Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Asymmetric Total Syntheses of Sarglamides A, C, D, E and F

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Contents

1. Experimental Section

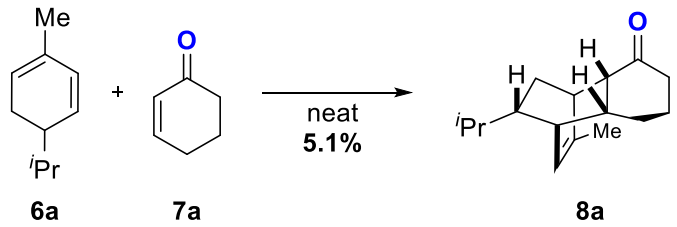
1.1 General Information:

Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane was freshly distilled before use from calcium hydride (CaH_2). All other solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Grace. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for 1H, 101 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C), dichloromethane (5.32 ppm for ^{1}H and 53.84 ppm for ^{13}C) or methanol (3.31 ppm for ^{1}H and 49.00 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter. High resolution mass spectra were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Center on either an Agilent GC/MS 5975C system or an API QSTAR XL System.

1.2 General Experimental Procedures and Characterization Data

1.2.1 Preparation of Diels-Alder products[1]

Compound 8a



6a **7a** **8a**

To a round-bottom flask cyclohexanone **7a** (192 mg, 2.0 mmol, 1.0 equiv.) under argon atmosphere, were added *α*-phellandrene **6a** (1.36 g, 10.0 mmol, 5.0 equiv.) in one pot. After being stirred for overnight at room temperature, the reaction mixture was purified by flash chromatography on silica gel (eluent: Acetone/*n*-Hexane, 1/20) to give compound **8a** (23.1 mg, yield: 5.1%) as a white powder.

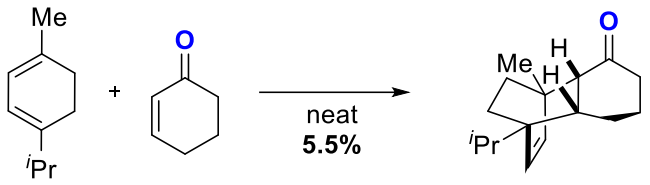
Rf = 0.6 (silica, Acetone/n-Hexane, 1/20);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.59 (d, 1H), 2.90 – 2.83 (m, 1H), 2.49 – 2.41 (m, 2H), 2.40 – 2.23 (m, 2H), 2.12 – 1.97 (m, 1H), 1.86 – 1.62 (m, 7H), 1.31 – 1.23 (m, 1H), 1.11 – 1.01 (m, 1H), 1.00 – 0.92 (m, 1H), 0.93 – 0.88 (m, 1H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.7, 143.0, 123.1, 51.8, 47.3, 43.8, 39.5, 39.0, 37.3, 33.3, 31.2, 29.2, 21.2, 21.0, 20.9, 20.5 ppm;

HRMS (ESI, TOF): calculated for $[C_{16}H_{25}O]^+$ 233.1900, found 233.1901.

Compound 8b



6b **7a** **8b**

To a round-bottom flask cyclohexanone **7a** (192 mg, 2.0 mmol, 1.0 equiv.) under argon atmosphere, were added *α*-terpinene **6b** (1.36 g, 10.0 mmol, 5.0 equiv.) in one pot. After being stirred for overnight at room temperature, the reaction mixture was purified by flash chromatography on silica gel (eluent: Acetone/*n*-Hexane, 1/20) to give compound **8b** (25.4 mg, yield: 5.5%) as a white powder.

Rf = 0.6 (silica, Acetone/*n*-Hexane, 1/20);

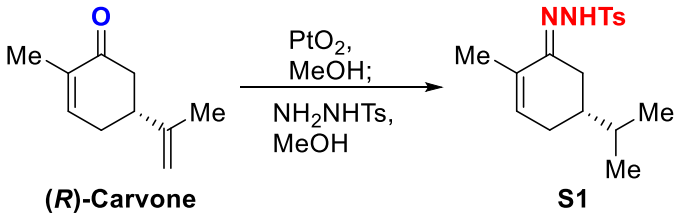
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.19 (d, *J* = 8.4 Hz, 1H), 5.82 (d, *J* = 8.4 Hz, 1H), 2.88 (d, *J* = 10.7 Hz, 1H), 2.52 (p, *J* = 6.9 Hz, 1H), 2.31 (dddt, *J* = 13.7, 9.2, 3.4, 1.1 Hz, 1H), 2.21 (td, *J* = 10.7, 5.2 Hz, 1H), 2.09 (ddd, *J* = 16.1, 9.4, 8.0 Hz, 1H), 1.88 – 1.73 (m, 2H), 1.69 – 1.62 (m, 1H), 1.50 – 1.38 (m, 1H), 1.37 – 1.28 (m, 1H), 1.28 – 1.19 (m, 1H), 1.19 – 1.11 (m, 1H), 1.09 (s, 3H), 0.98 – 0.89 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.5, 137.1, 135.6, 57.0, 49.3, 42.5, 38.7, 36.6, 36.5, 29.5, 25.5, 22.8, 22.5, 21.1, 18.7, 16.8 ppm;

HRMS (ESI, TOF): calculated for $[C_{16}H_{25}O]^+$ 233.1900, found 233.1904.

1.2.2 Preparation of sarglamide E (5)

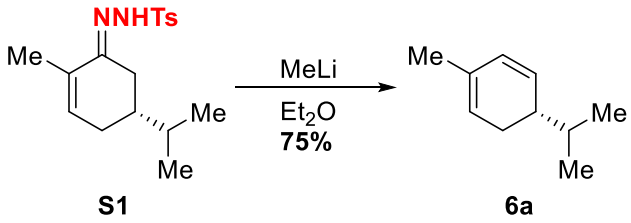
Compound S1



To a stirred suspension of PtO_2 (2.95 g, 13 mmol, 0.02 mol%) in MeOH (650 mL) was added (*R*)-Carvone (100 mL, 650 mmol, 1.0 equiv.) at room temperature. The mixture was evacuated and refilled with hydrogen gas and stirred at the same temperature for 2 days. The reaction was monitored by ^{1}H-NMR with a small amount of the reaction mixture. The reaction mixture was filtered through a celite pad with diethyl ether. The filtrate was concentrated under reduced pressure. The resulting crude enone was used directly for the next step without further purification.

To a solution of the abovementioned crude enone in MeOH (650 mL) under argon atmosphere, was added 4-Methylbenzenesulfonhydrazide (127.1 g, 682 mmol, 1.05 equiv.) in one portion at room temperature. The resulting mixture was heated to 70 °C and stirred for additional 2 h. The reaction was cooled to 25 °C, and then concentrated under reduced pressure. The resulting residue was used directly without further purification.

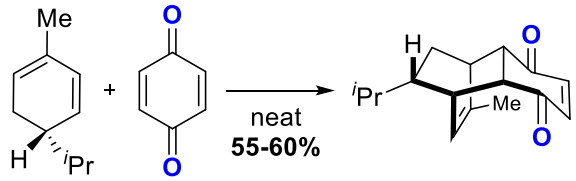
Compound 6a



To a cooled (0 °C) solution of the crude hydrazone (25.6 g, 80 mmol, 1 equiv.) obtained above in diethyl ether (320 mL) under argon atmosphere, was added MeLi (100 mL, 160 mmol, 2.0 equiv., 1.6 M in Et_2O) dropwise over 0.5 h at the same temperature. After being stirred for another 4 h at room temperature, the resulting mixture was allowed to stir at 0 °C for another

0.5 h, the reaction was quenched with a saturated aqueous NH_4Cl solution over 20 min. The mixture was allowed to warm to room temperature, the organic layer was collected, and aqueous phase was extracted with pentane (4 × 200 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: Pentane only) to give (*S*)-(+)-*α*-phellandrene **6a**[2] (8.17 g, 60 mmol, yield: 75%) as a colorless oil.

Compound 8



6a **7g** **8**

Procedure A (*Neat condition*): To a round-bottom flask 1,4-Benzoquinone (3.56 g, 33 mmol, 1.0 equiv.) under argon atmosphere, were added (*S*)-(+)-*α*-phellandrene (15.7 g, 115.5 mmol, 3.5 equiv.) obtained above in one pot. After being stirred for 7 days at room temperature, the reaction mixture was purified by flash chromatography on silica gel (eluent: Pentane only to EtOAc/*n*-Hexane, 1/9) to give compound **8** (4.91 g, yield: 60%) as a yellow solid.

Procedure B (*EtOH/H₂O as solvent*): To a round-bottom flask 1,4-Benzoquinone (21.6 g, 200 mmol, 1.0 equiv.) under argon atmosphere in EtOH/H_2O (500 mL, 1/1), were added (*S*)-(+)-*α*-phellandrene (32.8 g, 241 mmol, 1.2 equiv.) obtained above in one pot. After being stirred for 1 h at reflux temperature, Et_2O (200 mL) was then added, and the organic layer was separated. The aqueous phase was extracted with Et_2O (4 × 500 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to give compound **8** (26.8 g, yield: 55%)

Rf = 0.4 (silica, EtOAc/*n*-Hexane = 1:4);

$[\alpha]_D^{25}$ = +35.7 (*c* 1.0, DCM);

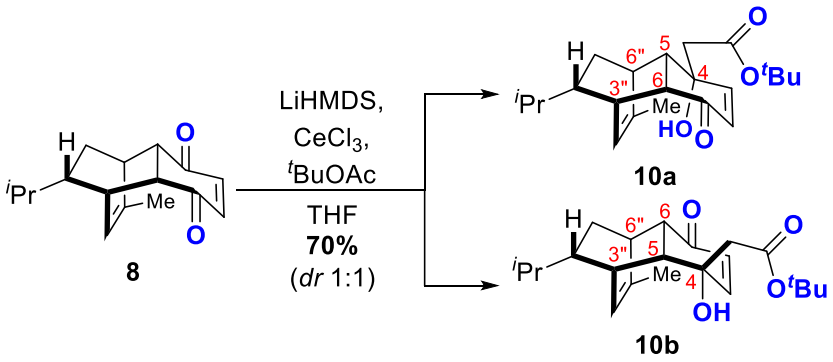
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.63 (s, 2H), 5.67 (d, *J* = 6.4 Hz, 1H), 3.19 (dt, *J* = 6.3, 2.3

Hz, 1H), 2.97 – 2.91 (m, 2H), 2.87 (dd, J = 9.1, 2.5 Hz, 1H), 1.86 (ddd, J = 13.0, 9.2, 2.5 Hz, 1H), 1.66 (d, J = 1.7 Hz, 3H), 1.40 (tdd, J = 9.3, 5.4, 2.0 Hz, 1H), 1.10 – 0.99 (m, 2H), 0.89 (d, J = 6.5 Hz, 3H), 0.78 (d, J = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.8, 199.5, 142.5, 142.4, 141.6, 123.2, 50.7, 48.6, 45.6, 41.7, 39.2, 33.3, 31.7, 21.0, 20.7, 20.2 ppm;

HRMS (ESI, TOF): calculated for $[C_{16}H_{20}O_2+Na]^+$ 267.1356, found 267.1368.

Compound 10a and 10b



$CeCl_3{\cdot}7H_2O$ (18.6 g, 50.0 mmol, 1.0 equiv.) was added to a Schlenk tube (250 mL) and evacuated. The tube was immersed in a pre-heated oil bath (140 ºC) with evacuation, while the water was trapped by liquid nitrogen. After 1 h heating without stirring, the cerium chloride was completely dried by a vigorous stirring at the same temperature for an additional 2 h. While the flask was still hot, the flask was filled with argon gas and then cooled to 0 ºC. Freshly distilled THF (100 mL) was added to the flask containing cerium chloride at the same temperature and allowed to stir for another 2 h at room temperature.

To a cooled (-78 ºC) solution of LHMDS (50.0 mL, 50.0 mmol, 1.0 equiv., 1.0 M in THF) under argon atmosphere in THF (50 mL), was added *t*-BuOAc (6.7 mL, 50.0 mmol, 1.0 equiv.). After 1.5 h of stirring at -78 ºC, the mixture containing cerium chloride made *in situ* above was added dropwise and stirred at -78 ºC for another 2 h.

After being stirred for 2 h, the mixture was added to compound **8** (12.2 g, 50.0 mmol, 1.0 equiv.) in THF (50 mL) dropwise at -78 ºC. After the addition, the reaction mixture was allowed to stir

for an additional 2 h at the same temperature. The mixture was quenched with saturated aqueous NH_4Cl. Et_2O (100 mL) and H_2O (100 mL) were then added, and the organic layer was separated. The aqueous phase was extracted with Et_2O (4 × 100 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: DCM/Et_2O/*n*-Hexane, 1/1/4 to 2/2/4) to give compound **10a** (6.3 g, 17.5 mmol) and compound **10b** (6.3 g, 17.5 mmol) respectively as a pale-yellow oil in 70% yield in total.

Compound 10a:

Rf = 0.35 (silica, DCM/Et_2O/*n*-Hexane = 1:1:3);

$[\alpha]_D^{25}$ = +27.8 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.57 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.75 (d, *J* = 10.3 Hz, 1H), 5.59 – 5.28 (m, 1H), 3.01 (ddd, *J* = 6.3, 3.7, 1.5 Hz, 1H), 2.89 (dq, *J* = 3.3, 1.5 Hz, 1H), 2.63 (dd, *J* = 8.3, 3.7 Hz, 1H), 2.49 (d, *J* = 15.9 Hz, 1H), 2.39 (d, *J* = 15.9 Hz, 1H), 2.21 (dt, *J* = 8.4, 1.7 Hz, 1H), 1.72 (d, *J* = 1.7 Hz, 3H), 1.70 – 1.58 (m, 1H), 1.44 (s, 9H), 1.40 – 1.28 (m, 1H), 1.10 (dh, *J* = 9.0, 6.5 Hz, 1H), 0.92 (d, *J* = 6.4 Hz, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.9, 171.6, 150.5, 144.5, 130.4, 121.8, 82.6, 70.1, 50.5, 49.7, 44.4, 44.0, 40.1, 35.4, 34.6, 33.2, 28.0, 21.2, 20.4, 20.2 ppm;

HRMS (ESI, TOF): calculated for $[C_{22}H_{32}O_4Si+Na]^+$ 383.2193, found 383.2195.

Compound 10b:

Rf = 0.35 (silica, DCM/Et_2O/*n*-Hexane = 1:1:3);

$[\alpha]_D^{25}$ = +53.4 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.60 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.84 (d, *J* = 10.3 Hz, 1H), 5.70 (dt, *J* = 6.3, 1.8 Hz, 1H), 3.17 – 3.10 (m, 1H), 2.77 (dt, *J* = 3.4, 1.6 Hz, 1H), 2.73 (dd, *J* = 8.5, 3.5 Hz, 1H), 2.50 (d, *J* = 15.9 Hz, 1H), 2.40 (d, *J* = 15.9 Hz, 1H), 2.21 (dt, *J* = 8.6, 1.6 Hz,

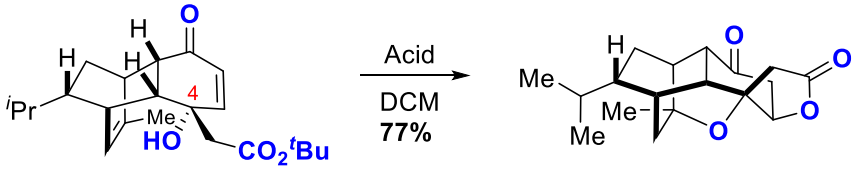
1H), 1.78 (ddd, *J* = 13.1, 9.1, 2.3 Hz, 1H), 1.56 (d, *J* = 1.7 Hz, 3H), 1.44 (s, 9H), 1.18 (dddd, *J* = 9.3, 6.6, 4.2, 2.0 Hz, 1H), 1.09 – 0.95 (m, 2H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 13C NMR (101 MHz, $CDCl_3$) δ 200.0, 171.5, 152.8, 139.7, 129.3, 124.7, 82.5, 70.0, 49.6, 49.1, 48.3, 47.3, 43.1, 33.2, 32.8, 30.7, 28.0, 21.1, 20.8, 20.4 ppm;

HRMS (ESI, TOF): calculated for $[C_{22}H_{32}O_4Si+Na]^+$ 383.2193, found 383.2199.

Compound 9b

Table 1. Optimization of cycloetherification and intramolecular *oxa*-Michael addition



10b **9b**

Entry	Acid (1.0 eq.)	Temp (^oC)	**9b** Yield (%)
1	*p*-TsOH	25-40	Complex
2	Amberlyst-15	25-40	74
3	CSA	25	No Pdt
4	PPTS	25-40	NR
5	BF_3-Et_2O	25	77
6	TMSOTf	25	74
7	TBSOTf	25	74
8	$Sc(OTf)_3$	25	NR
9	$FeCl_3$	25	**78**

[a] Reaction conditions: **11b** (0.035 mmol), Lewis acid (0.035 mmol), and DCM (0.5 mL) were mixed and stirred at room or specified temperature under N_2 atmosphere. [b] NMR yield with CH_2Br_2 as internal standard.

To a solution of compound **10b** (1.56 g, 4.33 mmol, 1.0 equiv.) in DCM (45 mL) under argon atmosphere, was added $FeCl_3$ (702 mg, 4.33 mmol, 1.0 equiv.). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 30 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4) to give the corresponding pentacyclic **9b** (1.02 g, yield: 77%) as a white powder.

Rf = 0.3 (silica, EtOAc/*n*-Hexane = 1:4);

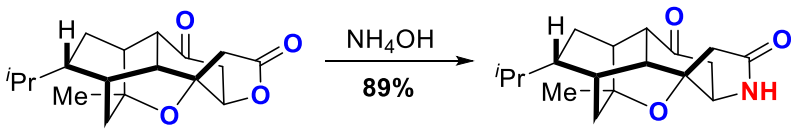
$[\alpha]_D^{25}$ = -33.1 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.37 (t, *J* = 8.1 Hz, 1H), 3.00 (dd, *J* = 13.1, 8.0 Hz, 1H), 2.90 (d, *J* = 17.2 Hz, 1H), 2.75 (d, *J* = 17.4 Hz, 1H), 2.65 (dd, *J* = 13.2, 8.1 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.32 (d, *J* = 4.6 Hz, 1H), 2.26 (d, *J* = 5.9 Hz, 1H), 2.17 (t, *J* = 6.5 Hz, 1H), 1.81 (ddd, *J* = 12.8, 7.8, 4.7 Hz, 1H), 1.53 – 1.47 (m, 1H), 1.46 – 1.32 (m, 3H), 1.10 – 1.04 (m, 1H), 1.08 (s, 3H), 0.90 (t, *J* = 6.2 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 208.5, 173.3, 81.1, 78.4, 76.1, 45.8, 42.2, 41.9, 41.3, 40.2, 35.0, 31.6, 29.5, 29.5, 27.0, 23.5, 21.5, 20.2 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{25}O_4]^+$ 305.1747, found 305.1758.

Compound 15b



9b **15b**

To a compound **9b** (1.02 g, 3.35 mmol, 1.0 equiv.) under argon atmosphere, was added NH_4OH (5 mL). After being stirred for overnight at the same temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: MeOH/DCM, 1/20) to give the corresponding amide **15b** (909 mg, yield:

89%) as a white powder.

Rf = 0.4 (silica, MeOH/DCM = 1:10);

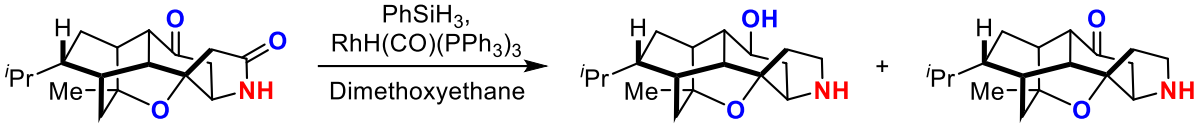
$[\alpha]_D^{25}$ = -19.8 (*c* 0.9, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.15 (s, 1H), 3.77 (dd, *J* = 8.9, 7.7 Hz, 1H), 2.80 (dd, *J* = 12.3, 7.7 Hz, 1H), 2.74 (d, *J* = 16.9 Hz, 1H), 2.64 – 2.54 (m, 2H), 2.43 (dd, *J* = 12.3, 8.9 Hz, 1H), 2.33 (d, *J* = 4.6 Hz, 1H), 2.20 (dd, *J* = 9.5, 5.9 Hz, 2H), 1.80 (ddd, *J* = 12.9, 7.8, 4.7 Hz, 1H), 1.55 – 1.30 (m, 4H), 1.08 (s, 4H), 0.90 (dd, *J* = 6.4, 4.6 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 210.2, 174.6, 79.3, 75.7, 59.9, 45.9, 42.7, 42.5, 41.7, 41.5, 35.9, 31.5, 29.6, 29.5, 27.3, 23.6, 21.6, 20.3 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{26}NO_3]^+$ 304.1907, found 304.1914.

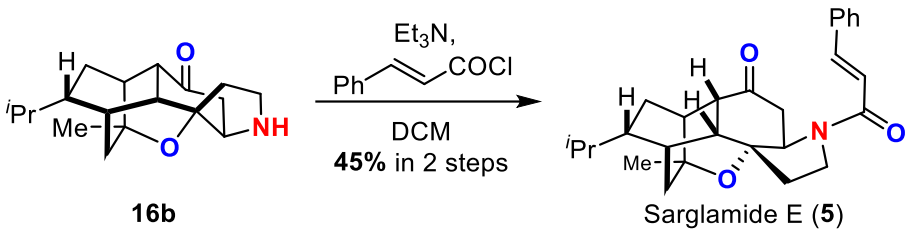
Compounds 16a and 16b



15b **16a** **16b**

To a cooled (0 °C) solution of compound **15b** (20 mg, 0.07 mmol, 1.0 equiv.) in dimethoxyethane (1.5 mL) under argon atmosphere, was added $RhH(CO)(PPh_3)_3$ (6.4 mg, 0.007 mmol, 0.1 equiv.). Then, $PhSiH_3$ (39 μL, 0.35 mmol, 5.0 equiv.) was added dropwise. After being stirred 1.5 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (2 mL), and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (3 × 3 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude amine **16a** and **16b** were used directly for the next step without further purification.

Sarglamide E (5)



To a cooled (0 °C) solution of amine **16b** obtained above in DCM (1 mL) under argon atmosphere, was added Et_3N (5.5 μL, 0.039 mmol, 1.1 equiv.) and cinnamoyl chloride (7.2 mg, 0.04 mmol, 1.1 equiv.). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 3 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/2) to give the corresponding sarglamide E (**5**) (13.1 mg, yield: 45% in 2 steps) as a white powder.

Rf = 0.4 (silica, EtOAc/*n*-Hexane = 1:1);

[α]D^{25} = -26.4 (*c* 0.5, MeOH); lit.[3] **[α]D^{22}** = -175 (*c* 0.3, MeOH)

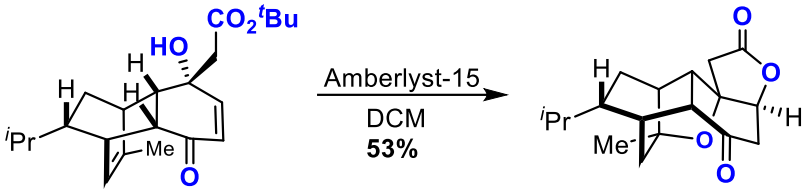
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 15.3 Hz, 1H), 7.67 (d, *J* = 15.3 Hz, 1H), 7.51 (m, 2H), 7.37 (m, 3H), 6.68 (d, *J* = 15.3 Hz, 1H), 6.54 (d, *J* = 15.3 Hz, 1H),4.16 (m, 1H), 4.00 (m, 1H), 3.94 (m, 1H), 3.92 (m, 1H), 3.73 (m, 1H), 3.49 (m, 1H), 3.05 (m, 1H), 2.60 (m, 1H), 2.59 (m, 1H), 2.55 (m, 1H), 2.40 (m, 1H), 2.39-2.38 (m, 1H), 2.37 (m, 3H), 2.23 (m, 1H), 2.22 (m, 1H), 2.19 (m, 1H), 2.08 (m, 1H), 1.98 (m, 1H), 1.81 (ddd, *J* = 12.8, 8.1, 4.7 Hz, 1H), 1.58-1.57 (m, 1H), 1.49 (m, 1H), 1.48-1.47 (m, 1H), 1.39 (m, 1H), 1.10-1.09 (s, 3H), 1.09 (m, 1H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.91 (d, *J* = 6.4 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 212.1, 211.2, 165.7, 142.8, 135.2, 130.0, 129.0, 128.1, 118.2, 83.4, 81.8, 75.7, 63.2, 62.9, 46.1, 45.7, 43.8, 41.9, 41.8, 35.2, 35.0, 34.4, 31.7, 29.9, 29.9, 29.8, 29.8, 28.1, 24.0, 21.8, 20.5 ppm;

HRMS (ESI, TOF): calculated for $[C_{27}H_{34}NO_3]^+$ 420.2533, found 420.2539.

1.2.3 Preparation of Sarglamide F (17)

Compound 9a



10a **9a**

To a solution of compound **10a** (1.3 g, 3.2 mmol, 1.0 equiv.) in DCM (30 mL) under argon atmosphere, was added amberlyst-15 (1.0 g, 3.2 mmol, 1.0 equiv.). After being stirred for 4 h at the reflux temperature, the reaction mixture was filtered with celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4) to give the corresponding pentacyclic **9a** (515 mg, yield: 53%) as a white powder.

Rf = 0.3 (silica, EtOAc/*n*-Hexane = 1:4);

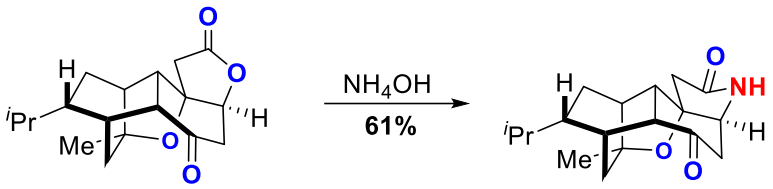
[α]D^{25} = -28.9 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.62 (dd, *J* = 9.3, 7.3 Hz, 1H), 2.95 (dd, *J* = 12.6, 7.3 Hz, 1H), 2.87 – 2.76 (m, 2H), 2.68 – 2.59 (m, 2H), 2.39 – 2.33 (m, 2H), 2.04 – 1.94 (m, 2H), 1.44 – 1.34 (m, 2H), 1.31 – 1.23 (m, 1H), 1.21 (s, 3H), 1.15 (ddd, *J* = 15.8, 7.2, 2.7 Hz, 1H), 1.02 – 0.93 (m, 1H), 0.86 (dd, *J* = 6.6, 5.4 Hz, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 207.6, 173.2, 82.2, 81.5, 81.0, 51.4, 45.6, 43.9, 42.8, 42.8, 42.7, 34.3, 32.3, 26.3, 24.6, 24.0, 20.8, 20.7 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{24}O_4+Na]^+$ 327.1567, found 327.1578.

Compound 15a



To a compound **9a** (150 mg, 0.5 mmol, 1.0 equiv.) under argon atmosphere, was added NH_4OH (2 mL) in the sealed tube. After being stirred for overnight at the 70 °C, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: MeOH/DCM, 1/20) to give the corresponding amide **15a** (95 mg, yield: 61%) as a white powder.

Rf = 0.4 (silica, MeOH/DCM = 1:10);

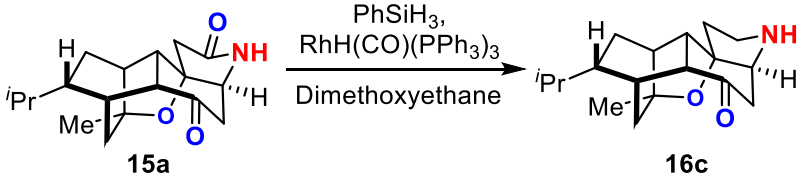
$[\alpha]_D^{25}$ = +11.1 (*c* 0.5, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.48 (s, 1H), 3.94 (dd, *J* = 10.5, 6.5 Hz, 1H), 2.84 (dd, *J* = 9.9, 3.3 Hz, 1H), 2.74 (dd, *J* = 11.8, 6.5 Hz, 1H), 2.65 (d, *J* = 17.7 Hz, 1H), 2.53 – 2.41 (m, 2H), 2.40 – 2.28 (m, 2H), 2.05 – 1.85 (m, 2H), 1.49 – 1.37 (m, 2H), 1.37 – 1.24 (m, 1H), 1.23 (s, 3H), 1.21 – 1.12 (m, 1H), 1.05 – 0.94 (m, 1H), 0.95 – 0.83 (m, 6H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 209.0, 174.3, 81.8, 81.8, 59.4, 51.9, 46.9, 45.5, 44.1, 44.0, 42.6, 34.6, 32.4, 26.3, 24.8, 24.1, 20.8, 20.8 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{26}NO_3]^+$ 304.1907, found 304.1913.

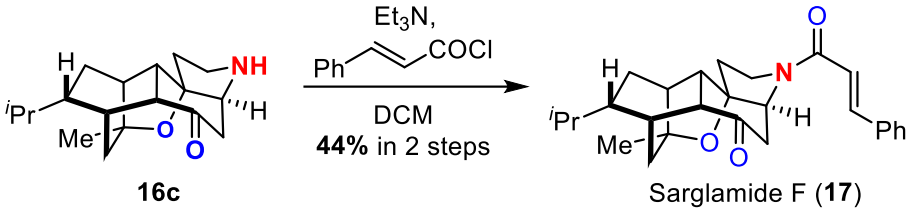
Compound 16c



To a cooled (0 °C) solution of compound **15a** (15 mg, 0.05 mmol, 1.0 equiv.) in

dimethoxyethane (1.5 mL) under argon atmosphere, was added $RhH(CO)(PPh_3)_3$ (4.5 mg, 0.005 mmol, 0.1 equiv.). Then, $PhSiH_3$ (28 μL, 0.25 mmol, 5.0 equiv.) was added dropwise. After being stirred 1.5 h at room temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (2 mL), and the organic layer was separated. The aqueous phase was extracted with ethyl acetate (3 × 3 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude amine **16c** was used directly for the next step without further purification.

Sarglamide F (17)



To a cooled (0 °C) solution of crude amine **16c** obtained above in DCM (1 mL) under argon atmosphere, was added Et_3N (4.3 μL, 0.03 mmol, 1.1 equiv.) and cinnamoyl chloride (5.1 mg, 0.03 mmol, 1.1 equiv.). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 5 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/2) to give the corresponding sarglamide F (**17**) (9.8 mg, yield: 44% in 2 steps) as a white powder.

Rf = 0.35 (silica, EtOAc/*n*-Hexane = 1:1);

$[\alpha]_D^{25}$ = -128.2 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$, Rotamer): δ = 7.71 (m, 1H), 7.51 (m, 2H), 7.36 (m, 3H), 6.60 (d, *J* = 15.2 Hz, 1H), 4.24 (m, 1H), 3.65 (m, 1H), 3.32 (m, 1H), 2.82 (m, 2H), 2.40 (m, 3H), 2.06 (m, 4H), 1.47 (m, 2H), 1.18-1.30 (m, 3H), 1.23 (m, 3H), 1.01 (m, 1H), 0.89 (m, 6H) ppm;

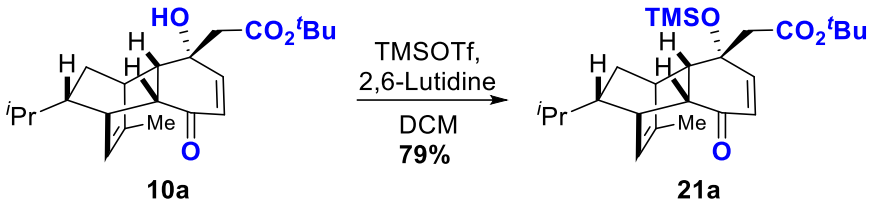
^{13}C NMR (101 MHz, $CDCl_3$, Rotamer): δ = 210.8, 210.0, 164.8, 143.2, 142.4, 134.9, 129.8, 128.8, 127.9, 118.1, 117.1, 87.8, 85.5, 81.4, 62.0, 51.4, 45.5, 45.3, 44.6, 44.3, 44.0, 43.1, 42.2,

38.7, 34.6, 32.5, 29.7, 27.5, 26.6, 24.7, 24.1, 20.8, 20.8 ppm;

HRMS (ESI, TOF): calculated for $[C_{27}H_{34}NO_3]^+$ 420.2533, found 420.2535.

1.2.4 Preparation of Sarglamide A (1)

Compound 21a



To a cooled (0 °C) solution of compound **10a** (1.08 g, 3.0 mmol, 1.0 equiv.) in DCM (30 mL) under argon atmosphere, was added 2,6-lutidine (0.38 mL, 3.3 mmol, 1.1 equiv.). After being stirred for another 5 min at the same temperature, TMSOTf (0.60 mL, 3.3 mmol, 1.1 equiv.) dropwise. After being stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/20) to give the corresponding silyl protected acetate **21a** (1.03 g, yield: 79%) as a colorless oil.

Rf = 0.21 (silica, EtOAc/*n*-Hexane = 1:20);

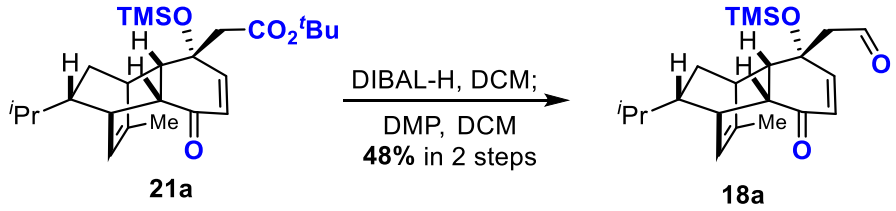
$[\alpha]_D^{25}$ = +39.5 (*c* 0.2, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (dd, *J* = 10.3, 1.7 Hz, 1H), 5.72 (d, *J* = 10.3 Hz, 1H), 5.45 (d, *J* = 6.2 Hz, 1H), 3.03 (m, 1H), 2.71 (m, 1H), 2.64 (dd, *J* = 8.4, 3.7 Hz, 1H), 2.58 (d, *J* = 14.6 Hz, 1H), 2.49 (d, *J* = 8.4 Hz, 1H), 2.45 (d, *J* = 14.6 Hz, 1H), 1.71 (m, 1H), 1.70 (d, *J* = 1.6 Hz, 3H), 1.43 (m, 1H), 1.42 (s, 9H), 1.11 (m, 1H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.82 (m, 1H), 0.77 (d, *J* = 6.6 Hz, 3H), 0.22 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.8, 168.3, 151.0, 144.4, 129.5, 121.9, 81.1, 74.0, 51.7, 50.9, 44.6, 43.8, 39.7, 36.4, 34.9, 33.2, 28.1, 21.2, 20.6, 20.2, 2.4 ppm;

HRMS (ESI, TOF): calculated for $[C_{25}H_{40}O_4Si+Na]^+$ 455.2588, found 455.2595.

Compound 18a



To a cooled (-78 °C) solution of silyl protected acetate **21a** (898 mg, 2.08 mmol, 1.0 equiv.) in DCM (20 mL), was added to DIBAL-H (8.3 mL, 8.32 mmol, 4.0 equiv., 1.0 M in hexane) dropwise. After being stirred for 1 h at the same temperature, the resulting mixture was quenched with saturated aqueous Rochelle salt carefully. The resulting mixture was allowed to stir at room temperature for another 3 h before the organic layer was separated. The aqueous phase was extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude diol was used directly for the next step without further purification.

To a cooled (0 °C) suspension of the above-mentioned diol and $NaHCO_3$ (1.7 g, 20.8 mmol, 10.0 equiv.) in DCM (24 mL) under argon atmosphere, was added DMP (2.5 g, 6.24 mmol, 3.0 equiv.) in 3 portions. After being stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated $NaHCO_3$ and $Na_2S_2O_3$ were added sequentially. After being stirred for 2 h at room temperature, the organic layer was separated, and the aqueous phases was extracted with DCM (3 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/20 to 1/16) to give compound **18a** (360 mg, yield: 48%, over 2 steps) as a colorless oil.

Rf = 0.65 (silica, EtOAc/*n*-Hexane = 1:4);

$[\alpha]_D^{25}$ = +28.8 (*c* 0.5, DCM);

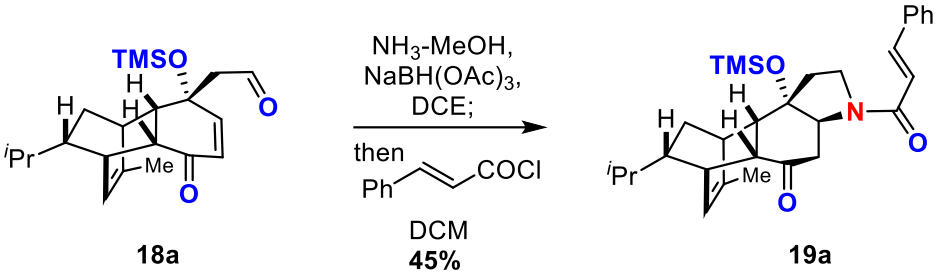
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.67 (t, *J* = 2.4 Hz, 1H), 6.63 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.66 (d, *J* = 10.3 Hz, 1H), 5.37 (d, *J* = 6.2 Hz, 1H), 2.98 (m, 1H), 2.66 (m, 1H), 2.62 (dd, *J* = 15.7,

2.24 Hz, 1H), 2.54, (dd, J = 8.3, 3.8 Hz, 1H), 2.48 (dd, J = 15.7, 3.04 Hz, 1H), 2.23 (d, J = 8.28 Hz, 1H), 1.63 (d, J = 1.6 Hz, 3H), 1.28 (m, 1H), 1.03 (m, 1H), 0.87 (m, 1H) 0.78 (d, J = 6.6 Hz, 3H), 0.75 (m, 1H), 0.69 (d, J = 6.6 Hz, 3H), 0.15 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.8, 199.7, 149.6, 144.2, 130.0, 122.0, 74.2, 58.6, 50.4, 45.5, 43.4, 39.8, 36.1, 34.6, 33.0, 21.0, 20.4, 20.0, 2.3 ppm;

HRMS (ESI, TOF): calculated for $[C_{21}H_{32}O_3Si+Na]^+$ 383.2013, found 383.2018.

Compound 19a



To a solution of compound **18a** (72 mg, 0.2 mmol, 1.0 equiv.) in DCE (2 mL) under argon atmosphere, was added a NH_3 (57 μL, 0.4 mmol, 2.0 equiv., 7M in MeOH). Once the starting material disappeared based on TLC, the resulting mixture was evacuated under reduced pressure.

To a cooled (0 °C) suspension of the abovementioned imine in MeOH (2 mL) under argon atmosphere, was added $NaBH(OAc)_3$ (127 mg, 0.6 mmol, 3.0 equiv.) in one portion. After being stirred for overnight at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with EtOAc (3 × 2 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting amine was used directly for the next step without further purification.

To a cooled (0 °C) suspension of the abovementioned amine in DCM (2 mL) under argon atmosphere, was added added triethylamine (31 μL, 0.22 mmol, 1.1 equiv.) and cinnamoyl chloride (33 mg, 0.2 mmol, 1.0 equiv.). After being stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was

separated, and the aqueous phase was extracted with DCM (3 × 2 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4 to 1/3) to give compound **19a** (44 mg, yield: 45%) as a colorless oil.

Rf = 0.43 (silica, EtOAc/*n*-Hexane = 2:1);

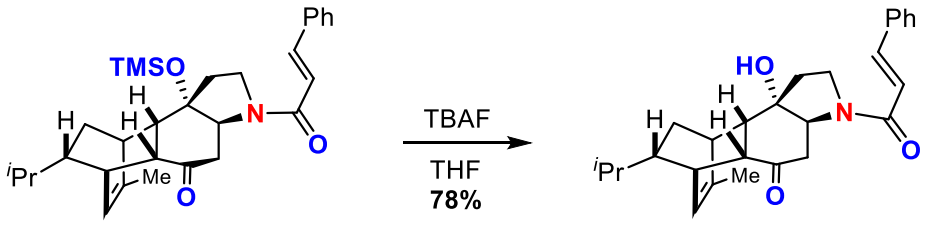
$[\alpha]_D^{25}$ = +20.8 (*c* 0.4, DCM);

^{1}H NMR (400 MHz, $CDCl_3$, Rotamer): δ = 7.68 (d, *J* = 15.4 Hz, 1H), 7.51 (m, 2H), 7.40 (m, 3H), 6.63 (d, *J* = 15.4 Hz, 1H), 5.75 (d, *J* = 6.3 Hz, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 3.66 (m, 1H), 3.66 (m, 1H), 3.11 (dd, *J* = 17.6, 10.9 Hz, 1H), 2.85 (m, 1H), 2.70 (td, *J* = 6.3, 2.24 Hz, 1H), 2.58 (m, 1H), 2.38 (td, *J* = 10.1, 1.52 Hz, 1H), 2.16 (td, *J* = 17.6, 1.9 Hz, 1H), 1.96 (d, *J* = 1.4 Hz, 3H), 1.94 (m, 1H), 1.80 (m, 1H), 1.69 (m, 1H), 1.34 (m, 1H), 1.05 (m, 1H), 0.95 (m, 1H), 0.84 (d, *J* = 6.5 Hz, 3H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.18 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$, Rotamer): δ = 214.9, 212.8, 164.3, 142.8, 142.7, 142.6, 142.4, 135.2, 135.1, 129.7, 128.8, 128.8, 127.9, 127.8, 123.8, 123.3, 118.1, 117.9, 82.5, 81.0, 62.5, 62.3, 53.7, 53.4, 47.6, 46.8, 46.6, 46.1, 45.8, 43.3, 42.5, 39.2, 39.1, 37.2, 35.0, 33.4, 33.4, 33.2, 33.1, 21.2, 20.6, 20.5, 20.3, 20.3, 2.2, 2.2 ppm;

HRMS (ESI, TOF): calculated for $[C_{30}H_{42}NO_3Si]^+$ 492.2928, found 492.2935.

Sarglamide A (1)



To a cooled (0 °C) suspension of compound **19a** (44 mg, 0.9 mmol, 1.0 equiv.) in THF (1 mL) under argon atmosphere, was added TBAF (0.1 mL, 0.1 mmol, 1.1 equiv., 1.0 M in THF), dropwise. The resulting mixture was stirred for 1 h at the same temperature. The reaction was quenched with saturated aqueous NH_4Cl, and then the organic layer was separated. The

aqueous phase was extracted with EtOAc (3 × 1 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4 to 1/2) to give compound Sarglamide A (**1**) (32 mg, yield: 78%) as a colorless crystal.

Rf = 0.35 (silica, EtOAc/*n*-Hexane = 1:1);

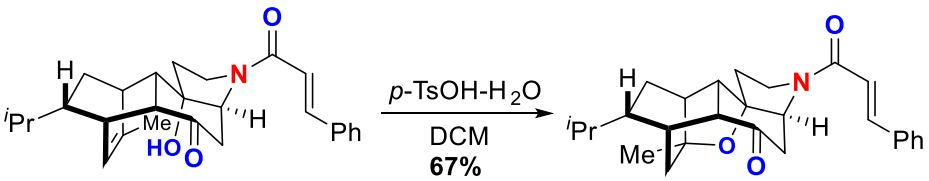
$[\alpha]_D^{25}$ = +25.1 (*c* 0.4, MeOH); lit.[3] **$[\alpha]_D^{22}$** = +17 (*c* 0.3, MeOH)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.60 (d, *J* = 15.6 Hz, 1H), 7.42 (m, 2H), 7.35, (m, 1H), 7.34 (m, 2H), 6.42 (d, *J* = 15.6 Hz, 1H), 5.80 (d, *J* = 6.2 Hz, 1H), 4.37 (d, *J* = 10.6 Hz, 1H), 3.55 (m, 1H), 3.47 (m, 1H), 3.21 (m, 1H), 3.04 (dd, *J* = 17.9, 10.8 Hz, 1H), 2.73 (m, 1H), 2.60 (m, 1H), 2.42 (dd, *J* = 10.4, 1.5 Hz, 1H), 2.15 (d, *J* = 1.3 Hz, 3H), 2.11 (m, 1H), 1.87 (m, 1H), 1.78 (m, 1H), 1.37 (m, 1H), 1.09 (m, 1H), 1.02 (m, 1H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): 215.0, 164.6, 143.2, 142.5, 134.9, 130.1, 129.0, 128.0, 123.3, 117.6, 76.5, 60.4, 53.7, 46.5, 46.4, 46.4, 43.7, 39.1, 37.8, 36.7, 33.5, 33.2, 21.2, 20.7, 20.4 ppm;

HRMS (ESI, TOF): calculated for $[C_{27}H_{33}NO_3+Na]^+$ 442.2353, found 442.2354.

Sarglamide F (17)



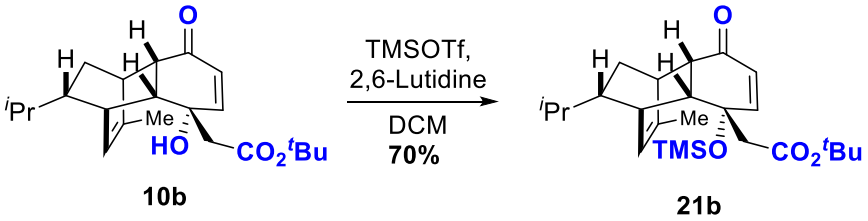
Sarglamide A (**1**) Sarglamide F (**17**)

To a solution of Sarglamide A (**1**) (15 mg, 0.036 mmol, 1.0 equiv.) in DCM (0.5 mL) under argon atmosphere, was added *p*-TsOH·H_2O (0.68 mg, 0.0036 mmol, 0.1 equiv.) at room temperature. After being stirred for 6 h at 50 °C, the reaction mixture was quenched by $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with DCM (3 × 1 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by PTLC (EtOAc/*n*-Hexane,

2/1) to give Sarglamide F (**17**) (10 mg, yield: 67%) as white solid.

1.2.5 Preparation of Sarglamide C (3)

Compound 21b



To a cooled (0 °C) solution of compound **10b** (4.1 g, 11.4 mmol, 1.0 equiv.) in DCM (110 mL) under argon atmosphere, was added 2,6-Lutidine (1.46 mL, 12.5 mmol, 1.1 equiv.). After being stirred for another 5 min at the same temperature, TMSOTf (2.27 mL, 12.5 mmol, 1.1 equiv.) dropwise. After being stirred for 1 h at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 15 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/20) to give the corresponding silyl protected acetate **21b** (3.4 g, 70%) as a colorless oil.

Rf = 0.21 (silica, EtOAc/*n*-Hexane = 1:20);

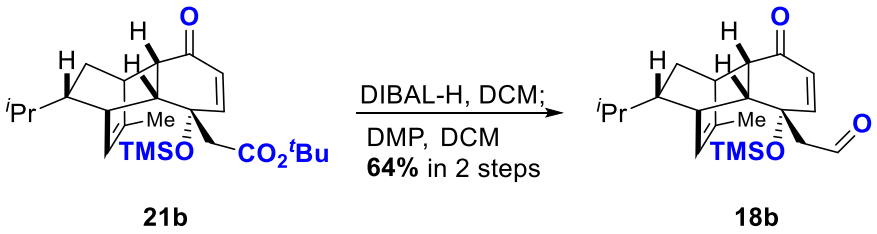
$[\alpha]_D^{25}$ = +25.6 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.79 (dd, *J* = 10.3, 1.3 Hz, 1H), 5.84 (d, *J* = 10.3 Hz, 1H), 5.66 (dt, *J* = 6.5, 1.8 Hz, 1H), 2.96 (dt, *J* = 6.6, 1.9 Hz, 1H), 2.84 (dt, *J* = 3.5, 1.6 Hz, 1H), 2.72 (dd, *J* = 9.0, 3.4 Hz, 1H), 2.59 (d, *J* = 14.3 Hz, 1H), 2.52 – 2.48 (m, 1H), 2.46 (d, *J* = 14.3 Hz, 1H), 1.78 (ddd, *J* = 13.1, 9.1, 2.4 Hz, 1H), 1.59 (d, *J* = 1.7 Hz, 3H), 1.42 (s, 9H), 1.22 (tt, *J* = 9.3, 3.2 Hz, 1H), 1.11 – 0.97 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.77 (d, *J* = 6.4 Hz, 3H), 0.18 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 199.8, 168.6, 152.5, 139.3, 129.1, 124.9, 81.0, 73.3, 52.0, 49.8, 48.6, 47.7, 42.1, 34.2, 32.9, 30.6, 28.1, 21.2, 20.8, 20.4, 2.3 ppm;

HRMS (ESI, TOF): calculated for $[C_{25}H_{40}O_4Si+Na]^+$ 455.2588, found 455.2594.

Compound 18b



21b **18b**

To a cooled (-78 ºC) solution of silyl protected acetate **21b** (3.4 g, 8.0 mmol, 1.0 equiv.) in DCM (80 mL), was added to DIBAL-H (32 mL, 32 mmol, 4.0 equiv., 1.0 M in hexane) dropwise. After being stirred for 1 h at the same temperature, the resulting mixture was quenched with saturated aqueous Rochelle salt carefully. The resulting mixture was allowed to stir at room temperature for another 3 h before the organic layer was separated. The aqueous phase was extracted with DCM (3 × 50 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude diol was used directly for the next step without further purification.

To a cooled (0 ºC) suspension of the above-mentioned diol and $NaHCO_3$ (6.72 g, 80 mmol, 10.0 equiv.) in DCM (80 mL) under argon atmosphere, was added DMP (10.2 g, 24 mmol, 3.0 equiv.) in 3 portions. After being stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated $NaHCO_3$ and $Na_2S_2O_3$ were added sequentially. After being stirred for 2 h at room temperature, the organic layer was separated, and the aqueous phases was extracted with DCM (3 × 100 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/20 to 1/16) to give compound **18b** (1.8 mg, yield: 64%, over 2 steps) as a colorless oil.

Rf = 0.65 (silica, EtOAc/*n*-Hexane = 1:4);

$[\alpha]_D^{25}$ = +116.2 (*c* 1.0, DCM);

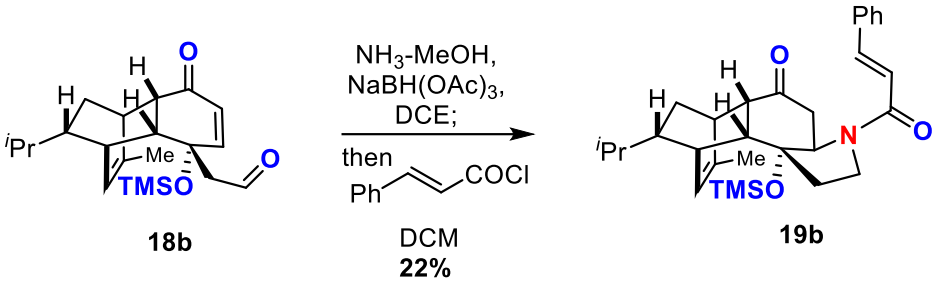
^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.76 (t, *J* = 2.3 Hz, 1H), 6.75 (dd, *J* = 10.3, 1.5 Hz, 1H), 5.85 (d, 10.3 Hz, 1H), 5.67 (d, *J* = 6.4 Hz, 1H), 2.99 (m, 1H), 2.84 (m, 1H), 2.74 (dd, *J* = 8.7, 3.6

Hz, 1H), 2.68 (dd, J = 15.2, 2.2 Hz, 1H,), 2.54 (dd, J = 15.2, 2.2 Hz, 1H), 2.27 (d, J = 8.7 Hz, 1H), 1.78 (m, 1H), 1.58 (d, J = 1.6 Hz, 3H), 1.21 (m, 1H), 1.04 (m, 1H), 1.00 (m, 1H), 0.87 (d, J = 6.4 Hz, 3H), 0.77 (d, J = 6.4 Hz, 3H), 0.21 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 200.3, 199.2, 151.2, 139.9, 129.7, 124.6, 74.0, 59.3, 49.3, 48.8, 48.8, 42.8, 33.9, 32.7, 30.2, 21.1, 20.8, 20.3, 2.3 ppm;

HRMS (ESI, TOF): calculated for $[C_{21}H_{32}O_3Si+Na]^+$ 383.2013, found 383.2021.

Compound 19b



To a solution of compound **18b** (150 mg, 0.45 mmol, 1.0 equiv.) in DCE (4.5 mL) under argon atmosphere, was added a NH_3 (129 μL, 0.45 mmol, 2.0 equiv., 7M in MeOH). Once the starting material disappeared based on TLC, the resulting mixture was evacuated under reduced pressure.

To a cooled (0 °C) suspension of the abovementioned imine in MeOH (4.5 mL) under argon atmosphere, was added $NaBH(OAc)_3$ (286 mg, 1.35 mmol, 3.0 equiv.) in one portion. After being stirred for overnight at 0 °C, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, and the aqueous phase was extracted with EtOAc (3 × 3 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting amine was used directly for the next step without further purification.

To a cooled (0 °C) suspension of the abovementioned amine in DCM (4.5 mL) under argon atmosphere, was added triethylamine (69 μL, 0.50 mmol, 1.1 equiv.) and cinnamoyl chloride (64 μL, 0.45 mmol, 1.0 equiv.). After being stirred for 2 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated, and

the aqueous phase was extracted with DCM (3 × 3 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4 to 1/3) to give compound **19b** (50 mg, yield: 22% in 2 steps) as a colorless powder.

Rf = 0.42 (silica, EtOAc/*n*-Hexane = 1:2);

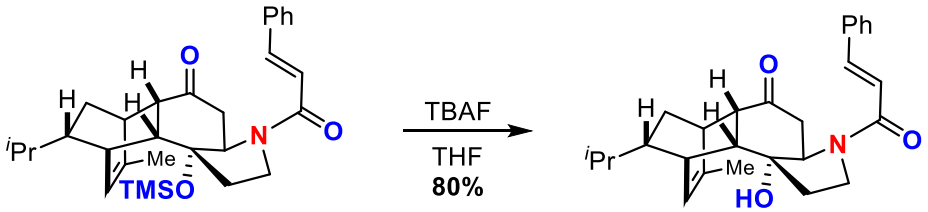
$[\alpha]_D^{25}$ = +64.9 (*c* 1.0, DCM);

^{1}H NMR (400 MHz, $CDCl_3$, Rotamer): δ = 7.69 (d, *J* = 15.4 Hz, 1H), 7.52 (m, 2H), 7.37 (m, 3H), 6.6 (d, *J* = 15.4 Hz, 1H), 5.93 (d, *J* = 6.08 Hz, 1H), 4.41 (d, *J* = 10.4 Hz, 1H), 3.66 (m, 2H), 3.13 (d, *J* = 6.5 Hz, 1H), 2.67 (m, 1H), 2.48 (m, 1H), 2.28 (d, *J* = 9.9 Hz, 1H), 2.19 (m, 1H), 1.95 (m, 2H), 1.81 (m, 1H), 1.77 (m, 1H), 1.77 (d, *J* = 1.5 Hz, 3H), 1.25 (m, 2H), 1.05 (m, 1H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.4 Hz, 3H), 0.18 (s, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$, Rotamer): δ = 214.6, 164.3, 142.6, 141.3, 135.1, 129.7, 128.7, 127.9, 127.9, 124.1, 117.9, 82.5, 80.9, 61.5, 60.4, 52.6, 48.3, 47.9, 46.1, 43.2, 42.4, 37.4, 37.2, 33.9, 33.2, 31.4, 21.3, 21.1, 20.5, 14.2, 2.2 ppm;

HRMS (ESI, TOF): calculated for $[C_{30}H_{42}NO_3Si]^+$ 492.2928, found 492.2931.

Sarglamide C (3)



19b Sarglamide C (**3**)

To a cooled (0 °C) suspension of compound **19b** (50 mg, 0.1 mmol, 1.0 equiv.) in THF (1 mL) under argon atmosphere, was added TBAF (0.11 mL, 0.11 mmol, 1.1 equiv., 1.0 M in THF), dropwise. The resulting mixture was stirred for 1 h

at the same temperature. The reaction was quenched with saturated aqueous NH_4Cl, and then the organic layer was separated. The aqueous phase was extracted with EtOAc (3 × 1 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and

concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4 to 1/2) to give compound Sarglamide C (**3**) (33 mg, yield: 80%) as a colorless crystal.

Rf = 0.38 (silica, EtOAc/*n*-Hexane = 1:1);

[α]$_D^{25}$ = -19.3 (*c* 1.0, MeOH); lit.[3] **[α]$_D^{22}$** = -21 (*c* 0.3, MeOH)

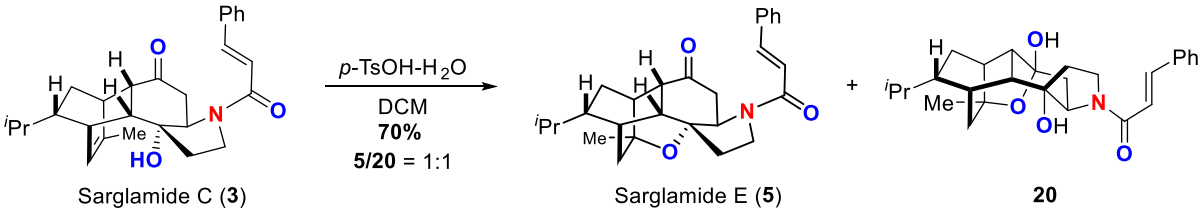
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 15.5 Hz, 1H), 7.45 (m, 2H), 7.35 (m, 1H), 7.33 (m, 2H), 6.54 (d, *J* = 15.4 Hz, 1H), 6.01 (d, *J* = 6.3 Hz, 1H), 4.43 (d, *J* = 10.2 Hz, 1H), 3.76 (q, *J* = 9.6 Hz, 1H), 3.57 (td, *J* = 8.9, 1.3 Hz, 1H), 3.33 (d, *J* = 6.4 Hz, 1H), 2.93 (dd, *J* = 17.8, 10.6 Hz, 1H), 2.68 (d, 9.9 Hz, 1H), 2.52 (m, 1H), 2.35 (d, *J* = 9.9 Hz, 1H), 2.17 (d, *J* = 17.8 Hz, 1H), 1.92 (m, 1H), 1.82 (d, *J* = 0.96 Hz, 1H), 1.78 (m, 1H), 1.31 (m, 1H), 1.09 (m,1H), 1.02 (m, 1H), 0.95 (d, *J* = 6.5 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 214.5, 164.9, 142.7, 141.8, 135.1, 130.0, 128.9, 128.1, 124.5, 118.0, 77.0, 61.1, 52.6, 48.1, 48.0, 45.8, 43.4, 42.2, 37.3, 33.7, 33.4, 31.7, 21.4, 20.5 ppm;

HRMS (ESI, TOF): calculated for $[C_{27}H_{33}NO_3Na]^+$ 442.2353, found 442.2360.

1.2.6 Preparation of Sarglamide D (4)

Sarglamide E (5) and compound 20



Sarglamide C (**3**) Sarglamide E (**5**) **20**

To a solution of Sarglamide C (**3**) (22 mg, 0.05 mmol, 1.0 equiv.) in DCM (0.5 mL) under argon atmosphere, was added *p*-TsOH·H_2O (0.95 mg, 0.005 mmol, 0.1 equiv.) at room temperature. After being stirred for 6 h at 50 °C, the reaction mixture was quenched by $NaHCO_3$. The organic phase was separated, and the aqueous phase was extracted with DCM (3 × 1 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered,

and concentrated under reduced pressure. The residue was purified by PTLC (EtOAc/*n*-Hexane, 2/1) to give Sarglamide E (**5**) (7 mg, yield: 35%) and compound **20** (8 mg, yield: 35%) as white powder.

Compound **20**:

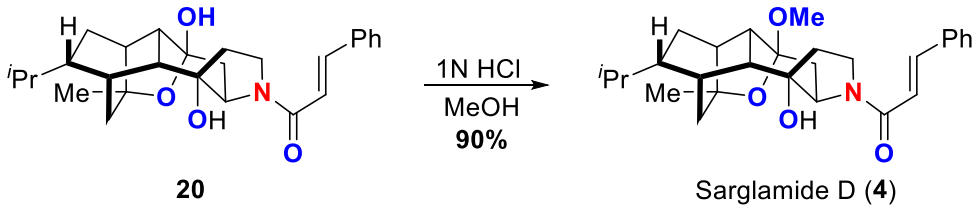
Rf = 0.5 (silica, EtOAc/*n*-Hexane = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 15.4 Hz, 1H), 7.72 (d, *J* = 15.5 Hz, 1H), 7.52 (m, 2H), 7.36-7.35 (m, 3H), 6.68 (d, *J* = 15.5 Hz, 1H),6.64 (d, *J* = 15.4 Hz, 1H), 4.34 (dd, *J* = 10.7, 6.4 Hz, 1H), 4.00 (dd, *J* = 11.2, 6.2 Hz, 1H), 3.83 (m, 1H), 3.81 (dd, *J* = 10.0, 8.4 Hz, 1H), 3.62 (t, *J* = 9.4 Hz, 1H), 3.57 (ddd, *J* = 12.8, 9.9, 1.6 Hz, 1H), 2.63 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.43-2.42 (m, 1H), 2.37 (m, 1H), 2.33 (dd, *J* = 14.2, 6.4 Hz, 1H), 2.33 (m, 1H), 2.31 (m, 1H), 2.29 (m, 1H), 2.27 (m, 1H), 2.09 (m, 1H), 2.02 (m, 1H), 1.97 (m, 1H), 1.88 (dd, *J* = 13.5, 8.2 Hz, 1H), 1.67 (m, 1H), 1.62-1.54 (m, 1H), 1.46 (m, 1H), 1.35 (s, 3H), 1.32 (s, 3H), 1.30-1.29 (m, 1H), 1.21-1.20 (m, 1H), 1.00-0.98 (m, 1H), 0.93-0.91 (d, *J* = 6.4 Hz, 3H), 0.89-0.87 (m, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 165.3, 165.1, 142.9, 142.4, 135.3, 135.2, 129.8, 128.9, 128.9, 128.2, 128.1, 118.3, 118.0, 101.3, 82.9, 82.5, 78.5, 77.4, 77.0, 61.4, 60.4, 46.6, 46.5, 45.5, 45.5, 44.6, 42.8, 42.3, 41.7, 39.7, 38.0, 37.7, 36.8, 35.2, 34.9, 33.0, 26.6, 26.4, 25.0, 24.1, 21.1, 20.9 ppm;

HRMS (ESI, TOF): calculated for $[C_{27}H_{35}NO_4Na]^+$ 460.2458, found 460.2455.

Sarglamide D (4)



20 Sarglamide D (**4**)

To a solution of compound **20** (4 mg, 0.009 mmol, 1.0 equiv.) in MeOH (0.5 mL), was added 1N HCl (100 uL) in one portion. After being stirred for 4 h at room temperature, the reaction mixture was purified by PTLC (EtOAc/*n*-Hexane, 1/2) to give Sargalmide **D** (4 mg, yield:

90%).

Rf = 0.6 (silica, EtOAc/*n*-Hexane = 1:1);

$[\alpha]_D^{25}$ = +12 (*c* 0.2, MeOH); lit.[3] **$[\alpha]_D^{22}$** = +3 (*c* 0.1, MeOH)

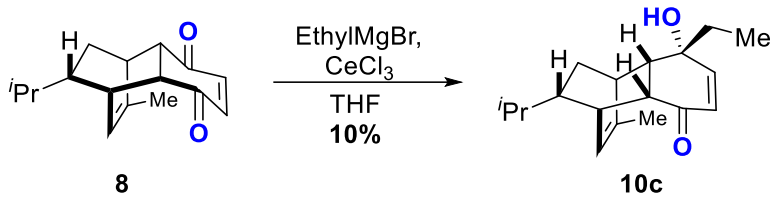
^{1}H NMR (400 MHz, $CDCl_3$, Rotamer): δ = 7.72 (d, *J* = 15.4 Hz, 1H), 7.72 (d, *J* = 15.4 Hz, 1H), 7.54 (m, 2H), 7.48 (m, 2H), 7.40 (m, 1H), 7.38 (m, 1H), 7.35 (m, 2H), 7.34 (m, 2H), 6.66 (d, *J* = 15.4 Hz, 1H), 6.65 (d, *J* = 15.4, 1H), 4.30 (dd, *J* = 10.9, 6.5 Hz, 1H), 3.94 (dd, *J* = 11.5, 6.3 Hz, 1H), 3.85 (m, 1H), 3.83 (m, 1H), 3.62 (m, 1H), 3.55 (m, 1H), 3.2-3.19 (s, 3H), 2.88 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.52 (dd, *J* = 14.0, 6.4 Hz, 1H), 2.38 (m, 1H), 2.36 (m, 1H), 2.34 (m, 1H), 2.33 (m, 1H), 2.27 (m, 1H), 2.22 (m, 1H), 2.18 (m, 1H), 2.11 (m, 1H), 2.08 (m, 1H), 1.99 (m, 1H), 1.98 (m, 1H), 1.96 (m, 1H), 1.87 (m, 1H), 1.74 (m, 1H), 1.62 (m, 1H), 1.56 (m, 1H), 1.52 (m, 1H), 1.35 (m, 1H), 1.33 (s, 3H), 1.31 (s, 3H), 1.30 (m, 1H), 1.17 (m, 1H), 1.16 (m, 1H), 1.15 (m, 1H), 0.97 (m, 1H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.88-0.87 (d, *J* = 6.5 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$, Rotamer): δ = 165.3, 165.0, 143.0, 142.8, 142.2, 135.4, 135.2, 129.8, 129.7, 128.9, 128.9, 128.3, 128.2, 128.1, 118.4, 118.0, 117.9, 103.5, 101.3, 101.3, 83.1, 82.9, 82.8, 82.6, 78.5, 78.4, 77.4, 61.3, 60.4, 48.6, 48.4, 46.8, 46.7, 46.5, 45.7, 45.6, 45.1, 44.9, 44.6, 42.9, 42.3, 42.2, 41.7, 38.0, 36.8, 36.7, 35.4, 35.0, 34.5, 33.0, 33.0, 32.4, 29.8, 26.5, 26.4, 26.2, 25.0, 24.4, 24.3, 24.2, 24.1, 21.2, 21.0, 20.9 ppm;

HRMS (ESI, TOF): calculated for $[C_{28}H_{37}NO_4+Na]^+$ 474.2615, found 474.2622.

1.2.7 Preparation of compound 10c and 9c

Compound 10c



8 **10c**

$CeCl_3 \cdot 7H_2O$ (745 mg, 2.0 mmol, 1.0 equiv.) was added to a Schlenk tube (100 mL) and evacuated. The tube was immersed in a pre-heated oil bath (140 °C) with evacuation, while the water was trapped by liquid nitrogen. After 1 h heating without stirring, the cerium chloride was completely dried by a vigorous stirring at the same temperature for an additional 2 h. While the flask was still hot, the flask was filled with argon gas and then cooled to 0 °C. Freshly distilled THF (20 mL) was added to the flask containing cerium chloride at the same temperature and allowed to stir for another 2 h at room temperature.

To the cooled (-78 °C) mixture containing cerium chloride made *in situ* above, ethyl magnesium bromide (2 mL, 2.0 mmol, 2.0 equiv., 1M in THF) was added dropwise and stirred at -78 °C. After being stirred for 2 h, the mixture was added to compound **8** (488 mg, 2.0 mmol, 1.0 equiv.) in THF (5 mL) dropwise at -78 °C. After the addition, the reaction mixture was allowed to stir for an additional 2 h at the 0 °C. The mixture was quenched with saturated aqueous NH_4Cl. Et_2O (10 mL) was then added, and the organic layer was separated. The aqueous phase was extracted with Et_2O (4 × 10 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4 and $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/8) to give compound **10c** (52 mg, 10%) as a white powder.

Compound 10c:

Rf = 0.7 (silica, EtOAc/*n*-Hexane, 1/4);

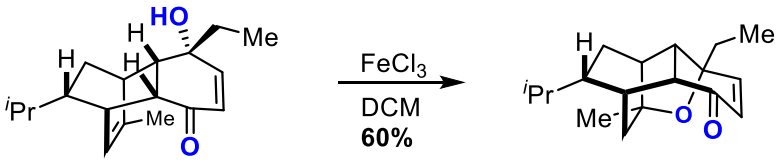
^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.50 (dd, *J* = 10.3, 1.6 Hz, 1H), 5.80 (d, *J* = 10.3 Hz, 1H), 5.52 – 5.44 (m, 1H), 3.04 (ddd, *J* = 6.4, 3.6, 1.6 Hz, 1H), 2.75 (dt, *J* = 3.1, 1.5 Hz, 1H), 2.64 (dd, *J* = 8.6, 3.6 Hz, 1H), 2.35 – 2.14 (m, 1H), 1.73 (d, *J* = 1.7 Hz, 3H), 1.71 (d, *J* = 3.4 Hz, 1H), 1.66 – 1.60 (m, 2H), 1.55 (dd, *J* = 13.9, 7.4 Hz, 1H), 1.43 – 1.29 (m, 1H), 1.16 – 1.04 (m,

1H), 0.91 (t, *J* = 7.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.77 (d, *J* = 6.6 Hz, 3H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.0, 151.6, 143.8, 130.1, 122.5, 72.3, 51.0, 44.9, 44.2, 40.0, 39.7, 36.3, 34.5, 33.3, 21.2, 20.5, 20.2, 7.4 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{26}O_2+Na]^+$ 297.1825, found 297.1826.

Compound 9c



10c **9c**

To a solution of compound **10c** (52 mg, 0.19 mmol, 1.0 equiv.) in DCM (2 mL) under argon atmosphere, was added $FeCl_3$ (51 mg, 0.19 mmol, 1.0 equiv.). After being stirred for 1 h at the same temperature, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and the organic layer was separated. The aqueous phase was extracted with DCM (3 × 2 mL). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/*n*-Hexane, 1/4) to give the corresponding pentacyclic **9c** (31 mg, yield: 60%) as a white powder.

Rf = 0.4 (silica, EtOAc/*n*-Hexane = 1:4);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.75 (d, *J* = 10.3 Hz, 1H), 6.09 (d, *J* = 10.3 Hz, 1H), 2.62 (dd, *J* = 8.9, 4.7 Hz, 1H), 2.47 (dt, *J* = 9.0, 1.5 Hz, 1H), 2.05 – 1.99 (m, 2H), 1.98 – 1.93 (m, 1H), 1.77 – 1.66 (m, 1H), 1.67 – 1.61 (m, 2H), 1.53 (dt, *J* = 15.2, 1.8 Hz, 1H), 1.37 – 1.27 (m, 1H), 1.26 (s, 3H), 1.25 – 1.17 (m, 2H), 0.96 – 0.77 (m, 9H) ppm;

^{13}C NMR (101 MHz, $CDCl_3$): δ = 201.8, 151.5, 128.9, 82.5, 75.6, 49.2, 45.0, 42.9, 42.2, 33.8, 33.8, 33.7, 32.8, 24.7, 23.8, 21.1, 20.5, 9.1 ppm;

HRMS (ESI, TOF): calculated for $[C_{18}H_{27}O_2]^+$ 275.2006, found 275.2010.

1.3 NMR Data Comparison[3]

^{1}H-NMR comparison of sarglamide A (**1**) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.57, td (9.9, 7.3)	*α* 3.55, m	0.02
β 3.48, m	*β* 3.47, m	0.01
1.87, m	1.87, m	0.00
2.42, dd (10.1, 2.0)	2.42, dd (10.4, 1.5)	0.00
2.61, ddd (10.1, 2.3, 2.3)	2.60, m	0.01
α 3.04, dd (17.8, 10.8)	*α* 3.04, dd (17.9, 10.8)	0.00
β 2.14, ddd (17.8, 2.2, 2.2)	*β* 2.11, m	0.03
4.38, ddd (10.8, 2.3, 2.3)	4.37, d (10.6)	0.01
6.44, d (15.5)	6.42, d (15.6)	0.02
7.61, d (15.5)	7.60, d (15.6)	0.01
7.43, m	7.42, m	0.01
7.34, m	7.34, m	0.00
7.35, m	7.35, m	0.00
5.81, ddq (6.4, 2.0, 1.6)	5.80, d (6.2)	0.01
2.74, ddd (6.4, 2.5, 2.0)	2.73, m	0.01
1.38, m	1.37, m	0.01
α 1.02, ddd (12.7, 5.6, 3.0)	*α* 1.02, m	0.00
β 1.78, ddd (12.7, 9.0, 2.9)	*β* 1.78, m	0.00
3.20, m	3.21, m	0.01
2.15, d (1.6)	2.15, d (1.3)	0.00
1.09, m	1.09, m	0.00
0.80, d (6.5)	0.79, d (6.5)	0.01
0.87, d (6.5)	0.86, d (6.5)	0.01

^{13}C-NMR comparison of sarglamide A (**1**) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
43.7	43.7	0.0
37.9	37.8	0.1
76.7	76.5	0.2
46.5	46.5	0.0
53.8	53.7	0.1
215.0	215.0	0.0
46.4	46.4	0.0
60.5	60.4	0.1
164.6	164.6	0.0
117.8	117.6	0.2
142.5	142.5	0.0
135.0	134.9	0.1
128.1	128.0	0.1
129.0	129.0	0.0
130.0	130.1	0.1
143.2	143.2	0.0
123.4	123.3	0.1
39.2	39.1	0.1
46.6	46.5	0.1
33.3	33.2	0.1
36.7	36.7	0.0
20.8	20.7	0.1
33.6	33.5	0.1
20.5	20.4	0.1
21.3	21.2	0.1

^{1}H-NMR comparison of sarglamide C (**3**) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.76, td (9.8, 7.6)	*α* 3.76 (q, 9.6)	0.00
β 3.56, td (9.3, 2.0)	*β* 3.57 (td, 8.9, 1.3)	0.01
1.92, m	1.92 (m)	0.00
2.35, dd (9.9, 1.6)	2.35, d (9.9)	0.00
2.68, ddd (9.9, 2.4, 2.4)	2.68, d (9.9)	0.00
α 2.93, dd (17.8, 10.6)	*α* 2.93, dd (17.8, 10.6)	0.00
β 2.17, dd (17.8, 2.2, 2.2)	*β* 2.17, d (17.8)	0.00
4.43, ddd (10.6, 2.2, 2.2)	4.43, d (10.2)	0.00
6.53, d (15.5)	6.54, d (15.4)	0.01
7.62, d (15.5)	7.63, d (15.5)	0.01
7.44, m	7.45, m	0.01
7.33, m	7.33, m	0.00
7.35, m	7.35, m	0.00
6.02, ddq (6.4, 1.8, 1.6)	6.01, d (6.3)	0.01
3.34, ddd (6.8, 1.8, 1.8)	3.33, d (6.4)	0.01
1.31, m	1.31, m	0.00
α 1.02, ddd (13.1, 3.9, 3.9)	*α* 1.02, m	0.00
β 1.79, m	*β* 1.78, m	0.01
2.52, m	2.52, m	0.00
1.82, d (1.6)	1.82, d (0.96)	0.00
1.09, m	1.09, m	0.00
0.79, d (6.5)	0.79, d (6.5)	0.00
0.95, d (6.5)	0.95, d (6.5)	0.00

^{13}C-NMR comparison of sarglamide C (**3**) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
43.4	43.4	0.0
37.3	37.3	0.0
77.0	77.0	0.0
48.0	48.0	0.0
52.7	52.6	0.1
214.6	214.5	0.1
45.8	45.8	0.0
61.1	61.1	0.0
165.0	164.9	0.1
118.1	118.0	0.1
142.6	142.7	0.1
135.0	135.1	0.1
128.1	128.1	0.0
128.9	128.9	0.0
130.0	130.0	0.0
141.6	141.8	0.2
124.6	124.5	0.1
33.7	33.7	0.0
48.2	48.1	0.1
31.7	31.7	0.0
42.3	42.2	0.1
21.4	21.4	0.0
33.4	33.4	0.0
20.5	20.5	0.0
21.4	21.4	0.0

^{1}H-NMR comparison of sarglamide D (**4**) (Rotamer A) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.83, m	*α* 3.83, m	0.00
β 3.56, m	*β* 3.55, m	0.01
α 1.87, m	*α* 1.87, m	0.00
β 2.27, m	*β* 2.27, m	0.00
2.08, m	2.08, m	0.00
2.22, dd (9.6, 4.2)	2.22, m	0.00
α 2.52, dd (14.1, 6.4)	*α* 2.52, dd (14.0, 6.4)	0.00
β 1.35, dd (14.1, 11.3)	*β* 1.35, m	0.00
3.94, dd (11.3, 6.4)	3.94, dd (11.5, 6.3)	0.00
6.64, d (15.5)	6.65, d (15.4)	0.01
7.68, d (15.5)	7.72, d (15.4)	0.04
7.48, m	7.48, m	0.00
7.34, m	7.34, m	0.00
7.35, m	7.35, m	0.00
α 1.62, m	*α* 1.62, m	0.00
β 1.52, m	*β* 1.52, m	0.00
2.38, m	2.38, m	0.00
0.97, m	0.97, m	0.00
α 1.15, m	*α* 1.15, m	0.00
β 1.98, m	*β* 1.98, m	0.00
2.34, m	2.34, m	0.00
1.30, s	1.31, s	0.01
1.30, m	1.30, m	0.00
0.90, d (6.5)	0.90, d (6.5)	0.00
0.88, d (6.5)	0.87, d (6.5)	0.01
3.19, s	3.19, s	0.00

^{13}C-NMR comparison of sarglamide D (**4**) (Rotamer A) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
41.6	41.7	0.1
36.7	36.7	0.0
78.6	78.5	0.1
45.7	45.7	0.0
44.9	443.9	0.0
103.5	103.5	0.0
34.5	34.5	0.0
61.3	61.3	0.0
165.1	165.0	0.1
118.4	118.4	0.0
142.3	142.2	0.1
135.3	135.2	0.1
128.3	128.3	0.0
128.9	128.9	0.0
129.8	129.8	0.0
82.8	82.8	0.0
35.1	35.0	0.1
26.3	26.2	0.1
46.7	46.7	0.0
24.1	24.1	0.0
42.2	42.2	0.0
24.3	24.3	0.0
33.0	33.0	0.0
20.9	20.9	0.0
21.2	21.2	0.0
48.6	48.6	0.0

^{1}H-NMR comparison of sarglamide D (**4**) (Rotamer B) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.85, m	*α* 3.85, m	0.00
β 3.62, m	*β* 3.62, m	0.00
α 1.96, m	*α* 1.96, m	0.00
β 2.33, m	*β* 2.33, m	0.00
2.11, m	2.10, m	0.01
2.18, dd (9.7, 4.2)	2.18, m	0.00
α 2.88, dd (13.7, 6.4)	*α* 2.88, dd (13.6, 6.4)	0.00
β 1.16, dd (13.7, 11.0)	*β* 1.16, m	0.00
4.30, dd (11.0, 6.4)	4.30, dd (10.9, 6.5)	0.00
6.66, d (15.5)	6.66, d (15.4)	0.00
7.77, d (15.5)	7.77, d (15.4)	0.00
7.54, m	7.54, m	0.00
7.38, m	7.38, m	0.00
7.40, m	7.40, m	0.00
α 1.74, m	*α* 1.74, m	0.00
β 1.56, m	*β* 1.56, m	0.00
2.36, m	2.36, m	0.00
0.97, m	0.97, m	0.00
α 1.17, m	*α* 1.17, m	0.00
β 1.99, m	*β* 1.99, m	0.00
2.34, m	2.34, m	0.00
1.33, s	1.33, s	0.00
1.30, m	1.30, m	0.00
0.90, d (6.5)	0.90, d (6.5)	0.00
0.88, d (6.5)	0.88, d (6.5)	0.00
3.20, s	3.2, s	0.00

^{13}C-NMR comparison of sarglamide D (**4**) (Rotamer B) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
42.8	42.9	0.1
38.0	38.0	0.0
77.1	77.4	0.3
45.6	45.6	0.0
45.2	45.1	0.1
103.5	103.5	0.0
32.4	32.4	0.0
60.4	60.4	0.0
165.3	165.3	0.0
118.0	118.0	0.0
143.0	143.0	0.0
135.4	135.4	0.0
128.1	128.1	0.0
128.9	128.9	0.0
129.8	129.8	0.0
83.1	83.1	0.0
35.4	35.4	0.0
26.5	26.5	0.0
46.8	46.8	0.0
24.1	24.1	0.0
42.2	42.2	0.0
24.3	24.3	0.0
33.0	33.0	0.0
20.9	20.9	0.0
21.2	21.2	0.0
48.5	48.4	0.1

^{1}H-NMR comparison of sarglamide E (**5**) (Rotamer A) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.73, m	*α* 3.73, m	0.00
β 3.92, m	*β* 3.92, m	0.00
α 2.40, m	*α* 2.39, m	0.01
β 2.08, m	*β* 2.08, m	0.01
2.60, m	2.59, m	0.01
2.23, m	2.22, m	0.01
α 2.37, dd (13.7, 8.1)	*α* 2.37, m	0.00
β 3.49, dd (13.7, 8.1)	*β* 3.49, m	0.00
3.94, dd (8.1, 8.1)	3.94, m	0.00
6.69, d (15.6)	6.68, d (15.3)	0.01
7.70, d (15.6)	7.69, d (15.3)	0.01
7.51, m	7.51, m	0.00
7.37, m	7.37, m	0.00
7.37, m	7.37, m	0.00
α 1.48, m	*α* 1.47, m	0.01
β 1.57, dd (13.7, 5.9)	*β* 1.58, m	0.01
2.19, m	2.19, m	0.00
1.39, m	1.39, m	0.00
α 1.81, ddd (12.9, 7.9, 4.7)	*α* 1.81, ddd (12.8, 8.1, 4.7)	0.00
β 1.09, m	*β* 1.09, m	0.00
2.38, m	2.37, m	0.01
1.10, s	1.09, s	0.01
1.49, m	1.49, m	0.00
0.91, d (6.5)	0.91, d (6.4)	0.00
0.93, d (6.5)	0.93, d (6.4)	0.00

^{13}C-NMR comparison of sarglamide E (**5**) (Rotamer A) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
46.1	46.1	0.0
35.0	35.0	0.0
81.8	81.8	0.0
35.2	35.2	0.0
45.7	45.7	0.0
212.1	212.1	0.0
43.8	43.8	0.0
63.2	63.2	0.0
165.7	165.7	0.0
118.2	118.2	0.0
142.8	142.8	0.0
135.2	135.2	0.0
128.0	128.1	0.1
129.0	129.0	0.0
130.0	130.0	0.0
75.7	75.7	0.0
31.7	31.7	0.0
28.2	28.1	0.1
41.8	41.8	0.0
29.9	29.9	0.0
42.0	41.9	0.1
24.0	24.0	0.0
29.8	29.8	0.0
20.5	20.5	0.0
21.8	21.8	0.0

^{1}H-NMR comparison of sarglamide E (**5**) (Rotamer B) with reported values

Yue's Isolated Sample (500 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 4.16, m	*α* 4.16, m	0.00
β 3.92, m	*β* 3.92, m	0.00
α 2.40, m	*α* 2.40, m	0.00
β 1.98, m	*β* 1.98, m	0.00
2.61, m	2.60, m	0.00
2.23, m	2.23, m	0.00
α 2.55, dd (13.7, 8.1)	*α* 2.55, m	0.00
β 3.05, dd (13.7, 8.1)	*β* 3.05, m	0.00
4.00, dd (8.1, 8.1)	4.00, m	0.00
6.54, d (15.6)	6.54, d (15.3)	0.00
7.67, d (15.6)	7.67, d (15.3)	0.00
7.51, m	7.51, m	0.00
7.37, m	7.37, m	0.00
7.37, m	7.37, m	0.00
α 1.48, m	*α* 1.48, m	0.00
β 1.57, dd (13.7, 5.9)	*β* 1.57, m	0.00
2.19, m	2.19, m	0.00
1.39, m	1.39, m	0.00
α 1.81, ddd (12.9, 7.9, 4.7)	*α* 1.81, ddd (12.8, 8.1, 4.7)	0.00
β 1.09, m	*β* 1.09, m	0.00
2.38, m	2.38, m	0.00
1.10, s	1.09, s	0.01
1.49, m	1.49, m	0.00
0.91, d (6.5)	0.91, d (6.4)	0.00
0.93, d (6.5)	0.93, d (6.4)	0.00

^{13}C-NMR comparison of sarglamide E (**5**) (Rotamer B) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
45.8	45.7	0.0
34.4	34.4	0.0
83.4	83.4	0.0
35.2	35.2	0.0
45.7	45.7	0.0
211.1	211.2	0.1
45.6	45.7	0.1
62.9	62.9	0.0
165.7	165.7	0.0
118.2	118.2	0.0
142.8	142.8	0.0
135.2	135.2	0.0
128.0	128.1	0.1
129.0	129.0	0.0
130.0	130.0	0.0
75.7	75.7	0.0
31.7	31.7	0.0
28.2	28.1	0.1
41.8	41.8	0.0
29.9	29.9	0.0
42.0	41.9	0.1
24.0	24.0	0.0
29.8	29.8	0.0
20.5	20.5	0.0
21.8	21.8	0.0

^{1}H-NMR comparison of compound **20** (Rotamer A) with reported values

Yue's Isolated Sample (600 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.81, dd (10.0, 8.4)	*α* 3.81, dd (10.0, 8.4)	0.00
β 3.57, ddd (12.8, 9.9, 1.6)	*β* 3.57, ddd (12.8, 9.9, 1.6)	0.00
α 1.87, dd (13.5, 8.4)	*α* 1.88, dd (13.5, 8.2)	0.01
β 2.29, m	*β* 2.29, m	0.00
2.09, m	2.09, m	0.00
α 2.33, dd (14.2, 6.4)	*α* 2.33, dd (14.2, 6.4)	0.00
β 1.67, dd (14.2, 11.3)	*β* 1.67, m	0.00
3.99, dd (11.3, 6.4)	4.00, dd (11.2, 6.2)	0.01
6.66, d (15.5)	6.64, d (15.4)	0.02
7.76, d (15.5)	7.76, d (15.4)	0.00
7.52, m	7.52, m	0.00
7.36, m	7.36, m	0.00
7.36, m	7.36, m	0.00
1.54-1.62, m	1.54-1.62, m	0.00
2.39, m	2.37, m	0.02
0.98, m	1.00, m	0.02
α 1.20, m	*α* 1.21, m	0.01
β 2.02, m	*β* 2.02, m	0.00
2.42, m	2.42, m	0.00
1.34, s	1.35, s	0.01
1.29, m	1.30, m	0.01
0.92, d (6.5)	0.93, d (6.4)	0.01
0.87, d (6.5)	0.89, m	0.02

^{13}C-NMR comparison of compound **20** (Rotamer A) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
41.7	41.7	0.0
36.9	36.8	0.1
78.6	78.5	0.1
45.5	45.5	0.0
44.6	44.6	0.0
101.3	101.3	0.0
39.7	39.7	0.0
61.4	61.4	0.0
165.3	165.3	0.0
118.1	118.1	0.0
142.9	142.9	0.0
135.2	135.2	0.0
128.2	128.2	0.0
128.9	128.9	0.0
129.8	129.8	0.0
83.0	82.9	0.1
35.2	35.2	0.0
26.4	26.4	0.0
46.5	46.5	0.0
24.1	24.1	0.0
42.3	42.3	0.0
25.0	25.0	0.0
33.0	33.0	0.0
20.9	20.9	0.0
21.1	21.1	0.0

^{1}H-NMR comparison of compound **20** (Rotamer B) with reported values

Yue's Isolated Sample (600 MHz, $CDCl_3$)	**Our Synthetic Sample (400 MHz, $CDCl_3$)**	**Δ/ppm**
α 3.83, ddd (10.0, 8.0,5.3)	α 3.83, m	0.00
β 3.62, t (9.4)	β 3.62, t (9.4)	0.00
α 1.97, dd (13.1, 8.0)	α 1.97, m	0.00
β 2.33, m	β 2.33, m	0.00
2.09, m	2.09, m	0.00
2.27, m	2.27, m	0.00
α 2.61, dd (13.9, 6.4)	α 2.63, dd (13.9, 6.3)	0.02
β 1.46, dd (13.9,11.0)	β 1.46, m	0.00
4.33, dd (11.0, 6.4)	4.34, dd (10.7, 6.4)	0.01
6.67, d (15.5)	6.68, d (15.5)	0.01
7.70, d (15.5)	7.72, d (15.5)	0.02
7.52, m	7.52, m	0.00
7.36, m	7.36, m	0.00
1.54-1.62, m	1.54-1.62, m	0.00
2.31, m	2.31, m	0.00
0.98, m	1.00, m	0.02
α 1.20, m	α 1.20, m	0.00
β 2.02, m	β 2.02, m	0.00
2.42, m	2.43, m	0.01
1.30, s	1.32, s	0.02
1.29, m	1.29, m	0.00
0.91, d (6.5)	0.91, d (6.4)	0.00
0.87, d (6.5)	0.87, d (6.4)	0.00

^{13}C-NMR comparison of compound **20** (Rotamer B) with reported values

Yue's Isolated Sample (125 MHz, $CDCl_3$)	**Our Synthetic Sample (101 MHz, $CDCl_3$)**	**Δ/ppm**
42.7	42.8	0.1
38.0	38.0	0.0
77.1	77.0	0.1
45.5	45.5	0.0
44.6	44.6	0.0
101.3	101.3	0.0
37.7	37.7	0.0
60.4	60.4	0.0
165.2	165.1	0.1
118.3	118.3	0.0
142.4	142.4	0.0
135.4	135.3	0.1
128.2	128.2	0.0
128.9	128.9	0.0
129.8	129.8	0.0
82.6	82.5	0.1
35.0	34.9	0.1
26.6	26.6	0.0
46.6	46.6	0.0
24.1	24.1	0.0
42.3	42.3	0.0
25.0	25.0	0.0
33.0	33.0	0.0
21.0	20.9	0.1
21.1	21.1	0.0

2. Crystallographic data

Crystal Data for **9b** ($C_{18}H_{24}O_4$)

```
Bond precision:   C-C = 0.0030 A          Wavelength=1.54184

Cell:            a=10.29909(12)     b=10.79136(13)     c=27.3078(3)
                 alpha=90           beta=90            gamma=90
Temperature:     100 K

                 Calculated                 Reported
Volume           3035.02(6)                 3035.02(6)
Space group      P 21 21 21                 P 21 21 21
Hall group       P 2ac 2ab                  P 2ac 2ab
Moiety formula   C18 H24 O4                 C18 H24 O4
Sum formula      C18 H24 O4                 C18 H24 O4
Mr               304.37                     304.37
Dx,g cm-3        1.332                      1.332
Z                8                          8
Mu (mm-1)        0.751                      0.751
F000             1312.0                     1312.0
F000'            1316.04
h,k,lmax         13,13,34                   12,13,33
Nref             6417[ 3623]                6230
Tmin,Tmax        0.861,0.874                0.920,1.000
Tmin'            0.861

Correction method= # Reported T Limits: Tmin=0.920 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.97        Theta(max)= 77.064

R(reflections)= 0.0344( 5743)                wR2(reflections)=
                                             0.0869( 6230)
S = 1.043                  Npar= 403
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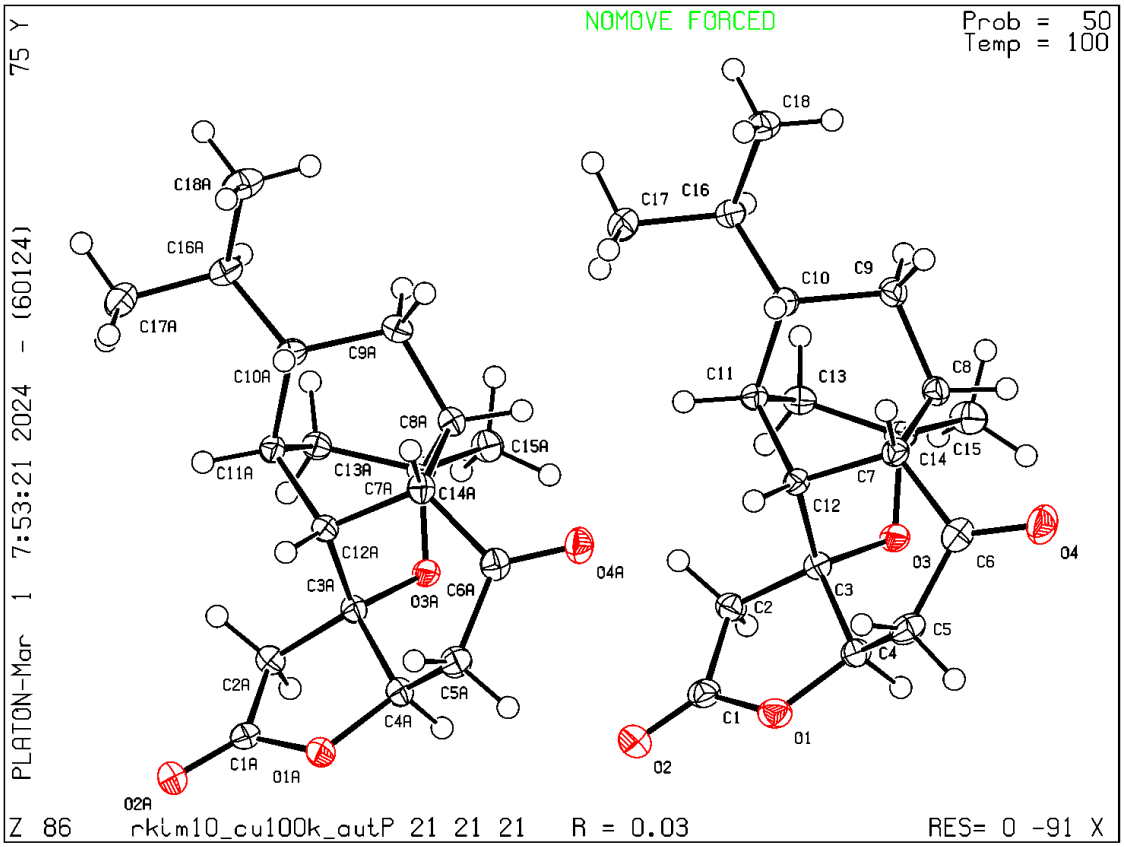

NOMOVE FORCED
Prob = 50
Temp = 100
PLATON-Mar 1 7:53:21 2024 - (60124)
75 Y
Z 86
rklm10_cu100k_autP 21 21 21
R = 0.03
RES= 0 -91 X
C18A
C16A
C17A
C10A
C9A
C8A
C15A
C11A
C13A
C7A
C14A
C12A
C3A
O3A
C6A
O4A
C2A
C5A
C4A
C1A
O1A
O2A
C18
C17
C16
C10
C9
C11
C13
C8
C7
C14
C15
C12
O3
C6
O4
C3
C2
C5
C4
C1
O1
O2

3. References

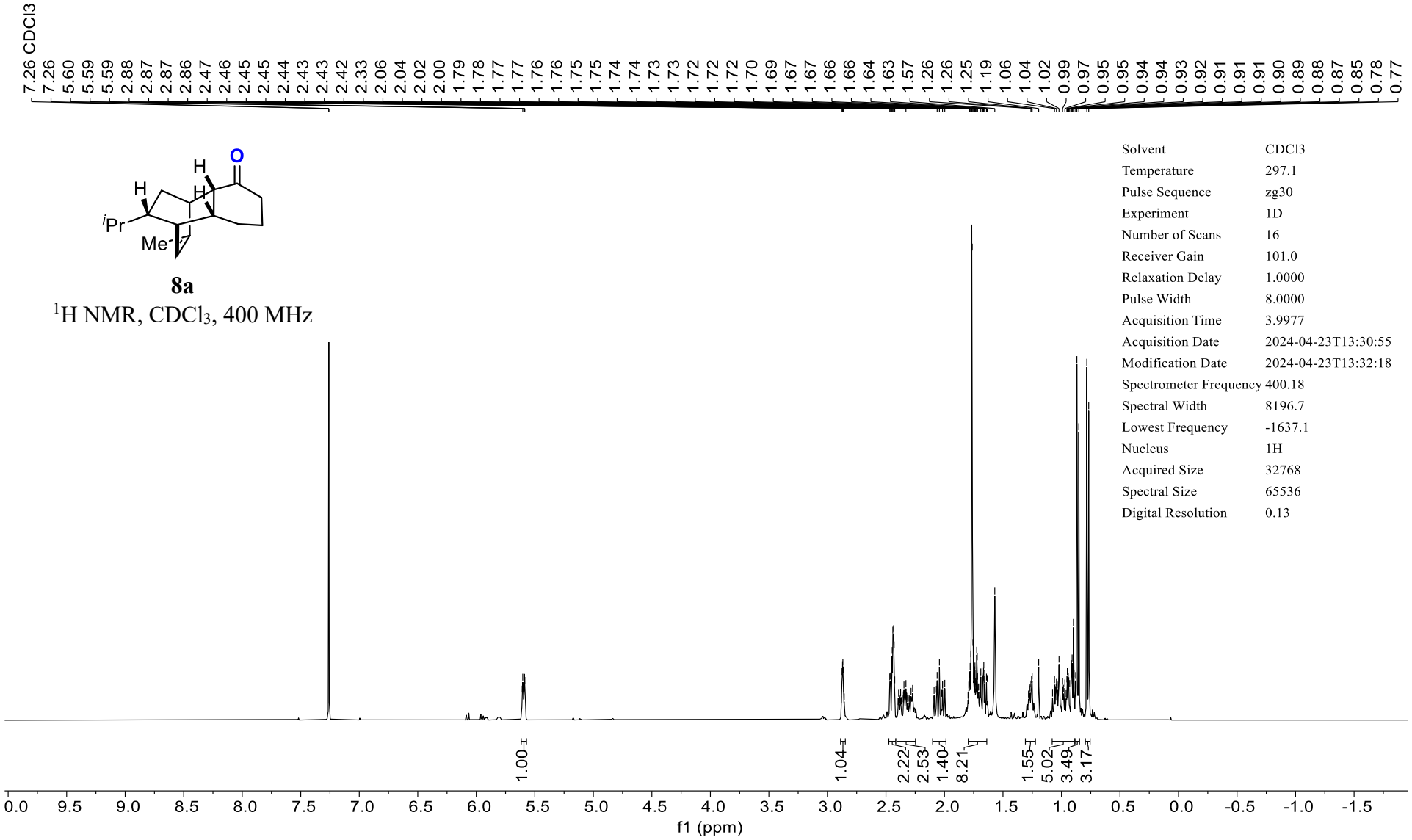
[1] a) F. Fringuelli, M. Guo, L. Minuti, F. Pizzo, A. Taticchi, E. Wenkert, *J. Org. Chem.* 1989, **54**, 710-712; b) R. K. Schmidt, K. Müther, C. Mück-Lichtenfeld, S. Grimme, M. Oestreich, *J. Am. Chem. Soc.* 2012, **134**, 4421-4428; c) R. A. Valiulin, T. M. Arisco, A. G. Kutateladze, *Org. Lett.* 2010, **12**, 3398-3401.

[2] S. J. Miller, H. Ishitani, Y. Furiya, S. Kobayashi, *Org. Proc. Res. Dev.* 2021, **25**, 192-198.

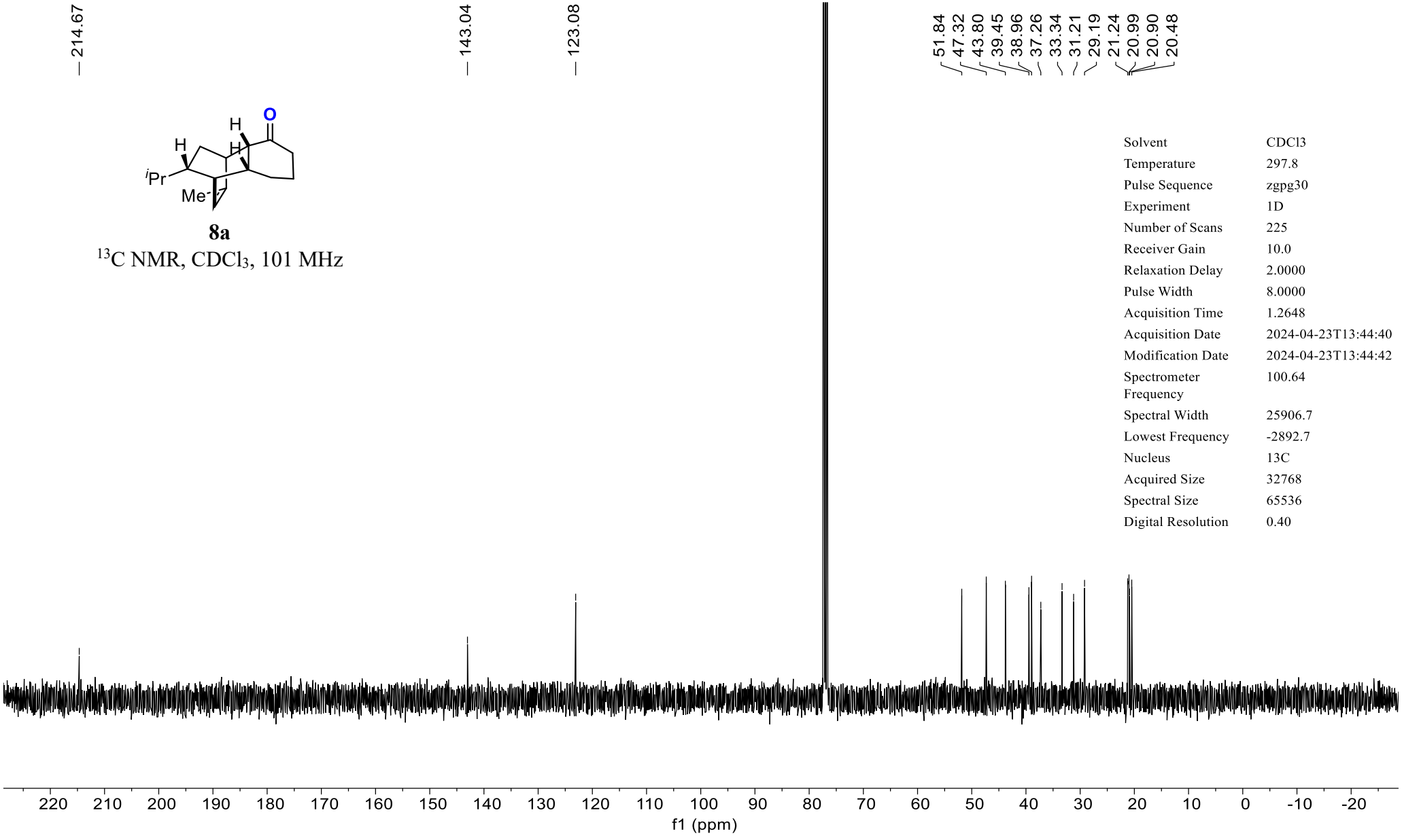
[3] B. Zhou, Q. Gong, Y. Fu, J.-S. Zhou, H.-Y. Zhang, J.-M. Yue, *Org. Lett.* 2023, **25**, 1464-1469.

4. ^{1}H and ^{13}C NMR Spectra

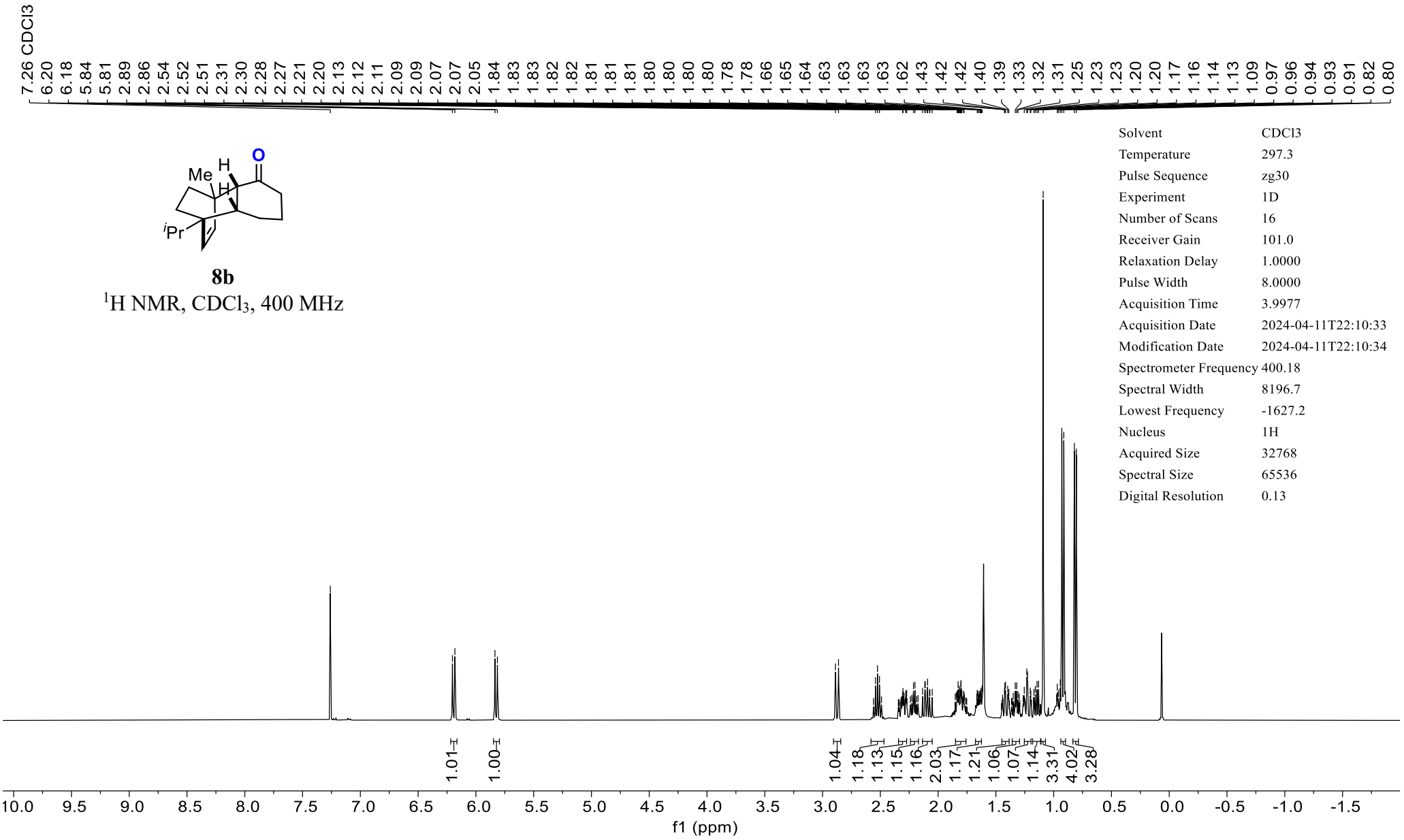
^{1}H NMR of **8a**



^{13}C NMR of **8a**


214.67
143.04
123.08
51.84
47.32
43.80
39.45
38.96
37.26
33.34
31.21
29.19
21.24
20.99
20.90
20.48
H
O
H
H
iPr
Me
H
8a
13C NMR, CDCl3, 101 MHz
Solvent CDCl3
Temperature 297.8
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 225
Receiver Gain 10.0
Relaxation Delay 2.0000
Pulse Width 8.0000
Acquisition Time 1.2648
Acquisition Date 2024-04-23T13:44:40
Modification Date 2024-04-23T13:44:42
Spectrometer Frequency 100.64
Spectral Width 25906.7
Lowest Frequency -2892.7
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

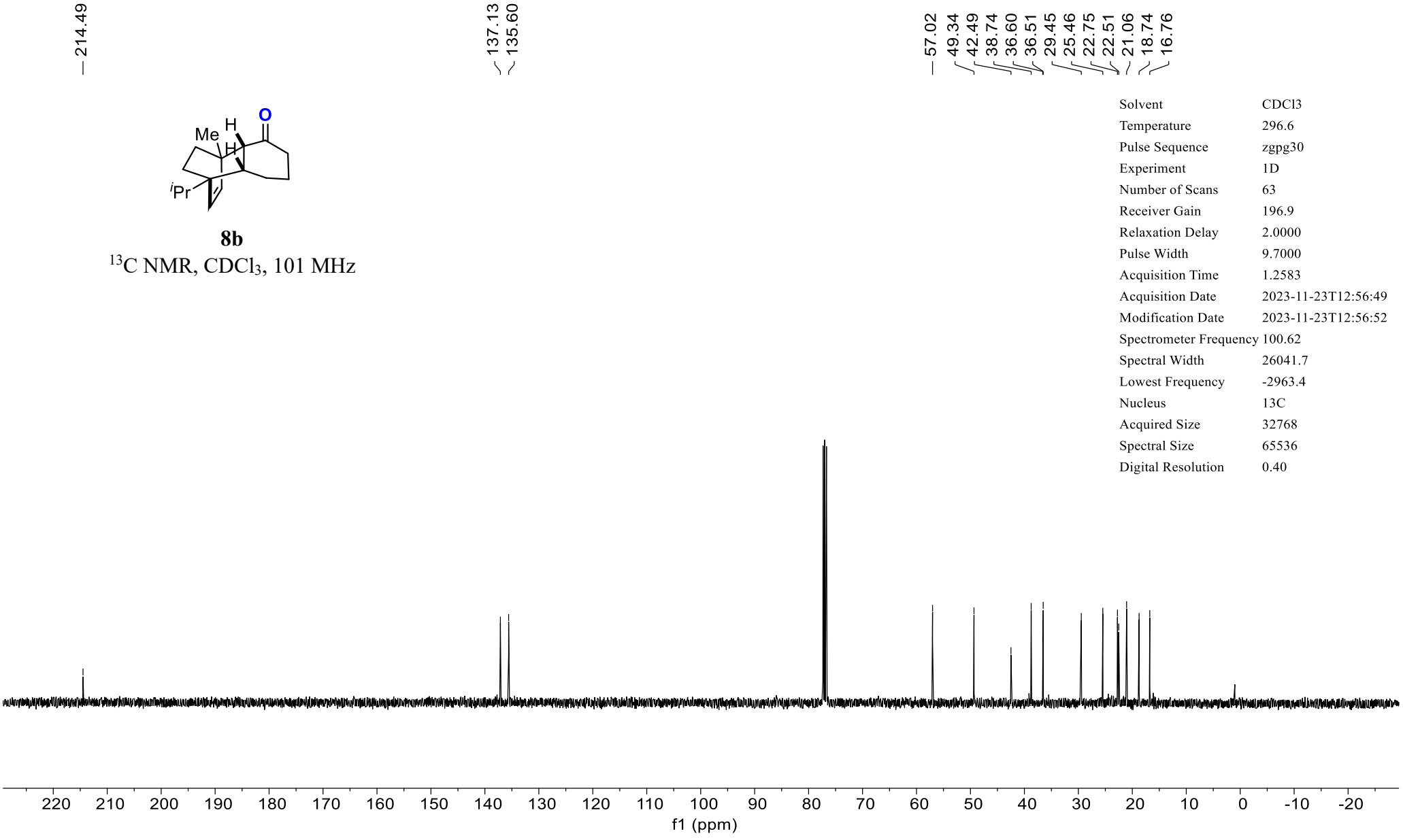
^{1}H NMR of **8b**



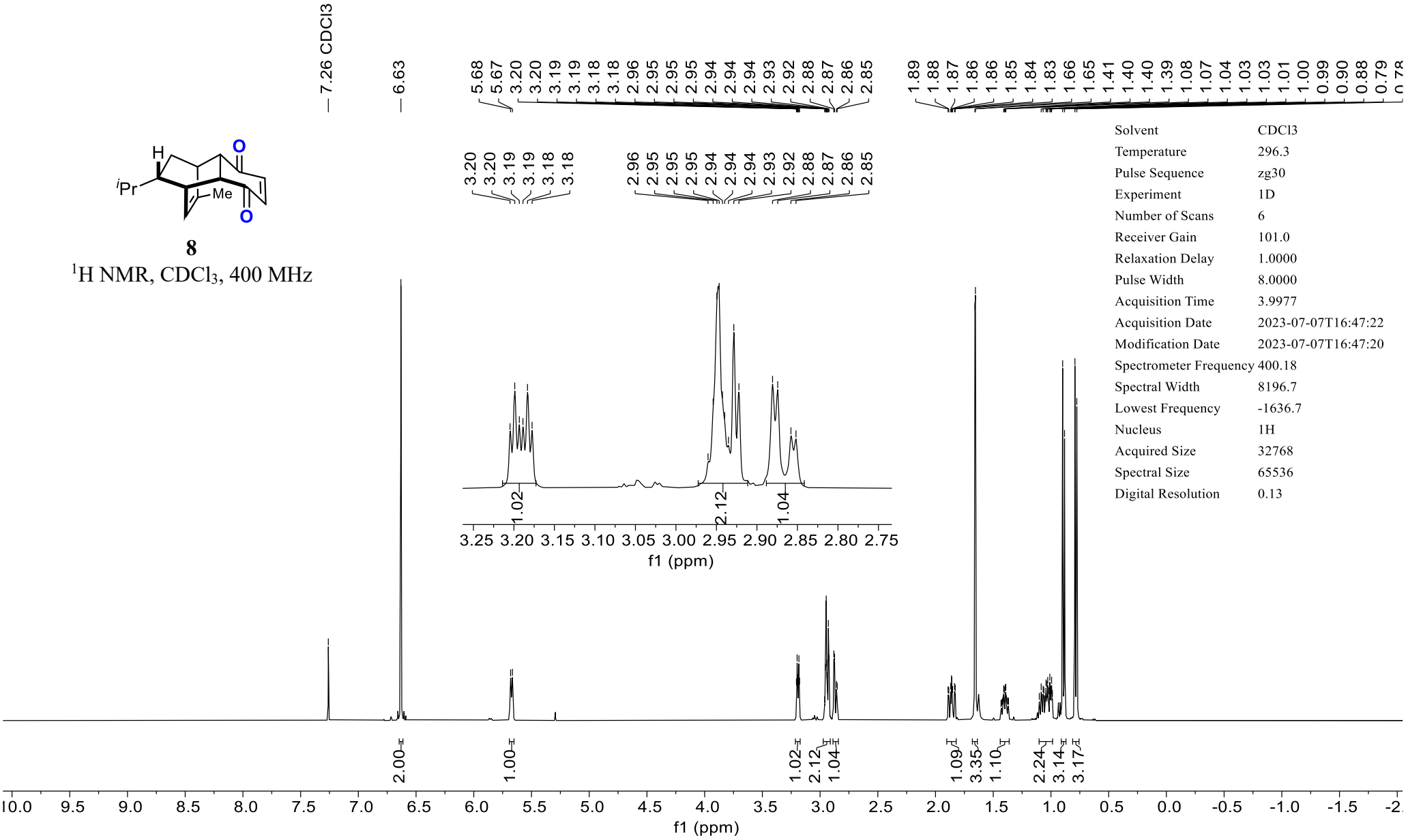
8b

^{1}H NMR, $CDCl_3$, 400 MHz

^{13}C NMR of **8b**


214.49
137.13
135.60
57.02
49.34
42.49
38.74
36.60
36.51
29.45
25.46
22.75
22.51
21.06
18.74
16.76
Me
H
H
O
iPr
8b
13C NMR, CDCl3, 101 MHz
Solvent CDCl3
Temperature 296.6
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 63
Receiver Gain 196.9
Relaxation Delay 2.0000
Pulse Width 9.7000
Acquisition Time 1.2583
Acquisition Date 2023-11-23T12:56:49
Modification Date 2023-11-23T12:56:52
Spectrometer Frequency 100.62
Spectral Width 26041.7
Lowest Frequency -2963.4
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

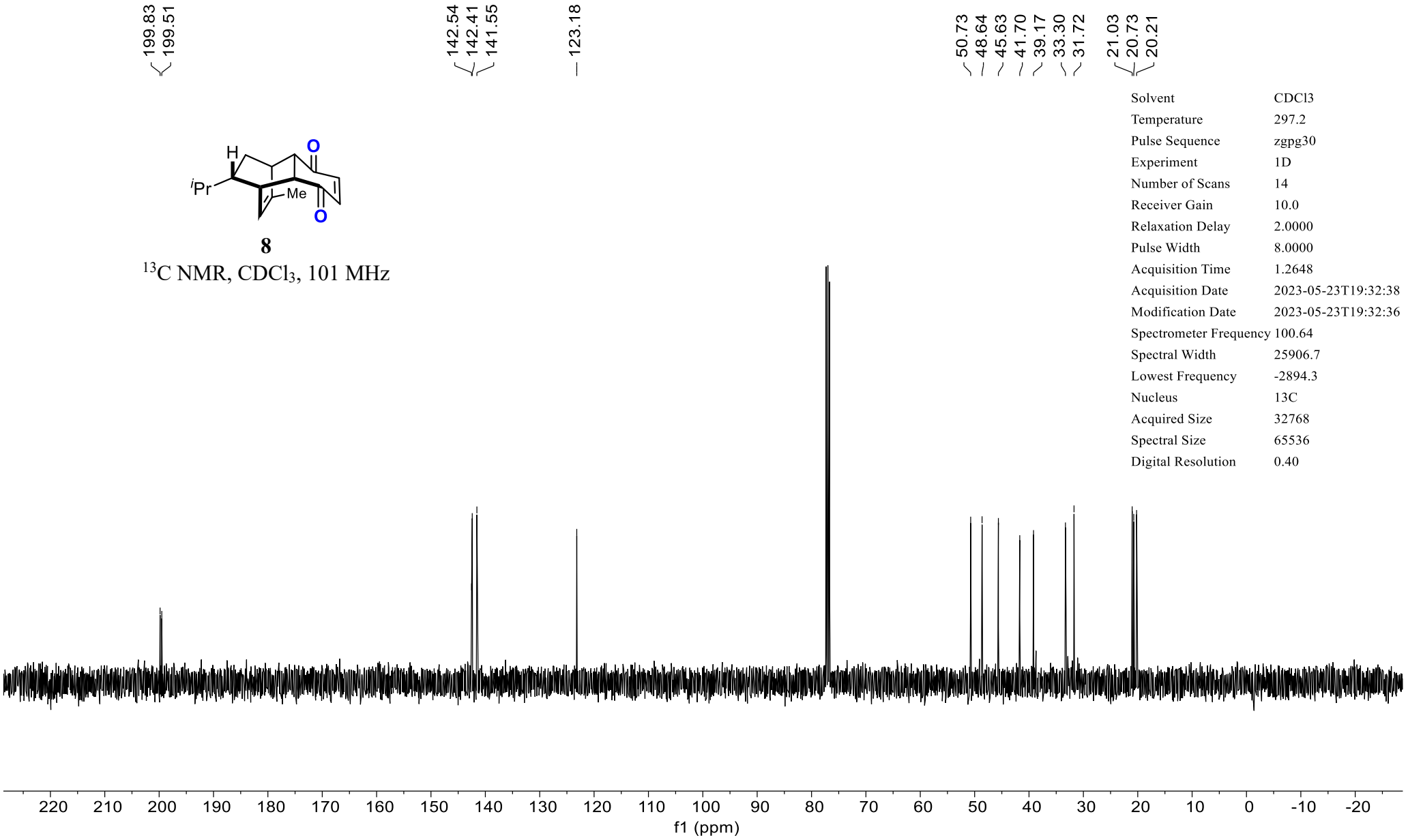
^{1}H NMR of **8**



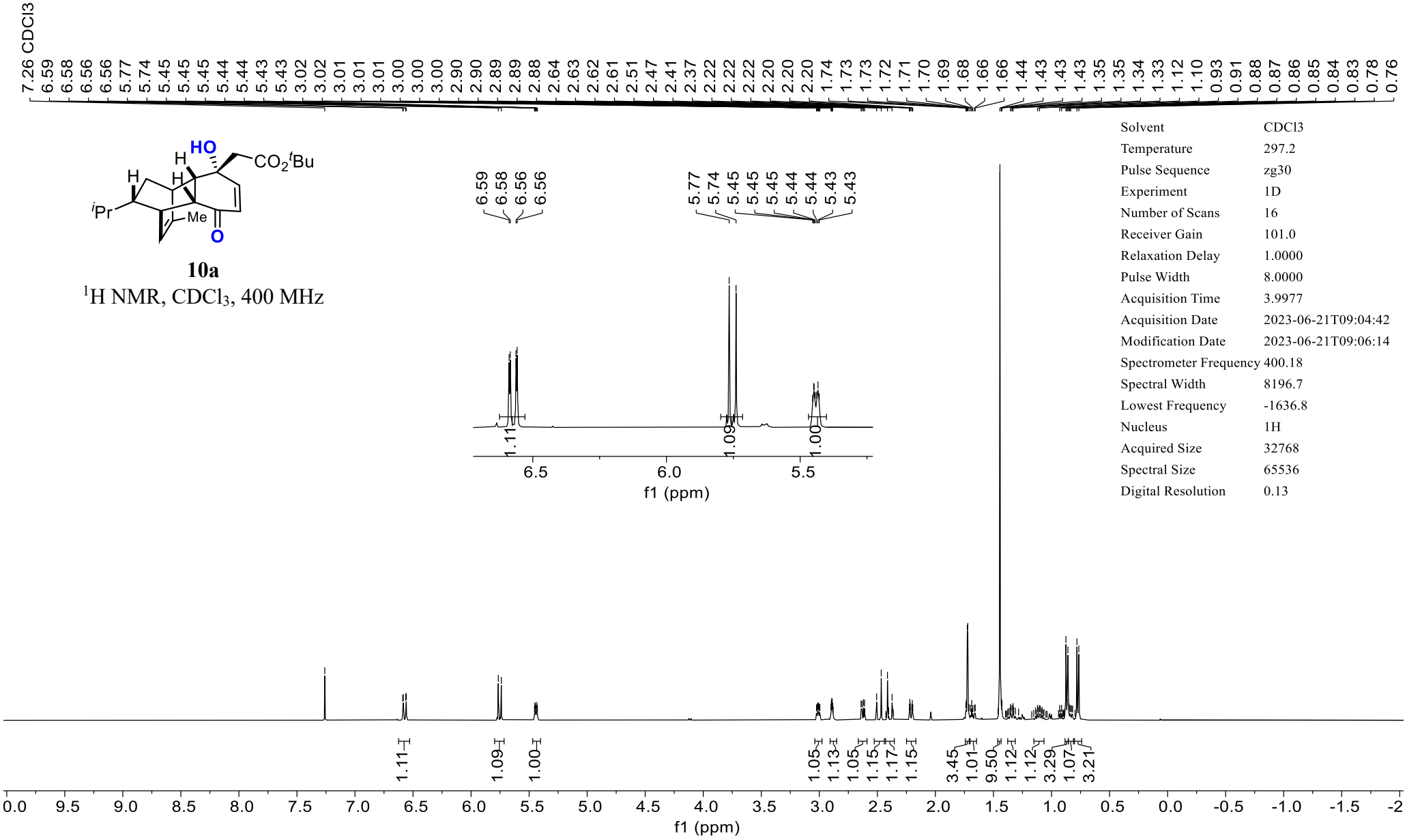
8

^{1}H NMR, $CDCl_3$, 400 MHz

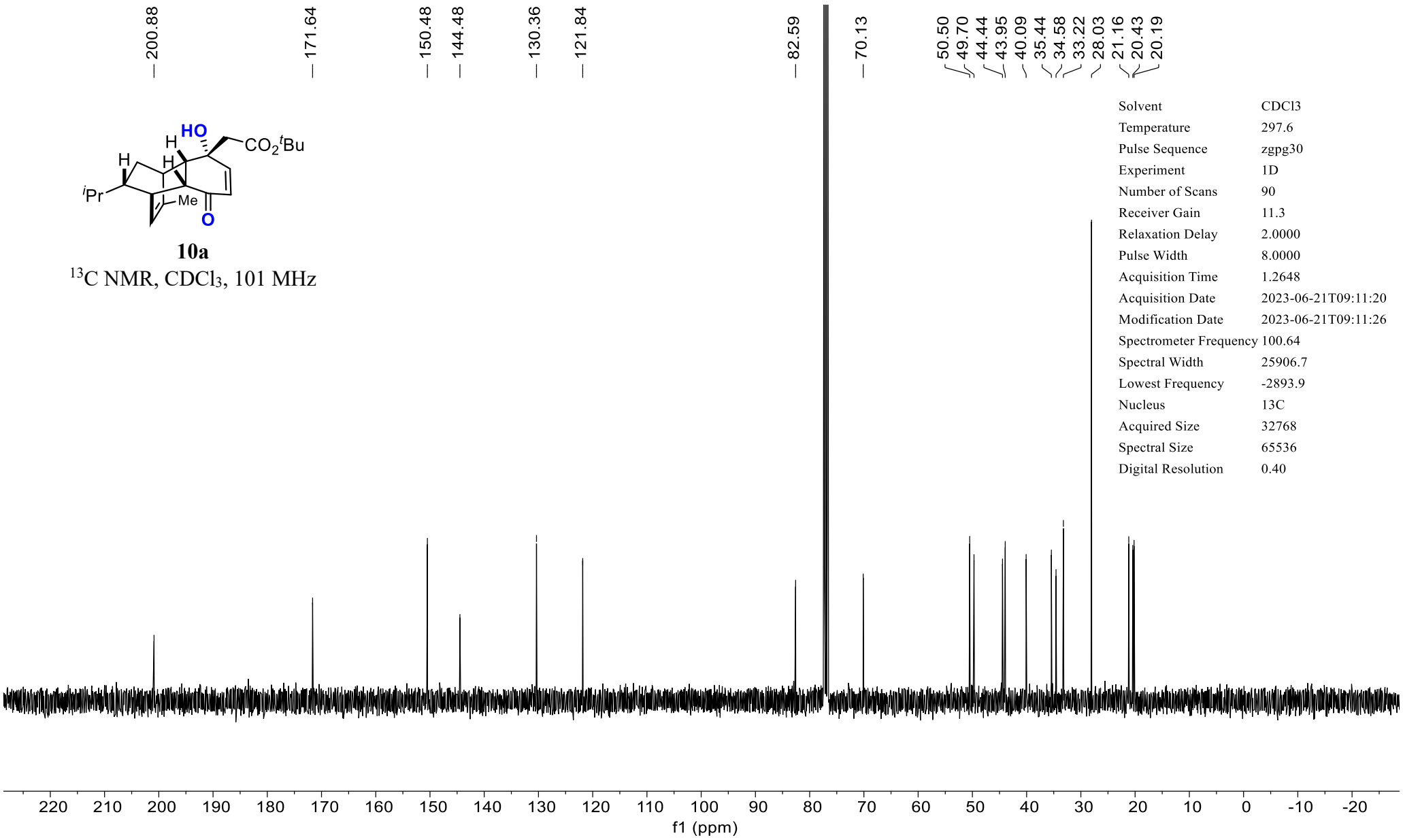
^{13}C NMR of **8**


199.83
199.51
142.54
142.41
141.55
123.18
50.73
48.64
45.63
41.70
39.17
33.30
31.72
21.03
20.73
20.21
H
O
iPr
Me
O
8
13C NMR, CDCl3, 101 MHz
Solvent CDCl3
Temperature 297.2
Pulse Sequence zgpg30
Experiment 1D
Number of Scans 14
Receiver Gain 10.0
Relaxation Delay 2.0000
Pulse Width 8.0000
Acquisition Time 1.2648
Acquisition Date 2023-05-23T19:32:38
Modification Date 2023-05-23T19:32:36
Spectrometer Frequency 100.64
Spectral Width 25906.7
Lowest Frequency -2894.3
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.40
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{1}H NMR of **10a**


7.26 CDCl3
6.59 6.58 6.56 6.56 5.77 5.74 5.45 5.45 5.45 5.44 5.44 5.43 5.43 3.02 3.02 3.01 3.01 3.01 3.00 3.00 3.00 2.90 2.90 2.89 2.89 2.88 2.64 2.63 2.62 2.61 2.51 2.47 2.41 2.37 2.22 2.22 2.22 2.20 2.20 2.20 1.74 1.73 1.73 1.72 1.71 1.70 1.69 1.68 1.66 1.66 1.44 1.43 1.43 1.43 1.35 1.35 1.34 1.33 1.12 1.10 0.93 0.91 0.88 0.87 0.86 0.85 0.84 0.83 0.78 0.76
HO
H
H
H
CO2tBu
iPr
Me
O
10a
1H NMR, CDCl3, 400 MHz
6.59 6.58 6.56 6.56
5.77 5.74 5.45 5.45 5.45 5.44 5.44 5.43 5.43
1.11 1.09 1.00
6.5 6.0 5.5
f1 (ppm)
Solvent CDCl3
Temperature 297.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-21T09:04:42
Modification Date 2023-06-21T09:06:14
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.8
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
1.11 1.09 1.00 1.05 1.13 1.05 1.15 1.17 1.15 3.45 1.01 9.50 1.12 1.12 3.29 1.07 3.21
0.0 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 -1.5 -2
f1 (ppm)

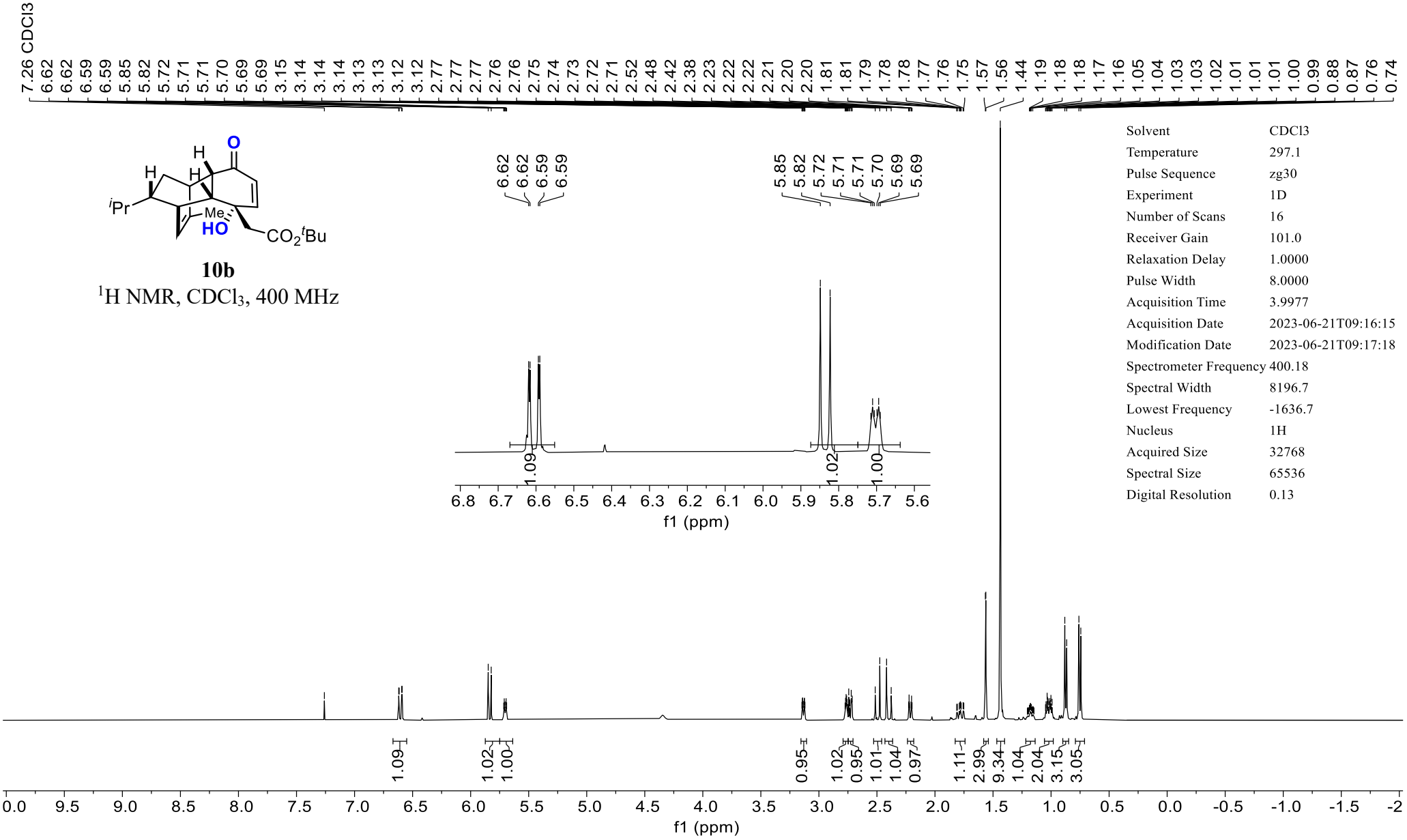
^{13}C NMR of **10a**



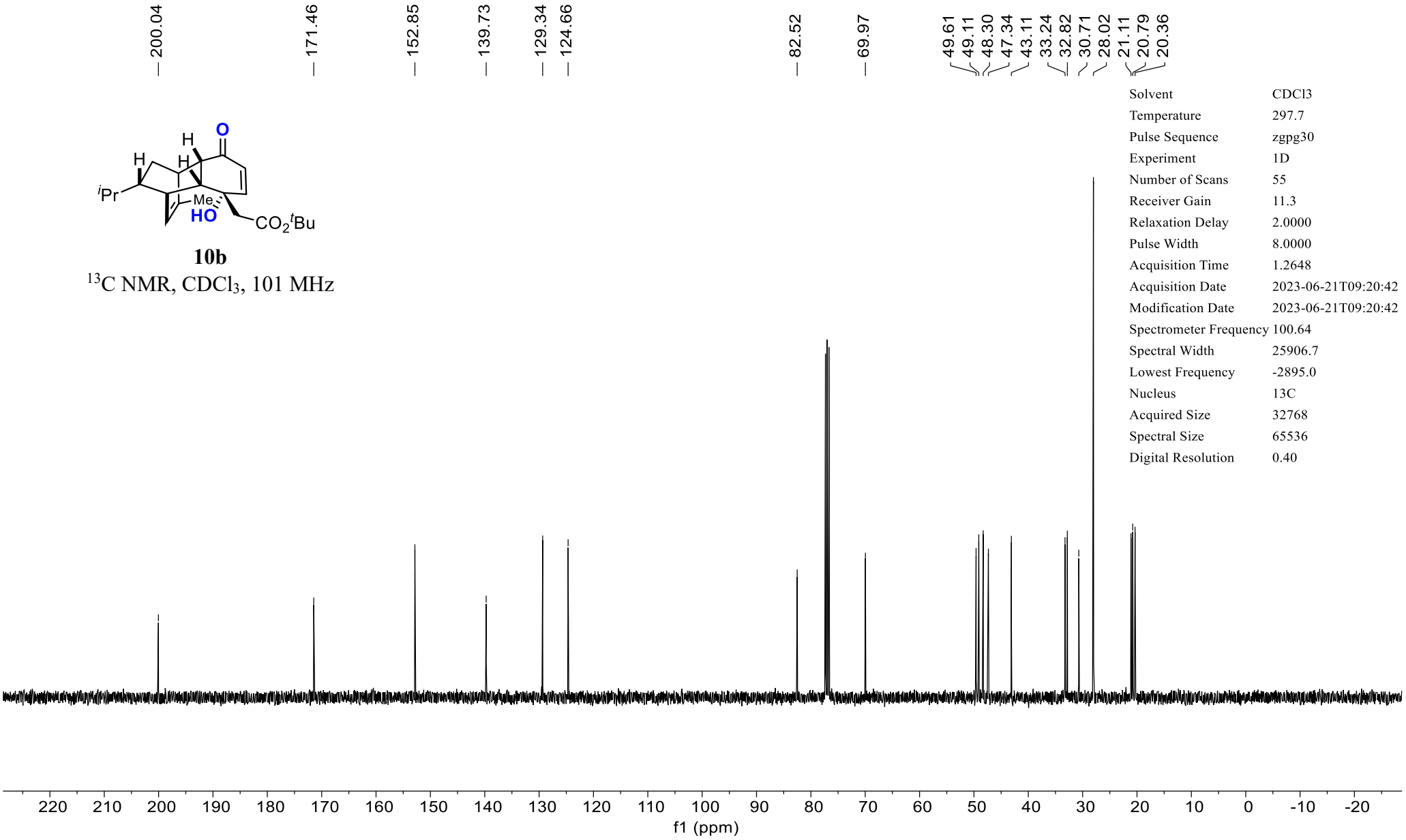
10a

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **10b**


7.26 CDCl3
6.62 6.62 6.59 6.59 5.85 5.82 5.72 5.71 5.71 5.70 5.69 5.69 3.15 3.14 3.14 3.14 3.13 3.13 3.12 3.12 2.77 2.77 2.77 2.76 2.76 2.75 2.74 2.73 2.72 2.71 2.52 2.48 2.42 2.38 2.23 2.22 2.22 2.21 2.20 2.20 1.81 1.81 1.79 1.78 1.78 1.77 1.76 1.75 1.57 1.56 1.44 1.19 1.18 1.18 1.17 1.16 1.05 1.04 1.03 1.03 1.02 1.01 1.01 1.01 1.00 0.99 0.88 0.87 0.76 0.74
O
H
H
H
iPr
Me
HO
CO2tBu
10b
1H NMR, CDCl3, 400 MHz
6.62 6.62 6.59 6.59
5.85 5.82 5.72 5.71 5.71 5.70 5.69 5.69
1.09 1.02 1.00
6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6
f1 (ppm)
Solvent CDCl3
Temperature 297.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-21T09:16:15
Modification Date 2023-06-21T09:17:18
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.7
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
1.09 1.02 1.00 0.95 1.02 0.95 1.01 1.04 0.97 1.11 2.99 9.34 1.04 2.04 3.15 3.05
0.0 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 -1.5 -2
f1 (ppm)

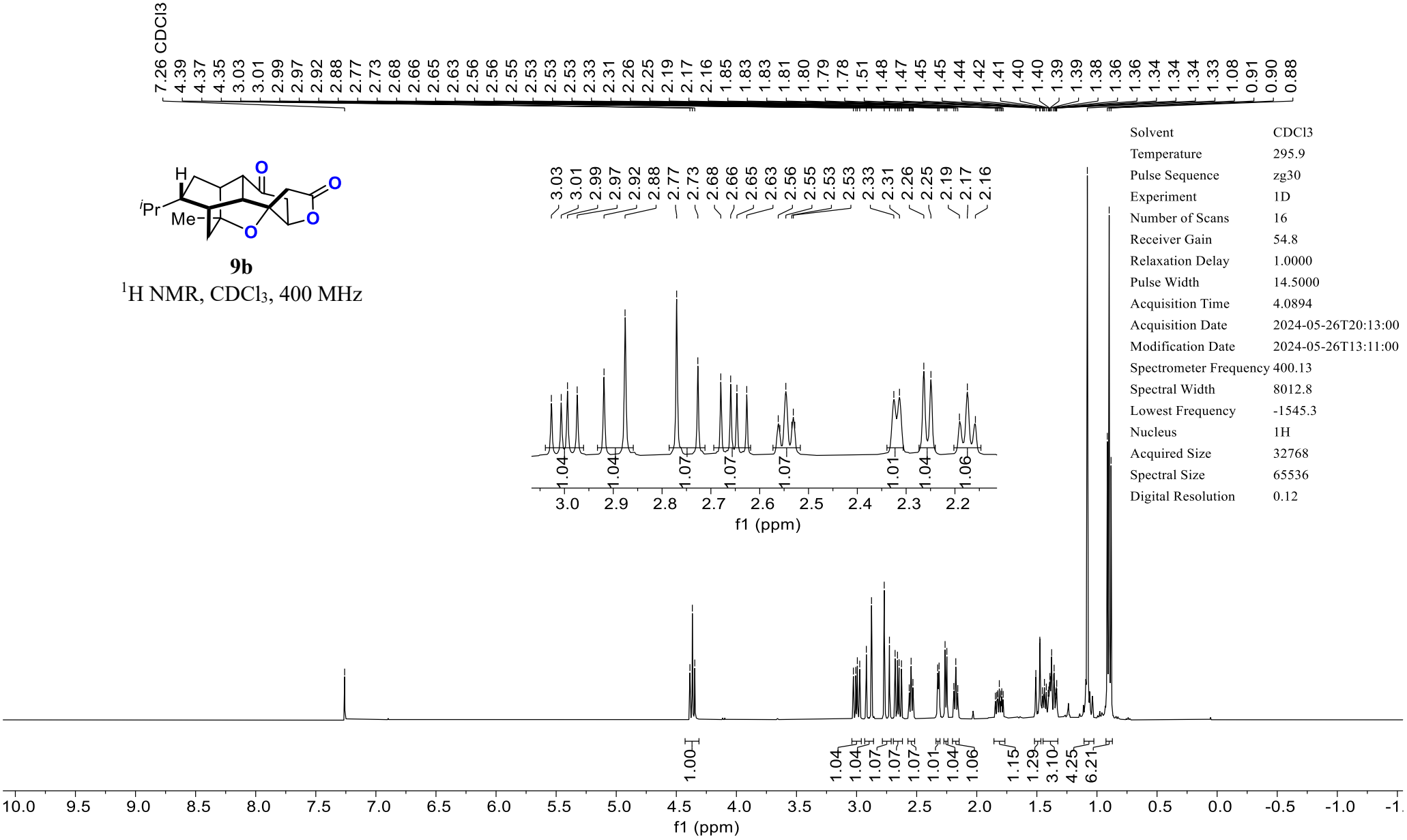
^{13}C NMR of **10b**



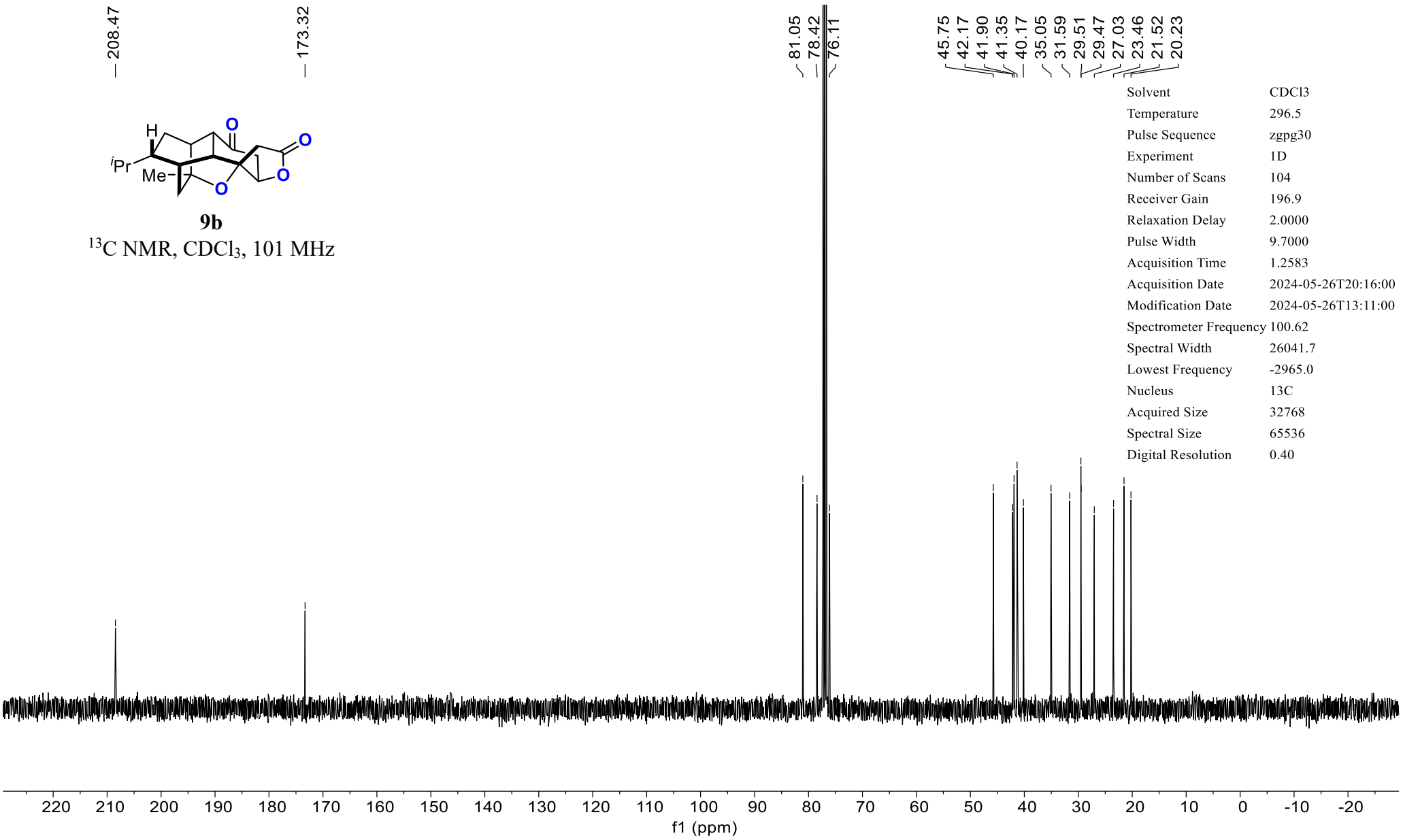
10b

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **9b**


7.26 CDCl3
4.39 4.37 4.35 4.03 3.01 2.99 2.97 2.92 2.88 2.77 2.73 2.68 2.66 2.65 2.63 2.56 2.56 2.55 2.53 2.53 2.53 2.33 2.31 2.26 2.25 2.19 2.17 2.16 1.85 1.83 1.83 1.81 1.80 1.79 1.78 1.51 1.48 1.47 1.45 1.45 1.44 1.42 1.41 1.40 1.40 1.39 1.39 1.38 1.36 1.36 1.34 1.34 1.34 1.33 1.08 0.91 0.90 0.88
H
O
O
O
O
iPr
Me
9b
1H NMR, CDCl3, 400 MHz
3.03 3.01 2.99 2.97 2.92 2.88 2.77 2.73 2.68 2.66 2.65 2.63 2.56 2.55 2.53 2.53 2.33 2.31 2.26 2.25 2.19 2.17 2.16
1.04 1.04 1.07 1.07 1.07 1.01 1.04 1.06
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2
f1 (ppm)
Solvent CDCl3
Temperature 295.9
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 54.8
Relaxation Delay 1.0000
Pulse Width 14.5000
Acquisition Time 4.0894
Acquisition Date 2024-05-26T20:13:00
Modification Date 2024-05-26T13:11:00
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.3
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.12
1.00 1.04 1.04 1.07 1.07 1.07 1.01 1.04 1.06 1.15 1.29 3.10 4.25 6.21
10.0 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)

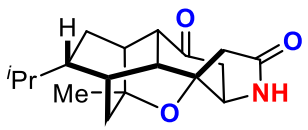
^{13}C NMR of **9b**



9b

^{13}C NMR, $CDCl_3$, 101 MHz

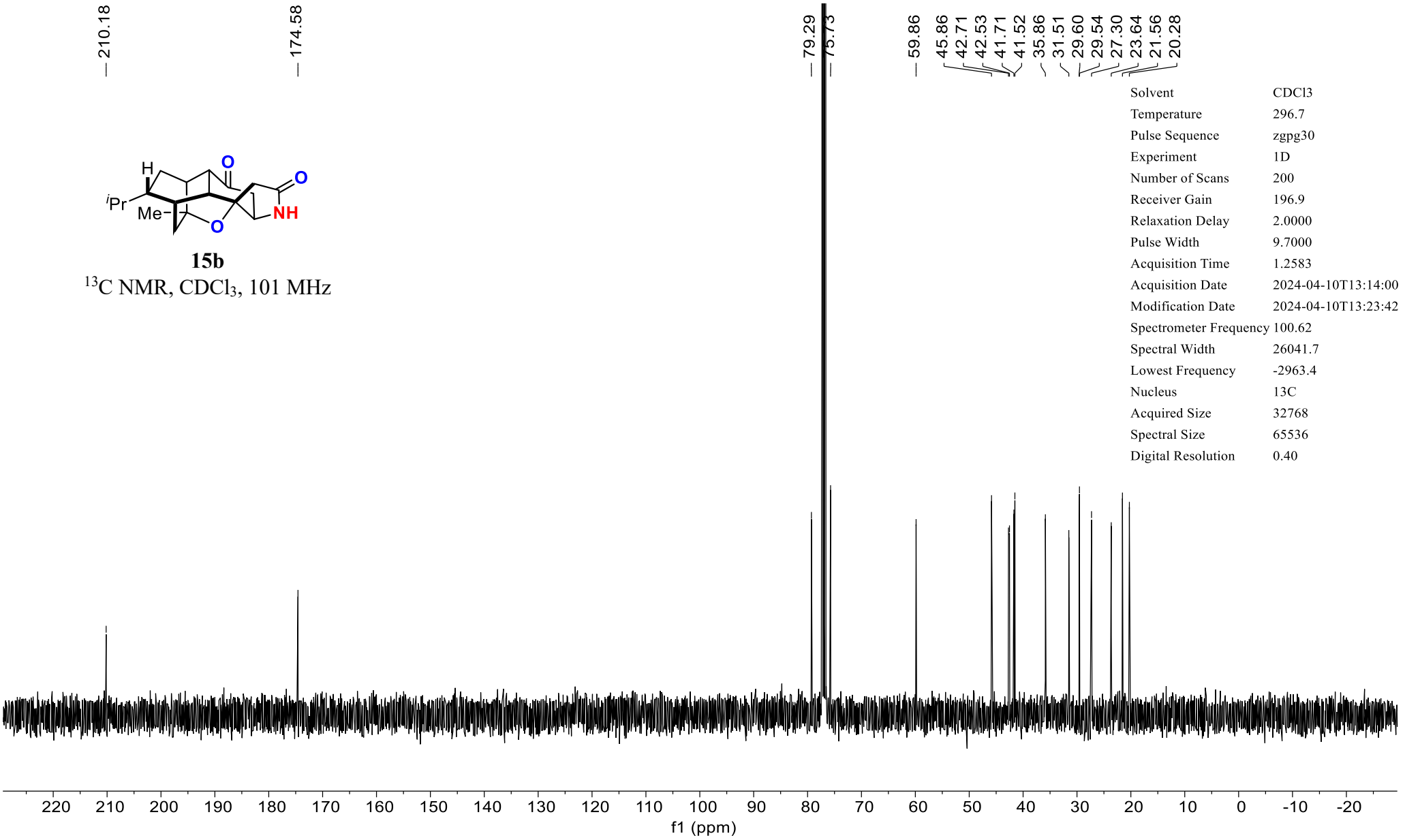
^{1}H NMR of **15b**



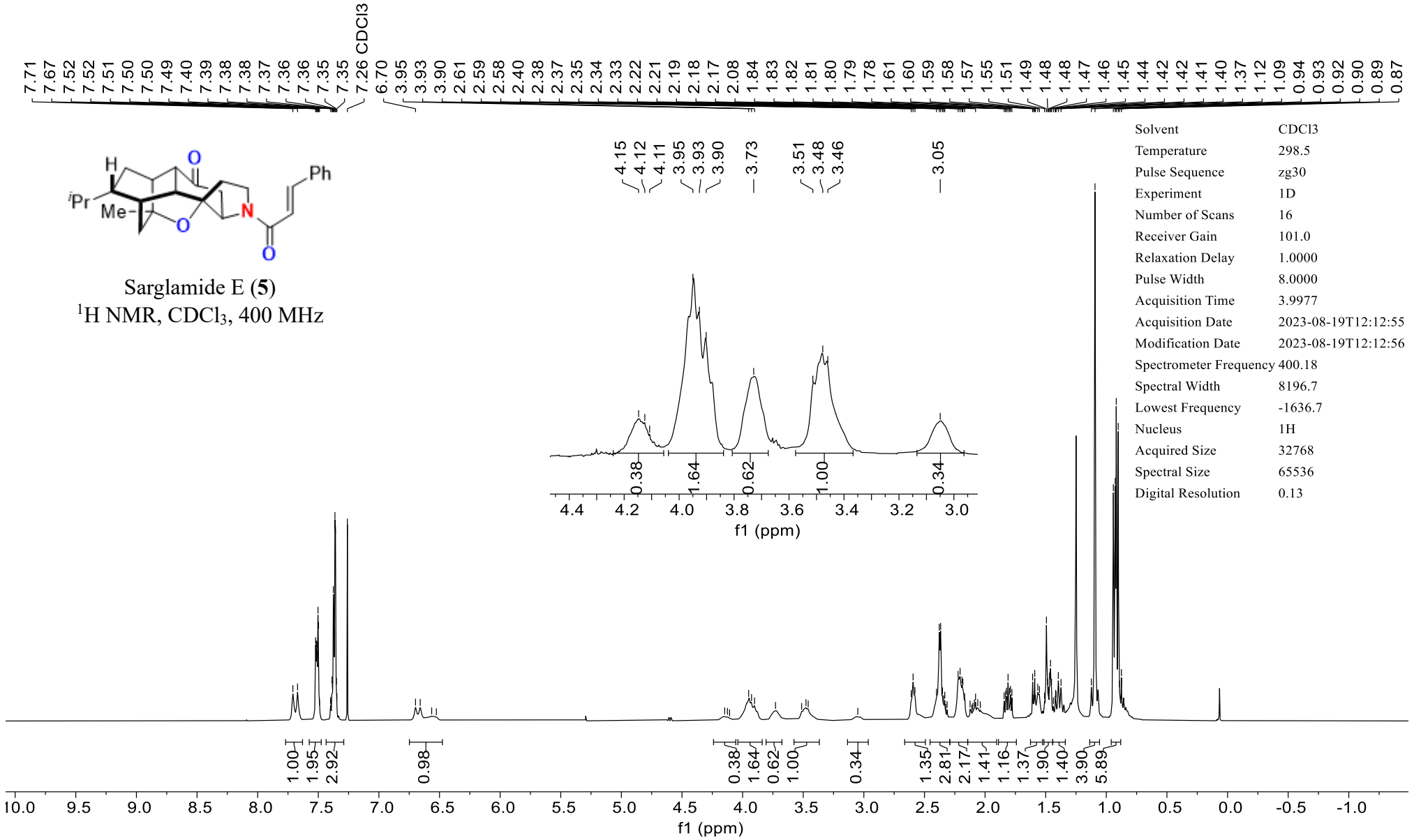
15b

^{1}H NMR, $CDCl_3$, 400 MHz

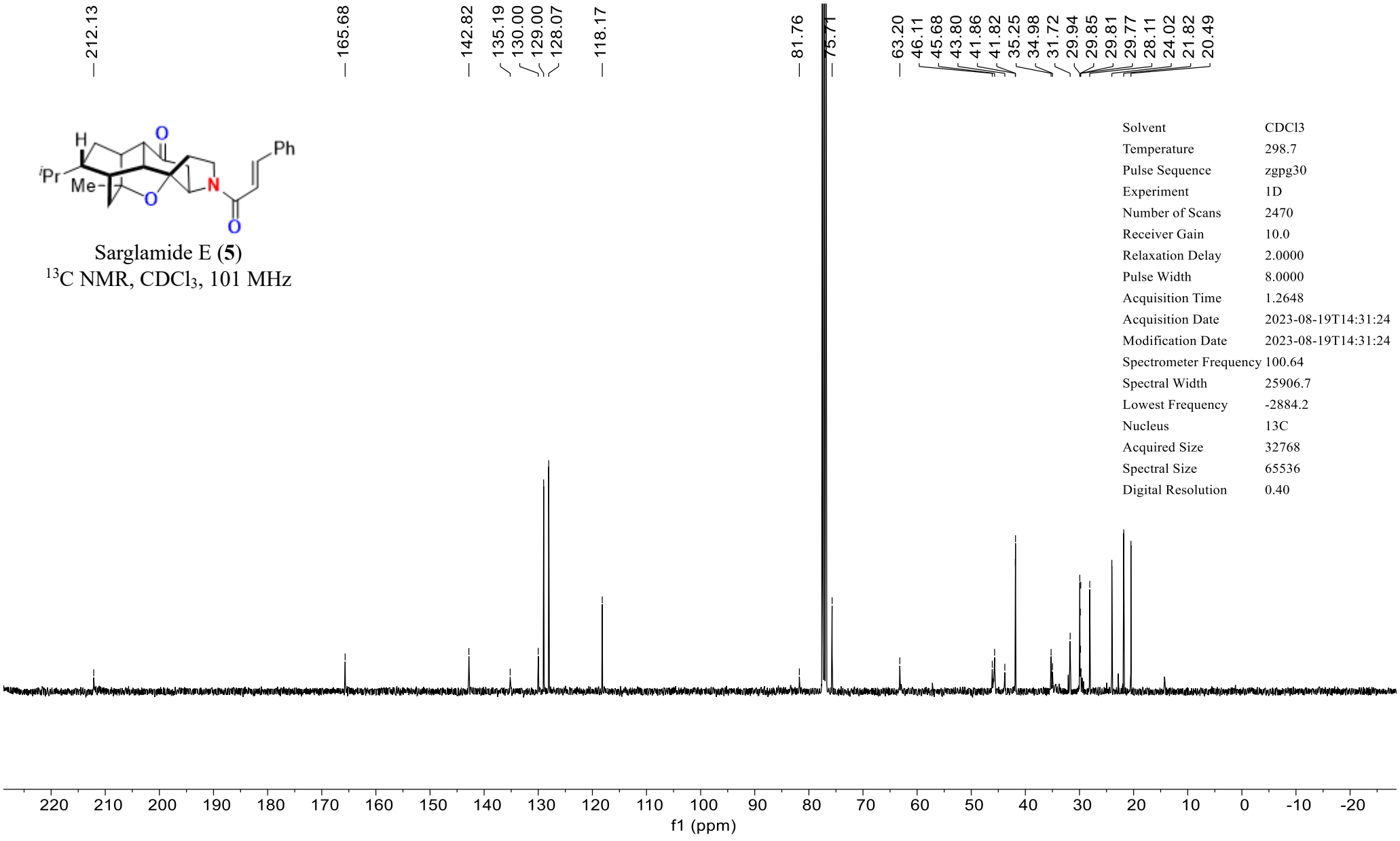
^{13}C NMR of **15b**



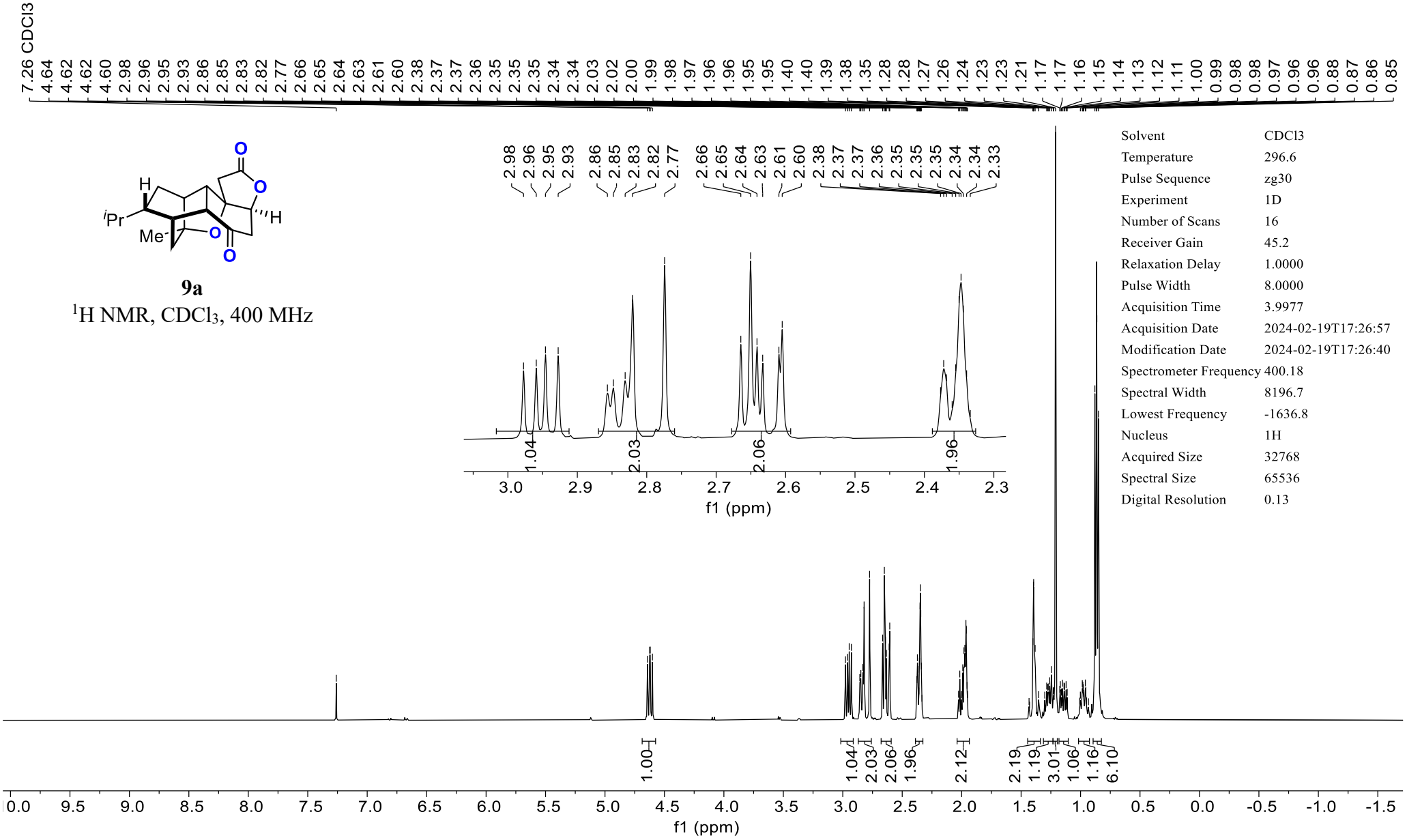
[1]H NMR of Sarglamide E (**5**)



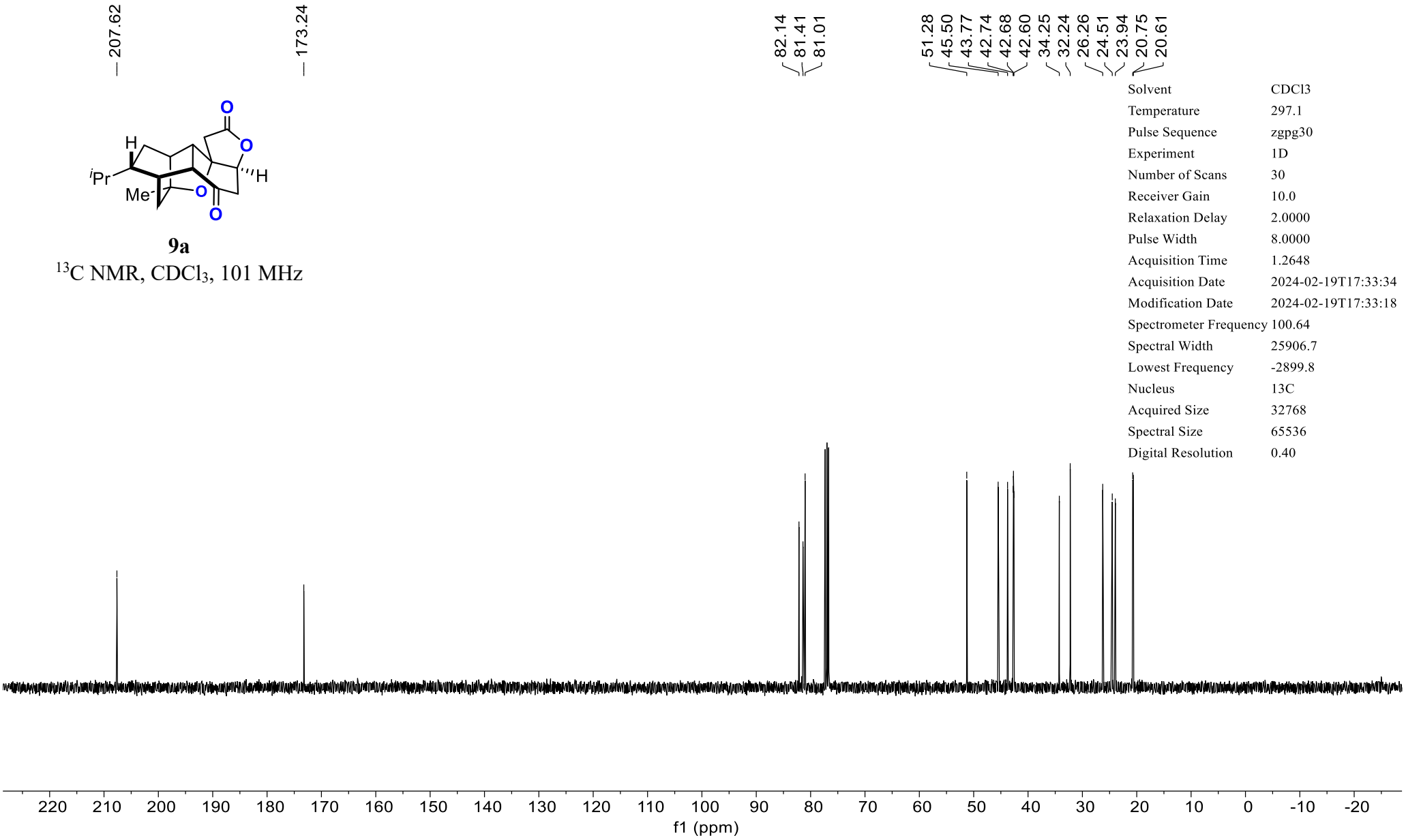
^{13}C NMR of Sarglamide E (**5**)



^{1}H NMR of **9a**


7.26 CDCl3
4.64 4.62 4.62 4.60 2.98 2.96 2.95 2.93 2.86 2.85 2.83 2.82 2.77 2.66 2.65 2.64 2.63 2.61 2.60 2.38 2.37 2.37 2.36 2.35 2.35 2.35 2.34 2.34 2.03 2.02 2.00 1.99 1.98 1.97 1.96 1.96 1.95 1.95 1.40 1.40 1.39 1.38 1.35 1.28 1.28 1.27 1.26 1.24 1.23 1.23 1.21 1.17 1.17 1.16 1.15 1.14 1.13 1.12 1.11 1.00 0.99 0.98 0.98 0.97 0.96 0.96 0.88 0.87 0.86 0.85
H
iPr
Me
O
O
O
O
H
9a
1H NMR, CDCl3, 400 MHz
2.98 2.96 2.95 2.93 2.86 2.85 2.83 2.82 2.77 2.66 2.65 2.64 2.63 2.61 2.60 2.38 2.37 2.37 2.36 2.35 2.35 2.35 2.34 2.34 2.33
1.04 2.03 2.06 1.96
3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3
f1 (ppm)
Solvent CDCl3
Temperature 296.6
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 45.2
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2024-02-19T17:26:57
Modification Date 2024-02-19T17:26:40
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.8
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
1.00 1.04 2.03 2.06 1.96 2.12 2.19 1.19 3.01 1.06 1.16 6.10
0.0 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 -1.5
f1 (ppm)

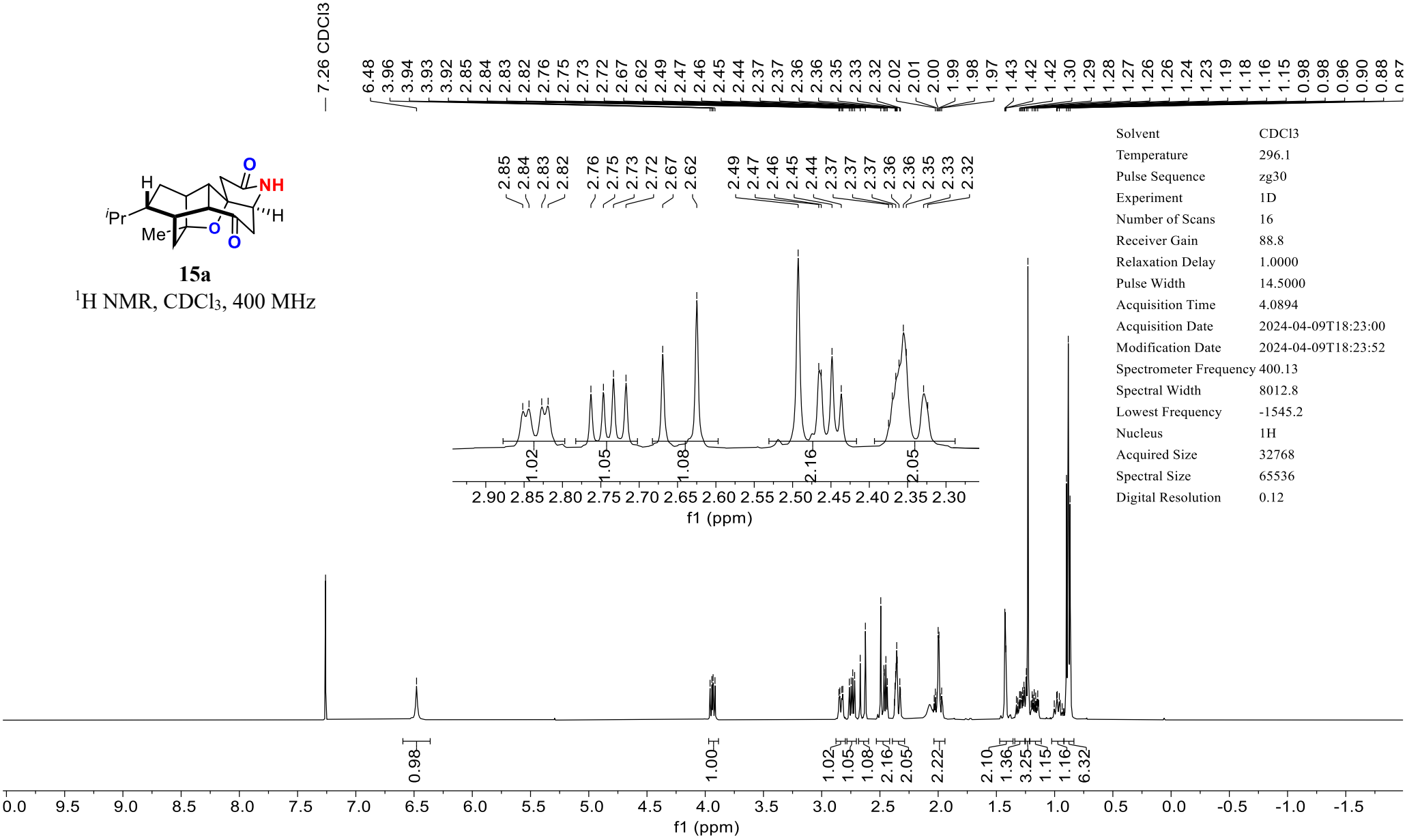
^{13}C NMR of **9a**



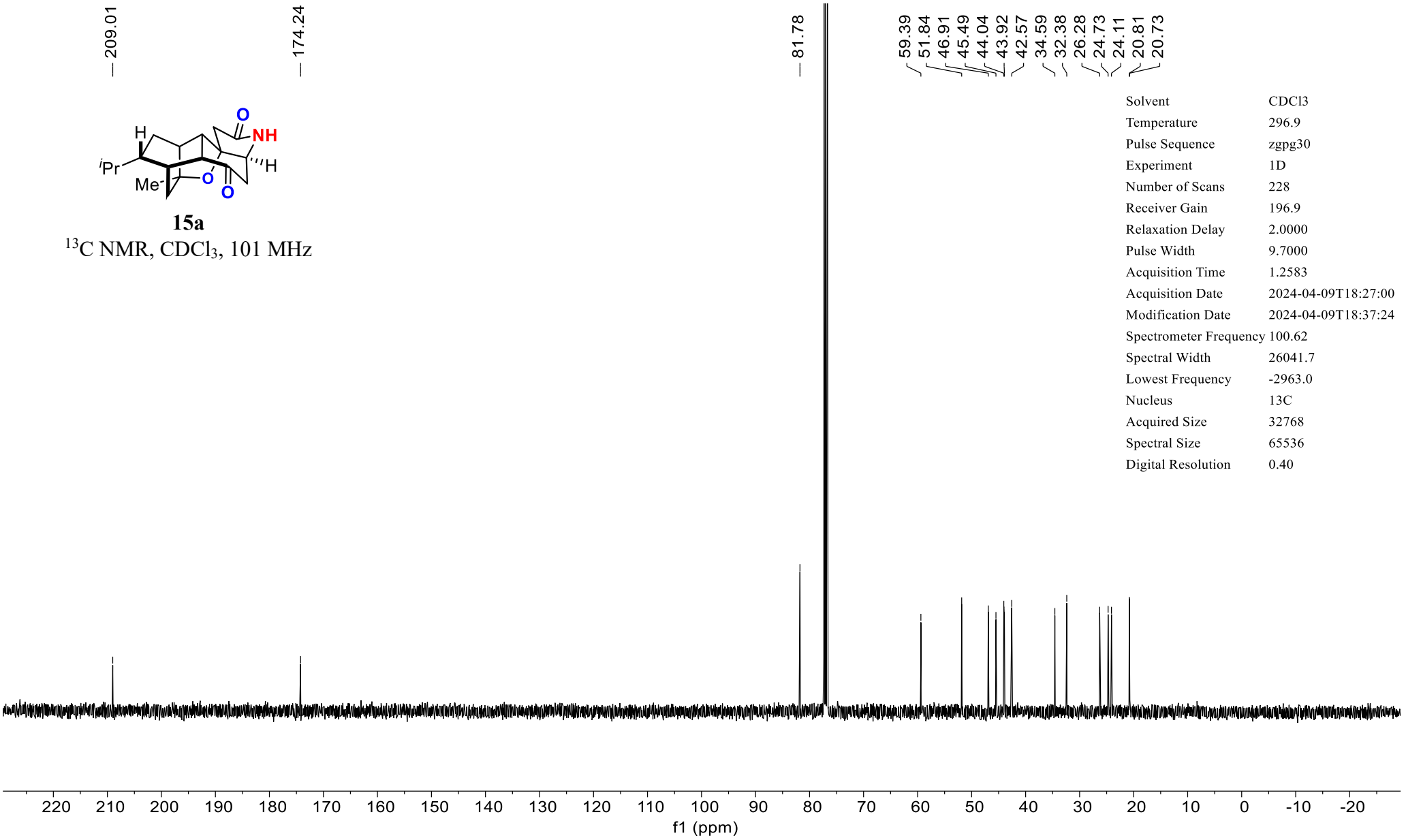
9a

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **15a**


7.26 CDCl3
6.48 3.96 3.94 3.93 3.92 2.85 2.84 2.83 2.82 2.76 2.75 2.73 2.72 2.67 2.62 2.49 2.47 2.46 2.45 2.44 2.37 2.37 2.36 2.36 2.35 2.33 2.32 2.02 2.01 2.00 1.99 1.98 1.97 1.43 1.42 1.42 1.30 1.29 1.28 1.27 1.26 1.26 1.24 1.23 1.19 1.18 1.16 1.15 0.98 0.98 0.96 0.90 0.88
O
NH
H
iPr
Me
O
O
H
15a
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 296.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 88.8
Relaxation Delay 1.0000
Pulse Width 14.5000
Acquisition Time 4.0894
Acquisition Date 2024-04-09T18:23:00
Modification Date 2024-04-09T18:23:52
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.12
2.85 2.84 2.83 2.82 2.76 2.75 2.73 2.72 2.67 2.62 2.49 2.47 2.46 2.45 2.44 2.37 2.37 2.37 2.36 2.36 2.35 2.33 2.32
1.02 1.05 1.08 2.16 2.05
2.90 2.85 2.80 2.75 2.70 2.65 2.60 2.55 2.50 2.45 2.40 2.35 2.30
f1 (ppm)
0.98 1.00 1.02 1.05 1.08 2.16 2.05 2.22 2.10 1.36 3.25 1.15 1.16 6.32
0.0 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 -1.5
f1 (ppm)

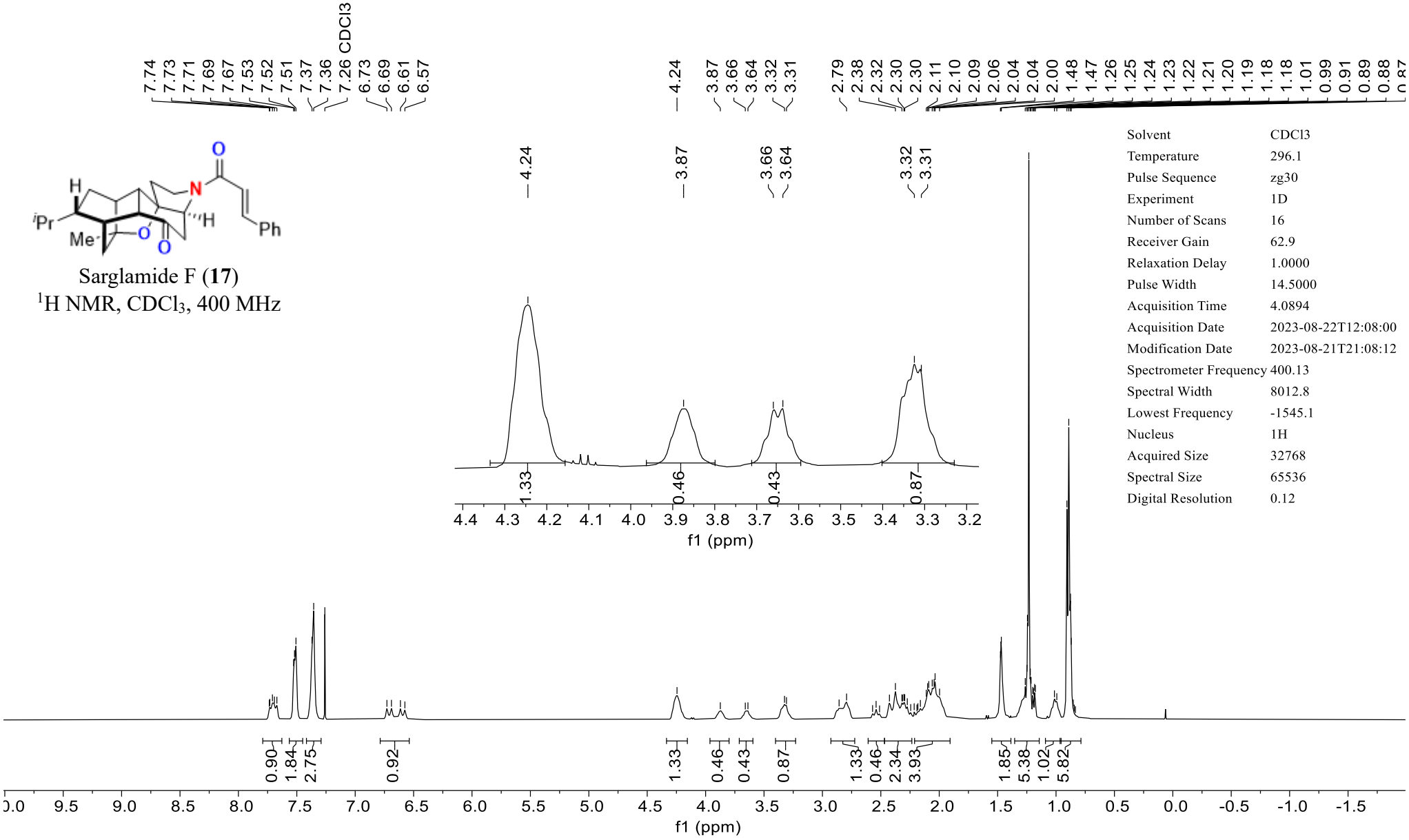
^{13}C NMR of **15a**



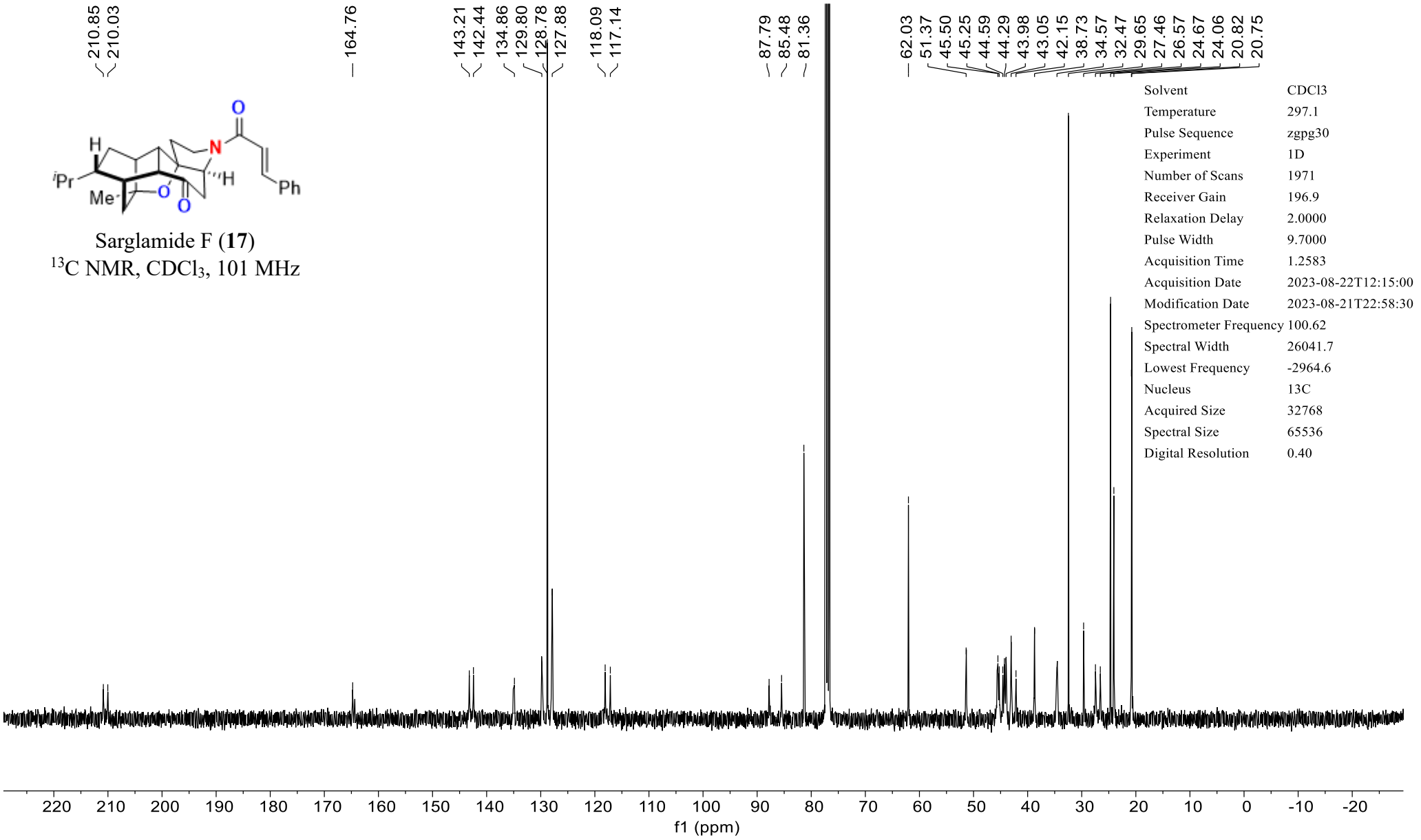
15a

^{13}C NMR, $CDCl_3$, 101 MHz

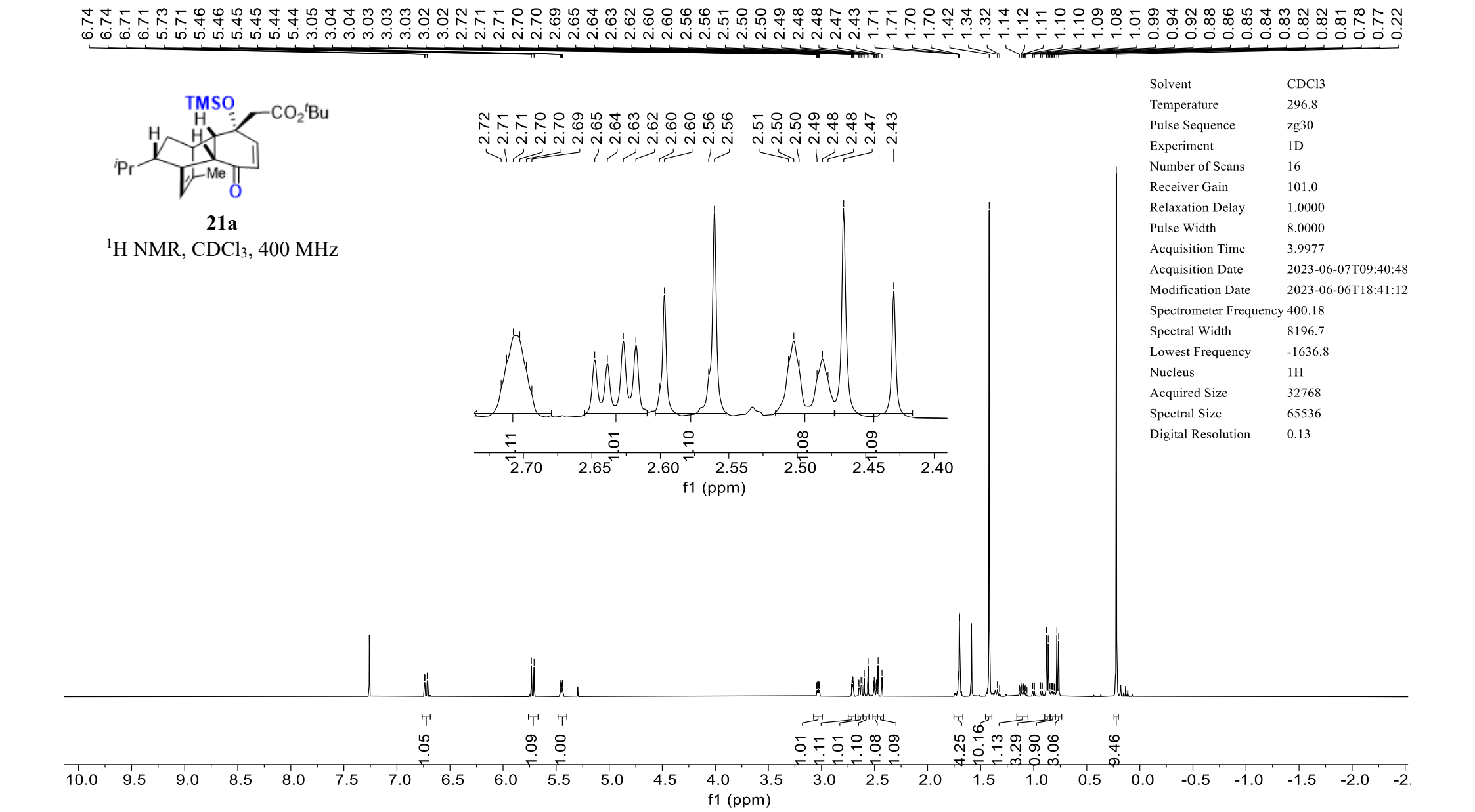
^{1}H NMR of sarglamide F (**17**)



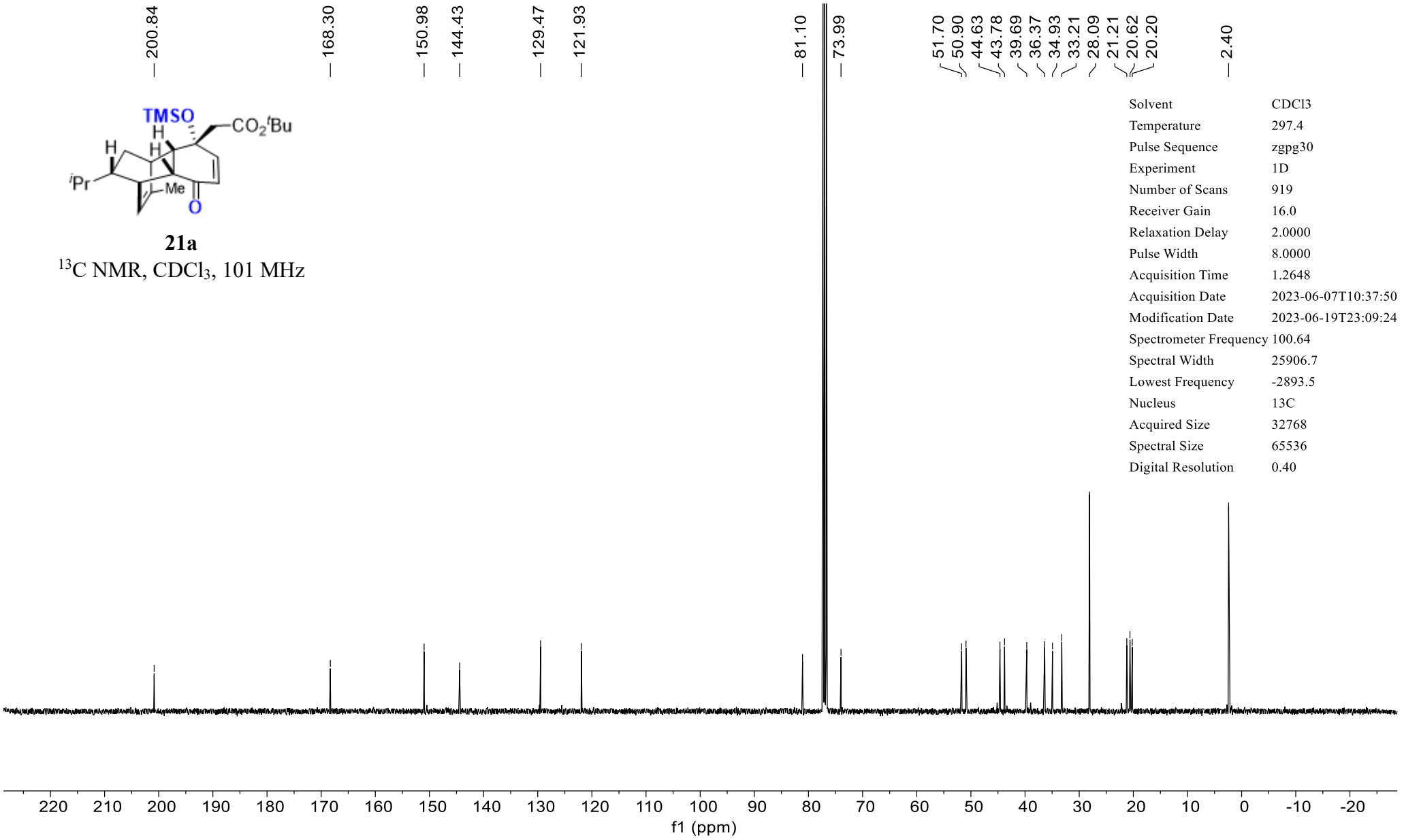
^{13}C NMR of Sarglamide F (**17**)



^{1}H NMR of **21a**


TMSO
H
H
H
$CO_2{}^tBu$
^{i}Pr
Me
O
21a
^{1}H NMR, $CDCl_3$, 400 MHz
Solvent CDCl3
Temperature 296.8
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-07T09:40:48
Modification Date 2023-06-06T18:41:12
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.8
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
f1 (ppm)
f1 (ppm)

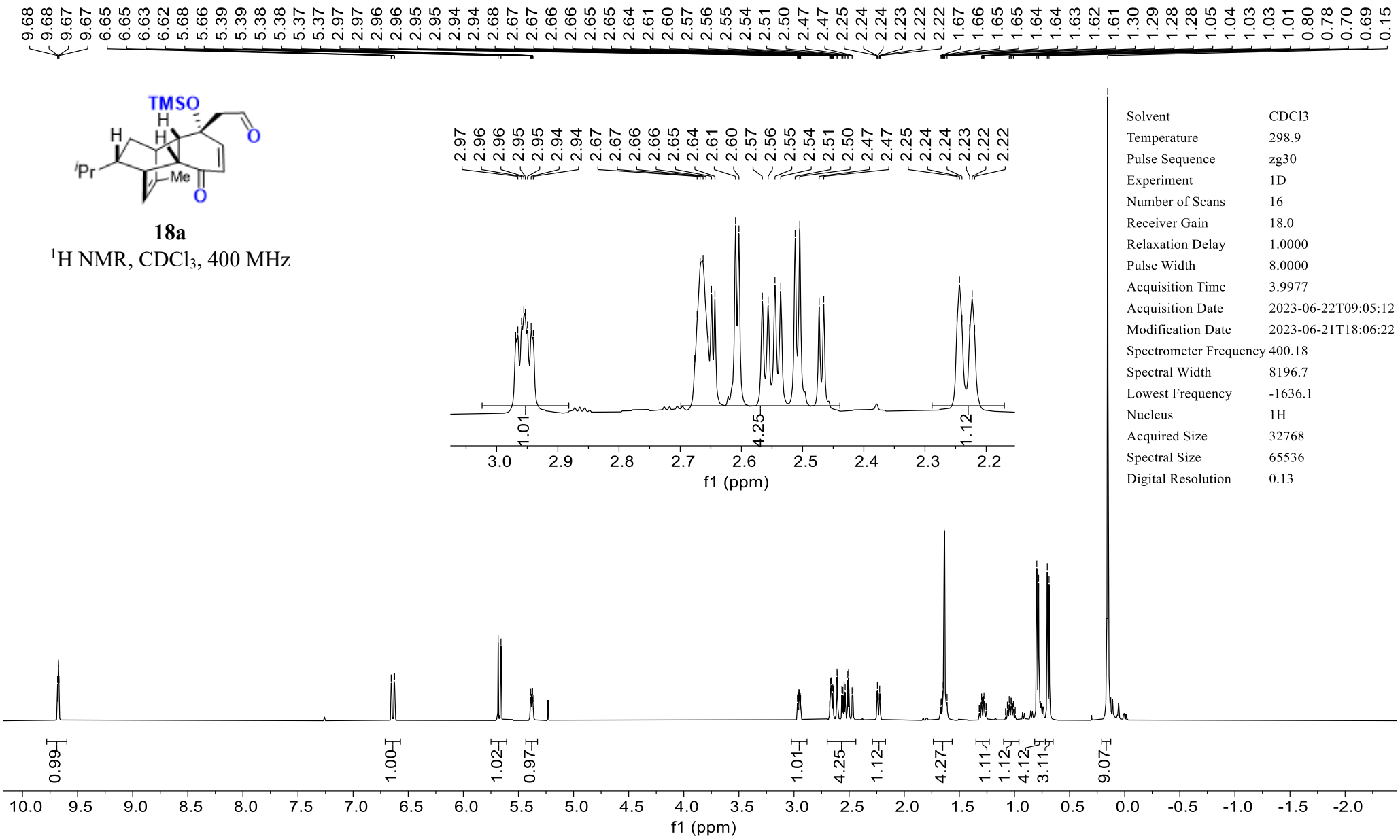
^{13}C NMR of **21a**



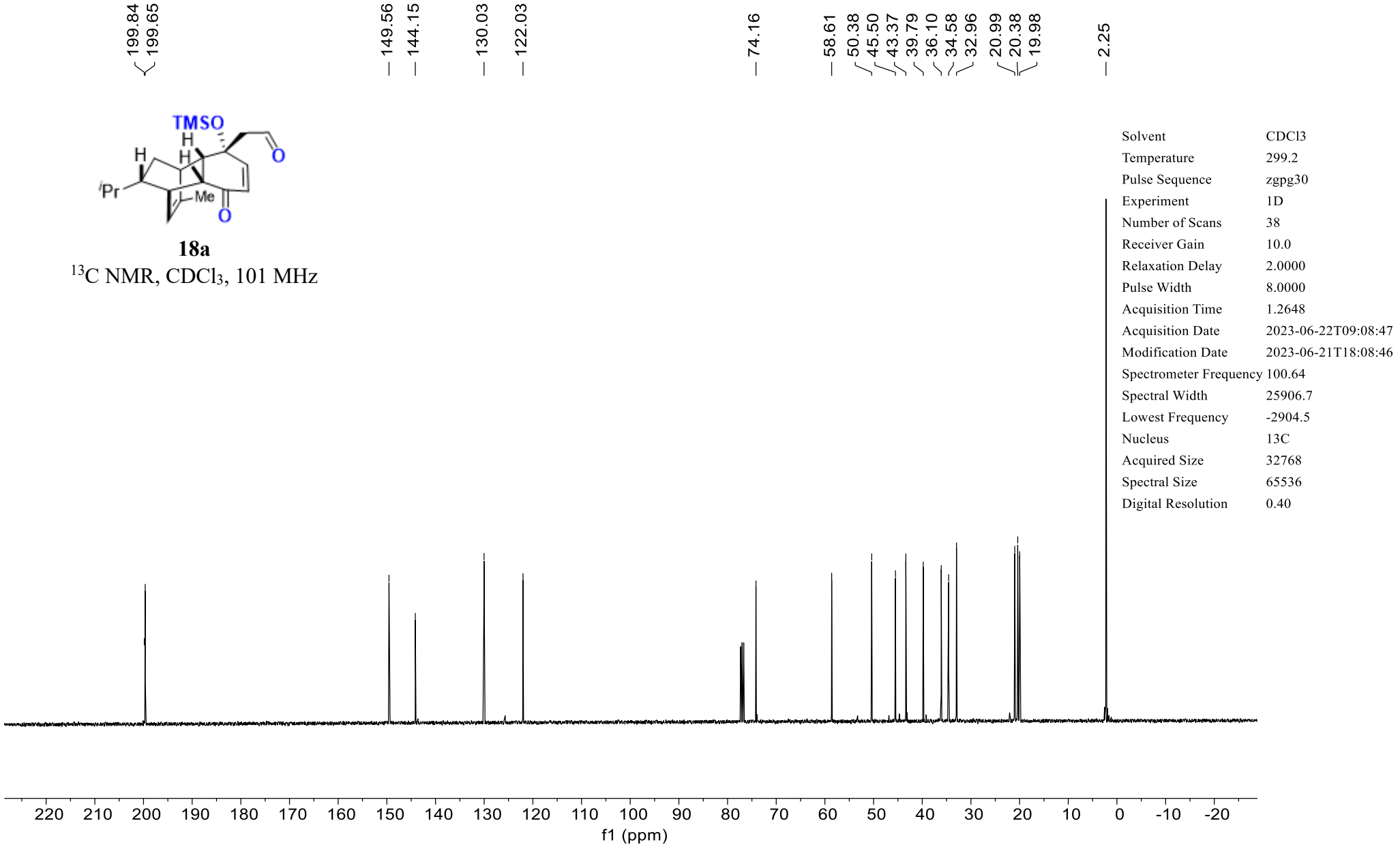
21a

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **18a**


TMSO
H
H
H
O
iPr
Me
O
18a
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 298.9
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 18.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-22T09:05:12
Modification Date 2023-06-21T18:06:22
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.1
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
f1 (ppm)
f1 (ppm)

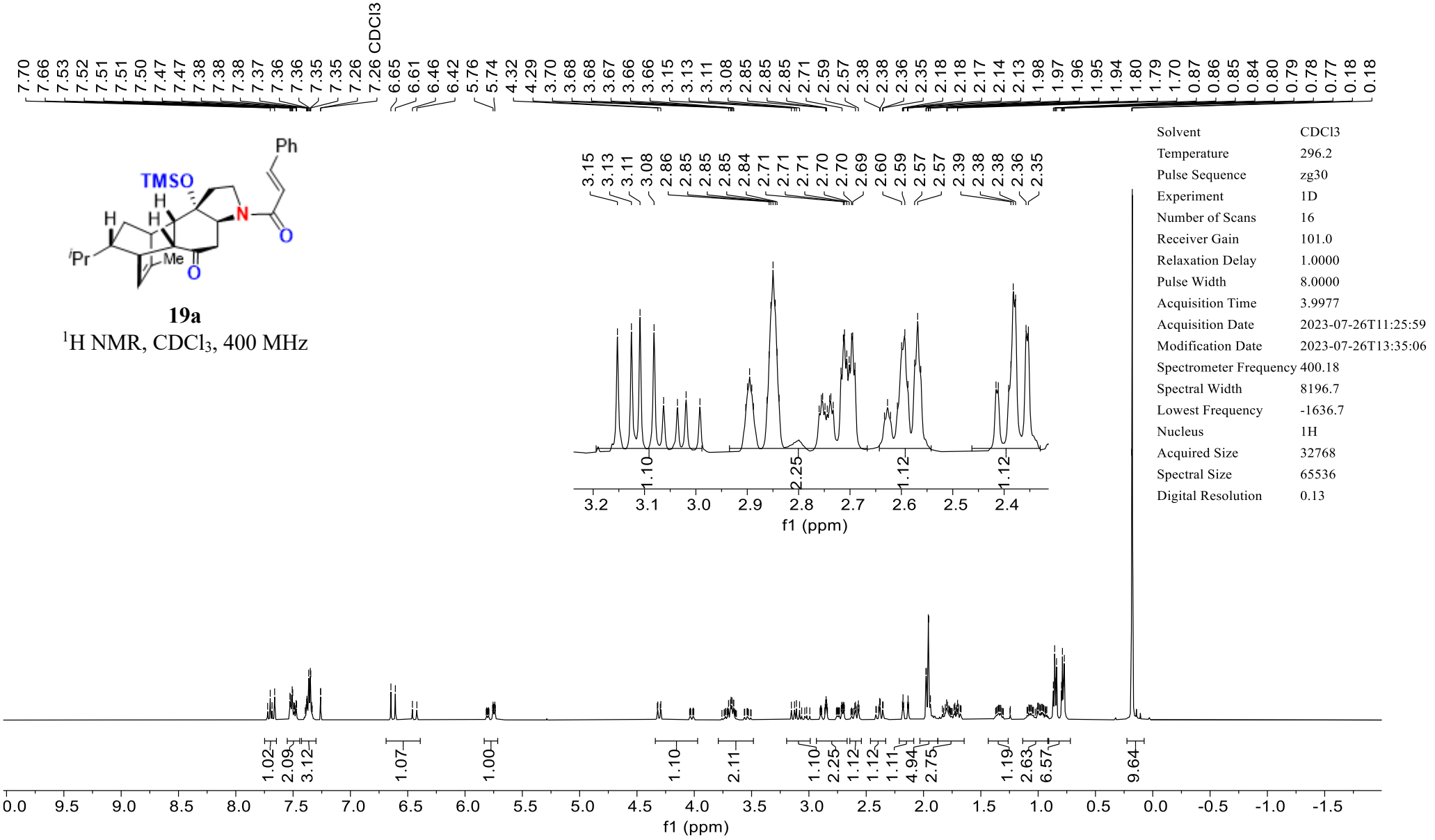
^{13}C NMR of **18a**



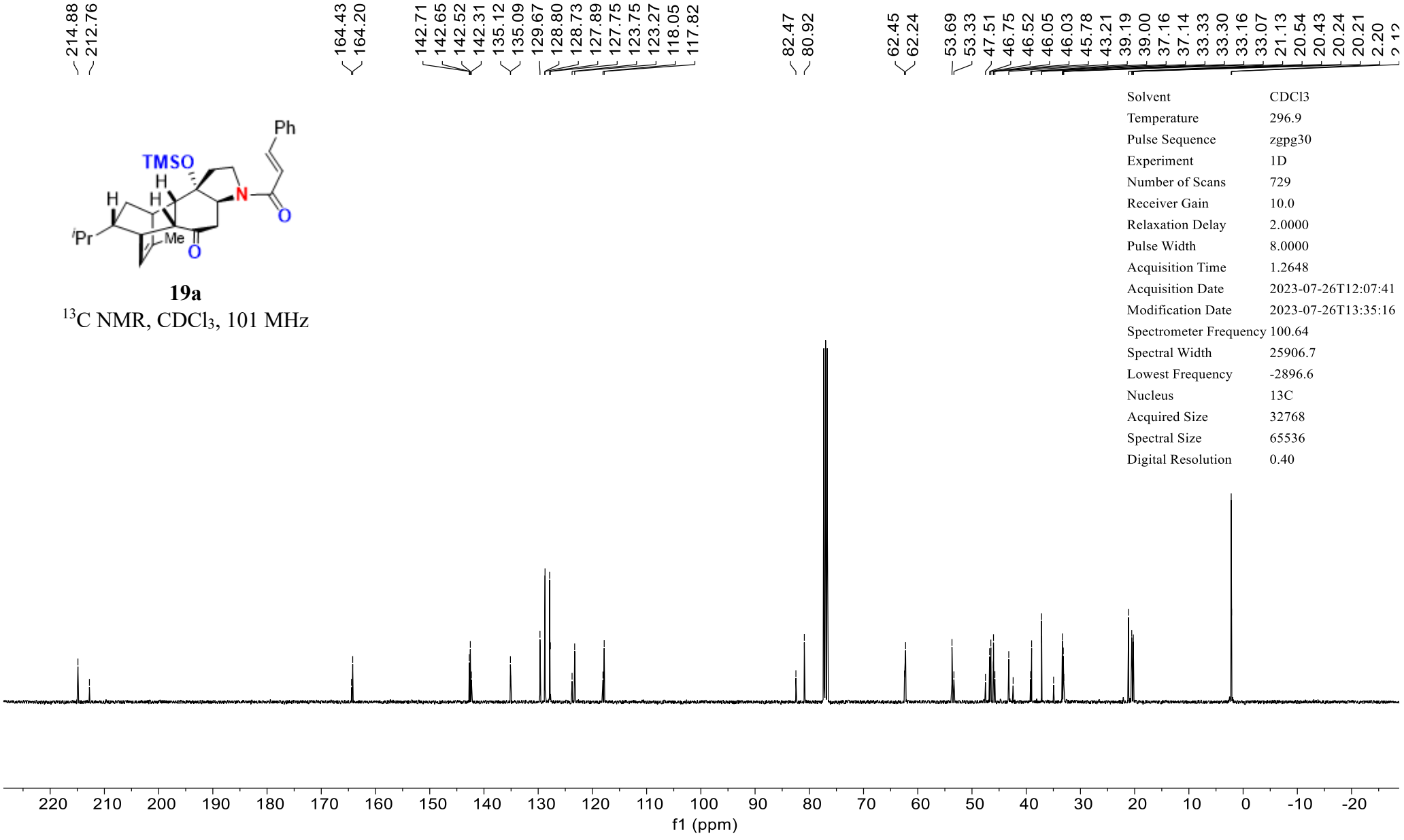
18a

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **19a**


CDCl3
TMSO
Ph
N
O
Me
O
iPr
19a
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 296.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-07-26T11:25:59
Modification Date 2023-07-26T13:35:06
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.7
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
f1 (ppm)
f1 (ppm)

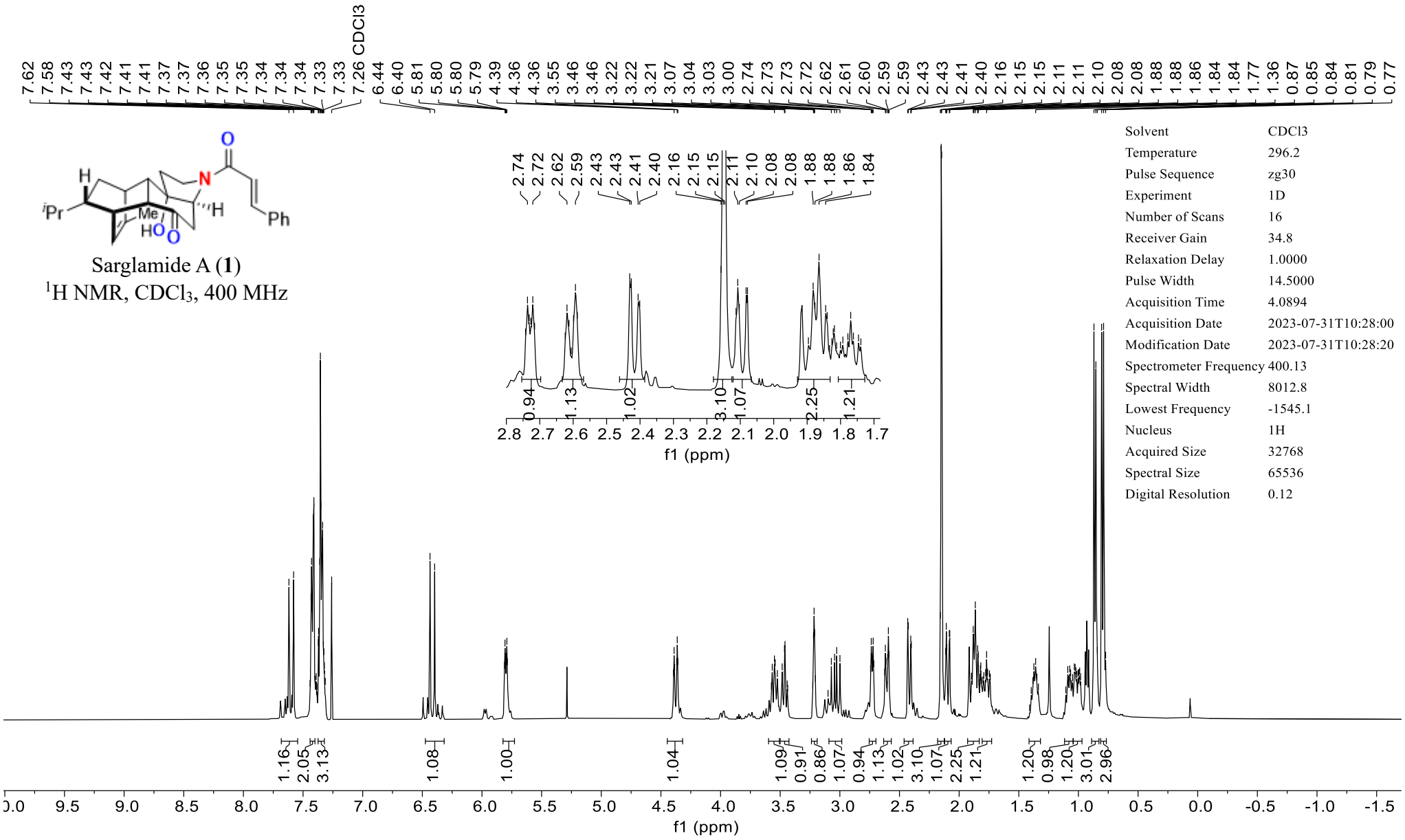
^{1}H NMR of **19a**



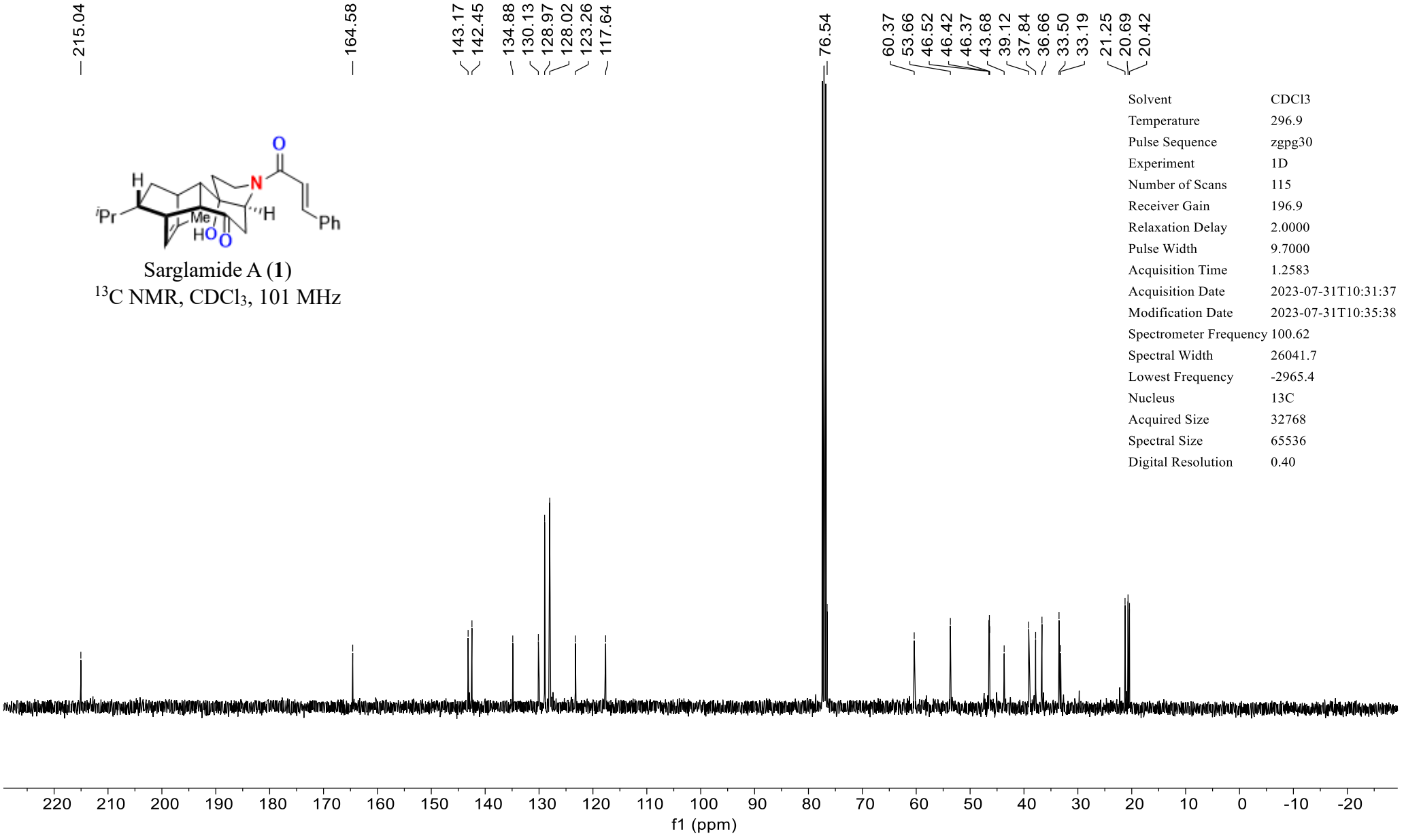
19a

^{13}C NMR, $CDCl_3$, 101 MHz

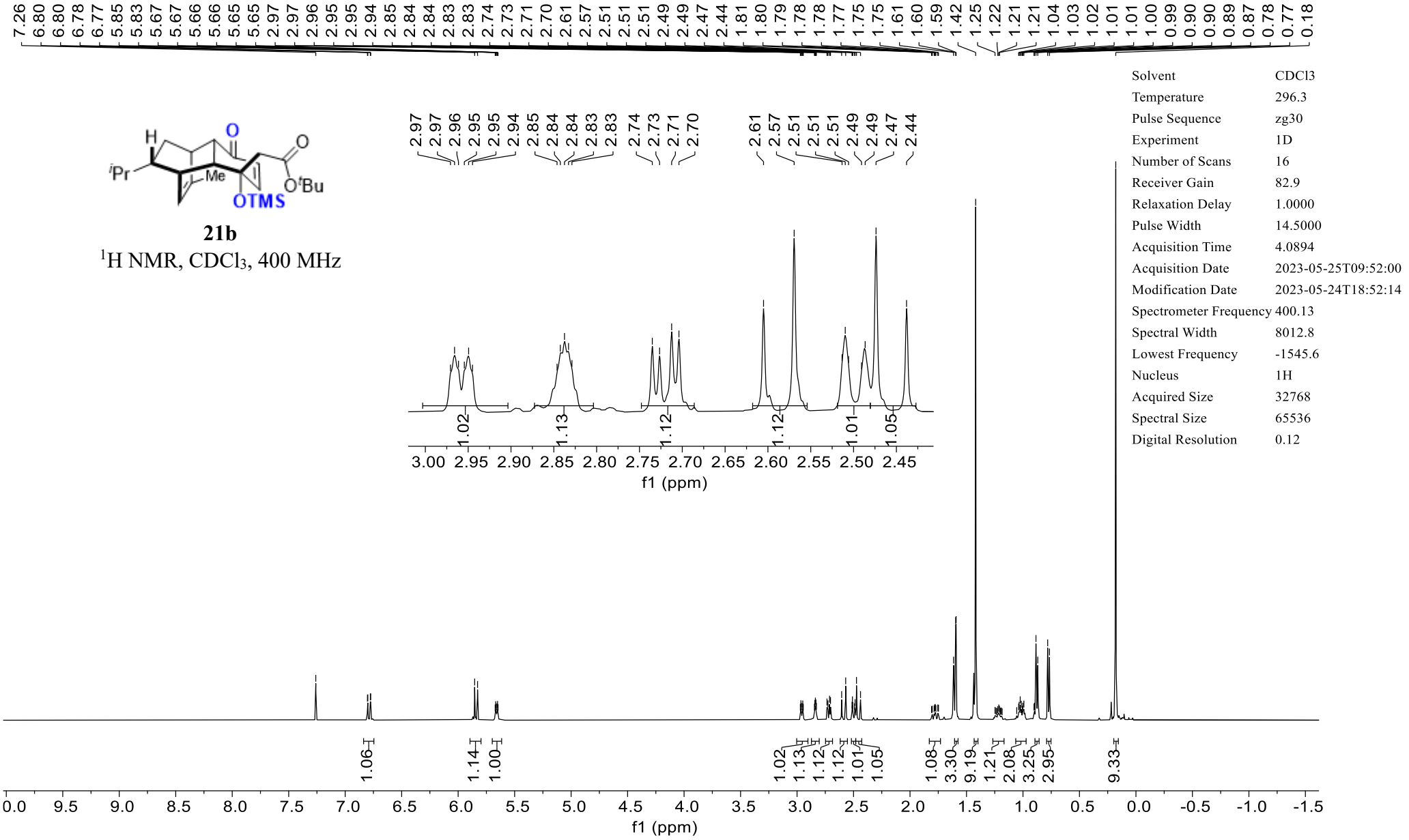
^{1}H NMR of Sarglamide A (**1**)



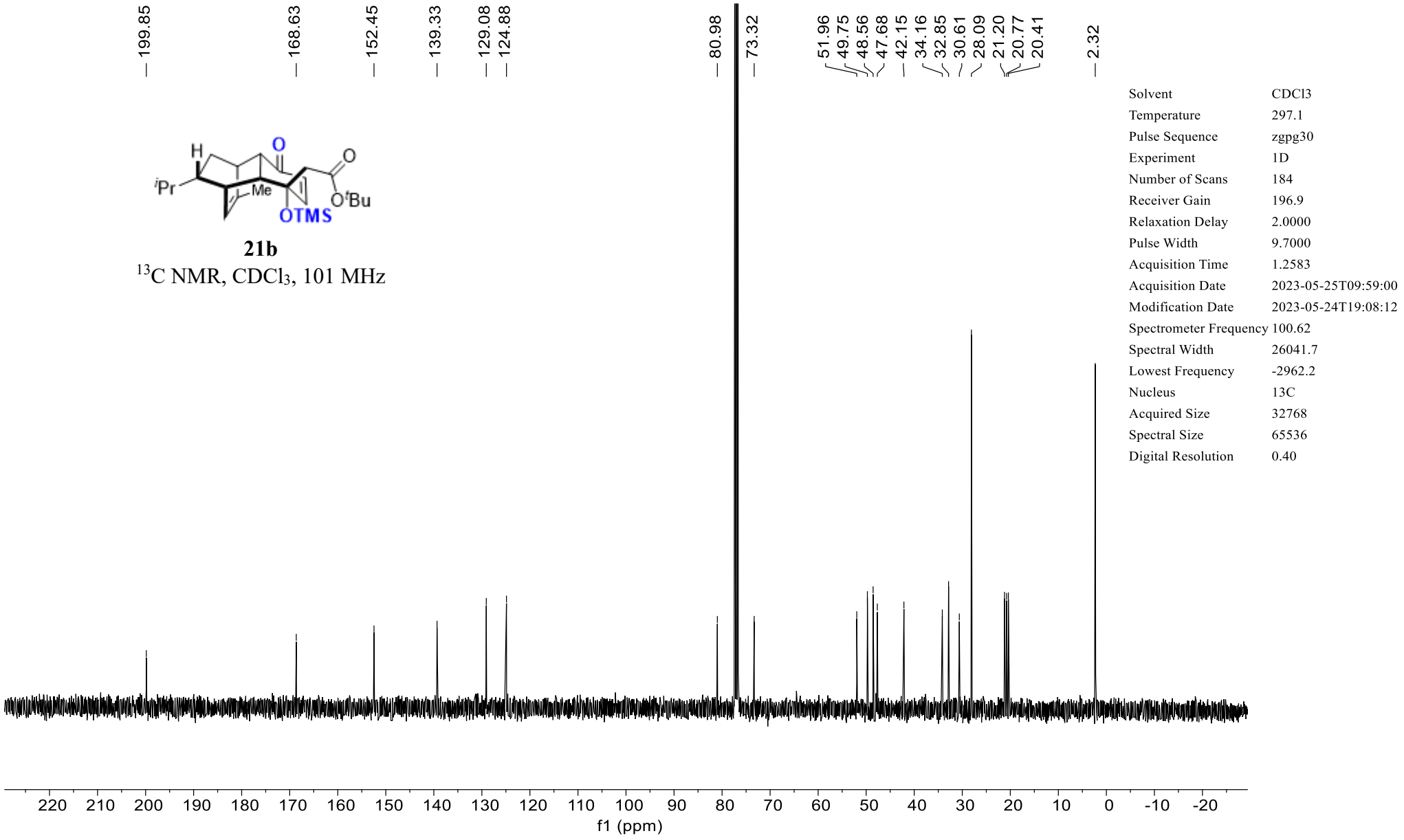
^{13}C NMR of Sarglamide A (**1**)



^{1}H NMR of **21b**


21b
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 296.3
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 82.9
Relaxation Delay 1.0000
Pulse Width 14.5000
Acquisition Time 4.0894
Acquisition Date 2023-05-25T09:52:00
Modification Date 2023-05-24T18:52:14
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.6
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.12
f1 (ppm)

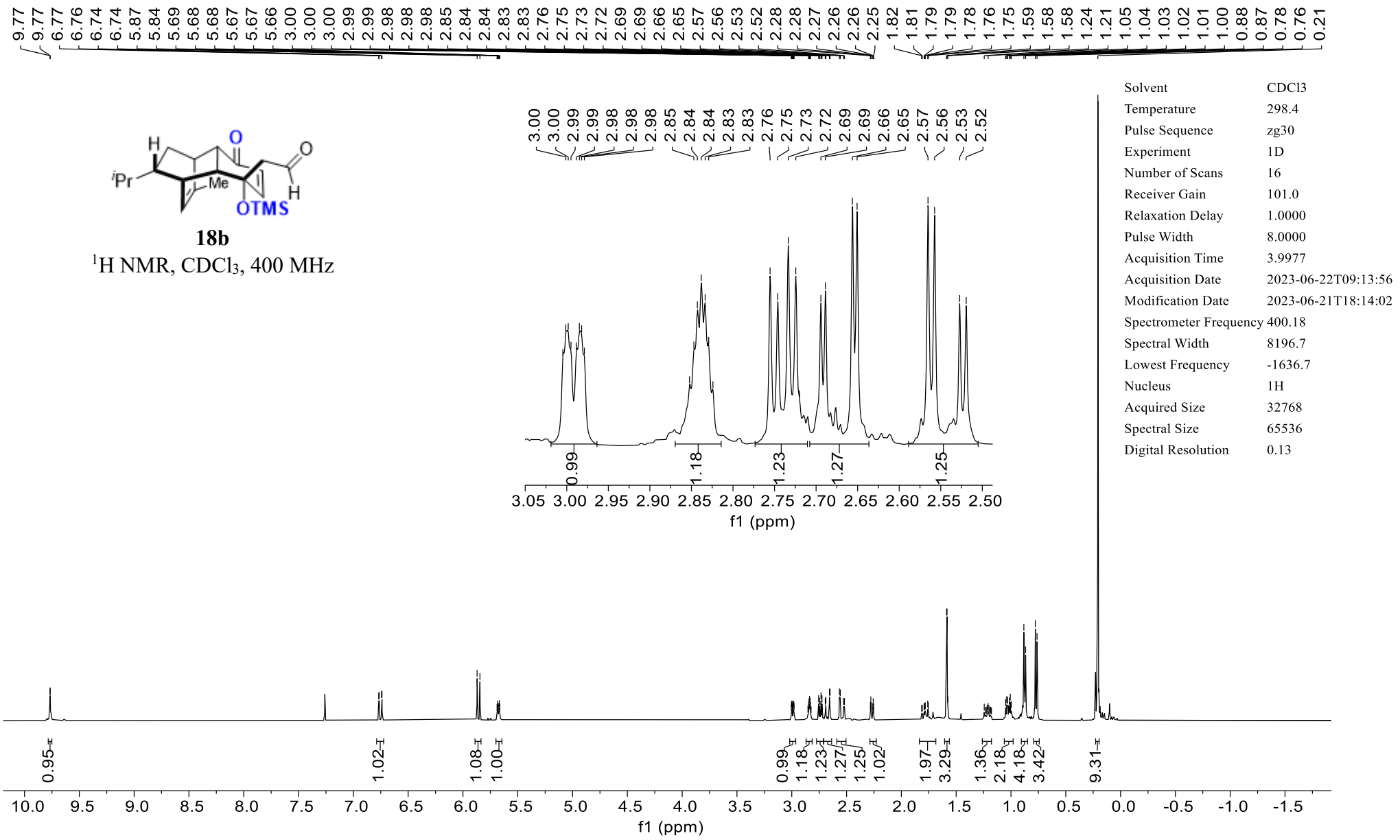
^{13}C NMR of **21b**



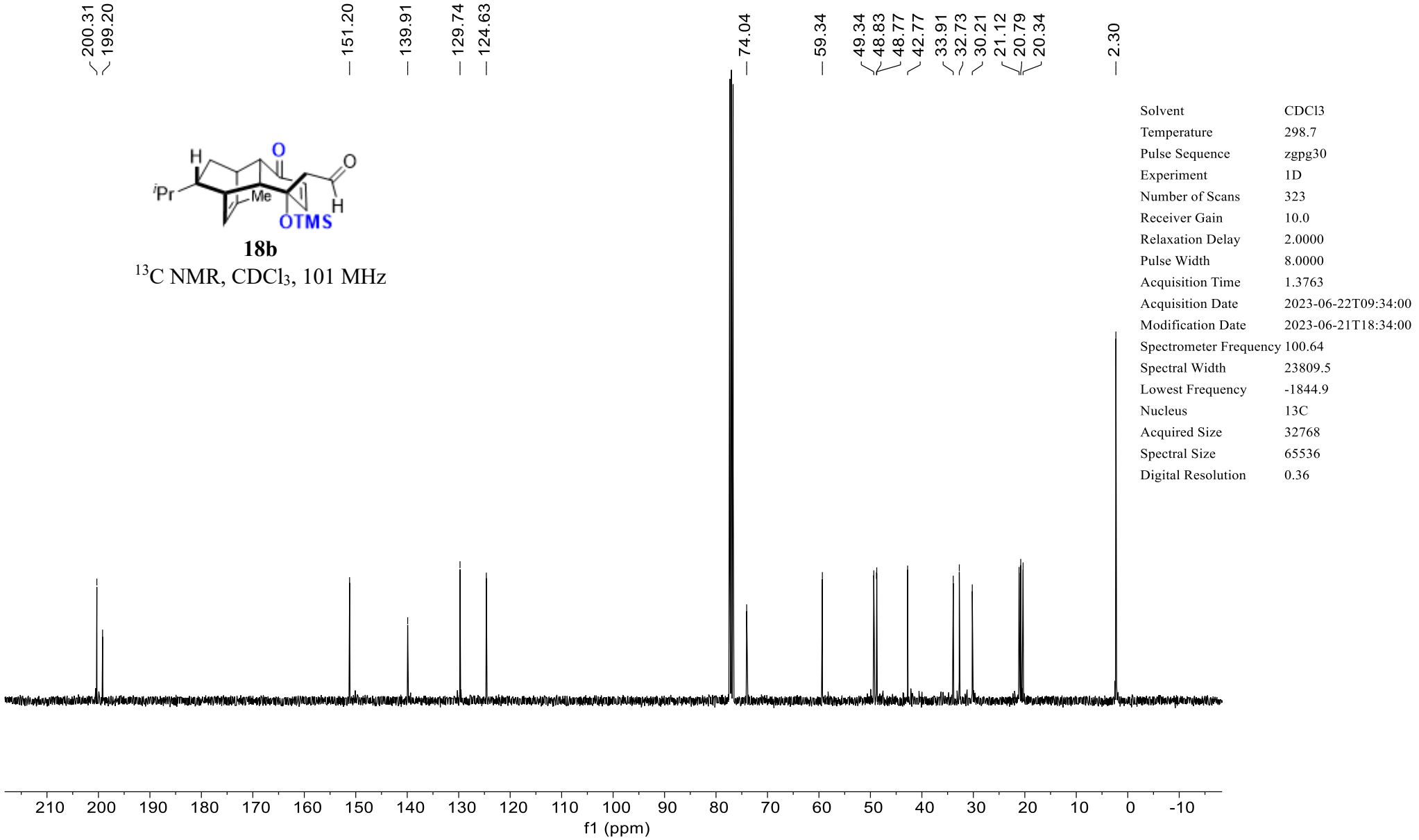
21b

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **18b**


18b
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 298.4
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-22T09:13:56
Modification Date 2023-06-21T18:14:02
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.7
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
f1 (ppm)

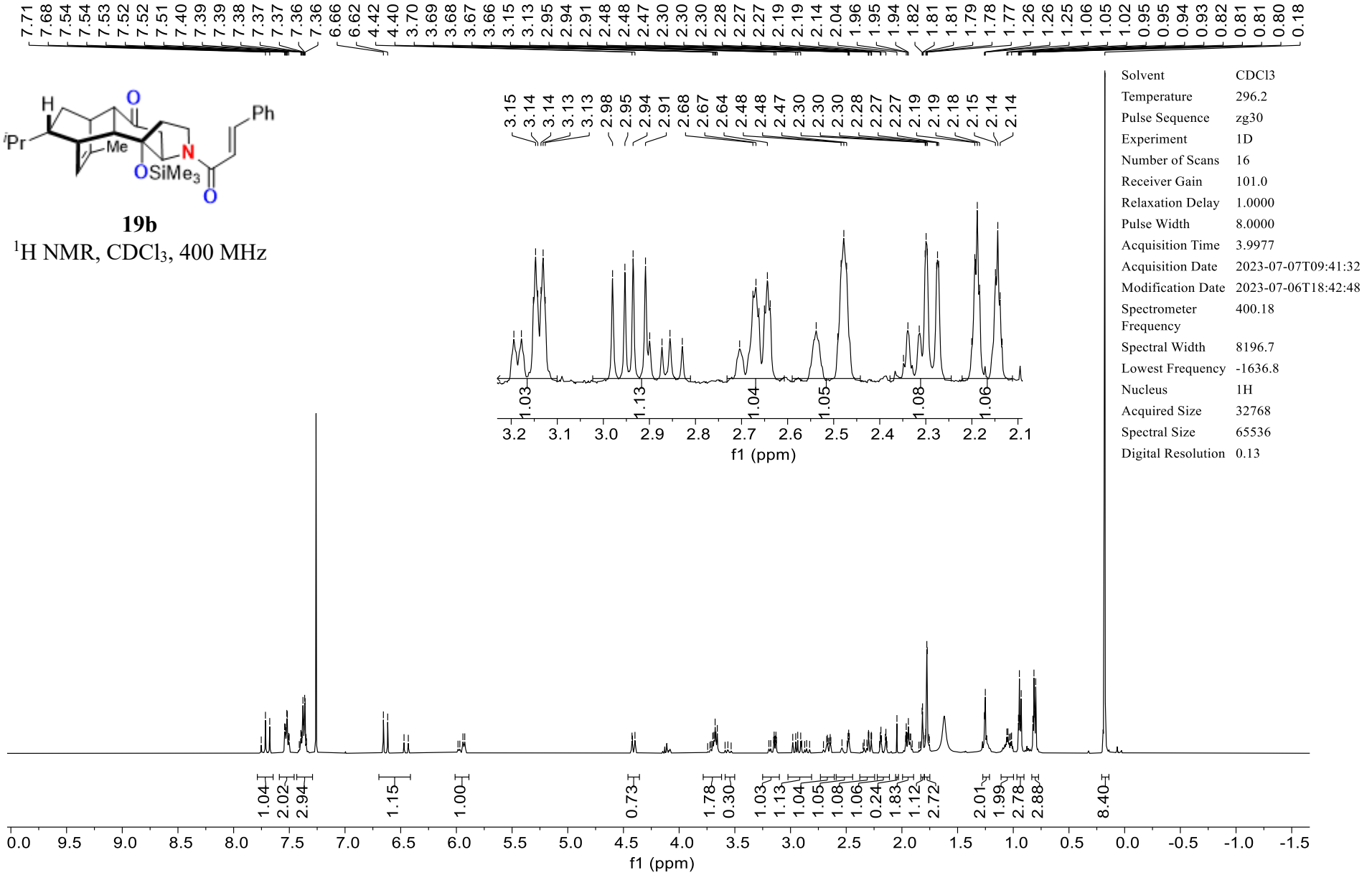
^{13}C NMR of **18b**



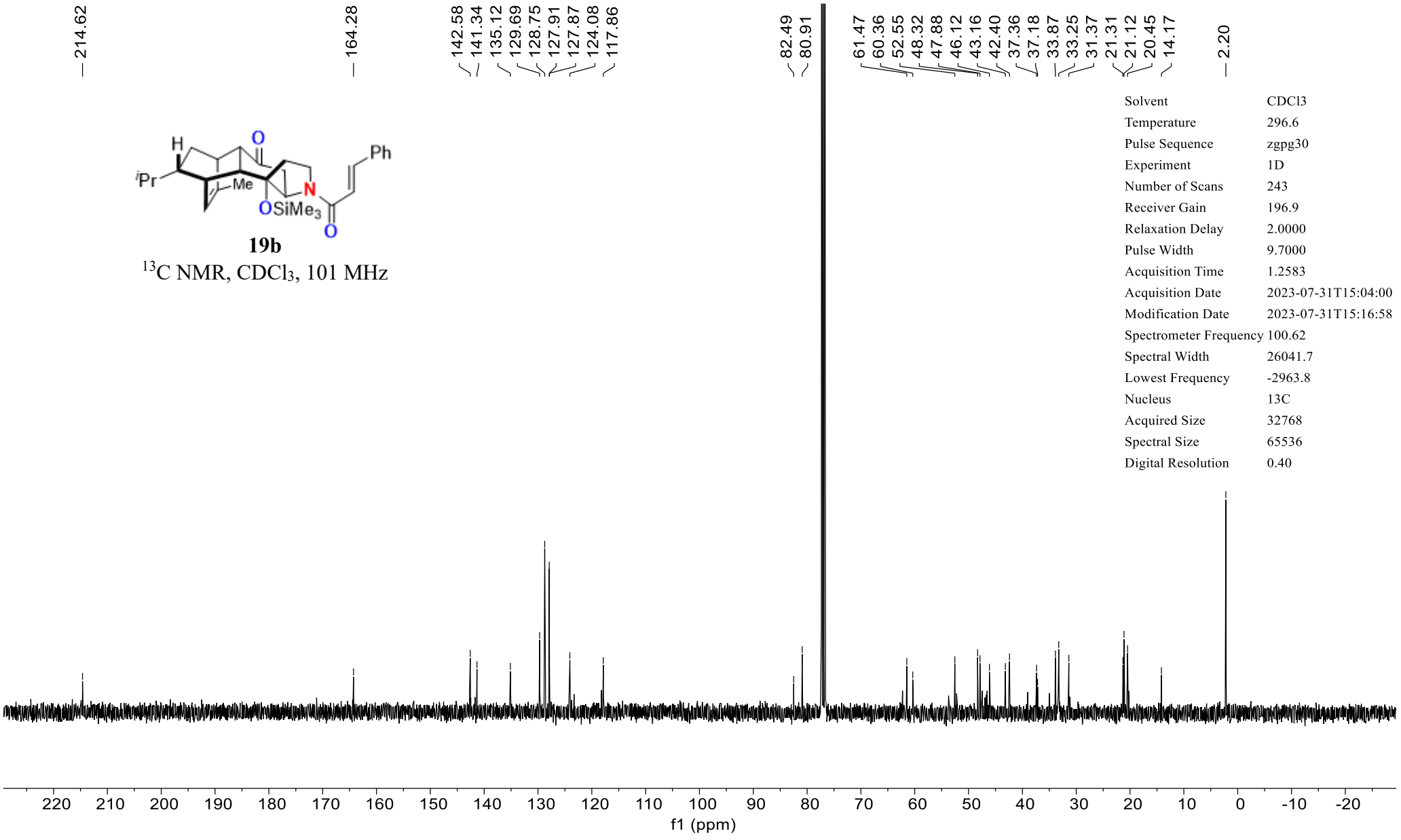
18b

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **19b**


19b
1H NMR, CDCl3, 400 MHz
Solvent CDCl3
Temperature 296.2
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-07-07T09:41:32
Modification Date 2023-07-06T18:42:48
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1636.8
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
f1 (ppm)

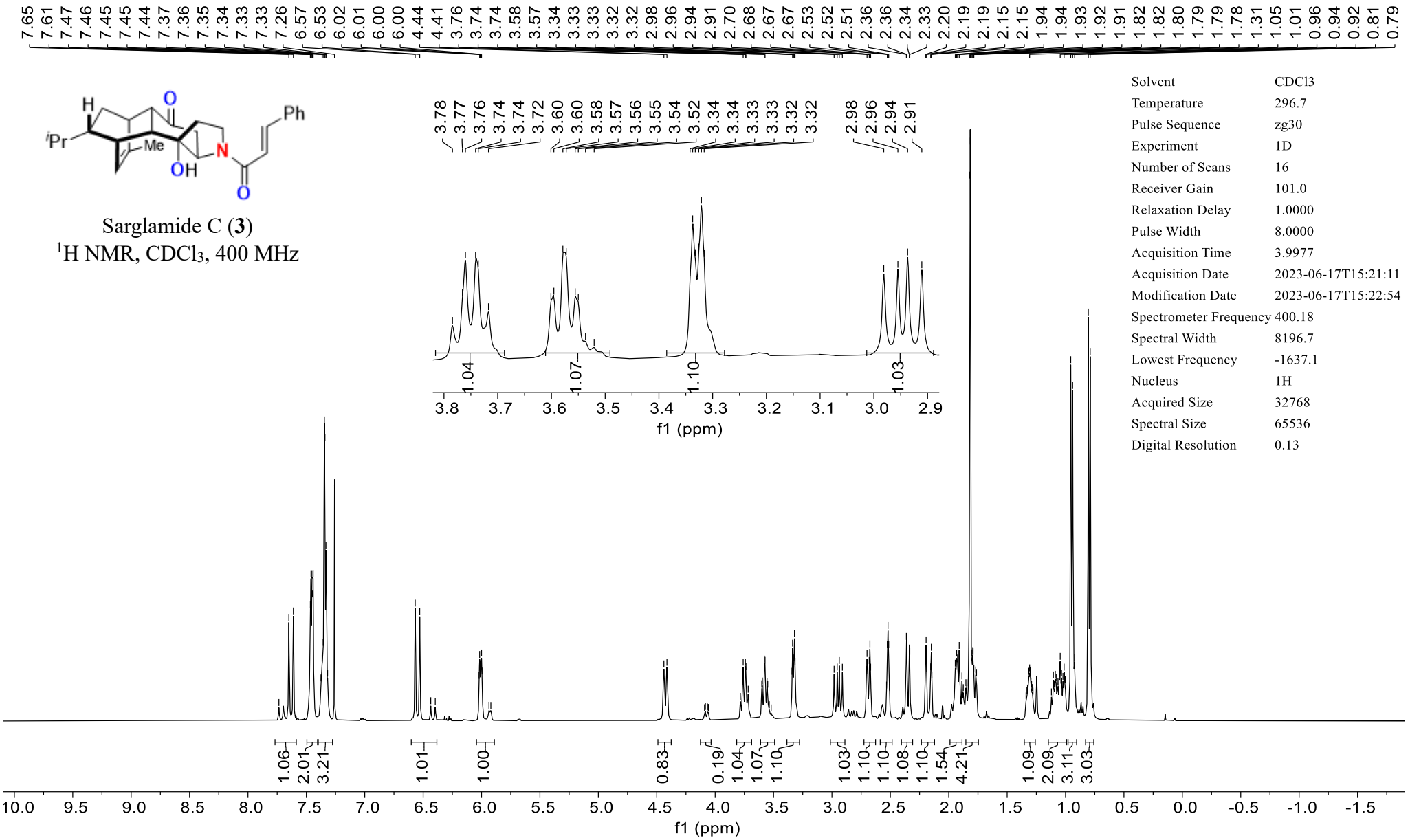
^{13}C NMR of **19b**



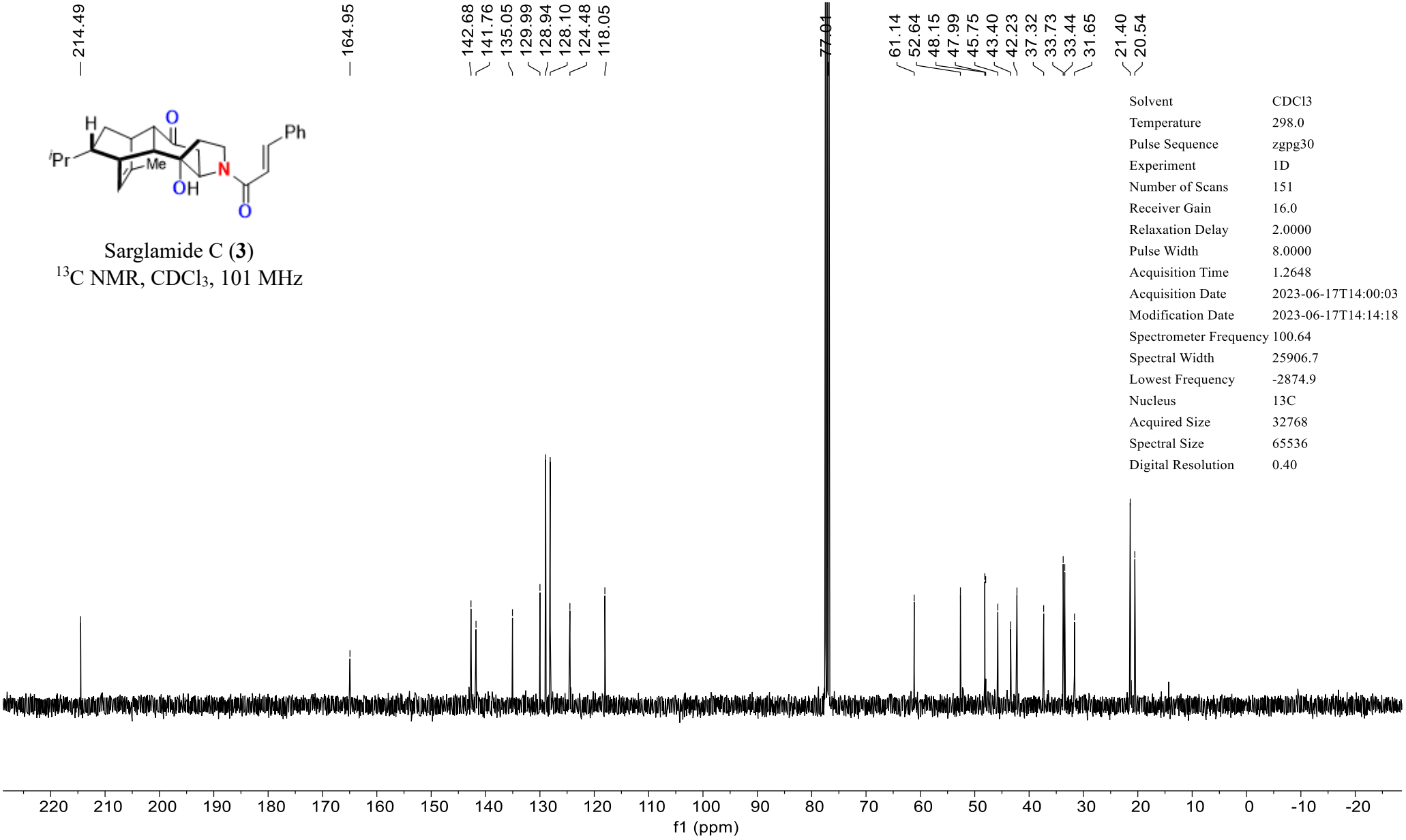
19b

^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of Sarglamide C (**3**)

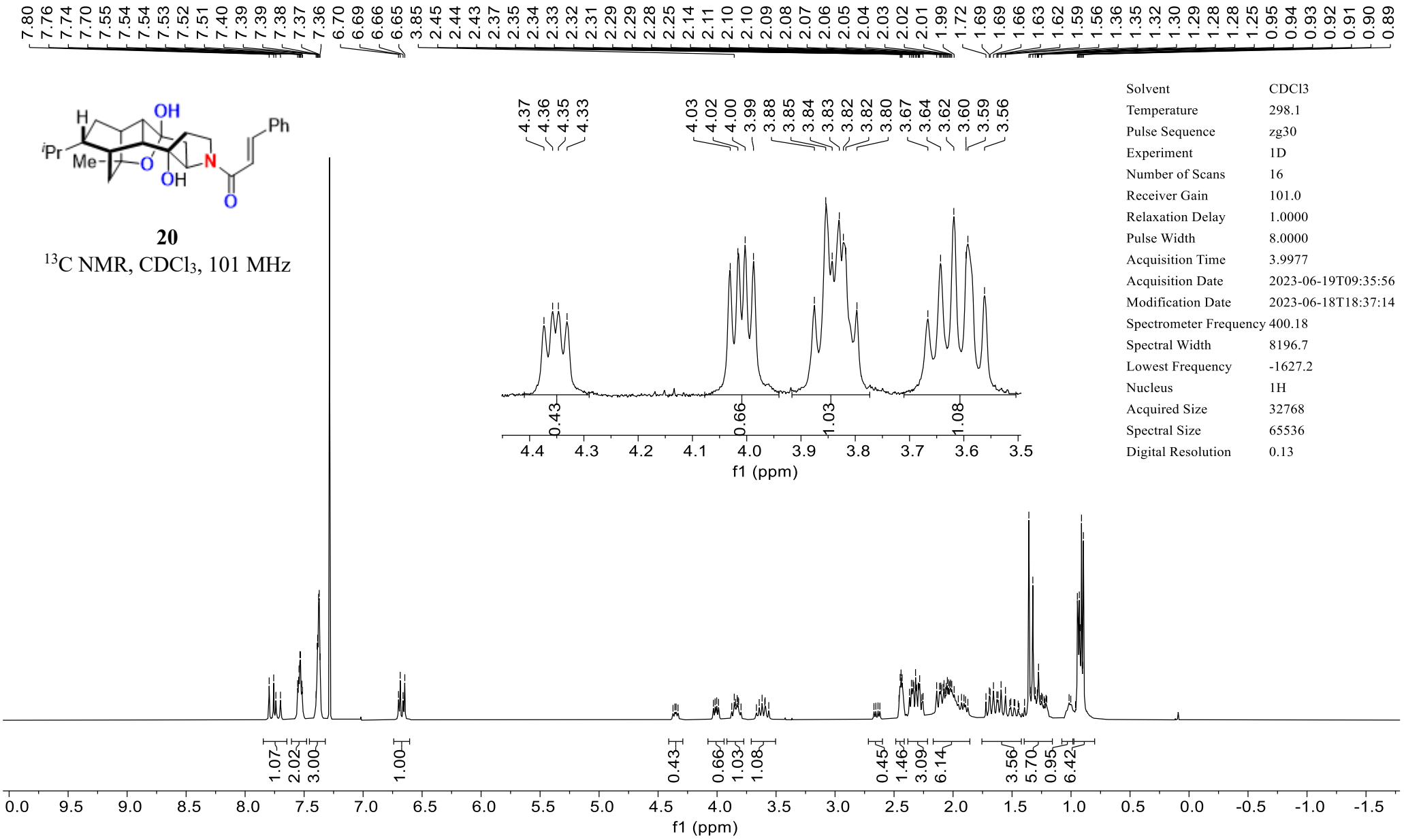


4.4 ^{1}H NMR of Sarglamide C (**3**)

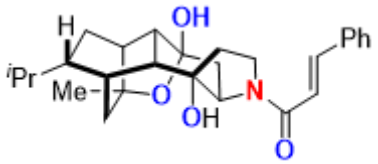


Sarglamide C (**3**)
^{13}C NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **20**


7.80 7.76 7.74 7.70 7.55 7.54 7.54 7.53 7.52 7.51 7.40 7.39 7.39 7.38 7.37 7.36 6.70 6.69 6.66 6.65 3.85 2.45 2.44 2.43 2.37 2.35 2.34 2.33 2.32 2.31 2.29 2.29 2.28 2.25 2.14 2.11 2.10 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.03 2.02 2.01 1.99 1.72 1.69 1.69 1.66 1.63 1.62 1.59 1.56 1.36 1.35 1.32 1.30 1.29 1.28 1.28 1.25 0.95 0.94 0.93 0.92 0.91 0.90 0.89
H
OH
Ph
iPr
Me
O
N
OH
O
20
13C NMR, CDCl3, 101 MHz
4.37 4.36 4.35 4.33 4.03 4.02 4.00 3.99 3.88 3.85 3.84 3.83 3.82 3.82 3.80 3.67 3.64 3.62 3.60 3.59 3.56
0.43 0.66 1.03 1.08
4.4 4.3 4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
f1 (ppm)
Solvent CDCl3
Temperature 298.1
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 8.0000
Acquisition Time 3.9977
Acquisition Date 2023-06-19T09:35:56
Modification Date 2023-06-18T18:37:14
Spectrometer Frequency 400.18
Spectral Width 8196.7
Lowest Frequency -1627.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.13
1.07 2.02 3.00 1.00 0.43 0.66 1.03 1.08 0.45 1.46 3.09 6.14 3.56 5.70 0.95 6.42
0.0 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 -1.5
f1 (ppm)

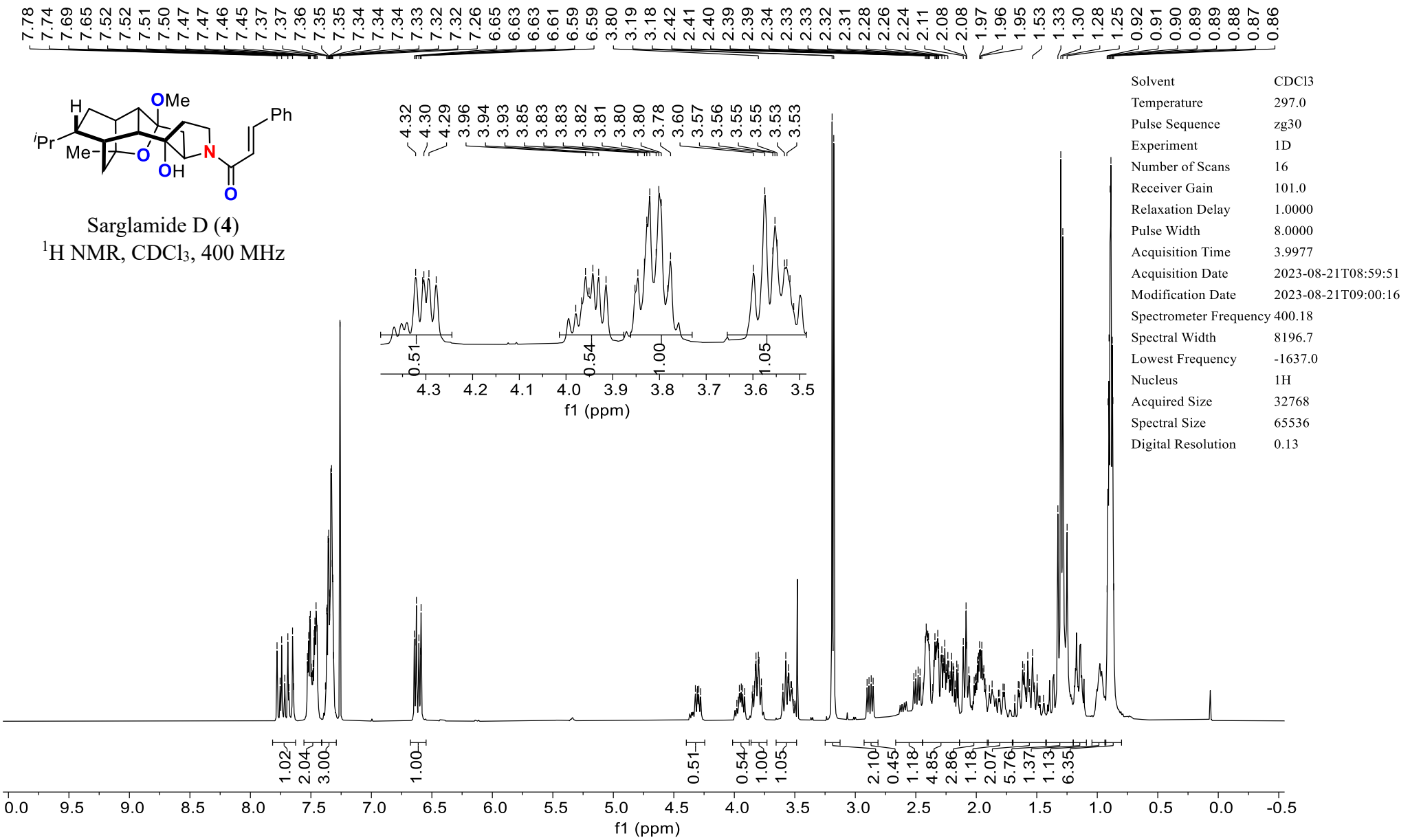
^{13}C NMR of **20**



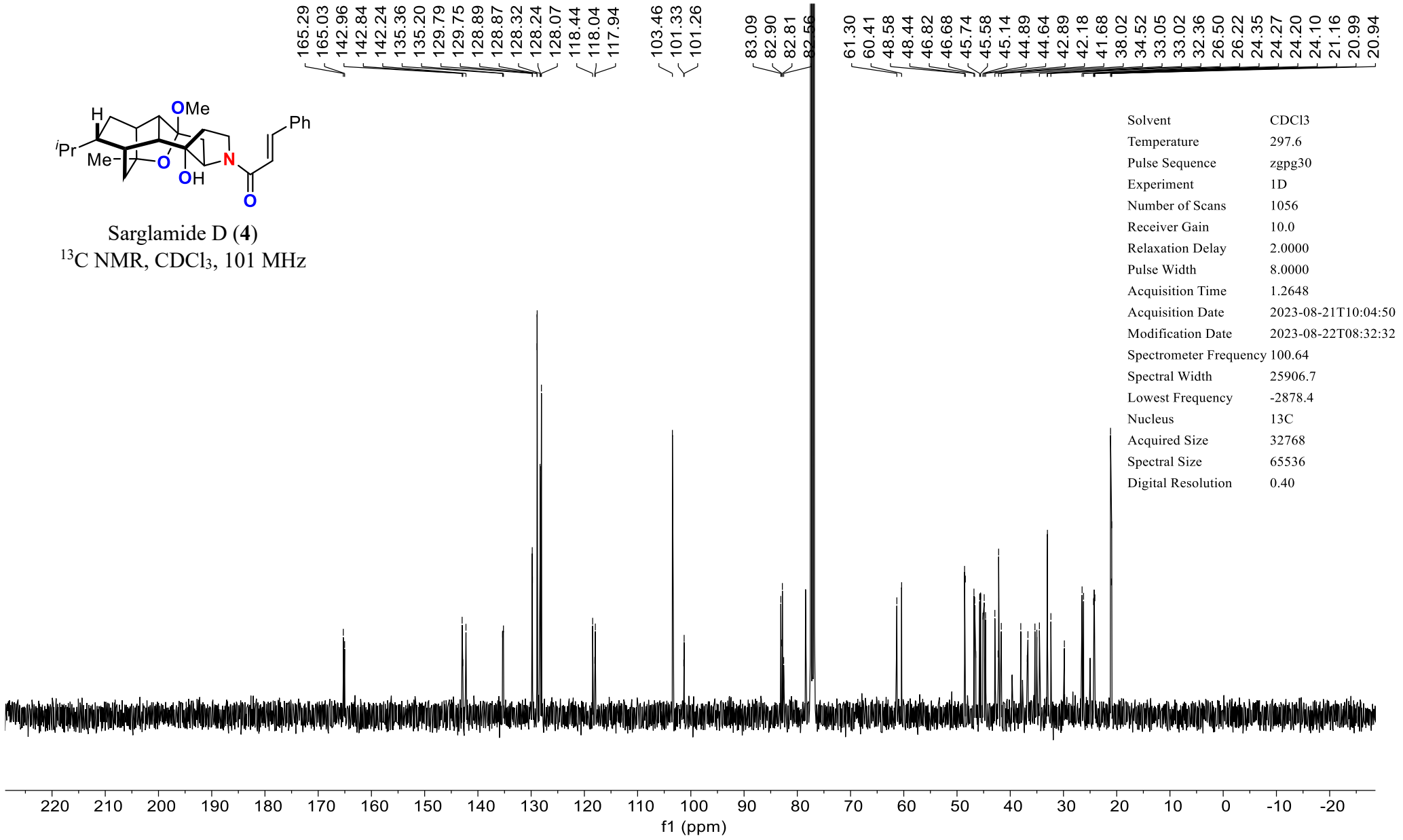
20

^{13}C NMR, $CDCl_3$, 101 MHz

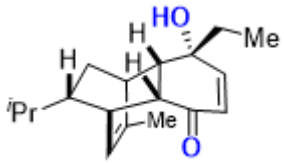
^{1}H NMR of Sarglamide D (**4**)



^{13}C NMR of Sarglamide D (**4**)



^{1}H NMR of **10c**

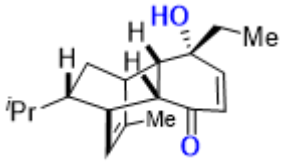


10c

^{1}H NMR, $CDCl_3$, 400 MHz

Solvent	CDCl3
Temperature	296.0
Pulse Sequence	zg30
Experiment	1D
Number of Scans	16
Receiver Gain	88.8
Relaxation Delay	1.0000
Pulse Width	14.5000
Acquisition Time	4.0894
Acquisition Date	2024-04-01T18:20:00
Modification Date	2024-04-01T18:20:30
Spectrometer Frequency	400.13
Spectral Width	8012.8
Lowest Frequency	-1545.2
Nucleus	1H
Acquired Size	32768
Spectral Size	65536
Digital Resolution	0.12

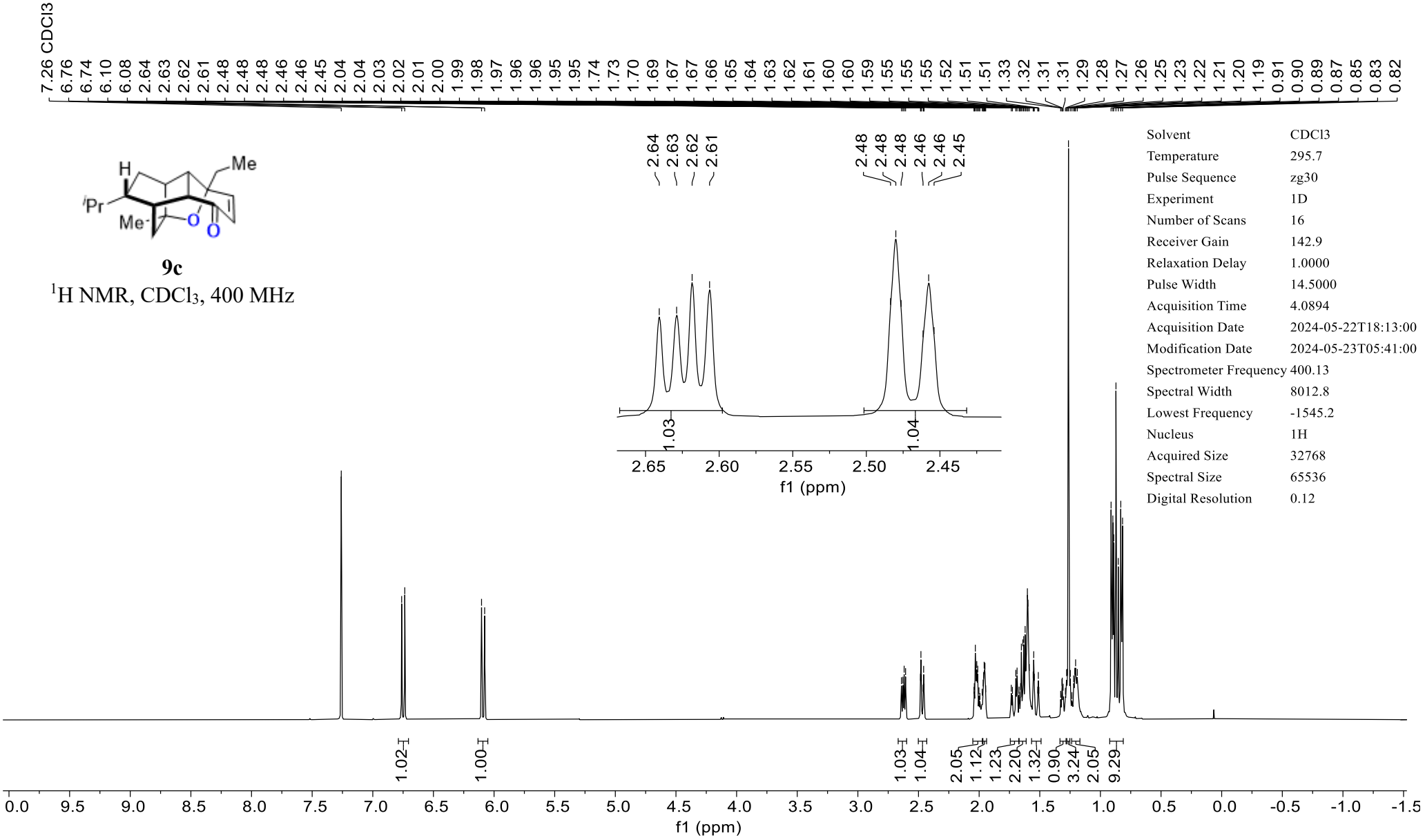
^{13}C NMR of **10c**



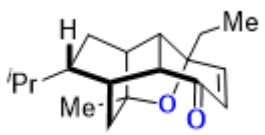
10c

^{13}H NMR, $CDCl_3$, 101 MHz

^{1}H NMR of **9c**


7.26 CDCl3
6.76 6.74 6.10 6.08 2.64 2.63 2.62 2.61 2.48 2.48 2.48 2.46 2.46 2.45 2.04 2.04 2.03 2.02 2.01 2.00 1.99 1.98 1.97 1.96 1.96 1.95 1.95 1.74 1.73 1.70 1.69 1.67 1.67 1.66 1.65 1.64 1.63 1.62 1.61 1.60 1.60 1.59 1.55 1.55 1.52 1.51 1.51 1.33 1.32 1.31 1.31 1.29 1.28 1.27 1.26 1.25 1.23 1.22 1.21 1.20 1.19 0.91 0.90 0.89 0.87 0.85 0.83 0.82
H
Me
iPr
Me
O
O
9c
1H NMR, CDCl3, 400 MHz
2.64 2.63 2.62 2.61
2.48 2.48 2.48 2.46 2.46 2.45
1.03
1.04
2.65 2.60 2.55 2.50 2.45
f1 (ppm)
Solvent CDCl3
Temperature 295.7
Pulse Sequence zg30
Experiment 1D
Number of Scans 16
Receiver Gain 142.9
Relaxation Delay 1.0000
Pulse Width 14.5000
Acquisition Time 4.0894
Acquisition Date 2024-05-22T18:13:00
Modification Date 2024-05-23T05:41:00
Spectrometer Frequency 400.13
Spectral Width 8012.8
Lowest Frequency -1545.2
Nucleus 1H
Acquired Size 32768
Spectral Size 65536
Digital Resolution 0.12
1.02 1.00 1.03 1.04 2.05 1.12 1.23 2.20 1.32 0.90 3.24 2.05 9.29
0.0 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 -1.5
f1 (ppm)

^{13}C NMR of **9c**



9c

^{1}H NMR, $CDCl_3$, 400 MHz