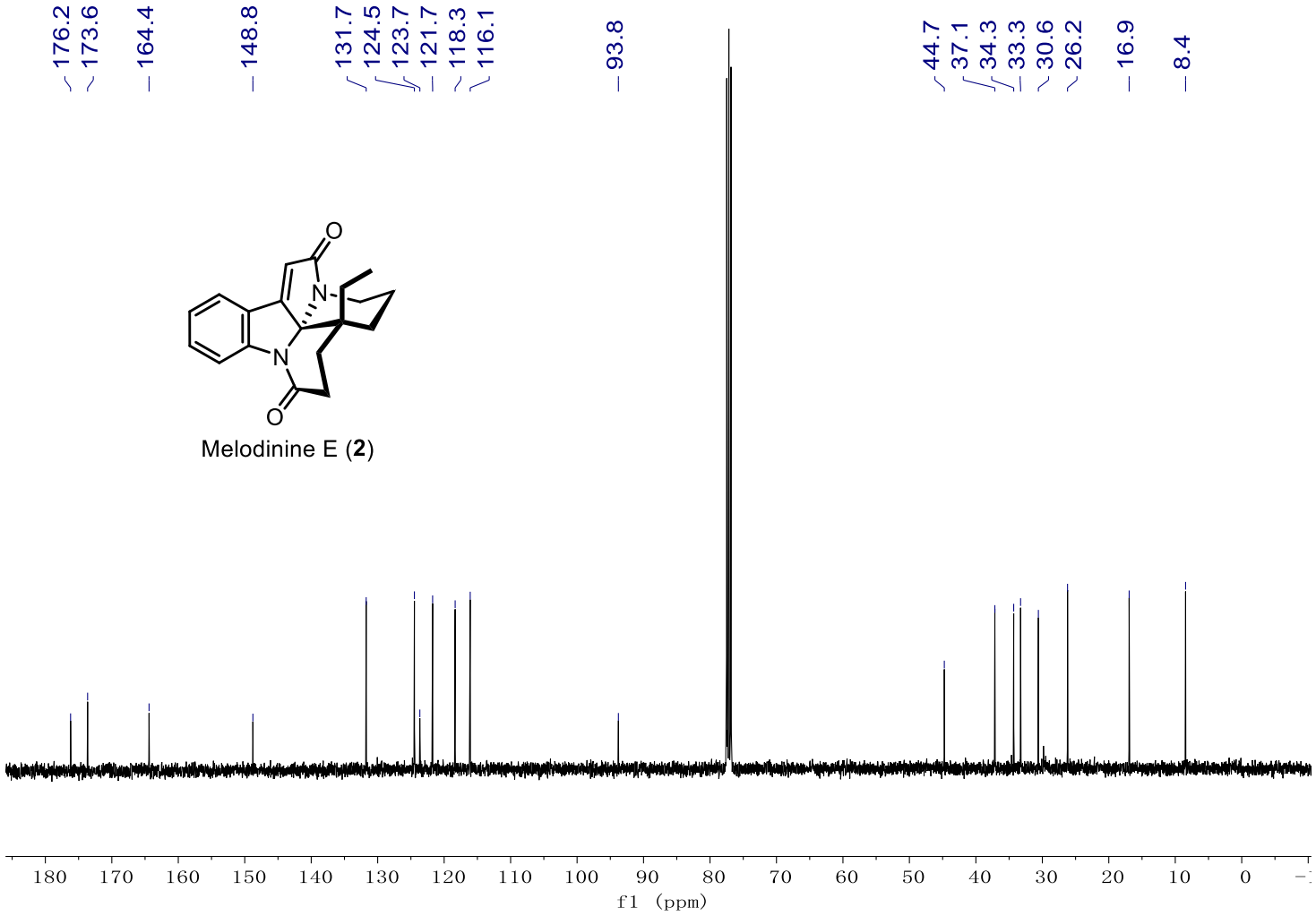
^{13}C NMR of Scholarisine G (1) ($CDCl_3$, 100Hz)



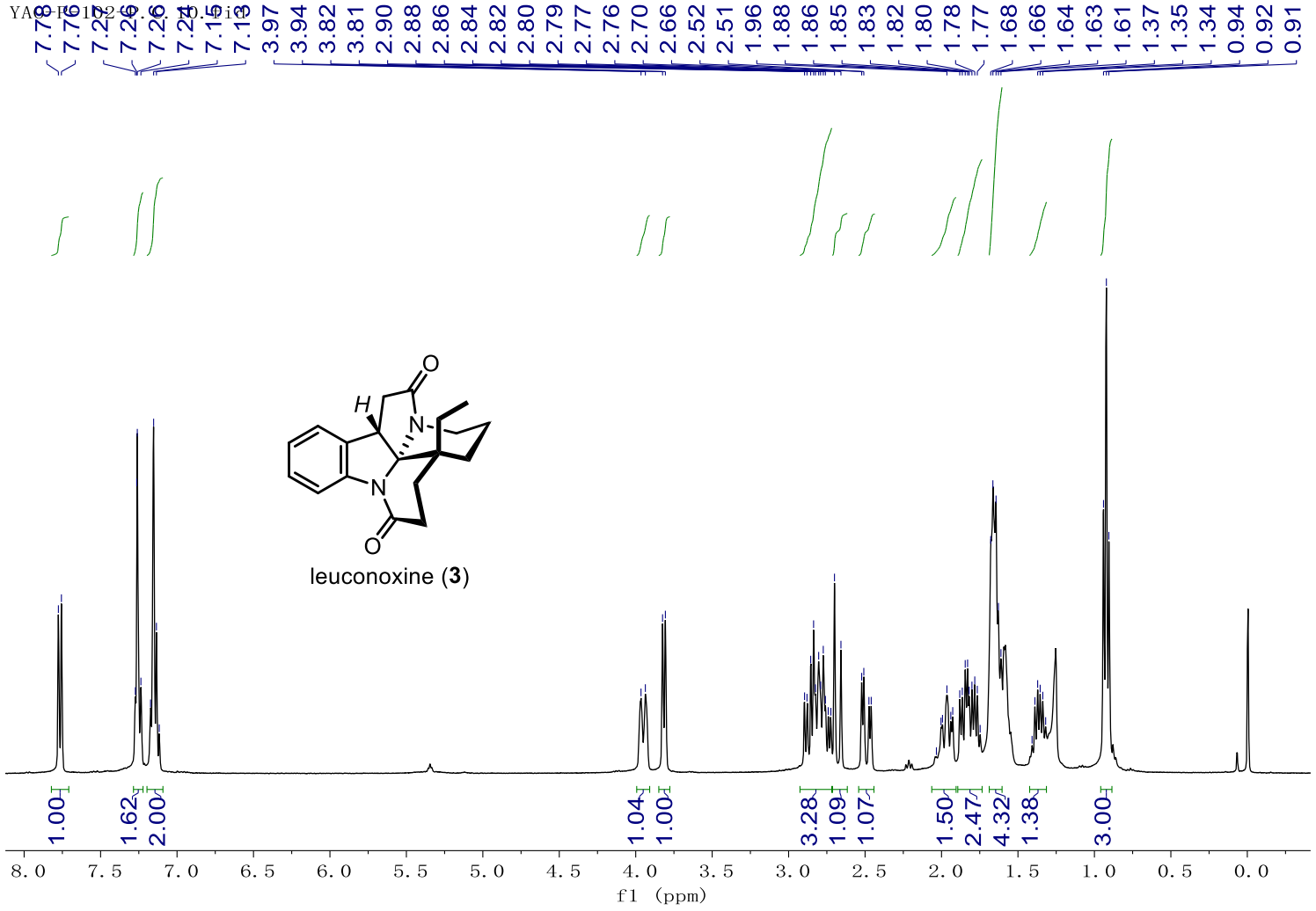
^{1}H NMR of Melodinine E (2) ($CDCl_3$, 400Hz)



^{13}C NMR of Melodinine E (2) ($CDCl_3$, 100Hz)



^{1}H NMR of leuconoxine (3) ($CDCl_3$, 400Hz)



^{13}C NMR of leuconoxine (3) ($CDCl_3$, 100Hz)