Supporting Information

Structures, Biological Activities, and Total Syntheses of 13-Hydroxy- and 13-Acetoxy-14-mordehydrocacalohastine, Novel Modified Furanoeremophilane Type Sesquiterpenes from *Trichilia cuneata*

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Natural 13-Hydroxy-14-nordehydrocacalohastine (2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (1H, d, *J* = 8.6 Hz), 7.89 (1H, s), 7.69 (1H, s), 7.34 (1H, dd, *J* = 8.6, 6.8 Hz), 7.28 (1H, br d, *J* = 6.8 Hz), 4.95 (2H, s), 4.36 (3H, s), 2.75 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2 (d), 142.7 (s), 138.9 (s), 134.0 (s), 130.8 (s), 129.8 (s), 125.3 (d), 124.9 (s), 124.1 (d), 120.5 (s), 120.4 (d), 107.7 (d), 60.9 (q), 56.1 (t), 20.3 (q); IR (neat) 3363, 2940, 2861, 1634, 1601, 1509, 1462, 1412, 1396, 1330, 1216, 1103, 1059, 1033, 1009, 942, 845, 820, 797, 753 cm^{-1}; UV λ_{max} (EtOH) 342 (ε 5437), 327 (ε 6360), 318 (ε 6568), 246 (ε 51624), 242 (ε 51229); EI-MS *m/z* (relative intensity) 243 [$(M + H)^+$, 17], 242 (M^+, 100), 227 (84); EI-HRMS calcd for $C_{15}H_{15}O_3$ [$(M + H)^+$] 243.1022, found 243.0999; EI-HRMS calcd for $C_{15}H_{14}O_3$ (M^+) 242.0943, found 242.0942.

Natural 13-Acetoxy-14-nordehydrocacalohastine (3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (1H, d, *J* = 8.5 Hz), 7.86 (1H, s), 7.76 (1H, s), 7.35 (1H, dd, *J* = 8.5, 6.8 Hz), 7.29 (1H, br d, *J* = 6.8 Hz), 5.36 (2H, s), 4.36 (3H, s), 2.76 (3H, s), 2.12 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9 (s), 146.0 (d), 142.5 (s), 139.0 (s), 133.9 (s), 130.9 (s), 129.1 (s), 125.4 (d), 124.9 (s), 124.2 (d), 120.4 (d), 116.1 (s), 107.5 (d), 60.9 (q), 56.6 (t), 20.9 (q), 20.4 (q); IR (KBr) 2975, 2935, 2858, 1734, 1633, 1606, 1594, 1508, 1450, 1396, 1246, 1185, 1088, 1040, 927, 844 cm^{-1}; UV λ_{max} (EtOH) 343 (ε

6617), 318 (ε 8442), 246 (ε 62329); EI-MS *m/z* (relative intensity) 284 (M^+, 100), 242 (35), 225 (26), 199 (21), 108 (24); EI-HRMS calcd for $C_{17}H_{16}O_4$ (M^+) 284.1027, found 284.1032.

Natural Maturinone (4): mp 155.5–156.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (1H, dd, *J* = 7.6, 1.0 Hz), 7.57 (1H, t, *J* = 7.6 Hz), 7.504 (1H, q, *J* = 1.2 Hz), 7.497 (1H, dq, *J* = 7.6, 1.0 Hz), 2.80 (3H, s), 2.37 (3H, d, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.4 (s), 173.6 (s), 152.0 (s), 145.8 (d), 142.0 (s), 138.2 (d), 134.3 (s), 132.6 (d), 130.8 (s), 129.8 (s), 125.8 (d), 121.9 (s), 23.0 (q), 8.76 (q); IR (KBr) 2980, 2930, 1725, 1685, 1597, 1534, 1415, 1381, 1285, 1222, 1207, 1150, 1108, 1092, 1022, 993, 837, 809, 762, 739 cm^{-1}; UV λ_{max} (EtOH) 350 (ε 2231), 306 (ε 1773), 250 (ε 14872); EI-MS *m/z* (relative intensity) 226 (M^+, 100), 197 (24), 141 (42), 115 (27); EI-HRMS calcd for $C_{14}H_{10}O_3$ (M^+) 226.0630, found 226.0614.

1- Penten-4-yn-3-ol (8). To a solution of trimethylsilylacetylene (4.32 mL, 30.0 mmol) in 120 mL of tetrahydrofuran was added dropwise *n*-butyllithium (18.8 mL, 30.0 mmol, 1.6 M in hexane) at 0 °C under a nitrogen atmosphere, and the solution was stirred at the same temperature for 30 min. To the solution was added dropwise a solution of acrolein (1.76 mL, 30.0 mmol) in 15 mL of tetrahydrofuran at 0 °C, and the solution was stirred at 45 °C for 1.5 h. After the solution was cooled to room temperature, a cold saturated aqueous solution of ammonium chloride (120 mL) was added to the reaction mixture, and the resulting mixture was extracted with ether (100 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo under 15 °C to afford a secondary alcohol, R_f = 0.50 (hexane/ethyl acetate = 4:1), which was taken to the next step without further purification.

To the solution of the above secondary alcohol in 100 mL of methanol was added a portion of potassium carbonate (6.0 g, 43.4 mmol) at room temperature, and the solution was stirred at 45 °C for 1.5 h. After the solution was cooled to room temperature, a cold saturated aqueous solution of ammonium chloride (600 mL) was added to the solution, and the resulting mixture was extracted with ether (200 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium

sulfate, and the ether solvent was distilled off under atmospheric pressure. The residue was subjected to column chromatography (pentane/ether = 6:1) on 270 g of silica gel to provide some fractions containing the product. Pentane and ether of the combined fractions were removed under atmospheric pressure, and the residue was distilled at 27–33 °C/20 mmHg to yield 1-penten-4-yn-3-ol (**8**) (1.98 g, 80.3% yield from trimethylsilylacetylene) as a colorless oil: R_f = 0.26 (hexane/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (1H, ddd, *J* = 17.1, 10.2, 5.4 Hz), 5.51 (1H, dt, *J* = 17.1, 1.2 Hz), 5.26 (1H, d, *J* = 10.2 Hz), 4.89 (1H, t, *J* = 5.0 Hz), 2.59 (1H, d, *J* = 2.2 Hz), 2.05 (1H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9 (d), 117.2 (t), 82.8 (s), 74.6 (d), 63.2 (d); IR (neat) 3350, 3300, 3091, 3023, 2987, 2960, 2877, 2118, 1644, 1422, 1409, 1309, 1254, 1122, 1022, 987, 935, 866, 846 cm^{-1}; EI-MS *m/z* (relative intensity) 82 (M^+, 5.0), 81 [$(M - H)^+$, 100], 55 (62), 53 (71), 39 (93); EI-HRMS calcd for C_5H_5O [$(M - H)^+$] 81.0340, found 81.0344.

Ester 10. *n*-Butyllithium (12.5 mL, 20.0 mmol, 1.6 M in hexane) was added dropwise to a solution of alcohol **8** (1.64 g, 20.0 mmol) in tetrahydrofuran (12.5 mL) at 0 °C under a nitrogen atmosphere, and the solution was allowed to reach room temperature (15 min). In a separate flask, *n*-butyllithium (0.625 mL, 1.0 mmol) was added dropwise to a well-stirred suspension of dichlorobis(triphenylphosphine)palladium(II) (350 mg, 0.5 mmol) in dimethyl sulfoxide (20 mL) (rt, 1 h) to give a dark red homogeneous solution. To this palladium solution were successively added dropwise a mixture of diethyl ethoxymethylenemalonate (**9**) (2.02 mL, 10.0 mmol) and 2-iodotoluene (**7**) (1.08 mL, 10.0 mmol) in tetrahydrofuran (10 mL), and the lithium alkoxide solution at room temperature. The reaction mixture was stirred at 40 °C for 12 h. A saturated aqueous solution of ammonium chloride (20 mL) and water (50 mL) were added to the reaction mixture, and the resulting mixture was filtered through a pad of Celite under reduced pressure. The filtrates were extracted with ether (40 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 50:1) on 270 g of silica gel to yield ester **10** (918 mg) and a mixture

containing mainly the precursor **11** (730 mg). A solution of potassium *tert*-butoxide (254 mg, 2.26 mmol) in tetrahydrofuran (5 mL) was added dropwise to a solution of the precursor **11** (730 mg, 1.88 mmol at most) in tetrahydrofuran (15 mL) at room temperature under a nitrogen atmosphere, and the reaction mixture was stirred at 40 °C for 12 h. Water (20 mL) was added to the reaction mixture, and the resulting mixture was extracted with ether (15 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 50:1) on 90 g of silica gel to furnish ester **10** (432 mg, total 1.35 g, 50.0% overall yield) as a colorless oil**:** R_f = 0.74 (hexane/ethyl acetate = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (1H, s), 7.15 (1H, d, *J* = 6.8 Hz), 7.09 (1H, t, *J* = 6.9 Hz), 7.05 (1H, t, *J* = 7.1 Hz), 6.82 (1H, d, *J* = 7.0 Hz), 6.29 (1H, dd, *J* = 17.4, 11.4 Hz), 5.67 (1H, d, *J* = 17.2 Hz), 5.16 (1H, d, *J* = 11.6 Hz), 4.16 (2H, q, *J* = 7.3 Hz), 4.03 (2H, s), 2.36 (3H, s), 1.17 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (s), 151.6 (s), 147.7 (d), 138.0 (s), 136.0 (s), 129.8 (d), 127.4 (d), 126.0 (d), 125.9 (d), 122.7 (d), 120.0 (s), 119.3 (s), 113.4 (t), 60.1 (t), 26.6 (t), 19.7 (q), 14.0 (q); IR (neat) 3022, 2980, 2925, 1723, 1640, 1607, 1530, 1432, 1309, 1238, 1160, 1102, 1025, 979, 907, 832, 769, 751 cm^{-1}; EI-MS *m/z* (relative intensity) 271 [$(M + H)^+$, 15], 270 (M^+, 79), 224 (100), 209 (55); EI-HRMS calcd for $C_{17}H_{18}O_3$ (M^+) 270.1256, found 270.1248.

Aldehyde 12. A portion of osmium tetroxide (6.0 mg, 24.0 μmol) was added to a solution of alkene **10** (3.23 g, 12.0 mmol) and sodium metaperiodate (7.70 g, 36.0 mmol) in tetrahydrofuran (117 mL) and water (39 mL) at 0 °C, and the solution was vigorously stirred at the same temperature for 30 min. The solution was further stirred at 35 °C for additional 2 h. Water (200 mL) was added to the solution, and the aqueous layer was extracted with ether (100 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 10:1) on 270 g of silica gel to give aldehyde **12** (1.63 g, 50.0% yield) as a colorless oil: R_f = 0.54 (hexane/ethyl acetate = 3:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (1H, s), 8.23 (1H, s), 7.19 (1H, d, *J* = 7.2 Hz), 7.14 (1H, t, *J* = 8.1 Hz),

7.08 (1H, t, *J* = 7.7 Hz), 6.85 (1H, d, *J* = 7.3 Hz), 4.39 (2H, s), 4.23 (2H, q, *J* = 7.2 Hz), 2.37 (3H, s), 1.23 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2 (d), 161.9 (s), 152.1 (d), 150.5 (s), 136.7 (s), 136.1 (s), 135.0 (s), 130.3 (d), 127.5 (d), 126.7 (d), 126.2 (d), 120.9 (s), 60.8 (t), 27.1 (t), 19.7 (q), 14.0 (q); IR (neat) 2870, 2725, 2685, 1732, 1695, 1589, 1460, 1420, 1377, 1294, 1244, 1200, 1163, 1094, 1026, 893, 862, 849, 826, 800, 770, 743 cm^{-1}; FAB-MS *m/z* (relative intensity) 273.1 [$(M + H)^+$, 100], 272.1 (M^+, 34), 227.1 (68), 154.1 (41), 137.1 (32), 136.1 (32); FAB-HRMS calcd for $C_{16}H_{17}O_4$ [$(M + H)^+$] 273.1126, found 273.1133.

Carboxylic Acid 6. Sodium dihydrogen phosphate (210 mg, 1.75 mmol), 2-methyl-2-butene (0.742 mL, 7.0 mmol), and sodium chlorite (127 mg, 1.4 mmol) were consecutively added to a solution of aldehyde **12** (94.7 mg, 0.35 mmol) in *tert*-butyl alcohol (6 mL) and water (2.4 mL) at 0 °C under a nitrogen atmosphere, and the solution was stirred at 40 °C for 1 h. Water (7.2 mL) was added to the solution, and the aqueous layer was adjusted to pH 2 with a 20% aqueous solution of phosphoric acid. The aqueous layer was extracted with dichloromethane (10 mL × 3). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The rresidue was subjected to column chromatography (chloroform/methanol = 9:1) on 45 g of silica gel to afford carboxylic acid **6** (81.0 mg, 80.4% yield) as an amorphous solid: R_f = 0.67 (chloroform/methanol = 4:1); mp 67–68 °C; ^{1}H NMR (300 MHz, CD_3OD) δ 8.28 (1H, s), 7.11 (1H, d, *J* = 6.8 Hz), 7.01 (1H, t, *J* = 8.0 Hz), 6.95 (1H, t, *J* = 7.5 Hz), 6.62 (1H, d, *J* = 7.2 Hz), 4.41 (2H, s), 4.11 (2H, q, *J* = 7.2 Hz), 2.39 (3H, s), 1.11 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 163.9 (s), 162.9 (s), 151.6 (d), 146.4 (s), 139.2 (s), 137.1 (s), 131.5 (s), 130.6 (d), 127.5 (d), 126.7 (d), 121.8 (s), 61.5 (t), 27.8 (t), 19.9 (q), 14.3 (q); IR (KBr) 3600–2500, 2980, 2936, 1728, 1599, 1536, 1423, 1286, 1152, 1107, 1093, 1021, 990, 836, 808, 762, 742 cm^{-1}; FAB-MS *m/z* (relative intensity) 289.1 [$(M + H)^+$, 92], 288.1 (M^+, 11), 243.1 (100), 242.1 (36); FAB-HRMS calcd for $C_{16}H_{17}O_5$ [$(M + H)^+$] 289.1076, found 289.1078.

Ester 13. To a solution of carboxylic acid **6** (81.0 mg, 0.28 mmol) in 6 mL of trifluoroacetic acid

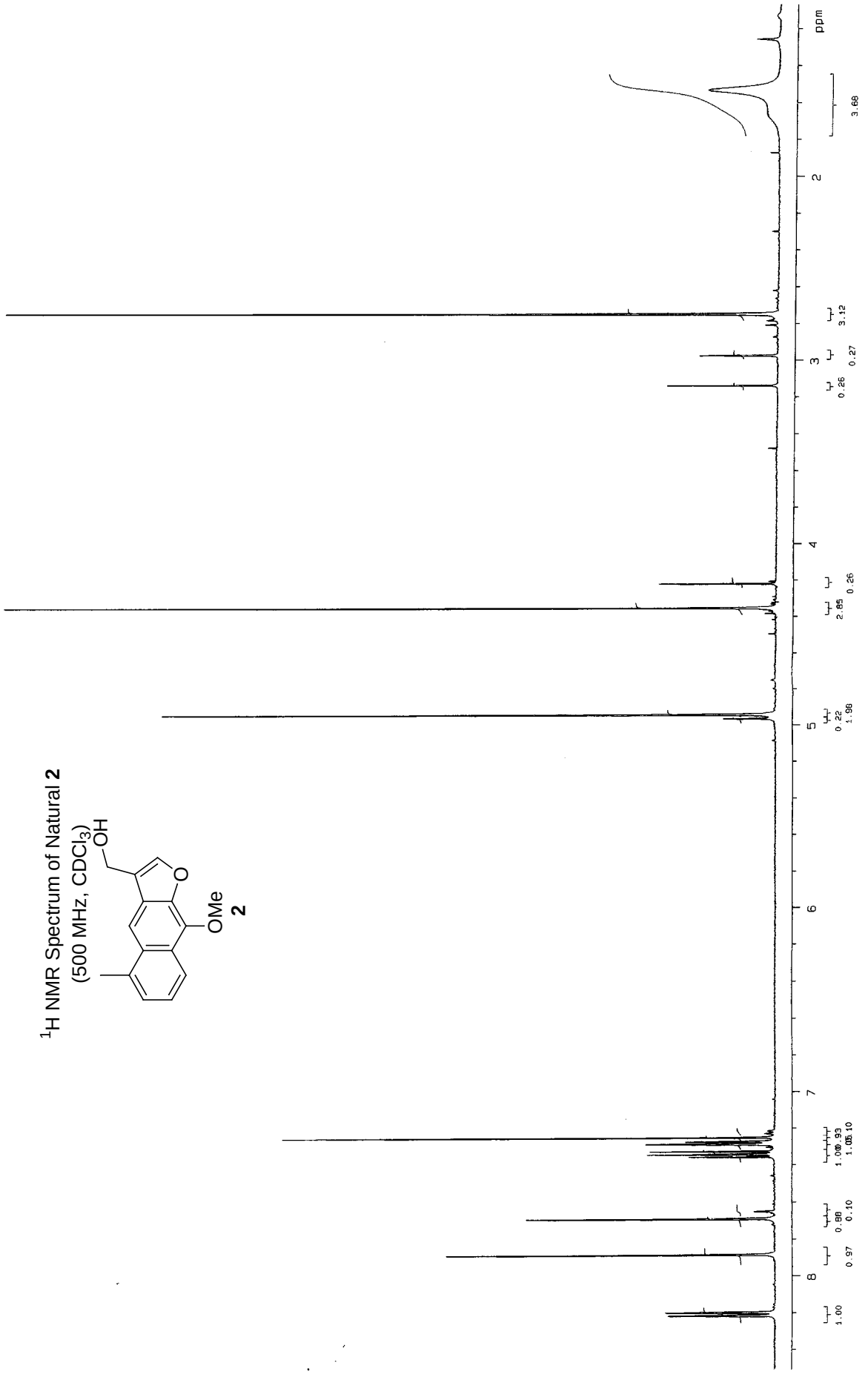
was added dropwise trifluoroacetic anhydride (0.5 mL, 1.4 mmol) at 0 °C under a nitrogen atmosphere, and the solution was stirred at 35 °C for 12 h. After the solution was cooled to 0 °C, water (20 mL) was added to the solution, and the solution was adjusted to pH 8 with a 50% aqueous solution of sodium hydroxide. The solution was stirred at 0 °C for 30 min, and the aqueous layer was extracted with dichloromethane (15 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was subjected to column chromatography (dichloromethane/methanol = 99:1) on 45 g of silica gel to provide a phenolic product (59.7 mg, 79.0% yield) as a colorless oil.

To a solution of the phenolic product (50 mg, 0.19 mmol) and potassium carbonate (315 mg, 2.28 mmol) in 20 mL of acetone was added dropwise dimethyl sulfate (0.128 mL, 0.76 mmol) at room temperature under a nitrogen atmosphere, and the solution was stirred at 56 °C for 12 h. After the solution was cooled to room temperature, the precipitates were filtered off through silica gel. To the filtrates was added water (20 mL), and the solution was stirred at room temperature for 30 min. The aqueous layer was extracted with ether (20 mL × 3). The organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 99:1) on 23 g of silica gel to yield ester **13** (37.4 mg, 67.9% yield) as a colorless oil: R_f = 0.56 (hexane/ethyl acetate = 4:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (1H, s), 8.33 (1H, s), 8.21 (1H, d, *J* = 8.3 Hz), 7.38 (1H, dd, *J* = 8.3, 6.7 Hz), 7.32 (1H, d, *J* = 6.8 Hz), 4.46 (2H, q, *J* = 7.2 Hz), 4.37 (3H, s), 2.78 (3H, s), 1.47 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5 (s), 153.1 (d), 142.7 (s), 139.1 (s), 134.5 (s), 131.6 (s), 126.3 (s), 125.8 (d), 124.9 (s), 124.6 (d), 120.4 (d), 114.7 (s), 110.3 (d), 61.0 (q), 60.6 (t), 20.1 (q), 14.3 (q); IR (neat) 2981, 2941, 2862, 1719, 1635, 1577, 1510, 1463, 1410, 1395, 1292, 1277, 1251, 1237, 1174, 1111, 1043, 1004, 939, 855, 829, 797, 771, 751 cm^{-1}; FAB-MS *m/z* (relative intensity) 285.2 [$(M + H)^+$, 29], 284.2 (M^+, 62), 269.1 (23), 154.1 (100), 136.1 (70); FAB-HRMS calcd for $C_{17}H_{16}O_4$ (M^+) 284.1048, found 284.1054.

Synthetic 13-Hydroxy-14-nordehydrocacalohastine (2). To a solution of ester **13** (18 mg, 62.5 μmol) in 5 mL of toluene was added dropwise diisobutylaluminum hydride (0.20 mL, 0.188 mmol, 0.94 M in hexane) at –78 °C under a nitrogen atmosphere, and the solution was stirred at the same temperature for 1 h. Water (18 μL) was added to the solution, and the mixture was vigorously stirred at 0 °C for 5 min. The resulting mixture was filtered through a pad of Celite, and the filtrates were concentrated under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate = 8:1) on 14 g of silica gel to give the synthetic 13-hydroxy-14-nordehydrocacalohastine (**2**) (12 mg, 79.4% yield) as a colorless oil: R_f = 0.41 (benzene/ethyl acetate = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (1H, d, *J* = 8.5 Hz), 7.86 (1H, s), 7.66 (1H, s), 7.34 (1H, dd, *J* = 8.5, 6.8 Hz), 7.27 (1H, d, *J* = 6.6 Hz), 4.92 (2H, s), 4.34 (3H, s), 2.74 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1 (d), 142.7 (s), 138.9 (s), 133.9 (s), 130.8 (s), 129.2 (s), 125.3 (d), 124.9 (s), 124.1 (d), 120.5 (s), 120.3 (d), 107.7 (d), 60.9 (q), 56.0 (t), 20.2 (q); IR (neat) 3363, 2939, 2861, 1635, 1601, 1509, 1462, 1412, 1396, 1329, 1216, 1170, 1103, 1050, 1031, 1008, 940, 844, 798, 750 cm^{-1}; UV λ_{max} (EtOH) 343 (ε 5708), 327 (ε 6766), 318 (ε 7047), 247 (ε 56637); FAB-MS *m/z* (relative intensity) 243.2 [$(M + H)^+$, 31], 242.2 (M^+, 90), 227.2 (33), 225.2 (40), 41.0 (100); FAB-HRMS calcd for $C_{15}H_{14}O_3$ (M^+) 242.0943, found 242.0942.

Synthetic 13-Acetoxy-14-nordehydrocacalohastine (3). A solution of the synthetic alcohol **2** (25 mg, 0.1 mmol) in pyridine (1.25 mL) and acetic anhydride (0.9 mL) was stirred at room temperature under a nitrogen atmosphere for 2 d. The solution was poured into ice water (10 mL), and the aqueous layer was extracted with ether (5 mL × 3). The organic layer was washed with 0.5 M aqueous hydrochloric acid, a saturated aqueous solution of sodium bicarbonate, and brine. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography (hexane/ethyl acetate = 8:1) on 45 g of silica gel to afford the synthetic 13-acetoxy-14-nordehydrocacalohastine (**3**) (25.0 mg, 88.0% yield) as a white solid: R_f =

0.41 (hexane/ethyl acetate = 4:1); mp 79.5–80.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (1H, d, *J* = 8.8 Hz), 7.86 (1H, s), 7.77 (1H, s), 7.36 (1H, dd, *J* = 8.7, 6.7 Hz), 7.30 (1H, d, *J* = 6.6 Hz), 5.36 (2H, s), 4.36 (3H, s), 2.76 (3H, s), 2.13 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3 (s), 146.2 (d), 142.5 (s), 139.1 (s), 134.1 (s), 131.0 (s), 129.2 (s), 125.5 (d), 124.9 (s), 124.3 (d), 120.5 (d), 116.1 (s), 107.6 (d), 60.9 (q), 56.6 (t), 20.8 (q), 20.2 (q); IR (KBr) 2976, 2942, 2860, 1741, 1635, 1594, 1507, 1451, 1393, 1365, 1335, 1249, 1173, 1097, 1039, 926, 838, 792 cm^{-1}; UV λ_{max} (EtOH) 343 (ε 5396), 318 (ε 6851), 246 (ε 54740); FAB-MS *m/z* (relative intensity) 285.1 [$(M + H)^+$, 28], 284.1 (M^+, 100), 225.1 (39), 154.1 (58), 136.1 (40); FAB-HRMS calcd for $C_{17}H_{16}O_4$ (M^+) 284.1048, found 284.1046. Anal. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67. Found: C, 71.81; H, 5.63.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(500 MHz, $CDCl_3$)
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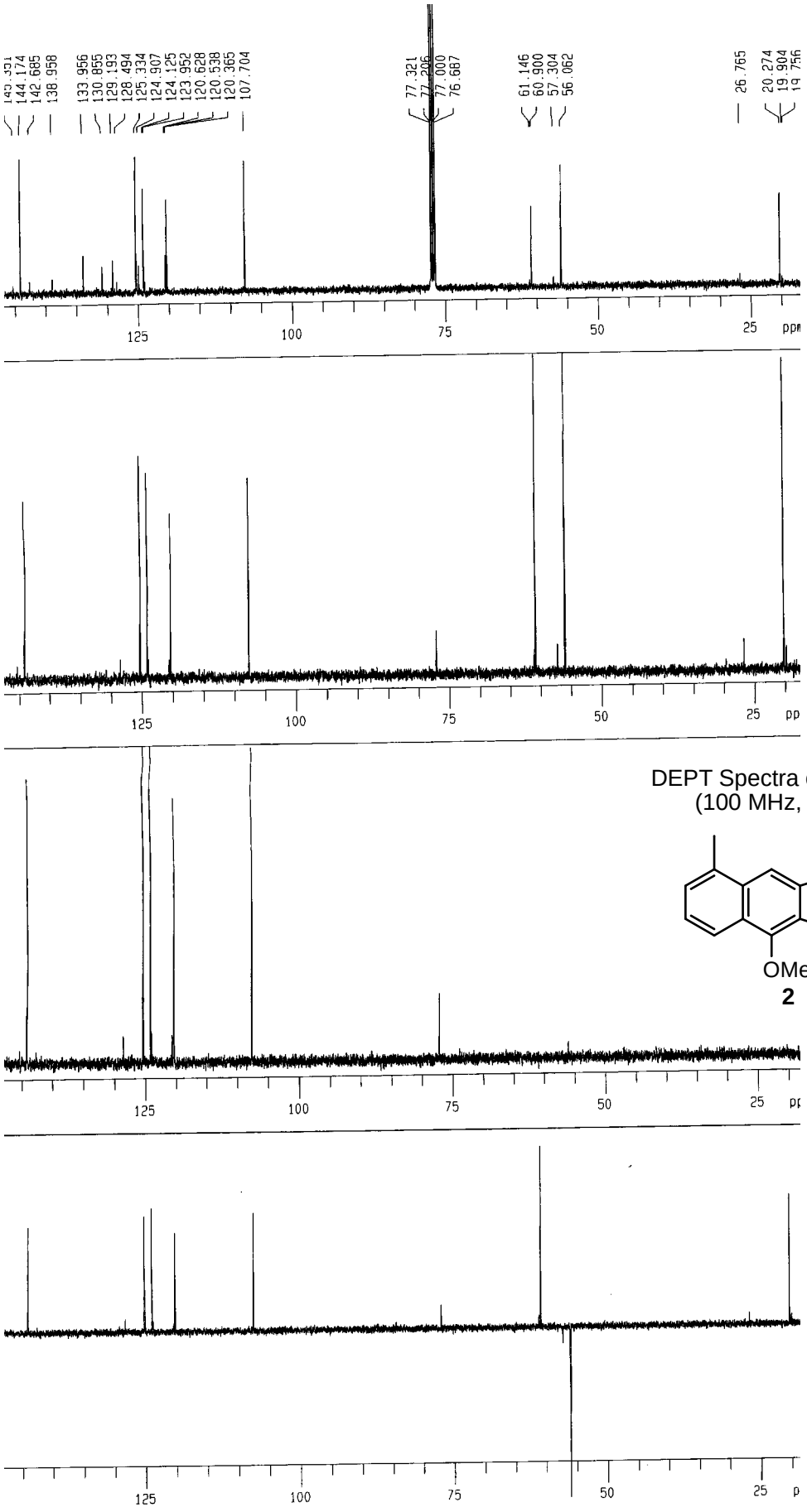
OMe
2
ppm



DEPT Spectra of Natural **2**
(100 MHz, $CDCl_3$)

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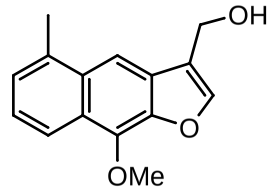
H-H COSY Spectrum of Natural **2**
(500 MHz, $CDCl_3$)



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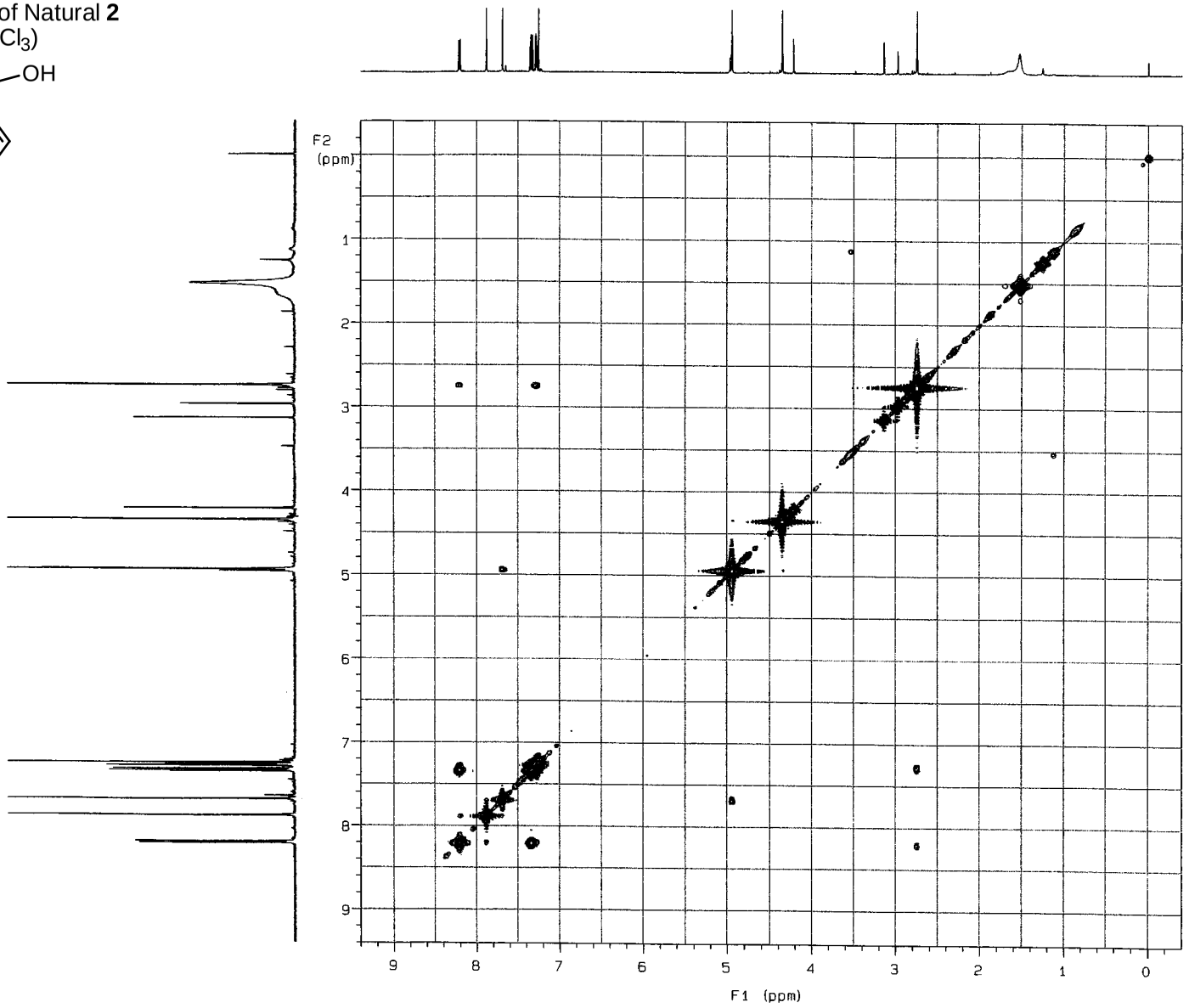
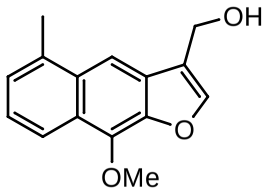


HMQC Spectrum of Natural **2**
(500 MHz, $CDCl_3$)



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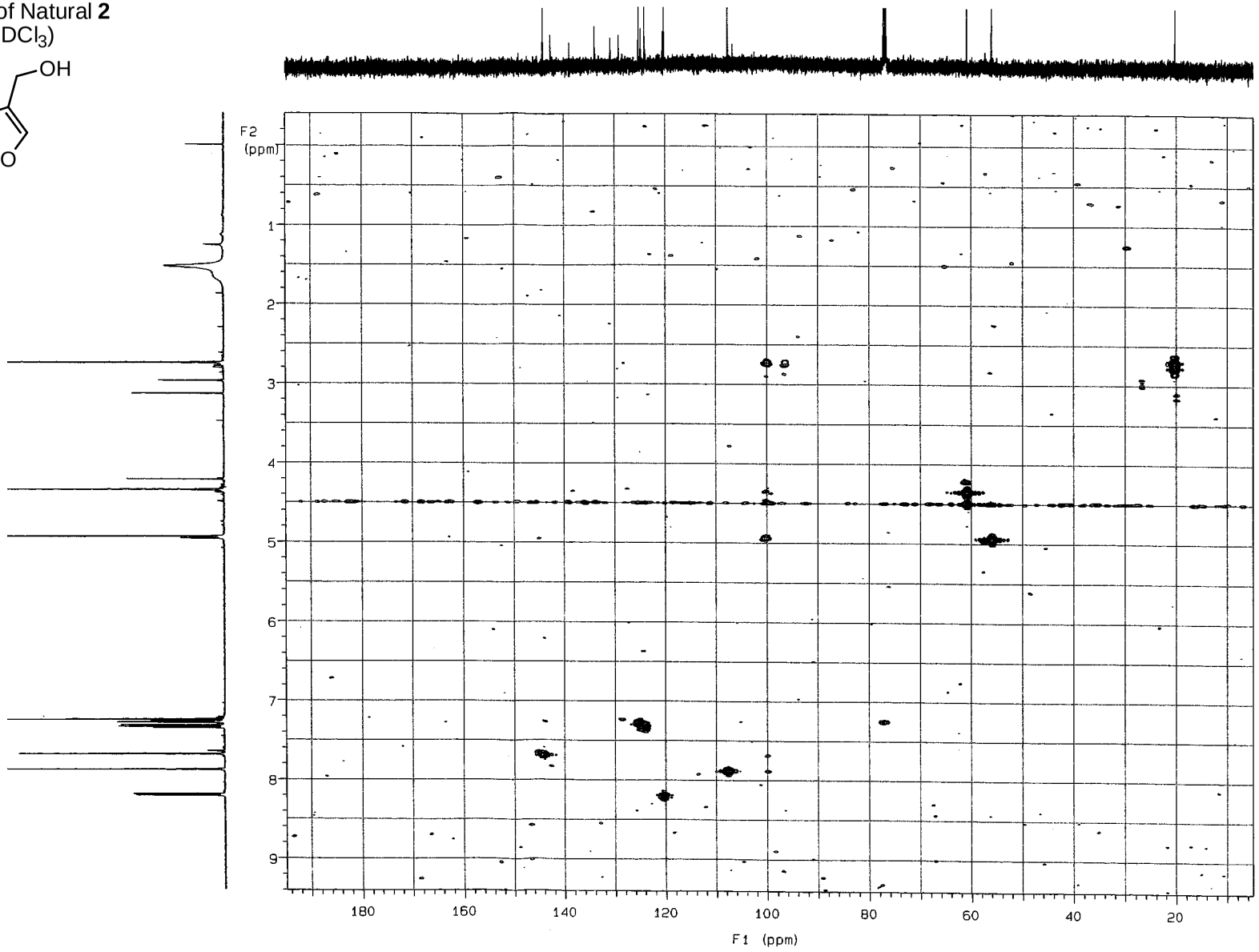
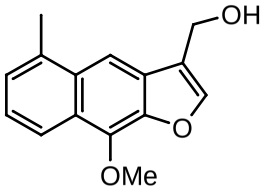


HMBC Spectrum of Natural **2**
(500 MHz, $CDCl_3$)



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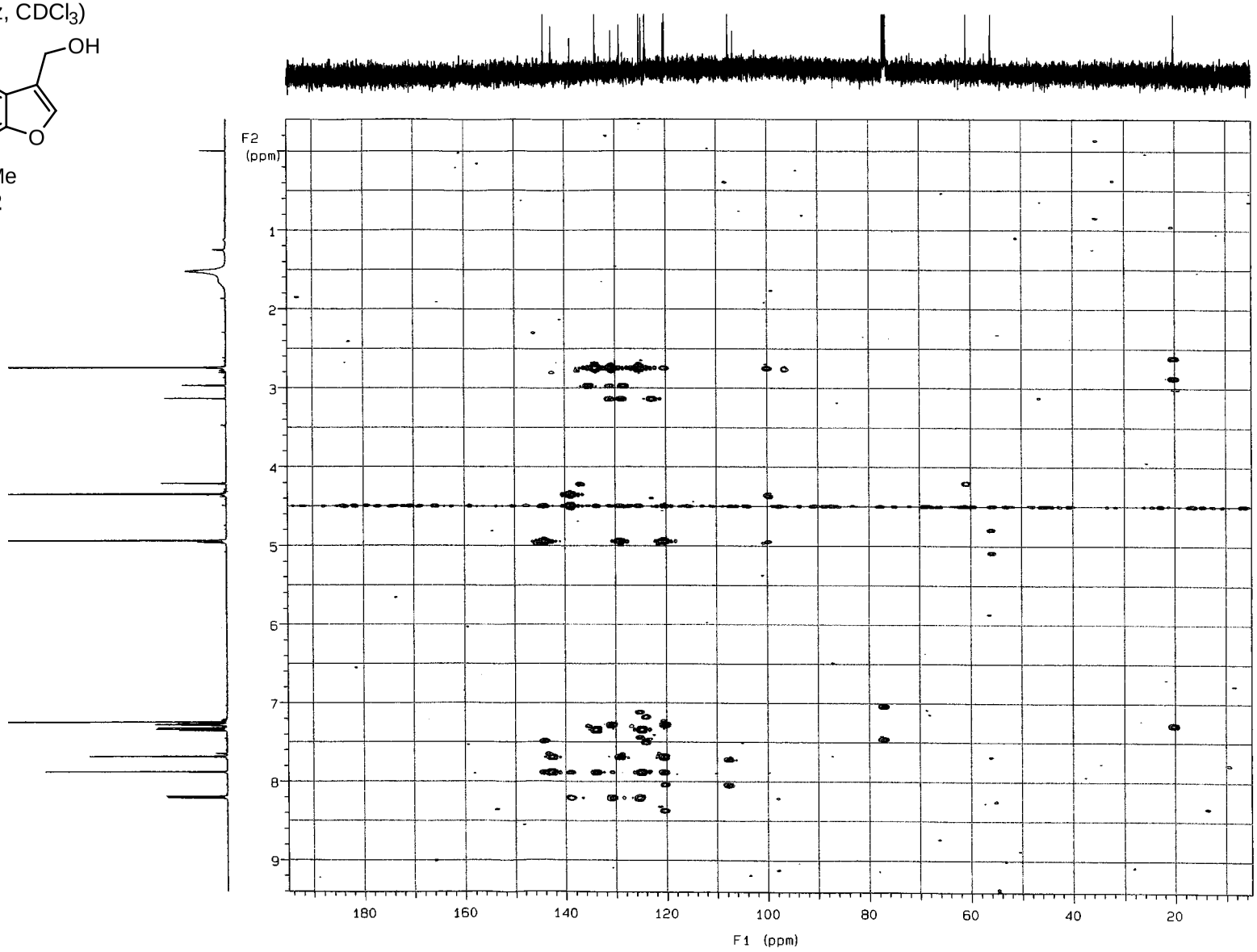
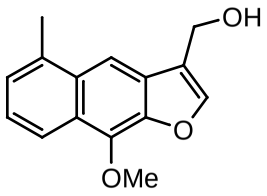
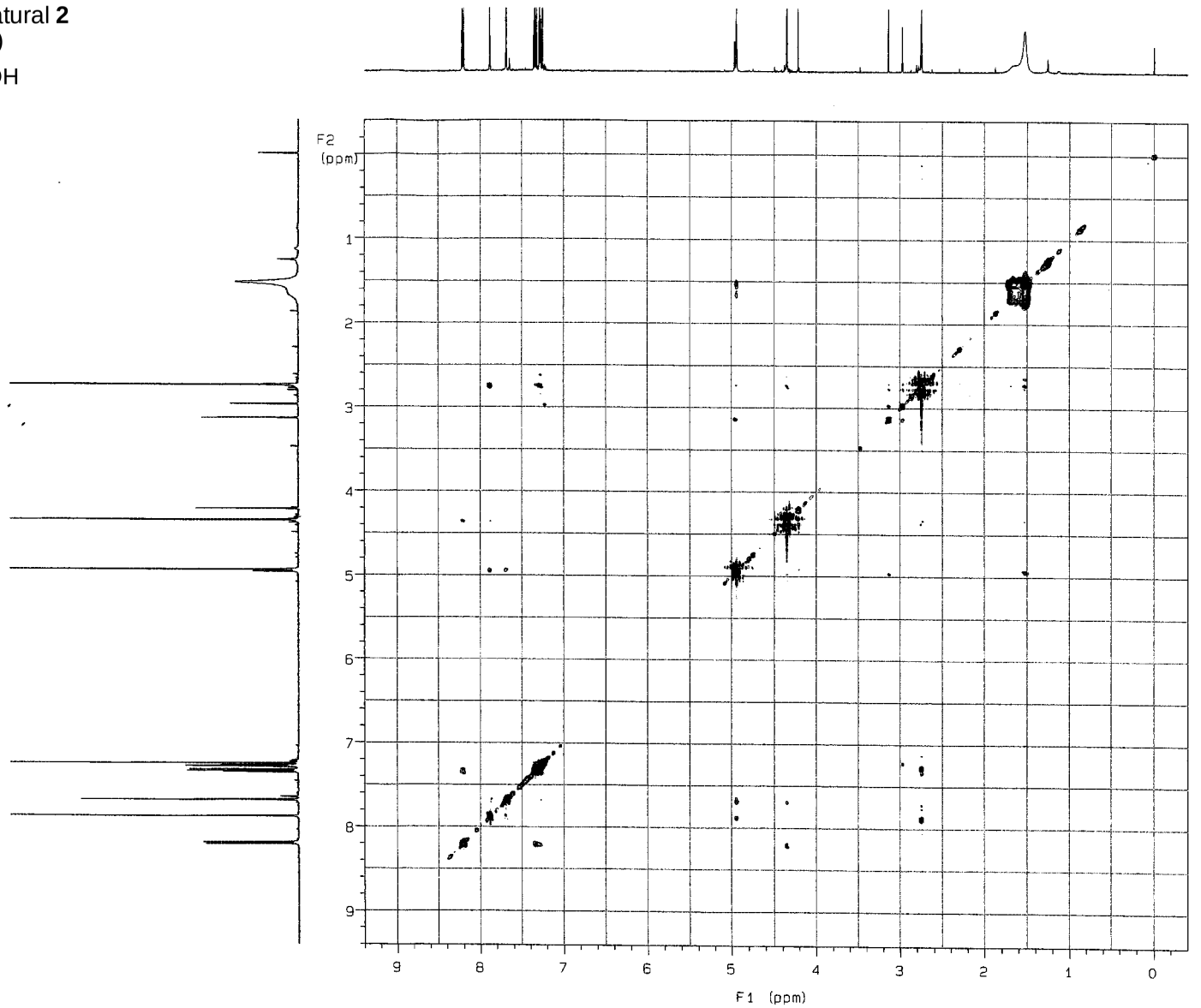


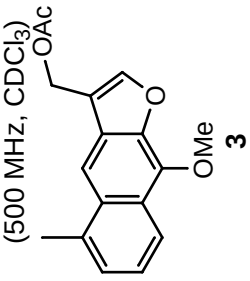
NOESY Spectrum of Natural **2**
(500 MHz, $CDCl_3$)



2



^{1}H NMR Spectrum of Natural **3**
(500 MHz, $CDCl_3$)



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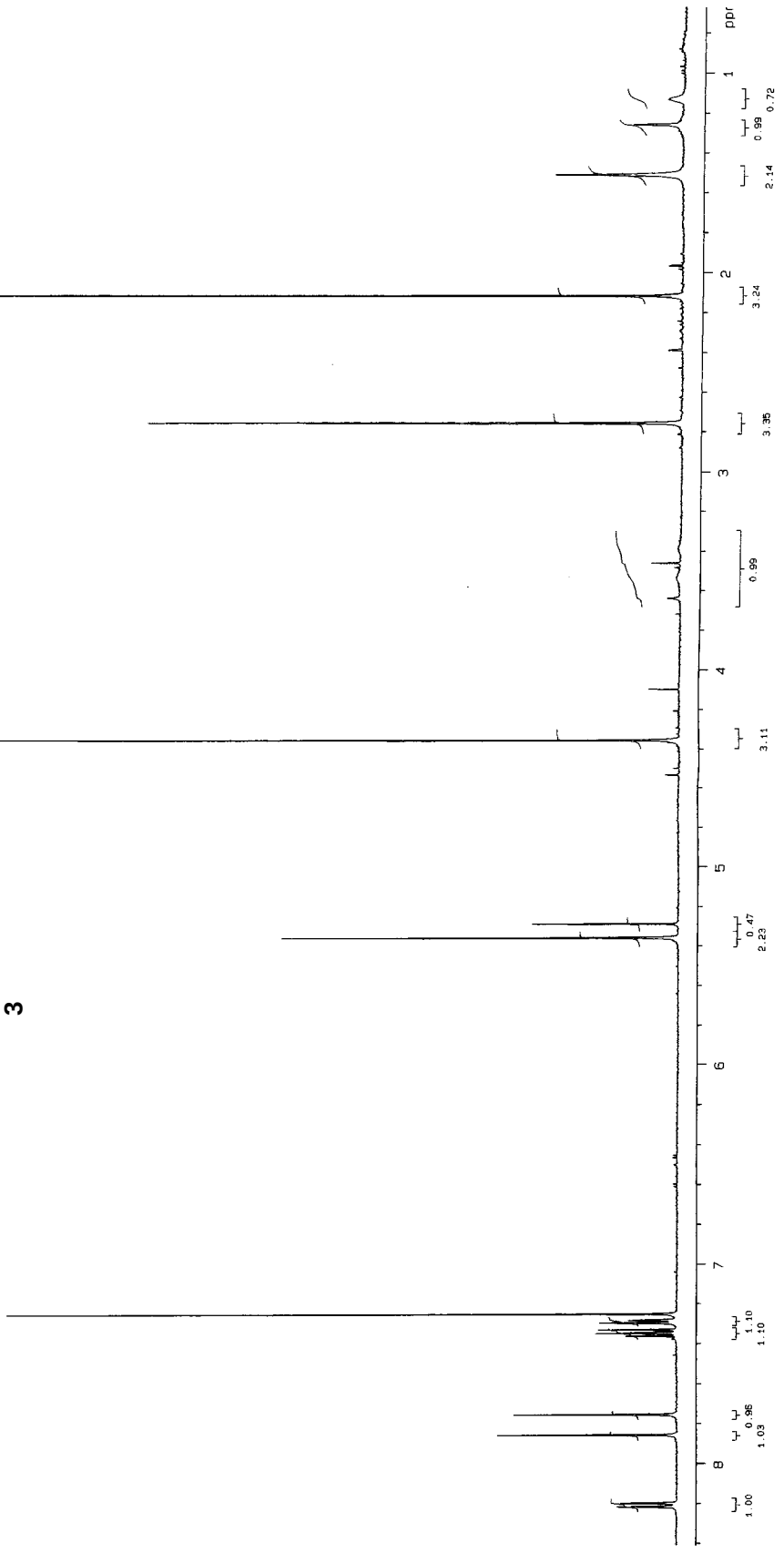
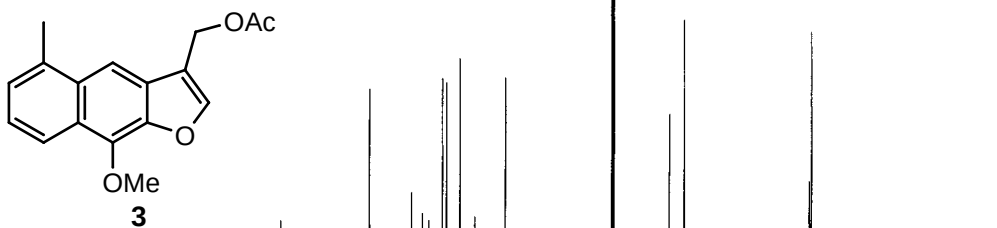
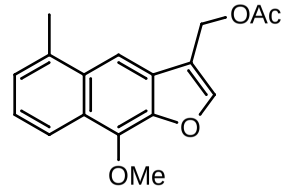


DEPT Spectra of Natural **3**
(100 MHz, $CDCl_3$)



3

H-H COSY Spectrum of Natural **3**
(500 MHz, $CDCl_3$)



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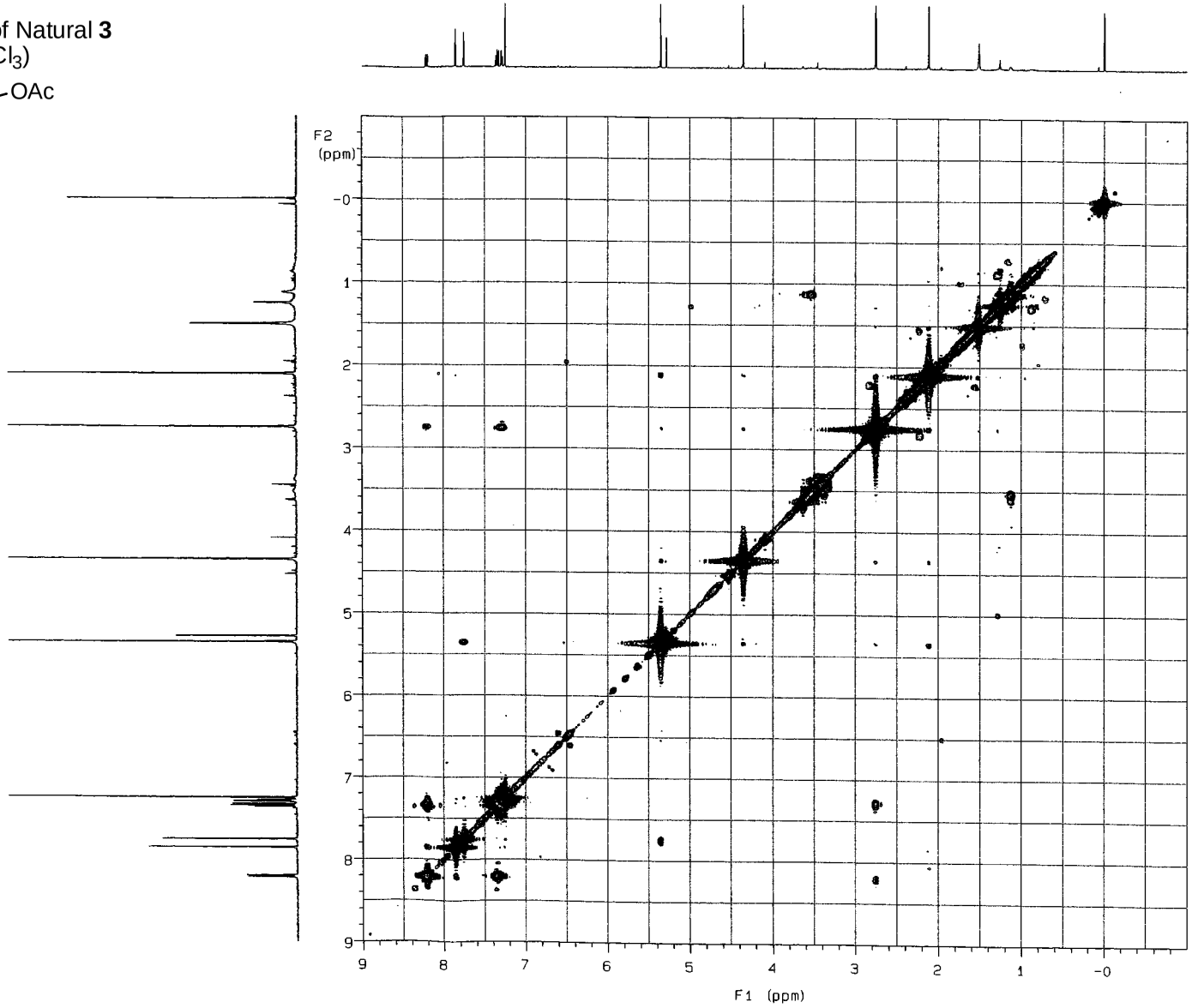
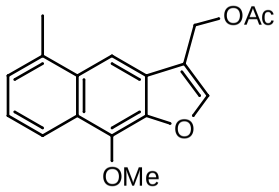
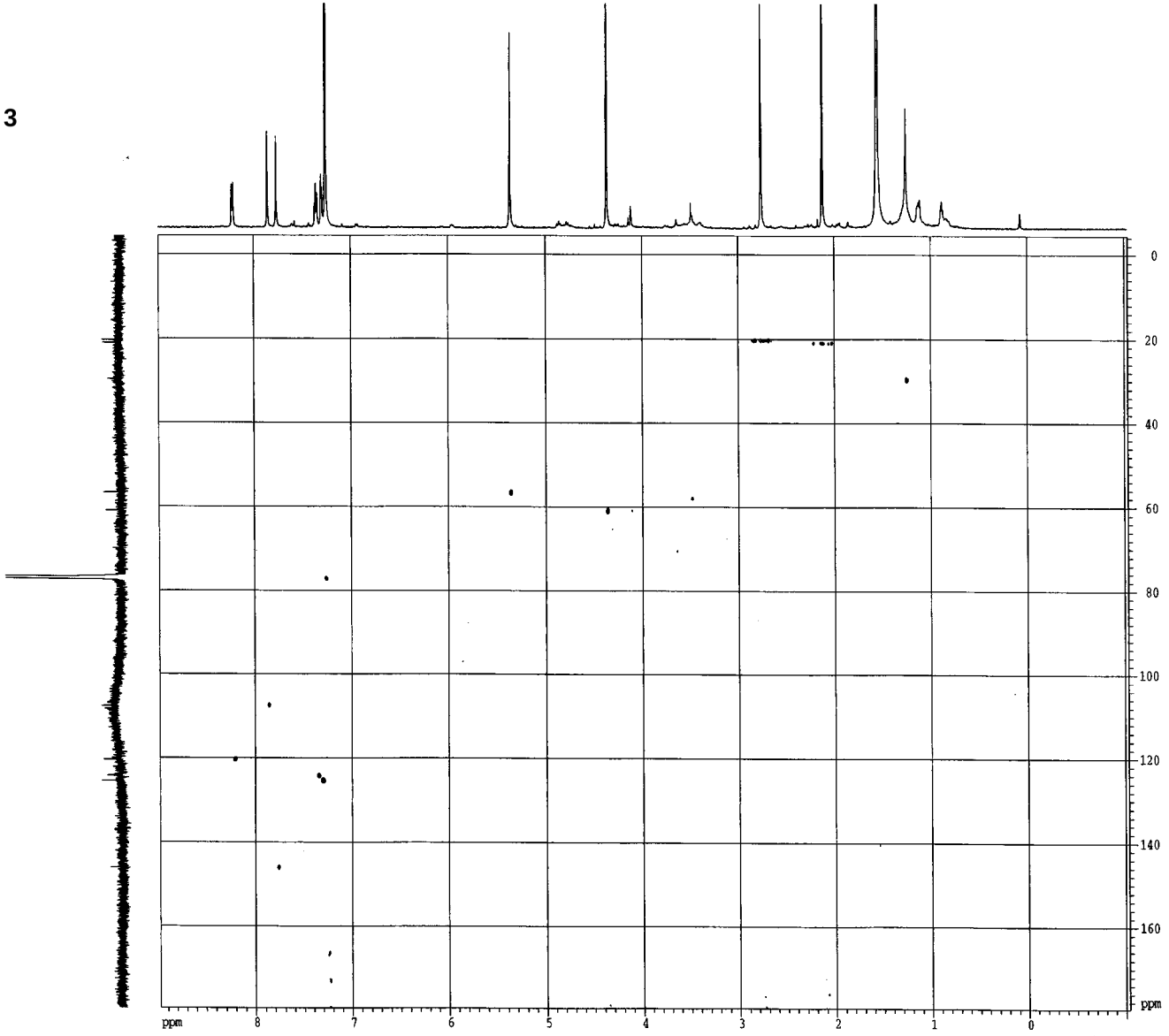


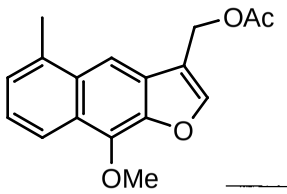
HMQC Spectrum of Natural **3**
(600 MHz, $CDCl_3$)



3



HMBC Spectrum of Natural **3**
(500 MHz, $CDCl_3$)



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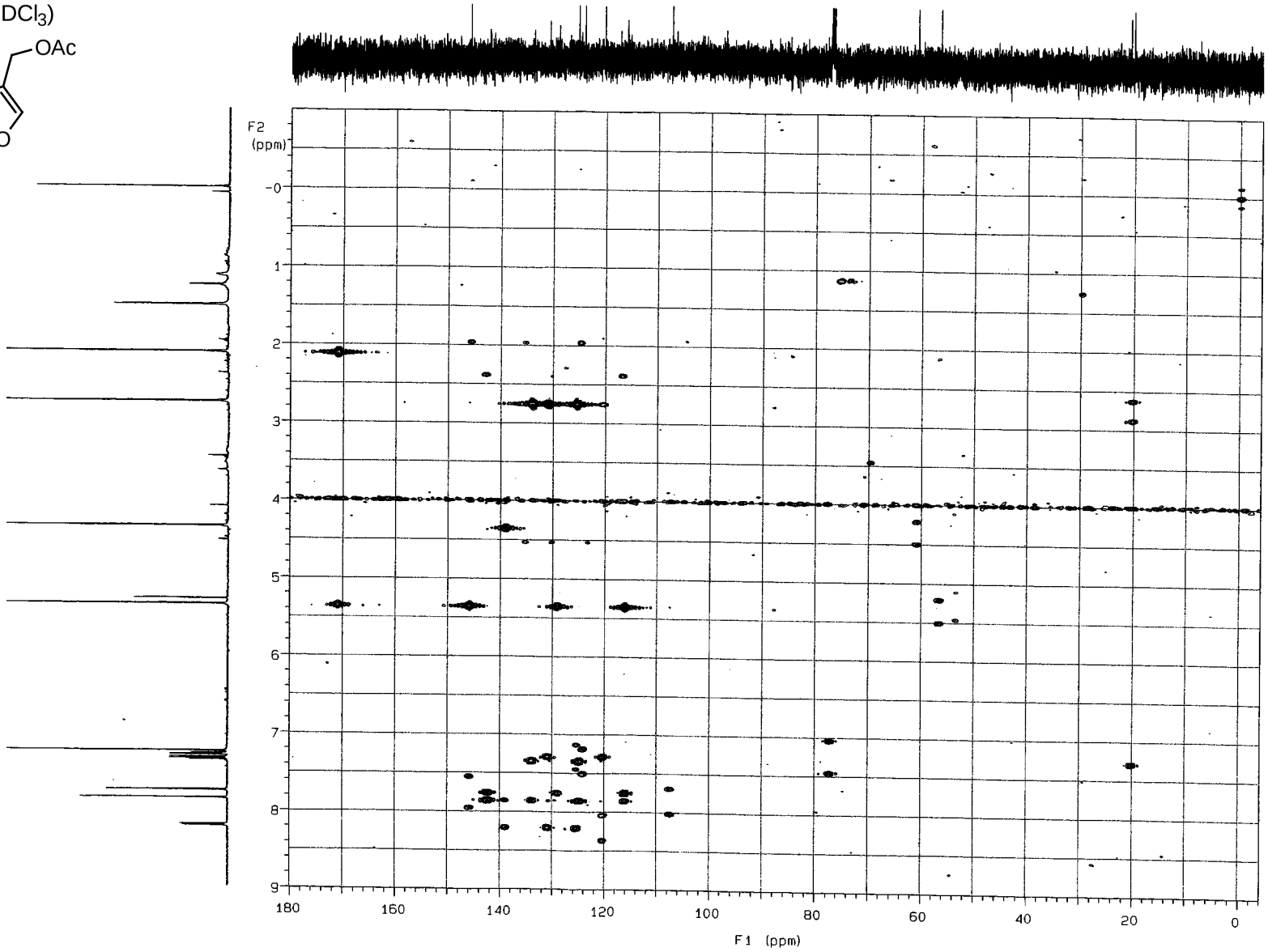
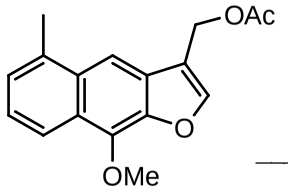
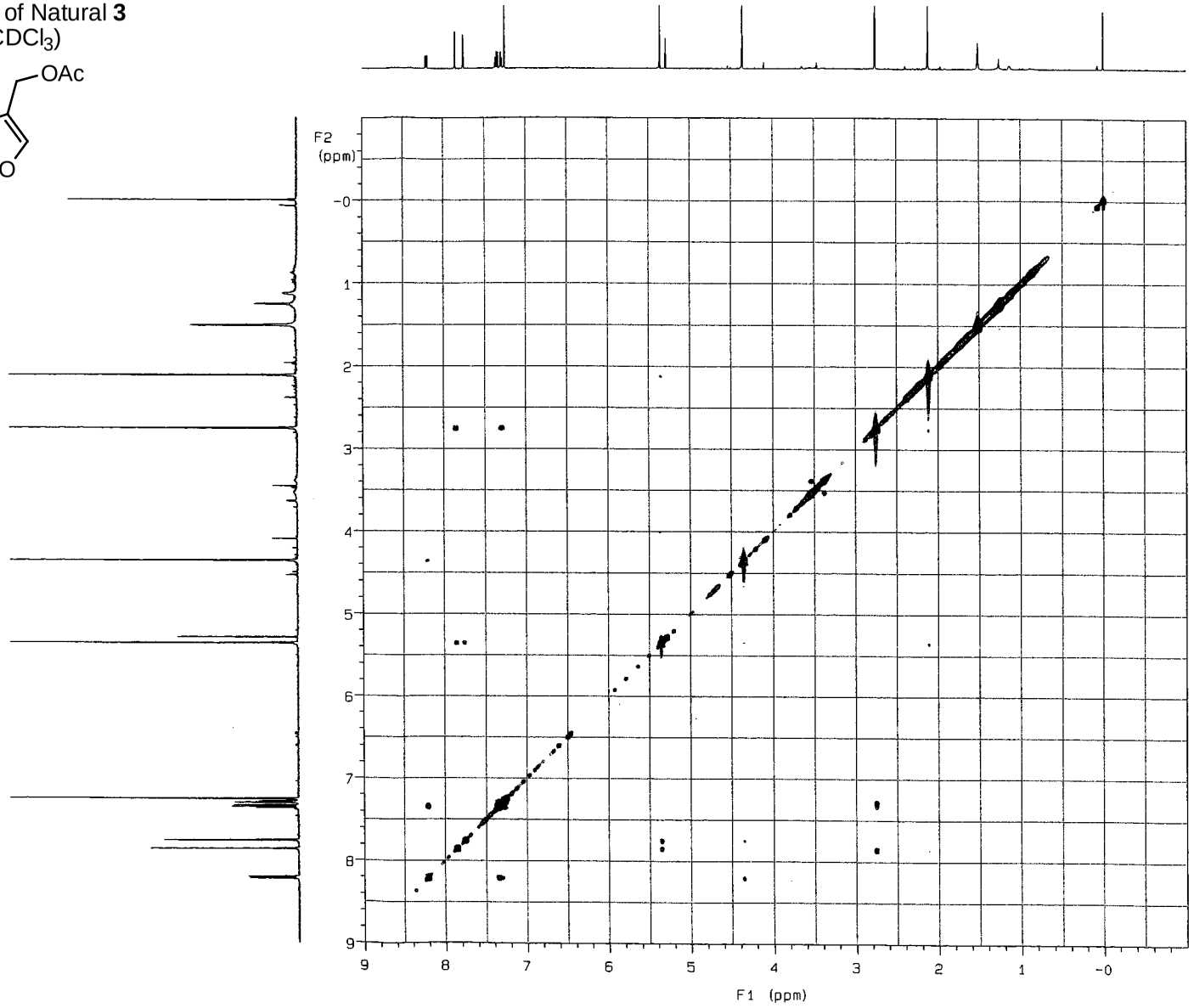


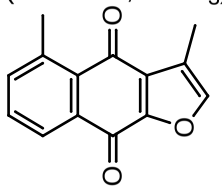
NOESY Spectrum of Natural **3**
(500 MHz, $CDCl_3$)



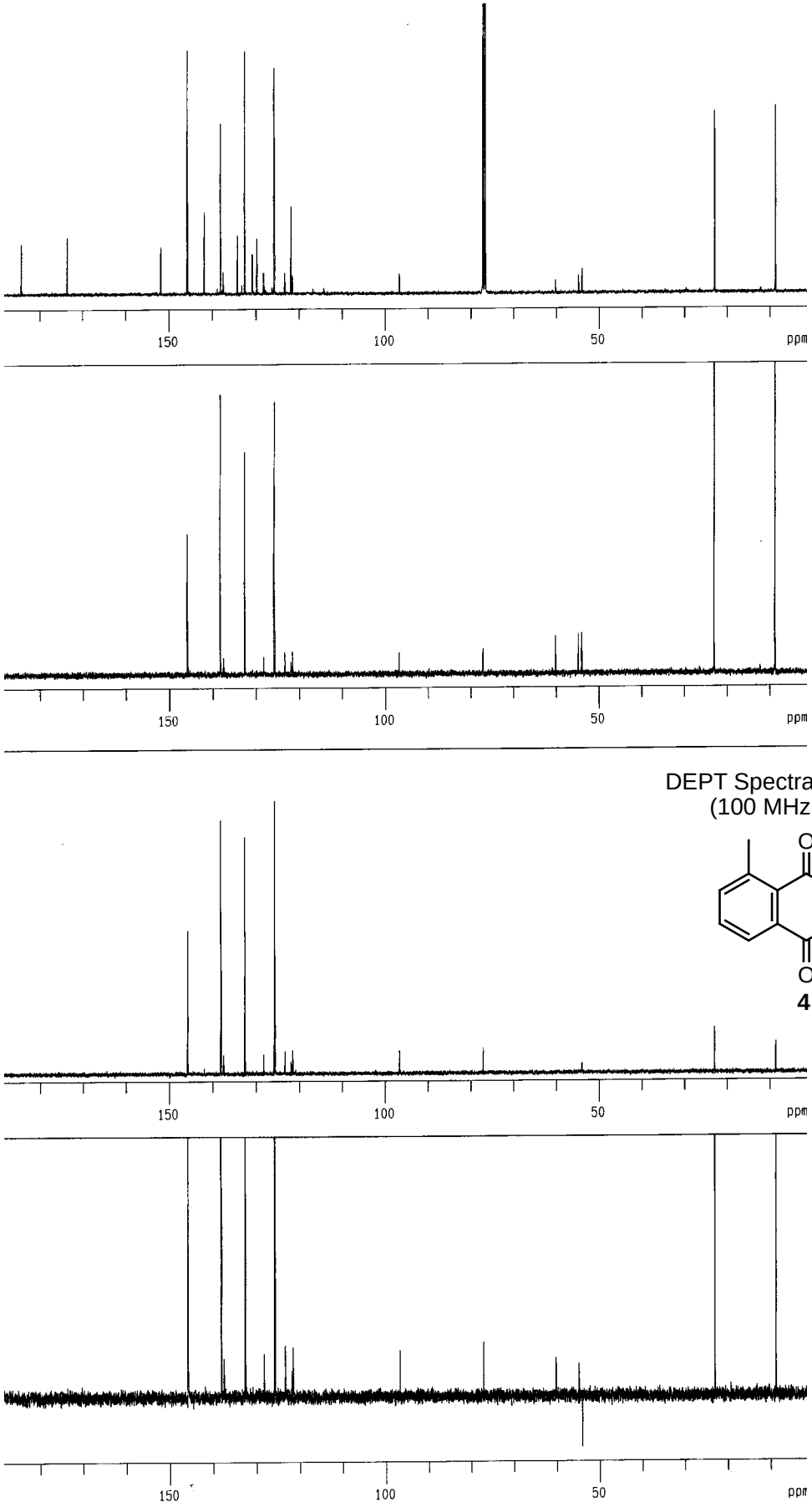
3



^{1}H NMR Spectrum of Natural **4**
(500 MHz, $CDCl_3$)



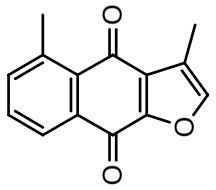
4



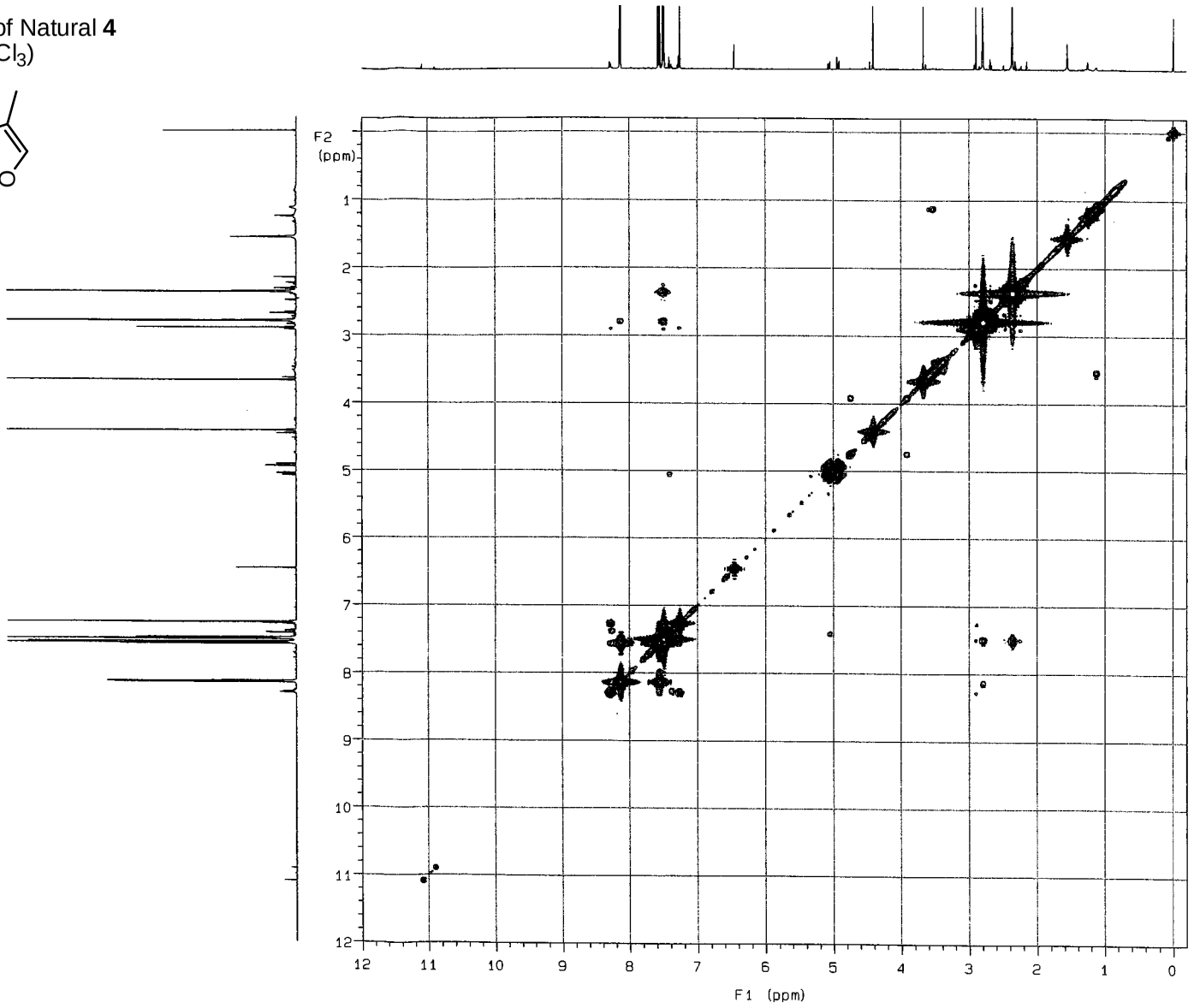
DEPT Spectra of Natural **4**
(100 MHz, $CDCl_3$)

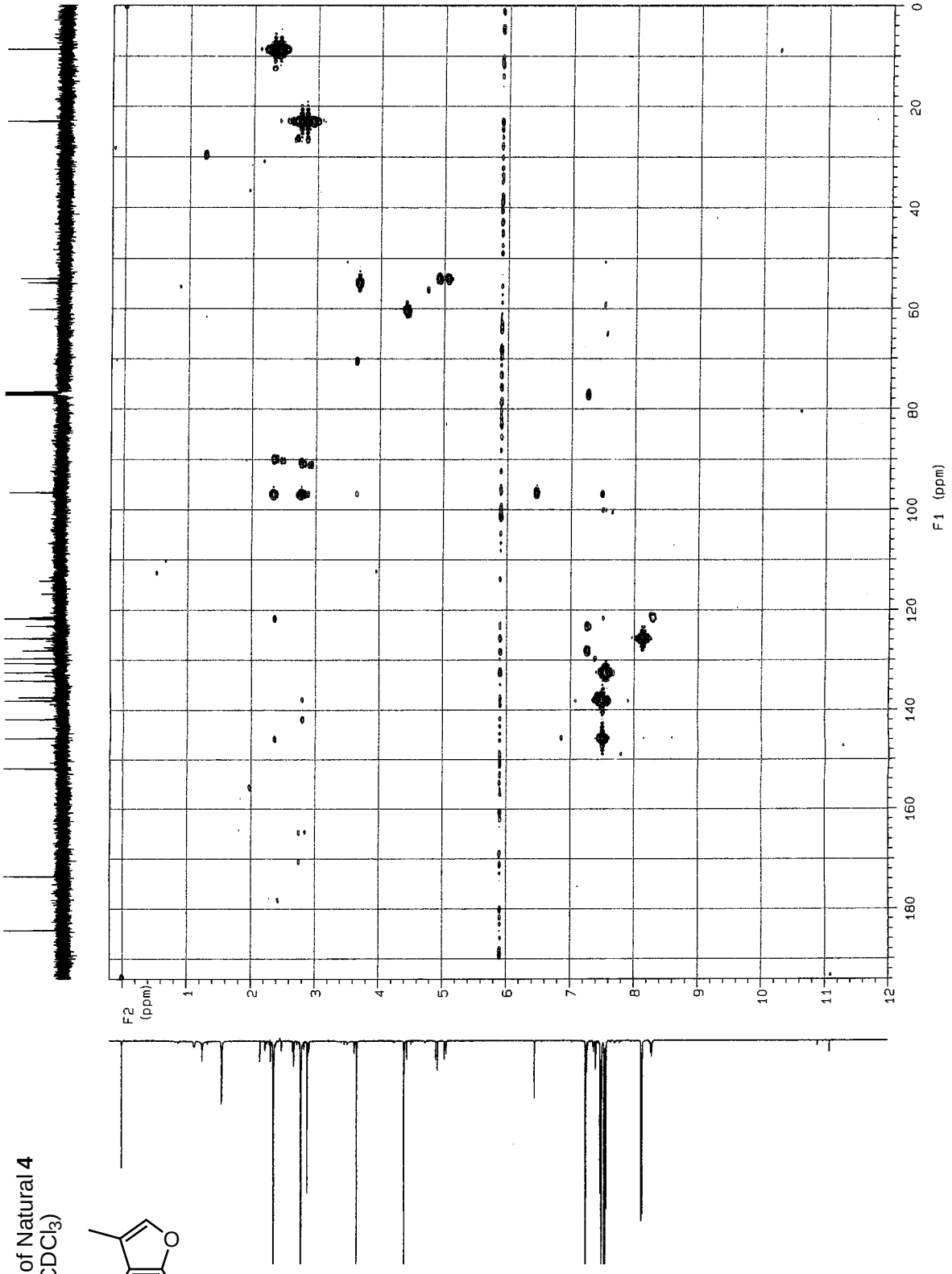
4

H-H COSY Spectrum of Natural **4**
(500 MHz, $CDCl_3$)



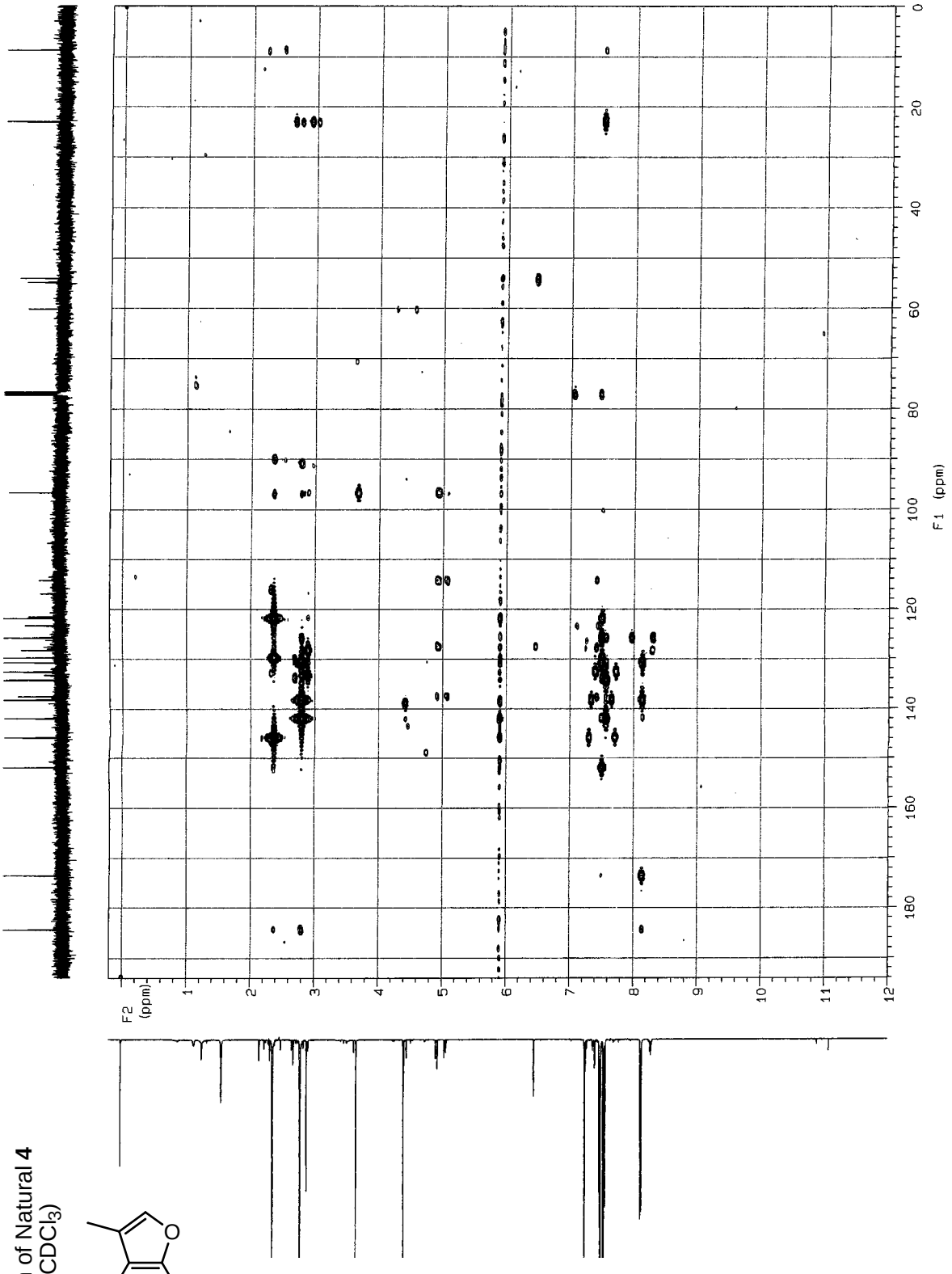
4





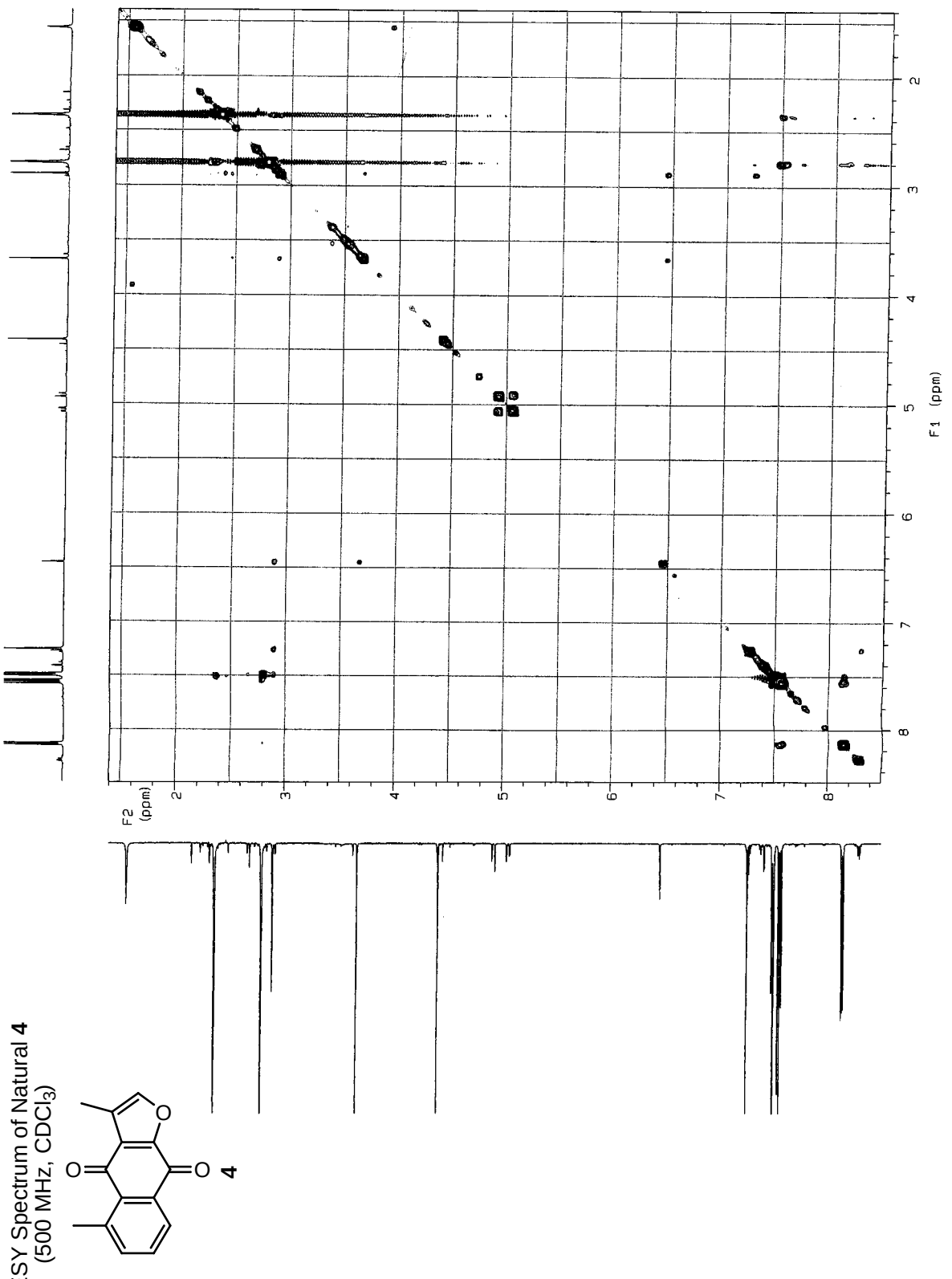
HMQC Spectrum of Natural **4**
(500 MHz, $CDCl_3$)

4



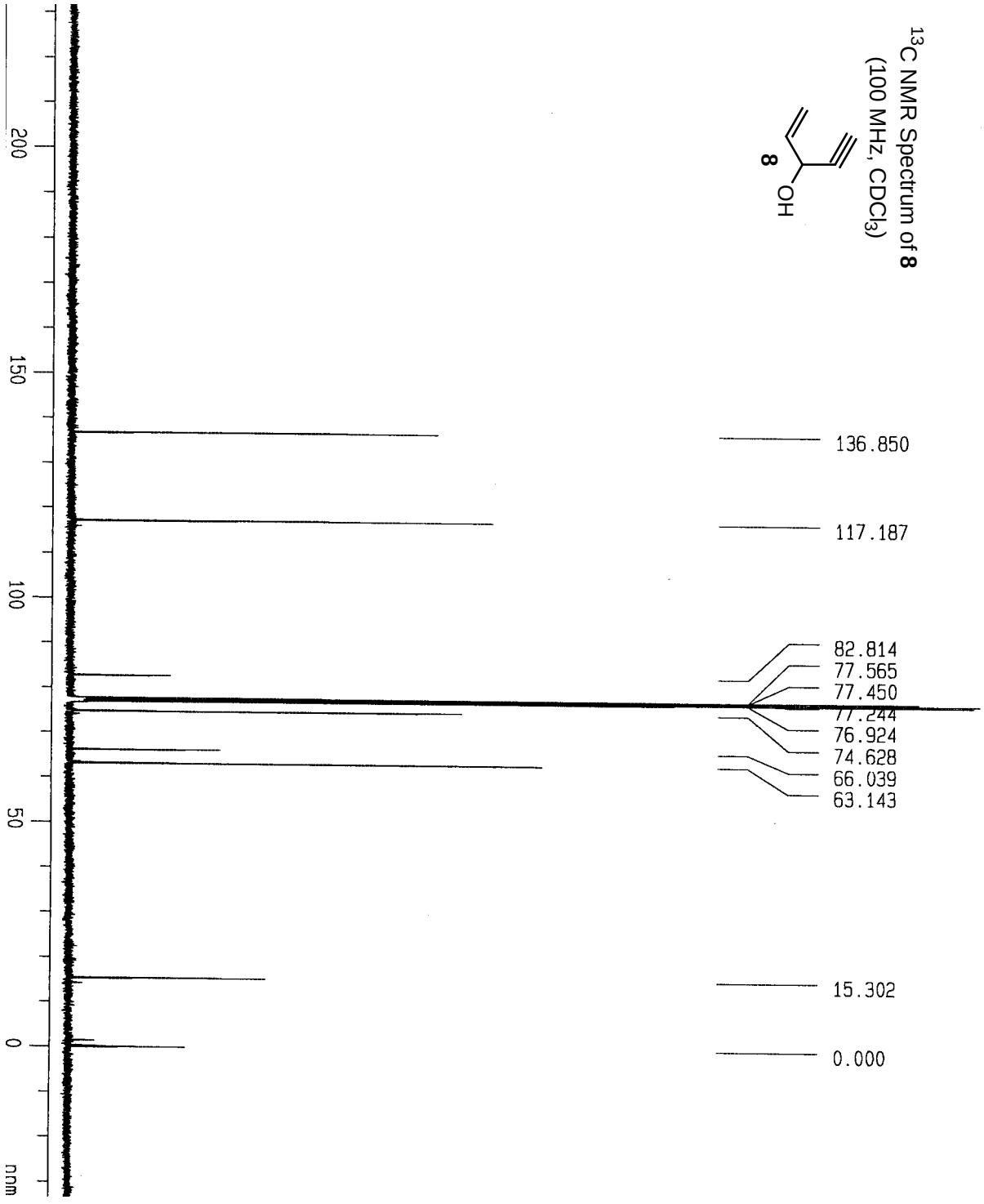
HMBC Spectrum of Natural **4**
(500 MHz, $CDCl_3$)

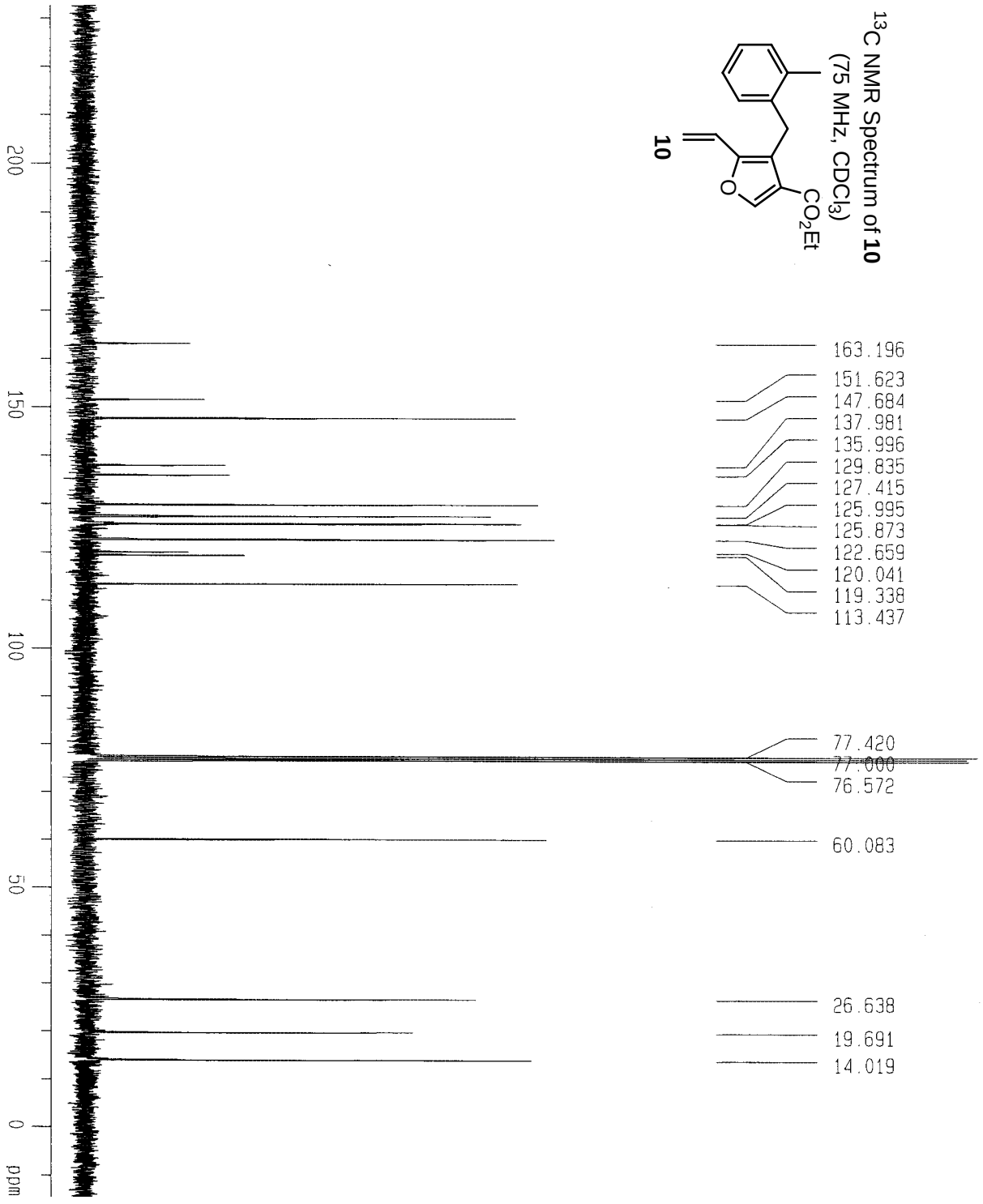
4

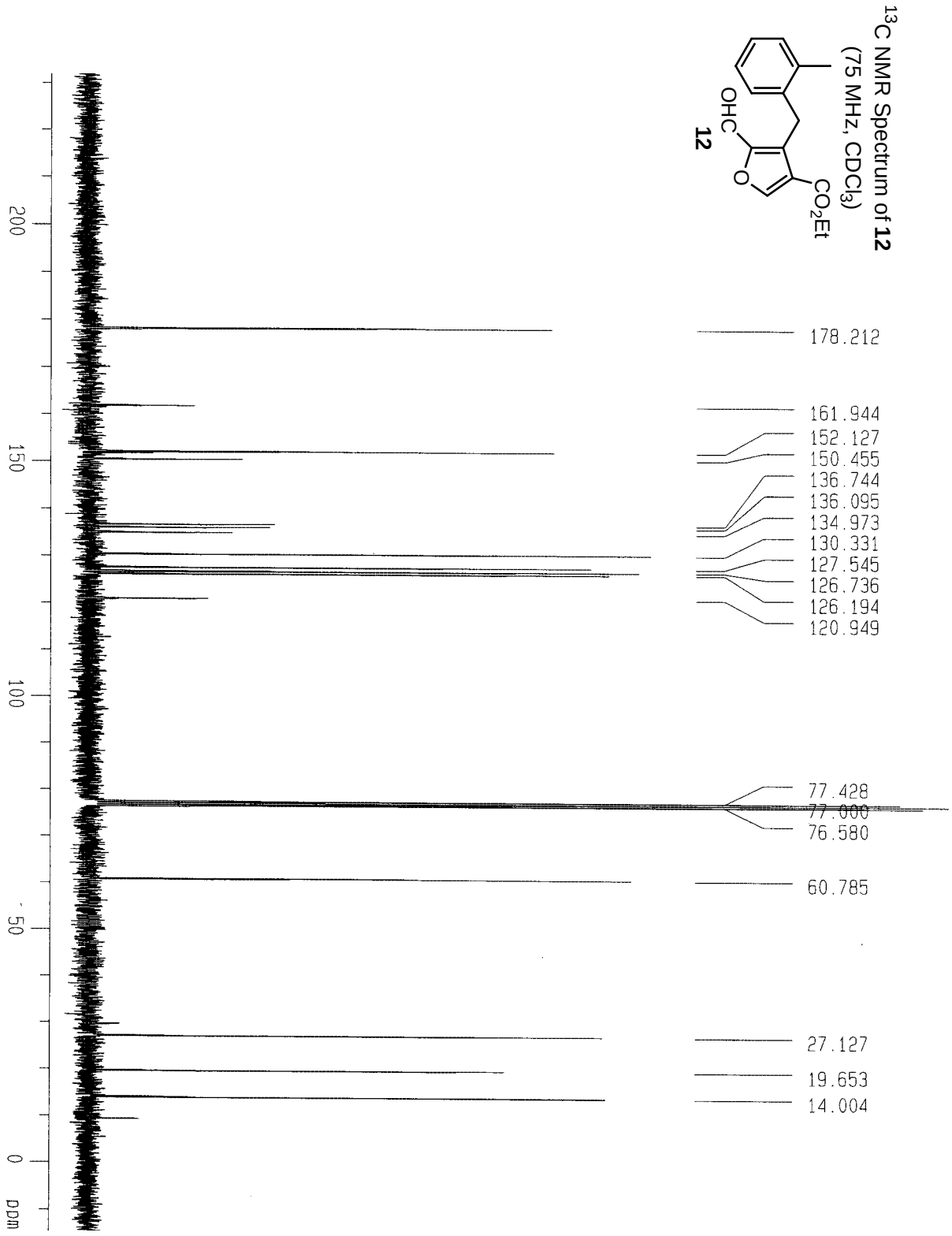


NOESY Spectrum of Natural **4**
(500 MHz, $CDCl_3$)

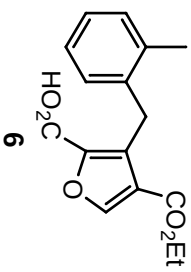
4


^{13}C NMR Spectrum of **8**
(100 MHz, $CDCl_3$)
8
OH
136.850
117.187
82.814
77.565
77.450
77.244
76.924
74.628
66.039
63.143
15.302
0.000
200
150
100
50
0
ppm

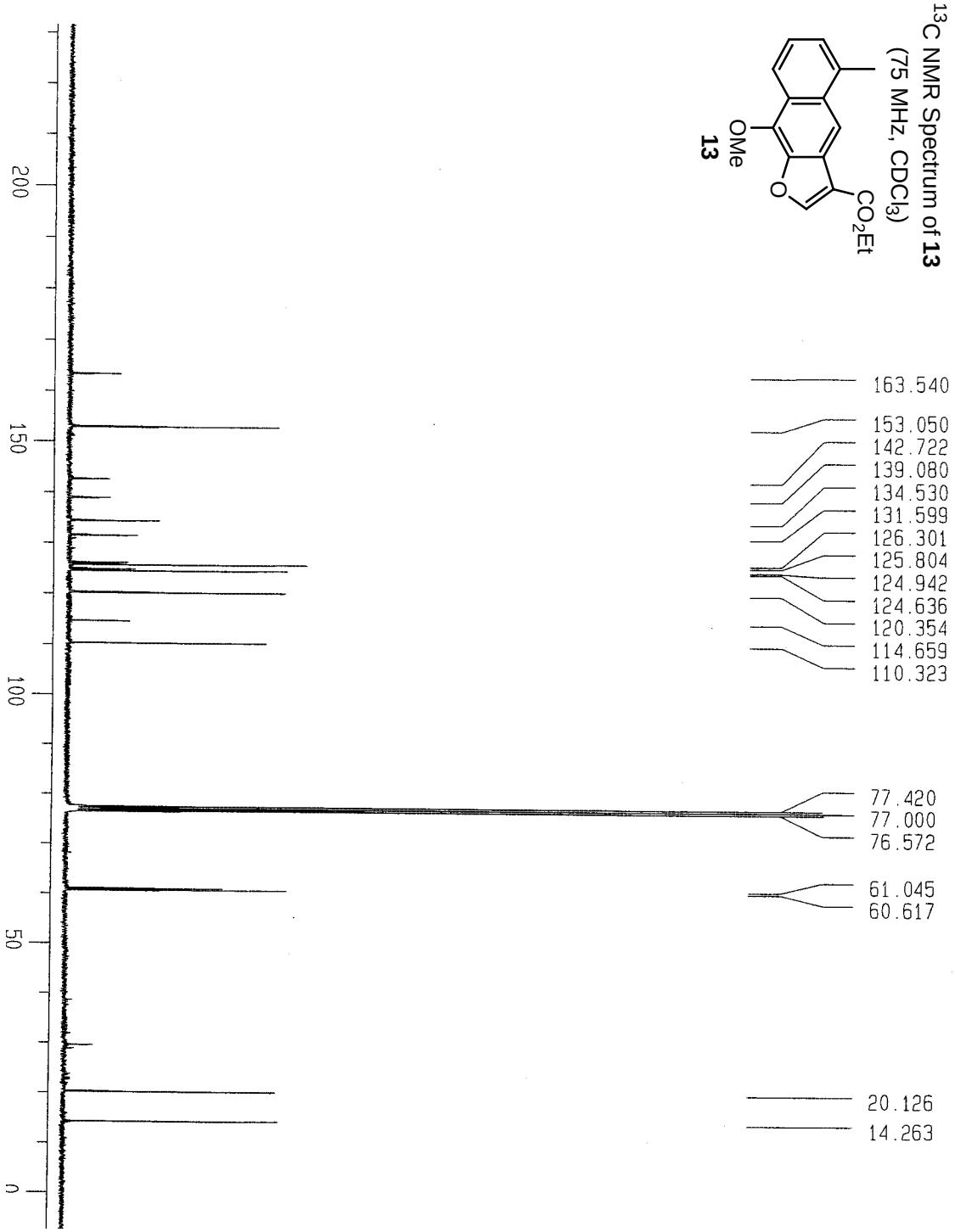

^{13}C NMR Spectrum of **10**
(75 MHz, $CDCl_3$)
CO_2Et
10
163.196
151.623
147.684
137.981
135.996
129.835
127.415
125.995
125.873
122.659
120.041
119.338
113.437
77.420
77.000
76.572
60.083
26.638
19.691
14.019
200
150
100
50
0
ppm

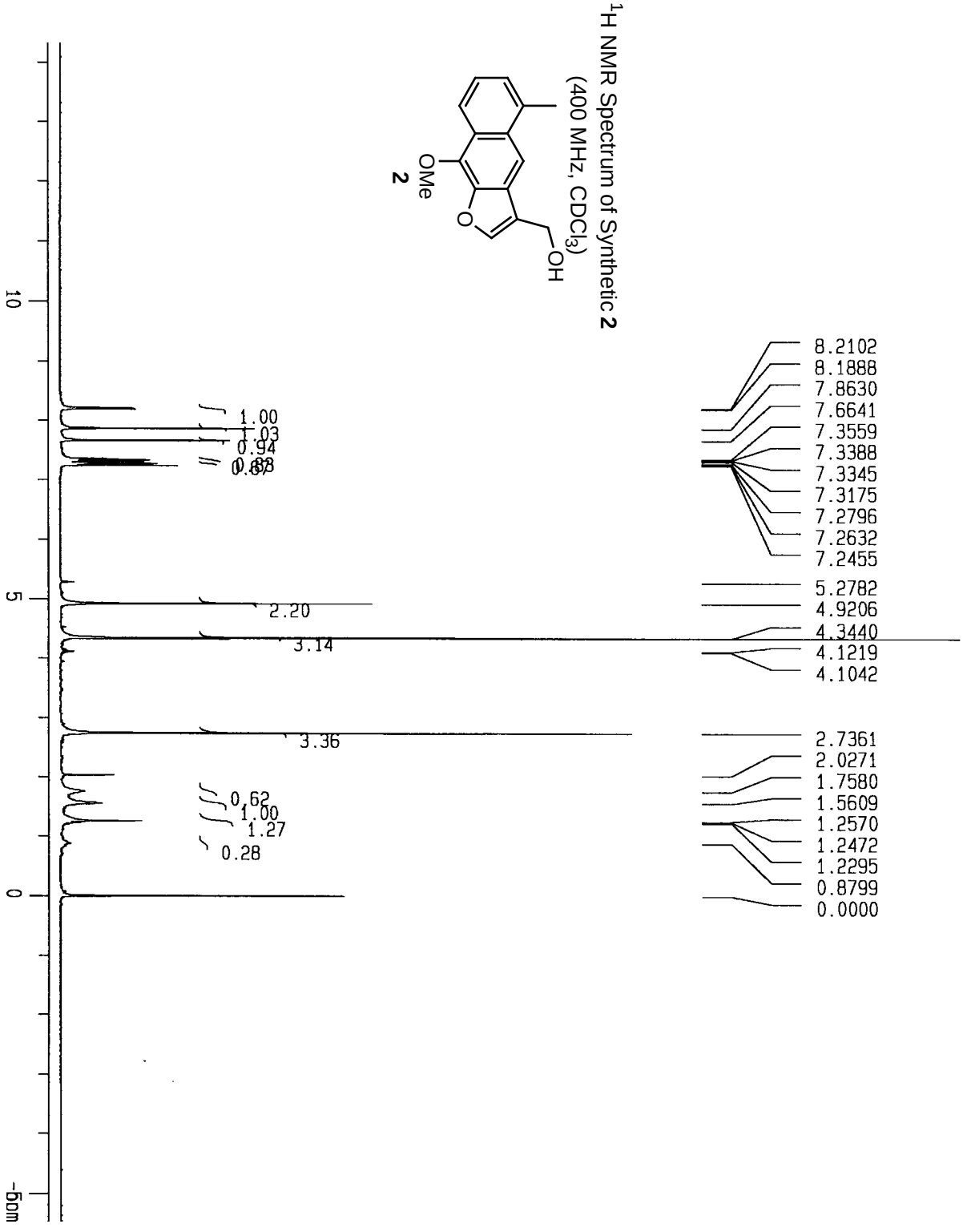

13C NMR Spectrum of 12
(75 MHz, CDCl3)
OHC
O
CO2Et
12
178.212
161.944
152.127
150.455
136.744
136.095
134.973
130.331
127.545
126.736
126.194
120.949
77.428
77.000
76.580
60.785
27.127
19.653
14.004
200
150
100
50
0
ppm

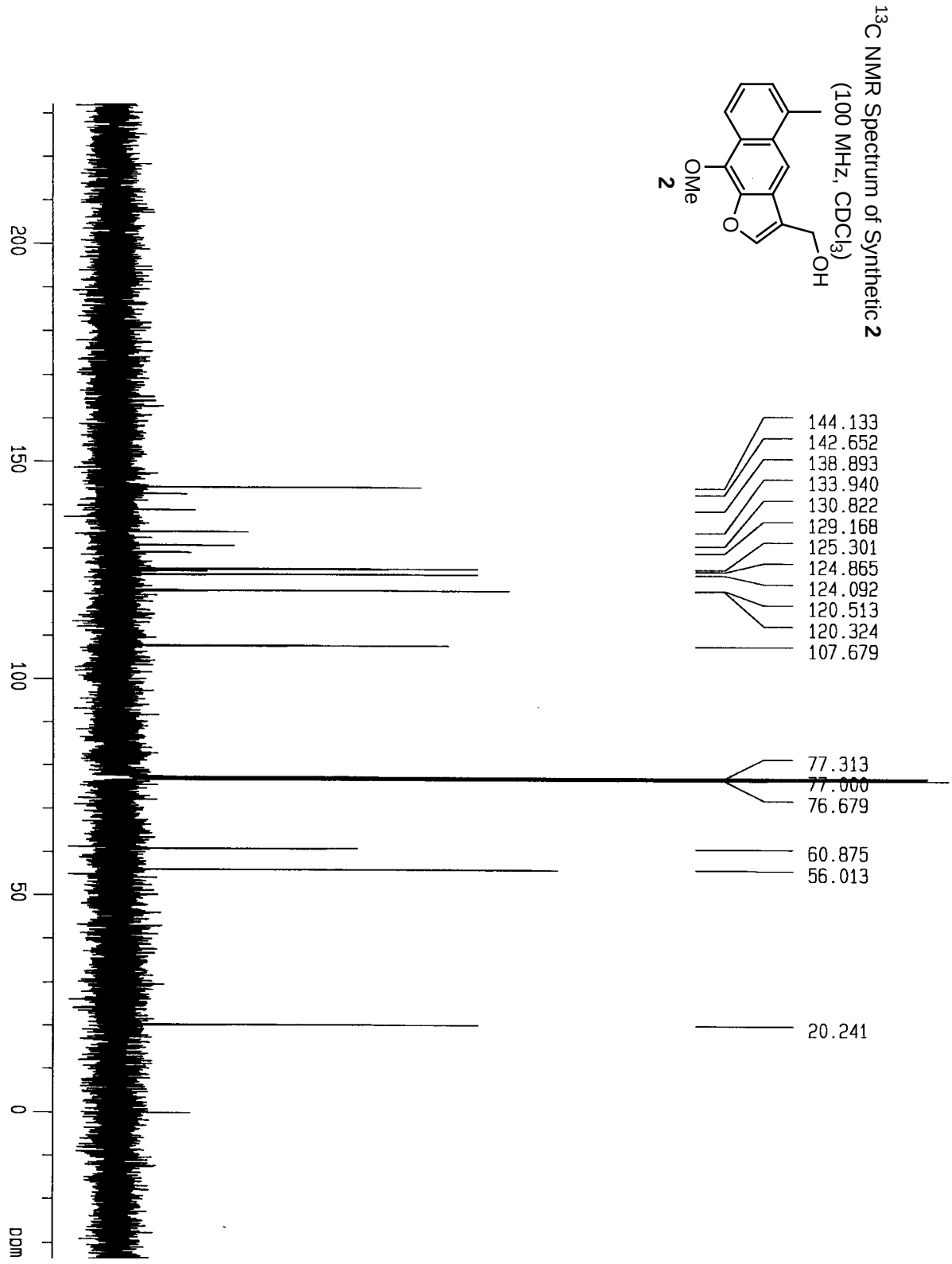
^{13}C NMR Spectrum of **6**
(75 MHz, CD_3OD)

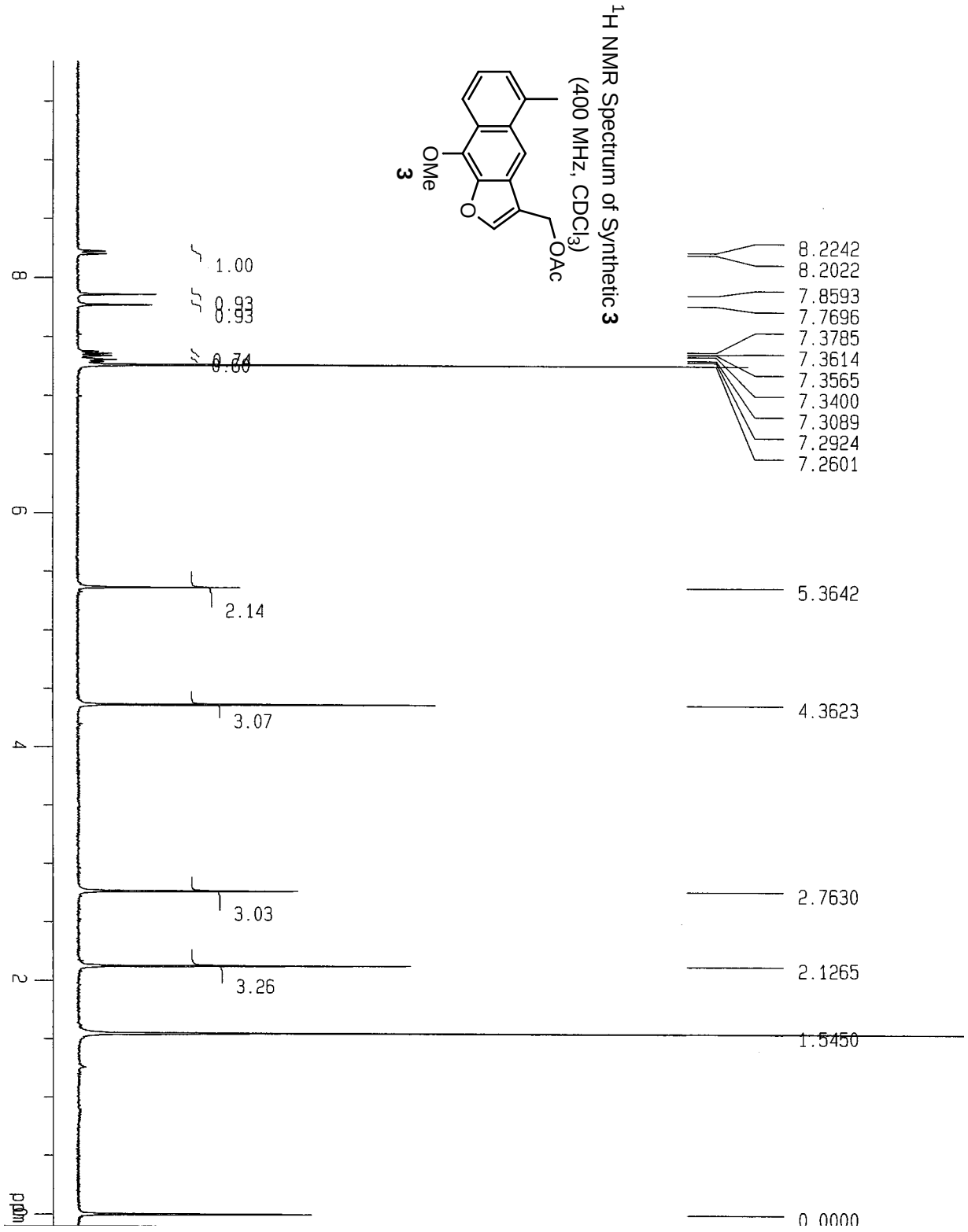


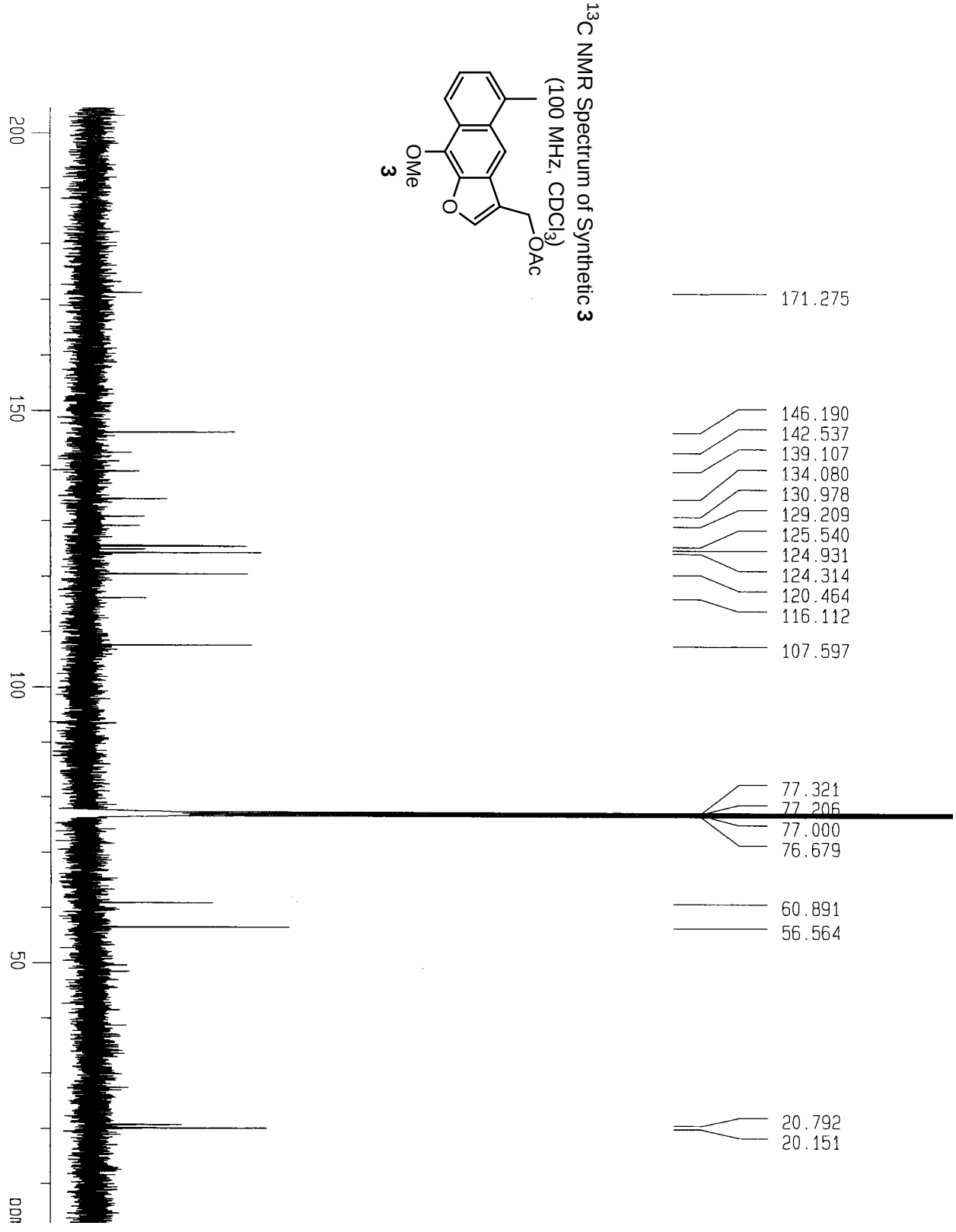
6


^{13}C NMR Spectrum of **13**
(75 MHz, $CDCl_3$)
OMe
13
CO_2Et
O
163.540
153.050
142.722
139.080
134.530
131.599
126.301
125.804
124.942
124.636
120.354
114.659
110.323
77.420
77.000
76.572
61.045
60.617
20.126
14.263
200
150
100
50
0


^{1}H NMR Spectrum of Synthetic **2**
(400 MHz, $CDCl_3$)
OMe
2
OH
O
10
5
0
-5ppm
1.00
1.03
0.94
2.20
3.14
3.36
0.62
1.00
1.27
0.28
8.2102
8.1888
7.8630
7.6641
7.3559
7.3388
7.3345
7.3175
7.2796
7.2632
7.2455
5.2782
4.9206
4.3440
4.1219
4.1042
2.7361
2.0271
1.7580
1.5609
1.2570
1.2472
1.2295
0.8799
0.0000


^{13}C NMR Spectrum of Synthetic **2**
(100 MHz, $CDCl_3$)
OMe
2
OH
O
144.133
142.652
138.893
133.940
130.822
129.168
125.301
124.865
124.092
120.513
120.324
107.679
77.313
77.000
76.679
60.875
56.013
20.241
200
150
100
50
0
ppm


^{1}H NMR Spectrum of Synthetic **3**
(400 MHz, $CDCl_3$)
OMe
3
O
OAc
1.00
0.93
0.93
8.2242
8.2022
7.8593
7.7696
7.3785
7.3614
7.3565
7.3400
7.3089
7.2924
7.2601
5.3642
2.14
4.3623
3.07
2.7630
3.03
2.1265
3.26
1.5450
0.0000
8
6
4
2
0
ppm


^{13}C NMR Spectrum of Synthetic **3**
(100 MHz, $CDCl_3$)
OMe
3
OAc
O
171.275
146.190
142.537
139.107
134.080
130.978
129.209
125.540
124.931
124.314
120.464
116.112
107.597
77.321
77.206
77.000
76.679
60.891
56.564
20.792
20.151
200
150
100
50
ppm