

Supporting Information

Palladium and Copper Co-Catalyzed Chloro-Arylation of *gem*-Difluorostyrenes – Use of a Nitrite Additive to Suppress β -F Elimination

Andrew J. Intelli,[†] Coriantumr Z. Wayment,[%] Ryan T. Lee,[‡]
Kedong Yuan,[&] Ryan A. Altman^{†,%,*}

[†] Borch Department of Medicinal Chemistry and Molecular Pharmacology, Purdue University, West Lafayette, Indiana 47907, United States

[%] James Tarpo Jr. and Margaret Tarpo Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

[‡] Department of Chemistry, Rutgers University, Piscataway, New Jersey, 08854, United States

[&] Guangzhou Municipal and Guangdong Provincial Key Laboratory of Molecular Target & Clinical Pharmacology, Guangzhou Medical University, Guangzhou 511436, China

* email address: raaltman@purdue.edu

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General Synthetic Information

Unless otherwise noted, reactions were performed under an atmosphere of dry nitrogen or argon using oven-dried scintillation vials sealed with a polytetrafluoro-ethylene-lined septum or oven-dried 15 mL sealed tubes with a screw-top cap. High density polyethylene or polypropylene 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. Elevated temperatures were maintained using thermostat-controlled heating mantles with a silicon oil heating bath and contained a thermometer for accurate readings. Organic solutions were concentrated using a rotary evaporator or BioChromato Smart Evaporator with a diaphragm vacuum pump. Thin-layer chromatography was performed on silica gel (VWR Common Silica Gel HLF UV₂₅₄ plates, and spots were visualized by quenching ultraviolet light ($\lambda = 254$ nm). Purification of products was accomplished by automated normal phase flash column chromatography on silica gel (VWR Common Silica Gel 60 Å, 40–60 μ m).

Reagents and solvents were purchased from various commercial sources and used as received. 1,4-Dioxane (99.5% extra dry over molecular sieves; sure seal) was purchased and used as received. Sodium nitrite (NaNO_2) was dried by evacuating and backfilling a 20 mL scintillation vial, which was subsequently heated with a butane torch (3x) under vacuum. The vial was then left under vacuum overnight and stored in a nitrogen-filled glovebox.

Proton nuclear magnetic resonance (^1H NMR) and fluorine nuclear magnetic resonance (^{19}F NMR) were taken on a Bruker DRX 500 spectrometer (500 and 470 MHz, respectively). Carbon nuclear magnetic resonance ($^{13}\text{C}\{^1\text{H}\}$ NMR) was taken on a Bruker Avance III 800 with a QCI cryoprobe (201 MHz). Chemical shifts (δ) for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are calibrated against residual solvent peak (CHCl_3 : $\delta = 7.26$ ppm). Chemical shifts (δ) for carbon are reported in ppm downfield from tetramethylsilane and are calibrated against the residual solvent peak (CDCl_3 : $\delta = 77.2$ ppm). Chemical shifts for fluorine are reported in ppm upfield from trichlorofluoromethane (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 determination was carried out by atmospheric-pressure chemical ionization (APCI-hexanes/PhMe) on a Waters Q-ToF Premier, in which samples were dissolved in hexanes or PhMe/hexanes, which was used as the ionization solvent or on an LTQ Orbitrap mass spectrometer (ThermoFisher Scientific, Bremen, Germany) using a high-resolution scan setting of 60,000. After tuning and calibrating the instrument in positive mode with a Thermo LTQ positive ion calibration solution, the samples were analyzed in APCI mode using low capillary temperature (150 °C) and low vaporizer temperature (150 °C) to prevent thermal decomposition of the compounds. Infrared spectra were measured on a Perkin Elmer Spectrum Two Fourier Transform Infrared Spectrometer by drying samples on a diamond ATR Sample base plate. Uncorrected melting points were measured on a

Chemglass Digital Melting Point apparatus. UV-Vis data was acquired on an Agilent Cary 6000i UV-Vis-NIR spectrophotometer.

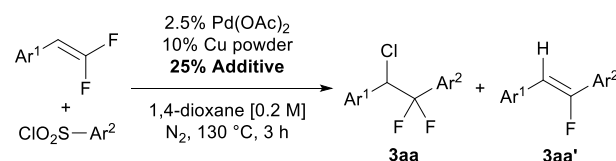
Safety. Sodium nitrite (NaNO_2) is an oxidizing agent and can form poisonous gases if mishandled. NaNO_2 reacts with strong acids to form nitrogen dioxide (a poisonous gas) and reacts with liquid ammonia and other ammonium compounds to form potentially explosive compounds. NaNO_2 is also not compatible with oxidizing agents (perchlorates, peroxides, nitrates, chlorine, bromine and fluorine); amines; chemically active metals (potassium, magnesium, zinc). Ensure reactants used with NaNO_2 do not contain known incompatible functional groups by checking the SDS of NaNO_2 .¹

Synthesis of *gem*-Difluoroalkenes. Substrates **1a–1q** were synthesized according to previously reported procedures.^{2,3}

General Procedure for the Chloro-Arylation of *gem*-Difluorostyrenes with Aryl Sulfonyl Chlorides. An oven dried 15 mL tube was charged with a Teflon-coated egg-shaped magnetic stir bar, copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.) and aryl sulfonyl chloride (2.0 mmol, 2.0 equiv.). The tube was then transferred into a nitrogen-filled glovebox. Then, $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 0.025 equiv.) and NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) were added to the tube. Next, 1,4-dioxane (5.0 mL) was added, followed by *gem*-difluorostyrene (1.0 mmol, 1.0 equiv.). The tube was sealed with a PTFE bushing lined with an O-ring and taken out of the glovebox. The tube was then stirred in a pre-heated silicone oil bath at 130 °C for 3 h, after which the sealed tube was removed from the oil bath and allowed to cool to rt. The sealed tube was opened and the crude reaction mixture was transferred to a separatory funnel along with 20 mL of water. The crude reaction mixture was extracted with EtOAc (3 x 20 mL). Then, the combined organic fractions were washed with saturated Na_2CO_3 (3 x 15 mL), brine (1 x 15 mL) and dried over sodium sulfate (Na_2SO_4). The combined organic fractions were then filtered to remove Na_2SO_4 , concentrated *in vacuo* onto diatomaceous earth, and purified by normal-phase silica gel chromatography.

Optimization Screens and Procedures

Table S1. M–X Additive Screen

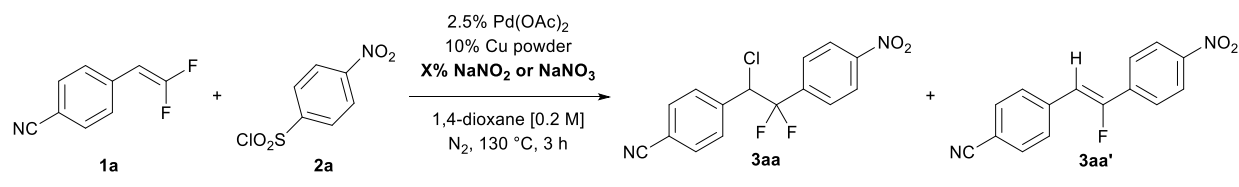


Ar¹ = 4-CN-Ph

Ar² = 4-NO₂-Ph

Entry	M-X	Conv.	3aa	3aa'	3aa/3aa'
1	none	91	31	21	1.5
2	Na ₂ CO ₃	98	33	21	1.6
3	NaOTf	97	31	20	1.6
4	NaCl	94	26	21	1.2
5	NaBr	54	-	12	-
6	Nal	40	-	trace	-
7	NaOAc	>95	36	18	2
8	NaPF ₆	>95	34	17	2
9	NaBF ₄	>95	34	19	1.8
10	NaTFA	88	24	16	1.5
11	NaNO ₃	96	41	16	2.5
12	NaNO₂	>95	51	11	4.8
13	NaNO₂	>95	54	2	27^a

Table S1. M–X Additive Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.050 equiv.), M–X additive (0.050 mmol, 0.25 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis. ^a 1.0 mmol scale.

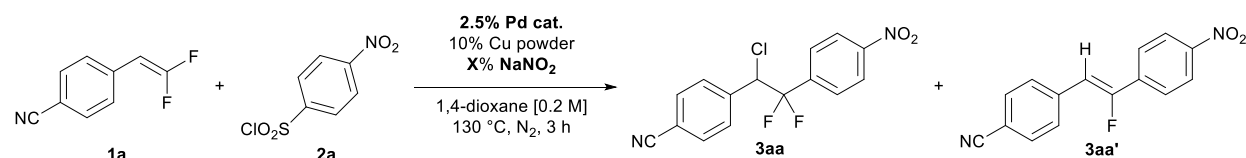
Table S2. NaNO_x Equivalents Screen**NaNO₂ Equivalents**

Entry	X% NaNO ₂	Conv.	3aa	3aa'	3aa/3aa'
1	0	>95	32	25	1.3
2	2.5	>95	41	18	2.2
3	5	>95	42	17	2.5
4	10	>95	52	12	4.4
5	20	>95	50	11	4.7
6	25	>95	51	11	4.8
7	50	>95	53	8	6.3
8	75	>95	51	7	7.7
9	100	93	51	5	10.9

NaNO₃ Equivalents

Entry	X% NaNO ₃	Conv.	3aa	3aa'	3aa/3aa'
10	0	89	27	24	1.1
11	2.5	94	32	21	1.5
12	5	91	31	22	1.4
13	10	96	39	20	2.0
14	20	95	38	17	2.2
15	25	96	41	16	2.5
16	50	96	43	16	2.6
17	75	94	46	13	3.7
18	100	95	46	12	3.9

Table S2. NaNO_x Equivalents Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.025 equiv.), NaNO₂ or NaNO₃ and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

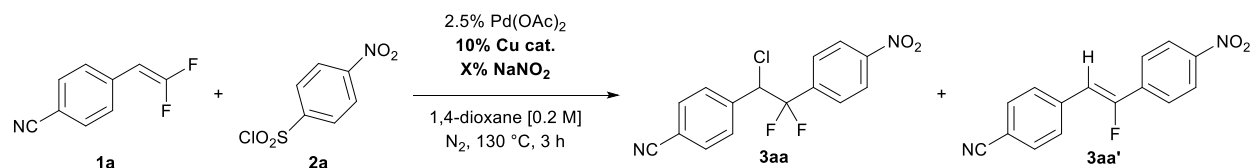
Table S3. Palladium Catalyst Screen**0% NaNO₂**

Entry	Pd catalyst	Conv.	3aa	3aa'
1	Pd black	75	24	27
2	Pd(dba) ₂	70	24	22
3	Pd(PPh ₃) ₄	48	13	21
4	PdO	24	2	3
5	Pd(NO ₃) ₂ ·H ₂ O	>95	55	14
6	PdCl ₂	64	19	23
7	PdCl ₂ (PPh ₃) ₂	46	9	16
8	Pd(TFA) ₂	78	28	28
9	Pd(OAc) ₂	95	33	29

100% NaNO₂

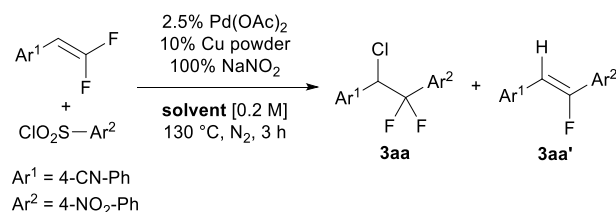
Entry	Pd catalyst	Conv.	3aa	3aa'
10	none	27	0	0
11	Pd black	90	56	4
12	Pd(dba) ₂	82	49	-
13	Pd(PPh ₃) ₄	50	23	10
14	PdO	14	4	-
15	Pd(NO ₃) ₂ ·H ₂ O	86	57	2
16	PdCl ₂	80	48	1
17	PdCl ₂ (PPh ₃) ₂	66	42	4
18	Pd(TFA) ₂	84	54	1
19	Pd(OAc) ₂	91	63	7

Table S3. Palladium Catalyst Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, palladium catalyst (0.0050 mmol, 0.025 equiv.), NaNO₂ (where applicable, 14 mg, 0.20 mmol, 1.0 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

Table S4. Copper Catalyst Screen

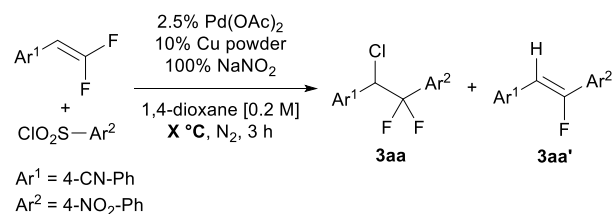
0% NaNO ₂					100% NaNO ₂				
Entry	Cu Source	Conv.	3aa	3aa'	Entry	Cu Source	Conv.	3aa	3aa'
1	none	19	0	2	16	none	21	0	2
2	Cu powder	75	19	30	17	Cu powder	92	63	7
3	CuCl	73	25	30	18	CuCl	81	49	3
4	CuBr	70	25	23	19	CuBr	83	52	3
5	CuI	80	24	28	20	CuI	77	53	2
6	Cu ₂ O	56	8	23	21	CuO	79	51	3
7	CuF ₂	90	32	30	22	CuF ₂	85	54	2
8	CuCl ₂	67	16	25	23	CuCl ₂	74	42	1
9	CuBr ₂	58	8	22	24	CuBr ₂	73	47	2
10	Cu(OAc) ₂	>95	32	26	25	Cu(OAc) ₂	89	62	5
11	Cu(acac) ₂	91	14	40	26	Cu(acac) ₂	93	55	15
12	Cu(C ₅ HF ₆ O) ₂ ·H ₂ O	69	17	28	27	Cu(C ₅ HF ₆ O) ₂ ·H ₂ O	89	59	3
13	Cu(NO ₃) ₂	>95	40	2	28	Cu(NO ₃) ₂	93	55	3
14	CuSO ₄	58	5	25	29	CuSO ₄	90	63	3
15	Cu(OTf) ₂	70	16	27	30	Cu(OTf) ₂	80	40	1

Table S4. Copper Catalyst Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper catalyst (0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.025 equiv.), NaNO₂ (where applicable, 14 mg, 0.20 mmol, 1.0 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

Table S5. Solvent Screen

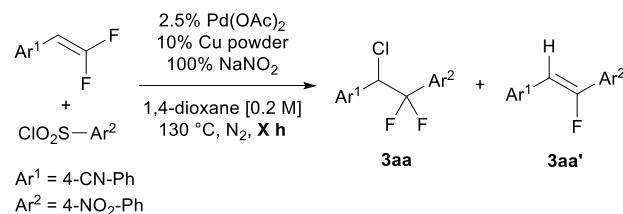
Entry	Solvent	Conv.	3aa	3aa'
1	1,2-DCB	67	28	7
2	CPME	35	8	3
3	Diglyme	47	16	-
4	DMA	30	-	-
5	<i>o</i> -Xylene	37	9	2
6	1,4-Dioxane	94	63	6

Table S5. Solvent Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.025 equiv.), NaNO₂ (14 mg, 0.20 mmol, 1.0 equiv.) and anhydrous solvent (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

Table S6. Temperature Screen

Exp	Temp. (°C)	Conv.	3aa	3aa'
1	110	>95	45	10
2	120	>95	47	8
3	130	>95	56	6
4	140	>95	43	11

Table S6. Temperature Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.025 equiv.), NaNO₂ (14 mg, 0.20 mmol, 1.0 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating blocks at different temperatures for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

Table S7. Reaction Time Screen

Exp	Time (h)	Conv.	3aa	3aa'
1	1	78	47	5
2	2	87	51	6
3	3	>95	60	6
4	4	>95	61	6

Table S7. Reaction Time Screen General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.) and 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.025 equiv.), NaNO₂ (14 mg, 0.20 mmol, 1.0 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 1–4 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α-trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ¹⁹F NMR analysis.

Table S8. ¹⁹F NMR Selectivities of Substrate Scope

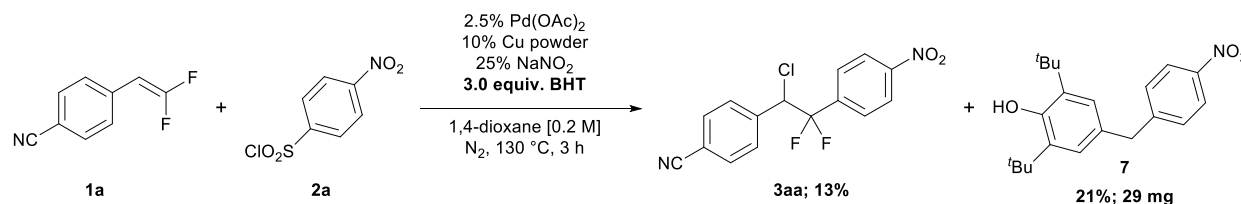
Entry	Ar ¹	Ar ²	A	B	C	D	A:(B+C+D)
1	3,4,5-tri-OMe-Ph	4-NO ₂ -Ph	53	1	3	1	11:1
2	2-(4- ^t Bu-Ph)	4-NO ₂ -Ph	43	2	2	0	11:1
3	3,5-di-OMe	4-NO ₂ -Ph	49	2	2	0	12:1
4	3,5-di-Me-Ph	4-NO ₂ -Ph	53	3	0	2	11:1
5	4- ^t Bu-Ph	4-NO ₂ -Ph	46	2	2	1	9:1
6	4-OBn	4-NO ₂ -Ph	55	1	1	1	18:1
7	3-OC(O)Ph	4-NO ₂ -Ph	50	3	6	2	5:1
8	3-CF ₃	4-NO ₂ -Ph	41	0	0	4	10:1
9	4-CN	4-NO ₂ -Ph	58	6	0	0	10:1
10	4-OTs	4-NO ₂ -Ph	62	2	1	0	21:1
11	4-CO ₂ Me	4-NO ₂ -Ph	45	3	0	2	9:1
12	3,5-di-Cl	4-NO ₂ -Ph	53	4	0	0	13:1
13	4-F	4-NO ₂ -Ph	58	3	0	3	10:1
14	4-Br	4-NO ₂ -Ph	57	2	2	0	14:1
15	3-indole	4-NO ₂ -Ph	56	0	0	0	56:1
16	2-benzofuran	4-NO ₂ -Ph	55	0	0	0	55:1
17	4-OMe-Ph	4-NO ₂ -Ph	55	1	3	2	9:1
18	4-OMe-Ph	4-CF ₃ -Ph	54	2	1	0	18:1
19	4-OMe-Ph	4-C(O)Me-Ph	61	0	3	2	12:1
20	4-OMe-Ph	4-F-Ph	61	1	2	3	10:1
21	4-OMe-Ph	4-Br-Ph	55	0	2	7	6:1
22	4-OMe-Ph	4-I-Ph	54	1	3	0	14:1
23	4-OMe-Ph	Ph	61	2	3	2	9:1
24	4-OMe-Ph	Naphthyl	54	2	3	5	5:1
25	4-OMe-Ph	4-Me-Ph	57	1	2	3	9:1
26	4-OMe-Ph	2-OMe-5-Br-Ph	57	0	4	5	6:1
27	4-OMe-Ph	6-Coumarin	56	1	4	4	6:1

Table S8. ¹⁹F NMR Selectivities of Substrate Scope Procedure: An oven dried 15 mL tube was charged with a Teflon-coated egg-shaped magnetic stir bar, copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.) and aryl sulfonyl chloride (2.0 mmol, 2.0 equiv.). The tube was then transferred into a nitrogen-filled glovebox. Then, Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.) and NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) were added to the tube. Next, 1,4-dioxane (5.0 mL) was added, followed by *gem*-difluorostyrene (1.0 mmol, 1.0 equiv.). The tube was sealed with a PTFE bushing lined with an O-ring and taken out of the glovebox. The tube was then stirred in a pre-heated silicone oil bath at 130 °C for 3 h, after which the sealed tube was removed from the oil bath and allowed to cool to rt. The sealed tube was opened and α,α,α-trifluorotoluene (8.2 μL) was added to each crude

reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ^{19}F NMR analysis.

Table S9. Radical Trapping Experiments

BHT Radical Trapping Experiment



Diphenylethylene (DPE) Radical Trapping Experiment

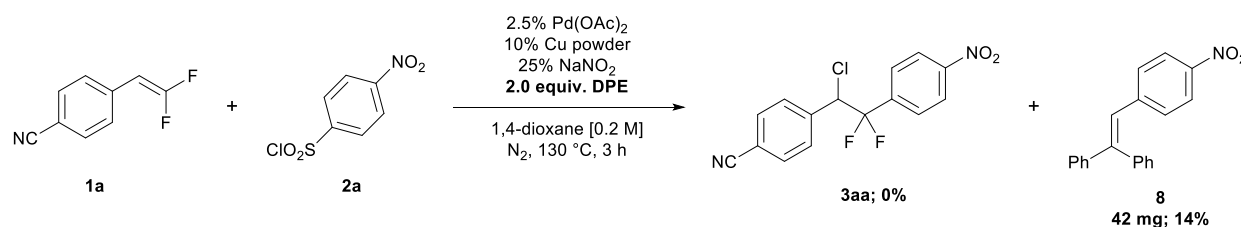


Table S9. Radical Trapping Experiments General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.033 g, 0.20 mmol, 1.0 equiv.), 4-nitrobenzenesulfonyl chloride **2a** (0.088 g, 0.40 mmol, 2.0 equiv.), and radical trap (BHT: 0.13 g, 0.60 mmol, 3.0 equiv. or DPE: 0.072 g, 0.40 mmol, 2.0 equiv.) before being transferred to a nitrogen-filled glove box. Then, Pd(OAc)₂ (1.1 mg, 0.0050 mmol, 0.050 equiv.), NaNO₂ (0.0035 g, 0.050 mmol, 0.25 equiv.) and anhydrous 1,4-dioxane (1.0 mL, 0.20 M) were added sequentially, and the vials were sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated 1-dram vial heating block at 130 °C for 3 h. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The crude reaction mixtures were diluted with EtOAc (1 mL). Then, α,α,α -trifluorotoluene (8.2 μL) was added to each crude reaction mixture, and the mixtures were thoroughly mixed to ensure proper mixing before taking an aliquot of the crude reaction mixture (0.5 mL) for ^{19}F NMR analysis. Then, the NMR sample was recombined with the crude reaction mixture and 50 μL of crude reaction mixture was filtered through a silica gel plug with EtOAc into a GC vial for GC-FID and GC-MS analysis. The GC sample was then

recombined with the crude reaction mixture and the workup outlined in the **General Procedure for the Chloro-Arylation of *gem*-Difluorostyrenes with Aryl Sulfonyl Chlorides** was performed. For the isolation of **7**, a preparatory TLC (20% EtOAc in hexanes) delivered 0.029 g (21%) as a yellow solid. For the isolation of **8**, a preparatory TLC (100% hexanes) delivered 0.042 g (14%) as a yellow solid.

Table S9. Radical Trapping Experiments Discussion:

- The reaction containing BHT had 45% conversion of 4-(2,2-difluorovinyl)benzonitrile **1a** with 13% of chloro-arylated product **3aa** and 14% of β -F elimination product **B** by ^{19}F NMR.
- The reaction containing DPE had 23% conversion of the *gem*-difluorostyrene **1a** with no arylated products (**A–D**) observed by ^{19}F NMR.

Table S10. UV-Vis Experiments

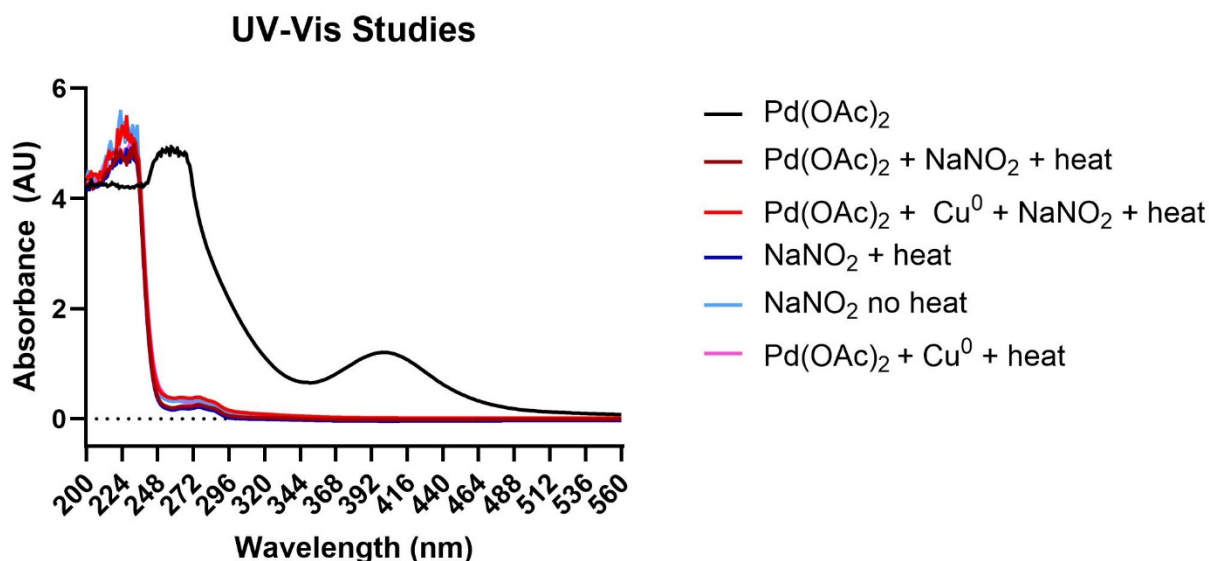


Table S10. UV-Vis Experiments General Procedure: Oven dried 1-dram vials equipped with magnetic stir bars were charged with (where applicable) copper powder (1.3 mg, 0.020 mmol, 0.10 equiv.), $\text{Pd}(\text{OAc})_2$ (1.1 mg, 0.0050 mmol, 0.050 equiv.), NaNO_2 (0.014 g, 0.20 mmol, 1.0 equiv.) and anhydrous 1,4-dioxane (2.0 mL, 0.10 M) in a nitrogen-filled glovebox and subsequently sealed with a screw-top cap containing a PTFE-lined septum. The vials were transferred out of the glove box and stirred on a pre-heated (or rt where

applicable) 1-dram vial heating block at 130 °C for 10 min. Upon completion, the vials were removed from the 1-dram vial heating block and allowed to cool to rt. The vials were then transferred to a nitrogen-filled glovebox, where 0.50 mL of crude reaction mixture was added to a quartz cuvette. The crude reaction mixture was then diluted with anhydrous 1,4-dioxane (2.5 mL) and sealed with J. Young valves. The vials were transferred out of the glove box and placed inside the UV-Vis spectrophotometer for analysis.

Table S10. UV-Vis Experiments Discussion:

- In the absence of other additives, Pd(OAc)₂ showed a prominent Pd²⁺ peak at 400 nm (black line).⁴
- Pd(OAc)₂ in the presence of Cu powder under the standard reaction temperature of 130 °C lost the Pd²⁺ peak at 400 nm (pink line), suggesting a reduction of Pd²⁺. Additionally, the redox couples Pd^{II}/Pd⁰ (+0.91 V)⁵ and Cu⁰/Cu^I (−0.52 V)⁵ supports a reduction of Pd^{II}. However, it is unlikely that Pd⁰ is formed due to the tolerance of Ar–I/Br (**3na**, **4qe**, **4qf**) under the standard reaction conditions for the chloro-arylation of *gem*-difluorostyrenes. Instead, a one-electron reduction to Pd^I is hypothesized to occur.
- Similarly, Pd(OAc)₂ with NaNO₂ produced a similar loss of of the Pd²⁺ peak for unknown reasons. Given the low oxidation potentials of NO^{2−} (NO^{3−}/ NO^{2−} = +0.42 V and NO^{2−}/NO = +0.38 V)⁶ relative to known oxidants for Pd^{II}/Pd^{IV} catalysis,^{7,8} it is unlikely that an oxidation occurred between Pd(OAc)₂ and NaNO₂.

Figure S1. Proposed Mechanism

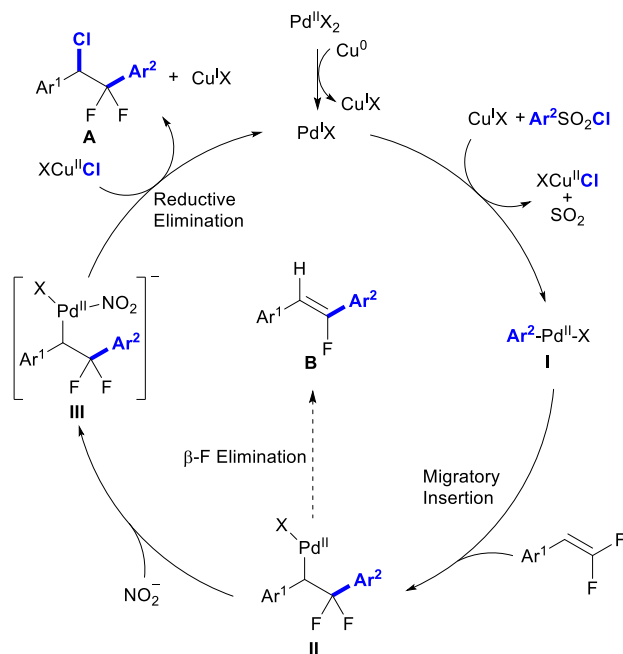


Figure S1. Proposed Mechanism Discussion:

- Based on UV-Vis experiments and the tolerance of Ar-I/Br (**3na**, **4qe**, **4qf**) in the reaction, Pd^{II} undergoes a single electron reduction in the presence of Cu^0 to give Pd^{I} and Cu^{I} as the active catalysts.
- Pd^{I} , Cu^{I} and $\text{Ar}^2\text{SO}_2\text{Cl}$ react to generate $\text{XCu}^{\text{II}}\text{Cl}$ and an aryl radical that combines with Pd^{I} to give $\text{Ar}^2\text{-Pd}^{\text{II}}\text{-X}$ species I. The activation of sulfonyl chlorides in the presence of Pd or Cu is well documented.^{9–14}
- Aryl-Pd complex I then undergoes a migratory insertion into the *gem*-difluorostyrene to give the Pd^{II} -benzyl intermediate II.
- In the absence of NO_2^- , II can competitively decompose via β -F elimination to give mixtures of monofluorovinyl alkene and chloro-arylated products, the former of which has been seen in other reactions that proceed via unstable organometal-alkyl intermediates to deliver monofluorovinyl alkenes.^{15–18}
- In the presence of NO_2^- , II then reacts with NO_2^- to deliver the Pd^{II} ate complex III.

- Pd ate complex **III** reacts with $\text{XCu}^{\text{II}}\text{Cl}$ through a bimetallic reductive elimination process to deliver chloro-arylated products and regenerates both Pd^{I} and Cu^{I} catalysts. Such processes have been proposed in oxidative functionalization of alkenes, though the details of the transformation have not been fully elucidated.^{19–24}
- Notably, this mechanism contrasts with other reported transition-metal-catalyzed oxidation reactions of alkenes with NO_x additives that exploited NO_x additives to facilitate reductive elimination via oxidation of Pd^{II} –alkyl intermediates to Pd^{IV} , due to our use of catalytic NO_2^- under *inert* conditions as opposed to oxygen-rich atmospheres.^{21,25–28} Subsequent use of catalytic NO_2^- under aerobic systems (air or O_2) in our system resulted in more non-productive consumption of the *gem*-difluorostyrene, lower yield of the chloro-arylated product and did not improve selectivity for chloro-arylated products vs. β -F elimination products. These results suggest a non-redox role for NO_2^- in this mechanism.

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Preparation and Characterization of Compounds

2,6-di-tert-butyl-4-(4-nitrobenzyl)phenol (7). Compound **7** was synthesized via the **Table S9 Radical Trapping Experiments General Procedure**. After the workup outlined in the **General Procedure for the Chloro-Arylation of gem-Difluorostyrenes with Aryl Sulfonyl Chlorides** was performed, a preparatory TLC (20% EtOAc in hexanes) delivered 0.029 g (21%) as a yellow solid. ¹H NMR matches the literature for this compound.²⁹

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.96 (s, 2H), 5.14 (s, 1H), 4.00 (s, 2H), 1.42 (s, 18H).

(2-(4-nitrophenyl)ethene-1,1-diyl)dibenzene (8). Compound **8** was synthesized via the **Table S9 Radical Trapping Experiments General Procedure**. After the workup outlined in the **General Procedure for the Chloro-Arylation of gem-Difluorostyrenes with Aryl Sulfonyl Chlorides** was performed, a preparatory TLC (hexanes) delivered 0.042 g (14%) as a yellow solid. ¹H NMR matches the literature for this compound.³⁰

¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 6.5 Hz, 8H), 7.19 – 7.16 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.00 (s, 1H).

5-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-1,2,3-trimethoxybenzene (3ba).

Compound **3ba** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 5-(2,2-difluorovinyl)-1,2,3-trimethoxybenzene **1b** (0.23 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→20% EtOAc in hexanes) provided 0.21 g (54%) of the title compound as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 8.32 – 8.15 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.47 (s, 2H), 5.14 (t, *J* = 10.2 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 6H). **¹³C{¹H}** (201 MHz, CDCl₃) δ 153.3, 149.4, 140.0 (t, *J* = 26.8 Hz), 128.3, 123.4, 119.4 (t, *J* = 250.8 Hz), 106.7, 64.3 (t, *J* = 31.9 Hz), 61.2, 56.5. **¹⁹F NMR** (470 MHz, CDCl₃) δ –100.36 (d, *J* = 246.8 Hz, 1F), –101.67 (d, *J* = 250.0 Hz, 1F). **IR(film)** 3656, 3086, 2980, 1593, 1530, 1237, 1127, 1089, 890, 857 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₇H₁₇ClF₂NO₅ [M+]⁺ 429.1307; found 429.1308.

4'-(tert-butyl)-2-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-1,1'-biphenyl (**3ca**).

Compound **3ca** was synthesized according to the general procedure 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 4'-(tert-butyl)-2-(2,2-difluorovinyl)-1,1'-biphenyl **1c** (0.27 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.18 g (42%) of the title compound as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.60 (ddd, *J* = 7.8, 1.9, 1.1 Hz, 1H), 7.52 – 7.48 (m, 5H), 7.46 – 7.43 (m, 2H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 5.30 (t, *J* = 10.3 Hz, 1H), 1.38 (s, 9H). **¹³C{¹H}** NMR (201 MHz, CDCl₃) δ 151.1, 149.2, 141.5, 139.8 (t, *J* = 26.6 Hz), 137.2, 133.6, 128.9, 128.4, 128.1 (t, *J* = 5.9 Hz), 127.8, 127.7, 126.8, 126.0, 123.3, 119.3 (t, *J* = 250.8 Hz), 63.9 (t, *J* = 31.6 Hz), 34.7, 31.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ –101.15 (br s, 2F). **IR(film)** 2968, 2870, 1532, 1486, 1356, 1087, 900, 856, 713, 629 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₂₄H₂₂ClF₂NO₂ [M]⁺ 429.1307; found 429.1308.

1-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-3,5-dimethoxybenzene (**3da**). Compound **3da** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-3,5-dimethoxybenzene **1d** (0.20 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 g, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic

purification (0→20% EtOAc in hexanes) provided 0.17 g (48%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.9 Hz, 2H), 7.50 (d, *J* = 8.9 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 1H), 6.39 (d, *J* = 2.2 Hz, 2H), 5.12 (t, *J* = 10.3 Hz, 1H), 3.73 (s, 6H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.7, 149.2, 139.9 (t, *J* = 26.7 Hz), 135.2, 128.1, 123.3, 119.2 (t, *J* = 250.9 Hz), 107.5, 101.5, 63.9 (t, *J* = 31.5 Hz), 55.6. **¹⁹F NMR** (470 MHz, CDCl₃) δ −100.49 (d, *J* = 245.7 Hz, 1F), −101.32 (d, *J* = 247.2 Hz, 1F). **IR(film)** 3656, 2980, 2920, 1548, 1530, 1468, 1058, 929, 867, 630 cm^{−1}. **HRMS** (APCI) *m/z*: calc'd for C₁₆H₁₅ClF₂NO₄ [M+H]⁺ 358.0658; found 358.0648. **mp** 124.3–125.2.

1-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-3,5-dimethylbenzene (3ea). Compound **3ea** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-3,5-dimethylbenzene **1e** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.16 g (49%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.99 (s, 1H), 6.86 (s, 2H), 5.12 (t, *J* = 10.5 Hz, 1H), 2.27 (s, 6H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.4, 140.2 (t, *J* = 26.5 Hz), 138.4, 133.2, 131.6, 128.3, 127.2, 123.3, 119.5 (t, *J* = 250.2 Hz), 64.1 (t, *J* = 31.7 Hz), 21.5. **¹⁹F NMR** (470 MHz, CDCl₃) δ −100.58 (d, *J* = 246.6 Hz, 1F), −101.59 (d, *J* = 235.0 Hz, 1F). **IR(film)** 2982, 2886, 1595, 1529, 1424, 1356, 1093, 932, 862, 631 cm^{−1}. **HRMS** (APCI) *m/z*: calc'd for C₁₆H₁₄ClF₂NO₂ [M]⁺ 325.0681; found 325.0690. **mp** 51.1–52.3 °C.

1-(tert-butyl)-4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzene (3fa). Compound **3fa** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(*tert*-butyl)-4-(2,2-difluorovinyl)benzene **1f** (0.20 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper

powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.16 g (45%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 5.21 (t, *J* = 10.5 Hz, 1H), 1.31 (s, 9H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 153.1, 149.2, 140.0 (t, *J* = 26.7 Hz), 130.1, 128.9, 128.0 (t, *J* = 5.9 Hz), 125.5, 123.2, 119.3 (t, *J* = 250.6 Hz), 63.7 (t, *J* = 31.6 Hz), 34.8, 31.3. **¹⁹F NMR** (470 MHz, CDCl₃) δ −100.69 (d, *J* = 251.0 Hz, 1F), −101.73 (dd, *J* = 246.3, 10.7 Hz, 1F). **IR(film)** 2981, 2889, 2815, 1595, 1464, 1424, 1239, 1090, 894, 631 cm^{−1}. **HRMS** (APCI) *m/z*: calc'd for C₁₈H₁₈ClF₂NO₂ [M]⁺ 353.0994; found 353.0990. **mp** 105.2–105.9 °C.

1-(benzyloxy)-4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzene (3ga). Compound **3ga** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(benzyloxy)-4-(2,2-difluorovinyl)benzene **1g** (0.25 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→20% EtOAc in hexanes) provided 0.21 g (53%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.55 – 7.35 (m, 6H), 7.35 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.17 (t, *J* = 10.3 Hz, 1H), 5.06 (s, 2H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 159.6, 149.0, 139.8 (t, *J* = 26.7 Hz), 136.4, 130.3, 128.7, 128.2, 127.9, 127.5, 125.3, 123.1, 119.1 (t, *J* = 250.6 Hz), 114.7, 70.1, 63.5 (t, *J* = 31.6 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ −100.75 (d, *J* = 245.5 Hz, 1F), −102.13 (d, *J* = 245.8 Hz, 1F). **IR(film)** 3657, 2981, 2917, 1712, 1511, 1383, 1237, 1089, 892, 629 cm^{−1}. **HRMS** (APCI) *m/z*: calc'd for C₂₁H₁₆F₂NO₃ [M-Cl]⁺ 368.1098; found 368.1084. **mp** 162.7–164.3 °C.

3-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)phenyl benzoate (3ha). Compound **3ha** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 3-(2,2-difluorovinyl)phenyl benzoate **1h** (0.26 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.18 g (44%) of the title compound as a yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 8.29 (dd, *J* = 17.0, 8.5 Hz, 4H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.60 (dd, *J* = 19.4, 8.4 Hz, 5H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 5.9 Hz, 2H), 5.35 (t, *J* = 10.1 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 164.9, 151.0, 149.2, 139.3 (t, *J* = 26.7 Hz), 134.7, 133.9, 130.3, 129.6, 129.2, 128.8, 128.0 (t, *J* = 5.7 Hz), 126.6, 123.4, 123.3, 122.8, 119.1 (t, *J* = 251.0 Hz), 63.2 (t, *J* = 31.7 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -100.82 (d, *J* = 256.3 Hz, 1F), -101.72 (d, *J* = 245.7 Hz, 1F). **IR(film)** 3077, 2977, 1736, 1528, 1237, 1082, 1062, 893, 708, 631 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₂₁H₁₄ClF₂NO₂ [M]⁺ 417.0579; found 417.0583.

1-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-3-(trifluoromethyl)benzene (3ia). Compound **3ia** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-3-(trifluoromethyl)benzene **1i** (0.21 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.15 g (40%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 6.7 Hz, 1H), 7.56 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 4H), 5.27 (dd, *J* = 11.5, 9.0 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.6, 139.5 (t, *J* = 26.5 Hz), 134.5, 132.7, 131.3 (q, *J* = 32.8 Hz), 129.4, 128.1, 126.8, 126.3 (d, *J* = 4.1 Hz), 123.6, 119.2 (t, *J* = 251.2 Hz), 63.1 (t, *J* = 32.4 Hz). **¹⁹F NMR**

(470 MHz, CDCl₃) δ -63.29 (s, 3F), -99.51 (d, J = 248.7 Hz, 1F), -103.50 (d, J = 248.7 Hz, 1F). **IR(film)** 3656, 2981, 1531, 1351, 1330, 1129, 1078, 899, 856, 737, 708 cm⁻¹. **HRMS** (APCI) m/z : calc'd for C₁₅H₉ClF₄NO₂ [M-F]⁺ 346.0258; found 346.0243. **mp** 58.3–59.7°C.

4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzonitrile (3aa). Compound **3aa** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 4-(2,2-difluorovinyl)benzonitrile **1a** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.18 g (55%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, J = 8.7 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H), 5.24 (dd, J = 11.7, 8.8 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.7, 139.4 (d, J = 25.9 Hz), 138.3, 132.5, 130.3, 128.1, 123.8, 119.1 (t, J = 251.4 Hz), 118.2, 114.1, 63.0 (t, J = 32.6 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -99.02 (d, J = 248.9 Hz, 1F), -103.60 (d, J = 260.9 Hz, 1F). **IR(film)** 3087, 2232, 1610, 1528, 1352, 1080, 871, 857, 780, 701 cm⁻¹. **HRMS** (APCI) m/z : calc'd for C₁₅H₁₀ClF₂N₂O₂ [M+H]⁺ 323.0399; found 323.0393. **mp**: 149.3–150.6°C.

4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)phenyl 4-methylbenzenesulfonate (3ja). Compound **3ja** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 4-(2,2-difluorovinyl)phenyl 4-methylbenzenesulfonate **1j** (0.31 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.24 g (51%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.21 – 8.15 (m, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.18 (t, *J* = 10.1 Hz, 1H), 2.47 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 150.7, 149.5, 146.1, 139.6 (t, *J* = 26.7 Hz), 132.5, 132.2, 130.8, 130.2, 128.8, 128.1 (t, *J* = 6.1 Hz), 123.5, 122.7, 119.2 (t, *J* = 251.0 Hz), 63.1 (t, *J* = 32.1 Hz), 22.04. **¹⁹F NMR** (470 MHz, CDCl₃) δ –100.96 (d, *J* = 247.2 Hz, 1F), –102.12 (d, *J* = 251.8 Hz, 1F). **IR(film)** 2981, 2920, 1530, 1375, 1236, 1178, 1157, 1091, 872, 662 cm^{–1}. **HRMS** (APCI) *m/z*: calc'd for C₂₁H₁₇ClF₂NO₅S [M+H]⁺ 468.0484; found 468.0472. **mp** 104.8–105.9 °C.

methyl 4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzoate (3ka). Compound **3ka** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), methyl 4-(2,2-difluorovinyl)benzoate **1k** (0.20 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.17 g (48%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.26 (t, *J* = 10.2 Hz, 1H), 3.93 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 166.3, 149.3, 139.4 (t, *J* = 26.5 Hz), 137.8, 131.5, 129.7, 129.3, 127.9 (t, *J* = 6.0 Hz), 123.4, 119.0 (t, *J* = 251.1 Hz), 63.2 (t, *J* = 32.0 Hz), 52.5. **¹⁹F NMR** (470 MHz, CDCl₃) δ –100.74 (d, *J* = 247.7 Hz, 1F), –101.69 (d, *J* = 247.6 Hz, 1F). **IR(film)** 2987, 2892, 1725, 1529, 1464, 1285, 1236, 1093, 878, 634 cm^{–1}. **HRMS** (APCI) *m/z*: calc'd for C₁₆H₁₂ClF₂NO₄ [M+H]⁺ 356.0501; found 356.0491. **mp** 130.6–131.4 °C.

1,3-dichloro-5-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzene (3la). Compound **3la** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1,3-dichloro-5-(2,2-difluorovinyl)benzene **1l** (0.21 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (11 mg, 0.050 mmol, 0.050 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup

outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.16 g (43%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.43 – 8.17 (m, 2H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 1.8 Hz, 1H), 7.22 (s, 2H), 5.11 (dd, *J* = 12.1, 8.5 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.7, 139.4 (t, *J* = 26.3 Hz), 136.5, 135.5, 130.3, 128.1 (t, *J* = 6.1 Hz), 128.0, 123.7, 119.0 (t, *J* = 251.4 Hz), 62.4 (t, *J* = 32.8 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ –98.63 (d, *J* = 256.3 Hz, 1F), –103.96 (d, *J* = 250.2 Hz, 1F). **IR(film)** 3661, 2981, 1530, 1353, 1236, 1089, 891, 857, 631 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₄H₈Cl₂F₂NO₂ [M-Cl]⁺ 335.6392; found 335.6399. **mp** 123.9–125.2 °C.

1-(2-chloro-1,1-difluoro-2-(4-fluorophenyl)ethyl)-4-nitrobenzene (3ma). Compound **3ma** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-fluorobenzene **1m** (0.16 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.15 g (48%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 7.26 (dd, *J* = 8.7, 5.0 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.21 (t, *J* = 10.3 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 164.0, 162.8, 149.3, 139.6 (t, *J* = 26.7 Hz), 131.1 (d, *J* = 8.5 Hz), 128.0 (t, *J* = 6.1 Hz), 123.4, 119.1 (t, *J* = 250.7 Hz), 115.7 (d, *J* = 22.0 Hz), 63.1 (t, *J* = 32.0 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ –101.10 (d, *J* = 247.7 Hz, 1F), –102.00 (dd, *J* = 246.8, 10.3 Hz), –111.35 (s, 1F). **IR(film)** 2984, 2894, 1614, 1535, 1513, 1234, 1090, 873, 856, 626 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₄H₉ClF₃NO₂ [M]⁺ 315.0274; found 315.0281. **mp** 68.1–69.1 °C.

1-bromo-4-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzene (3na). Compound **3na** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl

chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-bromo-4-(2,2-difluorovinyl)benzene **1n** (0.22 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase neutral alumina chromatographic purification (0→10% EtOAc in hexanes) provided 0.15 g (39%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.47 (dd, *J* = 8.6, 6.3 Hz, 4H), 7.15 (d, *J* = 8.3 Hz, 2H), 5.17 (t, *J* = 10.2 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.5, 139.6 (t, *J* = 26.7 Hz), 132.4, 132.0, 131.0, 128.2, 124.4, 123.6, 119.2 (t, *J* = 251.0 Hz), 63.3 (t, *J* = 32.4 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -100.72 (d, *J* = 244.1 Hz, 1F), -102.01 (d, *J* = 248.7 Hz, 1F). **IR(film)** 3656, 2981, 1610, 1594, 1529, 1490, 1353, 1077, 865, 856 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₄H₉BrClF₂NO₂ [M]⁺ 375.9551; found 375.9546. **mp** 97.9–99.8 °C.

3-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)-1-(phenylsulfonyl)-1H-indole (**3oa**).

Compound **3oa** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 3-(2,2-difluorovinyl)-1-(phenylsulfonyl)-1H-indole **1o** (0.32 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et₂O in hexanes) provided 0.21 g (44%) of the title compound as a yellow foam.

¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 3H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.23 (m, 1H), 5.46 (t, *J* = 10.3 Hz, 1H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 149.2, 139.5 (t, *J* = 26.6 Hz), 138.0, 135.1, 134.5, 129.6, 128.3, 127.8 (t, *J* = 5.5 Hz), 127.1, 126.9, 125.8, 124.0, 123.3, 120.7, 119.4 (t, *J* = 251.4 Hz), 115.6, 113.9, 57.0 (t, *J* = 33.9 Hz). **¹⁹F NMR** (470 MHz, CDCl₃) δ -99.88 (d, *J* = 246.7 Hz, 1F), -100.56 (d, *J* = 247.4 Hz, 1F). **IR(film)** 2978, 2889, 1532, 1451, 1377,

1356, 1177, 1087, 859, 729 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{22}\text{H}_{16}\text{ClF}_2\text{N}_2\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$ 477.0487; found 477.0486. **mp** 91.1–92.1 °C.

2-(1-chloro-2,2-difluoro-2-(4-nitrophenyl)ethyl)benzofuran (3pa). Compound **3pa** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 2-(2,2-difluorovinyl)benzofuran **1p** (0.18 g, 1.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et_2O in hexanes) provided 0.15 g (44%) of the title compound as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 8.24 (d, J = 8.9 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.56 (dt, J = 7.7, 1.1 Hz, 1H), 7.46 (dd, J = 8.3, 0.9 Hz, 1H), 7.35 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 7.27 (td, J = 7.6, 1.1 Hz, 1H), 6.82 (s, 1H), 5.42 (t, J = 10.0 Hz, 1H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (201 MHz, CDCl_3) δ 155.2, 149.4, 148.3, 139.5 (t, J = 26.3 Hz), 127.7 (t, J = 5.8 Hz), 127.3, 125.9, 123.6, 123.6, 121.8, 118.4 (t, J = 251.7 Hz), 111.7, 108.9, 56.7 (t, J = 33.9 Hz). **^{19}F NMR** (470 MHz, CDCl_3) δ -100.27 (d, J = 249.0 Hz, 1F), -100.91 (d, J = 250.1 Hz, 1F). **IR(film)** 2981, 2890, 1595, 1532, 1464, 1421, 1090, 897, 859, 629 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{16}\text{H}_{11}\text{ClF}_2\text{NO}_3$ $[\text{M}+\text{H}]^+$ 338.0317; found 338.0320. **mp** 133.6–134.2 °C.

1-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-4-nitrobenzene (4qa). Compound **4qa** was synthesized according to the general procedure using 4-nitrobenzenesulfonyl chloride **2a** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→15% Et_2O in hexanes) provided 0.20 g (61%) of the title compound as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 6.88 – 6.78 (m, 2H), 5.18 (t, J = 10.4 Hz, 1H), 3.80 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR**

(201 MHz, CDCl₃) δ 160.6, 149.2, 140.0 (t, J = 26.7 Hz), 130.5, 128.1 (t, J = 5.8 Hz), 125.2, 123.2, 119.3 (t, J = 250.5 Hz), 113.9, 63.7 (t, J = 31.5 Hz), 55.5. **¹⁹F NMR** (470 MHz, CDCl₃) δ -100.72 (d, J = 242.1 Hz, 1F), -102.09 (d, J = 246.1 Hz, 1F). **IR(film)** 2981, 2921, 2854, 1595, 1459, 1426, 1323, 1087, 867, 629 cm⁻¹. **HRMS** (APCI) m/z : calc'd for C₁₅H₁₃ClF₂NO₃ [M+H]⁺ 328.0547; found 328.0564. **mp** 103.8–104.7 °C.

1-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-4-(trifluoromethyl)benzene (**4qb**). Compound **4qb** was synthesized according to the general procedure using 4-(trifluoromethyl)benzenesulfonyl chloride **2b** (0.49 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→4% Et₂O in 99:1 hexanes:PhMe) provided 0.20 g (56%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.88 – 7.82 (m, 3H), 7.79 (d, J = 8.5 Hz, 1H), 7.54 (p, J = 7.1 Hz, 2H), 7.29 (dd, J = 8.7, 1.8 Hz, 1H), 7.21 (d, J = 8.3 Hz, 2H), 6.86 – 6.73 (m, 2H), 5.27 (t, J = 10.8 Hz, 1H), 3.78 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.5, 137.5 (t, J = 26.4 Hz), 132.5 (q, J = 32.8 Hz), 130.5, 127.2 (t, J = 6.1 Hz), 125.6, 125.1 (d, J = 3.9 Hz), 119.5 (t, J = 250.0 Hz), 113.8, 63.9 (t, J = 31.9 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ -63.42 (s, 3F), -100.86 (d, J = 244.5 Hz, 1F), -102.14 (d, J = 245.6 Hz, 1F). **IR(film)** 2978, 2919, 2848, 1594, 1464, 1421, 1247, 1090, 903, 631 cm⁻¹. **HRMS** (APCI) m/z : calc'd for C₁₆H₁₃ClF₅O [M+H]⁺ 351.0570; found 351.0611. **mp** 83.9–84.4 °C.

1-(4-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)phenyl)ethan-1-one (**4qc**). Compound **4qc** was synthesized according to the general procedure using 4-acetylbenzenesulfonyl chloride **2c** (0.44 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel

chromatographic purification (0→40% Et₂O in hexanes) provided 0.17 g (53%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 5.17 (t, *J* = 10.7 Hz, 1H), 3.79 (s, 3H), 2.60 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 197.5, 160.4, 138.2 (t, *J* = 26.2 Hz), 130.5, 129.5, 128.0, 127.5, 126.9 (t, *J* = 6.0 Hz), 119.6 (t, *J* = 250.0 Hz), 113.8, 63.9 (t, *J* = 31.6 Hz), 55.4, 26.8. **¹⁹F NMR** (470 MHz, CDCl₃) δ -99.65 (d, *J* = 241.5 Hz, 1F), -102.16 (d, *J* = 242.1 Hz, 1F). **IR(film)** 2916, 2848, 1715, 1595, 1459, 1421, 1088, 908, 768, 630 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₇H₁₆ClF₂O₂ [M+H]⁺ 325.0807; found 325.0809. **mp** 154.8–155.7 °C.

1-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-4-fluorobenzene (4qd). Compound **4qd** was synthesized according to the general procedure using 4-fluorobenzenesulfonyl chloride **2d** (0.39 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (100% hexanes) provided 0.15 g (51%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.23 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.13 (dd, *J* = 11.7, 9.3 Hz, 1H), 3.80 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 164.5, 160.4, 130.5, 129.8 (t, *J* = 27.1 Hz), 128.8 (q, *J* = 7.1, 6.7 Hz), 126.0, 119.8 (t, *J* = 249.6 Hz), 115.2 (d, *J* = 22.1 Hz), 113.7, 64.3 (t, *J* = 32.5 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ -99.21 (d, *J* = 242.6 Hz, 1F), -101.86 (d, *J* = 243.4 Hz, 1F), -110.79 (s, 1F). **IR(film)** 2981, 2905, 2852, 1595, 1464, 1421, 1236, 1090, 894, 634 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₅H₁₂ClF₃O [M]⁺ 300.0523; found 300.0521. **mp** 89.1–89.7 °C.

1-bromo-4-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)benzene (4qe). Compound **4qe** was synthesized according to the general procedure using 4-bromobenzenesulfonyl chloride **2e** (0.51 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q**

(0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (100% hexanes) provided 0.23 g (63%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.13 (t, *J* = 10.5 Hz, 1H), 3.80 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.4, 132.8 (t, *J* = 26.6 Hz), 131.3, 130.5, 128.3, 125.8, 125.0, 119.7 (t, *J* = 249.8 Hz), 113.8, 64.0 (t, *J* = 32.1 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ –100.04 (d, *J* = 243.7 Hz, 1F), –102.47 (d, *J* = 243.3 Hz, 1F). **IR(film)** 2983, 2889, 1592, 1464, 1421, 1226, 1093, 900, 765, 634 cm^{–1}. **HRMS** (APCI) *m/z*: calc'd for C₁₅H₁₂BrClF₂O [M]⁺ 359.9728; found 359.9638. **mp** 77.8–78.4 °C.

1-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-4-iodobenzene (4qf). Compound **4qf** was synthesized according to the general procedure using 4-iodobenzenesulfonyl chloride **2f** (0.60 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (100% hexanes) provided 0.20 g (50%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 5.16 – 5.08 (m, 1H), 3.80 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.4, 137.3, 133.5 (t, *J* = 26.7 Hz), 130.5, 128.3 (t, *J* = 5.9 Hz), 125.8, 119.8 (t, *J* = 249.8 Hz), 113.8, 97.1, 64.0 (t, *J* = 32.1 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ –100.35 (d, *J* = 243.2 Hz, 1F), –102.65 (d, *J* = 243.7 Hz, 1F). **IR(film)** 2984, 2895, 1595, 1464, 1421, 1239, 1092, 897, 858, 631 cm^{–1}. **HRMS** (APCI) *m/z*: calc'd for C₁₅H₁₂ClF₂IO [M]⁺ 407.9590; found 407.9592. **mp** 104.8–105.8 °C.

1-(1-chloro-2,2-difluoro-2-phenylethyl)-4-methoxybenzene (4qg). Compound **4qg** was synthesized according to the general procedure using benzenesulfonyl chloride **2g** (0.35

g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→5% Et₂O in hexanes) provided 0.15 g (53%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.03 (dd, *J* = 12.2, 9.6 Hz, 1H), 3.66 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.3, 133.9 (t, *J* = 26.1 Hz), 130.5, 130.3, 128.1, 126.5 (t, *J* = 6.1 Hz), 126.3, 120.0 (t, *J* = 249.5 Hz), 113.7, 64.4 (t, *J* = 32.1 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ -100.42 (dd, *J* = 242.6, 9.2 Hz, 1F), -103.19 (d, *J* = 245.4 Hz, 1F). **IR(film)** 2981, 2919, 2845, 1594, 1462, 1420, 1226, 1090, 903, 629 cm⁻¹. **HRMS** (APCI) *m/z*: calc'd for C₁₅H₁₃F₂O [M-Cl]⁺ 247.0932; found 247.0938. **mp** 101.3–101.9 °C.

2-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)naphthalene (4qh). Compound **4qh** was synthesized according to the general procedure using naphthalene-2-sulfonyl chloride **2h** (0.45 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), Pd(OAc)₂ (5.6 g, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO₂ (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→3% Et₂O in 99:1 hexanes:PhMe) provided 0.17 g (50%) of the title compound as a yellow solid.

¹H NMR (500 MHz, CDCl₃) δ 7.84 (td, *J* = 5.5, 2.7 Hz, 3H), 7.79 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.28 (dt, *J* = 8.5, 2.7 Hz, 1H), 7.21 (d, *J* = 6.5 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 5.27 (t, *J* = 11.7 Hz, 1H), 3.78 (s, 3H). **¹³C{¹H} NMR** (201 MHz, CDCl₃) δ 160.3, 134.0, 132.3, 131.3 (t, *J* = 26.2 Hz), 130.6, 128.8, 128.0, 127.9, 127.5, 126.8, 126.3, 123.2, 120.2 (t, *J* = 249.9 Hz), 113.7, 64.4 (t, *J* = 32.2 Hz), 55.4. **¹⁹F NMR** (470 MHz, CDCl₃) δ -100.70 (d, *J* = 243.6 Hz, 1F), -102.91 (d, *J* = 244.4 Hz, 1F). **IR(film)**

2943, 2918, 2840, 1592, 1462, 1424, 1089, 849, 753, 630 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{19}\text{H}_{15}\text{ClF}_2\text{O}$ $[\text{M}]^+$ 332.0780; found 332.0723. **mp** 154.8–155.3 °C.

1-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-4-methylbenzene (4qi). Compound **4qi** was synthesized according to the general procedure using 4-methylbenzenesulfonyl chloride **2i** (0.38 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (100% hexanes) provided 0.15 g (52%) of the title compound as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 7.19 (d, J = 8.4 Hz, 2H), 7.17 – 7.09 (m, 4H), 6.85 – 6.74 (m, 2H), 5.14 (dd, J = 12.0, 9.7 Hz, 1H), 3.80 (s, 3H), 2.35 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (201 MHz, CDCl_3) δ 160.2, 140.4, 131.0 (t, J = 26.3 Hz), 130.6, 128.8, 126.5, 126.4 (t, J = 6.1 Hz), 120.1 (t, J = 249.1 Hz), 113.7, 64.4 (t, J = 32.6 Hz), 55.4, 21.4. **^{19}F NMR** (470 MHz, CDCl_3) δ –99.79 (d, J = 242.0 Hz, 1F), –102.42 (d, J = 241.8 Hz, 1F). **IR(film)** 2981, 2892, 1595, 1464, 1424, 1228, 1128, 1003, 889, 783 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{16}\text{H}_{15}\text{F}_2\text{O}$ $[\text{M}-\text{Cl}]^+$ 261.1091; found 261.1090. **mp** 98.6–99.2 °C.

4-bromo-2-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-1-methoxybenzene (4qj). Compound **4qj** was synthesized according to the general procedure using 5-bromo-2-methoxybenzenesulfonyl chloride **2j** (0.38 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 mg, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL, 0.20 M). The reaction was stirred at 130 °C for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (100% hexanes) provided 0.20 g (52%) of the title compound as a yellow solid.

^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, J = 2.5 Hz, 1H), 7.47 (dd, J = 8.7, 2.5 Hz, 1H), 7.33 (d, J = 8.8 Hz, 2H), 6.83 (dd, J = 9.0, 2.6 Hz, 3H), 5.76 (t, J = 13.2 Hz, 1H), 3.92 (s, 3H), 3.79 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (201 MHz, CDCl_3) δ 160.3, 155.6 (d, J = 3.8 Hz), 134.7, 131.0

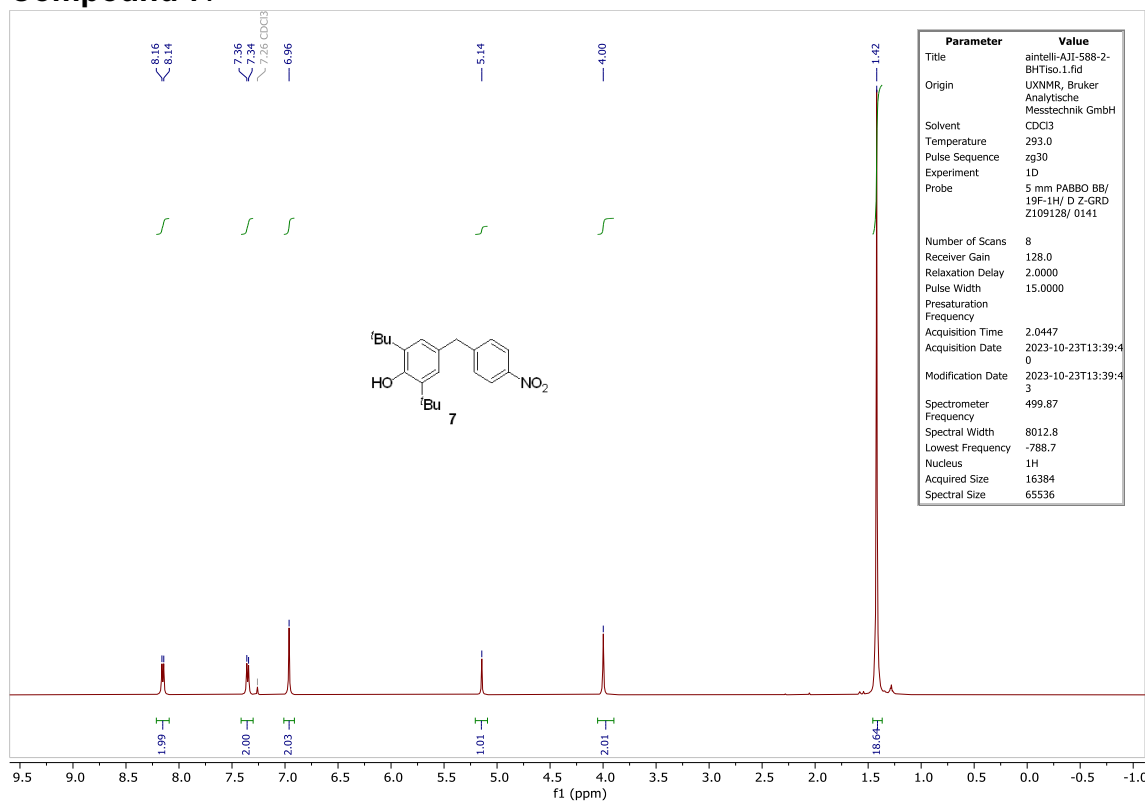
(t, $J = 9.1$ Hz), 130.4, 126.6, 124.8 (t, $J = 25.5$ Hz), 118.7 (t, $J = 250.1$ Hz), 113.8, 113.6, 113.0, 61.6 (t, $J = 28.7$ Hz), 56.4, 55.4. **^{19}F NMR** (470 MHz, CDCl_3) δ -100.05 (d, $J = 243.8$ Hz, 1F), -102.46 (d, $J = 243.5$ Hz, 1F). **IR(film)** 2984, 2887, 1595, 1462, 1424, 1090, 937, 897, 772, 631 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{16}\text{H}_{15}\text{BrClF}_2\text{O}_2$ $[\text{M}]^+$ 389.9834; found 389.9839. **mp** 117.3–118.1 $^\circ\text{C}$.

6-(2-chloro-1,1-difluoro-2-(4-methoxyphenyl)ethyl)-2H-chromen-2-one (4qk). Compound **4qk** was synthesized according to the general procedure using 2-oxo-2H-chromene-6-sulfonyl chloride **2k** (0.49 g, 2.0 mmol, 2.0 equiv.), 1-(2,2-difluorovinyl)-4-methoxybenzene **1q** (0.17 g, 1.0 mmol, 1.0 equiv.), $\text{Pd}(\text{OAc})_2$ (5.6 g, 0.025 mmol, 0.025 equiv.), copper powder (6.4 mg, 0.10 mmol, 0.10 equiv.), NaNO_2 (0.017 g, 0.25 mmol, 0.25 equiv.) and 1,4-dioxane (5.0 mL), 0.20 M. The reaction was stirred at 130 $^\circ\text{C}$ for 3 h. After the workup outlined in the general procedure, automated normal-phase silica gel chromatographic purification (0→30% Et_2O in hexanes) provided 0.18 g (50%) of the title compound as a yellow solid.

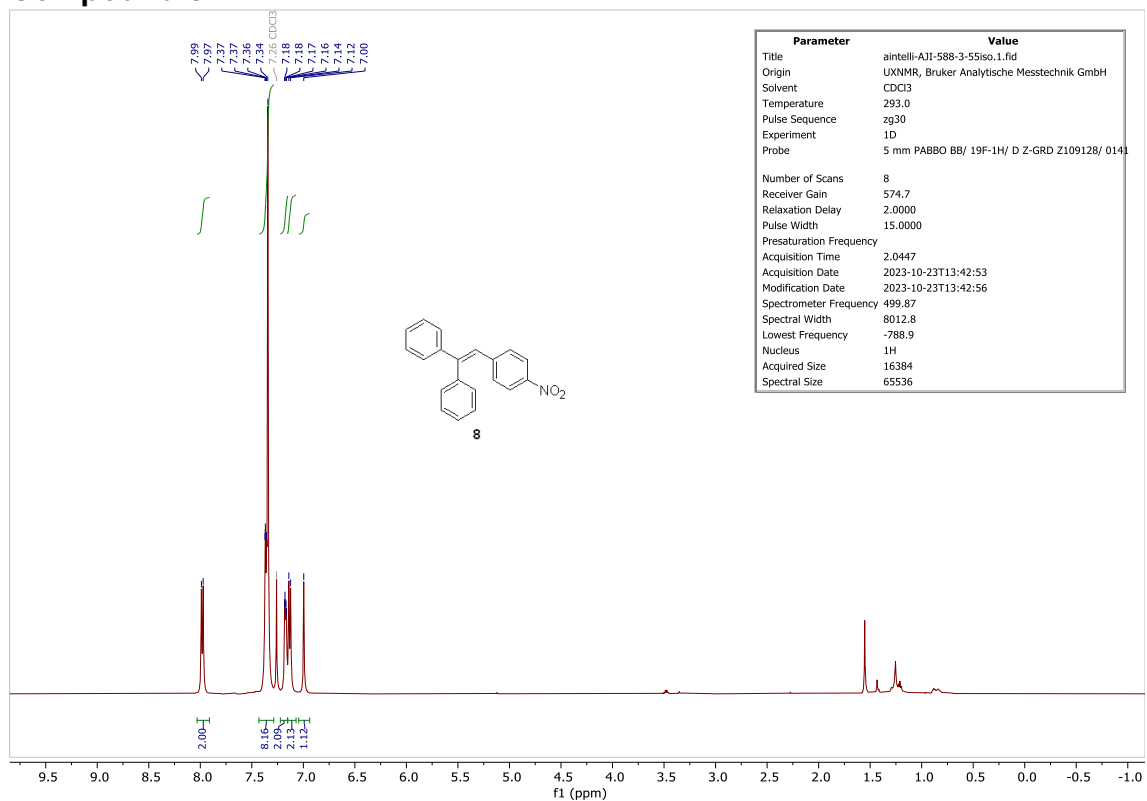
^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 9.6$ Hz, 1H), 7.53 (d, $J = 2.2$ Hz, 1H), 7.46 (dd, $J = 8.8, 2.2$ Hz, 1H), 7.38 (d, $J = 8.9$ Hz, 1H), 7.27 (d, $J = 8.3$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 6.57 (d, $J = 9.6$ Hz, 1H), 5.29 (t, $J = 10.2$ Hz, 1H), 3.90 (s, 3H). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (201 MHz, CDCl_3) δ 160.5, 160.1, 155.1, 143.0, 130.5, 130.1, 130.0 (t, $J = 6.0$ Hz), 126.7 – 126.5 (m), 125.6, 120.1 (t, $J = 250.2$ Hz), 118.3, 117.7, 116.8, 113.8, 64.0 (t, $J = 32.8$ Hz), 55.4. **^{19}F NMR** (470 MHz, CDCl_3) δ -99.70 (d, $J = 244.3$ Hz, 1F), -100.77 (d, $J = 245.5$ Hz, 1F). **IR(film)** 2981, 2921, 2845, 1733, 1592, 1421, 1228, 1087, 890, 634 cm^{-1} . **HRMS** (APCI) m/z : calc'd for $\text{C}_{18}\text{H}_{14}\text{ClF}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 351.0594; found 351.0606. **mp** 161.7–162.5 $^\circ\text{C}$.

NMR Spectra

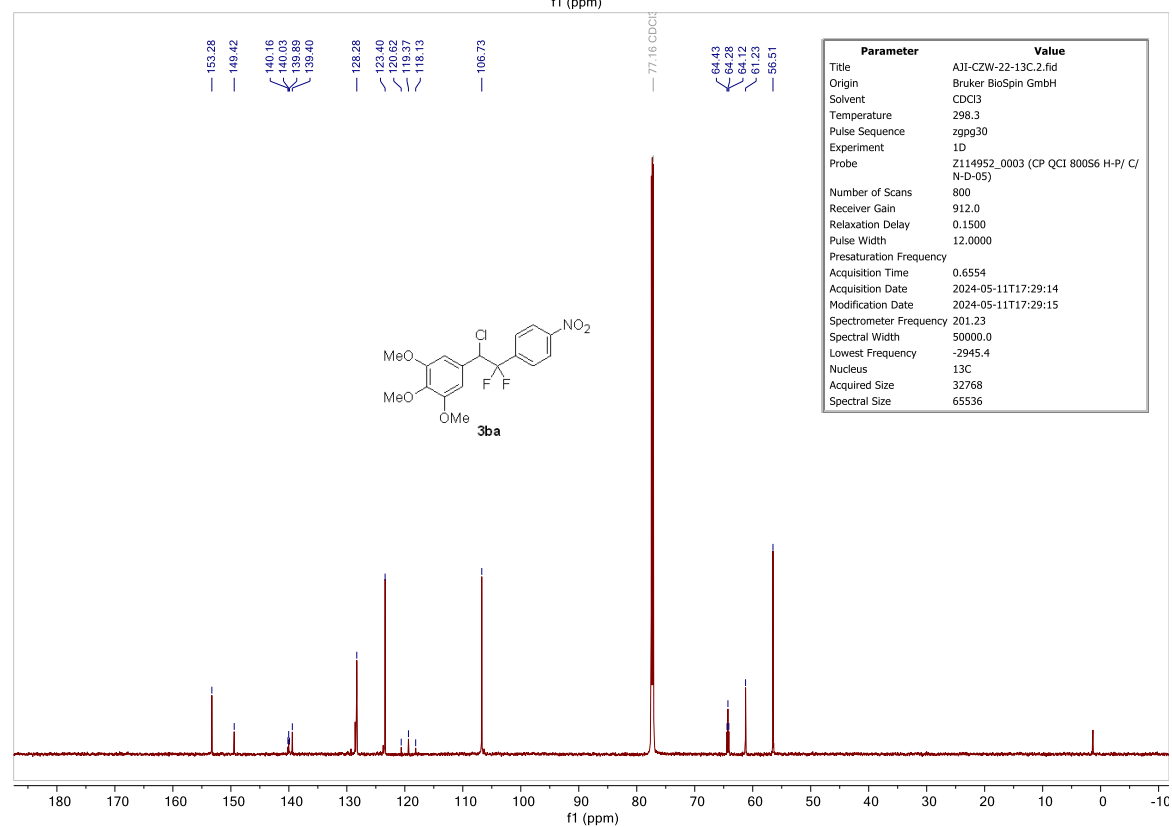
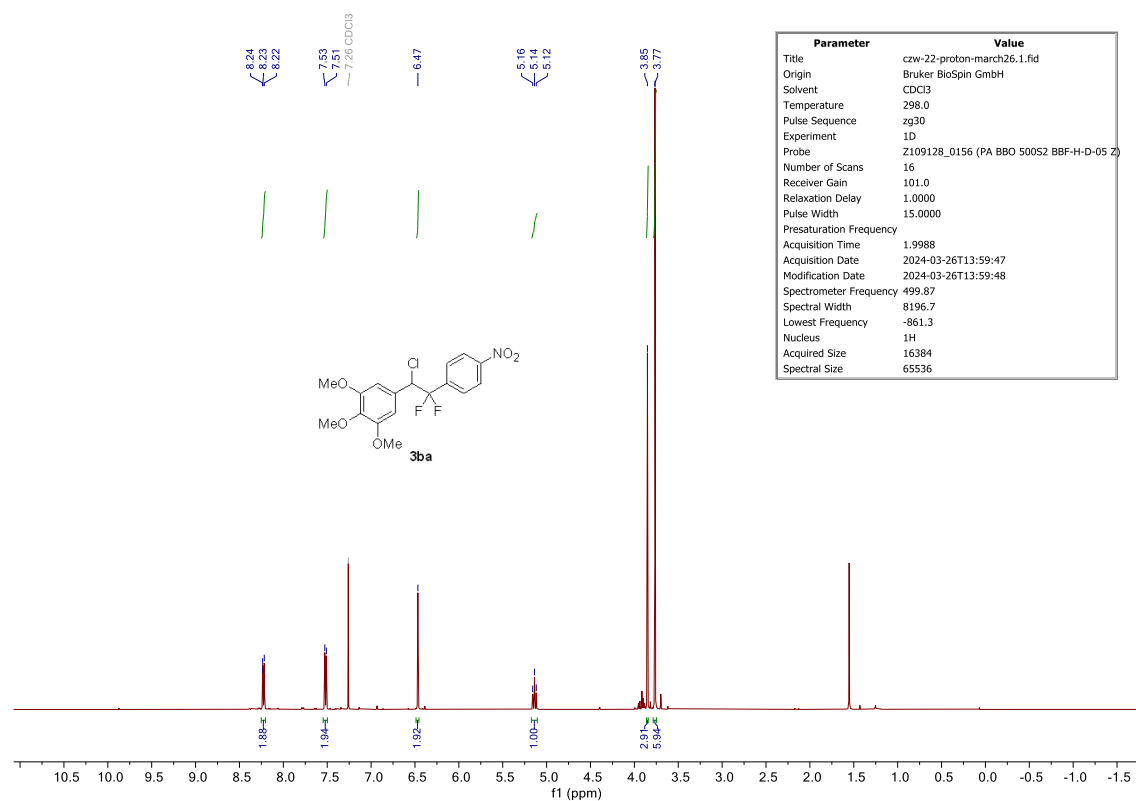
Compound 7:

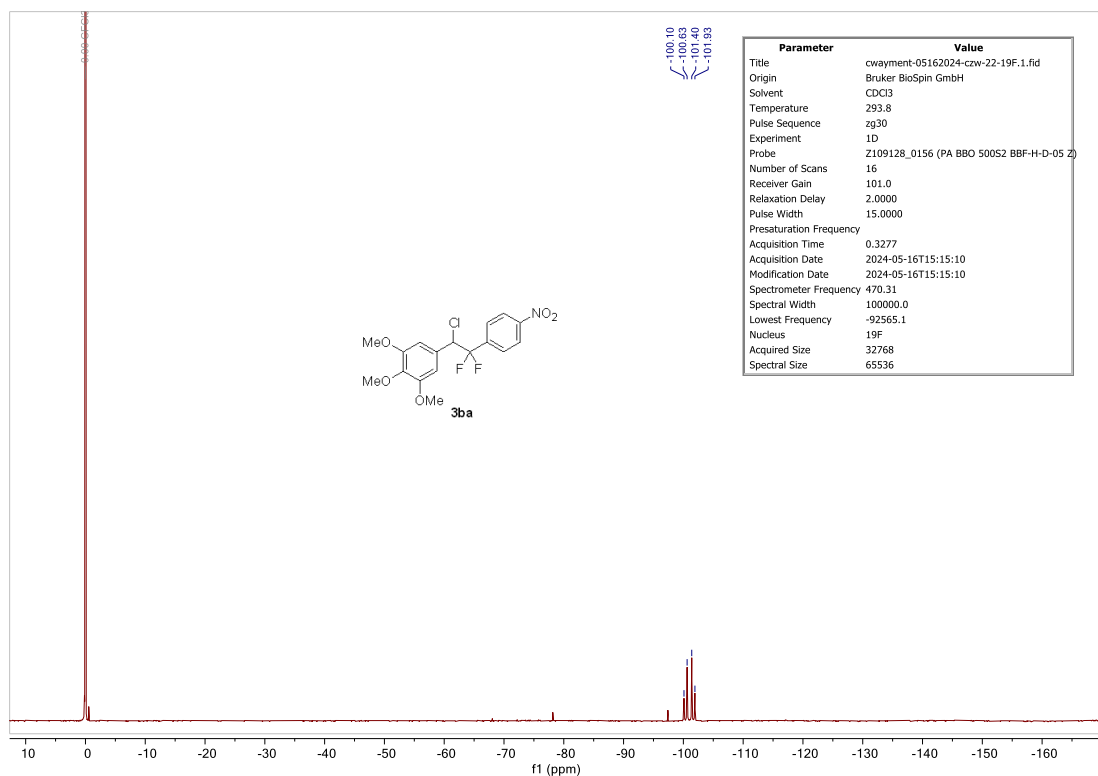


Compound 8:

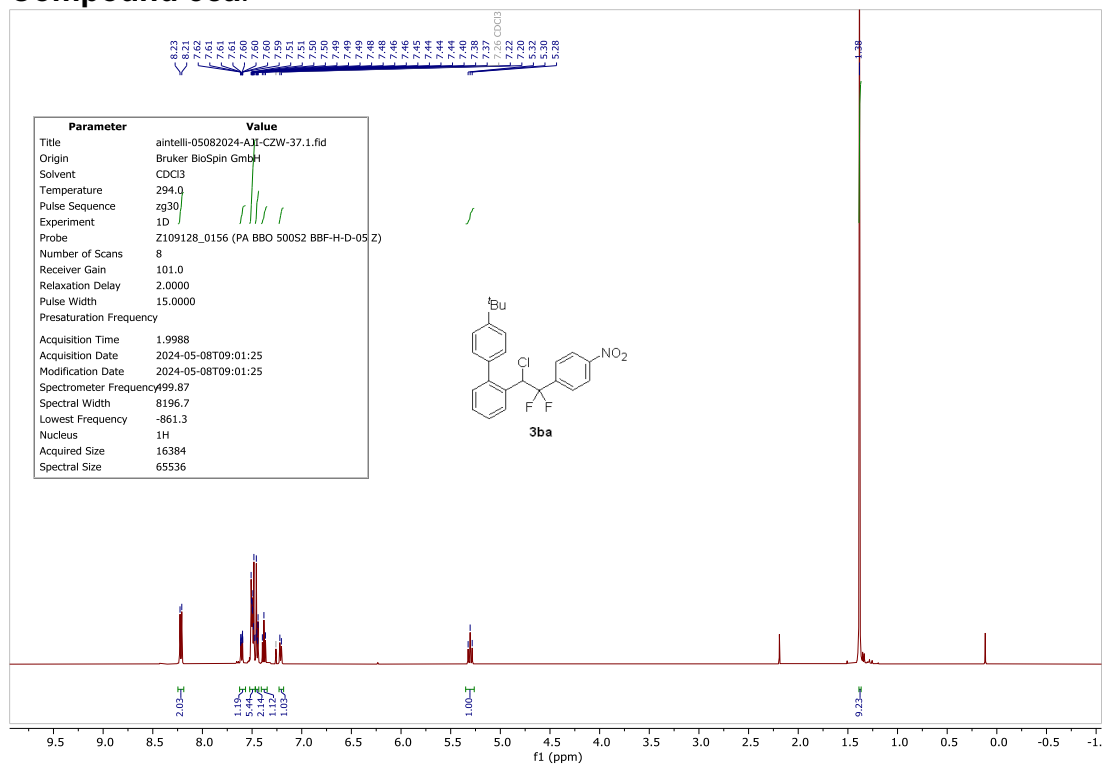


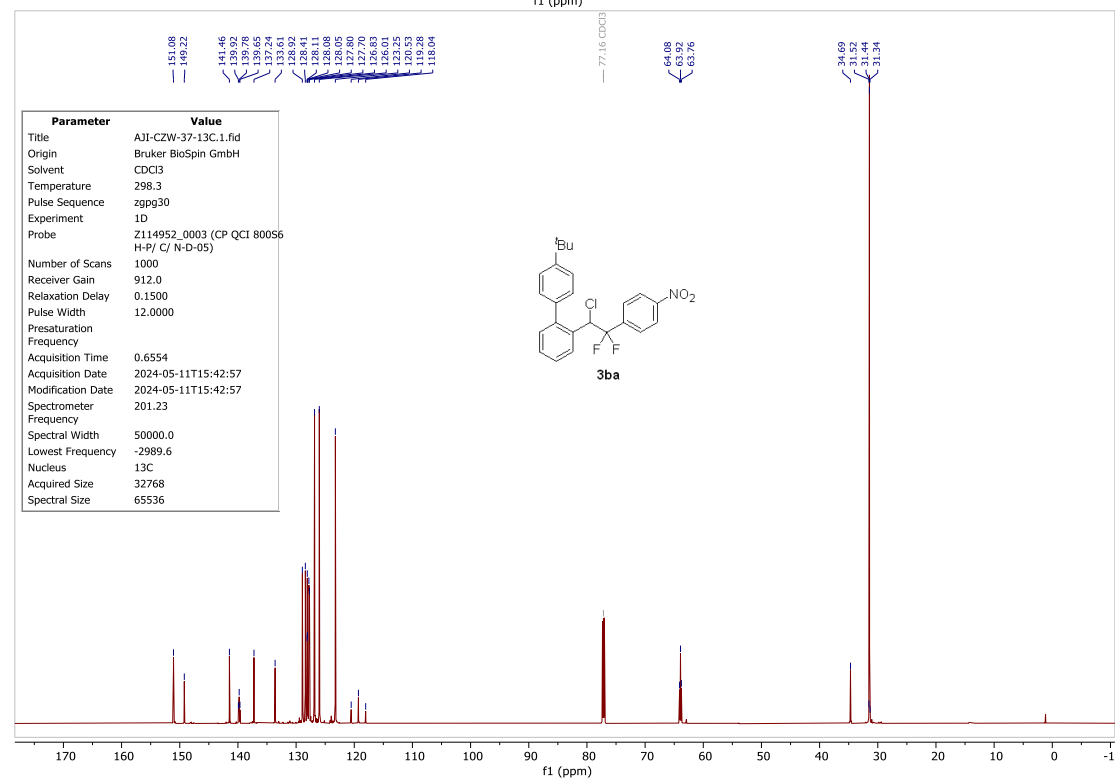
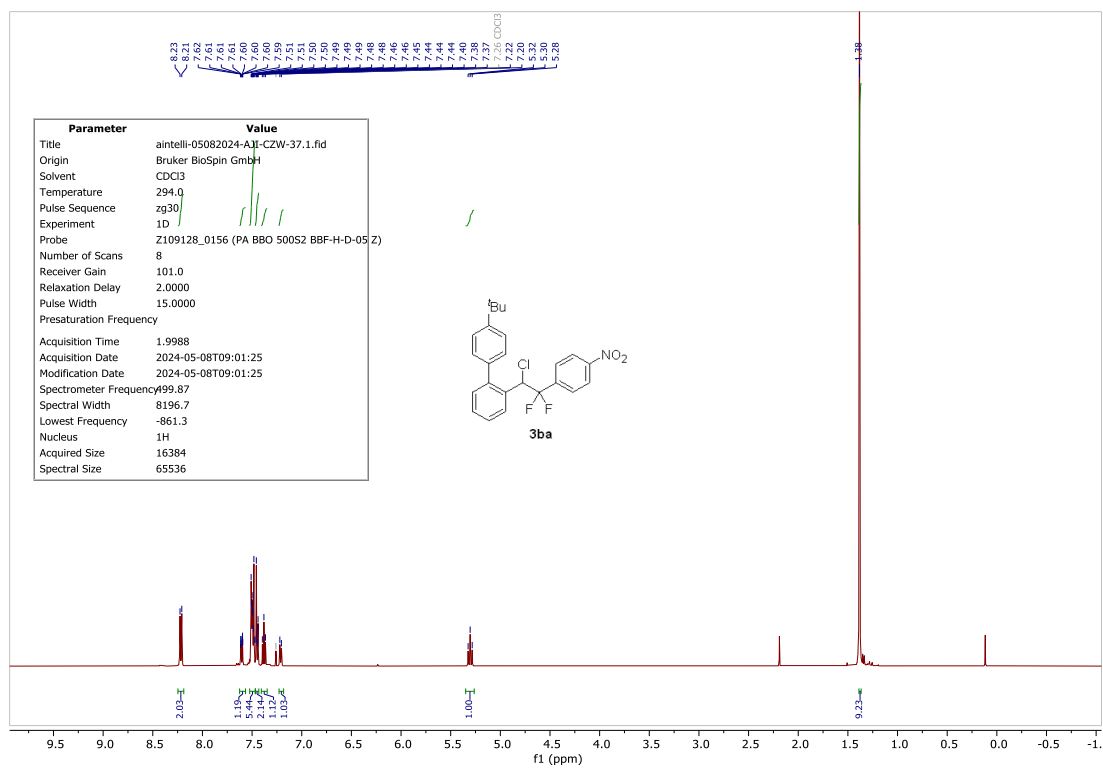
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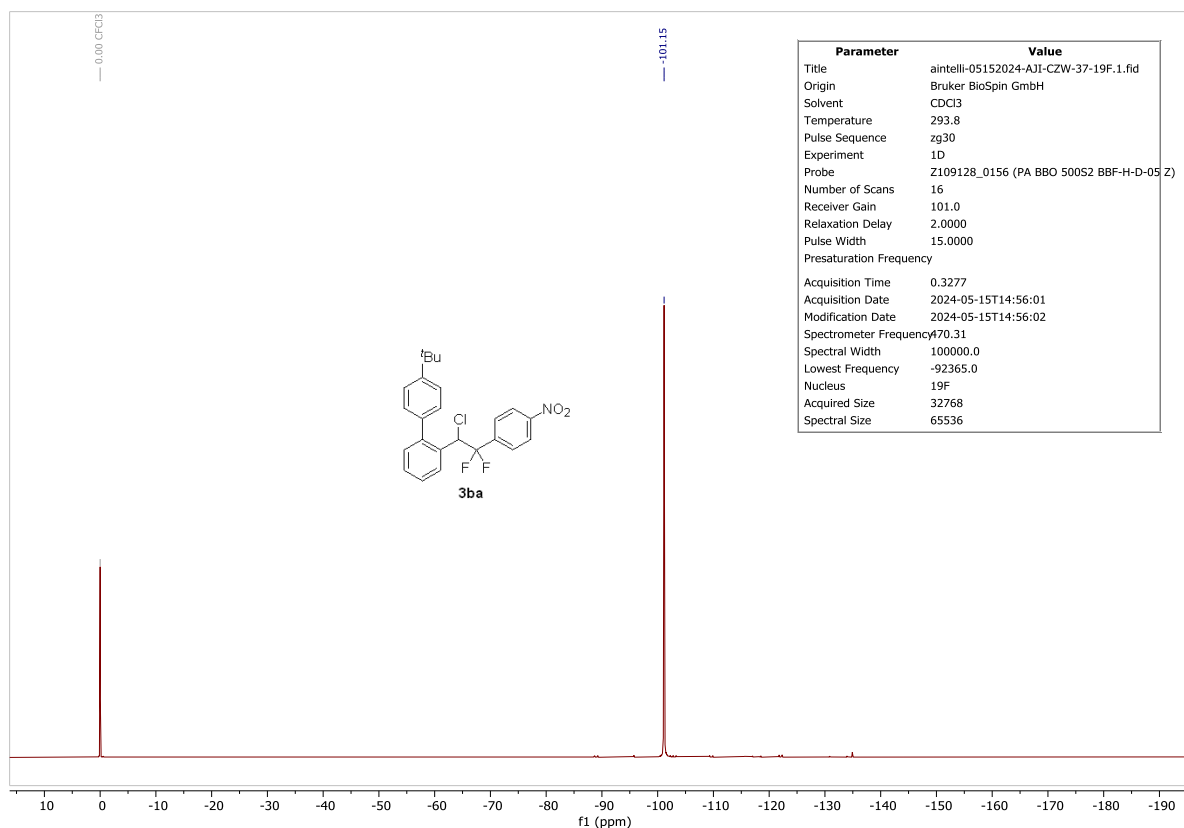




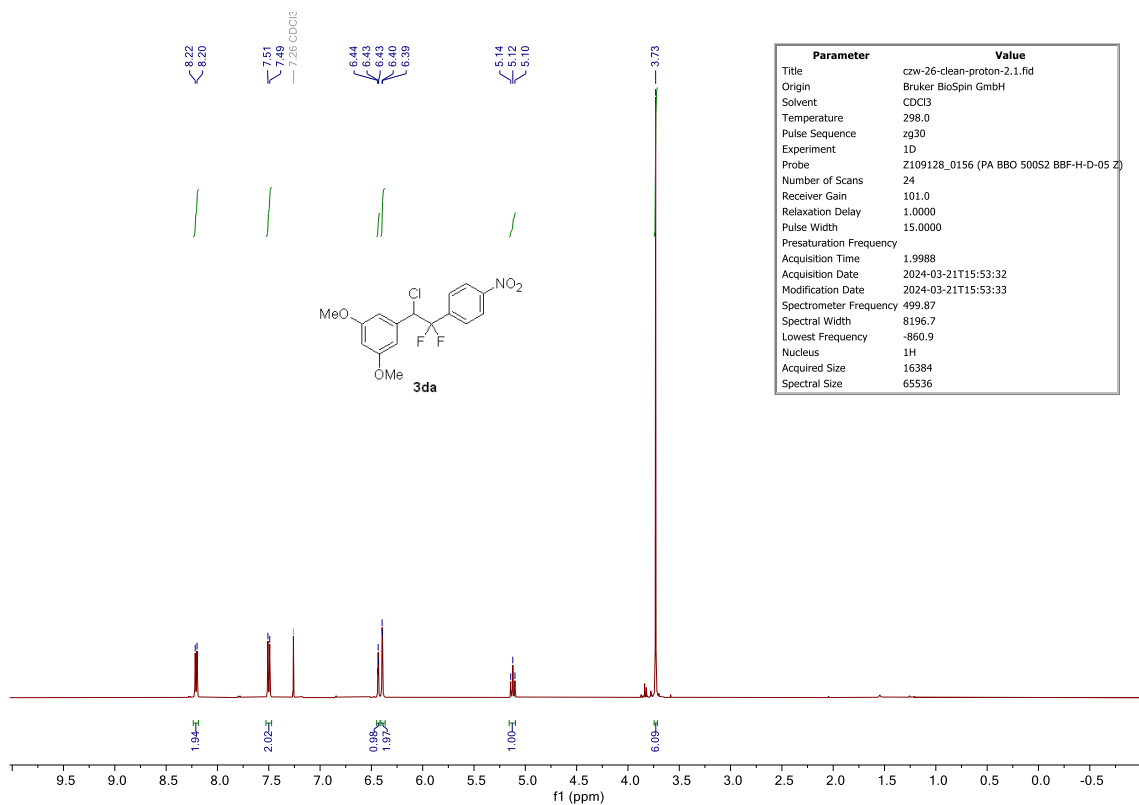
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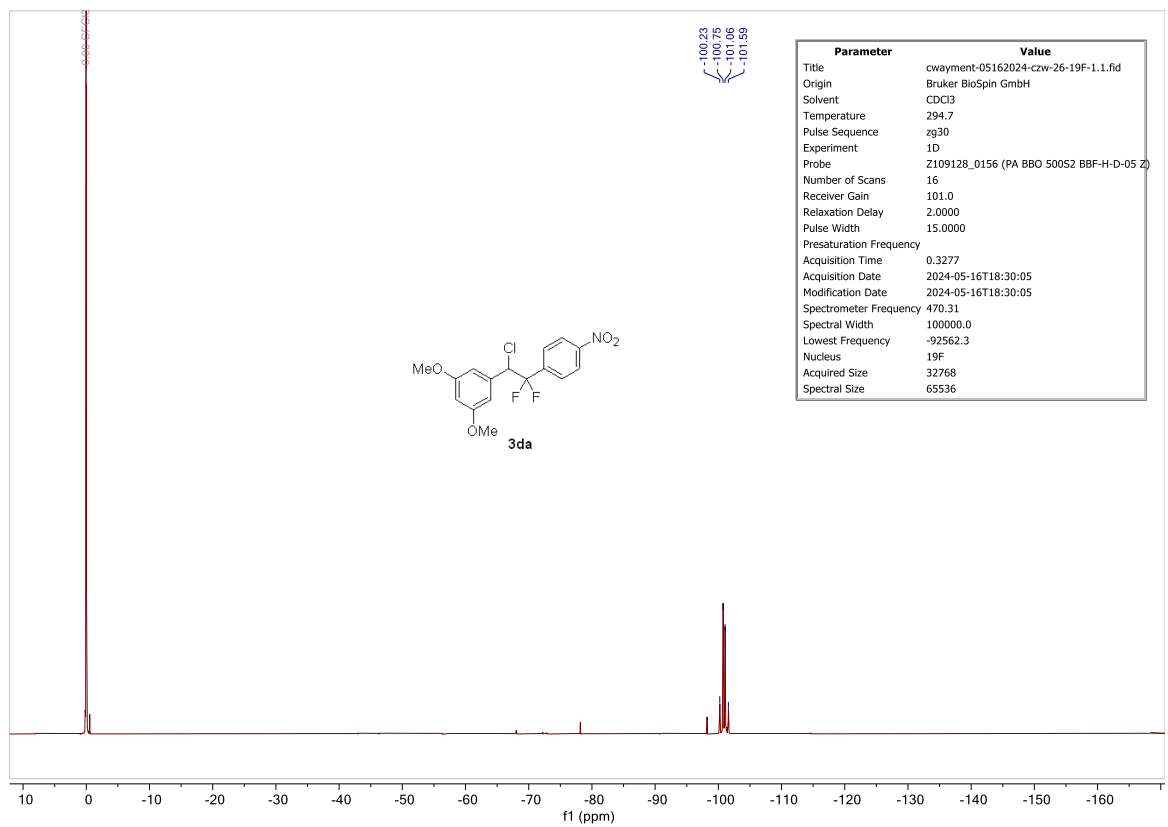
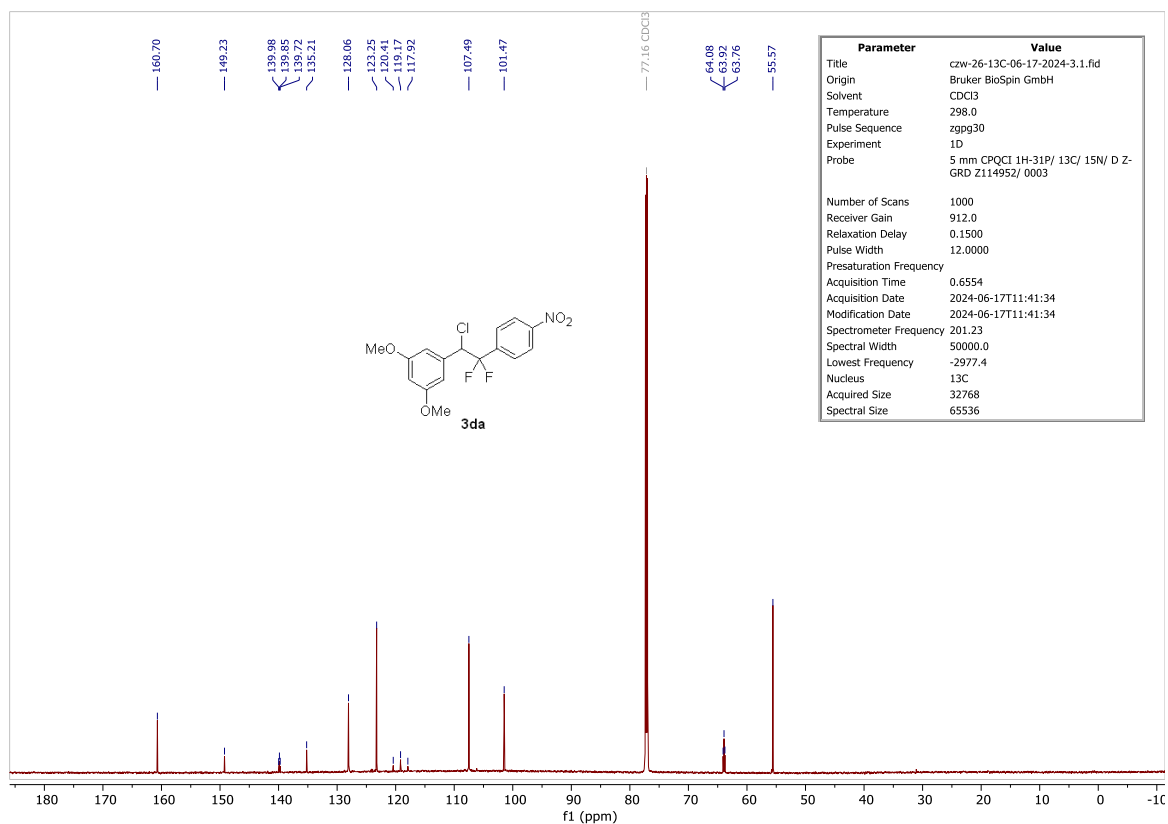




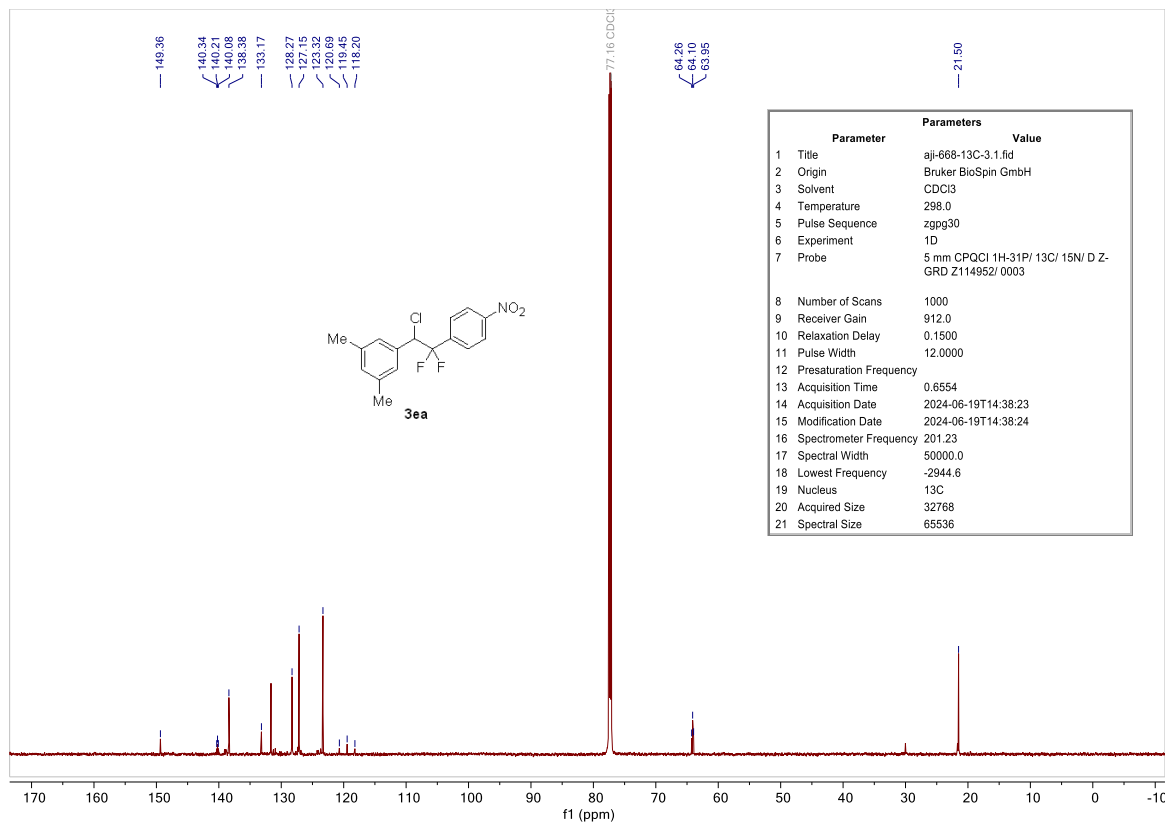
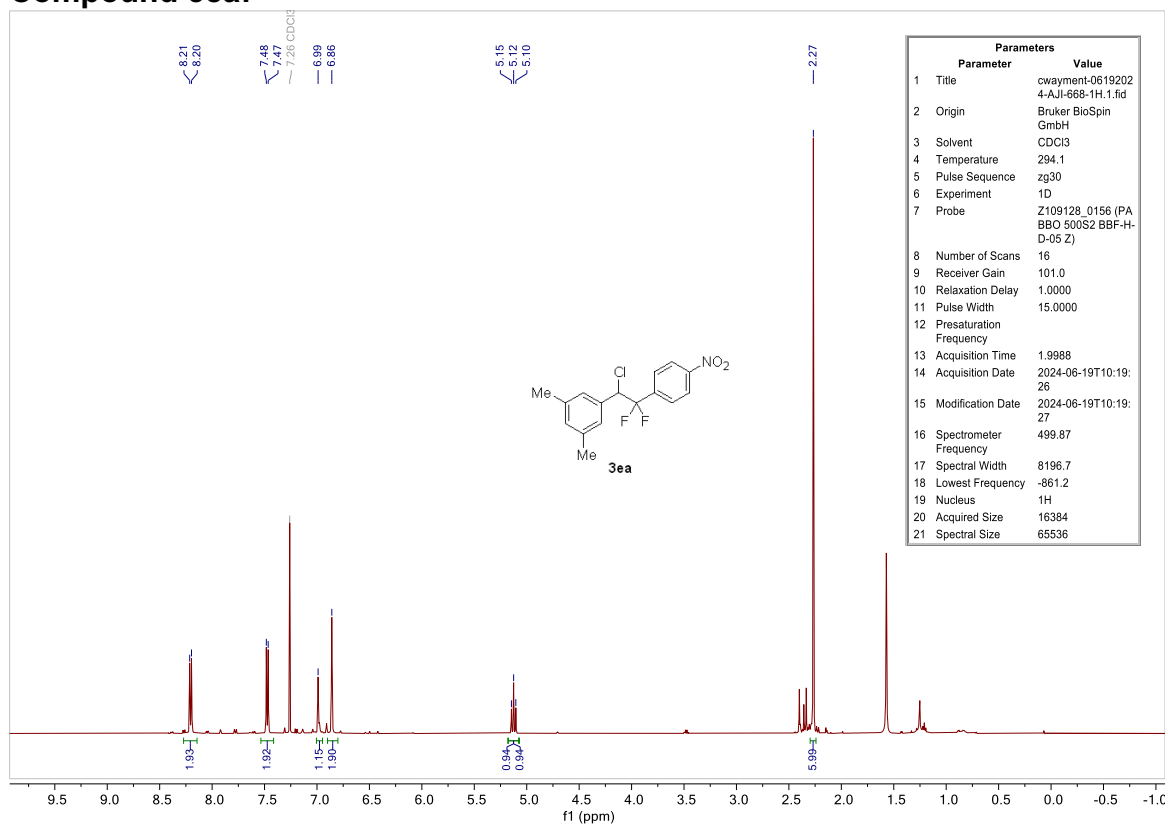


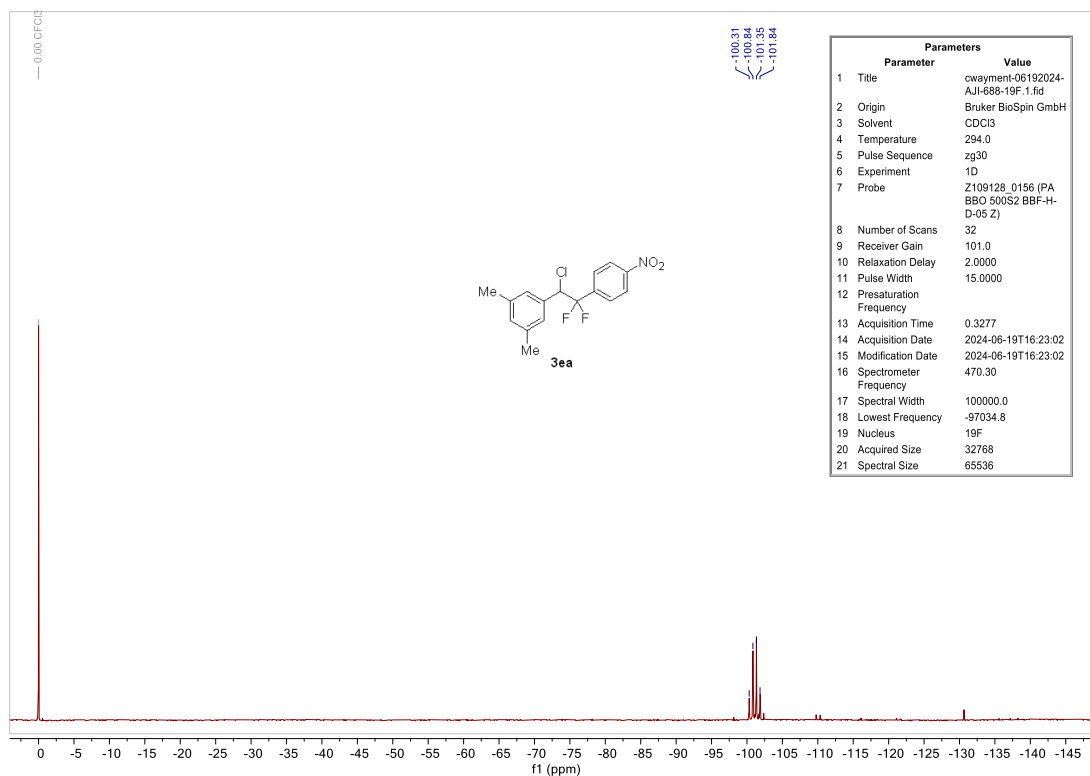
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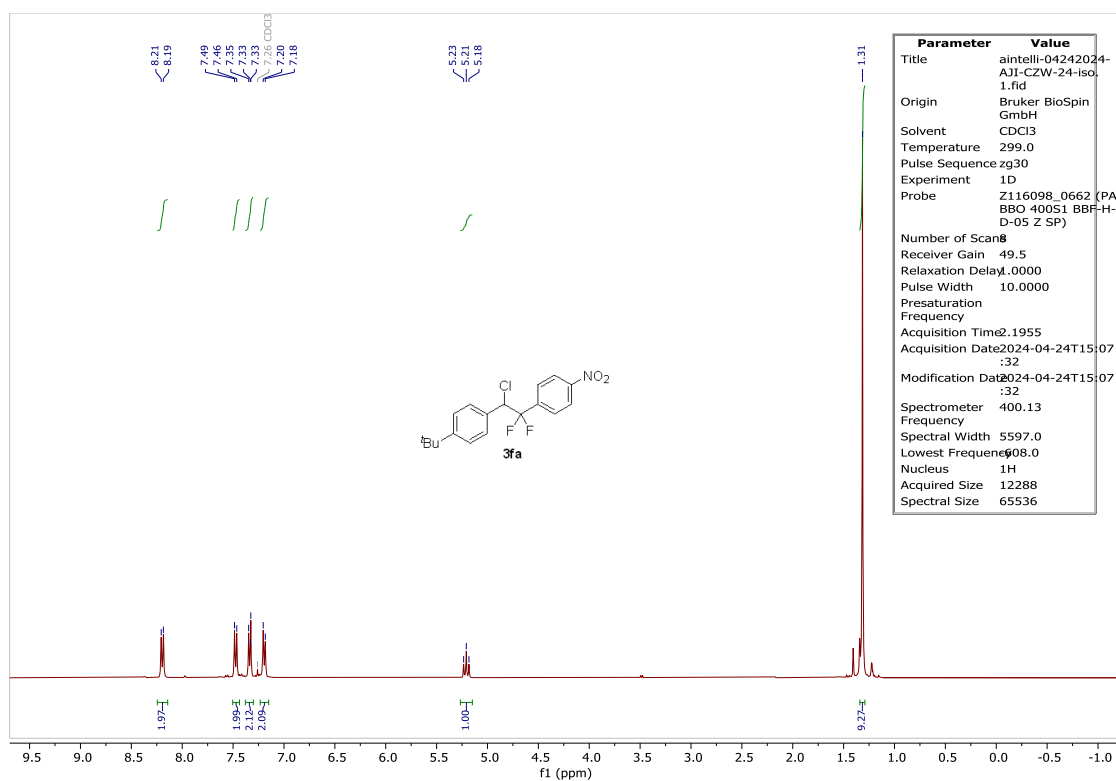


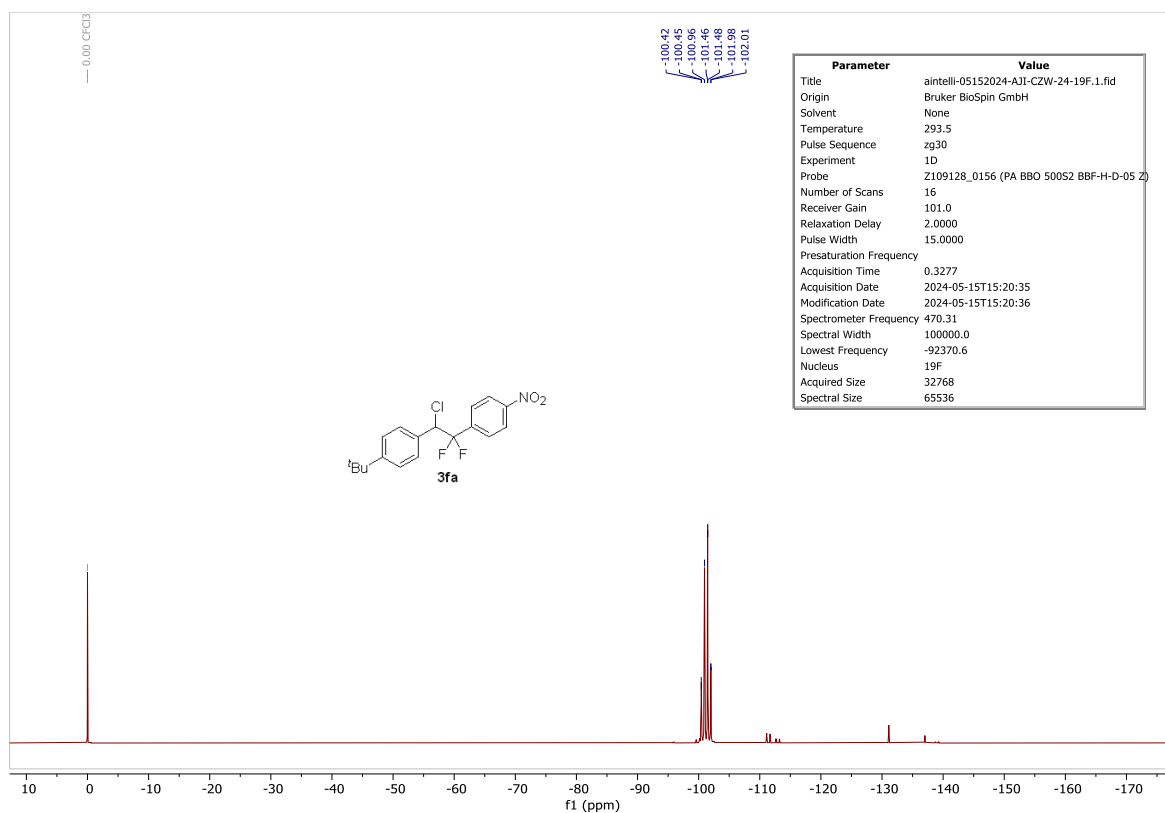
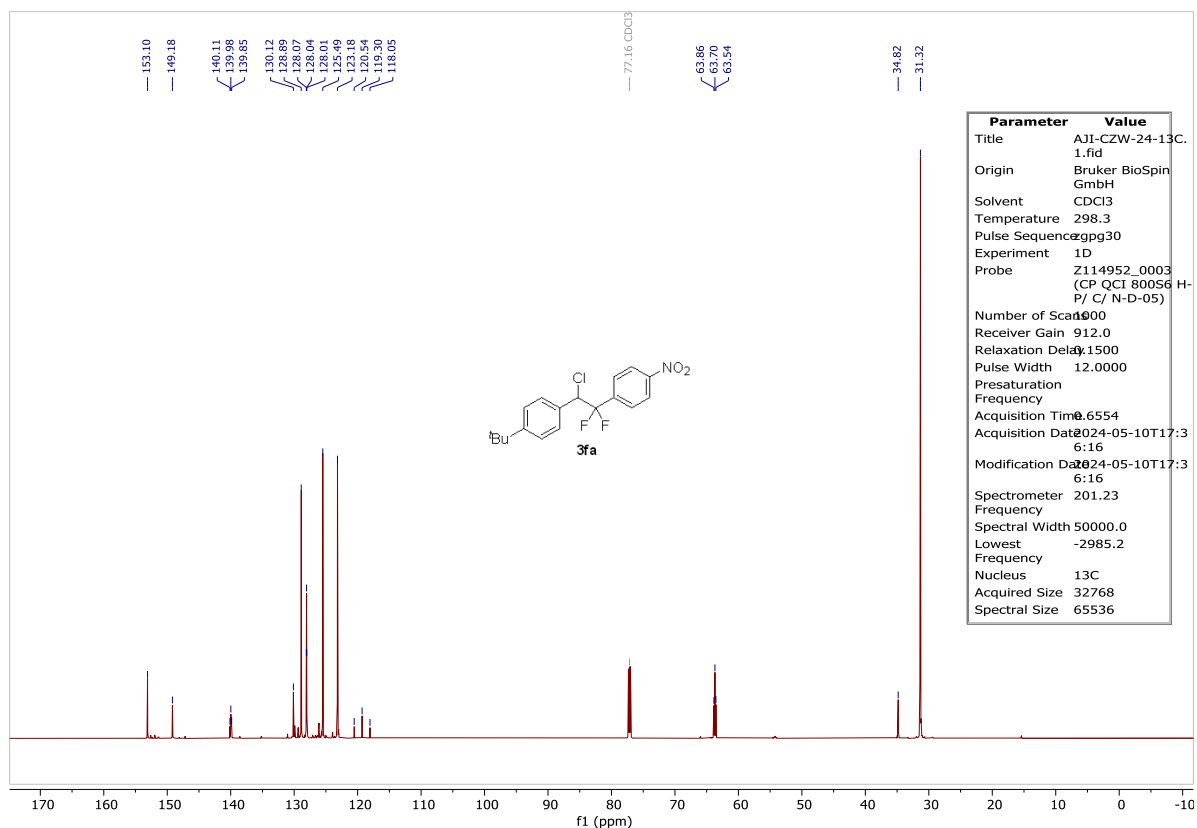
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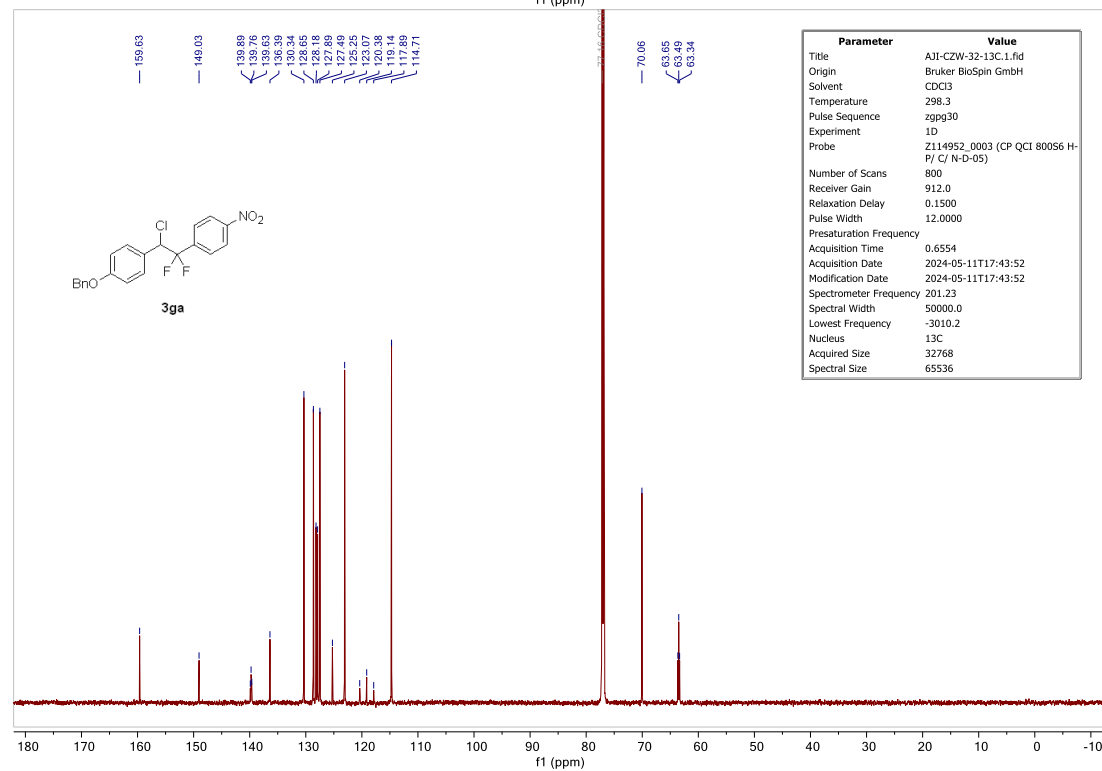
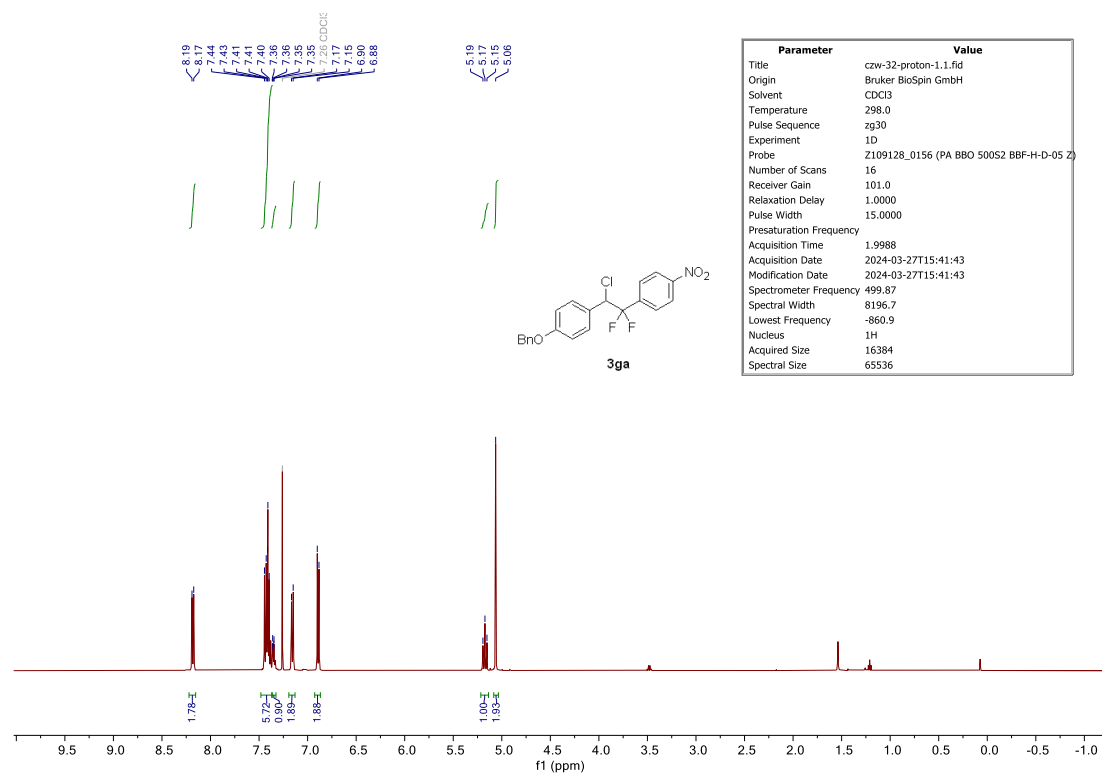


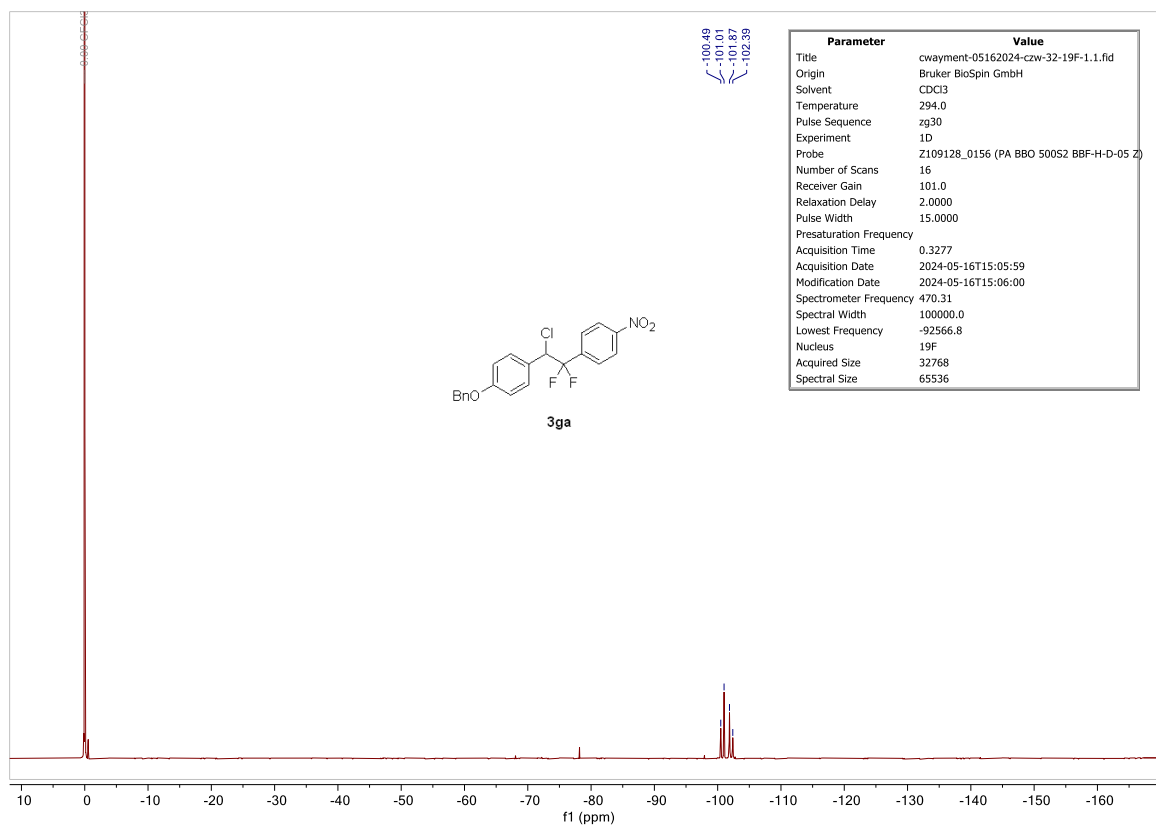
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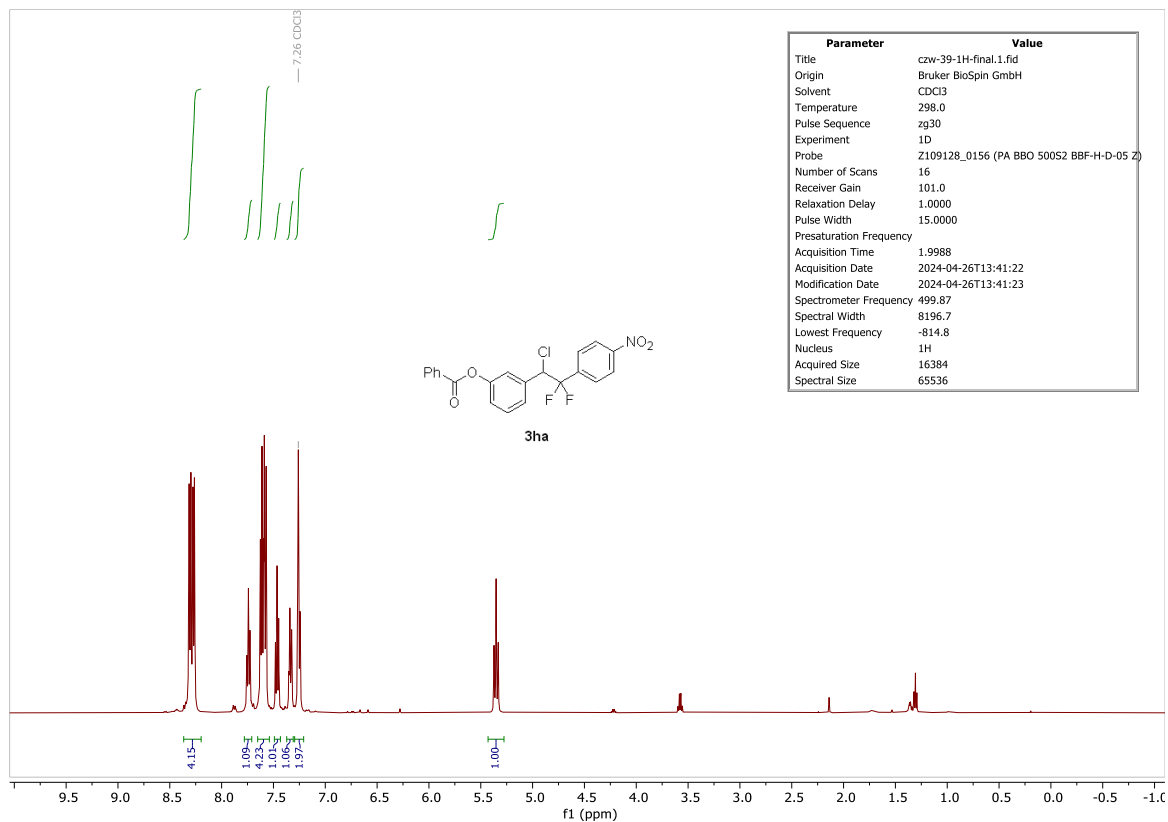


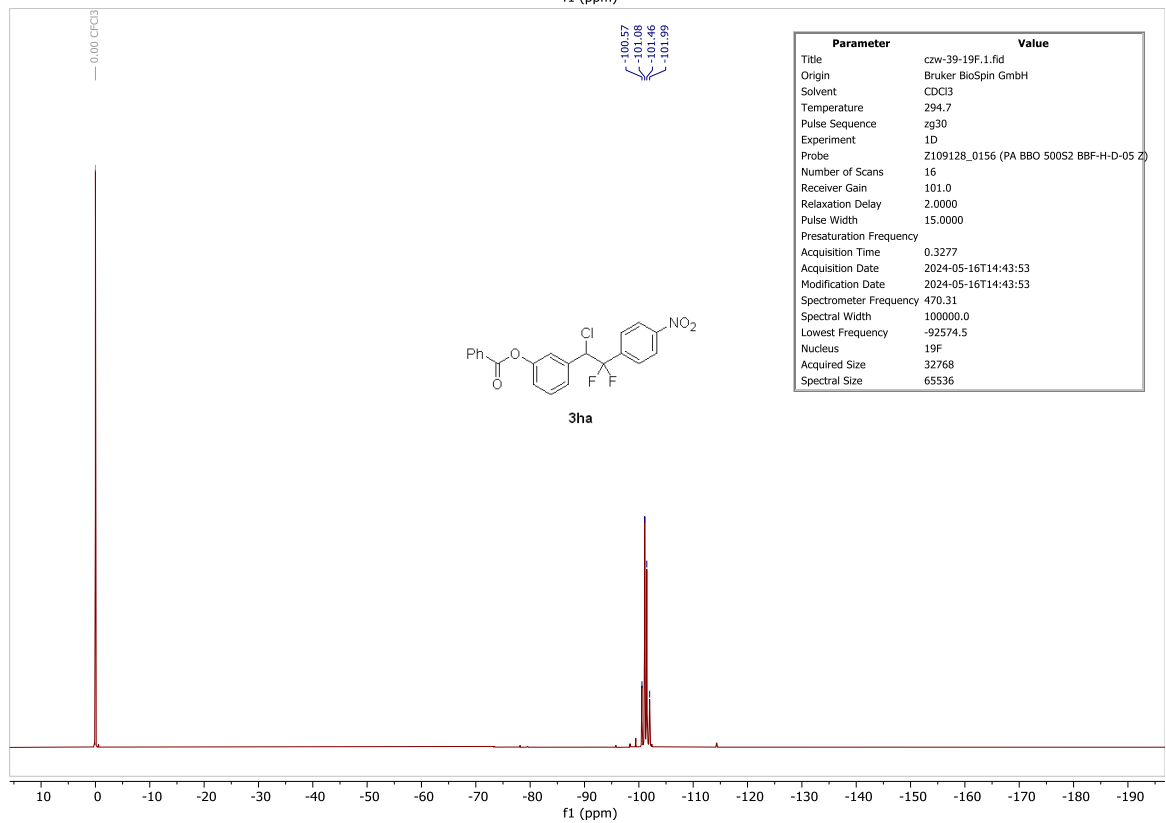
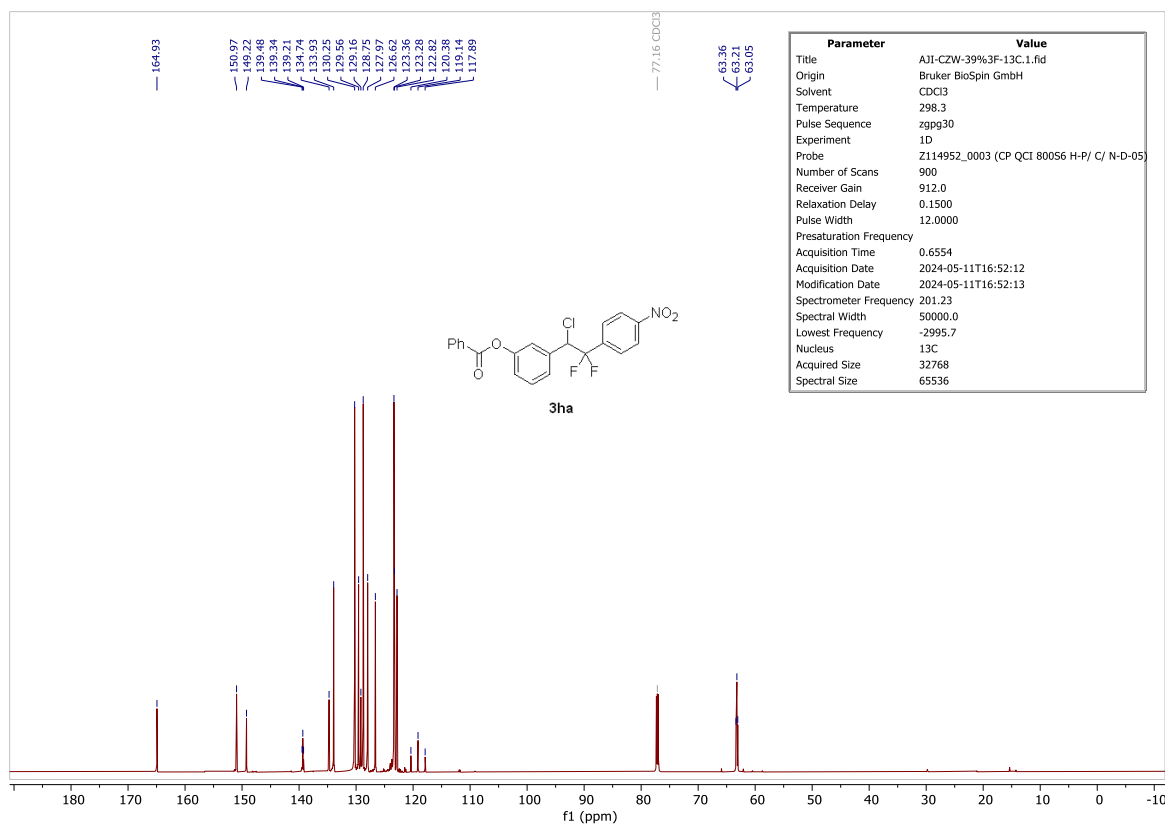
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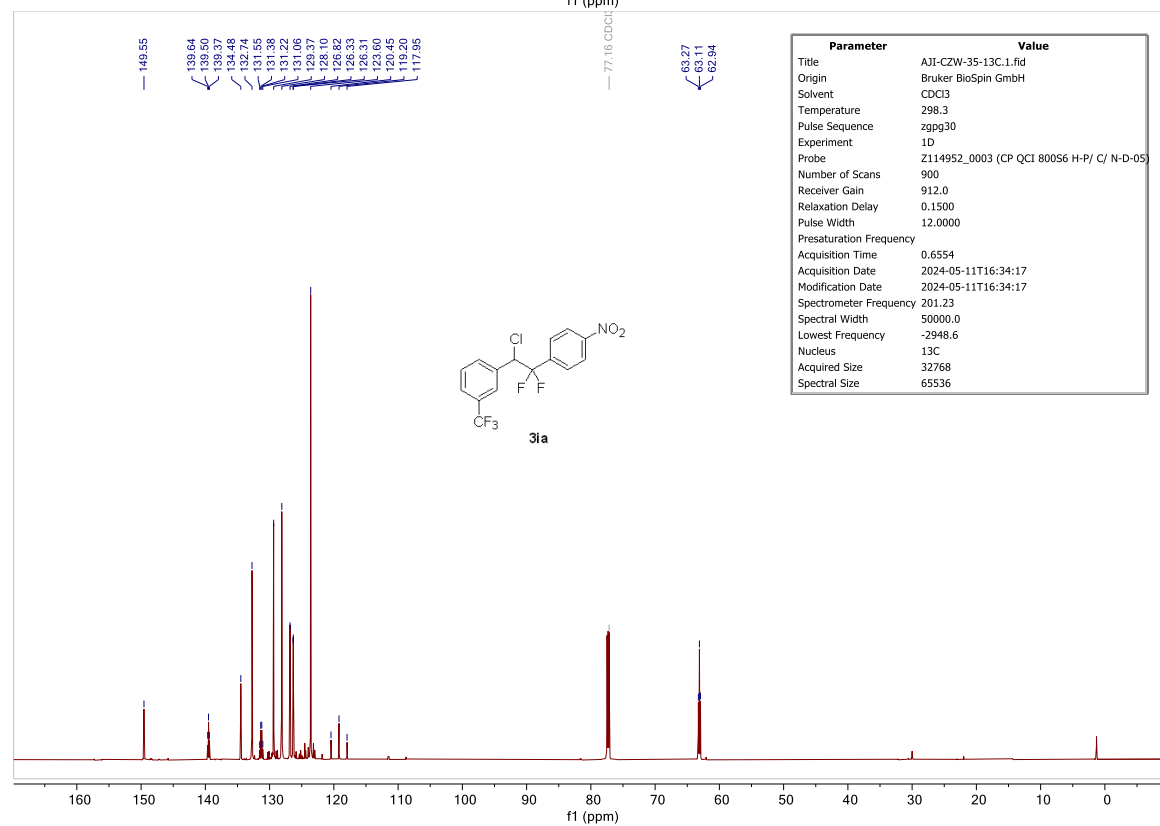
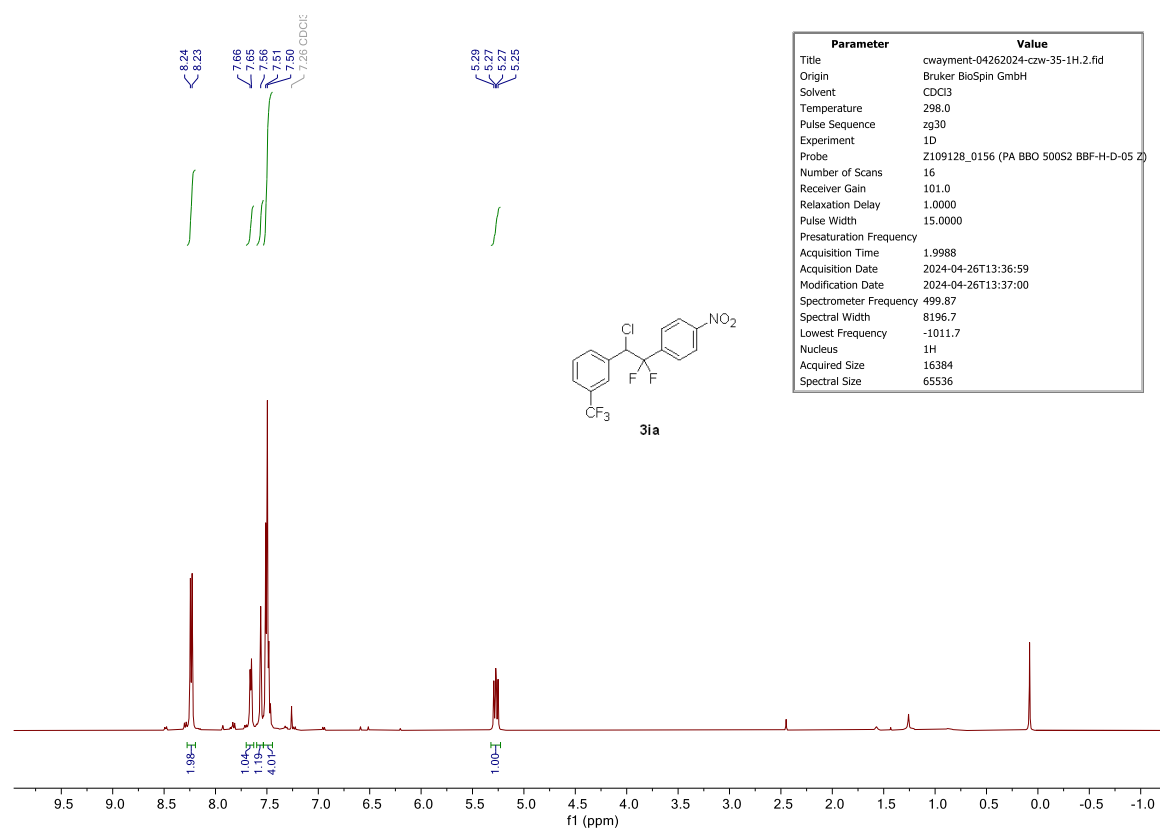


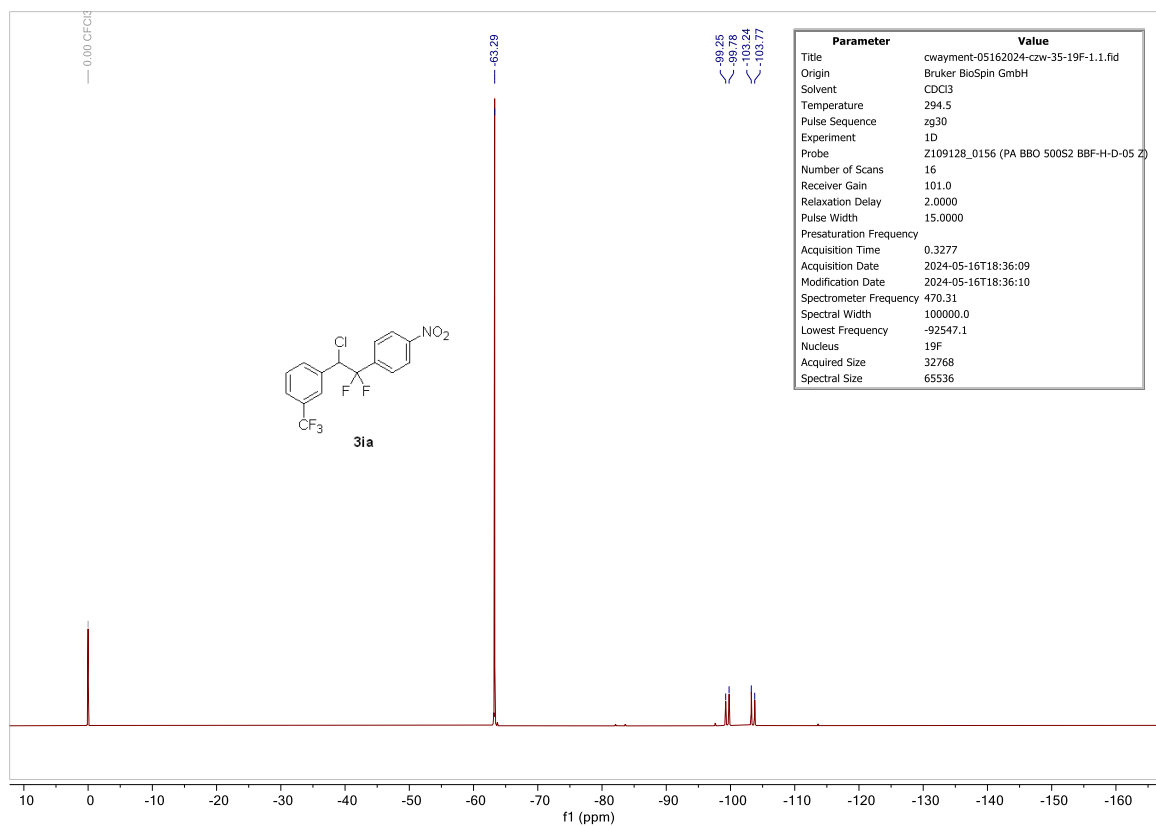
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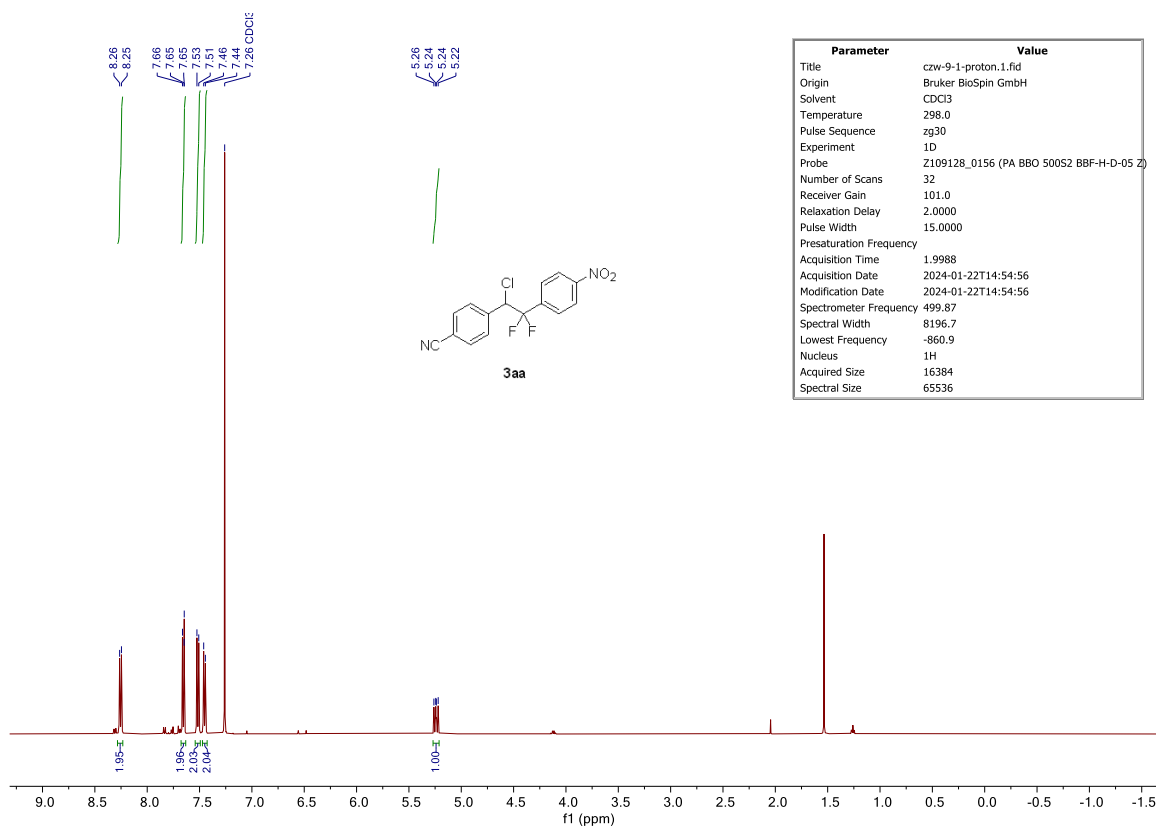


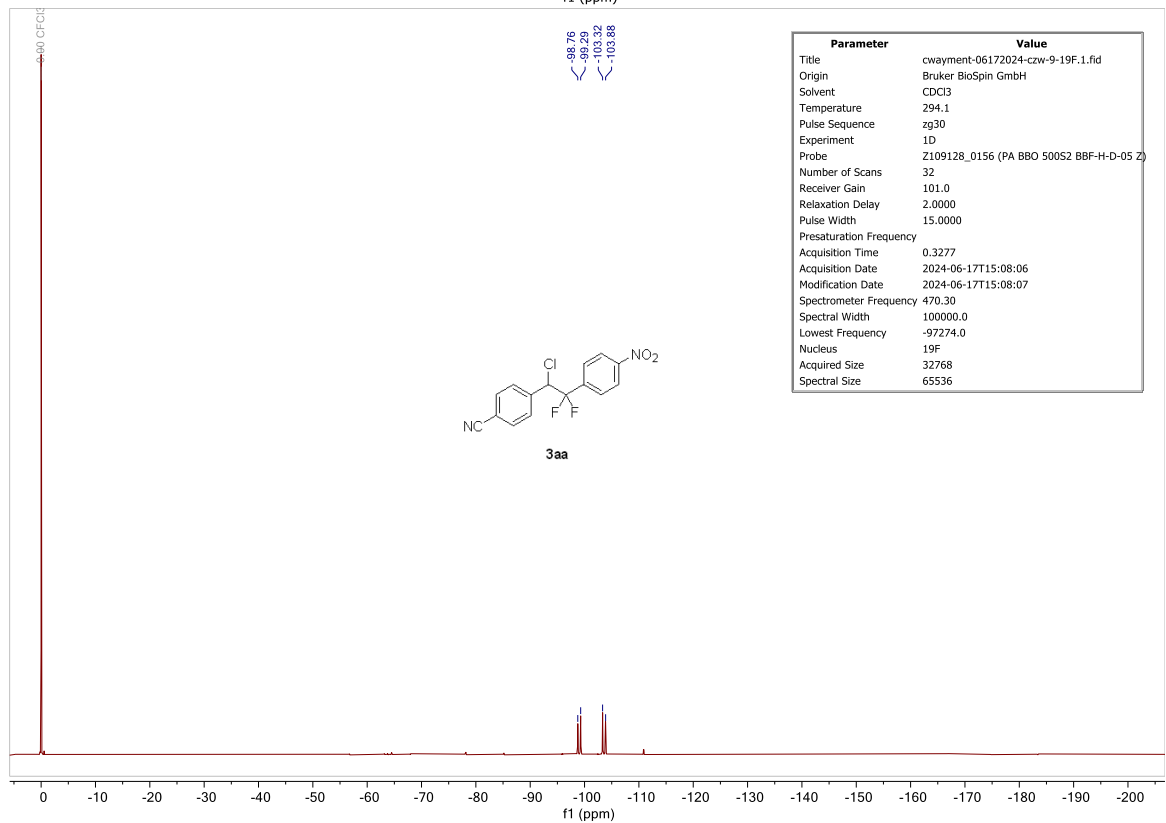
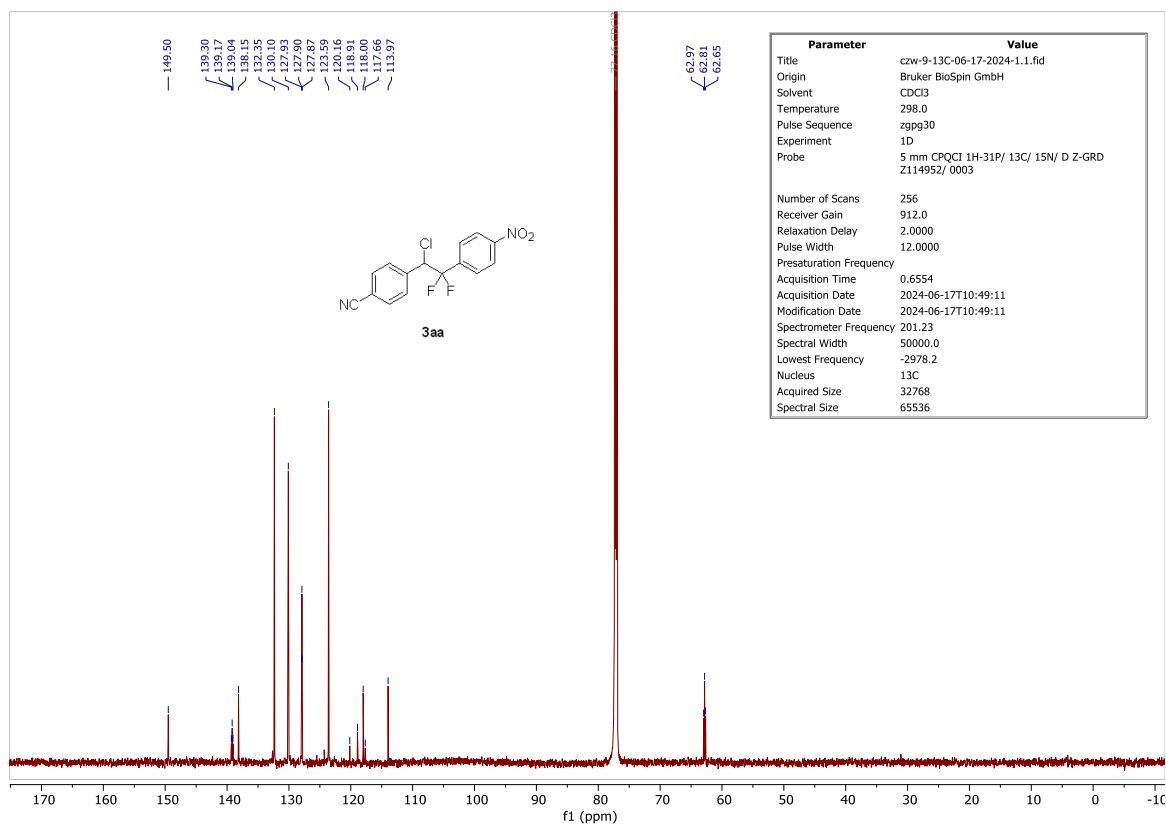
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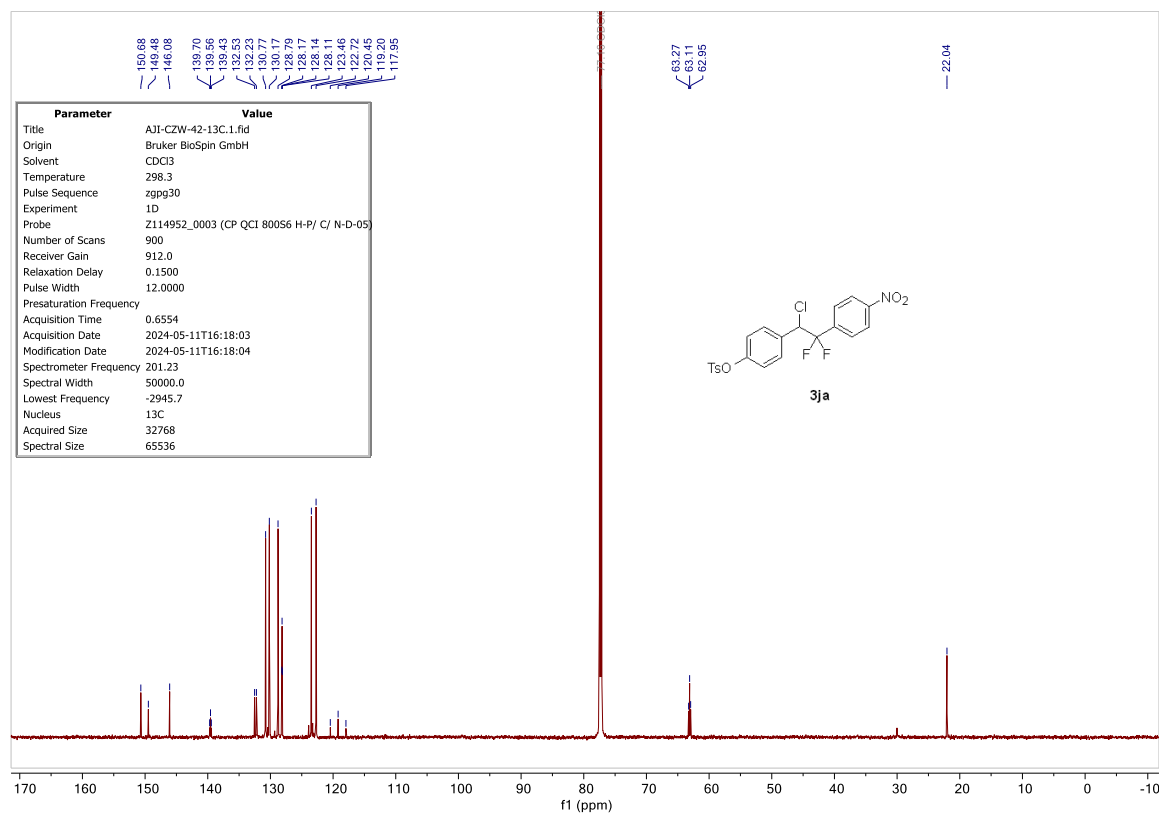
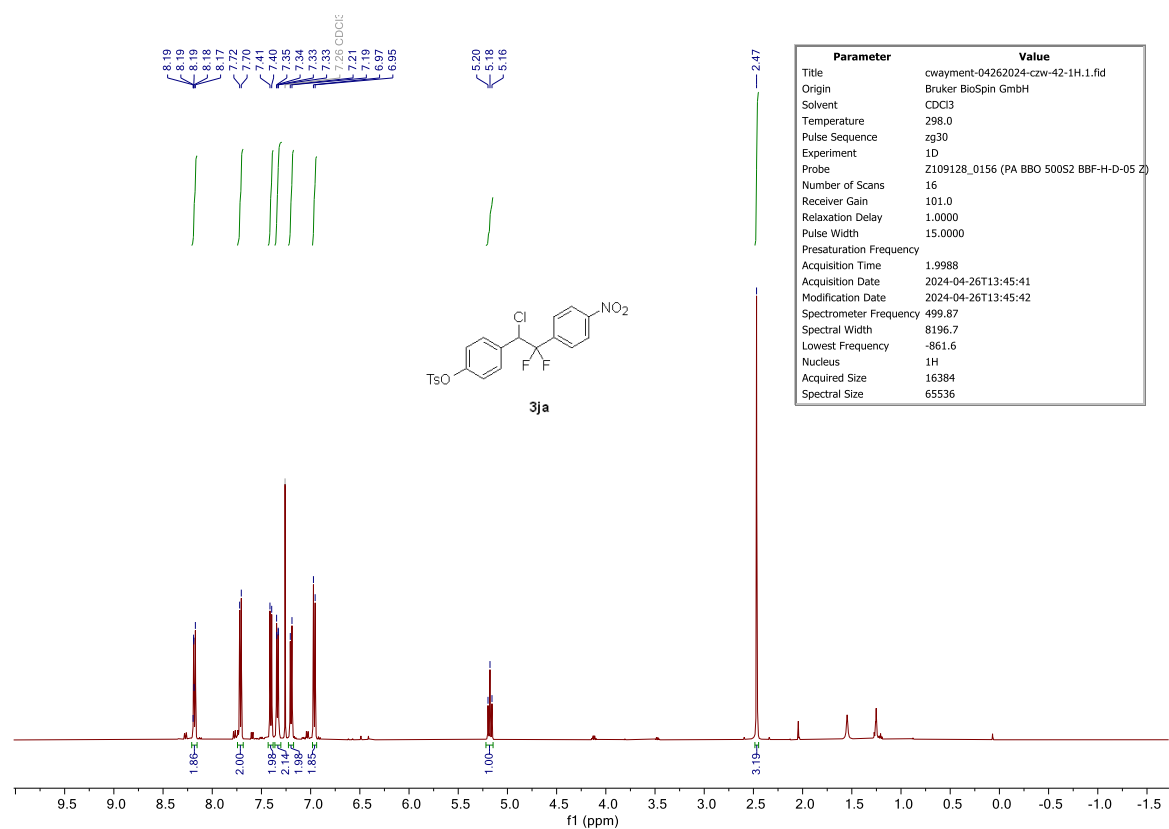


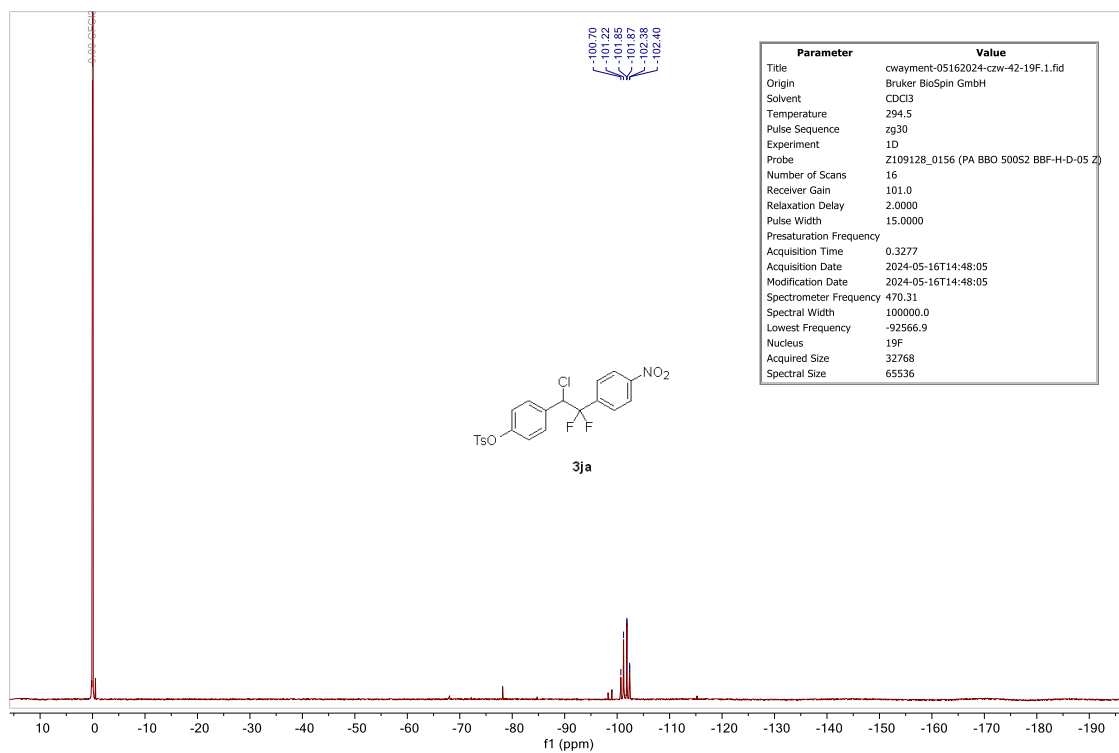
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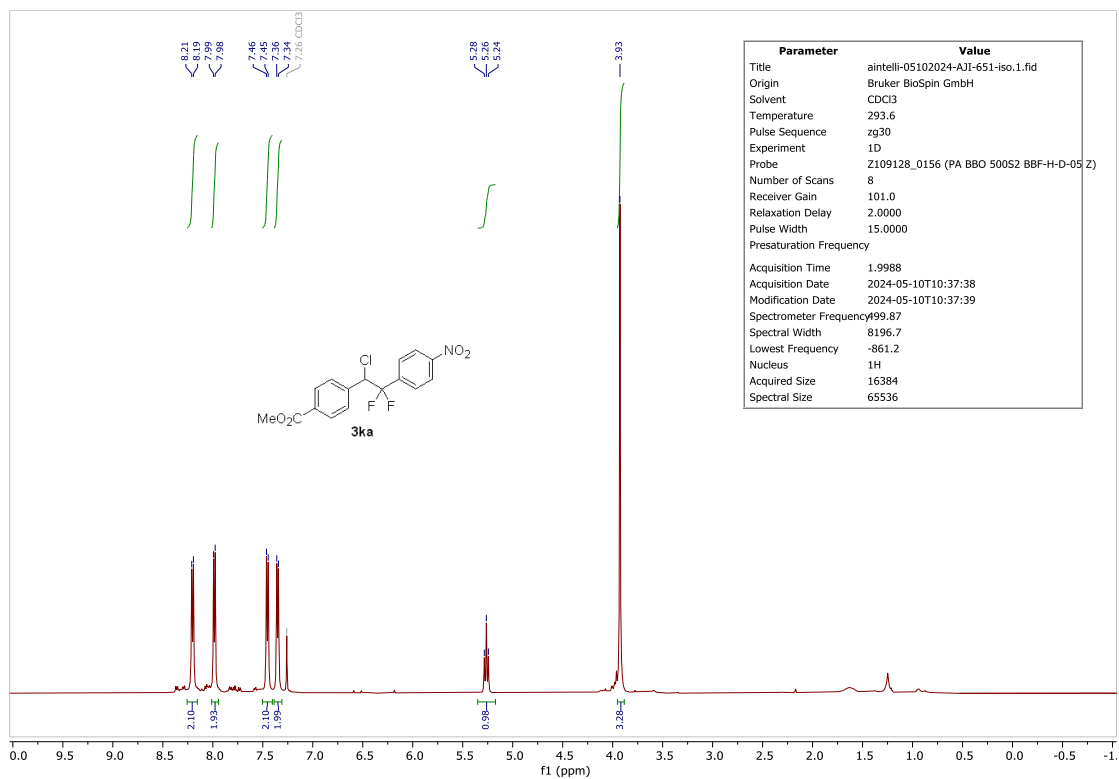


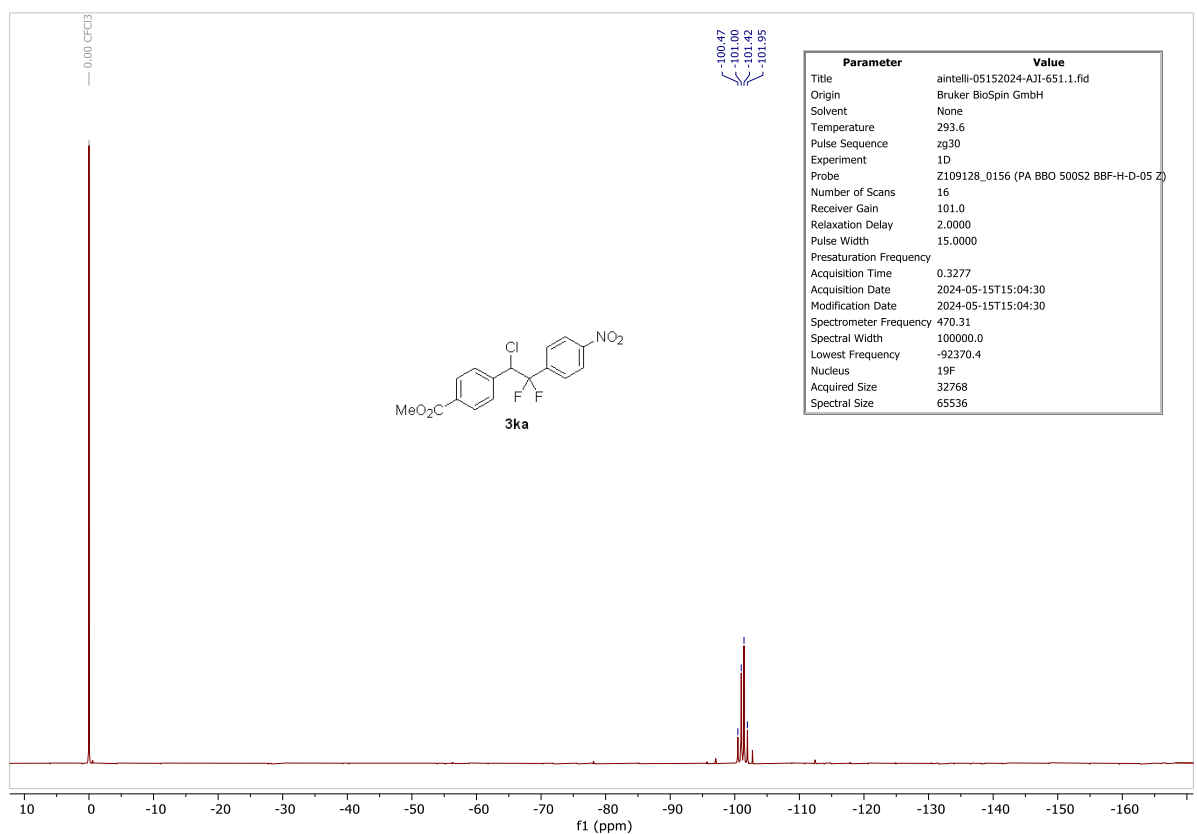
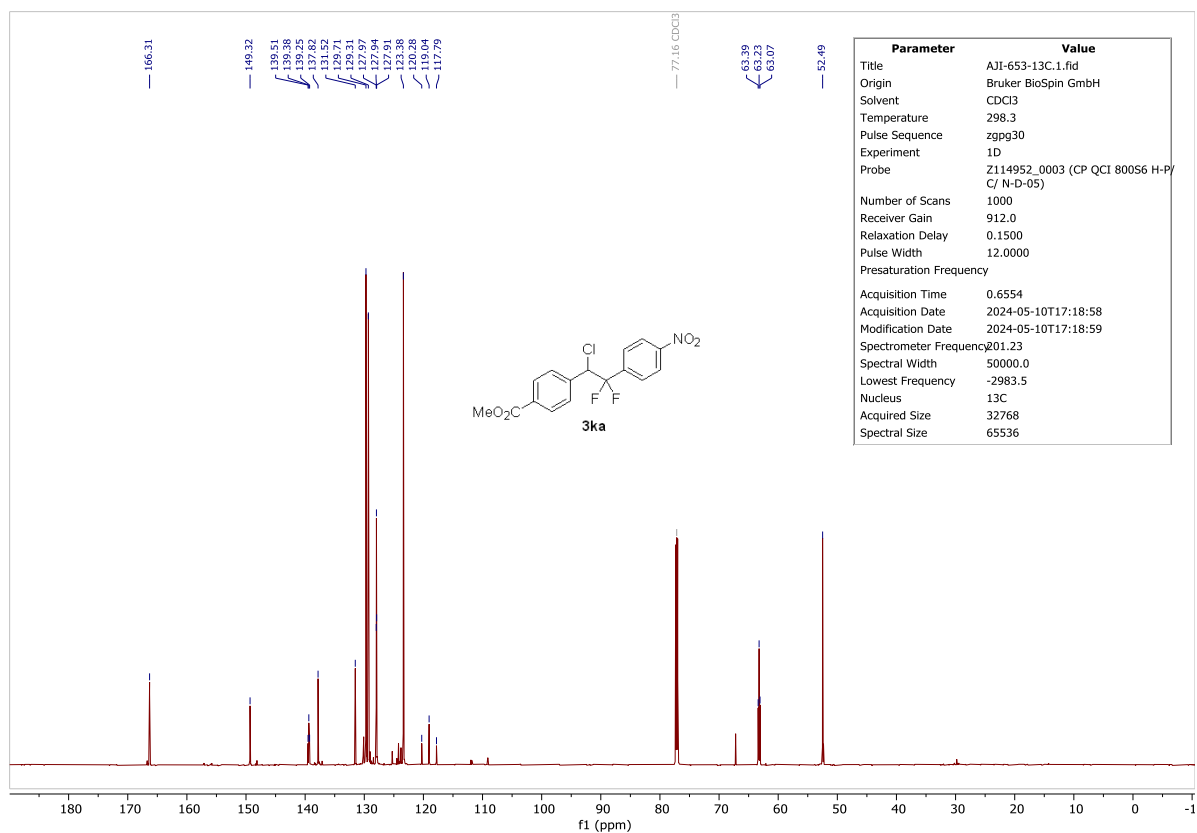
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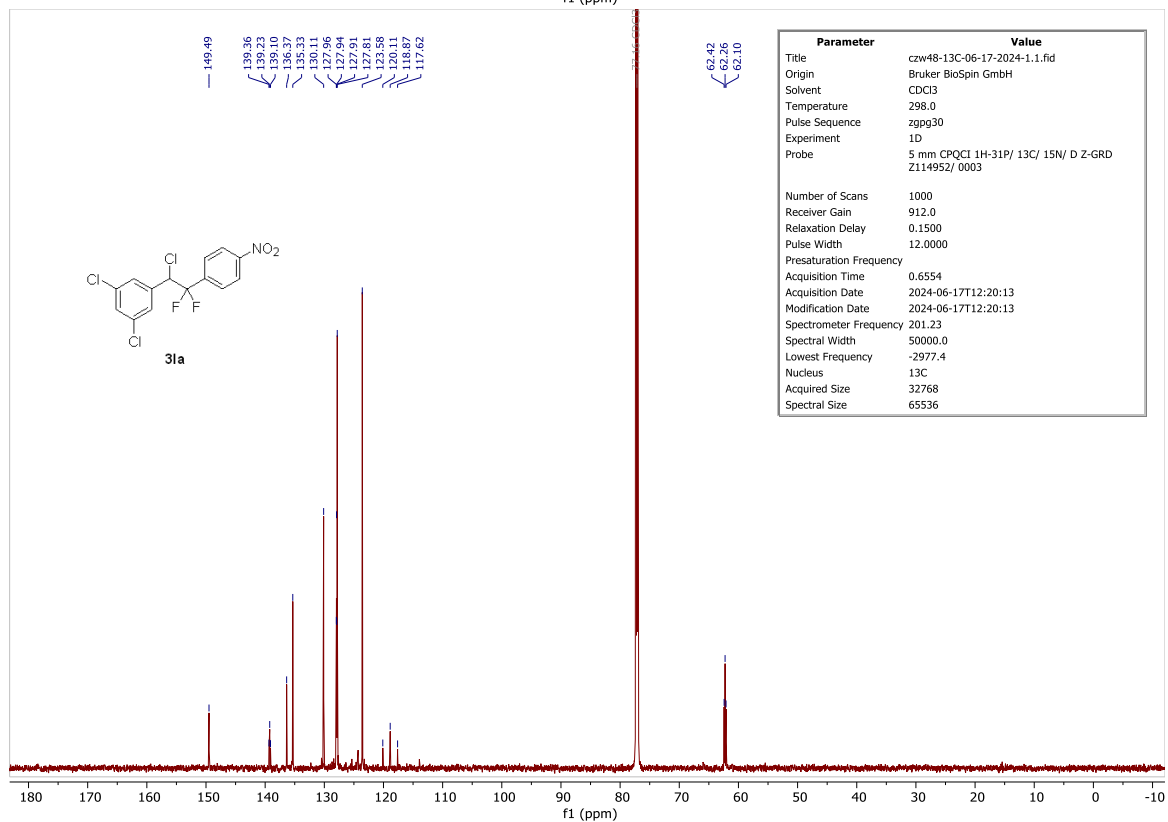
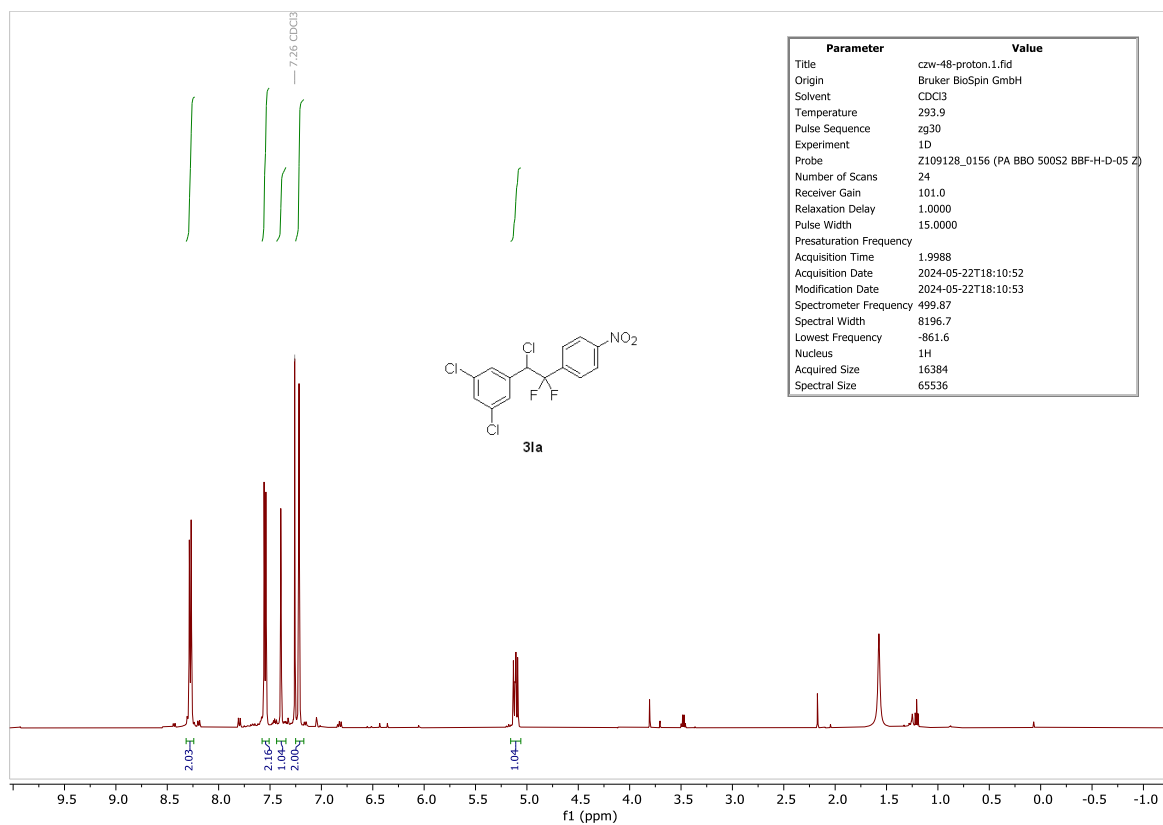


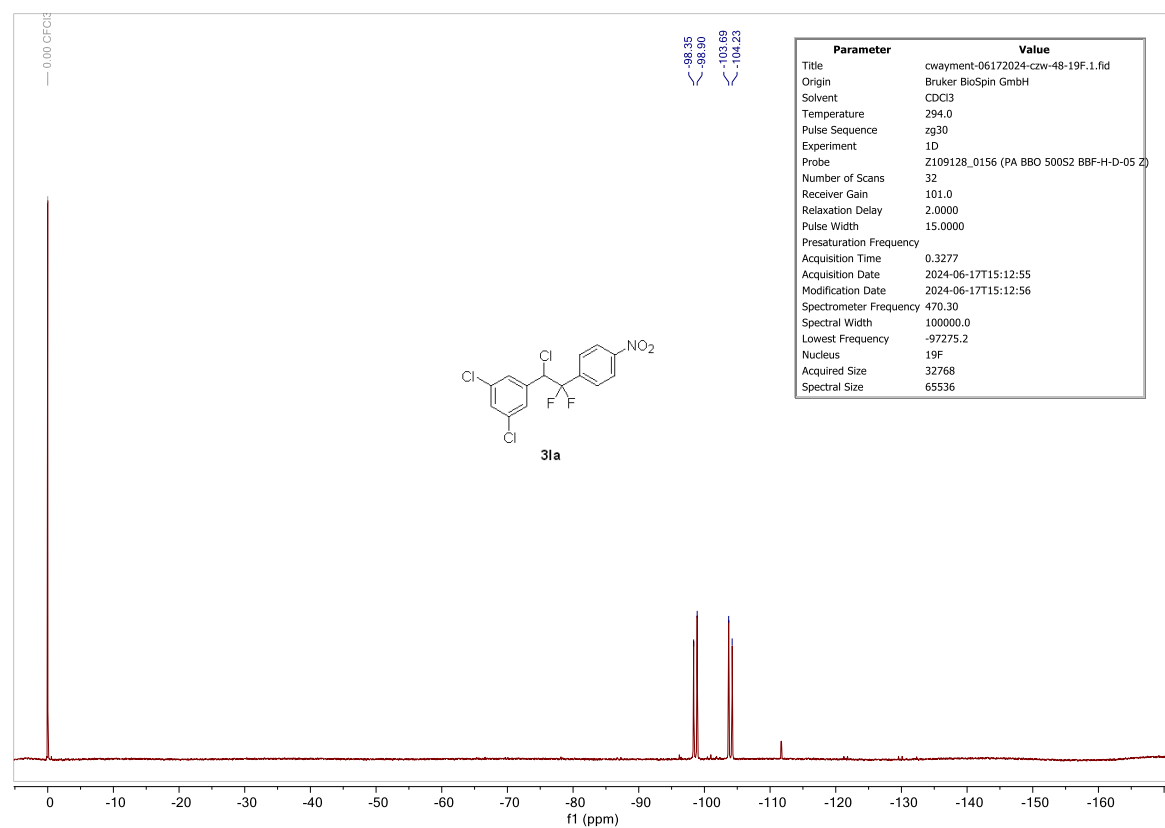
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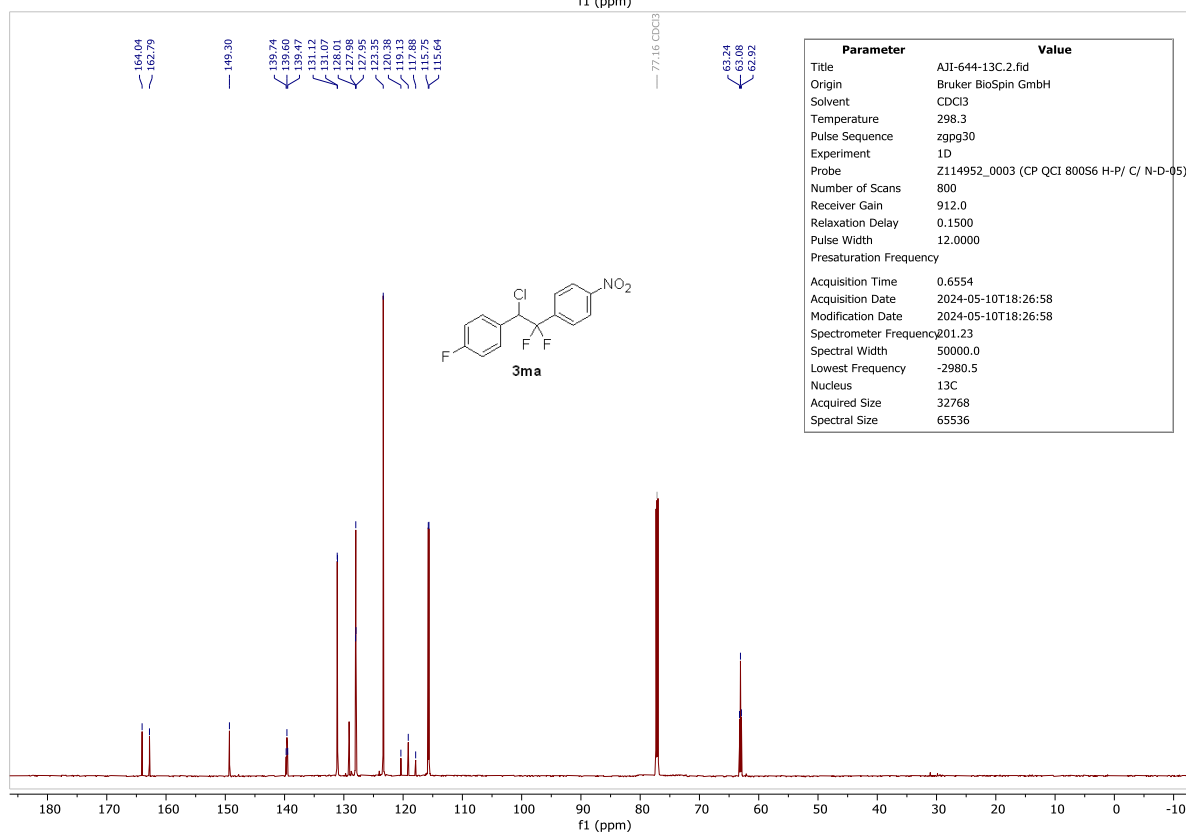
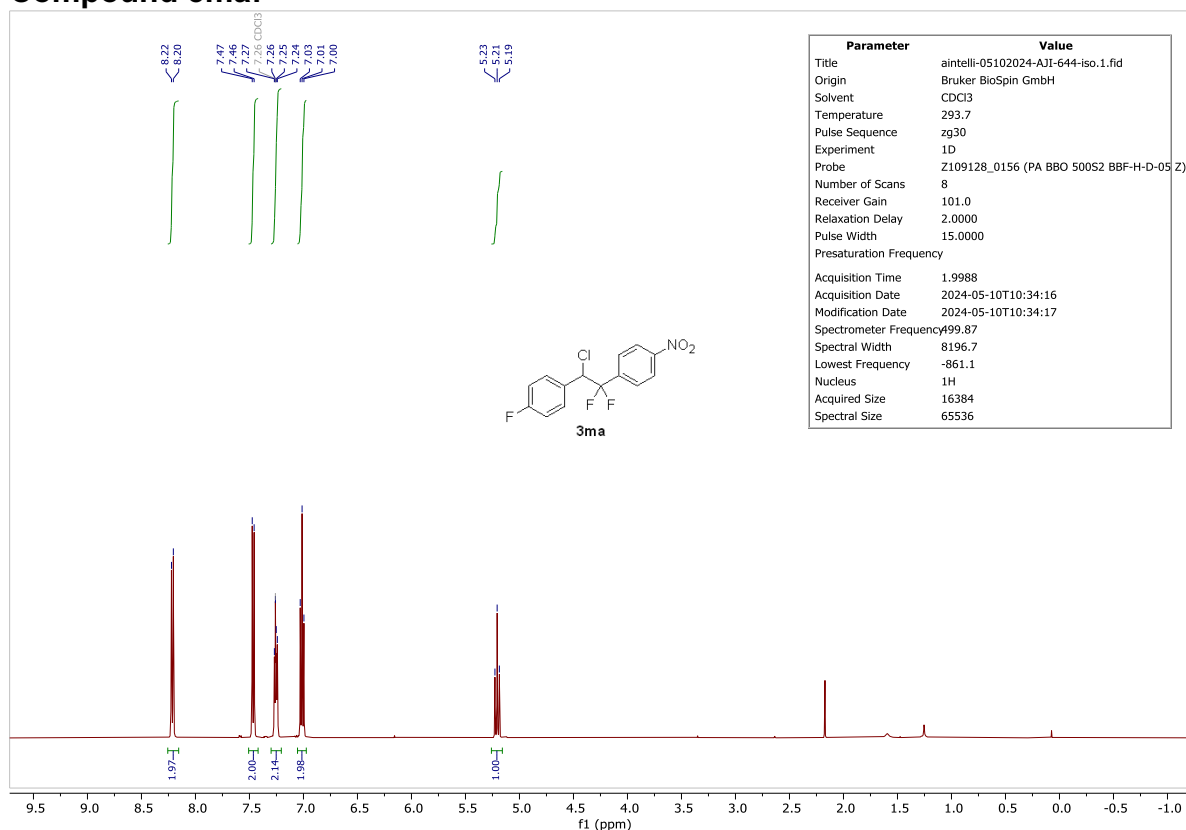


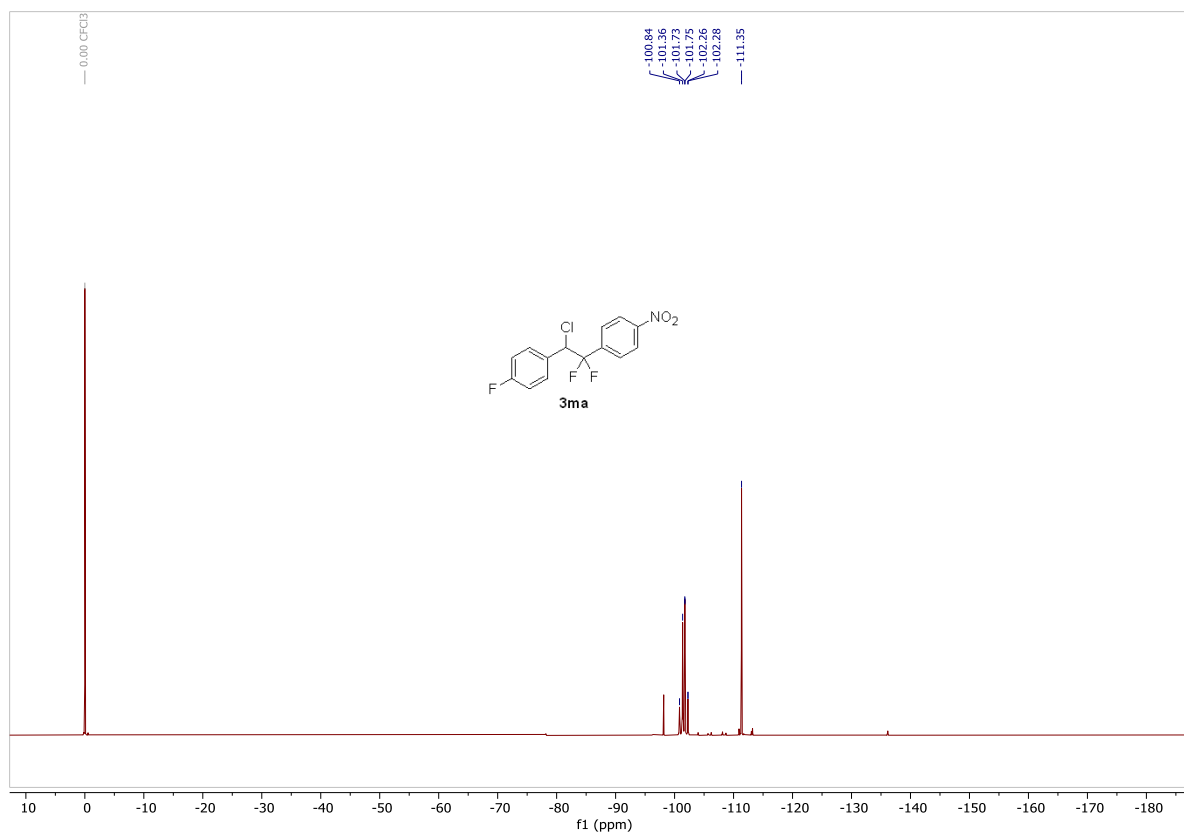
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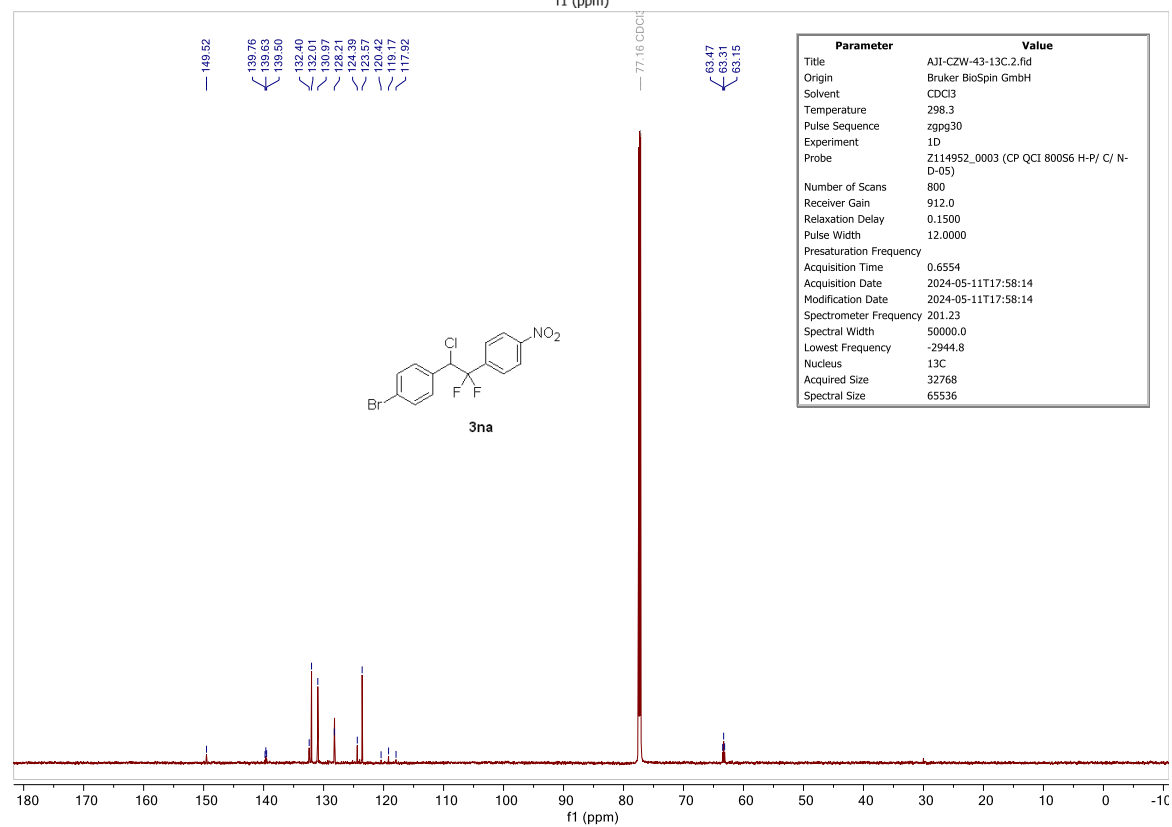
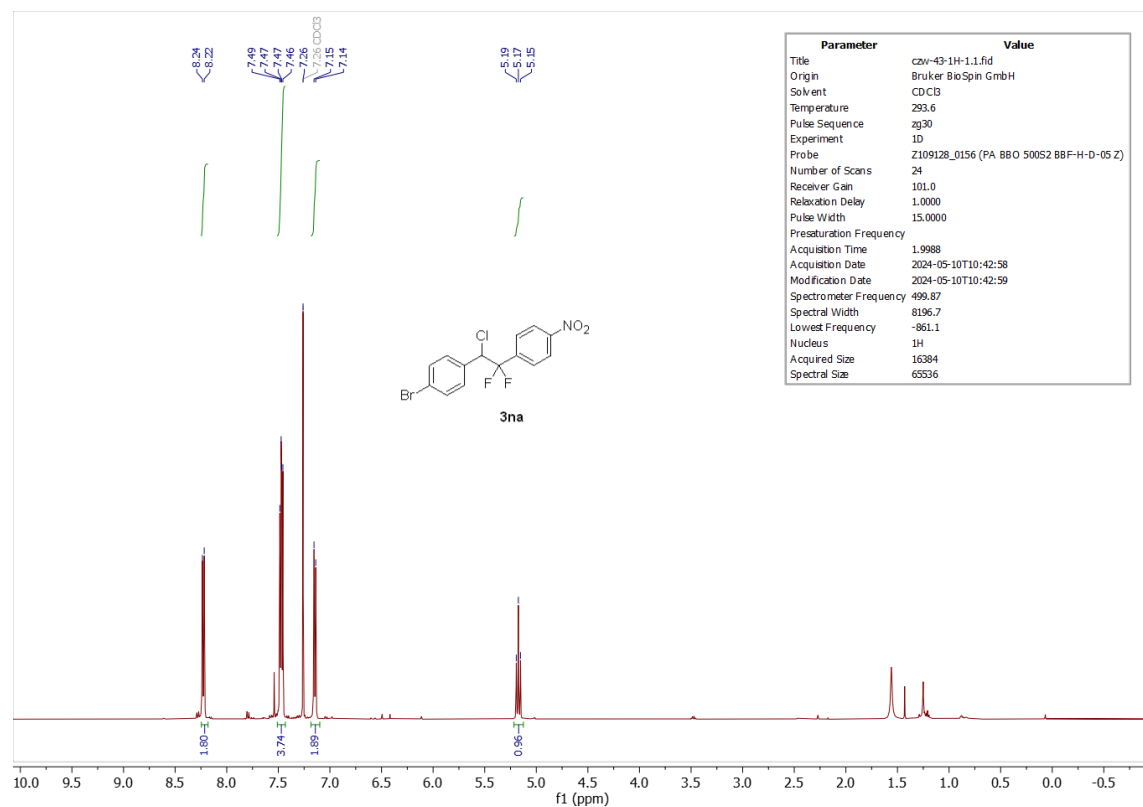


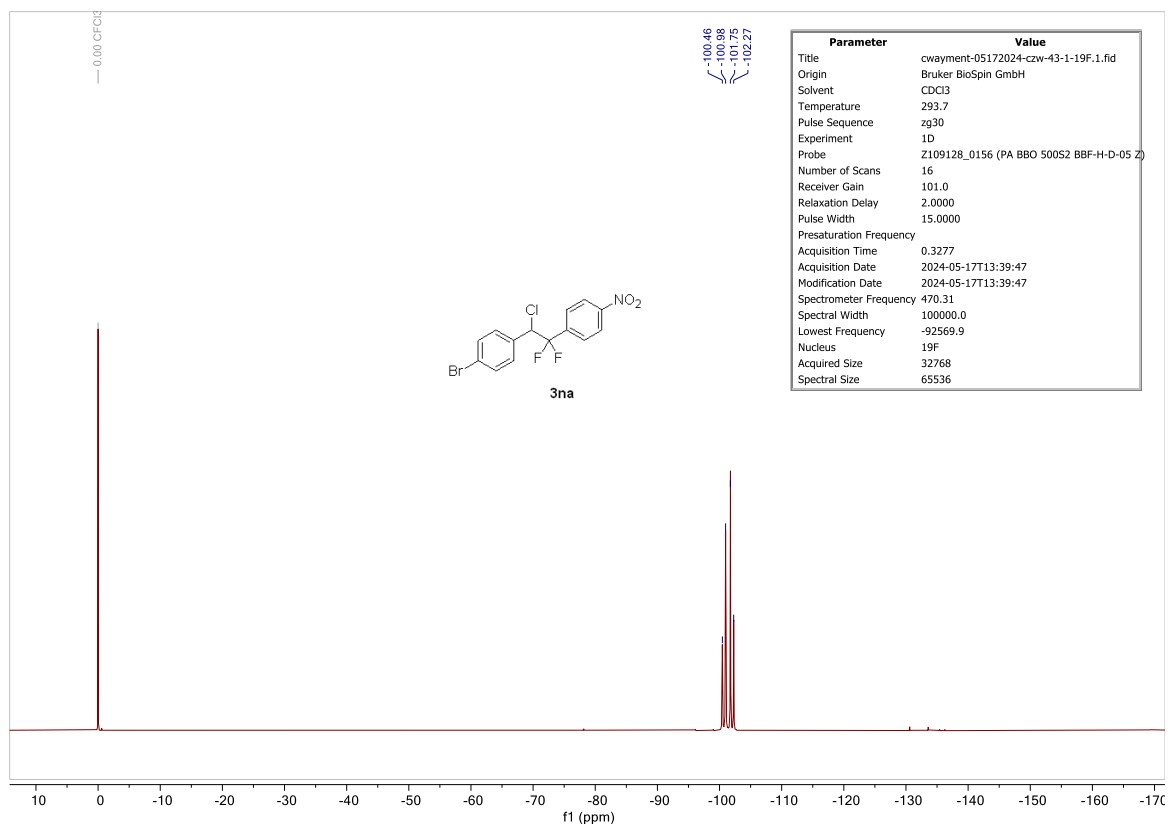
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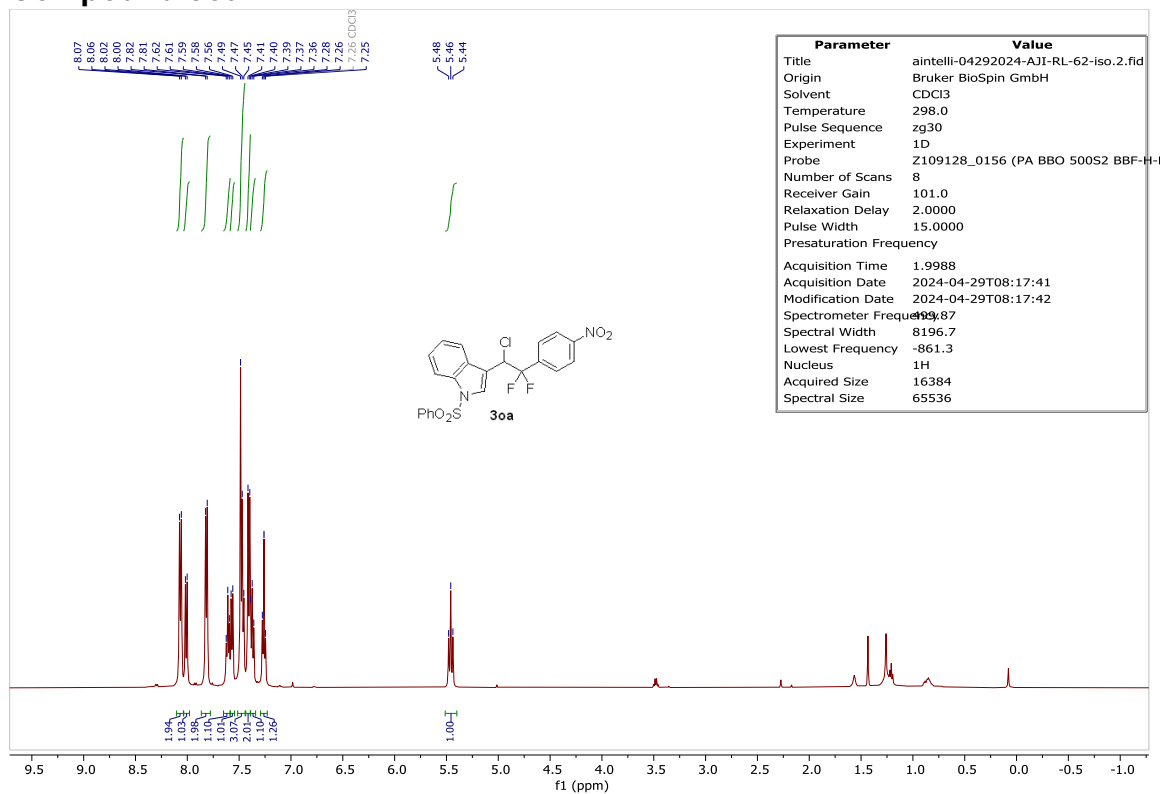


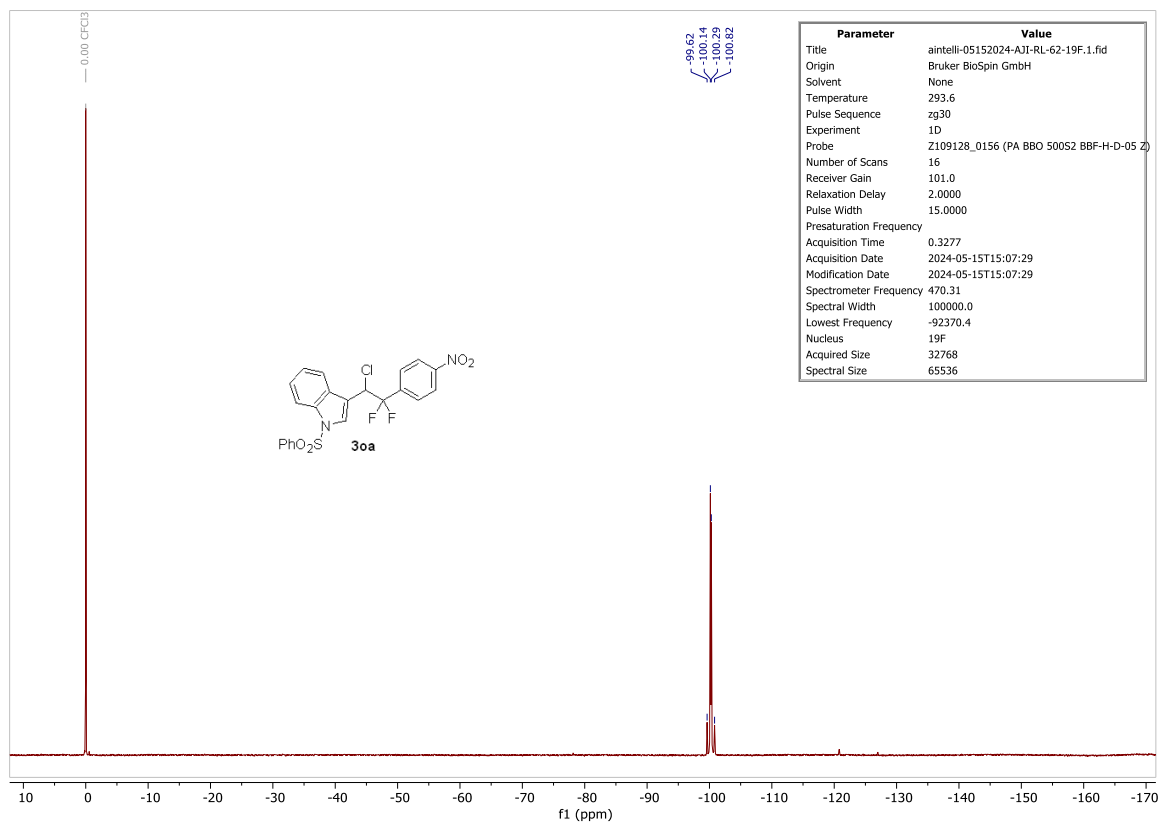
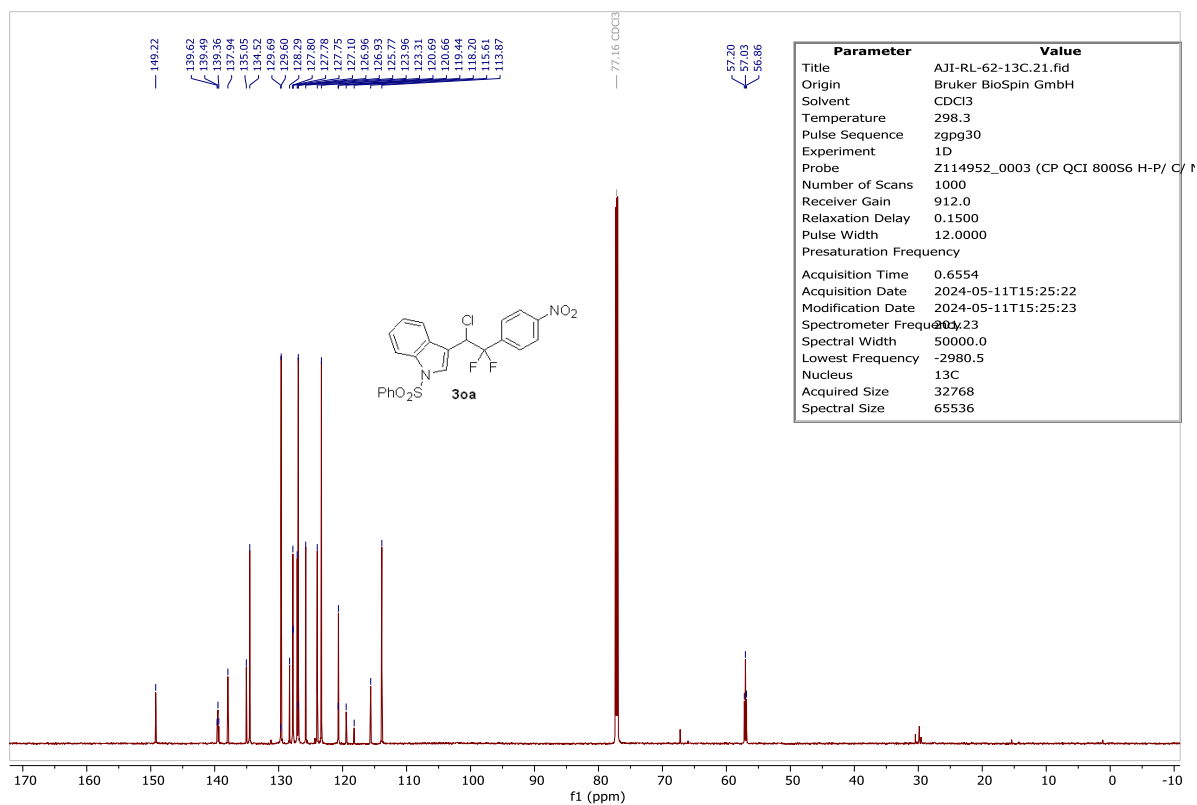
Compound 3na:





Compound 3oa:

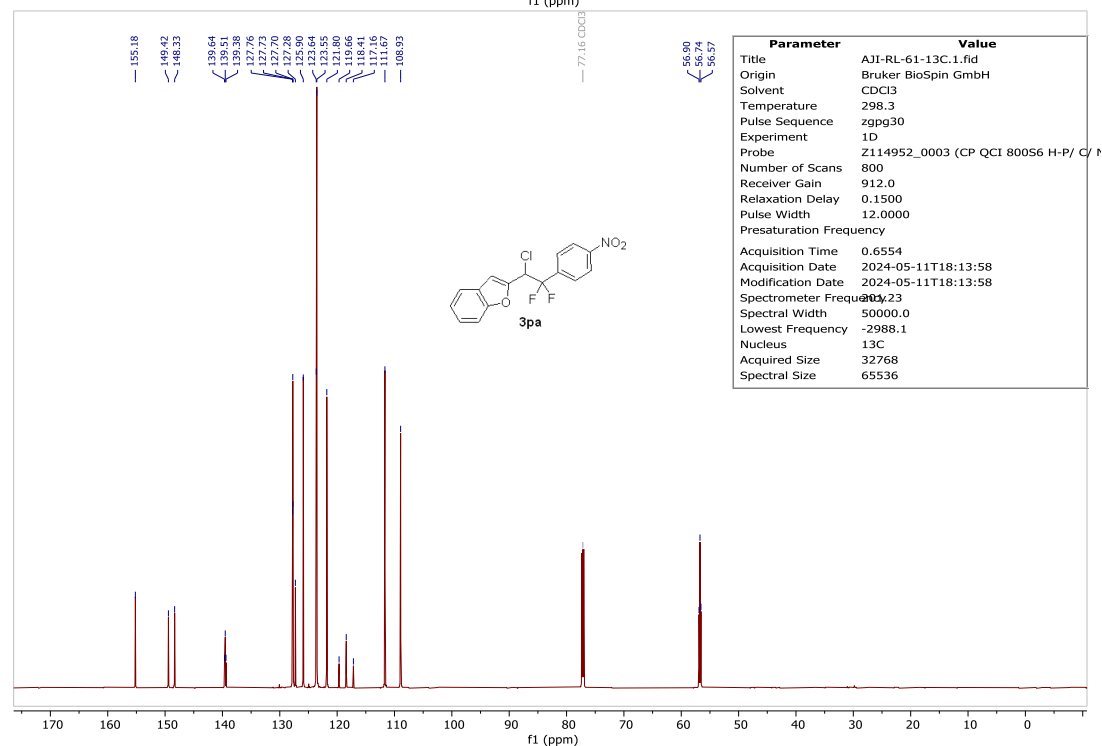


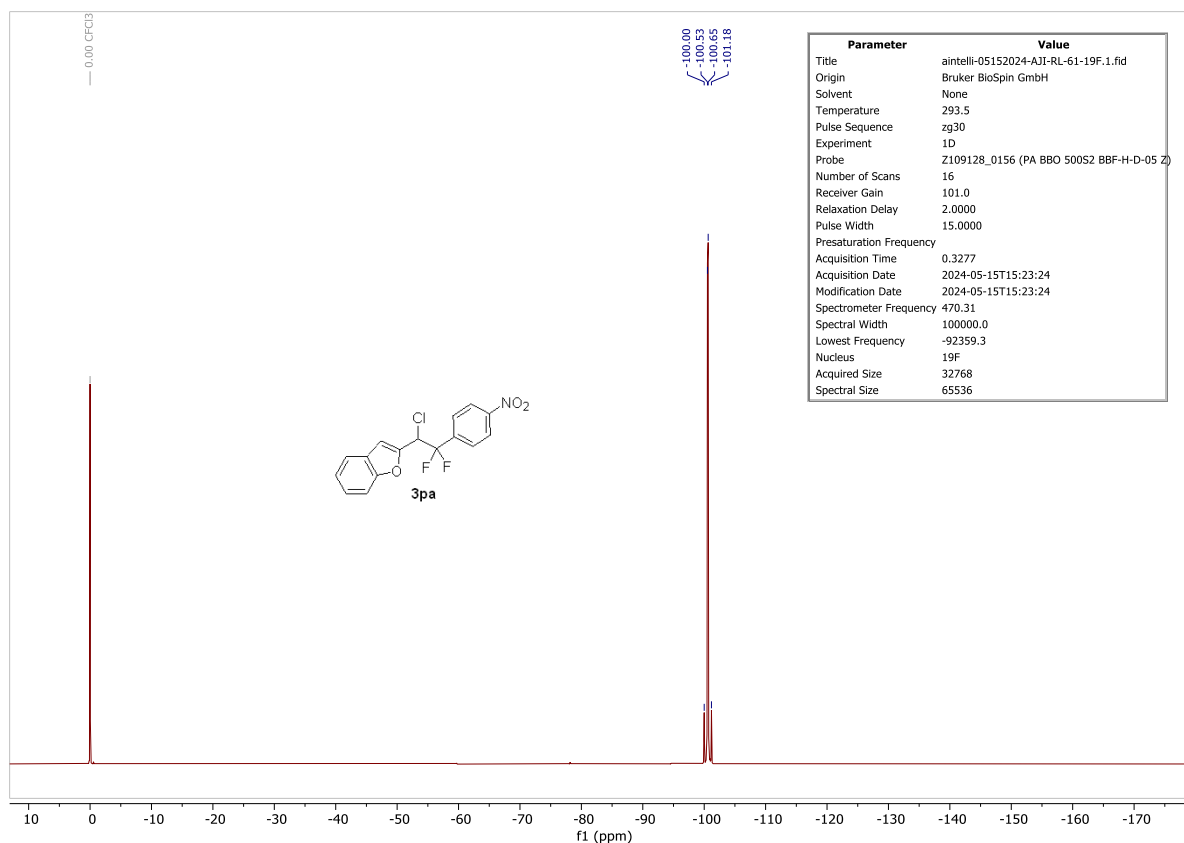


Chemical Structure of 3pa: c1ccc(cc1C2=CC=CC=C2O2)C(Cl)(F)Fc3ccc(cc3)[N+](=O)[O-]

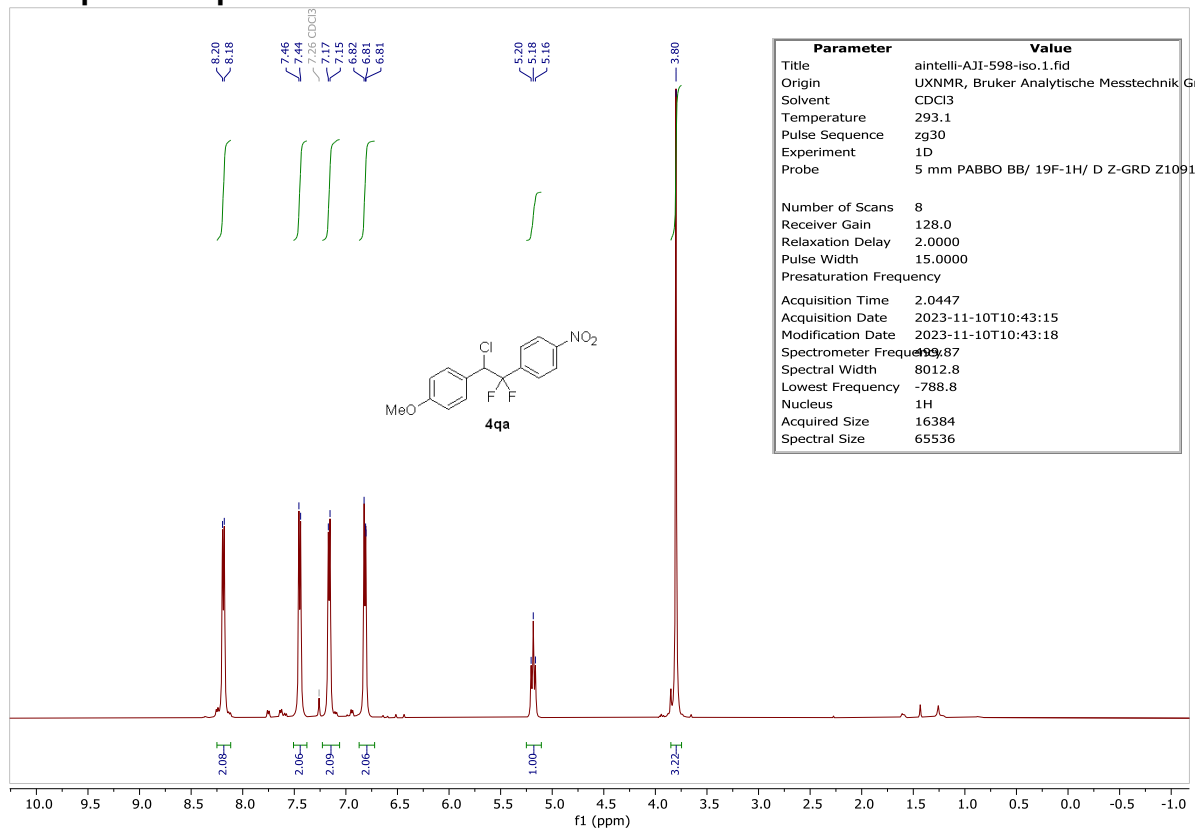
1H NMR Spectrum (CDCl₃):

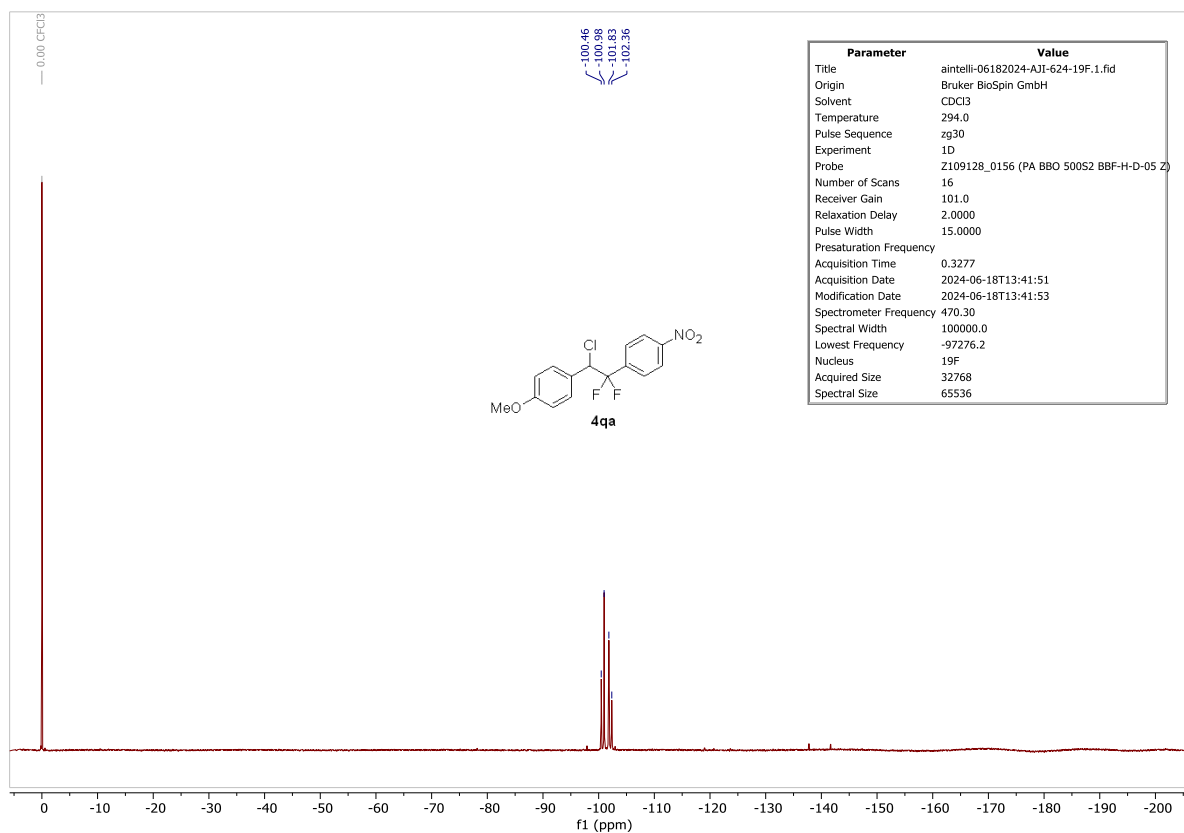
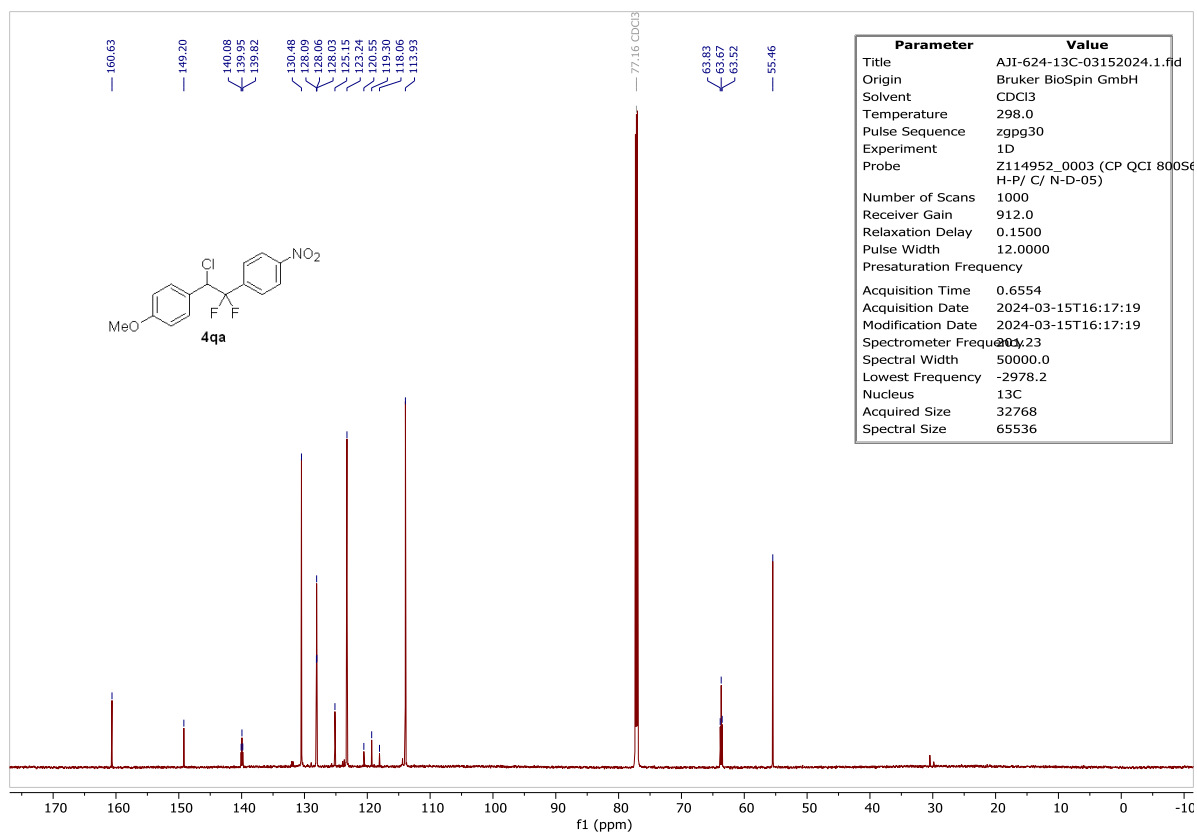
Chemical Shift (ppm)	Integration
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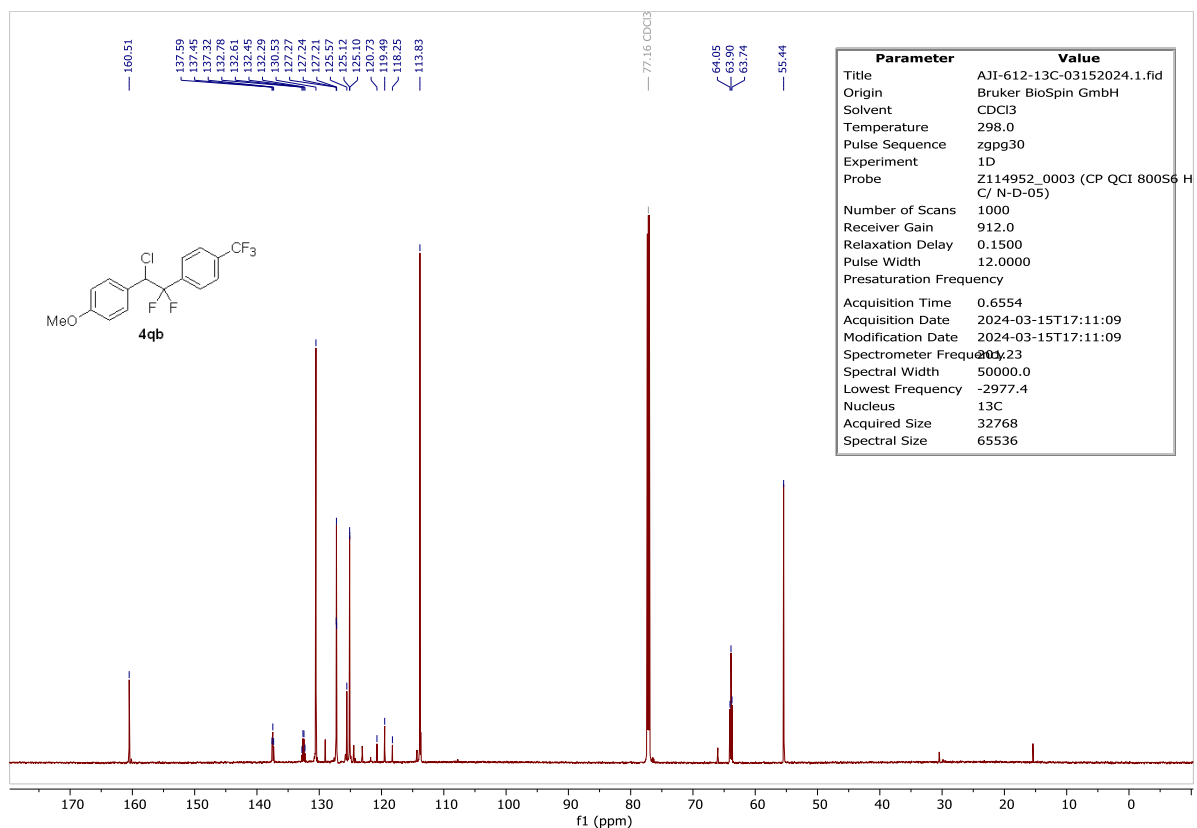
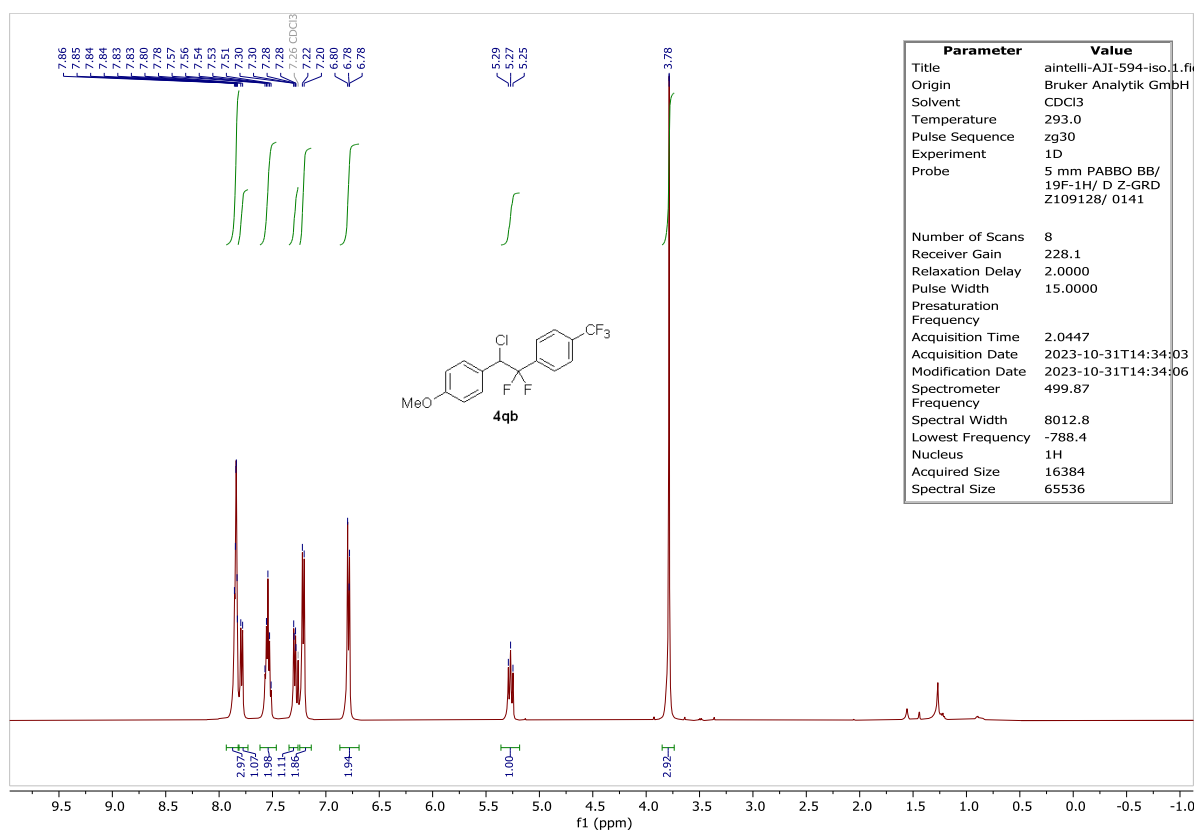


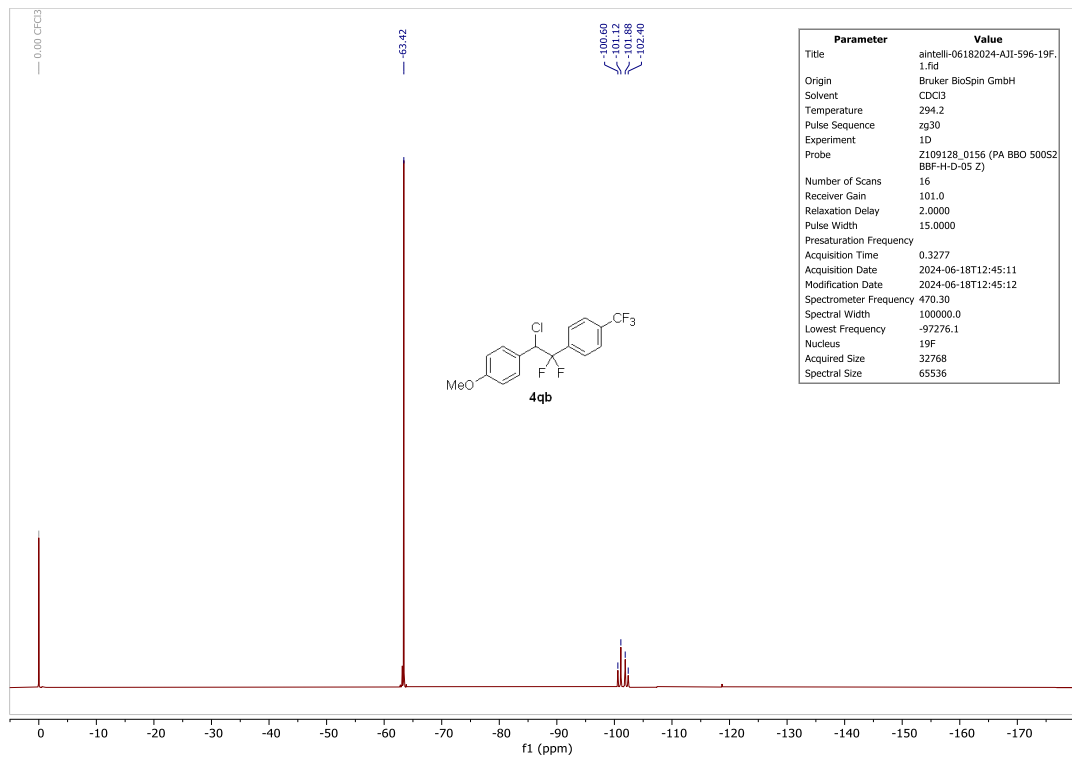
Compound 4qa:



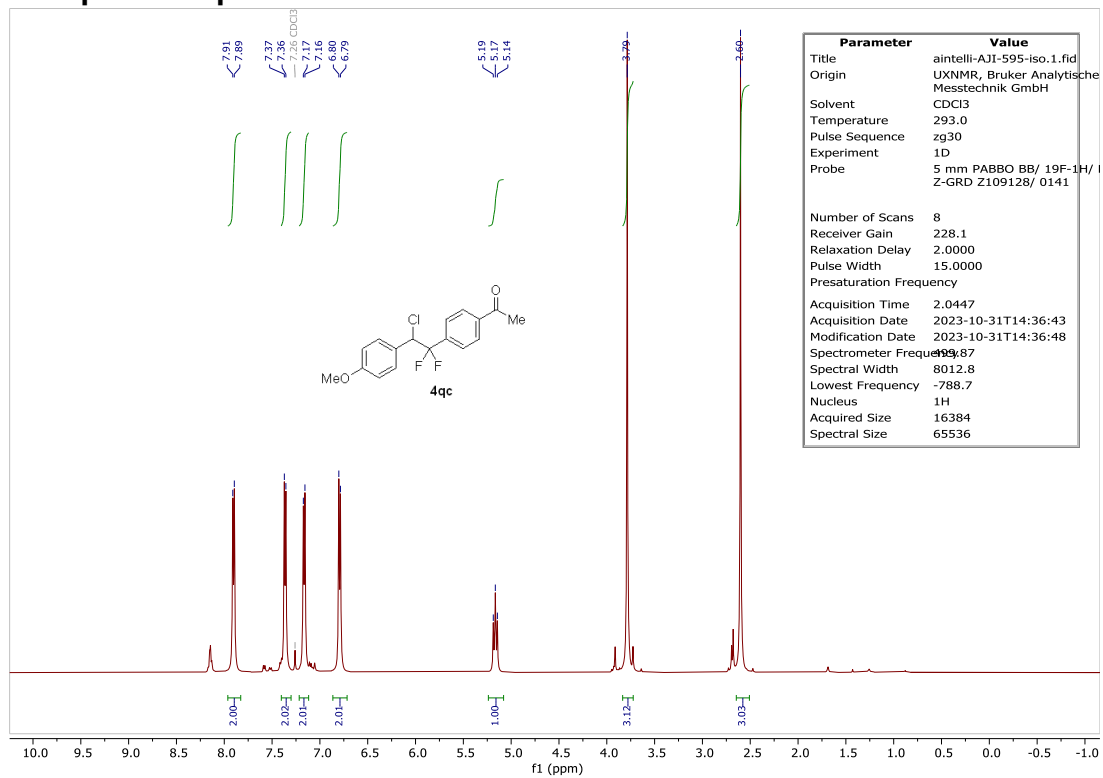


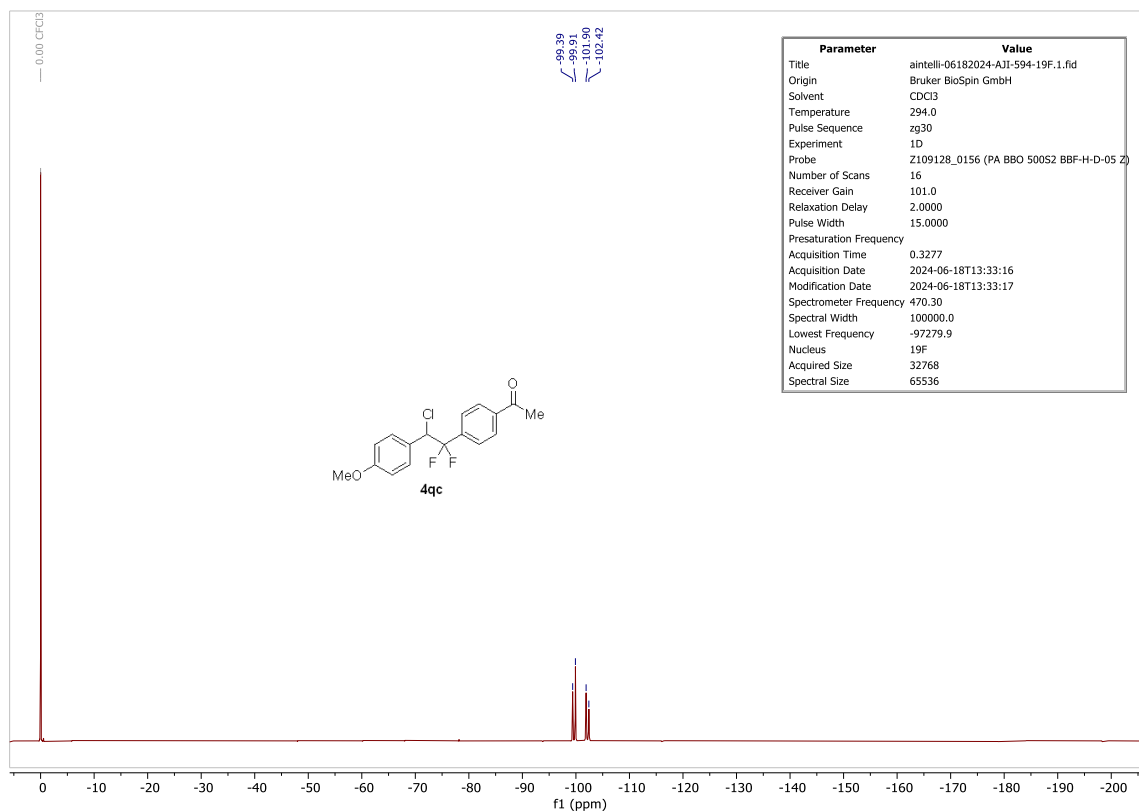
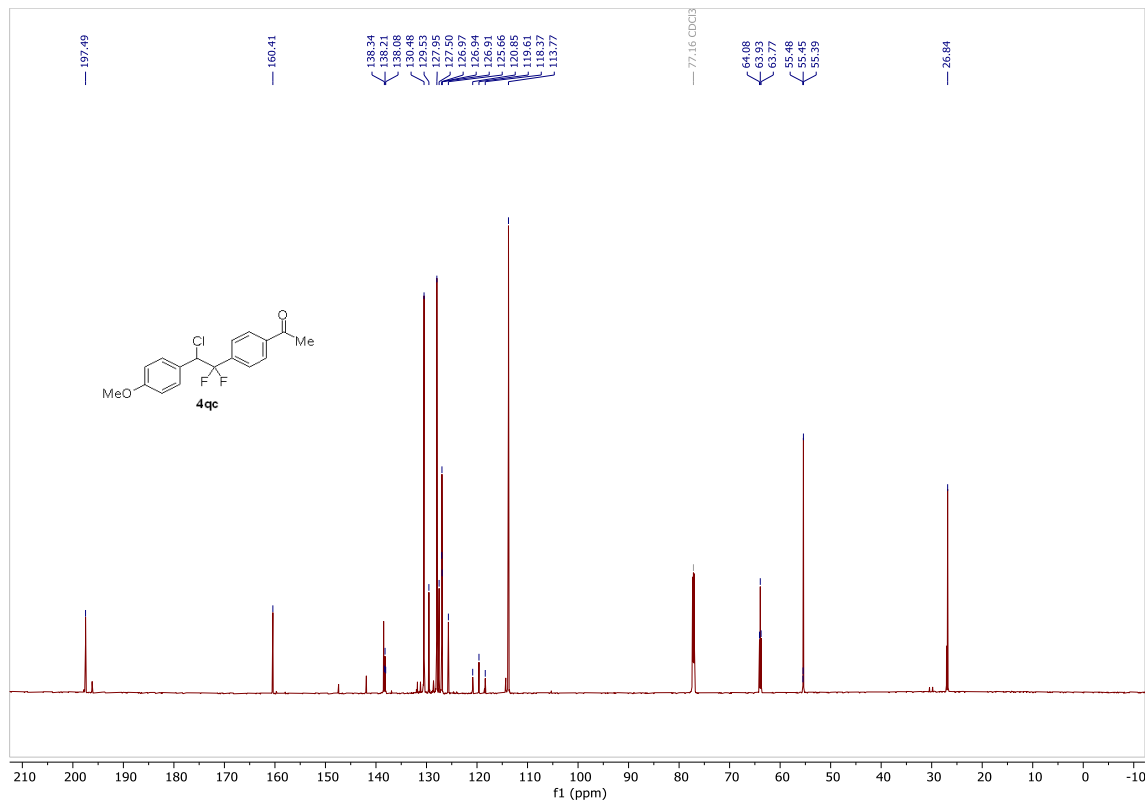
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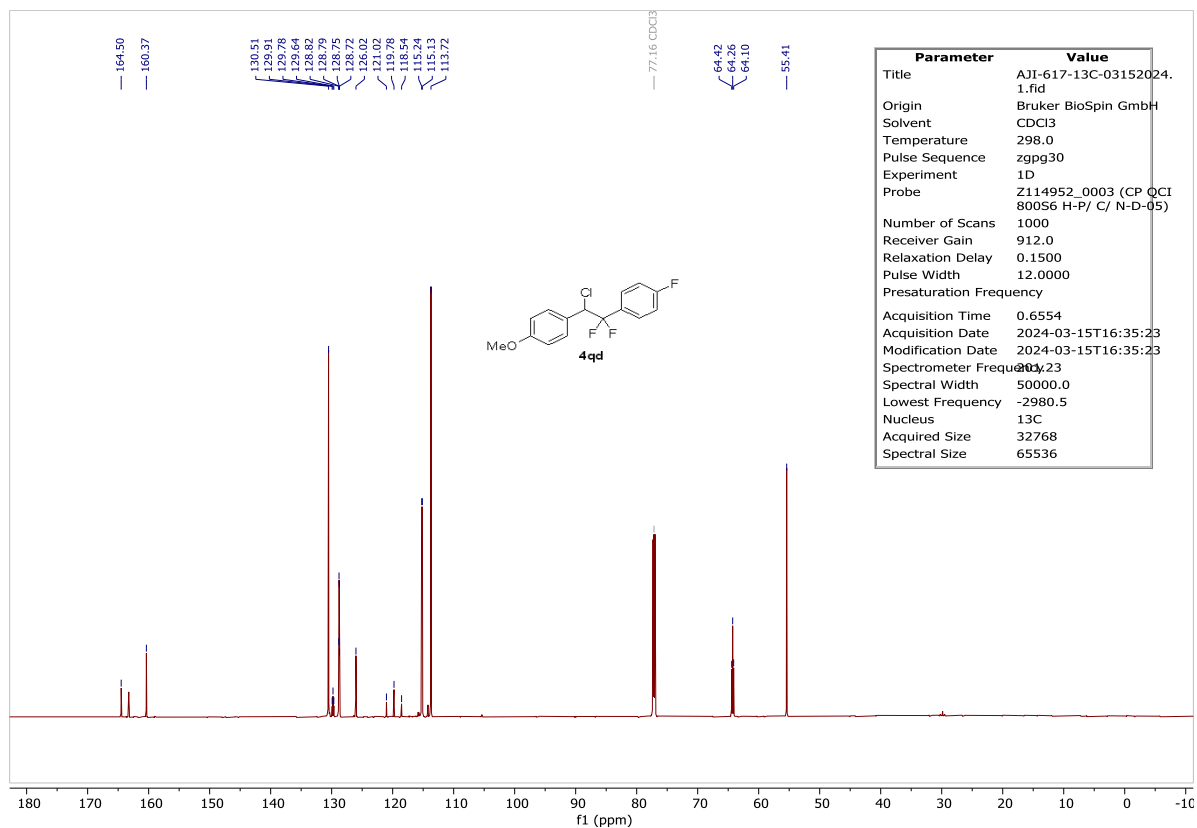
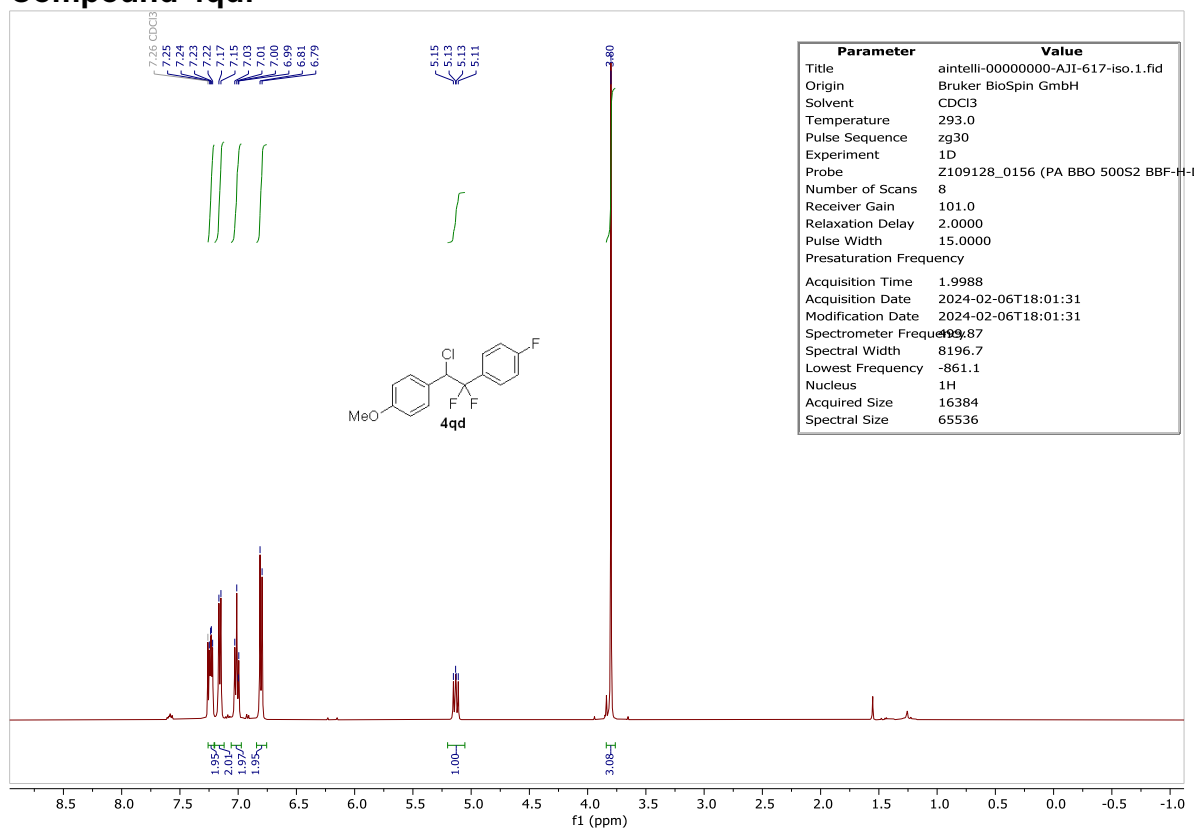


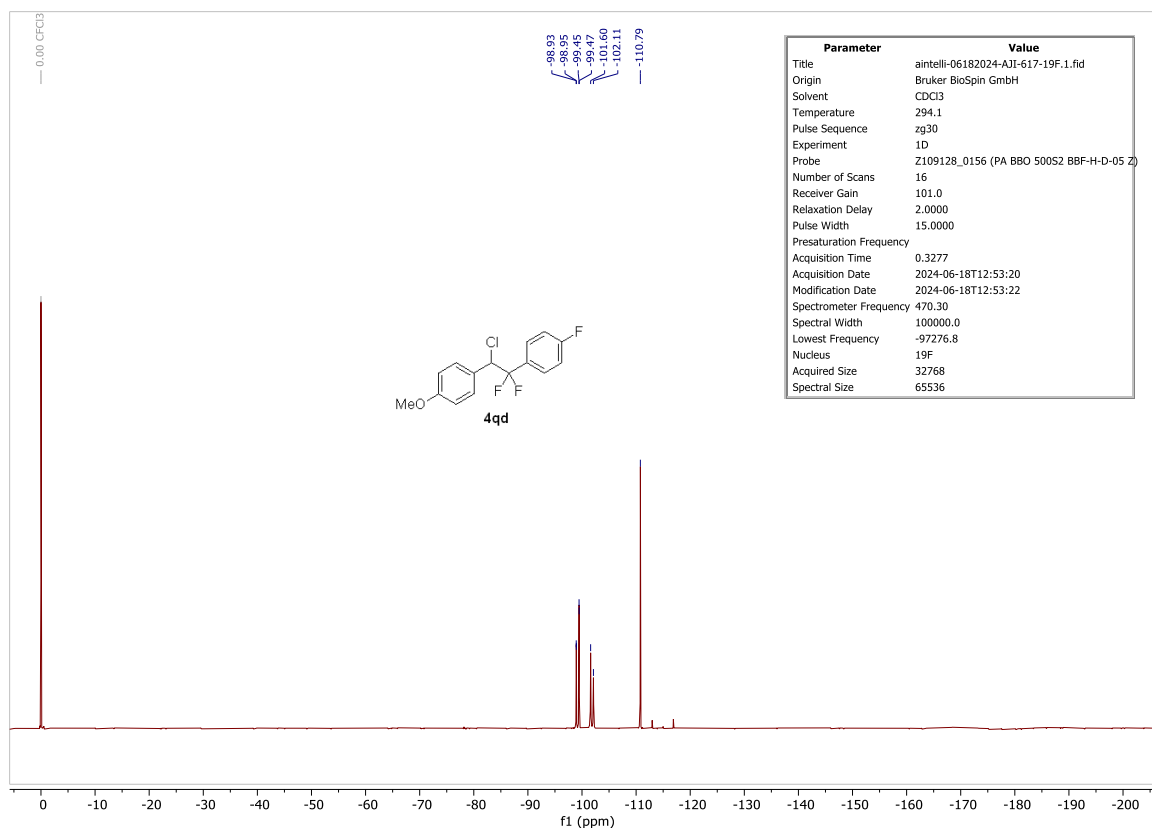
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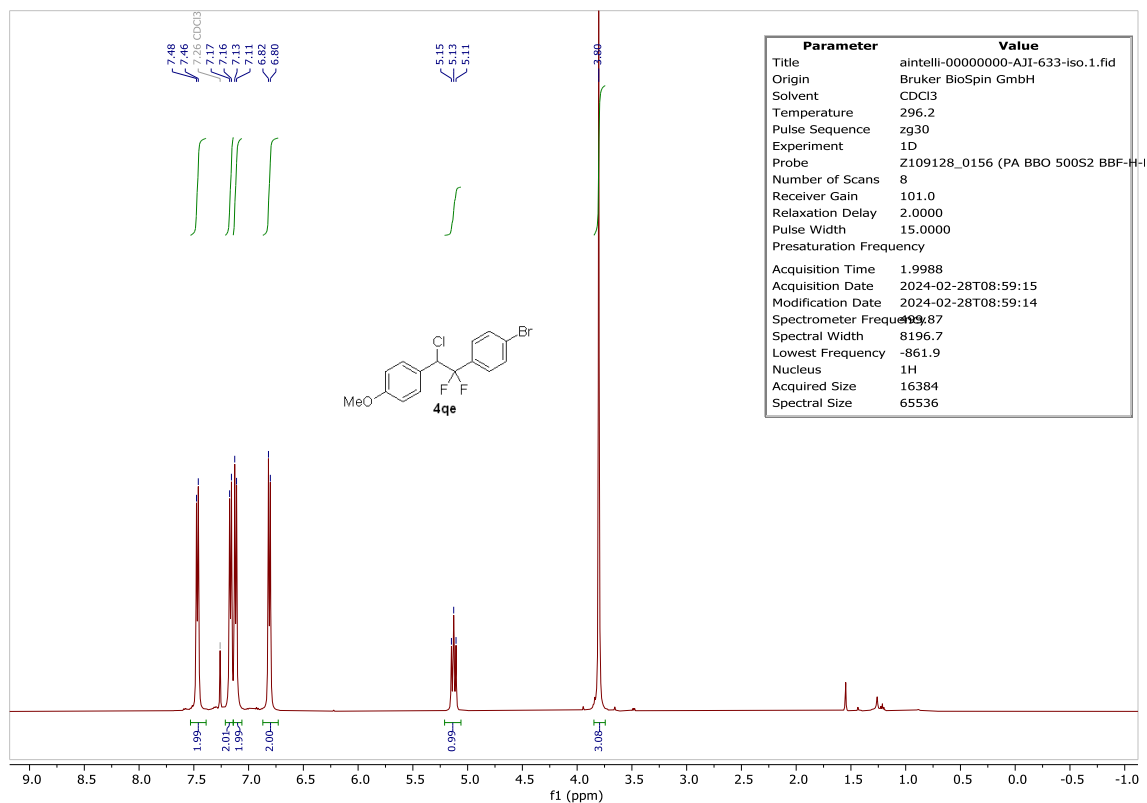


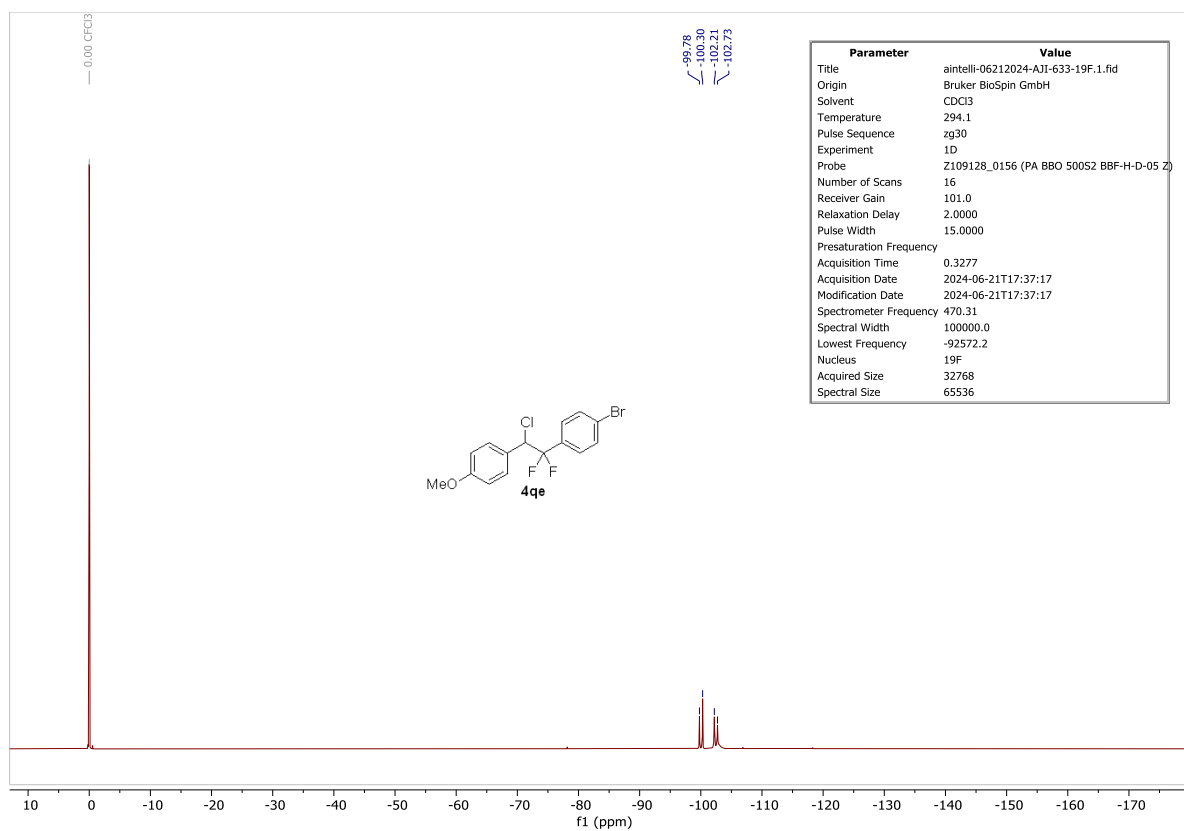
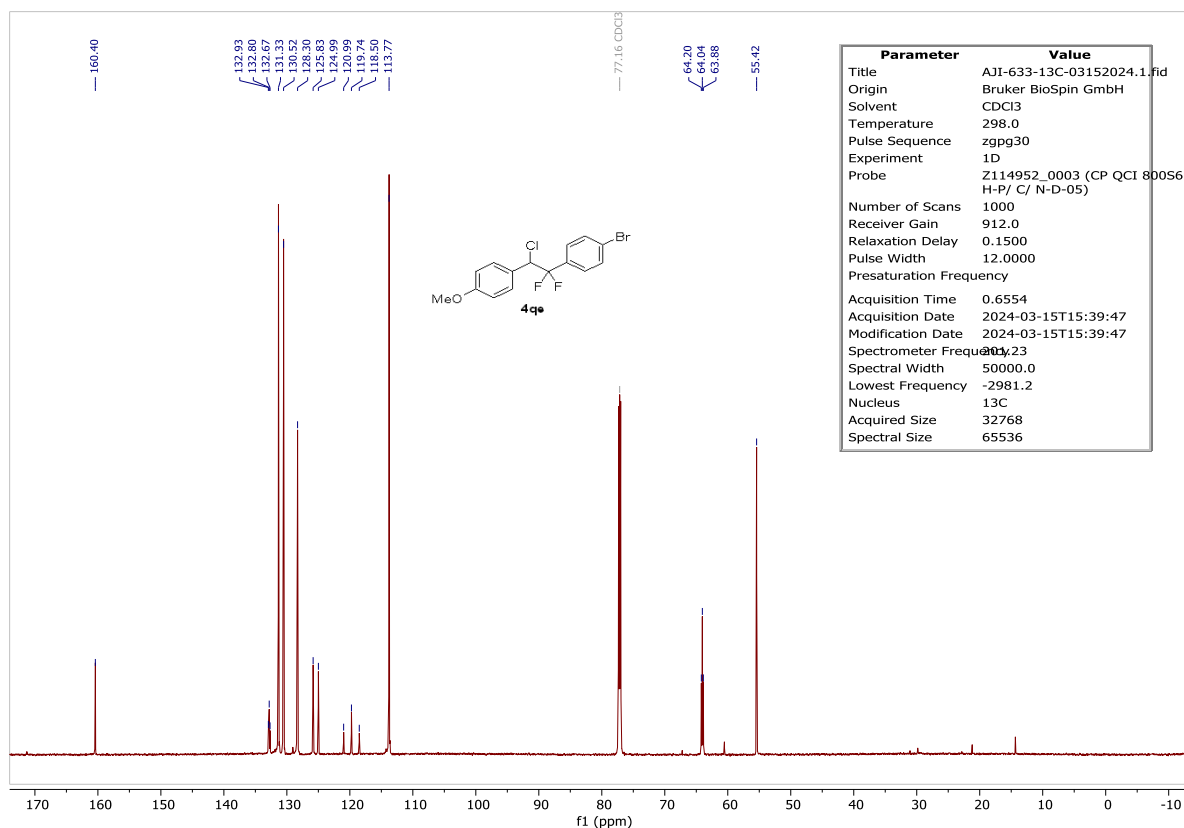
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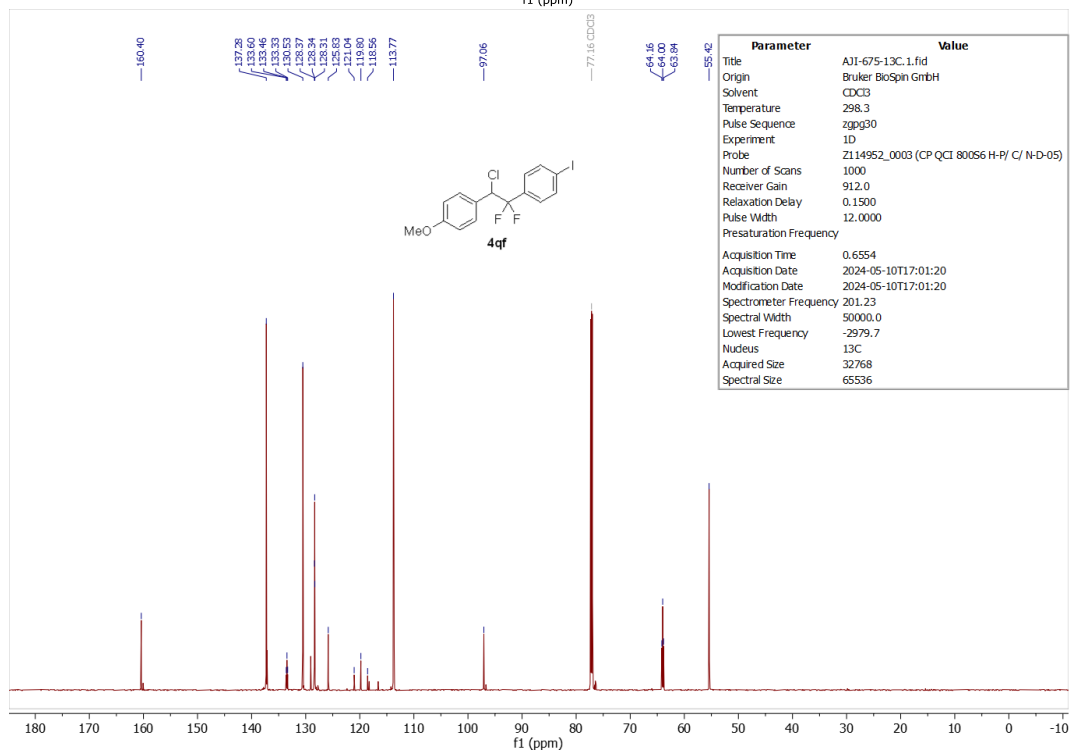
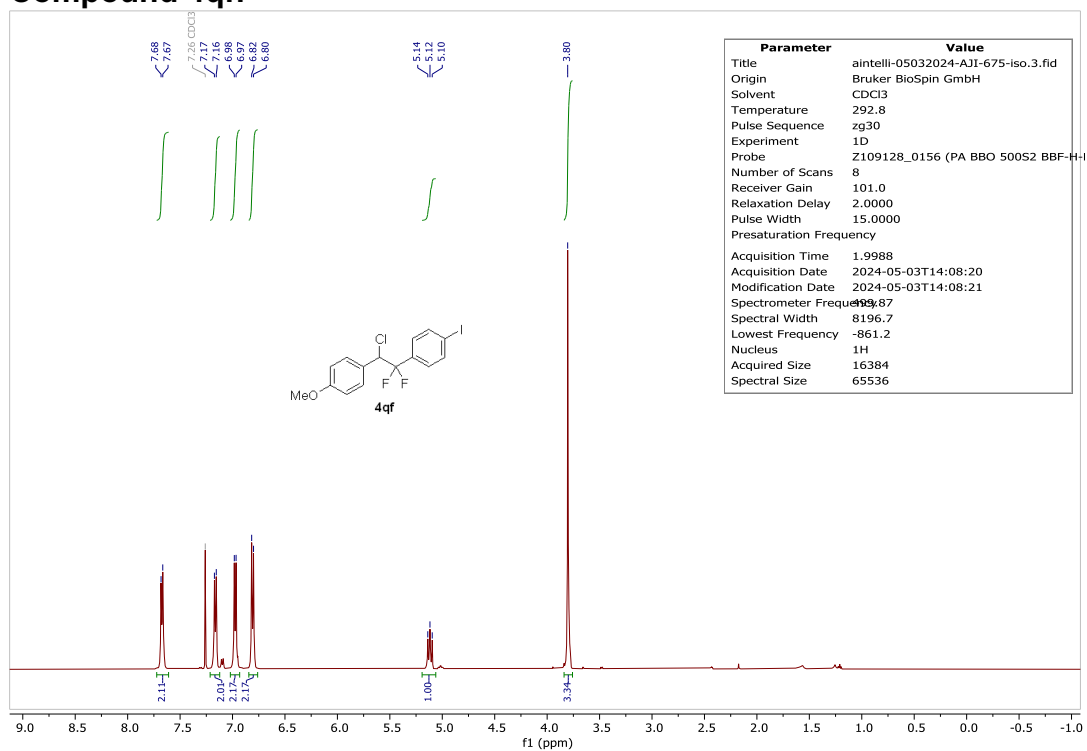


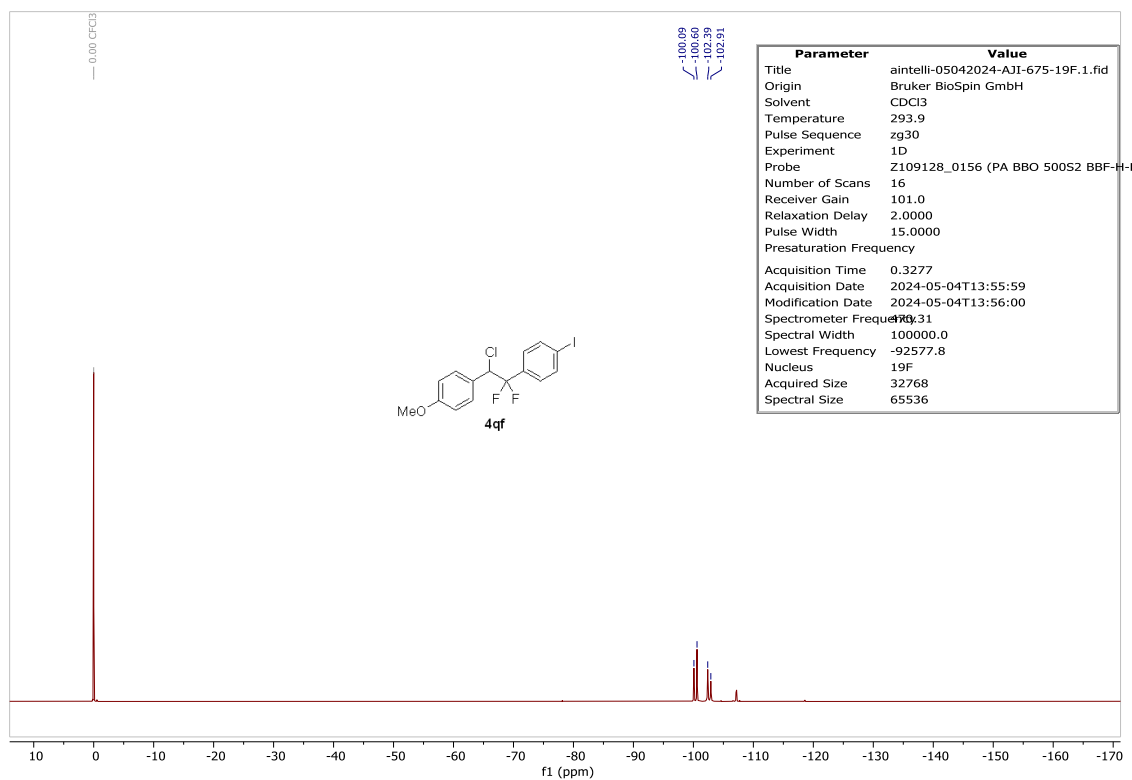
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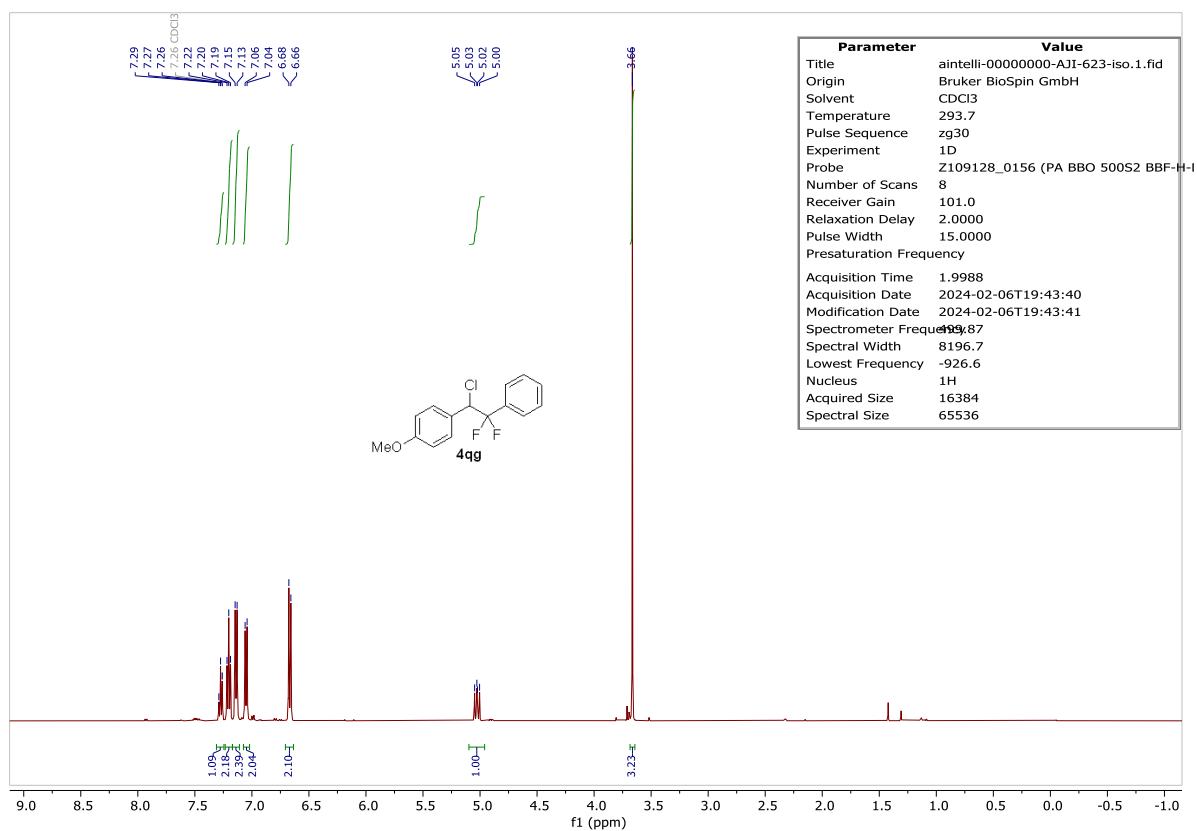


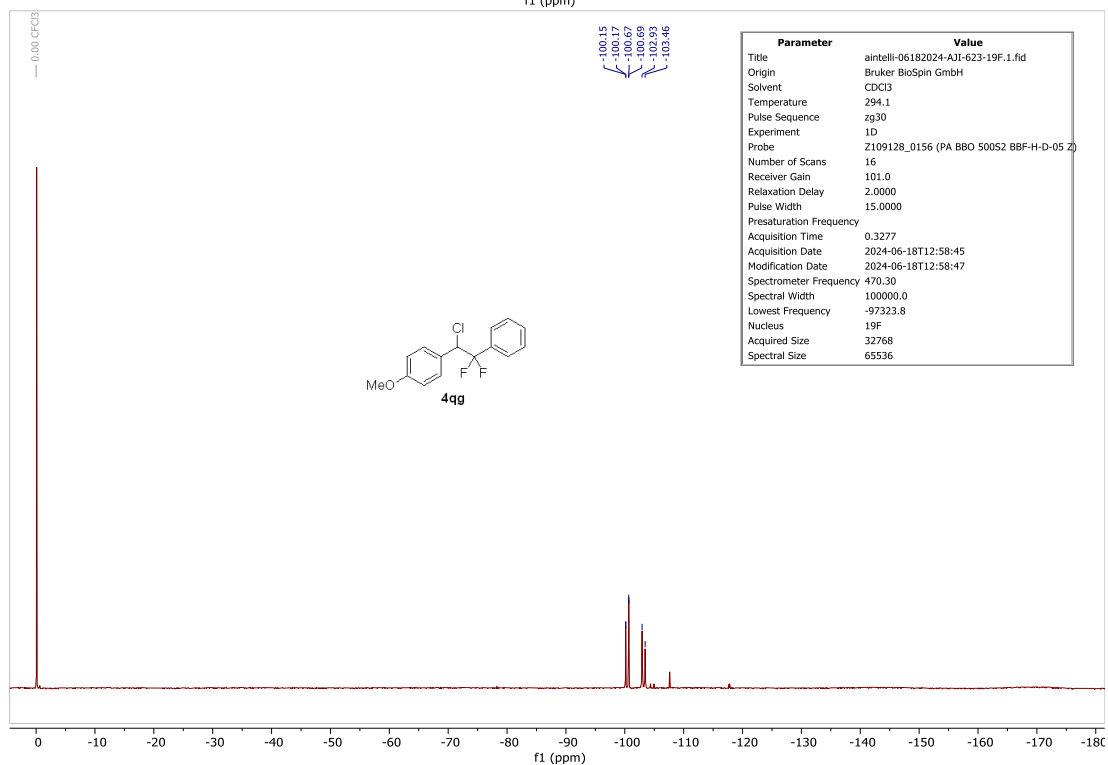
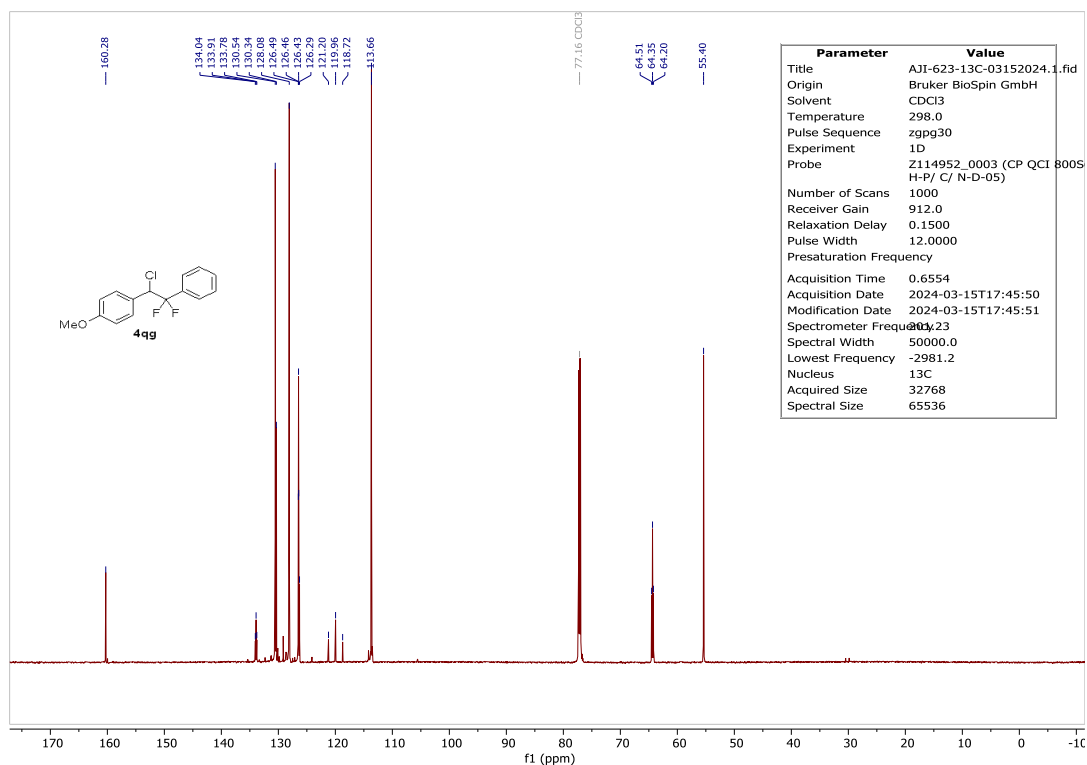
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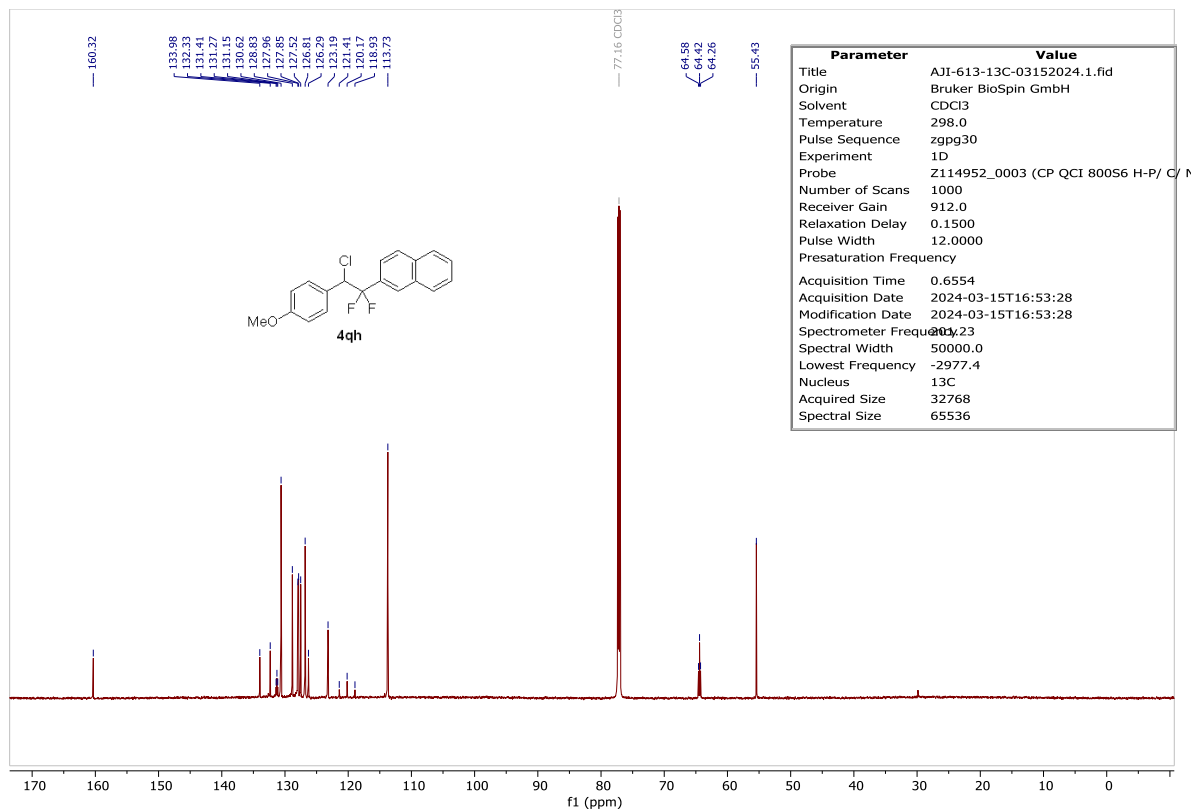
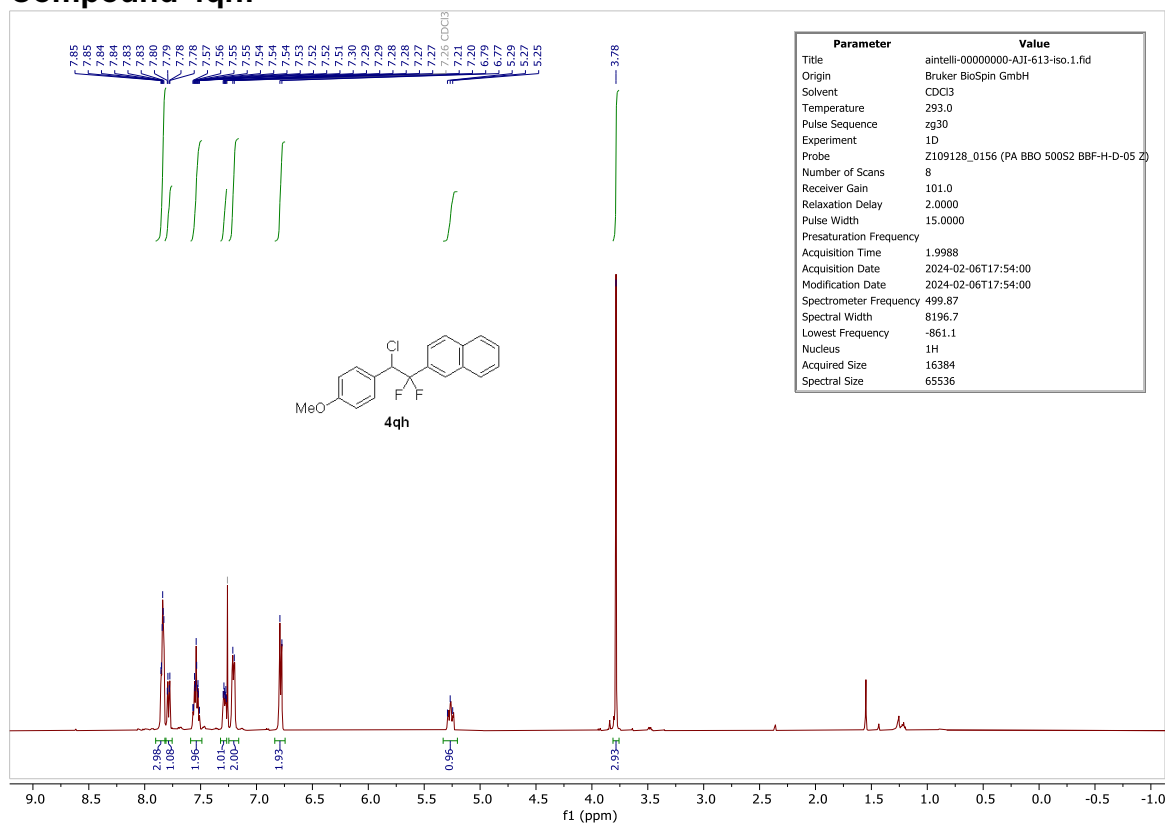


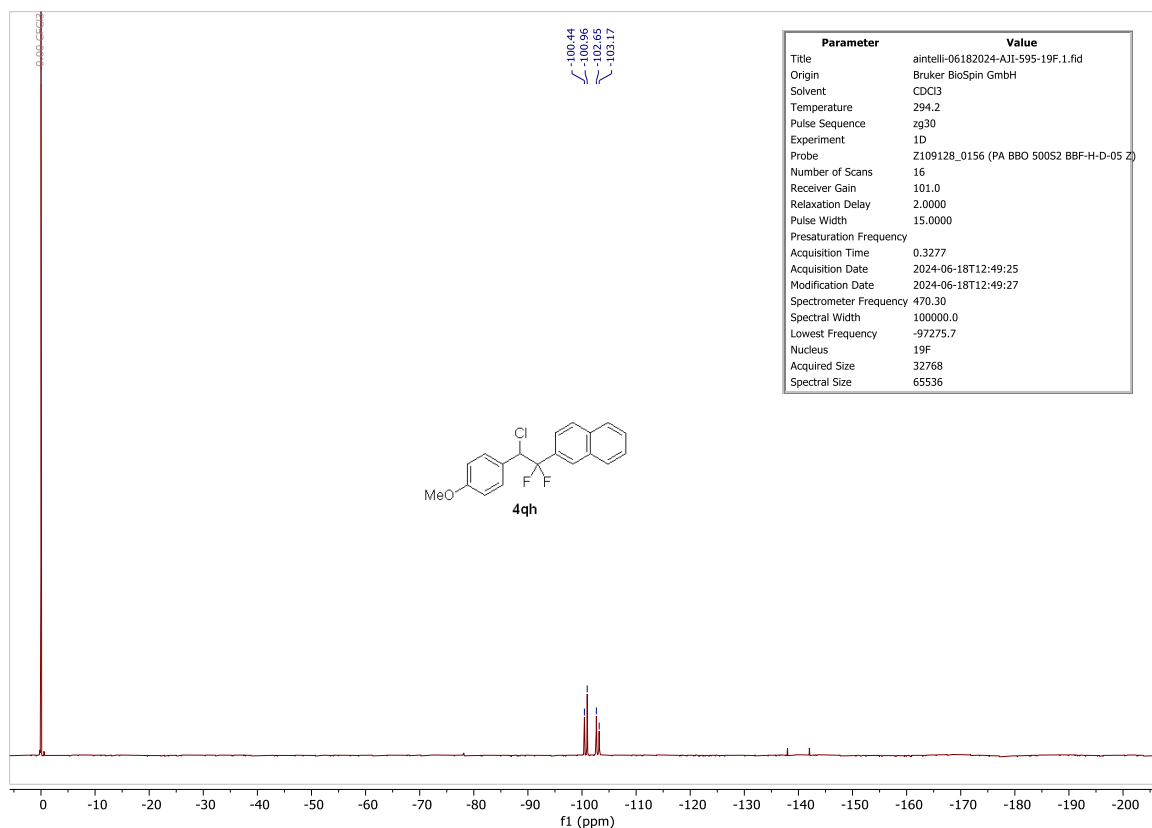
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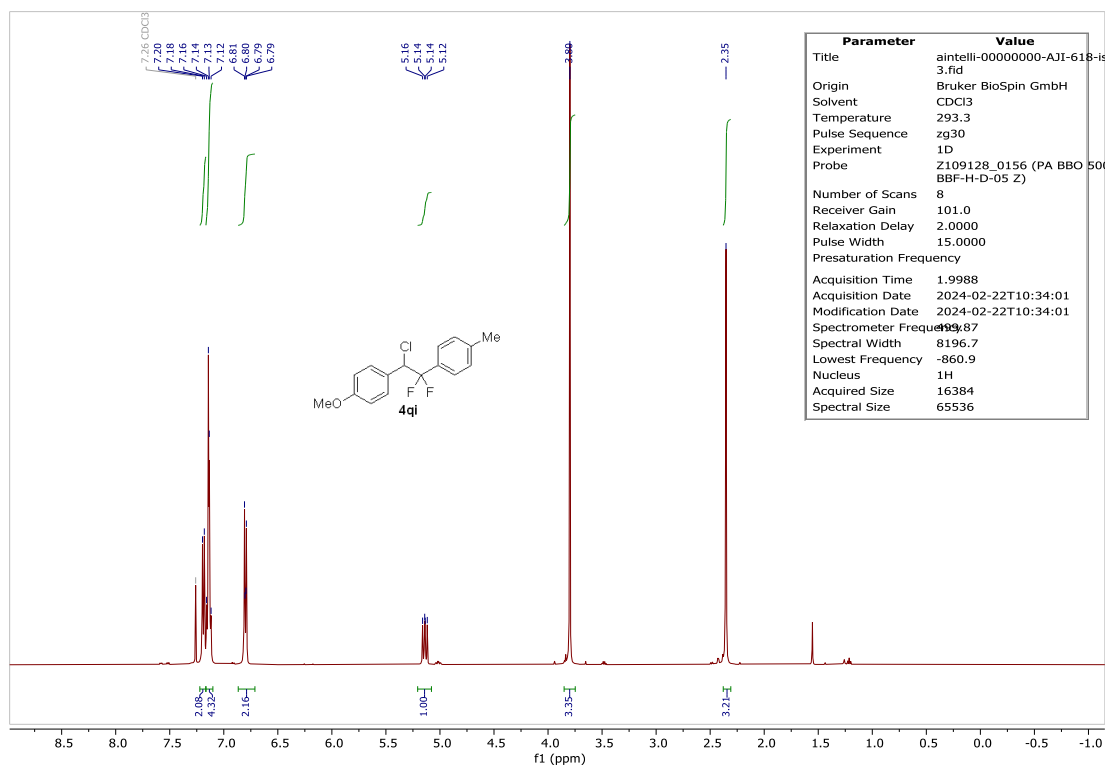


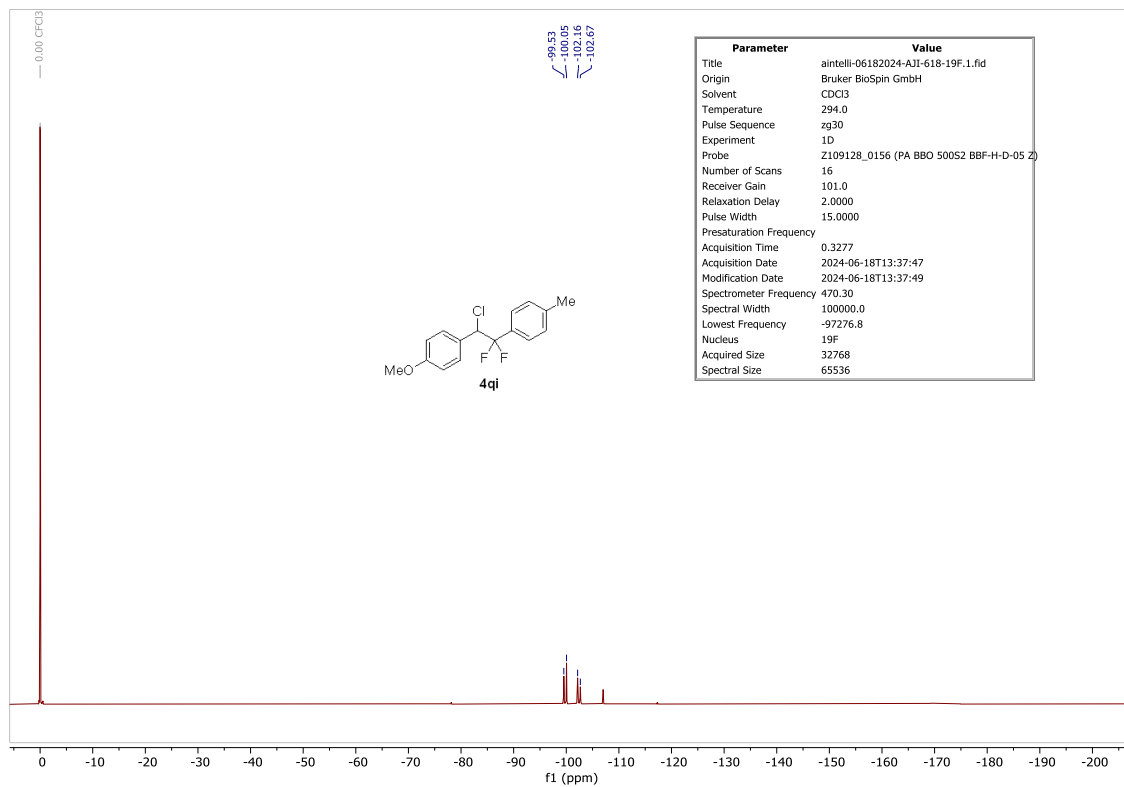
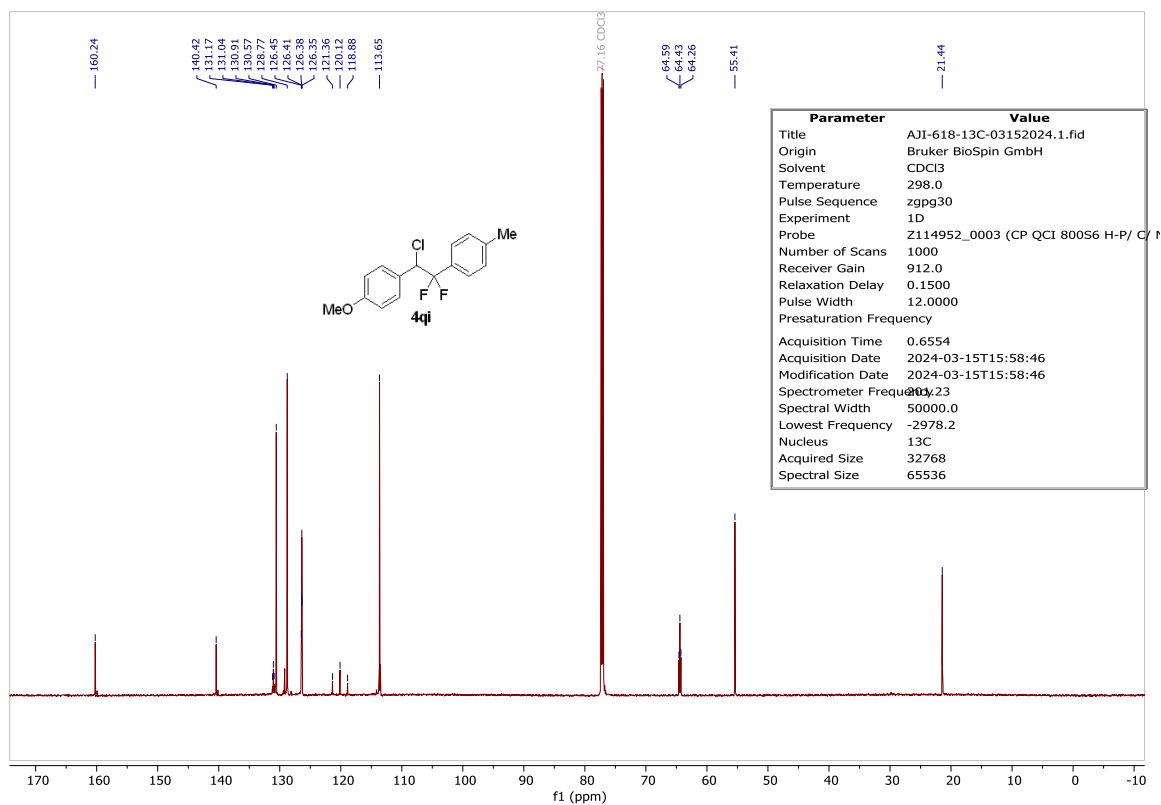
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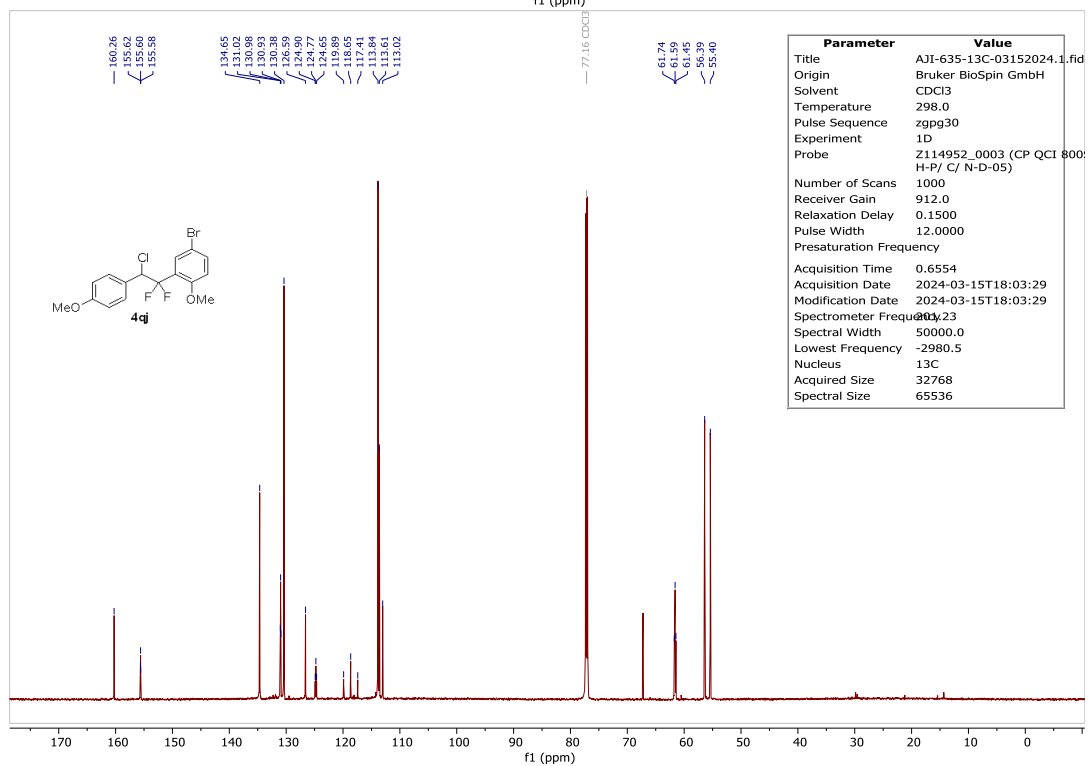
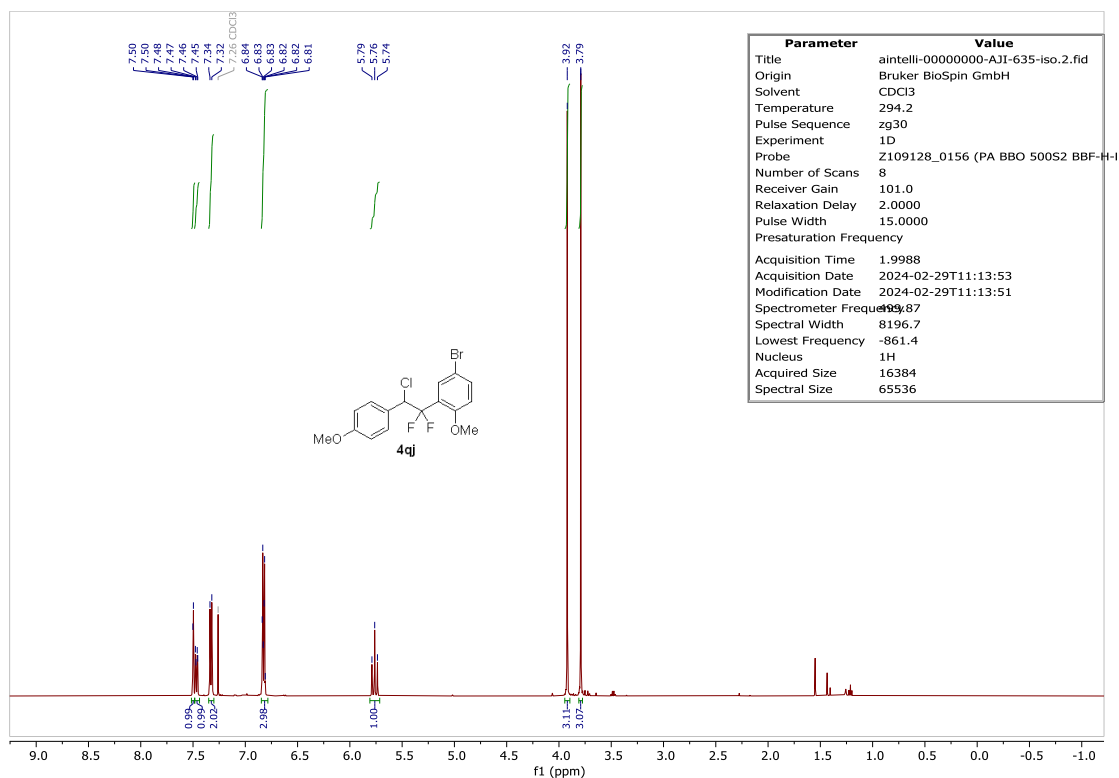


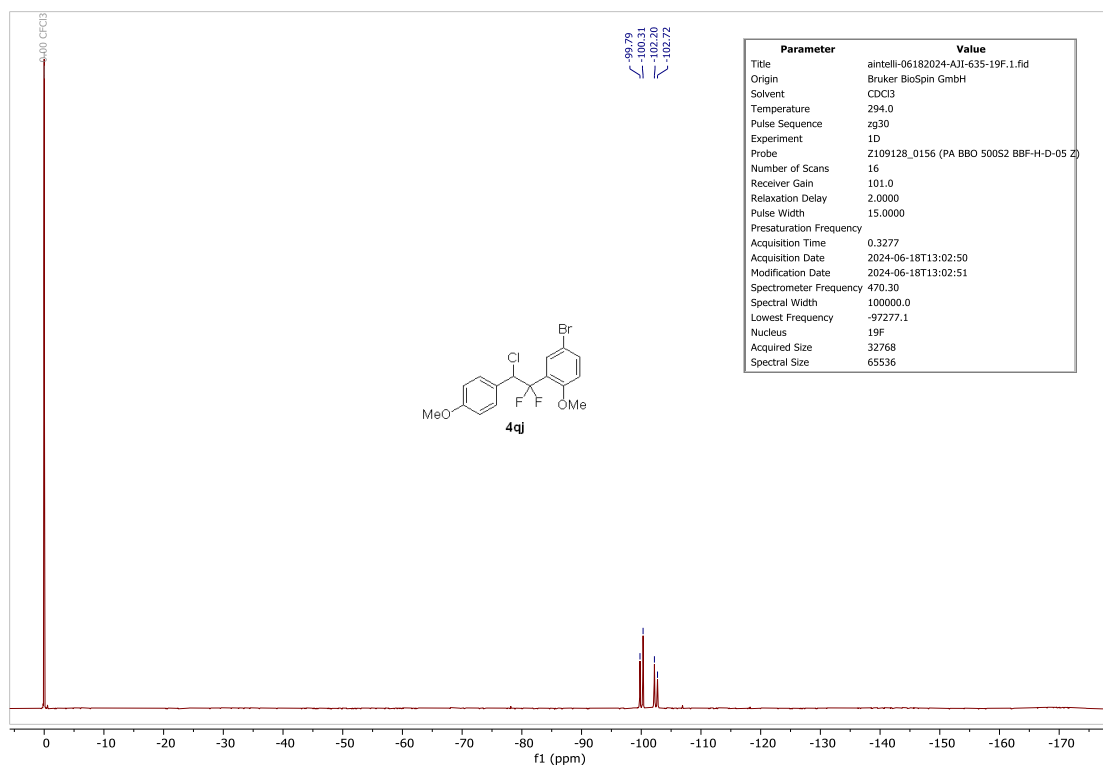
Compound 4qi:





Compound 4qj:





Compound 4qk:

