Supporting Information for

A rapid construction of ABC tricyclic skeleton of Malabanone A

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Contents

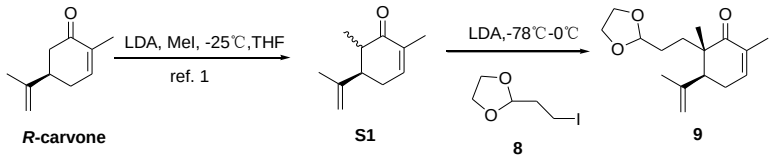
1. General Experimental Methods.

All reactions sensitive to air or moisture were carried out under argon atmosphere in dry and freshly distilled solvents under anhydrous conditions, unless otherwise noted. Column chromatography was performed on silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were obtained using 300 and 75MHz, 400 and 101MHz, or spectrometers respectively. Chemical shifts (δ) are given in ppm with reference to

solvent signals [^{1}H NMR: $CDCl_3$ (7.26); ^{13}C NMR: $CDCl_3$ (77.0)]. The high resolution mass spectra (HRMS) were recorded on an FT-ICR mass spectrometer using electrospray ionization (ESI). Optical rotations were measured on a precision automated polarimeter. Melting points were measured on a melting point apparatus.

2. Experimental procedures and characterization data of all synthetic new compounds

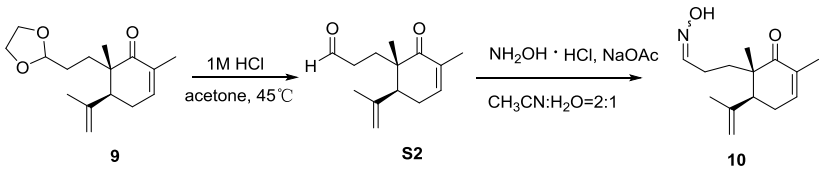
2.1 Preparation and spectra data of compound **9**



The known compound **S1** was prepared according to ref. 1 starting from commercially available (*R*)-carvone.

To a solution of diisopropylamine (11.60 mL, 82.90 mmol) in THF (100 mL) was added dropwise *n*-BuLi (2.5 M in THF, 29 mL, 73.10 mmol) at 0 ℃. After being stirred for 0.5 h, a solution of compound **S1** (8.0 g, 48.80 mmol) in THF (50 mL) was added dropwise. The resulting mixture was stirred for 4 h at -78 ℃ and treated with iodide **8** (22.20g, 97.50 mmol). After being stirred for an additional 16 h at 0 ℃, the reaction mixture was quenched with a saturated aqueous NH_4Cl solution. The aqueous phase was extracted with EtOAc. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuum. Flash chromatography on silica gel (petro ether / EtOAc, 100:1) afforded **9** (9.26 g, 71.8% yield) as colorless oil. $[\alpha]_D^{26}$ = -34.0°, (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.55 – 6.45 (m, 1H), 4.78 – 4.60 (m, 3H), 3.90 – 3.84 (m, 2H), 3.78 – 3.74 (m, 2H), 2.66 – 2.62 (m, 1H), 2.61 – 2.52 (m, 1H), 2.24 (dtd, *J* = 19.6, 4.4, 2.1 Hz, 1H), 1.69 (d, *J* = 1.5 Hz, 3H), 1.67 – 1.60 (m, 1H), 1.60 – 1.54 (m, 5H), 1.47 (ddd, *J* = 6.0, 5.3, 1.9 Hz, 1H), 0.95 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 203.6, 146.1 141.6 133.9 113.9, 104.4, 64.7 64.7 49.7 46.9 31.4, 28.6 28.5, 22.0, 19.1 16.3 pm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{16}H_{25}O_3$: 265.1798, found: 265.1796.

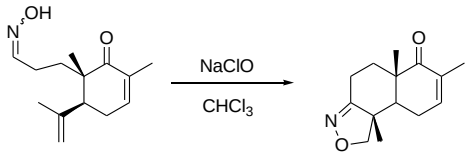
2.2 Preparation and spectra data of oxime **10**



A solution of compound **9** (2.71 g, 10.30 mmol) in acetone (80 mL) was treated with 1M HCl (51 mL) at 50℃ for 4 h. The reaction mixture was neutralized with saturated aqueous $NaHCO_3$ (25 mL). After evaporating most of the organic phase under reduced pressure, the residue was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure to afford compound S2 as colorless oil (2.12 g, 94.0% yield) which was used directly in the next step.

A solution of crude aldehyde S2 (2.53 g, 11.50 mmol) in acetonitrile (80 mL) was added to a solution of hydroxylamine hydrochloride (1.60 g, 2 equiv.) and sodium acetate (2.80 g, 3 equiv.) in water (40 mL).The resulting solution was stirred at ambient temperature for 3 h and then extracted with EtOAc (3 × 60 mL).The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (petro ether / EtOAc, 10:1 to 5:1) to afford compound **10** as colorless oil (2.02 g, 75.0% yield), which comprised a 1:1 mixture *E*- and *Z*-isomers. $[\alpha]_D^{26}$ = -55.0°, (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (s, 1H), 7.37 (t, *J* = 5.8 Hz, 1H), 6.58 (td, *J* = 4.0, 1.3 Hz, 1H), 4.80 (s, 1H), 4.73 (s, 1H), 2.71 (t, *J* = 5.9 Hz, 1H), 2.60 – 2.47 (m, 1H), 2.37 (dd, *J* = 4.0, 2.0 Hz, 1H), 2.22 – 2.03 (m, 2H), 1.83 – 1.77 (m, 1H), 1.76 (t, *J* = 3.1 Hz, 3H), 1.72 – 1.65 (m, 1H), 1.64 (s, 3H), 1.03 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 203.5, 151.8, 145.7, 142.2, 134.1, 114.5, 49.5, 47.4, 33.7, 28.7, 24.7, 22.3, 19.2, 16.4 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{22}NO_2$: 236.1645, found: 236.1643.

2.3 Preparation and spectra data of **7**

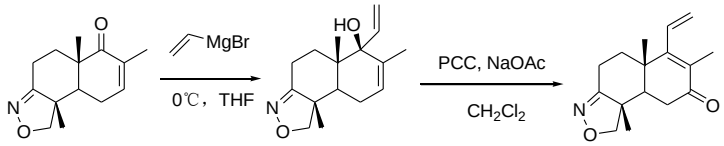


10 **7**

A solution of compound **10** (448.00 mg, 1.90 mmol) in $CHCl_3$(45 mL) was added 14.5% aqueous sodium hypochlorite (1.84 mL, 3.81 mmol) at room temperature. After stirring for 5 h, the reaction was quenched with aqueous sodium thiosulfate. After separation of the phases, the aqueous phase was extracted with chloroform and the combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (petro ether / EtOAc, 10:1) to afford compound **7** as a white solid (249.00 mg, 56.0% yield). Mp:78-83℃. $[\alpha]_D^{24}$ = -74.4°, (c = 0.9 , $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.66 (d, *J* = 5.7 Hz, 1H), 4.11 (d, *J* = 7.7 Hz, 1H), 3.78 (d, *J* = 7.7 Hz, 1H), 2.69 (ddd, *J* = 14.8, 4.5, 2.4 Hz, 1H), 2.57 – 2.46 (m, 1H), 2.37 (td, *J* = 14.5, 4.9 Hz, 1H), 2.24 (ddd, *J* = 14.1, 4.8, 2.4 Hz, 1H), 2.06 (dd, *J* = 11.6, 4.2 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.76 – 1.71 (m, 3H), 1.51 (td, *J* = 14.1, 4.5 Hz, 1H), 1.28 (s, 3H), 1.16 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 202.9, 163.5,

141.9, 133.7, 82.9, 53.6, 49.7, 44.8, 32.6, 25.8, 18.9, 18.6, 16.4, 16.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1489, found: 234.1487.

2.4 Preparation and spectra data of alcohol **6**

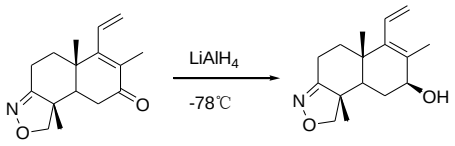


7 **S3** **6**

A solution of compound **7** (432.00 mg, 1.90 mmol) under argon at 0 ℃ in 50 mL of dry THF was slowly added 13.3 mL of a 1 M solution of vinylmagnesium bromide in THF. The reaction was allowed to warm to room temperature and stirred for 3 h. The reaction was quenched with aqueous saturated ammonium chloride and extracted with three 50 mL portions of EtOAc. The extracts were combined and dried over anhydrous Na_2SO_4, and the solvent was removed in vacuum and the residue was purified by flash column chromatography on silica gel (petro ether / EtOAc, 10:1) to afford compound **S3** as white solid (396.80 mg, 82.0% yield) which was used directly in the next step. The configuration of compound **S3** was determined by analogy with the literature 1b

To a magnetically stirred solution of crude alcohol **S3** (355.00 mg, 1.36 mmol) in anhydrous CH_2Cl_2 (30 mL) was added a homogeneous mixture of PCC (1.46 g, 6.79 mmol) , 4 Å molecular sieve(1.46 g) and sodium acetate(781 mg, 9.52 mmol) and stirred at room temperature for 3 h. The reaction mixture was filtered through a small pad of silica gel using ether (50 mL) as eluent. Evaporation of the solvent and further purification of the residue by flash chromatography on silica gel (petro ether / EtOAc, 5:1) furnished the ketone **6** (281.80 mg, 80.0% yield) as a white solid. Mp: 160−165℃. $[\alpha]_D^{24}$ = -1.0 °, (c = 1.0 , CH_2Cl_2) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.29 (ddd, *J* = 17.7, 11.7, 1.1 Hz, 1H), 5.55 (dd, *J* = 11.7, 1.8 Hz, 1H), 5.17 (dd, *J* = 17.7, 1.8 Hz, 1H), 4.13 (d, *J* = 7.8 Hz, 1H), 3.80 (d, *J* = 7.8 Hz, 1H), 2.77 – 2.64 (m, 2H), 2.46 (ddd, *J* = 15.0, 13.9, 5.0 Hz, 1H), 2.19 (d, *J* = 2.3 Hz, 1H), 2.08 (ddd, *J* = 13.4, 4.9, 2.5 Hz, 1H), 1.80 (d, *J* = 1.1 Hz, 3H), 1.60 (s, 1H), 1.49 (td, *J* = 13.8, 4.8 Hz, 1H), 1.28 (s, 3H), 1.27 (d, *J* = 0.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 198.0, 162.9, 162.3, 132.4, 129.8, 121.7, 83.1, 53.1, 49.9, 39.4, 36.6, 36.2, 19.1, 17.7, 17.5, 13.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{16}H_{22}NO_2$: 260.1645, found: 260.1644.

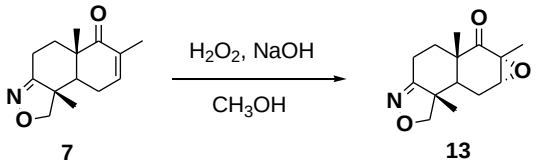
2.5 Preparation and spectra data of compound **11**



6 **11**

To a solution of **6** (42.00 mg, 0.16 mmol) in dry THF (20 mL) was added $LiAlH_4$(31.00 mg, 0.80 mmol) in batches at -78℃. The reaction was stirred for 0.5 h at -78℃ and quenched with saturated aqueous NH_4Cl (5 mL). After evaporating most of the organic phase under reduced pressure, the residue was extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography on silica gel (petro ether / EtOAc, 5:1) to afford product **11** as a white solid (41.00 mg, 98.0% yield). Mp:129−134℃. $[\alpha]_D^{24}$= 94.0°, (c = 1.0 , CH_2Cl_2) ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.08 (ddd, *J* = 12.2, 11.7, 6.1 Hz, 1H), 5.34 (dd, *J* = 11.3, 2.4 Hz, 1H), 5.00 (dd, *J* = 17.6, 2.4 Hz, 1H), 4.15 (dd, *J* = 14.9, 7.5 Hz, 2H), 3.77 (d, *J* = 7.7 Hz, 1H), 2.62 (ddd, *J* = 15.0, 4.5, 2.3 Hz, 1H), 2.45 – 2.32 (m, 1H), 1.97 (ddd, *J* = 13.2, 5.0, 2.4 Hz, 1H), 1.88 (d, *J* = 22.1 Hz, 1H), 1.75 (d, *J* = 3.5 Hz, 1H), 1.73 (s, 3H), 1.33 (dd, *J* = 13.7, 4.6 Hz, 1H), 1.26 (d, *J* = 8.3 Hz, 1H), 1.22 (d, *J* = 0.6 Hz, 3H), 1.16 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.2, 143.0, 133.7, 129.8, 120.5, 83.6, 72.0, 53.6, 49.7, 38.3, 36.7, 31.8, 19.3, 19.2, 17.9, 16.7 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO_2$: 262.1802, found: 262.1800.

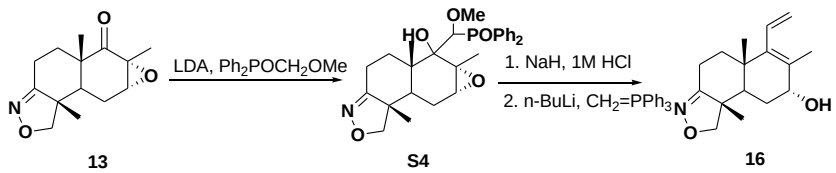
2.6 Preparation and spectra data of compound **13**



7 **13**

1 M NaOH (2.40 mL, 2.40 mmol) and 30% H_2O_2 (0.25 mL, 2.40 mmol) were added to a solution of the compound **7** (114.00 mg, 0.49 mmol) in MeOH (25 mL) at 0℃. The solution was stirred for 5 h at room temperature and then poured into a saturated aq. solution of $Na_2S_2O_3$. The solution was extracted with EtOAc and worked up as usual. The white solid residue obtained was purified by flash column chromatography (petro ether / EtOAc, 3:1) to afford **13** as a white solid (115.00 mg, 94.8% yield). Mp: 159−164℃. $[\alpha]_D^{26}$ = -45.0°, (c = 1.0 , CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.06 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 7.8 Hz, 1H), 3.36 (d, *J* = 1.3 Hz, 1H), 2.62 (ddd, *J* = 14.7, 4.5, 2.4 Hz, 1H), 2.26 (td, *J* = 14.5, 4.8 Hz, 1H), 2.20 – 2.09 (m, 2H), 1.98 (dd, *J* = 12.7, 3.9 Hz, 1H), 1.88 – 1.81 (m, 1H), 1.46 (dd, *J* = 14.1, 4.4 Hz, 1H), 1.37 (s, 3H), 1.19 (d, *J* = 2.7 Hz, 3H), 1.10 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 205.8, 163.1, 82.9, 58.8, 56.5, 52.6, 45.56, 39.8, 31.8, 24.0, 19.0, 18.3, 16.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{14}H_{20}NO_3$: 250.1438, found: 250.1436.

2.7 Preparation and spectra data of compound **16**



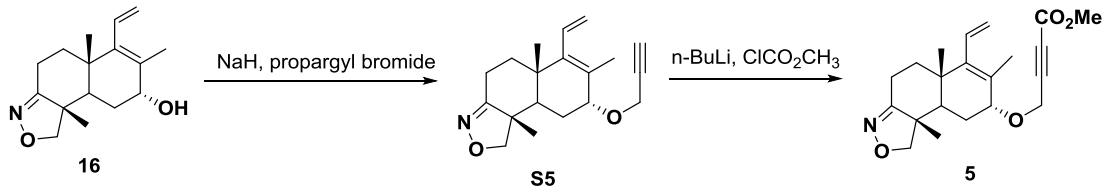
13 **S4** **16**

A solution of LDA in THF (1.47 mL, 2.0 M, 2.93 mmol) was added dropwise to a solution of $Ph_2POCH_2OCH_3$ (723.00 mg, 2.93 mmol) in dry THF (25 mL) at 0℃. After stirring for 0.5 h at 0℃ and then 30 min at room temperature, the mixture was cooled to -78℃and treated slowly with a solution of the epoxy-ketone **13** (244.00 mg, 0.98 mmol) in THF (10 mL). The reaction mixture was stirred for 2.5 h, during which time the temperature raised to -50℃, then treated with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. Workup as usual afforded a solid residue, which was purified by flash chromatography on silica gel (petro ether / EtOAc, 3:1), to afford a mixture of two epimeric β-hydroxyphosphine oxides **S4** as a white solid (439.00 mg, 90.5% yield).

To a suspension of NaH (68.60 mg of a 60% suspension in mineral oil, 1.71 mmol), previously washed with anhydrous pentane, in anhydrous THF (15 mL) maintained at 0℃, was added dropwise during 1 h a solution of the above mixture of β-hydroxyphosphine oxides **S4** (170.00 mg, 0.34 mmol) in the same THF (15 mL). The resulting suspension was stirred at the same temperature for 2 h, then raised to room temperature and cautiously treated with water (4 mL) to decompose the excess NaH. The homogeneous reaction mixture obtained was stirred at the same temperature until the hydrogen evolution ceased and then treated with 1 M HCl (8 mL). After stirring at room temperature for 1 h the mixture was poured into a saturated aq. solution of $NaHCO_3$ and the product was extracted with EtOAc and worked up. The crude product obtained was purified by flash column chromatography on silica gel (petro ether / ethyl acetate, 3:1) to give the hydroxyaldehyde **15** (68.00 mg, 75.0% yield from S4) as a white solid.

A suspension of methyltriphenylphosphonium bromide (521.00 mg, 1.46 mmol) in THF (20 mL) at 0℃ was treated with n-BuLi (0.58 mL of a 2.5 M solution in hexanes, 1.46 mmol). The mixture was stirred for 0.5 h while allowed to warm to room temperature. The resulting deep yellow solution was cooled to 0℃ and a solution of the aldehyde 15 (128.00 mg, 0.48 mmol) in THF (8 mL) was added to give a pale yellow mixture that was stirred for 1 min and then allowed to warm to room temperature for 1 h. The reaction was quenched with aq. NH_4Cl, extracted with EtOAc and worked up. The residue was purified by flash column chromatography on silica gel (petro ether / ethyl acetate 5:1) to furnish the dienol **16** (113.00 mg, 88.9% yield) as a white solid. Mp: 124−130℃. $[\alpha]_D^{26}$ = 89.0 °, (c = 1.0, CH_2Cl_2) ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.08 (dd, *J* = 17.7, 11.3 Hz, 1H), 5.34 (dd, *J* = 11.3, 2.3 Hz, 1H), 4.99 (dd, *J* = 17.7, 2.3 Hz, 1H), 4.11 (d, *J* = 7.7 Hz, 1H), 4.01 (d, *J* = 3.5 Hz, 1H), 3.83 (d, *J* = 7.7 Hz, 1H), 2.61 (ddd, *J* = 15.0, 4.5, 2.3 Hz, 1H), 2.43 – 2.32 (m, 1H), 2.20 (s, 1H), 1.93 (ddd, *J* = 7.3, 6.7, 3.4 Hz, 2H), 1.78 (s, 3H), 1.38 (d, *J* = 13.2 Hz, 1H), 1.35 – 1.21 (m, 2H), 1.19 (s, 3H), 1.07 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.5, 143.4, 1335, 128.3, 120.2, 83.6, 68.9, 53.5, 45.9, 38.1, 36.4, 31.1, 19.3, 18.9, 17.9, 17.6 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{16}H_{24}NO_2$: 262.1802, found: 262.1800.

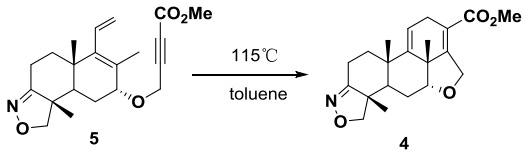
2.8 Preparation and spectra data of alkyne **5**



To a suspension of NaH (695.00 mg of a 60% suspension in mineral oil, 28.90 mmol), previously washed with anhydrous pentane, in anhydrous THF (35 mL), was evaporated with the aid of a current of argon to leave an oily residue, to which compound **16**, tetrabutylammonium iodide (TBAI) (1.28 g, 3.47 mmol) and propargyl bromide (3.30 mL, 34.70 mmol) were added successively. The mixture was vigorously stirred in a bath thermostated at 25 ℃ for 26 h. After this time, the brownish reaction mixture was poured into water, extracted with EtOAc. The brown oily residue obtained was purified by flash column chromatography (petro ether / ethyl acetate, 10:1) to afford propargyl ether **S5** (353.00 mg, 68.0% yield).

A solution of propargyl ether **S5** (313.00 mg, 1.04 mmol) in THF (20 mL) at -78℃ was treated dropwise with a solution of n-BuLi in hexanes (2.10 mL, 2.5 M, 5.25 mmol). After 30 minutes, the reaction mixture was treated with methyl chloroformate (0.57 mL, 7.30 mmol) and stirred at the same temperature for 3 h. Saturated aq. NH_4Cl and the aqueous phase was extracted with EtOAc. Work up followed by flash column chromatography on silica gel (petro ether / ethyl acetate, 5:1) afforded the acetylenic ester **5** (258.00 mg,72.0% yield).$[\alpha]_D^{26}$ = 23.0 °, (c = 1.0 , CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.10 (dd, *J* = 17.7, 11.3 Hz, 1H), 5.36 (dd, *J* = 11.3, 2.3 Hz, 1H), 5.03 (dd, *J* = 17.7, 2.3 Hz, 1H), 4.32 (s, 2H), 4.15 (d, *J* = 7.6 Hz, 1H), 3.83 (dd, *J* = 9.6, 5.7 Hz, 2H), 3.79 (s, 3H), 2.63 (ddd, *J* = 15.0, 4.4, 2.3 Hz, 1H), 2.38 (td, *J* = 14.4, 5.1 Hz, 1H), 1.94 (d, *J* = 13.4 Hz, 2H), 1.88 (dd, *J* = 13.6, 4.1 Hz, 1H), 1.78 (s, 3H), 1.54 (d, *J* = 13.6 Hz, 1H), 1.33 (td, *J* = 13.6, 4.5 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.1, 153.4, 144.8, 133.4, 126.6, 120.4, 84.1, 83.6, 77.7, 77.1, 56.5, 53.4, 52.8, 46.1, 38.0, 36.3, 26.4, 19.3, 18.7, 17.9, 17.6 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{21}H_{28}NO_4$: 358.2013, found: 358.2011.

2.9 Preparation and spectra data of **4**



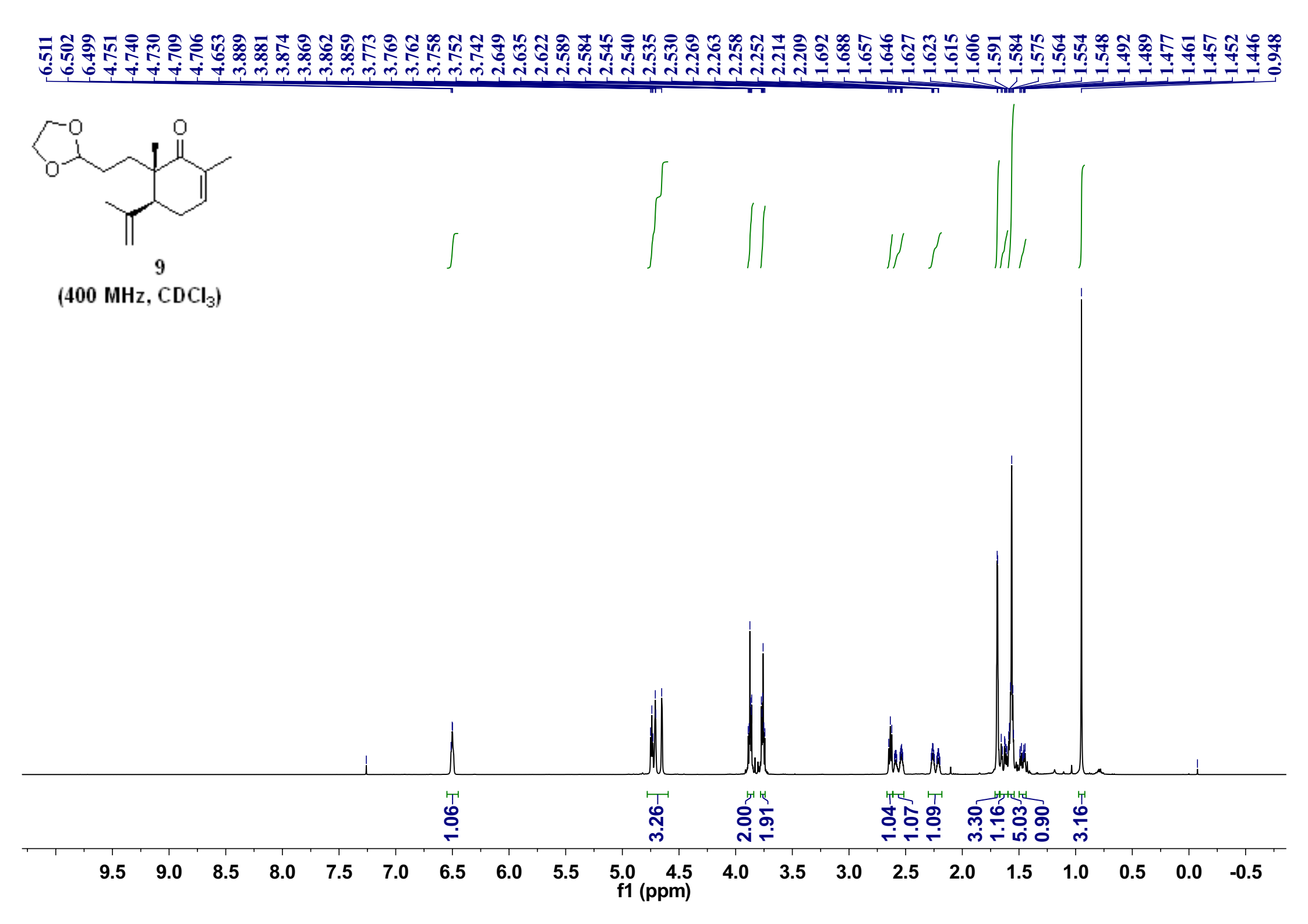
A solution of diene **5** (136.00 mg, 0.39 mmol) in degassed anhydrous toluene (2 mL) was heated in a vacuum sealed ampoule at 115℃ for 17 h. After evaporation of the solvent under reduced pressure, the residue was purified by flash chromatography on silica gel (petro ether / ethyl acetate, 3:1) to afford the Diels–Alder adduct **4** (121.00 mg, 89.0% yield) as a white solid. Mp: 182−186℃. $[\alpha]_D^{26}$ = 108.0 °, (c = 1.0 , CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.75 (d, *J* = 5.4 Hz, 1H), 4.95 (dd, *J* = 14.0, 2.2 Hz, 1H), 4.31 (dd, *J* = 14.0, 3.8 Hz, 1H), 4.11 (dd, *J* = 7.4, 4.6 Hz, 1H), 3.92 –

3.86 (m, 1H), 3.76 (d, *J* = 7.5 Hz, 4H), 3.36 (dd, *J* = 20.7, 6.5 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.41 (td, *J* = 14.5, 4.6 Hz, 1H), 2.31 – 2.15 (m, 2H), 1.62 (dd, *J* = 11.1, 3.0 Hz, 2H), 1.51 (td, *J* = 13.7, 4.3 Hz, 1H), 1.27 (s, 3H), 1.21 (s, 3H), 1.13 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.5, 164.1, 163.0, 151.9, 121.7, 119.4, 83.5, 81.7, 68.8, 53.4, 51.7, 45.7, 44.5, 38.1, 37.3, 27.1, 26.9, 24.5, 20.9, 19.1, 18.3 ppm. **HRMS (ESI)**: m/z $[M+H]^+$ calcd for $C_{21}H_{28}NO_4$: 358.2013, found: 358.2012.

3. References

1. (a) J. P. Gesson, S. A. M. Nieuwenhuis and B. Renoux, *Nat. Prod. Lett*, 1993, **2**, 129; (b) Z. Z. Zhong, G. Y. Zhao, D. Y. Xu, B. B. Dong, D. P. Song, X. G. Xie and X. G. She, *Chem. Asian J*., 2016, **11**, 1542.

4. NMR spectra of all synthetic new compounds.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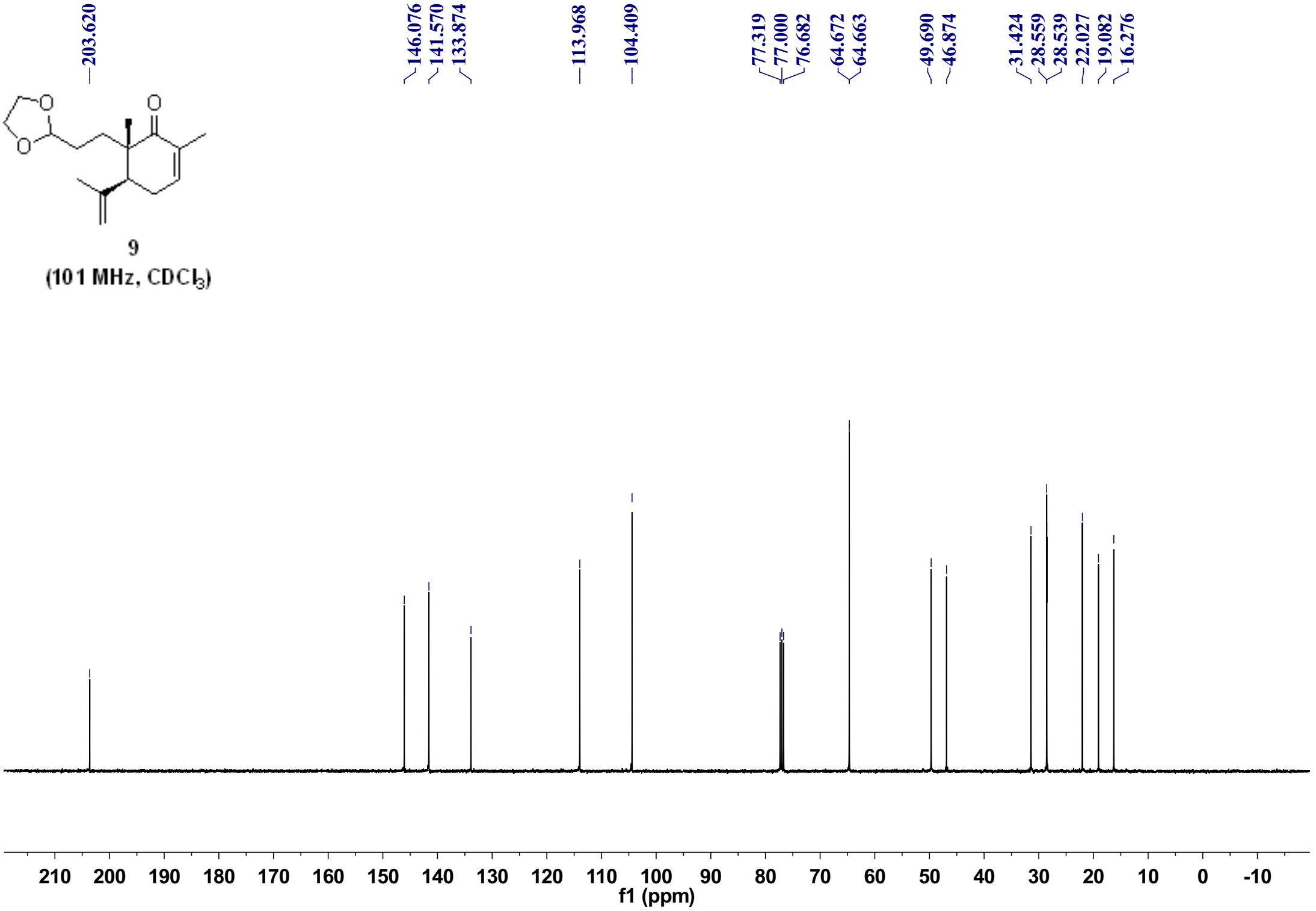
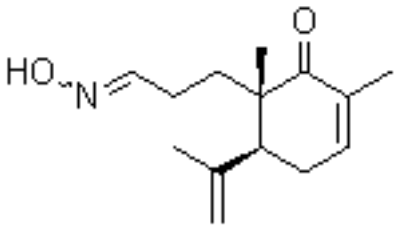
6.502
6.499
4.751
4.740
4.730
4.709
4.706
4.653
3.889
3.881
3.874
3.869
3.862
3.859
3.773
3.769
3.762
3.758
3.752
3.742
2.649
2.635
2.622
2.589
2.584
2.545
2.540
2.535
2.530
2.269
2.263
2.258
2.252
2.214
2.209
1.692
1.688
1.657
1.646
1.627
1.623
1.615
1.606
1.591
1.584
1.575
1.564
1.554
1.548
1.492
1.489
1.477
1.461
1.457
1.452
1.446
0.948
O
O
O
9
(400 MHz, CDCl3)
1.06
3.26
2.00
1.91
1.04
1.07
1.09
3.30
1.16
5.03
0.90
3.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


203.620
146.076
141.570
133.874
113.968
104.409
77.319
77.000
76.682
64.672
64.663
49.690
46.874
31.424
28.559
28.539
22.027
19.082
16.276
O
O
O
9
(101 MHz, CDCl3)
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)



10

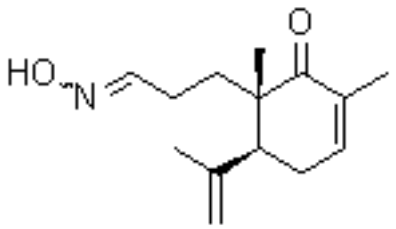
(400 MHz, $CDCl_3$)

8.291
7.386
7.371
7.357
7.260
6.594
6.591
6.584
6.581
6.574
6.571
4.802
4.733
2.720
2.706
2.691
2.147
2.093
1.795
1.782
1.766
1.754
1.750
1.708
1.695
1.678
1.666
1.641
1.627
-0.021

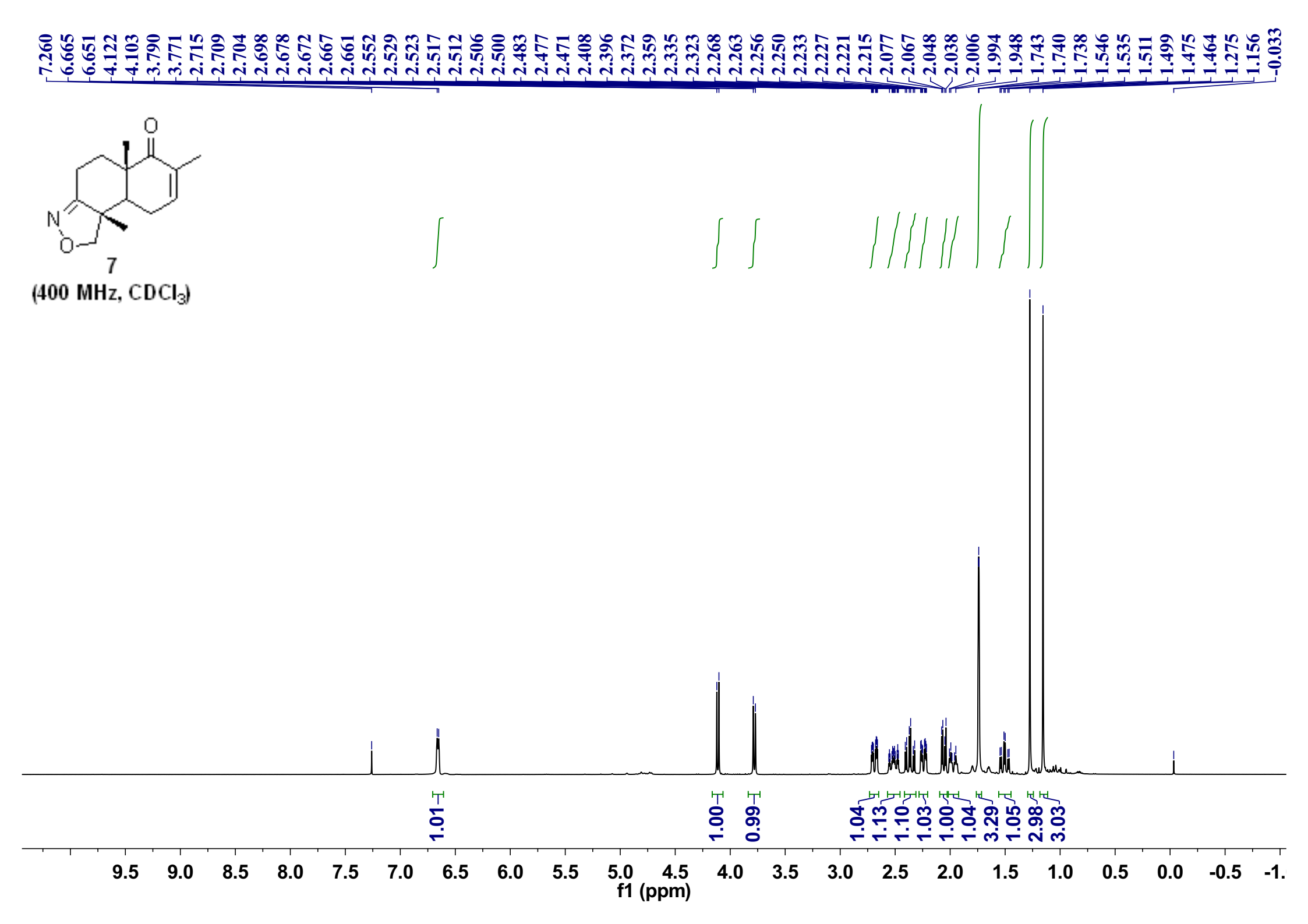
0.95
0.96
1.00
0.96
1.04
1.01
1.19
1.16
2.29
0.97
3.42
1.09
3.08
2.94

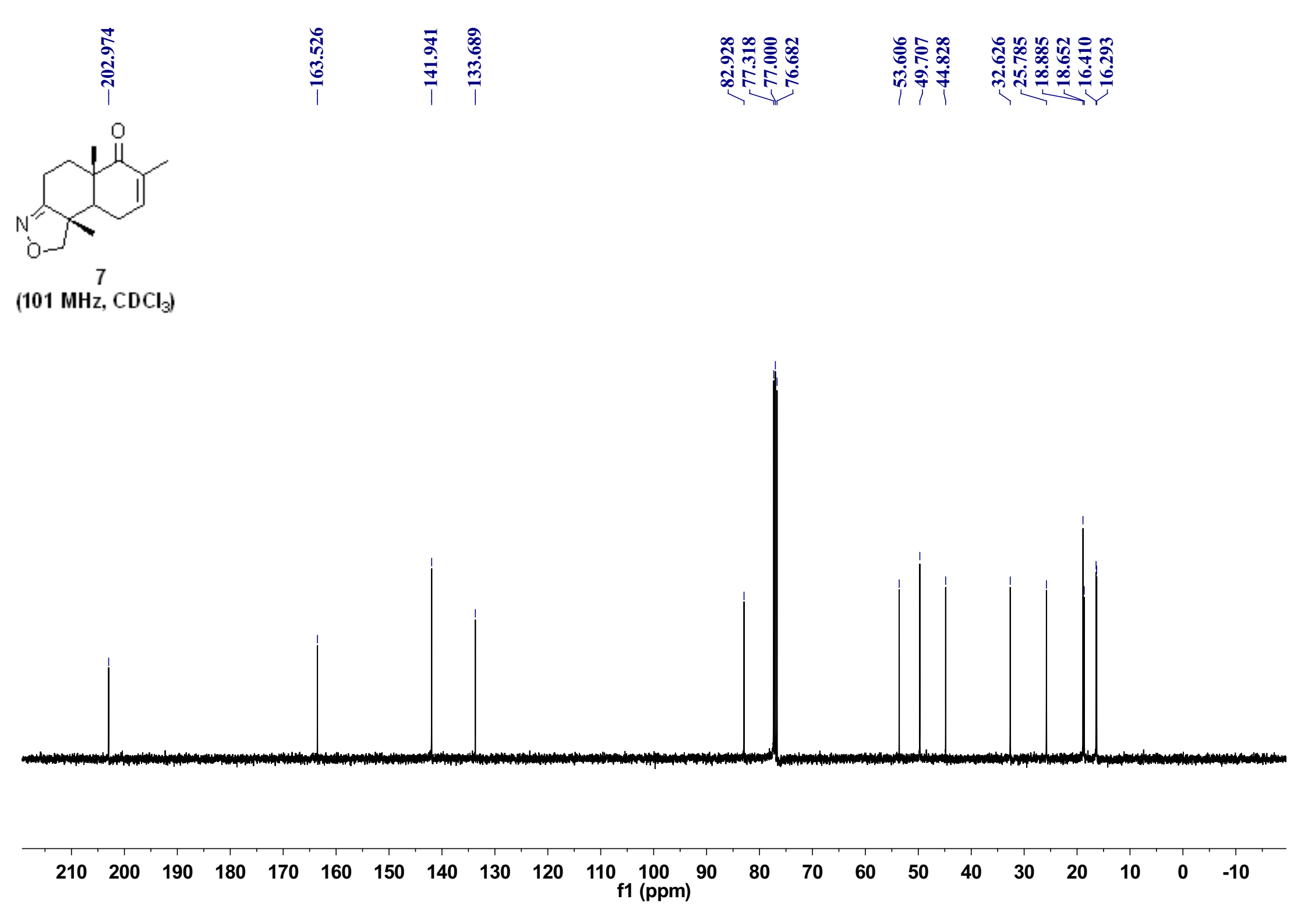
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

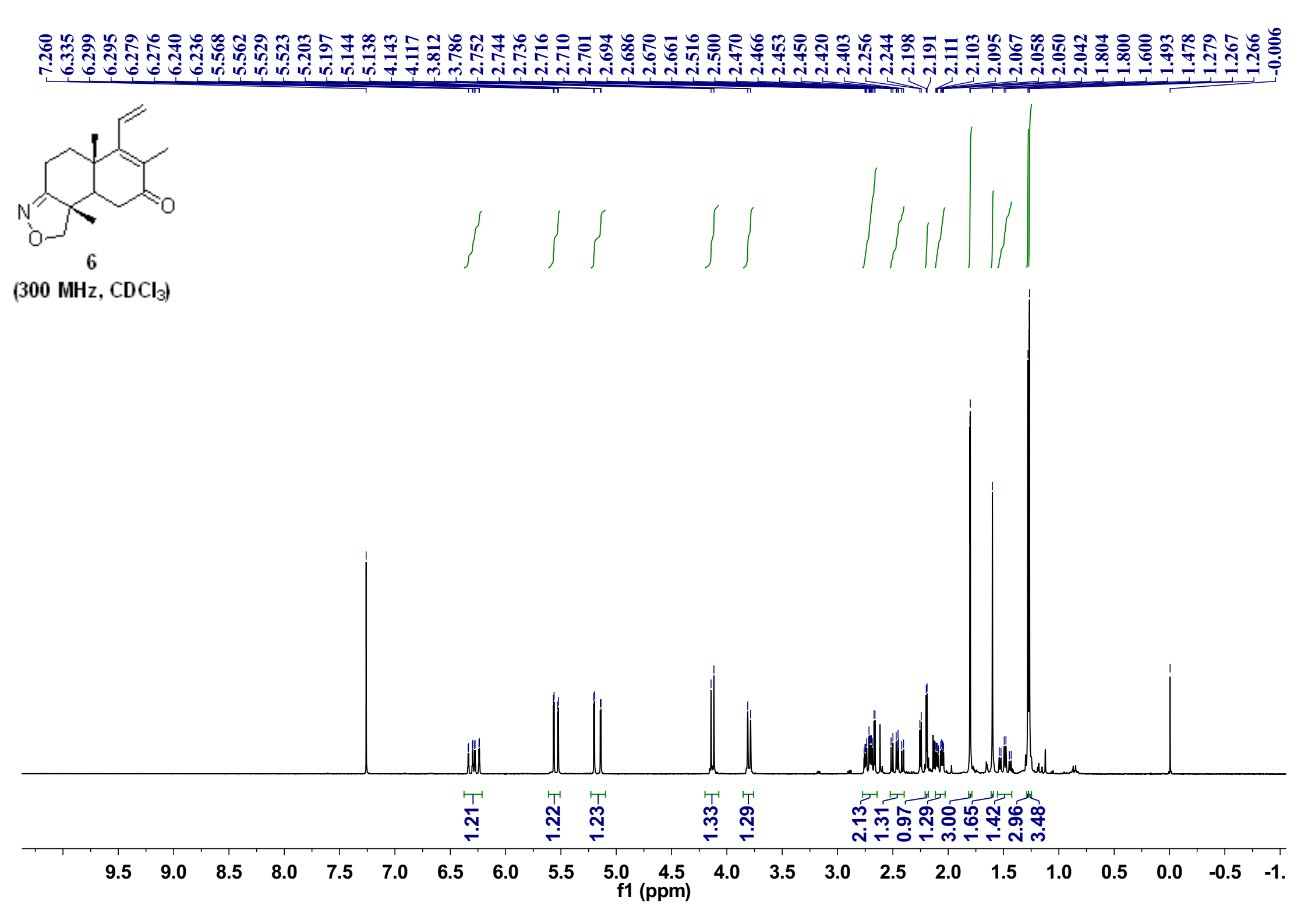
f1 (ppm)

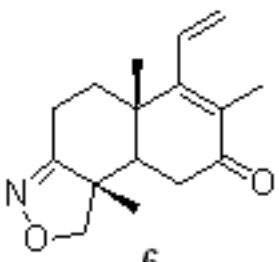


10
(101 MHz, $CDCl_3$)


7.260
6.665
6.651
4.122
4.103
3.790
3.771
2.715
2.709
2.704
2.698
2.678
2.672
2.667
2.661
2.552
2.529
2.523
2.517
2.512
2.506
2.500
2.483
2.477
2.471
2.408
2.396
2.372
2.359
2.335
2.323
2.268
2.263
2.256
2.250
2.233
2.227
2.221
2.215
2.077
2.067
2.048
2.038
2.006
1.994
1.948
1.743
1.740
1.738
1.546
1.535
1.511
1.499
1.475
1.464
1.275
1.156
-0.033
O
N
O
7
(400 MHz, CDCl3)
1.01
1.00
0.99
1.04
1.13
1.10
1.03
1.00
1.04
3.29
1.05
2.98
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


202.974
163.526
141.941
133.689
82.928
77.318
77.000
76.682
53.606
49.707
44.828
32.626
25.785
18.885
18.652
16.410
16.293
O
N
O
7
(101 MHz, CDCl3)
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)

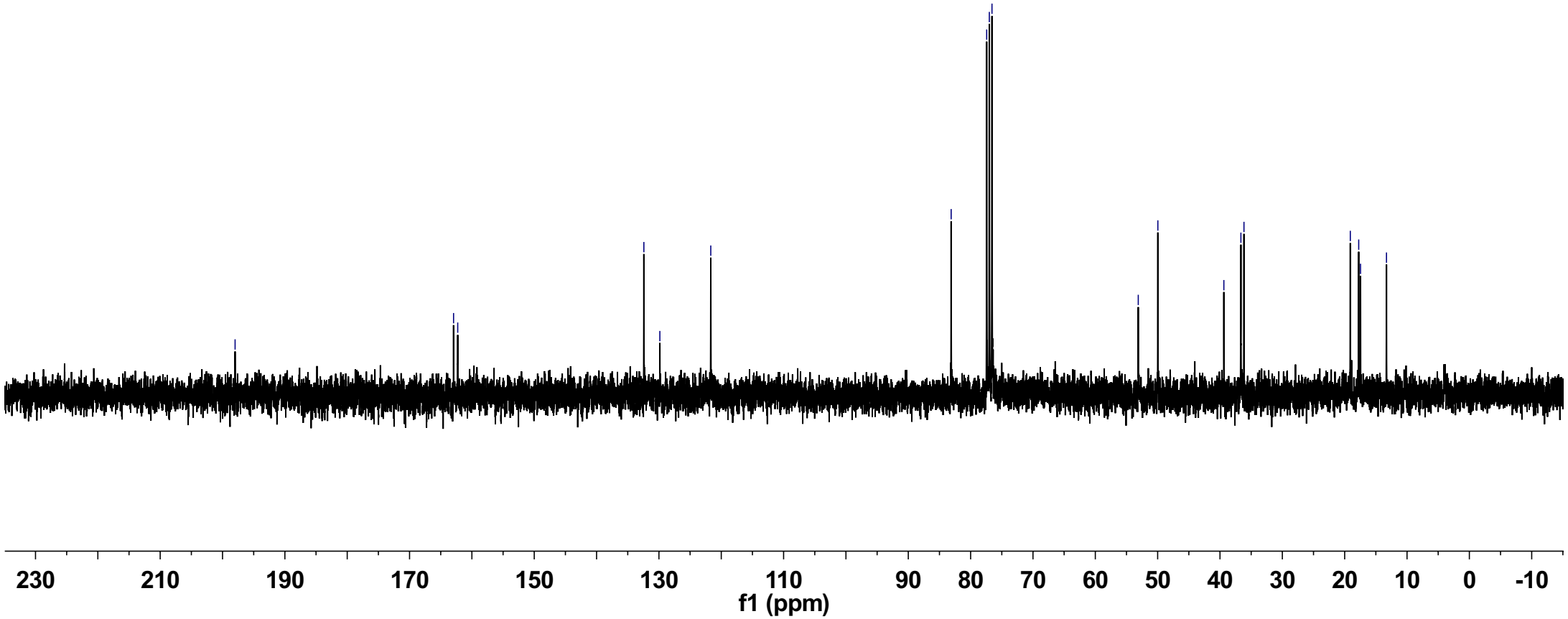

7.260
6.335
6.299
6.295
6.279
6.276
6.240
6.236
5.568
5.562
5.529
5.523
5.203
5.197
5.144
5.138
4.143
4.117
3.812
3.786
2.752
2.744
2.736
2.716
2.710
2.701
2.694
2.686
2.670
2.661
2.516
2.500
2.470
2.466
2.453
2.450
2.420
2.403
2.256
2.244
2.198
2.191
2.111
2.103
2.095
2.067
2.058
2.050
2.042
1.804
1.800
1.600
1.493
1.478
1.279
1.267
1.266
-0.006
N
O
O
6
(300 MHz, CDCl3)
1.21
1.22
1.23
1.33
1.29
2.13
1.31
0.97
1.29
3.00
1.65
1.42
2.96
3.48
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

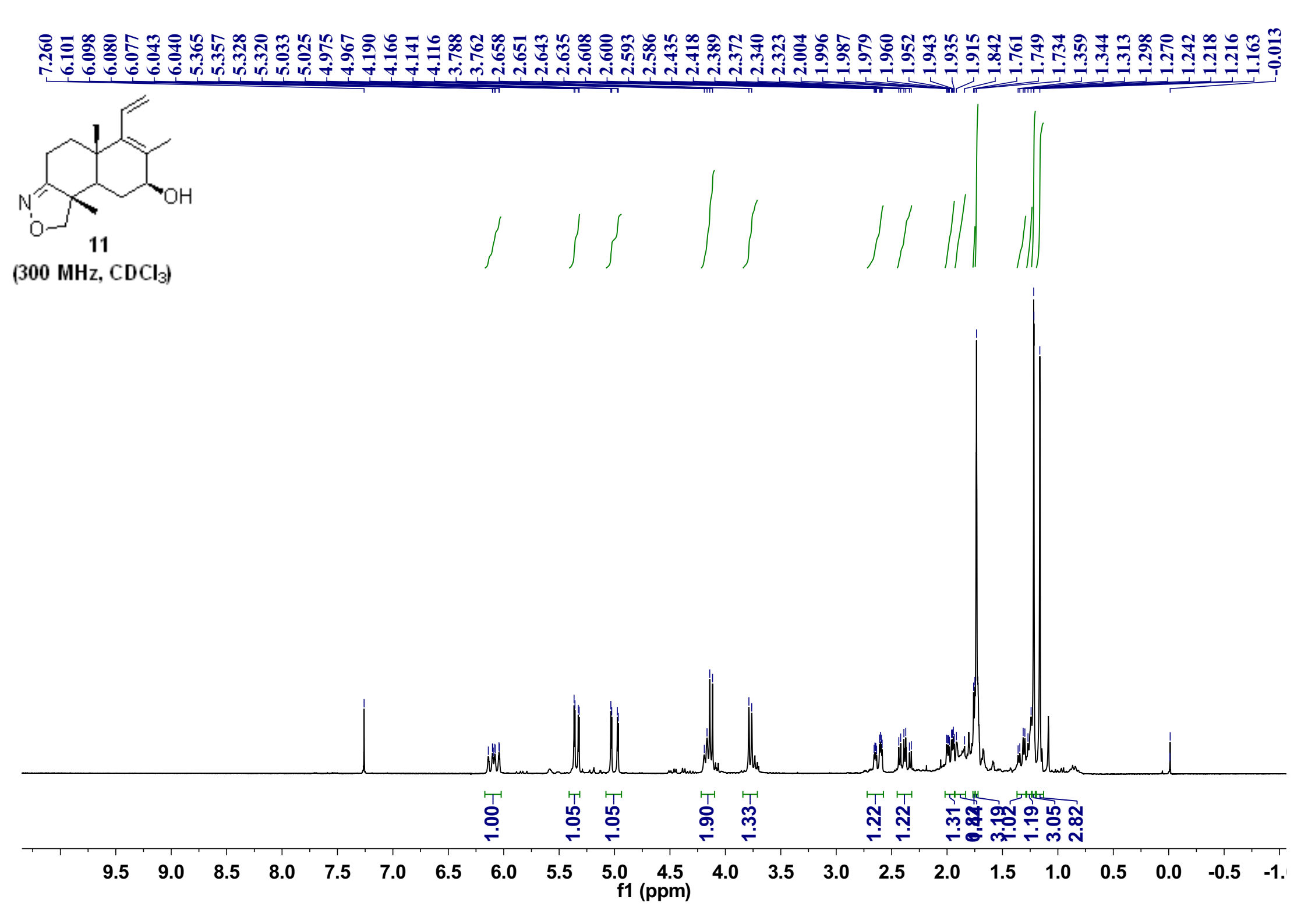


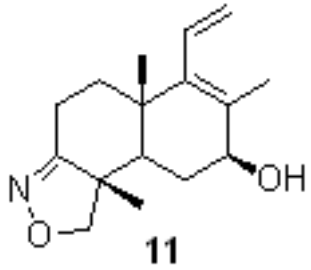
6

(75 MHz, $CDCl_3$)

197.985
162.940
162.273
132.415
129.850
121.682
83.124
77.423
77.000
76.576
53.110
49.968
39.380
36.645
36.154
19.098
17.749
17.460
13.294



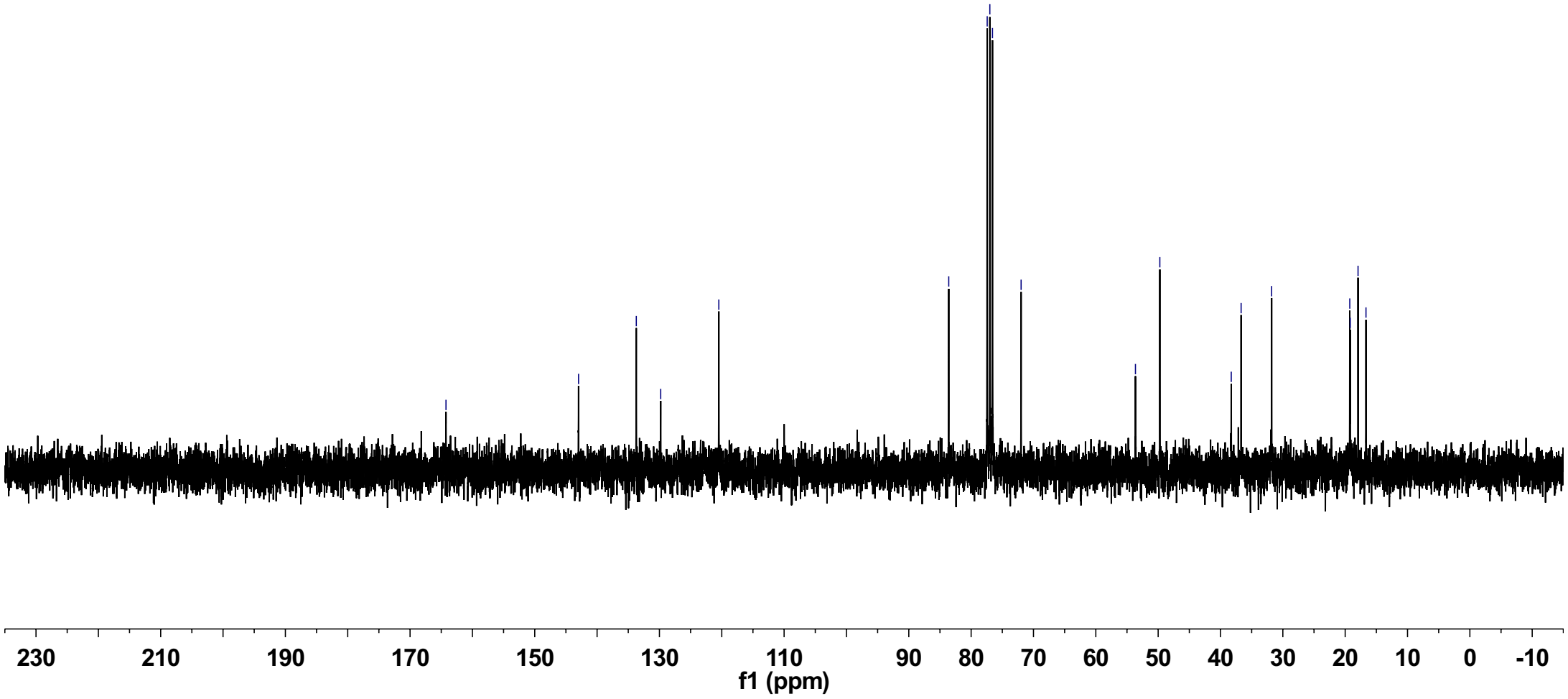

7.260
6.101
6.098
6.080
6.077
6.043
6.040
5.365
5.357
5.328
5.320
5.033
5.025
4.975
4.967
4.190
4.166
4.141
4.116
3.788
3.762
2.658
2.651
2.643
2.635
2.608
2.600
2.593
2.586
2.435
2.418
2.389
2.372
2.340
2.323
2.004
1.996
1.987
1.979
1.960
1.952
1.943
1.935
1.915
1.842
1.761
1.749
1.734
1.359
1.344
1.313
1.298
1.270
1.242
1.218
1.216
1.163
-0.013
N
O
OH
11
(300 MHz, CDCl3)
1.00
1.05
1.05
1.90
1.33
1.22
1.22
1.31
3.19
1.02
1.19
3.05
2.82
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

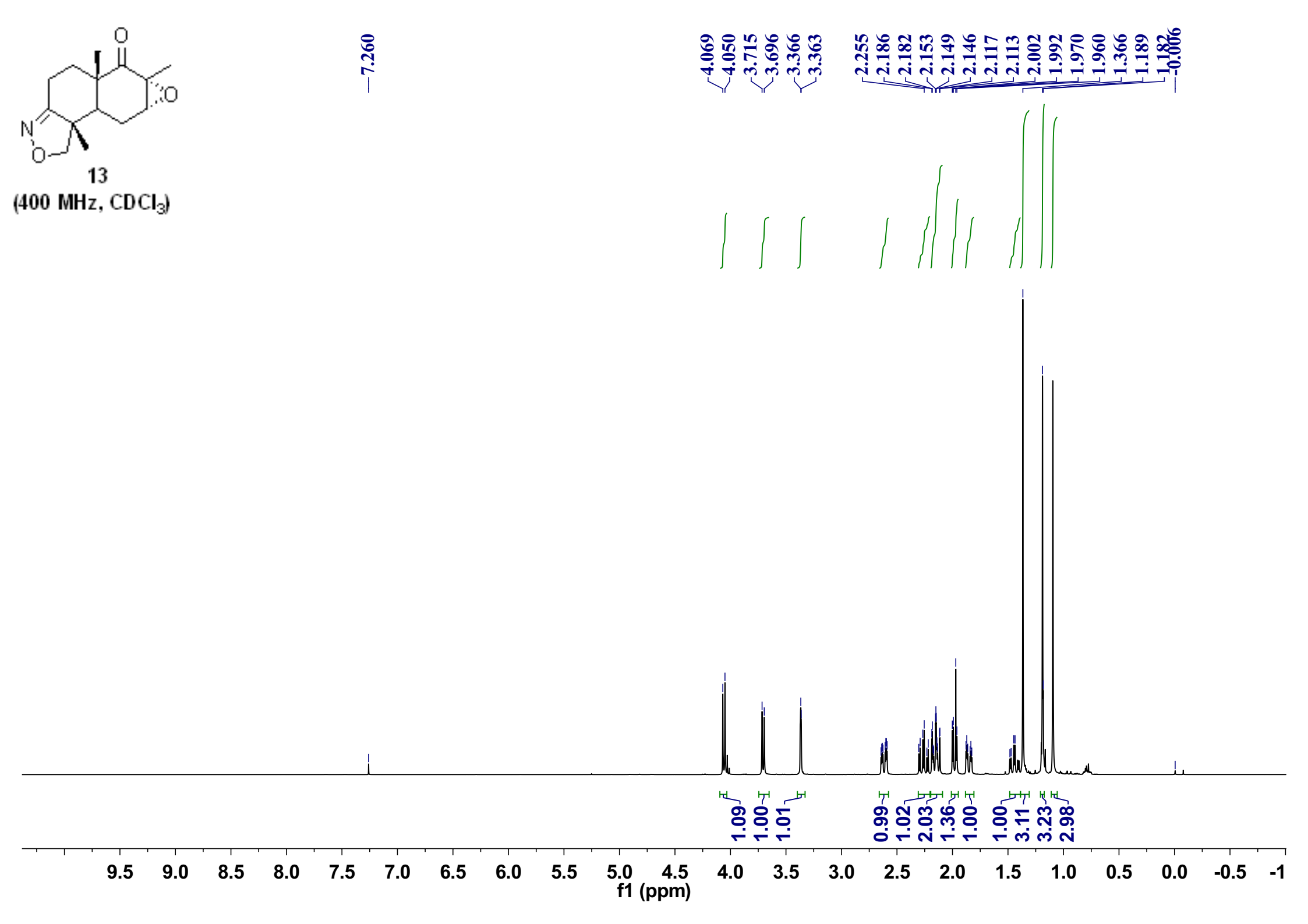


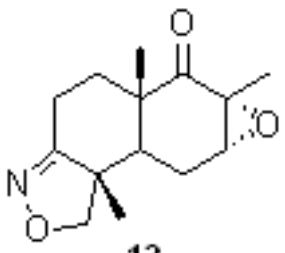
11

(75 MHz, $CDCl_3$)

164.237
142.969
133.710
129.794
120.471
83.591
77.424
77.000
76.576
71.983
53.644
49.730
38.277
36.694
31.797
19.262
19.186
17.938
16.663

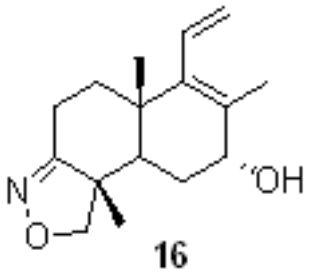



13
(400 MHz, CDCl3)
7.260
4.069
4.050
3.715
3.696
3.366
3.363
2.255
2.186
2.182
2.153
2.149
2.146
2.117
2.113
2.002
1.992
1.970
1.960
1.366
1.189
1.182
0.006
1.09
1.00
1.01
0.99
1.02
2.03
1.36
1.00
1.00
3.11
3.23
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



13

(101 MHz, $CDCl_3$)



16

(400 MHz, $CDCl_3$)

7.260

6.120 6.092 6.076 6.048

5.353 5.348 5.319

5.019 5.013

4.975 4.123 4.104 4.011 4.002

3.840 3.821

2.589 2.382 2.369

1.965 1.954 1.926 1.923 1.914

1.784

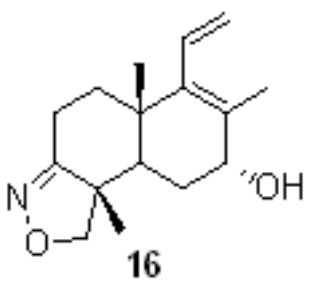
1.399 1.366 1.299 1.287 1.253 1.235 1.189

1.069 0.028

1.00 1.01 1.01 1.16 1.01 1.01 1.03 1.05 0.91 2.20 2.98 1.04 1.93 3.00 3.08

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

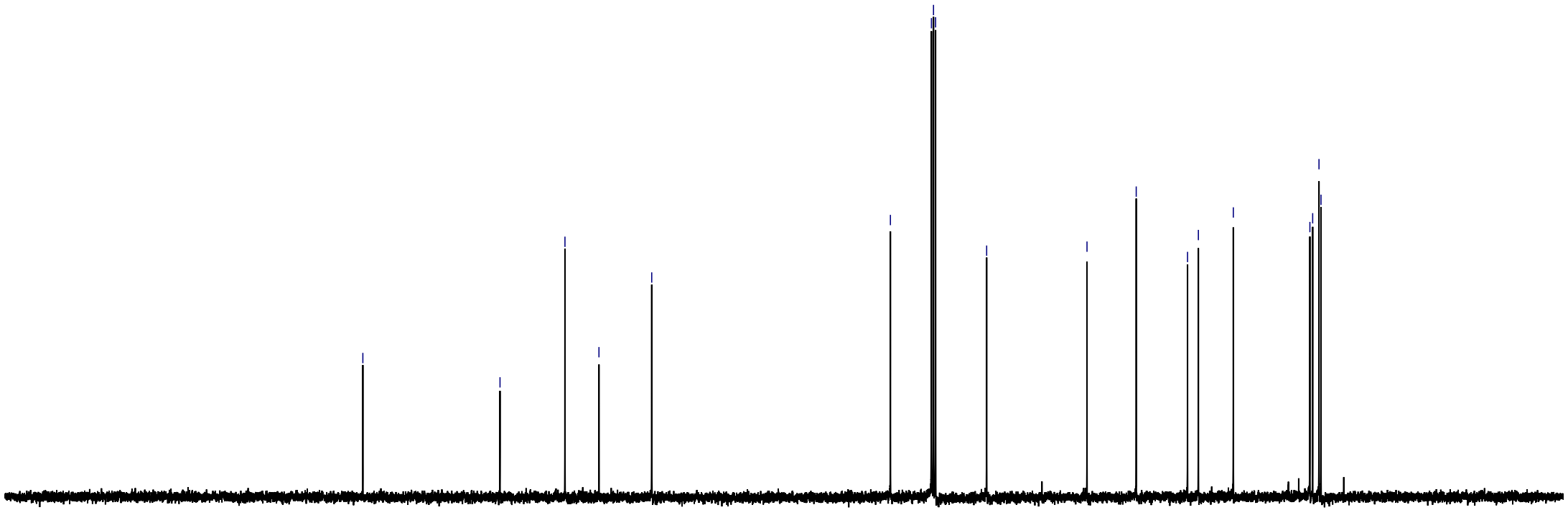
f1 (ppm)



16

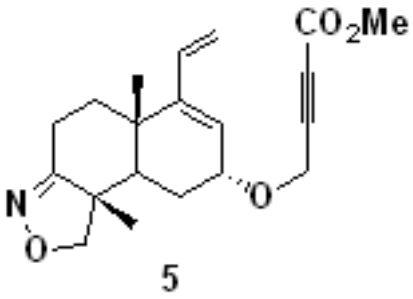
(101 MHz, $CDCl_3$)

164.457
143.437
133.483
128.272
120.186
83.604
77.317
77.000
76.682
68.853
53.474
45.931
38.065
36.404
31.049
19.312
18.887
17.919
17.611



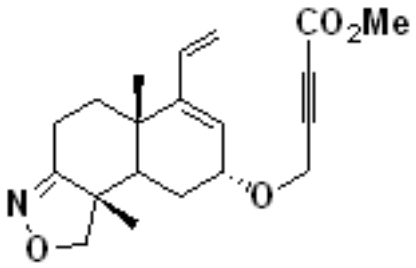
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



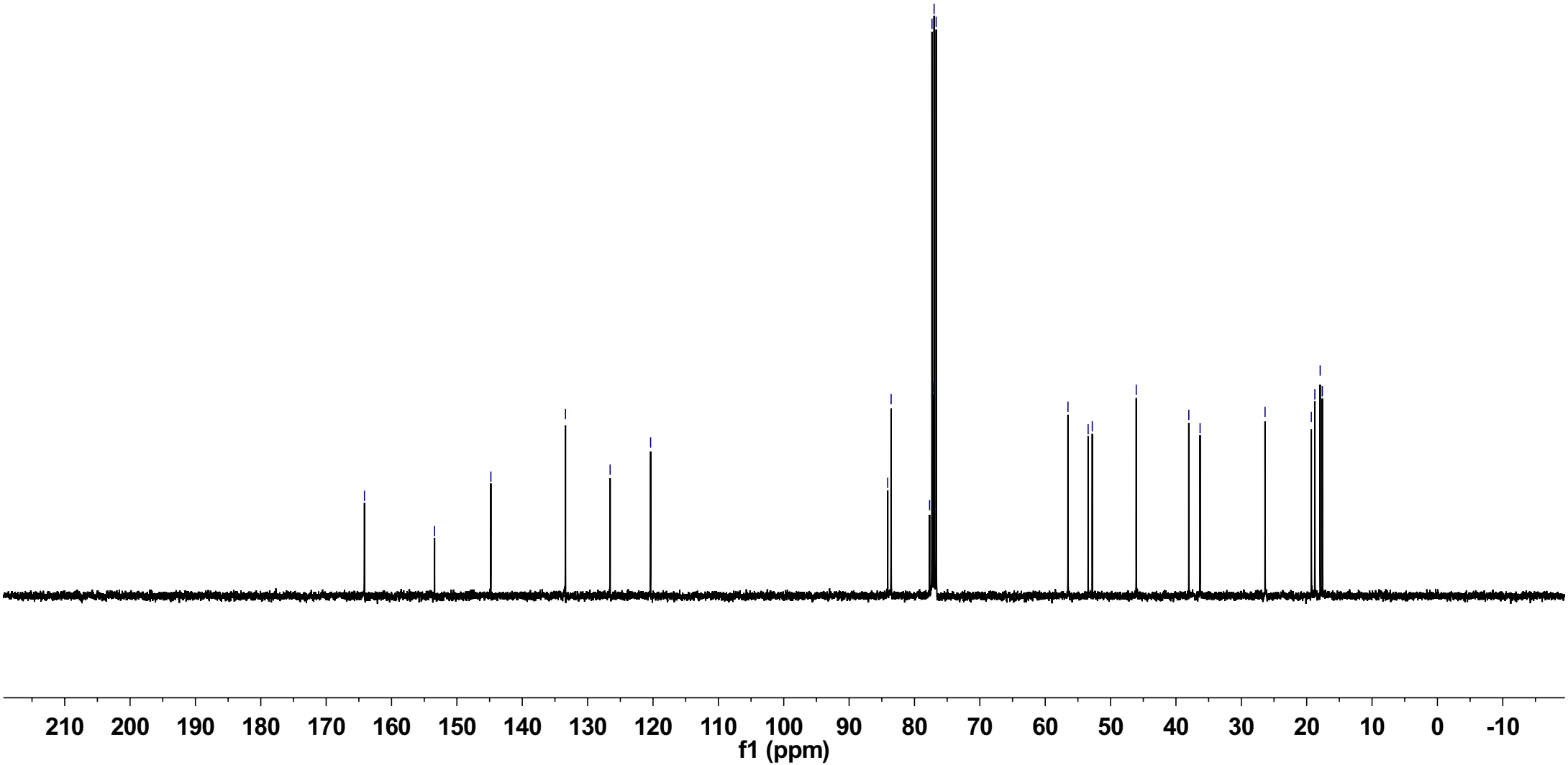
5

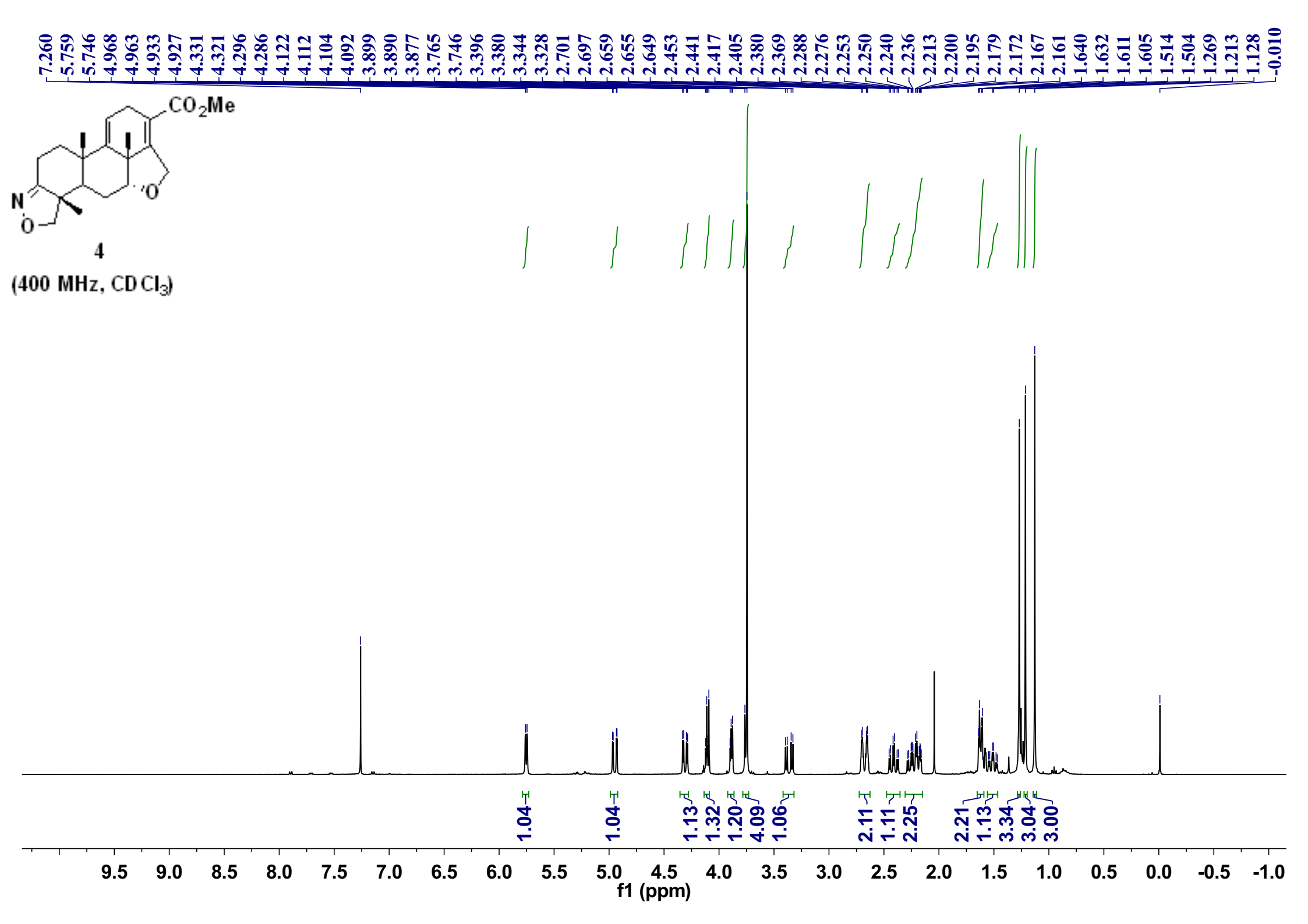
(400 MHz, $CDCl_3$)

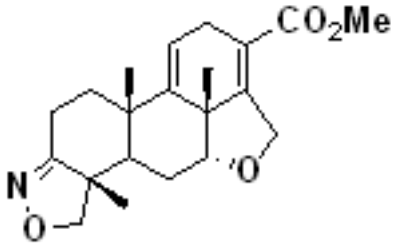


5
(101 MHz, $CDCl_3$)

164.141
153.420
144.802
133.390
126.559
120.366
84.095
83.572
77.687
77.318
77.076
77.000
76.683
56.518
53.434
52.800
46.074
38.032
36.308
26.366
19.290
18.752
17.938
17.604




7.260
5.759
5.746
4.968
4.963
4.933
4.927
4.331
4.321
4.296
4.286
4.122
4.112
4.104
4.092
3.899
3.890
3.877
3.765
3.746
3.396
3.380
3.344
3.328
2.701
2.697
2.659
2.655
2.649
2.453
2.441
2.417
2.405
2.380
2.369
2.288
2.276
2.253
2.250
2.240
2.236
2.213
2.200
2.195
2.179
2.172
2.167
2.161
1.640
1.632
1.611
1.605
1.514
1.504
1.269
1.213
1.128
-0.010
CO2Me
N
O
O
4
(400 MHz, CDCl3)
1.04
1.04
1.13
1.32
1.20
4.09
1.06
2.11
1.11
2.25
2.21
1.13
3.34
3.04
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



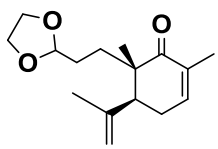
4

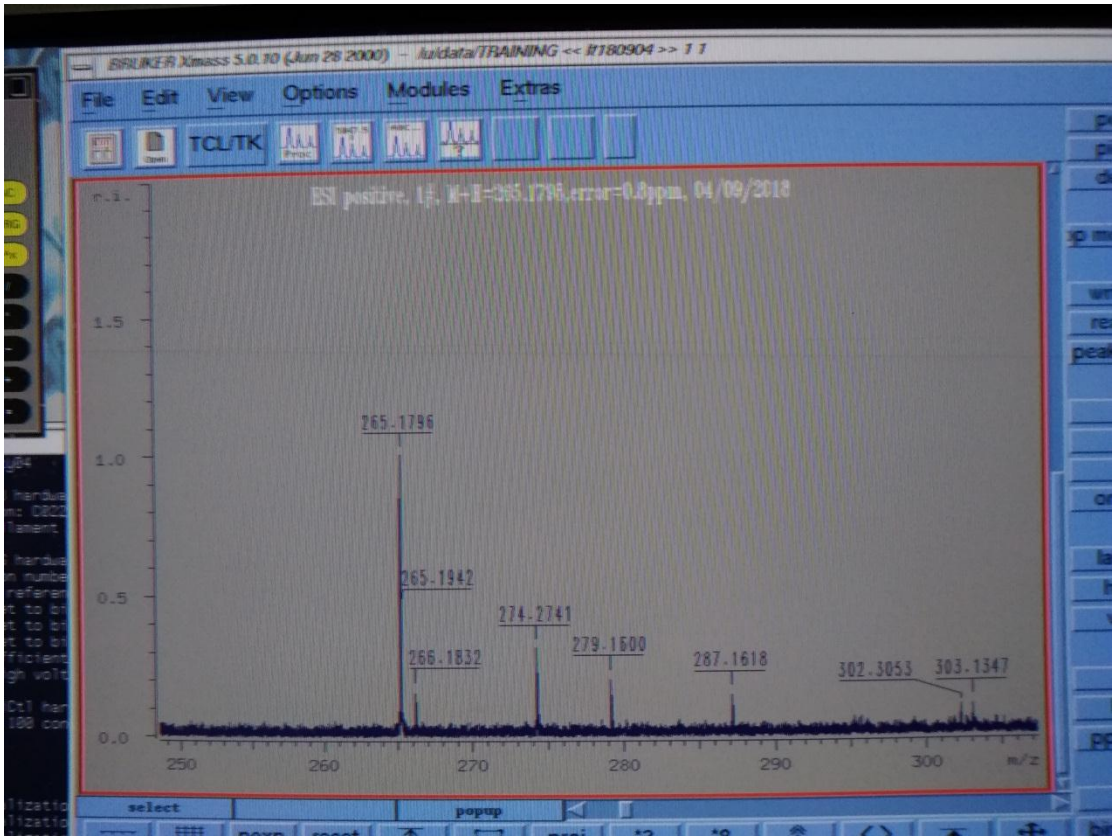
(101 MHz, $CDCl_3$)

166.458
164.096
162.995
151.936
121.661
119.356
83.466
81.691
77.318
77.000
76.683
68.818
53.370
51.679
45.656
44.465
38.054
37.324
27.151
26.934
24.461
20.916
19.061
18.330

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)

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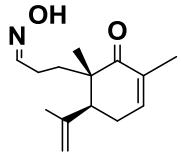
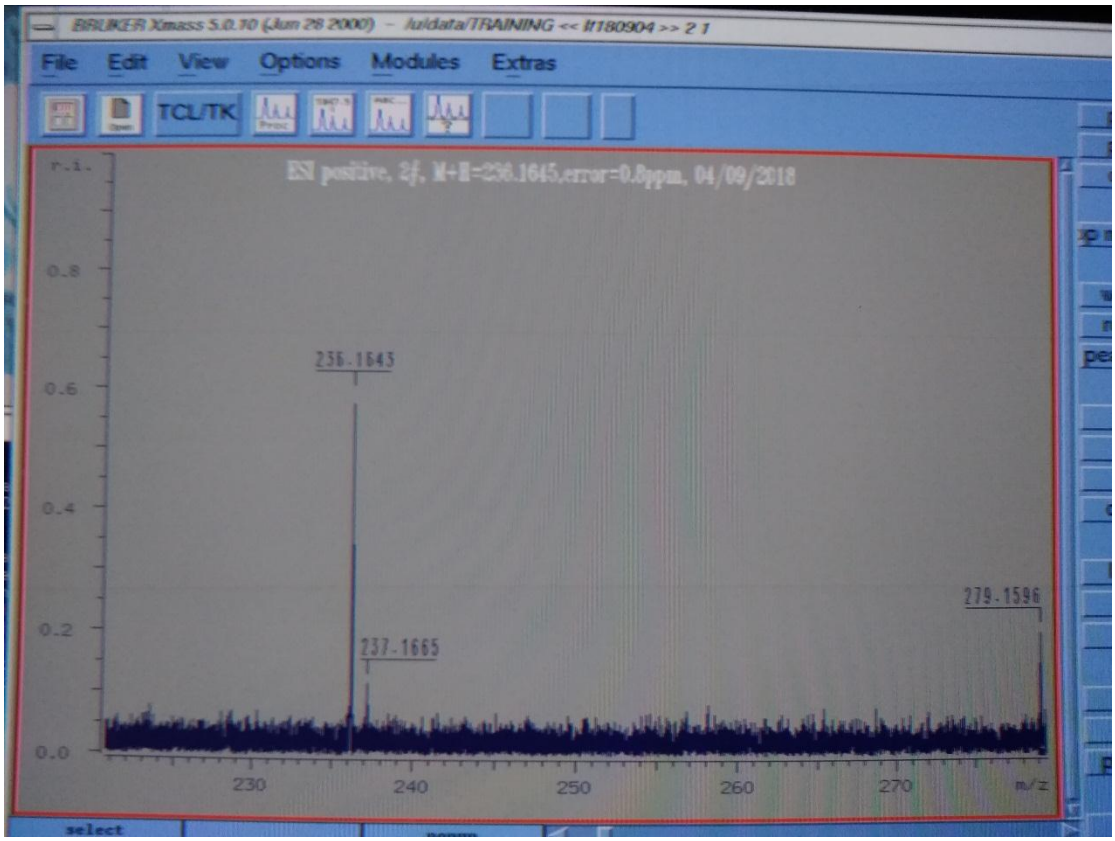
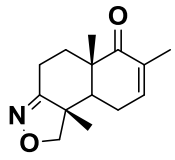
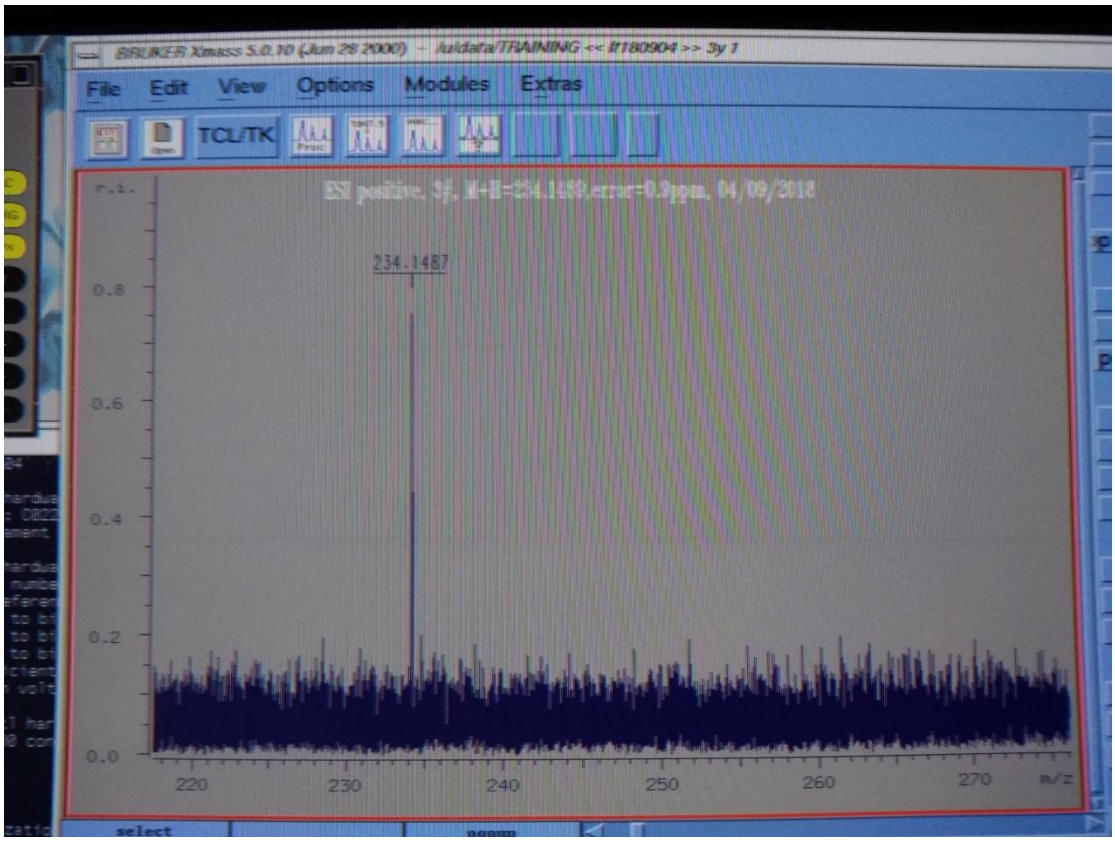
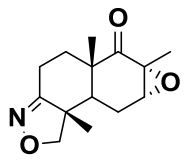
Edit
View
Options
Modules
Extras
TCL/TK
265.1796
265.1942
274.2741
266.1832
279.1600
287.1618
302.3053
303.1347
250
260
270
280
290
300
m/z
select
popup

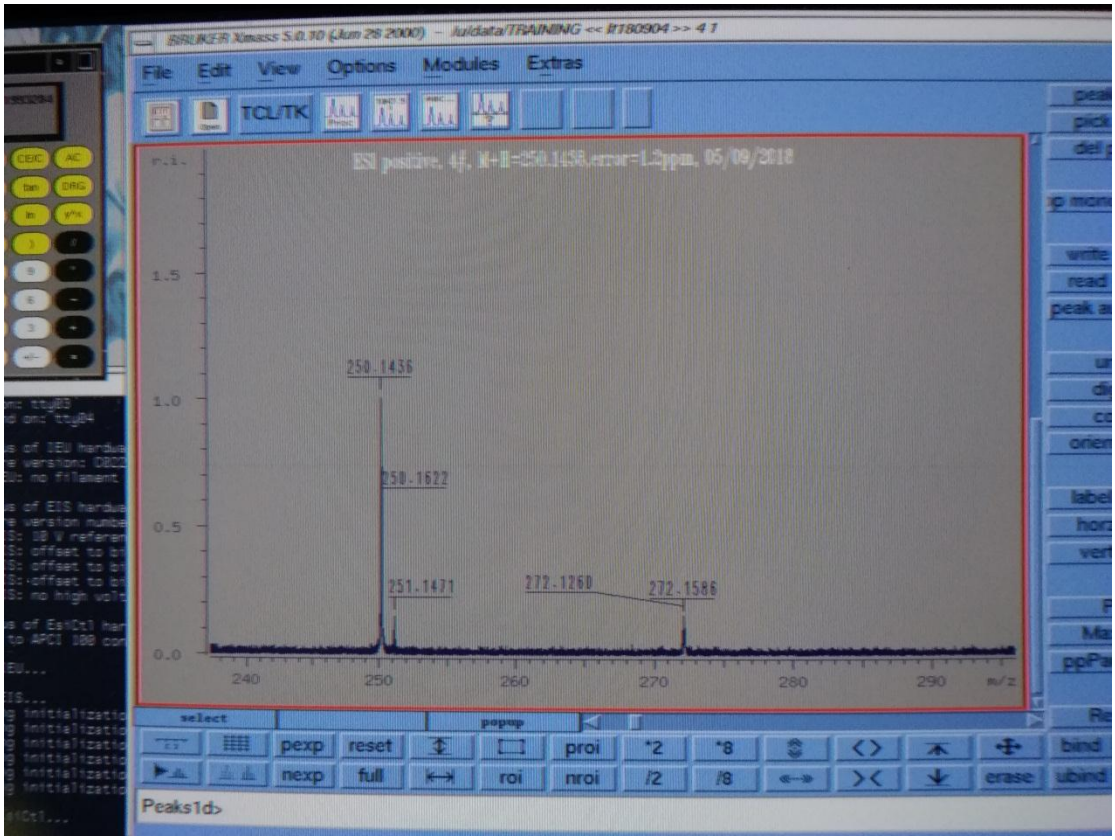

OH
N
O

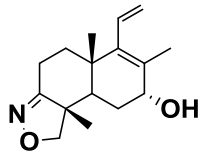

BRUKER Xmass 5.0.10 (Jun 28 2000) - /u/data/TRAINING << #180904 >> 2 1
File Edit View Options Modules Extras
TCL/TK
ESI positive, 2f, M+H=236.1645,error=0.8ppm, 04/09/2018
r.i.
0.8
0.6
0.4
0.2
0.0
236.1643
237.1665
279.1596
230
240
250
260
270
m/z
select

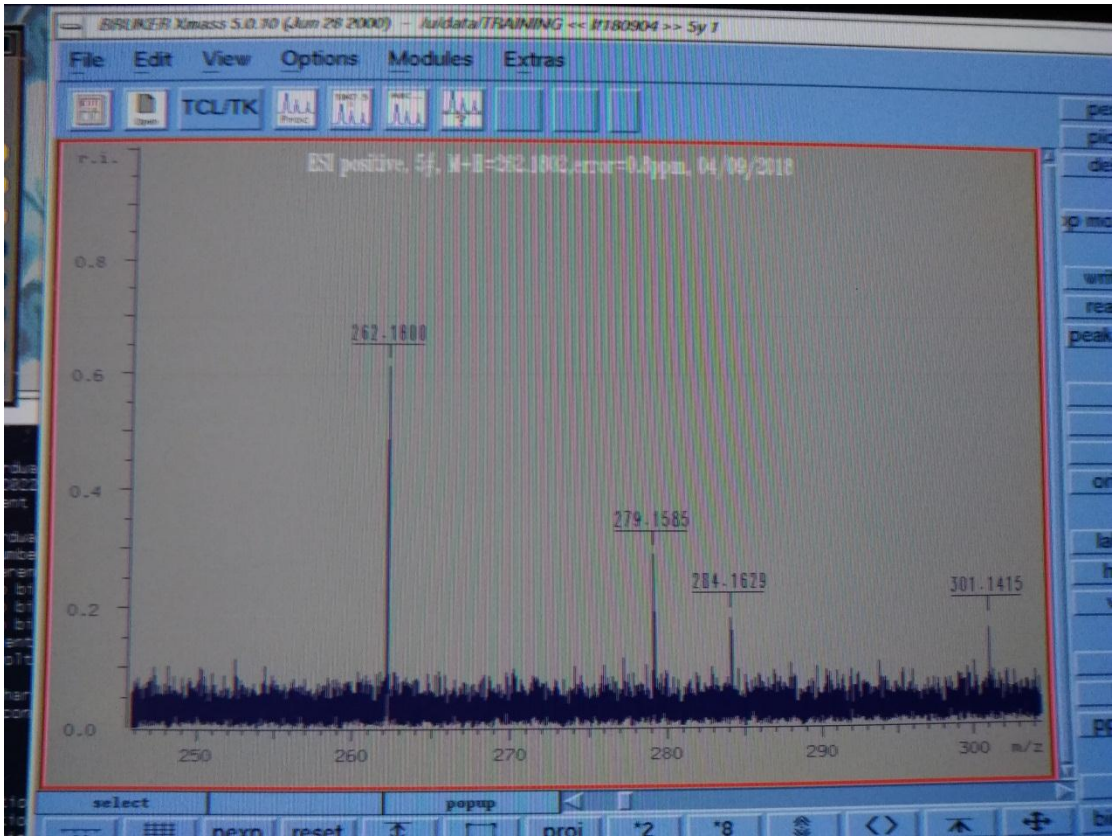

O
N
O

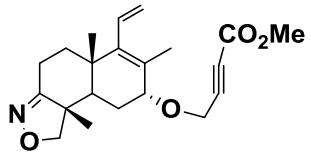

BRUKER Xmass 5.0.10 (Jun 26 2000) - /u/data/TRAINING << #180904 >> 3y 1
File
Edit
View
Options
Modules
Extras
TCL/TK
ESI positive, 3y, #-1=234.1489,error=0.9ppm, 04/09/2018
234.1487
r.i.
0.8
0.6
0.4
0.2
0.0
220
230
240
250
260
270
m/z

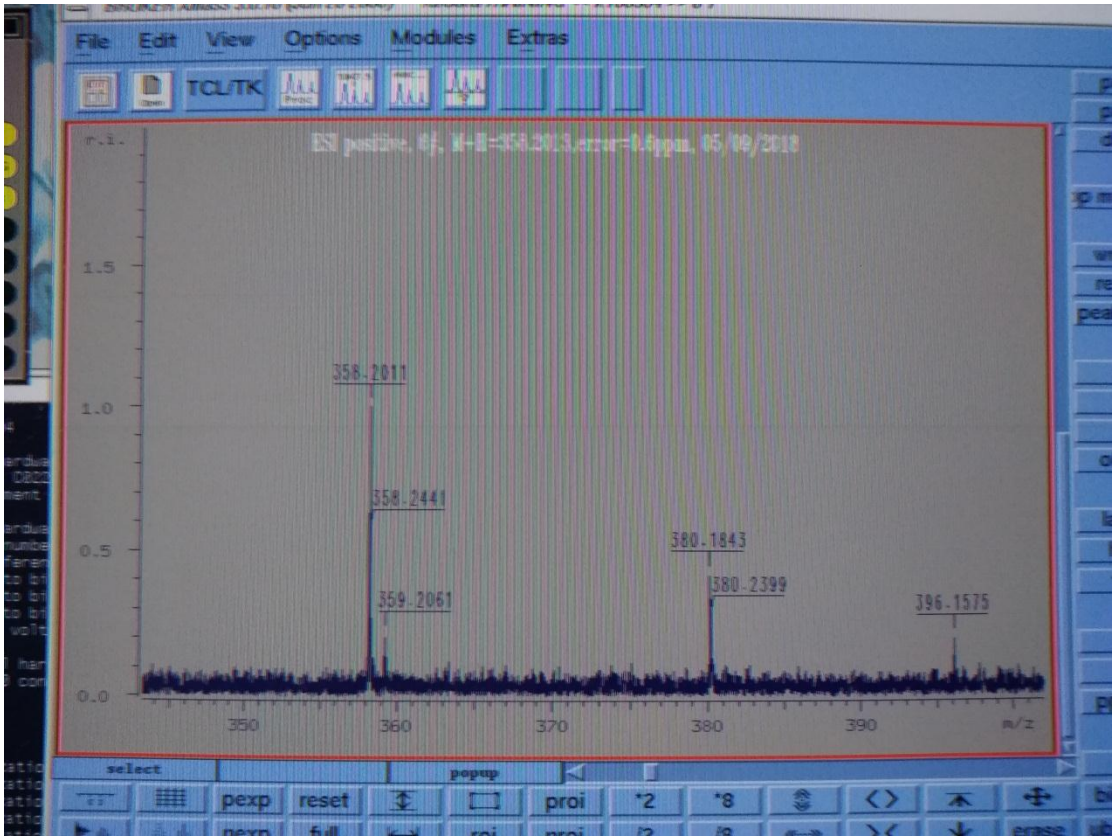

O
O
N
O

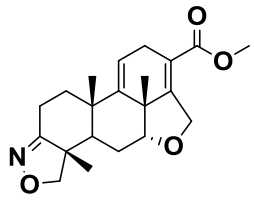

File Edit View Options Modules Extras
TCL/TK
ESI positive, 4f, M+H=250.1438,error=1.2ppm, 05/09/2018
250.1436
250.1622
251.1471
272.1260
272.1586
240
250
260
270
280
290
m/z
select
popup
pexp
reset
proi
*2
*8
bind
nexp
full
roi
nroi
/2
/8
erase
ubind
Peaks1d>

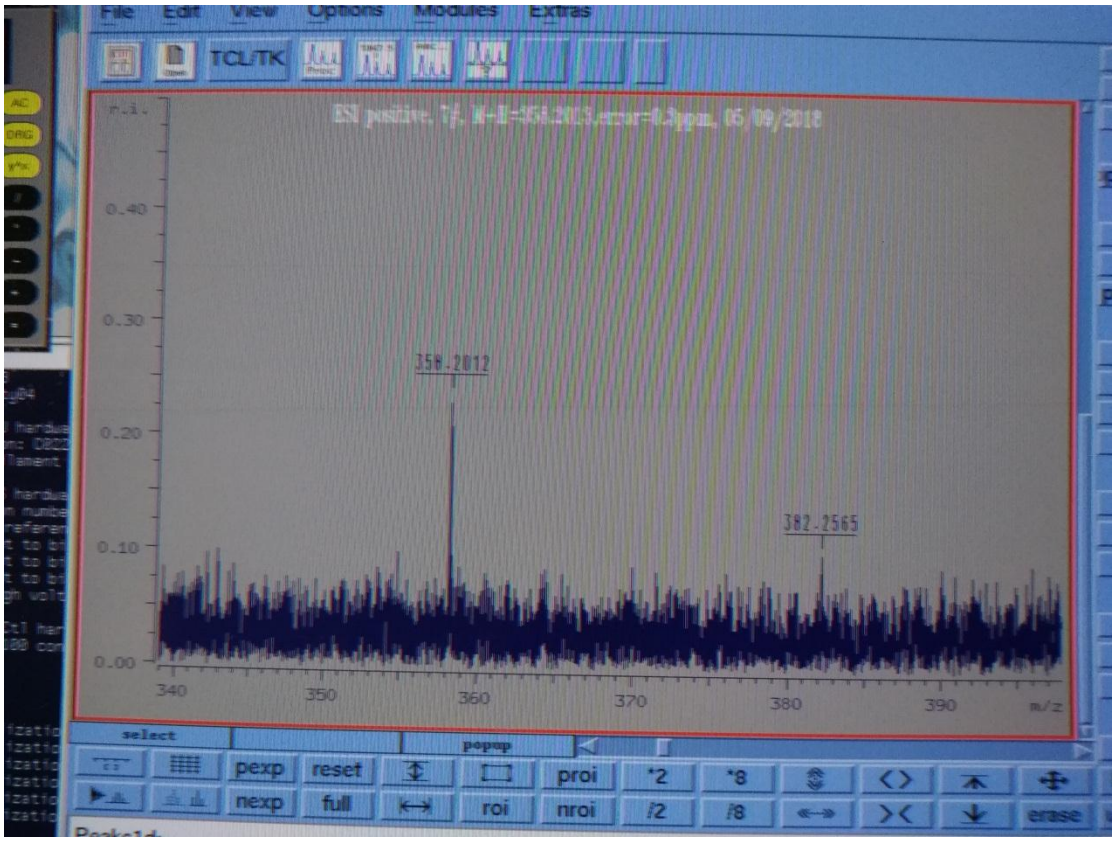

N
O
OH

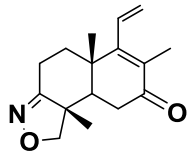

File
Edit
View
Options
Modules
Extras
TCL/TK
ESI positive, 5µ, M-H=282.1802,error=0.0ppm, 04/09/2018
r.i.
0.8
0.6
0.4
0.2
0.0
262.1600
279.1585
284.1629
301.1415
250
260
270
280
290
300
m/z
select
popup
reset
proj
*2
*8

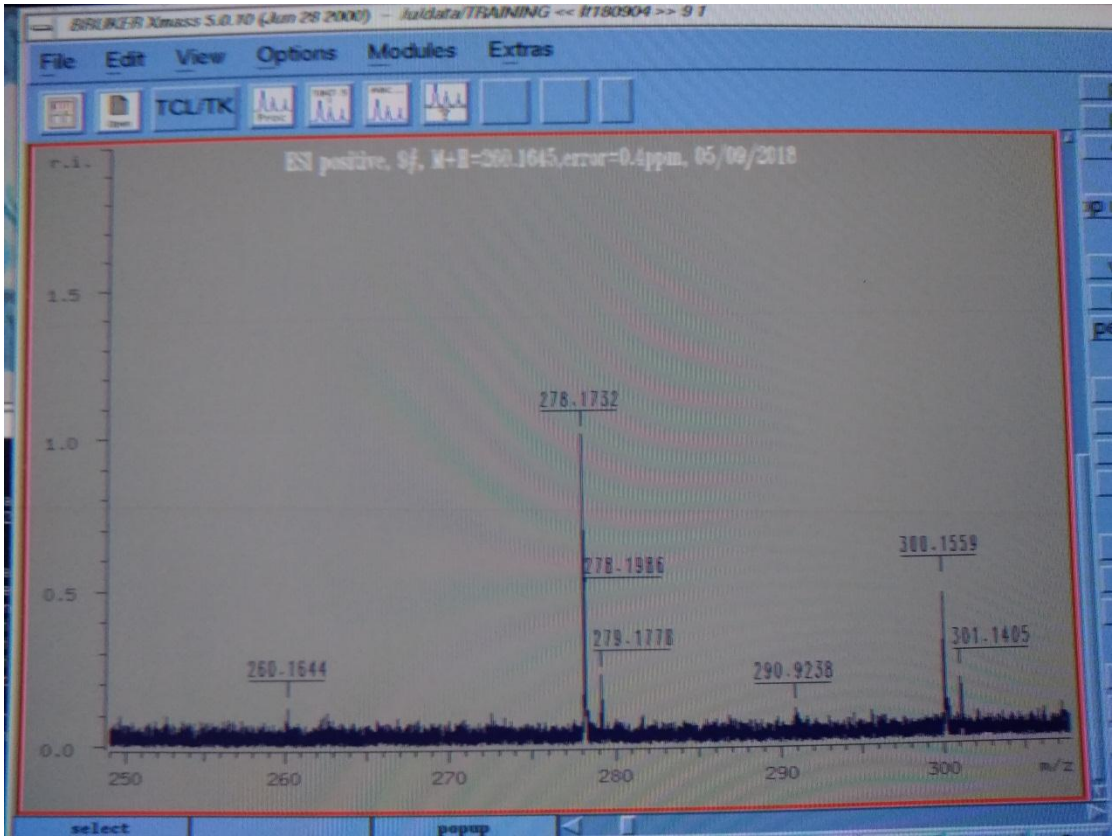

CO2Me
N
O
O

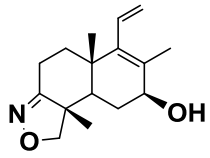

File
Edit
View
Options
Modules
Extras
TCL/TK
r.i.
1.5
1.0
0.5
0.0
358.2011
358.2441
359.2061
380.1843
380.2399
396.1575
350
360
370
380
390
m/z
select
popup
pexp
reset
proi
*2
*8

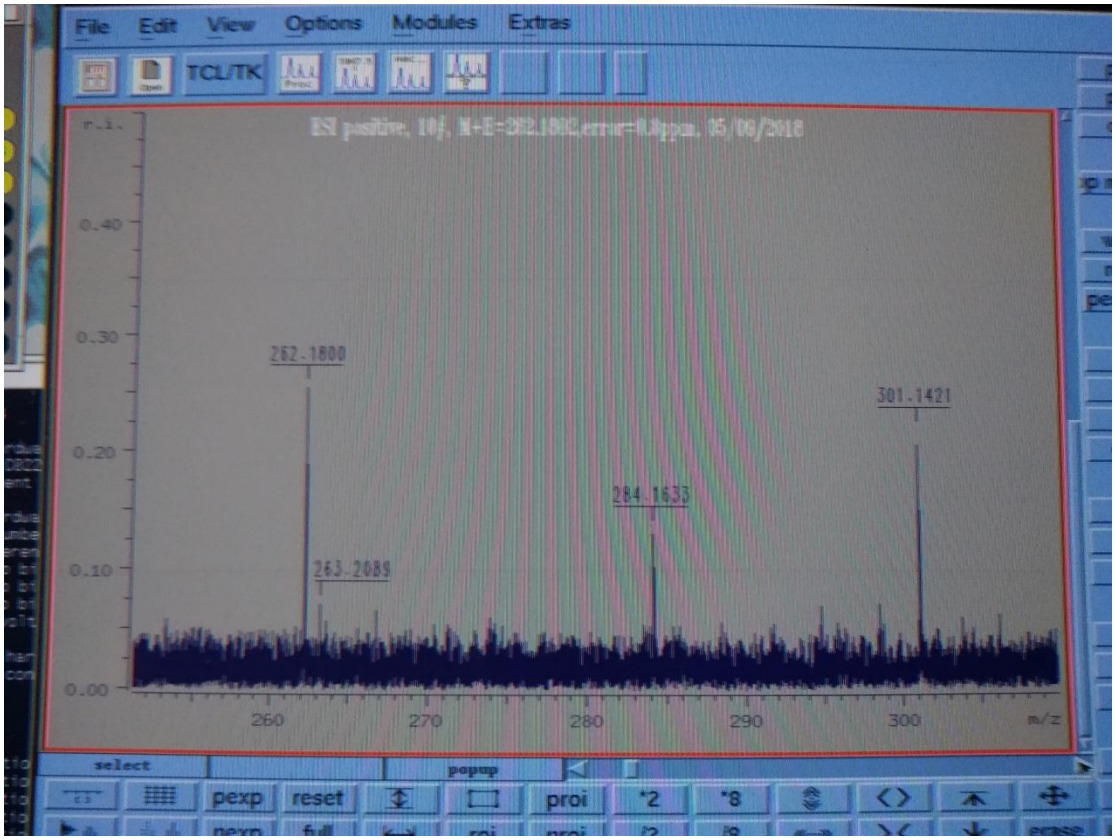

O
O
N
O
O


File Edit View Options Modules Extras
TCL/TK
ESI positive, 7T, M+1=358.2012,error=0.3ppm, 05/09/2018
0.40
0.30
0.20
0.10
0.00
358.2012
382.2565
340
350
360
370
380
390
m/z
select
popup
pexp
reset
proi
*2
*8
nexp
full
roi
nroi
/2
/8
erase


N
O
O


BRUKER Xmass 5.0.10 (Jun 28 2007) - /u/data/TRAINING << lt180904 >> 9 1
File
Edit
View
Options
Modules
Extras
TCL/TK
ESI positive, 9f, M+H=260.1645,error=0.4ppm, 05/09/2018
r.i.
1.5
1.0
0.5
0.0
278.1732
278.1986
300.1559
279.1778
301.1405
260.1644
290.9238
250
260
270
280
290
300
m/z
select
popup


N
O
OH


File
Edit
View
Options
Modules
Extras
TCL/TK
ESI positive, 10f, M+E=282.1802,error=0.0ppm, 05/06/2018
r.i.
0.40
0.30
0.20
0.10
0.00
262.1800
263.2089
284.1633
301.1421
260
270
280
290
300
m/z
select
popup
pexp
reset
proi
*2
*8