

Supporting Information

Cobalt-Catalyzed Selective Unsymmetrical Dioxidation of *gem*-Difluoroalkenes

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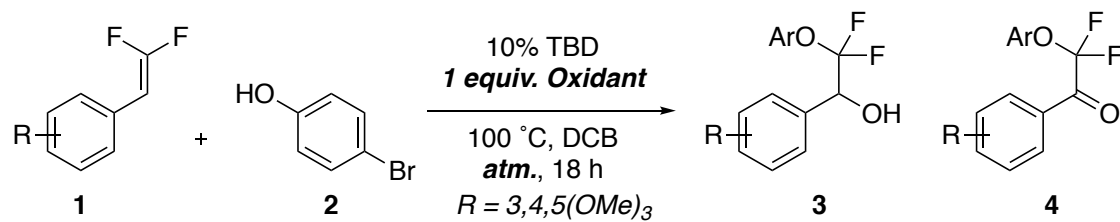
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General Procedure for the Selective Unsymmetric Dioxygenation of Difluoroalkenes with Phenols (B):

An oven-dried 20 mL scintillation vial, equipped with a magnetic stirbar, was charged with difluoroalkene (0.50 mmol), phenol (1.50 mmol), and Co(acac)₂ (0.050–0.20 mmol). The system was purged with O₂ gas for 1 min before anhydrous DCB (2.0 mL) was added to the system under a stream of O₂ gas. The system was sealed with a PTFE-lined screw-top cap and stirred for 1 min at R.T. Subsequently, the vial was placed into a pre-heated reaction block and stirred vigorously at 90–140 °C for 24–48 h. The vial was cooled to R.T., and 50 μL of TFT was added *via* microsyringe. The solution was diluted with approximately 1 mL of DCM and then stirred at R.T. for 10 min to allow adequate mixing. After mixing, an aliquot was removed from the vial and passed through a pad of silica gel into an NMR tube using acetone as eluent to remove Co(acac)₂, after which the reaction was analyzed by ¹⁹F NMR for completion and selectivity. After ¹⁹F NMR analysis, the aliquot was sampled for TLC analysis (visualized with 10% phosphomolybdic acid in EtOH) then returned to the vial. Aqueous base (sat. NaOH or Na₂CO₃) was added to the solution and stirred for 30 min, and then extracted with DCM (four times). The combined organic layers were washed with brine, dried over Na₂SO₄, concentrated *in vacuo*, and then purified by flash chromatography using EtOAc and hexanes.

Optimization of Reaction Conditions:

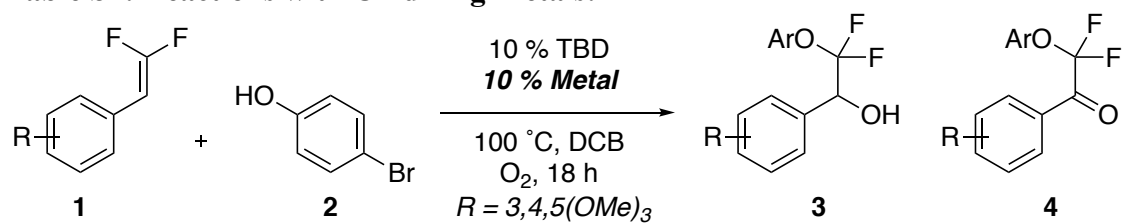
Table S1: Reactions with Oxidants:



Oxidant	Atmosphere	1	3	4
MnO ₂	O ₂	0	0	0
K ₂ S ₂ O ₈	O ₂	15	23	15
KMnO ₄	O ₂	38	13	9
Oxone	O ₂	48	5	1
DMP	O ₂	16	14	9
NMO	O ₂	53	3	7
IBX	O ₂	27	35	15
K ₂ S ₂ O ₈	air	21	8	0
KMnO ₄	air	46	0	0
mCPBA	air	23	0	0
IBX	air	61	0	0
H ₂ O ₂ (30 %)	air	40	11	6
^t BuOOH	air	34	0	0
Iodopentoxide	air	trace	trace	trace
Cumene Hydroperoxide	air	28	3	1
(^t BuO) ₂	air	40	trace	1.5
H ₂ O ₂ -Urea	air	39	6	6
Oxone	air	37	0	0
DMP*	air	36	0	0
NMO	air	67	0	0

* = Reacted on addition at room temperature

Following General Procedure B, 0.023 g (0.10 mmol) of compound **1** was reacted with 0.052 g (0.30 mmol) of 4-bromophenol in the presence of 0.0014 g (0.010 mmol) of TBD, and 0.10 mmol of oxidant in 0.40 mL of DCB at 100 °C for 18 h. Reactions were analyzed by ¹⁹F NMR with a 0.010 mL (0.080 mmol) TFT standard.

Table S2: Reactions with Oxidizing Metals:

Metal	1	3	4
Pd(OAc) ₂	5	38	26
Pd ₂ (dba) ₃	5	47	17
FeCl ₃	4	38	23
Fe(OAc) ₂	5	41	35
CuCl	4	24	23
Cu(OAc) ₂	0	30	33
AuCl ₃	0	0	0
Ag ₂ CO ₃	10	43	24
AgNO ₃	5	32	27
[Ir(cod)Cl] ₂	26	30	22
RhCl ₃ ·H ₂ O	6	46	29
Co(acac) ₂	6	74	13

Following General Procedure B, 0.023 g (0.10 mmol) of compound **1** was reacted with 0.052 g (0.30 mmol) of 4-bromophenol in the presence of 0.0014 g (0.010 mmol) of TBD, and 0.010 mmol of metal in 0.40 mL of DCB at 100 °C for 18 h. Reactions were analyzed by ¹⁹F NMR with a 0.01 mL (0.080 mmol) TFT standard.

Table S3: Solvent Screening:

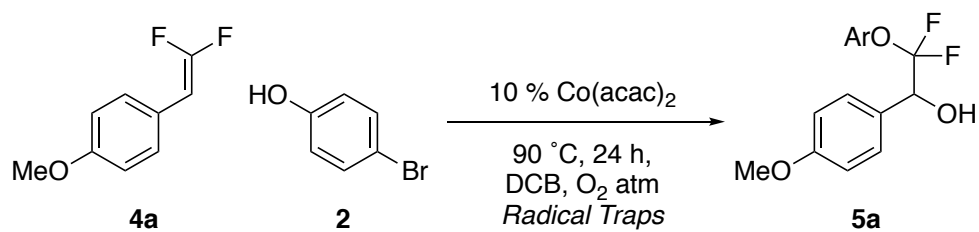
Reaction scheme showing the conversion of compound **1** (a substituted styrene derivative) and compound **2** (4-bromophenol) to products **3** and **4** (fluorinated alcohols/ketones) using 10% Co(acac)₂ in a solvent at 100 °C for 18 h under O₂. The substituent R is defined as 3,4,5-trimethoxyphenyl.

Solvent	1	3	4
DCB	7	63	5
H ₂ O	35	32	1
IPA	64	7	0.5
1,4-Dioxane	61	5	0
MeCN	45	20	2
DMF	55	15	5
PhMe	28	55	2
DMSO	49	9	5

Following General Procedure B, 0.023 g (0.10 mmol) of compound **1** was reacted with 0.052 g (0.30 mmol) of 4-bromophenol in the presence of 0.003 g (0.010 mmol) of Co(acac)₂ in 0.40 mL of solvent at 100 °C for 18 h. Reactions were analyzed by ¹⁹F NMR with a 0.010 mL (0.080 mmol) TFT standard.

Experimental Procedures for Mechanistic Experiments:

Table S4: Radical Trap Experiments:



<i>Radical Trap</i>	<i>Conv.</i>	<i>Pdt</i>	<i>Ketone</i>
	68%	0%	0%
	100%	0%	0%
	92%	54%	5.5%

Reaction with Butylated Hydroxy-Toluene (BHT):

Following General Procedure B, 0.085 g (0.50 mmol) of compound **4a** was reacted with 0.260 g (1.50 mmol) of 4-bromophenol in the presence of 0.331 g (1.50 mmol) of BHT and 0.013 g (0.050 mmol) of Co(acac)₂ at 110 °C for 15 h. The reaction was cooled to R.T., and 0.050 mL (0.40 mmol) of TFT was added. The resulting mixture was diluted with DCM and filtered through silica gel with acetone. The reaction yield and selectivity were determined by ¹⁹F NMR analysis of the crude reaction mixture, and non-fluorinated adducts were observed through GC-MS analysis.

Reaction with 1,4-Benzoquinone:

Following General Procedure B, 0.085 g (0.50 mmol) of compound **4a** was reacted with 0.260 g (1.50 mmol) of 4-bromophenol in the presence of 0.162 g (1.50 mmol) of 1,4-benzoquinone and 0.013 g (0.050 mmol) of Co(acac)₂ at 110 °C for 15 h. The reaction was cooled to R.T., and 0.050 mL (0.40 mmol) of TFT was added. The resulting mixture was diluted with DCM and filtered through silica gel with acetone. The reaction yield and selectivity were determined by ¹⁹F NMR analysis of the crude reaction mixture, and non-fluorinated adducts were observed through GC-MS analysis.

Reaction with 1,4-Dinitrobenzene:

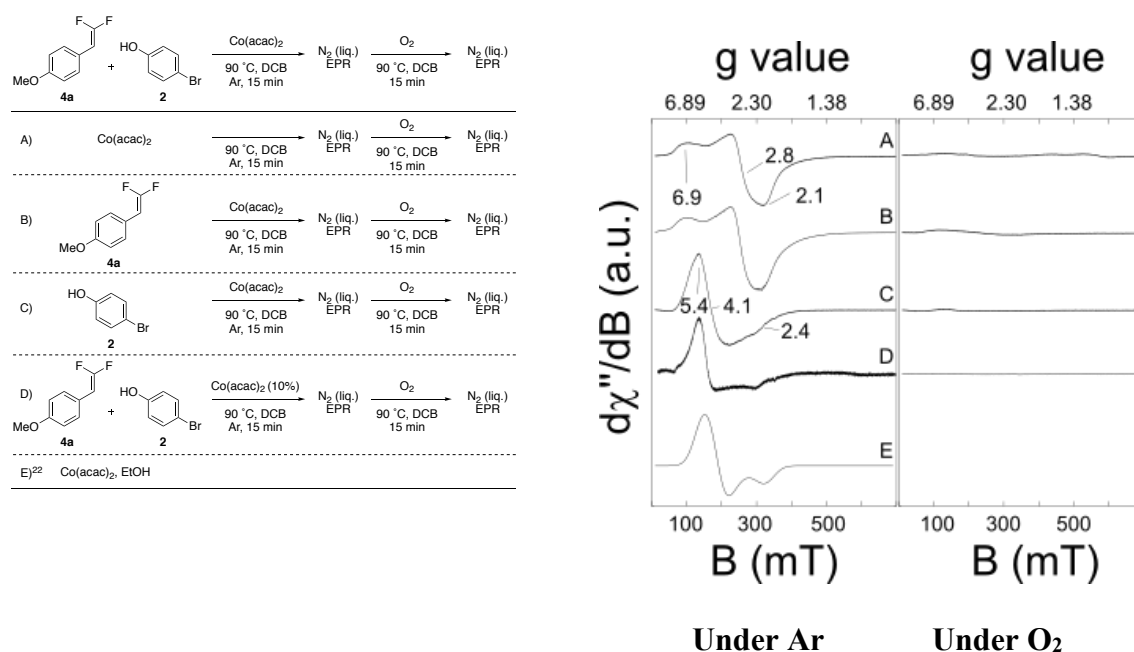
Following General Procedure B, 0.085 g (0.50 mmol) of compound **4a** was reacted with 0.260 g (1.50 mmol) of 4-bromophenol in the presence of 0.252 g (1.50 mmol) of 1,4-dinitrobenzene and 0.013 g (0.050 mmol) of Co(acac)₂ at 110 °C for 15 h. The reaction was cooled to R.T., and 0.050 mL (0.40 mmol) of TFT was added. The resulting mixture was diluted with DCM and filtered through silica gel with acetone. The reaction yield and selectivity were determined by ¹⁹F NMR analysis of the crude reaction mixture, and non-fluorinated adducts were observed through GC-MS analysis.

EPR Experiments:

Electron Paramagnetic Resonance (EPR), also known as Electron Spin Resonance (ESR) spectroscopy was used to probe the proposed reaction mechanism. EPR is a magnetic resonance spectroscopy sensitive to the oxidation state and molecular structure of molecules with unpaired electrons, such as transition metal complexes and stable radicals.² The proposed mechanism involves paramagnetic cobalt, reactive oxygen species, and organic radicals; thus, EPR was used to validate the role of these species in the general reaction.

Figure S1: EPR Experiments at 7 K to Analyze the Electronic Character of the Co:

EPR at 7 K revealed that Co does not interact with the difluoroalkene (A vs. B). The Co catalyst coordinates with phenol (A vs. C) in a similar fashion to a known (EtOH)₂Co(acac)₂ complex (E). However, the interaction with phenol does not involve a redox event, as the Co remains Co(II). The presumed (PhOH)₂Co(acac)₂ does not react with the difluoroalkene in the absence of O₂ (C vs. D). Upon addition of O₂, Co(II) (Left Frame) rapidly oxidizes to Co(III) (Right Frame), at which point the metal is no longer paramagnetic and EPR spectra cannot be obtained.



A) Reacting Co(acac)₂ and O₂:

Co(acac)₂ (0.021 g, 0.082 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (1.0 mL) was added, and a 100 μL aliquot of the reaction mixture was transferred to an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K. The reaction was then put under an O₂ balloon, and stirred at 90 °C for 30 min. A 100 μL aliquot of the reaction mixture was transferred into an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K.

B) Reacting Co(acac)₂ and 4a under O₂:

Following General Procedure B, in an oven-dried one dram vial compound **4a** (0.043 g, 0.25 mmol) was reacted with Co(acac)₂ (0.064 g, 0.25 mmol) in DCB (1.0 mL). An O₂ balloon was added, and a 100 μL aliquot of the reaction mixture was transferred to an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K. The reaction was then put under an O₂ balloon, and stirred at 90 °C for 30 min. A 100 μL aliquot of the reaction mixture was transferred into an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K.

C) Reacting Co(acac)₂ and 4-bromophenol under O₂:

Following General Procedure B, in an oven-dried one dram vial of 4-bromophenol (0.13 g, 0.75 mmol) was reacted with Co(acac)₂ (0.064 g, 0.25 mmol) in DCB (1.0 mL). An O₂ balloon was added, and a 100 μL aliquot of the reaction mixture was transferred to an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K. The reaction was then put under an O₂ balloon, and stirred at 90 °C for 30 min. A 100 μL aliquot of the reaction mixture was transferred into an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K.

D) Following Full Reaction Course:

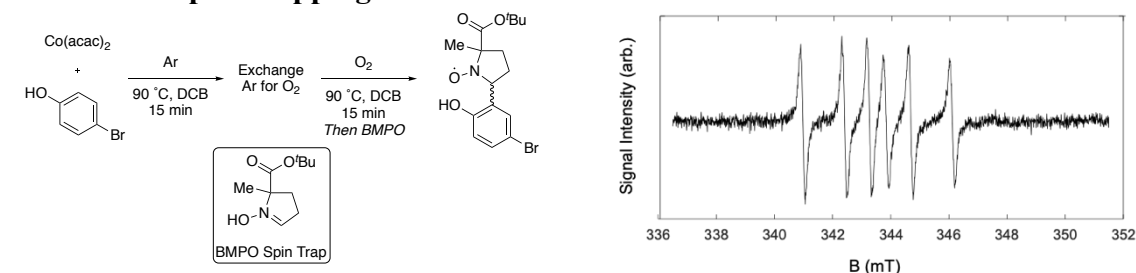
Following General Procedure B, in an oven-dried one dram vial of compound **4a** (0.043 g, 0.25 mmol) was reacted with 4-bromophenol (0.13 g, 0.75 mmol) in the presence of Co(acac)₂ (0.006 g, 0.03 mmol) in DCB (1.0 mL). An O₂ balloon was added, and a 100 μL aliquot of the reaction mixture was transferred to an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K. The reaction was then put under an O₂ balloon, and stirred at 90 °C for 30 min. A 100 μL aliquot of the reaction mixture was transferred into an EPR tube, frozen in liquid N₂, and then subjected to EPR analysis at 7 K.

EPR Parameters: Full Reaction Course and Co(acac)₂ with Phenol under Ar:

Spectrum ID	g-values	Line Width	Experiments
A	7, 2.5, 2.5	75	Co(II) and Ar Co(II) and 4a and Ar
B	5, 3, 2	150	Co(II) and O ₂ Co(II) and 4a and O ₂
C	5.8, 3.8, 2.5	50	Co(II), 2 , and Ar Co(II), 2 , 4a , and Ar
D	4.5, 2	75	Co(II), 2 , and O ₂ Co(II), 2 , 4a , and O ₂

Table S6: Summary of EPR Parameters for Full Dipolar Zero-Field-Splitting Hamiltonian		
	Spectrum A/B	Spectrum C/D
S	3/2	3/2
G	2.2	2.2
Nucleus	Co	Co
A (MHz)	0	0
Line Width	100	100
D (MHz)	500,000	500,000
E (MHz)	166,667	0

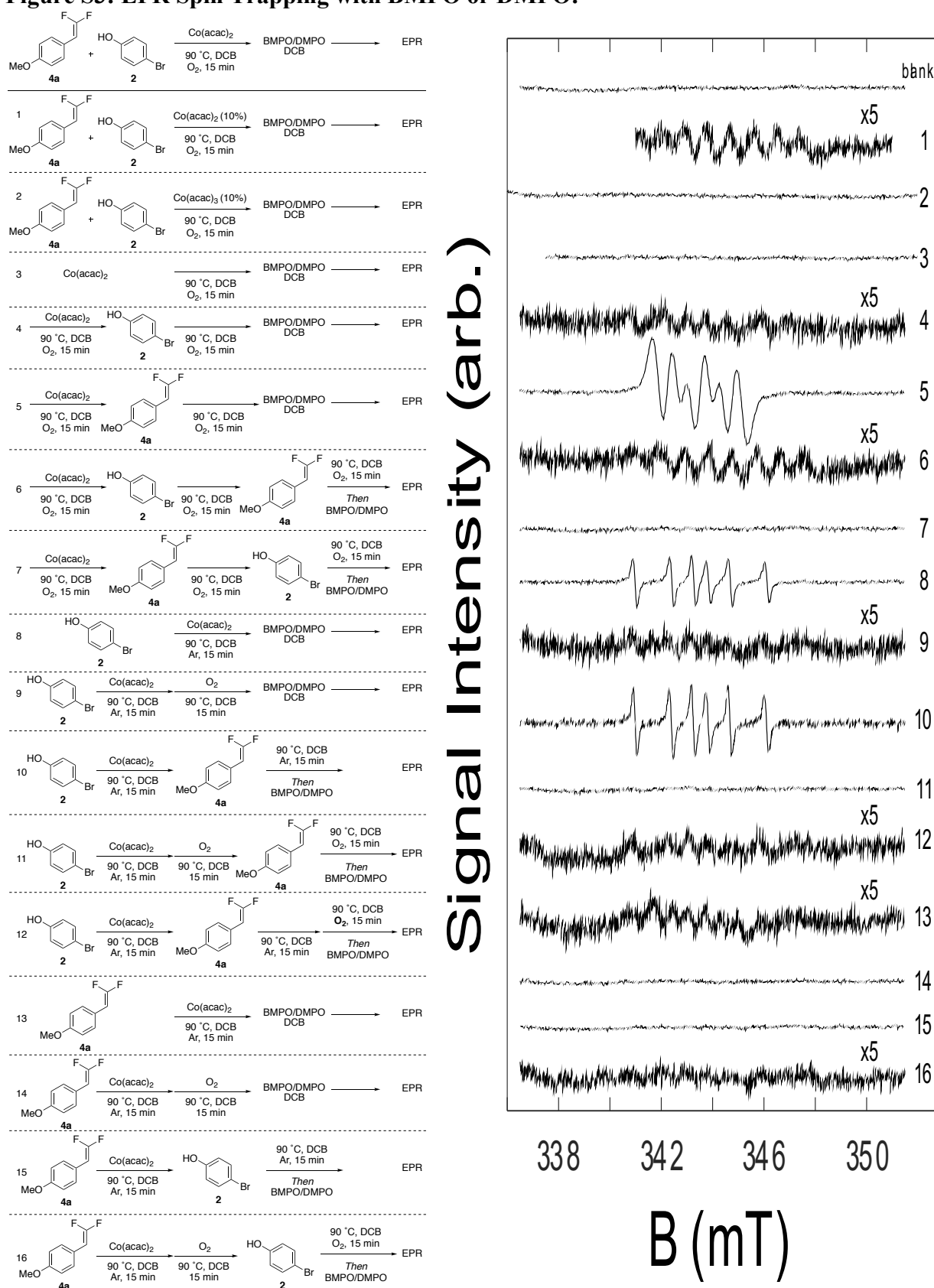
Figure S2: EPR Spin Trapping of Phenol Radical with BMPO:



EPR Spin Trapping with BMPO or DMPO:

To elucidate the presence and source of reactive oxygen species and organic radicals, EPR Spin Trapping analysis with the nitron spin traps BMPO and DMPO was performed (Figure S2). To determine the source of the reactive oxygen species and/or organic radicals, each potential reaction pathway was investigated in a string of half reactions, involving spin trapping reagents and EPR analysis (Figure S3). From these experiments, organic radicals and reactive oxygen species were only trapped in the presence of Co, phenol, and O_2 , consistent with our proposed mechanism in which Co activates O_2 to generate a reactive oxygen species that abstracts a hydrogen radical from phenol to generate a reactive organic radical. In all other conditions, no signal above baseline noise was observed, with the exception of difluoroalkene and Co in the presence of Ar. However, this signal likely results from the known background reaction between N–O species and difluoroalkenes and not along the Co-catalyzed reaction pathway.

Figure S3: EPR Spin Trapping with BMPO or DMPO:



Pathway A (spectrum 1): Following General Procedure A, in an oven-dried one dram vial of compound **4a** (0.017 g, 0.10 mmol) was reacted with 4-bromophenol (0.052 g, 0.30 mmol) in the presence of Co(acac)₂ (0.0026 g, 0.010 mmol) in DCB (0.40 mL). An O₂ balloon was added, and the reaction was stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 1).

Pathway A-2 (spectrum 2): Following General Procedure A, in an oven-dried one dram vial of compound **4a** (0.017 g, 0.10 mmol) was reacted with 4-bromophenol (0.052 g, 0.30 mmol) in the presence of Co(acac)₃ (0.0038 g, 0.010 mmol) in DCB (0.40 mL). An O₂ balloon was added, and the reaction was stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 2).

Pathway B (spectra 3, 4, and 6): Co(acac)₂ (0.026 g, 0.10 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an O₂ balloon and stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 3). Then 4-bromophenol (0.052 g, 0.30 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 4). Then **4a** (0.017 g, 0.10 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 6).

Pathway C (spectra 5 and 7): Co(acac)₂ (0.026 g, 0.10 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an O₂ balloon and stirred at 90 °C for 15 min. Then **4a** (0.017 g, 0.10 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 5). Then 4-bromophenol (0.052 g, 0.30 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 7). *Note:* Spectrum 5 demonstrates the background reaction of N-O oxides or radicals with difluoroalkenes, as observed in ¹⁹F NMR control reactions with BMPO or TEMPO in the absence of Co(acac)₂.

Pathway D (spectra 8, 9, and 11): Co(acac)₂ (0.026 g, 0.10 mmol) and 4-bromophenol (0.052 g, 0.30 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an Ar balloon and stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 8). Then Ar was exchanged for O₂, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 9). Then **4a** (0.017 g, 0.10 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 11).

Pathway E (spectra 10 and 12): Co(acac)₂ (0.026 g, 0.10 mmol) and 4-bromophenol (0.052 g, 0.30 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an Ar balloon and stirred at 90 °C for 15 min. Then **4a** (0.017 g, 0.10 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 10). Then Ar was exchanged for O₂, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 12).

Pathway F (spectra 13, 14, and 16): Co(acac)₂ (0.026 g, 0.10 mmol) and **4a** (0.017 g, 0.10 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an Ar balloon and stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 13). Then Ar was exchanged for O₂, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 14). Then 4-bromophenol (0.052 g, 0.30 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 16).

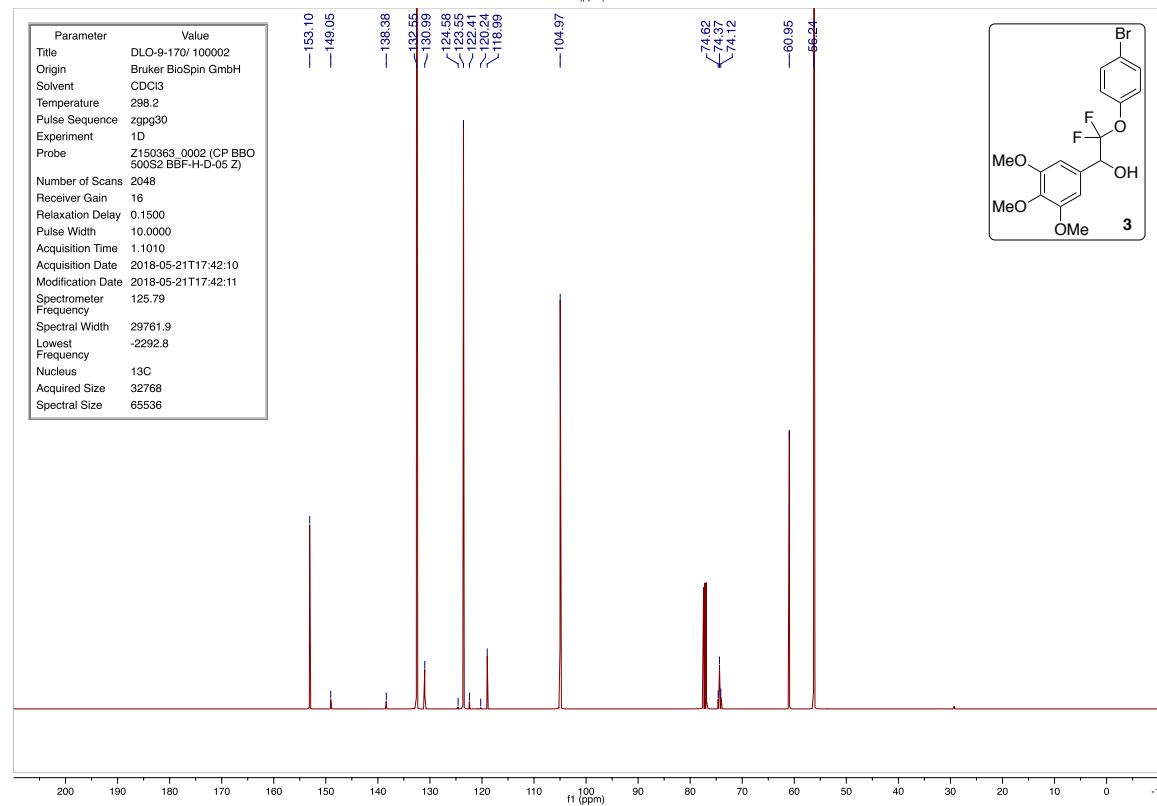
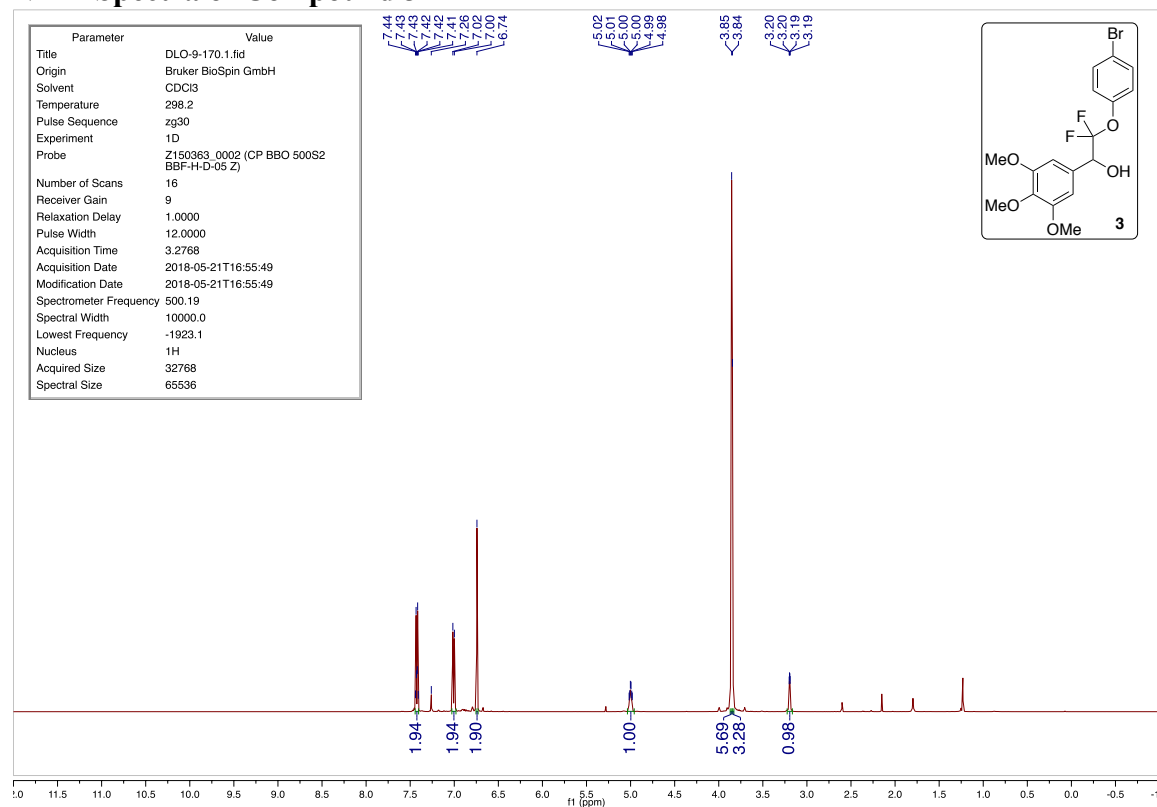
Pathway G (spectrum 15): Co(acac)₂ (0.026 g, 0.10 mmol) and **4a** (0.017 g, 0.10 mmol) was added to an oven dried one dram vial. The vial was sealed with a screw-top cap containing a PTFE-lined silicon septum, and the reaction was evacuated and backfilled three times with N₂. DCB (0.40 mL) was added, then put under an Ar balloon and stirred at 90 °C for 15 min. Then 4-bromophenol (0.052 g, 0.30 mmol) in 0.40 mL DCB was added, and the reaction stirred at 90 °C for 15 min. A 100 μL aliquot of the reaction mixture was transferred into an Eppendorf tube containing 10 μL of a 20 mg/200 μL DCB sample of BMPO or DMPO, mixed on a Vortex mixer, and then a capillary tube sample removed for EPR analysis at R.T. (Figure S3-1, Spectrum 15).

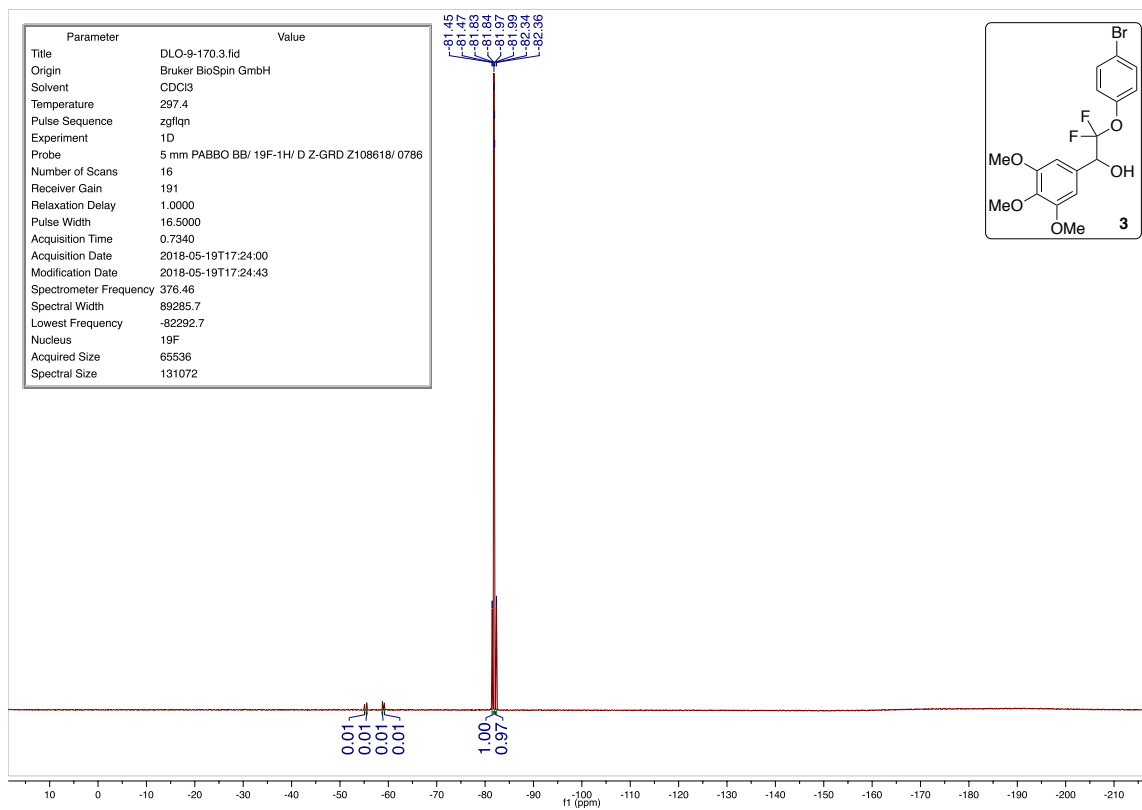
EPR Parameters from Spin Trapping Experimentation

Center Field (mT)	344		
Sweep Width (mT)	15		
Microwave Frequency (GHz)	9.6426		
G	2.0055		
A (MHz)	1 – ¹⁴ N	35.3525 (1.2615 mT)	N = 1
	2 – ¹ H	20.0400 (0.6161 mT)	N = 1
Iwpp (mT)	0.45		

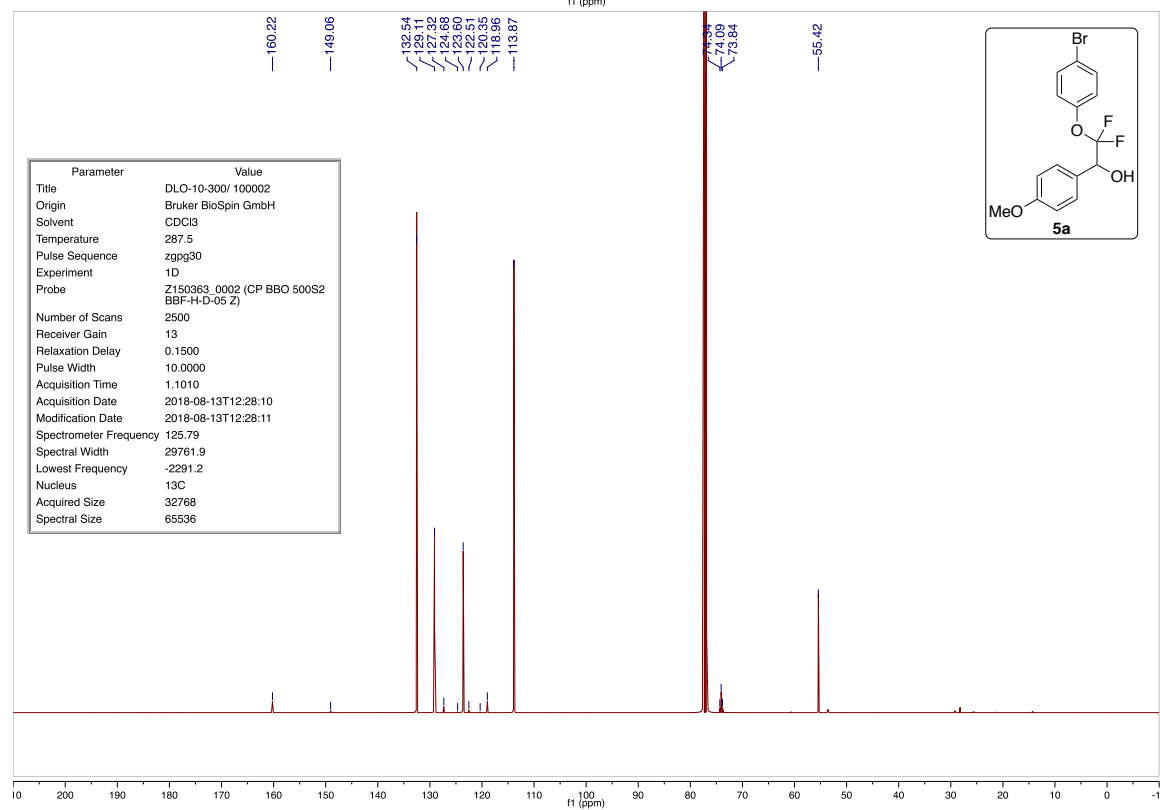
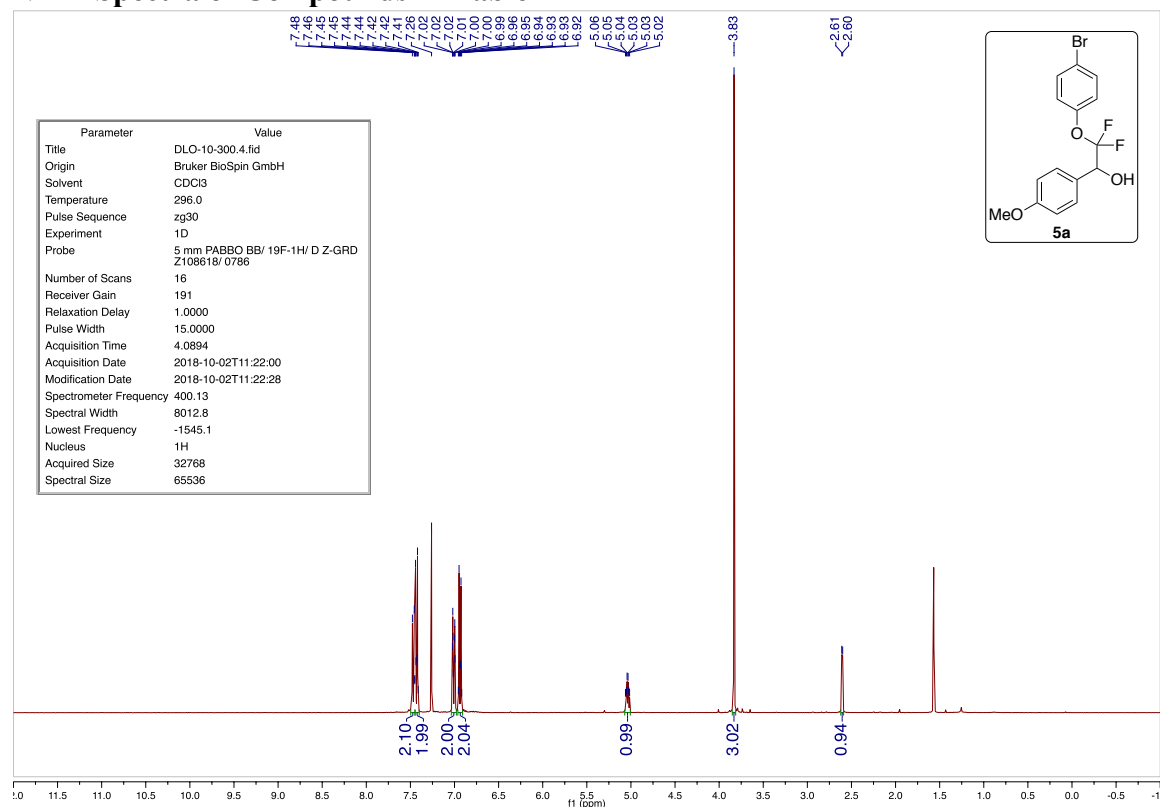
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Sweep Width (mT)	15		
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G	2.0055		
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Iwpp (mT)	0.45		

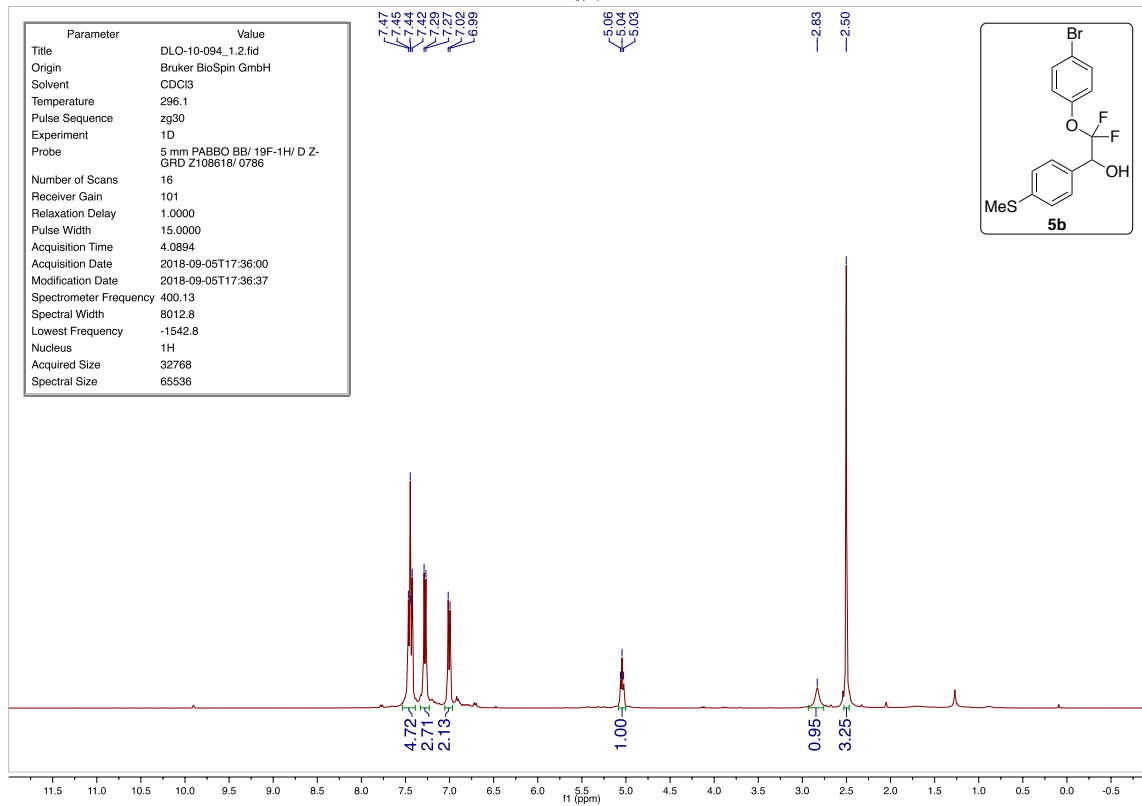
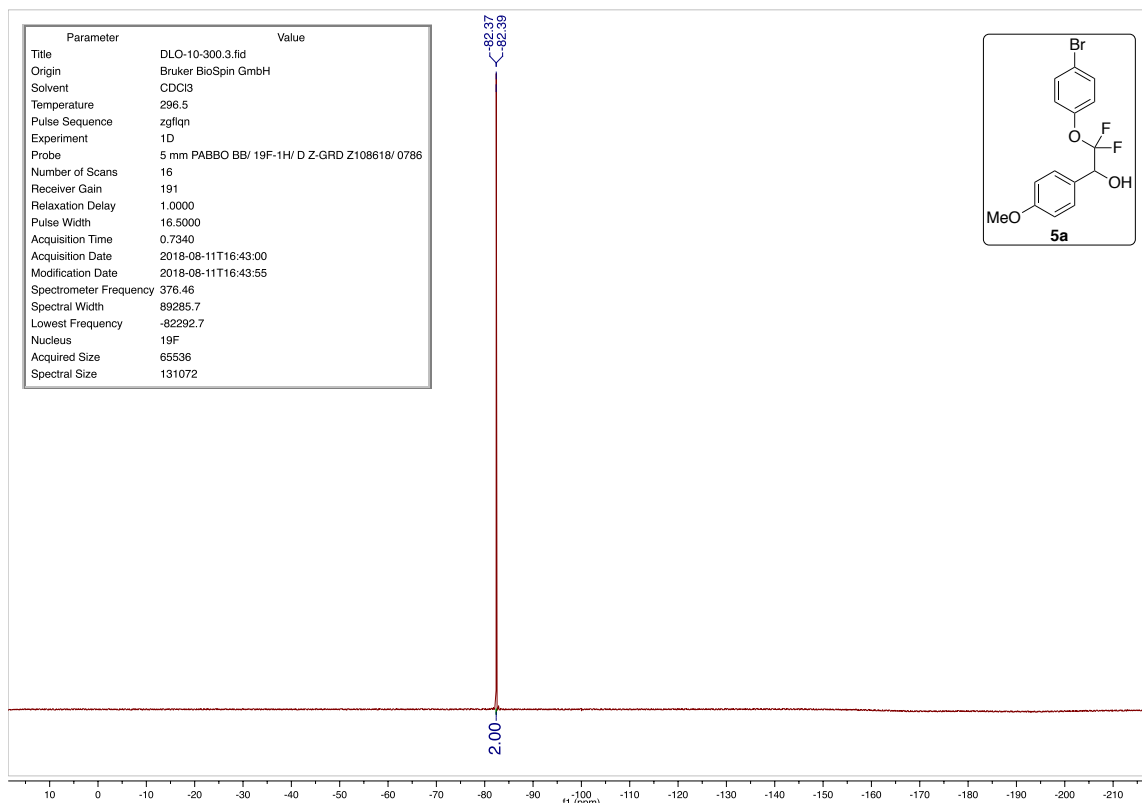
NMR Spectra of Compound 3

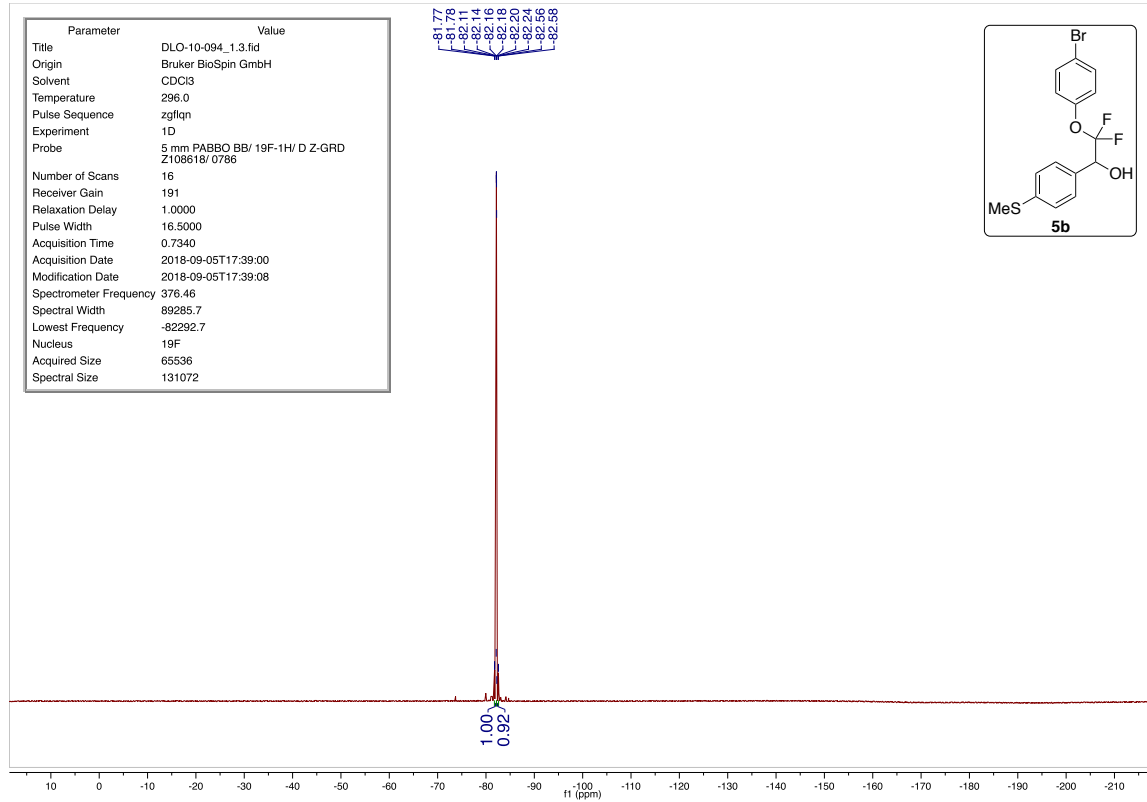
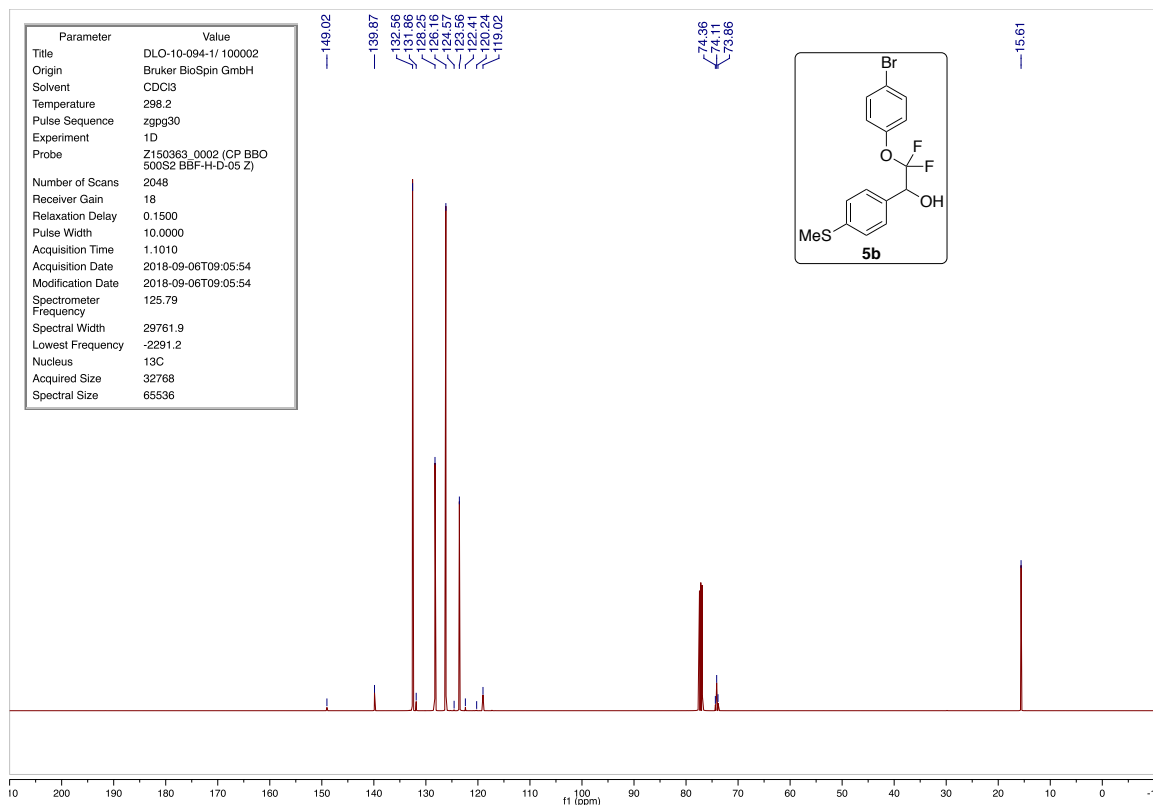


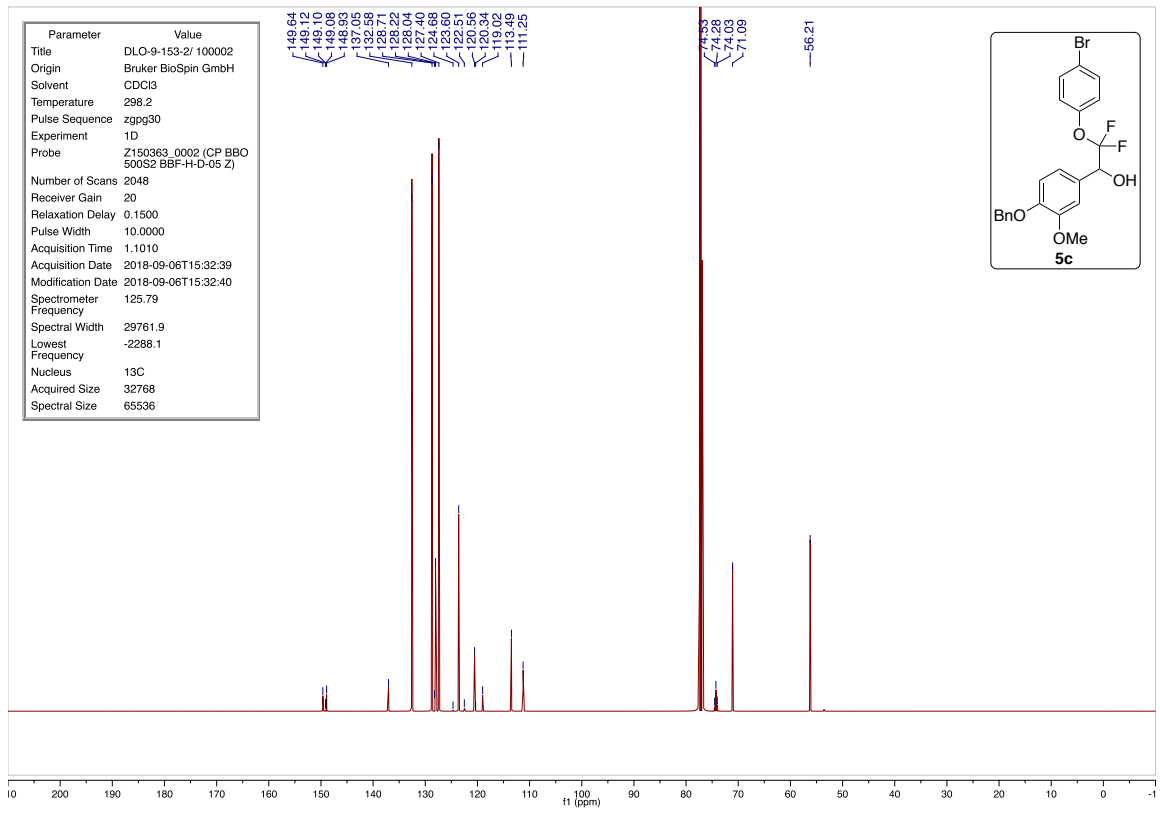
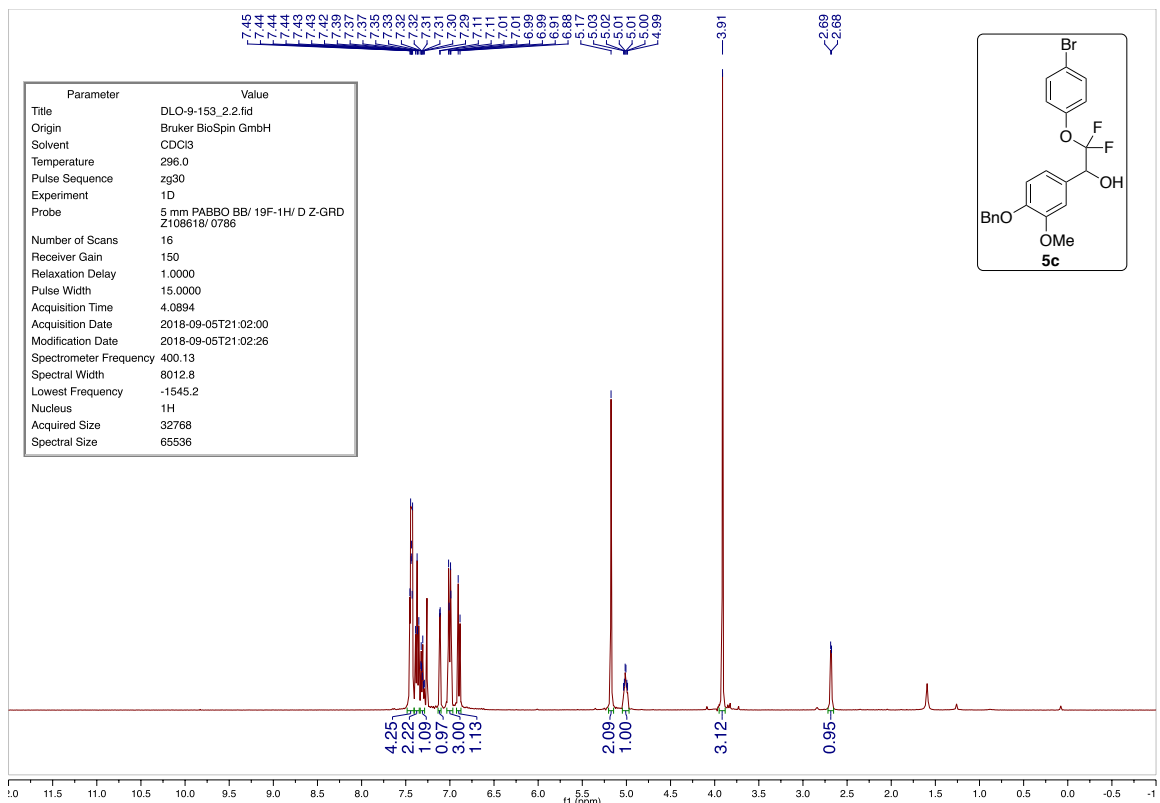


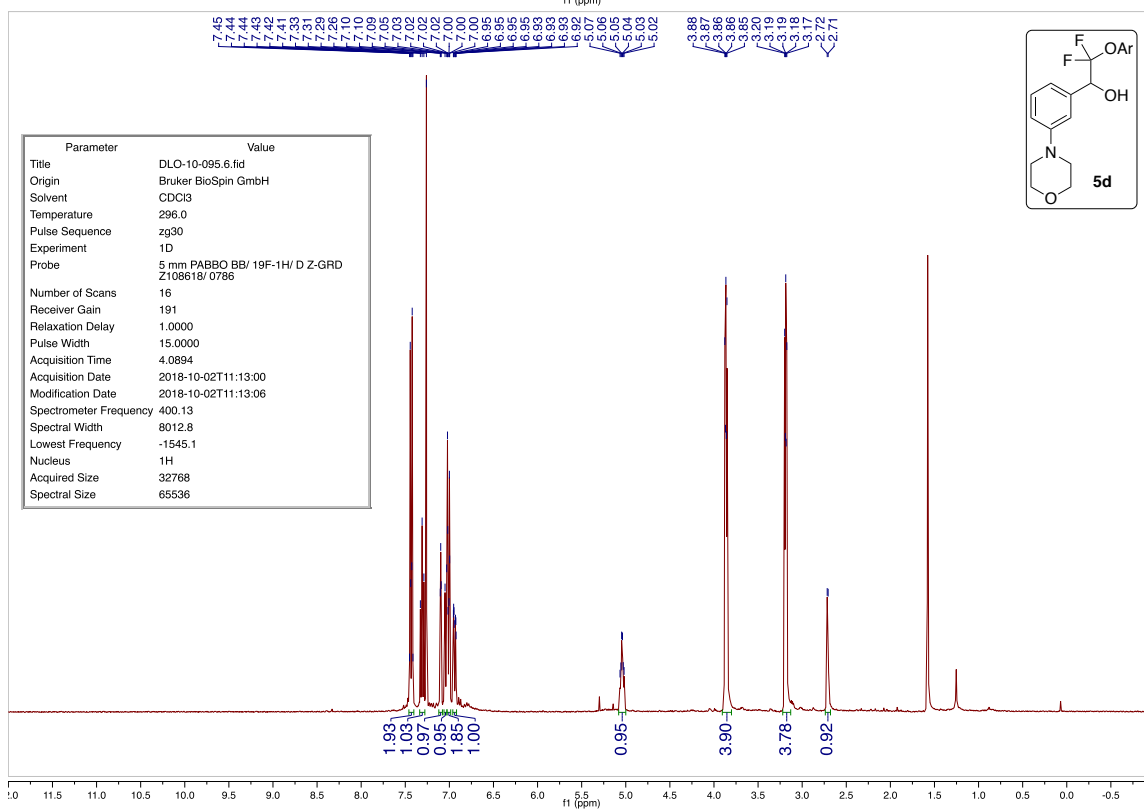
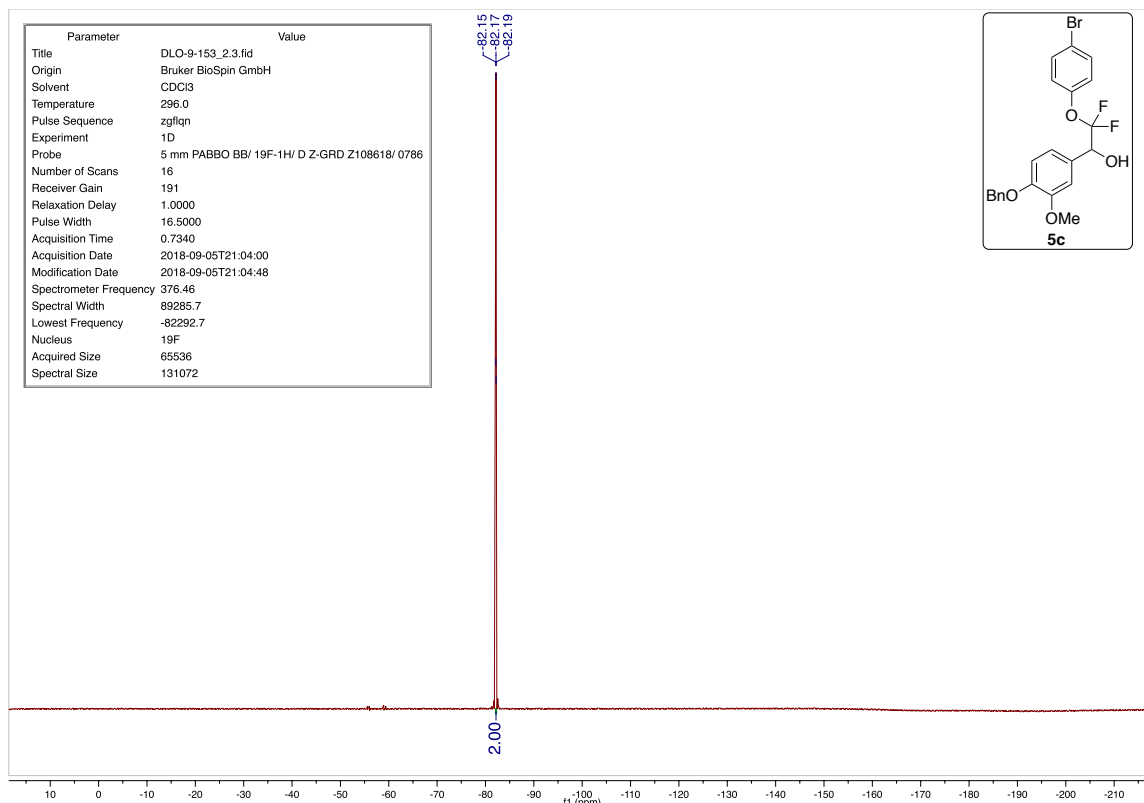
NMR Spectra of Compounds in Table 2

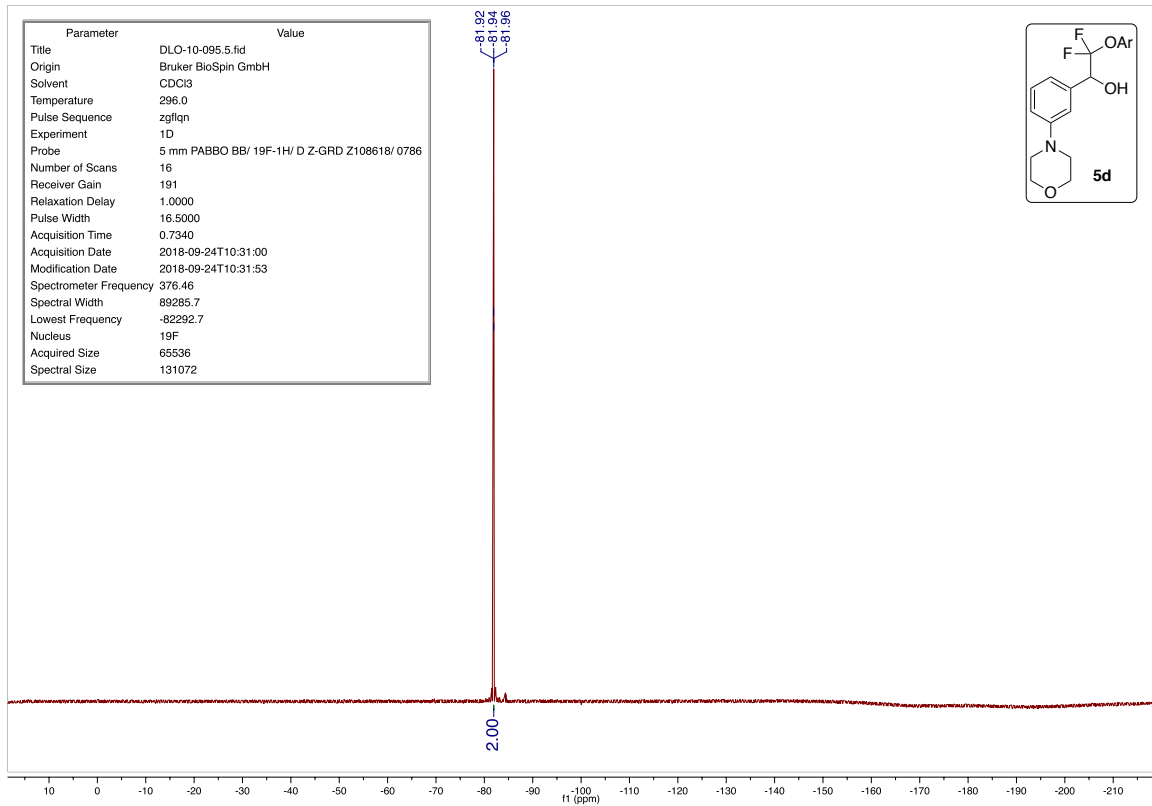
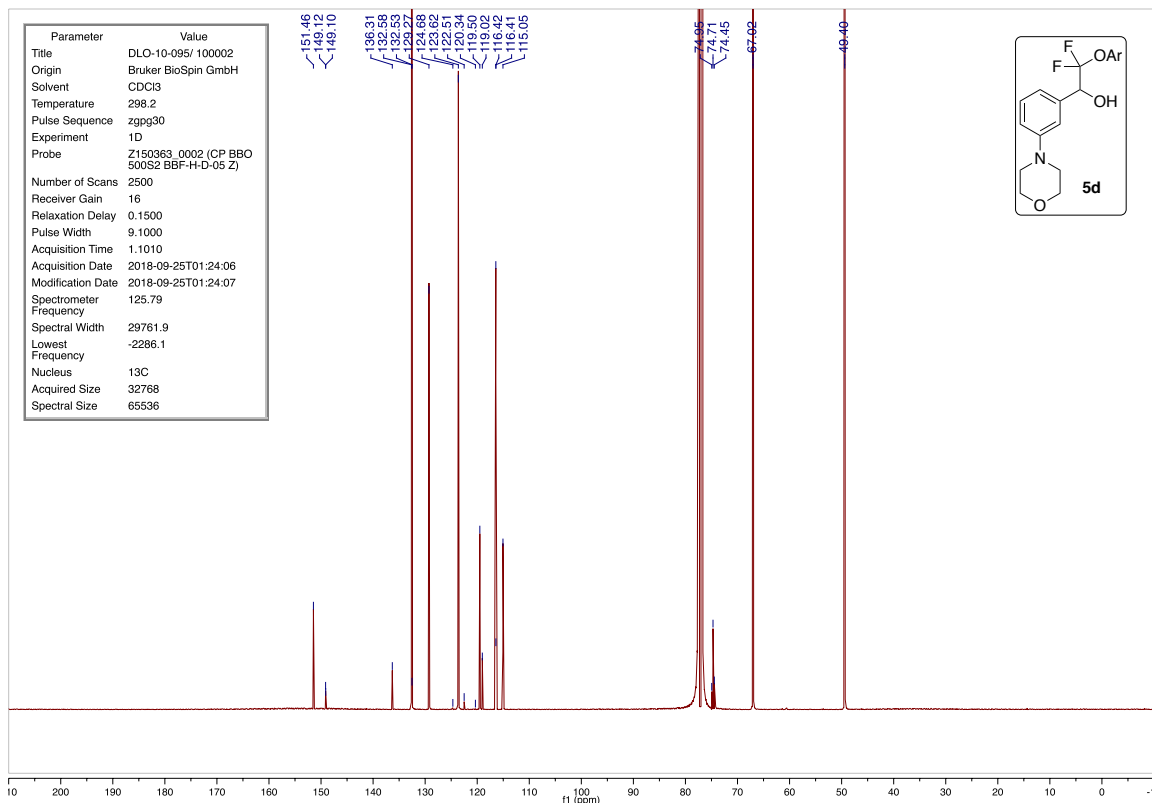


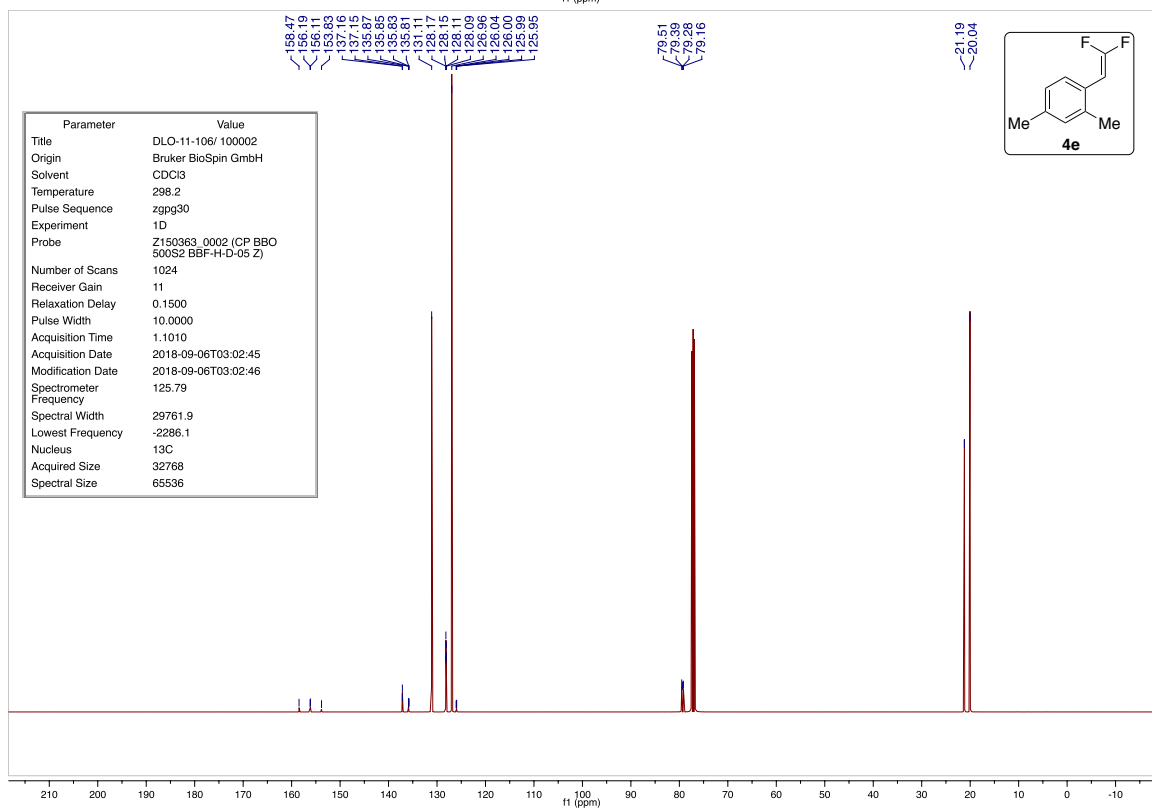
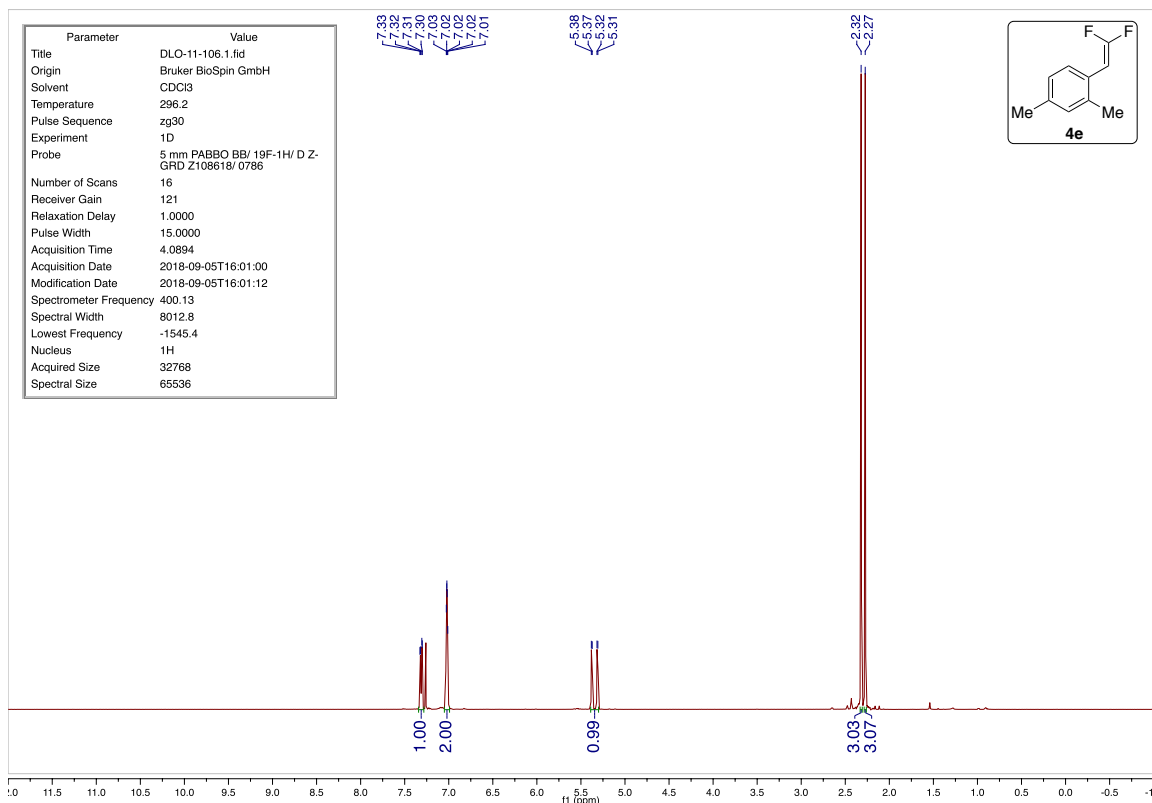


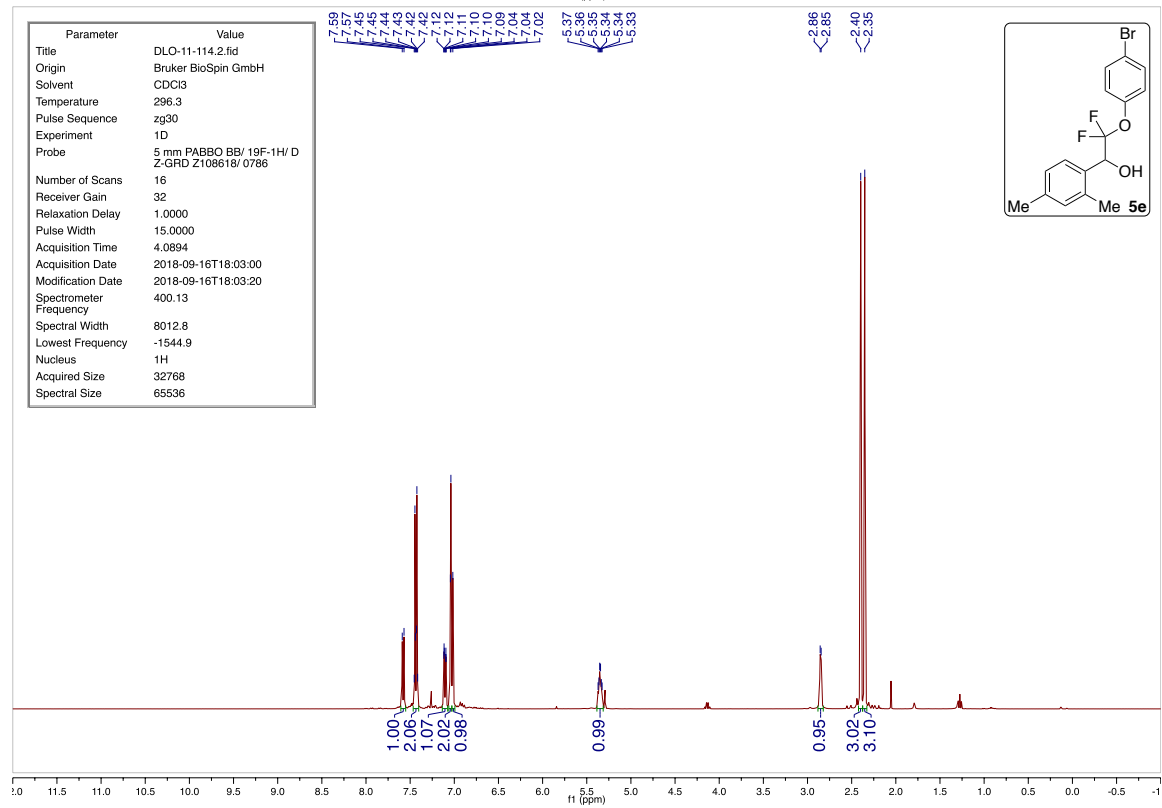
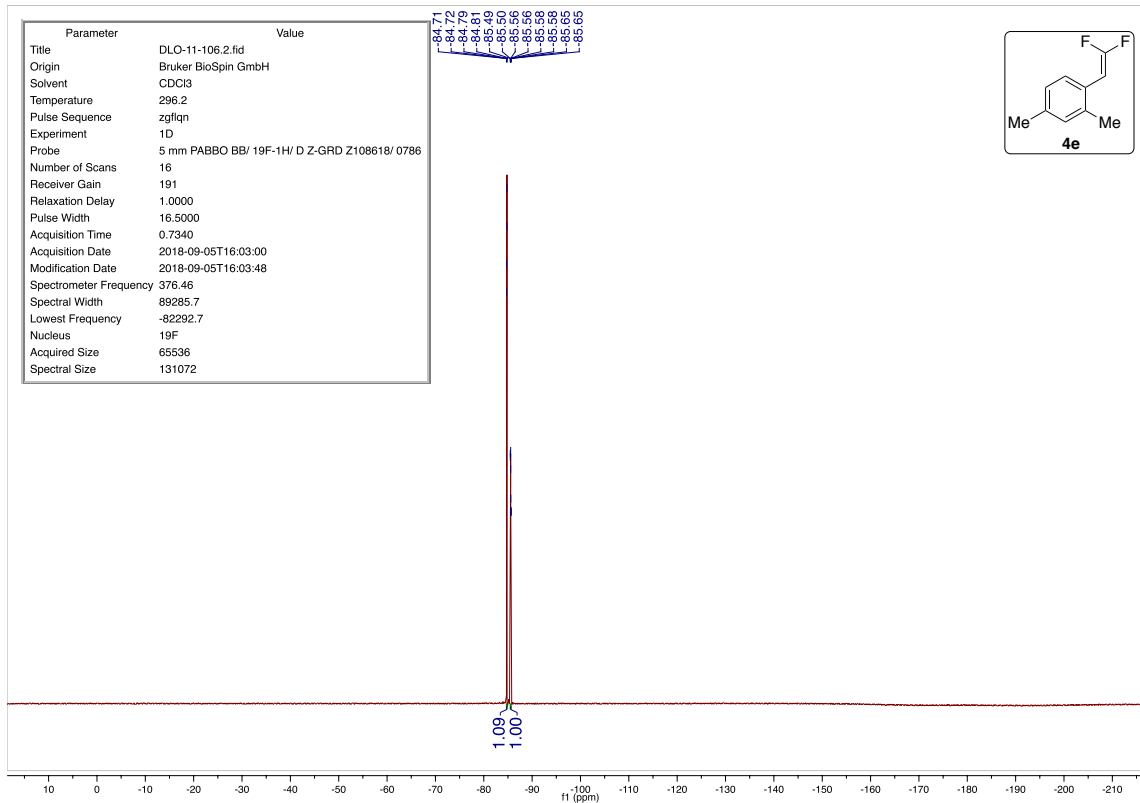


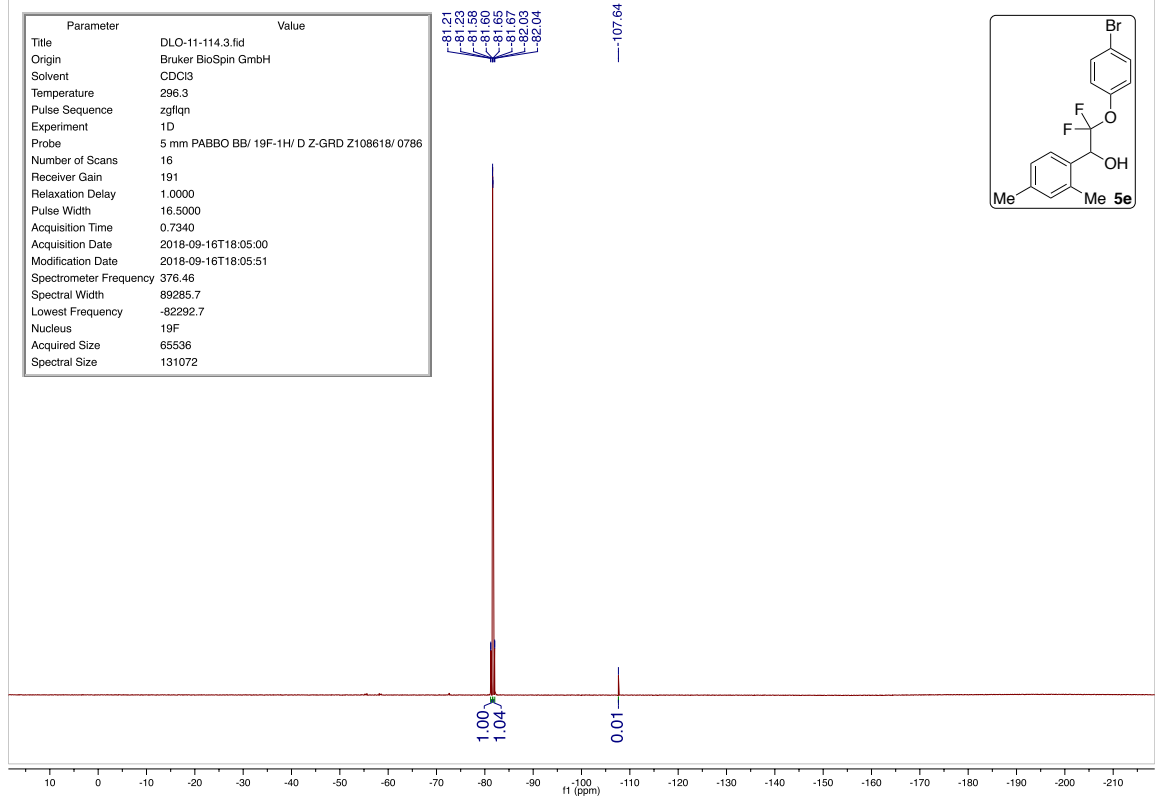
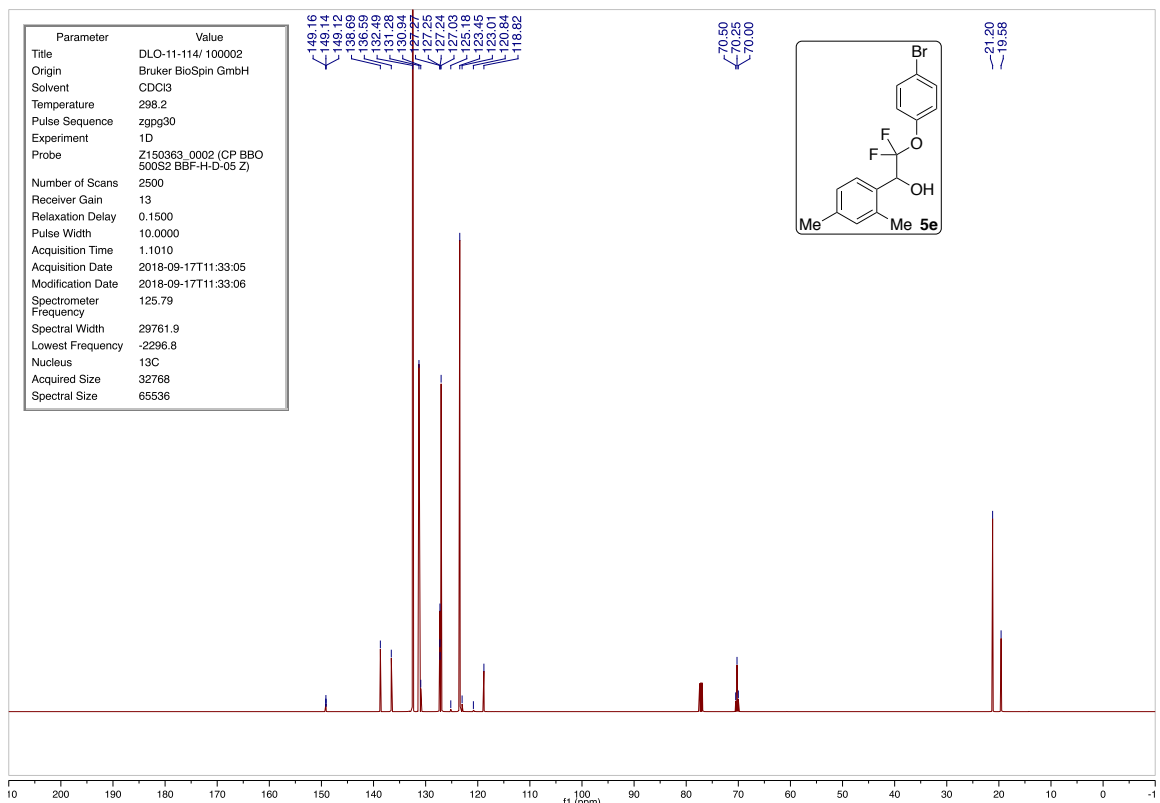


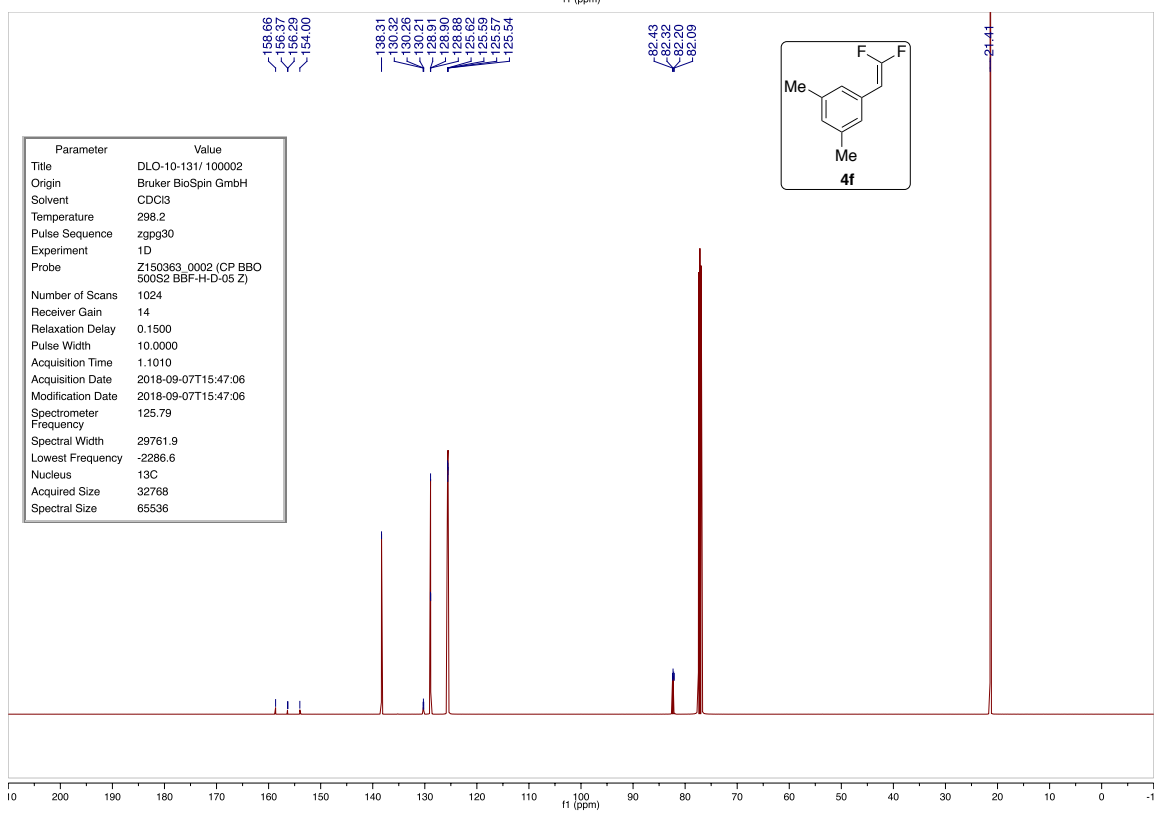
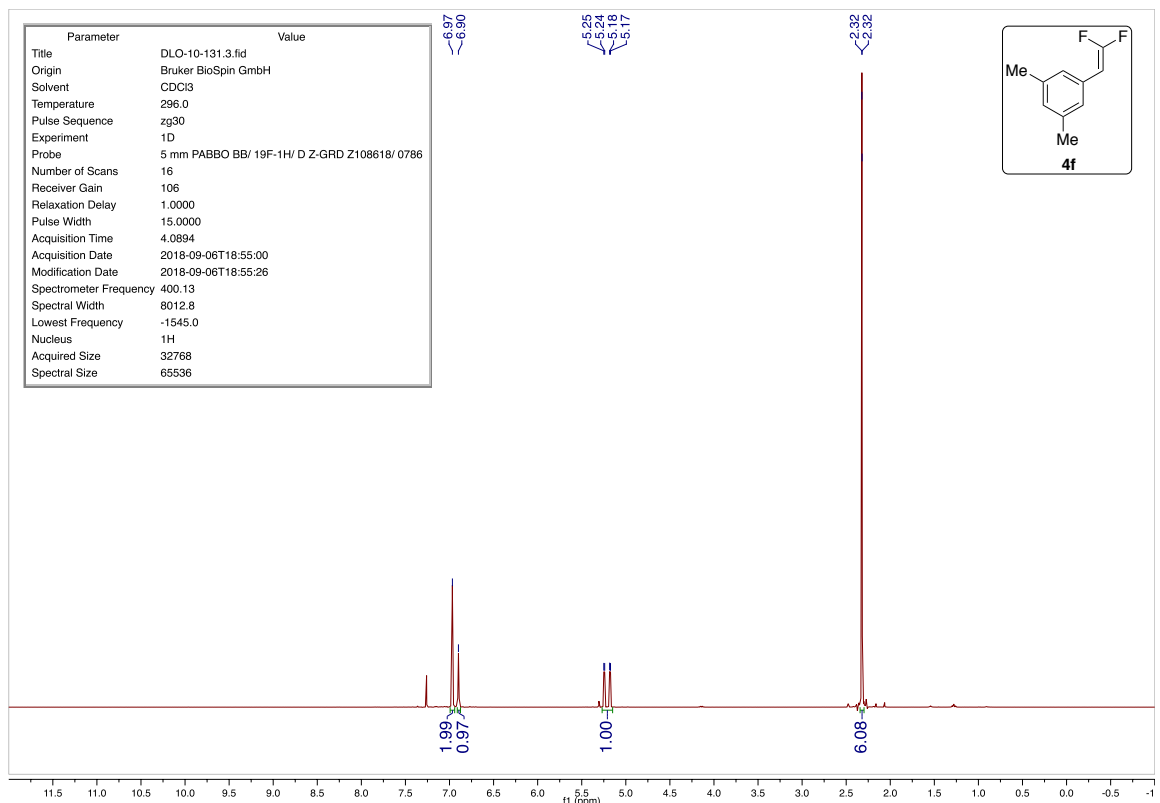


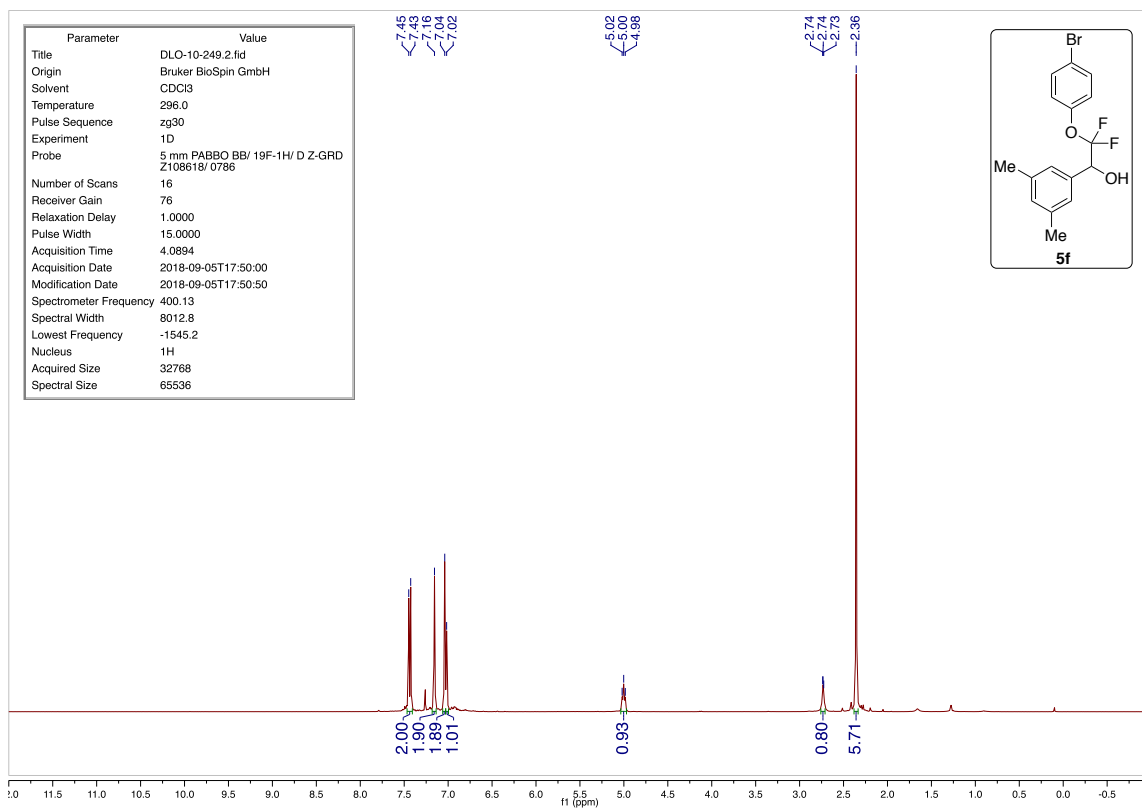
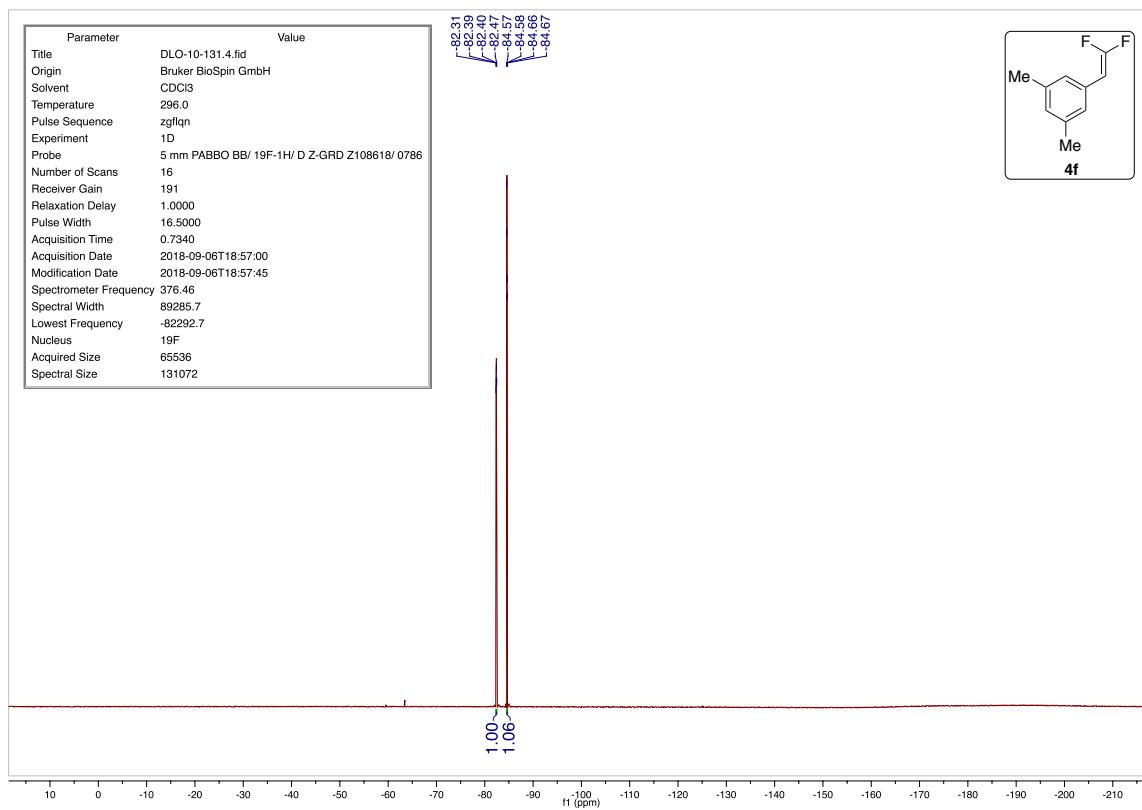


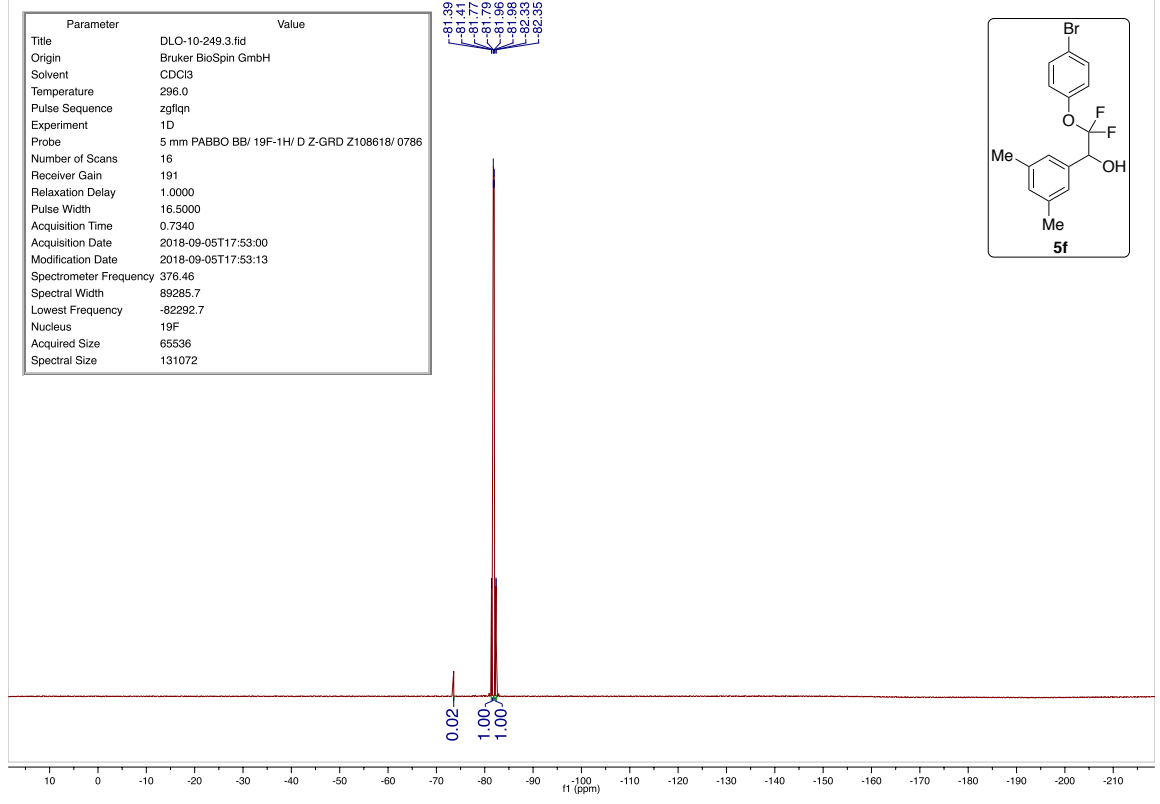
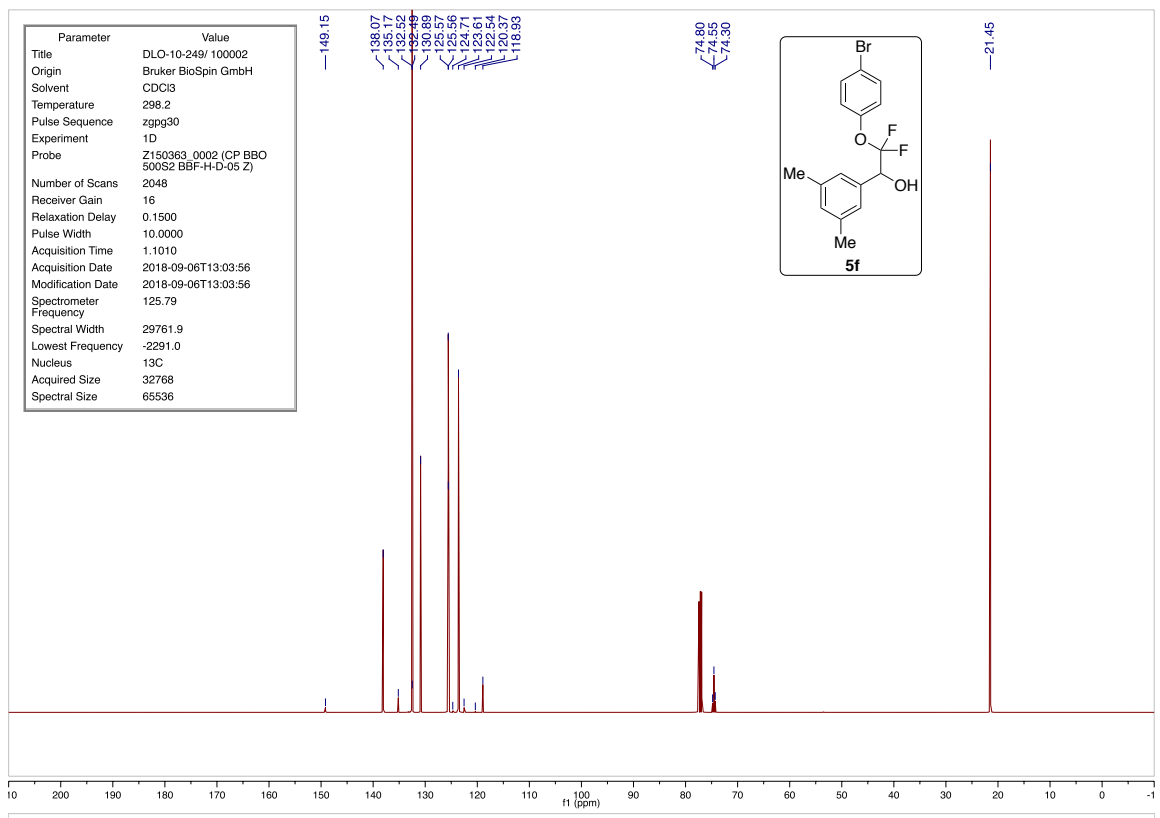


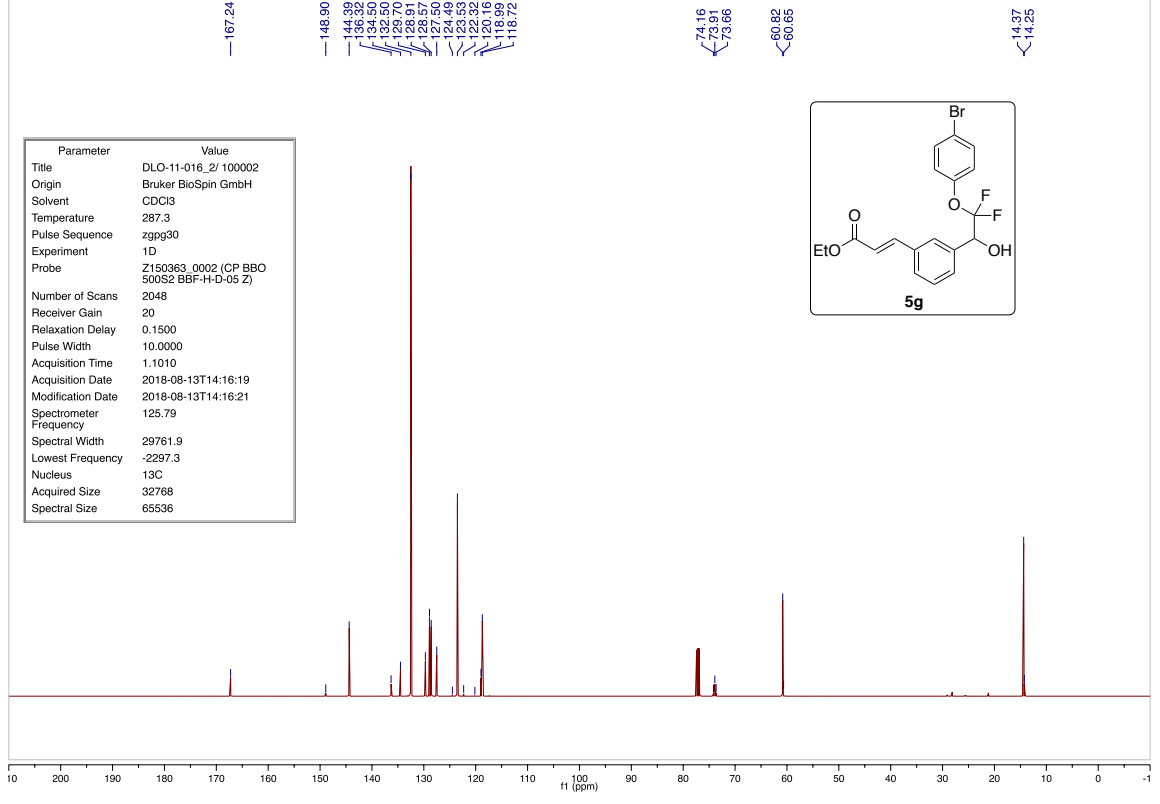
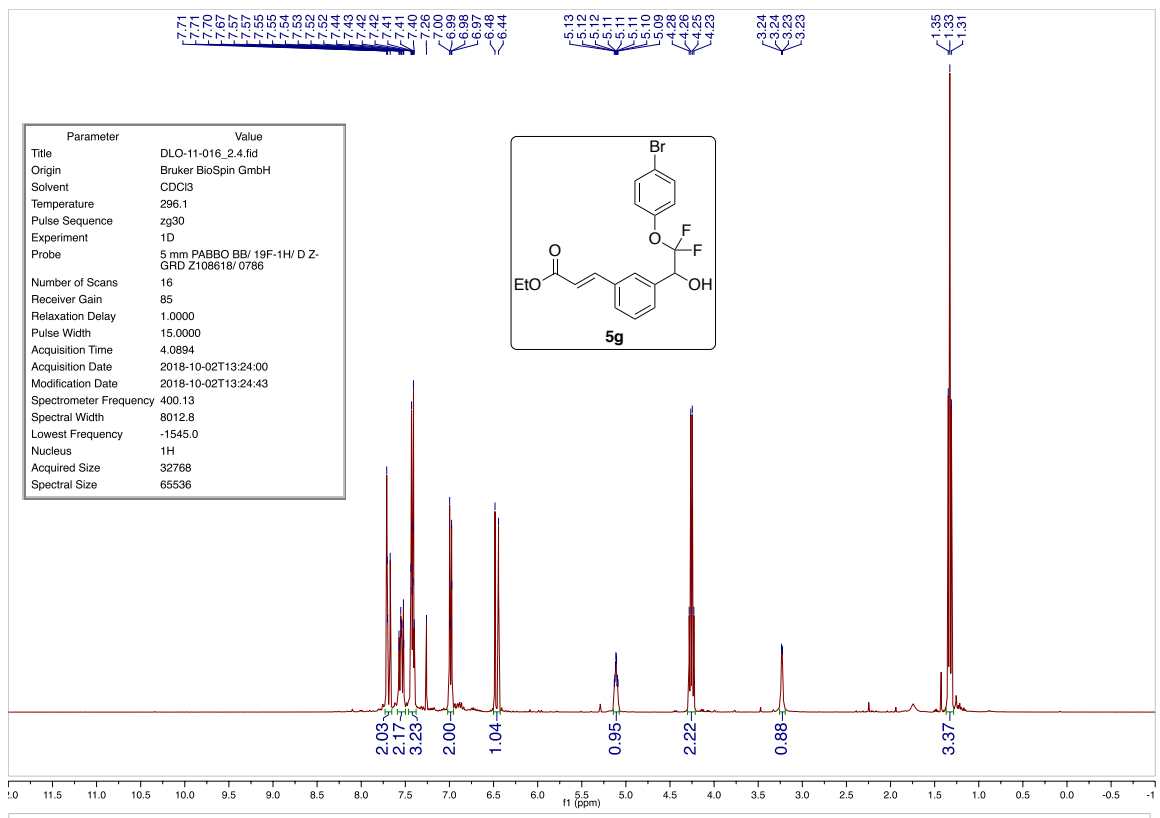


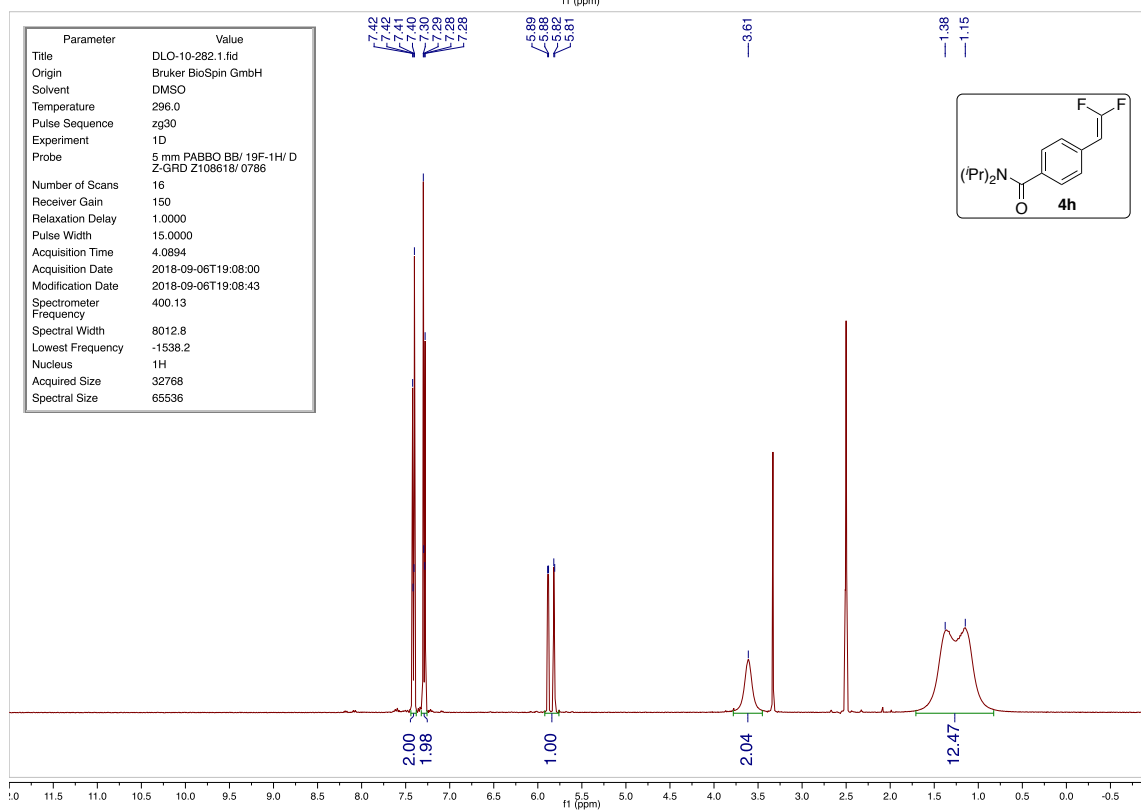
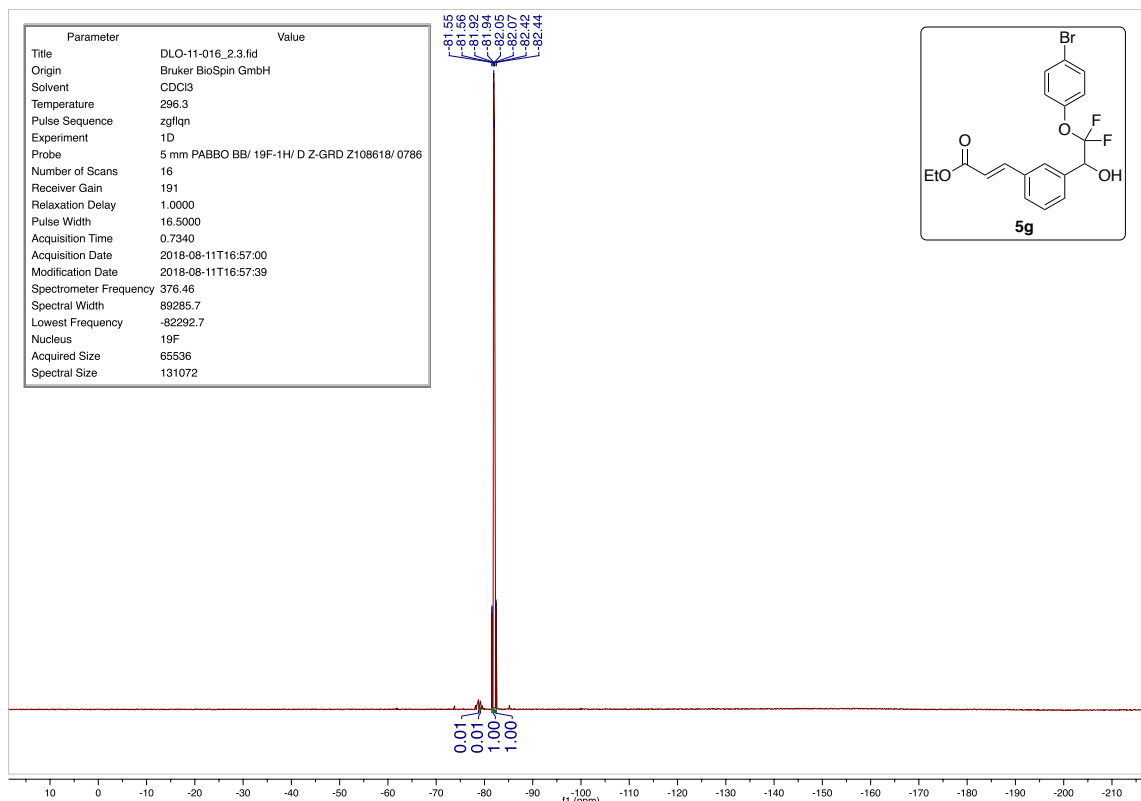


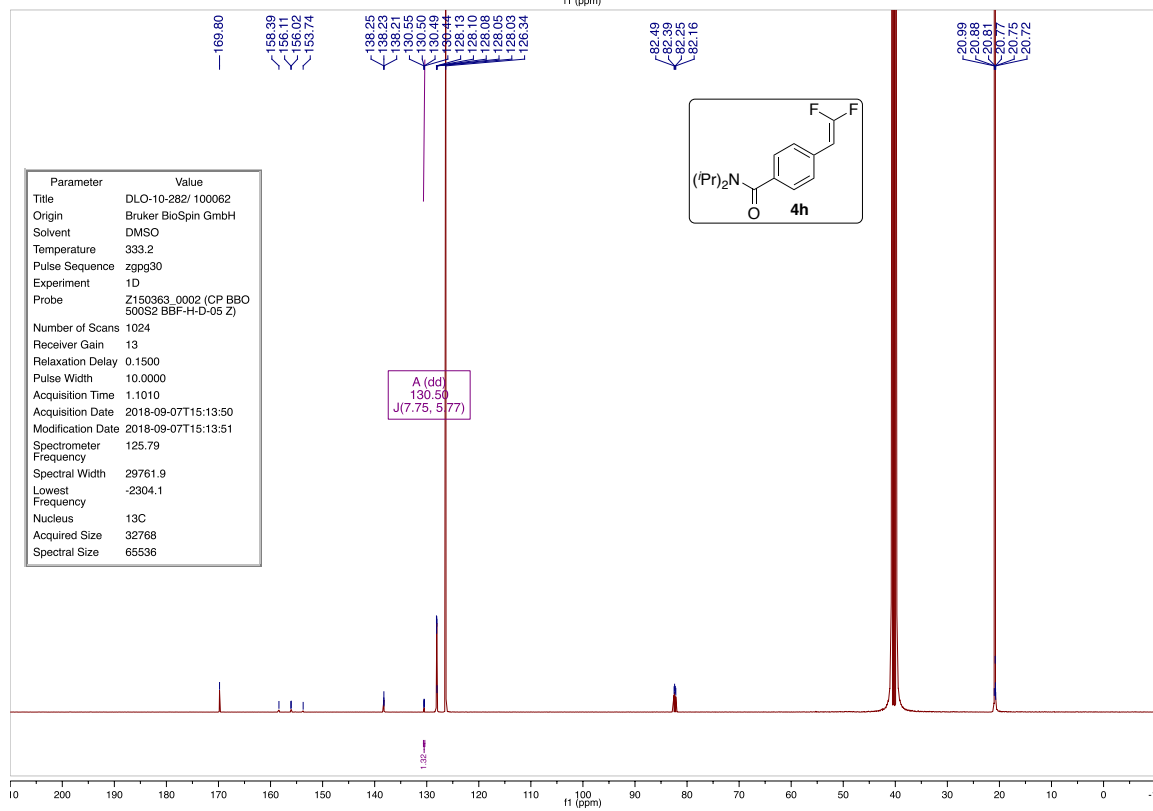
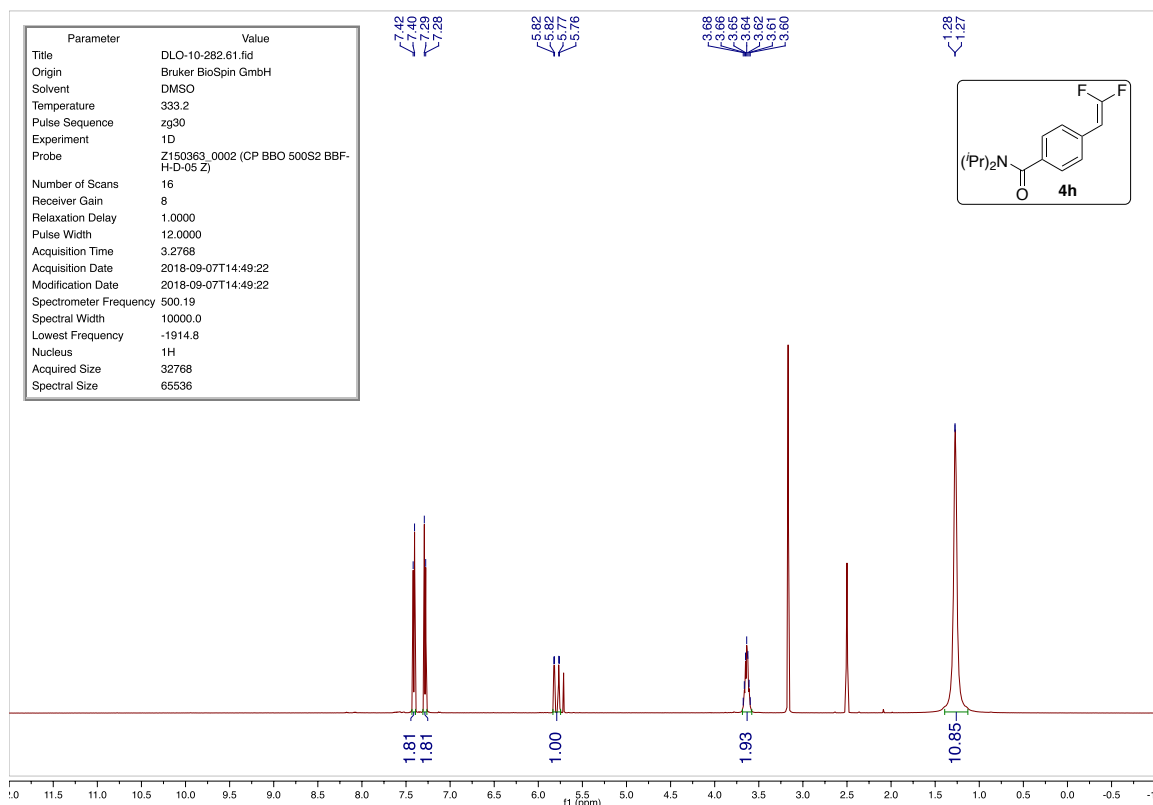


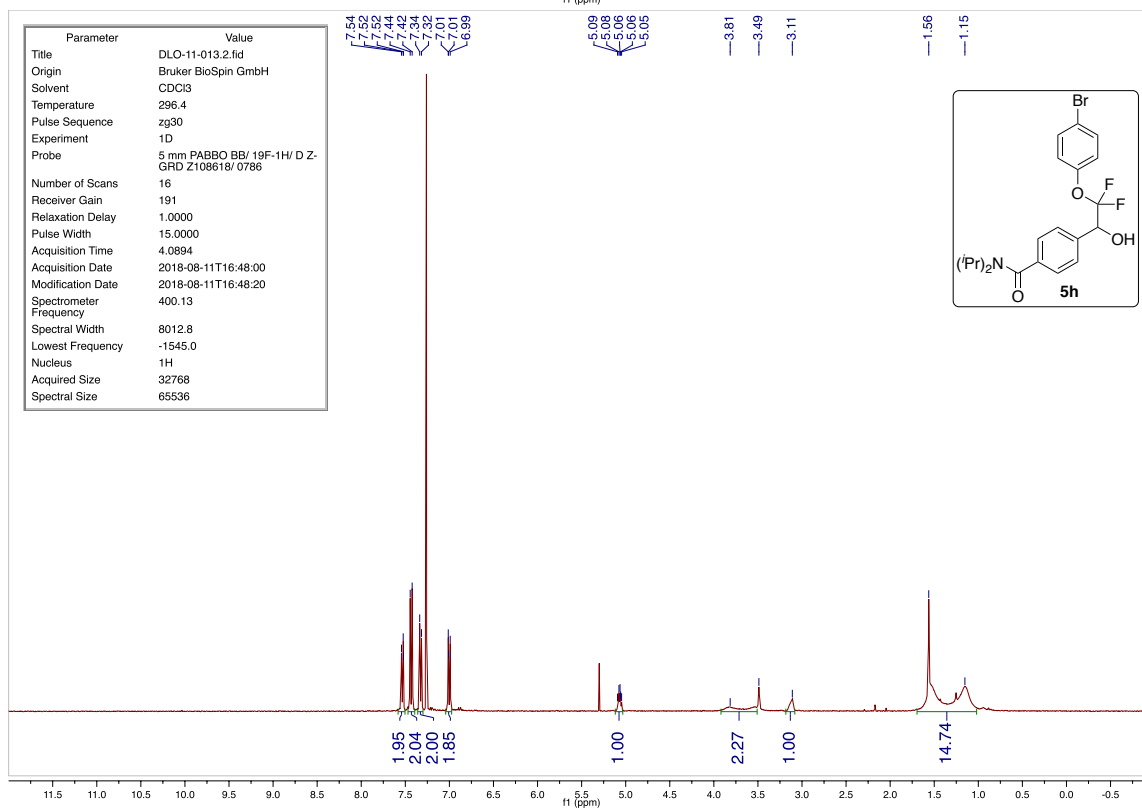
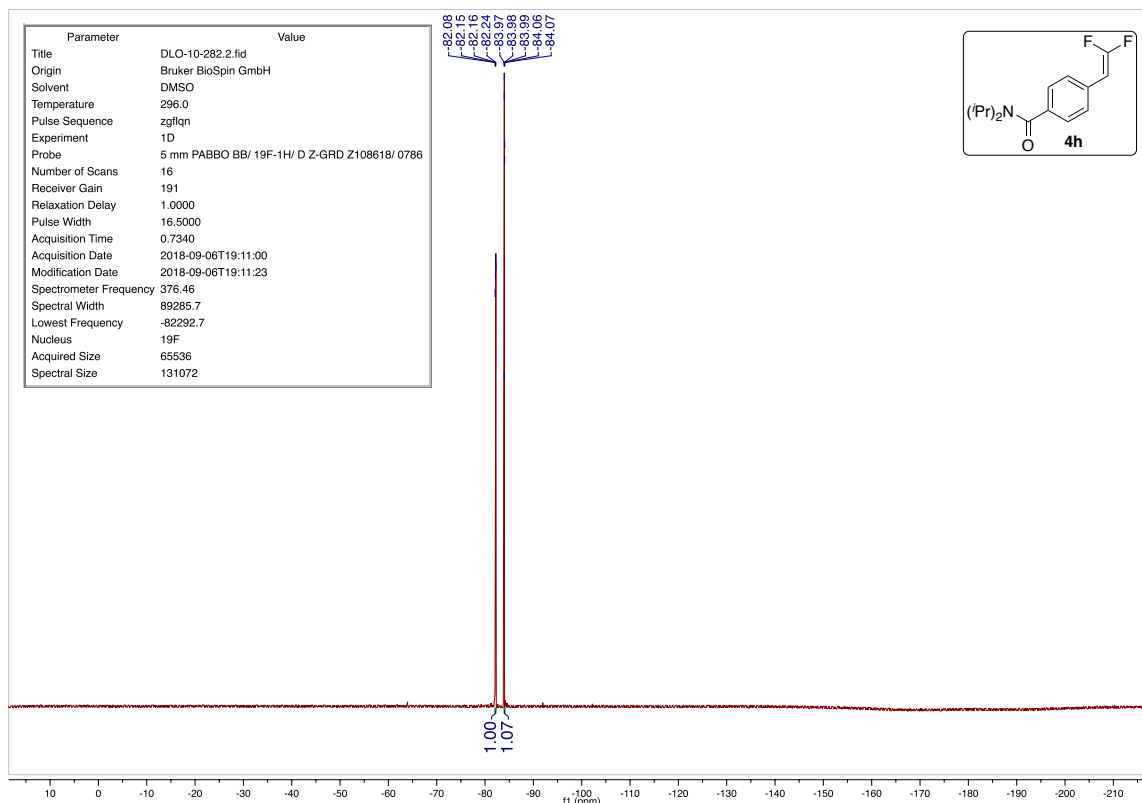


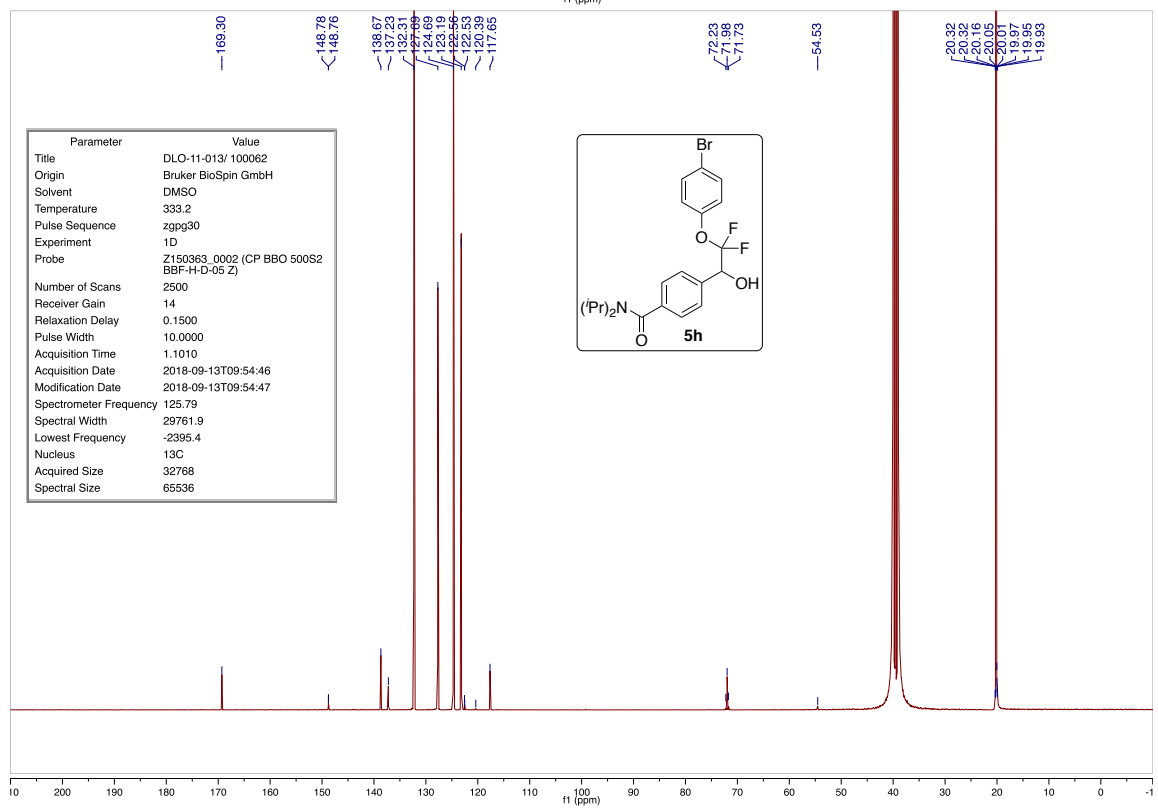
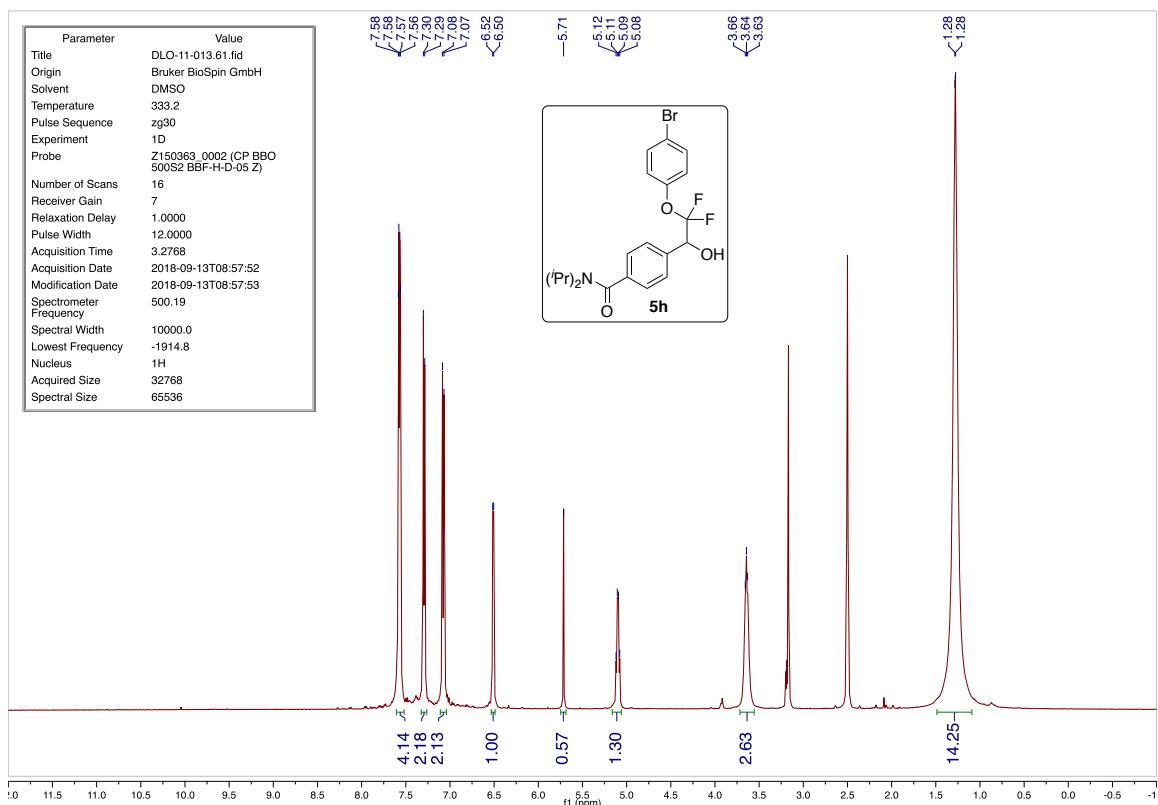


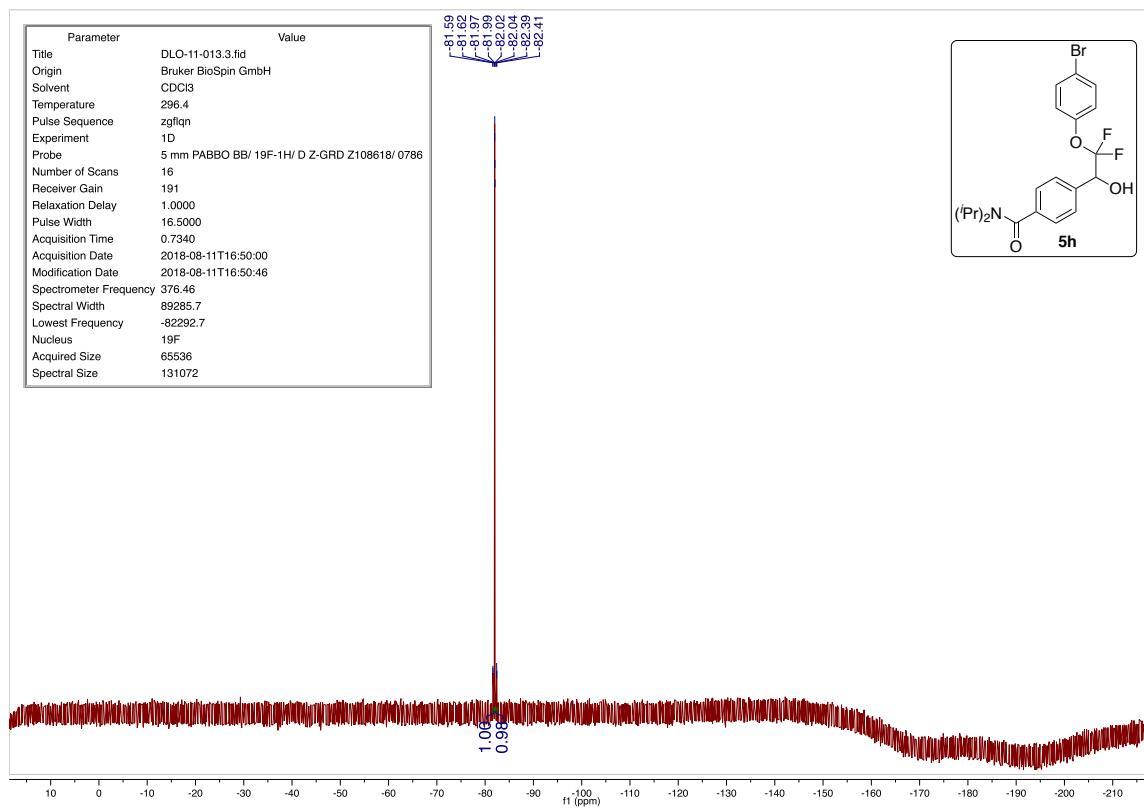


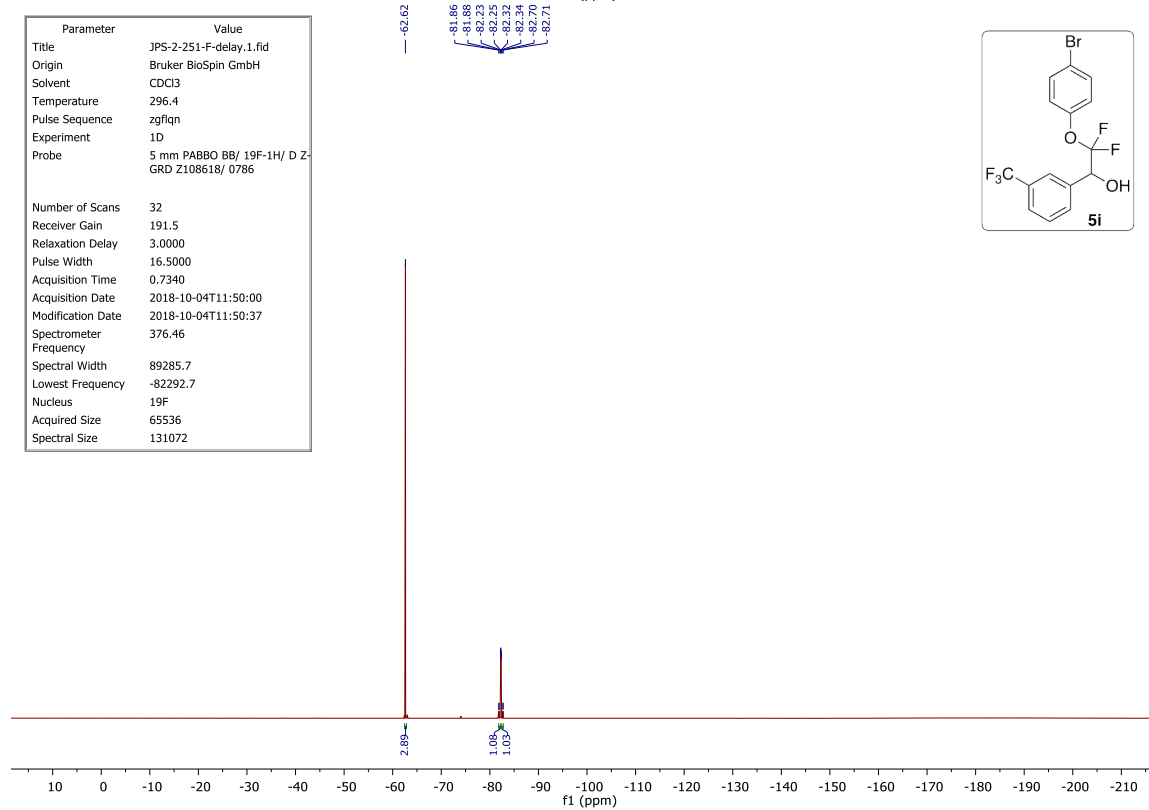
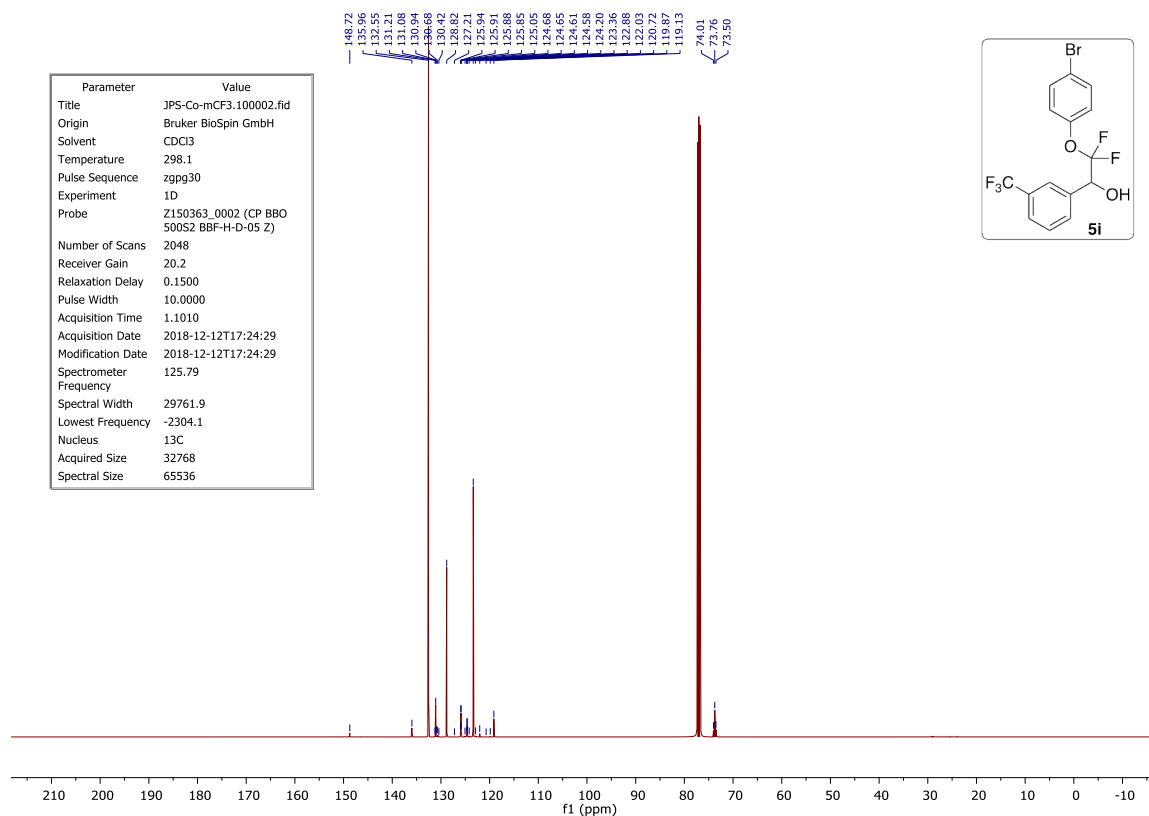


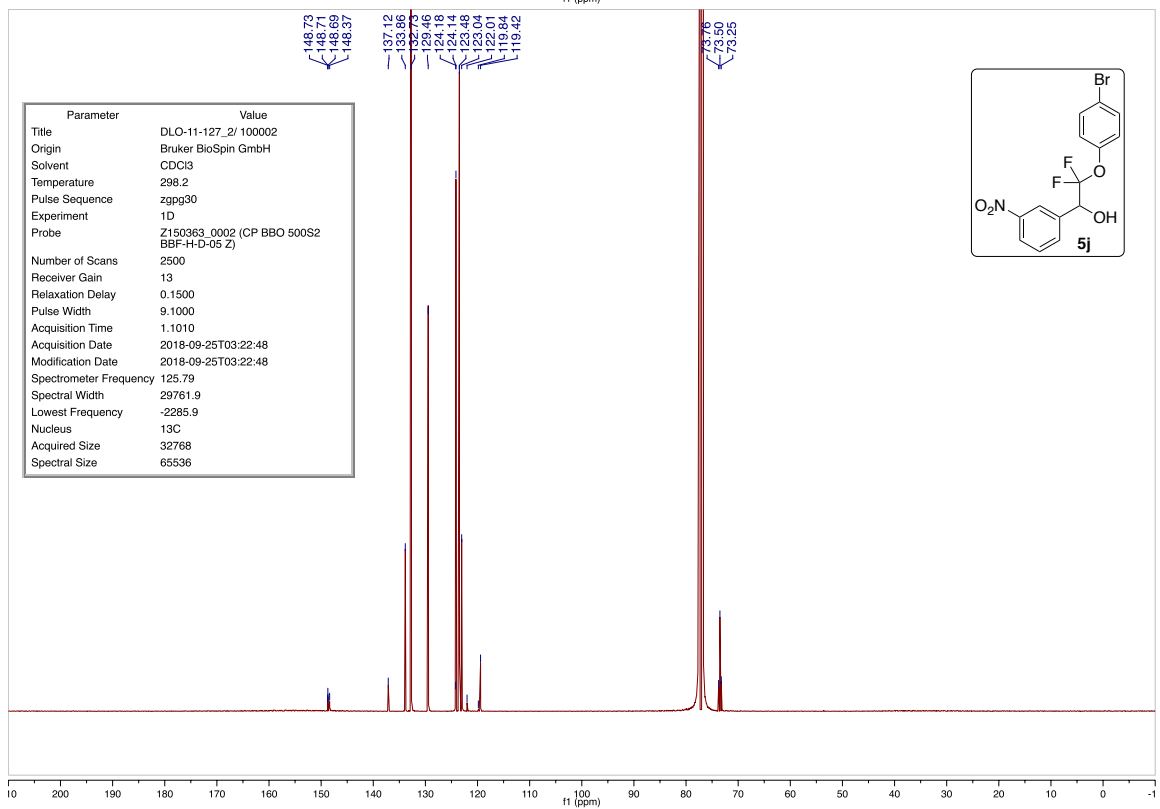
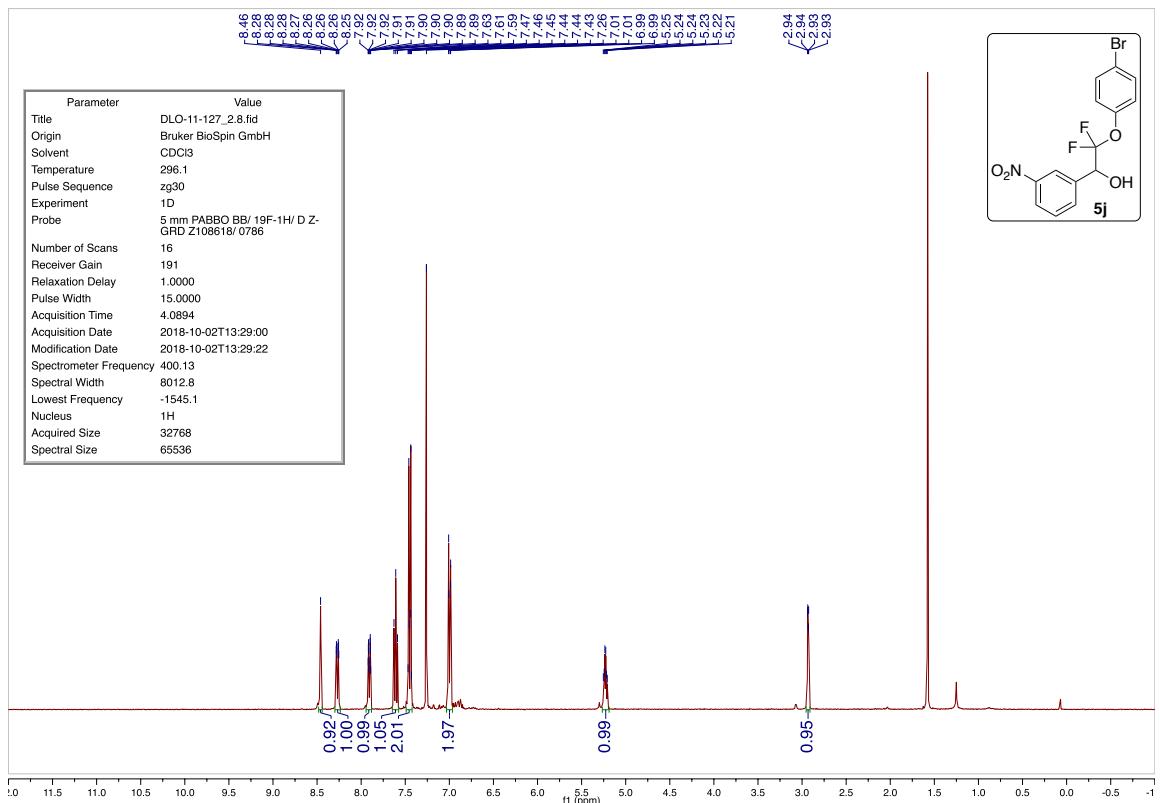


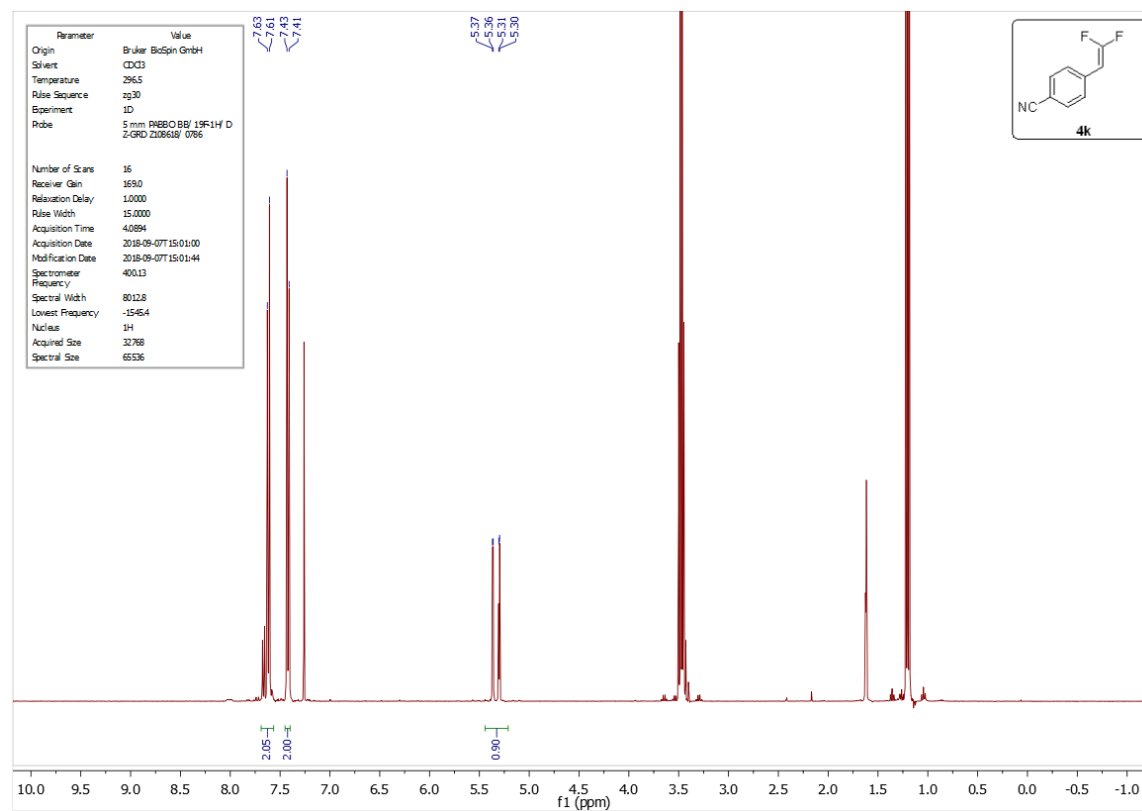
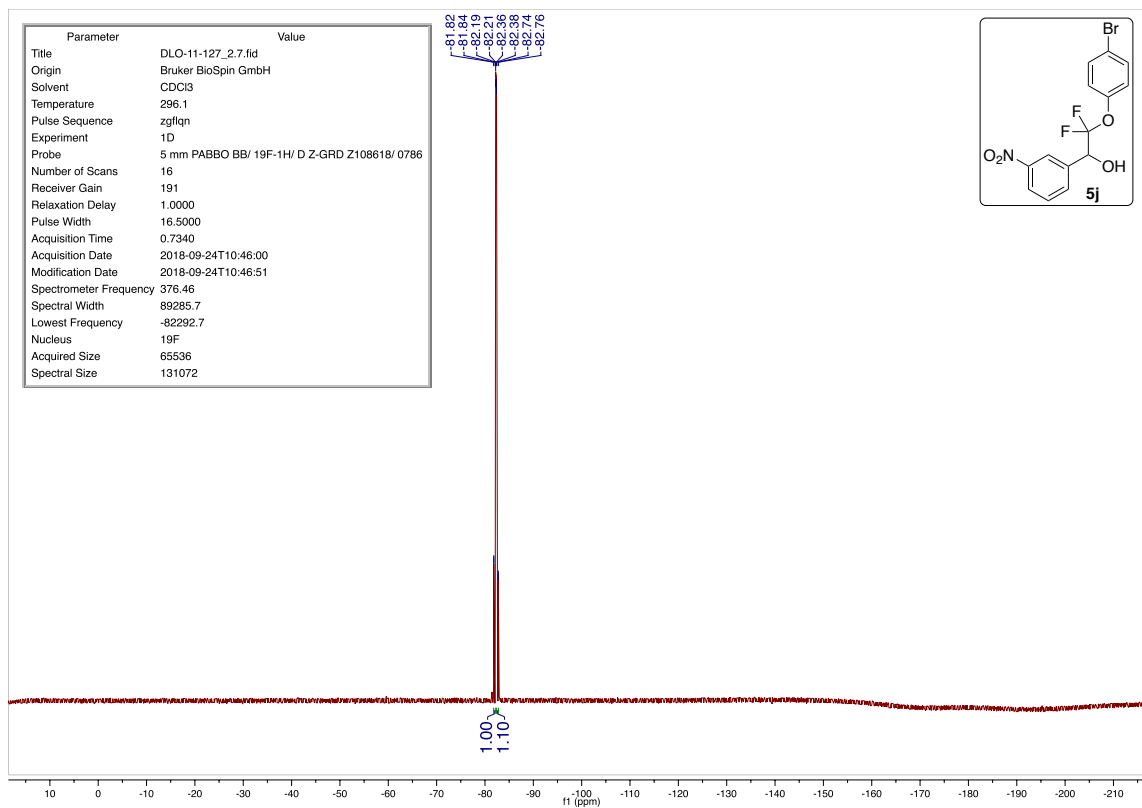






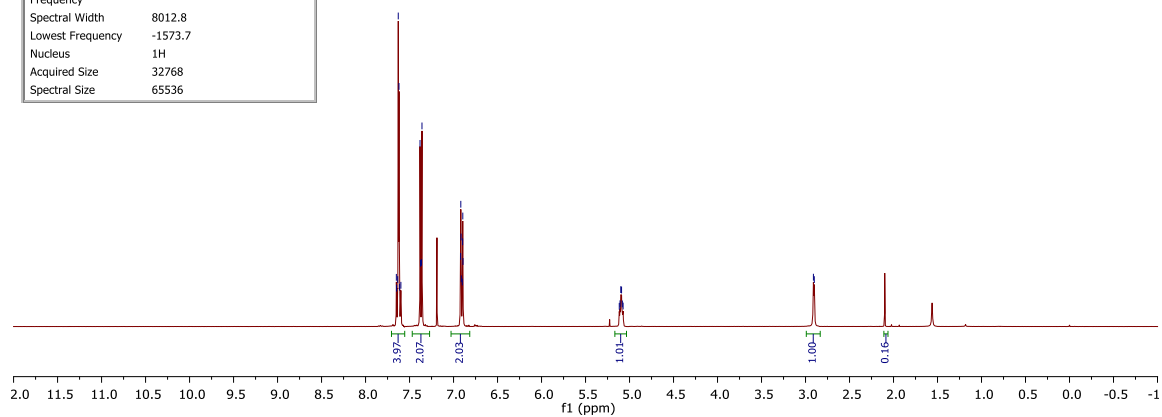
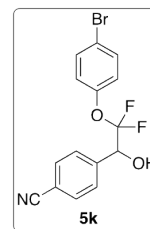






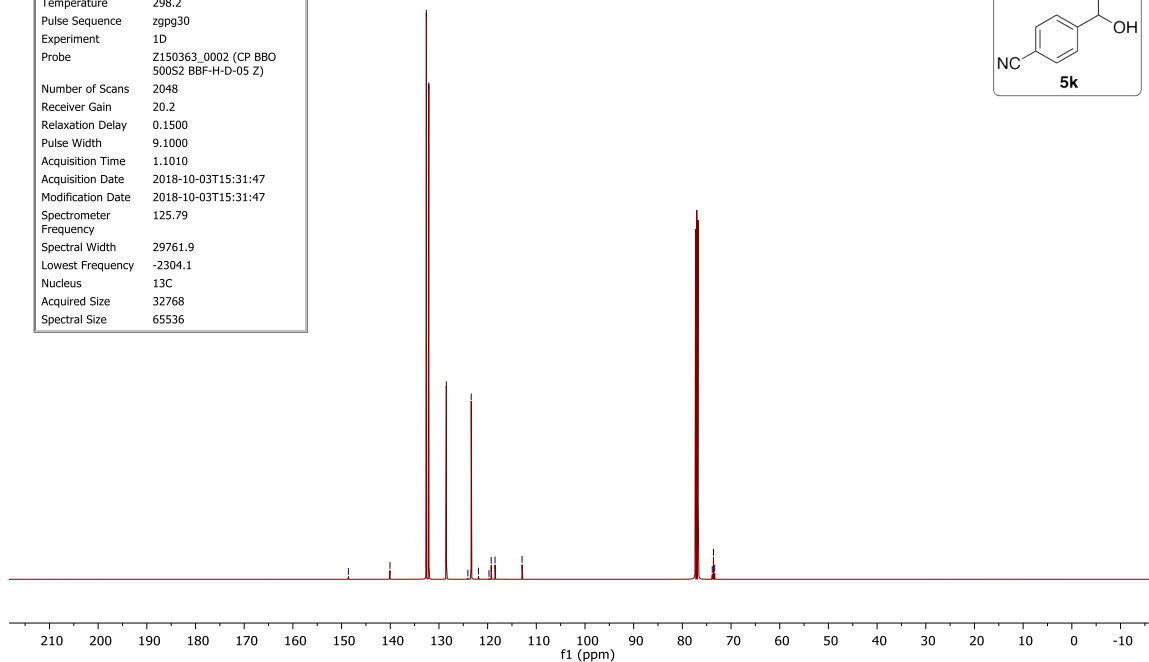
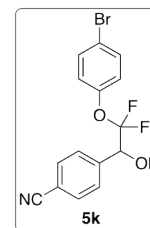
Parameter	Value
Title	JPS-2-292-F.5.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0786
Number of Scans	16
Receiver Gain	169.0
Relaxation Delay	1.0000
Pulse Width	15.0000
Acquisition Time	4.0894
Acquisition Date	2018-10-03T10:21:00
Modification Date	2018-10-03T10:21:12
Spectrometer	400.13
Frequency	
Spectral Width	8012.8
Lowest Frequency	-1573.7
Nucleus	1H
Acquired Size	32768
Spectral Size	65536

7.65
7.65
7.63
7.62
7.61
7.60
7.58
7.38
7.36
6.92
6.92
6.91
6.90
6.90
6.89
5.12
5.11
5.10
5.09
5.08
5.07
2.91
2.90



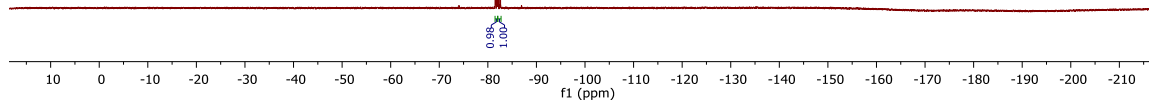
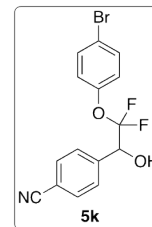
Parameter	Value
Title	JPS-2-292-F.100002.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	298.2
Pulse Sequence	zpgg30
Experiment	1D
Probe	Z150363_0002 (CP BBO 50052 BBF-H-D-05 Z)
Number of Scans	2048
Receiver Gain	20.2
Relaxation Delay	0.1500
Pulse Width	9.1000
Acquisition Time	1.1010
Acquisition Date	2018-10-03T15:31:47
Modification Date	2018-10-03T15:31:47
Spectrometer	125.79
Frequency	
Spectral Width	29761.9
Lowest Frequency	-2304.1
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

148.60
140.05
132.89
128.49
128.49
124.06
123.37
121.89
119.76
118.47
112.92
73.86
73.71
73.36



Parameter	Value
Title	JPS-2-292-F.7.fid
Origin	Bruker BioSpin GmbH
Solvent	CDCl3
Temperature	296.2
Pulse Sequence	zgfgq
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z108618/ 0786
Number of Scans	24
Receiver Gain	191.5
Relaxation Delay	1.0000
Pulse Width	16.5000
Acquisition Time	0.7340
Acquisition Date	2018-10-03T10:23:00
Modification Date	2018-10-03T10:23:49
Spectrometer	376.46
Frequency	
Spectral Width	89285.7
Lowest Frequency	-82292.7
Nucleus	19F
Acquired Size	65536
Spectral Size	131072

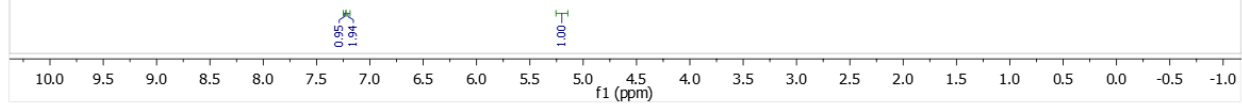
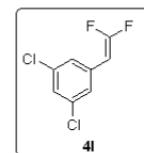
81.55
81.57
81.59
81.61
81.63
82.13
82.14
82.50

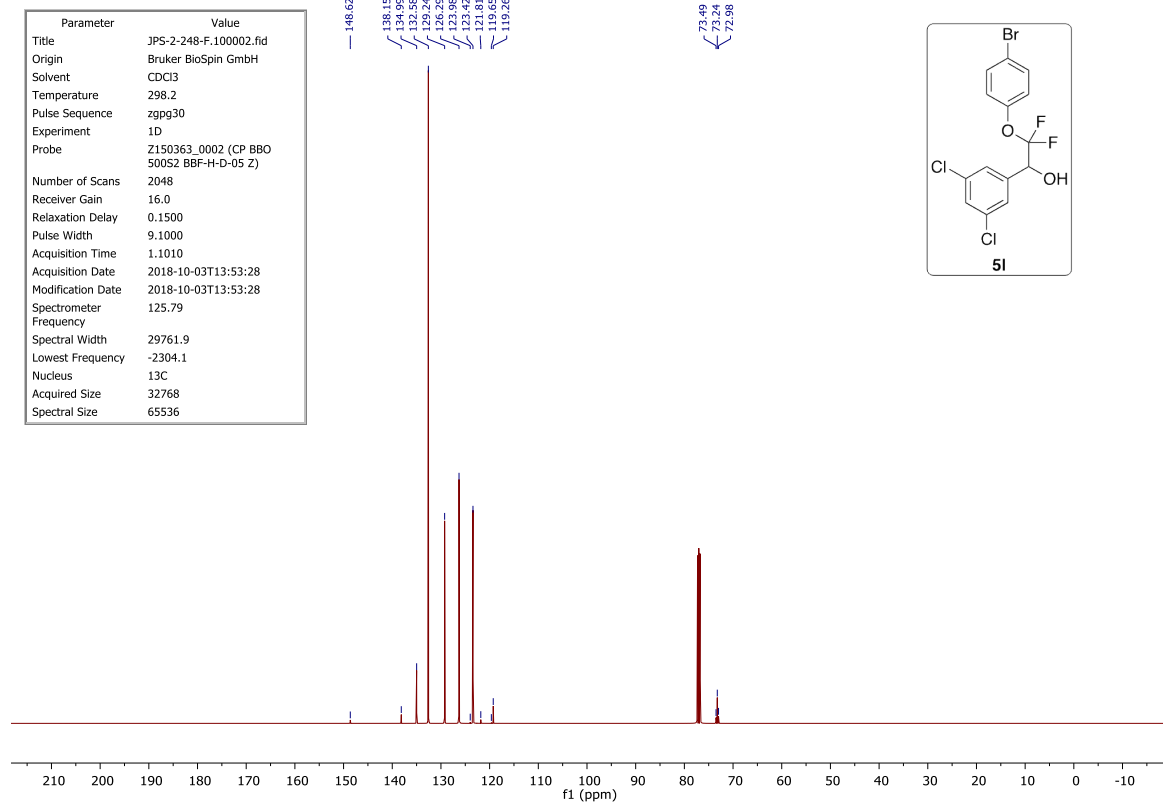
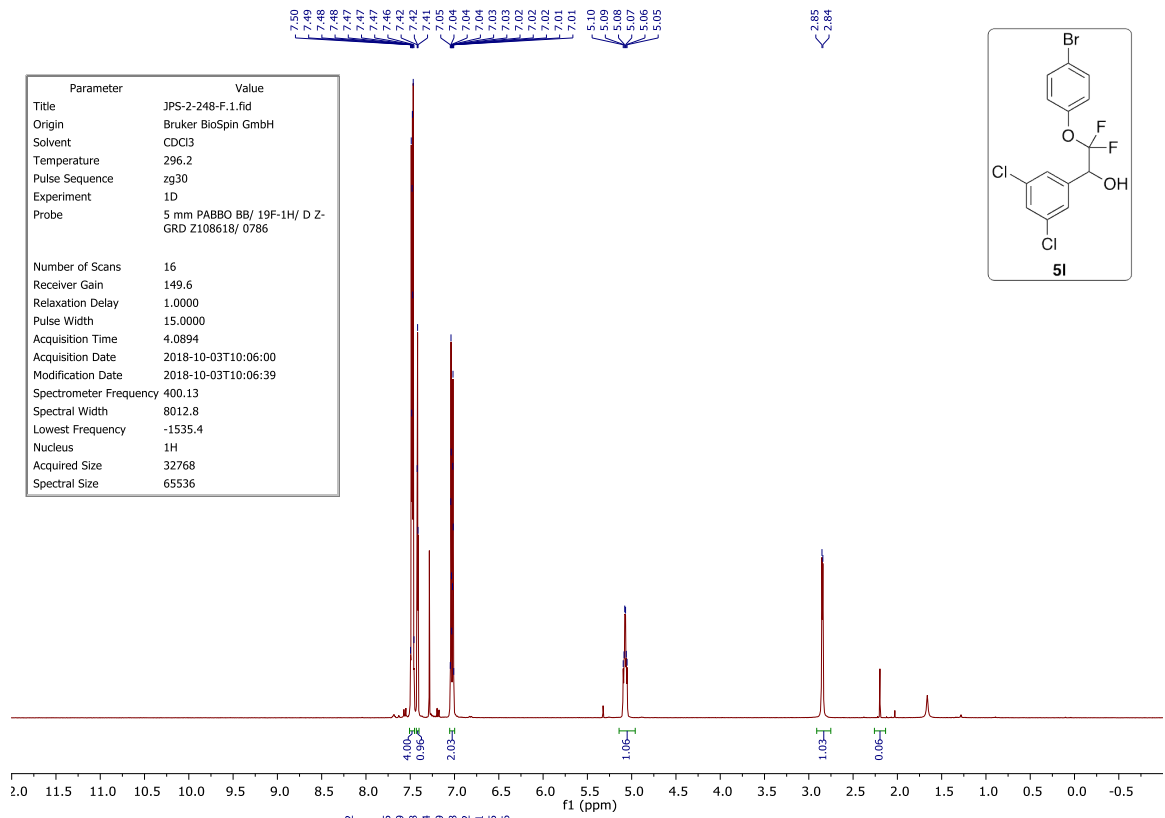


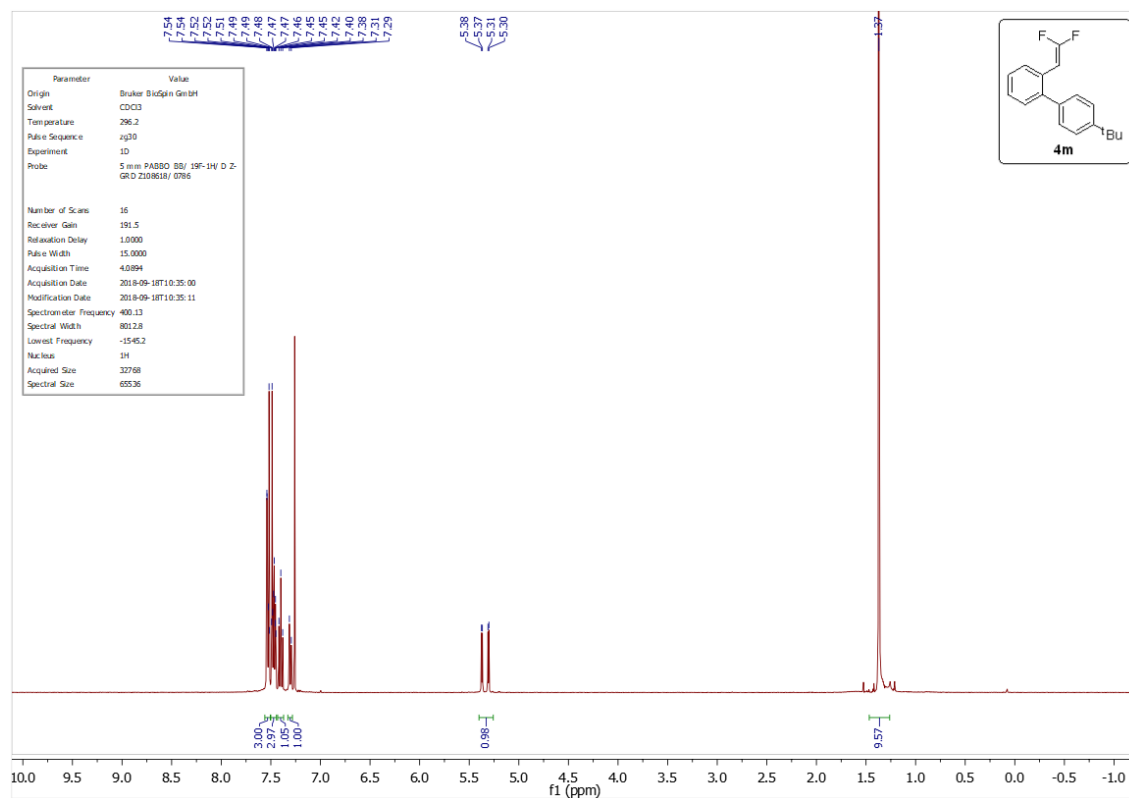
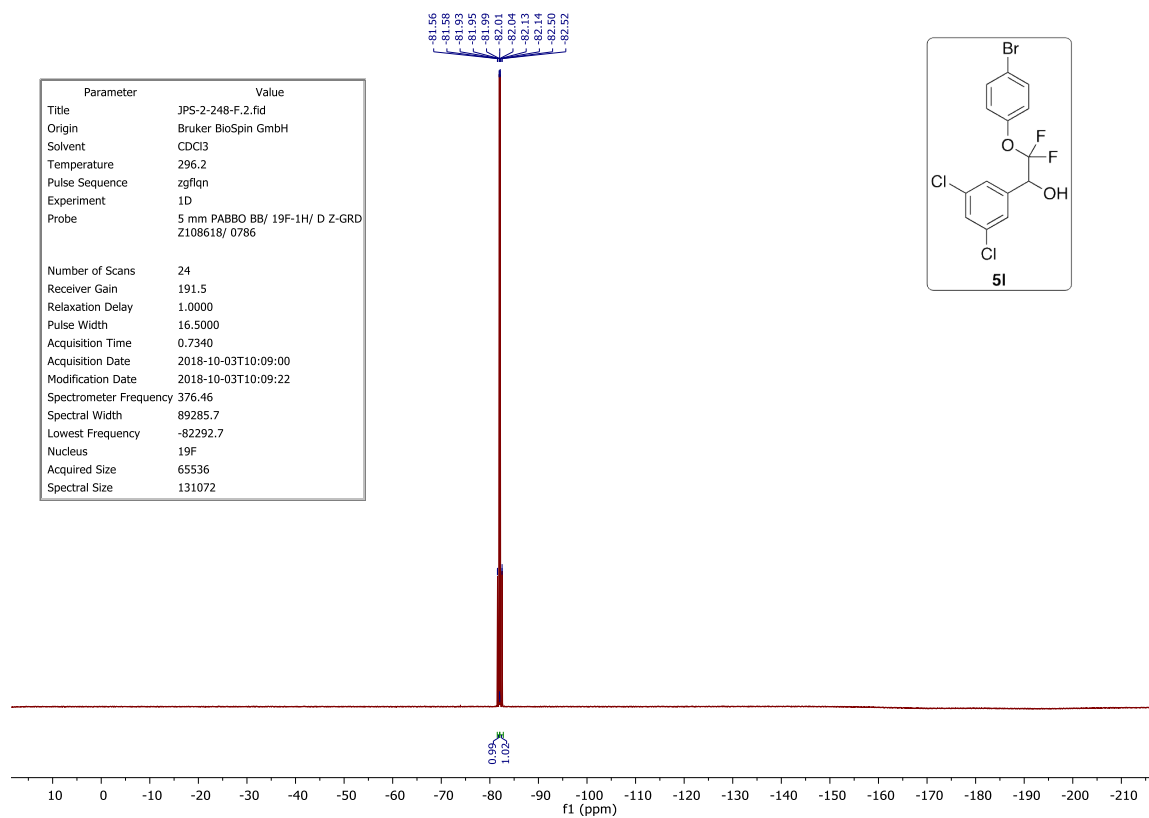
Parameter	Value
Origin	UKNMR, Bruker Analytische Messtechnik GmbH
Solvent	CDCl3
Temperature	301.7
Pulse Sequence	zg30
Experiment	1D
Probe	5 mm PABBO BB/ 19F-1H/ D Z-GRD Z10902/ 0011
Number of Scans	16
Receiver Gain	574.7
Relaxation Delay	1.0000
Pulse Width	15.2000
Acquisition Time	3.1719
Acquisition Date	2019-04-02T14:58:37
Modification Date	2019-04-02T14:58:40
Spectrometer Frequency	500.13
Spectral Width	10330.6
Lowest Frequency	-2089.8
Nucleus	1H
Acquired Size	32788
Spectral Size	65536

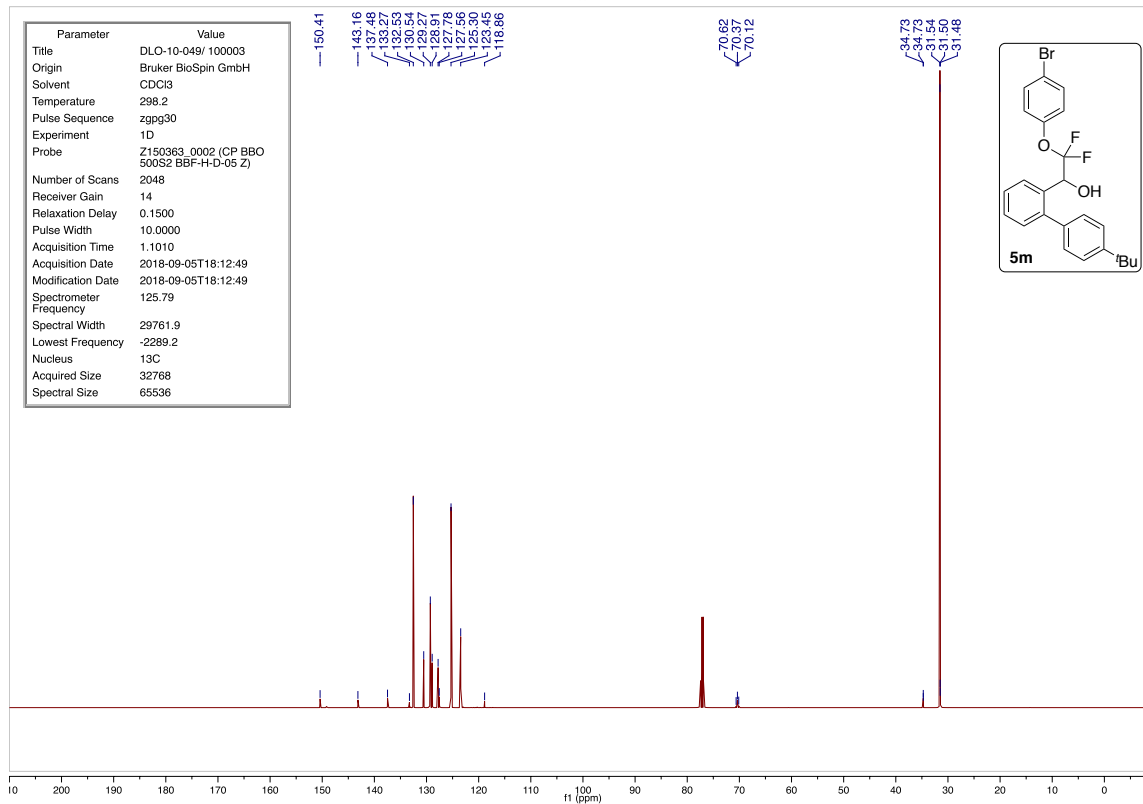
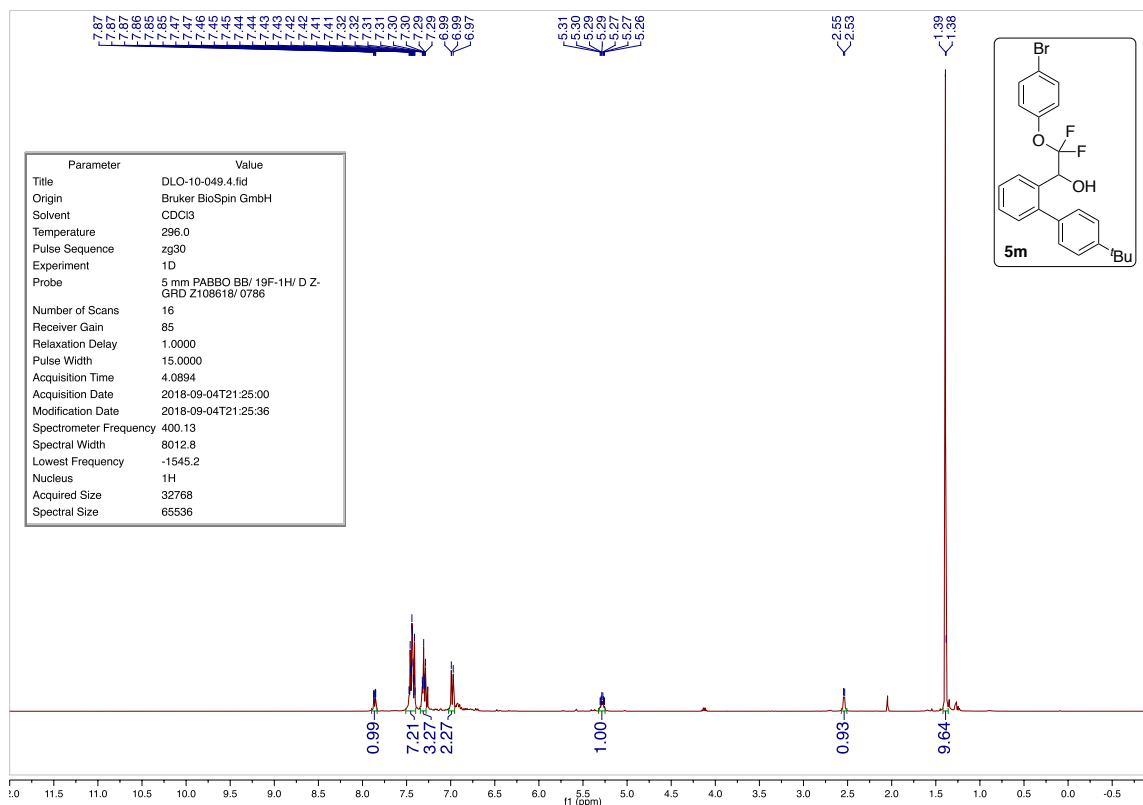
7.26
7.24
7.24
7.24
7.21

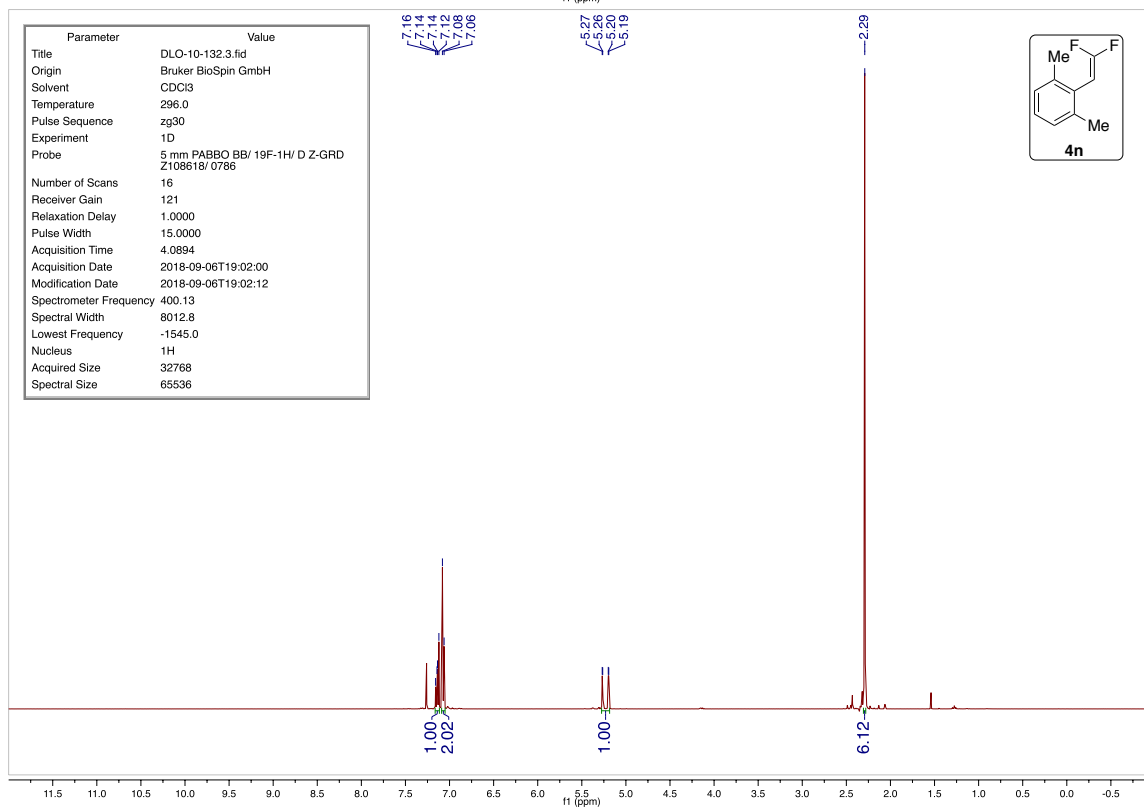
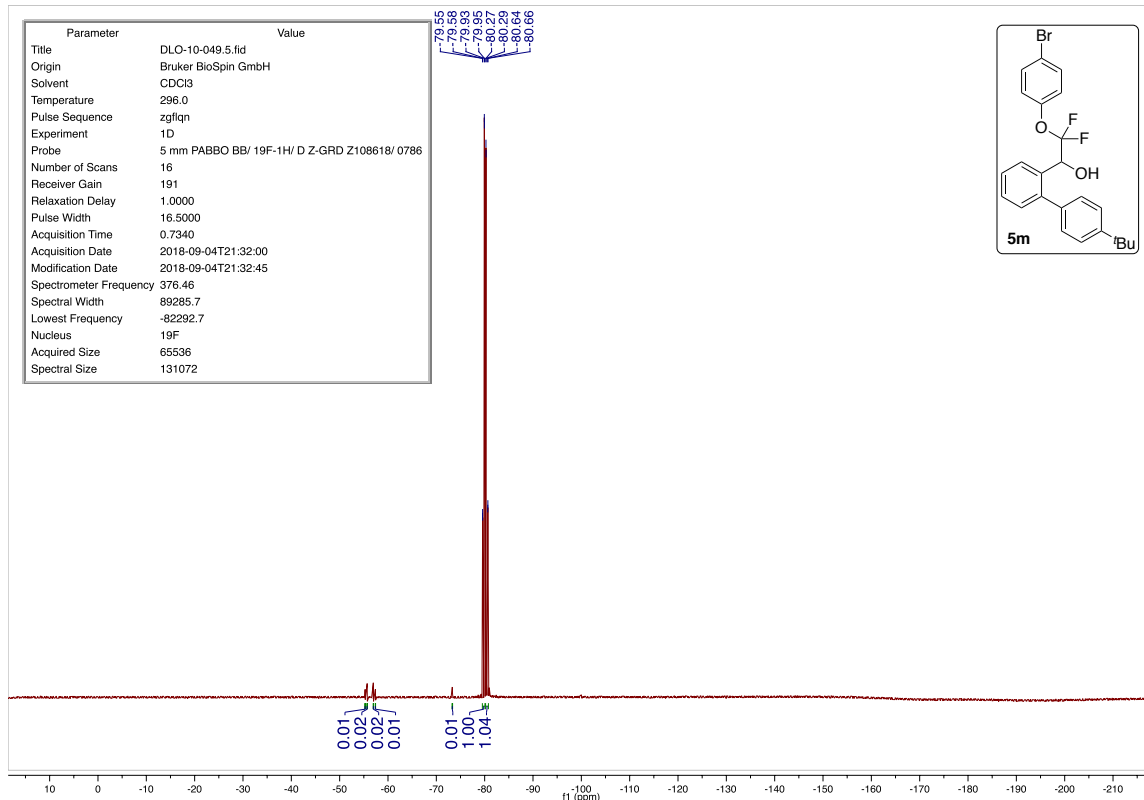
5.24
5.23
5.19
5.18

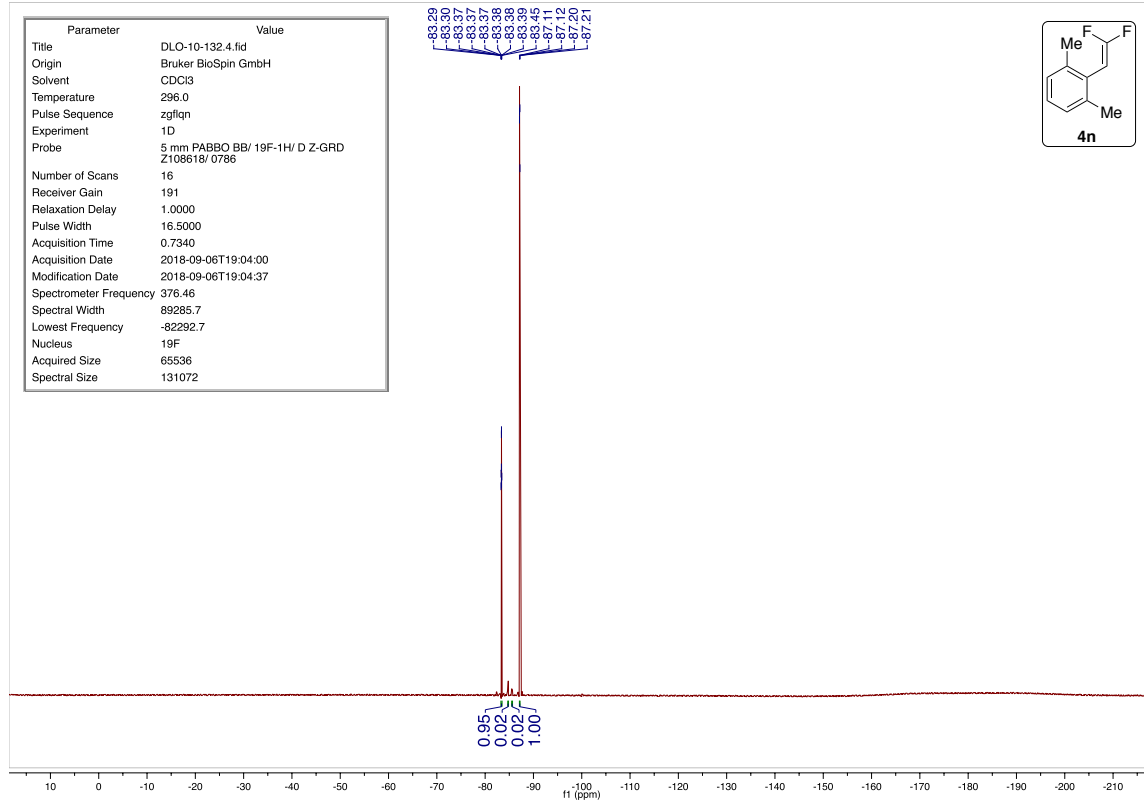
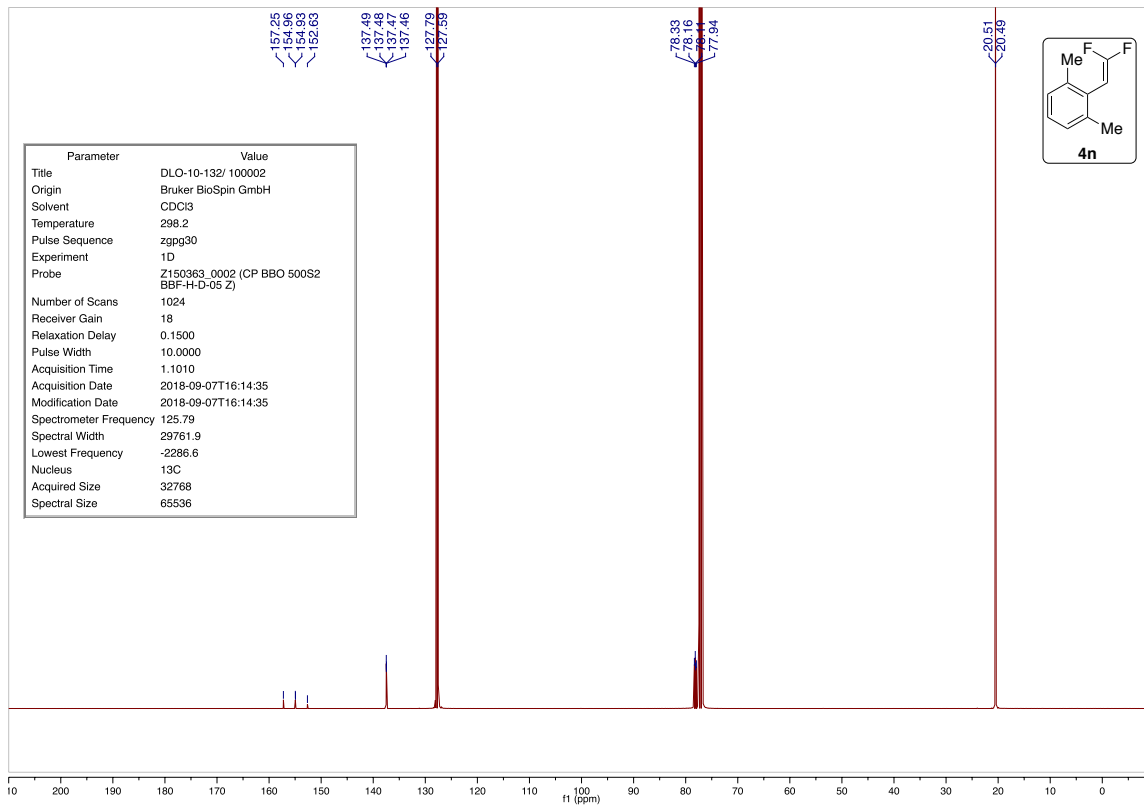




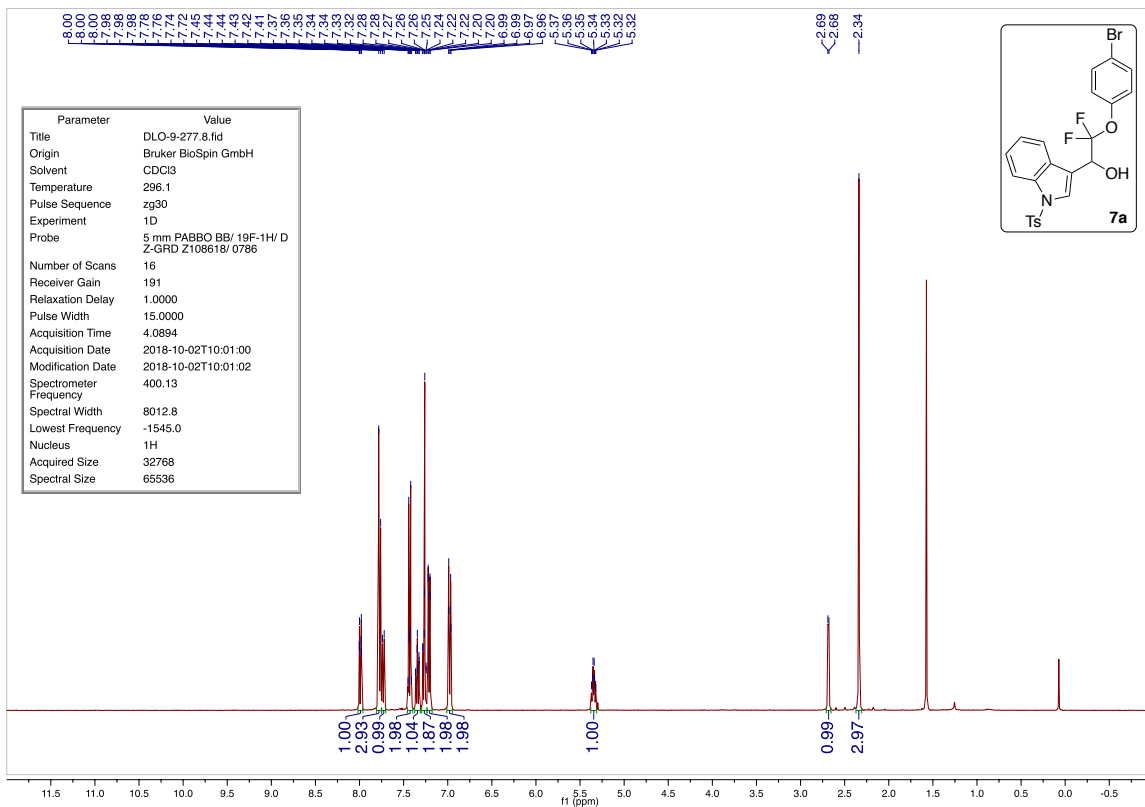
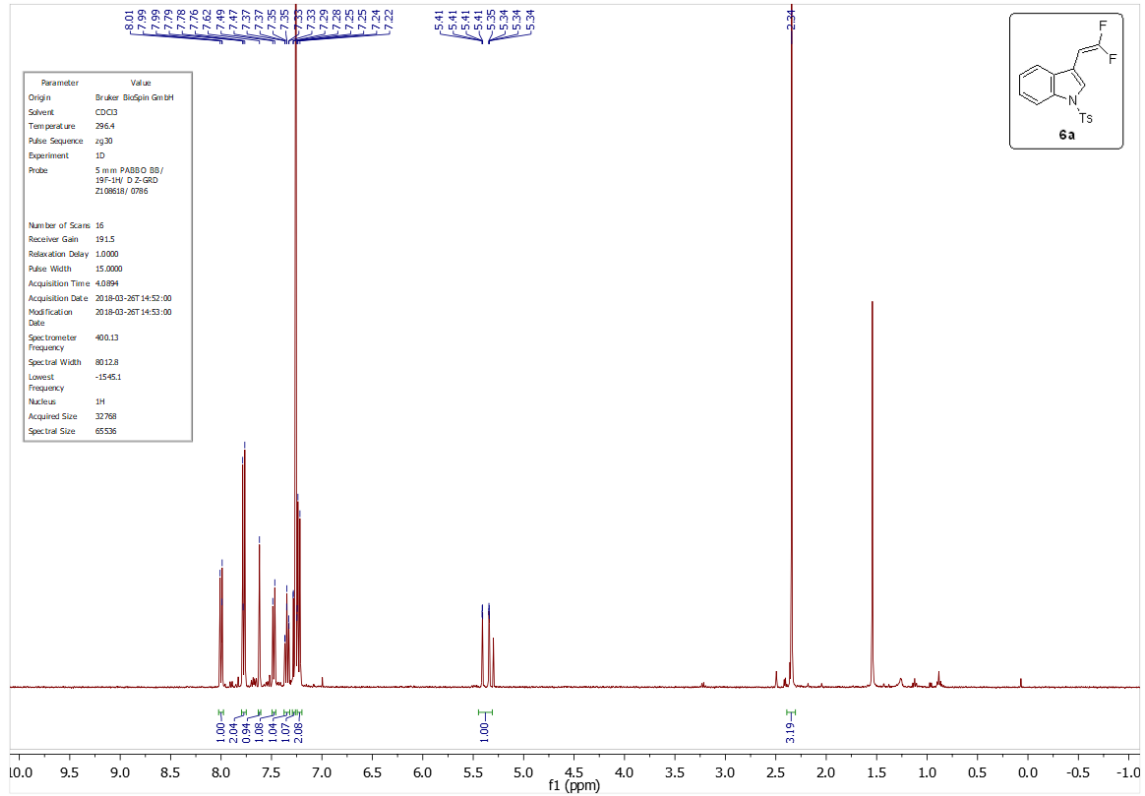


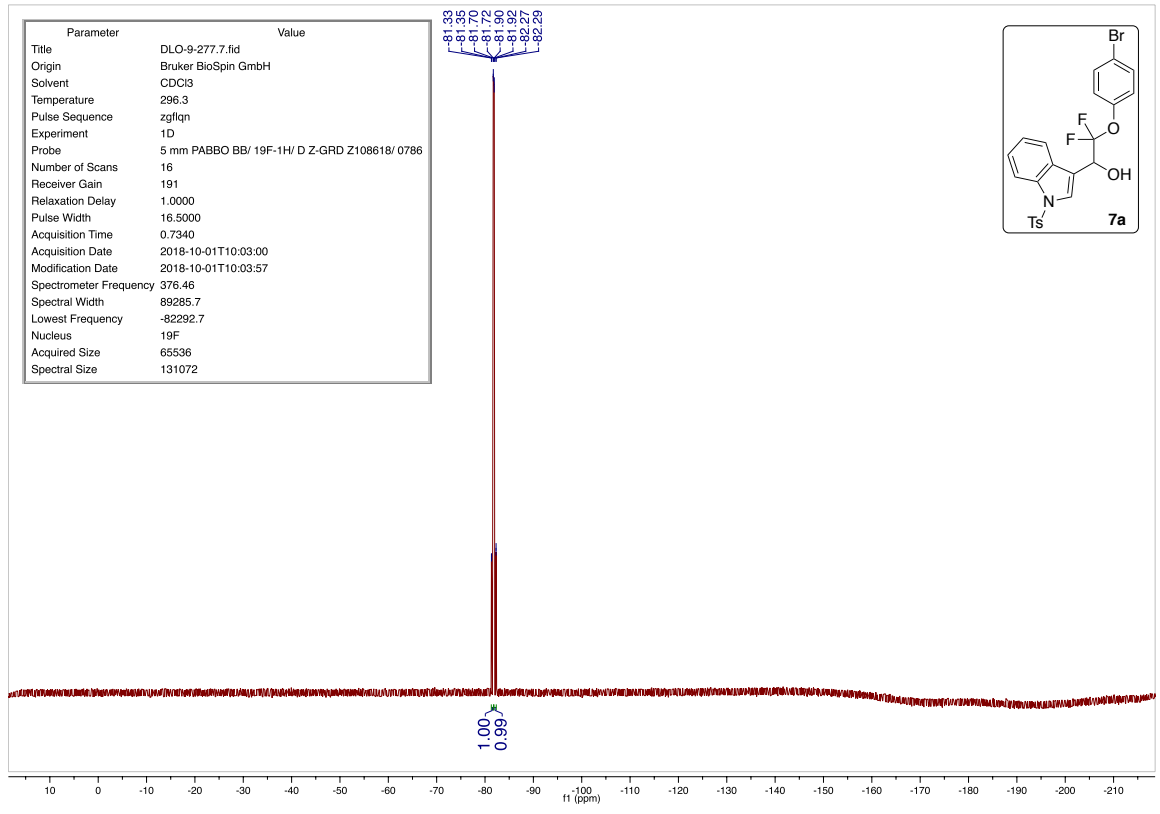
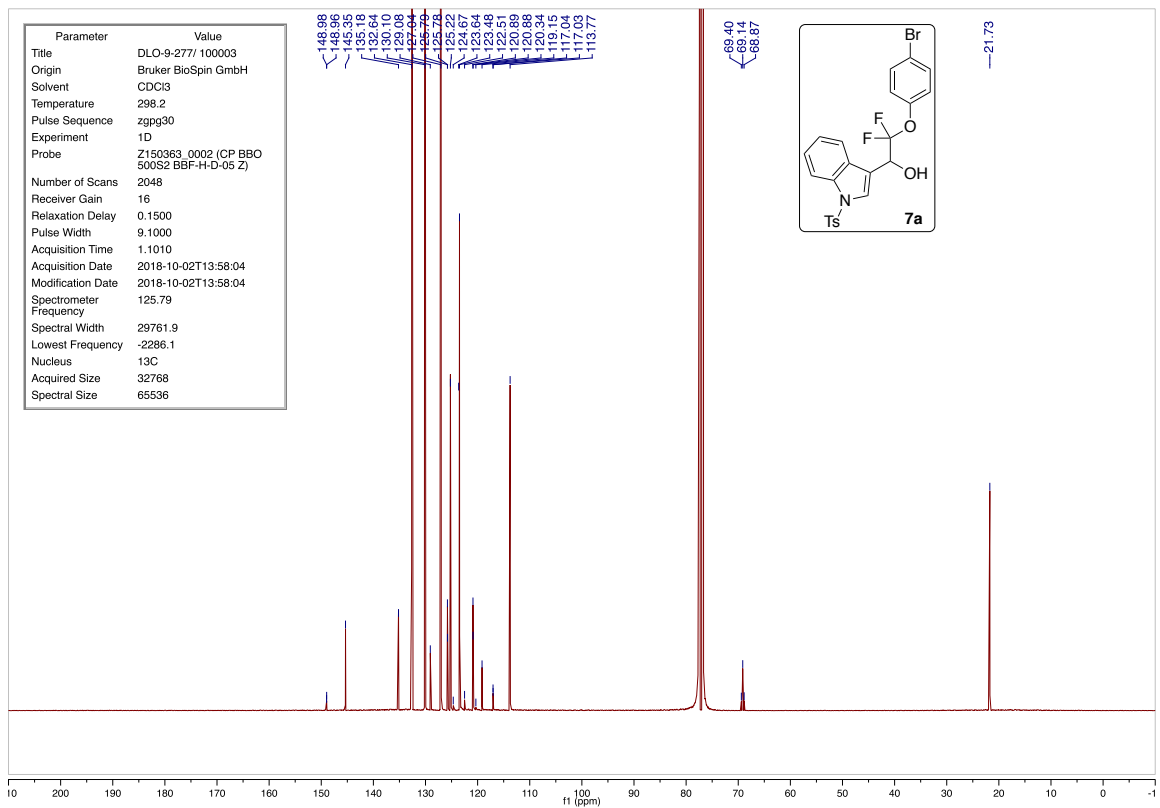


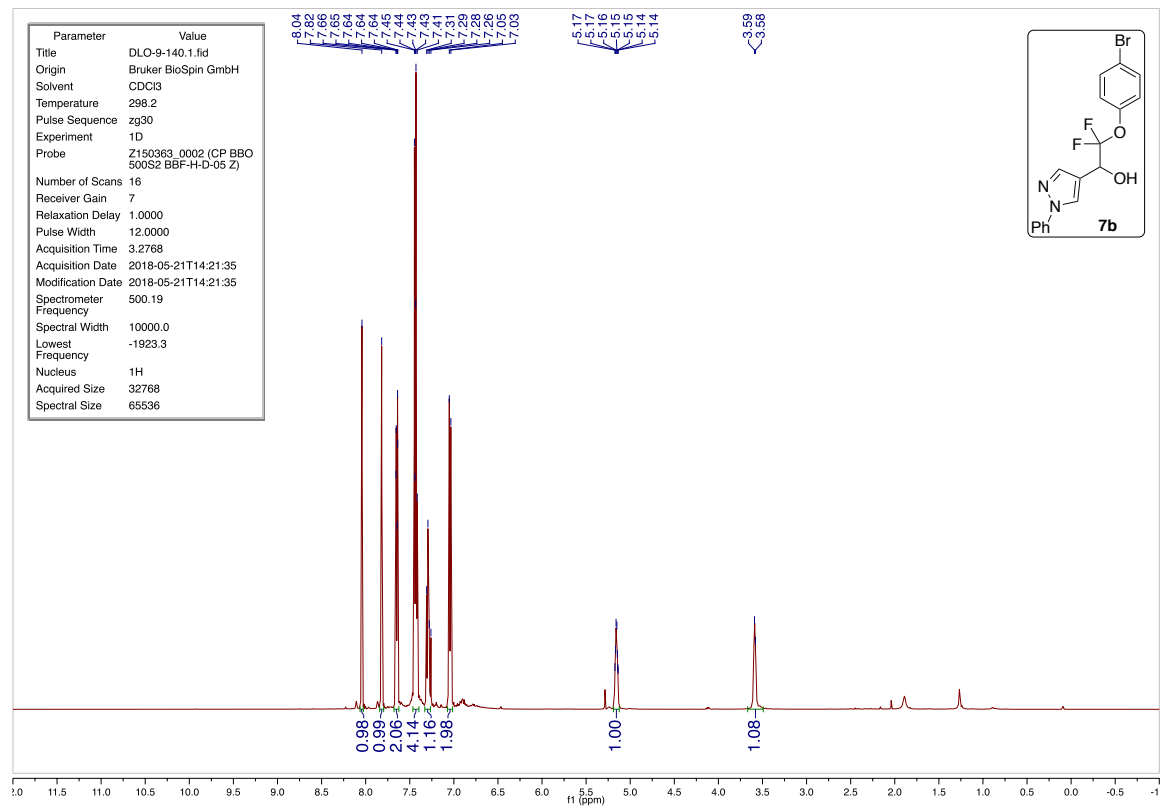
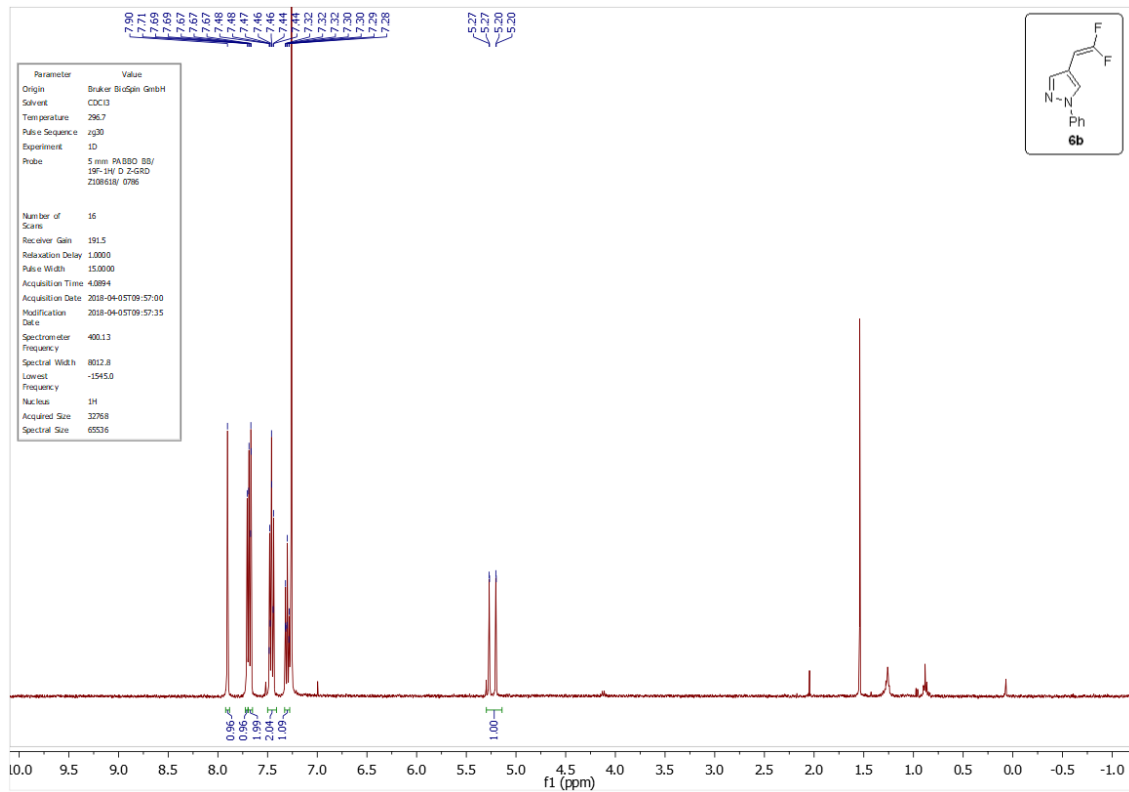


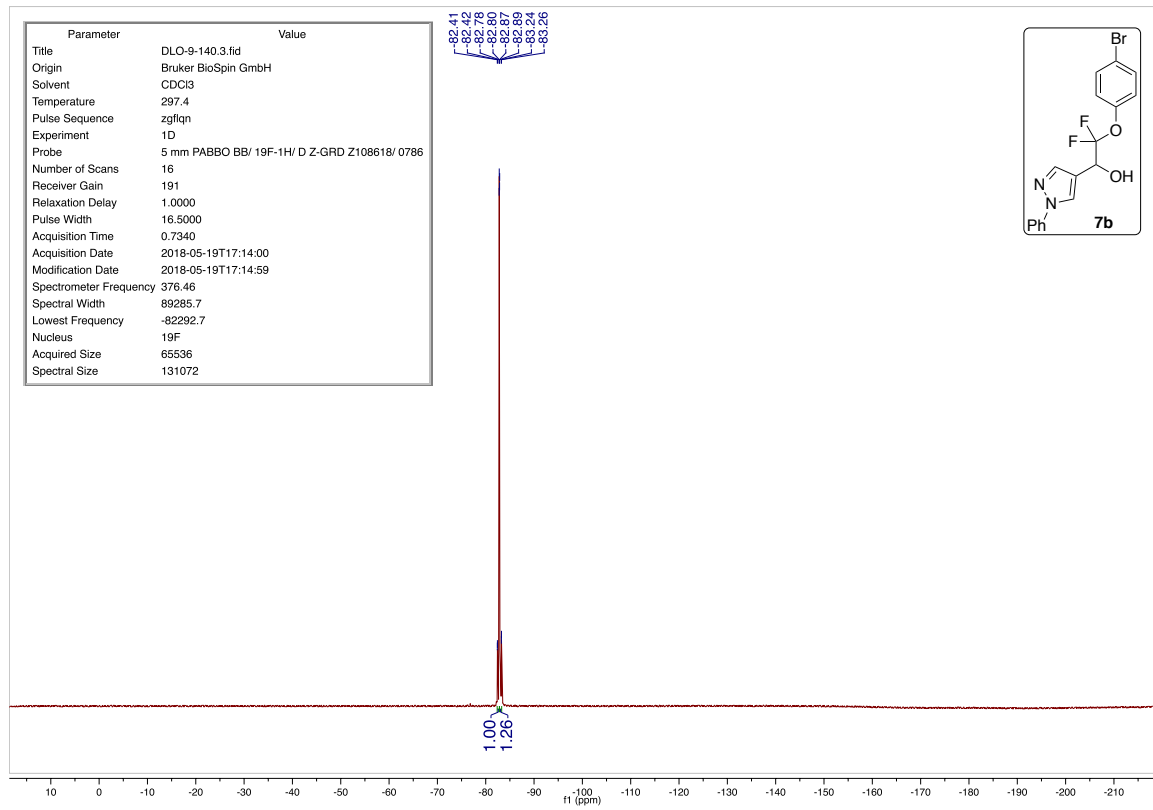
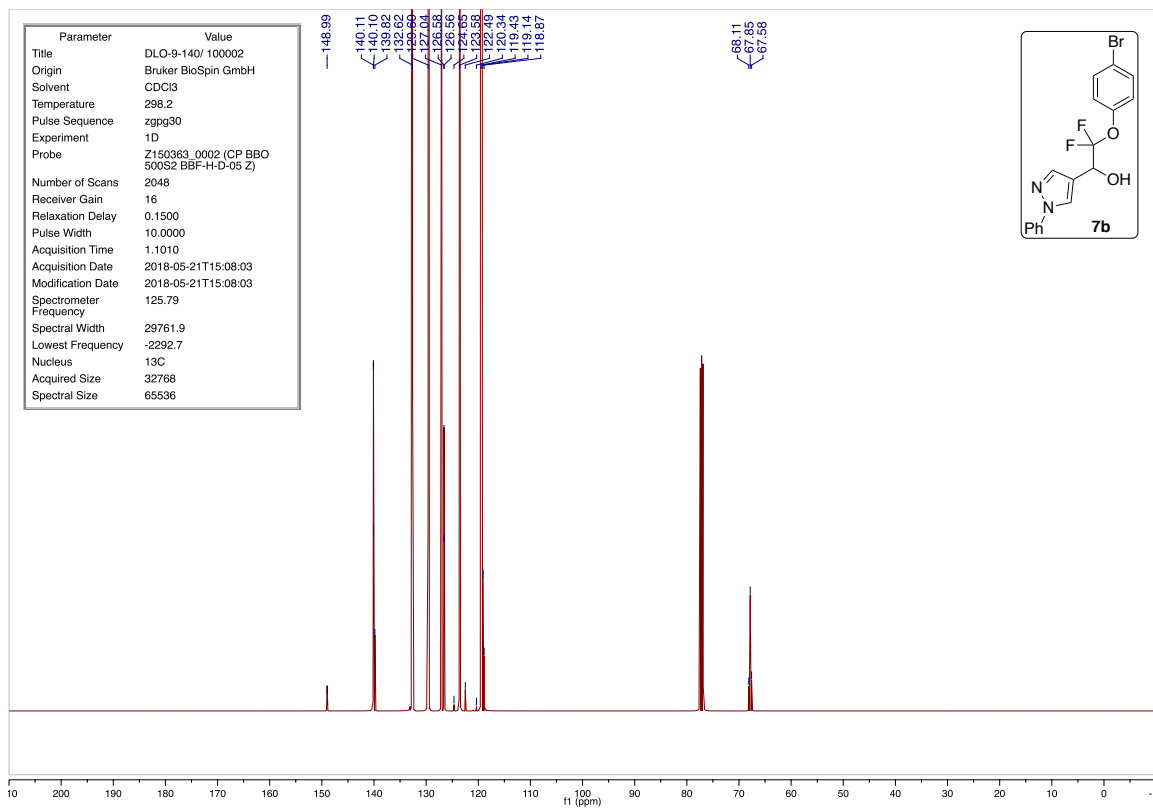


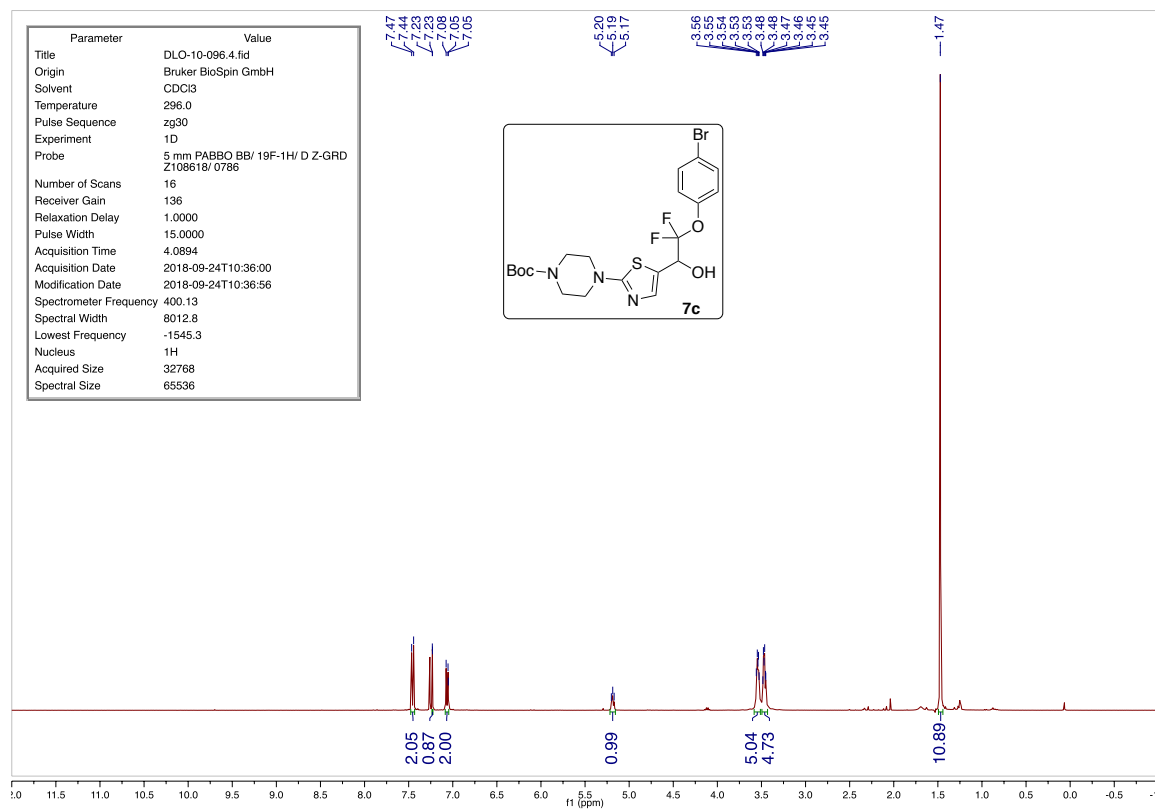
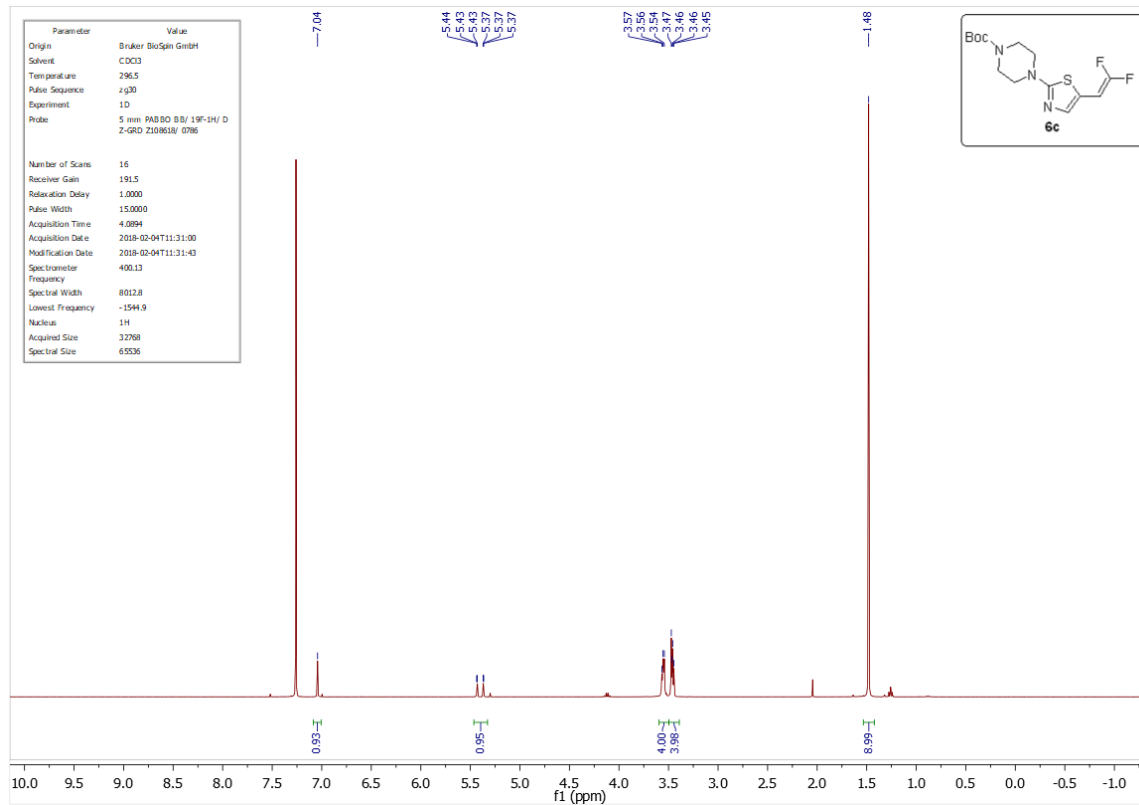
NMR Spectra of Compounds in Table 3:

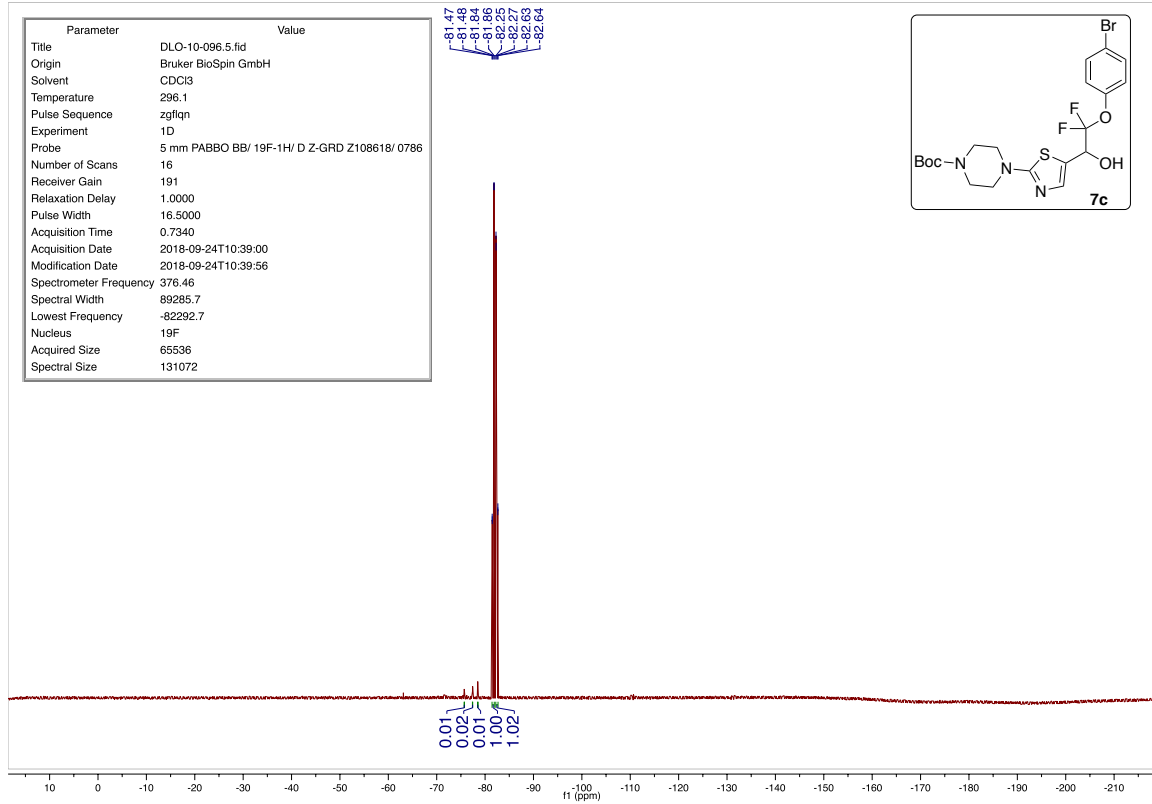
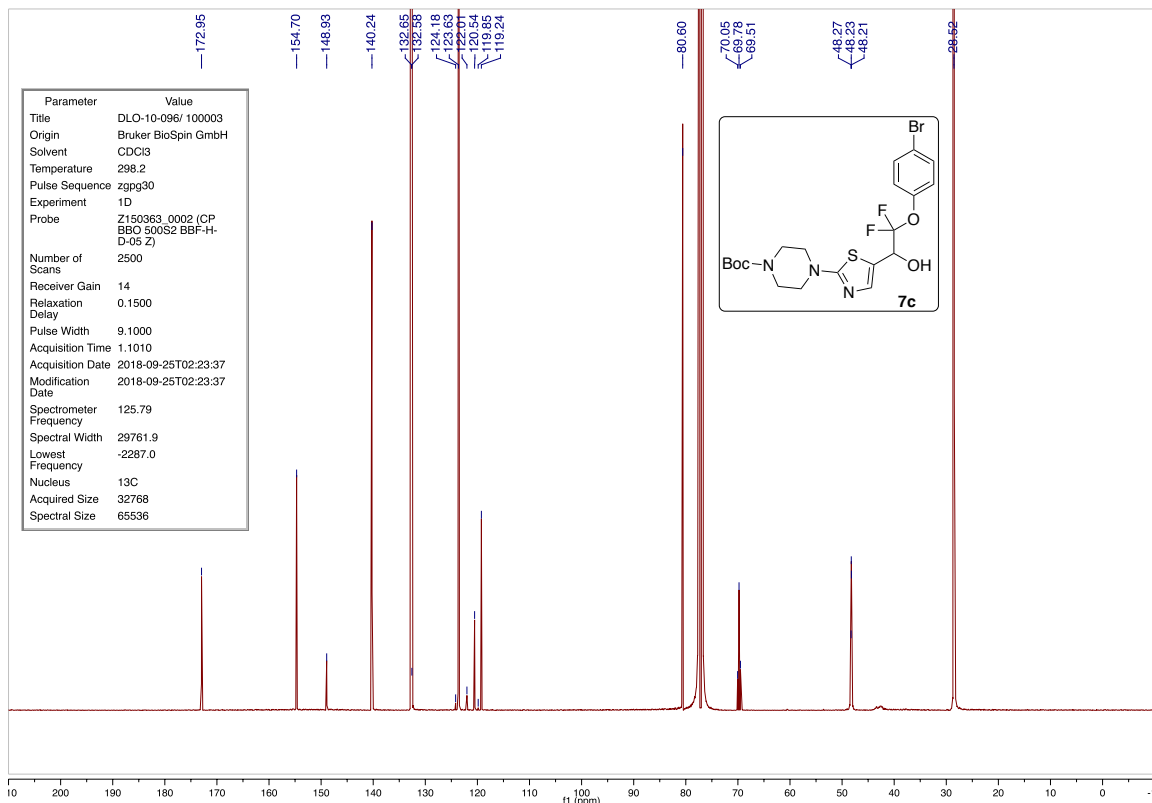


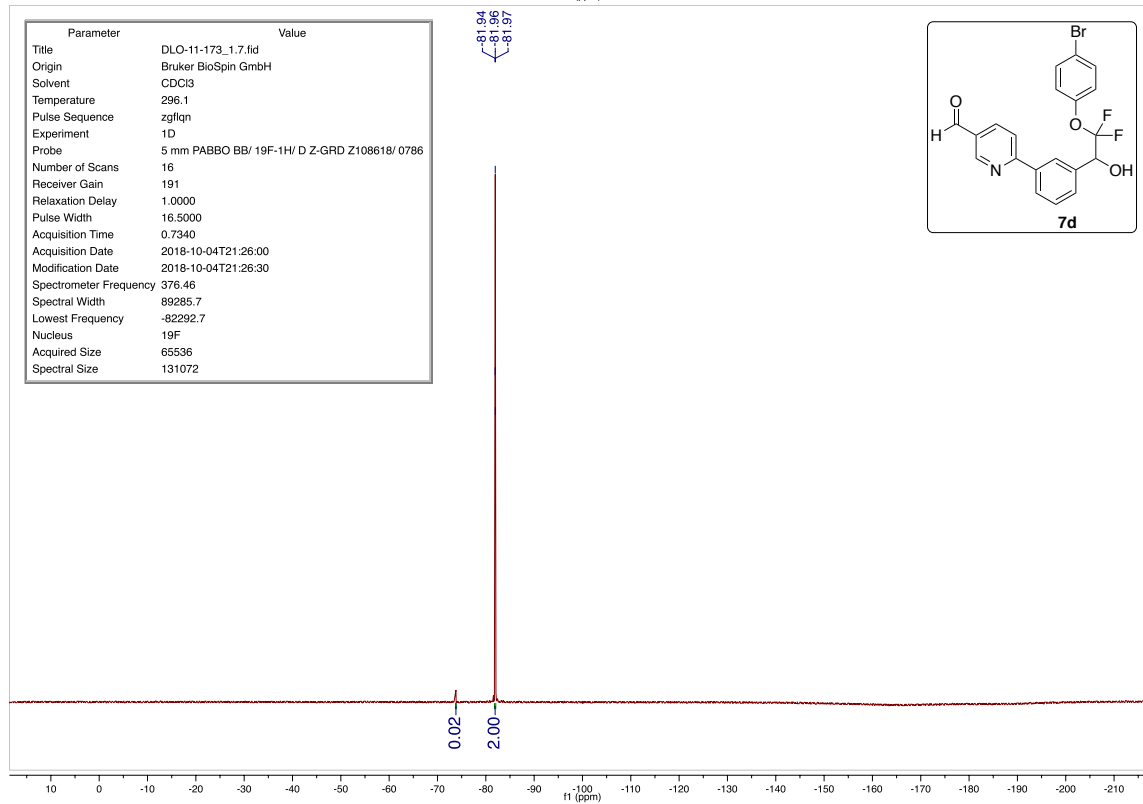
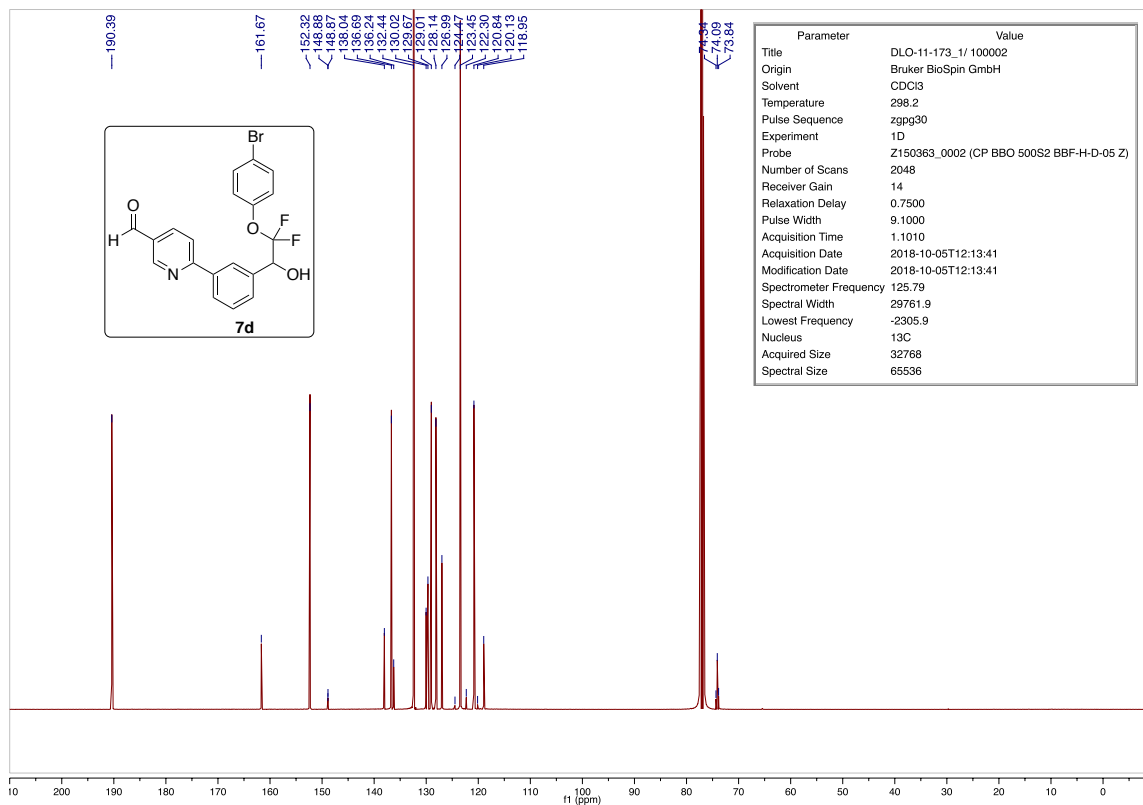


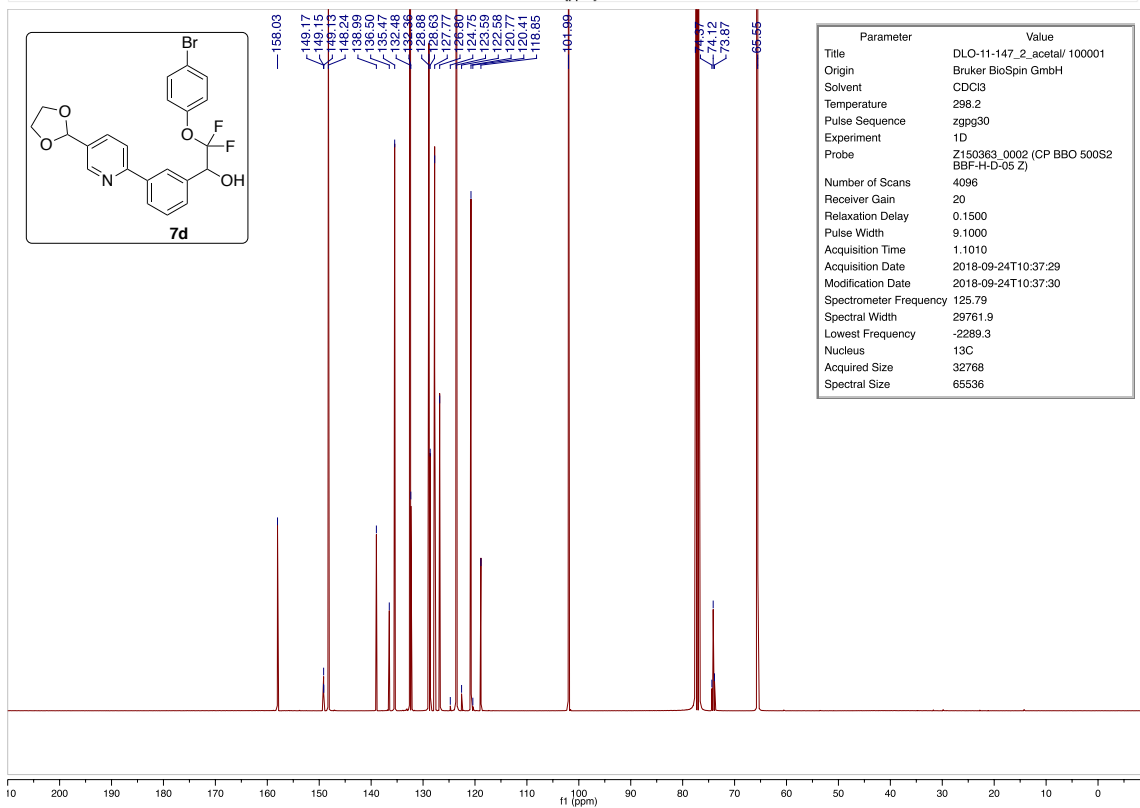
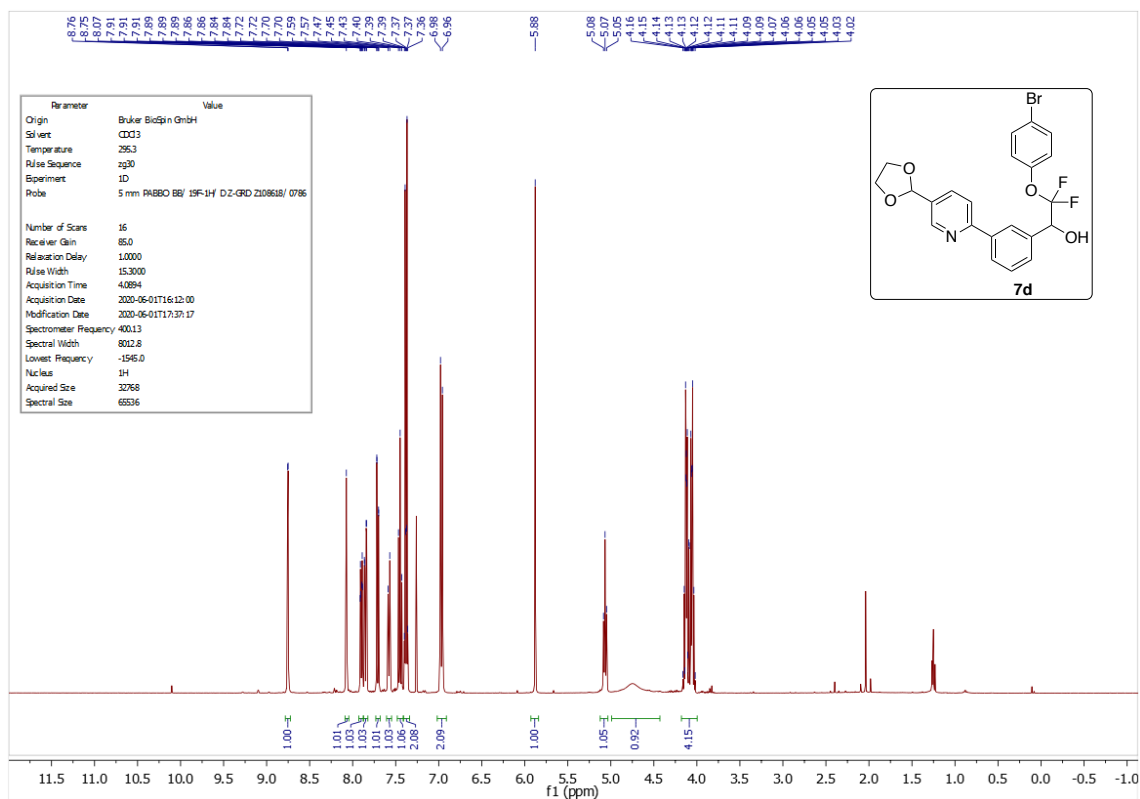


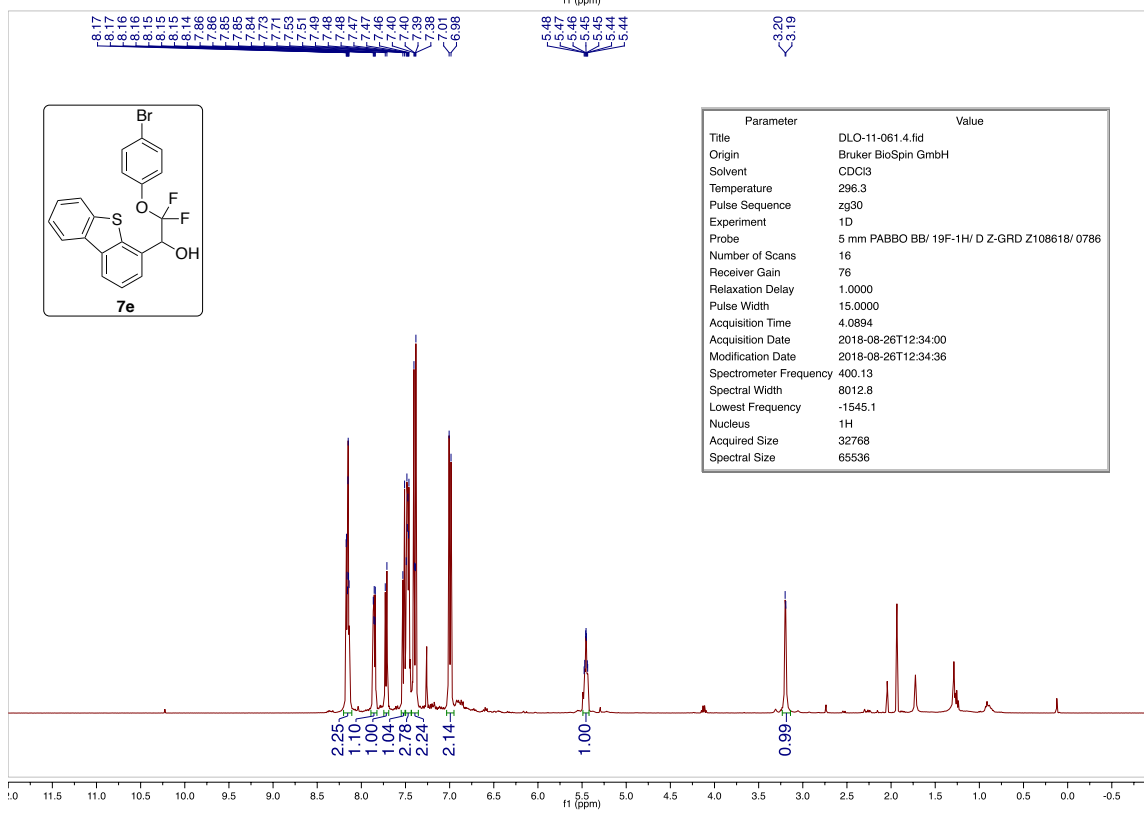
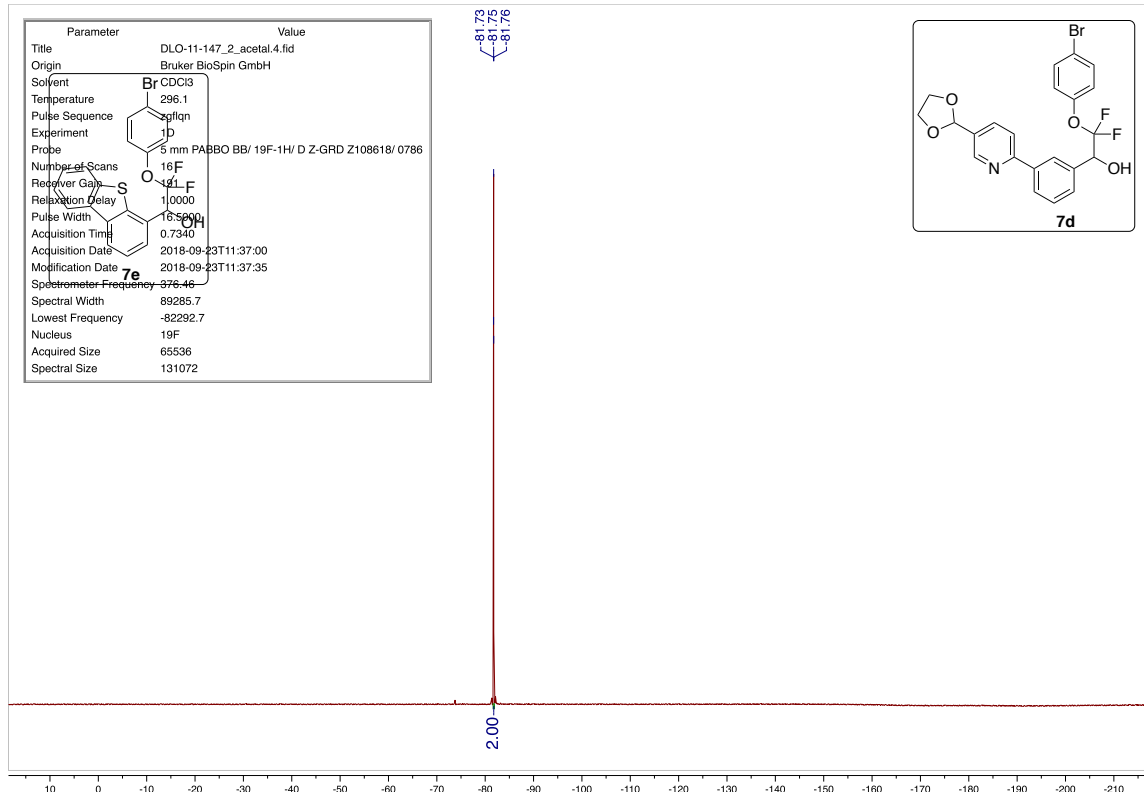


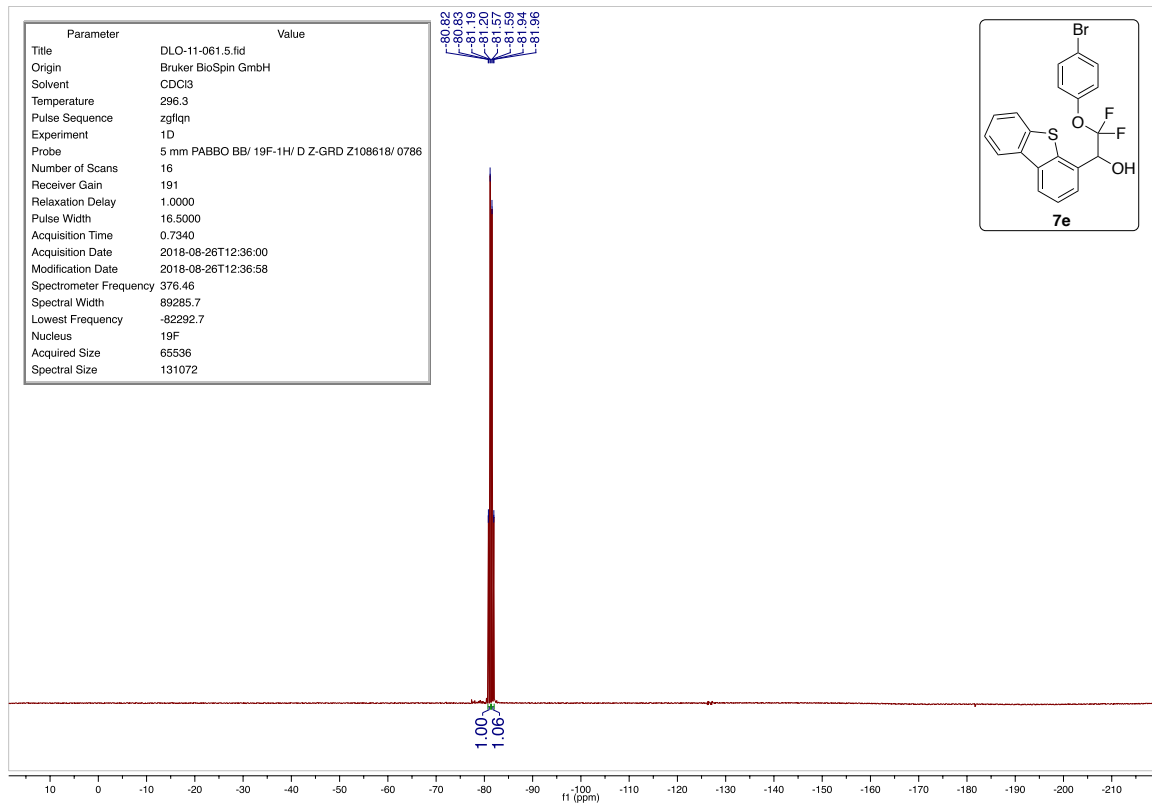
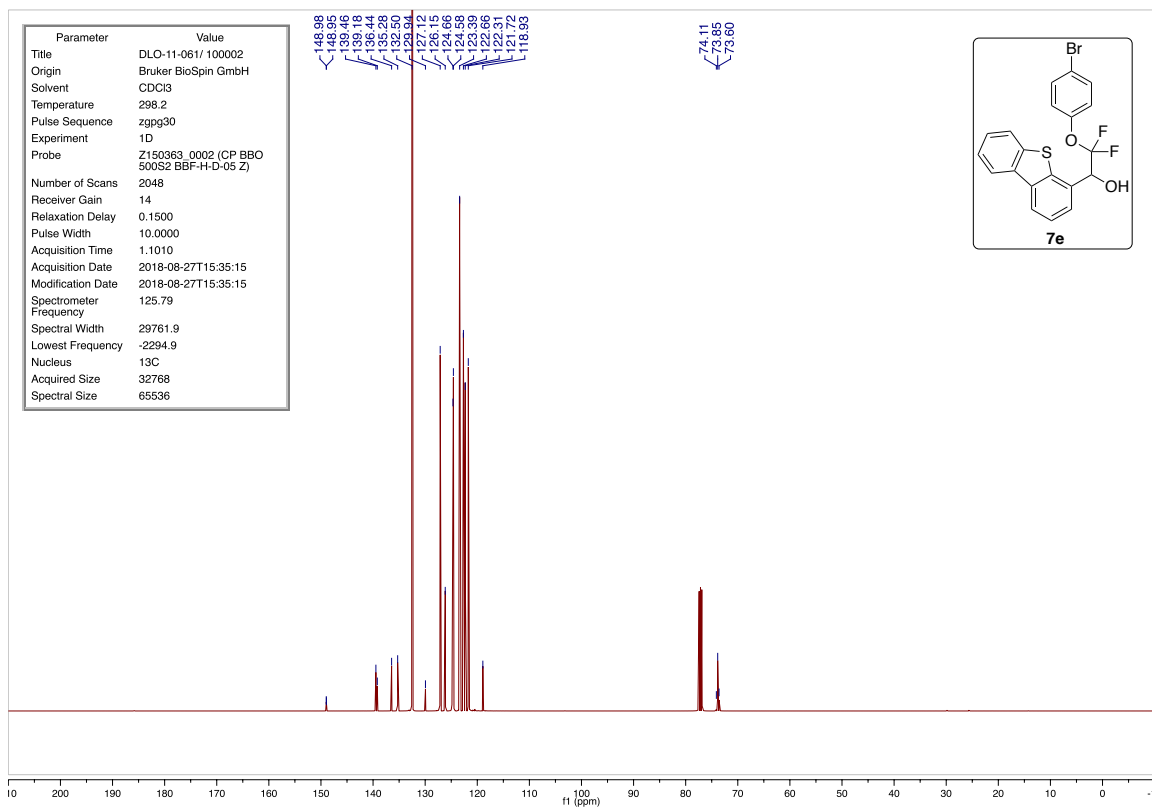












NMR Spectra of Compounds in Table 4:

