Supporting Information

Diselenide-Enabled Photocatalytic Hydroazolation of *gem*-Difluoroalkenes

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1. 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 PR160L 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 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), C18 silica gel (Teledyne RediSep Gold C18 High Performance Columns, 100 Å, 20–40 μm), or UNIPLATE Silica Gel HLF UV254 plates.

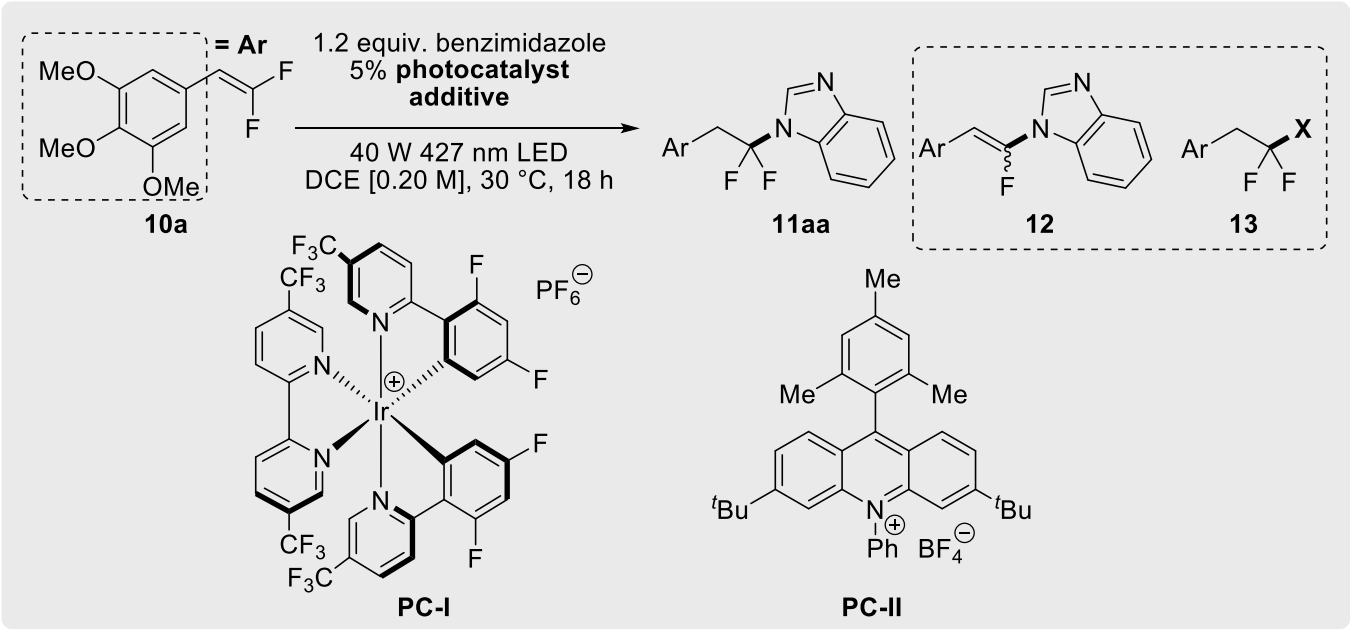
Unless otherwise noted, reagents were purchased from various commercial sources and used as received. Specifically, anhydrous PhMe (99.8%) and DCE (99.8%) were purchased from Thermo Fisher Scientific and stored in a N_2 glovebox. The highest available grade of purity of azoles were purchased and stored in a N_2 glovebox.

Nuclear magnetic resonance (NMR) spectroscopy was performed on either Bruker NEO 500 (^{1}H at 500 MHz, ^{13}C{^{1}H} at 126 MHz, and ^{19}F at 470 MHz) or Bruker Avance III 800 with QCI cryoprobe (^{1}H at 800 and ^{13}C{^{1}H} at 201 MHz) NMR spectrometers. ^{1}H NMR spectra were calibrated against the peak of the residual $CHCl_3$ (7.26 ppm). ^{13}C{^{1}H} NMR spectra were calibrated against the peak of $CDCl_3$ (77.2 ppm) or $(CD_3)_2CO$ (206.3 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. Uncorrected melting points were measured on a Chemglass Digital Melting Point apparatus.

The chemical abbreviations utilized in this document include nitrogen (N_2), water (H_2O), methanol (MeOH), ethyl acetate (EtOAc), 1,2-dichloroethane (DCE), toluene (PhMe), acetonitrile (MeCN), diethyl ether (Et_2O), acetic acid (AcOH), *N*,*N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), 2,4,6-triisopropylbenzenethiol (TRIP-SH), *N*-hydroxyphthalimide (NHP), *N*,*N*-dimethylformamide (DMF), sodium sulfate (Na_2SO_4), melting point (MP), glassy carbon (GC), tetra-*n*-butylammonium hexafluorophosphate (NBu_4PF_6), quasi reference electrode (QRE), ferrocene/ferrocenium (Fc/Fc^+), liquid chromatography mass spectroscopy (LCMS), electrospray ionization (ESI), and atmospheric pressure chemical ionization (APCI).

2. Reaction Development

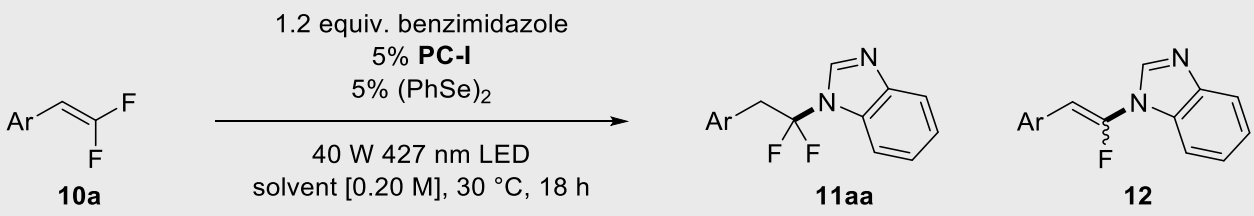
Table S1. Initial reaction development.



entry	photocatalyst	$E_{1/2}$ [PC*^{n}/PC^{n-1}] (V vs. Fc/Fc^{+})	additive	% conv. **10a**	% yield **11aa**	% yield **12**	% yield **13**
1	[Ir(dtbbpy)(ppy)$_2$]PF$_6$	+0.28 [1]	none	<5	0	0	N.A.
2	Rose Bengal lactone	+0.28 [2]	none	<5	0	0	N.A.
3	Eosin Y (dibasic)	+0.45 [2]	none	<5	0	0	N.A.
4	4CzIPN	+1.00 [2]	none	67	<1	66	N.A.
5	**PC-I**	+1.30 [3]	none	69	5	64	N.A.
6	**PC-II**	+1.70 [4]	none	66	<1	64	N.A.
7	**PC-I**	+1.30 [3]	*m*-anisidine (10%)	61	3	56	0
8	**PC-I**	"	TRIP-SH (30%)	53	3	44	0
9	**PC-I**	"	NHP (50%)	72	<1	66	0
10	**PC-I**	"	(TMS)$_3$SiH (50%)	70	8	56	0
11	**PC-I**	"	Ph$_3$SiH (50%)	>99	21	4	N.D.
12	**PC-I**	"	(PhS)$_2$ (20%)	>99	26	42	17 (X = SPh)
13	**PC-I**	"	(BnS)$_2$ (20%)	81	4	68	0
14	**PC-I**	"	(BnSe)$_2$ (20%)	82	21	44	<1 (X = F)
15	**PC-I**	"	(PhSe)$_2$ (20%)	>99	81	4	2 (X = F)
16	**PC-I**	"	(PhSe)$_2$ (5%)	>99	93	0	0
17	**PC-I**, no light	"	(PhSe)$_2$ (5%)	<5	0	0	0
18	none	"	(PhSe)$_2$ (5%)	<5	0	<1	0

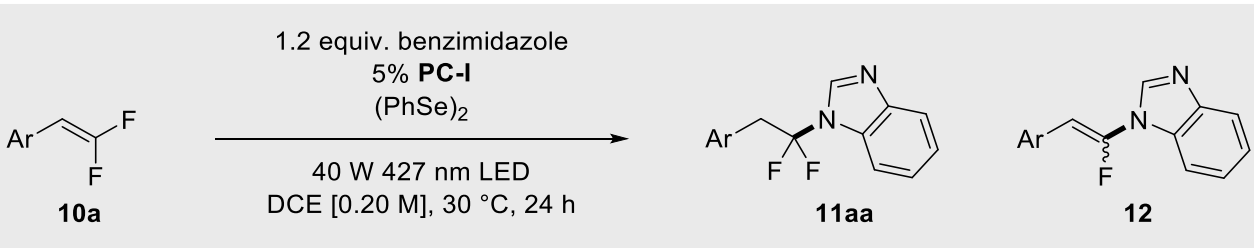
See S4–5 for reaction procedures.

Table S2. Solvent screening.



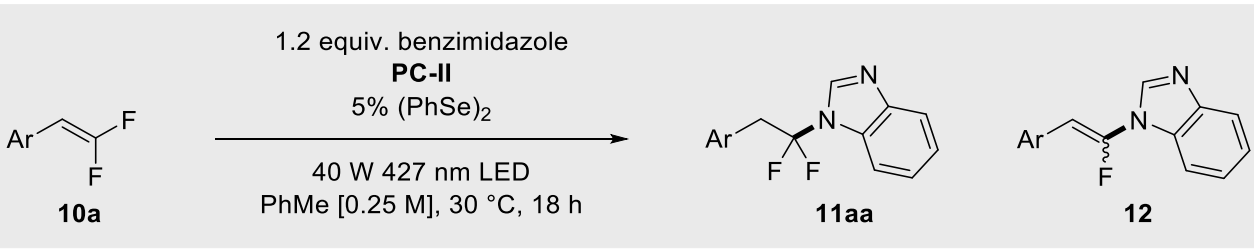
entry	solvent	% conv. **10a**	% yield **11aa**	% yield **12**
1	DCE	>99	93	0
2	MeCN	85	17	54
3	PhMe	>99	60	0
4	DMAc	71	0	46
5	THF	93	61	12

Table S3. $(PhSe)_2$ equivalents optimization.



entry	% $(PhSe)_2$	% conv. **10a**	% yield **11aa**	% yield **11**
1	0	77	4	64
2	5	>99	87	2
3	10	>99	64	3
4	20	>99	63	3

Table S4. PC-II equivalents optimization.



entry	% **PC-II**	% conv. **10a**	% yield **11aa**	% yield **12**
1	1.2	>99	61	4
2	3	>99	71	12
3	5	>99	68	16

Oven-dried one-dram vials equipped with magnetic stir bars were brought into a N_2 glovebox. The vials were each charged with *gem*-difluoroalkene **10a** (11.5 mg, 50.0 μmol), benzimidazole (7.1 mg, 60 μmol), additive (2.50–25.0 μmol), photocatalyst (0.50–2.5 μmol), and dry solvent (0.25 or 0.20 mL, 0.20 or 0.25 M). The vials were then removed from the glovebox, sealed with PTFE-lined septa, and irradiated by a 40 W 427 nm LED

lamp cooled by a fan (30 °C) for 18 or 24 h. Upon completion, an internal standard of (trifluoromethyl)benzene (4.1 µL, 33.3 µmol) was mixed into each crude reaction. The reactions were diluted with acetone or $CDCl_3$ (reaction solvent:dilution solvent = ~1:1). Aliquots of the reaction mixtures were subsequently transferred to NMR tubes and analyzed by ^{19}F NMR. Spectra were baseline corrected, phased, and integrated using MestReNova. Compound identity assignments were supported by LCMS (ESI^+) analysis.

^{19}F NMR (470 MHz, ~1:1 DCE/$CDCl_3$): (trifluoromethyl)benzene δ -64.00 (s); side product **13** (X = F) δ -67.28 (t, *J* = 9.93 Hz); side product **13** (X = SPh) δ -72.89 (t, *J* = 15.2 Hz); product **11aa** δ -79.44 (t, *J* = 12.8 Hz); *gem*-difluoroalkene **10a** δ -84.59 (t, *J* = 30.1 Hz), -86.60 (d, *J* = 34.6 Hz); side product **12** δ -87.18 (d, *J* = 8.8 Hz), -95.64 (d, *J* = 31.0 Hz); [ns = 16; D1 = 3 s].

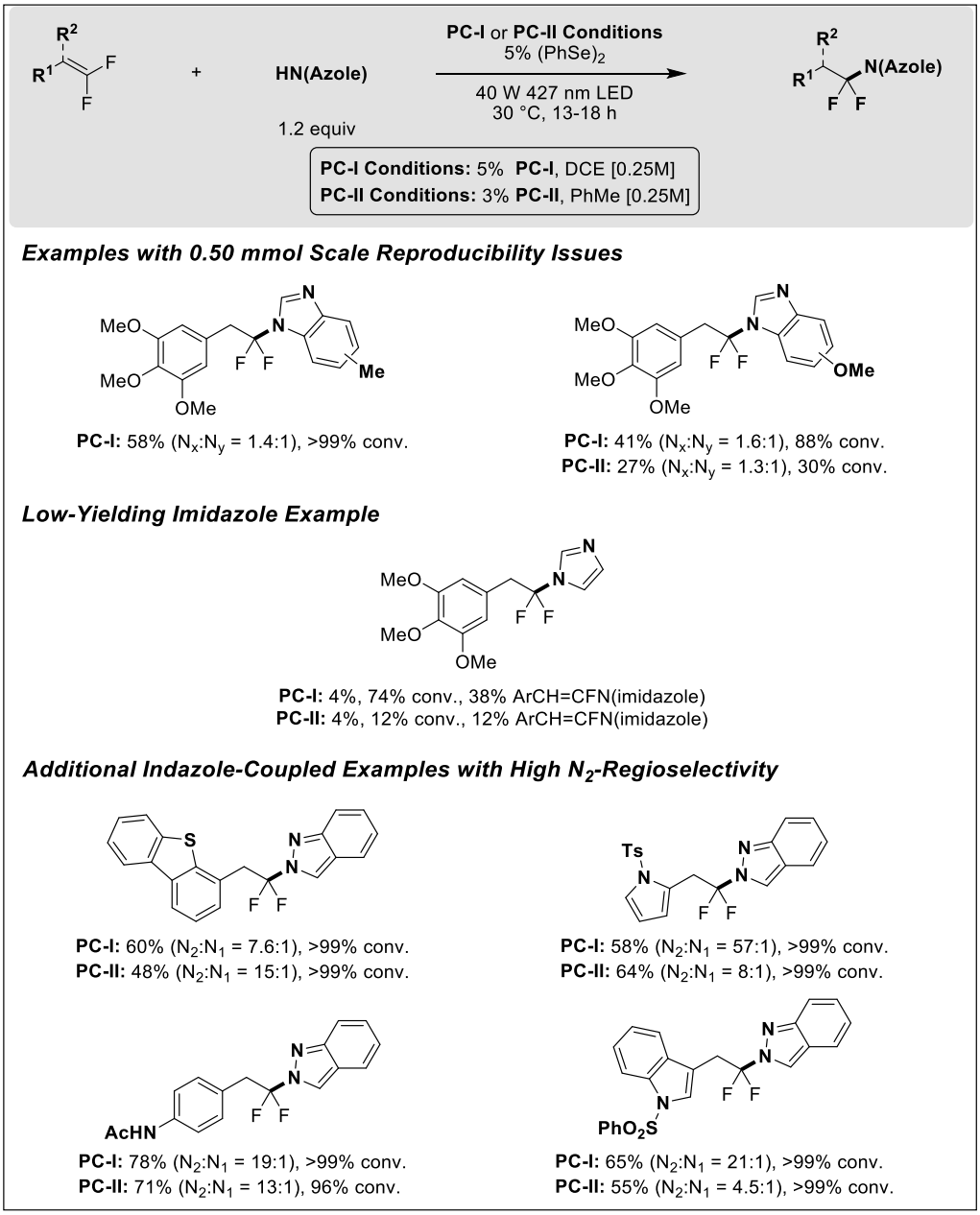
^{19}F NMR (470 MHz, ~1:1 MeCN:acetone): (trifluoromethyl)benzene δ -64.00 (s); product **11aa** δ -78.76 (t, *J* = 13.7 Hz); *gem*-difluoroalkene **10a** δ -85.96 (dd, *J* = 37.1, 25.9 Hz), -88.04 (d, *J* = 37.1 Hz); side product **12** δ -86.86 (d, *J* = 8.6 Hz), -96.62 (d, *J* = 32.0 Hz); [ns = 16; D1 = 3 s].

^{19}F NMR (470 MHz, ~1:1 PhMe:acetone): (trifluoromethyl)benzene δ -64.00 (s); product **11aa** δ -78.68 (t, *J* = 13.3 Hz); side product **12** δ -86.72 (d, *J* = 8.0 Hz), -96.60 (d, *J* = 32.1 Hz); [ns = 16; D1 = 3 s].

^{19}F NMR (470 MHz, ~1:1 DMAc:acetone): (trifluoromethyl)benzene δ -64.00 (s); *gem*-difluoroalkene **10a** δ -86.27 (dd, *J* = 38.6, 29.0 Hz), -88.41 (d, *J* = 38.6 Hz); side product **12** δ -86.58 (s), -96.85 (d, *J* = 32.4 Hz); [ns = 16; D1 = 3 s].

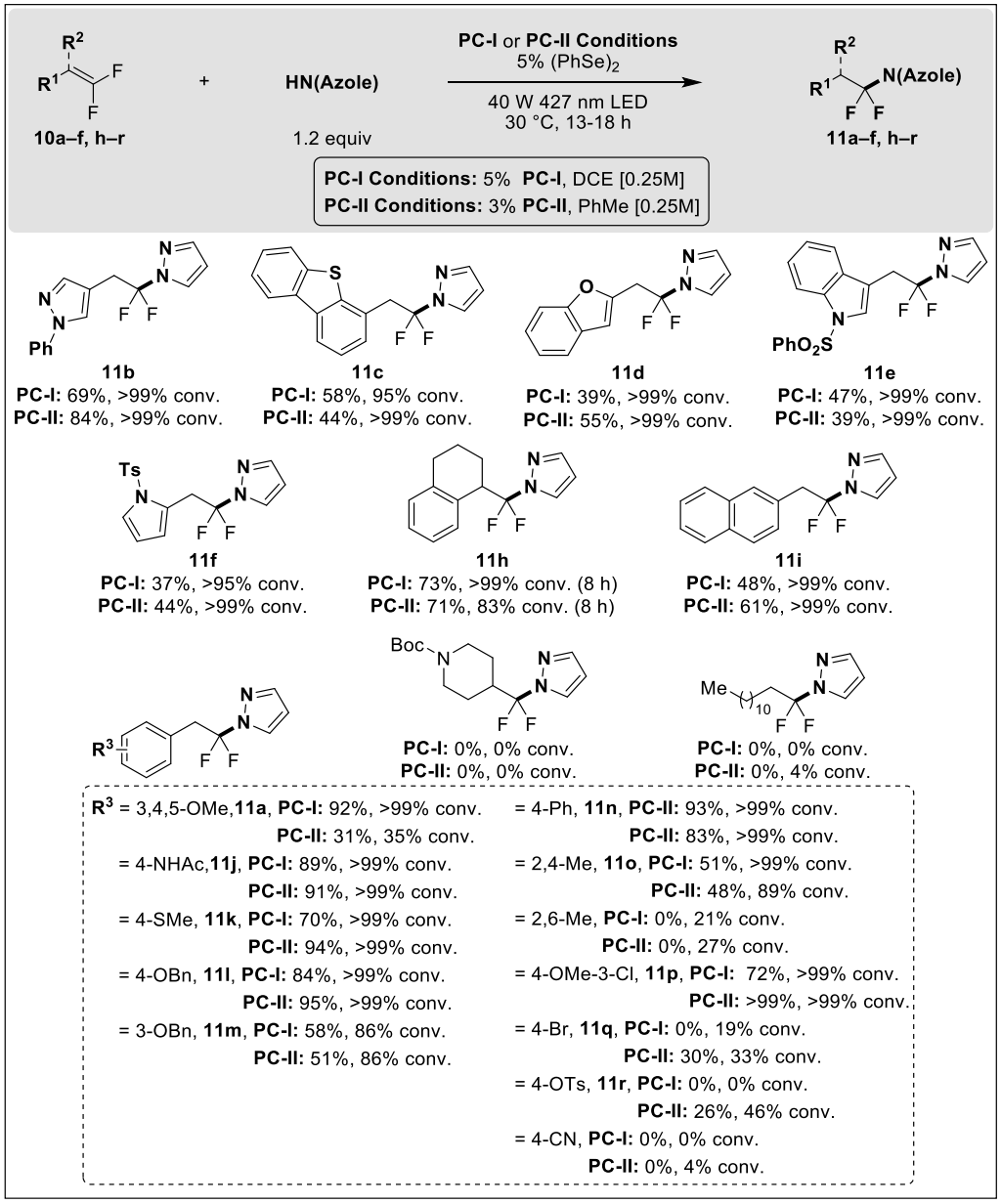
^{19}F NMR (470 MHz, ~1:1 THF:acetone): (trifluoromethyl)benzene δ -64.00 (s); product **11aa** δ -78.60 (t, *J* = 13.9 Hz); *gem*-difluoroalkene **10a** δ -86.18 (dd, *J* = 37.9, 27.5 Hz), -88.27 (d, *J* = 38.5 Hz); side product **12** δ -86.76 (d, *J* = 7.8 Hz), -96.60 (d, *J* = 32.4 Hz); [ns = 16; D1 = 3 s].

Table S5. 0.050 mmol scale substrate scope data.



See S7 for detailed reaction procedure.

Table S6. 0.050 mmol scale substrate scope data.

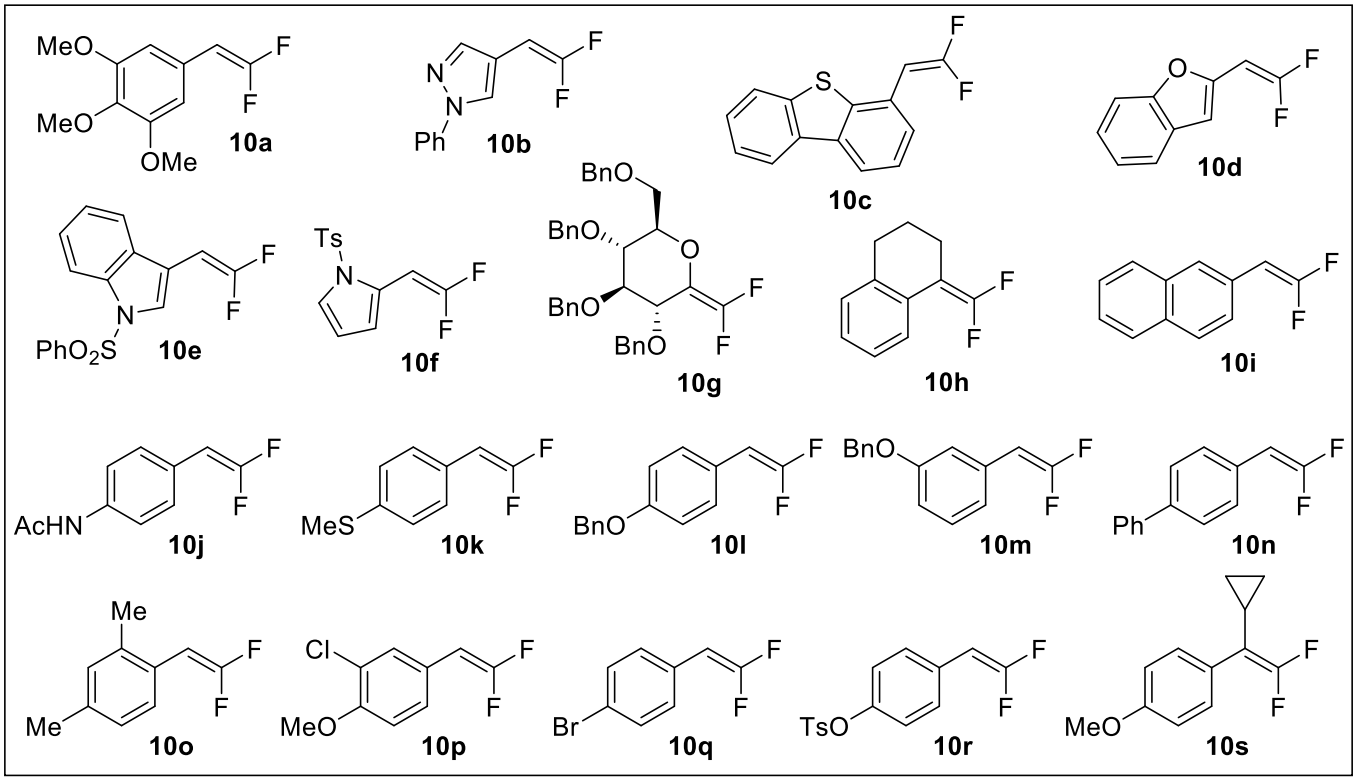


Oven-dried one-dram vials equipped with magnetic stir bars were brought into a N_2 glovebox. The vials were each charged with *gem*-difluoroalkene (50 µmol, 1.0 equiv.), azole (60 µmol, 1.0 equiv.) and 1,2-diphenyldiselane (0.8 mg, 3 µmol, 0.05 equiv). Then, either [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (**PC-I**, 2.9 mg, 2.5 µmol, 0.050 equiv) and dry DCE (0.20 mL, **PC-I Conditions**) or 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (**PC-II**, 0.9 mg, 2 µmol, 0.03 equiv) and dry PhMe (0.20 mL, **PC-II Conditions**) were added. The vials were then removed from the glovebox, sealed with PTFE-lined septa, and irradiated by a 40 W 427 nm LED lamp cooled by a fan (30 °C) for 13–18 h. Upon completion, an internal standard of (trifluoromethyl)benzene (10.0 µL, 81.4 µmol) was mixed into each crude reaction. The reactions were diluted with acetone (reaction solvent:acetone = ~1:1). Aliquots of the reaction mixtures were subsequently transferred to NMR tubes and analyzed by ^{19}F NMR. Spectra were baseline corrected, phased, and integrated using MestReNova. All yield, selectivity, and conversion values reported in Tables S1 and S2 were determined by ^{19}F NMR. Compound identity assignments were supported by LCMS (ESI^+) analysis.

3. Synthesis and Characterization

Preparation of *gem*-difluoroalkene substrates

Chart S1. Prepared *gem*-difluoroalkene substrates



gem-Difluoroalkenes **10a**,**b**,**c**,**k**,**l**,**n**,**q**,**r**,[5] **10d**,[6] **10e**,[7] **10g**,[8] and **10o**[9] were prepared according to reported procedures. **10d**, **10f**, **10h**, **10i**, **10j**, **10p**, and **10s** were prepared by procedures that had not previously been utilized for their syntheses (see below).

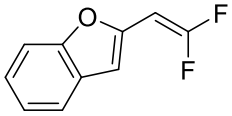
General Procedure A, for the Synthesis of *gem*-Difluoroalkenes

Following a previously reported procedure,[10] a flame-dried three-neck flask equipped with an addition funnel, thermometer adapter and thermometer, rubber septa, and PTFE-coated magnetic stir bar was charged with aldehyde (1.0 equiv.) and triphenylphosphine (1.5 equiv.). The flask was subsequently evacuated and backfilled with N_2 (3x), then charged with anhydrous DMF [0.33 M] and heated to 80 °C. Separately, potassium 2-bromo-2,2-difluoroacetate (1.8 equiv.) was added to a flask that was subsequently evacuated and backfilled with N_2 (3x) and charged with anhydrous DMF (enough to dissolve salt, ≥10 mL). This potassium 2-bromo-2,2-difluoroacetate solution was transferred to the addition funnel and dripped into the reaction mixture over the course of ~10 min such that the reaction temperature did not exceed 90 °C. The reaction was stirred at 80 °C for 1 h.

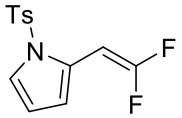
Upon completion, the reaction mixture was allowed to cool to rt, quenched with H_2O (equivalent volume to reaction DMF), and diluted with Et_2O (equivalent volume to reaction DMF). The Et_2O layer was then removed in a separatory funnel, and the aqueous layer was washed with additional Et_2O (3x). The combined organic fractions were washed with 10% LiCl in H_2O (3x), brine (1x), and dried over Na_2SO_4. MeI (2.0 equiv) was then added to the combined organic fractions, and the resulting mixture was stirred for 12–16 h at rt. The mixture was then pumped dry *in vacuo*, resuspended in Et_2O/hexanes (1:1), filtered through a plug of silica to remove methyltriphenylphosphonium iodide, and purified by normal-phase silica gel flash chromatography to provide the desired product in >95% purity.

General Procedure B, for the Synthesis of *gem*-Difluoroalkenes

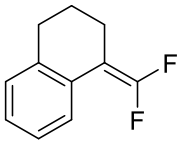
Following a previously reported procedure,[11] a flame-dried flask with a magnetic stir bar was charged with 2-((difluoromethyl)sulfonyl)pyridine (1.0 equiv.) and aldehyde/ketone (1.2 equiv.). The flask was then evacuated and backfilled with N_2 (3x), charged with anhydrous DMF [0.25 M], and cooled to –50 °C using a MeOH/H_2O (1:1) and dry ice bath. Separately, a flame-dried flask was charged with potassium 2-methylpropan-2-olate (1.80 equiv.), evacuated and backfilled with N_2 (3x), charged with anhydrous DMF [0.90 M], and cooled to –50 °C. This potassium 2-methylpropan-2-olate solution was then added to the reaction mixture in a dropwise fashion such that the reaction temperature remained between –50 and –40 °C. The resulting mixture was stirred at –50 °C for 1 h. Then, the reaction was quenched with sat. aq. NH_4Cl (one-half of reaction DMF volume) followed by dropwise addition of 6 M aq. HCl (5 equiv.). The resulting mixture was attached to a bubbler (extrusion of SO_2 gas occurs in this step of the reaction), removed from the cold bath, and stirred at 60 °C for 1 h. Upon completion of the reaction, the mixture was transferred to a separatory funnel, diluted with Et_2O, and then extracted with H_2O (3x) followed by 10% LiCl in H_2O (3x). The resulting organic layer was dried over Na_2SO_4 and purified by normal-phase silica gel flash chromatography to provide the desired product in >95% purity.



2-(2,2-difluorovinyl)benzofuran (**10d**): Following general procedure A, benzofuran-2-carbaldehyde (2.19 g, 15.0 mmol) reacted with triphenylphosphine (5.90 g, 22.5 mmol) and potassium 2-bromo-2,2-difluoroacetate (5.75 g, 27.0 mmol) in DMF (45 mL, [0.33 M]) at 80 °C for 1 h. The reaction was quenched and extracted according to the general procedure, then stirred with MeI (1.9 mL, 30 mmol) at rt for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using hexanes to furnish desired product **10d** as a dark red oil (2.41 g, 89%). ^{1}H NMR spectrum matches a previous report.[12]

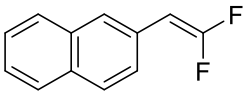


2-(2,2-difluorovinyl)-1-tosyl-1*H*-pyrrole (**10f**): Following general procedure A, 1-tosyl-1*H*-pyrrole-2-carbaldehyde (2.69 g, 10.8 mmol) reacted with triphenylphosphine (4.24 g, 16.2 mmol) and potassium 2-bromo-2,2-difluoroacetate (4.13 g, 19.4 mmol) in DMF (33 mL, [0.33 M]) at 80 °C for 1 h. The reaction was quenched and extracted according to the general procedure, then stirred with MeI (1.4 mL, 22 mmol) at rt for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to furnish desired product **10f** as a purple solid (2.15 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67–7.65 (m, 2H), 7.32 (dd, *J* = 3.3, 1.7 Hz, 1H), 7.30–7.28 (m, 2H), 6.35–6.33 (m, 1H), 6.29 (t, *J* = 3.4 Hz, 1H), 5.95 (dd, *J* = 24.8, 2.4 Hz, 1H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.4 (dd, *J* = 298.0, 288.1 Hz), 145.4, 135.9, 130.2, 126.9, 123.9 (t, *J* = 7.7 Hz), 123.0, 114.6 (dd, *J* = 9.7, 3.1 Hz), 112.7, 73.2 (dd, *J* = 36.6, 13.9 Hz), 21.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.59 (t, *J* = 23.7 Hz, 1F), -84.65 (d, *J* = 22.4 Hz, 1F). MP 71–73 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{13}H_{12}F_2NO_2S^+$ 284.0551, found 284.0545.

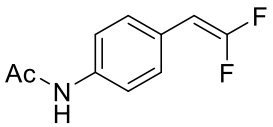


1-(difluoromethylene)-1,2,3,4-tetrahydronaphthalene (**10h**): Following general procedure B, 2-((difluoromethyl)sulfonyl)pyridine (0.750 g, 3.88 mmol), 3,4-dihydronaphthalene-1(2*H*)-one (0.620 mL, 4.66 mmol), and potassium 2-methylpropan-2-olate (0.784 g, 6.99 mmol) were reacted in DMF (23 mL, [0.20 M]) at –50 °C for 1 h. The reaction was then charged with sat. aq. NH_4Cl (12 mL) and 6 M aq. HCl (6 mL, 5 equiv.) and stirred at 60 °C for 1 h. The material was isolated according to the general procedure and purified by normal-

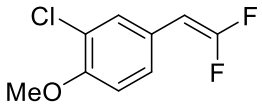
phase flash chromatography using pentane to furnish desired product **10h** as a colorless oil (0.420 g, 60%). ^{1}H NMR spectrum matches a previous report.[8]



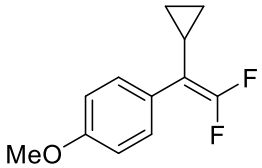
2-(2,2-difluorovinyl)naphthalene (**10i**): Following general procedure A, 2-naphthaldehyde (2.34 g, 15.0 mmol) reacted with triphenylphosphine (5.90 g, 22.5 mmol) and potassium 2-bromo-2,2-difluoroacetate (5.75 g, 27.0 mmol) in DMF (45 mL, [0.33 M]) at 80 °C for 1 h. The reaction was quenched and extracted according to the general procedure, then stirred with MeI (1.9 mL, 30 mmol) at rt for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using pentane to furnish desired product **10i** as a colorless solid (1.60, 56%). ^{1}H NMR spectrum matches a previous report.[13]



***N*-(4-(2,2-difluorovinyl)phenyl)acetamide** (**10j**): Following general procedure B, 2-((difluoromethyl)sulfonyl)pyridine (0.483 g, 2.50 mmol), 3,4-dihydronaphthalene-1(2*H*)-one (0.490 g, 3.00 mmol), and potassium 2-methylpropan-2-olate (0.505 g, 4.50 mmol) were reacted in DMF (12 mL, [0.20 M]) at –50 °C for 1 h. The reaction was then charged with sat. aq. NH_4Cl (6 mL) and 6 M aq. HCl (2 mL, 5 equiv) and stirred at 60 °C for 1 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→50% EtOAc) to afford desired product **10j** as a yellow solid (0.660 g, 67%). ^{1}H NMR spectrum matches a previous report.[6]



2-chloro-4-(2,2-difluorovinyl)-1-methoxybenzene (**10p**): Following general procedure A, 3-chloro-4-methoxybenzaldehyde (2.56 g, 15.0 mmol) reacted with triphenylphosphine (5.90 g, 22.5 mmol) and potassium 2-bromo-2,2-difluoroacetate (5.75 g, 27.0 mmol) in DMF (45 mL, [0.33 M]) at 80 °C for 1 h. The reaction was quenched and extracted according to the general procedure, then stirred with MeI (1.9 mL, 30 mmol) at rt for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to furnish desired product **10p** as a pale yellow oil (1.87 g, 61%). ^{1}H NMR spectrum matches a previous report.[14]



1-(1-cyclopropyl-2,2-difluorovinyl)-4-methoxybenzene (**10s**): Following a previously reported procedure,[15] a flame-dried flask equipped with a magnetic PTFE-coated stir bar was charged with cyclopropyl(4-methoxyphenyl)methanone (0.881 g, 5.00 mmol), 2,2-difluoro-2-(tris(dimethylamino)phosphonio)acetate (2.57 g, 10.0 mmol), and evacuated and backfilled with N_2. A mixture of PhMe/DMAc (3:1, 60 mL, [0.083 M]) was then added, and the reaction was stirred at 100 °C for 3 h. Upon completion, the reaction was cooled to rt, quenched with H_2O (60 mL) and diluted with Et_2O (60 mL). The organic layer was washed with H_2O (5x), 10% LiCl in H_2O (3x), and dried over Na_2SO_4. The material was then purified by normal-phase flash chromatography using EtOAc and hexanes (0→10% EtOAc) to furnish desired product **10s** as a yellow-orange oil (0.21 g, 20%). ^{1}H NMR spectrum matches a previous report.[14]

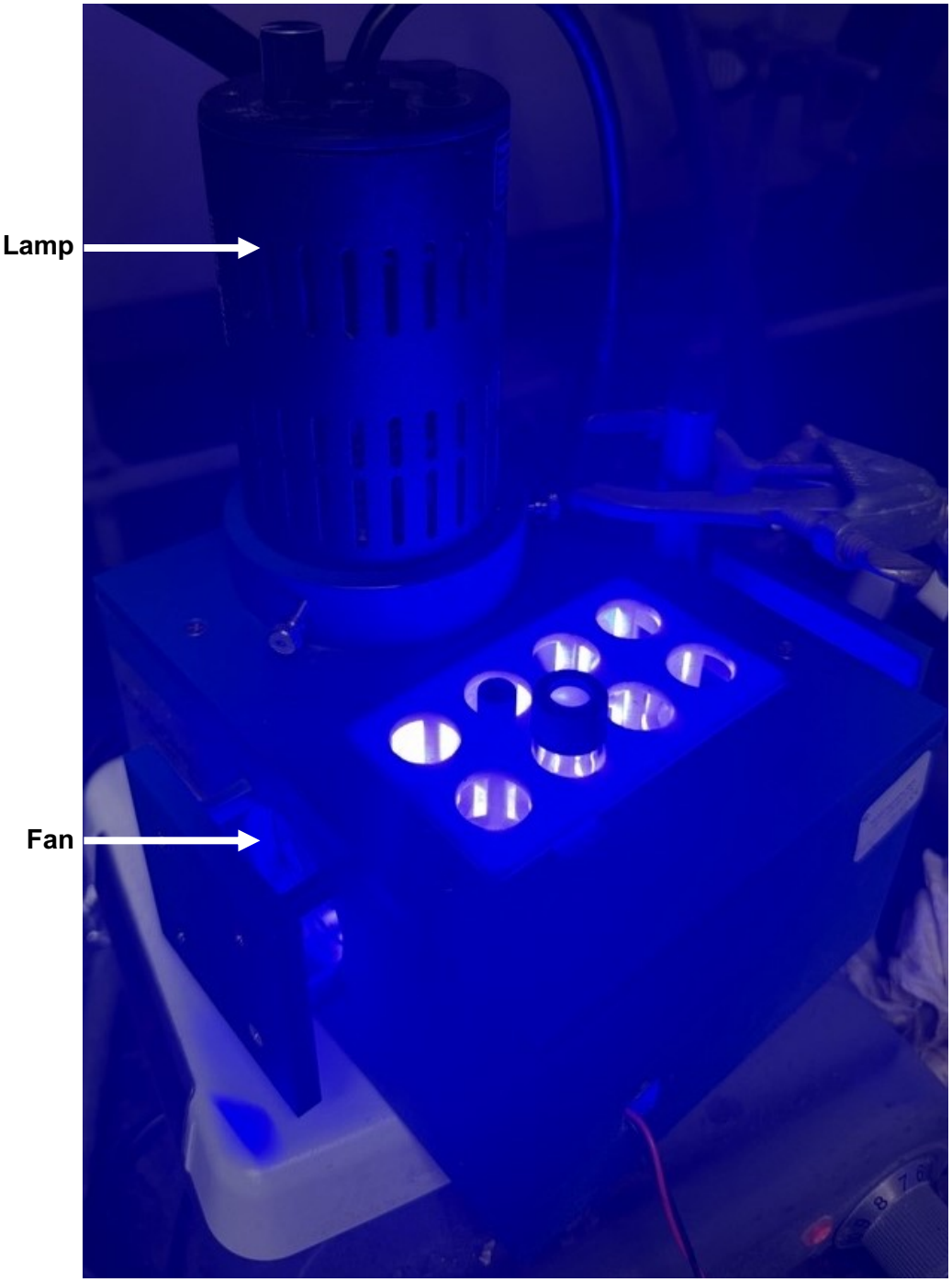
Hydroazolation of *gem*-difluoroalkenes

General Procedure C, for the Photochemical Hydroazolation of *gem*-Difluoroalkenes (PC-I Conditions): An oven-dried one-dram vial equipped with a magnetic stir bar was charged with *gem*-difluoroalkene (0.50 mmol, 1.0 equiv), azole (0.60 mmol, 1.2 equiv.), 1,2-diphenyldiselane (0.025 mmol, 0.050 equiv), and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (**PC-I**, 0.025 mmol, 0.050 equiv). The system was sealed with PTFE-lined septa and subsequently evacuated and backfilled with N_2 (3x). Dry DCE (2.0 mL, 0.25 M) 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 mixture was purified by flash chromatography* to provide the desired product in >95% purity.

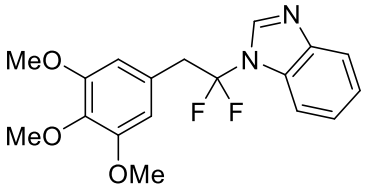
General Procedure D, for the Photochemical Hydroazolation of *gem*-Difluoroalkenes (PC-II Conditions): An oven-dried one-dram vial equipped with a magnetic stir bar was charged with *gem*-difluoroalkene (0.50 mmol, 1.0 equiv), azole (0.60 mmol, 1.2 equiv.), 1,2-diphenyldiselane (0.025 mmol, 0.050 equiv), and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (**PC-II**, 0.015 mmol, 0.030 equiv). The system was sealed with PTFE-lined septa and subsequently evacuated and backfilled with N_2 (3x). Dry PhMe (2.0 mL, 0.25 M) 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 mixture was filtered through a pad of silica using Et_2O or EtOAc (~100 mL) to remove the photocatalyst, concentrated *in vacuo*, and purified by flash chromatography* to provide the desired product in >95% purity.

* To separate $(PhSe)_2$, for normal-phase chromatographic purifications, the material was washed with 100% hexane or pentane until $(PhSe)_2$ eluted from the column

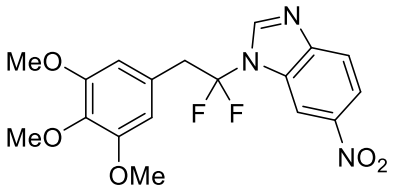
Photoreactor



Lamp: Kessil PR160L-427 (427 nm light at 40 W)
Fan: Orion Fans, 40x40x10.5 mm, 0.258 m^3/min (manufacturer part #: OD4010-12HB)
Photoreactor: EvoluChem PhotoRedOx Box

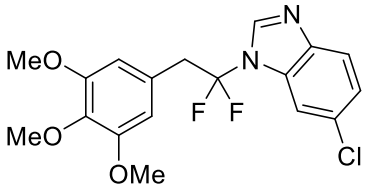


1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*]imidazole (**11aa**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with benzimidazole (0.071 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11aa** as a colorless oil (0.149 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.83 (dd, *J* = 6.6, 2.8 Hz, 1H), 7.53 (d, *J* = 6.0 Hz, 1H), 7.43–7.34 (m, 2H), 6.02 (s, 2H), 3.78 (s, 3H), 3.65 (t, *J* = 12.5 Hz, 2H), 3.61 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 139.6, 138.3, 131.2, 125.3, 124.9, 124.1, 120.6, 120.2, 112.0, 107.1, 61.0, 56.1, 43.20 (t, *J* = 30.1 Hz.). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.04 (t, *J* = 14.2 Hz, 2F). HRMS (APCI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{18}H_{19}F_2N_2O_3^{+}$ 349.1358, found 349.1366.



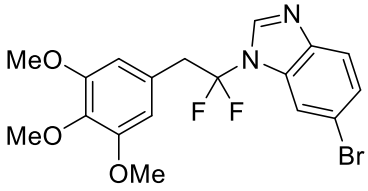
N1:N3 = (1.7:1)

1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-6- and -5-nitro-*1H*-benzo[d]imidazole (**11ab**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 5-nitro-1*H*-benzo[d]imidazole (0.098 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11ab** (N1:N3 = 1.7:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by reversed-phase flash chromatography using 0.1% AcOH in H_2O and MeCN (0→100% MeCN) to furnish a mixture of the two N-regioisomers of desired product **11ab** (N1:N3 = 1.7:1) as a yellow solid (0.081 g, 41%). NMR data are reported for the major regioisomer, for which a fractional amount was purified from the mixture of regioisomers by preparative TLC using EtOAc and hexanes (20% EtOAc). Melting point and HRMS data were obtained from the mixture of regioisomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (s, 1H), 8.28 (dd, *J* = 8.9, 2.2 Hz, 1H), 8.01 (s, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 6.04 (s, 2H), 3.75 (s, 3H), 3.67 (t, *J* = 13.6 Hz, 2H), 3.64 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.7, 147.7, 145.0, 143.7, 138.6, 130.8, 124.6 (t, *J* = 4.6 Hz), 121.1, 120.2 (t, *J* = 258.9 Hz), 119.5, 108.9 (t, *J* = 3.4 Hz), 107.1, 61.0, 56.2, 44.0 (t, *J* = 29.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.16 (t, *J* = 12.5 Hz, 2F). MP 161–166 °C. HRMS (APCI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{18}H_{18}F_2N_3O_5^{+}$ 394.1209, found 394.1215. The N-regiochemical assignment for the major product was made using ^{1}H{^{19}F} NOE (see S71) and X-ray crystallography (CCDC 2414748).



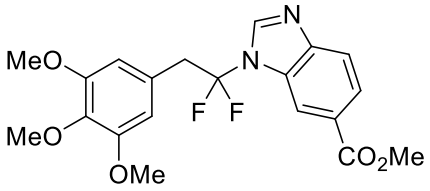
N1:N3 = (1.2:1)

6-chloro-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*]imidazole (**11ac**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 5-chloro-1*H*-benzo[d]imidazole (0.076 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11ac** (N_1:N_3 = 1.2:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish a mixture of the two N-regioisomers of desired product **11ac** (N1:N3 = 1.2:1) as a yellow solid (0.166 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.73 (m, 1H), 7.73–7.69 (m, 1H), 7.49–7.40 (m, 1H), 7.35–7.29 (m, 1H), 5.99 (d, *J* = 5.9 Hz, 2H), 3.78 (d, *J* = 1.6 Hz, 2H), 3.62 (m, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 144.8, 142.4, 140.7, 140.2, 138.3, 131.8, 130.4, 129.9, 129.5, 125.1, 124.5, 121.7, 120.7, 120.0 (t, *J* = 251.3 Hz), 112.6, 112.1, 107.0, 106.9, 61.0, 56.1, 43.4 (dt, *J* = 30.3, 7.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.61 (t, *J* = 12.6 Hz, 2F). MP 87–90 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{18}ClF_2N_2O_3^+$ 383.0969, found 383.0977. The N-regiochemical assignment for the major product is inferred based on structural data for similar examples **11ab** and **ad**.



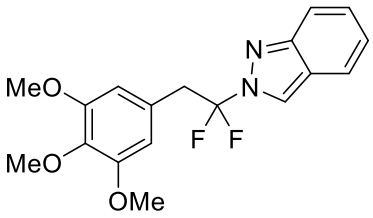
N1:N3 = (1.4:1)

6- and 5-bromo-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[d]imidazole (**11ad**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 5-bromo-1*H*-benzo[d]imidazole (0.118 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11ad** (N1:N3 = 1.2:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish a mixture of the two N-regioisomers of desired product **11ad** (N1:N3 = 1.4:1) as a yellow solid (0.191 g, 89%). NMR data are reported for the separated minor regioisomer. Melting point and HRMS data were obtained from the mixture of regioisomers. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.8 Hz, 1H), 7.71 (s, 1H), 7.46 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.39–7.34 (m, 1H), 5.98 (s, 2H), 3.79 (s, 3H), 3.62 (s, 6H), 3.58 (t, *J* = 12.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 145.2, 140.5, 138.2, 130.3, 127.7, 125.0, 123.7, 120.0 (t, *J* = 258.6 Hz), 116.8, 113.1, 106.9, 61.0, 56.1, 43.3 (t, *J* = 12.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.57 (t, *J* = 12.9 Hz, 2F). MP 78–82 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{18}BrF_2N_2O_3^+$ 427.0463, found 427.0470. The N-regiochemical assignment for the major product was made using ^{1}H{^{19}F} NOE (see S78).

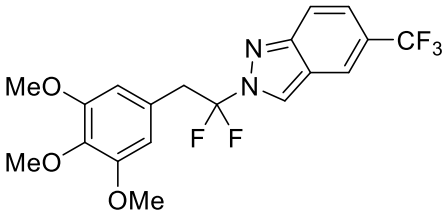


N1:N3 = (1.1:1)

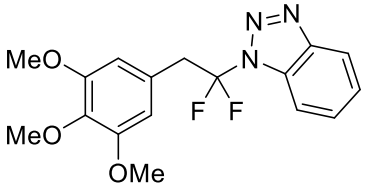
Methyl 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[d]imidazole-6- and -5-carboxylate (**11ae**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with methyl 1*H*-benzo[d]imidazole-5-carboxylate (0.132 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11ae** (N1:N3 = 1.2:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by reversed-phase flash chromatography using 0.1% AcOH in H_2O and MeCN (0→100% MeCN) to furnish a mixture of the two N-regioisomers of desired product **11ae** (N1:N3 = 1.1:1) as a colorless oil (0.185 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01–7.66 (m, 1H), 7.58–7.49 (m, 1H), 7.31–6.97 (m, 2H), 5.44 (s, 2H), 3.43 (t, *J* = 3.3 Hz, 3H), 3.23 (dd, J = 22.8, 12.6 Hz, 3H), 3.14–3.08 (m, 2H), 3.06 (d, J = 3.0 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.1, 167.0, 153.4, 147.2, 143.7, 142.0, 141.0, 138.3, 134.4, 131.1, 126.5, 126.1, 126.0, 125.1, 125.0, 123.1, 120.6, 120.2 (dt, *J* = 256.1, 3.4 Hz), 114.0, 111.6, 106.9, 106.8, 61.0, 60.9, 56.1, 56.0, 52.5, 52.4, 43.4 (dt, *J* = 30.1, 11.7 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.41 (t, *J* = 12.3 Hz, 2F), -78.56 (t, *J* = 12.8 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{20}H_{21}F_2N_2O_5^+$ 407.1413, found 407.1421. The N-regiochemical assignment for the major product is inferred based on structural data for similar examples **11ab** and **ad**.



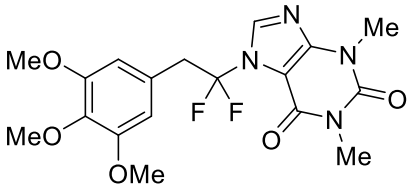
2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-2*H*-indazole (**11af**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1*H*-indazole (0.071 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11af** (N2:N1 = >20:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish the desired product **11af** as a colorless solid (0.156 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.77 (dd, *J* = 9.0, 1.0 Hz, 1H), 7.61 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.38–7.31 (m, 1H), 7.16–7.06 (m, 1H), 6.18 (s, 2H), 3.88 (t, *J* = 13.3 Hz, 2H), 3.76 (s, 3H), 3.56 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 149.7, 137.5, 128.0, 126.1, 123.1, 121.8, 121.2 (t, *J* = 258.4 Hz), 121.0, 120.8, 118.0, 107.0, 60.7, 55.7, 42.6 (t, *J* = 27.7 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -81.17 (t, *J* = 13.4 Hz, 2F). MP 85–87 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{19}F_2N_2O_3^+$ 349.1358, found 349.1365. The N2-regiochemical assignment for the major product was made using ^{1}H{^{19}F} NOE (see S85) and X-ray crystallography (CCDC 2414405).



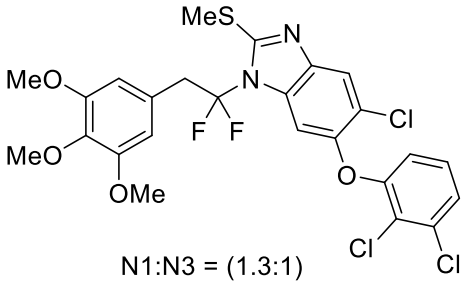
2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-5-(trifluoromethyl)-2*H*-indazole (**11ag**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 5-(trifluoromethyl)-1*H*-indazole (0.112 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced a mixture of the two N-regioisomers of desired product **11ag** (N2:N1 = >20:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by reversed-phase flash chromatography using 0.1% AcOH in H_2O and MeCN (0→100% MeCN) to furnish desired product **11ag** as a yellow oil (0.127 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.99 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.51 (d, *J* = 9.2 Hz, 1H), 6.20 (s, 2H), 3.88 (t, *J* = 13.6 Hz, 2H), 3.77 (s, 3H), 3.59 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.2, 149.9, 137.8, 129.3, 127.6, 125.7, 125.5, 123.9, 123.3, 122.9, 120.2 (q, *J* = 13.1 Hz), 119.8 (t, *J* = 258.7 Hz), 119.5, 107.1, 60.9, 55.9, 42.6 (t, *J* = 36.4 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.97 (s, 3F), -81.32 (t, *J* = 13.7 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{19}H_{18}F_5N_2O_3^+$ 417.1232, found 417.1236. The N1-regiochemical assignment for the major product was made using ^{1}H{^{19}F} NOE (see S89).



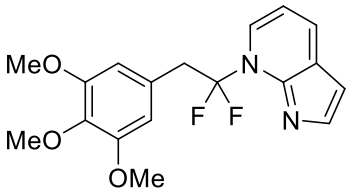
1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (**11ah**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1*H*-benzo[*d*][1,2,3]triazole (0.072 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11ah** as a colorless solid (0.168 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 6.52 (s, 2H), 4.11 (t, *J* = 14.3 Hz, 2H), 3.78 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.2, 146.1, 137.9, 131.6, 129.3, 125.8, 125.3, 121.1 (t, *J* = 254.7 Hz), 120.2, 111.7, 108.0, 60.9, 56.2, 42.2 (t, *J* = 25.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.99 (t, *J* = 14.7 Hz, 2F). MP 150–154 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{17}H_{18}F_2N_2O_3^+$ 350.1311, found 350.1317. The N1-regiochemical assignment for the major product was made using X-ray crystallography (CCDC 2414406).



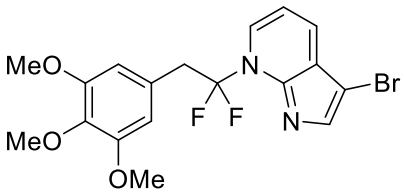
7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (**11ai**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (theophylline, 0.108 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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 reversed-phase flash chromatography using 0.1% AcOH in H_2O and MeCN (0→100% MeCN) to furnish desired product **11ai** as a colorless oil (0.088 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 6.32 (s, 2H), 3.94 (t, *J* = 14.6 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 6H), 3.60 (s, 3H), 3.49 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.1, 153.4, 151.4, 150.5, 139.1, 138.1, 125.9, 119.6 (t, *J* = 261.3 Hz), 107.3, 105.3, 61.0, 56.3, 43.0 (t, *J* = 27.1 Hz), 30.3, 28.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -77.75 (t, *J* = 15.1 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{21}F_2N_4O_5^+$ 411.1475, found 411.1479. The N-regiochemical assignment for the major product was made using ^{1}H{^{19}F} NOE (see S96).



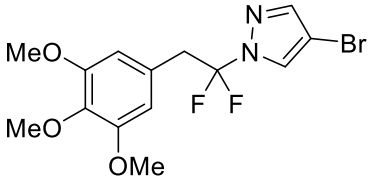
5-chloro-6-(2,3-dichlorophenoxy)-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-2-(methylthio)-1*H*-benzo[*d*]imidazole (**11aj**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 5-chloro-6-(2,3-dichlorophenoxy)-2-(methylthio)-1*H*-benzimidazole (triclabendazole, 0.198 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 24 h. The reaction produced an even mixture of the two N-regioisomers of desired product **11aj** (N1:N3 = 1:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish a mixture of the two N-regioisomers of desired product **11aj** (N1:N3 = 1.3:1) as a colorless solid (0.253 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.39 (m, 1H), 7.49–7.30 (m, 1H), 7.27 (m, 1H), 7.20–6.84 (m, 1H), 6.62 (ddd, *J* = 167.6, 8.3, 1.4 Hz, 1H), 6.19 (d, *J* = 23.7 Hz, 2H), 4.07–3.89 (m, 3H), 3.83–3.65 (m, 8H), 2.86 (d, *J* = 30.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 185.7, 154.9, 154.4, 154.3, 154.1, 153.4, 153.3, 147.9, 146.5, 142.4, 140.8, 138.3, 134.5, 134.3, 134.2, 132.1, 127.8, 127.7, 125.4, 125.1, 124.4, 122.2, 121.4, 120.8, 119.6, 116.8, 114.4, 113.3, 109.1, 107.5, 107.2, 105.6, 61.1, 61.0, 56.2, 56.1, 43.1- 41.8 (m), 15.3, 15.2. ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.42 (dt, *J* = 40.5, 12.5 Hz, 2F). MP 57–63 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{25}H_{22}Cl_3F_2N_2O_4S^+$ 589.0328, found 589.0340.



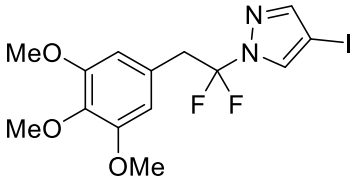
7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-7*H*-pyrrolo[2,3-*b*]pyridine (**11ak**)**:** With modification to general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1*H*-pyrrolo[2,3-*b*]pyridine (0.089 g, 0.75 mmol) in the presence of 1,2-diphenyldiselane (23.4 mg, 0.0750 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (5.7 mg, 0.0050 mmol) in dry DCE (2.0 mL) in a 20 mL scintillation vial using a 40 W 427 nm LED cooled by a fan for 46 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→75% EtOAc) to furnish desired product **11ak** as a bright yellow oil (0.024 g, 14%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.2 Hz, 1H), 7.97 (d, *J* = 2.6 Hz, 1H), 7.54 (d, *J* = 6.6 Hz, 1H), 6.72 (d, *J* = 2.6 Hz, 1H), 6.70 (t, *J* = 6.9 Hz, 1H), 5.94 (s, 2H), 4.32 (t, *J* = 13.9 Hz, 2H), 3.72 (s, 3H), 3.53 (s, 6H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 153.1, 146.2, 146.0, 137.7, 132.7, 132.6, 126.2 (t, *J* = 4.4 Hz), 123.9 (t, *J* = 9.0 Hz), 121.8 (t, *J* = 266.7 Hz), 108.1, 106.7, 102.0, 60.9, 55.9, 40.6 (t, *J* = 25.9 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -82.48 (t, *J* = 13.9 Hz, 2F). HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{18}H_{19}F_2N_2O_3^{+}$ 349.1358, found 349.1389. The N-regiochemistry was assumed to be the same for **11ak** as for **11al** (see below).



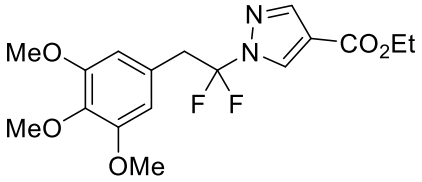
3-bromo-7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-7*H*-pyrrolo[2,3-*b*]pyridine (**11al**)**:** With modification to general procedure D, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 3-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (0.118 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (39.0 mg, 0.125 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) in a 20 mL scintillation vial using a 40 W 427 nm LED cooled by a fan for 44 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→25% EtOAc) to furnish a mixture of desired product **11al** and 3-bromo-1*H*-pyrrolo[2,3-*b*]pyridine. This mixture was further purified by crystallization. Specifically, the mixture was dissolved in a solution of hexanes and EtOAc (7.5 mL, 60% EtOAc) at 67 °C and then left to cool to rt for 2 h. The mixture was then cooled to ~0 °C and let sit for 14 h to ensure complete crystallization. Then, the liquor was removed and the remaining crystals were washed with a cold solution of pentane and EtOAc (0 °C, 10 x 3 mL, 50% EtOAc). Solvent was removed *in vacuo* to furnish dry, needle-like, bright yellow crystals of product **11al** (0.041 g, 19%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.3 Hz, 1H), 7.90 (s, 1H), 7.63 (d, *J* = 6.7 Hz, 1H), 6.82 (t, *J* = 7.0 Hz, 1H), 5.95 (s, 2H), 4.28 (t, *J* = 14.0 Hz, 2H), 3.73 (s, 3H), 3.56 (s, 6H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 153.2, 145.0, 144.2, 137.9, 132.9, 130.6, 125.7, 125.5, 121.8 (t, *J* = 268.2 Hz), 108.8, 106.7, 89.0, 60.9, 56.0, 40.8 (t, *J* = 25.5 Hz). ^{19}F NMR (282 MHz, $CDCl_3$) δ -82.49 (t, *J* = 14.0 Hz, 2F). MP 179–180 °C. HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{18}H_{18}BrF_2N_2O_3^{+}$ 427.0463, found 427.0427. The N-regiochemical assignment was made using X-ray crystallography (CCDC 2492669).



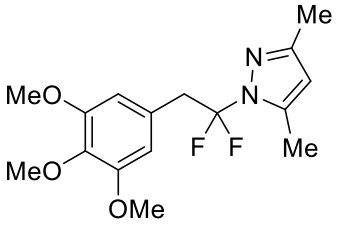
4-bromo-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-pyrazole (**11am**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 4-bromo-1*H*-pyrazole (0.088 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11am** as a colorless oil (0.175 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 2H), 6.32 (s, 2H), 3.81 (s, 3H), 3.77 (s, 6H), 3.73 (t, *J* = 13.5 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153.2, 142.3, 137.8, 129.3, 128.1, 126.1, 119.8 (t, *J* = 255.8 Hz), 107.4, 95.7, 60.9, 56.1, 41.6 (t, *J* = 27.3 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -79.52 (t, *J* = 13.2 Hz, 2F). HRMS (APCI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{14}H_{16}BrF_2N_2O_3^{+}$ 377.0307, found 377.0319.



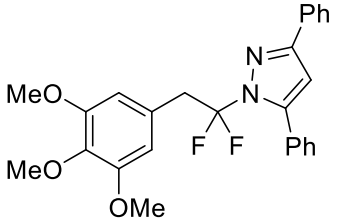
1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-4-iodo-1*H*-pyrazole (**11an**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 4-iodo-1*H*-pyrazole (0.116 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol), and N_2-sparged H_2O (4.5 µL, 0.25 mmol) in DCE (2.0 mL) 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% EtOAc) to furnish a mixture of desired product **11an** and two reaction side products [ArCH=CFN(Azole), $ArCH_2CF_2N$(Azole)]. This mixture was further purified by crystallization. Specifically, the mixture was dissolved in pentane (3 mL) at 39 °C and then left to cool to rt. Desired product crystallized over the course of 16 h. Then, the liquor was removed from the mixture and the remaining precipitate was washed with cold pentane (0 °C, 5 x 3 mL). This crystallization process was repeated for the liquor (2x) using crystals from the original batch as seed crystals. The solids from all three crystallizations were combined, and after removing residual pentane *in vacuo*, product **11an** was obtained as a colorless solid (0.171 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71–7.70 (m, 1H), 7.70 (d, *J* = 0.9 Hz, 1H), 6.31 (s, 2H), 3.82 (s, 3H), 3.78–3.72 (m, 8H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 153i.2, 146.6, 137.8, 132.4, 126.1, 119.6 (t, *J* = 255.9 Hz), 107.4, 60.9, 59.0, 56.2, 41.7 (t, *J* = 27.4 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -79.63 (t, *J* = 14.0 Hz, 2F). MP 55–57 °C. HRMS (APCI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{14}H_{16}F_2IN_2O_3^{+}$ 425.0168, found 425.0176.



Ethyl 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-pyrazole-4-carboxylate (**11ao**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with ethyl 1*H*-pyrazole-4-carboxylate (0.084 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol), and N_2-sparged H_2O (4.5 µL, 0.25 mmol) in DCE (2.0 mL) 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% EtOAc) to furnish desired product **11ao** as a colorless solid (0.167 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.09 (t, *J* = 1.67 Hz, 1H), 6.34 (s, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.80–3.74 (m, 8H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.2, 153.2, 142.6, 137.8, 131.3, 125.9, 119.9 (t, *J* = 252.6 Hz), 116.8, 107.4, 61.0, 60.8, 56.2, 41.8 (t, *J* = 27.2 Hz), 14.4. ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.42 (t, *J* = 13.7 Hz, 2F). MP 93–96 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{17}H_{21}F_2N_2O_5^+$ 371.1413, found 371.1422.

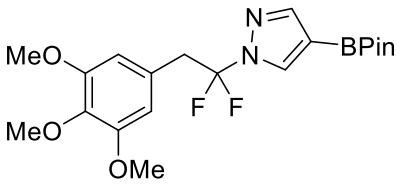


1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-3,5-dimethyl-1*H*-pyrazole (**11ap**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 3,5-dimethyl-1*H*-pyrazole (0.058 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11ap** as a colorless oil (0.148 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.48 (s, 2H), 5.86 (s, 1H), 3.82 (s, 3H), 3.82–3.75 (m, 8H), 2.24 (s, 3H), 2.22 (t, *J* = 1.1 Hz, 3H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.0, 149.6, 141.8, 137.5, 127.3, 121.0 (t, *J* = 250.7 Hz), 109.0, 107.9, 60.9, 56.1, 42.3 (t, *J* = 26.9 Hz), 13.6, 12.2 (t, *J* = 4.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -76.85 (t, *J* = 14.7 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{16}H_{21}F_2N_2O_3^+$ 327.1515, found 327.1523.

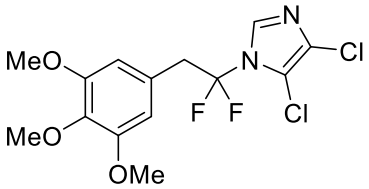


1-(1,1-Difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-3,5-diphenyl-1*H*-pyrazole (**11aq**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 3,5-diphenyl-1*H*-pyrazole (0.132 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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 reversed-phase flash

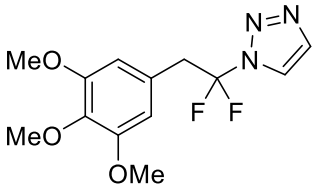
chromatography using 0.1% AcOH in H_2O and MeCN (0→100% MeCN) to furnish desired product **11aq** as a yellow oil (0.195 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 6.7, 1.4 Hz, 2H), 7.48–7.43 (m, 2H), 7.41–7.34 (m, 4H), 7.31–7.27 (m, 2H), 6.61 (s, 1H), 6.46 (s, 2H), 3.92 (t, *J* = 14.0 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.1, 151.9, 146.4, 137.6, 132.4, 130.6, 129.4, 128.9, 128.9, 128.7, 128.0, 127.1, 126.0, 121.3 (t, *J* = 254.1 Hz), 107.9, 107.5, 60.9, 56.1, 42.8 (t, *J* = 27.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.35 (t, *J* = 14.3 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{26}H_{25}F_2N_2O_3^+$ 451.1828, found 451.1835.



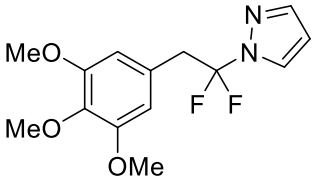
1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (**11ar**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with pyrazol-4-ylboronic acid pinacol ester (0.116 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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→25% EtOAc) to furnish the desired product **11ar** as a light orange solid (0.191 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (m, 2H), 6.30 (s, 2H), 3.80 (s, 3H), 3.75 (m, 8H), 1.30 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.1, 147.1, 137.7, 135.1, 126.4, 119.9 (t, *J* = 255.2 Hz), 107.5, 83.8, 60.9, 56.2, 42.1 (t, *J* = 25.6 Hz), 24.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.97 (t, J = 13.3 Hz, 2F). MP 88–91 °C. HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{20}H_{28}BF_2N_2O_5^+$ 425.2054, found 425.2063.



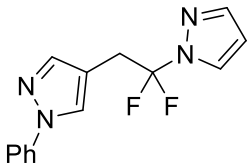
4,5-dichloro-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-imidazole (**11as**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 4,5-dichloro-1*H*-imidazole (0.082 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11as** as a colorless oil (0.176 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 1H), 6.14 (s, 2H), 3.76 (s, 3H), 3.72 (s, 6H), 3.55 (t, *J* = 13.2 Hz, 2H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.4, 138.2, 132.9, 129.5, 124.7, 119.2 (t, *J* = 261.8 Hz), 110.9, 106.7, 60.9, 56.1, 42.7 (t, *J* = 28.1 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -78.25 (t, *J* = 13.1 Hz, 2F). HRMS (APCI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{14}H_{15}Cl_2F_2N_2O_3^+$ 367.0422, found 367.0431.



1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-1,2,3-triazole (**11at**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1*H*-1,2,3-triazole (0.042 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) 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% EtOAc) to furnish the desired product **11at** as a colorless oil (0.139 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.71 (s, 1H), 6.34 (s, 2H), 3.91 (t, *J* = 13.8 Hz, 2H), 3.78 (s, 3H), 3.75 (s, 6H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.2, 137.8, 133.9, 125.3, 121.9, 119.6 (t, *J* = 258.7 Hz), 107.5, 60.9, 56.2, 42.2 (t, *J* = 26.1 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.23 (t, *J* = 13.9 Hz, 2F). HRMS (APCI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{13}H_{16}F_2N_3O_3^{+}$ 300.1154, found 300.1159.

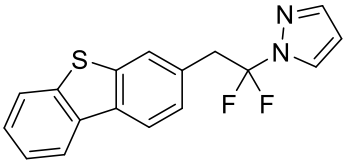


1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-pyrazole (**11a**): Following general procedure C, *gem*-difluoroalkene **10a** (0.115 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish desired product **11a** as a colorless solid (0.138 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.63 (d, *J* = 2.6 Hz, 1H), 6.33 (s, 1H), 6.32 (s, 2H), 3.80 (s, 3H), 3.78 (d, *J* = 13.4 Hz, 2H), 3.75 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.1, 141.8, 137.6, 128.0, 126.6, 112.0 (t, *J* = 254.1 Hz), 107.4, 107.2, 60.9, 56.1, 42.0 (t, *J* = 28.0 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.52 (t, *J* = 13.6 Hz, 2F). MP 64–65 °C. HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{14}H_{17}F_2N_2O_3^{+}$ 299.1202, found 299.1208.

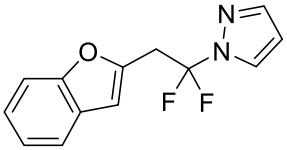


4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)-1-phenyl-1*H*-pyrazole (**11b**): Following general procedure D, *gem*-difluoroalkene **10b** (0.103 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→25% EtOAc) to furnish desired product **11b** as a dark yellow solid (0.115 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 2.7 Hz, 1H), 7.71 (s, 1H), 7.61 (d, *J* = 7.5 Hz, 2H), 7.52 (s, 1H), 7.42 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 6.36 (t, *J* = 2.1 Hz, 1H), 3.86 (t, *J* = 13.5 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.0, 141.9, 134.0, 129.5, 127.8, 127.2, 126.7, 119.7 (t, *J* = 252.3 Hz),

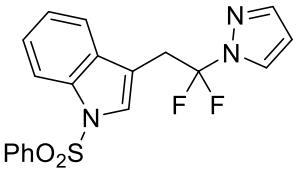
119.1, 112.7 (d, J = 4.6 Hz), 107.6, 31.5 (t, J = 29.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.27 (t, J = 13.5 Hz, 2F). MP 35–36 °C. HRMS (ESI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{14}H_{13}F_2N_4^+$ 275.1103, found 275.1108.



1-(2-(dibenzo[*b*,*d*]thiophen-3-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11c**): Following general procedure C, *gem*-difluoroalkene **10c** (0.123 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 38 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→10% EtOAc) to furnish desired product **11c** as a colorless solid (0.085 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15–8.13 (m, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.89–7.86 (m, 1H), 7.76 (d, J = 1.8 Hz, 1H), 7.71 (d, J = 2.6 Hz, 1H), 7.50–7.45 (m, 2H), 7.39 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.1 Hz, 1H), 6.37 (t, J = 2.2 Hz, 1H), 4.21 (t, J = 14.1 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.0, 141.5, 139.1, 136.2, 135.9, 128.9, 127.7, 127.1, 125.9, 124.8, 124.6, 122.9, 121.9, 121.3, 120.1 (t, J = 254.8 Hz), 107.6, 40.9 (t, J = 28.2 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -77.67 (t, J = 14.5 Hz, 2F). MP 114–118 °C. HRMS (ESI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{17}H_{13}F_2N_2S^+$ 315.0762, found 315.0767.

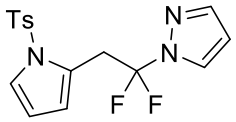


1-(2-(benzofuran-2-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11d**): With slight modification to general procedure D, *gem*-difluoroalkene **10d** (0.090 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (23.4 mg, 0.0750 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) 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→10% EtOAc) to afford the product **11d** as a pale yellow solid (0.073 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 2.6 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.50 (dd, J = 7.7, 1.3 Hz, 1H), 7.45 (d, J = 8.2 Hz, 1H), 7.29–7.25 (m, 1H), 7.20 (td, J = 7.5, 1.1 Hz, 1H), 6.54 (s, 1H), 6.38 (t, J = 2.1 Hz, 1H), 4.16 (t, J = 13.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.1, 148.5, 142.0, 128.4, 127.6, 124.4, 122.9, 121.0, 118.7 (t, J = 254.3 Hz), 111.3, 107.8, 106.9, 35.4 (t, J = 29.3 Hz).^{19}F NMR (470 MHz, $CDCl_3$) δ -77.78 (t, J = 13.5 Hz, 2F). MP 47–50 °C. HRMS (ESI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{13}H_{11}F_2N_2O^+$ 249.0834, found 249.0835.

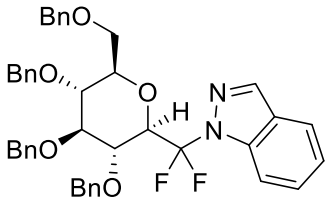


3-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)-1-(phenylsulfonyl)-1*H*-indole (**11e**): Following general procedure C, *gem*-difluoroalkene **10e** (0.160 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated

according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→40% EtOAc) to furnish desired product **11e** as a pale yellow solid (0.104 g, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.71 (s, 1H), 7.61 (d, *J* = 2.6 Hz, 1H), 7.54–7.50 (m, 2H), 7.41–7.38 (m, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 4.00 (t, *J* = 13.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 138.0, 134.9, 134.0, 130.8, 129.3, 127.6, 126.8, 126.4, 125.1, 123.6, 119.8 (t, *J* = 253.4 Hz), 119.7, 113.7, 112.7, 107.5, 31.7 (t, *J* = 29.3 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.10 (t, *J* = 13.4 Hz, 2F). MP 114–120 °C. HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{19}H_{16}F_2N_3O_2S^{+}$ 388.0926, found 388.0930.

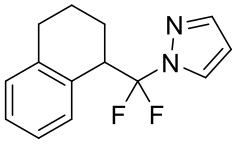


1-(1,1-difluoro-2-(1-tosyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrazole (**11f**): Following general procedure D, *gem*-difluoroalkene **10f** (0.142 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→20% EtOAc) to afford a mixture of desired product **11f** and unidentified impurities as a purple solid. The solid was washed with a Et_2O/pentane solution (20% Et_2O, 5 x 3 mL) and dried *in vacuo* to afford the product **11f** as a brown solid (0.075 g, 43%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 2.6 Hz, 1H), 7.69 (s, 1H), 7.68 (s, 1H), 7.64 (s, 1H), 7.32 (dd, *J* = 3.4, 1.6 Hz, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 6.36 (t, *J* = 2.1 Hz, 1H), 6.18 (t, *J* = 3.4 Hz, 1H), 5.96 (s, 1H), 4.23 (td, *J* = 13.4, 2.9 Hz, 2H), 2.40 (s, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.3, 141.8, 136.4, 130.2, 127.6, 126.9, 124.4, 123.7, 119.0 (t, *J* = 253.7 Hz), 116.0, 112.0, 107.6, 33.0 (t, *J* = 29.1 Hz), 21.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -78.30 (t, *J* = 13.6 Hz, 2F). MP 139–143 °C. HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{16}H_{16}F_2N_3O_2S^{+}$ 352.0926, found 352.0931.

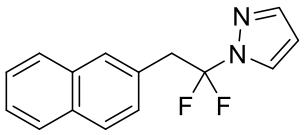


1-(difluoro((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)-1*H*-indazole (**11g**): Following general procedure C, *gem*-difluoroalkene **10g** (0.286 g, 0.500 mmol) was reacted with 1*H*-indazole (0.071 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 48 h. The reaction produced a mixture of the two N-regioisomers of desired product **11g** (N1:N2 = 13:1), as determined by ^{19}F NMR analysis of the crude reaction mixture. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→25% EtOAc) to deliver a mixture of desired product **11g** and its isomer. This mixture was further purified by crystallization to remove the undesired isomer of **11g**. Specifically, the mixture was dissolved in hexanes (5 mL) at 67 °C and then left to cool to rt. Desired product **11g** began to precipitate after 1 h, and the mixture was left undisturbed for 16 h at rt to ensure complete crystallization. Then, the liquor was removed from the mixture and the remaining precipitate was washed with cold pentane (0 °C, 5 x 3 mL). After removing residual pentane *in vacuo*, product **11g** was obtained as a colorless solid (0.167 g, 48%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.45 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.33–7.19 (m, 17H), 7.15–7.14 (m, 2H), 7.10–7.08 (m, 2H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.92 (d, *J* = 10.9 Hz, 1H), 4.84 (d, *J*

= 10.1 Hz, 1H), 4.82 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 10.1 Hz, 1H), 4.62–4.57 (m, 2H), 4.31 (d, *J* = 12.1 Hz, 1H), 4.22 (d, *J* = 12.1 Hz, 1H), 4.08 (t, *J* = 9.3 Hz, 1H), 3.84 (t, *J* = 9.0 Hz, 1H), 3.66 (t, *J* = 9.4 Hz, 1H), 3.58 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.53–3.49 (m, 2H). $^{13}C\{^1H\}$ NMR (201 MHz, $CDCl_3$) δ 139.9, 138.6, 138.4, 138.1, 137.9, 137.3, 128.6, 128.6, 128.4, 128.3, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.6, 127.5, 125.3, 122.6, 121.2, 120.5 (t, *J* = 257.5 Hz), 112.5, 87.0, 79.7, 78.0, 77.9, 77.6–77.3 (m), 76.1, 75.2, 75.2, 73.3, 68.5. $^{13}C\{^1H\}$ NMR (201 MHz, $(CD_3)_2CO$)* δ 140.7, 140.0, 139.7, 139.6, 139.4, 138.4, 129.3, 129.2, 129.1, 129.0, 129.0, 128.8, 128.6, 128.5, 128.4, 128.4, 128.2, 126.4, 123.5, 122.4, 121.8 (t, *J* = 257.1 Hz), 113.1 (t, *J* = 5.8 Hz), 87.5, 80.3, 78.9, 78.0 (dd, *J* = 32.5, 26.8 Hz), 76.3, 75.5, 75.4, 73.7, 69.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -83.00 (d, *J* = 212.8 Hz, 1F), -94.01 (dd, *J* = 212.3, 13.0 Hz, 1F). MP 60–62 °C. HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{42}H_{41}F_2N_2O_5^+$ 691.2978, found 691.2982. Absolute stereochemistry and the N_1-regiochemical assignment for the major product were made using X-ray crystallography (CCDC 2414370).



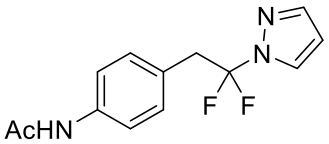
1-(difluoro(1,2,3,4-tetrahydronaphthalen-1-yl)methyl)-1*H*-pyrazole (**11h**): Following general procedure C, *gem*-difluoroalkene **10h** (0.090 g, 0.50 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to obtain a mixture of desired product **11h** with two additional uncharacterized compounds. This product-containing mixture was then further purified by normal-phase preparative TLC using pentane to furnish desired product **11h** as a pale yellow oil (0.106 g, 85%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.19 (td, *J* = 7.5, 1.4 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.04 (td, *J* = 7.5, 1.6 Hz, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 6.37 (t, *J* = 2.2 Hz, 1H), 4.32–4.24 (m, 1H), 2.89–2.75 (m, 2H), 2.02–1.85 (m, 3H), 1.76–1.69 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 142.1, 139.3, 130.4, 130.3, 129.4, 128.3, 127.5, 125.7, 122.0 (t, *J* = 260.0 Hz), 106.9, 42.8 (t, *J* = 24.7 Hz), 29.2, 23.2, 19.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.47 (dd, *J* = 203.1, 16.3 Hz, 1F), -84.92 (dd, *J* = 203.6, 14.0 Hz, 1F). HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{14}H_{15}F_2N_2^+$ 249.1198, found 249.1202.



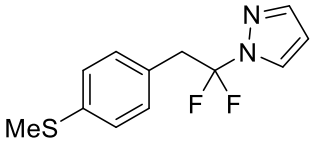
1-(1,1-difluoro-2-(naphthalen-2-yl)ethyl)-1*H*-pyrazole (**11i**): Following general procedure D, *gem*-difluoroalkene **10i** (0.090 g, 0.50 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→15% EtOAc) to obtain a mixture of desired product **11i** with two additional uncharacterized compounds. This product-containing mixture was then further purified by normal-phase preparative TLC using 5% EtOAc in pentane to furnish desired product **11i** as a dark yellow semisolid (0.064 g, 50%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.83–7.75 (m, 4H), 7.69 (s, 1H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.50–

* A $^{13}C\{^1H\}$ NMR in $(CD_3)_2CO$ was taken to account for the **11g** methine carbon signal [δ 78.0 (dd, *J* = 32.5, 26.8 Hz)] that was obscured by the trace $CHCl_3$ peak in the $CDCl_3$ $^{13}C\{^1H\}$ NMR.

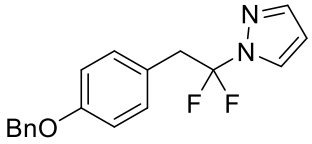
7.46 (m, 2H), 7.30 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 4.06 (t, *J* = 13.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 141.9, 133.3, 132.8, 129.9, 128.7 (t, *J* = 3.4 Hz), 128.1, 127.9, 127.8, 127.7, 126.3, 120.0 (t, *J* = 253.9 Hz), 107.3, 41.9 (t, *J* = 27.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.00 (t, *J* = 13.8 Hz, 2F). HRMS $(APCI)^+$ m/z: $[M + H]^+$ calc'd for $C_{15}H_{13}F_2N_2^+$ 259.1041, found 259.1043.



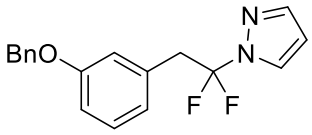
***N*-(4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)phenyl)acetamide** (**11j**): Following general procedure D, *gem*-difluoroalkene **10j** (0.099 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The crude reaction mixture was filtered through a pad of silica with EtOAc (~100 mL) to remove the photocatalyst. The resulting filtrate was dried *in vacuo* to afford a brown solid. This mixture was further purified by crystallization. Specifically, the mixture was dissolved in an EtOAc/hexanes solution (25% EtOAc, 5 mL) at 67 °C and then left to cool to rt. Desired product **11j** began to precipitate after 1 h, and the mixture was left undisturbed for 24 h at rt to ensure complete crystallization. Then, the liquor was removed from the mixture and the remaining precipitate was washed with a Et_2O/pentane solution (25% Et_2O, 5 x 3 mL). After removing residual solvent *in vacuo*, product **11j** was obtained as a colorless solid (0.109 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.65–7.60 (m, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 1H), 3.82 (t, *J* = 13.8 Hz, 2H), 2.15 (s, 3H). $^{13}C\{^{1}H\}$ NMR (201 MHz, $CDCl_3$) δ 168.4, 141.9, 137.6, 131.2, 127.8, 127.0, 119.9 (t, *J* = 253.7 Hz), 119.8, 107.3, 41.2 (t, *J* = 27.8 Hz), 24.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.40 (t, *J* = 13.8 Hz, 2F). MP 110–115 °C. HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{13}H_{14}F_2N_3O^+$ 266.1099, found 266.1105.



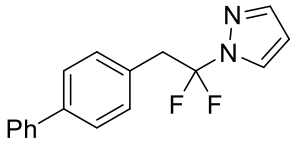
1-(1,1-difluoro-2-(4-(methylthio)phenyl)ethyl)-1*H*-pyrazole (**11k**): Following general procedure D, *gem*-difluoroalkene **10k** (0.093 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→20% EtOAc) to furnish desired product **11k** as a yellow semisolid (0.103 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.9 Hz, 1H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.32 (d, *J* = 1.6 Hz, 1H), 3.83 (t, *J* = 13.8 Hz, 2H), 2.45 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 141.9, 138.3, 131.0, 127.8, 126.4, 119.9 (t, *J* = 253.4 Hz), 107.3, 41.2 (t, *J* = 27.6 Hz), 15.7. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.32 (t, *J* = 13.7 Hz, 2F). HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{12}H_{13}F_2N_2S^+$ 255.0762, found 255.0763.



1-(2-(4-(benzyloxy)phenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11l**): Following general procedure D, *gem*-difluoroalkene **10l** (0.123 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 15 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→15% EtOAc) to furnish desired product **11l** as a yellow solid (0.130 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 2.6 Hz, 1H), 7.45–7.39 (m, 4H), 7.36–7.33 (m, 1H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.34 (t, *J* = 2.2 Hz, 1H), 5.04 (s, 2H), 3.83 (t, *J* = 13.9 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 141.8, 137.0, 131.7, 128.7, 128.1, 127.7, 127.6, 123.5 (d, *J* = 3.4 Hz), 120.0 (t, *J* = 253.4 Hz), 114.8, 107.2, 70.0, 40.9 (t, *J* = 27.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.61 (t, *J* = 13.9 Hz, 2F). MP 67–69 °C. HRMS (ESI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{17}F_2N_2O^+$ 315.1303, found 315.1308.

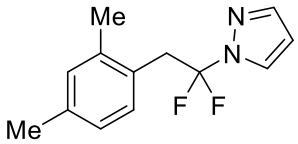


1-(2-(3-(benzyloxy)phenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11m**): Following general procedure C, *gem*-difluoroalkene **10m** (0.123 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 38 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→10% EtOAc) to furnish desired product **11m** as a colorless semisolid (0.089 g, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.66 (s, 1H), 7.46–7.39 (m, 5H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.98–6.87 (m, 2H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.34 (s, 1H), 5.01 (s, 2H), 3.88 (t, *J* = 13.8 Hz, 2H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 158.9, 141.8, 137.0, 132.6, 129.5, 128.7, 128.1, 127.8, 127.6, 123.3, 119.9 (t, *J* = 253.9 Hz), 117.0, 114.5, 107.3, 70.1, 41.8 (t, *J* = 27.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) -79.05 (t, *J* = 13.8 Hz, 2F). HRMS (ESI)$^+$ m/z: [M + H]$^+$ calc'd for $C_{18}H_{17}F_2N_2O^+$ 315.1303, found 315.1309.

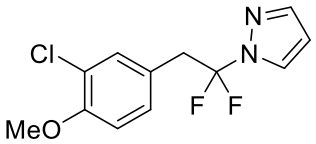


1-(2-([1,1'-biphenyl]-4-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11n**): Following general procedure D, *gem*-difluoroalkene **10n** (0.108 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→15% EtOAc) to obtain a mixture of desired product **11n**, $(PhSe)_2$, and an unidentified compound. This product-containing mixture was then further purified by normal-phase preparative TLC using EtOAc and hexanes (20% EtOAc) to furnish desired product **11n** as a pale yellow solid (0.124 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.69 (d, *J* = 2.6 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.35–

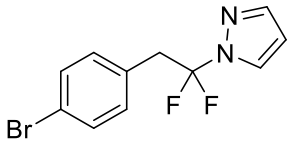
6.34 (m, 1H), 3.93 (t, J = 14.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.6, 140.5, 140.5, 130.8, 130.0, 128.7, 127.6, 127.3, 127.0, 127.0, 119.7 (t, J = 253.6 Hz), 107.1, 41.2 (t, J = 27.6 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.07 (t, J = 14.5 Hz, 2F). MP 74–77 °C. HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{17}H_{15}F_2N_2^+$ 285.1198, found 285.1203.



1-(2-(2,4-dimethylphenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11o**): Following general procedure D, *gem*-difluoroalkene **10o** (0.084 g, 0.50 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.600 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 44 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to afford the desired product **11o** as a yellow oil (0.083 g, 70%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.72–7.71 (m, 1H), 7.67 (d, J = 3.1 Hz, 1H), 7.01 (s, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.92 (d, J = 7.8 Hz, 1H), 6.36 (t, J = 2.1 Hz, 1H), 3.87 (t, J = 14.6 Hz, 2H), 2.32 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 141.7, 137.9, 137.7, 131.4, 131.3, 127.7, 126.8, 126.6, 120.3 (t, J = 253.9 Hz), 107.3, 38.2 (t, J = 27.3 Hz), 21.1, 19.8. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.03 (t, J = 14.6 Hz, 2F). HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{13}H_{15}F_2N_2^+$ 237.1198, found 237.1201.

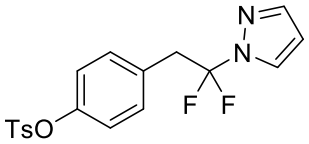


1-(2-(3-chloro-4-methoxyphenyl)-1, 1-difluoroethyl)-1*H*-pyrazole (**11p**): Following general procedure C, *gem*-difluoroalkene **10p** (0.102 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→12% EtOAc) to furnish desired product **11p** as a colorless oil (0.114 g, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 1.7 Hz, 1H), 7.26 (s, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.04 (dd, J = 8.4, 2.2 Hz, 1H), 6.81 (d, J = 8.5 Hz, 1H), 6.33 (t, J = 2.2 Hz, 1H), 3.86 (s, 3H), 3.79 (t, J = 13.7 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 154.7, 141.9, 132.2, 130.0, 127.8, 124.2, 122.3, 119.7 (t, J = 253.4 Hz), 111.9, 107.4, 56.2, 40.6 (t, J = 27.9 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.43 (t, J = 13.5 Hz, 2F). HRMS $(ESI)^+$ m/z: $[M + H]^+$ calc'd for $C_{14}H_{17}F_2N_2O_3^+$ 293.0601, found 293.0603.



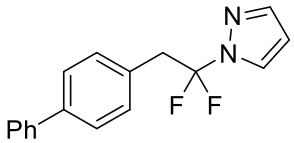
1-(2-(4-bromophenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11q**): Following general procedure D, *gem*-difluoroalkene **10q** (0.110 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 42 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→15% EtOAc) to obtain a mixture of desired product **11q** and two

additional uncharacterized compounds. This product-containing mixture was then further purified by normal-phase preparative TLC using EtOAc and pentane (5% EtOAc) to furnish desired product **11q** as a pale yellow oil (0.034 g, 24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.7 Hz, H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H), 3.84 (t, *J* = 13.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.9, 132.3, 131.7, 130.2, 127.7, 122.2, 119.6 (t, *J* = 253.9 Hz), 107.5, 41.2 (t, *J* = 27.8 Hz). ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.08 (t, *J* = 13.7 Hz, 2F). HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{11}H_{10}BrF_2N_2^{+}$ 286.9990, found 286.9994.



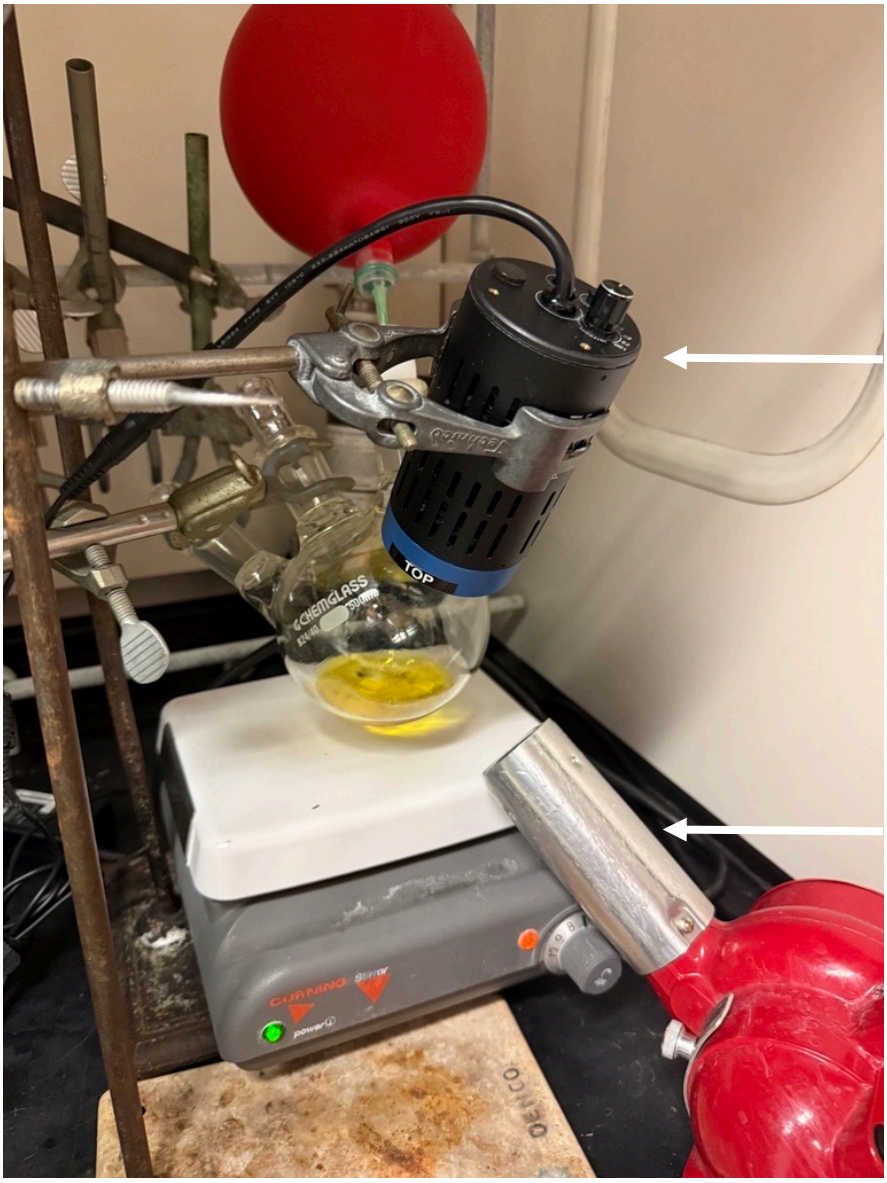
4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)phenyl 4-methylbenzenesulfonate (**11r**): Following general procedure D, *gem*-difluoroalkene **10r** (0.155 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 48 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→10% EtOAc) to obtain a mixture of desired product **11r**, the des-tosyl phenolic degradation product of **11r**, and additional uncharacterized compounds. This mixture was further purified by crystallization. Specifically, the mixture was dissolved in a 7% EtOAc in hexanes solution (5 mL) at 67 °C and then left to cool to rt. Desired product **11r** began to precipitate after 1 h, and the mixture was left undisturbed for 4 h at rt to ensure complete crystallization. Then, the liquor was removed from the mixture and the remaining precipitate was washed with a 10% Et_2O in pentane solution (5 x 3 mL). After removing residual solvent *in vacuo*, product **11r** was obtained as a colorless solid (0.048 g, 25%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.62 (m, 4H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.32 (t, *J* = 2.3 Hz, 1H), 3.84 (t, *J* = 13.7 Hz, 2H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 149.4, 145.5, 141.9, 132.5, 131.9, 130.3, 129.9, 128.6, 127.7, 122.5, 119.6 (t, *J* = 253.6 Hz), 107.5, 41.1 (t, *J* = 27.8 Hz), 21.9. ^{19}F NMR (470 MHz, $CDCl_3$) δ -79.11 (t, *J* = 13.9 Hz, 2F). MP 109–111 °C. HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{18}H_{17}F_2N_2O_3S^{+}$ 379.0922, found 379.0925.

4. Gram Scale Reaction



1-(2-([1,1'-biphenyl]-4-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11n**): A 500 mL 3-neck round bottom flask equipped with a thermometer and a stir bar was charged with *gem*-difluoroalkene **10n** (1.00 g, 4.62 mmol), 1*H*-pyrazole (0.378 g, 5.55 mmol), 1,2-diphenyldiselane (72.2 mg, 0.231 mmol), and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (79.6 mg, 0.139 mmol). The flask was then evacuated and backfilled with argon (3x), charged with dry PhMe (18.5 mL), and irradiated by a 40 W 427 nm LED cooled by a fan (30 °C) for 4 h (see next page for a photograph of the reaction setup). The crude reaction mixture was filtered through a pad of silica (~100 mL silica) using Et_2O (500 mL) to remove photocatalyst. The resulting filtrate was then dried onto diatomaceous earth *in vacuo* and purified by normal-phase flash chromatography using DCM and hexanes (0→70% DCM) to furnish desired product **11n** as a colorless solid (0.934 g, 71%). ^{1}H NMR and ^{19}F NMR spectra of the isolated material match the previous report (see S27–28).

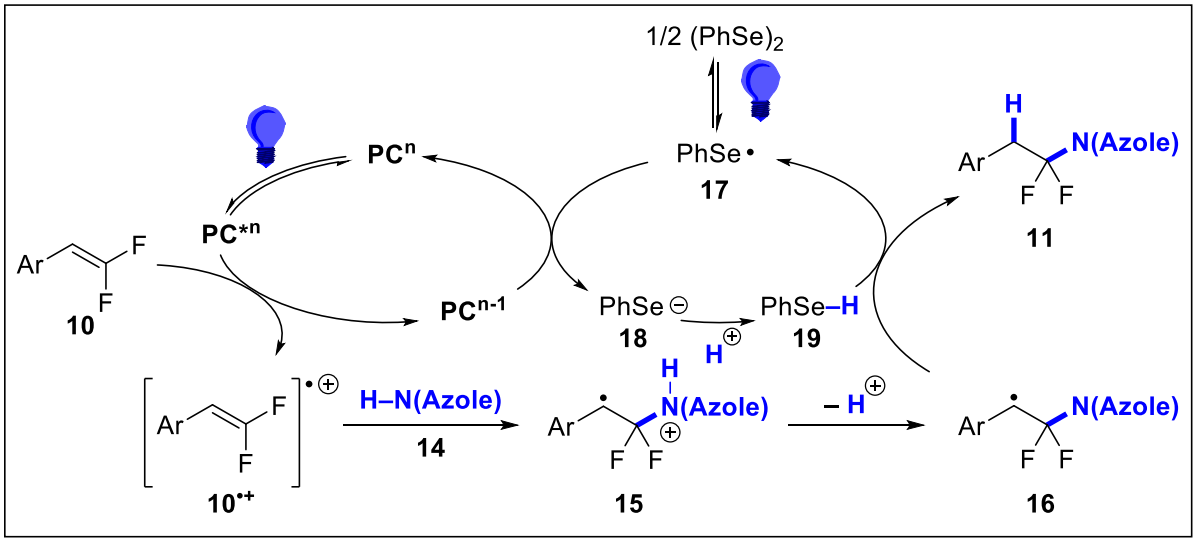
Gram Scale Reaction Setup



Lamp: Kessil PR160L-427 (427 nm light at 40 W); ~2 cm from glass
Fan: VARITEMP Heat Gun (on “no heat” setting; Model VT-750C); ~4 cm from glass

5. Mechanistic Studies

Scheme S1. Proposed reaction mechanism.



5.a. Luminescence Quenching and Cyclic Voltammetry

Luminescence Quenching Experimental Procedure

Following a previously reported procedure,[16] luminescence intensity measurements were performed with 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 606 nm (**PC-I**) or 517 nm (**PC-II**), which correspond to the absorption and emission maxima for **PC-I** [17] and **PC-II**,[4] respectively. 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** or **PC-II** (0.10 mM) alone in anhydrous MeCN or PhMe (150 µL total). The subsequent 4 wells contained increasing concentrations of quencher (see below for specific values) in addition to photocatalyst (0.10 mM) in anhydrous MeCN (150 µL total). All wells were repeated in triplicate. The 96-well plate was sealed with optical adhesive film (Applied Biosystems MicroAmp) prior to removal from the glovebox to prevent air exposure, and the plate was scanned within 5 minutes of film application to avoid condensation of solvent droplets on the film.

The recorded single-point luminescence intensities represent the average of 10 scans per well, with each scan consisting of concomitant excitation pulse and emission detection with a 100 µs integration time. These intensities were then used to construct Stern-Volmer plots with lines of best fit according to the following equation:

$$\frac{I^\circ}{I} = 1 + k_q\tau[Q] \qquad (1)$$

Where I° is the recorded luminescence intensity in the absence of quencher, I is the recorded luminescence 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 photocatalyst (**PC-I:** τ = 279 ns; **PC-II:** τ = 14.4 ns),[4,18] and k_q is the bimolecular quenching constant. Specifically, the "y-values" ($\frac{I^\circ}{I}$) were obtained by dividing each replicant luminescence intensity value from the wells containing photocatalyst 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 luminescence intensities ($I^\circ + I$). "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:

$$k_q = \frac{slope}{\tau} \quad (2)$$

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

Cyclic Voltammetry Experimental Procedure

Cyclic voltammograms were collected under an argon atmosphere (glovebox with H_2O and O_2 <1 ppm) using a CHI 6284E potentiostat (CH Instruments) at a scan rate of 50 mV/s. Samples were prepared in glass 20 mL scintillation vials with anhydrous, degassed DCE (5 mL),* NBu_4PF_6 (100 mM) as the supporting electrolyte, and analyte (1 mM). A three-electrode configuration was employed, which consisted of a freshly polished** glassy carbon (GC) working electrode (3 mm dia. disk), platinum wire counter electrode, and silver wire QRE.

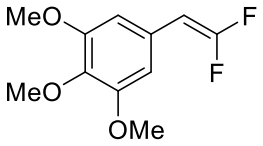
Specifically, prior to collecting data for the *gem*-difluorostyrene, azole, and $(PhSe)_2$ analytes, a cyclic voltammogram was obtained for a solution of ferrocene (Fc) between 0 and +2.5 V vs. QRE to establish an $E_{1/2}$ value for the reversible Fc/Fc^+ redox couple. Then, for each analyte, voltammograms were acquired for duplicate solutions (with no ferrocene). After completing these scans, another fresh solution of ferrocene was scanned to account for any drift in potential of the QRE, which was observed to be negligible over the duration of the experiments.

Data were analyzed using OriginPro software. The $E_{1/2}$ value for the reversible Fc/Fc^+ redox couple represents the average of the scans taken before and after studying the analytes. The reported peak potentials (E_p) were referenced to the $E_{1/2}(Fc/Fc^+)$ value and represent the average of the two independent measurements (rounded to the nearest 0.1 V). For compounds with multiple peaks, the reported E_p was determined from the first detected peak with respect to the scan direction. Pictured voltammograms represent one of the two independent measurements. The voltammograms are reported following the polarographic/US/Texas convention. Black arrows on the graphs indicate the scan direction.

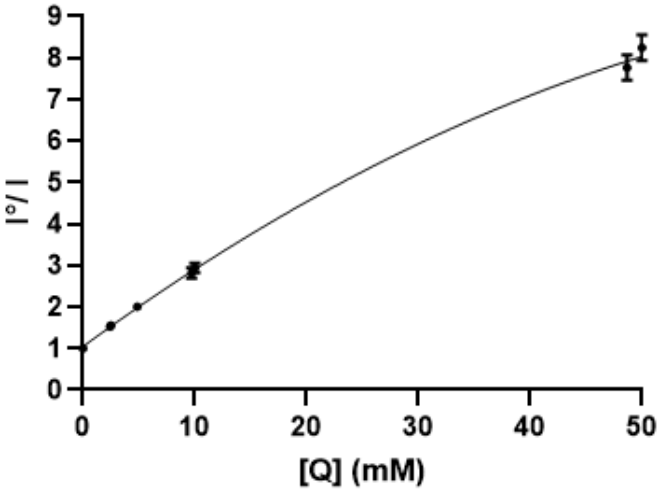
* DCE was dispensed using a clean, glass syringe and metal needle for most voltammograms (plastic syringe degradation affects the CVs).

** Prior to each experiment, the GC working electrode was polished using a 0.05 μm alumina powder suspension (Electron Microscopy Sciences) on a micro-cloth polishing pad (Buehler). Subsequently, the electrode was washed thoroughly with deionized H_2O and dried in the antechamber of the glovebox.

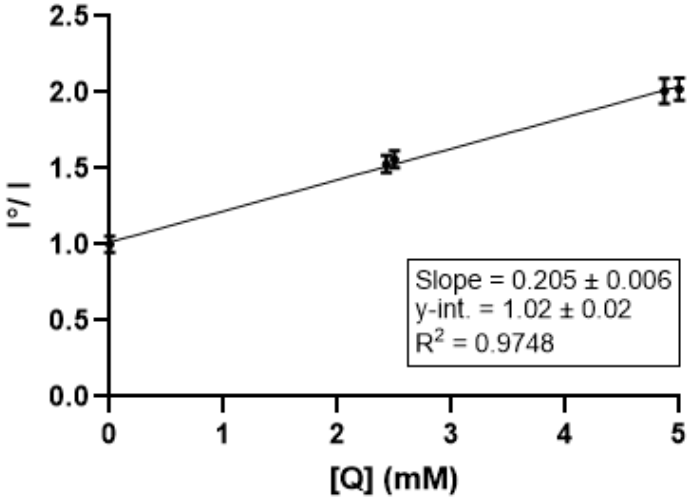
5-(2,2-difluorovinyl)-1,2,3-trimethoxybenzene (10a)



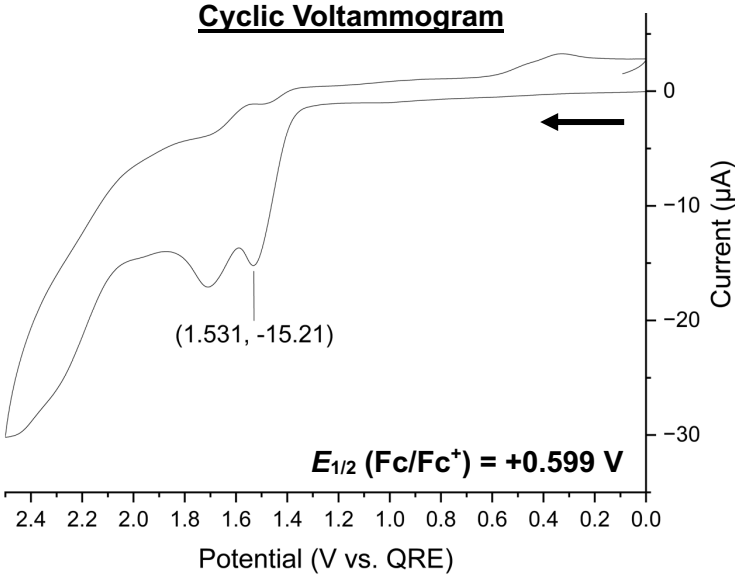
Stern-Volmer Plot (PC-I) Full Data†



Stern-Volmer Plot (PC-I) 0–5 mM



Cyclic Voltammogram



Summarized Data

E_p = +1.0 V

k_q **(PC-I)** = (7.3 ± 0.2) x 10^8 $M^{-1} \cdot s^{-1}$ †

k_q **(PC-II)**[15] = (8.33 ± 0.07) x 10^9 $M^{-1} \cdot s^{-1}$

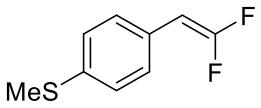
†Nonlinear luminescence quenching with negative curvature was observed in this experiment. This behavior can be caused by the existence of multiple emitters with different luminescence intensities and quenching rates.[19] The observed trend, then, may be indicative of the formation of a (**PC-I–10a**)* complex with an intrinsic luminescence lifetime ($\tau^{complex}$) and quenching rate ($k_q^{complex}$) that is distinct from **PC-I*** (τ^{PC}; k_q^{PC}), but still relevant at the experimental detection wavelength (606 nm). The following expression relates the contribution of both emitter species to observed luminescence quenching:[19]

$$\frac{I^\circ}{I} = \frac{1 + \left(k_q^{complex}\tau^{complex} + k_q^{PC}\tau^{PC}\right)[Q] + k_q^{complex}\tau^{complex}k_q^{PC}\tau^{PC}[Q]^2}{f(complex)\left(1 + k_q^{PC}\tau^{PC}[Q]\right) + f(PC)\left(1 + k_q^{complex}\tau^{complex}[Q]\right)} \quad (3)$$

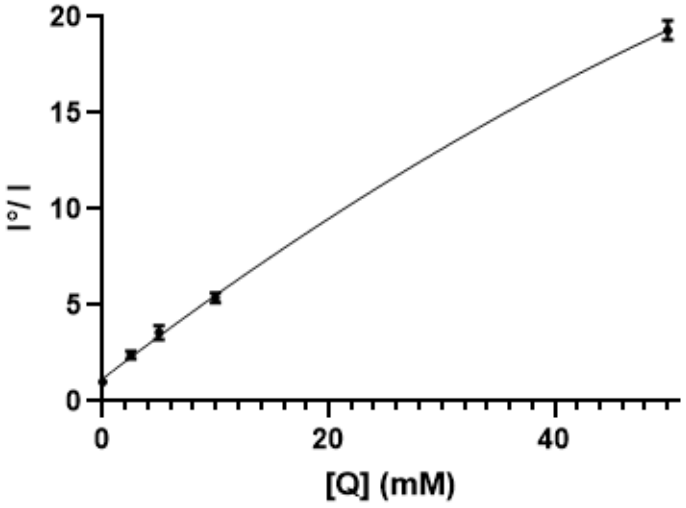
Where $f(complex)$ and $f(PC)$ are the respective fractional contributions to observed luminescence by **PC-I*** and the (**PC-I–10a**)* complex. Importantly, if **PC-I*** and the (**PC-I–10a**)* complex had identical fluorescent properties

($k_q^{complex}\tau^{complex} = k_q^{\boldsymbol{PC}}\tau^{\boldsymbol{PC}}$), this expression would simplify to give the original, linear Stern-Volmer equation (eq. 1). Absent specific values for $k_q^{complex}$ and $\tau^{complex}$, this expression fits the negative curvature observed in the above luminescence quenching plots. Notably, control experiments show no luminescence of **10a**, alone, at the experimental irradiation and detection wavelengths. Admittedly, then, the values for "k_q" that we determined from the linear-trimmed data using the Stern-Volmer relationship (a linear expression), cannot be taken as true k_q values for **10a** and used for quantitative comparison with other quenchers. However, given the thermodynamic favorability of oxidation of **10a** by **PC-I***, any observation of luminescence quenching, regardless of the specific "mode," supports the claim that oxidation of **10a** by **PC-I*** is feasible in this reaction.

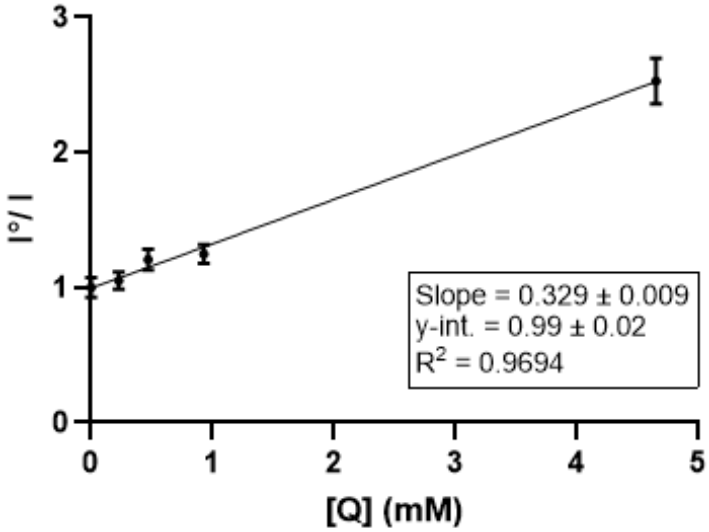
(4-(2,2-difluorovinyl)phenyl)(methyl)sulfane (10k)



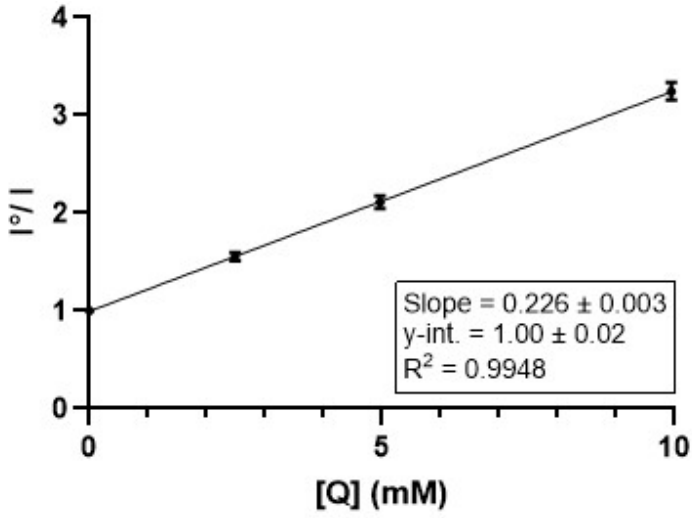
Stern-Volmer Plot (PC-I) Full Data†



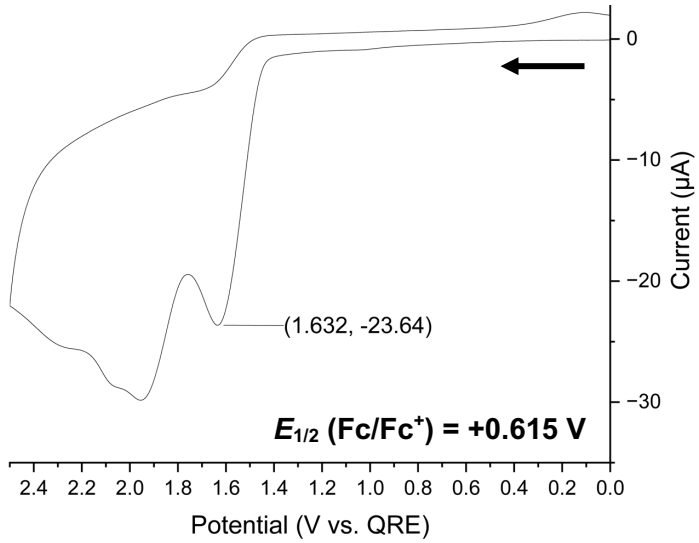
Stern-Volmer Plot (PC-I) 0–5 mM



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram



Summarized Data

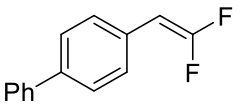
E_p = +1.0 V

k_q **(PC-I)** = (1.18 ± 0.06) x 10^9 $M^{-1} \cdot s^{-1}$

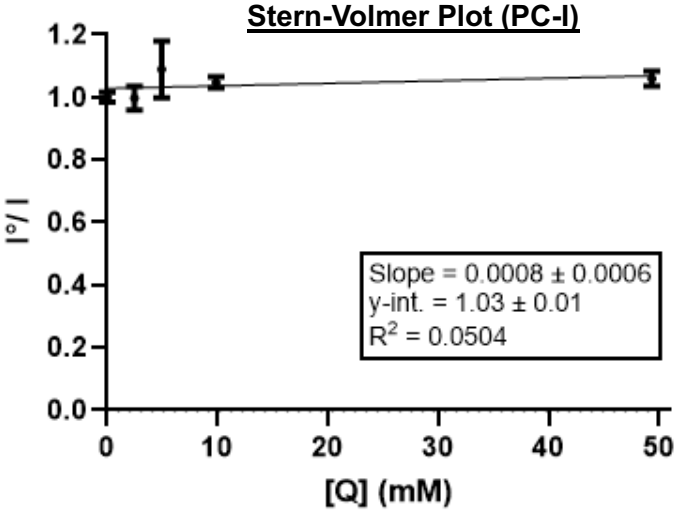
k_q **(PC-II)** = (1.57 ± 0.02) x 10^{10} $M^{-1} \cdot s^{-1}$

†See note on S33–34

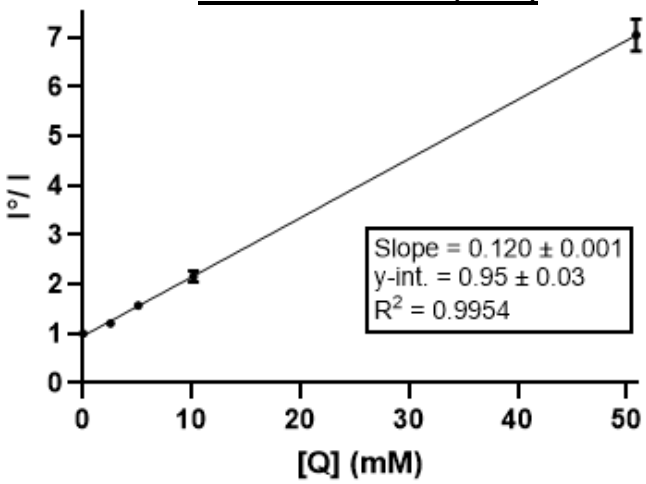
4-(2,2-difluorovinyl)-1,1'-biphenyl (10n)



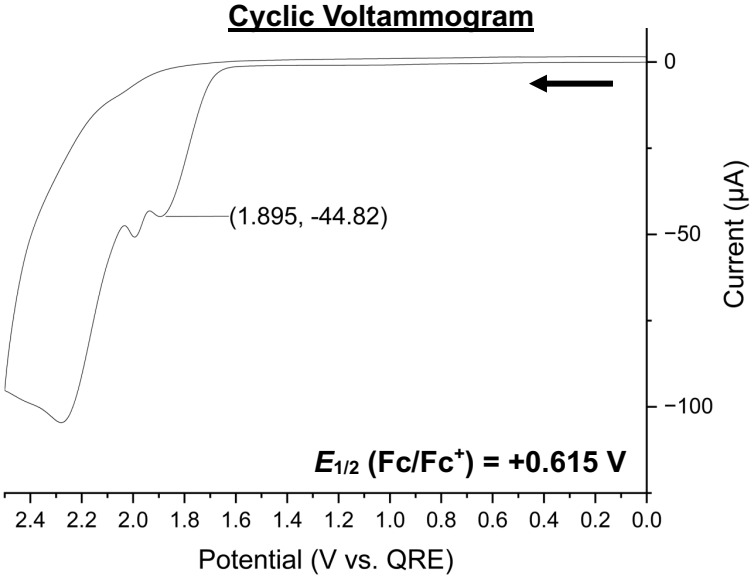
Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram



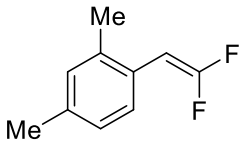
Summarized Data

E_p = +1.3 V

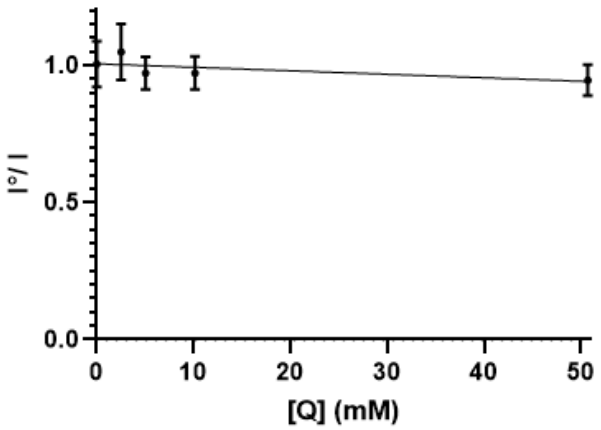
k_q **(PC-I)** = *no quenching*

k_q **(PC-II)** = (8.33 ± 0.07) x 10^9 $M^{-1} \cdot s^{-1}$

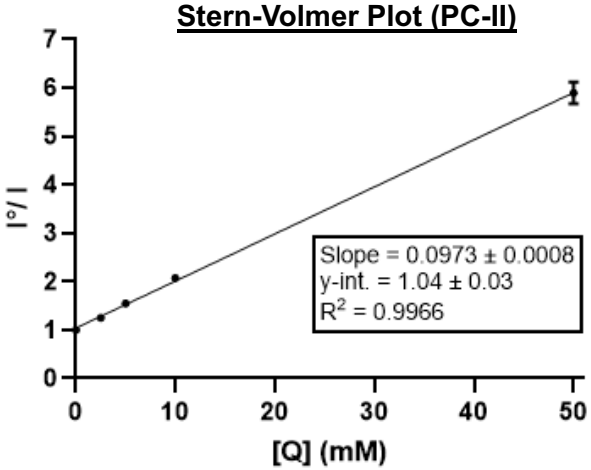
1-(2,2-difluorovinyl)-2,4-dimethylbenzene (10o)



Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)

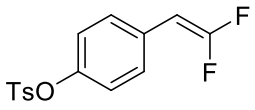


Summarized Data

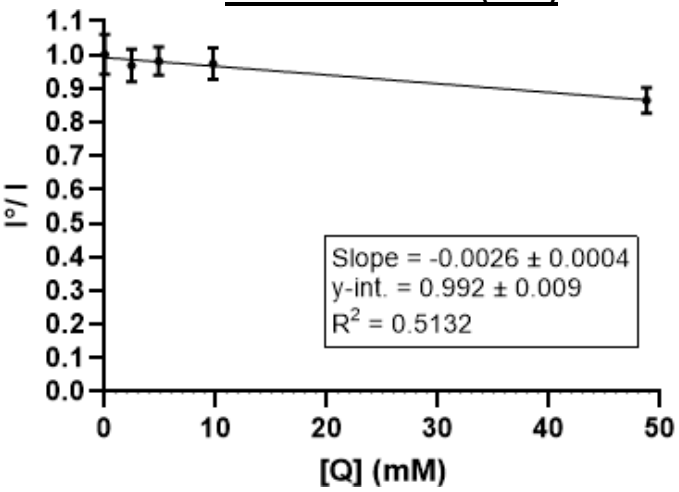
k_q (PC-I) = *no quenching*

k_q (PC-II) = $(6.76 \pm 0.06) \times 10^9\ M^{-1} \cdot s^{-1}$

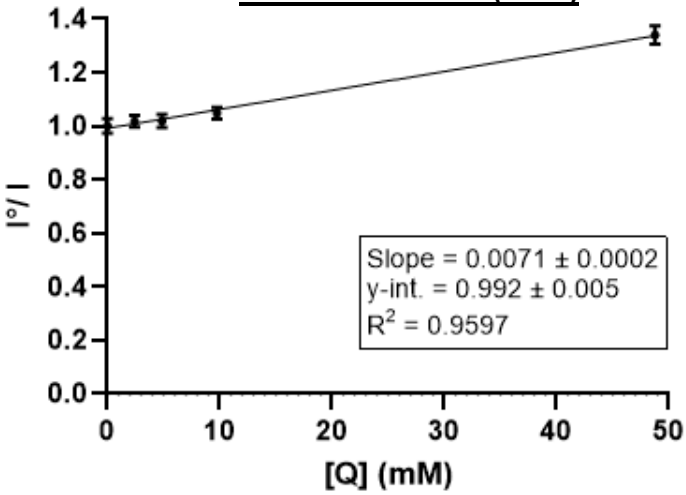
4-(2,2-difluorovinyl)phenyl 4-methylbenzenesulfonate (10r)



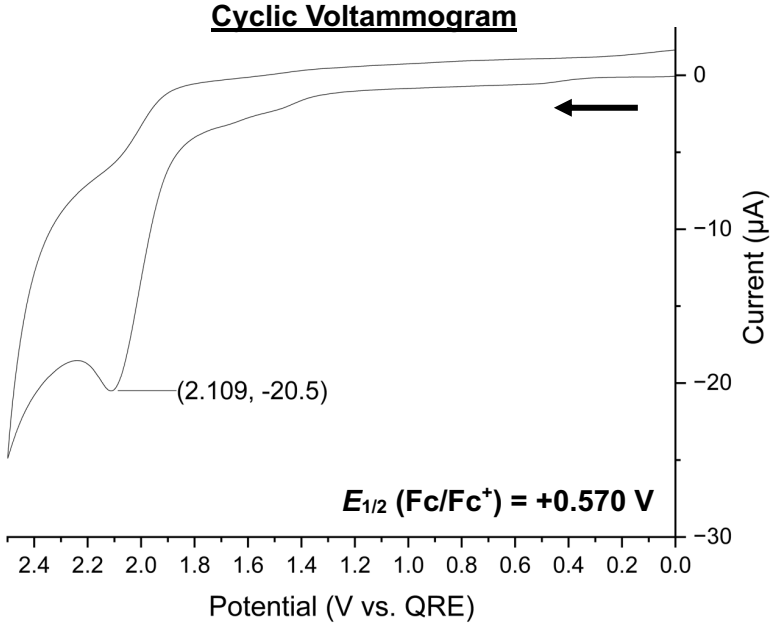
Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram



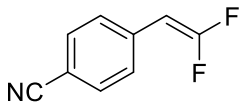
Summarized Data

E_p = +1.5 V

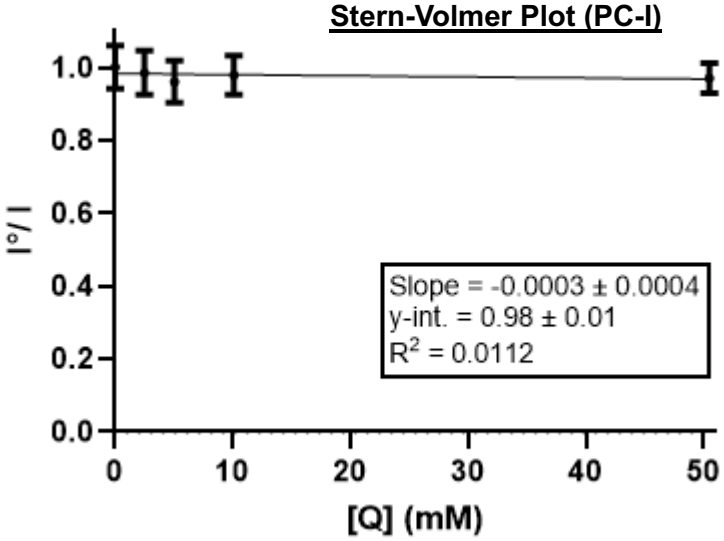
k_q **(PC-I)** = *no quenching*

k_q **(PC-II)** = (4.9 ± 0.1) x 10^8 $M^{-1} \cdot s^{-1}$

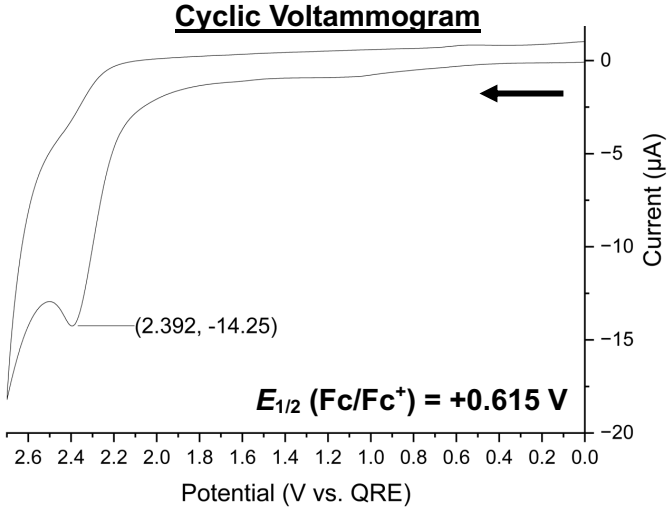
4-(2,2-difluorovinyl)benzonitrile (10t)



Stern-Volmer Plot (PC-I)



Cyclic Voltammogram



Summarized Data

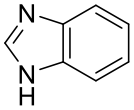
E_p = +1.8 V [!]

k_q **(PC-I)** = *no quenching*

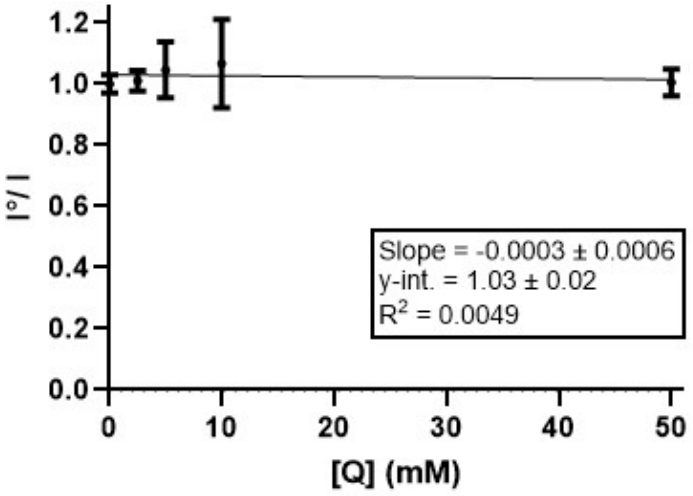
k_q **(PC-II)**[15] = *no quenching*

[!]This measured oxidation potential of **10t** in DCE (+1.8 V) is significantly different from the potential in THF previously reported by our research group (+1.3 V).[16] Interestingly, the measured potential of **10a** did not change between DCE and THF.

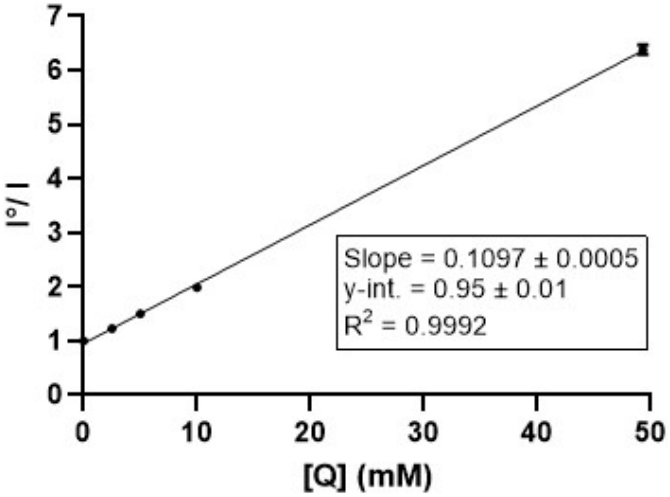
Benzimidazole



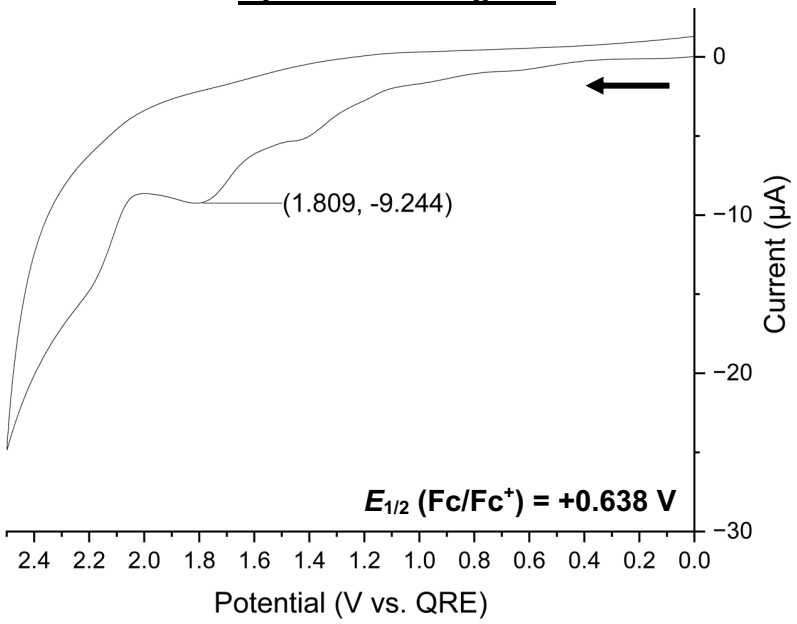
Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram*



Summarized Data

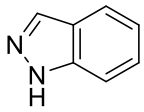
E_p = +1.1 V

k_q **(PC-I)** = *no quenching*

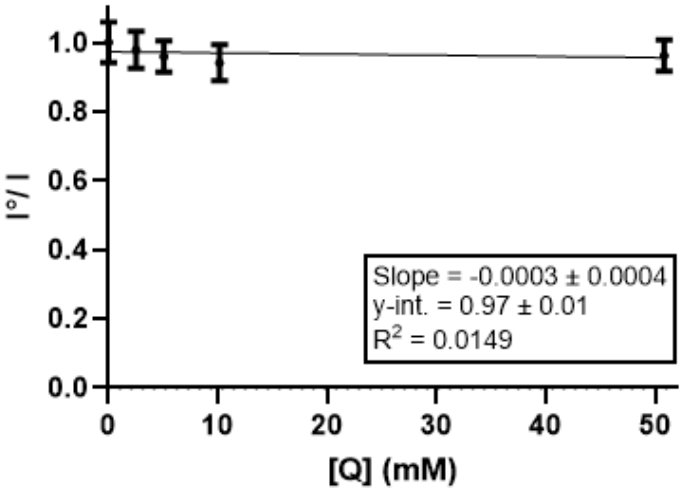
k_q **(PC-II)** = (7.62 ± 0.04) x 10^9 $M^{-1} \cdot s^{-1}$

*The small, unlabeled peaks prior to the first labeled peak are from the degradation of a plastic syringe used to dispense DCE.

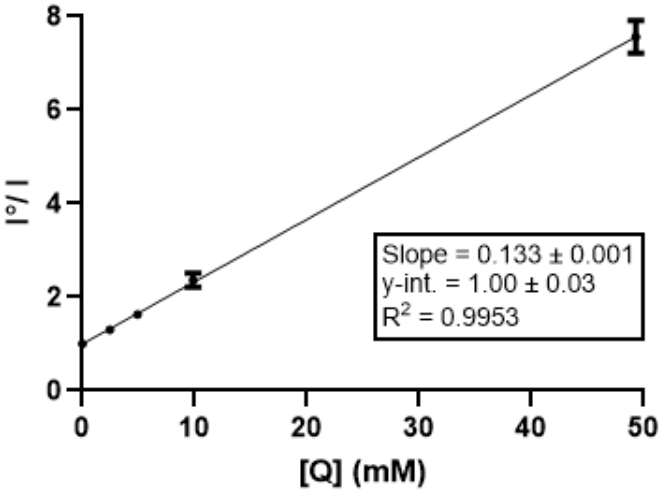
Indazole



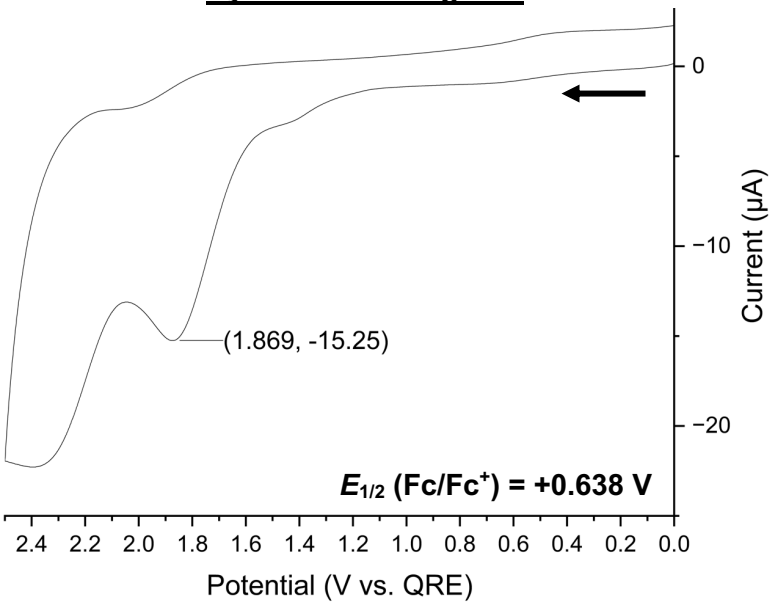
Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram*



Summarized Data

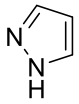
E_p = +1.2 V

k_q **(PC-I)** = *no quenching*

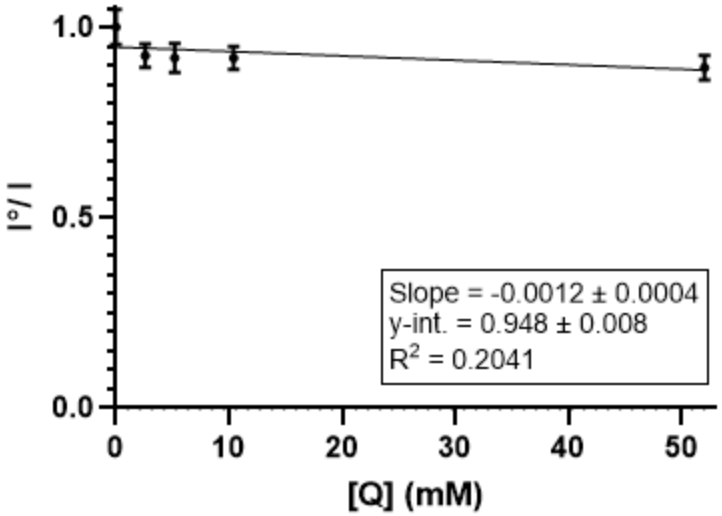
k_q **(PC-II)** = (9.23 ± 0.07) x 10^9 $M^{-1} \cdot s^{-1}$

*The small, unlabeled peaks prior to the first labeled peak are from the degradation of a plastic syringe used to dispense DCE.

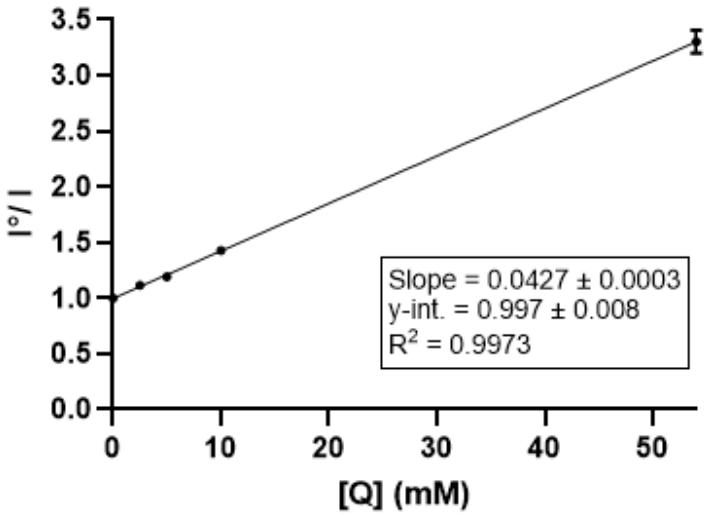
Pyrazole



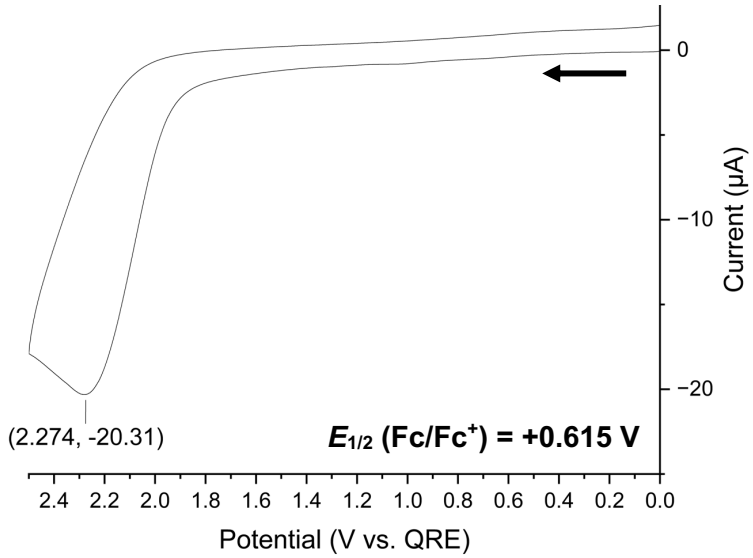
Stern-Volmer Plot (PC-I)



Stern-Volmer Plot (PC-II)



Cyclic Voltammogram



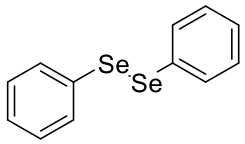
Summarized Data

E_p = +1.6 V

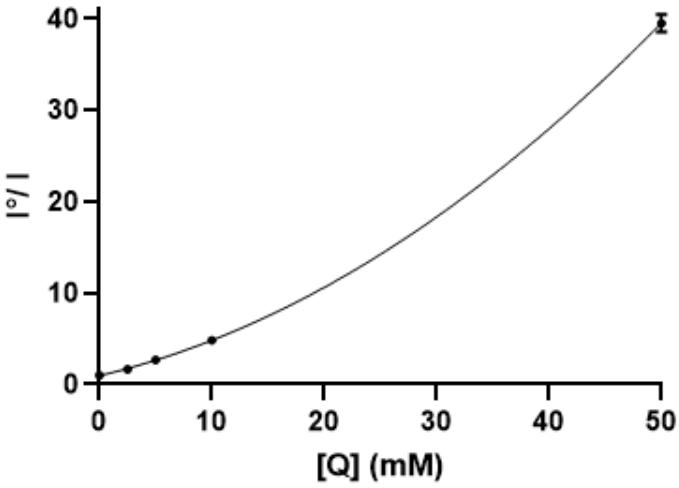
k_q **(PC-I)** = *no quenching*

k_q **(PC-II)** = (2.96 ± 0.02) x 10^9 $M^{-1} \cdot s^{-1}$

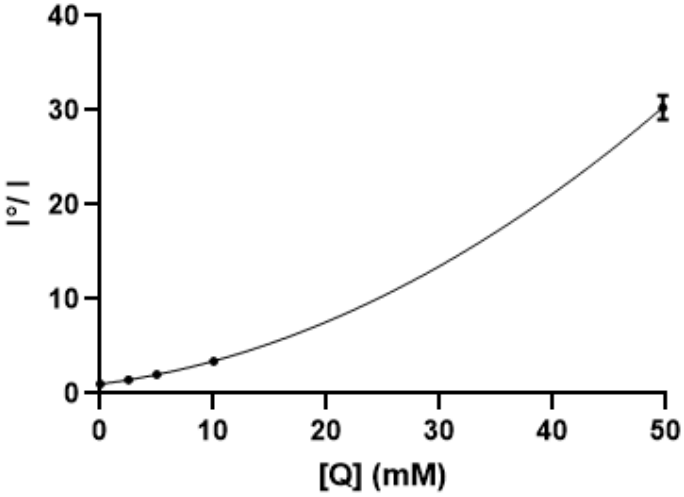
(PhSe)₂



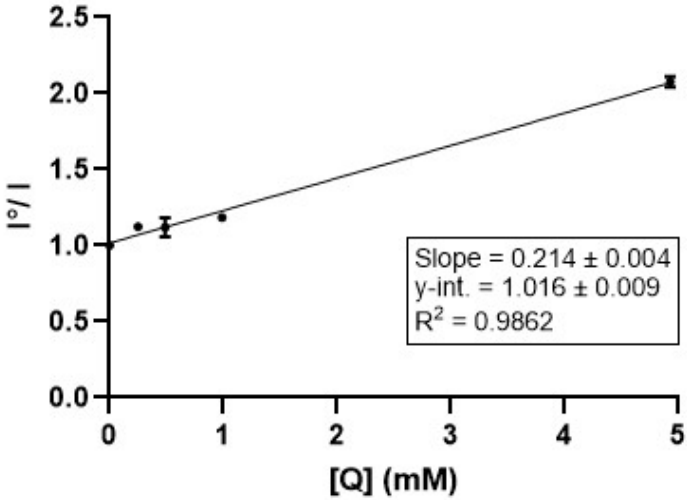
Stern-Volmer Plot (PC-I) Full Data‡



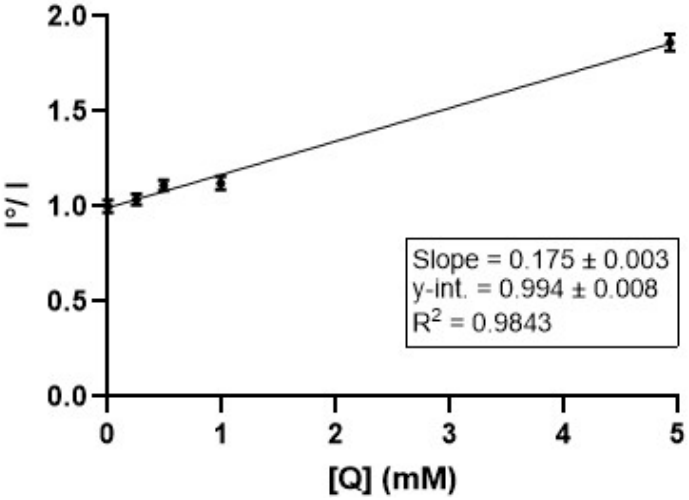
Stern-Volmer Plot (PC-II) Full Data‡



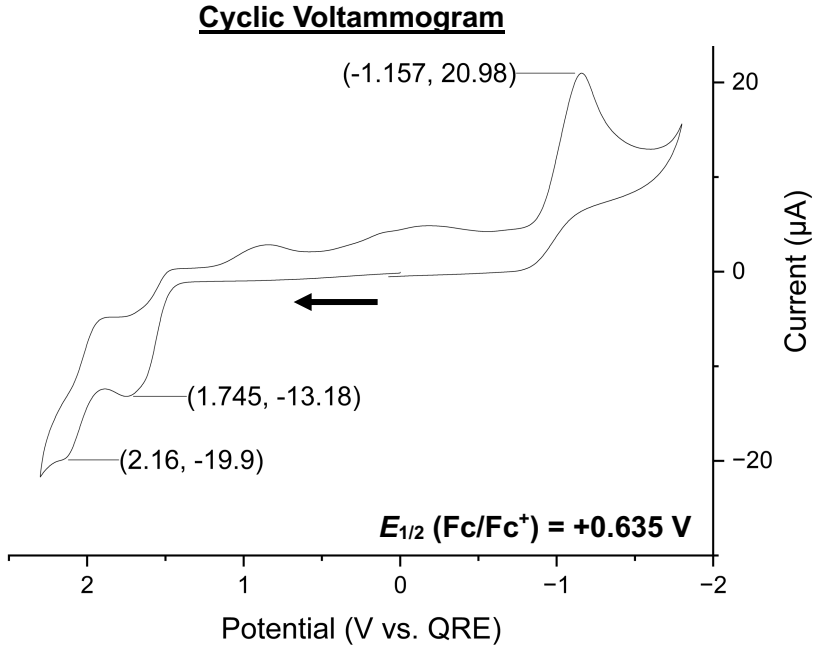
Stern-Volmer Plot (PC-I) 0–5.0 mM



Stern-Volmer Plot (PC-II) 0–5.0 mM



‡See explanation on S44



Summarized Data

E_p **(ox) =** +1.1 V

E_p **(red) =** –1.8 V

k_q **(PC-I)** = (7.7 ± 0.1) x 10^8 $M^{-1} \cdot s^{-1}$ ‡

k_q **(PC-II)** = (1.22 ± 0.02) x 10^{10} $M^{-1} \cdot s^{-1}$ ‡

‡$(PhSe)_2$ displayed nonlinear luminescence quenching with positive curvature of both photocatalysts. One possible explanation for this data is that energy transfer between **PC*** and $(PhSe)_2$ is occurring by static and dynamic mechanisms, simultaneously.[20] However, an alternative explanation that acknowledges and incorporates the intrinsic absorption of $(PhSe)_2$ at the experimental irradiation wavelength (420 nm) may be relevant in this case.[21,22] Specifically, $(PhSe)_2$ reduces the amount of light that reaches the ground state photocatalyst in a concentration-dependent manner, thus reducing the quantity of **PC*** and amplifying the observed suppression of photocatalyst luminescence. This alternative luminescence reduction "mode" would contribute a unique relationship between luminescence reduction $\left[\left(\frac{I^\circ}{I}\right)^{absorption}\right]$ and the concentration of $(PhSe)_2$ ($[Q]$) with a proportionality constant C that is dependent on both the respective relationships between 1) $[Q]$ and light transmittance and 2) irradiation intensity and photocatalyst luminescence:

$$\left(\frac{I^\circ}{I}\right)^{abs.} = 1 + C[Q] \tag{4}$$

The algebraic multiplication of this relationship by the Stern-Volmer equation (eq. 1) would lead to a quadratic expression that encompasses the combined effects of $(PhSe)_2$ on photocatalyst luminescence:[20]

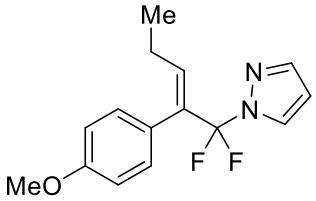
$$\frac{I^\circ}{I} = 1 + \left(C + k_q\tau\right)[Q] + \ C\ k_q\tau[Q]^2 \tag{5}$$

Absent specific values for C and k_q, this expression fits the positive curvature observed in the above luminescence quenching plots. Admittedly, then, the values for "k_q" that we determined from the linear-trimmed data using the Stern-Volmer relationship (a linear expression), cannot be taken as true k_q values and used for quantitative comparison with other quenchers. However, given the thermodynamic favorability of oxidation of $(PhSe)_2$ by either **PC-I*** or **PC-II***, it is likely that one of the observed luminescence quenching contributors is indeed an electron transfer.

5.b. Cyclopropane Ring Opening

In the speculative reaction mechanism, we propose carbon-centered radical intermediates **15** and **16** (Scheme S1). The existence of these intermediates is supported by the ring-opened styrene **11s** as the sole, detected azole-coupled product when vinyl cyclopropyl *gem*-difluoroalkene **10s** reacted with pyrazole under both **PC-I** and **PC-II** catalysis.

Experimental Procedure



(*E*)-1-(1,1-difluoro-2-(4-methoxyphenyl)pent-2-en-1-yl)-1*H*-pyrazole (**11s**)**:**

PC-I: Following general procedure C, *gem*-difluoroalkene **10s** (0.105 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-*C*]iridium(III) hexafluorophosphate (28.6 mg, 0.0250 mmol) in dry DCE (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to furnish a single diastereomer of desired product **11s** as a colorless oil (0.106 g, 76%). ^{1}H NMR (800 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.63 (d, *J* = 2.6 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.40 (t, *J* = 7.5 Hz, 1H), 6.27 (t, *J* = 2.2 Hz, 1H), 3.76 (d, *J* = 1.8 Hz, 3H), 2.02 (p, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (201 MHz, $CDCl_3$) δ 159.4, 141.9, 138.7 (t, *J* = 6.3 Hz), 132.4 (t, *J* = 26.4 Hz), 131.1, 128.4, 125.5, 118.0 (t, *J* = 252.7 Hz), 113.6, 106.8, 55.2, 22.2, 13.5. ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.24 (s, 2F). HRMS (ESI)$^{+}$ m/z: [M + H]$^{+}$ calc'd for $C_{15}H_{17}F_2N_2O^{+}$ 279.1303, found 279.1311. *E* stereochemical assignment is supported by 2D NMR data (see S189–194).

PC-II: Following general procedure D, *gem*-difluoroalkene **10s** (0.105 g, 0.500 mmol) was reacted with 1*H*-pyrazole (0.041 g, 0.60 mmol) in the presence of 1,2-diphenyldiselane (7.8 mg, 0.025 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (8.6 mg, 0.015 mmol) in dry PhMe (2.0 mL) using a 40 W 427 nm LED cooled by a fan for 14 h. The material was isolated according to the general procedure and purified by normal-phase flash chromatography using EtOAc and hexanes (0→5% EtOAc) to obtain a mixture of desired product **11s** and an unidentified impurity. The resulting mixture was further purified by preparative TLC (7% EtOAc in Hexanes) to furnish a single diastereomer of desired product **11s** as a colorless oil (0.105 g, 76%). The isolated ^{1}H and ^{19}F NMR spectra match the above data.

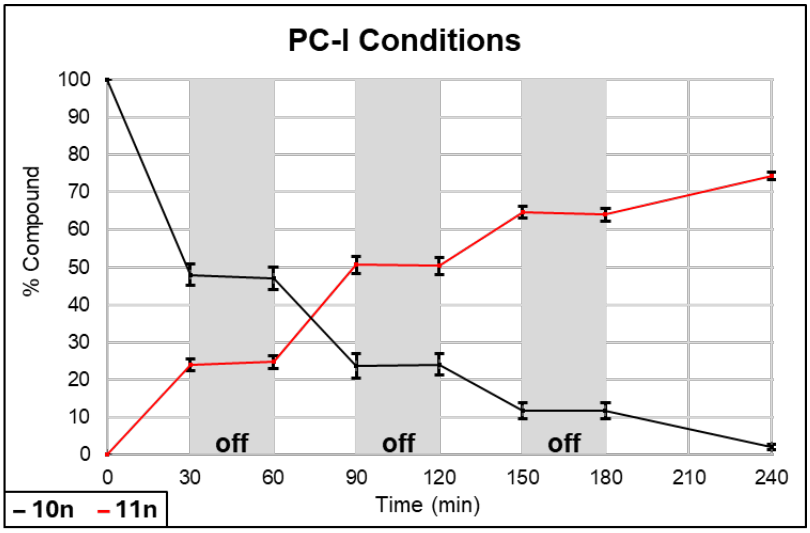
5.c. Light On/Off Experiments

In the speculative reaction mechanism (Scheme S1), we propose that, upon completion of a single photocatalytic cycle, radical intermediate **16** is converted to product **11**, and selenyl radical **17** does not engage in further on-cycle reactivity. Therefore, starting material consumption and product formation should not occur when the LED is turned off. Accordingly, light on/off experiments verified that no significant reaction progression occurred in dark periods when **PC-I** or **PC-II** were employed to couple pyrazole with *gem*-difluoroalkene **10n** by either general procedure C or D, respectively.

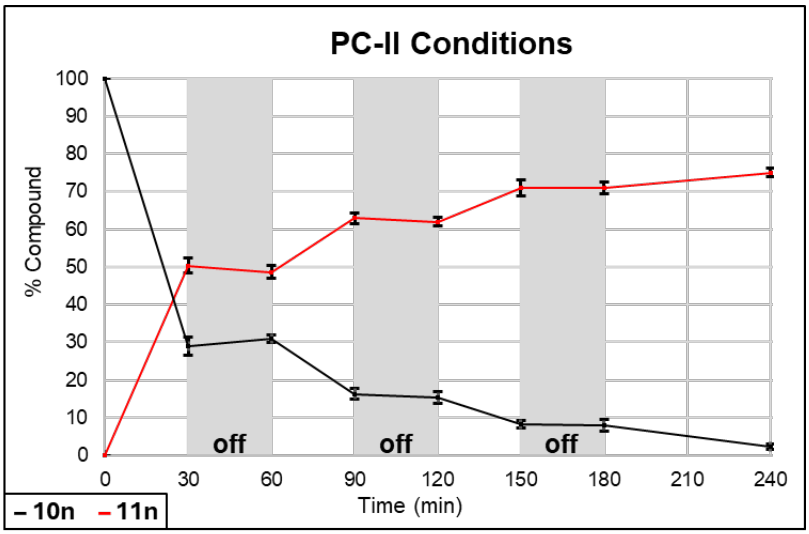
Experimental Procedure

PC-I: With slight modification to general procedure C, *gem*-difluoroalkene **10n** (0.54 g, 0.25 mmol) was reacted with 1*H*-pyrazole (0.020 g, 0.30 mmol) in the presence of 1,2-diphenyldiselane (3.9 mg, 0.013 mmol) and [5,5′-bis(trifluoromethyl)-2,2′-bipyridine-*N*1,*N*1′]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl-*N*]phenyl-

C]iridium(III) hexafluorophosphate (14.3 mg, 0.0130 mmol) in dry DCE (1.0 mL) under an argon balloon. (Trifluoromethyl)benzene (31 µL, 0.024 mmol) was added to the initial reaction mixture to serve as an internal standard for ^{19}F NMR analysis. The reaction was exposed to either 40 W 427 nm LED irradiation or covered from outside light in an alternating pattern for a total of 4 h. Specifically, the light was kept on for 30 min, then off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, and finally on for 60 min. A 5 µL aliquot was withdrawn *via* syringe and analyzed by ^{19}F NMR at the end of each of the aforementioned time periods. The data in the graph below was generated from ^{19}F NMR analysis of triplicate experiments, with error bars representing standard deviation.



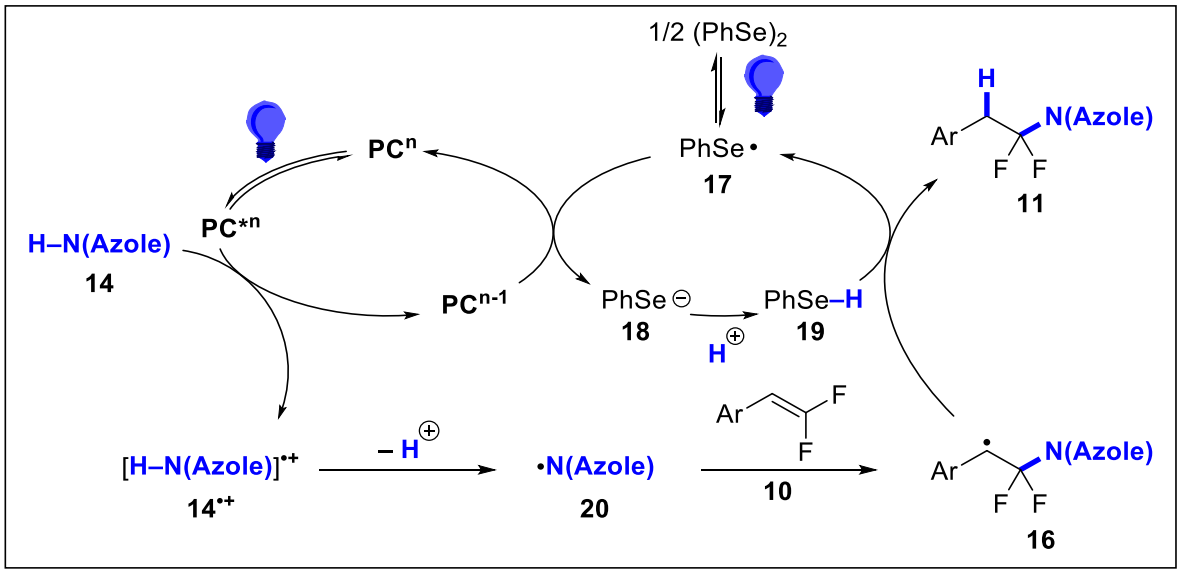
PC-II: With slight modification to general procedure D, *gem*-difluoroalkene **10n** (0.54 g, 0.25 mmol) was reacted with 1*H*-pyrazole (0.020 g, 0.30 mmol) in the presence of 1,2-diphenyldiselane (3.9 mg, 0.013 mmol) and 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (4.3 mg, 0.0080 mmol) in dry PhMe (1.0 mL) under an argon balloon. (Trifluoromethyl)benzene (31 µL, 0.024 mmol) was added to the initial reaction mixture to serve as an internal standard for ^{19}F NMR analysis. The reaction was exposed to either 40 W 427 nm LED irradiation or covered from outside light in an alternating pattern for a total of 4 h. Specifically, the light was kept on for 30 min, then off for 30 min, on for 30 min, off for 30 min, on for 30 min, off for 30 min, and finally on for 60 min. A 5 µL aliquot was withdrawn *via* syringe and analyzed by ^{19}F NMR at the end of each of the aforementioned time periods. The data in the graph below was generated from ^{19}F NMR analysis of triplicate experiments, with error bars representing standard deviation.



5.d. Alternative Hypotheses

5.d.i. Azole Radical Addition

Scheme S2. A possible mechanism initiated by the generation of azole radicals.

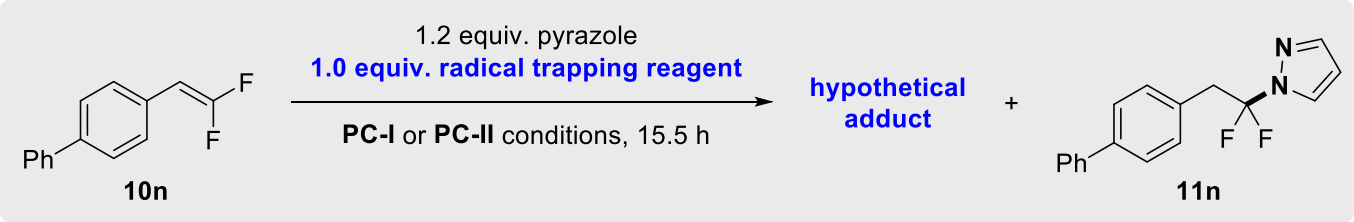


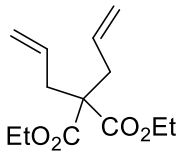
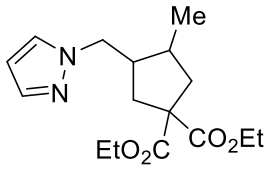
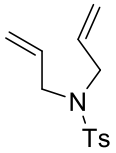
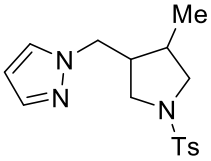
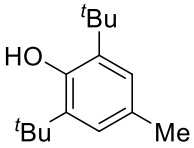
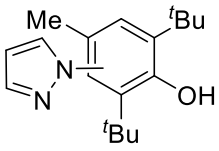
An alternative mechanism that could explain both the formation of intermediate **16** and a lack of reaction progression in the dark might involve attack of an azole-based radical (**20**) into the neutral gem-difluoroalkene (**10**, Scheme S2). Further, this hypothesis is supported by photophysical data that suggests oxidation of azoles (**14**→**14**$^{\bullet+}$) is possible in this system: pyrazole, indazole, and benzimidazole quench the luminescence of **PC-II** (but not **PC-I**) at a rate comparable to both *gem*-difluorostyrenes and $(PhSe)_2$ (see S33–44), and the measured oxidation potentials of these azoles (benzimidazole: $E_{p,ox}$ = +1.1 V; indazole: $E_{p,ox}$ = +1.2 V; pyrazole: $E_{p,ox}$ = +1.6 V) are comparable the excited state reduction potentials of **PC-I** and **PC-II** (see S39–42).

To test this hypothesis, a series of radical trapping agents were employed (Table S7). A pyrazole cyclization adduct was detected when diethyl 2,2-diallylmalonate (entry 4) and *N*,*N*-diallyl-4-methylbenzenesulfonamide (entry 6) were reacted in the presence of **PC-II**. However, conversion in the *gem*-difluoroalkene hydroazolation reaction was not inhibited (compare to entry 2). Additionally, these pyrazole cyclization adducts were not observed for reactions under **PC-I** catalysis (entries 3 and 5), and likewise, conversion was unaffected (compare to entry 1). Taken together, these results suggest that while **PC-II** catalysis does generate some azole radicals, they are unlikely to possess a significant mechanistic role in the desired *gem*-difluoroalkene hydroazolation process.

However, 2,6-di-*tert*-butyl-4-methylphenol (BHT) slightly inhibited conversion (compare entries 1–2 with 7–8), and a BHT-pyrazole adduct was detected by LCMS (ESI^+) and $APCI^+$ mass spectrometry. Notably, BHT has been previously reported as a pyrazole radical trapping reagent.[23–25] However, this adduct was also detected in the absence of light or photocatalyst (entries 9–10), which suggests that the mechanism responsible for the formation of the BHT-pyrazole adduct is not relevant to the *gem*-difluoroalkene hydroazolation reaction. Consumption of pyrazole by this off-cycle reaction with BHT may explain the conversion inhibition observed in entries 7–8.

Table S7. Pyrazole radical trapping experiments.

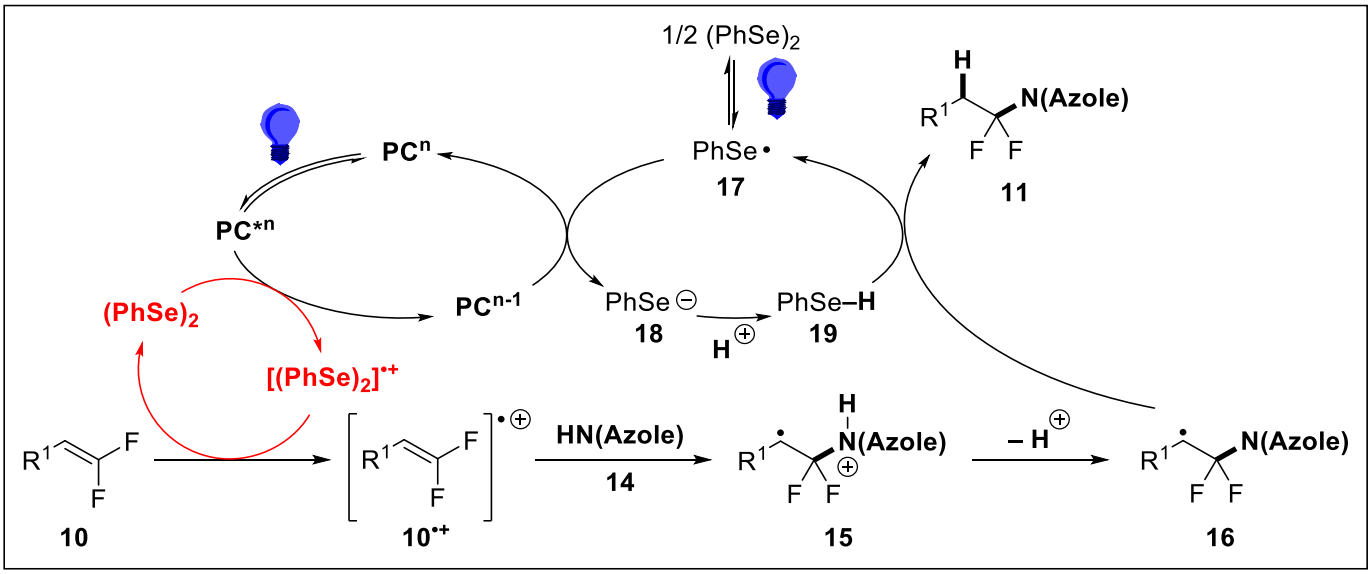


entry	radical trapping reagent	hypothetical adduct	photocat.	% Conversion 10n	% Yield 11n
1[a]	none	N.A.	PC-I	>99	93
2[b]	none	N.A.	PC-II	>99	83
3[c]			PC-I	>99	91
4[c]	"	not detected by LCMS (ESI$^+$) or APCI$^+$ above adduct detected by LCMS (ESI$^+$) and APCI$^+$	PC-II	>99	82
5[d]			PC-I or PC-II	>99	88
6[d]	"	not detected by LCMS (ESI$^+$) or APCI$^+$ above adduct detected by LCMS (ESI$^+$) and APCI$^+$	PC-II	>99	79
7[e]			PC-I	81	70
8[e]	"	detected by LCMS (ESI$^+$) and APCI$^+$ above adduct detected by LCMS (ESI$^+$) and APCI$^+$	PC-II	96	85
9[f]	"	above adduct detected by LCMS (ESI$^+$) and APCI$^+$	PC-I	N.A.	N.A.
10[g]	"	above adduct detected by LCMS (ESI$^+$) and APCI$^+$	none	N.A.	N.A.

[a]*gem*-Difluorostyrene **10n** (50 µmol), pyrazole (1.2 equiv.), 1,2-diphenyldiselane (5 mol%), {Ir[dF(CF$_3$)ppy]$_2$-(5,5'-dCF$_3$bpy)}PF$_6$ (**PC-I**, 5 mol%), in DCE (0.2 mL) irradiated with a 40 W 427 nm LED under an atmosphere of N$_2$ at 30 °C for 15.5 h. [b]*gem*-Difluorostyrene **10n** (50 µmol), pyrazole (1.2 equiv.), 1,2-diphenyldiselane (5 mol%), 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (**PC-II**, 3 mol%), in PhMe (0.2 mL) irradiated with a 40 W 427 nm LED under an atmosphere of N$_2$ at 30 °C for 15.5 h. [c]Conditions (a) or (b) plus diethyl 2,2-diallylmalonate (1.0 equiv.). [d]Conditions ([a]) or ([b]) plus *N*,*N*-diallyl-4-methylbenzenesulfonamide (1.0 equiv.). [e]Conditions ([a]) or ([b]) plus 2,6-di-*tert*-butyl-4-methylphenol (1.0 equiv.). [f]Conditions ([a]), but in the dark instead of under LED irradiation. [g]Conditions ([a]), but without **PC-I**.

5.d.ii. $(PhSe)_2$ Redox Mediation

Scheme S3. A possible mechanism involving *gem*-difluoroalkene oxidation mediation by $(PhSe)_2$.



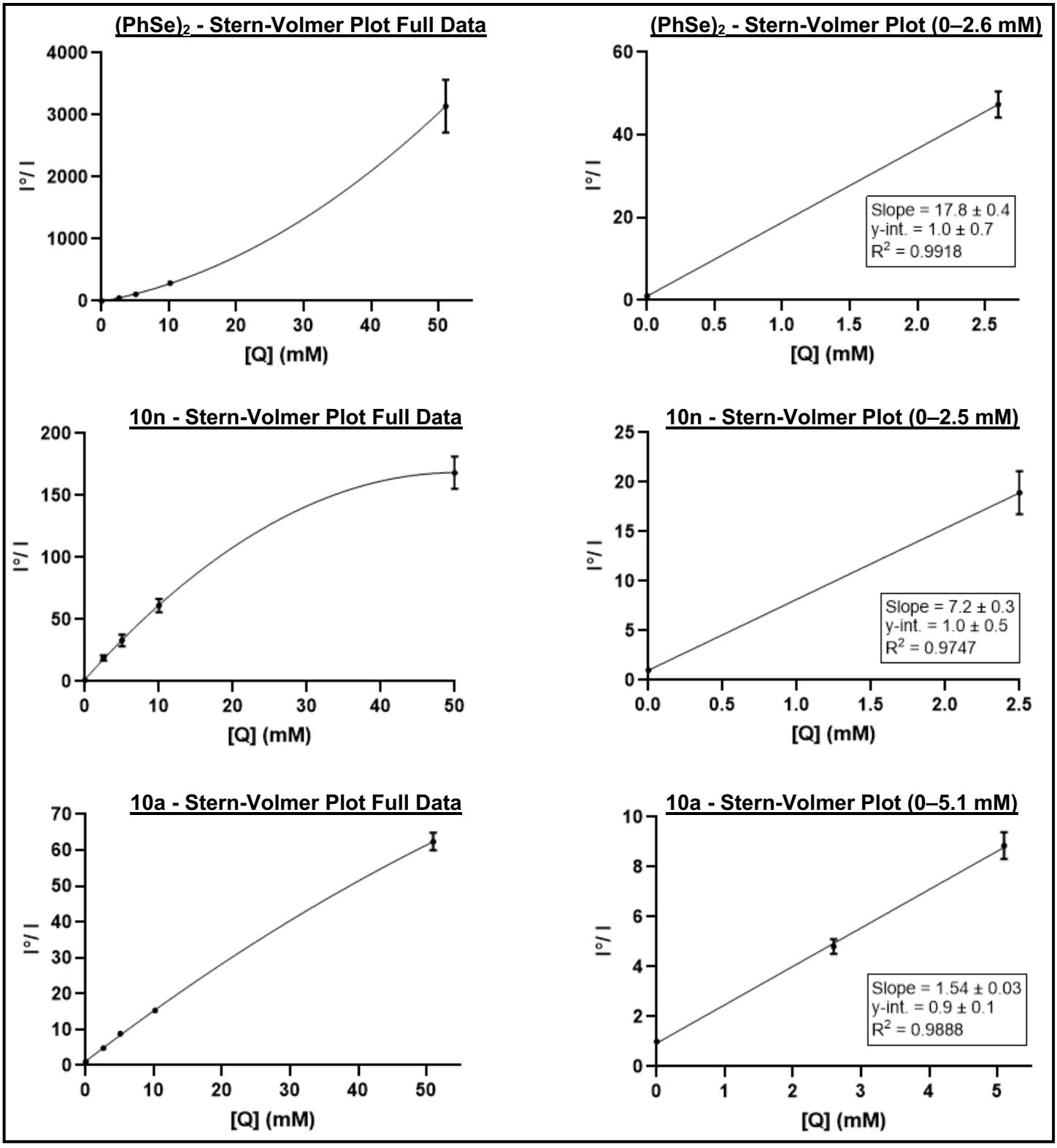
From the main text: "…in contrast to this general correlation between luminescence of photocatalyst quenching and *gem*-difluorostyrene conversion, *gem*-difluorostyrenes **10n** (E_p = +1.3 V) and **10o** only quench the luminescence of **PC-II** despite reacting successfully under both **PC-I** and **PC-II** catalysis (entries 5 and 6). In these reactions, only $(PhSe)_2$ quenched **PC-I** luminescence…" An alternate mechanism consistent with this data might involve redox mediation by $(PhSe)_2$ (Scheme S3). Specifically, oxidation of $(PhSe)_2$ by **PC-I*** might form $[(PhSe)_2]^{\bullet+}$, which could then oxidize *gem*-difluoroalkene **10** to generate **10**$^{\bullet+}$. If true, alternate photocatalysts that are capable of oxidizing $(PhSe)_2$, but not *gem*-difluorostyrenes **10n** and **10o**, should be able to facilitate product formation when used in place of **PC-I**.

To test this hypothesis, an alternate photocatalyst, {Ir[dF(CF_3)ppy]$_2$-(dtbbpy)}PF_6 (**PC-III**; $E_{1/2}$(**PC-III***^{III}/**PC-III**^{II}) = +0.83 V; $E_{1/2}$(**PC-III***^{III}/**PC-III**^{IV}) = –1.27 V)[26] was chosen due to its potential to oxidize $(PhSe)_2$ selectively over *gem*-difluorostyrene **10n**. Specifically, while $(PhSe)_2$ and **10n** both quench the luminescence of **PC-III*** (Chart S2), an analysis of relevant redox potentials reveals that the mechanisms of energy transfer to both quenchers are likely to be an oxidation of or triplet energy transfer to $(PhSe)_2$ ($E_{p,ox}$ = +1.1 V; $E_{p,red}$ = –1.8 V) and a reduction of or triplet energy transfer to **10n** ($E_{p,ox}$ = +1.3 V; $E_{p,red}$ = –1.18 V),[27] respectively. Additional support for the ability of **PC-III** to oxidize $(PhSe)_2$ to form $[(PhSe)_2]^{\bullet+}$ comes from the efficacy of **PC-III** in a previously reported reaction[28] that is presumedly facilitated by a photocatalyst-generated $[(PhSe)_2]^{\bullet+}$ intermediate (entry 1, Table S8).

Experimentally, a control reaction with *gem*-difluorostyrene **10n** in the presence of **PC-III** confirmed that **PC-III** was not capable of reacting **10n** with pyrazole in the absence of $(PhSe)_2$ (entry 2, Table S9). However, the introduction of $(PhSe)_2$ did not rescue conversion in the reaction of **10n** (entry 3), which suggests that *gem*-difluoroalkene oxidation mediation by $(PhSe)_2$ was not feasible in this reaction.

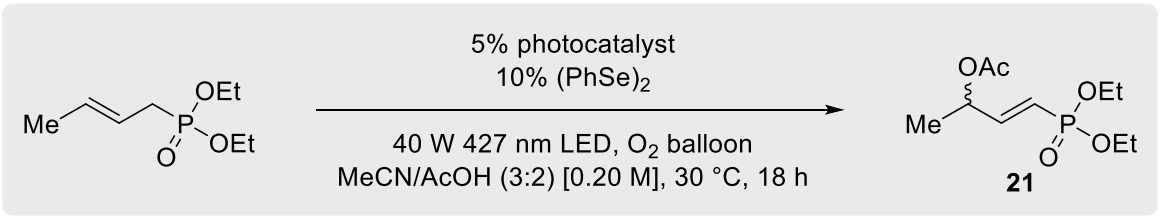
Importantly, control reactions with *gem*-difluorostyrene **10a** ($E_{p,ox}$ = +1.0 V) confirmed that **PC-III** was a competent photocatalyst in this system when reacting a *gem*-difluorostyrene capable of donating an electron to **PC-III*** (Chart S2), as **10a** successfully reacted with pyrazole in either the absence or presence of $(PhSe)_2$ (entries 4 and 5, Table S9).

Chart S2. PC-III luminescence quenching data.



Experiments were performed according the luminescence quenching experimental procedure (S29–30), but an excitation wavelength of 400 nm and emission detection wavelength of 470 nm were used.[26]

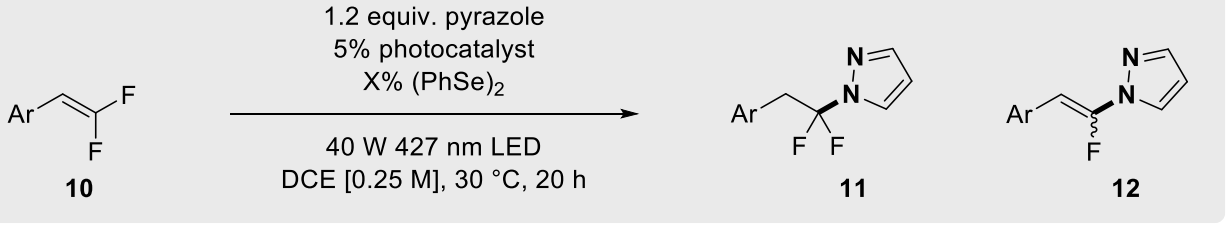
Table S8. The ability of **PC-III**, **I**, and **II** to generate $[(PhSe)_2)]^{\bullet+}$ in a previously reported reaction.[28]



entry	photocatalyst	% yield **21**
1	**PC-III**	64
2	**PC-I**	52
3	**PC-II**	76

One-dram vials with magnetic stir bars were charged with diethyl (*E*)-but-2-en-1-ylphosphonate (19.2 mg, 100 µmol), 1,2-diphenyldiselane (3.1 mg, 10 µmol), and either {Ir[dF(CF_3)ppy]$_2$-(dtbbpy)}PF_6 (**PC-III**, 5.6, 5.0 µmol), {Ir[dF(CF_3)ppy]$_2$-(5,5'-dCF_3bpy)}PF_6 (**PC-I**, 5.7 mg, 5.0 µmol), or 9-mesityl-3,6-di-*tert*-butyl-10-phenylacridinium tetrafluoroborate (**PC-II**, 2.9 mg, 5.0 µmol). MeCN/AcOH (3:2, 0.50 mL) was added to the vials, and they were then sealed with PTFE-lined septa and placed under an O_2 balloon. The reactions were then irradiated by a 40 W 427 nm LED lamp cooled by a fan (30 °C) for 18 h. Upon completion, solvent was removed from the vials *in vacuo*. The resulting residues were resuspended in $CDCl_3$ (2 mL), and an internal standard of 2-(trimethylsilyl)ethan-1-ol (20.0 µL, 140 µmol) was mixed into each vial. Aliquots of the reaction mixtures were subsequently transferred to NMR tubes and analyzed by ^{1}H NMR. Spectra were baseline corrected, phased, and integrated using MestReNova. Yields in the table represent crude yields as determined by comparative integration of the internal standard 2-(trimethylsilyl)ethan-1-ol methyl peak and the product **21** methine proton peak. Product **21** mass was independently confirmed by LCMS (ESI^+) analysis. ^{1}H NMR (500 MHz, $CDCl_3$): **21** δ 6.70 (ddd, *J* = 22.5, 17.2, 4.4 Hz), 5.81 (ddd, *J* = 19.1, 17.2, 1.7 Hz), 5.47–5.41 (m), 4.12–4.03 (m), 2.08 (s), 1.36–1.30 (m); 2-(trimethylsilyl)ethan-1-ol δ 3.75–3.71 (m), 0.98–0.93 (m), 0.01 (s); [ns = 32; D1 = 2 s].

Table S9. Exploration of $(PhSe)_2$ redox mediation under the hydroazolation conditions.

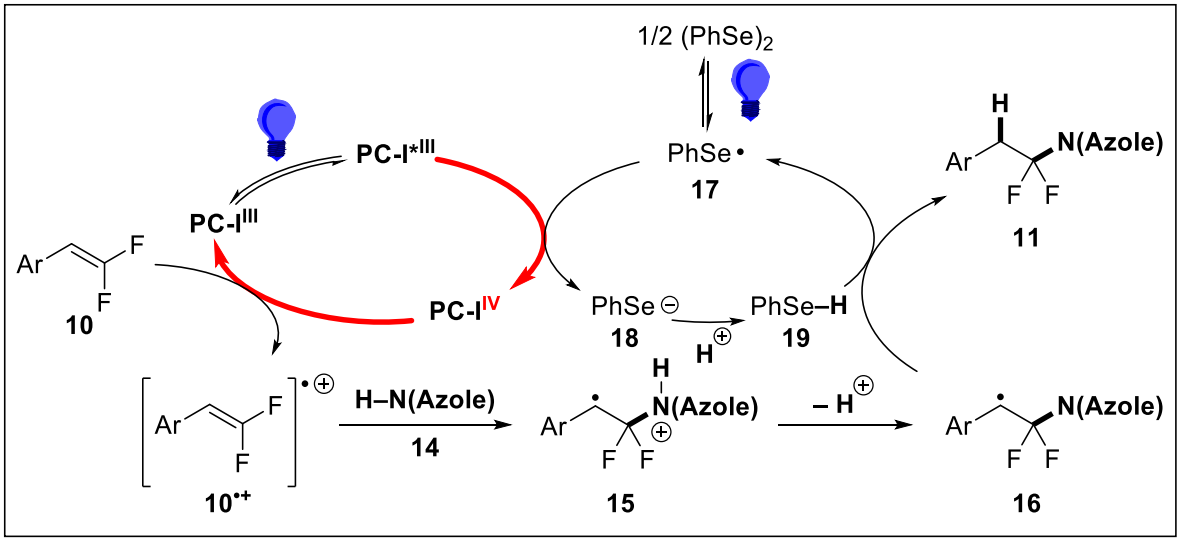


entry	difluorostyrene	photocatalyst	% $(PhSe)_2$	% conv. **10**	% yield **11**	% yield **12**
1	**10n**	**PC-I**	5	>99	93	0
2	**10n**	**PC-III**	5	0	0	0
3	**10n**	**PC-III**	0	1	0	0
4	**10a**	**PC-III**	5	>99	71	10
5	**10a**	**PC-III**	0	38	<1	30

Reaction conditions: *gem*-difluorostyrene **10n** or **10a** (50 µmol), pyrazole (1.2 equiv.), 1,2-diphenyldiselane (5 or 0 mol%), and either {Ir[dF(CF_3)ppy]$_2$-(5,5'-dCF_3bpy)}PF_6 (**PC-I**, 5 mol%) or {Ir[dF(CF_3)ppy]$_2$-(dtbbpy)}PF_6 (**PC-III**, 5 mol%) in DCE (0.2 mL) irradiated with a 40 W 427 nm LED under an atmosphere of N_2 at 30 °C for 20 h. Yield and conversion were determined by ^{19}F NMR using $PhCF_3$ as an internal standard.

5.d.iii. PC-I Oxidative Quenching Cycle

Scheme S4. Alternate oxidative quenching cycle for PC-I.



From the main text: "…for certain substrates, a plausible alternate mechanistic hypothesis for **PC-I** might involve an oxidative quenching cycle (Scheme S4) as opposed to a reductive quenching cycle (Scheme 2). Specifically, **PC-I*** [$E_{1/2}$(**PC-I*^{III}**/**PC-I^{IV}**) = –0.81 V][29] might first reduce selenyl radical **17**, thus generating strong oxidant **PC-I^{IV}** [E_p(**PC-I^{III}**/**PC-I^{IV}**) = +1.56 V][29] which oxidizes *gem*-difluorostyrenes **10n** and **10o**."

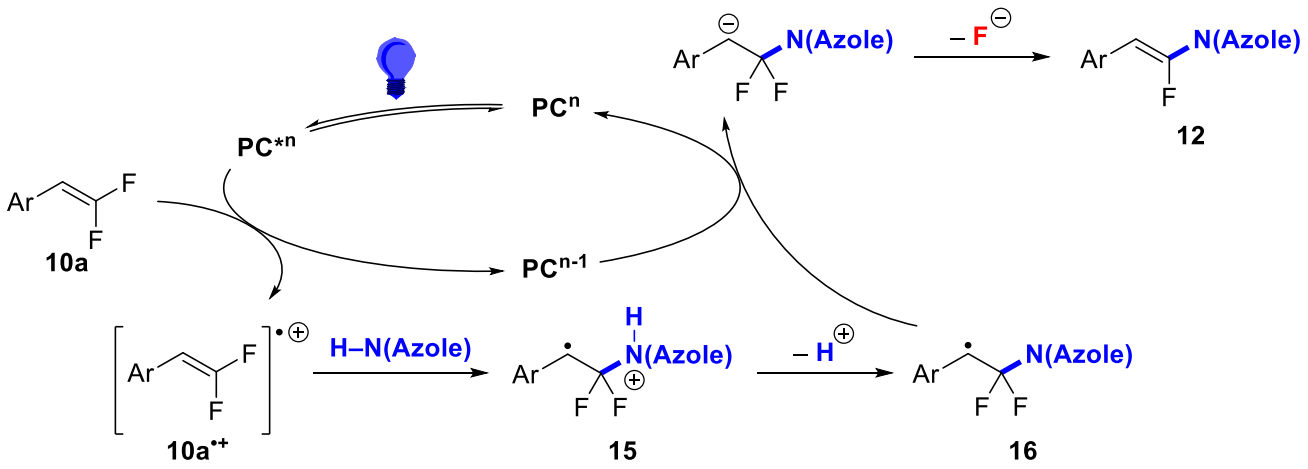
To clarify further, this hypothesis could explain the absence of observed luminescence quenching of **PC-I*** by *gem*-difluorostyrenes **10n** (E_p = +1.3 V) and **10o** (S36–37), which, despite this apparent lack of energy transfer, react successfully in **PC-I**-catalyzed reactions. **PC-I*^{III}** [$E_{1/2}$(**PC-I*^{III}**/**PC-I^{II}**) = +1.30 V][3] might not be a strong enough oxidant to react with these styrenes. However, if **PC-I** proceeds through an oxidative quenching cycle in these reactions, it will generate strong oxidant **PC-I^{IV}** [E_p(**PC-I^{III}**/**PC-I^{IV}**) = +1.56 V][29] which may be able to oxidize **10**→**10$^{•+}$**, and that energy transfer would not be detectable by our luminescence quenching experiments.

Notably, **PC-I^{IV}** is likely still not a strong enough oxidant to oxidize electron-deficient *gem*-difluorostyrenes **10r** (E_p = +1.5 V) and **10t** (E_p = +1.8 V), which is supported by the failure of **PC-I** to react these substrates.

5.e. Proposed Mechanisms for Side Product Formation

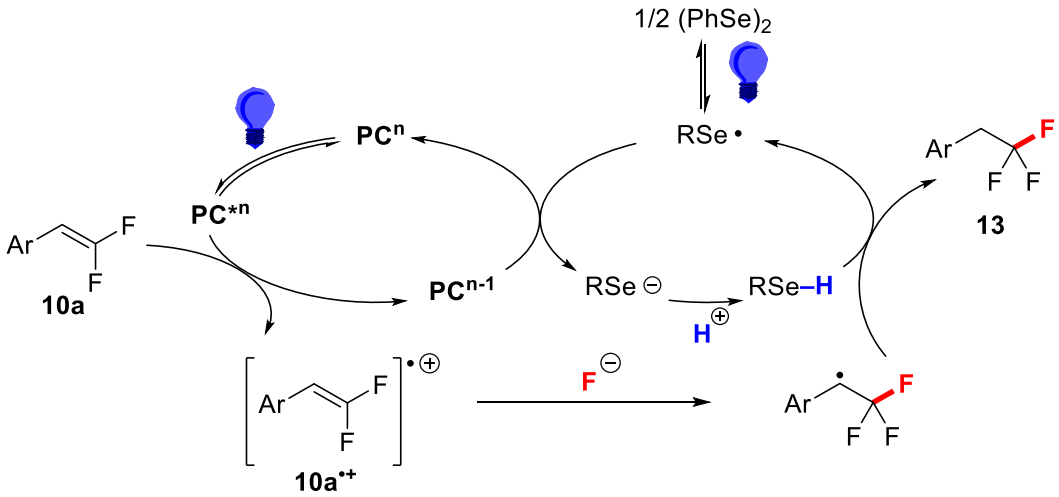
Scheme S5. Possible mechanisms of side product formation

A. ***Proposed Mechanism for Defluorinative Azolation***

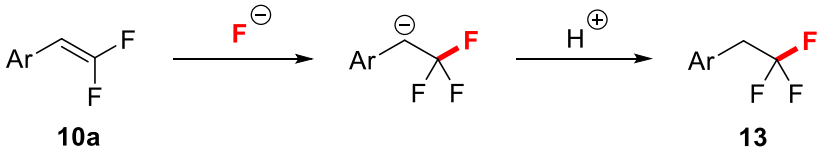


Ar = C_6H_2(3,4,5-OMe) Azole = benzimidazole

B. ***Photocatalyst-Mediated Mechanism for gem-Difluorostyrene Hydrofluorination***



C. ***Non-Photocatalyst-Mediated Mechanism for gem-Difluorostyrene Hydrofluorination***



A mechanism (Scheme S5A) that might account for the undesired formation of monofluorovinyl azole side product **12** (entries 4–14, Table 1) involves oxidation of *gem*-difluorostyrene **10a** to radical cation **10a**$^{\bullet+}$ by the excited state photocatalyst, nucleophilic attack by benzimidazole to generate acidic radical cation **15**, and deprotonation to afford carbon-based radical **16**. In the absence of a hydrogen atom donor to quench radical **16** or an exogenous oxidant, **16** subsequently oxidizes the reduced state photocatalyst to regenerate ground state photocatalyst and release an unstable anionic intermediate. This anionic intermediate then liberates a fluoride anion to generate undesired monofluorovinyl azole **12**.

Further, this defluorinative pathway might explain the formation benzyl trifluoromethyl side product **13** in reactions that contain diselenide co-catalyst yet still form monofluorovinyl azole **12** (entries 13 and 14, Table 4). Specifically, the aforementioned fluoride anion can attack radical cation **10a**$^{\bullet+}$ to generate a carbon-based radical,[14,30] which forms **13** after hydrogen atom transfer with a selenol intermediate (Scheme S5B). Alternatively, direct hydrofluorination of neutral *gem*-difluorostyrene **10a** might explain the trace quantities of **13** in these reactions (Scheme S5C).[31,32]

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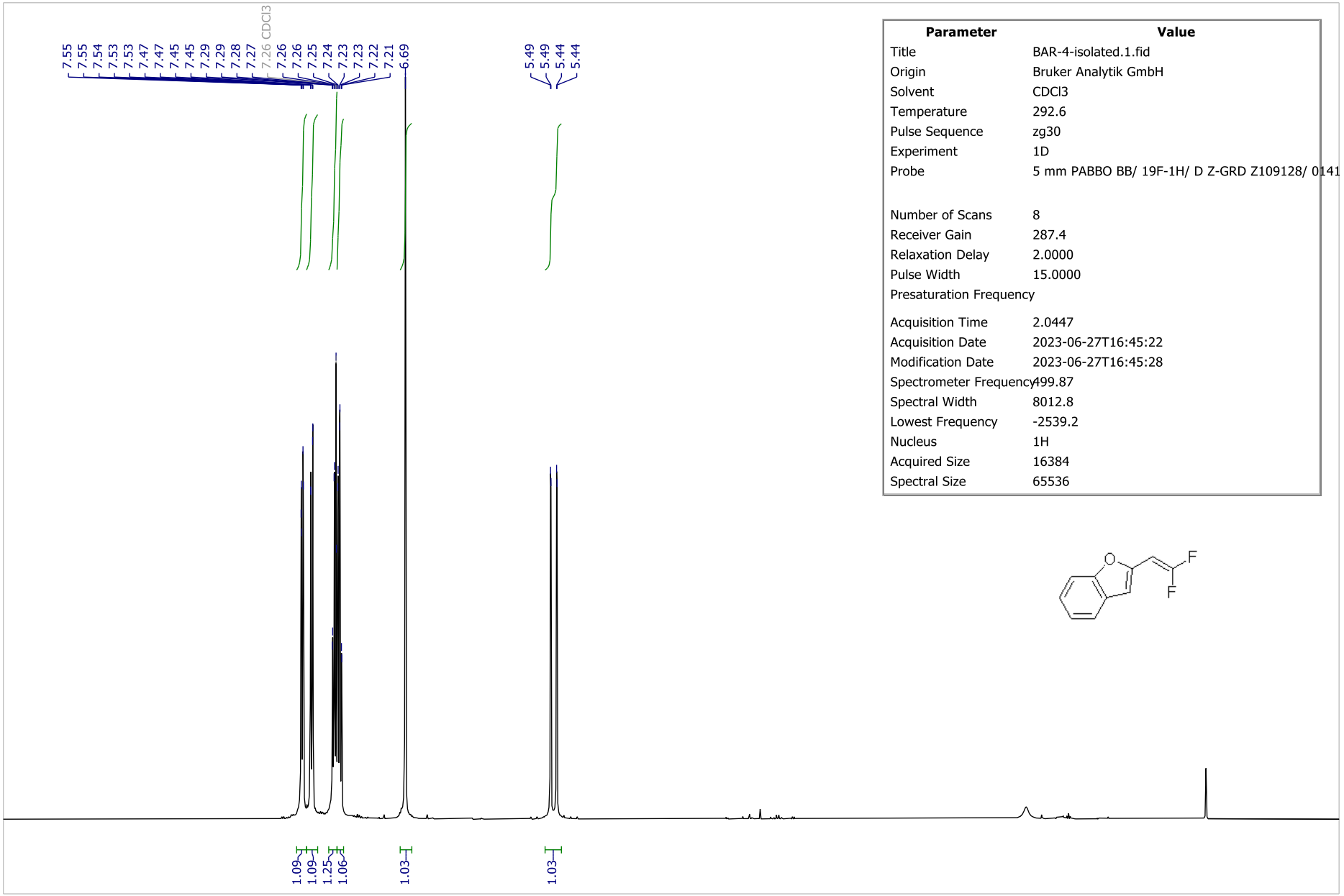
NMR spectra for 2-(2,2-difluorovinyl)benzofuran (**10d**)



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Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	287.4
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-06-27T16:45:22
Modification Date	2023-06-27T16:45:28
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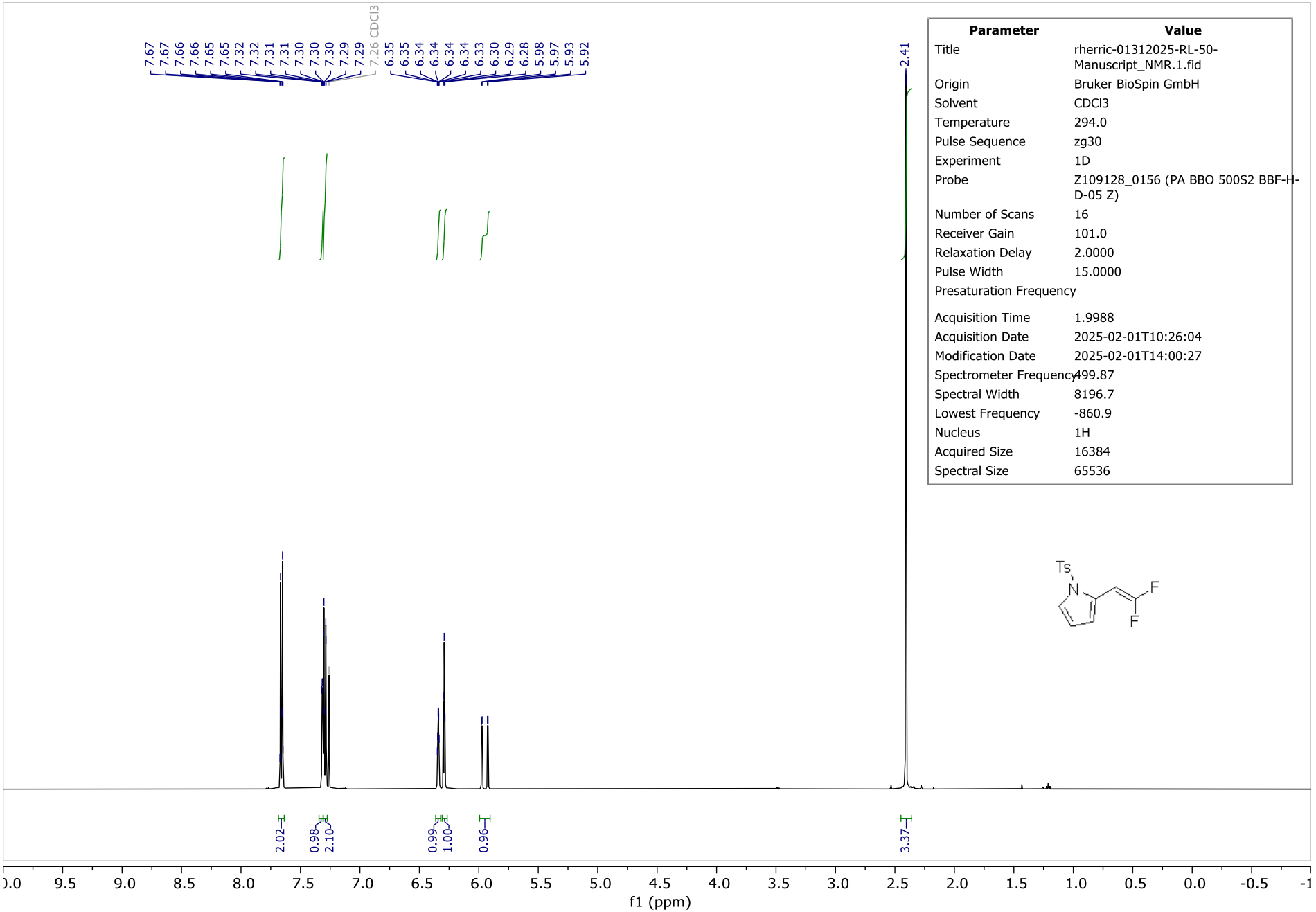
Lowest Frequency	-2539.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

NMR spectra for 2-(2,2-difluorovinyl)-1-tosyl-1*H*-pyrrole (**10f**)



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Experiment	1D
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Receiver Gain	101.0
Relaxation Delay	0.1500
Pulse Width	10.0000
Presaturation Frequency	
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Lowest Frequency	-1245.2
Nucleus	13C
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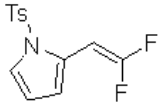
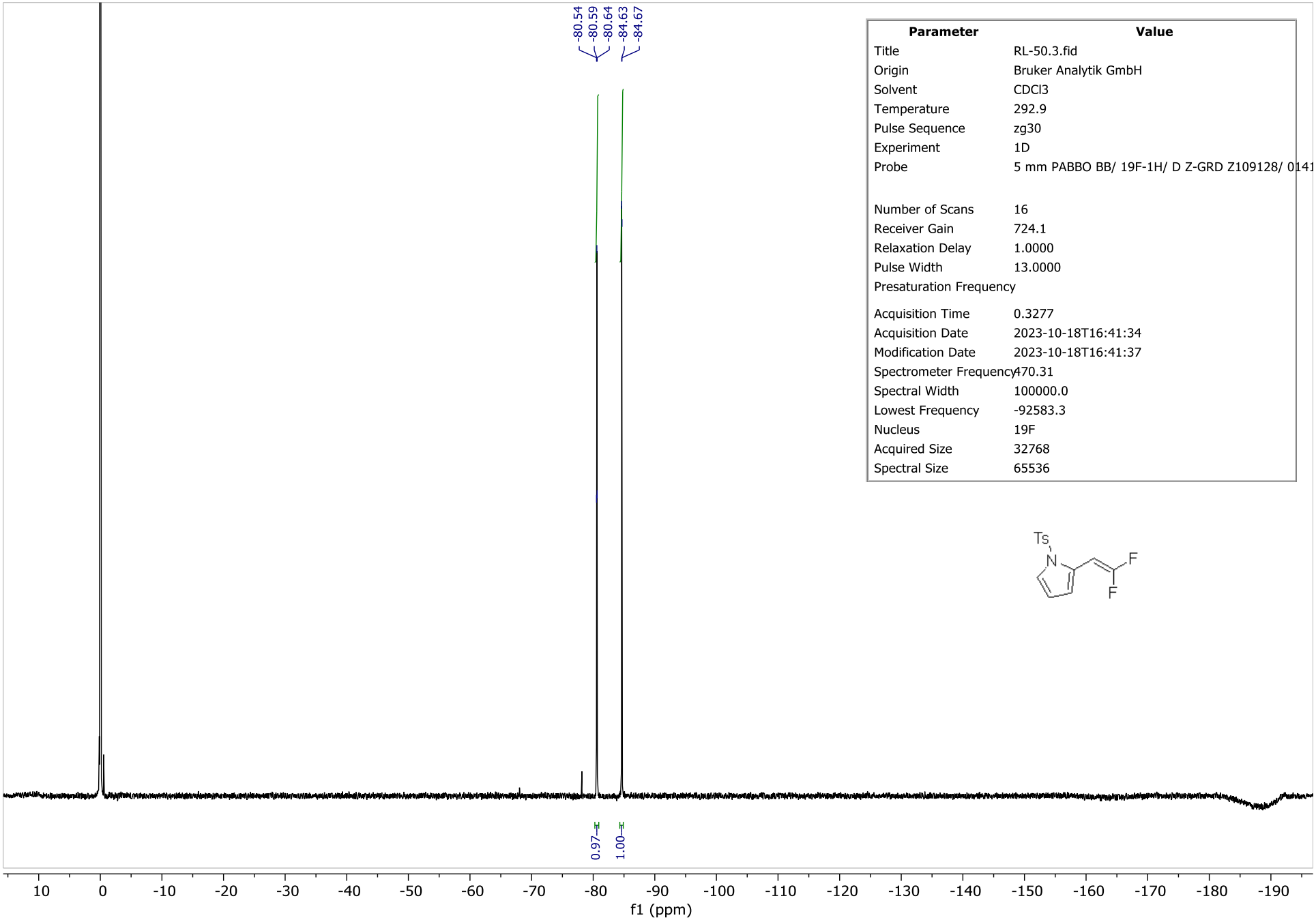
Spectral Size	65536





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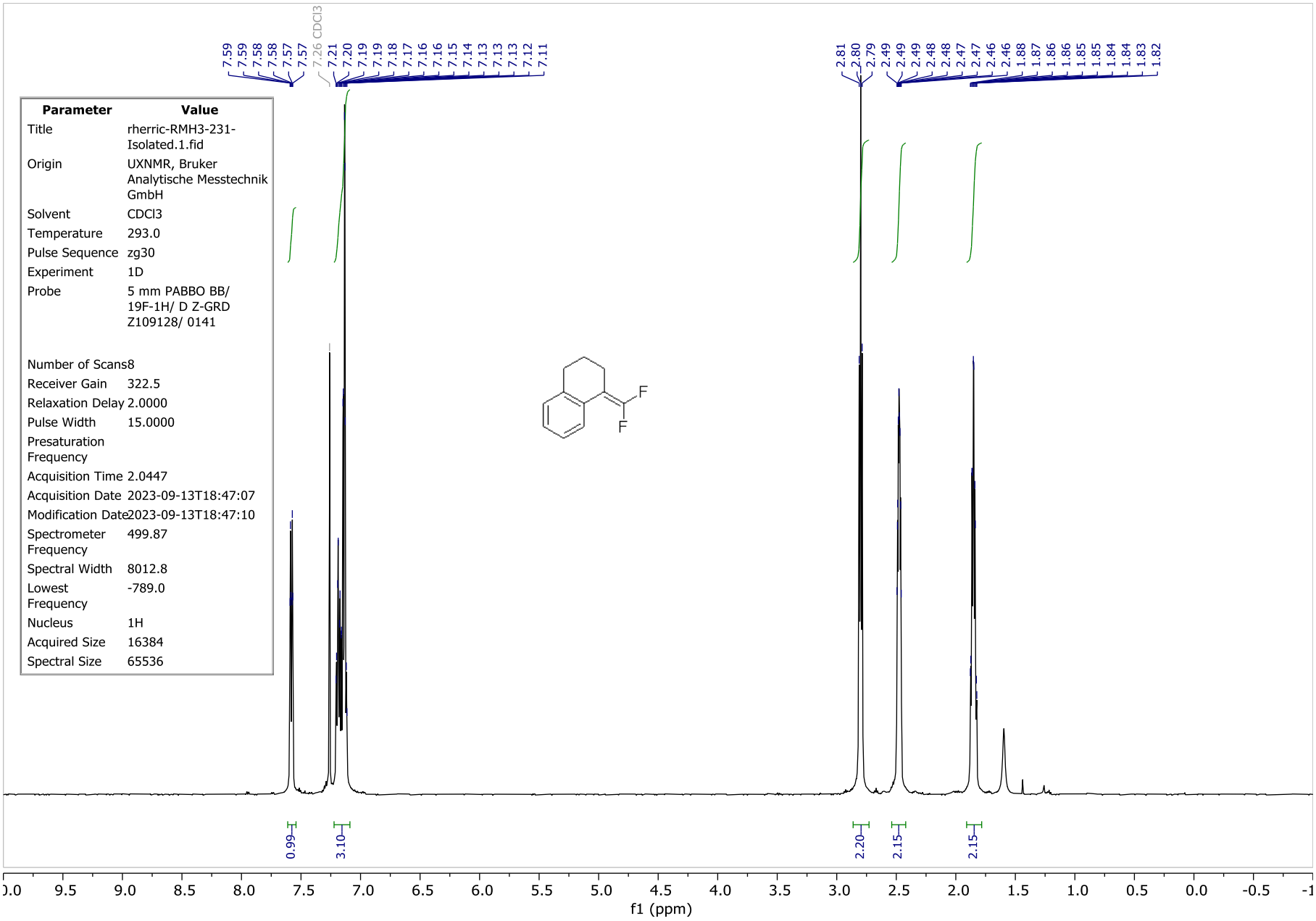
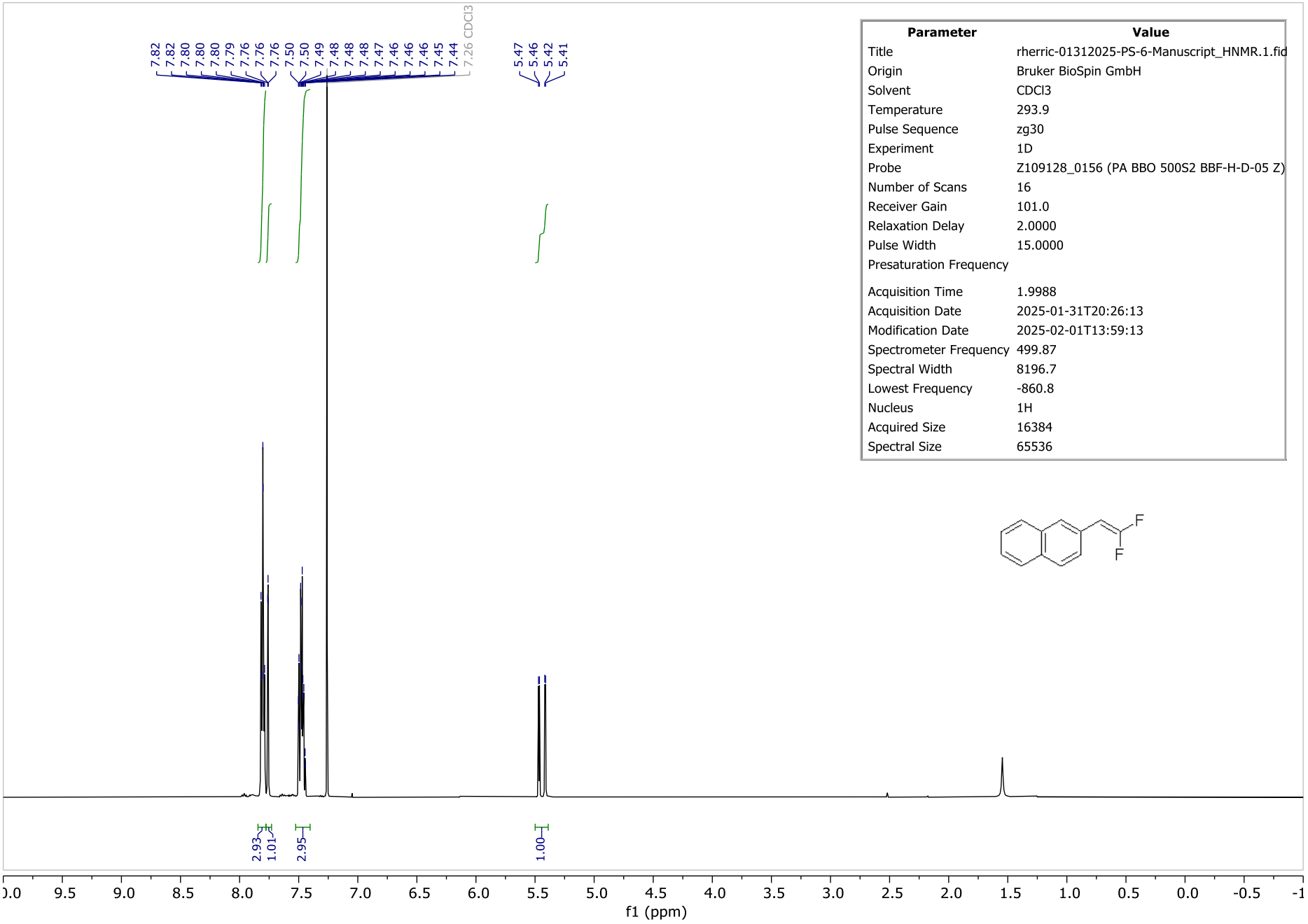
Number of Scans	16
Receiver Gain	724.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-10-18T16:41:34
Modification Date	2023-10-18T16:41:37
Spectrometer Frequency	470.31
Spectral Width	100000.0
Lowest Frequency	-92583.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(difluoromethylene)-1,2,3,4-tetrahydronaphthalene (**10h**)

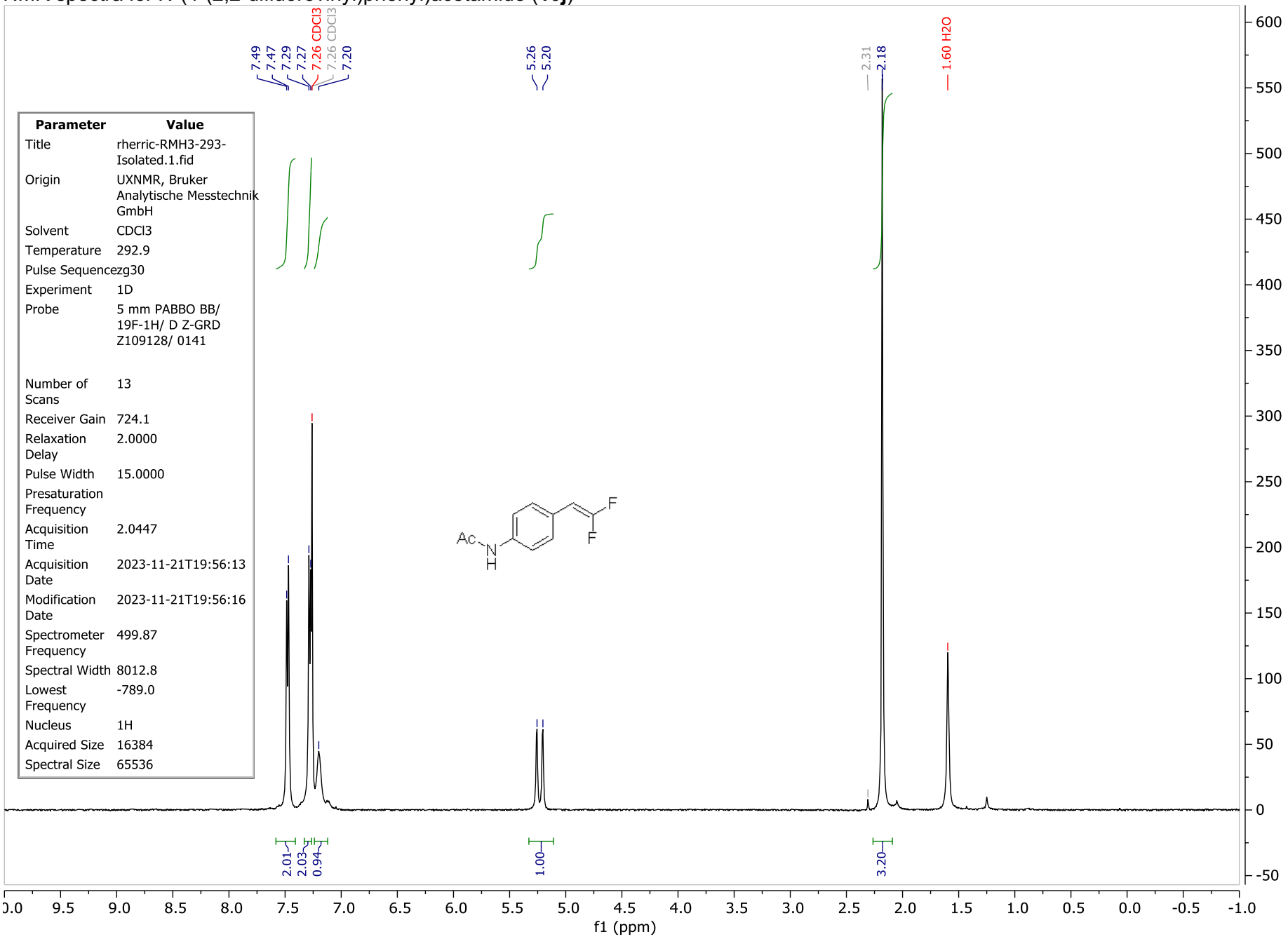


NMR spectra for 2-(2,2-difluorovinyl)naphthalene (**10i**)



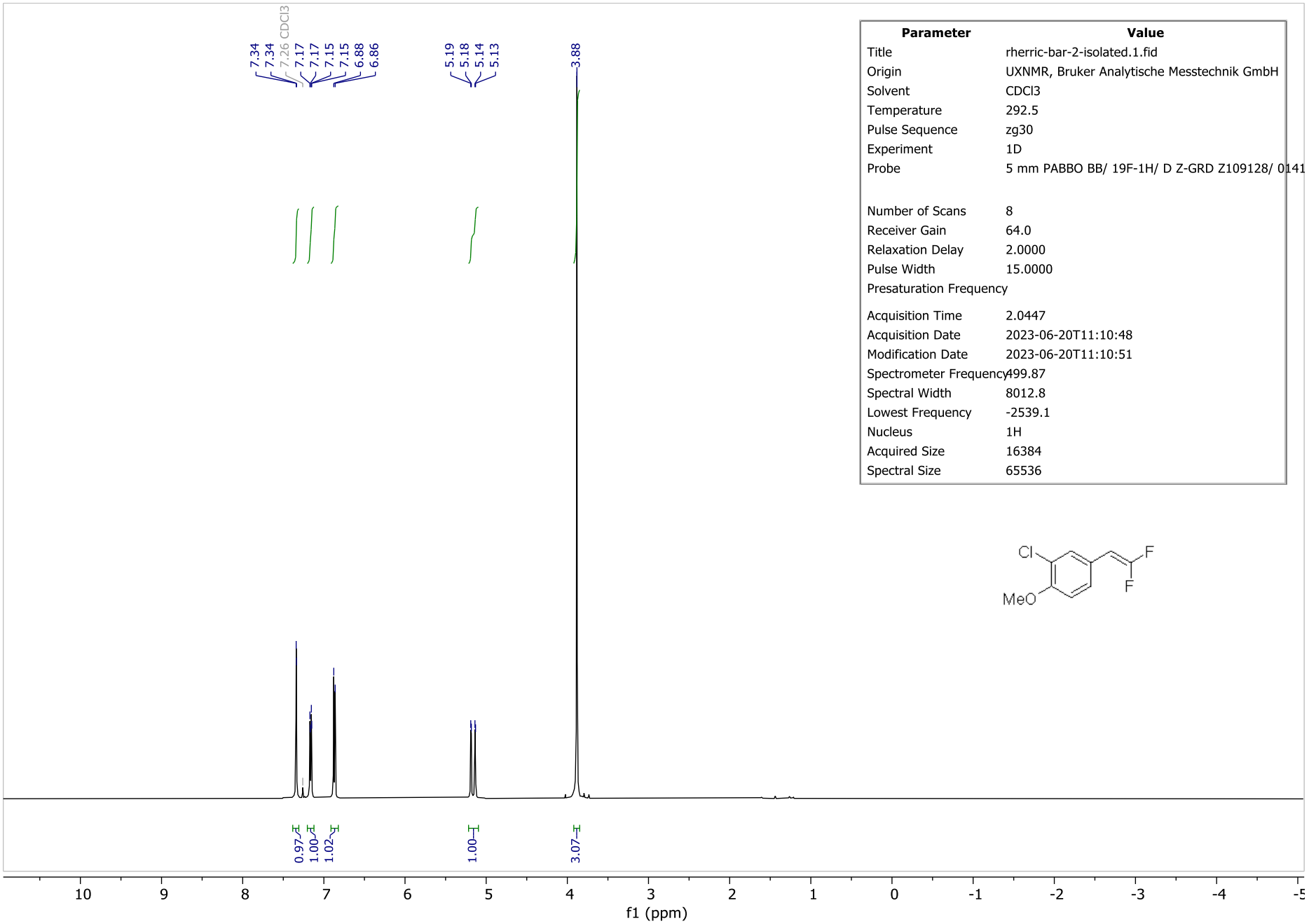
Parameter	Value
Title	rherric-01312025-PS-6-Manuscript_HNMR.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	1.9988
Acquisition Date	2025-01-31T20:26:13
Modification Date	2025-02-01T13:59:13
Spectrometer Frequency	499.87
Spectral Width	8196.7
Lowest Frequency	-860.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

NMR spectra for *N*-(4-(2,2-difluorovinyl)phenyl)acetamide (**10j**)



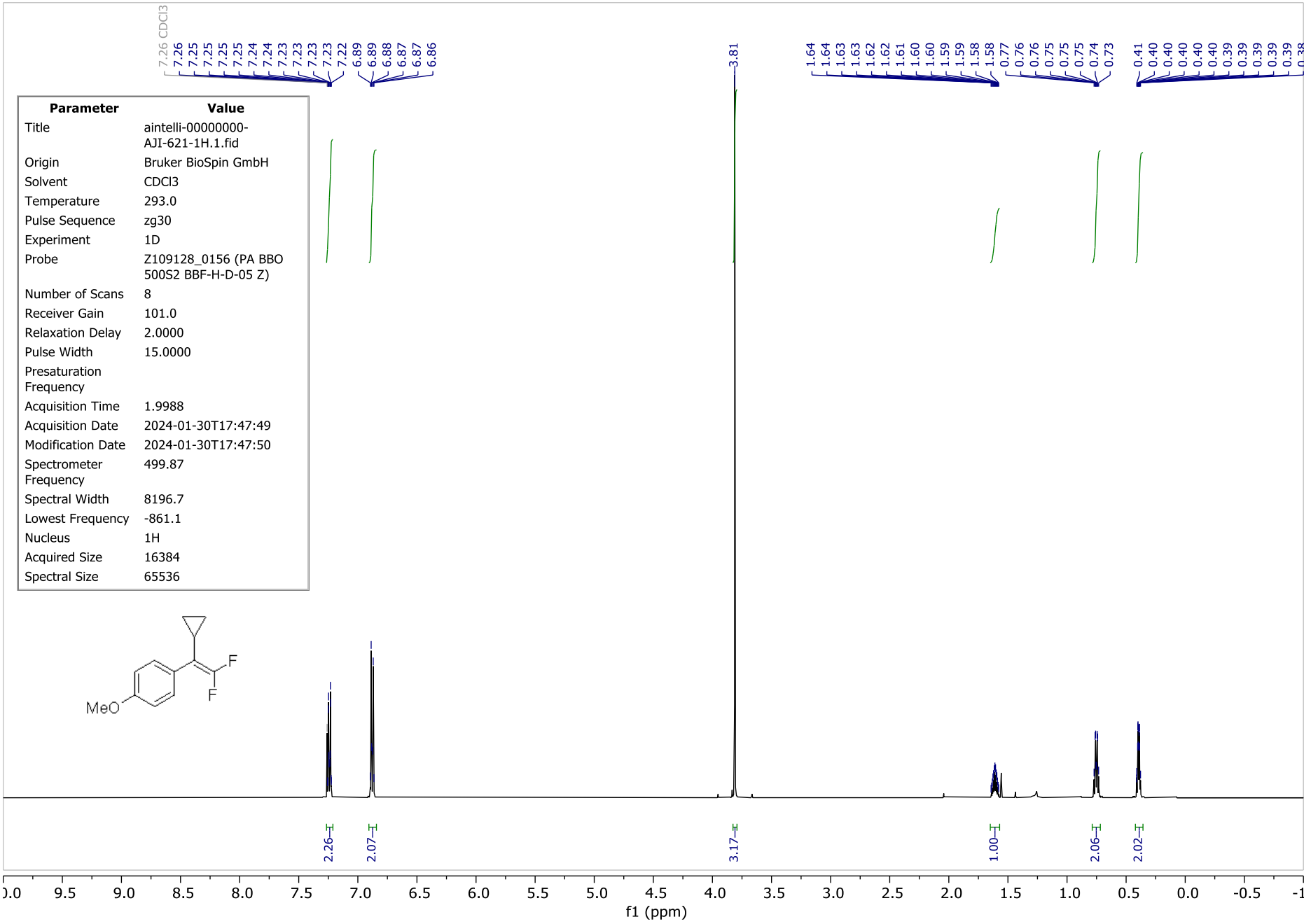
Parameter	Value
Title	rherric-RMH3-293-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	13
Receiver Gain	724.1
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-11-21T19:56:13
Modification Date	2023-11-21T19:56:16
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

NMR spectra for 2-chloro-4-(2,2-difluorovinyl)-1-methoxybenzene (**10p**)

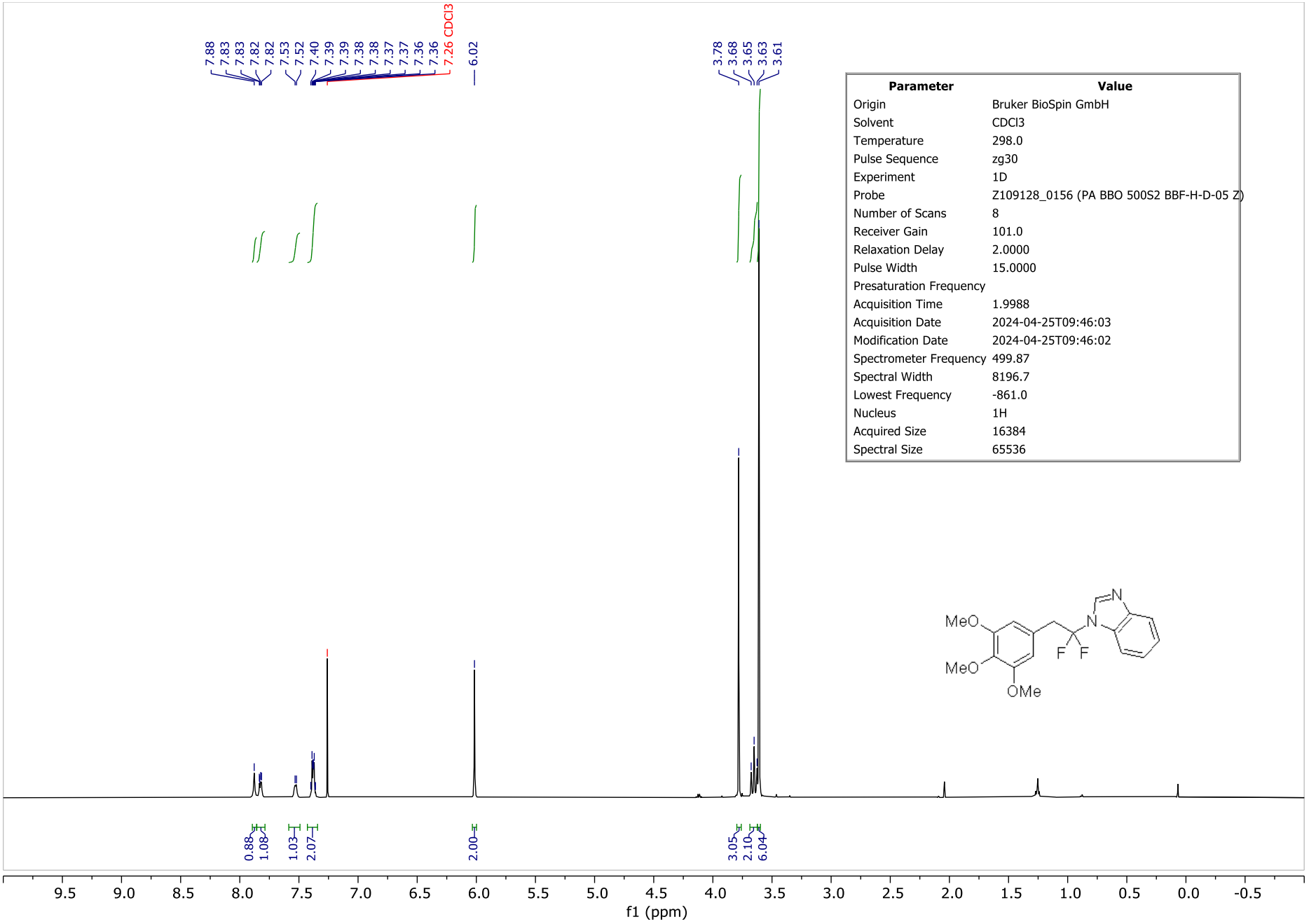


Parameter	Value
Title	rherric-bar-2-isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	64.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-06-20T11:10:48
Modification Date	2023-06-20T11:10:51
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2539.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

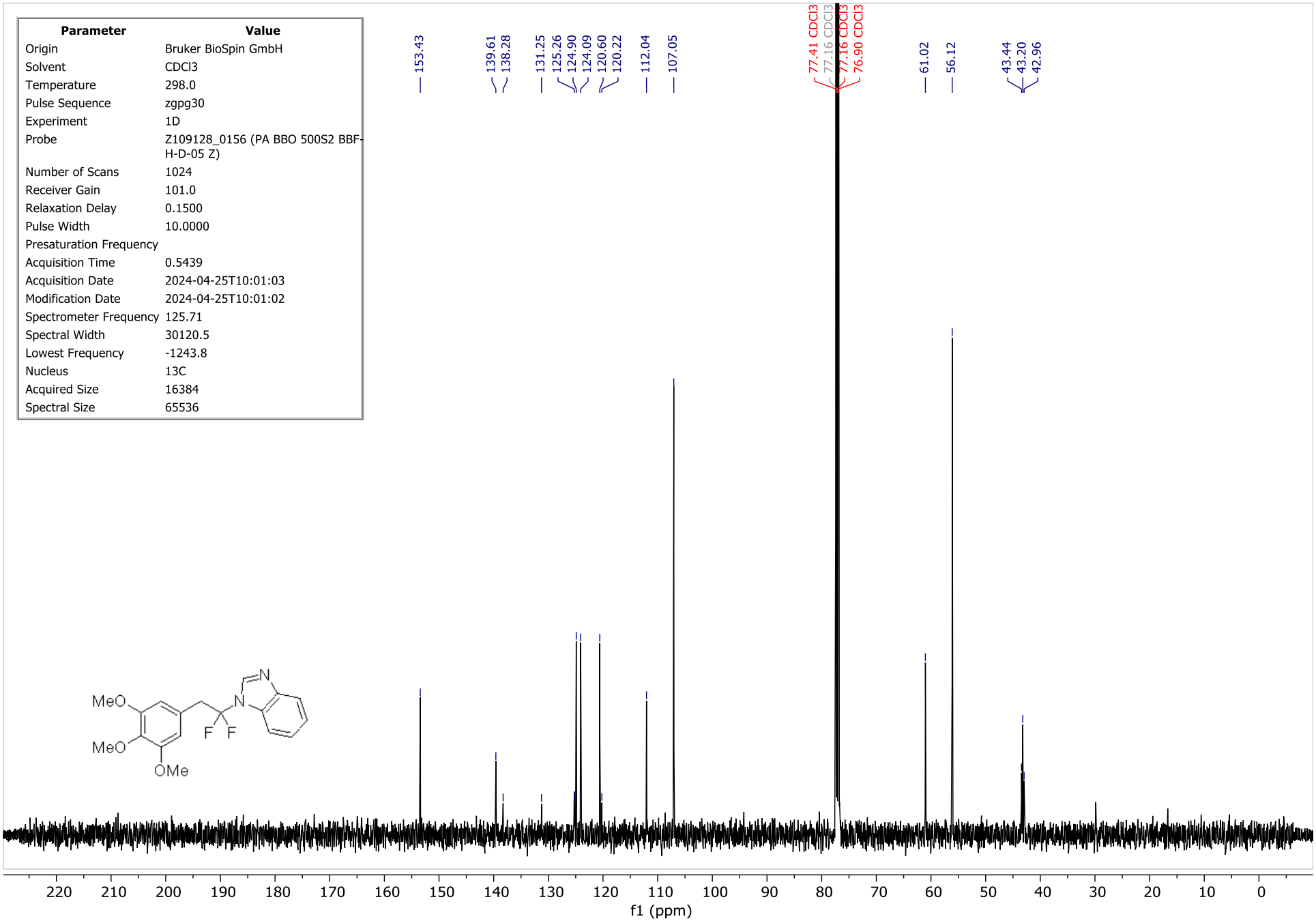
NMR spectra for 1-(1-cyclopropyl-2,2-difluorovinyl)-4-methoxybenzene (**10s**)

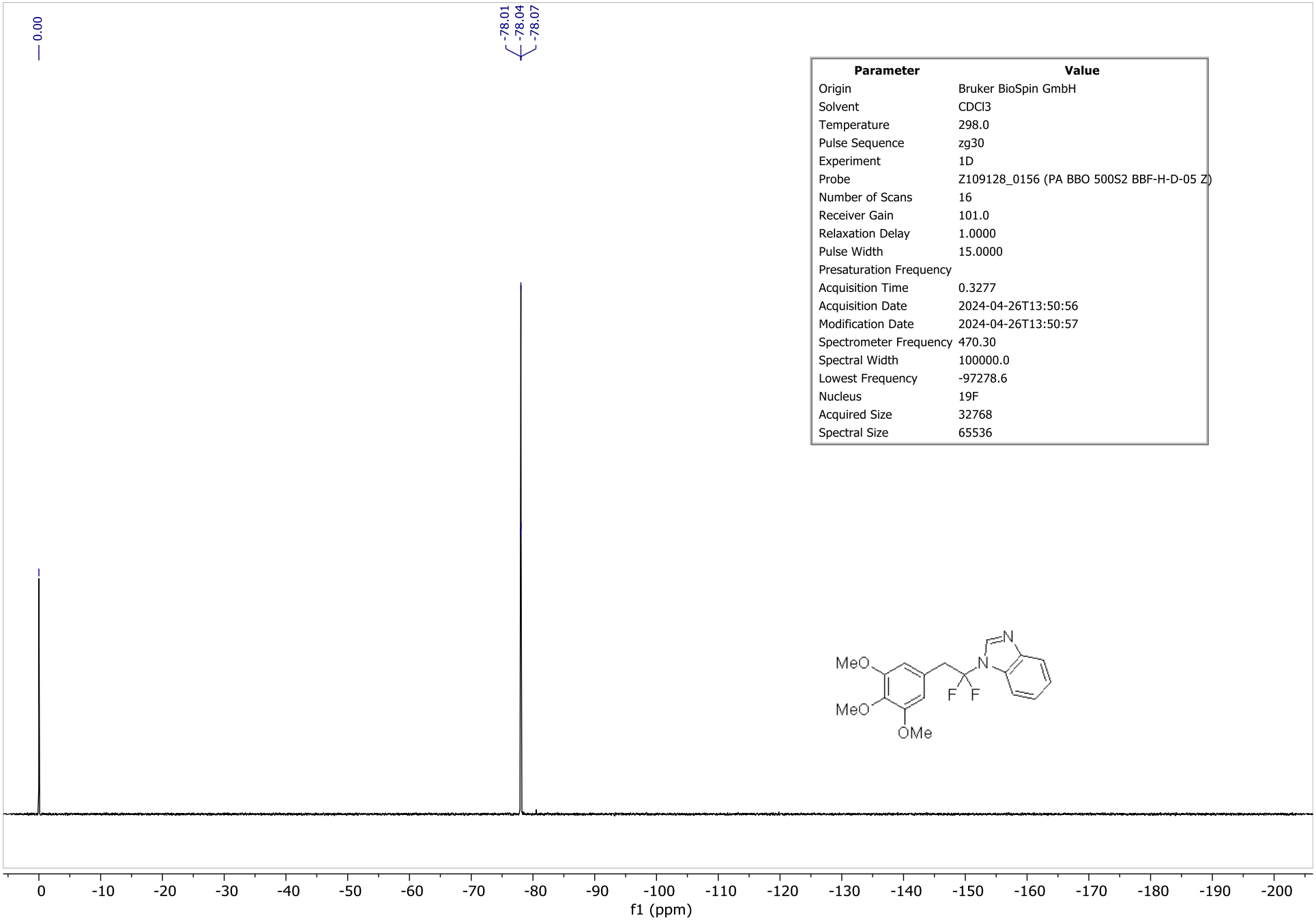


NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*]imidazole (**11aa**)

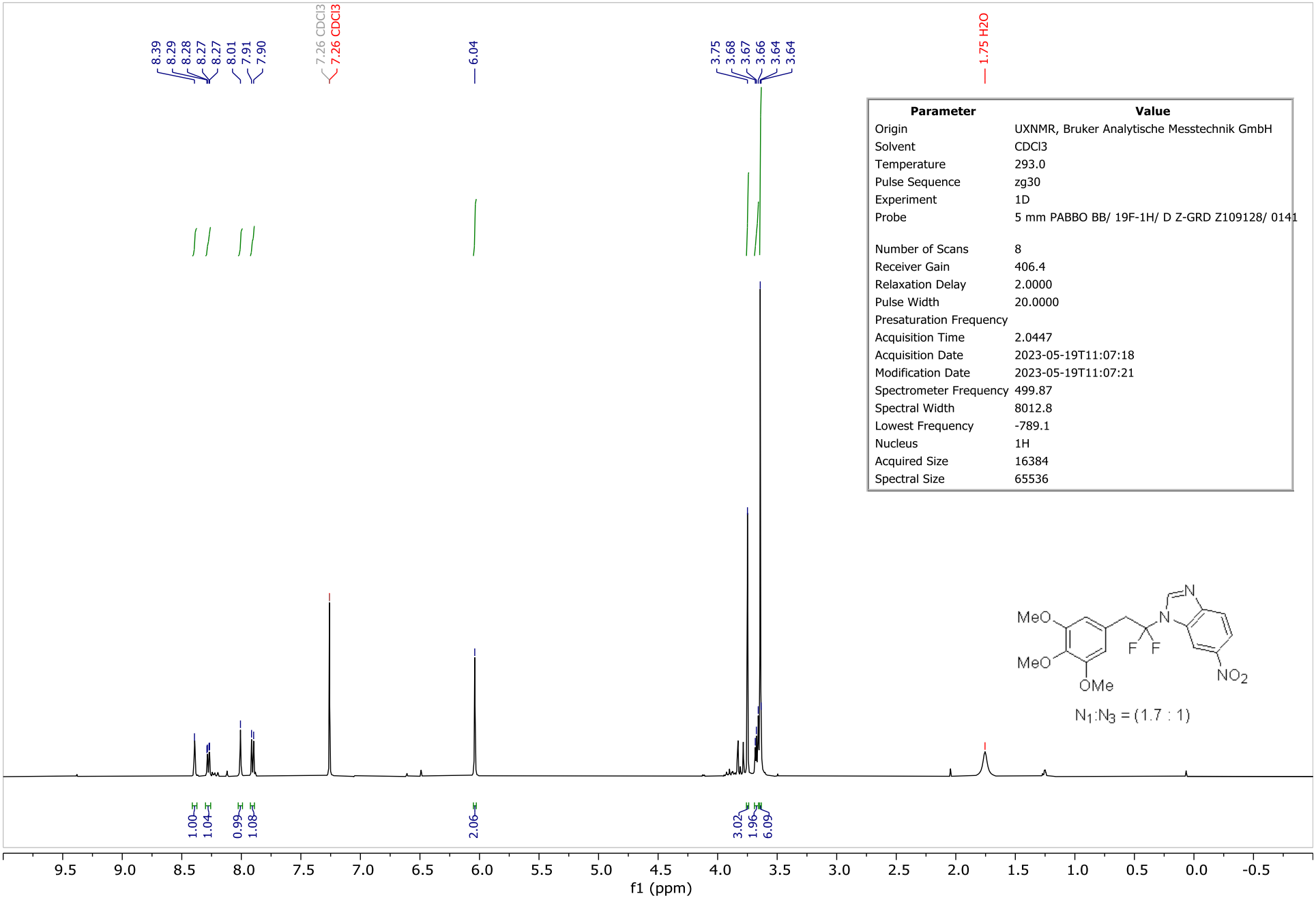


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	1024
Receiver Gain	101.0
Relaxation Delay	0.1500
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	0.5439
Acquisition Date	2024-04-25T10:01:03
Modification Date	2024-04-25T10:01:02
Spectrometer Frequency	125.71
Spectral Width	30120.5
Lowest Frequency	-1243.8
Nucleus	13C
Acquired Size	16384
Spectral Size	65536




0.00
-78.01
-78.04
-78.07
Parameter Value
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2024-04-26T13:50:56
Modification Date 2024-04-26T13:50:57
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97278.6
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
MeO
MeO
OMe
N
N
F
F
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

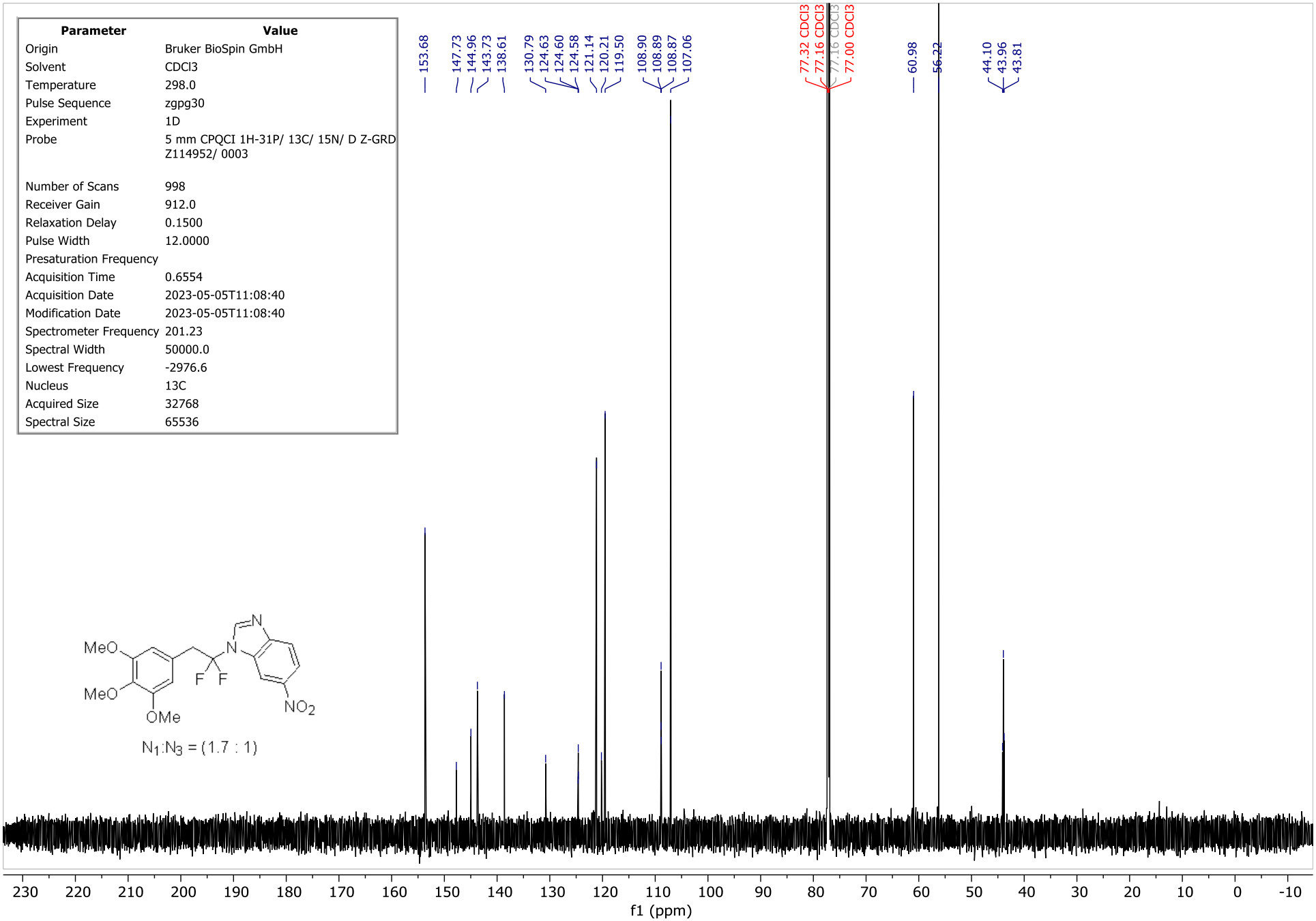
NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-6- and -5-nitro-1*H*-benzo[*d*]imidazole (**11ab**)

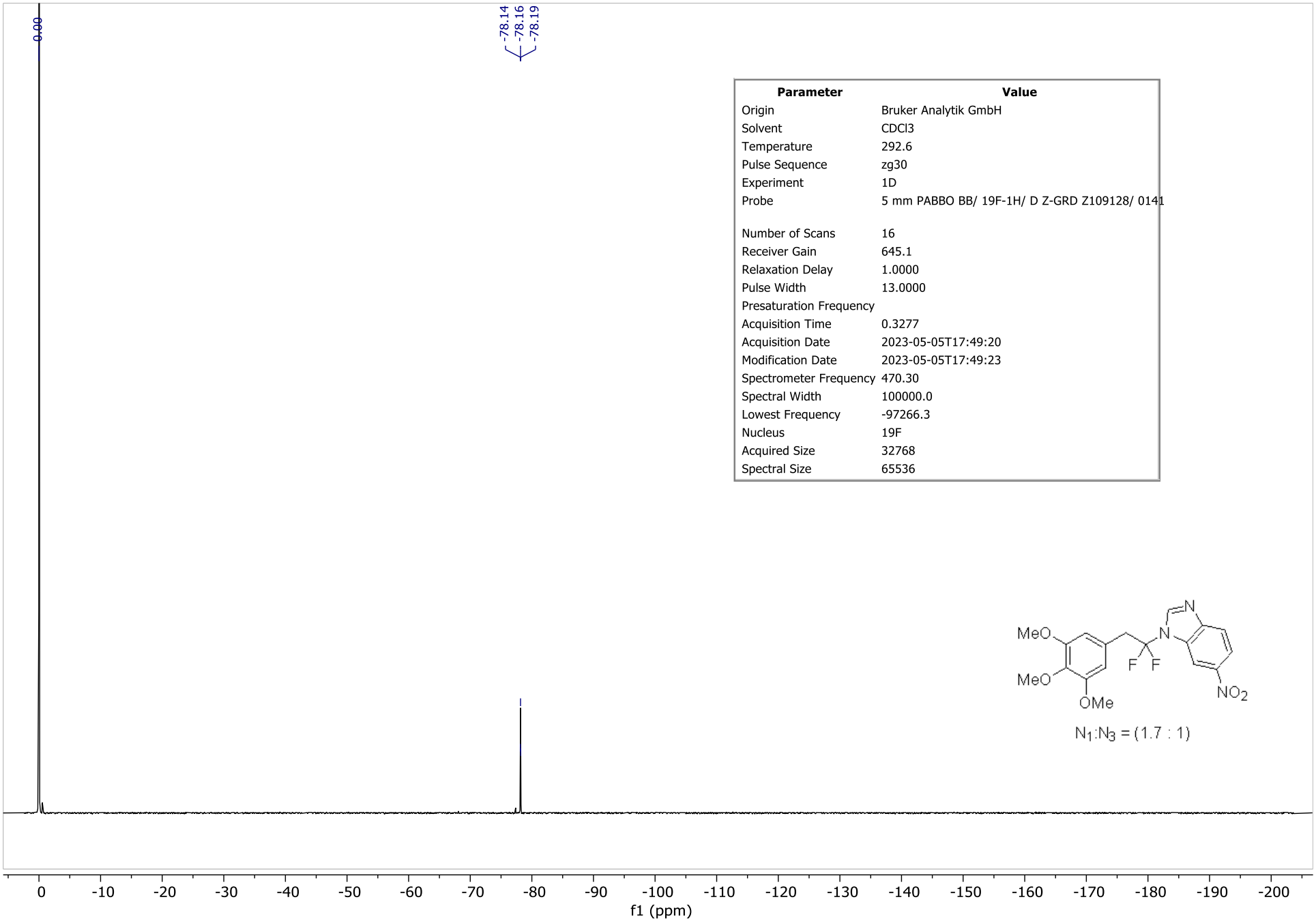


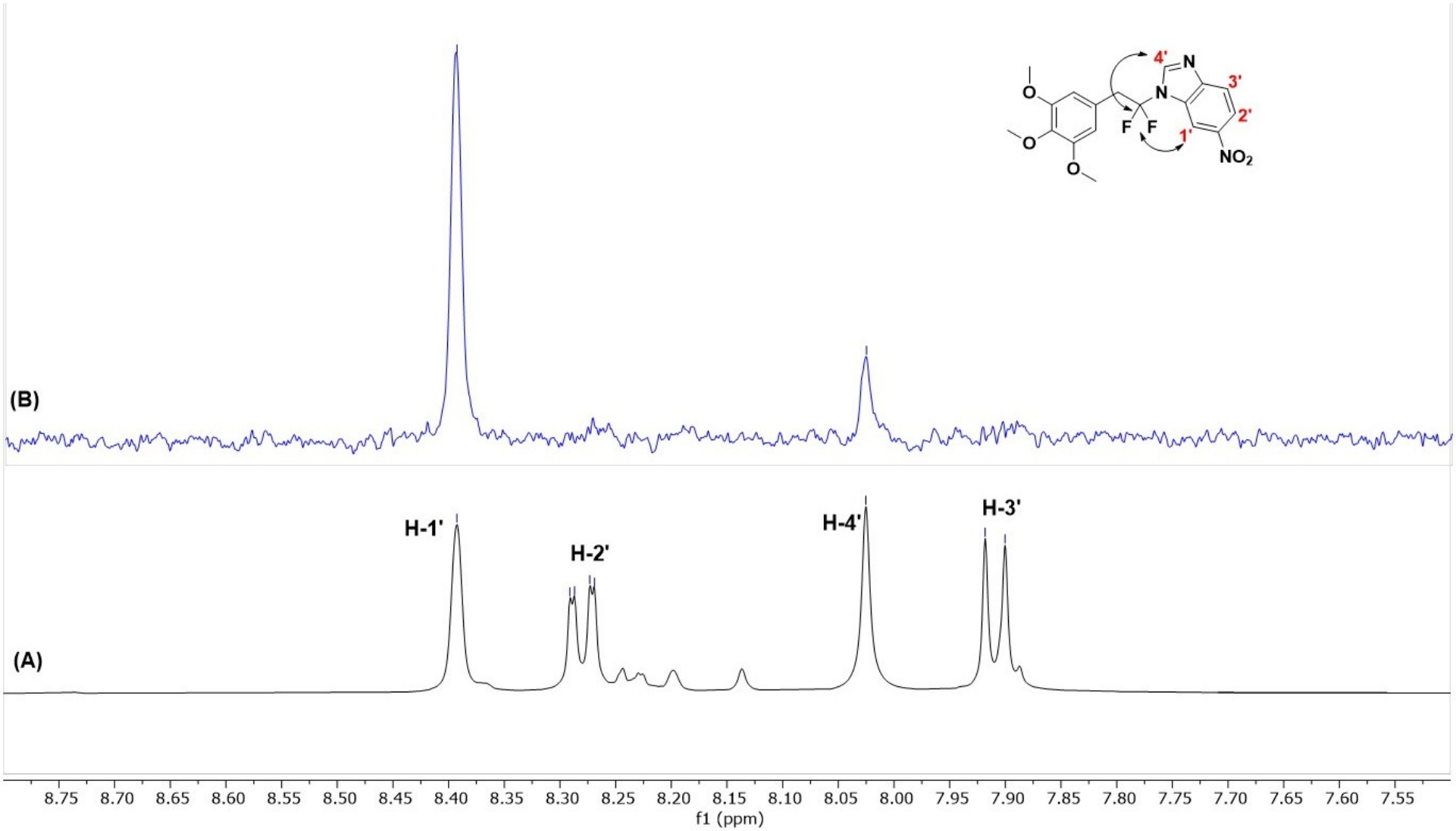
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	406.4
Relaxation Delay	2.0000
Pulse Width	20.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-05-19T11:07:18
Modification Date	2023-05-19T11:07:21
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

N_1:N_3 = (1.7 : 1)

Parameter	Value
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	998
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2023-05-05T11:08:40
Modification Date	2023-05-05T11:08:40
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-2976.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

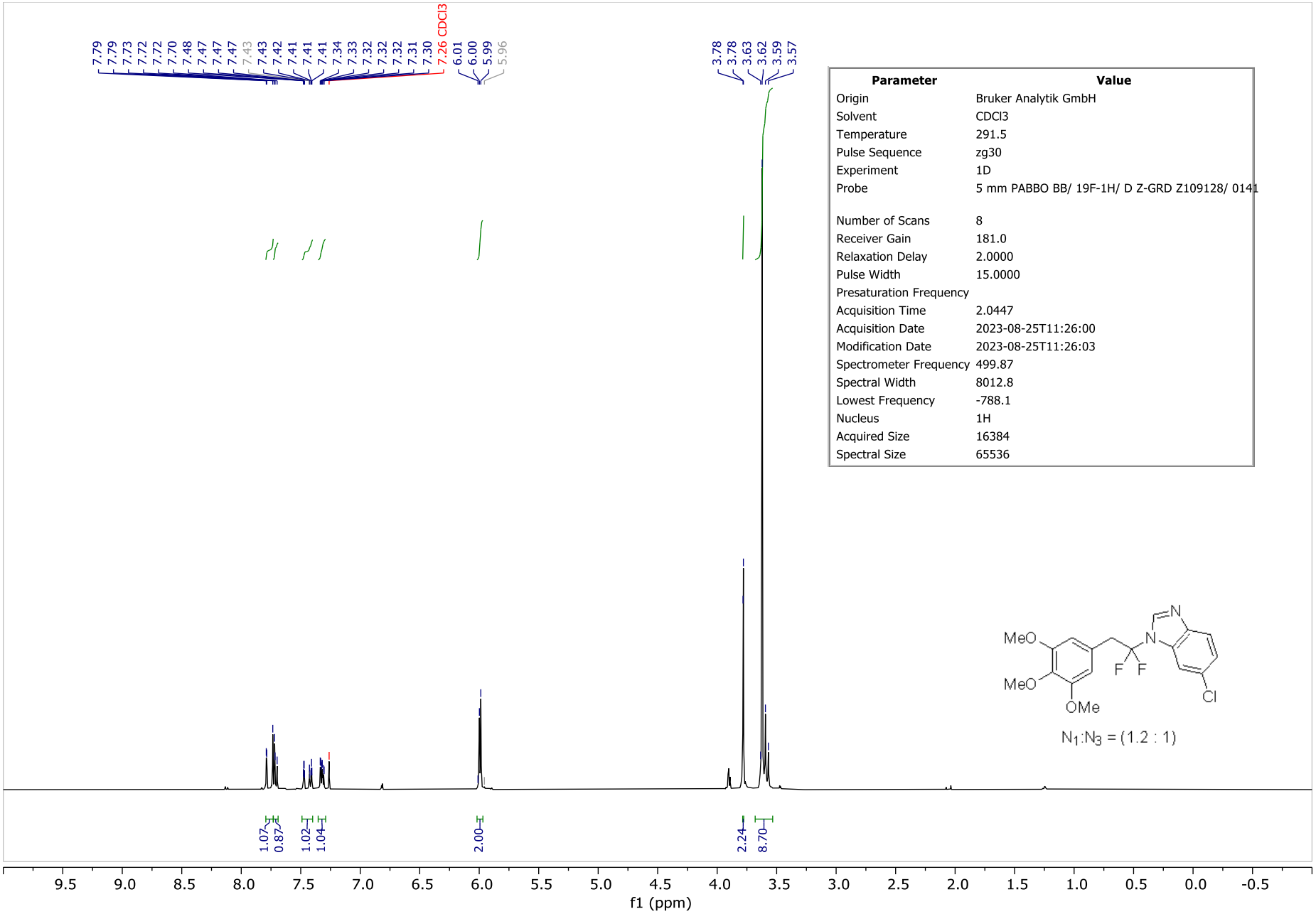



0.00
-78.14
-78.16
-78.19
Parameter Value
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 292.6
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 16
Receiver Gain 645.1
Relaxation Delay 1.0000
Pulse Width 13.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2023-05-05T17:49:20
Modification Date 2023-05-05T17:49:23
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97266.3
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
MeO
MeO
OMe
N
N
F F
NO2
N1:N3 = (1.7 : 1)
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)



(**A**) Aromatic region of ^{1}H NMR spectrum of **11ab**. (**B**) ^{1}H {^{19}F} NOE difference spectrum after preirradiation of ^{19}F δ -78.16.

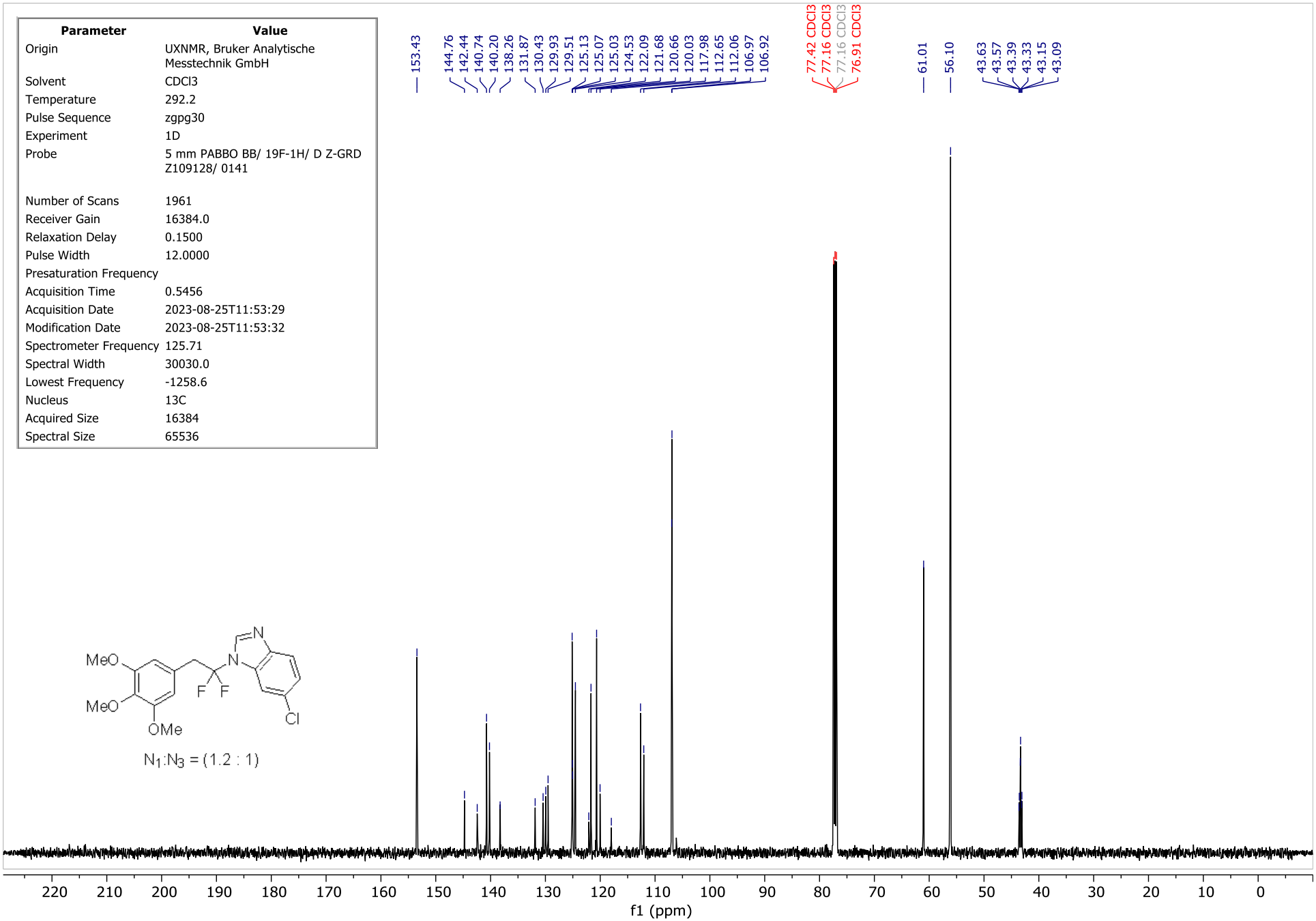
NMR spectra for 6- and 5-chloro-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*]imidazole (**11ac**)

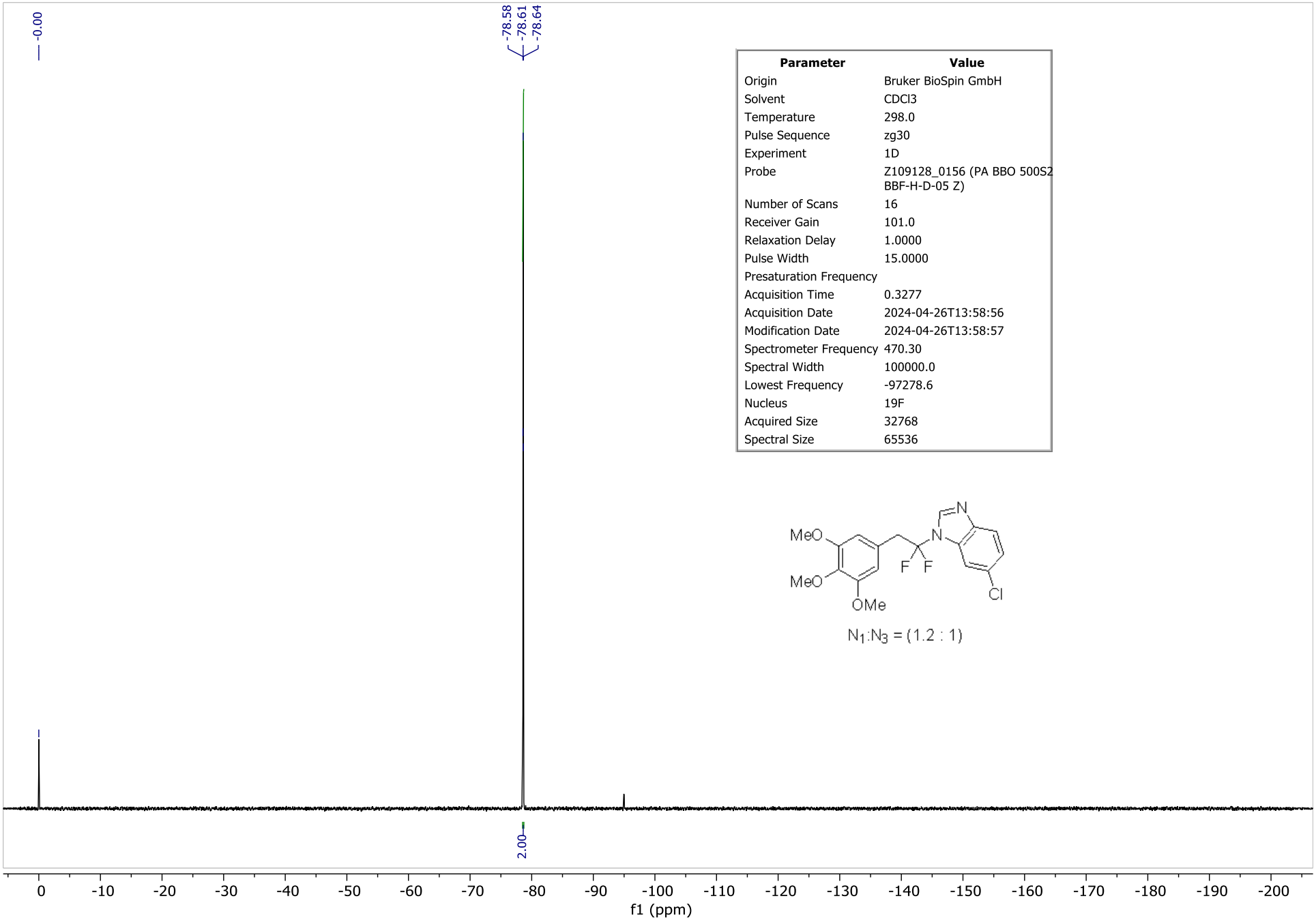


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	181.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-08-25T11:26:00
Modification Date	2023-08-25T11:26:03
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

N_1:N_3 = (1.2 : 1)

Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1961
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-08-25T11:53:29
Modification Date	2023-08-25T11:53:32
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1258.6
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

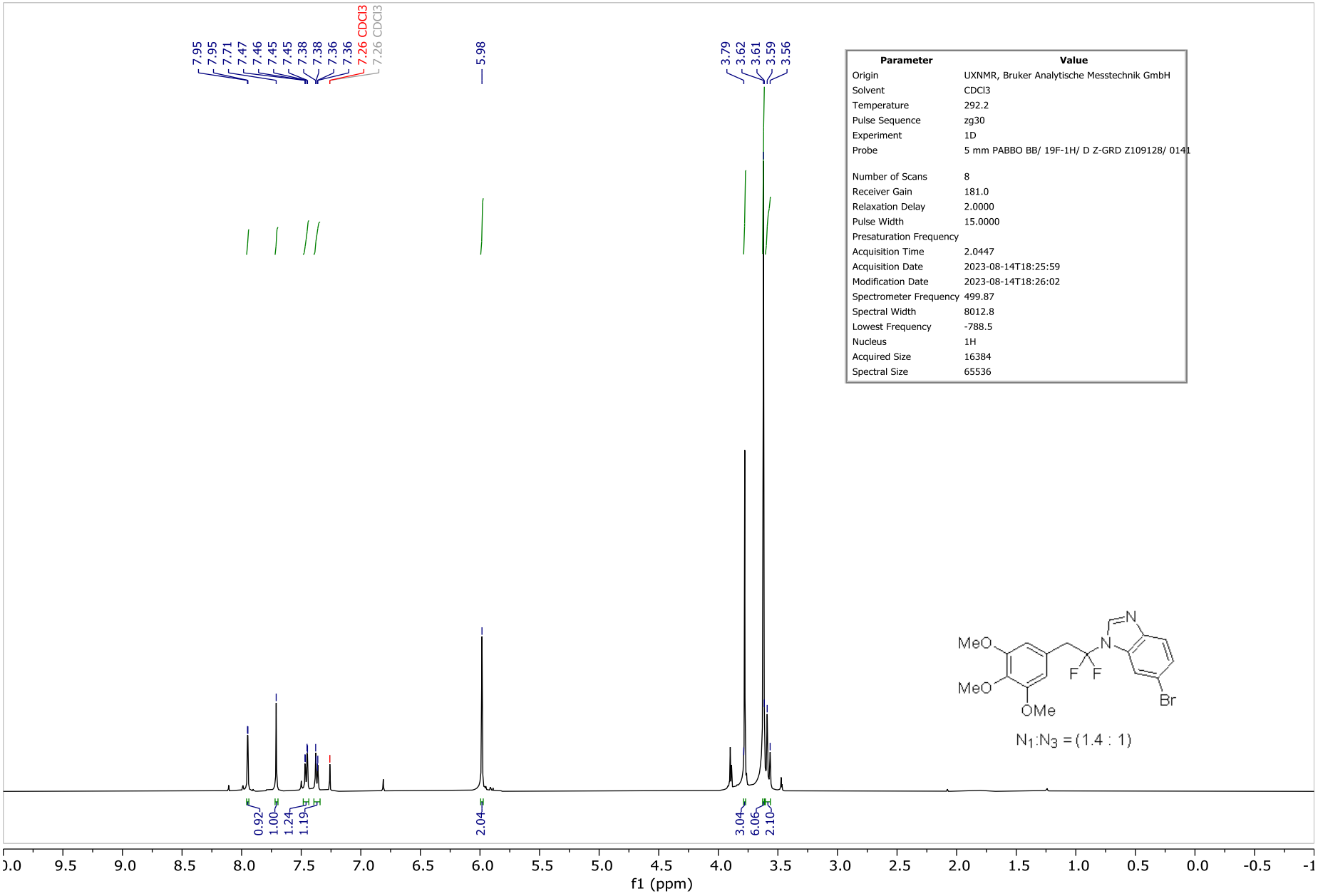




Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-04-26T13:58:56
Modification Date	2024-04-26T13:58:57
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97278.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

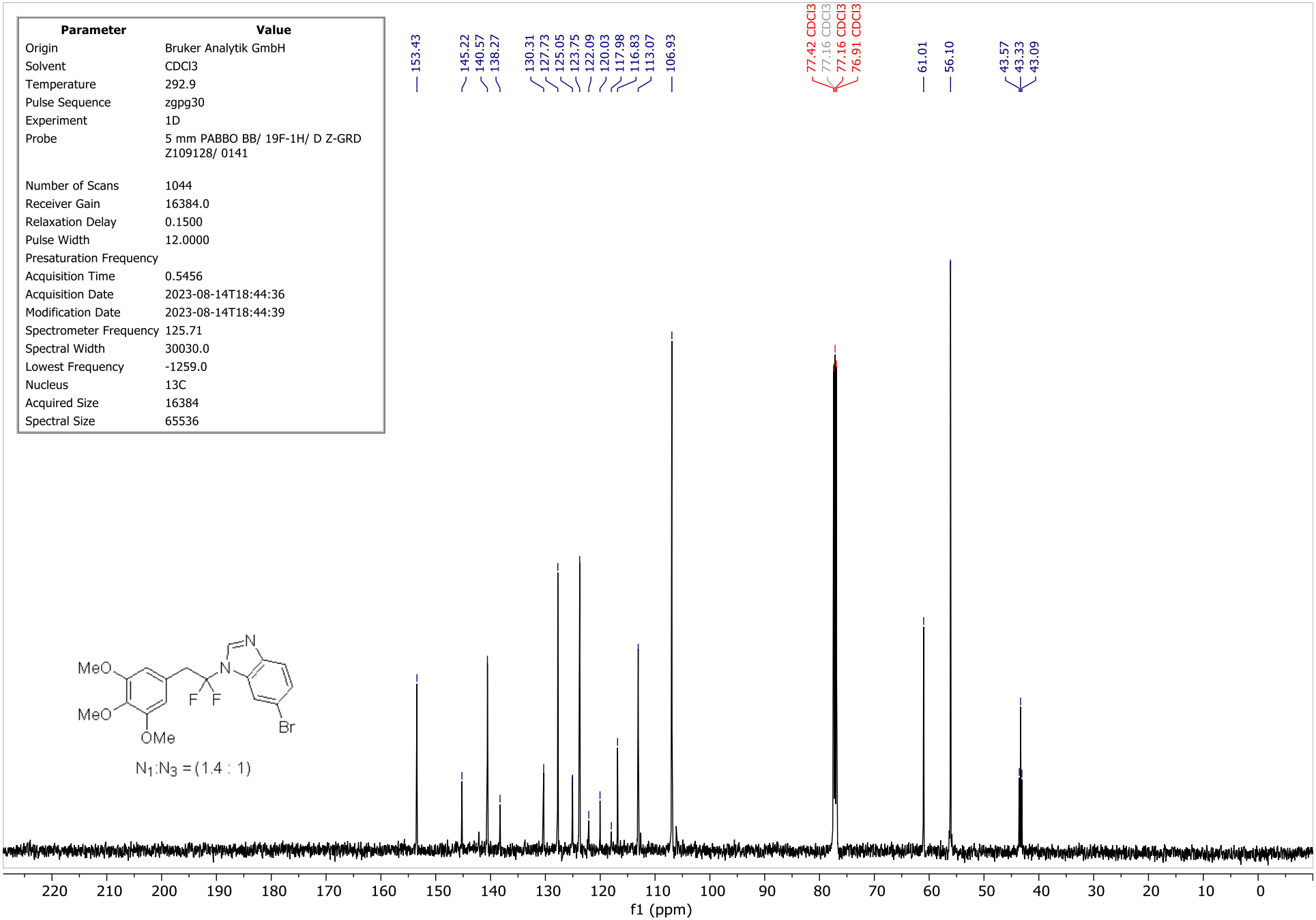
N_1:N_3 = (1.2 : 1)

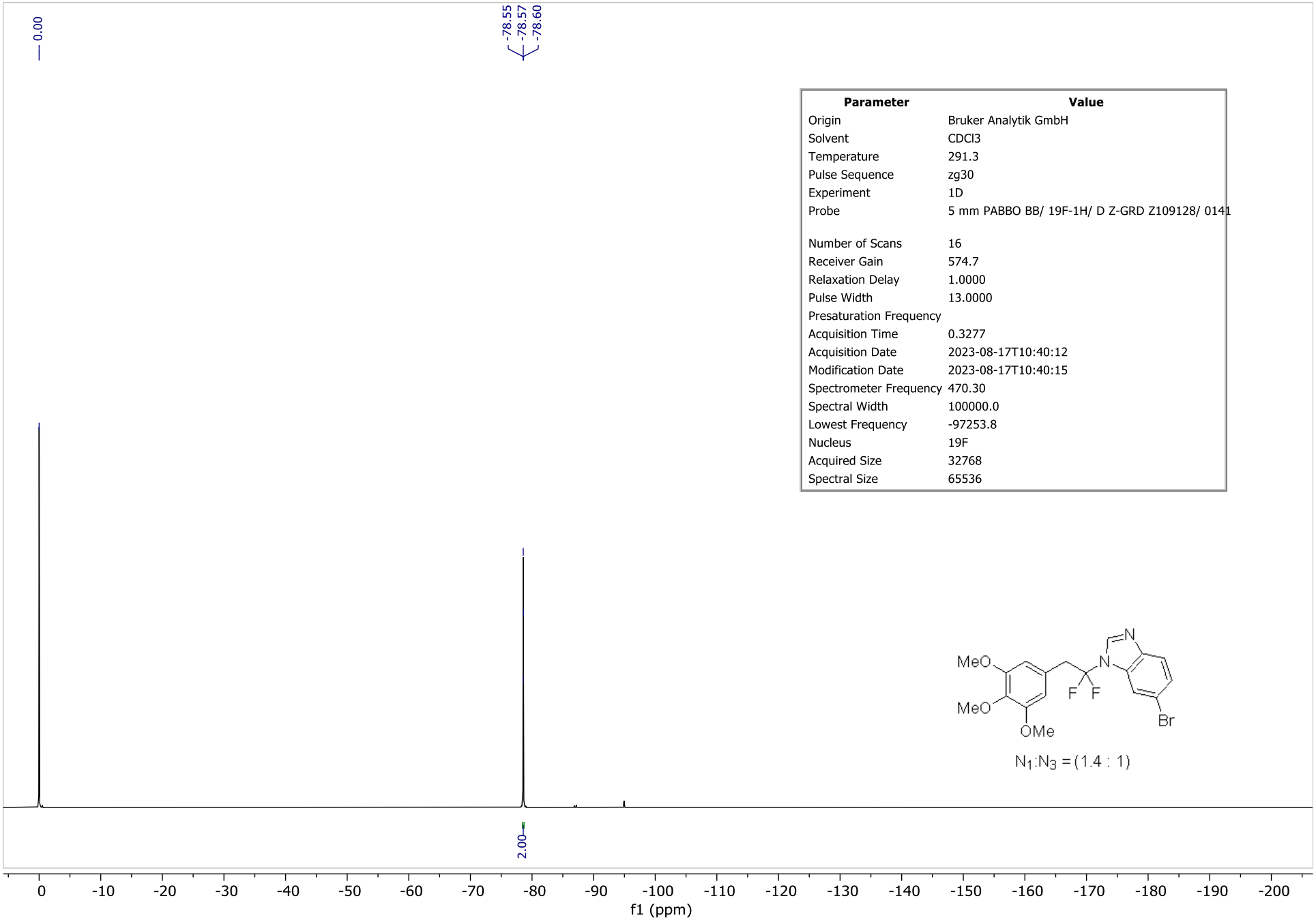
NMR spectra for 6- and 5-bromo-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-*1H*-benzo[d]imidazole (**11ad**)

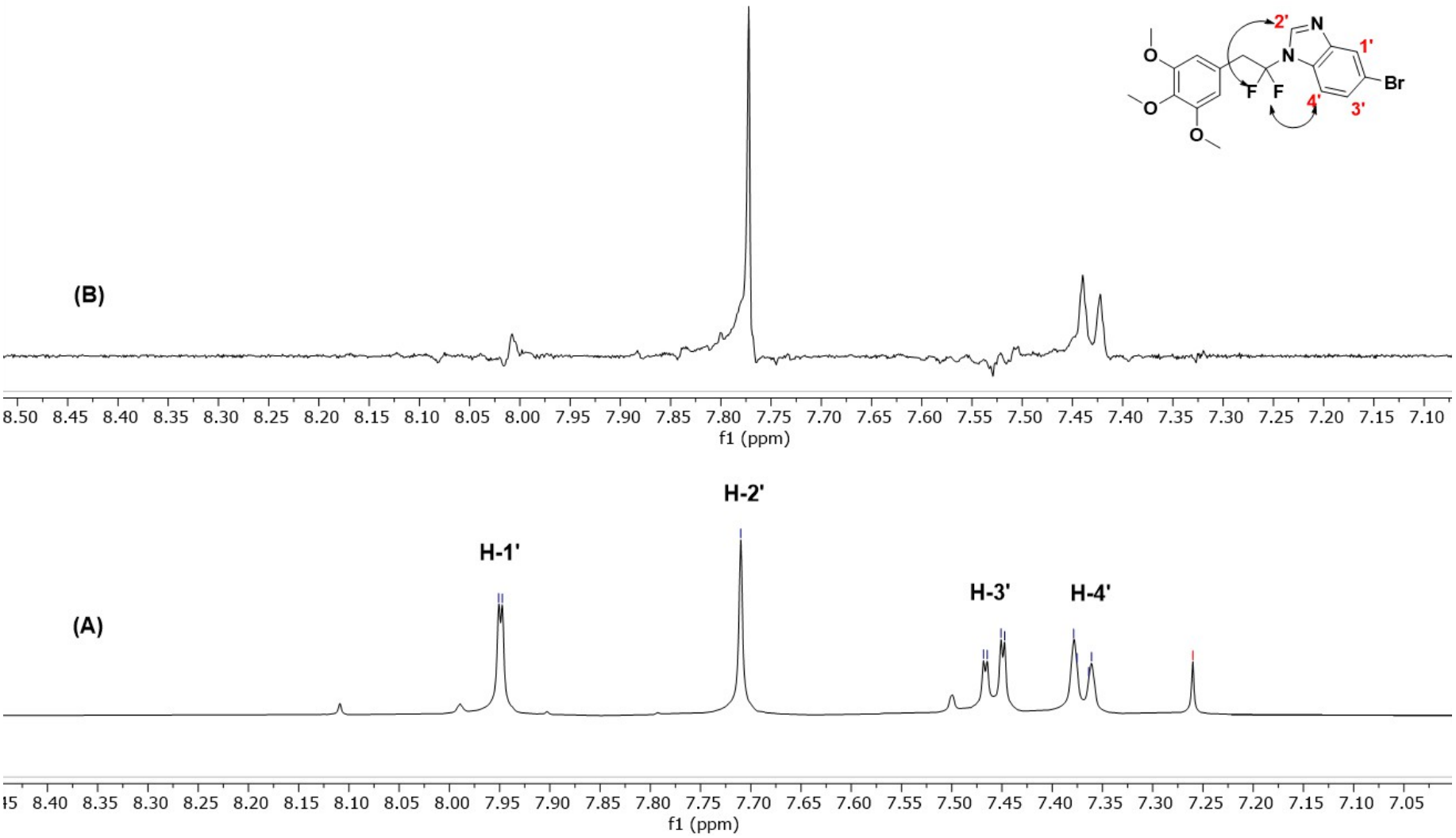


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	181.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-08-14T18:25:59
Modification Date	2023-08-14T18:26:02
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.5
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

Parameter	Value
Origin	Bruker Analytik 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	1044
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-08-14T18:44:36
Modification Date	2023-08-14T18:44:39
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

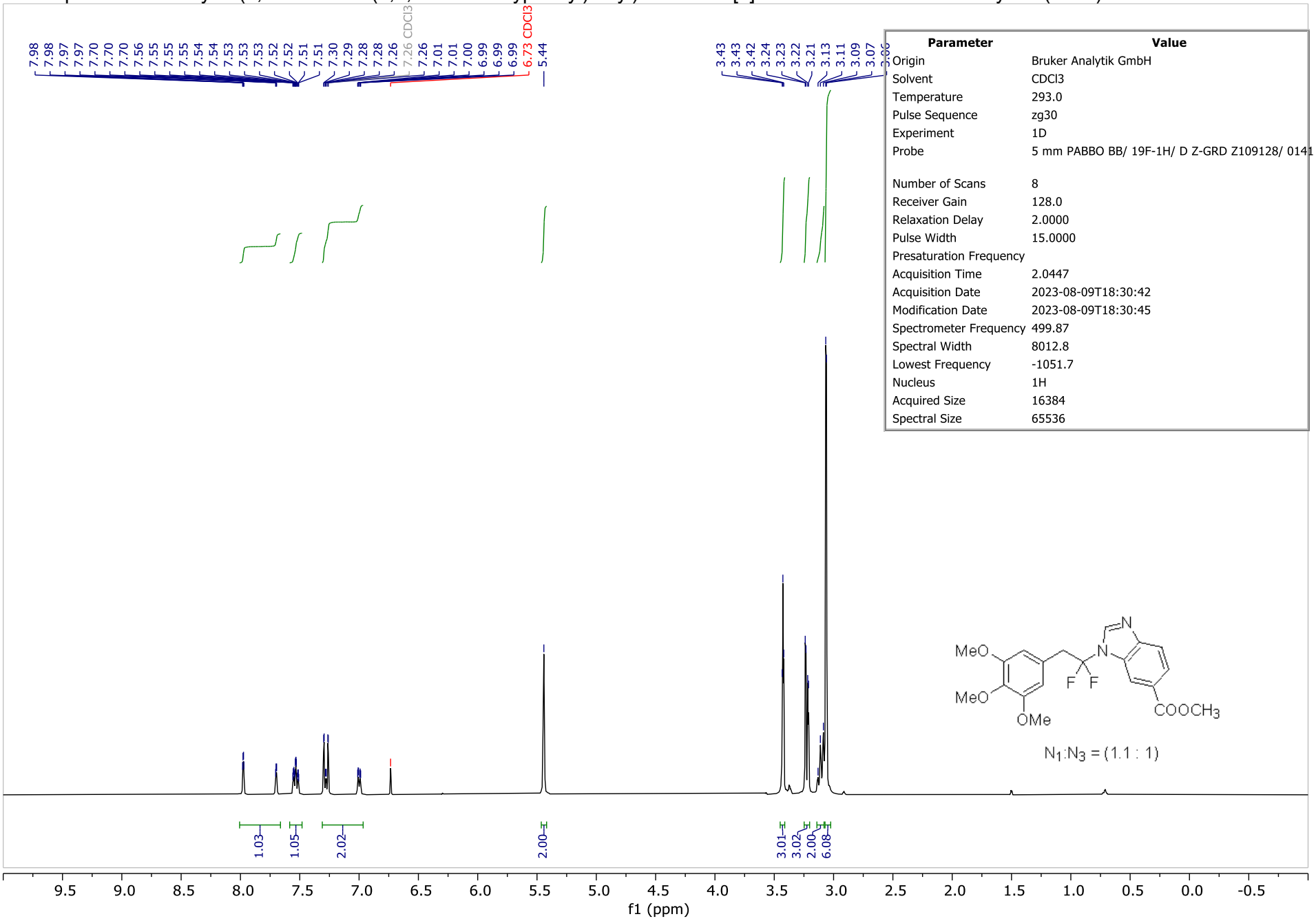



0.00
-78.55
-78.57
-78.60
Parameter Value
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 291.3
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 16
Receiver Gain 574.7
Relaxation Delay 1.0000
Pulse Width 13.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2023-08-17T10:40:12
Modification Date 2023-08-17T10:40:15
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97253.8
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
MeO
MeO
OMe
F F
N
N
Br
N1:N3 = (1.4 : 1)
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)



(**A**) Aromatic region of ^{1}H NMR spectrum of **11ad**. (**B**) ^{1}H {^{19}F} NOE difference spectrum after preirradiation of ^{19}F δ -78.57.

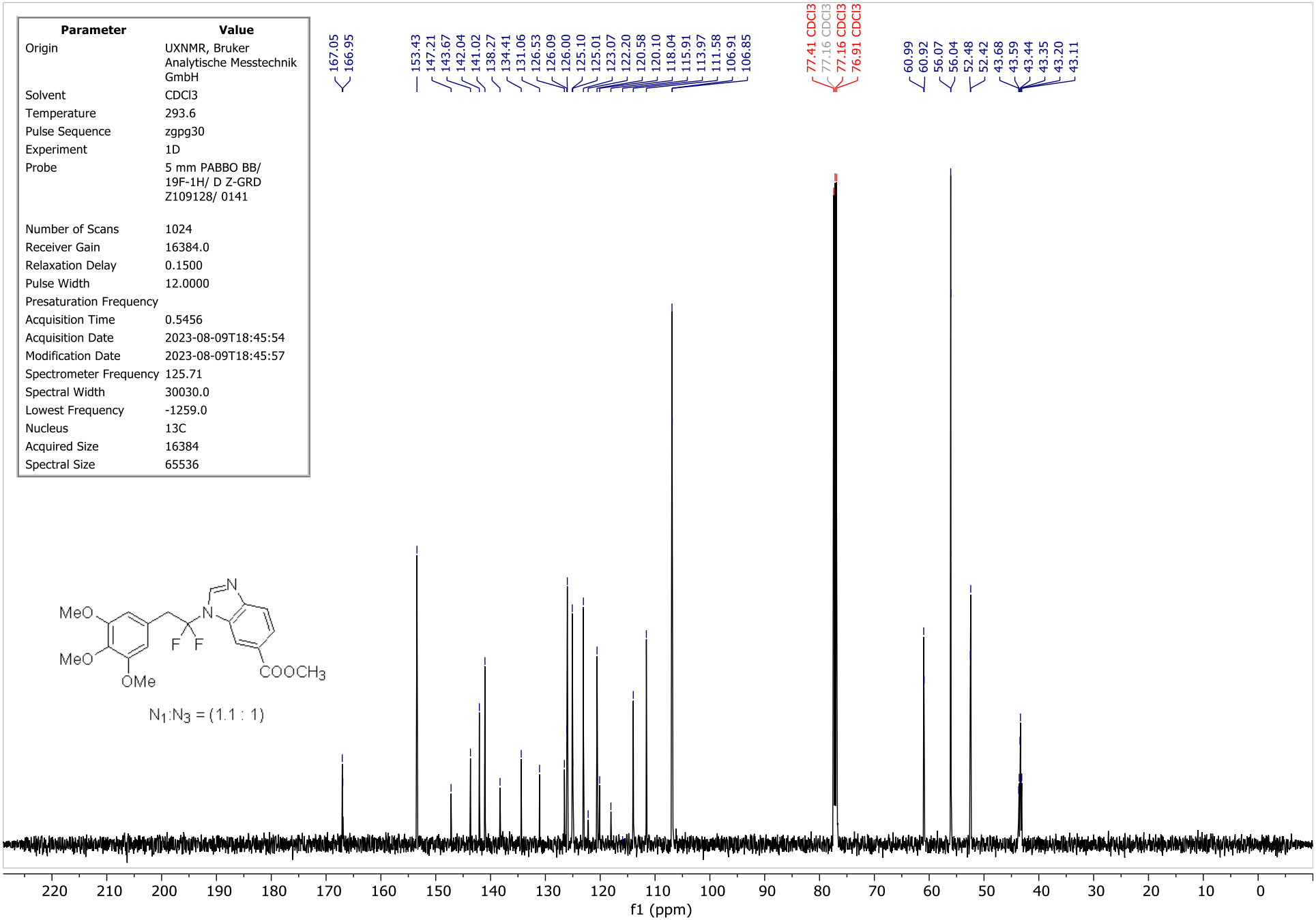
NMR spectra for methyl 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-*1H*-benzo[d]imidazole-6- and -5-carboxylate (**11ae**)

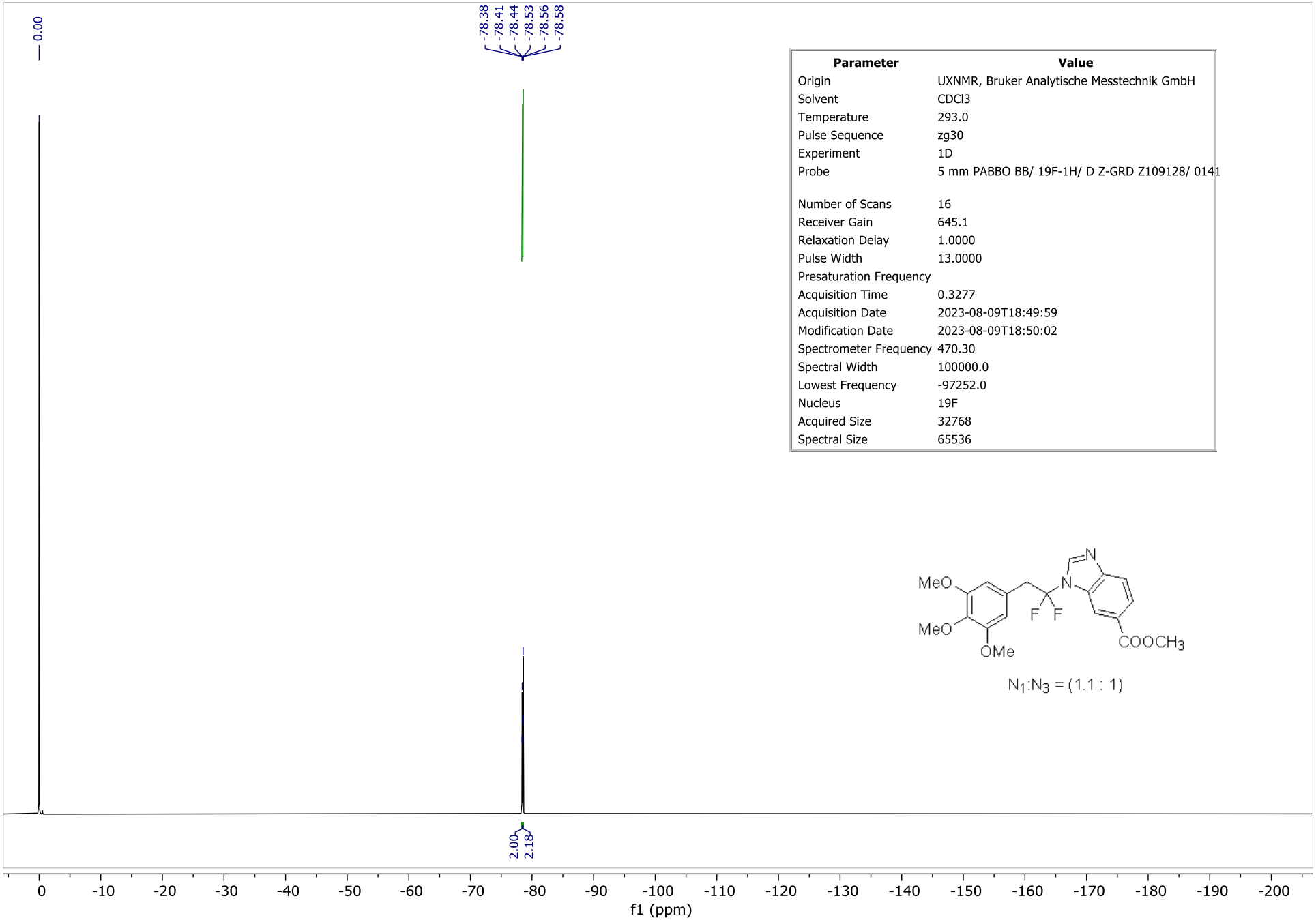


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-08-09T18:30:42
Modification Date	2023-08-09T18:30:45
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-1051.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

N_1:N_3 = (1.1 : 1)

Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1024
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-08-09T18:45:54
Modification Date	2023-08-09T18:45:57
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

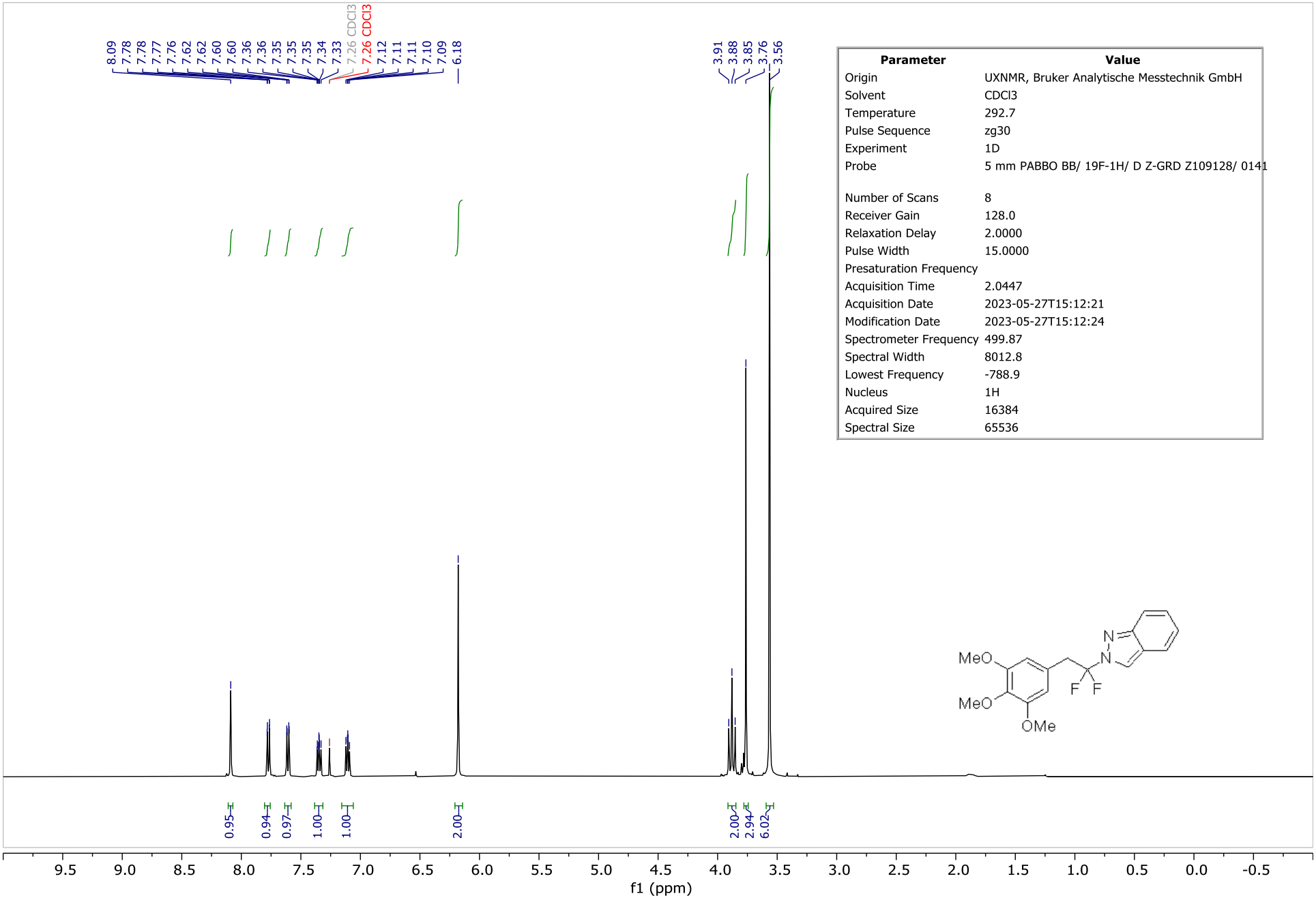




Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-08-09T18:49:59
Modification Date	2023-08-09T18:50:02
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97252.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

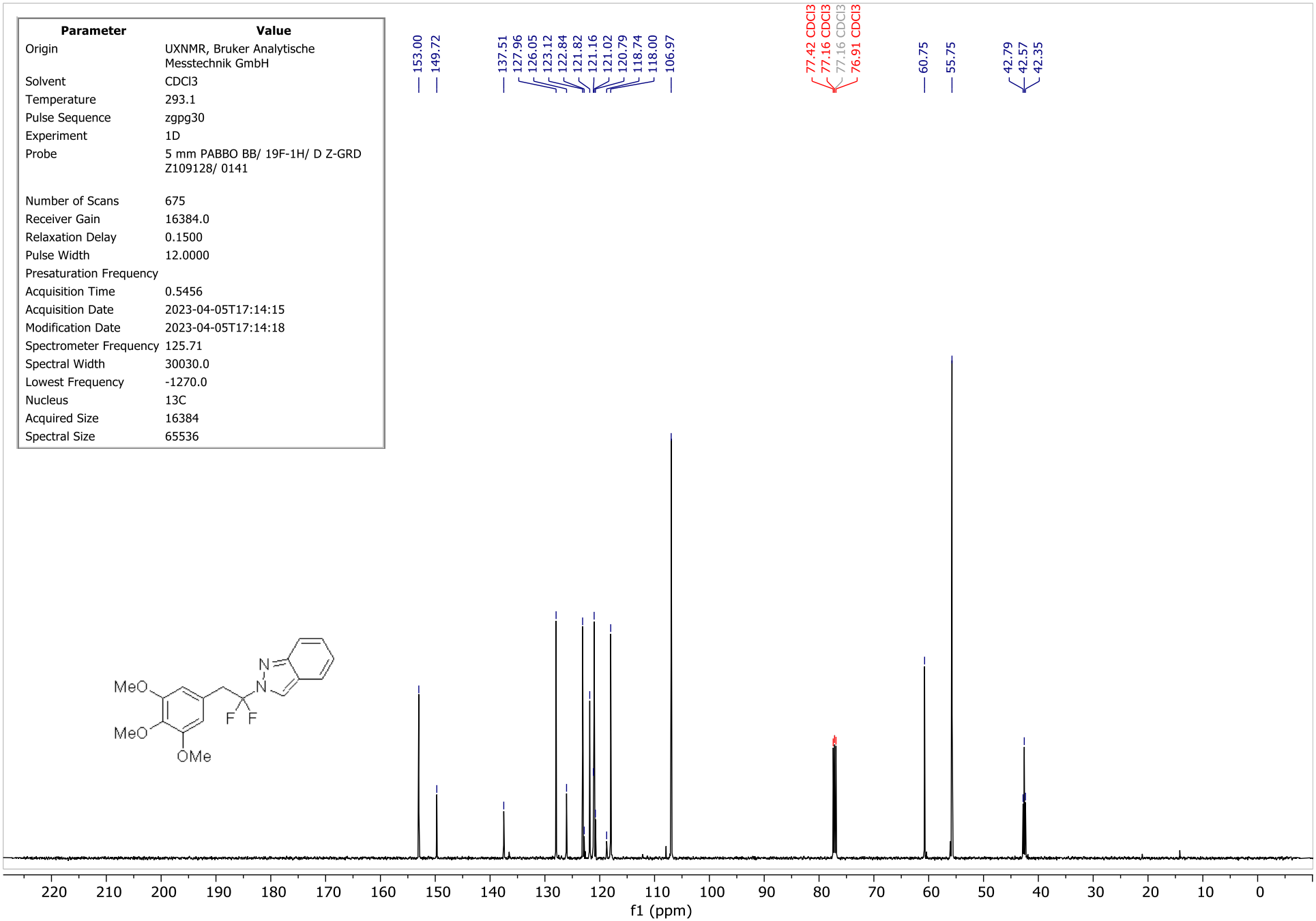
N_1:N_3 = (1.1 : 1)

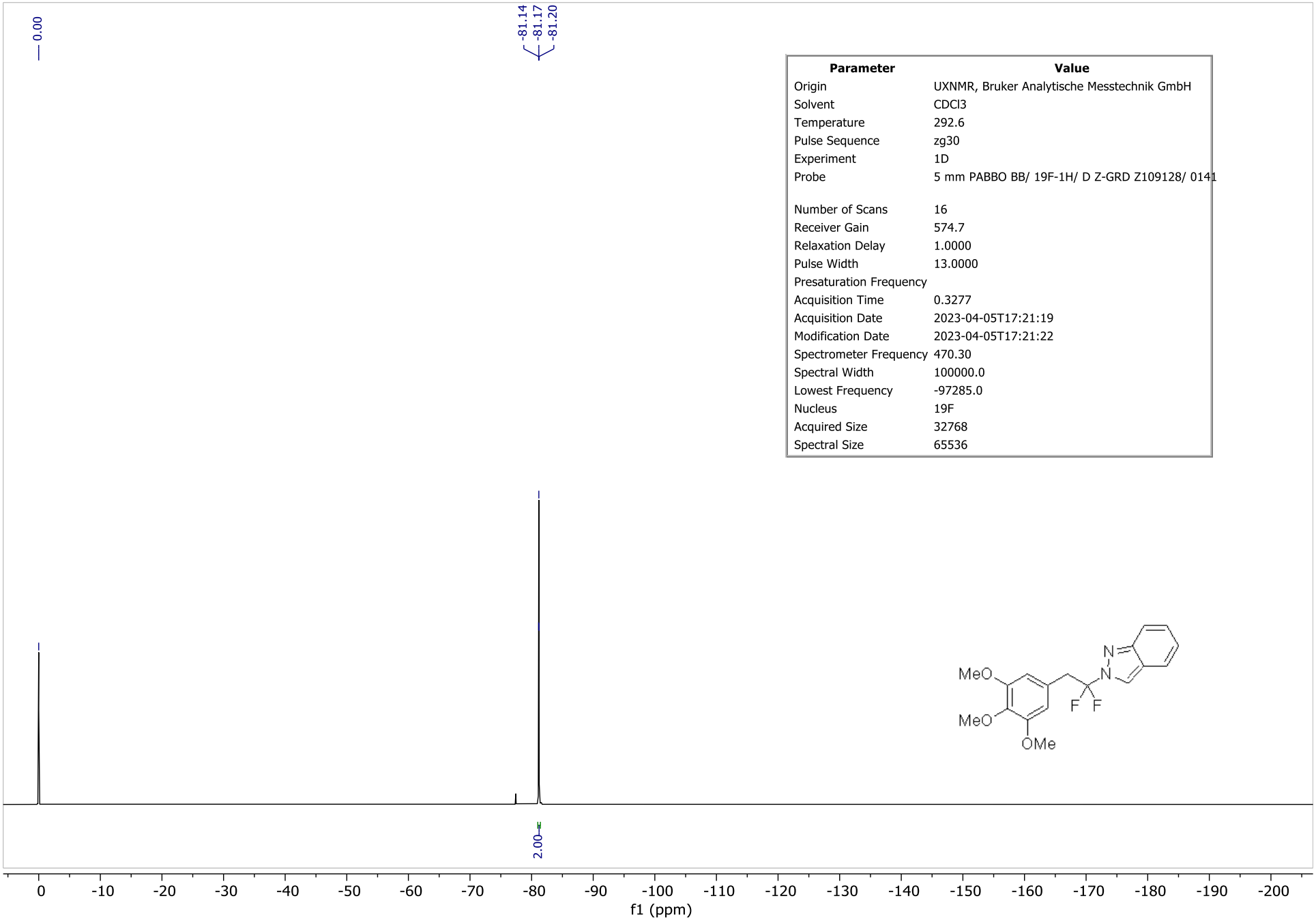
NMR spectra for 2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-2*H*-indazole (**11af**)



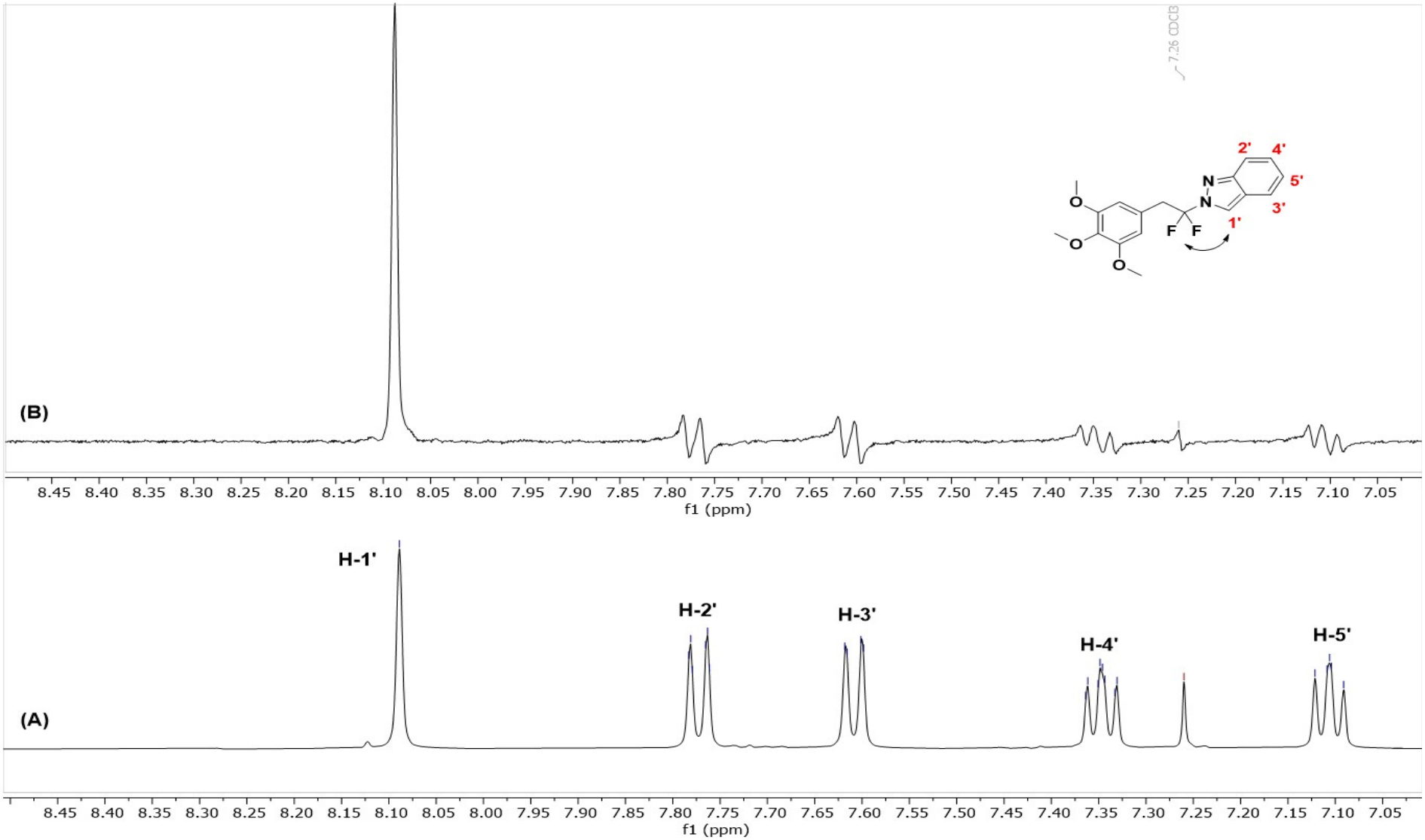
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-05-27T15:12:21
Modification Date	2023-05-27T15:12:24
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.9
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	675
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-04-05T17:14:15
Modification Date	2023-04-05T17:14:18
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1270.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



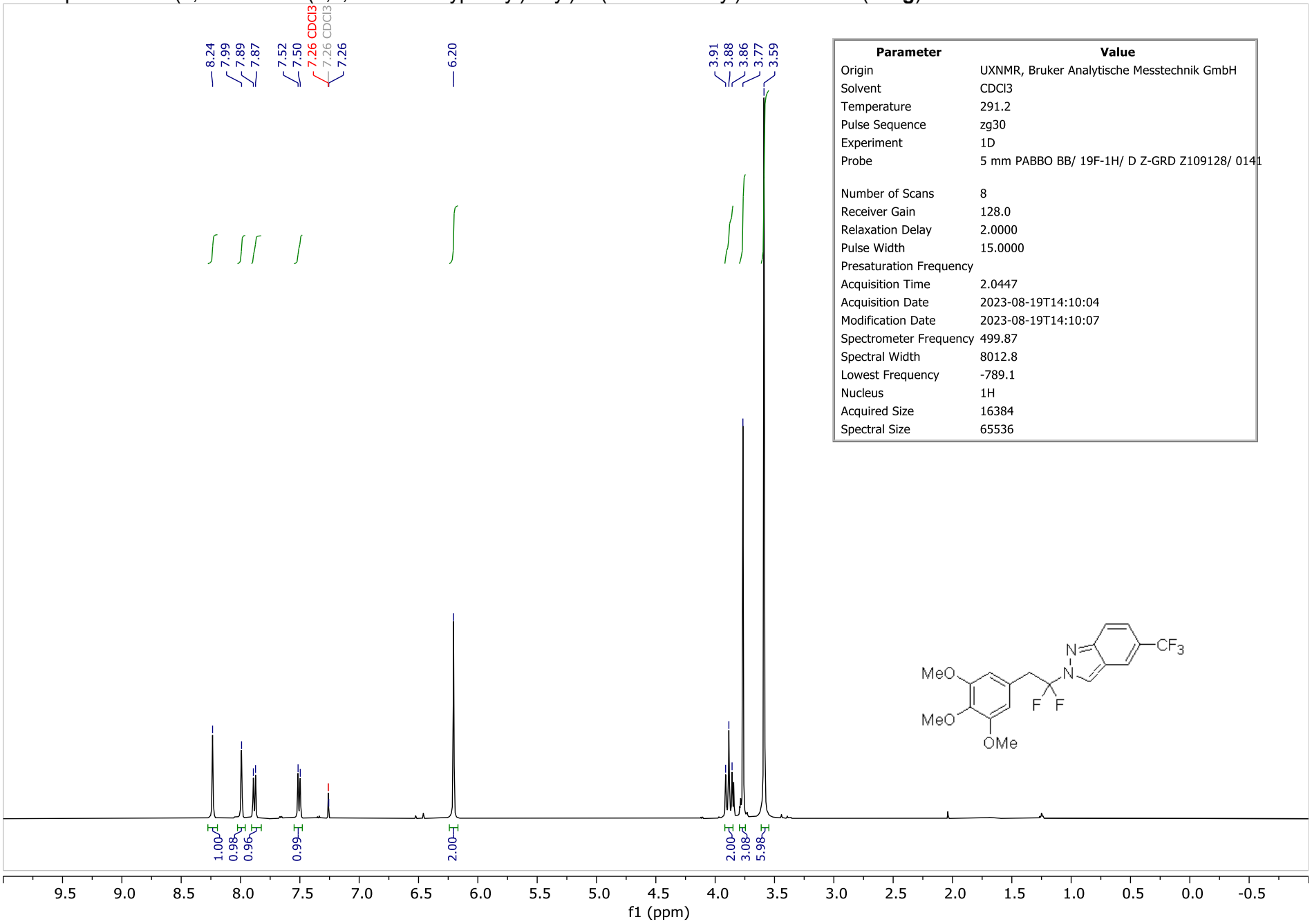


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-04-05T17:21:19
Modification Date	2023-04-05T17:21:22
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97285.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

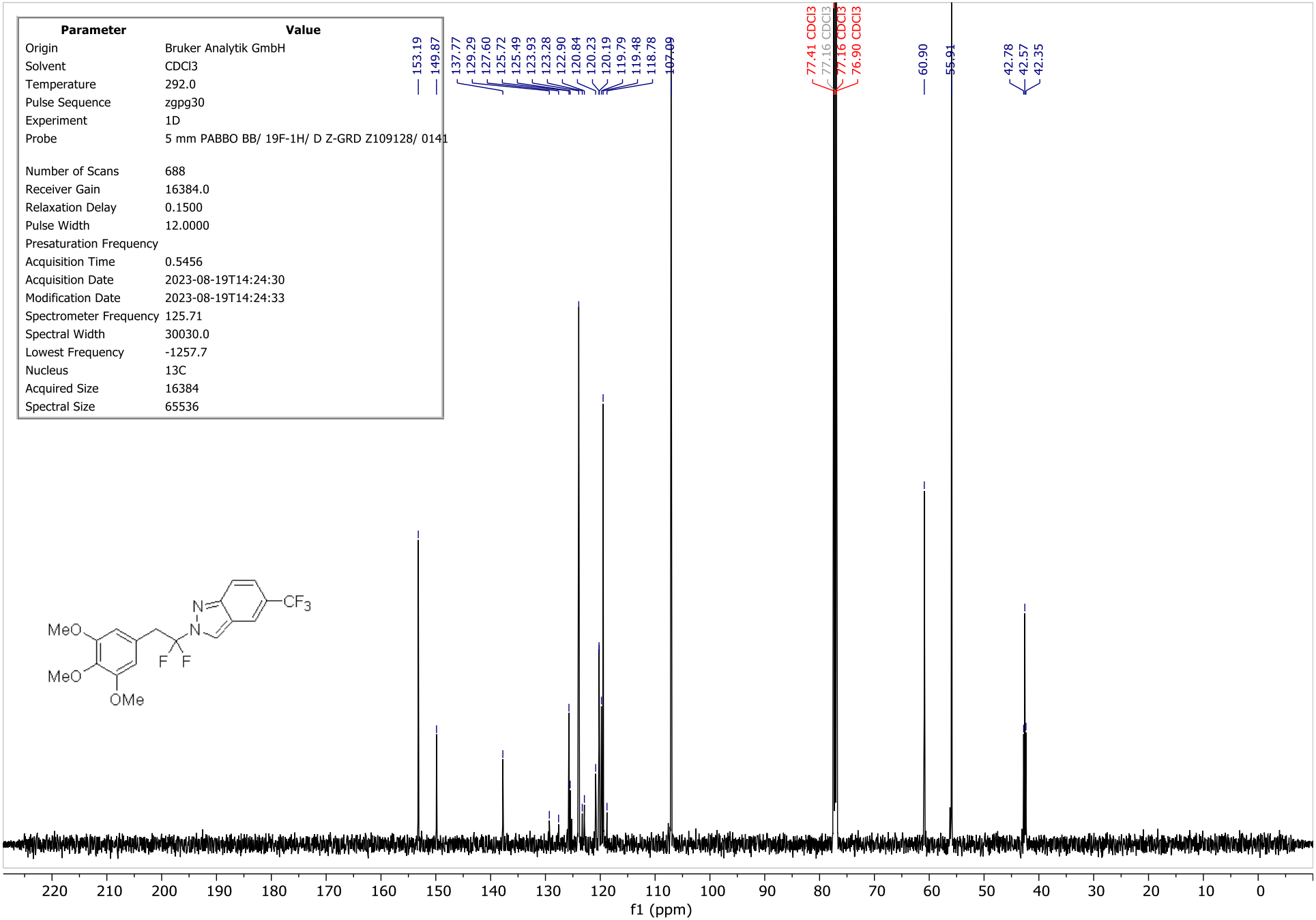


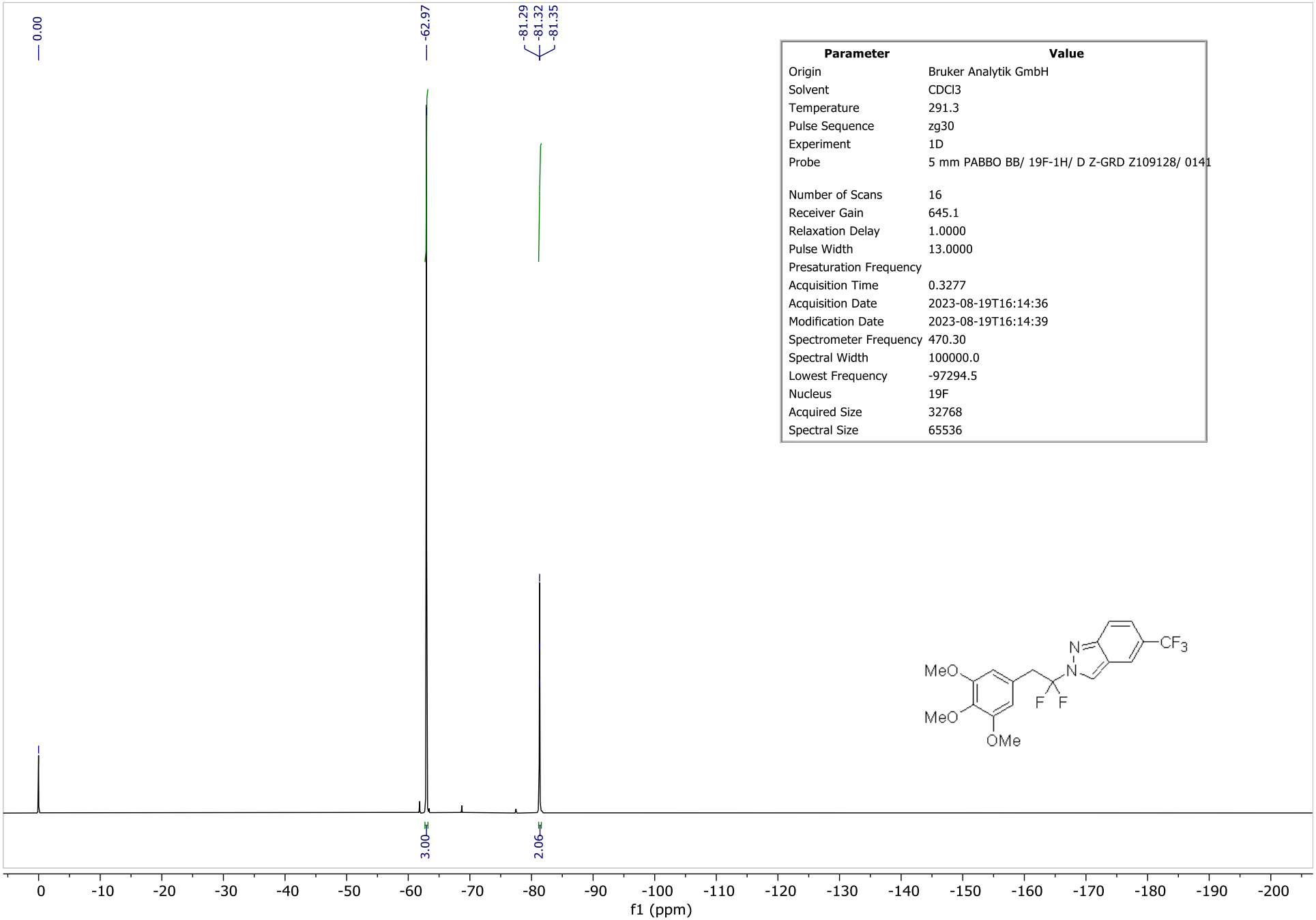
(**A**) Aromatic region of ^{1}H NMR spectrum of **11af**. (**B**) ^{1}H {^{19}F} NOE difference spectrum after preirradiation of ^{19}F δ -81.17.

NMR spectra for 2-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-5-(trifluoromethyl)-2*H*-indazole (**11ag**)

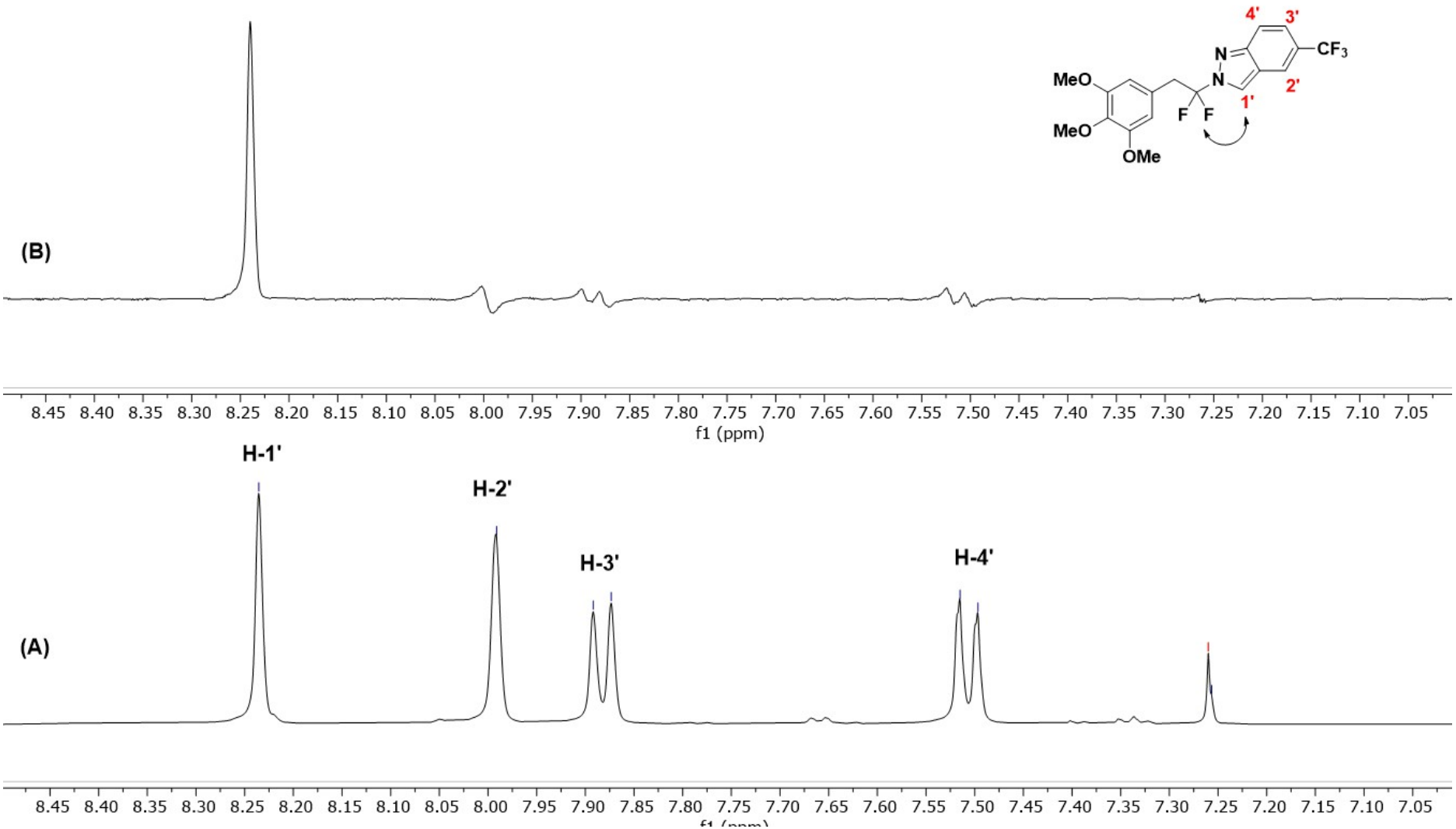


Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-08-19T14:10:04
Modification Date	2023-08-19T14:10:07
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536


Parameter Value
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 292.0
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 688
Receiver Gain 16384.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.5456
Acquisition Date 2023-08-19T14:24:30
Modification Date 2023-08-19T14:24:33
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -1257.7
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
153.19
149.87
137.77
129.29
127.60
125.72
125.49
123.93
123.28
122.90
120.84
120.23
120.19
119.79
119.48
118.78
107.09
77.41 CDCl3
77.16 CDCl3
76.90 CDCl3
60.90
55.91
42.78
42.57
42.35
MeO
MeO
OMe
F F
N
N
CF3
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)

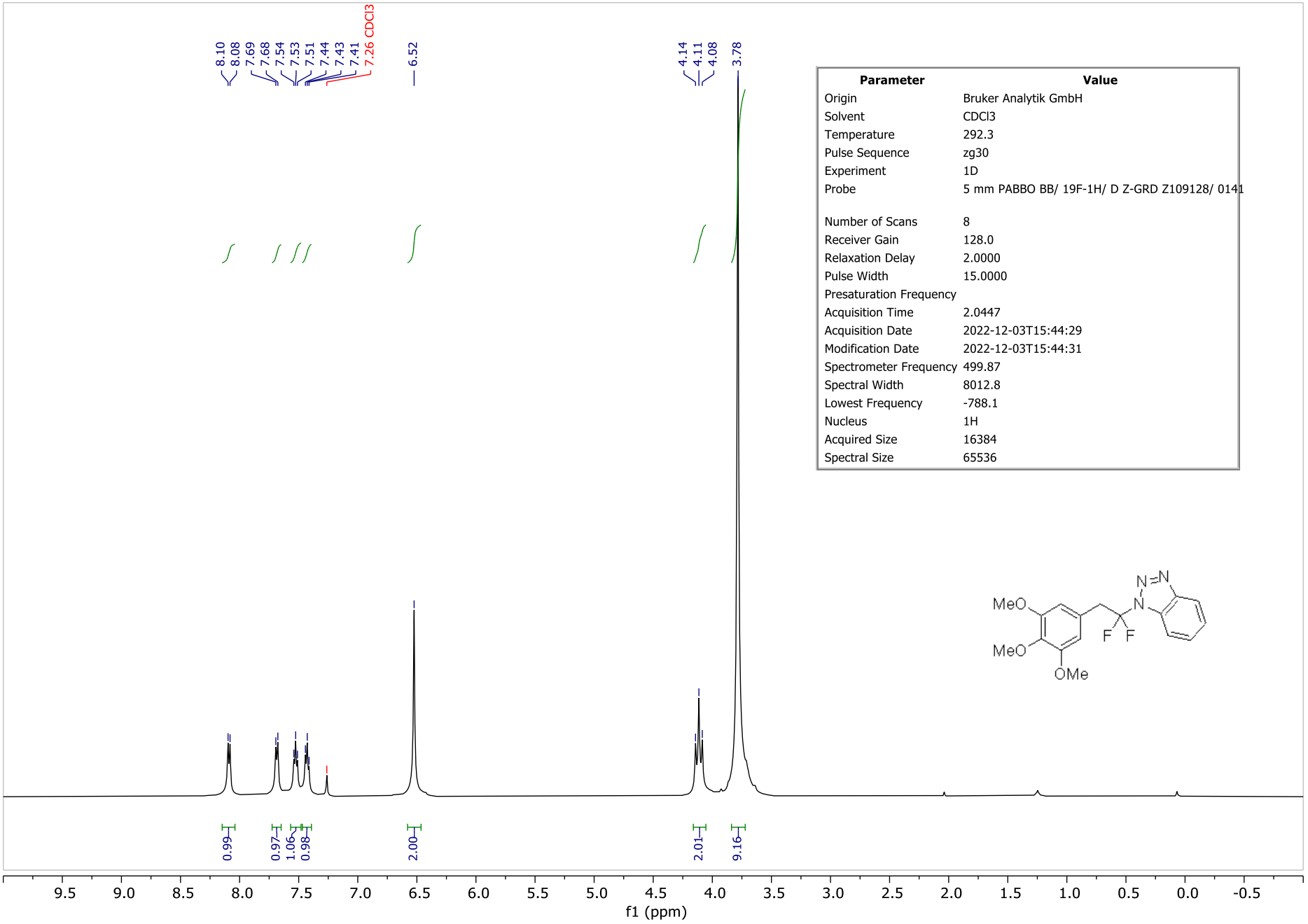


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.3
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-08-19T16:14:36
Modification Date	2023-08-19T16:14:39
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97294.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536



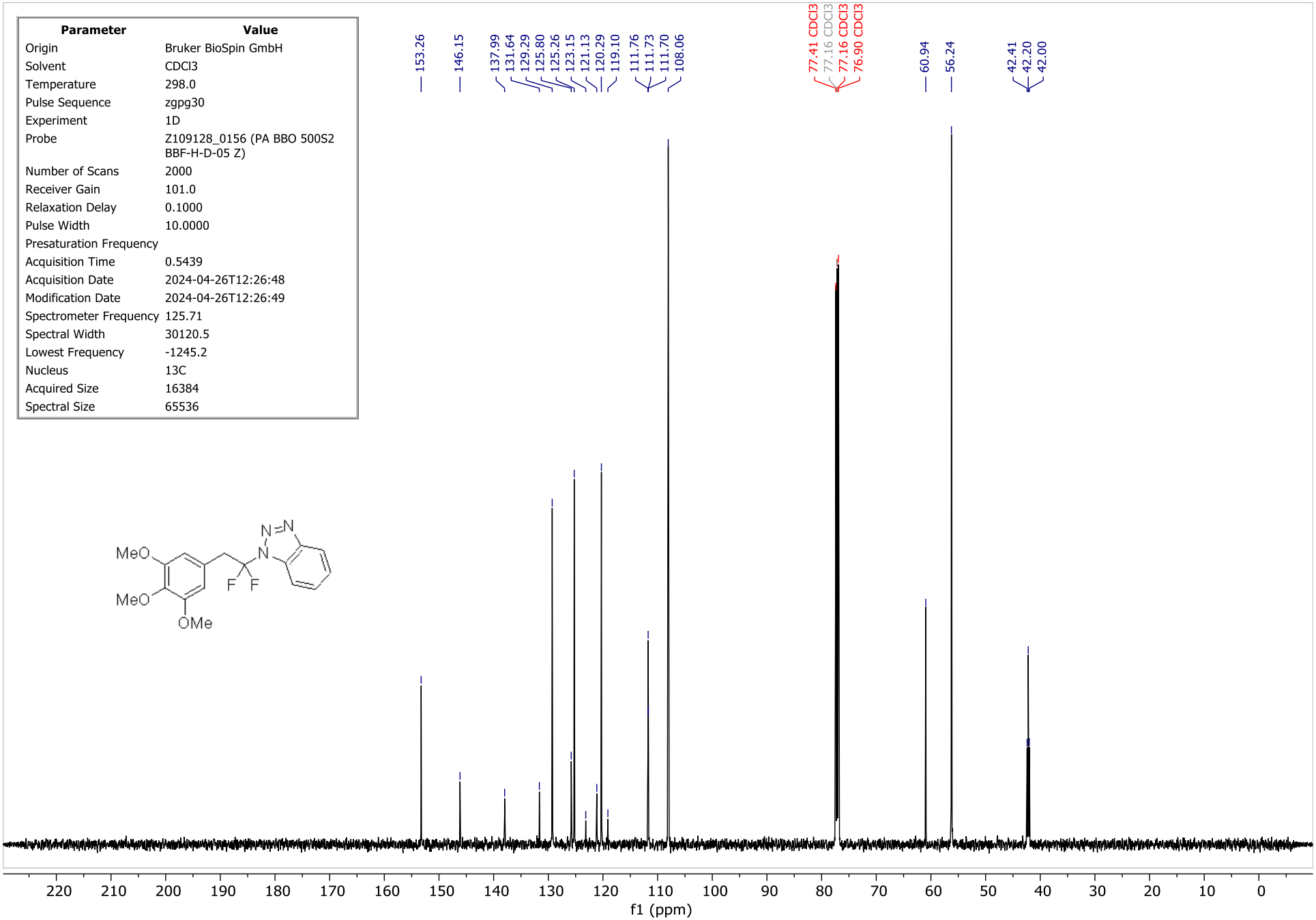
(**A**) Aromatic region of ^{1}H NMR spectrum of **11ag**. (**B**) ^{1}H {^{19}F} NOE difference spectrum after preirradiation of ^{19}F δ -81.32.

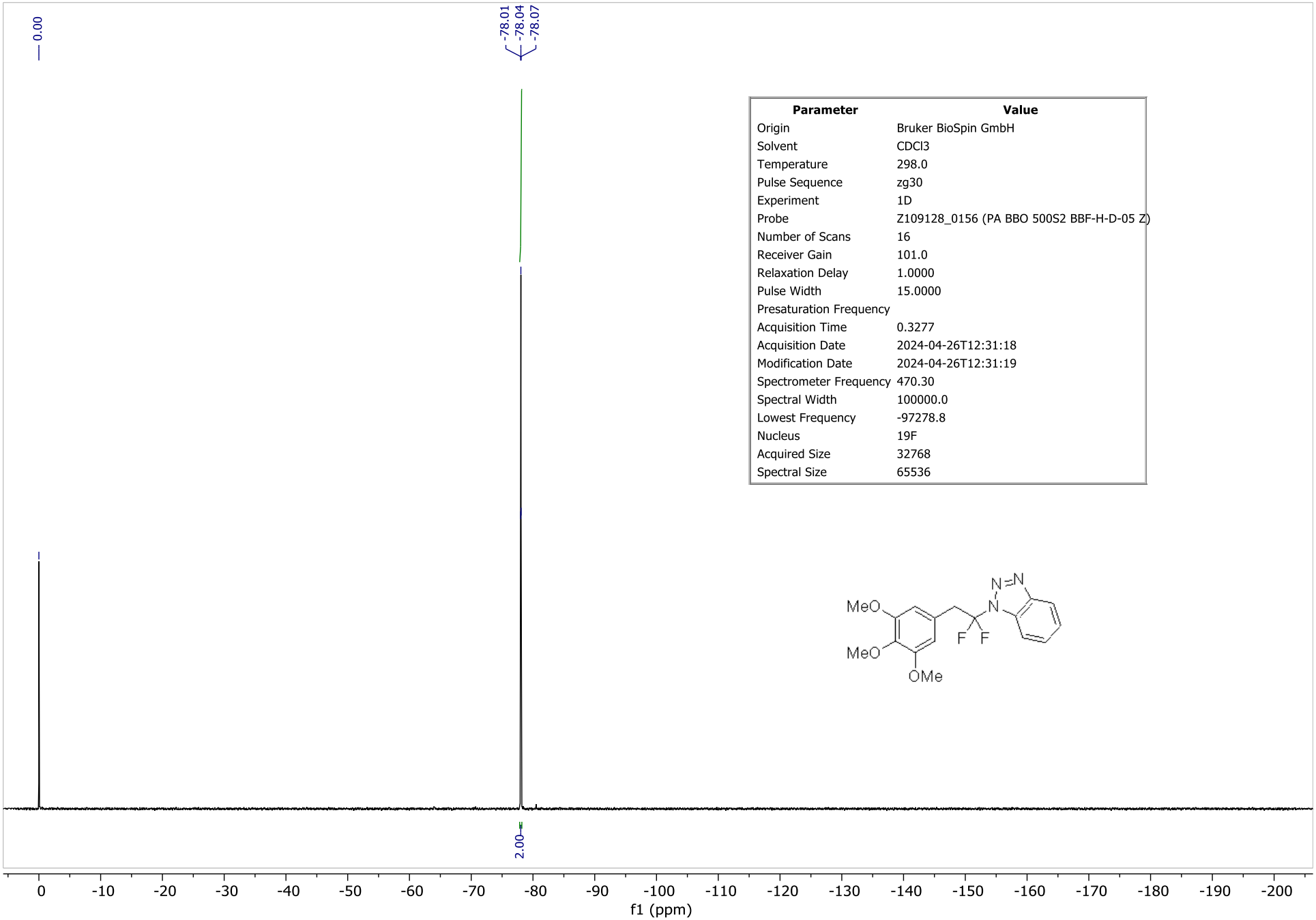
NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole (**11ah**)



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	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-03T15:44:29
Modification Date	2022-12-03T15:44:31
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

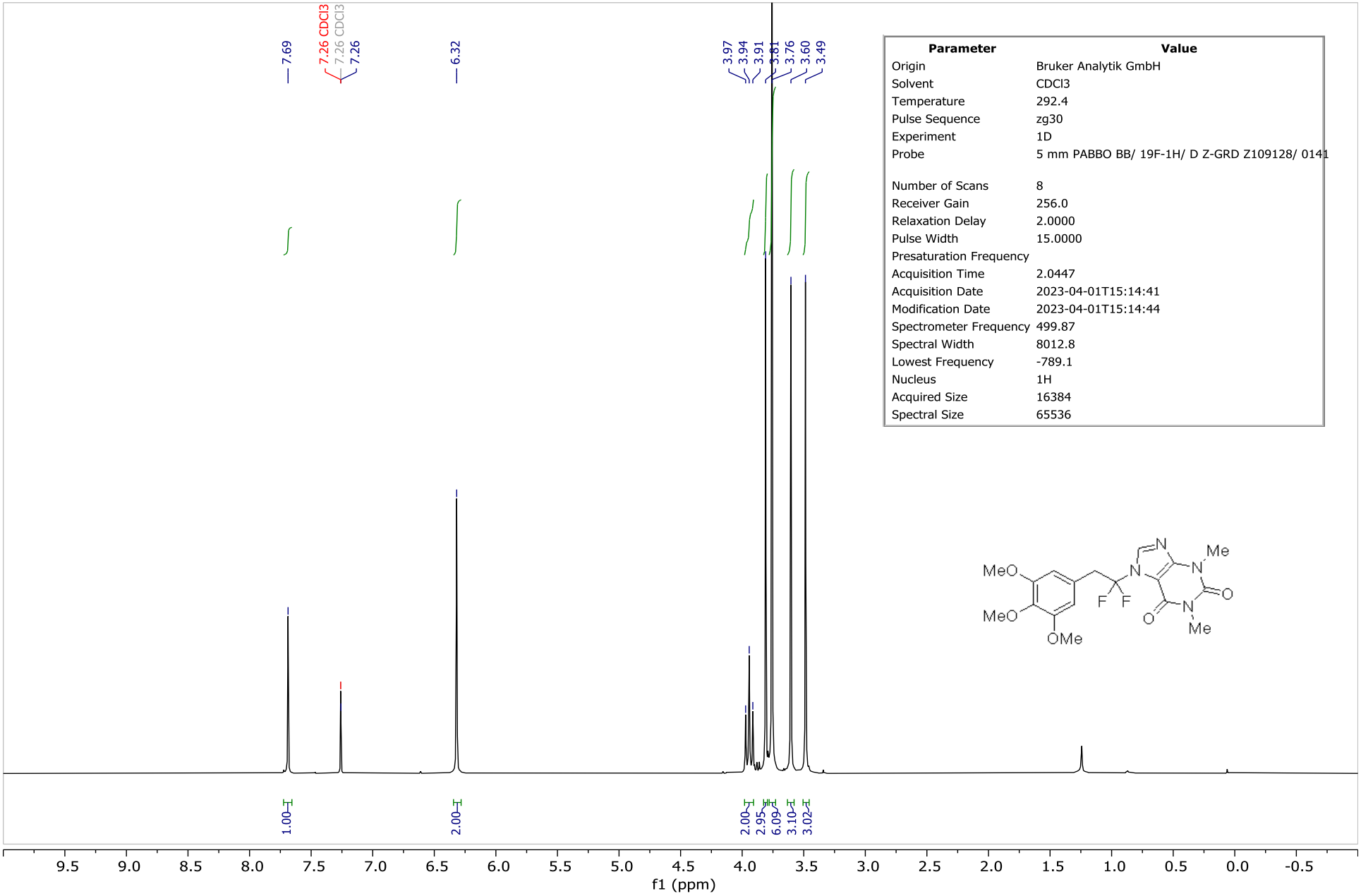
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	2000
Receiver Gain	101.0
Relaxation Delay	0.1000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	0.5439
Acquisition Date	2024-04-26T12:26:48
Modification Date	2024-04-26T12:26:49
Spectrometer Frequency	125.71
Spectral Width	30120.5
Lowest Frequency	-1245.2
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



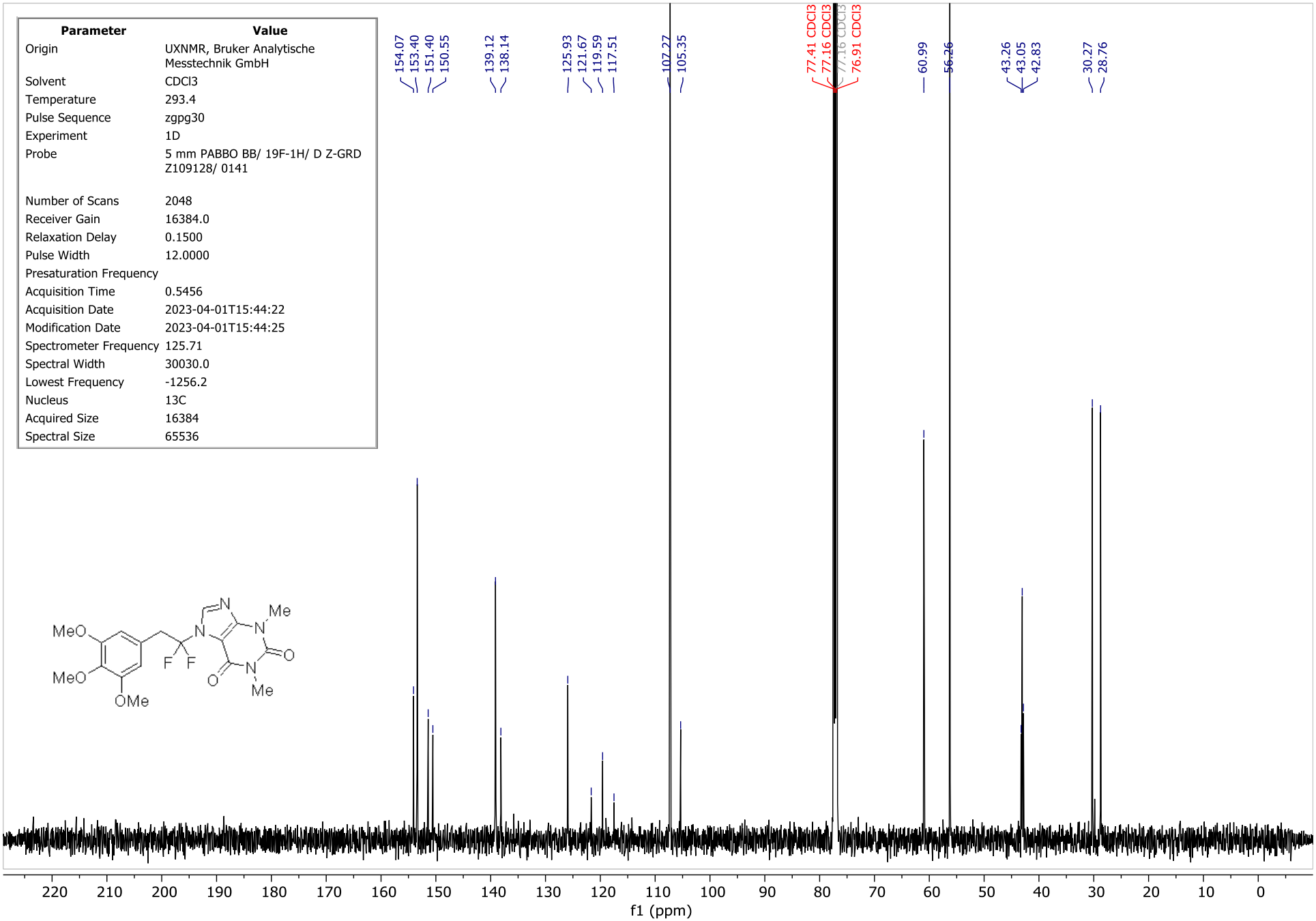


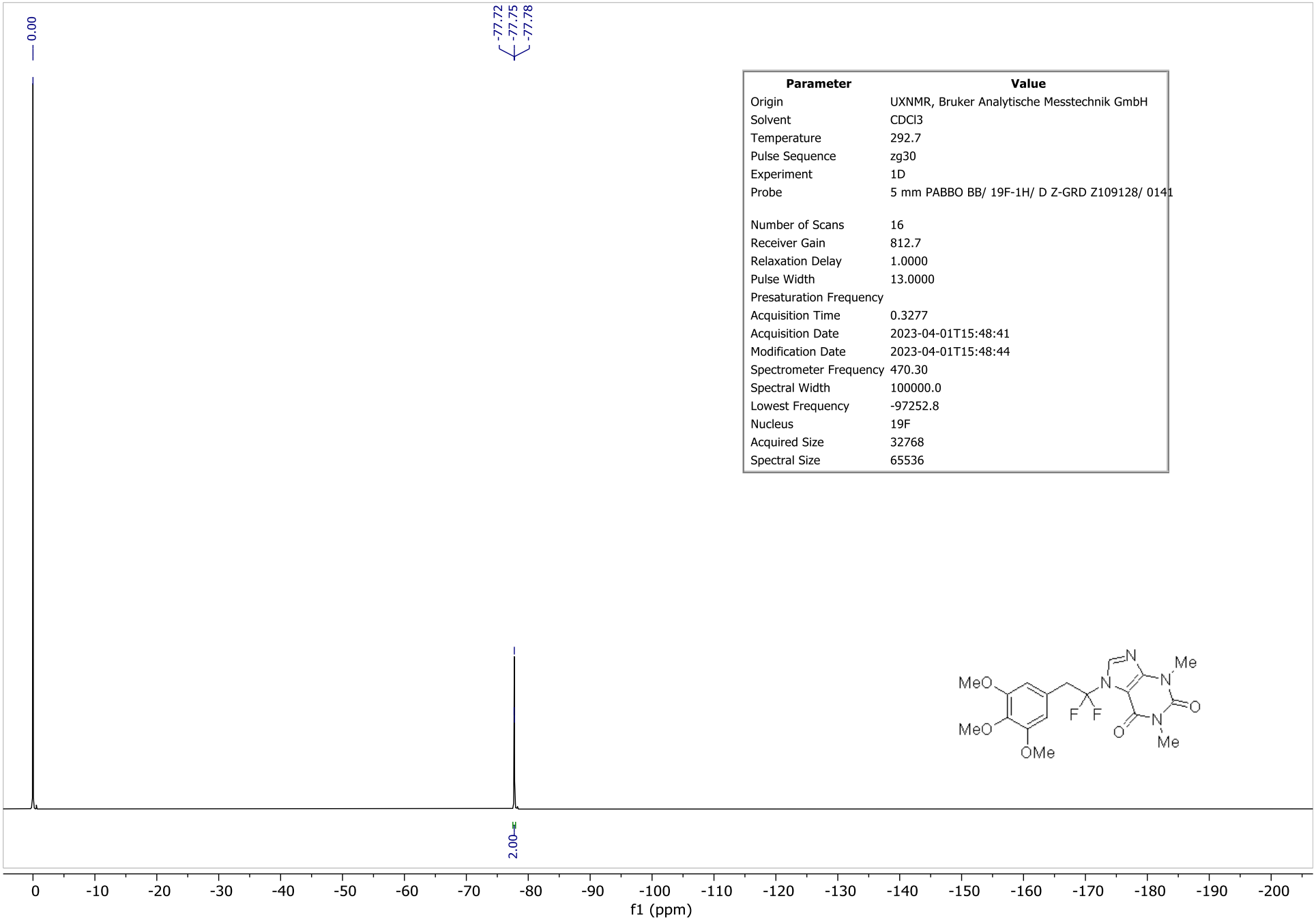
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-04-26T12:31:18
Modification Date	2024-04-26T12:31:19
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97278.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1,3-dimethyl-3,7-dihydro-1*H*-purine-2,6-dione (**11ai**)

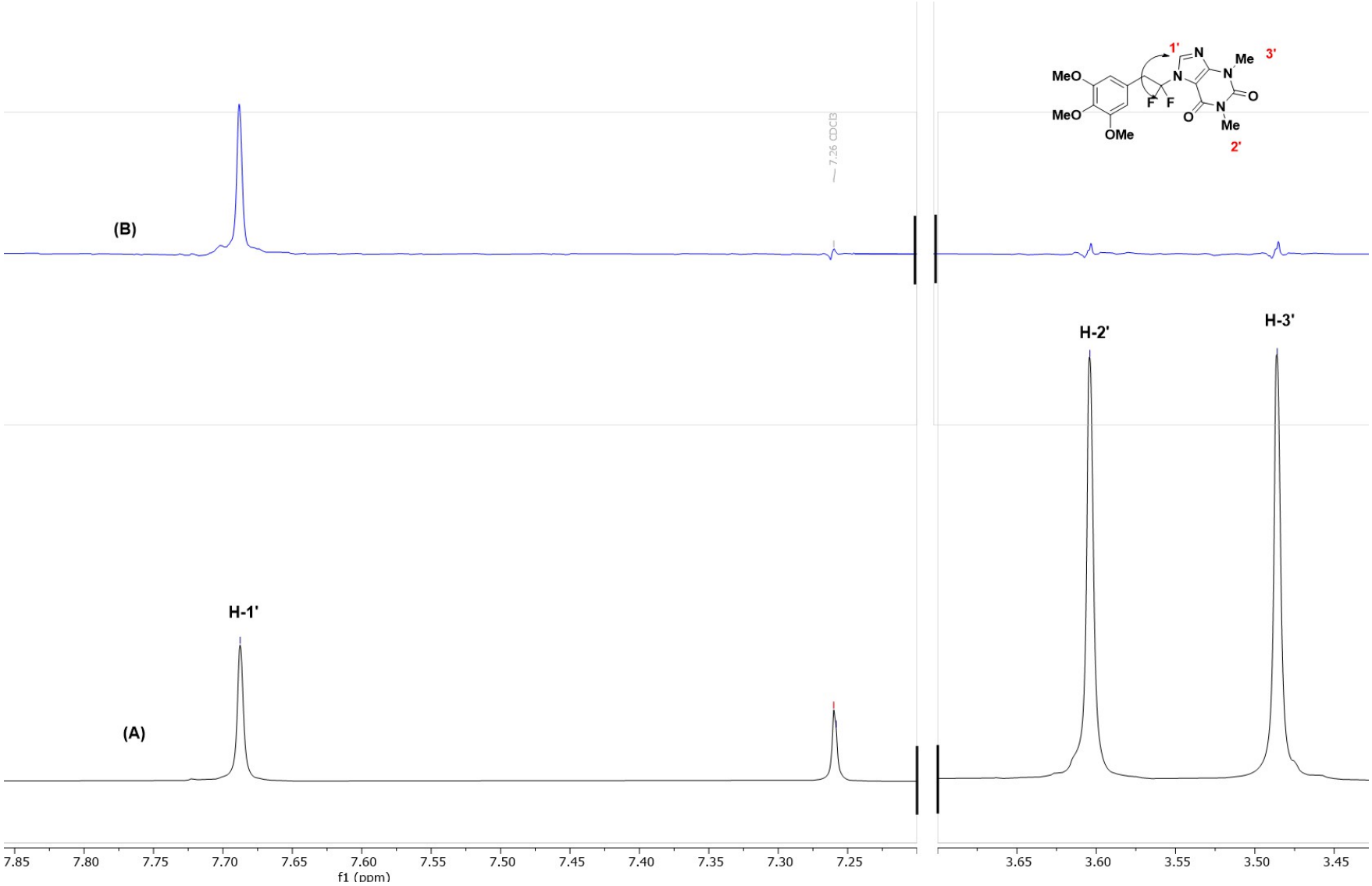


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	256.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-04-01T15:14:41
Modification Date	2023-04-01T15:14:44
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536


Parameter Value
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 293.4
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 2048
Receiver Gain 16384.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.5456
Acquisition Date 2023-04-01T15:44:22
Modification Date 2023-04-01T15:44:25
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -1256.2
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
154.07
153.40
151.40
150.55
139.12
138.14
125.93
121.67
119.59
117.51
107.27
105.35
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
60.99
56.26
43.26
43.05
42.83
30.27
28.76
MeO
MeO
OMe
F
F
N
N
N
N
Me
Me
O
O
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)

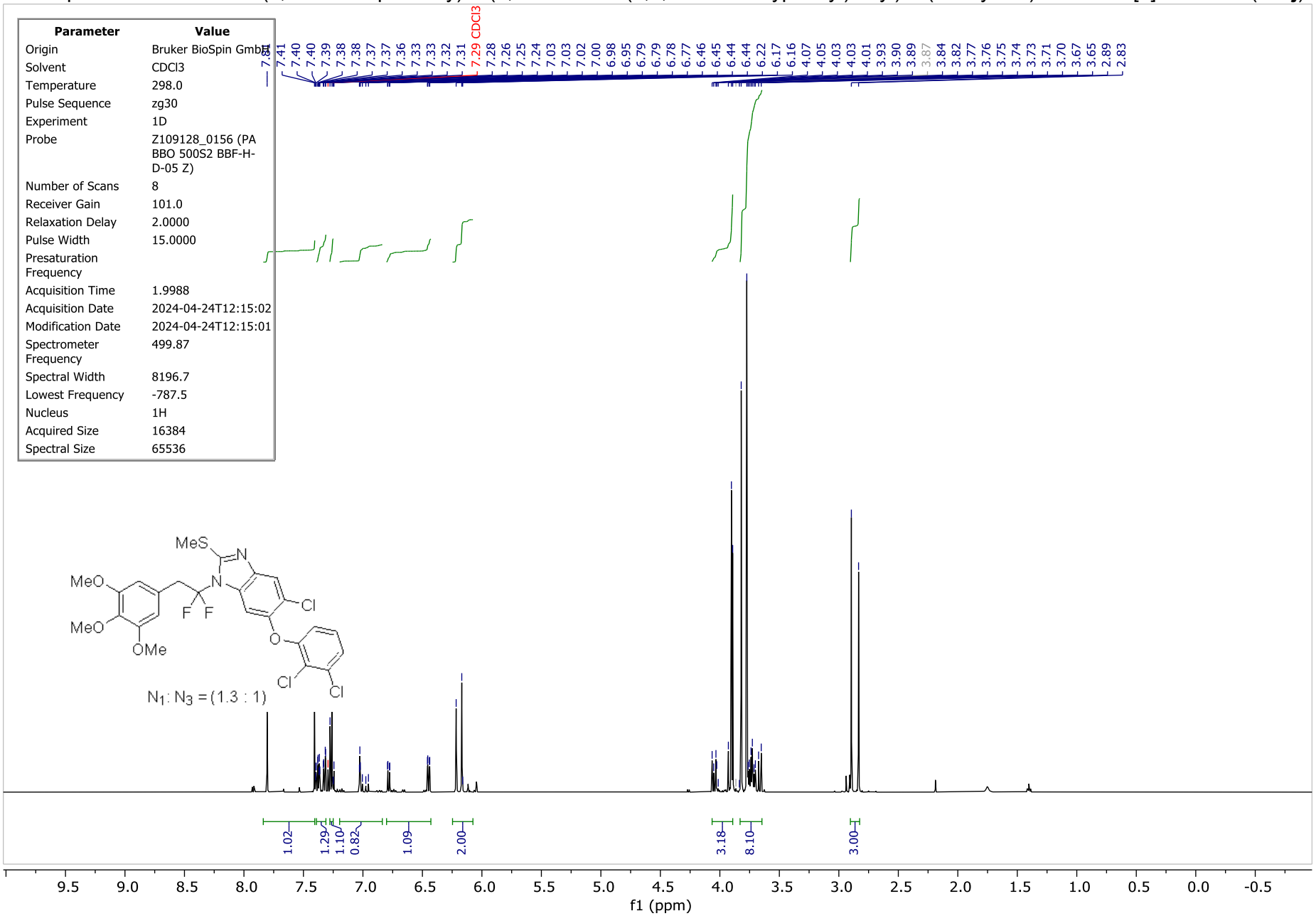


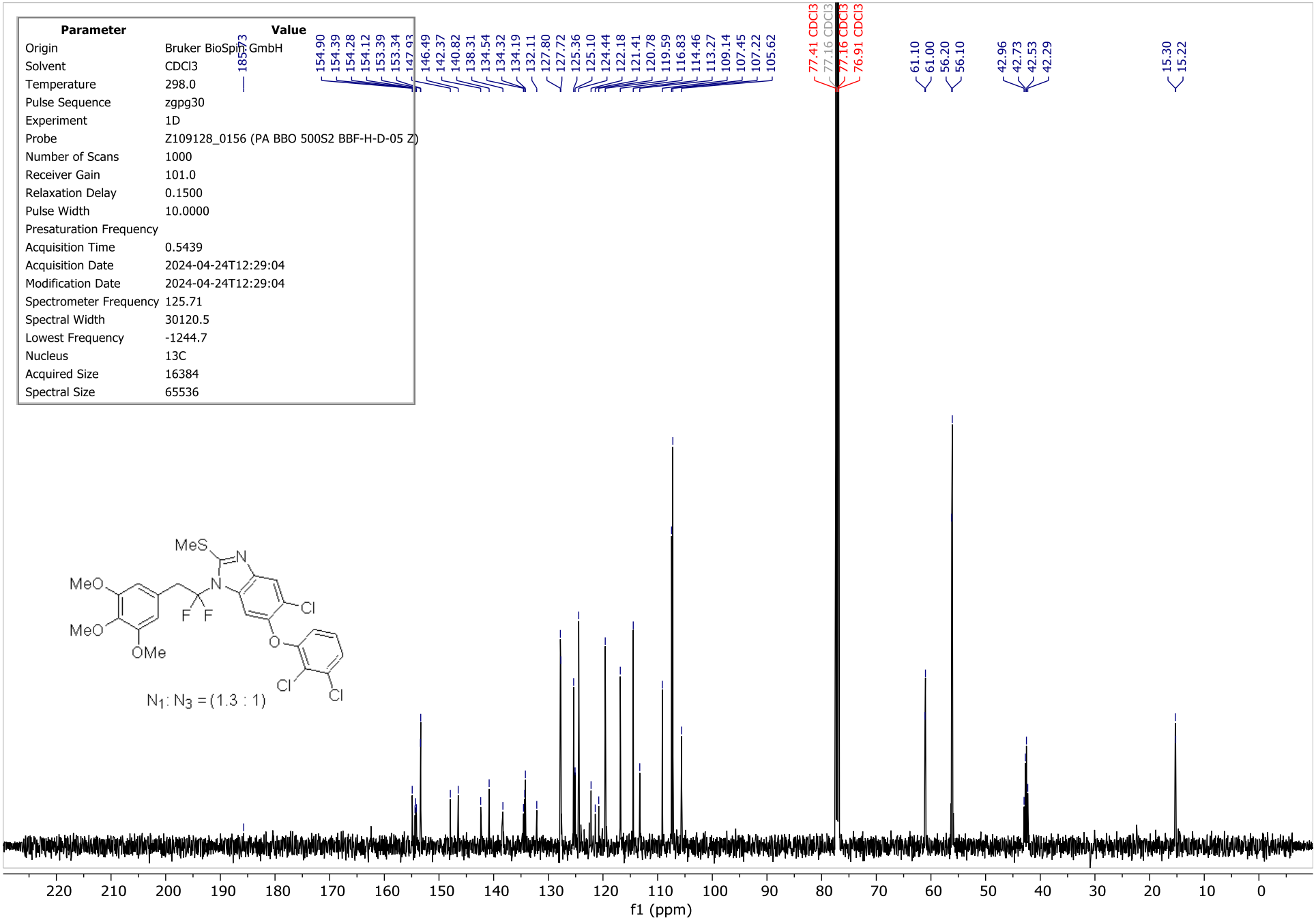
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	812.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-04-01T15:48:41
Modification Date	2023-04-01T15:48:44
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97252.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

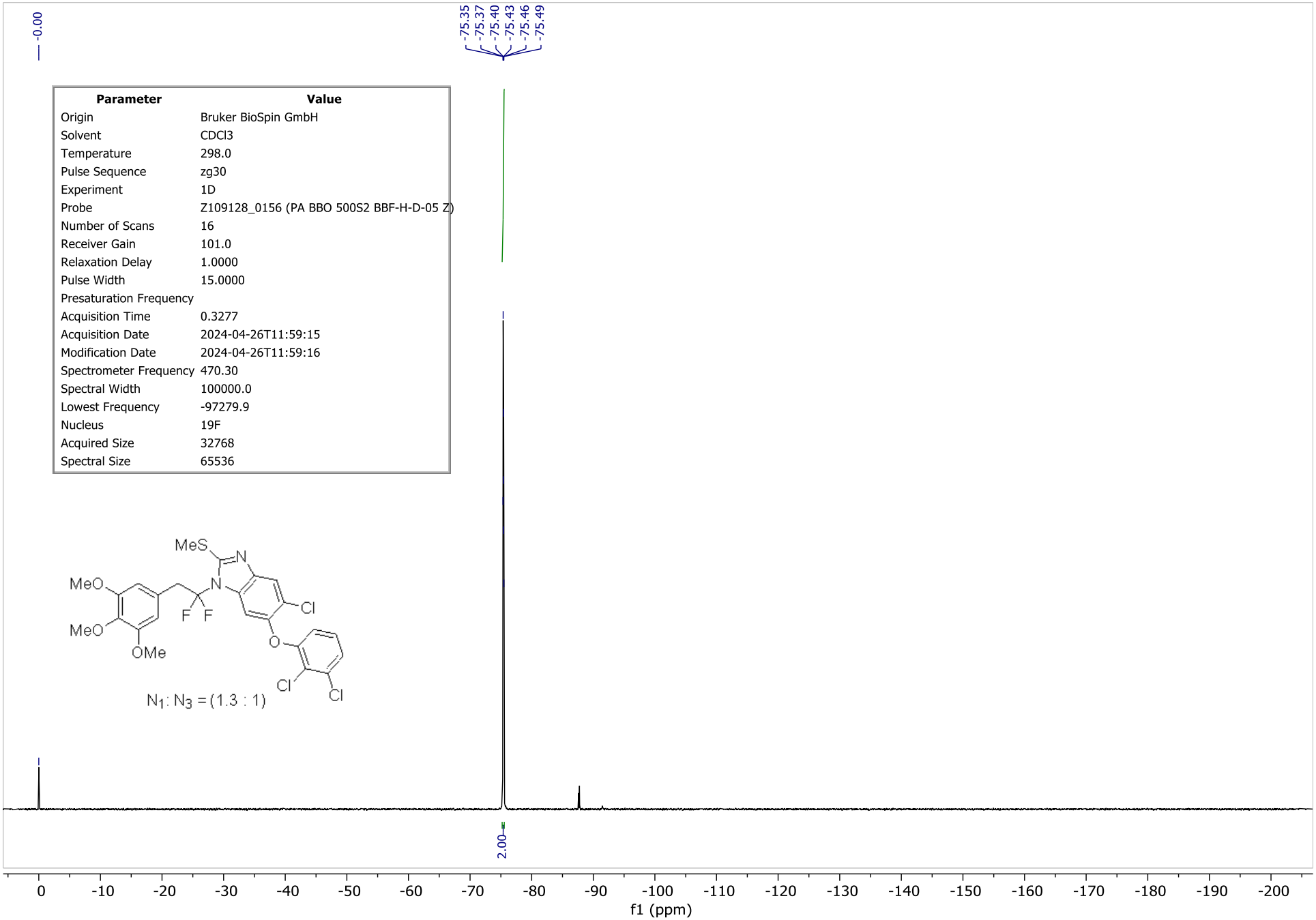


(**A**) ^{1}H NMR spectrum of **11ai**. (**B**) ^{1}H {^{19}F} NOE difference spectrum after preirradiation of ^{19}F δ -77.15.

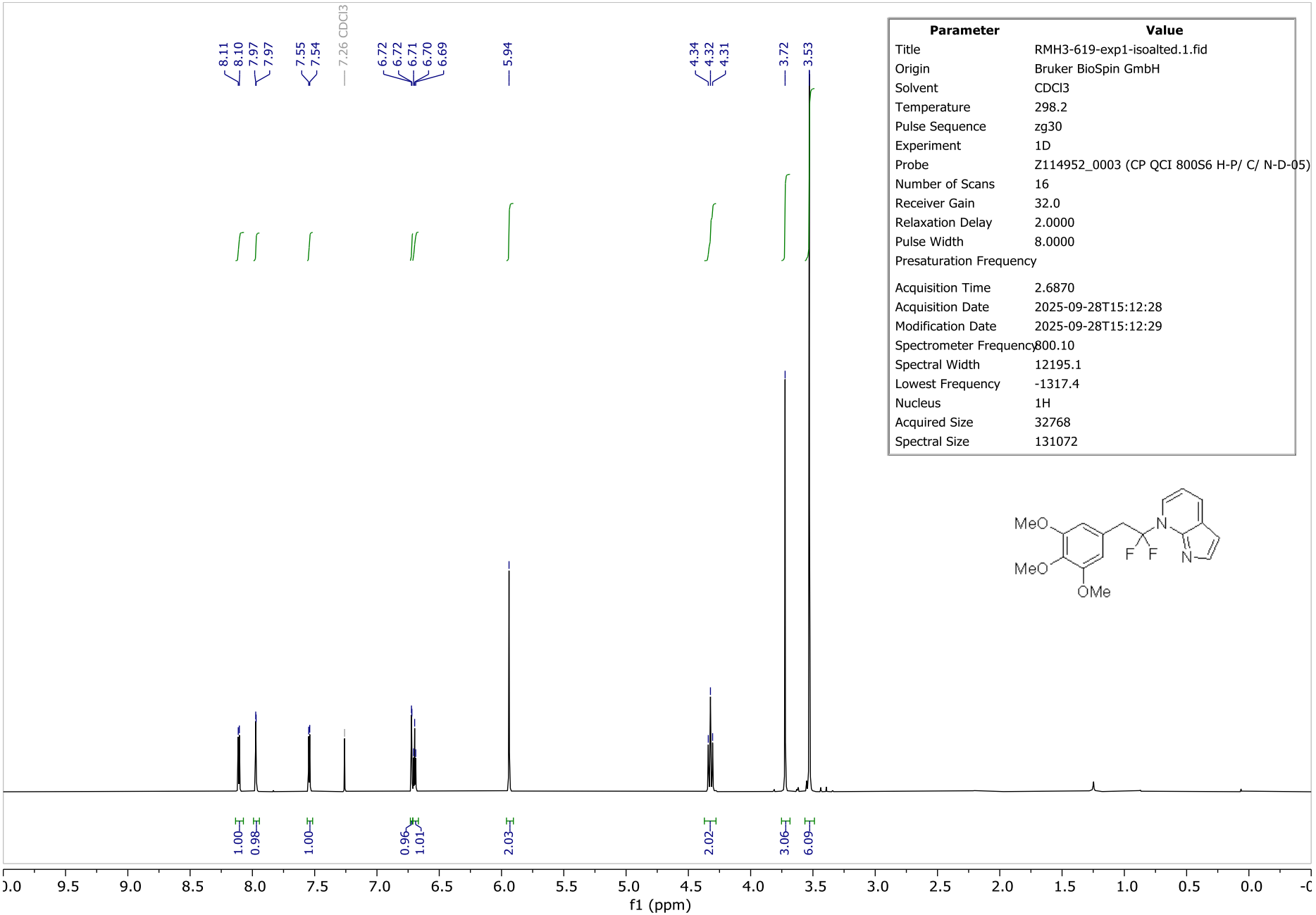
NMR spectra for 5-chloro-6-(2,3-dichlorophenoxy)-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-2-(methylthio)-1*H*-benzo[*d*]imidazole (**11aj**)




Parameter Value
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Pulse Sequence zgpg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 1000
Receiver Gain 101.0
Relaxation Delay 0.1500
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 0.5439
Acquisition Date 2024-04-24T12:29:04
Modification Date 2024-04-24T12:29:04
Spectrometer Frequency 125.71
Spectral Width 30120.5
Lowest Frequency -1244.7
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
185.73
154.90
154.39
154.28
154.12
153.39
153.34
147.93
146.49
142.37
140.82
138.31
134.54
134.32
134.19
132.11
127.80
127.72
125.36
125.10
124.44
122.18
121.41
120.78
119.59
116.83
114.46
113.27
109.14
107.45
107.22
105.62
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
61.10
61.00
56.20
56.10
42.96
42.73
42.53
42.29
15.30
15.22
MeS
N
N
MeO
MeO
OMe
F F
Cl
O
Cl
Cl
N1 : N3 = (1.3 : 1)
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)

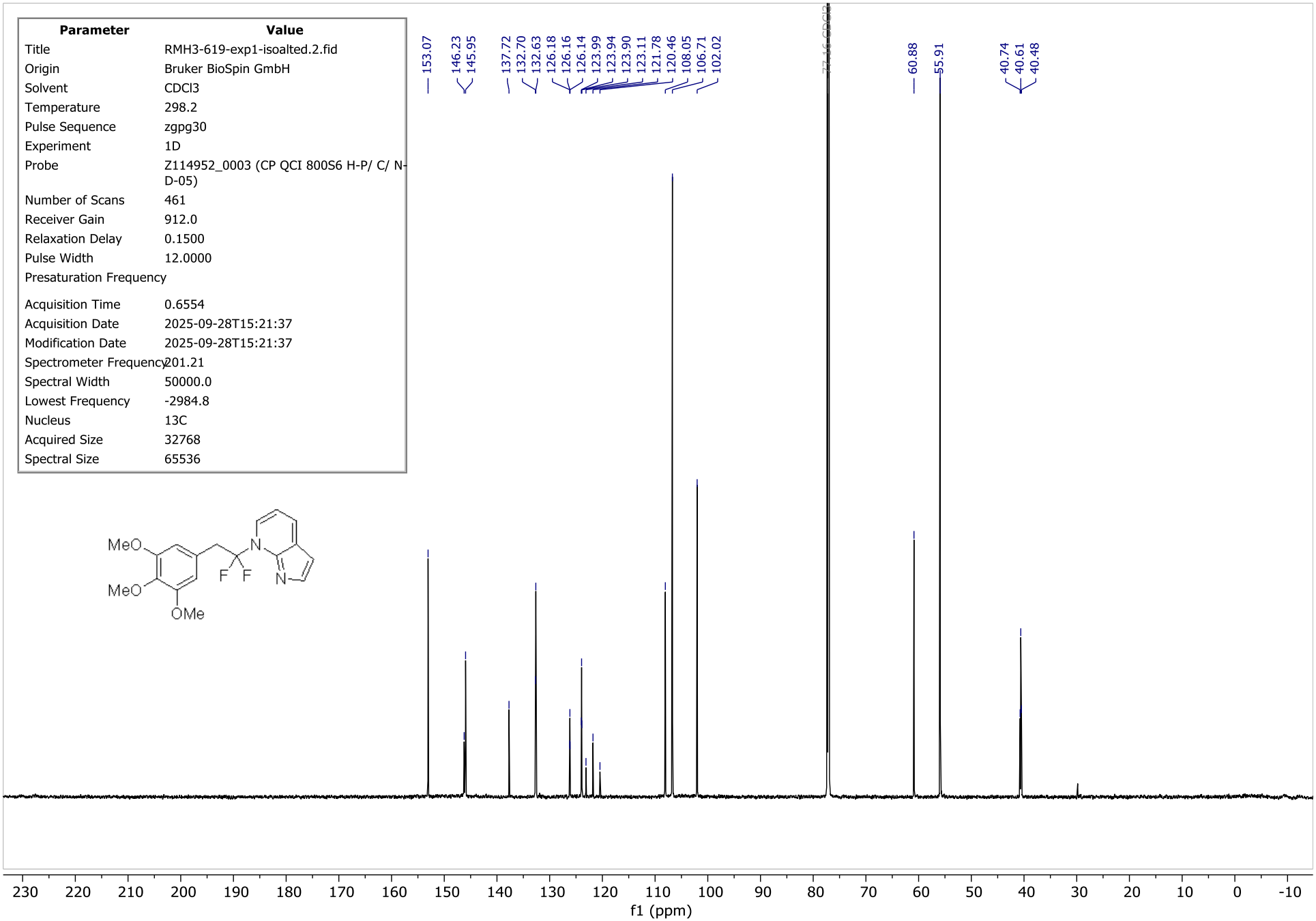

-0.00
-75.35
-75.37
-75.40
-75.43
-75.46
-75.49
Parameter Value
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Pulse Sequence zg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2024-04-26T11:59:15
Modification Date 2024-04-26T11:59:16
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97279.9
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
MeS
N
N
MeO
MeO
OMe
F F
Cl
O
Cl
Cl
N1: N3 = (1.3 : 1)
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)

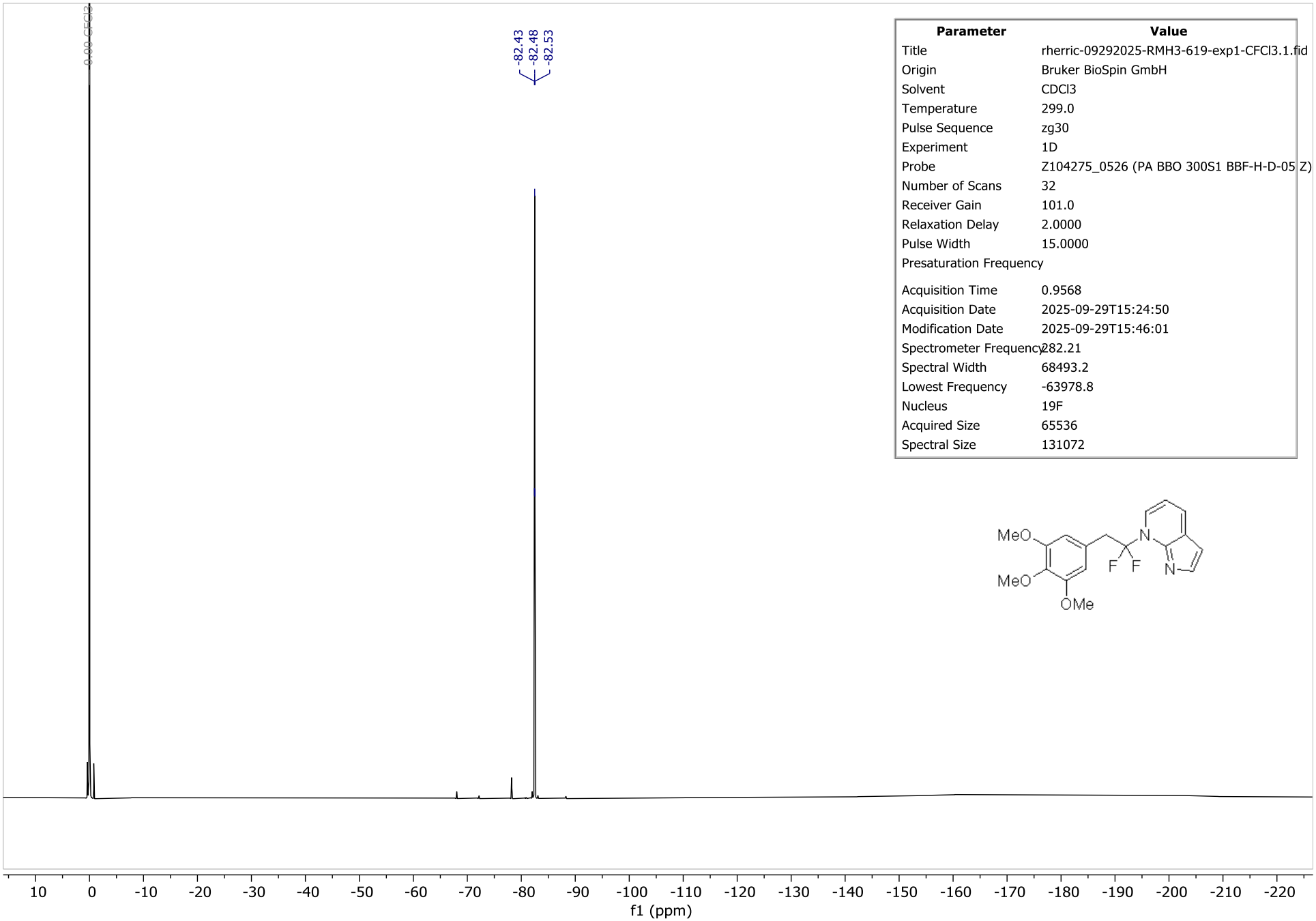
NMR spectra for 7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-7*H*-pyrrolo[2,3-*b*]pyridine (**11ak**)



Parameter	Value
Title	RMH3-619-exp1-isoalted.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	16
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Presaturation Frequency	
Acquisition Time	2.6870
Acquisition Date	2025-09-28T15:12:28
Modification Date	2025-09-28T15:12:29
Spectrometer Frequency	800.10
Spectral Width	12195.1
Lowest Frequency	-1317.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

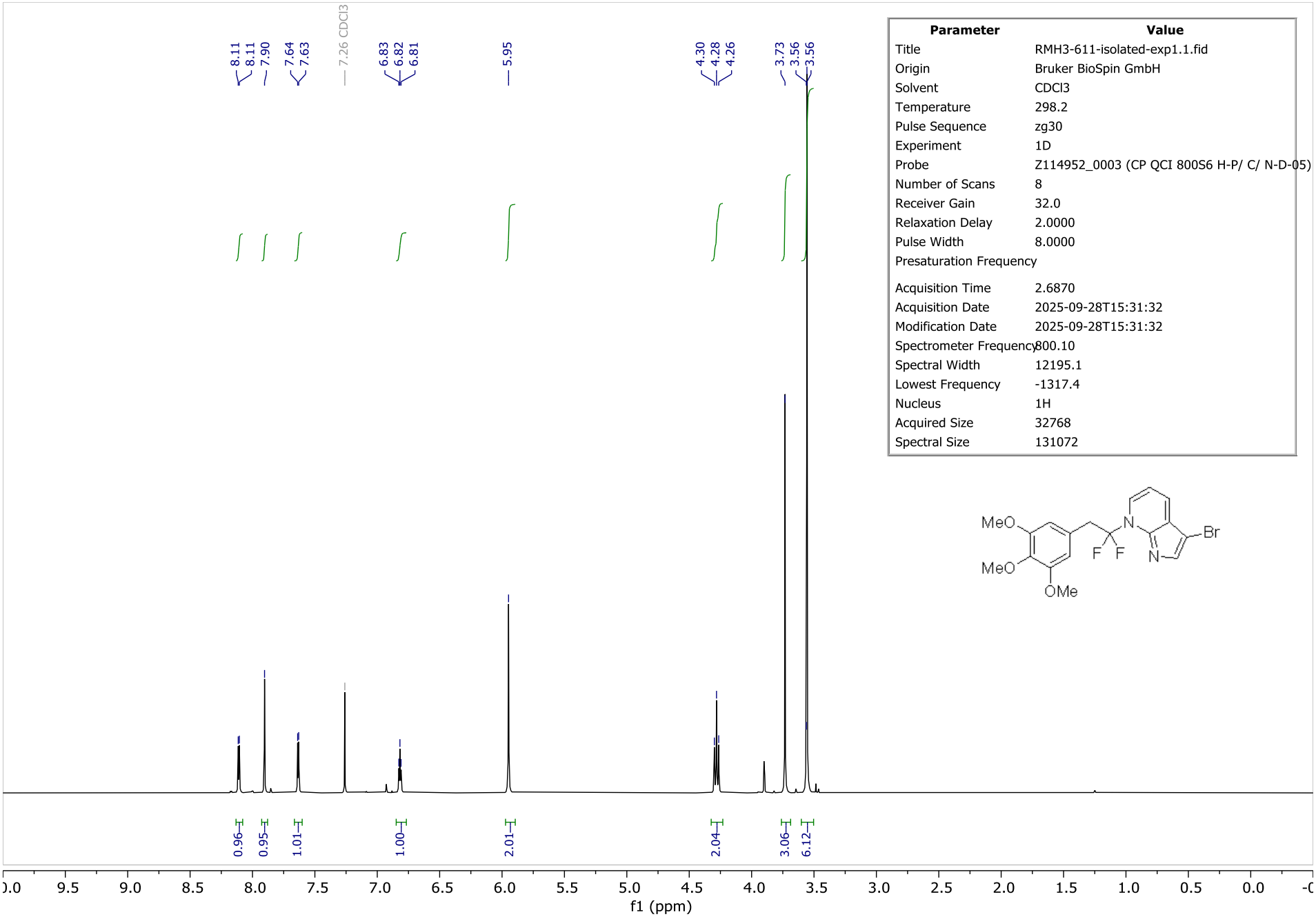
Parameter	Value
Title	RMH3-619-exp1-isoalted.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	461
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2025-09-28T15:21:37
Modification Date	2025-09-28T15:21:37
Spectrometer Frequency	201.21
Spectral Width	50000.0
Lowest Frequency	-2984.8
Nucleus	13C
Acquired Size	32768
Spectral Size	65536





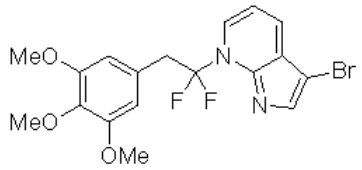
Parameter	Value
Title	rherric-09292025-RMH3-619-exp1-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	299.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z104275_0526 (PA BBO 300S1 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.9568
Acquisition Date	2025-09-29T15:24:50
Modification Date	2025-09-29T15:46:01
Spectrometer Frequency	282.21
Spectral Width	68493.2
Lowest Frequency	-63978.8
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

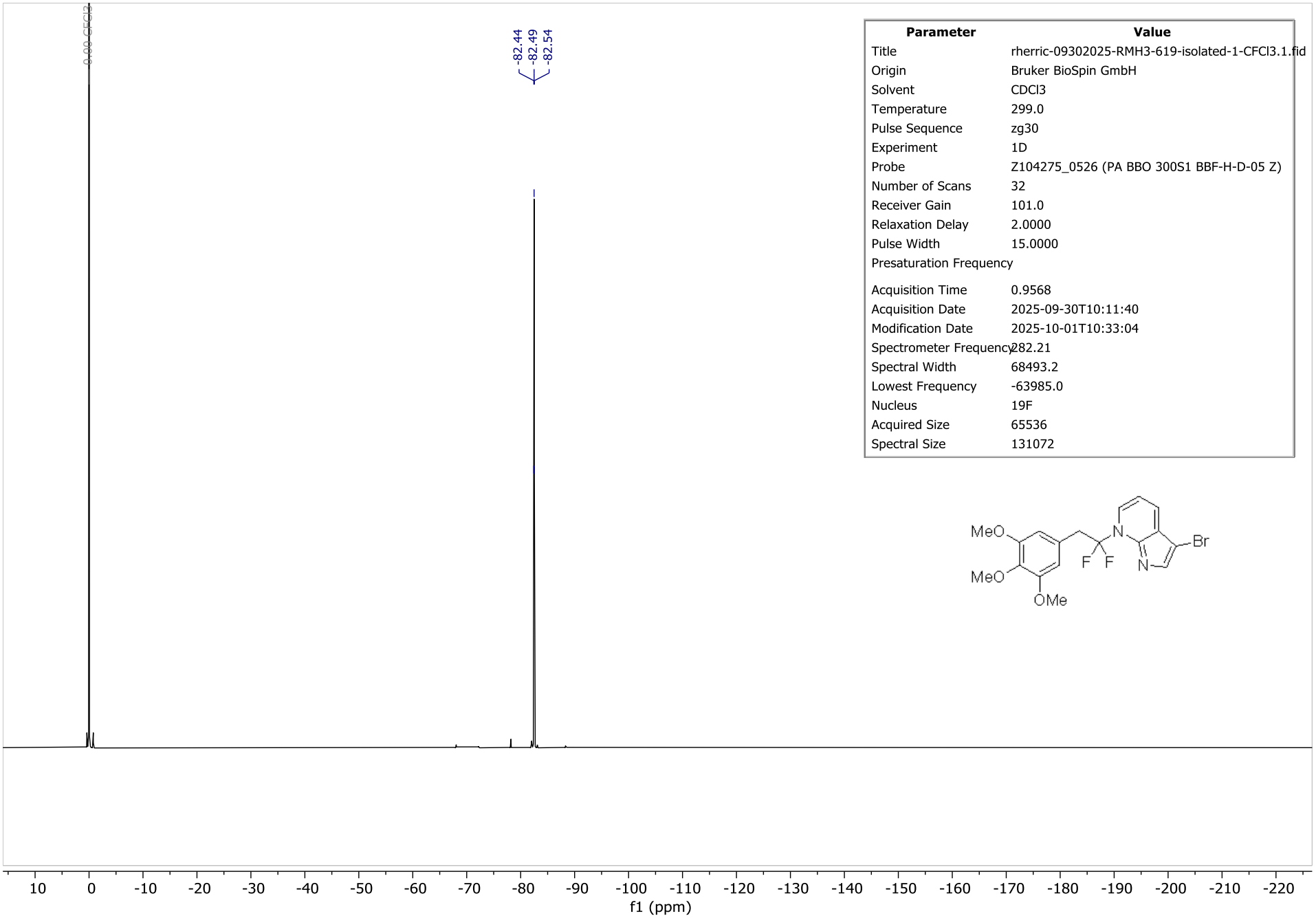
NMR spectra for 3-bromo-7-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-7*H*-pyrrolo[2,3-*b*]pyridine (**11al**)



Parameter	Value
Title	RMH3-611-isolated-exp1.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Presaturation Frequency	
Acquisition Time	2.6870
Acquisition Date	2025-09-28T15:31:32
Modification Date	2025-09-28T15:31:32
Spectrometer Frequency	800.10
Spectral Width	12195.1
Lowest Frequency	-1317.4
Nucleus	1H
Acquired Size	32768
Spectral Size	131072

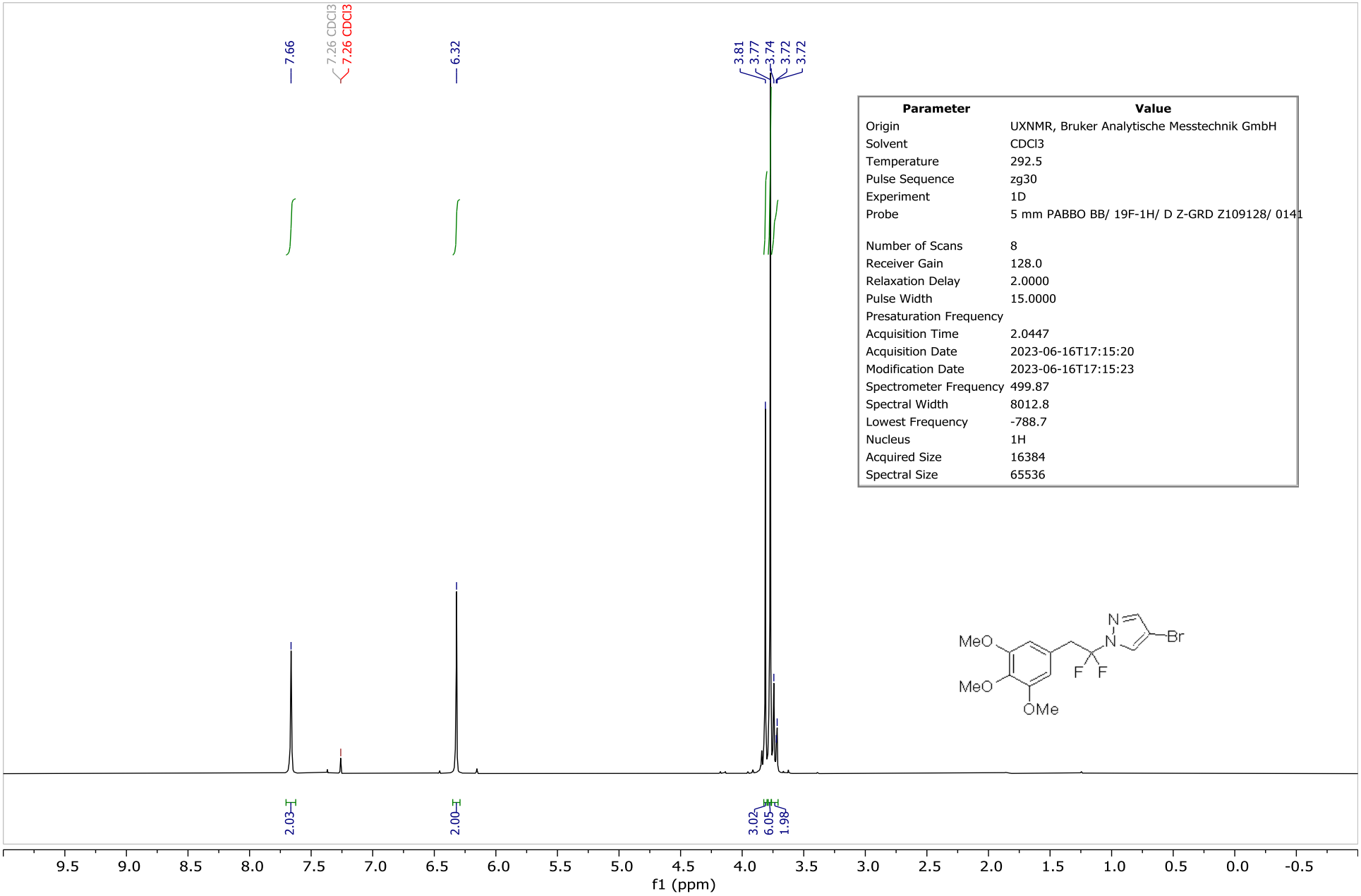
Parameter	Value
Title	RMH3-611-isolated-exp1.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z114952_0003 (CP QCI 800S6 H-P/ C/ N-D-05)
Number of Scans	1000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2025-09-28T15:47:33
Modification Date	2025-09-28T15:47:33
Spectrometer Frequency	201.21
Spectral Width	50000.0
Lowest Frequency	-2982.4
Nucleus	13C
Acquired Size	32768
Spectral Size	65536



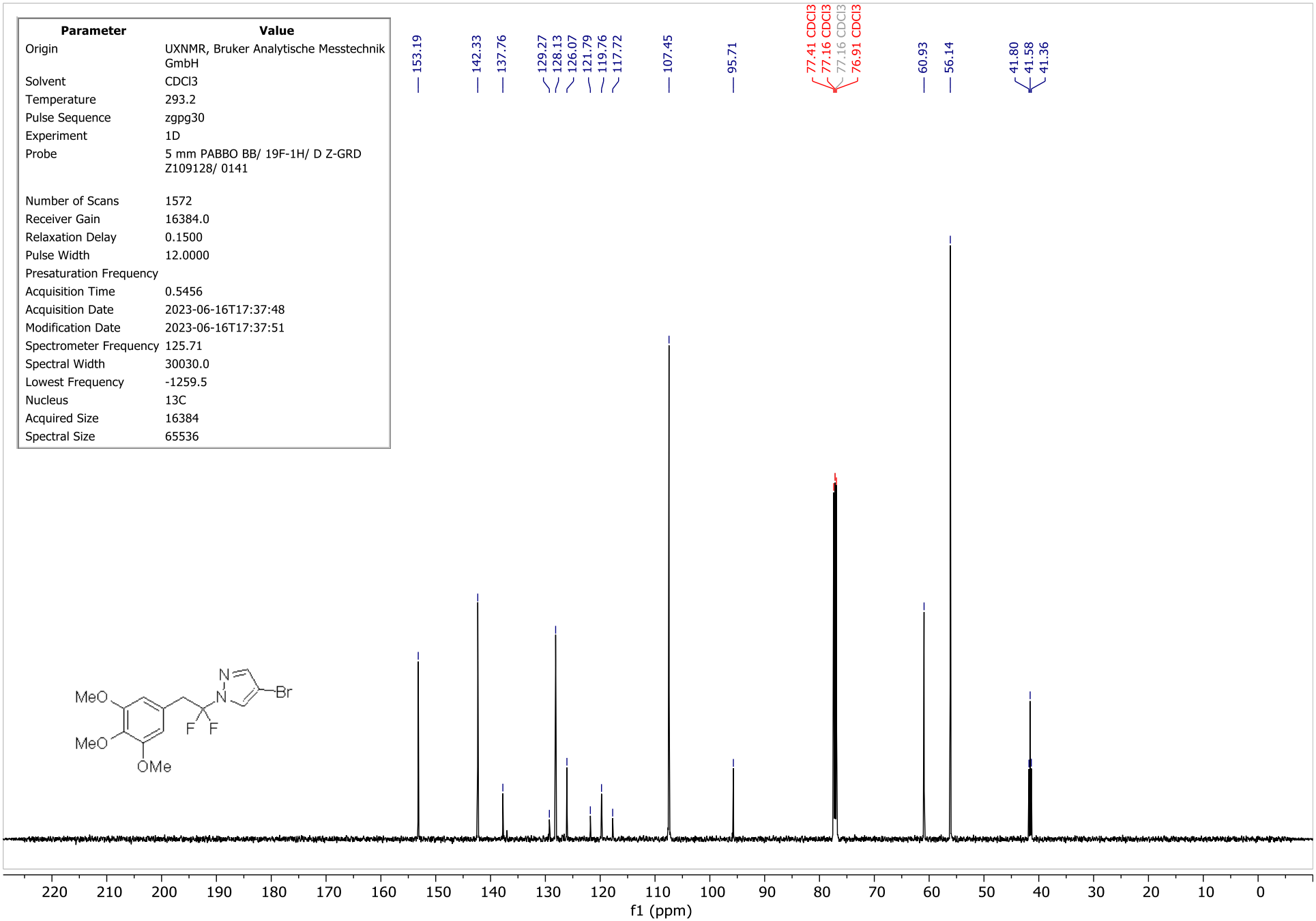


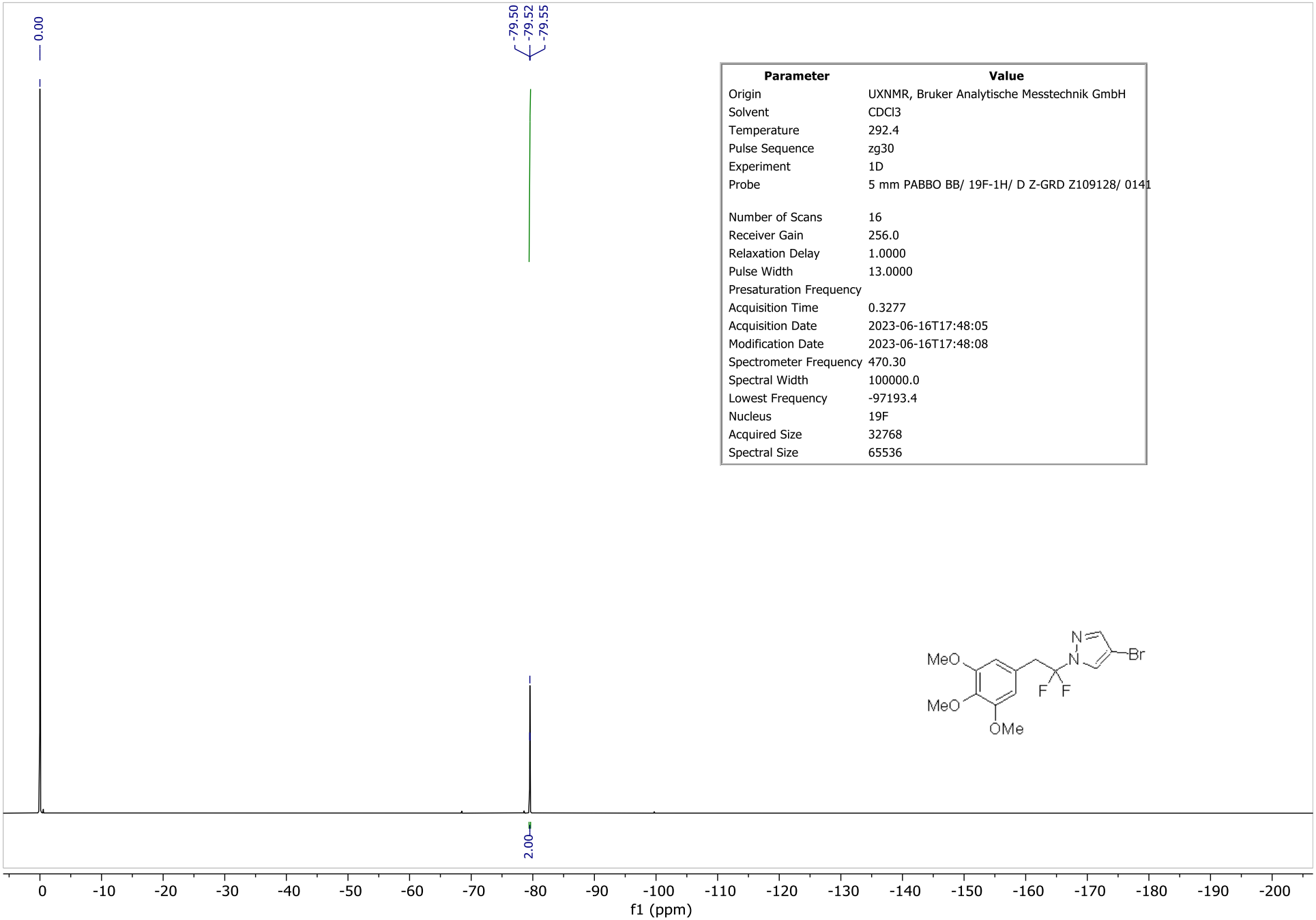
Parameter	Value
Title	rherric-09302025-RMH3-619-isolated-1-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	299.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z104275_0526 (PA BBO 300S1 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.9568
Acquisition Date	2025-09-30T10:11:40
Modification Date	2025-10-01T10:33:04
Spectrometer Frequency	282.21
Spectral Width	68493.2
Lowest Frequency	-63985.0
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

NMR spectra for 4-bromo-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-pyrazole (**11am**)



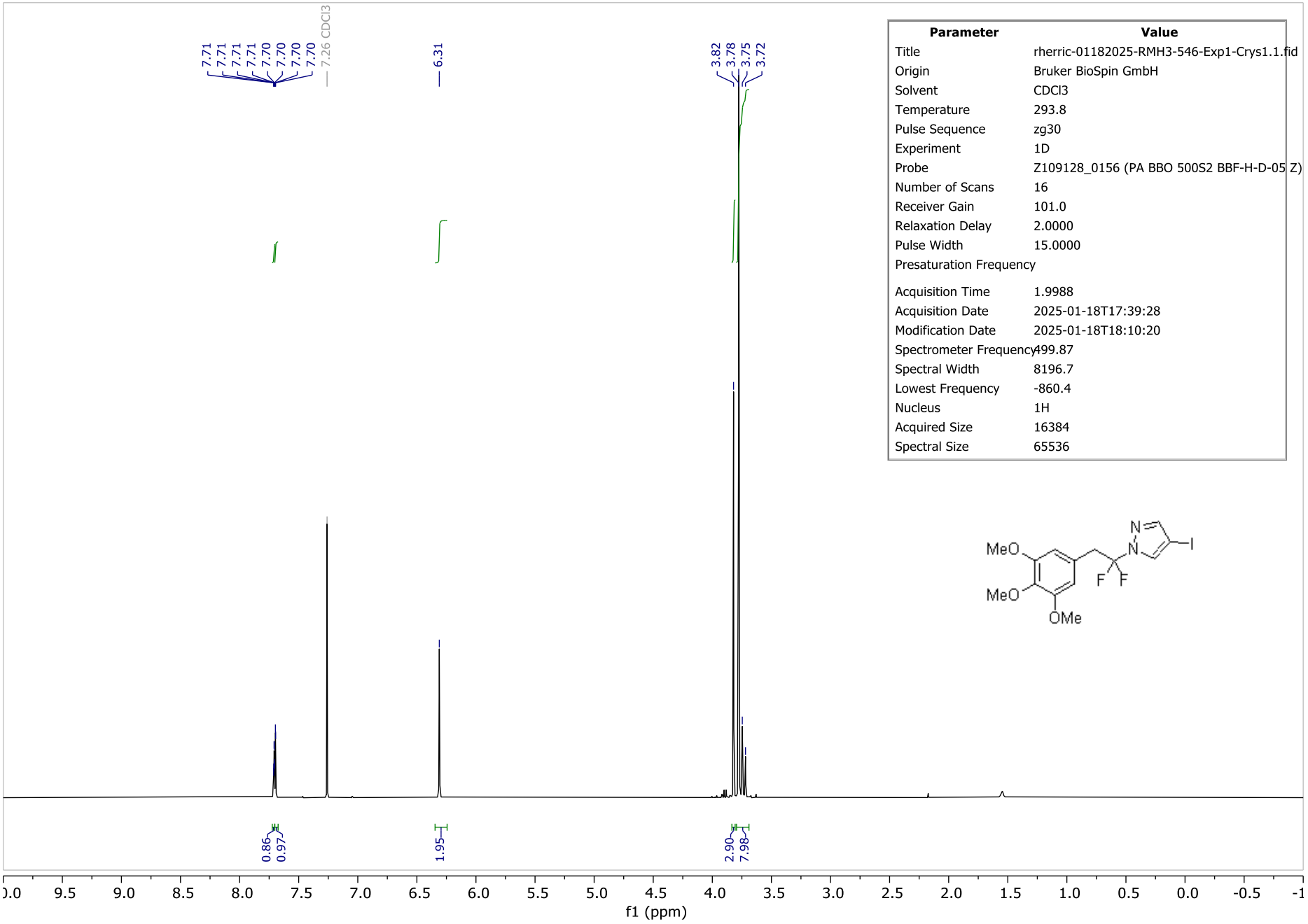
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1572
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-06-16T17:37:48
Modification Date	2023-06-16T17:37:51
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.5
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



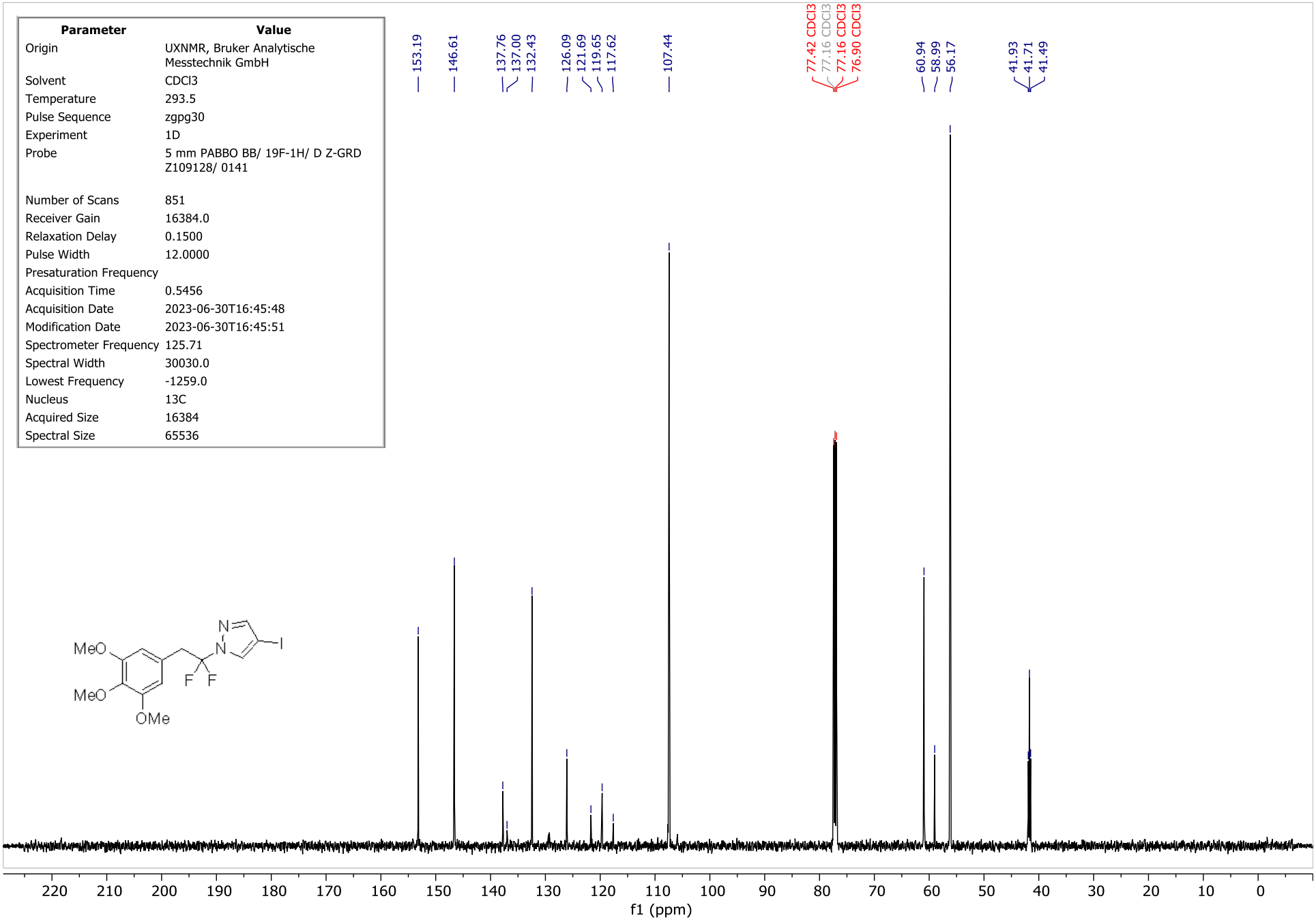


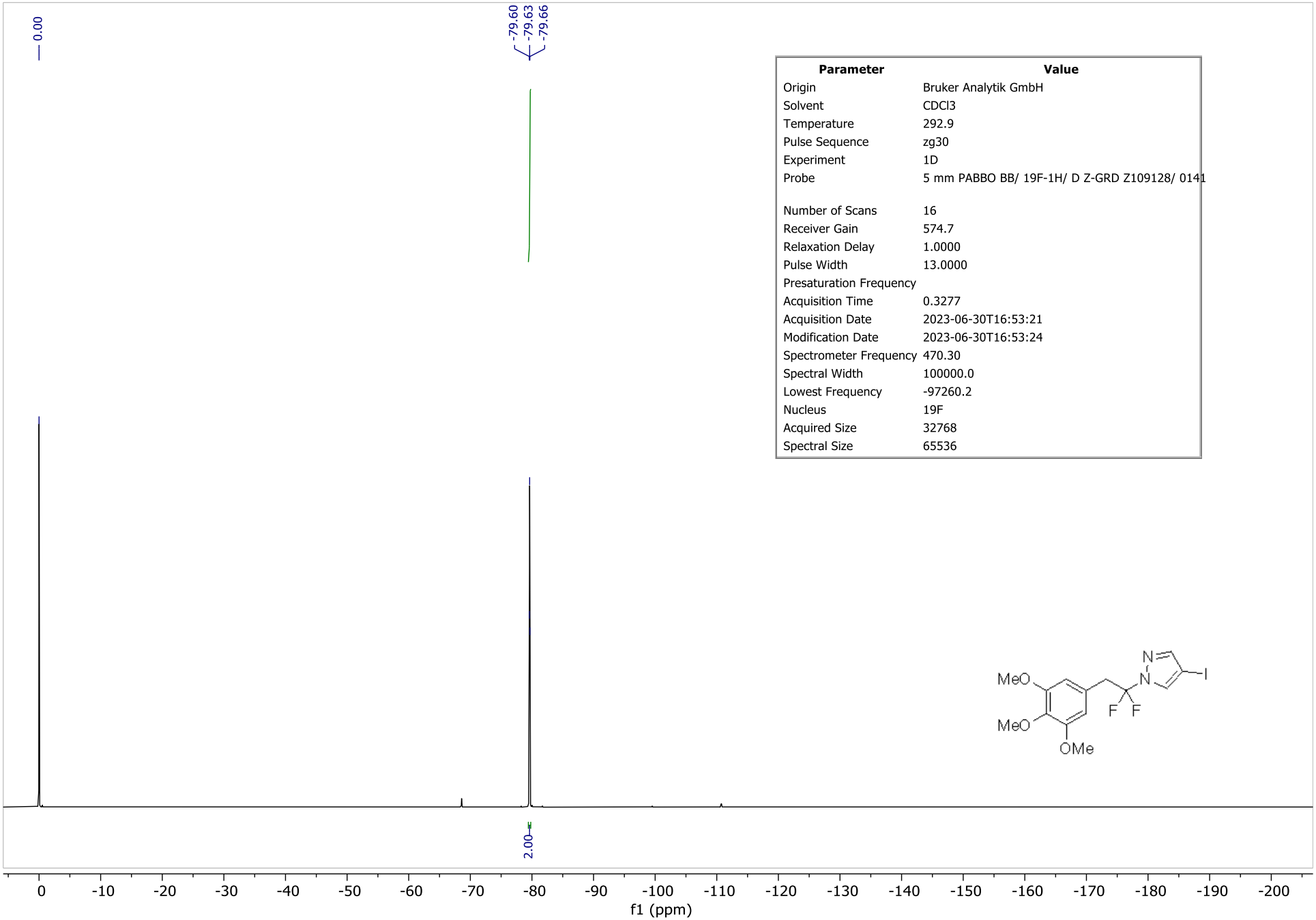
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-06-16T17:48:05
Modification Date	2023-06-16T17:48:08
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97193.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-4-iodo-1*H*-pyrazole (**11an**)



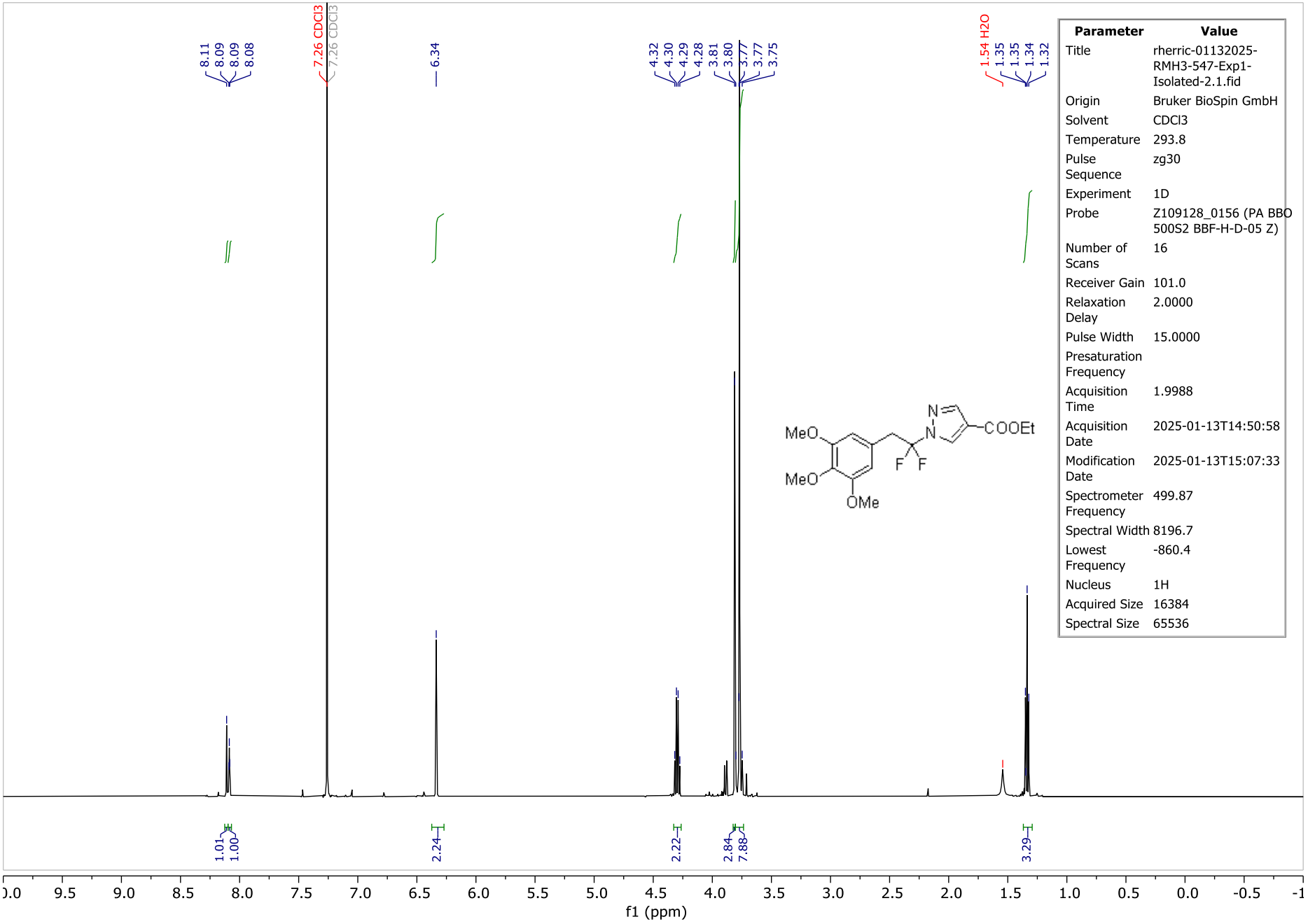
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	851
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-06-30T16:45:48
Modification Date	2023-06-30T16:45:51
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





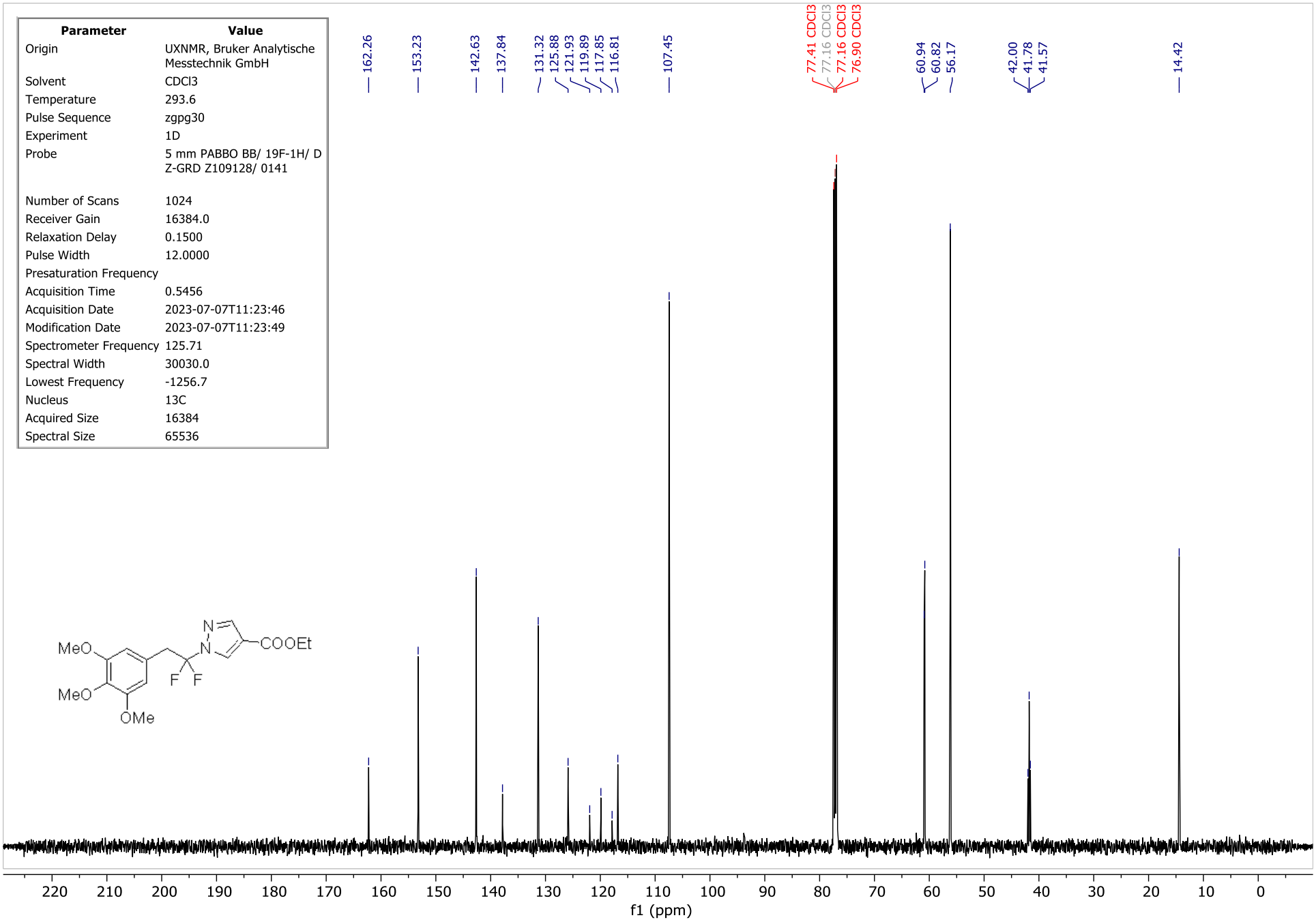
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.9
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-06-30T16:53:21
Modification Date	2023-06-30T16:53:24
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97260.2
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

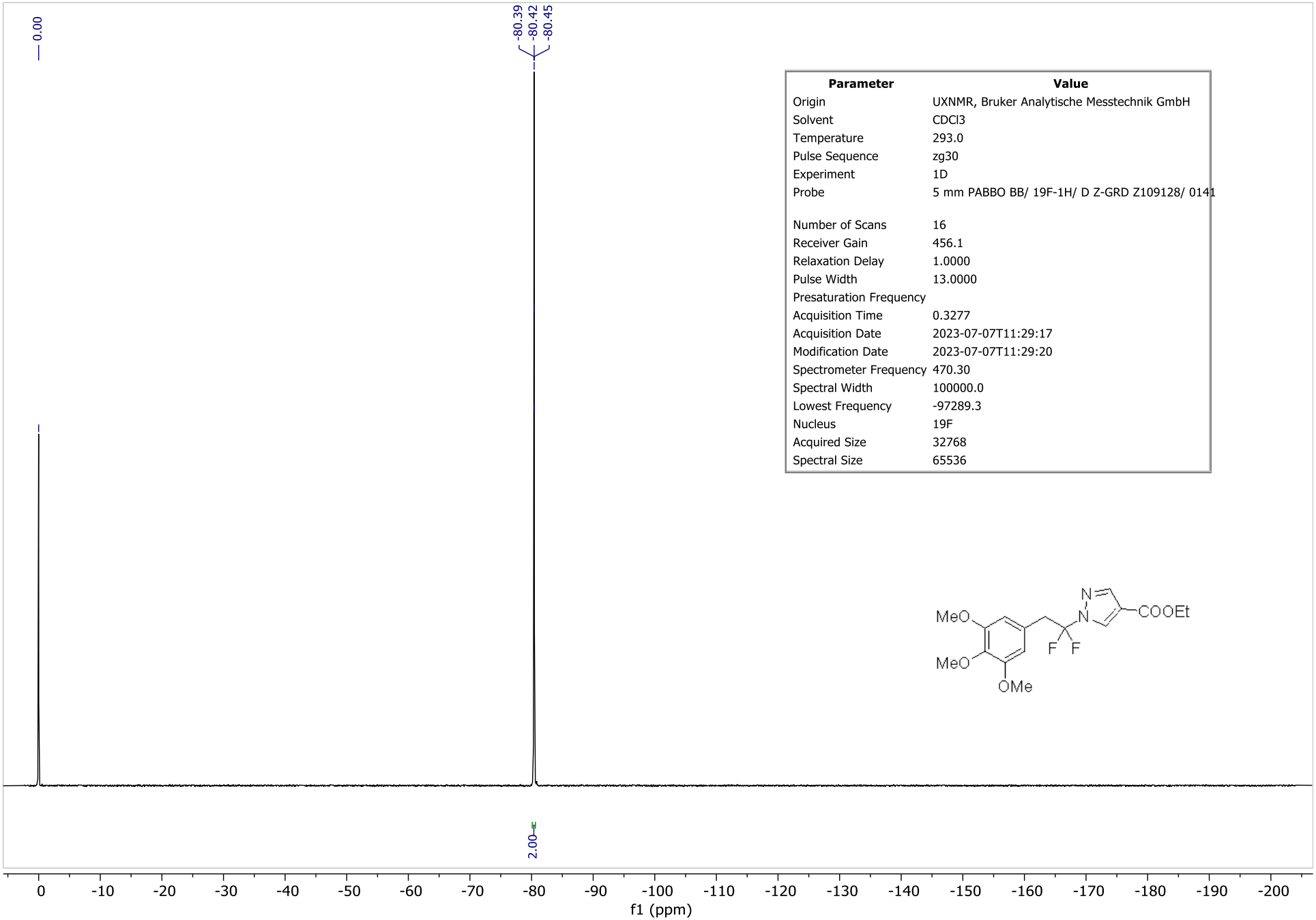
NMR spectra for ethyl 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-*1H*-pyrazole-4-carboxylate (**11ao**)



Parameter	Value
Title	rherric-01132025-RMH3-547-Exp1-Isolated-2.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	1.9988
Acquisition Date	2025-01-13T14:50:58
Modification Date	2025-01-13T15:07:33
Spectrometer Frequency	499.87
Spectral Width	8196.7
Lowest Frequency	-860.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

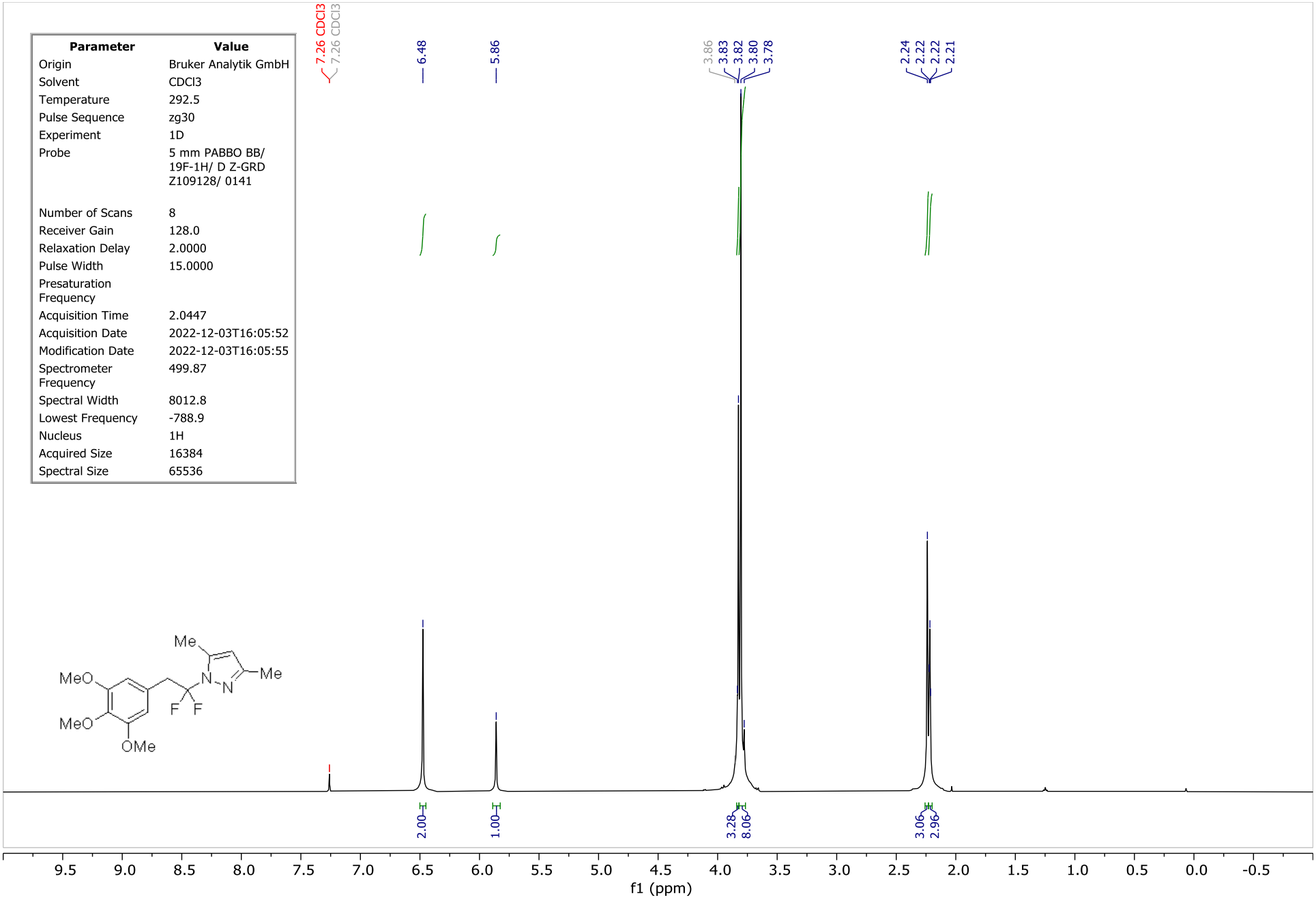
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.6
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1024
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-07-07T11:23:46
Modification Date	2023-07-07T11:23:49
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1256.7
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





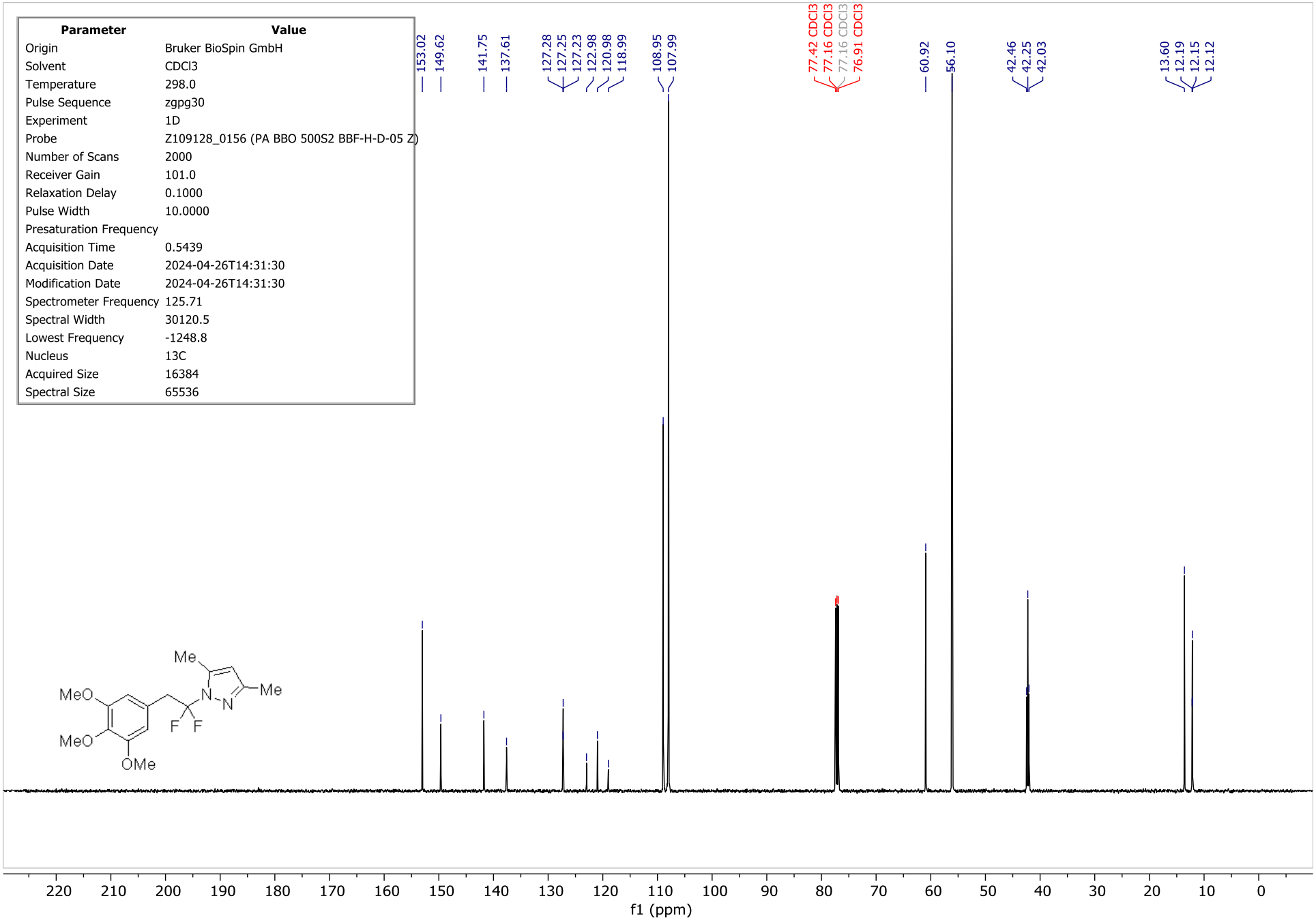
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	456.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-07-07T11:29:17
Modification Date	2023-07-07T11:29:20
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97289.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

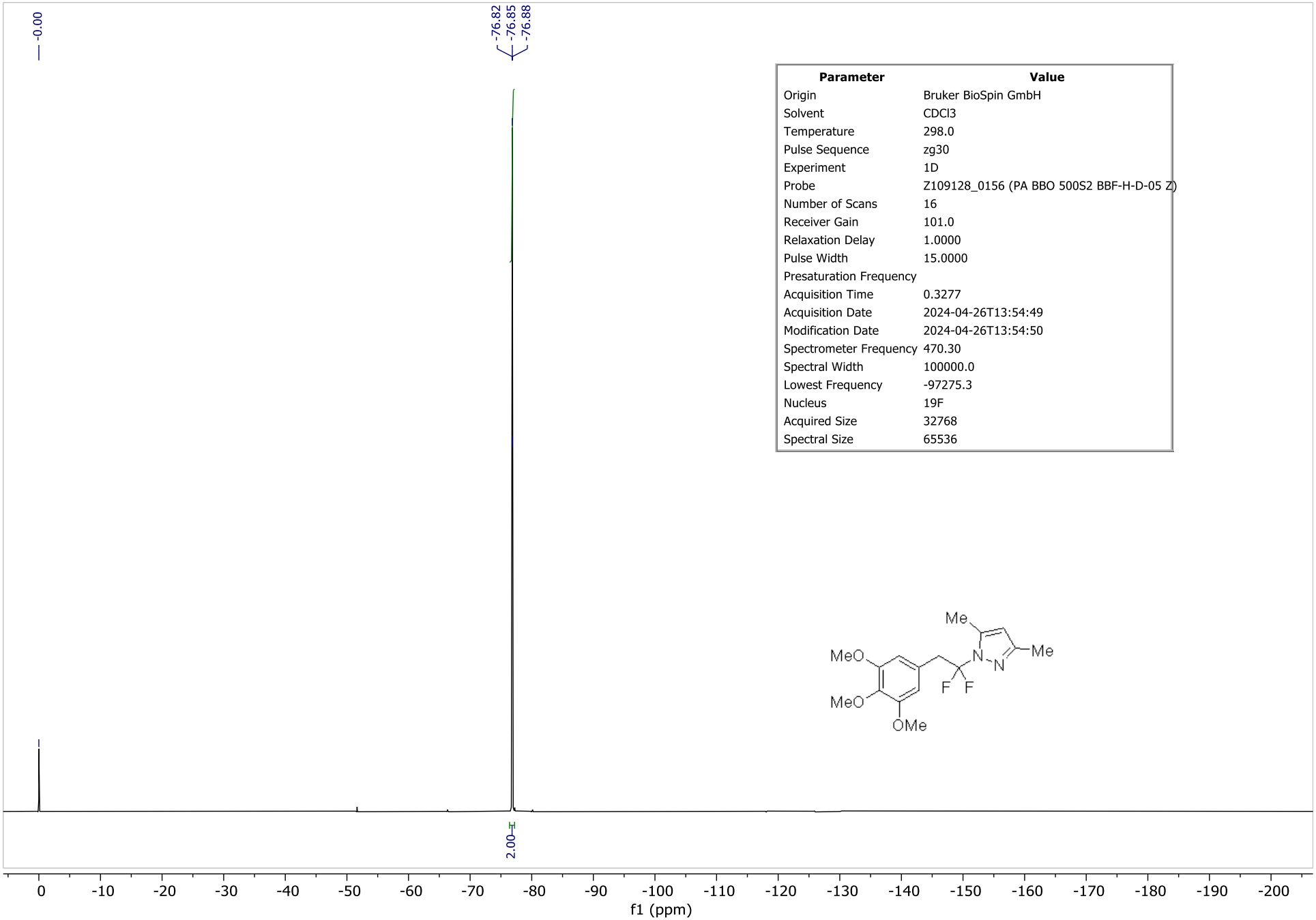
NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-3,5-dimethyl-1*H*-pyrazole (**11ap**)



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	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2022-12-03T16:05:52
Modification Date	2022-12-03T16:05:55
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

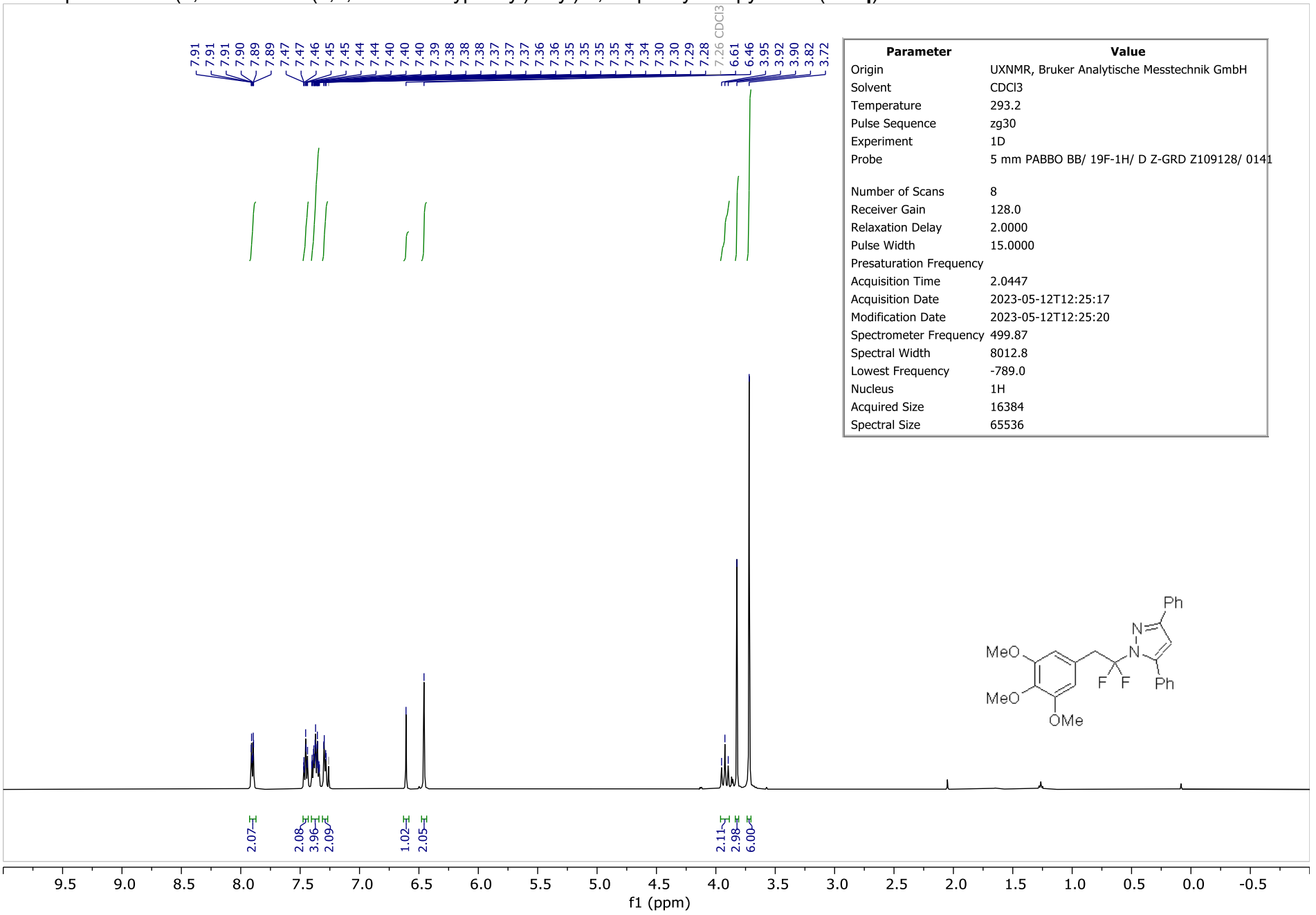
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	2000
Receiver Gain	101.0
Relaxation Delay	0.1000
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	0.5439
Acquisition Date	2024-04-26T14:31:30
Modification Date	2024-04-26T14:31:30
Spectrometer Frequency	125.71
Spectral Width	30120.5
Lowest Frequency	-1248.8
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

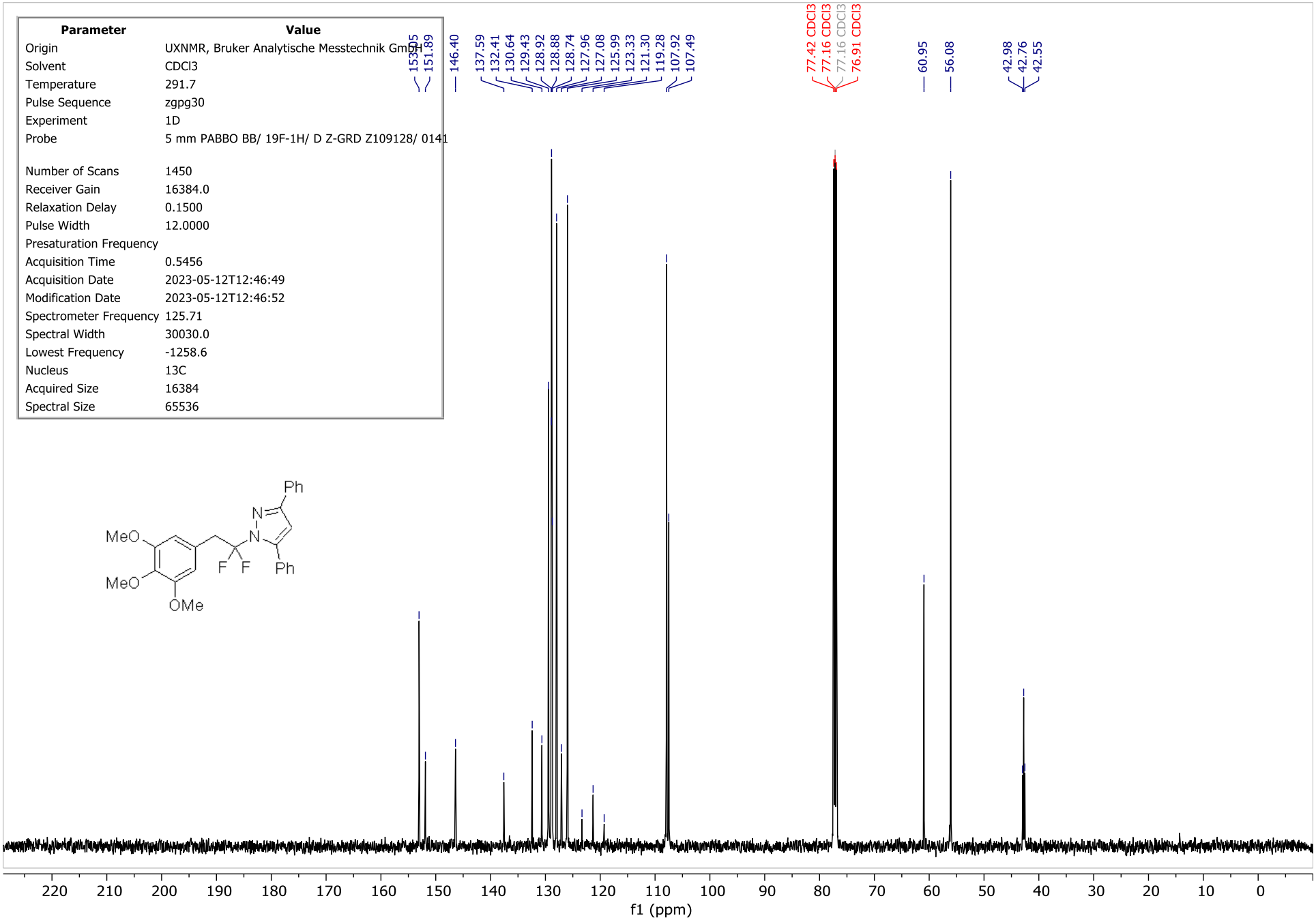


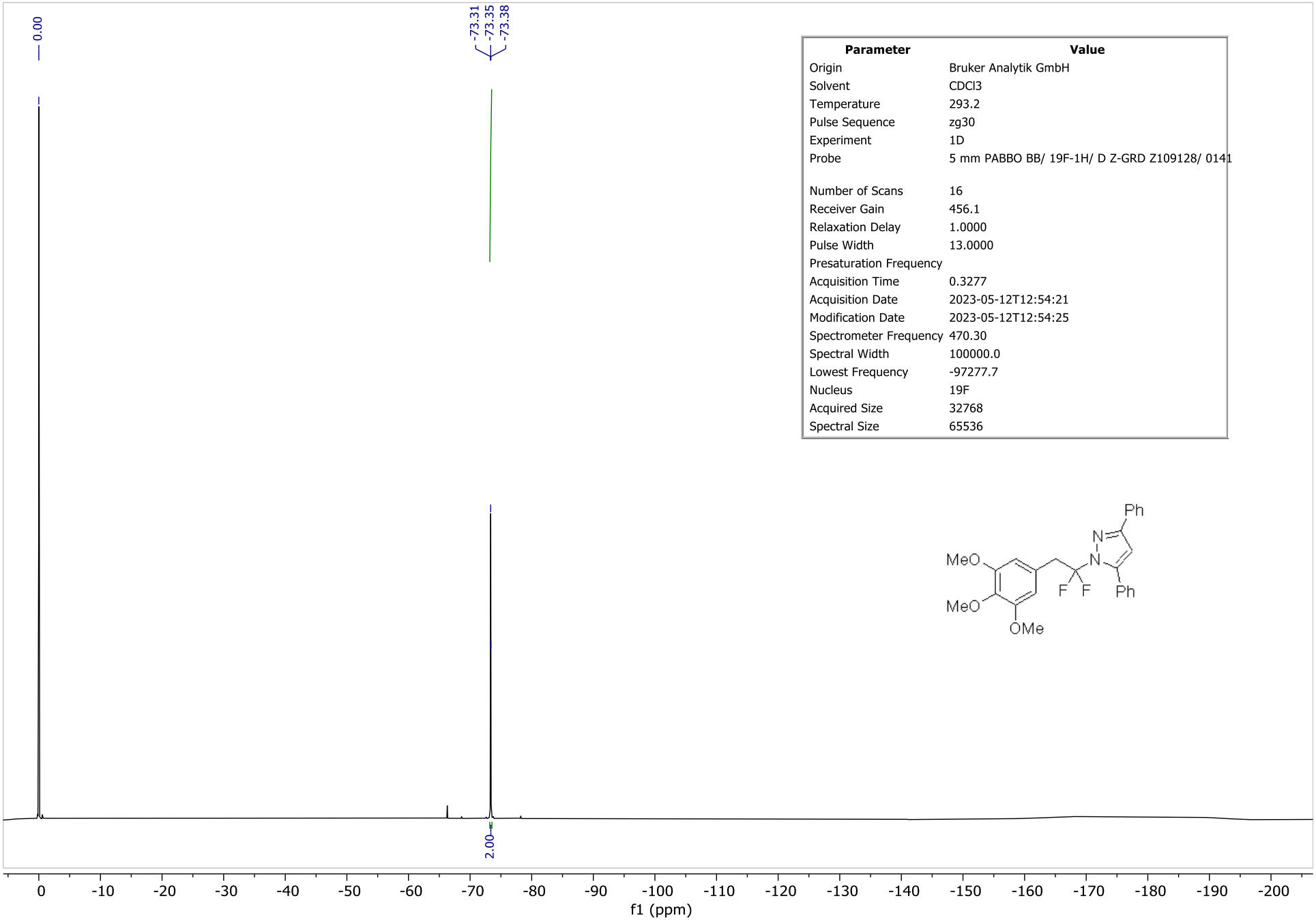


Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-04-26T13:54:49
Modification Date	2024-04-26T13:54:50
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97275.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(1,1-Difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-3,5-diphenyl-1*H*-pyrazole (**11aq**)

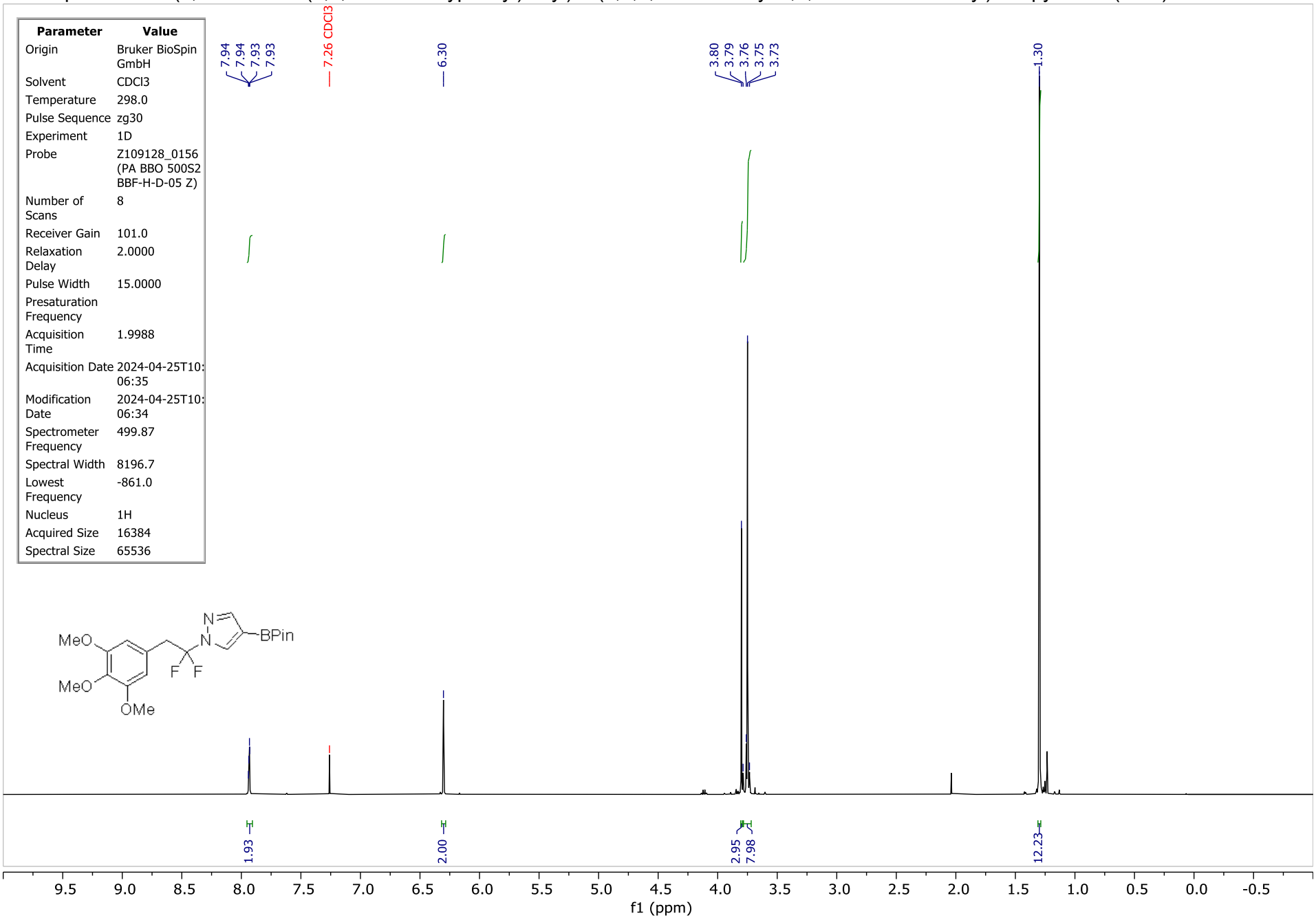


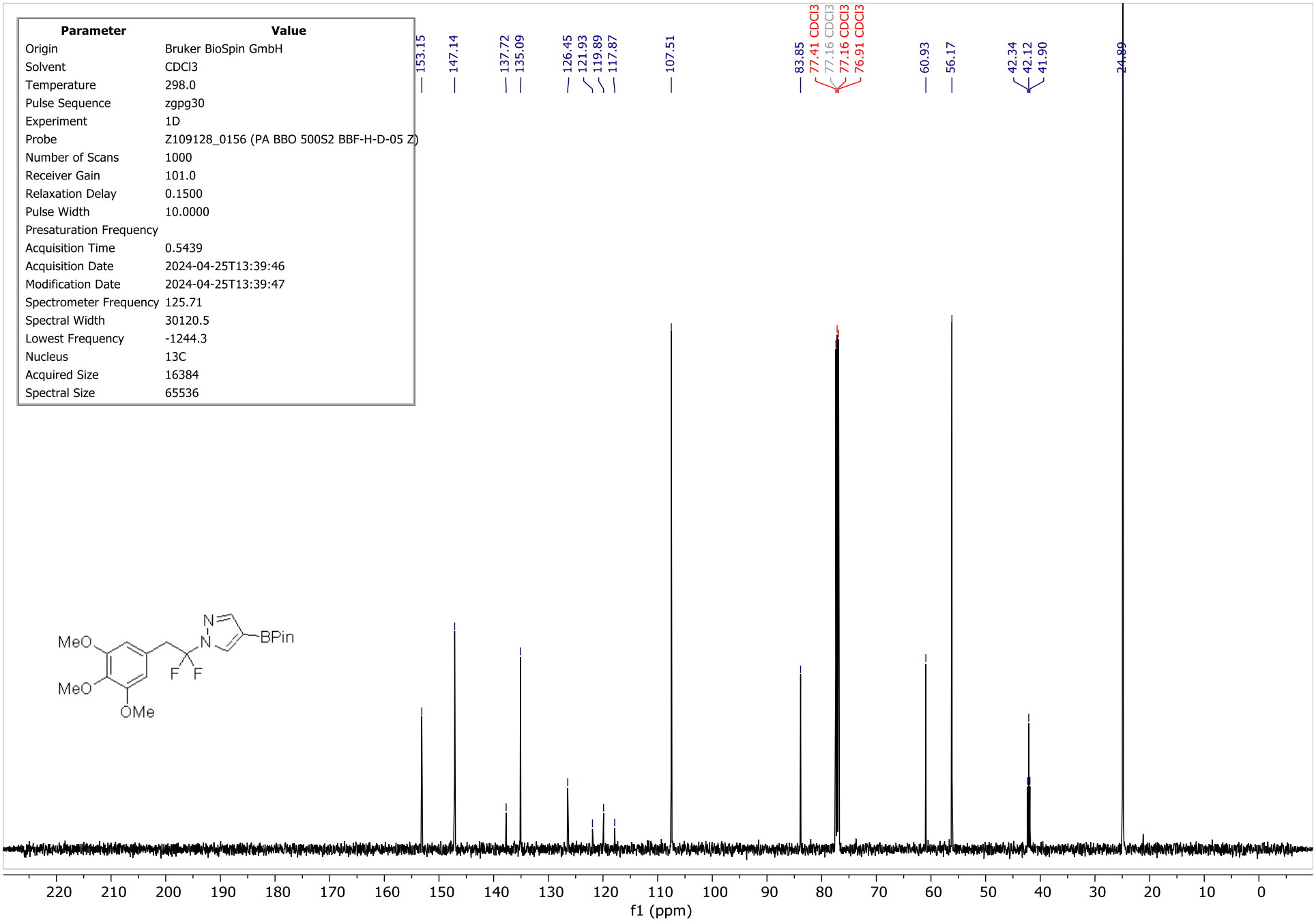

Parameter Value
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 291.7
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 1450
Receiver Gain 16384.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.5456
Acquisition Date 2023-05-12T12:46:49
Modification Date 2023-05-12T12:46:52
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -1258.6
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
153.55
151.89
146.40
137.59
132.41
130.64
129.43
128.92
128.88
128.74
127.96
127.08
125.99
123.33
121.30
119.28
107.92
107.49
77.42 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
60.95
56.08
42.98
42.76
42.55
Ph
N
N
MeO
MeO
OMe
F
F
Ph
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)

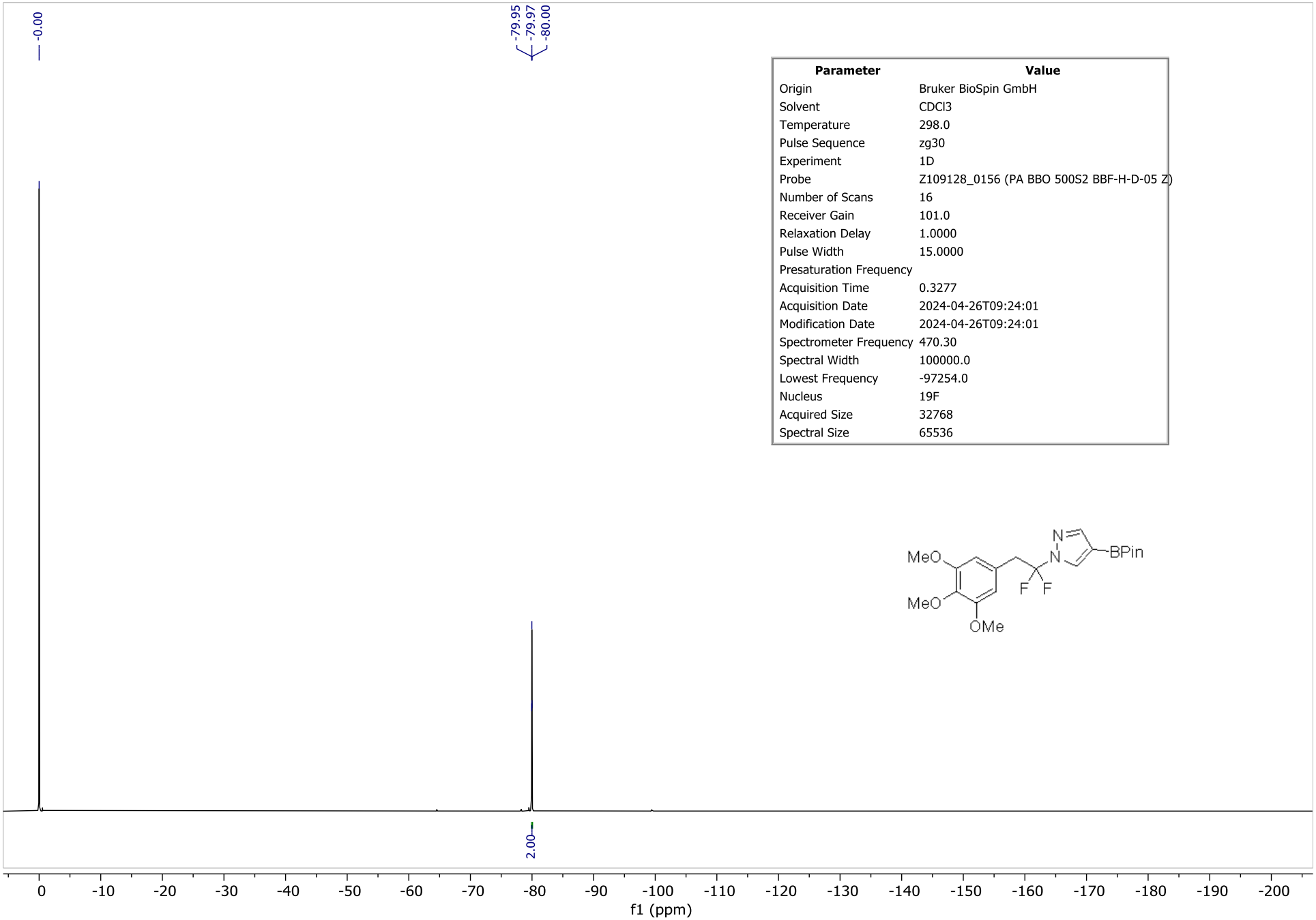


Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	456.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-05-12T12:54:21
Modification Date	2023-05-12T12:54:25
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97277.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (**11ar**)

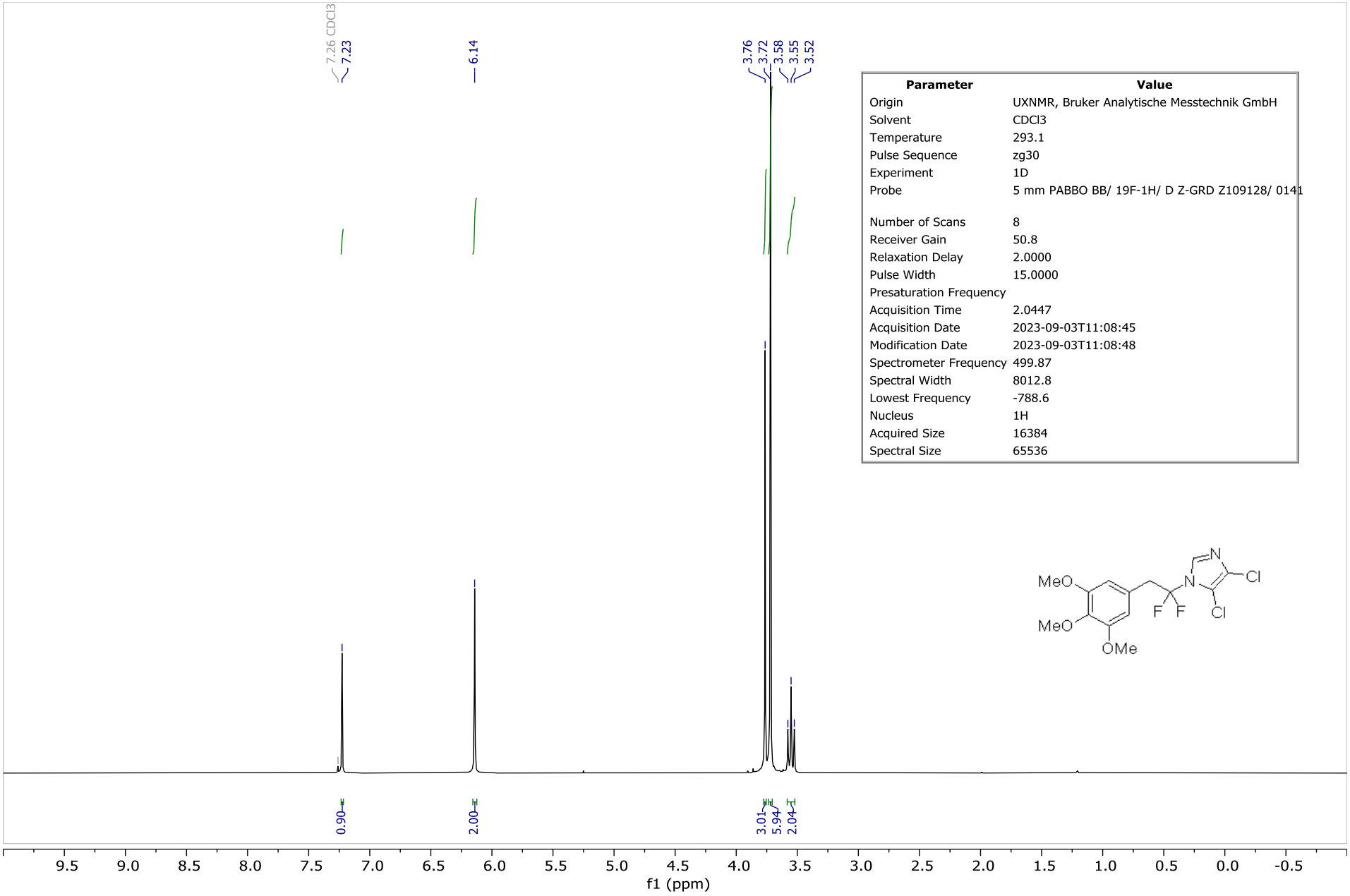



Parameter Value
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Pulse Sequence zgpg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 1000
Receiver Gain 101.0
Relaxation Delay 0.1500
Pulse Width 10.0000
Presaturation Frequency
Acquisition Time 0.5439
Acquisition Date 2024-04-25T13:39:46
Modification Date 2024-04-25T13:39:47
Spectrometer Frequency 125.71
Spectral Width 30120.5
Lowest Frequency -1244.3
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
153.15
147.14
137.72
135.09
126.45
121.93
119.89
117.87
107.51
83.85
77.41 CDCl3
77.16 CDCl3
77.16 CDCl3
76.91 CDCl3
60.93
56.17
42.34
42.12
41.90
24.89
MeO
MeO
OMe
N
N
BPin
F F
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)



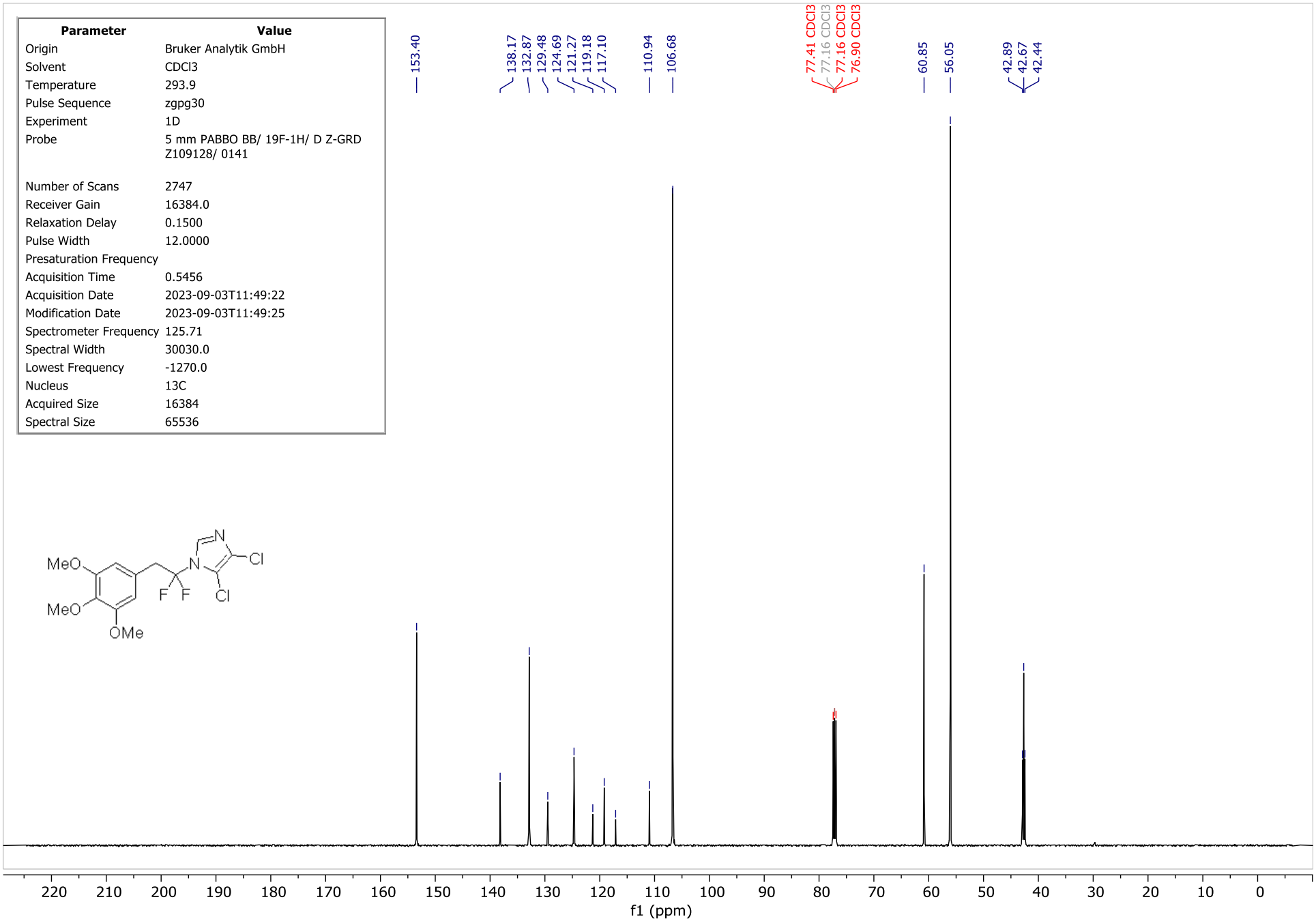
Parameter	Value
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-04-26T09:24:01
Modification Date	2024-04-26T09:24:01
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97254.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

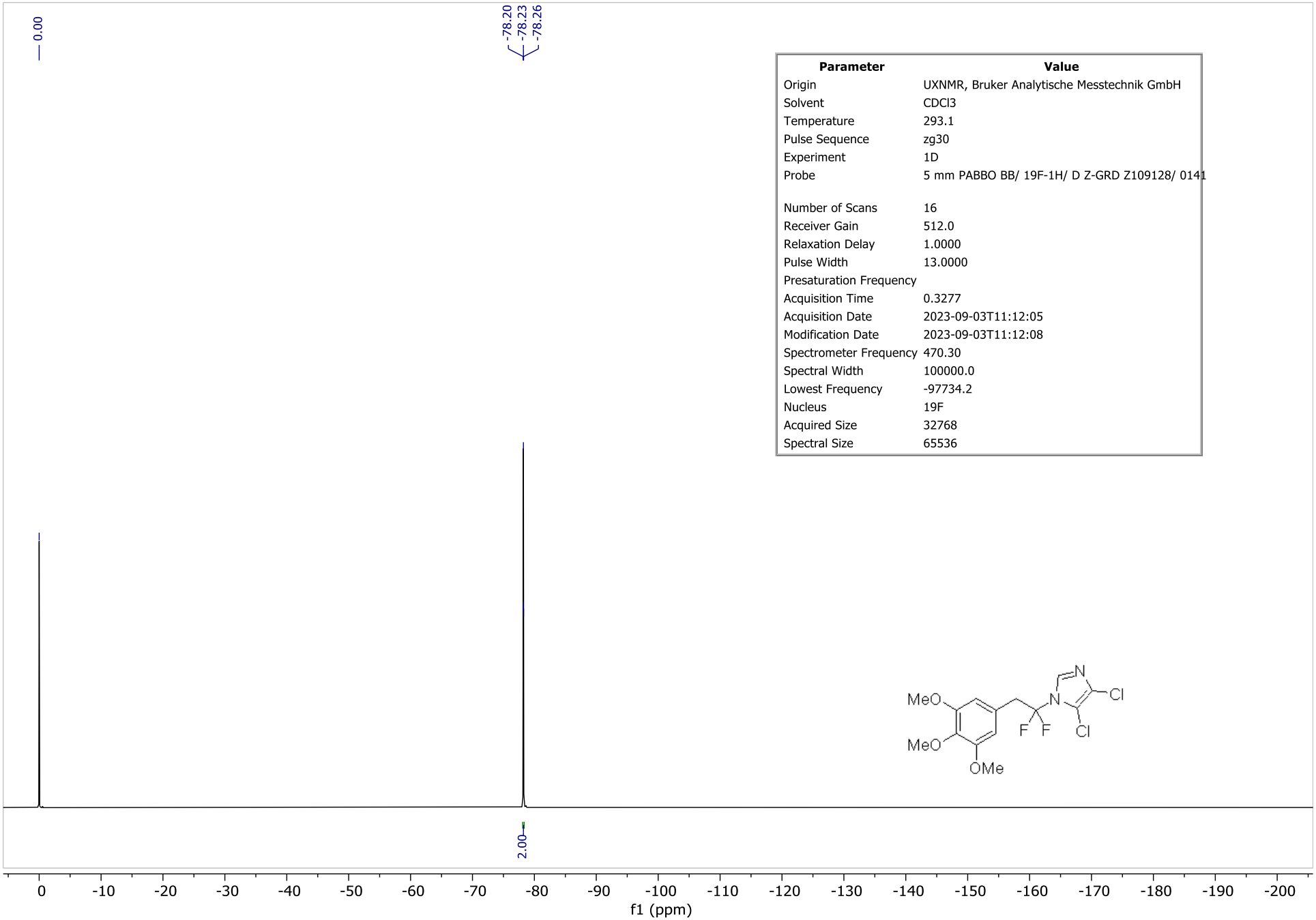
NMR spectra for 4,5-dichloro-1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-imidazole (**11as**)



Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.1
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	2023-09-03T11:08:45
Modification Date	2023-09-03T11:08:48
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

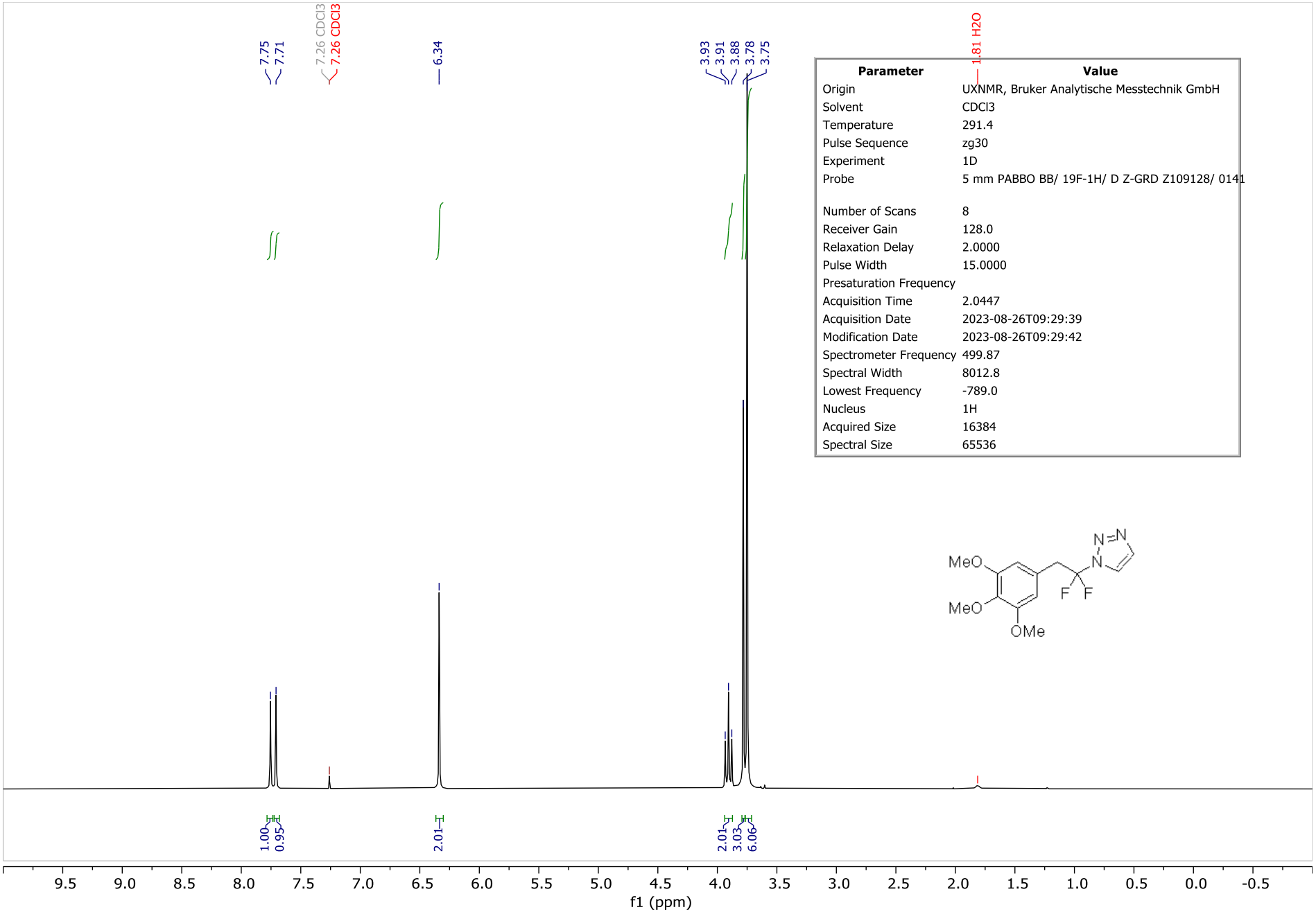
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	2747
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-09-03T11:49:22
Modification Date	2023-09-03T11:49:25
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1270.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





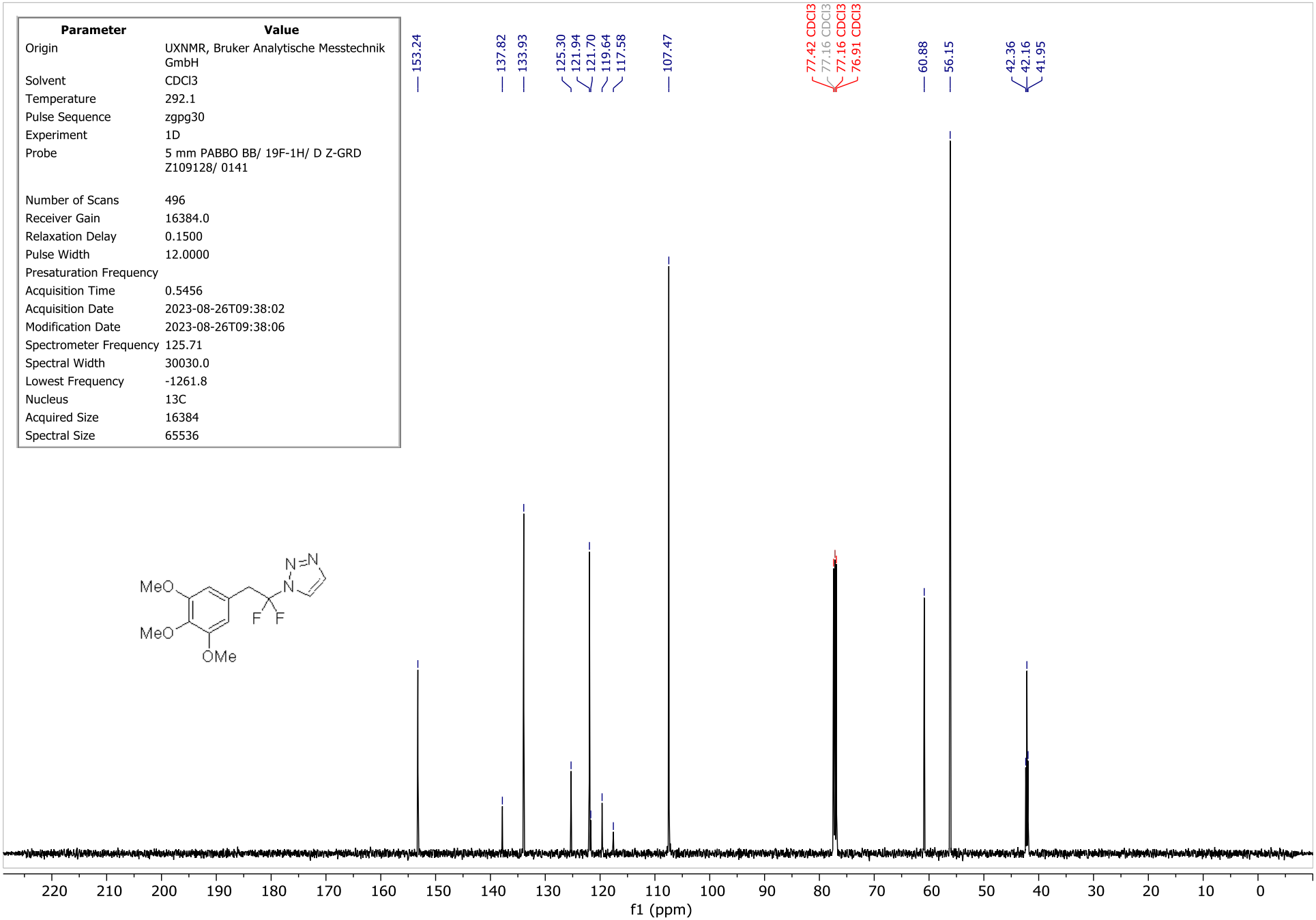
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-09-03T11:12:05
Modification Date	2023-09-03T11:12:08
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97734.2
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

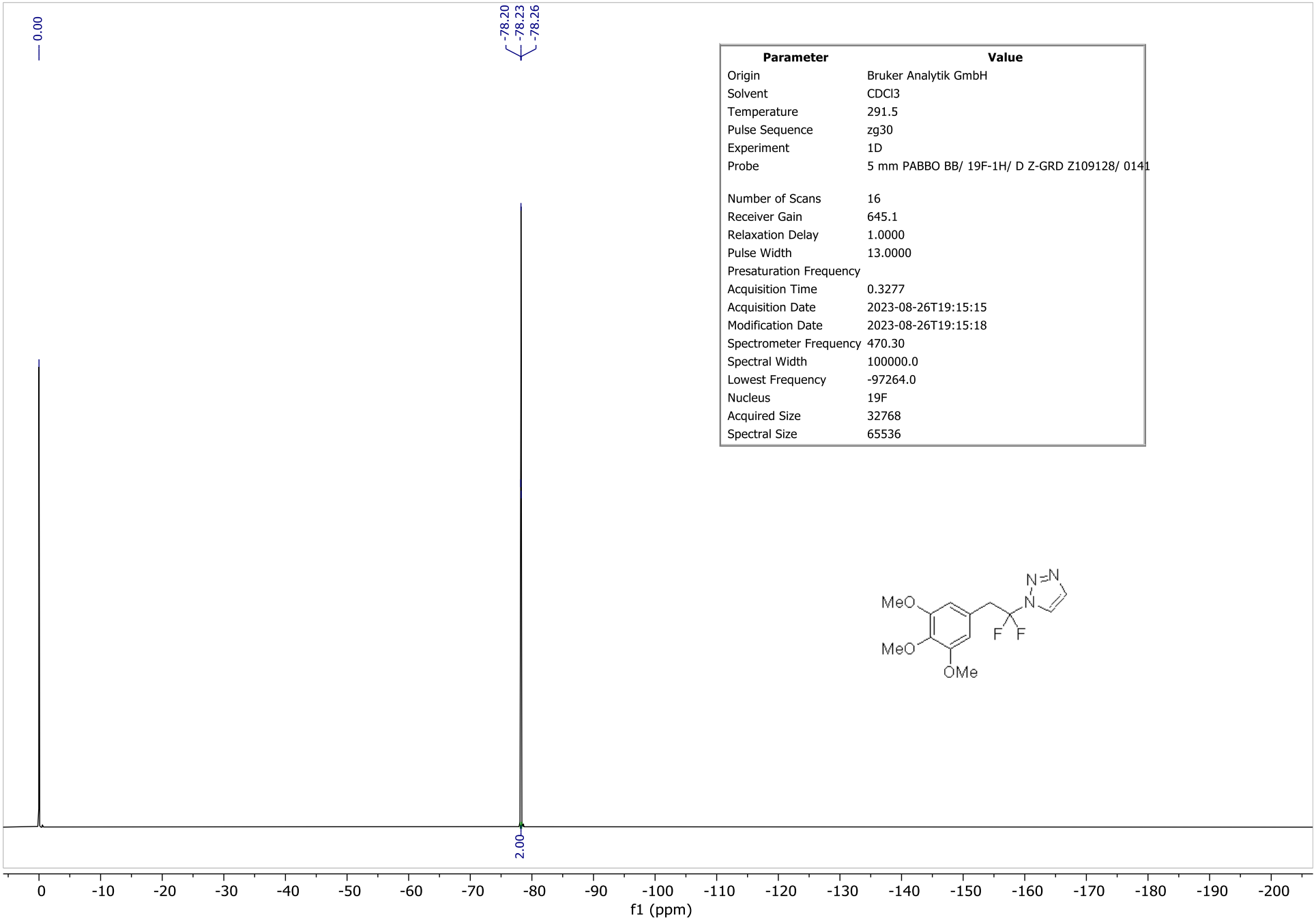
NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-1,2,3-triazole (**11at**)



Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.4
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	2023-08-26T09:29:39
Modification Date	2023-08-26T09:29:42
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

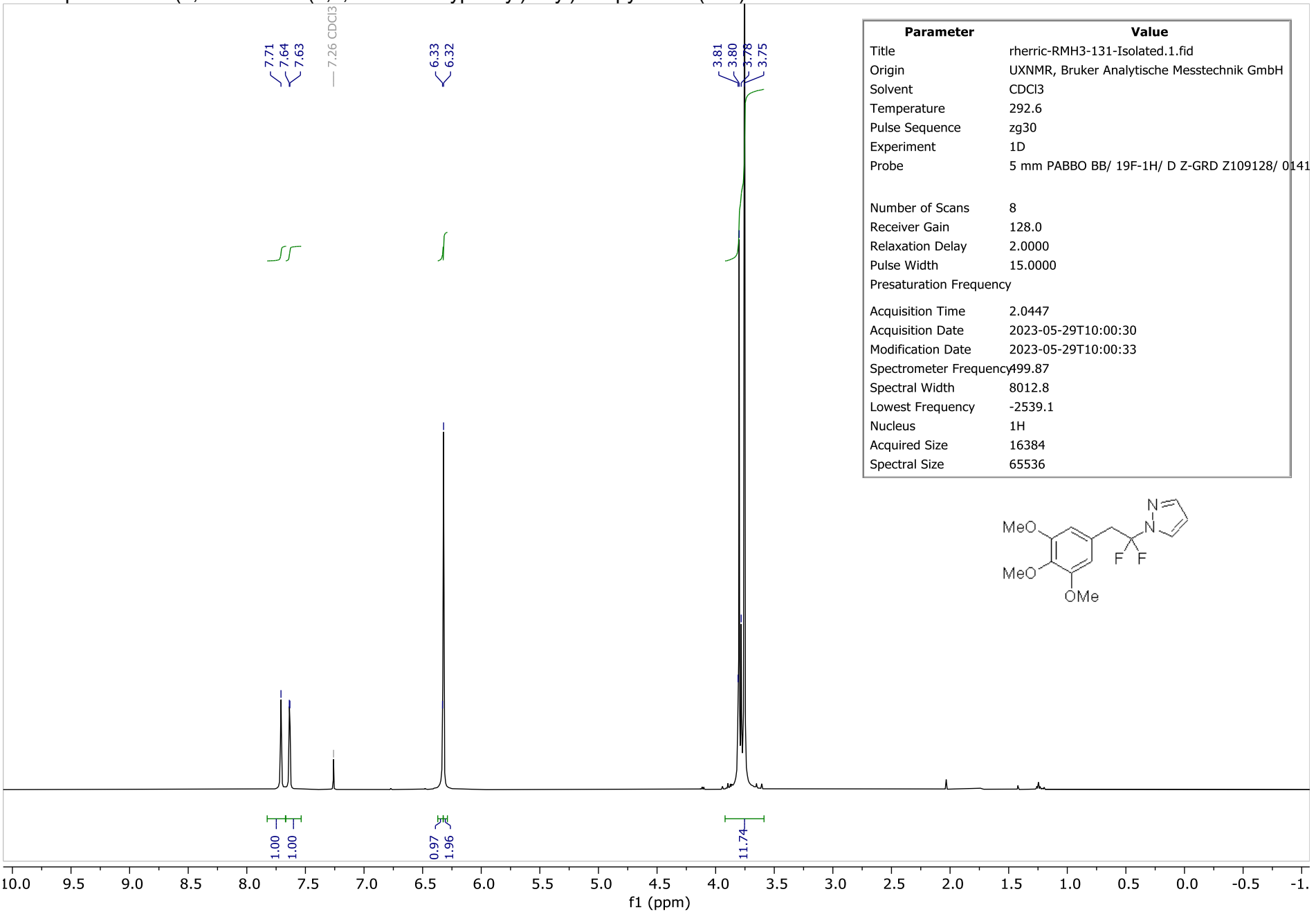
Parameter	Value
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	496
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-08-26T09:38:02
Modification Date	2023-08-26T09:38:06
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1261.8
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



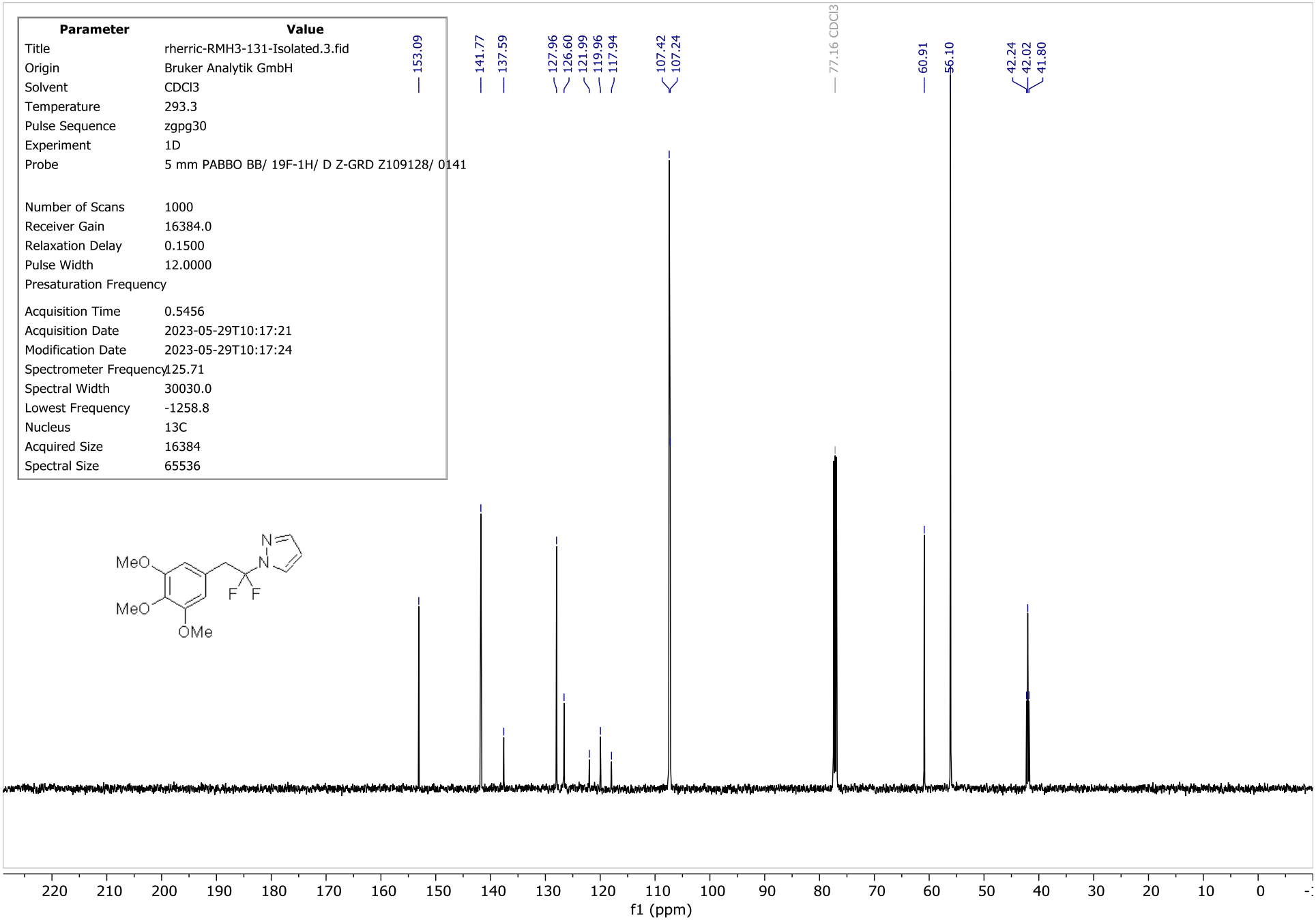


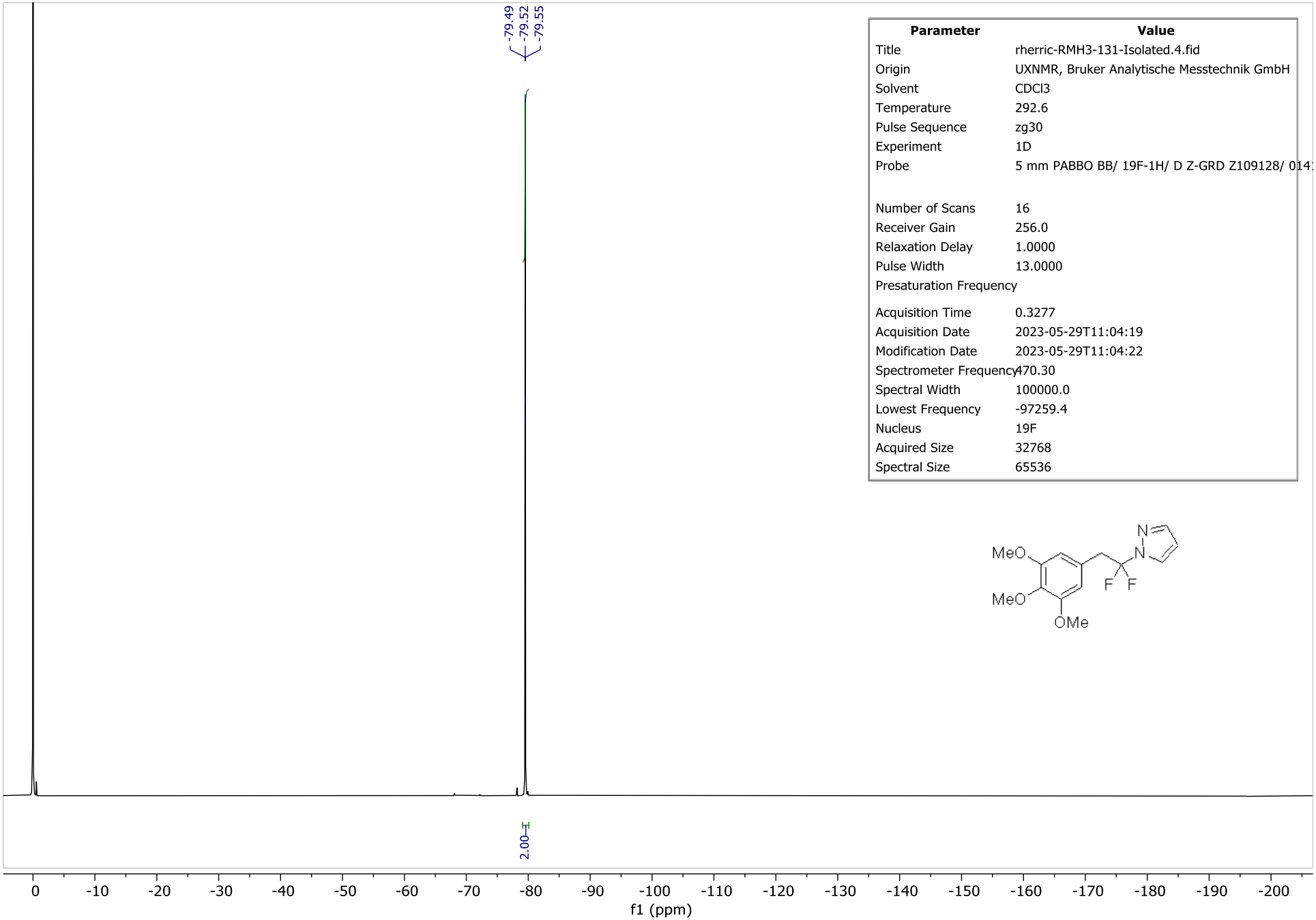
Parameter	Value
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-08-26T19:15:15
Modification Date	2023-08-26T19:15:18
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97264.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(1,1-difluoro-2-(3,4,5-trimethoxyphenyl)ethyl)-1*H*-pyrazole (**11a**)



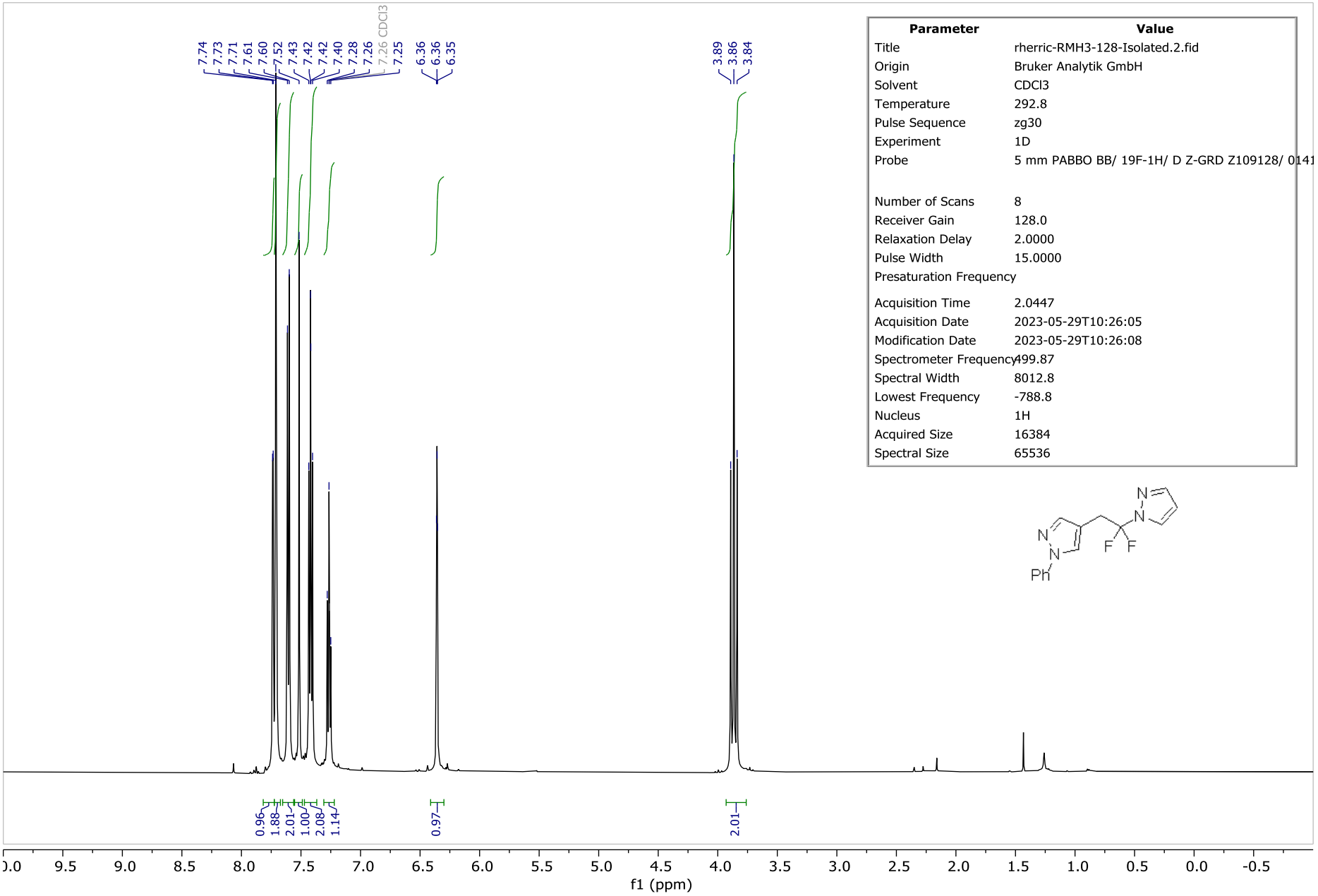
Parameter	Value
Title	rherric-RMH3-131-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-05-29T10:00:30
Modification Date	2023-05-29T10:00:33
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2539.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536


Parameter Value
Title rherric-RMH3-131-Isolated.3.fid
Origin Bruker Analytik GmbH
Solvent CDCl3
Temperature 293.3
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 2023-05-29T10:17:21
Modification Date 2023-05-29T10:17:24
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -1258.8
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
153.09
141.77
137.59
127.96
126.60
121.99
119.96
117.94
107.42
107.24
77.16 CDCl3
60.91
56.10
42.24
42.02
41.80
MeO
MeO
OMe
F
F
N
N
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)



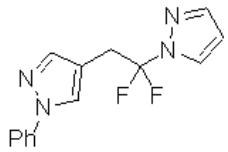
Parameter	Value
Title	rherric-RMH3-131-Isolated.4.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 014
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-05-29T11:04:19
Modification Date	2023-05-29T11:04:22
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97259.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

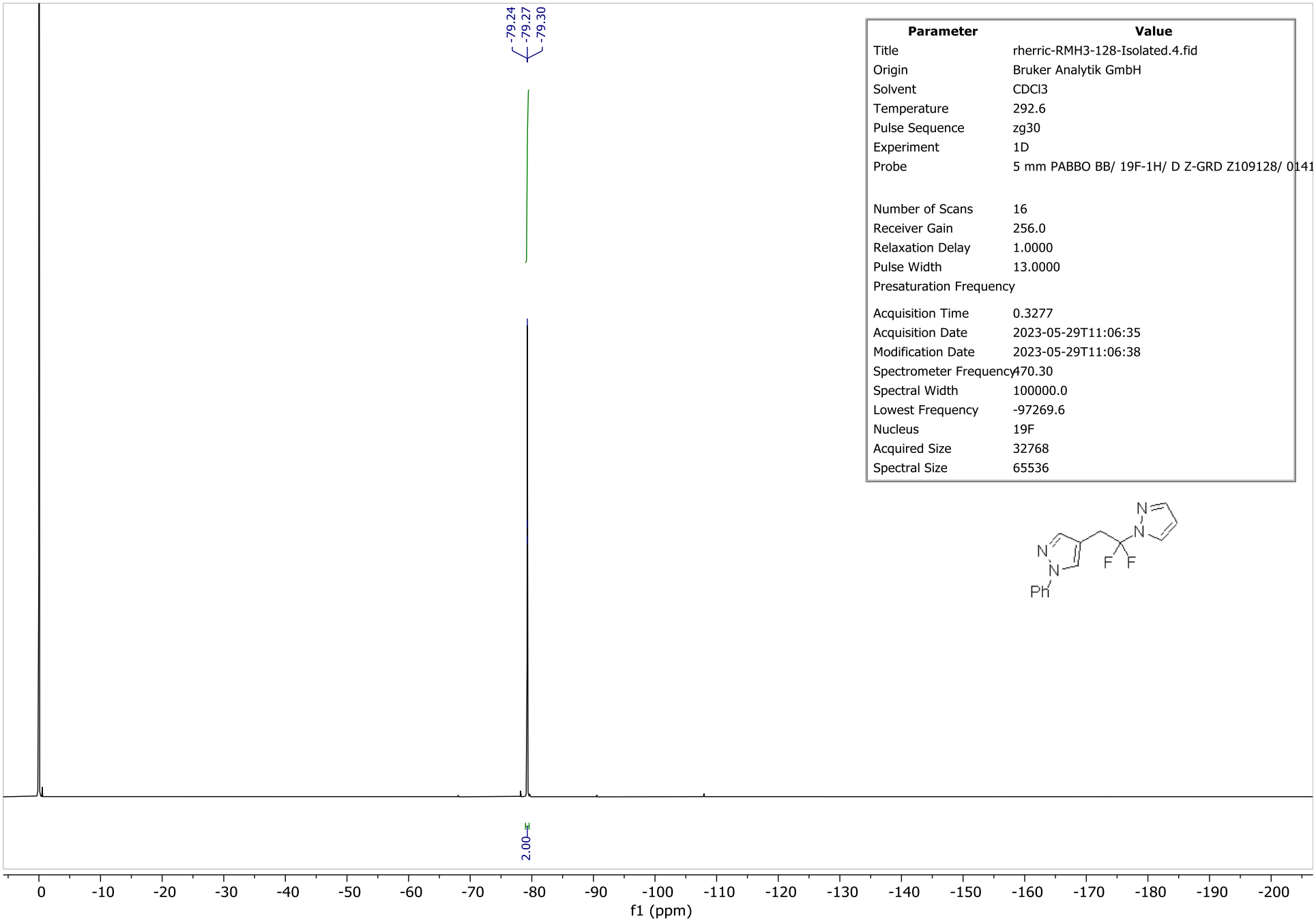
NMR spectra for 4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)-1-phenyl-1*H*-pyrazole (**11b**)



Parameter	Value
Title	rherric-RMH3-128-Isolated.2.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.8
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	2023-05-29T10:26:05
Modification Date	2023-05-29T10:26:08
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

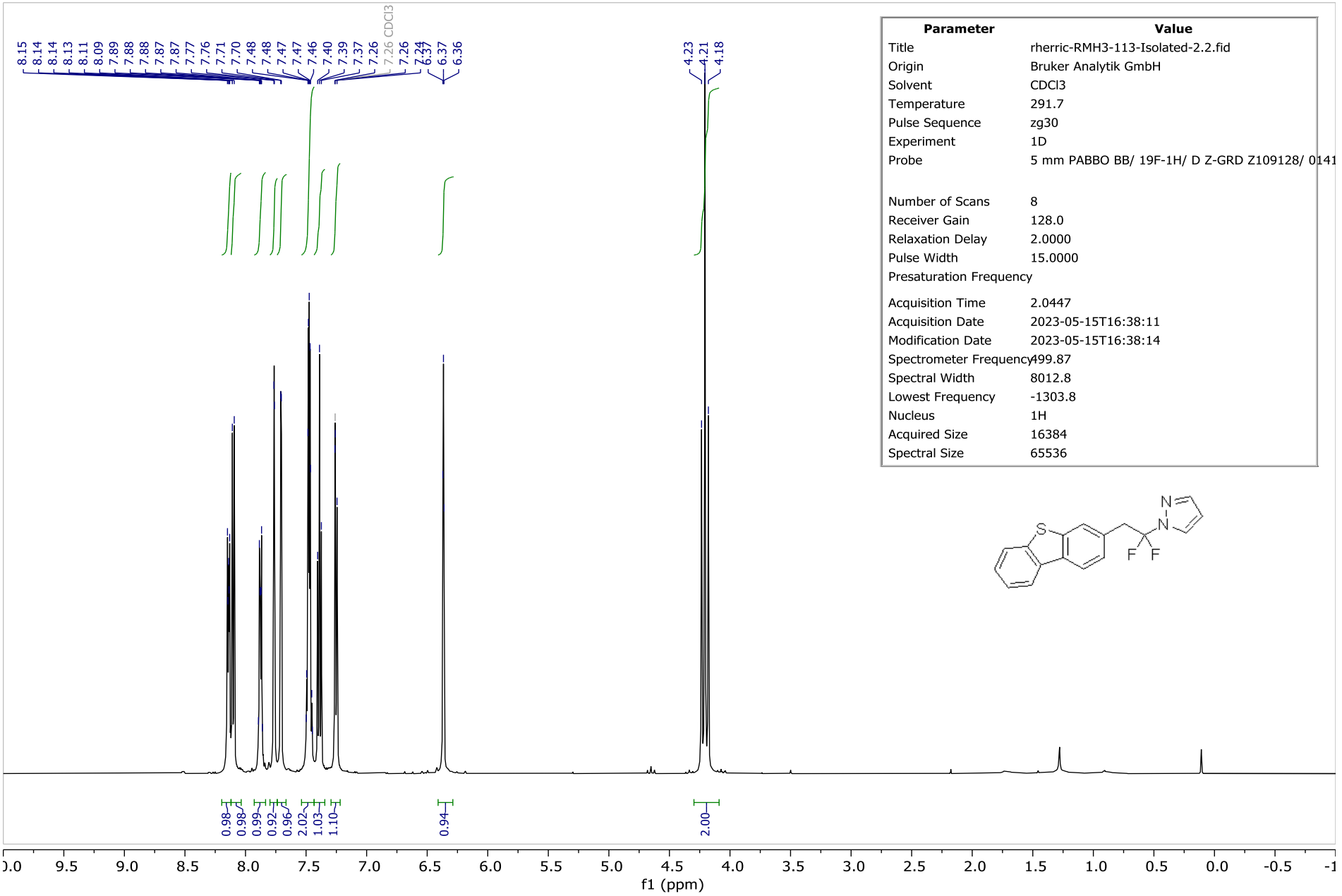
Parameter	Value
Title	rherric-RMH3-128-Isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1024
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-05-29T10:41:22
Modification Date	2023-05-29T10:41:25
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1260.4
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





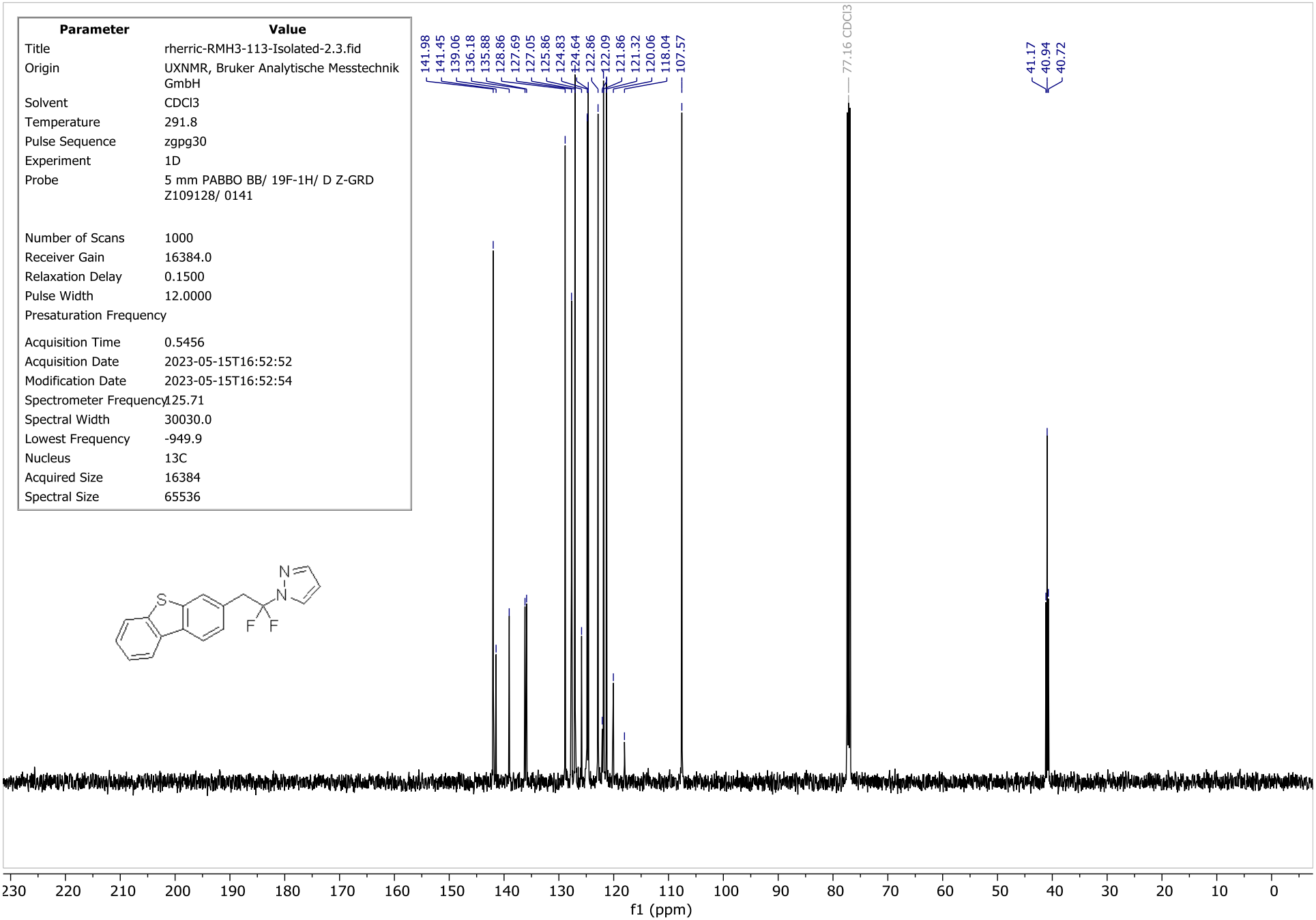
Parameter	Value
Title	rherric-RMH3-128-Isolated.4.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-05-29T11:06:35
Modification Date	2023-05-29T11:06:38
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97269.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

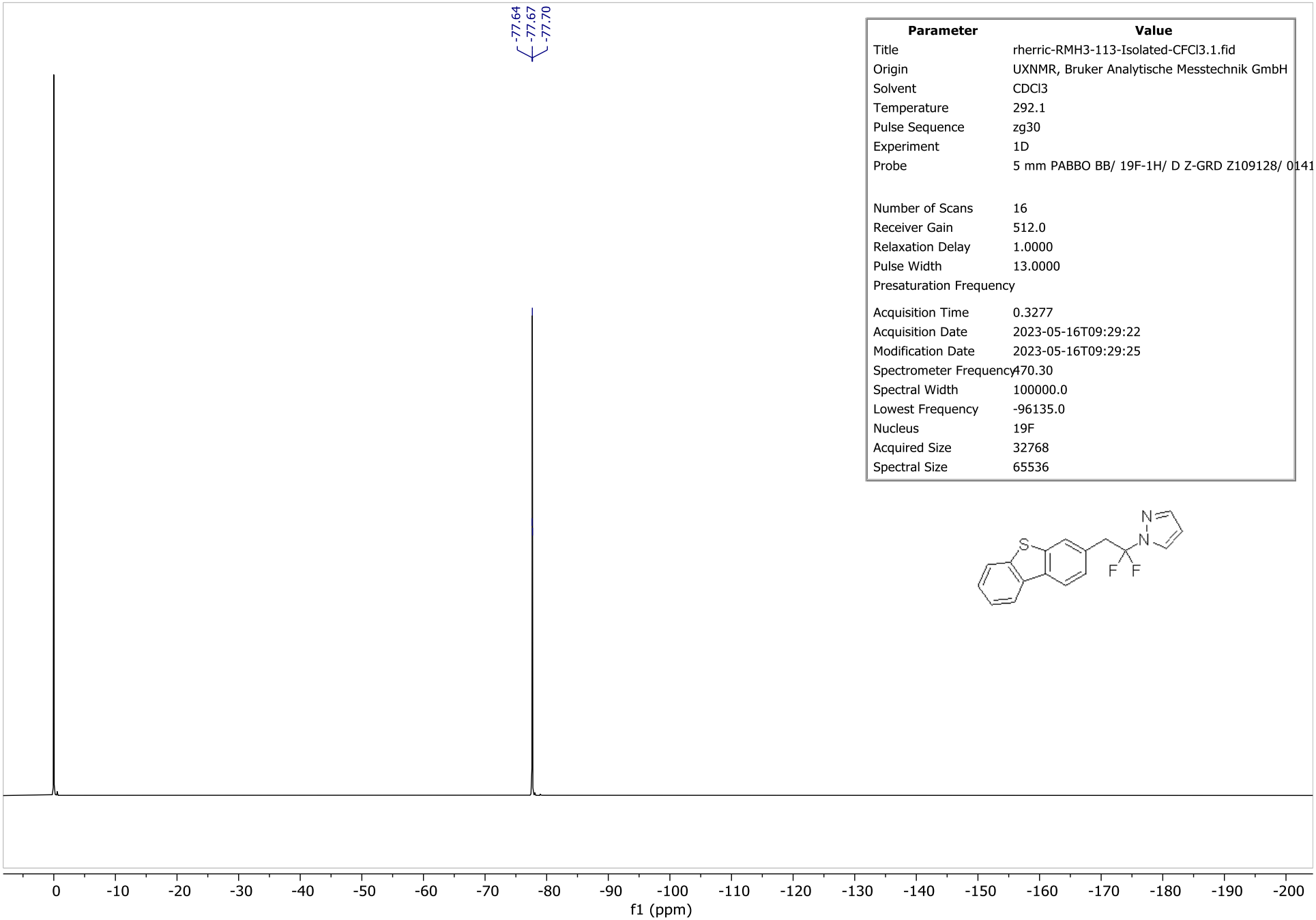
NMR spectra for 1-(2-(dibenzo[*b*,*d*]thiophen-3-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11c**)



Parameter	Value
Title	rherric-RMH3-113-Isolated-2.2.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	291.7
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	2023-05-15T16:38:11
Modification Date	2023-05-15T16:38:14
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-1303.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

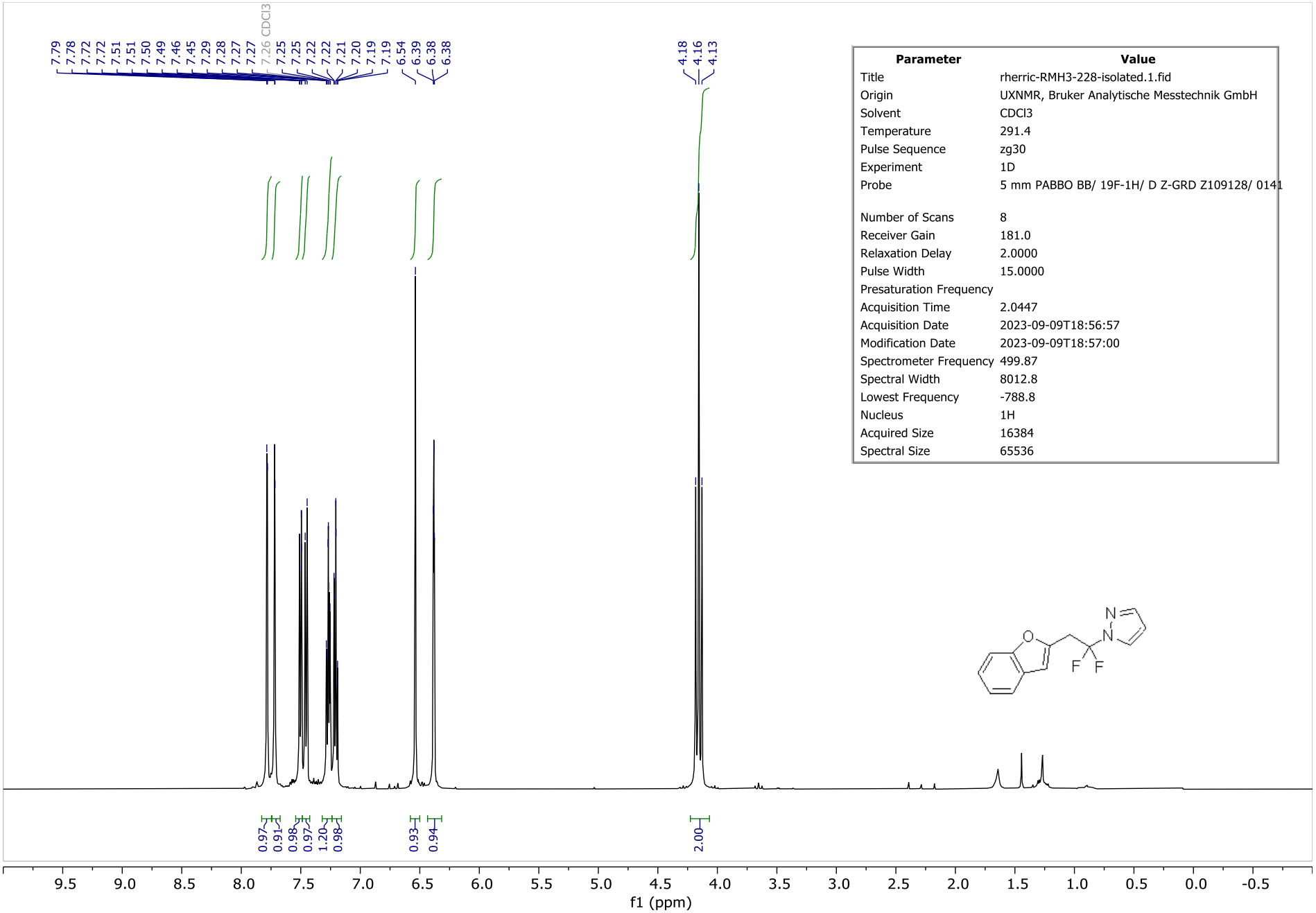
Parameter	Value
Title	rherric-RMH3-113-Isolated-2.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-05-15T16:52:52
Modification Date	2023-05-15T16:52:54
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-949.9
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





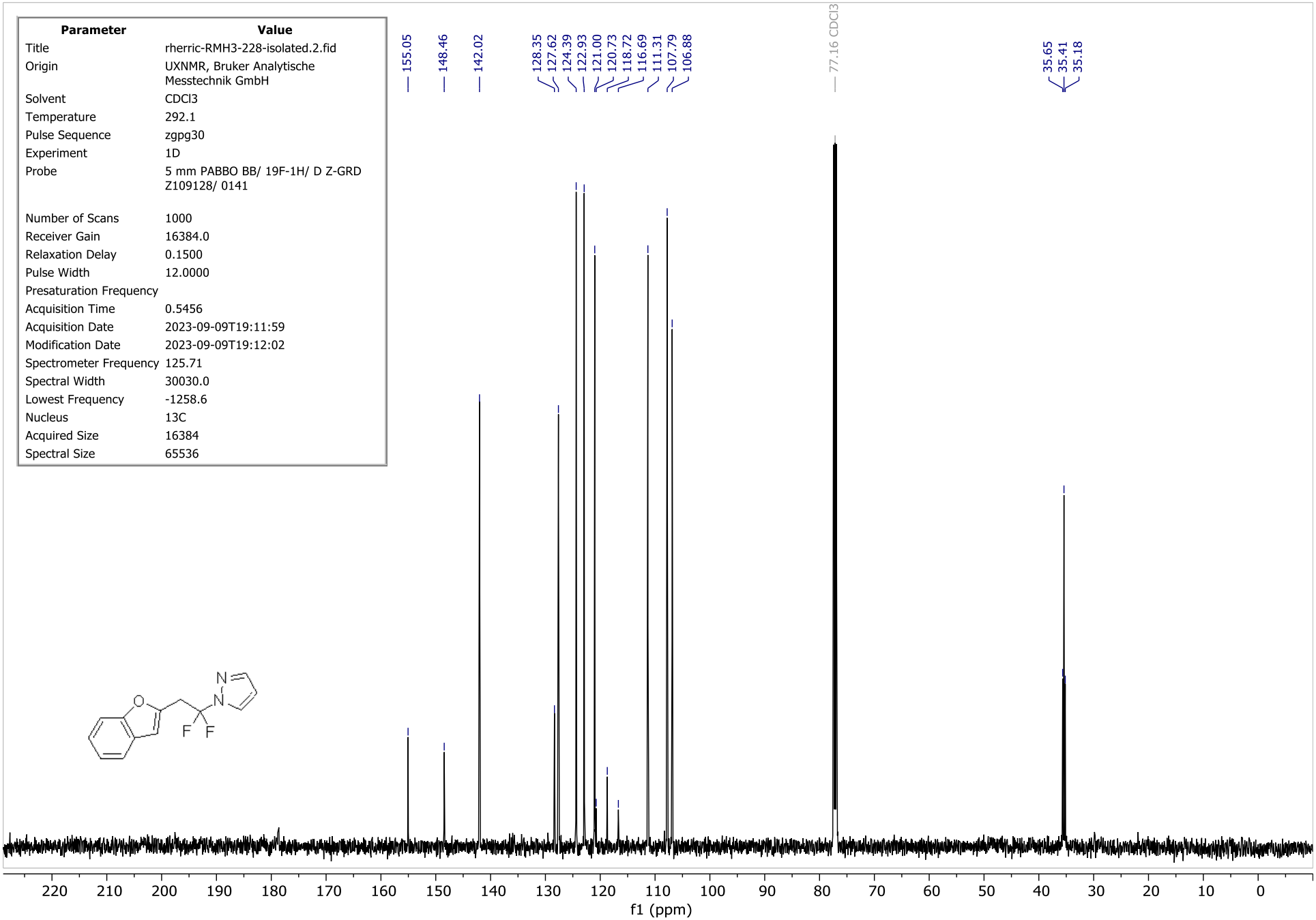
Parameter	Value
Title	rherric-RMH3-113-Isolated-CFCl3.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-05-16T09:29:22
Modification Date	2023-05-16T09:29:25
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96135.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

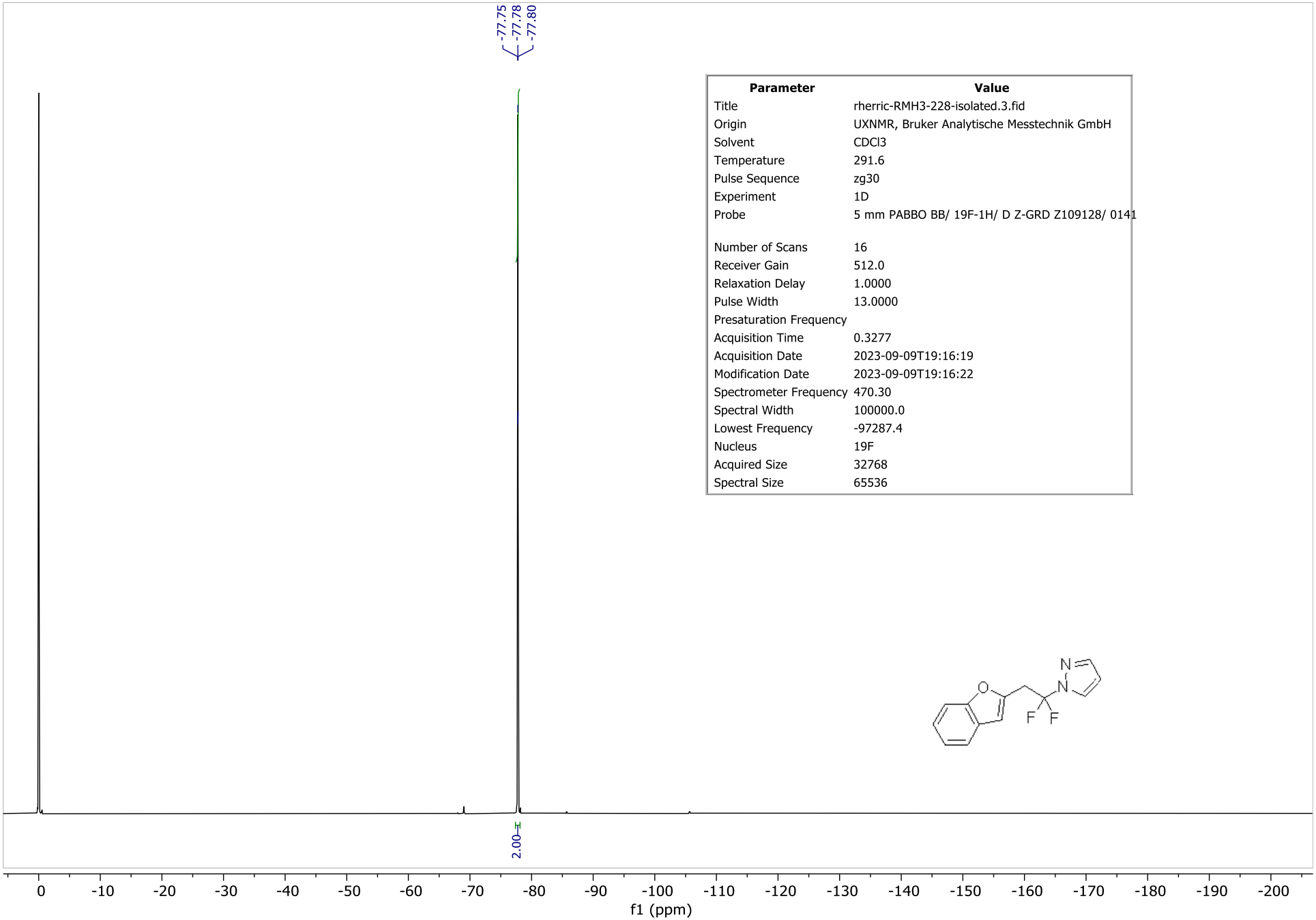
NMR spectra for 1-(2-(benzofuran-2-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11d**)



Parameter	Value
Title	rherric-RMH3-228-isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.4
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	181.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-09-09T18:56:57
Modification Date	2023-09-09T18:57:00
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.8
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

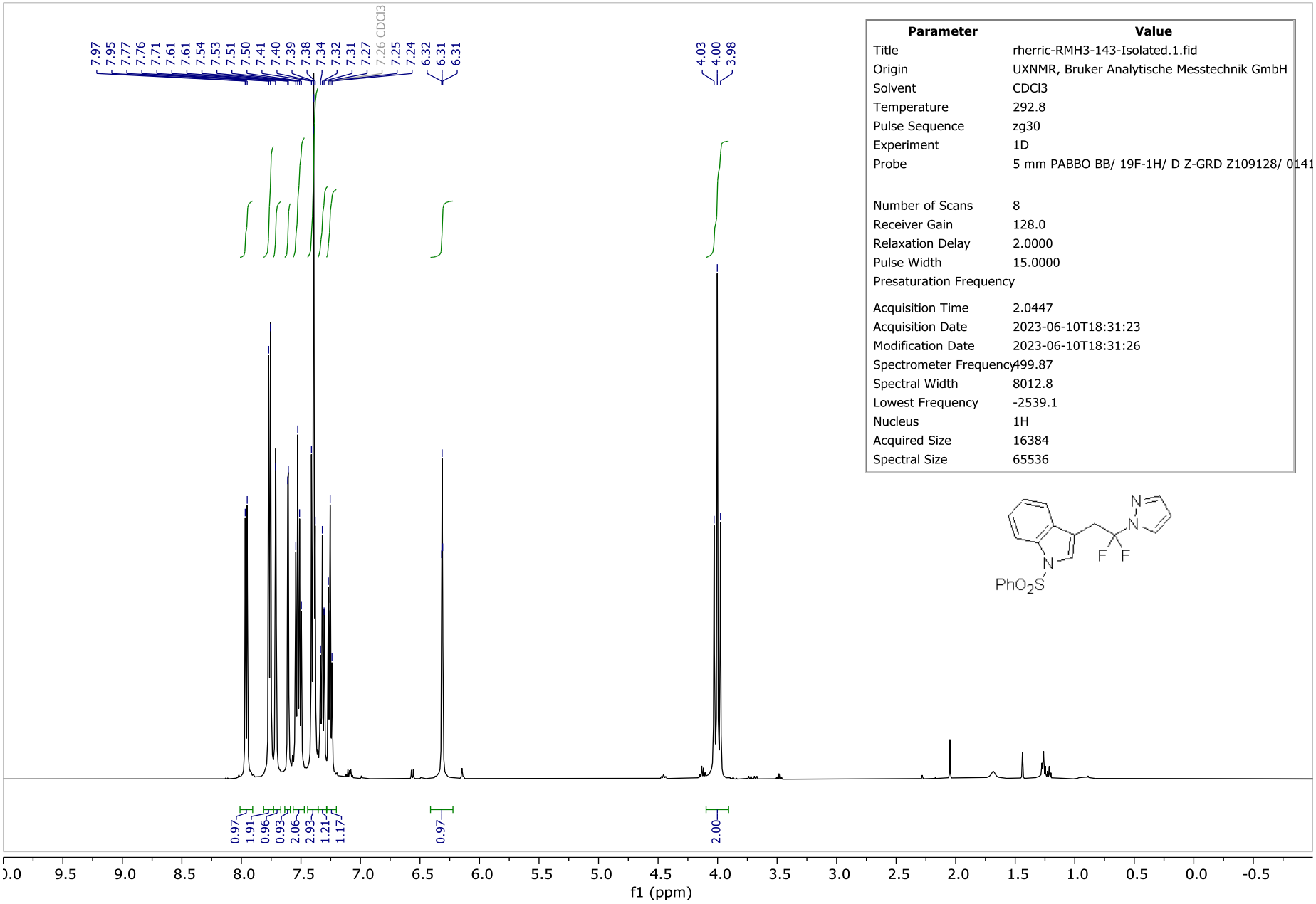
Parameter	Value
Title	rherric-RMH3-228-isolated.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.1
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-09-09T19:11:59
Modification Date	2023-09-09T19:12:02
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1258.6
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





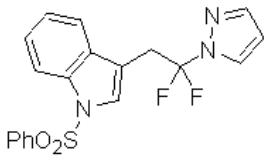
Parameter	Value
Title	rherric-RMH3-228-isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-09-09T19:16:19
Modification Date	2023-09-09T19:16:22
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97287.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

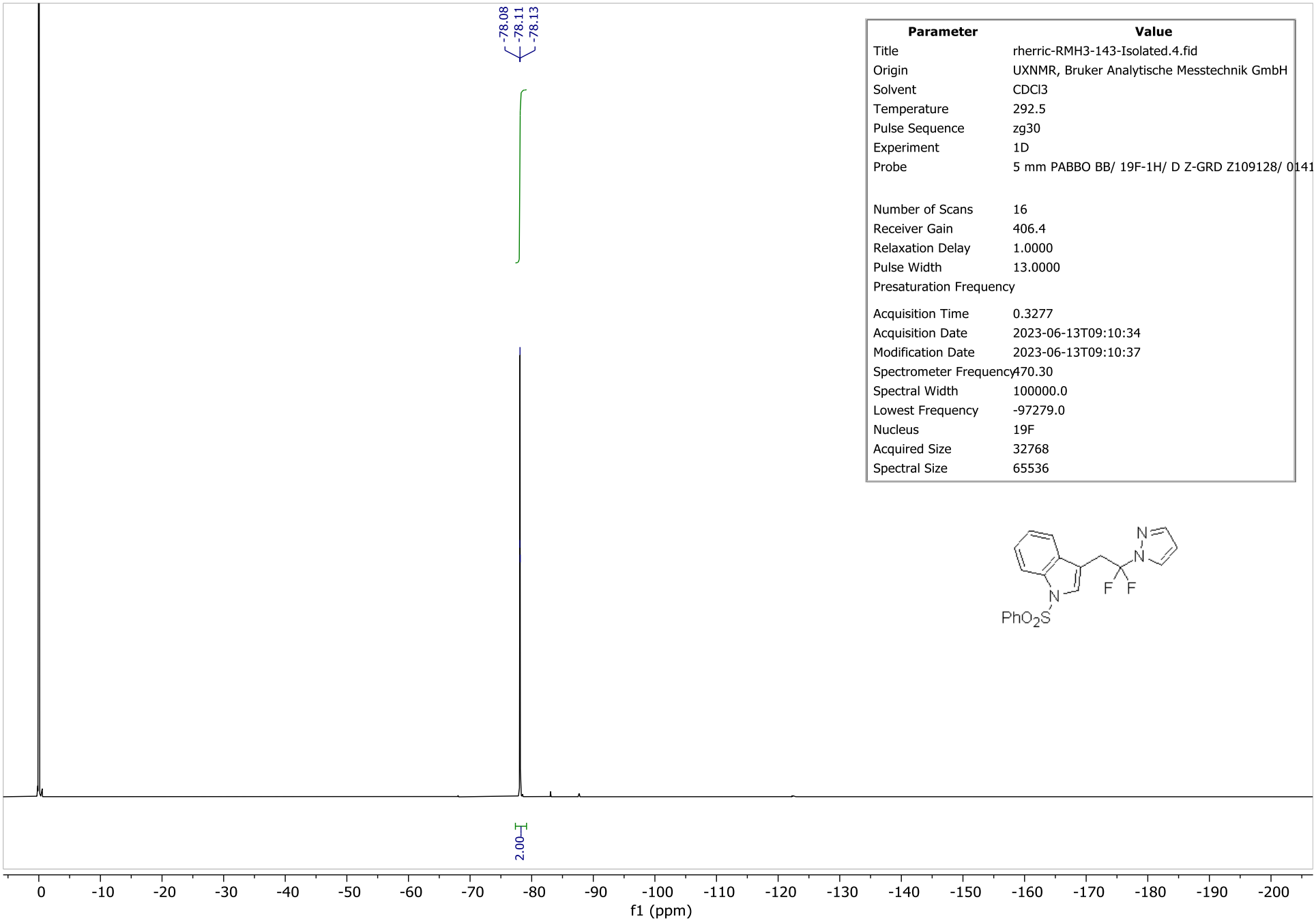
NMR spectra for 3-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)-1-(phenylsulfonyl)-1*H*-indole (**11e**)



Parameter	Value
Title	rherric-RMH3-143-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
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	2023-06-10T18:31:23
Modification Date	2023-06-10T18:31:26
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2539.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

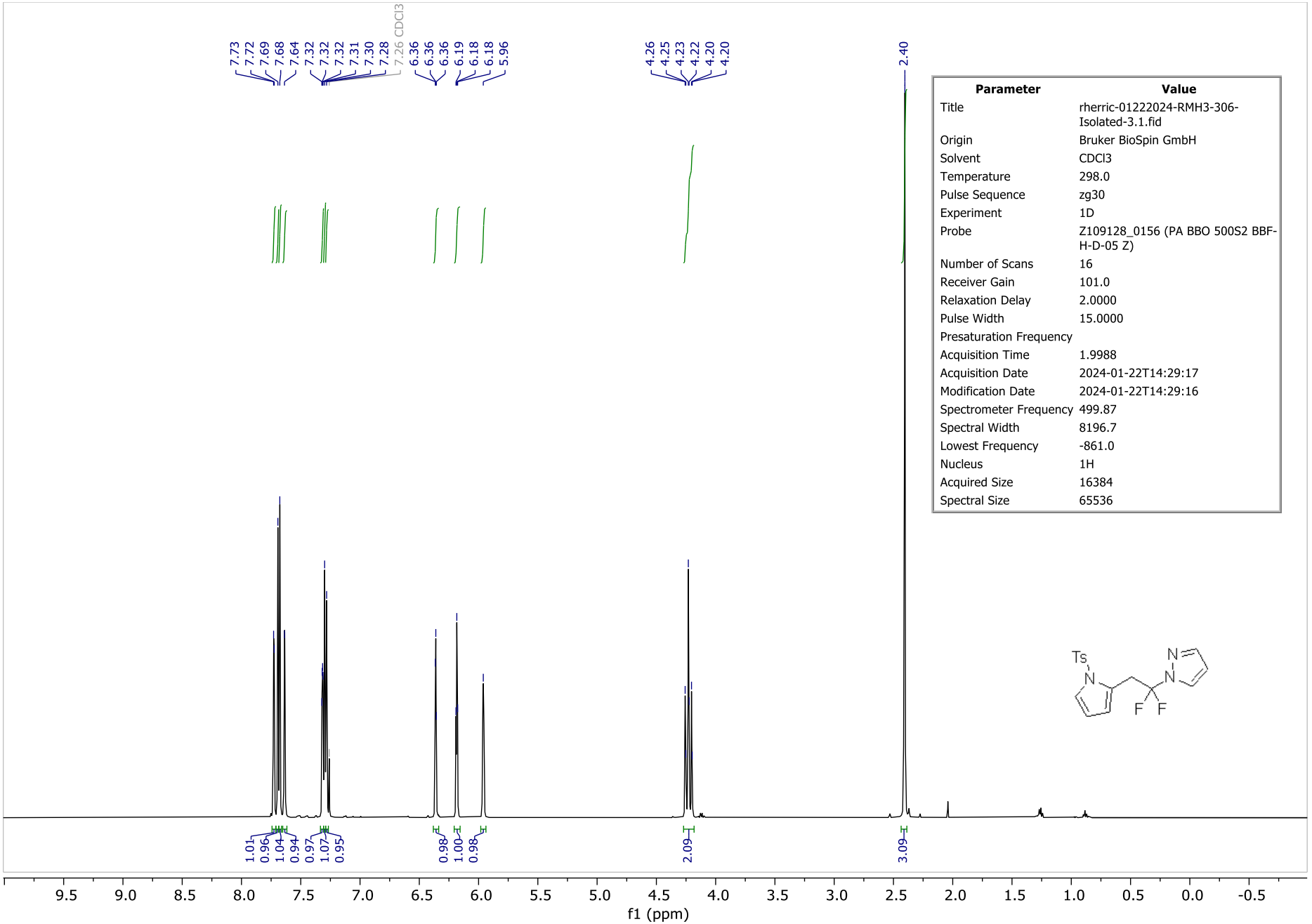
Parameter	Value
Title	rherric-RMH3-143-Isolated.3.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-06-10T18:48:08
Modification Date	2023-06-10T18:48:14
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1259.9
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





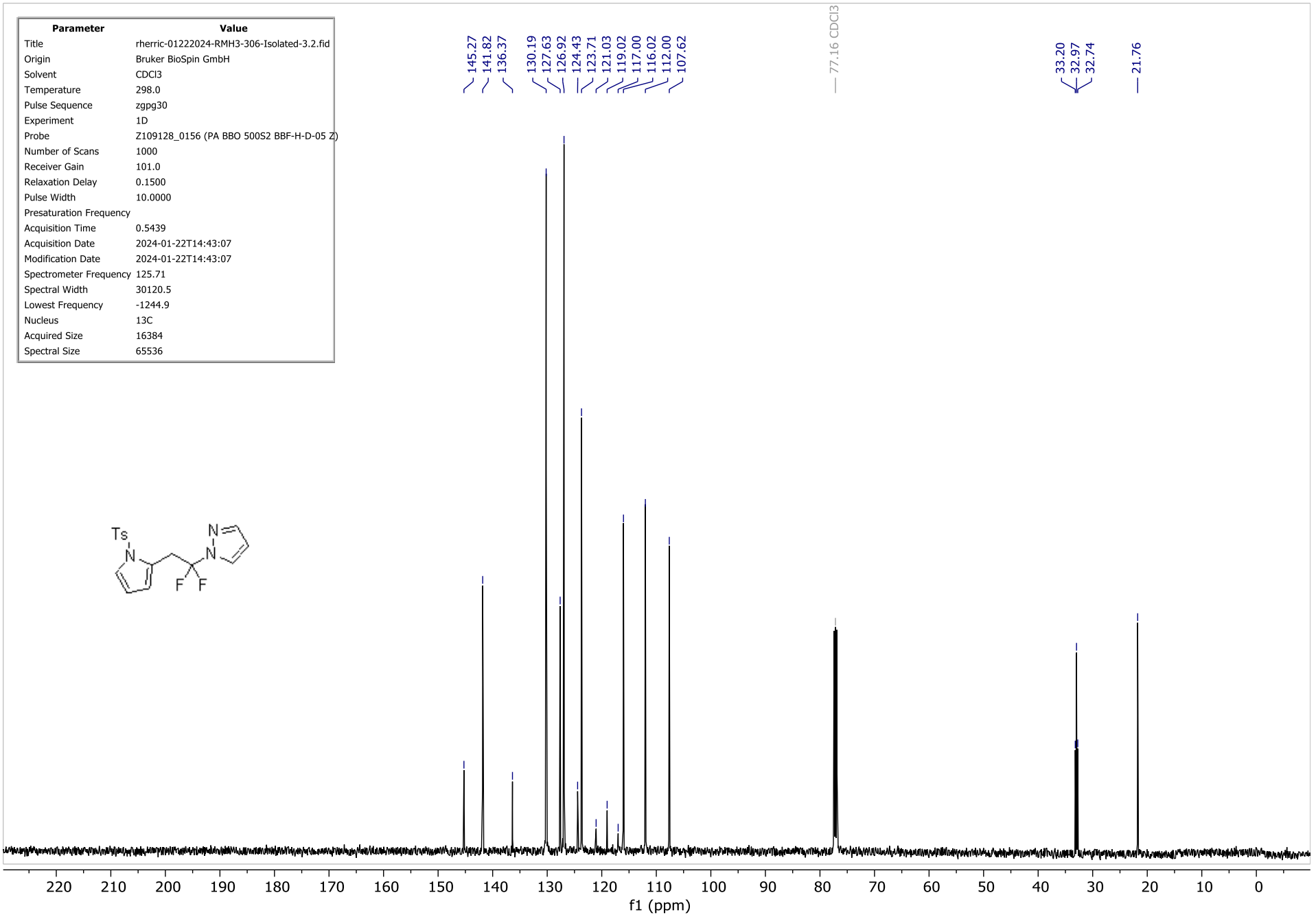
Parameter	Value
Title	rherric-RMH3-143-Isolated.4.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.5
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	406.4
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-06-13T09:10:34
Modification Date	2023-06-13T09:10:37
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97279.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

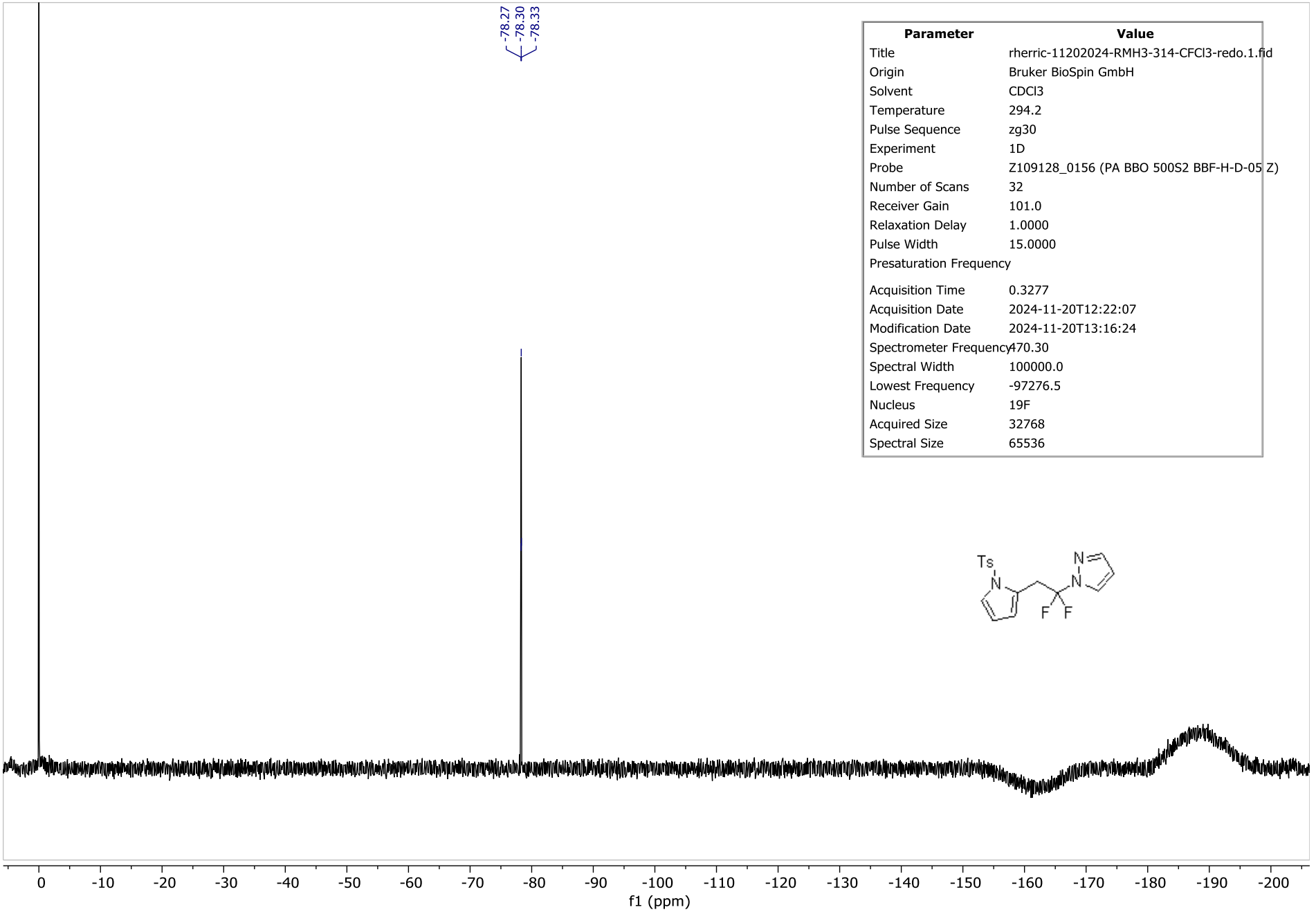
NMR spectra for 1-(1,1-difluoro-2-(1-tosyl-1*H*-pyrrol-2-yl)ethyl)-1*H*-pyrazole (**11f**)



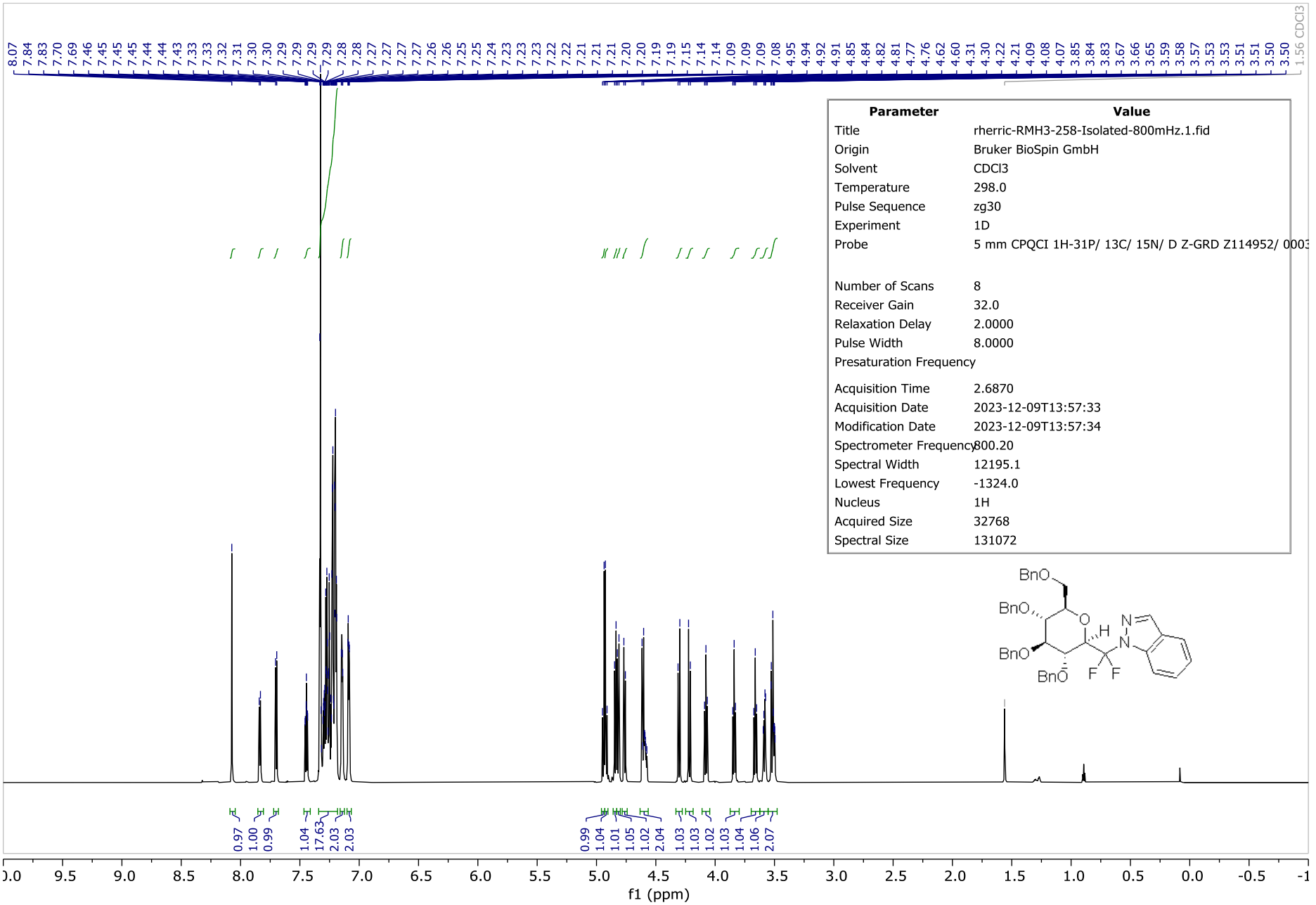
Parameter	Value
Title	rherric-01222024-RMH3-306-Isolated-3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	1.9988
Acquisition Date	2024-01-22T14:29:17
Modification Date	2024-01-22T14:29:16
Spectrometer Frequency	499.87
Spectral Width	8196.7
Lowest Frequency	-861.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

Parameter	Value
Title	rherric-01222024-RMH3-306-Isolated-3.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	1000
Receiver Gain	101.0
Relaxation Delay	0.1500
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	0.5439
Acquisition Date	2024-01-22T14:43:07
Modification Date	2024-01-22T14:43:07
Spectrometer Frequency	125.71
Spectral Width	30120.5
Lowest Frequency	-1244.9
Nucleus	13C
Acquired Size	16384
Spectral Size	65536

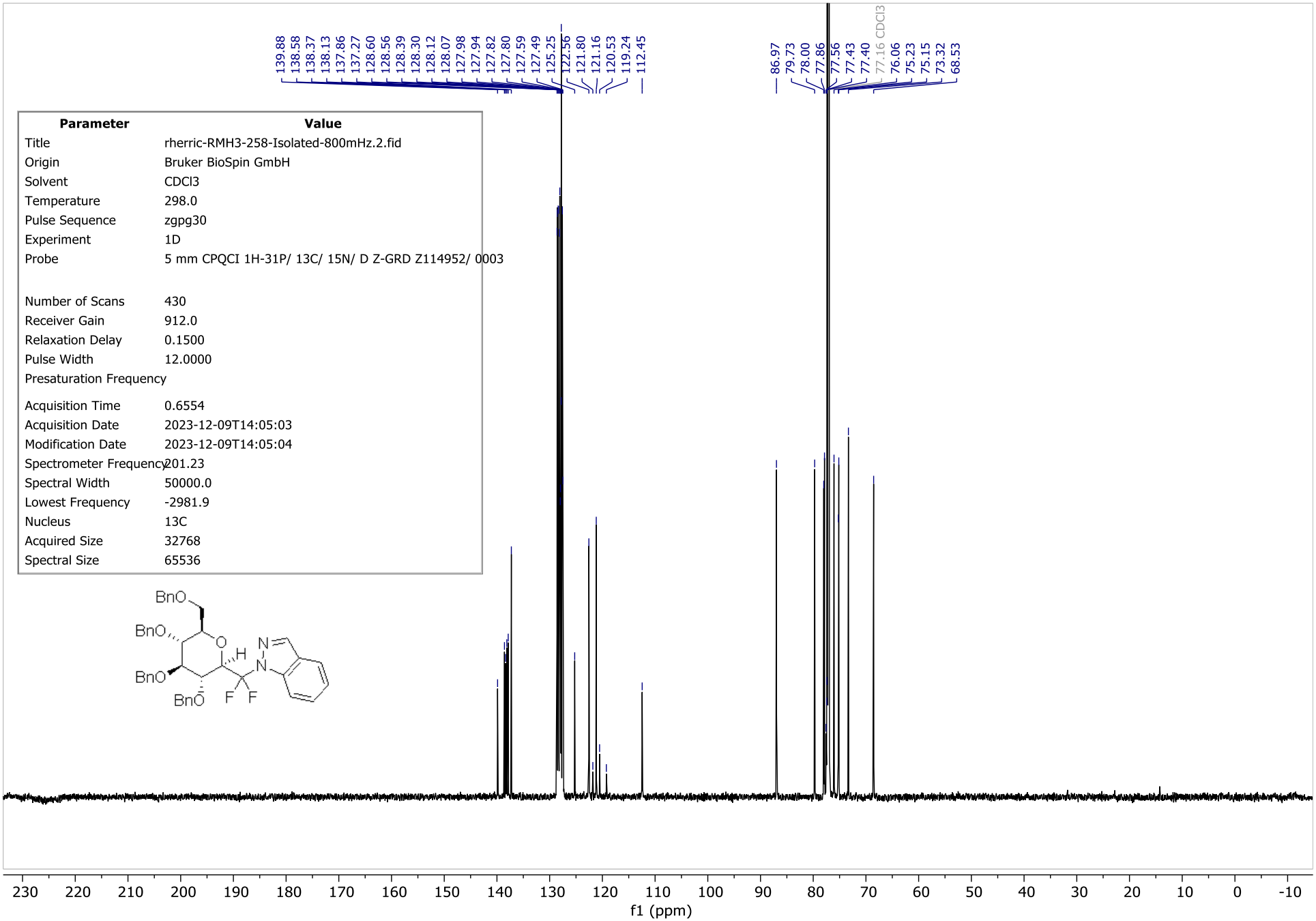


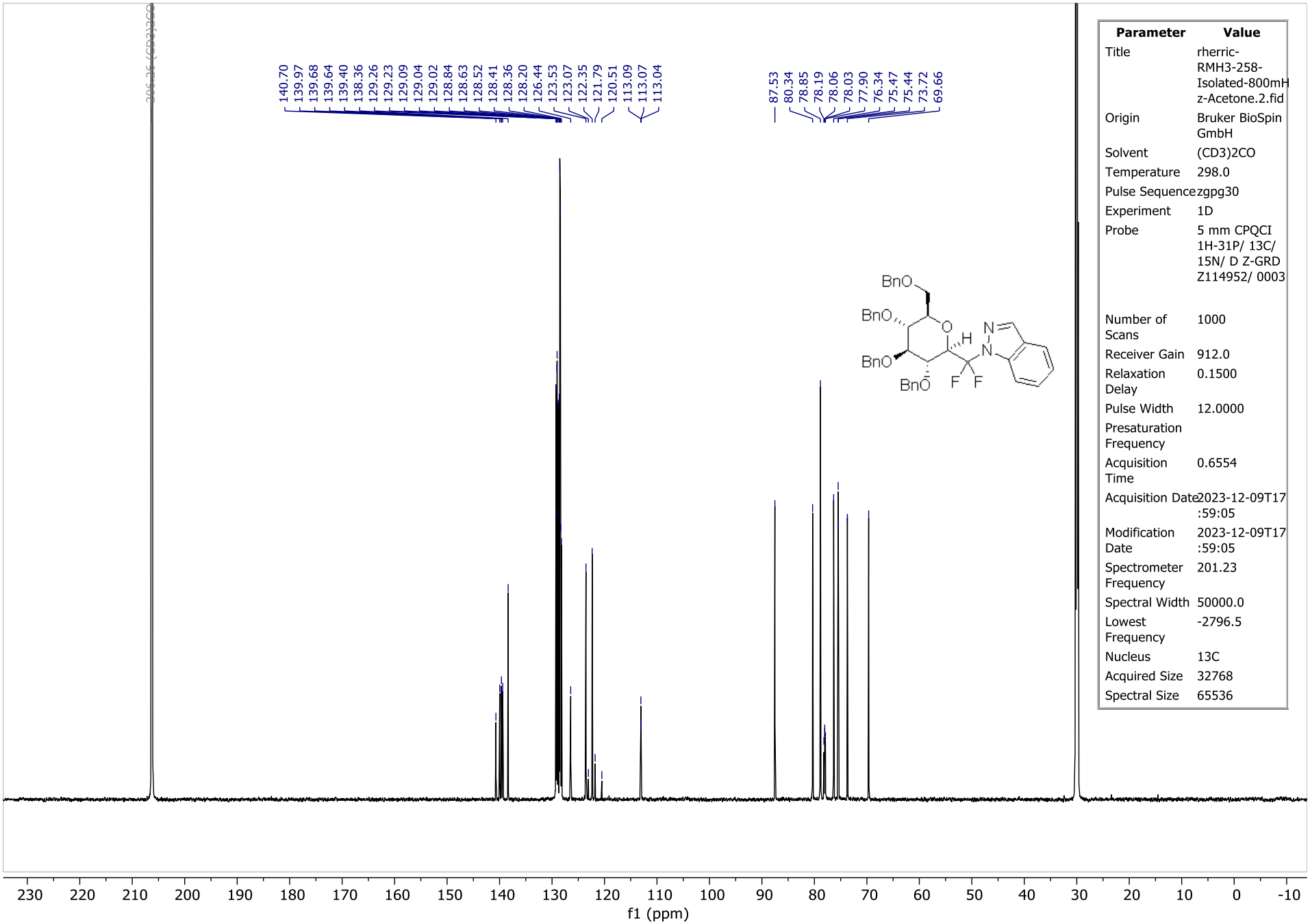

-78.27
-78.30
-78.33
Parameter Value
Title rherric-11202024-RMH3-314-CFCl3-redo.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 294.2
Pulse Sequence zg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 32
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2024-11-20T12:22:07
Modification Date 2024-11-20T13:16:24
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97276.5
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
Ts
N
N
N
F
F
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 1-(difluoro((2*R*,3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)methyl)-1*H*-indazole (**11g**)

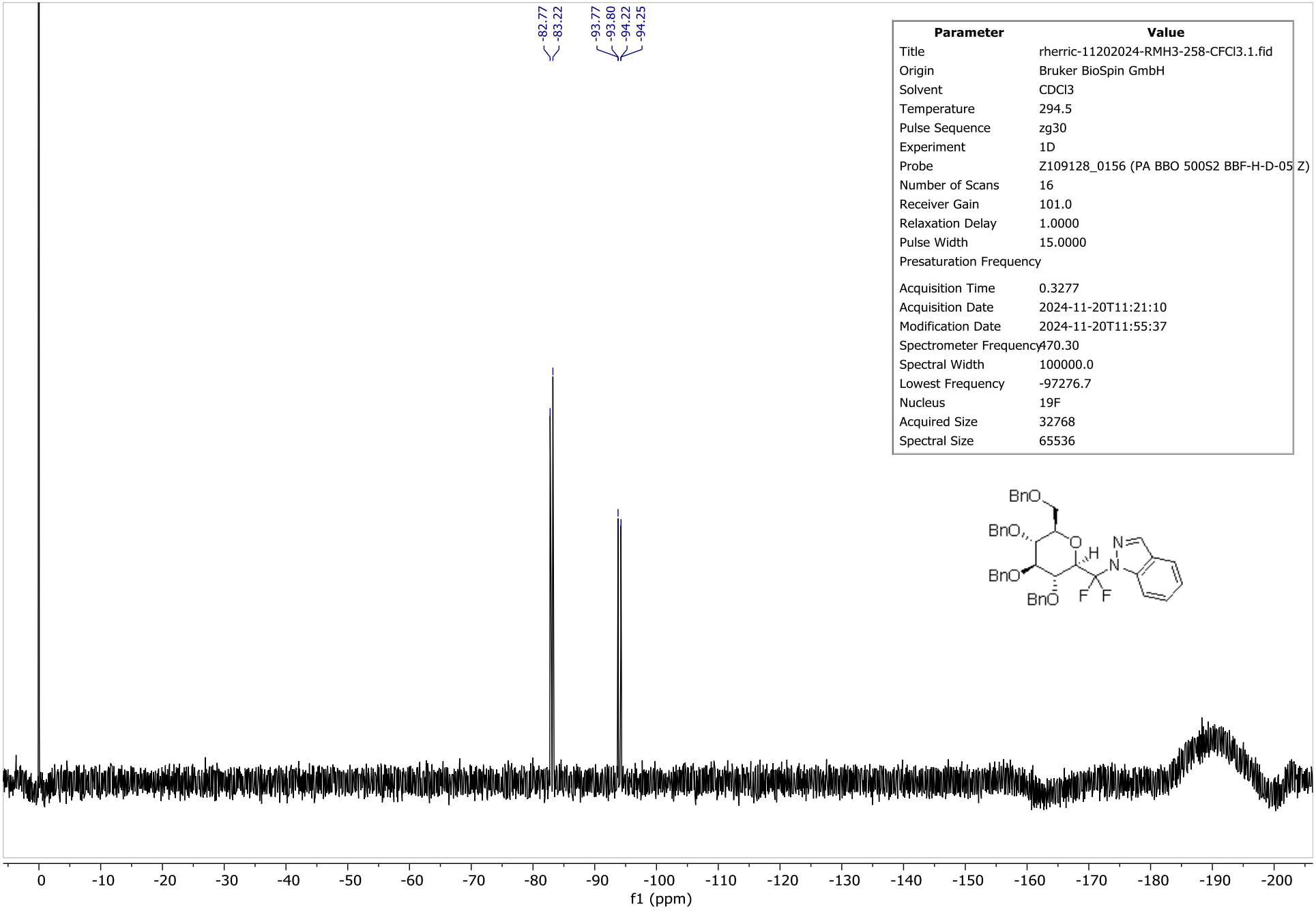


Parameter	Value
Title	rherric-RMH3-258-Isolated-800mHz.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	8
Receiver Gain	32.0
Relaxation Delay	2.0000
Pulse Width	8.0000
Presaturation Frequency	
Acquisition Time	2.6870
Acquisition Date	2023-12-09T13:57:33
Modification Date	2023-12-09T13:57:34
Spectrometer Frequency	800.20
Spectral Width	12195.1
Lowest Frequency	-1324.0
Nucleus	1H
Acquired Size	32768
Spectral Size	131072


139.88
138.58
138.37
138.13
137.86
137.27
128.60
128.56
128.39
128.30
128.12
128.07
127.98
127.94
127.82
127.80
127.59
127.49
125.25
122.56
121.80
121.16
120.53
119.24
112.45
86.97
79.73
78.00
77.86
77.56
77.43
77.40
77.16 CDCl3
76.06
75.23
75.15
73.32
68.53
Parameter
Value
Title
rherric-RMH3-258-Isolated-800mHz.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
430
Receiver Gain
912.0
Relaxation Delay
0.1500
Pulse Width
12.0000
Presaturation Frequency
Acquisition Time
0.6554
Acquisition Date
2023-12-09T14:05:03
Modification Date
2023-12-09T14:05:04
Spectrometer Frequency
201.23
Spectral Width
50000.0
Lowest Frequency
-2981.9
Nucleus
13C
Acquired Size
32768
Spectral Size
65536
BnO
BnO
BnO
BnO
O
H
N
N
F
F
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

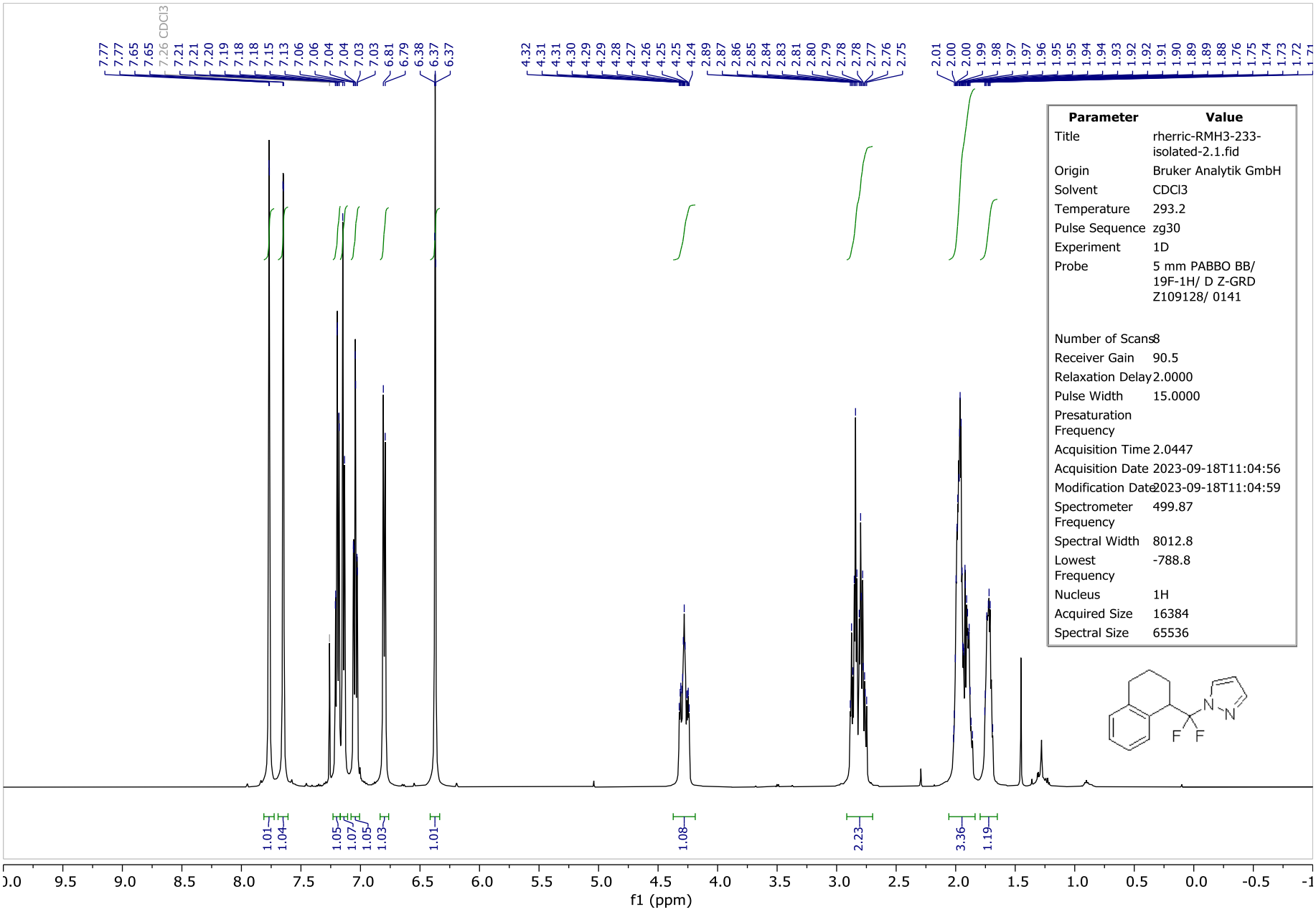


Parameter	Value
Title	rherric-RMH3-258-Isolated-800mHz-Acetone.2.fid
Origin	Bruker BioSpin GmbH
Solvent	(CD3)2CO
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	1000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2023-12-09T17:59:05
Modification Date	2023-12-09T17:59:05
Spectrometer Frequency	201.23
Spectral Width	50000.0
Lowest Frequency	-2796.5
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

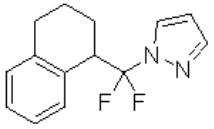


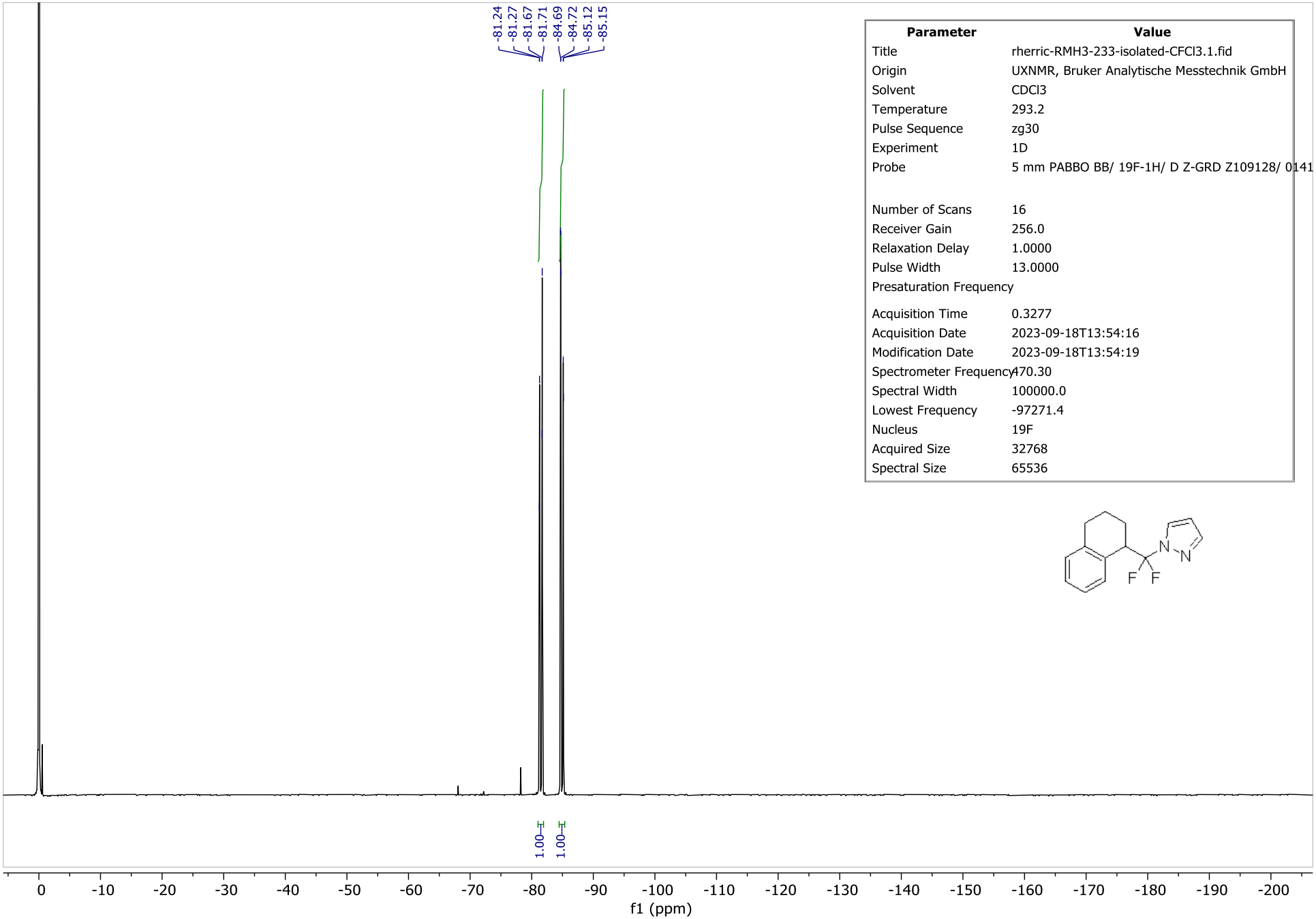
Parameter	Value
Title	rherric-11202024-RMH3-258-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.5
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-11-20T11:21:10
Modification Date	2024-11-20T11:55:37
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97276.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(difluoro(1,2,3,4-tetrahydronaphthalen-1-yl)methyl)-1*H*-pyrazole (**11h**)



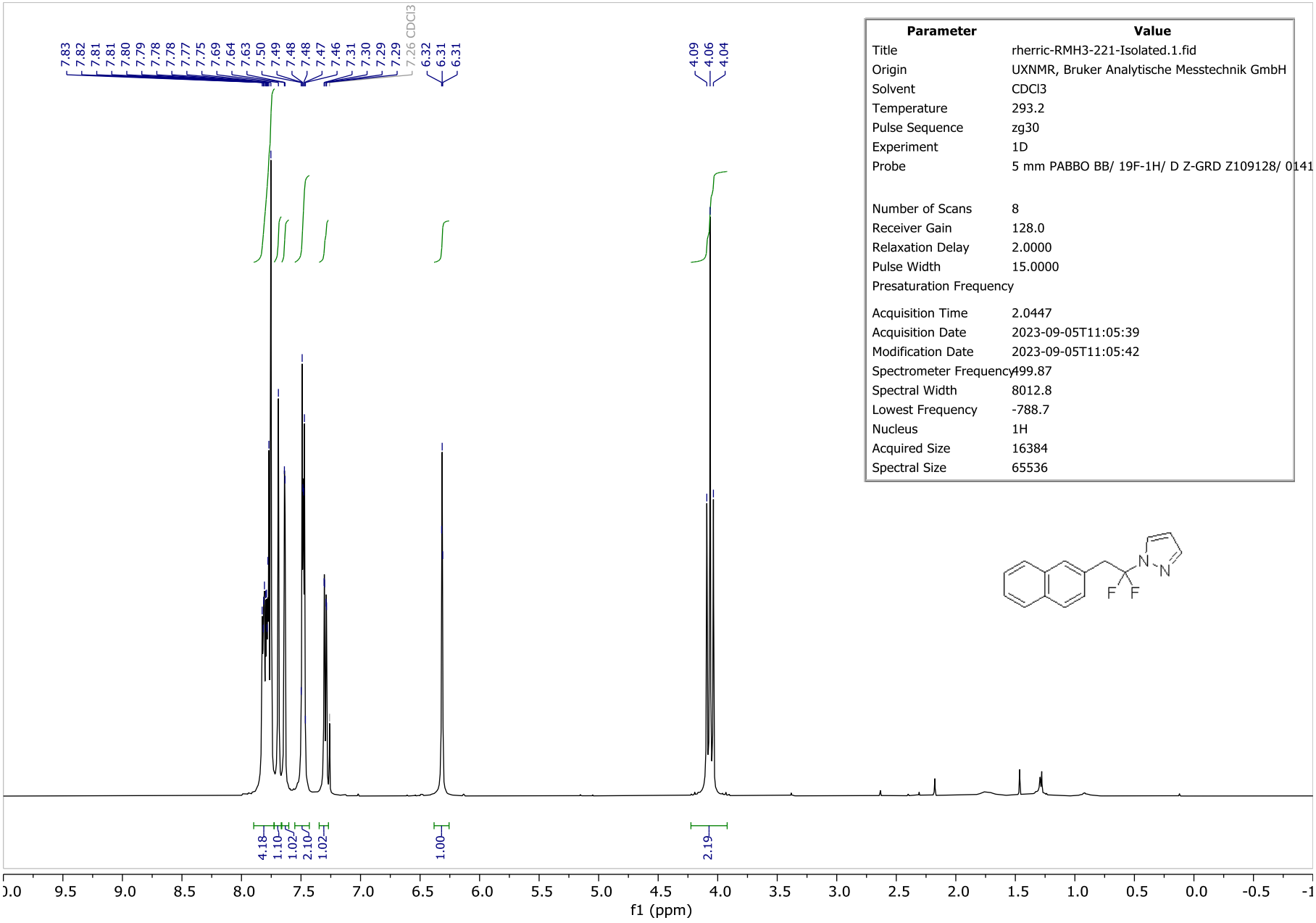
Parameter	Value
Title	rherric-RMH3-233-isolated-2.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	751
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-09-18T11:16:30
Modification Date	2023-09-18T11:16:33
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1261.3
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





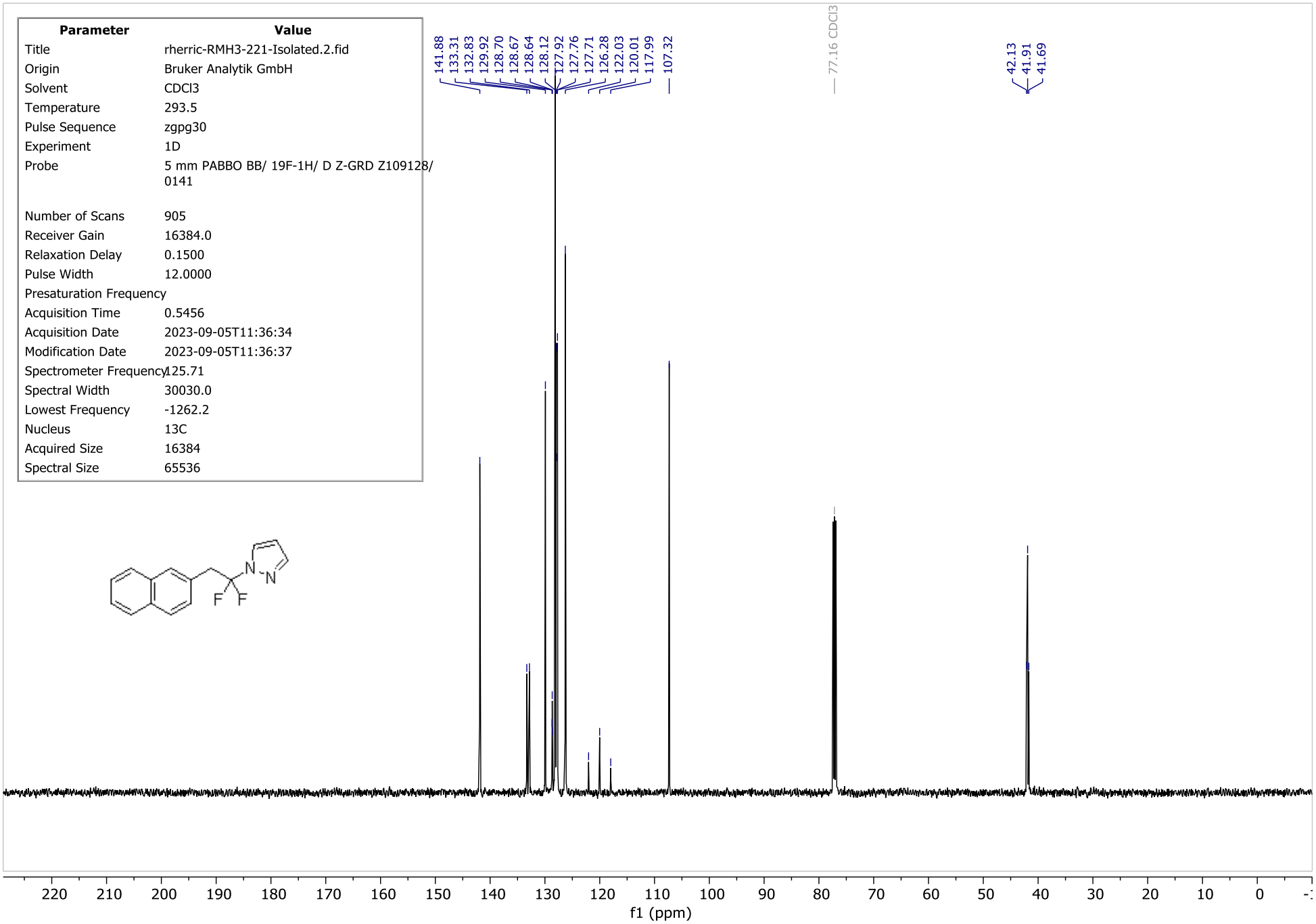
Parameter	Value
Title	rherric-RMH3-233-isolated-CFCl3.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-09-18T13:54:16
Modification Date	2023-09-18T13:54:19
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97271.4
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

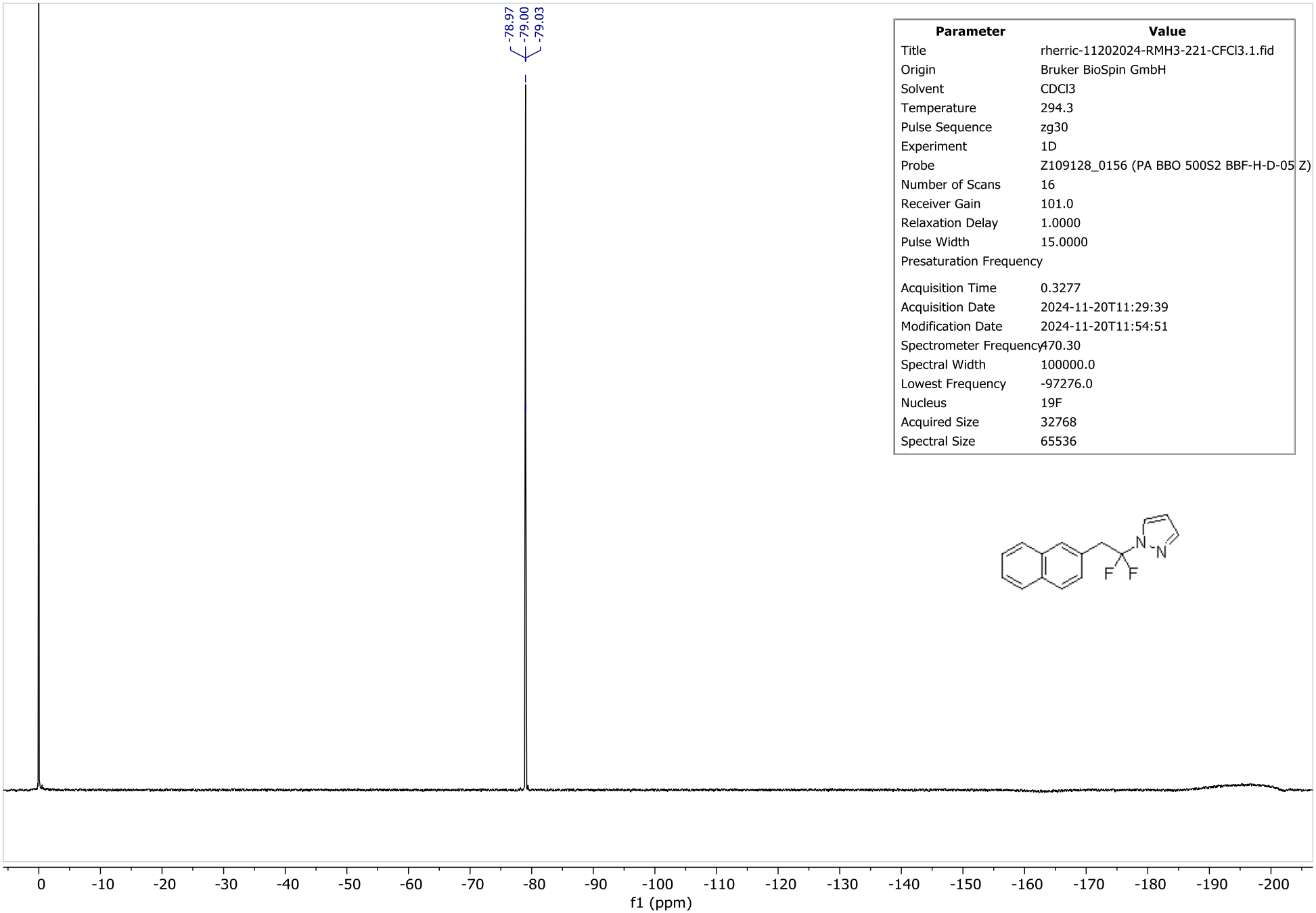
NMR spectra for 1-(1,1-difluoro-2-(naphthalen-2-yl)ethyl)-1*H*-pyrazole (**11i**)



Parameter	Value
Title	rherric-RMH3-221-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.2
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	2023-09-05T11:05:39
Modification Date	2023-09-05T11:05:42
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

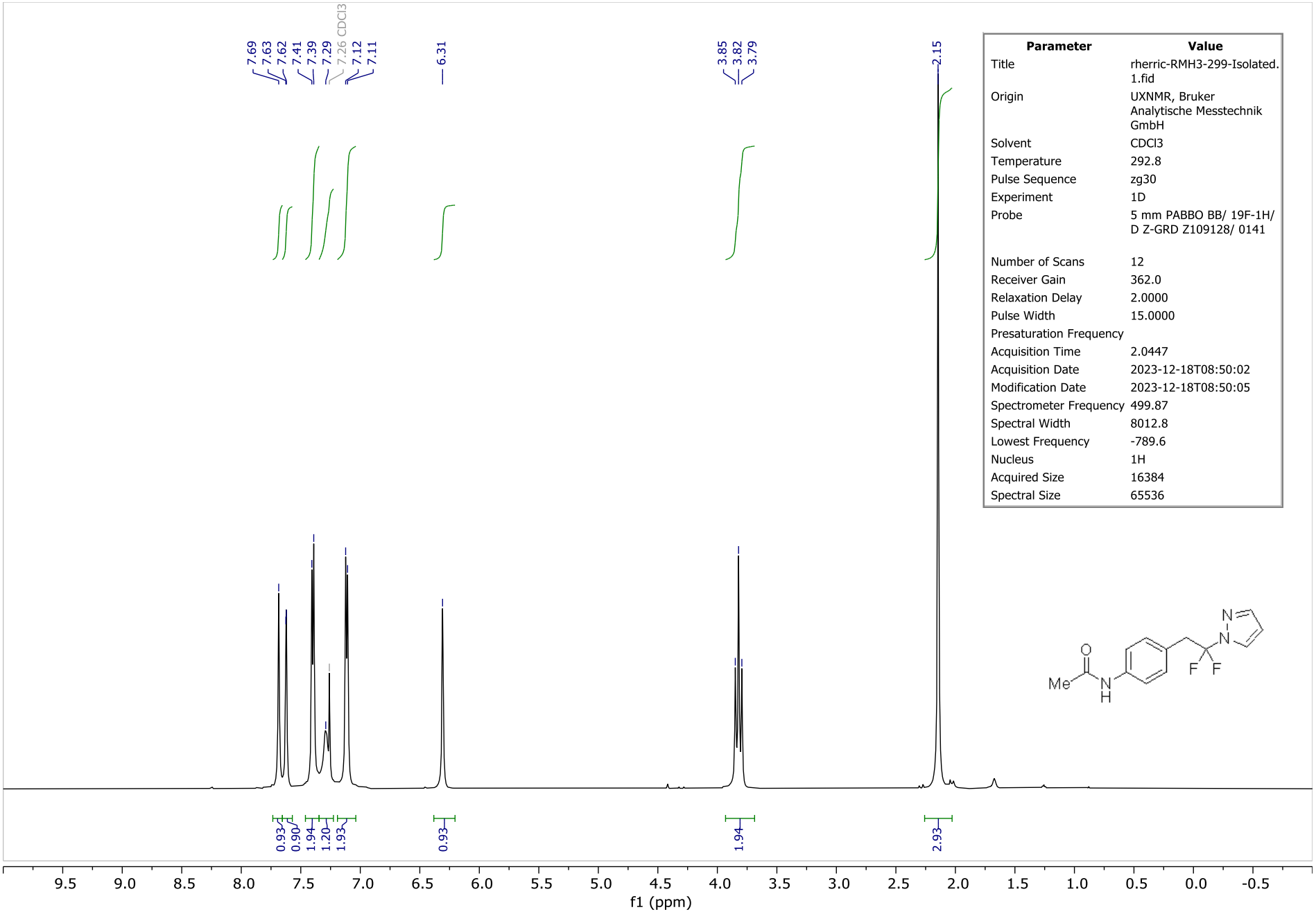
Parameter	Value
Title	rherric-RMH3-221-Isolated.2.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.5
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	905
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-09-05T11:36:34
Modification Date	2023-09-05T11:36:37
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1262.2
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



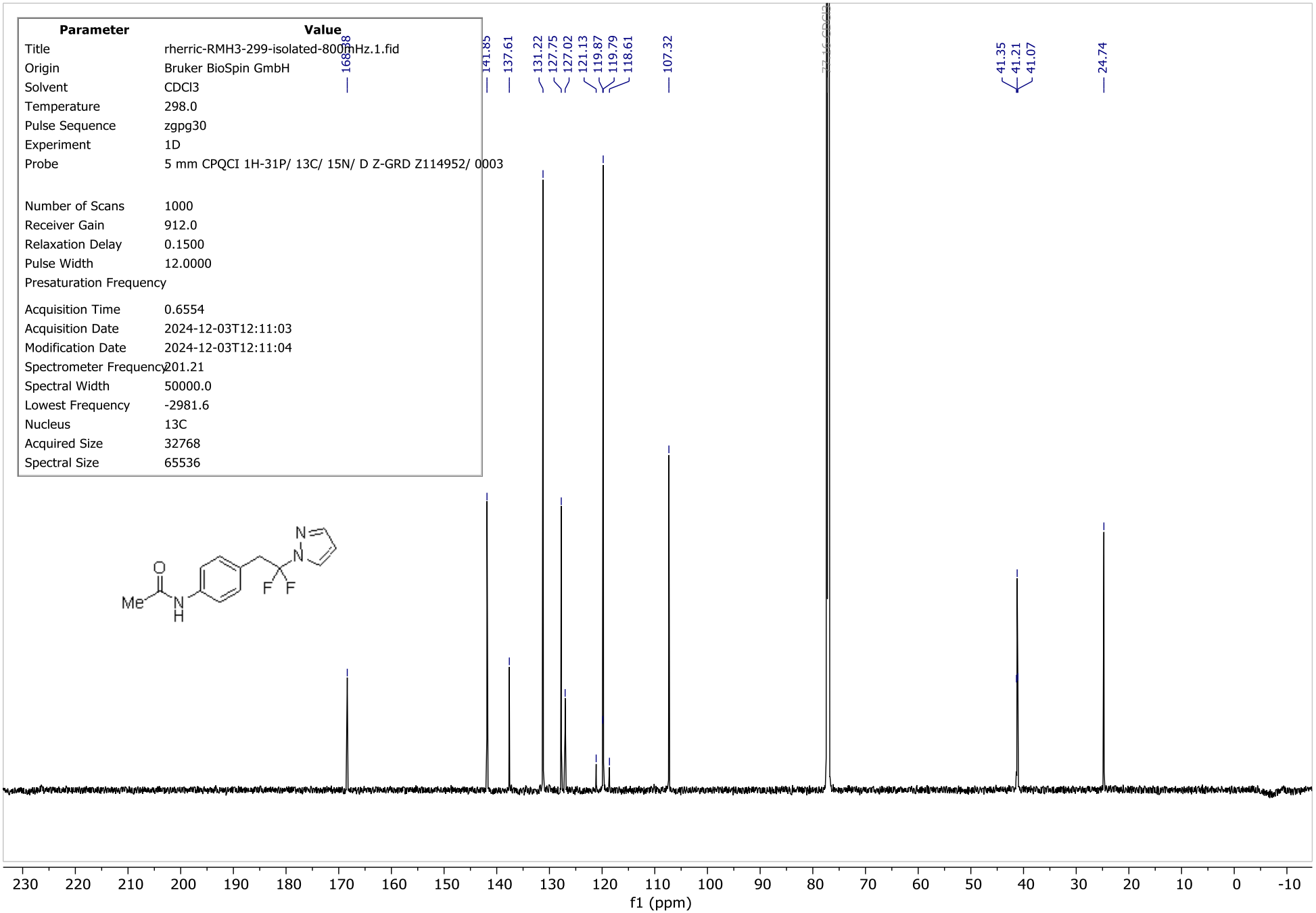


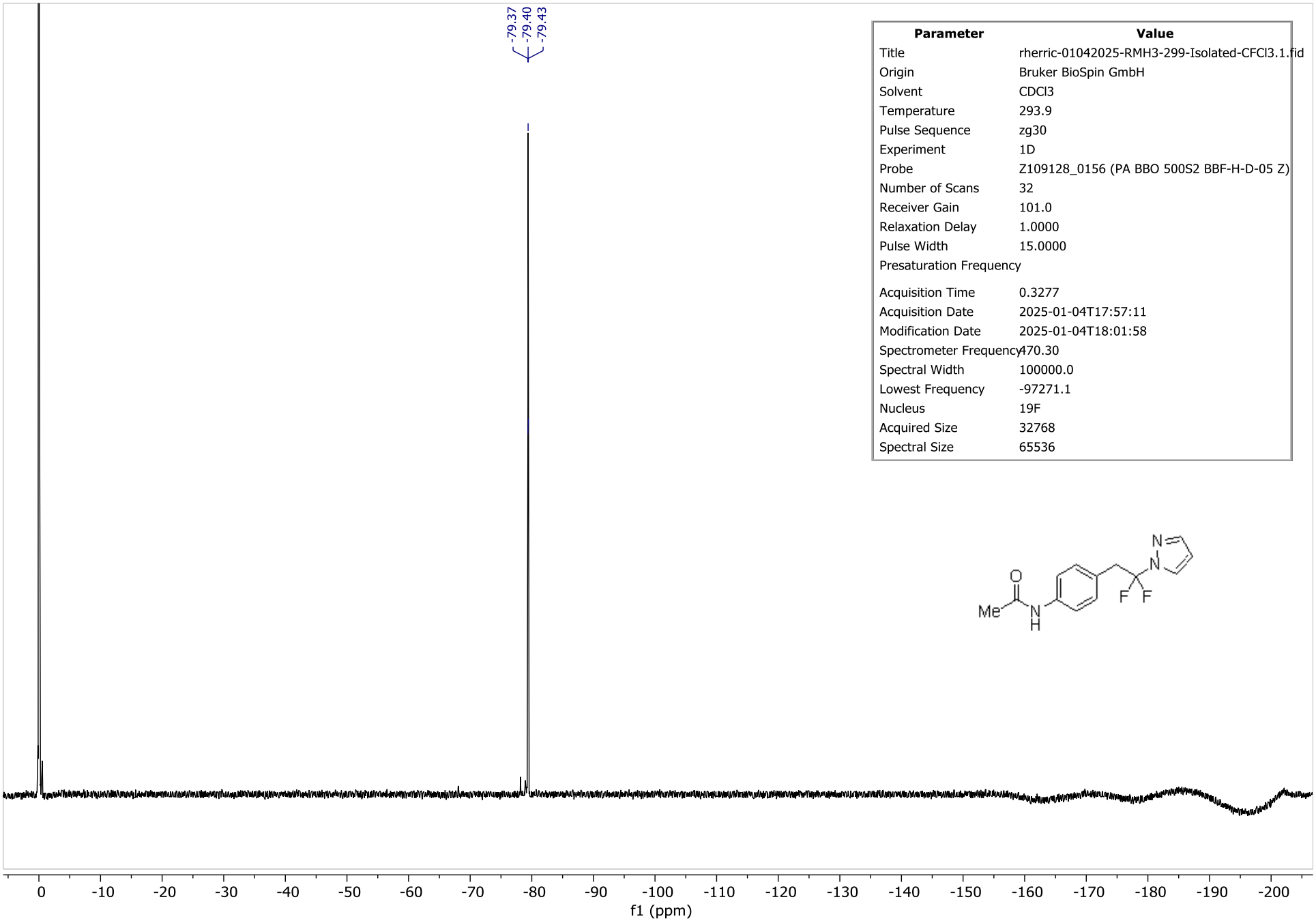
Parameter	Value
Title	rherric-11202024-RMH3-221-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.3
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-11-20T11:29:39
Modification Date	2024-11-20T11:54:51
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97276.0
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for *N*-(4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)phenyl)acetamide (**11j**)



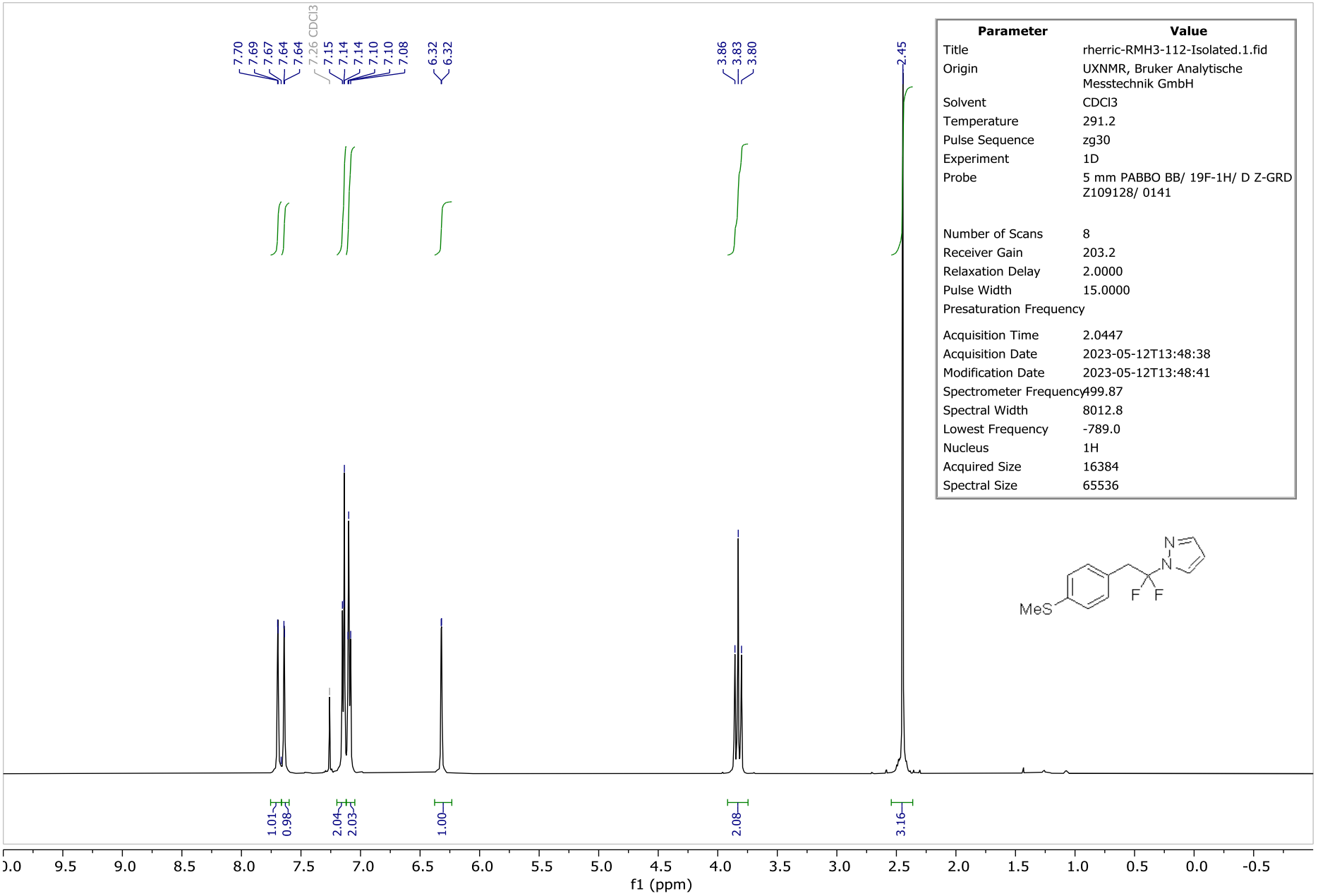
Parameter	Value
Title	rherric-RMH3-299-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/D Z-GRD Z109128/ 0141
Number of Scans	12
Receiver Gain	362.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-12-18T08:50:02
Modification Date	2023-12-18T08:50:05
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.6
Nucleus	1H
Acquired Size	16384
Spectral Size	65536


Parameter Value
Title rherric-RMH3-299-isolated-800MHz.1.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 1000
Receiver Gain 912.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.6554
Acquisition Date 2024-12-03T12:11:03
Modification Date 2024-12-03T12:11:04
Spectrometer Frequency 201.21
Spectral Width 50000.0
Lowest Frequency -2981.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
168.38
141.85
137.61
131.22
127.75
127.02
121.13
119.87
119.79
118.61
107.32
77.16 CDCl3
41.35
41.21
41.07
24.74
Me
O
N
H
F
F
N
N
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

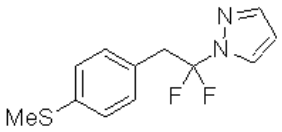


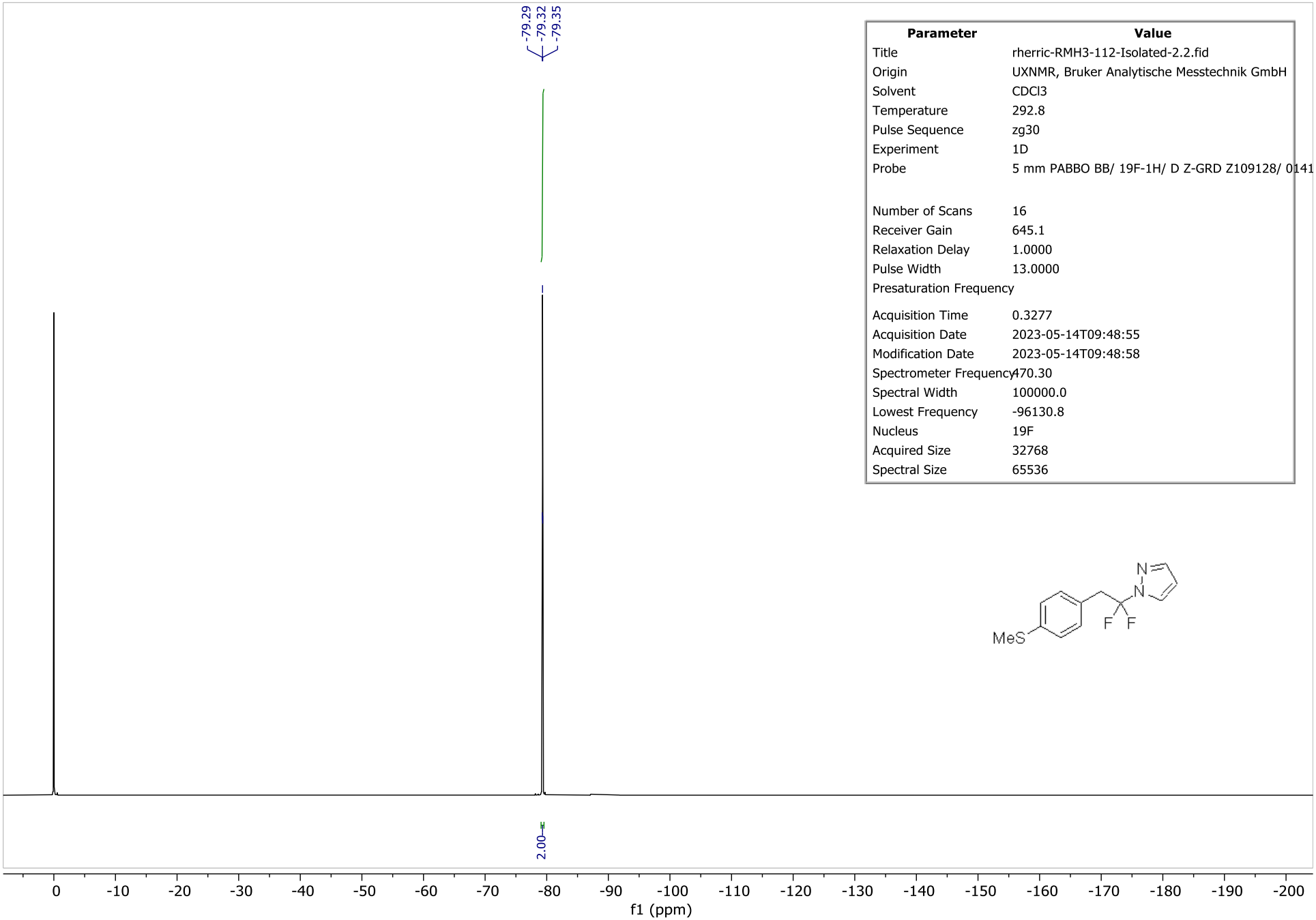
Parameter	Value
Title	rherric-01042025-RMH3-299-Isolated-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.9
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2025-01-04T17:57:11
Modification Date	2025-01-04T18:01:58
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97271.1
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(1,1-difluoro-2-(4-(methylthio)phenyl)ethyl)-1*H*-pyrazole (**11k**)



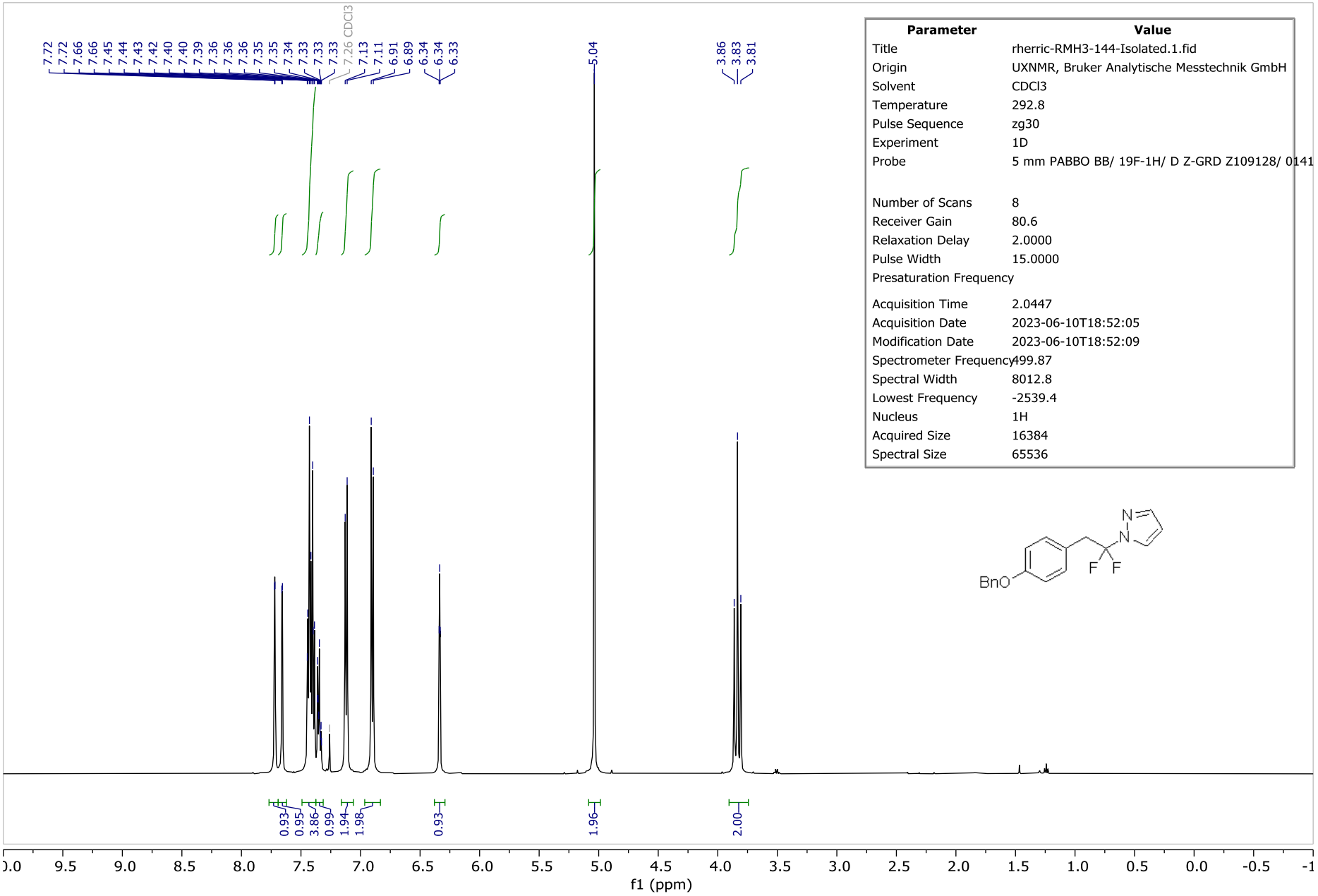
Parameter	Value
Title	rherric-RMH3-112.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	291.5
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-05-12T14:27:59
Modification Date	2023-05-12T14:28:06
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-946.2
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



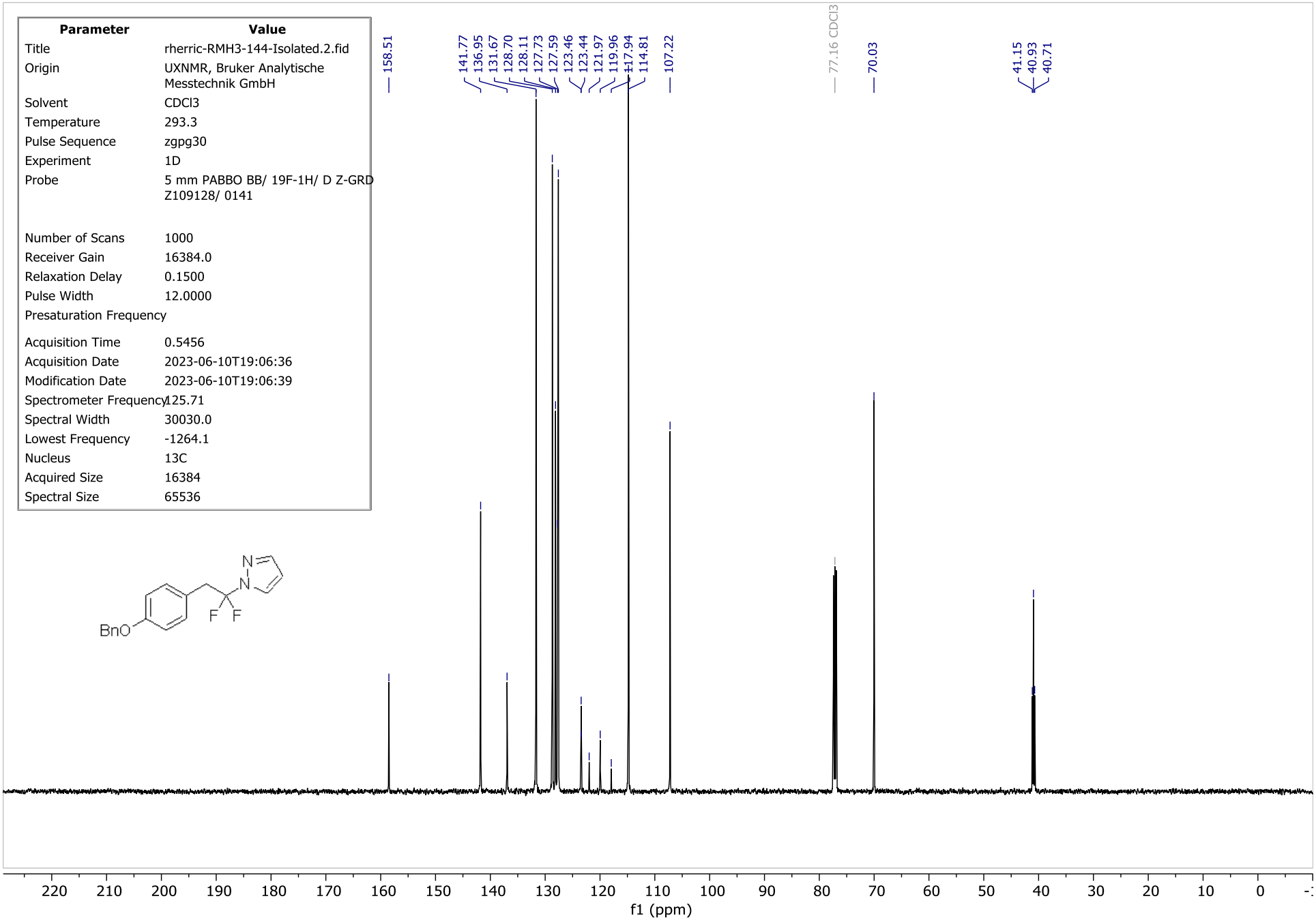


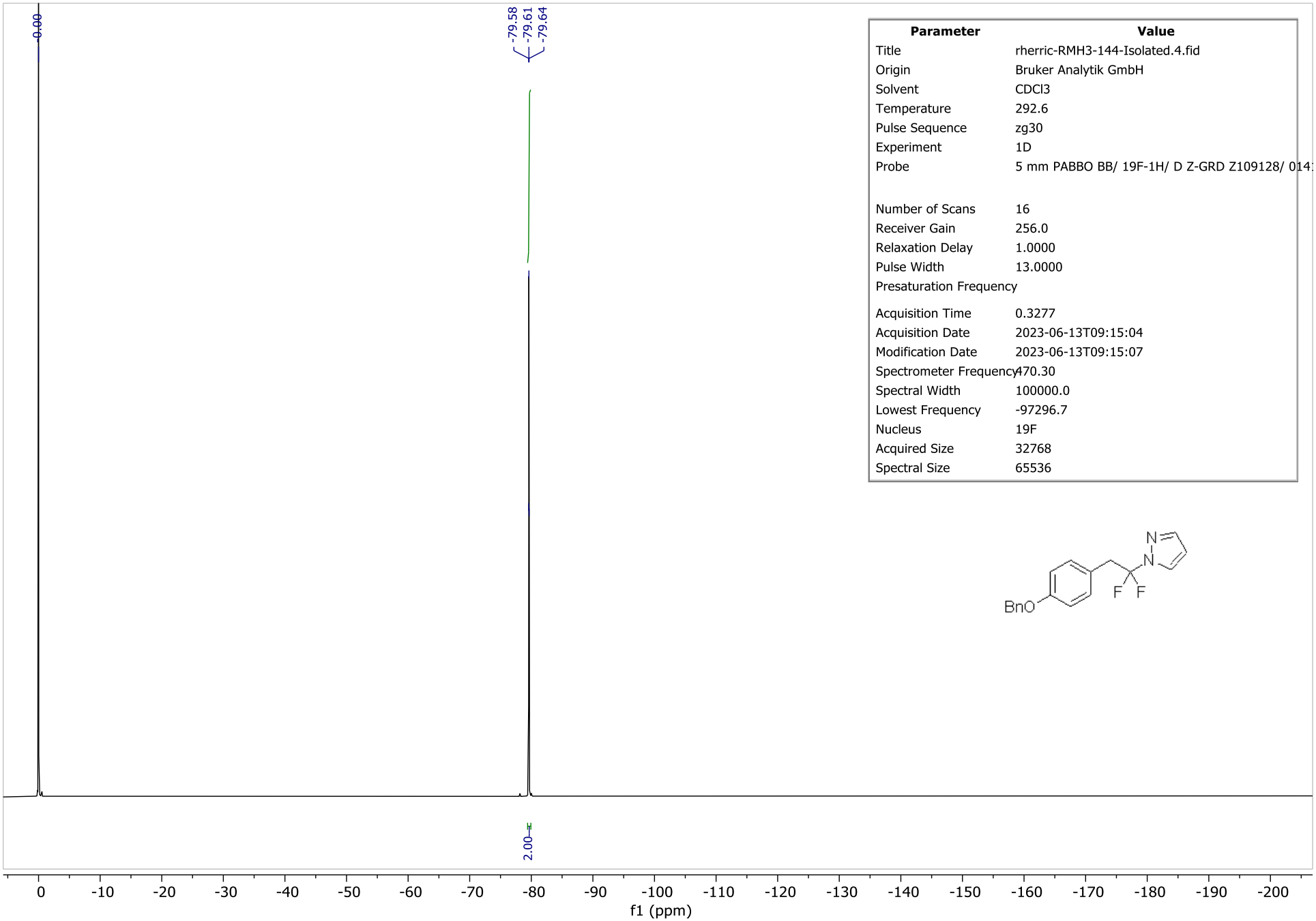
Parameter	Value
Title	rherric-RMH3-112-Isolated-2.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	645.1
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-05-14T09:48:55
Modification Date	2023-05-14T09:48:58
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-96130.8
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

NMR spectra for 1-(2-(4-(benzyloxy)phenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11l**)



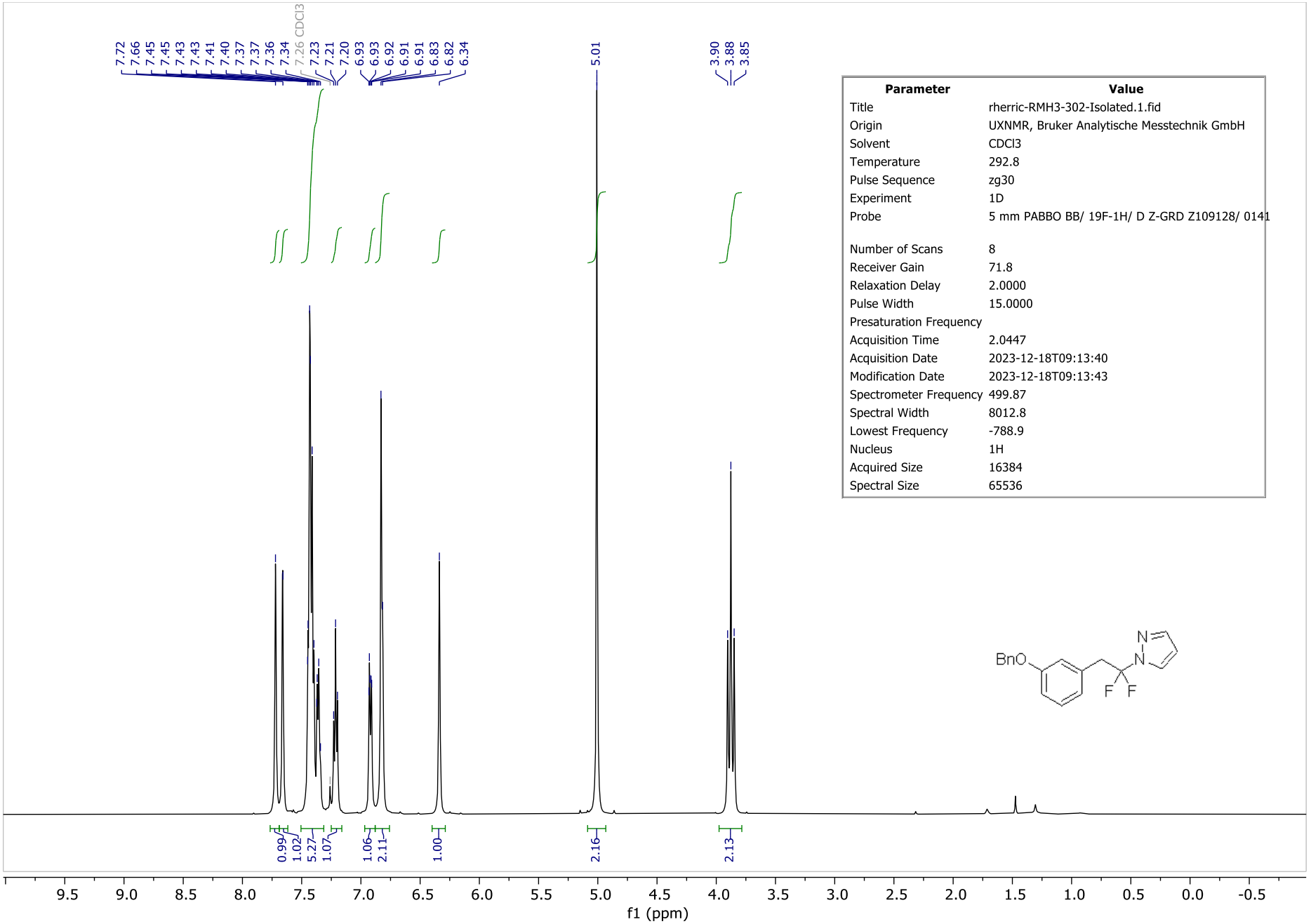
Parameter	Value
Title	rherric-RMH3-144-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	80.6
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-06-10T18:52:05
Modification Date	2023-06-10T18:52:09
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2539.4
Nucleus	1H
Acquired Size	16384
Spectral Size	65536


Parameter Value
Title rherric-RMH3-144-Isolated.2.fid
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 293.3
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 2023-06-10T19:06:36
Modification Date 2023-06-10T19:06:39
Spectrometer Frequency 125.71
Spectral Width 30030.0
Lowest Frequency -1264.1
Nucleus 13C
Acquired Size 16384
Spectral Size 65536
158.51
141.77
136.95
131.67
128.70
128.11
127.73
127.59
123.46
123.44
121.97
119.96
117.94
114.81
107.22
77.16 CDCl3
70.03
41.15
40.93
40.71
N
N
F
F
BnO
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)



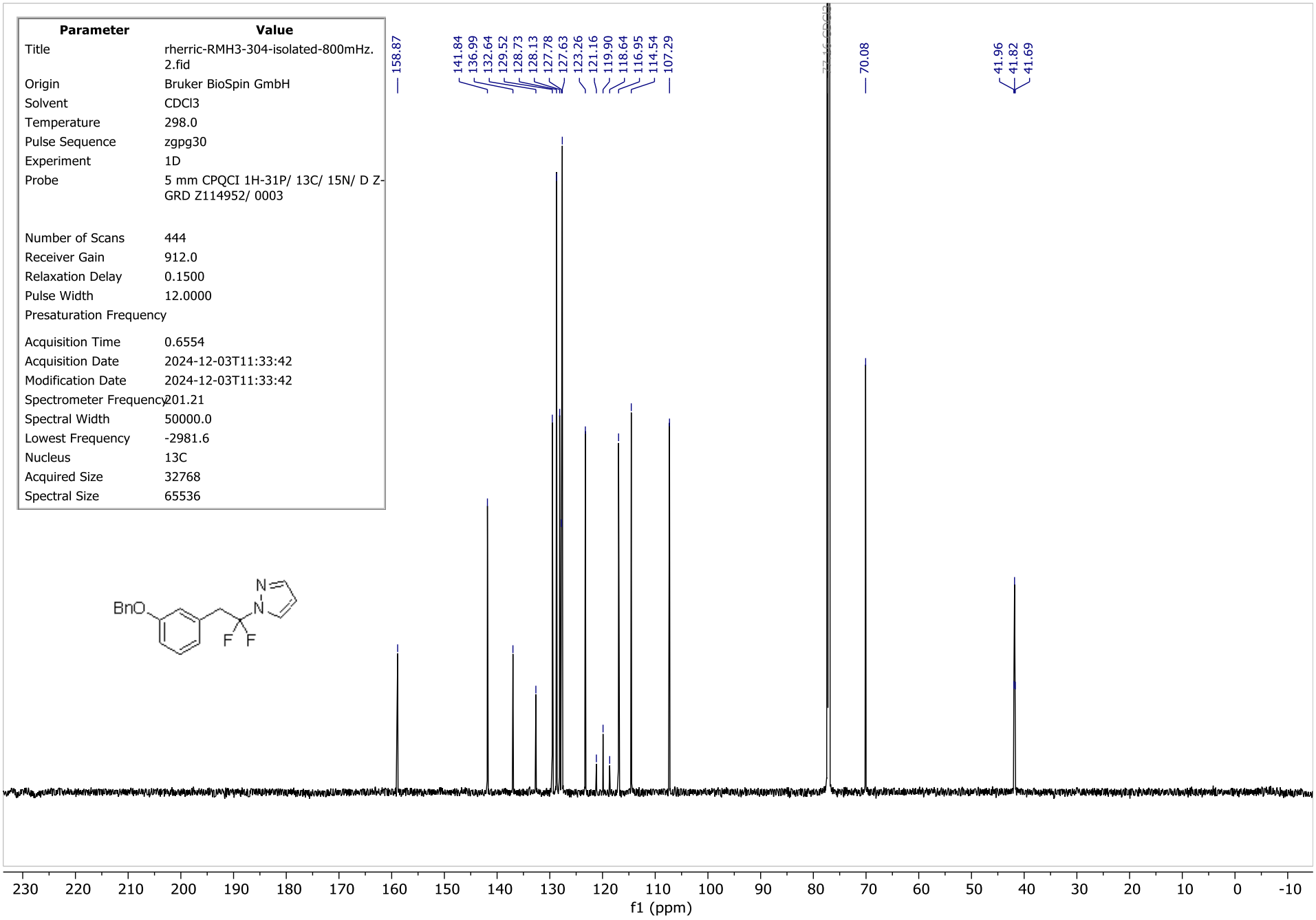
Parameter	Value
Title	rherric-RMH3-144-Isolated.4.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 014
Number of Scans	16
Receiver Gain	256.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-06-13T09:15:04
Modification Date	2023-06-13T09:15:07
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97296.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

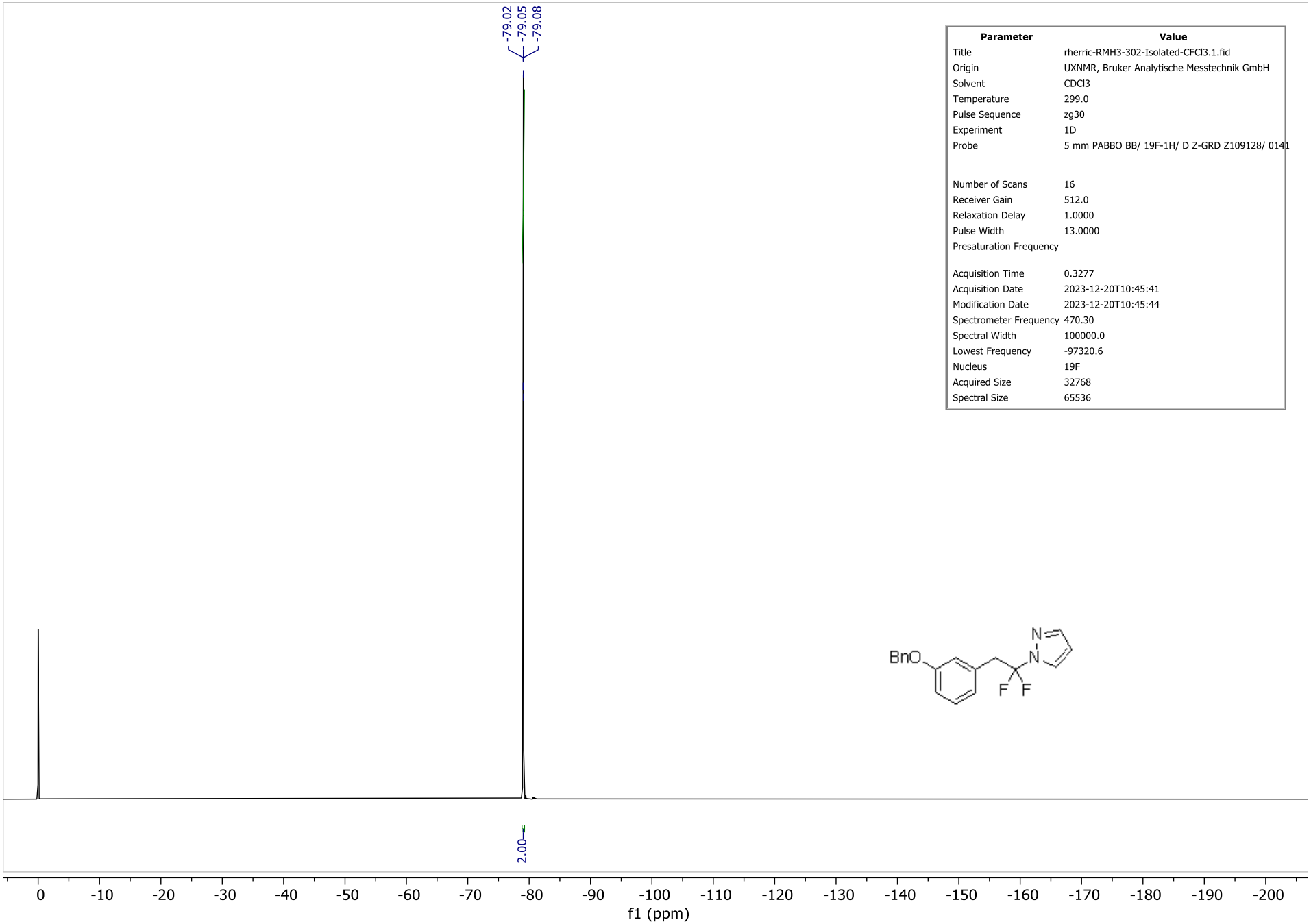
NMR spectra for 1-(2-(3-(benzyloxy)phenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11m**)



Parameter	Value
Title	rherric-RMH3-302-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	71.8
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-12-18T09:13:40
Modification Date	2023-12-18T09:13:43
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.9
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

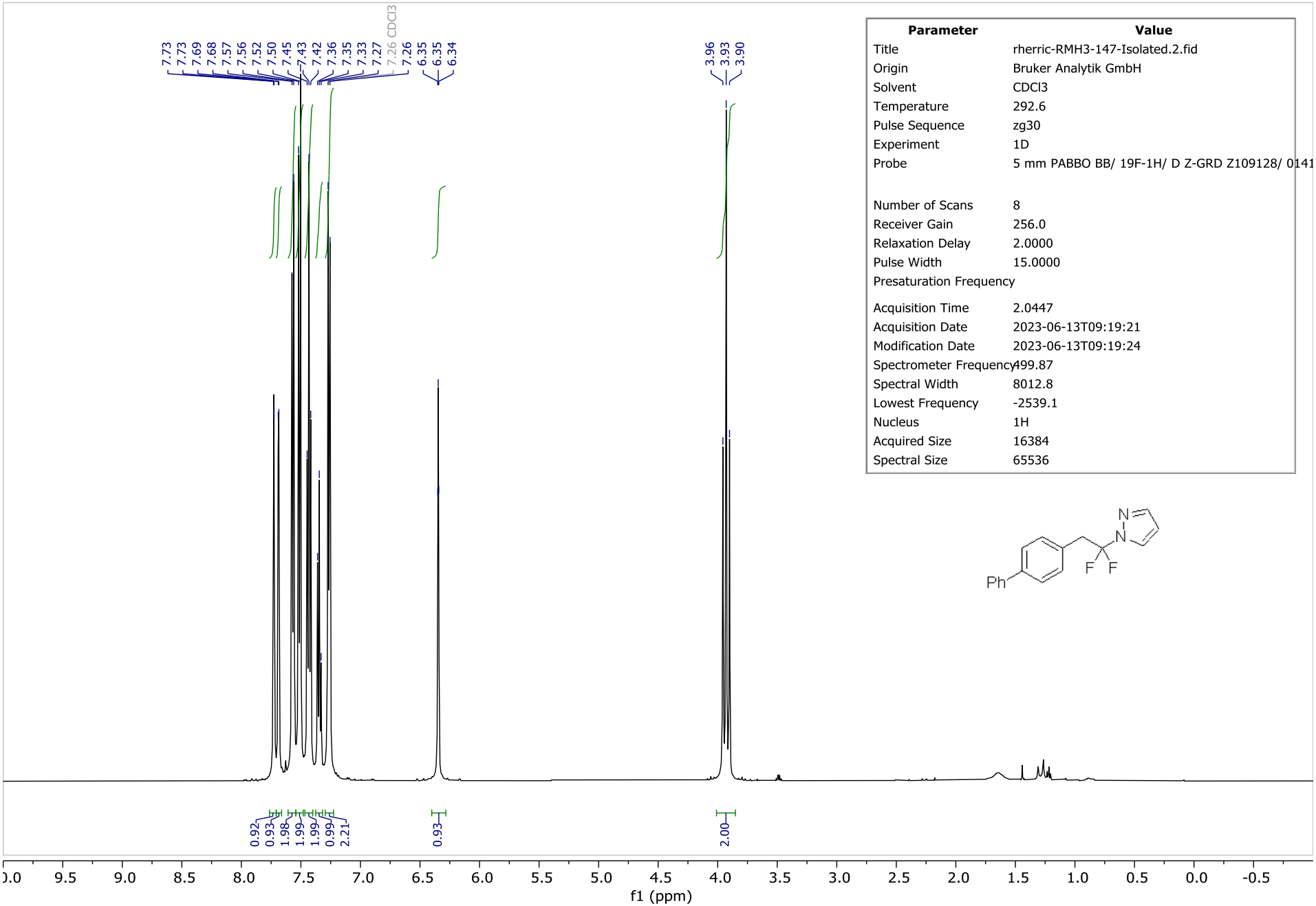
Parameter	Value
Title	rherric-RMH3-304-isolated-800mHz.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	444
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2024-12-03T11:33:42
Modification Date	2024-12-03T11:33:42
Spectrometer Frequency	201.21
Spectral Width	50000.0
Lowest Frequency	-2981.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536





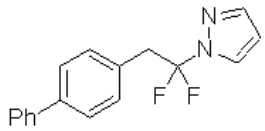
Parameter	Value
Title	rherric-RMH3-302-Isolated-CFCl3.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	299.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	512.0
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-12-20T10:45:41
Modification Date	2023-12-20T10:45:44
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97320.6
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

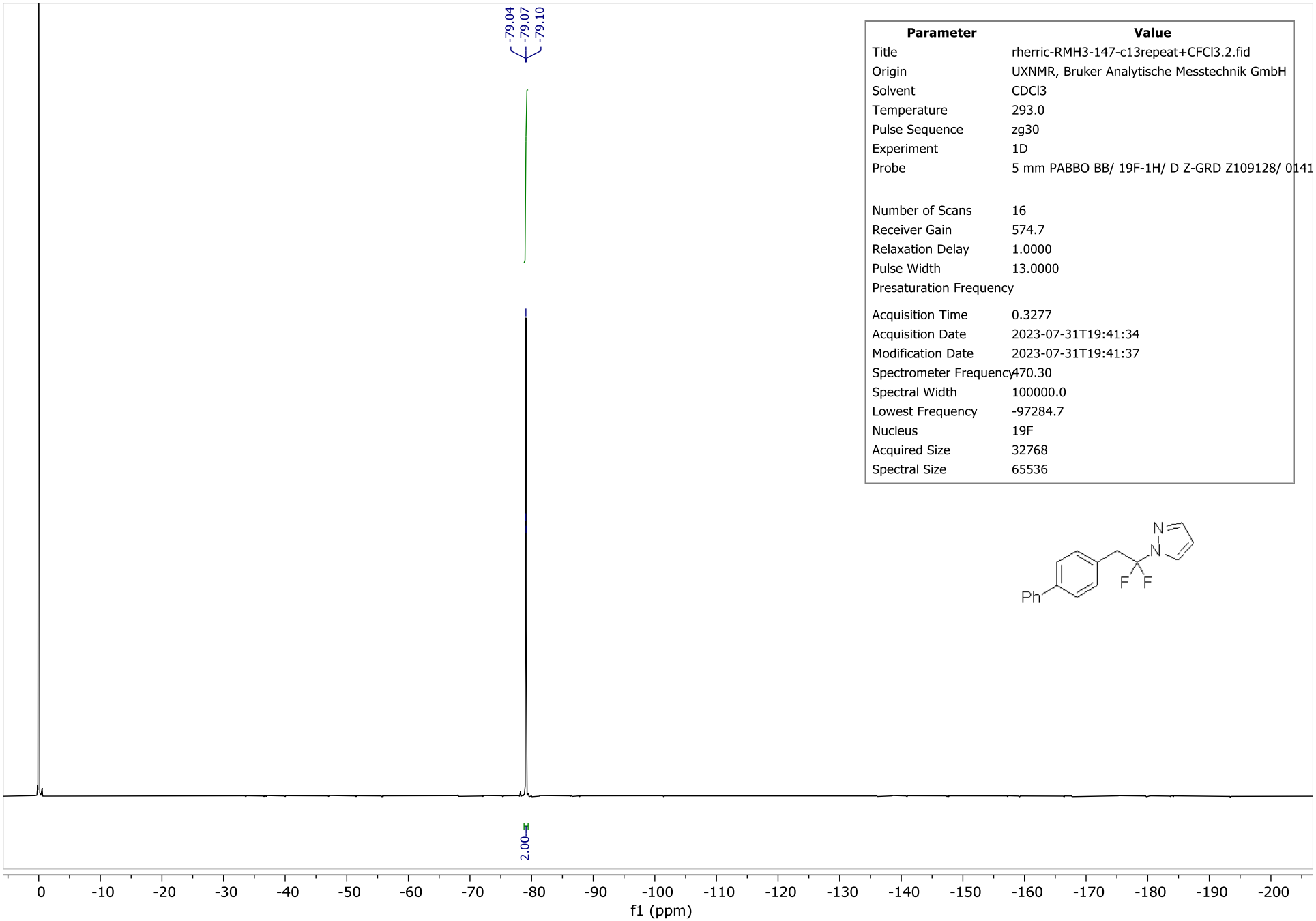
NMR spectra for 1-(2-([1,1'-biphenyl]-4-yl)-1,1-difluoroethyl)-1*H*-pyrazole (**11n**)



Parameter	Value
Title	rherric-RMH3-147-Isolated.2.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	292.6
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	256.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-06-13T09:19:21
Modification Date	2023-06-13T09:19:24
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-2539.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

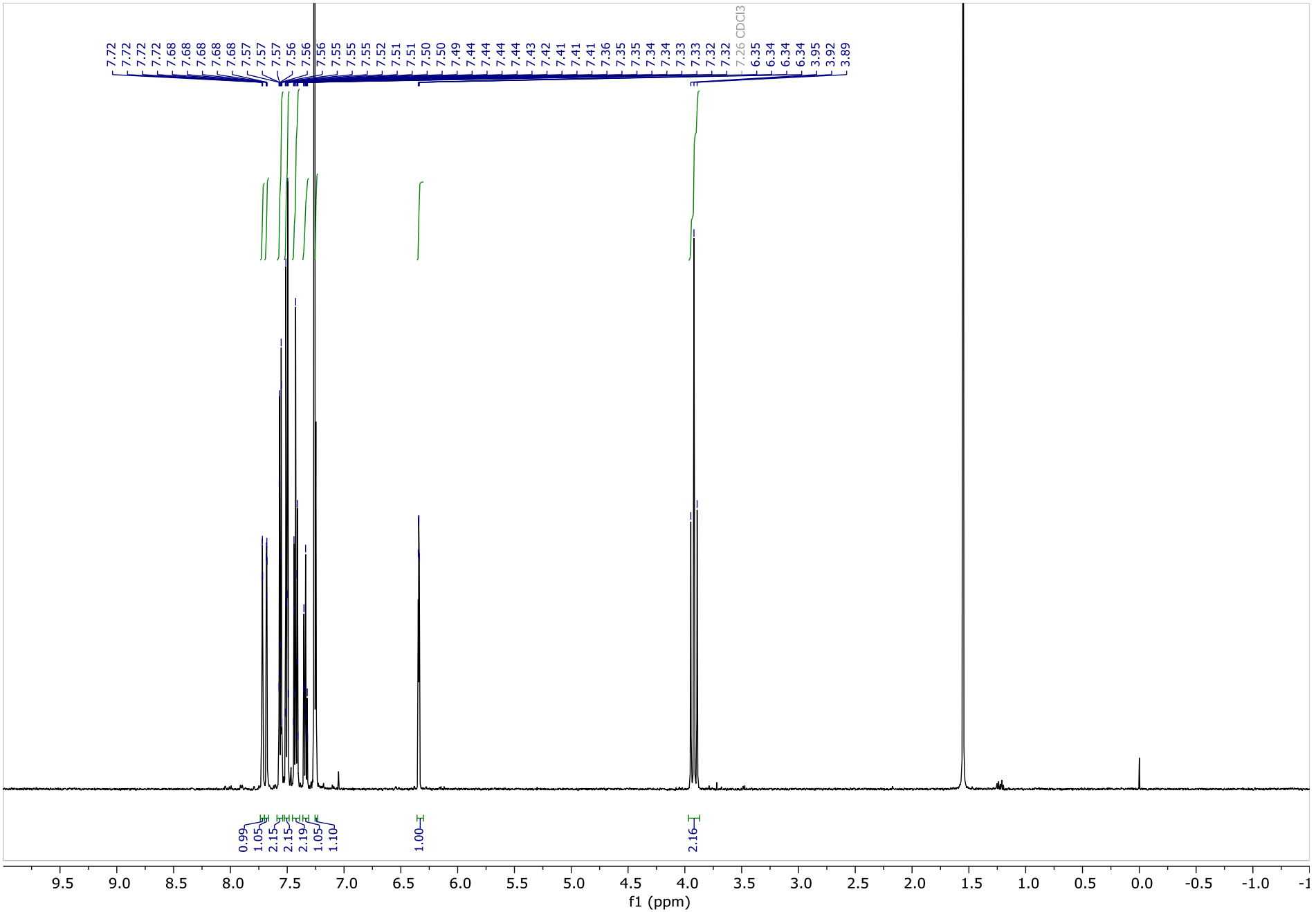
Parameter	Value
Title	rherric-RMH3-147-Isolated.3.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-06-13T09:33:39
Modification Date	2023-06-13T09:33:42
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1286.0
Nucleus	13C
Acquired Size	16384
Spectral Size	65536



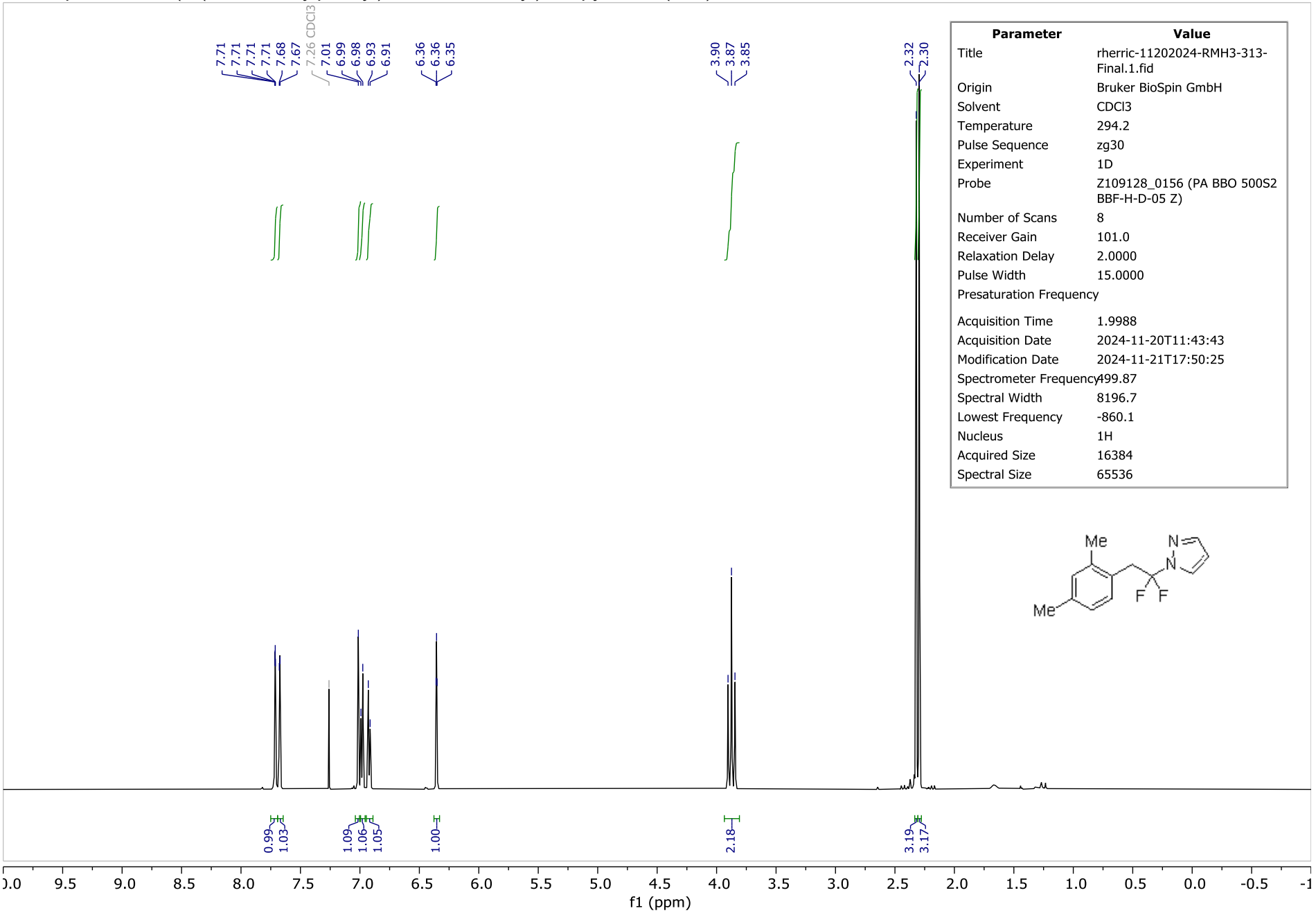


Parameter	Value
Title	rherric-RMH3-147-c13repeat+CFCl3.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-07-31T19:41:34
Modification Date	2023-07-31T19:41:37
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97284.7
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

^{1}H NMR spectra of **11n** (gram scale reaction)

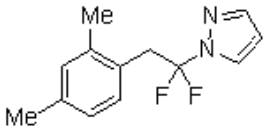


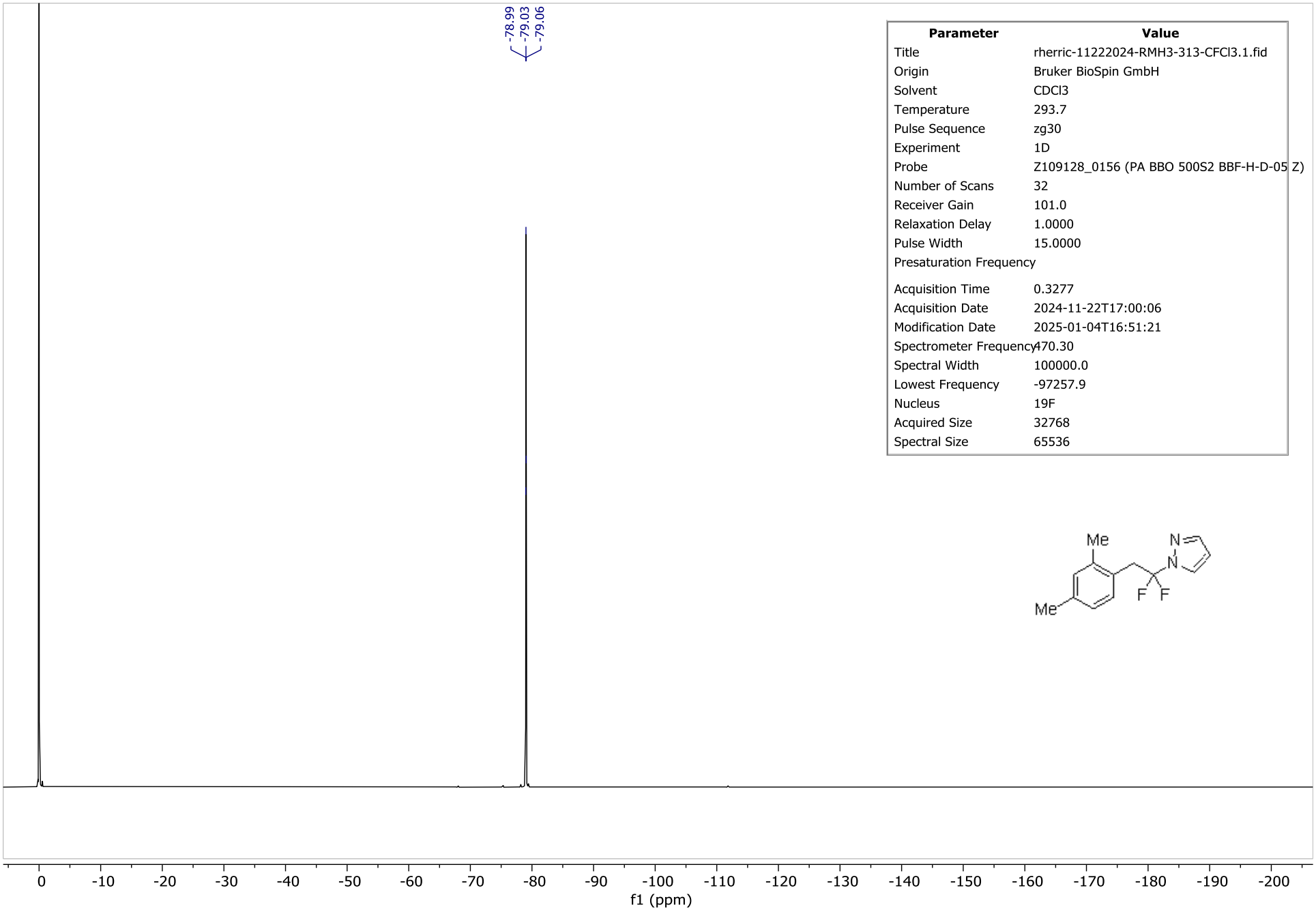
NMR spectra for 1-(2-(2,4-dimethylphenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11o**)



Parameter	Value
Title	rherric-11202024-RMH3-313-Final.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.2
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	8
Receiver Gain	101.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	1.9988
Acquisition Date	2024-11-20T11:43:43
Modification Date	2024-11-21T17:50:25
Spectrometer Frequency	499.87
Spectral Width	8196.7
Lowest Frequency	-860.1
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

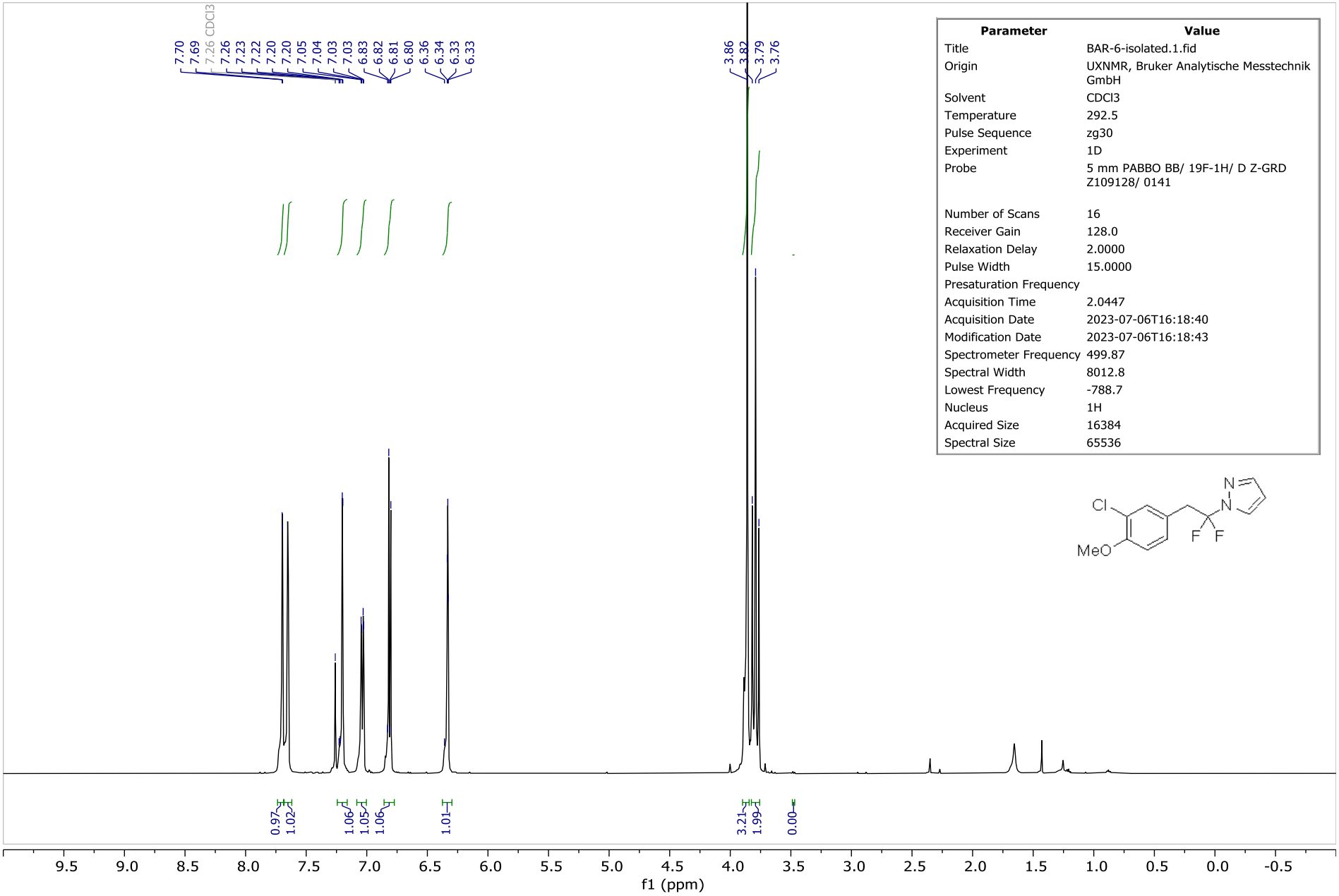
Parameter	Value
Title	rherric-11202024-RMH3-313-Final.2.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	295.8
Pulse Sequence	zgpg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	2000
Receiver Gain	101.0
Relaxation Delay	0.1500
Pulse Width	10.0000
Presaturation Frequency	
Acquisition Time	0.5439
Acquisition Date	2024-11-20T22:26:38
Modification Date	2024-11-21T17:50:26
Spectrometer Frequency	125.71
Spectral Width	30120.5
Lowest Frequency	-1246.4
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





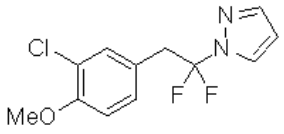
Parameter	Value
Title	rherric-11222024-RMH3-313-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	32
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-11-22T17:00:06
Modification Date	2025-01-04T16:51:21
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97257.9
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

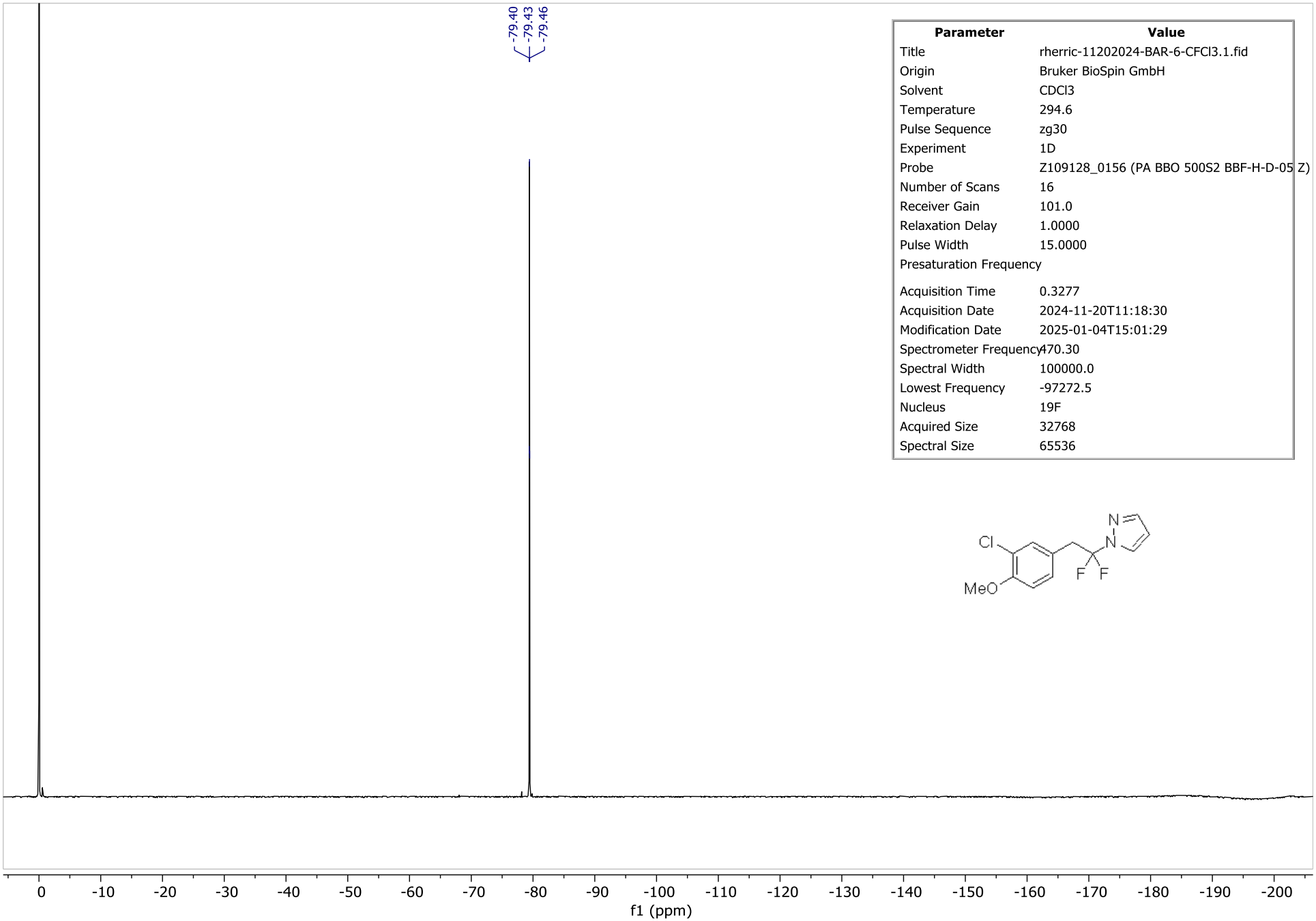
NMR spectra for 1-(2-(3-chloro-4-methoxyphenyl)-1, 1-difluoroethyl)-1*H*-pyrazole (**11p**)



Parameter	Value
Title	BAR-6-isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik 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	16
Receiver Gain	128.0
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-07-06T16:18:40
Modification Date	2023-07-06T16:18:43
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-788.7
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

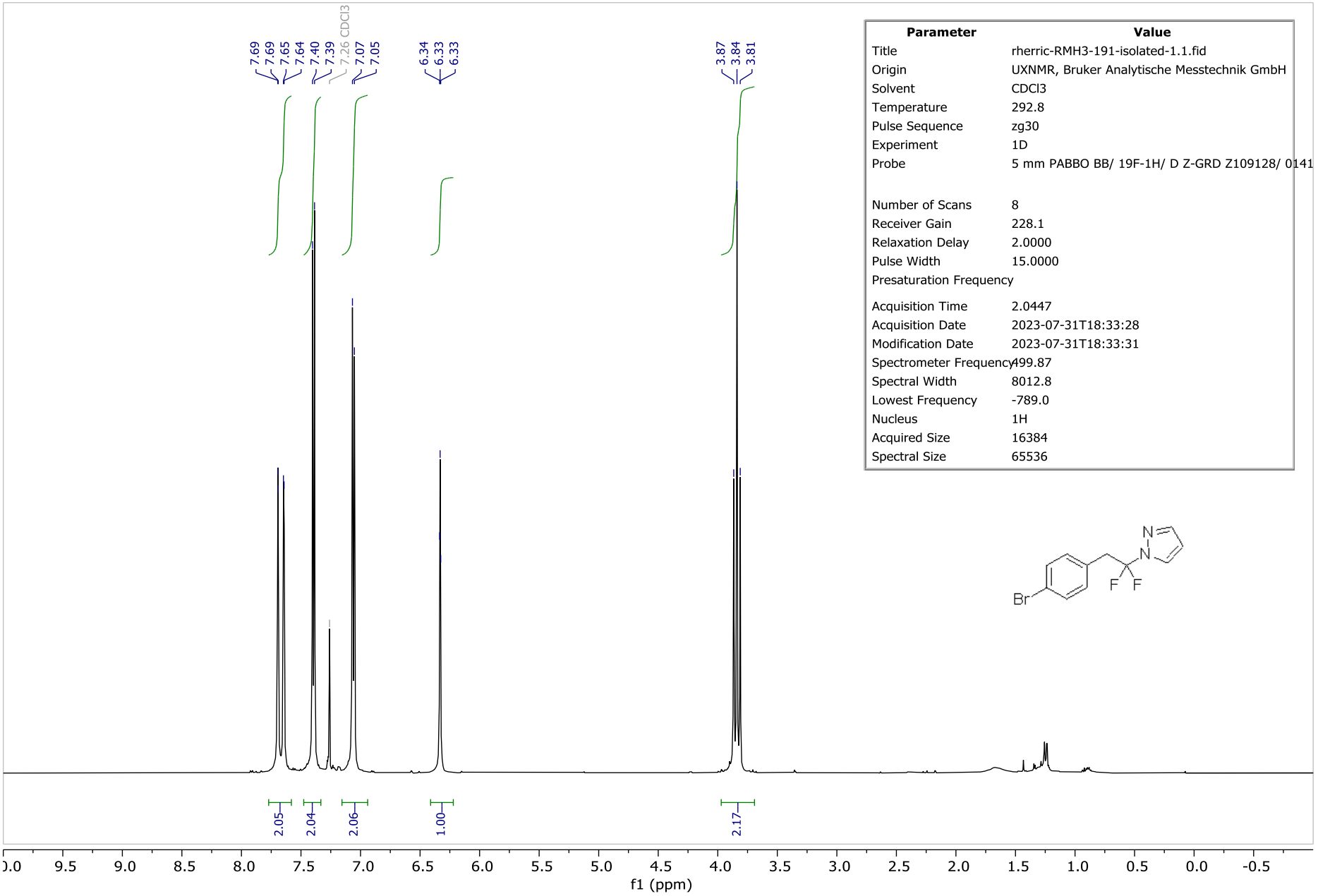
Parameter	Value
Title	BAR-6-isolated.3.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.4
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.5100
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-07-06T16:45:55
Modification Date	2023-07-06T16:45:58
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1257.3
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





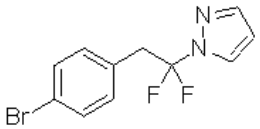
Parameter	Value
Title	rherric-11202024-BAR-6-CFCl3.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	294.6
Pulse Sequence	zg30
Experiment	1D
Probe	Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans	16
Receiver Gain	101.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2024-11-20T11:18:30
Modification Date	2025-01-04T15:01:29
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97272.5
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

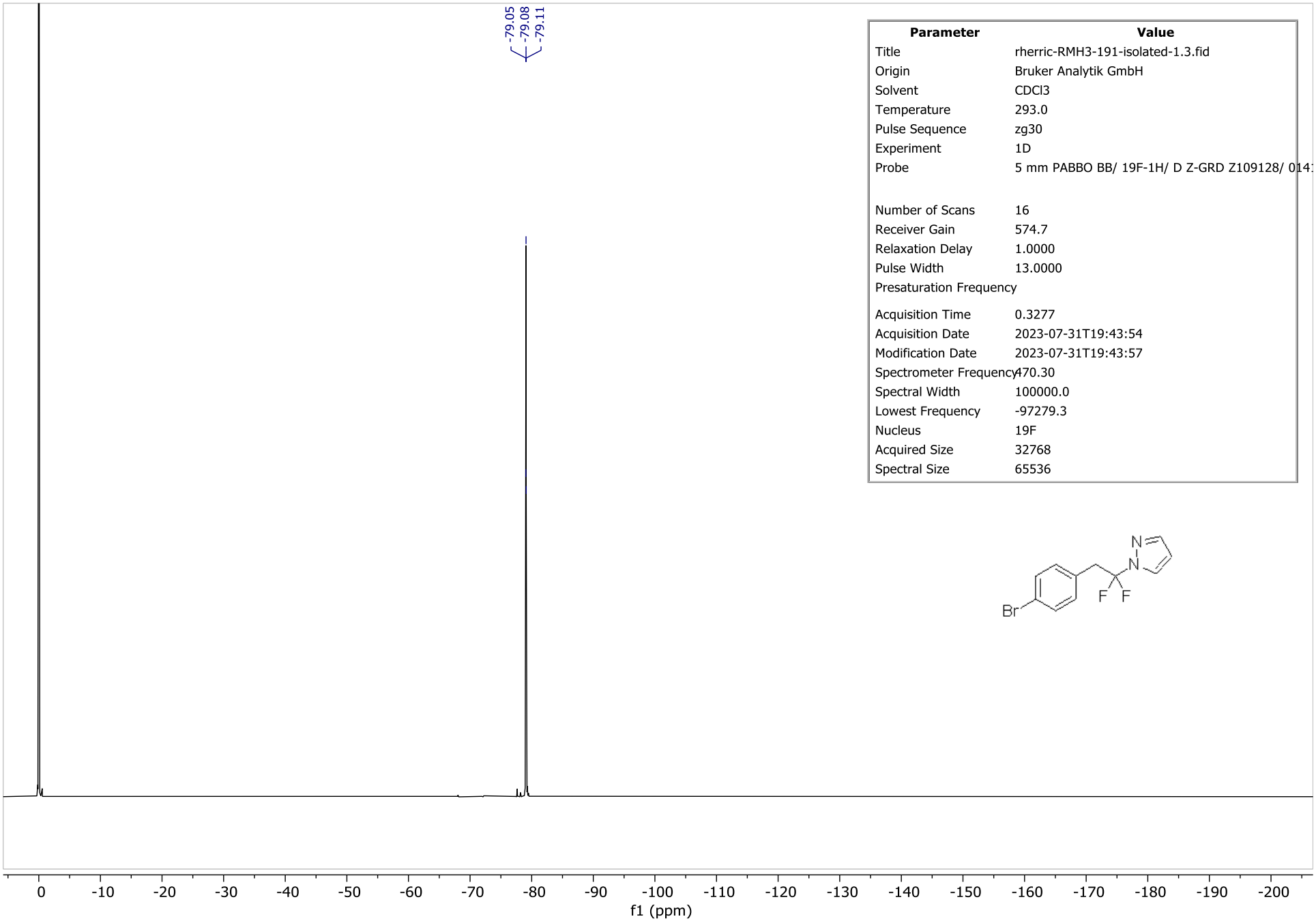
NMR spectra for 1-(2-(4-bromophenyl)-1,1-difluoroethyl)-1*H*-pyrazole (**11q**)



Parameter	Value
Title	rherric-RMH3-191-isolated-1.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.8
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	8
Receiver Gain	228.1
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-07-31T18:33:28
Modification Date	2023-07-31T18:33:31
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.0
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

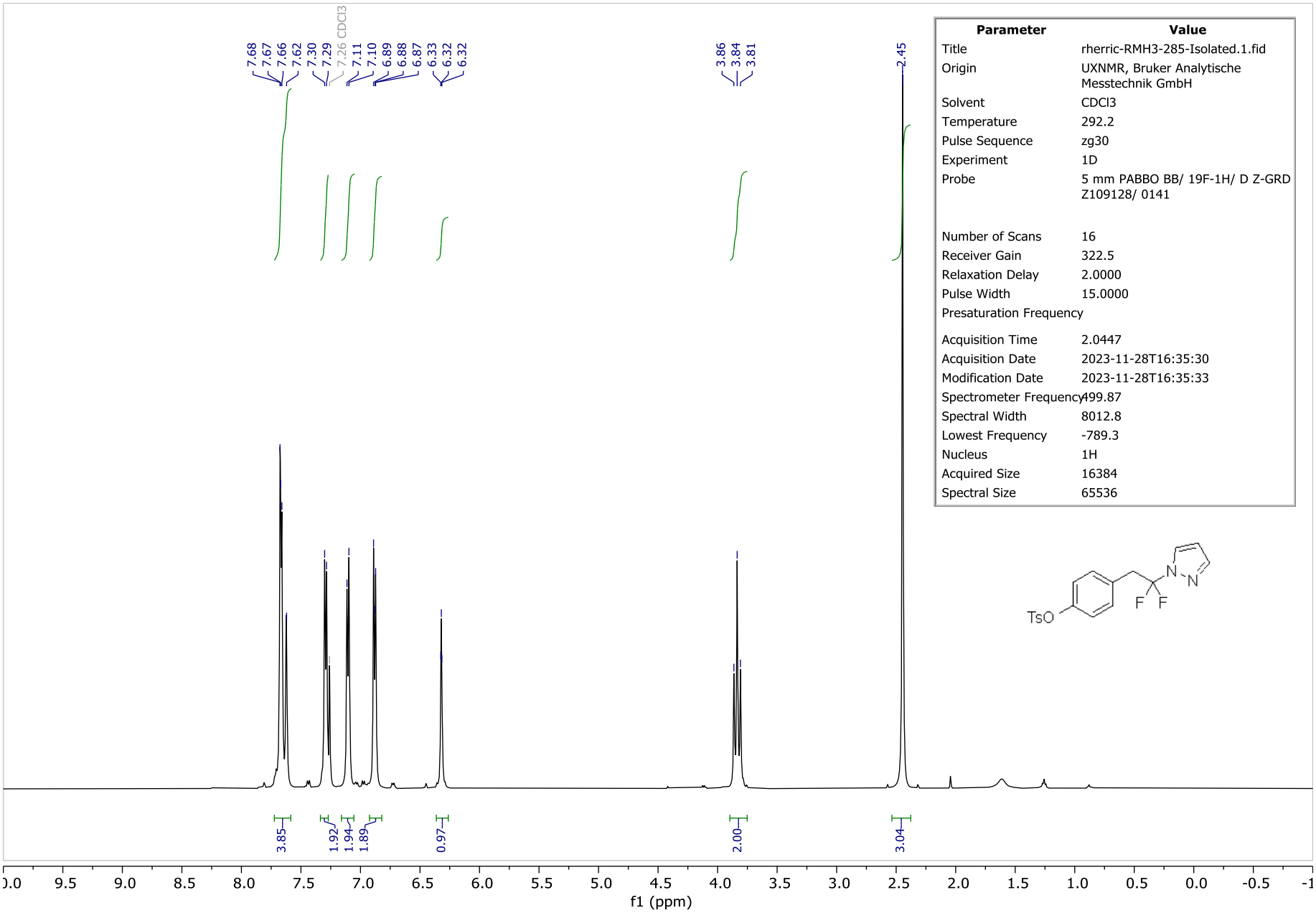
Parameter	Value
Title	rherric-RMH3-191-isolated-1.2.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	293.7
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	1000
Receiver Gain	16384.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.5456
Acquisition Date	2023-07-31T19:20:17
Modification Date	2023-07-31T19:20:20
Spectrometer Frequency	125.71
Spectral Width	30030.0
Lowest Frequency	-1256.5
Nucleus	13C
Acquired Size	16384
Spectral Size	65536





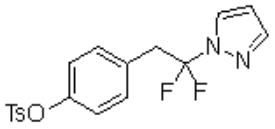
Parameter	Value
Title	rherric-RMH3-191-isolated-1.3.fid
Origin	Bruker Analytik GmbH
Solvent	CDCl3
Temperature	293.0
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 014
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	13.0000
Presaturation Frequency	
Acquisition Time	0.3277
Acquisition Date	2023-07-31T19:43:54
Modification Date	2023-07-31T19:43:57
Spectrometer Frequency	470.30
Spectral Width	100000.0
Lowest Frequency	-97279.3
Nucleus	19F
Acquired Size	32768
Spectral Size	65536

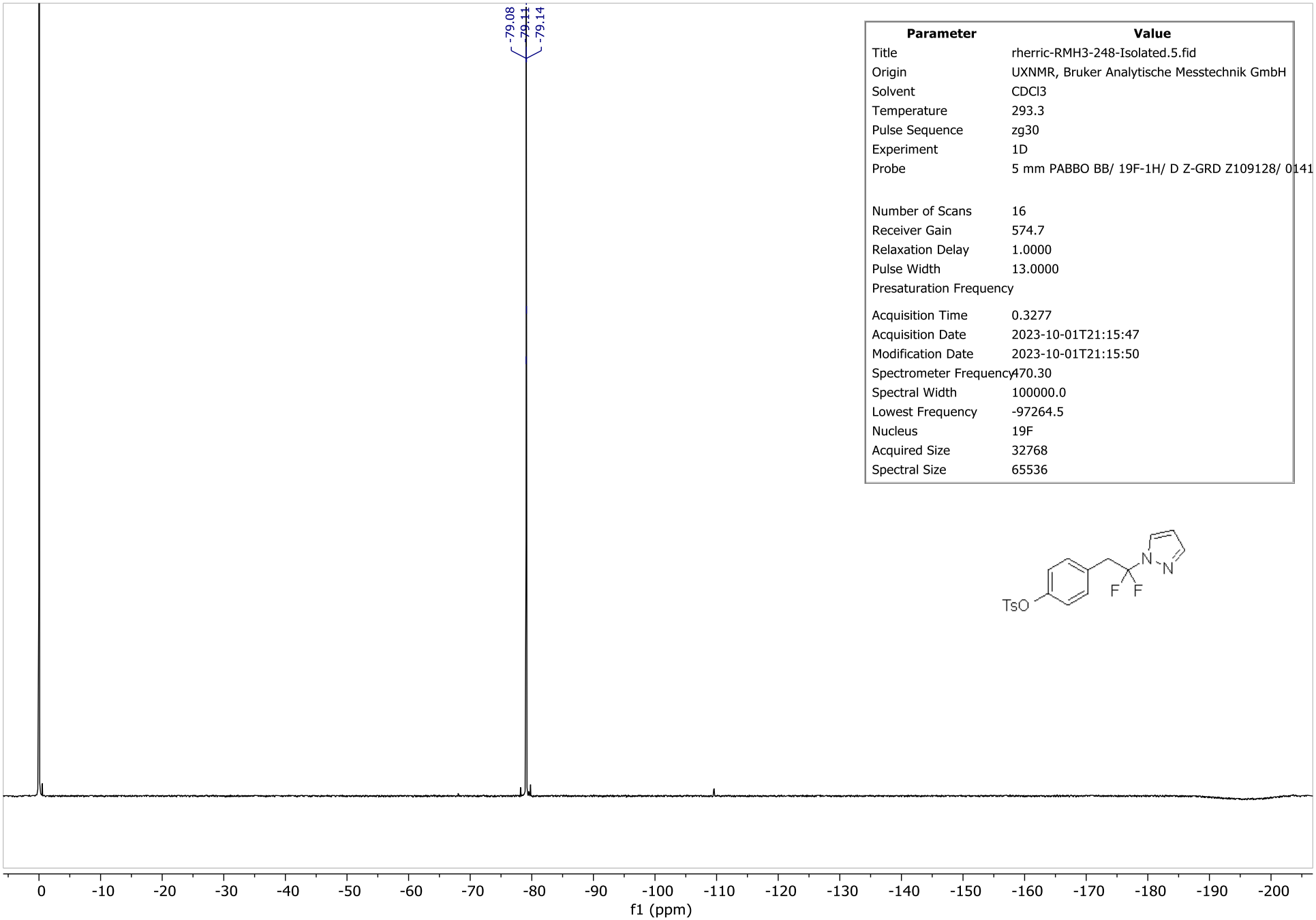
NMR spectra for 4-(2,2-difluoro-2-(1*H*-pyrazol-1-yl)ethyl)phenyl 4-methylbenzenesulfonate (**11r**)



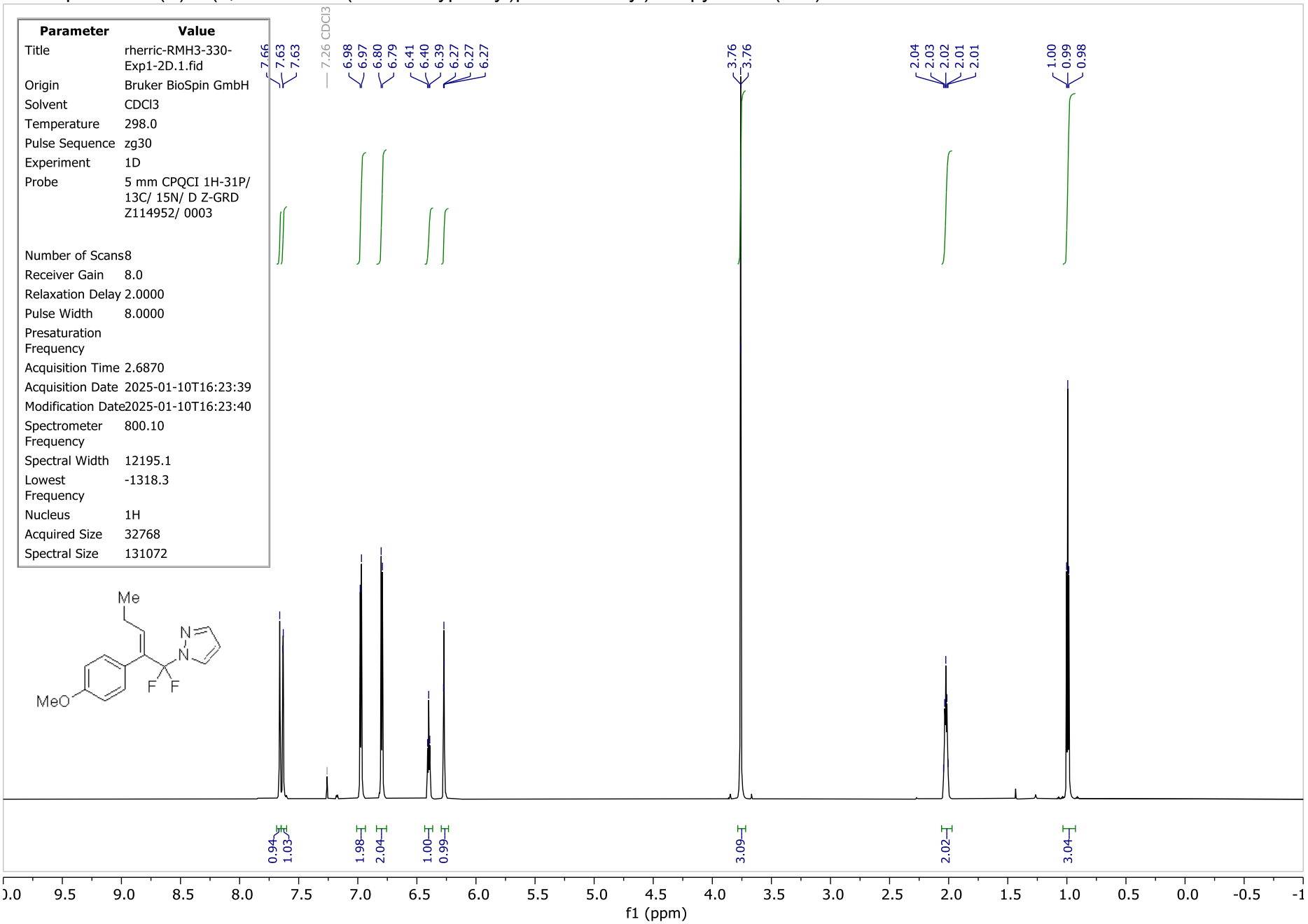
Parameter	Value
Title	rherric-RMH3-285-Isolated.1.fid
Origin	UXNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	292.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans	16
Receiver Gain	322.5
Relaxation Delay	2.0000
Pulse Width	15.0000
Presaturation Frequency	
Acquisition Time	2.0447
Acquisition Date	2023-11-28T16:35:30
Modification Date	2023-11-28T16:35:33
Spectrometer Frequency	499.87
Spectral Width	8012.8
Lowest Frequency	-789.3
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

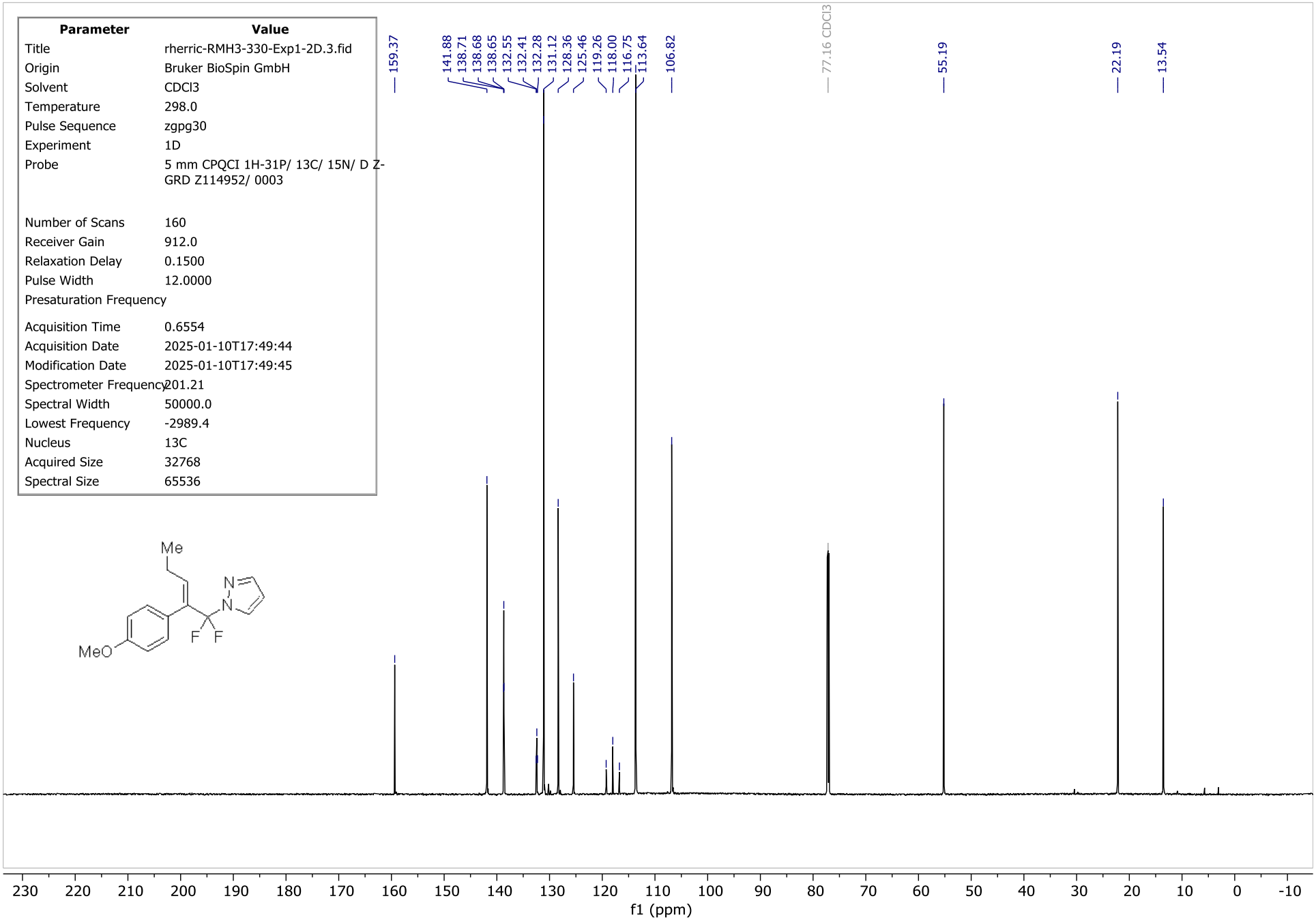
Parameter	Value
Title	rherric-RMH3-248-isolated-800mHz.1.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.0
Pulse Sequence	zgpg30
Experiment	1D
Probe	5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans	1000
Receiver Gain	912.0
Relaxation Delay	0.1500
Pulse Width	12.0000
Presaturation Frequency	
Acquisition Time	0.6554
Acquisition Date	2024-12-03T11:51:39
Modification Date	2024-12-03T11:51:40
Spectrometer Frequency	201.21
Spectral Width	50000.0
Lowest Frequency	-2980.9
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

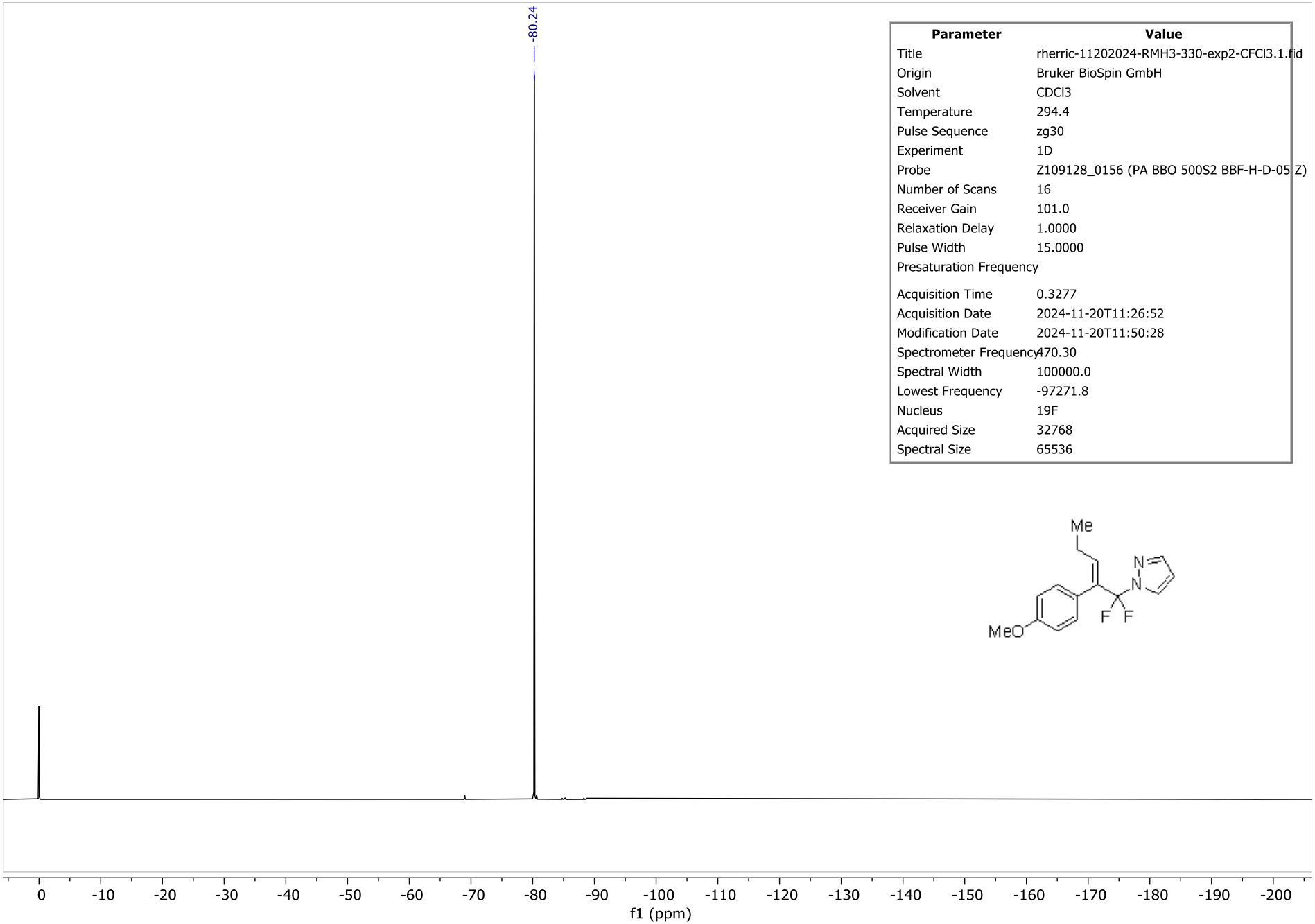


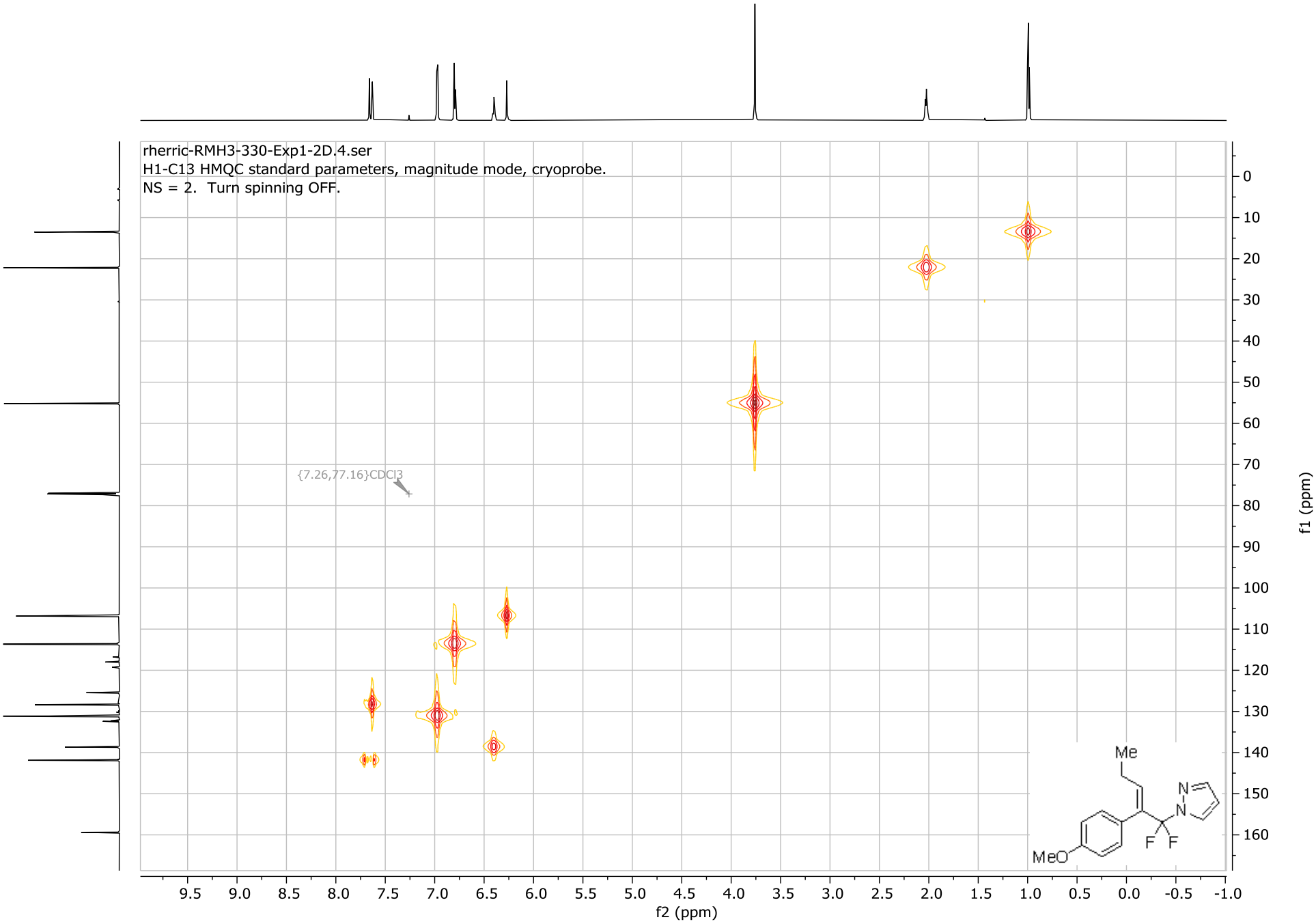

-79.08
-79.11
-79.14
Parameter Value
Title rherric-RMH3-248-Isolated.5.fid
Origin UXNMR, Bruker Analytische Messtechnik GmbH
Solvent CDCl3
Temperature 293.3
Pulse Sequence zg30
Experiment 1D
Probe 5 mm PABBO BB/ 19F-1H/ D Z-GRD Z109128/ 0141
Number of Scans 16
Receiver Gain 574.7
Relaxation Delay 1.0000
Pulse Width 13.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2023-10-01T21:15:47
Modification Date 2023-10-01T21:15:50
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97264.5
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
TsO
N
N
F
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

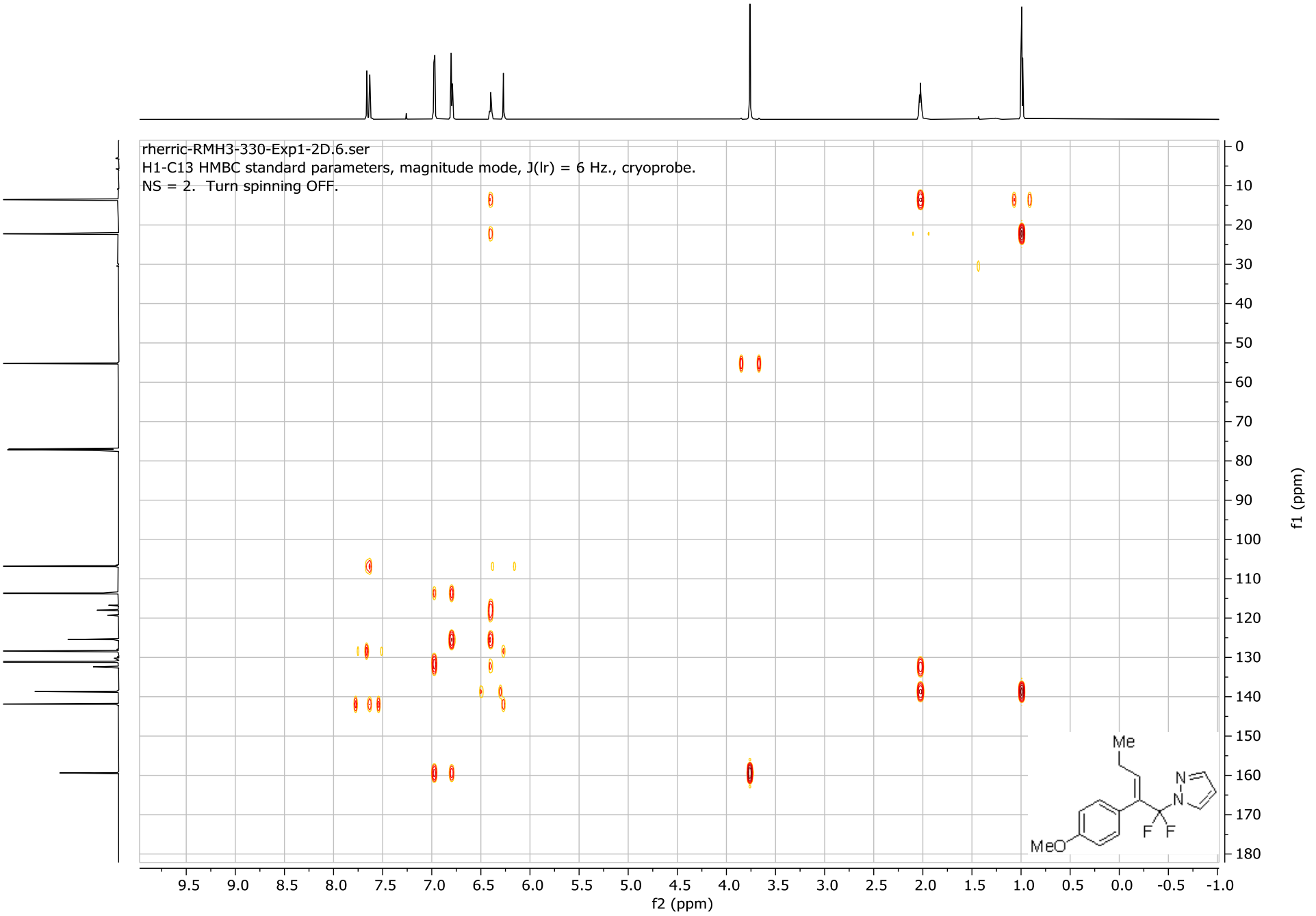
NMR spectra for (*E*)-1-(1,1-difluoro-2-(4-methoxyphenyl)pent-2-en-1-yl)-1*H*-pyrazole (**11s**)

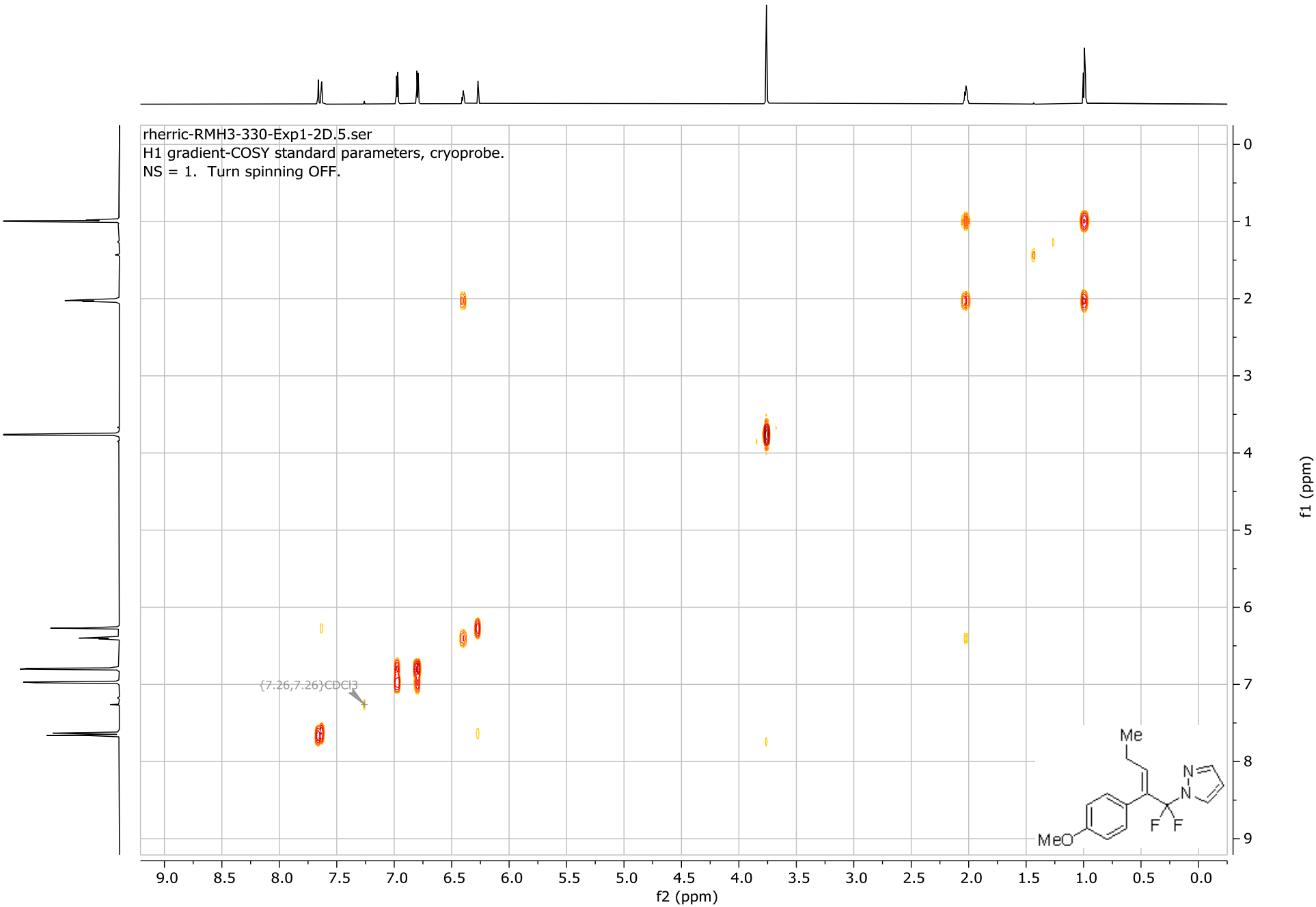


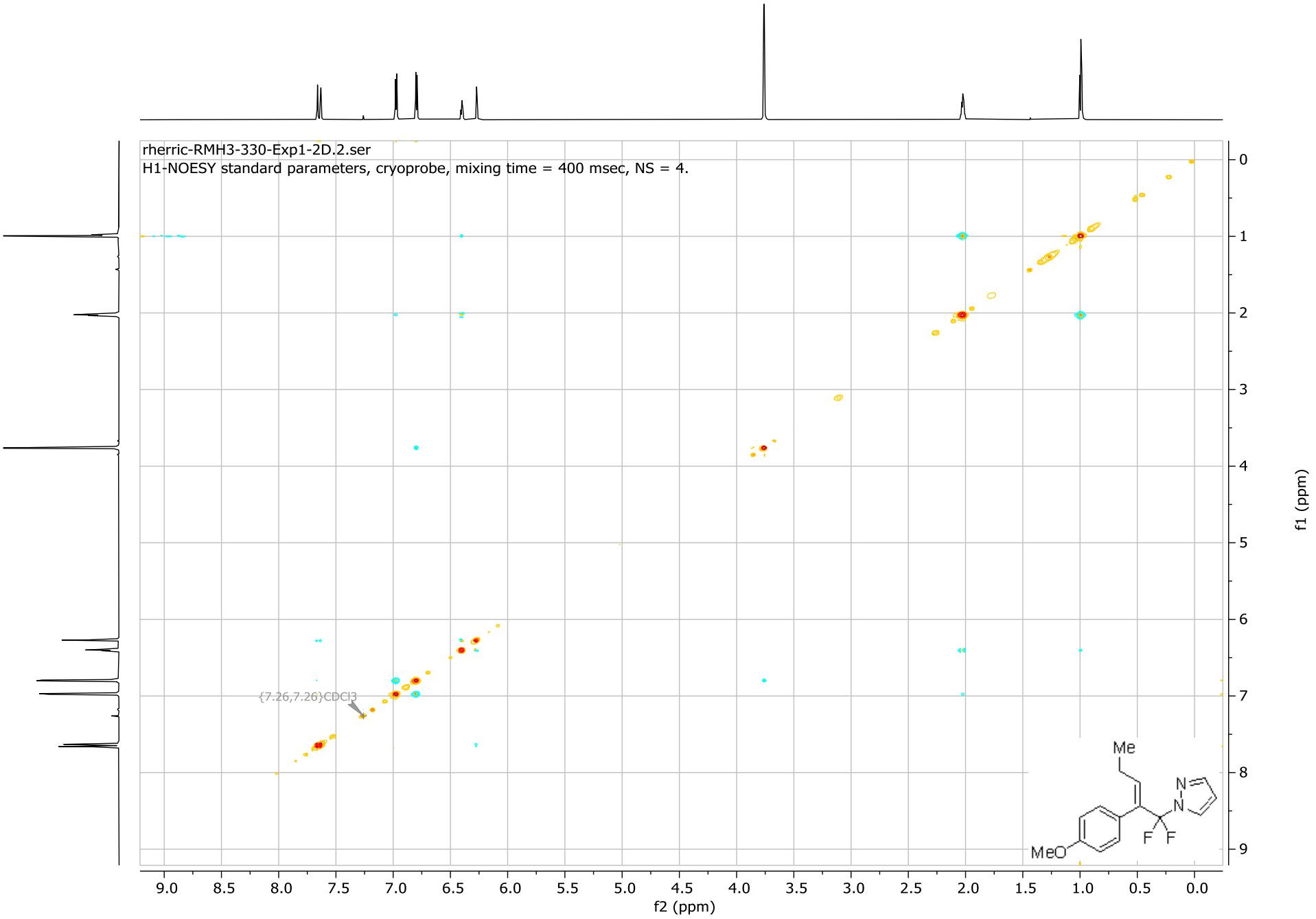

Parameter Value
Title rherric-RMH3-330-Exp1-2D.3.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 298.0
Pulse Sequence zgpg30
Experiment 1D
Probe 5 mm CPQCI 1H-31P/ 13C/ 15N/ D Z-GRD Z114952/ 0003
Number of Scans 160
Receiver Gain 912.0
Relaxation Delay 0.1500
Pulse Width 12.0000
Presaturation Frequency
Acquisition Time 0.6554
Acquisition Date 2025-01-10T17:49:44
Modification Date 2025-01-10T17:49:45
Spectrometer Frequency 201.21
Spectral Width 50000.0
Lowest Frequency -2989.4
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
159.37
141.88
138.71
138.68
138.65
132.55
132.41
132.28
131.12
128.36
125.46
119.26
118.00
116.75
113.64
106.82
77.16 CDCl3
55.19
22.19
13.54
Me
N
N
F
F
MeO
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

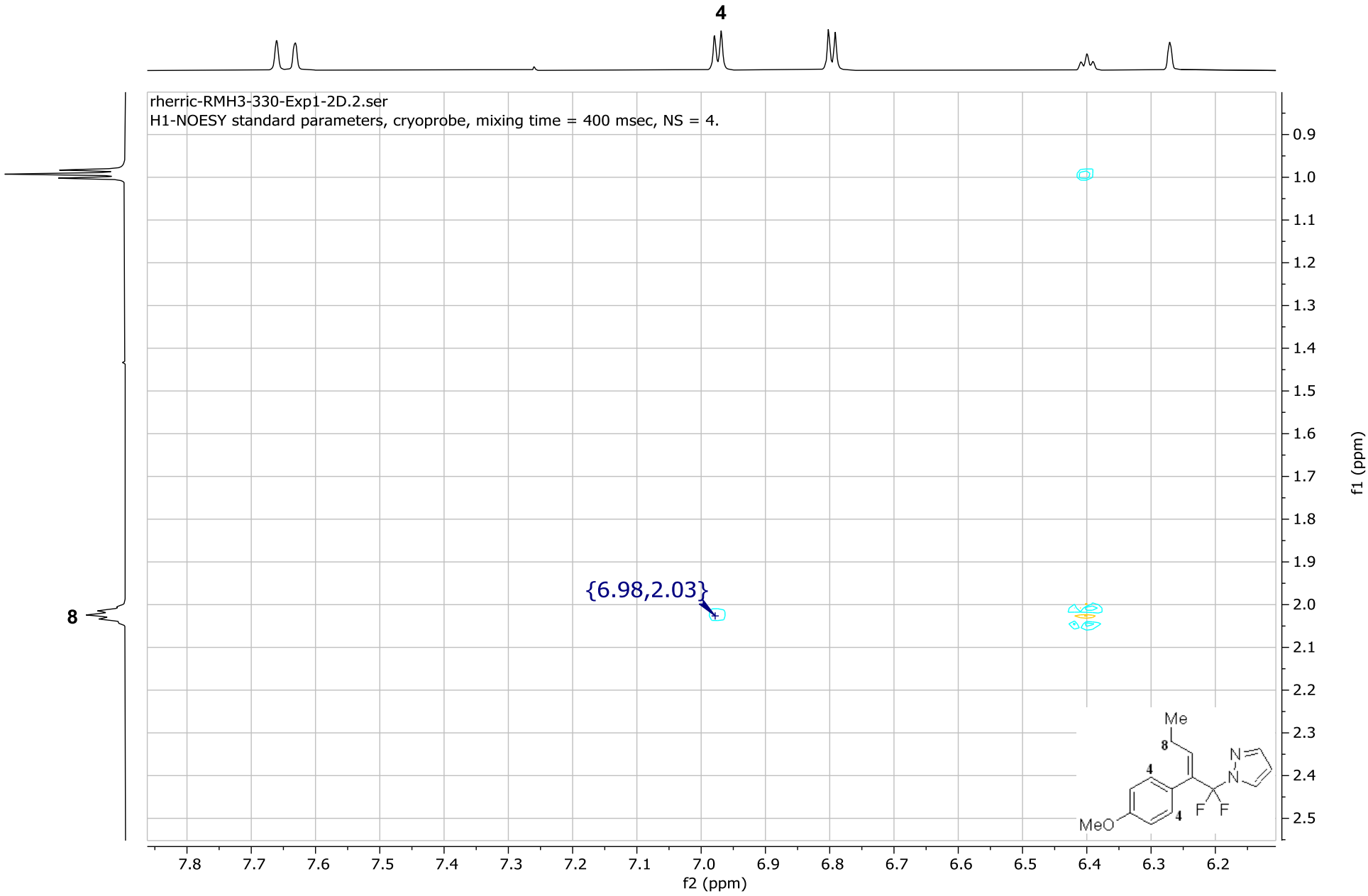

-80.24
Parameter Value
Title rherric-11202024-RMH3-330-exp2-CFCl3.1.fid
Origin Bruker BioSpin GmbH
Solvent CDCl3
Temperature 294.4
Pulse Sequence zg30
Experiment 1D
Probe Z109128_0156 (PA BBO 500S2 BBF-H-D-05 Z)
Number of Scans 16
Receiver Gain 101.0
Relaxation Delay 1.0000
Pulse Width 15.0000
Presaturation Frequency
Acquisition Time 0.3277
Acquisition Date 2024-11-20T11:26:52
Modification Date 2024-11-20T11:50:28
Spectrometer Frequency 470.30
Spectral Width 100000.0
Lowest Frequency -97271.8
Nucleus 19F
Acquired Size 32768
Spectral Size 65536
Me
N
N
F F
MeO
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

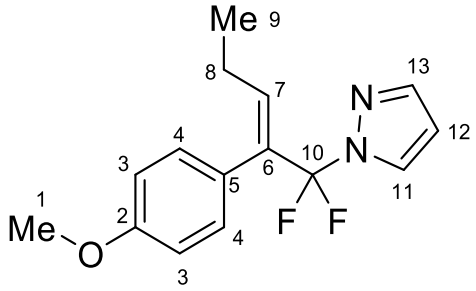

rherric-RMH3-330-Exp1-2D.4.ser
H1-C13 HMQC standard parameters, magnitude mode, cryoprobe.
NS = 2. Turn spinning OFF.
{7.26,77.16}CDCl3
f2 (ppm)
f1 (ppm)
Me
MeO
F
F
N
N


rherric-RMH3-330-Exp1-2D.6.ser
H1-C13 HMBC standard parameters, magnitude mode, J(lr) = 6 Hz., cryoprobe.
NS = 2. Turn spinning OFF.
f2 (ppm)
f1 (ppm)
Me
MeO
N
N
F
F


rherric-RMH3-330-Exp1-2D.5.ser
H1 gradient-COSY standard parameters, cryoprobe.
NS = 1. Turn spinning OFF.
{7.26,7.26}CDCl3
Me
N
N
F
F
MeO
f2 (ppm)
f1 (ppm)


rherric-RMH3-330-Exp1-2D.2.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
{7.26,7.26}CDCl3
Me
MeO
F
F
N
N
f2 (ppm)
f1 (ppm)


4
rherric-RMH3-330-Exp1-2D.2.ser
H1-NOESY standard parameters, cryoprobe, mixing time = 400 msec, NS = 4.
{6.98,2.03}
8
Me
8
4
4
N
N
F
F
MeO
f2 (ppm)
f1 (ppm)
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
6.3
6.2
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5



^{1}H (800 MHz) and ^{13}C (201 MHz) Data **Solvent: $CDCl_3$**

Atom	^{1}H shift (ppm)	^{1}H mult.	^{1}H *J* value (Hz)	^{13}C shift (ppm)	^{13}C mult.	^{13}C *J* value (Hz)	HMBC	COSY	NOESY
1	3.76	s		55.2	s		2		3
2				159.4	s		1		
3	6.80	d	8.7	113.6	s		2, 3, 4, 5	4	1, 4
4	6.97	d	8.7	131.1	s		2, 3, 4, 7, 8	3	3, 8
5				125.5	s		3, 6		
6				132.4	t	26.4	7, 8		
7	6.40	t	7.5	138.7	t	6.3	5, 6, 8, 9, 10	8	8, 9
8	2.02	p	7.5	22.2	s		6, 7, 9	7, 9	4, 7, 9
9	0.99	t	7.6	13.5	s		7, 8	8	7, 8
10				118.0	t	252.7	7		
11	7.66	s		141.9	s		12, 13	12	12
12	6.27	t	2.2	106.8	s		11, 13	11, 13	11, 13
13	7.63	d	2.6	128.4	s		11, 12	12	12