Electronic Supplementary Information

Synthesis of the 6,6,5,7-Tetracyclic Core of Daphnilongeranin B

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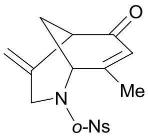
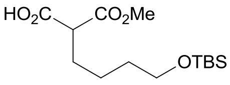
I Experimental Procedures and Spectroscopic Data of Compounds

General Procedures. All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Anhydrous acetonitrile (MeCN) and toluene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Tetrahydrofuran (THF) was distilled immediately before use from sodium-benzophenone ketyl. Methylene chloride (CH_2Cl_2), *N*,*N*-dimethylformamide (DMF), triethylamine (Et_3N), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 2,6-lutidine, and hexamethylphosphoramide (HMPA) were distilled from calcium hydride and stored under an argon atmosphere. Methanol (MeOH) was distilled form magnesium and stored under an argon atmosphere. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents for chromatography were used as supplied by Sinopharm Chemicals. Reactions were monitored by thin layer chromatography (TLC) carried out on S-2 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and aqueous ammonium cerium nitrate/ammonium molybdate or basic aqueous potassium permanganate as developing agent. E. Merck silica gel (60, particle size 0.040–0.063 mm) was used for flash column chromatography. Preparative thin layer chromatography separations were carried out on 0.25 or 0.50 mm E. Merck silica gel plates (60F-254). NMR spectra were recorded on Bruker AV-400 or Agilent 500 instrument and calibrated by using residual undeuterated chloroform (δ_H = 7.26 ppm) and $CDCl_3$ (δ_C = 77.16 ppm) as internal references. The following abbreviations are used to designate multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, quint = quintet, br = broad. IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker APEXIII 7.0 Tesla ESI-FT mass spectrometer at a 4000 V emitter voltage.



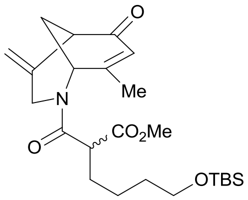
10

[3.3.1]-Bicyclic compound 10: To a stirred solution of enone sulfonamide **7** (2.36 g, 6.77 mmol) in CH_2Cl_2 (40 mL) were sequentially added 2,6-lutidine (872 mg, 0.94 mL, 8.13 mmol) and freshly prepared TBDPSOTf [1] (7.45 mL, 1.0 M in CH_2Cl_2, 7.45 mmol) at −78 °C. After stirring at that temperature for 10 min, the reaction mixture was quenched with saturated aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were sequentially washed with aq. citric acid (50 mL, 10 wt%), water (50 mL), and brine (50 mL) before they were dried over anhydrous Na_2SO_4 and filtered. The solvent was evaporated under vacuum, and the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:10) to give the silyl enol ether as a pale yellow oil. This oil was immediately dissolved in toluene (65.0 mL) and MeOH (6.5 mL). To the solution was added $[Au(PPh_3)]NTf_2$ (501 mg, 0.677 mmol) at 22 °C. The resulting mixture was stirred at that temperature for 10 min before it was directly subjected to flash column chromatography for purification using EtOAc/petroleum ether (1:5 → 1:3) as eluent to give [3.3.1]-bicyclic compound **10** (1.79 g, 5.14 mmol, 76% over the 2 steps) as a pale yellow powder. **10**: $R_f = 0.48$ (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 3093, 2915, 2849, 1677, 1633, 1542, 1439, 1370, 1164, 1126, 920, 778, 740, 608, 569 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.12–8.07 (m, 1 H), 7.77–7.71 (m, 2 H), 7.70–7.66 (m, 1 H), 6.10 (t, J = 1.2 Hz, 1 H), 5.00 (t, J = 0.8 Hz, 1 H), 4.91 (d, J = 1.7 Hz, 1 H), 4.59 (t, J = 2.95 Hz, 1 H), 4.13 (d, J = 15.5 Hz, 1 H), 3.89 (dt, J = 15.5, 1.7 Hz, 1 H), 3.18 (t, J = 2.6 Hz, 1 H), 2.31 (dt, J = 13.1, 3.1 Hz, 1 H), 2.08 (dt, J = 13.1, 3.0 Hz, 1 H), 2.05 (d, J = 1.4 Hz, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 196.48, 155.32, 147.71, 137.00, 134.10, 133.23, 132.12, 130.78, 129.37, 124.56, 114.44, 51.64, 50.11, 45.87, 32.72, 21.83 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{16}H_{16}N_2O_5SNa^+$ 371.0672, found 371.0669.



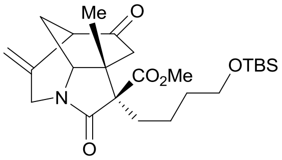
11

Carboxylic acid 11: To a stirred solution of dimethyl malonate (10.2 g, 8.82 mL, 77.2 mmol) in THF (80.0 mL) was added NaH (3.09 g, 60 wt% in mineral oil, 77.2 mmol) at 0 °C. The resulting mixture was stirred at that temperature for 10 min before iodide **12**[2] (20.2 g, 64.3 mmol) was added. The reaction mixture was warmed to 60 °C and stirred at that temperature for 4 h before it was cooled to 22 °C and quenched with aq. $NaHCO_3$ (150 mL). The resulting mixture was extracted with EtOAc (3 × 200 mL). The combined organic phases were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under vacuum, the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:5) to give the corresponding alkylated malonate as a pale yellow oil. This oil was dissolved in MeOH (50.0 mL). To the solution was added aq. LiOH (49.4 mL, 1.0 M, 49.4 mmol) at 22 °C. The reaction mixture was stirred at that temperature for 12 h before it was quenched with saturated aq. $NaHCO_3$ (100 mL) and extracted with EtOAc (3 × 200 mL). The aqueous phase was acidified with aq. HCl (1.0 M) until pH reached 3 and then extracted with EtOAc (3 × 100 mL). The combined organic phases were washed with brine (100 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was subjected to flash column chromatography using EtOAc/petroleum ether (1:2 → 2:1) as eluent to give carboxylic acid **11** (5.63 g, 27.0 mmol, 42% for the 2 steps). **11**: R_f = 0.34 (silica, EtOAc:petroleum ether 2:1); IR (film): ν_{max} = 2955, 2926, 2859, 1752, 1730, 1715, 1472, 1462, 1437, 1256, 1160, 1101, 837, 777, 665 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.74 (s, 3 H), 3.60 (t, J = 6.3 Hz, 2 H), 3.39 (t, J = 7.5 Hz, 1 H), 1.99–1.86 (m, 2 H), 1.57–1.50 (m, 2 H), 1.43–1.35 (m, 2 H), 0.87 (s, 9 H), 0.03 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.91, 169.90, 62.83, 52.73, 51.70, 32.36, 28.76, 26.05, 23.78, 18.44, −5.20 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{14}H_{28}O_5SiNa^+$ 327.1598, found 327.1593.



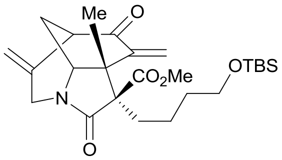
13

Bicyclic amide 13: To a stirred solution of [3.3.1]-bicyclic compound **10** (1.62 g, 4.66 mmol) in DMF (2.0 mL) were sequentially added K_2CO_3 (1.29 g, 9.32 mmol) and *p*-toluenethiol (868 mg, 6.99 mmol) at 22 ℃. After stirring at that temperature for 1.5 h, the resulting mixture was directly subjected to flash column chromatography using EtOAc/petroleum ether (1:10) and then MeOH/CH_2Cl_2 (1:100 → 1:10) as eluent to give the corresponding secondary amine as a pale yellow oil. This oil was dissolved in CH_2Cl_2 (40 mL). To the solution were sequentially added carboxylic acid **11** (1.70 g, 5.60 mmol), Et_3N (1.42 g, 1.95 mL, 14.0 mmol), HOBt (1.26 g, 9.30 mmol), and EDC•HCl (1.78 g, 9.30 mmol) at 22 ℃. The resulting mixture was stirred at that temperature for 12 h before it was quenched with saturated aq. $NaHCO_3$ (50 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were washed with brine (30 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:5 → 1:2) to give bicyclic amide **13** (1.62 g, 3.62 mmol, 78% for the 2 steps) as a white foam. **13**: R_f = 0.32 (silica, EtOAc:petroleum ether 1:2); IR (film): ν_{max} = 2952, 2935, 2857, 1747, 1681, 1651, 1435, 1273, 1230, 1183, 1100, 837, 777 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, a mixture of inconsequential diastereomers and amide C−N bond rotamers): δ = 6.19 (s, 0.03 H), 6.06 (s, 0.78 H), 6.04 (s, 0.14 H), 5.42 (s, 0.17 H), 5.38 (s, 0.62 H), 5.03 (s, 0.27 H), 5.01 (s, 0.79 H), 4.97 (s, 0.09 H), 4.95 (s, 0.17 H), 4.93 (s, 0.16 H), 4.90 (s, 0.61 H), 4.49 (s, 0.14 H), 4.31 (d, *J* = 15.0 Hz, 0.62 H,), 4.61 (d, *J* = 15.0 Hz, 0.2 H), 3.86 (d, *J* = 14.2 Hz, 0.73 H), 3.81 (s, 0.08 H), 3.75–3.65 (m, 3.12 H), 3.61–3.53 (m, 2.83 H), 3.48–3.43 (m, 0.19 H), 3.25 (s, 0.23 H,), 3.22 (s, 0.79 H), 2.39–2.33 (m, 0.26 H), 2.31–2.27 (m, 0.74 H), 2.02–1.88 (m, 6 H), 1.54–1.47 (m, 2.03 H), 1.39–1.37 (m, 2.10 H), 0.84 (s, 9 H), 0.01 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$, a mixture of inconsequential diastereomers and amide C−N bond rotamers): δ = 196.98, 196.88, 196.43, 170.33, 170.21, 167.97, 167.57, 157.12, 156.66, 154.82, 138.07, 137.93, 137.55, 129.43, 129.09, 128.63, 114.66, 114.00, 113.82, 77.48, 77.36, 77.16, 76.84, 62.81, 62.72, 52.54, 52.46, 52.09, 50.82, 50.76, 50.69, 49.86, 49.41, 49.12, 47.17, 46.95, 46.57, 46.37, 43.04, 33.94, 32.71, 32.65, 32.57, 29.76, 29.05, 28.90, 26.01, 24.08, 24.05, 22.16, 21.74, 18.38, −5.24. ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{24}H_{39}NO_5SiNa^+$ 472.2490, found 472.2498.



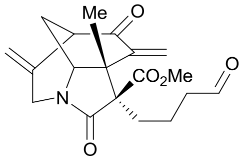
14

Tricyclic compound 14: To a stirred solution of bicyclic amide **13** (1.02 g, 2.27 mmol) in MeCN (30.0 mL) was added K_2CO_3 (1.57 g, 11.4 mmol) at 22 ℃. The resulting mixture was heated to 100 ℃ and stirred at that temperature for 3 h before it was cooled to 22 ℃ and quenched with saturated aq. $NaHCO_3$ (100 mL). After extraction with EtOAc (3 × 100 mL), the combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under vacuum, and the residue so obtained was subjected to flash column chromatography using EtOAc/petroleum ether (1:5 → 1:1) as eluent to give tricyclic compound **14** (834 mg, 1.85 mmol, 82%) as a white foam. **14**: R_f = 0.43 (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2953, 2928, 2857, 1715, 1688, 1419, 1275, 1256, 1195, 1170, 1140, 1099, 776, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 4.93 (s, 1 H), 4.90 (s, 1 H), 4.50 (d, *J* = 16.5 Hz, 1 H), 3.91 (d, *J* = 5.5 Hz, 1 H), 3.66 (s, 3 H), 3.60–3.51 (m, 2 H), 3.48 (dd, *J* = 16.6, 2.2 Hz, 1 H), 2.91 (s, 1 H), 2.54–2.51 (m, 1 H), 2.29 (dd, *J* = 14.7, 4.1 Hz, 1 H), 2.18–2.12 (m, 2 H), 1.90–1.82 (m, 1 H), 1.79–1.73 (m, 1 H), 1.56–1.41 (m, 3 H), 1.36–1.26 (m, 1 H), 1.17 (s, 3 H,), 0.82 (s, 9 H), −0.03 (s, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 207.26, 172.85, 170.43, 143.28, 112.33, 62.77, 61.33, 57.83, 52.11, 50.71, 48.35, 45.12, 40.49, 33.65, 29.94, 25.94, 23.43, 20.92, 20.90, 18.26, −5.26, −5.30 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{24}H_{39}NO_5SiNa^+$ 472.2490, found 472.2495.



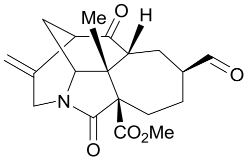
16

Tricyclic enone 16: To a stirred solution of **14** (692 mg, 1.54 mmol) in CH_2Cl_2 (15 mL) were sequentially added DBU (1.17 g, 1.08 mL, 7.70 mmol) and Eschenmoser′s salt **15** (566 mg, 3.08 mmol) at 22 °C. The resulting mixture was warmed to 55 °C and stirred that temperature for 6 h before it was cooled to 22 °C. The volatile was removed under vacuum, and the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:4 → 1:2) to give **16** (452 mg, 2.17 mmol, 64%) as a colorless oil. **16**: R_f = 0.52 (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2952, 2928, 2856, 1727, 1462, 1417, 1251, 1195, 1090, 837, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.98 (s, 1 H), 5.41 (s, 1 H), 5.09 (s, 1 H), 4.96 (s, 1 H), 4.63 (d, J = 16.5 Hz, 1 H), 3.94 (d, J = 5.5 Hz, 1 H), 3.74 (s, 3 H), 3.61–3.50 (m, 3 H), 3.00 (d, J = 2.9 Hz, 1 H), 2.19–2.08 (m, 1 H), 2.10 (dd, J = 14.2, 3.9 Hz, 1 H), 1.95–1.87 (m, 1 H), 1.66 (d, J = 6.2 Hz, 1 H), 1.52–1.33 (m, 4 H), 1.31 (s, 3 H), 0.87 (s, 9 H), 0.02 (s, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 200.60, 172.32, 170.36, 148.47, 143.81, 126.58, 112.56, 63.21, 61.03, 57.90, 54.12, 52.36, 48.09, 40.27, 33.96, 32.29, 26.11, 22.62, 21.07, 19.46, 18.46, −5.10, −5.13 ppm; HRMS (m/z): $[M + Na]^+$ calcd for $C_{25}H_{39}NO_5SiNa^+$ 484.2490, found 484.2492.



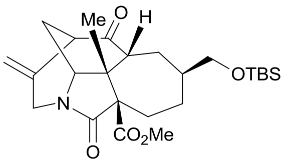
17

Tricyclic aldehyde 17: To a stirred solution of tricyclic enone **16** (427 mg, 0.915 mmol) in THF (10.0 mL) was added HF•py (2.0 mL) at 0 °C. The resulting mixture was stirred at that temperature for 10 min before it was poured to saturated aq. $NaHCO_3$ (50 mL). After extraction with EtOAc (3 × 50 mL), the combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under vacuum, and the residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:1 → 4:1) as eluent to give the corresponding primary alcohol as a white foam. This foam was dissolved in CH_2Cl_2 (20.0 mL). To the solution was added Dess–Martin periodione (582 mg, 1.37 mmol) at 22 °C. The resulting mixture was stirred at that temperature for 10 min before it was quenched with saturated aq. $NaHCO_3$ (50 mL) and extracted with EtOAc (3 × 50 mL). The combined organic phases were washed with brine (40 mL) and dried over anhydrous Na_2SO_4. After filtration and removal of the solvent under vacuum, the residue was subjected to flash column chromatography using EtOAc/petroleum ether (1:1 → 3:1) as eluent to give the tricyclic aldehyde **17** (259 mg, 0.750 mmol, 81%) as a pale yellow foam. **17**: $R_f = 0.35$ (silica, EtOAc:petroleum ether 2:1); IR (film): ν_{max} = 3518, 2970, 2952, 2920, 2836, 2730, 1730, 1694, 1420, 1286, 1241, 734, 700, 629 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 9.62 (s, 1 H), 5.88 (s, 1 H), 5.34 (s, 1 H), 5.02 (s, 1 H), 4.90 (s, 1 H), 4.54 (d, *J* = 16.5 Hz, 1 H), 3.91 (d, *J* = 5.7 Hz, 1 H), 3.70 (s, 3 H), 3.52 (dt, *J* = 16.5, 2.3 Hz, 1 H), 2.94 (d, *J* = 3.0 Hz, 1 H), 2.37–2.21 (m, 3 H), 2.15–2.10 (m, 1 H), 2.05 (dd, *J* = 14.3, 4.0 Hz, 1 H), 1.63–1.54 (m, 1 H), 1.53–1.44 (m, 1 H), 1.23 (s, 3 H), 1.20–1.16 (m, 1 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 202.50, 200.65, 171.96, 169.83, 148.23, 143.55, 126.30, 112.42, 60.62, 57.77, 54.00, 52.39, 47.87, 44.47, 40.12, 31.65, 22.40, 19.11, 17.56 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{19}H_{23}NO_5Na^+$ 368.1468, found 368.1472.



18

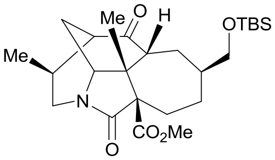
Tetracyclic aldehyde 18: To a stirred solution of tricyclic aldehyde **17** (167 mg, 0.484 mmol) in CH_2Cl_2 (10.0 mL) was added Et_3N (489 mg , 674 μL, 4.84 mmol) at 22 °C. The resulting mixture was warmed to 60 °C and stirred at that temperature for 5 h before it was cooled to 22 °C and quenched with saturated aq. $NaHCO_3$ solution (30 mL). After extraction with EtOAc (3 × 50 mL) and washing with brine (40 mL), the combined organic phases were dried over anhydrous Na_2SO_4 and filtered. The volatile was removed under vacuum, and the residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:2 → 3:1) to give the tetracyclic aldehyde **18** (54.4 mg, 0.158 mmol, 33%) and its C10 epimer (45.8 mg, 0.133 mmol, 27%) both as colorless oil. The latter compound was dissolved in *t*-BuOH (2.0 mL). To this solution was added *t*-BuOK (270 μL, 1.0 M in *t*-BuOH, 0.270 mmol) at 0 ℃. The reaction mixture was stirred at that temperature for 10 min before it was quenched with saturated aq. $NaHCO_3$ (10 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, and filtered. After removal of the solvent under vacuum, the residue was subjected to flash column chromatography using EtOAc/petroleum ether (1:1 → 3:1) as eluent to give a second portion of **18** (20.5 mg). Thus, the combined yield of **18** from **17** was 45%. **18**: $R_f = 0.32$ (silica, EtOAc:petroleum ether 2:1); IR (film): ν_{max} = 2953, 2928, 1713, 1697, 1447, 1433, 1250, 1223, 1030, 902, 739, 641cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.66 (s, 1 H), 5.06 (s, 1 H), 4.99 (s, 1 H), 4.65 (d, *J* = 16.5 Hz, 1 H), 4.08 (d, *J* = 5.8 Hz, 1 H), 3.70 (s, 3 H), 3.61 (dt, *J* = 16.5, 2.4 Hz, 1 H), 3.41–3.36 (m, 1 H), 2.96 (d, *J* = 3.8 Hz, 1 H), 2.73 (d, *J* = 4.7 Hz, 1 H), 2.37 (dd, *J* = 14.8, 4.2 Hz, 1 H), 2.24–2.20 (m, 1 H), 2.16–2.02 (m, 3 H), 1.97–1.92 (m, 1 H), 1.70–1.63 (m, 1 H), 1.44–1.36 (m, 1 H), 1.27 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.41, 204.66, 171.44, 171.01, 143.18, 112.70, 64.54, 58.98, 53.46, 53.24, 52.65, 48.64, 46.74, 40.68, 23.96, 22.45, 21.97, 20.26, 19.18 ppm; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_{19}H_{23}NO_5Na^+$ 368.1468, found 368.1476.



20

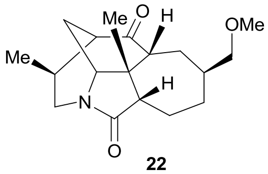
TBS ether 20: To a stirred solution of tetracyclic aldehyde **18** (42.6 mg, 0.123 mmol) in CH_2Cl_2 (2.0 mL) was added LiAlH(O*t*-Bu)$_3$ (185 μL, 1.0 M in THF, 0.185 mmol) at −40 °C. The resulting mixture was stirred at that temperature for 15 min before it was quenched with saturated aq. $NaHCO_3$ (20 mL). After extraction with EtOAc (3 × 10 mL), the combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under vacuum, and the residue so obtained was purified by flash column chromatography with EtOAc/petroleum ether (1:1 →

4:1) to give the corresponding primary alcohol as a colorless oil. This oil was dissolved in CH_2Cl_2 (2.0 mL). To the solution were sequentially added Et_3N (62 mg, 86 μL, 0.62 mmol) and TBSOTf (65 mg, 56 μL, 0.25 mmol) at −78 °C. The resulting mixture was allowed to stir at that temperature for 5 min before it was quenched with saturated aq. $NaHCO_3$ (20 mL). The mixture so obtained was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were dried over anhydrous Na_2SO_4 and filtered. After removal of the volatile under vacuum, the residue was subjected to flash column chromatography using EtOAc/petroleum ether (1:3 → 1:1) as eluent to give TBS ether **20** (38.6 mg, 0.0837 mmol, 67% for the 2 steps) as a pale yellow oil. **20**: $R_f = 0.34$ (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2952, 2928, 2855, 1739, 1715, 1694, 1431, 1253, 1224, 1091, 836, 776, 669, 647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 5.04 (s, 1 H), 4.96 (s, 1 H), 4.64 (d, *J* = 16.5 Hz, 1 H), 4.05 (d, *J* = 5.7 Hz, 1 H), 3.70 (s, 3 H), 3.59 (d, *J* = 16.5 Hz, 1 H), 3.42 (d, *J* = 6.4 Hz, 2 H), 2.93 (d, *J* = 3.3 Hz, 1 H), 2.68–2.59 (m, 2 H), 2.33 (dd, *J* = 14.7, 4.1 Hz, 1 H), 2.19 (dd, *J* = 14.6, 5.7 Hz, 1 H), 2.08–1.96 (m, 2 H), 1.93–1.86 (m, 1 H), 1.65–1.59 (m, 1 H), 1.47–1.40 (m, 1 H), 1.24 (s, 3 H), 1.18–1.11 (m, 1 H), 0.88 (s, 9 H), 0.03 (s, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.00, 171.93, 171.66, 143.40, 112.37, 67.57, 64.65, 59.02, 54.00, 52.94, 52.47, 48.74, 40.68, 34.48, 26.05, 23.75, 23.37, 22.82, 22.45, 22.19, 18.37, −5.24, −5.25 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{25}H_{40}NO_5Si^+$ 462.2670, found 462.2670.



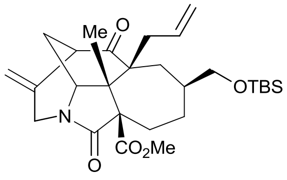
21

Hydrogenated compound 21: To a stirred solution of **20** (18.3 mg, 0.0397 mmol) in CH_2Cl_2 (2.0 mL) was added Crabtree′s catalyst (6.4 mg, 0.0079 mmol) at 22 °C. The resulting mixture was stirred at that temperature under a hydrogen atmosphere (balloon pressure) for 20 min. After removal of the solvent under vacuum, the residue was purified by flash column chromatography with EtOAc/petroleum ether (1:1 → 3:1) to give the hydrogenated compound **21** (15.1 mg, 0.0326 mmol, 82%) as a pale yellow oil. **21**: $R_f = 0.35$ (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2951, 2928, 2855, 1735, 1708, 1694, 1459, 1433, 1291, 1252, 1225, 1207, 1126, 1104, 1091, 913, 837, 775, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.11 (dd, *J* = 8.8, 13.6 Hz, 1 H), 3.95 (d, *J* = 4.9 Hz, 1 H), 3.68 (s, 3 H), 3.44–3.39 (m, 2 H), 2.86–2.76 (m, 1 H), 2.72–2.63 (m, 1 H), 2.60 (dd, *J* = 1.6, 6.1 Hz, 1 H), 2.37 (dd, *J* = 9.8, 13.6 Hz, 1 H), 2.14–1.95 (m, 5 H), 1.91–1.84 (m, 1 H), 1.68–1.59 (m, 1 H), 1.43–1.36 (m, 1 H), 1.29–1.26 (m, 4 H), 1.04 (d, *J* = 6.93, 3 H), 0.89 (s, 9 H), 0.04 (s, 6 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 214.09, 171.76, 171.21, 67.60, 64.65, 60.12, 54.51, 52.85, 52.40, 46.85, 41.05, 36.88, 34.87, 26.06, 23.75, 23.52, 22.93, 22.10, 19.03, 18.39, 18.38, −5.24 ppm; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_{25}H_{41}NO_5SiNa^+$ 486.2646, found 486.2650.



22

Decarboxylated compound 22: To a stirred solution of **21** (10.6 mg, 0.0229 mmol) in THF (2.0 mL) was added HF•py (500 *μ*L) at 0 ℃. The resulting mixture was stirred at that temperature for 5 min before it was poured to saturated aq. $NaHCO_3$ (10 mL). After extraction with EtOAc (3 × 5 mL), the combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under vacuum, and the residue so obtained was dissolved in CH_2Cl_2 (2.0 mL). To this solution were sequentially added 2,6-di-*tert*-butylpyridine (85.2 mg, 100 *μ*L, 0.445 mmol) and MeOTf (36.3 mg, 25.0 *μ*L, 0.220 mmol) at 0 ℃. The reaction mixture was warmed to 22 ℃ and stirred at that temperature for 20 min before it was quenched with saturated aq. $NaHCO_3$ (5 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 5 mL), and the combined organic phases were washed with brine (5.0 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent under vacuum, the residue was purified by flash column chromatography with EtOAc/petroleum ether (3:1 → 8:1) as eluent to give the corresponding methyl ether as a colorless oil. This oil was dissolved in DMSO (2.0 mL), and LiCl•H_2O (27.5 mg, 0.458 mmol) was added at 22 ℃. The resulting mixture was heated to 170 ℃ and stirred at that temperature for 5 h before it was cooled to 22 ℃ and quenched with saturated aq. $NaHCO_3$ (5 mL). After extraction with CH_2Cl_2 (3 × 5 mL), the combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated under vacuum, and the residue so obtained was subjected to flash column chromatography using EtOAc/petroleum ether (2:1 → 6:1) as eluent to give **22** (2.9 mg, 0.0092 mmol, 42%) as a pale yellow oil. 22: R_f = 0.24 (silica, EtOAc:petroleum ether 8:1); IR (film): ν_{max} = 2953, 2923, 2870, 1704, 1689, 1457, 1430, 1384, 1290, 1116, 1084, 1054, 950, 890, 736, 668, 641 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 4.06 (dd, *J* = 13.6, 8.9 Hz, 1 H), 3.63 (t, *J* = 3.0 Hz, 1 H), 3.33 (s, 3 H), 3.26–3.17 (m, 2 H), 2.87–2.79 (m, 1 H), 2.57–2.52 (m, 1 H), 2.47 (dd, *J* = 5.5, 2.2 Hz, 1 H), 2.39–2.37 (m, 1 H), 2.27–2.21 (m, 1 H), 2.08–2.06 (m, 2 H), 1.98–1.87 (m, 3 H), 1.62–1.48(m, 3 H), 1.38–1.31 (m, 1 H), 1.33 (s, 3 H), 1.02 (d, *J* = 7.0 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.40, 174.16, 78.46, 61.35, 58.77, 53.29, 52.00, 50.56, 46.72, 40.53, 37.38, 32.21, 24.65, 24.49, 24.30, 18.95, 18.49, 18.36 ppm; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{18}H_{27}NO_3Na^+$ 328.1883, found 328.1887.



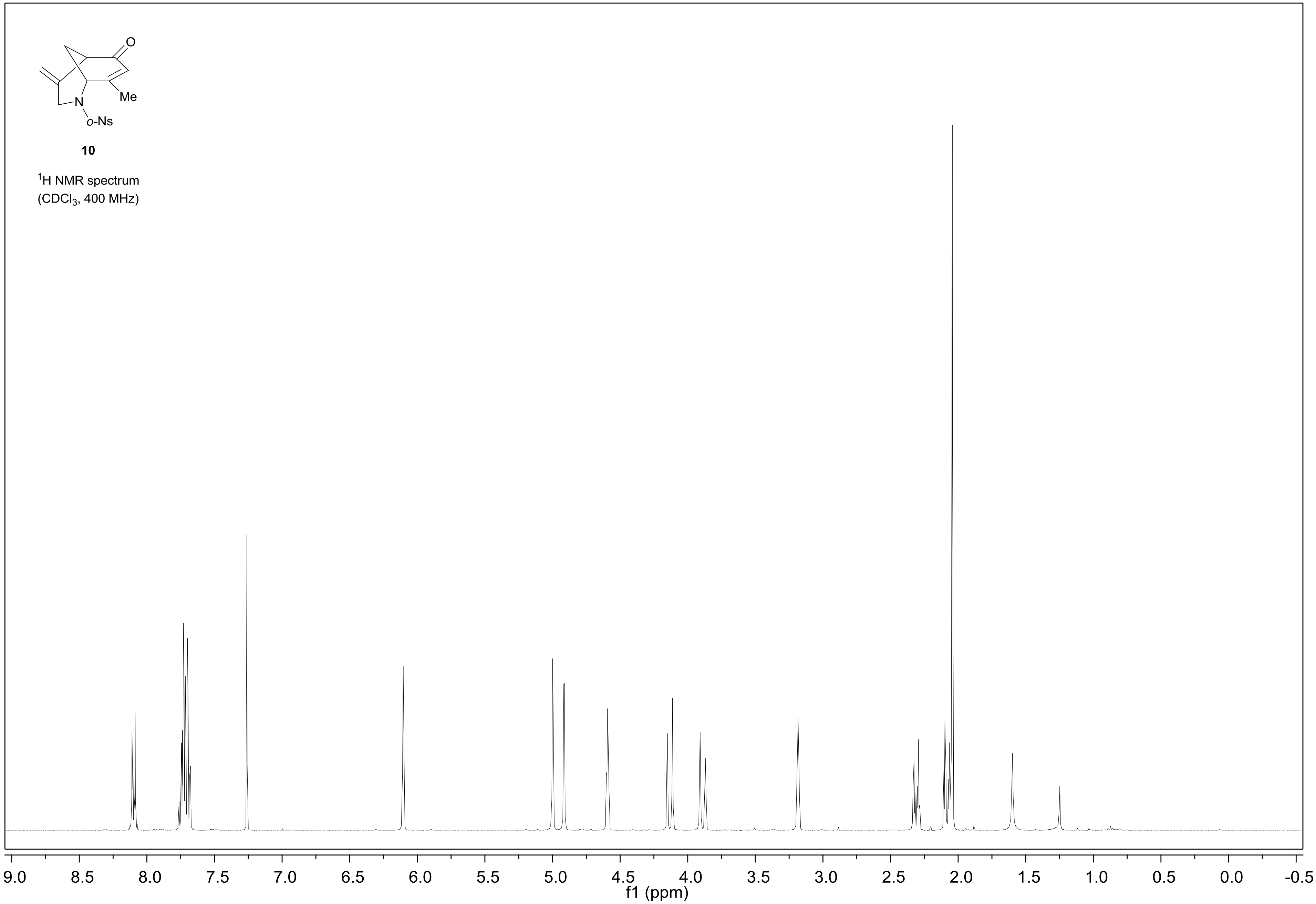
23

***C*-allylated tetracyclic compound 23:** To a stirred solution of TBS ether **20** (21.7 mg, 0.0470 mmol) and allyl iodide (23.6 mg, 12.8 μL, 0.141 mmol) in THF/HMPA (1.65 mL, 10:1) was added KHMDS (190 μL, 0.5 M in toluene, 0.0950 mmol) at −78 ℃. The reaction mixture was warmed to 0 ℃ and stirred at that temperature for 10 min before it was quenched with saturated aq. $NaHCO_3$ (10 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic phases were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent under vacuum, the residue was dissolved in mesitylene (2.5 mL). The resulting solution was heated to 170 ℃ and allowed to stir at that temperature for 4 h before it was cooled to 22 ℃. The solvent was evaporated under vacuum, and the residue so obtained was subjected to flash column chromatography using EtOAc/petroleum ether (1:4 → 1:1) as eluent to give *C*-allylated tetracyclic compound **23** (15.1 mg, 0.0301 mmol, 64% for the 2 steps) as a pale yellow oil. **23**: R_f = 0.43 (silica, EtOAc:petroleum ether 1:1); IR (film): ν_{max} = 2961, 2926, 2852, 1727, 1706, 1697, 1453, 1432, 1412, 1261, 1098, 1027, 801, 680, 668 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ = 5.55–5.47 (m, 1 H), 5.08 (d, *J* = 9.5 Hz, 1 H), 5.06 (d, *J* = 17.0, 1 H), 5.01 (s, 1 H), 4.91 (s, 1 H), 4.63 (d, *J* = 16.7 Hz, 1 H), 3.90 (d, *J* = 5.8 Hz, 1 H), 3.70 (s, 3 H), 3.59 (d, *J* = 16.7 Hz, 1 H), 3.48–3.41(m, 2 H), 2.81 (d, *J* = 4.3 Hz, 1 H), 2.72 (d, *J* = 5.4 Hz, 1 H), 2.69 (d, *J* = 5.4 Hz, 1 H), 2.21–1.98 (m, 5 H), 1.82 (dd, *J* = 15.1, 2.7 Hz, 1 H), 1.58–1.45 (m, 2 H), 1.34 (dd, *J* = 15.2, 10.2 Hz, 1 H), 1.22 (s, 3 H), 0.86 (d, *J* = 1.0 Hz, 9 H), 0.01 (s, 3 H), 0.01 (s, 3 H) ppm; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 208.65, 172.60, 171.69, 144.82, 133.74, 119.16, 111.58, 68.14, 66.86, 59.44, 58.52, 55.48, 52.61, 48.58, 44.19, 40.28, 33.91, 33.30, 26.08, 24.59, 23.68, 22.47, 18.41, 16.87, −5.21, −5.25 ppm; HRMS (*m/z*): $[M + H]^+$ calcd for $C_{28}H_{44}NO_5Si^+$ 502.2983, found 502.2984.

II References

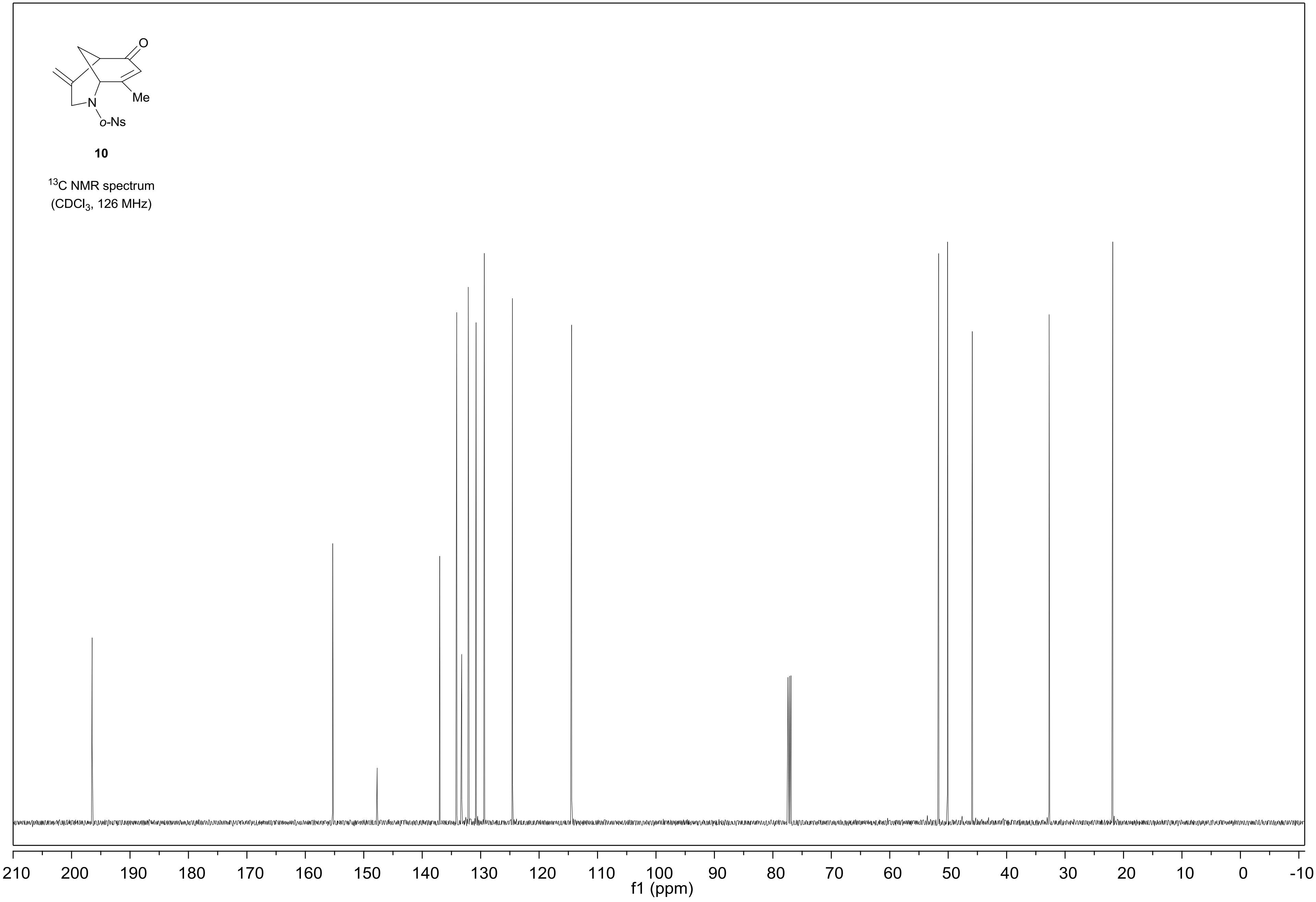
1. M. Uyanik, K. Ishihara, H. Yamamoto, *Org. Lett.*, 2006, **8**, 5649.
2. J.-E. Nystroem, T. D. McCanna, P. Helquist, R. Amouroux, *Synthesis*, 1988, 56.

III ^{1}H and ^{13}C NMR Spectra of Compounds



10

^{1}H NMR spectrum
($CDCl_3$, 400 MHz)

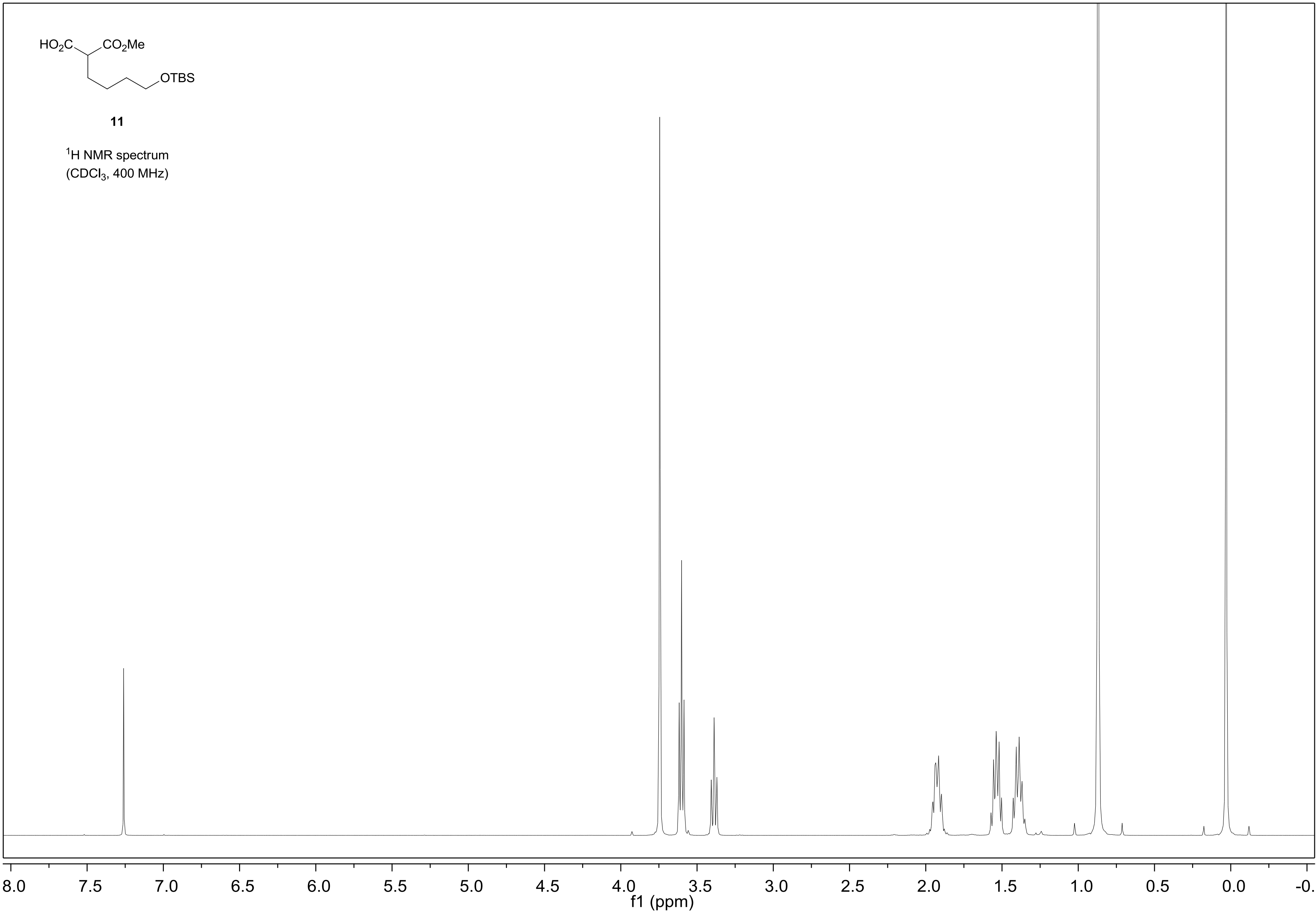


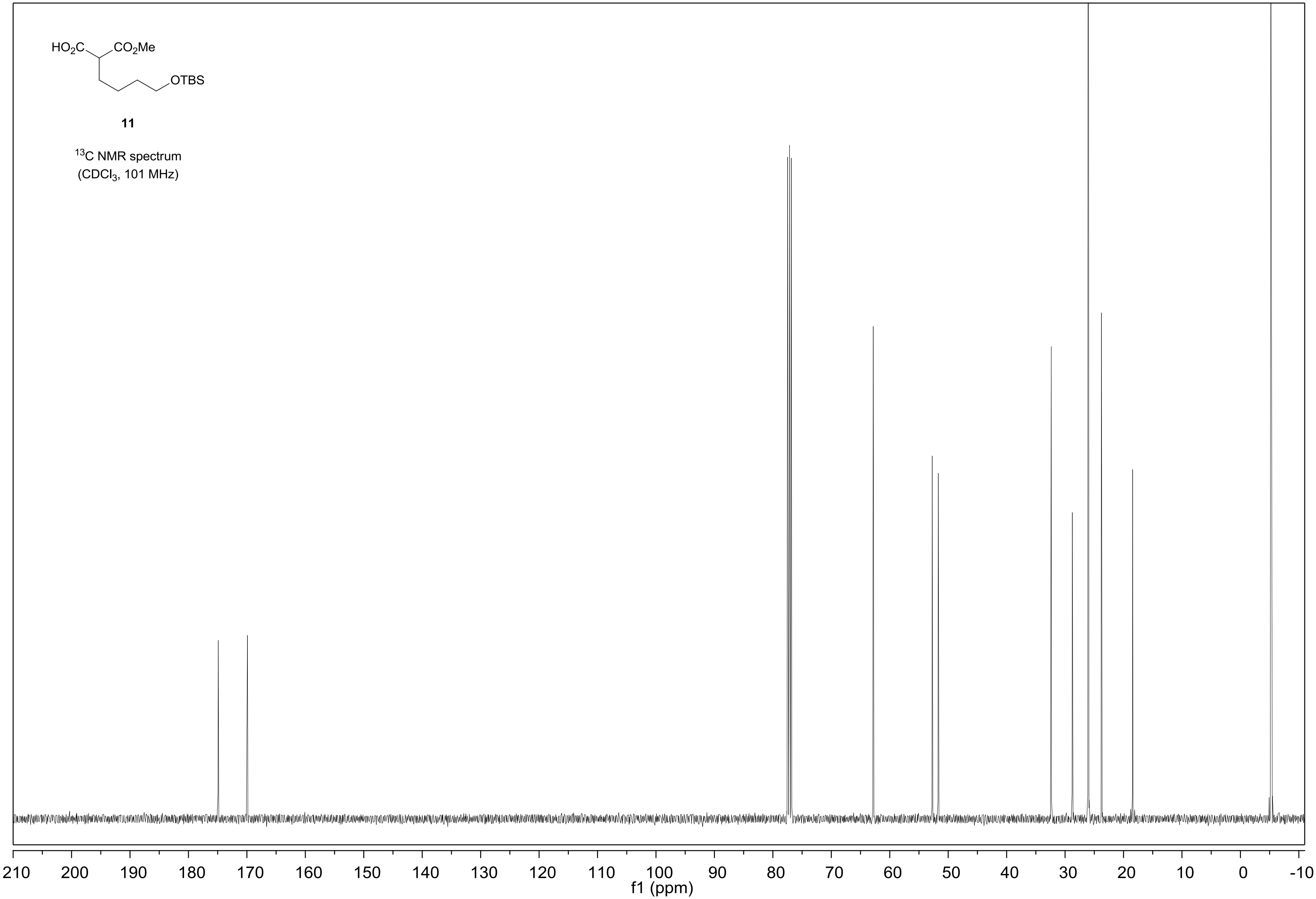
10

^{13}C NMR spectrum
($CDCl_3$, 126 MHz)

11

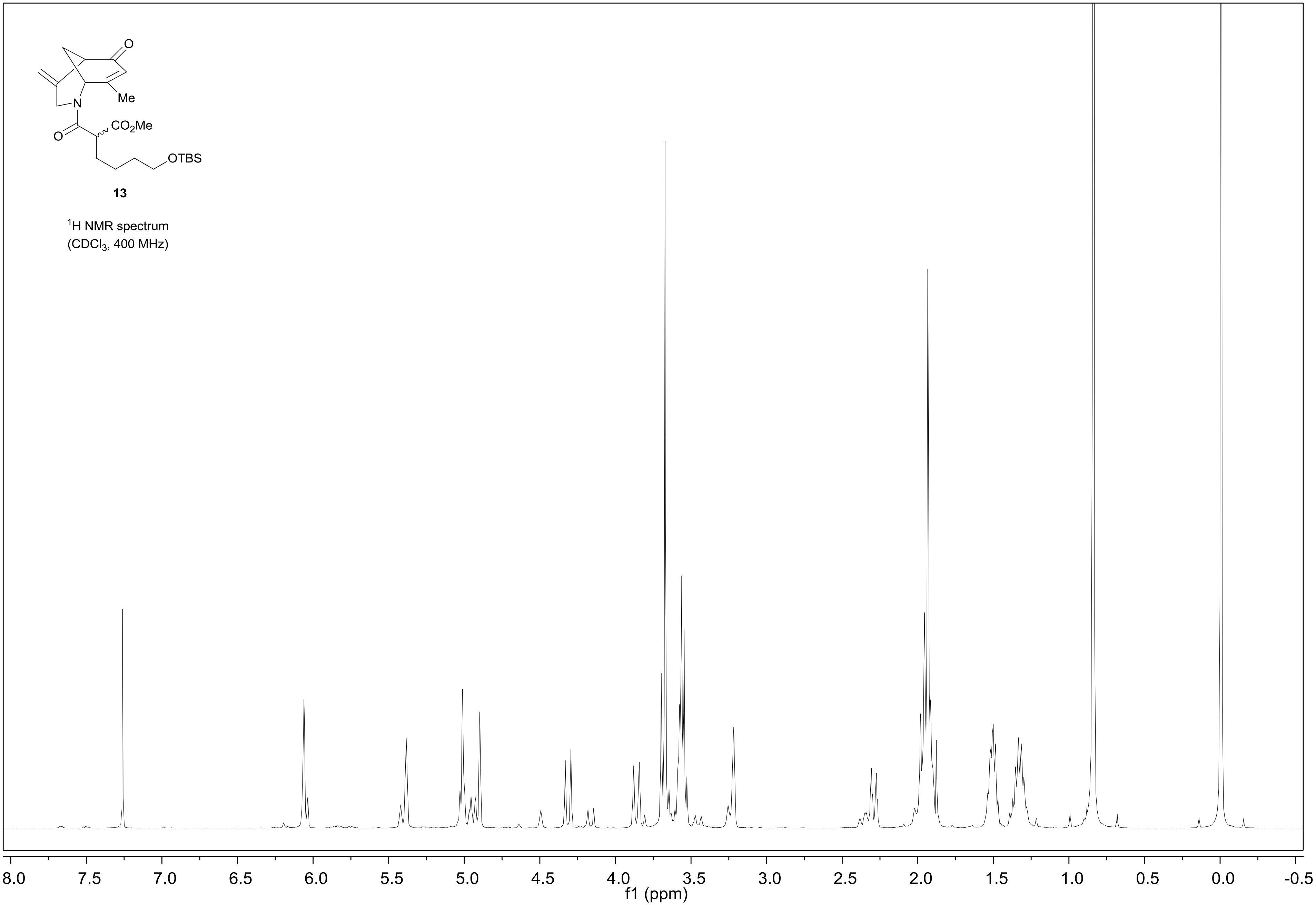
^{1}H NMR spectrum
($CDCl_3$, 400 MHz)

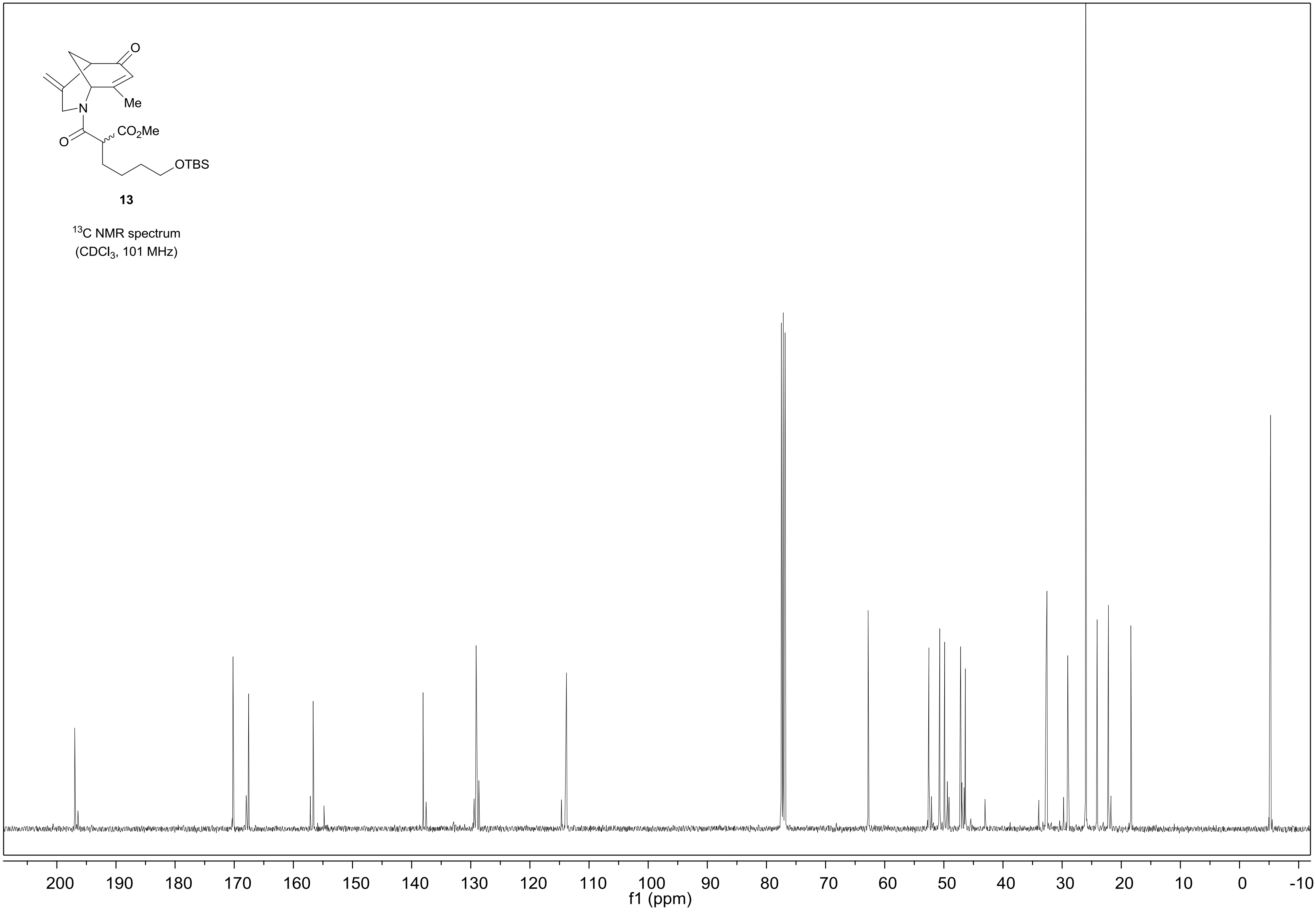




11

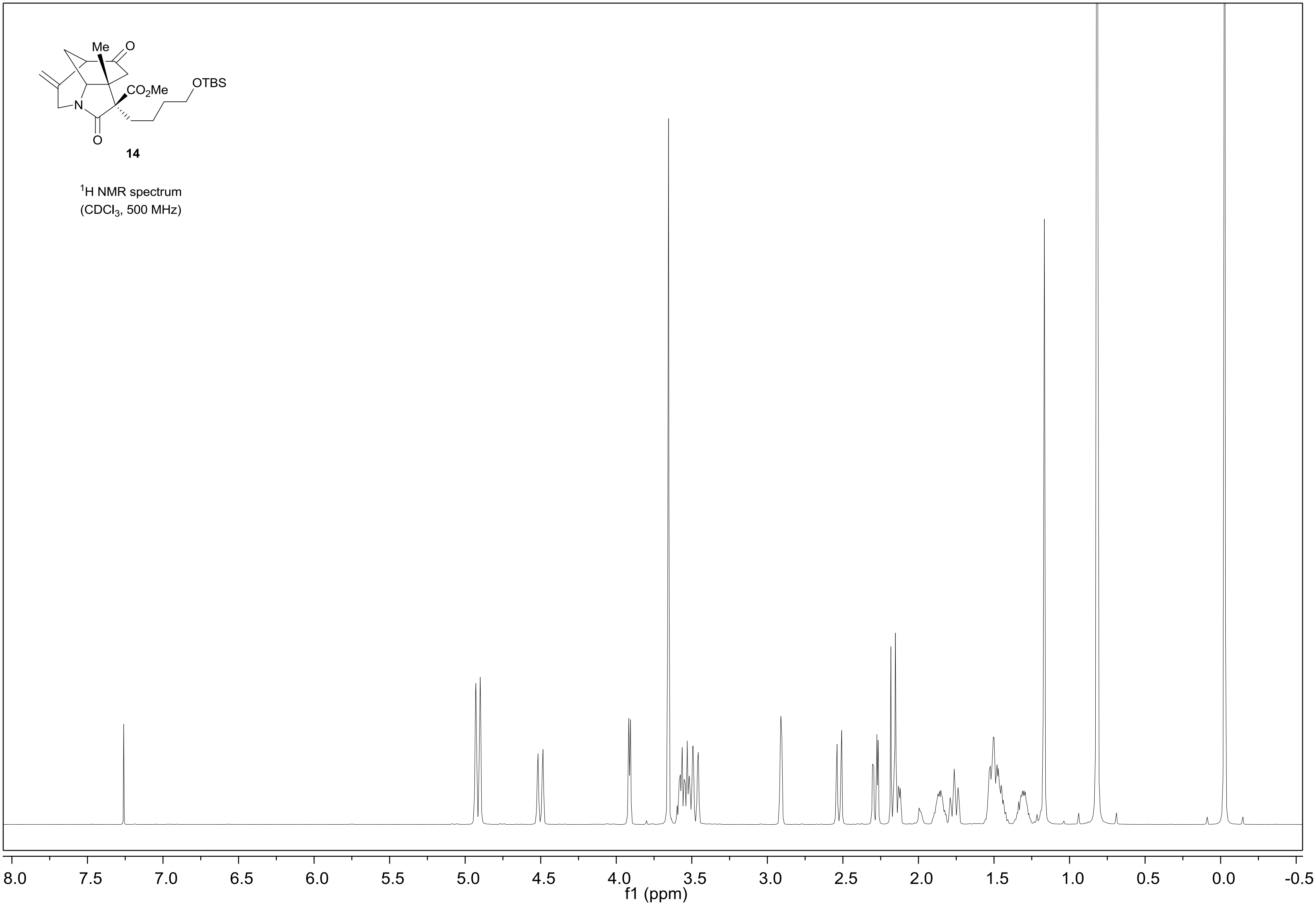
^{13}C NMR spectrum
($CDCl_3$, 101 MHz)


O
Me
N
CO_2Me
O
OTBS
13
^1H NMR spectrum
($CDCl_3$, 400 MHz)
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
f1 (ppm)



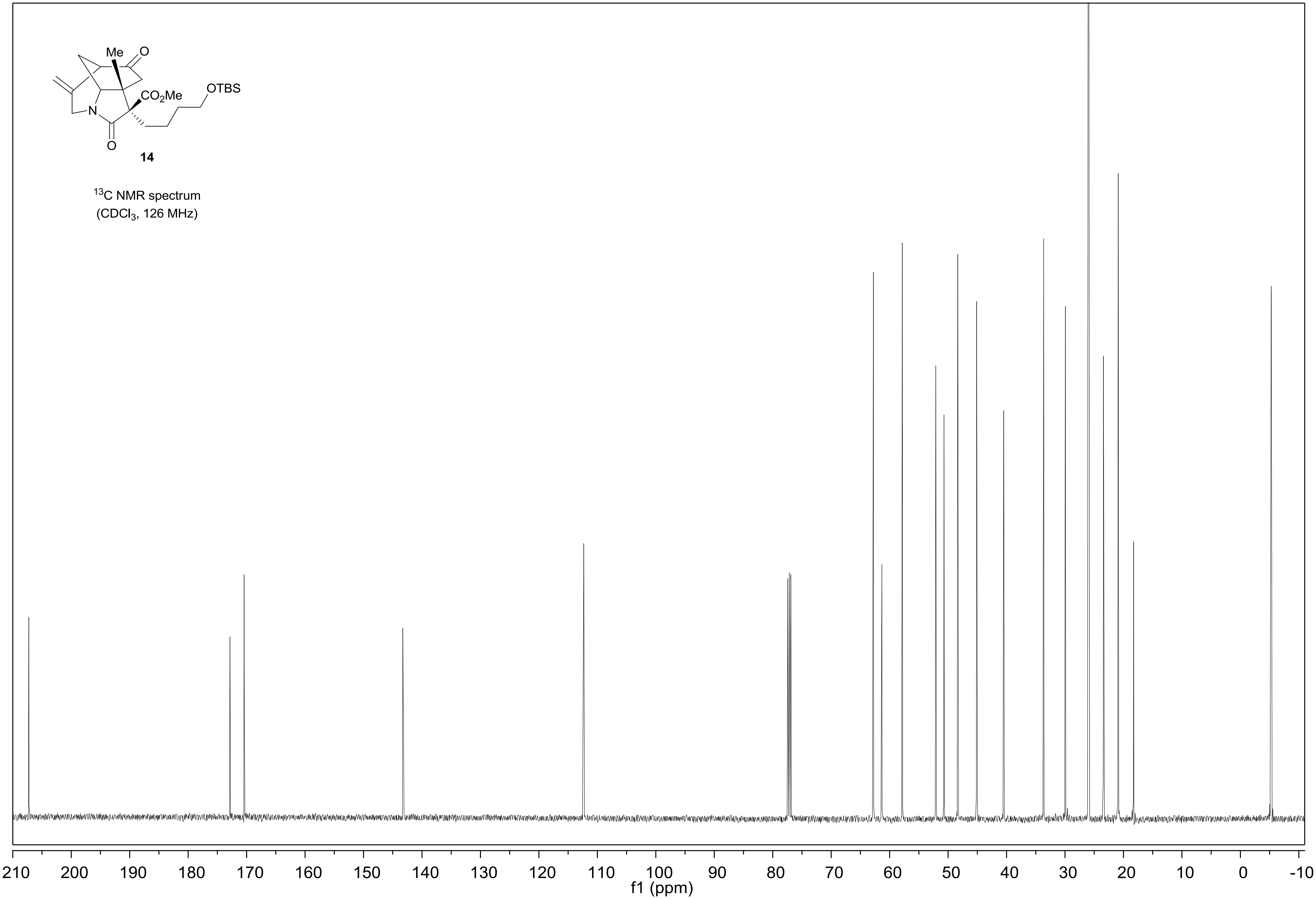
13

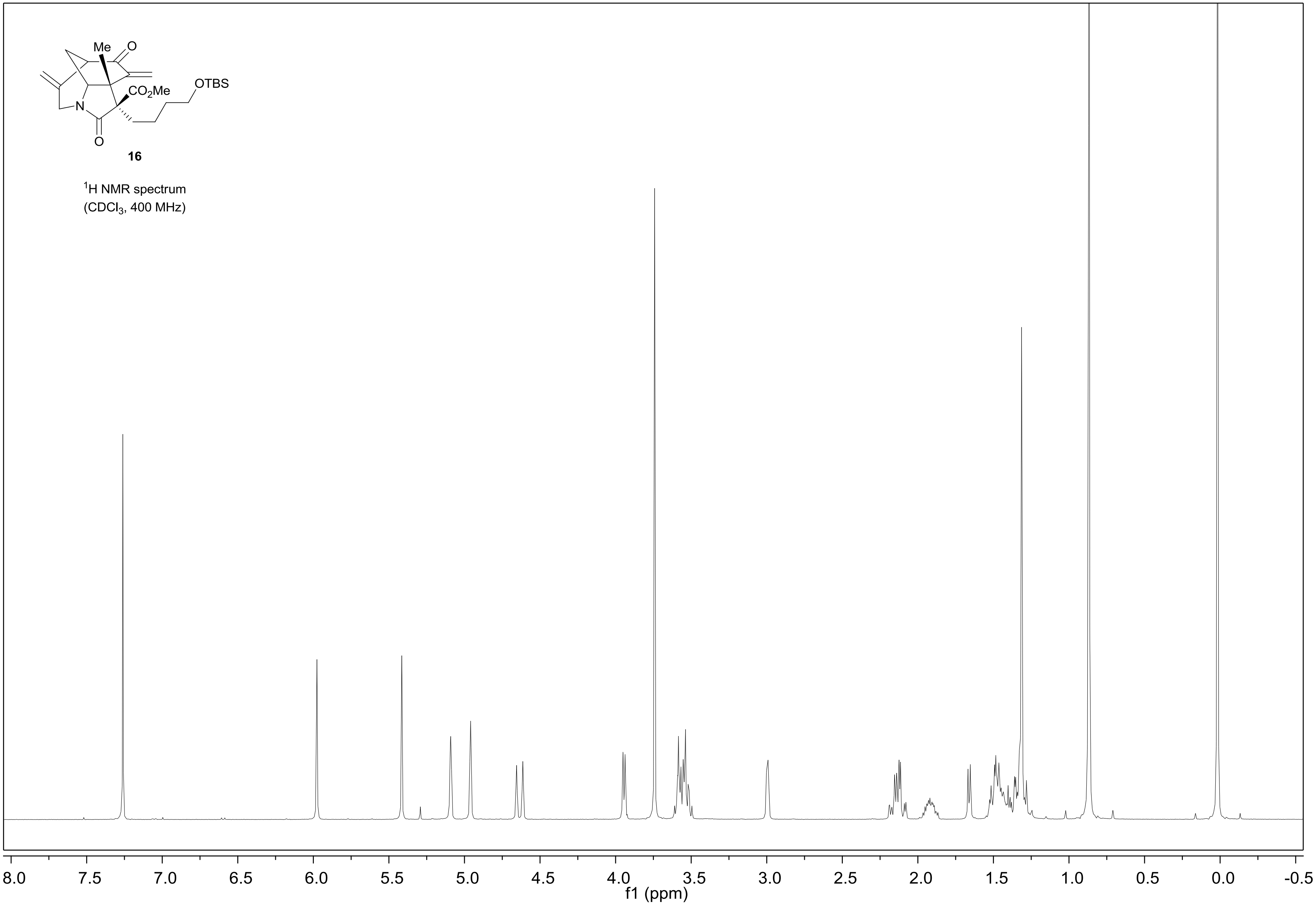
^{13}C NMR spectrum
($CDCl_3$, 101 MHz)

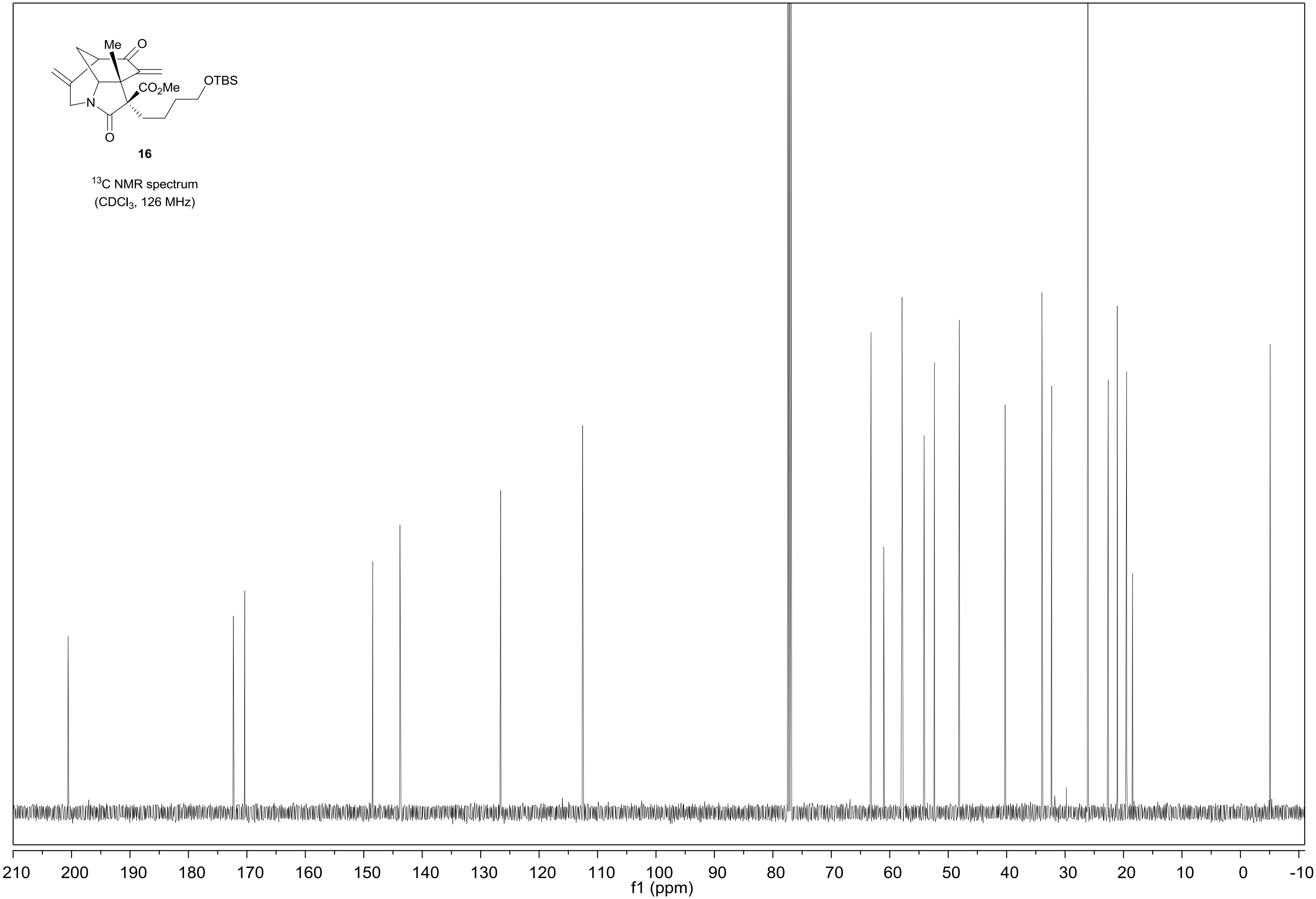


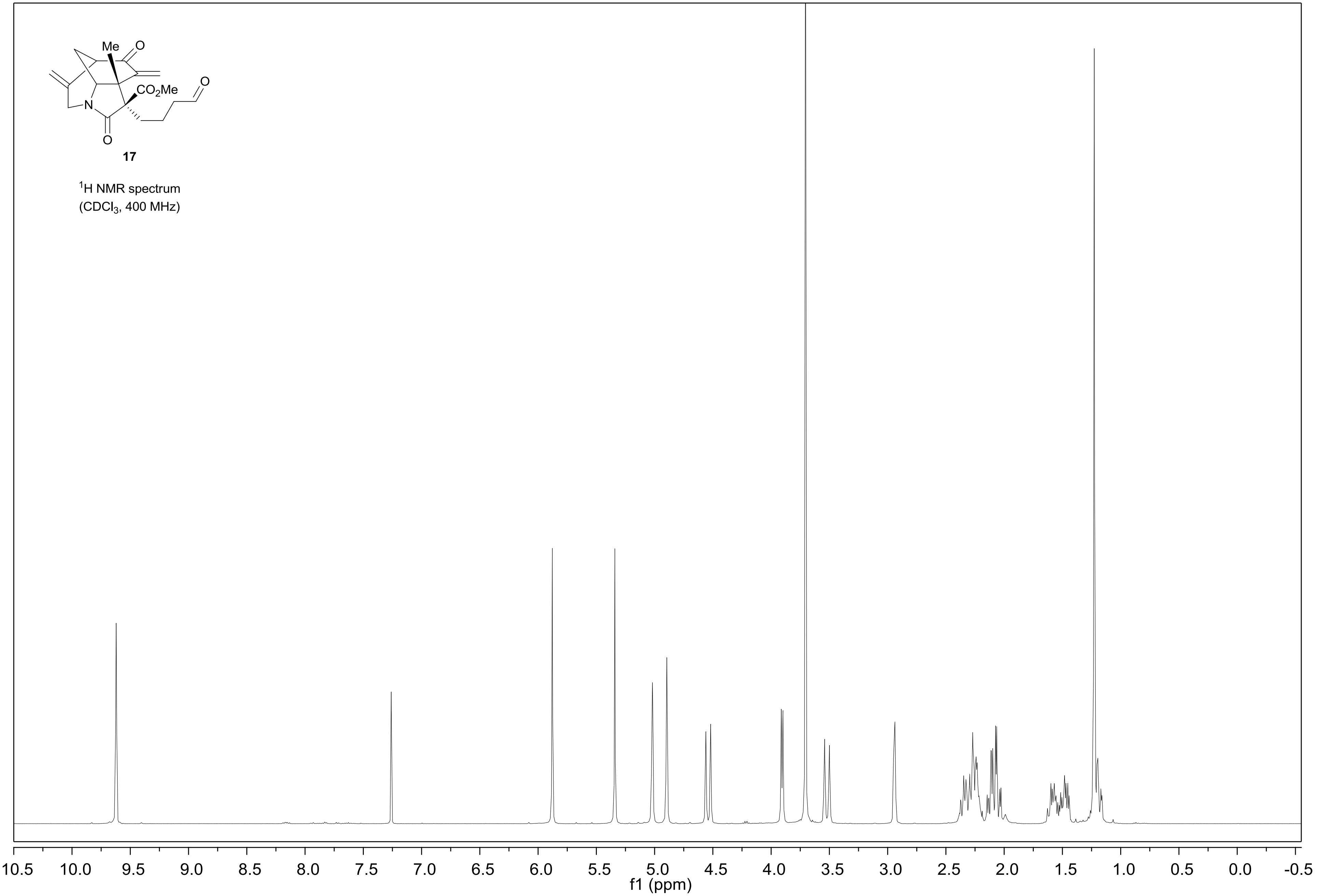
14

^{1}H NMR spectrum
(CDCl$_3$, 500 MHz)


Me
O
CO$_2$Me
OTBS
N
O
14
^{13}C NMR spectrum
(CDCl$_3$, 126 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

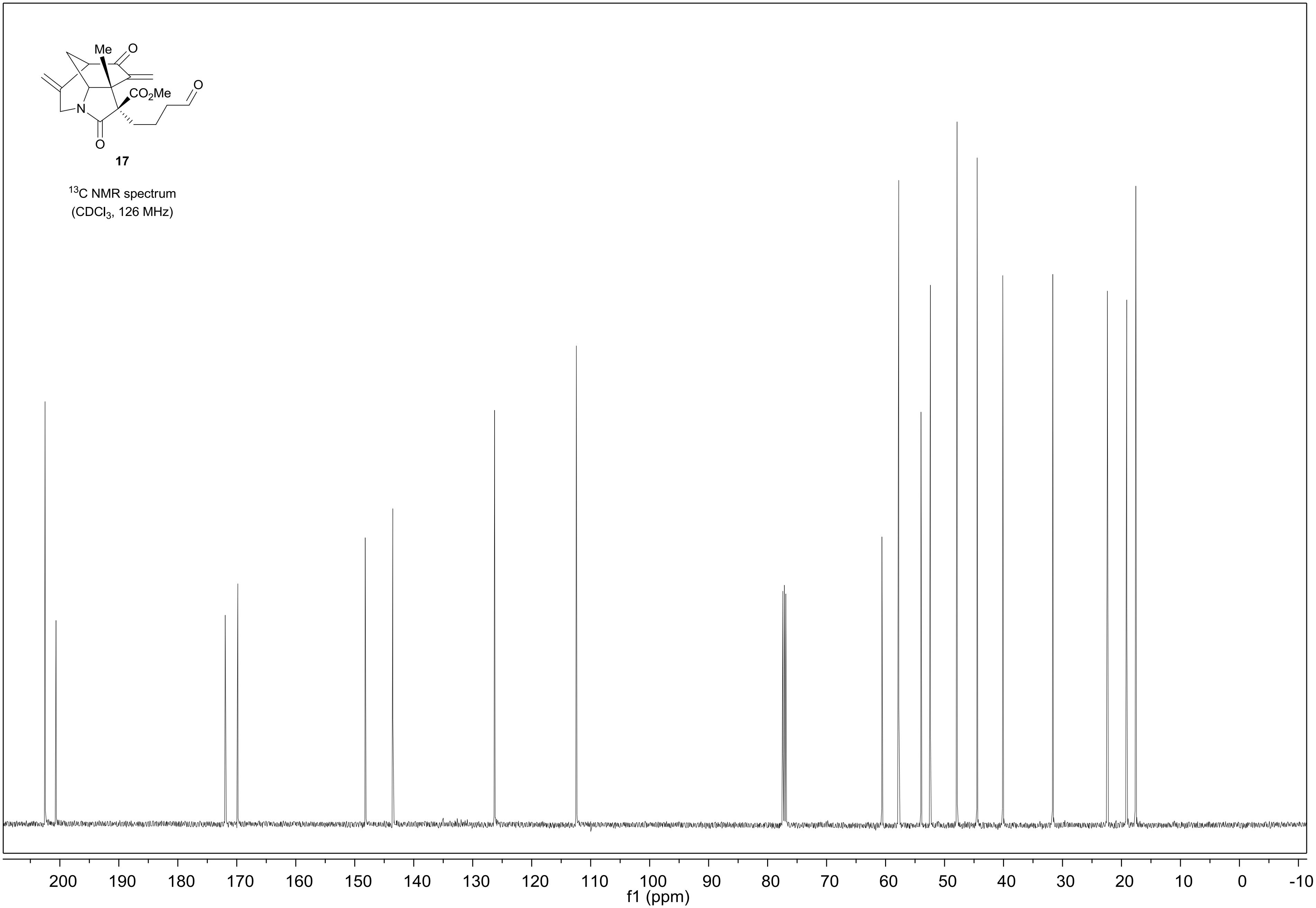

Me
O
CO2Me
OTBS
N
O
16
1H NMR spectrum
(CDCl3, 400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

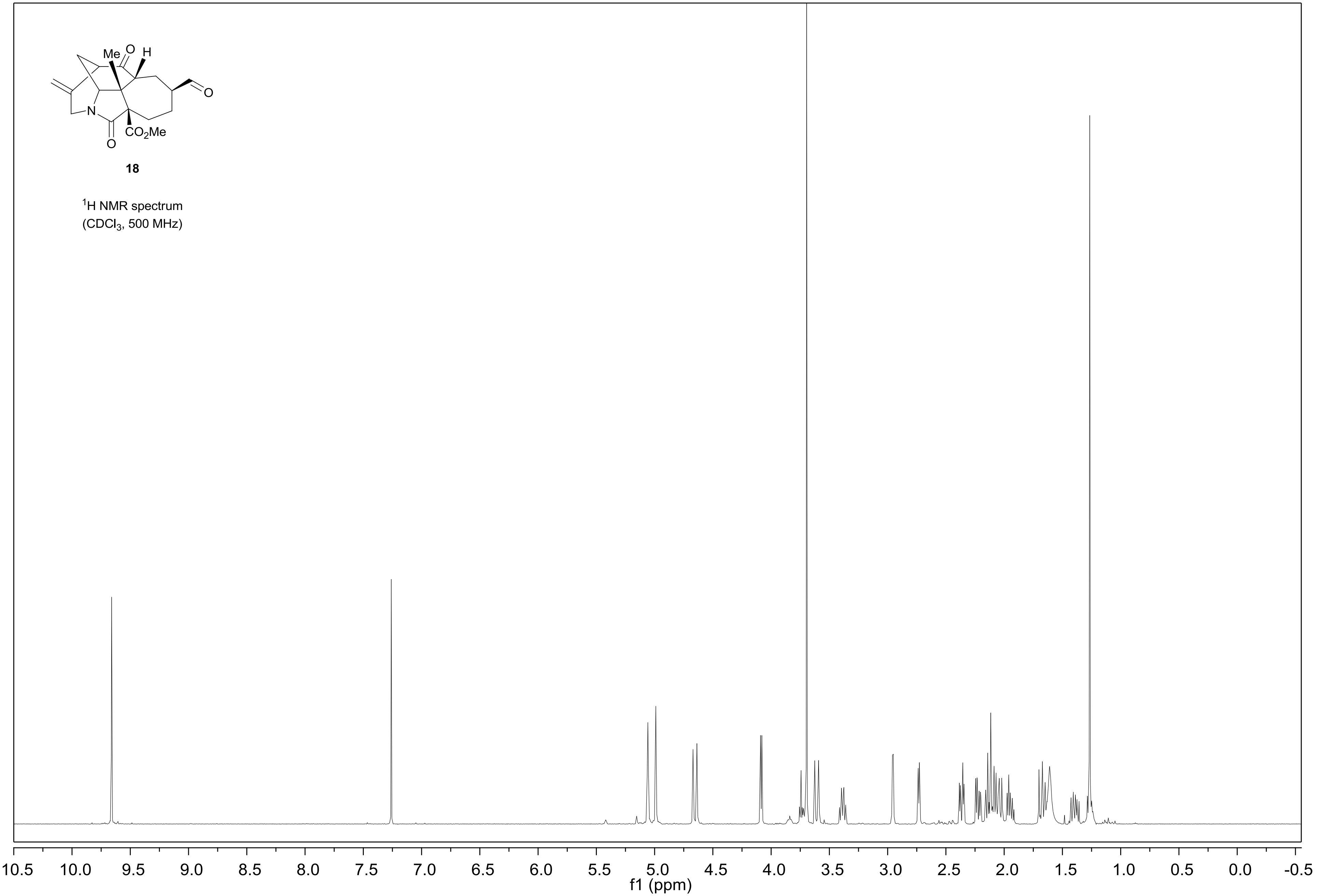

Me
O
CO2Me
OTBS
N
O
16
13C NMR spectrum
(CDCl3, 126 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



17

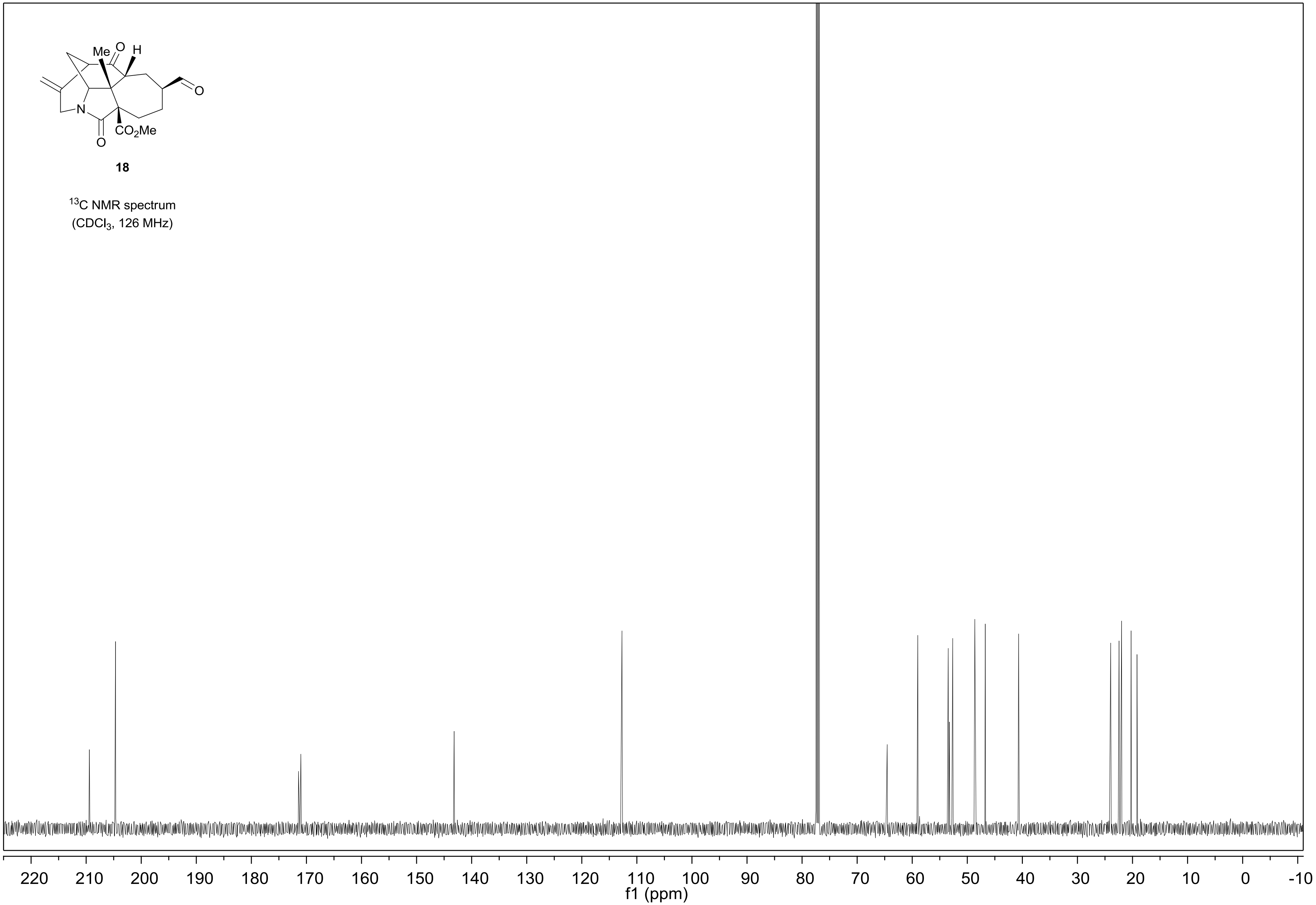
^{1}H NMR spectrum
($CDCl_3$, 400 MHz)

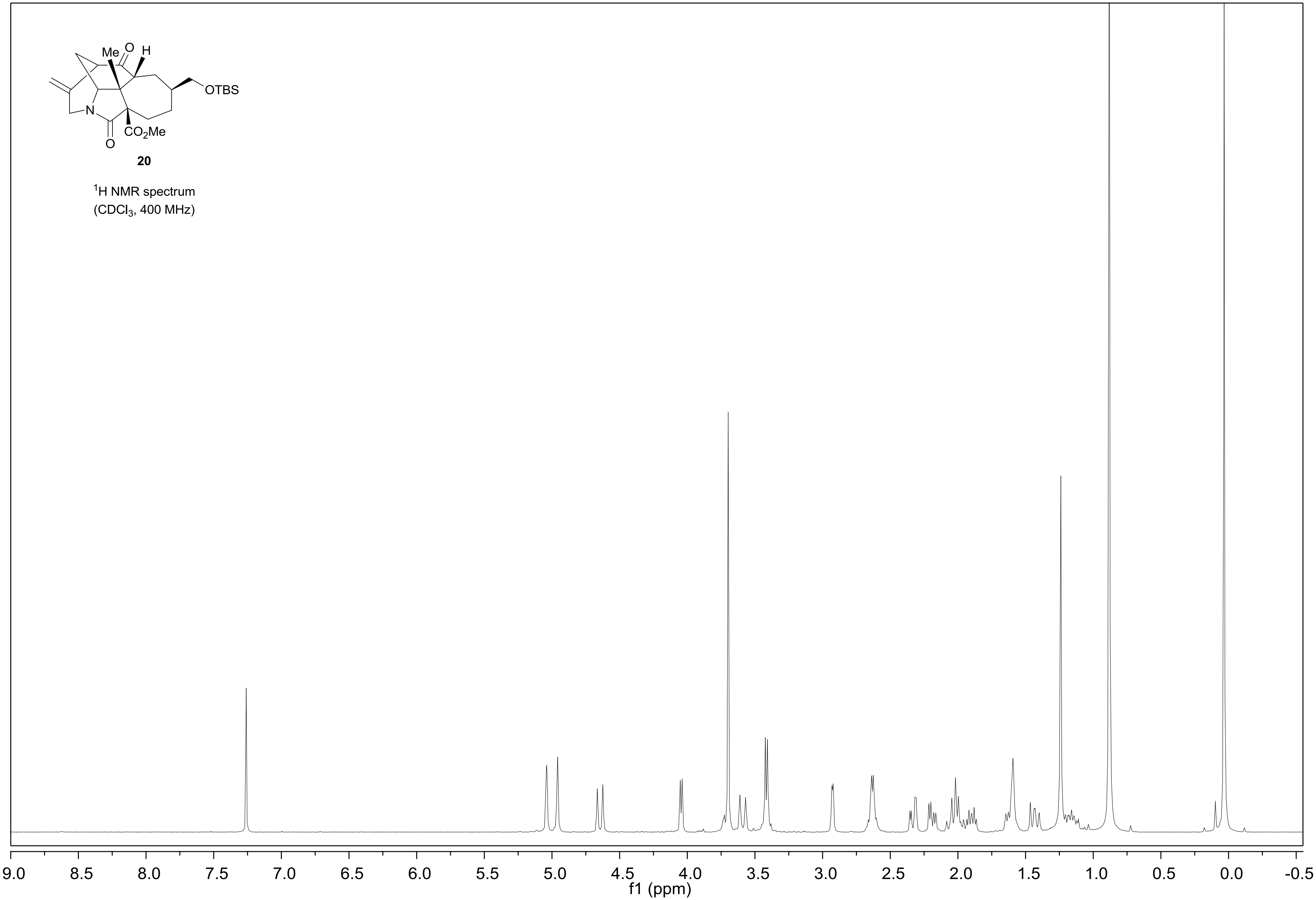

Me
O
CO2Me
O
N
O
17
13C NMR spectrum
(CDCl3, 126 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



18

^{1}H NMR spectrum
($CDCl_3$, 500 MHz)


Me
O
H
N
O
CO_2Me
O
18
^{13}C NMR spectrum
($CDCl_3$, 126 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Me
O
H
OTBS
N
CO_2Me
O
20
^{1}H NMR spectrum
($CDCl_3$, 400 MHz)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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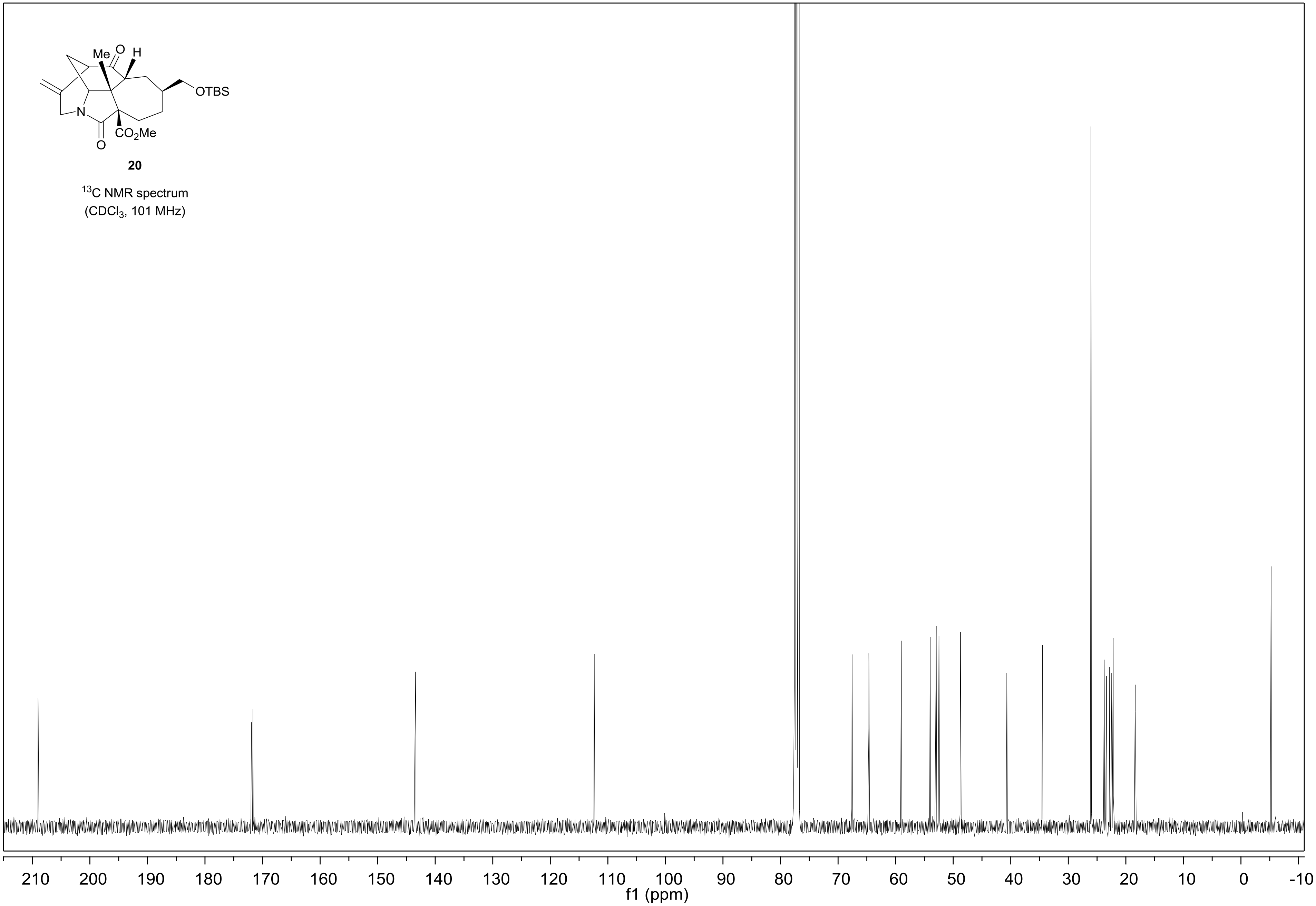
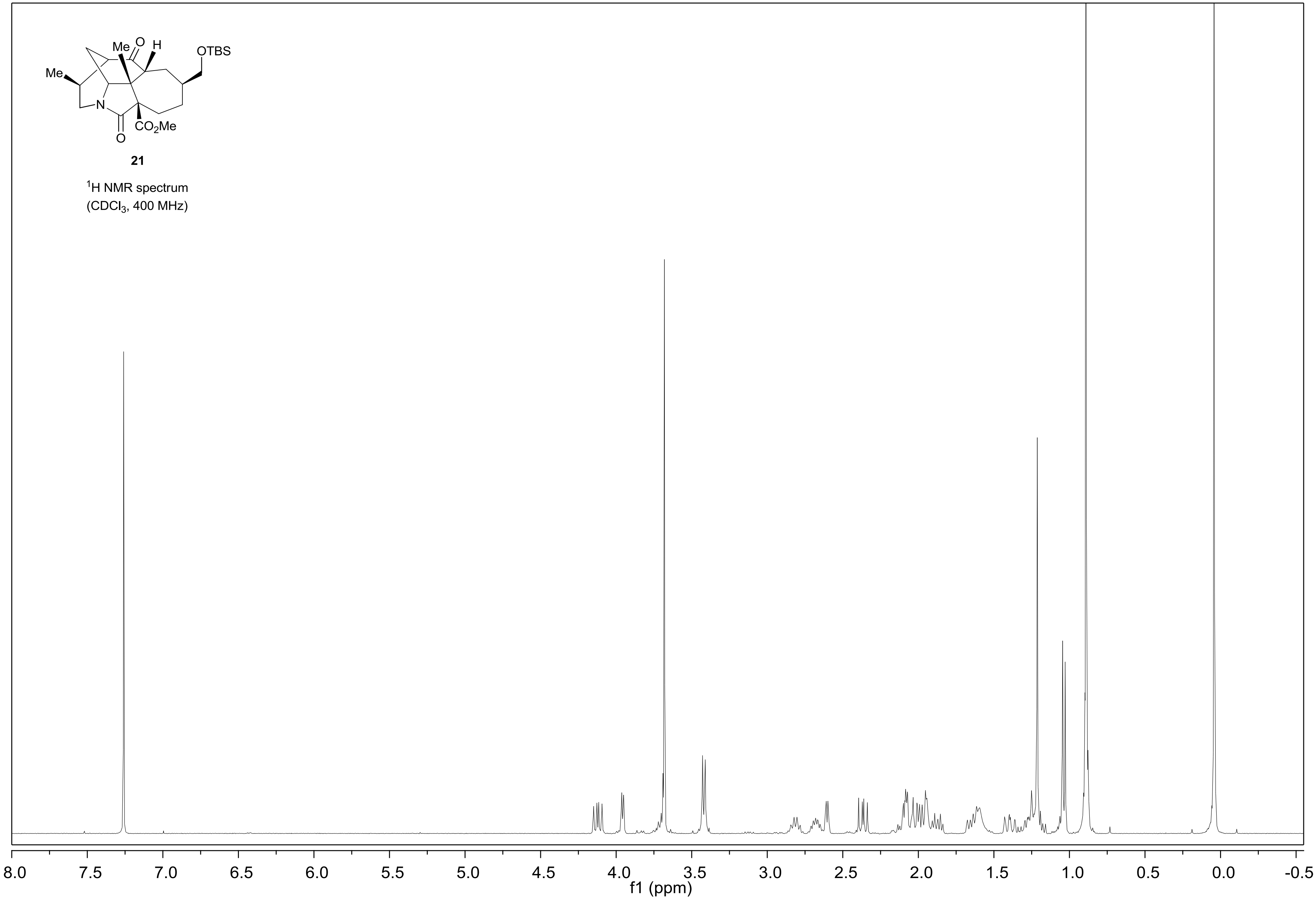
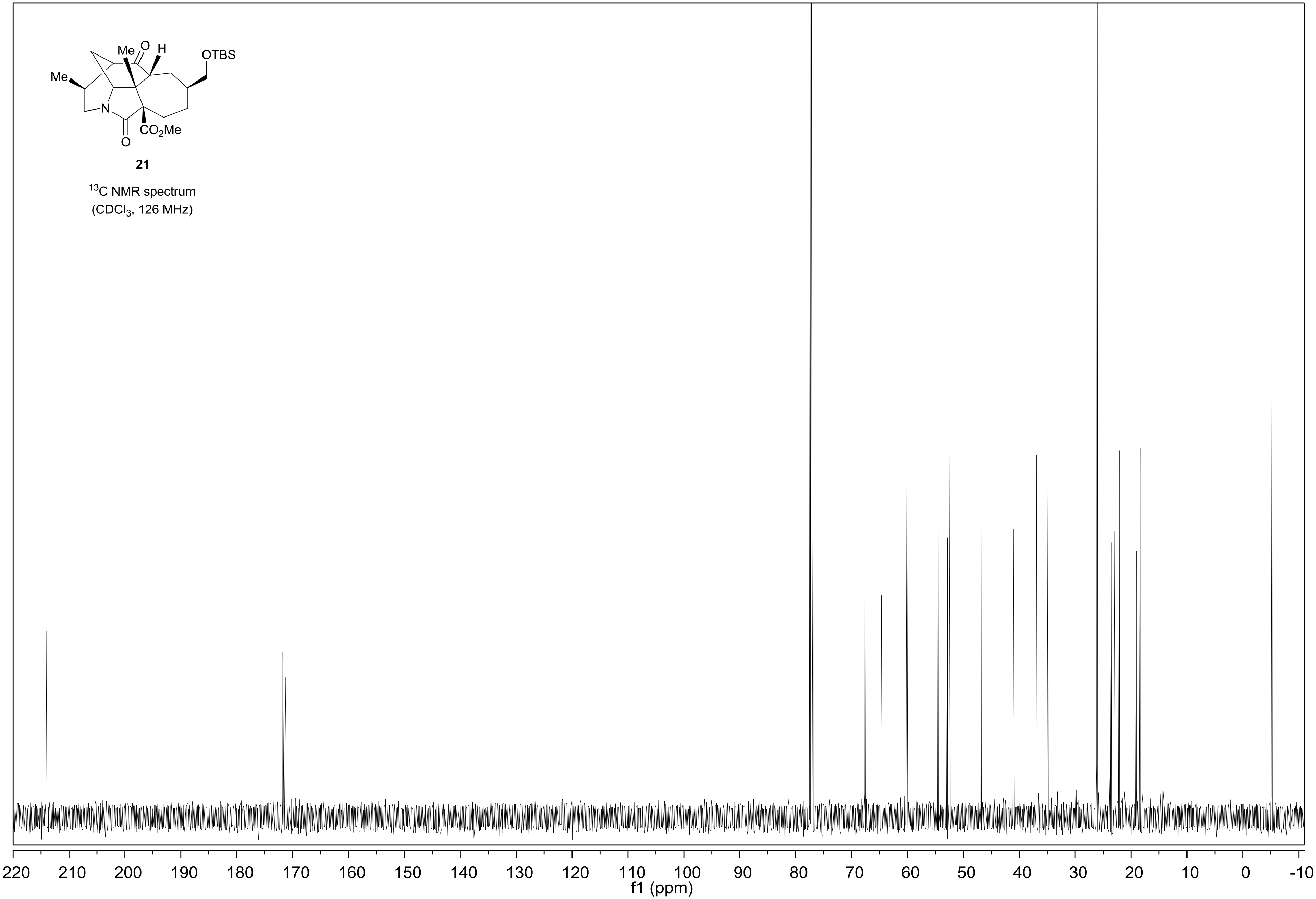
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

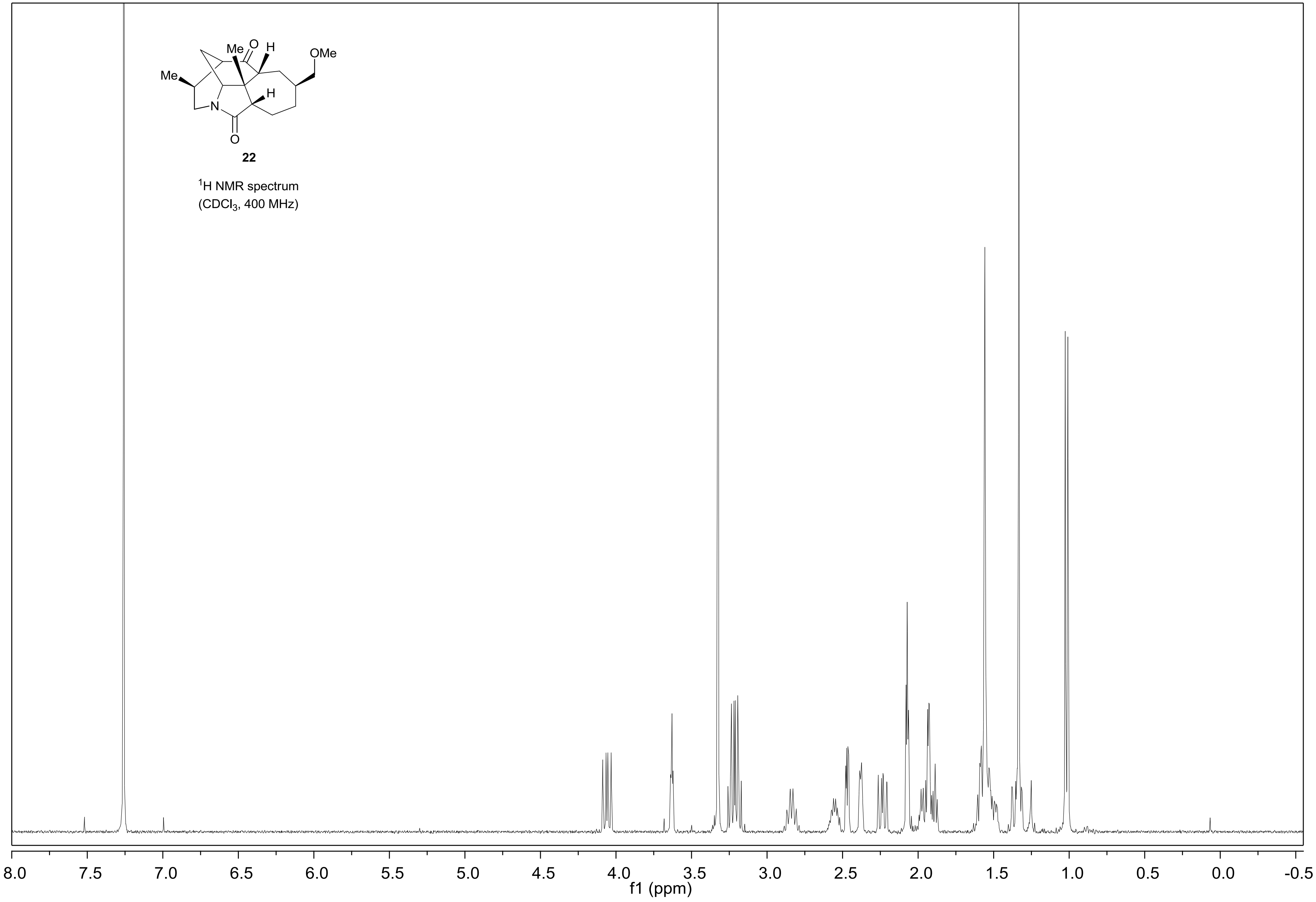


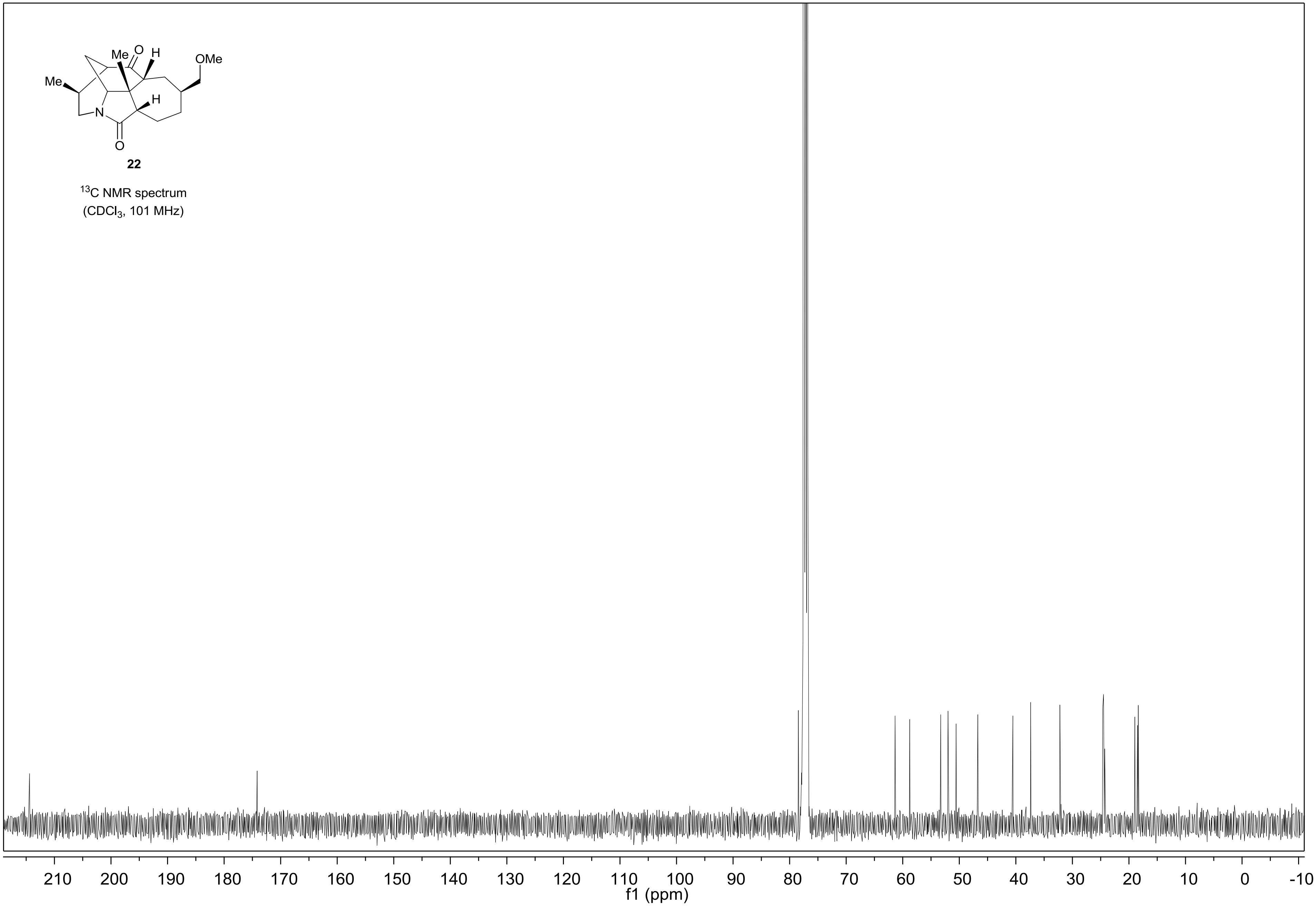
20

^{13}C NMR spectrum
($CDCl_3$, 101 MHz)


Me
O
H
OTBS
Me
N
O
CO_2Me
21
^{1}H NMR spectrum
($CDCl_3$, 400 MHz)
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
f1 (ppm)

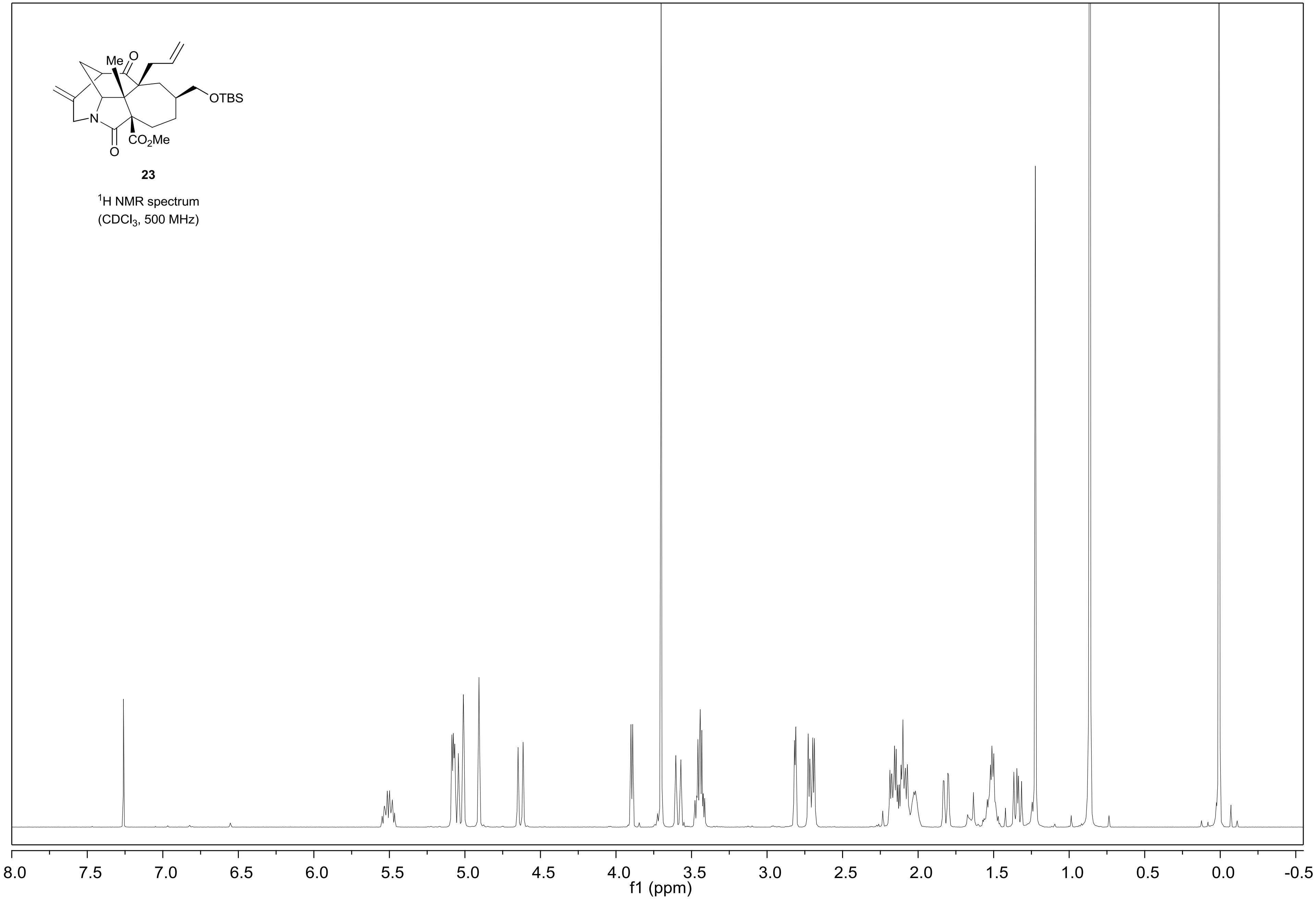

Me
O
H
OTBS
Me
N
CO2Me
O
21
13C NMR spectrum
(CDCl3, 126 MHz)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

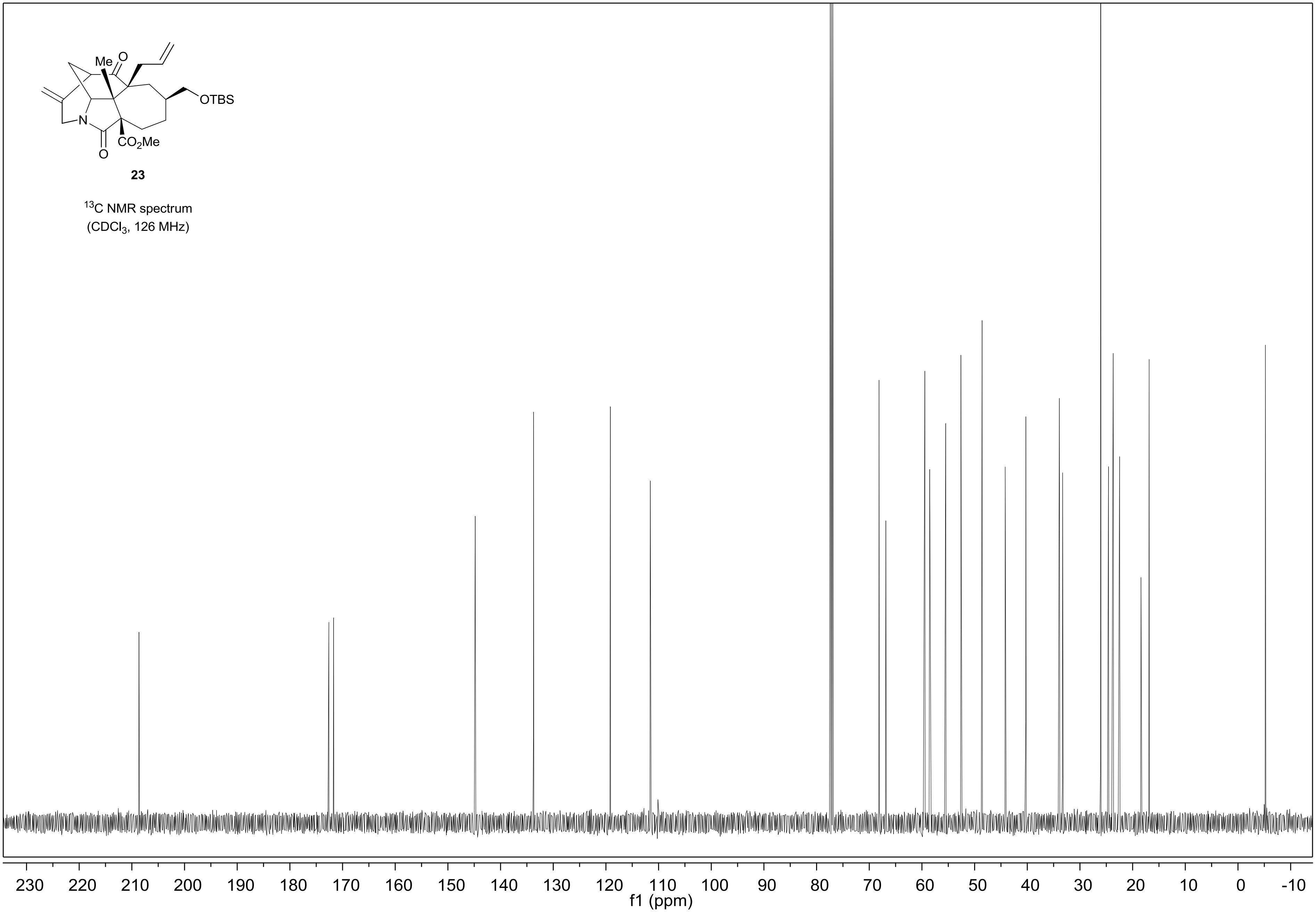

Me
O
H
OMe
Me
N
H
O
22
^{1}H NMR spectrum
($CDCl_3$, 400 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



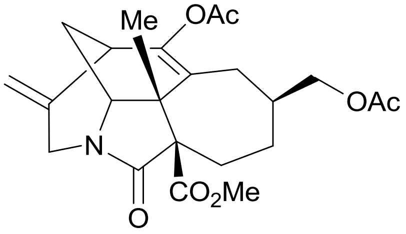
22

^{13}C NMR spectrum
($CDCl_3$, 101 MHz)

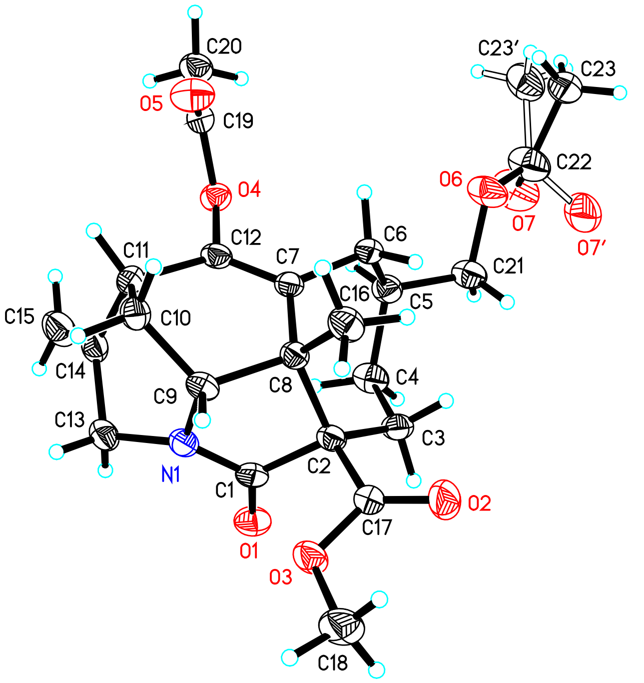

Me
O
OTBS
N
CO2Me
O
23
1H NMR spectrum
(CDCl3, 500 MHz)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
O
OTBS
N
O
CO2Me
23
13C NMR spectrum
(CDCl3, 126 MHz)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

VI Crystallographic Data of Compound 19



19



ORTEP of compound **19**

Crystal data

$C_{23}H_{29}NO_7$

M_r = 431.47

Monoclinic, $P2_1/n$

a = 8.2542 (9) Å

b = 26.236 (3) Å

c = 10.2531 (12) Å

β = 104.029 (2) °

$F(000)$ = 920

D_x = 1.330 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å

Cell parameters from 1308 reflections

θ = 5.1–40.6 °

μ = 0.10 mm^{-1}

T = 293 K

$V = 2154.1\ (4)\ \text{Å}^3$

$Z = 4$

Prismatic, colorless

0.31 × 0.27 × 0.04 mm

Data collection

CCD area detector diffractometer

Radiation source: fine-focus sealed tube

graphite

phi and ω scans

Absorption correction: empirical (using intensity measurements) *SADABS*

$T_{\text{min}} = 0.669$, $T_{\text{max}} = 1.000$

11005 measured reflections

3990 independent reflections

2414 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.055$

$\theta_{\text{max}} = 25.5°$, $\theta_{\text{min}} = 1.6°$

$h = -9\rightarrow9$

$k = -31\rightarrow21$

$l = -12\rightarrow11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.081$

$wR(F^2) = 0.212$

$S = 1.10$

3990 reflections

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0955P)^2 + 0.6358P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.007$

303 parameters	$\Delta\rho_{max} = 1.06$ e Å^{-3}
27 restraints	$\Delta\rho_{min} = -0.50$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
N1	0.1679 (4)	0.19003 (13)	0.6093 (3)	0.0393 (8)	
O1	−0.1052 (4)	0.19127 (13)	0.6209 (3)	0.0523 (8)	
O2	0.0159 (5)	0.03328 (15)	0.6668 (3)	0.0732 (11)	
O3	0.1240 (4)	0.10060 (12)	0.7887 (3)	0.0510 (8)	
O4	0.1383 (3)	0.19323 (11)	0.1771 (2)	0.0405 (7)	
O5	0.3796 (4)	0.16531 (14)	0.1417 (3)	0.0589 (9)	
O6	−0.2428 (4)	0.06154 (15)	0.0196 (3)	0.0659 (11)	

C1	0.0171 (5)	0.16958 (17)	0.6012 (4)	0.0389 (10)
C2	0.0201 (5)	0.11355 (16)	0.5543 (3)	0.0365 (10)
C3	−0.1511 (5)	0.09915 (19)	0.4632 (4)	0.0450 (11)
H3A	−0.1441	0.0646	0.4311	0.054*
H3B	−0.2325	0.0991	0.5174	0.054*
C4	−0.2162 (5)	0.1339 (2)	0.3410 (4)	0.0501 (12)
H4A	−0.3371	0.1349	0.3222	0.060*
H4B	−0.1755	0.1682	0.3642	0.060*
C5	−0.1657 (5)	0.11763 (18)	0.2128 (4)	0.0425 (11)
H5	−0.1748	0.1476	0.1542	0.051*
C6	0.0157 (5)	0.09914 (17)	0.2440 (4)	0.0380 (10)
H6A	0.0207	0.0644	0.2774	0.046*
H6B	0.0538	0.0989	0.1616	0.046*
C7	0.1315 (5)	0.13217 (16)	0.3467 (4)	0.0348 (9)
C8	0.1798 (4)	0.11360 (16)	0.4923 (4)	0.0348 (9)
C9	0.2901 (5)	0.15359 (16)	0.5824 (4)	0.0378 (10)
H9	0.3505	0.1377	0.6667	0.045*
C10	0.4125 (5)	0.18036 (18)	0.5164 (4)	0.0444 (11)
H10A	0.4865	0.2022	0.5808	0.053*
H10B	0.4797	0.1556	0.4829	0.053*
C11	0.3104 (5)	0.21177 (17)	0.4015 (4)	0.0420 (11)
H11	0.3850	0.2265	0.3503	0.050*
C12	0.1895 (5)	0.17628 (17)	0.3122 (3)	0.0376 (10)

C13	0.1952 (6)	0.24488 (17)	0.5957 (4)	0.0473 (11)
H13A	0.2925	0.2558	0.6636	0.057*
H13B	0.0992	0.2639	0.6079	0.057*
C14	0.2215 (5)	0.25487 (18)	0.4567 (4)	0.0435 (11)
C15	0.1738 (7)	0.2973 (2)	0.3910 (5)	0.0634 (14)
H15A	0.1217	0.3226	0.4295	0.076*
H15B	0.1921	0.3021	0.3058	0.076*
C16	0.2684 (6)	0.06225 (17)	0.5010 (4)	0.0492 (12)
H16A	0.1906	0.0366	0.4580	0.074*
H16B	0.3123	0.0533	0.5936	0.074*
H16C	0.3582	0.0645	0.4567	0.074*
C17	0.0518 (5)	0.07757 (19)	0.6738 (4)	0.0426 (10)
C18	0.1560 (7)	0.0694 (2)	0.9089 (4)	0.0662 (15)
H18A	0.0526	0.0623	0.9323	0.099*
H18B	0.2294	0.0873	0.9814	0.099*
H18C	0.2073	0.0380	0.8925	0.099*
C19	0.2503 (5)	0.18669 (17)	0.1010 (4)	0.0393 (10)
C20	0.1890 (6)	0.20890 (19)	−0.0353 (4)	0.0503 (12)
H20A	0.2620	0.1991	−0.0910	0.075*
H20B	0.1870	0.2454	−0.0288	0.075*
H20C	0.0783	0.1966	−0.0744	0.075*
C21	−0.2864 (5)	0.0784 (2)	0.1409 (4)	0.0515 (12)
H21A	−0.2862	0.0494	0.1998	0.062*

H21B	−0.3981	0.0927	0.1183	0.062*	
C22	−0.3532 (6)	0.0498 (3)	−0.0859 (5)	0.0721 (17)	
O7	−0.4691 (12)	0.0832 (4)	−0.1158 (9)	0.101 (3)	0.55
C23	−0.3068 (13)	0.0202 (4)	−0.1913 (9)	0.066 (3)	0.65
H23A	−0.3520	0.0360	−0.2768	0.098*	0.65
H23B	−0.3505	−0.0137	−0.1919	0.098*	0.65
H23C	−0.1873	0.0188	−0.1748	0.098*	0.65
O7'	−0.4917 (11)	0.0422 (4)	−0.0761 (9)	0.117 (4)	0.45
C23'	−0.307 (3)	0.0504 (9)	−0.213 (2)	0.078 (6)	0.35
H23D	−0.3897	0.0326	−0.2788	0.118*	0.35
H23E	−0.2007	0.0339	−0.2025	0.118*	0.35
H23F	−0.2992	0.0850	−0.2408	0.118*	0.35

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.051 (2)	0.035 (2)	0.0326 (17)	−0.0009 (17)	0.0118 (14)	−0.0026 (15)
O1	0.0524 (18)	0.058 (2)	0.0522 (18)	0.0096 (16)	0.0224 (14)	−0.0025 (15)
O2	0.123 (3)	0.049 (2)	0.0456 (19)	−0.029 (2)	0.0170 (18)	−0.0004 (17)
O3	0.075 (2)	0.044 (2)	0.0308 (15)	−0.0031 (16)	0.0059 (13)	−0.0012 (13)
O4	0.0385 (15)	0.049 (2)	0.0334 (14)	−0.0014 (13)	0.0079 (11)	0.0022 (13)
O5	0.0526 (19)	0.076 (3)	0.0492 (18)	0.0186 (18)	0.0146 (15)	0.0081 (16)
O6	0.0443 (18)	0.107 (3)	0.0420 (17)	−0.0125 (18)	0.0025 (14)	−0.0283 (18)
C1	0.045 (2)	0.047 (3)	0.0256 (19)	0.003 (2)	0.0091 (17)	−0.0001 (18)

C2	0.043 (2)	0.039 (3)	0.0281 (18)	0.0005 (19)	0.0093 (16)	−0.0022 (17)
C3	0.041 (2)	0.060 (3)	0.037 (2)	−0.006 (2)	0.0156 (17)	−0.007 (2)
C4	0.038 (2)	0.069 (4)	0.041 (2)	0.005 (2)	0.0045 (18)	−0.006 (2)
C5	0.042 (2)	0.051 (3)	0.032 (2)	−0.002 (2)	0.0053 (17)	−0.0017 (19)
C6	0.043 (2)	0.043 (3)	0.0307 (19)	−0.005 (2)	0.0132 (16)	−0.0045 (18)
C7	0.034 (2)	0.042 (3)	0.0285 (18)	−0.0015 (19)	0.0086 (15)	−0.0056 (18)
C8	0.034 (2)	0.038 (3)	0.0329 (19)	−0.0006 (18)	0.0094 (16)	−0.0025 (17)
C9	0.042 (2)	0.042 (3)	0.0266 (19)	0.0050 (19)	0.0041 (16)	−0.0022 (17)
C10	0.036 (2)	0.056 (3)	0.039 (2)	−0.010 (2)	0.0034 (17)	−0.008 (2)
C11	0.043 (2)	0.048 (3)	0.036 (2)	−0.016 (2)	0.0122 (18)	−0.003 (2)
C12	0.040 (2)	0.047 (3)	0.0250 (18)	0.000 (2)	0.0071 (16)	−0.0019 (18)
C13	0.065 (3)	0.035 (3)	0.043 (2)	−0.003 (2)	0.016 (2)	−0.009 (2)
C14	0.050 (2)	0.042 (3)	0.034 (2)	−0.012 (2)	0.0023 (17)	−0.003 (2)
C15	0.091 (4)	0.051 (4)	0.043 (3)	−0.009 (3)	0.007 (2)	−0.003 (2)
C16	0.053 (3)	0.043 (3)	0.050 (3)	0.007 (2)	0.011 (2)	−0.004 (2)
C17	0.051 (3)	0.042 (3)	0.037 (2)	−0.007 (2)	0.0155 (18)	−0.005 (2)
C18	0.090 (4)	0.070 (4)	0.033 (2)	0.001 (3)	0.005 (2)	0.008 (2)
C19	0.041 (2)	0.037 (3)	0.040 (2)	−0.004 (2)	0.0106 (18)	−0.0053 (19)
C20	0.062 (3)	0.053 (3)	0.035 (2)	−0.001 (2)	0.0102 (19)	−0.001 (2)
C21	0.046 (2)	0.068 (4)	0.041 (2)	0.002 (2)	0.0105 (19)	−0.008 (2)
C22	0.041 (3)	0.104 (5)	0.063 (3)	0.013 (3)	−0.004 (2)	−0.026 (3)
O7	0.115 (6)	0.085 (6)	0.093 (5)	−0.002 (5)	0.007 (4)	0.015 (5)
C23	0.074 (5)	0.077 (7)	0.047 (4)	−0.012 (5)	0.018 (4)	−0.015 (5)

O7'	0.060 (5)	0.178 (9)	0.112 (7)	−0.040 (6)	0.021 (5)	−0.089 (7)
C23'	0.080 (9)	0.089 (10)	0.060 (8)	0.002 (9)	0.006 (7)	−0.015 (8)

Geometric parameters (Å, º)

N1—C1	1.340 (5)	C10—C11	1.515 (6)
N1—C9	1.464 (5)	C10—H10A	0.9700
N1—C13	1.469 (5)	C10—H10B	0.9700
O1—C1	1.218 (5)	C11—C12	1.503 (6)
O2—C17	1.197 (5)	C11—C14	1.529 (6)
O3—C17	1.329 (5)	C11—H11	0.9800
O3—C18	1.450 (5)	C13—C14	1.516 (6)
O4—C19	1.358 (5)	C13—H13A	0.9700
O4—C12	1.418 (4)	C13—H13B	0.9700
O5—C19	1.188 (5)	C14—C15	1.311 (7)
O6—C22	1.272 (5)	C15—H15A	0.9300
O6—C21	1.446 (5)	C15—H15B	0.9300
C1—C2	1.549 (6)	C16—H16A	0.9600
C2—C17	1.518 (6)	C16—H16B	0.9600
C2—C3	1.540 (5)	C16—H16C	0.9600
C2—C8	1.596 (5)	C18—H18A	0.9600
C3—C4	1.537 (6)	C18—H18B	0.9600
C3—H3A	0.9700	C18—H18C	0.9600
C3—H3B	0.9700	C19—C20	1.485 (6)

C4—C5	1.532 (5)	C20—H20A	0.9600
C4—H4A	0.9700	C20—H20B	0.9600
C4—H4B	0.9700	C20—H20C	0.9600
C5—C21	1.496 (6)	C21—H21A	0.9700
C5—C6	1.533 (5)	C21—H21B	0.9700
C5—H5	0.9800	C22—O7'	1.188 (9)
C6—C7	1.512 (5)	C22—O7	1.278 (9)
C6—H6A	0.9700	C22—C23'	1.44 (2)
C6—H6B	0.9700	C22—C23	1.456 (11)
C7—C12	1.333 (6)	C23—H23A	0.9600
C7—C8	1.529 (5)	C23—H23B	0.9600
C8—C16	1.526 (6)	C23—H23C	0.9600
C8—C9	1.541 (5)	C23'—H23D	0.9600
C9—C10	1.518 (6)	C23'—H23E	0.9600
C9—H9	0.9800	C23'—H23F	0.9600
C1—N1—C9	113.5 (4)	C14—C11—H11	109.1
C1—N1—C13	123.2 (4)	C7—C12—O4	119.4 (3)
C9—N1—C13	119.6 (3)	C7—C12—C11	127.2 (3)
C17—O3—C18	116.5 (4)	O4—C12—C11	113.4 (3)
C19—O4—C12	116.0 (3)	N1—C13—C14	108.6 (3)
C22—O6—C21	122.0 (4)	N1—C13—H13A	110.0
O1—C1—N1	126.7 (4)	C14—C13—H13A	110.0
O1—C1—C2	124.8 (4)	N1—C13—H13B	110.0

N1—C1—C2	108.4 (3)	C14—C13—H13B	110.0
C17—C2—C3	106.9 (3)	H13A—C13—H13B	108.3
C17—C2—C1	110.6 (3)	C15—C14—C13	122.4 (4)
C3—C2—C1	109.9 (3)	C15—C14—C11	123.3 (4)
C17—C2—C8	108.9 (3)	C13—C14—C11	114.3 (4)
C3—C2—C8	118.9 (3)	C14—C15—H15A	120.0
C1—C2—C8	101.5 (3)	C14—C15—H15B	120.0
C4—C3—C2	115.9 (4)	H15A—C15—H15B	120.0
C4—C3—H3A	108.3	C8—C16—H16A	109.5
C2—C3—H3A	108.3	C8—C16—H16B	109.5
C4—C3—H3B	108.3	H16A—C16—H16B	109.5
C2—C3—H3B	108.3	C8—C16—H16C	109.5
H3A—C3—H3B	107.4	H16A—C16—H16C	109.5
C5—C4—C3	114.9 (4)	H16B—C16—H16C	109.5
C5—C4—H4A	108.5	O2—C17—O3	123.1 (4)
C3—C4—H4A	108.5	O2—C17—C2	124.3 (4)
C5—C4—H4B	108.5	O3—C17—C2	112.6 (4)
C3—C4—H4B	108.5	O3—C18—H18A	109.5
H4A—C4—H4B	107.5	O3—C18—H18B	109.5
C21—C5—C4	109.1 (3)	H18A—C18—H18B	109.5
C21—C5—C6	112.7 (4)	O3—C18—H18C	109.5
C4—C5—C6	111.3 (3)	H18A—C18—H18C	109.5
C21—C5—H5	107.9	H18B—C18—H18C	109.5

C4—C5—H5	107.9	O5—C19—O4	122.4 (4)
C6—C5—H5	107.9	O5—C19—C20	126.1 (4)
C7—C6—C5	112.6 (3)	O4—C19—C20	111.5 (4)
C7—C6—H6A	109.1	C19—C20—H20A	109.5
C5—C6—H6A	109.1	C19—C20—H20B	109.5
C7—C6—H6B	109.1	H20A—C20—H20B	109.5
C5—C6—H6B	109.1	C19—C20—H20C	109.5
H6A—C6—H6B	107.8	H20A—C20—H20C	109.5
C12—C7—C6	121.3 (3)	H20B—C20—H20C	109.5
C12—C7—C8	120.7 (3)	O6—C21—C5	111.0 (3)
C6—C7—C8	118.0 (4)	O6—C21—H21A	109.4
C16—C8—C7	110.2 (3)	C5—C21—H21A	109.4
C16—C8—C9	111.2 (3)	O6—C21—H21B	109.4
C7—C8—C9	110.2 (3)	C5—C21—H21B	109.4
C16—C8—C2	114.0 (3)	H21A—C21—H21B	108.0
C7—C8—C2	110.2 (3)	O7'—C22—O6	118.3 (6)
C9—C8—C2	100.8 (3)	O7'—C22—O7	57.0 (6)
N1—C9—C10	110.2 (4)	O6—C22—O7	112.3 (6)
N1—C9—C8	102.9 (3)	O7'—C22—C23'	123.4 (10)
C10—C9—C8	114.1 (3)	O6—C22—C23'	118.1 (10)
N1—C9—H9	109.8	O7—C22—C23'	97.1 (11)
C10—C9—H9	109.8	O7'—C22—C23	113.9 (7)
C8—C9—H9	109.8	O6—C22—C23	119.8 (6)

C11—C10—C9	107.1 (3)	O7—C22—C23	120.2 (7)
C11—C10—H10A	110.3	C23'—C22—C23	33.0 (9)
C9—C10—H10A	110.3	C22—C23—H23A	109.5
C11—C10—H10B	110.3	C22—C23—H23B	109.5
C9—C10—H10B	110.3	C22—C23—H23C	109.5
H10A—C10—H10B	108.6	C22—C23'—H23D	109.5
C12—C11—C10	107.4 (4)	C22—C23'—H23E	109.5
C12—C11—C14	112.1 (3)	H23D—C23'—H23E	109.5
C10—C11—C14	110.0 (3)	C22—C23'—H23F	109.5
C12—C11—H11	109.1	H23D—C23'—H23F	109.5
C10—C11—H11	109.1	H23E—C23'—H23F	109.5
C9—N1—C1—O1	178.8 (4)	C16—C8—C9—C10	85.0 (4)
C13—N1—C1—O1	−22.9 (6)	C7—C8—C9—C10	−37.5 (4)
C9—N1—C1—C2	−4.2 (4)	C2—C8—C9—C10	−153.8 (3)
C13—N1—C1—C2	154.0 (3)	N1—C9—C10—C11	−49.0 (4)
O1—C1—C2—C17	−85.7 (5)	C8—C9—C10—C11	66.2 (4)
N1—C1—C2—C17	97.2 (4)	C9—C10—C11—C12	−55.4 (4)
O1—C1—C2—C3	32.0 (5)	C9—C10—C11—C14	66.8 (4)
N1—C1—C2—C3	−145.0 (3)	C6—C7—C12—O4	1.6 (6)
O1—C1—C2—C8	158.8 (4)	C8—C7—C12—O4	−178.0 (3)
N1—C1—C2—C8	−18.3 (4)	C6—C7—C12—C11	−177.2 (4)
C17—C2—C3—C4	174.9 (3)	C8—C7—C12—C11	3.2 (6)
C1—C2—C3—C4	54.9 (4)	C19—O4—C12—C7	−102.3 (4)

C8—C2—C3—C4	−61.4 (5)	C19—O4—C12—C11	76.7 (4)
C2—C3—C4—C5	90.3 (5)	C10—C11—C12—C7	24.5 (6)
C3—C4—C5—C21	84.4 (5)	C14—C11—C12—C7	−96.3 (5)
C3—C4—C5—C6	−40.6 (5)	C10—C11—C12—O4	−154.3 (3)
C21—C5—C6—C7	−164.8 (3)	C14—C11—C12—O4	84.8 (4)
C4—C5—C6—C7	−41.9 (5)	C1—N1—C13—C14	−103.0 (4)
C5—C6—C7—C12	−80.1 (5)	C9—N1—C13—C14	54.0 (5)
C5—C6—C7—C8	99.5 (4)	N1—C13—C14—C15	147.7 (4)
C12—C7—C8—C16	−120.4 (4)	N1—C13—C14—C11	−33.3 (5)
C6—C7—C8—C16	60.0 (4)	C12—C11—C14—C15	−85.1 (5)
C12—C7—C8—C9	2.6 (5)	C10—C11—C14—C15	155.5 (4)
C6—C7—C8—C9	−177.0 (3)	C12—C11—C14—C13	95.9 (4)
C12—C7—C8—C2	113.0 (4)	C10—C11—C14—C13	−23.5 (5)
C6—C7—C8—C2	−66.7 (4)	C18—O3—C17—O2	−1.0 (6)
C17—C2—C8—C16	34.2 (4)	C18—O3—C17—C2	178.8 (4)
C3—C2—C8—C16	−88.5 (4)	C3—C2—C17—O2	38.8 (6)
C1—C2—C8—C16	151.0 (3)	C1—C2—C17—O2	158.4 (4)
C17—C2—C8—C7	158.7 (3)	C8—C2—C17—O2	−90.8 (5)
C3—C2—C8—C7	36.1 (5)	C3—C2—C17—O3	−140.9 (4)
C1—C2—C8—C7	−84.5 (4)	C1—C2—C17—O3	−21.3 (5)
C17—C2—C8—C9	−84.9 (4)	C8—C2—C17—O3	89.4 (4)
C3—C2—C8—C9	152.4 (4)	C12—O4—C19—O5	4.4 (6)
C1—C2—C8—C9	31.8 (3)	C12—O4—C19—C20	−176.1 (4)

C1—N1—C9—C10	147.9 (3)	C22—O6—C21—C5	−145.1 (5)
C13—N1—C9—C10	−11.3 (4)	C4—C5—C21—O6	−179.5 (4)
C1—N1—C9—C8	25.8 (4)	C6—C5—C21—O6	−55.3 (5)
C13—N1—C9—C8	−133.3 (3)	C21—O6—C22—O7'	−15.9 (11)
C16—C8—C9—N1	−155.6 (3)	C21—O6—C22—O7	47.4 (9)
C7—C8—C9—N1	81.9 (3)	C21—O6—C22—C23'	159.1 (12)
C2—C8—C9—N1	−34.4 (4)	C21—O6—C22—C23	−163.1 (7)