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Enantioselective total synthesis of cytotoxic taiwaniaquinones A and F

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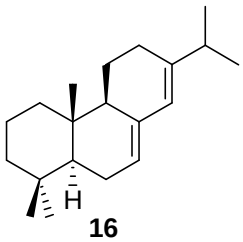
Experimental Section

(4aS,10aS)-7-isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene (16).

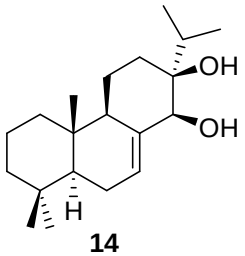


16

To a solution of **15** (1.4 g, 5.69 mmol) in dry THF (25 mL) was added slowly at -20 ºC, *i*-PrMgCl.LiCl (7 mL, 7 mmol, 1 M in THF), and the resulting mixture was stirred at this temperature for 30 min, at which time TLC showed no starting material. Then, a 2N HCl solution (1 mL) was added and the mixture was stirred for an additional 5 min. Then, the solvent was removed under vacuum and ether – water (80 : 20 mL) was added and the phases were shaken and separated. The organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded a crude product which was directly purified by flash chromatography on silica gel (2 % ether/hexanes) to yield 1.2 g of **16** (77%) as a yellow oil.

$[\alpha]_D^{25}$ = -135.6 (c 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.79 (s, 3H), 0.87 (s, 3H), 0.92 (s, 3H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.00 (ddd, *J* = 13.3, 13.3, 3.4 Hz, 1H), 1.01 (d, *J*= 6.9 Hz, 1H), 1.02 (d, *J* = 4.8 Hz, 3H), 1.15 - 1.29 (m, 3H), 1.40 - 1.49 (m, 2H), 1.55 (m, 1H), 1.77 - 1.88 (m, 3H), 1.96 (m, 1H), 2.02 - 2.17 (m, 3H), 2.22 (h, *J* = 6.8 Hz, 1H), 5.43 (br s, 1H), 5.78 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 39.5 (C-1), 19.2 (C-2), 42.7 (C-3), 33.1 (C-4), 50.5 (C-5), 24.4 (C-6), 121.7 (C-7), 135.7 (C-8), 51.3 (C-9), 35.2 (C-10), 23.0 (C-11), 27.7 (C-12), 144.2 (C-13), 123.7 (C-14), 35.3 (C-15), 21.7 (C-16), 22.1 (C-17), 33.5 (C-18), 21.1 (C-19), 13.9 (C-20). IR (film): 1461, 1385, 1364, 1163, 1029, 887, 801 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{20}H_{32}Na$ ($M+Na^+$) 295.2402, found: 295.2405.

(4bS,8aS)-2-isopropyl-4b,8,8-trimethyl-1,2,3,4,4a,4b,5,6,7,8,8a,9-dodecahydrophenanthrene-1,2-diol (14).



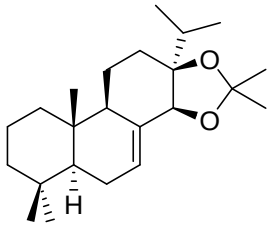
14

To a solution of **16** (1 g, 3.67 mmol) in strictly deoxygenated *t*-BuOH - H_2O (35 : 5 mL) were added trimethylamine *N*-oxide dihydrate (0.9 g, 8.1 mmol) and pyridine (0.1 mL) under argon atmosphere. The solution was stirred for 10 min at room temperature, and 2% aq. OsO_4 (2 mL) was added and the reaction mixture was further stirred under argon atmosphere at reflux for 24 h. At which time TLC indicated no remaining starting material, and then the solvent was removed under vacuum to afford a crude product that was dissolved in ether (40 mL) and washed with water and brine. The organic phase was dried over Na_2SO_4 and concentrated to give a crude product which was directly purified by flash chromatography on silica gel (25 % ether/hexanes) to yield 977 mg of pure **14** (87%) as a colourless syrup.

$[\alpha]_D^{25}$ = -27.5 (c 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.84 (s, 3H), 0.88 (s, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.93 (s, 3H), 0.95 (d, *J* = 6.9 Hz, 3H), 1.00 (ddd, *J* = 13.3, 13.3, 3.4 Hz, 1H), 1.10 (dd, *J* = 12.1, 4.2 Hz, 1H), 1.17 (ddd, *J* = 13.3, 13.3, 3.4 Hz, 1H), 1.25 - 1.60 (m, 7H), 1.68 (br s, 1H), 1.73 (s, 1H), 1.84 (dq, *J* = 12.8, 2.4 Hz, 1H), 1.91 (m, 1H), 2.05 (m, 1H), 2.17 (h, *J* = 6.9 Hz, 1H), 3.95 (br s, 1H), 5.95 (br s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 40.2 (C-1), 18.9 (C-2), 42.3 (C-3), 33.1 (C-4), 50.0 (C-5), 26.8 (C-6), 120.7 (C-7), 137.8 (C-8), 51.4 (C-9), 35.7 (C-10), 23.3 (C-11), 19.5 (C-12), 76.2 (C-13), 73.4 (C-14), 32.8 (C-15), 16.4 (C-16)*, 17.8 (C-17)*, 33.6 (C-18), 22.4 (C-19), 15.1 (C-20). IR (film): 3395, 1465, 1386, 1299, 1083, 1031, 803, 761 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{20}H_{34}O_2Na$ ($M+Na^+$) 329.2457, found: 329.2463.

* interchangeable signals

(3aS,5aS,9aS,11aS)-11a-isopropyl-2,2,6,6,9a-pentamethyl-3a,5,5a,6,7,8,9,9a,9b,10,11,11a-dodecahydrophenanthro[2,1-d][1,3]dioxole (17).



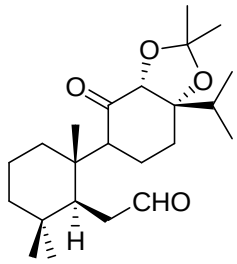
17

To a solution of **14** (4.27 g, 13.85 mmol) in dry acetone (50 mL) were added 2,2-dimethoxypropane (3 mL, 24.4 mmol) and PTSA (0.2 g, 1.05 mmol) and the reaction mixture was stirred at room temperature for 6 h, at which time TLC showed no starting material. Then, the solvent was removed under vacuum and ether – water (90 : 20 mL) was added. The phases were shaken, separated and the organic phase was washed with brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded a crude product which was directly purified by flash chromatography on silica gel (2 % ether/hexanes) to yield 4.65 g of **17** (97%) as a colourless syrup.

$[\alpha]_D^{25}$ = +12.0 (c 3.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.77 (s, 3H), 0.81 (d, *J* = 6.8 Hz, 3H), 0.83 (s, 3H), 0.86 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.14 (ddd, *J* = 13.3, 13.3, 3.4 Hz, 1H), 1.30 (dd, *J* = 12.0, 5.6 Hz, 1H), 1.34 (s, 3H), 1.39 (s, 3H), 1.35 - 1.77 (m, 9H), 1.83 (h, *J* = 6.8 Hz, 1H), 1.95 (m, 1H), 2.16 (m, 1H), 4.20 (s, 1H), 5.80 (br s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 38.6 (C-1), 16.7 (C-2), 42.3 (C-3), 33.1 (C-4), 50.7 (C-5), 30.4 (C-6), 128.4 (C-7), 133.5 (C-8), 53.0 (C-9), 34.8 (C-10), 24.6 (C-11), 18.9 (C-12), 84.1 (C-13), 81.9 (C-14), 37.7 (C-15), 16.9 (C-16)*, 17.7 (C-17)*, 32.8 (C-18), 21.1 (C-19), 13.6 (C-20), 106.3 (C-acetonide), 26.7 (CH_3-acetonide), 28.1 (CH_3-acetonide). IR (film): 1460, 1377, 1366, 1252, 1210, 1168, 1029, 1012, 888 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{23}H_{38}O_2Na$ ($M+Na^+$) 369.2770, found: 369.2775.

* interchangeable signals

2-((1S,2S)-2-((3aR,5R,7aS)-7a-isopropyl-2,2-dimethyl-4-oxo-hexahydrobenzo[d][1,3]dioxol-5-yl)-2,6,6-trimethylcyclohexyl)acetaldehyde (13).

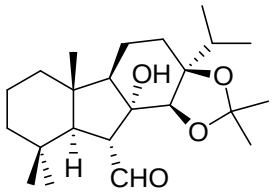


13

A stirred solution of **17** (1.6 g, 4.62 mmol) in CH_2Cl_2 – MeOH (45 : 15 mL) was slowly bubbled with an O_3/O_2 mixture at -78 ºC, and the course of the reaction was monitored by TLC. When the starting material was consumed (45 min), the solution was flushed with argon, and methyl sulfide (5 mL) was added. The mixture was further stirred at room temperature under argon atmosphere for 4 h and the solvent was removed. Flash chromatography on silica gel (35 % ether/hexanes) gave ketoaldehyde **13** (1.45 g, 83%). $[\alpha]_D^{25}$ = 36.3 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.80 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H), 0.93 (s, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 1.09 (s, 3H), 1.15 - 1.28 (m, 2H), 1.38 (s, 3H), 1.47 (s, 3H), 1.29 - 1.68 (m, 4H), 1.71 - 1.82 (m, 2H), 1.91 – 2.00 (m, 2H), 2.02 (dd, *J* = 6.0, 3.6 Hz, 1H), 2.35 (ddd, *J* = 18.4, 3.5, 1.6 Hz, 1H), 1.48 (ddd, *J*= 18.4, 6.1, 1.7 Hz, 1H) (m, 2H), 3.97 (s, 1H), 9.79 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 41.5 (C-1), 18.5 (C-2), 42.1 (C-3), 34.9 (C-4), 43.2 (C-5), 34.4 (C-6), 210.3 (C-7), 202.6 (C-8), 57.7 (C-9), 40.6 (C-10), 27.0 (C-11), 19.7 (C-12), 85.0 (C-13), 90.2 (C-14), 36.7 (C-15), 18.3 (C-16)*, 19.6 (C-17)*, 34.2 (C-18), 22.5 (C-19), 16.7 (C-20), 110.0 (C-acetonide), 27.3 (CH_3-acetonide), 27.6 (CH_3-acetonide). IR (film): 1460, 1377, 1366, 1252, 1210, 1167, 1029, 1012, 888 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{23}H_{38}O_4Na$ ($M+Na^+$) 401.2668, found: 401.2662.

* interchangeable signals

(3aS,5bS,9aS,10R,10aR,10bS)-10a-hydroxy-3a-isopropyl-2,2,5b,9,9-pentamethyl-dodecahydro-3aH-fluoren[2,1-d][1,3]dioxole-10-carbaldehyde (12).



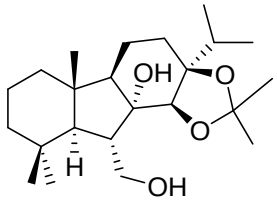
12

1,8-Diazabicyclo [5.4.0]undec-7-ene (DBU) (520 mg, 3.42 mmol) was added to a stirred solution of ketoaldehyde **13** (0.5 g, 1.32 mmol) in benzene (15 mL) and the mixture was stirred under reflux for 1 h, at which time TLC showed no **13**. Then, it was diluted with ether (30 mL) and washed with 1M HCl, water and brine. The organic phase was dried over Na_2SO_4 and concentrated under vacuum to yield hydroxyl aldehyde **12** (474 mg, 95%) as a yellow syrup.

$[\alpha]_D^{25}$ = + 22.6 (c 1.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.88 (s, 3H), 0.92 (s, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 1.00 (d, *J* = 6.8 Hz, 3H), 1.01 (s, 3H), 1.12 (ddd, *J* = 12.7, 12.7, 3.4 Hz, 1H), 1.21 (ddd, *J* = 13.9, 13.9, 4.7 Hz, 1H), 1.32 (s, 3H), 1.42 (s, 3H), 1.28 - 1.68 (m, 9H), 1.72 (br d, *J* = 12.5 Hz, 1H), 1.87 (h, *J* = 6.8 Hz, 1H), 1.97 (d, *J* = 13.1 Hz, 1H), 3.01 (dd, *J* = 13.1, 3.3 Hz, 1H), 3.18 (s, 1H), 3.98 (s, 1H), 9.98 (d, *J* = 3.3 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 40.0 (C-1), 16.1 (C-2), 41.8 (C-3), 33.3 (C-4), 56.3 (C-5), 58.0 (C-6), 208.6 (C-7), 80.5 (C-8), 62.2 (C-9), 42.8 (C-10), 28.3 (C-11), 19.7 (C-12), 85.7 (C-13), 80.0 (C-14), 37.5 (C-15), 16.5 (C-16)*, 18.0 (C-17)*, 36.0 (C-18), 22.5 (C-19), 16.5 (C-20), 106.6 (C-acetonide), 26.5 (CH_3-acetonide), 26.9 (CH_3-acetonide). IR (film): 3468, 1706, 1465, 1378, 1258, 1210, 1182, 1051, 995, 758 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{23}H_{38}O_4Na$ ($M+Na^+$) 401.2668, found: 401.2654.

* interchangeable signals

(3aS,5bS,9aS,10S,10aR,10bS)-10-(hydroxymethyl)-3a-isopropyl-2,2,5b,9,9-pentamethyl-dodecahydro-3aH-fluoren[2,1-d][1,3]dioxol-10a-ol (28).

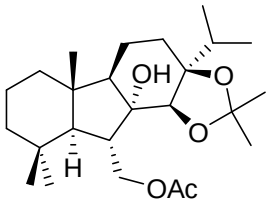


28

Sodium borohydride (0.32 g, 8.42 mmol) was added to a stirred solution of hydroxy aldehyde **12** (1.3 g, 3.44 mmol) in EtOH (10 mL) and the reaction mixture was stirred at room temperature for 15 min, at which time TLC showed no **12**. The reaction mixture was quenched with water (1 mL), the solvent was evaporated, and the crude product was diluted with ether (30 mL) and washed with water and brine. The organic phase was dried over Na_2SO_4 and concentrated to give **28** (1.28 g, 98%) as a colorless oil. $[\alpha]_D^{25}$ = + 2.3 (c 1.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.91 (s, 3H), 0.96 (s, 6H), 0.98 (d, *J* = 6.8 Hz, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.06 (ddd, *J* = 13.3, 13.3, 4.2 Hz, 1H), 1.19 (ddd, *J* = 13.3, 13.3, 4.2 Hz, 1H), 1.36 (s, 3H), 1.44 (s, 3H), 1.30-1.49 (m, 6H), 1.52-1.70 (m, 4H), 1.92 (h, *J* = 6.8 Hz, 1H), 2.16 (br s, 1H), 2.32 (ddd, *J* = 13.1, 7.6, 4.2 Hz, 1H), 3.85 (dd, *J* = 11.3, 7.6 Hz, 1H), 4.15 (dd, *J* = 11.3, 4.2 Hz, 1H), 4.16 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 40.4 (C-1), 16.1 (C-2), 43.0 (C-3), 33.1 (C-4), 54.5 (C-5), 45.5 (C-6), 63.2 (C-7), 80.1 (C-8), 61.4 (C-9), 42.1 (C-10), 28.5 (C-11), 19.9 (C-12), 86.0 (C-13), 81.0 (C-14), 37.7 (C-15), 18.3 (C-16)*, 18.4 (C-17)*, 35.0 (C-18), 22.3 (C-19), 17.0 (C-20), 106.5 (C-acetonide), 26.8 (CH_3-acetonide), 27.2 (CH_3-acetonide). IR (film): 3420, 1461, 1378, 1258, 1209, 1182, 1050, 994, 937, 758 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{23}H_{40}O_4Na$ ($M+Na^+$) 403.2824, found: 403.2831.

* interchangeable signals

((3aS,5bS,9aS,10S,10aR,10bS)-10a-hydroxy-3a-isopropyl-2,2,5b,9,9-pentamethyl-dodecahydro-3aH-fluoren[2,1-d][1,3]dioxol-10-yl)methyl acetate (18).



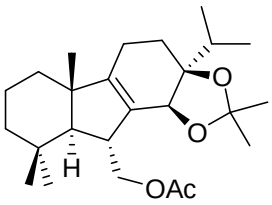
18

To a solution of **28** (2.3 g, 6.05 mmol) in pyridine (10 ml) at 0 ºC was added acetic anhydride (6 mL) and the reaction mixture was stirred at room temperature for 1 h, at which time TLC showed no starting material. Then, the reaction mixture was cooled at 0 ºC, water (10 mL) was added to quench the reaction and the mixture was stirred for an additional 10 min. Then, it was diluted with ether (100 mL) and washed with water (1 x 20 mL), 2N HCl (5 x 20 mL), again water (1 x 20 mL), sat. aq $NaHCO_3$ (5 x 20 mL) and brine, and the organic phase was dried over Na_2SO_4. Removal of the solvent under vacuum afforded a crude product which was purified by flash chromatography on silica gel (15 % ether/hexanes) to yield 2.45 g of **18** (96%) as a colourless syrup.

$[\alpha]_D^{25}$ = + 3.7 (c 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.921 (s, 3H), 0.925 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 0.99 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.17 (ddd, *J* = 13.3, 4.6 Hz, 1H), 1.30 (dd, *J* = 6.0, 6.0 Hz, 1H), 1.35 (s, 3H), 1.45 (s, 3H), 1.22 -1.62 (m, 10H), 1.68 (br d, *J* = 15.6 Hz, 2H), 1.88 (h, *J* = 6.9 Hz, 1H), 2.08 (s, 3H), 2.51 (ddd, *J* = 13.0, 9.5, 4.9 Hz, 1H), 4.01 (s, 1H), 4.18 (dd, *J* = 11.2, 9.6 Hz, 1H), 4.56 (dd, *J* = 11.2, 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 40.3 (C-1), 16.1 (C-2), 43.0 (C-3), 32.9 (C-4), 55.5 (C-5), 44.1 (C-6), 64.5 (C-7), 78.7 (C-8), 61.4 (C-9), 42.0 (C-10), 28.8 (C-11), 19.7 (C-12), 85.7 (C-13), 80.5 (C-14), 37.6 (C-15), 18.1 (C-16)*, 18.2 (C-17)*, 34.9 (C-18), 22.1 (C-19), 16.8 (C-20), 106.4 (C-acetonide), 26.6 (CH_3-acetonide), 27.1 (CH_3-acetonide), 21.1 (CH_3-OAC), 170.9 (C-OAc). IR (film): 3473, 1742, 1458, 1377, 1246, 1210, 1045, 995, 773, 669 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{25}H_{42}O_5Na$ ($M+Na^+$) 445.2930, found: 445.2919.

* interchangeable signals

((3aS,5bS,9aS,10R,10bS)-3a-isopropyl-2,2,5b,9,9-pentamethyl-4,5,5b,6,7,8,9,9a,10,10b-decahydro-3aH-fluoren[2,1-d][1,3]dioxol-10-yl)methyl acetate (19).



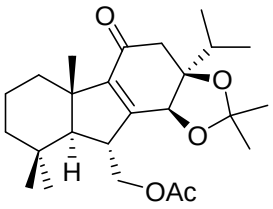
19

$SOCl_2$ (0.5 mL, 6.85 mmol) was added slowly to a solution of **18** (2 g, 4.74 mmol) and pyridine (1 mL) in dry CH_2Cl_2 (10 mL) at -60 ºC. The reaction mixture was stirred at this temperature under argon atmosphere for 5 min, at which time TLC showed no starting material. The reaction mixture was quenched with sat. aq. $NaHCO_3$ (1 mL) and the cooling bath was removed. The mixture was poured into ether - water (90 : 20 mL) and the phases were shaken and separated. The organic phase was washed with 2N HCl (3 x 10 mL), brine and dried over Na_2SO_4 Removal of the solvent under vacuum afforded a crude product which was directly purified by flash chromatography on silica gel (10 % ether/hexanes) to yield 1.7 g of **19** (89%) as a yellow syrup.

$[\alpha]_D^{25}$ = -18.2 (c 0.9, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.98 (d, *J* = 6.9 Hz, 3H), 0.92 (s, 3H), 0.96 (s, 3H), 1.00 (d, *J* = 6.9 Hz, 3H), 1.03 (s, 3H), 1.18 (ddd, *J*= 14.5, 24.5, 5.0 Hz, 1H), 1.21 (ddd, *J* = 12.9, 12.9, 3.9 Hz, 1H), 1.32 (s, 3H), 1.39 (s, 3H), 1.41 (m, 1H), 1.54 (d, *J* = 11.0 Hz, 1H), 1.50 -1.79 (m, 4H), 1.80 -1.90 (m, 2H), 1.97 (h, *J* = 6.9 Hz, 1H), 2.03 (s, 3H), 2.86 (br d, *J* = 10.8 Hz, 1H), 4.32 (dd, *J* = 11.9, 3.8 Hz, 1H), 4.32 (s, 1H), 4.52 (dd, *J* = 11.9, 2.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.1 (C-1), 17.2 (C-2), 42.2 (C-3), 33.5 (C-4), 58.5 (C-5), 41.8 (C-6), 63.3 (C-7), 132.0 (C-8), 150.5 (C-9), 46.5 (C-10), 24.7 (C-11), 19.4 (C-12), 84.9 (C-13), 73.3 (C-14), 33.7 (C-15), 17.8 (C-16)*, 18.8 (C-17)*, 33.3 (C-18), 22.3 (C-19), 16.2 (C-20), 108.3 (C-acetonide), 28.7 (CH_3-acetonide), 28.8 (CH_3-acetonide), 20.8 (CH_3-OAC), 171.0 (C-OAc). IR (film): 1743, 1461, 1376, 1238, 1163, 1033, 979, 944, 862, 758 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{25}H_{40}O_4Na$ ($M+Na^+$) 427.2824, found: 427.2831.

* interchangeable signals

((3aS,5bS,9aS,10R,10bS)-3a-isopropyl-2,2,5b,9,9-pentamethyl-5-oxo-4,5,5b,6,7,8,9,9a,10,10b-decahydro-3aH-fluoren[2,1-d][1,3]dioxol-10-yl)methyl acetate (11).



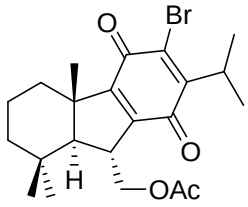
11

Pyridinium chlorochromate (PCC) (1.13 g, 5.24 mmol), pyridine (1 g, 12.65 mmol) and celite (2 g) were added to a stirred solution of **19** (0.5 g, 1.237 mmol) in dry benzene (25 mL) and the mixture was kept stirring at reflux under argon atmosphere for 3 days, at which time TLC showed no remaining starting material. Then, the reaction was worked up by the addition of ether (50 mL) and the resulting mixture was filtered through a silica gel pad and washed with ether (30 mL). The filtrate was washed with 2N HCl (3 x 15 mL) and brine. The solvent was evaporated to yield a crude product, which was chromatographed on silica gel (30% ether/hexanes) to yield **11** (413 mg, 80%).

$[\alpha]_D^{25}$ = + 15.7 (c 1.0, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.90 (d, *J* = 6.9 Hz, 3H), 0.97 (s, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.04 (s, 3H), 1.08 (s, 3H), 1.19 (ddd, *J* = 13.4, 13.4, 4.6 Hz, 1H), 1.29 (s, 3H), 1.41 (s, 3H), 1.22 – 1.80 (m, 5H), 1.68 (d, *J* = 11.7 Hz, 1H), 2.06 (s, 3H), 2.27 (dt, *J* = 12.9, 3.8 Hz, 1H), 2.52 (d, *J* = 16.5 Hz, 1H), 2.62 (d, *J* = 16.5 Hz, 1H), 3.03 (br d, *J* = 11.7 Hz, 1H), 4.44 (dd, *J* = 12.1, 3.5 Hz, 1H), 4.58 (s, 1H), 4.60 (dd, *J* = 12.1, 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 41.4 (C-1), 19.32 (C-2), 41.9 (C-3), 33.4 (C-4), 57.5 (C-5), 43.4 (C-6), 62.5 (C-7), 147.4 (C-8), 157.3 (C-9), 45.9 (C-10), 194.6 (C-11), 34.5 (C-12), 87.7 (C-13), 72.7 (C-14), 34.8 (C-15), 18.2 (C-16)*, 19.31 (C-17)*, 33.6 (C-18), 22.2 (C-19), 16.0 (C-20), 109.5 (C-acetonide), 28.7 (CH_3-acetonide), 28.9 (CH_3-acetonide), 20.8 (CH_3-OAC), 170.7 (C-OAc). IR (film): 1745, 1678, 1461, 1378, 1236, 1153, 1054, 1031, 845, 771, 669 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{25}H_{38}O_5Na$ ($M+Na^+$) 441.2617, found: 441.2622.

* interchangeable signals

((4aS,9R,9aS)-6-bromo-7-isopropyl-1,1,4a-trimethyl-5,8-dioxo-2,3,4,4a,5,8,9,9a-octahydro-1H-fluoren-9-yl)methyl acetate (20).



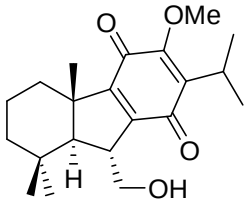
20

Bromine (0.2 ml, 7.81 mmol) was added to a solution of **11** (380 mg, 0.936 mmol) in CH_2Cl_2 (15 mL) and the mixture was stirred at room temperature for 30 min, at which time TLC showed no **11**. Then, 5% $NaHSO_3$ (1 mL) was added and the mixture was diluted with ether (60 mL). The organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded the resulting crude residue which was purified by flash chromatography on silica gel (30% ether/hexanes) giving the bromoquinone derivative **20** (330 mg, 81%) as a yellow syrup.

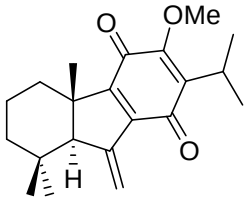
$[\alpha]_D^{25}$ = + 75.7 (c 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.01 (s, 3H), 1.06 (s, 3H), 1.10 (s, 3H), 1.24 (m, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.40 – 1.78 (m, 5H), 1.80 (d, *J* = 11.4 Hz, 1H), 1.98 (s, 3H), 2.34 (dt, *J* = 12.8, 3.7 Hz, 1H), 3.22 (dt, *J* = 11.4, 2.6 Hz, 1H), 3.38 (h, *J* = 7.0 Hz, 1H), 4.45 (dd, *J* = 11.7, 2.3 Hz, 1H), 4.95 (dd, *J* = 11.7, 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.2 (C-1), 19.3 (C-2), 41.8 (C-3), 33.7 (C-4), 56.5 (C-5), 42.8 (C-6), 62.5 (C-7), 146.7 (C-8), 154.7 (C-9), 47.5 (C-10), 183.7 (C-11), 152.7 (C-12), 134.7 (C-13), 177.6 (C-14), 34.1 (C-15), 19.9 (C-16)*, 20.1 (C-17)*, 33.6 (C-18), 22.2 (C-19), 19.6 (C-20), 20.8 (CH_3-OAC), 170.6 (C-OAc). IR (film): 1744, 1664, 1566, 1461, 1381, 1364, 1300, 1238, 1086, 1031, 801, 754, 617 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{22}H_{29}BrO_4Na$ (M+Na$^+$) 459.1147, found: 459.1143.

* interchangeable signals

(4bS,8aS,9R)-9-(hydroxymethyl)-2-isopropyl-3-methoxy-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1,4-dione (21) and (4bS,8aR)-2-isopropyl-3-methoxy-4b,8,8-trimethyl-9-methylene-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1,4-dione (22).



21



22

To a solution of **20** (203 mg, 0.465 mmol) in dried methanol (10 mL) was added sodium methoxide (130 mg, 2.41 mmol) and the solution was stirred at room temperature for 10 min, at which time TLC showed no **20**. Then, the solvent was removed and ether – water (40 : 10 mL) was added, and the phases were shaken and separated. The organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent in vacuum afforded a crude product which was purified by flash chromatography on silica gel (15% ether/hexanes) giving 92 mg of **21** (57%) as a yellow syrup and 59 mg of **22** (39%) as a yellow syrup.

21: $[\alpha]_D^{25}$ = -94.5 (c 0.6, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.07 (s, 3H), 1.09 (s, 3H), 1.12 (s, 3H), 1.19 (d, *J* = 7.1 Hz, 1H), 1.21 (d, *J* = 7.1 Hz, 1H), 1.22 (m, 1H), 1.40 – 1.80 (m, 5H), 1.58 (d, *J* = 11.4 Hz, 1H), 2.17 (s, 1H), 2.31 (dt, *J* = 12.8, 4.1 Hz 1H), 3.11 (ddd, *J* = 11.4, 7.2, 2.4 Hz, 1H), 3.22 (h, *J* = 7.1 Hz, 1H), 3.60 (dd, *J* = 11.7, 7.2 Hz, 1H), 3.95 (s, 3H), 4.35 (dd, *J* = 11.7, 2.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.3 (C-1), 19.3 (C-2), 41.9 (C-3), 33.8 (C-4), 57.6 (C-5), 48.0 (C-6), 62.5 (C-7), 148.5 (C-8), 156.0 (C-9), 47.3 (C-10), 182.0 (C-11), 154.7 (C-12), 137.3 (C-13), 189.0 (C-14), 24.7 (C-15), 20.5 (C-16)*, 20.6 (C-17)*, 34.8 (C-18), 22.5 (C-19), 20.4 (C-20), 61.0 (C-OMe). IR (film): 3422, 1644, 1589, 1458, 1314, 1263, 1148, 1049, 1018, 940, 815, 760, 668 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{21}H_{30}O_4Na$ ($M+Na^+$) 369.2042, found: 369.2037.

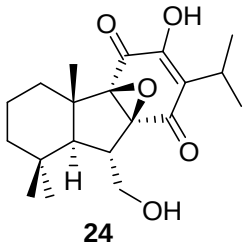
* interchangeable signals

22: $[\alpha]_D^{25}$ = -92.7 (c 0.5, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.09 (s, 3H), 1.14 (s, 3H), 1.15 (s, 3H), 1.21 (d, *J* = 7.1 Hz, 3H), 1.22 (d, *J* = 7.1 Hz, 3H), 1.45-1.64 (m, 4H), 1.74 (m, 1H), 2.25 (t, *J* = 2.6 Hz, 1H), 2.35 (dt, *J* = 12.8, 3.2 Hz, 1H), 3.23 (h, *J* = 7.1 Hz, 1H), 3.94 (s, 3H), 5.48 (d, *J* = 2.6 Hz, 1H), 6.18 (d, *J* = 2.6 Hz, 1H). ^{13}C NMR

($CDCl_3$, 125 MHz) δ: 33.9 (C-1), 19.1 (C-2), 42.9 (C-3), 33.1 (C-4), 63.2 (C-5), 141.4 (C-6), 116.3 (C-7), 144.8 (C-8), 156.2 (C-9), 47.2 (C-10), 182.7 (C-11), 153.1 (C-12), 137.6 (C-13), 186.9 (C-14), 24.5 (C-15), 20.68 (C-16)*, 20.69 (C-17)*, 32.9 (C-18), 20.66 (C-19)*, 20.5 (C-20)*, 61.1 (C-OMe). IR (film): 1656, 1575, 1458, 1284, 1260, 1147, 1101, 1058, 1017, 799, 772, 669 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{21}H_{28}O_3Na$ ($M+Na^+$) 351.1936, found: 351.1947.

* interchangeable signals

(4aR,4bS,8aS,9S,9aS)-3-hydroxy-4a,9a-epoxy-9-(hydroxymethyl)-2-isopropyl-4b,8,8-trimethyl-4b,5,6,7,8,8a,9,9a-octahydro-4aH-fluoren-1,4-dione (24).



24

2N KOH in MeOH (1 mL) was added to a solution of **21** (78 mg, 0.225 mmol) in MeOH (5 mL) and the mixture was stirred at room temperature for 10 h, at which time TLC showed no remaining starting material. Then, the solvent was removed in vacuum and ether – water (30 : 10 mL) was added, and the phases were shaken and separated. 2N HCl (2 mL) was added slowly to the aqueous phase and the mixture was diluted with ether (30 mL). The organic phase was washed with water and brine, dried over Na_2SO_4 and concentrated to afford a crude product, which was purified by flash chromatography on silica on silica gel (35% ether/hexanes) to give **24** (54 mg, 69%) as a yellow syrup .

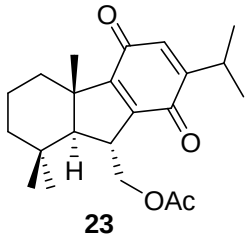
$[\alpha]_D^{25}$ = -31.8 (c 0.2, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 1.00 (s, 3H), 1.01 (s, 3H), 1.07 (s, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.23 (d, *J* = 7.1 Hz, 3H), 1.45 (dt, *J* = 13.4, 4.6 Hz, 1H), 1.52-1.71 (m, 5H), 2.16 (dt, *J* = 12.8, 3.8, 1H), 2.54 (ddd, 11.5, 8.2, 2.7 Hz, 1H), 3.13 (h, *J* = 7.1 Hz, 1H), 3.65 (dd, *J* = 11.5, 8.2 Hz, 1H), 4.22 (dd, *J* = 11.5, 8.2 Hz, 1H), 6.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 32.1 (C-1), 19.0 (C-2), 41.6 (C-3), 33.4 (C-4), 48.3 (C-5), 42.0 (C-6), 61.9 (C-7), 66.1 (C-8), 67.8 (C-9), 42.0 (C-10), 188.0 (C-11), 152.7 (C-12), 127.6 (C-13), 194.3 (C-14), 25.4 (C-15), 19.3 (C-16)*, 19.8 (C-17)*, 34.8 (C-18), 23.1 (C-19), 19.3 (C-20). IR (film): 3398, 1696, 1638, 1463, 1382, 1286, 1258, 1094, 1041, 969, 904, 798. HRMS (FAB) *m/z*: calcd for $C_{20}H_{28}O_5Na$ ($M+Na^+$) 371.1834, found: 371.1844.

* interchangeable signals

Synthesis of 24 from 11.

KOH (500 mg, 12.5 mmol) was added to a solution of **11** (138 mg, 0.33 mmol) in MeOH (10 mL) and the mixture was stirred at room temperature for 13 h under oxygen atmosphere, at which time TLC showed no remaining starting material. Following the same work-up previously described for **24**, 84 mg of quinone **24** was obtained (73%).

((4aS,9R,9aS)-7-isopropyl-1,1,4a-trimethyl-5,8-dioxo-2,3,4,4a,5,8,9,9a-octahydro-1H-fluoren-9-yl)methyl acetate (23).



23

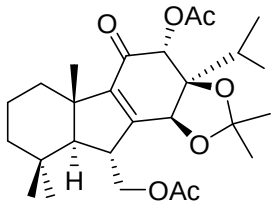
KOH (100 mg, 2.5 mmol) was added to a solution of **11** (103 mg, 0.253 mmol) in MeOH (6 mL) at -30 ºC and the mixture was stirred for 4 h under oxygen atmosphere, at which time TLC showed no remaining starting material. Then, the solvent was removed in vacuum and ether – water (30 - 10 mL) was added, and the phases were shaken and separated. The organic phase was washed with water and brine, dried over Na_2SO_4 and concentrated to afford a crude product, which was purified by flash chromatography on silica gel (10% ether/hexanes) to give quinone **23** (56 mg, 62%) as a yellow syrup.

$[\alpha]_D^{25}$ = -34.4 (c 0.9, $CHCl_3$). 1.01(s, 3H), 1.06 (s, 3H), 1.08 (d, *J* = 6.9 Hz, 3H), 1.10 (s, 3H), 1.12 (d, *J* = 6.9 Hz, 3H), 1.24 (dt, *J* = 13.4, 4.6 Hz, 1H), 1.43-1.65 (m, 4H), 1.73 (m, 1H), 1.82 (d, *J* = 11.4 Hz, 1H), 1.98 (s, 3H), 2.34 (dt, *J* = 12.8, 3.8 Hz, 1H), 3.02 (dh, *J* = 6.9, 1.1 Hz, 1H), 3.22 (dt, *J* = 11.4, 2.6 Hz), 4.49 (dd, *J* = 11.7, 2.4 Hz, 1H), 5.00 (dd, *J* = 11.7, 2.8 Hz, 1H), 6.31 (d, *J* = 1.2 Hz, 1H).). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.5 (C-1), 19.4 (C-2), 41.9 (C-3), 33.7 (C-4), 56.6 (C-5), 42.8 (C-6), 62.7 (C-7), 145.7 (C-8), 155.8 (C-9)*, 46.9 (C-10), 186.6 (C-11), 130.2 (C-12), 155.1 (C-13)*, 186.9 (C-14), 26.5 (C-15), 21.2 (C-16)&, 21.9 (C-17)&, 33.7 (C-18), 22.4 (C-19), 20.2 (C-20), 20.9 (CH_3-OAc), 170.8 (C-OAc). IR (film): 1740, 1647, 1595, 1460, 1385,

1311, 1243, 1068, 1037, 929, 902, 772 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{22}H_{30}O_4Na$ ($M+Na^+$) 381.2042, found: 381.2052.

*& interchangeable signals

((3aR,4R,5bS,9aS,10R,10bS)-4-acetoxy-3a-isopropyl-2,2,5b,9,9-pentamethyl-5-oxo-4,5,5b,6,7,8,9,9a,10,10b-decahydro-3aH-fluoren[2,1-d][1,3]dioxol-10-yl)methyl acetate (25).

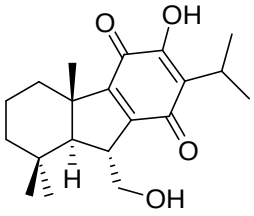


25

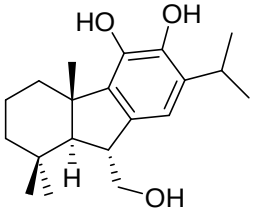
Lead (IV) acetate (1 g, 2.25 mmol) was added to a solution of ketone **11** (317 mg, 0.758 mmol) in dry benzene (25 mL) and the mixture was stirred at reflux for 3 days, at which time TLC showed no **11**. The reaction was filtered through a silica gel pad and washed with ether (50 mL). The organic phase was then washed with 5% aq $NaHSO_3$ (10 mL), satd. aq $NaHCO_3$ (3 x 10 mL) and brine, and dried over Na_2SO_4. Removal of the solvent in vacuum gave a crude product which was purified by flash chromatography on silica gel (15% ether/hexanes) to afford pure **25** (300 mg, 83%) as a colourless oil. $[\alpha]_D^{25}$ = + 6 (c 0.8, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ: 0.79 (d, *J* = 7.1 Hz, 3H), 0.98 (s, 3H), 1.01 (d, *J* = 7.1 Hz, 3H), 1.05 (s, 3H), 1.06 (s, 3H), 1.20 – 1.72 (m, 5H), 1.42 (s, 3H), 1.53 (s, 3H), 1.75 (d, *J* = 11.6, Hz, 1H), 2.07 (s, 3H), 2.23 (s, 3H), 2.27 (dt, *J* = 13.6, 3.9, 3.9 Hz, 1H), 2.41 (h, *J* = 7.1 Hz, 1H), 3.14 (dt, *J* = 11.7, 3.3, 3.3 Hz, 1H), 4.41 (dd, *J* = 12.3, 3.9 Hz, 1H), 4.53 (s, 1H), 4.61 (dd, *J* = 12.3, 2.3 Hz, 1H), 5.70 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.9 (C-1), 19.32 (C-2), 41.8 (C-3), 33.3 (C-4), 58.3 (C-5), 44.0 (C-6), 62.0 (C-7), 148.7 (C-8), 153.8 (C-9), 46.5 (C-10), 189.3 (C-11), 69.6 (C-12), 87.8 (C-13), 78.3 (C-14), 30.1 (C-15), 18.4 (C-16)*, 19.35 (C-17)*, 33.7 (C-18), 22.1 (C-19), 17.3 (C-20), 110.4 (C-acetonide), 27.1 (CH_3-acetonide), 28.0 (CH_3-acetonide), 20.7 (CH_3-OAC), 20.8 (CH_3-OAc), 170.1 (C-OAc), 170.5 (C-OAc). IR (film): 1749, 1696, 1458, 1373, 1229, 1047, 886, 761 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{27}H_{40}O_7Na$ ($M+Na^+$) 499.2672, found: 499.2684.

* interchangeable signals

(4bS,8aS,9R)-3-hydroxy-9-(hydroxymethyl)-2-isopropyl-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1,4-dione (26) and (4bS,8aS,9R)-9-(hydroxymethyl)-2-isopropyl-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-3,4-diol (27).



26



27

Conc. hydrochloric acid (2 mL) was added to a stirred solution of **25** (240 mg, 0.504 mmol) in MeOH (12 mL) under oxygen atmosphere and the reaction mixture was heated at 40 ºC for 13 h, at which time TLC showed no starting material remaining. Then, the solvent was removed in vaccum and ether -water (30 : 10 mL) was added. The phases were shaken, separated and the organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded a crude product which was directly purified by flash chromatography (10 % ether/hexanes) to yield 134 mg of **26** (80%) as a yellow syrup and 13 mg of **27** (8%) as a colourless syrup.

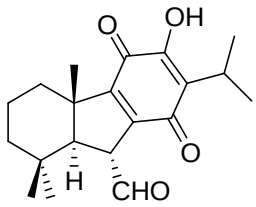
26: $[\alpha]_D^{25}$ = -117.5 (c 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.08 (s, 3H), 1.10 (s, 3H), 1.13 (s, 3H), 1.22 (d, *J* = 7.3 Hz, 3H), 1.23 (d, *J* = 7.3 Hz, 3H), 1.24 (m, 1H), 1.42 – 1.58 (m, 2H), 1.61 (d, *J* = 11.4 Hz, 1H), 1.62 (m, 1H), 1.75 (m, 1H), 2.28 (dt, *J* = 12.9, 4.1, 4.1 Hz, 1H), 3.14 (ddd, *J* = 11.4, 7.2, 1.8, Hz, 1H), 3.19 (h, *J* = 7.1 Hz, 1H), 3.60 (dd, *J* = 11.7, 7.2 Hz, 1H), 4.14 (br s, 1H), 4.36 (dd, *J* = 11.7, 1.8 Hz, 1H), 6.97 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.3 (C-1), 19.3 (C-2), 41.9 (C-3), 33.8 (C-4), 57.7 (C-5), 48.6 (C-6), 62.4 (C-7), 149.2 (C-8), 152.8 (C-9), 48.7 (C-10), 181.0 (C-11), 151.2 (C-12), 124.6 (C-13), 185.3 (C-14), 24.2 (C-15), 19.8 (C-16)*, 19.9 (C-17)*, 35.0 (C-18), 21.8 (C-19), 20.2 (C-20). IR (film): 3384, 1647, 1597, 1458, 1393, 1374, 1311, 1286, 1160, 1108, 1044, 975, 759 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{20}H_{28}O_4Na$ ($M+Na^+$) 355.1885, found: 355.1881.

27: $[\alpha]_D^{25}$ = +31.9 (c 1.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.10 (s, 3H), 1.14 (s, 3H), 1.17 (s, 3H), 1.23 (d, *J* = 6.9 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.27-1.37 (m, 2H),

1.49 (dt, *J* = 14.0, 3.9, 3.9 Hz, 1H), 1.68 (m, 1H), 1.79 (m, 1H), 1.86 (d, *J* = 11.6 Hz, 1H), 2.28 (dt, *J* = 11.6, 3.9, 3.9 Hz, 1H), 3.07 (dt, *J* = 11.6, 2.4, 2.4 Hz, 1H), 3.14 (h, *J* = 6.9 Hz, 1H), 4.10 (dd, *J* = 11.8, 3.2 Hz, 1H), 4.31 (dd, *J* = 11.8, 2.4 Hz, 1H), 5.04 (br.s, 1H), 6.69 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 36.4 (C-1), 19.8 (C-2), 42.0 (C-3), 33.8 (C-4), 58.2 (C-5), 44.8 (C-6), 61.8 (C-7), 134.2 (C-8), 136.5 (C-9), 45.7 (C-10), 138.9 (C-11)*, 140.2 (C-12)*, 132.5 (C-13), 119.5 (C-14), 27.5 (C-15), 22.4 (C-16)&, 22.6 (C-17)&, 33.7 (C-18), 21.5 (C-19), 23.0 (C-20). IR (film): 3436, 1445, 1373, 1287, 1216, 1098, 1031, 991, 938, 759, 669 cm^{-1}. HRMS (FAB) *m/z*: calcd for $C_{20}H_{30}O_3Na$ ($M+Na^+$) 341.2093, found: 341.2099.

*& interchangeable signals

Taiwaniaquinone A (5).



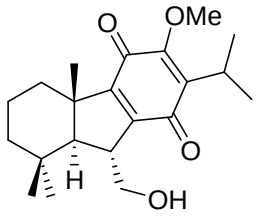
5

Pyridinium dichromate (PDC; 0.6 g, 1.59 mmol) was added to a stirred solution of **26** (88 mg, 0.265 mmol) in dry CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature under argon atmosphere for 24 h, at which time TLC showed no remaining starting material. Then, the reaction was worked up by the addition of ether (10 mL), and the resulting mixture was filtered through a silica gel pad and washed with ether (2 x 15 mL). The filtrate was washed with 2N HCl (2 x 10 mL), water and brine, dried over anhydrous Na_2SO_4 and the solvent was evaporated to give 80 mg of taiwaniaquinone A (**5**), (91%) as a colourless syrup.

$[\alpha]_D^{25}$ = -118.2 (c 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.81 (s, 3H), 1.08 (s, 3H), 1.17 (s, 3H), 1.20 (d, *J* = 7.1 Hz, 3H), 1.21 (d, *J* = 7.1 Hz, 3H), 1.20 - 1.83 (m, 5H), 1.77 (m, 1H), 2.15 (d, *J* = 11.5 Hz, 1H), 2.29 (dt, *J* = 12.7, 3.2, 3.2 Hz, 1H), 3.15 (h, *J* = 7.1 Hz, 1H), 3.78 (dd, *J* = 11.5, 3.8 Hz, 1H), 6.93 (s, 1H), 9.86 (d, *J* = 3.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.4 (C-1), 19.3 (C-2), 41.1 (C-3), 33.7 (C-4), 61.5 (C-5), 54.4 (C-6), 200.1 (C-7), 149.2 (C-8), 152.8 (C-9), 48.7 (C-10), 181.0 (C-11), 151.2 (C-12), 124.6 (C-13), 185.3 (C-14), 24.2 (C-15), 19.8 (C-16), 19.9 (C-17), 35.0

(C-18), 21.8 (C-19), 20.2 (C-20). IR (film): 3386, 1731, 1652, 1606, 1460, 1394, 1374, 1310, 1262, 1101, 803, 758 cm^{-1}.

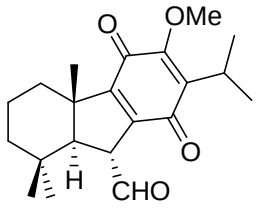
(4bS,8aS,9R)-9-(hydroxymethyl)-2-isopropyl-3-methoxy-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1,4-dione (21) from 26.



21

K_2CO_3 (100 mg, 0.72 mmol) was added to a solution of quinone **26** (65 mg, 0.196 mmol) in acetone (10 mL), and the reaction was kept stirring at room temperature for 5 min. Then, dimethyl sulfate (90 mg, 0.713 mmol) was added, and the reaction mixture was stirred at room temperature for 3 h. Then, the solvent was removed in vacuum and ether - water (40 : 15 mL) was added. The phases were shaken, separated and the organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. Removal of the solvent under vacuum afforded a crude product which was directly purified by flash chromatography (10 % ether/hexanes) to yield 50 mg of **21** (74%) as a yellow syrup.

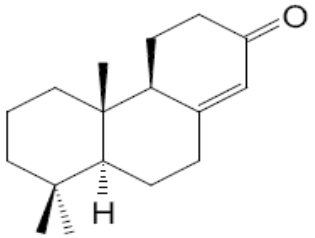
Taiwaniaquinone F (6).



6

Pyridinium dichromate (PDC; 0.5 g, 1.33 mmol) was added to a stirred solution of **21** (70 mg, 0.20 mmol) in dry CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature under argon atmosphere for 34 h, at which time TLC showed no remaining starting material. Following the same work-up used for taiwaniaquinone A (**5**), 80 mg, of taiwaniaquinone F (**6**) (91%) was obtained as a yellow syrup.

$[\alpha]_D^{25}$ = -131.9 (c, 0.9 $CHCl_3$). ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 0.81 (s, 3H), 1.07 (s, 3H), 1.16 (s, 3H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.19 (d, *J* = 7.1 Hz, 3H), 1.21 (m, 1H), 1.50 (dt, *J* = 13.8, 3.4 Hz, 1H), 1.58 (ddd, *J* = 12.8, 12.8, 4.1 Hz, 1H), 1.66 (m, 1H), 1.76 (m, 1H), 2.12 (d, *J* = 11.5 Hz, 1H), 2.32 (dt, *J* = 12.9, 3.3 Hz, 1H), 3.17 (h, *J* = 7.1 Hz, 1H), 3.76 (dd, *J* = 11.5, 3.9 Hz, 1H), 3.76 (dd, *J* = 11.5, 3.9 Hz, 1H), 3.94 (s, 3H), 9.86 (d, *J* = 3.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 34.4 (C-1), 19.3 (C-2), 41.1 (C-3), 33.7 (C-4), 61.5 (C-5), 54.0 (C-6), 200.5 (C-7), 146.4 (C-8), 156.4 (C-9), 49.1 (C-10), 181.5 (C-11), 155.1 (C-12), 137.0 (C-13), 185.8 (C-14), 24.7 (C-15), 20.48 (C-16), 20.5 (C-17), 35.0 (C-18), 21.8 (C-19), 20.1 (C-20), 61.1 (C-OMe). IR (film): 1727, 1662, 1588, 1459, 1378, 1263, 1148, 1017, 928, 759 cm^{-1}.



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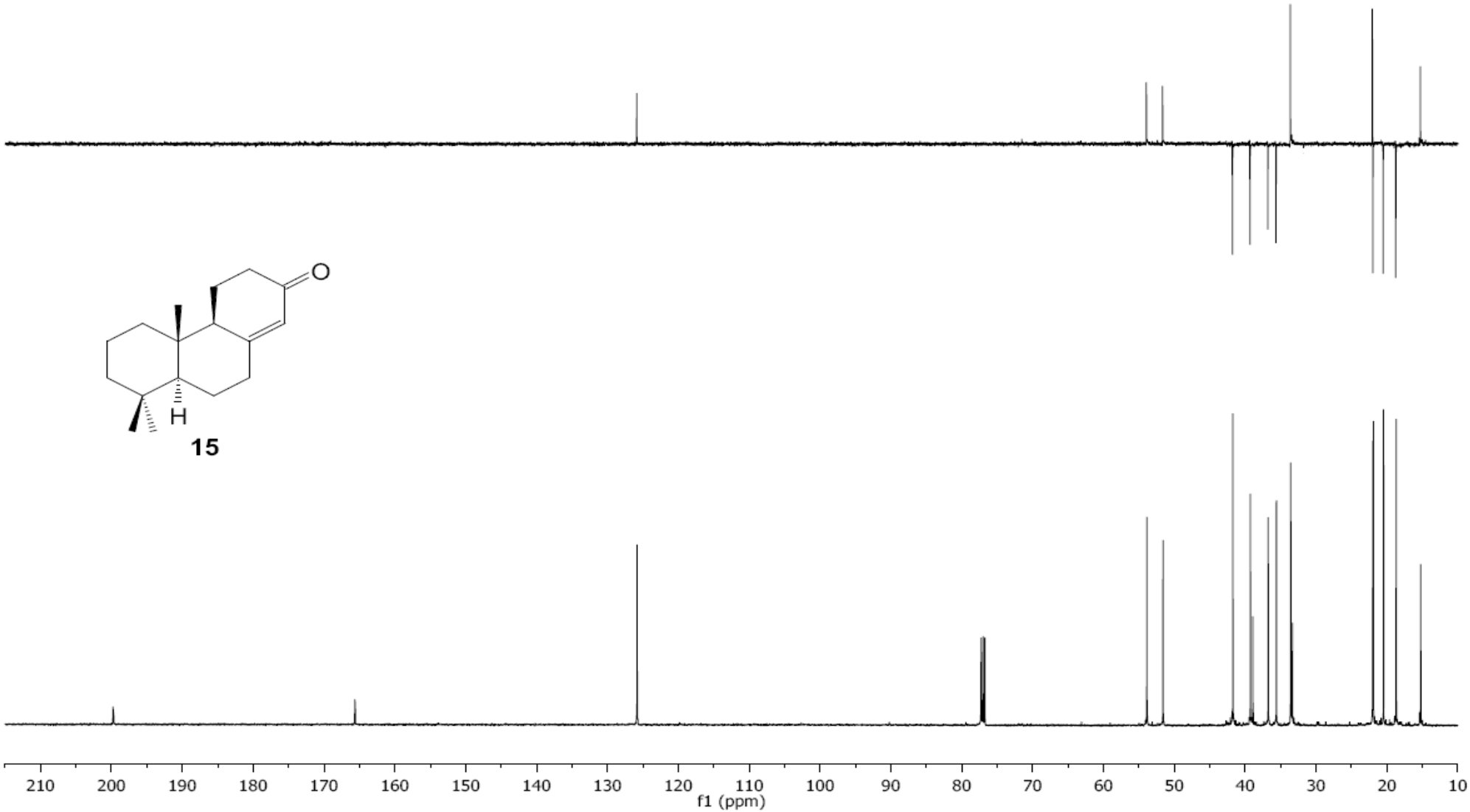
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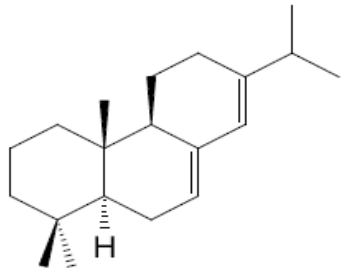

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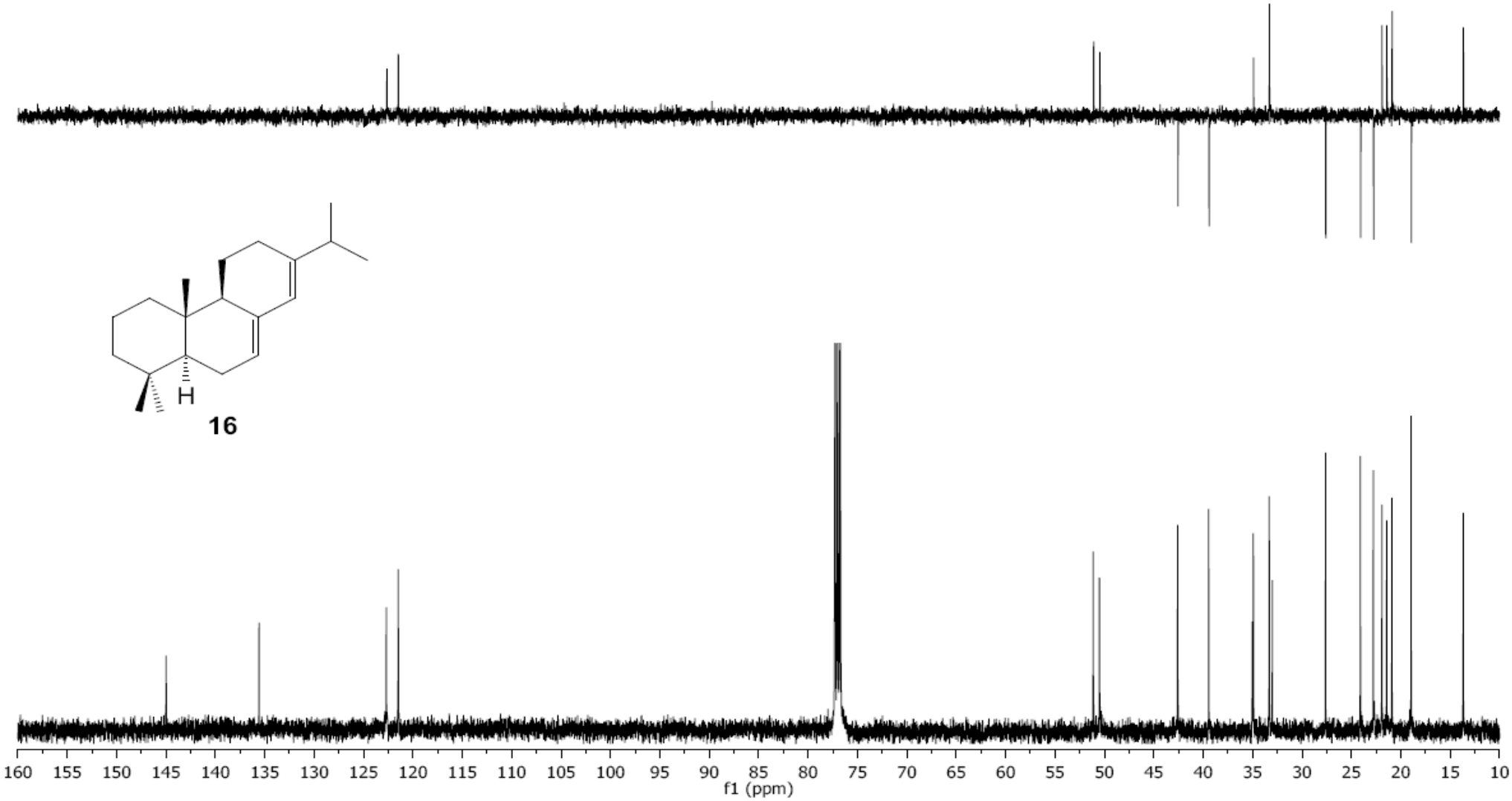
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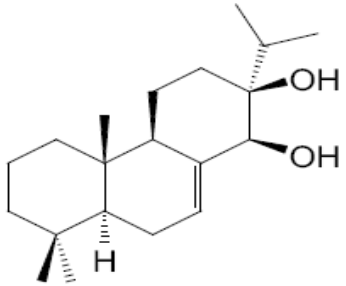

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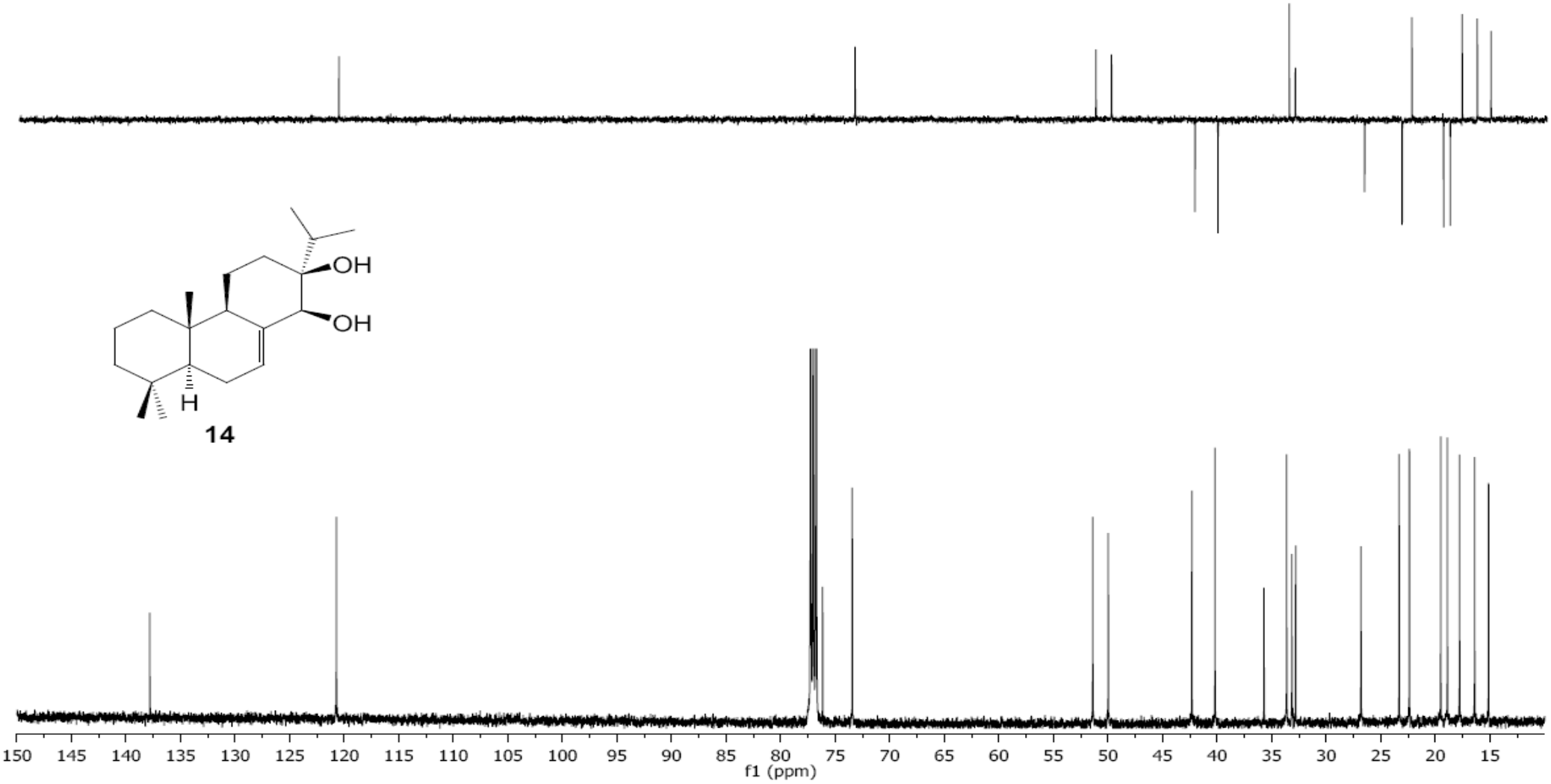
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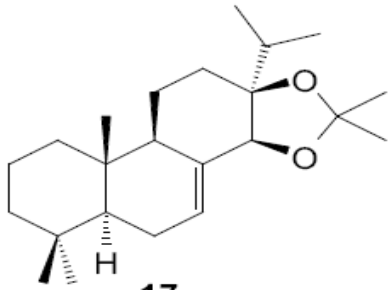

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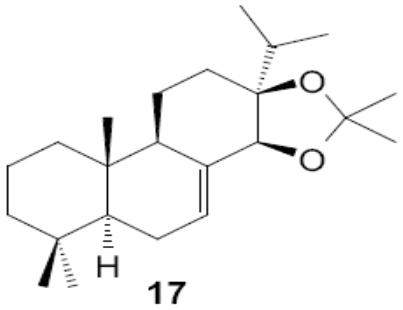
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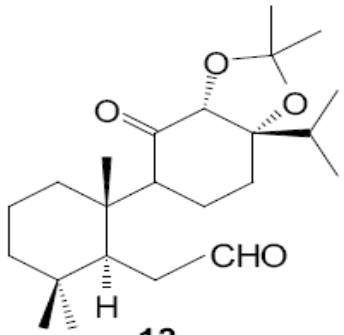
f1 (ppm)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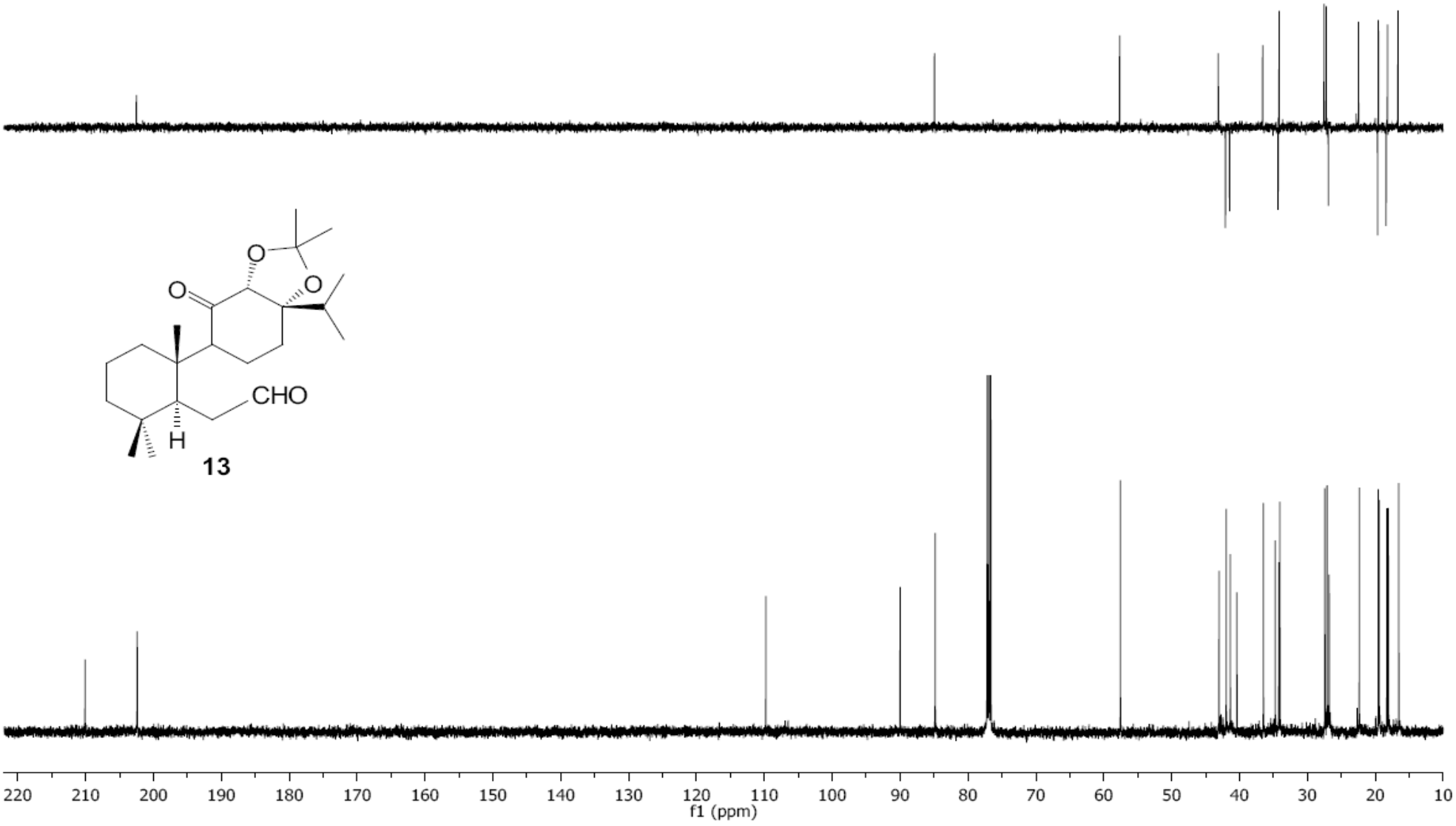
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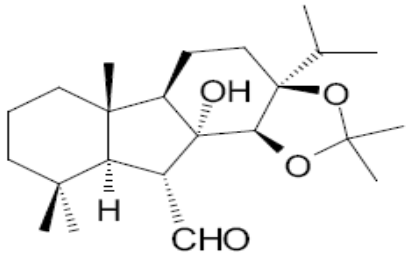
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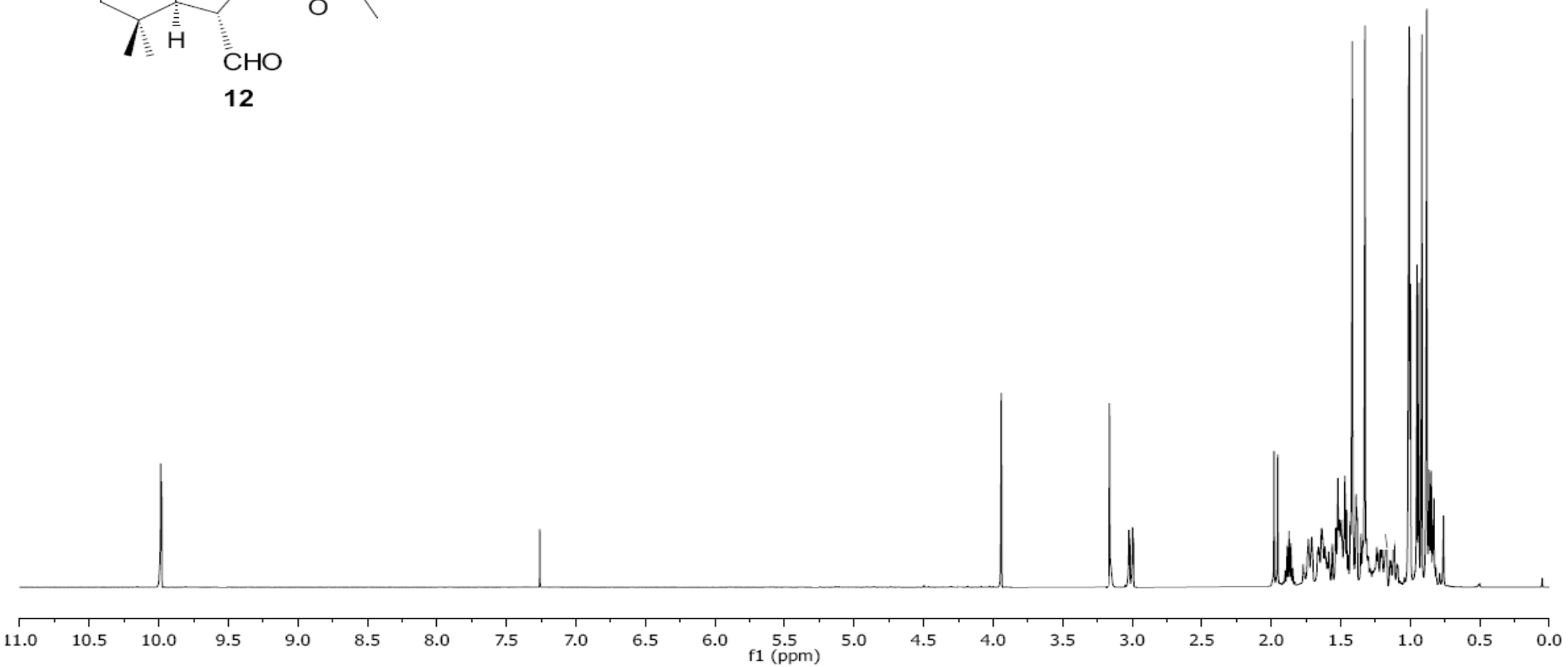
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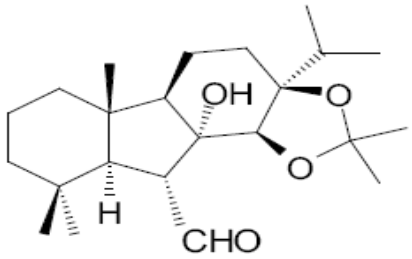
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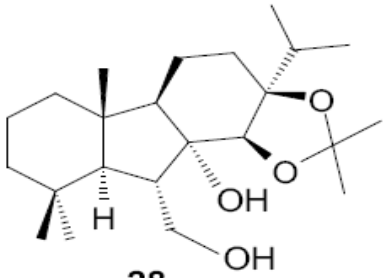

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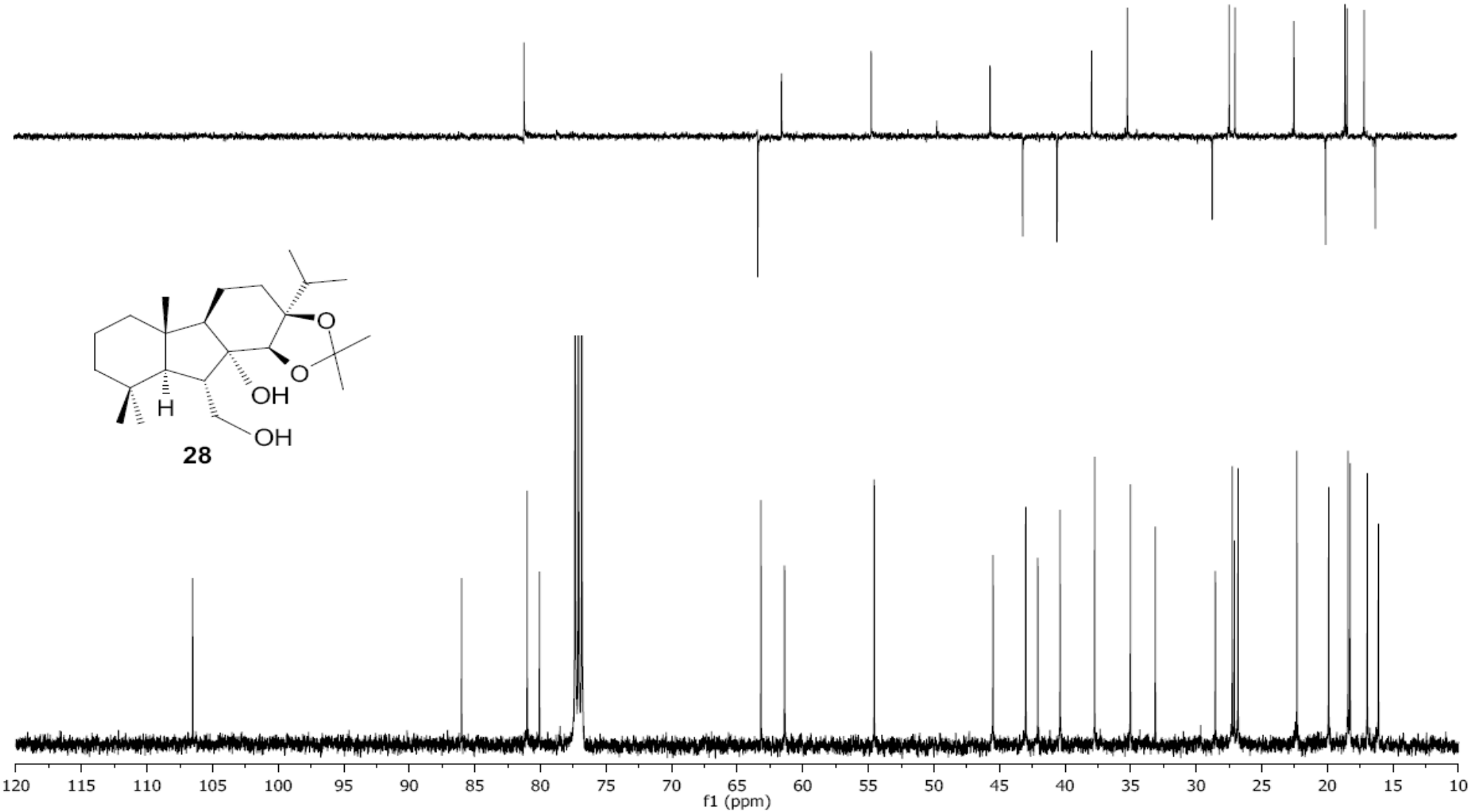
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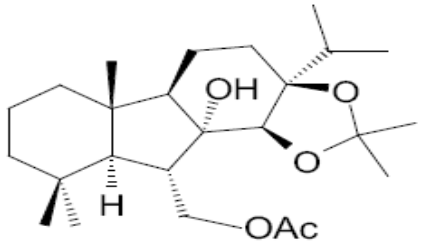

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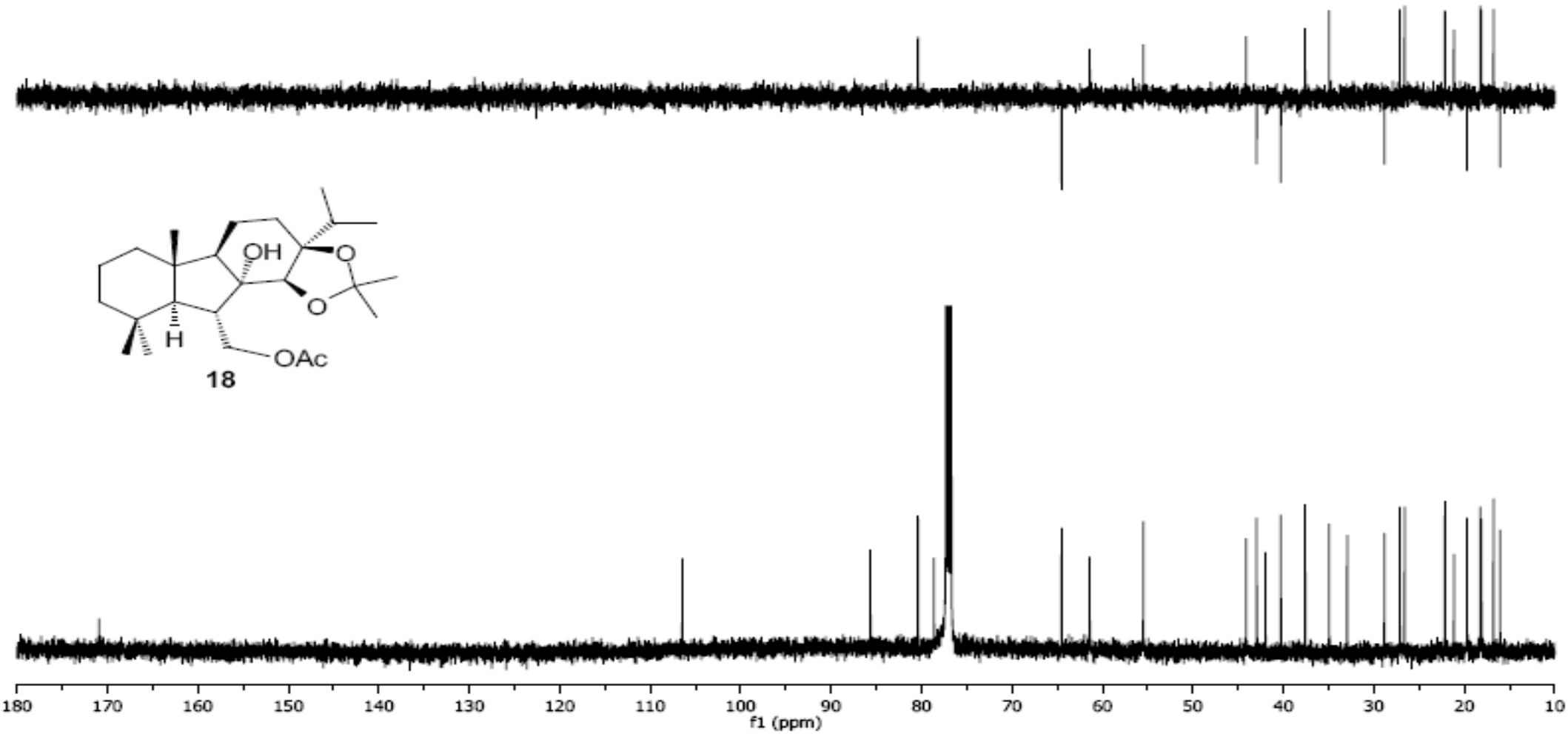
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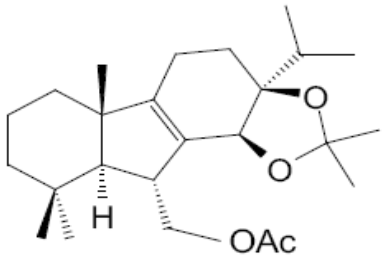

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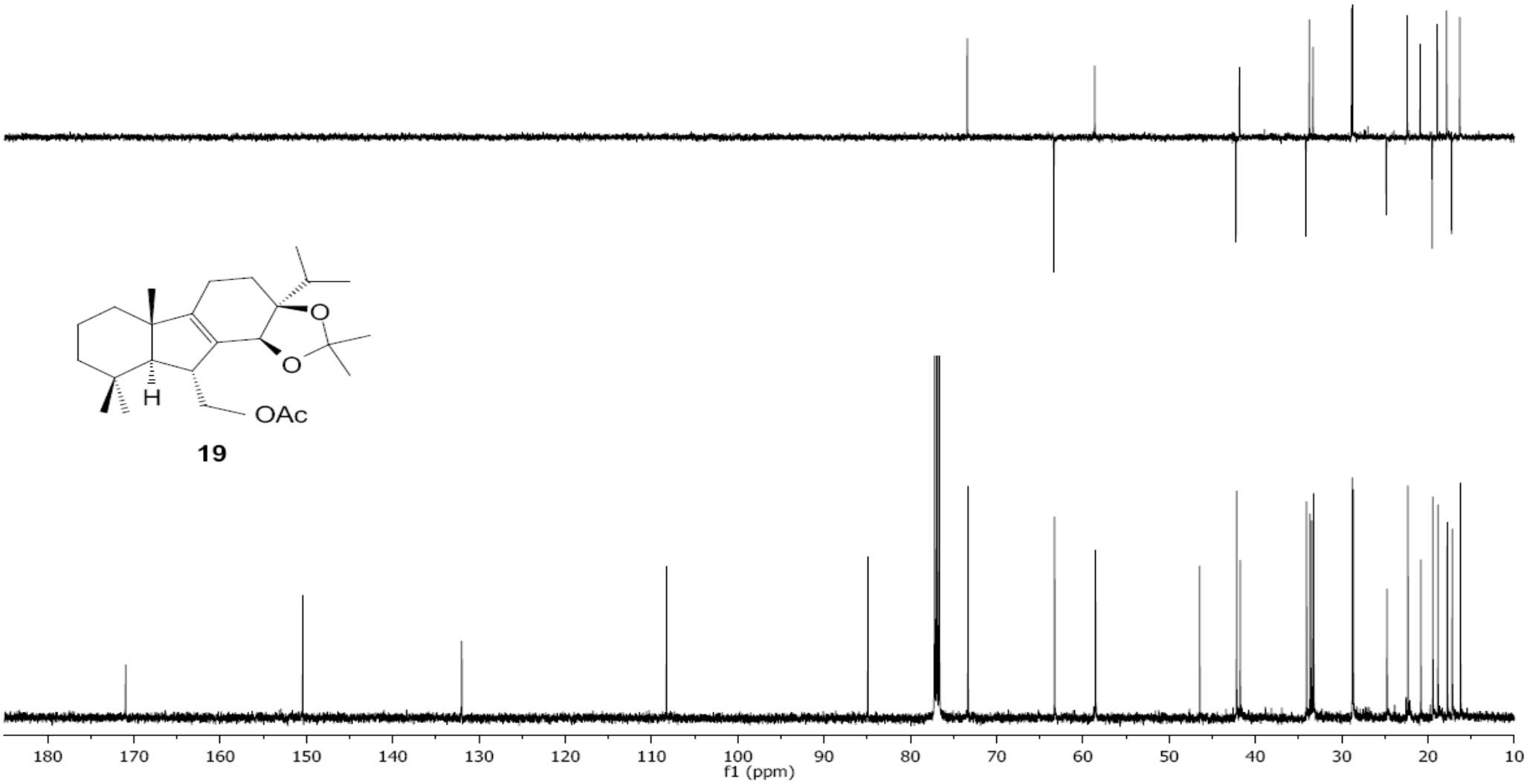
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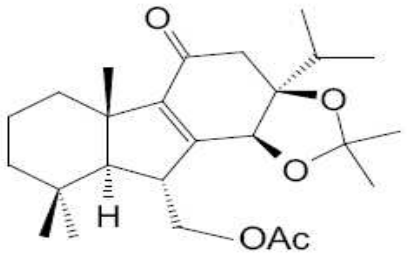

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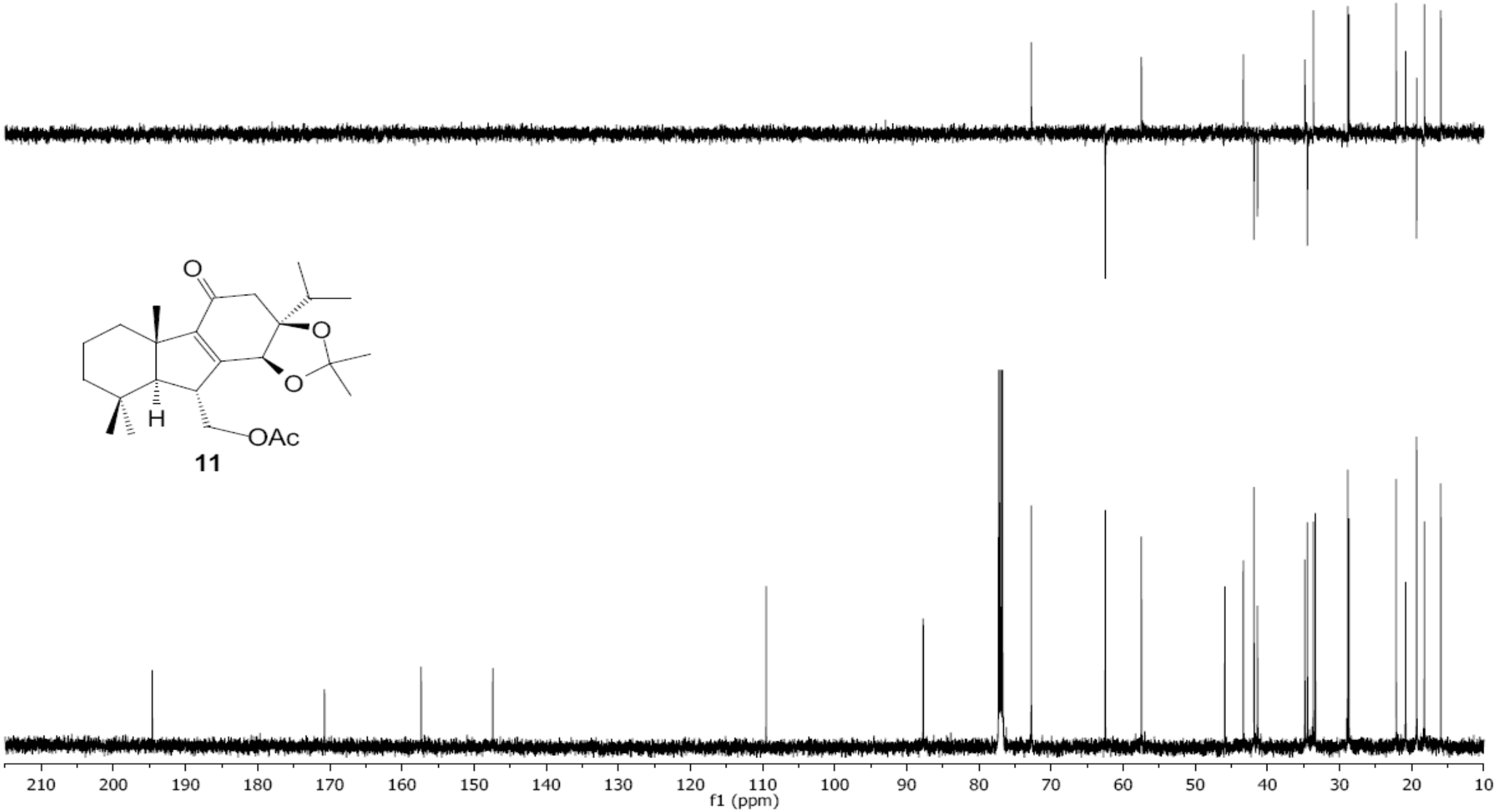
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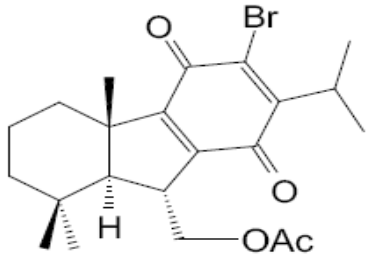

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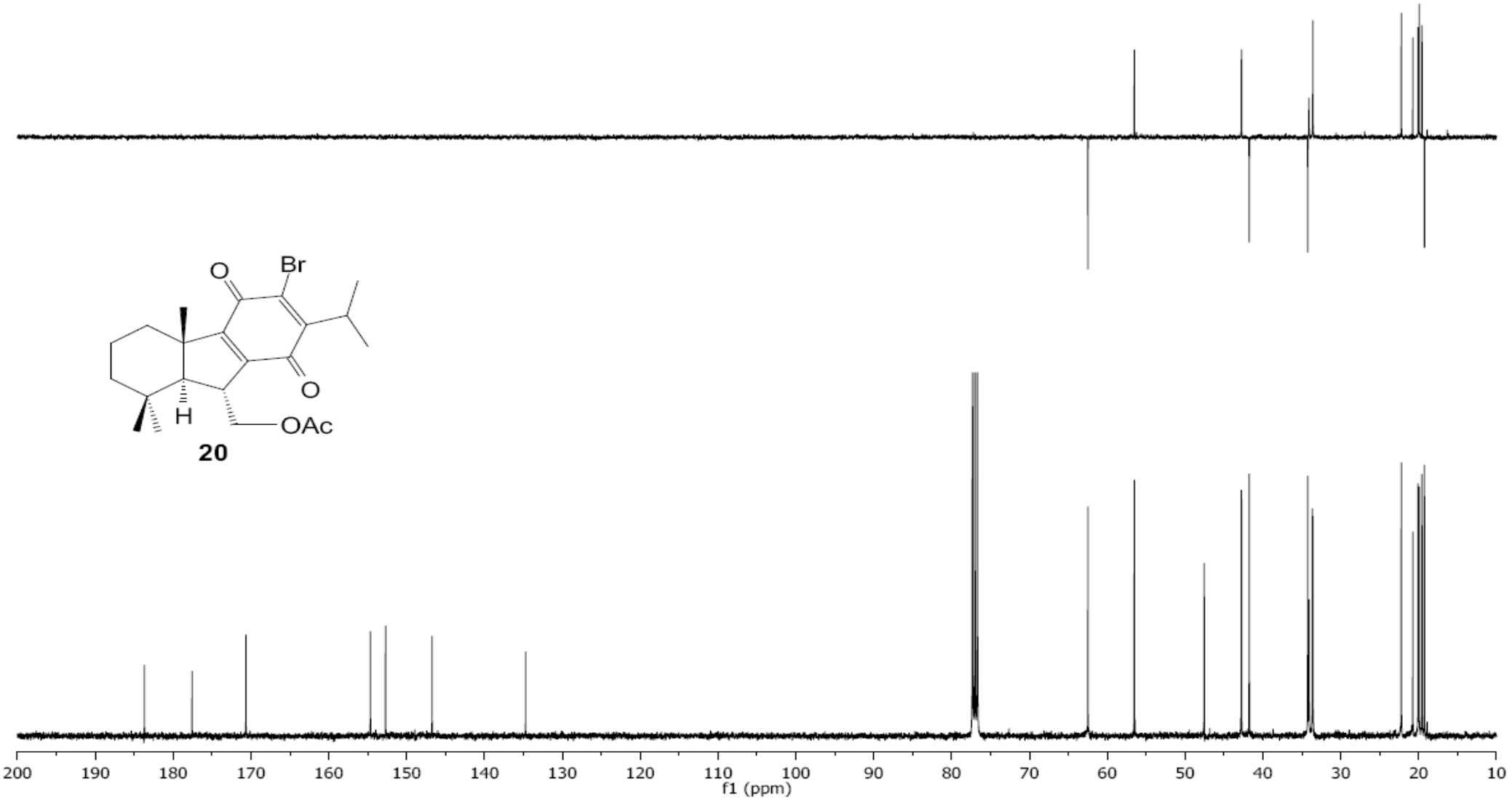
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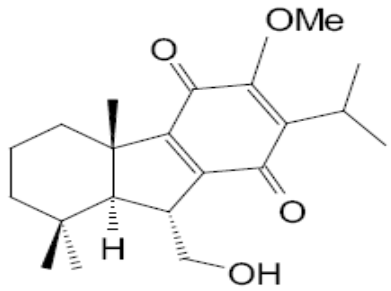

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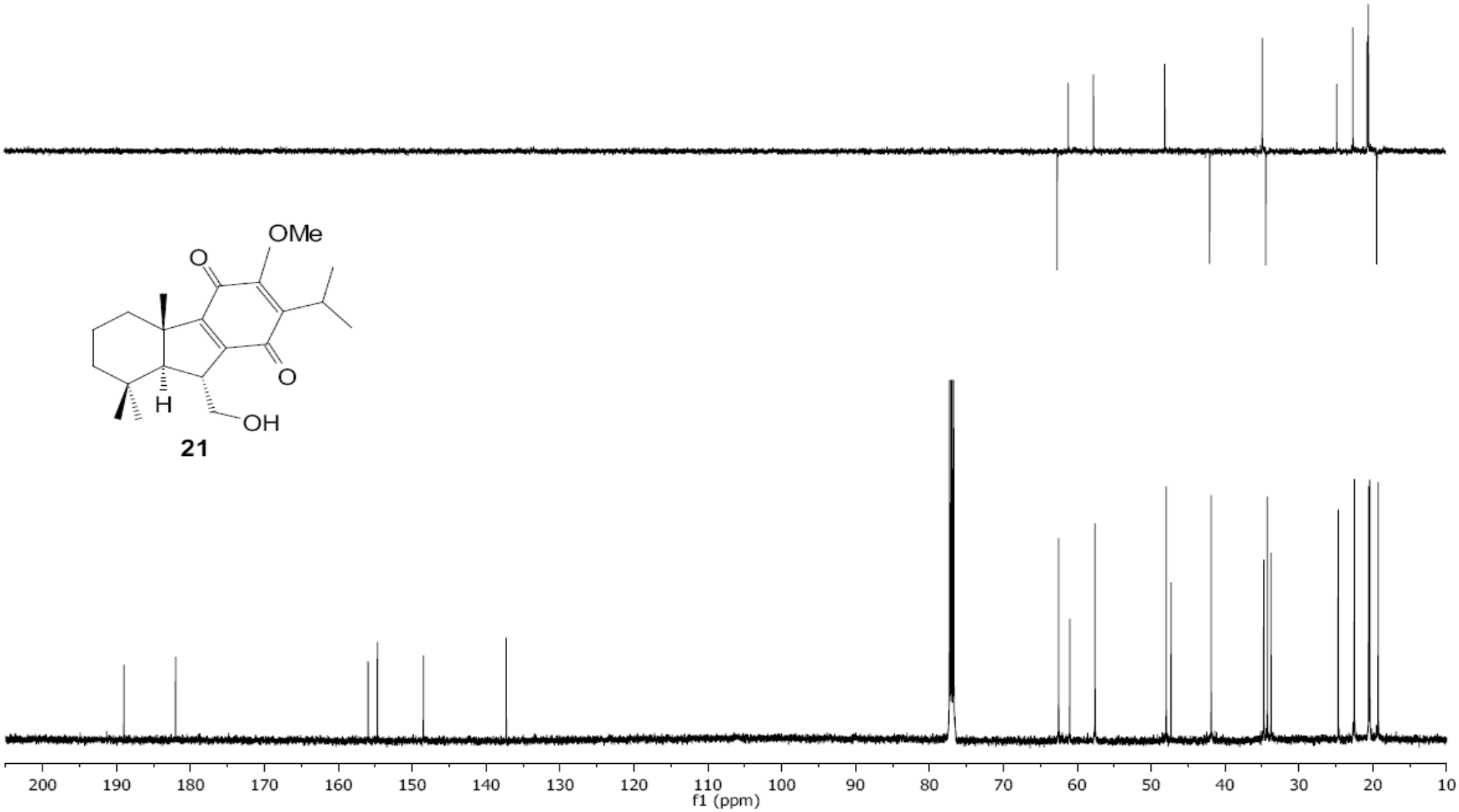
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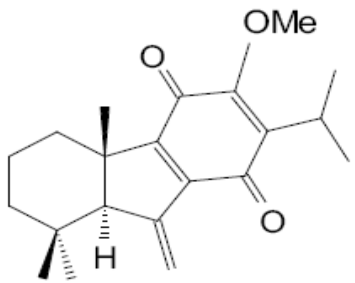

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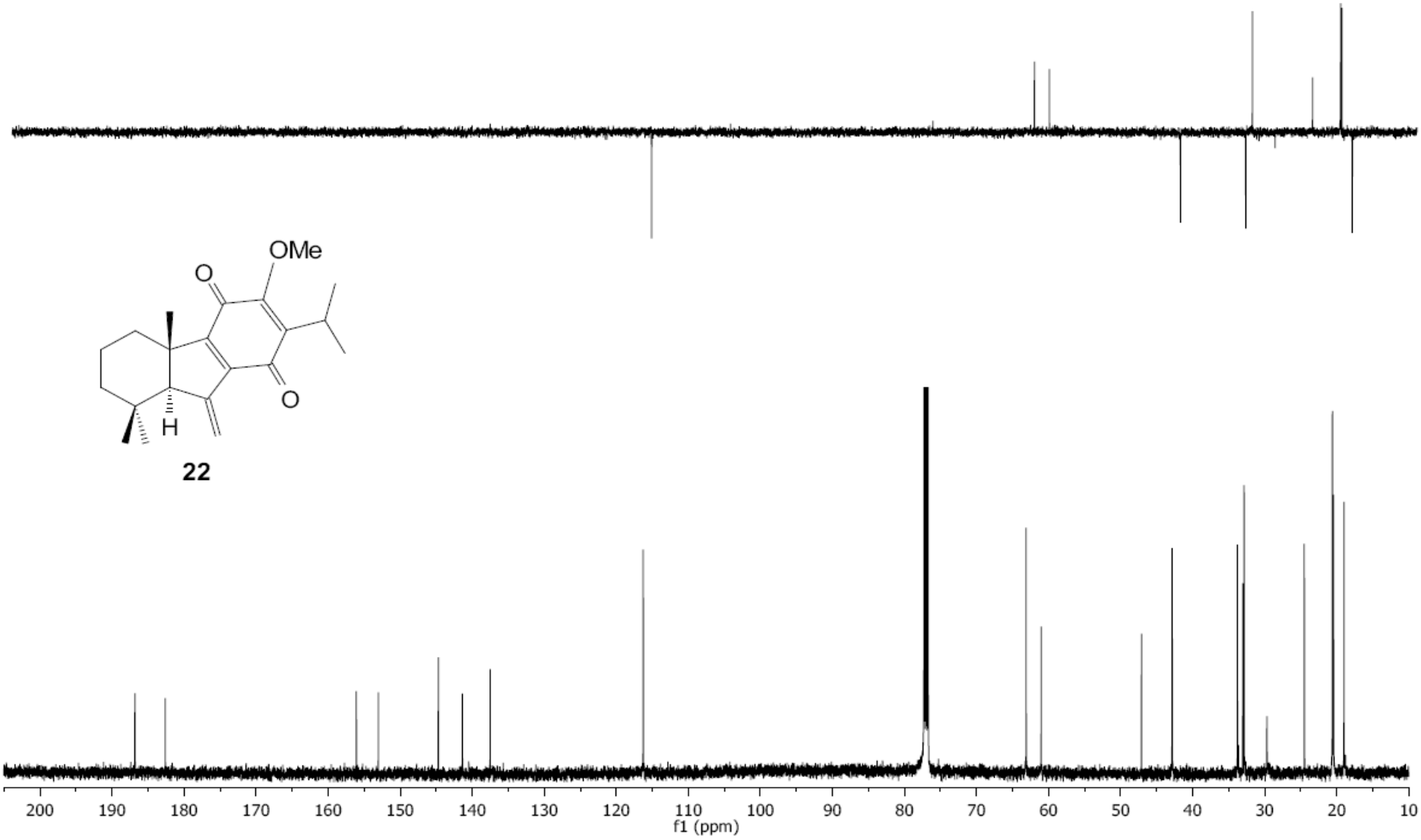
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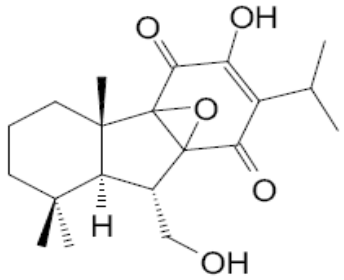
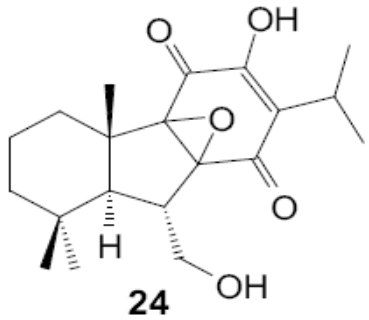
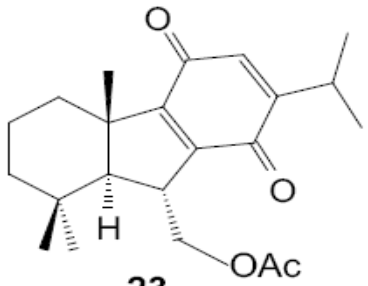


24

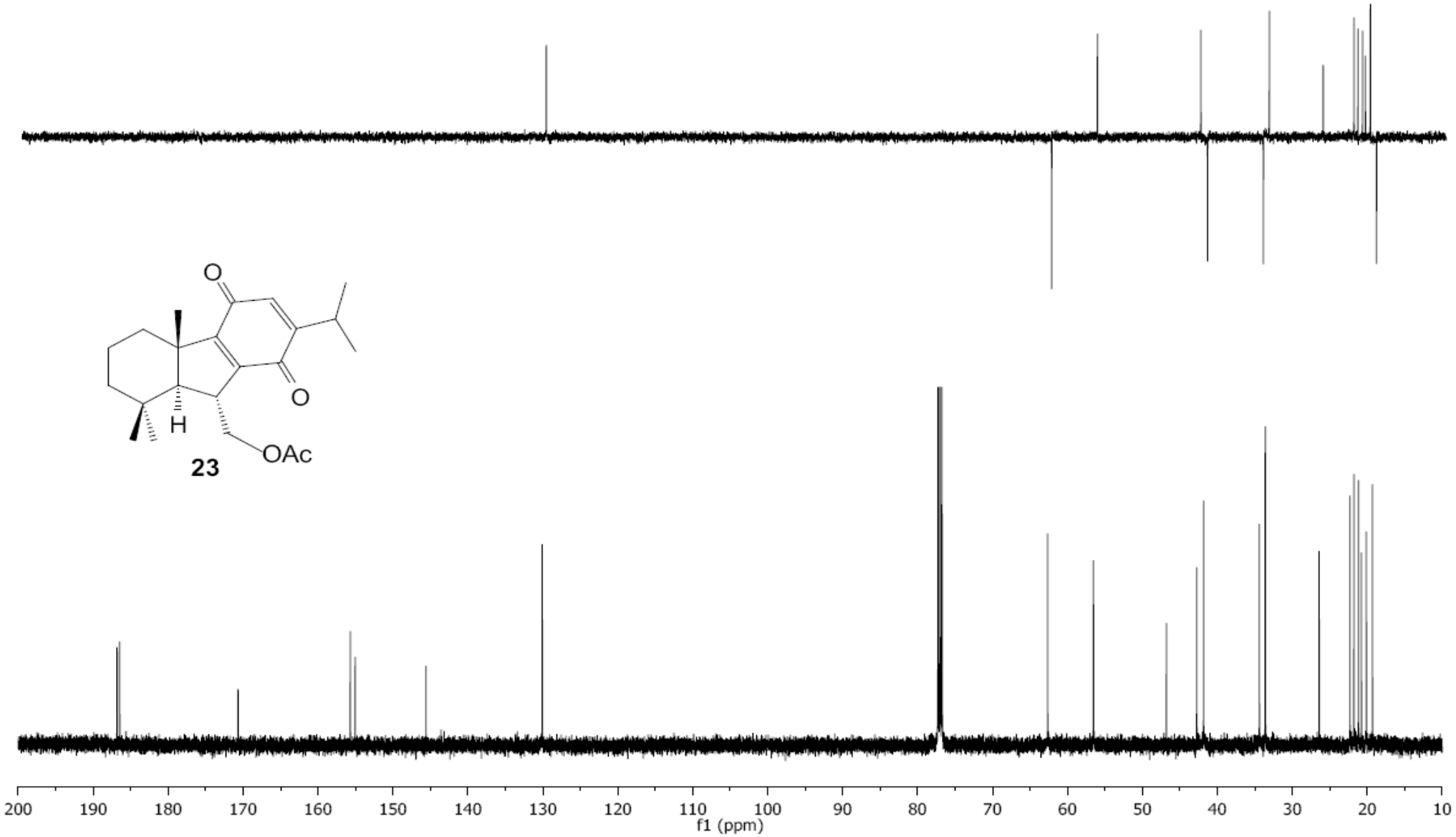

O
OH
O
O
H
OH

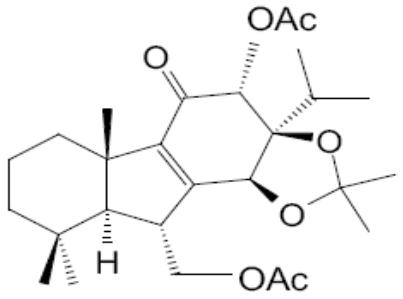
24

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

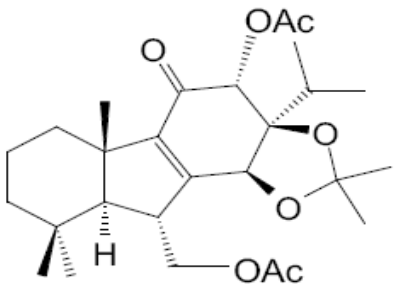


23


O
O
H
OAc
23
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

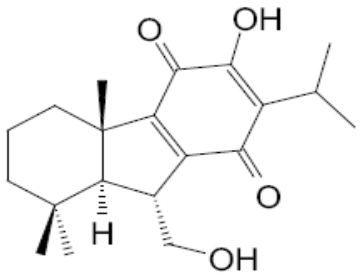


25

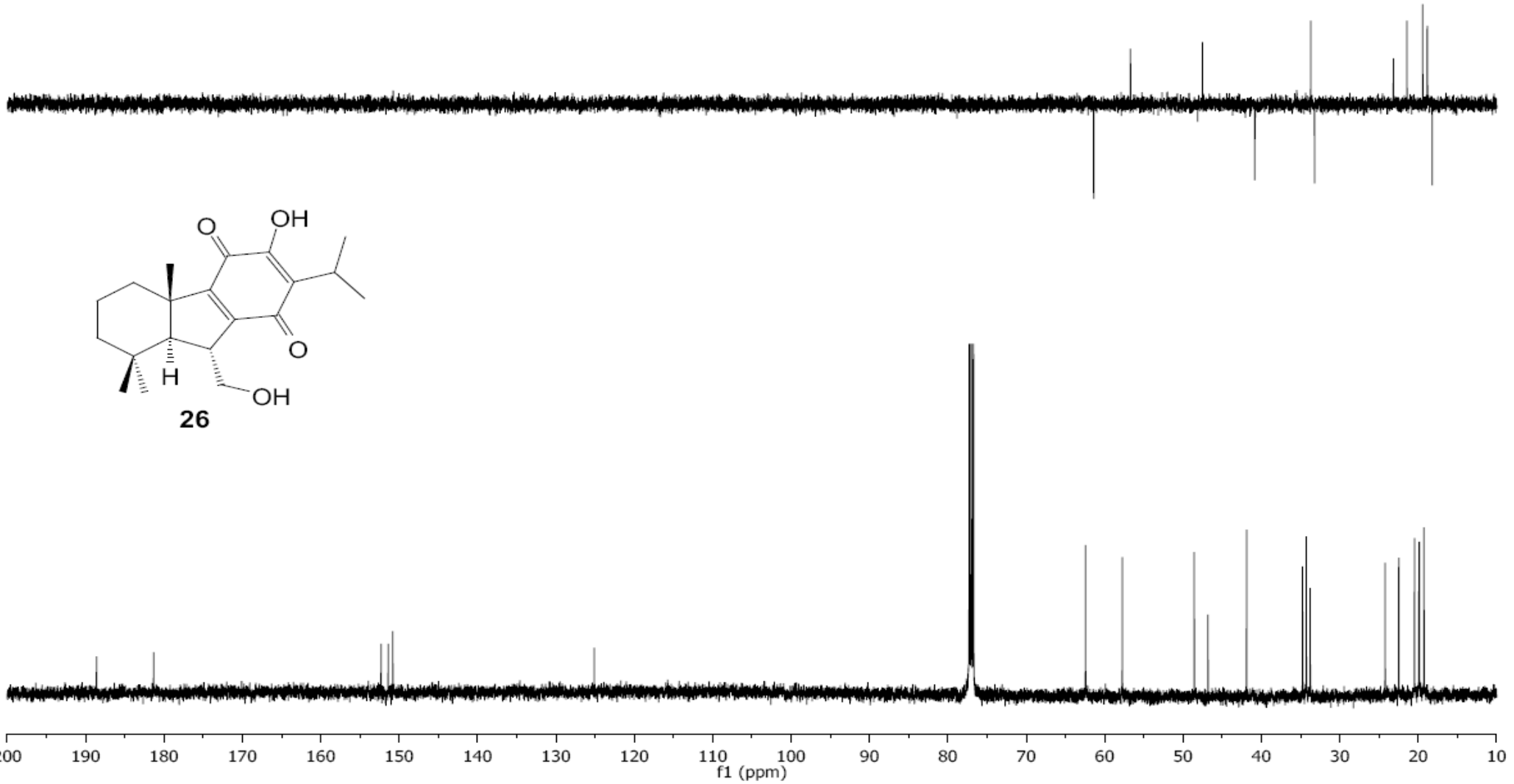

OAc
O
O
O
H
OAc

25

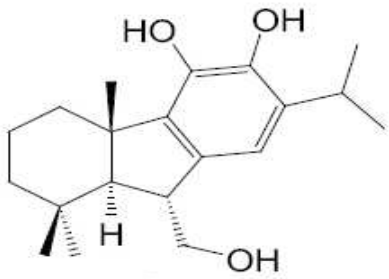
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



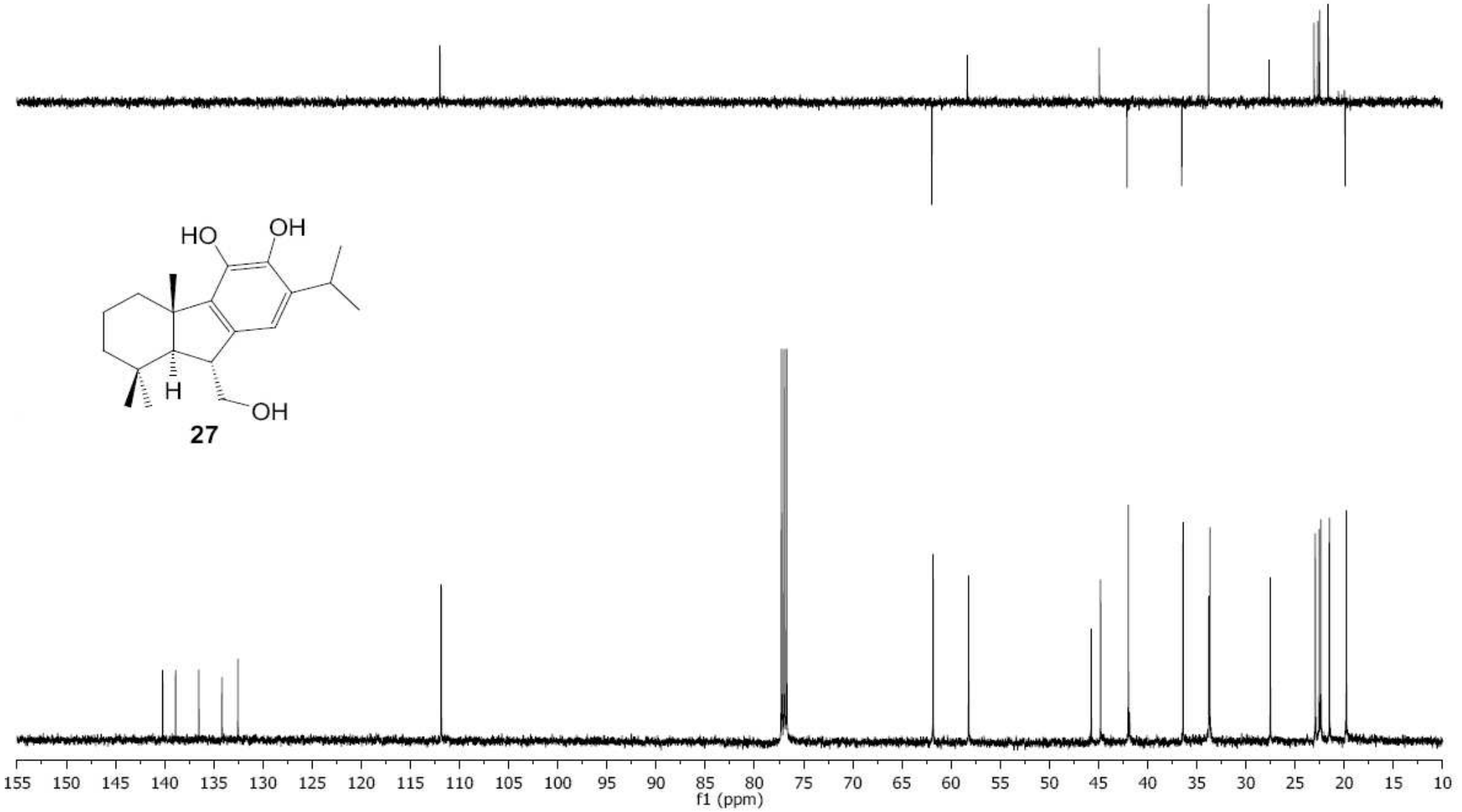
26

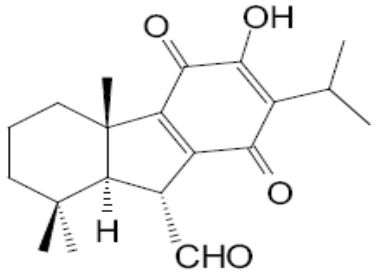

O
OH
O
H
OH
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

26



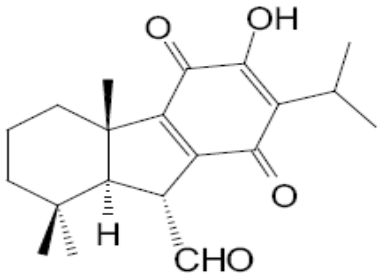
27


HO
OH
H
OH
27
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)


O
OH
O
H
CHO

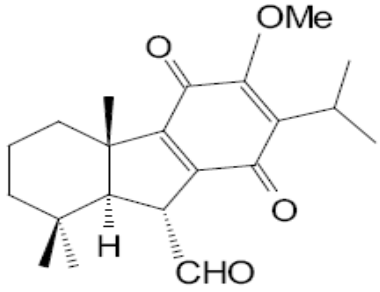
5

11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


O
OH
O
H
CHO

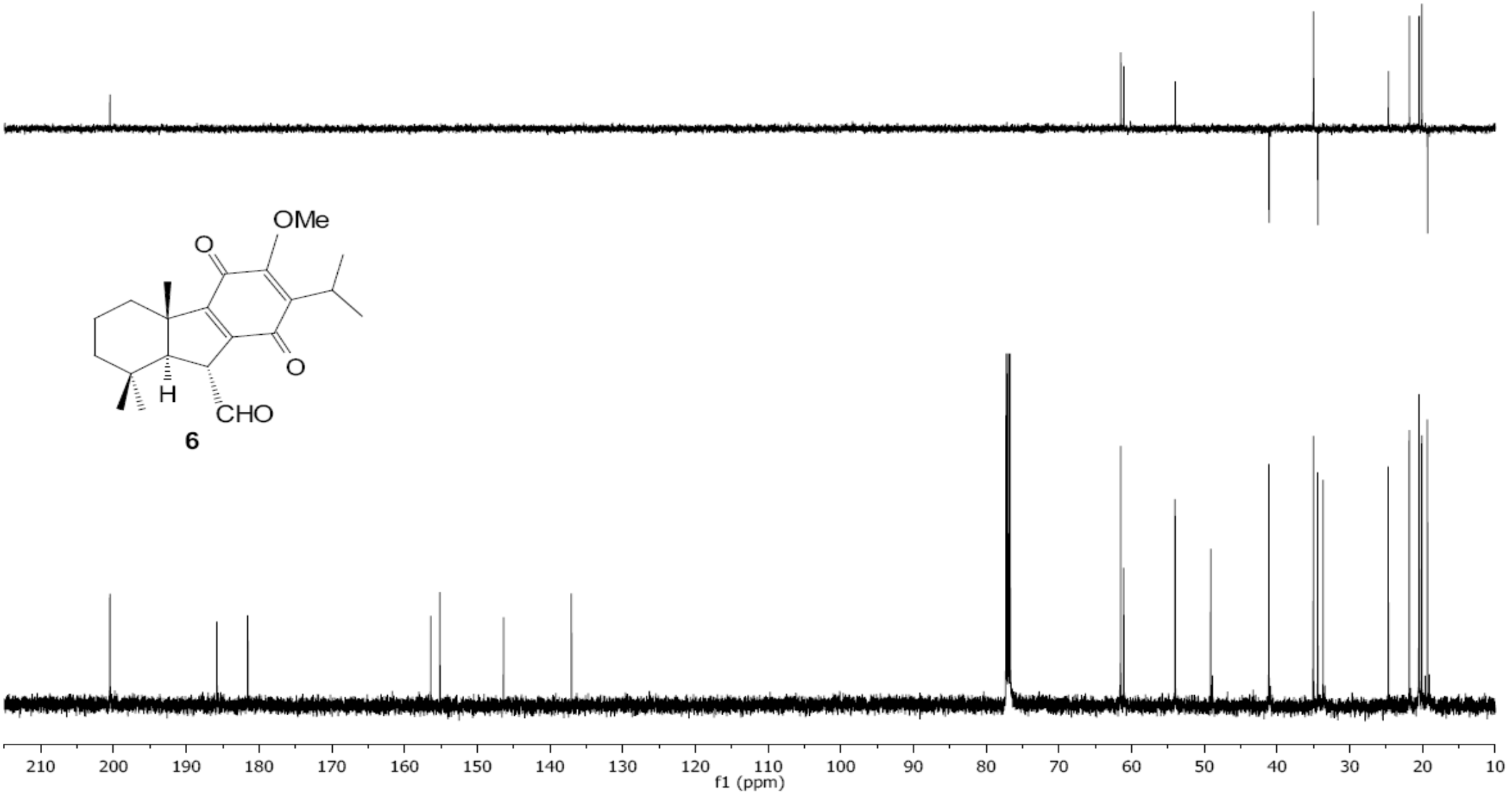
5

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


OMe
O
O
H
CHO

6

11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


OMe
O
O
H
CHO
6
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)