Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Total Synthesis of (–)-Depyranoversicolamide B

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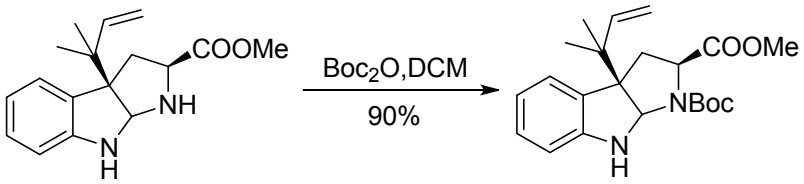
Contents of Supporting Information

General methods:

All commercially available reagents were used without further purification. All solvents were dried and distilled before use; THF were distilled from sodium/benzophenone ketyl; DCM and DMF were distilled from calcium hydride. Chromatography was conducted by using 200-300 mesh silica gel. All new compounds gave satisfactory spectroscopic analyses (^{1}H NMR, ^{13}C NMR, HRMS). NMR spectra were recorded on 400 MHz NMR or 600 MHz NMR spectrometer. HRMS spectra were obtained by the ESI method.

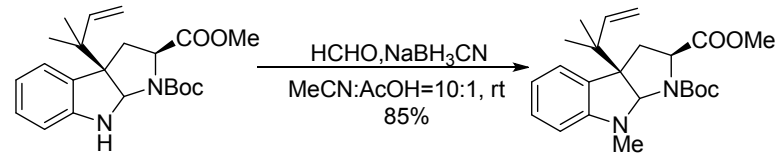


20 N2-Boc pyrroloindoline

Synthesis of N2-Boc pyrroloindoline

Pyrroloindoline **20** (15.0 g, 52.4 mmol) in dichloromethane (500 mL) was reacted with di-*tert*-butyl-dicarbonate (45.80 g, 209.6 mmol) at room temperature for 24 h. The reaction mixture was then quenched by addition of saturated $NaHCO_3$ and extracted with DCM (500 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10) to give N2-Boc pyrroloindoline as a pair of inseparable amide rotamers A and B (18.86 g, 90%) as white solids. $[\alpha]^{20}_D = -301.9$ (*c* 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$; a mixture of rotamer A and B in 1:4 ratio) δ 7.17-7.08 (rotamer A and B; m, 2H), 6.75-6.71 (rotamer A and B; m, 1H), 6.60 (rotamer A and B; d, J = 8.0 Hz, 1H), 5.41 (rotamer A; s, 1H), 5.35 (rotamer B; s, 1H), 5.07 (rotamer A and B; dd, J = 25.6, 11.2 Hz, 2H), 3.94 (rotamer A and B; t, J = 8.0 Hz, 1H), 3.72 (rotamer B; s, 3H), 3.71 (rotamer A; s, 3H), 2.43-2.34 (rotamer A and B; m, 2H), 1.36 (rotamer A and B; s, 9H), 1.06 (rotamer B; s, 3H), 1.05 (rotamer A; s, 3H), 1.00 (rotamer B; s, 3H), 0.98 (rotamer A; s, 3H) ppm. ^{13}C NMR (100 MHz,

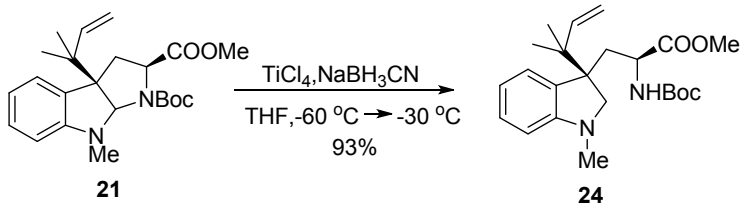
$CDCl_3$; a mixture of rotamer A and B in a 1:4 ratio) rotamer B: δ 173.4, 153.7, 149.8, 143.9, 130.1, 128.6, 124.9, 118.7, 113.9, 109.1, 80.8, 78.4, 61.7, 59.3, 52.1, 41.0, 36.4, 28.5, 22.9, 22.3 ppm. rotamer A:δ 173.4, 153.7, 149.8, 143.9, 130.1, 128.6, 124.9, 118.2, 113.9, 109.3, 80.8, 79.1, 61.7, 59.3, 51.9, 41.0, 37.1, 28.1, 22.9, 22.3 ppm. HRESIMS *m*/*z* 409.2103 $[M+Na]^+$ (calcd for $C_{22}H_{30}N_2O_4Na$ 409.2115); IR (neat): ν = 2977, 1753, 1693, 1607, 1394, 1365, 1172, 734 cm^{-1}.



N2-Boc pyrroloindoline **21**

(3a*R*)-1-*tert*-butyl 2-methyl 8-methyl-3a-(2-methylbut-3-en-2-yl)-3,3a,8,8a -tetrah ydropyrrolo[2,3-*b*]indole-1,2(2*H*)-dicarboxylate 21

To a solution of N2-Boc pyrroloindoline (2.1 g, 5.4 mmol) in 10% acetic acid (7.0 mL) in acetonitrile (63.0 mL), sodium cyanoborohydride (1.02 g, 16.3 mmol) and formaldehyde (37 % aqueous solution, 63 mL) was added. The reaction mixture was stirred at room temoperature for 30 min and then quenched by addition of saturated $NaHCO_3$. The mixture was extracted with EtOAc (50 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10) to afford **21** (1.85 g, 85%) as a white solid. $[\alpha]^{20}_D$ = −256.6 (*c* 0.5, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) δ 7.15-7.11 (m, 1H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.67-6.64 (m, 1H), 6.38 (d, *J* = 7.2 Hz, 1H), 5.88 (dd, *J* = 17.2, 11.2 Hz, 1H), 5.35 (s, 1H), 5.16-4.99 (m, 2H), 3.99-3.95 (m, 1H), 3.70 (s, 3H), 3.07-3.01 (m, 3H), 2.35 (d, *J* = 8.4 Hz, 2H), 1.37 (s, 9H), 1.00 (s, 3H), 0.93 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 153.7, 151.4, 143.9, 130.2, 128.8, 124.4, 116.8, 113.7, 106.3, 85.0, 80.3, 61.3, 59.5, 51.8, 40.9, 37.6, 34.9, 28.0, 27.3, 23.1, 22.0 ppm. HRESIMS *m*/*z* 400.2362 $[M]^+$ (calcd for $C_{23}H_{32}N_2O_4$ 400.2372). IR (neat): ν = 2977, 1753, 1704, 1605, 1495, 1394, 1169, 738 cm^{-1}.



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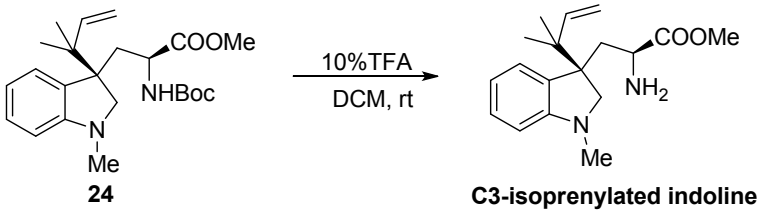
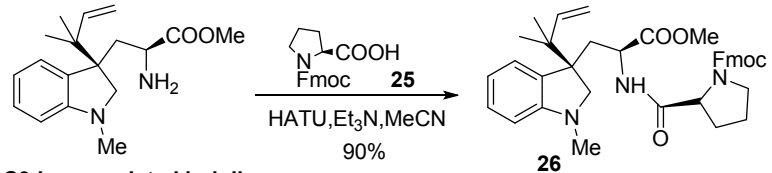
Methyl 2-((*tert*-butoxycarbonyl)amino)-3-((*R*)-1-methyl-3-(2-methylbut-3-en-2-yl) indolin-3-yl)propanoate 24

To a solution of **21** (3.2 g, 8.0 mmol) in THF (125 mL) was added $NaBH_3CN$ (5.0 g, 80.0 mmol) at −60 °C. After stirred for 10 min, a solution of $TiCl_4$ (3.2 mL) in DCM (200 mL) was added dropwise. The reaction mixture was warmed up to −30 °C, stirred for additional 24 h, and then quenched by addition of saturated $NaHCO_3$. The residue was extracted with EtOAc (100 mL × 3), and then combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10) to afford 2**4** (2.57 g, 80%) as a white solid. $[\alpha]^{20}_D$ = +0.6 (*c* 0.6, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 7.06 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.59 (t, *J* = 6.8 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.96 (dd, *J* = 17.2,10.8 Hz, 1H), 5.04 (dd, *J* = 17.2, 10.8 Hz, 2H), 4.99 (s, 1H), 4.06 (s, 1H), 3.45 (d, *J* = 9.6 Hz, 1H), 3.38 (s, 3H), 3.29 (d, *J* = 10.4 Hz, 1H), 2.73 (s, 3H), 2.39 (dd, *J* = 14.4, 6.0 Hz, 1H), 1.87 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.41 (s, 9H), 1.01 (s, 3H), 0.98 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.7, 154.7, 153.9, 144.8, 130.2, 128.1, 125.5, 116.4, 113.2, 106.6, 60.9, 52.3, 52.0, 51.6, 43.4, 37.3, 35.3, 30.9, 28.2, 22.6, 22.4 ppm. HRESIMS *m*/*z* 425.2416 $[M+Na]^+$ (calcd for $C_{23}H_{34}N_2$ Na O_4 425.2418). IR (neat): ν = 2928, 2857, 1718, 1604, 1499, 1366, 1168, 799 cm^{-1}.



Methyl 2-amino-3-((*R*)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl) propanoate

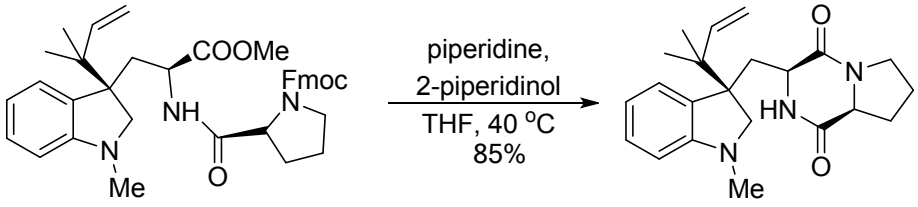
To a solution of **24** (3.0 g, 7.4 mmol) in DCM (100 mL), 10% TFA (20 mL) in DCM (80 mL) was added dropwise at 0 °C. The reaction mixture was warmed up to room temperature and stirred for additional 2 h. After completion of the reaction, it was quenched by addition of saturated $NaHCO_3$ at 0 °C and extracted with DCM (100 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ solution (100 mL) and brine (100 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 to 1:1) to afford C3-isoprenylated indoline (2.1 g, 93%) as a white solid. $[\alpha]^{20}_D$ = +11.6 (*c* 0.4, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 7.07 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.59 (t, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.96 (dd, *J* = 17.2, 10.8 Hz, 1H), 5.04 (dd, *J* = 11.2, 10.0 Hz, 2H), 3.54 (d, *J* = 10.0 Hz, 1H), 3.47 (s, 3H), 3.42 (d, *J* = 10.4 Hz, 1H), 2.74 (s, 3H), 2.44 (dd, *J* = 14.0, 4.8 Hz, 1H), 1.71 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.87 (dd, *J* = 14.0, 6.8 Hz, 1H), 1.03 (s, 3H), 1.00 (s, 3H) ppm.^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 154.1, 145.1, 130.8, 128.0, 125.7, 116.3, 112.9, 106.6, 61.5, 52.8, 52.5, 51.8, 43.7, 39.7, 35.4, 22.7, 22.5 ppm. HRESIMS *m*/*z* 303.2073 $[M+H]^+$ (calcd for $C_{18}H_{27}N_2O_2$ 303.2067); IR (neat): ν = 3611, 3289, 2966, 1681, 1262, 1208, 1144, 1019, 801 cm^{-1}.



(9*H*-fluoren-9-yl)methyl 2-((1-methoxy-3-((*R*)-1-methyl-3-(2-methylbut-3-en -2-yl) indolin-3-yl)-1-oxopropan-2-yl)carbamoyl)pyrrolidine-1-carboxylate 26

Under N_2, C3-isoprenylated indoline (2.0 g, 6.6 mmol) and HATU (3.0 g, 7.9 mmol) was stirred in dry acetonitrile (100 mL) at 0 °C. After stirring for five minutes, triethylamine (1.8 mL, 13.2 mmol) was added slowly to the mixture and reacted at 0 °C for another five minutes when Fmoc-*L*-proline **25**(4.5 g, 13.2 mmol) was introduced to the mixture by syringe. The mixture was warmed up to room temperature and stirred for additional 2 h. After completion of the reaction, it was quenched by addition of H_2O at 0 °C and extracted with EtOAc (100 mL × 3). The

combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:3) to afford **26** (3.7 g, 90%) as a white solid. $[\alpha]^{20}_D$ = −60.7 (*c* 0.8, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) 7.76 (s, 2H), 7.59-7.52 (m, 2H), 7.40-7.26 (m, 4H), 7.07-6.97 (m, 3H), 6.58 (t, *J* = 8.0 Hz, 1H), 6.37-6.35 (m, 1H), 5.89-5.85 (m, 1H), 4.95 (t, *J* = 10.4 Hz, 2H), 4.42-4.26 (m, 5H), 3.52 (s, 2H), 3.38 (s, 3H), 3.33 (d, *J* = 10.0 Hz, 1H), 3.19 (d, *J* = 10.4 Hz, 1H), 2.70-2.63 (m, 3H), 2.43-2.26 (m, 2H), 1.98-1.88 (m, 4H), 0.96 (s, 3H), 0.91 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.8, 170.6, 155.9, 153.9, 144.6, 143.7, 141.2, 130.3, 128.2, 127.6, 127.0, 125.3, 124.9, 119.9, 116.4, 113.0, 106.6, 67.6, 60.5, 60.2, 52.3, 52.0, 50.4, 47.1, 46.8, 43.2, 38.4, 36.9, 35.2, 28.0, 24.5, 22.5, 22.3 ppm. HRESIMS *m*/*z* 622.3281 $[M+H]^+$ (calcd for $C_{38}H_{44}N_3O_5$ 622.3278); IR (neat): ν = 2951, 1744, 1695, 1451, 1419, 1355, 1201, 1121, 742 cm^{-1}.

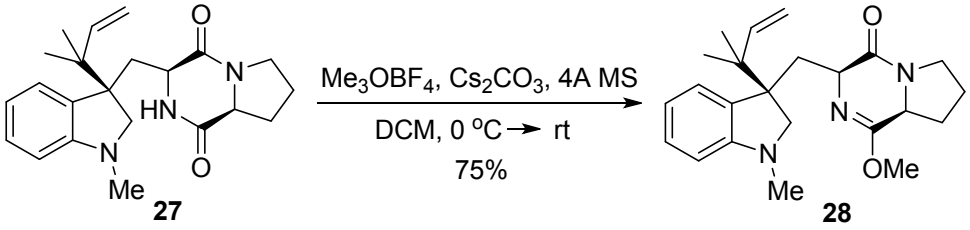


26 **27**

3-(((*R*)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)hexahydropyrrolo[1,2-a]pyrazine-1,4-dione 27

To a solution of **26** (3.7 g, 6.0mmol) in dry THF (100 mL) was added 2-piperidinol (1.2 g, 12.0 mmol) in one portion. After stirring at 0 °C for five minutes, a solution of piperdine (15 mL) in THF (85 mL) was added slowly to the mixture. The mixture was warmed up to room temperature and stirred for additional 24 h. After completion of the reaction, it was quenched by addition of saturated NH_4Cl at 0 °C and extracted with EtOAc (100 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:10 to 1:2) to afford **27** (1.8 g, 85%) as a yellow oil. $[\alpha]^{20}_D$ = −60.9 (*c* 0.7, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) 7.20 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 1H), 6.71 (t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.00-

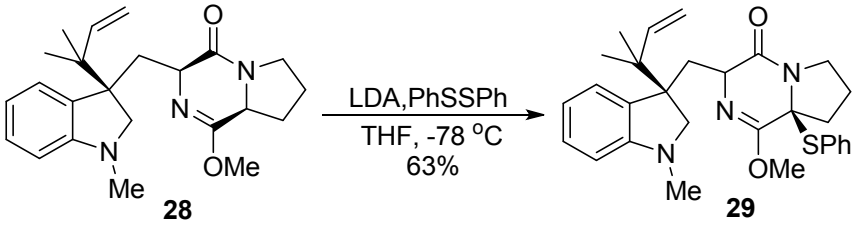
5.97 (m, 1H), 5.08 (t, *J* = 9.6 Hz, 2H), 3.87 (t, *J* = 7.2 Hz, 1H), 3.58-3.56 (m, 1H), 3.45-3.41 (m, 3H), 3.21 (d, *J* = 15.6 Hz, 1H), 3.12(d, *J* = 10.2 Hz, 1H), 2.80 (s, 3H), 2.28-2.26 (m, 1H), 1.97-1.94 (m, 2H), 1.97-1.94 (m, 2H), 1.81-1.77 (m, 2H), 1.12 (s, 3H), 1.11 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.6, 165.6, 152.8, 145.0, 131.3, 128.4, 125.2, 118.8, 113.4, 108.7, 64.1, 58.7, 54.5, 52.2, 45.4, 43.3, 37.6, 35.7, 28.5, 23.5, 23.1, 22.2 ppm. HRESIMS *m*/*z* 390.2157 $[M+Na]^+$ (calcd for $C_{22}H_{29}N_3NaO_2$ 390.2153); IR (KBr) ν_{max} 3609, 2971, 1680, 1419, 749 cm^{-1}.



1-methoxy-3-(((*R*)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)-6,7,8,8a-tetrahydropyrrolo[1,2-*a*]pyrazin-4(3*H*)-one 28

27 (500 mg, 1.4 mmol), $CsCO_3$ (2.9 g, 8.9 mmol), and 4Å molecular sieves (150 mg) were mixed and stirred in dry DCM (50 mL), when trimethyloxonium tetrafluoroborate (2.0 g, 14.0 mmol) was introduced by syringe and stirred at 0 °C under nitrogen. The mixture was warmed up to room temperature and stirred for additional 3h. After completion of the reaction, it was quenched by addition of saturated NaCl and extracted with DCM (50 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:5) to afford **28** (389.3 mg, 75%) as a yellow oil. $[\alpha]^{20}_D = -126.4$ (*c* 0.3, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$) 7.07-7.03 (m, 2H), 6.56 (t, *J* = 7.2 Hz, 1H), 6.33 (d, *J* = 7.8 Hz, 1H), 6.01 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.02 (t, *J* = 10.8 Hz, 2H), 4.00 (d, *J* = 9.6 Hz, 1H), 3.83 (s, 1H), 3.63 (s, 3H), 3.59-3.58 (m, 1H), 3.51 (dd, *J* = 20.4, 9.6 Hz, 1H), 3.42 (d, *J* = 9.6 Hz, 1H), 3.37 (t, *J* = 9.6 Hz, 1H), 3.13 (d, *J* = 15.0 Hz, 1H), 2.69 (s, 3H), 2.18-2.16 (m, 1H), 1.95 (s, 1H), 1.79-1.75 (m, 2H), 1.07 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0, 160.8, 154.5, 145.5, 131.6, 127.6, 126.0, 116.0, 112.3, 105.6, 60.5, 58.1, 56.4, 53.4, 44.5, 43.7, 35.2, 34.4, 31.8, 29.6, 28.7, 22.6, 22.4 ppm.

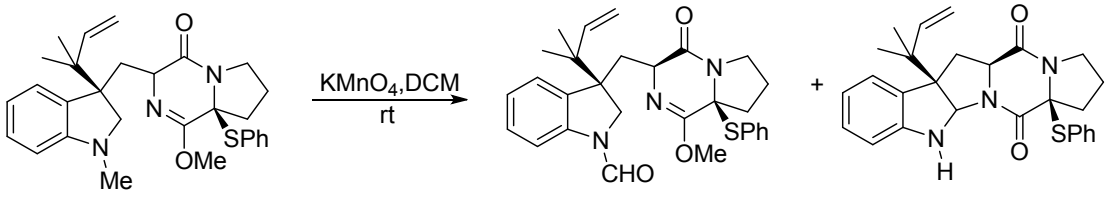
HRESIMS *m/z* 382.2495 $[M+H]^+$ (calcd for $C_{23}H_{32}N_3O_2$ 382.2494). IR (neat): ν = 3626, 2943, 1673, 1603, 1499, 1433, 1258, 750 cm^{-1}.



28 **29**

(8a*S*)-1-methoxy-3-(((*R*)-1-methyl-3-(2-methylbut-3-en-2-yl)indolin-3-yl)methyl)-8a-(phenylthio)-6,7,8,8a-tetrahydropyrrolo[1,2-a]pyrazin-4(3*H*)-one 29

LDA (1.5 M solution in tetrahydrofuran, 15.7 mmol) was added slowly to a solution of 2**8** (1.0 g, 2.6 mmol) in anhydrous THF (50 mL) at −78 °C. After stirring for 30 min, diphenyl disulfide (3.4 g, 15.7 mmol) was added and the mixture was stirred for another 30 min at the same temperature. The reaction mixture was then quenched by addition of saturated NH_4Cl and extracted with EtOAc (50 mL × 3). The combined organic layers were washed with saturated $NaHCO_3$ solution (50 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:20) to give **29** (0.8 g, 63%) as a yellow oil. $[\alpha]^{20}_D$ = −289.5 (*c* 0.4, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$) 7.13-7.08 (m, 3H), 6.99 (t, *J* = 7.2 Hz, 1H), 6.93-6.89 (m, 3H), 6.60 (t, *J* = 7.2 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 5.89 (dd, *J* = 17.4, 10.8 Hz, 1H), 4.94 (dd, *J* = 22.2, 10.8 Hz, 2H), 3.84-3.79 (m, 1H), 3.66 (d, *J* = 9.6 Hz, 1H), 3.59 (s, 3H), 3.29 (d, *J* = 10.2 Hz, 1H), 2.76 (d, *J* = 15.0Hz, 1H), 2.69 (m, 3H), 2.28-2.19 (m, 4H), 2.02-1.97 (m, 1H), 1.43 (dd, *J* = 14.4, 9.6Hz, 1H), 0.95 (s, 3H), 0.90 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 156.4, 154.5, 145.5, 137.0, 131.2, 130.3, 129.2, 128.4, 127.6, 126.0, 116.3, 112.2, 105.9, 74.1, 60.1, 57.1, 53.4, 53.1, 43.8, 43.5, 36.2, 35.6, 35.5, 22.5, 22.2, 20.3 ppm. HRESIMS *m/z* 490.2528 $[M+H]^+$ (calcd for $C_{29}H_{36}N_3O_2S$ 490.2536); IR (neat): ν = 3479, 2919, 1680, 1604, 1440, 1421, 1302, 749 cm^{-1}.



29

30a and **30b**
rotamers: a/b=4:1
55%

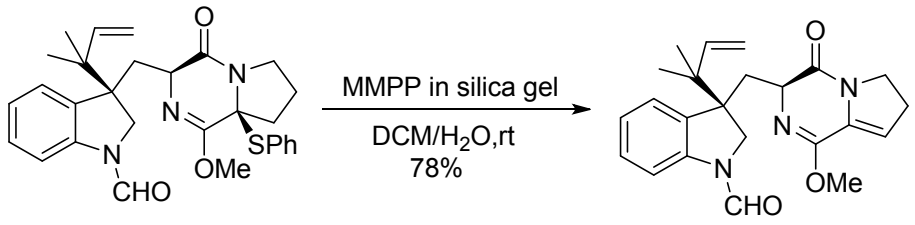
31, 25%

(3*R*)-3-(((8a*S*)-1-methoxy-4-oxo-8a-(phenylthio)-3,4,6,7,8,8a-hexahydropyrrolo[1,2-*a*]pyrazin-3-yl)methyl)-3-(2-methylbut-3-en-2-yl)indoline-1-carbaldehyde 30

To a stirred solution of **29** (200 mg, 0.4 mmol) in DCM (20 mL) was added potassium permanganate (194 mg, 1.2 mmol) and stirred at 0 °C. The mixture was warmed up to room temperature and stirred for additional 20 h. After completion of the reaction, it was quenched by saturated $NaHSO_3$ and extracted with DCM (20 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamer **30a** and **30b** (113.1 mg, 55%, 1:4) as a yellow oil. $[\alpha]^{20}_D = -265.2$ (*c* 0.2, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$; a mixture of rotamers **30a** and **30b**) δ 8.90 (rotamer **a**; s, 1H), 8.92 (rotamer **b**; s, 1H), 8.15 (rotamer **b**; d, *J* = 12.0 Hz, 1H), 7.33-7.26 (rotamers **a** and **b**; m, 1H), 7.27 (rotamers **a** and **b**; d, *J* = 7.8 Hz, 1H), 7.19 (rotamers **a** and **b**; d, *J* = 7.8 Hz, 1H), 7.08-7.05 (rotamers **a** and **b**; m, 3H), 6.68 (rotamers **a** and **b**; t, *J* = 7.2 Hz, 1H), 6.88 (rotamers **a** and **b**; t, *J* = 7.2 Hz, 1H), 5.71 (rotamers **a** and **b**; dd, *J* = 16.2, 10.8 Hz, 1H), 5.01-4.91 (rotamers **a** and **b**; m, 2H), 4.48 (rotamer **b**; d, *J* = 11.4 Hz, 1H), 4.13 (rotamer **a**; d, *J* = 12.6 Hz, 1H), 4.02 (rotamer **a**; d, *J* = 13.2 Hz, 1H), 3.95 (rotamer **b**; d, *J* = 6.8 Hz, 1H), 3.82-3.79 (rotamers **a** and **b**; m, 1H), 2.28-2.20 (rotamers **a** and **b**; m, 3H), 2.07-1.99 (rotamers **a** and **b**; m, 1H),1.55 (rotamers **a** and **b**; dd, d, *J* = 13.8, 9.6 Hz, 1H), 0.92 (rotamers **a** and **b**; s, 3H), 0.89 (rotamers **a** and **b**; s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$; all signals for the amide rotamers are listed) δ 169.7, 159.0, 157.2, 156.8, 143.9, 143.6, 142.5, 137.1, 137.0, 134.2, 129.9, 129.3, 128.4, 128.2, 127.3, 126.1, 123.8, 123.5, 116.1, 113.8, 74.0, 56.8, 53.4, 53.1, 52.7, 52.6, 50.8, 43.8, 36.0, 35.1, 22.2, 21.8, 20.2 ppm. HRESIMS *m*/*z* 526.2140 $[M+Na]^+$ (calcd for

$C_{29}H_{33}N_3O_3NaS$ 526.2157); IR (neat): ν = 2938, 1794, 1671, 1484, 1385, 1238, 1118, 1039, 898, 753 cm^{-1}.

31 (51.4 mg, 25%) as a yellow oil. $[\alpha]^{20}_D$ = −198.8 (*c* 0.4, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$) 7.28 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 2H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 5.86 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.37 (s, 1H), 5.06-4.97 (m, 3H), 3.73-3.68 (m, 1H), 3.73-3.68 (m, 1H), 3.48 (s, 0.5H), 3.10 (s, 0.5H), 2.43-2.36 (m, 3H), 2.20-2.00 (m, 4H), 1.00 (s, 3H), 0.91 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 166.8, 164.9, 149.9, 143.4, 137.3, 130.0, 129.2, 128.8, 128.6, 124.9, 118.5, 114.2, 108.9, 74.4, 76.2, 61.2, 60.2, 59.2, 44.9, 40.4, 43.5, 36.1, 35.5, 22.5, 22.6, 22.2, 20.9 ppm. HRESIMS *m/z* 482.1878 $[M+Na-CH_2]^+$ (calcd for $C_{27}H_{29}N_3O_2S$ 482.1878); IR (neat): ν = 3508, 2661, 1415, 753, 693 cm^{-1}.



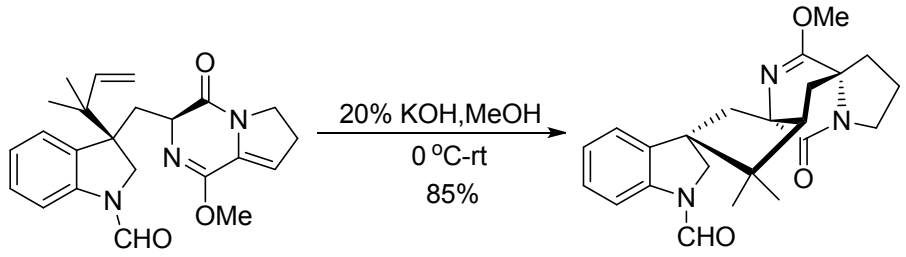
30a and **30b**
rotamers: a/b=4:1

18a and **18b**
rotamers: a/b=4:1

(3*R*)-3-((1-methoxy-4-oxo-3,4,6,7-tetrahydropyrrolo[1,2-*a*]pyrazin-3-yl)methyl)-3-(2-methylbut-3-en-2-yl)indoline-1-carbaldehyde 18

Monoperoxyphthalic acid magnesium salt hexahydrate (MMPP) (704 mg, 1.4 mmol) and silica gel (54-75um) (3.0 g) in 2.25 mL H_2O was vigorously stirred for 5 minutes. The freshly prepared mixture was then added to a solution of **30a** and **30b** (180 mg, 0.36 mmol) in DCM (18 mL) in one portion and stirred for another 30 minutes. After completion of the reaction, it was quenched by addition of saturated $NaHSO_3$ and extracted with DCM (20 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of diene **18a** and **18b** (109.7 mg, 78%) as a white solid. $[\alpha]^{20}_D$ = −265.2 (*c* 0.2, CH_2Cl_2). ^1H NMR (600 MHz, $CDCl_3$; a mixture of rotamer **a** and **b** in a 1:4 ratio) *δ* 8.88 (rotamer **a**; s, 1H),

8.44 (rotamer **b**; s, 1H), 8.08 (rotamer **a**; d, *J* = 7.8 Hz, 1H), 7.43-7.40 (rotamers **a** and **b**; m, 1H), 7.21 (rotamers **a** and **b**; d, *J* = 7.2 Hz, 1H), 7.16 (rotamer **a**; d, *J* = 8.0 Hz, 1H), 7.09 (rotamers **a** and **b**; t, *J* =7.2 Hz, 1H), 5.82 (rotamers **a** and **b**; dd, *J*=17.2,10.8 Hz, 1H), 5.51(rotamers **a** and **b**; s, 1H), 5.05 (rotamers **a** and **b**; dd, *J* =17.2, 10.8 Hz, 2H), 4.73 (rotamer **b**; d, *J* = 7.2 Hz, 1H), 4.53 (rotamer **a**; d, *J* = 8.4 Hz, 1H), 4.13 (rotamer **a**; d, *J* = 8.4 Hz, 1H), 4.08 (rotamer **b**; d, *J* = 6.8 Hz, 1H), 3.94-3.81 (rotamers **a** and **b**; m, 3H), 3.64-3.62 (rotamers **a** and **b**; m, 3H), 2.95-2.92 (rotamers **a** and **b**; m, 1H), 2.71-2.69 (rotamers **a** and **b**; m, 2H),1.82 (rotamers **a** and **b**; dd, *J* = 13.6, 10.8 Hz, 1H), 1.02 (rotamers **a** and **b**; s, 3H), 1.00 (rotamers **a** and **b**; s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$; all signals for the amide rotamers are listed) *δ* 166.7, 159.1, 157.0, 150.8, 143.7, 142.8, 134.1, 129.6, 128.1, 127.6, 126.4, 123.9, 123.5, 116.2, 114.1, 111.0, 108.7, 60.5, 53.1, 53.0, 52.9, 52.1, 44.4, 44.0, 38.4, 27.8, 22.4, 22.0 ppm. HRESIMS *m/z* 416.1950 $[M+Na]^+$ (calcd for $C_{23}H_{27}N_3O_3Na$ 416.1949). IR (neat): ν = 3613, 2924, 2855, 1681, 1626, 1261, 1019, 801 cm^{-1}.



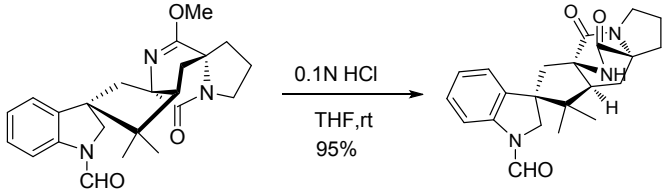
18a and **18b**
rotamers: a/b=4:1

19a and **19b**
rotamers:a/b=4:1

(3'*R*,5a*S*,8a*R*,9a*R*)-10-methoxy-8,8-dimethyl-5-oxo-1,2,3,5,6,8,8a,9-octahydrospiro[5a,9a-(azenometheno)cyclopenta[f]indolizine-7,3'-indoline]-1'-carbaldehyde 19

To a solution of diene **18a** and **18b** (175 mg, 0.405 mmol) in MeOH (28 mL) at 0 ºC was added 20% aqueous KOH (7 mL). The reaction mixture was slowly warmed to room temperature over 1 hour and stirred for another 5 hours. After completion of the reaction, it was quenched by addition of H_2O at 0 °C and extracted with EtOAc (30 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamer **19a** and **19b** (148.7

mg, 85%) in 1:4 ratio as a white solid. $[\alpha]^{20}_D = -92.4$ (*c* 0.2, CH_2Cl_2); ^1H NMR (600 MHz, $CDCl_3$; a mixture of rotamers **a** and **b** in a 1:4 ratio) δ 8.80 (rotamer **a**; s, 1H), 8.43 (rotamer **a**; s, 1H), 7.19 (rotamer **b**; d, *J* = 7.8 Hz, 1H), 8.06 (rotamer **b**; d, *J* = 7.8 Hz, 1H), 7.43 (rotamer **b**; d, *J* = 7.2 Hz, 1H), 7.28-7.23 (rotamers **a** and **b**; m, 1H), 7.19 (rotamer **a**; d, *J* = 7.8 Hz, 1H), 7.13-7.11 (rotamers **a** and **b**; m, 1H), 4.64 (rotamer **a**; d, *J* = 12.6 Hz, 1H), 4.38 (rotamer **b**; d, *J* = 11.4 Hz, 1H), 3.84 (rotamer **b**; d, *J* = 11.4 Hz, 1H), 3.79 (rotamers **a** and **b**; s, 3H), 3.54 (rotamer **a**; d, *J* = 12.0 Hz, 2H), 3.41-3.36 (rotamers **a** and **b**; m, 2H), 2.99 (rotamers **a** and **b**; t, *J* = 15.6 Hz, 1H), 2.87 (rotamers **a** and **b**; t, *J* = 15.6 Hz, 1H), 2.59-2.56 (rotamers **a** and **b**; m, 1H), 2.49-2.46 (rotamers **a** and **b**; m, 1H), 2.04-2.00 (v; m, 1H), 1.98-1.88 (rotamers **a** and **b**; m, 2H), 1.85-1.81 (rotamers **a** and **b**; m, 1H), 1.50-1.45 (rotamers **a** and **b**; m, 1H), 0.73 (rotamer **b**; s, 3H),0.72 (rotamer **a**; s, 3H), 0.69 (rotamer **b**; s, 3H), 0.68 (rotamer **a**; s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$; all signals for the amide rotamers are listed) δ 172.3, 170.8, 158.3, 156.8, 141.2, 134.6, 128.2, 127.2, 125.9, 124.0, 123.7, 116.6, 109.7, 72.4, 67.3, 59.8, 59.0, 57.3, 54.3, 54.1, 53.6, 46.8, 46.7, 43.1, 41.8, 41.6, 30.5, 30.4, 29.6, 28.8, 25.1, 21.5, 21.0, 19.8, 19.6 ppm. HRESIMS *m*/*z* 416.1950 $[M+Na]^+$ (calcd for $C_{23}H_{27}N_3O_3Na$ 416.1949); IR (neat): ν = 3600, 2947, 1679, 1590, 1489, 1362 cm^{-1}.

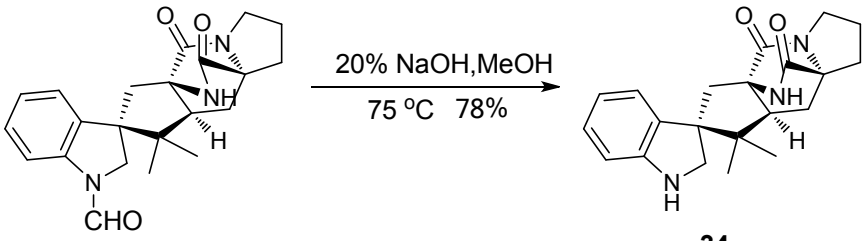


19a and **19b** **33a** and **33b**

(3'*R*,5a*S*,8a*R*,9a*R*)-8,8-dimethyl-5,10-dioxo-1,2,3,5,6,8,8a,9-octahydrospiro[5a,9a-(epiminomethano)cyclopenta[f]indolizine-7,3'-indoline]-1'-carbaldehyde 33

To a solution of rotamers **19a** and **19b** (100 mg, 0.254 mmol) in THF (5 mL) at 0 ºC was added 0.1N HCl (5 mL). The reaction mixture was slowly warmed to room temperature and stirred for another 20 mintues. After completion of the reaction, it was then quenched by addition of $NaHCO_3$ at 0 °C and extracted with EtOAc (10 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and

concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to give a mixture of two amide rotamers **33a** and **33b** (91.6 mg, 95%) in 1:4 ratio as a white solid. $[\alpha]^{20}_{D} = -91.2$ (*c* 0.1, CH_2Cl_2). ^{1}H NMR (600 MHz, $CDCl_3$; a mixture of rotamer **a** and **b** in a 1:4 ratio) δ 8.82 (rotamer **a**; s, 1H), 8.45 (rotamer **b**; s, 1H), 0.08 (rotamer **b**; d, *J* = 7.8 Hz, 1H), 7.96 (rotamer **b**; s, 1H), 7.80 (rotamer **a**; s, 1H), 7.42 (rotamers **a** and **b**; d, *J* = 7.8 Hz, 1H), 7.32-7.28 (rotamers **a** and **b**; m, 1H), 7.20 (rotamers **a** and **b**; d, *J* = 7.8 Hz, 1H), 7.15-7.12 (rotamers **a** and **b**; m, 1H), 4.64 (rotamer **a**; d, *J* = 12.6 Hz, 1H), 4.37 (rotamer **b**; d, *J* = 11.4Hz, 1H), 3.83 (rotamer **a**; d, *J* = 10.8 Hz, 1H), 3.52 (rotamer **a**; d, *J* = 12.6 Hz, 1H), 3.50-3.43 (rotamers **a** and **b**; m, 2H), 2.92 (rotamers **a** and **b**; t, *J* = 15.0 Hz,1H), 2.80-2.74 (rotamers **a** and **b**; m, 1H), 2.51-2.41(rotamers **a** and **b**; m, 2H), 2.09-2.00 (rotamers **a** and **b**; m, 2H), 1.99-1.96 (rotamers **a** and **b**; m, 1H), 1.96-1.86 (rotamers **a** and **b**; m, 1H), 1.80-1.75 (rotamers **a** and **b**; m, 1H), 0.83 (rotamer **a**; s, 3H), 0.80 (rotamer **b**; s, 3H); 0.79 (rotamer **b**; s, 3H), 0.74 (rotamer **a**; s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$; all signals for the amide rotamers are listed) δ 173.8, 169.7, 158.2, 156.8, 141.1, 133.4, 128.6, 126.8, 125.6, 124.2, 123.9, 116.8, 110.0, 68.9, 66.7, 59.6, 58.9, 58.7, 53.3, 52.8, 46.8, 43.8, 38.6, 38.4, 29.0, 28.9, 24.9, 21.7, 21.3, 19.3; 19.1 ppm. HRESIMS *m*/*z* 402.1794 $[M+Na]^+$ (calcd for $C_{22}H_{25}N_3O_3Na$ 402.1798); IR (neat): ν = 3646, 2955, 1675, 1589, 1493, 1370, 760 cm^{-1}.

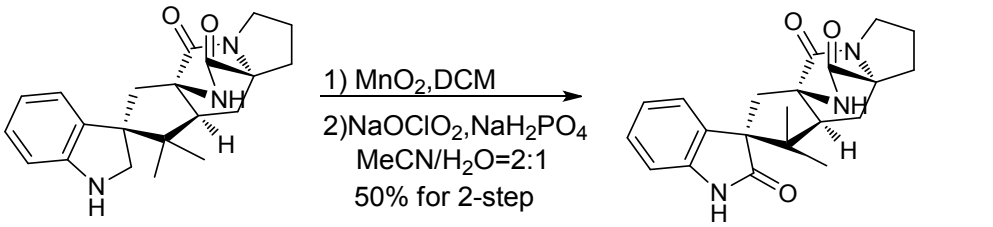


33a and **33b** **34**

(3'*R*,5a*S*,8a*R*,9a*R*)-8,8-dimethyl-2,3,6,8,8a,9-hexahydrospiro[5a,9a-(epiminomethano)cyclopenta[f]indolizine-7,3'-indoline]-5,10(1*H*)-dione 34

To a solution of **33a** and **33b** (100 mg, 0.405 mmol) in MeOH (10 mL) at 0 ºC was added 20% aqueous NaOH (2.5 mL). The reaction mixture was heated to 75°C and stirred for 4 hours. After completion of the reaction, it was cooled to room temperature and quenched by cold water at 0 °C and extracted with EtOAc (15 mL ×

3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:2) to afford **34** (72.2 mg, 78%) as a white solid. $[\alpha]^{20}_D = -12.0$ (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) 7.11-7.07 (m, 2H), 6.76 (t, *J* = 7.2 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 1H), 3.79 (d, *J* = 10.0 Hz, 1H), 3.47-3.40 (m, 3H), 2.89 (d, *J* = 15.6 Hz, 1H), 2.78-2.72 (m, 1H), 2.44 (t, *J* = 8.4 Hz, 1H), 2.20 (d, *J* = 15.6 Hz, 1H), 2.06-1.99 (m, 2H), 1.97-1.94 (m, 1H), 1.91-1.67 (m, 2H), 0.93 (s, 3H), 0.87 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 170.2, 152.1, 129.9, 128.2, 125.6, 118.0, 110.0, 69.0, 66.8, 59.9, 53.1, 46.4, 43.8, 40.6, 31.9, 25.0, 22.6, 22.2, 19.6, 14.1 ppm. HRESIMS *m*/*z* 352.2025 $[M+H]^+$ (calcd for $C_{21}H_{26}N_3O_2$ 325.2029). IR (neat): ν = 3521, 2917, 2849, 1651, 1261, 1018, 799 cm^{-1}.

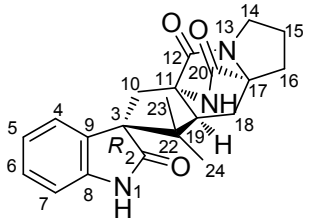


34 (-)-Depyranoversicolamide B **(12)**

Synthesis of (–)-Depyranoversicolamide B (12)

To a solution of **34** (20 mg, 0.057 mmol) in DCM (2 mL) was added MnO_2 (99 mg, 1.14 mmol). The reaction mixture was stirred for 2 hours and then filtered and concentrated in vacuum. The residue was dissolved in a mixture of MeCN (1 mL) and H_2O (0.5 mL) and added with $NaOClO_2$ (10.4 mg, 0.114 mmol) and NaH_2PO_4 (18.0 mg, 0.114 mmol). The reaction mixture was stirred at room temperature for 3 hours. After completion of the reaction, it was quenched by addition of $Na_2S_2O_3$ at 0 °C and extracted with EtOAc (5 mL × 3). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/petroleum 1:1) to afford (–)-depyranoversicolamide B **(12)** (10.4 mg, 50%) as a white solid. $[\alpha]^{20}_D = -12.60$ (*c* 0.1, CH_2Cl_2). ^{1}H NMR (600 MHz, CD_3OD: （$CD_3)_2SO$ = 6:1) 7.43-7.40 (m, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 3.46-3.43 (m, 1H), 3.41-3.39 (m, 1H), 3.03

(dd, *J* = 15.6, 3.6 Hz, 1H), 2.67-2.62 (m, 1H), 2.20 (dt, *J* = 15.0, 3.0 Hz, 1H), 2.12-2.07 (m, 1H), 2.05-1.89 (m, 3H), 1.78 (dd, *J* = 13.2, 7.2 Hz, 1H), 1.10 (s, 3H), 0.81 (s, 3H) ppm. ^{13}C NMR (150 MHz, CD_3OD: $(CD_3)_2SO$ = 6:1) δ 184.3, 178.3, 171.9, 143.6, 130.9, 129.6, 127.4, 122.6, 110.5, 70.7, 69.1, 64.3, 52.1, 49.3, 44.9, 35.2, 29.8, 29.3, 25.8, 23.5, 21.1 ppm. HRESIMS *m/z* 388.1637 $[M+Na]^+$ (calcd for $C_{21}H_{23}N_3NaO_3$ 388.1641). IR (neat): ν = 3613, 3290, 1699, 1572, 694 cm^{-1}

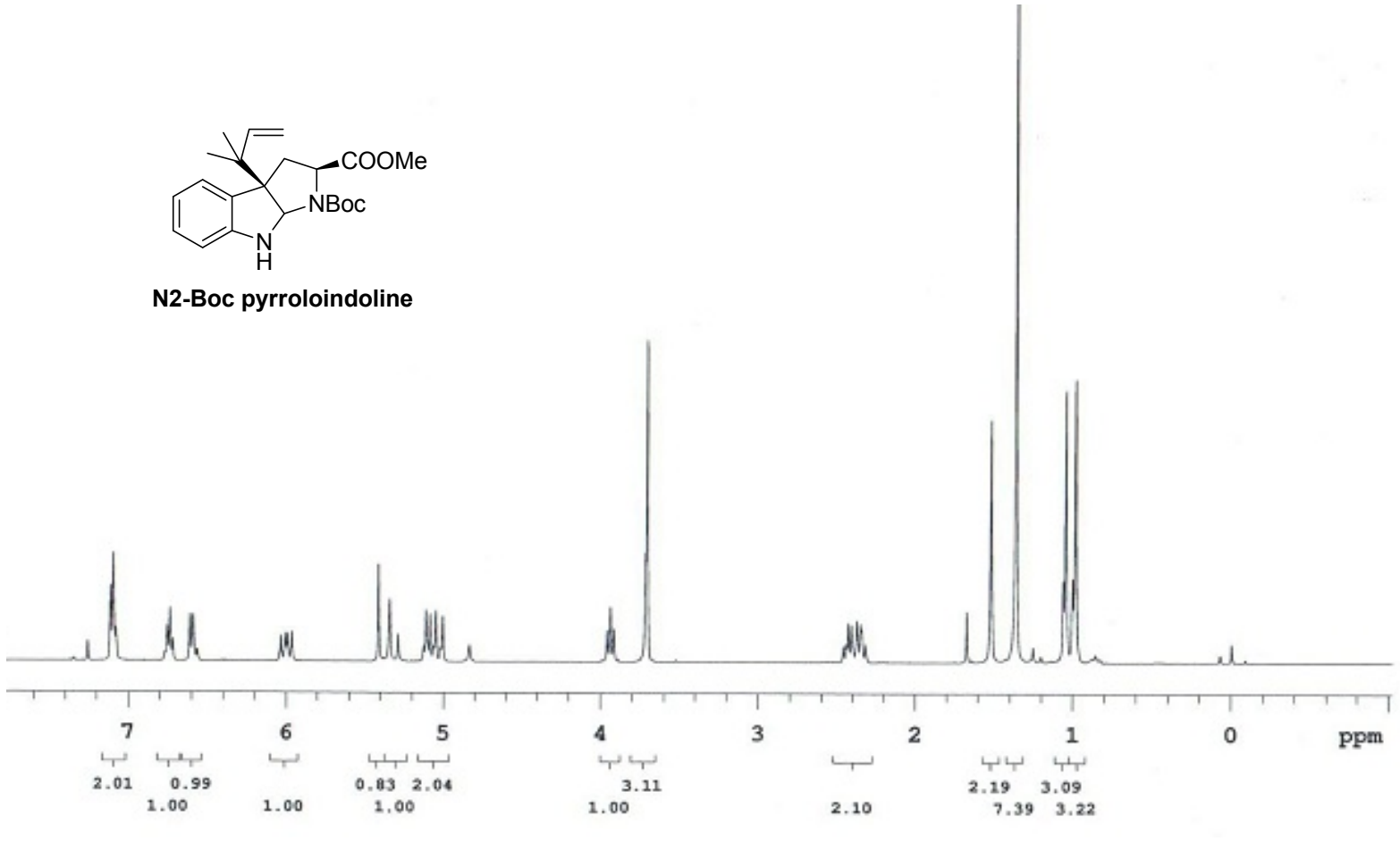


(-)-depyranoversicolamide B (**12**)

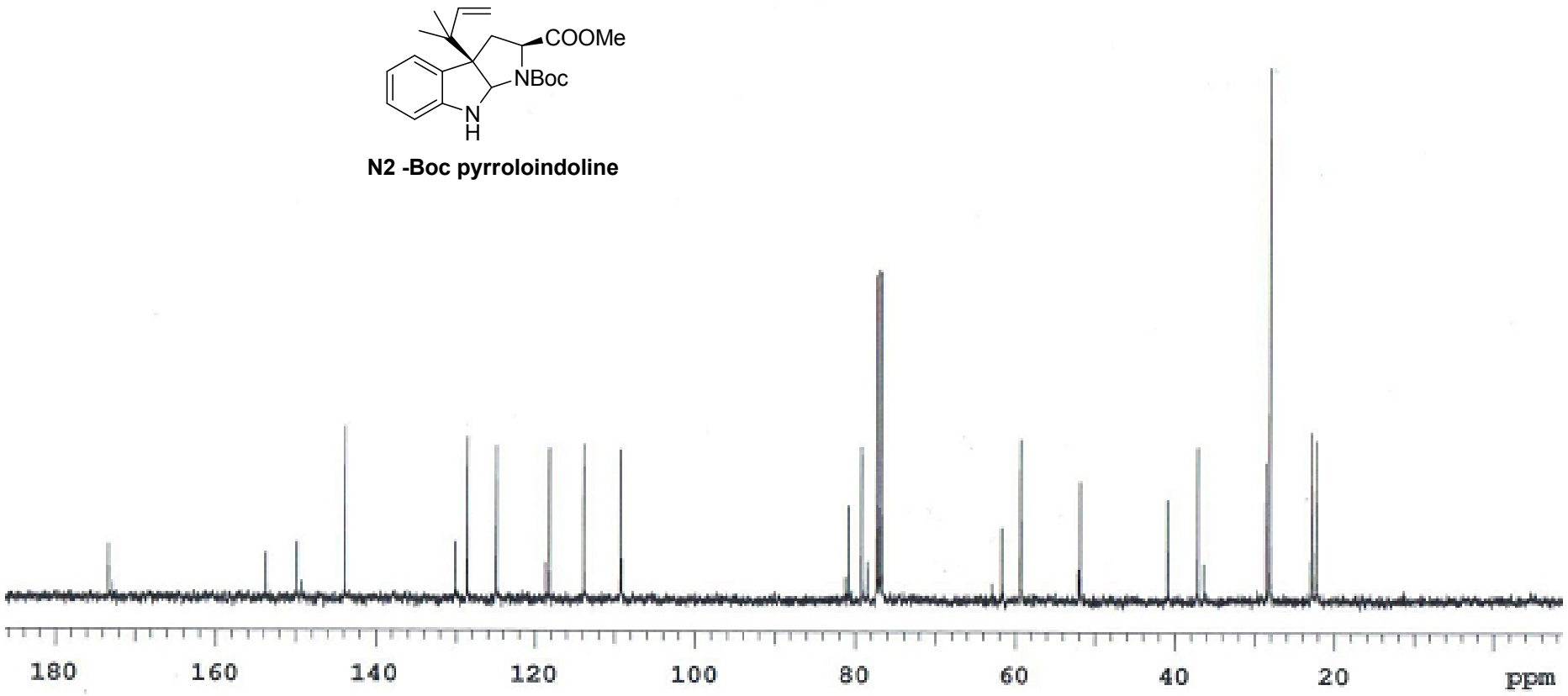
2D NMR spectrum data of (–)-depyranoversicolamide B (12)

Position	C	H	HMBC (H→C)	H-H COSY
2	184.2	-	-	-
3	64.2	-	-	-
4	127.4	7.43-7.40m	C6, C9	H5
5	122.6	7.04 (t, *J* = 7.2 Hz)	C7, C8	H4, H6
6	129.6	7.25 (t, *J* = 7.8 Hz)	C4, C9	H5, H7
7	110.5	6.89 (d, *J* = 7.2 Hz)	C5, C8	H6
8	130.9	-	-	-
9	143.6	-	-	-
10	35.2	3.03 (dd, *J* = 15.6, 3.6 Hz) (a)	C2, C3, C11, C12, C22	H10b
		2.20 (dt, *J* = 15.0, 3.0 Hz) (b)	C2, C3, C11, C19	H10a
11	69.1	-	-	-
12	171.9	-	-	-
14	44.9	3.46-4.43m	C16	H15a, H16b
15	25.8	2.12-2.07 m (a)	C14, C16,C17	H14, H15b, H16b
		2.00-1.95 m (b)	C14, C16,C17	H14, H15a,H16b

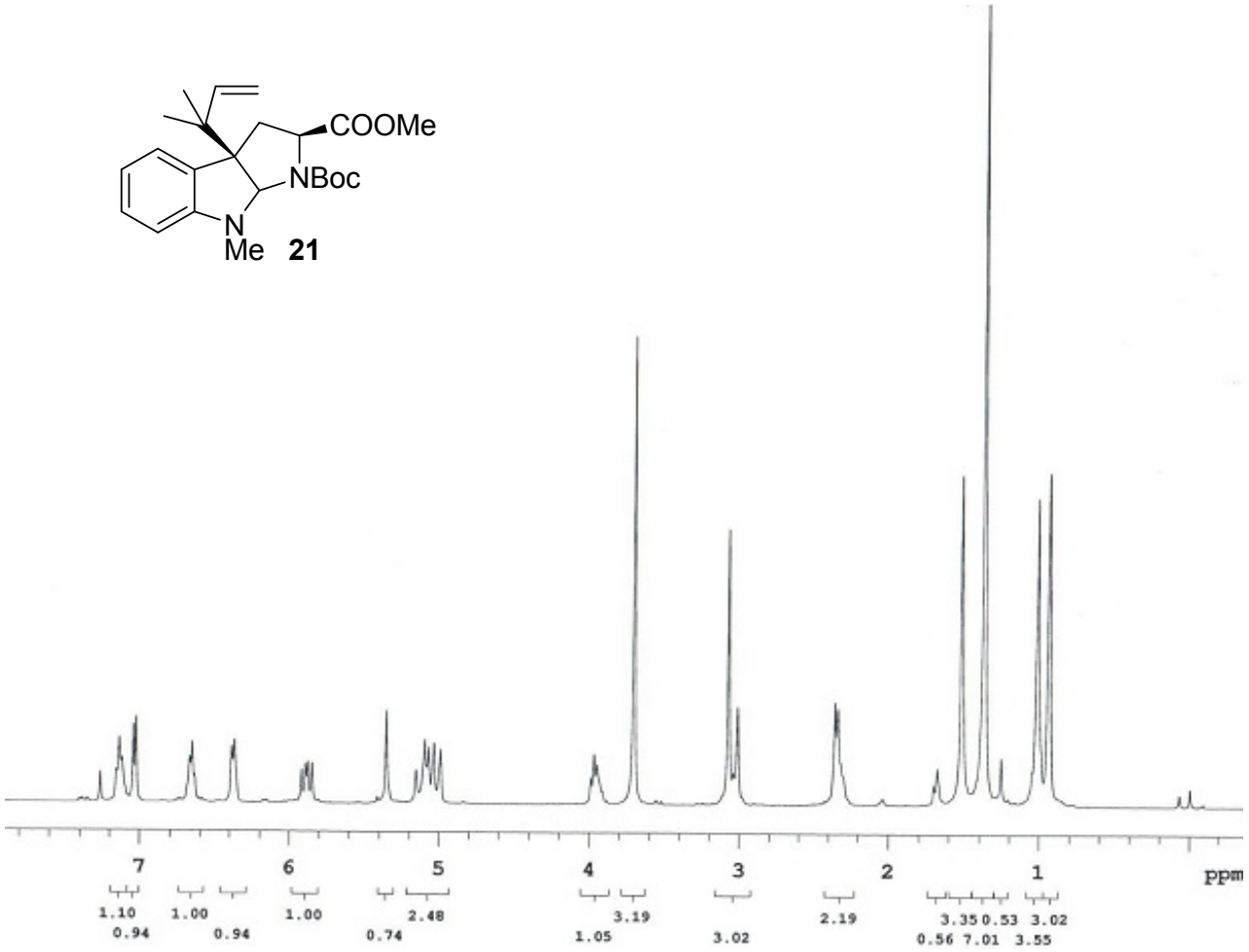
16	29.8	2.67-2.62 m (a)	C14, C15, C17, C18, C20	H16b
		1.94-1.89 m (b)	C14, C15, C17, C18, C20	H16a, H15a, H15b
17	70.7	-	-	-
18	29.3	2.05-2.00 m (a)	C11, C16, C17, C20	H18b, H19
		1.78 (dd, *J* = 13.2, 7.2 Hz) (b)	C11,C17,C19,C20	H18a, H19
19	52.1	3.41-3.39 m	C12, C18, C22, C23, C24	H18a, H18b
20	178.3	-	-	-
22	49.3	-	-	-
23	21.1	1.10 s	C3, C10, C19, C22, C24	-
24	23.5	0.81 s	C3, C10, C19, C22, C23	-



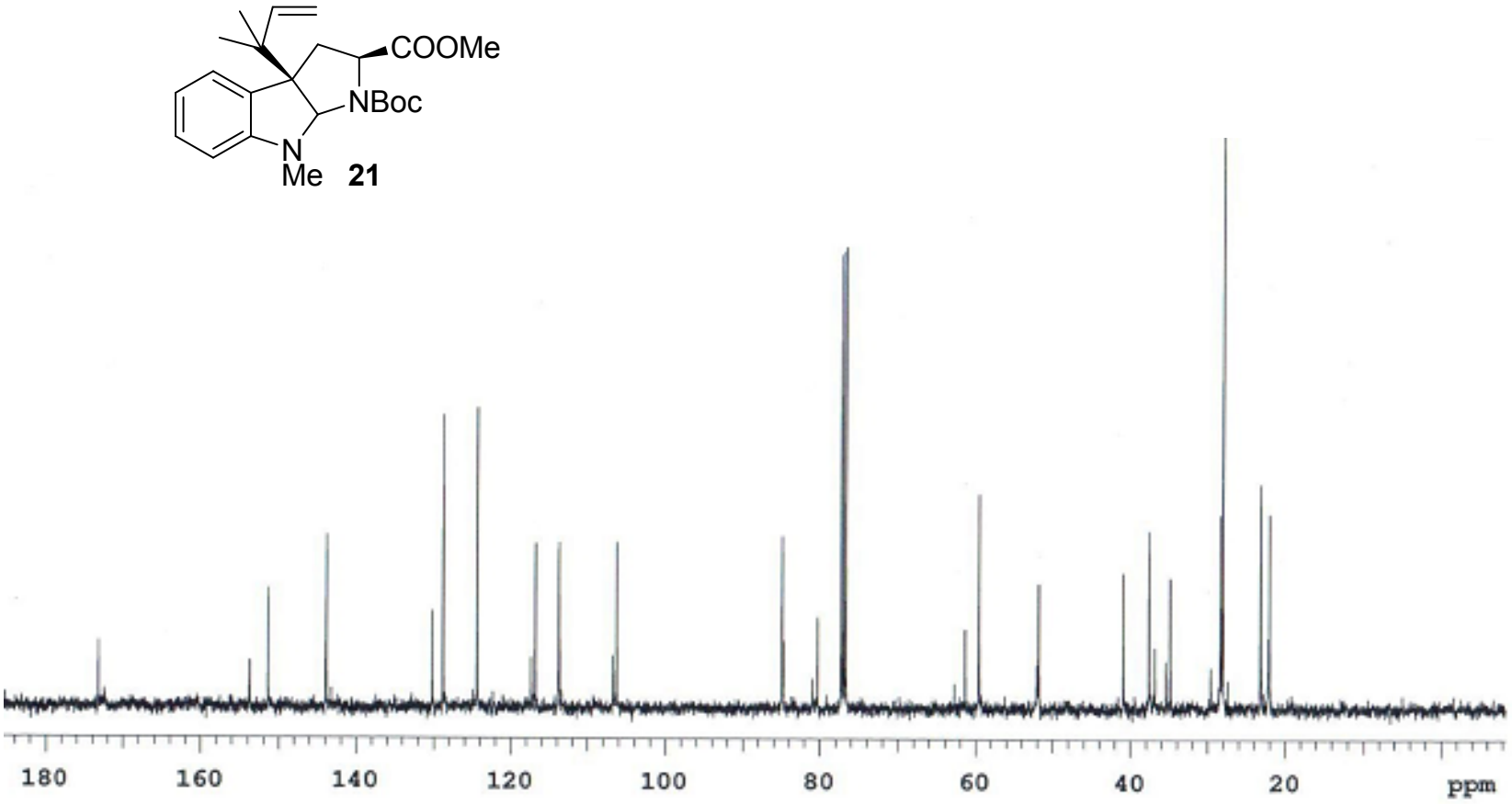
^{1}H NMR spectrum of compound **N2-Boc pyrroloindoline**



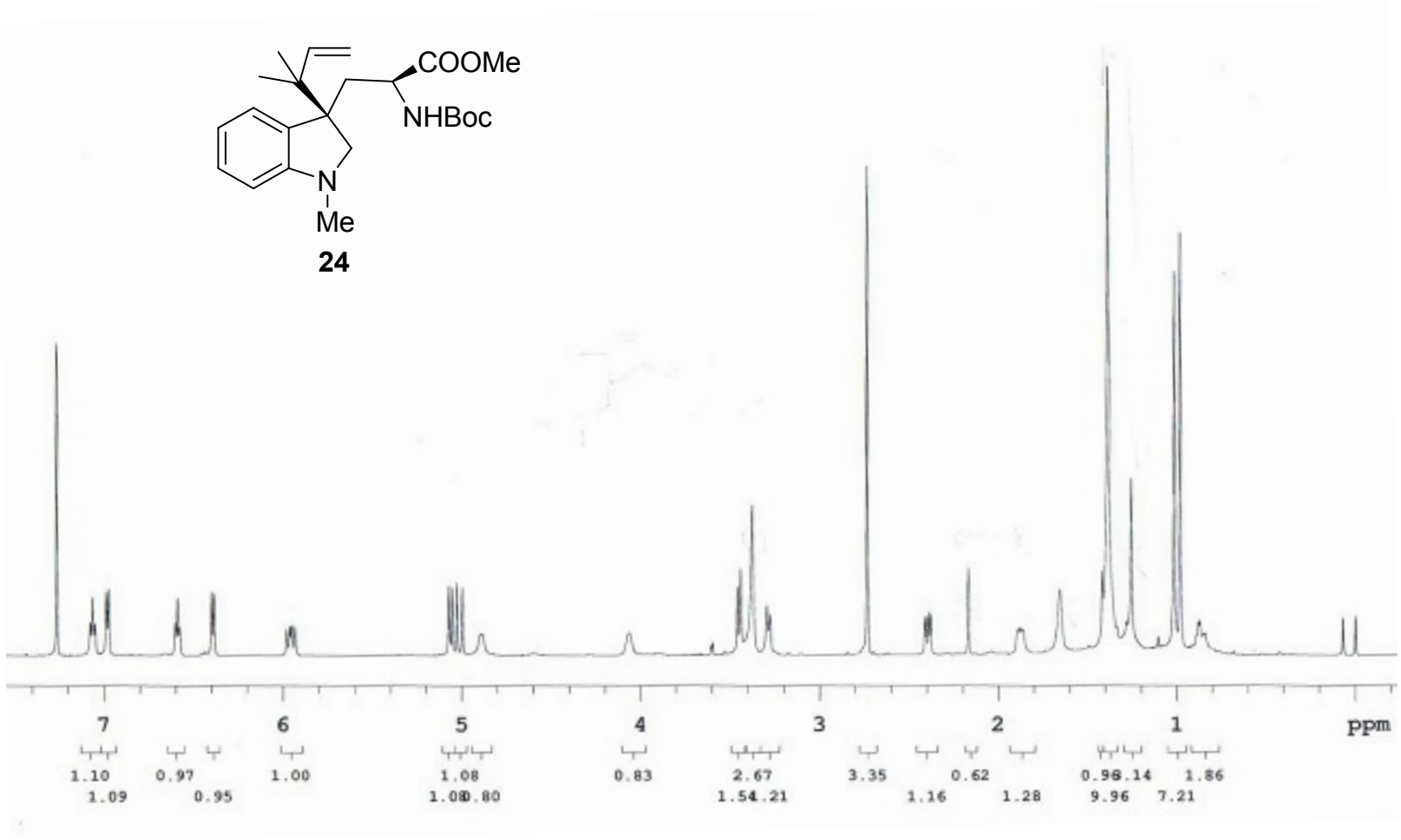
^{13}C NMR spectrum of compound **N2-Boc pyrroloindoline**



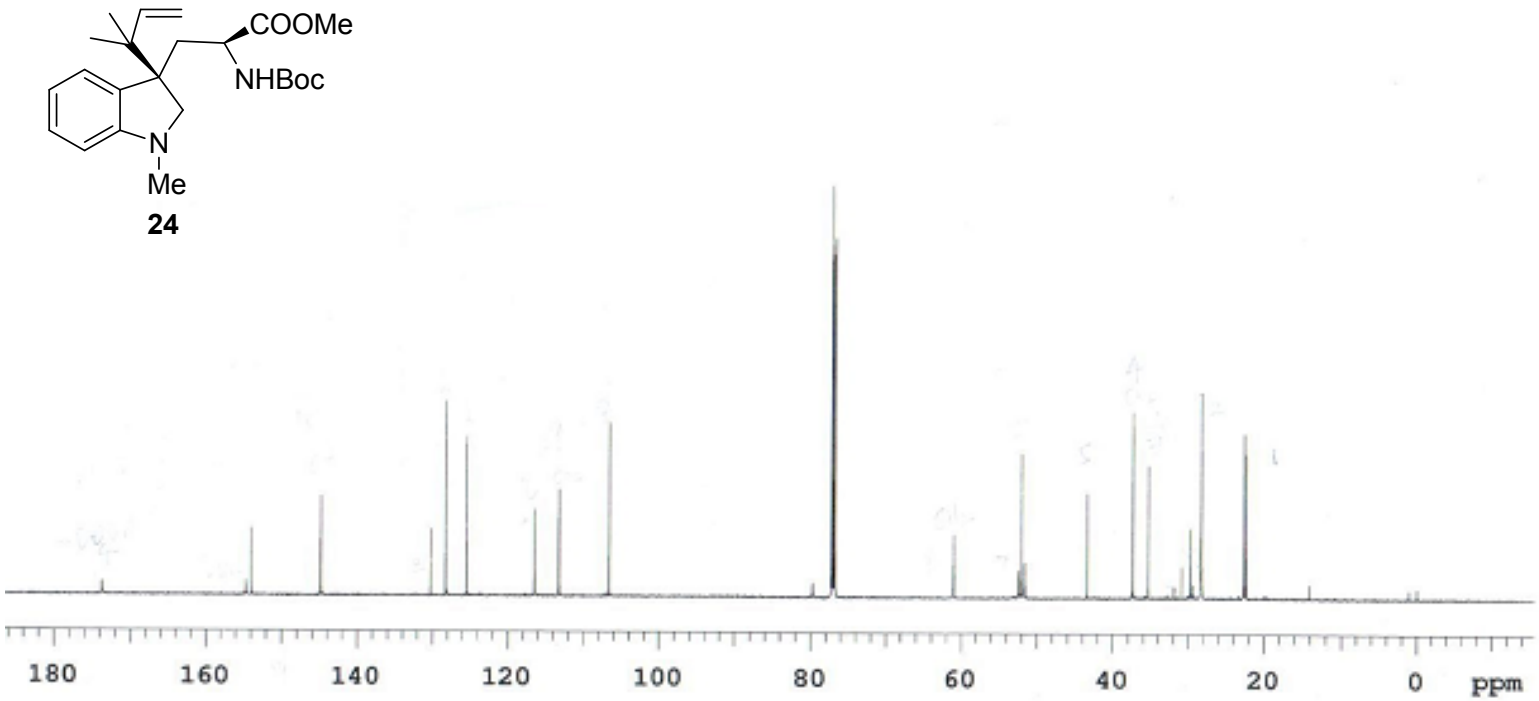
^{1}H NMR spectrum of compound **21**



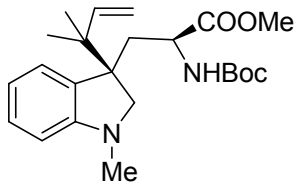
^{13}C NMR spectrum of compound **21**



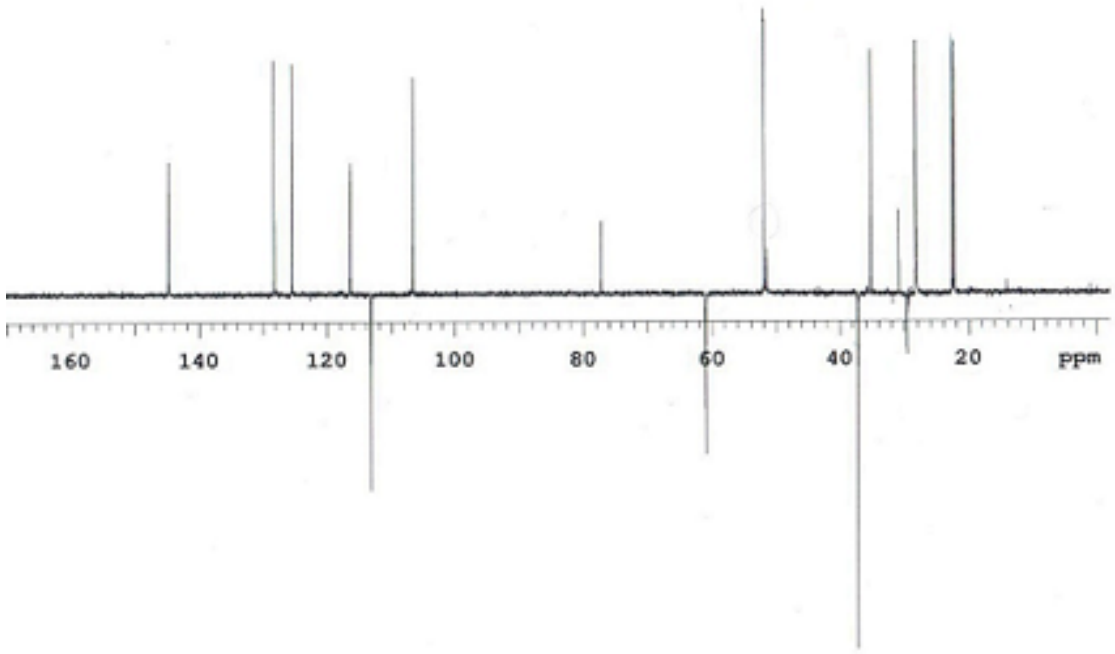
^{1}H NMR spectrum of compound **24**



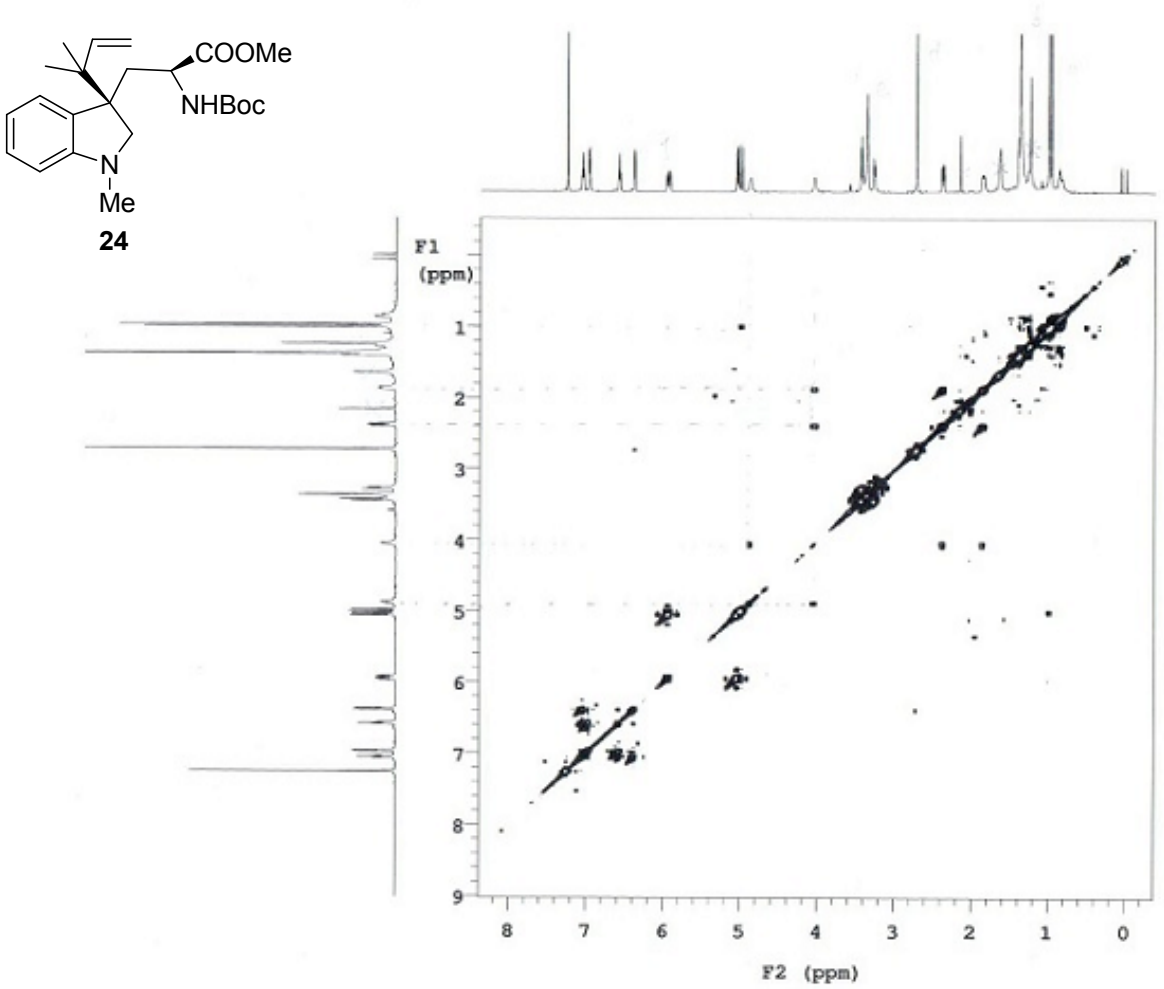
^{13}C NMR spectrum of compound **24**



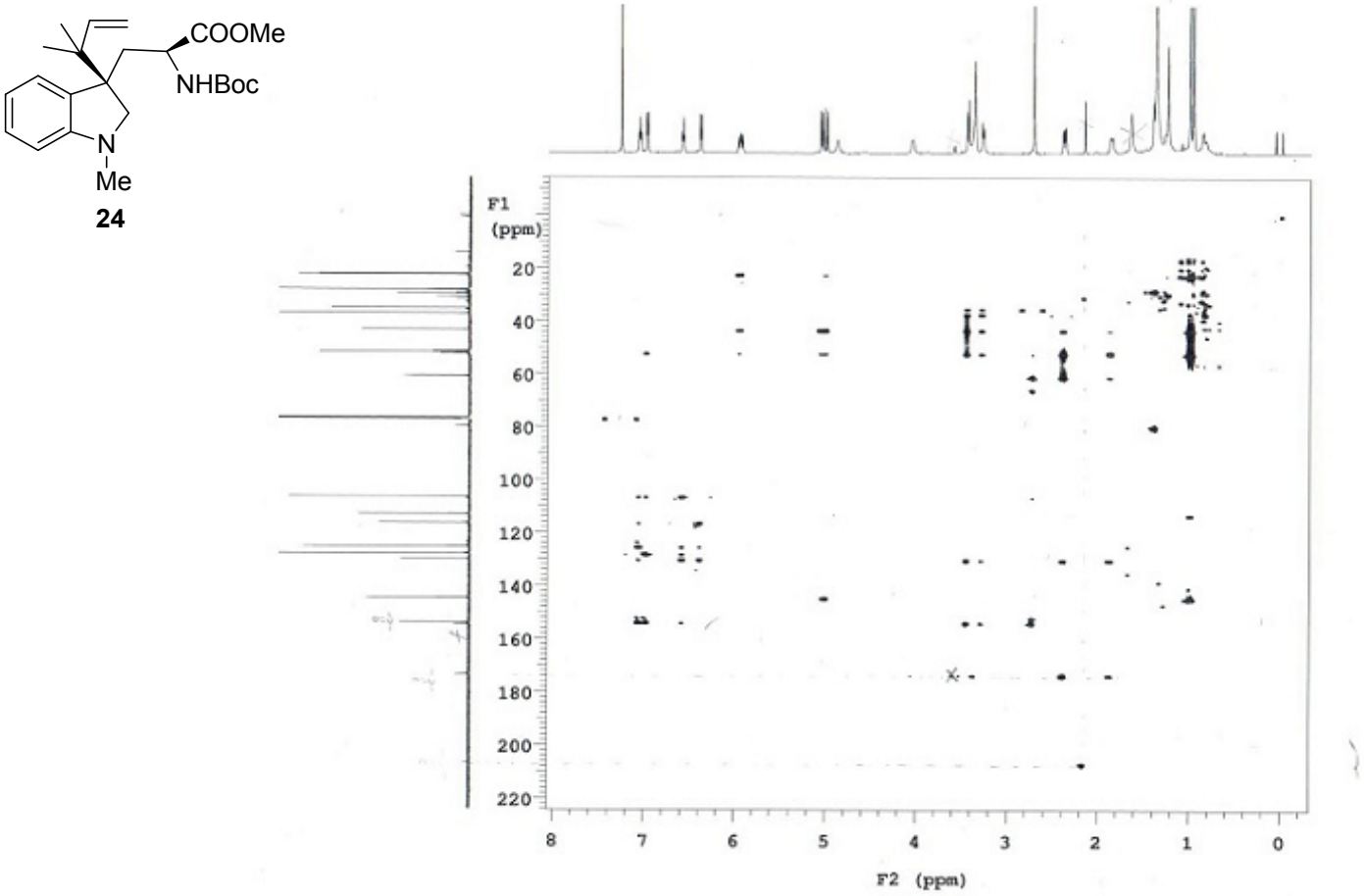
24



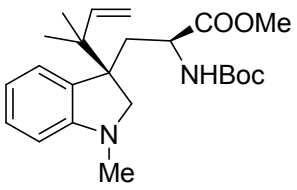
DEPT spectrum of compound **24**



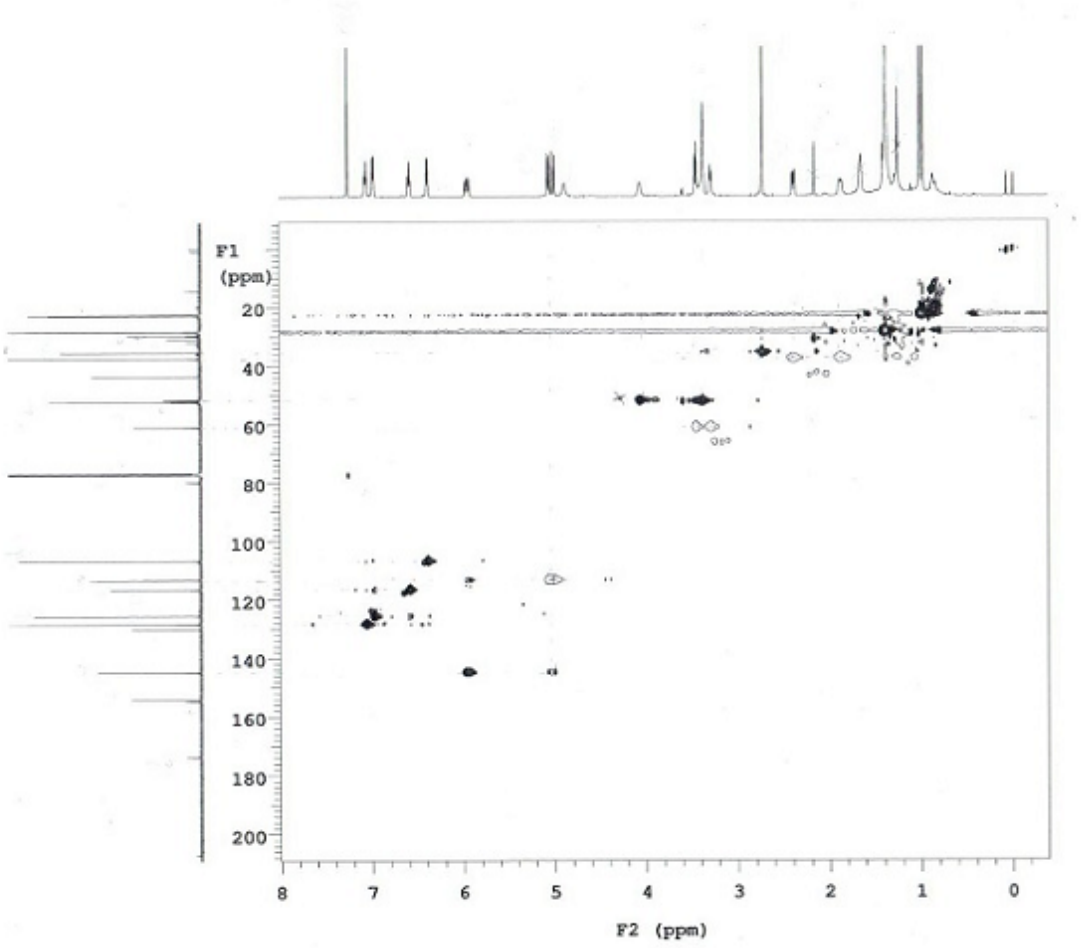
gCOSY spectrum of compound **24**



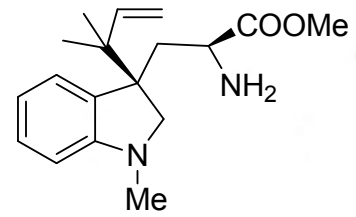
gHMBC spectrum of compound **24**



24

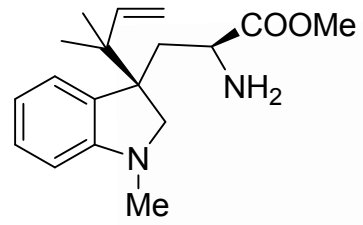


gHMQC spectrum of compound **24**



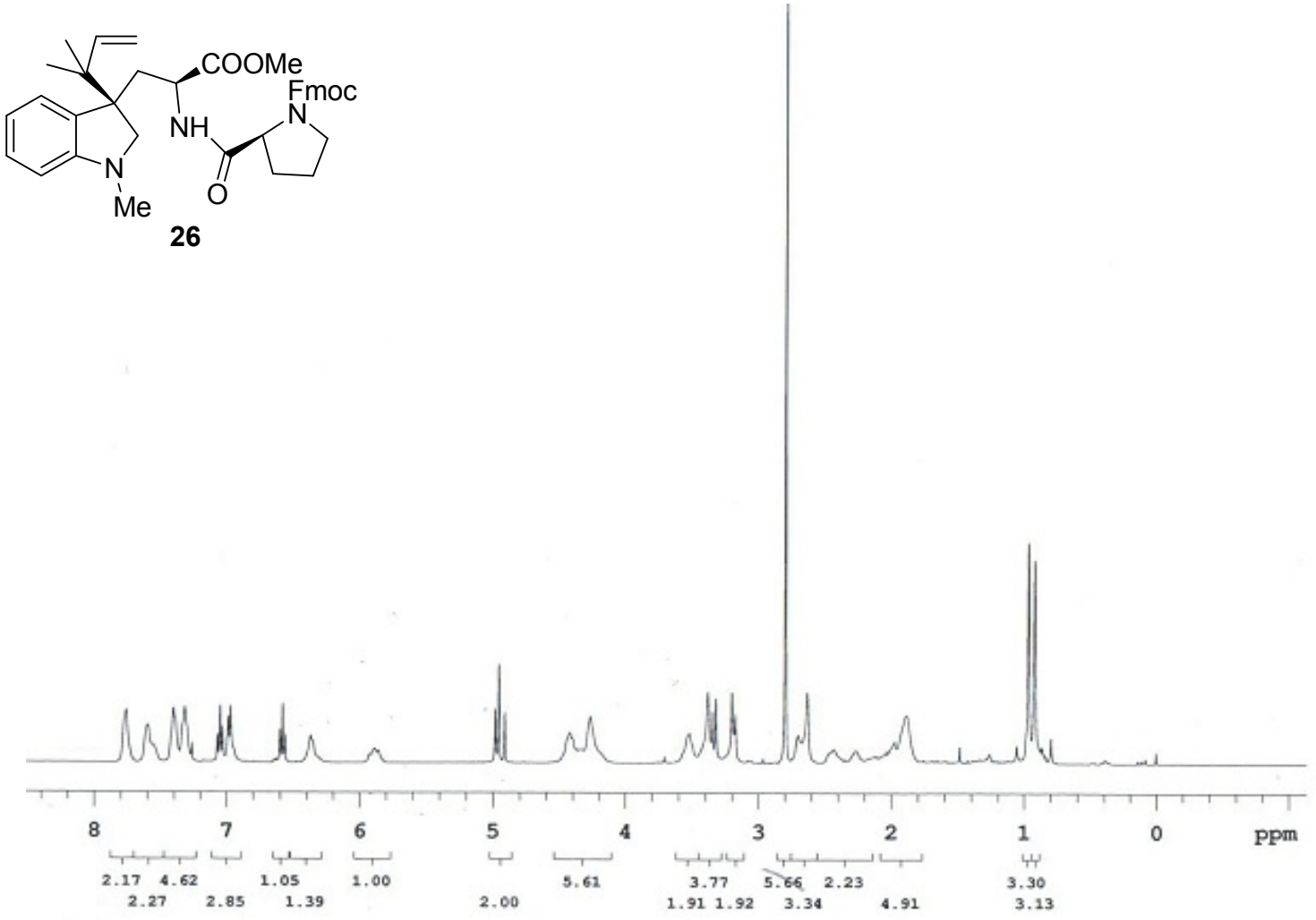
C3-isoprenylated indoline

^{1}H NMR spectrum of **C3-isoprenylated indoline**

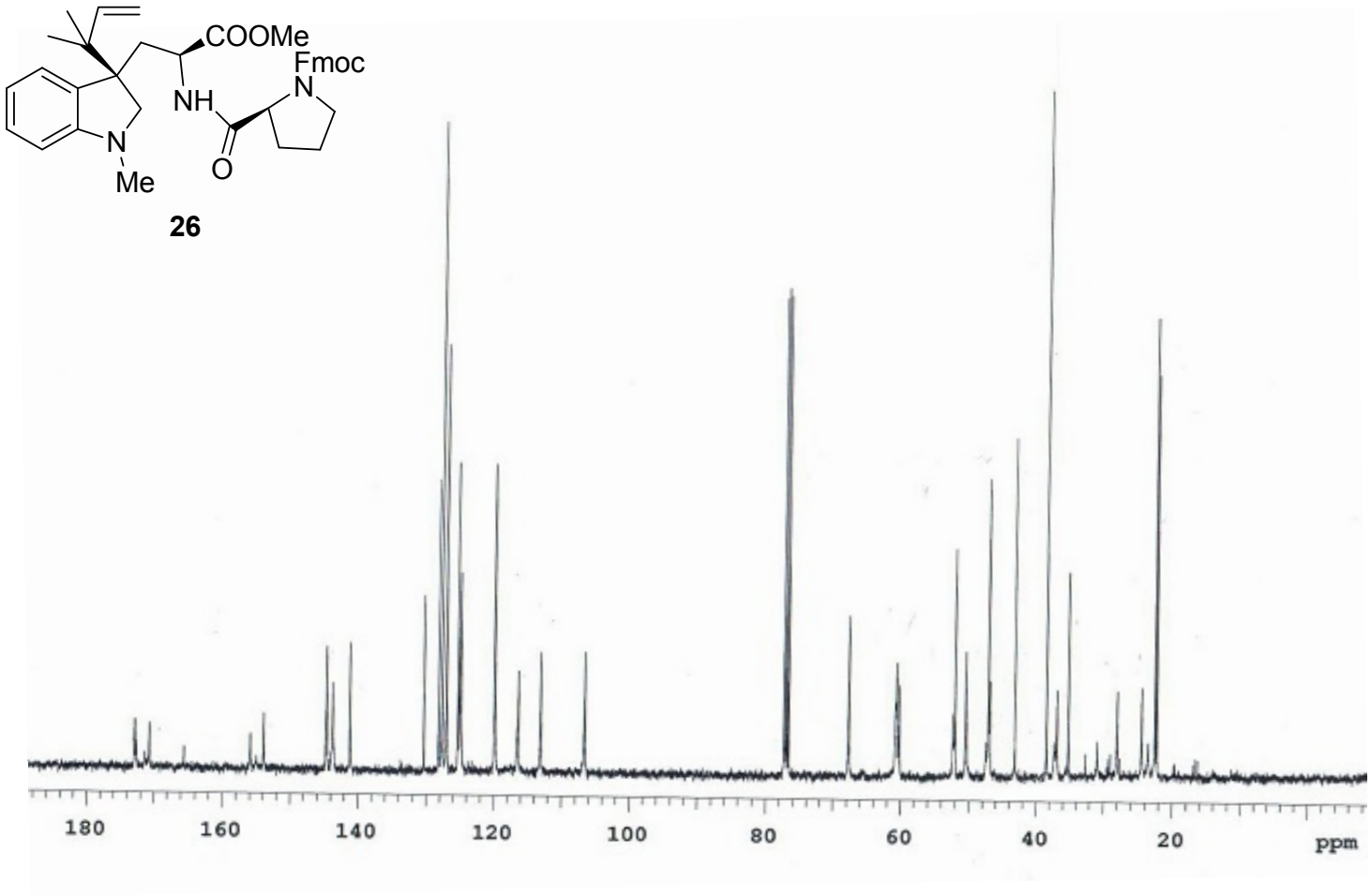


C3-isoprenylated indoline

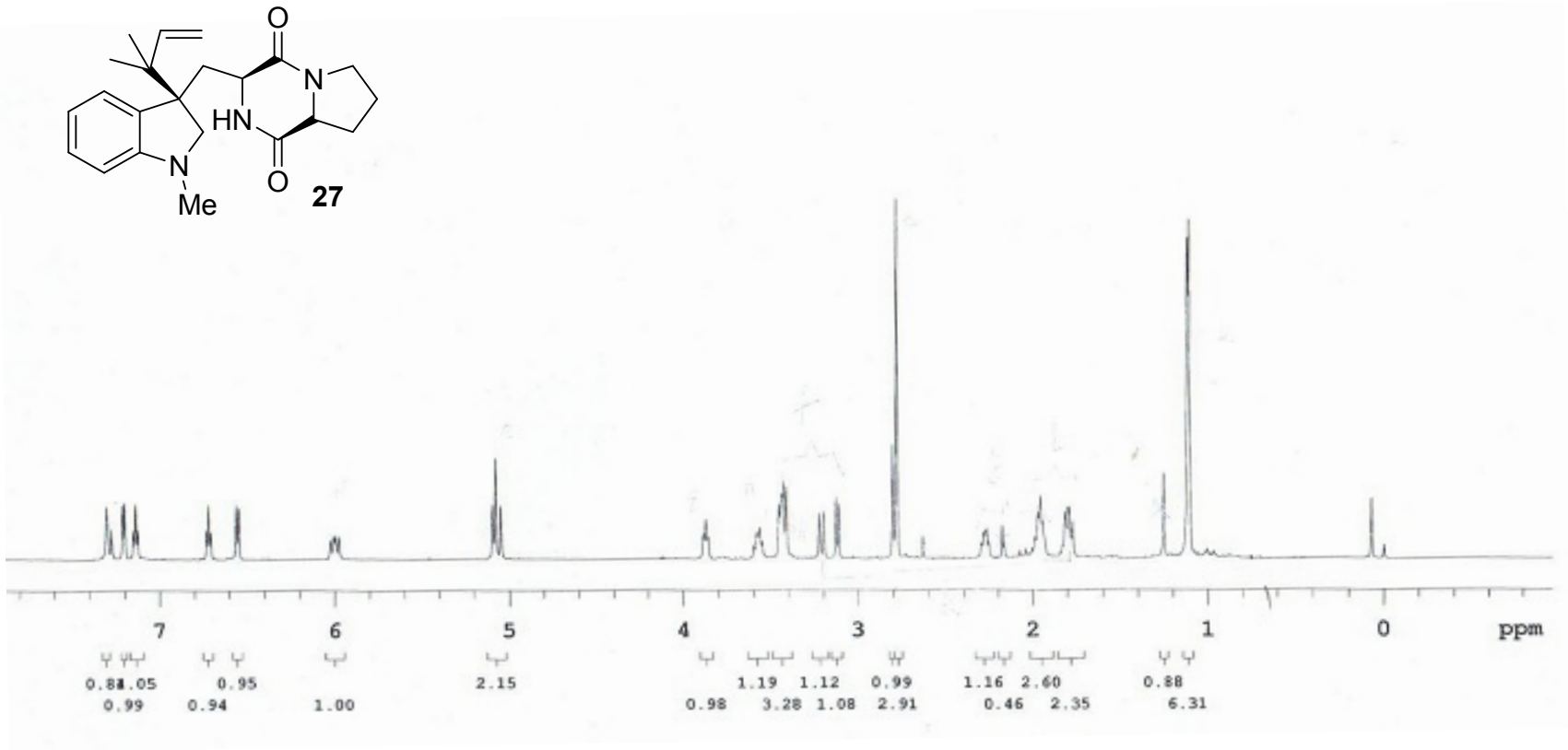
^{13}C NMR spectrum of C3-isoprenylated indoline



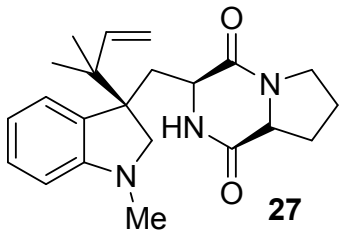
^{1}H NMR spectrum of compound **26**



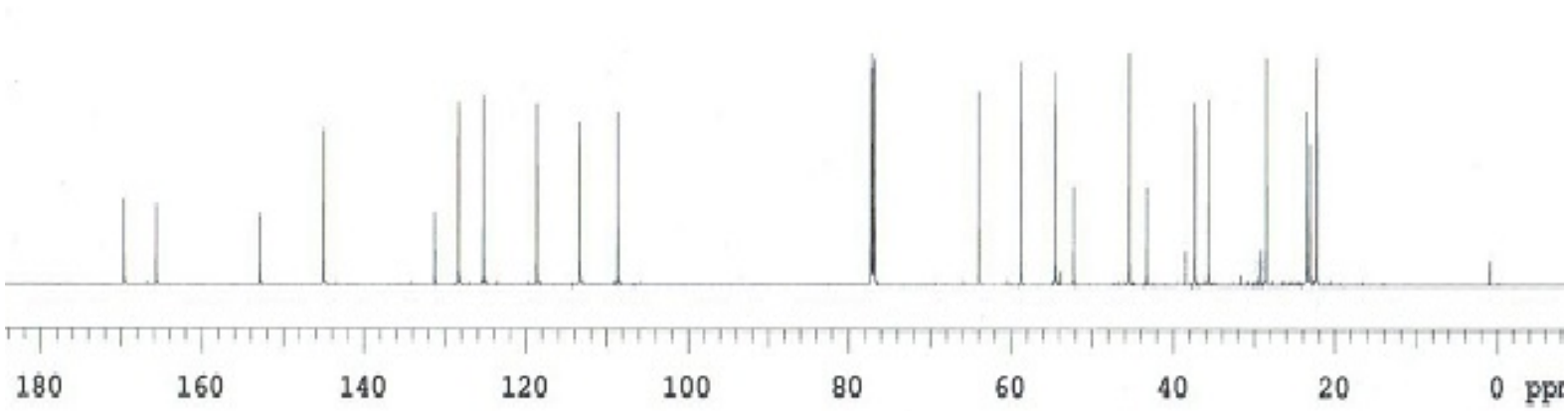
^{13}C NMR spectrum of compound **26**



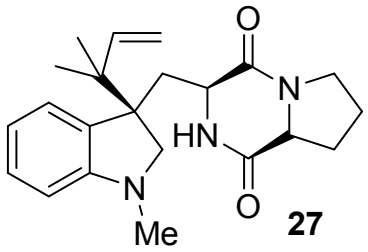
^{1}H NMR spectrum of compound **27**



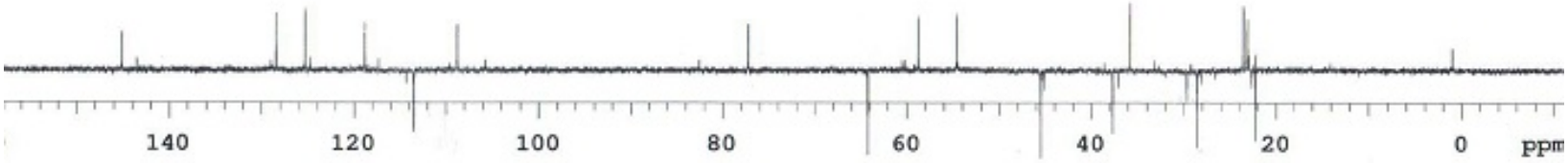
27



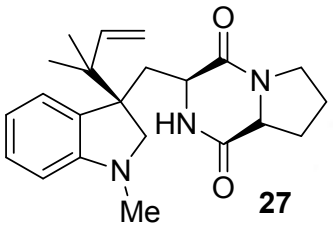
^{13}C NMR spectrum of compound **27**



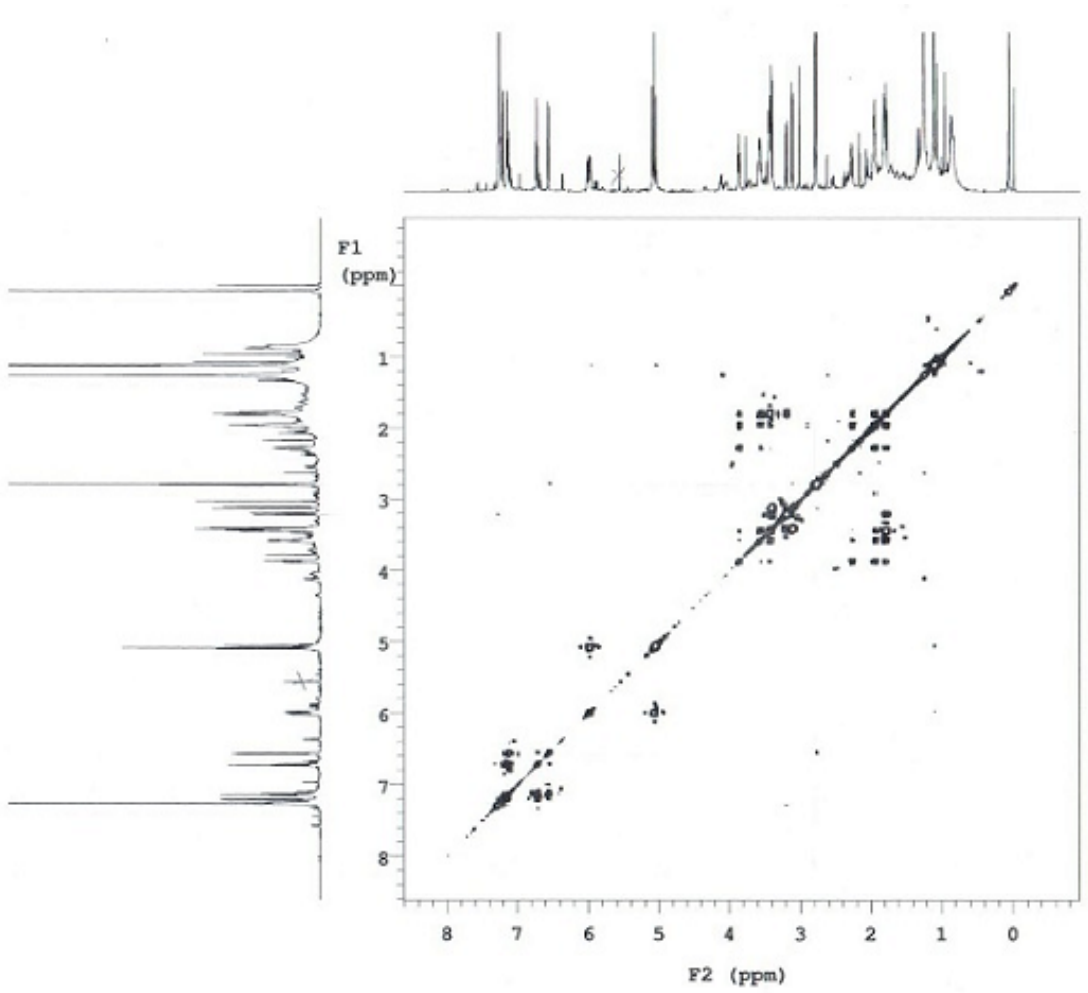
27



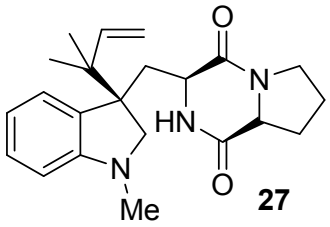
DEPT spectrum of compound **27**



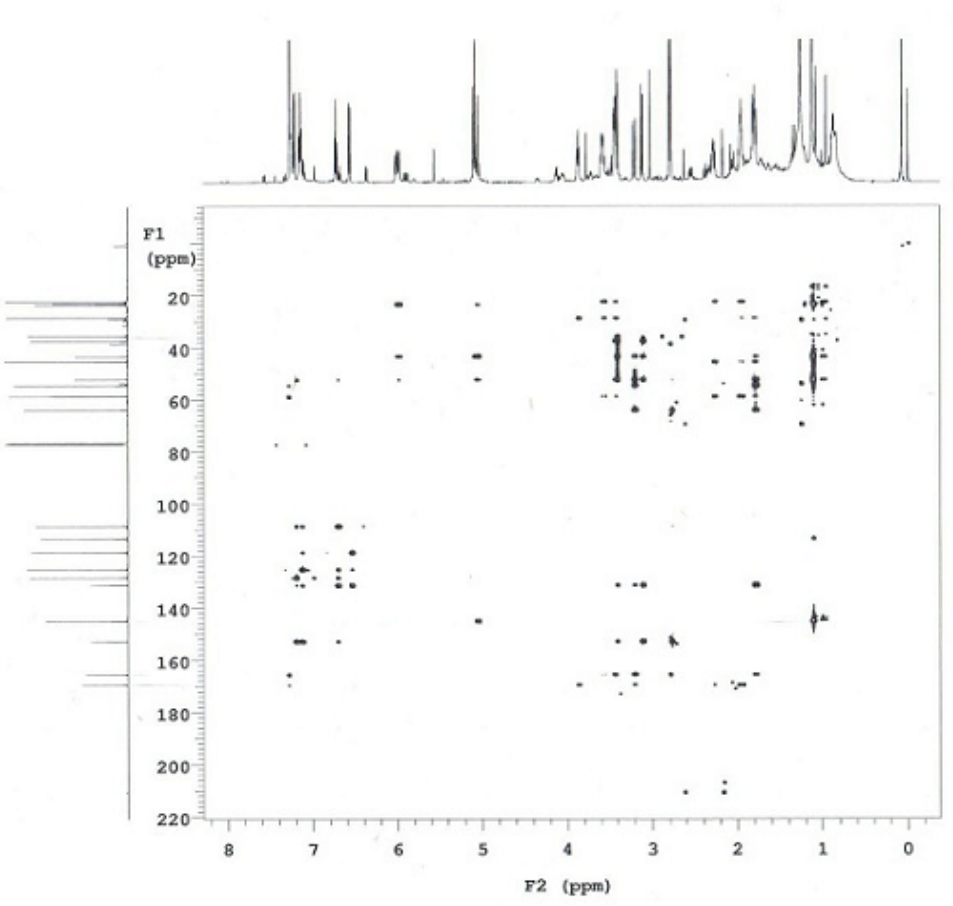
27



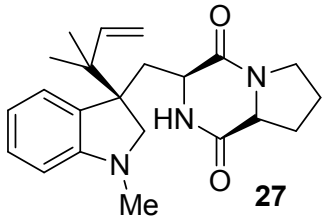
gCOSY spectrum of compound **27**



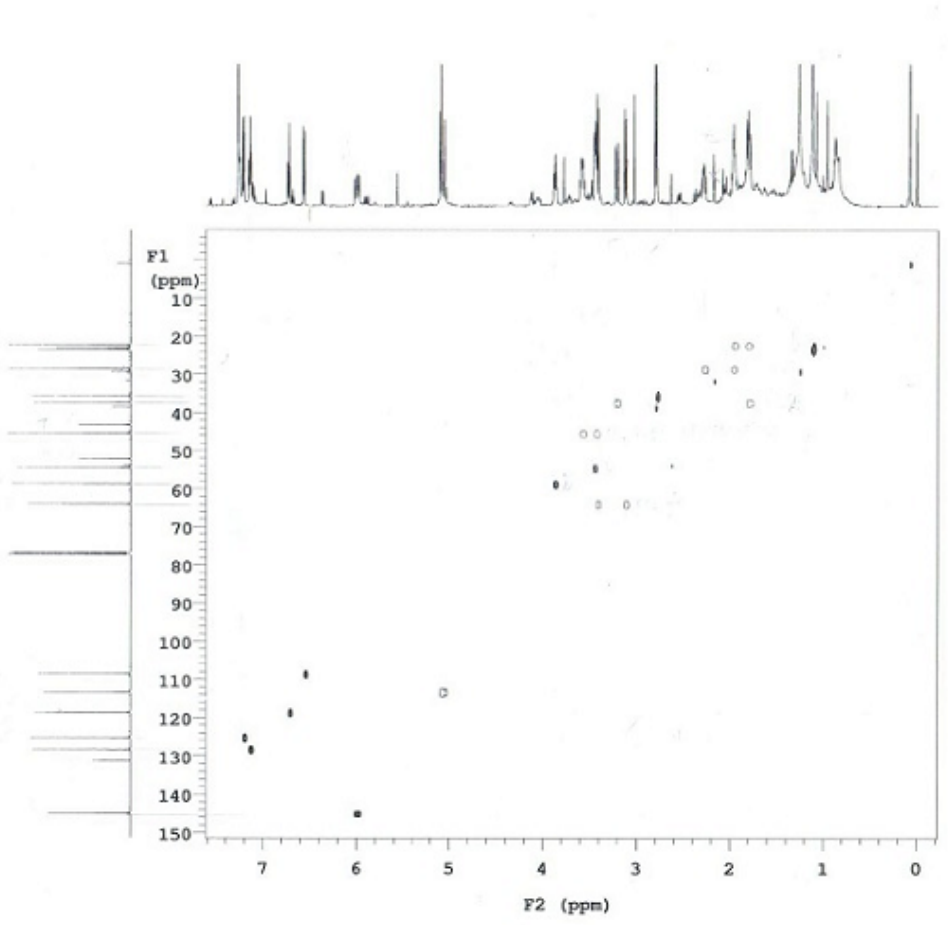
27



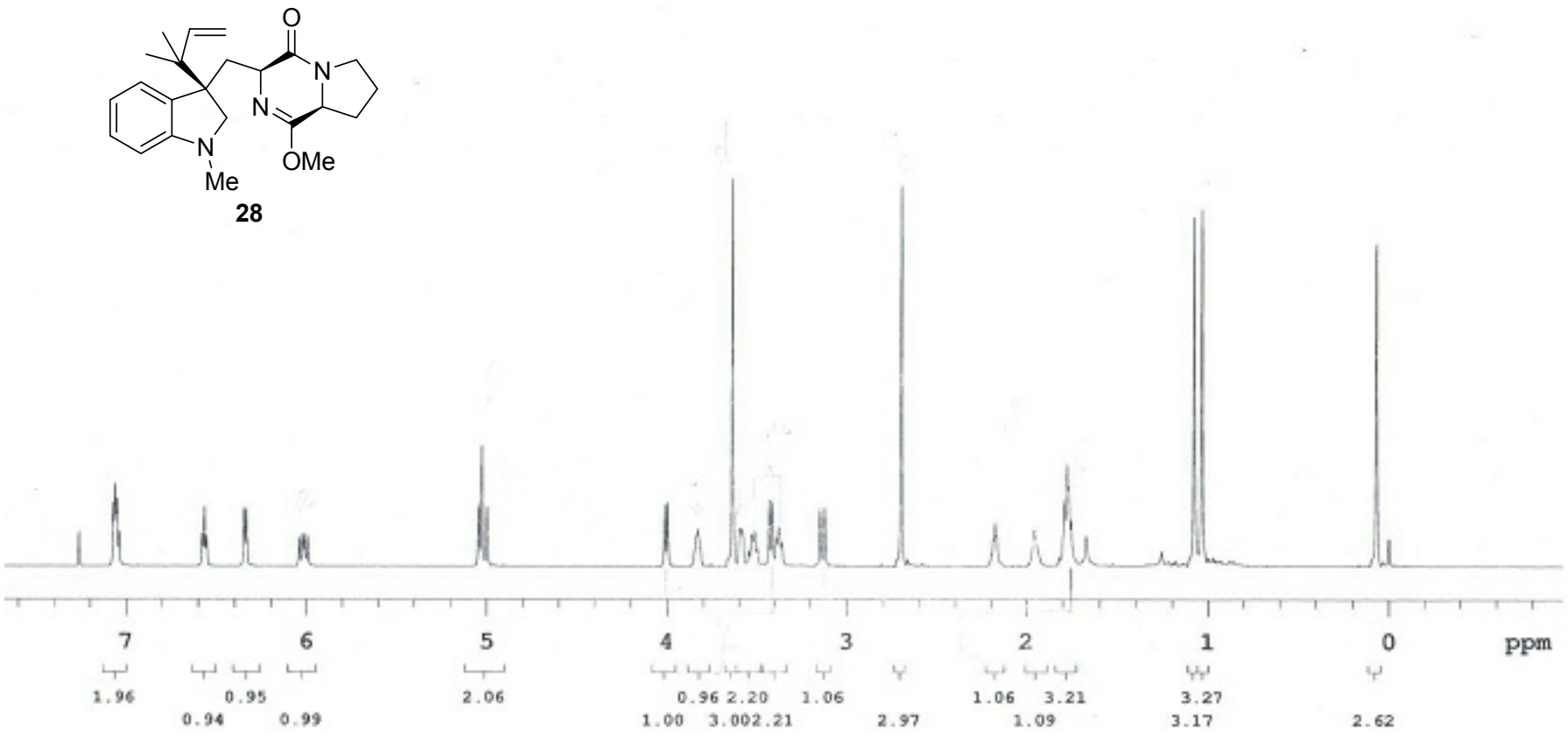
gHMBC spectrum of compound **27**



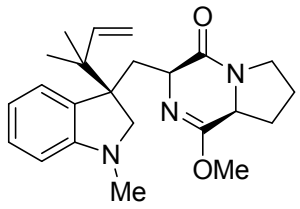
27



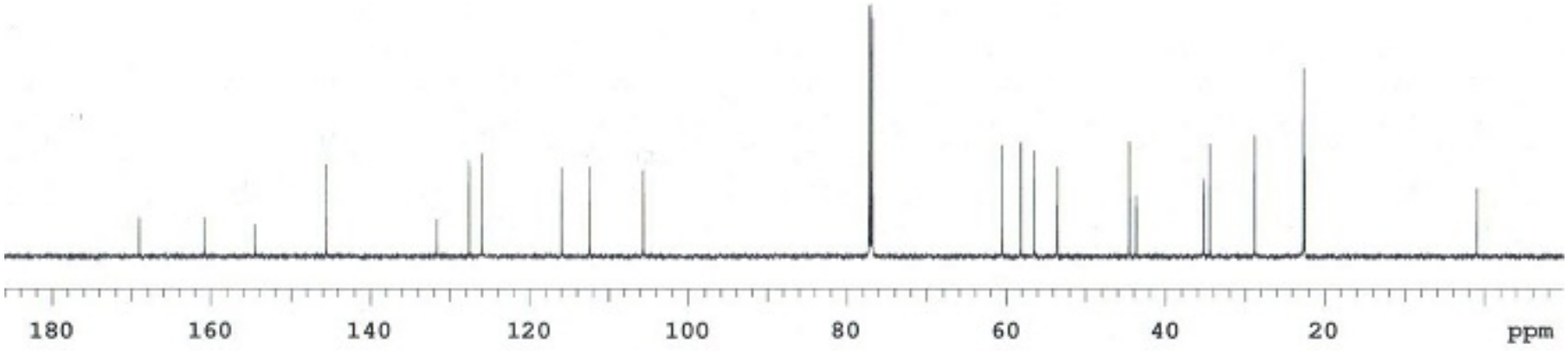
gHMQC spectrum of compound **27**



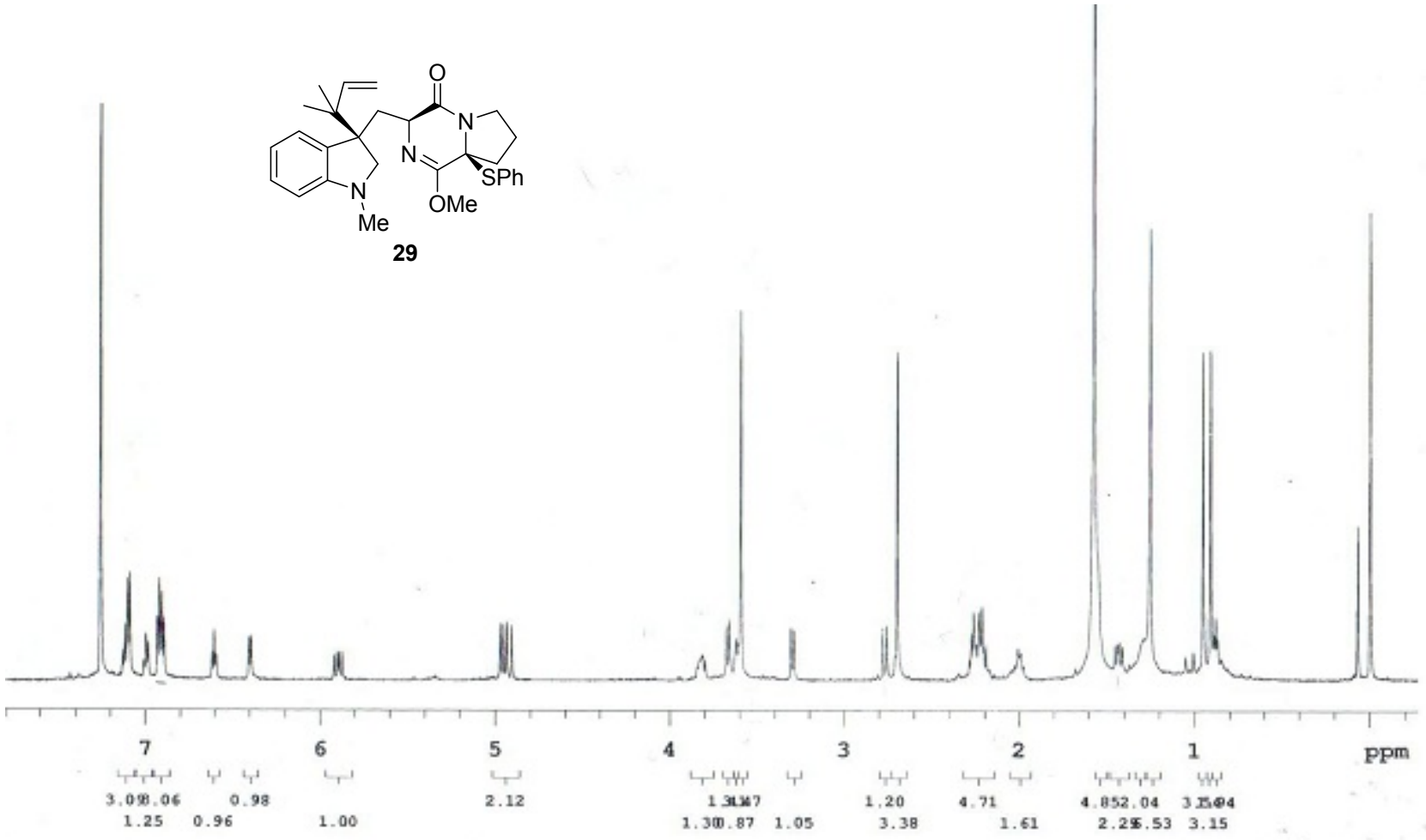
^{1}H NMR spectrum of compound **28**



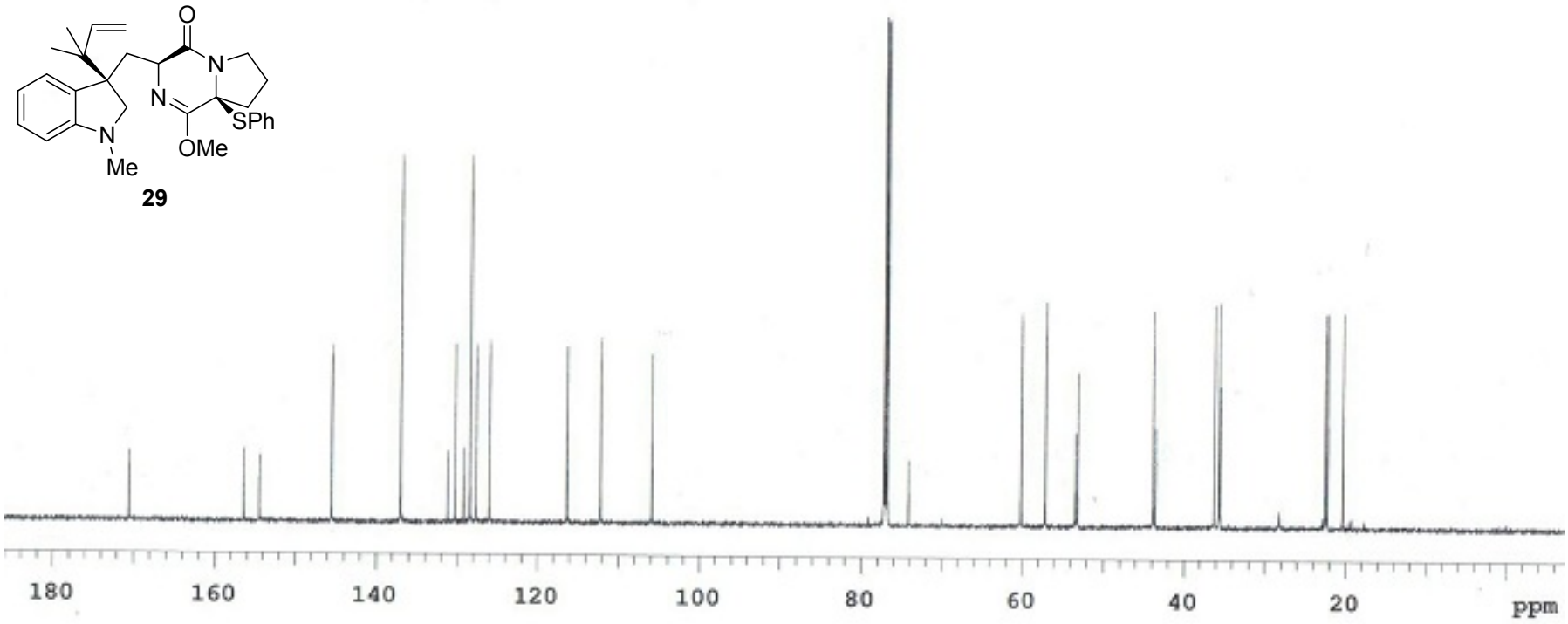
28



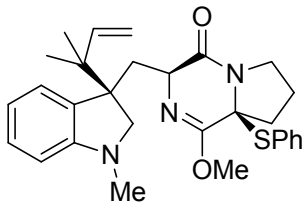
^{13}C NMR spectrum of compound **28**



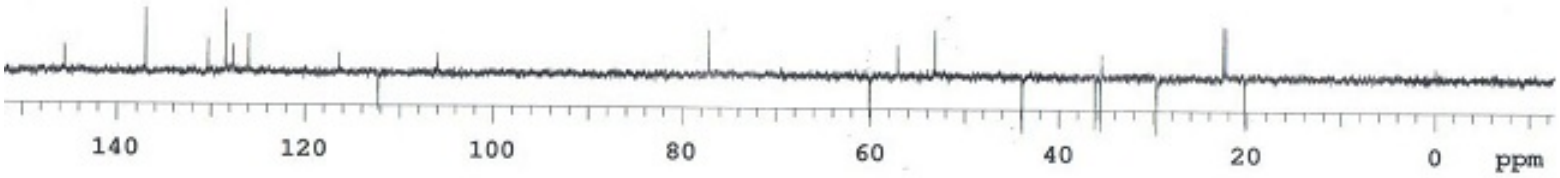
^{1}H NMR spectrum of compound **29**



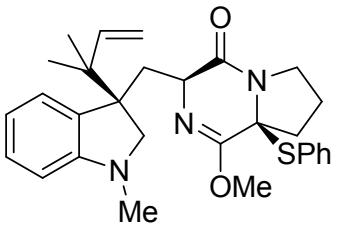
^{13}C NMR spectrum of compound **29**



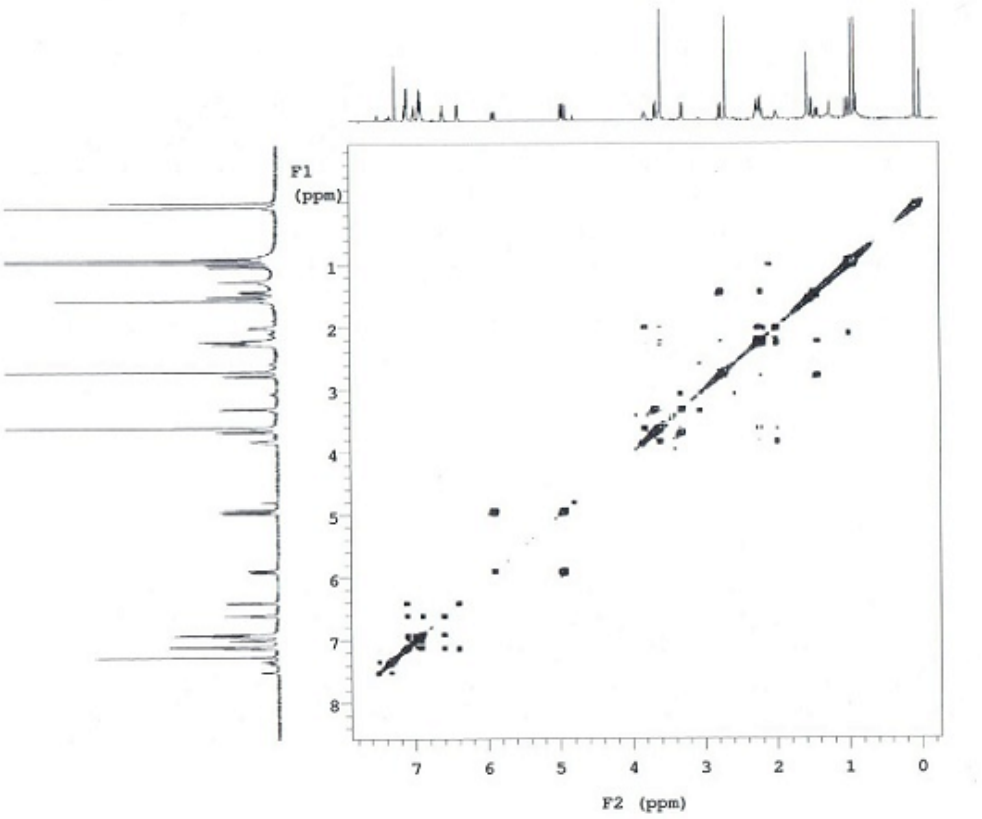
29



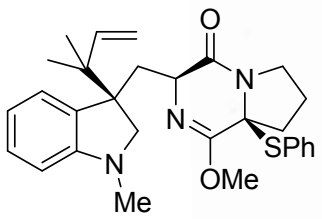
DEPT spectrum of compound **29**



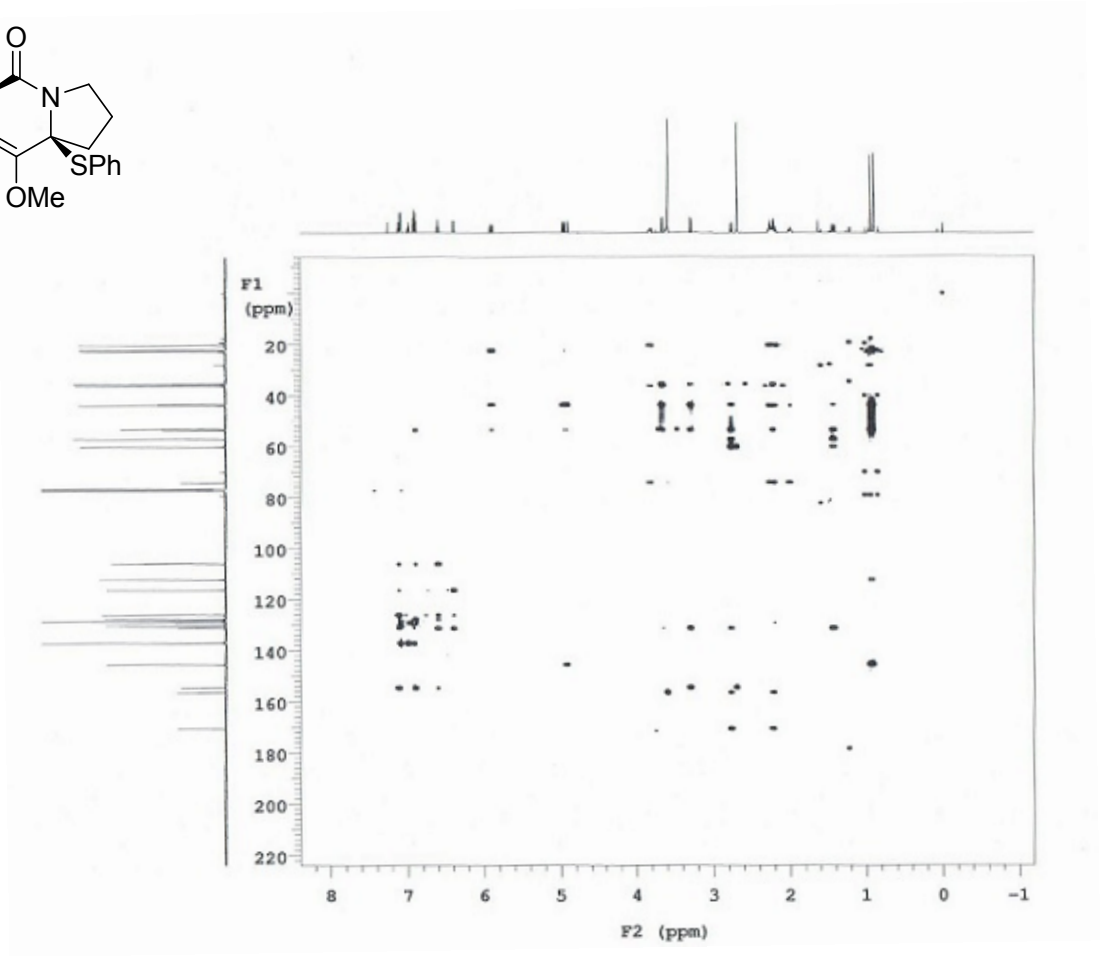
29



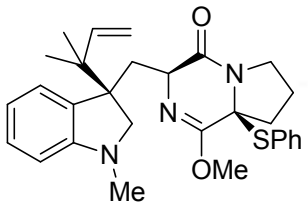
gCOSY spectrum of compound **29**



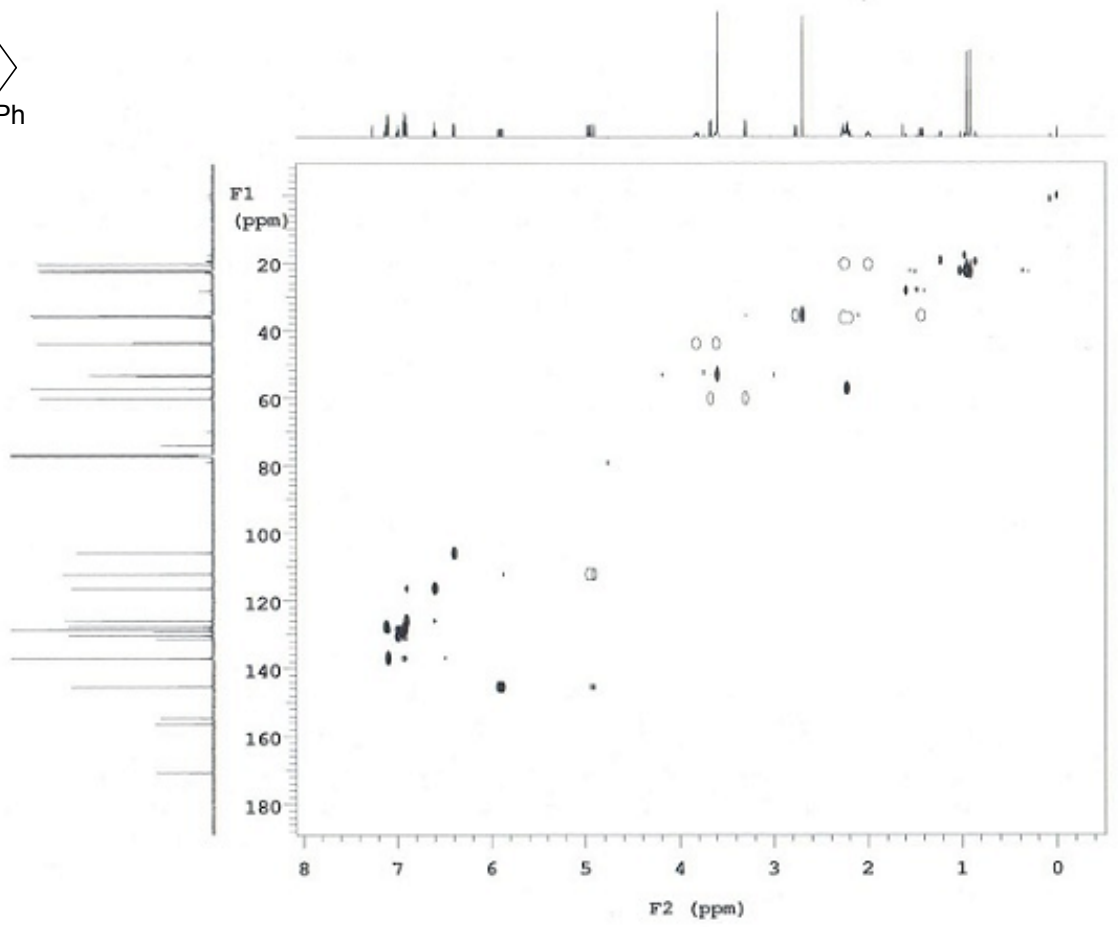
29



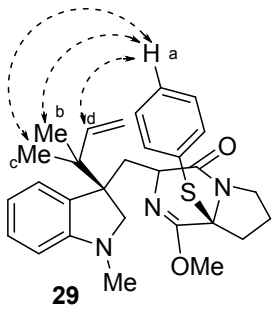
gHMBC spectrum of compound **29**



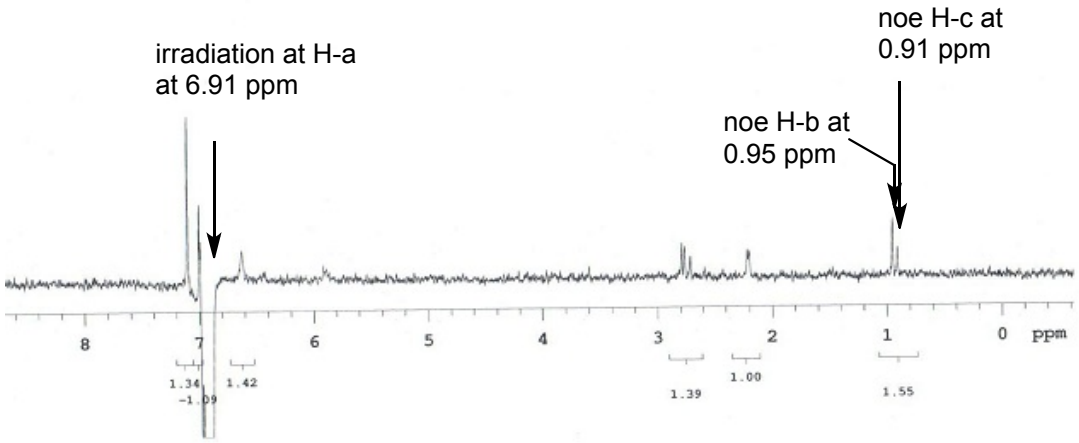
29



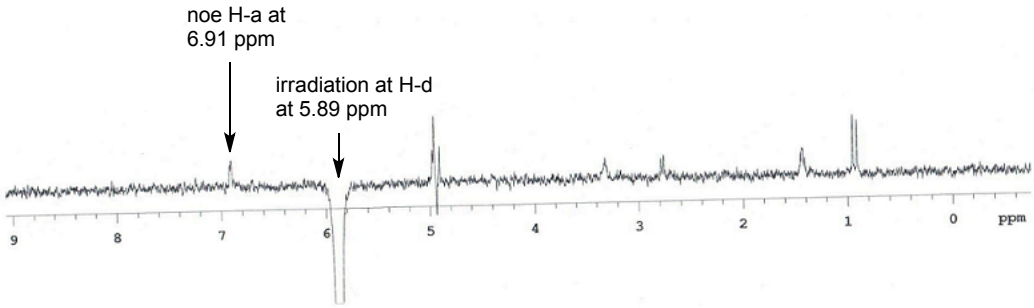
gHMQC spectrum of compound **29**



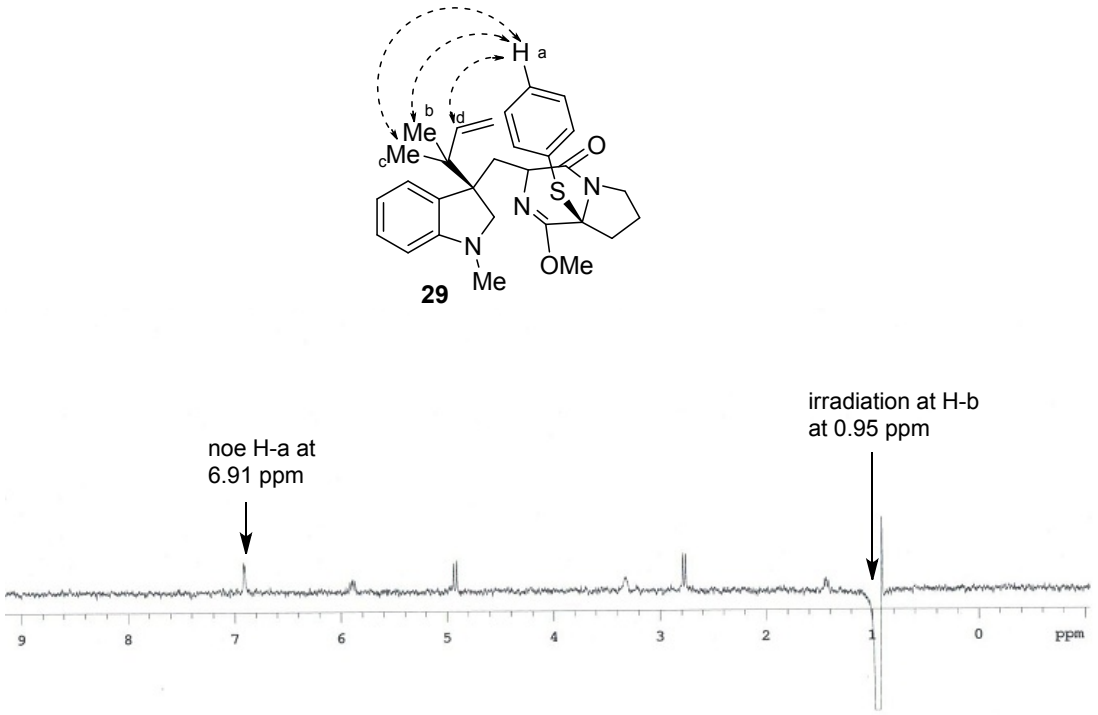
29



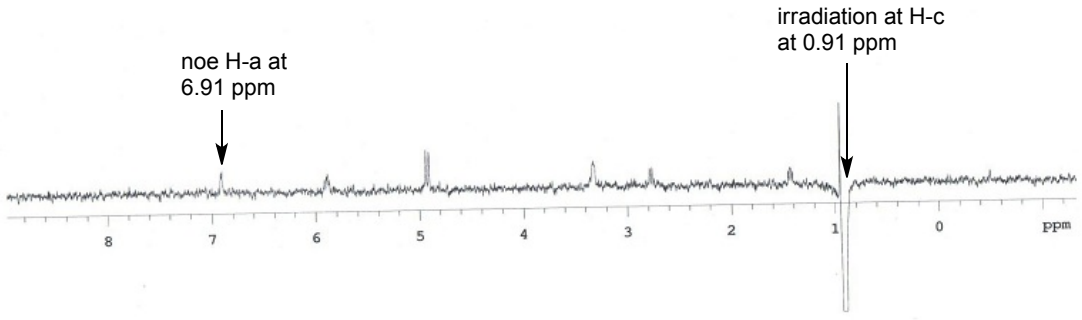
NOEDS spectrum of compound **29**（1）



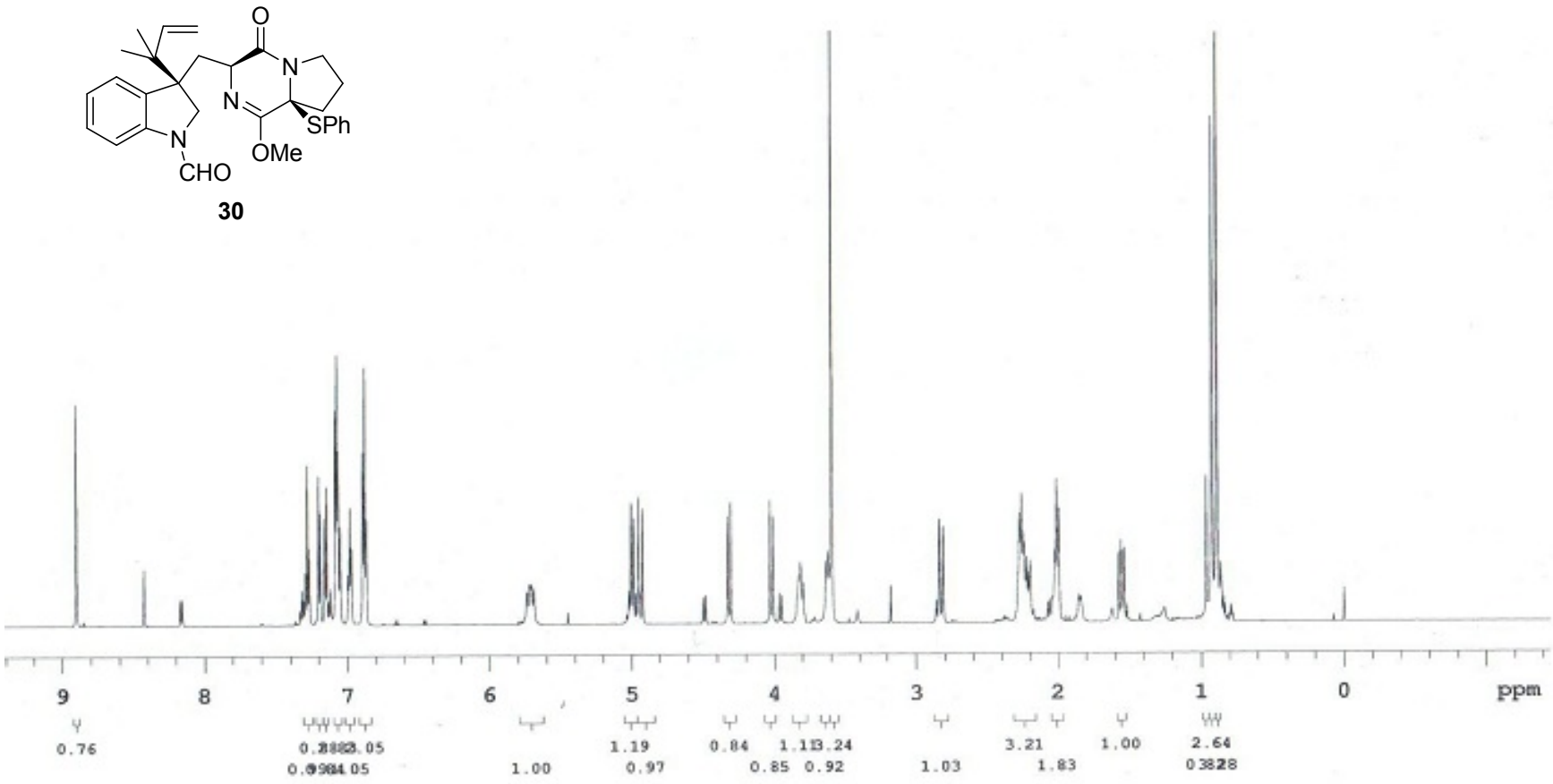
NOEDS spectrum of compound **29**（2）



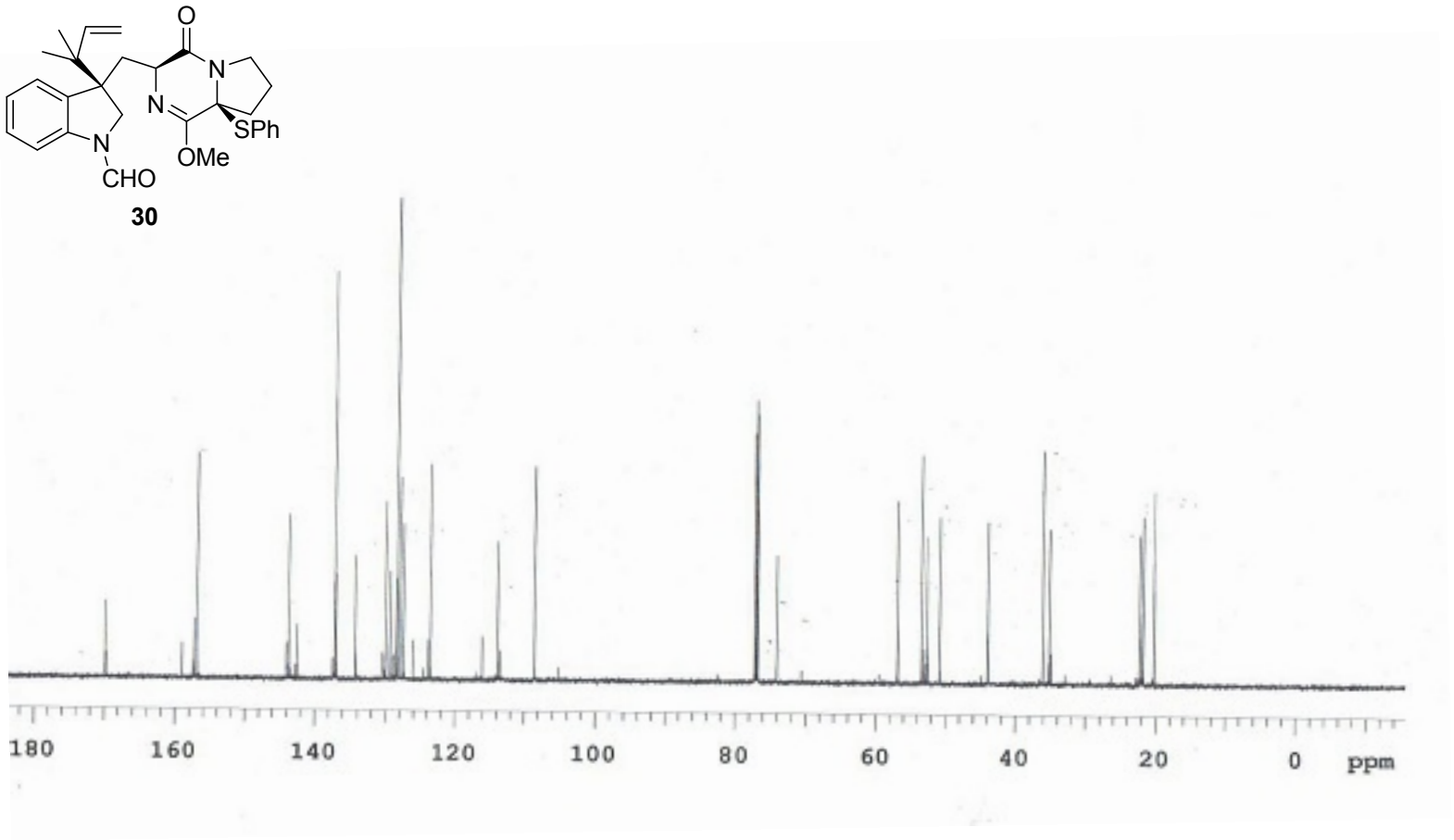
NOEDS spectrum of compound **29**（3）



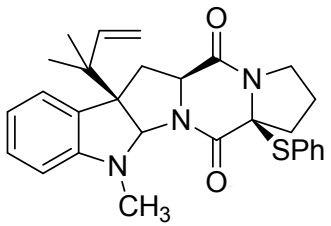
NOEDS spectrum of compound **29**（4）



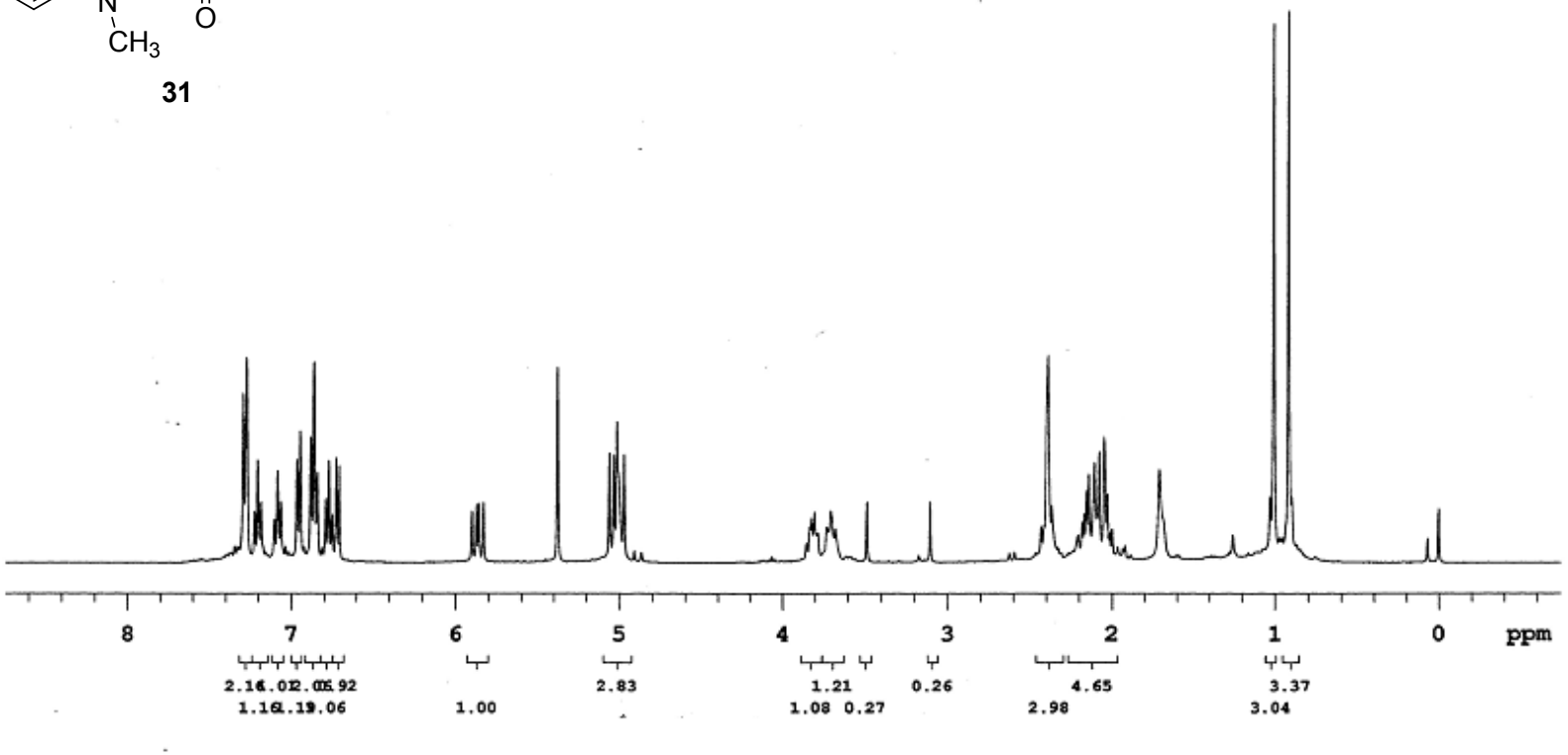
^{1}H NMR spectrum of compound **30**



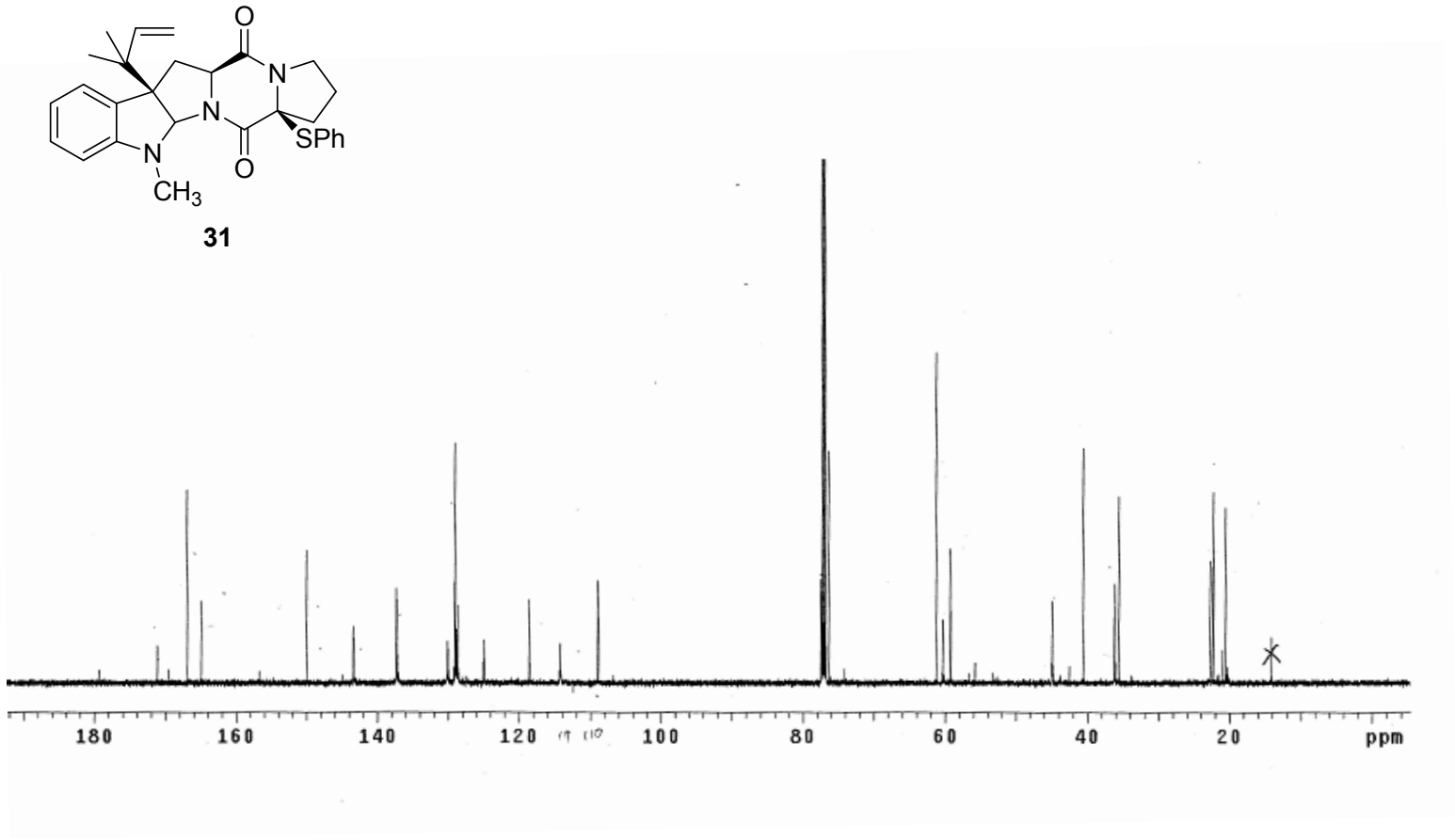
^{13}C NMR spectrum of compound **30**



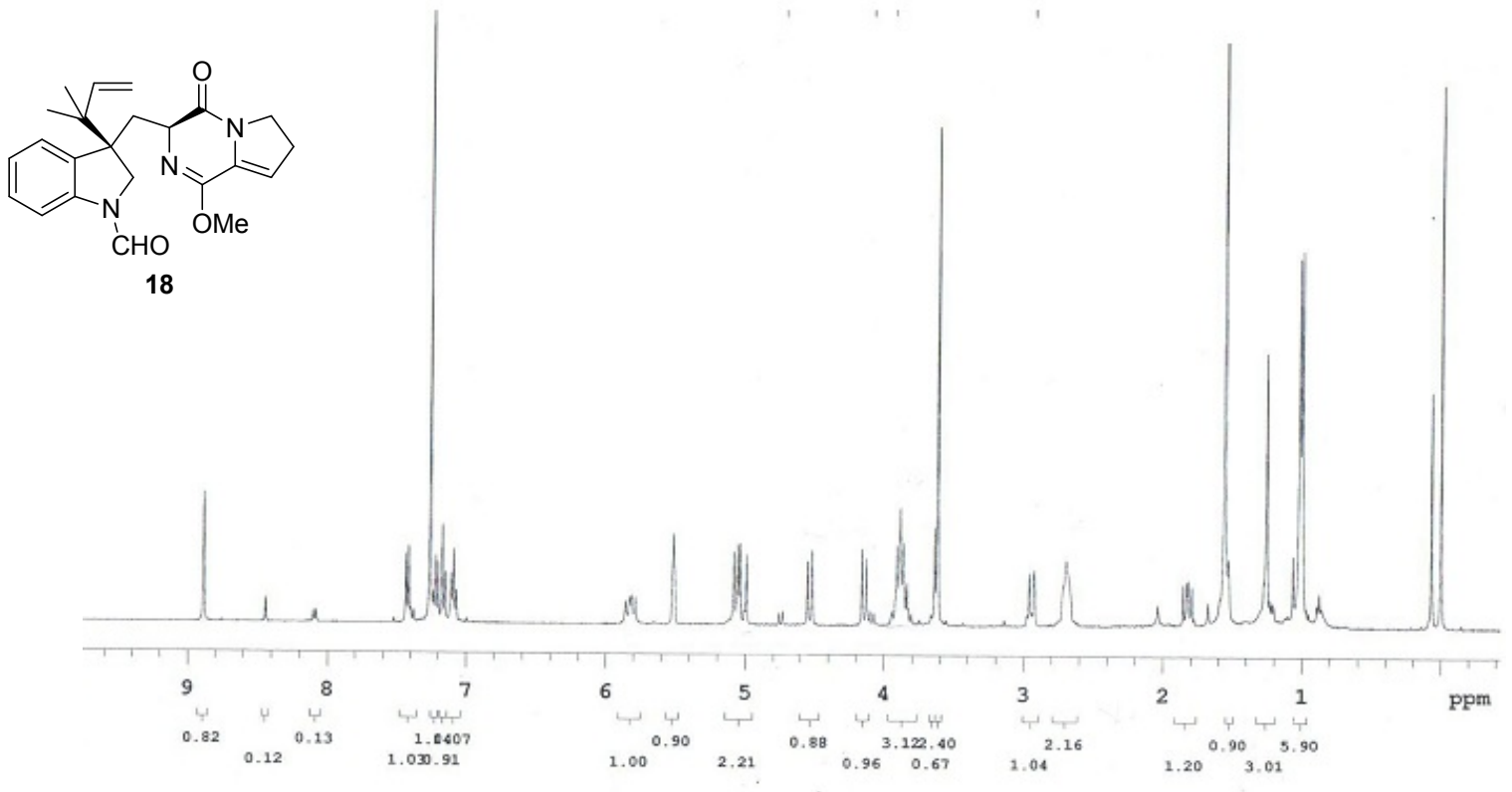
31



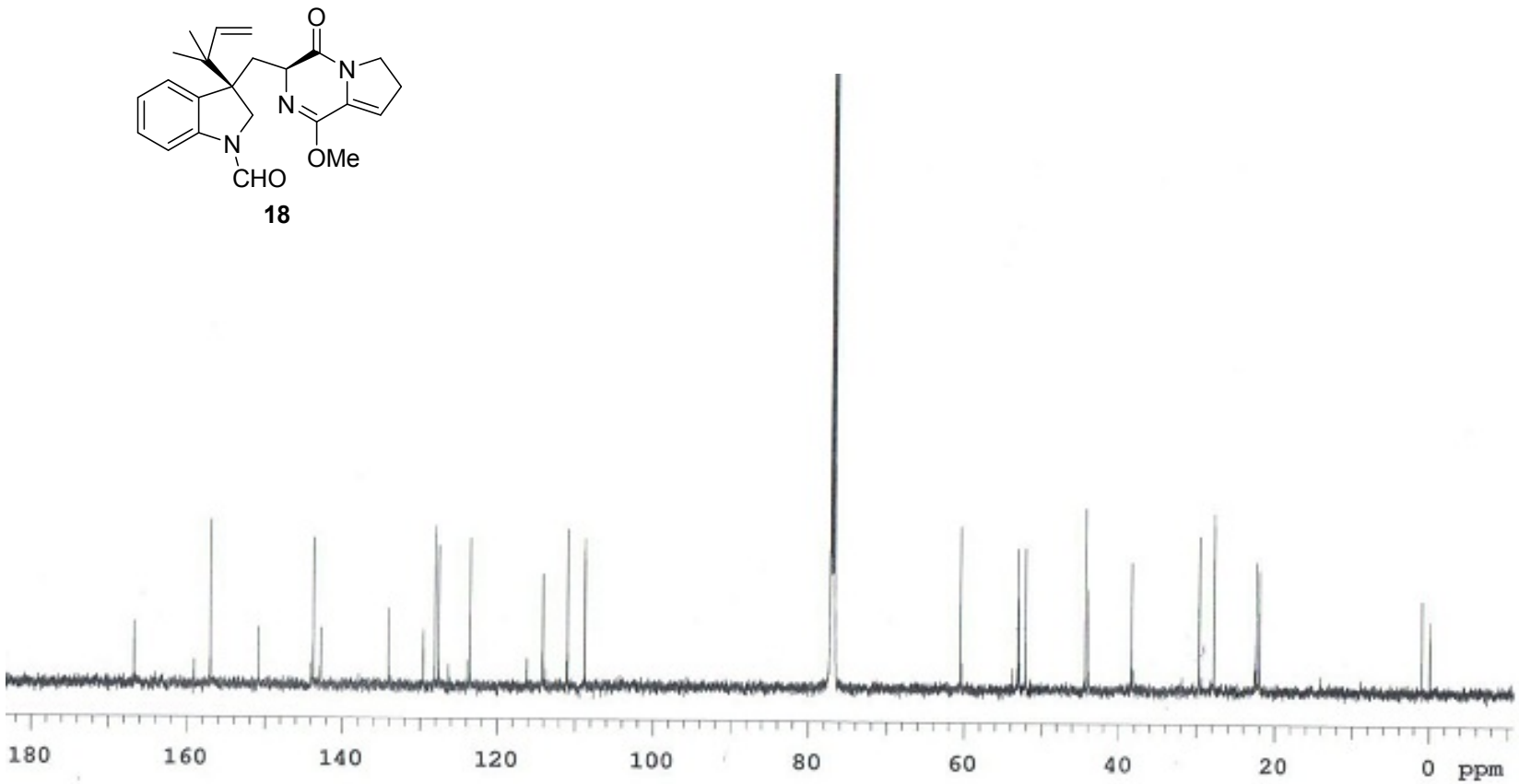
^{1}H NMR spectrum of compound **31**



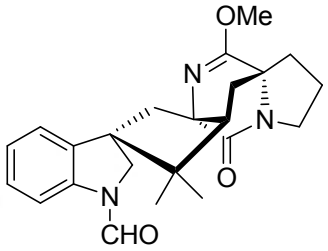
^{13}C NMR spectrum of compound **31**



^{1}H NMR spectrum of compound **18**

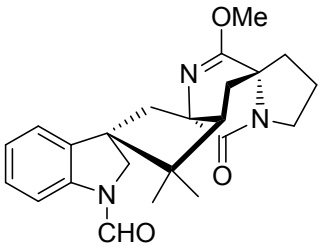


^{13}C NMR spectrum of compound **18**

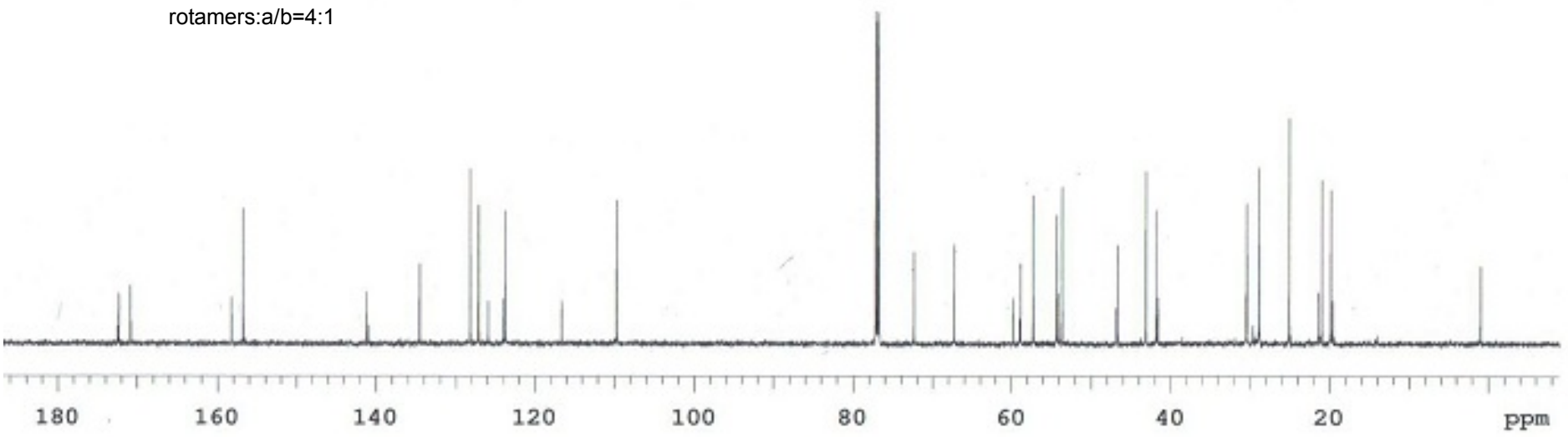


19a and **19b**
rotamers:a/b=4:1

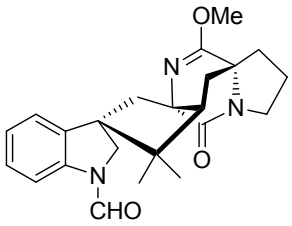
^{1}H NMR spectrum of compound **19**



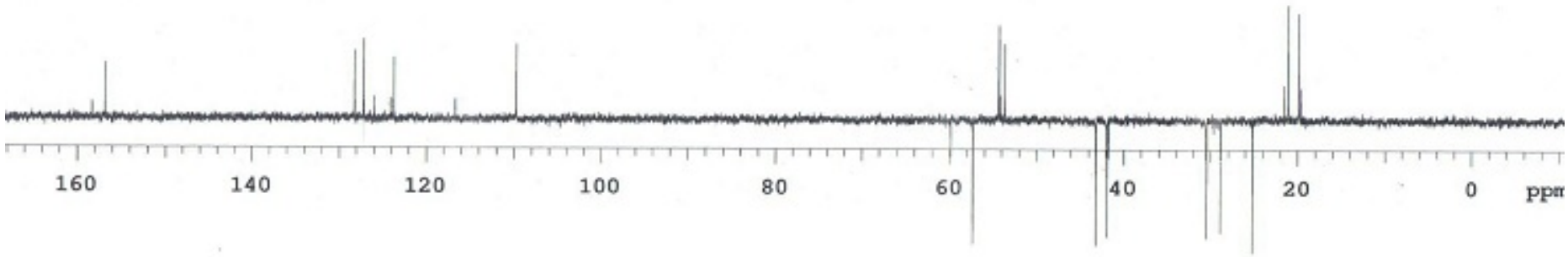
19a and **19b**
rotamers:a/b=4:1



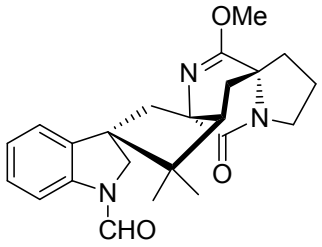
^{13}C NMR spectrum of compound **19**



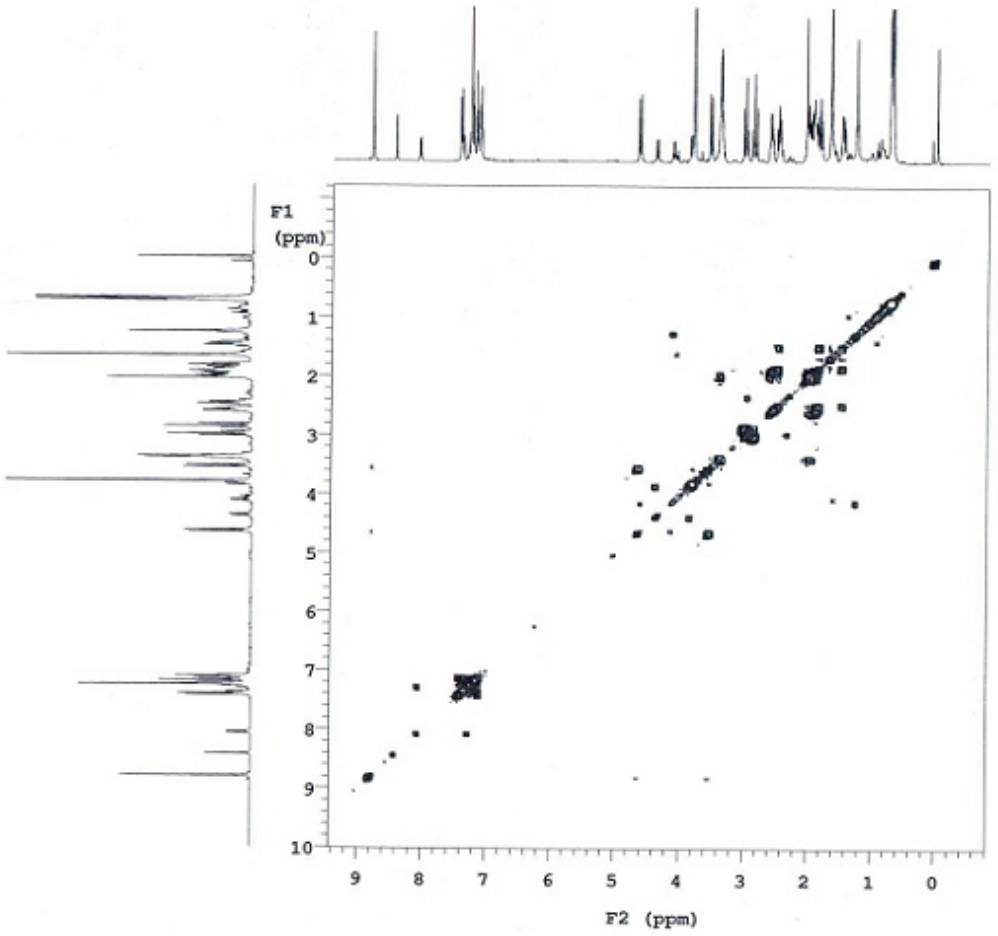
19a and **19b**
rotamers:a/b=4:1



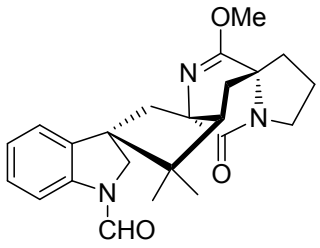
DEPT spectrum of compound **19**



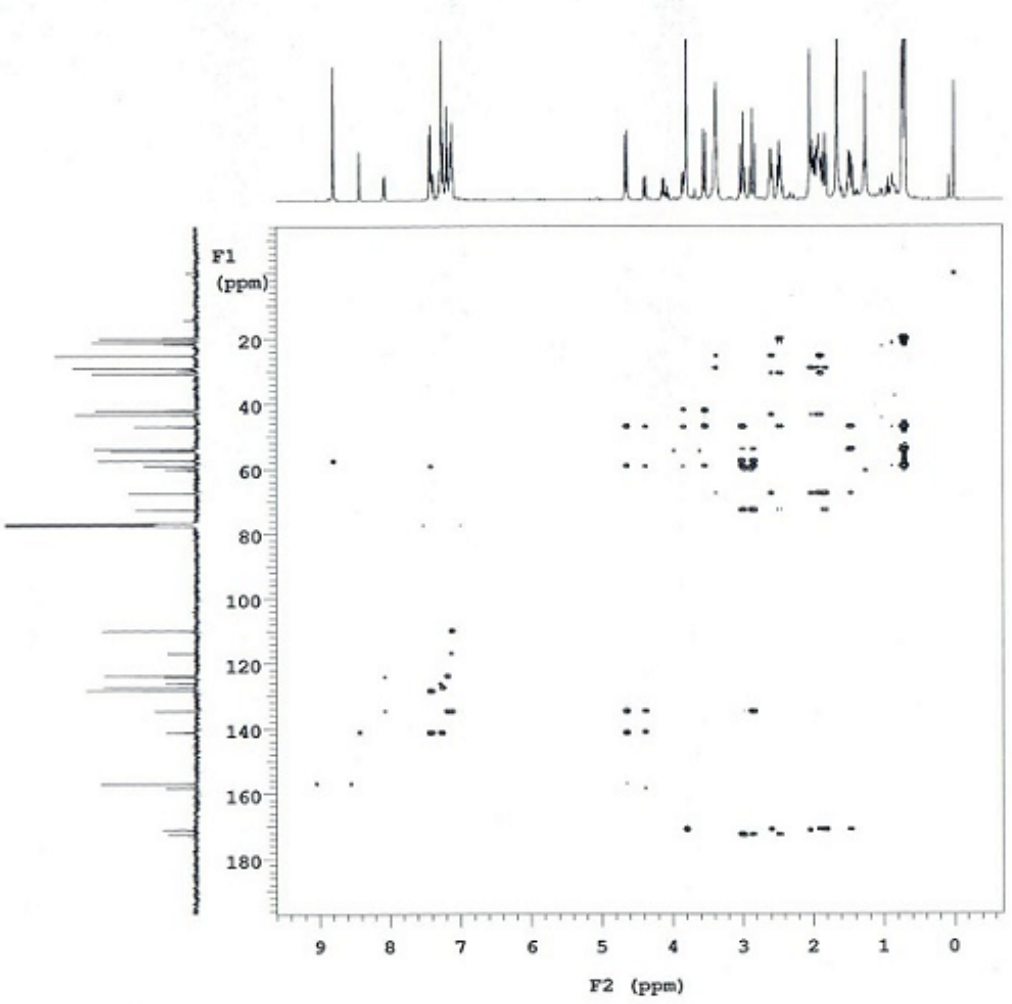
19a and **19b**
rotamers:a/b=4:1



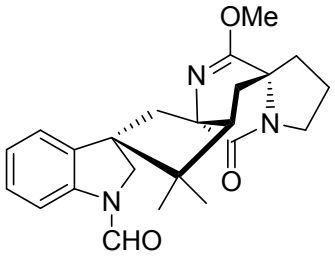
gCOSY spectrum of compound **19**



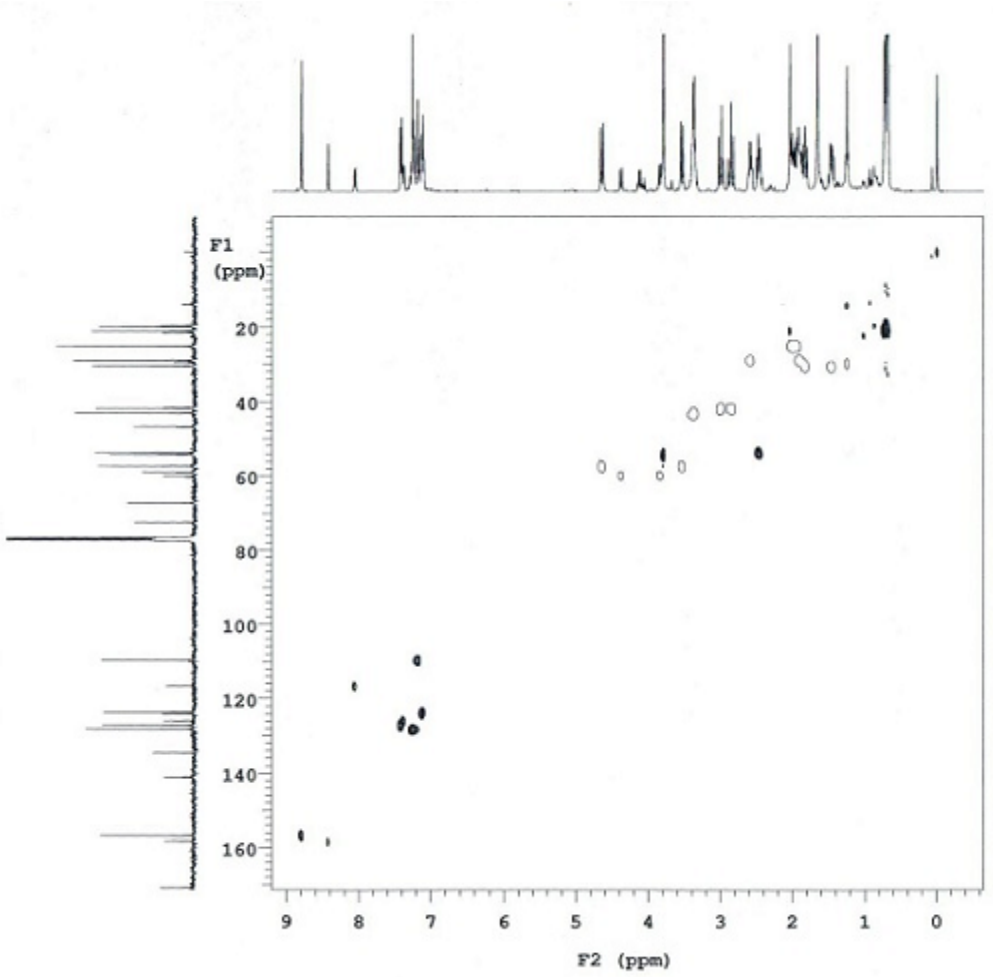
19a and **19b**
rotamers:a/b=4:1



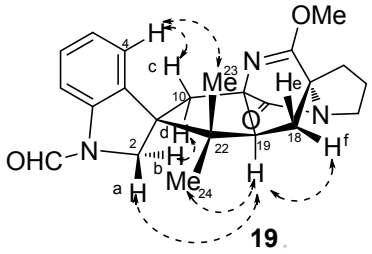
gHMBC spectrum of compound **19**



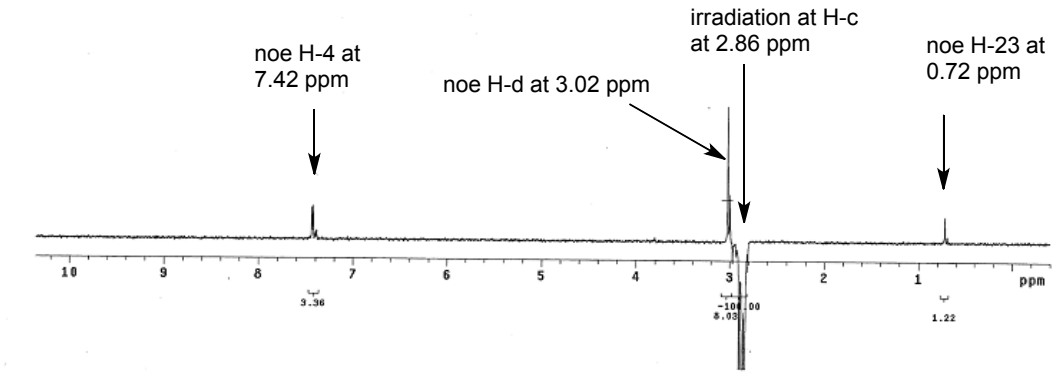
19a and **19b**
rotamers:a/b=4:1



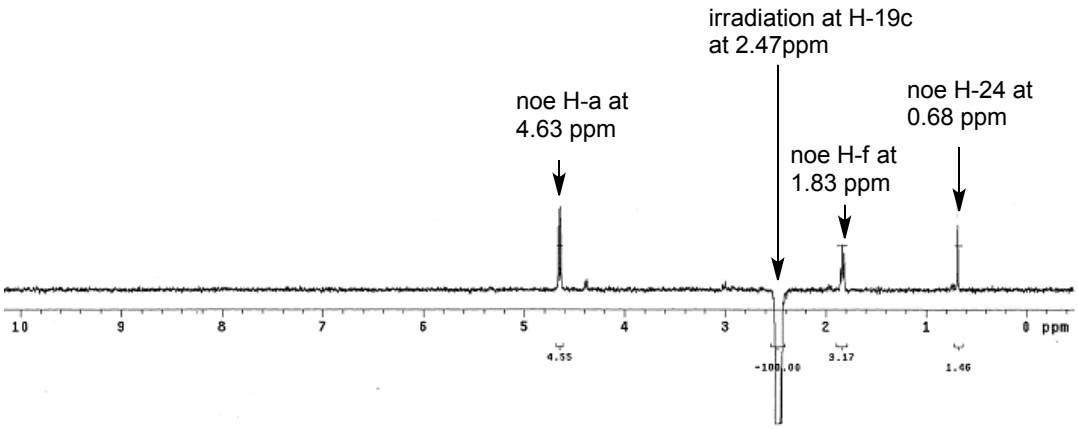
gHMQC spectrum of compound **19**



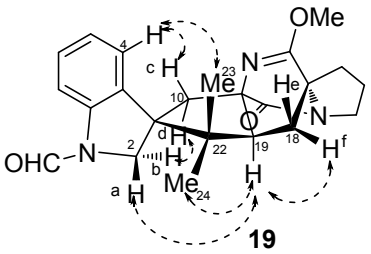
19



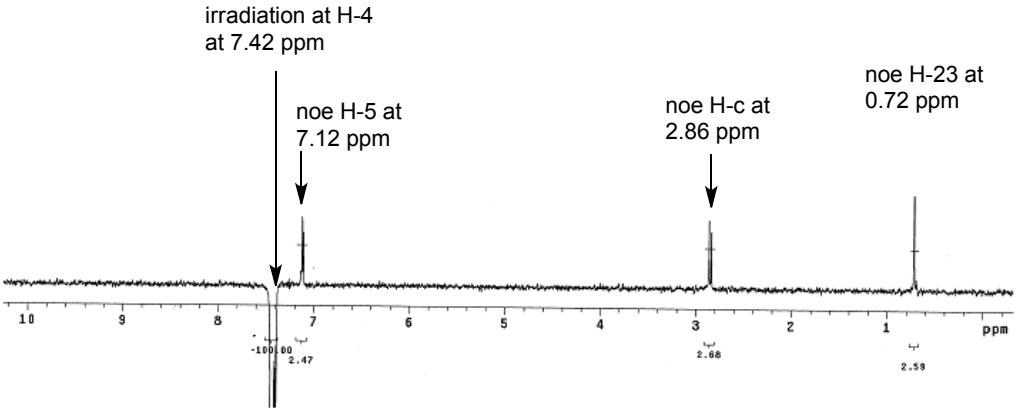
NOEDS spectrum of compound **19 (1)**



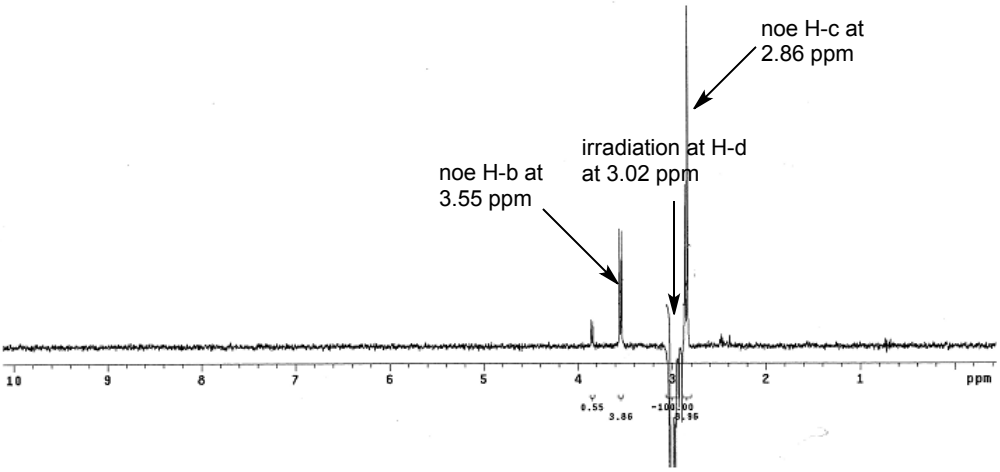
NOEDS spectrum of compound **19 (2)**



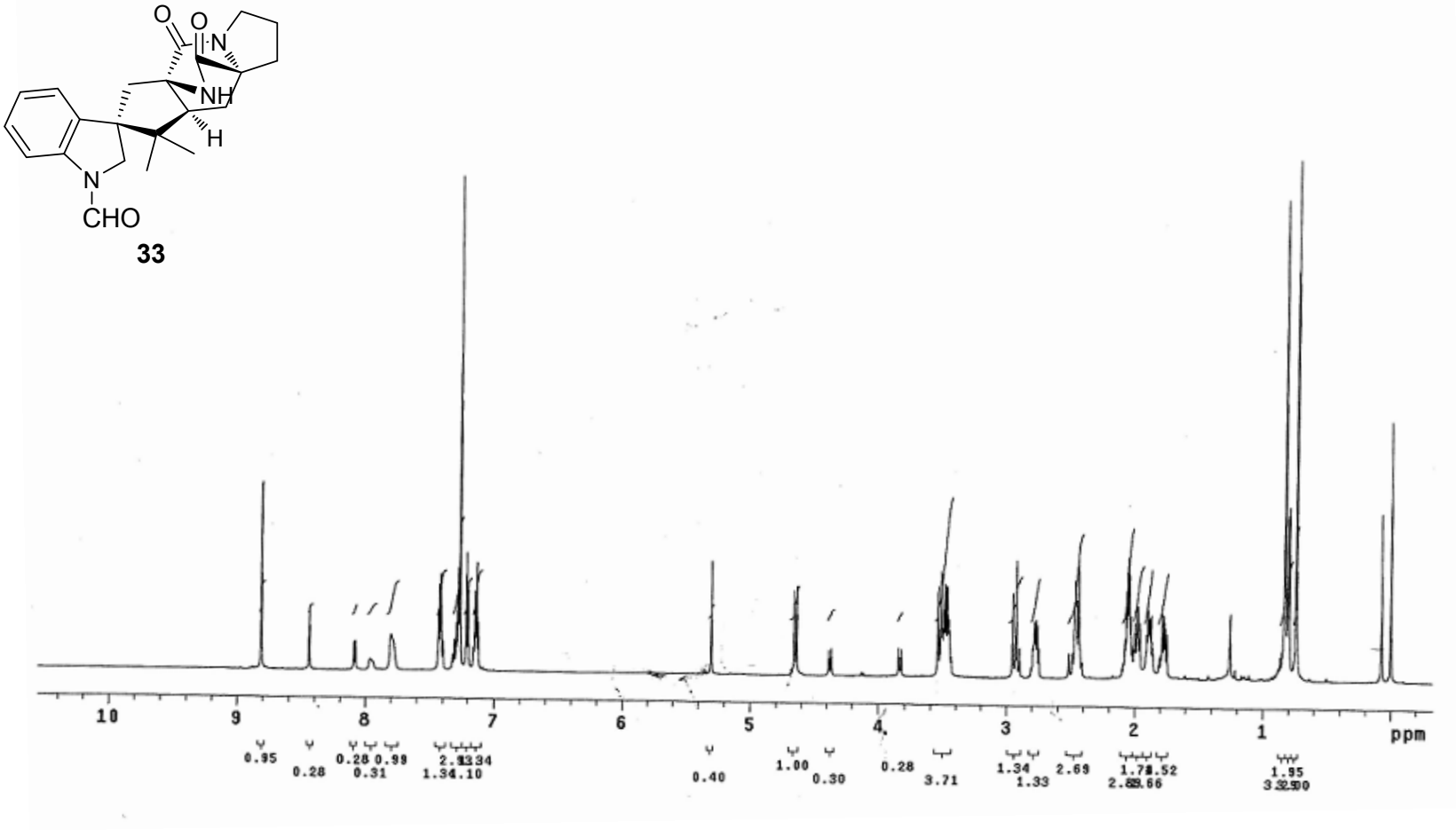
19



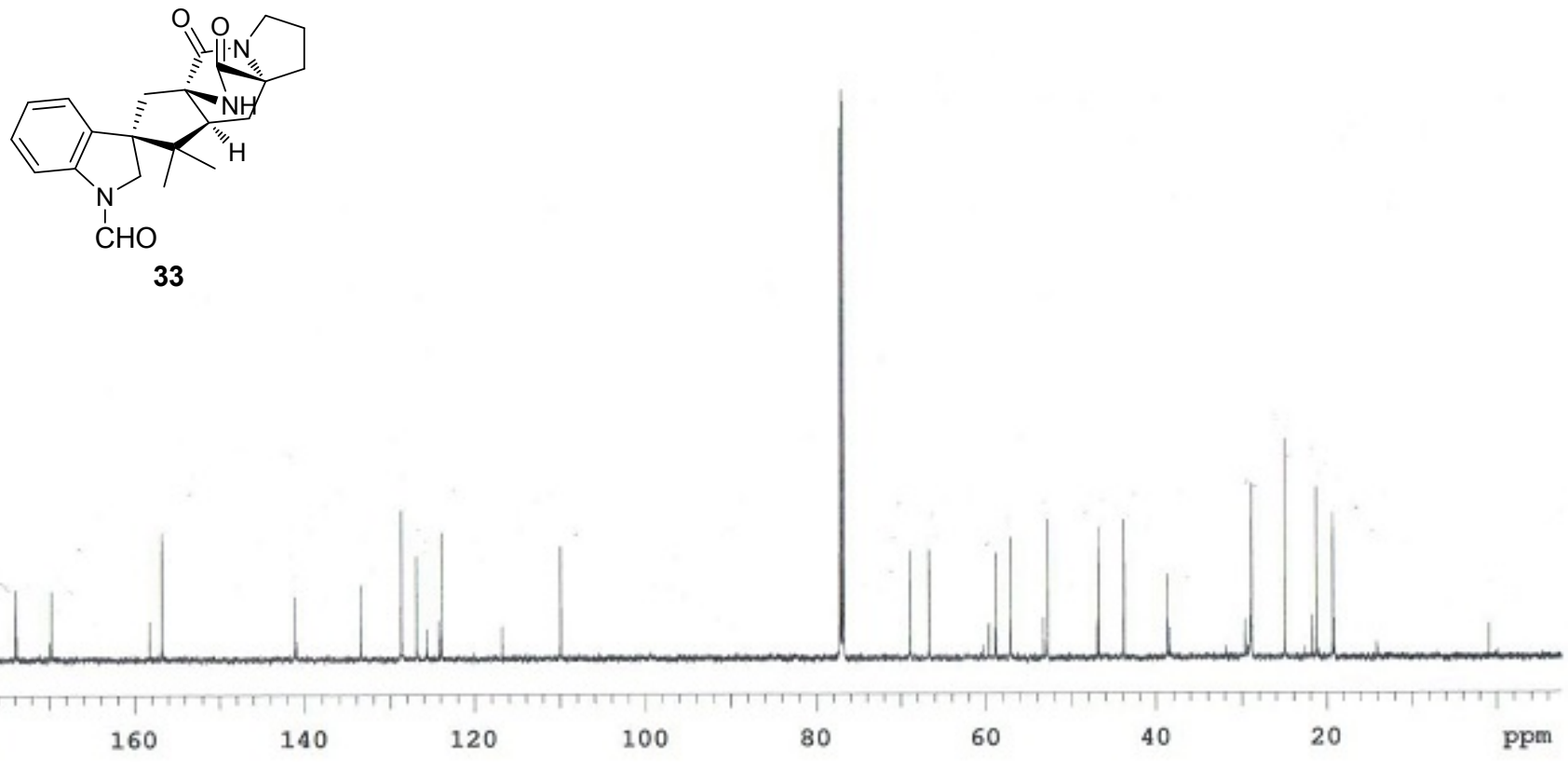
NOEDS spectrum of compound **19 (3)**



NOEDS spectrum of compound **19 (4)**

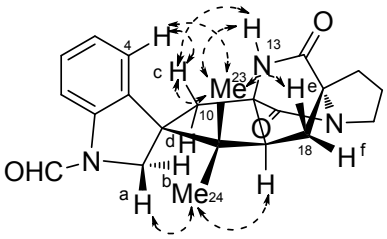


^{1}H NMR spectrum of compound **33**

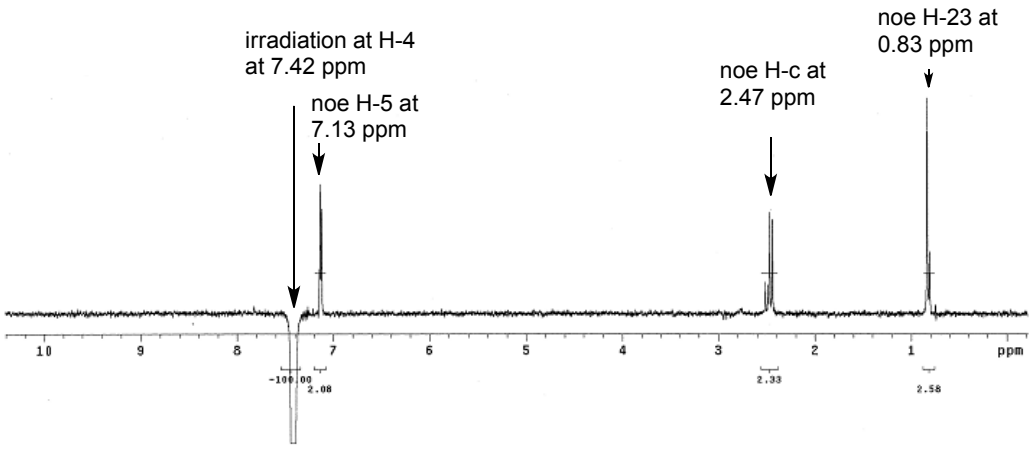


33

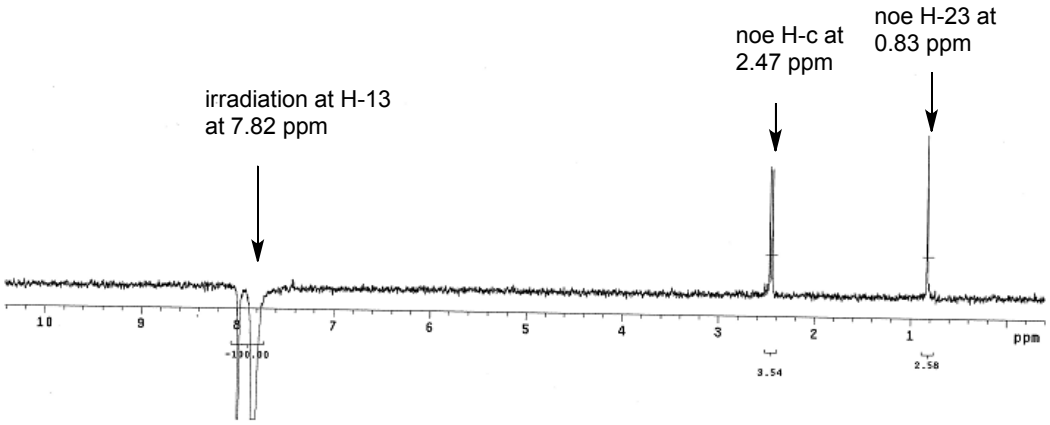
^{13}C NMR spectrum of compound **33**



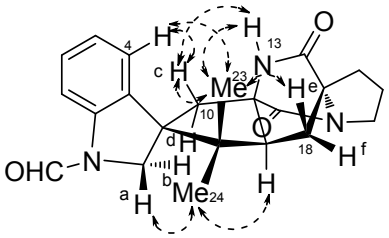
33



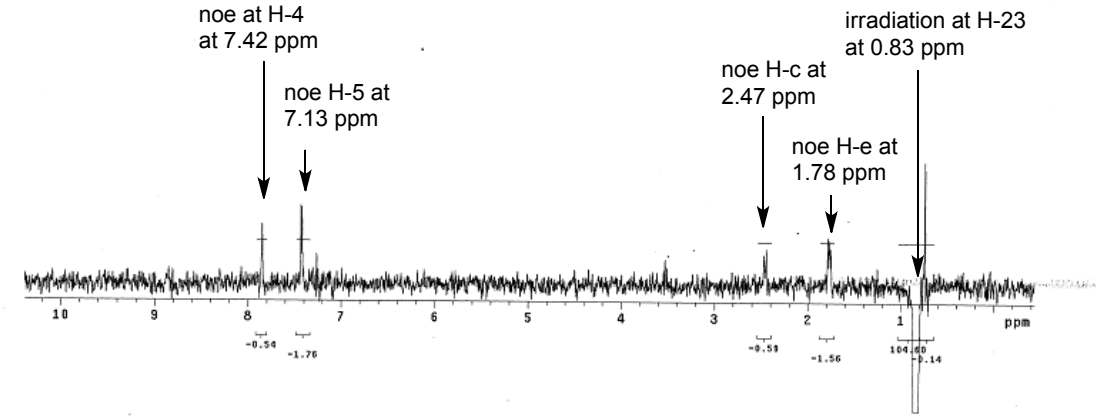
NOEDS spectrum of compound **33 (1)**



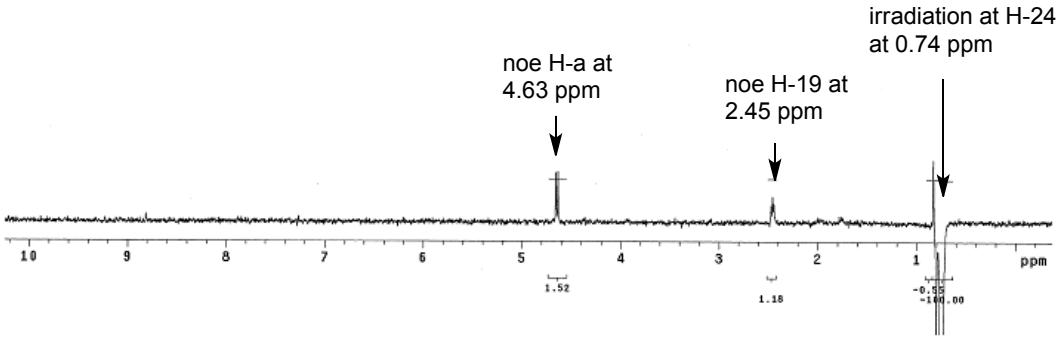
NOEDS spectrum of compound **33 (2)**



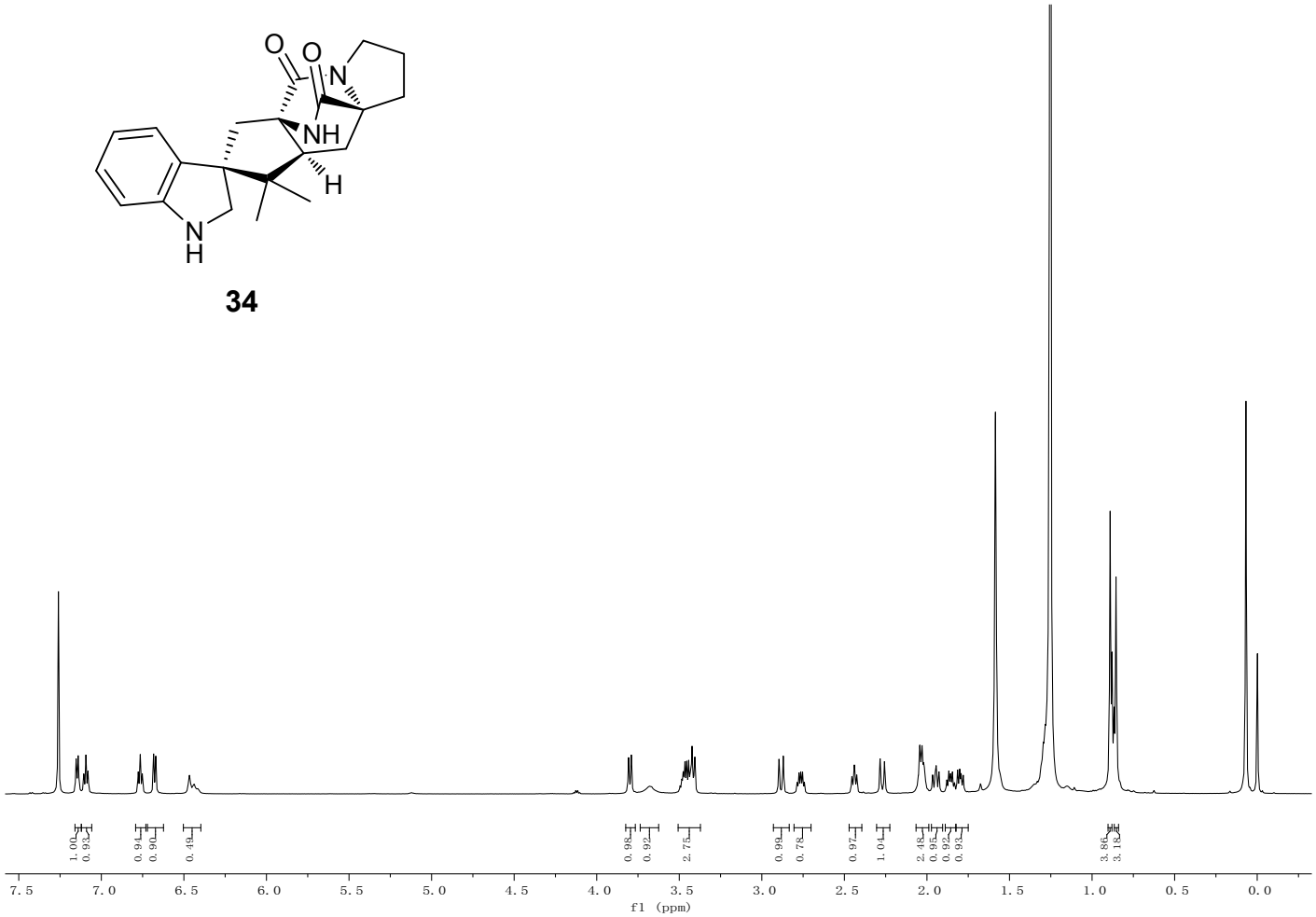
33



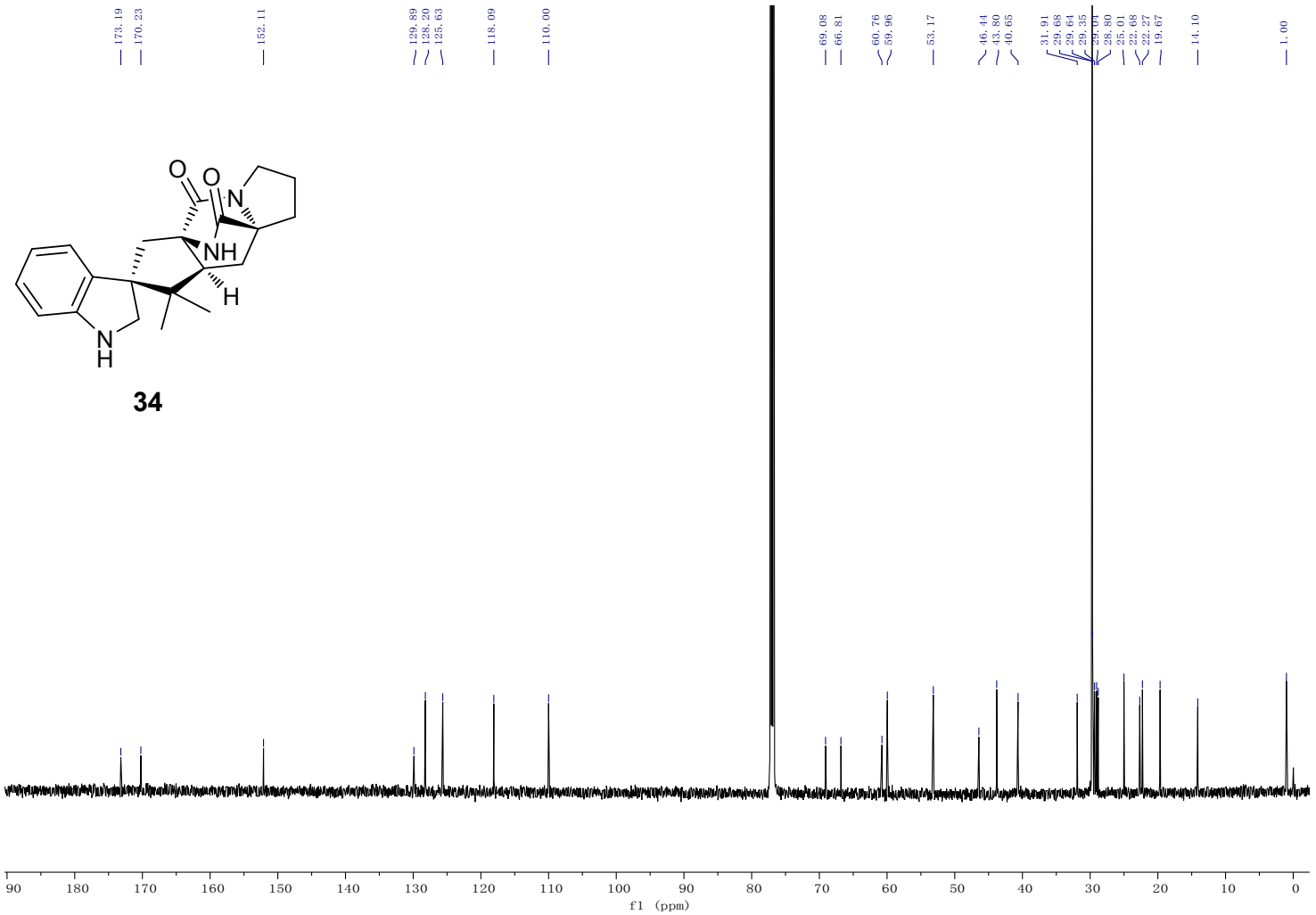
NOEDS spectrum of compound **33 (3)**



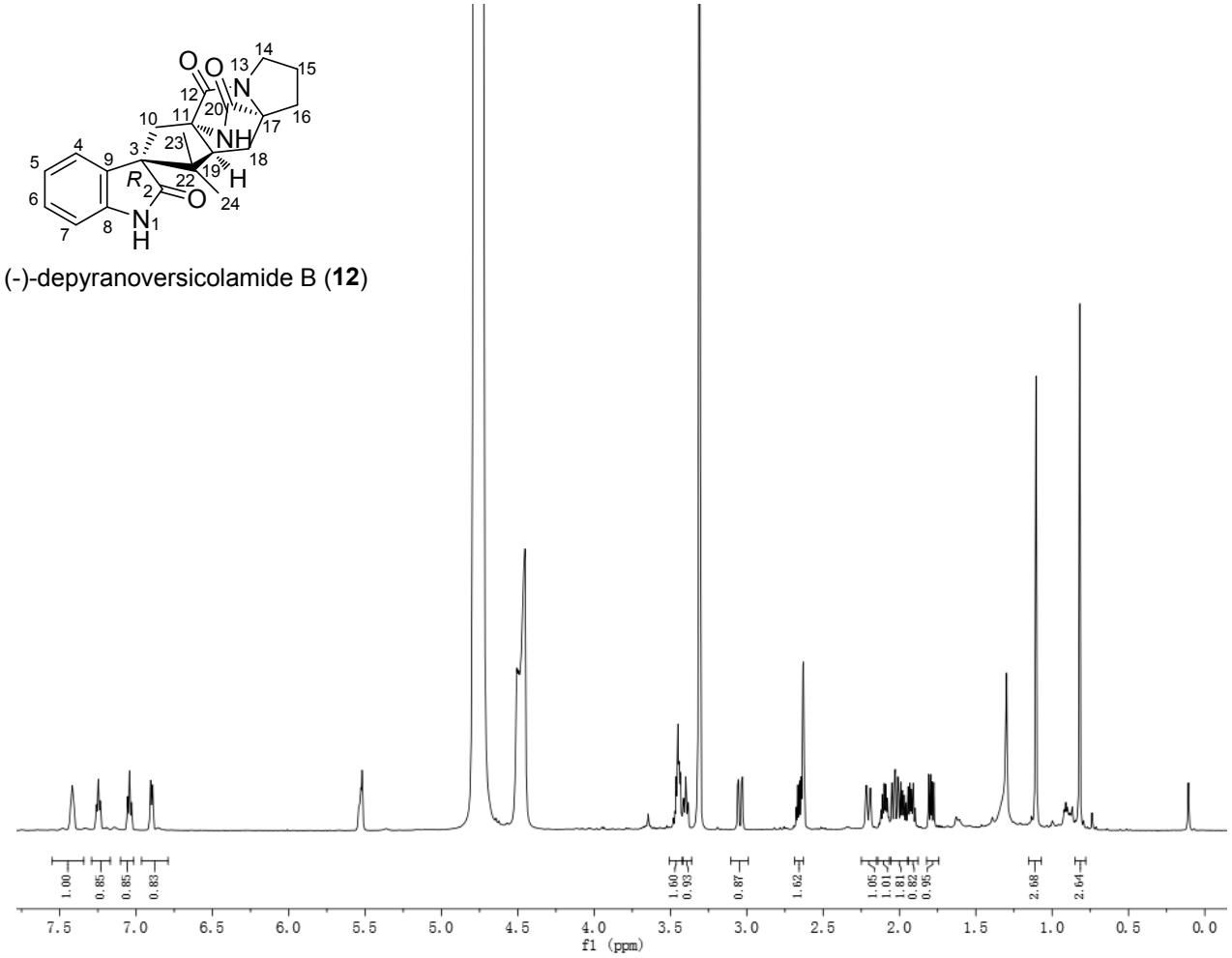
NOEDS spectrum of compound **33 (4)**



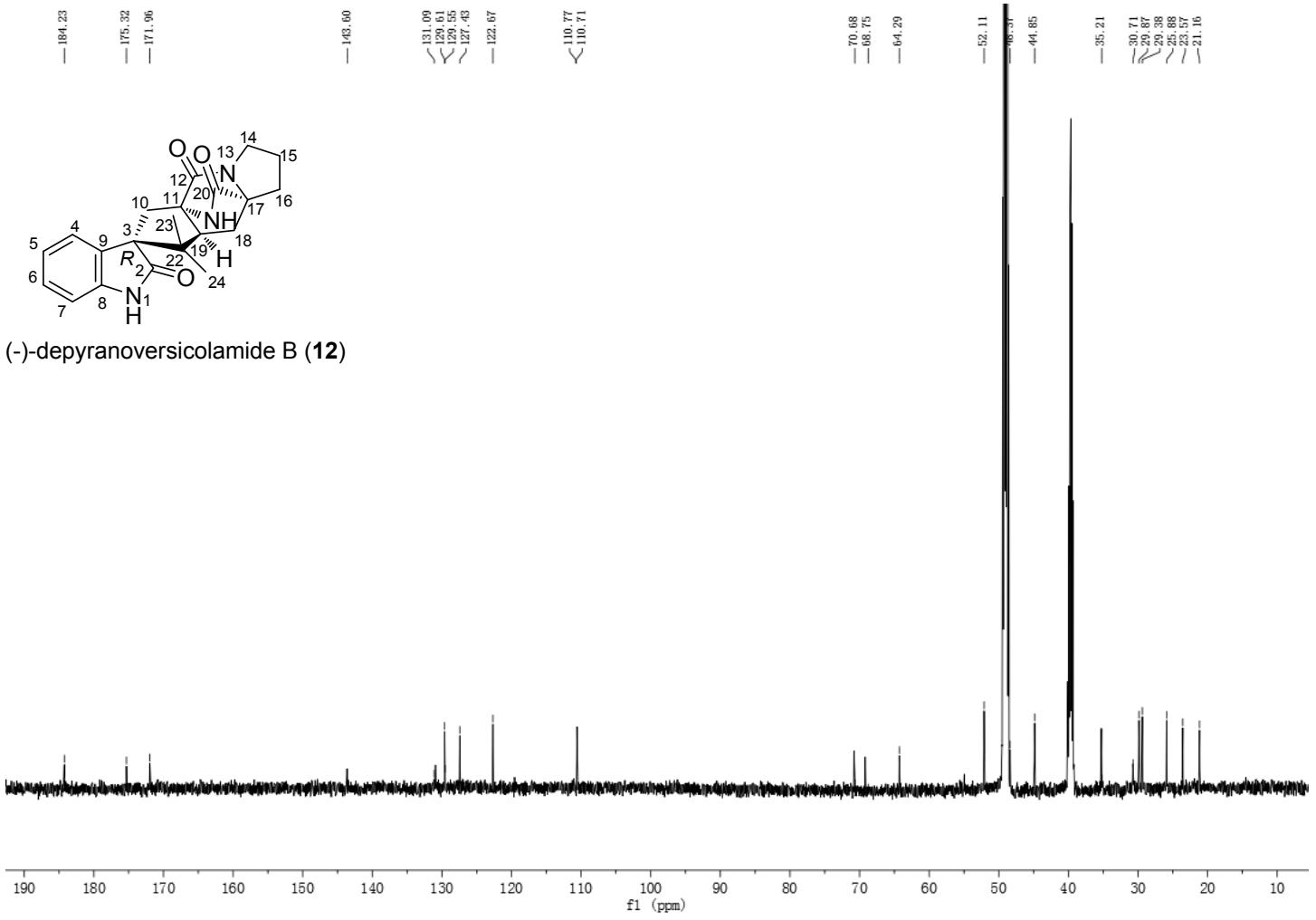
^{1}H NMR spectrum of compound **34**



^{13}C NMR spectrum of compound **34**

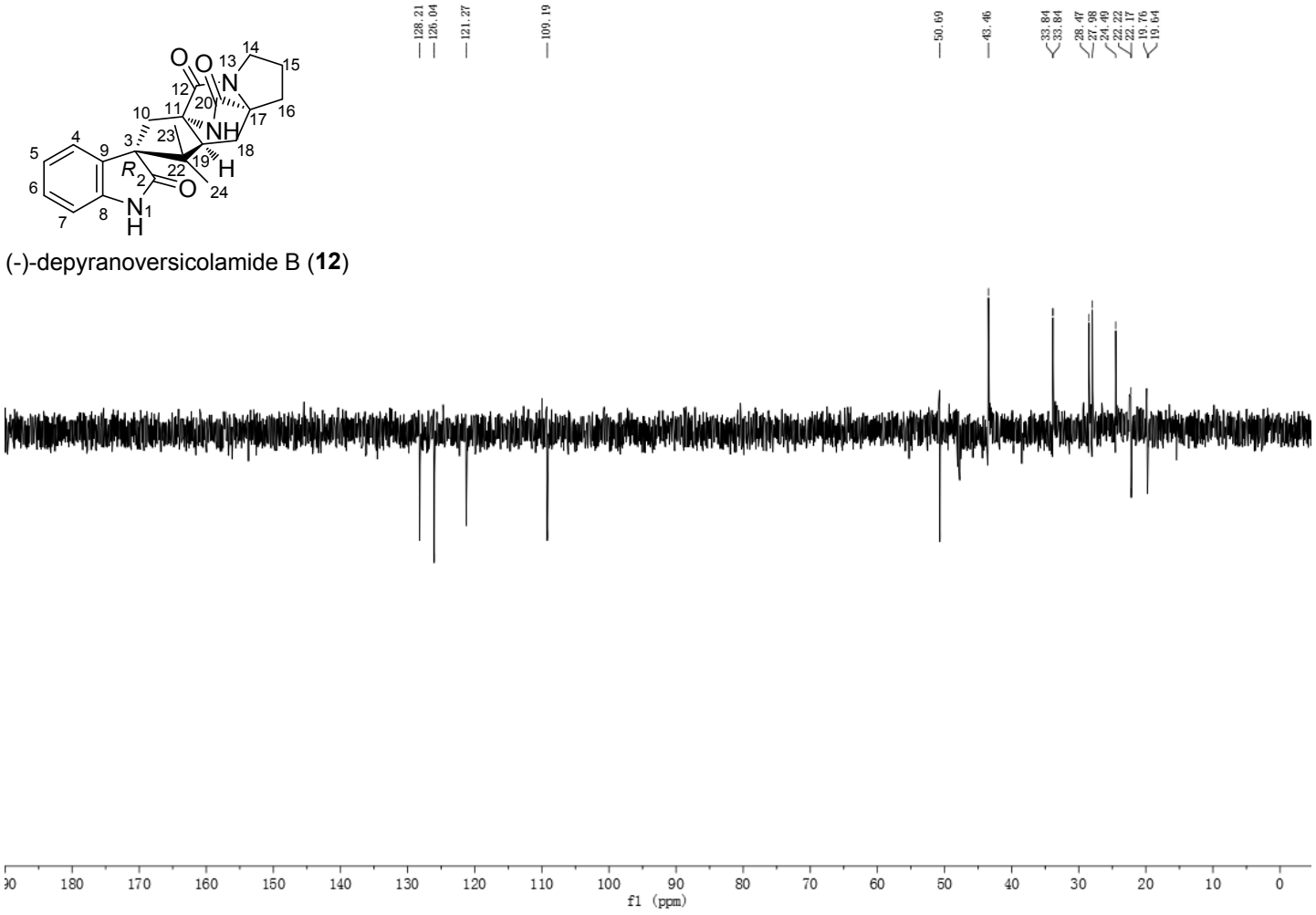


^{1}H NMR spectrum of (–)-depyranoversicolamide B (**12**)



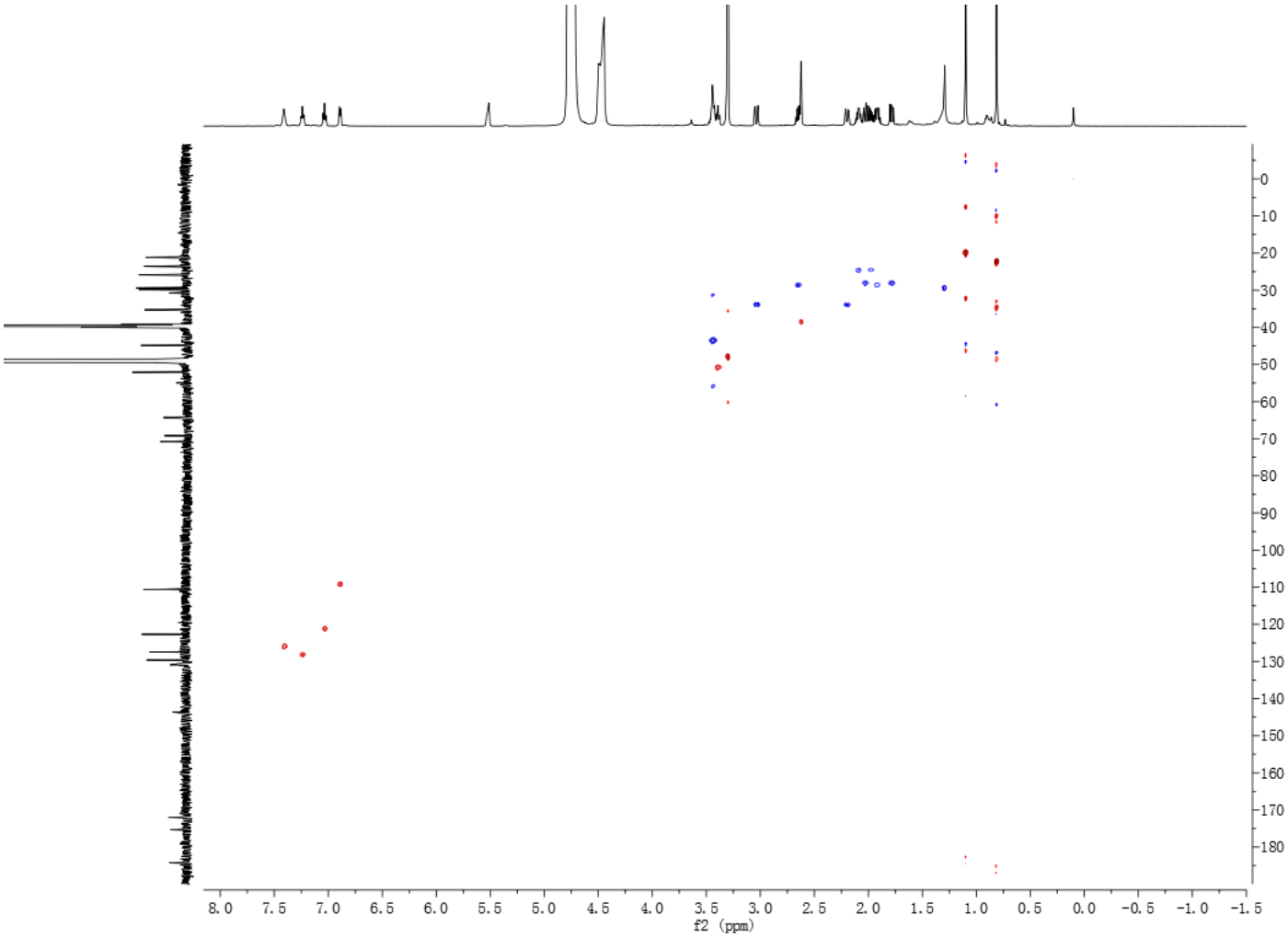
(-)-depyranoversicolamide B (**12**)

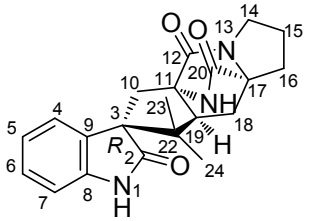
^{13}C NMR spectrum of (–)-depyranoversicolamide B (**12**)



(-)-depyranoversicolamide B (**12**)

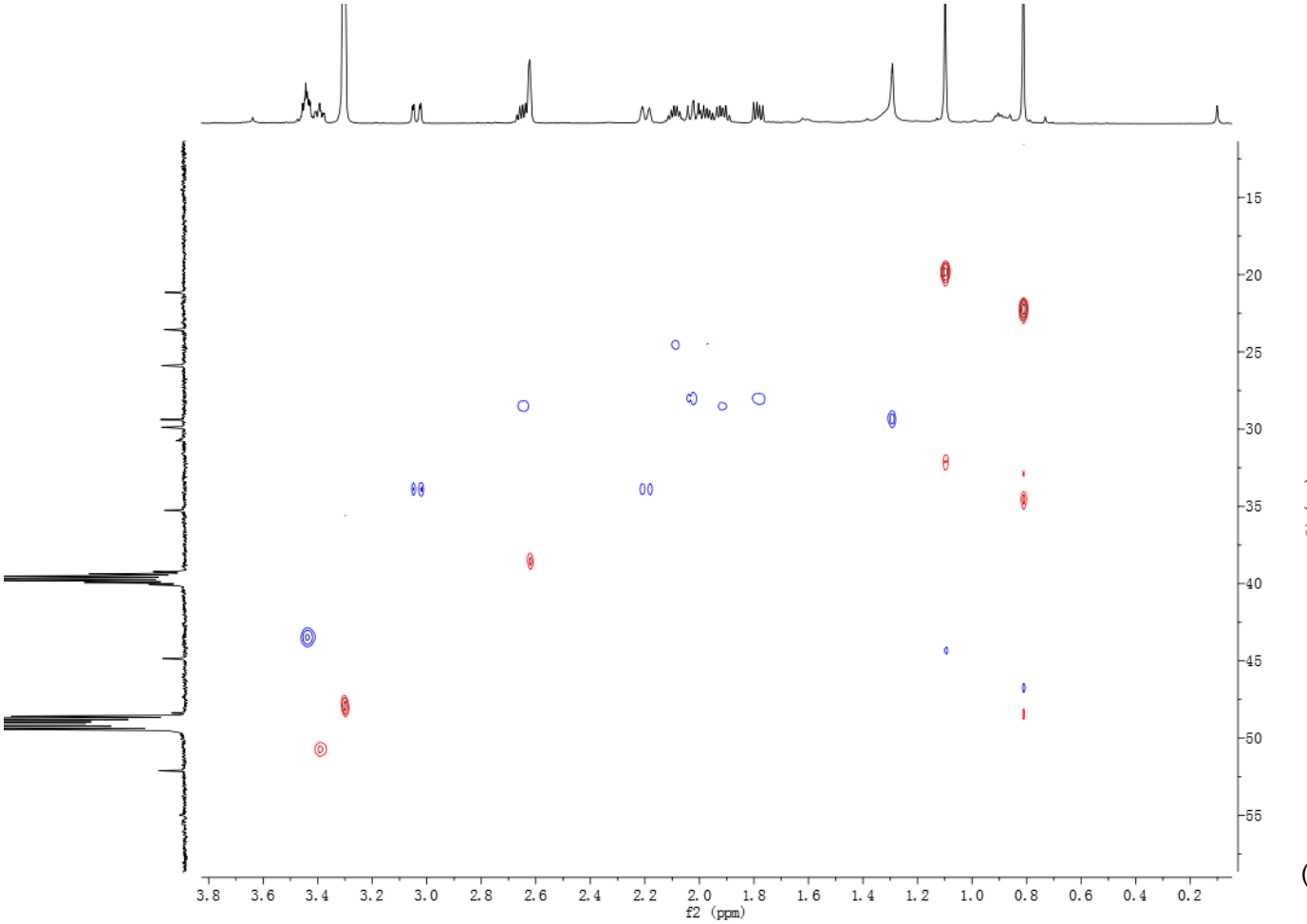
DEPT spectrum of (–)-depyranoversicolamide B (**12**)

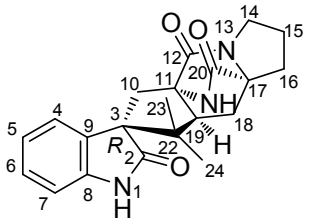




(-)-depyranoversicolamide B (**12**)

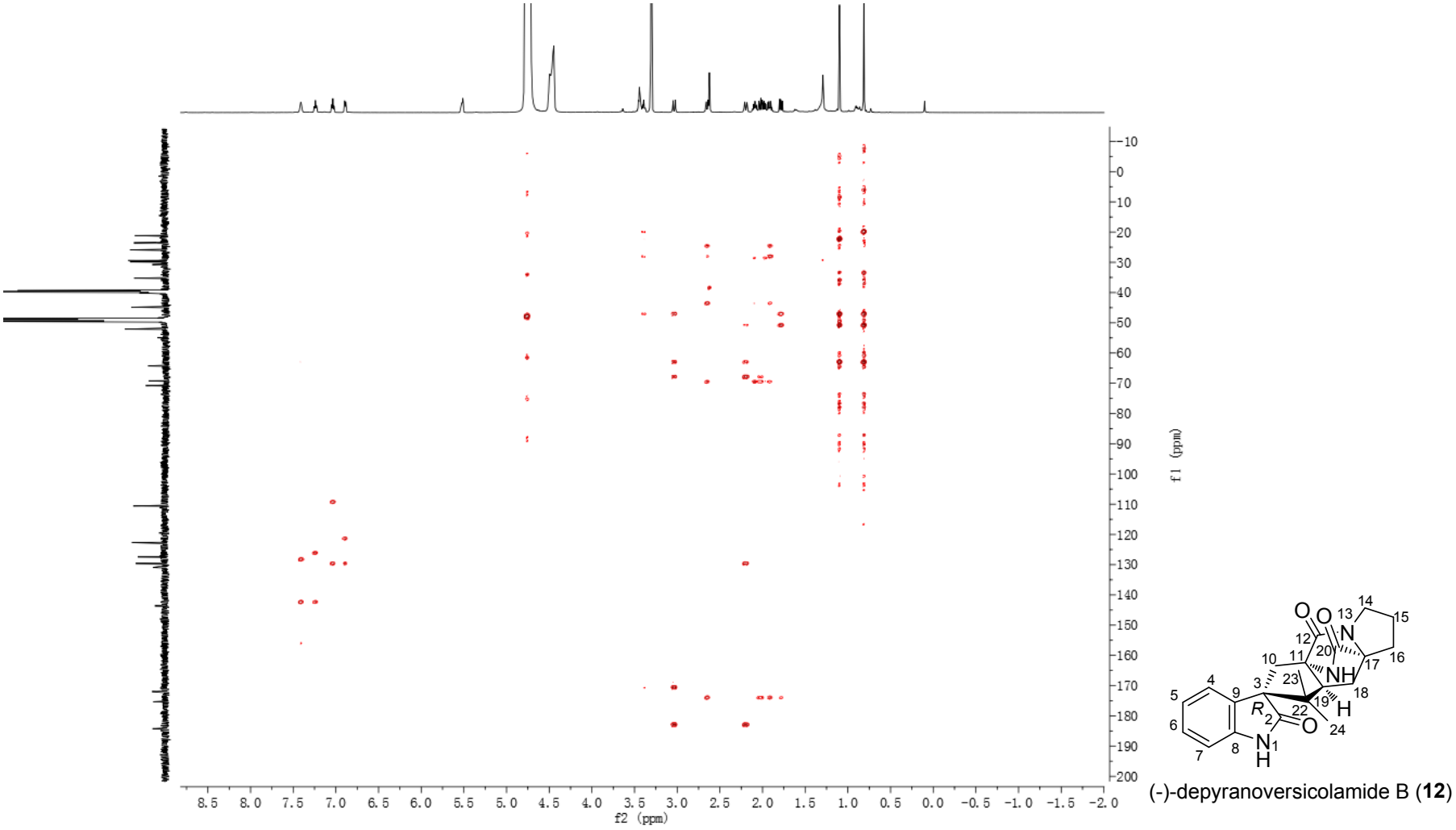
HSQC spectrum of (–)-depyranoversicolamide B (**12**)





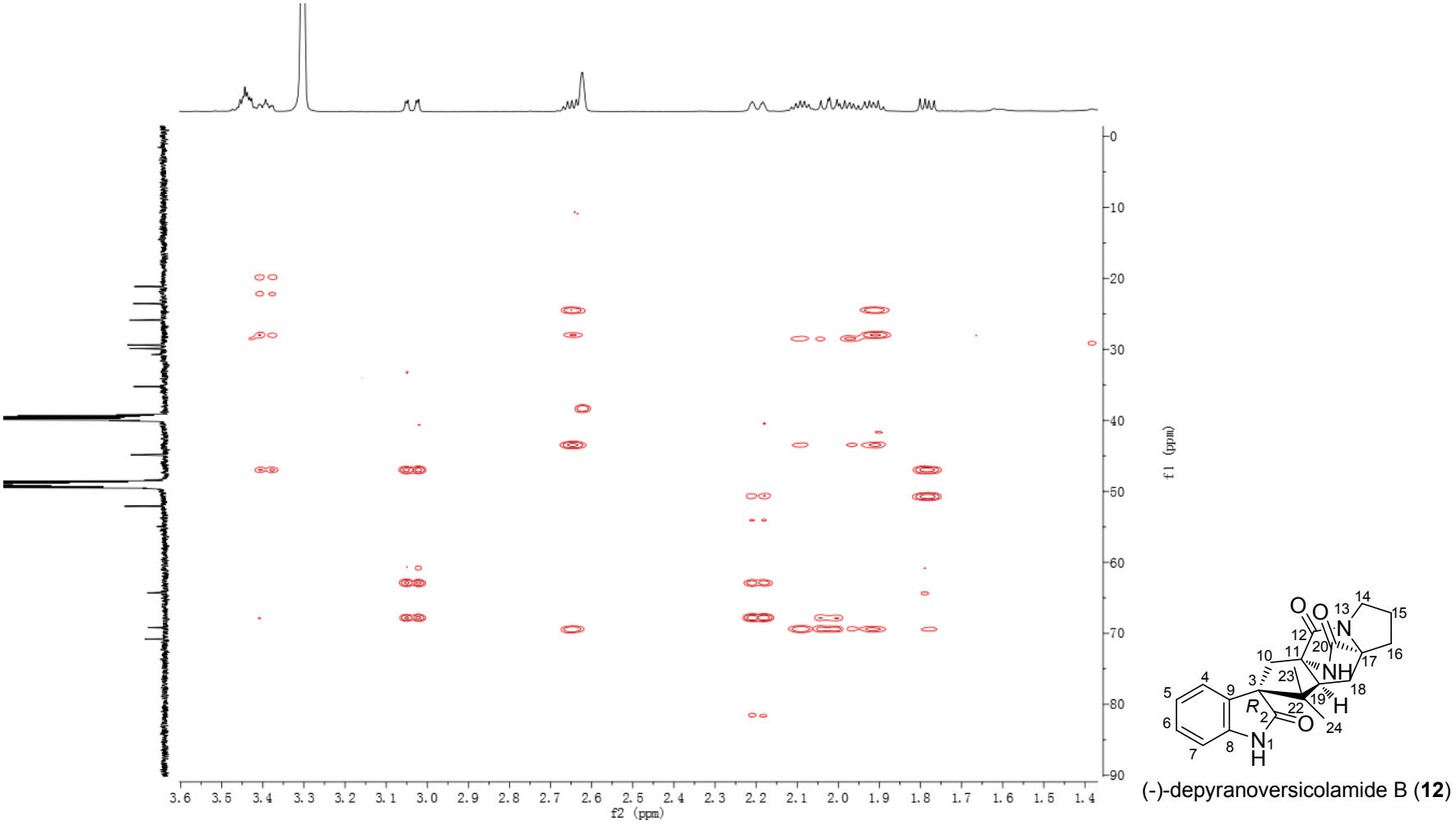
(-)-depyranoversicolamide B (**12**)

HSQC spectrum of (–)-depyranoversicolamide B (**12**)

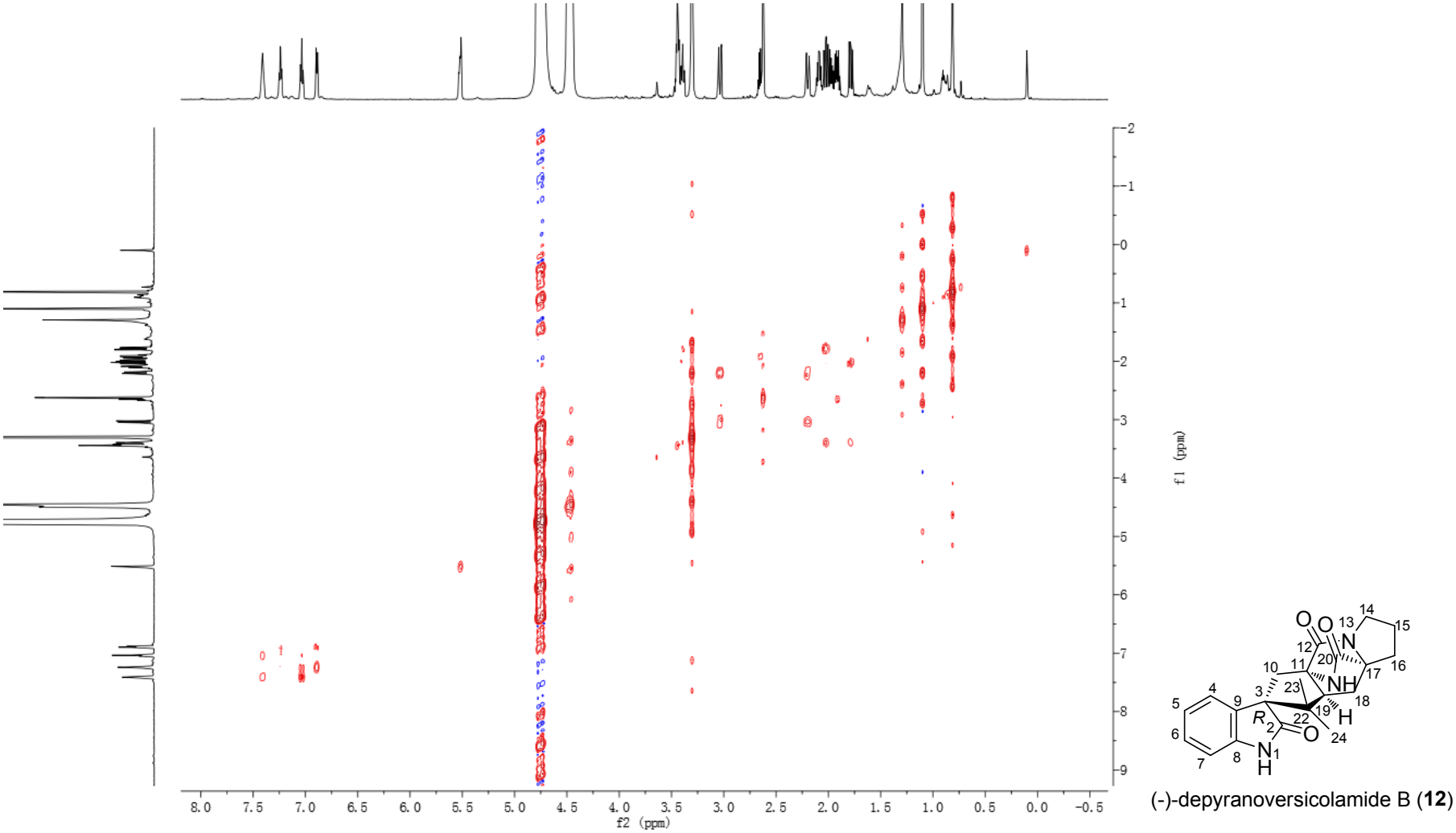


(-)-depyranoversicolamide B (**12**)

HMBC spectrum of (–)-depyranoversicolamide B (**12**)

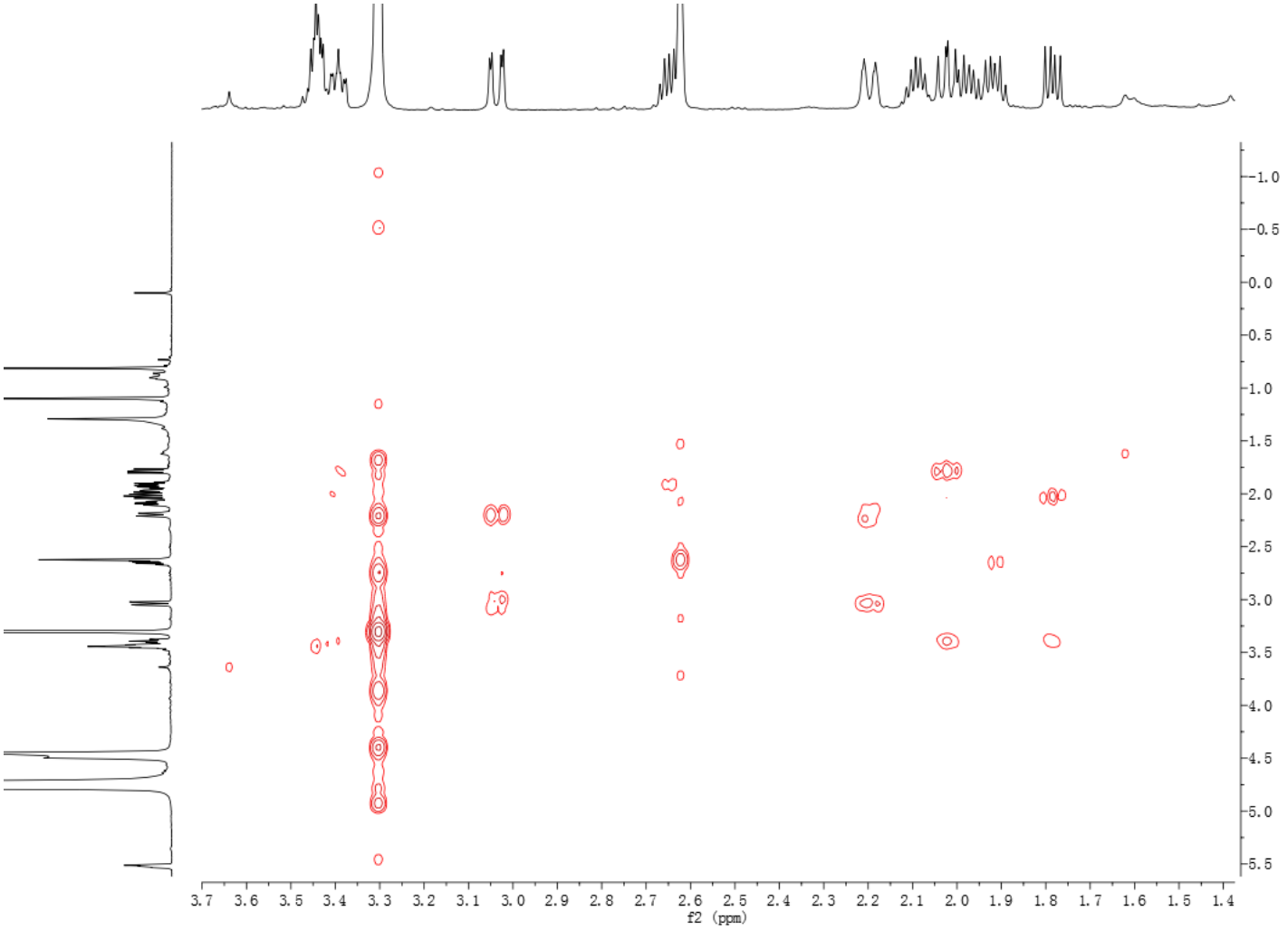


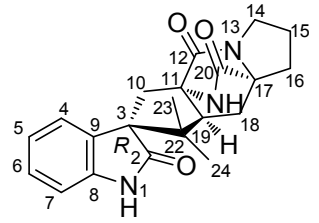
HMBC spectrum of **(–)**-depyranoversicolamide B (**12**)



(-)-depyranoversicolamide B (**12**)

COSY spectrum of (–)-depyranoversicolamide B (**12**)





(-)-depyranoversicolamide B (**12**)

COSY spectrum of (–)-depyranoversicolamide B (**12**)