Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Total Synthesis of (±)-*epi*-Stemodan-13α, 17-diol

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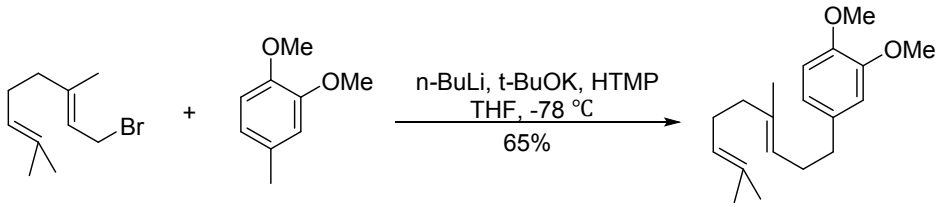
General Information

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. DCM and toluene were distilled from calcium hydride under argon; THF were distilled from sodium-benzophenone under argon. All the other chemicals were purchased commercially and used without further purification, unless otherwise stated. Flash chromatography was performed using silica gel (200-300 mesh). Reactions were monitored by thin layer chromatography (TLC). Visualization was achieved under a UV lamp (254 nm and 365 nm), I_2 and by developing the plates with *p*-anisaldehyde or phosphomolybdic acid. ^{1}H and ^{13}C NMR were recorded on Bruker DRX-400 MHz NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^{1}H NMR = 7.26, ^{13}C NMR = 77.16). The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded by using FTMS-7 spectrometers. Infrared (IR) spectra were recorded on a NEXUS 670 FT-IR Fourier transform infrared spectrophotometer and are reported in wavenumbers (cm^{-1}).

Experimental Procedures

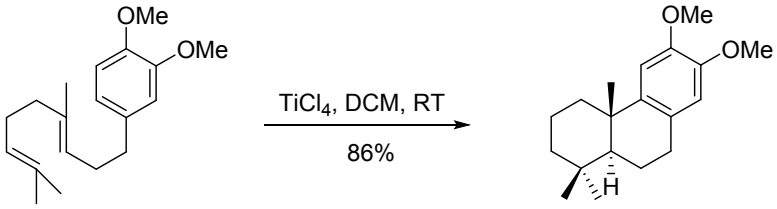
Procedure for the preparation of Compound 12



13 **14** **12**

To a solution of t-BuOK (20.11 g, 179.20 mmol) in dry THF (600 ml) at room temperature was added 1, 2-dimethoxy-4-methylbenzene (**14**, 17.15 mL, 119.45 mmol) and HTMP (1.00 mL, 5.97 mmol). The solution was allowed to cool down at -78 ℃. Then was added n-BuLi (2.5 M in hexane, 71.68 mL, 179.20 mmol) dropwise slowly at -78 ℃. The solution became wine red. After the addition of n-BuLi, the solution was stirred for 30 min. Then geranyl bromide (**13**, 26.10 mL, 131.40 mmol) was added dropwsie into the reaction system to get a yellow solution. After completion of addition of geranyl bromide, the mixture was quenched with saturated NH_4Cl solution (400 mL) at -78 ℃. The aqueous layer was extracted with EtOAc (200 mL × 4). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:10) to afford the corresponding compound **12** (22.38 g, 65%) as a yellow oil. Note that all NMR data matched that reported by Snyder and co-workers.[1]

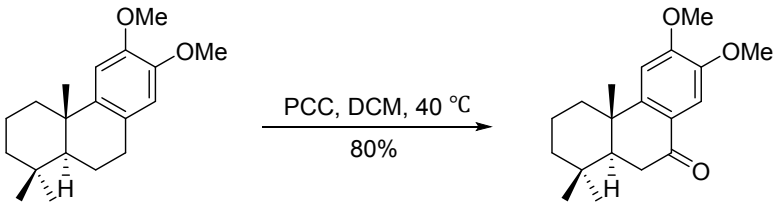
Procedure for the preparation of compound 4



12 **11**

To a solution of compound **12** (8.68 g, 30.11 mmol) in dry DCM (100 mL) at room temperature was slowly added $TiCl_4$ (3.30 mL, 30.11 mmol). The solution became deep red. The solution was stirred for 2 days at room temperature. The reaction was quenched with saturated $NaHCO_3$ solution (500 mL). The aqueous layer was extracted with DCM (200 mL × 1) and EtOAc (100 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:10) to afford the corresponding compound **11** (7.47 g, 86%) as a yellow oil. Note that all NMR data matched that reported by Tada and co-workers.[2]

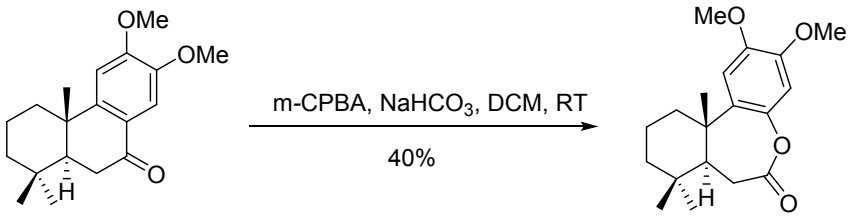
Procedure for the preparation of compound 15



11 **15**

To a solution of compound **11** (7.47 g, 25.91 mmol) in dry DCM (100 mL) at room temperature was added PCC (26.62 g, 123.45 mmol) in one-portion. The solution became black. After stirred for 12 hours at 40 ℃, the reaction was filtered through a pad of silica gel and washed with EtOAc (50 mL × 5). The organic phase was concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:5) to afford the corresponding compound **15** (6.29 g, 80%) as a foam. Note that all NMR data matched that reported by Tada and co-workers.[2]

Procedure for the preparation of compound 10



15 **10**

To a solution of compound **15** (3.84 g, 12.70 mmol) in dry DCM (0.01 M, 1.30 L) at room temperature, was added $NaHCO_3$ (5.87 g, 69.85 mmol) and m-CPBA (11.60 g, 57.15 mmol). The solution was stirred for 2 days at room temperature. Then was quenched with saturated NaS_2O_3 solution (200 mL) and $NaHCO_3$ (200 mL). The aqueous layer was extracted with DCM (100 mL × 1) and EtOAc (100 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:5) to afford the corresponding compound **10** (1.64 g, 40%) as a foam.

Compound **10**:

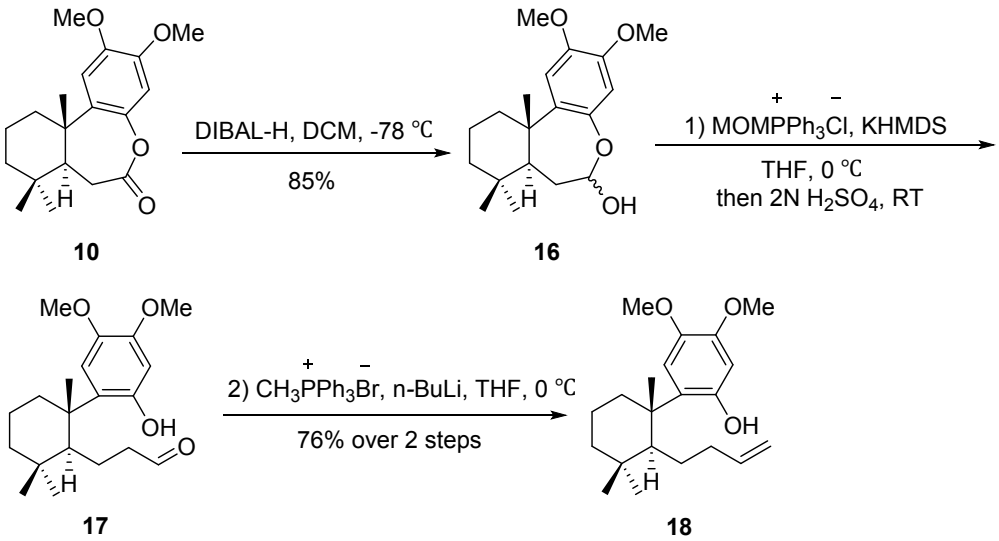
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.65 (s, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 2.64 – 2.52 (m, 2H), 1.98 – 1.87 (m, 1H), 1.85 (dd, *J* = 9.1, 3.4 Hz, 1H), 1.80 (dd, *J* = 9.4, 2.9 Hz, 2H), 1.74 – 1.66 (m, 1H), 1.55 – 1.49 (m, 1H), 1.48 (s, 3H), 1.20 (dd, *J* = 13.4, 4.5 Hz, 1H), 1.12 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 148.0, 146.0, 144.8, 132.4, 108.1, 104.8, 56.45, 56.2, 56.0, 41.2, 39.8, 39.1, 36.1, 33.3, 32.0, 21.5, 20.7, 18.9.

IR (neat, cm^{-1}): 2297, 2931, 2869, 2254, 1750, 1509, 1140, 1001, 772.

HRMS (ESI): *m/z* calcd for $C_{19}H_{26}O_4$ $[M]^+$: 318.1831; Found: 318.1831.

Procedure for the preparation of compound 16, 17 and 18



10 **16** **17** **18**

1) To a solution of compound **10** (761.5 mg, 2.39 mmol) in dry DCM (50 ml) at -78 ℃ was added DIBAL-H (1.5 M in toluene, 2.40 mL, 3.59 mmol) quickly. After stirred for 6 hours, the reaction was quenched with CH_3OH (2.00 ml) at -78 ℃. Then it was added saturated potassium sodium tartrate solution (30 mL) and stirred for 1 hour at room temperature. The aqueous layer was extracted with DCM (30 mL × 1) and EtOAc (25 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:3) to afford the corresponding compound **16** (649.5 mg, 85%) as a foam.

2) To a suspension of methoxymethyltriphenylphosphonium chloride (3.48 g, 10.14 mmol) in dry THF (50 ml) at 0 ℃ was added KHMDS (1 M in THF, 9.95 mL, 9.95 mmol) dropwise. The solution became wine red. After the addition of KHMDS, the solution was stirred for 30 min at 0 ℃. The compound **16** (649.5 mg, 2.03 mmol) in THF (10 mL) was added into the solution. After stirred for 2 hours, the mixture was treated with H_2SO_4 (2 M, 10 mL) and stirred for overnight at room temperature. The aqueous layer was extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by

column chromatography (EtOAc/petroleum ether = 1:2) to afford the corresponding compound **17** as a foam.

3) To a suspension of methoxymethyltriphenylphosphonium bromide (3.65 g, 10.15 mmol) in dry THF (50 ml) at 0 ℃ was added n-BuLi (2.5 M in hexane, 3.65 mL, 9.14 mmol) dropwise slowly. The solution became wine red. After the addition of *n*-BuLi, the solution was stirred for another 30 min. The compound **17** (2.03 mmol) in THF (10 mL) was added dropwise into the solution. After stirred for overnight, the reaction was quenched with saturated NH_4Cl solution (20 mL) at 0 ℃. The aqueous layer was extracted with EtOAc (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:8) to afford the corresponding compound **18** (495.5 mg, 76% for 2 steps) as a white solid.

Compound **18**:

m.p. 136-142.5 ℃.

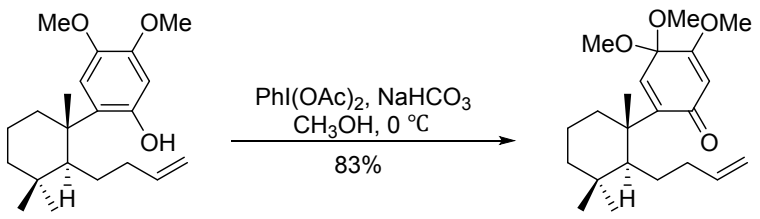
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.26 (s, 1H), 5.48 (dq, *J* = 10.3, 6.4 Hz, 1H), 4.69 (dd, *J* = 24.1, 6.2 Hz, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 2.62 (s, 1H), 2.18 (s, 1H), 1.81 – 1.64 (m, 2H), 1.57 – 1.45 (m, 1H), 1.43 (s, 1H), 1.39 (dd, *J* = 13.0, 3.5 Hz, 1H), 1.33 (s, 3H), 1.32 – 1.23 (m, 3H), 1.08 (d, *J* = 14.5 Hz, 1H), 0.94 (s, 3H), 0.91 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 147.8, 142.5, 140.0, 127.9, 114.3, 113.6, 102.5, 57.3, 56.0, 47.9, 42.5, 41.7, 36.4, 36.3, 34.9, 34.1, 27.7, 22.7, 21.5, 19.6.

IR (neat, cm^{-1}): 3447, 2933, 2867, 2360, 1520, 1299.

HRMS (ESI): *m/z* calcd for $C_{21}H_{32}O_3$ $[M]^+$: 332.2351; Found: 332.2344.

Procedure for the preparation of compound 9



18 **9**

To a solution of compound **18** (495.6 mg, 1.54 mmol) in CH_3OH (30 mL) at 0 ℃, was added $NaHCO_3$ (385.8 mg, 4.61 mmol) at 0 ℃ and stirred for 10 min. Then $PhI(OAc)_2$ (993.4 g, 3.07 mmol) was added in one-portion. After stirred for 30 min, the reaction was quenched with saturated $NaHCO_3$ solution (20 mL) at 0 ℃. The aqueous layer was extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:6) to afford the corresponding compound **9** (462.6 mg, 83%) as a white solid.

Compound **9**:

m.p. 75.2-78.9 ℃.

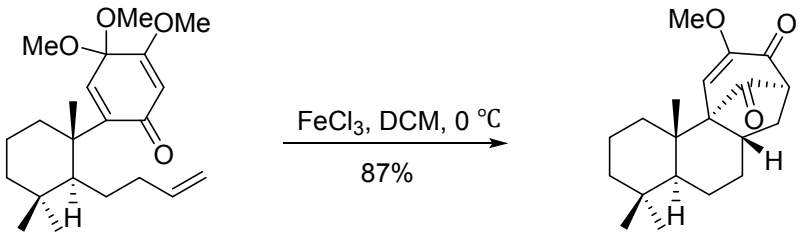
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 5.63 (ddt, *J* = 16.8, 10.3, 6.4 Hz, 1H), 5.54 (s, 1H), 4.87 – 4.77 (m, 2H), 3.79 (s, 3H), 3.26 (s, 3H), 3.25 (s, 3H), 2.48 (s, 1H), 2.25 (t, *J* = 4.1 Hz, 1H), 1.95 – 1.80 (m, 1H), 1.74 – 1.55 (m, 2H), 1.52 – 1.35 (m, 3H), 1.36 – 1.23 (m, 1H), 1.12 (s, 4H), 1.06 – 0.94 (m, 1H), 0.91 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7, 166.6, 148.8, 139.2, 137.9, 113.9, 106.7, 95.2, 56.1, 51.7, 51.6, 47.0, 43.9, 41.1, 36.4, 36.3, 34.6, 34.2, 27.0, 22.6, 20.8, 19.1.

IR (neat, cm^{-1}): 2936, 2360, 1656, 1610, 1460, 1260, 1072, 750.

HRMS (ESI): *m/z* calcd for $C_{22}H_{35}O_4$ $[M+H]^+$: 363.2350; Found: 363.2528.

Procedure for the preparation of compound 8



9 **8**

To a suspension of $FeCl_3$ (418.7 mg, 2.55 mmol) in dry DCM (0.01 M, 120 mL) at 0 ℃ was added compound **9** (462.6 mg, 1.28 mmol) in DCM (15 mL) dropwise, and it was stirred for 10 hours at the same temperature. Then reaction concentrated under reduced pressure, then the crude product was purified by column chromatography (EtOAc/petroleum ether = 1:3) to afford the corresponding compound **8** (353.4 mg, 87%) as a white solid.

Compound **8**:

m.p. 174.5-177.8 ℃.

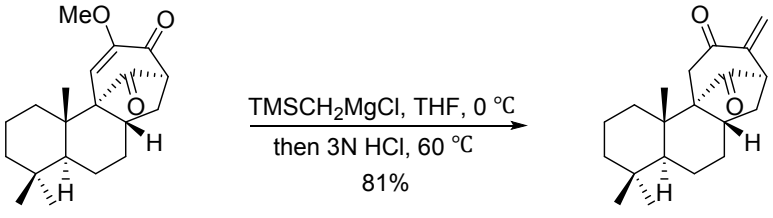
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.12 (s, 1H), 3.68 (s, 3H), 3.42 (dd, *J* = 6.2, 4.2 Hz, 1H), 2.19 (ddd, *J* = 12.8, 9.3, 5.6 Hz, 1H), 2.11 (td, *J* = 13.0, 3.9 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.75 (dd, *J* = 6.1, 3.8 Hz, 2H), 1.70 (dd, *J* = 12.6, 2.6 Hz, 1H), 1.61 – 1.49 (m, 2H), 1.48 – 1.42 (m, 1H), 1.42 – 1.27 (m, 4H), 1.20 (s, 3H), 1.05 (qd, *J* = 13.4, 4.5 Hz, 1H), 0.88 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 192.6, 152.8, 119.2, 63.4, 61.8, 55.6, 46.6, 41.1, 37.7, 36.6, 33.6, 33.5, 33.3, 33.2, 30.1, 22.4, 21.3, 18.6, 18.3.

IR (neat, cm^{-1}): 2947, 2360, 1756, 1693, 1698, 1458, 1276.

HRMS (ESI): *m/z* calcd for $C_{20}H_{28}O_3$ $[M]^+$: 316.2038; Found: 316.2038.

Procedure for the preparation of compound 19



8 **19**

To a solution of compound **8** (353.4 mg, 1.12 mmol) in dry THF (40 mL) at 0 ℃ was added $TMSCH_2MgCl$ (1.3 M in THF, 4.30 mL, 5.59 mmol) dropwise. After stirred for 2 hours, the reaction was treated with HCl (3N, 30 mL) and stirred for 30 min at 0 ℃, then stirred for 3 hours at 60 ℃. It was allowed to cool down to room temperature and diluteed with H_2O (20 mL). The aqueous layer was extracted with EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:20) to afford the corresponding compound **19** (271.7 mg, 81%) as a white solid.

Compound **19**:

m.p. 126.1-132.1 ℃.

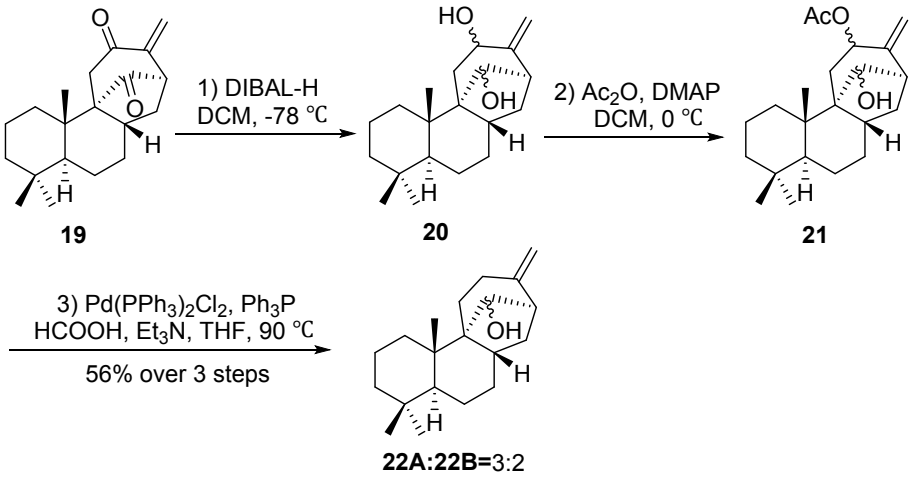
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.71 (s, 1H), 5.14 (s, 1H), 3.09 (dd, *J* = 7.7, 3.5 Hz, 1H), 2.74 (dd, *J* = 98.1, 19.3 Hz, 2H), 2.33 – 2.17 (m, 2H), 1.87 (tdd, *J* = 7.5, 5.7, 2.1 Hz, 3H), 1.60 – 1.43 (m, 4H), 1.42 – 1.25 (m, 4H), 0.97 (dd, *J* = 13.5, 4.3 Hz, 1H), 0.92 (s, 3H), 0.87 (s, 3H), 0.84 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.3, 199.3, 149.3, 118.5, 57.4, 50.5, 47.5, 47.2, 41.3, 39.0, 38.0, 34.0, 33.8, 33.4, 31.6, 31.5, 22.5, 21.5, 18.6, 17.0.

IR (neat, cm^{-1}): 3005, 2947, 2360, 2341, 1744, 1700, 1275.

HRMS (ESI): *m/z* calcd for $C_{20}H_{28}O_2$ $[M]^+$: 300.2089; Found: 300.2091.

Procedure for the preparation of compound 20, 21 and 22



1) To a solution of compound **19** (179.8 mg, 0.60 mmol) in dry DCM (30 mL) at -78 ℃ was added DIBAL-H (1.5 M in toluene, 2.00 mL, 2.99 mmol) dropwise. After stirred for 3 hours, the reaction was quenched with CH_3OH (2 ml) at -78 ℃. Then added saturated potassium sodium tartrate solution (30 mL) to the reaction system. And it was stirred for 1 hours at 0 ℃. The aqueous layer was extracted with DCM (20 mL × 1) and EtOAc (30 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:4) to afford the corresponding mixture **20**.
2) To a solution of mixture **20** in dry DCM (25 mL) was added DMAP (81.2 mg, 0.65 mmol) and then added Ac_2O (0.06 mL, 0.65 mmol) dropwise at 0 ℃. After stirred for 2 hours, the reaction was quenched with saturated $NaHCO_3$ solution (15 mL) at 0 ℃. The aqueous layer was extracted with DCM (20 mL × 1) and EtOAc (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:40) to afford the corresponding mixture **21**.
3) To a solution of $Pd(PPh_3)_2Cl_2$ (83.5 mg, 0.12 mmol) and PPh_3 (467.3 mg, 1.77 mmol) in dry THF (30 mL) at room temperature, was added Et_3N (0.57 mL, 4.13 mmol) and HCOOH (0.16 mL, 4.13 mmol), and it was stirred for 10 min. The mixture **21** in THF (5 mL) was added into the solution. After stirred 10 hours at 100 ℃, it was allowed to cool down to room temperature and added H_2O_2 (0.20 mL) stirred for another 10 min. It was added H_2O (20 mL) to dilute the reaction. The aqueous layer was extracted with EtOAc (20 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography

(EtOAc/petroleum ether = 1:20) to afford the corresponding compound **22A** and **22B** as a colourless oil (97.1 mg, 56% for 3 steps, **22A**:**22B**=3:2).

Compoud **22A**:

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.52 (t, *J* = 2.0 Hz, 1H), 4.45 (d, *J* = 2.0 Hz, 1H), 3.76 (d, *J* = 3.6 Hz, 1H), 2.54 (d, *J* = 7.3 Hz, 1H), 2.23 – 2.02 (m, 3H), 1.99 (dd, *J* = 14.7, 6.3 Hz, 1H), 1.90 (d, *J* = 7.8 Hz, 1H), 1.88 – 1.82 (m, 1H), 1.67 (ddd, *J* = 11.1, 7.3, 3.7 Hz, 2H), 1.60 – 1.48 (m, 3H), 1.49 – 1.43 (m, 1H), 1.44 – 1.36 (m, 3H), 1.31 (d, *J* = 3.9 Hz, 1H), 1.28 – 1.16 (m, 3H), 0.93 (s, 3H), 0.88 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 103.7, 85.8, 54.5, 54.0, 49.4, 41.9, 39.5, 38.9, 38.4, 38.1, 35.7, 35.2, 33.5, 31.7, 27.7, 23.5, 21.8, 20.3, 19.0.

IR (neat, cm^{-1}): 3462, 3005, 2934, 2360, 1654, 1275, 1260.

HRMS (ESI): *m/z* calcd for $C_{20}H_{33}O$ $[M+H]^+$: 289.2528; Found: 289.2526.

Compoud **22B**:

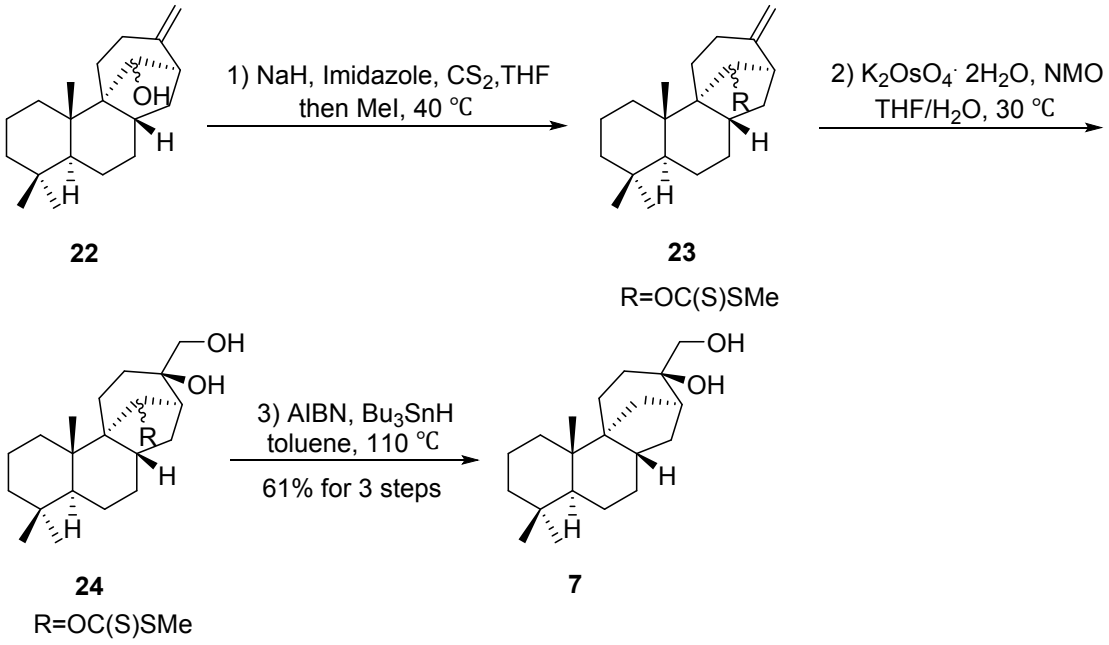
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (t, *J* = 2.2 Hz, 1H), 4.68 (t, *J* = 2.1 Hz, 1H), 4.50 – 4.45 (t, *J*=6.8 Hz , 1H), 2.69 (t, *J* = 6.8 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.08 (dd, *J* = 14.6, 6.9 Hz, 1H), 2.03 – 1.89 (m, 2H), 1.84 (dt, *J* = 12.1, 4.3 Hz, 2H), 1.75 (dt, *J* = 12.8, 6.5 Hz, 1H), 1.69 (d, *J* = 8.8 Hz, 1H), 1.54 – 1.46 (m, 2H), 1.46 – 1.40 (m, 2H), 1.41 – 1.35 (m, 2H), 1.36 – 1.33 (m, 1H), 1.32 – 1.29 (m, 1H), 1.24 (dd, *J* = 15.9, 13.0 Hz, 3H), 0.95 (s, 3H), 0.90 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 109.2, 73.2, 50.5, 50.0, 47.6, 41.8, 39.5, 37.7, 37.0, 35.5, 34.7, 34.2, 33.6, 27.8, 26.3, 23.2, 22.8, 19.5, 18.8.

IR (neat, cm^{-1}): 3554, 3005, 2941, 2360, 1652, 1276, 1261.

HRMS (ESI): *m/z* calcd for $C_{20}H_{33}O$ $[M+H]^+$: 289.2528; Found: 289.2525.

Procedure for the preparation of compound 7



1) To a suspension of NaH (60.0 mg, 1.50 mmol) in dry THF (3 mL) at room temperature, was added imidazole (2.30 mg, 0.02 mmol), followed by addition of the compound **22** (43.3 mg, 0.15 mmol) in THF (5 mL). It was stirred for 10 min. Then CS_2 (0.50 mL) was added into the solution. After stirred for 1 hour at 40 ℃, it was allowed to cool down to room temperature, and MeI (0.20 mL) was added stirred for 10 hours at 40 ℃, it was allowed to cool down to room temperature again and quenched with saturated NH_4Cl solution (10 mL) at 0 ℃. The aqueous layer was extracted with EtOAc (25 mL × 3). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (petroleum ether) to afford the corresponding mixture **23**.
2) To a solution of compound **23** in THF/H_2O (5/1 mL) at room temperature, was added NMO (0.20 mL) followed by the addition of K_2OsO_4•$2H_2O$ (12.3 mg, 0.03 mmol) with carefully. After stirred for 10 hours at 30 ℃, it was allowed to cool down to room temperature and quenched with saturated $Na_2S_2O_3$ solution (20 mL). The aqueous layer was extracted with EtOAc (20 mL × 4). The combined

organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:2) to afford the corresponding mixture **24**.

3) To a solution of compound **24** in toluene (20 mL) at room temperature was added AIBN (50.3 mg, 0.30 mmol) and Bu_3SnH (0.12 mL, 0.30 mmol) with carefully. After stirred for 5 hours at 110 ℃, it was allowed to cool down to room temperature, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1:1) to afford the corresponding compound **7** (28.5 mg, 61% for 3 steps) as a white solid.

Compound **7**:

m.p. 141.0-144.5℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 – 3.53 (dd, *J*=11.2, 2H), 2.17 – 2.05 (m, 2H), 1.93 (ddd, *J* = 13.3, 7.5, 3.2 Hz, 1H), 1.84 (ddd, *J* = 11.8, 5.9, 2.9 Hz, 1H), 1.75 (t, *J* = 8.2 Hz, 1H), 1.63 (dt, *J* = 4.8, 3.8 Hz, 1H), 1.57 (dd, *J* = 8.7, 6.5 Hz, 1H), 1.49 – 1.40 (m, 2H), 1.40 – 1.32 (m, 5H), 1.28 – 1.21 (m, 3H), 1.19 (t, *J* = 3.8 Hz, 1H), 1.18 – 1.16 (m, 1H), 1.14 – 1.07 (m, 2H), 0.94 (s, 3H), 0.87 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 74.8, 66.7, 50.4, 47.5, 42.3, 42.0, 38.4, 37.8, 36.7, 36.3, 35.5, 34.7, 33.3, 31.9, 29.0, 28.9, 22.9, 22.4, 19.2, 18.9.

IR (neat, cm^{-1}): 3281, 2928, 2866, 2360, 2341, 1449, 1357.

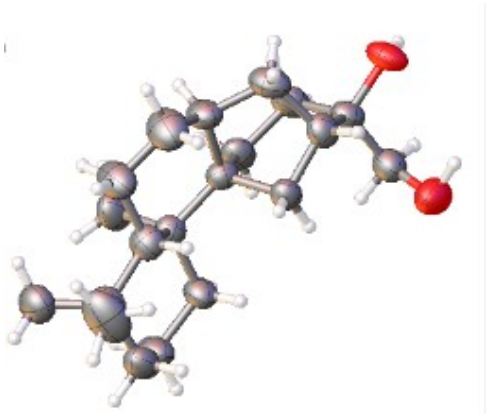
HRMS (ESI): *m/z* calcd for $C_{20}H_{34}NaO_2$ $[M+Na]^+$: 329.2453; Found: 329.2451.

References

1) S. A. Snyder, D. S. Treitler and A. P. Brucks, *J. Am. Chem. Soc.* 2010, **132**, 14303.

2) M. Tada, J. Kurabe, T. Yoshida, T. Ohkanda and Y. Matsumoto, *Chem. Pharm. Bull.* 2010, **58**, 818.

X-ray Crystal Structures of compound 7 (CCDC1900612)



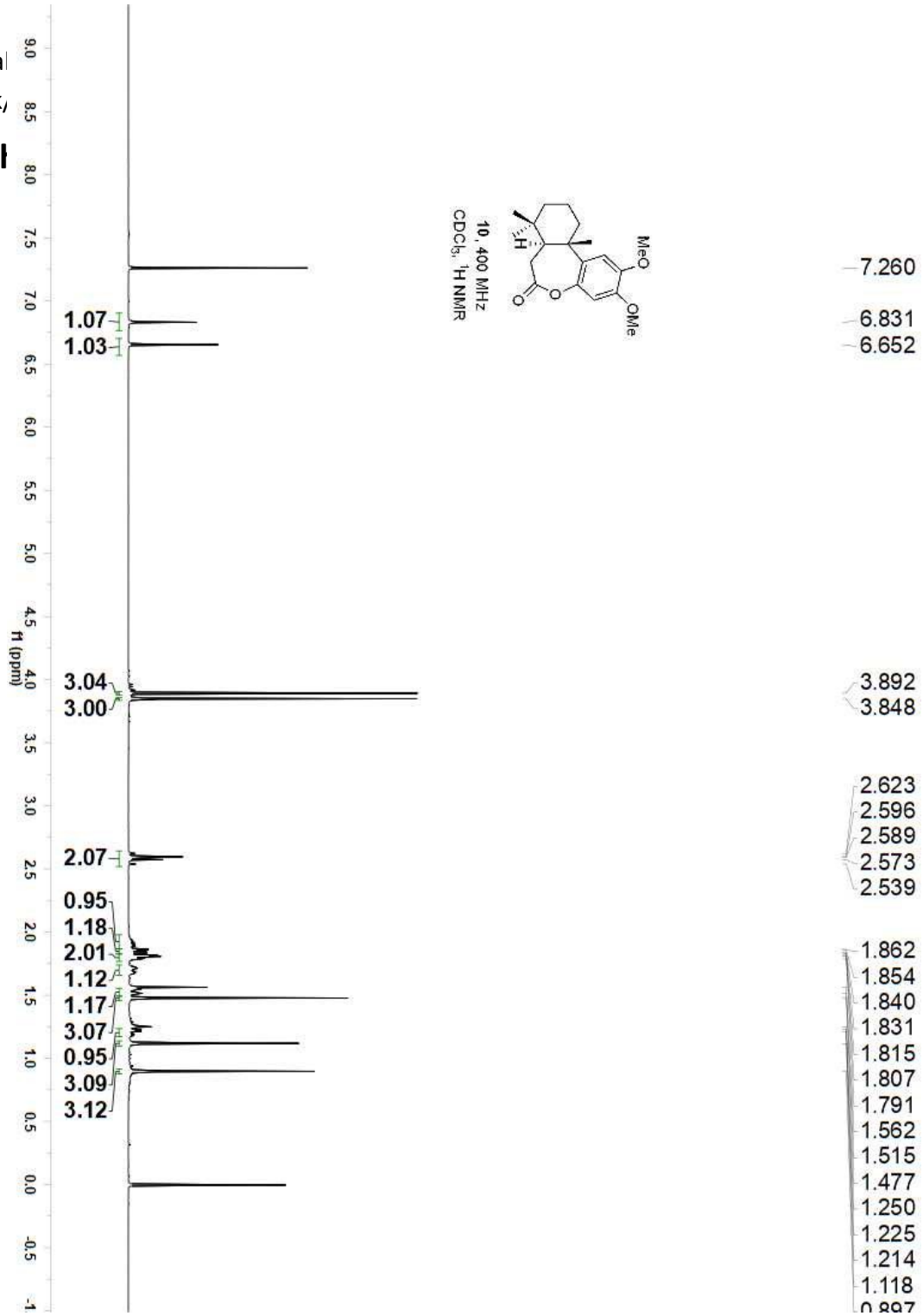
Crystal data and structure refinement for **7**.

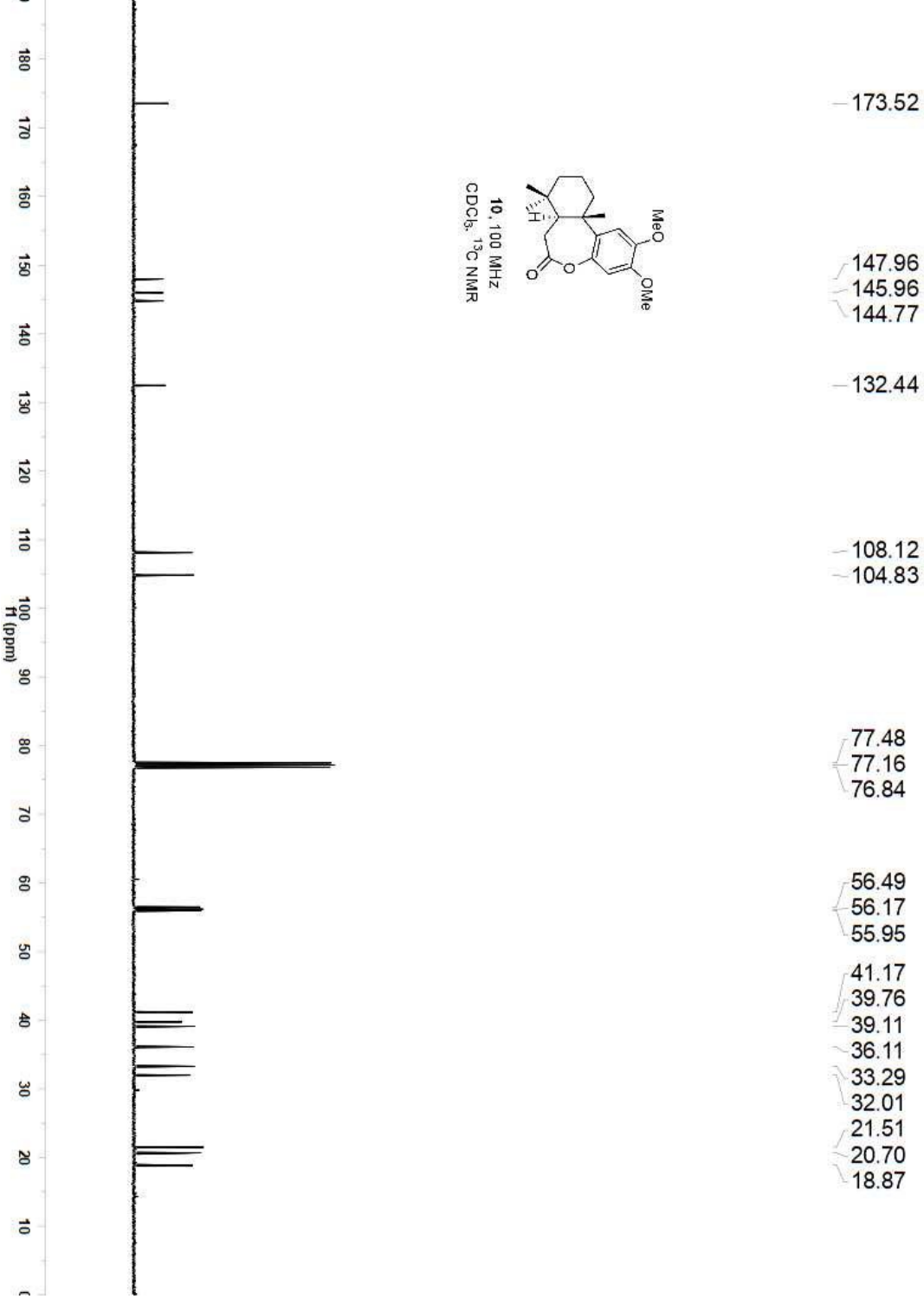
Identification code	**7**
Empirical formula	$C_{20}H_{34}O_2$
Formula weight	306.47
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	9.1145(5)
b/Å	18.1803(17)
c/Å	18.6882(17)
α/°	115.886(9)
β/°	99.779(6)
γ/°	99.493(6)
Volume/Å^3	2643.8(4)
Z	6
ρ_{calc}g/cm^3	1.155
μ/mm^{-1}	0.072
F(000)	1020.0
Crystal size/mm^3	0.35 × 0.3 × 0.25
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.916 to 52.742
Index ranges	-11 ≤ h ≤ 9, -21 ≤ k ≤ 22, -23 ≤ l ≤ 22
Reflections collected	20338
Independent reflections	10807 [R_{int} = 0.0455, R_{sigma} = 0.0967]
Data/restraints/parameters	10807/1/619
Goodness-of-fit on F^2	1.284
Final R indexes [I>=2σ (I)]	R_1 = 0.1359, wR_2 = 0.3946

Final R indexes [a

Largest diff. peak,

Spectra for t




10, 100 MHz
CDCl3, 13C NMR
MeO
OMe
O
O
H
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
173.52
147.96
145.96
144.77
132.44
108.12
104.83
77.48
77.16
76.84
56.49
56.17
55.95
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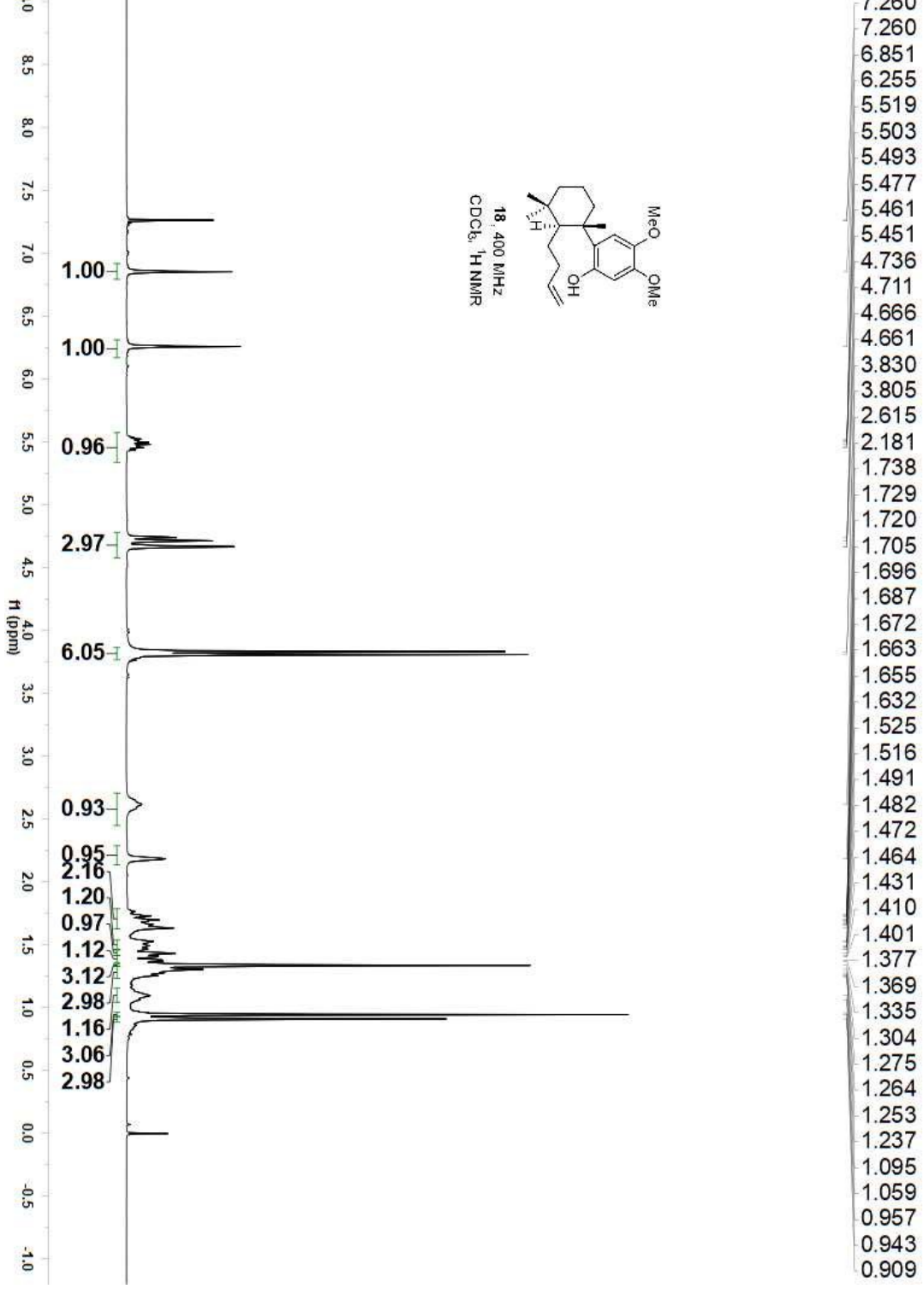
36.11
33.29
32.01
21.51
20.70
18.87


18, 400 MHz
CDCl3, 1H NMR
MeO
OMe
OH
H
f1 (ppm)
1.00
1.00
0.96
2.97
6.05
0.93
0.95
2.16
1.20
0.97
1.12
3.12
2.98
1.16
3.06
2.98
7.260
7.260
6.851
6.255
5.519
5.503
5.493
5.477
5.461
5.451
4.736
4.711
4.666
4.661
3.830
3.805
2.615
2.181
1.738
1.729
1.720
1.705
1.696
1.687
1.672
1.663
1.655
1.632
1.525
1.516
1.491
1.482
1.472
1.464
1.431
1.410
1.401
1.377
1.369
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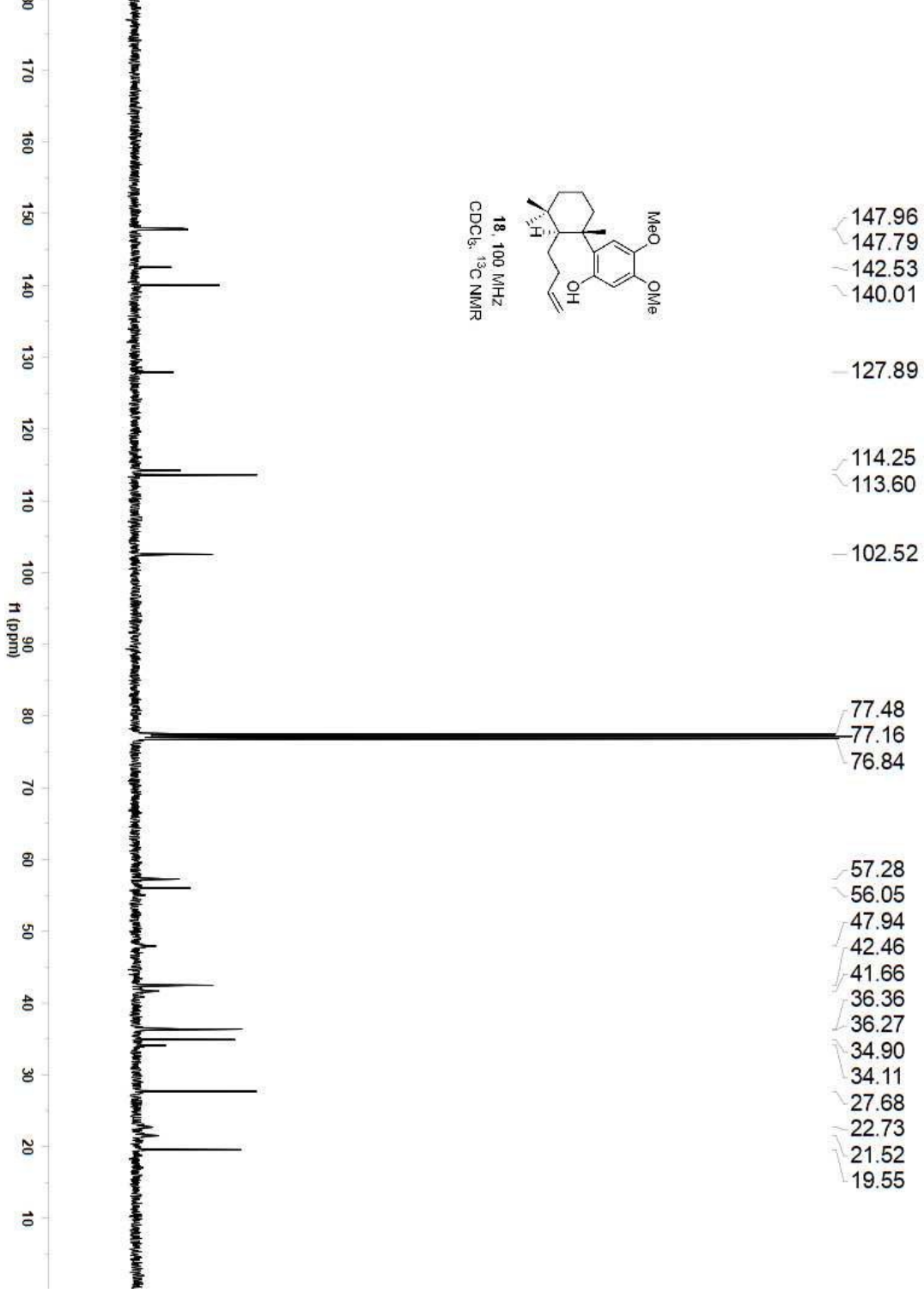
1.264
1.253
1.237
1.095
1.059
0.957
0.943
0.909


18, 100 MHz
CDCl3, 13C NMR
MeO
OMe
OH
H
f1 (ppm)
147.96
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114.25
113.60
102.52
77.48
77.16
76.84
57.28
56.05
47.94
42.46
41.66
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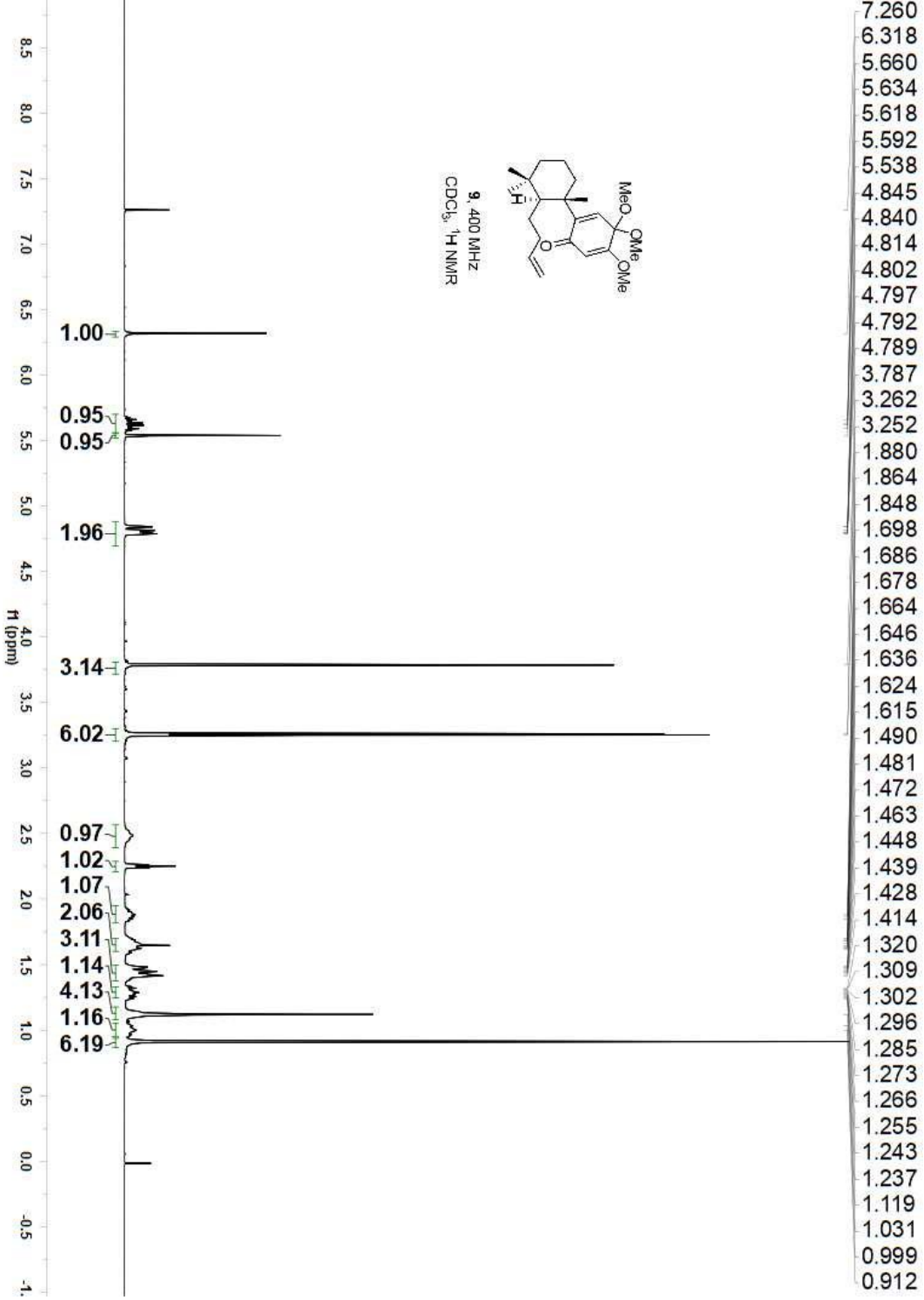
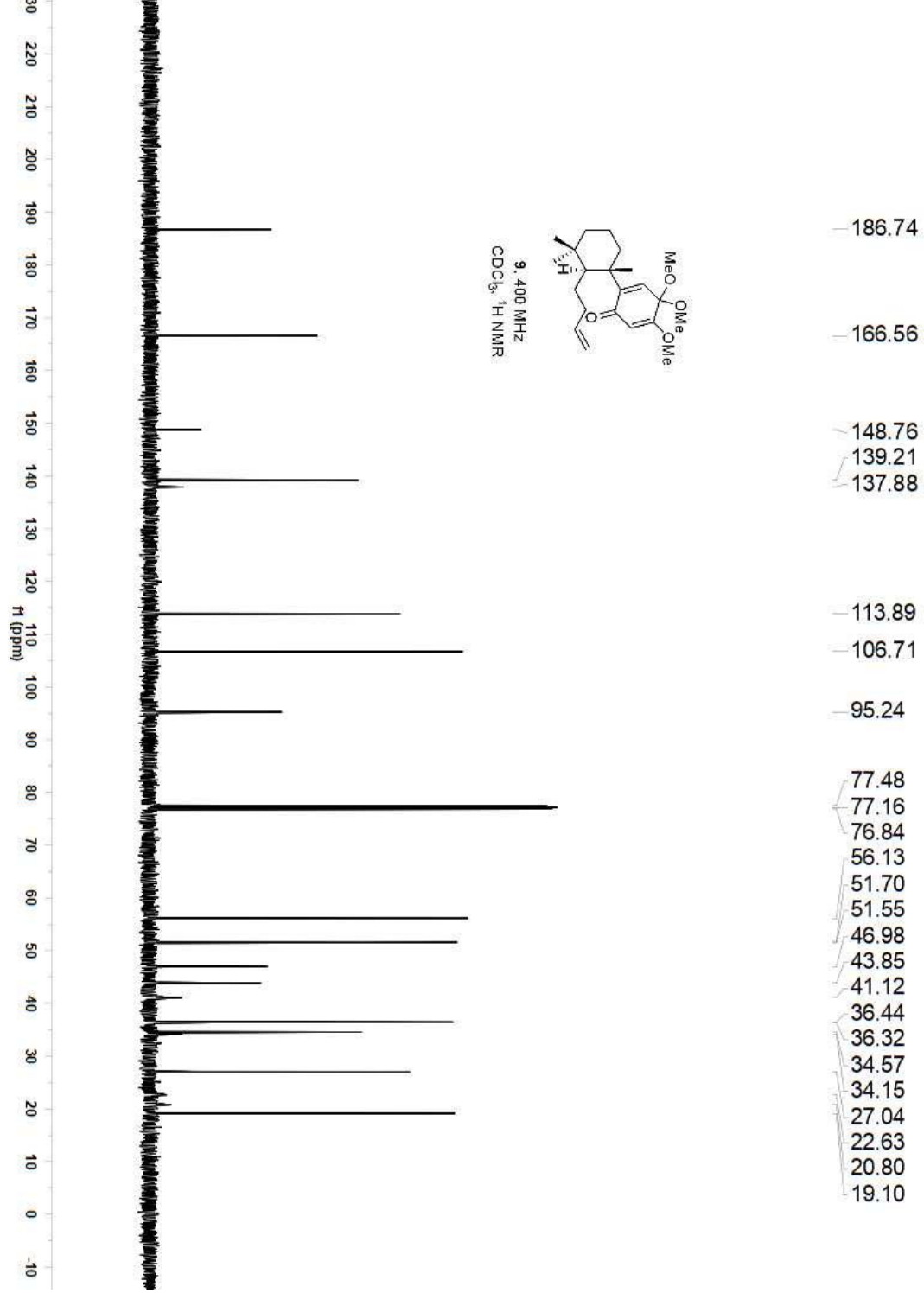
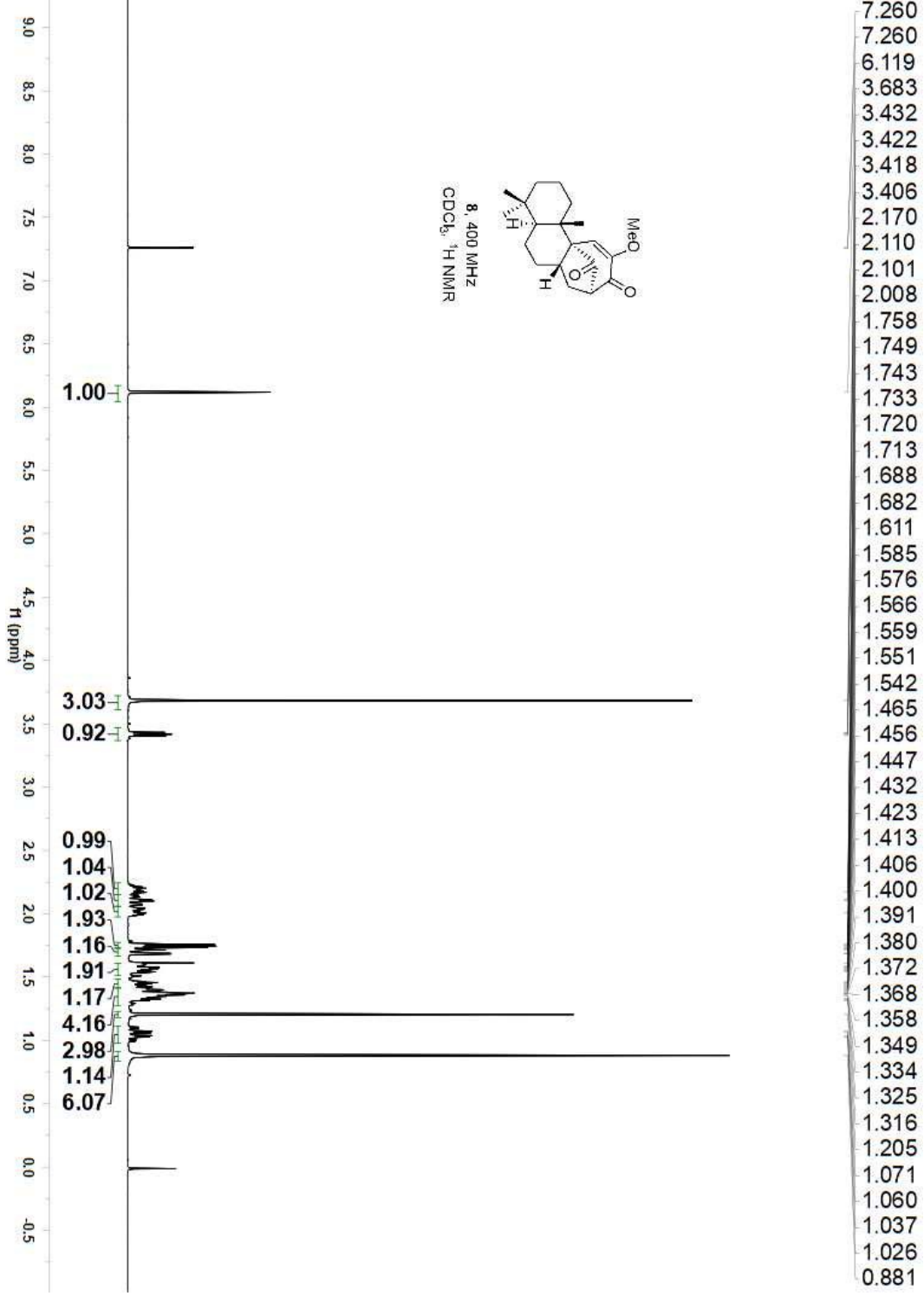
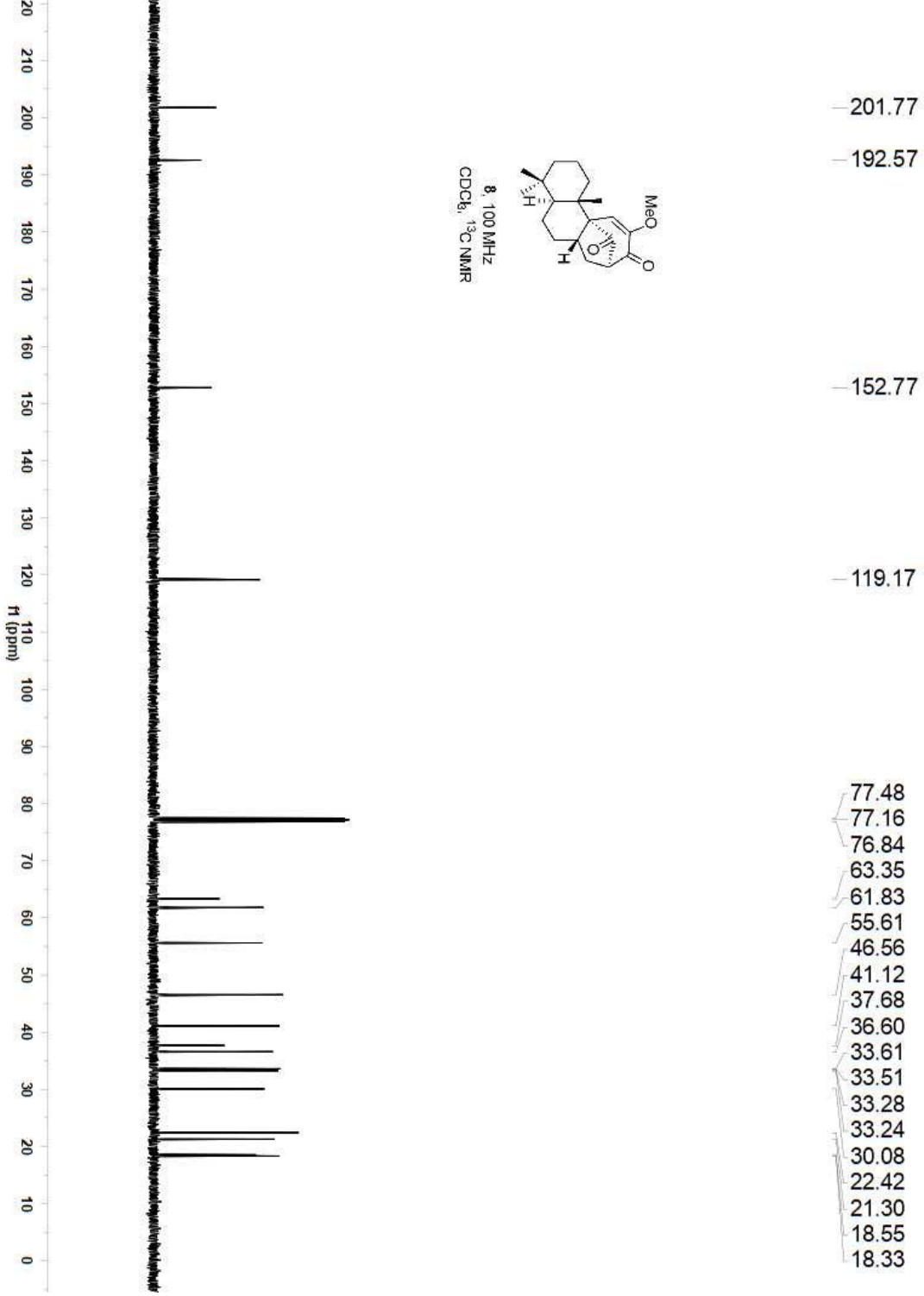
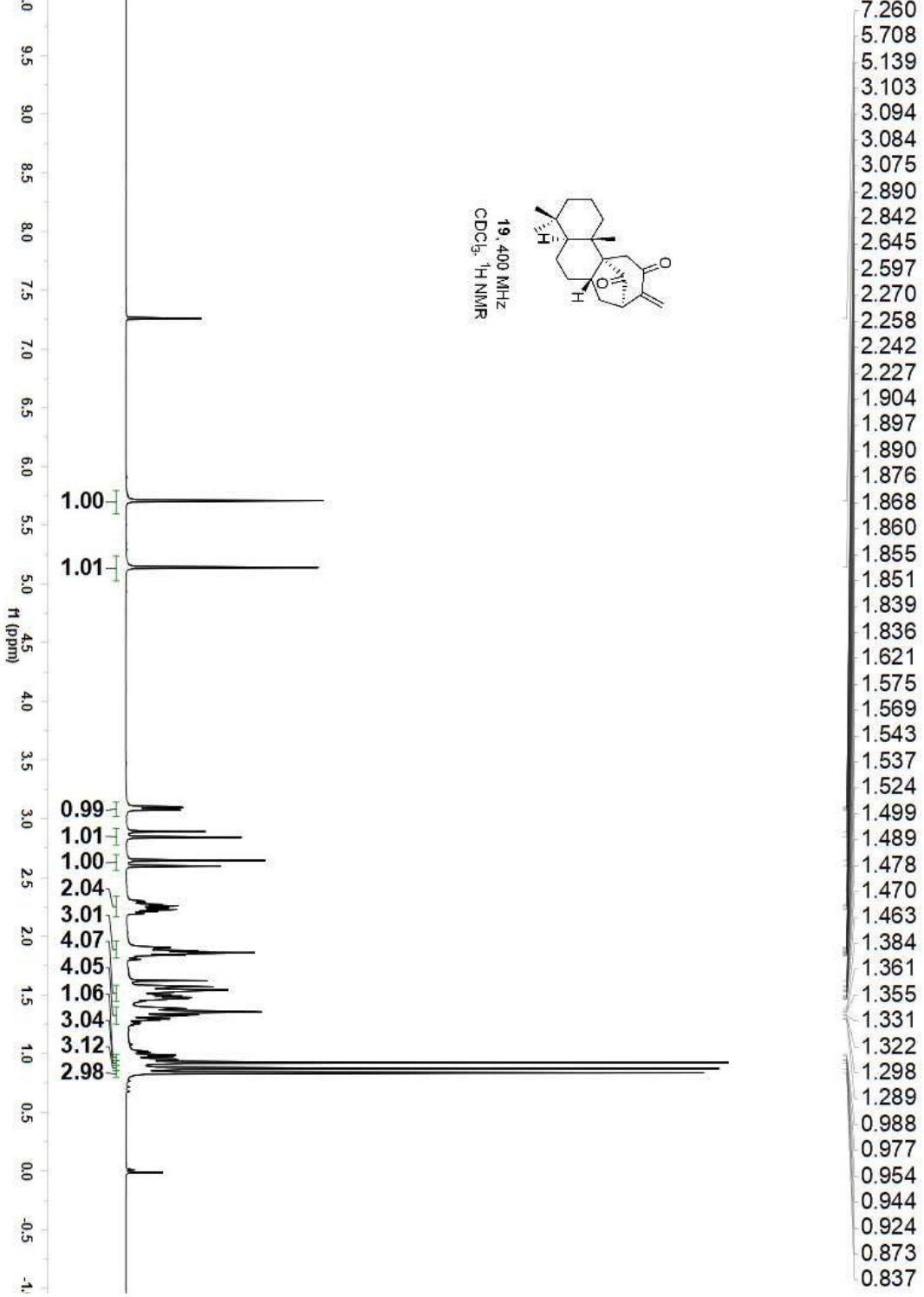
36.27
34.90
34.11
27.68
22.73
21.52
19.55

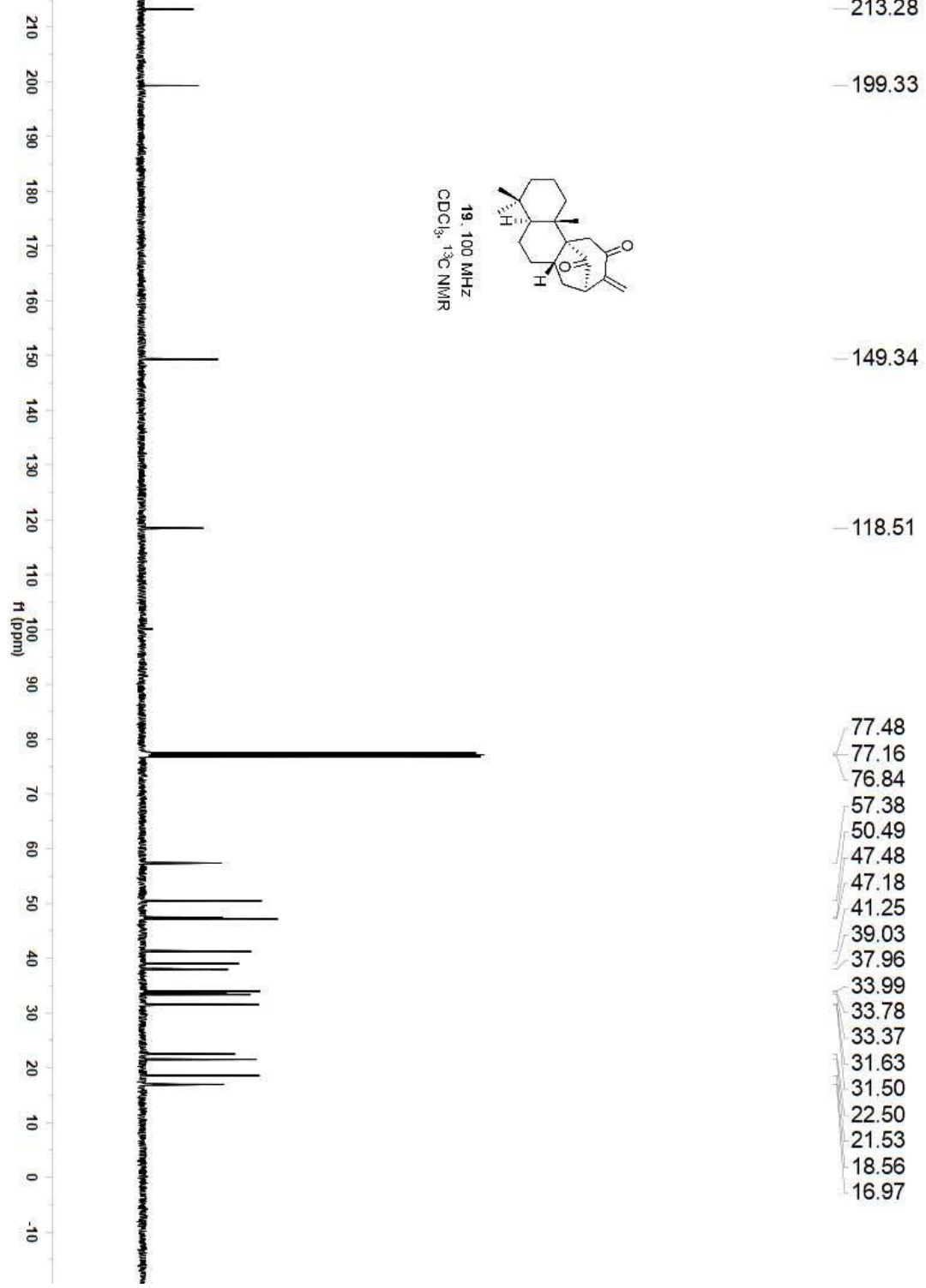

9, 400 MHz
$CDCl_3$, ^1H NMR
MeO
OMe
OMe
O
H
f1 (ppm)
1.00
0.95
0.95
1.96
3.14
6.02
0.97
1.02
1.07
2.06
3.11
1.14
4.13
1.16
6.19
7.260
6.318
5.660
5.634
5.618
5.592
5.538
4.845
4.840
4.814
4.802
4.797
4.792
4.789
3.787
3.262
3.252
1.880
1.864
1.848
1.698
1.686
1.678
1.664
1.646
1.636
1.624
1.615
1.490
1.481
1.472
1.463
1.448
1.439
1.428
1.414
1.320
1.309
1.302
1.296
1.285
1.273
1.266
1.255
1.243
1.237
1.119
1.031
0.999
0.912

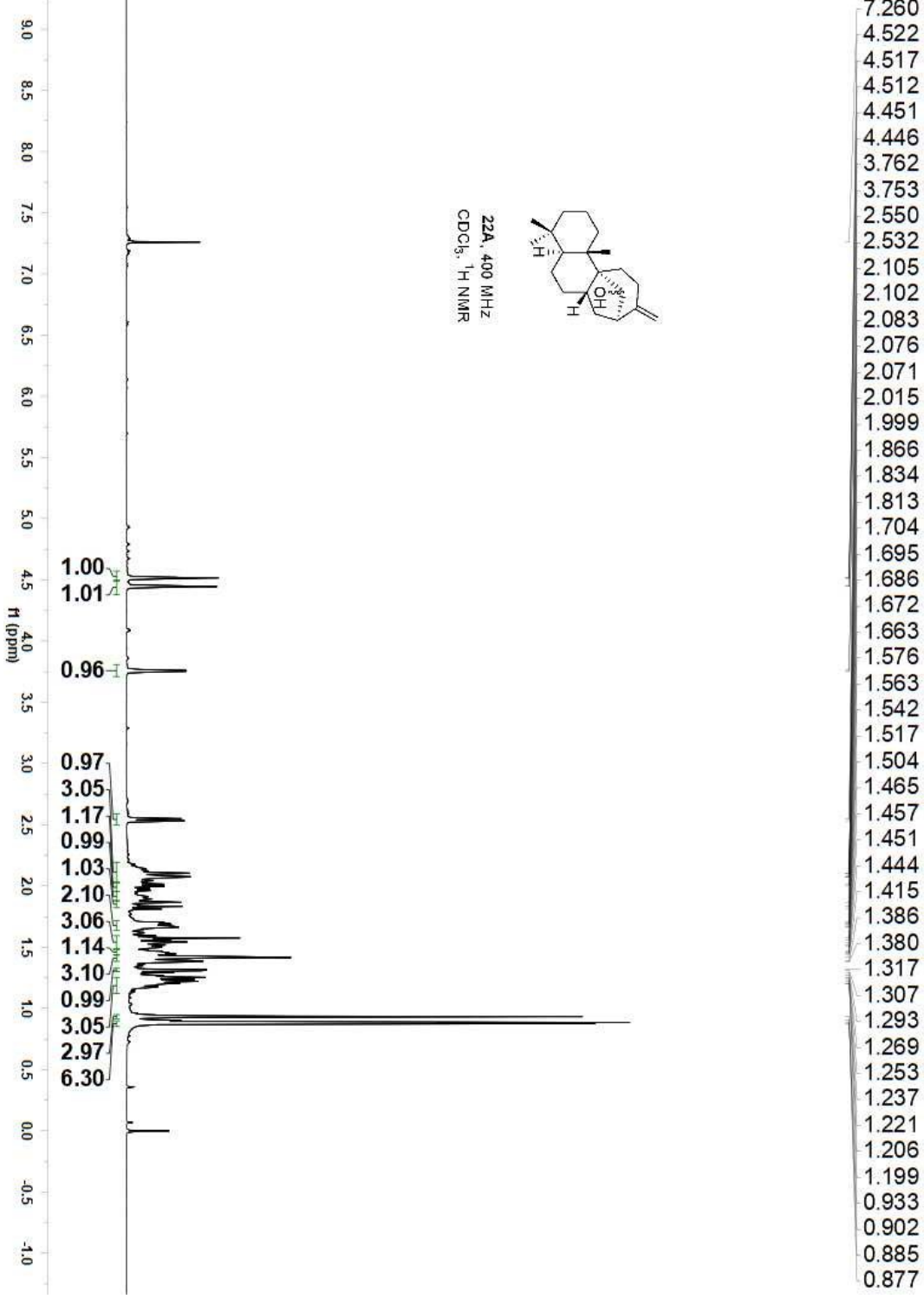

9, 400 MHz
CDCl3, 1H NMR
MeO
OMe
OMe
186.74
166.56
148.76
139.21
137.88
113.89
106.71
95.24
77.48
77.16
76.84
56.13
51.70
51.55
46.98
43.85
41.12
36.44
36.32
34.57
34.15
27.04
22.63
20.80
19.10
f1 (ppm)

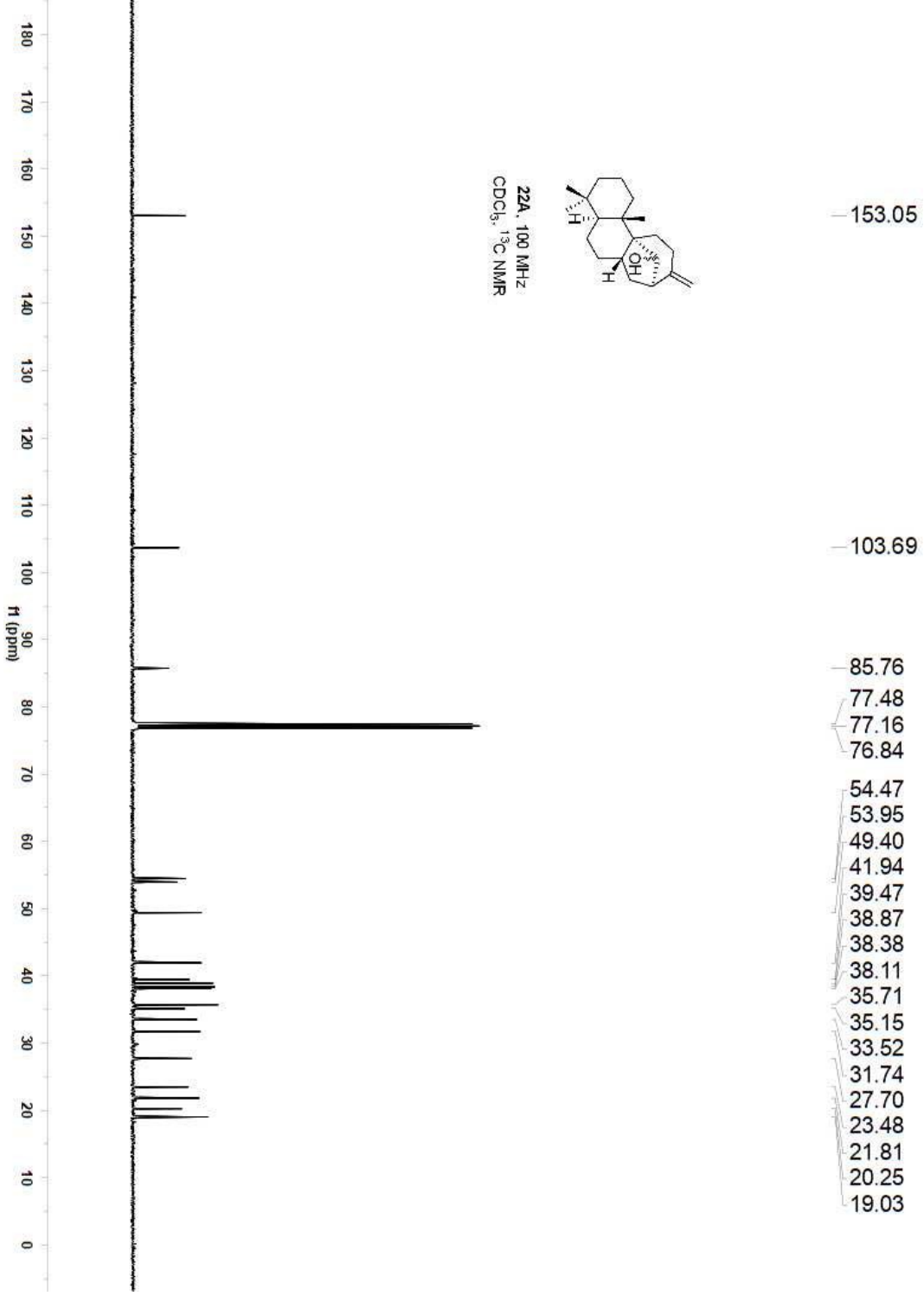

8, 400 MHz
CDCl3, 1H NMR
MeO
O
H
H
O
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
1.00
3.03
0.92
0.99
1.04
1.02
1.93
1.16
1.91
1.17
4.16
2.98
1.14
6.07
7.260
7.260
6.119
3.683
3.432
3.422
3.418
3.406
2.170
2.110
2.101
2.008
1.758
1.749
1.743
1.733
1.720
1.713
1.688
1.682
1.611
1.585
1.576
1.566
1.559
1.551
1.542
1.465
1.456
1.447
1.432
1.423
1.413
1.406
1.400
1.391
1.380
1.372
1.368
1.358
1.349
1.334
1.325
1.316
1.205
1.071
1.060
1.037
1.026
0.881

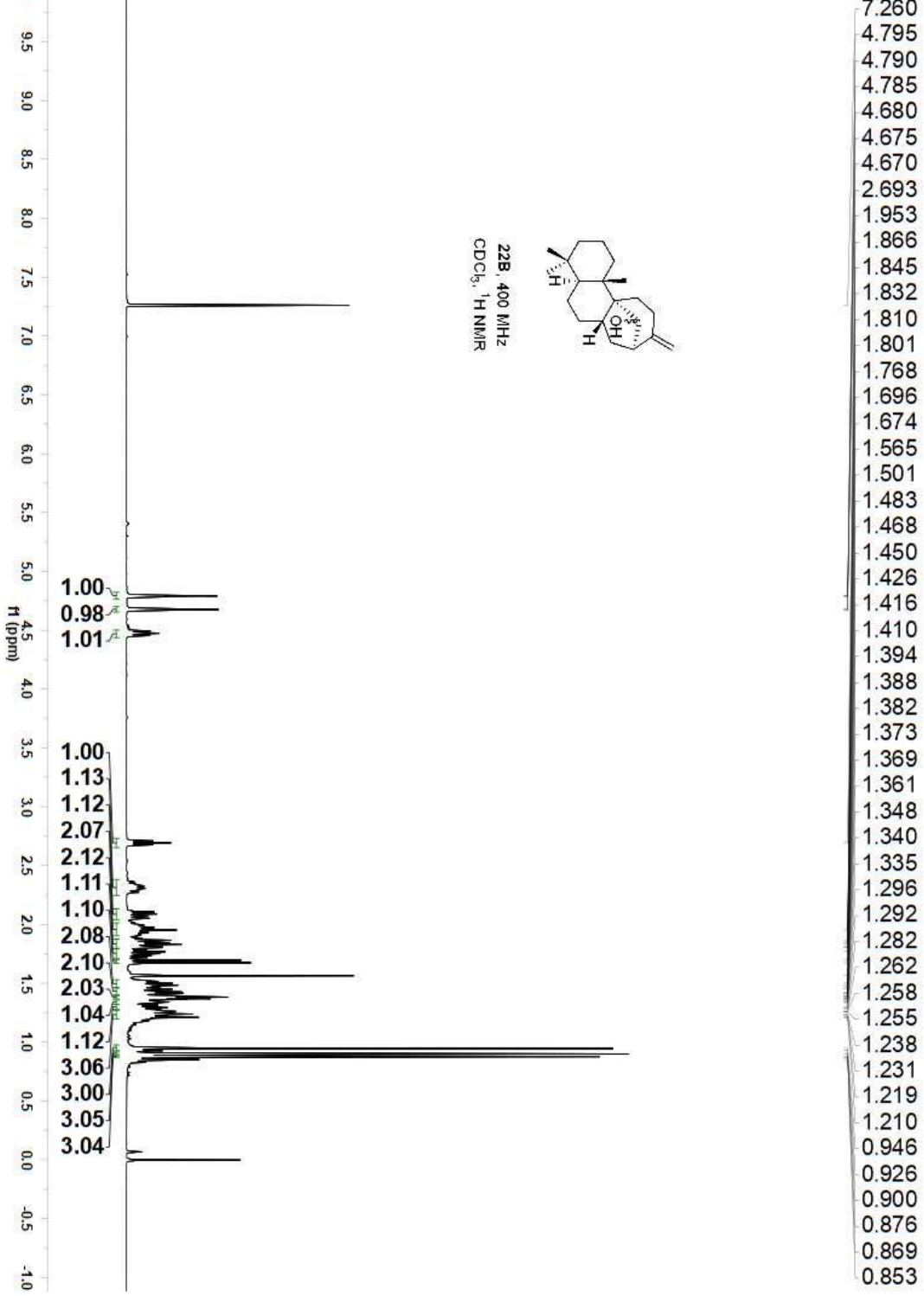

8, 100 MHz
CDCl3, 13C NMR
MeO
O
H
H
O
f1 (ppm)
201.77
192.57
152.77
119.17
77.48
77.16
76.84
63.35
61.83
55.61
46.56
41.12
37.68
36.60
33.61
33.51
33.28
33.24
30.08
22.42
21.30
18.55
18.33

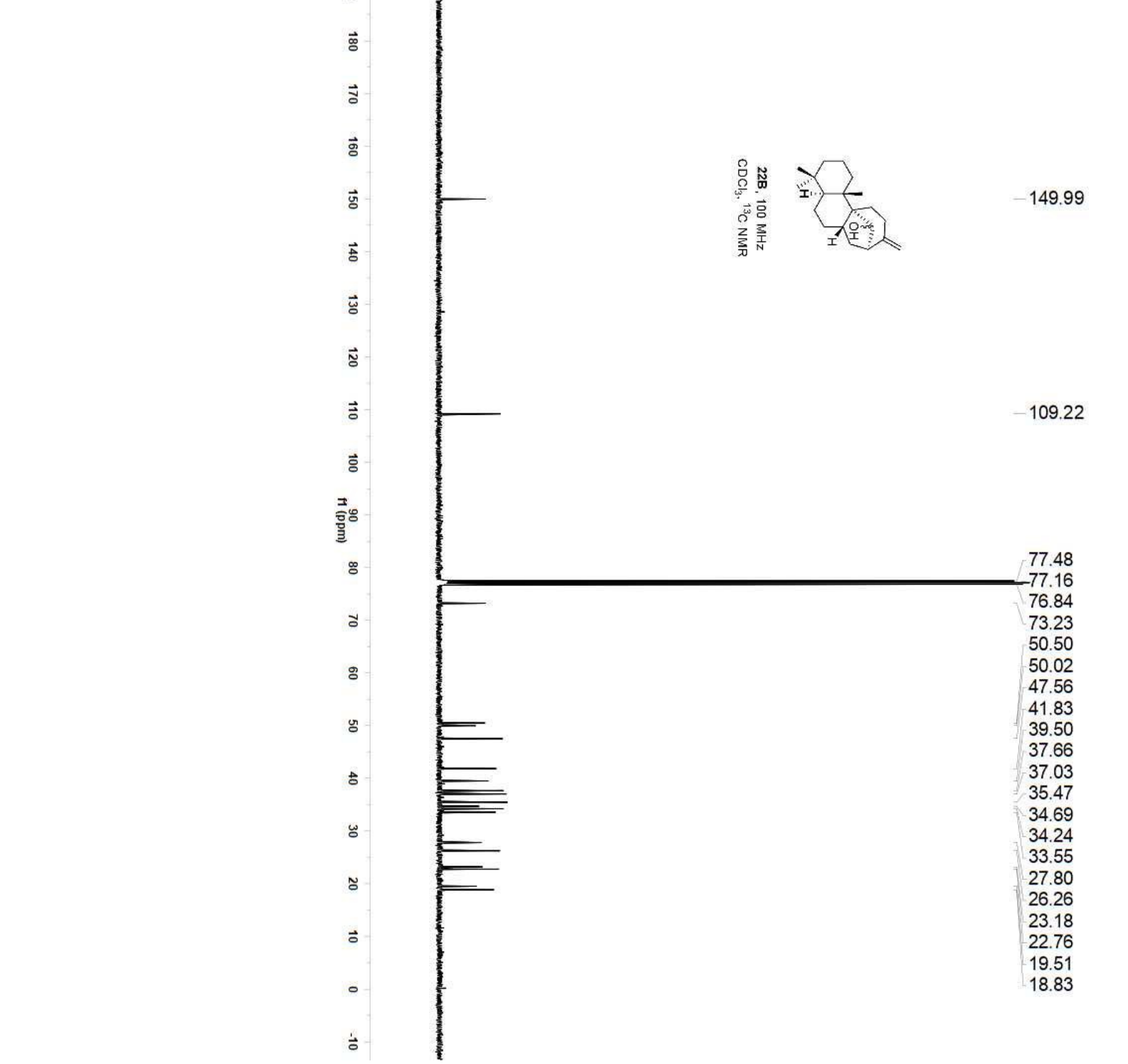

19, 400 MHz
$CDCl_3$, ^1H NMR
f1 (ppm)
1.00
1.01
0.99
1.01
1.00
2.04
3.01
4.07
4.05
1.06
3.04
3.12
2.98
7.260
5.708
5.139
3.103
3.094
3.084
3.075
2.890
2.842
2.645
2.597
2.270
2.258
2.242
2.227
1.904
1.897
1.890
1.876
1.868
1.860
1.855
1.851
1.839
1.836
1.621
1.575
1.569
1.543
1.537
1.524
1.499
1.489
1.478
1.470
1.463
1.384
1.361
1.355
1.331
1.322
1.298
1.289
0.988
0.977
0.954
0.944
0.924
0.873
0.837

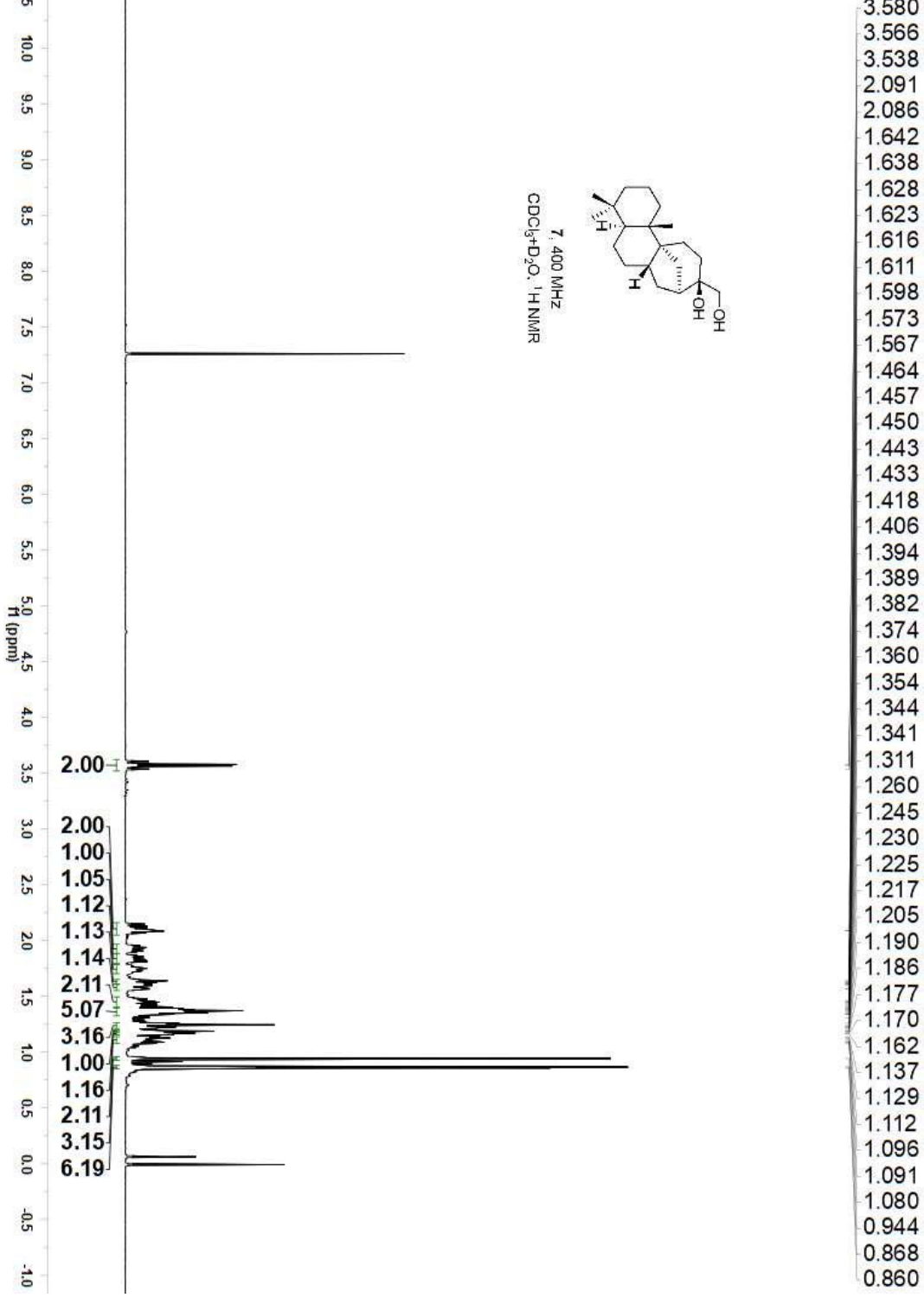

213.28
199.33
149.34
118.51
77.48
77.16
76.84
57.38
50.49
47.48
47.18
41.25
39.03
37.96
33.99
33.78
33.37
31.63
31.50
22.50
21.53
18.56
16.97
19. 100 MHz
CDCl3, 13C NMR
f1 (ppm)


22A, 400 MHz
CDCl3, 1H NMR
f1 (ppm)
1.00
1.01
0.96
0.97
3.05
1.17
0.99
1.03
2.10
3.06
1.14
3.10
0.99
3.05
2.97
6.30
7.260
4.522
4.517
4.512
4.451
4.446
3.762
3.753
2.550
2.532
2.105
2.102
2.083
2.076
2.071
2.015
1.999
1.866
1.834
1.813
1.704
1.695
1.686
1.672
1.663
1.576
1.563
1.542
1.517
1.504
1.465
1.457
1.451
1.444
1.415
1.386
1.380
1.317
1.307
1.293
1.269
1.253
1.237
1.221
1.206
1.199
0.933
0.902
0.885
0.877


22A, 100 MHz
CDCl3, 13C NMR
OH
H
H
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
153.05
103.69
85.76
77.48
77.16
76.84
54.47
53.95
49.40
41.94
39.47
38.87
38.38
38.11
35.71
35.15
33.52
31.74
27.70
23.48
21.81
20.25
19.03


22B, 400 MHz
$CDCl_3$, ^1H NMR
OH
H
H
f1 (ppm)
1.00
0.98
1.01
1.00
1.13
1.12
2.07
2.12
1.11
1.10
2.08
2.10
2.03
1.04
1.12
3.06
3.00
3.05
3.04
7.260
4.795
4.790
4.785
4.680
4.675
4.670
2.693
1.953
1.866
1.845
1.832
1.810
1.801
1.768
1.696
1.674
1.565
1.501
1.483
1.468
1.450
1.426
1.416
1.410
1.394
1.388
1.382
1.373
1.369
1.361
1.348
1.340
1.335
1.296
1.292
1.282
1.262
1.258
1.255
1.238
1.231
1.219
1.210
0.946
0.926
0.900
0.876
0.869
0.853


22B, 100 MHz
CDCl3, 13C NMR
OH
H
H
149.99
109.22
77.48
77.16
76.84
73.23
50.50
50.02
47.56
41.83
39.50
37.66
37.03
35.47
34.69
34.24
33.55
27.80
26.26
23.18
22.76
19.51
18.83
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


7, 400 MHz
$CDCl_3$+D_2O, ^1H NMR
OH
OH
f1 (ppm)
2.00
2.00
1.00
1.05
1.12
1.13
1.14
2.11
5.07
3.16
1.00
1.16
2.11
3.15
6.19
3.580
3.566
3.538
2.091
2.086
1.642
1.638
1.628
1.623
1.616
1.611
1.598
1.573
1.567
1.464
1.457
1.450
1.443
1.433
1.418
1.406
1.394
1.389
1.382
1.374
1.360
1.354
1.344
1.341
1.311
1.260
1.245
1.230
1.225
1.217
1.205
1.190
1.186
1.177
1.170
1.162
1.137
1.129
1.112
1.096
1.091
1.080
0.944
0.868
0.860

77.48
77.16
76.84
74.76
66.69
50.41
47.53
42.33
41.95
38.38
37.82
36.74
36.30
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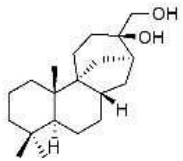
28.99
28.90
22.92
22.39
19.21
18.88



7, 100 MHz
$CDCl_3$, ^{13}C NMR