Configurations on pages S8 and S11 and structures on pages S36-39 for 39A and 40A were in correct in the version published February 14, 2007. The corrected version was published July 12, 2007.

A Versatile Strategy for Divergent and Diastereoselective Synthesis of Natural Product-Like Polyhydroxylated Indolizidines

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Melting points are uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded in $CDCl_3$ otherwise as indicated. THF was distilled from sodium benzophenone ketyl. Petroleum ether refers to that of bp 60-90 °C. The starting material *cis*-(3*S*, 4*R*)-3,4-isopropylidenedioxypyrrolidin-2-ylidene acetate **17** was prepared according to the method described in the literatures. [(a) Buchanan, J. G.; Jigajinni, V. B.; Singh, G.; Wightman, R. H. *J. Chem. Soc., Perkin Trans. 1* **1987**, *(11),* 2377-2384. (b) Buchanan, J. G.; Singh, G.; Wightman, R. H. *J. Chem. Soc., Chem. Commun.* **1984**, *(19)*, 1299-1300.]

1. General procedure for the reactions of heterocyclic enamine 17 with methyl alkenoic carboxylates or methyl allenic carboxylate.

Under nitrogen atmosphere, a solution of heterocyclic enamine **17** (1 mmol) in dry THF (10 mL) was added dropwise to the suspension of NaH (0.5 mmol, 50% in mineral oil) in THF (10 mL) cooled in an ice bath. The resulting mixture was stirred at 0 °C until no evolution of hydrogen gas. To this mixture, the solution of alkenoic carboxylate (methyl acrylate, methyl crotonate or methyl 2-hexenoate) (1.25 mmol) or methyl allenic carboxylate (1.5 mmol) in THF (10 mL) was then added dropwise at 0 °C. The reaction mixture was stirred for another 4 h at ambient temperature for the alkenoic carboxylate or for 1 h at 0 °C for the methyl allenic carboxylate. After removal of the solvent, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (4:1 to 1:1). The hexahydro-5-indolizinones **18**, **22,** and **23** were obtained, respectively, from the reactions of enamine **17** with alkenoic carboxylates, while tetrahydro-5-indolizinone **30** was isolated from the reaction of enamine **17** with allenic carboxylate.

Methyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-1,2,3,5,6,7-hexahydro-5-indolizinone-8-carboxylate 18: 82 %, 122-123 °C, $[\alpha]_D^{20}$ = -204.3° (c = 0.635, $CHCl_3$). IR ν (cm^{-1}) 1700, 1675, 1656; ^{1}H NMR δ (ppm) 5.75 (d, J = 6.1 Hz, 1H), 4.84 (dt, J = 5.9, 1.7 Hz, 1H), 3.97(dd, J = 13.1, 1.6 Hz, 1H), 3.81 (s, 3H), 3.77

(dd, J = 13.1, 5.8 Hz, 1H), 2.78-2.84 (m, 1H), 2.56-2.65 (m, 3H), 1.46 (s, 3H), 1.44 (s, 3H); ^{13}C NMR δ (ppm) 169.0, 166.2, 149.9, 112.4, 105.0, 80.3, 75.1, 51.7, 50.9, 30.4, 27.2, 25.4, 21.5. MS (FT-ICR): 268 (M+1). Anal. Calcd for $C_{13}H_{17}NO_5$ C 58.42, H 6.41, N 5.24; Found: C 58.43, H 6.50, N 5.08.

Methyl (1S, 2R, 7S)-1,2-*O*-isopropylidenedioxy-7-methyl-1,2,3,5,6,7-hexahydro-5-indolizinone-8-carboxylate 22A: 54%, mp 97-98 °C, $[\alpha]_D^{20}$ = -61.28° (C = 0.545, $CHCl_3$). IR v (cm^{-1}) 1705, 1689, 1647; ^{1}H NMR δ (ppm) 5.69 (d, J = 6.1 Hz, 1H), 4.78 (dt, J = 5.7, 1.5 Hz, 1H), 3.93 (d, J = 13.1 Hz, 1H), 3.81 (dd, J = 13.2, 5.6 Hz, 1H), 3.78 (s, 3H), 2.97-3.00 (m, 1H), 2.59 (dd, J = 16.9, 7.1 Hz, 1H), 2.42 (dd, J = 16.8, 1.2 Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H), 1.11 (d, J = 7.0 Hz, 3H); ^{13}CNMR δ (ppm) 169.1, 166.5, 149.2, 112.2, 109.3, 80.6, 75.0, 51.5, 51.0, 38.1, 28.0, 27.6, 26.0, 18.7; MS (EI): 43 (100), 59 (55), 266 (68), 281 (M^+, 45%). Anal. Calcd for $C_{14}H_{19}NO_5$: C 59.78, H 6.81, N 4.98. Found C 59.69, H 7.01, N 4.77.

Methyl (1S, 2R, 7R)-1,2-*O*-isopropylidenedioxy-7-methyl-1,2,3,5,6,7-hexahydro-5-indolizinone-8-carboxylate 22B: 35%, mp 120-121 °C, $[\alpha]_D^{20}$ = -234.39° (C = 0.535, $CHCl_3$). IR v (cm^{-1}) 1702, 1677, 1650; ^{1}H NMR δ (ppm) 5.71 (d, J = 6.1 Hz, 1H), 4.83 (t, J = 5.8 Hz, 1H), 4.00 (d, J = 13.0 Hz, 1H), 3.79 (s, 3H), 3.67 (dd, J = 13.0, 5.7 Hz, 1H), 3.08-3.10 (m, 1H), 2.70 (dd, J = 16.1, 7.2 Hz, 1H), 2.38 (dd, J = 16.1, 1.6 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H), 1.02 (d, J = 7.1 Hz, 3H); ^{13}C NMR δ (ppm) 168.4, 165.9, 148.7, 112.3, 110.8, 80.5, 75.2, 51.7, 50.5, 37.9, 27.6, 27.2, 25.2, 18.8; MS (EI): 43 (100), 59 (55), 266 (15), 281 (M^+, 10%). Anal. Calcd for $C_{14}H_{19}NO_5$: C 59.78, H 6.81, N 4.98. Found C 59.70, H 6.38, N 4.94.

Methyl (1S, 2R, 7S)-1,2-*O*-isopropylidenedioxy-7-propyl-1,2,3,5,6,7-hexahydro-5-indolizinone-8-carboxylate 23A: 52%, mp 46-47 °C, $[\alpha]_D^{20}$ = -40.43° (C = 0.470, $CHCl_3$). IR v (cm^{-1}) 1709, 1685, 1648; ^{1}H NMR δ (ppm) 5.73 (d, J = 6.1 Hz, 1H), 4.81 (t, J = 5.7 Hz, 1H), 3.95 (d, J = 12.1 Hz, 1H), 3.84 (dd, J = 13.2, 5.6 Hz, 1H), 3.81 (s, 3H), 2.91-2.94 (m, 1H), 2.60 (dd, J = 16.9, 1.5 Hz, 1H), 2.54 (dd, J = 17.0, 6.7 Hz, 1H), 1.51-1.55 (m, 1H), 1.36-1.46 (m, 2H), 1.43 (s, 3H), 1.41 (s, 3H), 1.27-1.32 (m, 1H), 0.91 (t, J = 7.1 Hz, 3H). ^{13}C NMR δ (ppm) 169.5, 166.6, 149.9, 112.2, 108.6, 80.7, 75.0, 51.5,

51.0, 35.4, 34.7, 32.4, 27.6, 26.0, 19.5, 13.9; MS (EI): 49 (83), 84 (100), 176 (45), 266 (85), 309 (M^+, 8%). Anal. Calcd for $C_{16}H_{23}NO_5$: C 62.12, H 7.49, N 4.53. Found: C 62.01, H 7.80, N 4.48.

Methyl (1S, 2R, 7R)-1,2-*O*-isopropylidenedioxy-7-propyl-1,2,3,5,6,7-hexahydro-5-indolizinone-8-carboxylate 23B: 33%, mp 107-108 °C, $[\alpha]_D^{20}$ = -220.25° (C = 0.400, $CHCl_3$). IR ν (cm^{-1}) 1712, 1688, 1650; ^{1}H NMR δ (ppm) 5.76 (d, *J* = 6.0 Hz, 1H), 4.85 (dt, *J* = 5.7, 1.2 Hz, 1H), 4.03 (d, *J* = 13.0 Hz, 1H), 3.81 (s, 3H), 3.66 (dd, *J* = 13.0, 5.6 Hz, 1H), 3.00-3.03 (m, 1H), 2.66 (dd, *J* = 16.2, 7.1 Hz, 1H), 2.56 (dd, *J* = 16.2, 1.5 Hz, 1H), 1.44 (s, 3H), 1.43 (s, 3H), 1.36-1.41 (m, 2H), 1.24-1.29 (m, 2H), 0.90 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR δ (ppm) 168.7, 166.2, 148.9, 112.3, 110.2, 80.4, 75.2, 51.7, 50.4, 35.2, 35.0, 32.1, 27.2, 25.3, 19.4, 14.0; MS (EI): 49 (100), 81 (65), 176 (55), 266 (95), 309 (M^+, 7%). Anal. Calcd for $C_{16}H_{23}NO_5$: C 62.12, H 7.49, N 4.53. Found: C 61.97, H 7.25, N 4.55.

Methyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-7-ethyl-1,2,3,5-tetrahydro-5-indolizinone-8-carboxylate 30: 87%, mp 81-82 °C, $[\alpha]_D^{20}$ = -208.5° (C = 0.530, CH_3OH). IR ν (cm^{-1}) 1716, 1673, 1658; ^{1}H NMR δ (ppm) 6.44 (s, 1H), 5.90 (brs, 1H), 4.95 (brs, 1H), 4.47 (d, *J* = 13.2 Hz, 1H), 4.10 (d, *J* = 12.2 Hz, 1H), 3.90 (s, 3H), 2.73-2.85 (m, 2H), 1.42 (s, 3H), 1.25 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ (ppm) 165.7, 161.2, 157.2, 151.6, 118.0, 112.5, 109.5, 82.6, 74.7, 52.8, 52.2, 27.2, 26.7, 26.0, 13.9; MS (ESI-TOF): 294 (M+1), 316 ($M+Na^+$). Anal. Calcd for $C_{15}H_{19}NO_5$: C 61.42, H 6.53, N 4.78. Found C 61.11, H 6.46, N 4.53.

2. Preparation of trimethyl (3S, 4R)-3-(3',4'-isopropylidenedioxypyrrolidin-2-ylidene)-1-propene-1,2,3-tricarboxylate 33 and dimethyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-1,2,3,5-tetrahydro-5-indolizinone-7,8-dicarboxylate 34.

A mixture of enamine **17** (0.7 mmol) with DMAD (0.8 mmol) in methanol (10 mL) was stirred at room temperature for 2 h. After removal of methanol, the intermediate adduct **33** and cyclization product **34** were isolated in 74% and 18% yields, respectively, by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (1:1).

A mixture of enamine **17** (0.7 mmol) with DMAD (0.8 mmol) in methanol (10 mL) was stirred at room temperature for 2 h and then refluxed for another 10 h. After removal of methanol, the product

1,2,3,5-tetrahydro-5-indolizinone-7,8-dicarboxylate **34** was isolated in 88% yield by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (1:1 to 1:5).

Trimethyl (3S, 4R)-3-(3',4'-isopropylidenedioxypyrrolidin-2-ylidene)-1-propene-1,2,3-tricarboxylate 33: 74%, mp 119-121 °C, $[\alpha]_D^{20}$ = -231.9° (C = 0.580, $CHCl_3$). IR ν (cm^{-1}) 3358, 1737, 1733, 1683, 1603; ^{1}H NMR δ (ppm) 8.38 (br, 1H), 6.93 (s, 1H), 5.23 (s, 1H), 4.73 (s, 1H), 3.73-3.83 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 3.64 (s, 3H), 1.32 (s, 6H); ^{13}C NMR δ (ppm) 169.0, 167.9, 166.0, 163.0, 142.3, 130.4, 126.9, 112.6, 81.6, 76.2, 52.3, 51.7, 51.6, 50.8, 26.9, 26.2. HRMS (ESI-TOF): 356.1250 (M+1); Calcd for $C_{16}H_{22}NO_8$: 356.1345.

Dimethyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-1,2,3,5-tetrahydro-5-indolizinone-7,8-dicarboxylate 34: 88%, oil, $[\alpha]_D^{20}$ = -199.7° (C = 1.01, CH_3OH). IR ν (cm^{-1}) 1732, 1670, 1604, 1528; ^{1}H NMR δ (ppm) 6.72 (s, 1H), 5.95 (d, *J* = 5.7 Hz, 1H), 5.00 (t, *J* = 5.0 Hz, 1H), 4.49 (d, *J* = 14.5 Hz, 1H), 4.12 (dd, *J* = 14.5, 4.9 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 1.43 (s, 3H), 1.29 (s, 3H); ^{13}C NMR δ (ppm) 166.2, 164.2, 160.3, 152.6, 144.3, 119.6, 112.8, 106.8, 82.2, 74.5, 53.6, 53.0, 52.5, 27.1, 25.7. HRMS (ESI-TOF): 324.1071 (M+1); Calcd for $C_{15}H_{18}NO_7$: 324.1083.

3. Preparation of methyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-7-hydroxyl-1,2,3,5-tetrahydro-5-indolizinone-8-carboxylate 37.

A solution of malonyl dichloride (2.0 mmol) in dry dichloromethane (5 mL) was added dropwise to enamine **17** (1.5 mmol) in dichloromethane (10 mL) at -10 °C to 0 °C. The reaction mixture was stirred at ambient temperature for about 3 h until the starting material **17** was consumed. After removal of dichloromethane, the residue was chromatographed on silica gel eluting with petroleum ether and ethyl acetate (1:1) to pure ethyl acetate to give product **37**.

Methyl (1S, 2R)-1,2-*O*-isopropylidenedioxy-7-hydroxyl-1,2,3,5-tetrahydro-5-indolizinone-8-carboxylate 37: 81%, mp 190-191 °C, $[\alpha]_D^{20}$ = -209.0° (C = 0.745, CH_3OH). IR ν (cm^{-1}) 3433, 1732, 1655, 1613, 1544; ^{1}H NMR δ (ppm) 11.12 (s, 1H), 5.98 (s, 1H), 5.92 (d, *J* = 6.1Hz, 1H), 5.00 (t, *J* = 5.3Hz, 1H), 4.44 (d, *J* = 15.0Hz, 1H), 4.13 (dd, *J* = 14.2, 5.3Hz, 1H), 3.99 (s, 3H), 1.44 (s, 3H), 1.32 (s,

3H); ^{13}C NMR δ (ppm) 168.7, 168.0, 162.0, 155.1, 112.3, 99.7, 97.4, 83.4, 74.0, 53.8, 52.7, 27.1, 25.5; MS (ESI-TOF): 282 (M+1). Anal. Calcd for $C_{13}H_{15}NO_6$: C 55.51, H 5.38, N 4.98; Found: C 55.60, H 5.22, N 4.84.

4. General procedure for hydrogenation of hexahydro-5-indolizinones and tetrahydro-5-indolizinones.

The hexahydro-5-indolizinone **18**, **22** or **23** (0.75 mmol), or tetrahydro-5-indolizinone **30**, **34** or **37** (0.75 mmol) was dissolved in methanol (20 mL), and Palladium on activated carbon (10%) (0.2-0.5g) was added. The reaction mixture was stirred under hydrogen (10-15 atm) for 24 h at room temperature for hexahydroindolizinone, or for 30-72 h at 40-50 °C for tetrahydroindolizinone. The catalyst was filtered off and washed with methanol (2×10 mL). The filtrate was concentrated under vacuum, and the residue was purified on a silica gel column. While the octahydro-5-indolizinone **19** and 7-alkyl-octahydro-5-indolizinones **24**, **25** and **31** were eluted, respectively, from the column with ethyl acetate and acetone (9:1), the 7-methoxycarbonyl- and 7-hydroxyl-octahydro-5-indolizinones **35** and **39** were obtained respectively from eluting with ethyl acetate and acetone (9:1 to 5:1).

Methyl (1S, 2R, 8S, 9R)-1,2-*O*-isopropylidenedioxy-octahydro-5-indolizinone-8-carboxylate 19:

94%, mp 90-93 °C, $[\alpha]_D^{20}$ = -114.3° (C = 0.545, $CHCl_3$). IR ν (cm^{-1}) 1732, 1626; ^{1}H NMR δ (ppm) 4.78 (t, J = 5.5 Hz, 1H), 4.67 (t, J = 5.2 Hz, 1H), 4.42 (d, J = 13.3 Hz, 1H), 3.77 (s, 3H), 3.67 (dd, J = 7.4, 3.6 Hz, 1H), 3.09-3.12 (m, 1H), 2.90 (dd, J = 13.2, 4.4 Hz, 1H), 2.60 (dt, J = 16.4, 3.9 Hz, 1H), 2.13-2.30 (m, 3H), 1.37 (s, 3H), 1.26 (s, 3H); ^{13}C NMR δ (ppm) 171.7 169.8, 111.8, 80.5, 77.6, 60.0, 52.0, 50.0, 39.4, 31.2, 26.0, 24.3, 22.4; MS (EI): 152 (100), 194 (95), 211 (50), 270 (M+1, 92%). Anal. Calcd for $C_{13}H_{19}NO_5$: C 57.98, H 7.11, N 5.20; Found: C 57.93, H 7.04, N 5.22.

Methyl (1S, 2R, 7S, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-methyl-octahydro-5-indolizinone-8-carboxylate 24A: 97%, mp 174-176 °C, $[\alpha]_D^{20}$ = -142.7° (C = 0.475, $CHCl_3$). IR ν (cm^{-1}) 1734, 1650, 1624; ^{1}H NMR δ (ppm) 4.76-4.80 (m, 2H), 4.15 (d, J = 13.8 Hz, 1H), 3.68 (s, 3H), 3.28 (dd, J = 13.5, 4.4 Hz, 1H), 2.97 (s, 1H), 2.62 (dd, J = 17.5, 12.3 Hz, 1H), 2.38 (dd, J = 17.6, 6.0 Hz, 1H), 2.26-2.29 (m, 1H), 1.40 (s, 3H), 1.31 (s, 3H), 1.27 (t, J = 7.2 Hz, 1H), 1.05 (d, J = 6.7 Hz, 3H); ^{13}C NMR δ (ppm)

170.8, 169.4, 112.7, 80.7, 77.1, 62.9, 51.2, 50.3, 43.8, 36.2, 31.7, 25.4, 24.5, 18.4; MS (EI): 166 (72), 208 (100), 284 (M+1, 48%). Anal. Calcd for $C_{14}H_{21}NO_5$: C 59.35, H 7.47, N 4.94. Found C 59.16, H 7.35, N 4.95.

Methyl (1S, 2R, 7R, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-methyl-octahydro-5-indolizinone-8-carboxylate 24B: 93%, mp 121-122 °C, $[\alpha]_D^{20}$ = -129.1° (C = 0.525, $CHCl_3$). IR ν (cm^{-1}) 1744, 1644; ^1H NMR δ (ppm) 4.68 (t, *J* = 5.4 Hz, 1H), 4.59 (dd, *J* = 5.7, 3.5 Hz, 1H), 4.38 (d, *J* = 13.3 Hz, 1H), 3.76 (s, 3H), 3.67 (dd, *J* = 7.5, 3.4 Hz, 1H), 3.09-3.12 (m, 1H), 2.93 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.82 (dd, *J* = 9.3, 7.7 Hz, 1H), 2.66 (d, *J* = 4.8 Hz, 1H), 2.59-2.63 (m, 2H), 2.02 (dd, *J* = 16.3, 9.7 Hz, 1H), 1.39 (s, 3H), 1.28 (s, 3H), 1.11 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR δ (ppm) 171.3, 169.4, 112.1, 80.5, 77.9, 60.0, 51.7, 50.1, 46.0, 38.8, 28.1, 26.2, 24.5, 20.4; MS (EI): 166 (100), 208 (90), 284 (M+1, 20%). Anal. Calcd for $C_{14}H_{21}NO_5$: C 59.35, H 7.47, N 4.94. Found C 59.19, H 7.23, N 4.91.

Methyl (1S, 2R, 7S, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-propyl-octahydro-5-indolizinone-8-carboxylate 25A: 93%, mp 204-205 °C, $[\alpha]_D^{20}$ = -68.2° (C = 0.245, $CHCl_3$). IR ν (cm^{-1}) 1730, 1638, 1627; ^1H NMR δ (ppm) 4.78 (m, 2H), 4.15 (d, *J* = 13.6 Hz, 1H), 3.67 (s, 4H), 3.28 (dd, *J* = 13.5, 4.5 Hz, 1H), 3.05 (t, *J* = 3.7 Hz, 1H), 2.57 (dd, *J* = 17.6, 12.4 Hz, 1H), 2.43 (dd, *J* = 17.7, 6.2 Hz, 1H), 2.11-2.13 (m, 1H), 1.41 (s, 3H), 1.31-1.40 (m, 4H), 1.31 (s, 3H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ (ppm) 170.9, 169.5, 112.7, 80.8, 77.2, 62.9, 51.2, 50.3, 42.1, 36.6, 35.4, 34.8, 25.4, 24.4, 19.8, 13.9. MS (EI): 97 (100), 194 (67), 210 (64), 236 (82), 253 (55), 312 (M+1, 73%). Anal. Calcd for $C_{16}H_{25}NO_5$: C 61.72, H 8.09, N 4.53. Found C 61.27, H 8.11, N 4.53.

Methyl (1S, 2R, 7R, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-propyl-octahydro-5-indolizinone-8-carboxylate 25B: 95%, oil, $[\alpha]_D^{20}$ = -94.8° (C = 0.515, $CHCl_3$). IR ν (cm^{-1}) 1740, 1639; ^1H NMR δ (ppm) ^1H NMR: 4.71 (t, *J* = 5.4 Hz, 1H), 4.65 (t, *J* = 5.5 Hz, 1H), 4.33 (d, *J* = 13.3 Hz, 1H), 3.74 (s, 3H), 3.66 (dd, *J* = 6.3, 3.9 Hz, 1H), 3.04 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.92 (t, *J* = 7.2 Hz, 1H), 2.86 (dd, *J* = 17.1, 5.3 Hz, 1H), 2.41-2.42 (m, 1H), 2.06 (dd, *J* = 17.1, 7.7 Hz, 1H), 1.52-1.58 (m, 1H), 1.40-1.44 (m, 1H), 1.40 (s, 3H), 1.30-1.33 (m, 1H), 1.30 (s, 3H), 1.20-1.23 (m, 1H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR

δ (ppm) 171.6, 169.5, 112.2, 80.6, 77.7, 59.5, 51.6, 50.2, 43.8, 36.4, 35.4, 33.1, 26.0, 24.6, 19.6, 13.9. HRMS (ESI-TOF): 311.1735, $C_{16}H_{25}NO_5$ required 311.1733.

Methyl (1S, 2R, 7S, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-ethyl-octahydro-5-indolizinone-8-carboxylate 31: 88%, 184-186 °C, $[\alpha]_D^{20}$ = -56.4° (C = 0.560, CH_3OH). IR *v* (cm^{-1}) 1730, 1639, 1627; ^1H NMR δ (ppm) 4.77-4.81 (m, 2H), 4.15 (d, *J* = 13.5 Hz, 1H), 3.68 (s, 3H), 3.30 (dd, *J* = 13.6, 4.4 Hz, 1H), 3.10 (s, 1H), 2.57 (dd, *J* = 17.5, 12.5 Hz, 1H), 2.45 (dd, *J* = 17.6, 6.1 Hz, 1H), 2.02 (br, 1H), 1.41 (s, 3H), 1.34-1.38 (m, 1H), 1.31 (s, 3H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ (ppm) 170.9, 169.5, 112.7, 80.8, 77.2, 62.9, 51.2, 50.3, 41.7, 38.8, 34.7, 26.2, 25.4, 24.4, 11.4; MS (ESI-TOF): 298 (M+1), 320 ($M+Na^+$). Anal. Calcd for $C_{15}H_{23}NO_5$: C 60.59, H 7.80, N 4.71. Found C 60.36, H 7.55, N 4.45.

Dimethyl (1S, 2R, 7S, 8S, 9R)-1,2-*O*-isopropylidenedioxy-octahydro-5-indolizinone-7,8-dicarboxylate 35: 88%, mp 204-205 °C; $[\alpha]_D^{20}$ = -57.0° (C = 0.560, CH_3OH). IR *v* (cm^{-1}) 1734, 1726, 1640; ^1H NMR δ (ppm) 4.80 (d, *J* = 2.5 Hz, 1H), 4.15 (d, *J* = 13.6 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.69 (brs, 1H), 3.46 (s, 1H), 3.28 (dd, *J* = 16.4, 12.5 Hz, 1H), 3.07-3.10 (m, 1H), 2.71 (dd, *J* = 17.5, 5.6 Hz, 1H), 1.39 (s, 3H), 1.31 (s, 3H); ^{13}CNMR δ (ppm) 171.5, 170.3, 167.8, 112.8, 80.6, 77.2, 62.1, 52.4, 51.6, 50.5, 41.8, 39.2, 30.7, 25.8, 24.8; MS (ESI-TOF): 328 (M+1), 350 ($M+Na^+$). Anal. Calcd for $C_{15}H_{21}NO_7$: C 55.04, H 6.47, N 4.28. Found C 54.91, H 6.48, N 4.10.

Methyl (1S, 2R, 7S, 8S, 9R)-1,2-*O*-isopropylidenedioxy-7-hydroxy-octahydro-5-indolizinone-8-carboxylate 39A: 63 %, mp 130-131 °C, $[\alpha]_D^{20}$ = -24.7° (C = 0.580, CH_3OH). IR *v* (cm^{-1}) 3226, 1742, 1625; ^1H NMR δ (ppm) 4.73-4.77 (m, 2H), 4.30 (d, *J* = 13.4 Hz, 2H), 3.86 (s, 3H), 3.62 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.04-3.09 (m, 2H), 2.85 (d, *J* = 13.2 Hz, 1H), 2.44 (d, *J* = 16.7, 10.1 Hz, 1H), 1.44 (s, 3H), 1.34 (s, 3H); ^{13}C NMR δ (ppm) 172.1, 166.6, 112.2, 79.8, 77.5, 66.7, 59.9, 52.7, 49.8, 47.0, 39.4, 26.4, 24.7; MS (ESI-TOF): 286 (M+1). Anal. Calcd for $C_{13}H_{19}NO_6$: C 54.73, H 6.71, N 4.91. Found C 54.63, H 7.50, N 4.68.

Methyl (1S, 2R, 7S, 8R, 9R)-1,2-*O*-isopropylidenedioxy-7-hydroxy-octahydro-5-indolizinone-8-carboxylate 39B: 11 %, mp 170-171 °C, $[\alpha]_D^{20}$ = -56.2° (C = 0.710, CH_3OH). IR *v* (cm^{-1}) 3227, 1728,

1621; ^{1}H NMR δ (ppm) ^{1}H NMR: 5.02 (dd, *J* = 5.8, 3.4 Hz, 1H), 4.78 (t, *J* = 5.4 Hz, 1H), 4.58 (brs, 1H), 4.46 (d, *J* = 13.4 Hz, 1H), 3.83-3.85 (m, 1H), 3.83 (s, 3H), 3.44 (dd, *J* = 8.0, 2.7 Hz, 1H), 2.97 (dd, *J* = 13.4, 4.9 Hz, 1H), 2.80 (dd, *J* = 17.0, 3.5 Hz, 1H), 2.57 (dd, *J* = 16.9, 3.6 Hz, 1H), 1.47 (s, 3H), 1.35 (s, 3H). ^{13}C NMR: 169.6, 166.9, 112.4, 79.2, 77.6, 64.4, 59.6, 52.3, 49.7, 44.5, 40.2, 25.4, 24.1. HRMS (ESI-TOF): 286.1286 (M+1). Calcd for $C_{13}H_{20}NO_6$: 286.1291.

5. General procedure for reduction and deprotection of the octahydro-5-indolizinone-8-carboxylates 19, **24**, **25**, **31**, **35** and **39**.

At ambient temperature, boron trifluoride etherate (ca. 48% BF_3, 15 mL, 57 mmol) was added dropwise very slowly to the suspension of $NaBH_4$ (4.0 g, 105 mmol) in dry THF (20 mL) within 2 h. During this period, the borane gas generated was continuously bubbled into the solution of octahydro-5-indolizinone-8-carboxylates (0.5 mmol) in THF (10 mL). After addition of boron trifluoride, the mixture of $NaBH_4$ with boron trifluoride in THF was warmed to 60-70 ^{o}C, and the vapor of borane ether complex was bubbled into the reaction solution. The reaction mixture was stirred at room temperature for 3 h and then refluxing for another 3 h. The reaction mixture was cooled in an ice-bath, and 10 mL of methanol was added to quench the reaction (Caution: hydrogen evolution). After removal of the solvent, the thick oily residue was dissolved in methanol (20 mL) and refluxed for 3 h to decompose the boron complex of product. The volatiles were removed again under vacuum, and the residue was chromatographed on a neutral aluminum oxide column. The borane derivatives were eluted with a mixture of ethyl acetate and petroleum ether (1:1), and the pure 1,2-*O*-isopropylidenedioxy-octahydroindolizines were obtained by eluting with ethyl acetate to a mixture of ethyl acetate and acetone (1:2). Deprotection procedure was performed by the treatment of 1,2-*O*-isopropylidenedioxy-octahydroindolizines with 6 N HCl (10 mL) at room temperature for 4h. The acidic reaction mixture was basified using Na_2CO_3 powder to pH~9, and then concentrated under vacuum to dryness. The polyhydroindolizidine products were isolated from repeating extraction of inorganic salts with dichloromethane (for **21**, **28**, **29** and **32**) or acetone (for **36** and **40**) (10×10 mL).

(1S, 2R, 8S, 9R)-Octahydro-8-hydroxymethyl-1,2-indolizinediol 21: 84%, oil, $[\alpha]_D^{20}$ = -23.8° (C = 0.630, $CHCl_3$). IR ν (cm^{-1}) 3279; ^1H NMR δ (ppm) 4.10-4.72 (br, 3H), 4.29 (dd, *J* = 5.5, 3.8 Hz, 1H), 4.28-4.30 (m, 1H), 4.20 (t, *J* = 5.1 Hz, 1H), 4.13 (dd, *J* = 10.9, 8.1 Hz, 1H), 3.17 (d, *J* = 10.7 Hz, 1H), 3.07 (dd, *J* = 11.0, 1.9 Hz, 1H), 2.42 (brs, 1H), 2.26 (brs, 1H), 2.20 (d, *J* = 2.8 Hz, 1H), 2.01 (brs, 1H), 2.01-2.07 (m, 1H), 1.80 (dd, *J* = 11.0, 1.9 Hz, 1H), 1.59-1.68 (m, 1H), 1.46-1.54 (m, 2H); ^{13}C NMR δ (ppm) 72.0, 69.3, 63.1, 62.6, 61.8, 54.7, 37.5, 29.9, 21.7. HRMS (ESI-TOF): 187.1210, $C_9H_{17}NO_3$ required 187.1208.

(1S, 2R, 7S, 8S, 9R)-Octahydro-8-hydroxymethyl-7-methyl-1,2-indolizinediol 28A: 76%, mp 82-83 °C, $[\alpha]_D^{20}$ = -81.67° (C = 0.60, CH_3OH). IR ν (cm^{-1}) 3423, 3117; ^1H NMR δ (ppm) 4.28 (t, *J* = 4.7 Hz, 1H), 4.23 (t, *J* = 5.5 Hz, 1H), 4.01 (dd, *J* = 11.3, 5.9 Hz, 1H), 3.86 (dd, *J* = 11.3, 4.0 Hz, 1H), 3.15-3.18 (m, 1H), 3.12 (dd, *J* = 11.0, 1.6 Hz, 1H), 2.33 (dd, *J* = 10.9, 6.7 Hz, 1H), 2.26 (dd, *J* = 4.7, 2.2 Hz, 1H), 1.99-2.04 (m, 2H), 1.63-1.69 (m, 1H), 1.46-1.49 (m, 2H), 1.07 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR δ (ppm) 72.4, 71.5, 69.9, 61.3, 58.3, 54.2, 42.0, 35.7, 29.9, 19.3. MS (ESI-TOF): 201 (M^+). Anal. Calcd for $C_{10}H_{19}NO_3$: C 59.68, H 9.52, N 6.96. Found: C 59.37, H 9.37, N 6.91.

(1S, 2R, 7R, 8S, 9R)-Octahydro-8-hydroxymethyl-7-methyl-1,2-indolizinediol 28B: 79%, mp 107-108 °C, $[\alpha]_D^{20}$ = -32.4° (C = 0.965, $CHCl_3$). IR ν (cm^{-1}) 3396; ^1H NMR δ (ppm) 4.35 (brs, 1H), 4.24 (brs, 1H), 4.10 (t, *J* = 7.3 Hz, 1H), 3.76 (d, *J* = 8.3 Hz, 1H), 3.05 (d, *J* = 11.2 Hz, 1H), 3.00 (d, *J* = 11.2 Hz, 1H), 2.63 (brs, 2H), 2.41 (brs, 1H), 2.00 (brs, 1H), 1.84-1.91 (m, 2H), 1.38 (d, *J* = 11.2 Hz, 1H), 1.06 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR δ (ppm) 72.3, 69.6, 64.4, 63.7, 61.7, 49.7, 43.5, 31.2, 28.5, 18.6. HRMS (ESI-TOF): 202.1450 (M+1), Calcd for $C_{10}H_{20}NO_3$: 202.1443.

(1S, 2R, 7S, 8S, 9R)-Octahydro-8-hydroxymethyl-7-propyl-1,2-indolizinediol 29A: 80%, oil, $[\alpha]_D^{20}$ = -55.03° (C = 0.830, CH_3OH). IR ν (cm^{-1}) 3278; ^1H NMR δ (ppm) 4.27-4.30 (m, 1H), 4.00 (t, *J* = 3.5 Hz, 1H), 3.76 (t, *J* = 10.0 Hz, 1H), 3.53 (d, *J* = 11.0 Hz, 1H), 2.93 (d, *J* = 10.5 Hz, 1H), 2.77 (dd, *J* = 11.0, 4.0 Hz, 1H), 2.48 (t, *J* = 10.5 Hz, 1H), 2.31 (s, 1H), 2.01 (t, *J* = 10.5 Hz, 1H), 1.96 (d, *J* = 7.5 Hz, 1H), 1.44-1.36 (m, 1H), 1.39 (d, *J* = 13.9 Hz, 1H), 1.22-1.23 (m, 4H), 1.04-1.09 (m, 1H), 0.78 (t, *J* = 6.3

Hz, 3H); ^{13}C NMR: 72.3, 71.6, 69.9, 61.4, 58.1, 54.4, 40.7, 40.5, 35.7, 28.4, 20.3, 14.2. HRMS (ESI-TOF): 230.1762 (M+1), Calcd for $C_{12}H_{24}NO_3$: 230.1756.

(1S, 2R, 7R, 8S, 9R)-Octahydro-8-hydroxymethyl-7-propyl-1,2-indolizinediol 29B: 78%, mp 93-94 °C, $[\alpha]_D^{20}$ = -58.5° (C = 0.535, CH_3OH). IR ν (cm^{-1}) 3418; ^{1}H NMR (D_2O) δ (ppm) 4.28 (t, J = 5.5 Hz, 1H), 4.14-4.28 (m, 2H), 3.70 (dd, J = 10.9, 3.2 Hz, 1H), 3.05 (d, J = 11.0 Hz, 1H), 2.93 (d, J = 10.7 Hz, 1H), 2.43 (brs, 1H), 2.22 (t, J = 11.1Hz, 1H), 1.98 (brs, 1H), 1.79-1.84 (m, 1H), 1.73 (brs, 1H), 1.32-1.45 (m, 5H), 0.93 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ (ppm) 71.7, 69.3, 63.9, 63.3, 60.8, 50.6, 41.9, 35.2, 34.4, 26.6, 20.2, 14.2; MS (ESI-TOF): 230 (M+1). Anal. Calcd for $C_{12}H_{23}NO_3$: C 62.85, H 10.11, N 6.11; Found C 62.87, H 9.84, N 6.06.

(1S, 2R, 7S, 8S, 9R)-Octahydro-7-ethyl-8-hydroxymethyl-1,2-indolizinediol 32: 82%, 93-95 °C, $[\alpha]_D^{20}$ = -69.4 ° (C = 0.820, $CHCl_3$). IR ν (cm^{-1}) 3424, 3113; ^{1}H NMR (D_2O) δ (ppm) 4.27-4.31 (m, 1H), 4.01 (d, J = 3.4 Hz, 1H), 3.76 (t, J = 10.1 Hz, 1H), 3.52 (d, J = 11.5 Hz, 1H), 2.94 (d, J = 10.9 Hz, 1H), 2.78 (dd, J = 11.1, 3.9 Hz, 1H), 2.48 (t, J = 9.3 Hz, 1H), 2.30 (brs, 1H), 1.99-2.03 (m, 2H), 1.41 (d, J = 13.7 Hz, 1H), 1.33 (brs, 1H), 1.26 (qt, J = 7.3 Hz, 2H), 1.06 (dq, J = 12.7, 3.7 Hz, 1H), 0.80 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ (ppm) 72.3, 71.6, 69.9, 61.3, 58.1, 54.3, 42.9, 40.0, 28.1, 26.2, 11.8. MS (ESI-TOF): 216.1590 (M+1); Calcd for $C_{11}H_{22}NO_3$: 216.1600.

(1S, 2R, 7S, 8S, 9R)-7,8-dihydromethyl-1,2-indolizinediol 36: 61%, mp 186-187 °C; $[\alpha]_D^{20}$ = -52.9° (C = 0.480, CH_3OH). IR ν (cm^{-1}) 3313, 3227; ^{1}H NMR δ (ppm) 4.30-4.32 (m, 1H), 4.07 (t, J = 4.0 Hz, 1H), 3.83 (dd, J = 11.5, 9.0 Hz, 1H), 3.46-3.54 (m, 4H), 3.03 (d, J = 9.7 Hz, 1H), 2.83 (dd, J = 11.0, 3.9 Hz, 1H), 2.53 (t, J = 10.6 Hz, 1H), 2.37 (s, 1H), 2.06-2.13 (m, 2H), 1.67-1.70 (m, 1H), 1.48 (d, J = 12.7 Hz, 1H), 1.17 (dq, J = 16.9, 3.8 Hz, 1H); ^{13}C NMR (D2O) δ (ppm) 71.5, 69.5, 69.2, 63.7, 58.6, 56.7, 53.3, 41.8, 39.0, 24.0. HRMS (ESI-TOF): 218.1380 (M+1), Calcd for $C_{10}H_{20}NO_4$: 218.1392.

(1S, 2R, 7S, 8R, 9R)-Octahydro-8-hydroxymethyl-1,2,7-indolizinetriol 40A: 67 %, oil, $[\alpha]_D^{20}$ = -34.6° (C = 0.650, CH_3OH). IR ν (cm^{-1}) 3357; ^{1}H NMR (D_2O) δ (ppm) 4.29-4.32 (m, 1H), 4.16 (dd, J = 6.0, 3.5 Hz, 1H), 3.83 (dd, J = 11.5, 3.5 Hz, 1H), 3.72 (dd, J = 6.0, 11.5 Hz, 1H), 3.62 (dt, J = 10.5, 5.0

Hz, 1H), 2.93 (d, J = 10.5 Hz, 1H), 2.79 (dd, J = 11.0, 2.0 Hz, 1H), 2.42 (dd, J = 11.0, 8.0 Hz, 1H), 1.99-2.04 (m, 2H), 1.90-1.94 (m, 1H), 1.64-1.69 (m, 1H), 1.50 (dq, J = 11.5, 4.0 Hz, 1H); ^{13}C NMR (D_2O) δ (ppm) 69.7, 69.5, 68.4, 67.0, 59.7, 58.7, 49.5, 43.9, 32.7. HRMS (ESI-TOF): 204.1228 (M+1), Calcd for $C_9H_{18}NO_4$: 204.1236.

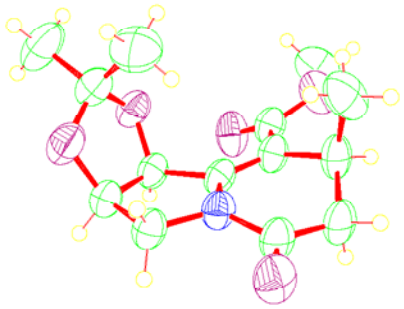


Figure S1. The Ortep drawing of single crystal structure of **22A**.

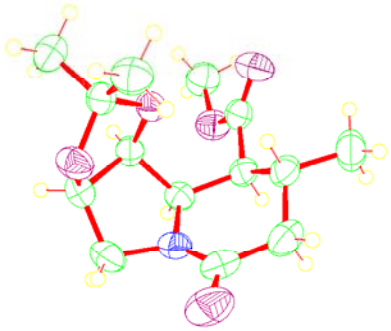


Figure S2. The Ortep drawing of single crystal structure of **24B**.

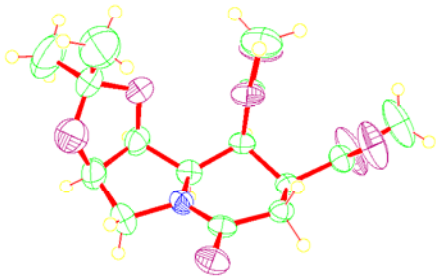


Figure S3. The Ortep drawing of single crystal structure of **35**.

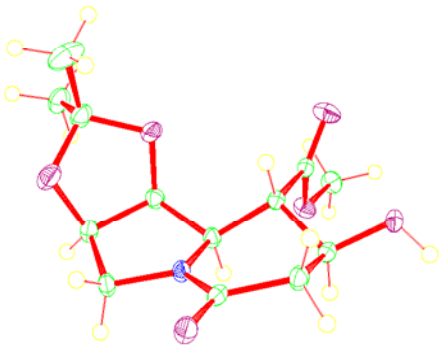
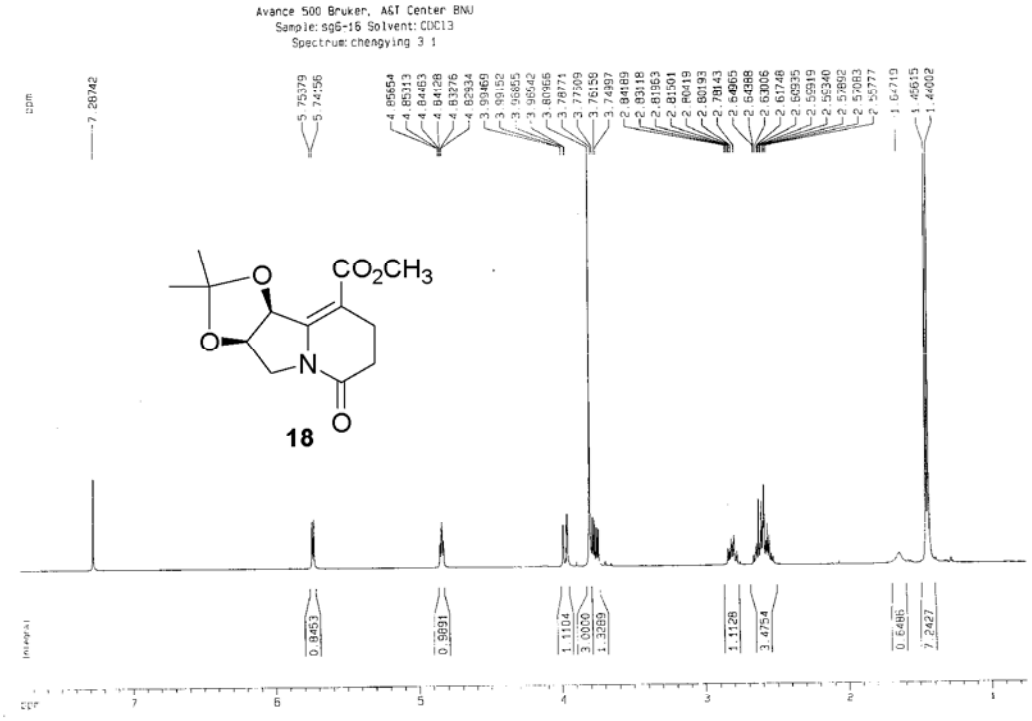
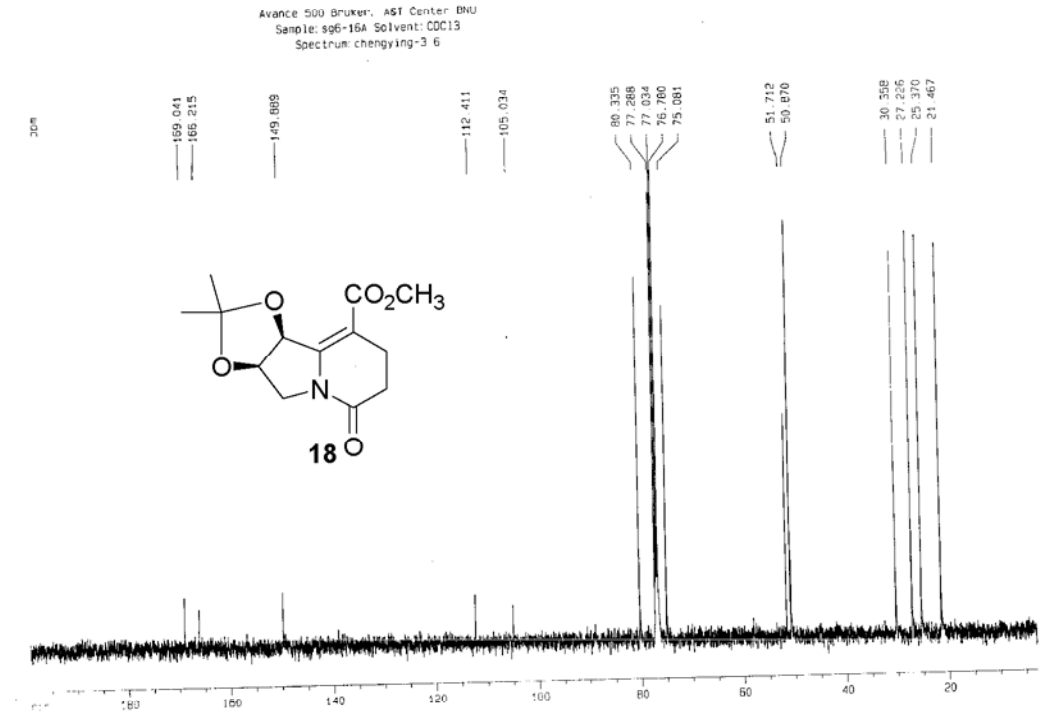


Figure S4. The Ortep drawing of single crystal structure of **39A**.

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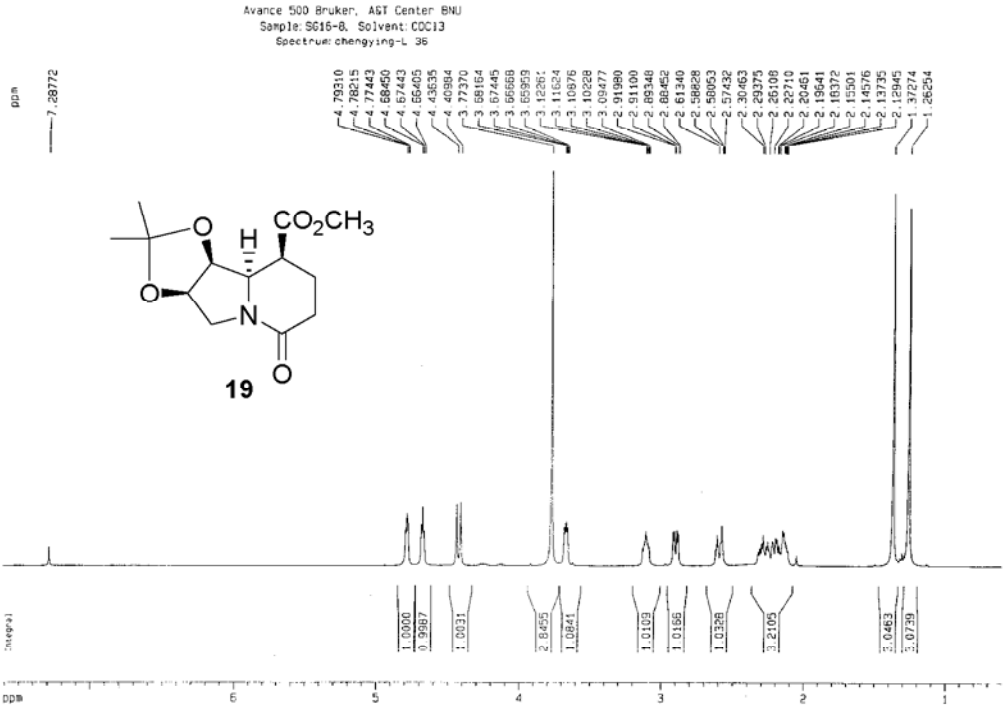
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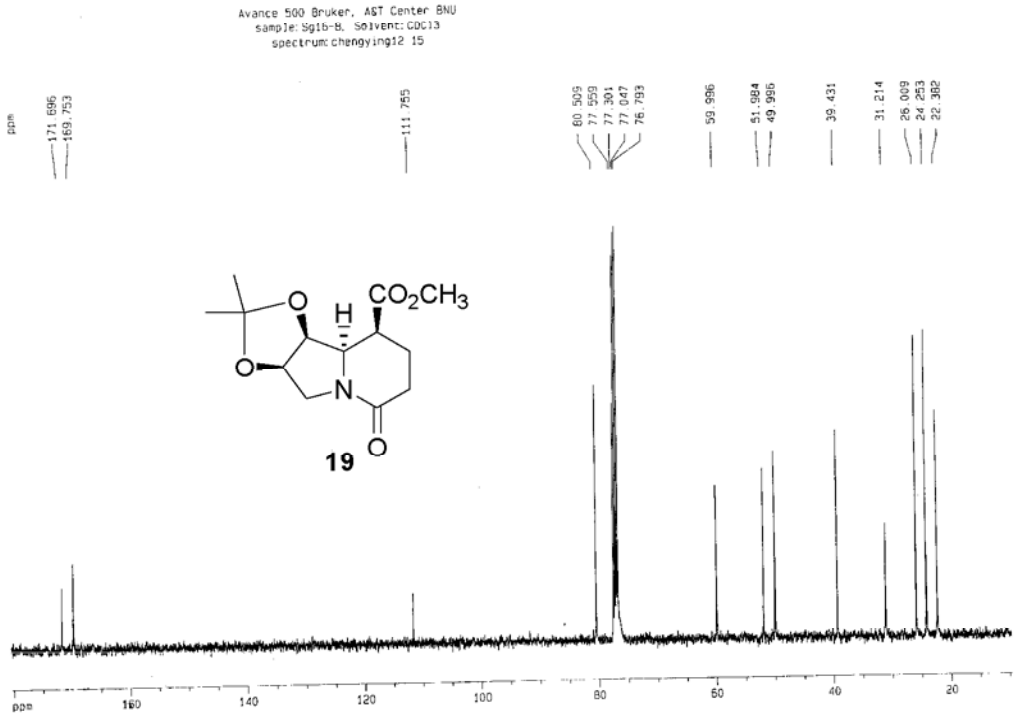
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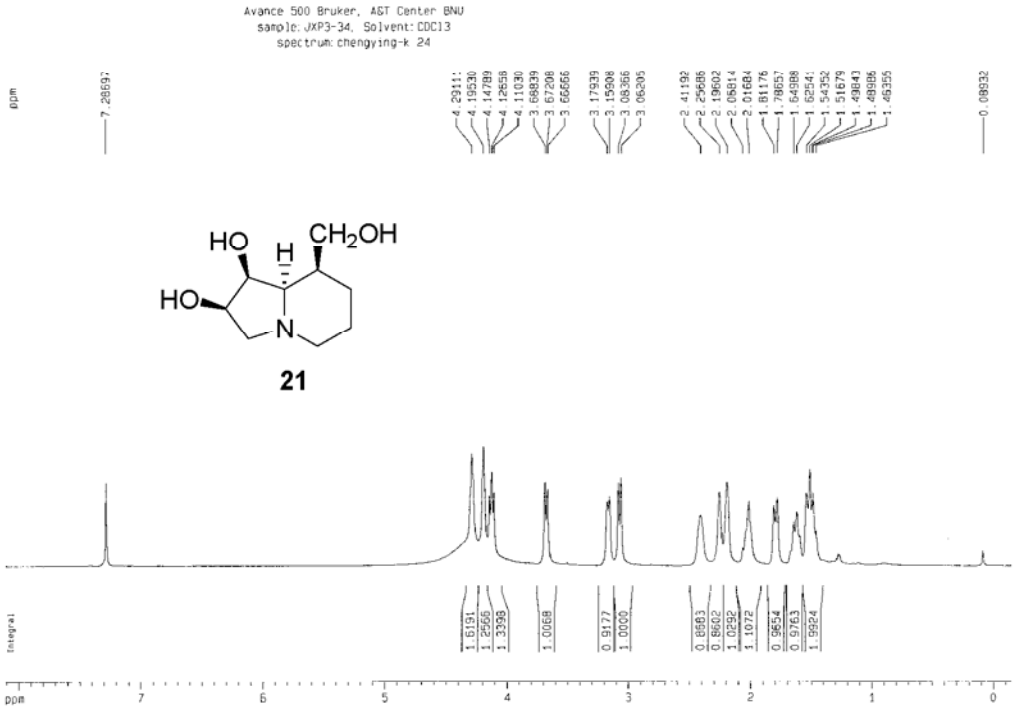
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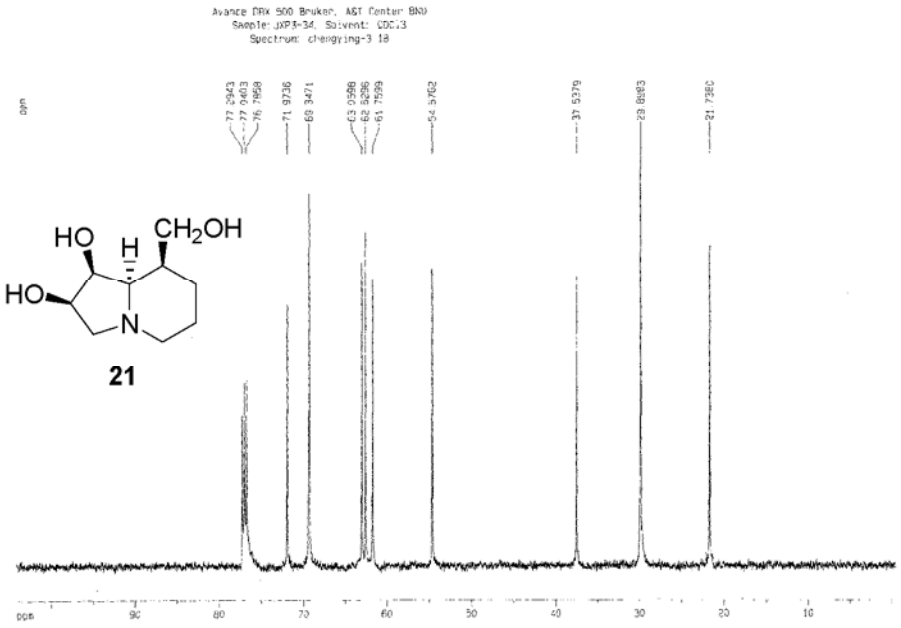
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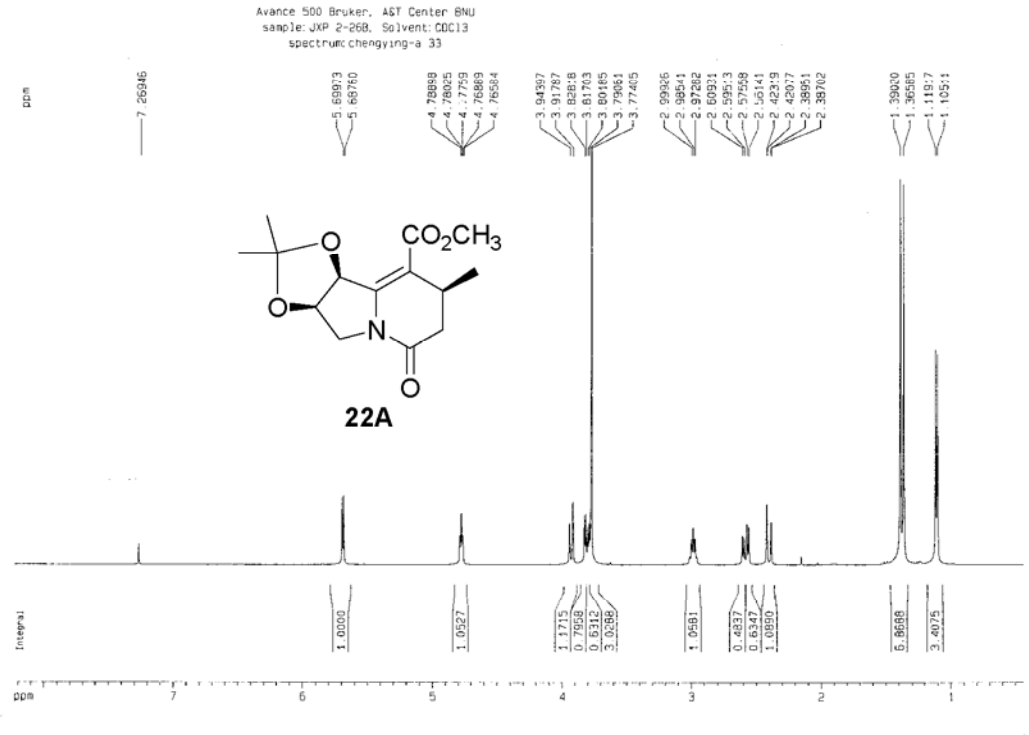
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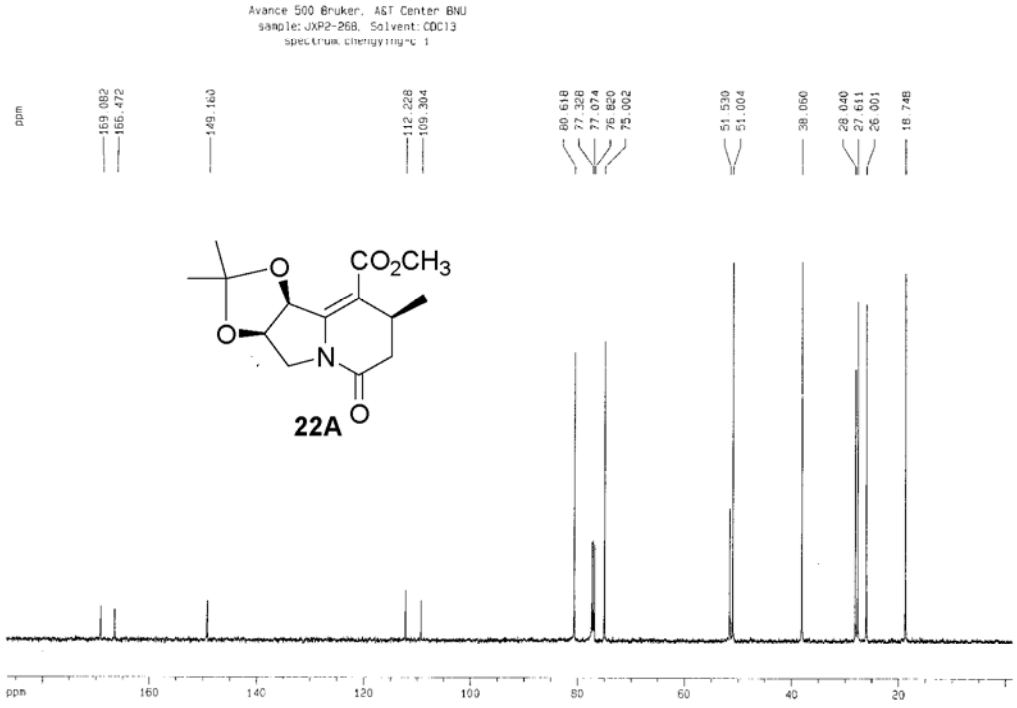
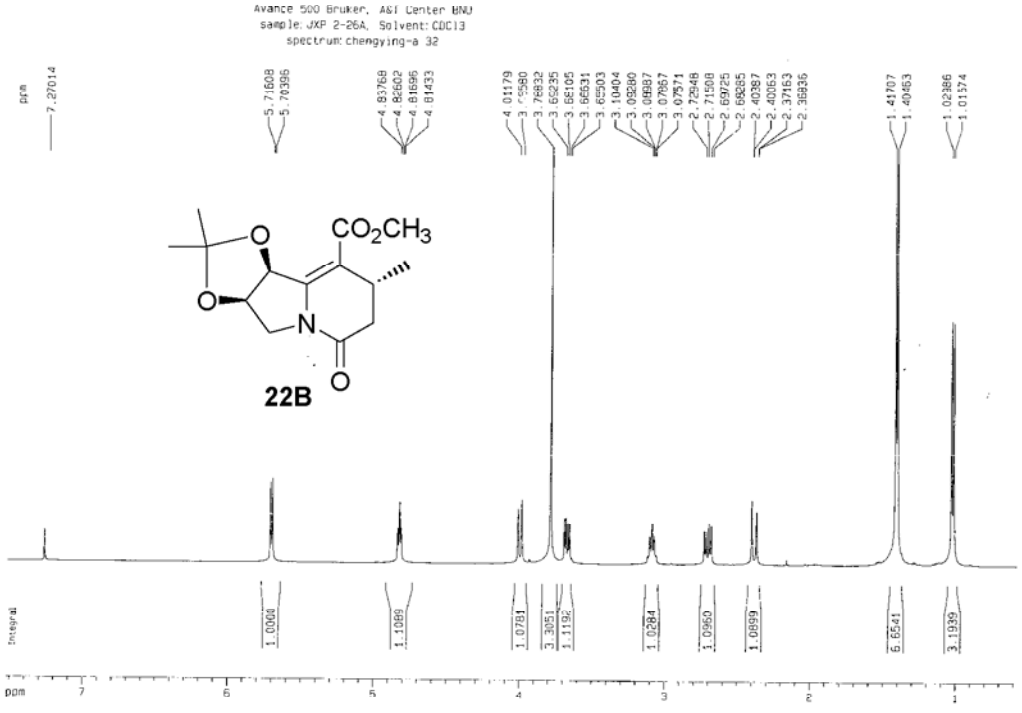
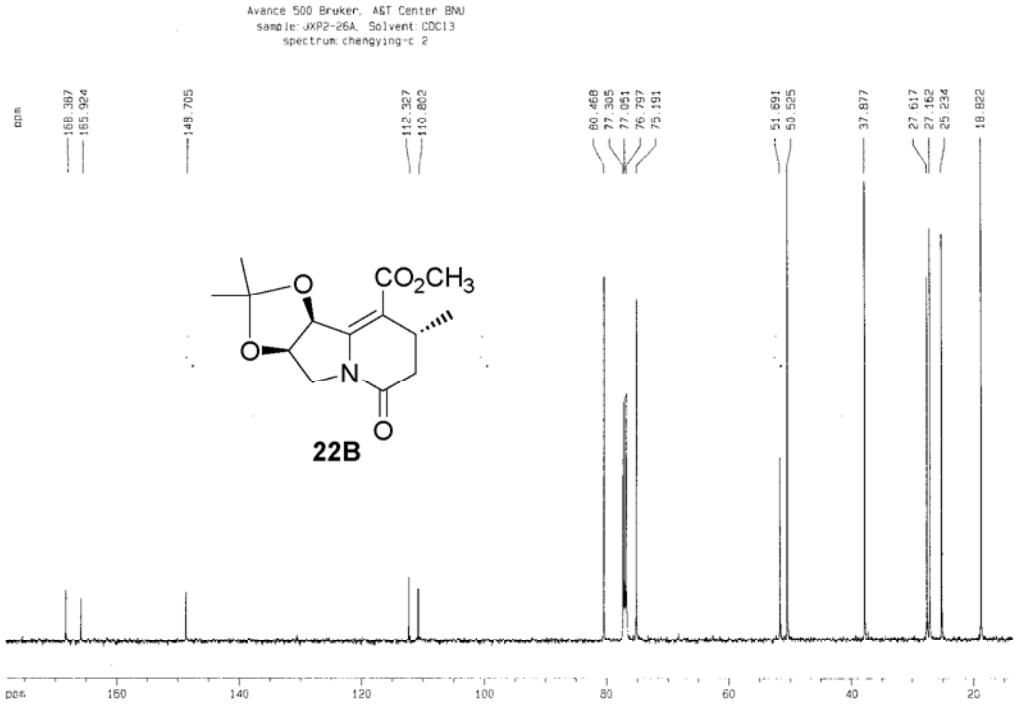
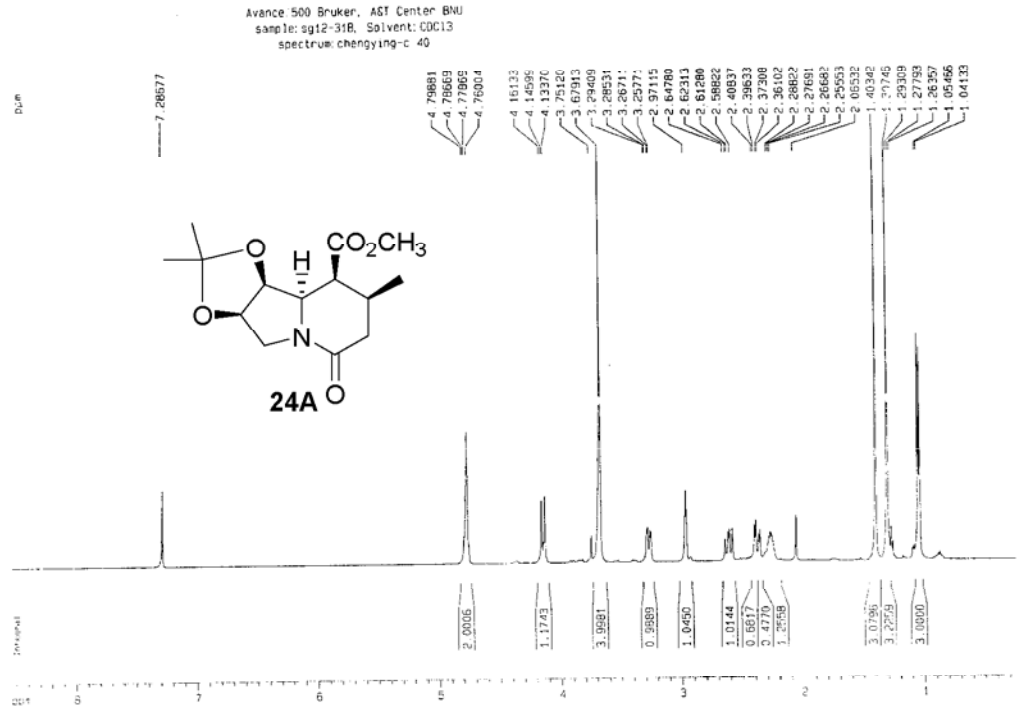
5.68760
4.78888
4.78025
4.77759
4.76869
4.76584
3.94397
3.91787
3.82818
3.81703
3.80185
3.79861
3.77405
2.99926
2.98641
2.97282
2.60931
2.59513
2.57558
2.56141
2.42319
2.42077
2.38961
2.38702
1.39010
1.36585
1.11917
1.10511
CO2CH3
O
O
N
O
22A
Integral
1.0000
1.0527
1.1715
0.7958
0.6312
3.0088
1.0581
0.4837
0.6347
1.0890
5.8688
3.4075
ppm


Avance 500 Bruker, A&T Center BNU
sample: JXP2-26B, Solvent: CDCl3
ppm
169.082
166.472
149.160
112.228
109.304
80.618
77.328
77.074
76.820
75.002
51.539
51.004
38.060
28.040
27.611
26.001
18.748
CO2CH3
O
O
N
O
22A
ppm
160
140
120
100
80
60
40
20


Avance 500 Bruker, A&T Center BNU
sample: JXP 2-26A, Solvent: CDCl3
spectrum: chengying-a 32
ppm
7.27014
5.77608
5.76396
4.83768
4.82602
4.81696
4.81433
4.01179
3.99580
3.76832
3.65235
3.66105
3.66531
3.65503
3.10404
3.09280
3.08687
3.07867
3.07571
2.72948
2.71508
2.69725
2.69285
2.40387
2.40053
2.37163
2.36836
1.41707
1.40453
1.02386
1.01574
CO2CH3
O
O
N
O
22B
Integral
1.0068
1.1089
1.0781
3.3051
1.1192
1.0284
1.0960
1.0899
6.6541
3.1939
ppm
7
6
5
4
3
2
1


Avance 500 Bruker, A&T Center BNU
sample: JXP2-26A, Solvent: CDCl3
spectrum: chengying-c 2
ppm
168.387
165.924
149.705
112.327
110.802
80.468
77.305
77.051
76.797
75.191
51.691
50.525
37.877
27.617
27.162
25.234
18.822
CO2CH3
O
O
N
O
22B
ppm
160
140
120
100
80
60
40
20


Avance 500 Bruker, A&T Center BNU
sample: sg12-31B, Solvent: CDCl3
spectrum: chengying-c 40
ppm
7.28577
4.79881
4.78669
4.77969
4.76504
4.16133
4.14596
4.13370
3.75120
3.67913
3.29409
3.28531
3.26717
3.25777
2.97115
2.64780
2.62311
2.61280
2.58822
2.40837
2.39633
2.37308
2.36102
2.28822
2.27691
2.26682
2.25553
2.06532
1.40342
1.29309
1.27793
1.26357
1.05466
1.04133
CO2CH3
H
O
O
N
O
24A
2.0006
1.1743
3.9981
0.9889
1.0490
1.0144
0.6617
0.4770
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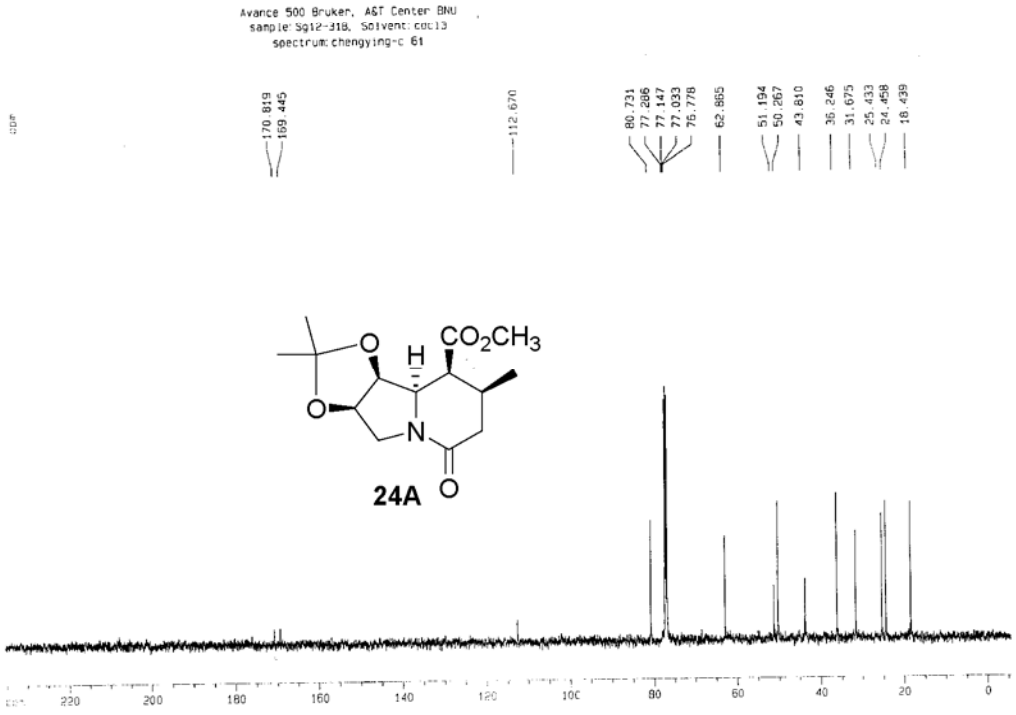
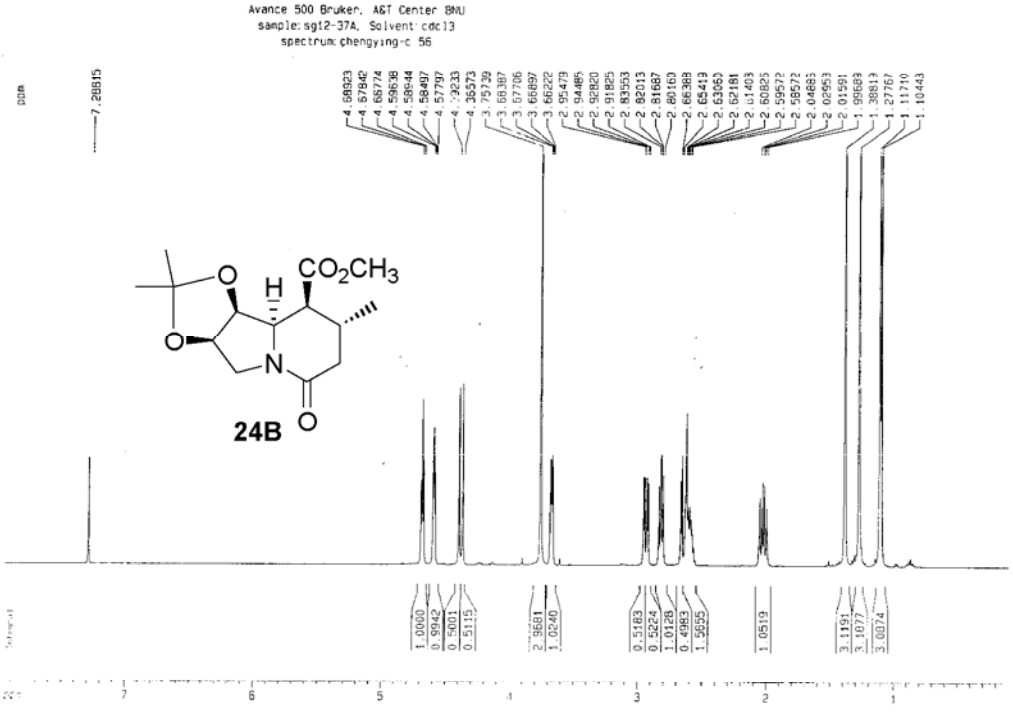
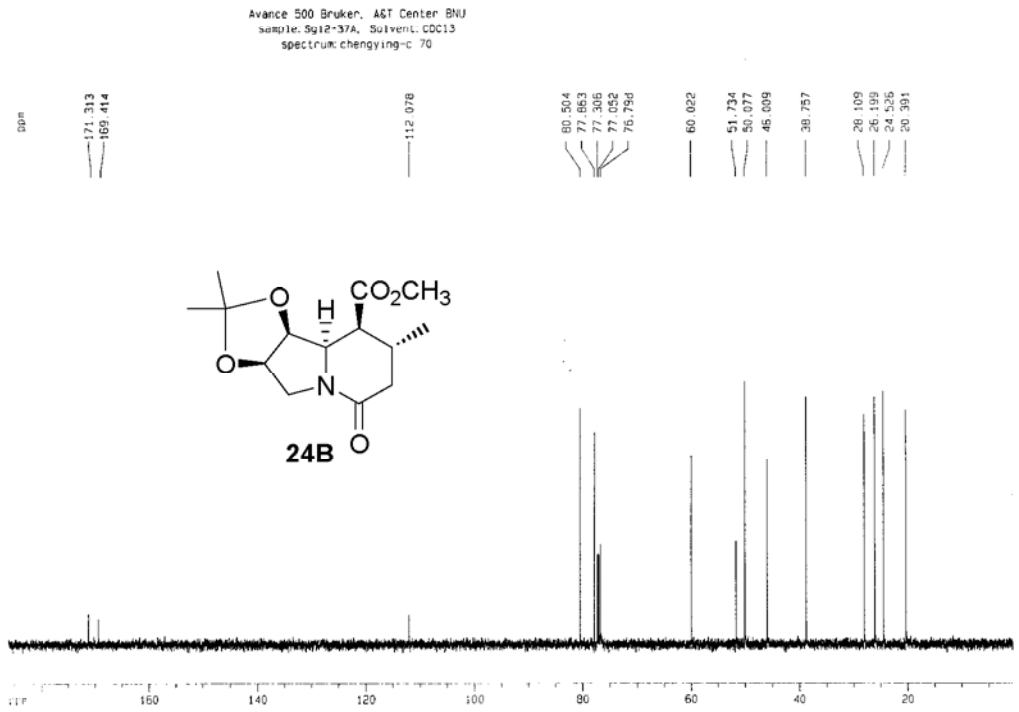
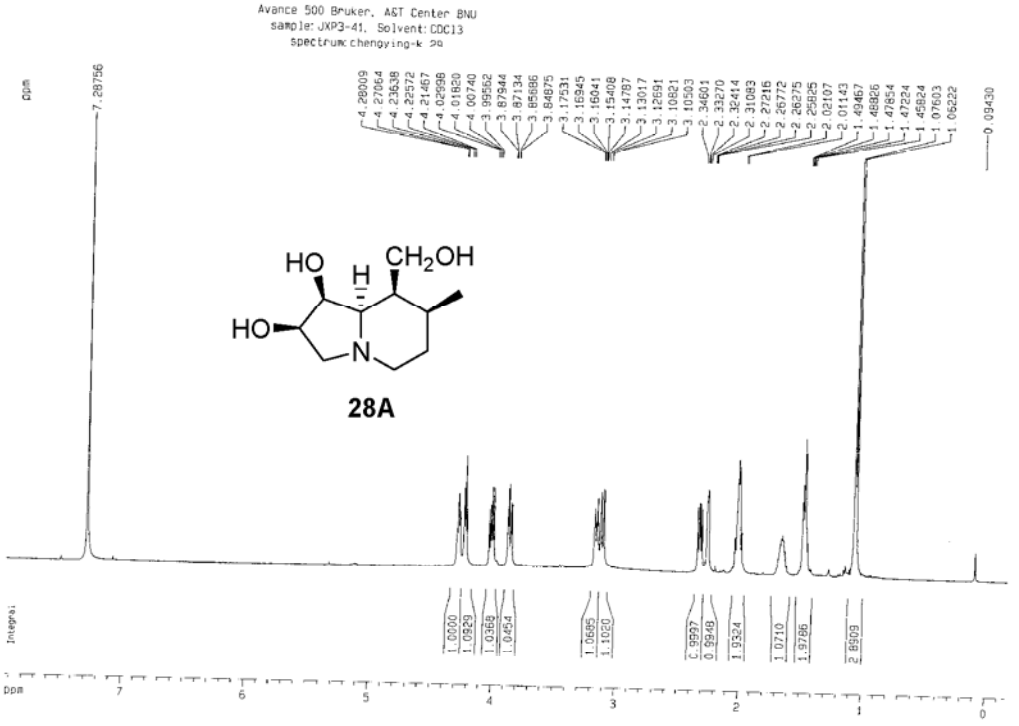
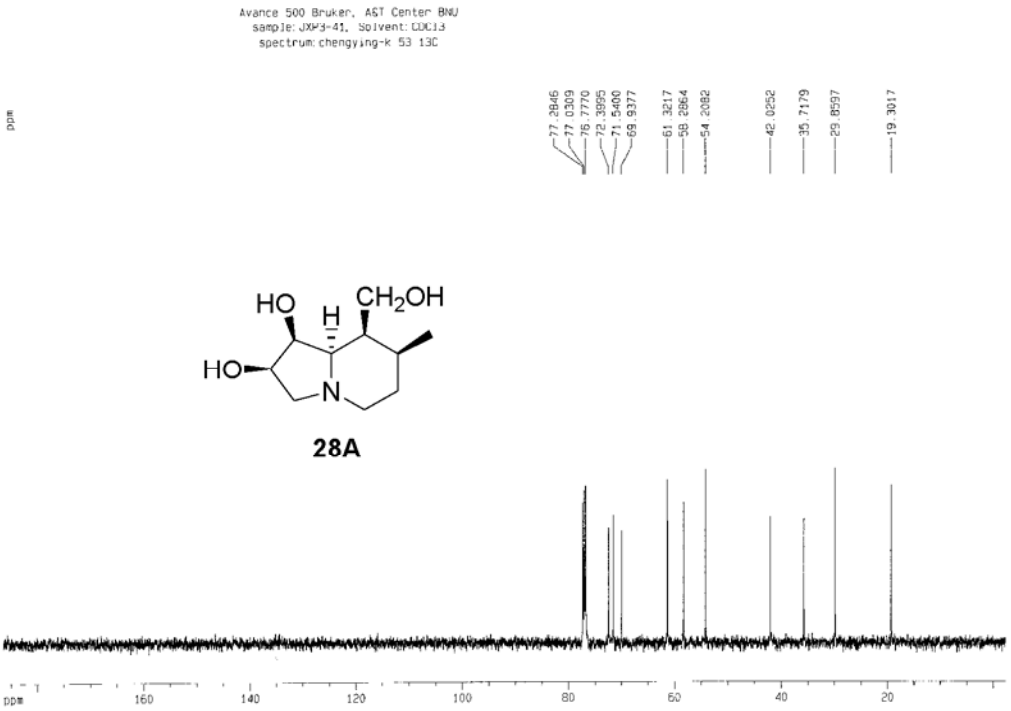
3.0796
3.2759
3.0000
ppm
8
7
6
5
4
3
2
1

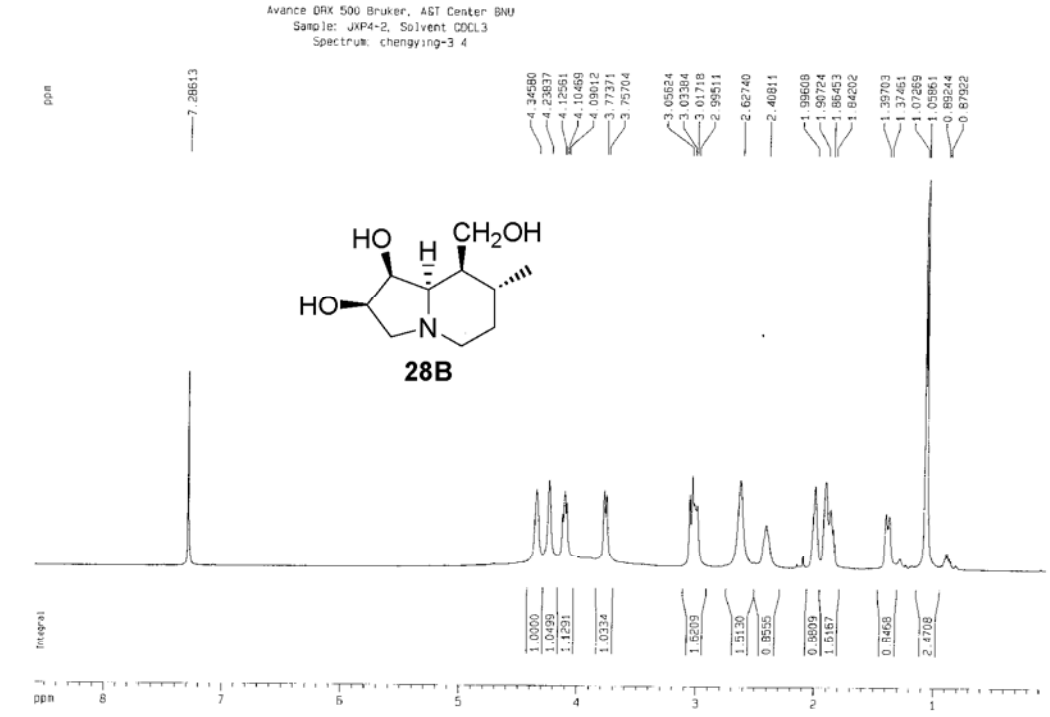

Avance 500 Bruker, A&T Center BNU
sample: Sg12-318, Solvent: cdcl3
spectrum: chengying-c 61
170.819
169.445
112.670
80.731
77.286
77.147
77.033
76.778
62.865
51.194
50.267
43.810
36.246
31.675
25.433
24.458
18.439
O
H
CO2CH3
N
O
O
24A
220
200
180
160
140
120
100
80
60
40
20
0

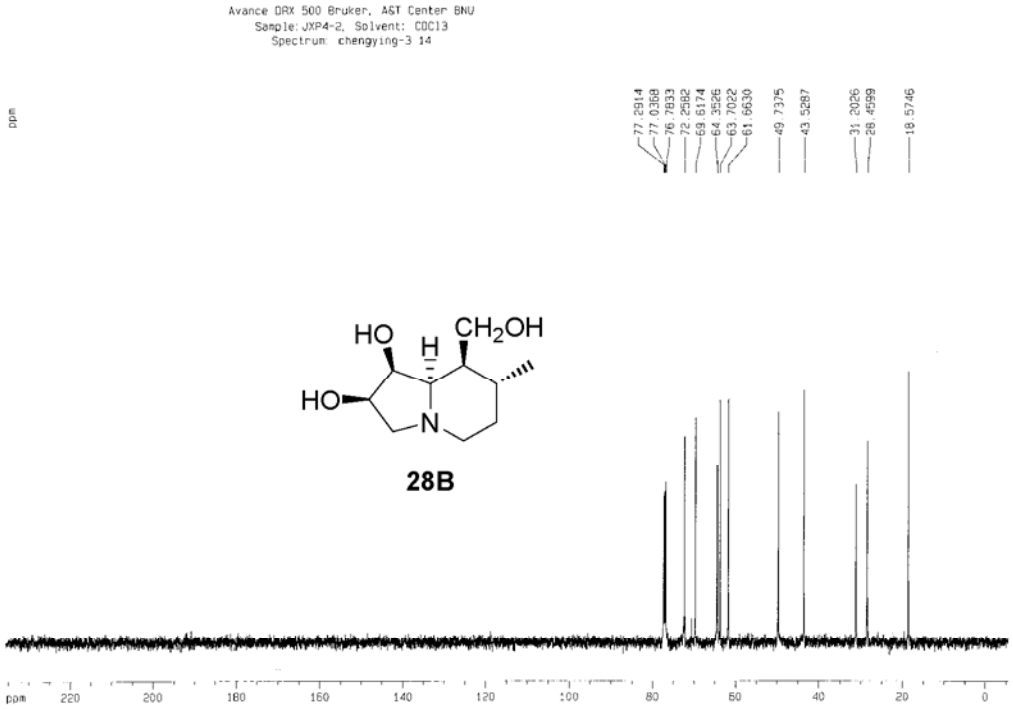

Avance 500 Bruker, A&T Center BNU
sample: sg12-37A, Solvent: cdcl3
spectrum: chengying-c 56
ppm
7.28815
4.58923
4.57842
4.56774
4.56038
4.55844
4.55497
4.54797
4.53233
4.36573
3.79739
3.68387
3.67706
3.66897
3.66222
2.95479
2.94485
2.92820
2.91825
2.89353
2.82013
2.81687
2.80160
2.66383
2.65419
2.63063
2.62181
2.61403
2.60825
2.59572
2.59572
2.04883
2.02953
2.01591
1.99583
1.38813
1.27767
1.11710
1.10443
O
H
CO2CH3
N
O
O
24B
1.0000
0.9942
0.5001
0.5115
2.9681
1.0240
0.5183
0.5224
1.0128
0.4983
1.5655
1.0519
3.1191
3.1077
3.0874
7
6
5
4
3
2
1

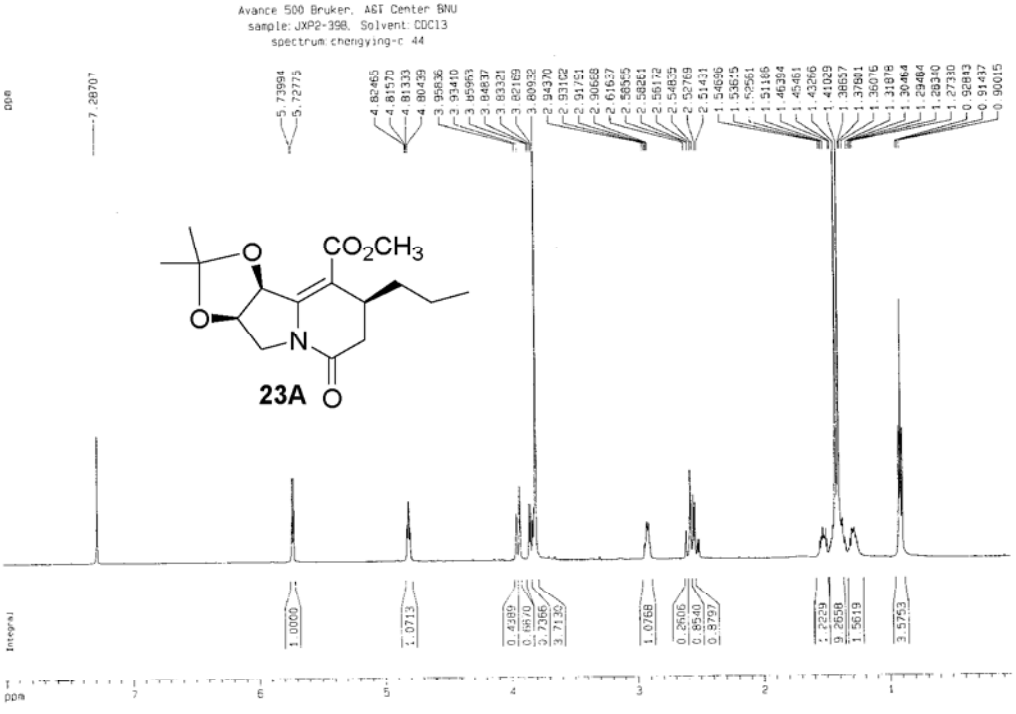

Avance 500 Bruker, A&T Center BNU
Sample. Sgl2-37A, Solvent: CDCl3
spectrum: chengying-c 70
ppm
171.313
169.414
112.078
80.504
77.863
77.306
77.052
76.798
60.022
51.734
50.077
46.009
38.757
28.109
26.199
24.525
20.391
O
H
CO2CH3
O
N
O
24B
160
140
120
100
80
60
40
20

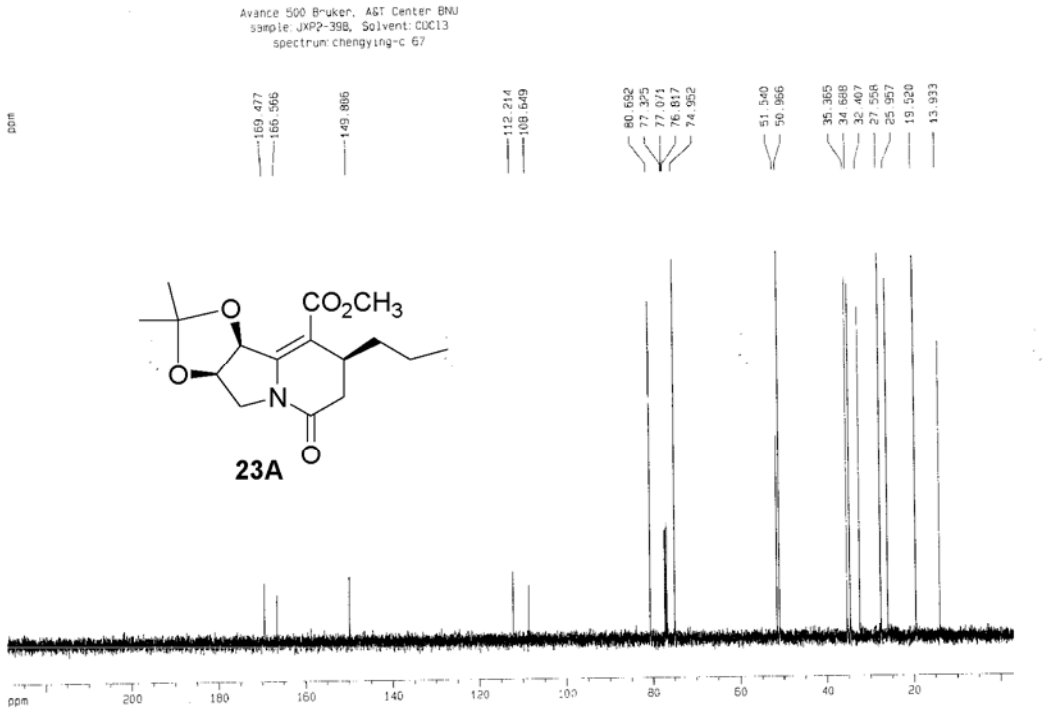

Avance 500 Bruker, A&T Center BNU
sample: JXP3-41, Solvent: CDCl3
spectrum: chengying-k 2g
ppm
7.28756
4.28009
4.27064
4.23638
4.22572
4.21467
4.02996
4.01820
4.00740
3.99562
3.87944
3.87134
3.85686
3.84875
3.17531
3.16945
3.16041
3.15408
3.14787
3.13017
3.12691
3.10821
3.10503
2.34601
2.33270
2.32414
2.31083
2.27216
2.26772
2.26275
2.25825
2.02107
2.01143
1.49467
1.48926
1.47854
1.47224
1.45824
1.07603
1.06222
0.09430
HO
H
CH2OH
HO
N
28A
Integral
1.0000
1.0829
1.0368
1.0454
1.0695
1.1020
0.9997
0.9949
1.9324
1.0710
1.9786
2.8909
ppm
7
6
5
4
3
2
1
0

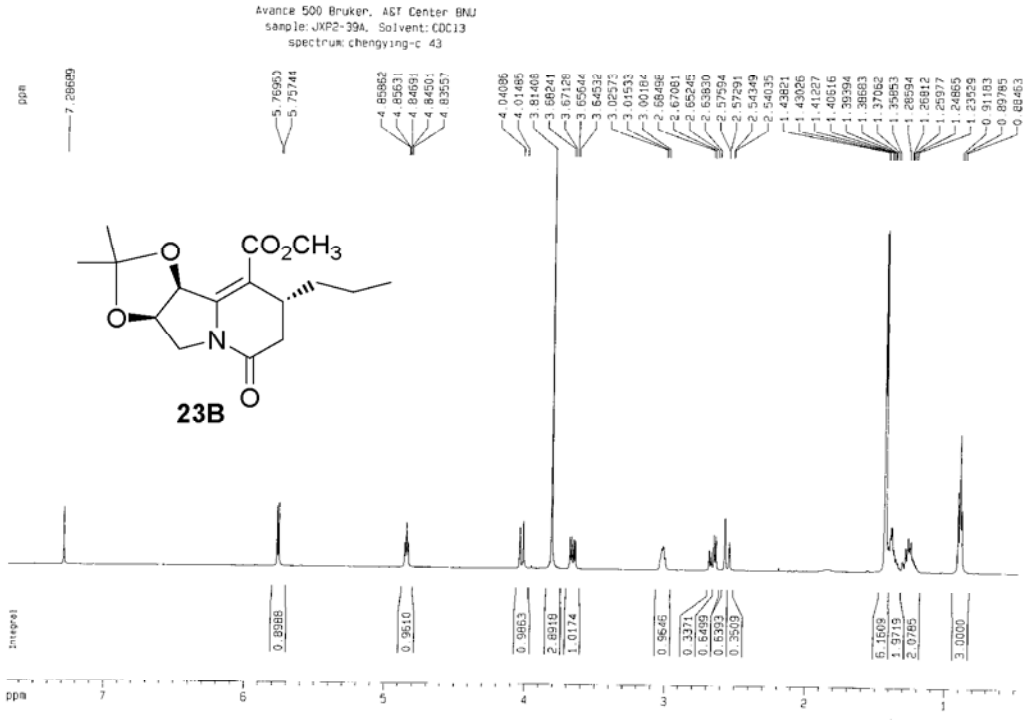

Avance 500 Bruker, A&T Center BNU
sample: JXP3-41, Solvent: CDCl3
spectrum: chengying-k 53 13C
ppm
77.2846
77.0309
76.7770
72.3995
71.5400
69.9377
61.3217
58.2864
54.2082
42.0252
35.7179
29.8597
19.3017
HO
H
CH2OH
HO
N
28A
ppm
160
140
120
100
80
60
40
20

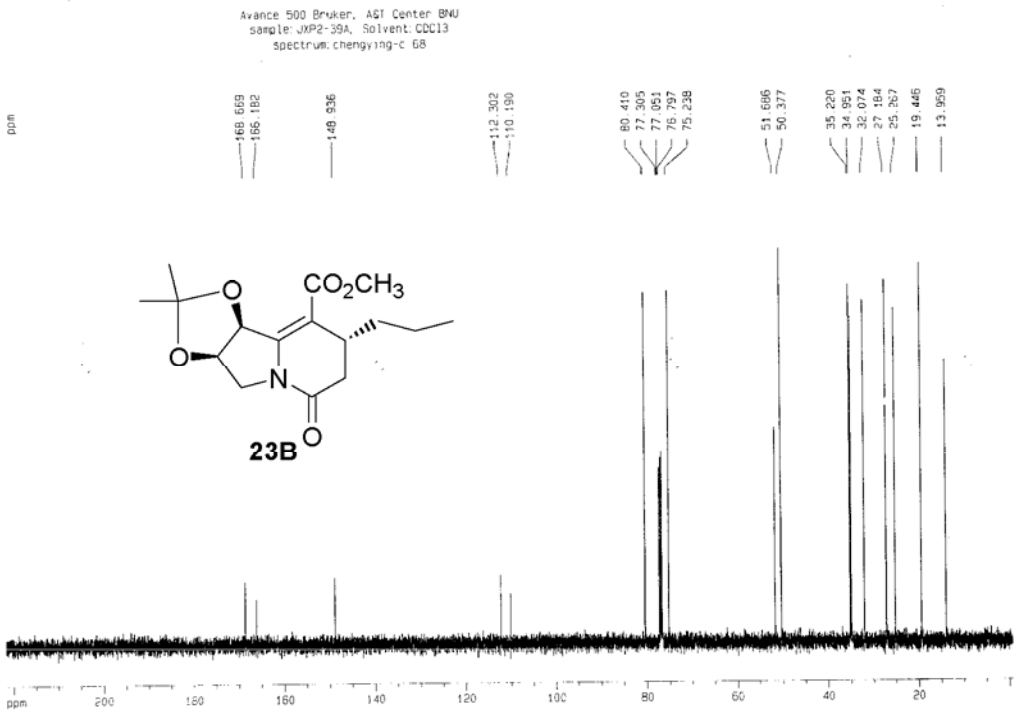

Avance DRX 500 Bruker, A&T Center BNU
Sample: JXP4-2, Solvent CDCL3
Spectrum: chengying-3 4
ppm
7.28613
4.34580
4.23837
4.12561
4.10459
4.09612
3.77371
3.75704
3.05624
3.03384
3.01718
2.99511
2.62740
2.40811
1.99608
1.96724
1.86453
1.84202
1.39703
1.37461
1.07269
1.05861
0.89244
0.87922
HO
H
CH2OH
HO
N
28B
Integral
1.0000
1.0499
1.4291
1.0334
1.6209
1.5130
0.9555
0.8809
1.5167
0.8468
2.4708
ppm
8
7
6
5
4
3
2
1

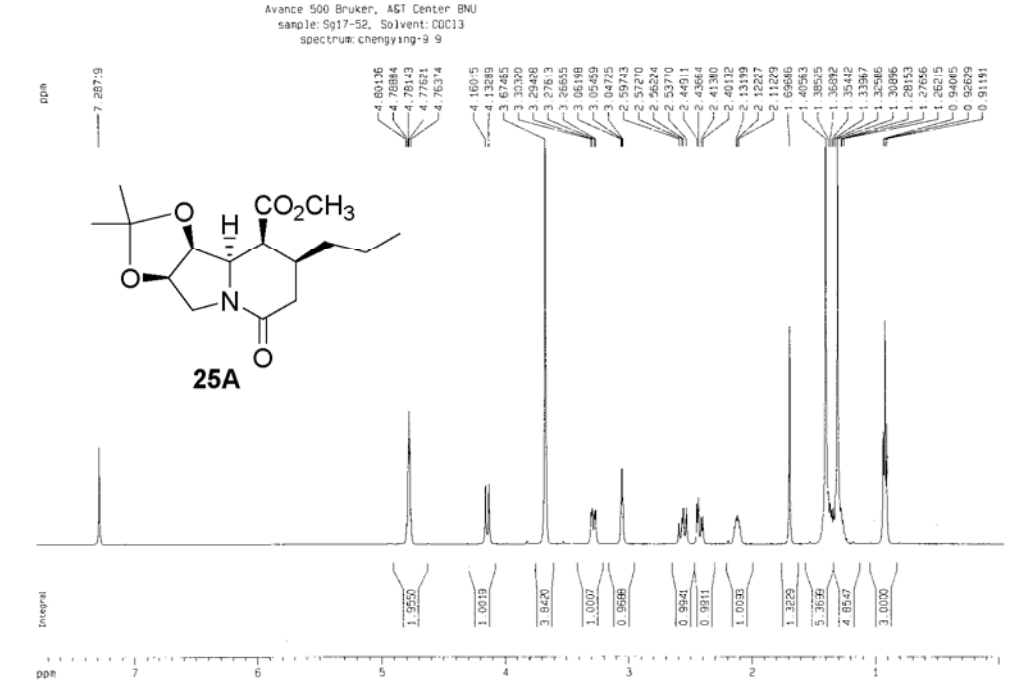

Avance DRX 500 Bruker, A&T Center BNU
Sample: JXP4-2, Solvent: CDCl3
Spectrum: chengying-3 14
ppm
77.2914
77.0388
76.7833
72.2582
69.6174
64.3526
63.7022
61.6630
49.7375
43.5287
31.2026
28.4599
18.5746
HO
H
CH2OH
HO
N
28B
ppm 220 200 180 160 140 120 100 80 60 40 20 0

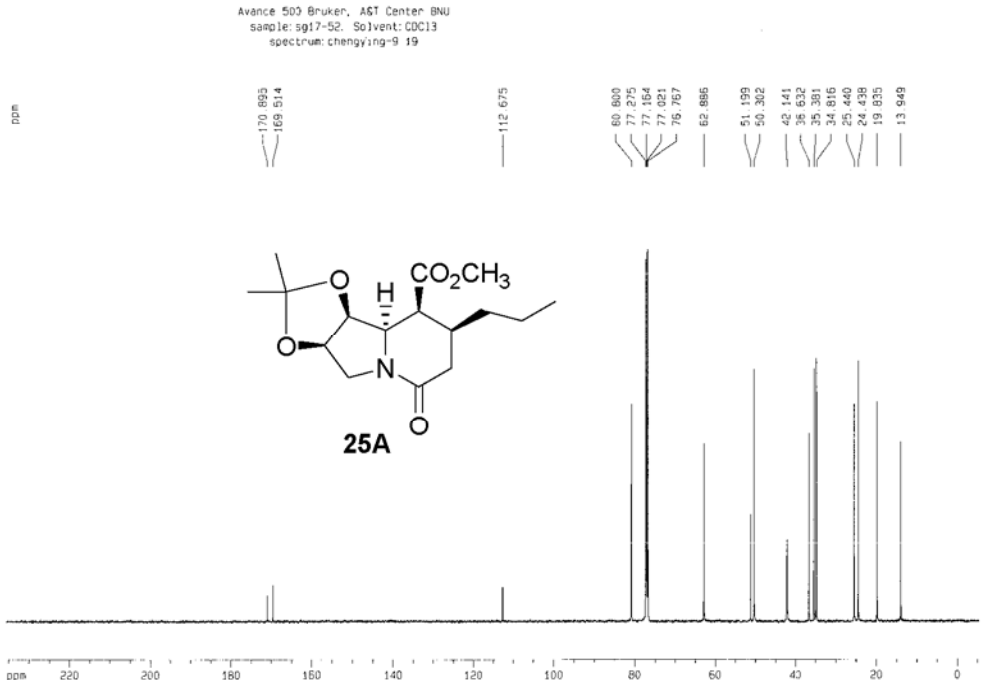

Avance 500 Bruker, A&T Center BNU
sample: JXP2-398, Solvent: CDCl3
spectrum: chengying-c 44
ppm
7.28707
5.73994
5.72775
4.82465
4.81570
4.81333
4.80459
3.95836
3.93410
3.85963
3.84837
3.83321
3.82169
3.80932
2.94370
2.93102
2.91751
2.90668
2.61627
2.58955
2.58261
2.56172
2.54835
2.52769
2.51431
1.54696
1.53615
1.52561
1.51165
1.46354
1.45461
1.43296
1.41029
1.38657
1.37981
1.36076
1.31878
1.30464
1.29464
1.28340
1.27330
0.92813
0.91437
0.90015
CO2CH3
O
O
N
O
23A
Integral
1.0000
1.0713
0.4589
0.6670
0.7366
3.7135
1.0768
0.2606
0.8540
0.8797
7.7229
9.2658
1.5619
3.5753
ppm 7 6 5 4 3 2 1

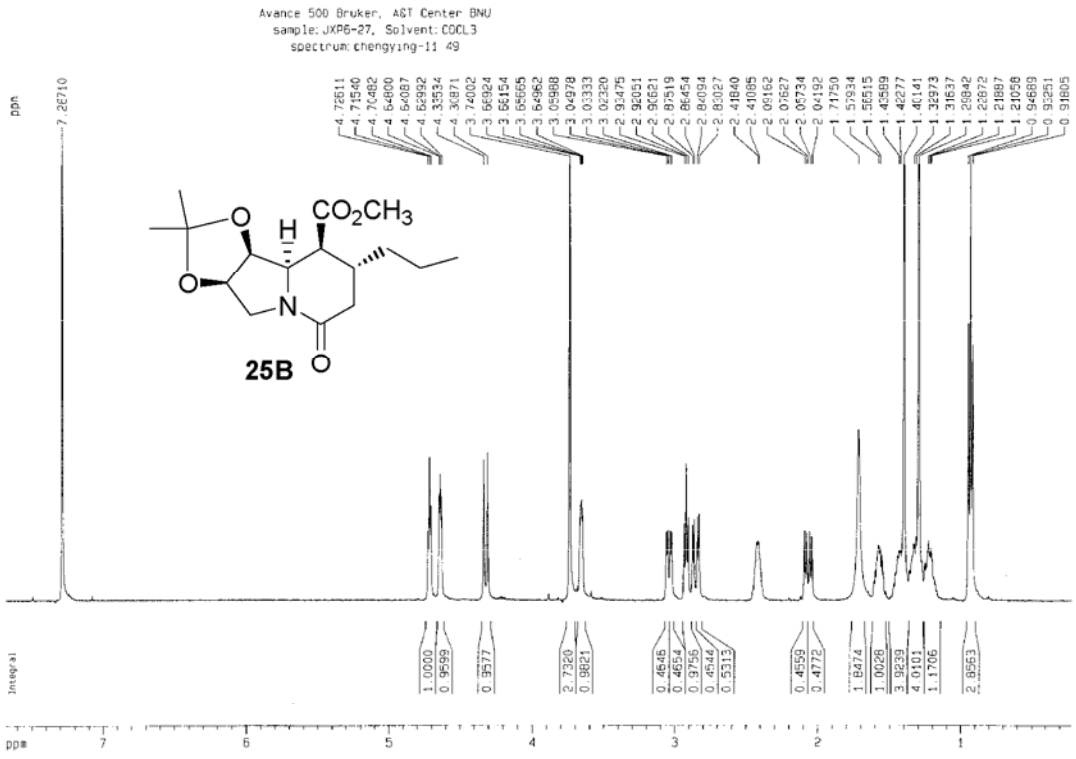

Avance 500 Bruker, A&T Center BNU
sample: JXP2-39B, Solvent: CDCl3
spectrum: chengying-c 67
ppm
169.477
166.566
149.886
112.214
108.649
80.692
77.375
77.071
76.817
74.952
51.540
50.966
35.365
34.688
32.467
27.556
25.957
19.520
13.933
CO2CH3
O
O
N
O
23A
ppm
200
180
160
140
120
100
80
60
40
20

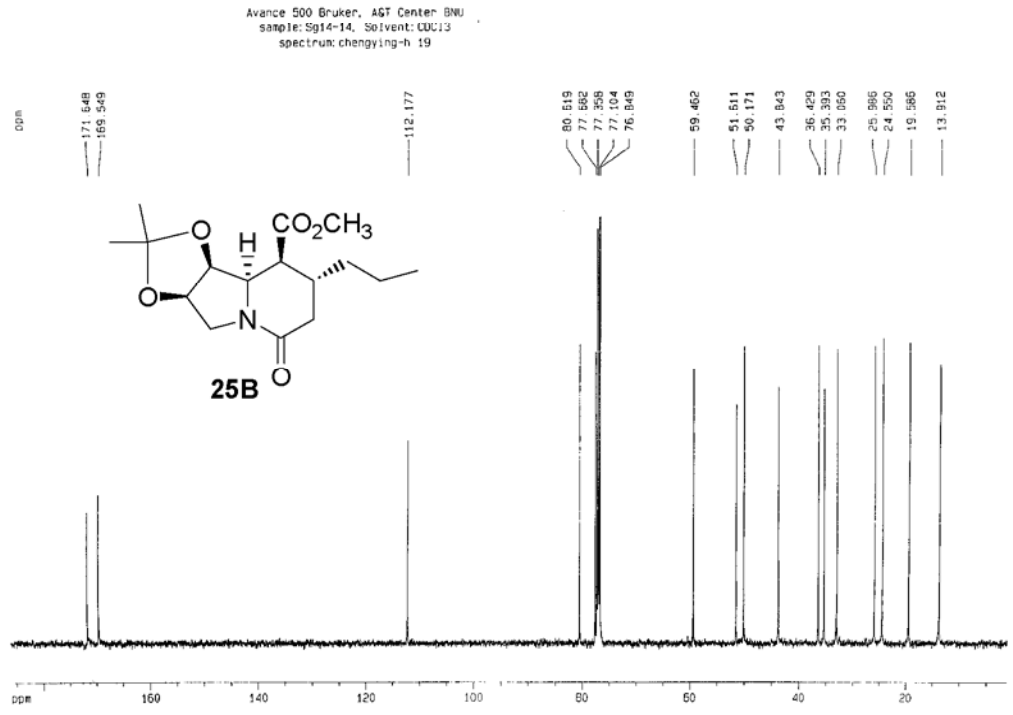

Avance 500 Bruker, A&T Center BNU
sample: JXP2-39A, Solvent: CDCl3
spectrum: chengying-c 43
ppm
7.28689
5.76953
5.75744
4.85962
4.85631
4.84691
4.84500
4.83557
4.04086
4.01486
3.81408
3.68241
3.67128
3.65644
3.64538
3.02573
3.01533
3.00184
2.68458
2.67081
2.65245
2.63830
2.57594
2.57291
2.54349
2.54035
1.43821
1.43026
1.41227
1.40516
1.39394
1.38683
1.37062
1.35953
1.28594
1.26812
1.25977
1.24865
1.23529
0.91183
0.89785
0.88463
CO2CH3
O
O
N
O
23B
Integral
0.8988
0.9610
0.9863
2.8818
1.0174
0.9645
0.3371
0.6499
0.6393
0.3509
6.1609
1.9719
2.0785
3.0000
ppm
7
6
5
4
3
2
1

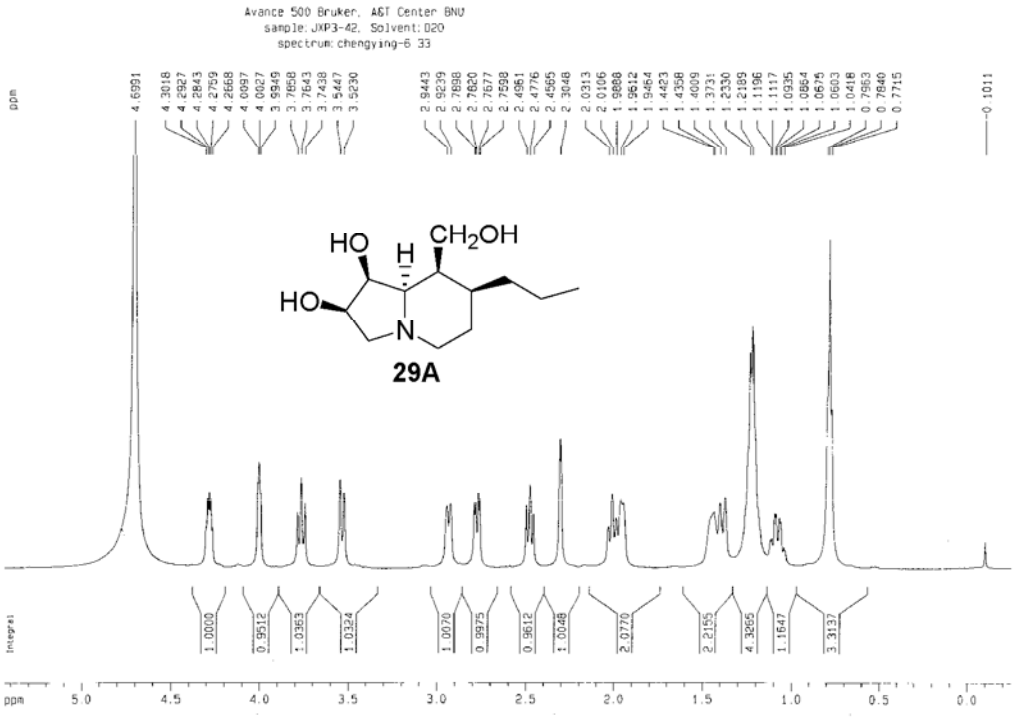

Avance 500 Bruker, A&T Center BNU
sample: JXP2-39A, Solvent: CDCl3
spectrum: chengying-c 68
ppm
168.669
166.182
148.936
112.302
110.190
80.410
77.305
77.051
76.797
75.238
51.686
50.377
35.220
34.951
32.074
27.184
25.267
19.446
13.959
CO2CH3
O
O
N
O
23B
ppm
200
180
160
140
120
100
80
60
40
20

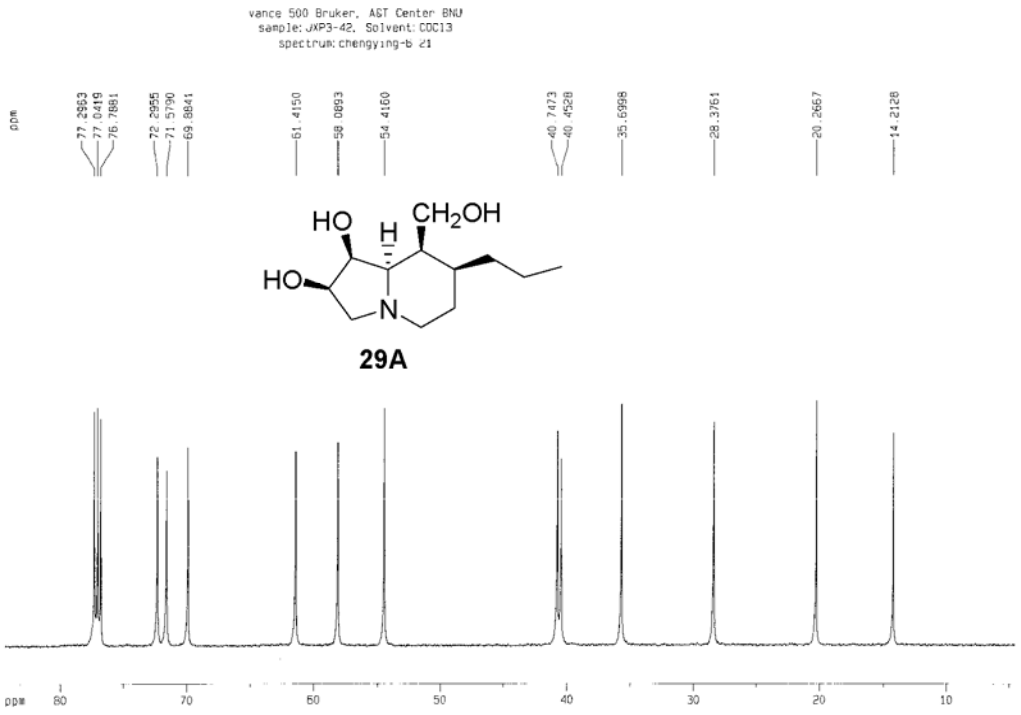

Avance 500 Bruker, A&T Center BNU
sample: Sg17-52, Solvent: CDCl3
spectrum: chengying-9 9
ppm
7.28799
4.80136
4.78884
4.78143
4.77621
4.76374
4.16015
4.13289
3.67485
3.30300
3.29488
3.27613
3.26655
3.06198
3.05459
3.04725
2.59743
2.57210
2.56224
2.53770
2.44911
2.43664
2.41380
2.40132
2.13199
2.12227
2.11209
1.69586
1.40563
1.38525
1.36892
1.35442
1.33367
1.32586
1.30896
1.28153
1.27656
1.26215
0.94065
0.92629
0.91191
CO2CH3
H
O
O
N
O
25A
Integral
1.9550
1.0019
3.8420
1.0007
0.9688
0.9941
0.9911
1.0038
1.3229
5.3699
4.8547
3.0000
ppm
7
6
5
4
3
2
1

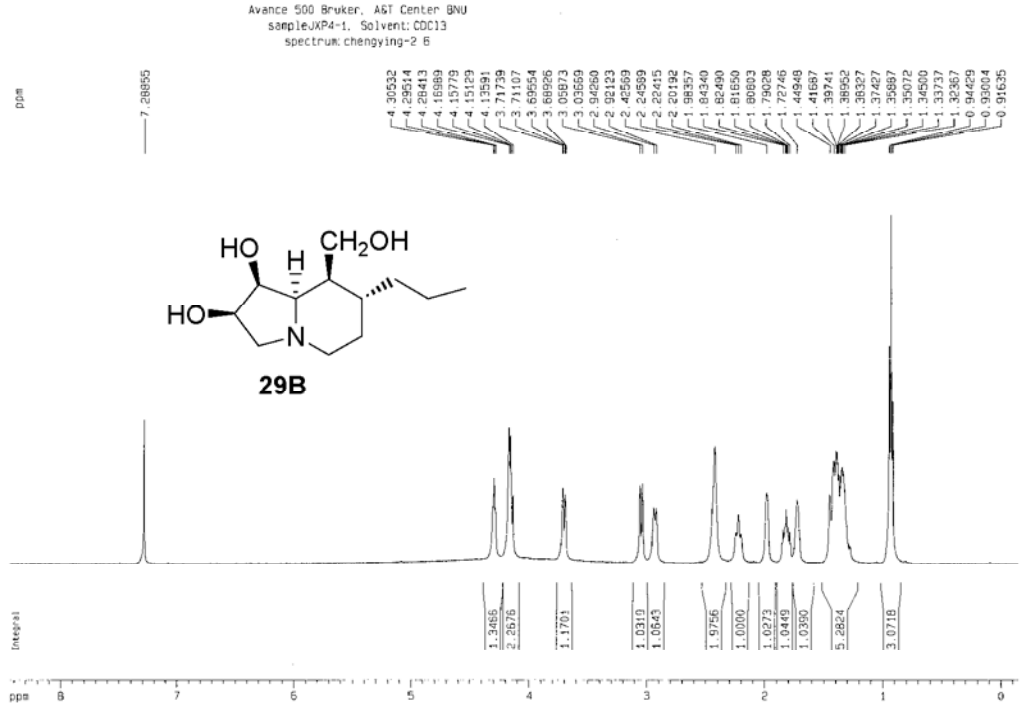

Avance 500 Bruker, A&T Center BNU
sample: sg17-52, Solvent: CDCl3
spectrum: chengying-9 19
ppm
170.895
169.514
112.675
60.800
77.275
77.164
77.021
76.767
62.886
51.199
50.302
42.141
36.632
35.381
34.816
25.440
24.438
19.835
13.949
CO2CH3
H
O
N
O
25A
ppm 220 200 180 160 140 120 100 80 60 40 20 0

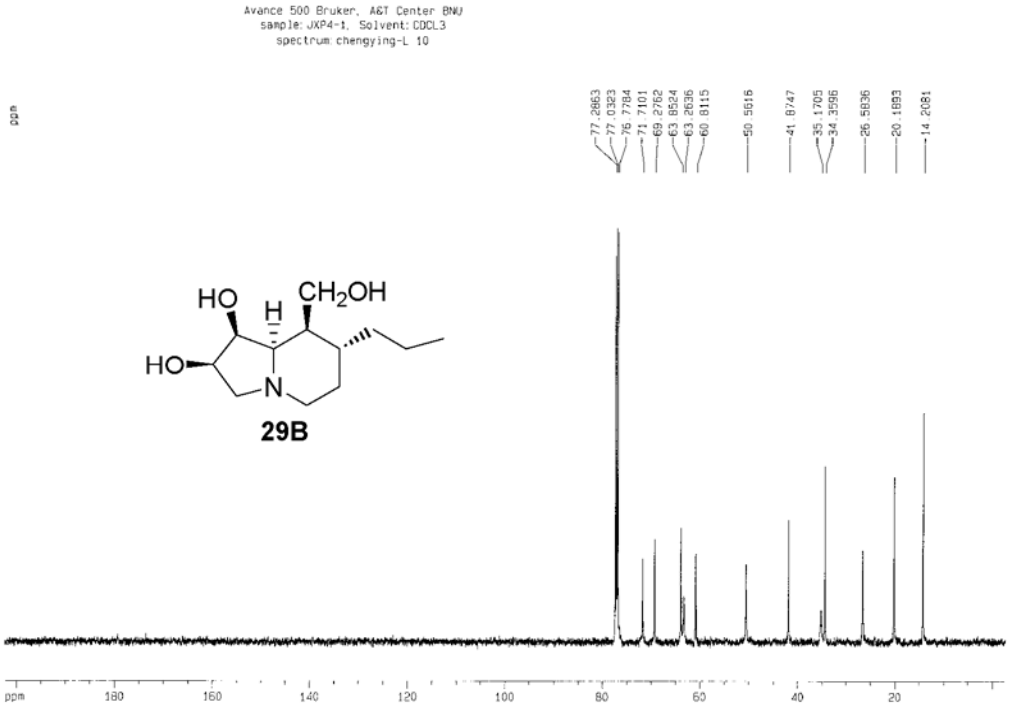

Avance 500 Bruker, A&T Center BNU
sample: JXP6-27, Solvent: CDCL3
spectrum: chengying-11 49
ppm
7.26710
CO2CH3
H
O
N
O
25B
Integral
1.0000
0.9599
0.9577
2.7320
0.9821
0.4646
0.4654
0.9756
0.4544
0.5313
0.4559
0.4772
1.8474
1.0026
3.9239
4.0101
1.1706
2.8563
ppm 7 6 5 4 3 2 1

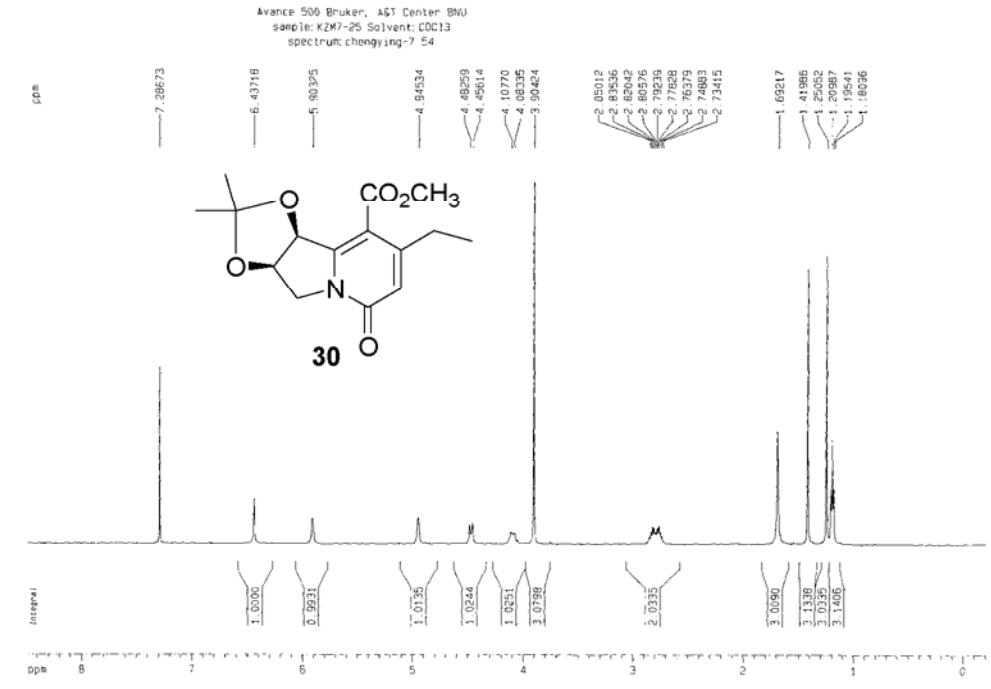

Avance 500 Bruker, A&T Center BNU
sample: Sg14-14, Solvent: CDCl3
spectrum: chengying-h 19
ppm
171.648
169.549
112.177
80.519
77.582
77.358
77.104
76.849
59.462
51.611
50.171
43.843
36.429
35.393
33.060
25.986
24.550
19.585
13.912
CO2CH3
H
O
O
N
O
25B
ppm
160
140
120
100
80
60
40
20

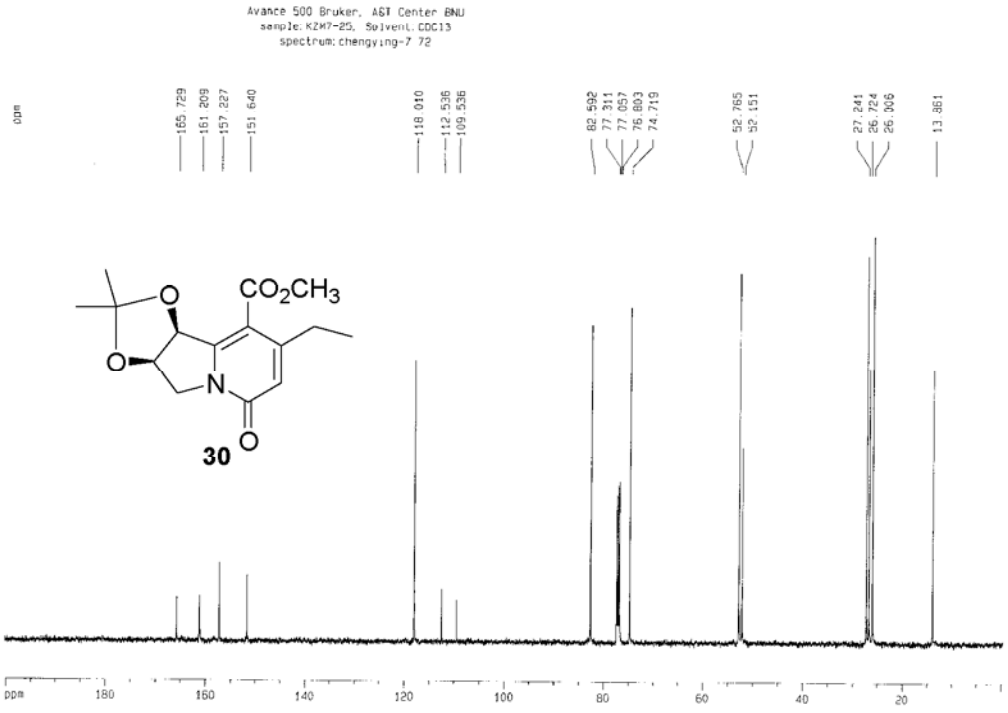

Avance 500 Bruker, A&T Center BNU
sample: JXP3-42, Solvent: D2O
spectrum: chengying-6 33
ppm
4.6991
4.3018
4.2927
4.2843
4.2759
4.2668
4.0097
4.0027
3.9945
3.7658
3.7643
3.7438
3.5447
3.5230
2.9443
2.9239
2.7698
2.7620
2.7677
2.7598
2.4961
2.4776
2.4565
2.3048
2.0313
2.0106
1.9888
1.9612
1.9464
1.4423
1.4358
1.4009
1.3731
1.2330
1.2189
1.1196
1.1117
1.0935
1.0864
1.0675
1.0603
1.0418
0.7963
0.7840
0.7715
0.1011
HO
H
CH2OH
HO
N
29A
Integral
1.0000
0.9512
1.0363
1.0324
1.0070
0.9975
0.9612
1.0048
2.0770
2.2155
4.3265
1.1647
3.3137
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

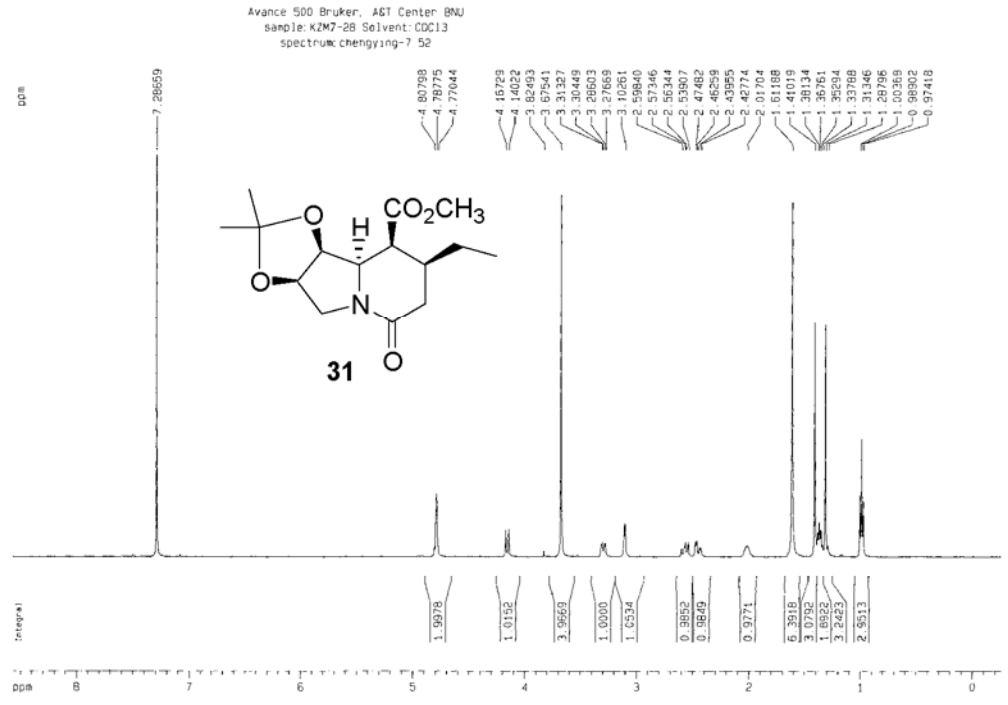

vance 500 Bruker, A&T Center BNU
sample: JXP3-42, Solvent: CDCl3
spectrum: chengying-b 21
ppm
77.2963
77.0419
76.7881
72.2955
71.5790
69.8841
61.4150
58.0893
54.4160
40.7473
40.4528
35.6998
28.3761
20.2667
14.2126
HO
H
CH2OH
HO
N
29A
ppm
80
70
60
50
40
30
20
10

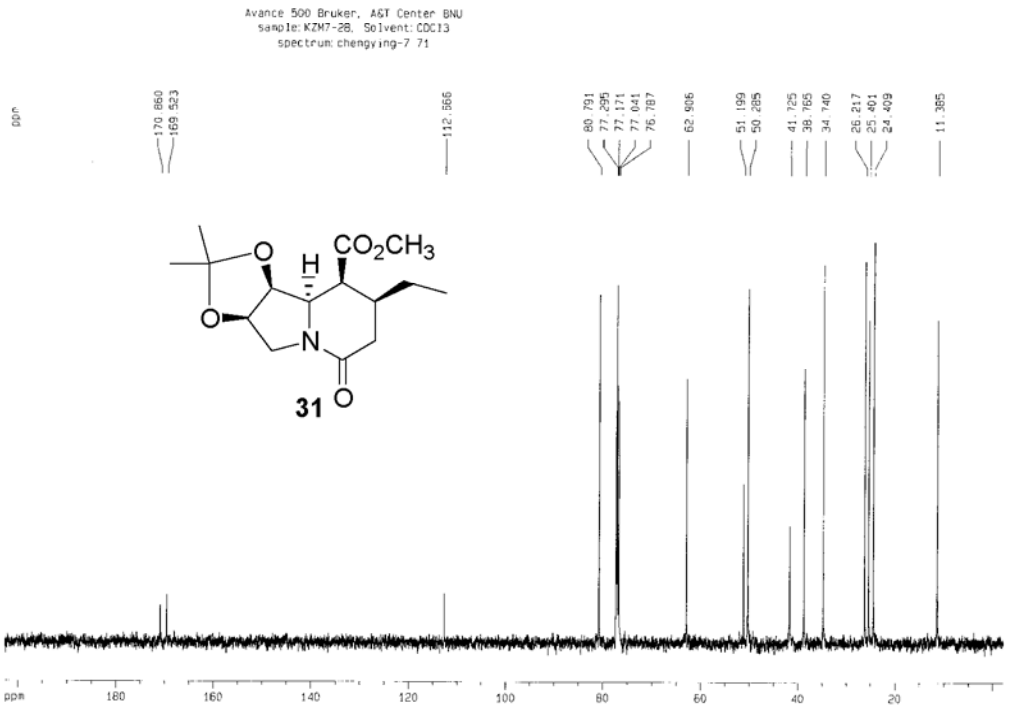

Avance 500 Bruker, A&T Center BNU
sampleJXP4-1, Solvent: CDCl3
spectrum: chengying-2 6
ppm
7.28855
4.30532
4.29514
4.28413
4.16989
4.15779
4.15129
4.13591
3.71739
3.71107
3.69554
3.68926
3.05873
3.03569
2.94269
2.92123
2.42569
2.24599
2.22415
2.20192
1.98357
1.84340
1.82490
1.81650
1.80603
1.79028
1.72746
1.44948
1.41687
1.39741
1.38962
1.38327
1.37427
1.35887
1.35072
1.34500
1.33737
1.32367
0.94429
0.93004
0.91635
HO
H
CH2OH
HO
N
29B
Integral
1.3466
2.2676
1.1701
1.0319
1.0643
1.9756
1.0000
1.0273
1.0449
1.0390
5.2824
3.0718
ppm
8
7
6
5
4
3
2
1
0

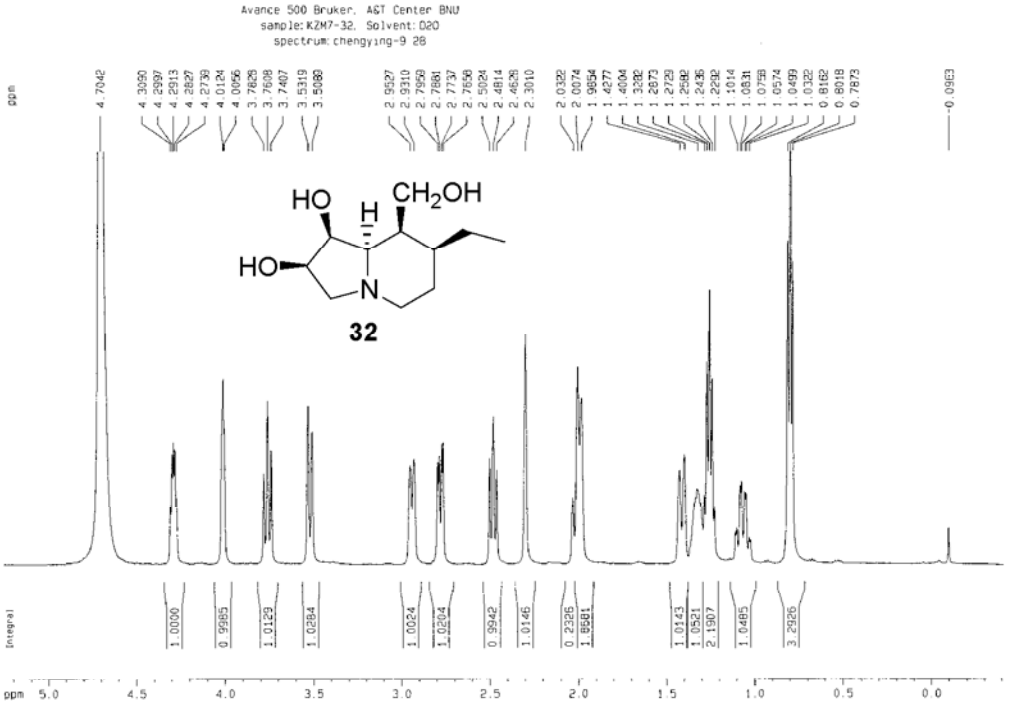

Avance 500 Bruker, A&T Center BNU
sample: JXP4-1, Solvent: CDCL3
spectrum: chengying-L 10
ppm
77.2863
77.0323
76.7784
71.7101
69.2762
63.8524
63.2636
60.8115
50.5616
41.8747
35.1705
34.3596
26.5836
20.1893
14.2081
HO
H
CH2OH
HO
N
29B
ppm
180
160
140
120
100
80
60
40
20

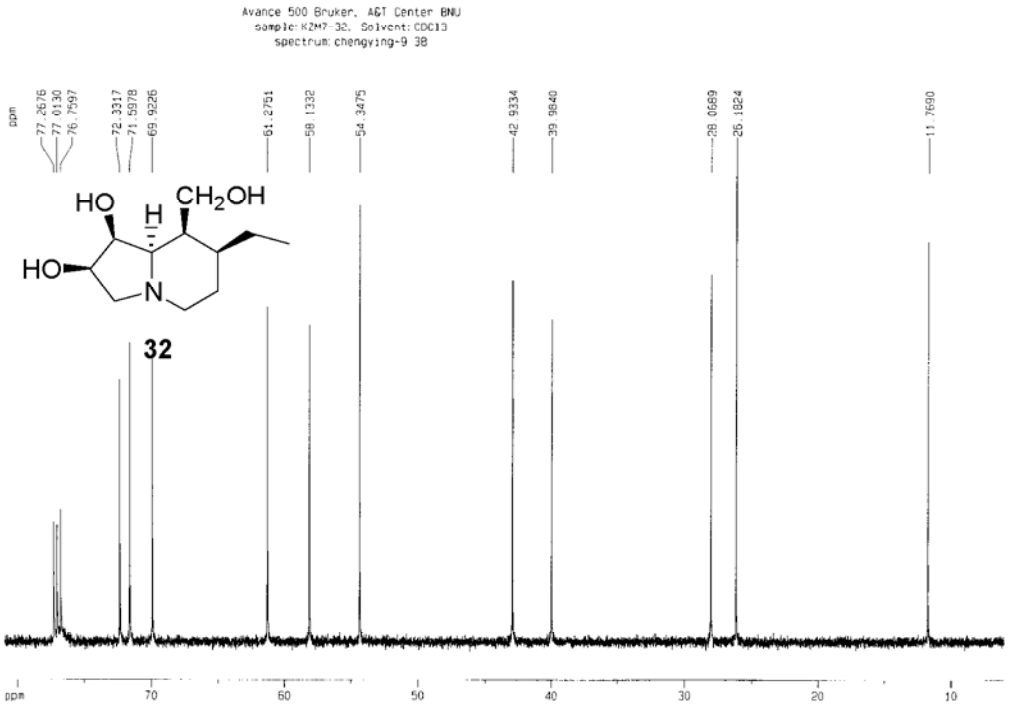

Avance 500 Bruker, A&T Center BNU
sample: KZM7-25 Solvent: CDCl3
spectrum: chengying-7 54
ppm
7.28673
6.43718
5.90395
4.94534
4.48259
4.45614
4.10770
4.08335
3.90424
2.05012
2.83536
2.82042
2.80576
2.79239
2.77628
2.76379
2.74883
2.73415
1.69217
1.41986
1.25052
1.20987
1.19541
1.18096
CO2CH3
O
O
N
O
30
Integral
1.0000
0.9931
1.0135
1.0244
1.0251
3.0798
2.0335
3.0090
3.1338
3.0335
3.1406
ppm
8
7
6
5
4
3
2
1
0

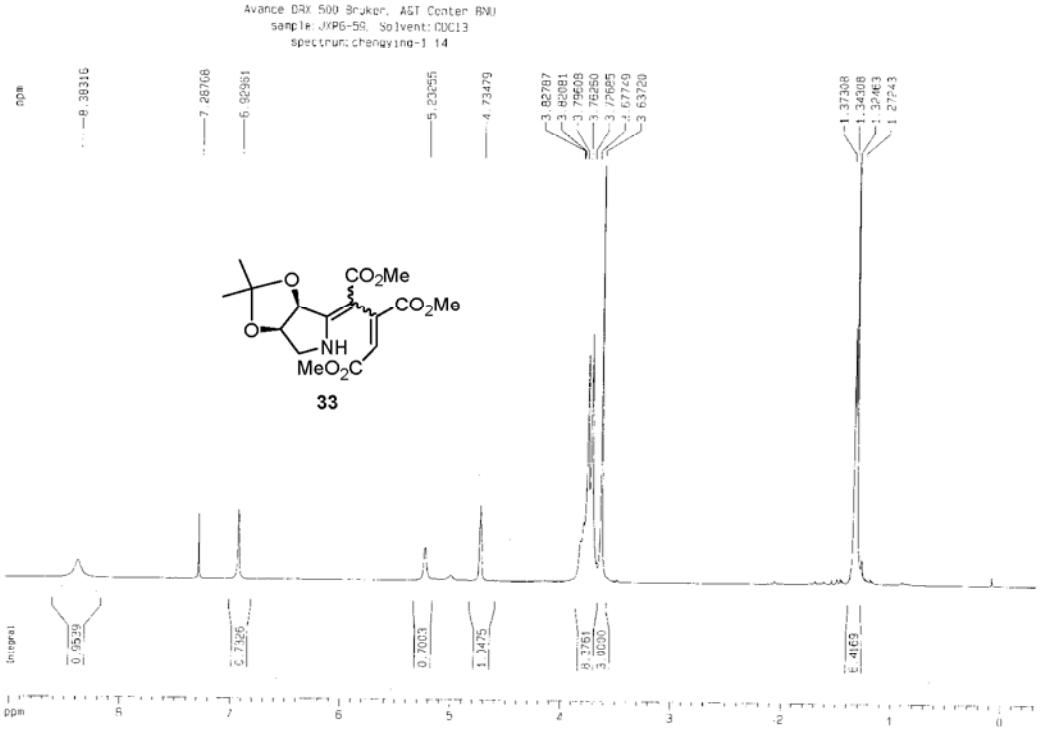

Avance 500 Bruker, A&T Center BNU
sample: KZM7-25, Solvent: CDCl3
spectrum: chengying-7 72
ppm
165.729
161.209
157.227
151.640
118.010
112.536
109.536
82.592
77.311
77.057
76.803
74.719
52.765
52.151
27.241
26.724
26.006
13.861
CO2CH3
O
O
N
O
30
ppm
180
160
140
120
100
80
60
40
20

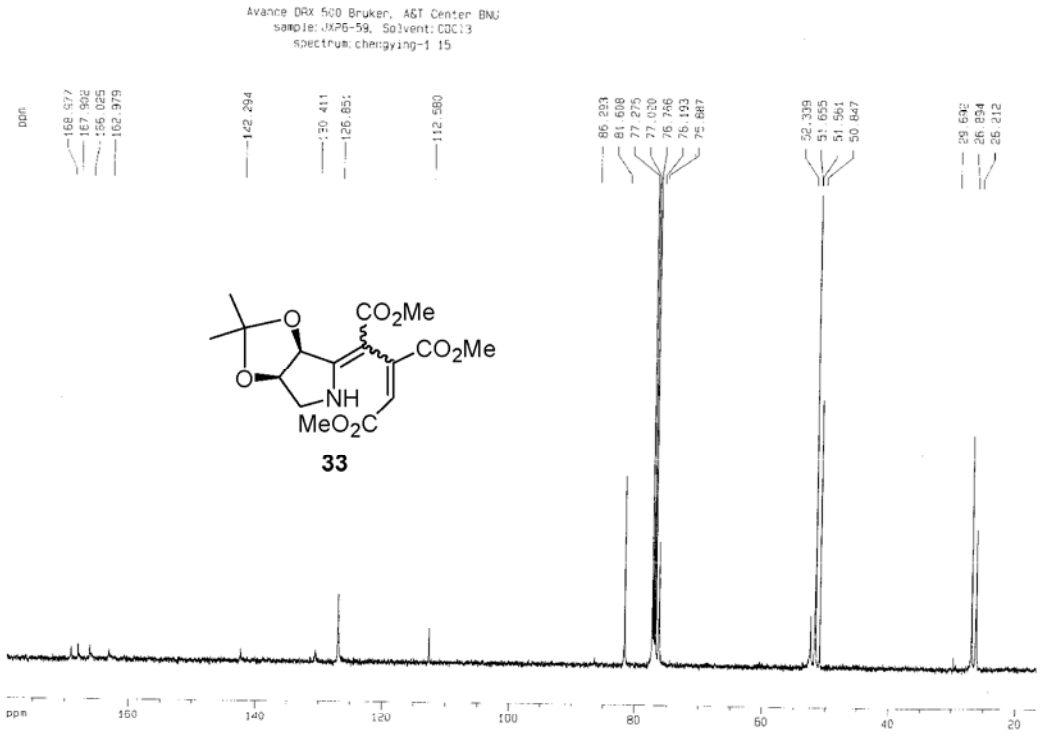

Avance 500 Bruker, A&T Center BNU
sample: KZM7-28 Solvent: CDCl3
spectrum: chengying-7 52
ppm
7.28659
4.80798
4.78775
4.77644
4.16729
4.14022
3.82493
3.67541
3.31327
3.30449
3.28603
3.27669
3.10261
2.59840
2.57346
2.56344
2.53907
2.47482
2.46259
2.43955
2.42774
2.01704
1.61188
1.41019
1.38134
1.36761
1.35294
1.33788
1.31346
1.28796
1.00365
0.98902
0.97418
CO2CH3
H
O
O
N
O
31
Integral
1.9978
1.0152
3.9669
1.0000
1.6534
0.3852
0.3849
0.9771
6.3918
3.0792
1.8622
3.2423
2.9513
ppm
8
7
6
5
4
3
2
1
0

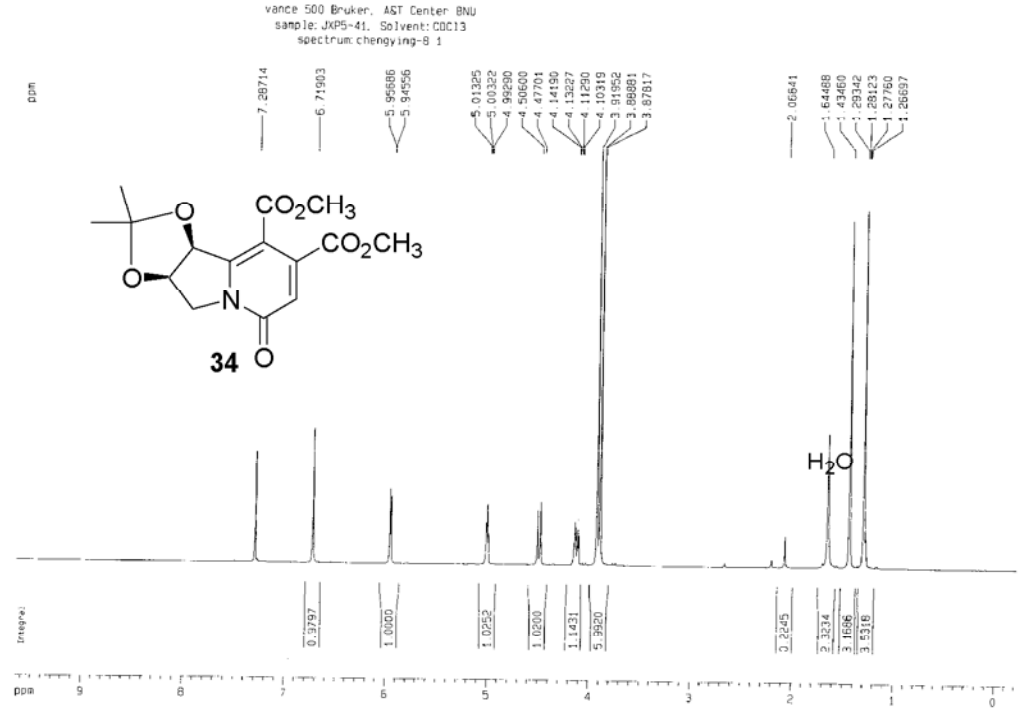

Avance 500 Bruker, A&T Center BNU
sample: KZM7-28, Solvent: CDCl3
spectrum: chengying-7 71
ppm
170.860
169.523
112.566
80.791
77.295
77.171
77.041
76.787
62.906
51.199
50.285
41.725
38.765
34.740
26.217
25.401
24.409
11.385
CO2CH3
H
O
O
N
O
31
ppm
180
160
140
120
100
80
60
40
20

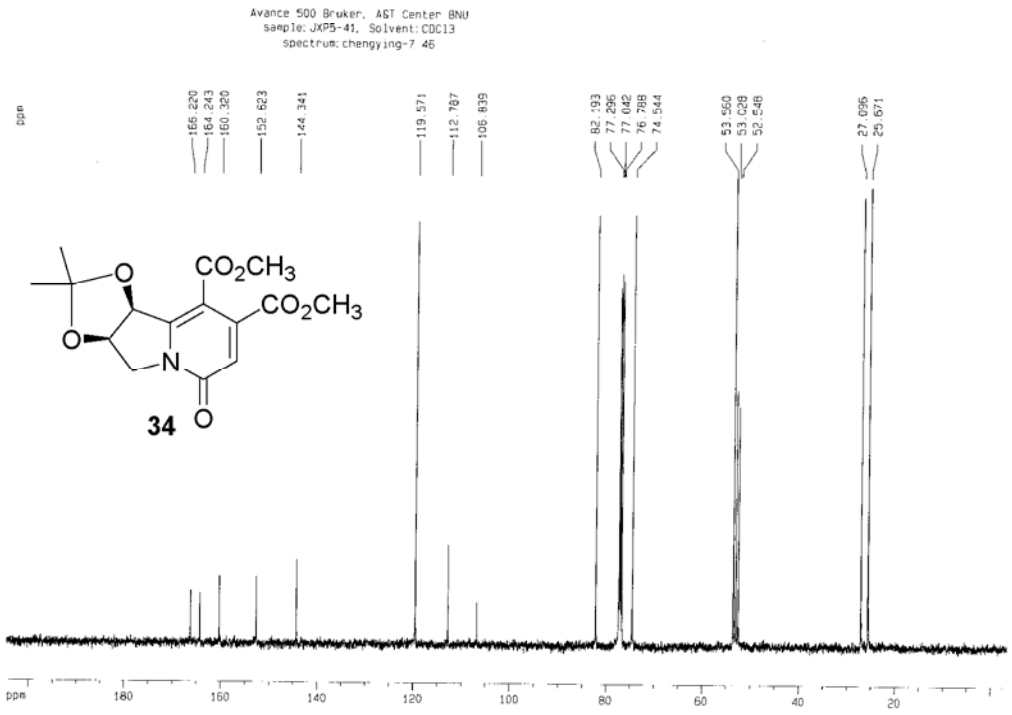

Avance 500 Bruker, A&T Center BNU
sample: KZM7-32, Solvent: D2O
spectrum: chengying-9 28
ppm
4.7042
4.3090
4.2997
4.2913
4.2827
4.2739
4.0124
4.0056
3.7825
3.7608
3.7407
3.5319
3.5088
2.9527
2.9310
2.7959
2.7881
2.7737
2.7656
2.5024
2.4814
2.4626
2.3010
2.0322
2.0074
1.9854
1.4277
1.4004
1.3282
1.2873
1.2729
1.2586
1.2436
1.2292
1.1014
1.0831
1.0758
1.0574
1.0499
1.0322
0.8162
0.8018
0.7873
-0.0963
HO
H
CH2OH
HO
N
32
Integral
1.0000
0.9985
1.0129
1.0284
1.0024
1.0204
0.9942
1.0146
0.2386
1.8681
1.0143
1.0521
2.1907
1.0485
3.2926
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

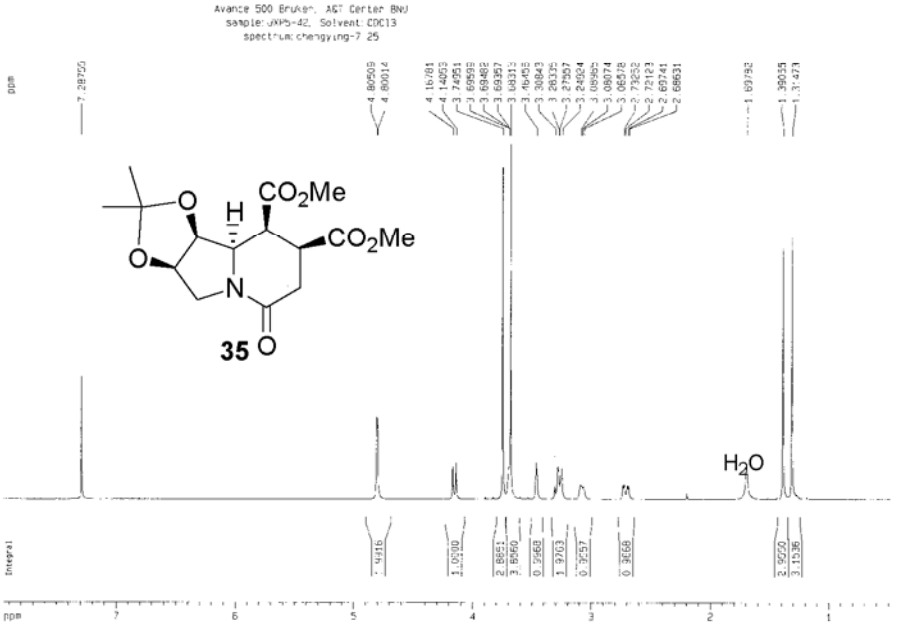

Avance 500 Bruker, A&T Center BNU
Sample: KZM7-32, Solvent: CDCl3
spectrum: chengying-9 3B
ppm
77.2676
77.0130
76.7597
72.3317
71.5978
69.9226
61.2751
58.1332
54.3475
42.9334
39.9840
28.0689
26.1824
11.7690
HO
H
CH2OH
HO
N
32
ppm
70
60
50
40
30
20
10

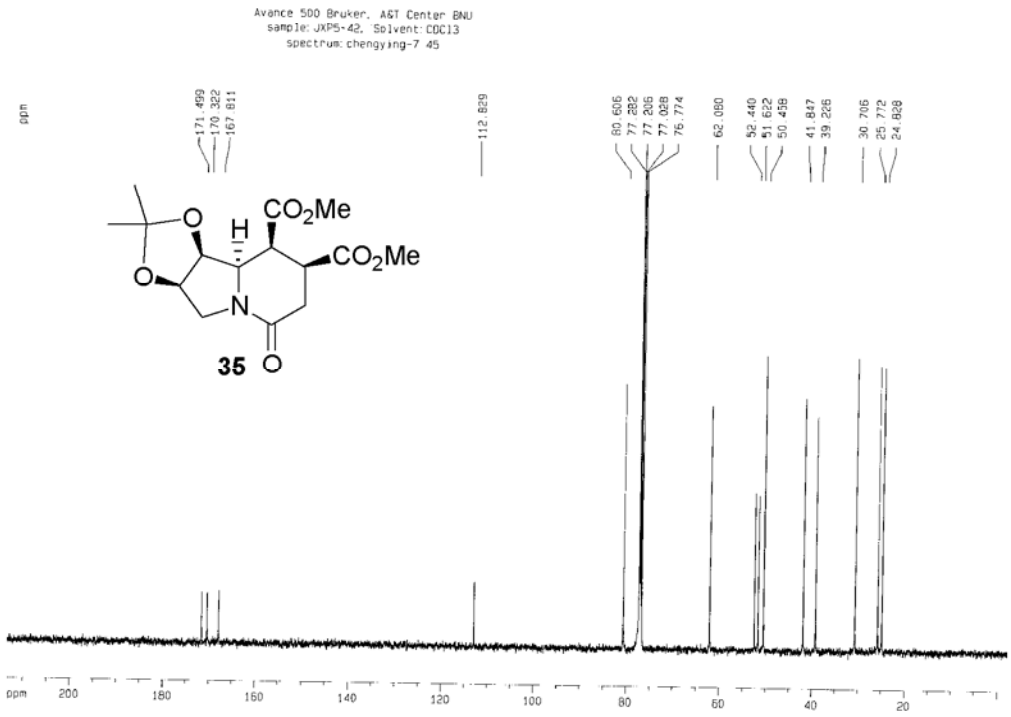

Avance DRX 500 Bruker, A&T Center BNU
sample: JXP6-59, Solvent: CDCl3
spectrum: chengying-1 14
ppm
8.38316
7.28708
6.92961
5.23255
4.73479
3.82787
3.82081
3.79608
3.76260
3.77685
3.67749
3.63720
1.37308
1.34308
1.31463
1.27243
CO2Me
CO2Me
O
O
O
NH
MeO2C
33
Integral
0.6529
2.7326
0.7003
1.1475
9.3761
3.0000
6.4169
ppm
7
6
5
4
3
2
1
0

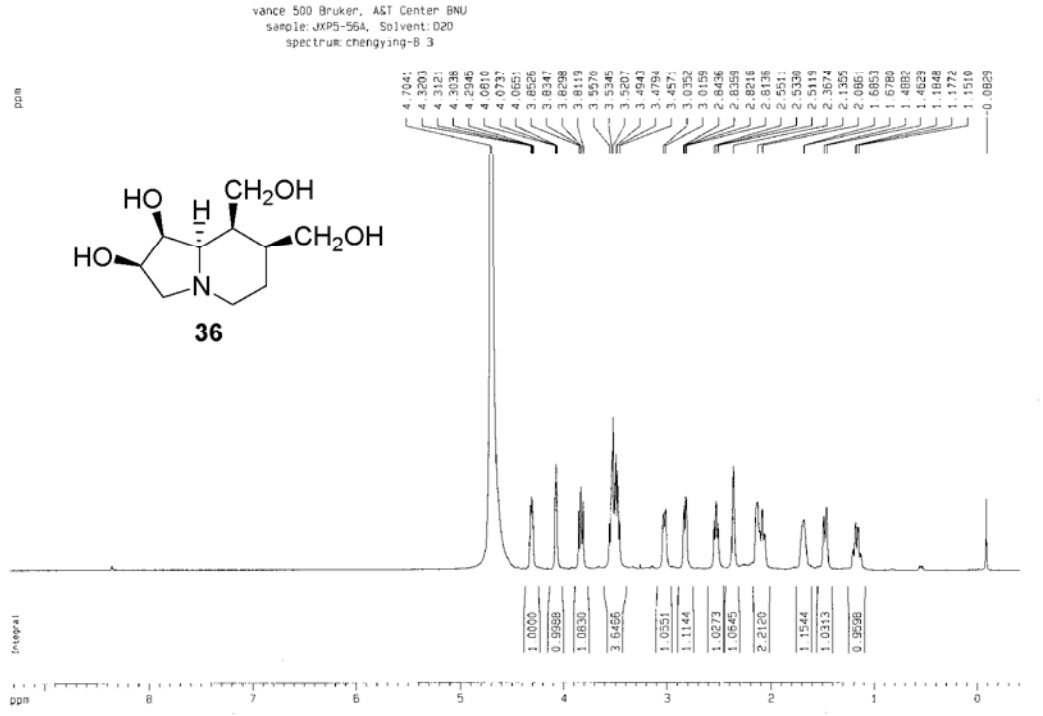

Avance DRX 500 Bruker, A&T Center BNU
sample: JXP6-59, Solvent: CDCl3
spectrum: chengying-1 15
ppm
168.977
167.902
155.025
102.979
142.294
130.411
126.851
112.580
86.293
81.698
77.275
77.020
76.756
76.193
75.887
52.339
51.655
51.561
50.847
29.642
26.894
25.212
CO2Me
CO2Me
O
O
NH
MeO2C
33
ppm
160
140
120
100
80
60
40
20

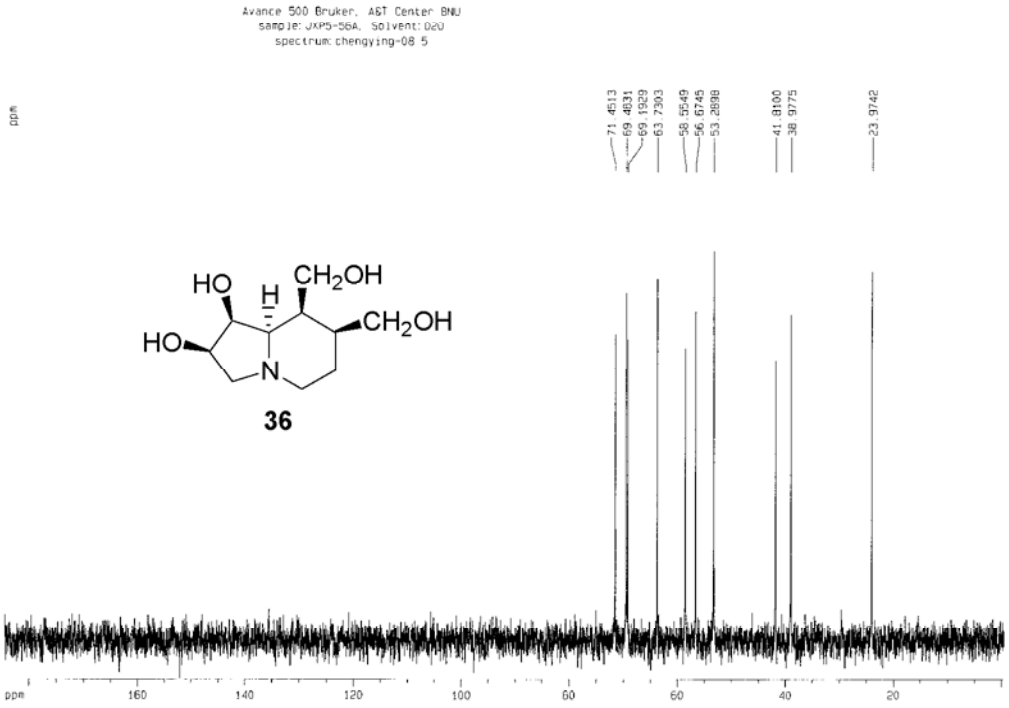

vance 500 Bruker, A&T Center BNU
sample: JXP5-41, Solvent: CDCl3
spectrum: chengying-8 1
ppm
7.26714
6.71903
5.95686
5.94556
5.01325
5.00332
4.99290
4.50600
4.47701
4.14190
4.13227
4.11290
4.10319
3.91952
3.88881
3.87817
2.06641
1.64488
1.43460
1.29342
1.28123
1.27760
1.26697
CO2CH3
CO2CH3
O
O
N
O
34
H2O
Integral
0.3797
1.0000
1.0252
1.0200
1.1431
5.9920
2.2245
2.3234
3.1686
3.5316
ppm
9
8
7
6
5
4
3
2
1
0

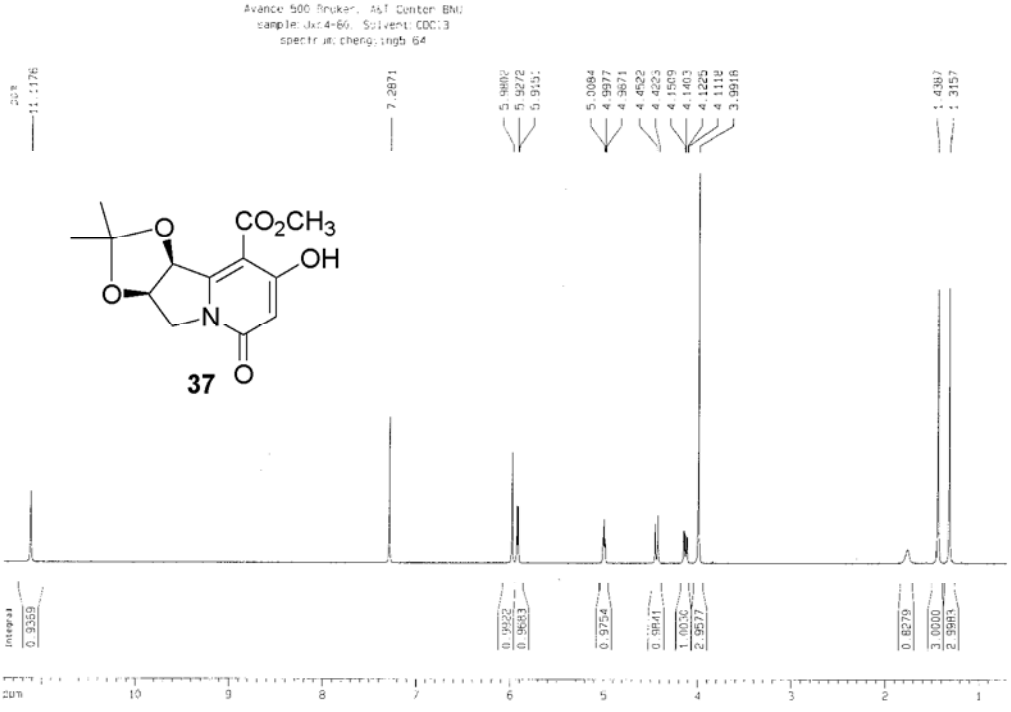

Avance 500 Bruker, AST Center BNU
sample: JXP5-41, Solvent: CDCl3
spectrum: chengying-7 46
ppm
166.220
164.243
160.320
152.623
144.341
119.571
112.787
106.839
82.193
77.296
77.042
76.788
74.544
53.560
53.028
52.548
27.096
25.671
CO2CH3
CO2CH3
O
O
N
O
34
ppm
180
160
140
120
100
80
60
40
20

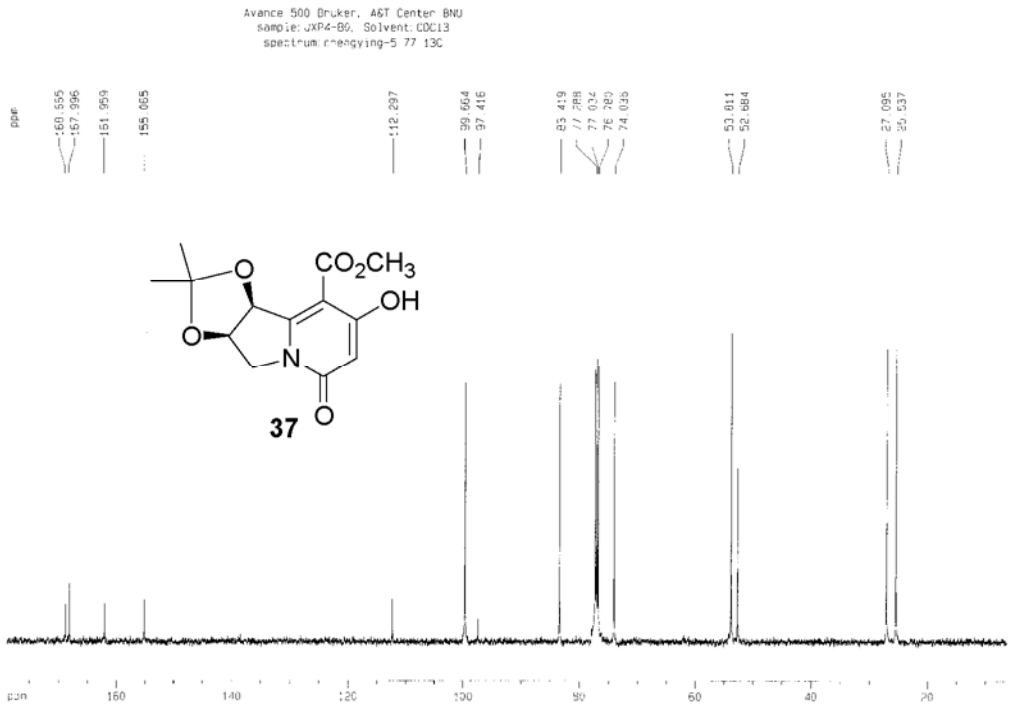

Avance 500 Bruker, AST Center BNU
sample: JXP5-42, Solvent: CDCl3
spectrum: chengying-7 25
ppm
7.28750
4.80509
4.80014
4.16481
4.14053
3.74951
3.69598
3.69482
3.69357
3.69315
3.46405
3.30843
3.28335
3.27957
3.24824
3.09985
3.08074
3.06578
2.79252
2.72123
2.69341
2.68631
1.69798
1.39055
1.37473
CO2Me
CO2Me
H
O
O
N
O
35
H2O
Integral
1.4416
1.0000
2.8851
3.8060
0.2988
1.9703
0.3257
0.3668
2.9050
3.1536
ppm
7
6
5
4
3
2
1

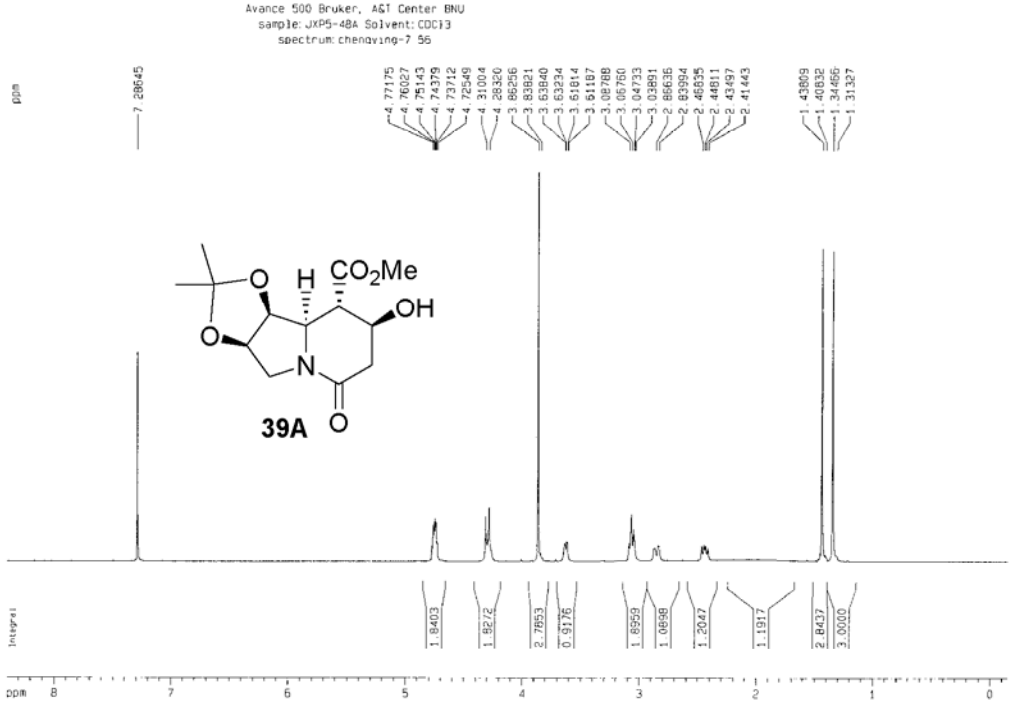

Avance 500 Bruker, A&T Center BNU
sample: JXP5-42, Solvent: CDCl3
spectrum: chengying-7 45
ppm
171.499
170.322
167.811
112.829
80.606
77.282
77.206
77.028
76.774
62.080
52.440
51.622
50.458
41.847
39.266
30.706
25.772
24.828
CO2Me
CO2Me
H
O
O
N
O
35
ppm 200 180 160 140 120 100 80 60 40 20

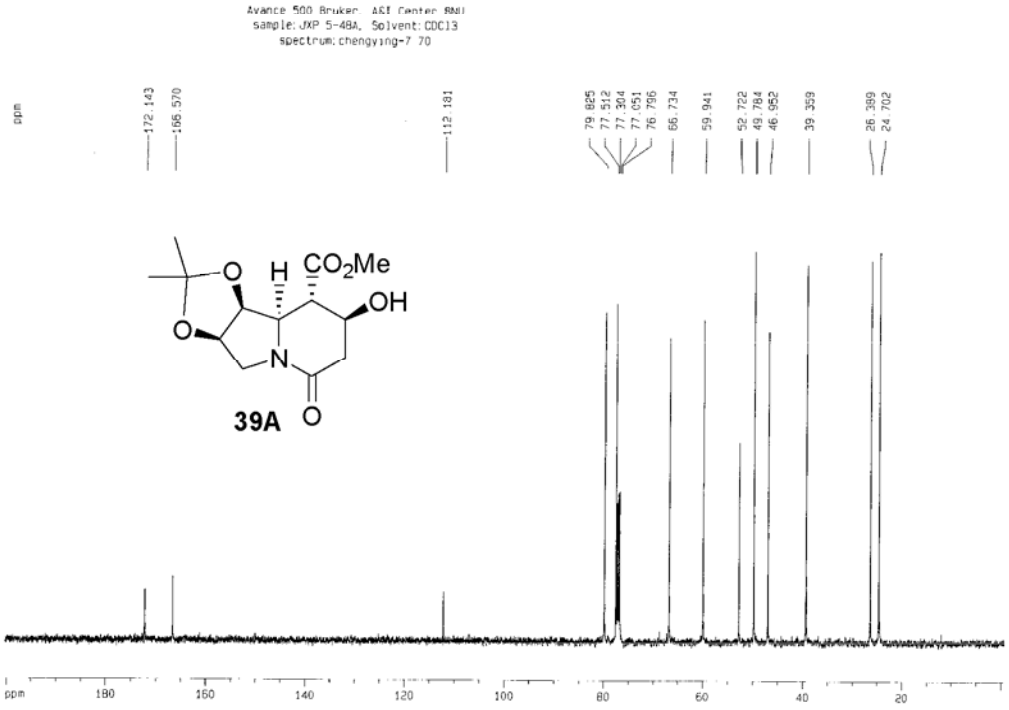

vance 500 Bruker, A&T Center BNU
sample: JXP5-56A, Solvent: D2O
spectrum: chengying-B 3
ppm
4.704
4.320
4.312
4.303
4.294
4.061
4.073
4.065
3.852
3.834
3.829
3.811
3.557
3.534
3.520
3.494
3.479
3.457
3.035
3.015
2.843
2.835
2.821
2.813
2.551
2.533
2.511
2.367
2.135
2.086
1.685
1.678
1.468
1.462
1.184
1.177
1.151
-0.082
HO
H
CH2OH
HO
CH2OH
N
36
Integral
1.0000
0.9968
1.0830
3.6466
1.0351
1.1144
1.0273
1.0645
2.2120
1.1544
1.0313
0.9598
ppm 8 7 6 5 4 3 2 1 0

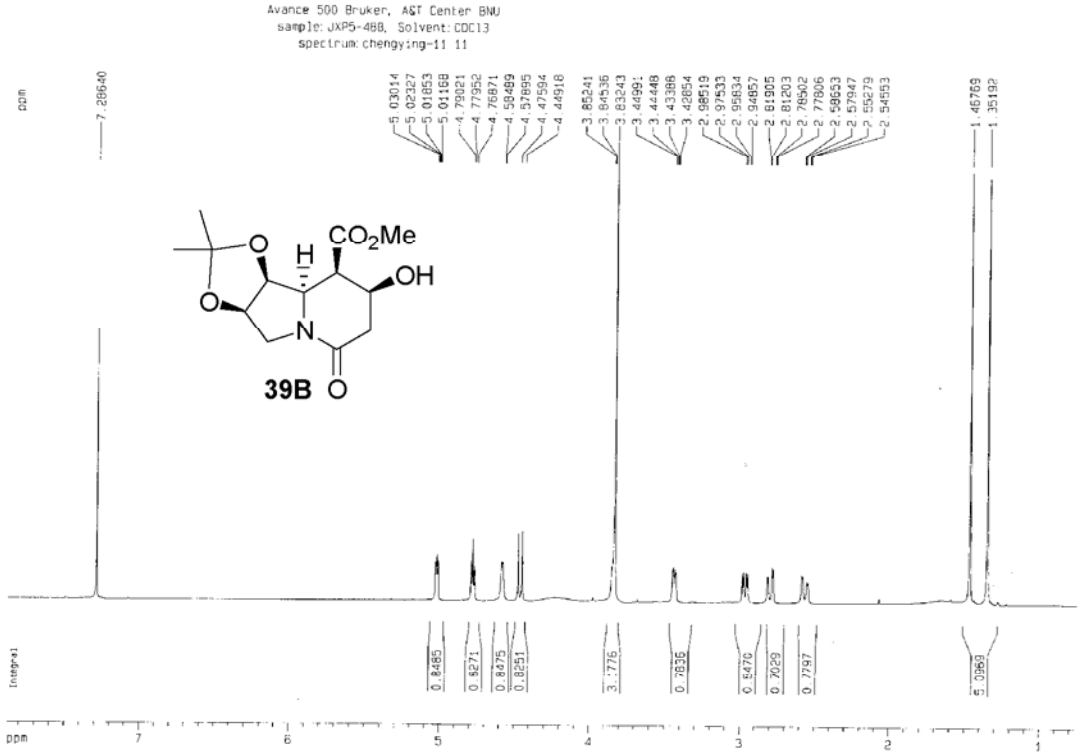

Avance 500 Bruker, A&T Center BNU
sample: JXP5-56A, Solvent: D2O
spectrum: chengying-08 5
ppm
71.4513
69.4631
69.1929
63.7303
58.5549
56.6745
53.2898
41.8100
38.9775
23.9742
HO
H
CH2OH
HO
CH2OH
N
36
ppm
160
140
120
100
80
60
40
20

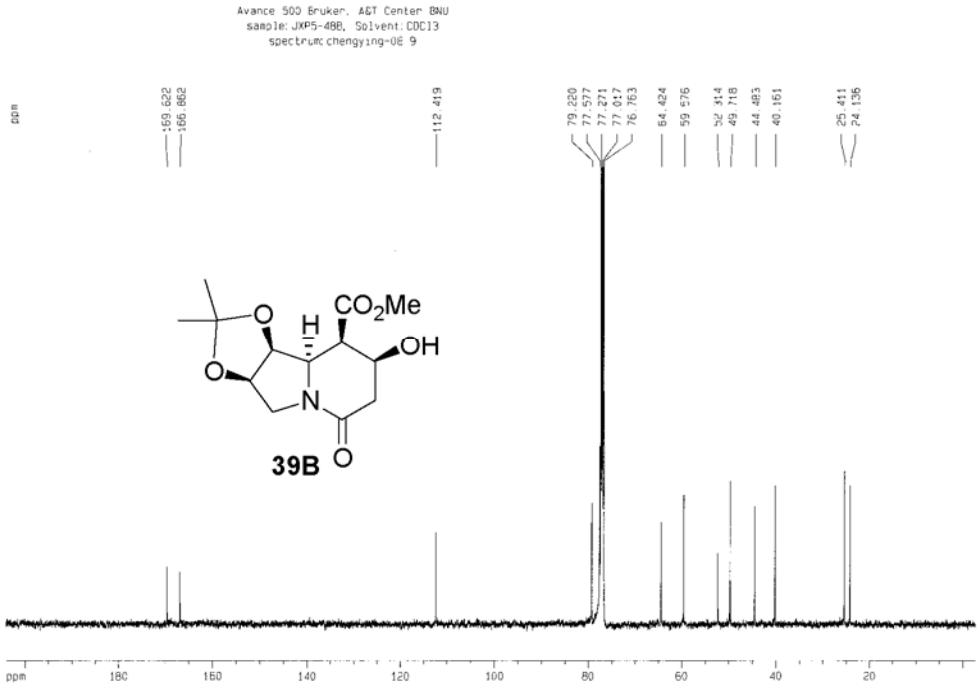

Avance 500 Bruker, A&T Center BNU
sample: Jxc4-86, Solvent: CDCl3
spectr um: cheng;ing5 64
11.1176
7.2871
5.9802
5.9272
5.9151
5.0084
4.9997
4.9671
4.4522
4.4223
4.1509
4.1403
4.1225
4.1110
3.9918
1.4387
1.3157
CO2CH3
OH
O
O
N
O
37
Integral
0.9359
0.9922
0.9683
0.9754
0.9841
1.0036
2.9577
0.8279
3.0000
2.9983
ppm
10
9
8
7
6
5
4
3
2
1

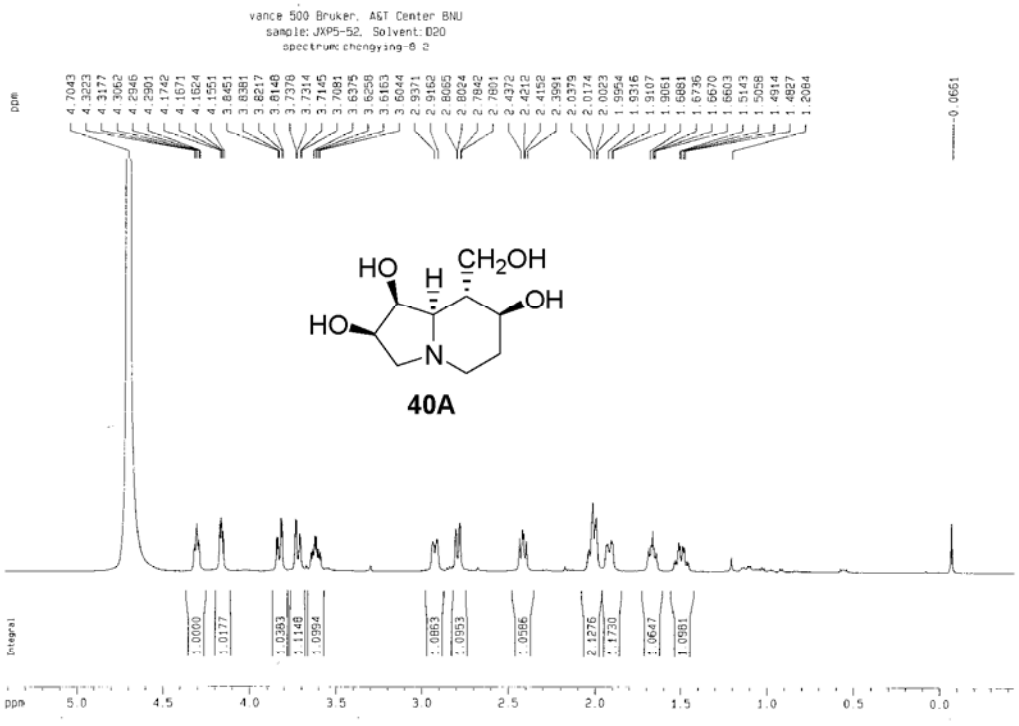

Avance 500 Bruker, A&T Center BNU
sample: JXP4-B9, Solvent: CDCl3
spectrum: chengying-5 77 13C
ppm
160.555
157.996
151.959
155.065
112.297
99.664
97.416
83.419
77.288
77.034
76.780
74.036
53.011
52.684
27.095
26.537
CO2CH3
OH
O
O
N
O
37
ppm
160
140
120
100
80
60
40
20

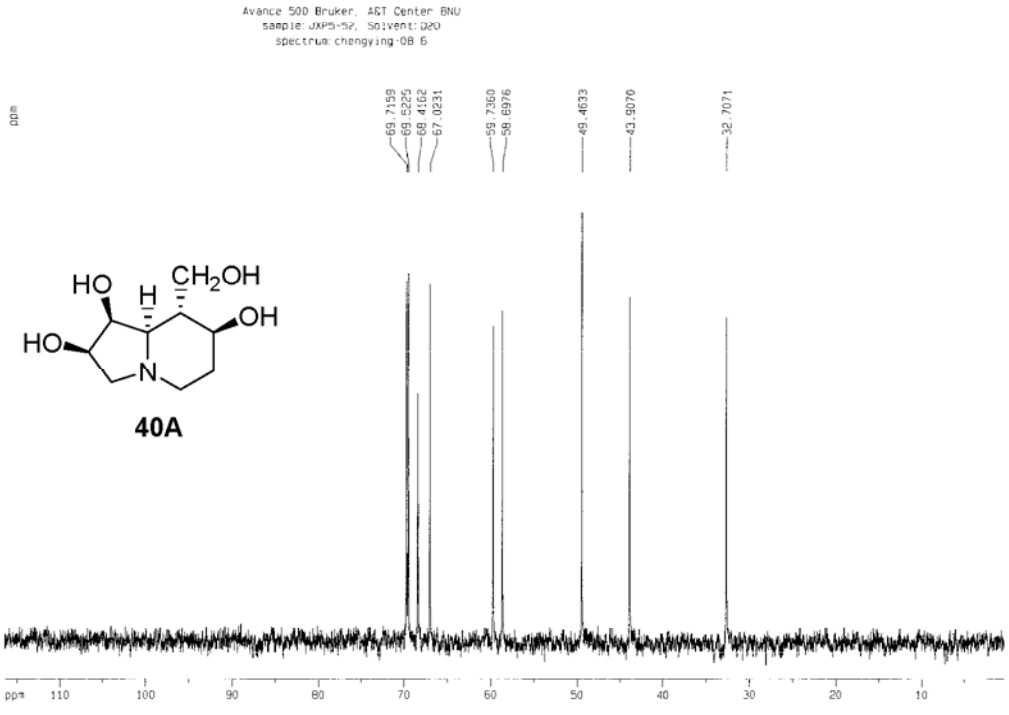

Avance 500 Bruker, A&T Center BNU
sample: JXP5-48A Solvent: CDCl3
spectrum: chengying-7 56
ppm
7.28645
4.77175
4.76027
4.75143
4.74379
4.73712
4.72549
4.31004
4.28320
3.86256
3.83821
3.63840
3.63234
3.61814
3.61187
3.08788
3.06760
3.04733
3.03891
2.86636
2.83994
2.46535
2.44811
2.43497
2.41443
1.43869
1.40832
1.34466
1.31327
H
CO2Me
OH
O
O
N
O
39A
Integral
1.8403
1.9272
2.7853
0.9176
1.8959
1.0698
1.2047
1.1917
2.8437
3.0000
ppm
8
7
6
5
4
3
2
1
0


Avance 500 Bruker A&I Center BNU
sample: JXP 5-48A, Solvent: CDCl3
spectrum: chengying-7 70
ppm
172.143
166.570
112.181
79.825
77.512
77.304
77.051
76.796
66.734
59.941
52.722
49.784
46.952
39.359
26.399
24.702
CO2Me
H
O
OH
N
O
39A
ppm
180
160
140
120
100
80
60
40
20


Avance 500 Bruker, A&T Center BNU
sample: JXP5-48B, Solvent: CDCl3
spectrum: chengying-11 11
ppm
7.26640
5.03014
5.02327
5.01853
5.01168
4.79021
4.77952
4.76871
4.59489
4.57895
4.47594
4.44918
3.85241
3.84536
3.83243
3.44991
3.44448
3.43388
3.42654
2.98519
2.97533
2.95834
2.94857
2.81905
2.81203
2.78502
2.77806
2.59653
2.57947
2.55279
2.54593
1.46769
1.35192
CO2Me
H
O
OH
N
O
39B
Integral
0.8485
0.8271
0.8475
0.8251
3.1776
0.7836
0.5476
0.7029
0.7797
5.0969
ppm
7
6
5
4
3
2
1


Avance 500 Bruker, A&T Center BNU
sample: JXP5-48B, Solvent: CDCl3
spectrum: chengying-0E 9
ppm
159.622
166.662
112.419
79.220
77.577
77.271
77.017
76.763
64.424
59.676
52.314
49.718
44.483
40.161
25.411
24.136
CO2Me
OH
O
H
N
O
39B
ppm
180
160
140
120
100
80
60
40
20


vance 500 Bruker, A&T Center BNU
sample: JXP5-52, Solvent: D2O
spectrum: chengying-0 2
ppm
4.7043
4.3223
4.3177
4.3062
4.2946
4.2901
4.1742
4.1671
4.1624
4.1551
3.8451
3.8381
3.8217
3.8148
3.7378
3.7314
3.7145
3.7081
3.6375
3.6258
3.6163
3.6044
2.9371
2.9162
2.8065
2.8024
2.7842
2.7801
2.4372
2.4212
2.4152
2.3991
2.0379
2.0174
2.0023
1.9954
1.9316
1.9107
1.9061
1.6881
1.6736
1.6670
1.6603
1.5143
1.5058
1.4914
1.4827
1.2084
0.0661
HO
H
CH2OH
OH
HO
N
40A
Integral
1.0000
1.0177
0.0383
0.1148
0.0994
0.0863
0.0953
0.0586
2.1276
2.1730
1.0647
1.0981
ppm
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


Avance 500 Bruker, A&T Center BNU
sample: JXP5-52, Solvent: D2O
spectrum: chengying-DB 6
ppm
69.7159
69.5225
68.4162
67.0231
59.7360
59.6976
49.4633
43.9070
32.7071
HO
H
CH2OH
OH
HO
N
40A
ppm 110 100 90 80 70 60 50 40 30 20 10