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Supporting Information

A Diselenide Additive Enables a Photocatalytic Hydroalkoxylation of *gem*-Difluoroalkenes

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Table of Contents

General Synthetic Information

Air- and moisture-sensitive reactions were carried out in oven-dried one-dram vials sealed with poly(tetrafluoroethylene) (PTFE)-lined septa or glassware sealed with rubber septa under an atmosphere of dry nitrogen or argon. Plastic syringes equipped with stainless-steel needles were used to transfer air- and moisture-sensitive liquid reagents. Reactions were stirred using Teflon-coated magnetic stir bars, and elevated temperatures were maintained using thermostat-controlled heating mantles. Light-promoted reactions were conducted using an EvoluChem PhotoRedOx Box photoreactor equipped with a Kessil PR160 427 nm light with a peak intensity at 427 nm operating at 40 W. Organic solvents were removed using a rotary evaporator with a diaphragm vacuum pump. Thin-layer analytical chromatography was performed on silica gel UNIPLATE Silica Gel HLF UV254 plates, and spots were visualized by quenching of ultraviolet light (λ = 254 nm). Purification of products was accomplished by automated flash column chromatography on silica gel (VWR Common Silica Gel 60 Å, 40–60 μm) or C18 silica gel (Teledyne RediSep Gold C18 High Performance Columns, 100 Å, 20–40 μm).

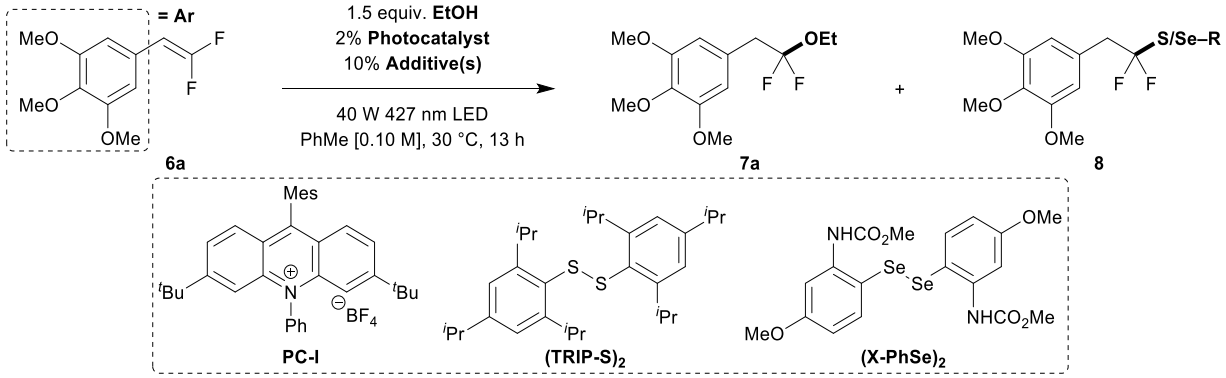
Unless otherwise noted, reagents were purchased from various commercial sources and used as received. Specifically, anhydrous PhMe (99.8%) was purchased from Thermo Fisher Scientific and stored in an N_2 glovebox. When commercially available, anhydrous grade alcohols were purchased and stored in an N_2 glovebox. When anhydrous alcohols were not available, the highest available grade of purity was purchased and used as received.

NMR spectra were recorded on Bruker DRX 500 MHz (^{1}H at 500 MHz, $^{13}C\{^{1}H\}$ at 126 MHz, and ^{19}F at 470 MHz) or Bruker Avance III 800 with a QCI cryoprobe (^{1}H at 800 and $^{13}C\{^{1}H\}$ at 201 MHz) nuclear magnetic resonance spectrometers. ^{1}H NMR spectra were calibrated against the peak of the residual $CHCl_3$ (7.26 ppm)

or DMF-d_7 (8.03 ppm). $^{13}C\{^1H\}$ NMR spectra were calibrated against the peak of $CDCl_3$ (77.2 ppm) or DMF-d_7 (163.2 ppm). ^{19}F NMR spectra were calibrated against the peak of $CFCl_3$ (0.0 ppm). NMR data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constant in hertz (Hz), integration. High-resolution mass determinations were obtained by electrospray ionization (ESI) or atmospheric-pressure chemical ionization (APCI) on a Waters LCT Premier mass spectrometer. Infrared spectra were measured on a PerkinElmer Spectrum Two Fourier Transform Infrared Spectrometer by drying samples on a diamond ATR sample base plate. Uncorrected melting points were measured on a Chemglass Digital Melting Point apparatus.

Reaction Development

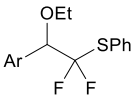
Table S1: Initial Reaction Development



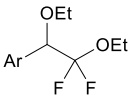
Entry	Photocatalyst (PC)	$E_{1/2}[PC^*/PC^{n-1}]$ (V)	Additive(s)	% Conv. 6a	% Yield 7a	% Yield 8
1	$\{Ir[dF(CF_3)ppy]_2$-(5,5'-$dCF_3bpy)\}PF_6$	–	10% $(PhS)_2$, 10% lutidine	77	11	5
2	$\{Ir[dF(CF_3)ppy]_2$-(5,5'-$dCF_3bpy)\}PF_6$	+ 1.30 [1]	$(PhS)_2$	47	12	6
3	$[Ir(dtbbpy)(ppy)_2]PF_6$	+ 0.28 [2]	$(PhS)_2$	33	0	0
4	Rose Bengal	+ 0.28 [3]	$(PhS)_2$	<5	0	0
5	Eosin Y (dibasic)	+ 0.45 [3]	$(PhS)_2$	<5	0	0
6	$\{Ir[dF(CF_3)ppy]_2$-(dtbbpy)$\}PF_6$	+ 0.83 [1]	$(PhS)_2$	48	5	2
7	**PC-I**	+ 1.70 [4]	$(PhS)_2$	45	20	5
8	**PC-I**	–	$(TRIP\text{-}S)_2$	>95	57	5
9	**PC-I**	–	$(PhSe)_2$	>95	70	0
10	**PC-I**	–	$(X\text{-}PhSe)_2$	26	10	0
11	**PC-I**	–	$(4\text{-}CF_3\text{-}PhSe)_2$	>95	30	0
12	**PC-I**	–	$(BnSe)_2$	>95	75	0
13	–	–	$(BnSe)_2$	0	0	0
14	**PC-I**	–	–	22	<5	0

Oven-dried one-dram vials equipped with magnetic stir bars were each charged with *gem*-difluoroalkene **6a** (0.023 g, 0.10 mmol), additive(s) (10 μmol), and photocatalyst (2.0 μmol). The vials were then sealed with PTFE-lined septa and subsequently evacuated and backfilled with dry argon (3x). Dry PhMe (1.0 mL, 0.10 M) and EtOH (8.7 μL, 0.15 mmol) were added *via* a syringe, and the vials were irradiated by a 40 W 427 nm LED lamp (entries 1–3, 6–14) or a 40 W 525 nm LED lamp (entries 4, 5) cooled by a fan (30 °C) for 13 h. Upon completion, an internal standard of α,α,α-trifluorotoluene (10 μL) was added to each crude reaction mixture, and the resultant mixtures were thoroughly mixed. Aliquots of each reaction mixture were subsequently transferred to NMR tubes and analyzed by ^{19}F NMR (470 MHz, PhMe): α,α,α-trifluorotoluene δ -66.0 (s); side product **8** (entries 1-7) δ -76.96 (t, J = 10.8 Hz); side product **8** (entry 8) δ -74.3 (m); product **7a** δ -77.0 (t, J = 10.9 Hz); *gem*-difluoroalkene **6a** δ -87.8 (dd, J = 35.8, 25.8 Hz), -89.4 (d, J = 35.9 Hz); [ns = 8; D1 = 5 s]. Spectra were baseline corrected, phased, and integrated using MestReNova. Additional observed side products are listed in Chart S1.

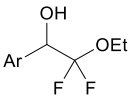
Chart S1. Additional Side Products from Table S1



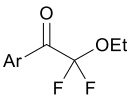
Entries 2, 7



Entries 2, 6, 7



Entry 2



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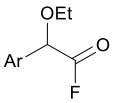
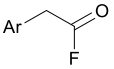
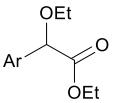


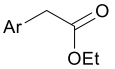
Entry 2



Entries 2, 6



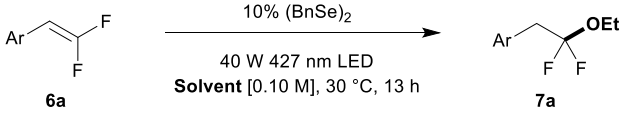
Entries 2, 6



Entries 2, 6, 7, 9, 12

Compound identities were assigned based on interpretations of mass spec data obtained by GC-MS. “Entry X” indicates the reaction(s) from Table S1 in which the compound was observed.

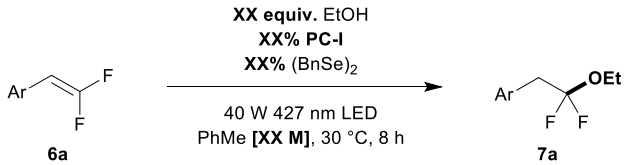
Table S2: Solvent Screening



Entry	Solvent	% Conv. 6a	% Yield 7a
1	PhMe	>95	75
2	$PhCF_3$	Full	<5
3	DCE	Full	0
4	THF	0	0
5	MeCN	0	0
6	DMF	0	0

Oven-dried one-dram vials equipped with magnetic stir bars were each charged with *gem*-difluoroalkene **6a** (0.023 g, 0.10 mmol), 1,2-dibenzyldiselane (3.4 mg, 10 μmol), and **PC-I**: 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (1.2 mg, 2.0 μmol). The vials were then sealed with PTFE-lined septa and subsequently evacuated and backfilled with dry argon (3x). Dry PhMe (1.0 mL, 0.10 M) and EtOH (8.7 μL, 0.15 mmol) were added *via* a syringe, and the vials were irradiated by a 40 W 427 nm LED lamp cooled by a fan (30 °C) for 13 h. Upon completion, an internal standard of α,α,α-trifluorotoluene (10 μL) (entries 1, 3-6) or fluorobenzene (10 μL) (entry 2) was added to each crude reaction mixture, and the resultant mixtures were thoroughly mixed. Aliquots of each reaction mixture were subsequently transferred to NMR tubes and analyzed by ^{19}F NMR (470 MHz, PhMe): α,α,α-trifluorotoluene δ -66.0 (s); product **7a** δ -77.0 (t, *J* = 10.9 Hz); *gem*-difluoroalkene **6a** δ -87.8 (dd, *J* = 35.8, 25.8 Hz), -89.4 (d, *J* = 35.9 Hz); ^{19}F NMR (470 MHz, $PhCF_3$): product **7a** δ -76.4 – -76.5 (m); fluorobenzene δ -113.0 (s); ^{19}F NMR (470 MHz, THF): α,α,α-trifluorotoluene δ -66.0 (s); *gem*-difluoroalkene **6a** δ -88.1 (dd, *J* = 37.5, 27.0 Hz), -90.1 (d, *J* = 37.5 Hz); ^{19}F NMR (470 MHz, MeCN): α,α,α-trifluorotoluene δ -66.0 (s); *gem*-difluoroalkene **6a** δ -87.7 (dd, *J* = 37.5, 26.7 Hz), -89.7 (d, *J* = 37.2 Hz); ^{19}F NMR (470 MHz, DMF): α,α,α-trifluorotoluene δ -66.0 (s); *gem*-difluoroalkene **6a** δ -88.4 (d, *J* = 32.1 Hz), -90.5 (d, *J* = 37.7 Hz); [ns = 8; D1 = 5 s]. Spectra were baseline corrected, phased, and integrated using MestReNova.

Table S3: Optimization of Reagent Loading and Reaction Concentration on a 0.50 mmol Scale



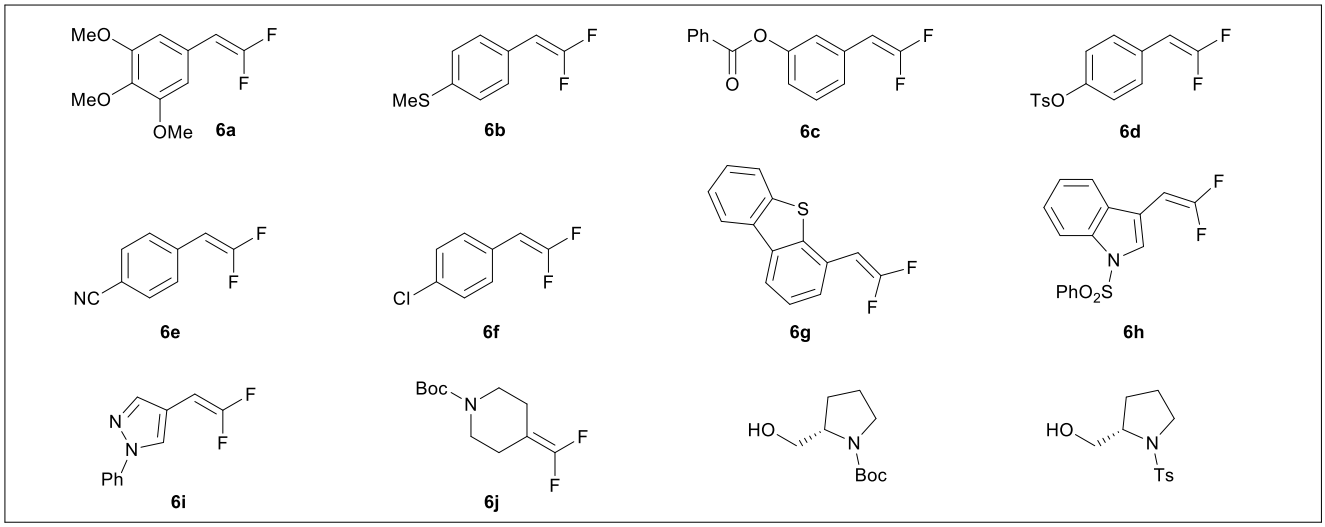
6a **7a**

Entry	Equiv. EtOH	% PC, [PC]	% $(BnSe)_2$	[6a]	% Conv. 6a	% Yield 7a
1	1.1	2.0%, 5.0 mM	5.0%	0.25 M	66	61
2	1.5	2.0%, 5.0 mM	5.0%	0.25 M	67	64
3	2.0	2.0%, 5.0 mM	5.0%	0.25 M	71	68
4	4.0	2.0%, 5.0 mM	5.0%	0.25 M	22	19
5	1.5	0.6%, 1.5 mM	5.0%	0.25 M	90	82
6	1.5	1.0%, 2.5 mM	5.0%	0.25 M	88	81
7	**1.5**	**1.2%, 3.0 mM**	**5.0%**	**0.25 M**	**88**	**85**
8	1.5	1.4%, 3.5 mM	5.0%	0.25 M	80	72
9	1.5	1.2%, 1.7 mM	5.0%	0.14 M	57	49
10	1.5	1.2%, 2.4 mM	5.0%	0.20 M	40	34
11	1.5	1.2%, 3.5 mM	5.0%	0.30 M	20	16
12	1.5	1.2%, 4.3 mM	5.0%	0.36 M	64	57
13	1.5	0.8%, 3 mM	5.0%	0.36 M	Full	78
14	1.5	2.1%, 3 mM	5.0%	0.14 M	90	82
15	1.5	1.2%, 3.0 mM	2.5%	0.25 M	48	45
16	1.5	1.2%, 3.0 mM	10%	0.25 M	86	82

Oven-dried one-dram vials equipped with magnetic stir bars were each charged with *gem*-difluoroalkene **6a** (0.115 g, 0.50 mmol), 1,2-dibenzyldiselane (see table), and **PC-1**: 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (see table). The vials were then sealed with PTFE-lined septa and subsequently evacuated and backfilled with dry argon (3x). Dry PhMe (see table) and EtOH (see table) were added *via* a syringe, and the vials were irradiated by a 40 W 427 nm LED lamp cooled by a fan (30 °C) for 8 h. Upon completion, an internal standard of α,α,α-trifluorotoluene (10 µL) was added to each crude reaction mixture, and the resultant mixtures were thoroughly mixed. Aliquots of each reaction mixture were subsequently transferred to NMR tubes and analyzed by ^{19}F NMR (470 MHz, PhMe): α,α,α-trifluorotoluene δ -66.0 (s); product **7a** δ -77.0 (t, J = 10.9 Hz); *gem*-difluoroalkene **6a** δ -87.8 (dd, J = 35.8, 25.8 Hz), -89.4 (d, J = 35.9 Hz); [ns = 8; D1 = 5 s]. Spectra were baseline corrected, phased, and integrated using MestReNova.

Synthesis and Characterization

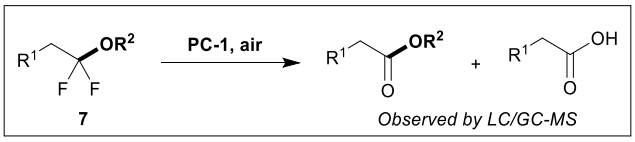
Chart S2. Prepared Substrates

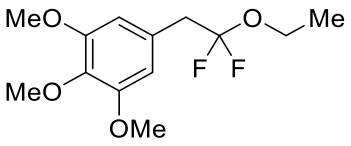


Preparation and Characterization of Substrates: *gem*-Difluoroalkenes **6a**–**6g** and **6i**,[5] **6h**,[6] and **6j** [7] were prepared according to previously reported procedures. Alcohols *tert*-butyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate [8] and (*S*)-(1-tosylpyrrolidin-2-yl)methanol [9] were prepared according to previously reported procedures.

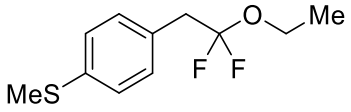
General Procedure A, for the Photochemical Hydroalkoxylation of *gem*-Difluoroalkenes: An oven-dried one-dram vial equipped with a magnetic stir bar was charged with *gem*-difluoroalkene (0.50 mmol, 1.0 equiv), 1,2-dibenzyldiselane (0.025 mmol, 0.050 equiv), and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (6.0 μmol, 0.012 equiv). When relevant, solid alcohol (1.0 mmol, 1.5 equiv) was then added. The system was sealed with PTFE-lined septa and subsequently evacuated and backfilled with dry N_2 or argon (3x). Dry PhMe (0.50 M) and, when relevant, liquid alcohol (1.0 mmol, 1.5 equiv) was added *via* a syringe, and the vial was irradiated by a 40 W 427 nm LED lamp cooled by a fan (30 °C). Upon completion, the reaction was immediately filtered through a pad of silica using Et_2O (~100 mL) to remove photocatalyst, as some α,α-difluorinated products degraded to form carboxylic acid and ester side-products when exposed to air in the presence of the photocatalyst (Scheme S1). The resultant filtrate was then concentrated onto diatomaceous earth and purified by normal-phase flash chromatography to provide the desired product in >95% purity.

Scheme S1. Common Degradation Side-Products

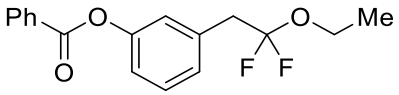




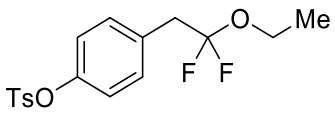
5-(2-ethoxy-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (**7a**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and pentane (0 → 50%) to furnish desired product **7a** as a yellow oil (0.123 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (s, 2H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 6H), 3.83 (s, 3H), 3.16 (t, *J* = 10.8 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 137.3, 128.4, 124.5 (t, *J* = 261.9 Hz), 107.4, 60.9, 59.1 (t, *J* = 7.0 Hz), 56.1, 42.4 (t, *J* = 31.3 Hz), 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.28 (t, *J* = 11.0 Hz, 2F). IR (Film) 2941, 2988, 1593, 1509, 1461, 1424, 1325, 1236, 1128, 1028 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{13}H_{18}F_2O_4$ [M + H]$^{+}$ 276.1173, found 276.1173.



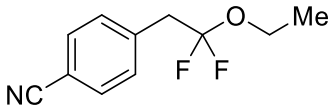
(4-(2-ethoxy-2,2-difluoroethyl)phenyl)(methyl)sulfane (**7b**): Following general procedure A, *gem*-difluoroalkene **6b** (0.093 g, 0.50 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 10%) to furnish desired product **7b** as a colorless oil (0.108 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 4H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.21 (t, *J* = 10.8 Hz, 2H), 2.49 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 137.5, 130.8, 129.6, 126.6, 124.4(t, *J* = 262.8 Hz), 59.1 (t, *J* = 7.0 Hz), 41.5 (t, *J* = 31.3 Hz), 15.8, 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.41 (t, *J* = 11.4 Hz, 2F). IR (Film) 2986, 2921, 1496, 1350, 1287, 1269, 1251, 1234, 1018, 817 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{11}H_{14}F_2OS$ [M]$^{+}$ 232.0733, found 232.0719.



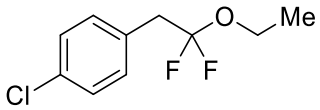
4-(2-ethoxy-2,2-difluoroethyl)phenyl benzoate (**7c**): Following general procedure A, *gem*-difluoroalkene **6c** (0.130 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using acetone and pentane (0 → 20%) to furnish desired product **7c** as a colorless oil (0.118 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.68 – 7.64 (m, 1H), 7.54 (td, *J* = 8.0, 1.9 Hz, 2H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.18 (m, 3H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 10.7 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.2, 150.9, 134.5, 133.7, 130.3, 129.6, 129.3, 128.7, 128.0, 124.3 (t, *J* = 263.2 Hz), 123.7, 120.8, 59.2 (t, *J* = 7.0 Hz), 41.9 (t, *J* = 31.6 Hz), 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.02 (t, *J* = 9.9 Hz, 2F). IR (Film) 3064, 2936, 1738, 1490, 1449, 1266, 1236, 1148, 1025, 706cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{17}H_{16}F_2O_3$ [M – F]$^{+}$ 287.1083, found 287.1074.



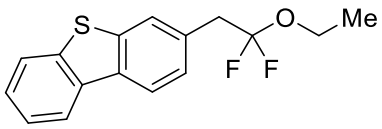
4-(2-ethoxy-2,2-difluoroethyl)phenyl 4-methylbenzenesulfonate (**7d**): Following general procedure A, *gem*-difluoroalkene **6d** (0.155 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 40%) to furnish desired product **7d** as a colorless solid (0.143 g, 80%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.93 (d, *J* = 8.3 Hz, 2H), 3.88 (q, *J* = 7.1 Hz, 2H), 3.18 (t, *J* = 10.6 Hz, 2H), 2.45 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 149.0, 145.5, 132.6, 132.0, 131.7, 129.9, 128.7, 124.2 (t, *J* = 262.0 Hz), 122.2, 59.2 (t, *J* = 6.9 Hz), 41.6 (t, *J* = 31.6 Hz), 21.8, 15.00. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.32 (t, *J* = 10.7 Hz, 2F). IR (Film) 2919, 1505, 1374, 1199, 1178, 1155, 1094, 1020, 865 cm $^{-1}$. MP 80–88 °C. HRMS (ESI)$^{+}$ *m/z* calc'd $C_{17}H_{18}F_2O_4S$ [M – F]$^{+}$ 337.0910, found 337.0904.



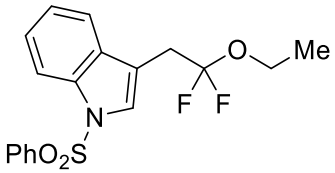
4-(2-ethoxy-2,2-difluoroethyl)benzonitrile (**7e**): Following general procedure A, *gem*-difluoroalkene **6e** (0.083 g, 0.50 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 10%) to furnish desired product **7e** as a colorless oil (0.094 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 3.89 (q, *J* = 7.1 Hz, 2H), 3.28 (t, *J* = 10.3 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.2, 131.2, 126.0, 123.8 (t, *J* = 261.9 Hz), 118.8, 111.5, 59.3 (t, *J* = 6.9 Hz), 42.3 (t, *J* = 31.8 Hz), 14.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.51 – -73.67 (m, 2F). IR (Film) 2920, 2850, 2231, 1612, 1350, 1275, 1251, 1024, 827, 749 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{11}H_{11}F_2NO$ [M + H]$^{+}$ 212.0887, found 212.0883.



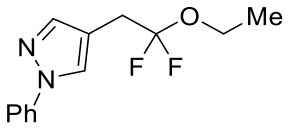
1-chloro-4-(2-ethoxy-2,2-difluoroethyl)benzene (**7f**): Following general procedure A, *gem*-difluoroalkene **6f** (0.087 g, 0.50 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 10%) to furnish desired product **7f** as a colorless oil (0.086 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 6.8 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 3.90 (q, *J* = 7.2 Hz, 2H), 3.20 (t, *J* = 10.5 Hz, 2H), 1.22 (t, *J* = 6.9 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 133.4, 131.8, 131.3, 128.5, 124.3 (t, *J* = 261.8 Hz), 59.2 (t, *J* = 7.1 Hz), 41.5 (t, *J* = 31.6 Hz), 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.57 (t, *J* = 14.9 Hz, 2F). IR (Film) 2987, 2936, 1494, 1350, 1291, 1251, 1271, 1018, 843, 801 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{11}H_{14}F_2OS$ [M + H]$^{+}$ 221.0545, found 221.0550.



3-(2-ethoxy-2,2-difluoroethyl)dibenzo[*b*,*d*]thiophene (**7g**): Following general procedure A, *gem*-difluoroalkene **6g** (0.123 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 10%) to furnish desired product **7g** as a colorless oil (0.122 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.00 (m, 2H), 7.93 – 7.83 (m, 1H), 7.62 – 7.32 (m, 4H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.57 (t, *J* = 10.7 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.1, 139.2, 136.0, 128.9, 127.5, 126.9, 124.7, 124.3 (t, *J* = 260.9 Hz), 122.8, 121.8, 120.8, 59.3 (t, *J* = 6.9 Hz), 41.3 (t, *J* = 32.1 Hz), 15.0. ^{19}F NMR (470 MHz, CDCl3) δ -72.98 (t, *J* = 10.7 Hz, 2F). IR (Film) 3062, 2984, 1732, 1443, 1403, 1260, 1155, 1128, 1093, 750 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{16}H_{14}F_2OS$ [M]$^{+}$ 292.0733, found 292.0703.

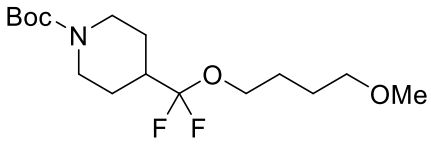


3-(2-ethoxy-2,2-difluoroethyl)-1-(phenylsulfonyl)-1H-indole (**7h**): Following general procedure A, *gem*-difluoroalkene **6h** (0.160 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 13.5 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 35%) to furnish desired product **7h** as a viscous, colorless oil (0.158 g, 90%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.63 – 7.48 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.29 (m, 1H), 7.29 – 7.17 (m, 1H), 3.90 (q, *J* = 7.1 Hz, 2H), 3.32 (t, *J* = 10.4 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 138.3, 135.1, 133.9, 131.0, 129.3, 126.9, 125.8, 124.9, 124.3 (t, *J* = 261.9 Hz), 123.4, 120.1, 114.4, 113.7, 59.3 (t, *J* = 6.9 Hz), 32.3 (t, *J* = 33.5 Hz), 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.96 (t, *J* = 11.4 Hz, 2F). IR (Film) 2989, 1448, 1373, 1274, 1247, 1177, 1122, 1086, 1030, 977 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{18}H_{17}F_2NO_3S$ [M]$^{+}$ 365.0897, found 365.0889.

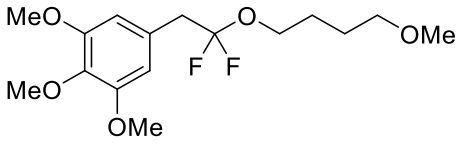


4-(2-ethoxy-2,2-difluoroethyl)-1-phenyl-1*H*-pyrazole (**7i**): Following general procedure A, *gem*-difluoroalkene **6i** (0.103 g, 0.500 mmol) was reacted with ethanol (43.8 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 18 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 10%) to furnish desired product **7i** as a colorless oil (0.106 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.70 – 7.65 (m, 3H), 7.46 – 7.39 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.20 (t, *J* = 10.7 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 140.1, 129.4, 126.7, 126.4, 124.2 (t, *J* = 263.3 Hz), 119.0, 114.3, 59.2 (t, *J* = 7.1 Hz), 31.7 (t, *J* = 33.3 Hz), 15.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.20 (t, *J* = 10.9 Hz, 2F). IR (Film)

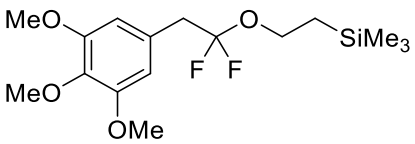
2987, 2936, 1601, 1505, 1402, 1279, 1246, 1026, 756, 691 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{13}H_{14}F_2N_2O$ [M + H]$^{+}$ 253.1145, found 253.1152.



***tert*-butyl 4-(difluoro(4-methoxybutoxy)methyl)piperidine-1-carboxylate** (**7j**): Following general procedure A, *gem*-difluoroalkene **6j** (0.117 g, 0.500 mmol) was reacted with 4-methoxybutan-1-ol (84.0 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 13.5 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 40%) to furnish desired product **7j** as a pale yellow oil (0.114 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.14 (s, 2H), 3.83 (t, *J* = 5.8 Hz, 2H), 3.37 (t, *J* = 5.9 Hz, 1H), 3.31 (d, *J* = 1.5 Hz, 3H), 2.62 (s, 2H), 2.04 – 1.90 (m, 1H), 1.77 (d, *J* = 13.2 Hz, 2H), 1.69 – 1.55 (m, 4H), 1.46 – 1.30 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.8, 125.8 (t, *J* = 262.9 Hz), 79.6, 72.2, 62.7 (t, *J* = 6.6 Hz), 58.7, 43.4, 42.3 (t, *J* = 28.8 Hz), 28.5, 26.1, 26.0, 25.3. ^{19}F NMR (470 MHz, $CDCl_3$) δ -82.52 (s, 2F). IR (Film) 2960, 2935, 2867, 1695, 1423, 1366, 1328, 1236, 1157, 1040 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{11}H_{20}F_2NO_2$ [M + H – F]$^{+}$ 218.1556, found 218.1555.

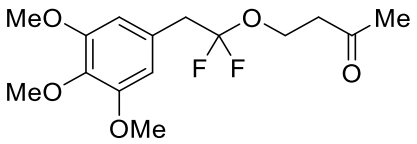


5-(2,2-difluoro-2-(4-methoxybutoxy)ethyl)-1,2,3-trimethoxybenzene (**7k**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with 4-methoxybutan-1-ol (84 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 16 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish desired product **7k** as a colorless oil (0.122 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 2H), 3.91 – 3.74 (m, 11H), 3.34 (t, *J* = 6.0 Hz, 2H), 3.29 (s, 3H), 3.15 (t, *J* = 10.7 Hz, 2H), 1.67 – 1.57 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.9, 137.3, 128.3, 124.3 (t, *J* = 262.1 Hz), 107.4, 72.7, 72.1, 70.6, 62.8 (t, *J* = 6.5 Hz), 60.9, 58.6, 56.1, 42.3 (t, *J* = 31.4 Hz), 26.5, 26.1, 26.0. ^{19}F NMR (470 MHz, CDCl3) δ -74.12 (t, *J* = 10.9 Hz, 2F). IR (Film) 2939, 2839, 1732, 1507, 1423, 1318, 1239, 1123, 1007, 971 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{16}H_{24}F_2O_5$ [M – F]$^{+}$ 315.1608, found 315.1215.

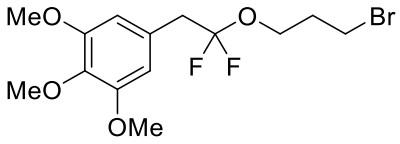


(2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)ethyl)trimethylsilane (**7l**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with 2-(trimethylsilyl)ethan-1-ol (108 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and further purified by normal-phase flash chromatography using EtOAc and pentane (0 → 20%) to obtain a mixture of unreacted **6a** and desired product **7l**. This starting material and product mixture was then purified by normal-phase preparative TLC using EtOAc and pentane (20%) to furnish desired product **7l** as a pale brown oil (0.124 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (s, 2H), 3.96 (t, *J* = 8.2 Hz, 2H),

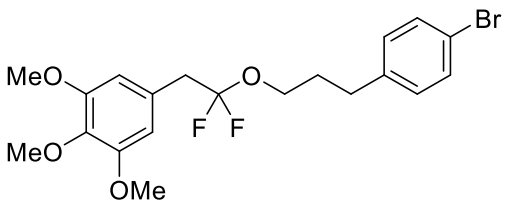
3.85 (s, 6H), 3.83 (s, 3H), 3.15 (t, *J* = 10.7 Hz, 2H), 0.94 (t, *J* = 8.3 Hz, 2H), -0.00 (s, 9H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.0, 137.3, 128.4, 124.5 (t, *J* = 261.7 Hz), 107.5, 61.2 (t, *J* = 7.2 Hz), 60.9, 56.1, 42.6 (t, *J* = 31.5 Hz), 17.8, -1.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.82 (t, *J* = 10.0 Hz, 2F). IR (Film) 2954, 2841, 1593, 1463, 1325, 1278, 1246, 1130, 1028, 838 cm $^{-1}$. HRMS $(APCI)^+$ *m/z* calc'd $C_{16}H_{26}F_2O_4Si$ $[M]^+$ 348.1568, found 348.1579.



4-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)butan-2-one (**7m**): Following general procedure A, *gem*-difluoroalkene **6a** 0.115 g, 0.500 mmol) was reacted with 4-hydroxybutan-2-one (65 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 16 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish desired product **7m** as a colorless oil (0.081 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.46 (s, 2H), 4.13 (t, *J* = 6.2 Hz, 2H), 3.87 – 3.81 (m, 9H), 3.14 (t, *J* = 10.8 Hz, 2H), 2.69 (t, *J* = 6.2 Hz, 2H), 2.11 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 205.9, 153.0, 137.3, 128.0, 124.3 (t, *J* = 263.8 Hz),107.4, 60.9, 58.5 (t, *J* = 6.3 Hz), 56.1, 43.0, 42.2 (t, *J* = 31.0 Hz), 30.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.48 (t, *J* = 11.4 Hz, 2F). IR (Film) 2941, 2840, 1733, 1591, 1508, 1320, 1241, 1125, 1007, 838 cm $^{-1}$. HRMS $(APCI)^+$ *m/z* calc'd $C_{15}H_{20}F_2O_5$ $[M - F]^+$ 299.1295, found 299.1378.

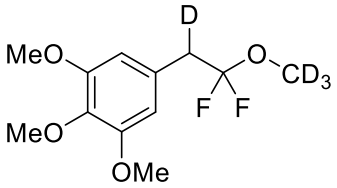


5-(2-(3-bromopropoxy)-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (**7n**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with 3-bromopropan-1-ol (65 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 16 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish desired product **7n** as a colorless oil (0.099 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 2H), 3.99 (t, *J* = 5.6 Hz, 2H), 3.91 – 3.82 (m, 9H), 3.40 (t, *J* = 6.1 Hz, 2H), 3.17 (t, *J* = 10.7 Hz, 2H), 2.12 (p, *J* = 6.3 Hz, 2H).$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.0, 137.4, 128.1, 126.5, 124.4 (t, *J* = 261.1 Hz), 122.3, 107.4, 61.0, 60.8 (t, *J* = 12.7 Hz), 56.2, 42.2 (t, *J* = 30.9 Hz), 32.4, 29.4.^{19}F NMR (470 MHz, CDCl3) δ -74.13 – -74.29 (m, 2F).IR (Film) 2960, 2940, 2839, 1733, 1590, 1459, 1240, 1125, 1008, 974 cm $^{-1}$. HRMS $(APCI)^+$ *m/z* calc'd $C_{14}H_{19}BrF_2O_4$ $[M - F]^+$ 349.0451, found 349.0465.

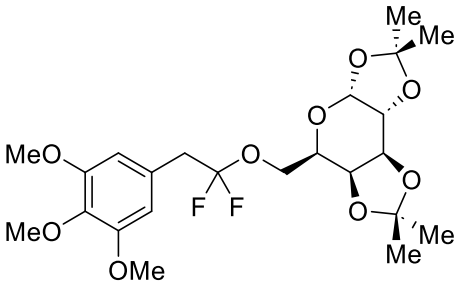


5-(2-(3-(4-bromophenyl)propoxy)-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (**7o**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with 3-(4-bromophenyl)propan-1-ol (0.12 mL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 8 h. The

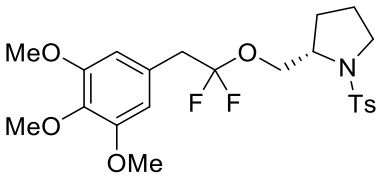
material was isolated according to the general procedure and purified by normal-phase flash chromatography using Et_2O and pentane (0 → 20%) to furnish desired product **7o** as a yellow oil (0.163 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 2H), 3.90 – 3.80 (m, 11H), 3.18 (t, *J* = 10.5 Hz, 2H), 2.59 (t, *J* = 7.6 Hz, 2H), 1.94 – 1.83 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.1, 140.2, 137.4, 131.6, 130.3, 128.4, 124.3 (t, *J* = 262.1 Hz), 119.8, 107.5, 61.8 (t, *J* = 6.4 Hz), 61.0, 56.2, 42.7, 42.3 (t, *J* = 31.2 Hz), 42.2, 31.4, 30.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -74.14 (t, *J* = 11.2 Hz, 2F). IR (Film) 2935, 2840, 1591, 1460, 1324, 1233, 1127, 1010, 835, 707 cm $^{-1}$. HRMS (APCI)$^+$ *m/z* calc'd $C_{20}H_{32}F_2O_9$ [M – F]$^+$ 425.0764, found 425.0766.



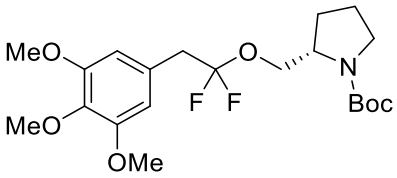
5-(2,2-difluoro-2-(methoxy-d$_3$)ethyl-1-d)-1,2,3-trimethoxybenzene (**7p**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with methanol-d$_4$ (31 µL, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 16 h. The material was isolated according to the general procedure, then subjected to normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish the desired product **7p** as a pale yellow oil (0.130 g, 98%).^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (s, 2H), 3.83 (m, 9H), 3.14 (t, *J* = 10.5 Hz, 1H). ^{2}H NMR (77 MHz, $CDCl_3$) δ 5.83 (s, 3^{2}H), 5.50 (s, 1^{2}H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 137.3, 128.1, 124.5 (t, *J* = 262.5 Hz), 107.4, 60.8, 56.1, 42.0 – 41.4 (m). ^{19}F NMR (470 MHz, $CDCl_3$) -76.70 – -76.84 (m, 2F). IR (Film) 2942, 2841, 1591, 1459, 1422, 1324, 1240, 1126, 1095, 1008 cm $^{-1}$. HRMS (APCI)$^+$ *m/z* calc'd $C_{12}H_{12}D_4F_2O_4$ [M + H]$^+$ 267.1346, found 267.1338.



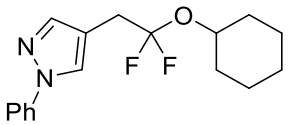
(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-5-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (**7q**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (195 mg, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 16 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish desired product **7q** as a yellow oil (0.157 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 – 6.46 (m, 2H), 5.55 – 5.45 (m, 1H), 4.62 – 4.49 (m, 1H), 4.35 – 4.24 (m, 1H), 4.16 – 4.09 (m, 1H), 4.06 – 3.94 (m, 2H), 3.94 – 3.79 (m, 10H), 3.17 (t, *J* = 10.7 Hz, 2H), 1.50 – 1.37 (m, 6H), 1.35 – 1.26 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.9, 137.2, 128.1, 124.4 (t, *J* = 263.1 Hz), 109.6, 108.8, 107.4, 96.3, 71.0, 70.7, 70.5, 66.6, 62.4 (t, *J* = 6.2 Hz), 60.8, 56.1, 42.1 (t, *J* = 30.7 Hz), 26.0, 25.9, 25.0, 24.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.78 – -75.01 (m, 2F). IR (Film) 2988, 2939, 1592, 1460, 1325, 1212, 1127, 1070, 1005, 888 cm $^{-1}$. HRMS (APCI)$^+$ *m/z* calc'd $C_{23}H_{32}F_2O_9$ [M – F]$^+$ 471.2030, found 471.2019.



(*S*)-2-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)-1-tosylpyrrolidine (**7r**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with (*S*)-(1-tosylpyrrolidin-2-yl)methanol (0.191 g, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 80%) to furnish desired product **7r** as a pale yellow oil (0.123 g, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 6.49 (s, 2H), 4.08 (dd, *J* = 10.0, 3.7 Hz, 1H), 3.87 – 3.79 (m, 10H), 3.73 (tt, *J* = 7.6, 3.3 Hz, 1H), 3.34 – 3.30 (m, 1H), 3.17 (t, *J* = 10.6 Hz, 2H), 3.07 (dt, *J* = 9.5, 7.1 Hz, 1H), 2.42 (s, 2H), 1.75 – 1.62 (m, 2H), 1.59 – 1.40 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 143.7, 137.4, 134.2, 129.8, 128.1, 127.6, 124.3 (t, *J* = 263.0 Hz), 107.5, 65.3 (t, *J* = 5.41 Hz), 60.9, 58.3, 56.2, 49.3, 42.2 (t, *J* = 31.0 Hz), 28.5, 23.9, 21.6. ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.11 (dt, *J* = 141.7, 10.8 Hz, 1F), -73.78 (dt, *J* = 141.3, 10.8 Hz, 1F). IR (Film) 3019, 2942, 1594, 1509, 1463, 1326, 1234, 1161, 1129, 754 cm $^{-1}$. HRMS (APCI)$^{+}$ *m/z* calc'd $C_{23}H_{29}F_2NO_6S$ $[M + H]^{+}$ 486.1762, found 486.1755.



***tert*-butyl (*S*)-2-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)pyrrolidine-1-carboxylate** (**7s**): Following general procedure A, *gem*-difluoroalkene **6a** (0.115 g, 0.500 mmol) was reacted with *tert*-butyl (*S*)-2-(hydroxymethyl)pyrrolidine-1-carboxylate (0.151 g, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and purified by reverse-phase flash chromatography using MeCN and 0.1% AcOH in H_2O (10 → 100%) to furnish desired product **7s** as a pale yellow oil (0.153 g, 71%). ^{1}H NMR (500 MHz, DMF-d_7, 60 °C) δ 6.70 (s, 2H), 4.06 – 3.95 (m, 1H), 3.92 (d, *J* = 7.0 Hz, 2H), 3.86 (s, 6H), 3.76 (s, 3H), 3.32 (t, *J* = 10.1 Hz, 3H), 3.26 – 3.11 (m, 1H), 2.02 – 1.93 (m, 1H), 1.91 – 1.68 (m, 3H), 1.46 (s, 9H).^{13}C{^{1}H} NMR (126 MHz, DMF-d_7, 62 °C) δ 155.1, 154.4, 139.3, 129.5, 125.97 (t, *J* = 261.9 Hz), 109.7, 79.8, 64.9, 61.0, 57.2, 47.8, 42.6 (t, *J* = 31.2 Hz), 29.0, 24.2. ^{19}F NMR (470 MHz, DMF-d_7, 61 °C) δ -71.68 (d, *J* = 143.2 Hz, 1F), -72.42 (d, *J* = 144.6 Hz, 1F). ^{19}F NMR (470 MHz, DMF-d_7, 19 °C) δ -71.45 – -72.79 (m, 2F). IR (Film) 2974, 2941, 1694, 1593, 1461, 1393, 1325, 1236, 1129, 1032 cm $^{-1}$. HRMS (ESI)$^{+}$ *m/z* calc'd $C_{21}H_{31}F_2NO_6$ $[M - C_5H_9O_2]^{+}$ 332.1673, found 332.1698.



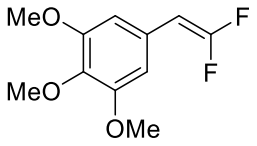
4-(2-(cyclohexyloxy)-2,2-difluoroethyl)-1-phenyl-1H-pyrazole (**7t**): Following general procedure A, *gem*-difluoroalkene **6i** (0.103 g, 0.500 mmol) was reacted with cyclohexanol (0.075 g, 0.750 mmol) in the presence of 1,2-dibenzyldiselane (8.5 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (3.4 mg, 6.0 µmol) using a 40 W 427 nm LED cooled by a fan for 24 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0 → 20%) to furnish desired product **7t** as a pale yellow oil (0.115 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.86 (s, 1H), 7.69 – 7.66 (m, 3H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 6.3 Hz, 1H), 4.28 (tt, *J* = 9.0, 3.9 Hz, 1H), 3.20 (t, *J* = 10.5 Hz, 2H), 1.89 – 1.85 (m, 2H), 1.75 – 1.71 (m, 2H), 1.54 – 1.40 (m, 3H), 1.37 – 1.29 (m, 2H), 1.27 – 1.19 (m, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 142.0, 140.2, 129.5, 126.7, 126.4, 124.7 (t, *J* = 261.3 Hz), 119.0, 114.7, 73.2, 33.4, 32.2 (t, *J* = 33.7 Hz), 25.4, 24.0. ^{19}F NMR (470 MHz, $CDCl_3$) δ -72.13 (t, *J* = 11.4 Hz, 2F). IR (Film) 2939, 2860, 1601, 1506, 1402, 1291, 1239, 1093, 1012, 954 cm^{-1}. HRMS $(APCI)^+$ *m/z* calc'd $C_{17}H_{20}F_2N_2O$ $[M + H]^+$ 307.1622, found 307.1660.

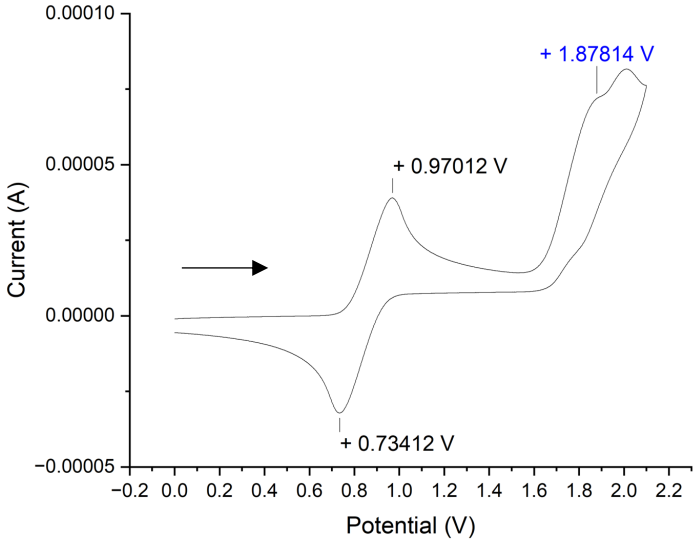
Cyclic Voltammetry

Samples were prepared with anhydrous, degassed THF (5 mL), tetra-*n*-butylammonium hexafluorophosphate (0.10 M), ferrocene (3 μmol), and analyte (5 μmol). A three-electrode configuration was employed, which consisted of a glassy carbon working electrode (3 mm diameter disk), platinum wire counter electrode, and silver wire pseudoreference electrode. Cyclic voltammograms were collected under an N_2 atmosphere (glovebox) with a Gamry Interface 1000 potentiostat at a scan rate of 100 mV/s. Data was analyzed using OriginPro software. All reported peak potentials (E_p) were referenced to the $E_{1/2}$ value for the reversible Fc/Fc^+ redox couple and represent the average of two independent measurements (rounded to the nearest 0.1 V), while pictured cyclic voltammograms represent one of the two independent measurements. Black arrows on the graphs indicate the scan direction.

Cyclic Voltammogram of *gem*-Difluoroalkene 6a

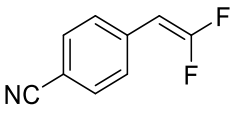


6a

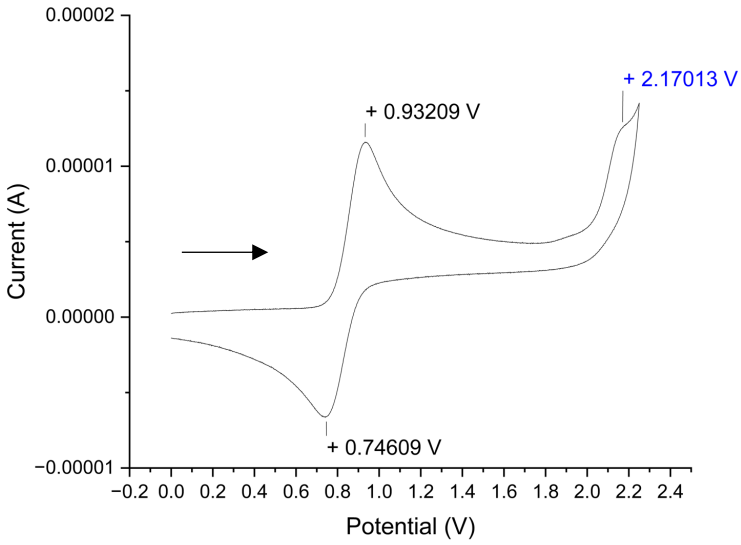


6a (vs. Fc/Fc^+): E_p = +1.0 V

Cyclic Voltammogram of *gem*-Difluoroalkene 6e

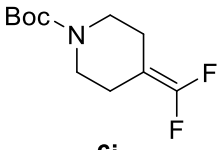


6e

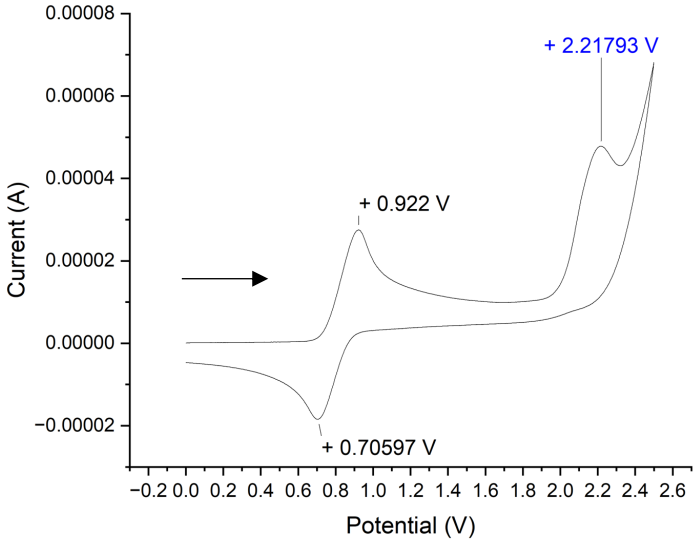


6e (vs. Fc/Fc$^+$): E_p = +1.3 V

Cyclic Voltammogram of *gem*-Difluoroalkene 6j

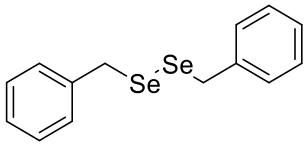


6j

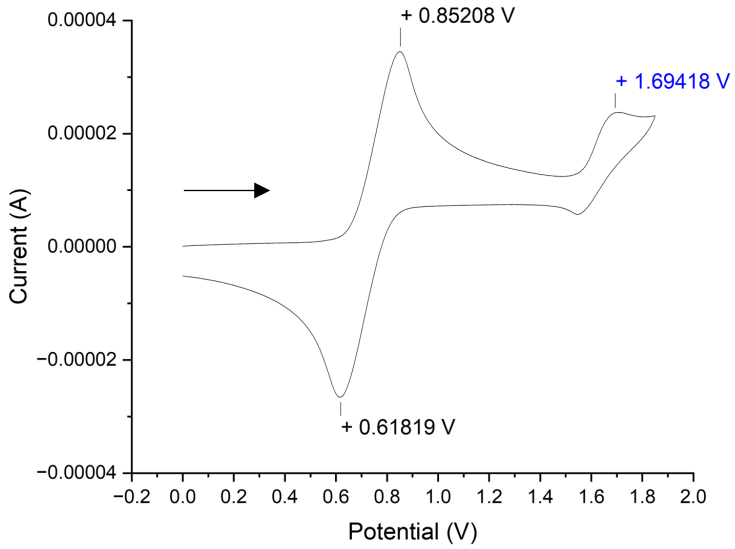


6j (vs. Fc/Fc$^+$): E_p = +1.4 V

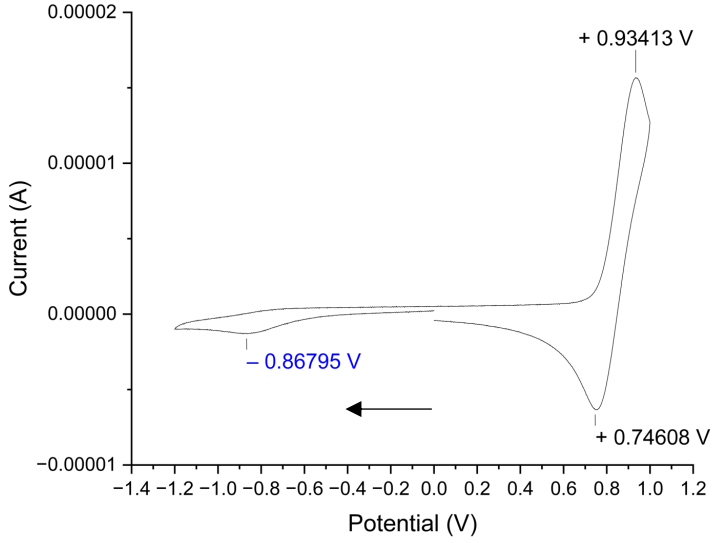
Cyclic Voltammograms of 1,2-Dibenzyldiselane



$(BnSe)_2$



$(BnSe)_2$ (vs. Fc/Fc^+): E_p = +1.0 V



$(BnSe)_2$ (vs. Fc/Fc^+): E_p = –1.7 V

Fluorescence Quenching Experiments

Fluorescence intensity measurements were measured using a BioTek Synergy NEO2 microplate reader using the instrument's monochromator functionality at an excitation wavelength of 420 nm (<6 nm bandwidth) and an emission detection wavelength of 517 nm, which correspond to the absorption and emission maxima for **PC-I**, respectively.[4] Specifically, samples were prepared in an N_2 glovebox in polypropylene opaque flat-bottomed 96-well plates. For a given experiment, one well contained **PC-I** (0.10 mM) alone in anhydrous MeCN or PhMe (150 µL total). The subsequent wells (3–6 total) contained increasing concentrations of quencher (see below for specific values) in addition to **PC-I** (0.10 mM) in anhydrous MeCN or PhMe (150 µL total). All wells were repeated (3–6 replicants each per experiment). The 96-well plate was sealed with optical adhesive film (Applied Biosystems MicroAmp) prior to removal from the glovebox, and the plate was read within 5 minutes of application of the film to prevent solvent condensation.

The recorded single-point fluorescence intensities were then used to construct Stern-Volmer plots according to the following equation:

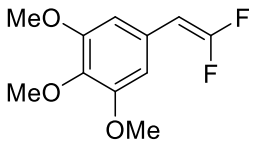
$$\frac{I°}{I} = 1 + k_q\tau[Q]$$

Where $I°$ is the recorded fluorescence intensity in the absence of quencher, I is the recorded fluorescence intensity in the presence of quencher, $[Q]$ is the concentration of quencher, τ is the literature-reported value for the lifetime of the excited state **PC-I** in the absence of quencher (14.4 ns),[4] and k_q is the bimolecular quenching constant. Specifically, the "y-values" ($\frac{I°}{I}$) were obtained by dividing each replicant fluorescence intensity value from the wells containing **PC-I** alone by each replicant fluorescent intensity value from the wells containing quencher. This treatment of data better incorporates error into the full dataset and results in an expansion of data such that the total number of "y-values" is the square of the number of experimentally determined fluorescence intensities ($I° + I$). "x-Values" were simply $[Q]$. Stern-Volmer plots using the full dataset were then constructed in GraphPad Prism, which returned values for slope, y-intercept, R^2, and error bars representing standard error. The slope of the graph was used to calculate k_q in units of (M^{-1} • s^{-1}) using the following relationship:

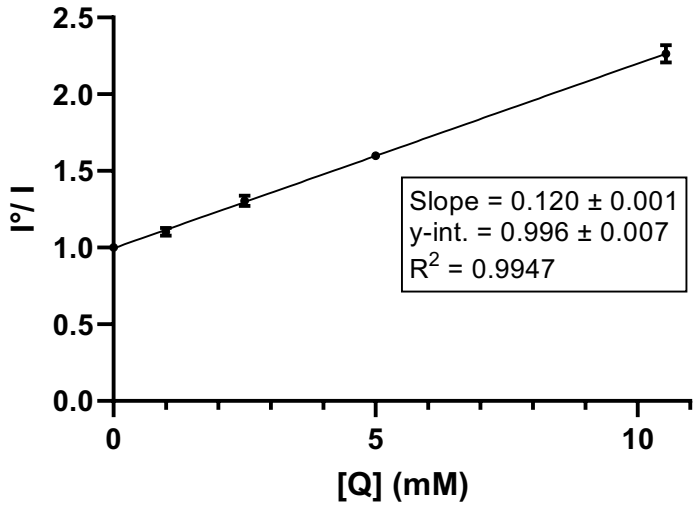
$$k_q = \frac{slope}{\tau}$$

k_q was not determined for plots with fitted lines having $R^2 < 0.5$, and these experiments were interpreted as failing to show fluorescence quenching of **PC-1** by the tested compound.

Stern-Volmer Plot for Compound 6a – in MeCN



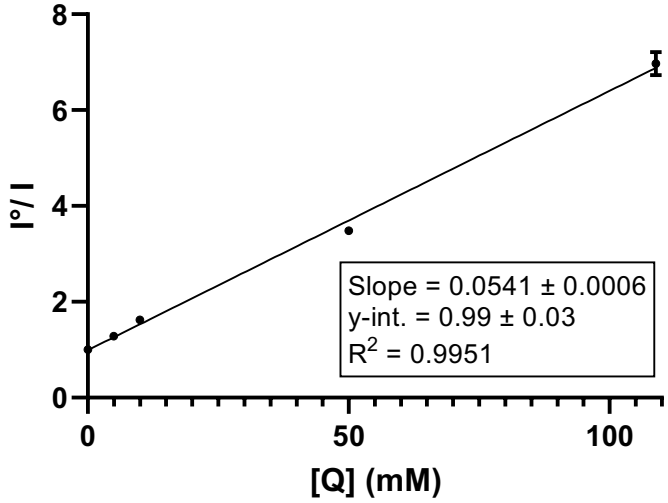
6a



Tested concentrations of 6a: 0, 1.00, 2.50, 5.00, and 10.54 mM

k_q **=** (8.33 ± 0.07) x 10^9 M^{-1} • s^{-1}

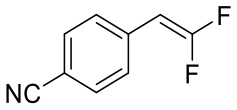
Stern-Volmer Plot for Compound 6a – in PhMe



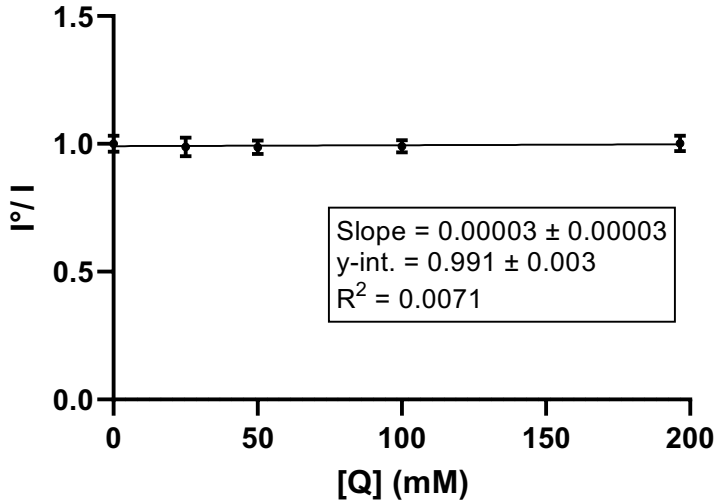
Tested concentrations of 6a: 0, 5.00, 10.00, 50.00, and 108.85 mM

k_q **=** (3.76 ± 0.04) x 10^9 M^{-1} • s^{-1}

Stern-Volmer Plot for Compound 6e – in MeCN



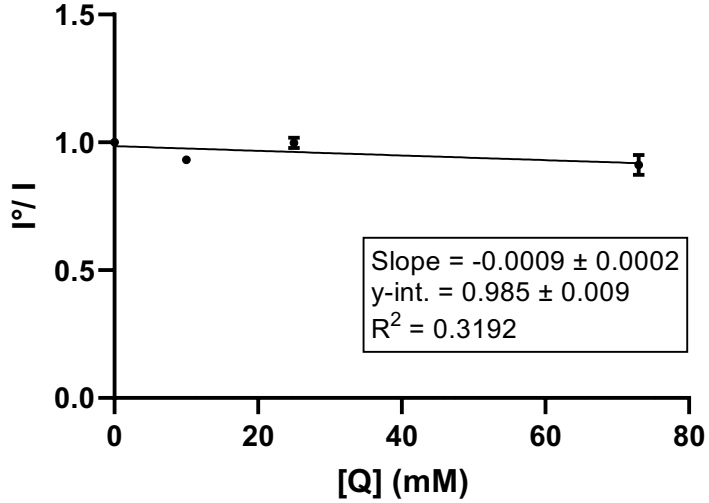
6e



Tested concentrations of 6e: 0, 25.0, 50.0, 100.0, and 196.5 mM

k_q **=** N.D. due to absence of trend

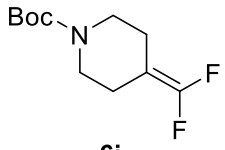
Stern-Volmer Plot for Compound 6e – in PhMe



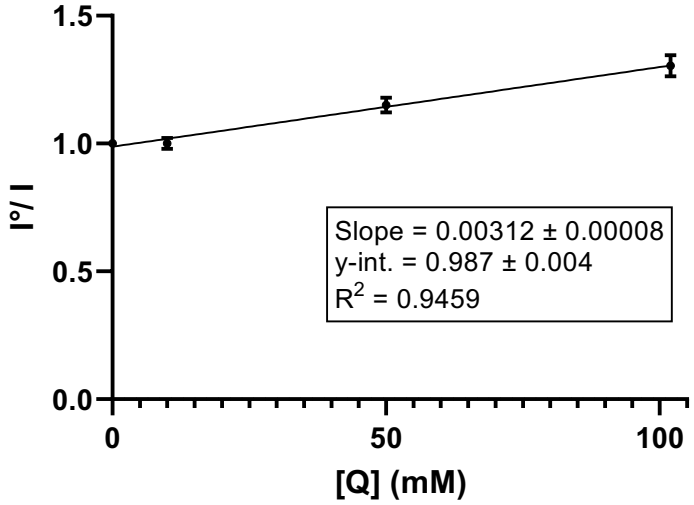
Tested concentrations of 6e: 0, 10.00, 25.00, and 73.02 mM

k_q **=** N.D. due to absence of trend

Stern-Volmer Plot for Compound 6j – in MeCN



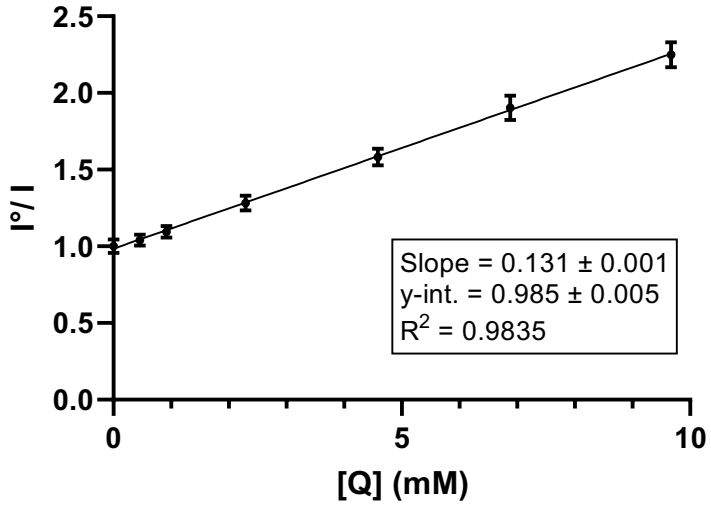
6j



Tested concentrations of 6j: 0, 10.0, 50.0, and 102.0 mM

k_q **=** (2.16 ± 0.06) x 10^8 M^{-1} • s^{-1}

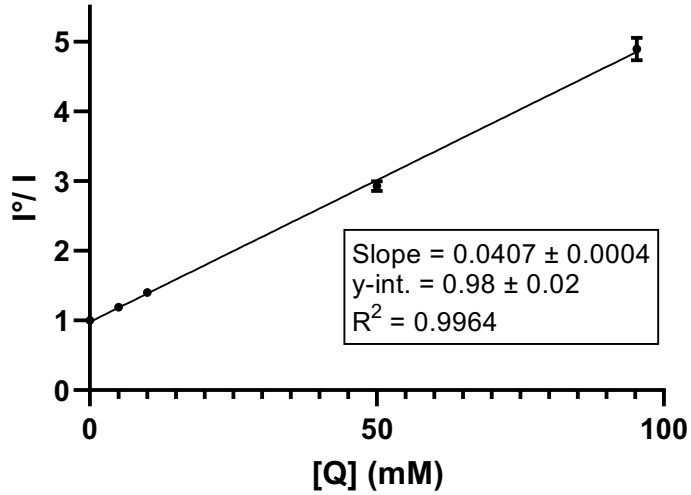
Stern-Volmer Plot for $(BnSe)_2$ – in MeCN



Tested concentrations of $(BnSe)_2$: 0, 0.46, 0.92, 2.29, 4.59, 6.88, and 9.67 mM

k_q **=** $(9.10 \pm 0.07) \times 10^9\ M^{-1} \cdot s^{-1}$

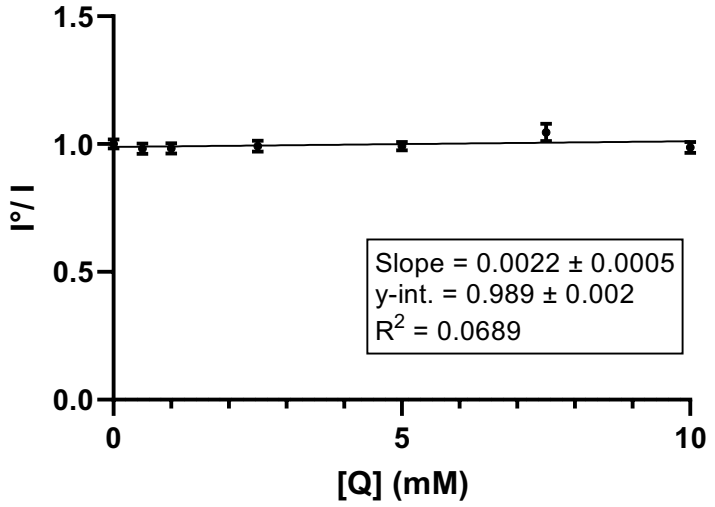
Stern-Volmer Plot for $(BnSe)_2$ – in PhMe



Tested concentrations of $(BnSe)_2$: 0, 5.00, 10.00, 50.00, and 95.33 mM

k_q **=** $(2.83 \pm 0.03) \times 10^9\ M^{-1} \cdot s^{-1}$

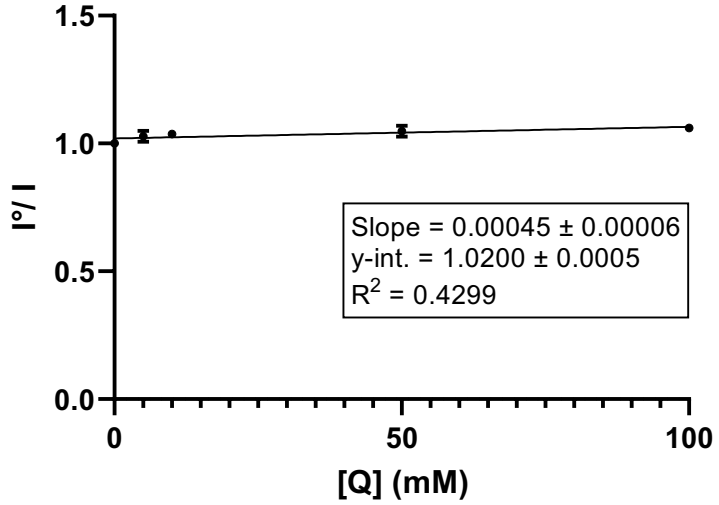
Stern-Volmer Plot for EtOH – in MeCN



Tested concentrations of EtOH: 0, 0.50, 1.00, 2.50, 5.00, 7.50, and 10.00 mM

k_q **=** N.D. due to absence of trend

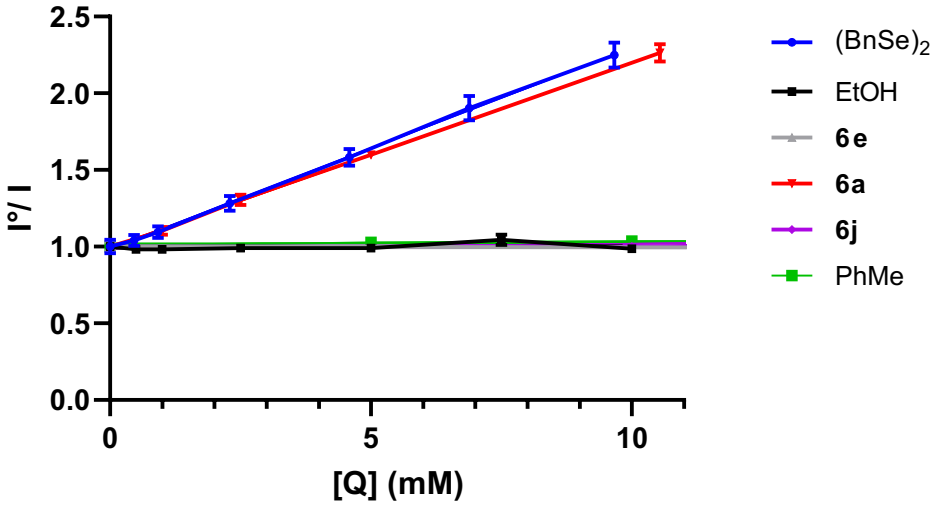
Stern-Volmer Plot for PhMe – in MeCN



Tested concentrations of PhMe: 0, 5.00, 10.00, 50.00, 100.00 mM

k_q **=** N.D. due to absence of trend

Combined Stern-Volmer Plot – in MeCN



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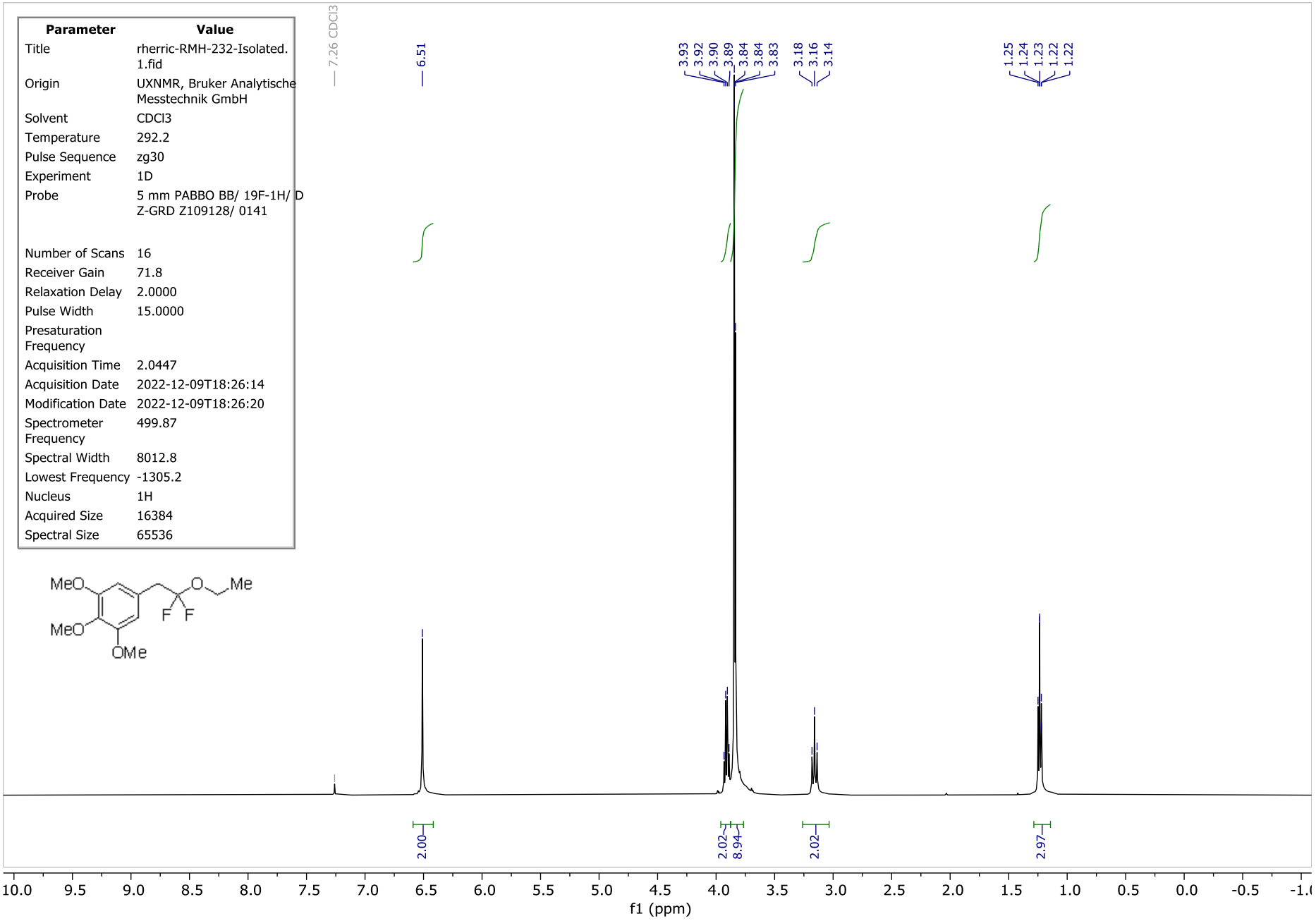
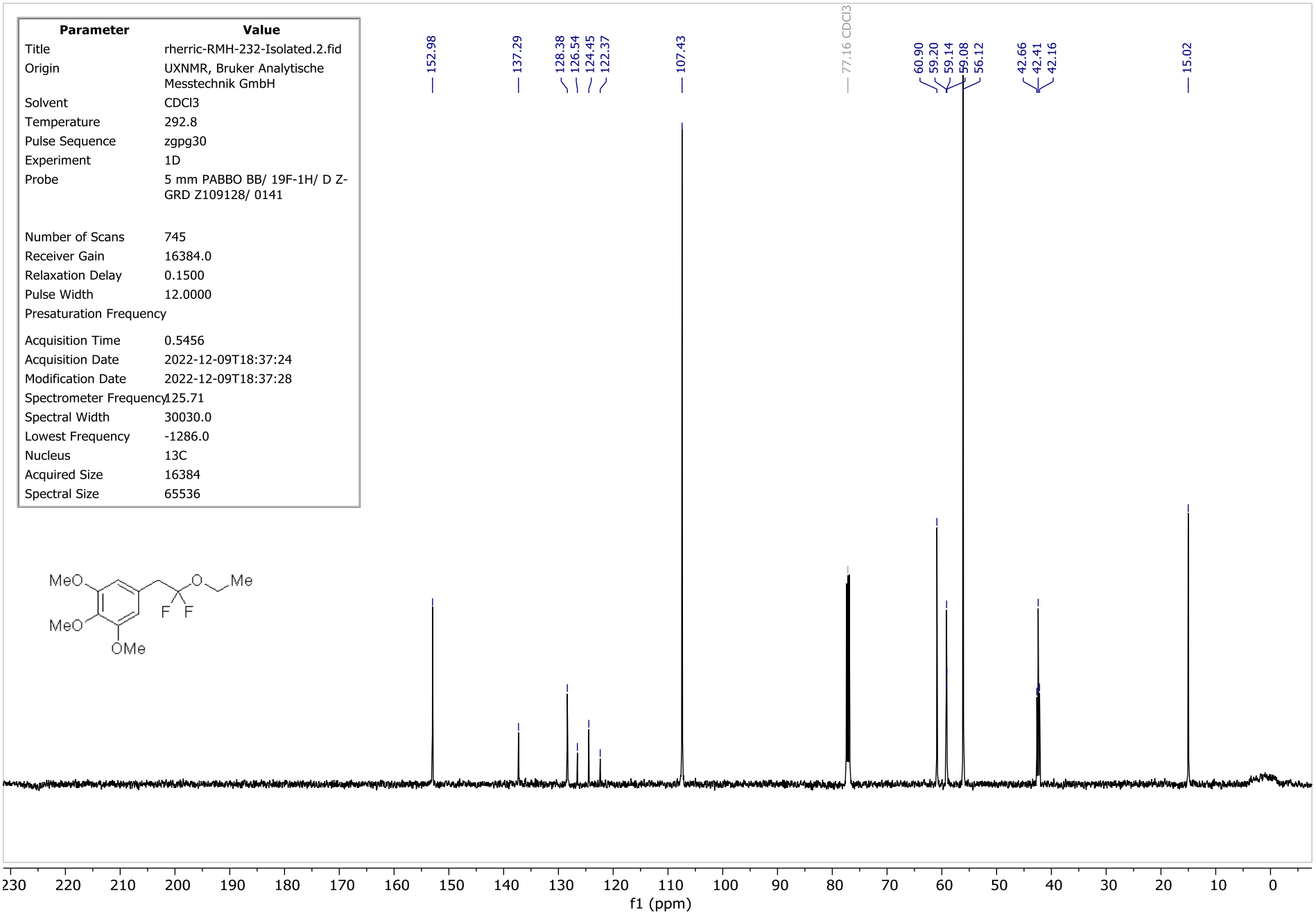
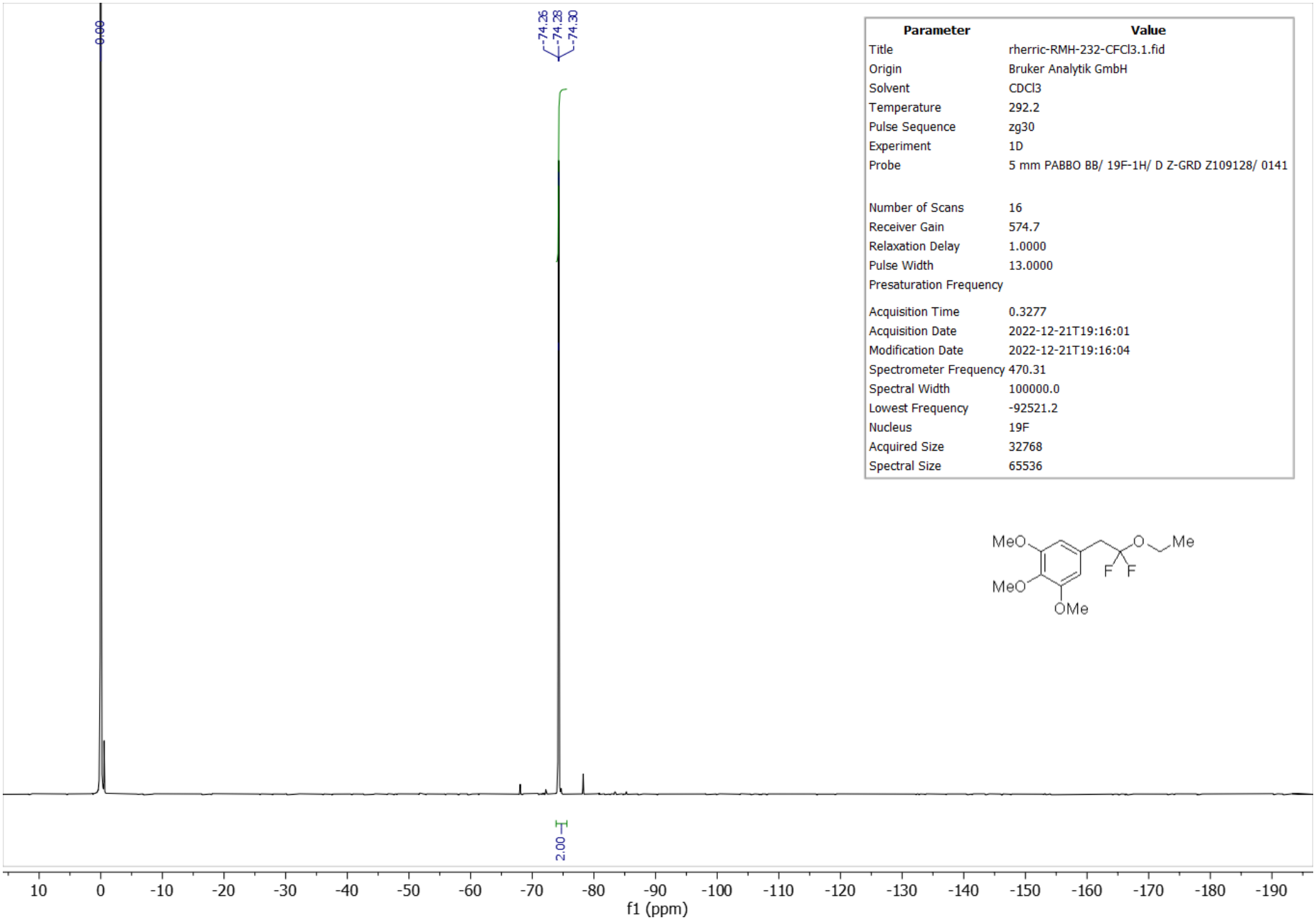
NMR Spectra for Compound **5-(2-ethoxy-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (7a)**

Parameter	Value
Title	rherric-RMH-232-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	71.8
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-09T18:26:14
Modification Date	2022-12-09T18:26:20
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-1305.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536



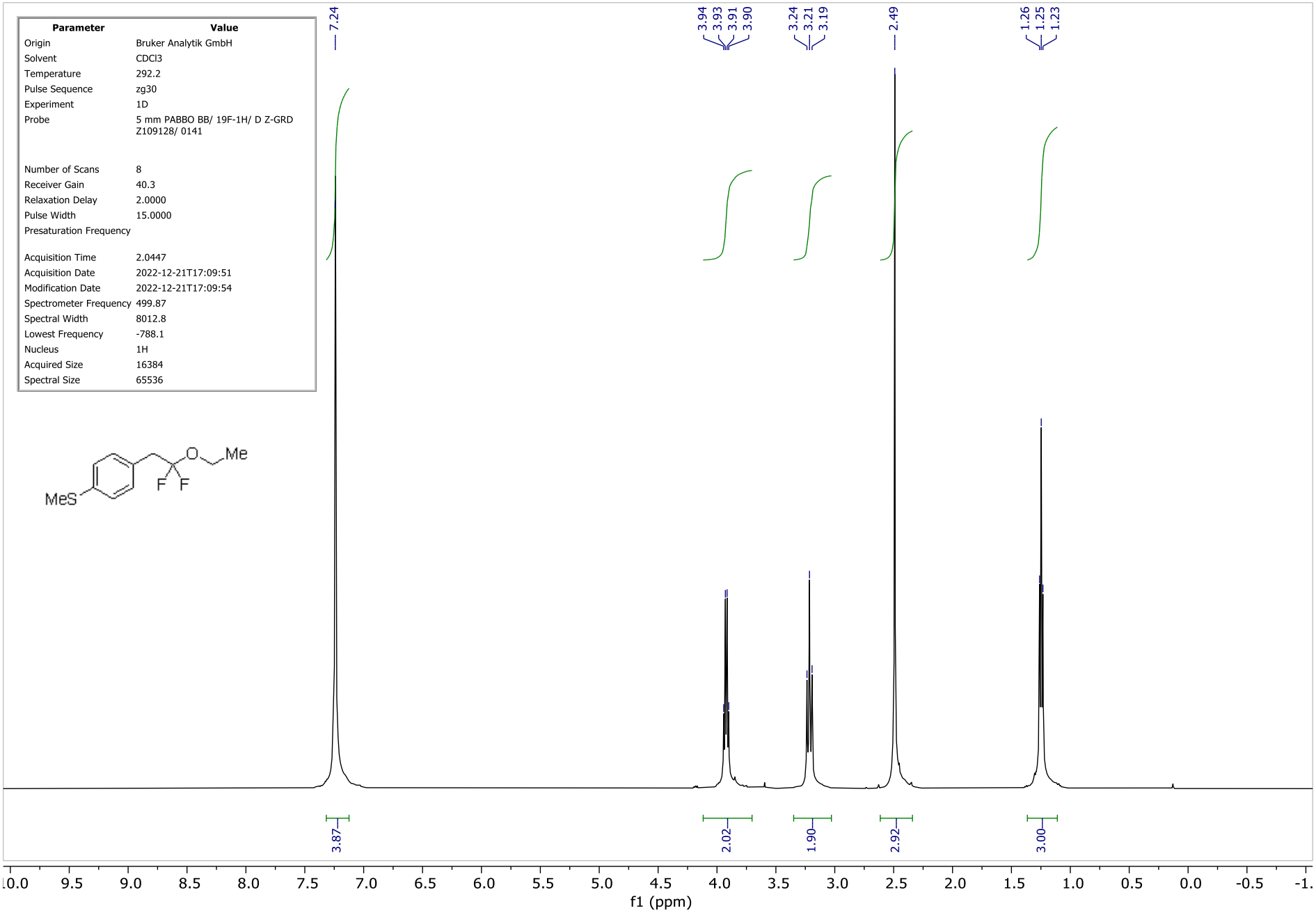
Parameter	Value
Title	rherric-RMH-232-Isolated.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	745
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-09T18:37:24
Modification Date	2022-12-09T18:37:28
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



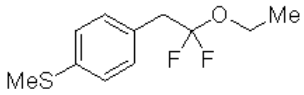


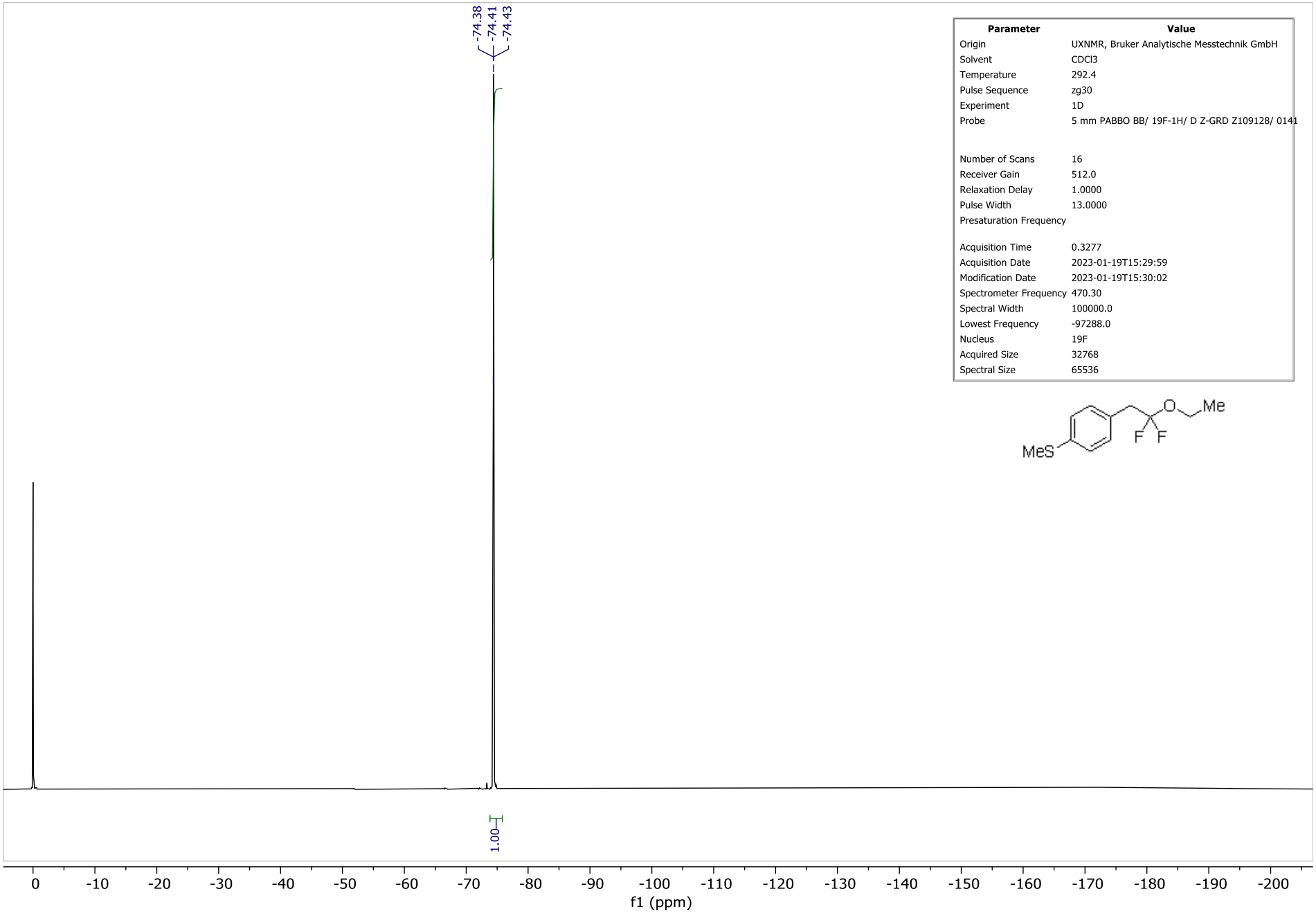
Parameter	Value
Title	rherric-RMH-232-CFCl3.1.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2022-12-21T19:16:01
Modification Date	2022-12-21T19:16:04
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92521.2
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **(4-(2-ethoxy-2,2-difluoroethyl)phenyl)(methyl)sulfane (7b)**



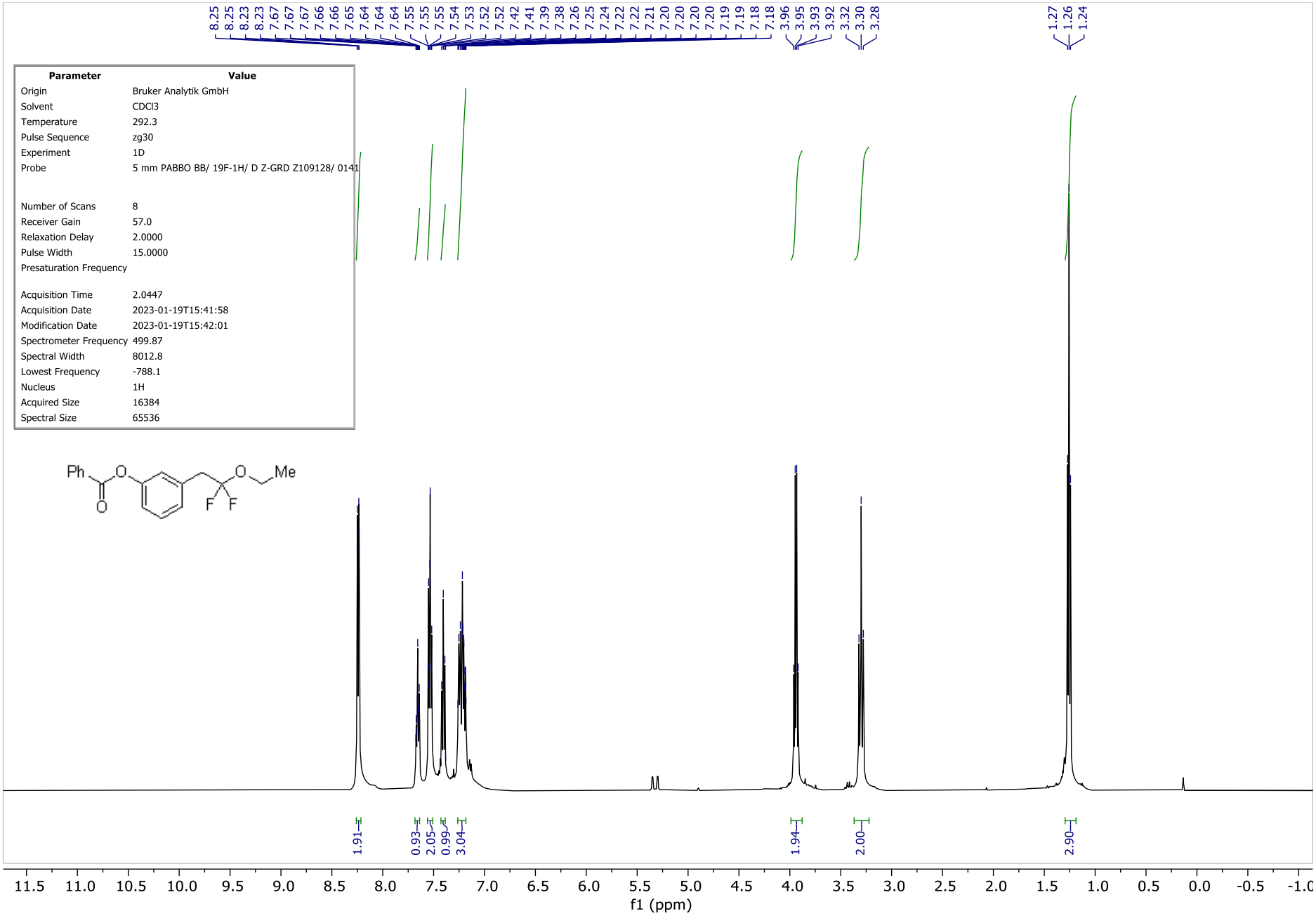
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-21T17:28:29
Modification Date	2022-12-21T17:28:32
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



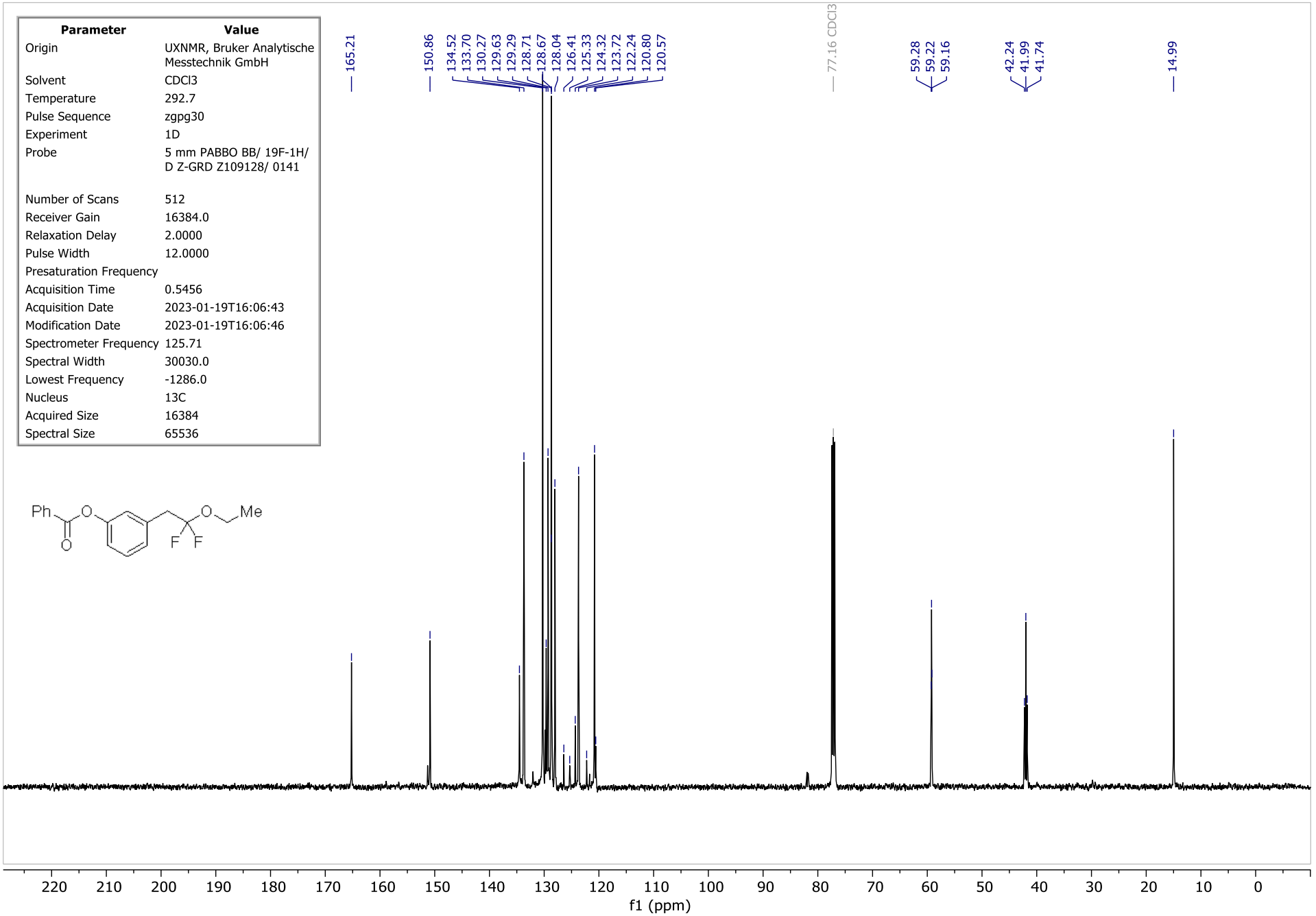


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-19T15:29:59
Modification Date	2023-01-19T15:30:02
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97288.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

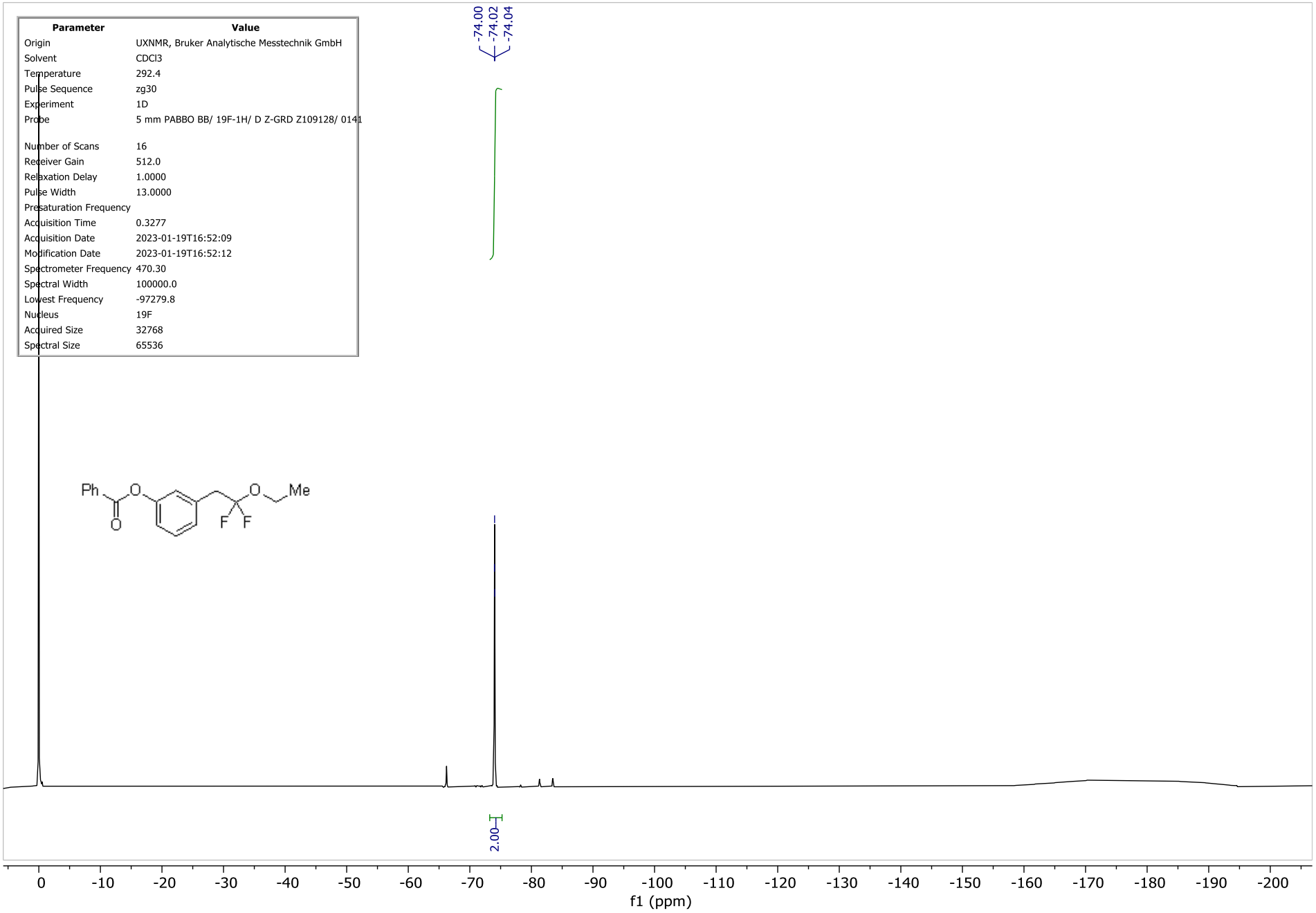
NMR Spectra for Compound **4-(2-ethoxy-2,2-difluoroethyl)phenyl benzoate (7c)**



Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.7
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	512
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-01-19T16:06:43
Modification Date	2023-01-19T16:06:46
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

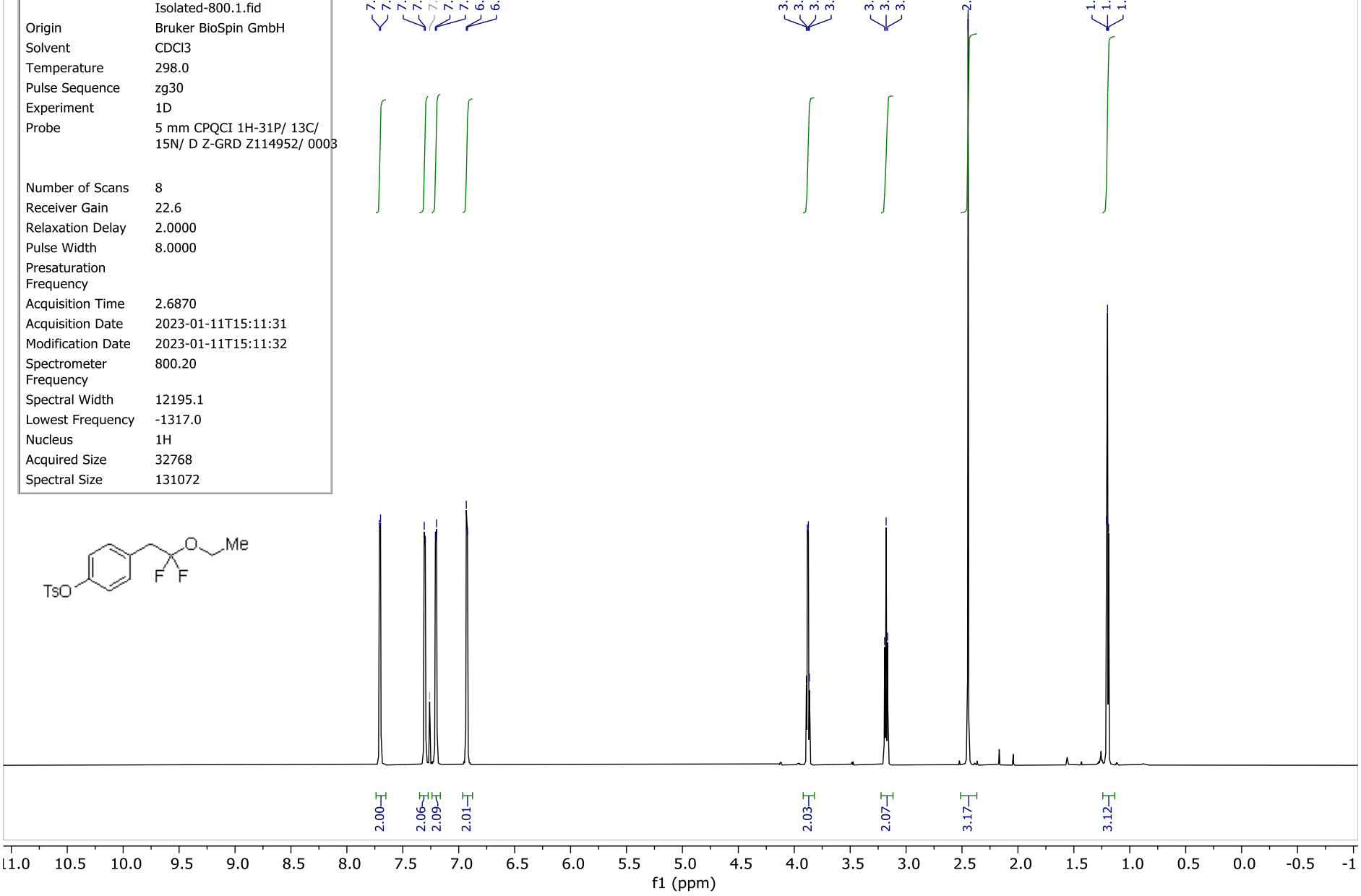


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-19T16:52:09
Modification Date	2023-01-19T16:52:12
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97279.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

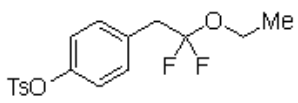


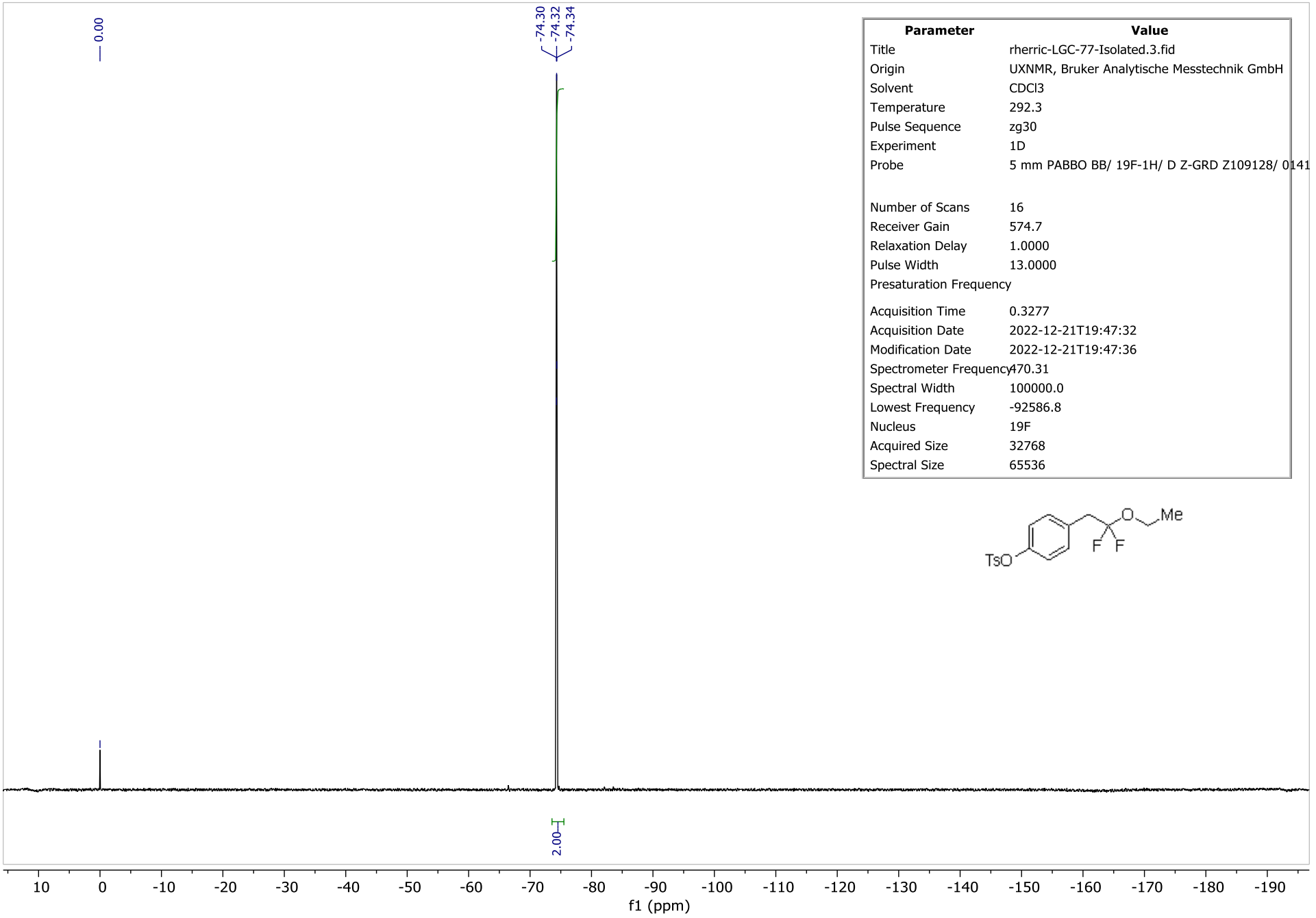
NMR Spectra for Compound **4-(2-ethoxy-2,2-difluoroethyl)phenyl 4-methylbenzenesulfonate (7d)**

Parameter	Value
Title	rherric-LGC-77-Isolated-800.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	22.6
Relaxation Delay	2.0000
Pulse Width	8.0000
Presaturation Frequency	
Acquisition Time	2.6870
Acquisition Date	2023-01-11T15:11:31
Modification Date	2023-01-11T15:11:32
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1317.0
Nucleus	1H
Acquired Size	32768
Spectral Size	131072



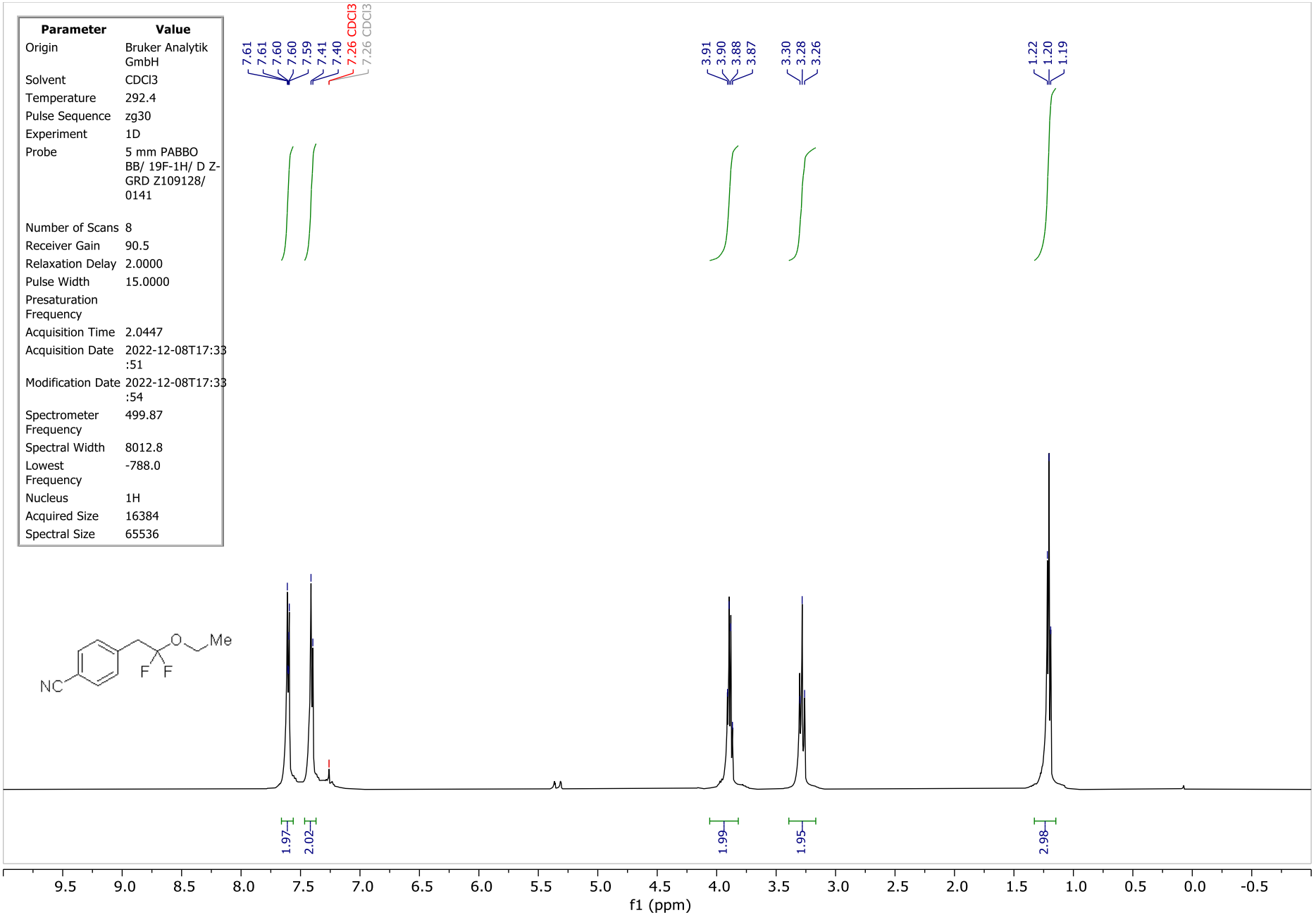
Parameter	Value
Title	rherric-LGC-77-Isolated-800.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	586
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2023-01-11T15:23:26
Modification Date	2023-01-11T15:23:27
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-2979.7
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



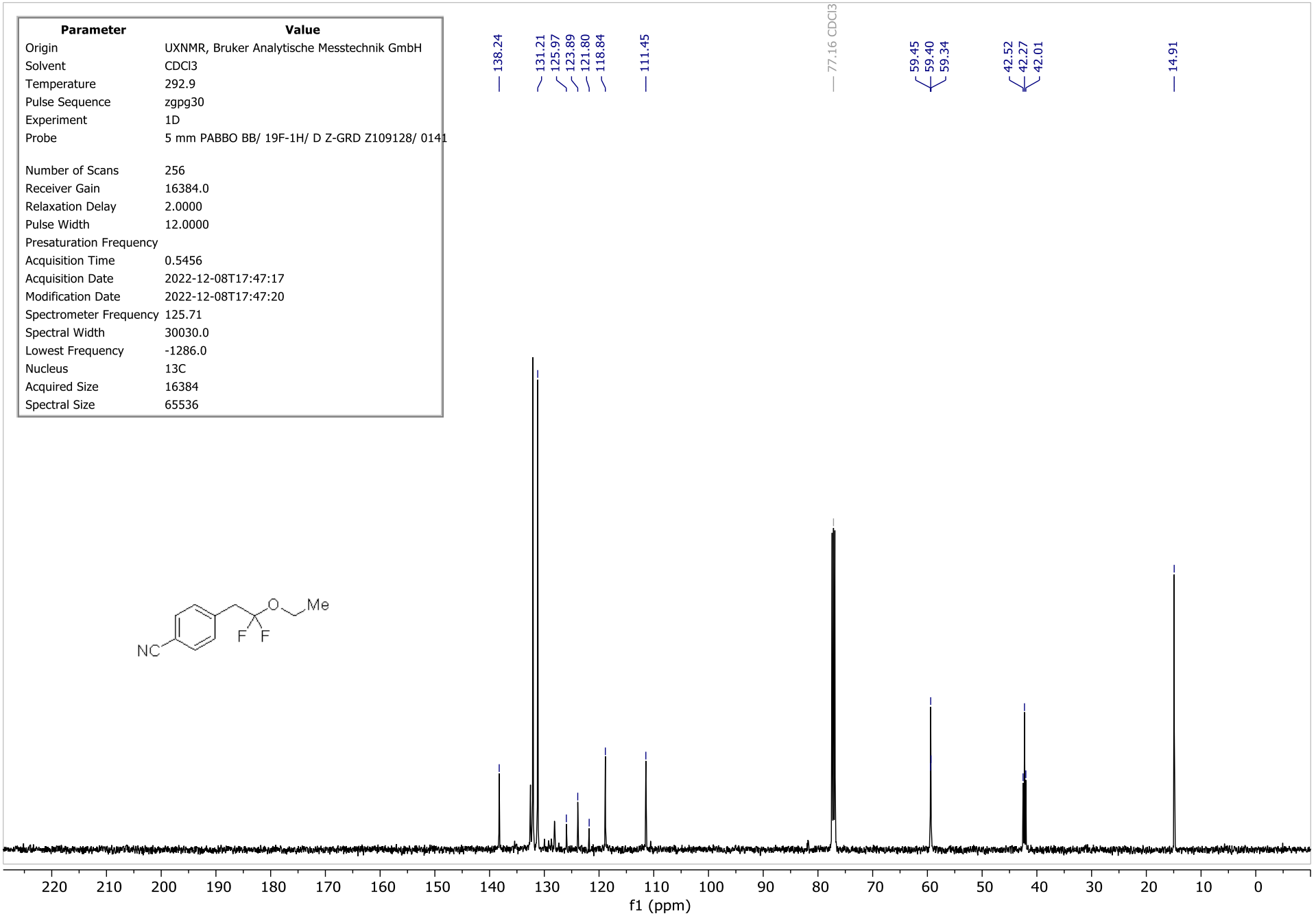


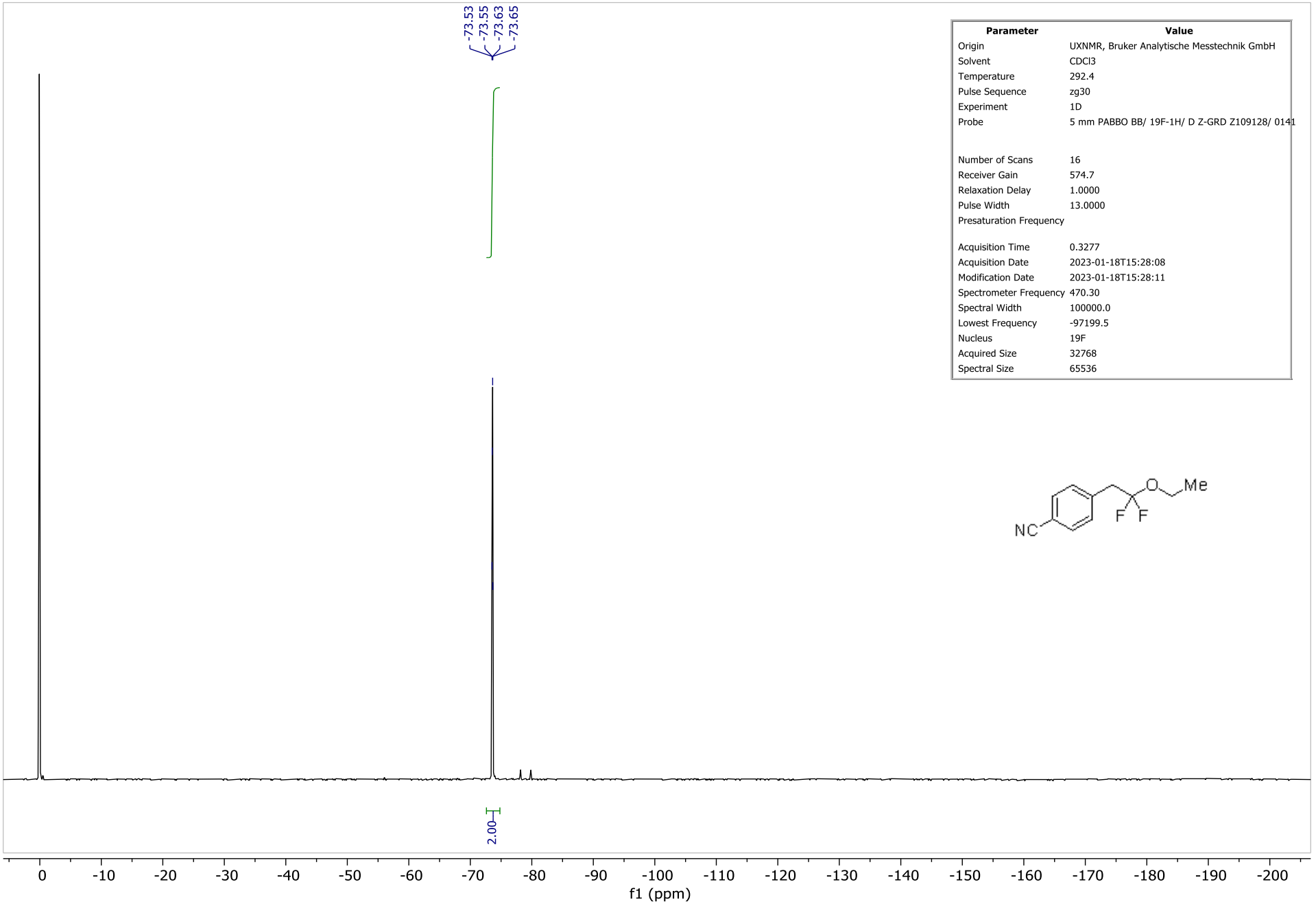
Parameter	Value
Title	rherric-LGC-77-Isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2022-12-21T19:47:32
Modification Date	2022-12-21T19:47:36
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92586.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **4-(2-ethoxy-2,2-difluoroethyl)benzonitrile (7e)**



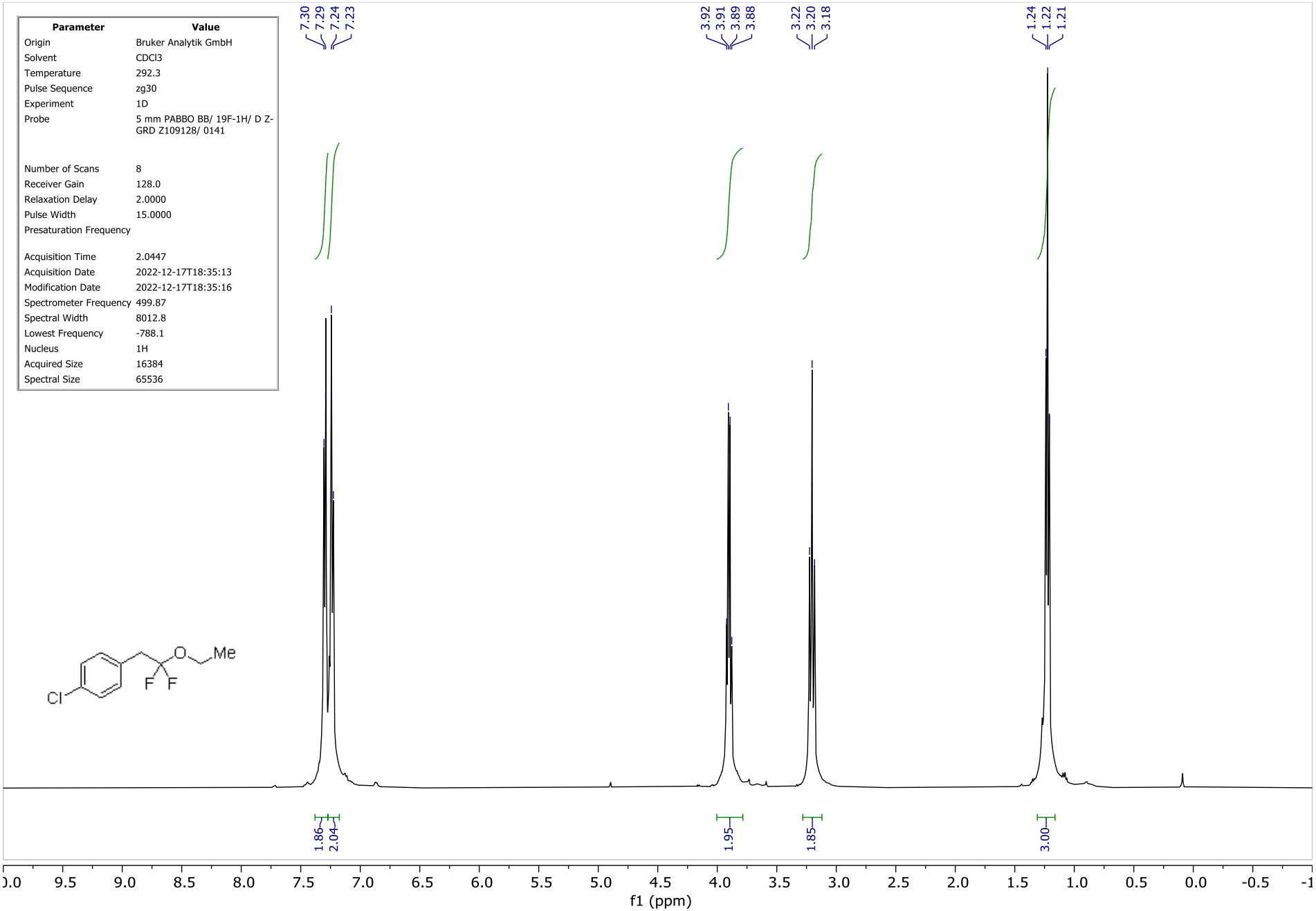
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-08T17:47:17
Modification Date	2022-12-08T17:47:20
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



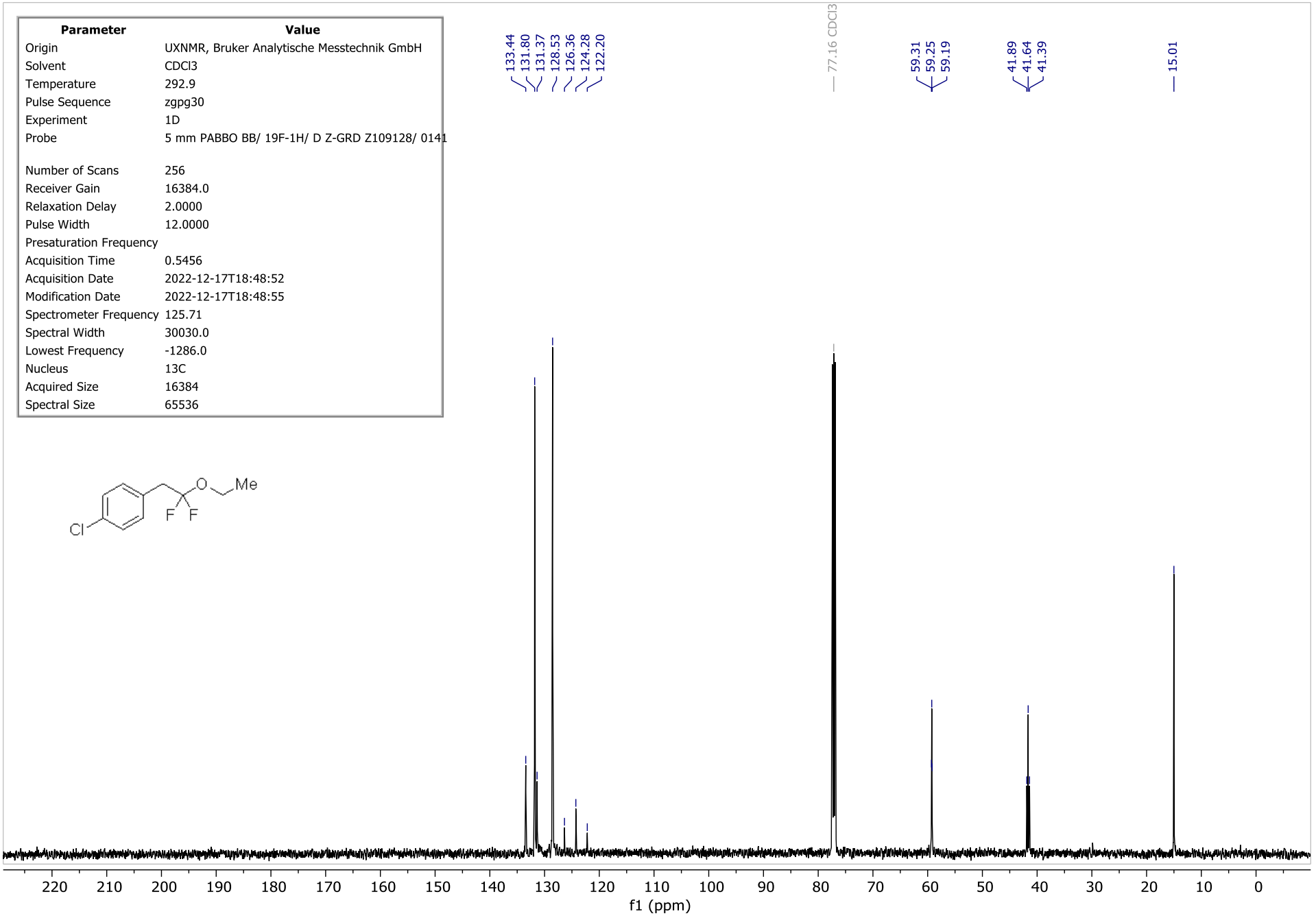


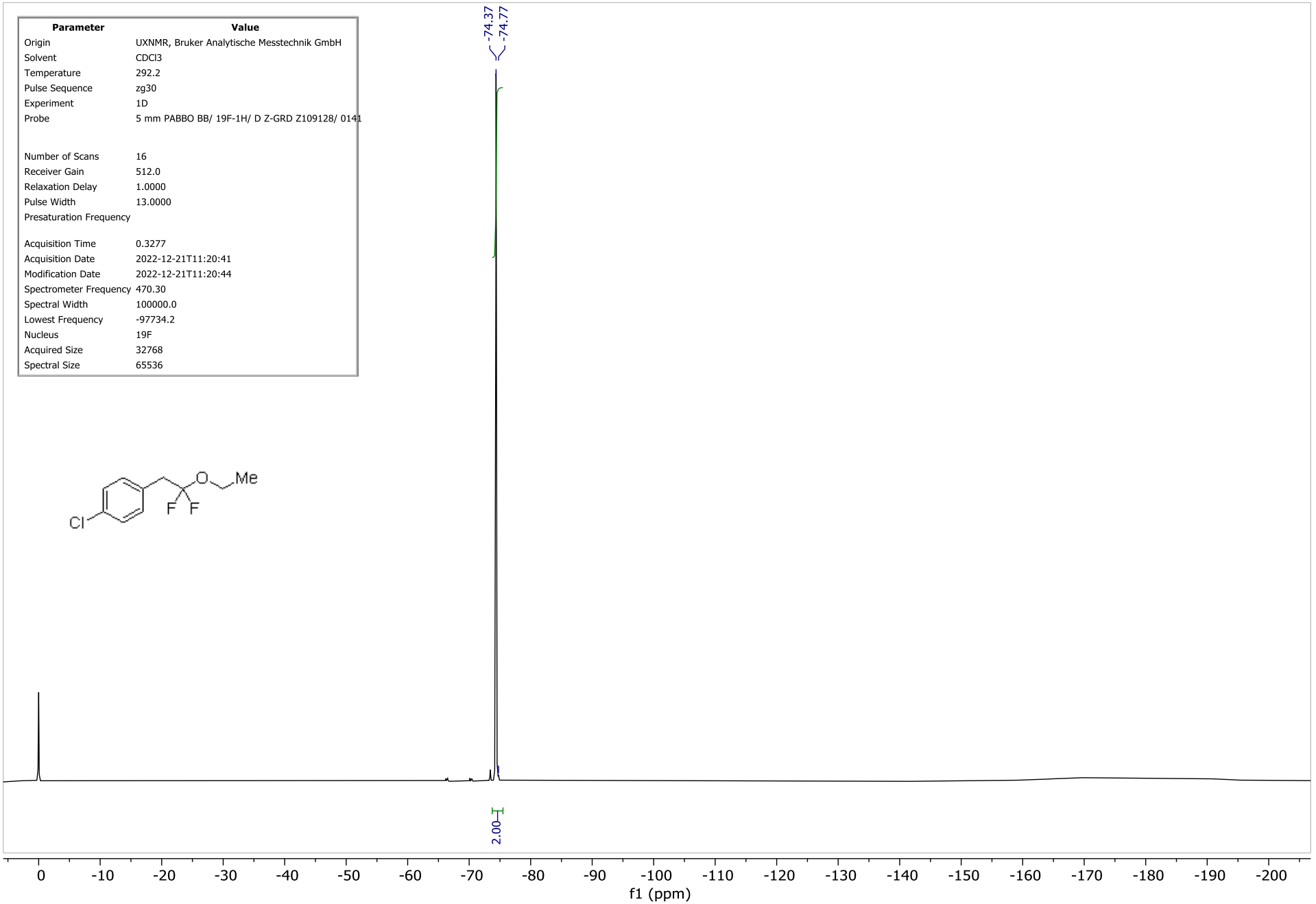
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-18T15:28:08
Modification Date	2023-01-18T15:28:11
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97199.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **1-chloro-4-(2-ethoxy-2,2-difluoroethyl)benzene (7f)**

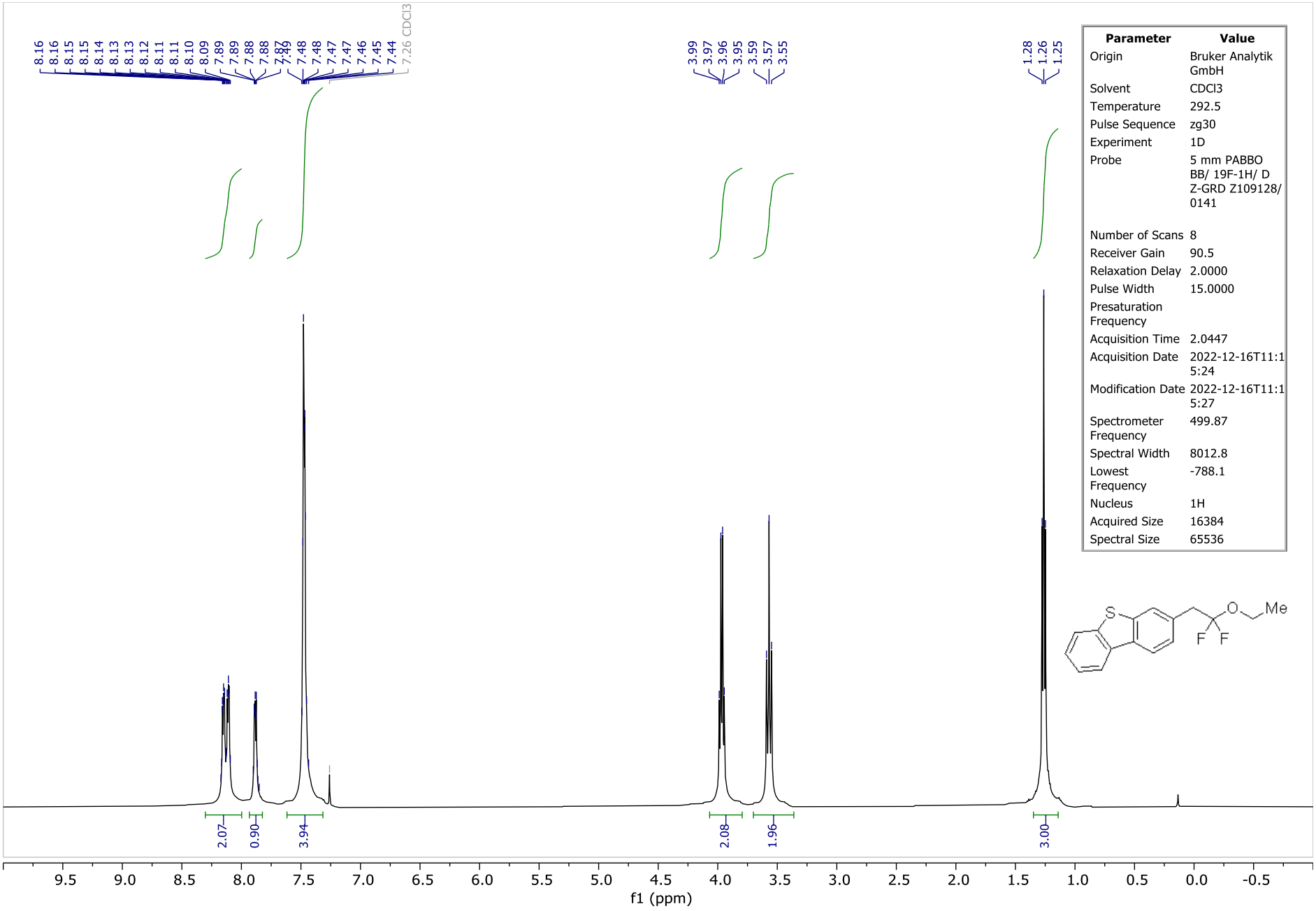


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-17T18:48:52
Modification Date	2022-12-17T18:48:55
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



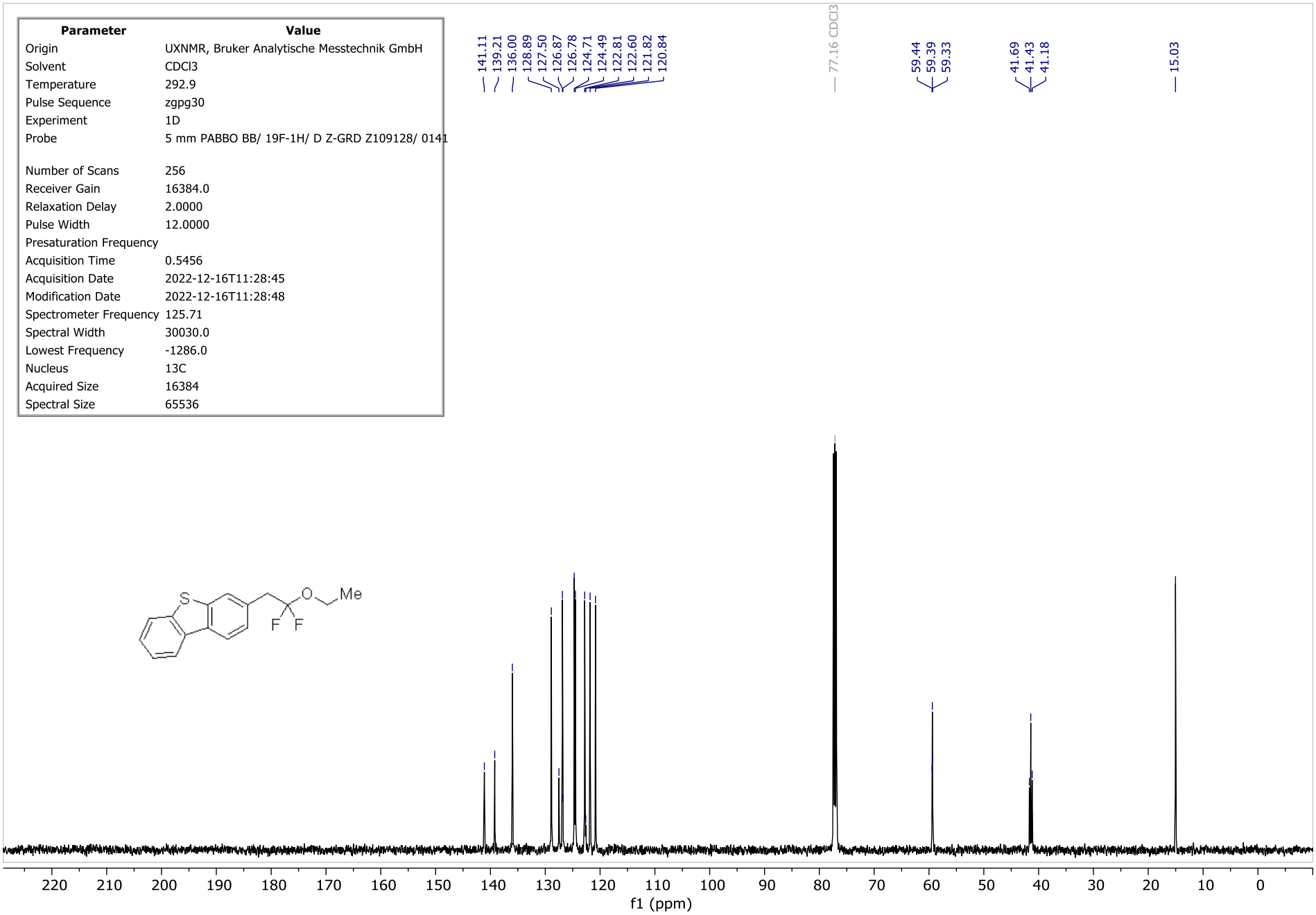

Parameter Value
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 292.2
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 16
Receiver Gain 512.0
Relaxation Delay 1.0000
Pulse Width 13.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2022-12-21T11:20:41
Modification Date 2022-12-21T11:20:44
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97734.2
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
-74.37
-74.77
Cl
F F
O
Me
2.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

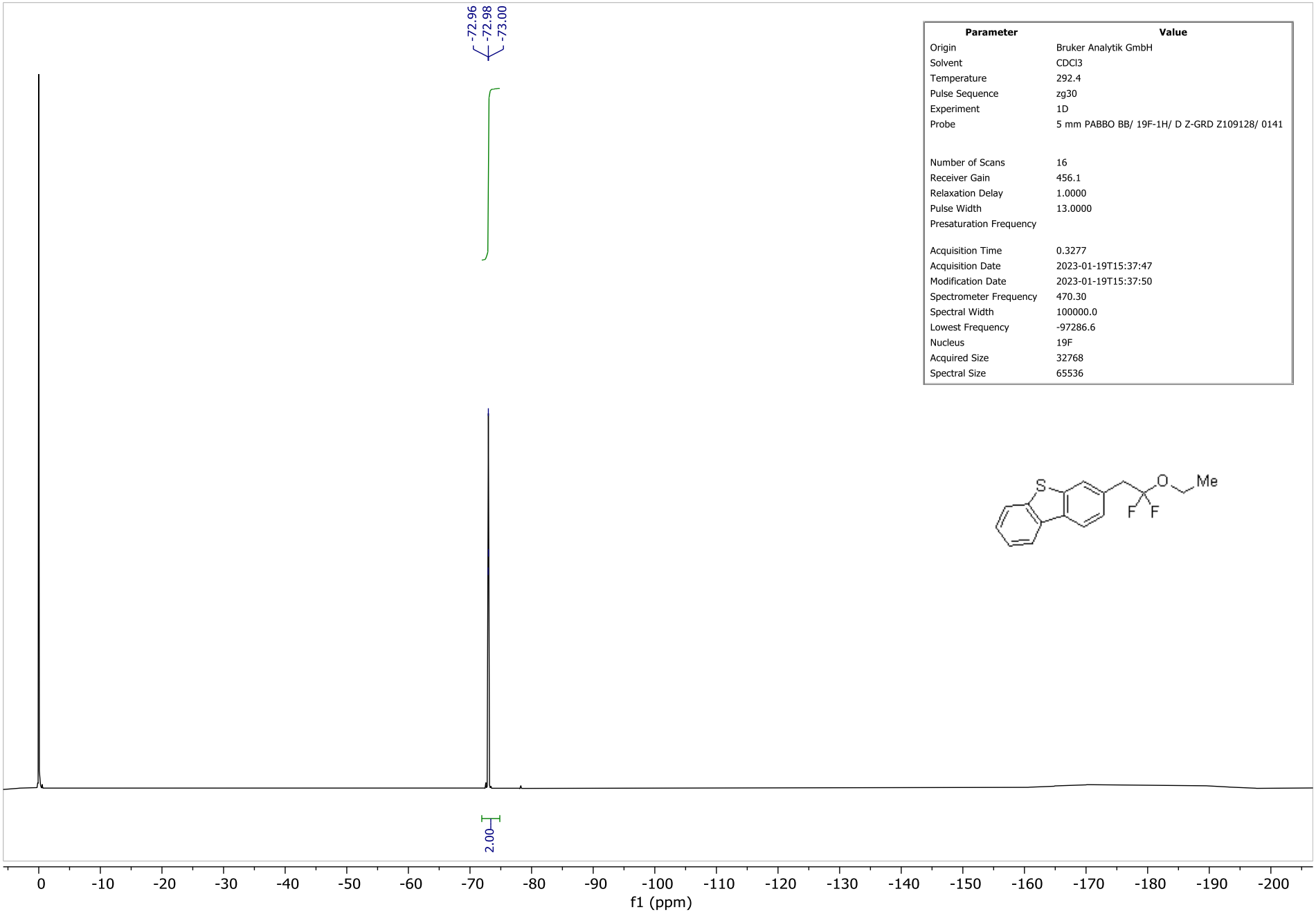
NMR Spectra for Compound **3-(2-ethoxy-2,2-difluoroethyl)dibenzo[*b*,*d*]thiophene (7g)**



Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	90.5
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-16T11:15:24
Modification Date	2022-12-16T11:15:27
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

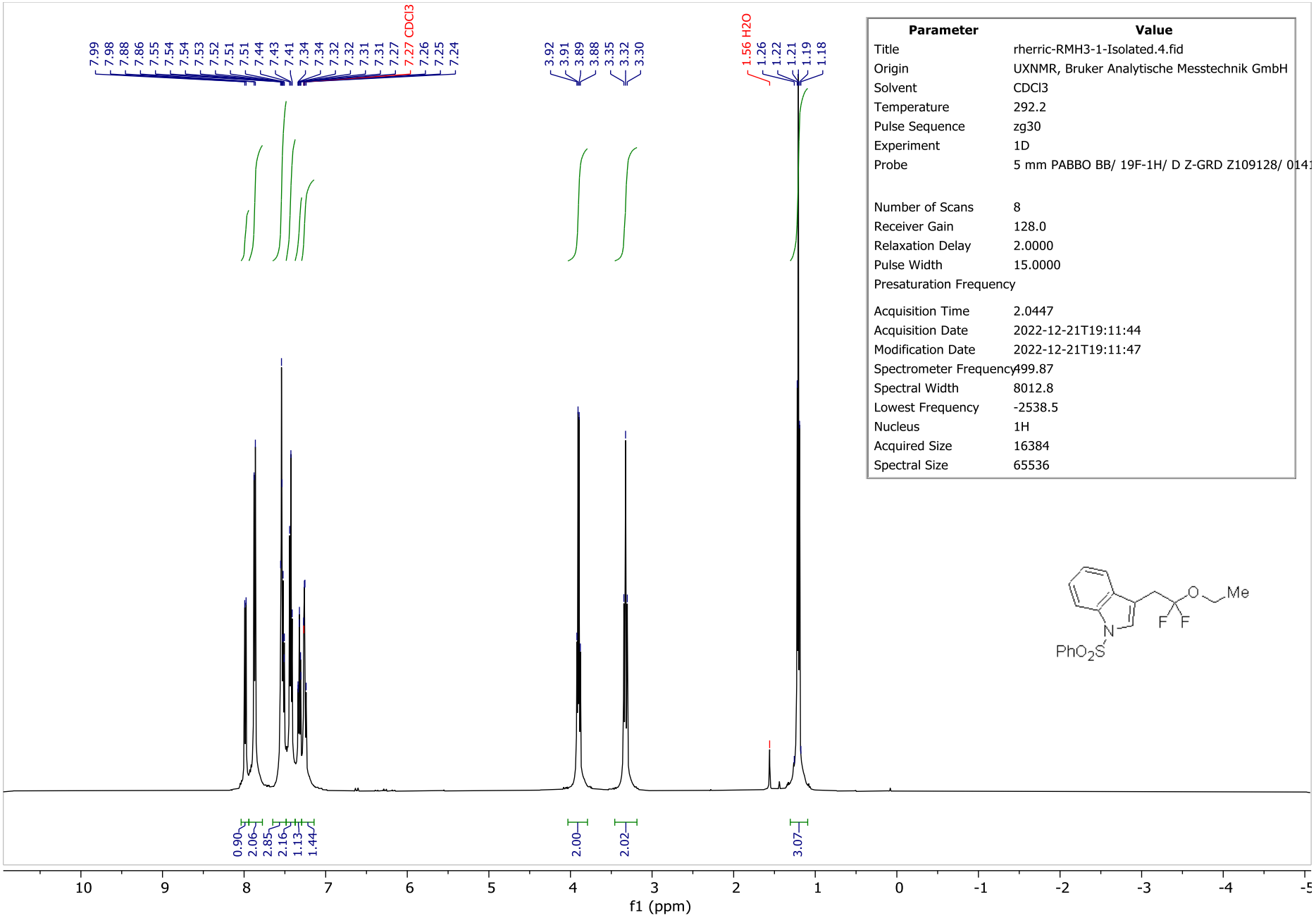
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-16T11:28:45
Modification Date	2022-12-16T11:28:48
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





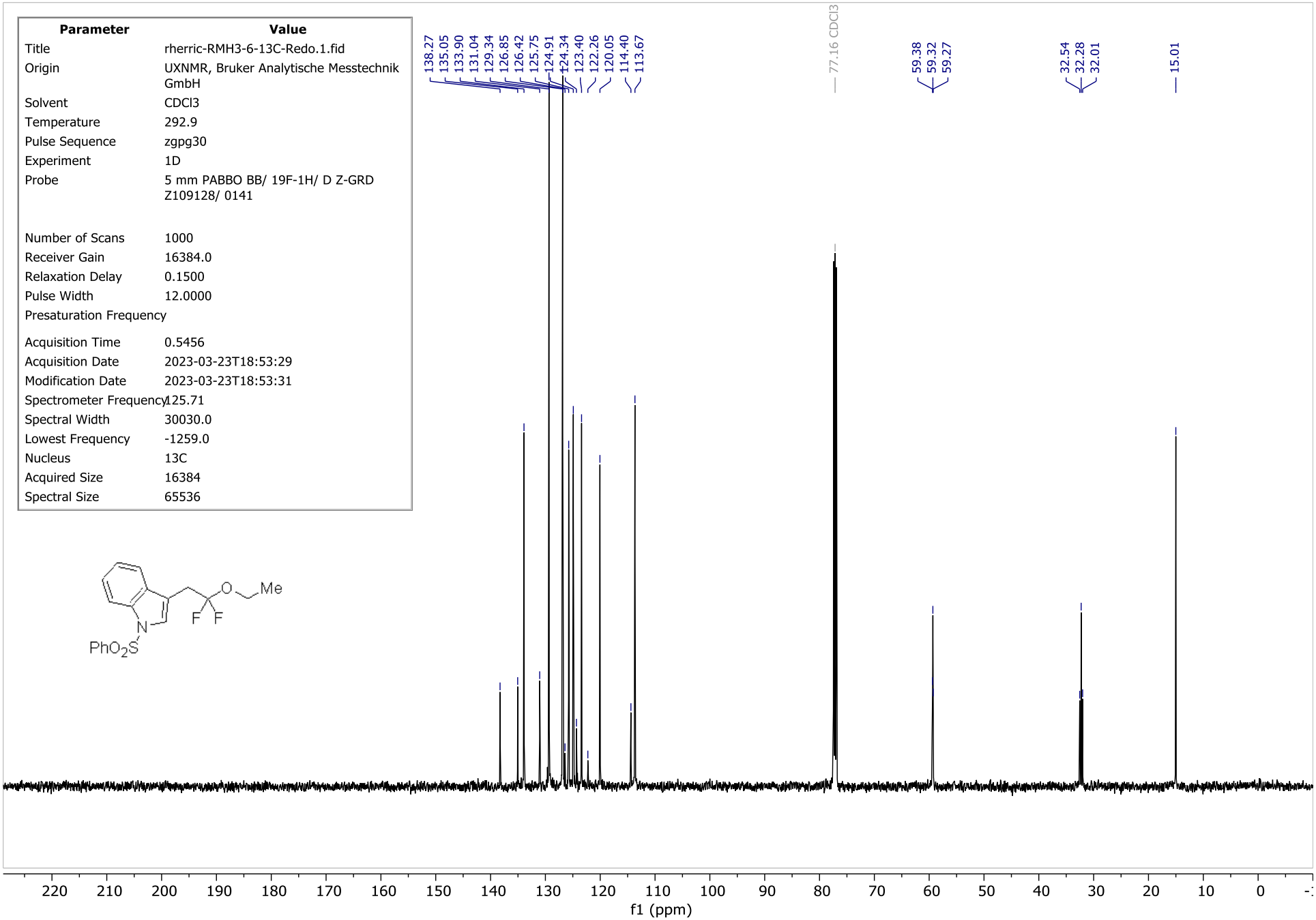
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	456.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-19T15:37:47
Modification Date	2023-01-19T15:37:50
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97286.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

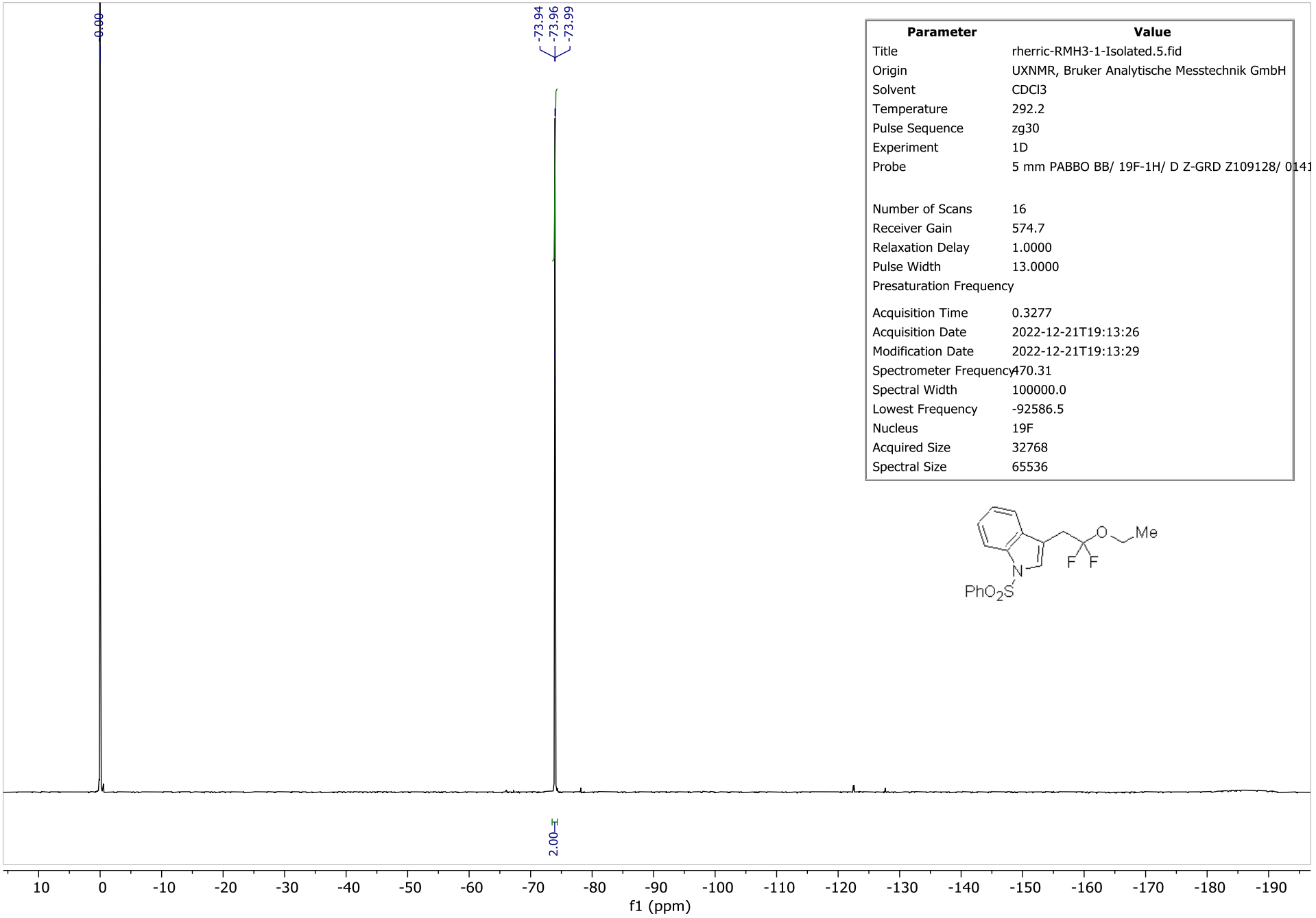
NMR Spectra for Compound **3-(2-ethoxy-2,2-difluoroethyl)-1-(phenylsulfonyl)-1H-indole (7h)**



Parameter	Value
Title	rherric-RMH3-1-Isolated.4.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-21T19:11:44
Modification Date	2022-12-21T19:11:47
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2538.5
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

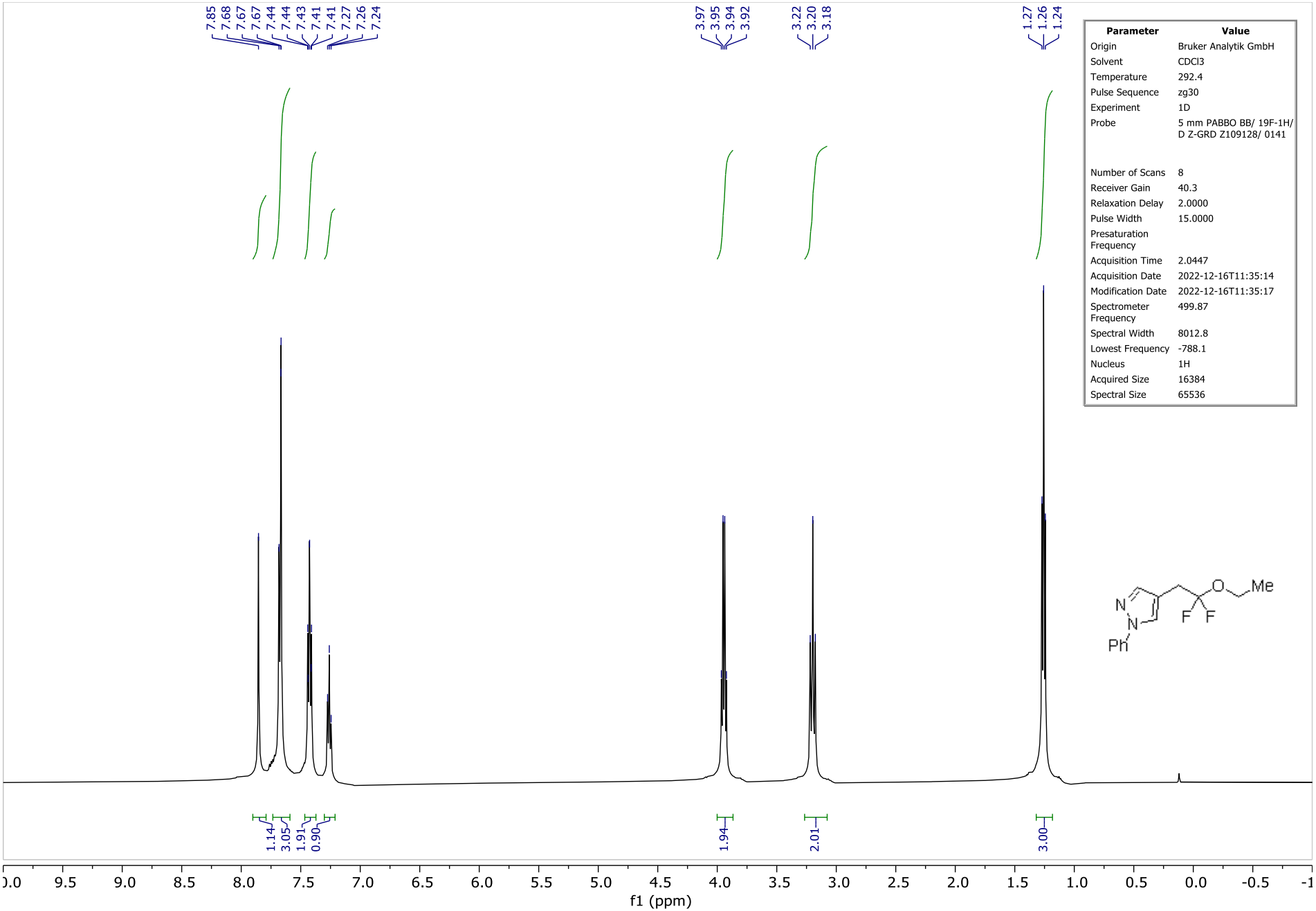
Parameter	Value
Title	rherric-RMH3-6-13C-Redo.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-03-23T18:53:29
Modification Date	2023-03-23T18:53:31
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



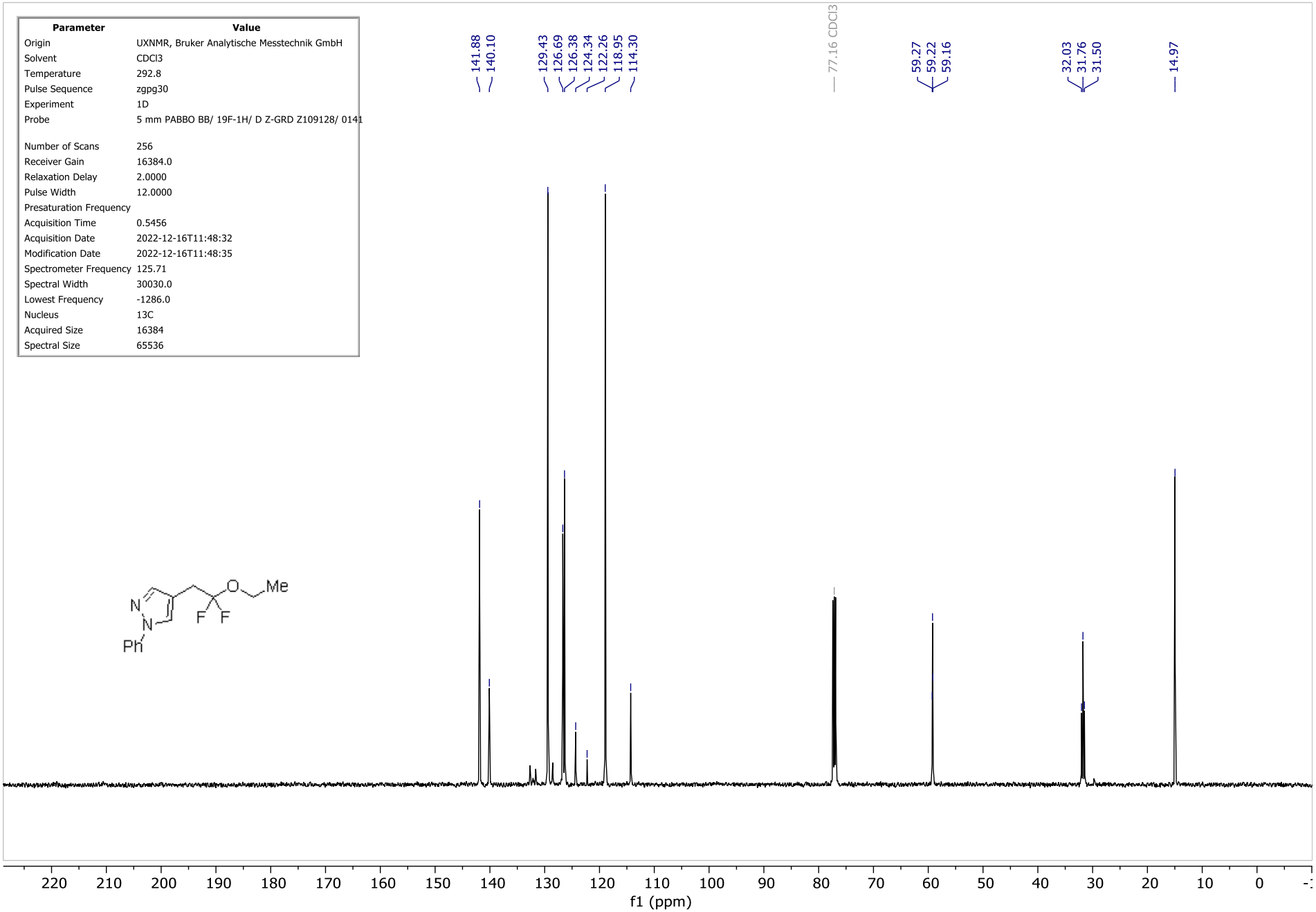


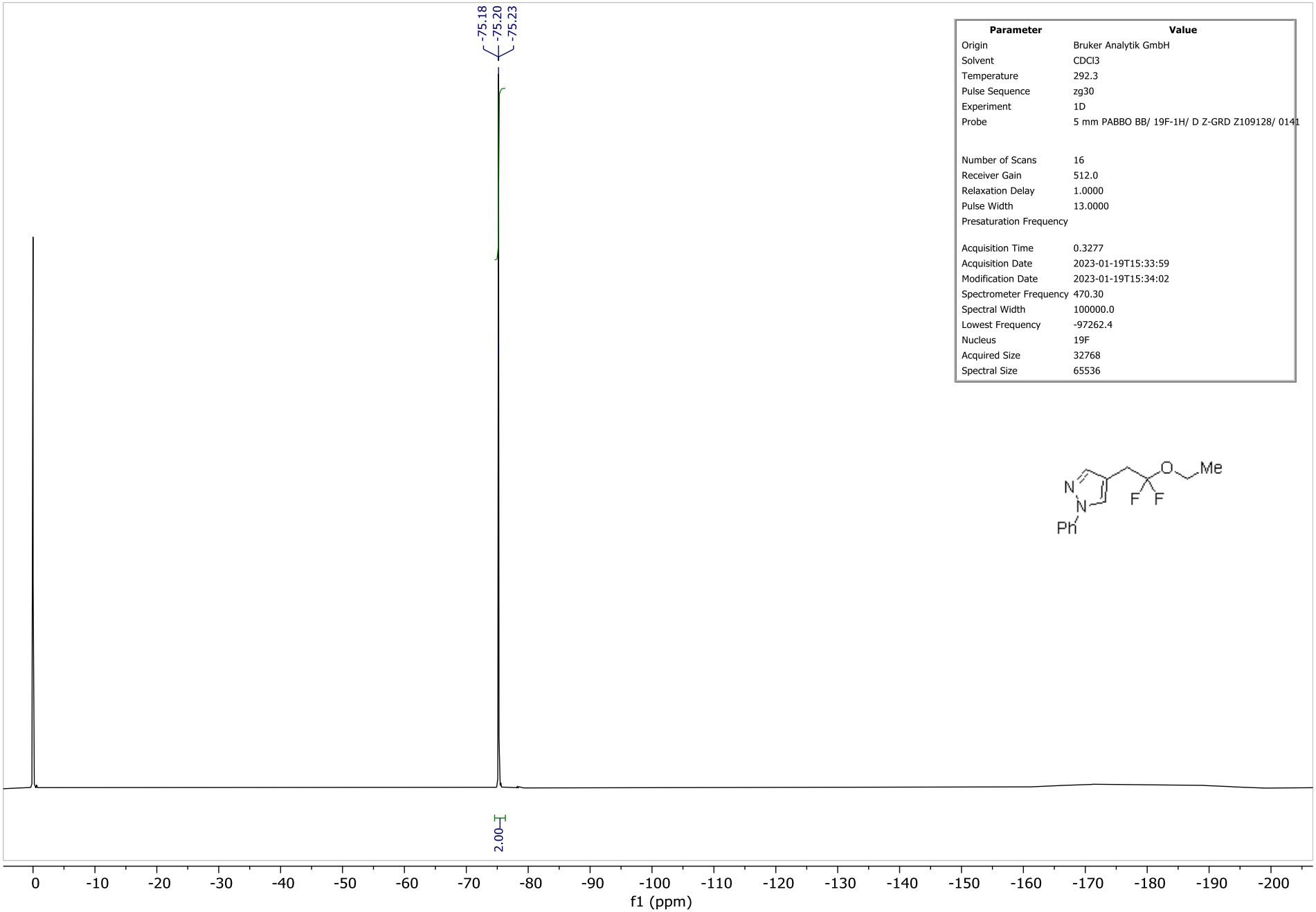
Parameter	Value
Title	rherric-RMH3-1-Isolated.5.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2022-12-21T19:13:26
Modification Date	2022-12-21T19:13:29
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92586.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **4-(2-ethoxy-2,2-difluoroethyl)-1-phenyl-1*H*-pyrazole (7i)**



Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2022-12-16T11:48:32
Modification Date	2022-12-16T11:48:35
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

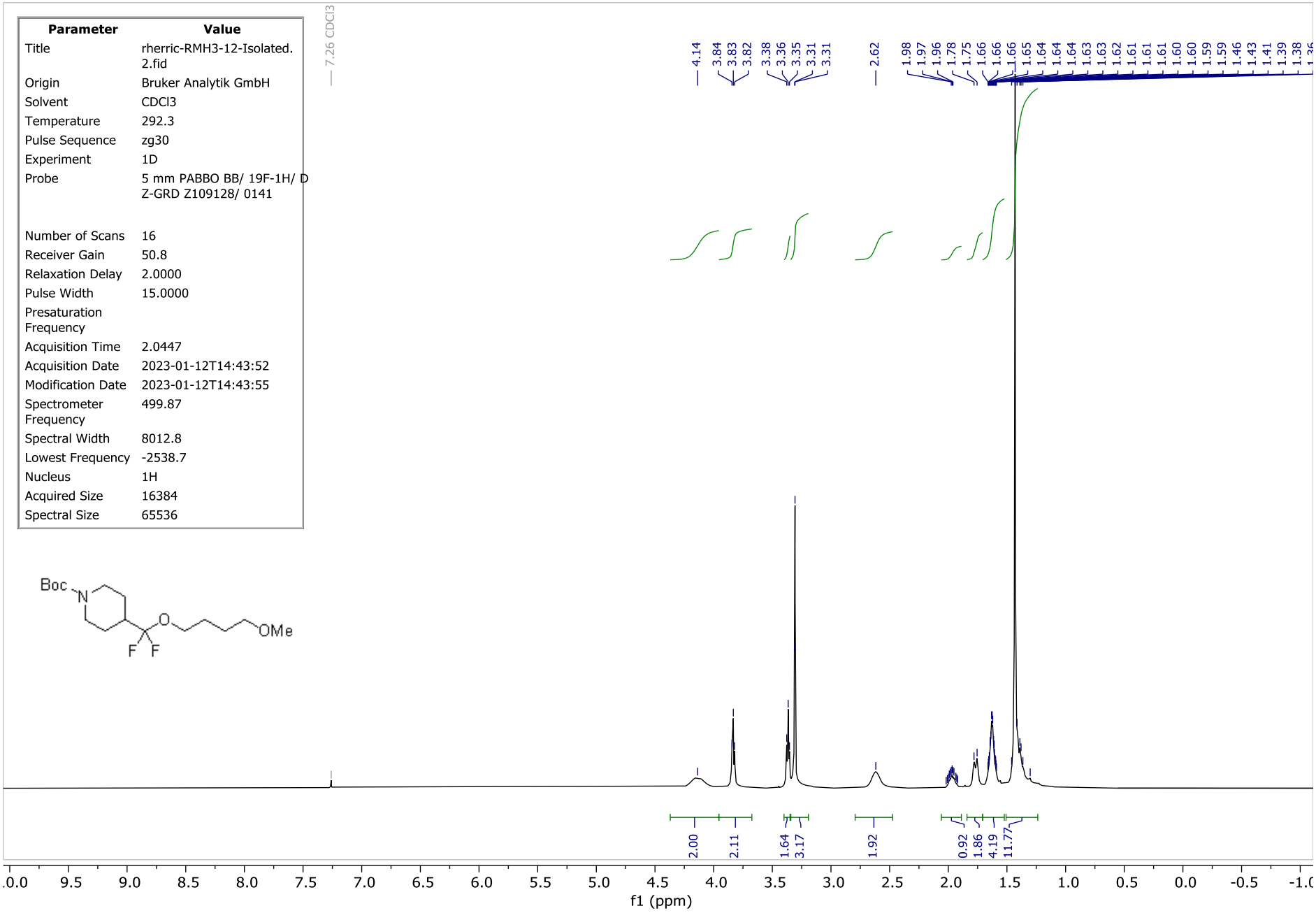




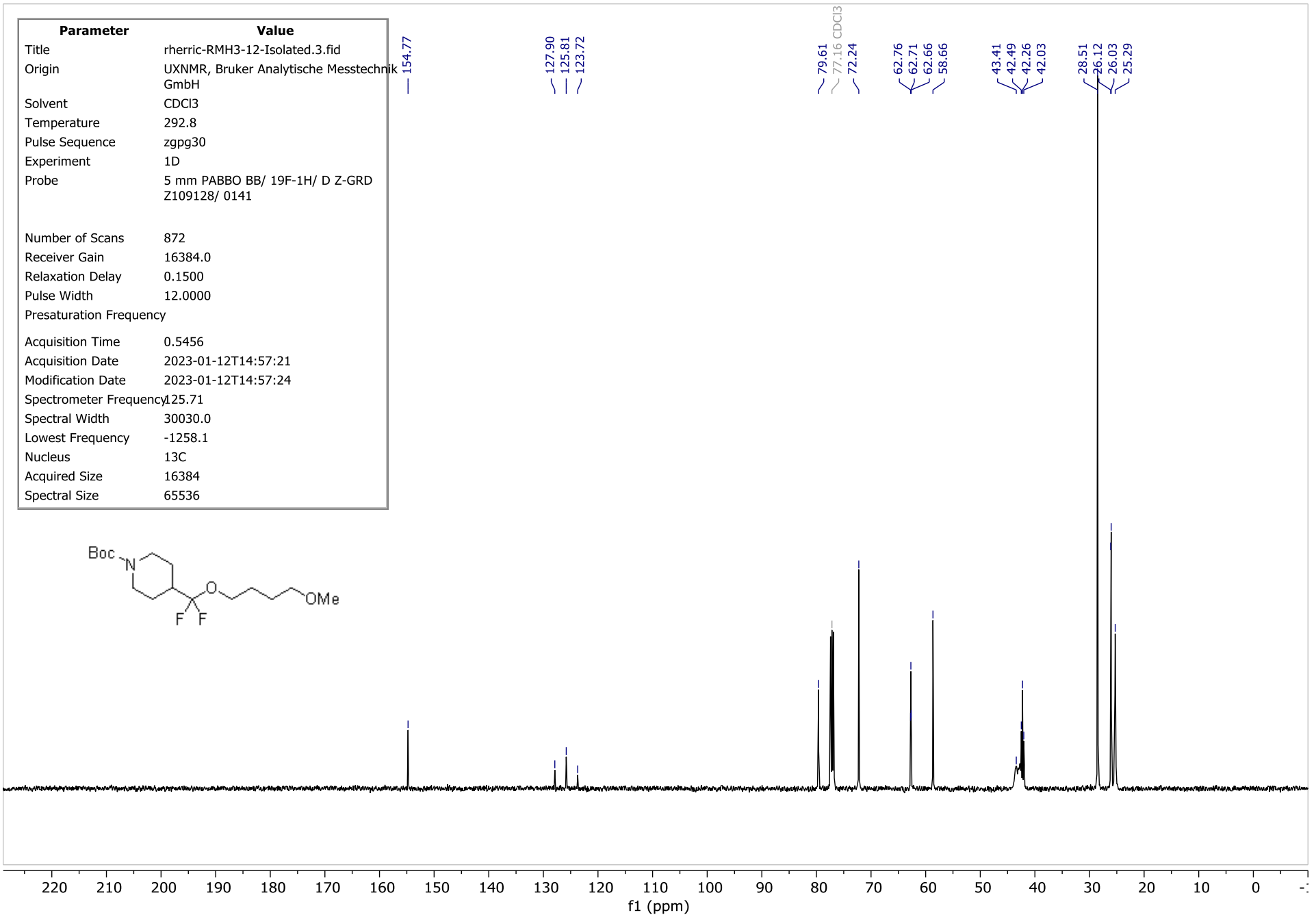
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-19T15:33:59
Modification Date	2023-01-19T15:34:02
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97262.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

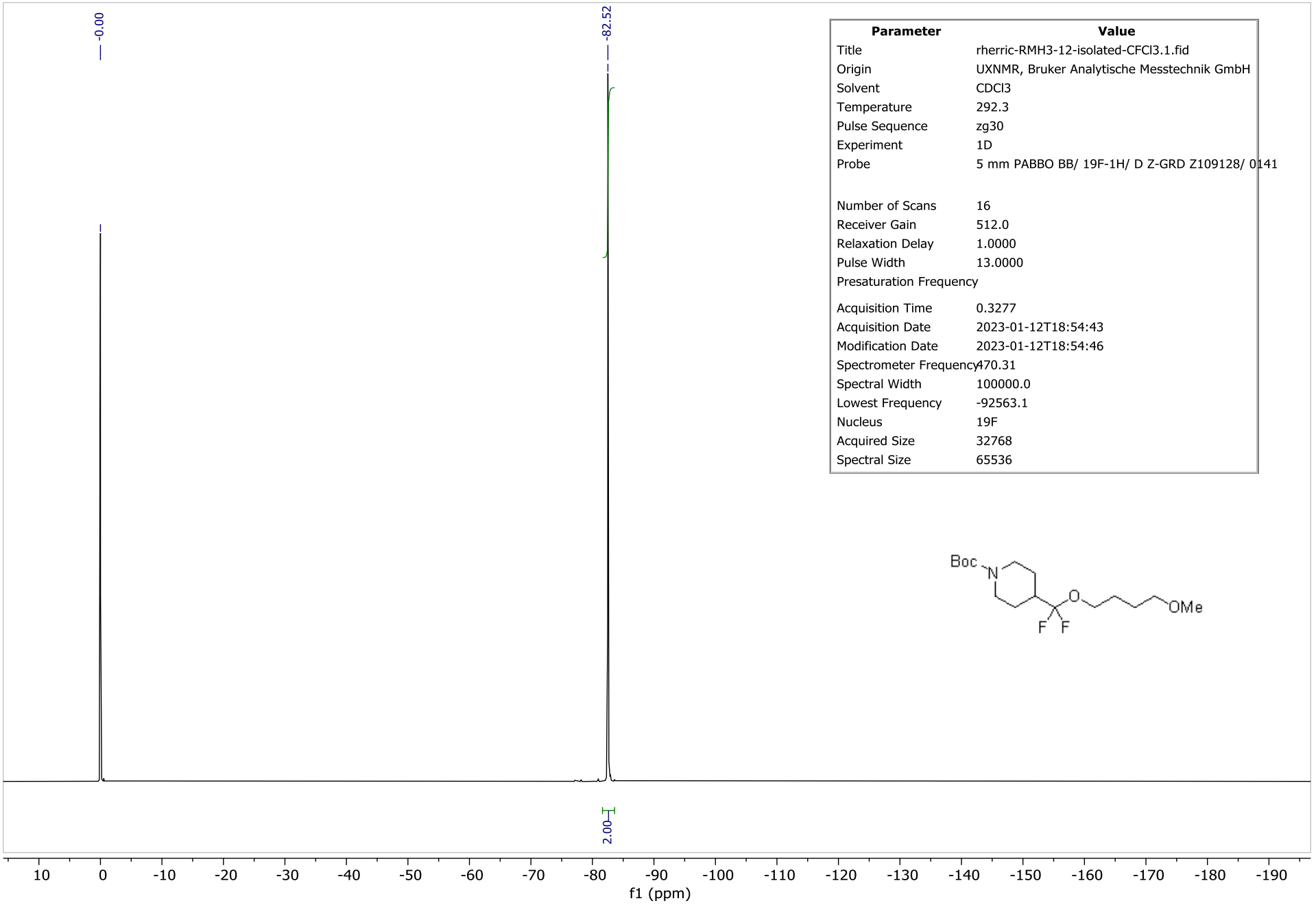
NMR Spectra for Compound ***tert*-butyl 4-(difluoro(4-methoxybutoxy)methyl)piperidine-1-carboxylate (7j)**

Parameter	Value
Title	rherric-RMH3-12-Isolated.2.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	50.8
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-01-12T14:43:52
Modification Date	2023-01-12T14:43:55
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2538.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536



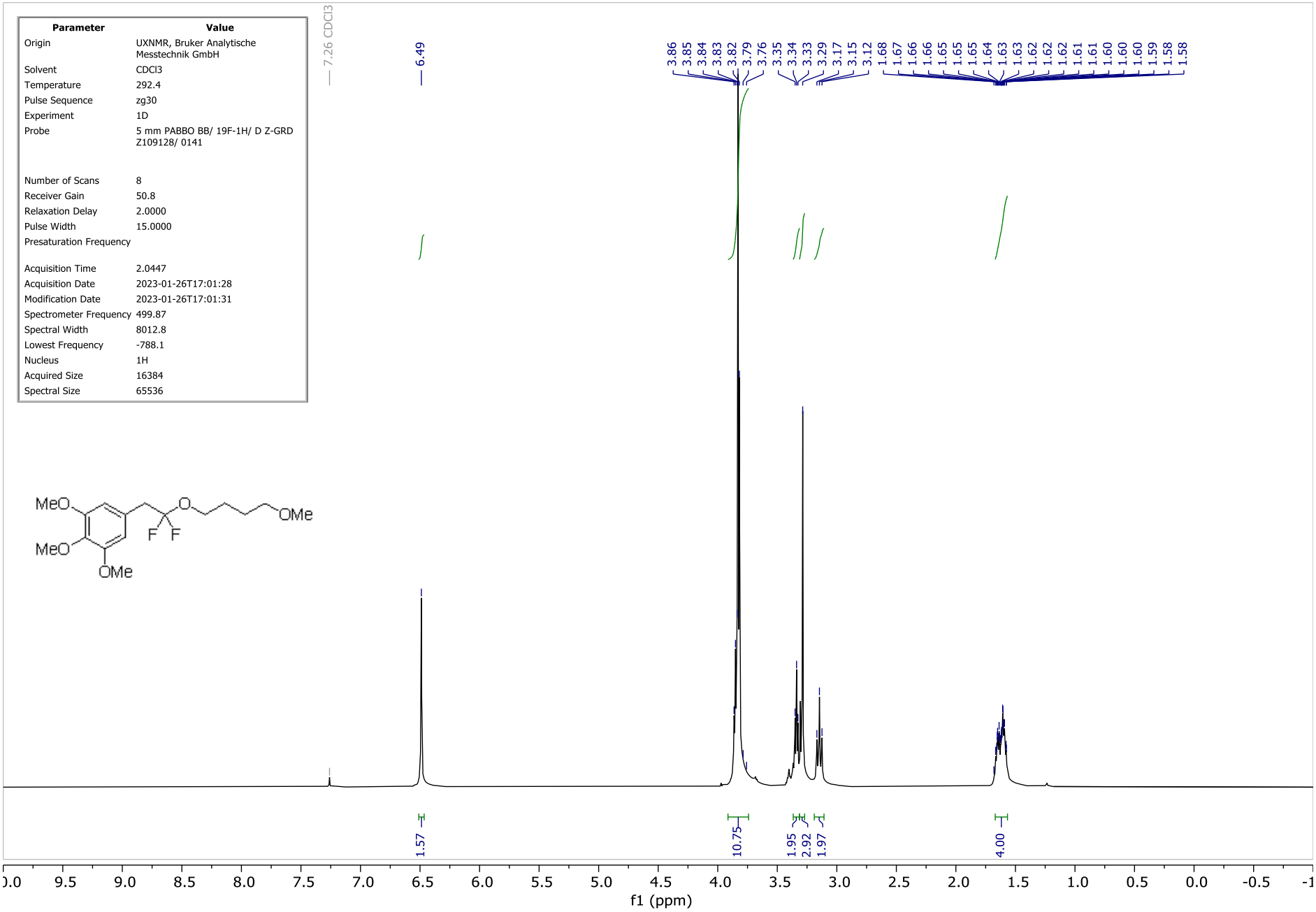
Parameter	Value
Title	rherric-RMH3-12-Isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	872
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-01-12T14:57:21
Modification Date	2023-01-12T14:57:24
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1258.1
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



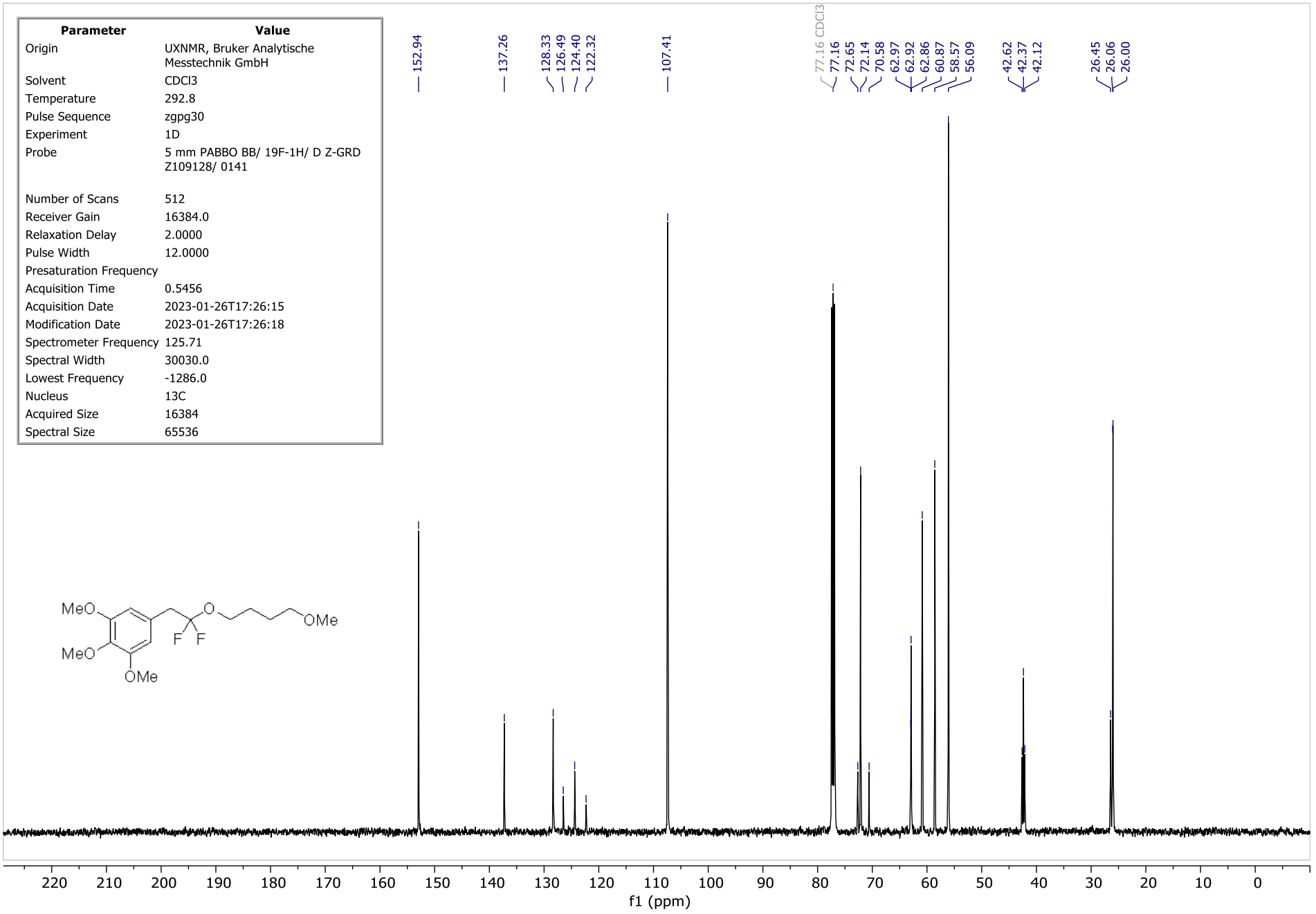


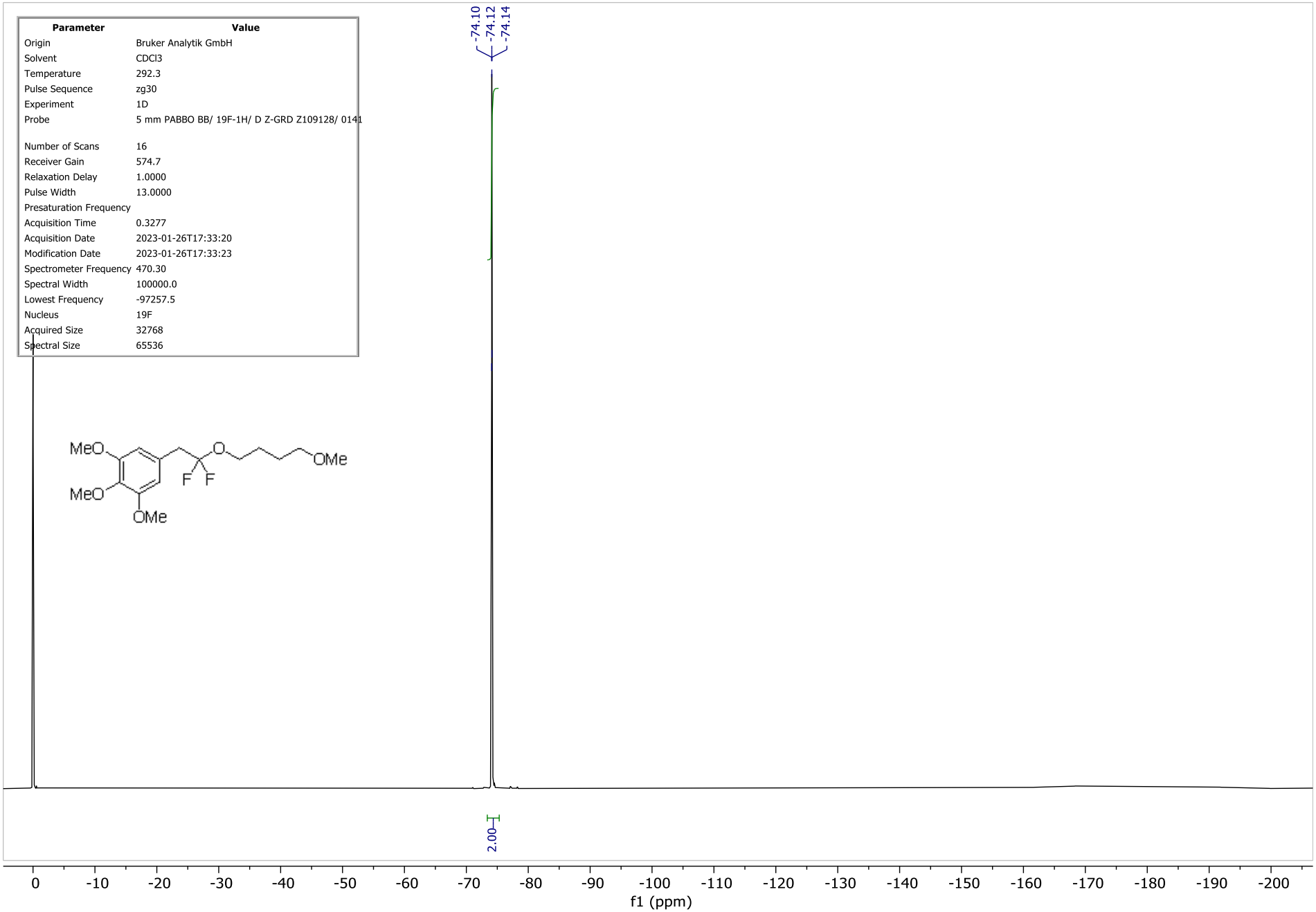
Parameter	Value
Title	rherric-RMH3-12-isolated-CFCl3.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-12T18:54:43
Modification Date	2023-01-12T18:54:46
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92563.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **5-(2,2-difluoro-2-(4-methoxybutoxy)ethyl)-1,2,3-trimethoxybenzene (7k)**


Parameter Value
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 292.4
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 8
Receiver Gain 50.8
Relaxation Delay 2.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 2.0447
Acquisition Date 2023-01-26T17:01:28
Modification Date 2023-01-26T17:01:31
Spectrometer Frequency 499.87
Spectral Width 8012.8
Lowest Frequency -788.1
Nucleus 1H
Acquired Size 16384
Spectral Size 65536
7.26 CDCl3
6.49
3.86 3.85 3.84 3.83 3.82 3.79 3.76 3.35 3.34 3.33 3.29 3.17 3.15 3.12
1.68 1.67 1.66 1.66 1.65 1.65 1.65 1.64 1.63 1.63 1.62 1.62 1.62 1.61 1.61 1.60 1.60 1.60 1.59 1.58 1.58
MeO
MeO
OMe
O
F F
OMe
1.57
10.75
1.95
2.92
1.97
4.00
f1 (ppm)

Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	512
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-01-26T17:26:15
Modification Date	2023-01-26T17:26:18
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

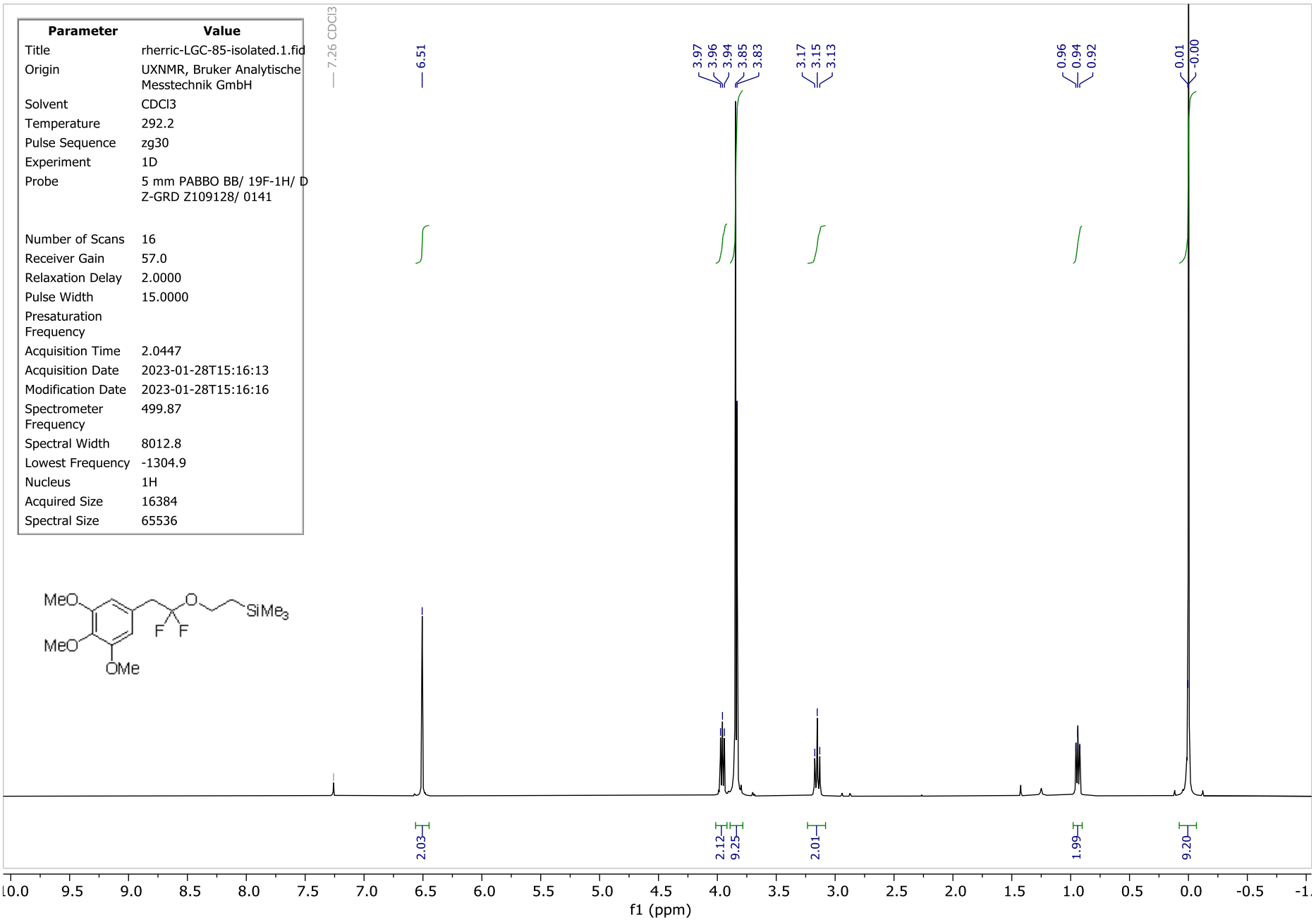


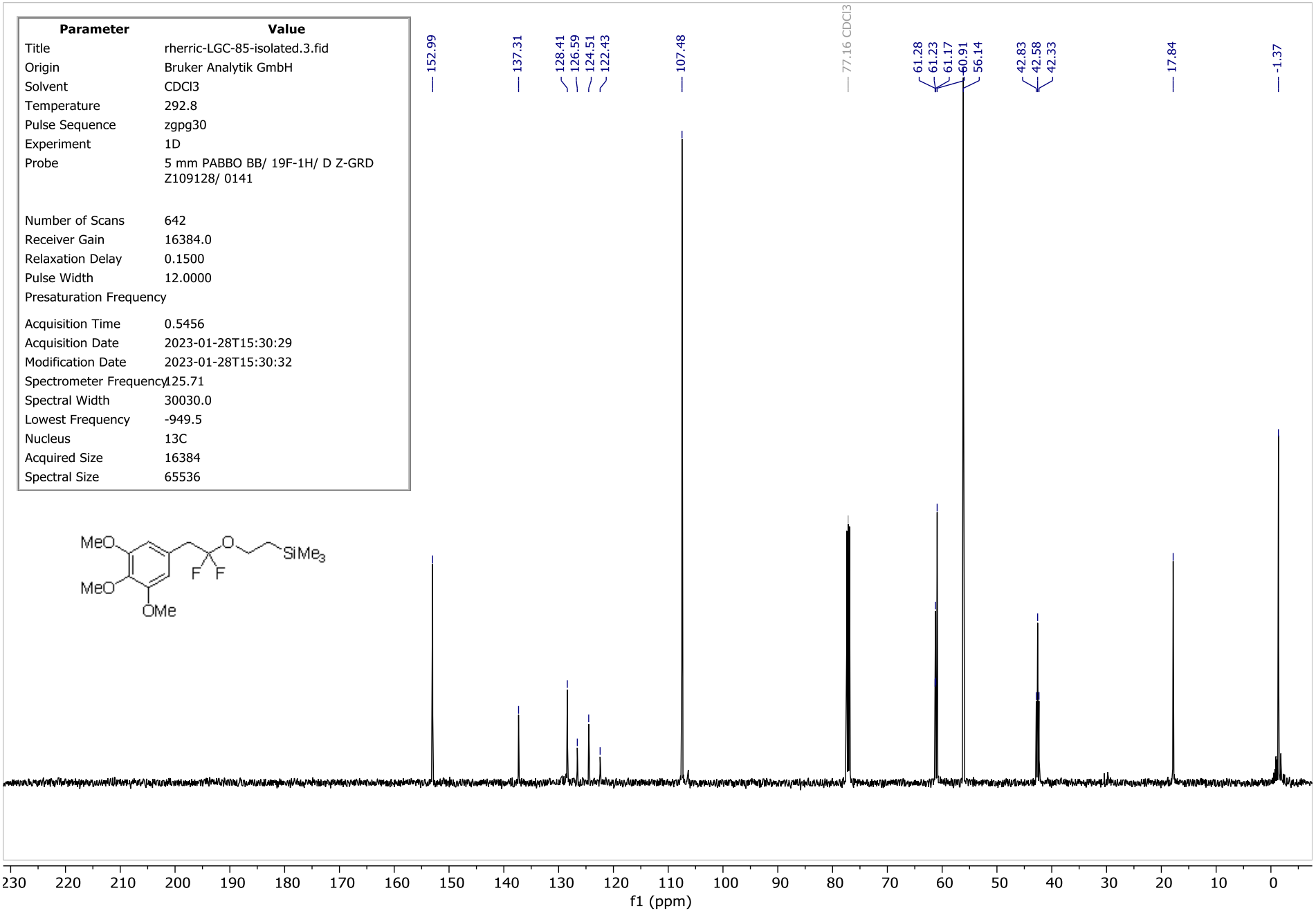


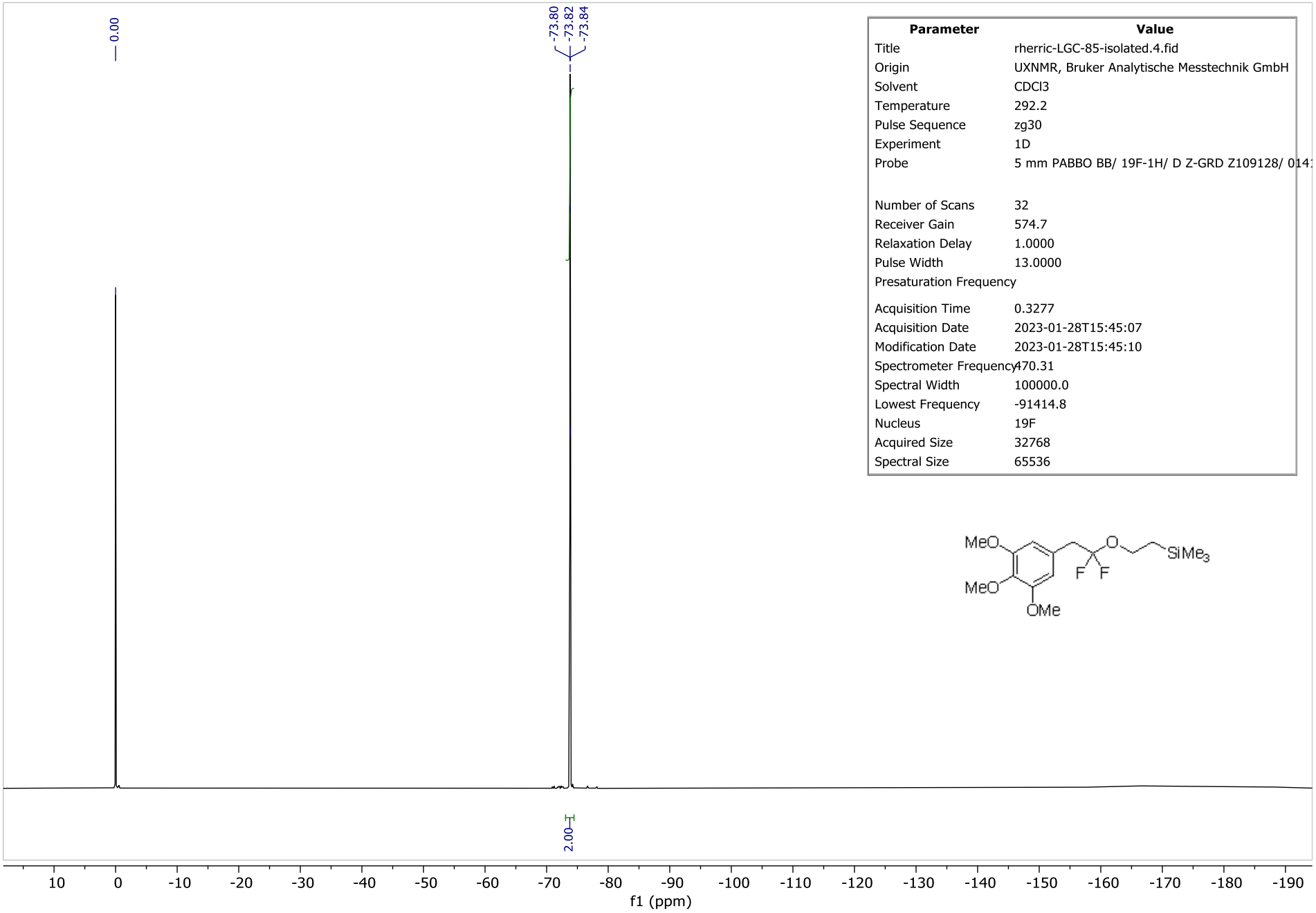
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-26T17:33:20
Modification Date	2023-01-26T17:33:23
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97257.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **(2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)ethyl)trimethylsilane (7l)**

Parameter	Value
Title	rherric-LGC-85-isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	57.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-01-28T15:16:13
Modification Date	2023-01-28T15:16:16
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-1304.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

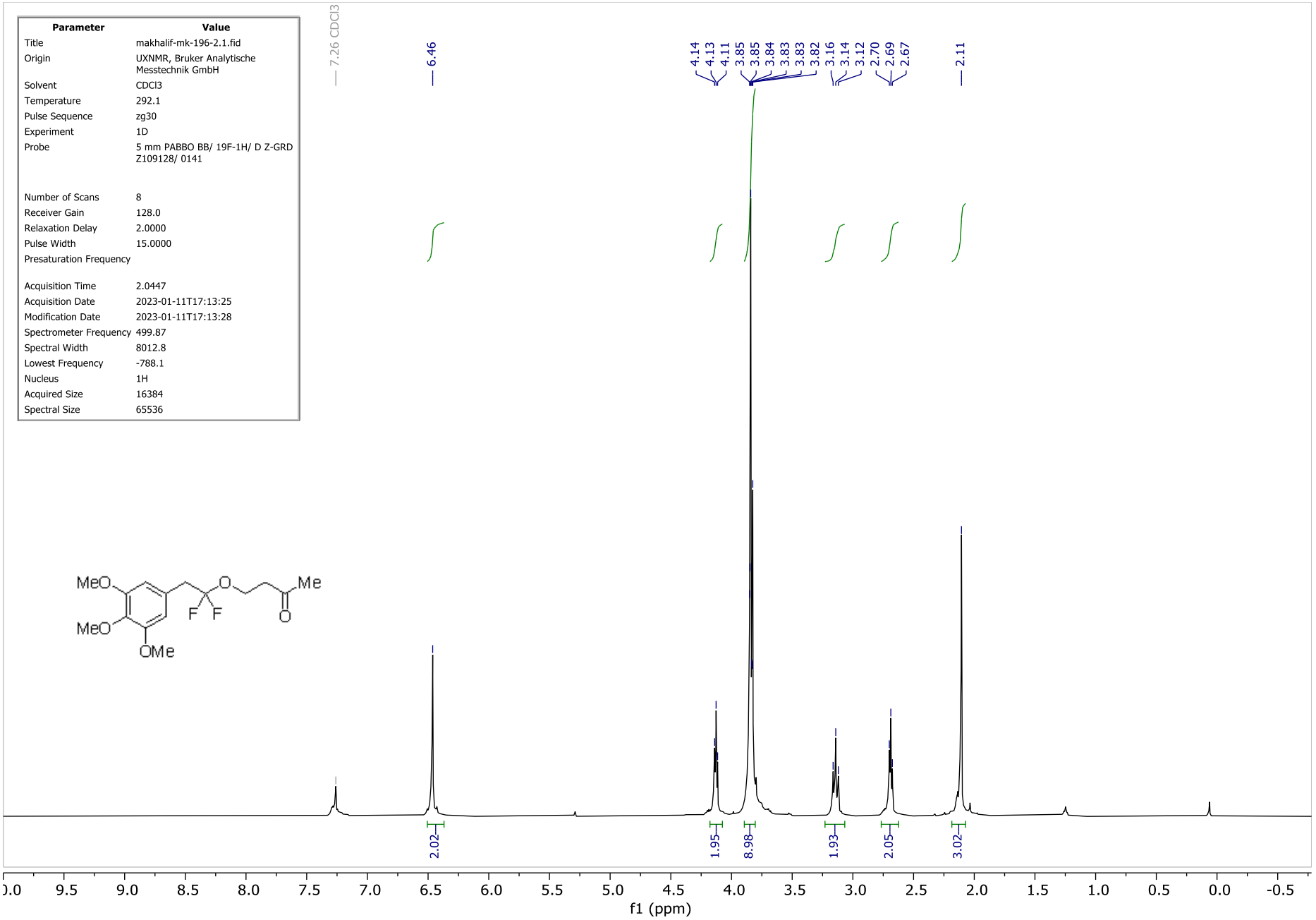



Parameter Value
Title rherric-LGC-85-isolated.3.fid
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 292.8
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 642
Receiver Gain 16384.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.5456
Acquisition Date 2023-01-28T15:30:29
Modification Date 2023-01-28T15:30:32
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -949.5
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
152.99
137.31
128.41
126.59
124.51
122.43
107.48
77.16 CDCl3
61.28
61.23
61.17
60.91
56.14
42.83
42.58
42.33
17.84
-1.37
MeO
MeO
OMe
O
F F
SiMe3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

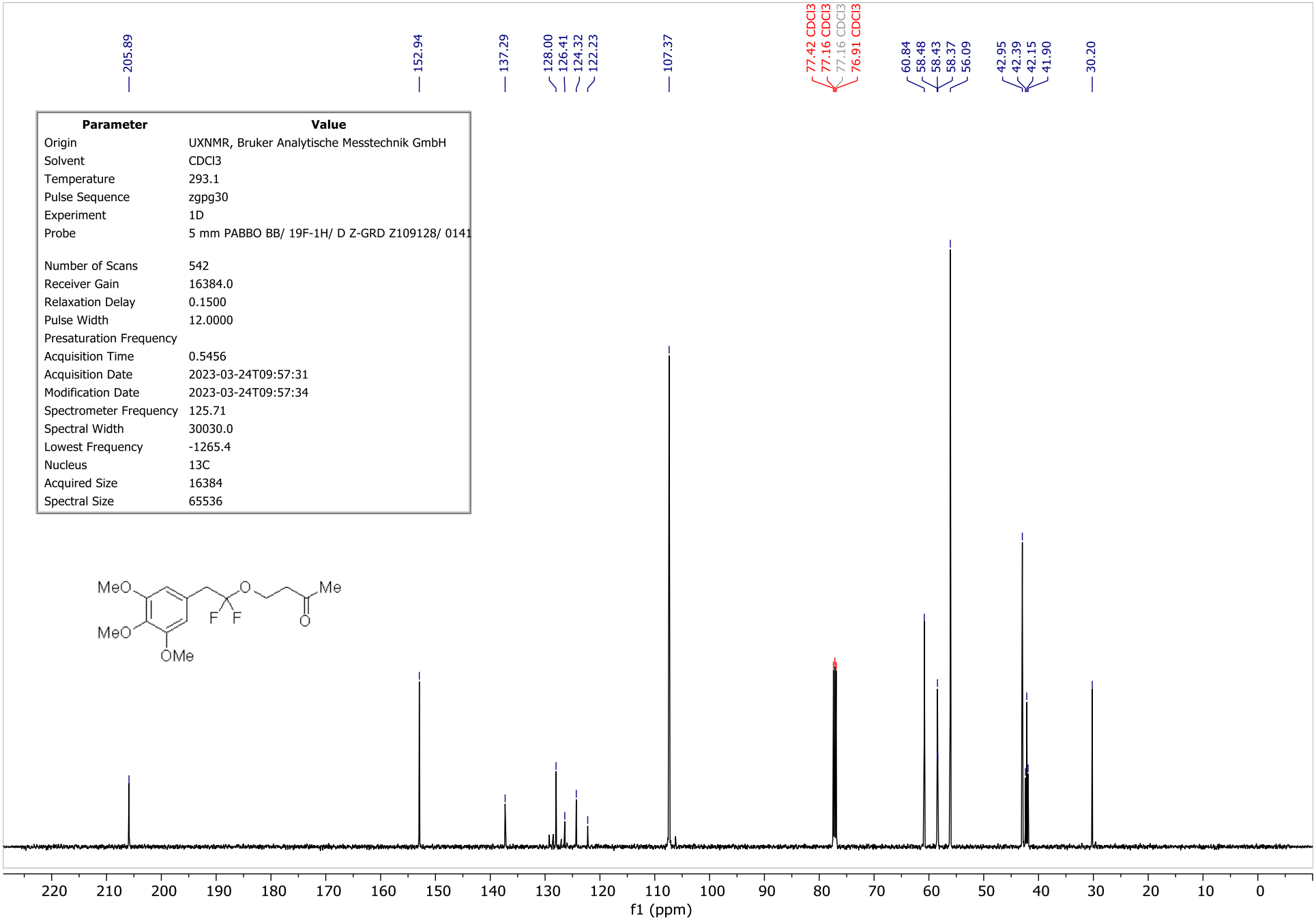


Parameter	Value
Title	rherric-LGC-85-isolated.4.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 014
Number of Scans	32
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-28T15:45:07
Modification Date	2023-01-28T15:45:10
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-91414.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

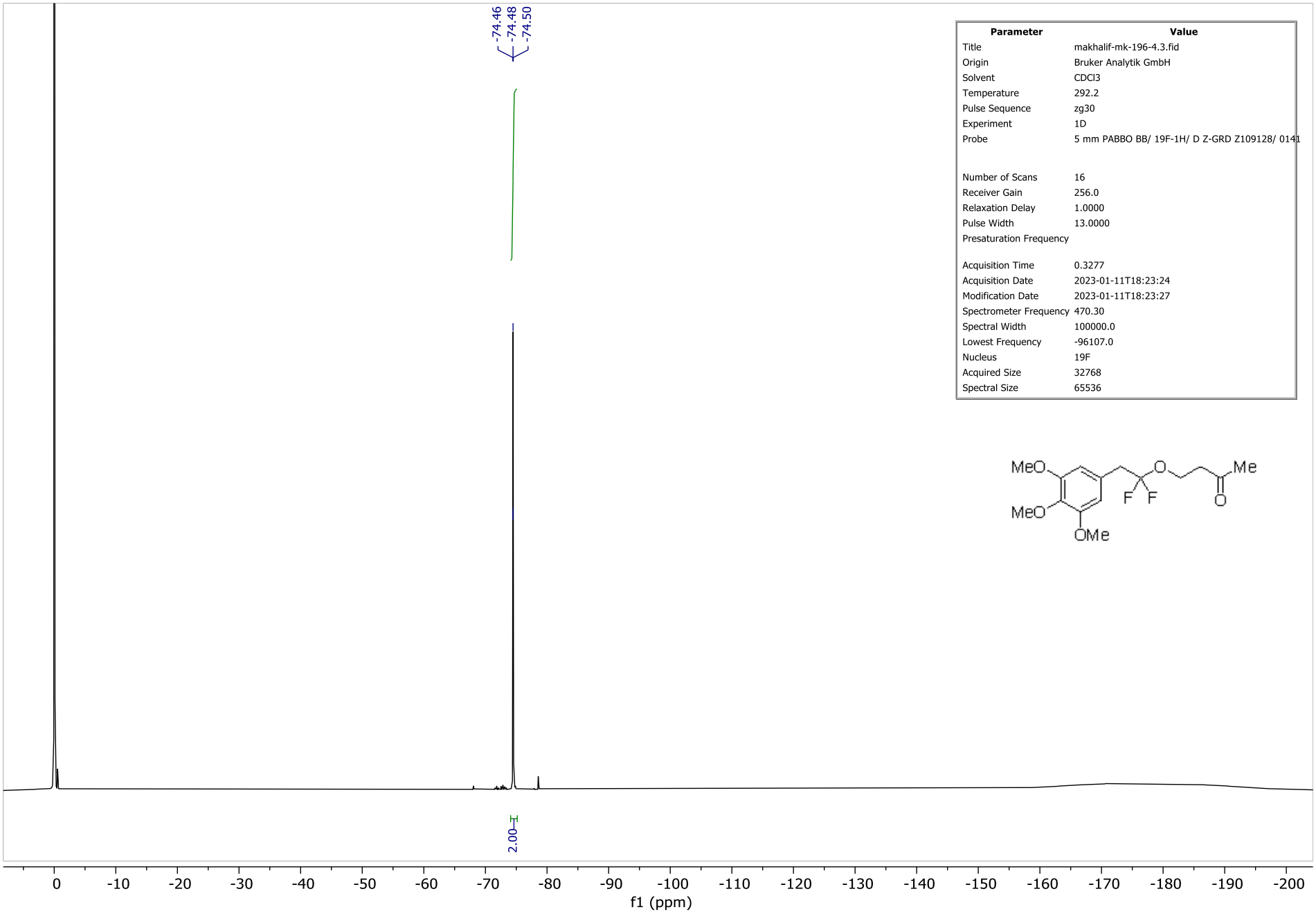
NMR Spectra for Compound **4-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)butan-2-one (7m)**



Parameter	Value
Title	makhalif-mk-196-2.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-01-11T17:13:25
Modification Date	2023-01-11T17:13:28
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

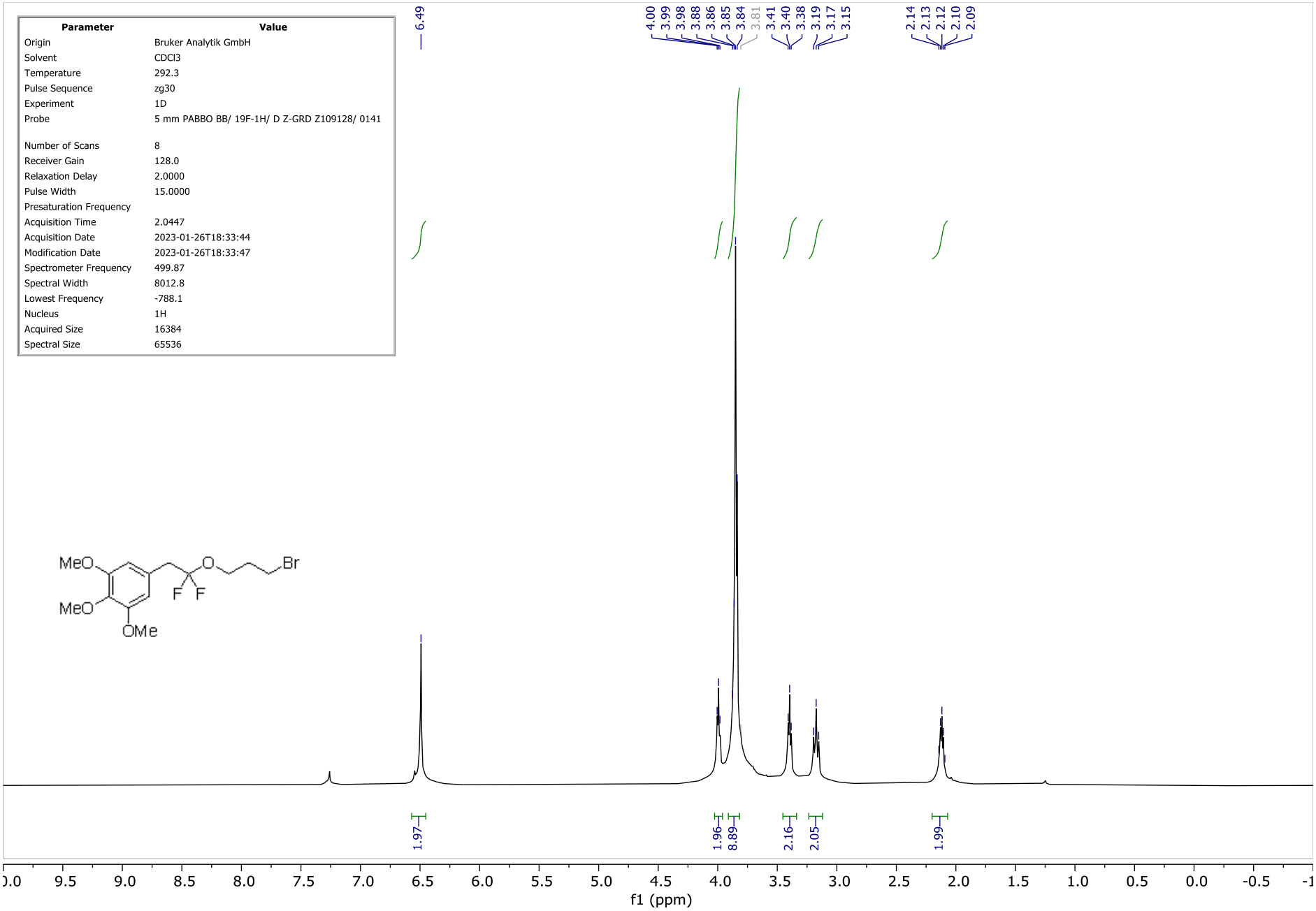


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	542
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-03-24T09:57:31
Modification Date	2023-03-24T09:57:34
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1265.4
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

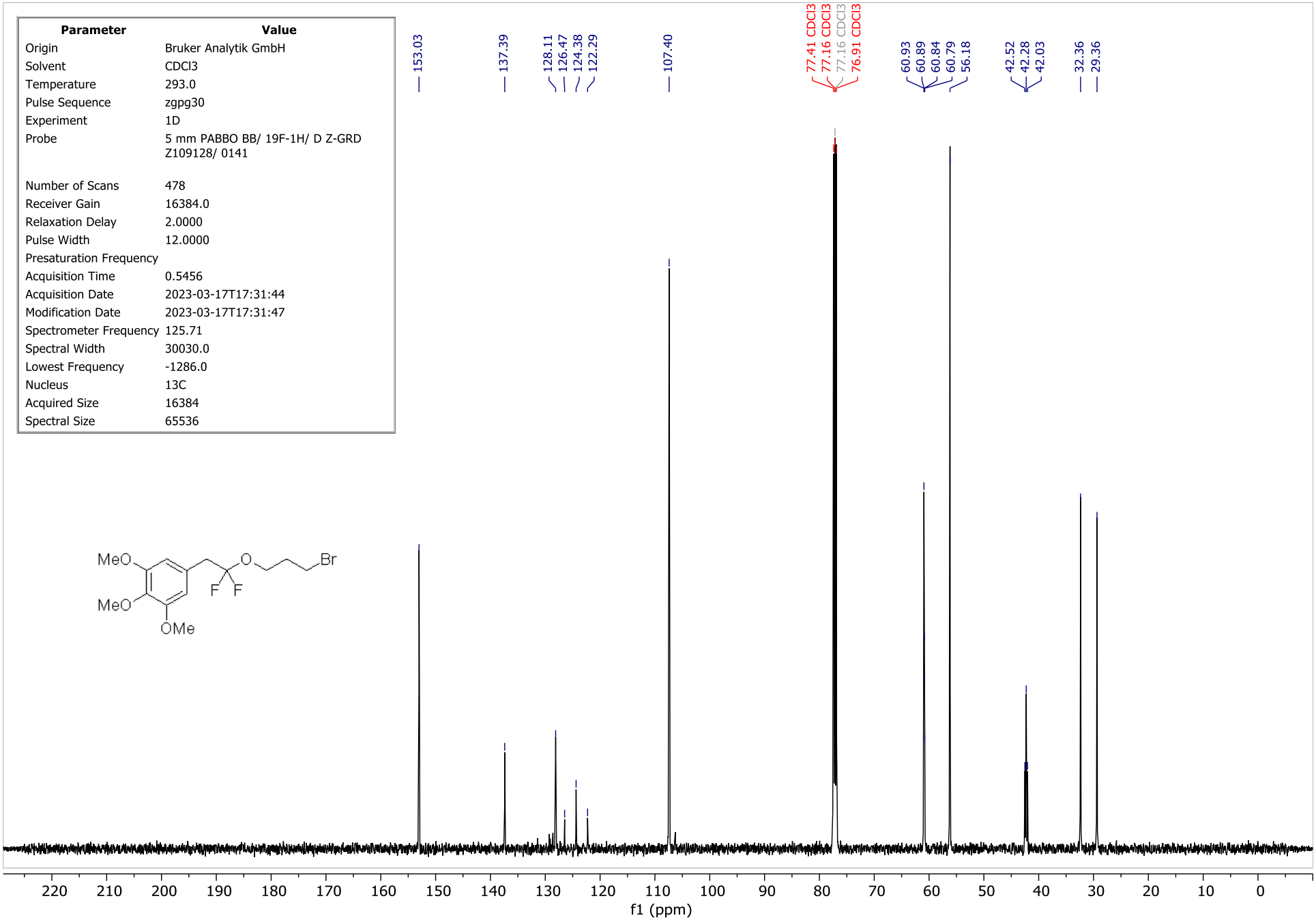


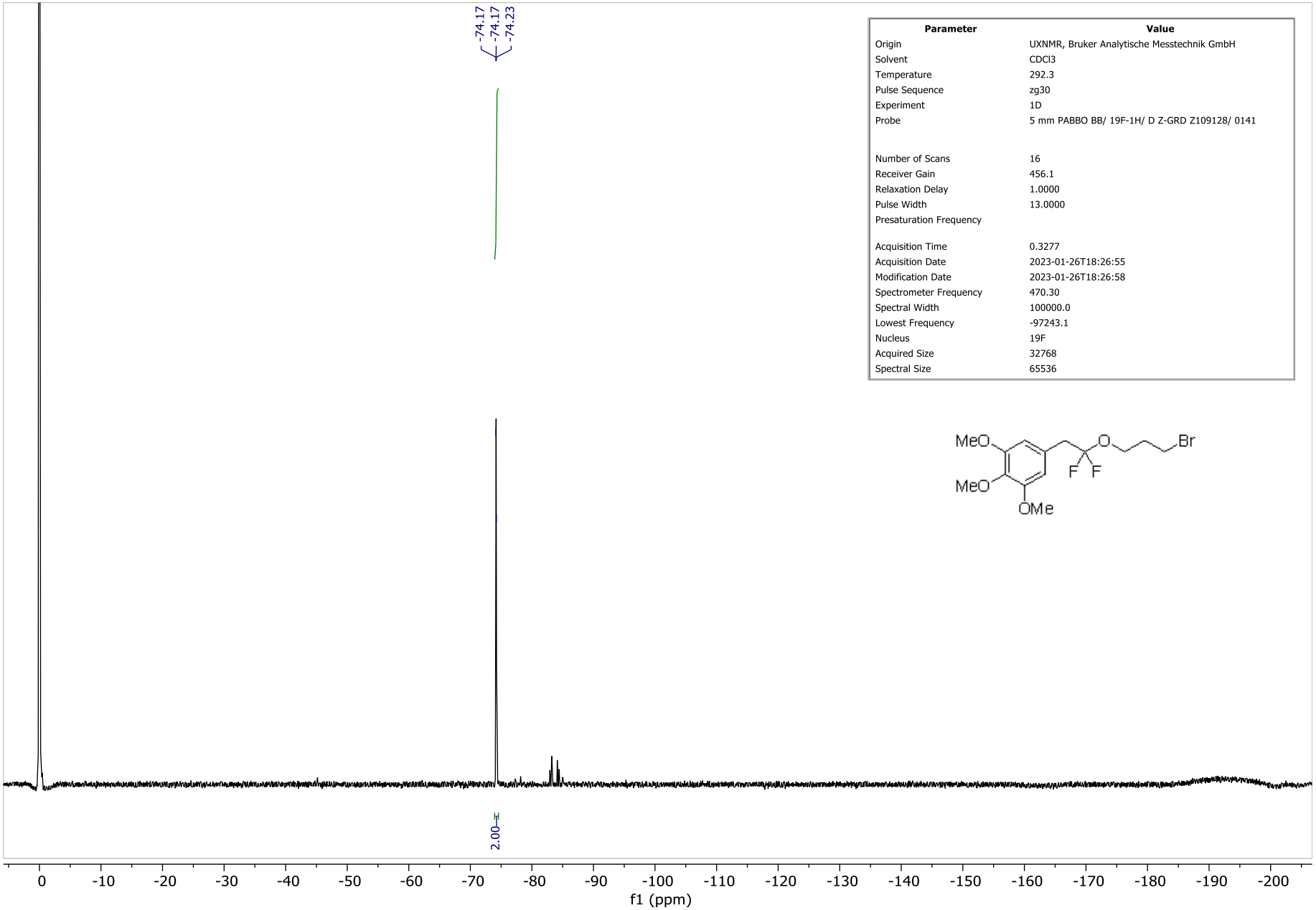
Parameter	Value
Title	makhalif-mk-196-4.3.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-11T18:23:24
Modification Date	2023-01-11T18:23:27
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96107.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **5-(2-(3-bromopropoxy)-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (7n)**



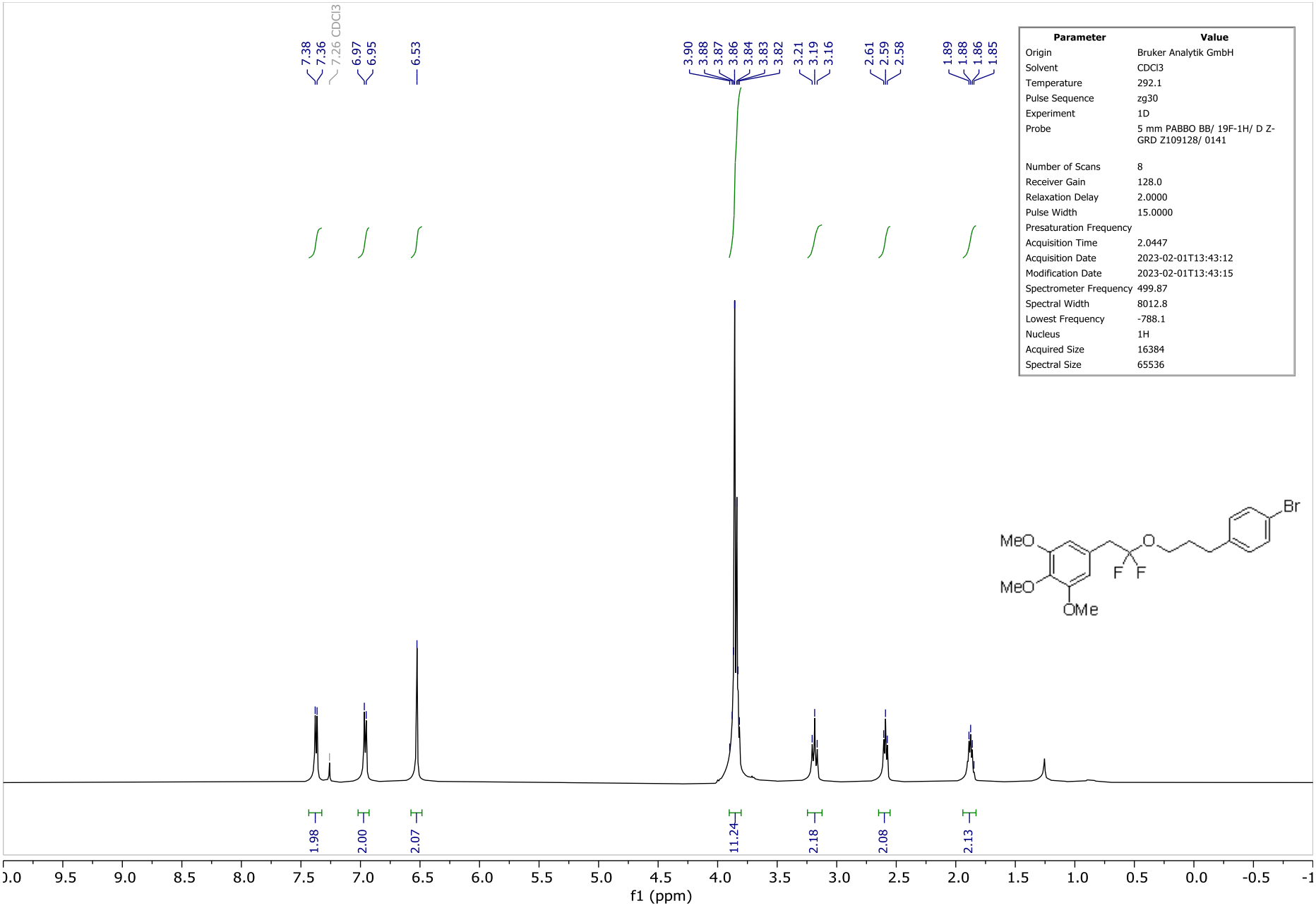
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	478
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-03-17T17:31:44
Modification Date	2023-03-17T17:31:47
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





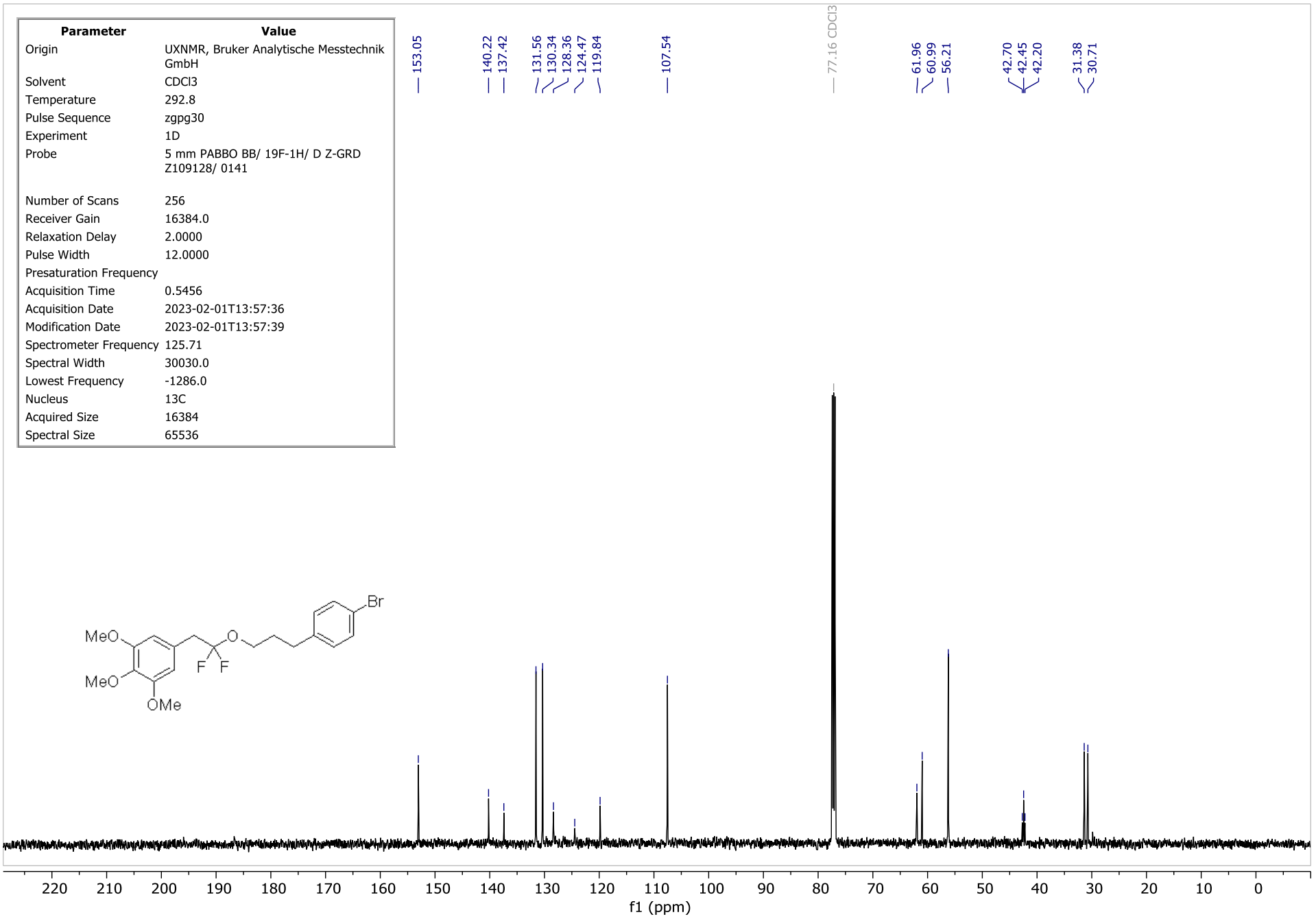
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	456.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-26T18:26:55
Modification Date	2023-01-26T18:26:58
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97243.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

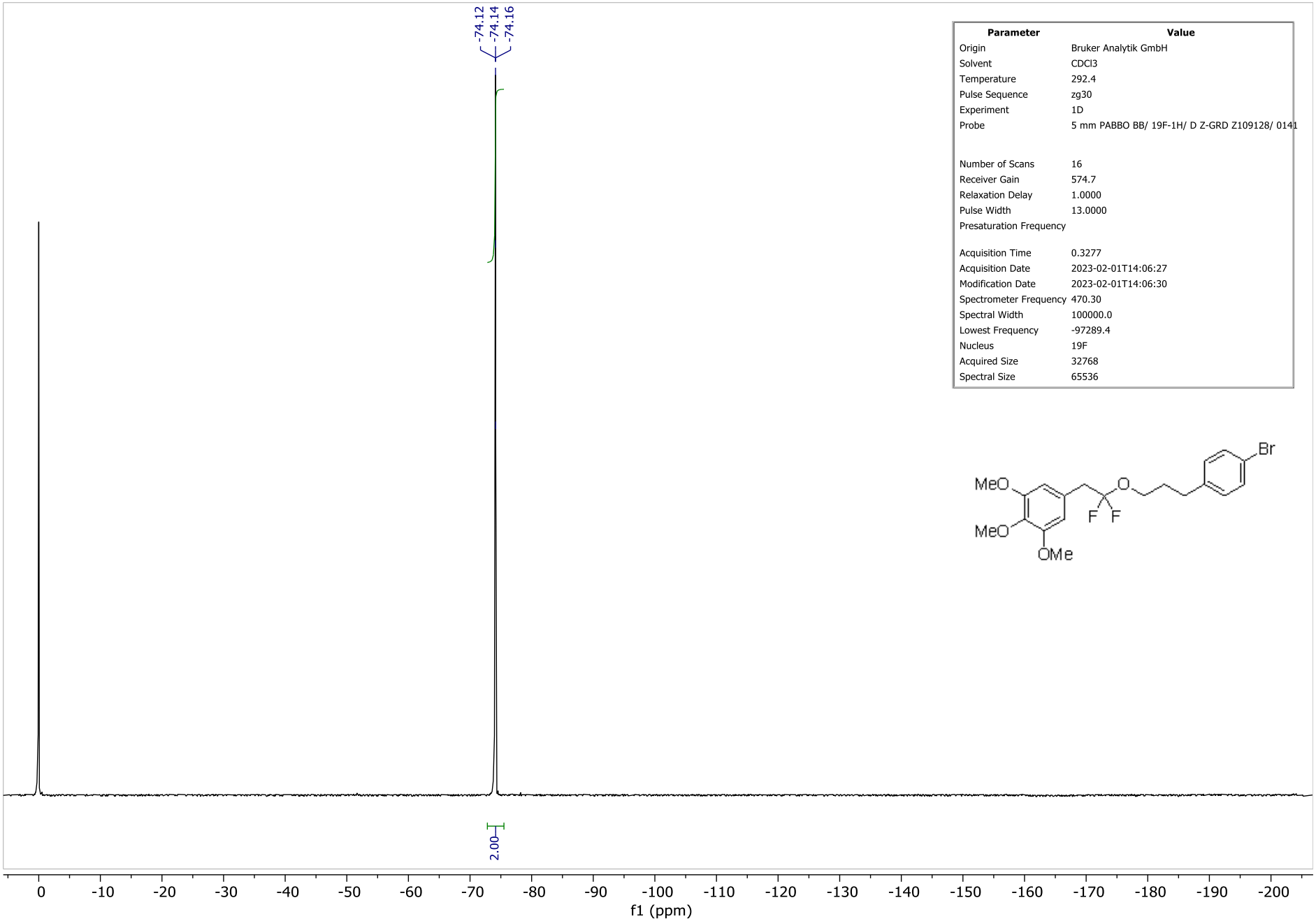
NMR Spectra for Compound **5-(2-(3-(4-bromophenyl)propoxy)-2,2-difluoroethyl)-1,2,3-trimethoxybenzene (7o)**



Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-02-01T13:43:12
Modification Date	2023-02-01T13:43:15
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

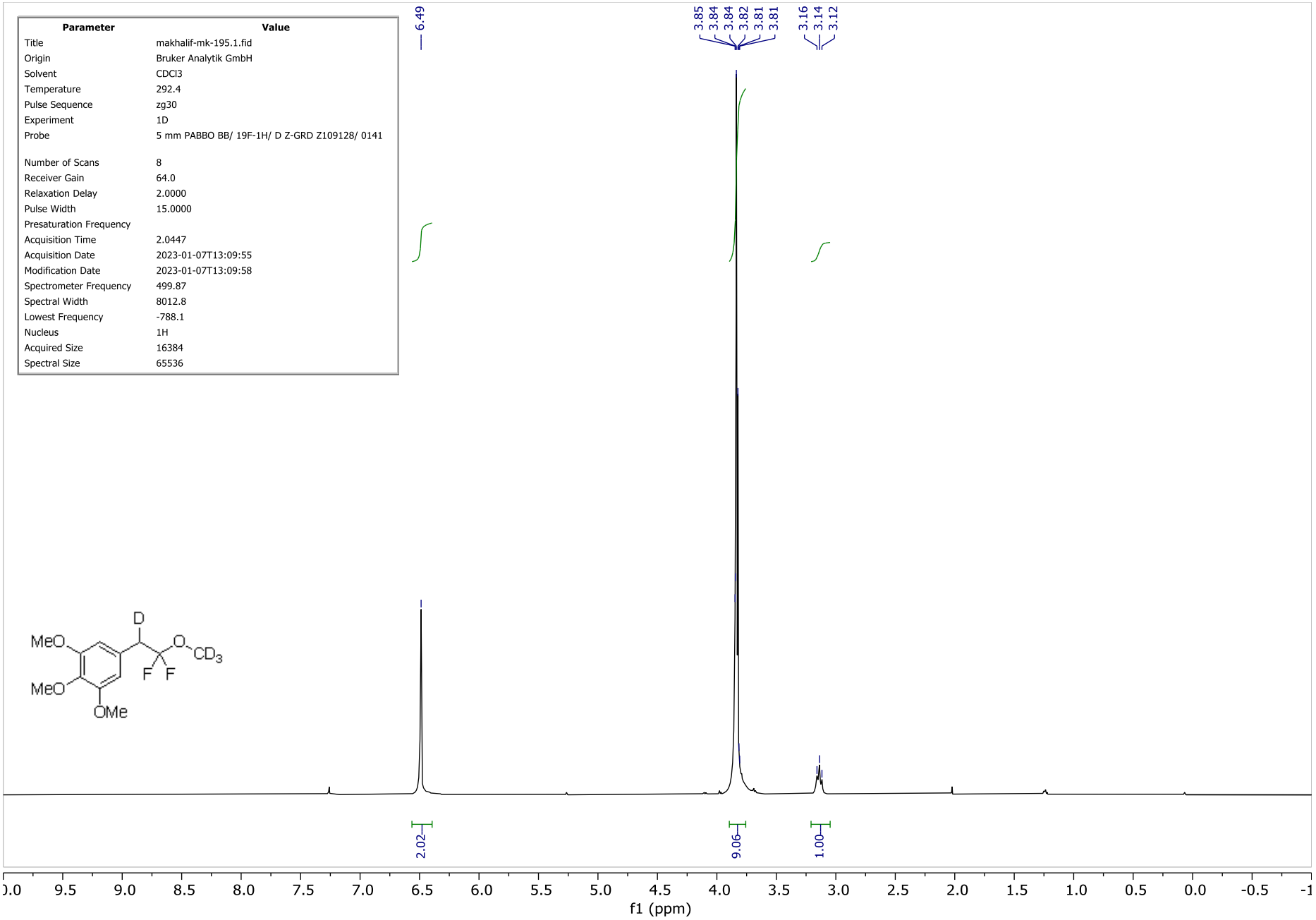
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-02-01T13:57:36
Modification Date	2023-02-01T13:57:39
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



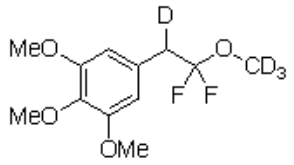


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-02-01T14:06:27
Modification Date	2023-02-01T14:06:30
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97289.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

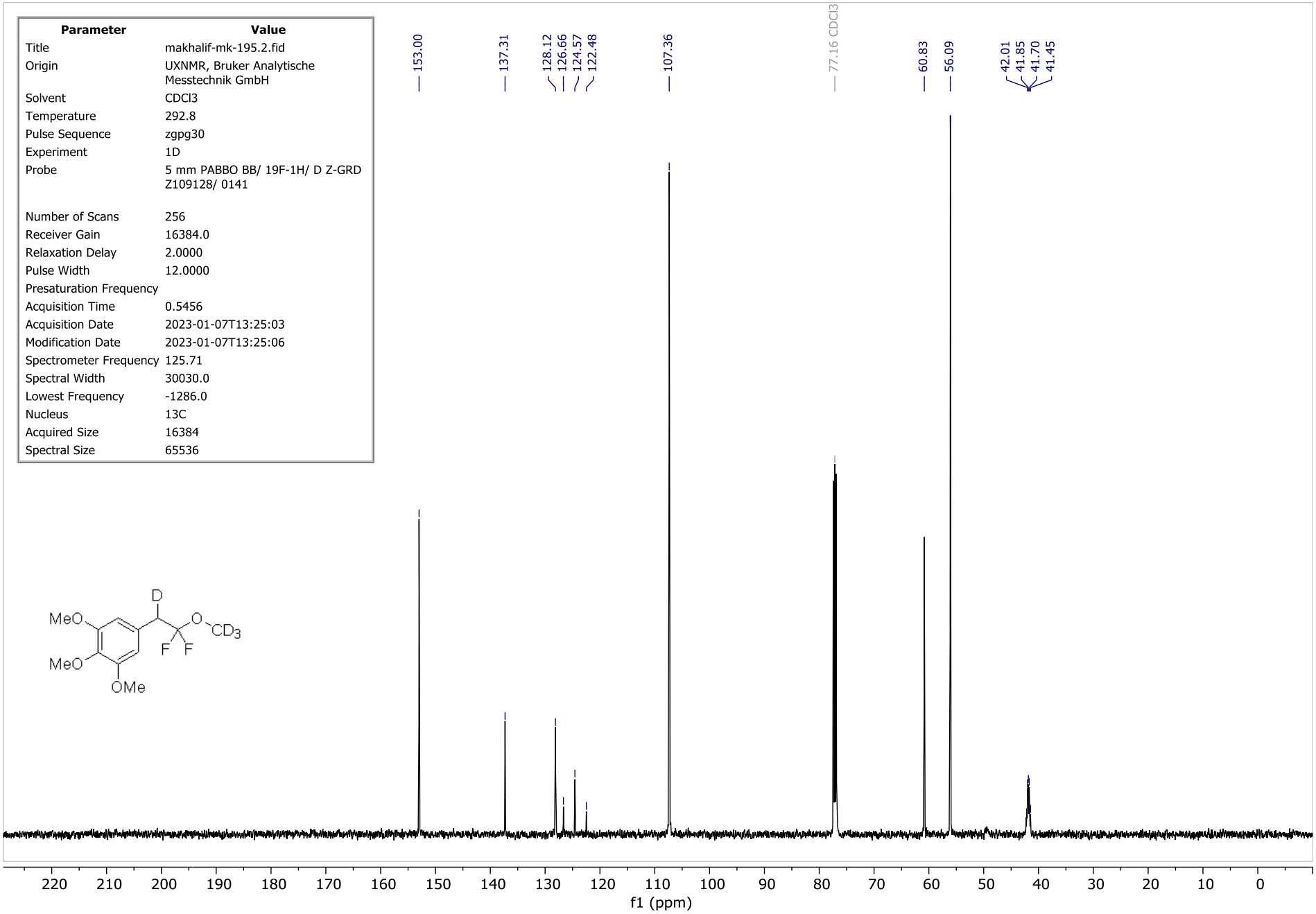
NMR Spectra for Compound **5-(2,2-difluoro-2-(methoxy-d_3)ethyl-1-d)-1,2,3-trimethoxybenzene (7p)**

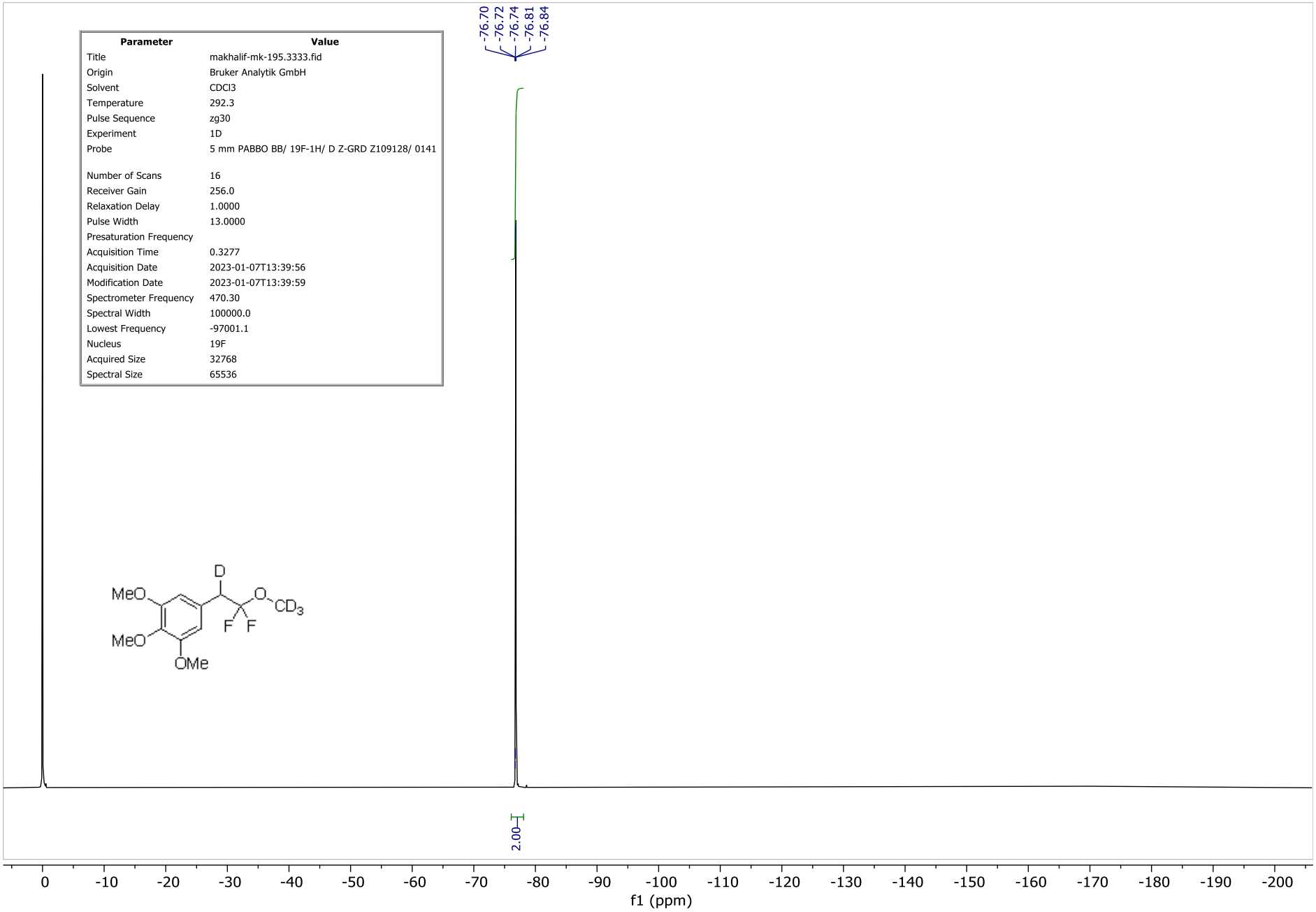


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	D2O
Temperature	292.4
Pulse Sequence	zg2hf3.jsh
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	64
Receiver Gain	1625.5
Relaxation Delay	2.0000
Pulse Width	80.0000
Presaturation Frequency	
Acquisition Time	1.3369
Acquisition Date	2023-01-13T11:40:16
Modification Date	2023-01-13T11:40:20
Spectrometer Frequency	76.73
Spectral Width	3063.7
Lowest Frequency	-1160.9
Nucleus	2H
Acquired Size	4096
Spectral Size	8192

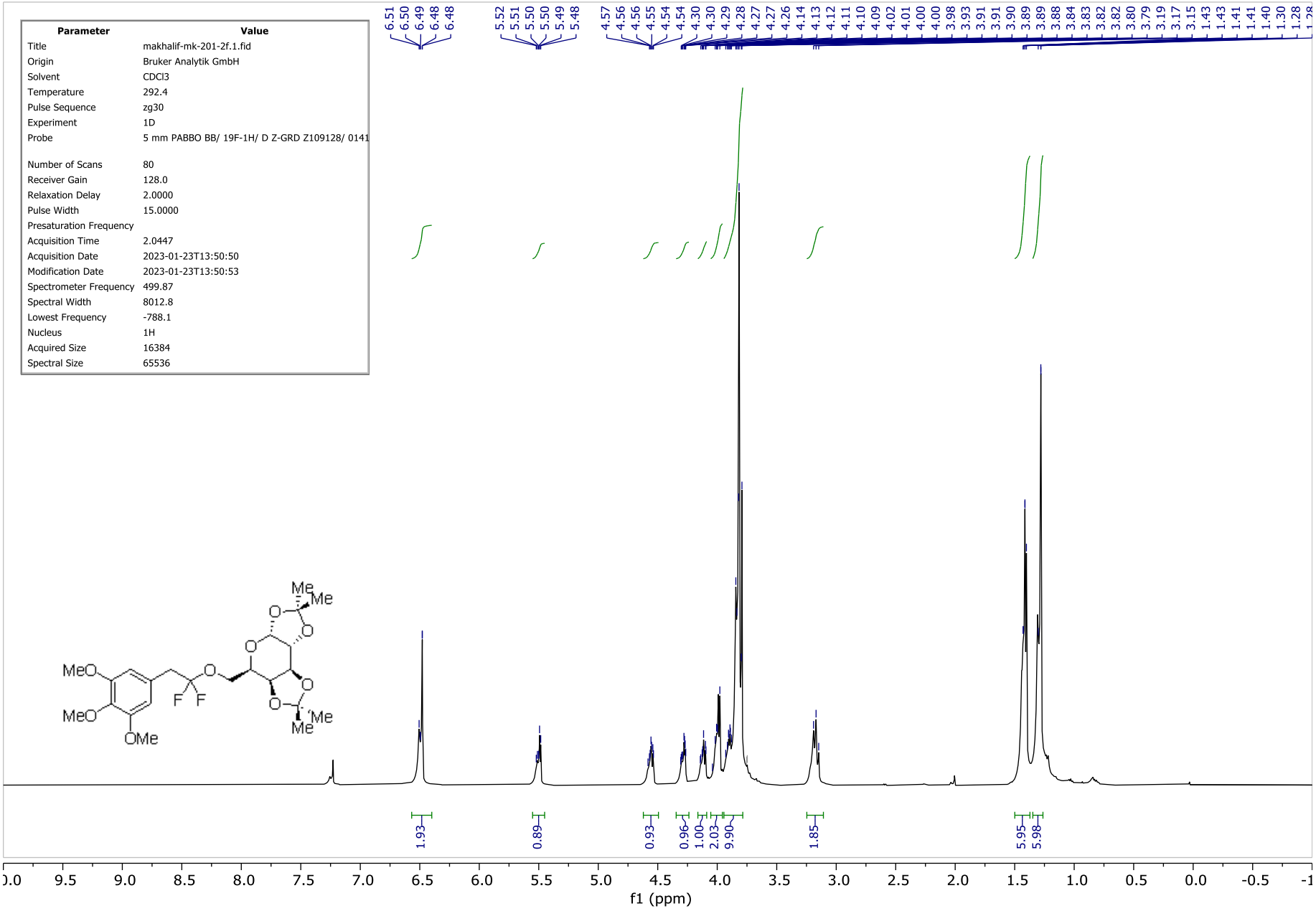


Parameter	Value
Title	makhalif-mk-195.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	256
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-01-07T13:25:03
Modification Date	2023-01-07T13:25:06
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

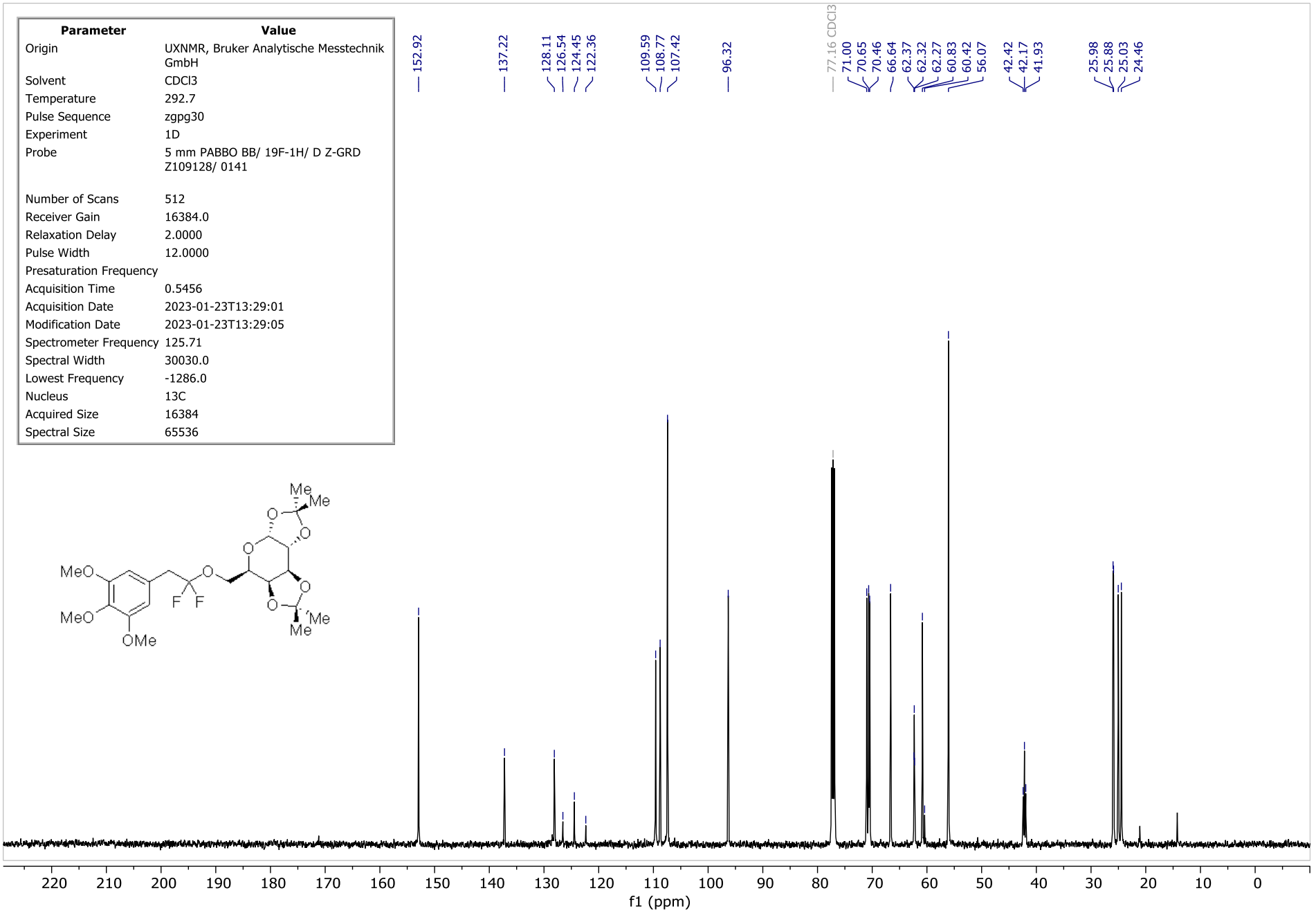


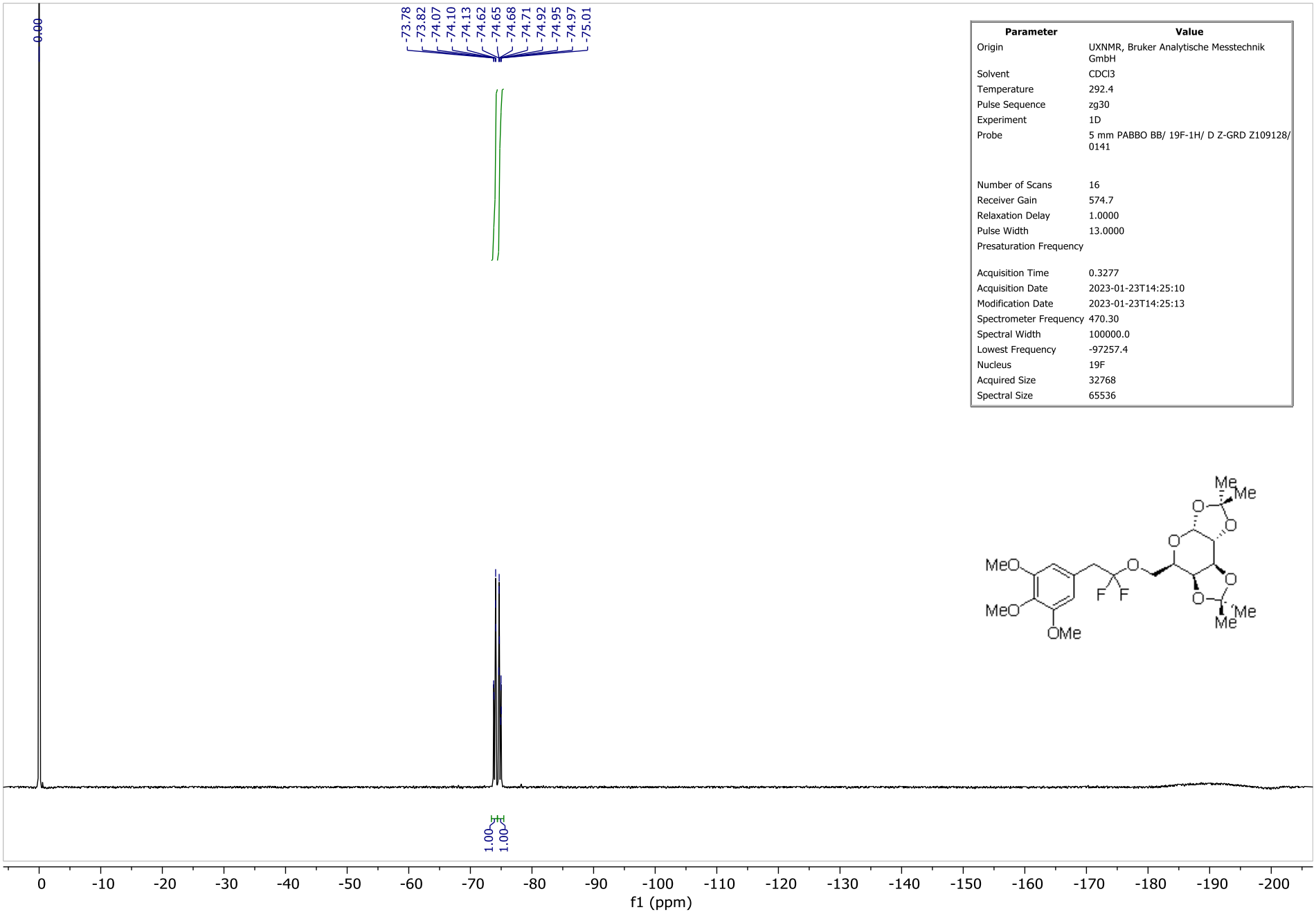

-76.70
-76.72
-76.74
-76.81
-76.84
Parameter Value
Title makhalif-mk-195.3333.fid
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 292.3
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 16
Receiver Gain 256.0
Relaxation Delay 1.0000
Pulse Width 13.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2023-01-07T13:39:56
Modification Date 2023-01-07T13:39:59
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97001.1
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
D
MeO
MeO
OMe
O
CD3
F
F
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

NMR Spectra for Compound **(3a*S*,5*S*,5a*R*,8a*R*,8b*S*)-5-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran (7q)**



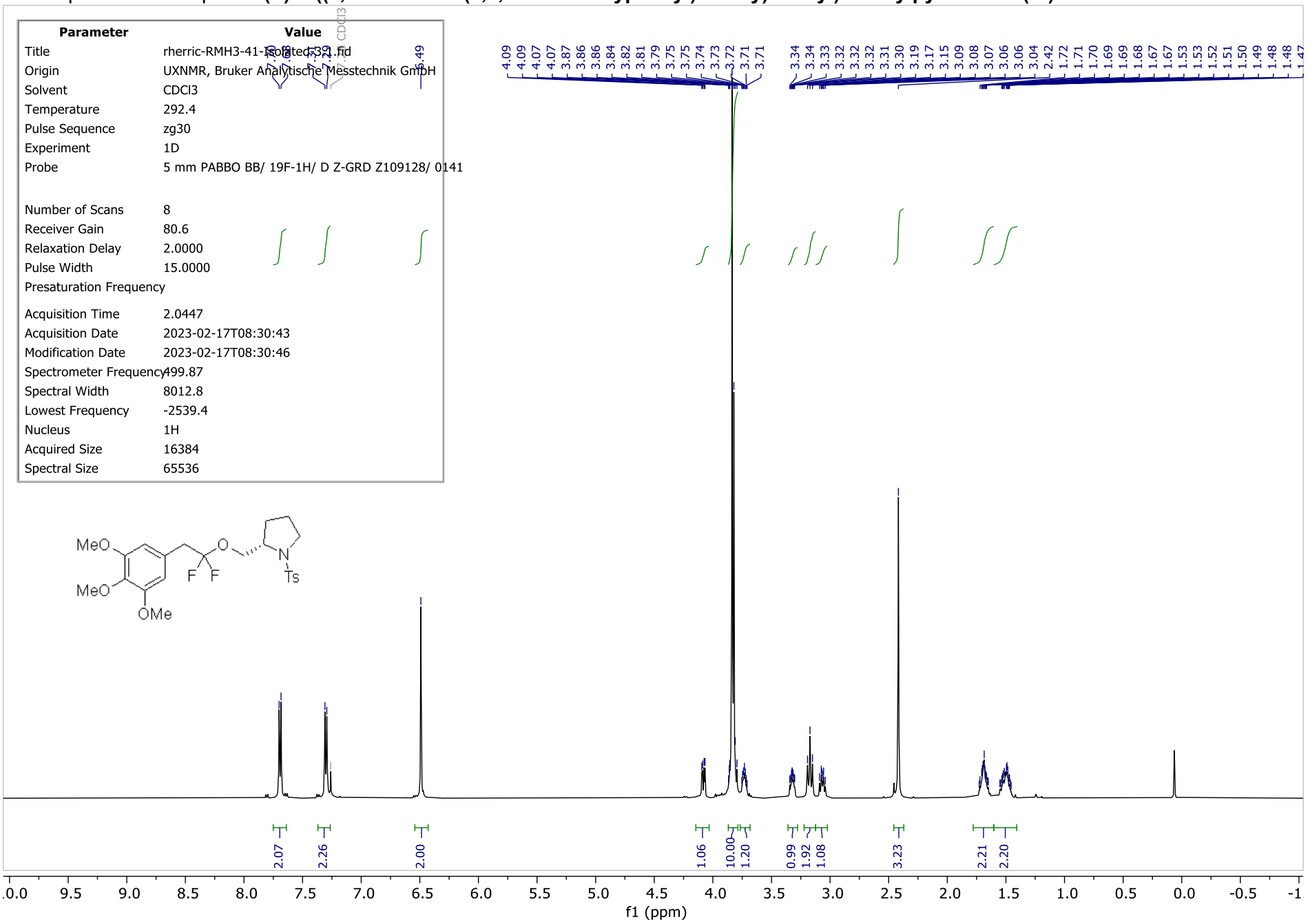
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.7
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	512
Receiver Gain	16384.0
Relaxation Delay	2.0000
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-01-23T13:29:01
Modification Date	2023-01-23T13:29:05
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



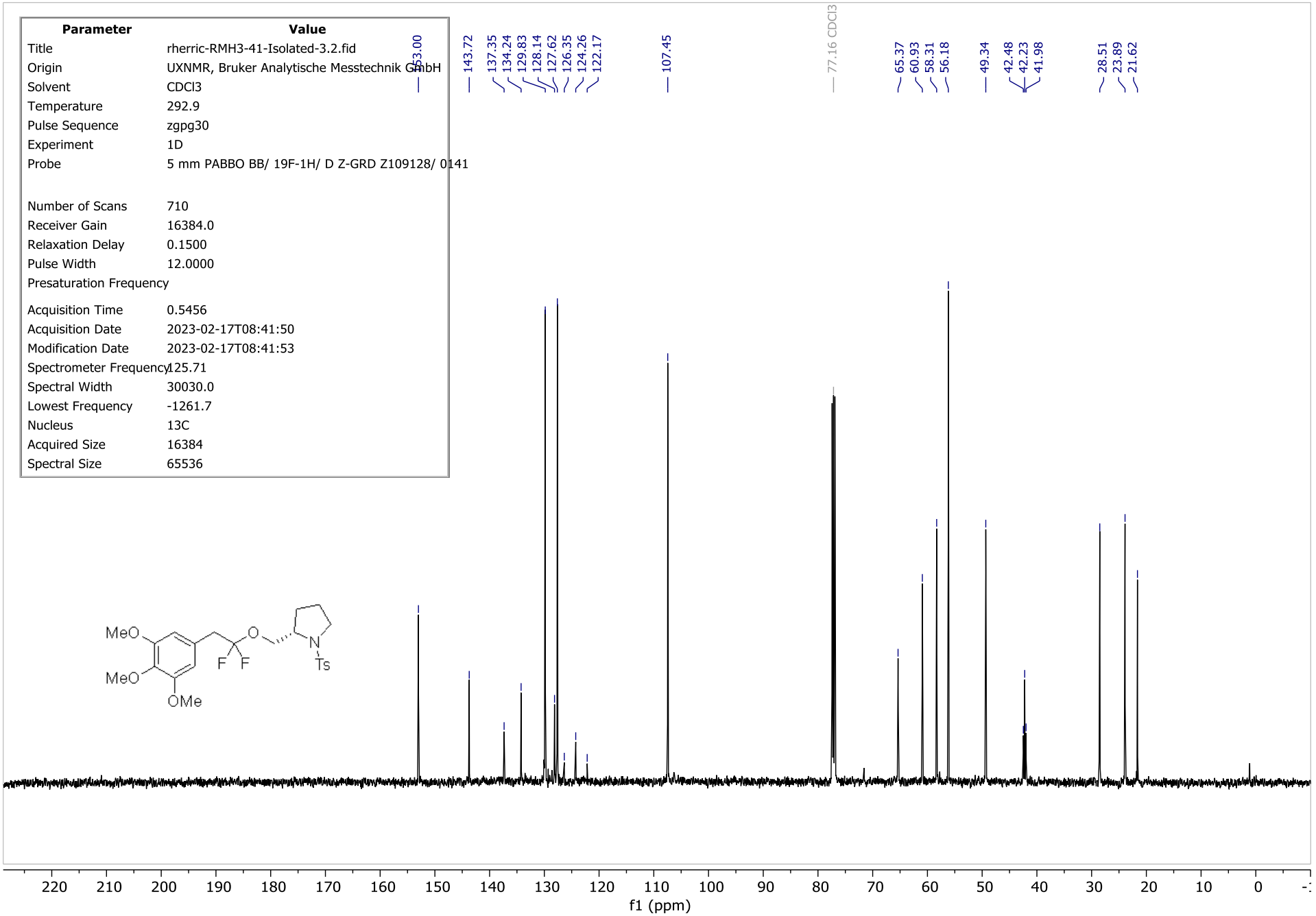


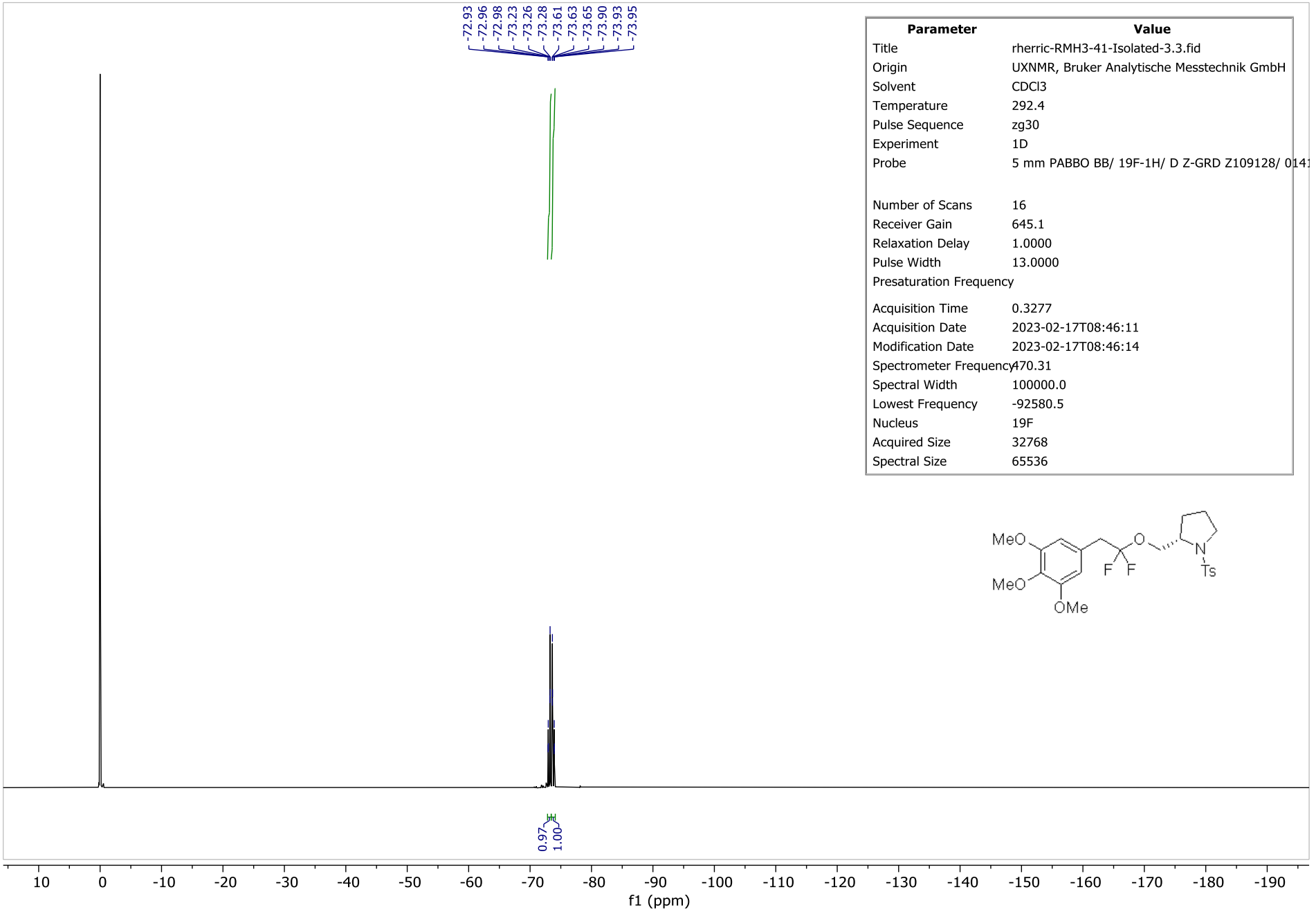
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-01-23T14:25:10
Modification Date	2023-01-23T14:25:13
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97257.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **(*S*)-2-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)-1-tosylpyrrolidine (7r)**



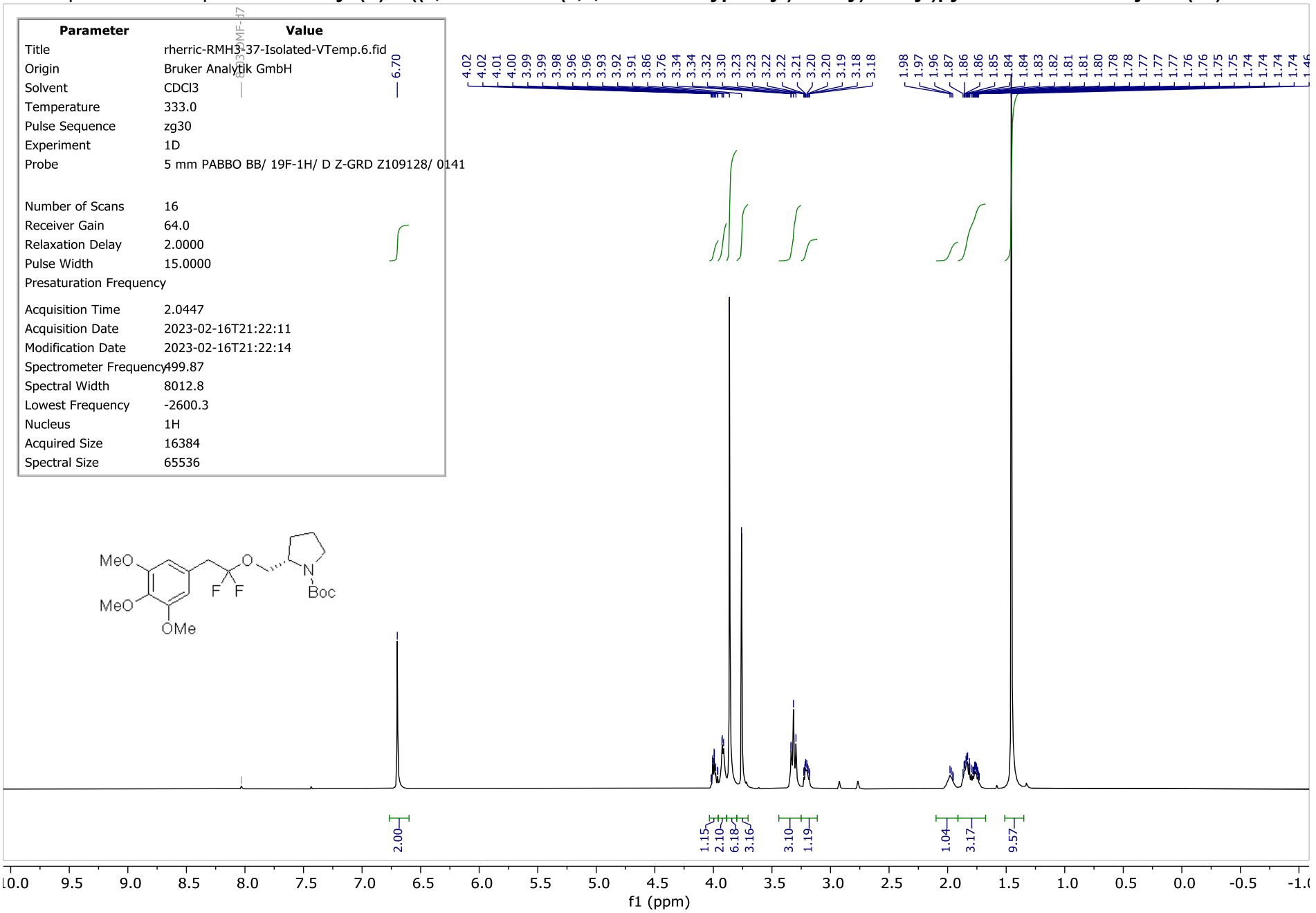
Parameter	Value
Title	rherric-RMH3-41-Isolated-3.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	710
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-02-17T08:41:50
Modification Date	2023-02-17T08:41:53
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1261.7
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



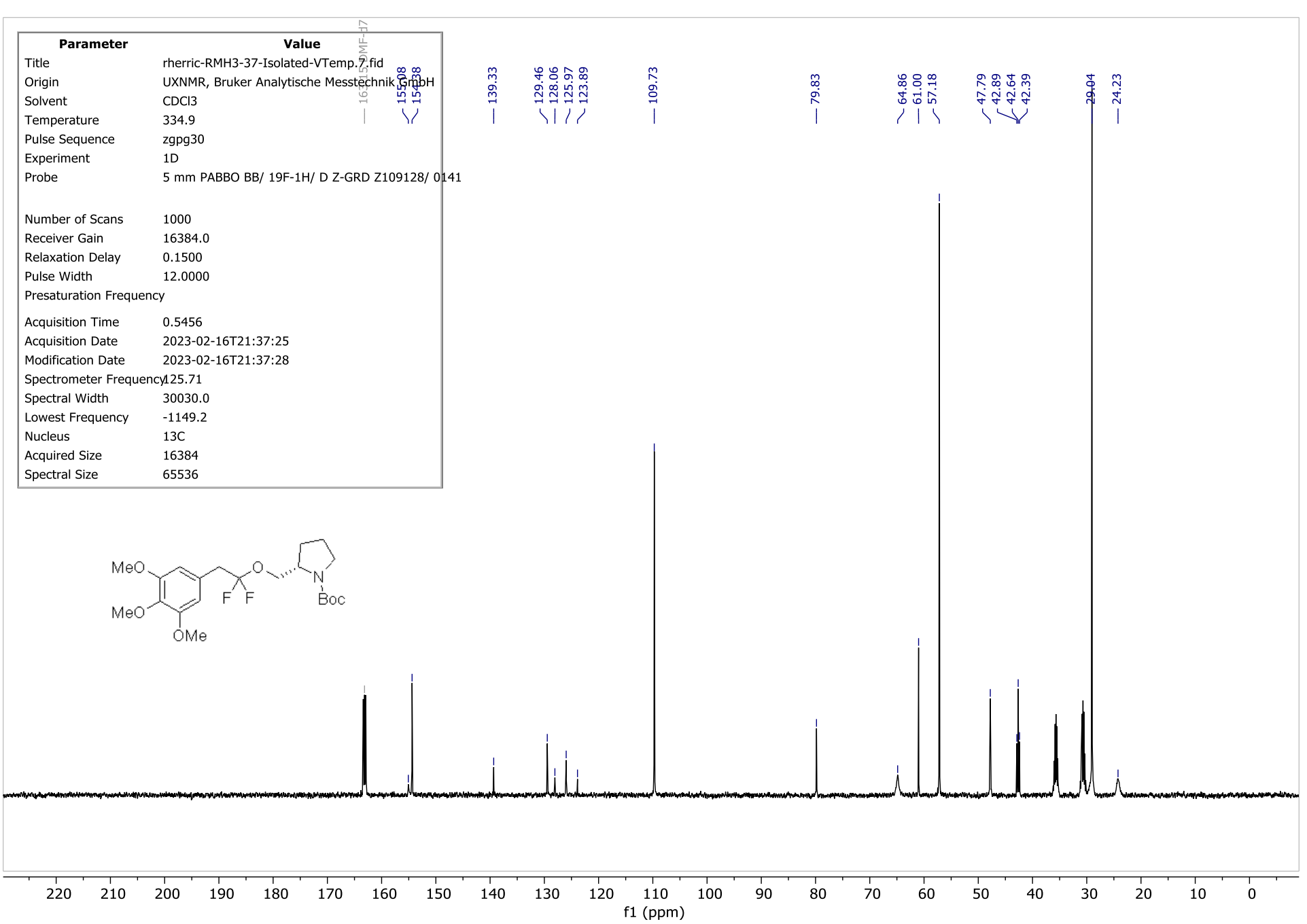


Parameter	Value
Title	rherric-RMH3-41-Isolated-3.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 014
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-02-17T08:46:11
Modification Date	2023-02-17T08:46:14
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92580.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

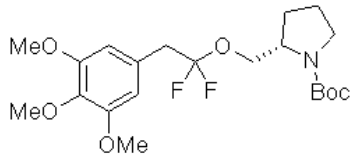
NMR Spectra for Compound ***tert*-butyl (*S*)-2-((1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethoxy)methyl)pyrrolidine-1-carboxylate (7s)**

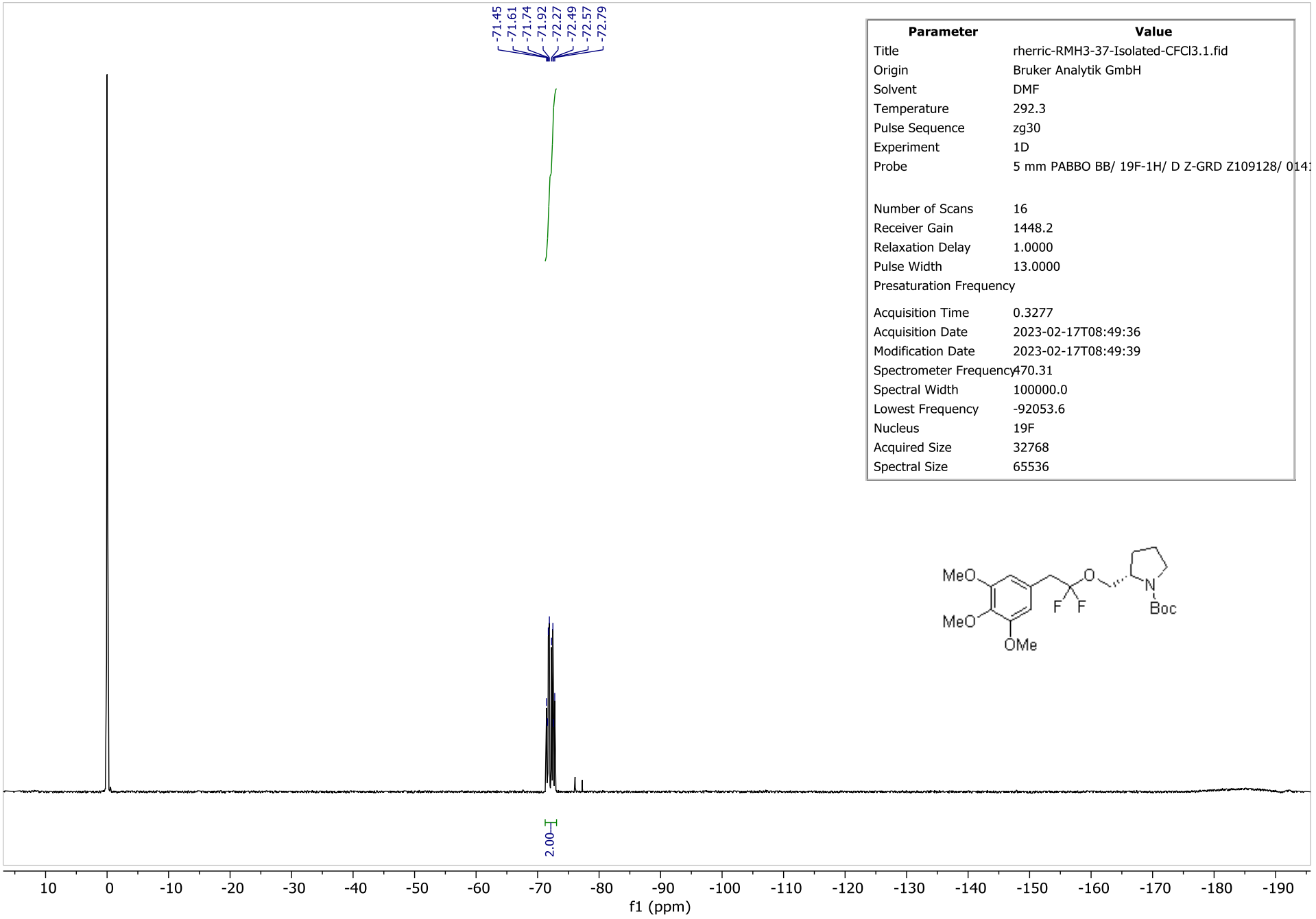


Parameter	Value
Title	rherric-RMH3-37-Isolated-VTemp.7.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	334.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-02-16T21:37:25
Modification Date	2023-02-16T21:37:28
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1149.2
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



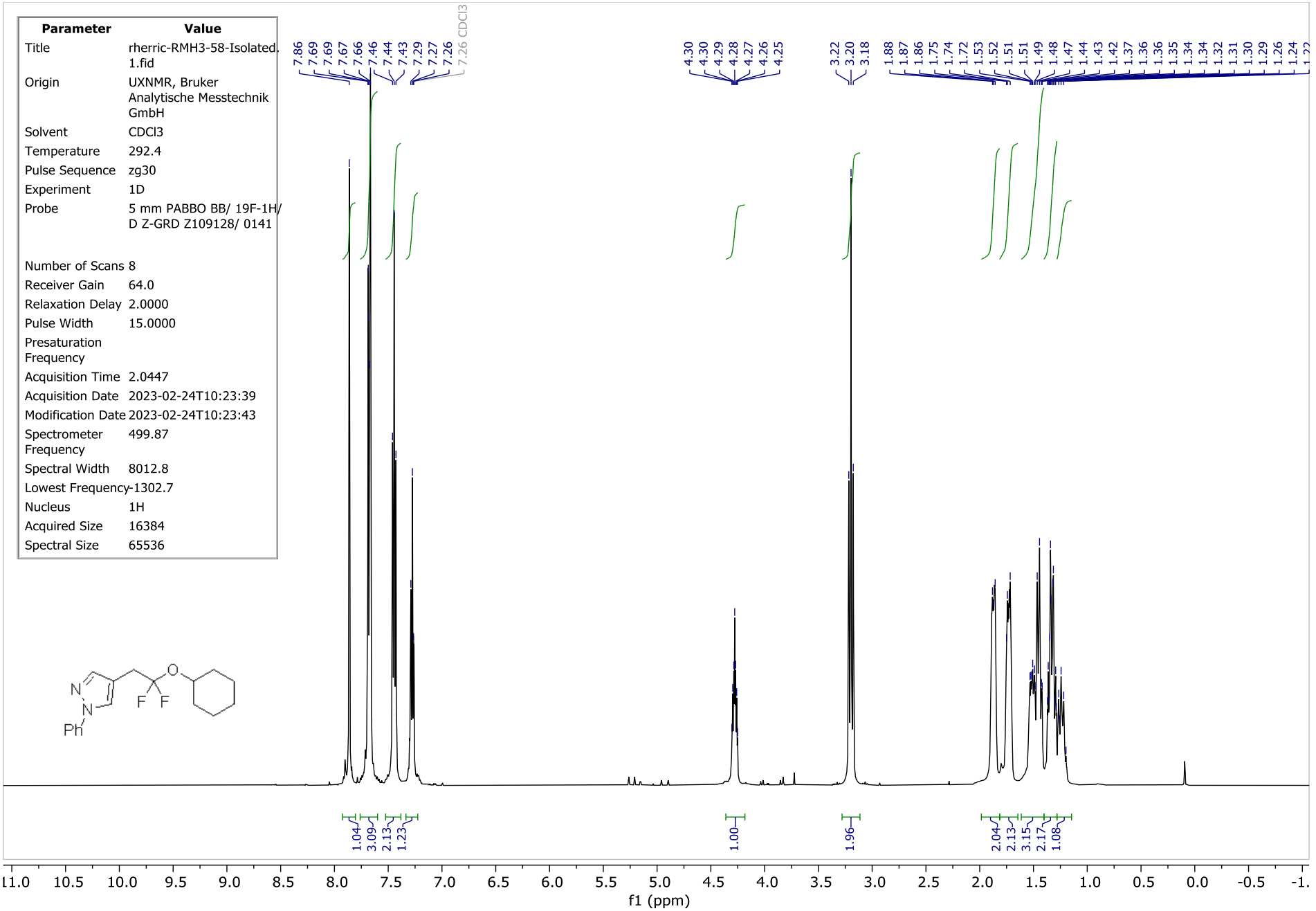
Parameter	Value
Title	rherric-RMH3-37-Isolated-VTemp.5.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	334.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-02-16T21:19:09
Modification Date	2023-02-16T21:19:12
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96959.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536



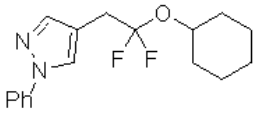


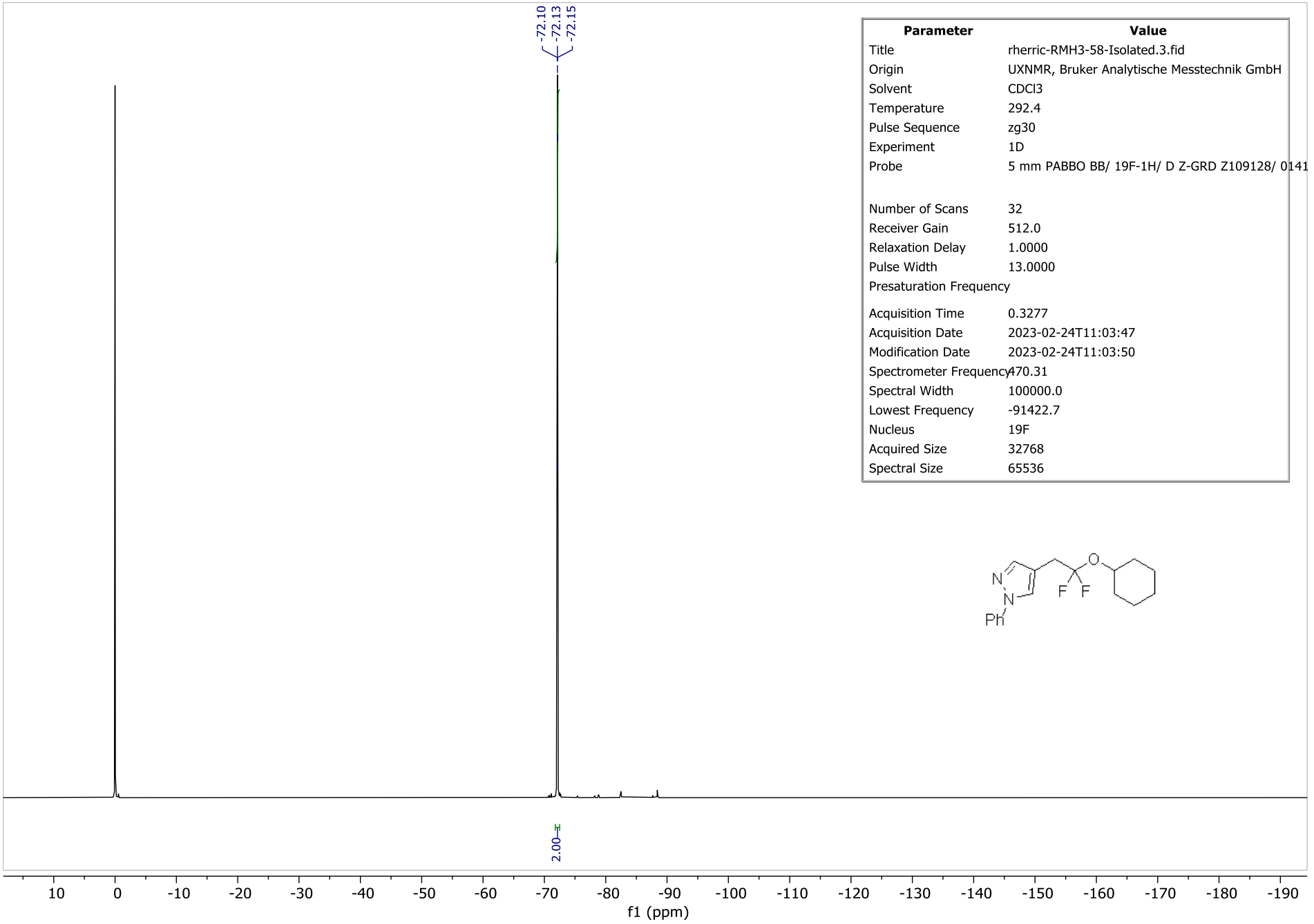
Parameter	Value
Title	rherric-RMH3-37-Isolated-CFCl3.1.fid
Origin	Bruker Analytik GmbH
Solvent	DMF
Temperature	292.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	1448.2
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-02-17T08:49:36
Modification Date	2023-02-17T08:49:39
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92053.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR Spectra for Compound **4-(2-(cyclohexyloxy)-2,2-difluoroethyl)-1-phenyl-1H-pyrazole** (**7t**)



Parameter	Value
Title	rherric-RMH3-58-Isolated.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	501
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-02-24T10:32:19
Modification Date	2023-02-24T10:32:23
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-949.9
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





Parameter	Value
Title	rherric-RMH3-58-Isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	32
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-02-24T11:03:47
Modification Date	2023-02-24T11:03:50
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-91422.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536