En Route to D-Ring Inverted Phorbol Esters

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Supporting Information

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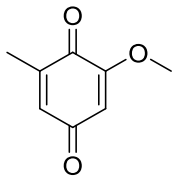
List of abbreviations

^{o}C	degree
Δ	chemical shift
^{1}H	hydrogen isotope
^{13}C	carbon isotope
DCM	dichloromethane
calcd	calculated
cm^{-1}	reciprocal centimetre
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DIBAL-H	diisobutylaluminium hydride
DMAP	4-(*N,N*-dimethylamino)pyridine
DMDO	dimethyldioxirane
DMF	*N,N*-dimethylformamide
DMOS	dimethylsulfoxide
EI	electron ionisation
equiv	equivalents
ESI	electrospray ionisation
et al	et alii/et aliae (and others)
g	gram
GCMS	gas chromatography/mass spectroscopy
h	hour(s)
HRMS	high resolution mass spectrometry
Hz	hertz
in situ	on site (in the reaction vessel)
in vacuo	in a vacuum
J	coupling constant
L	litre
LDA	lithium *N,N*-diisopropylamide
M	molar
m.p.	melting point
m/z	mass to charge ratio
MHz	megahertz
min	minute(s)
mmol	millimole(s)
mol	mole(s)
Ms	methylsulfonyl
n-	normal
ppm	parts per million
rt	room temperature
t-	tertiary
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl
TMSCl	trimethylsilyl chloride
TPAP	tetrapropylammonium perruthenate

Experimental Procedures

General information

^{1}H and ^{13}C NMR spectra were recorded on Bruker AV300 (300.13 MHz; 75.47 MHz), AV400 (400.13 MHz; 100.62 MHz), AV500/AS500 (500.13 MHz; 125.76 MHz) or AS700 (700.47 MHz; 176.13 MHz) instruments. Coupling constants are given in hertz (Hz) and chemical shifts are reported as δ values in parts-per-million (ppm) with the solvent resonance as the internal standard (^{1}H NMR-$CDCl_3$: δ 7.26 and ^{13}C NMR-$CDCl_3$: δ 77.0, ^{1}H NMR-C_6D_6: δ 7.16 and ^{13}C NMR- C_6D_6: δ 128.39). Data are reported as followed: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintuplet, sext = sextuplet, spt = septet, m = multiplet), coupling constants (Hz), and integration. HRMS measurements were recorded in positive ionisation mode on a Bruker MicrOTOF-Q instrument with a Bruker ESI source using electron ionisation. Sodium formate was used as a reference calibrant. Column chromatography was performed using distilled solvents on silica (silica gel 230 – 400 mesh) or aluminium oxide (neutral). Anhydrous DCM, triethylamine, and cyclohexane were distilled from calcium hydride under argon before use. Anhydrous THF was freshly distilled from sodium under argon before use. All catalysts used in this work [TPAP, $Rh_2(OAc)_4$ and AuCl] were sourced from Sigma. Infrared spectroscopy (IR) was acquired using a Perkin Elmer-400 model, with the scanning range of 4000 to 650 cm^{-1}. Melting points are uncorrected. X-Ray crystallographic data, obtained from the University of Queensland, was carried out on an Oxford Diffraction Gemini S Ultra CCD diffractometer using Cu-Kα radiation (l=1.54180 Å). The crystals were kept at 190 K using an Oxford Cryosystems Desktop Cooler.



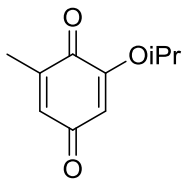
2-Methoxy-6-methylphenol (15)

According to the literature procedure,[1] *o*-vanillin (**12**) (19.7 g, 0.123 mol), hydrazine hydrate (55 – 60% wt. in water, 25 mL, approx. 0.280 mol) and triethylene glycol (100 mL) were mixed and then heated to 110 ^{o}C. Potassium hydroxide (45.5 g, 0.813 mol) was then added in portions to the bright yellow solution over 20 – 30 min. Effervesce was observed after each addition of the base. The resulting orange solution was stirred at 150 ^{o}C for 20 h. After cooling to room temperature, the reaction was carefully poured into ice cold hydrochloric acid (HCl) (1 M, 450 mL) and further acidified with additional concentrated HCl until reaching pH 2. A white precipitate was formed during this process. The mixture was then extracted with chloroform (4 x 80 mL). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure to give a pale orange liquid that still contained a small amount of chloroform. The crude phenol **13** was separated into 2 portions for the oxidation process. The first portion of the crude phenol (9.36 g, 67.7 mmol) was taken up in DMF (60 mL) and added salcomine **14** (2.14 g, 6.08 mmol). Oxygen was then gently bubbled into the brown suspension for 1 d, or until no starting material was detected by TLC. A mixture of ethyl acetate and diethyl ether (1:1, 300 mL) was then added and stirred for 30 min. The suspension was then filtered *via* a pad of celite and the pad was rinsed with fresh solvent (100 mL). The combined filtrates were washed with water (3 x 200 mL). The aqueous layers were then reextracted with fresh solvent (3 x 100 mL). On combining all the organic extracts, washes were performed firstly with a saturated $NaHCO_3$ solution (50 mL) and then brine (80 mL) respectively. Upon drying with $MgSO_4$ and concentrating under reduced pressure, the residue was purified by flash silica gel chromatography (DCM, collected in 100 mL fractions) to give the titled product **15** as a yellow solid. The total product weight was measured at 17.3 g (88% over 2 steps) after repeating the oxidation with the second half of the crude phenol. Spectroscopic data and the melting point matched that described in literature.[2,3]

m.p. 148 – 149 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.07 (d, *J*=1.5 Hz, 3 H), 3.82 (s, 3 H), 5.88 (d, *J*=2.5 Hz, 1 H), 6.53 – 6.55 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 56.3, 107.3, 133.8, 143.6, 158.8, 182.4, 187.4.



2-Isopropoxy-6-methylcyclohexa-2,5-diene-1,4-dione (16)

An adaptation of the procedure reported by Wurm *et.al* was utilised.[4] Methoxy-quinone **15** (1.05 g, 6.90 mmol) was dissolved in isopropanol (70 mL) and potassium carbonate (1.31 g, 9.49 mmol) added in one portion. The suspension was stirred until TLC showed that no further starting material was present after 6.5 h. The mixture was filtered and the filtrate was partitioned between brine and DCM (3 x 30 mL). The

combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. After flash silica gel chromatography (2% ethyl acetate in DCM), the desired isopropoxy-quinone **16** was obtained as a bright yellow liquid which solidified on standing (0.90 g, 73%).

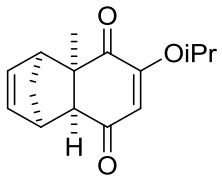
m.p. 53 – 54 ^{o}C

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (d, *J*=6.2 Hz, 6 H), 2.05 (d, *J*=1.7 Hz, 3 H), 4.45 (spt, *J* =6.0 Hz, 1 H), 5.83 (d, *J* =2.4 Hz, 1 H), 6.50 – 6.52 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 15.7, 21.2, 72.4, 108.0, 133.7, 143.8, 157.0, 182.9, 188.0.

IR (thin film) ν_{max}: 2980, 2920, 1678, 1649, 1595, 1312, 1230, 1190, 1104, 1053, 986, 897 cm^{-1}.

HRMS (EI+) calculated for $C_{10}H_{12}NaO_3$: 203.0684; found: 203.0679.



(1*R,4*S**,4a*R**,8a*S**)-6-Isopropoxy-4a-methyl-1,4,4a,8a-tetrahydro-1,4-methanonaphthalene-5,8-dione (17)**

Isopropoxy-quinone **16** (0.982 g, 5.46 mmol) and freshly cracked cyclopentadiene (3.20 mL, 38.1 mmol) were stirred in anhydrous DCM over 3 d or until no starting material was detected by TLC. The solvent and residual diene was removed under reduced pressure, leaving behind the crude product, which was purified by flash silica gel chromatography (20% ethyl acetate in petroleum spirit) to give the product **17** as a clear liquid (1.26 g, 93%) which solidified on standing.

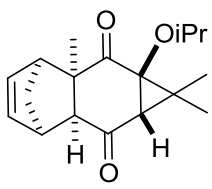
m.p. 79 – 81 ^{o}C

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (d, *J*=6.2 Hz, 3 H), 1.35 (d, *J*=6.2 Hz, 3 H), 1.48 (s, 3 H), 1.54 (dt, *J*=8.8, 1.8 Hz, 1 H), 1.68 (dt, *J*=9.2, 1.5 Hz, 1 H), 2.83 (d, *J*=4.0 Hz, 1 H), 3.10 – 3.12 (m, 1 H), 3.38 – 3.45 (m, 1 H), 4.35 (sptd, *J*=6.2, 0.7 Hz, 1 H), 5.86 (s, 1 H), 6.03 (dd, *J*=5.9, 2.9 Hz, 1 H), 6.13 (dd, *J*=5.9, 2.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 20.93, 20.98, 26.5, 46.4, 48.7, 52.5, 53.8, 57.4, 72.3, 114.6, 135.1, 137.5, 160.7, 197.8, 198.8.

IR (thin film) ν_{max}: 2984, 1697, 1639, 1593, 1229, 1212, 1098, 1048, 1036, 865, 722 cm^{-1}.

HRMS (EI+) calculated for $C_{15}H_{18}NaO_3$: 269.1145; found: 269.1148.



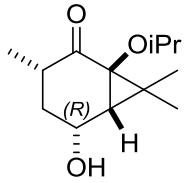
((1a*R,2a*R**,3*S**,6*R**,6a*S**,7a*S**)-1a-Isopropoxy-1,1,2a-trimethyl-1a,2a,3,6,6a,7a-hexahydro-1H-3,6-methanocyclopropa[b]naphthalene-2,7-dione (19)**

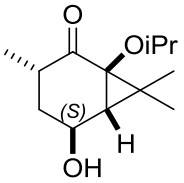
Following the literature procedure,[5] sodium hydride (60% dispersion in mineral oil, 0.261 g, 2.98 mmol) in anhydrous DMF (20 mL) was cooled to 0 °C using an ice bath under an argon atmosphere. Triisopropylsulfoxonium tetrafluoroborate[Error! Bookmark not defined.] (0.788 g, 2.98 mmol) was added in one-portion and stirred for 30 min. Minor effervescence was observed during the deprotonation. The substrate **17** (0.605 g, 2.46 mmol) in anhydrous DMF (4 mL) was then added slowly to the sulfoxonium ylid over 10 min. It was crucial to maintain the temperature of the reaction below 5 °C during the addition. The reaction was stirred for 2 h at 0 °C and then warmed gradually to room temperature. Stirring was continued until no starting material was detected by TLC (*ca* 4 h). The dark brown solution was poured onto an ice cold saturated NH_4Cl solution with caution, and extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified *via* flash silica gel chromatography (20% ethyl acetate in petroleum spirit) to give the desired product **19** as a clear oil (0.50 g, 70%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.02 (d, *J*=6.1 Hz, 3 H), 1.26 (d, *J*=6.1 Hz, 3 H), 1.31, (s, 3 H), 1.32 (s, 3 H), 1.44 (dt, *J*=9.2, 1.6 Hz, 1 H), 1.49 (s, 3 H), 1.66 (dt, *J*=9.2, 1.3 Hz, 1 H), 2.14 (s, 1 H), 2.59 (d, *J*=4.2 Hz, 1 H), 3.18 – 3.26 (m, 1 H), 3.50 (qd, *J*=3.9, 1.9 Hz, 1 H), 3.68 (spt, *J*=6.2 Hz, 1 H), 6.21 – 6.26 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 19.5, 22.9, 23.5, 23.7, 26.9, 33.9, 47.3, 48.2, 51.0, 53.1, 58.4, 59.0, 72.6, 76.2, 136.9, 137.4, 206.3, 210.3.

HRMS (EI+) calculated for $C_{18}H_{24}NaO_3$: 311.1618; found: 311.1630.





(1*S,3*R**)-5-Hydroxy-1-isopropoxy-3,7,7-trimethylbicyclo[4.1.0]heptan-2-one (22)**

The retro-Diels Alder reaction was carried out in a Kulgehrohr distillation apparatus by heating the cyclopropyl adduct **19** (1.82 g, 6.31 mmol) to 140 °C at 520 – 570 mmHg (Büchi vacuum controller). The reaction was monitored by TLC, which showed no starting material after 2 h. The bright yellow liquid, containing relatively pure endione **20**, was taken up in methanol (25 mL) and cooled to 0 °C. To this was added $NaBH_4$ (0.70 g, 5.3 mmol) in small portions over 2 min. The reaction was stirred for 2 h while the bath temperature warmed to 6 °C. TLC indicated endione **20** was fully consumed. The reaction was quenched by adding a cold solution of saturated NH_4Cl. To assist with the extraction process, the methanol was partially removed under reduced pressure. The residue was then partitioned with water and ethyl acetate (3 x 15 mL). The organic extracts were combined and washed with brine. After drying the organic layer over anhydrous Na_2SO_4, the solvent was removed *via* rotary evaporation. The yellow residue was purified by flash silica gel chromatography (40% ethyl acetate in petroleum spirit) affording two diastereomers (5*R**)-**22** and (5*S**)-**22** (1.47 g, 92% over 2 steps, dr 2:3), as a colourless oil, that were collected as a mixture. The two diastereomers were separated for characterisation purposes.

(5*R**)-**22**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 3 H), 1.10 (d, *J*=6.6 Hz, 3 H), 1.15 (d, *J*=6.2 Hz, 3 H), 1.16 (d, *J*=6.2 Hz, 3 H), 1.23 (s, 3 H), 1.46 (t, *J*=2.2 Hz, 1 H), 1.73 (ddd, *J*=15.8, 12.8, 3.7 Hz, 1 H), 1.76 (br. s, 1 H), 2.00 (ddt, *J*=15.1, 6.6, 2.2 Hz, 1 H), 2.65 (dt, *J*=12.9, 6.6 Hz, 1 H), 3.71 (spt, *J*=6.2 Hz, 1 H), 4.43 (br. s, 1 H).

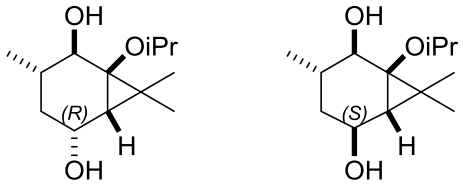
^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 17.9, 23.0, 23.2, 24.6, 27.3, 36.7, 38.66, 38.73, 63.9, 70.2, 72.6, 211.1.

(5*S**)-**22**

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (d, *J*=6.2 Hz, 3 H), 1.12 (d, *J*=6.2 Hz, 3 H), 1.13 (d, *J*=6.2 Hz, 3 H), 1.71 (br. s, 1 H), 1.20 (s, 3 H), 1.24 (s, 3 H), 1.55 – 1.64 (m, 2 H), 2.15 – 2.30 (m, 1 H), 2.25 (tt, *J*=12.8, 6.6 Hz, 1 H), 3.62 (spt, *J*=6.2 Hz, 1 H), 4.65 (ddd, *J*=11.3, 6.9, 5.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 19.0, 22.8, 23.2, 24.8, 28.2, 36.7, 37.5, 42.7, 66.5, 71.7, 72.0, 209.6.

HRMS (EI+) calculated for $C_{13}H_{22}NaO_3$: 249.1467; found: 249.1461.



(1*R,2*R**,3*S**)-1-Isopropoxy-3,7,7-trimethylbicyclo[4.1.0]heptane-2,5-diol (23)**

A diastereomeric mixture of (*R*)- and (*S*)-ketone **22** (1.40 g, 6.18 mmol) in anhydrous THF (20 mL) was cooled to 0 °C under an argon atmosphere. To this was added DIBAL-H (1.0 M in hexane, 18.5 mL) dropwise over 15 min. The reaction was stirred for 2 h while the bath temperature was gradually warmed to 10 °C, at which no starting material was detected by TLC. On re-cooling to 0 °C, a saturated potassium sodium tartrate (Rochelle's salt) solution was added. A gel-like material was formed initially. The heterogeneous solution was stirred for 1 h at the same temperature and then at room temperature until all gel-like material redissolved. The solution was extracted with ethyl acetate (3 x 25 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was subjected to flash silica gel chromatography (40% ethyl acetate in petroleum spirit) giving the diol as mainly two diastereomers (1.20 g, 85%, colourless oil), collected as one fraction. Separation of the diastereomers by flash chromatography was attempted for characterisation purposes.

(5*R**)-**23** (off-white solid)

m.p. 79 – 81 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (s, 3 H), 1.03 (d, *J*=6.6 Hz, 3 H), 1.16 (s, 3 H), 1.18 (d, *J*=6.2 Hz, 3 H), 1.15 – 1.21 (m, 2 H), 1.31 (d, *J*=6.2 Hz, 3 H), 1.57 (ddt, *J*=15.4, 3.7, 1.8, 1.8 Hz, 1 H), 1.63 (br. s, 1 H), 1.74 – 1.85 (m, 1 H), 3.16 (d, *J*=10.6 Hz, 1 H), 3.24 (br. s, 1 H), 3.78 (spt, *J*=6.2 Hz, 1 H), 4.01 (dd, *J*=2.6, 1.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 16.1, 18.3, 22.8, 23.2, 23.5, 24.4, 31.4, 32.8, 39.7, 63.9, 66.2, 70.3, 72.5.

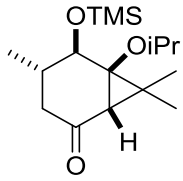
IR (thin film) ν_{max}: 3436, 2922, 1381, 1368, 1154, 1131, 1110, 1095, 1089, 1013, 958, 932, 839 cm^{-1}.

(5*S**)-**23** [colourless oil, the sample was mixed with a small amount of (5*R**)-**23**]

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, *J*=6.5 Hz, 3 H), 1.16 – 1.19 (m, 1 H), 1.18 (d, *J*=6.2 Hz, 3 H), 1.19 (s, 3 H), 1.21 (s, 3 H), 1.23 (d, *J*=6.2 Hz, 3 H), 1.31 (d, *J*=6.2 Hz, 1 H), 1.40 (d, *J*=7.3 Hz, 1 H), 1.43 – 1.54 (m, 2 H), 1.84 (ddd, *J*=13.5, 7.5, 2.8 Hz, 1 H), 3.29 (d, *J*=10.6 Hz, 1 H), 3.68 (spt, *J*=6.2 Hz, 1 H), 4.38 (dt, *J*=10.9, 7.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 17.5, 18.3, 23.2, 23.4, 23.5, 26.9, 31.3, 36.8, 38.9, 67.7, 69.4, 70.1, 72.1.

HRMS (EI+) calculated for $C_{13}H_{24}NaO_3$: 251.1623; found: 251.1618.



(1*S,4*S**,5*R**,6*R**)-6-Isopropoxy-4,7,7-trimethyl-5-((trimethylsilyl)oxy)bicyclo[4.1.0]heptan-2-one (24)**

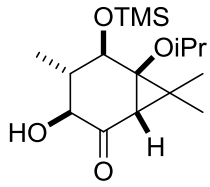
Under an argon atmosphere, diol **23** (1.18 g, 5.17 mmol) in anhydrous DCM (8 mL) was cooled to 0 ^{o}C. Triethylamine (1.3 mL, 8.4 mmol) was added, followed by TMSCl (0.60 mL, 4.8 mmol). The reaction was left to stir while the temperature increased gradually to room temperature. No starting material was observed by TLC after 15 h. The suspension was poured into a cold saturated $NaHCO_3$ solution, followed by extraction with DCM (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The crude material was taken up in methanol (24 mL) and cooled to 0 ^{o}C. Citric acid (29 mg, 0.15 mmol) in methanol (1 mL) was then added. The reaction was closely followed by TLC until the mono-deprotection was completed. While still maintaining the same temperature, a saturated $NaHCO_3$ solution was added and subsequently approximately half of the methanol was removed under reduced pressure. The remaining solution was partitioned with water and ethyl acetate (3 x 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude oil was redissolved in anhydrous DCM (10 mL) was added *N*-methylmorpholine *N*-oxide (0.95 g, 8.1 mmol), TPAP (71 mg, 0.20 mmol) and a spatula of 4 Å molecular sieves powder respectively. The dark green suspension was stirred for 3 h, at which point no starting material could be detected by TLC. The reaction mixture was passed through a plug of silica gel. The plug was then rinsed with freshly distilled DCM. The combined DCM solutions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the desired ketone **24** as a colourless oil (0.75 g, 66% over 3 steps). Ketone **24** was used in the following reaction without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9 H), 1.00 (d, *J*=6.2 Hz, 3 H), 1.07 (d, *J*=6.2 Hz, 3 H), 1.18 (s, 3 H), 1.22 (d, *J*=6.2 Hz, 3 H), 1.28 (s, 3 H), 1.69 (dd, *J*=17.5, 13.5 Hz, 1 H), 1.86 (dd, *J*=2.1, 0.6 Hz, 1 H), 2.04 – 2.18 (m, 1 H), 2.37 (ddd, *J*=17.5, 4.0, 1.9 Hz, 1 H), 3.60 (d, *J*=10.9 Hz, 1 H), 3.99 (spt, *J*=6.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2 (3C), 17.9, 18.3, 22.8, 23.5, 23.8, 34.5, 39.4, 42.3, 47.2, 71.6, 71.9, 72.2, 207.2.

IR (thin film) ν_{max}: 2960, 1680, 1250, 1159, 1102, 1084, 1066, 928, 890, 862, 839 cm^{-1}.

HRMS (EI+) calculated for $C_{16}H_{30}NaO_3Si$: 321.1862; found: 321.1856.



(3*S,4*S**,5*R**,6*R**)-3-Hydroxy-6-isopropoxy-4,7,7-trimethyl-5-((trimethylsilyl)oxy)bicyclo[4.1.0]heptan-2-one (26)**

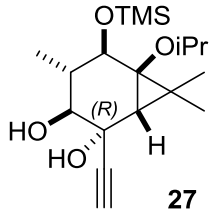
In a round bottom flask, LDA was freshly prepared by slowly adding ^{n}BuLi (1.95 M in cyclohexane, 1.6 mL, 3.0 mmol) to *N*,*N*-diisopropylamine (0.46 mL, 3.3 mmol) in anhydrous THF (8 mL) at 0 ^{o}C under an argon atmosphere. After stirring at the same temperature for 20 min, the colourless LDA solution was added dropwise to ketone **24** (0.75 g, 2.5 mmol) in anhydrous THF (10 mL) precooled to -78 ^{o}C under an argon atmosphere. Once the addition was completed, the reaction was stirred for 30 min before neat TMSCl (freshly distilled from CaH_2, 0.38 mL, 3.0 mmol) was added slowly, which formed a white precipitate over time. The reaction was followed by TLC and stirred until all the starting material was consumed. Quenching of the reaction was performed by pouring the suspension into cold aqueous $NaHCO_3$ solution and extracted with diethyl ether (3 x 15 mL). The combined ether extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude TMS enol ether **25**. The crude **25** was redissolved in acetone (3 mL) and cooled to 0 ^{o}C. DMDO solution[6] (approx. 0.05 M in acetone) was added to the acetone solution of **25** in 3 mL portions with a minute of stirring in between each addition. Once 40 mL of the DMDO solution was added, the reaction was then stirred for 20 min before another 3 portions of DMDO was added. The temperature of the reaction was maintained at 0 ^{o}C the entire time. After stirring for another 45 min, the reaction was stirred for an extra 15 min at room temperature before concentrating under reduced pressure. The residue was partitioned between a saturated aqueous NH_4Cl solution and diethyl ether (3 x 15 mL). The combined ether extracts were dried with anhydrous Na_2SO_4, followed by concentration under reduced pressure. The crude product was subjected to flash silica gel chromatography (15% ethyl acetate in petroleum spirit), which afforded the desired hydroxyl-ketone **26** (0.38 g, 49% over 2 steps, colourless oil) was obtained and starting ketone **24** (0.22 g, 29%) were recovered.

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.16 (s, 9 H), 1.07 (d, *J*=6.2 Hz, 3 H), 1.17 (d, *J*=6.5 Hz, 3 H), 1.20 (d, *J*=6.2 Hz, 3 H), 1.22 (s, 3 H), 1.31 (s, 3 H), 1.93 (tq, *J*=11.2, 6.2 Hz, 1 H), 2.08 (s, 1 H), 3.40 (dd, *J*=12.3, 2.3 Hz, 1 H), 3.68 (d, *J*=11.2 Hz, 1 H), 3.88 (d, *J*=2.6 Hz, 1 H), 4.00 (spt, *J*=6.2 Hz, 1 H).

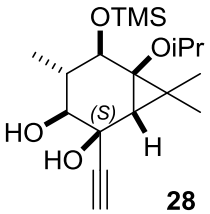
^{13}C NMR (100 MHz, $CDCl_3$) δ -0.2 (3C), 15.3, 17.9, 23.0, 23.3, 23.7, 36.1, 42.7, 48.5, 70.0, 72.2, 75.2, 77.1, 206.7.

IR (thin film) ν_{max}: 3436, 2922, 1381, 1368, 1154, 1131, 1110, 1080, 1013, 958, 932, 839 cm^{-1}.

HRMS (EI+) calculated for $C_{16}H_{30}NaO_4Si$: 337.1811; found: 337.1806.



27



28

(3*S,4*S**,5*R**,6*R**)-2-Ethynyl-6-isopropoxy-4,7,7-trimethyl-5-((trimethylsilyl)oxy)bicyclo[4.1.0]heptane-2,3-diol [27 (*anti*) & 28 (*syn*)]**

At ambient temperature, commercially available ethynyl magnesium bromide solution (Sigma-Aldrich, 0.5 M in THF, 5.1 mL) was added slowly in one-portion to a solution of hydroxy-ketone **26** (0.20 g, 0.64 mmol) in anhydrous THF (3 mL) under an argon atmosphere. The orange solution was stirred for 24 h at which point no starting material was detected by TLC. The reaction was quenched by pouring the mixture into a cold saturated NH_4Cl solution, which was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was subjected to flash silica gel chromatography (20% ethyl acetate in petroleum spirit), which gave diols **27** (73 mg, 34%) and **28** (87 mg, 40%) in two fractions.

27 (colourless oil)

^{1}H NMR (500 MHz, C_6D_6) δ 0.18 (s, 9 H), 1.06 (s, 3 H), 1.15 (d, *J*=6.6 Hz, 3 H), 1.18 (d, *J*=6.2 Hz, 3 H), 1.24 (s, 3 H), 1.34 (d, *J*=6.2 Hz, 3 H), 1.70 (d, *J*=9.5 Hz, 1 H), 1.77 (s, 1 H), 1.93 (tq, *J*=11.0, 6.2 Hz, 1 H), 2.01 (s, 1 H), 2.52 (br. s, 1 H), 3.03 (dd, *J*=11.4, 9.5 Hz, 1 H), 3.34 (d, *J*=10.6 Hz, 1 H), 3.98 (spt, *J*=6.2 Hz, 1 H).

^{13}C NMR (100 MHz, C_6D_6) δ 0.4 (3C), 14.7, 18.0, 24.1, 24.5, 24.6, 28.8, 38.6, 43.6, 68.2, 72.48, 72.54, 74.4, 74.7, 78.9, 86.0.

IR (thin film) ν_{max}: 3461, 3310, 1260, 1249, 1142, 1101, 1048, 1023, 876, 839, cm^{-1}.

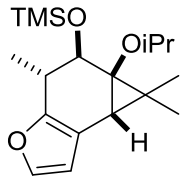
28 (off-white solid)

m.p. 141.5 – 143.0 ^oC

^{1}H NMR (500 MHz, C_6D_6) δ 0.20 (s, 9 H), 1.03 (d, *J*=5.9 Hz, 3 H), 1.04 (s, 3 H), 1.15 (d, *J*=6.2 Hz, 3 H), 1.29 (s, 3 H), 1.30 (d, *J*=5.9 Hz, 3 H), 1.70 (s, 1 H), 1.71 (d, *J*=5.5 Hz, 1 H), 1.98 (s, 1 H), 1.99 (tq, *J*=11.0, 6.6 Hz, 1 H), 2.86 (dd, *J*=11.2, 5.7 Hz, 1 H), 3.22 (d, *J*=11.0 Hz, 1 H), 3.28 (s, 1 H), 4.02 (spt, *J*=6.2 Hz, 1 H).

^{13}C NMR (100 MHz, C_6D_6) δ 0.4 (3C), 14.7, 17.5, 23.8, 23.9, 24.5, 25.2, 38.4, 39.0, 64.7, 67.8, 71.2, 71.5, 72.5, 78.7, 87.7.

HRMS (EI+) calculated for $C_{18}H_{32}NaO_4Si$: 363.1968; found: 363.1962.



(((4*R,5*R**,5*aR**,6*aR**)-5a-Isopropoxy-4,6,6-trimethyl-5,5a,6,6a-tetrahydro-4H-cyclopropa[e]benzofuran-5-yl)oxy)trimethylsilane (29)**

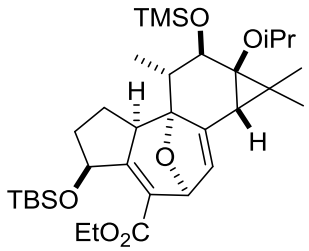
A modified procedure of that reported by Aponick *et.al.*[7] was used. A gold(I) chloride solution was freshly prepared by stirring commercially available gold(I) chloride (1.1 mg, 4.7 µmol) in anhydrous THF (1 mL) under an argon atmosphere. After a few minutes, the undissolved catalyst was allowed to settle and only the yellow solution was used in the subsequent reaction.

To **27** (38 mg, 0.11 mmol) in anhydrous THF (4 mL) under an atmosphere of argon was added the catalyst solution above (0.8 mL). The reaction was left to stir in the dark and was monitored closely by TLC. The colour of the reaction intensified gradually and turned to a deep pink. Upon completion of reaction, the solvent was immediately removed under *in vacuo* under ambient temperature. The residue was redissolved in a small amount of petroleum spirit and passed through a plug of neutral aluminium oxide (petroleum spirit) to give the desired furan **29** as a colourless liquid (29 mg, 80%). [Notes: 1) Fresh catalyst is essential; 2) The product is highly sensitive to acid and base.]

^{1}H NMR (500 MHz, C_6D_6) δ 0.20 (s, 9 H), 0.82 (s, 3 H), 1.04 (d, *J*=6.2 Hz, 3 H), 1.27 (d, *J*=6.2 Hz, 3 H), 1.40 (s, 3 H), 1.44 (d, *J*=7.0 Hz, 3 H), 1.72 (d, *J*=1.1 Hz, 1 H), 2.99 (dqt, *J*=9.9, 6.6, 1.5 Hz, 1 H), 3.45 (d, *J*=9.9 Hz, 1 H), 3.96 (spt, *J*=6.2 Hz, 1 H), 6.09 (d, *J*=2.0 Hz, 1 H), 7.09 (dd, *J*=2.0, 1.1 Hz, 1 H).

^{13}C NMR (100 MHz, C_6D_6) δ 0.4 (3C), 14.5, 17.3, 22.3, 23.9, 24.4, 27.0, 31.4, 37.5, 65.6, 71.8, 75.1, 111.4, 114.3, 141.9, 154.8.

HRMS (EI+) calculated for $C_{18}H_{30}NaO_3Si$: 345.1862; found: 345.1856.



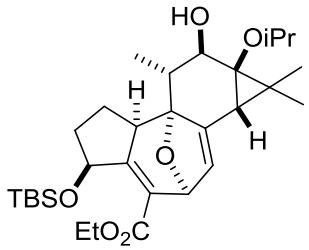
Ethyl (1*aR,3*S**,5*S**,7*aR**,7*bR**,8*R**,9*R**,9*aR**)-5-((tert-butyldimethylsilyl)oxy)-9a-isopropoxy-1,1,8-trimethyl-9-((trimethylsilyl)oxy)-1,1a,3,5,6,7,7a,8,9,9a-decahydro-3,7b-epoxycyclopropa[3,4]benzo[1,2-e]azulene-4-carboxylate (30)**

Furan **29** (29 mg, 90 µmol) and $Rh_2(OAc)_4$ (0.7 mg, 1.6 µmol) were mixed in anhydrous cyclohexane (0.3 mL) and heated to 60 ^{o}C under an argon atmosphere. The solubility of the catalyst increased as the temperature increased. The diazo compound **9**[8] (39 mg, 0.13 mmol) in anhydrous cyclohexane (0.4 mL) was added dropwise to the hot solution. Once the addition was completed, the reaction was stirred for 1 h. Upon cooling to ambient temperature, the solution was passed through a plug of neutral alumina (20 % ethyl acetate in petroleum spirit). After removal of solvent, the residue was subjected to further chromatography using neutral alumina (5% ethyl acetate in petroleum spirit) to give the desired product **30** as a slightly yellow resinous oil (36 mg, 66%).

^{1}H NMR (500 MHz, C_6D_6) δ 0.14 (s, 3 H), 0.21 (s, 9 H), 0.27 (s, 3 H), 0.94 (s, 9 H), 0.98 (s, 3 H), 0.99 (t, *J*=7.0 Hz, 3 H), 1.04 (d, *J*=5.9 Hz, 3 H), 1.26 (s, 3 H), 1.30 – 1.43 (m, 3 H), 1.38 (d, *J*=6.2 Hz, 3 H), 1.40 (d, *J*=7.0 Hz, 3 H), 1.58 (dt, *J*=10.5, 5.2 Hz, 1 H), 1.70 (dd, *J*=12.5, 5.1 Hz, 1 H), 2.40 (dq, *J*=11.4, 6.8 Hz, 1 H), 2.75 (dd, *J*=12.7, 6.4 Hz, 1 H), 3.37 (d, *J*=11.4 Hz, 1 H), 3.99 (spt, *J*=6.2 Hz, 1 H), 4.01 (dq, *J*=10.6, 7.0 Hz, 1 H), 4.12 (dq, *J*=10.6, 7.0 Hz, 1 H), 5.08 (d, *J*=2.2 Hz, 1 H), 5.18 (d, *J*=5.1 Hz, 1 H), 6.37 (t, *J*=2.4 Hz, 1 H).

^{13}C NMR (100 MHz, C_6D_6) δ -4.4, -3.5, 0.6 (3C), 11.7, 14.7, 18.7, 18.8, 23.0, 24.6, 24.7, 25.2, 26.0, 26.55 (3C), 26.64, 36.0, 43.3, 46.8, 60.2, 68.5, 70.3, 72.0, 72.1, 77.7, 90.1, 132.1, 136.6, 139.6, 155.7, 165.6.

HRMS (EI+) calculated for $C_{33}H_{56}NaO_6Si_2$: 627.3513; found: 627.3508.



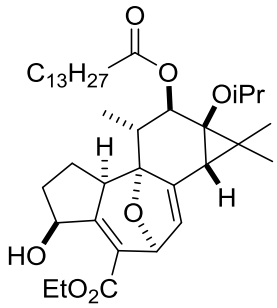
Ethyl (1*aR,3*S**,5*S**,7*aR**,7*bR**,8*R**,9*R**,9*aR**)-5-((tert-butyldimethylsilyl)oxy)-9-hydroxy-9a-isopropoxy-1,1,8-trimethyl-1,1a,3,5,6,7,7a,8,9,9a-decahydro-3,7b-epoxycyclopropa[3,4]benzo[1,2-e]azulene-4-carboxylate (31)**

Compound **30** (8.0 mg, 13 µmol) was dissolved in methanol (1.2 mL) and stirred with a catalytic amount of Amberlyst I15 for 2.5 h at which point no starting material could be detected by TLC. The resin was filtered off and rinsed with ethyl acetate. The combined filtrates were concentrated *in vacuo* and the residue purified *via* chromatography with neutral alumina (15% ethyl acetate in petroleum spirit) to give the desired product **31** (6.0 mg, 85%) as a colourless oil.

^{1}H NMR (500 MHz, C_6D_6) δ 0.15 (s, 3 H), 0.28 (s, 3 H), 0.89 (d, *J*=5.5 Hz, 3 H), 0.90 (s, 3 H), 0.94 (s, 9 H), 0.99 (t, *J*=7.2 Hz, 3 H), 1.15 (s, 3 H), 1.16 (d, *J*=7.0 Hz, 3 H), 1.31 – 1.38 (m, 2 H), 1.44 (d, *J*=2.2 Hz, 1 H), 1.47 – 1.52 (m, 1 H), 1.59 (d, *J*=7.0 Hz, 3 H), 1.68 – 1.72 (m, 1 H), 2.17 (dq, *J*=12.1, 7.0 Hz, 1 H), 2.71 – 2.78 (m, 1 H), 2.83 (d, *J*=6.2 Hz, 1 H), 3.38 (dd, *J*=11.9, 6.4 Hz, 1 H), 3.75 (spt, *J*=6.2 Hz, 1 H), 4.02 (dq, *J*=10.6, 7.0 Hz, 1 H), 4.11 (dq, *J*=10.6, 7.0 Hz, 1 H), 5.04 (d, *J*=2.2 Hz, 1 H), 5.15 – 5.20 (m, 1 H), 6.35 (t, *J*=2.4 Hz, 1 H).

^{13}C NMR (125 MHz, C_6D_6) δ -4.5, -3.5, 11.1, 14.7, 18.2, 18.7, 22.4, 24.3, 24.5, 25.2, 25.5, 26.6 (3C), 27.3, 36.1, 43.1, 46.5, 60.3, 68.9, 70.9, 71.9, 73.6, 77.7, 89.9, 132.1, 136.0, 140.2, 155.6, 165.5.

HRMS (EI+) calculated for $C_{33}H_{56}NaO_6Si_2$: 627.3513; found: 627.3508.



Ethyl (1a*R,3*S**,5*S**,7a*R**,7b*R**,8*R**,9*R**,9a*R**)-5-hydroxy-9a-isopropoxy-1,1,8-trimethyl-9-(tetradecanoyloxy)-1,1a,3,5,6,7,7a,8,9,9a-decahydro-3,7b-epoxycyclopropa[3,4]benzo[1,2-e]azulene-4-carboxylate (32)**

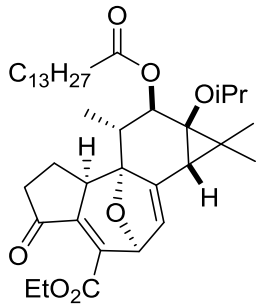
The procedure was modified from the Yamaguchi esterification described by Santa Lucia et.al.[9] Alcohol **31** (20 mg, 38 µmol) was dissolved in anhydrous THF (0.5 mL) and to this was added benzoyl chloride (20 µL, 0.17 mmol), myristic acid (39 mg, 0.17 mmol), triethylamine (40 µL, 0.29 mmol) and DMAP (8.9 mg, 73 µmol) under an argon atmosphere. The reaction mixture was then stirred for 2 d, followed by workup through partitioning between a saturated $NaHCO_3$ solution and 15% ethyl acetate in petroleum spirit (3 x 1.5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude residue was purified *via* chromatography with neutral alumina (4% ethyl acetate in petroleum spirit)

to afford the TBS-myristate as a colourless oil (22 mg), which was then treated with methanol (4 mL) and a catalytic amount of Amberlyst I15 (5 mg) for 7 d. After filtration and concentration, the crude was purified *via* chromatography with neutral alumina (20% ethyl acetate in petroleum spirit) to give the desired hydroxy-myristate **32** as a clear oil (10 mg, 40% over 2 steps [63% brsm over 2 steps]). Note: The unreacted TBSO-myristate (8.6 mg, 39%) was recovered from the silyl deprotection (Step 2).

^{1}H NMR (500 MHz, C_6D_6) δ 0.86 (t, *J*=7.2 Hz, 3 H), 0.92 (t, *J*=7.0 Hz, 3 H), 0.96 (d, *J*=6.2 Hz, 3 H), 1.24 – 1.35 (m, 33 H), 1.43 – 1.52 (m, 1 H), 1.52 – 1.65 (m, 2 H), 1.68 (quin, *J*=7.2 Hz, 2 H), 2.03 (dd, *J*=13.0, 6.4 Hz, 1 H), 2.34 (td, *J*=7.4, 1.7 Hz, 2 H), 2.47 (dq, *J*=12.1, 7.0 Hz, 1 H), 2.75 (dd, *J*=13.2, 6.2 Hz, 1 H), 3.78 (spt, *J*=6.1 Hz, 1 H), 3.87 (qd, *J*=7.0, 0.7 Hz, 2 H), 4.49 (d, *J*=12.5 Hz, 1 H), 4.99 (t, *J*=1.8 Hz, 1 H), 5.10 (dd, *J*=7.3, 1.1 Hz, 1 H), 5.20 (d, *J*=1.8 Hz, 1 H), 6.07 (t, *J*=2.4 Hz, 1 H).

^{13}C NMR (176 MHz, C_6D_6) δ 11.1, 14.3, 14.7, 18.5, 22.7, 23.5, 24.4, 24.6, 25.6, 25.7, 26.1, 28.0, 29.9, 30.1, 30.2, 30.3, 30.42, 30.47, 30.48, 30.51, 32.7, 33.7, 34.8, 40.2, 47.7, 61.3, 68.0, 72.07, 72.13, 72.8, 76.8, 89.4, 129.6, 136.7, 139.0, 163.0, 166.6, 172.4.

HRMS (EI+) calculated for $C_{38}H_{60}NaO_7$: 651.4237; found: 651.4231.



Ethyl (1a*R,3*S**,7a*S**,7b*R**,8*R**,9*R**,9a*R**)-9a-isopropoxy-1,1,8-trimethyl-5-oxo-9-(tetradecanoyloxy)-1,1a,3,5,6,7,7a,8,9,9a-decahydro-3,7b-epoxycyclopropa[3,4]benzo[1,2-e]azulene-4-carboxylate (33)**

The hydroxy-myristate **32** (10 mg, 16 µmol) was treated with Dess-Martin periodinane (11 mg, 26 µmol) and $NaHCO_3$ (4.0 mg, 48 µmol) in anhydrous DCM. The reaction was stirred for 20 h at which point TLC indicated no sign of starting material. The reaction mixture was then partitioned with a saturated $NaHCO_3$ solution and DCM (3 x 1 mL), and the combined organic extracts dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The desired keto-myristate **33** was obtained as a clear liquid (10 mg, quantitative) after chromatography with neutral alumina (20% ethyl acetate in petroleum spirit).

^{1}H NMR (500 MHz, C_6D_6) δ 0.73 (qd, *J*=12.0, 7.9 Hz, 1 H), 0.92 (t, *J*=7.0 Hz, 3 H), 0.96 (d, *J*=6.2 Hz, 3 H), 1.08 (d, *J*=2.2 Hz, 1 H), 1.16 (t, *J*=7.2 Hz, 3 H), 1.21 (s, 3 H), 1.24 – 1.33 (m, 28 H), 1.38 (dt, *J*=11.4, 7.7 Hz, 1 H), 1.69 (s, 3 H), 1.64 – 1.74 (m, 1 H), 1.90 (dd, *J*=17.6, 7.7 Hz, 1 H), 2.30 (dt, *J*=12.5, 6.6 Hz, 1 H), 2.34 (td, *J*=7.3, 1.5 Hz, 2 H), 2.72 (dd, *J*=12.8, 7.0 Hz, 1 H), 3.63 (spt, *J*=6.2 Hz, 1 H), 4.23 (dq, *J*=10.6, 7.0 Hz, 1 H), 4.25 (dq, *J*=10.6, 7.0 Hz, 1 H), 4.40 (d, *J*=12.1 Hz, 1 H), 4.79 (dt, *J*=2.2, 1.1 Hz, 1 H), 6.10 (t, *J*=2.4 Hz, 1 H).

^{13}C NMR (125 MHz, C_6D_6) δ 11.1, 14.5, 14.7, 18.4, 22.4, 22.7, 23.5, 24.4, 24.6, 25.7, 25.9, 28.2, 29.9, 30.1, 30.2, 30.3, 30.4, 30.48 (2C), 30.51, 32.7, 34.8, 38.3, 39.7, 41.3, 61.8, 67.9, 71.9, 72.7, 78.0, 89.9, 135.8, 137.6, 139.2, 140.2, 166.5, 172.4, 201.7.

HRMS (EI+) calculated for $C_{38}H_{58}NaO_7$: 649.4080; found: 649.4075.

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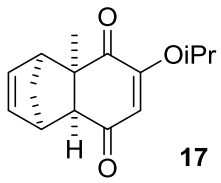
X-ray crystallography data for compounds 17, 19, 24, 28 & 30



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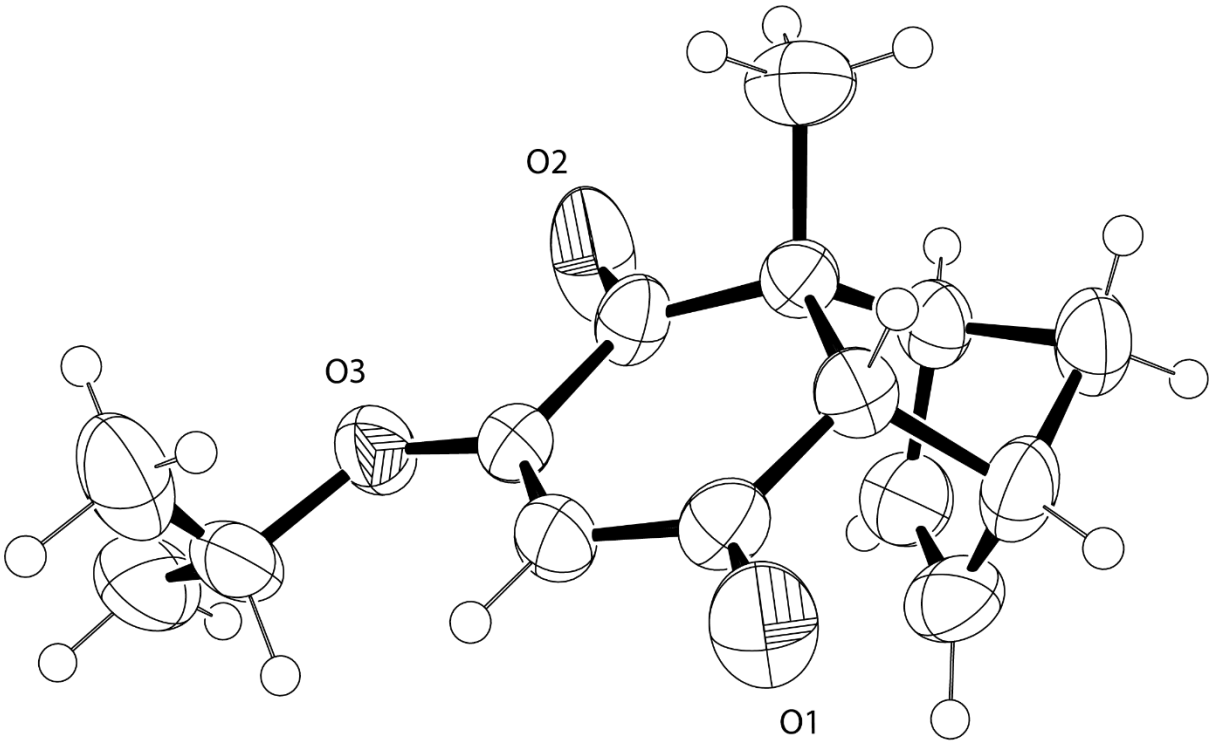
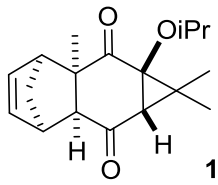


Identification code	860tk3 (CCDC 1955317)	
Empirical formula	$C_{15}\ H_{18}\ O_3$	
Formula weight	246.29	
Temperature	190(2) K	
Wavelength	0.7107 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/c$	
Unit cell dimensions	a = 6.365(2) Å	α= 90°.
	b = 21.464(5) Å	β= 100.69(3)°.
	c = 9.837(3) Å	γ = 90°.
Volume	1320.6(7) $Å^3$	
Z	4	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	528	
Crystal size	0.600 x 0.600 x 0.400 mm^3	
Theta range for data collection	3.257 to 24.999°.	
Index ranges	-6<=h<=7, -25<=k<=24, -11<=l<=11	
Reflections collected	9703	
Independent reflections	2329 [R(int) = 0.0260]	
Completeness to theta = 24.999°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.969	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2329 / 0 / 166	
Goodness-of-fit on F^2	1.043	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1090	
R indices (all data)	R1 = 0.0603, wR2 = 0.1158	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.171 and -0.146 e.$Å^{-3}$	



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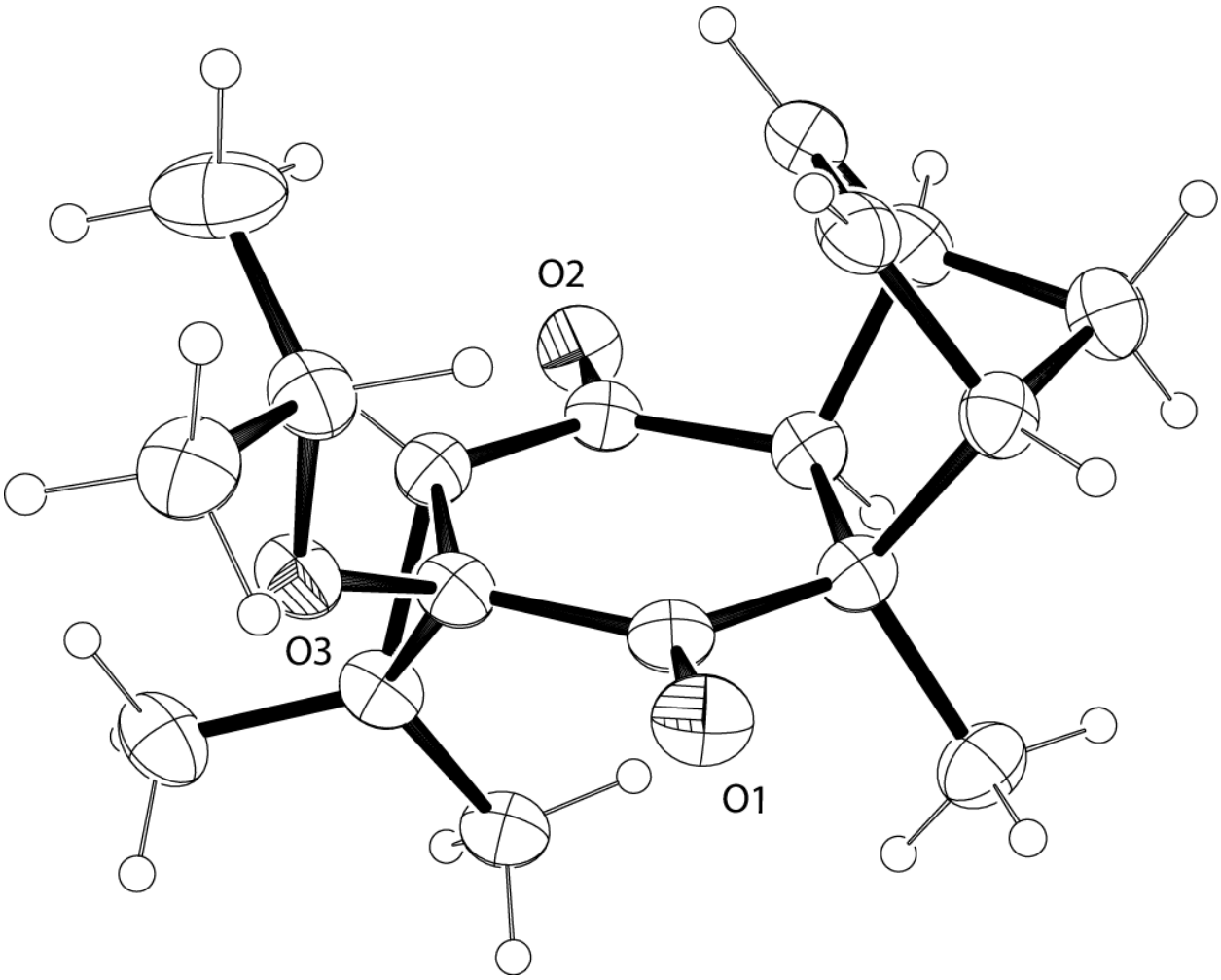
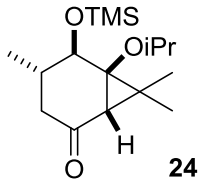


Identification code	1112tk-111-75 (CCDC 1955318)	
Empirical formula	$C_{18}H_{24}O_3$	
Formula weight	288.37	
Temperature	190(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	*P* $2_1/n$	
Unit cell dimensions	a = 8.3706(8) Å	α= 90°.
	b = 17.0190(15) Å	β= 99.617(8)°.
	c = 11.1609(9) Å	γ = 90°.
Volume	1567.6(2) $Å^3$	
Z	4	
Density (calculated)	1.222 Mg/m^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	624	
Crystal size	0.2 x 0.2 x 0.2 mm^3	
Theta range for data collection	4.785 to 62.478°.	
Index ranges	-9<=h<=9, -19<=k<=11, -10<=l<=12	
Reflections collected	6198	
Independent reflections	2484 [R(int) = 0.0393]	
Completeness to theta = 62.478°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.605	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2484 / 0 / 195	
Goodness-of-fit on F^2	1.076	
Final R indices [I>2sigma(I)]	R1 = 0.0631, wR2 = 0.1548	
R indices (all data)	R1 = 0.0759, wR2 = 0.1676	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.393 and -0.226 e.$Å^{-3}$	



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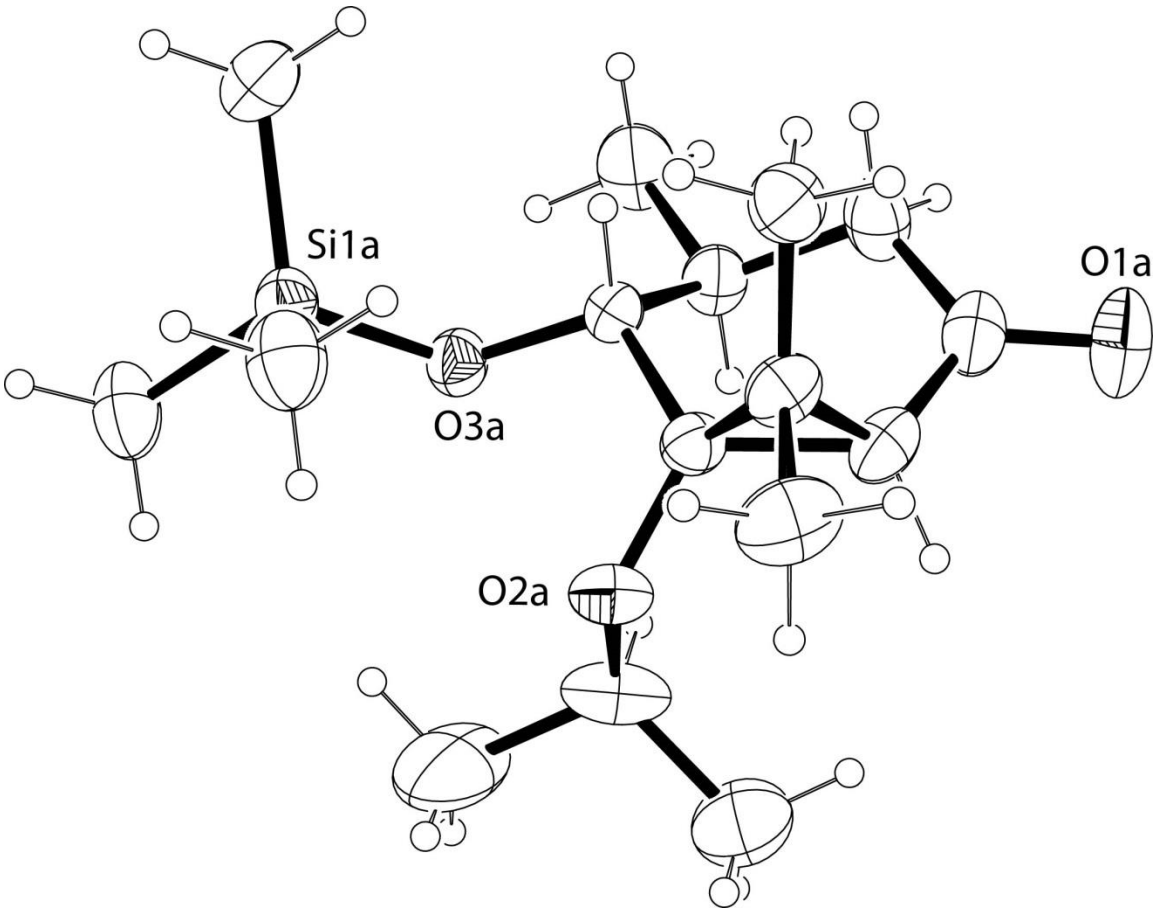
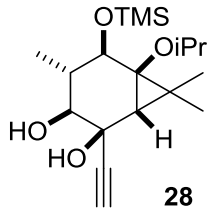


Identification code	1096sc1 (CCDC 1955319)	
Empirical formula	$C_{16}\ H_{30}\ O_3\ Si$	
Formula weight	298.49	
Temperature	190(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 10.034(3) Å	α= 80.65(2)°.
	b = 12.968(3) Å	β= 88.39(2)°.
	c = 14.934(3) Å	γ = 84.63(2)°.
Volume	1908.9(8) $Å^3$	
Z	4	
Density (calculated)	1.039 Mg/m^3	
Absorption coefficient	0.128 mm^{-1}	
F(000)	656	
Crystal size	0.4 x 0.2 x 0.1 mm^3	
Theta range for data collection	2.97 to 29.42°.	
Index ranges	-13<=h<=12, -17<=k<=17, -20<=l<=12	
Reflections collected	19545	
Independent reflections	9071 [R(int) = 0.0499]	
Completeness to theta = 25.00°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.38943	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9071 / 0 / 365	
Goodness-of-fit on F^2	1.021	
Final R indices [I>2sigma(I)]	R1 = 0.0746, wR2 = 0.1711	
R indices (all data)	R1 = 0.1323, wR2 = 0.2068	
Largest diff. peak and hole	0.286 and -0.216 $e.Å^{-3}$	



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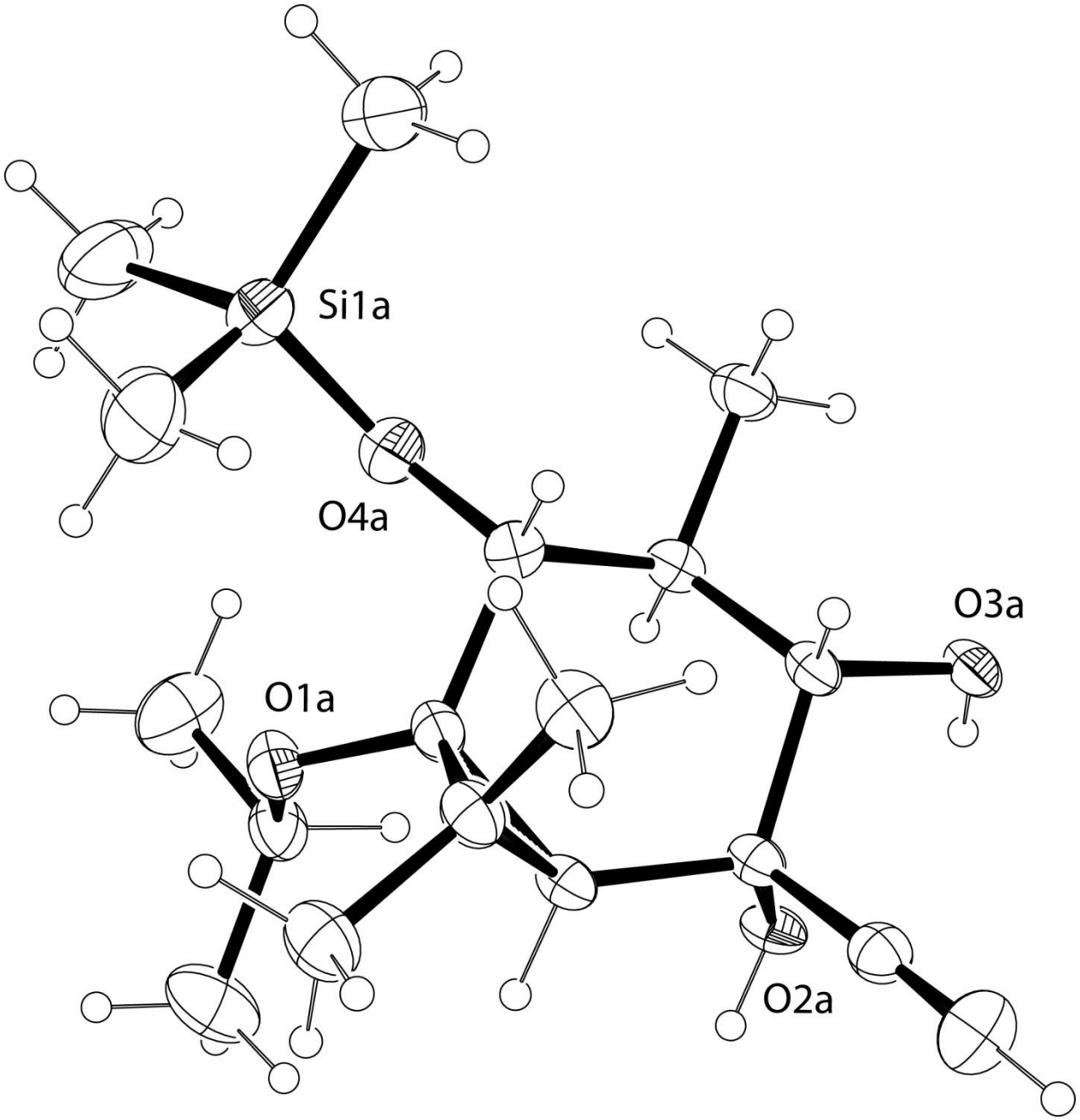
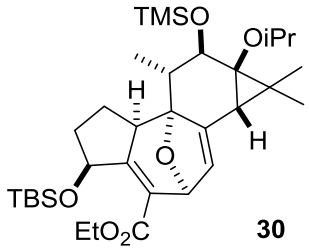


Identification code	1323sc2 (CCDC 1955320)	
Empirical formula	C_{18} H_{32} O_4 Si	
Formula weight	340.53	
Temperature	190(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	$P\ \bar{1}$	
Unit cell dimensions	a = 10.3455(10) Å	α= 73.468(7)°.
	b = 13.8560(13) Å	β= 86.752(7)°.
	c = 15.6403(12) Å	γ = 74.998(8)°.
Volume	2075.7(3) Å^3	
Z	4	
Density (calculated)	1.090 Mg/m^3	
Absorption coefficient	1.123 mm^{-1}	
F(000)	744	
Crystal size	0.3 x 0.1 x 0.04 mm^3	
Theta range for data collection	3.44 to 62.50°.	
Index ranges	-11<=h<=10, -12<=k<=15, -17<=l<=17	
Reflections collected	16171	
Independent reflections	6526 [R(int) = 0.0539]	
Completeness to theta = 62.50°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.87037	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6526 / 0 / 419	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R1 = 0.0711, wR2 = 0.2017	
R indices (all data)	R1 = 0.0917, wR2 = 0.2370	
Largest diff. peak and hole	1.012 and -0.483 e.Å^{-3}	



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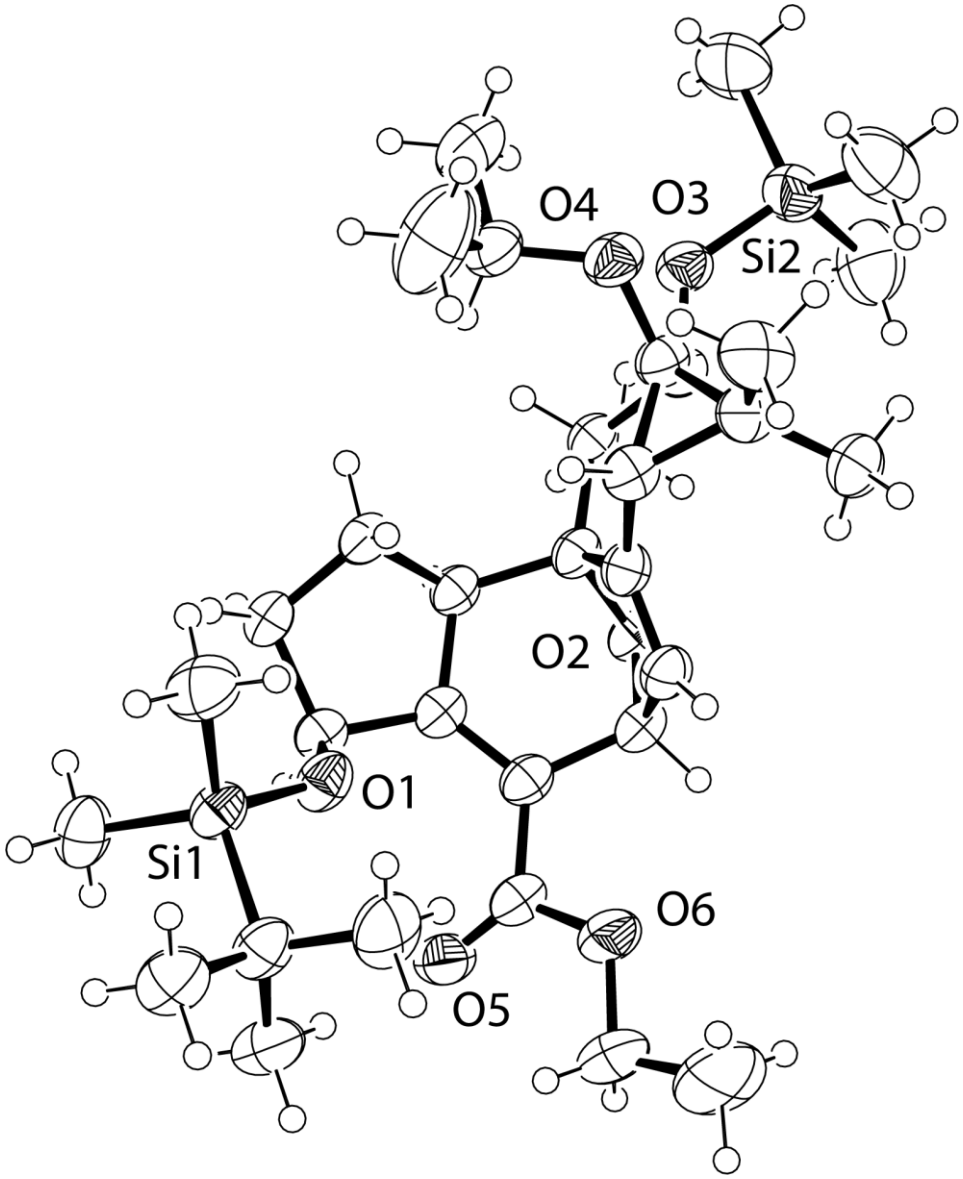

Identification code	1207sc1 (CCDC 1955321)	
Empirical formula	$C_{33}\ H_{56}\ O_6\ Si_2$	
Formula weight	604.95	
Temperature	190(2) K	
Wavelength	1.5418 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 13.2671(6) Å	α= 90°.
	b = 13.5663(8) Å	β= 93.323(4)°.
	c = 20.4372(13) Å	γ = 90°.
Volume	3672.2(4) $Å^3$	
Z	4	
Density (calculated)	1.094 Mg/m^3	
Absorption coefficient	1.173 mm^{-1}	
F(000)	1320	
Crystal size	0.5 x 0.5 x 0.2 mm^3	
Theta range for data collection	3.337 to 62.496°.	
Index ranges	-10<=h<=15, -15<=k<=14, -22<=l<=23	
Reflections collected	17861	
Independent reflections	5727 [R(int) = 0.0644]	
Completeness to theta = 62.496°	97.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1 and 0.47	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5727 / 0 / 384	
Goodness-of-fit on F^2	1.067	
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1715	
R indices (all data)	R1 = 0.0666, wR2 = 0.1843	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.452 and -0.409 e.$Å^{-3}$	

NMR spectra

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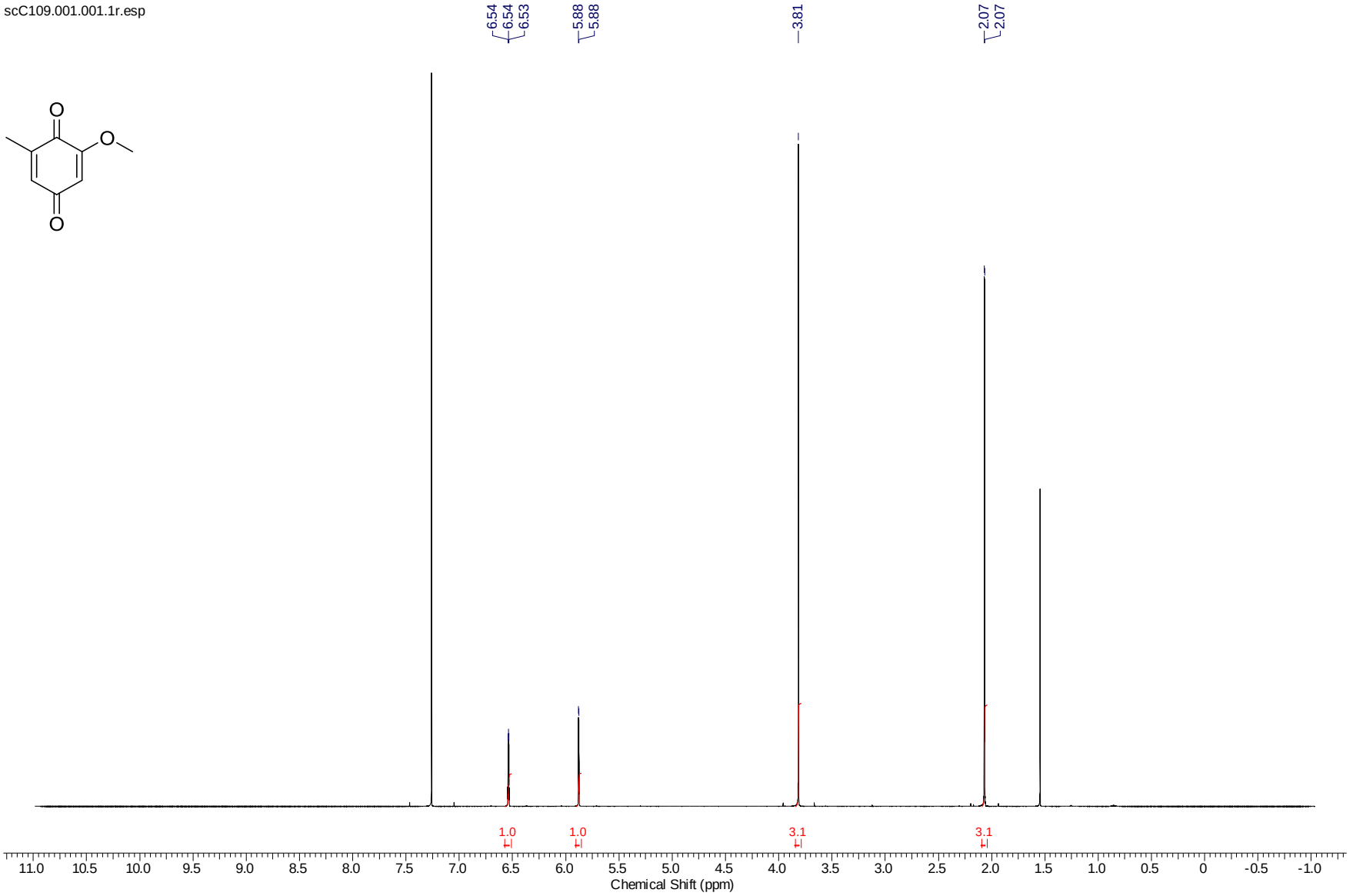
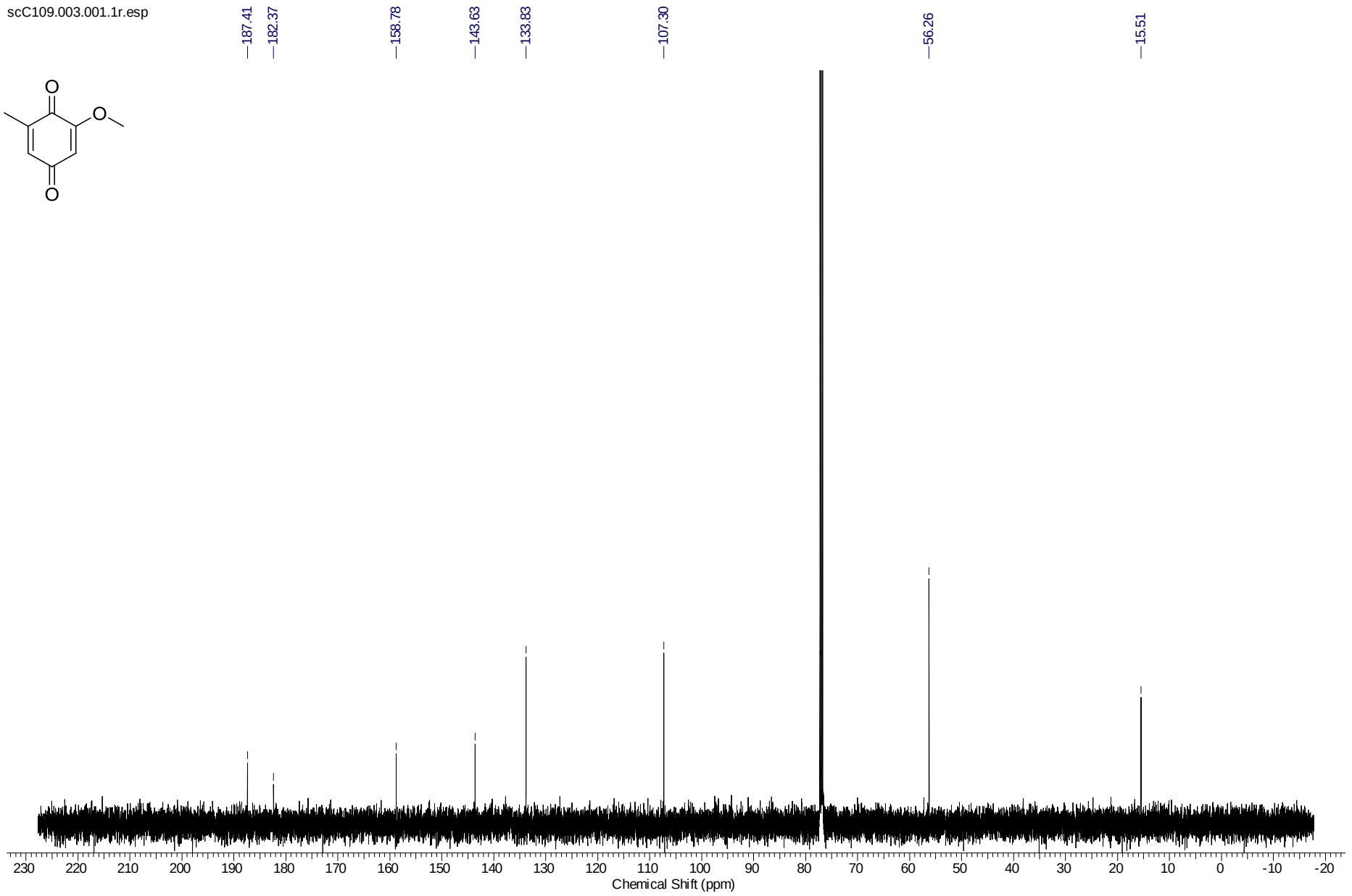
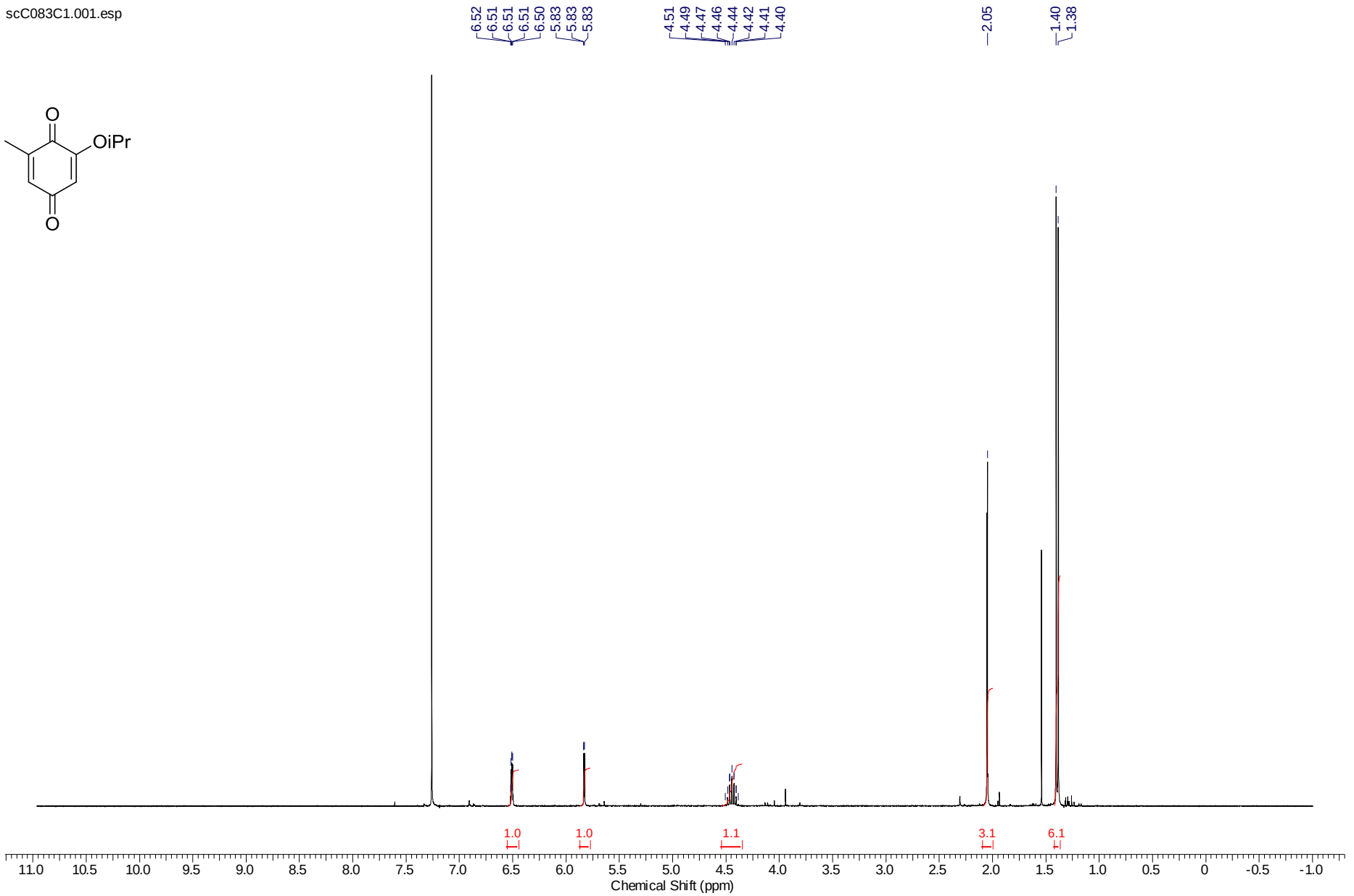


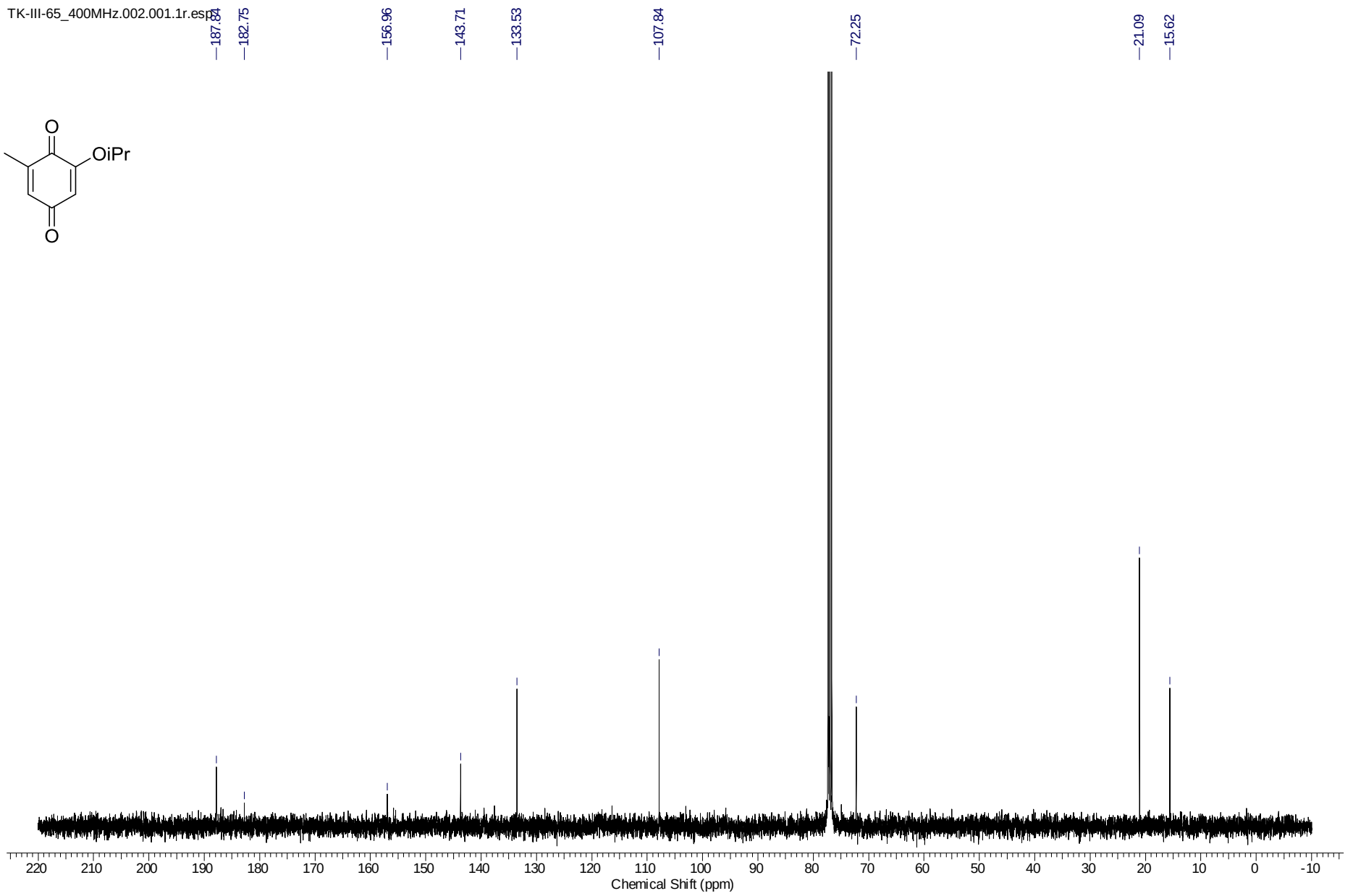
500 MHz ^{1}H NMR spectrum of **15** ($CDCl_3$).



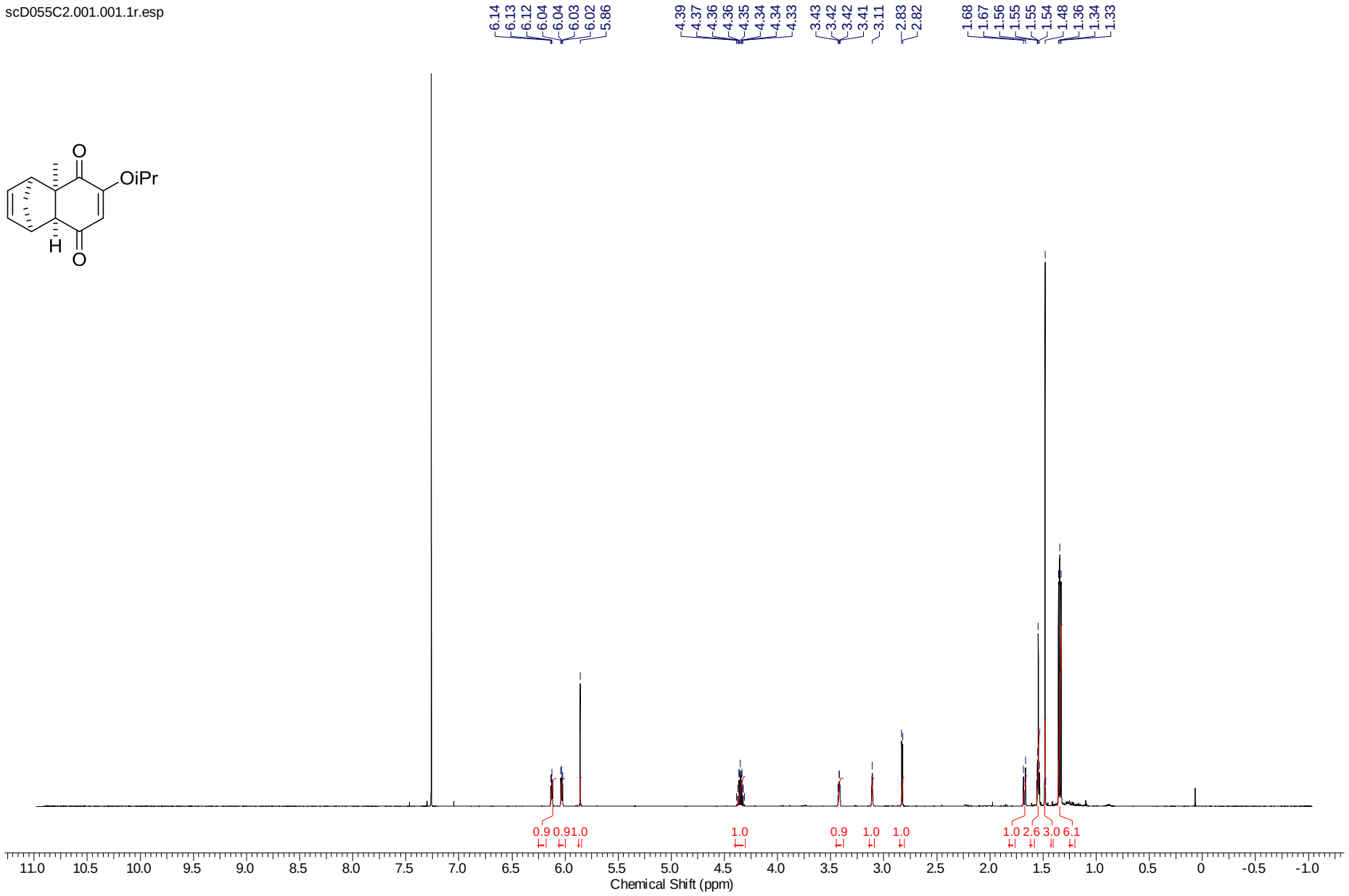
125 MHz ^{13}C NMR spectrum of **15** ($CDCl_3$).



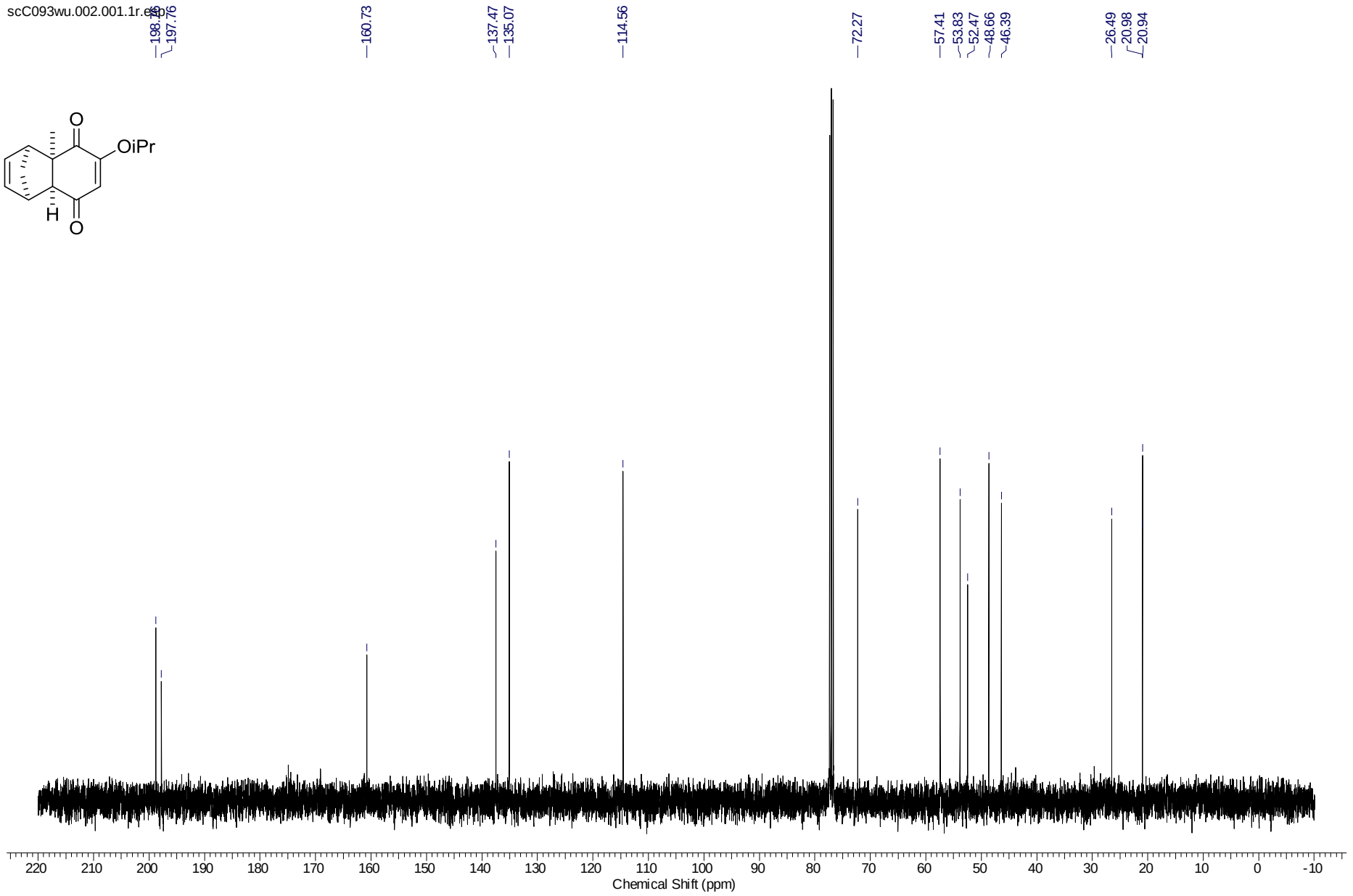
300 MHz ^{1}H NMR spectrum of **16** ($CDCl_3$).



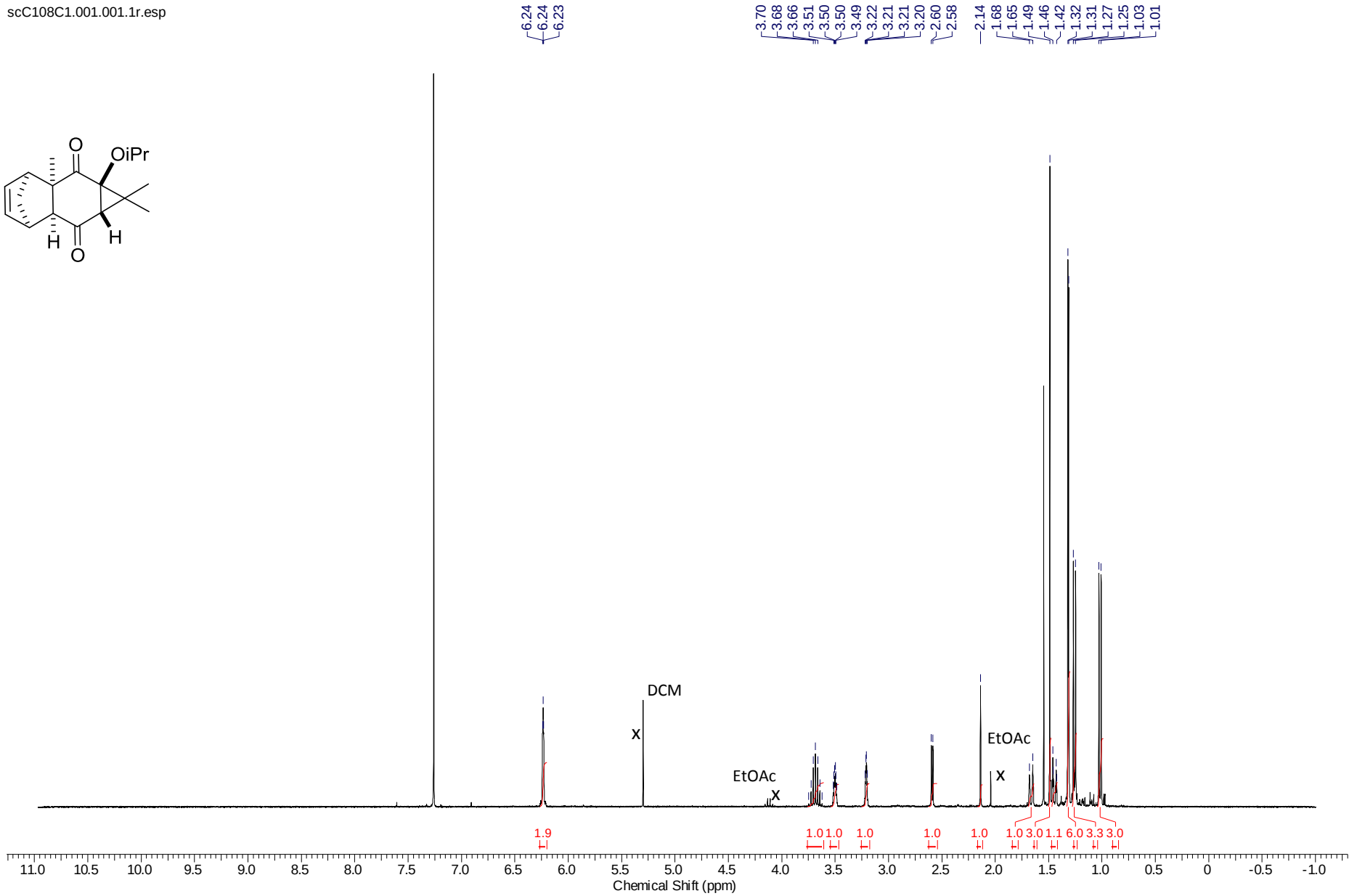
100 MHz ^{13}C NMR spectrum of **16** ($CDCl_3$).



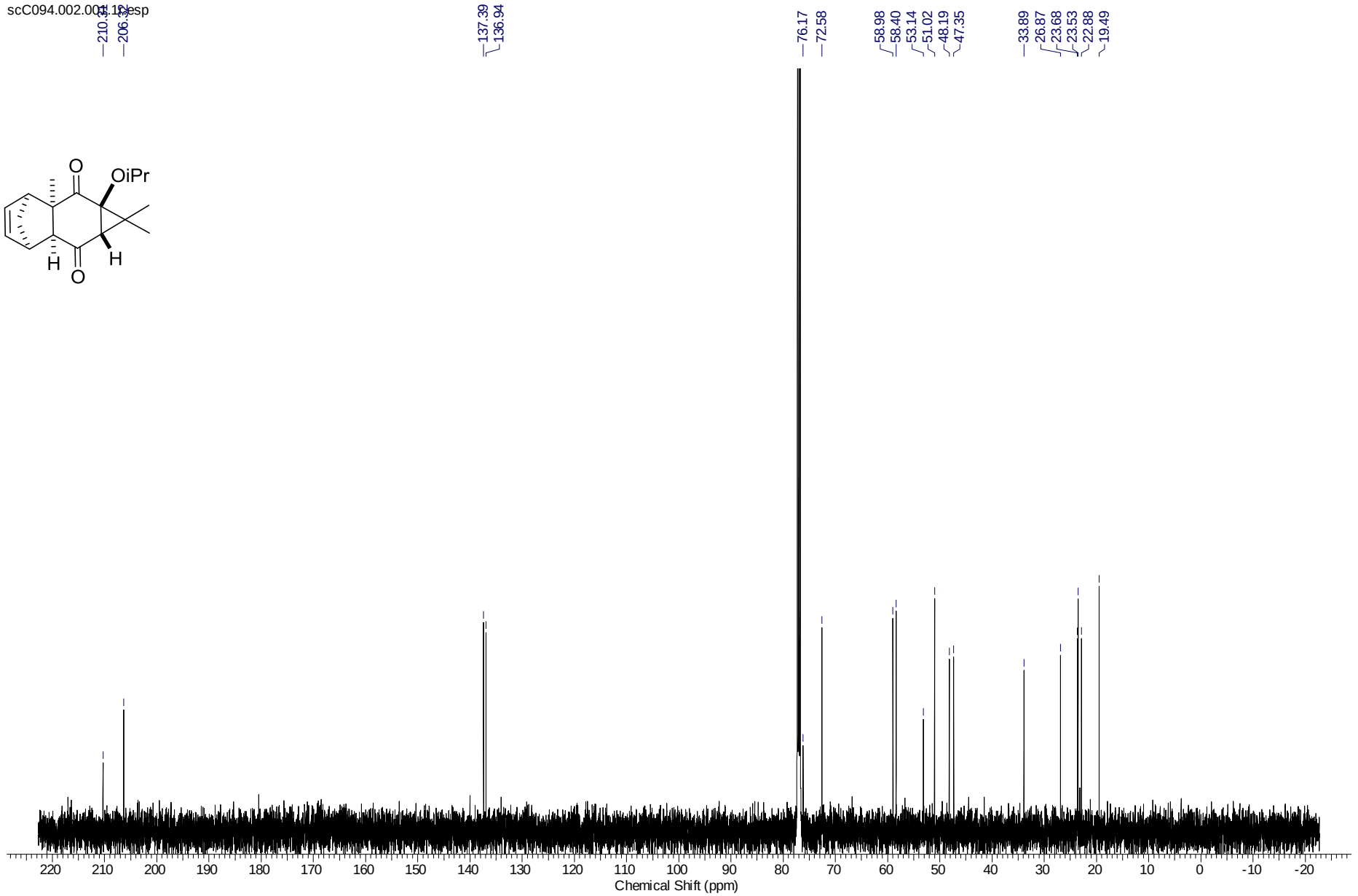
400 MHz ^{1}H NMR spectrum of **17** ($CDCl_3$).



100 MHz ^{13}C NMR spectrum of **17** ($CDCl_3$).



400 MHz ^{1}H NMR spectrum of **19** ($CDCl_3$).



125 MHz ^{13}C NMR spectrum of **19** ($CDCl_3$).

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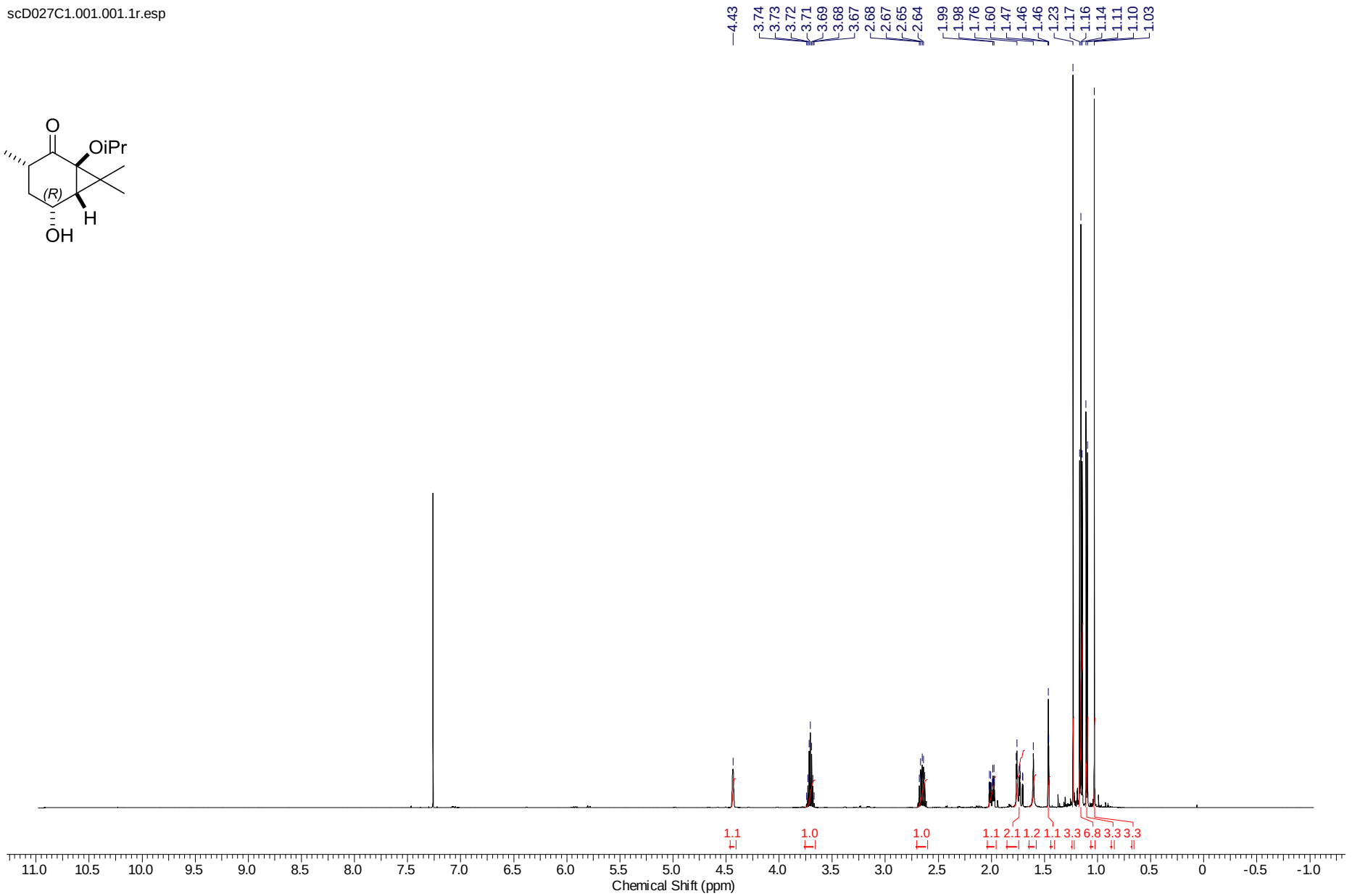
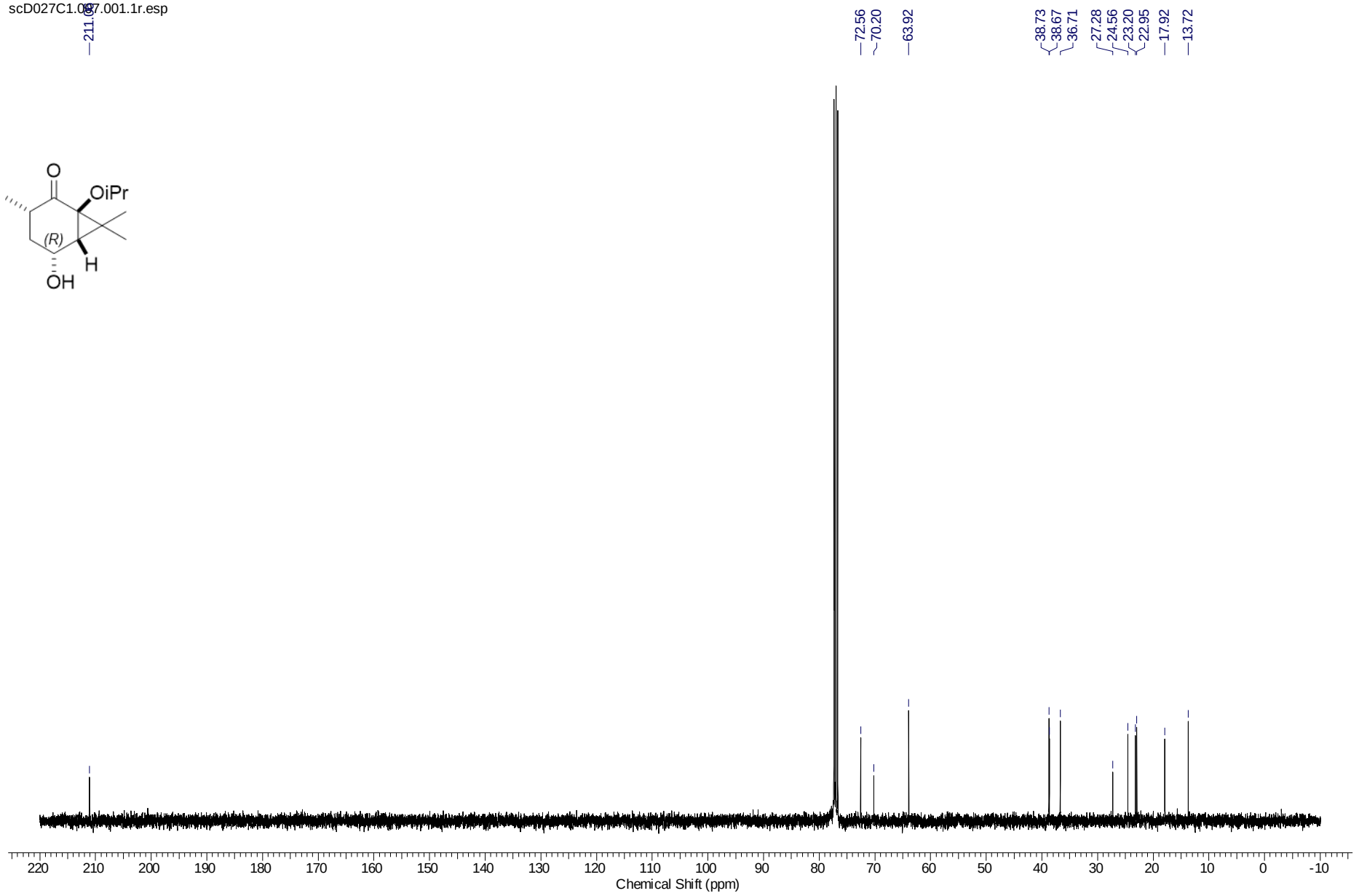
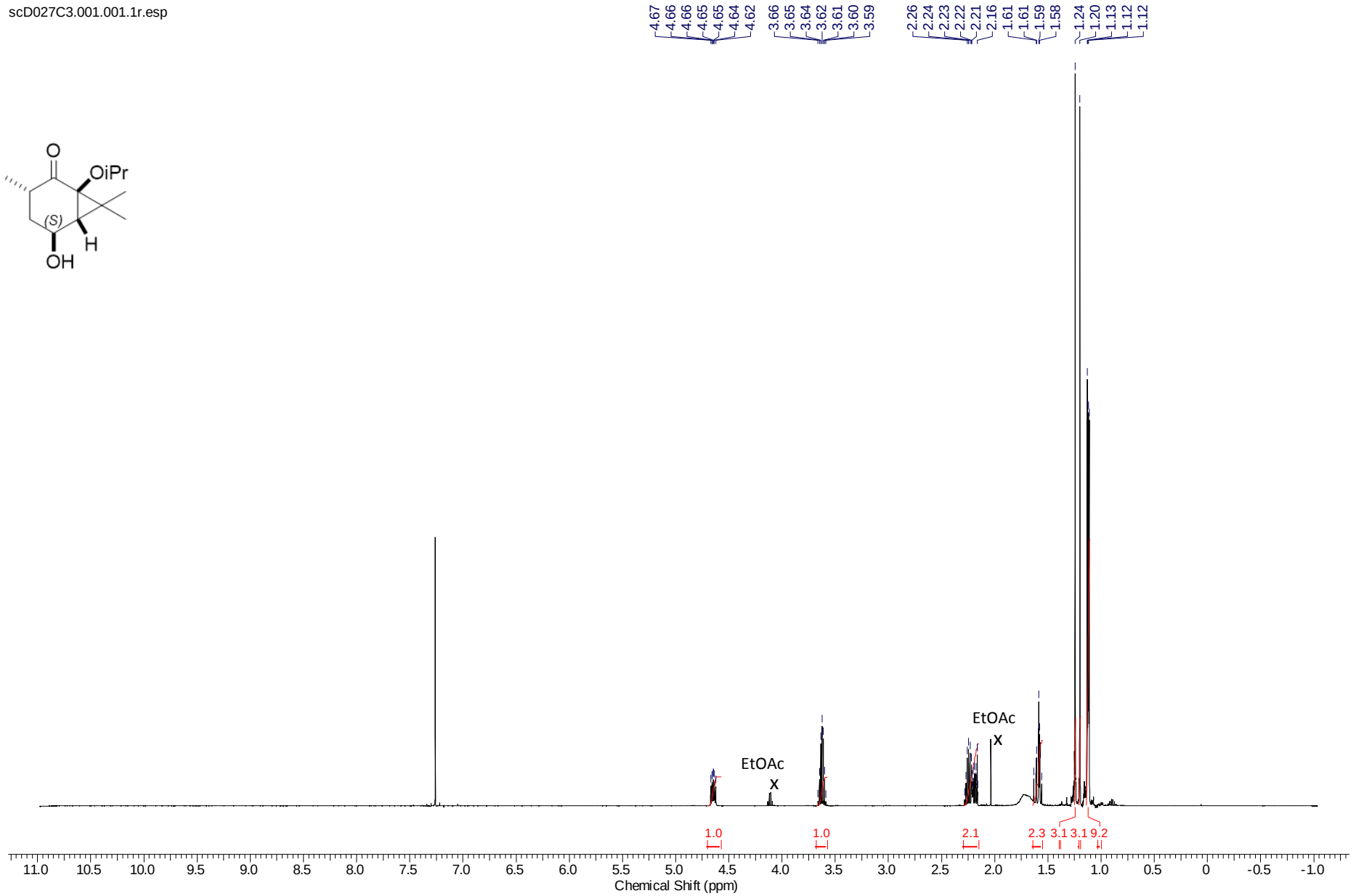


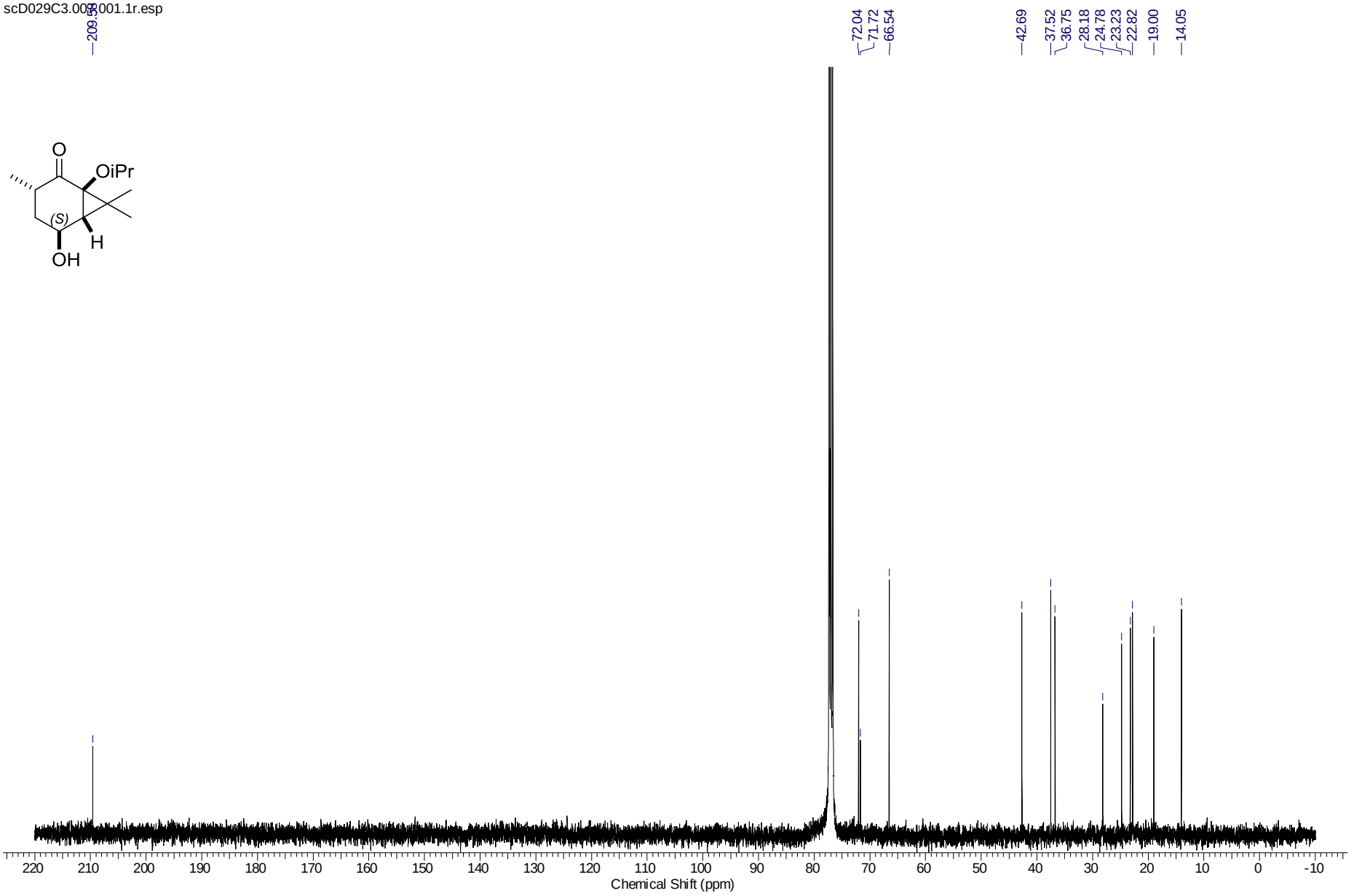
500 MHz ^{1}H NMR spectrum of (5*R**)-**22** ($CDCl_3$).



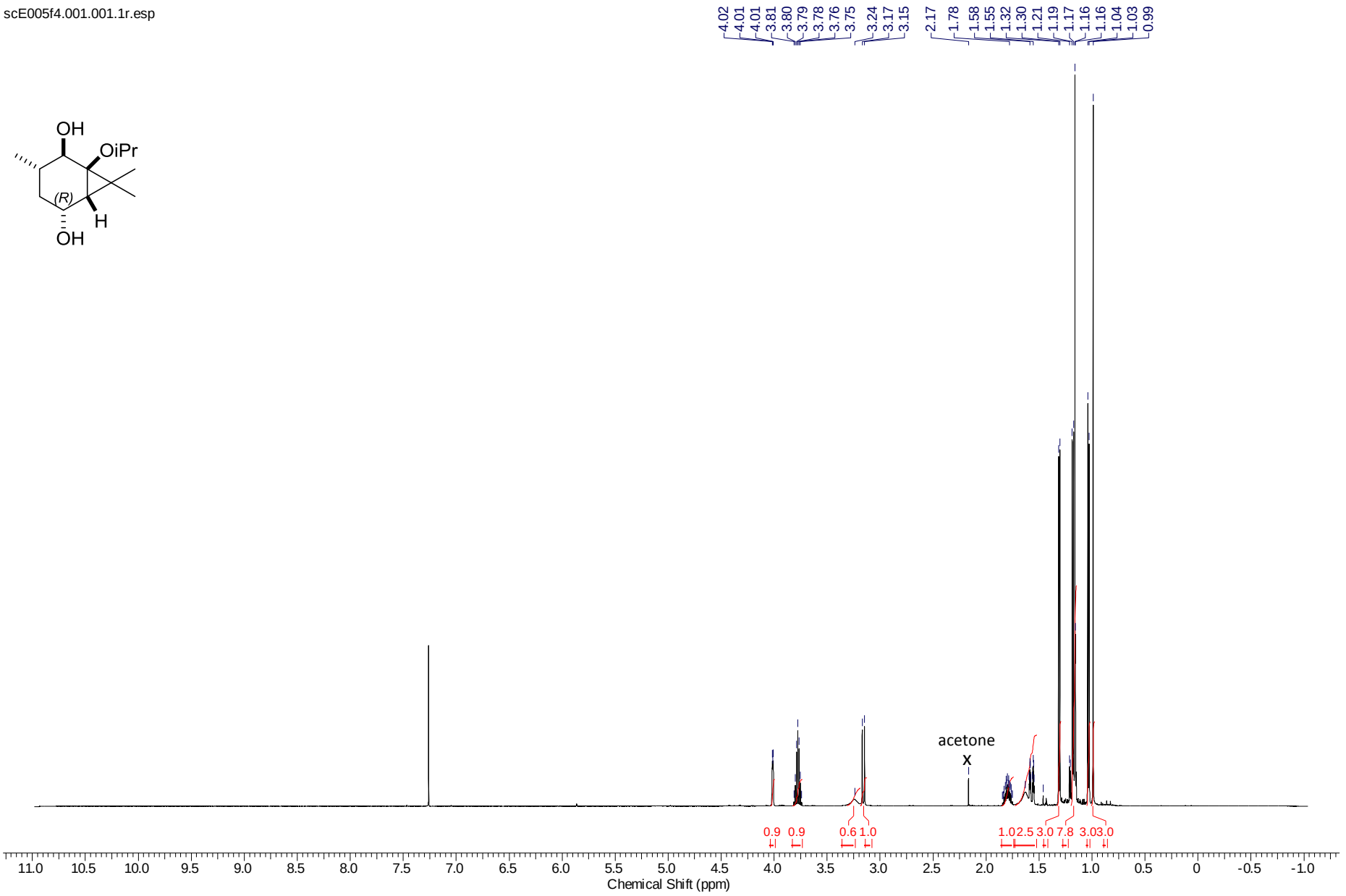
100 MHz ^{13}C NMR spectrum of (5*R**)-**22** ($CDCl_3$).



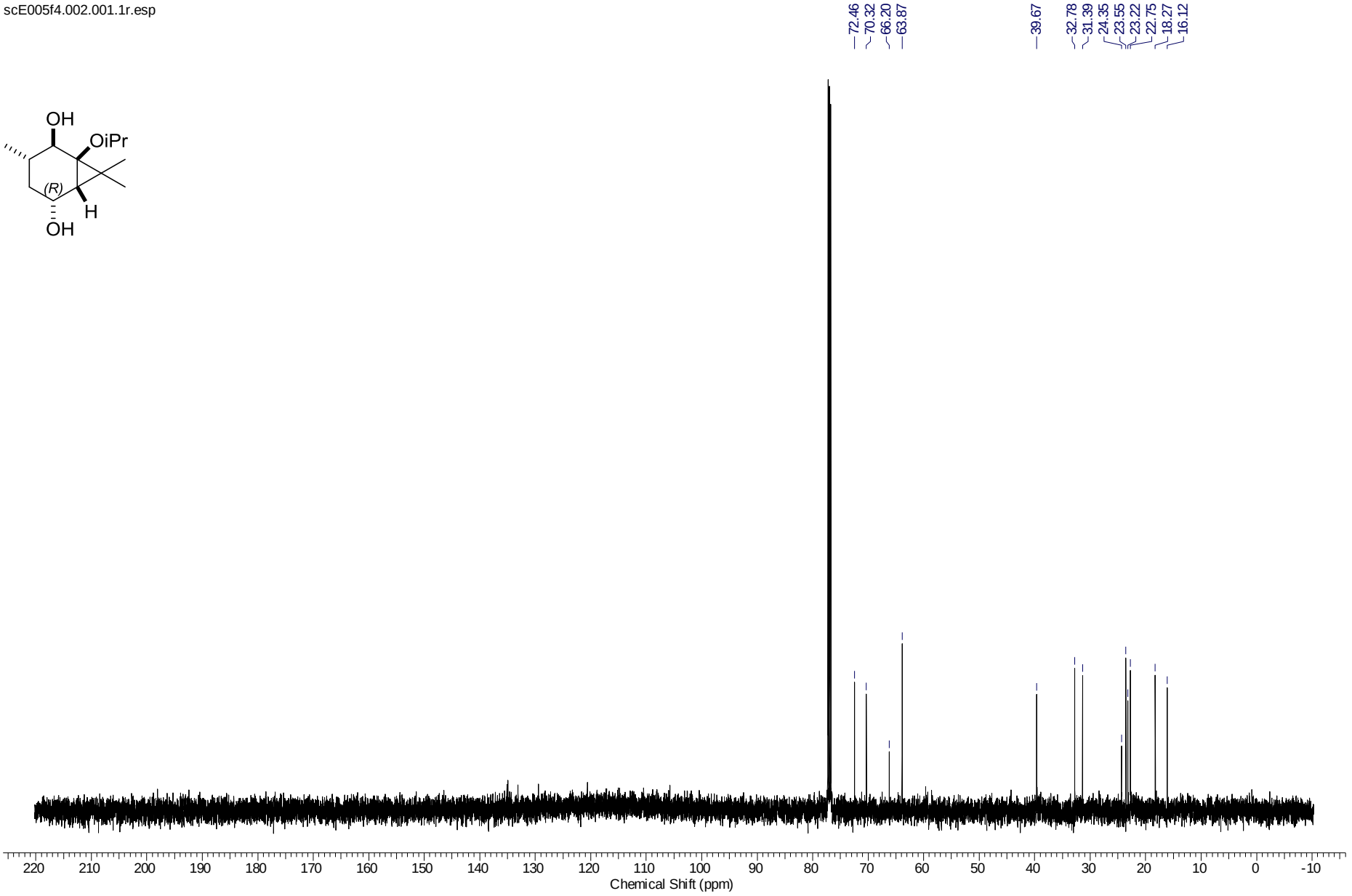
500 MHz ^{1}H NMR spectrum of (5*S**)-**22** ($CDCl_3$).



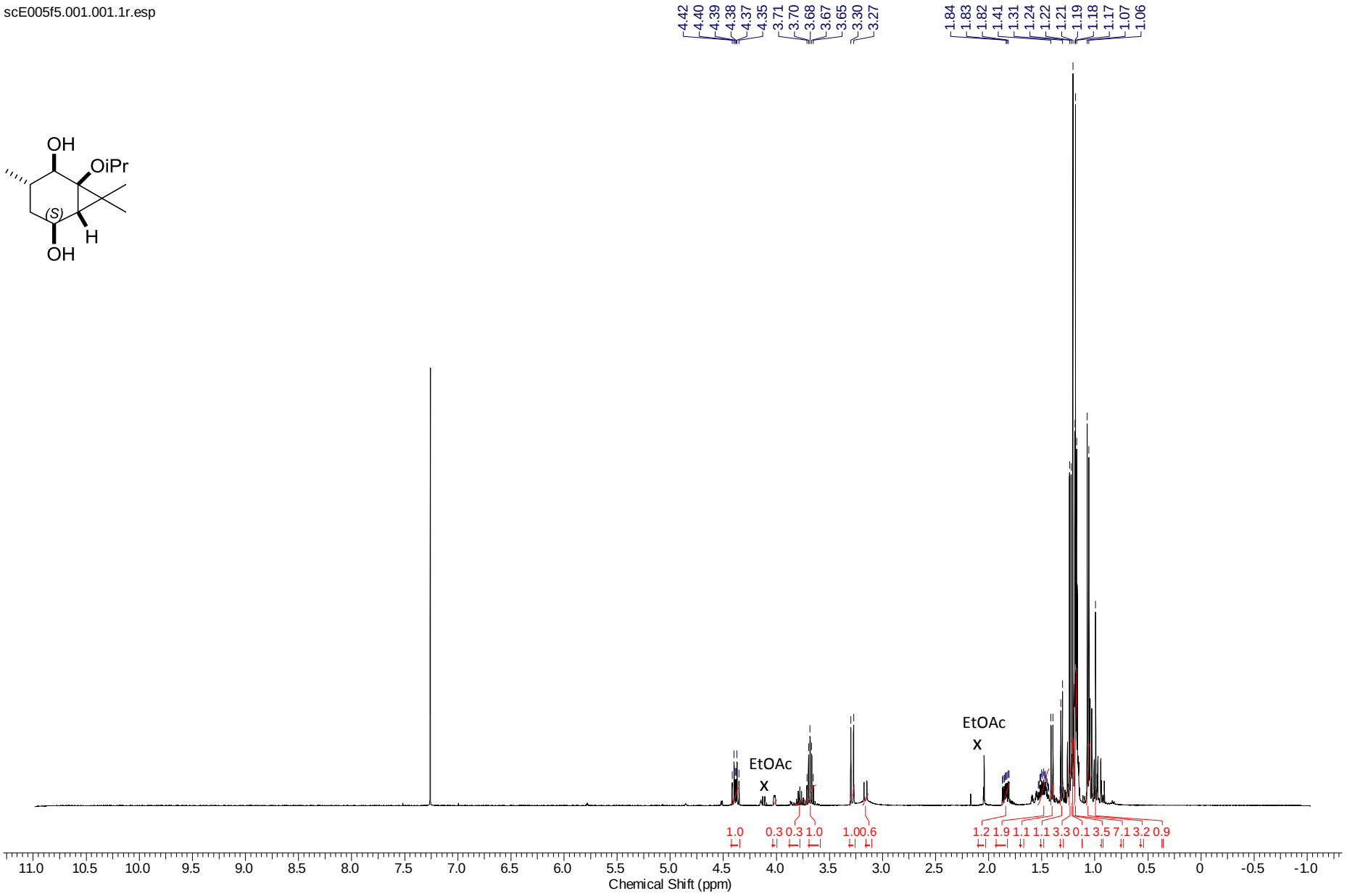
100 MHz ^{13}C NMR spectrum of (5*S**)-**22** ($CDCl_3$).



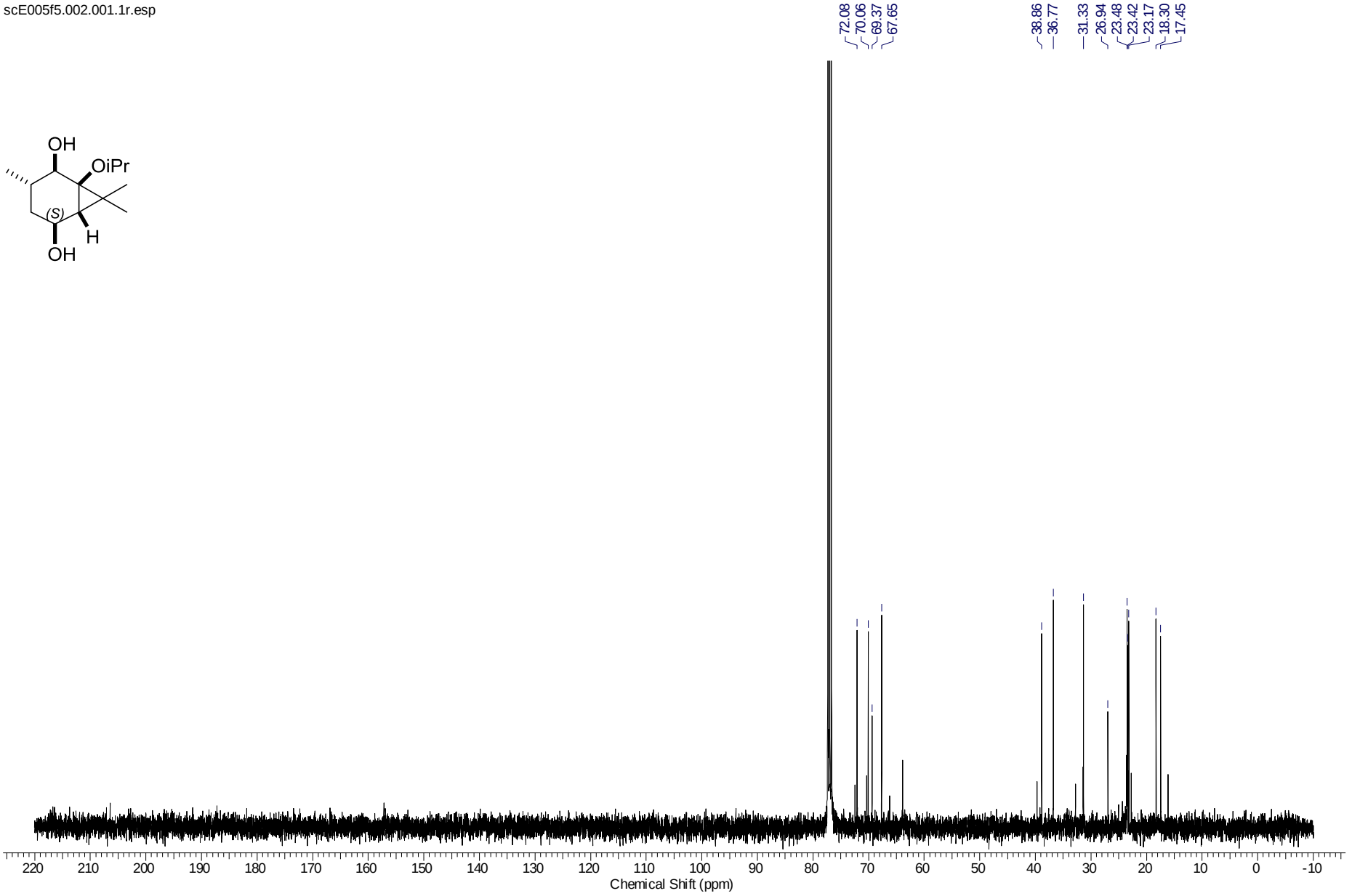
500 MHz ^{1}H NMR spectrum of (5*R**)-**23** ($CDCl_3$).



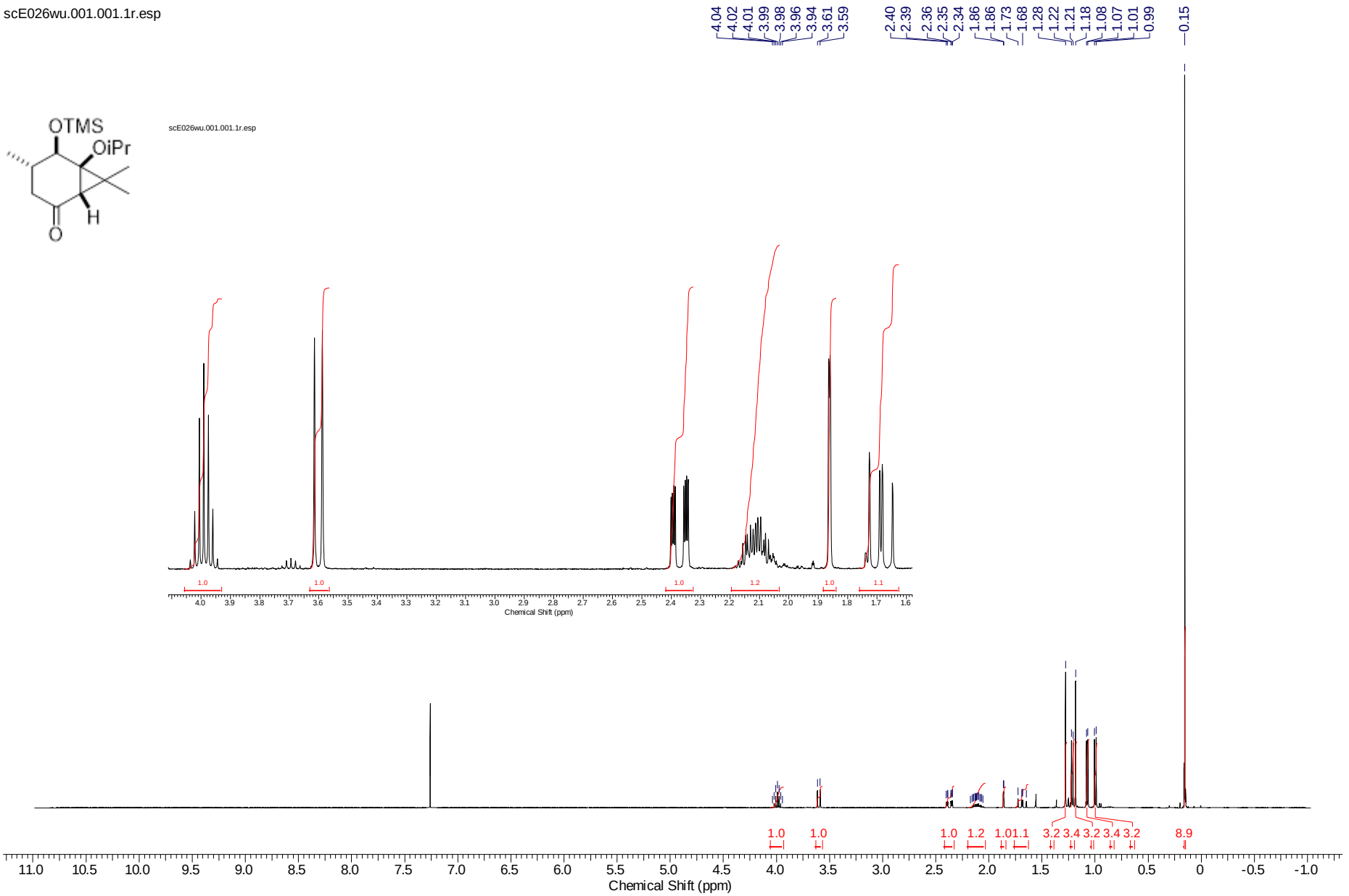
100 MHz ^{13}C NMR spectrum of (5*R**)-**23** ($CDCl_3$).



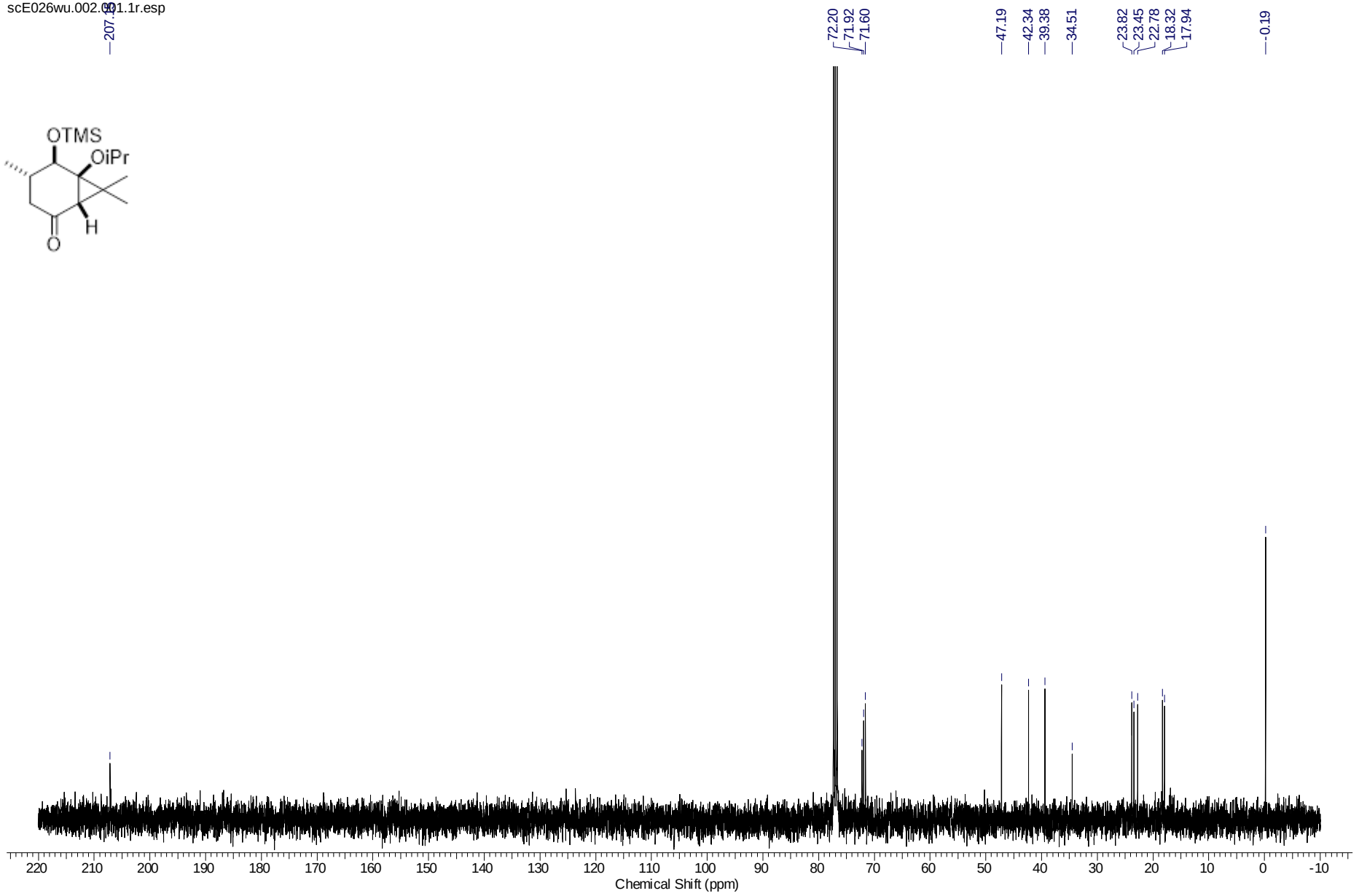
400 MHz ^{1}H NMR spectrum of (5*S**)-**23** ($CDCl_3$), containing ~ 23% of (5*R**)-**23**.



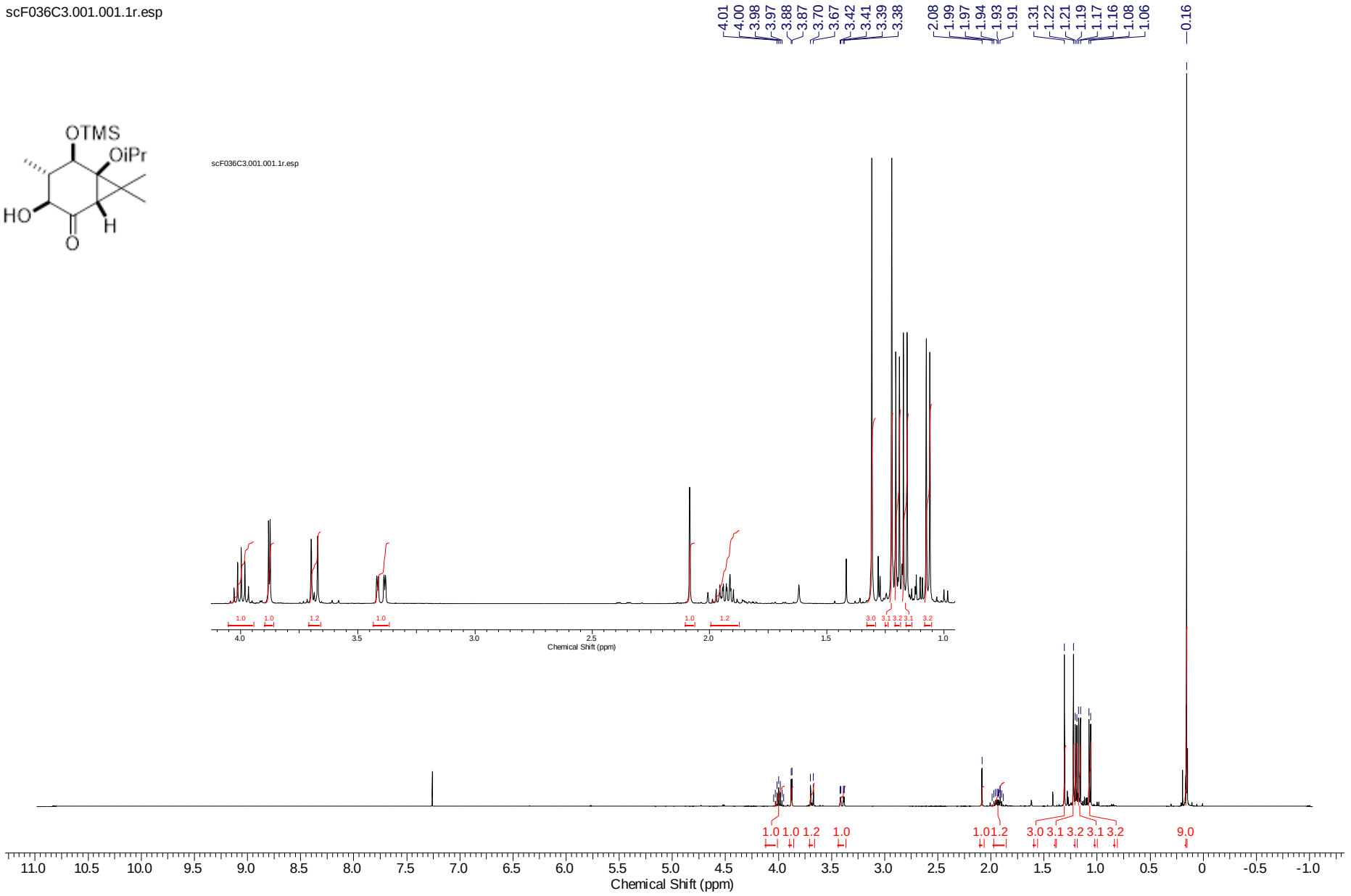
100 MHz ^{13}C NMR spectrum of (5*S**)-**23** ($CDCl_3$), containing ~ 23% of (5*R**)-**23**.



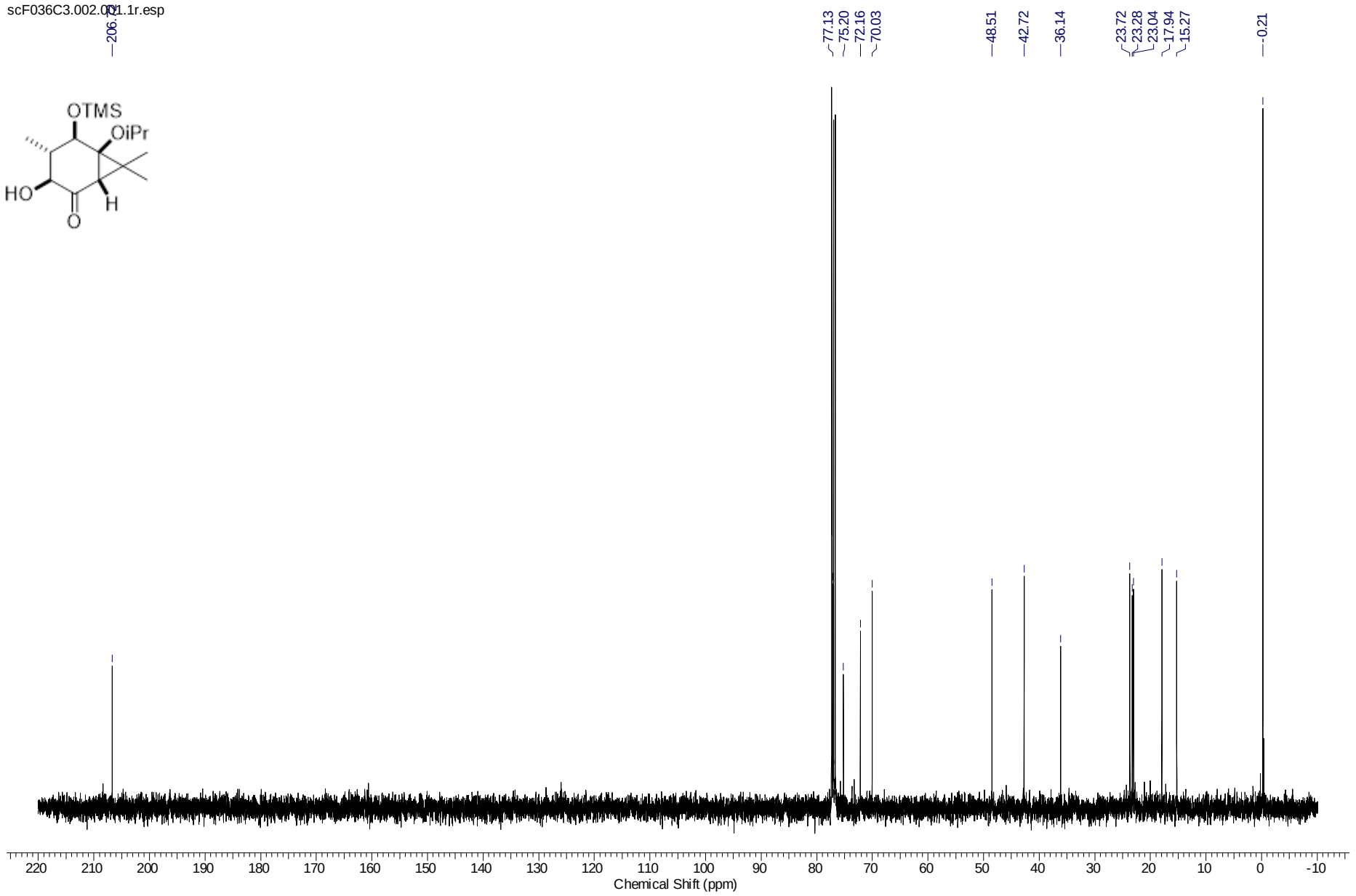
400 MHz ^{1}H NMR spectrum of **24** ($CDCl_3$).



100 MHz ^{13}C NMR spectrum of **24** ($CDCl_3$).



400 MHz ^{1}H NMR spectrum of **26** ($CDCl_3$).



100 MHz ^{13}C NMR spectrum of **26** ($CDCl_3$).

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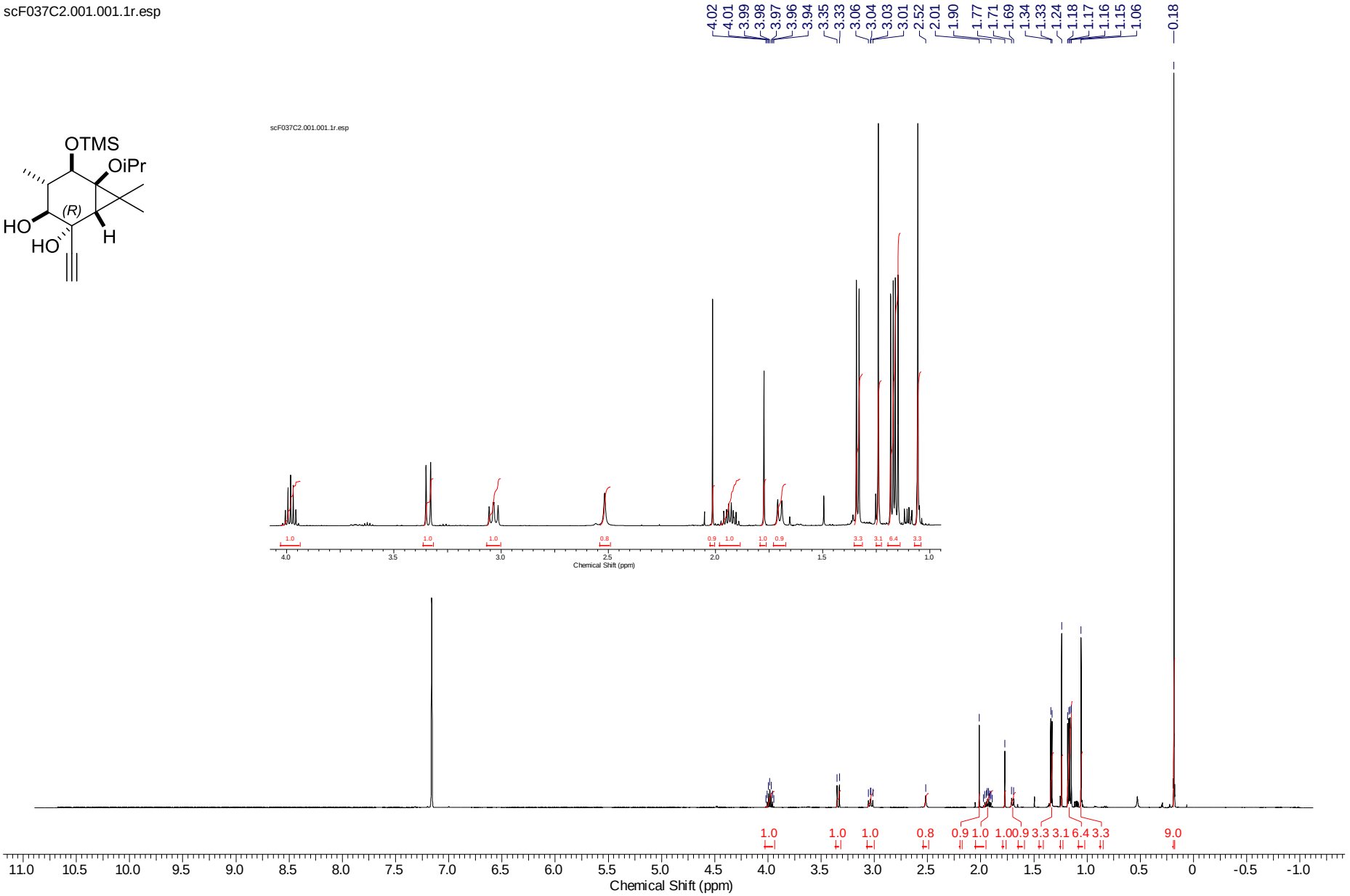
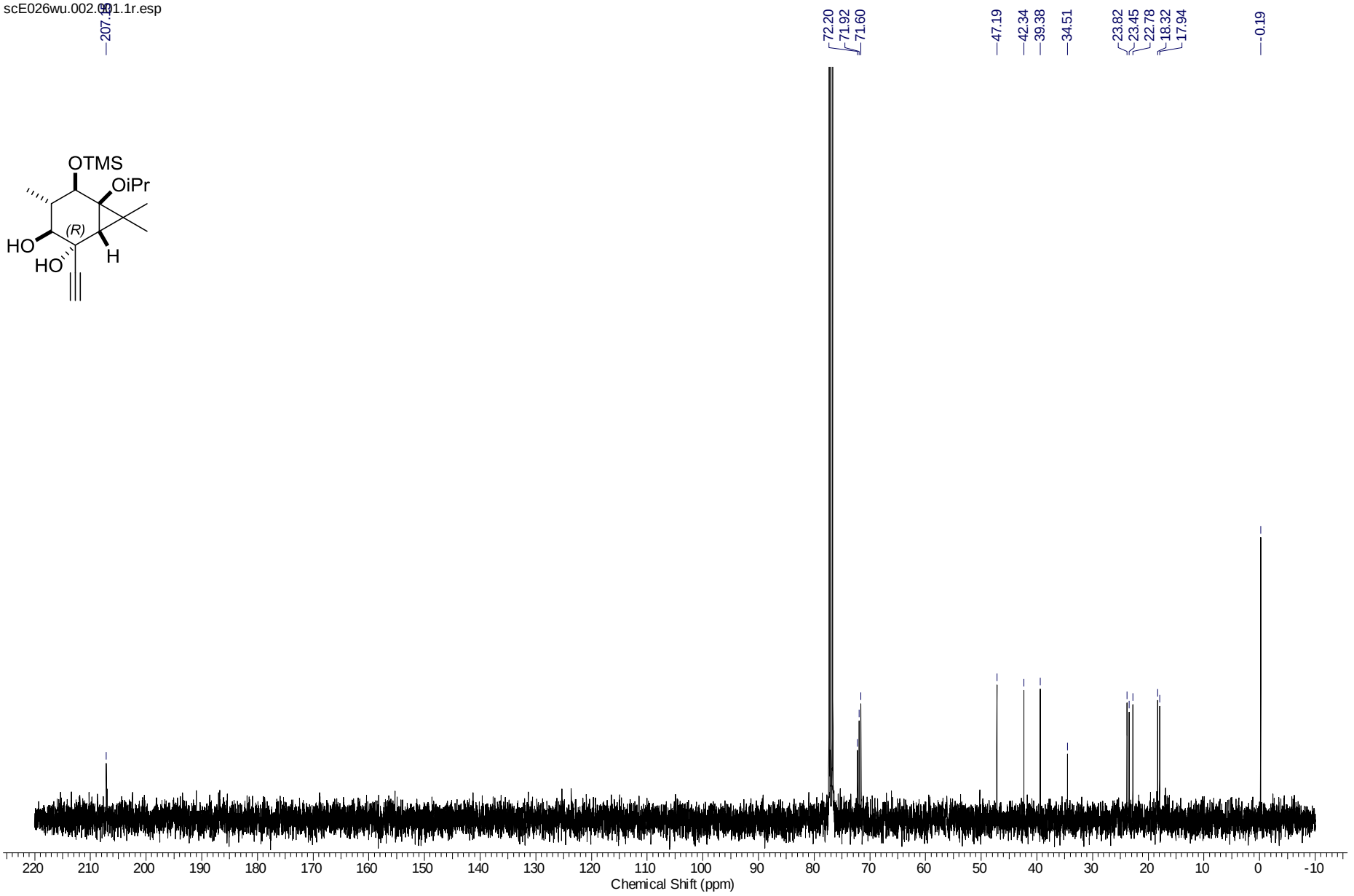


500 MHz ^{1}H NMR spectrum of **27** (C_6D_6).



100 MHz ^{13}C NMR spectrum of **27** (C_6D_6).

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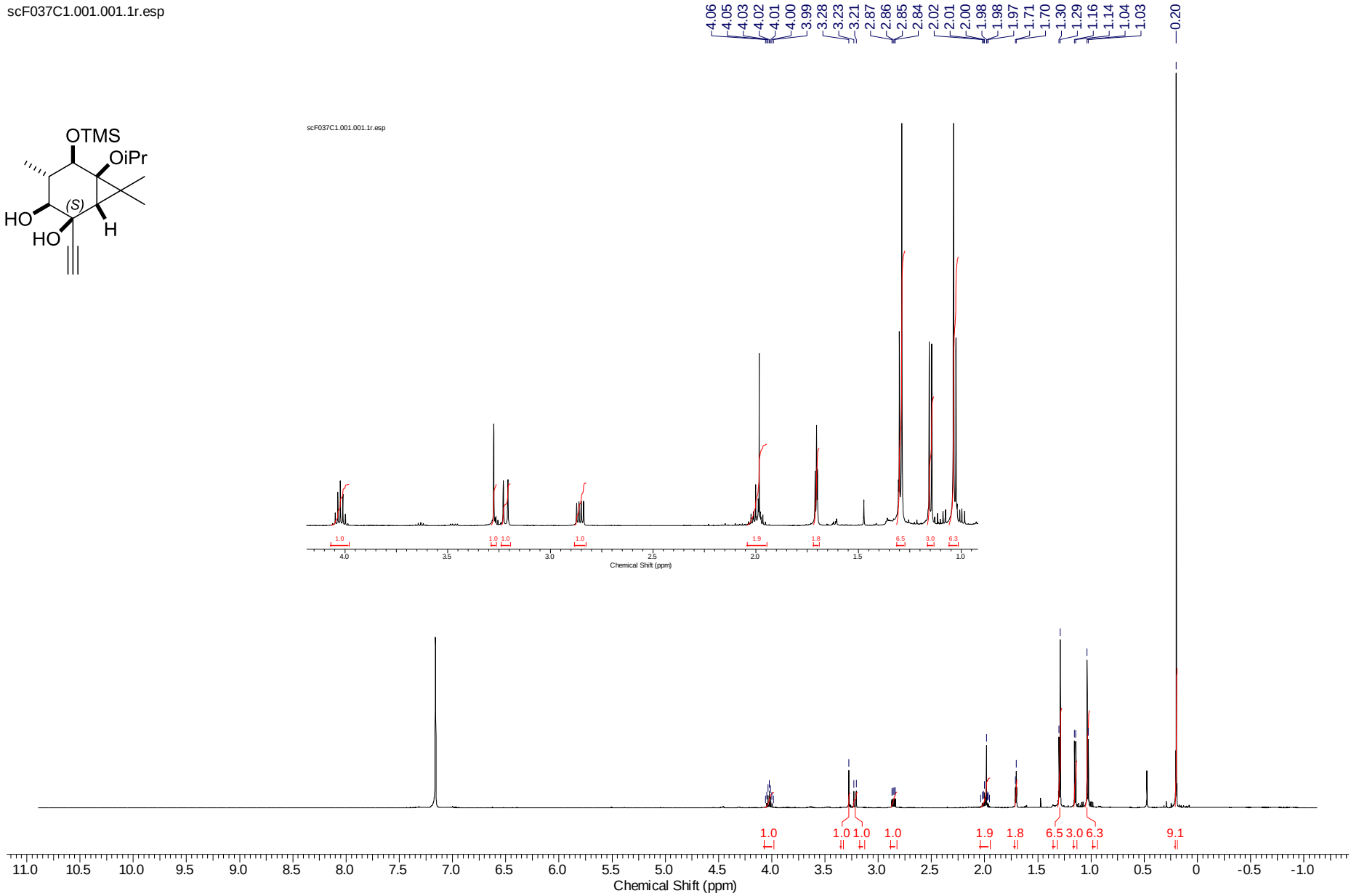
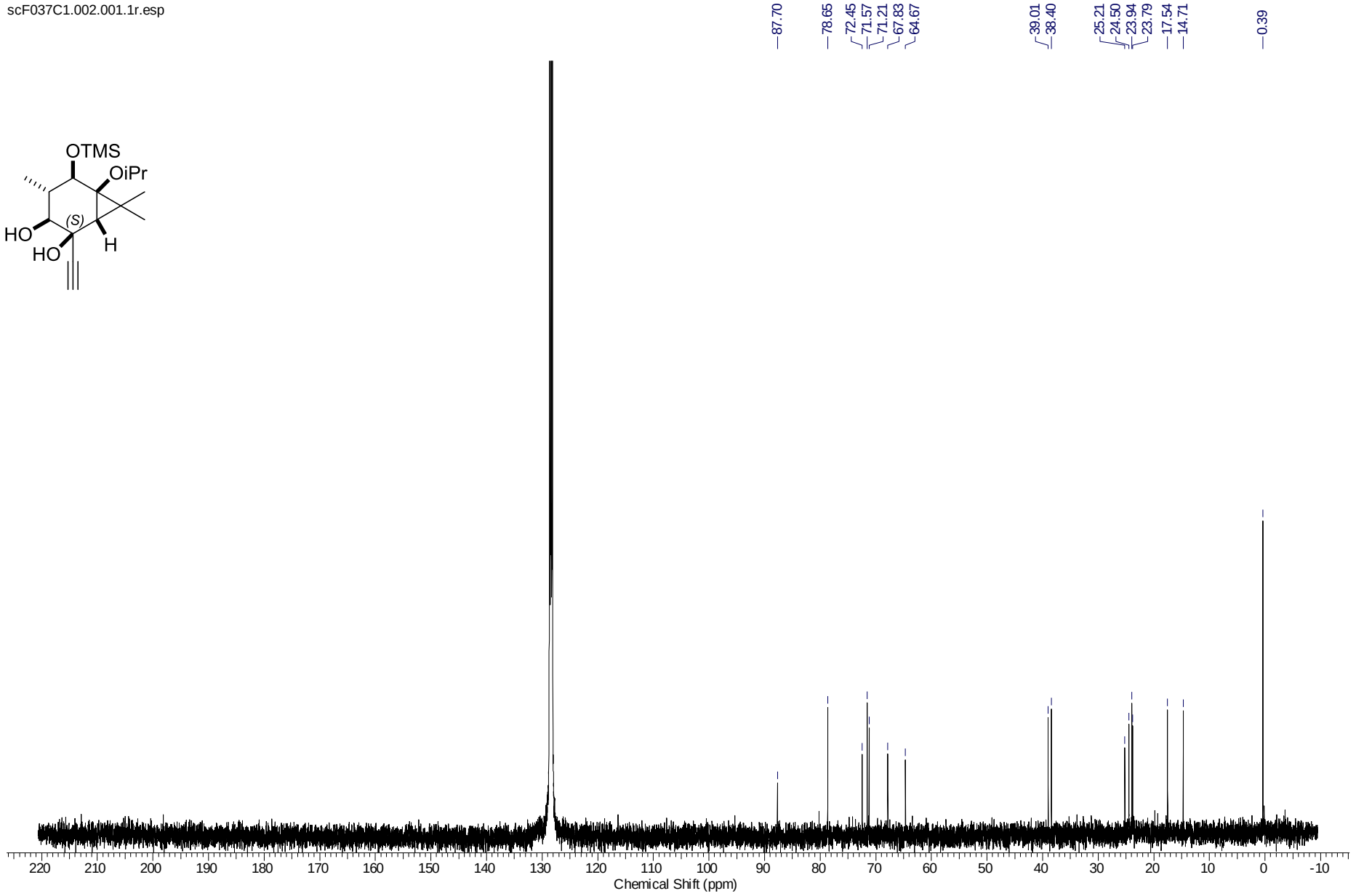
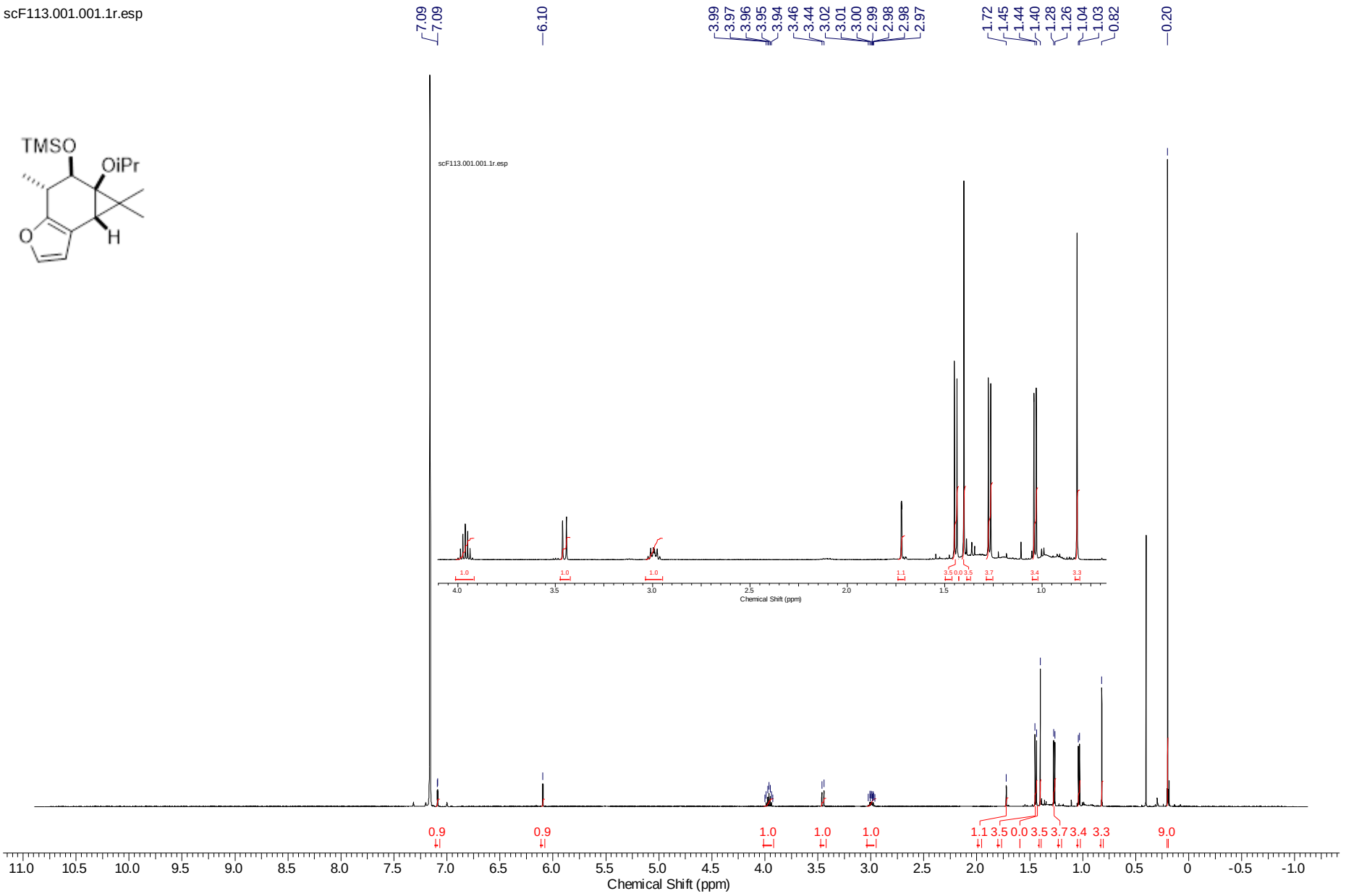


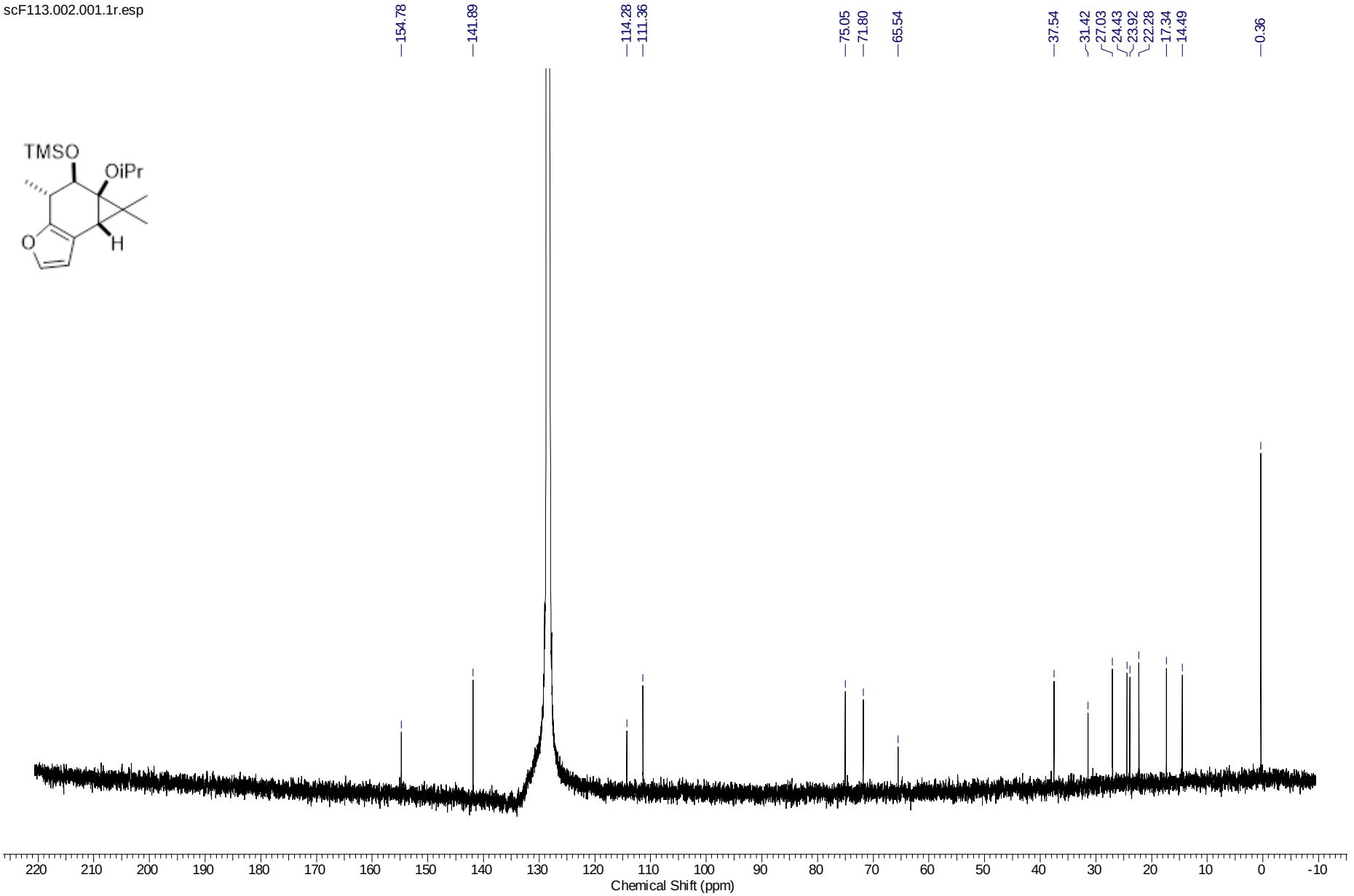
500 MHz ^{1}H NMR spectrum of **28** (C_6D_6).



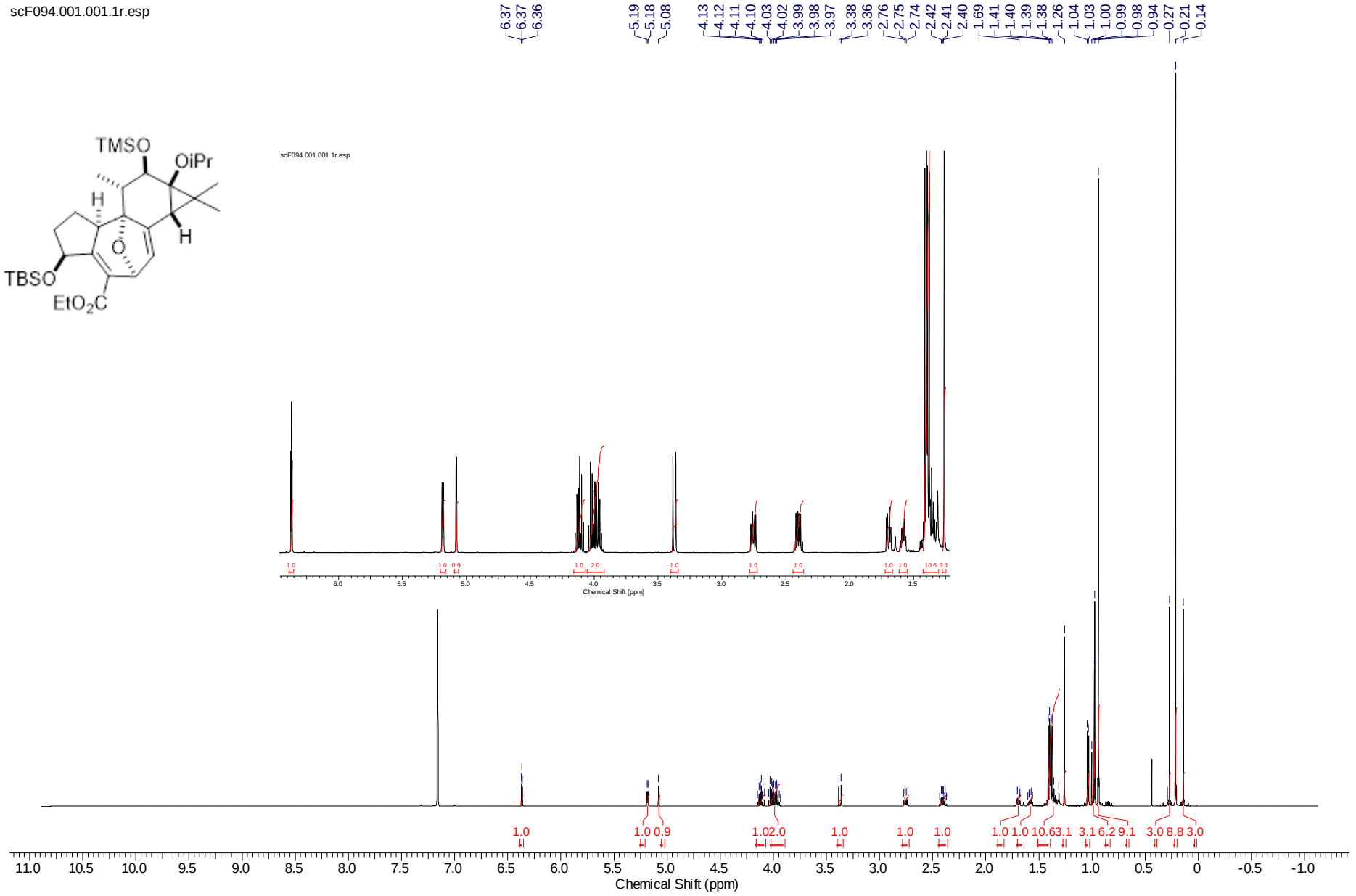
100 MHz ^{13}C NMR spectrum of **28** (C_6D_6).



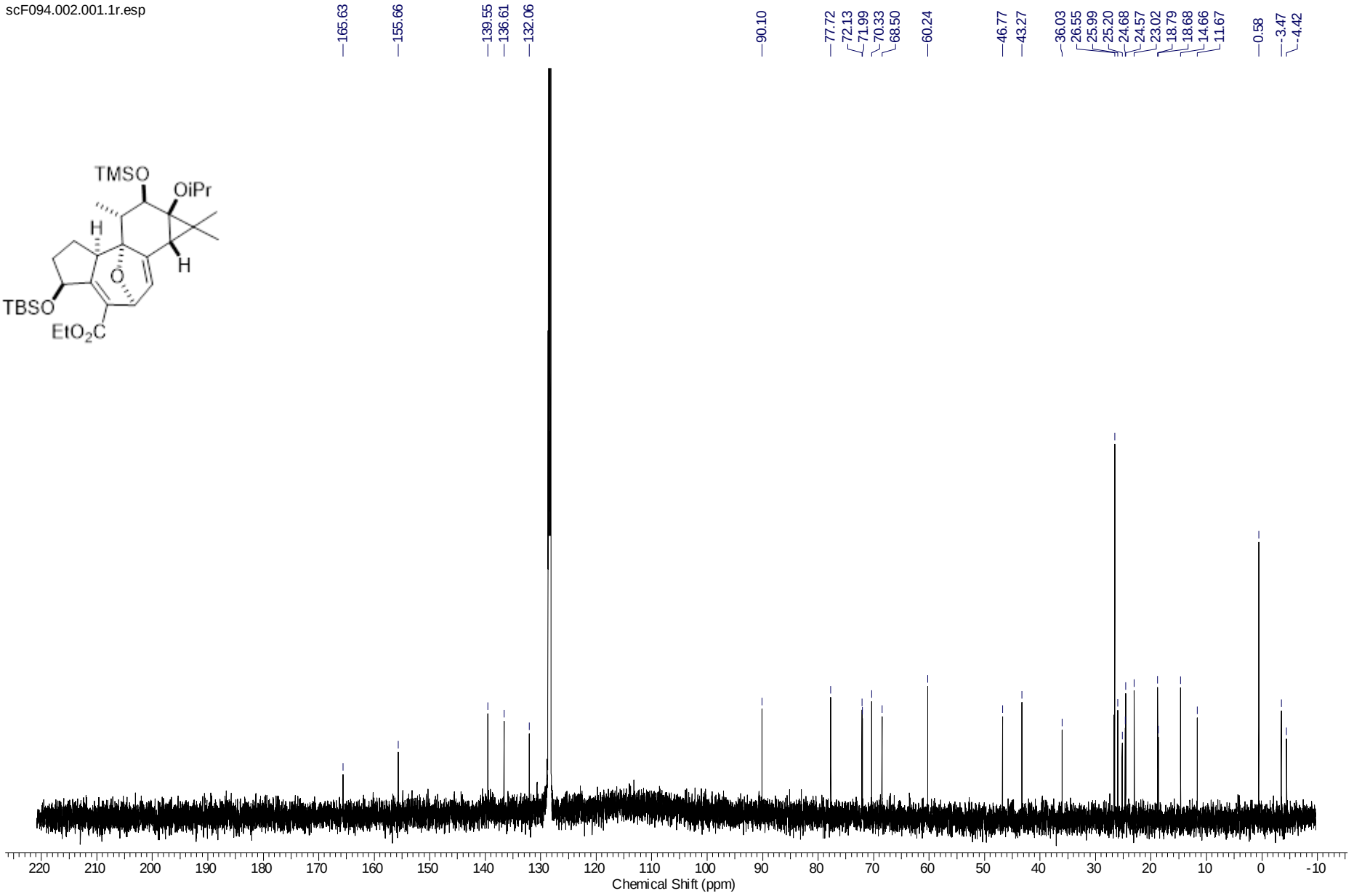
500 MHz ^{1}H NMR spectrum of **29** (C_6D_6).



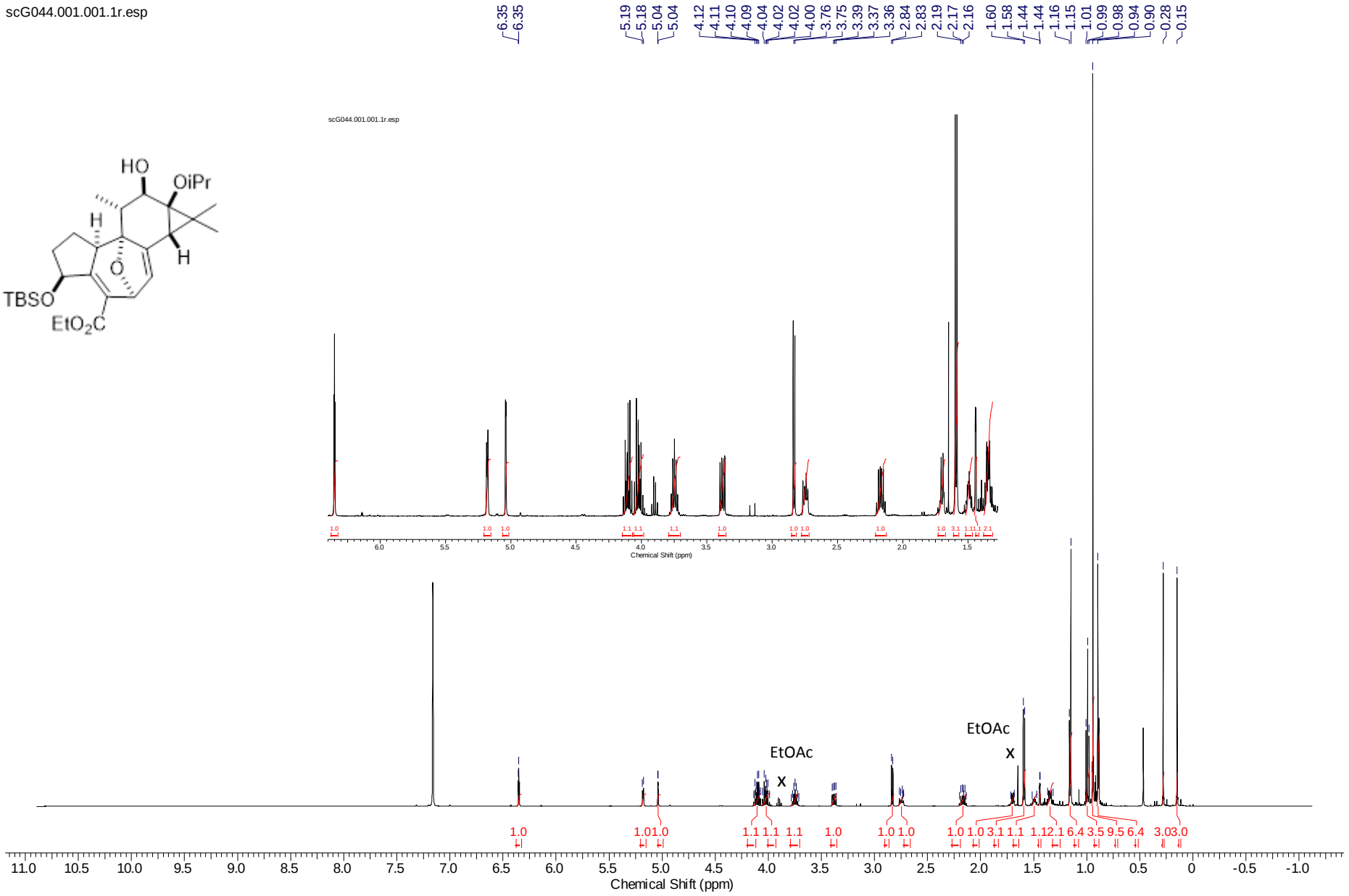
100 MHz ^{13}C NMR spectrum of **29** (C_6D_6).



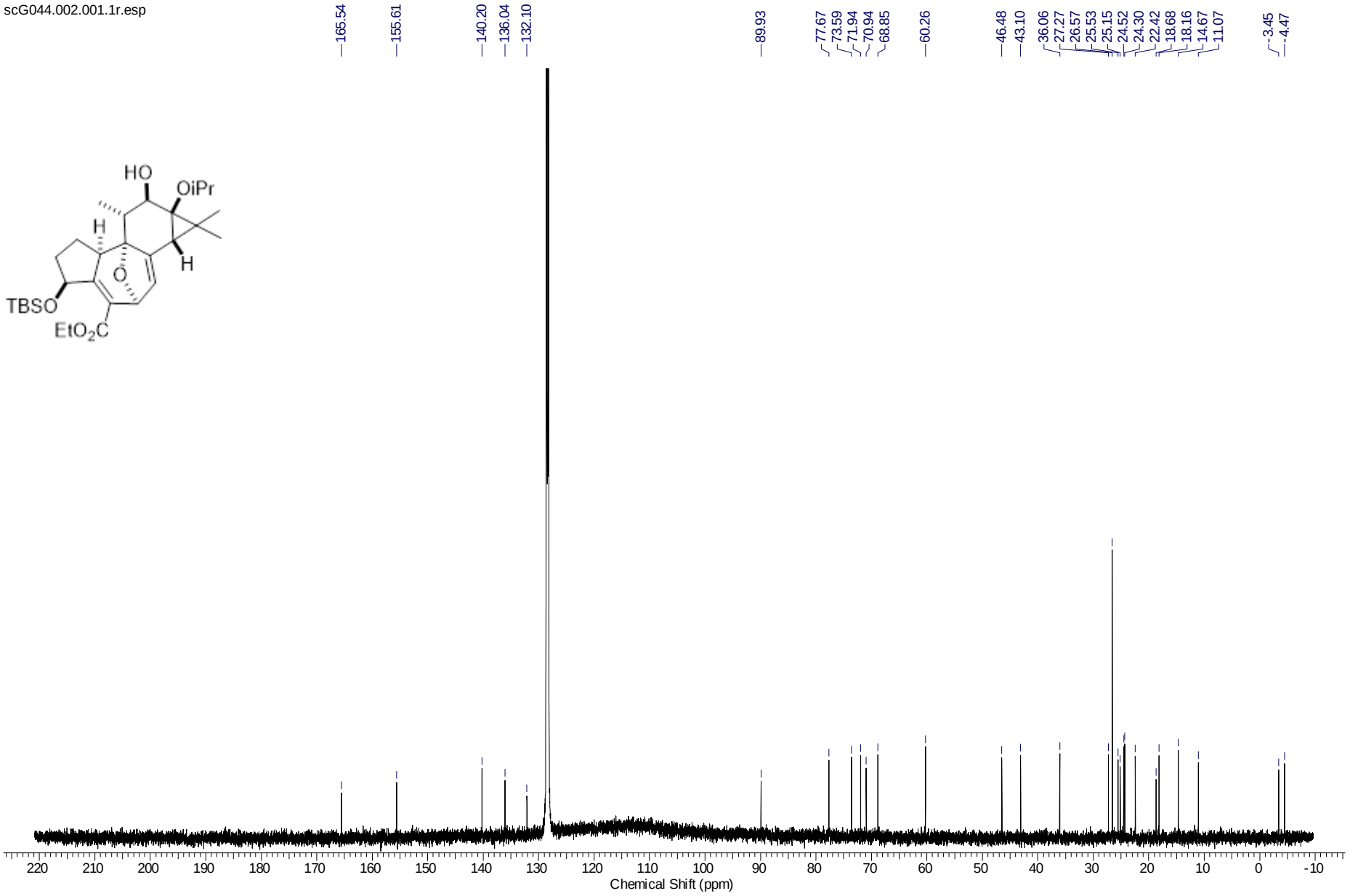
500 MHz ^{1}H NMR spectrum of **30** (C_6D_6).



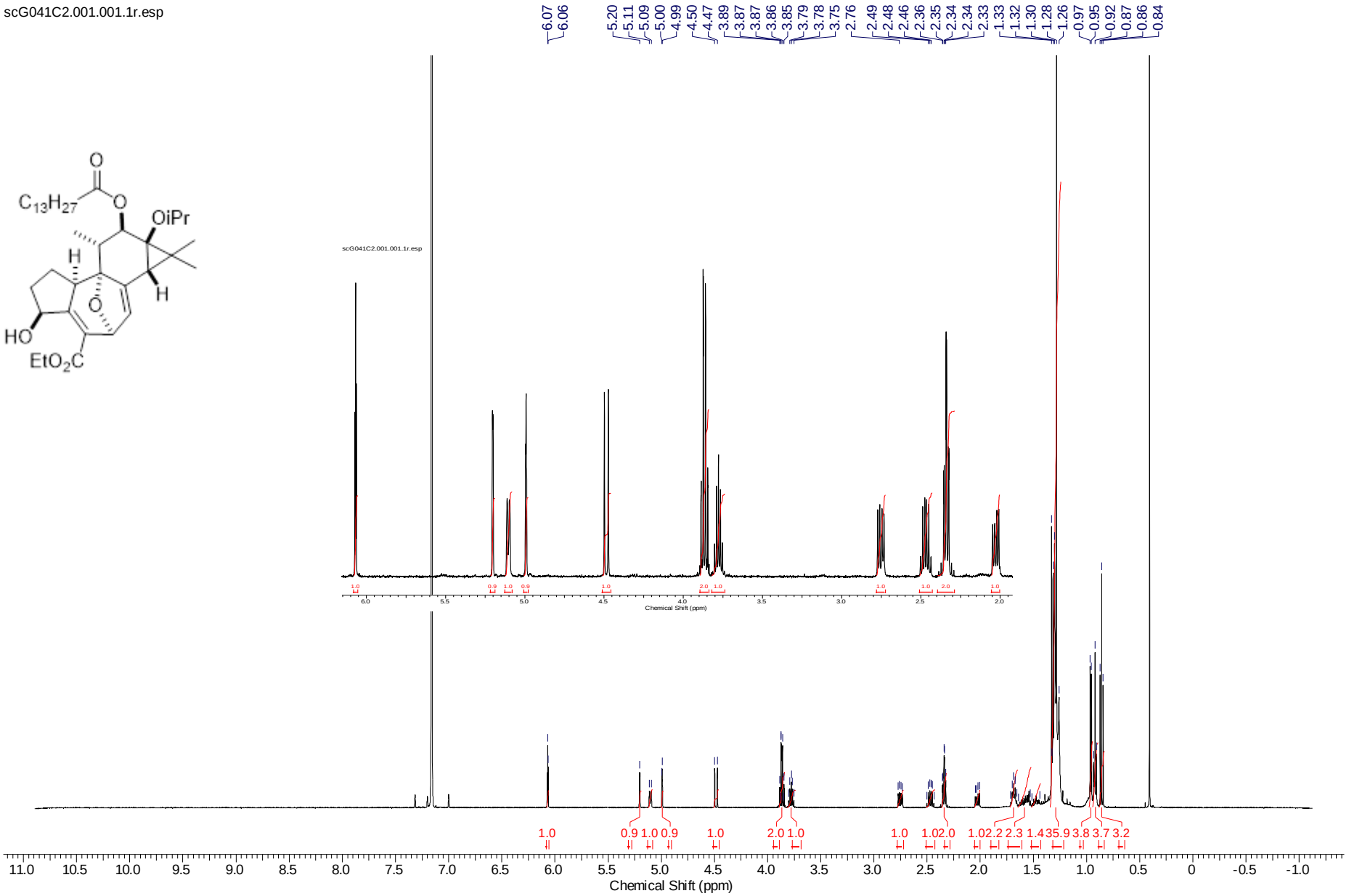
100 MHz ^{13}C NMR spectrum of **30** (C_6D_6).



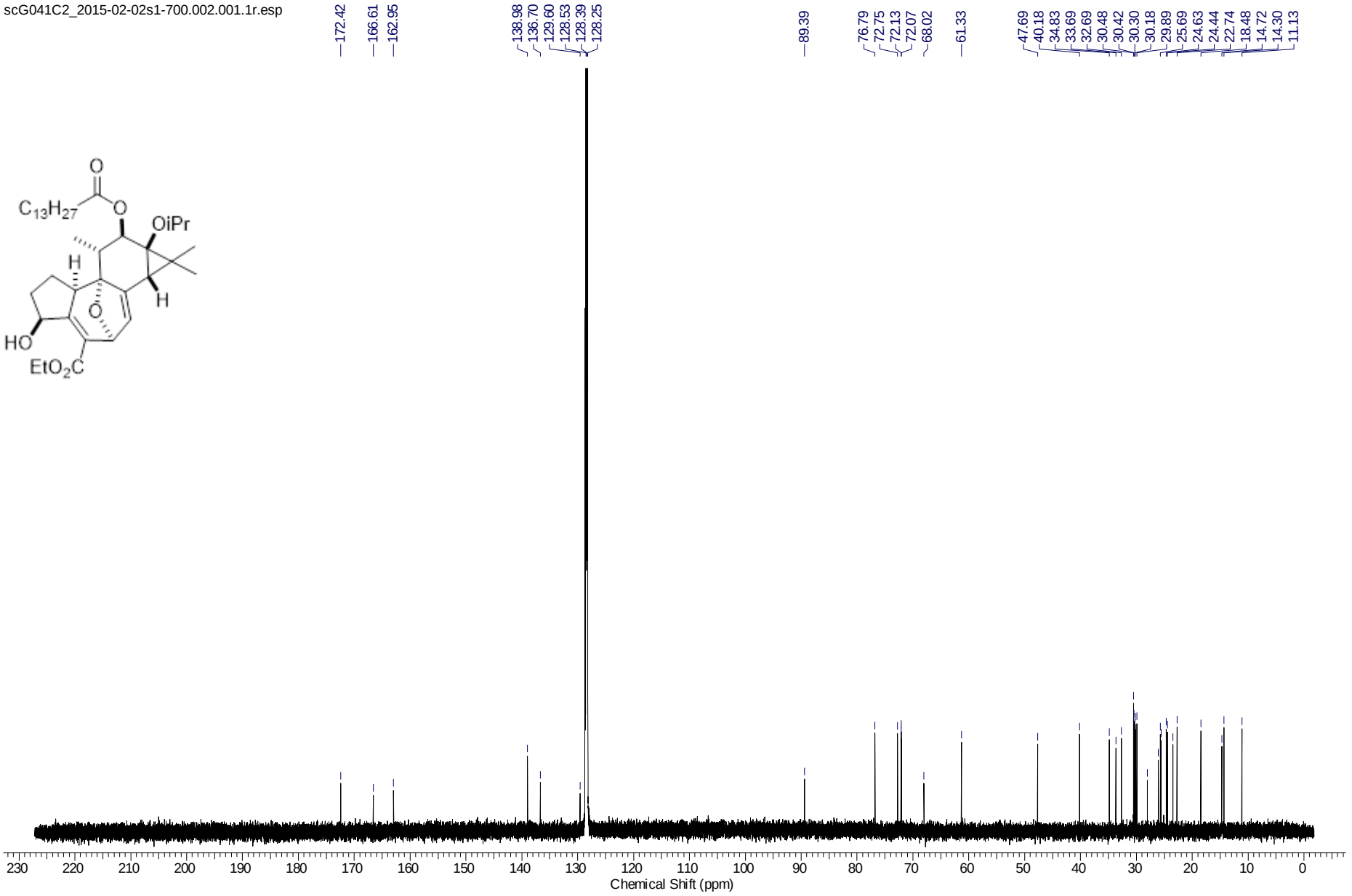
500 MHz ^{1}H NMR spectrum of **31** (C_6D_6).



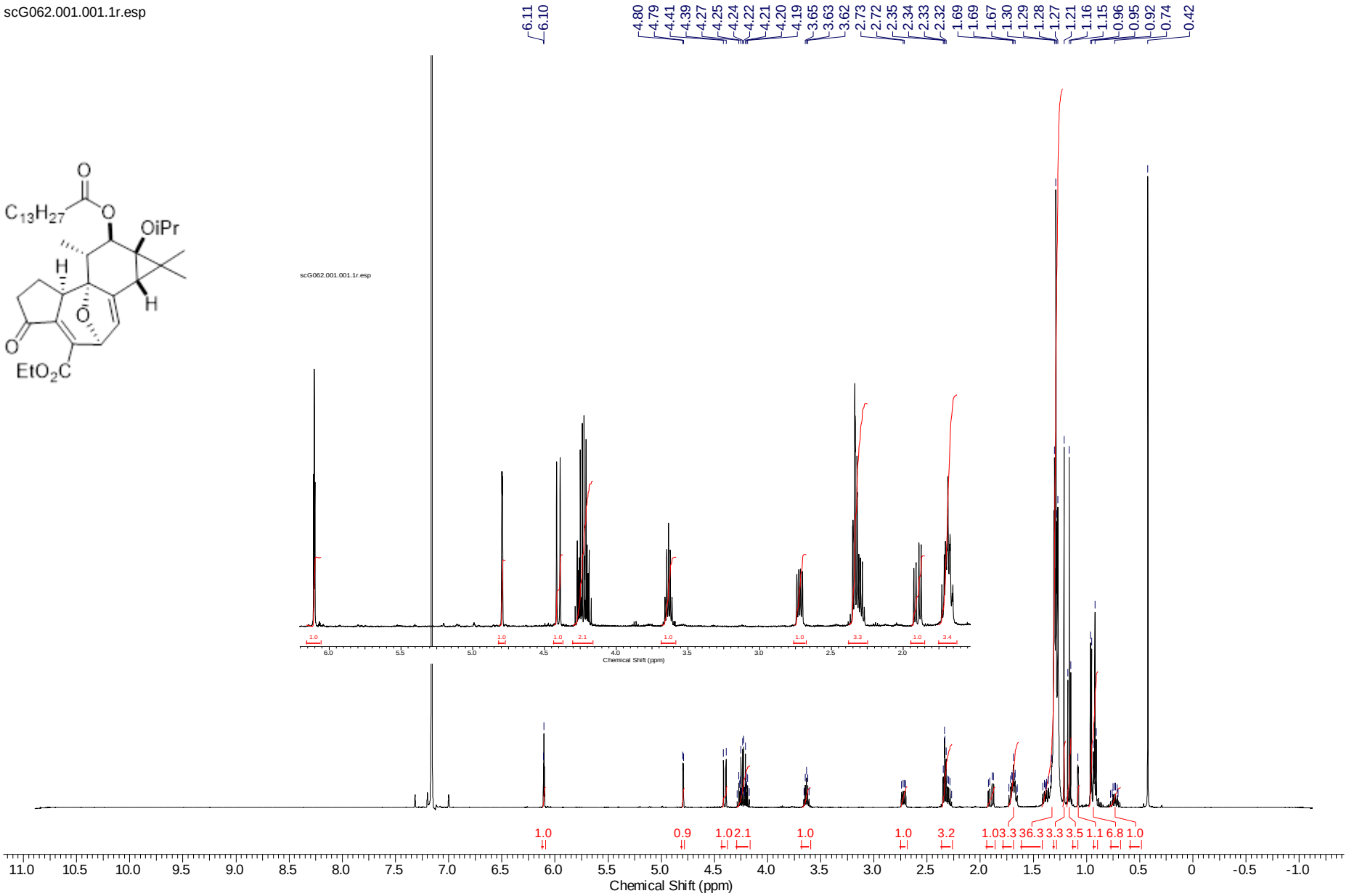
125 MHz ^{13}C NMR spectrum of **31** (C_6D_6).



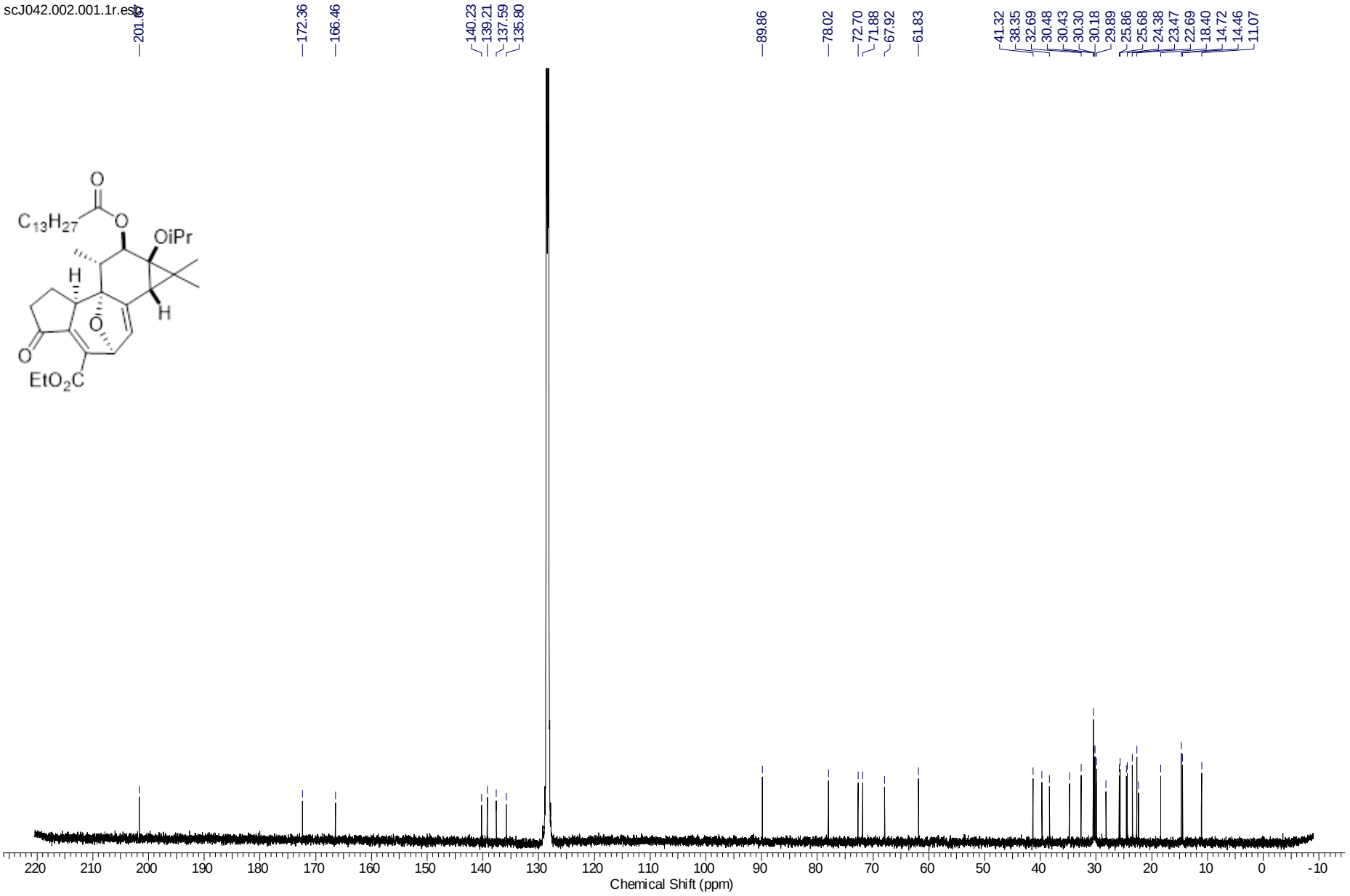
500 MHz ^{1}H NMR spectrum of **32** (C_6D_6).



176 MHz ^{13}C NMR spectrum of **32** (C_6D_6).



500 MHz ^{1}H NMR spectrum of **33** (C_6D_6).



125 MHz ^{13}C NMR spectrum of **33** (C_6D_6).