Electronic Supplementary Information (ESI)

A thermal 6π electrocyclization strategy towards taiwaniaquinoids. First enantiospecific synthesis of (-)-taiwaniaquinone G

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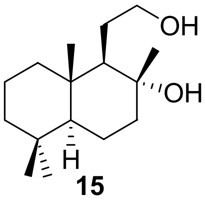
Experimental Section

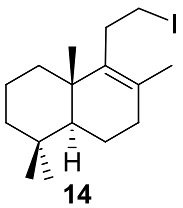
(1*R*,2*R*,8a*S*)-1-(2-Hydroxyethyl)-2,5,5,8a-tetramethyl-decahydronaphthalen-2-ol (15):



15

To a solution of (+)-sclareolide (**17**) (8.6 g, 34.4 mmol) in ethanol (25 mL) was added potassium borohydride (4.3 g, 79.7 mmol) and the reaction mixture was kept at reflux for 10 h, at which time TLC showed no starting material. Then, the reaction mixture was allowed to cool to room temperature and water (5 mL) was carefully added. The solvent was removed in vacuum, and ether (60 mL) – water (15 mL) were added. The phases were shaken and separated and the organic phase was washed with water, brine, dried over anhydrous Na_2SO_4, and the solvent was removed in vacuum to give pure diol **15** (8.39 g, 96%).

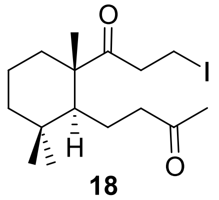
(4a*S*)-5-(2-Iodoethyl)-1,1,4a,6-tetramethyl-1,2,3,4,4a,7,8,8a-octahydronaphthalene (14):



14

Iodine (5.3 g, 20.88 mmol) was added to a solution of triphenylphosphine (PPh_3) (5.3 g, 20.2 mmol) in CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature for 10 min. A solution of diol **15** (5 g, 19.68 mmol) in CH_2Cl_2 (20 mL)was then added and the resulting mixture was further stirred at room temperature for 3h 30 min, at which time TLC showed no **15**. Then aqueous 5% $NaHSO_3$ solution (10 mL) was added and the mixture was vigorously stirred for an additional 5 min and then, the solvent was removed in vacuum. Ether (80 mL) was added and the phases were shaken and separated, the organic phase was washed with water (3 x 20 mL), brine. After drying over anhydrous Na_2SO_4, the solvent was removed in vacuum and the crude product was purified by flash column chromatography on silica gel (5% ether-hexanes), 5 cm x 12 cm) to give 5.65 g, of **14** (83%) as a colourless oil.

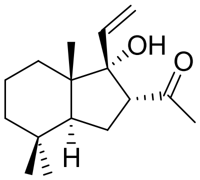
4-((2*S*)-2-(3-Iodopropanoyl)-2,6,6-trimethylcyclohexyl)butan-2-one (18):



18

A stirred solution of **14** (1.7 g, 4.913 mmol) in CH_2Cl_2 (60 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 (3 h), the solution was flushed with argon, and dimethyl sulfide (5 mL) was added. The reaction mixture was then slowly warmed to room temperature over 15 min and further stirred for 12 h. The solvent was removed, and the crude product was purified by flash column chromatography on silica gel (15% ether/hexanes, 1.5 cm x 25 cm) to give 1.39 g of **18** (75%) as a colourless oil.

1-((1*R*,2*R*,3a*S*,7a*S*)-1-Hydroxy-4,4,7a-trimethyl-1-vinyl-octahydro-1H-inden-2-yl)ethanone (13):

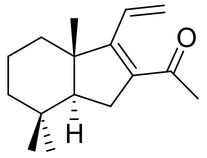


13

Diazabicyclo[5.4.0]undec-7-ene (DBU) (2.74 g, 17.99 mmol) was added to a solution of **18** (3.3 g, 8.73 mmol) in benzene (15 mL) and the mixture was stirred at room temperature for 12 h, at which time TLC showed no **18**. Then, it was diluted with ether (30 mL) - water (10 mL) and the phases were shaken and separated. The organic phase was washed with 1 M HCl (3 x 10 mL), water, brine, dried over anhydrous Na_2SO_4 and concentrated under vacuum to yield 1.96 g of hydroxy ketone **13** (90%) as a yellow syrup. $[\alpha]_D^{25}$ = -43.2 (c 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.78 (s, 3H), 0.83 (s, 3H), 0.84 (s, 3H), 1.08 (ddd, *J*= 13.5, 13.5, 3.9 Hz, 1H), 1.11 (m, 1H), 1.35 (dt, *J* =

13.3, 1H), 1.40-1.55 (m, 2H), 1.73 (d, *J* = 12.5 Hz, 1H), 1.86 (ddd, *J* = 12.5, 8.1, 5.0 Hz, 1H), 2.00 (dd, *J* = 12.5, 4.4 Hz, 1H), 2.10 (s, 3H), 3.12 (dd, *J* = 11.7, 5.0 Hz, 1H), 3.58 (bs, 1H), 5.13 (dd, *J* = 10.8, 1.5 Hz, 1H), 5.19 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.95 (dd, *J* = 17.3, 10.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ : 16.9 (CH$_3$), 19.2 (CH$_2$), 20.9 (CH$_3$), 24.8 (CH$_2$), 29.4 (CH$_2$), 31.3 (CH$_3$), 33.37 (CH$_3$), 33.47 (C), 41.3 (CH$_2$), 50.0 (C), 51.3 (CH), 55.2 (CH), 84.9 (C), 114.8 (CH$_2$), 140.4 (CH), 212.3 (C); IR (cm^{-1}) ν: 3472, 1692, 1459, 1360, 1260, 1176, 1136, 1092, 1003, 977, 921, 817, 756; HRMS (FAB) *m/z*: calcd for $C_{16}H_{26}O_2Na$ 273.1830, found: 273.1821.

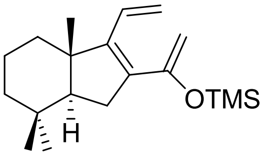
1-((3aS,7aS)-3a,7,7-trimethyl-3-vinyl-3a,4,5,6,7,7a-hexahydro-1H-inden-2-yl)ethanone (19):



19

To a solution of **13** (0.2 g, 0 .8 mmol) in 1,4-dioxane (7 mL) was added 3 drops of concd H_2SO_4 and the reaction mixture was stirred at room temperature for 4 h at which time TLC showed no starting material. Then water (3 mL) was slowly added and the solvent was removed in vacuum, and the mixture was diluted with ether (20 mL), washed with water (3 x 6 mL), brine, dried over anhydrous Na_2SO_4 to give a crude product which was purified by flash chromatography on silica gel (5% ether/hexane, 2.5 cm x 18 cm) to give 135 mg of **19** (73%) as a colourless oil. $[\alpha]_D^{25}$ = -59.5 (*c* 1.1, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 500 MHz) δ : 0.90 (s, 3H), 0.97 (s, 3H), 1.04 (s, 3H), 1.12 (ddd, *J* = 13.6, 13.6, 4.5 Hz, 1H), 1.43 (m, 1H), 1.46 (ddd, *J* = 12.8, 12.8, 4.1 Hz, 1H), 1.52 (dd, *J* = 11.8, 6.7 Hz, 1H), 1.60 (m, 1H), 1.73 (qt, *J* = 13.7, 3.9 Hz, 1H), 1.98 (dt, *J* = 12.3, 3.4 Hz, 1H), 2.24 (s, 3H), 2.36 (dd, *J* = 15.1, 11.8 Hz, 1H), 2.42 (dd, *J* = 15.1, 6.7 Hz, 1H), 5.32 (d, *J* = 11.8 Hz, 1H), 5.57 (d, *J* = 18.2 Hz, 1H), 6.94 (dd, *J* = 18.2, 11.8 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ : 17.7 (CH$_3$), 19.9 (CH$_2$), 21.3 (CH$_3$), 30.3 (C), 30.9 (CH$_2$), 32.9 (CH$_3$), 33.0 (C), 35.9 (CH$_2$), 40.9 (CH$_2$), 50.0 (C), 57.3 (CH), 120.1 (CH$_2$), 130.7 (CH), 137.7 (C), 159.9 (C), 199.8 (C); IR (cm^{-1}) ν: 1669, 1545, 1459, 1355, 1232, 1208, 1114, 1078, 1011, 972, 912; HRMS (FAB) *m/z*: calcd for $C_{16}H_{24}ONa$ 255.1725, found: 255.1737.

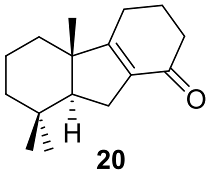
Trimethyl(1-((3a*S*,7a*S*)-3a,7,7-trimethyl-3-vinyl-3a,4,5,6,7,7a-hexahydro-1H-inden-2-yl)vinyloxy)silane (12):



12

To a solution of **19** (533 mg, 2.29 mmol) and *i*-Pr$_2$NEt (0.5 mL, 2.87 mmol) in CH$_2$Cl$_2$ (12 mL) was added at 0 ºC trimethylsilyl trifluoromethanesulphonate (0.5 mL, 2.76 mmol) and the reaction mixture was stirred at this temperature for 30 min, at which time TLC showed no starting material. Then the mixture was poured into ice (10g) and diluted with ether (40 mL), washed with water (3 x 10 mL), brine, dried over anhydrous Na$_2$SO$_4$ to give 0.7 g of compound **12**, which was utilized in the next reaction without purification.

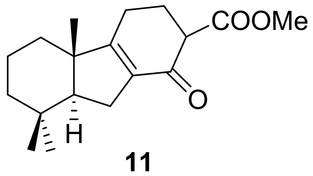
(4b*S*,8a*S*)-4b,8,8-Trimethyl-3,4,5,6,7,8,8a,9-octahydro-2H-fluoren-1(4bH)-one (20):



20

A solution of **12** (2.4 g, 7.89 mmol) in xylene (8 mL) was stirred at reflux for 4 h (monotorized by TLC). Then the solvent was removed in vacuum, and the crude product was purified by flash column chromatography on silica gel (H:E, 9:1) to give 1.68 g (92%) of **20** as a yellow syrup. $[\alpha]_D^{25}$ = -66.1 (*c* 1.0, CHCl$_3$); ^{1}H NMR (CDCl$_3$, 500 MHz) δ : 0.89 (s, 3H), 0.92 (s, 3H), 0.96 (s, 3H), 1.12 (ddd, *J* = 13.3, 13.3, 4.4 Hz, 1H), 1.28 (ddd, *J* = 12.5, 12.5, 3.9 Hz, 1H), 1.44-1.52 (m, 2H), 1.56-1.67 (m, 2H), 1.73 (qt, *J* = 13.9, 3.9 Hz, 1H), 1.95-2.02 (m, 2H), 2.08 (ddt, *J* = 14.7, 12.1, 3.0 Hz, 1H), 2.24 (ddd, *J* = 4.4, 2.9, 1.5 Hz, 1H), 2.28 (ddd, *J* = 4.5, 2.9, 1.5 Hz, 1H), 2.27-2.42 (m, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ : 17.1 (CH$_3$), 19.7 (CH$_2$), 21.3 (CH$_3$), 22.0 (CH$_2$), 23.6 (CH$_2$), 25.6 (CH$_2$), 33.0 (CH$_3$), 33.0 (C), 33.9 (CH$_2$) 38.0 (CH$_2$), 41.4 (CH$_2$), 49.1 (C), 58.3 (CH), 136.1 (C), 175.4 (C), 198.3 (C); IR (cm^{-1}) ν: 1665, 1612, 1456, 1383, 1231, 1202, 1104, 980, 853 cm^{-1}; HRMS (FAB) *m/z*: calcd for $C_{16}H_{24}ONa$ 255.1725, found: 255.1719.

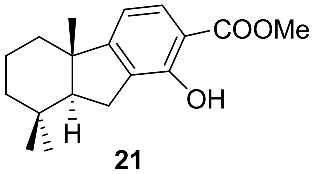
(4b*S*,8a*S*) Methyl 4b,8,8-trimethyl-1-oxo-2,3,4,4b,5,6,7,8,8a,9-decahydro-1H-fluorene-2-carboxylate (11):



11

To a flame dried 20 mL round bottom flask was added *i*-Pr_2NH (2 mL, 28.3 mmol) and THF (10 mL). The solution was cooled to 0 ºC and n-BuLi (8 mL, 2.5 M hexanes, 20 mmol) was added dropwise and the solution was stirred for 20 min. The solution was cooled at -78 ºC and a solution of **20** (3.1 g, 13.36 mmol) in THF (10 mL) was added, and the reaction mixture was stirred for 30 min. Then methyl cyanoformate (2 mL, 25.2 mmol) was added and the reaction mixture was slowly warmed to -36 ºC over 3 h, then quenched by the addition of water (1 mL), diluted with ether (50 mL) and water (10 mL), the phases were shaken and separated, and the aqueous phase was extracted with ether (2 x 10 mL). The combined organic phases were washed with a saturated aqueous NaCl solution (2 x 10 mL) dried over anhydrous Na_2SO_4 to give a crude product which was purified by flash chromatography on silica gel (20% ether/hexane, 2.5cm x 16cm) to give 3.75 g of an unresolvable 1:1 mixture of epimers **11** (97%) as a colourless oil; ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.75 (s, 6H), 0.78 (s, 3H), 0.79 (s, 3H), 0.82 (s, 3H), 0.823 (s, 3H), 0.91 (ddd, *J* = 13.4, 13.4, 3.8 Hz, 2H), 1.17 (ddd, *J* = 12.1, 12.1, 3.9 Hz, 2H), 1.30-1.39 (m, 4H), 1.40-1.53 (m, 4H), 1.59 (qt, *J* = 13.8, 3.6 Hz, 2H), 1.80-2.40 (m, 12H), 3.19 (dd, *J* = 9.0, 4.9 Hz, 1H), 3.24 (dd, *J* = 9.0, 4.8 Hz, 1H), 3.65 (s, 3H), 3.66 (s, 3H); IR (cm^{-1}) ν: 1708, 1618, 1457, 1236, 1078, 757; HRMS (FAB) *m/z*: calcd for $C_{18}H_{26}O_3Na$ 313.1780, found: 313.1787.

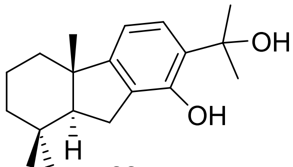
(4b*S*,8a*S*) Methyl 1-hydroxy-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluorene-2-carboxylate (21):



21

To a solution of **11** (723 mg, 2.493 mmol) in dioxane (15 ml) was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (622 mg, 2.74 mmol) and the reaction mixture was stirred at reflux for 30 min. Then, the solvent was removed in vacuum and water (10 mL), ether (30 mL) were added to the crude product. The phases were shaken, separated and the organic phase was washed with 5% aqueous $NaHCO_3$ (3 x 5 mL), brine, and the organic phase was dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (10% ether/hexane, 2,5 cm x 15cm) to give 674 mg, of **21** (94%) as a colourless syrup. $[\alpha]_D^{25}$ = -14.7 (*c* 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.98 (s, 3H), 1.03 (s, 3H), 1.04 (s, 3H), 1.20 (ddd, *J* = 13.2, 13.2, 3.9 Hz, 1H), 1.45 (ddd, *J* = 12.7, 12.7, 3.9 Hz, 1H), 1.54 (dt, *J* = 13.2, 2.9 Hz, 1H), 1.67 (m, 1H), 1.70 (dd, *J* = 12.7, 5.8 Hz, 1H), 1.83 (qt, *J* = 13.7, 3.9 Hz, 1H), 2.02 (dt, *J* = 12.2, 3.4 Hz, 1H), 2.54 (dd, *J* = 14.7, 12.7 Hz, 1H), 2.83 (dd, *J* = 14.7, 5.8 Hz, 1H), 3.91 (s, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 10.81 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 20.0 (CH_2), 21.14 (CH_3), 21.16 (CH_3), 25.6 (CH_2), 33.21 (CH_3), 33.22 (C), 35.3 (CH_2), 41.5 (CH_2), 46.8 (C), 52.1 (CH_3), 59.9 (CH), 110.3 (C), 111.8 (CH), 129.23 (CH), 158.0 (C), 164.6 (C), 171.1 (C); IR (cm^{-1}) ν: 3431, 1671, 1449, 1296, 1196, 1142, 1096, 953, 791, 740; HRMS (FAB) *m/z*: calcd for $C_{18}H_{24}O_3Na$ 311.1623, found: 311.1635.

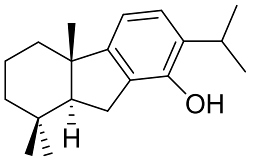
(4b*S*,8a*S*)-2-(2-Hydroxypropan-2-yl)-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1-ol (22):



22

To a solution of **21** (423 mg, 1.468 mmol) in anhydrous THF (30 mL) was added dropwise a solution of methylmagnesium bromide (5.2 mL of a 1.4 M solution in Toluene/THF, 7.28 mmol) at 0 °C. The mixture was stirred under argon atmosphere at room temperature for 13 h, at which time TLC showed no starting material. Then, 5% aqueous NH_4Cl (5 mL) was added slowly at 0 ºC and the mixture was extracted with ether (2 x 20 ml).The combined organic layers was washed with water and brine, and dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification by flash column chromatography on silica gel (35% ether/hexanes, 2 cm x 15 cm) gave 0.57 g of **22** (97%). $[\alpha]_D^{25}$ = -17.4 (*c* 0.9, $CHCl_3$); ^{1}H NMR (CD_3COCD_3, 500 MHz) δ : 0.98 (s, 3H), 1.01 (s, 3H), 1.06 (s, 3H), 1.22 (ddd, *J* = 13.3, 13.3, 3.8 Hz, 1H), 1.42 (ddd, *J* = 12.8, 12.8, 3.4 Hz, 1H), 1.55 (dt, *J* = 13.3, 3.2 Hz, 1H), 1.59 (s, 3H), 1.60 (m, 1H), 1.61 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.62 (s, 3H), 1.86 (qt, *J* = 13.8, 3.9 Hz, 1H), 2.02 (dt, *J* = 12.3, 3.2 Hz, 1H), 2.45 (dd, *J* = 14.1, 12.6 Hz, 1H), 2.83 (dd, *J* = 14.1, 6.2 Hz, 1H), 5.31 (s, 1H), 6.48 (d, *J* = 7.7 Hz, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 9.55 (s, 1H); ^{13}C NMR (CD_3COCD_3, 125 MHz) δ : 20.6 (CH_2), 21.3 (CH_3), 21.9 (CH_3), 26.4 (CH_2), 30.9 (CH_3), 31.0 (CH_3), 33.59 (CH_3), 33.6 (C), 36.5 (CH_2), 42.3 (CH_2), 46.4 (C), 60.9 (CH), 75.8 (C), 111.4 (CH), 124.6 (CH), 129.3 (C), 130.2 (C), 153.4 (C), 156.9 (C); IR (cm^{-1}) ν: 3372, 1629, 1579, 1458, 1368, 1265, 1233, 1157, 1098, 1055, 981, 946, 897, 808; HRMS (FAB) *m/z*: calcd for $C_{19}H_{28}O_2Na$ 311.1987, found: 311.1975.

(4b*S*,8a*S*)-2-Isopropyl-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluoren-1-ol (10):

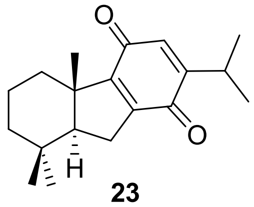


10

To a solution of **22** (376 mg, 1.305 mmol) in CH_2Cl_2 (20 mL) was added at -40 ºC triethylsilane (0.7 mL, 4.38 mmol) and trifluoroacetic acid (0.2 mL, 2.69 mmol) and the mixture was stirred at this temperature for 1 h, at which time TLC showed no starting material. Then, sat. $NaHCO_3$ solution (1 mL) was slowly added to quench the reaction and the solvent was removed in vacuum. Ether (40 mL) was added to the crude product and the organic phase was washed with sat. $NaHCO_3$ solution (3 x 10 mL), water, brine, dried over anhydrous Na_2SO_4 and concentrated in vacuum. Purification by flash column chromatography on silica gel (20% ether/hexanes) gave 337 mg of **10** (95%). $[\alpha]_D^{25}$ = -

19.4 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.99 (s, 3H), 1.04 (s, 3H), 1.06 (s, 3H), 1.21 (ddd, *J* = 13.2, 13.2, 3.4 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 3H), 1.27 (d, *J* = 6.9 Hz, 3H), 1.47 (ddd, *J* = 12.8, 12.8, 3.6 Hz, 1H), 1.55 (bd, *J* = 13.3 Hz, 1H), 1.67 (m, 1H), 1.77 (dd, *J* = 13.2, 6.2 Hz, 1H), 1.83 (qt, *J* = 13.7, 3.9 Hz, 1H), 2.04 (bd, *J* = 12.4 Hz, 1H), 2.52 (dd, *J* = 13.8, 13.2 Hz, 1H), 2.65 (dd, *J* = 13.8, 6.2 Hz, 1H), 3.20 (h, *J* = 6.9 Hz, 1H), 4.57 (bs, 1H), 6.64 (d, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 20.1 (CH_2), 21.1 (CH_3), 21.8 (CH_3), 22.8 (CH_2), 23.1 (CH_3), 25.4 (CH_2), 27.1 (CH), 33.1 (C), 33.3 (CH_3), 35.8 (CH_2), 41.7 (CH_2), 46.1 (C), 60.4 (CH), 112.7 (CH), 124.6 (CH), 126.7 (C), 131.7 (C), 149.3 (C), 154.9 (C); IR (cm^{-1}) ν: 3430, 1646, 1458, 1436, 1369, 1261, 1188, 1144, 1097, 959, 813; HRMS (FAB) *m/z*: calcd for $C_{19}H_{28}ONa$ 295.2038, found: 295.2047.

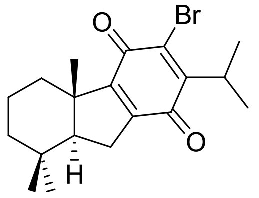
(4b*S*,8a*S*)-2-Isopropyl-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluorene-1,4-dione (23):



23

Potassium nitrosodisulfonate (0.54 g, 2.01 mmol) and disodium hydrogen phosphate buffer PH-7 (2 mL) were added to a solution of **10** (0.25 g, 0.796 mmol) in acetone (15 ml) and water (3 ml), and the reaction mixture was stirred at room temperature for 15 h. Then, the solvent was evaporated and the mixture was extracted with ether (2 x 20 ml). The combined organic phases were washed with brine, dried over anhydrous. Na_2SO_4, and concentrated to give 222 mg of **23** (94%) as a red oil. $[\alpha]_D^{25}$ = -26.3 (*c* 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.87 (s, 3H), 0.93 (s, 3H), 1.00 (s, 3H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.05 (d, *J* = 6.9 Hz, 3H), 1.05 (ddd, *J* = 13.9, 13.9, 4.4 Hz, 1H), 1.40 (ddd, *J* = 12.8, 12.8, 3.8 Hz, 1H), 1.44 (bd, *J* = 13.1 Hz, 1H), 1.55 (m, 1H), 1.59 (dd, *J* = 12.5, 6.3 Hz, 1H), 1.70 (qt, *J* = 13.8, 3.5 Hz, 1H), 2.22 (bd, *J* = 14.1 Hz, 1H), 2.27 (dd, *J* = 16.7, 12.5 Hz, 1H), 2.54 (dd, *J* = 16.7, 6.3 Hz, 1H), 2.96 (h, *J* = 6.9 Hz, 1H), 6.25 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 18.1 (CH_3), 19.7 (CH_2), 21.1 (CH_3), 21.8 (CH_3), 26.5 (CH), 27.0 (CH_2), 32.9 (C), 33.1 (CH_3), 34.9 (CH_2), 41.1 (CH_2), 48.1 (C), 58.3 (CH), 130.7 (CH), 148.1 (CH), 154.4 (C), 155.8 (C), 186.7 (C), 186.8 (C); IR (cm^{-1}) ν: 1650, 1593, 1459, 1370, 1315, 1265, 1223, 1132, 1081, 1023, 893, 771 cm $^{-1}$; HRMS (FAB) *m/z*: calcd for $C_{19}H_{26}O_2Na$ 309.1830, found: 309.1816.

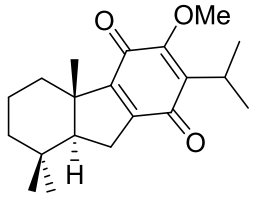
(4b*S*,8a*S*)-3-Bromo-2-isopropyl-4b,8,8-trimethyl-5,6,7,8,8a,9-hexahydro-4bH-fluorene-1,4-dione (24):



24

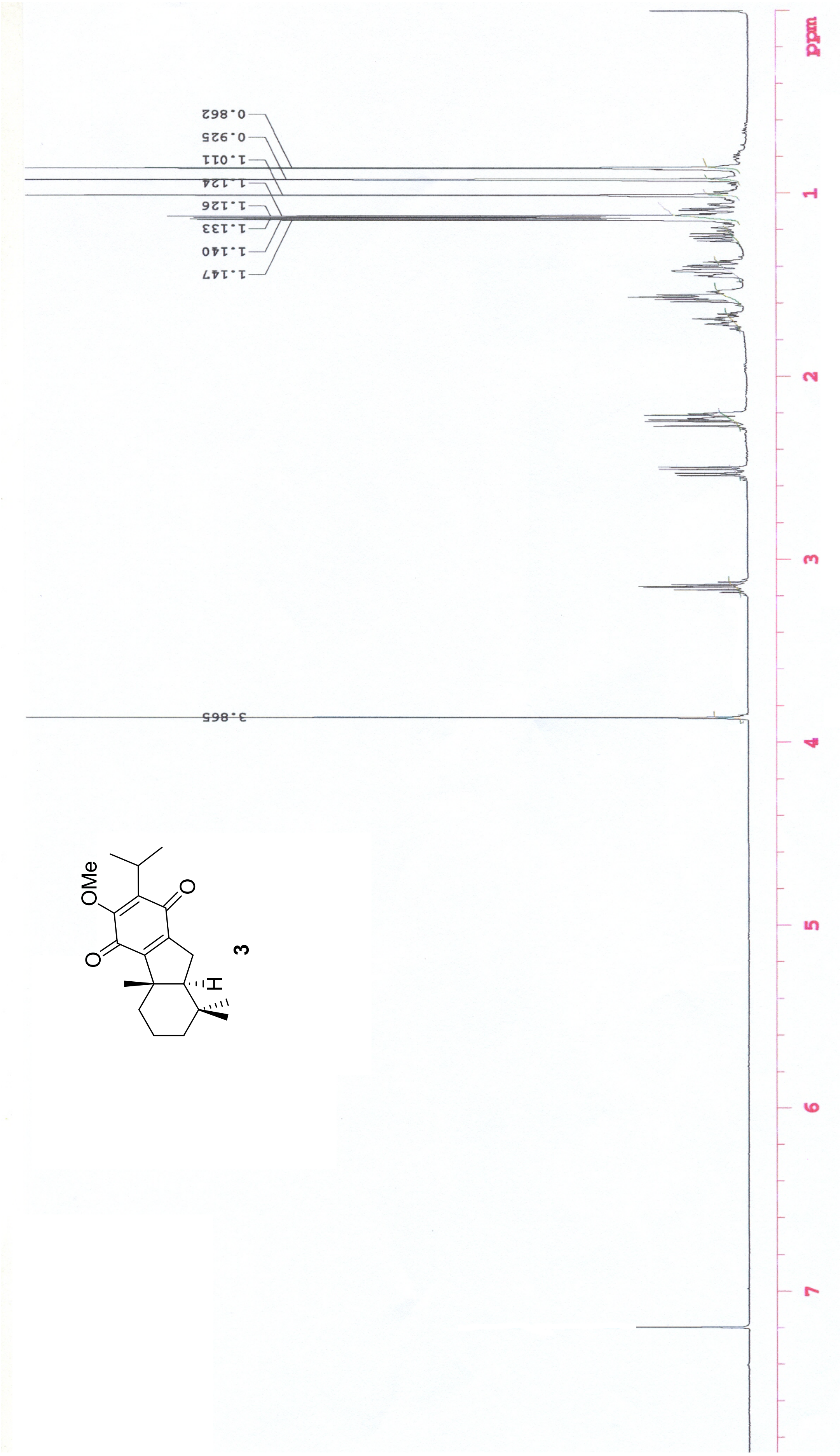
A solution of bromine (0.15 ml, 2.93 mmol) was added to a solution of **23** (0.57 mg, 1.993 mmol) in acetic acid (7 ml), and the reaction mixture was stirred for 5 min. 5% $NaHSO_3$ solution (1 mL) was added to quench the reaction and the mixture was stirred for an additional 5 min. Then ether (25 mL) was added and the organic phase was washed with water (10 x 10 mL), brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the crude product was purified by flash column chromatography on silica gel to give 645 mg of **24** (89%) as a yellow syrup. $[\alpha]_D^{25}$ = -23.6°(*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz) δ : 0.93 (s, 3H), 0.99 (s, 3H), 1.08 (s, 3H), 1.25 (ddd, *J* = 13.2, 13.2, 3.8 Hz, 1H), 1.29 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.45 (ddd, *J* = 13.1, 13.1, 4.2 Hz, 1H), 1.51 (bd, *J* = 13.4 Hz, 1H), 1.62 (m, 1H), 1.66 (dd, *J* = 12.6, 6.3 Hz, 1H), 1.76 (qt, *J* = 13.7, 3.4 Hz, 1H), 2.30 (dt, *J* = 13.1, 3.3 Hz, 1H), 2.35 (dd, *J* = 16.9, 12.6 Hz, 1H), 2.61 (dd, *J* = 16.9, 6.3 Hz, 1H), 3.42 (h, *J* = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 18.1 (CH_3), 19.7 (CH_2), 19.99 (CH_3), 20.04 (CH_3), 21.1 (CH_3), 27.1 (CH), 27.2 (CH_2), 32.9 (C), 33.0 (CH_3), 34.7 (CH_2), 41.1 (CH_2), 48.7 (C), 58.3 (CH), 135.9 (CH), 148.9 (CH), 151.9 (C), 154.9 (C), 177.7 (C), 183.7 (C); IR (cm^{-1}) ν: 1690, 1663, 1561, 1370, 1298, 1247, 1216, 1068, 1027, 916, 769, 739; HRMS (FAB) *m/z*: calcd for $C_{19}H_{25}O_2BrNa$ 387.0936, found: 387.0948.

(-)-Taiwaniaquinone G (3)



3

To a solution of **24** (193 mg, 0.53 mmol) in dried methanol (10 mL) was added sodium methoxide (220 mg, 4.07 mmol) and the solution was stirred at room temperature for 30 min, at which time TLC showed no **24**. Then the solvent was removed and ether (20 mL) and water (6 mL) were added to the crude product and the organic phase was washed with water, brine, dried over anhydrous Na_2SO_4. The solvent was removed in vacuum to give162 mg of **3** (97%) as a yellow syrup.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6
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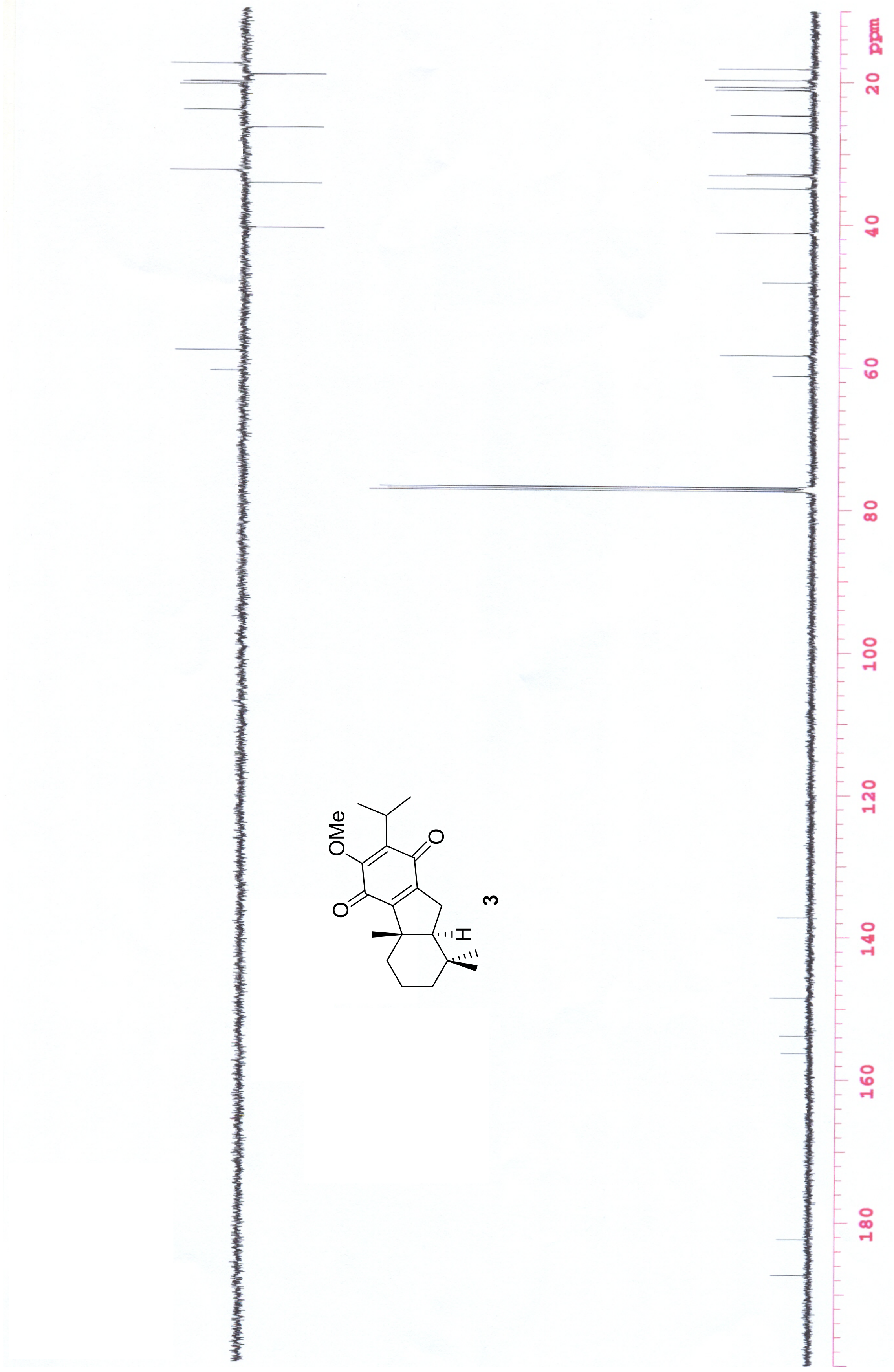
O
O
H

3



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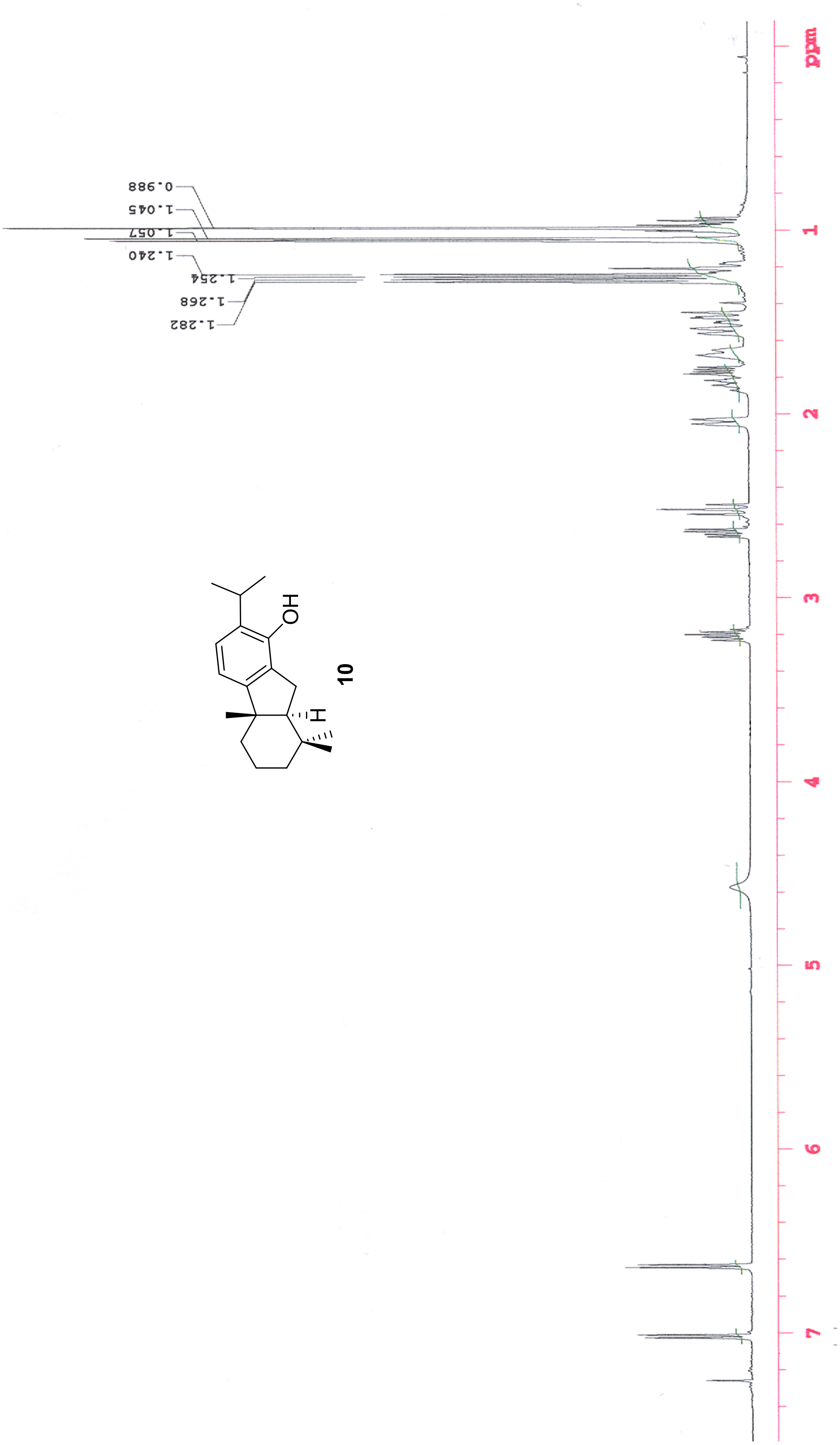

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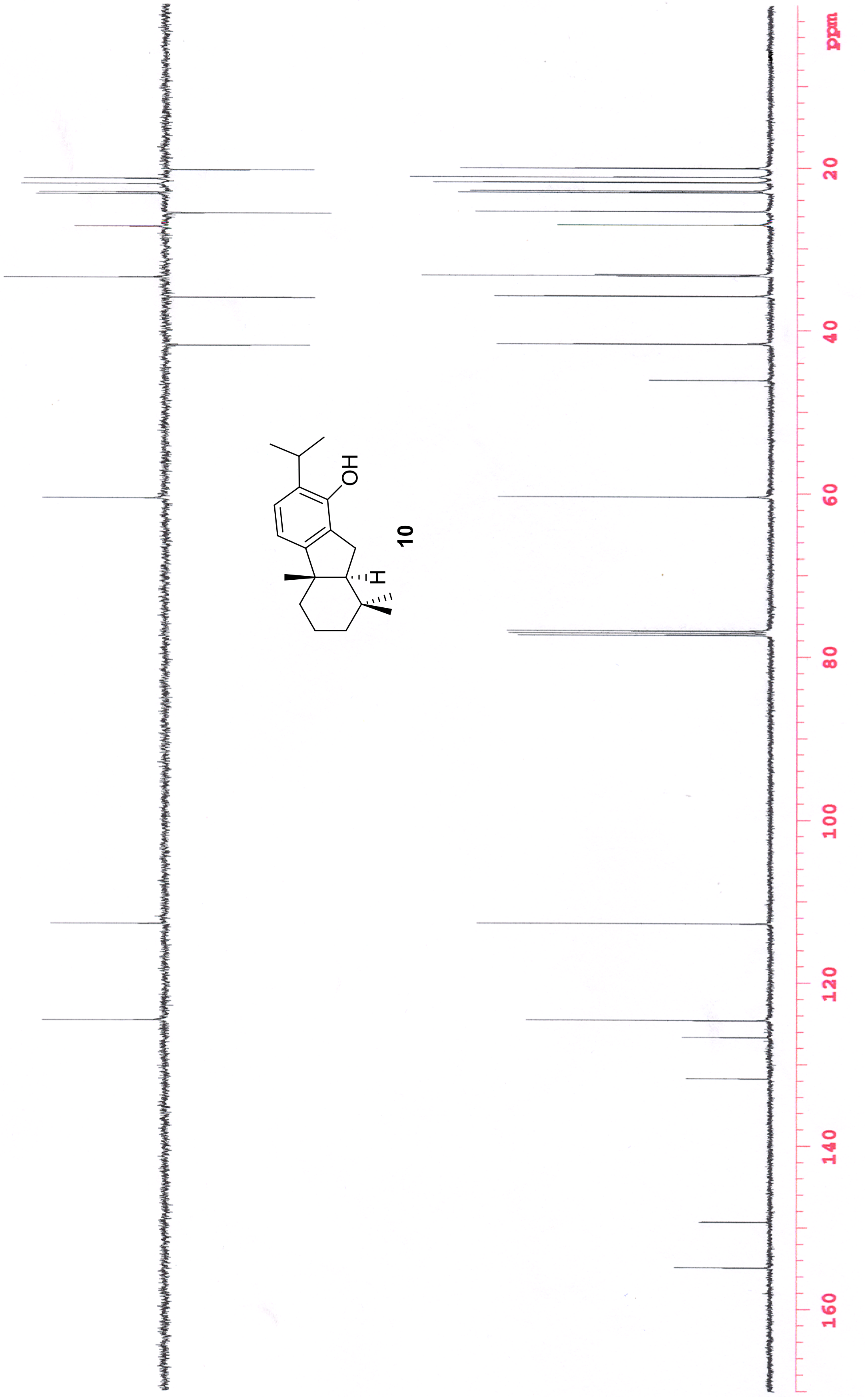

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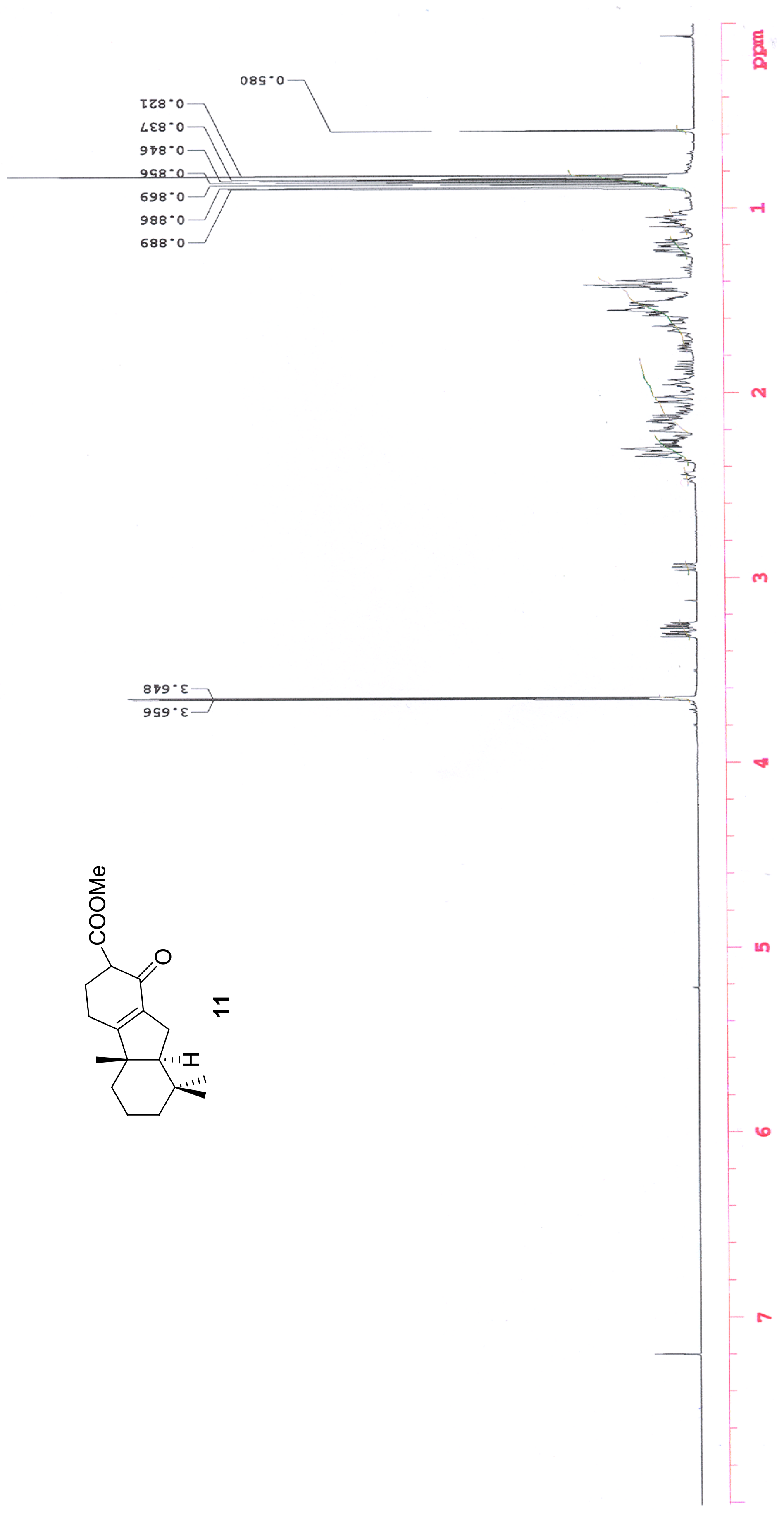
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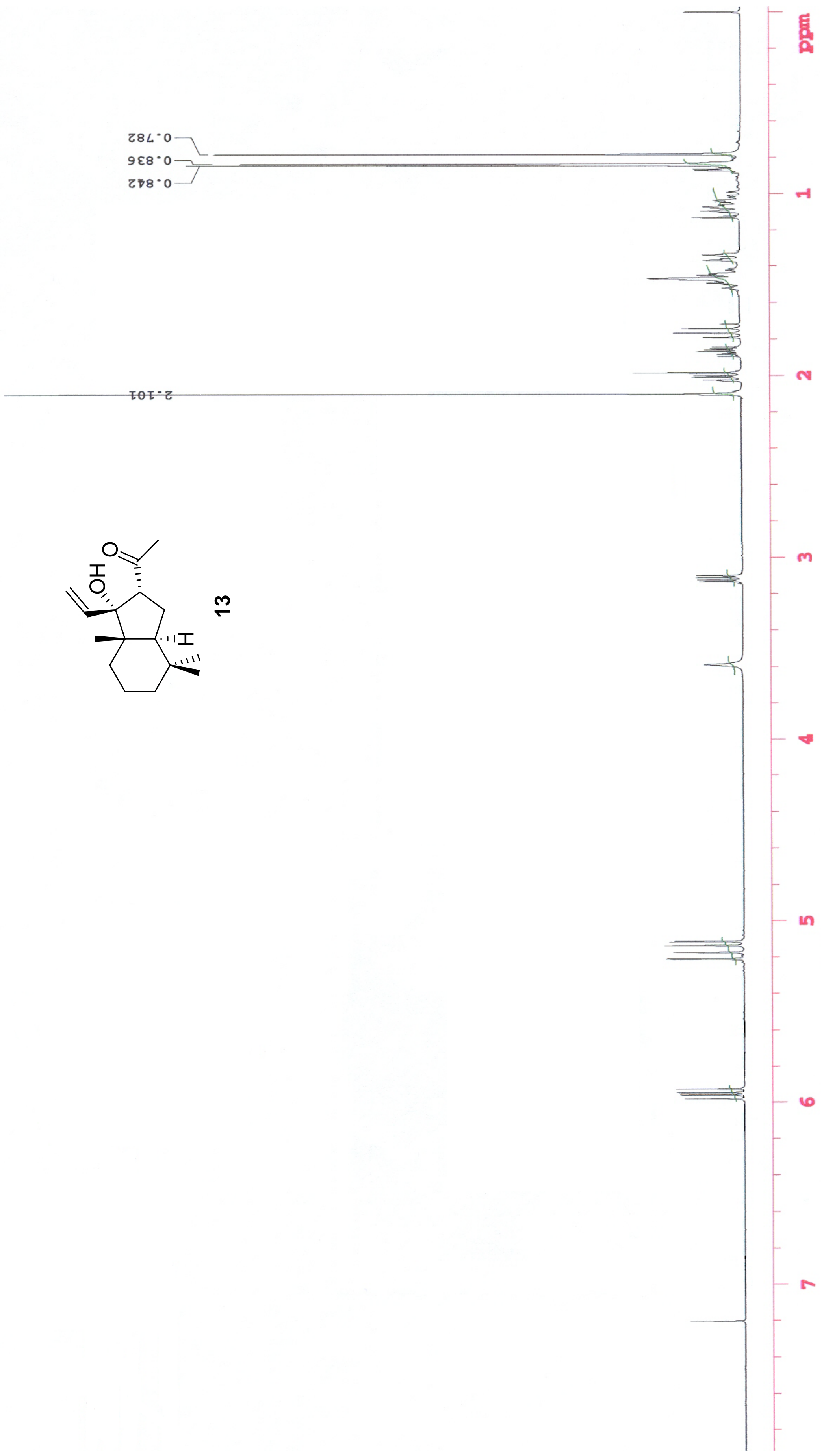
O
H

11



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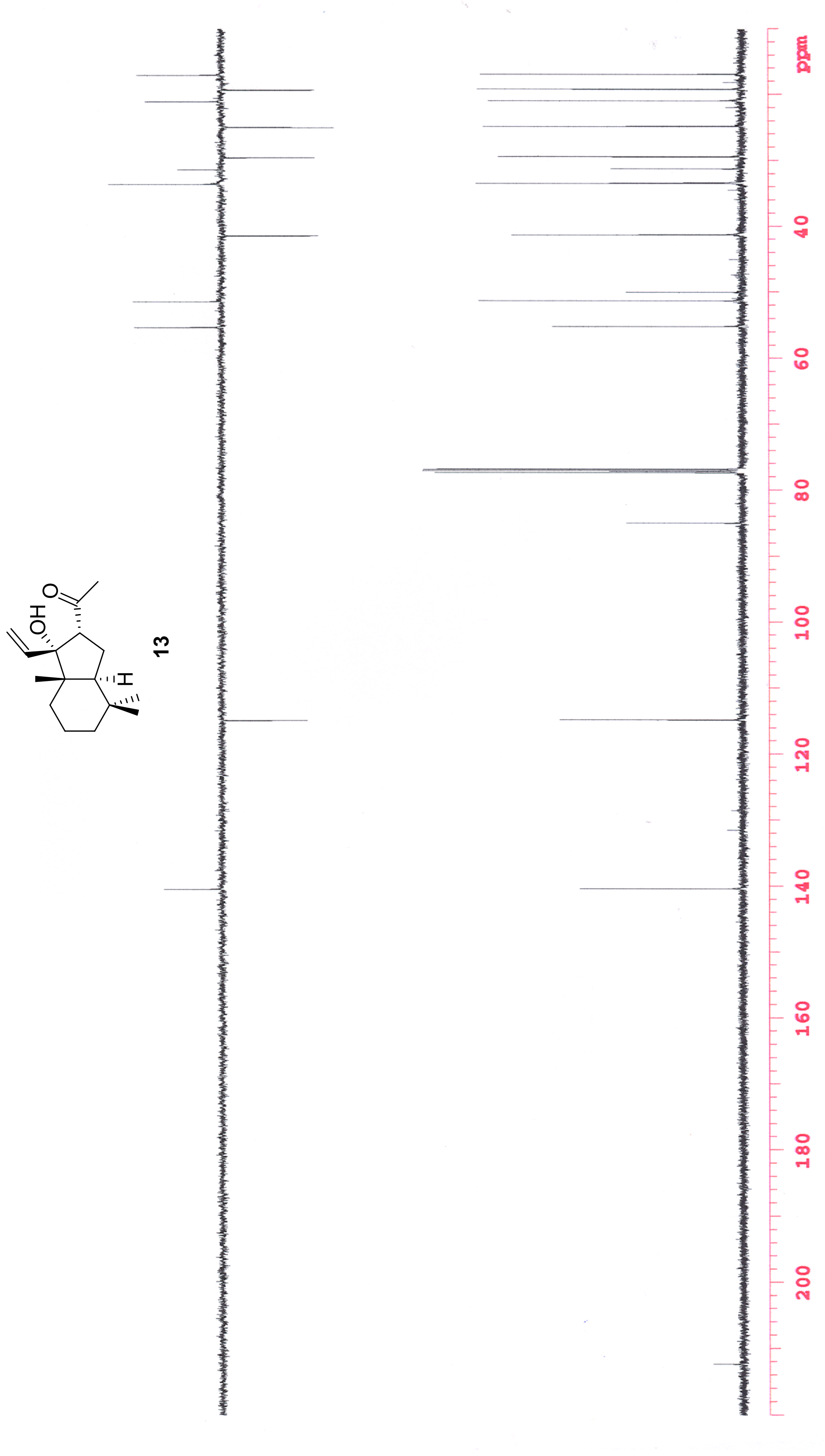
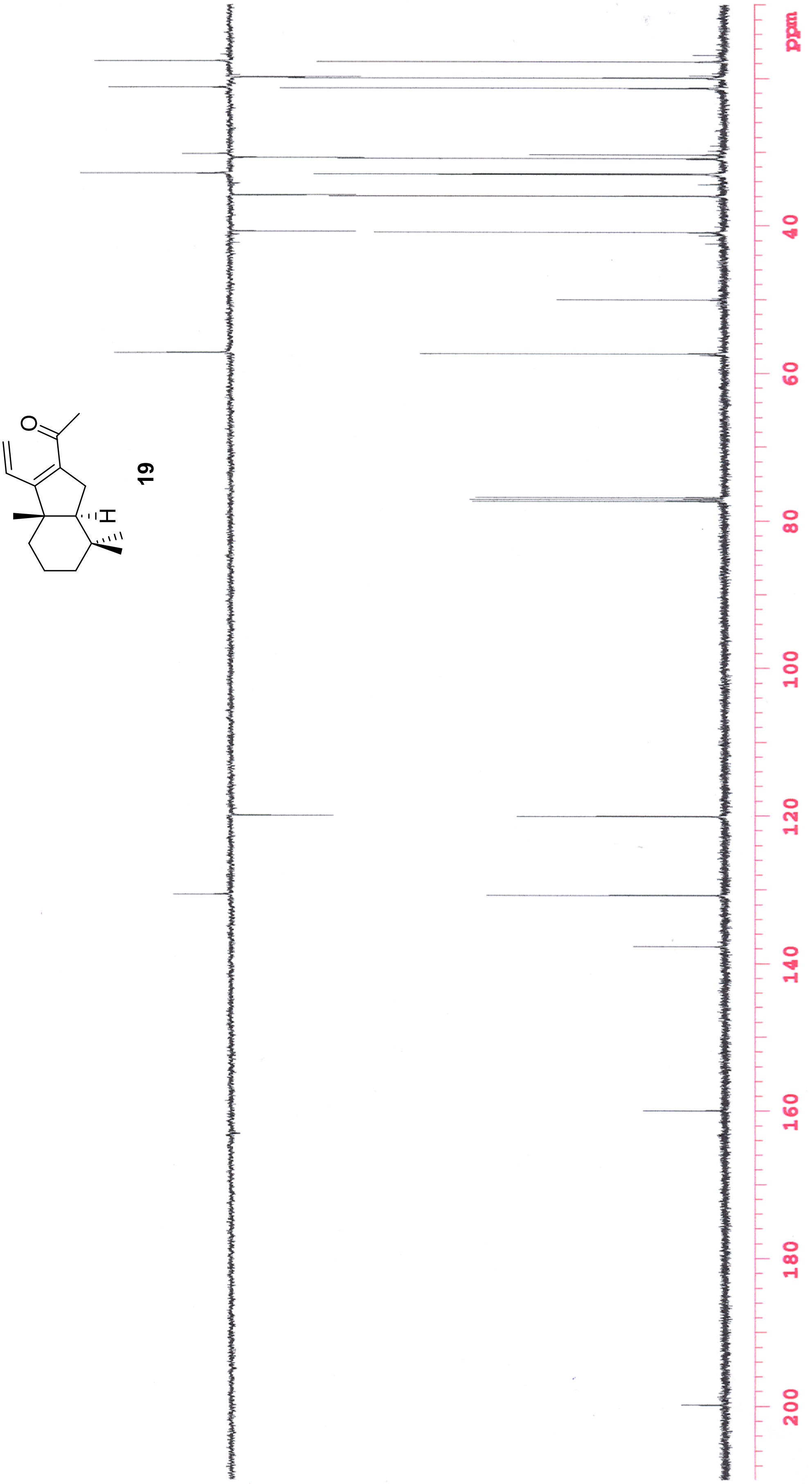


13

19



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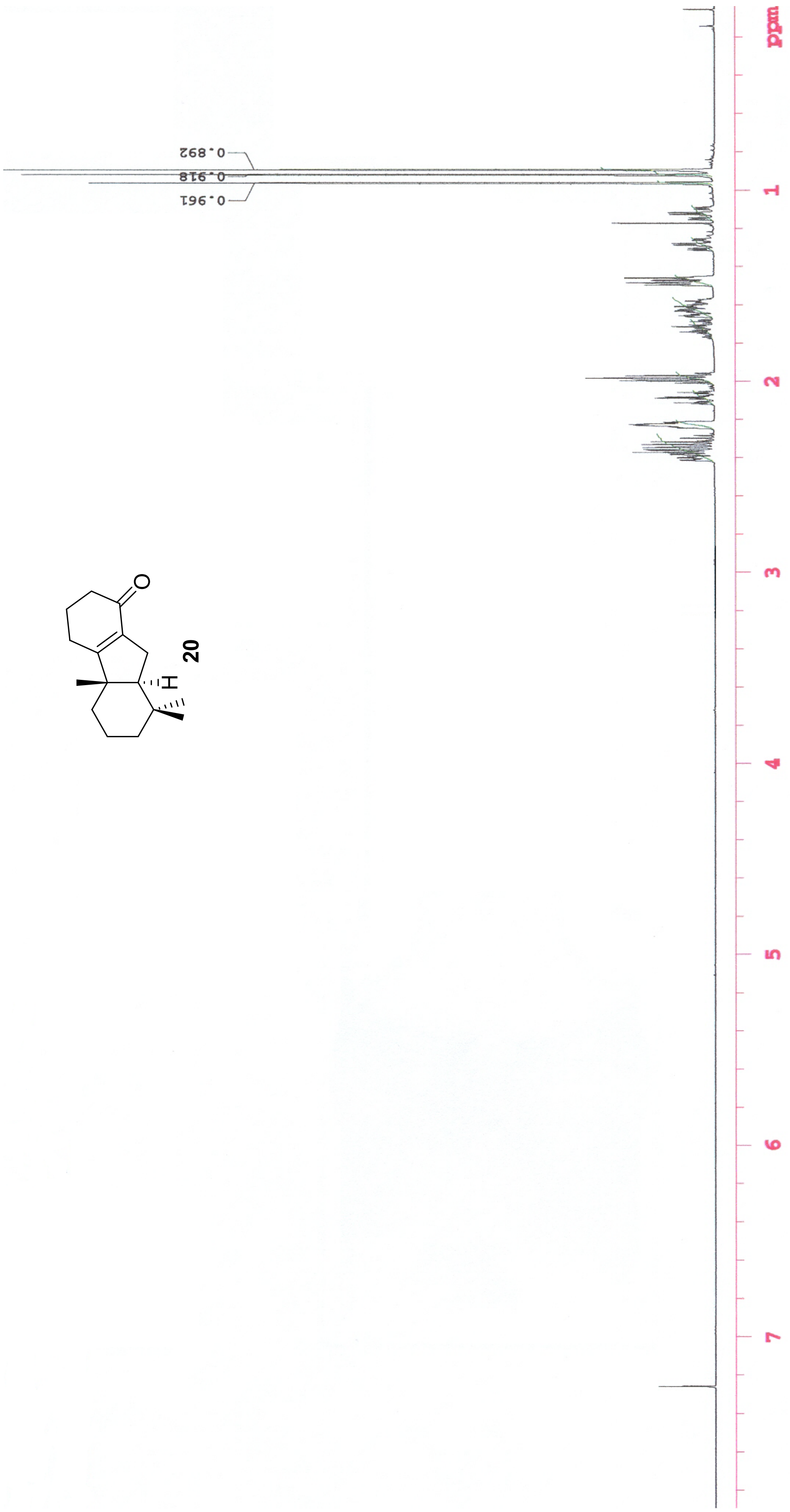

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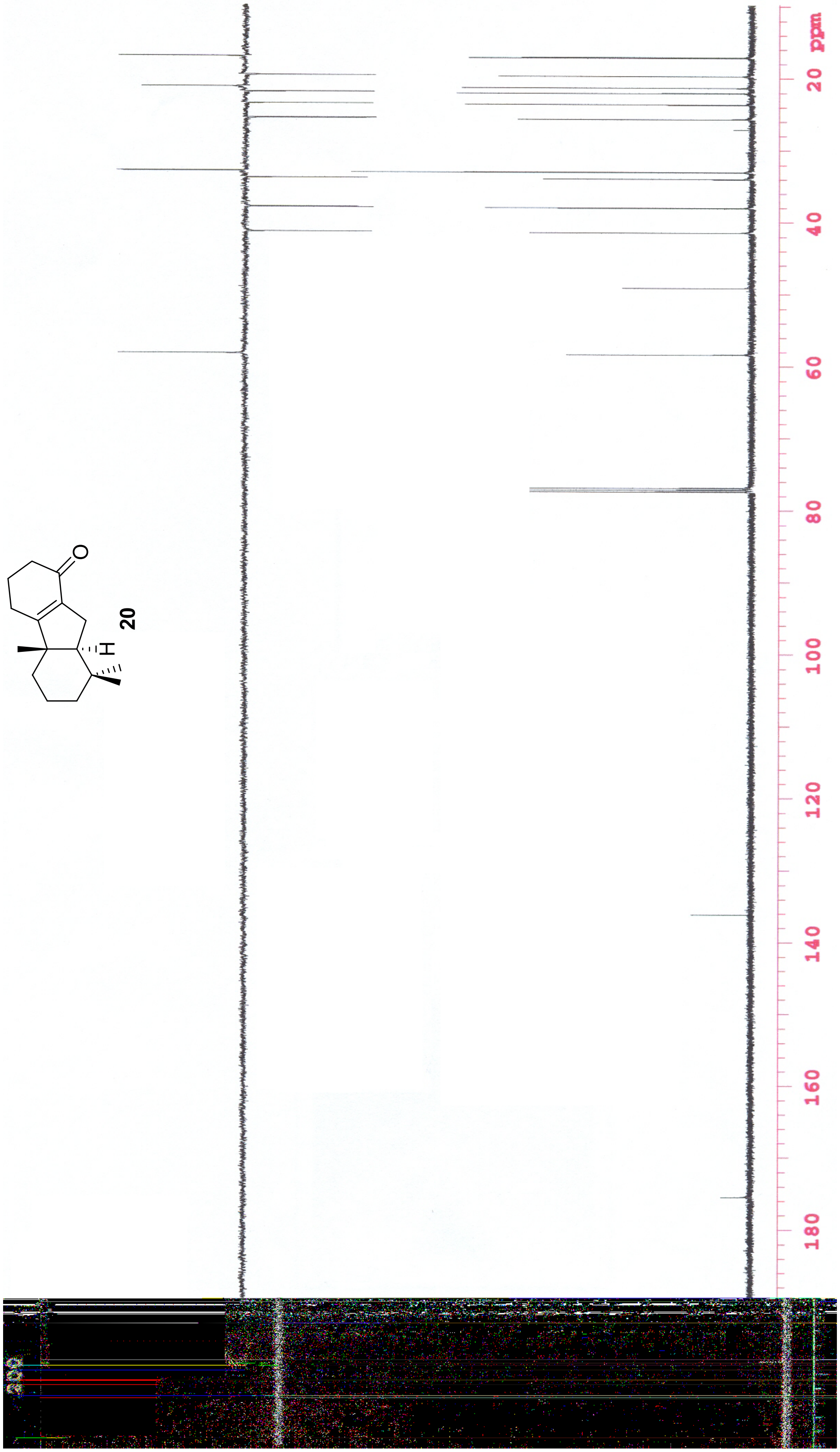
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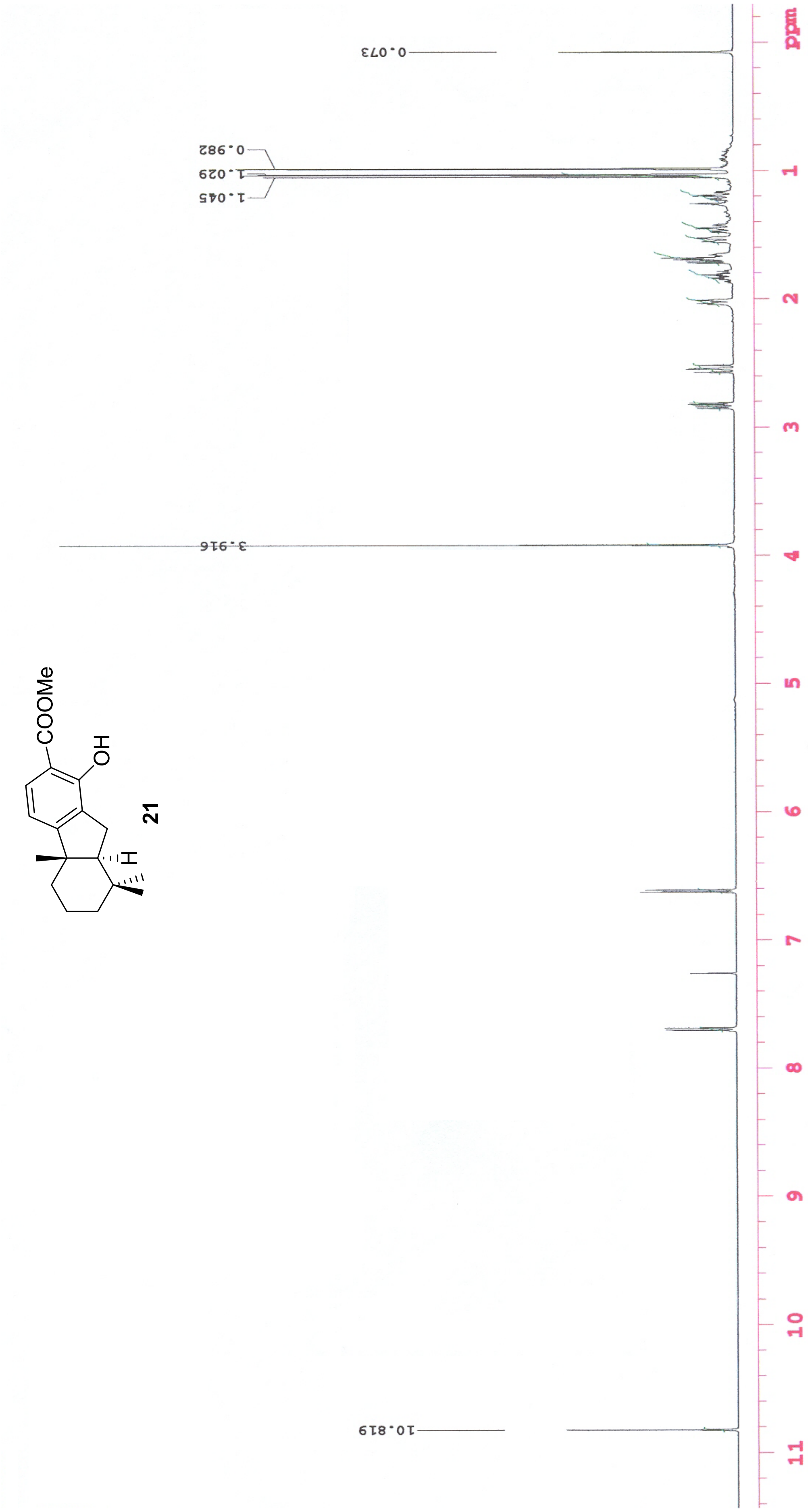
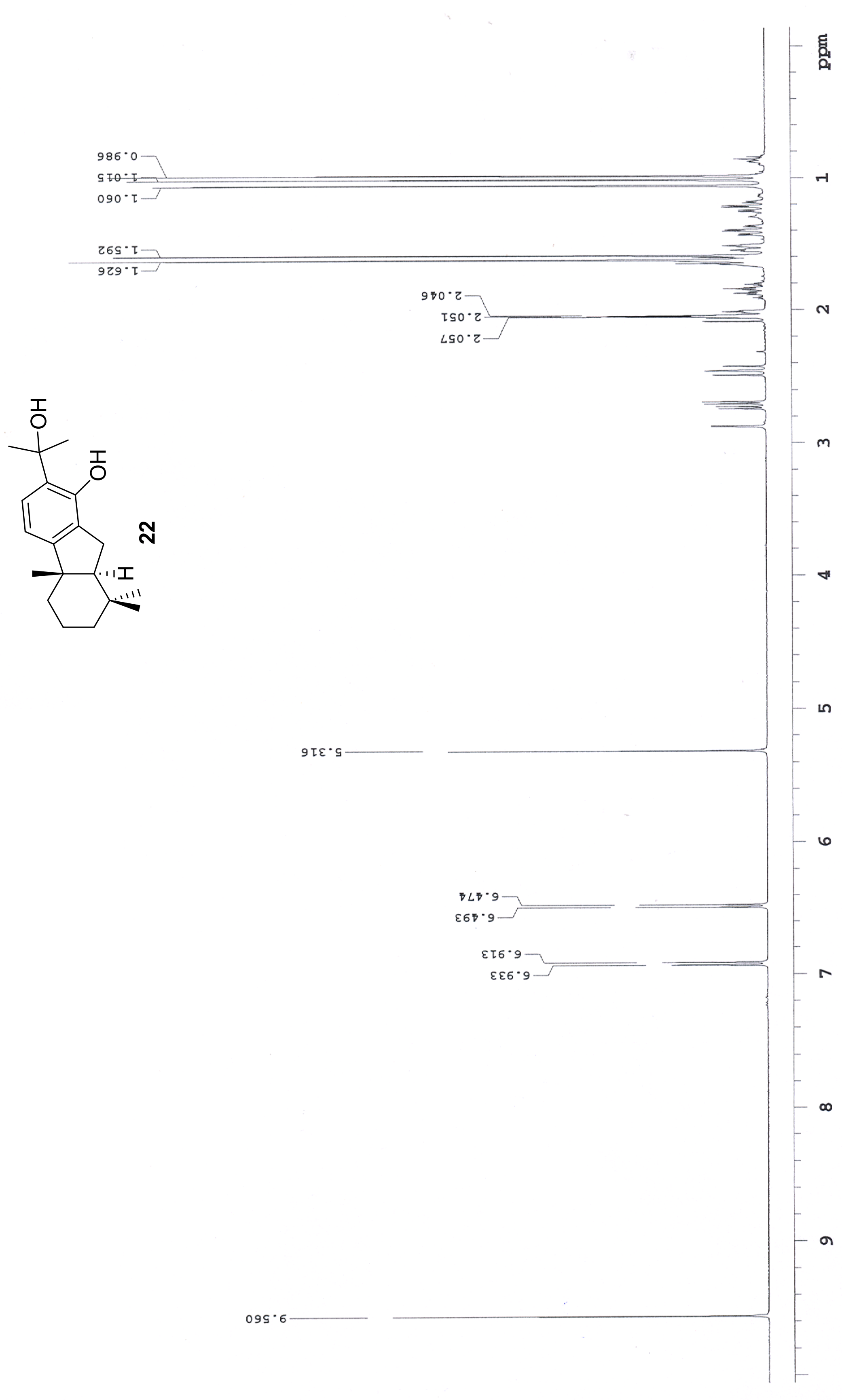

21

21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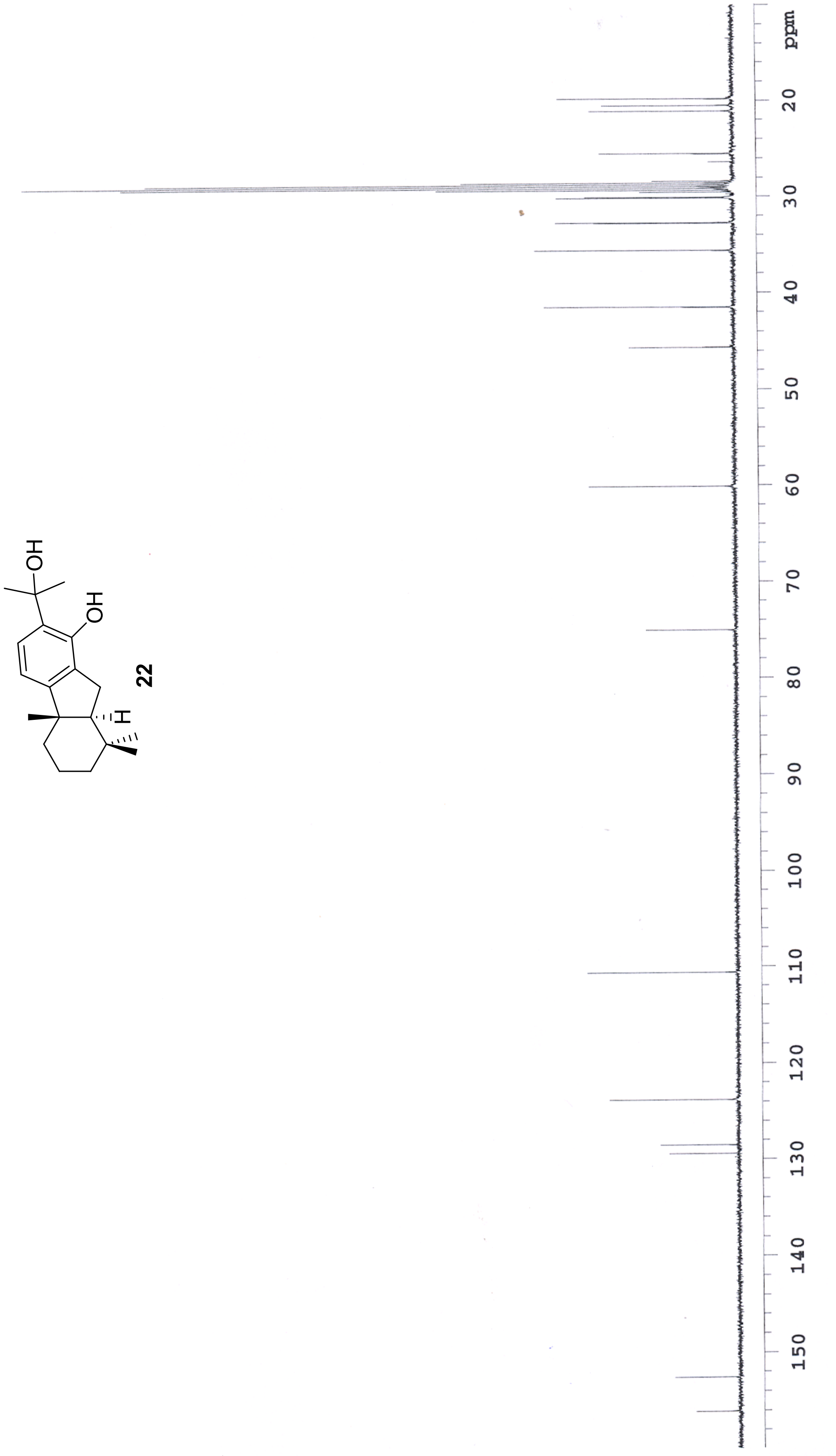
22



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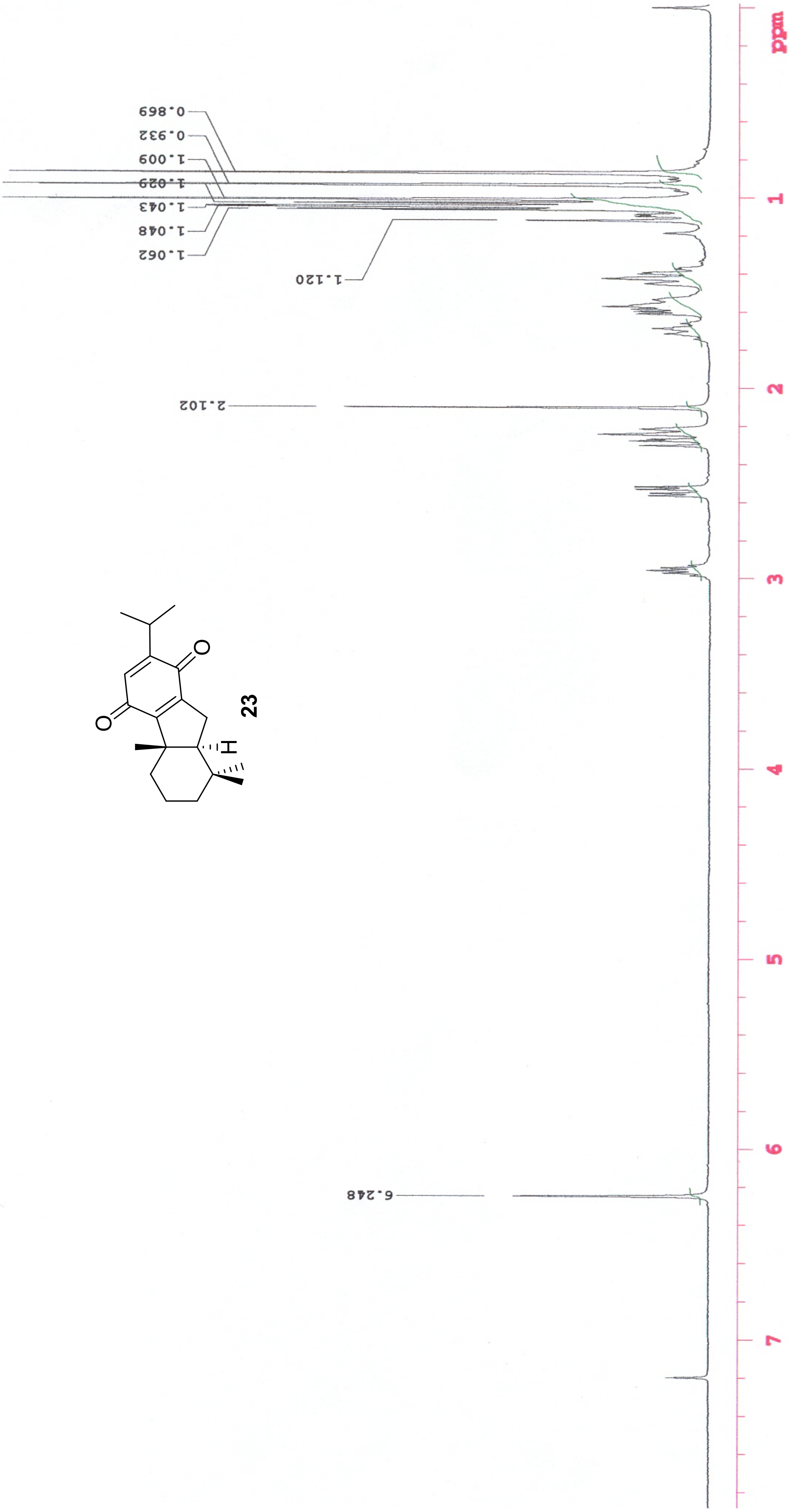
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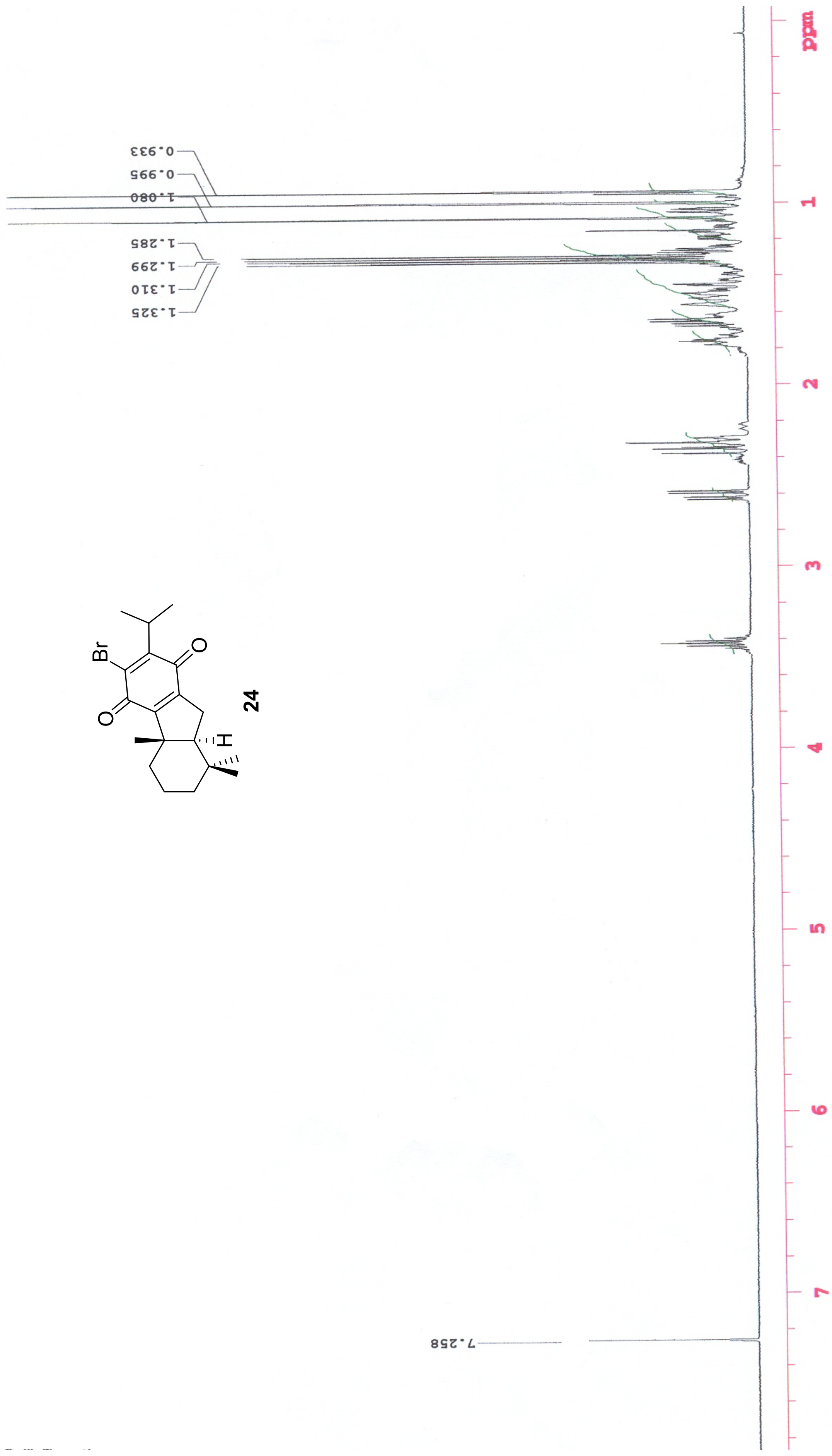
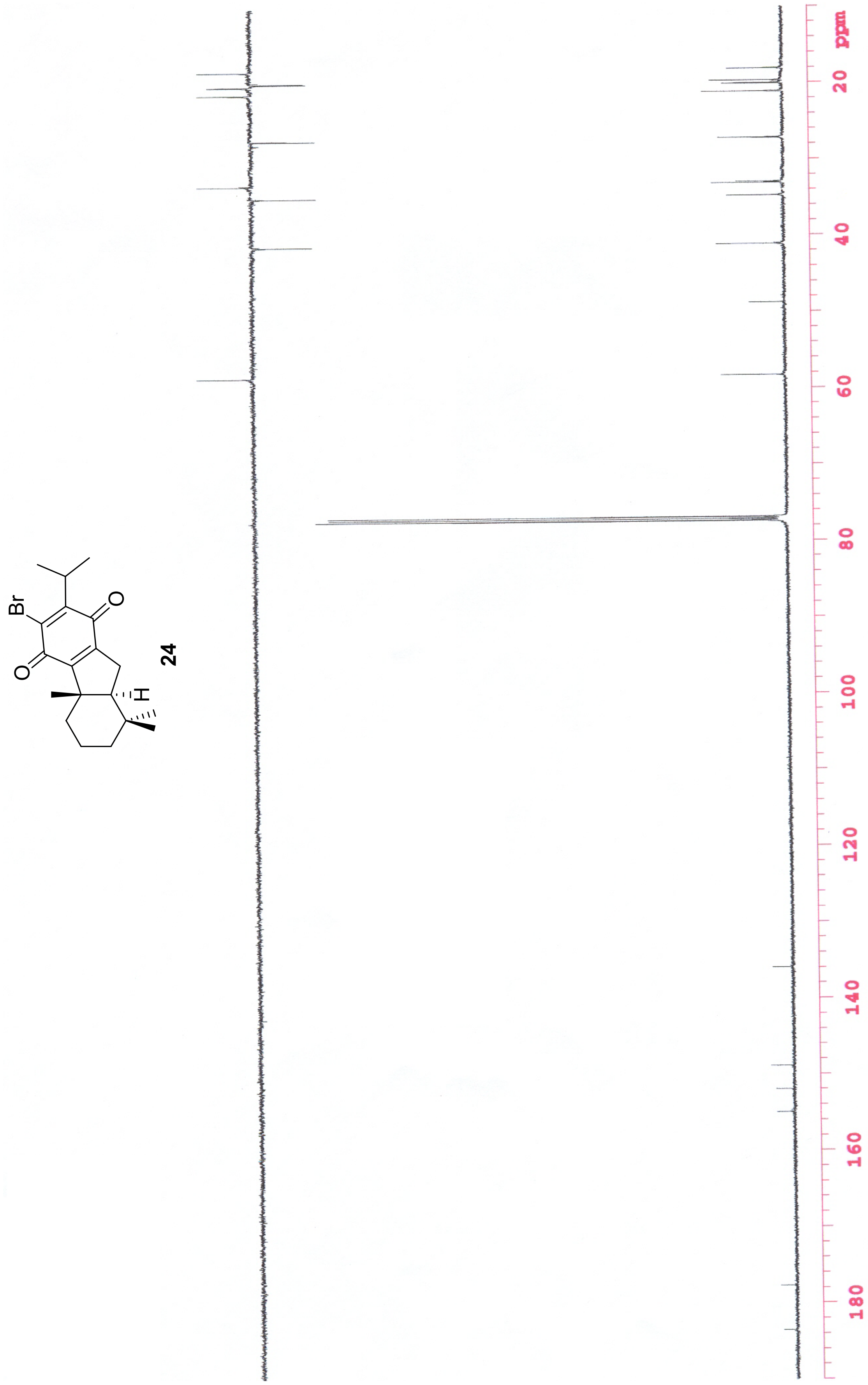
O
H
23

23



24



24