Trifluoromethylation of Secondary Nitroalkanes

Amber A. S. Gietter-Burch,[‡] Vijayarajan Devannah,[‡] Donald A. Watson*

Department of Chemistry and Biochemistry, University of Delaware,

Newark, Delaware 19716

Supporting Information

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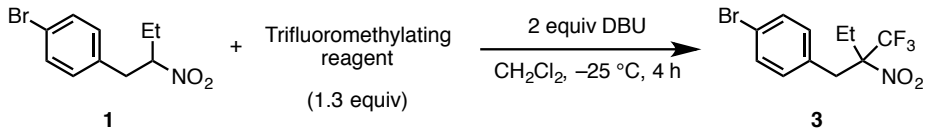
1. General Experimental Details: Benzene, diethyl ether, dichloromethane, and dioxane were dried on alumina according to a published procedure.[1] Copper bromide, sodium methoxide and sodium trimethylsilanolate were purchased commercially; the bulk was stored in a N_2 filled glovebox; samples were removed from the glovebox and stored in a desiccator under air for up to two weeks prior to use. All hot glassware was oven dried for a minimum of two hours or flame-dried under vacuum prior to use. 4-nitrobutyl acetate,[2] methyl-4-nitrobutyrate,[3] *N,N*-dimethyl-4-nitrobutanamide,[4] (*E*)-*N*-((*Z*)-4-(2,6-dimethylphenylamino)pent-3-en-2-ylidene)-2,6-dimethylaniline,[5] 3-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropyl 2-bromopropanoate[6] 3-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropyl 2-methyl-3-nitropentanoate[6] 5-bromo-1-(*p*-toluenesulfonyl)-1H-indole,[7] benzyl-4-nitrobutanote,[8] 1-bromo-4-(2-nitrobutyl)benzene,[9] *N*-(3,4-dichlorobenzyl)-2-ethyl-3-nitropentanamide,[6] *rac*-2-(4-trifluoromethylphenyl)-1-nitrocyclohexane,[10] 4-acetyl-(1-nitropropyl)benzene,[11] methyl 4-nitropentanoate,[12] 1-ethyl 6-methyl 3-nitro-2-propylhexanedioate,[6] ethyl-5-(*tert*-butoxycarbonylamino)-2,2-dimethyl-3-nitropentanoate,[6] *N*-methoxy-*N*,2-dimethyl-3-nitropentanamide,[6] 2-(2-nitrobutyl)pyridine,[9] and 2-(2-nitrobutyl)benzo[*d*]oxazole (**22**)[9] were synthesized according to published procedures. All other substrates and reagents were purchased in highest analytical purity from commercial suppliers and used as received. Reaction optimization (Table 1 and Table S.1 and S.2) was conducted on a 300 μmol scale in 17 x 60 mm vials with Teflon lined caps. All NMR yields and diastereoselectivity are reported using 1,3,5-trimethoxybenzene as an internal standard. All reactions were set up using standard Schlenk technique. Reactions were heated with stirring in temperature controlled oil baths and cooled with stirring using Cryo cooling units. "Double manifold" refers to a standard Schlenk-line gas manifold equipped with N_2 and vacuum (ca. 0.1 mm Hg).

2. Instrumentation and Chromatography: 400 MHz ^{1}H, 101 MHz ^{13}C, and 376 MHz ^{19}F spectra were obtained on a 400 MHz FT-NMR spectrometer equipped with a Bruker CryoPlatform. 600 MHz ^{1}H and 151 MHz ^{13}C spectra were obtained on a 600 MHz FTNMR spectrometer equipped with a Bruker SMART probe. ^{13}C spectra were recorded using Attached Proton Test phase pulse sequence; carbons with an odd number of protons are phased down and those with an even number of protons are phased up.[13] All samples were analyzed in the indicated deutero-solvent and were recorded at ambient temperatures. Chemical shifts are reported in ppm. ^{1}H NMR spectra were calibrated using the residual protio-signal in deutero-solvents as a standard. ^{13}C NMR spectra were calibrated using the deutero-solvent as a standard. IR spectra were recorded on a Nicolet Magma-IR 560 FT-IR spectrometer as thin films on NaCl plates or using KBr pellets. Unless otherwise noted, column chromatography was performed with 40-63 μm silica gel with the eluent reported in parentheses. Where noted 5-20 μm silica gel was used to improve separation. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with $KMnO_4$. GCMS data was collected using an Agilent 6850 series GC and 5973 MS detector. Low resolution ESI data was collected on a Thermo LCQ Advantage running in positive ion mode. High resolution MS data was obtained on a Waters GCT Premier spectrometer using chemical ionization (CI) or liquid injection field desorption ionization (LIFDI) or on a Thermo Scientific, Q Exactive model orbitrap using electrospray ionization (ESI).

3. Screen of Additional Trifluoromethylation Sources

As shown in Table S1, additional trifluoromethylating reagents proved ineffective for the desired transformation.

Table S1: Optimization of Trifluoromethylating Reagent



1 **3**

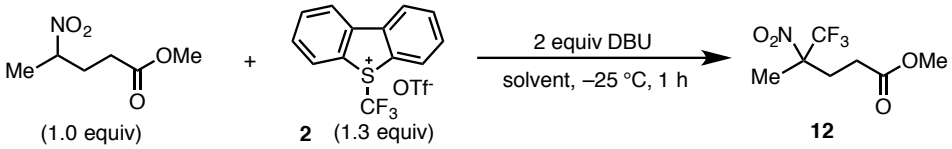
Entry	Trifluoromethylating reagent	% Yield **3**[a]
1	$TMSCF_3$	0
2	Togni's reagent	31
3	CF_3I	45
4	Umemoto's reagent	90

[a]Yield determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

4. Screen of Additional Solvents

As shown in Table S2, DCM found to be optimal solvent for the desired transformation

Table S2: Optimization of Solvents

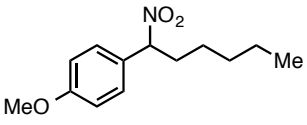


(1.0 equiv) **2** (1.3 equiv) **12**

Entry	Solvent	% Yield **12**[a]
1	benzene	22
2	MeCN	36
3	DMF	45
4	DMA	47
5	DCM	72

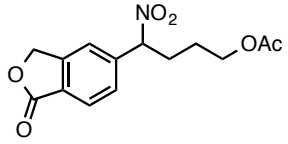
[a]Yield determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

5. Synthesis of Novel Nitroalkane Starting Materials:

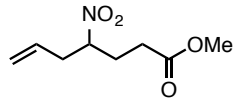


(S1) S1 was synthesized by modification of a previously published procedure.[11] A hot 200 mL Schlenk equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and allowed to cool. Once cool, the flask was backfilled with N_2, the septum was removed and tris(dibenzylideneacetone)dipalladium(0) (129 mg, 141 μmol), BrettPhos (177 mg, 330 μmol), cesium carbonate (3.68 g, 11.3 mmol), and 4-bromoanisole (1.76 g, 9.42 mmol) were added. The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous dioxane (47 mL) and 1-nitrohexane (2.62 mL, 18.8 mmol) were added via syringe. The resulting heterogeneous solution was heated in an oil bath at 50 °C for 40 h. Once complete, the reaction was cooled to rt. Saturated NH_4Cl (10 mL) was added and the reaction was stirred for 10 minutes. Another 10 mL saturated NH_4Cl (10 mL) was added and the reaction was stirred for another 10 minutes.

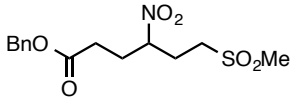
The reaction was then diluted with diethyl ether (25 mL), washed twice with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo.* The crude reaction was purified using flash silica gel chromatography (65:35 hexanes : ethyl acetate) to afford **S1** (1.83 g, 82%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.7 Hz, 2H), 6.94 - 6.87 (m, 2H), 5.40 (dd, *J* = 8.6, 6.7 Hz, 1H), 3.81 (s, 3H), 2.51 - 2.38 (m, 1H), 2.05 (dt, *J* = 12.3, 6.5 Hz, 1H), 1.36 - 1.23 (m, 6H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 129.2, 126.9, 114.3, 91.2, 55.4, 33.8, 31.2, 25.8, 22.4, 14.0; FTIR (cm^{-1}): 2957, 2860, 1550, 1253, 1179. HRMS (LIFDI) m/z calculated for $[C_{13}H_{19}NO_3]^+$: 237.1365; found: 237.1339.



(S2) S2 was synthesized by modification of a previously published procedure.[11] A hot 100 mL Schlenk equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and allowed to cool. Once cool, the flask was backfilled with N_2, the septum was removed and tris(dibenzylideneacetone)dipalladium(0) (110 mg, 120 μmol), BrettPhos (147 mg, 280 μmol), cesium carbonate (3.13 g, 9.60 mmol), and 5-bromophthalide (1.70 g, 8.0 mmol). The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous dioxane (30 mL) and nitroethane (855 μL, 12.0 mmol) were added via syringe. The resulting heterogeneous solution was heated in an oil bath at 50 °C for 24 h. Once complete, the reaction was cooled to rt. Saturated NH_4Cl (10 mL) was added and the reaction was stirred for 10 minutes. Another 10 mL saturated NH_4Cl (10 mL) was added and the reaction was stirred for another 10 minutes. The reaction was then diluted with diethyl ether (25 mL), washed twice with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo.* The crude reaction was purified using flash silica gel chromatography (80:20 hexanes : ethyl acetate) to afford **S2** (757 mg, 32%) as a thick orange oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 2H), 5.62 (dd, *J* = 9.1, 6.1 Hz, 1H), 5.36 (s, 2H), 4.19 - 4.08 (m, 2H), 2.68 - 2.58 (m, 1H), 2.23 - 2.13 (m, 1H), 2.06 (s, 3H), 1.78 - 1.63 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 170.1, 147.5, 140.2, 129.0, 127.4, 126.7, 121.7, 90.4, 69.6, 63.0, 31.0, 25.4, 21.0; FTIR (cm^{-1}): 2961, 1780, 1767, 1553, 1245, 1050; HRMS (LIFDI) m/z calculated for $[C_{14}H_{16}NO_6]^+$: 294.0978; found: 294.0983.

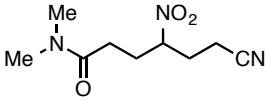


(S3) S3 was synthesized by modification of a previously published procedure.[14] A hot 100 mL Schlenk equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and allowed to cool. Once cool, the flask was backfilled with N_2, the septum was removed and bis(triphenylphosphine)palladium (II) chloride (386 mg, 550 μmol) and sodium methoxide (1.19 g, 22.0 mmol) were added. The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous methanol (22 mL) and methyl 4-nitrobutanoate (2.56 mL, 20.0 mmol) were added via syringe. The resulting yellow suspension was heated in an oil bath at 65 °C for 5 min, during which time the suspension turned brown. The reaction was cooled to rt and transfered to pre-cooled bath at 15 °C. allyl acetate (4.32 mL, 40 mmol) was added via syringe and the reaction was allowed to stir at 15 °C for 24 h. Once complete, the reaction was warmed to rt. The reaction was then diluted with diethyl ether (40 mL), washed thrice with brine (30 mL), dried over magnesium sulfate and concentrated *in vacuo.* The crude reaction was purified using flash silica gel chromatography (100:0 → 95:5 hexanes : ethyl acetate) to afford (**S3**) (552 mg, 15%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 - 5.63 (m, 1H), 5.20 - 5.16 (m, 1H), 5.15 (s, 1H), 4.67 - 4.57 (m, 1H), 3.69 (s, 3H), 2.77 - 2.64 (m, 1H), 2.60 - 2.48 (m, 1H), 2.49 - 2.29 (m, 2H), 2.30 - 2.18 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 131.2, 119.9, 87.0, 52.0, 38.0, 30.0, 28.1; FTIR (cm^{-1}): 2954, 2918, 2849, 1734, 1654, 1558, 993, 927 ; GC/MS (EI) 156.1 $(M\text{-}OCH_3)^+$. HRMS (CI) m/z calculated for $[C_8H_{14}NO_4]^+$: 188.0923; found: 188.0917.

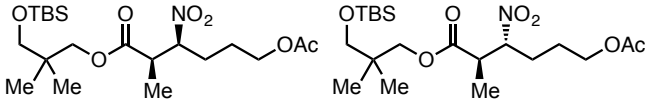


(S4) To a 50 mL round bottom equipped with a magnetic stir bar was added benzyl-γ-nitrobutanote (2.63 g, 12.7 mmol), dichloromethane (2.5 mL), water (21 mL), methyl vinyl sulfone (1.06 mL, 12.7 mmol) and sodium hydroxide (61.0 μg, 1.52 mmol). The biphasic reaction was vigorously stirred at room temperature for 4 days. Dichloromethane (20 mL) was added and the aqueous layer was extracted with dichloromethane (10 mL). The organic layers were combined, dried with magnesium sulfate and concentrated *in vacuo*. The crude reaction was purified using flash silica gel chromatography (70:30

benzene : ethyl acetate) to afford **S4** (513 mg, 12%) as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.31 (m, 5H), 5.13 (s, 2H), 4.83 - 4.70 (m, 1H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.94 (s, 3H), 2.56 - 2.42 (m, 3H), 2.42 - 2.24 (m, 2H), 2.23 - 2.12 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 135.5, 128.8, 128.6, 128.5, 85.5, 67.0, 50.7, 41.3, 30.0, 28.7, 26.0; FTIR (cm^{-1}): 2931, 1733, 1550, 1299, 1133; mp = 68-69 °C.ESI-MS: 352.3 $(M+Na)^+$ HRMS (ESI) m/z calculated for $[C_{14}H_{20}NO_6S]^+$: 330.10058; found: 330.09975.

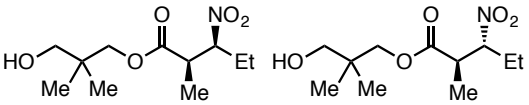


(S5) To a 200 mL round bottom flask equipped with a magnetic stir bar was added *N,N*-dimethyl-4-nitrobutanamide (5.23 mL, 40.0 mmol), acrylonitrile (2.62 mL, 40.0 mmol), dichloromethane (8 mL), sodium hydroxide (192 mg, 4.80 mmol), and water (67 mL). The flask was sealed with a polypropylene cap and stirred at room temperature for 42 h. The reaction was then diluted with dichloromethane (20 mL) and the organic layer was separated. The aqueous layer was extracted with dichloromethane (20 mL), dried over magnesium sulfate, and concentrated *in vacuo*. The crude reaction was purified using flash silica gel chromatography (18:80:2 hexanes : ethyl acetate : triethylamine) to afford **S5** (1.65 g, 19%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (tt, *J* = 8.7, 4.4 Hz, 1H), 2.96 (d, *J* = 6.4 Hz, 6H), 2.50 - 2.33 (m, 5H), 2.28 - 2.12 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 117.9, 86.4, 37.1, 35.7, 29.6, 28.9, 28.8, 14.4; FTIR (cm^{-1}): 2938, 2248, 1645, 1550, 1150; mp = 53-55 °C; GC/MS (EI) 167.1 $(M-NO_2)^+$. HRMS (CI) m/z calculated for $[C_9H_{16}N_3O_3]^+$: 214.1192; found: 214.1192.



S6A **dr: 46 : 54** **S6B**

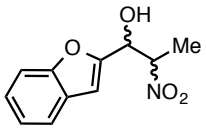
(S6) A hot 50 mL Schlenk equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and cooled under vacuum.[6] Once cool, the septum was removed and CuBr (84.3 mg, 588 μmol), (*E*)-*N*-((*Z*)-4-(2,6-dimethylphenylamino)pent-3-en-2-ylidene)-2,6-dimethylaniline (180 mg, 588 μmol), and sodium trimethylsilanolate (429 mg, 3.82 mmol) were added. The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous benzene (17 mL), 4-nitrobutyl acetate (663 mg, 4.12 mmol), and 3-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropyl 2-bromopropanoate (1.04 g, 2.91 mmol) were added via syringe. The reaction was heated to 60 °C with rapid stirring for 48 h. Once completed, the reaction was cooled to room temperature, the septum was removed and the reaction mixture was diluted with diethyl ether (50 mL). The crude reaction mixture was filtered through a plug of magnesium sulfate and concentrated *in vacuo*. NMR analysis revealed a 46:54 mixture of syn and anti isomers. The crude reaction was purified by flash silica chromatography (90:10:1 hexanes : ethyl acetate : acetic acid) to afford a mixture of diastereomers of β-nitroester **S6** (760 mg, 60%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed. See attached spectra for details) δ **S6A**: 4.69 (ddd, *J* = 10.6, 9.2, 3.2 Hz, 1H), 2.99 (dq, *J* = 9.0, 7.0 Hz, 1H), 1.87 - 1.80 (m, 1H); **S6B**: 4.77 (td, *J* = 8.9, 3.6 Hz, 1H), 3.19 (p, *J* = 7.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **S6A:** 172.2, 89.8, 68.4, 63.2, 43.8, 29.0, 25.3, 21.6, 14.7; **S6B**: 172.5, 88.1, 68.5, 63.3, 42.5, 27.1, 24.8, 21.5, 13.5; FTIR (cm^{-1}): 2956, 1741, 1555, 1248, 1099, 776; GC/MS (EI) 376.3 $(M-C_4H_9)^+$; 329.1 $(M-C_4H_{10}NO_2)^+$. HRMS (CI) m/z, calculated for $[C_{20}H_{40}NO_7Si]^+$: 434.2574; found: 434.2575 and 434.2573.



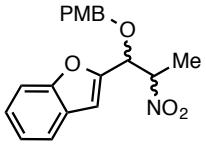
S7A **62 : 38** **S7B**

(S7) To a 500 mL round bottom flask with a stir bar was added 3-(*tert*-butyldimethylsilyloxy)-2,2-dimethylpropyl 2-methyl-3-nitropentanoate (800 mg, 2.22 mmol), THF (74 mL), and 3M HCl (55 mL). The flask was sealed with a polyethylene stopper and stirred vigorously at rt for 4.5 h. Once complete, the reaction was diluted with brine (20 mL) and extracted with ethyl acetate (3x, 35 mL). The organic layers were combined, washed with brine (1x, 20 mL), dried with magnesium sulfate, and concentrated *in vacuo*. NMR analysis revealed a 62:38 mixture of syn and anti isomers. The crude reaction was purified by flash silica chromatography (60:40 hexanes: ethyl acetate) to afford alcohol **S7** (463 mg, 84%) as a clear oil: ^{1}H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed. See attached spectra for details) δ **S7A**: 3.05 - 2.96 (m, 1H), 0.93 (s, 6H); **S7B**: 3.20 (dq, *J* = 9.1, 7.3 Hz, 1H), 0.91 (apparent d, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **S7A**: 173.0, 91.5, 68.2, 43.5, 36.5, 25.5, 14.4, 10.6; **S7B**: 173.7, 89.8, 68.1, 42.0, 36.6, 24.0, 13.9, 9.5; FTIR (cm^{-1}):

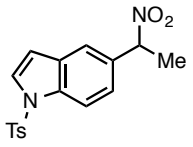
3446, 2971, 1734, 1552, 1375; ESI-MS: 270.2 $(M+Na)^+$; HRMS (ESI) m/z, calculated for $[C_{11}H_{22}NO_5]^+$: 248.14925; found: 248.14849.



(S8) To a 100 mL round bottom flask equipped with a magnetic stir bar was added 2-benzofurancarboxaldehyde (4.15 mL, 34.2 mmol) and nitroethane (24.4 mL, 342 mmol). The reaction was cooled to 0 °C in an ice bath and tetramethylguanidine (216 μL, 1.71 mmol) was added dropwise via syringe. Once the addition was complete, the ice bath was removed and the flask was allowed to warm to rt where it was stirred for 12 h. The crude reaction was transferred to a seperatory funnel and diluted with brine (15 mL). The reaction was acidified with 5% HCl. The aqueous layer was extracted with ethyl acetate. The organic layer was dried with magnesium sulfate and concentrated *in vacuo*. NMR analysis revealed a 63:37 mixture of isomers. The crude reaction was purified via flash silica gel chromatography (93:7 hexanes : ethyl acetate) to afford α-nitroalcohol **S8** (6.60 g, 87%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed. See attached spectra for details) δ **S8** (major): 6.81 (s, 1H), 5.22 (dd, *J* = 8.5, 6.2 Hz, 1H), 5.14 - 5.05 (m, 1H), 2.81 (d, *J* = 6.2 Hz, 1H), 1.49 (d, *J* = 6.8 Hz, 3H); **S8** (minor): 6.80 (s, 1H), 5.57 (t, *J* = 4.2 Hz, 1H), 5.01 (qd, *J* = 6.9, 3.6 Hz, 1H), 2.89 (d, *J* = 5.3 Hz, 1H), 1.62 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **S8** (major): 155.1, 153.1, 127.5, 125.4, 123.5, 121.6, 111.7, 106.4, 86.1, 70.2, 16.5; **S8** (minor): 155.0, 153.8, 127.7, 124.9, 121.5,123.4, 111.5, 105.1, 84.7, 69.3, 12.9; FTIR (cm^{-1}): 3508, 3066, 2993, 1553, 1454, 753; mp = 68-70 °C; GC/MS (EI) retention time= 11.566, 174.0 $(M-HNO_2)^+$; retention time= 11.633, 173.9 $(M-HNO_2)^+$. HRMS (CI) m/z, calculated for $[C_{11}H_{12}NO_4]^+$: 222.0766; found: 222.0759 and 222.0755.

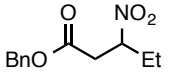


(S9) A hot 100 mL round bottom flask equipped with a magnetic stir bar and a septum was attached to a double manifold and allowed to cool. Once cooled, the flask was backfilled with N_2, septum was removed and **S8** (2.00 g, 9.00 mmol) was added. The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous diethyl ether (45 mL) and 4-methoxybenzyl-2,2,2-trichloroacetimidate (3.33 g, 11.8 mmol) were added via syringe. The reaction was stirred for five minutes then trimethylsilyl trifluoromethanesulfonate (90.0 μL, 494 μmol) was added dropwise via syringe. Once addition was complete, the reaction was stirred at rt for 20 h. Once complete, the reaction was washed with $NaHCO_3$ (2x, 15 mL), 1M HCl (1x, 15 mL), and brine (1x, 15 mL). The reaction was dried with magnesium sulfate and concentrated *in vacuo*. NMR analysis revealed a 79:21 mixture of isomers. The crude reaction was purified via flash silica chromatography (95:5 hexanes : ethyl acetate) to afford **S9** (358 mg, 12%) as a yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed. See attached spectra for details) δ **S9 Major**: 4.53 (d, *J* = 11.4 Hz, 1H), 4.30 (d, *J* = 11.4 Hz, 1H), 3.79 (s, 3H), 1.36 (d, *J* = 6.8 Hz, 3H); **S9 Minor**: 4.63 (d, *J* = 11.3 Hz, 1H), 4.39 (d, *J* = 11.3 Hz, 1H), 3.81 (s, 3H), 1.65 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ **S9 Major:** 159.6, 155.5, 151.2, 129.8, 128.6, 127.5, 125.4, 123.4, 121.5, 113.9, 111.8, 108.5, 85.3, 75.5, 71.0, 55.4, 16.4; **S9 Minor:** 159.7, 155.3, 152.5, 129.9, 128.8, 127.7, 125.0, 123.3, 121.5, 114.0, 111.7, 106.8, 84.4, 74.9, 71.8, 55.4, 13.7;FTIR (cm^{-1}): 2937, 2837, 1556, 1251, 1175; mp: 72-74 °C; GC/MS (EI) 235.0 $(M-C_7H_7O)^+$; 234.9 $(M-C_7H_7O)^+$. HRMS (LIFDI) m/z, calculated for $[C_{19}H_{19}NO_5]^+$: 341.1263; found: 341.1247.



(S10) S10 was synthesized by modification of a previously published procedure.[11] A hot 100 mL Schlenk equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and allowed to cool. Once cool, the flask was backfilled with N_2, the septum was removed and tris(dibenzylideneacetone)dipalladium(0) (82.0 mg, 90.0 μmol), BrettPhos (110 mg, 210 μmol), cesium carbonate (2.35 g, 7.20 mmol), and 5-bromo-1-(*p*-toluenesulfonyl)-1H-indole (2.09 g, 6.00 mmol). The septum was replaced, the flask was reattached to the double manifold and evacuated and backfilled with N_2 three times. Anhydrous dioxane (40 mL) and 4-nitrobutyl acetate (2.58 g, 16.0 mmol) were added via syringe. The resulting heterogeneous solution was heated in an oil bath at 50 °C for 24 h. Once complete, the reaction was cooled to rt. Saturated NH_4Cl (10 mL) was added and the reaction was stirred for 10 minutes. Another 10 mL saturated NH_4Cl (10 mL) was added and the reaction was stirred for another 10 minutes. The reaction was then diluted with diethyl ether (25 mL), washed twice with brine (25 mL), dried over magnesium

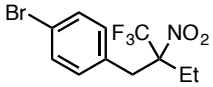
sulfate and concentrated *in vacuo*. The crude reaction was purified using flash silica gel chromatography (65:35 hexanes : ethyl acetate) to afford **S10** (911 mg, 44%) as a thick yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 14.3, 2.6 Hz, 2H), 7.40 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 3.7 Hz, 1H), 5.68 (q, *J* = 6.9 Hz, 1H), 2.35 (s, 3H), 1.92 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 135.4, 135.1, 131.1, 130.7, 130.2, 127.6, 127.0, 123.9, 120.8, 114.1, 109.0, 86.4, 21.8, 19.7; FTIR (cm^{-1}): 3144, 2989, 1550, 1373, 1175; HRMS (LIFDI) m/z calculated for $[C_{17}H_{16}N_2O_4S]^+$: 344.0831; found: 344.0845.



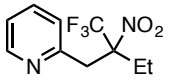
(25) A hot 150 mL high-pressure reaction vessel equipped with a magnetic stir bar and a Teflon cap and a Kontes cap was attached to a double manifold and cooled under vacuum. Once cool, the flask was backfilled with N_2, the Teflon cap was removed, and CuBr (940 mg, 6.55 mmol), (*E*)-*N*-((*Z*)-4-(2,6-dimethylphenylamino)pent-3-en-2-ylidene)-2,6-dimethylaniline (2.00 g, 6.55 mmol), and sodium trimethylsilanolate (2.06 g, 18.3 mmol) were added. The Teflon cap was replaced, the flask was attached to a double manifold, and evacuated and backfilled with N_2 five times. The Kontes cap was removed and replaced with a rubber septum, and anhydrous dichloromethane (77 mL), 1-nitropropane (1.52 mL, 17.0 mmol) and benzyl bromoacetate (2.10 mL, 13.1 mmol) were added via syringe. The Kontes cap was replaced and the resulting hetereogenous solution was submerged in an oil bath. The reaction was heated at 60 °C with rapid stirring for 21 h. Once completed, the reaction was cooled to room temperature, the septum was removed and the reaction mixture was diluted with diethyl ether (50 mL). The crude reaction mixture was filtered through a plug of Celite and concentrated *in vacuo*. The crude reaction was purified by silica gel flash chromatography (82:15:3 hexanes : benzene : ethyl acetate) to afford β-nitroester **S11** (1.23 g, 40%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 5H), 5.15 (s, 2H), 4.86 (dddd, *J* = 9.8, 7.5, 5.7, 4.5 Hz, 1H), 3.20 (dd, *J* = 17.3, 9.4 Hz, 1H), 2.73 (dd, *J* = 17.4, 4.3 Hz, 1H), 2.04 - 1.89 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 135.3, 128.8, 128.7, 128.5, 84.4, 67.3, 36.8, 27.2, 10.0; FTIR (cm^{-1}):3066, 2975, 2883, 1738, 1552; GC/MS (EI) 107.0 $(M\text{-}C_5H_8NO_3)^+$. HRMS (CI) m/z calculated for $[C_{12}H_{16}NO_4]^+$: 238.1079; found: 238.1072.

6. General Protocol for the Synthesis of α-Trifluoromethylnitroalkanes:

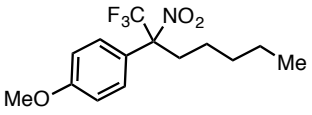
General Protocol A: Synthesis of α-Trifluoromethylnitroalkanes: A hot 25 mL round bottom flask equipped with a magnetic stir bar and a rubber spectrum was attached via needle to a double manifold and cooled under vacuum. Once cooled, the flask was backfilled with N_2, the septum was removed, and nitroalkane (1 equiv) and 5-(trifluoromethyl)dibenzothiophenium trifluoromethanesulfonate (Umemoto's reagent, **2**, 1.3 equiv) were added. The septum was replaced, the flask was reattached to a double manifold and evacuated and backfilled with N_2 three times. Anhydrous dichloromethane was added via syringe and the flask was lowered into a precooled –25 °C cooling bath and stirred. 1,8-Diazabicycloundec-7-ene (DBU, 2 equiv) was then added dropwise via syringe. The resulting homogenous solution was stirred at –25 °C for 4 h after which the flask was removed from the cooling unit and the septum was removed. The reaction mixture was washed with brine (1x), dried over magnesium sulfate, and concentrated *in vacuo* onto Celite. The product was purified by silica gel flash chromatography.



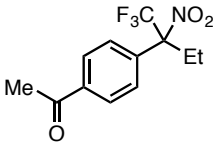
(3) According to general protocol A: 1-bromo-4-(2-nitrobutyl)benzene (257 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (100:0 → 99:1 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **3** (270 mg, 83%) as a clear oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 3.51 (d, *J* = 14.7 Hz, 1H), 3.34 (d, *J* = 14.7 Hz, 1H), 2.22 (dq, *J* = 15.9, 8.4 Hz, 1H), 2.05 (dq, *J* = 14.8, 7.3 Hz, 1H), 1.08 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ132.1, 132.0, 131.0, 122.6, 123.2 (q, *J* = 286 Hz), 94.3 (q, *J* = 25.9 Hz), 38.9, 26.1, 8.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.5; FTIR (cm^{-1}): 2987, 2957, 1561, 1490, 1195, 839, 812; GC/MS (EI) 278.0 $(M\text{-}NO_2)^+$. HRMS (CI) m/z calculated for $[C_{11}H_{11}NO_2BrF_3]^+$: 324.9925; found: 324.9930.



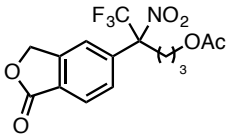
(4) According to general protocol A: 2-(2-Nitrobutyl)pyridine (180 mg, 1.00 mmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (75:25 hexanes : ethyl acetate). A second column (50:50 hexanes : ethyl acetate) to remove trace dibenzothiophene afforded α-trifluoromethylnitroalkane 4 (158 mg, 64%) as a orange oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.55 - 8.51 (m, 1H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1H), 7.20 (dd, *J* = 7.1, 5.3 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 3.83 (d, *J* = 14.8 Hz, 1H), 3.53 (d, *J* = 14.8 Hz, 1H), 2.41 - 2.26 (m, 2H), 1.10 - 1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 149.6, 136.8, 124.8, 123.8 (q, *J* = 288 Hz), 122.8, 94.0 (q, *J* = 26.3 Hz), 39.6, 25.1, 8.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.3; FTIR (cm^{-1}): 2986, 2955, 1563, 1439, 1241, 1186; GC/MS (EI) 202.1 $(M\text{-}NO_2)^+$. HRMS (CI) m/z calculated for $[C_{10}H_{12}N_2O_2F_3]^+$: 249.0851; found: 249.0850.



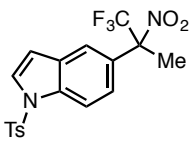
(5) According to general protocol A: **S1** (237 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (90:10 petroleum ether : benzene) to afford α-trifluoromethylnitroalkane **5** (263 mg, 86%) as a clear oil: ^{1}H NMR (600 MHz, C_6D_6) δ 7.03 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 9.0 Hz, 2H), 3.16 (s, 3H), 2.41 - 2.30 (m, 2H), 1.43 (m, 1H), 1.31 (m, 1H), 1.09 - 0.96 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 128.6, 123.8, 123.0 (q, *J* = 286 Hz), 114.2, 96.3 (q, *J* = 27.3 Hz), 55.5, 34.5, 31.9, 23.6, 22.3, 14.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.2; FTIR (cm^{-1}): 2960, 1563, 1518, 1263, 1180, 832. HRMS (LIFDI) m/z calculated for $[C_{14}H_{18}NO_3F_3]^+$: 305.1239; found: 305.1242.



(6) According to general protocol A: 4-Acetyl-(1-nitropropyl)benzene (207 mg, 1.00 mmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (99:05 → 90:10 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **6** (214 mg, 78%) as a clear oil **6**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 2.69 (hept, *J* = 7.8 Hz, 2H), 2.63 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.0, 138.3, 136.3, 128.8, 127.5, 122.7 (q, *J* = 285 Hz), 96.8 (q, *J* = 27.2 Hz), 28.2, 26.8, 8.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -68.7; FTIR (cm^{-1}): 2955, 1692, 1565, 1411, 1269, 1169, 824**.** HRMS (CI) m/z calculated for $[C_{12}H_{13}NO_3F_3]^+$: 276.0848; found: 276.0823.

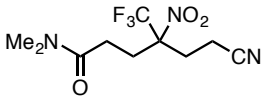


(7) According to general protocol A: **S2** (248 mg, 850 μmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (65:35 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **7** (246 mg, 80%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 8.2 Hz, 1H), 7.45 (s, 1H), 5.38 (s, 2H), 4.13 (t, *J* = 6.1 Hz, 2H), 2.72 (dt, *J* = 10.6, 4.9 Hz, 2H), 2.08 (s, 3H), 1.96 - 1.86 (m, 1H), 1.77 - 1.67 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 169.6, 147.3, 137.5, 127.9, 127.9, 126.7, 122.4 (q, *J*= 286 Hz), 121.2, 96.2 (q, *J*= 28.1 Hz), 69.6, 63.2, 31.9, 23.6, 21.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -68.5; FTIR (cm^{-1}): 2960, 1773, 1739, 1567, 1240; mp = 109-110 °C; HRMS (LIFDI) m/z calculated for $[C_{15}H_{14}NO_6F_3]^+$: 361.0773; found: 361.0766.

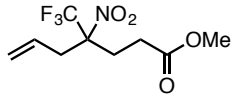


(8) According to general protocol A: **S10** (344 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the

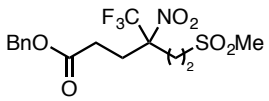
general protocol and purified by flash silica gel chromatography (80:20 hexanes : ethyl acetate) to afford **8** (309 mg, 75%) as a light yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 4.8, 2.9 Hz, 2H), 7.39 - 7.31 (m, 1H), 7.29 - 7.24 (m, 2H), 6.69 (d, *J* = 3.7 Hz, 1H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 135.4, 135.0, 130.9, 130.24, 127.9, 127.0, 126.6, 122.8 (q, *J* = 283 Hz), 122.7, 120.3, 114.0, 108.9, 92.6 (q, *J* = 28.7 Hz), 21.8, 20.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.3; FTIR (cm^{-1}): 3146, 2925, 1564, 1376, 1173, 1135; mp: 104-105 °C; HRMS (LIFDI) m/z calculated for $[C_{18}H_{15}N_2O_4SF_3]^+$: 412.0705; found: 412.0703.



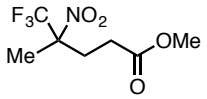
(9) According to general protocol A: **S5** (213 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to -25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica get chromatography (60:40 benzene : ethyl acetate) to afford α-trifluoromethylnitroalkane **9** (198 mg, 70%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.98 (d, *J* = 10.7 Hz, 6H), 2.75 - 2.48 (m, 6H), 2.46 - 2.35 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3. 122.7 (q, *J* = 286 Hz), 117.4, 91.7 (q, *J* = 27.4 Hz), 37.1, 35.9, 28.8, 28.4, 27.0, 12.8 (q, *J* = 2.1 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -70.57; FTIR (cm^{-1}):2940, 2254, 1644, 1558, 1189; mp = 52-54 °C; GC/MS (EI) 235.1 $(M\text{-}NO_2)^+$; HRMS (ESI) m/z calculated for $[C_{10}H_{15}N_3O_3F_3]^+$: 282.10600; found: 282.10552.



(10) According to general protocol A: methyl 4-nitrohept-6-enoate **S3** (187 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 18 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (100:0 → 95:5 hexanes : ethyl acetate) to afford **10** (119 mg, 47%) as a clear oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.69 (dd, *J* = 17.2, 7.5 Hz, 1H), 5.33 - 5.25 (m, 2H), 3.71 (s, 3H), 2.98 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.90 (dd, *J* = 14.9, 7.3 Hz, 1H), 2.65 - 2.57 (m, 1H), 2.56 - 2.42 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.8, 128.1, 122.7, 122.9 (q, *J* = 286 Hz), 92.5 (q, *J* = 26.8 Hz), 52.2, 37.6, 28.2, 27.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.1; FTIR (cm^{-1}): 3089, 2957, 1742, 1652, 1563, 1439, 1201, 936; GC/MS (EI) 224.0 $(M\text{-}OCH_3)^+$; HRMS (CI) m/z calculated for $[C_9H_{13}NO_4F_3]^+$: 256.0797; found: 256.0810.

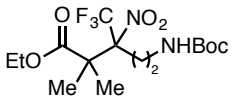


(11) According to general protocol A: benzyl 6-(methylsulfonyl)-4-nitrohexanoate **S4** (315 mg, 960 μmol), Umemoto's reagent **2** (500 mg, 1.24 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (95:5 → 80:20 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **11** (250 mg, 66%) as a clear oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 - 7.32 (m, 5H), 5.15 (s, 2H), 3.19 (dt, *J* = 12.9, 4.2 Hz, 1H), 3.12 (dt, *J* = 12.7, 4.3 Hz, 1H), 2.98 (s, 3H), 2.81 - 2.72 (m, 1H), 2.69 - 2.45 (m, 5H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 135.3, 128.8, 128.7, 128.5, 122.6 (q, *J* = 286 Hz), 91.5 (q, *J* = 27.4 Hz), 67.3, 49.0, 41.0, 28.2, 28.1, 25.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -70.8; FTIR (cm^{-1}): 3011, 1731, 1565, 1451, 1308, 1176, 755 **;** ESI-MS 420.3 $(M+Na)^+$**.** HRMS (ESI) m/z calculated for $[C_{15}H_{19}NO_6F_3S]^+$: 398.0880; found: 398.0869.

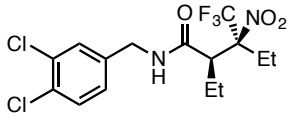


(12) According to general protocol A: Methyl 4-nitropentanoate (484 mg, 3.00 mmol), Umemoto's reagent **2** (1.57 g, 3.90 mmol) and anhydrous dichloromethane (30 mL) were combined under N_2 and cooled to –25 °C. DBU (897 μL, 6.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified via silica gel flash chromatography (95:5 → 80:20 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **12** (624 mg, 91%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.77 - 2.63 (m, 1H), 2.48 - 2.27 (m, 3H), 1.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 123.0 (q, *J* = 287 Hz), 90.0 (q, *J* = 29.1 Hz), 52.3, 28.7, 28.05, 17.6; ^{19}F NMR (565

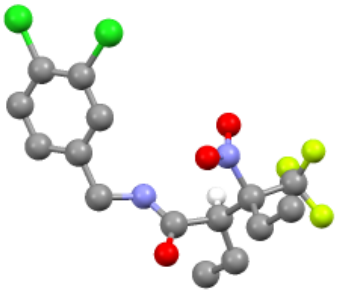
MHz, $CDCl_3$) δ -75.7; FTIR (cm^{-1}): 2361, 1652, 1559, 1540, 1175; GC/MS (EI) 198.1 $(M\text{-}OCH_3)^+$. HRMS (CI) m/z calculated for $[C_7H_{11}NO_4F_3]^+$: 230.0640; found: 230.0626.

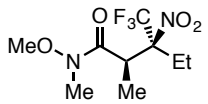


(14) According to general protocol A: Ethyl 5-(*tert*-butoxycarbonylamino)-2,2-dimethyl-3-nitropentanoate (318 mg, 1.00 mmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL. 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 48 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (89:11 hexanes : ethyl acetate) to afford **14** (141 mg, 36%) as a pale yellow solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.76 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.47 - 3.32 (m, 1H), 2.96 (ddt, *J* = 14.3, 10.3, 5.0 Hz, 1H), 2.65 - 2.40 (m, 2H), 1.49 - 1.34 (m, 15H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 155.7, 123.1 (q, *J* = 287 Hz), 96.1 (q, *J* = 26.3 Hz), 79.9, 62.4, 49.2, 36.2, 32.0, 28.5, 23.3, 23.1, 13.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.6; FTIR (cm^{-1}): 3350, 2981, 1720, 1568, 1174; mp: 58-60 °C; ESI-MS: 409.1 $(M+Na)^+$. HRMS (ESI) m/z calculated for $[C_{15}H_{25}N_2O_6F_3Na]^+$: 409.15569; found: 409.15437.



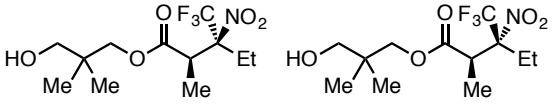
(15) According to general protocol A: *N*-(3,4-dichlorobenzyl)-2-ethyl-3-nitropentanamide (332 mg, 1.00 mmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 24 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (75:25 hexanes : ethyl acetate). A second column (50:50 hexanes : ethyl acetate) to remove trace dibenzothiophene afforded α-trifluoromethylnitroalkane **15** (291 mg, 73%) as a light yellow solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.06 (dd, *J* = 8.2, 1.9 Hz, 1H), 5.84 (s, 1H), 4.32 (qd, *J* = 15.1, 5.8 Hz, 2H), 3.07 - 2.98 (m, 1H), 2.74 - 2.64 (m, 1H), 2.06 (dq, *J* = 14.7, 7.2 Hz, 1H), 1.93 (tq, *J* = 14.2, 7.2 Hz, 1H), 1.65 (dd, *J* = 12.8, 6.8 Hz, 1H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 137.6, 132.9, 131.9, 130.8, 129.8, 127.1, 122.7 (q, *J* = 287 Hz), 96.8 (q, *J* = 25.8), 54.0, 43.0, 21.9, 21.0, 12.6, 8.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -65.5; FTIR (cm^{-1}): 3297, 3088, 1658, 1563, 1201, 1088, 1032; 116-118 °C; ESI-MS: 401.2 $(M+H)^+$. HRMS (ESI) m/z calculated for $[C_{15}H_{18}N_2O_3Cl_2F_3]^+$: 401.06411; found: 401.06349; X-ray crystals were obtained by vapor diffusion (dichloromethane/ hexanes).





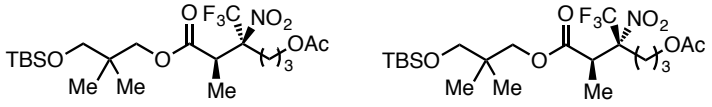
(16) According to general protocol A: *N*-methoxy-*N*,2-dimethyl-3-nitropentanamide (204 mg, 1.0 mmol), Umemoto's reagent **2** (532 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (95:5 → 90:10 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **16** (172 mg, 63%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (q, *J* = 7.1 Hz, 1H), 3.71 (s, 3H), 3.15 (s, 3H), 2.90 (ddd, *J* = 15.9, 7.5, 2.5 Hz, 1H), 2.16 (dd, *J* = 15.7, 7.6 Hz, 1H), 1.36 (d, *J* = 7.2 Hz, 3H), 1.11 (td, *J* = 7.4, 1.8 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.1, 123.1 (q, *J* = 287 Hz), 95.3 (q, *J* = 25.6 Hz), 61.6, 39.2, 32.4, 22.7, 13.8, 8.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.9; FTIR (cm^{-1}): 2985, 2951, 1670, 1565, 1203,

1179 ; GC/MS (EI) 226.1 $(M\text{-}NO_2)^+$. HRMS (CI) m/z calculated for $[C_9H_{16}N_2O_4F_3]^+$: 273.1062; found: 273.1064.



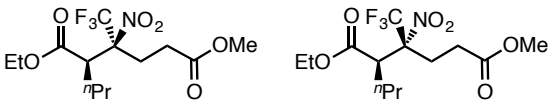
17A **83:17** **17B**

(17) According to general protocol A: 3-Hydroxy-2,2-dimethylpropyl 2-methyl-3-nitropentanoate **S7** (315 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 83:17 mixture of syn and anti isomers. The crude reaction was purified by flash silica gel chromatography (95:5 → 80:20 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **17** (157 mg, 50%) as a clear oil: The product was isolated as a mixture of diastereomers (dr: 88:12): ^{1}H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed) δ **17A:** 3.87 (d, *J* = 10.9 Hz, 1H), 3.72 (q, *J* = 7.2 Hz, 1H), 1.39 (d, *J* = 7.2 Hz, 3H); **17B:** 3.60 (q, *J* = 7.1 Hz, 1H), 2.00 (d, *J* = 2.0 Hz, 1H), 1.31 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **17A:** 170.5, 122.8 (q, *J* = 287 Hz), 95.0 (q, *J* = 26 Hz), 68.1, 44.5, 36.2, 22.7, 21.5, 12.8, 8.5; **17B**: 170.3, 123,0 (q, *J* = 287 Hz), 95.2 (q, *J* = 26 Hz), 68.3, 43.9, 23.8, 13.0;^{19}F NMR (565 MHz, $CDCl_3$) δ **17A:** -66.8, **17B:** -67.1; FTIR (cm^{-1}): 3435, 2962, 1742, 1569, 1470, 1245, 1203, 824; GC/MS (EI) 212.0 $(M\text{-}C_5H_{11}O_2)^+$; 212.1 $(M\text{-}C_5H_{11}O_2)^+$. HRMS (CI) m/z calculated for $[C_{12}H_{21}NO_5F_3]^+$: 316.1372; found: 316.1364.



18A **85:15** **18B**

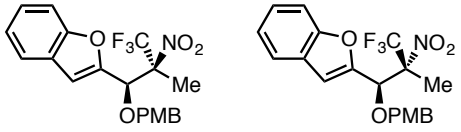
(18) According to general protocol A: **S6** (433 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 85:15 mixture of syn and anti isomers. The crude reaction was purified flash silica gel chromatography (100:0 → 95:5 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **18** (292 mg, 58%) as a clear oil. The product was isolated as a mixture of diastereomers (dr: 92:08): ^{1}H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed) δ **18A:** 3.81 (d, *J* = 10.6 Hz, 1H), 3.76 (q, *J* = 7.2 Hz, 1H), 1.40 (d, *J* = 7.2 Hz, 3H), 0.88 (s, 9H), 0.86 (d, *J* = 2.4 Hz, 6H), 0.03 (d, *J* = 5.2 Hz, 6H); **18B:** 3.88 (d, *J* = 10.6 Hz, 1H), 3.61 (q, *J* = 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **18A:** 170.9, 169.8, 122.8, (q, *J* = 288 Hz), 94.2, (q, *J* = 26 Hz), 71.5, 63.8, 44.4, 43.9, 36.2, 26.1, 25.9, 23.2, 21.5, 21.4, 20.9, 18.3, 12.9, -5.5, -5.6; **18B:** 71.4, 63.7, 43.9, 13.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ **18A:** -67.2, **18B:** -67.5; FTIR (cm^{-1}): 2957, 2897, 1745, 1572, 1473, 1365, 1236, 838, 776; GC/MS (ESI) 524.3 $(M+Na)^+$. HRMS (ESI) m/z calculated for $[C_{21}H_{39}NO_7F_3Si]^+$: 502.2442; found: 502.24267.



19A **67:33** **19B**

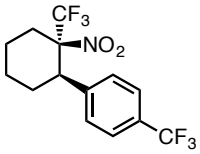
(19) According to the general protocol: 1-Ethyl 6-methyl 3-nitro-2-propylhexanedioate (275 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed a 67:33 mixture of syn and anti isomers. The reaction was purified by silica gel flash chromatography (100:0 → 95:5 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **19** (254 mg, 74%) as a yellow oil. The product was isolated as a mixture of diastereomers (dr: 73: 27): ^{1}H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed. See attached spectra for details): δ **19A:** 4.15 (q, *J* = 7.1 Hz, 2H), 3.71 (s, 3H), 3.44 (dd, *J* = 12.1, 2.4 Hz, 1H), 0.91 (t, 3H); **19B:** 4.25 - 4.19 (m, 2H), 3.73 (s, 3H), 3.50 (dd, *J* = 12.0, 2.6 Hz, 1H), 0.95 (t, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **19A:** 172.0, 169.2, 122.7 (q, *J* = 286 Hz), 62.2, 50.3, 29.3, 28.5, 24.8, 21.3, 13.9, 13.7, 13.5; **19B:** 172.1, 169.5, 122.6 (q, *J* = 287 Hz), 62.1, 49.5, 29.9, 23.9, 28.6, 20.8, 14.0, 13.5; ^{19}F

NMR (565 MHz, $CDCl_3$) δ **19A**: -66.2, **19B**: -68.1; FTIR (cm^{-1}): 2965, 2878, 1743, 1570, 1190; GC/MS (EI) 297.1 $(M\text{-}NO_2)^+$; 297.1 $(M\text{-}NO_2)^+$. HRMS (CI) m/z calculated for $[C_{13}H_{21}NO_6F_3]^+$: 344.1321; found: 344.1329.

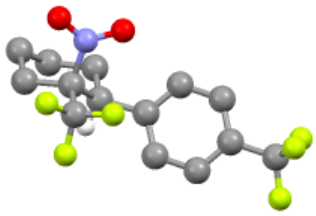


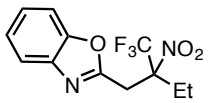
20A **89:11** **20B**

(20) According to general protocol A: **S9** (341 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol) and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 89:11 mixture of syn and anti isomers. The crude reaction was purified by flash silica gel chromatography (100:0 → 95:05 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **20** (236 mg, 58%) as a clear oil: ^1H NMR (600 MHz, $CDCl_3$: mixture of diastereomers; useful diagnostic peaks for each compound are listed) δ **20A:** 7.57 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.36 - 7.32 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.15 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.78 (s, 1H), 5.53 (s, 1H), 4.62 (d, *J* = 11.1 Hz, 1H), 4.42 (d, *J* = 11.1 Hz, 1H), 1.89 (s, 3H); **20B:** 7.54 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H), 4.50 (d, *J* = 11.0 Hz, 1H), 4.27 (d, *J* = 11.2 Hz, 1H), 2.03 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **20A:** 159.9, 155.6, 149.5, 130.1, 128.1, 125.5, 123.5, 122.7 (q, *J* = 287 Hz), 119.9, 111.8, 109.7, 109.3, 93.16, (q, *J* = 26.5 Hz), 74.5, 72.3, 55.4, 13.5; **20B:** 159.8, 155.7, 149.3, 129.9, 128.0, 125.6, 109.7, 73.9, 71.6, 12.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ **20A:** -72.0, **20B:** -73.2; FTIR (cm^{-1}): 2936, 2838, 1613, 1566, 1453, 1254, 751; GC/MS (EI) 409.0 $(M)^+$. HRMS (CI) m/z calculated for $[C_{20}H_{18}NO_5F_3]^+$: 409.1137; found: 409.1135.



(21) According to general protocol A: *rac*-2-(4-Trifluoromethylphenyl)-1-nitrocyclohexane (410 mg, 1.50 mmol), Umemoto's reagent **2** (785 mg, 1.95 mmol), and anhydrous dichloromethane (15 mL) were combined under N_2 and cooled to –25 °C. DBU (448 μL, 3.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and purified by flash silica gel chromatography (77:20:3 hexanes : benzene : ethyl acetate) to afford α-trifluoromethylnitroalkane **21** (333 mg, 65%) as a light yellow solid: ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 3.33 (dd, *J* = 12.6, 3.8 Hz, 1H), 2.66 (d, *J* = 14.7 Hz, 1H), 2.38 (qd, *J* = 13.0, 3.7 Hz, 1H), 2.11 - 1.96 (m, 2H), 1.96 - 1.71 (m, 3H), 1.52 (ddp, *J* = 17.0, 8.7, 4.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 130.2 (q, *J* = 35.5 Hz), 129.9, 125.3 (q, *J* = 3.64 Hz), 124.1 (q, *J* = 272 Hz), 122.9 (q, *J* = 284 Hz), 92.9 (q, *J* = 25.4 Hz), 46.4, 31.5, 29.1, 24.8, 20.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -70.9; FTIR (cm^{-1}): 2947, 1561, 1328, 1161, 1123; mp = 43-45 °C; GC/MS (EI) 341.1 $(M)^+$. HRMS (CI) m/z calculated for $[C_{14}H_{13}NO_2F_6]^+$: 341.0871; found: 341.0850; crystals for X-ray analysis were obtained by slow evaporation of hexanes.

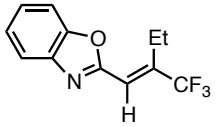




(23) A hot 25 mL round bottom flask equipped with a magnetic stir bar and a rubber spectrum was attached to a double manifold and cooled under vacuum. Once cooled, the flask was backfilled with N_2, the septum was removed, and 2-(2-nitrobutyl)benzo[*d*]oxazole (220 mg, 1.00 mmol) and Umemoto's reagent **2** (523 mg, 1.30 mmol) were added. The septum was replaced, the flask was reattached to a double manifold and evacuated and backfilled with N_2 three times. Anhydrous dichloromethane (10 mL) was added via syringe and the flask was lowered into a precooled –25 °C cooling bath and stirred. 1,1,3,3,-Tetramethylguanidine (121 μL, 1.00 mmol) was then added dropwise via syringe. The resulting homogenous solution was stirred at –25 °C for 4 h, after which the flask was removed from the cooling unit and warmed to rt. The

reaction mixture was washed with brine (1x), dried over magnesium sulfate, and concentrated *in vacuo* onto Celite. The product was purified by silica gel flash chromatography (100:0 → 95:5 hexanes : ethyl acetate) to afford α-trifluoromethylnitroalkane **23** (128 mg, 44%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 - 7.68 (m, 1H), 7.56 - 7.50 (m, 1H), 7.41 - 7.32 (m, 2H), 3.99 (d, *J* = 16.0 Hz, 1H), 3.81 (d, *J* = 16.0 Hz, 1H), 2.54 (q, *J* = 7.5 Hz, 2H), 1.15 (dd, *J* = 7.4, 1.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.7, 150.8, 140.9, 125.7, 124.9, 122.8 (q, *J* = 291 Hz), 120.4, 110.9, 92.4 (q, *J* = 26.9 Hz), 30.39 (q, *J* = 1.41 Hz), 25.2, 8.45 (d, *J* = 1.66 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.9; FTIR (cm^{-1}): 2985, 1567, 1455, 1180, 1169; GC/MS (EI) 288.1 $(M)^+$. HRMS (CI) m/z calculated for $[C_{12}H_{12}N_2O_3F_3]^+$: 289.0800; found: 289.0794.

7. Synthesis of Trifluoromethylalkenes:



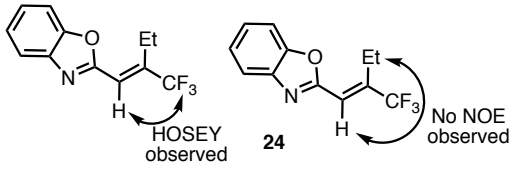
(24) According to general protocol A: 2-(2-Nitrobutyl)benzo[*d*]oxazole (220 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis revealed a >95:5 mixture of E and Z isomers. The crude reaction was purified flash silica gel chromatography (100:0 → 98:2 hexanes : ethyl acetate) to afford vinyltrifluoromethylalkene **24** (147 mg, 61%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 7.7, 1H), 7.40 (pd, *J* = 7.2, 1.1 Hz, 2H), 6.96 (s, 1H), 2.97 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 150.4, 142.6 (q, J = 28.9 Hz), 141.9, 126.3, 125.1, 123.2, 120.8, 117.3 (q, J = 6.9 Hz), 110.9, 21.0, 13.2; ^{19}F NMR (565 MHz, $CDCl_3$) δ -68.3; FTIR (cm^{-1}): 2981, 2944, 2883, 1652, 1451, 1181, 745; GC/MS (EI) 241.1 $(M)^+$. HRMS (CI) m/z calculated for $[C_{12}H_{11}NOF_3]^+$: 242.0793; found: 242.0780. The relative stereochemistry of compound **24** was determined using a combination of 1D nOe and ^{19}F:^{1}H HOSEY correlations.[15] The results from these experiments is summarized in the tables and figures below:

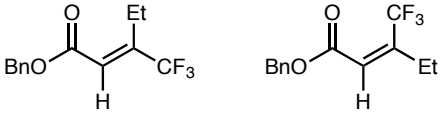
1D nOe Correlation For **24**

Shift Irradiated (ppm)	1 D nOe Correlation Seen (ppm)
6.99	n/a

2D HOSEY Correlation for **24**: ^{1}H to ^{19}F

^{19}F Shift (ppm)	^{1}H Correlations Seen (ppm)
-68.3	1.23
-68.3	2.90
-68.3	6.88





27A **88:12** **27B**

(27) According to general protocol A: **25** (238 mg, 1.00 mmol), Umemoto's reagent **2** (523 mg, 1.30 mmol), and anhydrous dichloromethane (10 mL) were combined under N_2 and cooled to –25 °C. DBU (299 μL, 2.00 mmol) was added dropwise and the reaction was stirred at –25 °C for 4 h. The reaction was worked up according to the general protocol and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 88:12 mixture of E and Z isomers. The crude reaction was purified flash silica gel chromatography (100:0 → 98:2 hexanes : ethyl acetate) to afford mixture of vinyltrifluoromethylalkene **27A** and **27B** (154 mg, 60%) as a clear oil. An analytically pure sample of product **27A** was obtained by column chromatography. Alkene **27B** was isolated contaminated

with alkene **27A**. Diagnostic peaks for alkene **27A** are listed below: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 - 7.32 (m, 5H), 6.35 (s, 1H), 5.21 (s, 2H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.17 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 148.4 (q, *J* = 28.9 Hz), 135.5, 128.8, 128.7, 123.6 (q, *J* = 276 Hz) 121.5, (q, *J* = 6.20 Hz), 120.9, 66.9, 20.4, 13.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.2; FTIR (cm^{-1}): 3036, 2982, 1731, 1669, 1309, 1191, 696; GC/MS (EI) 258.1 $(M)^+$. HRMS (CI) m/z calculated for $[C_{13}H_{13}O_2F_3]^+$: 258.0868; found: 258.0896.

Alkene **27B** was isolated contaminated with alkene **27A**. Diagnostic peaks for alkene **27B** are listed below: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (s, 1H), 5.20 (s, 2H), 2.33 (qd, *J* = 7.3, 1.6 Hz, 2H), 1.13 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.8, 135.3, 128.8, 128.7, 128.6, 123.5, 67.4, 24.5, 11.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.5; GC/MS (EI) 258.1 $(M)^+$. HRMS (CI) m/z calculated for $[C_{13}H_{13}O_2F_3]^+$: 258.0868; found: 258.0859.

The relative stereochemistry for alkenes **27A** and **27B** was determined using 1D nOe and ^{1}H:^{19}F HOSEY. The results from these experiments is summarized in the tables and figures below:

1D nOe Correlation For **27A**

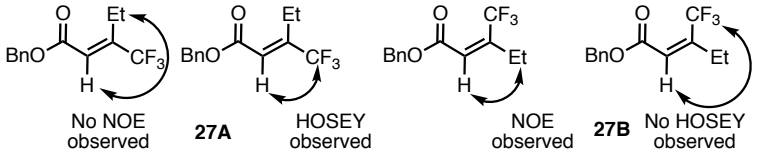
Shift Irradiated (ppm)	1 D nOe Correlation Seen (ppm)
6.38	n/a

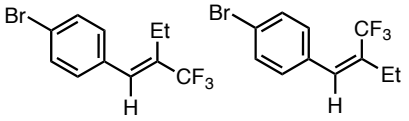
2D HOSEY Correlation For **27A**: ^{1}H to ^{19}F

^{19}F Shift (ppm)	^{1}H Correlations Seen (ppm)
-69.2	1.17
-69.2	2.69
-69.2	6.34

1D nOe Correlation For **27B**

Shift Irradiated (ppm)	1 D nOe Correlation Seen (ppm)
6.10	2.35, 1.16
2.36	6.10, 1.16
1.16	2.36, 1.16





(28) A hot 25 mL round bottom flask equipped with a magnetic stir bar and a rubber spectrum was attached to a double manifold and cooled under vacuum. Once cooled, the flask was backfilled with N_2, the septum was removed, and 1-bromo-4-(2-nitro-2-(trifluoromethyl)butyl)benzene **3** (163 mg, 0.5 mmol), potassium *tert*-butoxide (84.0 mg, 0.75 mmol) and anhydrous dichloromethane (5 mL) were added and the reaction was stirred in an oil bath at 40 °C for 5 h. The reaction mixture was washed with NH_4Cl (1x15 mL), dried over magnesium sulfate, and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 72:28 mixture of E and Z isomers. The product was purified by silica gel flash chromatography (100 % hexanes) to afford a mixture of vinyltrifluoromethylalkene **28A** and **28B** (130 mg, 93%) as a clear oil. The product was isolated as a mixture of E:Z (72:28) isomers. ^{1}H NMR (600 MHz, C_6D_6: mixture of E and Z isomer; useful diagnostic peaks for each compound are listed; see attached spectra for details) δ **28A:** 7.14 - 7.10 (m, 2H), 6.72 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 2.09 (q, *J* = 7.6 Hz, 2H), 0.90 (t, *J* = 7.5 Hz, 3H); **28B:** 6.78 (d, *J* = 8.3 Hz, 2H), 6.12 (s, 1H), 1.99 (qd, *J* = 7.4, 1.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ **28A:** 133.6, 133.2, 131.9, 130.8 (q, *J* = 6.5 Hz), 130.5, 124.9 (q, *J* = 274 Hz), 122.6, 19.8, 13.4; **28B:** 134.4, 133.1, 132.7 (q, *J* = 3.9 Hz), 131.3, 130.2 (q, J = 2.5 Hz), 124.0 (q, *J* = 276 Hz), 122.1, 25.9, 13.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.4, -66.7. FTIR (cm^{-1}): 2975, 2942, 1653,

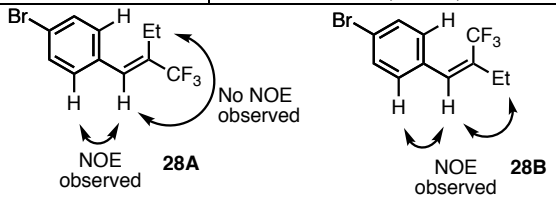
1489, 1251, 1161, 1115, 901; GC/MS (EI) 278.0 $(M)^+$. HRMS (CI) m/z calculated for $[C_{11}H_{10}F_3Br]^+$: 277.9918; found: 277.9909.

1D nOe Correlation For **28A**

Shift Irradiated (ppm)	1 D nOe Correlation Seen (ppm)
6.73	6.55

1D nOe Correlation For **28B**

Shift Irradiated (ppm)	1 D nOe Correlation Seen (ppm)
6.12	6.78, 1.99, 0.86

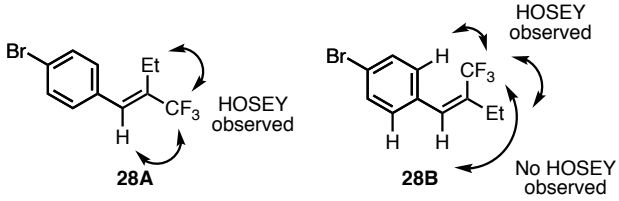


2D HOSEY Correlation For **28A**: ^1H to ^{19}F

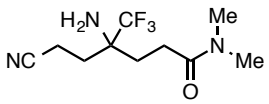
^{19}F Shift (ppm)	^1H Correlations Seen (ppm)
-66.7	0.90
-66.7	2.09
-66.7	6.72

2D HOSEY Correlation For **28B**: ^1H to ^{19}F

^{19}F Shift (ppm)	^1H Correlations Seen (ppm)
-59.4	0.90
-59.4	1.99
-59.4	6.78

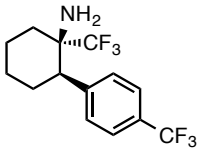


8. Reduction of Trifluoromethylnitroalkanes to Trifluoromethylamines

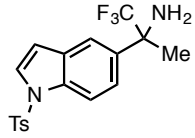


(29) To a 10 mL round bottom flask equipped with a magnetic stir bar was added α-trifluoromethylnitroalkane **9** (100 mg, 356 μmol) and acetic acid (1.19 mL). The flask was cooled to 0 °C in an ice bath and zinc dust (233 mg, 3.56 mmol) was added portionwise. Once addition of zinc was complete, the reaction was warmed to rt and stirred for 13 h. The crude reaction was filtered through Celite and diluted with ethyl acetate (10 mL). The reaction was washed with $NaHCO_3$ (3x, 10 mL). The aqueous layer was basified with 1 M NaOH. The water was removed *in vacuo* and the crude solid was washed with chloroform (25 mL). The mother liquor was concentrated *in vacuo* to afford α-trifluoromethylamine 29 (70.1 mg, 78%) as a light pink solid: ^1H NMR (400 MHz, $CDCl_3$) δ 3.02 (s, 3H), 2.93 (s, 3H), 2.82 - 2.70 (m, 1H), 2.70 - 2.57 (m, 1H), 2.58 - 2.45 (m, 2H), 2.36 - 2.05 (m, 4H); ^{13}C NMR (101 MHz, D_2O) δ 173.7, 156.0, 125.4 (q, J = 286 Hz), 73.3 (q, J = 27.7 Hz), 37.2, 35.5, 25.9, 24.2, 24.0, 21.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.7;

FTIR (cm^{-1}): 3412, 2239, 1687, 1635, 1160; mp: 180-182 °C; ESI-MS: 268.1 $(M+OH)^+$. HRMS (ESI) m/z calculated for $[C_{10}H_{17}N_3OF_3]^+$: 252.13182; found: 252.13130.



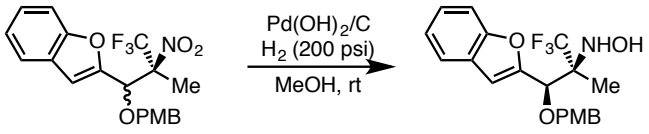
(30) To a 25 mL round bottom flask equipped with a magnetic stir bar was added α-trifluoromethylnitroalkane **21** (75.0 mg, 220 μmol), methanol (2.2 mL), and Pd/C (15.0 mg, 20 wt %) The flask was equipped with a rubber septum and a needle was inserted into the septum. The flask was placed in a Parr reactor and evacuated and backfilled with H_2 five times. On the last refill, the reactor was sealed at a H_2 pressure of 400 psi. The reactor was placed on a stir plate and the reaction was stirred at rt for 24 h. Once complete, the reactor was vented and the crude reaction was diluted with ethyl acetate and filtered through Celite and concentrated *in vacuo* to afford α-trifluoromethylamine **30** (66.8 mg, 98%) as a thick colorless oil. NMR analysis revealed a >99:1 mixture of syn and anti isomers: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.62 (s, 1H), 4.30 (s, 1H), 3.13 (dd, *J* = 13.0, 3.7 Hz, 1H), 2.57 (ddd, *J* = 13.4, 4.7, 3.0 Hz, 1H), 2.16 (qd, *J* = 13.2, 3.8 Hz, 1H), 2.00 - 1.87 (m, 1H), 1.83 - 1.39 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 129.5 (q, *J* = 30.2 Hz), 129.3, 127.0 (q, *J* = 288 Hz), 125.4 (q, *J* = 3.53 Hz), 124.2 (q, *J* = 273 Hz), 64.9 (q, *J* = 22.3), 46.3, 29.1, 26.3, 26.1, 20.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -69.5, -78.5; FTIR (cm^{-1}): 3307, 2943, 2865, 1166, 1120; GC/MS (EI) 310.1 $(M-H)^+$**.** HRMS (CI) m/z, calculated for $[C_{14}H_{16}NF_6]^+$: 312.1187; found: 312.1190.



(31) To a 25 mL round bottom flask equipped with a magnetic stir bar was added α-trifluoromethylnitroalkane **8** (100 mg, 242 μmol), Pearlman's catalyst (10 mg, 10 wt %), and methanol (2.42 mL). The flask was equipped with a rubber septum and a needle was inserted into the septum. The flask was placed in a Parr reactor and evacuated and backfilled with H_2 five times. On the last refill, the reactor was sealed at a H_2 pressure of 200 psi. The reactor was placed on a stir plate and the reaction was stirred at rt for 16 h. Once complete, the reactor was vented and the crude reaction was diluted with ethyl acetate, filtered through Celite and concentrated *in vacuo*. The crude reaction was purified via flash silica chromatography (80:20 hexanes : ethyl acetate) to afford α-trifluoromethylamine **31** (60.1 mg, 65%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 1H), 7.81 - 7.75 (m, 3H), 7.59 (d, *J* = 3.6 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.24 (d, *J* = 8.3 Hz, 2H), 6.67 (d, *J* = 3.5 Hz, 1H), 5.48 (d, *J* = 3.5 Hz, 1H), 4.48 (d, *J* = 3.6 Hz, 1H), 2.35 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 135.3, 134.6, 131.4, 130.9, 130.1, 127.1, 127.0, 126.2 (*J* = 285 Hz), 123.7, 120.7, 113.5, 109.1, 66.5 (q, *J* = 23.7 Hz), 21.8, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.1; FTIR (cm^{-1}): 3422, 2923, 1371, 1170, 1132; mp = 93-95 °C; HRMS (LIFDI) m/z calculated for $[C_{18}H_{17}N_2O_2F_3S]^+$: 382.0963; found: 382.1037.

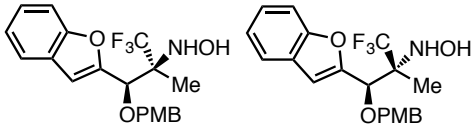
9. Determination of Relative Stereochemistry of S12

The relative stereochemistry was determined by X-ray after converting compound **20** into hydroxylamine **S12**.



20 — **93:07 mixture of diastereomers**

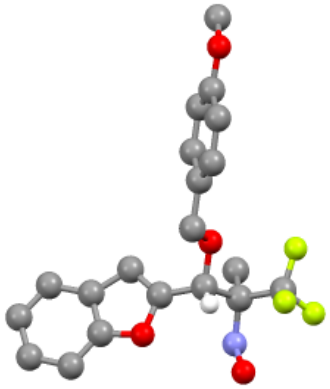
S12 (Xray) — **93:07 (NMR)** — **(isolated as 99:01 diastereomer)**



S12A **93:07** **S12B**

(S12) To a 50 mL round bottom flask equipped with a magnetic stir bar was added α-trifluoromethylnitroalkane **20** (825 mg, 2.0 mmol), Pearlman's catalyst (165 mg, 20 wt %), and methanol (20.0 mL). The flask was equipped with a rubber septum and a needle was inserted into the septum. The flask was placed in a Parr reactor was purged with H_2 five times. On the last refill, the reactor was sealed at a H_2 pressure of 200 psi. The reactor was placed on a stir plate and the reaction was stirred at rt for 20 h. Once complete, the reactor was vented and the crude reaction

was diluted with ethyl acetate, filtered through Celite and concentrated *in vacuo*. NMR analysis of the crude reaction mixture revealed an 93:07 mixture of syn and anti isomers. The crude reaction was purified via flash silica chromatography (90:10 hexanes : ethyl acetate) to afford α-trifluoromethylhydroxylamine **S12** (551 mg, 70%) as a white solid: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 6.0 Hz, 1H), 7.52 (d, *J* = 7.0 Hz, 1H), 7.32 (td, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.27 (d, 1H), 7.25 – 7.22 (m, 2H), 6.90 – 6.84 (m, 2H), 6.83 (s, 1H), 5.39 (d, *J* = 3.5 Hz, 1H), 5.20 (s, 1H), 4.65 (d, *J* = 3.4 Hz, 1H), 4.56 (d, *J* = 11.1 Hz, 1H), 4.37 (d, *J* = 11.1 Hz, 1H), 3.80 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.6, 155.3, 153.4, 129.8, 129.3, 127.9, 126.5 (q, *J* = 288 Hz), 124.7, 123.3, 121.3, 113.9, 111.6, 107.4, 73.8, 71.9, 66.9 (q, *J* = 24 Hz), 55.4, 13.2. ^{19}F NMR (565 MHz, $CDCl_3$) δ -71.9; FTIR (cm^{-1}): 3282, 2937, 2837, 1612, 1585, 1514, 1613, 1566, 1453, 1251, 752; mp = 97-99 °C; HRMS (ESI) $(M-H)^+$ m/z calculated for $[C_{20}H_{21}NO_4F_3]$: 396.14357; found: 396.14172; Crystals for X-ray analysis were obtained by slow evaporation of diethylether.

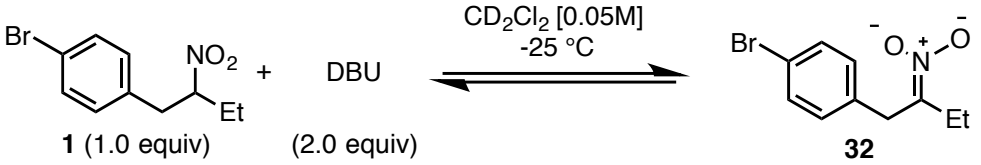


10. X-ray Structural Solution and Refinement:

X-ray structural analysis for **15**, **21** and **S12**: Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data was collected on a Bruker-AXS APEX II DUO CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å) monochromated with graphite for **15** and **21**, and with Cu- Kα radiation (λ = 1.54178 Å) focused with Goebel mirrors for **S12**. Unit cell parameters were obtained from 36 data frames, 0.5º ω, from three different sections of the Ewald sphere. The systematic absences in the diffraction data are uniquely consistent with *Pbca* for **15**, $P2_1/c$ for **21,** and $P2_1/n$ for **S12**. The data-sets were treated with multi-scan absorption corrections[16]. The structures were solved using direct methods and refined with full-matrix, least-squares procedures on F[217]. Four symmetry unique compound molecules were located in the asymmetric unit of **21** different from each only in C-C and C-N single bond rotations of the $–CF_3$ and $–NO_2$ groups, respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The amine H-atoms in **15** and **S12** were located from the electron density difference map and assigned an idealized fixed N-H distance of 0.87(2) Å with U_{iso} equal to 1.2 U_{eq} of the attached nitrogen atom. All other hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2, or 1.5 for methyl, U_{eq} of the attached atom. Atomic scattering factors are contained in various versions of the SHELXTL program library[17]. Structural information has been deposited with the Cambridge Structural Crystallographic Centre under depositary numbers CCDC 1411931 for **15**, CCDC 1411932 for **21,** and CCDC 1532771 for **S12**

11. Deprotonation Studies:

To understand the kinetics of deprotonation of **1** Starting material, we treated 1 with DBU in CD_2Cl_2 at –25 °C. We monitored the reaction using ^1H NMR spectroscopy.



1 (1.0 equiv) (2.0 equiv) **32**

In a nitrogen-filled glove-box to a 1 dram vial was added **1** (9 mg, 0.035 mmol), hexamethyldisiloxane (3.7 μL, 17.5 μmol) (internal standard) CD_2Cl_2 (0.7mL, [0.05 M]) This solution was transferred to a NMR tube via pipette, sealed with septa cap and removed from the glovebox. The sample was cooled to –25 °C in NMR probe. DBU (11 μL, 70.0 μmol) was added at –25 °C by quickly removing the sample from the NMR probe and the data were collected at –25 °C in 400 MHz NMR incrementally for 30 min.
Yield of starting material **1** and nitronate anion **32** was determined by integrating signals shown in the table below:

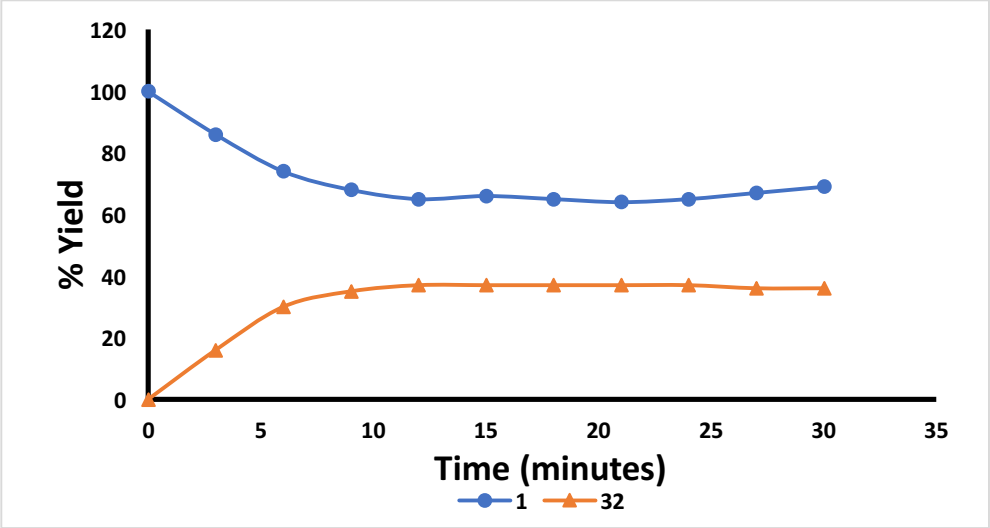
Compound	^1H NMR signal
1	δ 7.42 (d, *J* = 8.1 Hz, 2H),
32	δ 7.33 (d, *J* = 8.1 Hz, 2H),

Compound 1 equilibrates to nitronate anion **32** with approximate ratio of 67:33 in ten minutes. As shown in the tableS3.The ratio of **1:32** is shown in the chart below as a function of time.

Time(min)	Yield **1**[a]	Nitronate anion **32**[a]
0	100	0
3	86	16
6	74	30
9	68	35
12	65	37
15	66	37
18	65	37
21	64	37
24	65	37
27	67	36
30	69	36

[a]Yield determined by 1H NMR using hexamethyldisiloxane as an internal standard

TableS3: Yield of **1** and Nitronate anion **32** over time using DBU as base

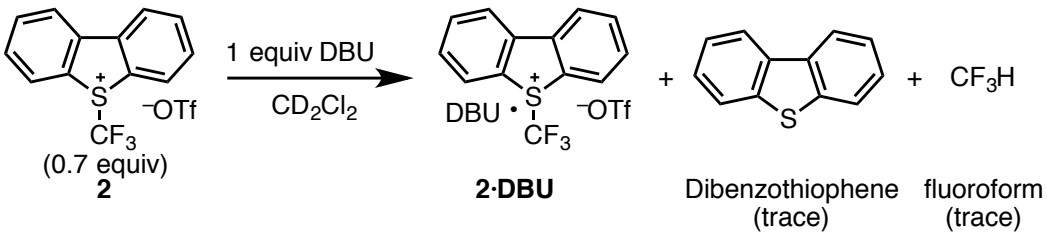


ChartS1: Ratio of compound **1** and Nitronate anion 32 over time

From this experiment, we learn that a substantial concentration of nitronate anion is formed under these conditions, but that the kinetic for formation are relatively slow.

12. Interaction of DBU with Umemoto's Reagent – ^{1}H NMR study.

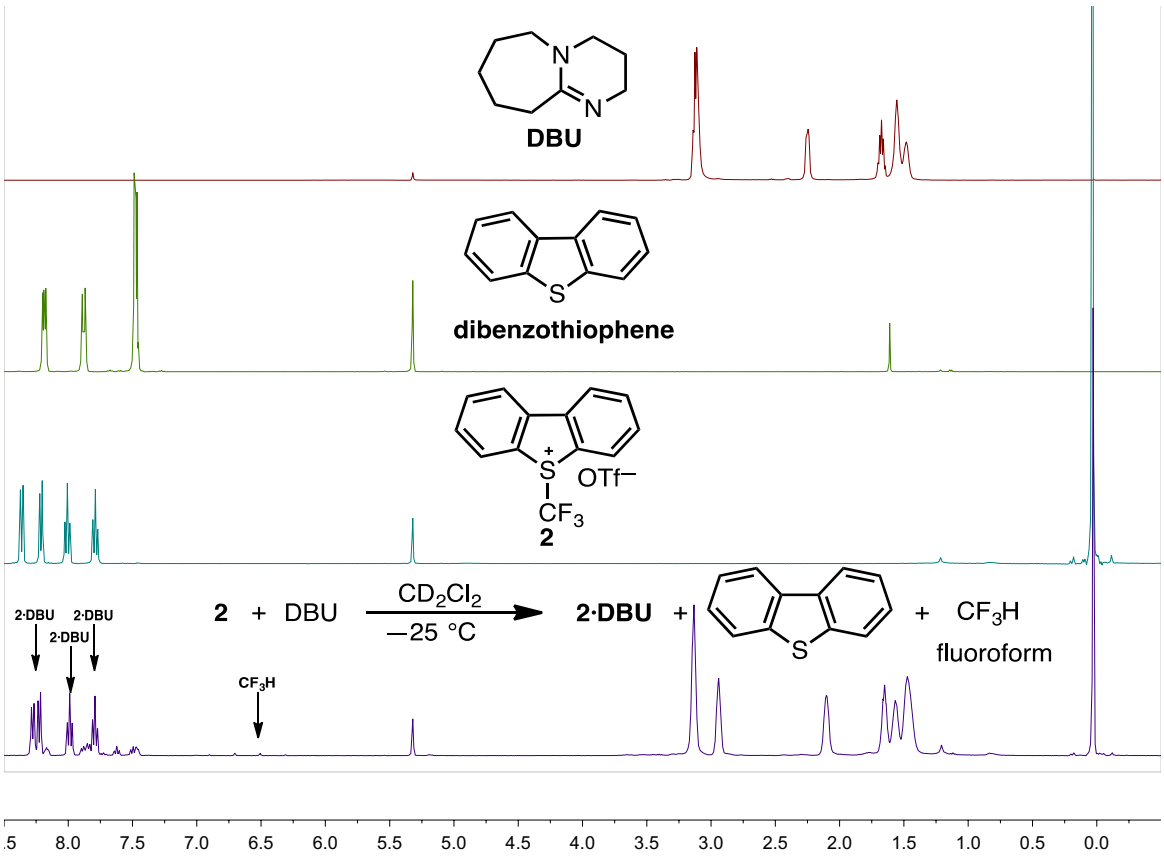
To understand possible interactions between DBU and Umemoto's reagent, we studied their reaction by ^{1}H NMR at –25 °C in CD_2Cl_2 in the absence of other reagents.



In a nitrogen-filled glove-box to a 1 dram vial was added, Umemoto's reagent **2** (0.0183 mg, 0.045 mmol), hexamethyldisiloxane (3.7 μL, 17.5 μmol) (internal standard) CD_2Cl_2 (0.7mL, [0.05 M]). This solution was transferred to a NMR tube via pipette, sealed with septa cap and removed from the glovebox. The sample was cooled to –25 °C in NMR probe. DBU (11 μL, 70.0 μmol) was added at –25 °C by quickly removing the sample from the NMR probe and the data were collected at –25 °C.

From the ^{1}H NMR spectra we observed the complete disappearance of Umemoto's reagent and formation of new adduct, which we believe to be EDA complex of the two (**2·DBU**), along with traces of dibenzothiophene, and fluoroform. The conversion happens within seconds, and the resulting solution is stable at –25 °C for extended time (as judged by ^{1}H NMR). ^{1}H NMR signals are tabulated below.

Compound	^{1}H NMR signal
dibenzothiophene	δ 8.19 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.88 (dt, *J* = 7.1, 3.6 Hz, 2H), 7.53 – 7.42 (m, 4H)
CF_3H	δ 6.61 (q, *J* = 79, 1H)
Umemoto's reagent 2	δ 8.40 (d, *J* = 8.1 Hz, 2H), 8.23 (td, *J* = 7.8, 1.2 Hz, 2H), 8.03 (td, *J* = 7.7, 1.1 Hz, 2H) 7.82 (td, *J* = 7.9, 1.3 Hz, 2H)
2·DBU	δ 8.28 (d, *J* = 8.1 Hz, 2H) 8.23 (d, *J* = 7.8 Hz, 2H) 7.99 (t, *J* = 7.7 Hz, 2H) 7.79 (t, *J* = 7.8 Hz, 2H)

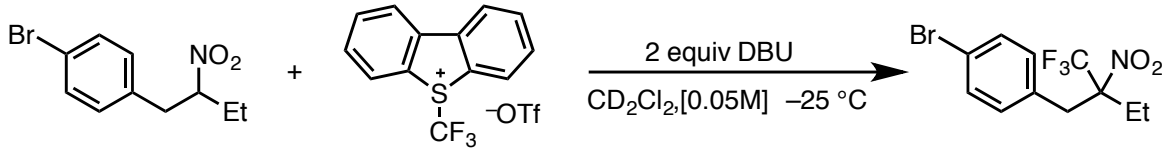


FiguareS1: ^{1}H NMR study of Interaction between Umemoto's reagent **2** and **DBU,** 0.05 M CD_2Cl_2, –25 °C, compared to spectra of reagents and products under the same conditions.

From this data, we find that: (1) a DBU adduct of Umemoto's reagent can form; (2) the reaction kinetics are fast; (3) we are able to identify its ^{1}H NMR signals for use in the studies below.

13. ^{1}H NMR Monitoring of Trifluoromethylation of Secondary Nitroalkane:

We monitored trifluoromethylation of nitroalkane reaction using ^{1}H NMR at –25 °C in CD_2Cl_2. Under the optimized reaction conditions [0.1 M], a very rapid reaction was observed that was too fast to adequately monitor by NMR. Spectra traces from this reaction are shown below. Further, the optimized reaction conditions are slightly heterogeneous for the first few minutes of the transformation, due to the saturation of Umemoto's reagent in methylene chloride at the reaction temperature. We were concerned that such heterogeneous behavior might obscure the reaction profile due to mass transport issues. To address both problems, we diluted the reaction (2-fold, to 0.05 M) for NMR studies. Under these conditions, the reaction slowed enough to allow better observation by transient NMR experiments, and was fully homogenous at the start of the reaction.



1 (1.0 equiv) **2** (1.3 equiv) **3**

In a nitrogen-filled glovebox to a 1 dram vial was added **1** (9 mg, 0.035 mmol), Umemoto's reagent **2** (0.0183 mg, 0.045 mmol), hexamethyldisiloxane (3.7 μL, 17.5 μmol) (internal standard) and CD_2Cl_2 (0.7mL, [0.05 M]). This solution was transferred to a NMR tube via pipette, sealed with septa cap and removed from the glove box. The sample was cooled to –25 °C in NMR probe. DBU (11 μL, 70.0 μmol) was added at –25 °C by quickly removing the sample from the NMR probe and the data started to collect at –25 °C.

Data were collected periodically for first 30 minutes then, collected for every 30 minutes.
Yield of starting material **1,** product **3, 2·DBU and 33** was determined by integrating signals shown in the table below:

Compound	^{1}H NMR signal
1	δ 0.93 (t, *J* = 7.4 Hz, 3H)
3	δ 1.01 (t, *J* = 7.4 Hz, 3H)
33	δ 7.27 (d, *J* = 7.9 Hz, 2H)
2·DBU	δ 7.73 (t, *J* = 7.8 Hz, 2H)

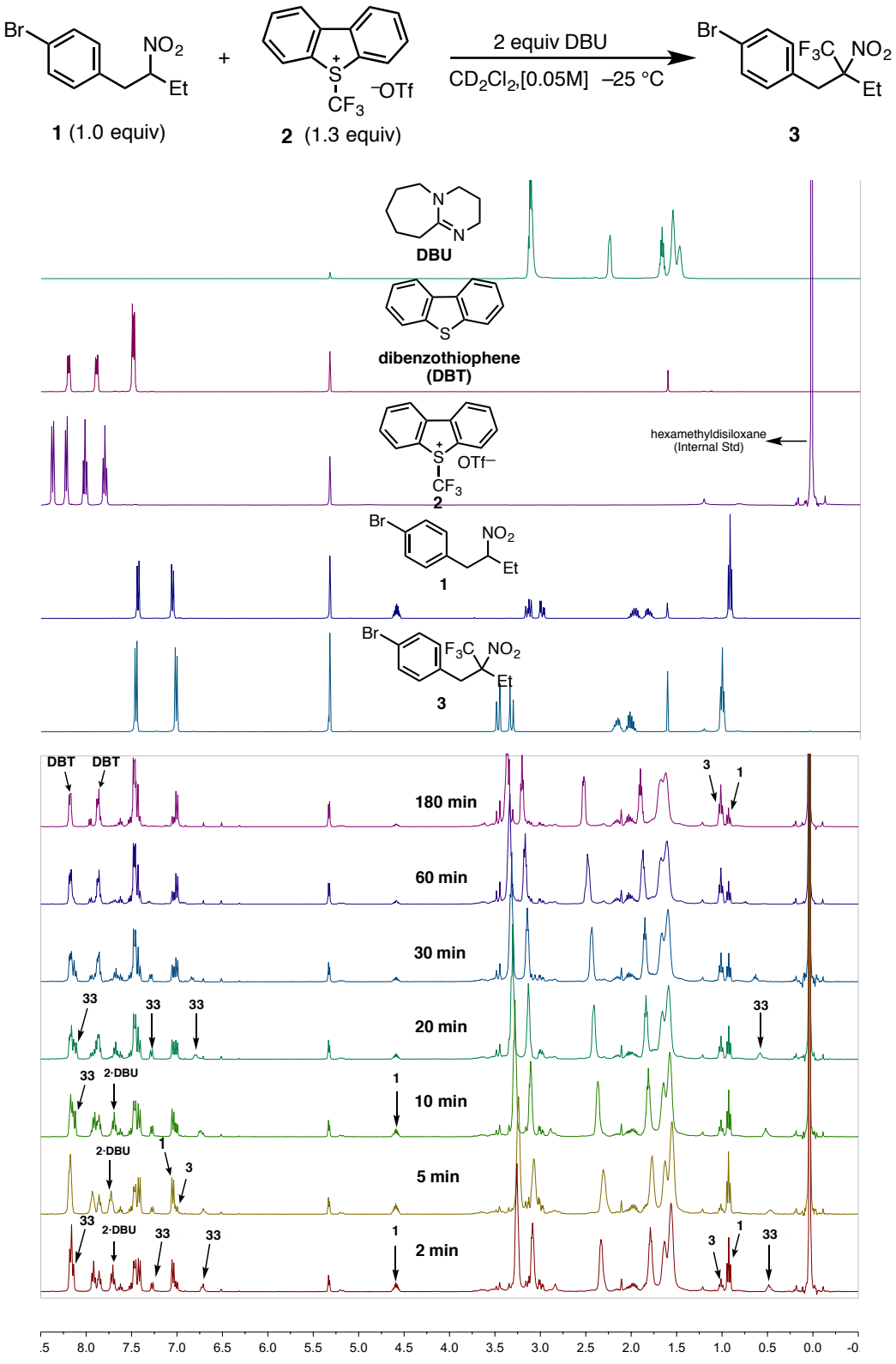
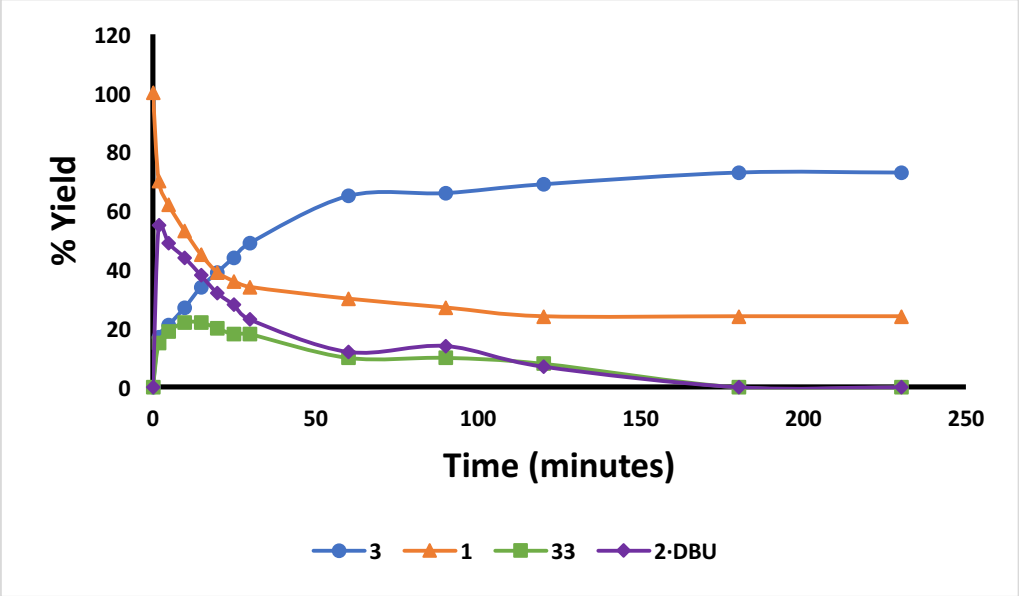


Figure S2: ^{1}H NMR monitoring of Trifluoromethylation of **1** [0.05] M CD_2Cl_2, –25 °C, compared to spectra of reagents and products under the same conditions.



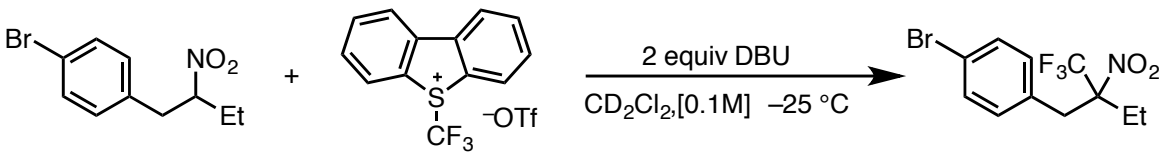
ChartS2: Kinetic Profile of Trifluoromethylation of **1** [0.05 M] $CD_2Cl_2$and Change of **1,3,33** and **2·DBU** over time.

From the ^{1}H NMR time study, we observed formation of product **3** and disappearance of starting material **1**. Further, we also noticed that high concentration buildup of peak at δ 7.73ppm, a peak that matches **2·DBU**, at the beginning of the reaction then it gradually disappears at the end.

In addition, we also observed another compound with ^{1}H NMR signals at δ 8.13, 7.27, 6.80, 0.6ppm. These rise and fall in together. Further, these signals corresponds to features in the spectra of both the nitroalkane **1** and Umemoto's reagent (**2**), but are not identical to either. Based upon this spectra data, we believe that this intermediate is the associated ion pair **33**, where in the nitronate anion has replaced triflate in Umemoto's reagent .

Based on our NMR study of DBU interaction with Umemoto's reagent we propose that the peak at δ 7.7ppm is adduct **2·DBU** which is formed between Umemoto's reagent and DBU and the peak at δ 8.13, 7.27, 6.80, 0.6ppm is an ion pair **33**, which is formed reversibly between **2·DBU** and nitronate anion **32**.

14. ^{1}H NMR monitoring of Trifluoromethylation of Secondary Nitroalkane (optimal reaction condition):



1 (1.0 equiv) **2** (1.3 equiv) **3**

To a 1 dram vial was added **1** (18 mg, 0.070 mmol), Umemoto's reagent **2** (0.0366 mg, 0.090 mmol),1,3,5 trimethoxy benzene (5.8 mg, 0.035 mmol) added as Internal Standard) (0.7mL, [0.1 M] CD_2Cl_2). This solution was transferred to a NMR tube via pipette sealed with septa cap and removed from the glove box. The sample was cooled to –25 °C in NMR probe. DBU (22 μL, 140.0 μmol) was added at –25 °C by removing the sample quickly from the NMR probe. Data were collected periodically for first 30 minutes then, collected for every 30 minutes.

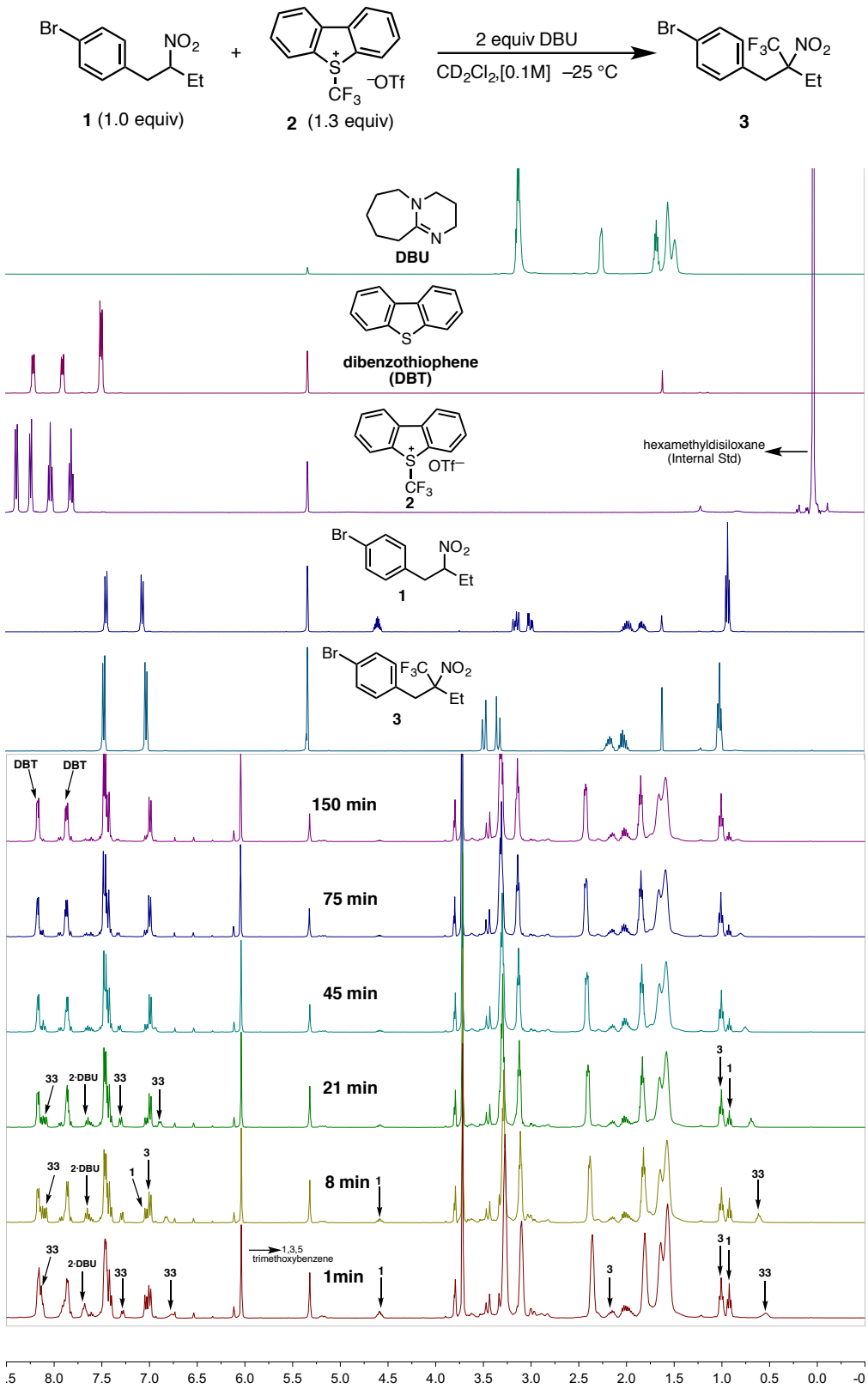
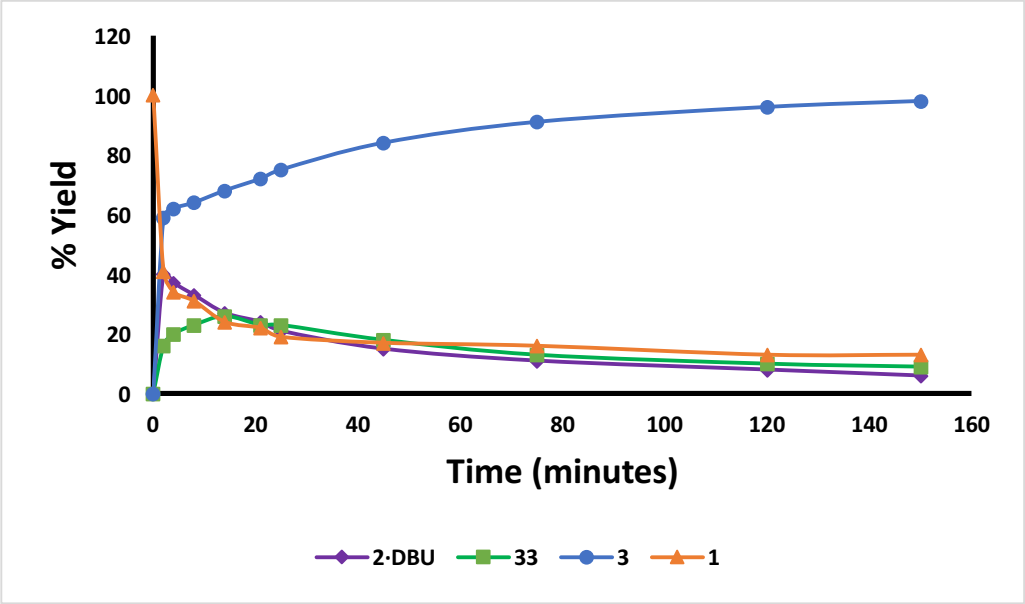


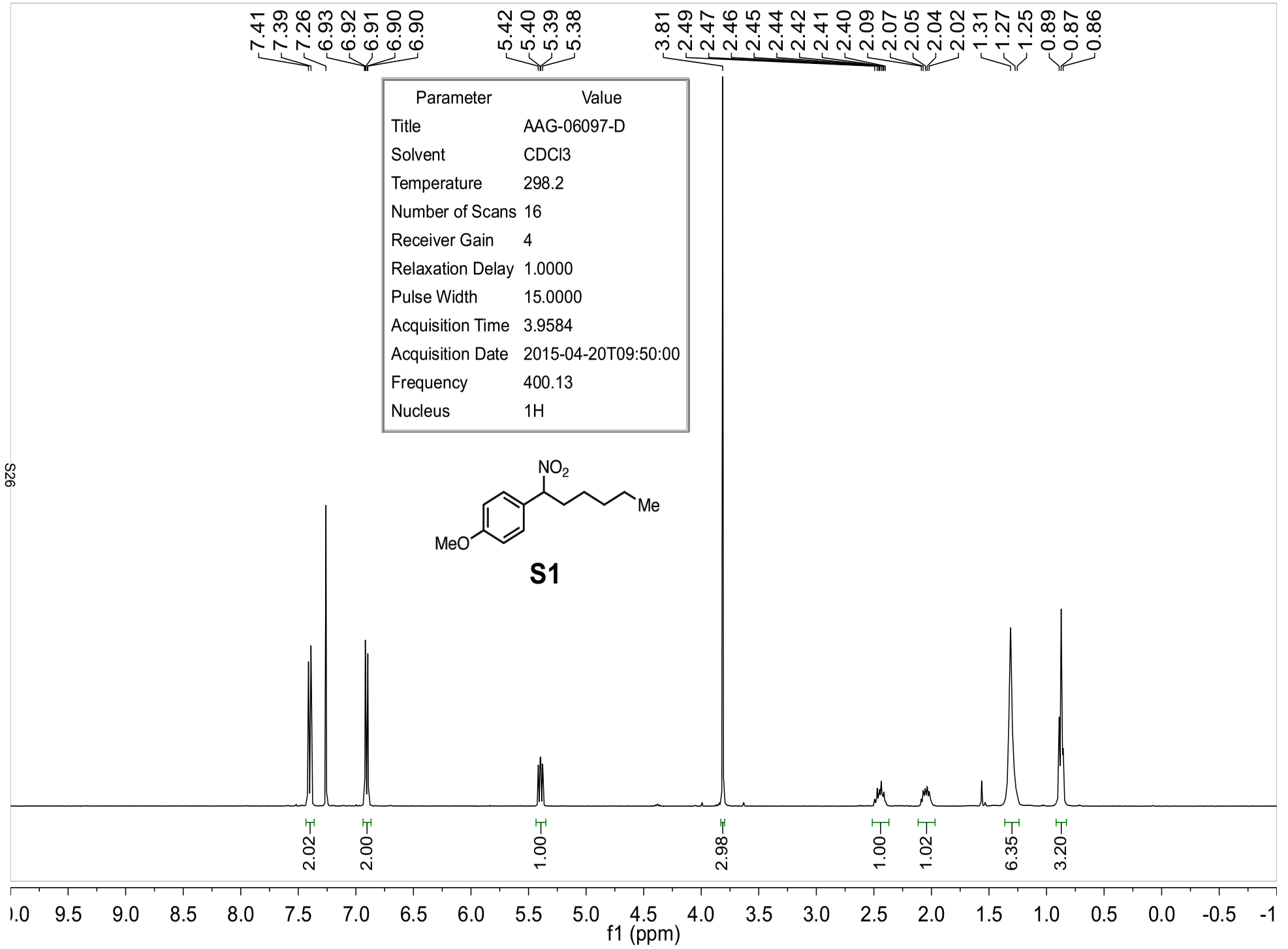
Figure S3: ^{1}H NMR monitoring of Trifluoromethylation of **1** [0.1 M] CD_2Cl_2, –25 °C, compared to spectra of reagents and products under the same conditions.



ChartS3: Kinetic Profile of Trifluoromethylation of **1** [0.1 M] CD_2Cl_2 and Change of **1,3,33** and **2·DBU** over time

15. References

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996,** *15* (5), 1518-1520.
(2) Ballini, R.; Barboni, L.; Giarlo, G., *J. Org. Chem* **2004,** *69* (20), 6907-6908.
(3) Bobál, P.; Lightner, D. A., *J. Heterocycl. Chem.* **2001,** *38* (2), 527-530.
(4) Zhang, H.-Z.; Zhang, H.; Kemnitzer, W.; Tseng, B.; Cinatl, J.; Michaelis, M.; Doerr, H. W.; Cai, S. X., *J. Med. Chem.* **2006,** *49* (3), 1198-1201.
(5) Budzelaar, Peter H. M.; Moonen, Nicolle N. P.; Gelder, René d.; Smits, Jan M. M.; Gal, Anton W., *Eur. J. Inorg. Chem.* **2000,** *2000* (4), 753-769.
(6) Gietter, A. A. S.; Gildner, P. G.; Cinderella, A. P.; Watson, D. A., *Org. Lett.* **2014,** *16* (11), 3166-3169.
(7) Zanon, J.; Klapars, A.; Buchwald, S. L., *J. Am. Chem. Soc.* **2003,** *125* (10), 2890-2891.
(8) Newkome, G. R.; Kim, H. J.; Moorefield, C. N.; Maddi, H.; Yoo, K.-S., *Macromolecules* **2003,** *36* (12), 4345-4354.
(9) Gildner, P. G.; Gietter, A. A. S.; Cui, D.; Watson, D. A., *J. Am. Chem. Soc.* **2012,** *134* (24), 9942-9945.
(10) Hayashi, T.; Senda, T.; Ogasawara, M., *J. Am. Chem. Soc.* **2000,** *122* (43), 10716-10717.
(11) Vogl, E. M.; Buchwald, S. L., *J. Org. Chem* **2001,** *67* (1), 106-111.
(12) Ballini, R.; Bosica, G., *Eur. J. Org. Chem.* **1998,** *1998* (2), 355-357.
(13) Patt, S. L.; Shoolery, J. N., *J. Magn. Reson.* **1982,** *46* (3), 535-539.
(14) Aleksandrowicz, P.; Piotrowska, H.; Sas, W., *Pol. J. Chem.* **1981,** *55*, 1469.
(15) Alam, T. M.; Pedrotty, D. M.; Boyle, T. J., *Magn. Reson. Chem.* **2002,** *40* (5), 361-365.
(16) Apex3 software suite; Bruker AXS, I., Madison, WI, 2015.
(17) Sheldrick, G., *Acta Cryst.A* **2008,** *64* (1), 112-122.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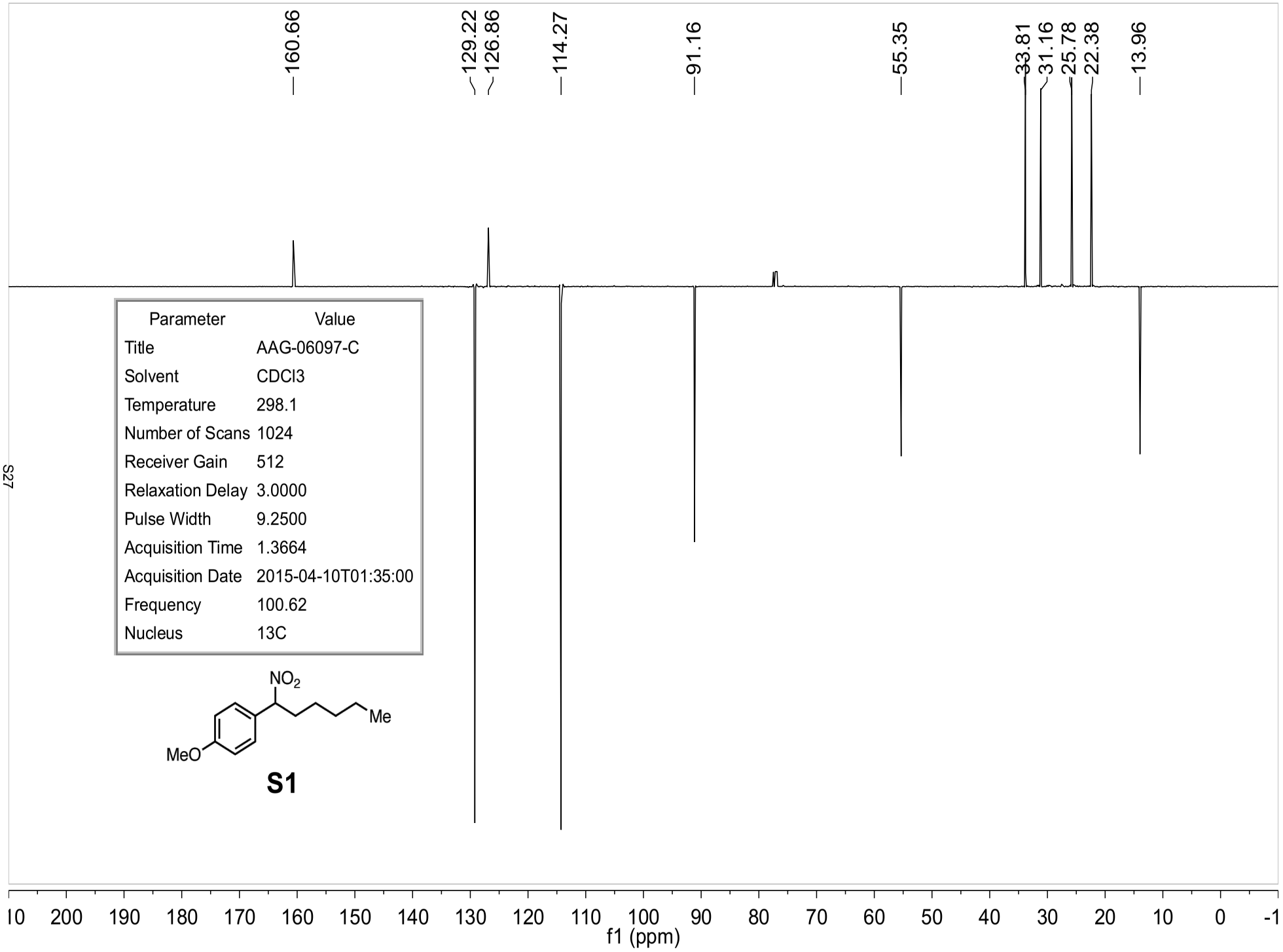
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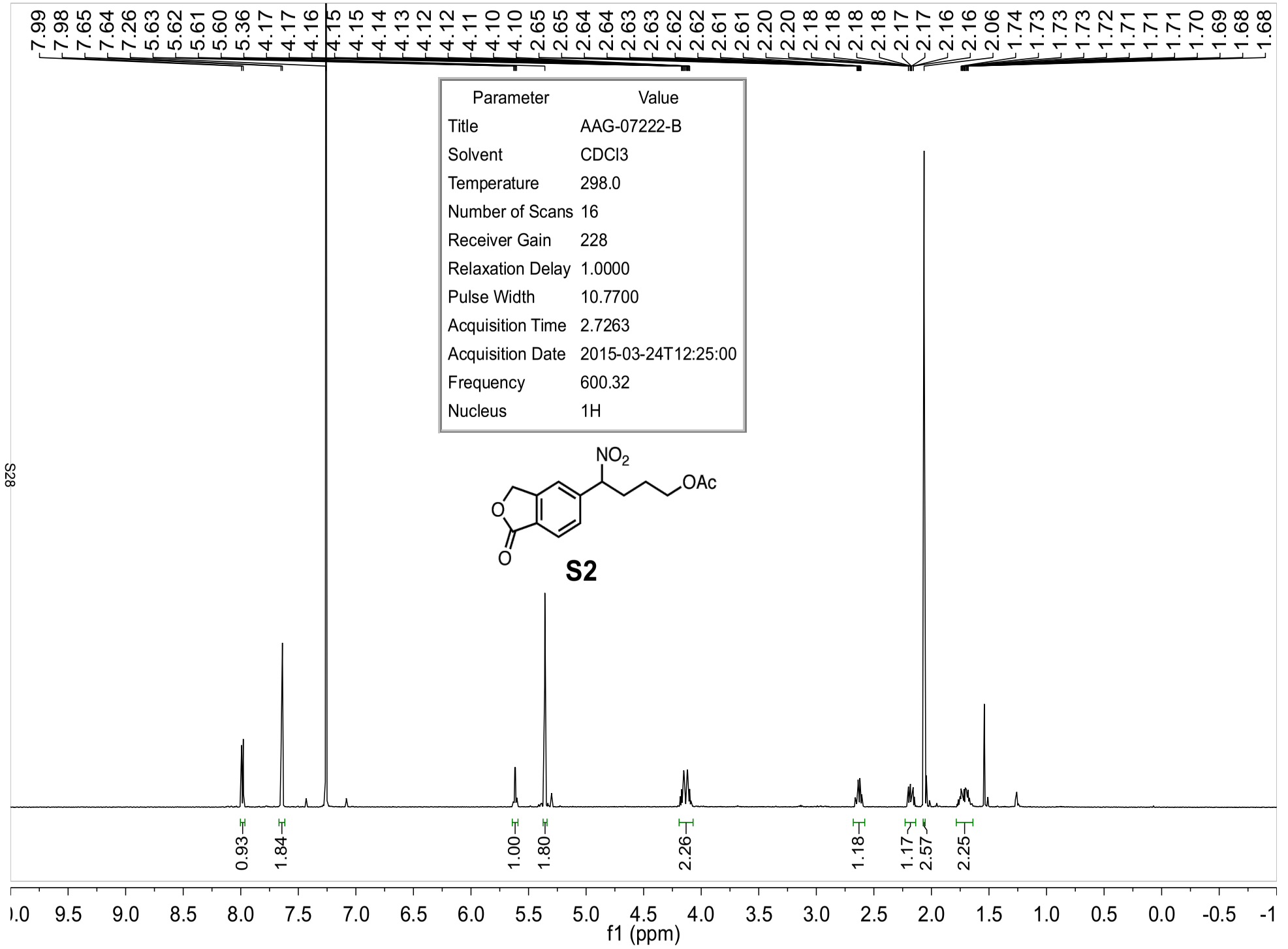
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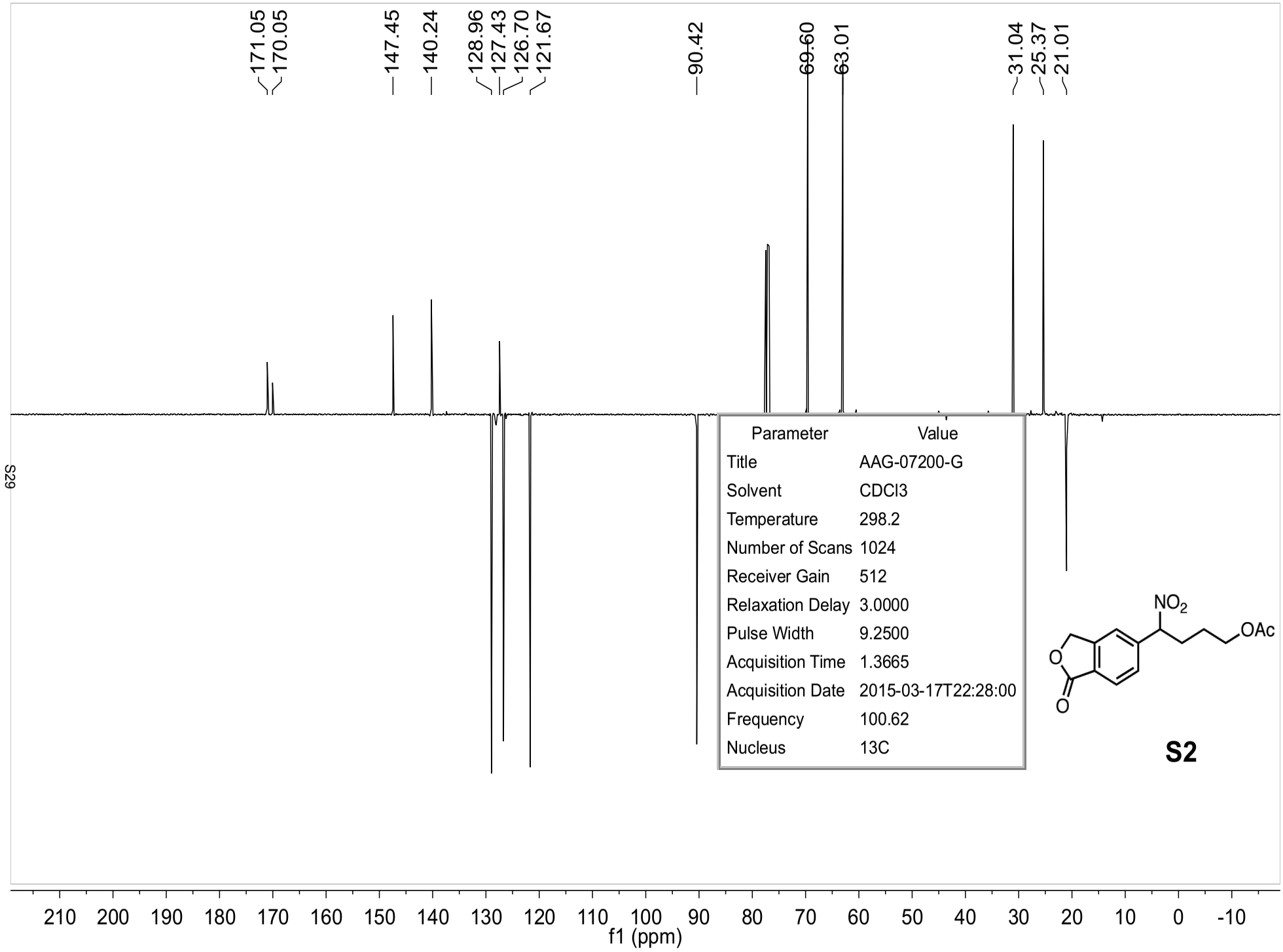
f1 (ppm)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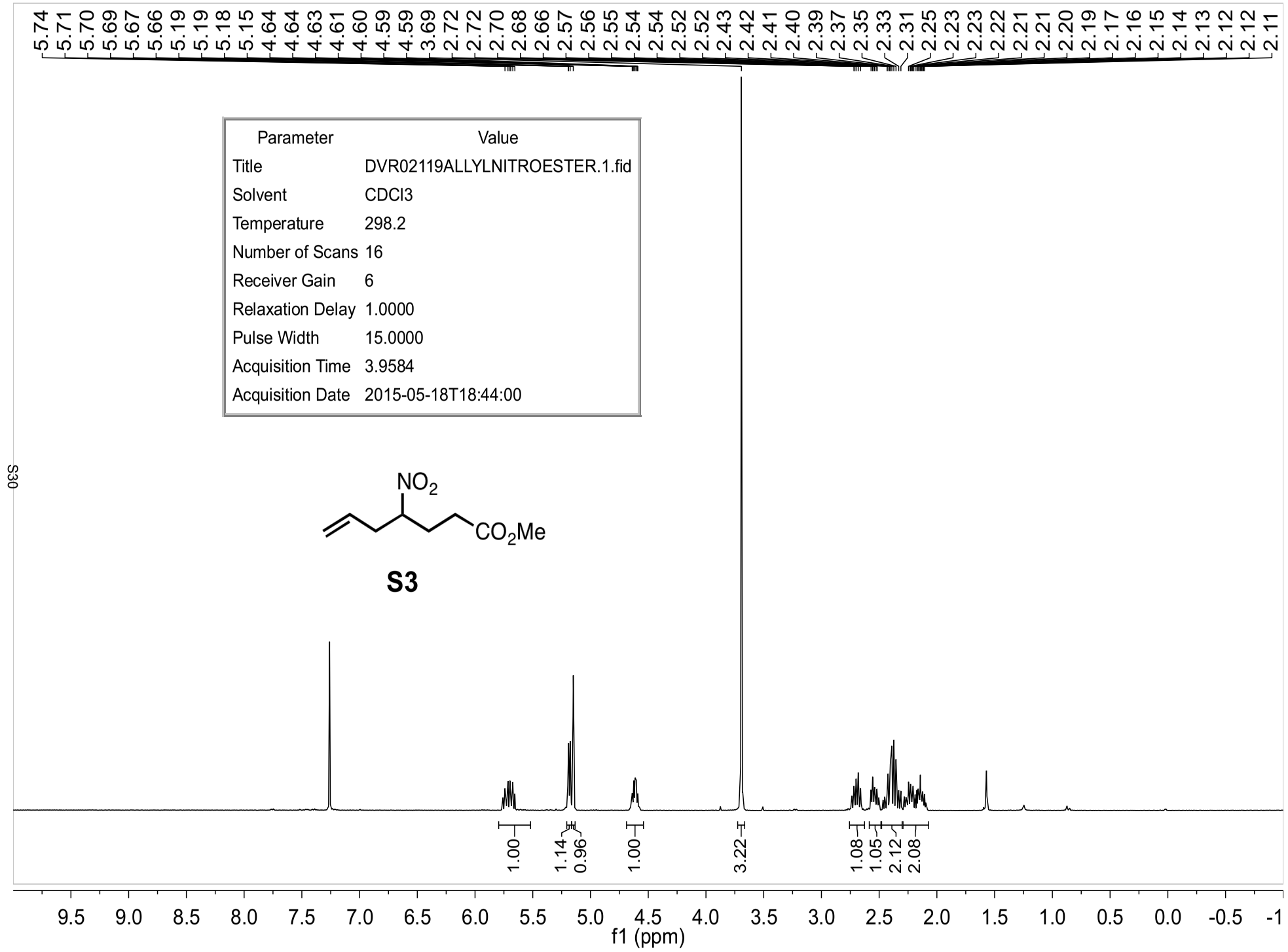
f1 (ppm)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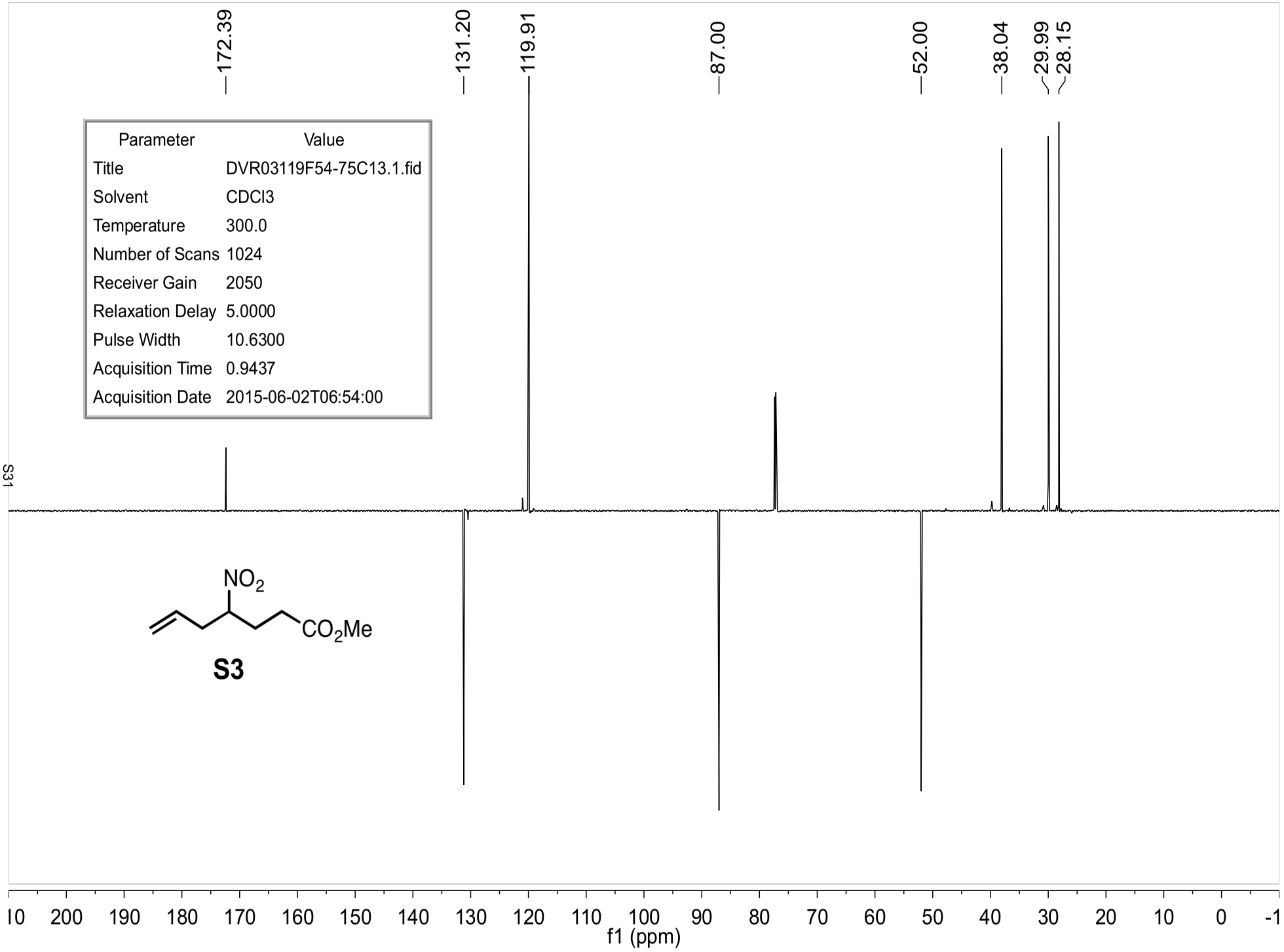
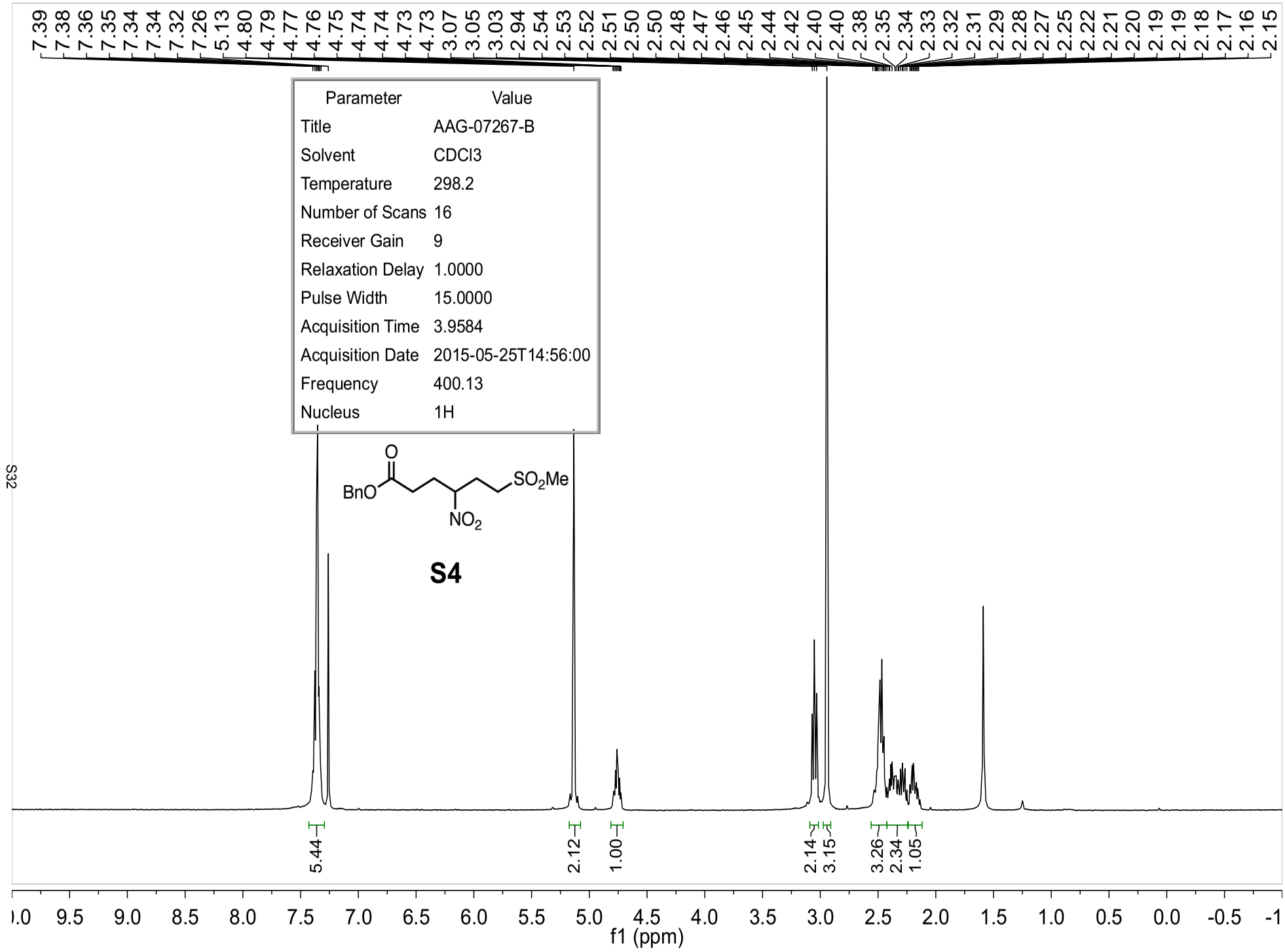
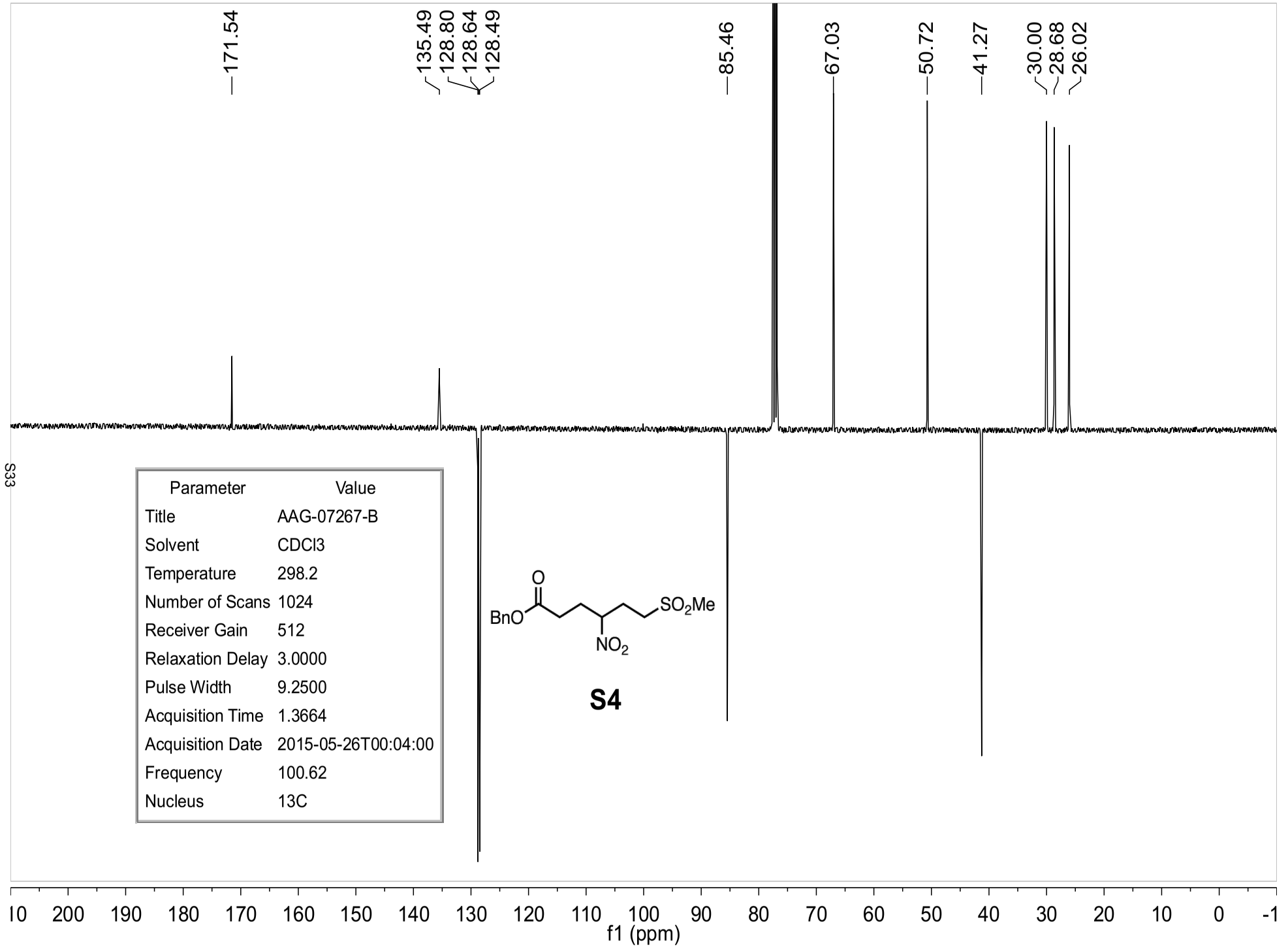
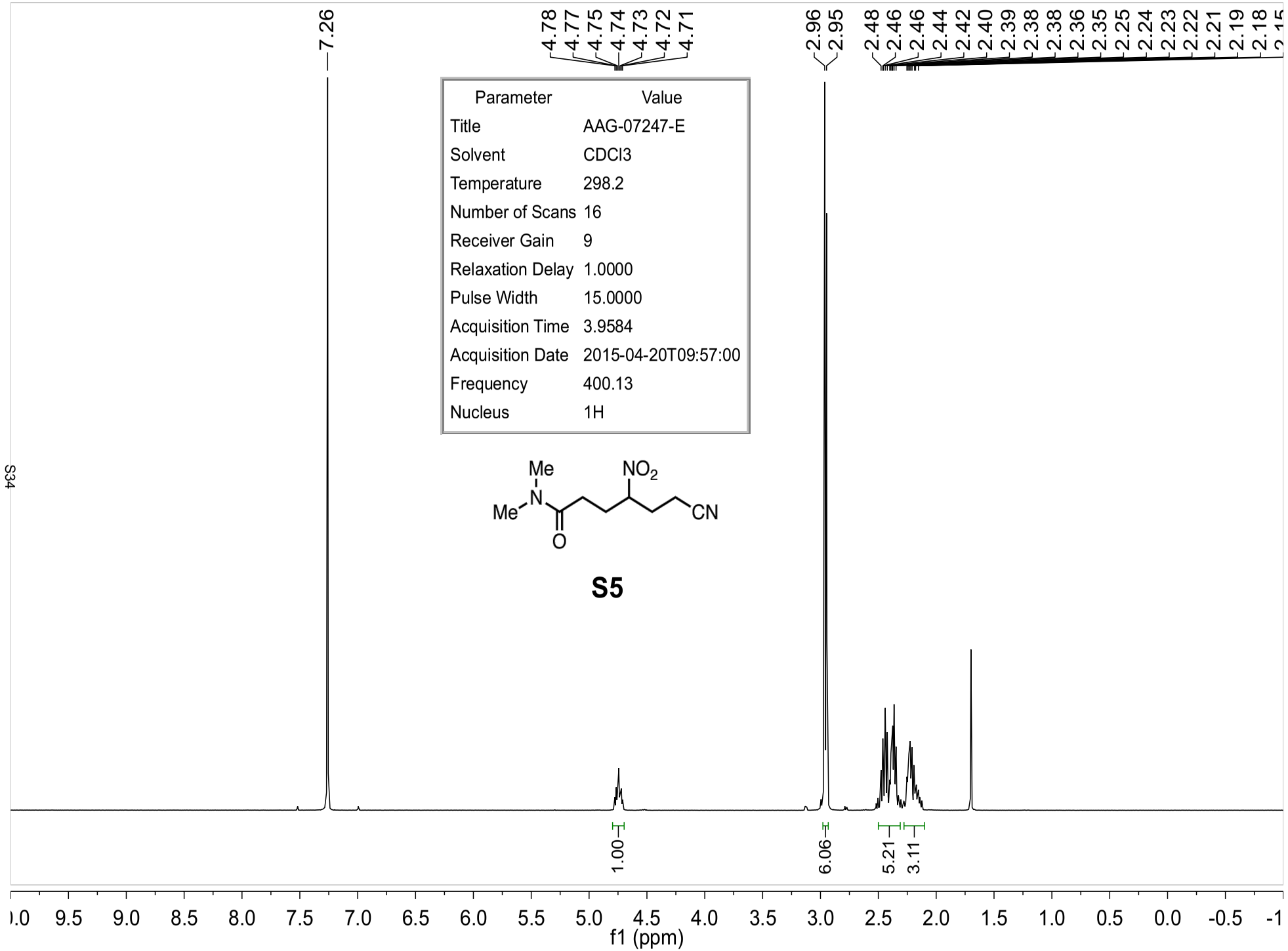
1.08
1.05
2.12
2.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

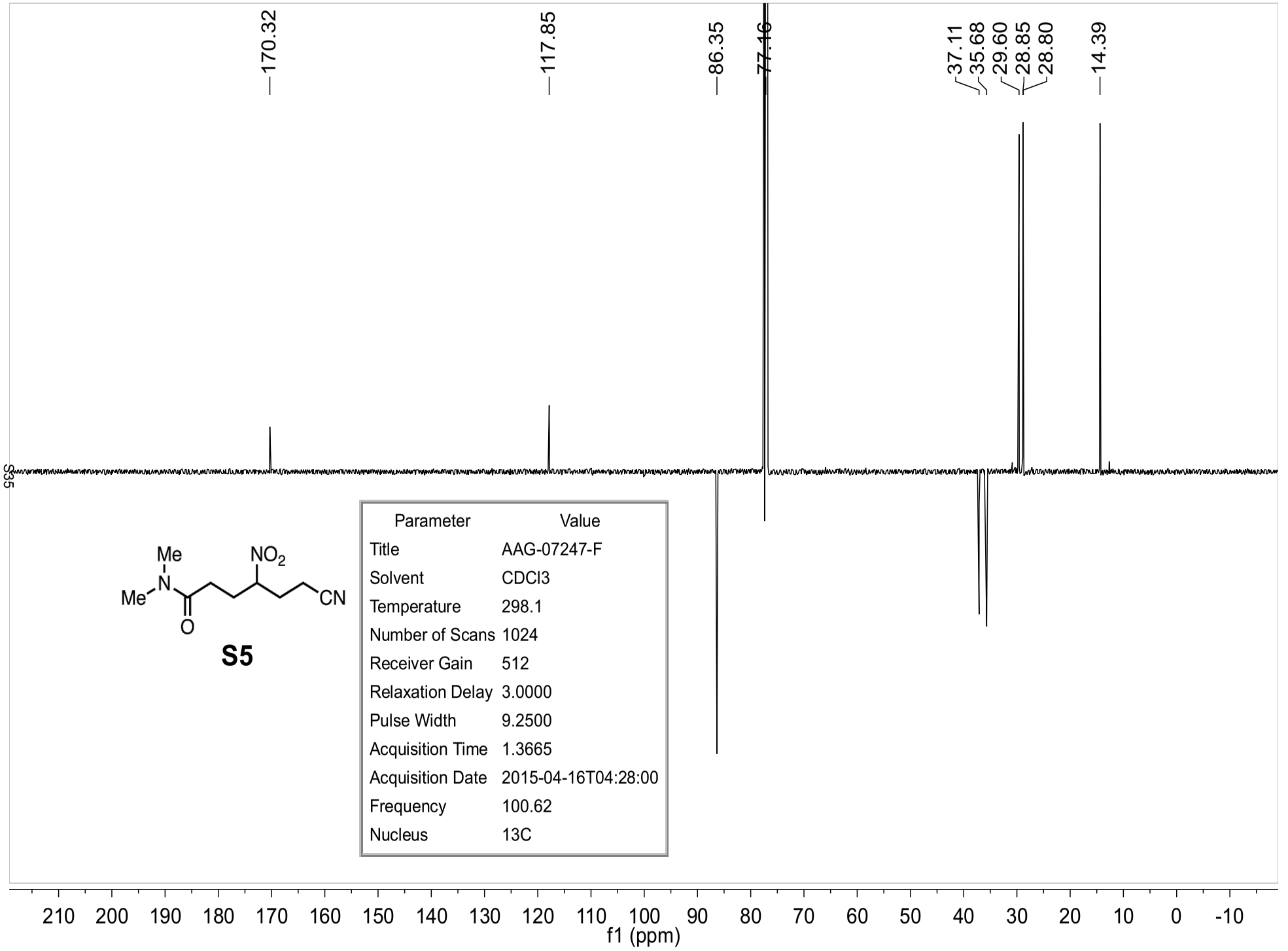

172.39
131.20
119.91
87.00
52.00
38.04
29.99
28.15
Parameter Value
Title DVR03119F54-75C13.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-02T06:54:00
S34
NO2
CO2Me
S3
f1 (ppm)

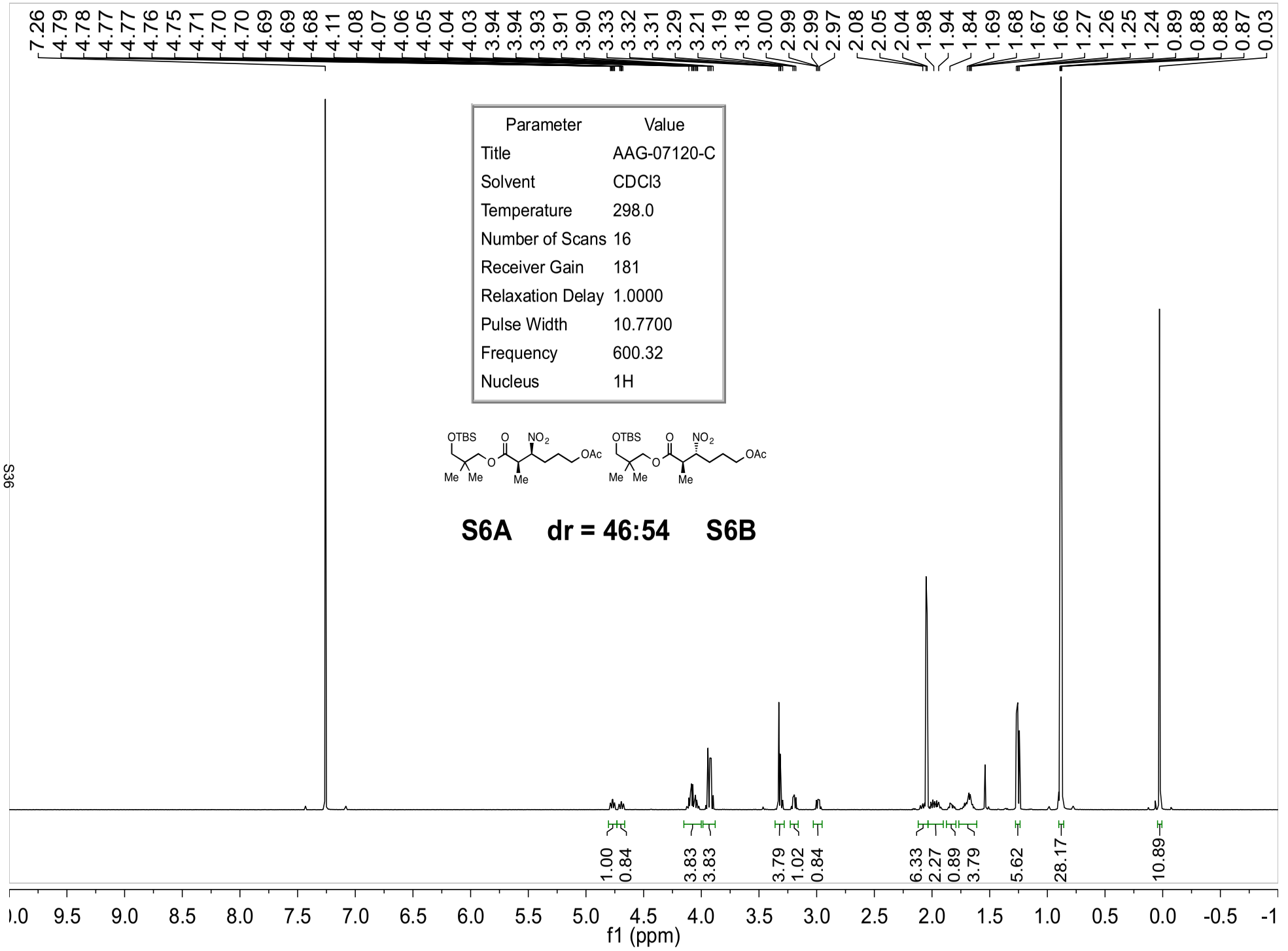

7.39 7.38 7.36 7.35 7.34 7.34 7.32 7.26 5.13 4.80 4.79 4.77 4.76 4.75 4.74 4.74 4.73 4.73 3.07 3.05 3.03 2.94 2.54 2.53 2.52 2.51 2.50 2.50 2.48 2.47 2.46 2.45 2.44 2.42 2.40 2.40 2.38 2.35 2.34 2.33 2.32 2.31 2.29 2.28 2.27 2.25 2.22 2.21 2.20 2.19 2.19 2.18 2.17 2.16 2.15
Parameter Value
Title AAG-07267-B
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 9
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-05-25T14:56:00
Frequency 400.13
Nucleus 1H
O
BnO
SO2Me
NO2
S4
S32
5.44
2.12
1.00
2.14
3.15
3.26
2.34
1.05
f1 (ppm)

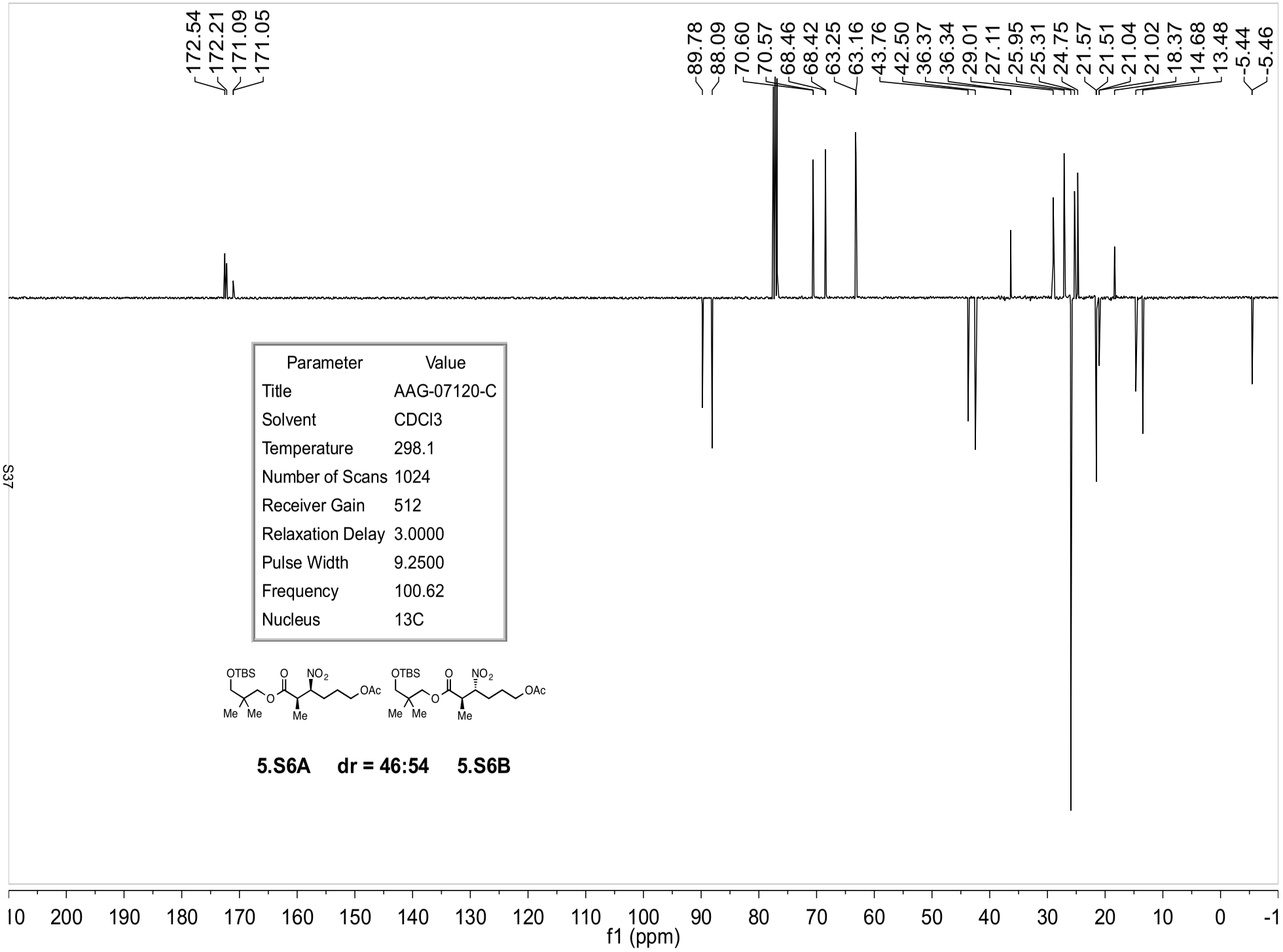

171.54
135.49
128.80
128.64
128.49
85.46
67.03
50.72
41.27
30.00
28.68
26.02
S33
Parameter Value
Title AAG-07267-B
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3664
Acquisition Date 2015-05-26T00:04:00
Frequency 100.62
Nucleus 13C
BnO
O
SO2Me
NO2
S4
f1 (ppm)


7.26
4.78
4.77
4.75
4.74
4.73
4.72
4.71
2.96
2.95
2.48
2.46
2.46
2.44
2.42
2.40
2.39
2.38
2.38
2.36
2.35
2.25
2.24
2.23
2.22
2.21
2.19
2.18
Parameter Value
Title AAG-07247-E
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 9
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-04-20T09:57:00
Frequency 400.13
Nucleus 1H
Me
NO2
N
Me
CN
O
1.00
6.06
5.21
3.11
f1 (ppm)

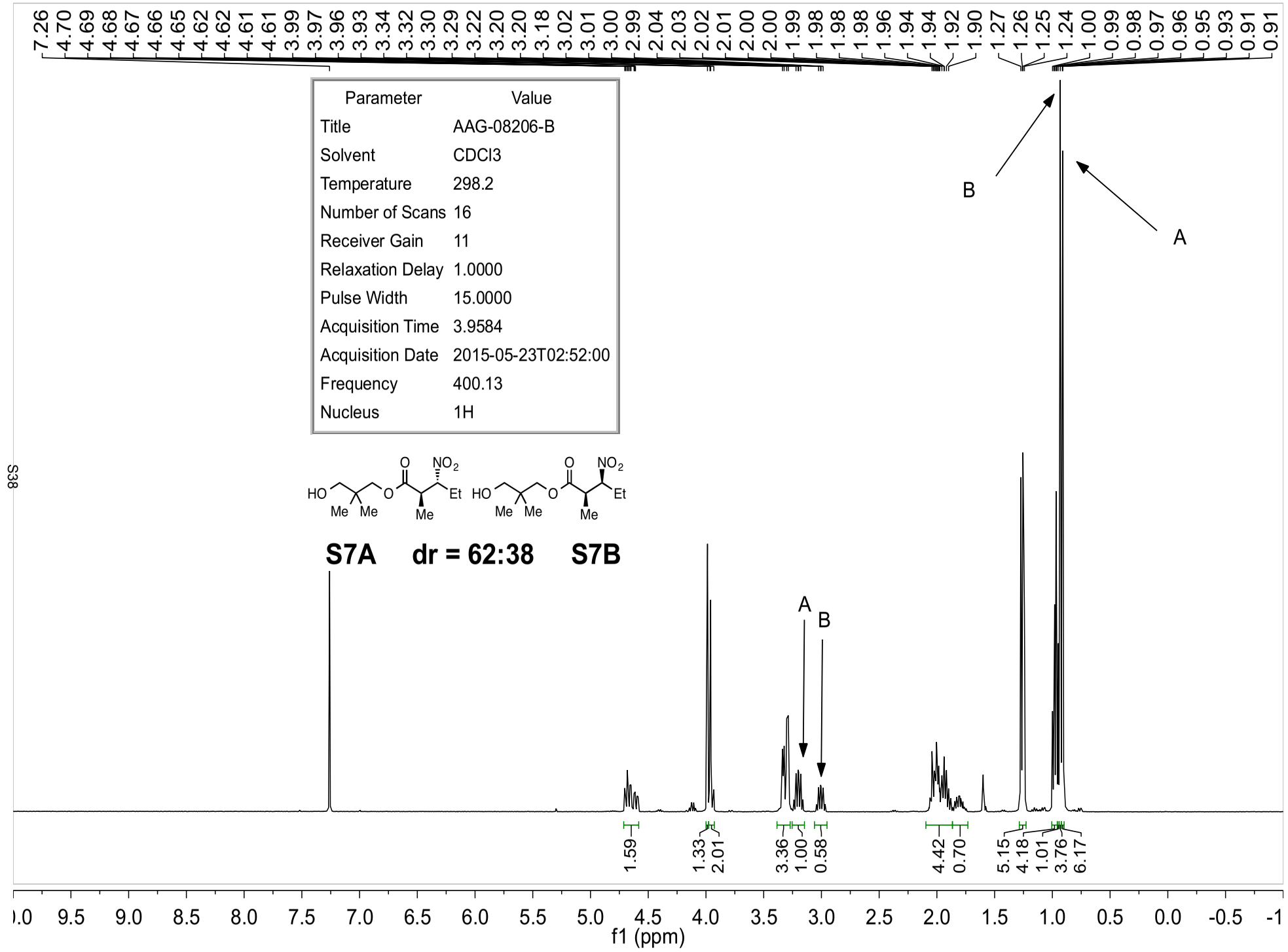
S5

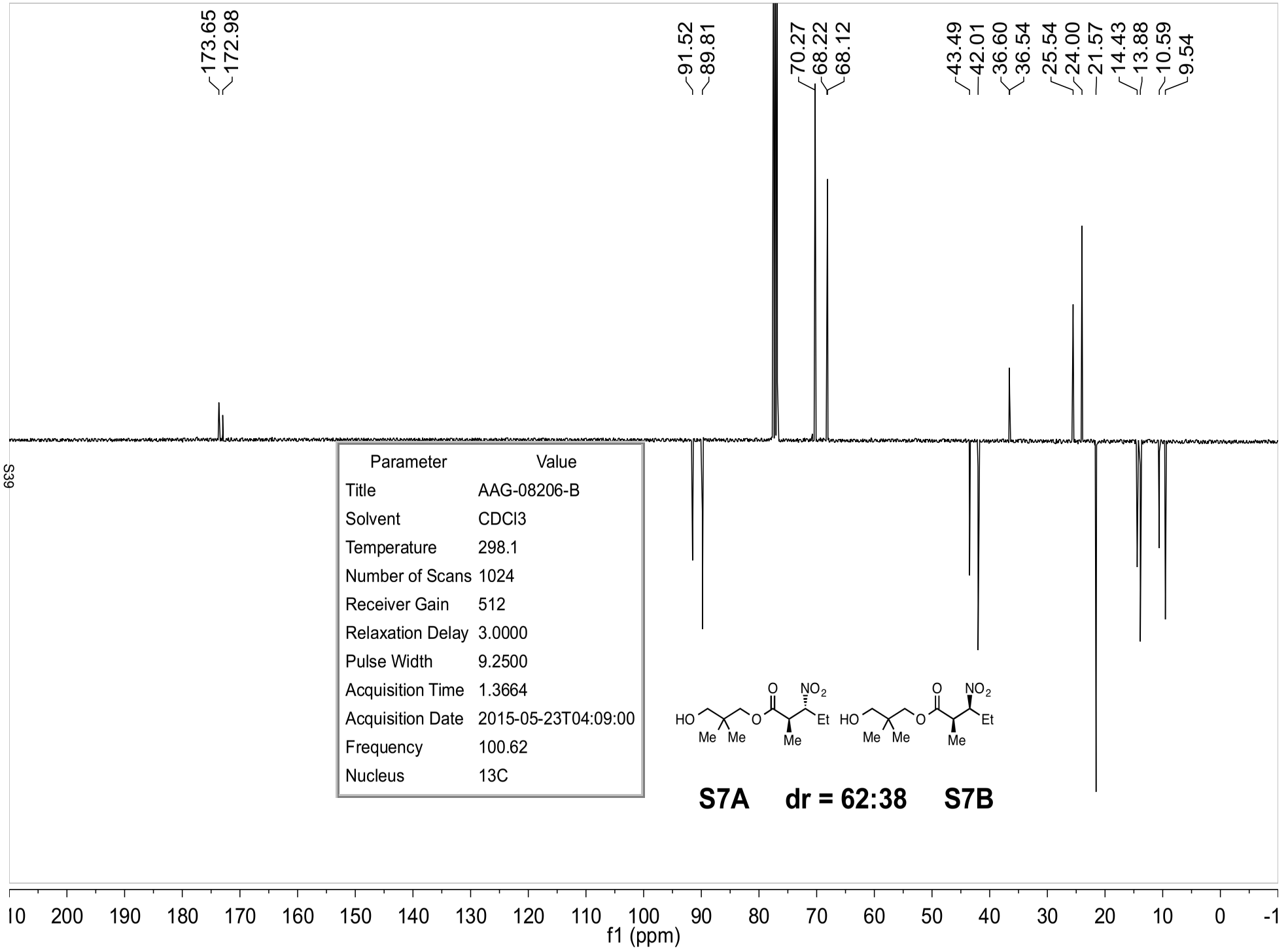

170.32
117.85
86.35
77.16
37.11
35.68
29.60
28.85
28.80
14.39
S35
Me
N
Me
NO2
CN
O
S5
Parameter Value
Title AAG-07247-F
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-04-16T04:28:00
Frequency 100.62
Nucleus 13C
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

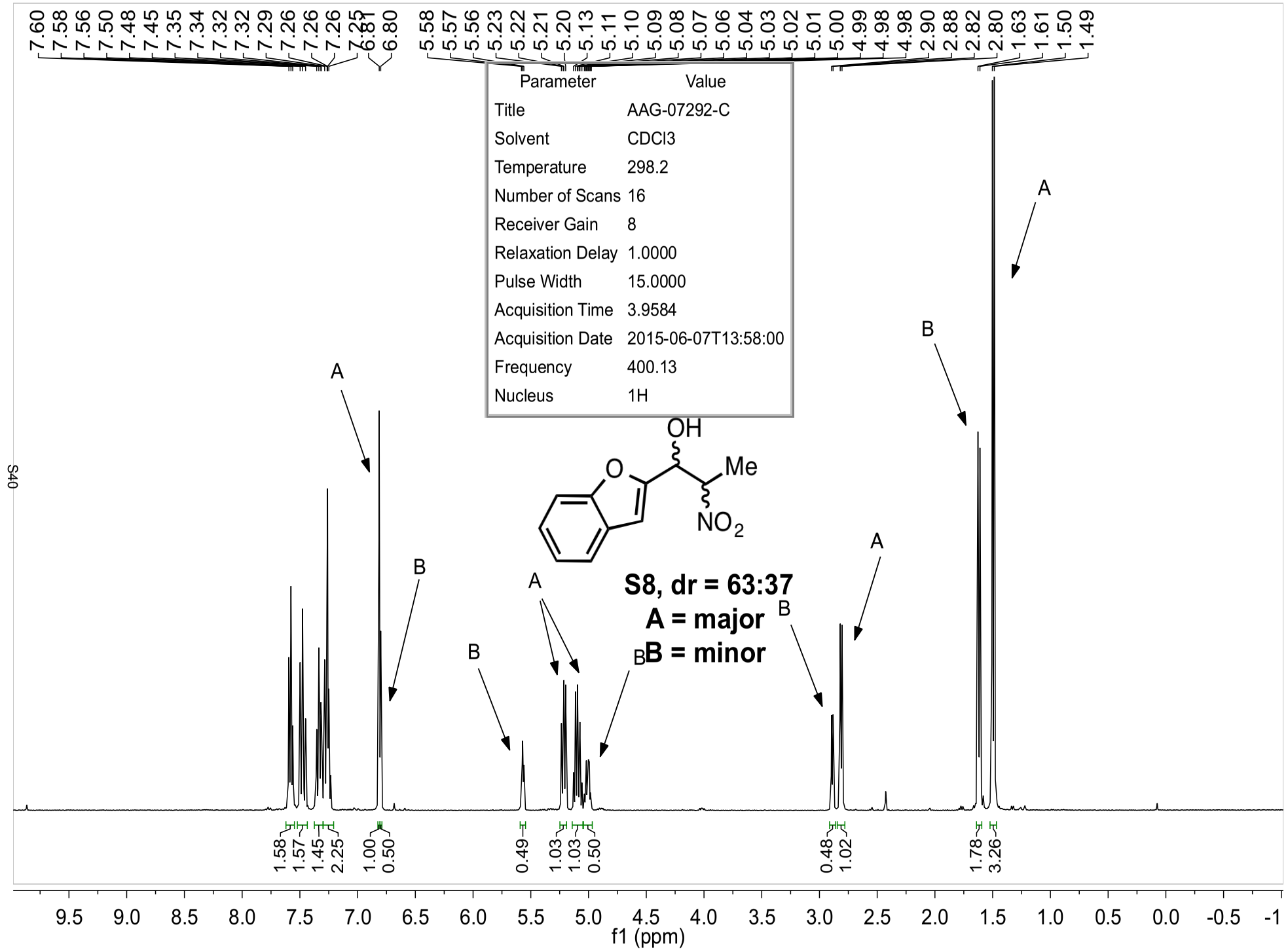

7.26 4.79 4.78 4.77 4.77 4.76 4.75 4.71 4.70 4.70 4.69 4.69 4.68 4.11 4.08 4.07 4.06 4.05 4.04 4.03 3.94 3.94 3.93 3.91 3.90 3.33 3.32 3.31 3.29 3.21 3.19 3.18 3.00 2.99 2.99 2.97 2.08 2.05 2.04 1.98 1.94 1.84 1.69 1.68 1.67 1.66 1.27 1.26 1.25 1.24 0.89 0.88 0.88 0.87 0.03
Parameter Value
Title AAG-07120-C
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 10.7700
Frequency 600.32
Nucleus 1H
OTBS O NO2 OAc Me Me Me
OTBS O NO2 OAc Me Me Me
S6A dr = 46:54 S6B
S36
1.00 0.84 3.83 3.83 3.79 1.02 0.84 6.33 2.27 0.89 3.79 5.62 28.17 10.89
f1 (ppm)

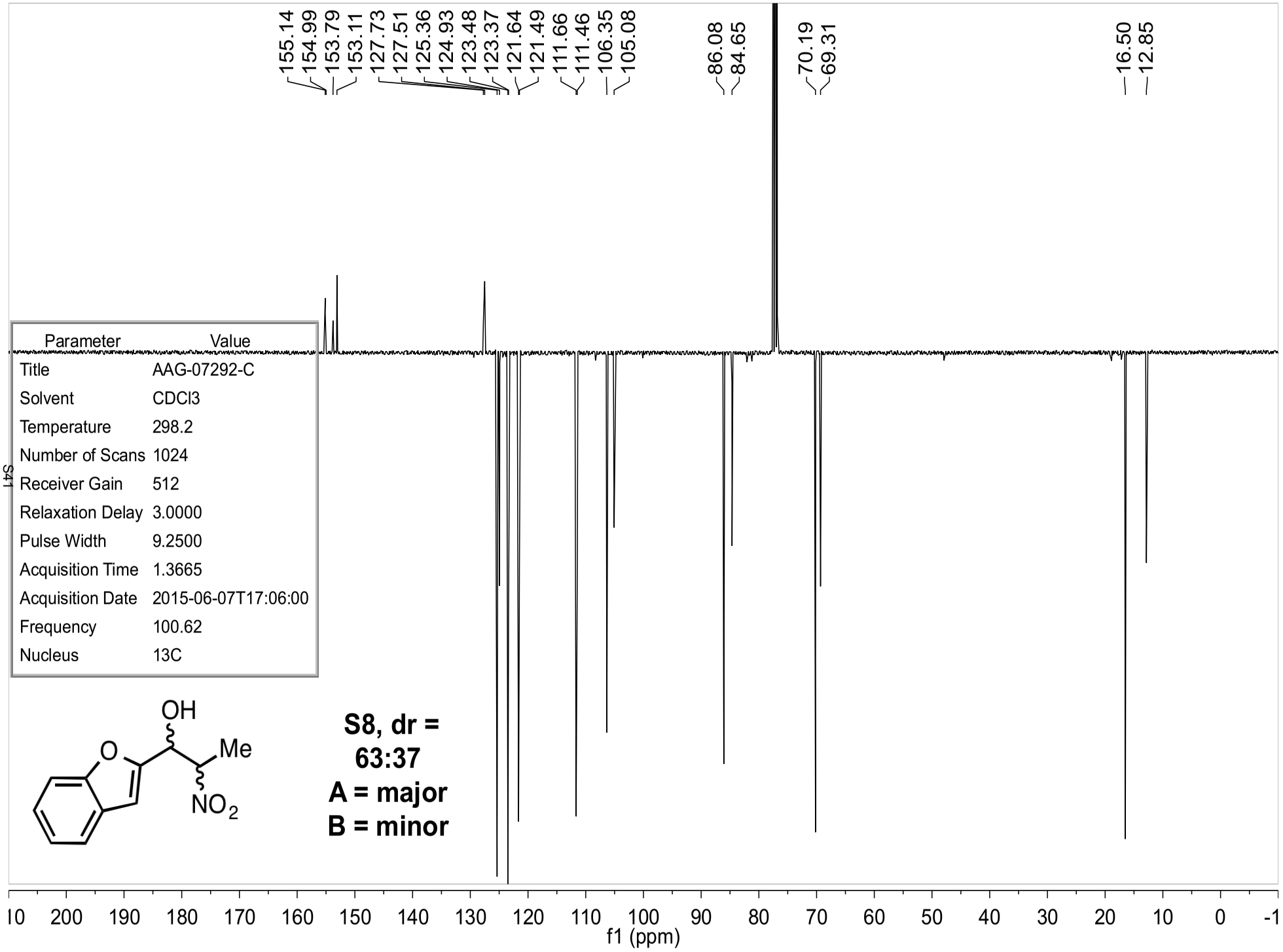


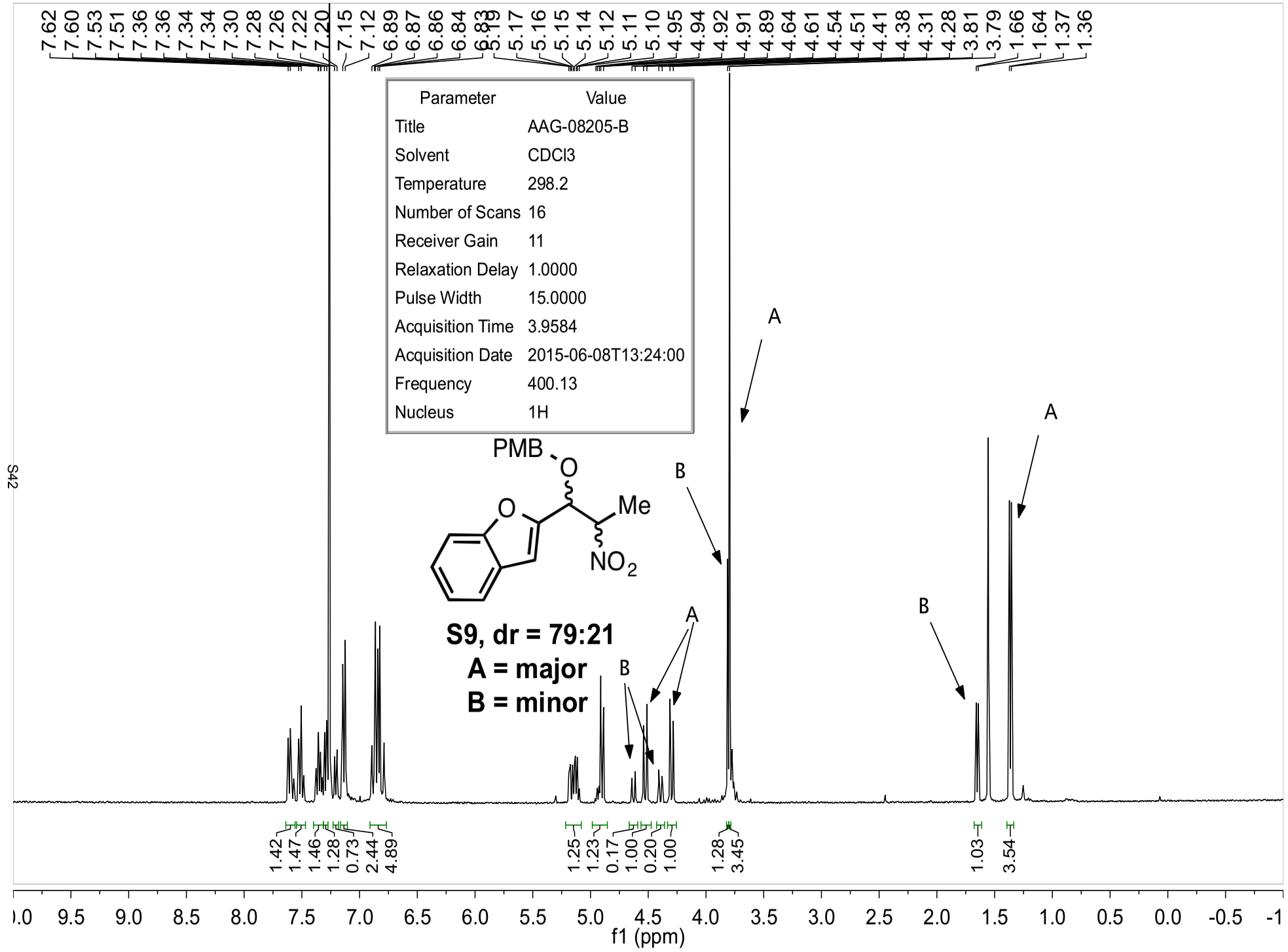
5.S6A dr = 46:54 5.S6B

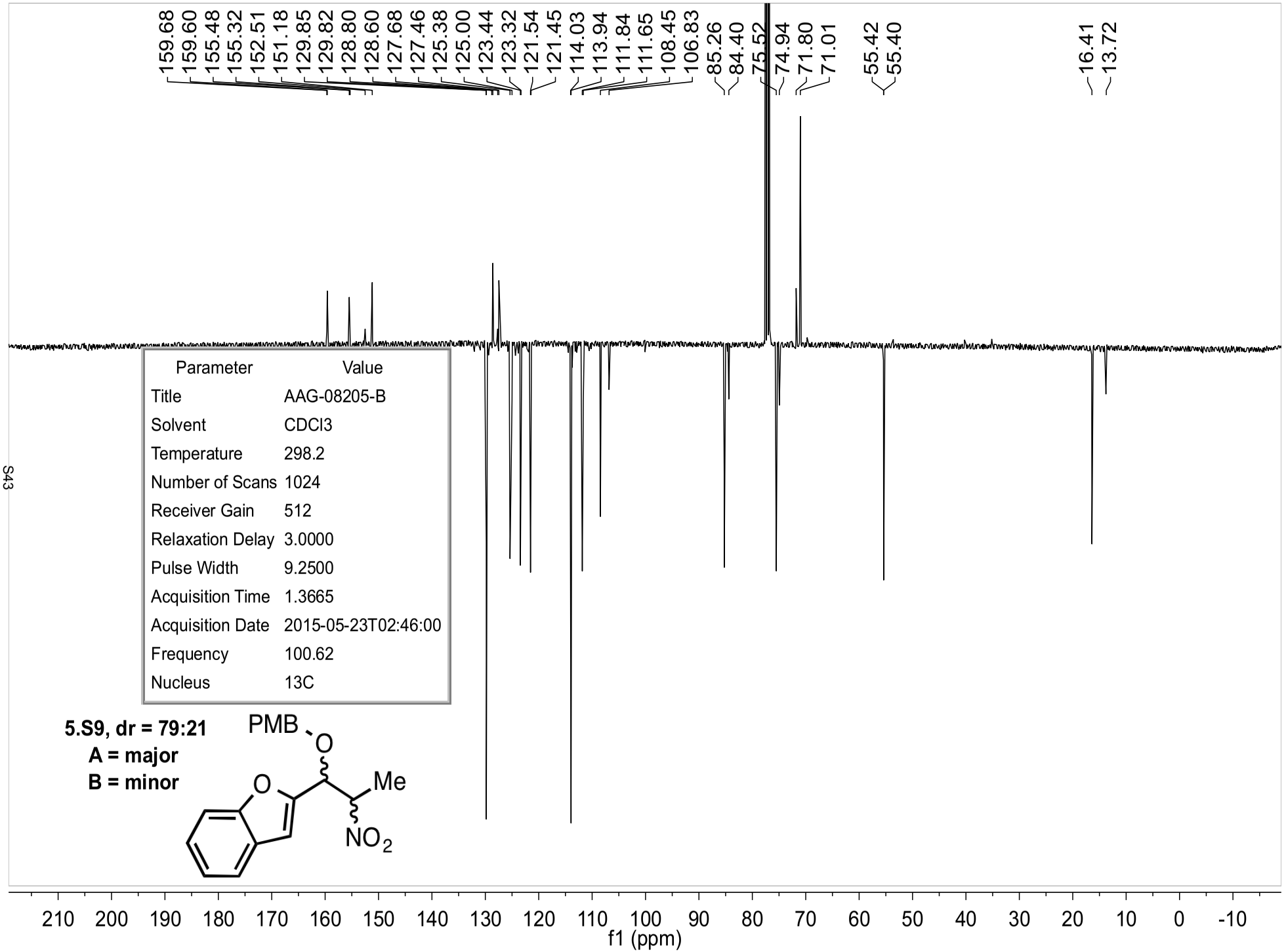

7.26 4.70 4.69 4.68 4.67 4.66 4.65 4.62 4.62 4.61 4.61 3.99 3.97 3.96 3.93 3.34 3.32 3.30 3.29 3.22 3.20 3.20 3.18 3.02 3.01 3.00 2.99 2.04 2.03 2.02 2.01 2.00 2.00 1.99 1.98 1.98 1.98 1.96 1.94 1.94 1.92 1.90 1.27 1.26 1.25 1.24 1.00 0.99 0.98 0.97 0.96 0.95 0.93 0.91 0.91
Parameter Value
Title AAG-08206-B
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-05-23T02:52:00
Frequency 400.13
Nucleus 1H
B
A
S38
S7A dr = 62:38 S7B
A
B
1.59 1.33 2.01 3.36 1.00 0.58 4.42 0.70 5.15 4.18 1.01 3.76 6.17
f1 (ppm)

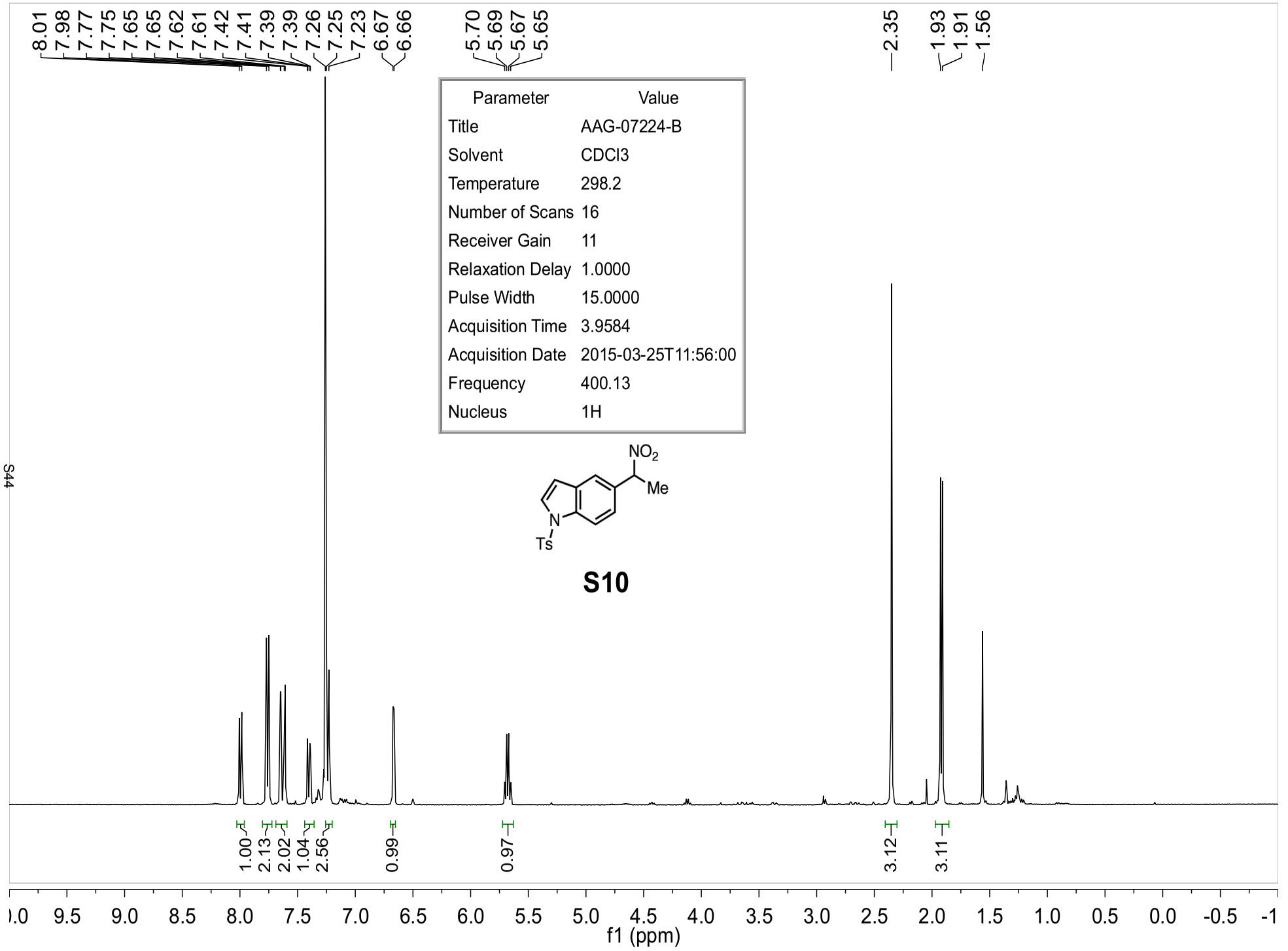

173.65
172.98
91.52
89.81
70.27
68.22
68.12
43.49
42.01
36.60
36.54
25.54
24.00
21.57
14.43
13.88
10.59
9.54
S39
Parameter Value
Title AAG-08206-B
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3664
Acquisition Date 2015-05-23T04:09:00
Frequency 100.62
Nucleus 13C
HO
Me Me
O
O
NO2
Et
Me
S7A dr = 62:38 S7B
f1 (ppm)

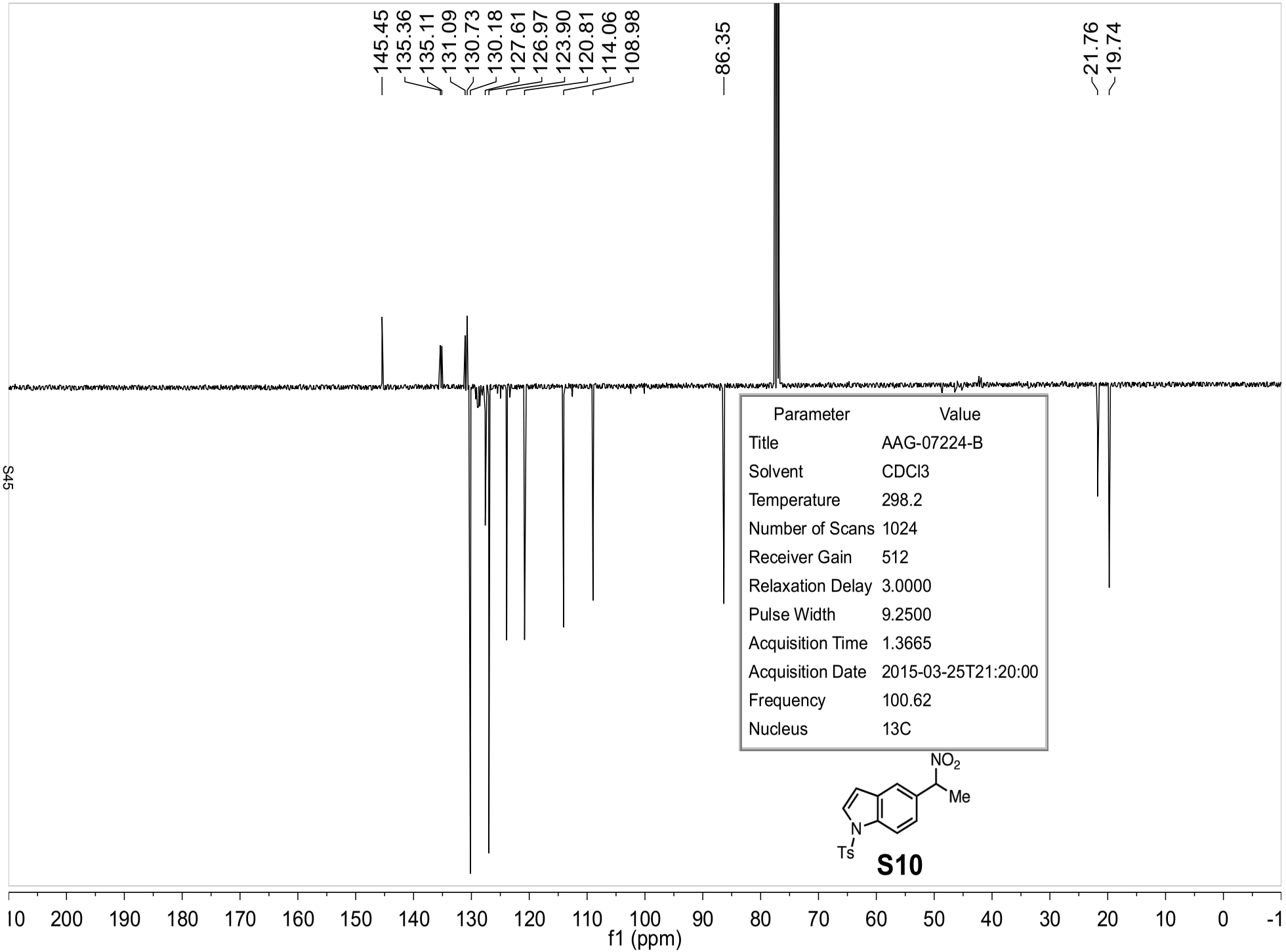

7.60 7.58 7.56 7.50 7.48 7.45 7.35 7.34 7.32 7.32 7.29 7.26 7.26 7.26 7.25 6.81 6.80
5.58 5.57 5.56 5.23 5.22 5.21 5.20 5.13 5.11 5.10 5.09 5.08 5.07 5.06 5.04 5.03 5.02 5.01 5.00 4.99 4.98 4.98 2.90 2.88 2.82 2.80 1.63 1.61 1.50 1.49
Parameter Value
Title AAG-07292-C
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-06-07T13:58:00
Frequency 400.13
Nucleus 1H
OH
O
Me
NO2
S8, dr = 63:37
A = major
B = minor
A
B
S40
1.58 1.57 1.45 2.25 1.00 0.50 0.49 1.03 1.03 0.50 0.48 1.02 1.78 3.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


155.14
154.99
153.79
153.11
127.73
127.51
125.36
124.93
123.48
123.37
121.64
121.49
111.66
111.46
106.35
105.08
86.08
84.65
70.19
69.31
16.50
12.85
Parameter Value
Title AAG-07292-C
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-06-07T17:06:00
Frequency 100.62
Nucleus 13C
OH
O
Me
NO2
S8, dr = 63:37
A = major
B = minor
S41
f1 (ppm)

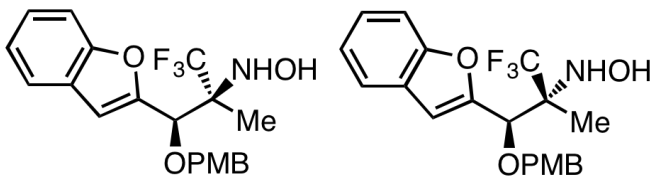

7.62 7.60 7.53 7.51 7.36 7.36 7.34 7.34 7.30 7.28 7.26 7.22 7.20 7.15 7.12 6.89 6.87 6.86 6.84 6.83 5.19 5.17 5.16 5.15 5.14 5.12 5.11 5.10 4.95 4.94 4.92 4.91 4.89 4.64 4.61 4.54 4.51 4.41 4.38 4.31 4.28 3.81 3.79 1.66 1.64 1.37 1.36
Parameter Value
Title AAG-08205-B
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-06-08T13:24:00
Frequency 400.13
Nucleus 1H
PMB
O
O
Me
NO2
S9, dr = 79:21
A = major
B = minor
A
B
A
B
A
B
1.42 1.47 1.46 1.28 0.73 2.44 4.89
1.25 1.23 0.17 1.00 0.20 1.00
1.28 3.45
1.03 3.54
f1 (ppm)


159.68
159.60
155.48
155.32
152.51
151.18
129.85
129.82
128.80
128.60
127.68
127.46
125.38
125.00
123.44
123.32
121.54
121.45
114.03
113.94
111.84
111.65
108.45
106.83
85.26
84.40
75.52
74.94
71.80
71.01
55.42
55.40
16.41
13.72
Parameter Value
Title AAG-08205-B
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-05-23T02:46:00
Frequency 100.62
Nucleus 13C
5.S9, dr = 79:21
A = major
B = minor
PMB
O
O
Me
NO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.01
7.98
7.77
7.75
7.65
7.65
7.62
7.61
7.42
7.41
7.39
7.39
7.26
7.25
7.23
6.67
6.66
5.70
5.69
5.67
5.65
2.35
1.93
1.91
1.56
Parameter Value
Title AAG-07224-B
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-03-25T11:56:00
Frequency 400.13
Nucleus 1H
NO2
Me
N
Ts
S10
S44
1.00
2.13
2.02
1.04
2.56
0.99
0.97
3.12
3.11
f1 (ppm)

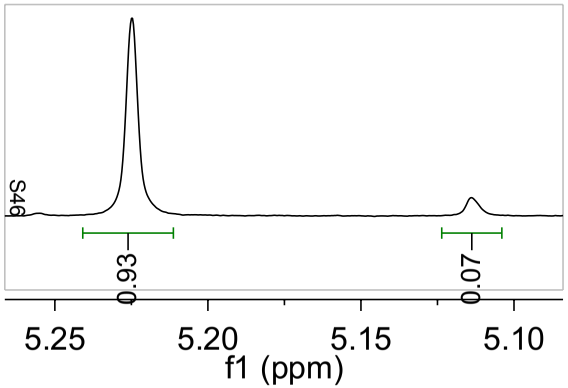

145.45
135.36
135.11
131.09
130.73
130.18
127.61
126.97
123.90
120.81
114.06
108.98
86.35
21.76
19.74
Parameter Value
Title AAG-07224-B
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-03-25T21:20:00
Frequency 100.62
Nucleus 13C
NO2
Me
N
Ts
S10
f1 (ppm)

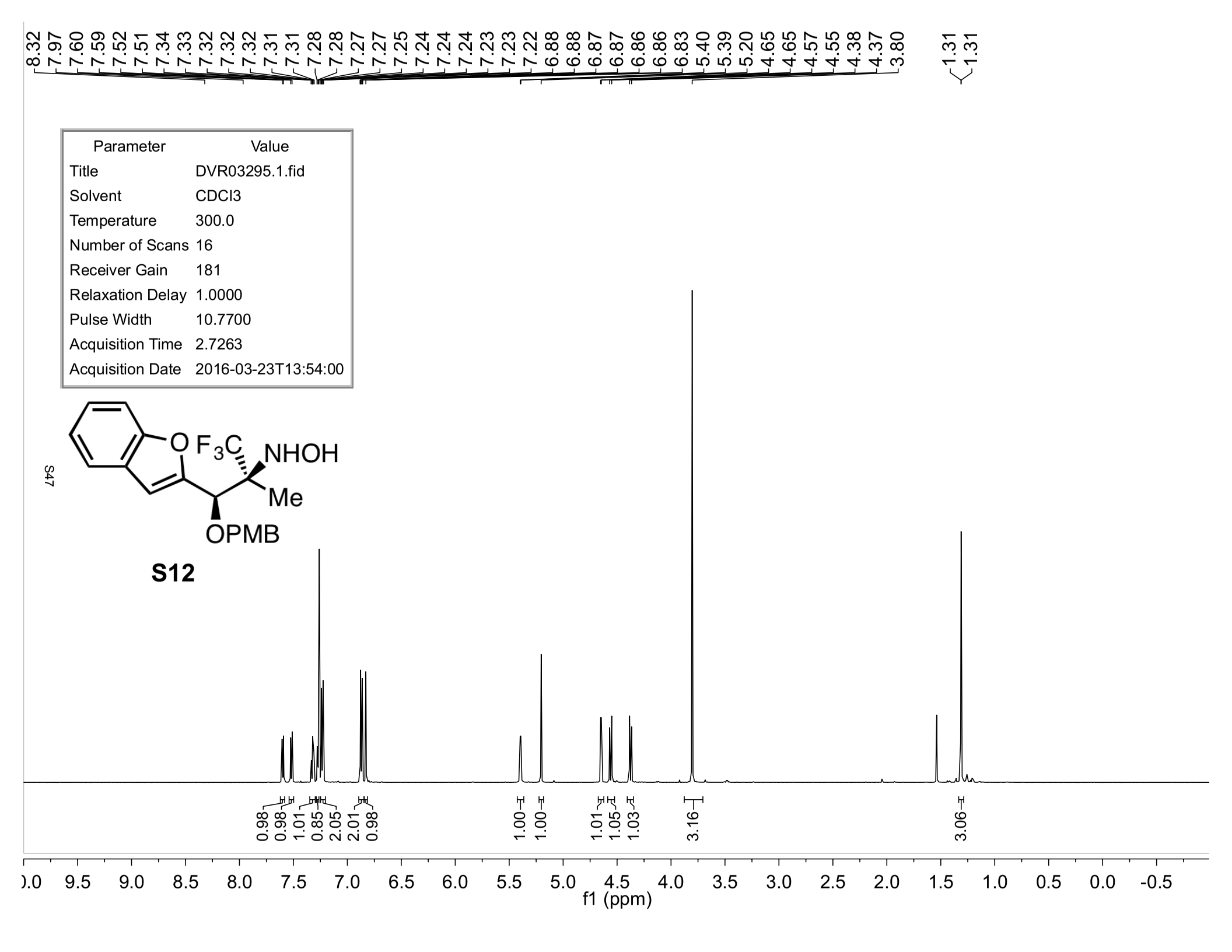
Parameter	Value
1 Title	DVR03295CRD.1.fid
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	9
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	400.13
9 Nucleus	1H

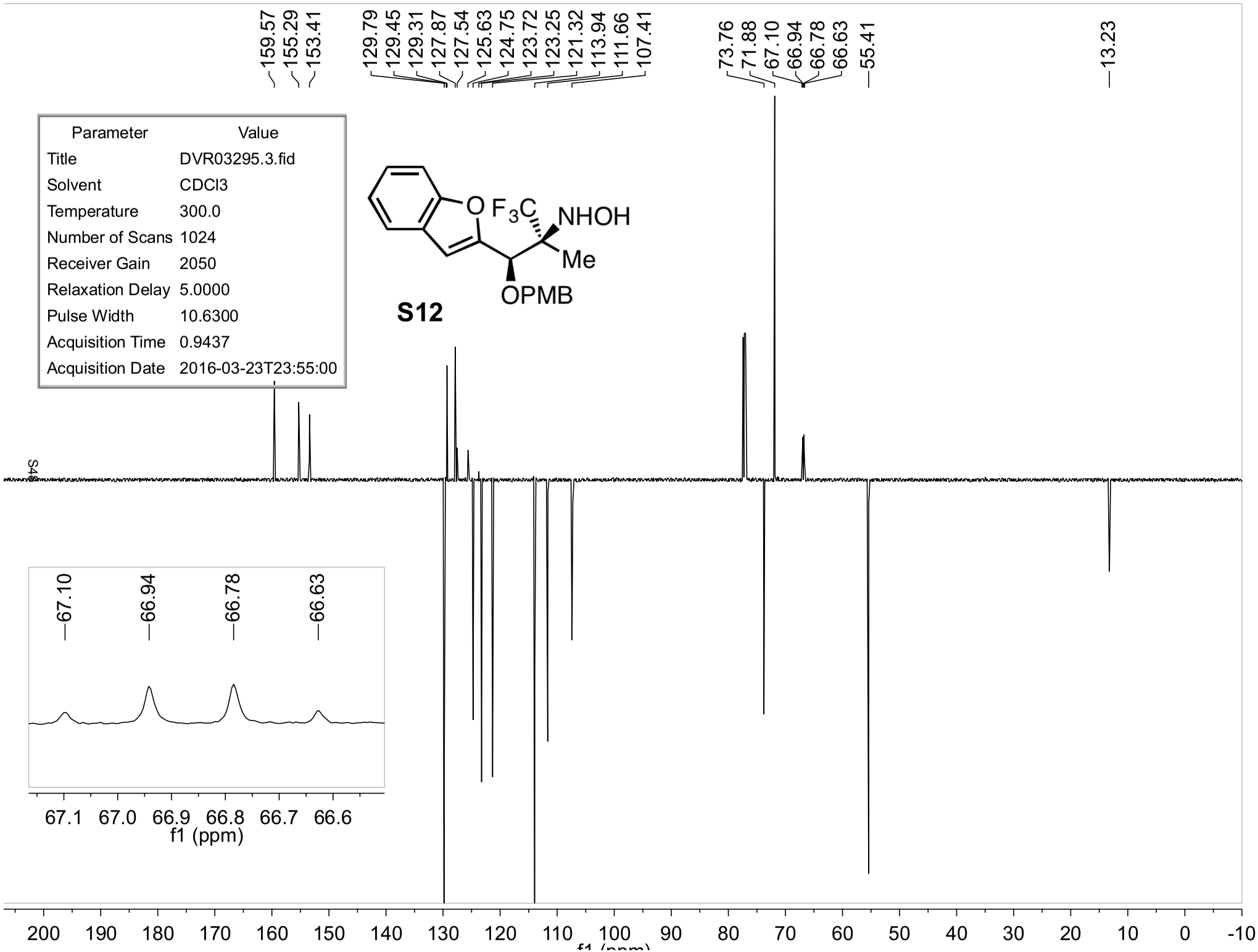


crude-S12

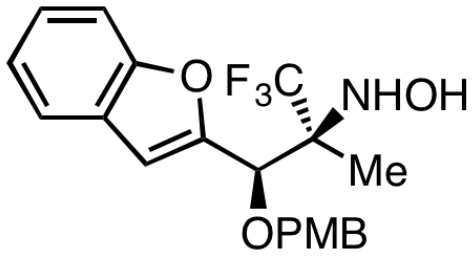
S12A 93:07



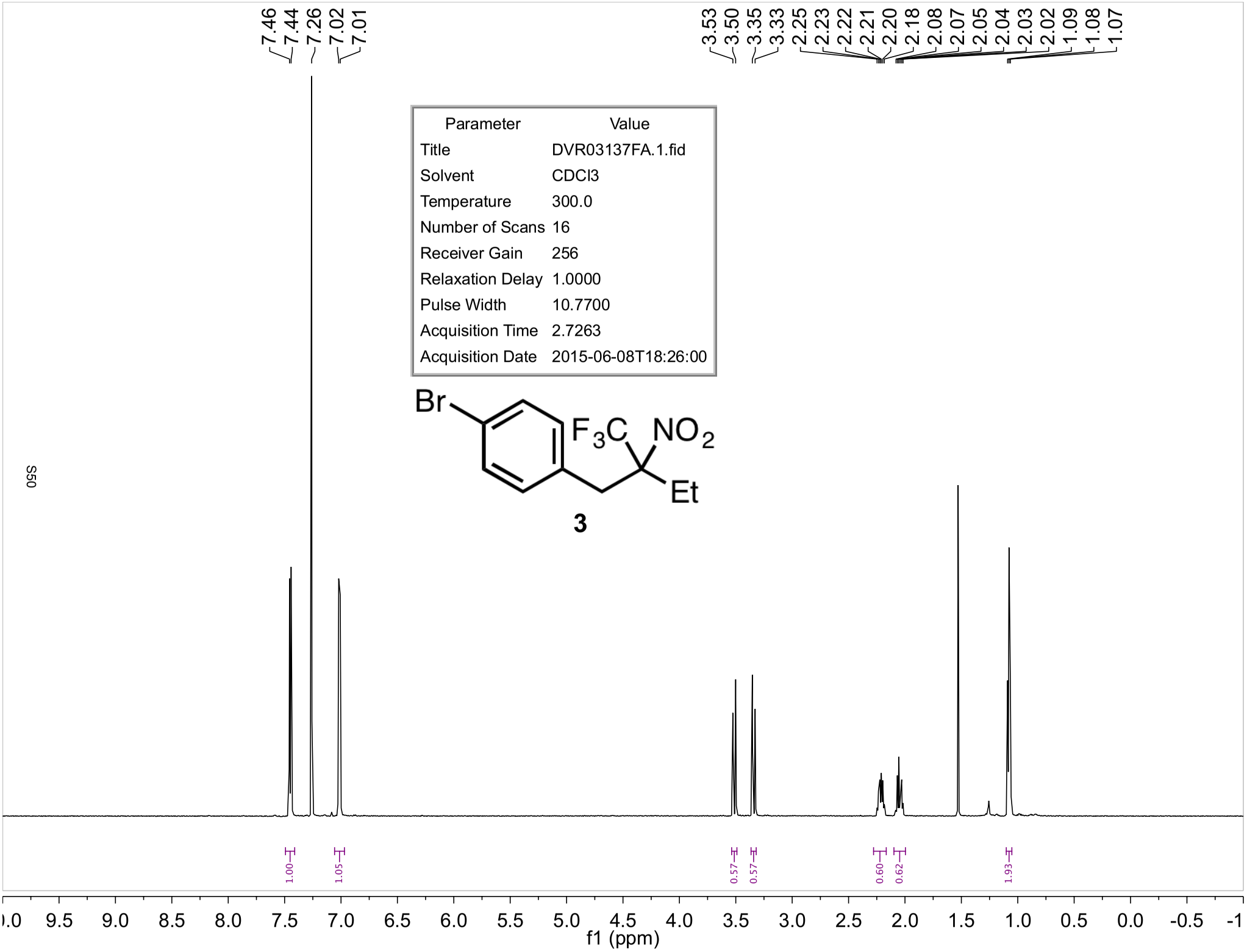

8.32 7.97 7.60 7.59 7.52 7.51 7.34 7.33 7.32 7.32 7.32 7.31 7.31 7.28 7.28 7.27 7.27 7.25 7.24 7.24 7.24 7.23 7.23 7.22 6.88 6.88 6.87 6.87 6.86 6.86 6.83 5.40 5.39 5.20 4.65 4.65 4.57 4.55 4.38 4.37 3.80 1.31 1.31
Parameter Value
Title DVR03295.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2016-03-23T13:54:00
O F3C NHOH Me OPMB
S12
S47
0.98 0.98 1.01 0.85 2.05 2.01 0.98 1.00 1.00 1.01 1.05 1.03 3.16 3.06
f1 (ppm)

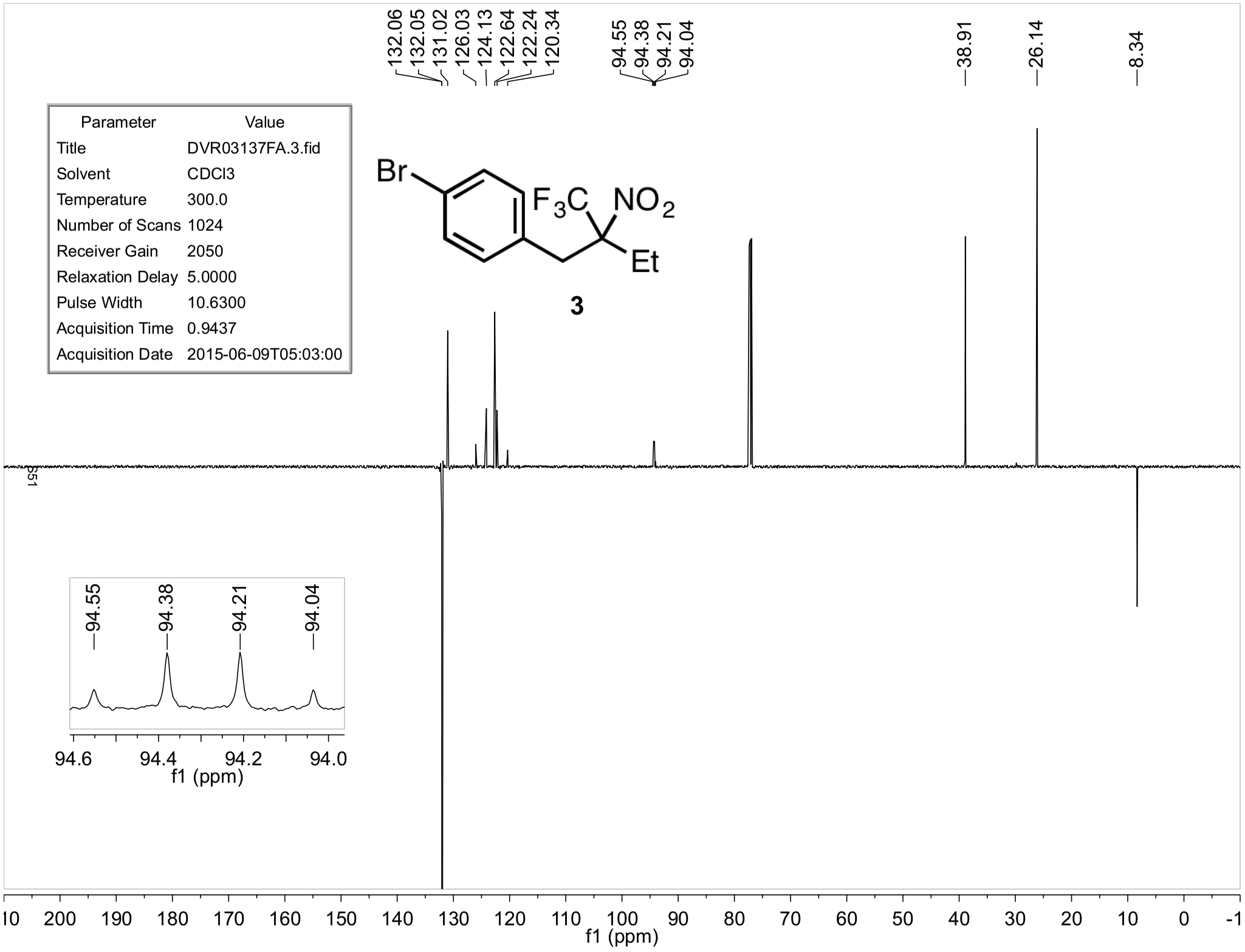

159.57
155.29
153.41
129.79
129.45
129.31
127.87
127.54
125.63
124.75
123.72
123.25
121.32
113.94
111.66
107.41
73.76
71.88
67.10
66.94
66.78
66.63
55.41
13.23
Parameter Value
Title DVR03295.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2016-03-23T23:55:00
O
F3C
NHOH
Me
OPMB
S12
67.10
66.94
66.78
66.63
67.1 67.0 66.9 66.8 66.7 66.6
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Parameter	Value
Title	DVR03295.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2016-03-23T13:57:00



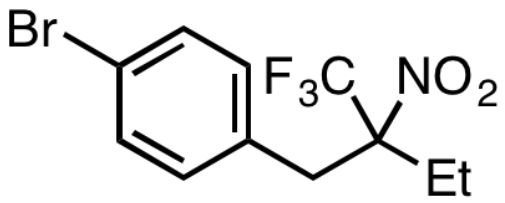
S12


7.46
7.44
7.26
7.02
7.01
3.53
3.50
3.35
3.33
2.25
2.23
2.22
2.21
2.20
2.18
2.08
2.07
2.05
2.04
2.03
2.02
1.09
1.08
1.07
Parameter Value
Title DVR03137FA.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 256
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-08T18:26:00
Br
F3C
NO2
Et
3
S50
1.00
1.05
0.57
0.57
0.60
0.62
1.93
f1 (ppm)

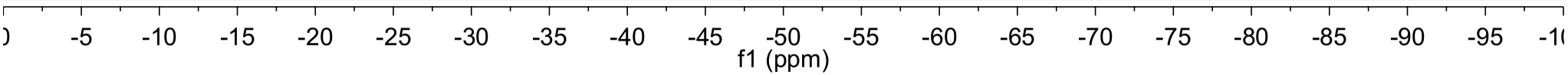

132.06
132.05
131.02
126.03
124.13
122.64
122.24
120.34
94.55
94.38
94.21
94.04
38.91
26.14
8.34
Br
F3C
NO2
Et
3
Parameter Value
Title DVR03137FA.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-09T05:03:00
94.55
94.38
94.21
94.04
94.6
94.4
94.2
94.0
f1 (ppm)
f1 (ppm)

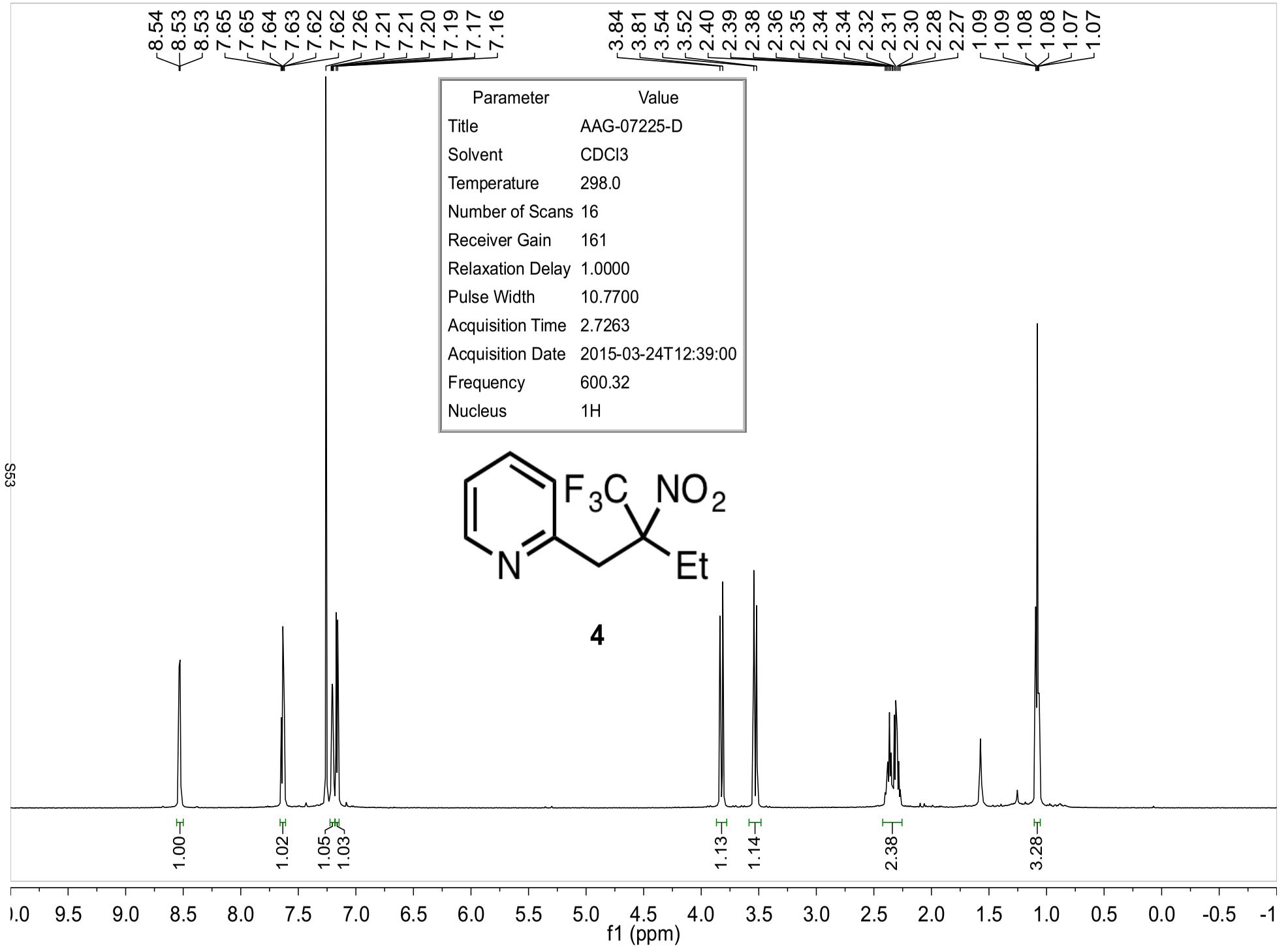
-69.51

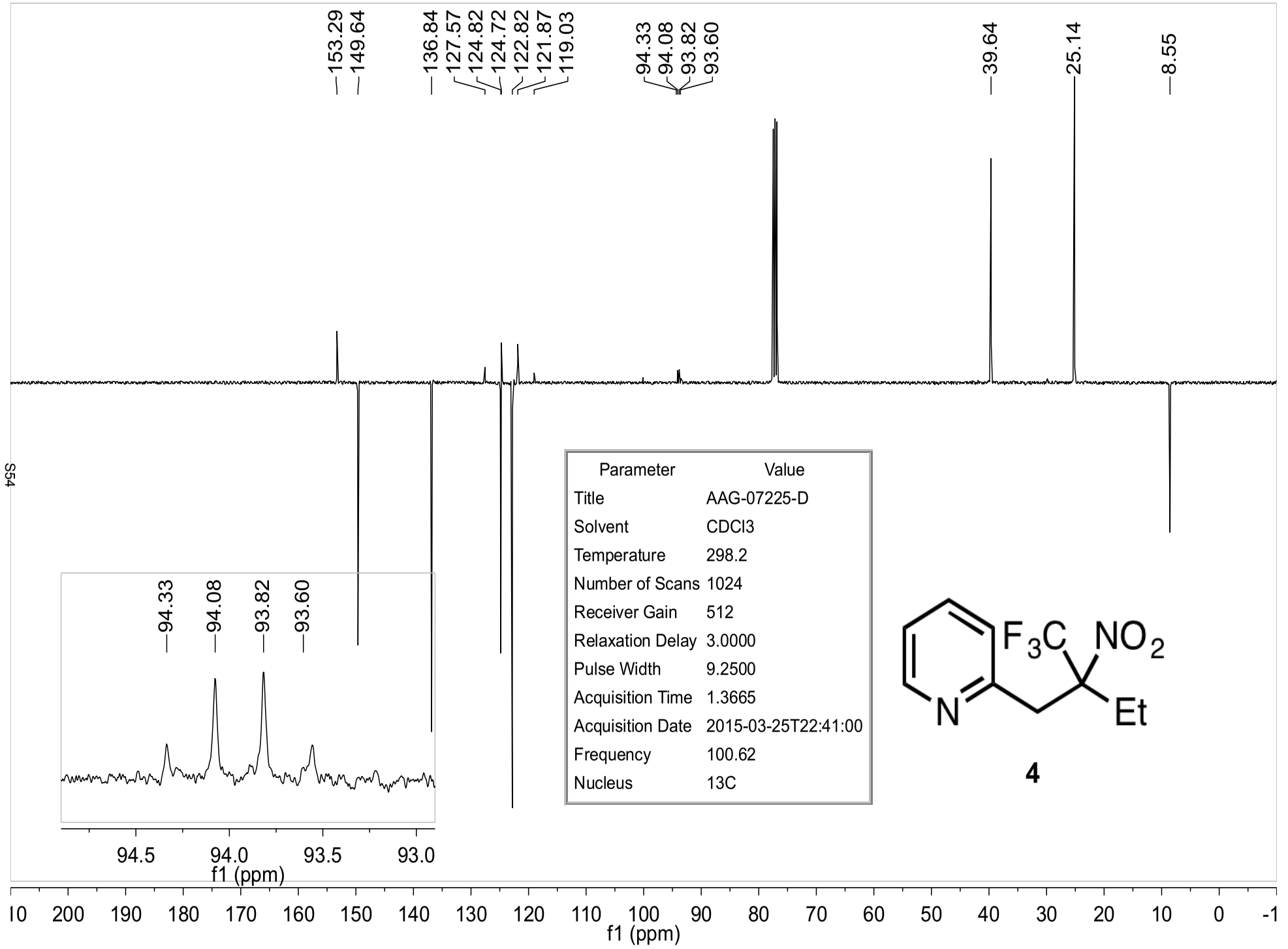
Parameter	Value
Title	DVR03137FA.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-06-08T18:29:00



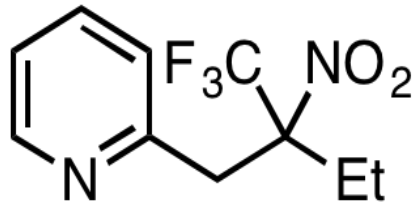
3



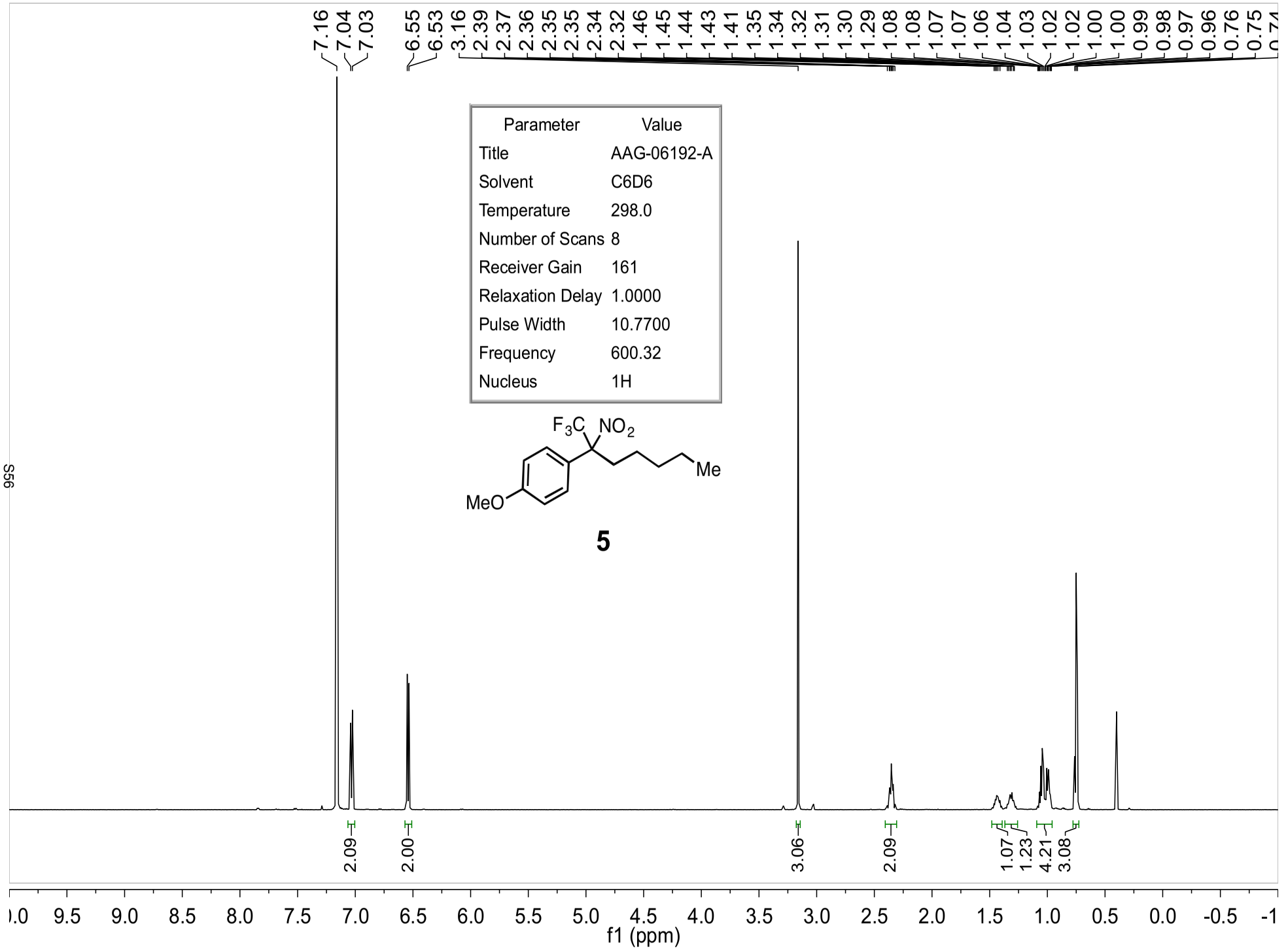

8.54 8.53 8.53 7.65 7.65 7.64 7.63 7.62 7.62 7.26 7.21 7.21 7.20 7.19 7.17 7.16
3.84 3.81 3.54 3.52 2.40 2.39 2.38 2.36 2.35 2.34 2.34 2.32 2.31 2.30 2.28 2.27
1.09 1.09 1.08 1.08 1.07 1.07
Parameter Value
Title AAG-07225-D
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Receiver Gain 161
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-03-24T12:39:00
Frequency 600.32
Nucleus 1H
F3C NO2
N
Et
4
S53
1.00 1.02 1.05 1.03 1.13 1.14 2.38 3.28
f1 (ppm)

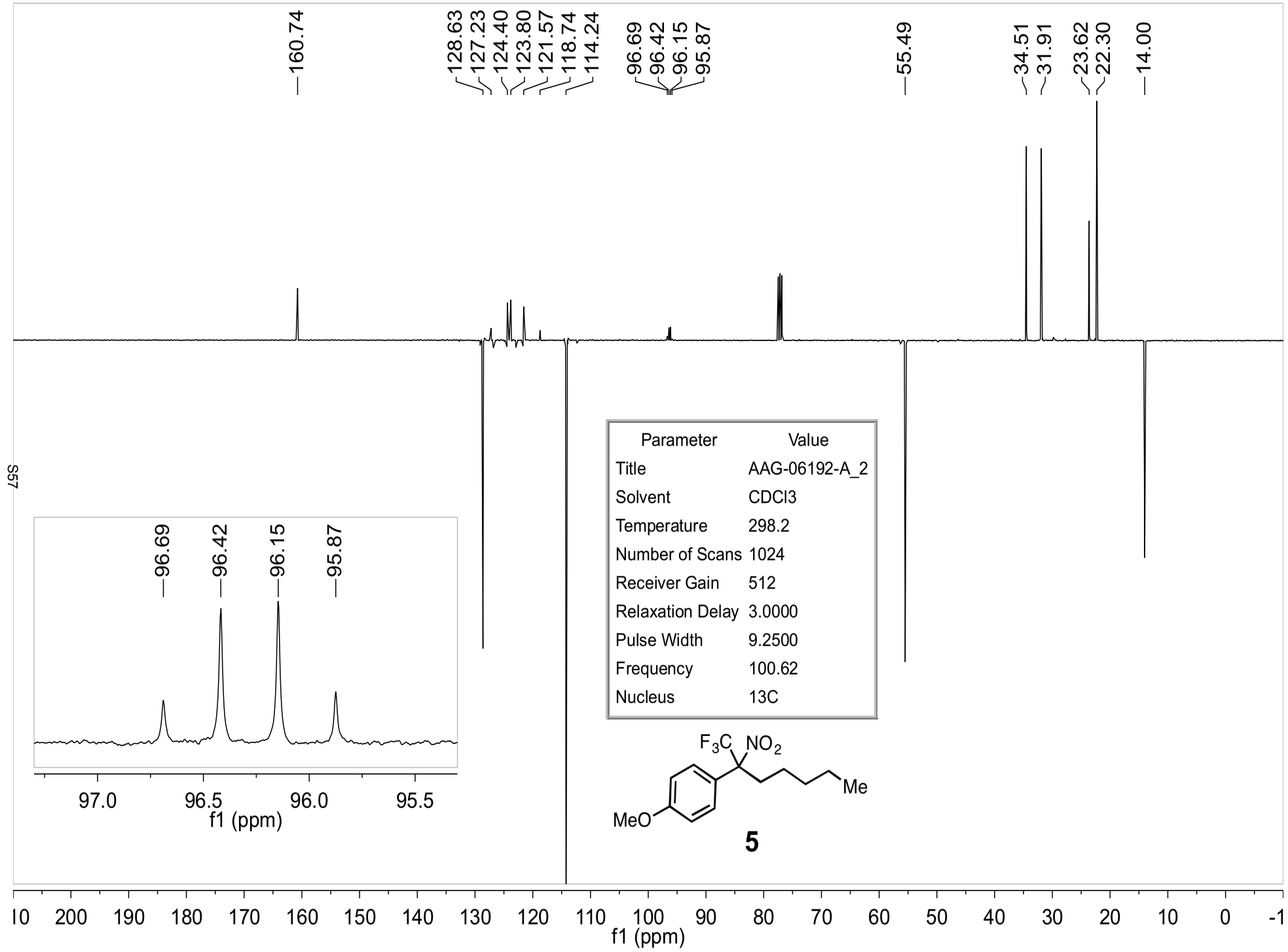

153.29
149.64
136.84
127.57
124.82
124.72
122.82
121.87
119.03
94.33
94.08
93.82
93.60
39.64
25.14
8.55
S54
94.33
94.08
93.82
93.60
94.5
94.0
93.5
93.0
f1 (ppm)
Parameter Value
Title AAG-07225-D
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-03-25T22:41:00
Frequency 100.62
Nucleus 13C
F3C
NO2
N
Et
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

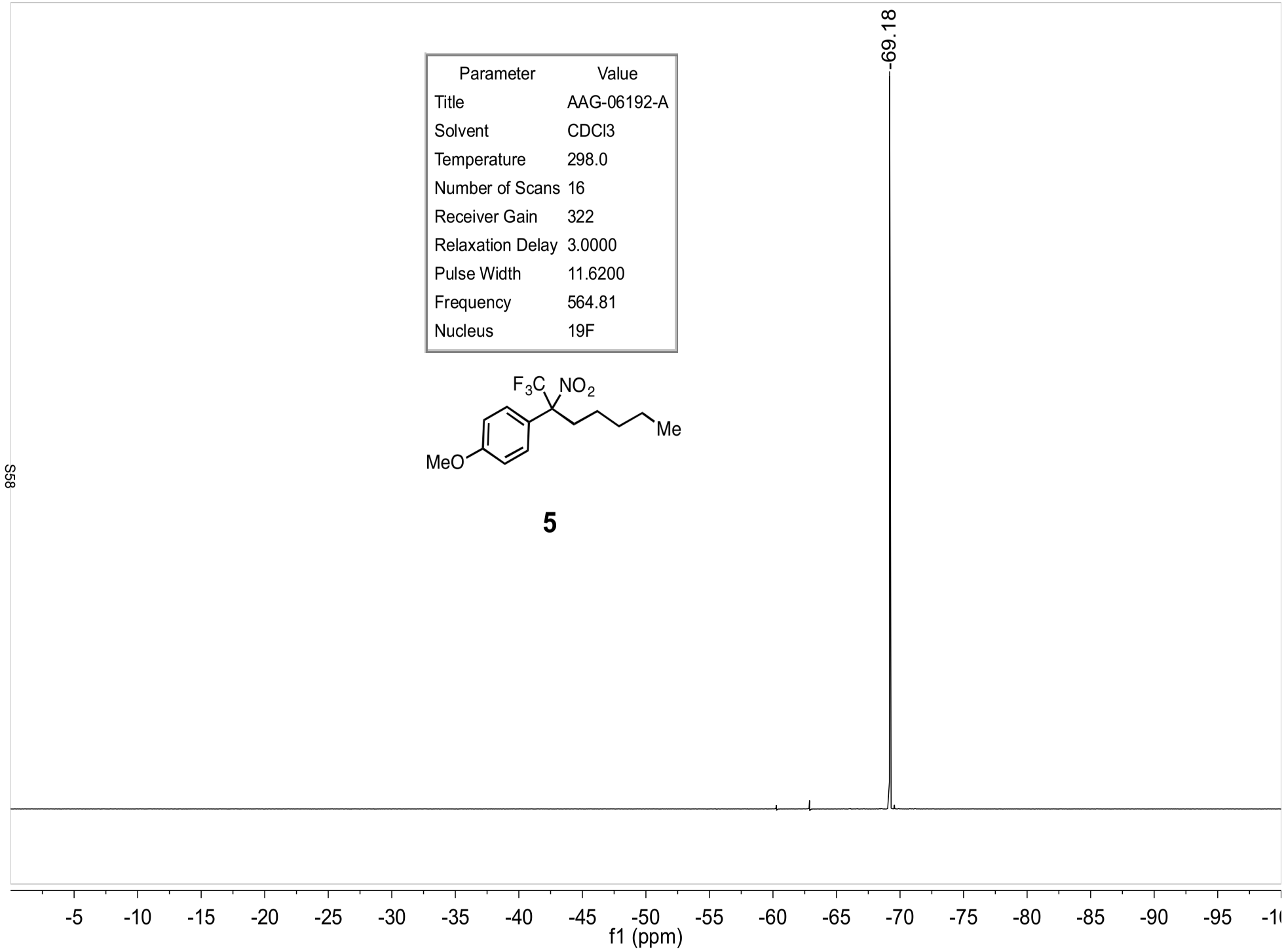
Parameter	Value
Title	AAG-07225-D/ 20
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4888
Acquisition Date	2015-03-23T22:03:27
Frequency	564.81
Nucleus	19F

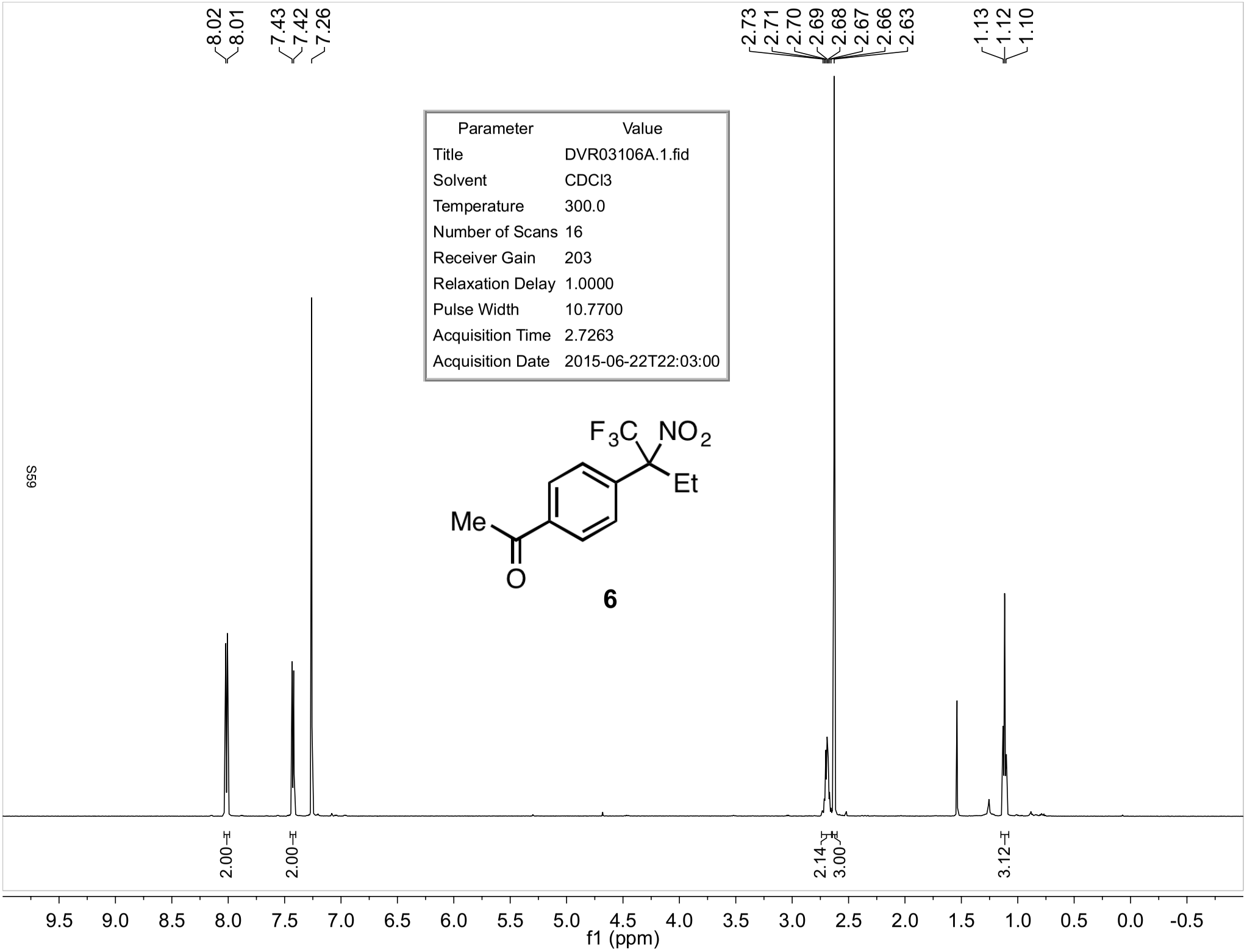


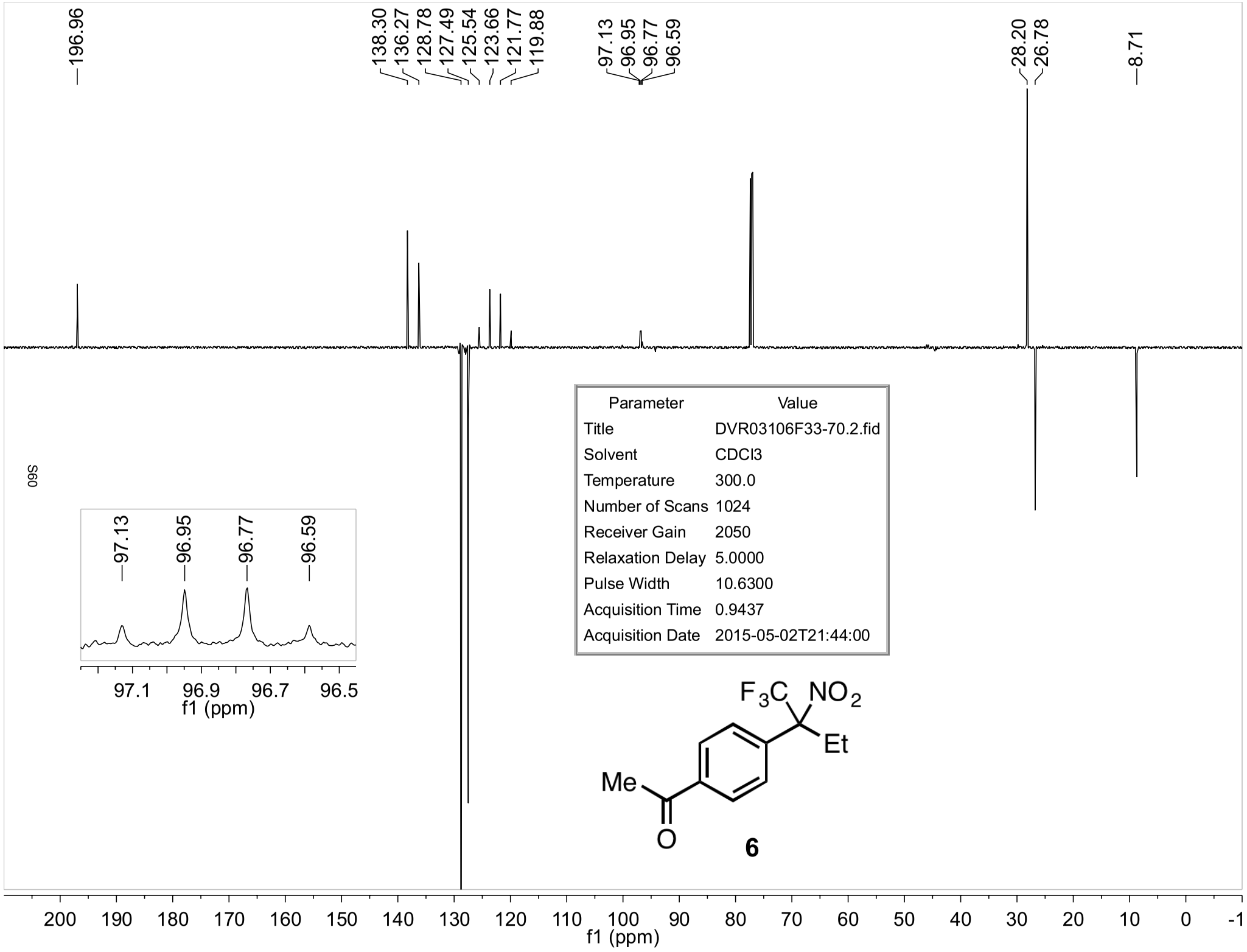
4


7.16 7.04 7.03 6.55 6.53 3.16 2.39 2.37 2.36 2.35 2.35 2.34 2.32 1.46 1.45 1.44 1.43 1.41 1.35 1.34 1.32 1.31 1.30 1.29 1.08 1.08 1.07 1.07 1.06 1.04 1.03 1.02 1.02 1.00 1.00 0.99 0.98 0.97 0.96 0.76 0.75
Parameter Value
Title AAG-06192-A
Solvent C6D6
Temperature 298.0
Number of Scans 8
Receiver Gain 161
Relaxation Delay 1.0000
Pulse Width 10.7700
Frequency 600.32
Nucleus 1H
F3C NO2
Me
MeO
5
S56
2.09 2.00 3.06 2.09 1.07 1.23 4.21 3.08
f1 (ppm)


160.74
128.63
127.23
124.40
123.80
121.57
118.74
114.24
96.69
96.42
96.15
95.87
55.49
34.51
31.91
23.62
22.30
14.00
S57
96.69
96.42
96.15
95.87
97.0
96.5
96.0
95.5
f1 (ppm)
Parameter Value
Title AAG-06192-A_2
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
F3C NO2
Me
MeO
5
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

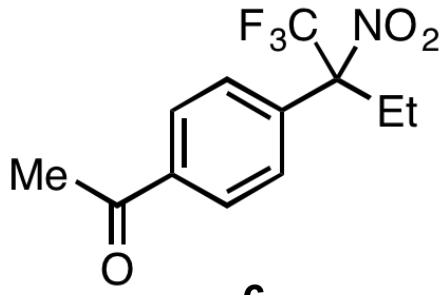

-69.18
Parameter Value
Title AAG-06192-A
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Receiver Gain 322
Relaxation Delay 3.0000
Pulse Width 11.6200
Frequency 564.81
Nucleus 19F
F3C NO2
Me
MeO
5
S58
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)


8.02
8.01
7.43
7.42
7.26
2.73
2.71
2.70
2.69
2.68
2.67
2.66
2.63
1.13
1.12
1.10
Parameter Value
Title DVR03106A.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-22T22:03:00
S59
F3C NO2
Et
Me
O
6
2.00
2.00
2.14
3.00
3.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

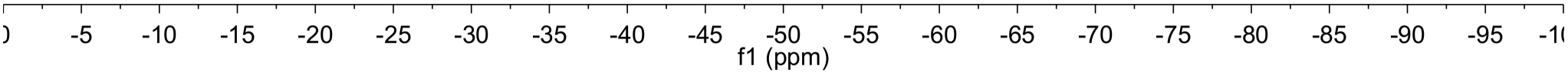

196.96
138.30
136.27
128.78
127.49
125.54
123.66
121.77
119.88
97.13
96.95
96.77
96.59
28.20
26.78
8.71
S60
97.13
96.95
96.77
96.59
97.1
96.9
96.7
96.5
f1 (ppm)
Parameter Value
Title DVR03106F33-70.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-05-02T21:44:00
F3C
NO2
Et
Me
O
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

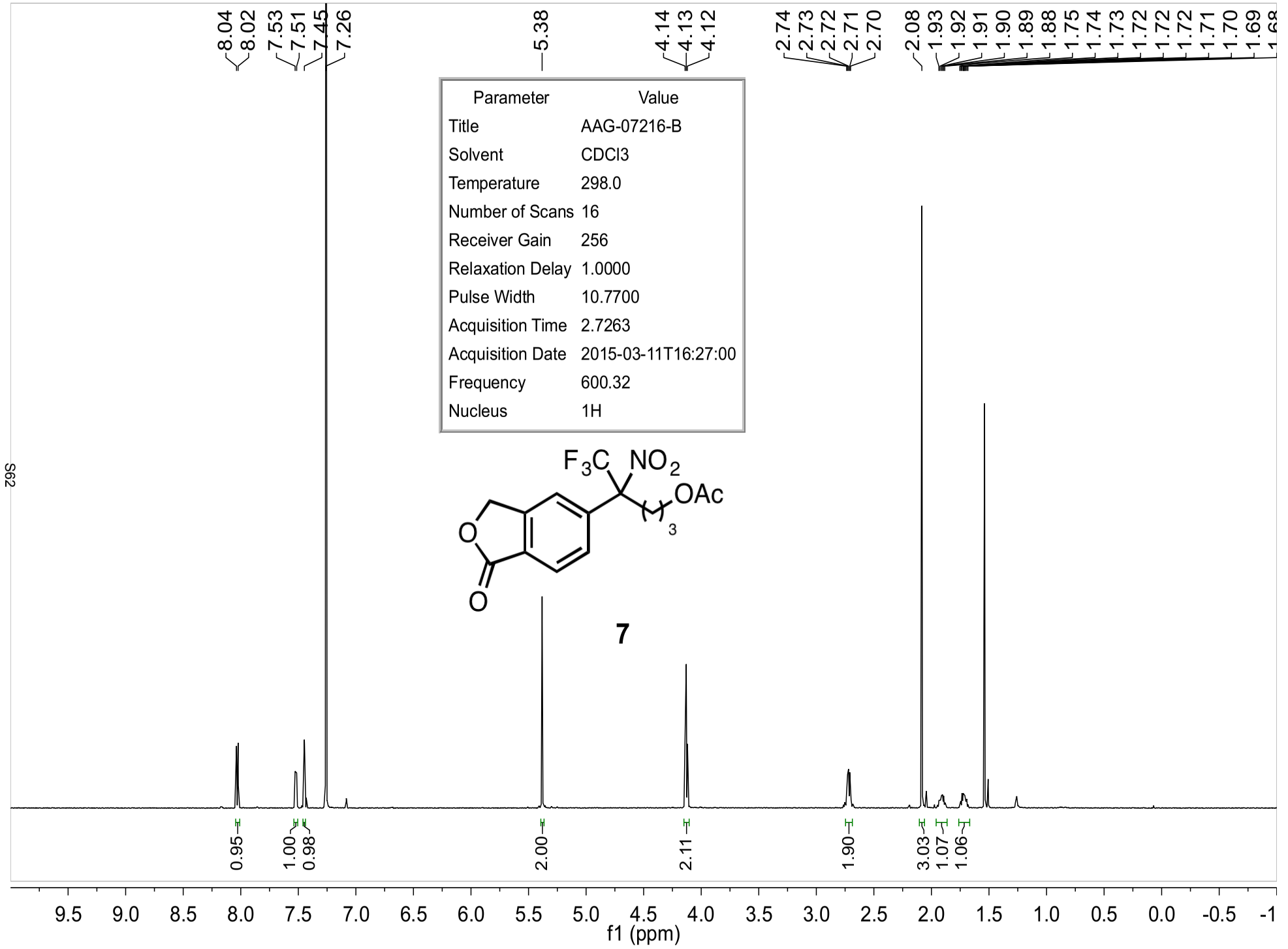
-68.67

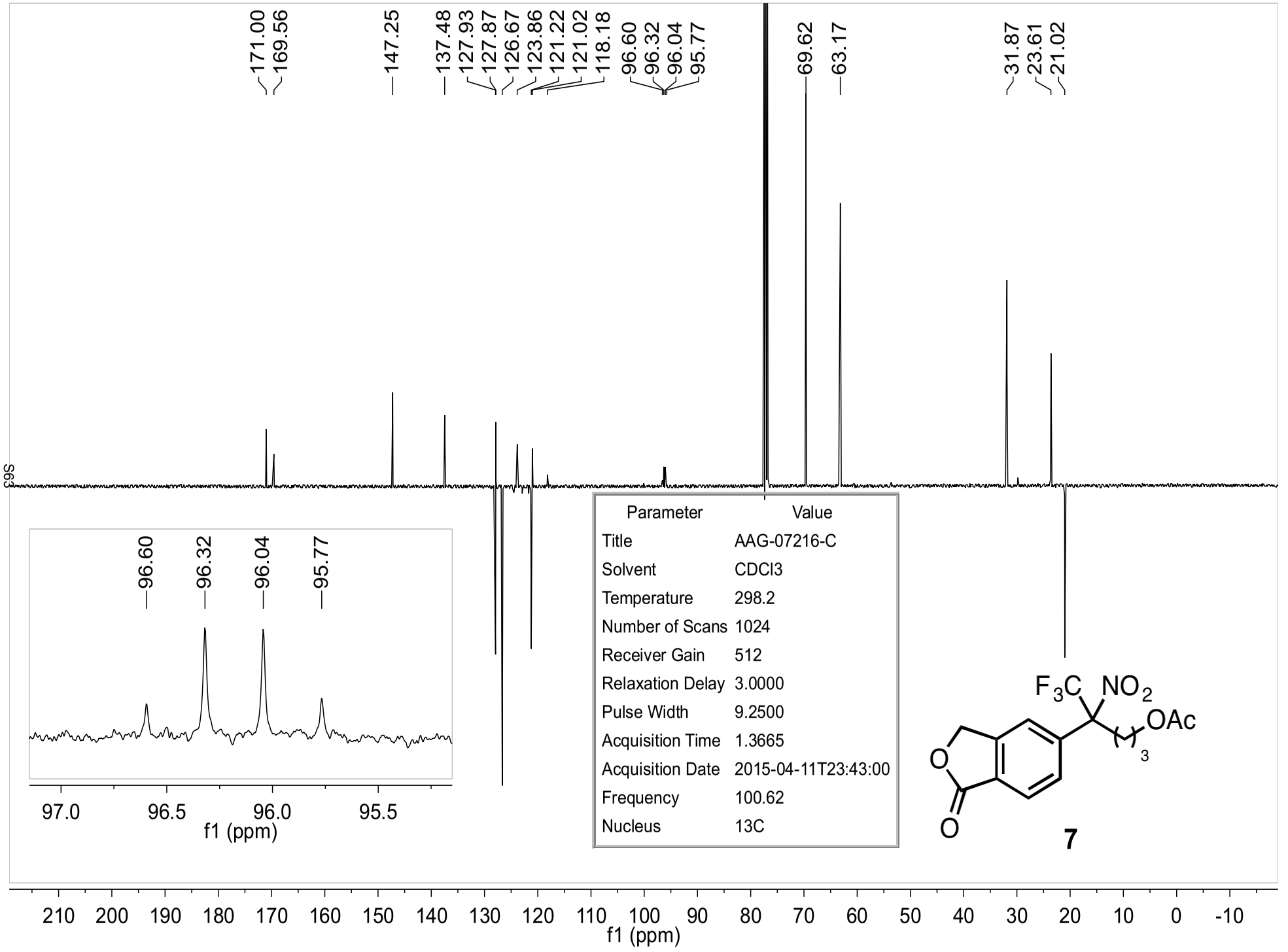
Parameter	Value
Title	DVR03106F33-70.4.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-06-09T17:42:00



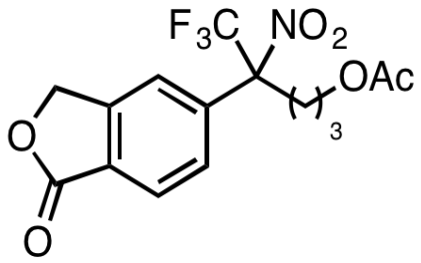
6



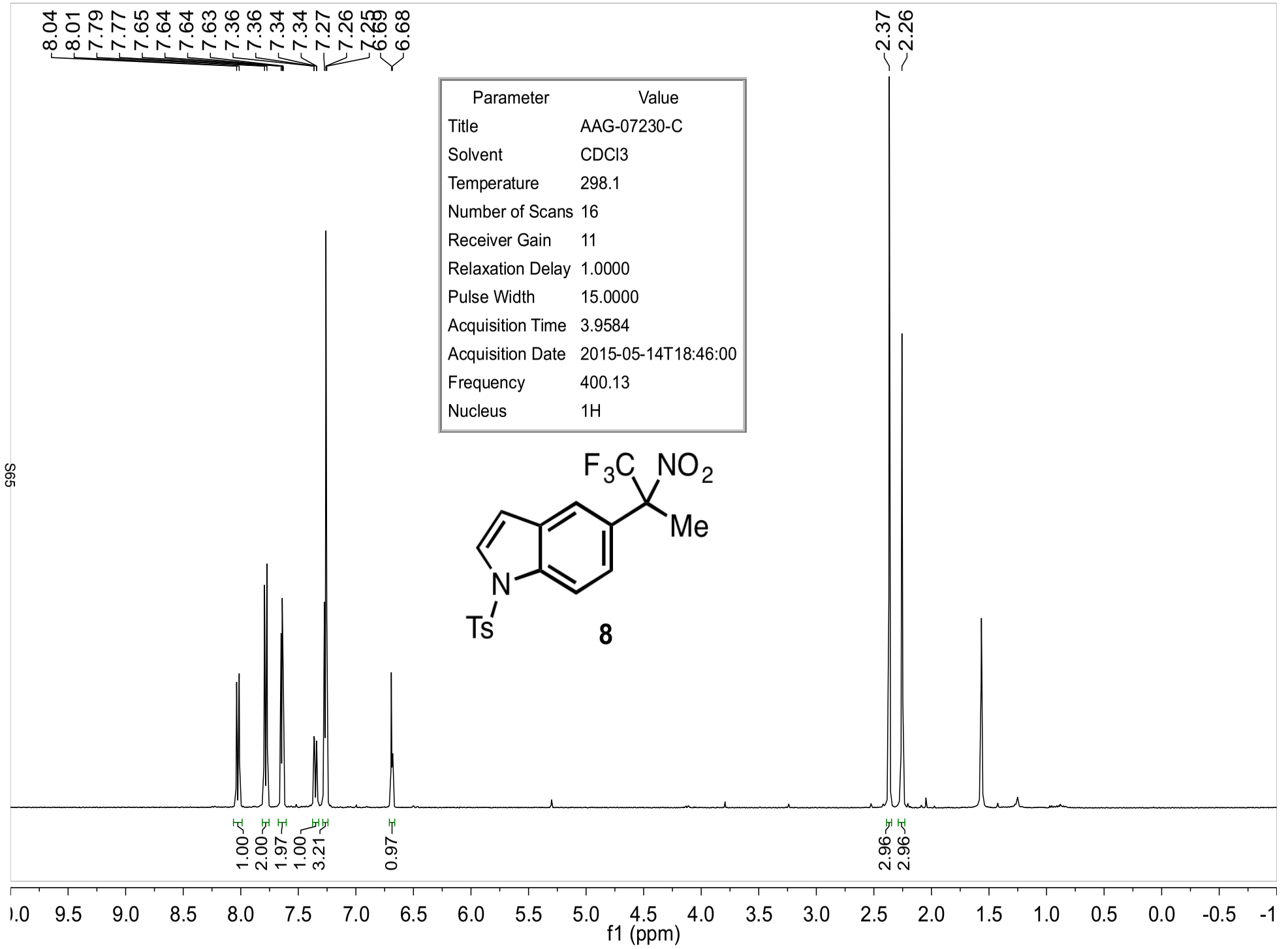

8.04
8.02
7.53
7.51
7.45
7.26
5.38
4.14
4.13
4.12
2.74
2.73
2.72
2.71
2.70
2.08
1.93
1.92
1.91
1.90
1.89
1.88
1.75
1.74
1.73
1.72
1.72
1.72
1.71
1.70
1.69
Parameter Value
Title AAG-07216-B
Solvent CDCl3
Temperature 298.0
Number of Scans 16
Receiver Gain 256
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-03-11T16:27:00
Frequency 600.32
Nucleus 1H
F3C NO2
OAc
3
O
O
7
S62
0.95
1.00
0.98
2.00
2.11
1.90
3.03
1.07
1.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

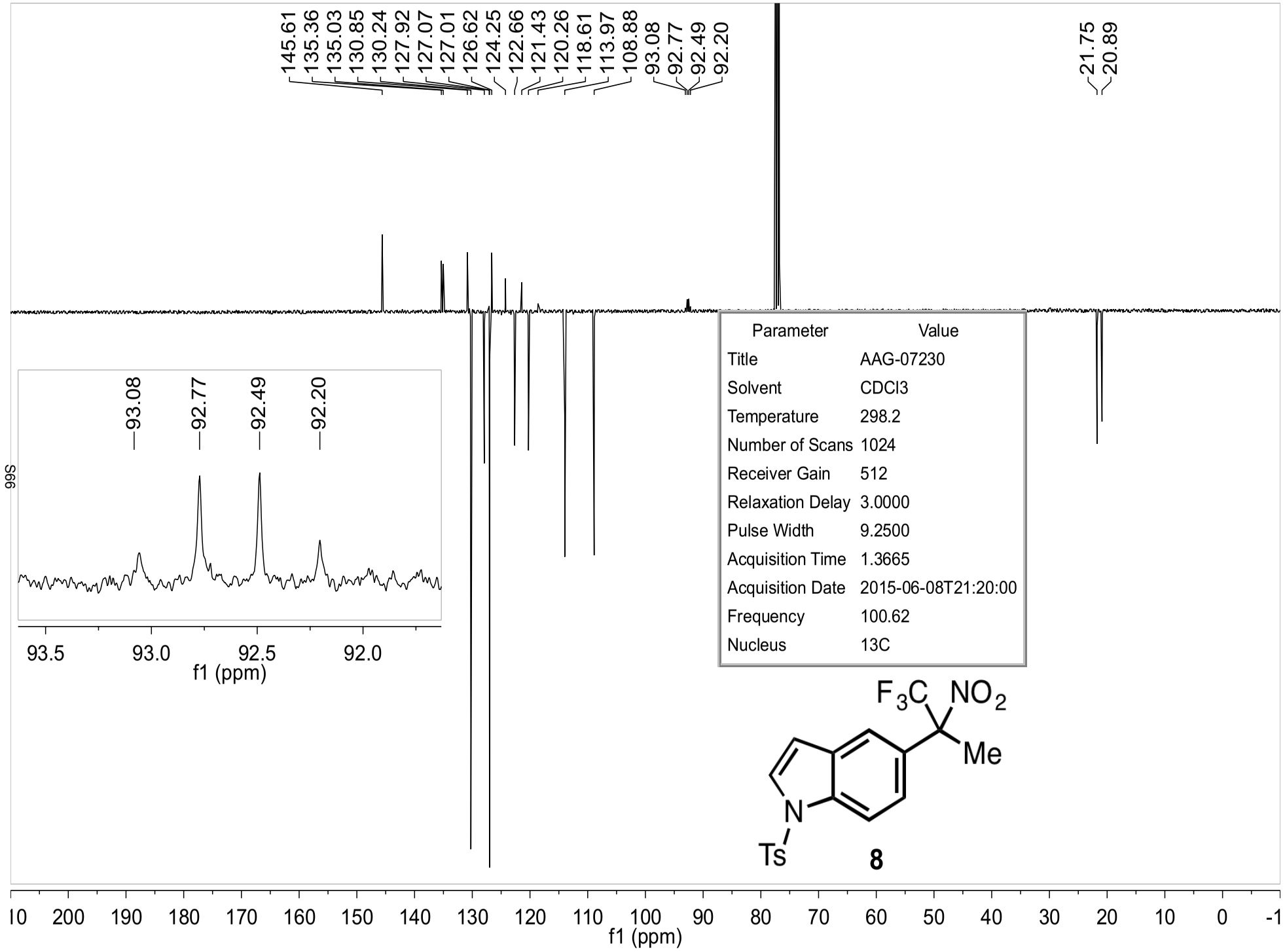

171.00
169.56
147.25
137.48
127.93
127.87
126.67
123.86
121.22
121.02
118.18
96.60
96.32
96.04
95.77
69.62
63.17
31.87
23.61
21.02
S63
96.60
96.32
96.04
95.77
97.0
96.5
96.0
95.5
f1 (ppm)
Parameter Value
Title AAG-07216-C
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-04-11T23:43:00
Frequency 100.62
Nucleus 13C
F3C
NO2
OAc
3
O
O
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
Title	AAG-07216-B
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-03-11T16:30:00
Frequency	564.81
Nucleus	19F

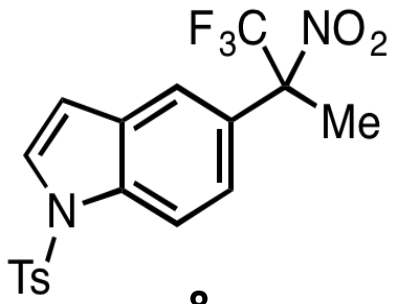


7

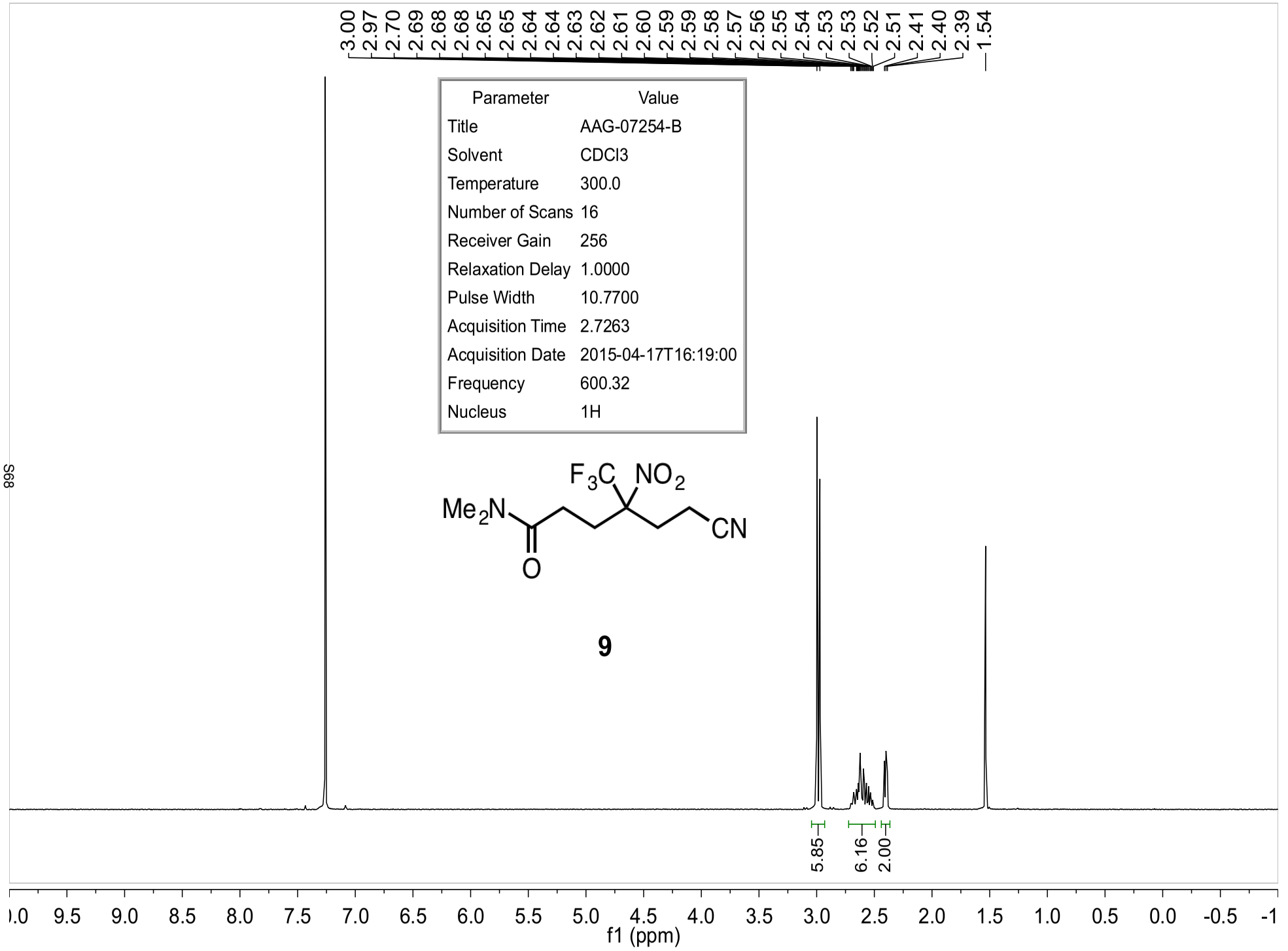

8.04
8.01
7.79
7.77
7.65
7.64
7.64
7.63
7.36
7.36
7.34
7.34
7.27
7.26
7.25
6.69
6.68
2.37
2.26
S65
Parameter Value
Title AAG-07230-C
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-05-14T18:46:00
Frequency 400.13
Nucleus 1H
F3C
NO2
Me
N
Ts
8
1.00
2.00
1.97
1.00
3.21
0.97
2.96
2.96
f1 (ppm)

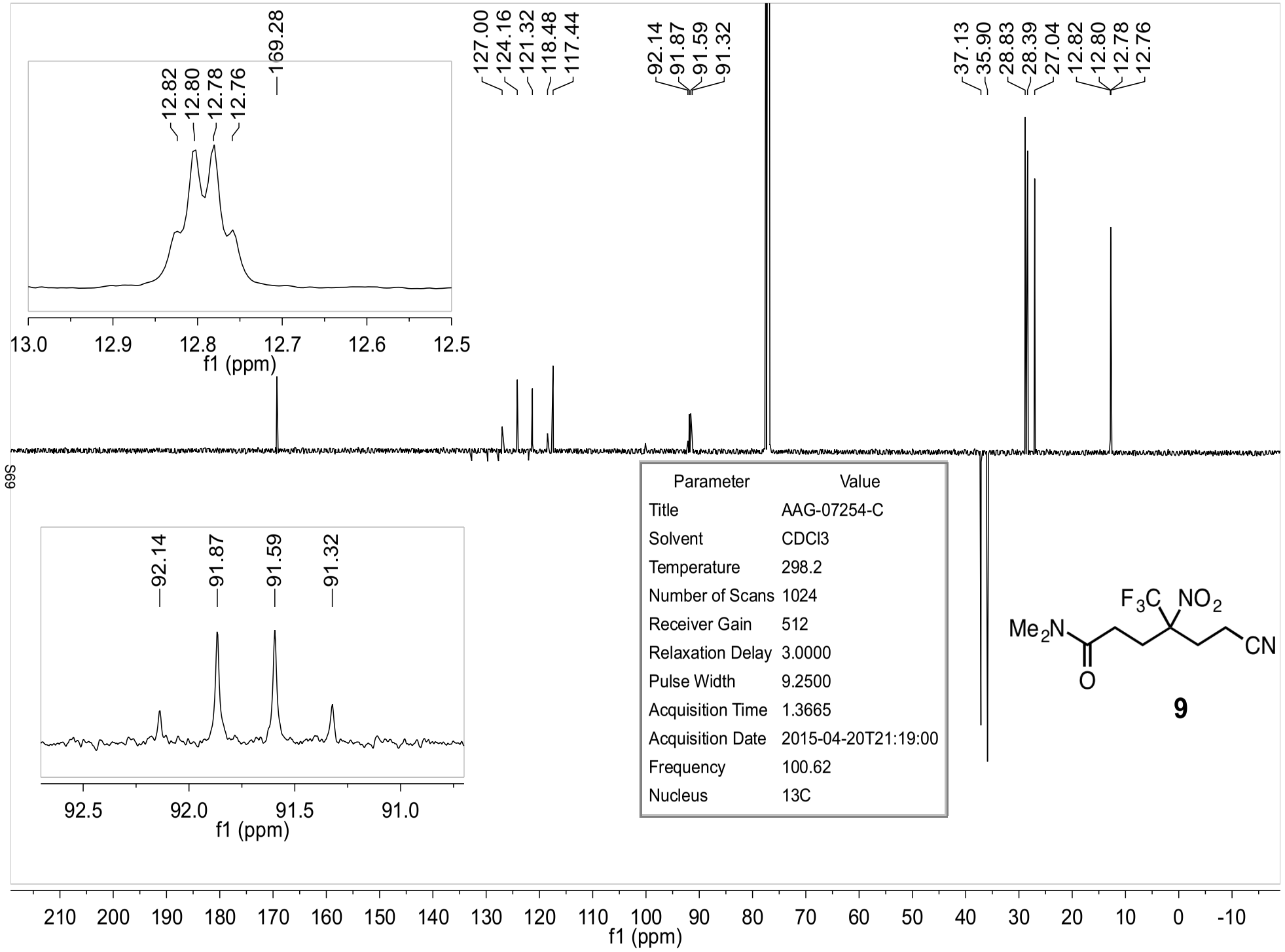

145.61
135.36
135.03
130.85
130.24
127.92
127.07
127.01
126.62
124.25
122.66
121.43
120.26
118.61
113.97
108.88
93.08
92.77
92.49
92.20
21.75
20.89
93.08
92.77
92.49
92.20
93.5
93.0
92.5
92.0
f1 (ppm)
Parameter Value
Title AAG-07230
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-06-08T21:20:00
Frequency 100.62
Nucleus 13C
F3C
NO2
Me
N
Ts
8
f1 (ppm)

Parameter	Value
Title	AAG-07230-C
Solvent	CDCl3
Temperature	298.2
Number of Scans	16
Receiver Gain	1626
Relaxation Delay	2.0000
Pulse Width	15.0300
Acquisition Time	0.8717
Acquisition Date	2015-05-14T18:48:00
Frequency	376.46
Nucleus	19F

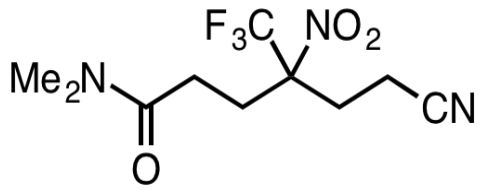


8

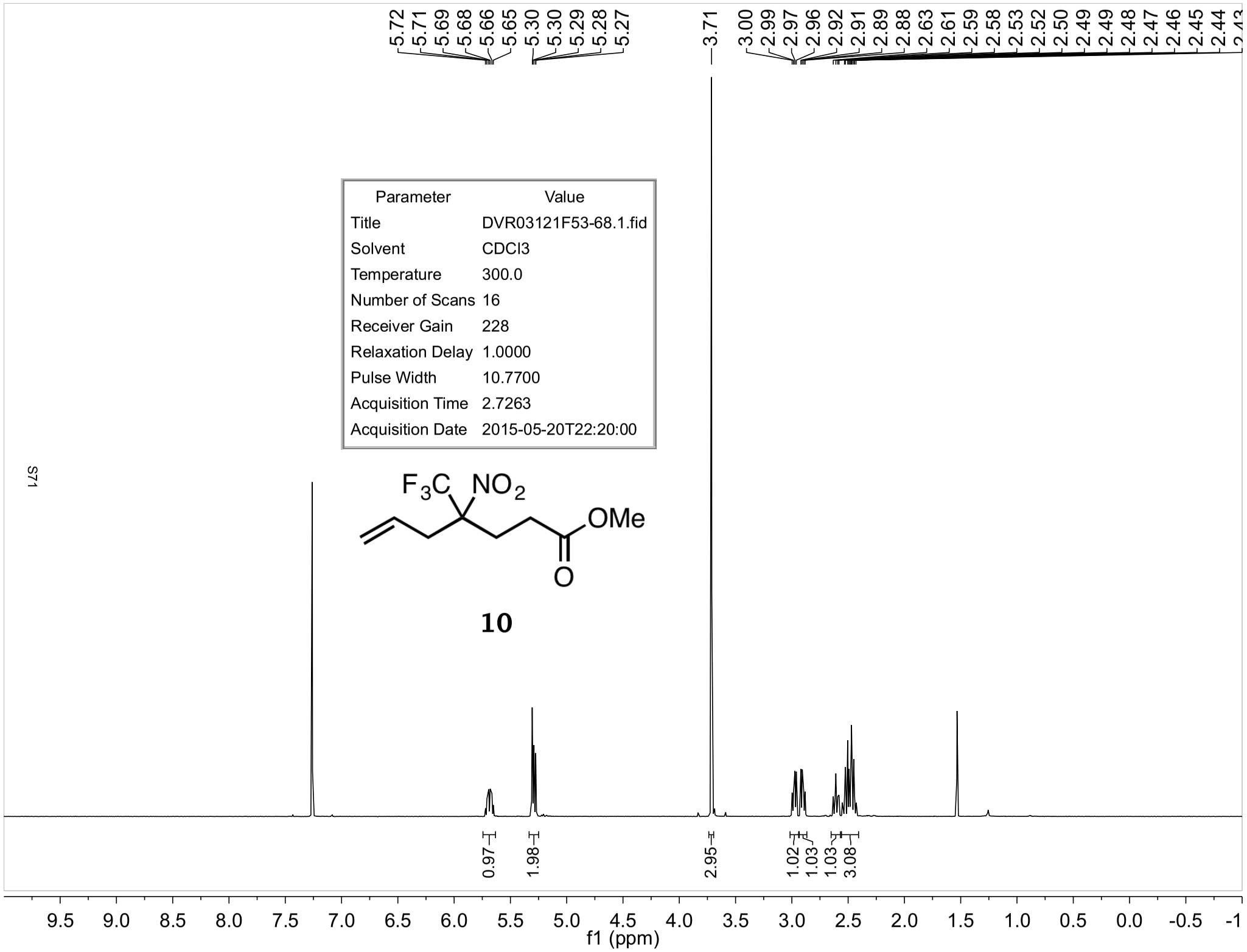

3.00 2.97 2.70 2.69 2.68 2.68 2.65 2.65 2.64 2.64 2.63 2.62 2.61 2.60 2.59 2.59 2.58 2.57 2.56 2.55 2.54 2.53 2.53 2.52 2.51 2.41 2.40 2.39 1.54
Parameter Value
Title AAG-07254-B
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 256
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-04-17T16:19:00
Frequency 600.32
Nucleus 1H
S68
F3C NO2
Me2N
CN
O
9
5.85
6.16
2.00
f1 (ppm)

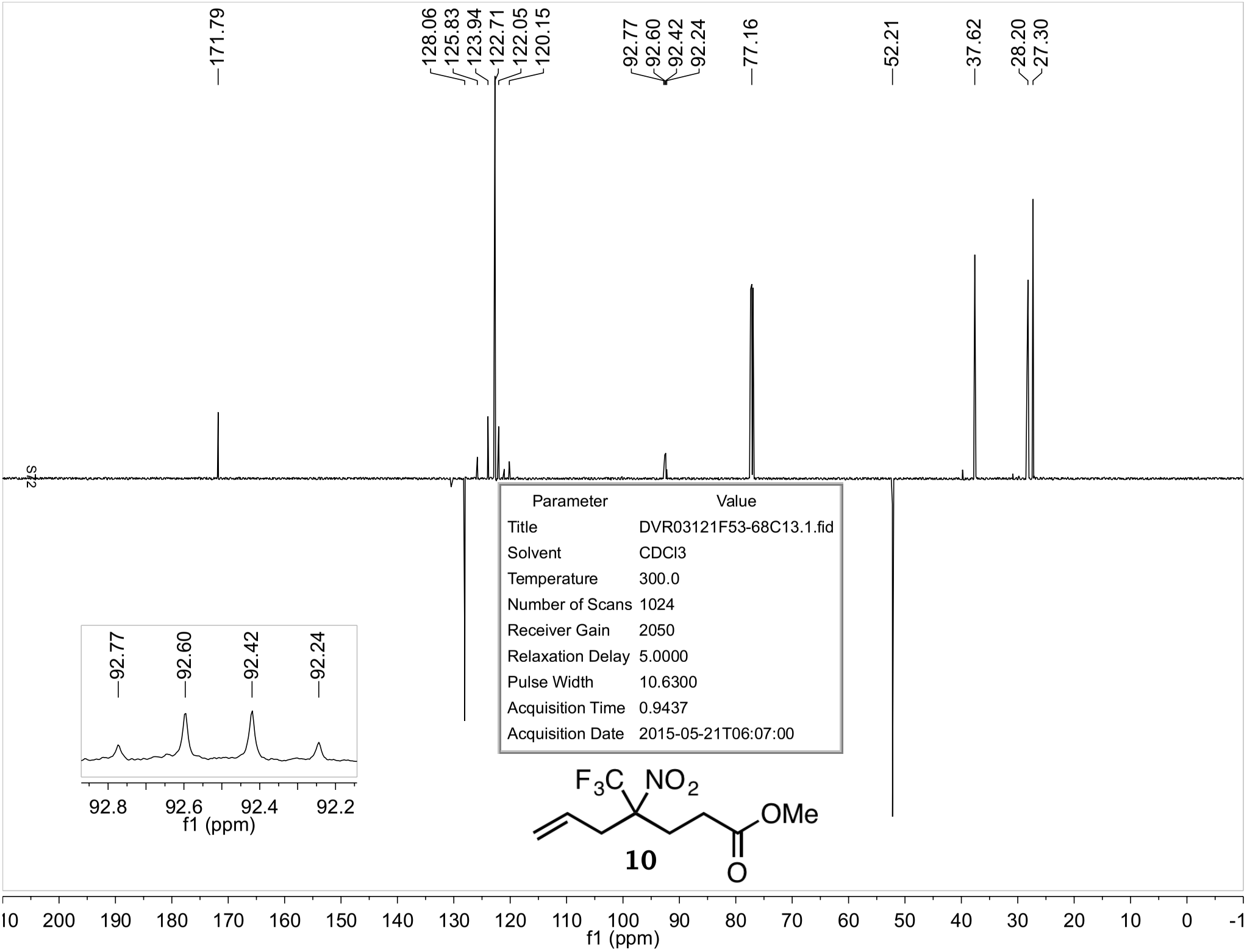

169.28
127.00
124.16
121.32
118.48
117.44
92.14
91.87
91.59
91.32
37.13
35.90
28.83
28.39
27.04
12.82
12.80
12.78
12.76
12.82
12.80
12.78
12.76
13.0
12.9
12.8
12.7
12.6
12.5
f1 (ppm)
92.14
91.87
91.59
91.32
92.5
92.0
91.5
91.0
f1 (ppm)
S69
Parameter Value
Title AAG-07254-C
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-04-20T21:19:00
Frequency 100.62
Nucleus 13C
F3C NO2
Me2N
CN
O
9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
Title	AAG-07254-B
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-04-16T18:22:00
Frequency	564.81
Nucleus	19F



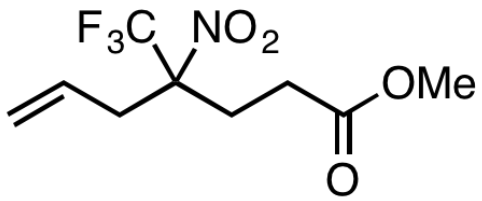
9


5.72 5.71 5.69 5.68 5.66 5.65 5.30 5.30 5.29 5.28 5.27
3.71
3.00 2.99 2.97 2.96 2.92 2.91 2.89 2.88 2.63 2.61 2.59 2.58 2.53 2.52 2.50 2.49 2.49 2.48 2.47 2.46 2.45 2.44
Parameter Value
Title DVR03121F53-68.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 228
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-05-20T22:20:00
S71
F3C NO2
OMe
O
10
0.97 1.98 2.95 1.02 1.03 1.03 3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


171.79
128.06
125.83
123.94
122.71
122.05
120.15
92.77
92.60
92.42
92.24
77.16
52.21
37.62
28.20
27.30
S12
Parameter Value
Title DVR03121F53-68C13.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-05-21T06:07:00
92.8
92.6
92.4
92.2
f1 (ppm)
F3C NO2
OMe
O
10
f1 (ppm)

-71.06

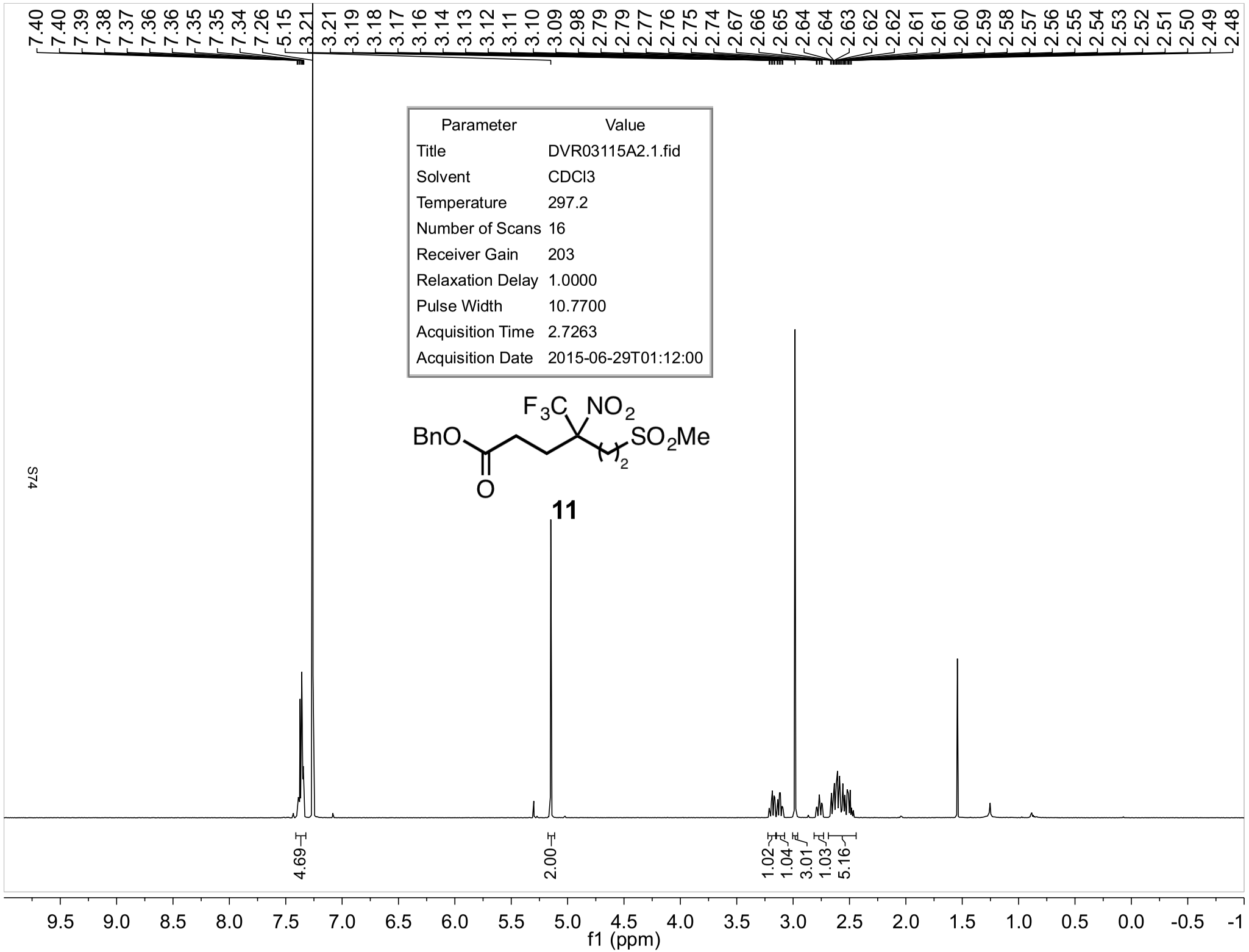
Parameter	Value
Title	DVR03121F53-68.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-05-20T22:22:00

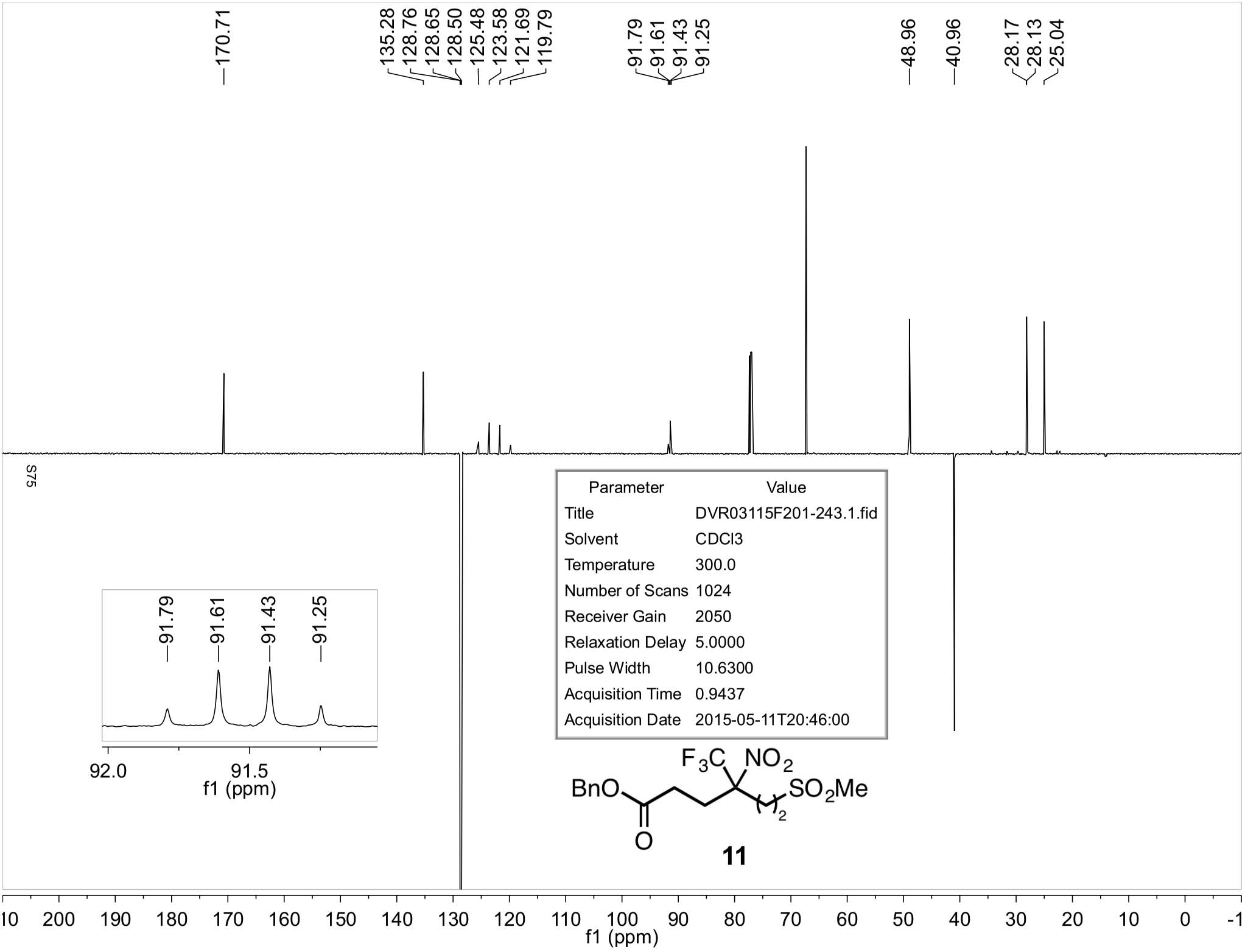


10

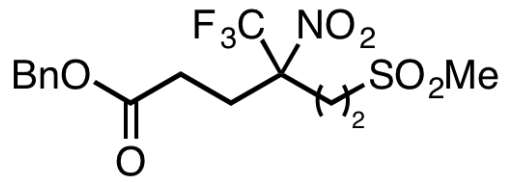
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95

f1 (ppm)

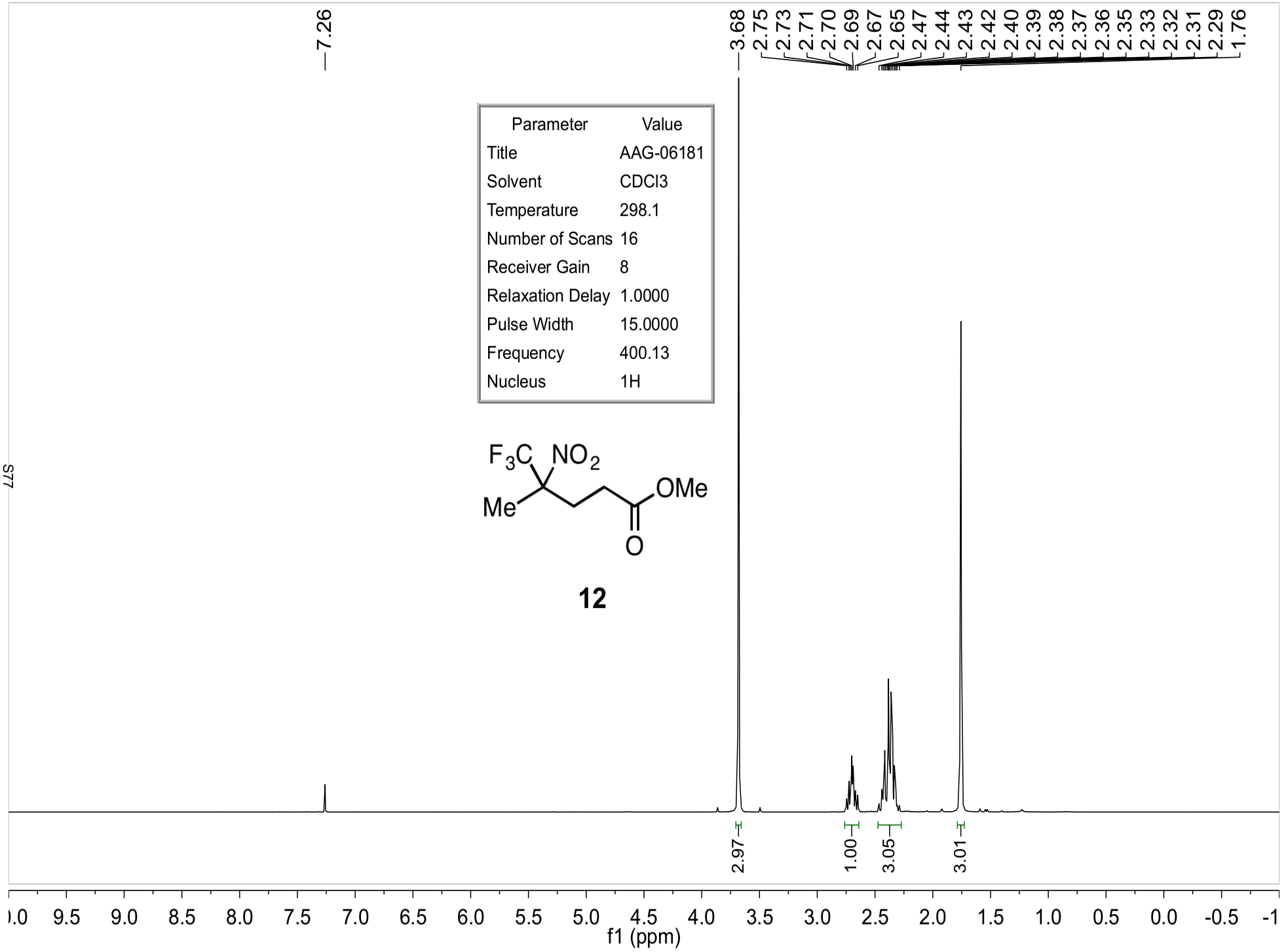

7.40 7.40 7.39 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.26 5.15 3.21 3.21 3.19 3.18 3.17 3.16 3.14 3.13 3.12 3.11 3.10 3.09 2.98 2.79 2.79 2.77 2.76 2.75 2.74 2.67 2.66 2.65 2.64 2.64 2.63 2.62 2.62 2.61 2.61 2.60 2.59 2.58 2.57 2.56 2.55 2.54 2.53 2.52 2.51 2.50 2.49 2.48
Parameter Value
Title DVR03115A2.1.fid
Solvent CDCl3
Temperature 297.2
Number of Scans 16
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-29T01:12:00
F3C NO2
BnO
SO2Me
2
O
11
S74
4.69
2.00
1.02
1.04
3.01
1.03
5.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

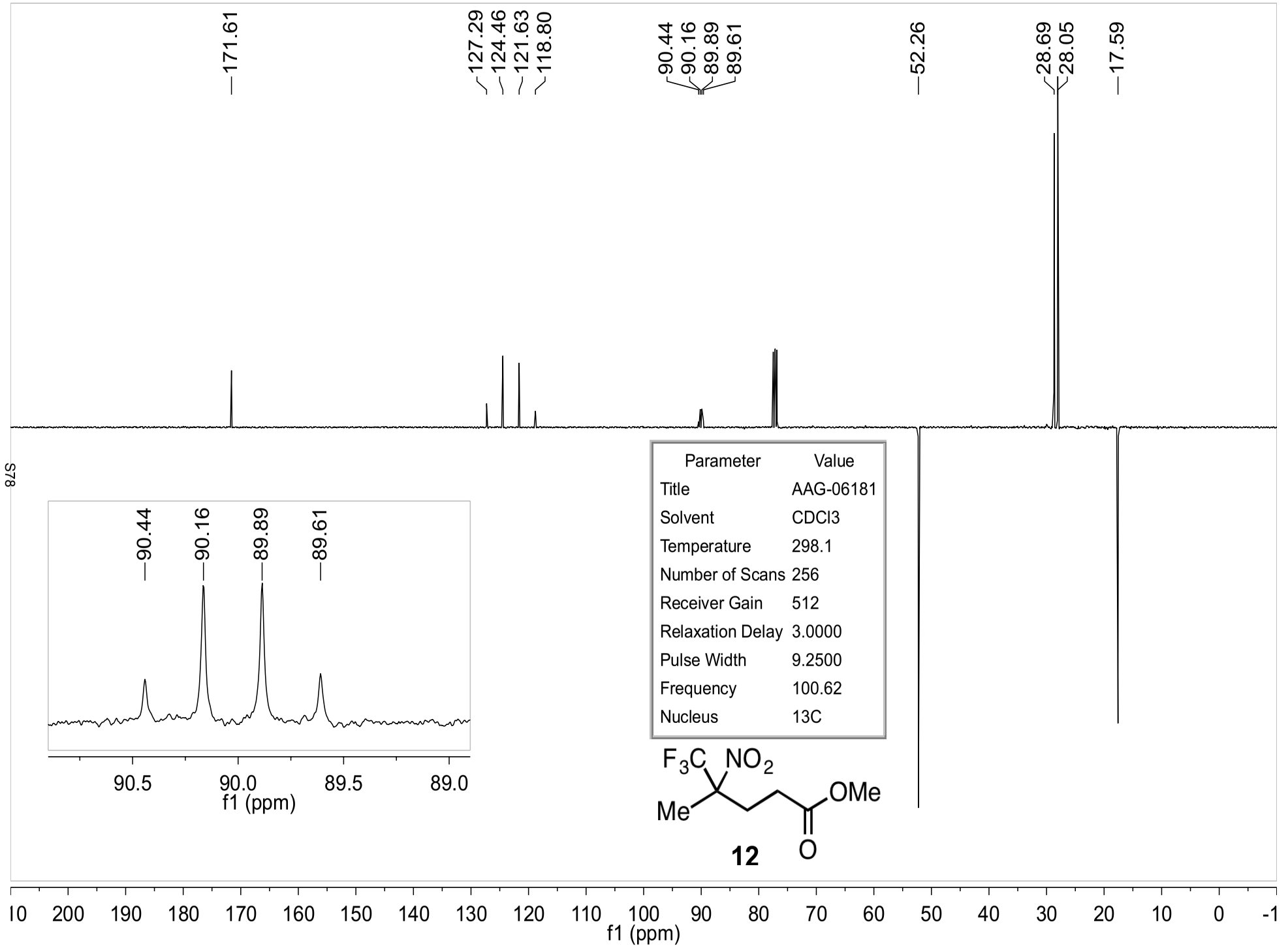

170.71
135.28
128.76
128.65
128.50
125.48
123.58
121.69
119.79
91.79
91.61
91.43
91.25
48.96
40.96
28.17
28.13
25.04
S75
91.79
91.61
91.43
91.25
92.0
91.5
f1 (ppm)
Parameter Value
Title DVR03115F201-243.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-05-11T20:46:00
F3C NO2
BnO
SO2Me
O
11
f1 (ppm)

Parameter	Value
Title	DVR03115F201-240.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-05-11T12:38:00

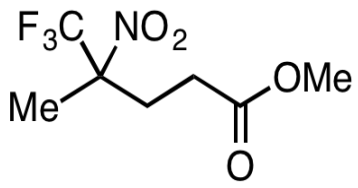


11

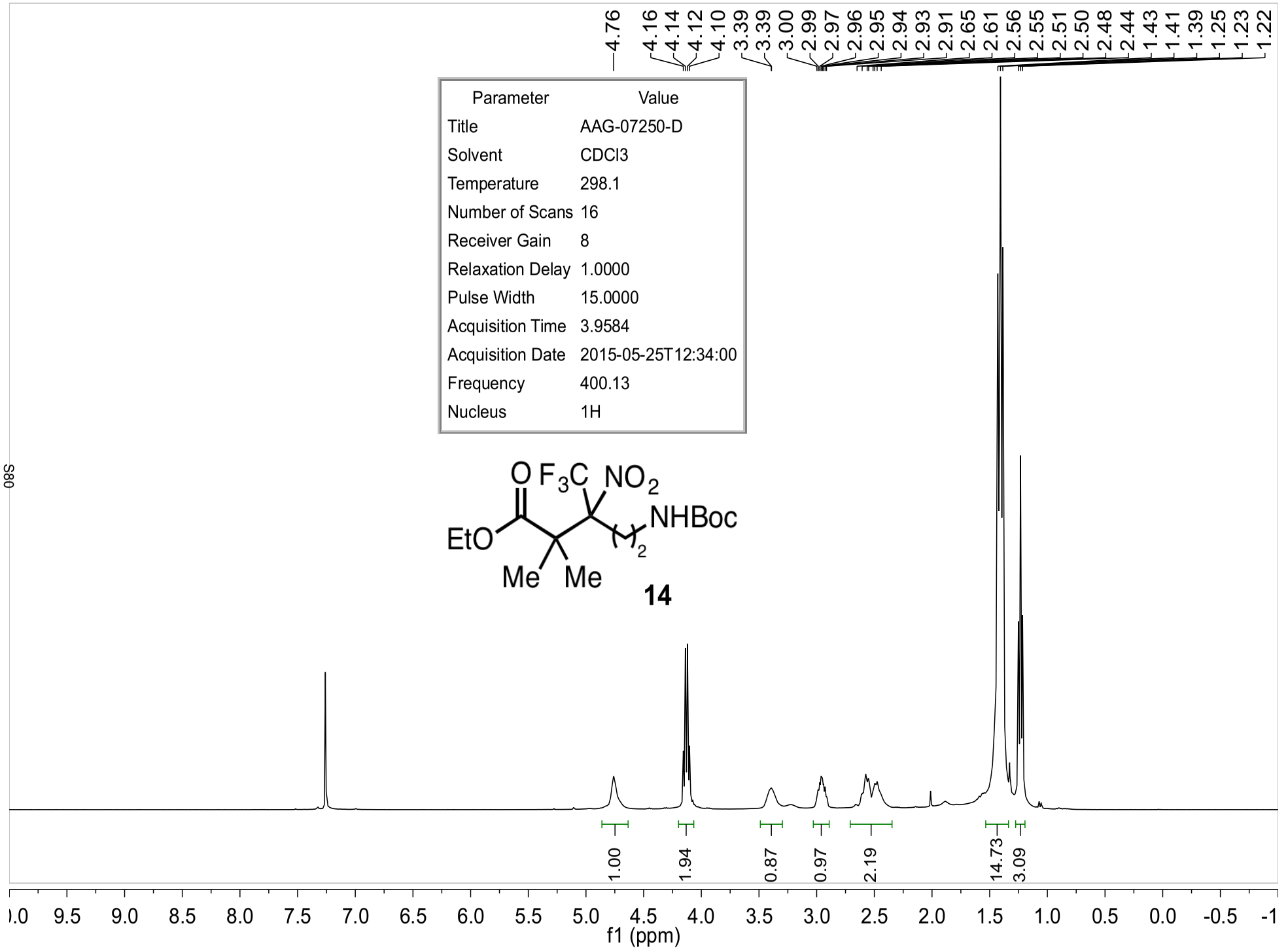

7.26
3.68
2.75
2.73
2.71
2.70
2.69
2.67
2.65
2.47
2.44
2.43
2.42
2.40
2.39
2.38
2.37
2.36
2.35
2.33
2.32
2.31
2.29
1.76
Parameter Value
Title AAG-06181
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
F3C NO2
Me
OMe
O
12
2.97
1.00
3.05
3.01
S77
f1 (ppm)

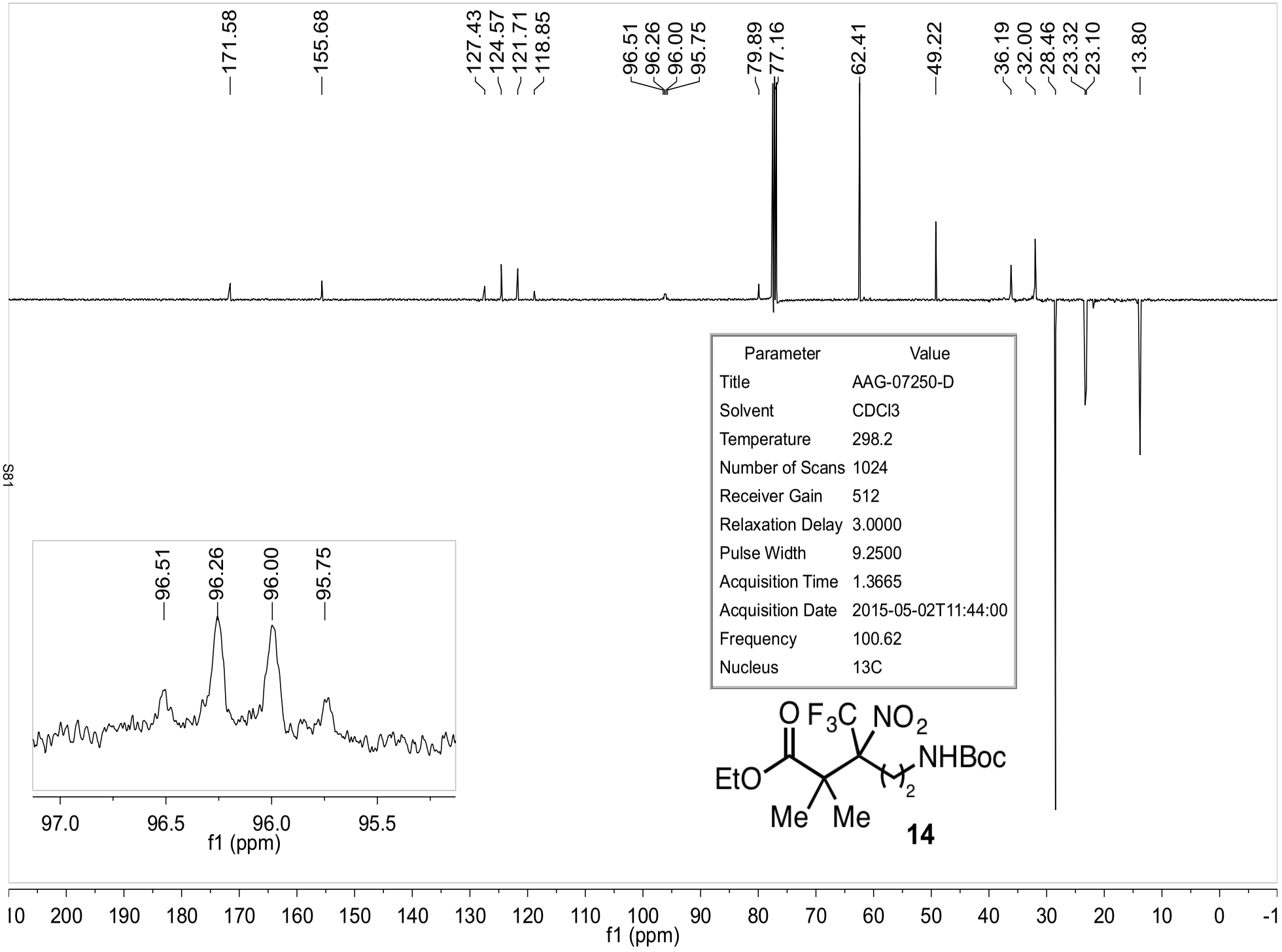

171.61
127.29
124.46
121.63
118.80
90.44
90.16
89.89
89.61
52.26
28.69
28.05
17.59
S78
90.44
90.16
89.89
89.61
90.5
90.0
89.5
89.0
f1 (ppm)
Parameter Value
Title AAG-06181
Solvent CDCl3
Temperature 298.1
Number of Scans 256
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
F3C NO2
Me
OMe
O
12
f1 (ppm)

Parameter	Value
Title	AAG-06181-B
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Receiver Gain	322
Relaxation Delay	3.0000
Pulse Width	11.6200
Frequency	564.81
Nucleus	19F

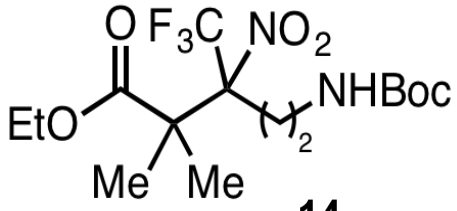


12

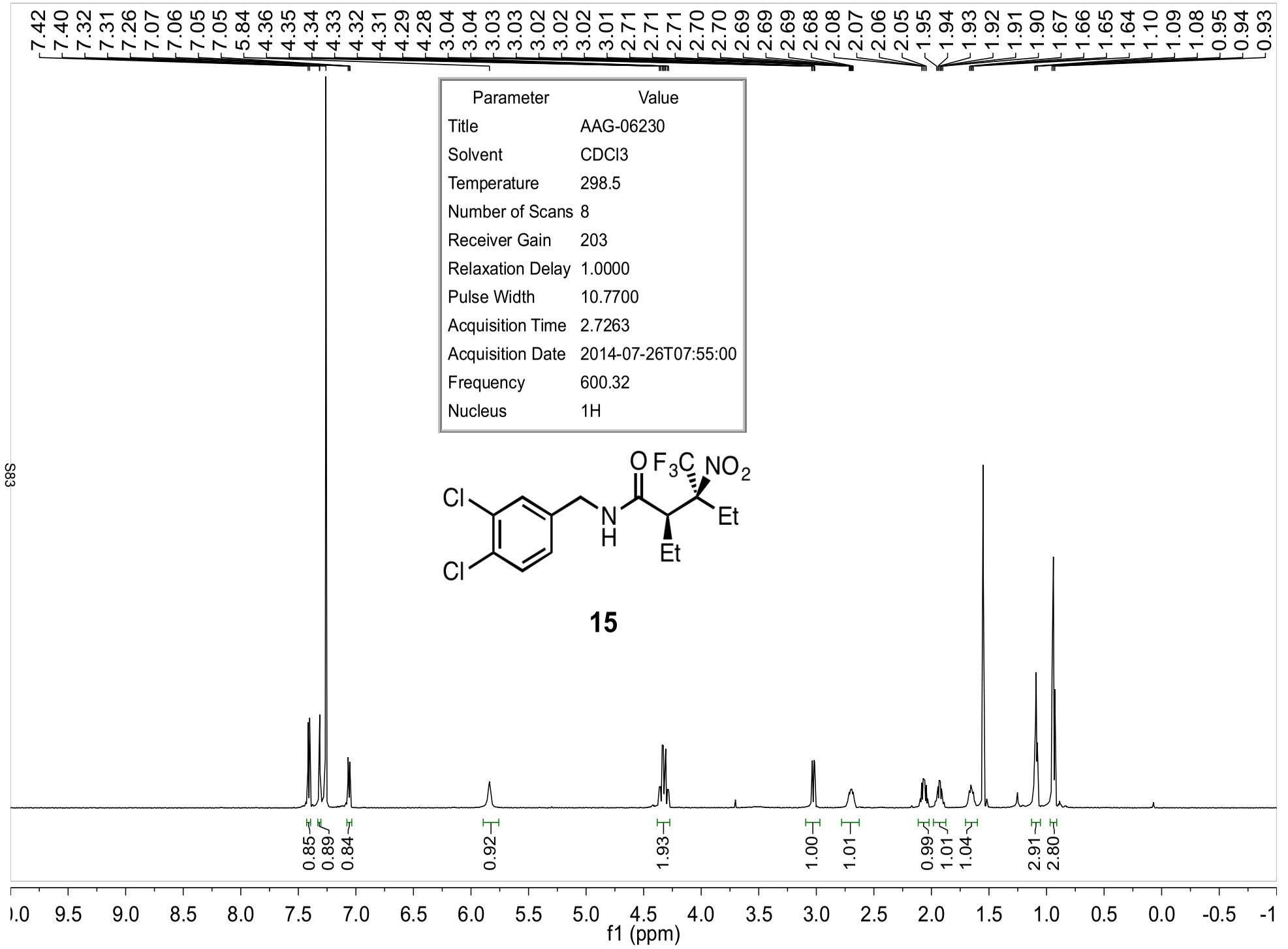

4.76
4.16
4.14
4.12
4.10
3.39
3.39
3.00
2.99
2.97
2.96
2.95
2.94
2.93
2.91
2.65
2.61
2.56
2.55
2.51
2.50
2.48
2.44
1.43
1.41
1.39
1.25
1.23
1.22
Parameter Value
Title AAG-07250-D
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-05-25T12:34:00
Frequency 400.13
Nucleus 1H
S80
O
F3C
NO2
NHBoc
EtO
2
Me
Me
14
1.00
1.94
0.87
0.97
2.19
14.73
3.09
f1 (ppm)

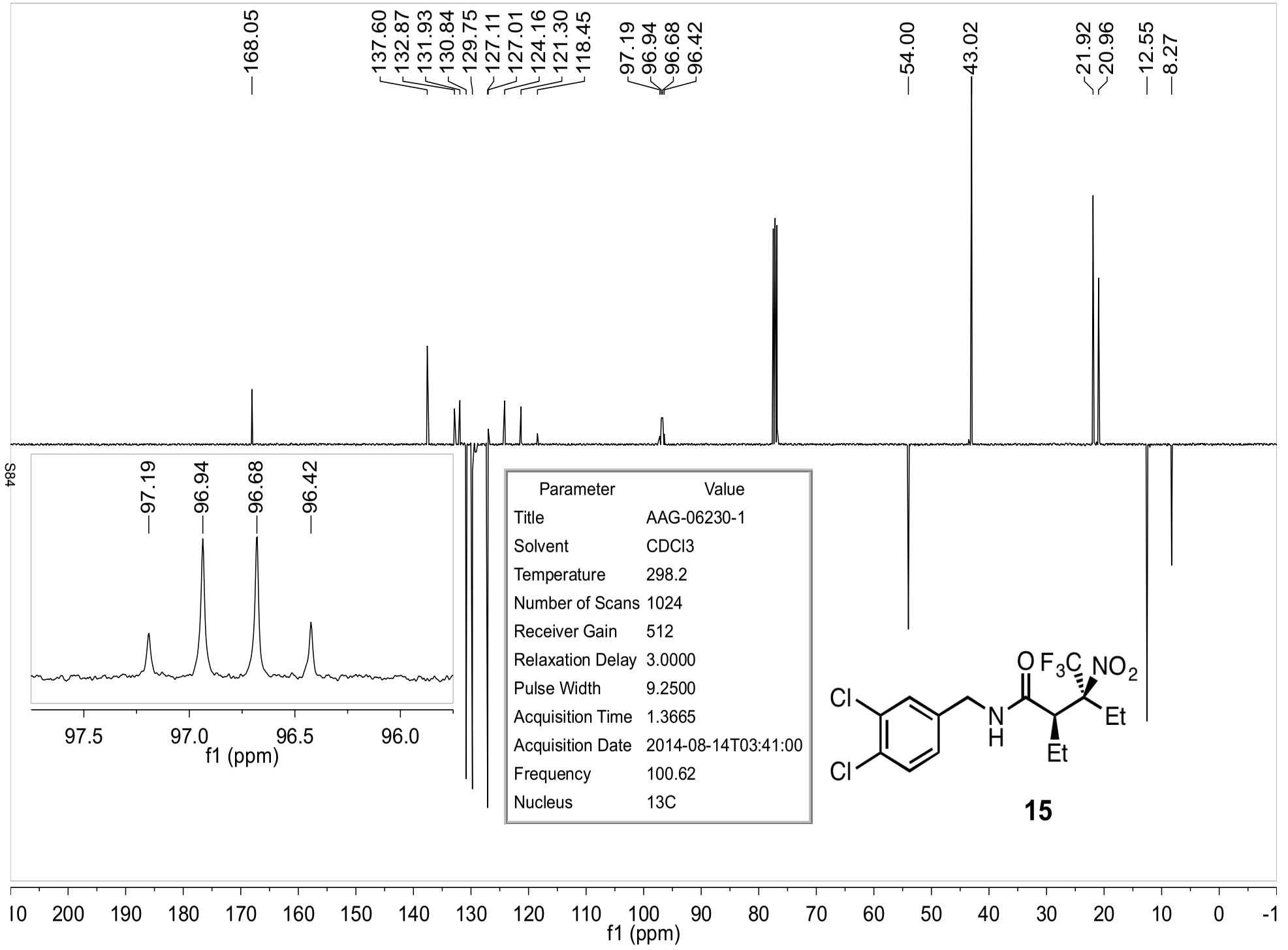

171.58
155.68
127.43
124.57
121.71
118.85
96.51
96.26
96.00
95.75
79.89
77.16
62.41
49.22
36.19
32.00
28.46
23.32
23.10
13.80
Parameter Value
Title AAG-07250-D
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-05-02T11:44:00
Frequency 100.62
Nucleus 13C
O F3C NO2
EtO
NHBoc
2
Me Me
14
96.51
96.26
96.00
95.75
97.0
96.5
96.0
95.5
f1 (ppm)
S81
f1 (ppm)

Parameter	Value
Title	AAG-07250-D
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-05-01T11:43:00
Frequency	564.81
Nucleus	19F

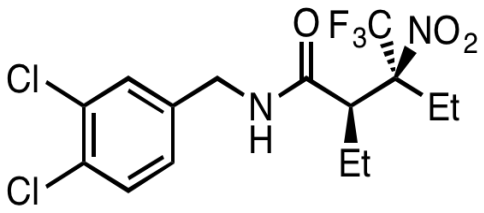


14

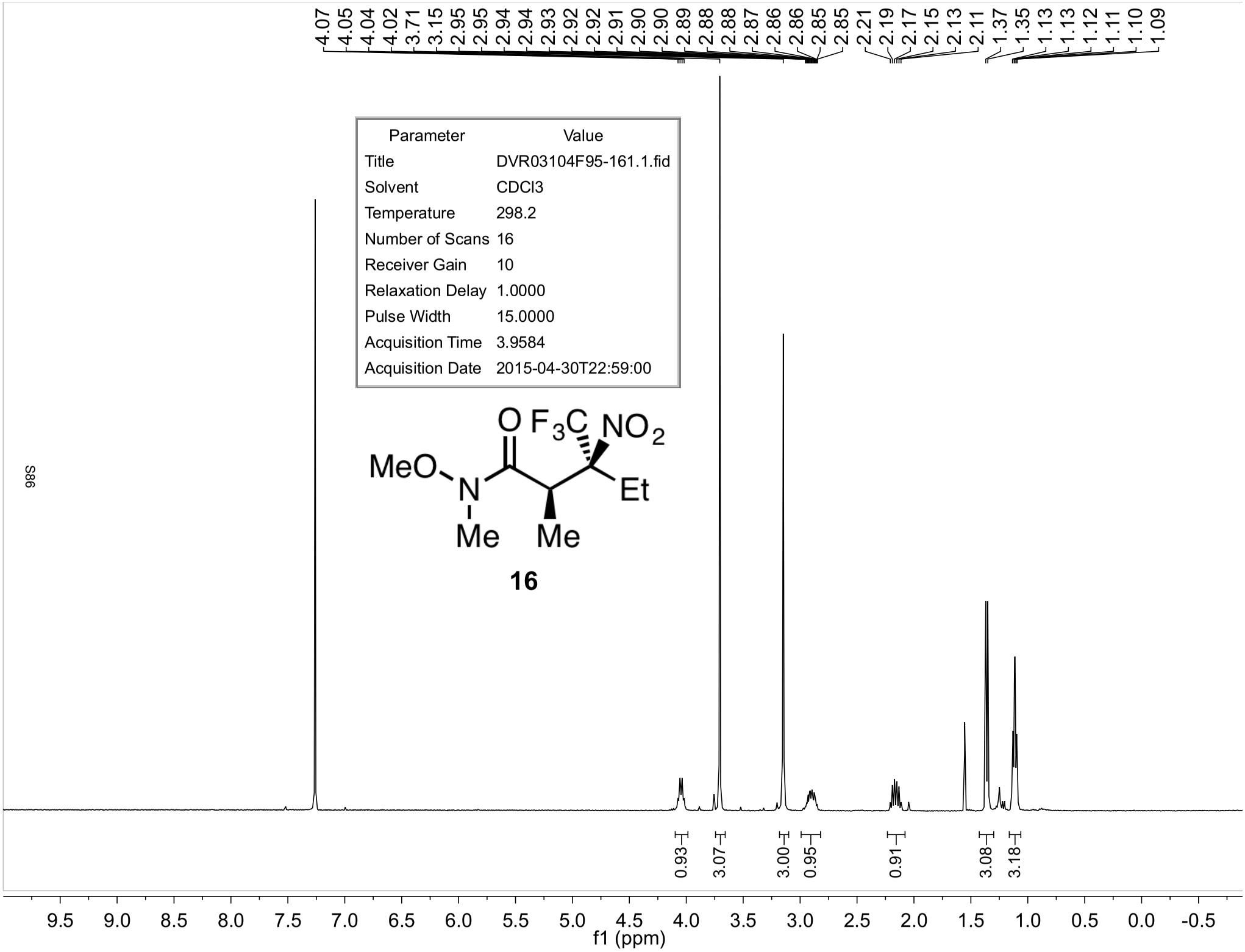

7.42 7.40 7.32 7.31 7.26 7.07 7.06 7.05 7.05 5.84 4.36 4.35 4.34 4.33 4.32 4.31 4.29 4.28 3.04 3.04 3.03 3.03 3.02 3.02 3.02 3.01 2.71 2.71 2.71 2.70 2.70 2.69 2.69 2.69 2.68 2.08 2.07 2.06 2.05 1.95 1.94 1.93 1.92 1.91 1.90 1.67 1.66 1.65 1.64 1.10 1.09 1.08 0.95 0.94 0.93
Parameter Value
Title AAG-06230
Solvent CDCl3
Temperature 298.5
Number of Scans 8
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2014-07-26T07:55:00
Frequency 600.32
Nucleus 1H
S83
Cl
Cl
N
H
O
F3C
NO2
Et
Et
15
0.85
0.89
0.84
0.92
1.93
1.00
1.01
0.99
1.01
1.04
2.91
2.80
f1 (ppm)

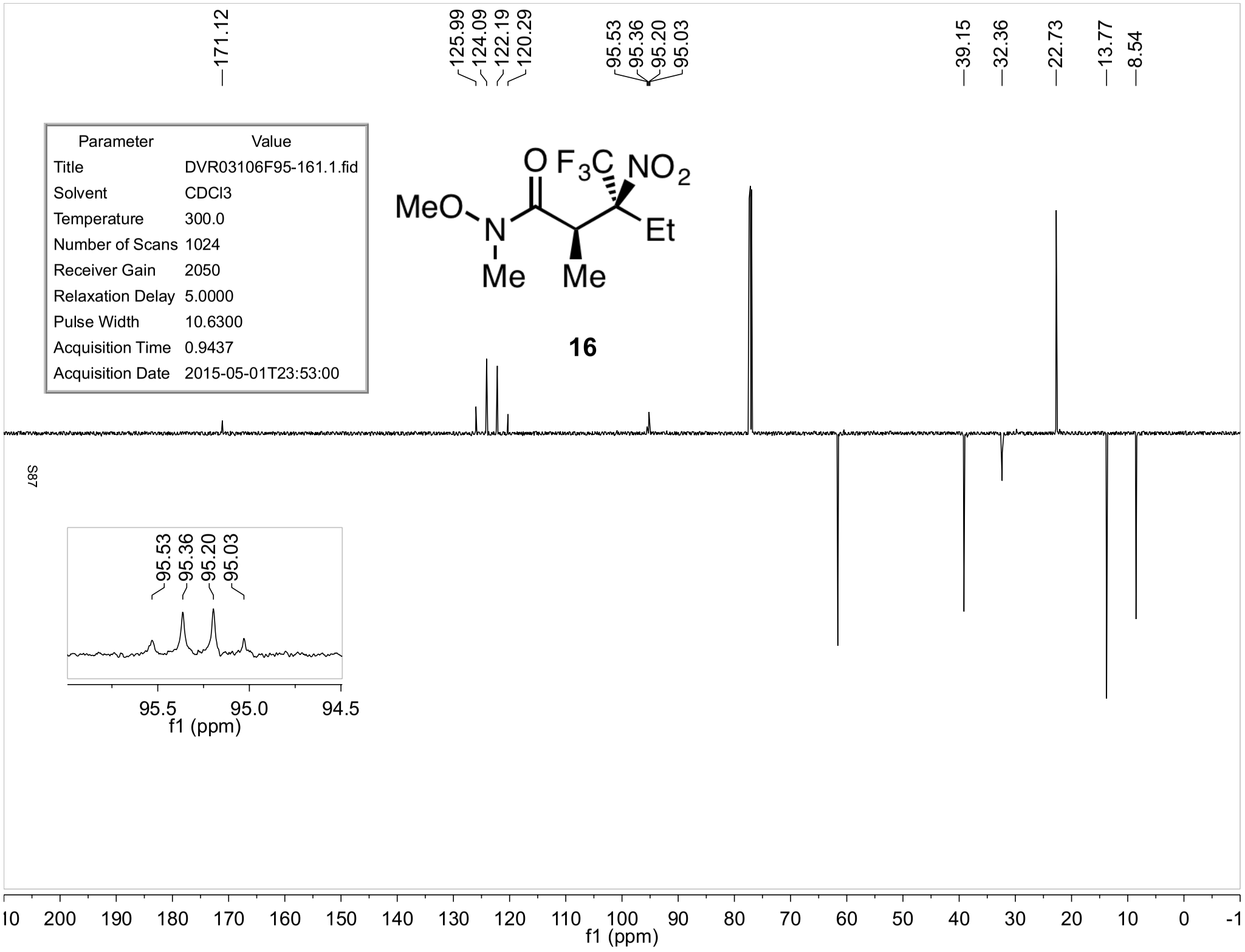

168.05
137.60
132.87
131.93
130.84
129.75
127.11
127.01
124.16
121.30
118.45
97.19
96.94
96.68
96.42
54.00
43.02
21.92
20.96
12.55
8.27
S84
97.19
96.94
96.68
96.42
97.5
97.0
96.5
96.0
f1 (ppm)
Parameter Value
Title AAG-06230-1
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2014-08-14T03:41:00
Frequency 100.62
Nucleus 13C
Cl
Cl
N
H
O
F3C
NO2
Et
Et
15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

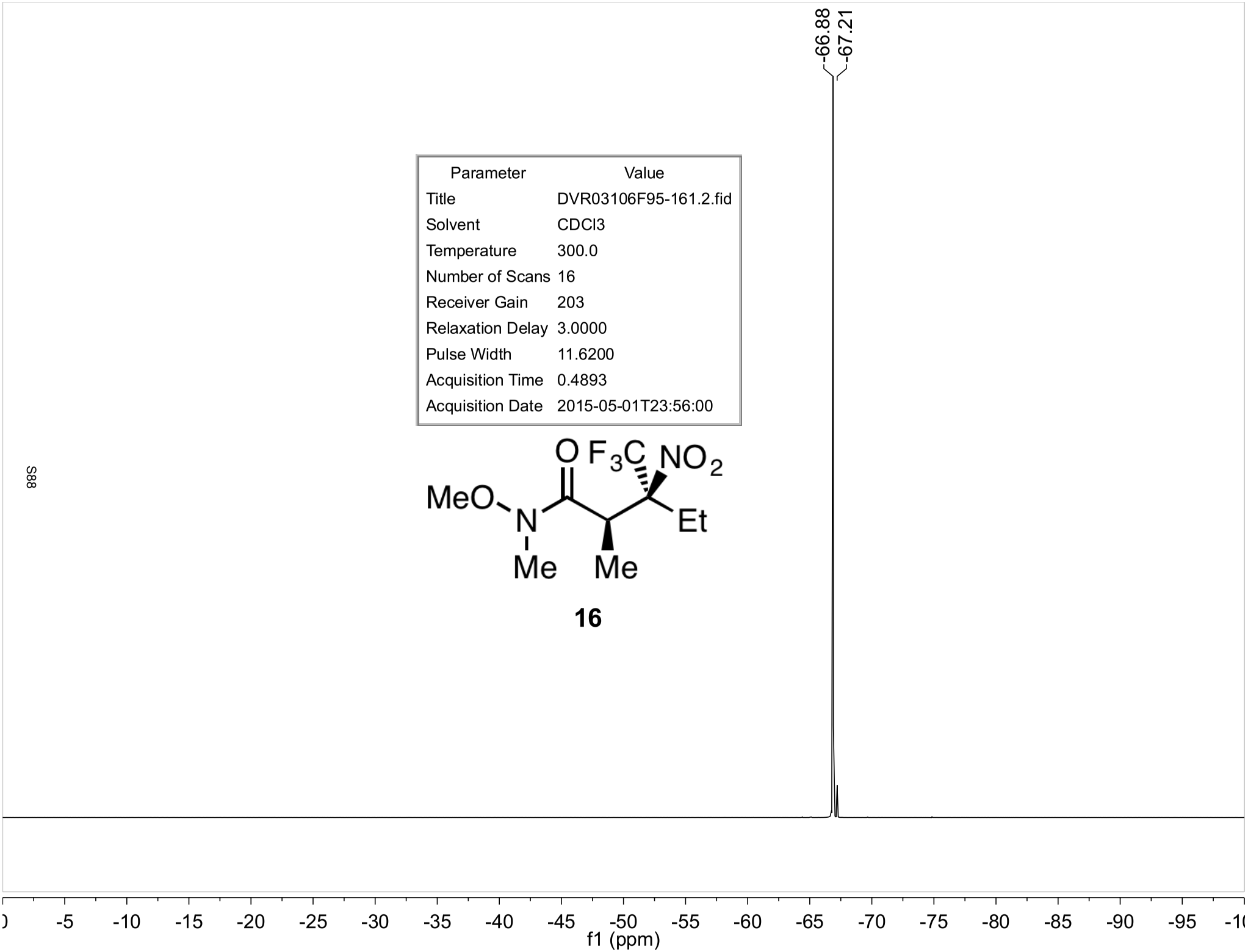
Parameter	Value
Title	AAG-06230
Solvent	CDCl3
Temperature	298.4
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2014-07-26T07:58:00
Frequency	564.81
Nucleus	19F



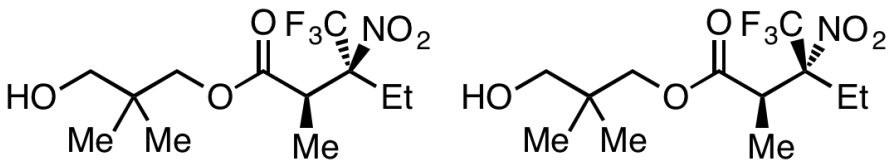
15


4.07 4.05 4.04 4.02 3.71 3.15 2.95 2.95 2.94 2.94 2.93 2.92 2.92 2.91 2.90 2.90 2.89 2.88 2.88 2.87 2.86 2.86 2.85 2.85 2.21 2.19 2.17 2.15 2.13 2.11 1.37 1.35 1.13 1.13 1.12 1.11 1.10 1.09
Parameter Value
Title DVR03104F95-161.1.fid
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 10
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-04-30T22:59:00
O F3C NO2
MeO N Et
Me Me
16
S86
0.93 3.07 3.00 0.95 0.91 3.08 3.18
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.12
125.99
124.09
122.19
120.29
95.53
95.36
95.20
95.03
39.15
32.36
22.73
13.77
8.54
Parameter Value
Title DVR03106F95-161.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-05-01T23:53:00
MeO
N
Me
O
F3C
NO2
Et
Me
16
S87
95.53
95.36
95.20
95.03
95.5
95.0
94.5
f1 (ppm)
f1 (ppm)

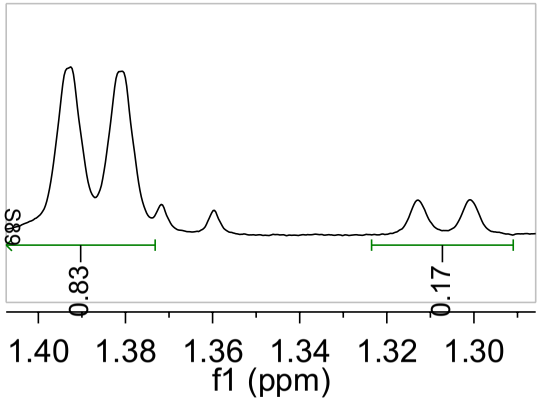

-66.88
-67.21
S88
Parameter Value
Title DVR03106F95-161.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 203
Relaxation Delay 3.0000
Pulse Width 11.6200
Acquisition Time 0.4893
Acquisition Date 2015-05-01T23:56:00
O
F3C
NO2
MeO
N
Et
Me
Me
16
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)

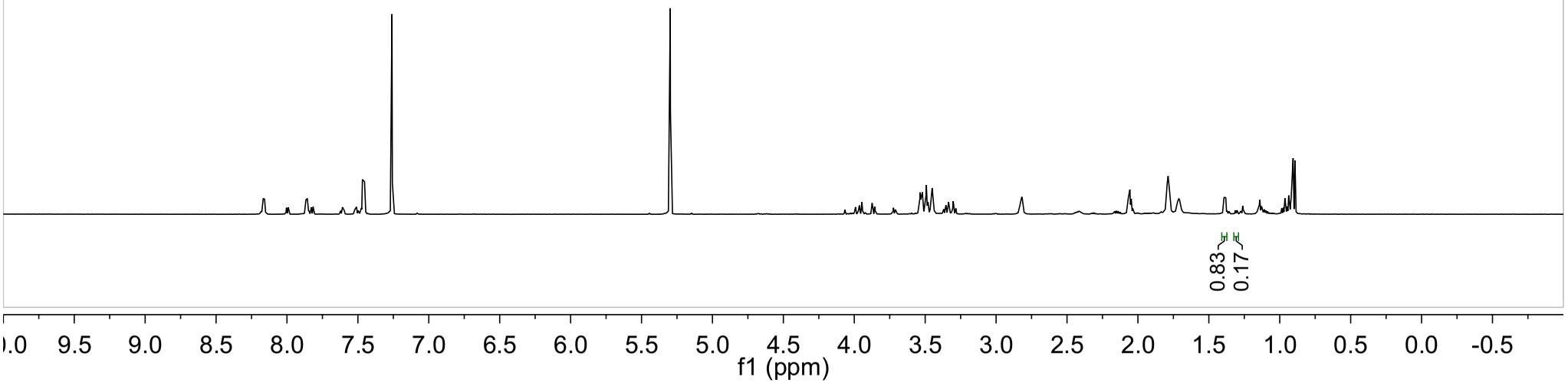
Parameter	Value
1 Title	DVR03126CRD.1.fid
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	203
6 Relaxation Delay	1.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

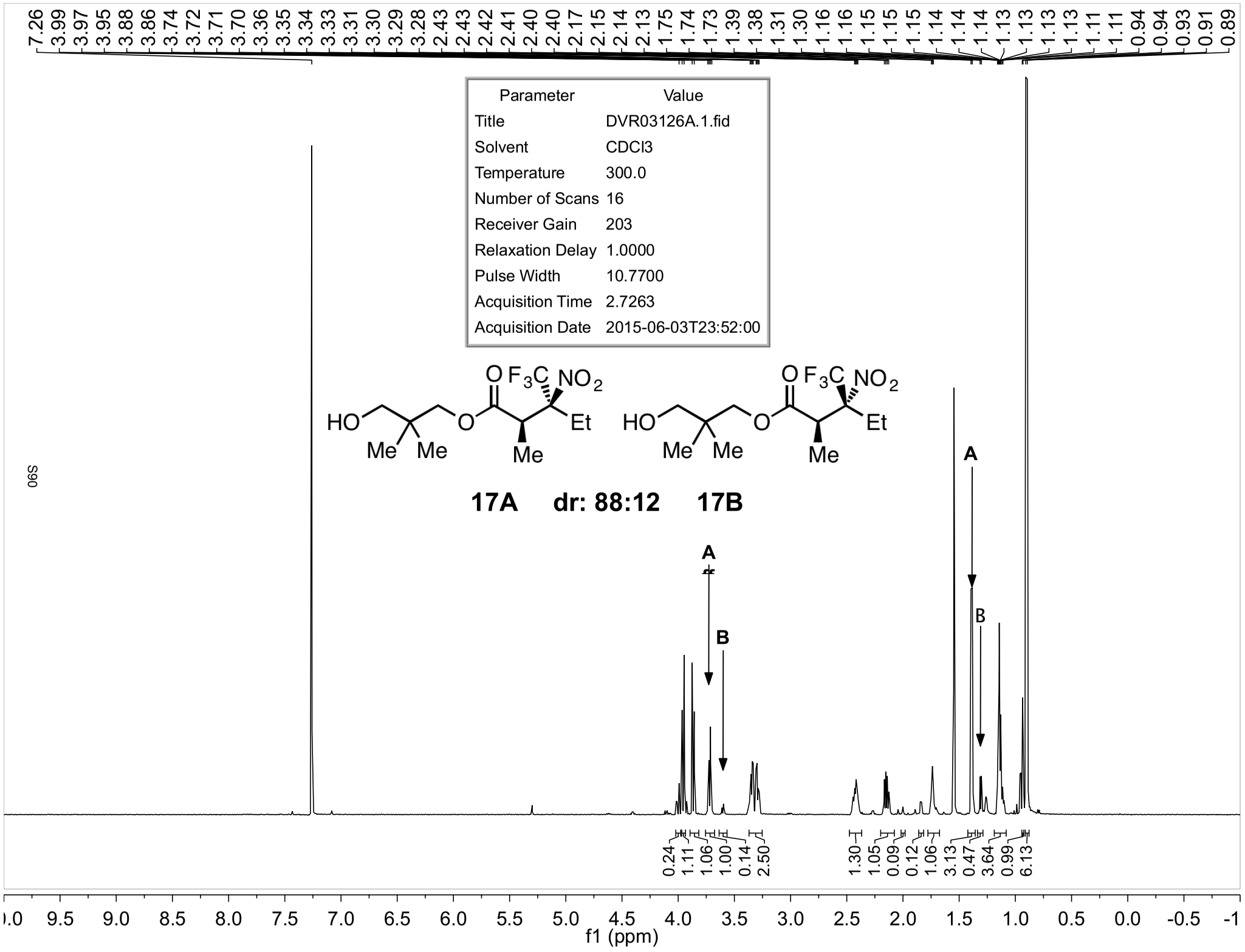


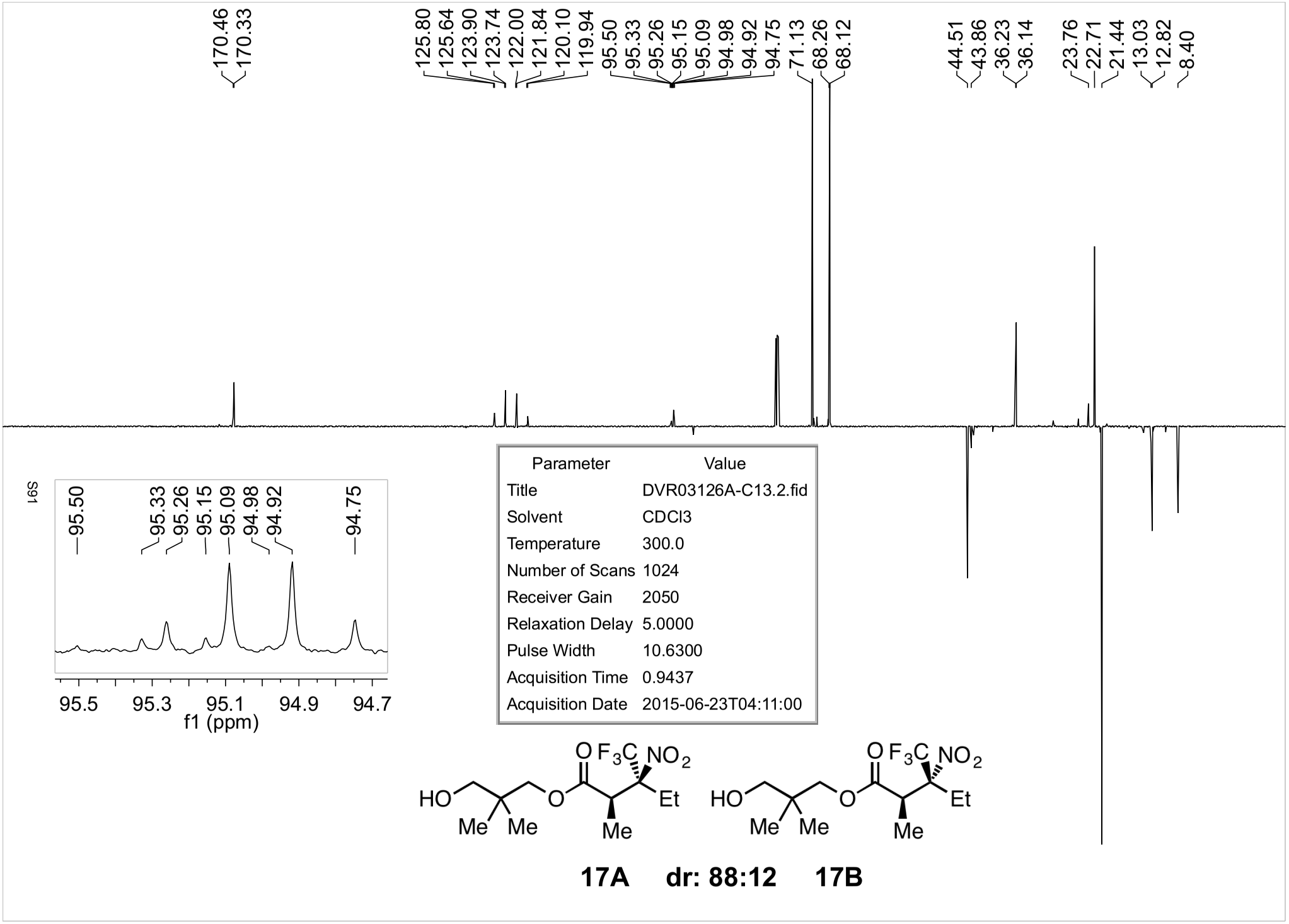
Crude

17A dr: 83:17 17B



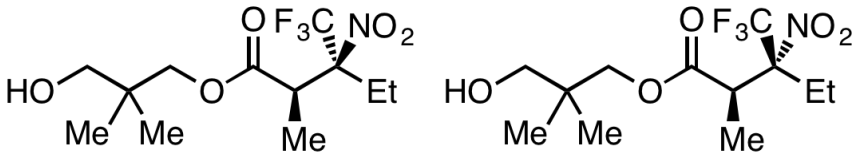



7.26 3.99 3.97 3.95 3.88 3.86 3.74 3.72 3.71 3.70 3.36 3.35 3.34 3.33 3.31 3.30 3.29 3.28 2.43 2.43 2.42 2.41 2.40 2.40 2.17 2.15 2.14 2.13 1.75 1.74 1.73 1.39 1.38 1.31 1.30 1.16 1.16 1.15 1.15 1.15 1.14 1.14 1.14 1.13 1.13 1.13 1.13 1.11 1.11 0.94 0.94 0.93 0.91 0.89
Parameter Value
Title DVR03126A.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-03T23:52:00
HO Me Me O O F3C NO2 Et Me
HO Me Me O O F3C NO2 Et Me
17A dr: 88:12 17B
A
B
A
B
S90
0.24 1.11 1.06 1.00 0.14 2.50
1.30 1.05 0.09 0.12 1.06 3.13 0.47 3.64 0.99 6.13
f1 (ppm)


170.46
170.33
125.80
125.64
123.90
123.74
122.00
121.84
120.10
119.94
95.50
95.33
95.26
95.15
95.09
94.98
94.92
94.75
71.13
68.26
68.12
44.51
43.86
36.23
36.14
23.76
22.71
21.44
13.03
12.82
8.40
S91
95.5
95.3
95.1
94.9
94.7
f1 (ppm)
Parameter Value
Title DVR03126A-C13.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-23T04:11:00
HO
Me
Me
O
O
F3C
NO2
Et
Me
17A dr: 88:12 17B
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

-66.83
-67.07

Parameter	Value
Title	DVR03126A.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-06-03T23:55:00

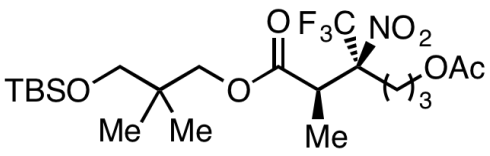


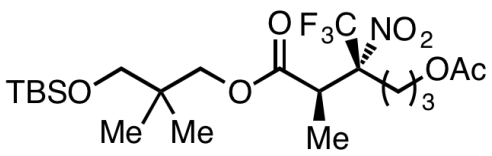
17A dr: 88:12 17B

-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -10

f1 (ppm)

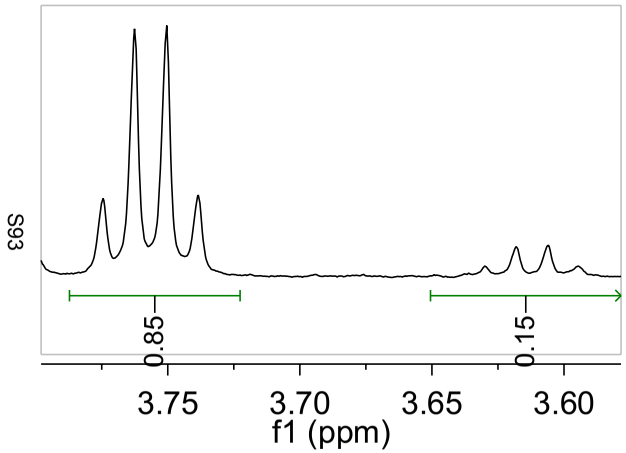
	Parameter	Value
1	Title	DVR03122CRD.1.fid
2	Solvent	CDCl3
3	Temperature	300.0
4	Number of Scans	16
5	Receiver Gain	144
6	Relaxation Delay	1.0000
7	Pulse Width	10.7700
8	Spectrometer Frequency	600.32
9	Nucleus	1H

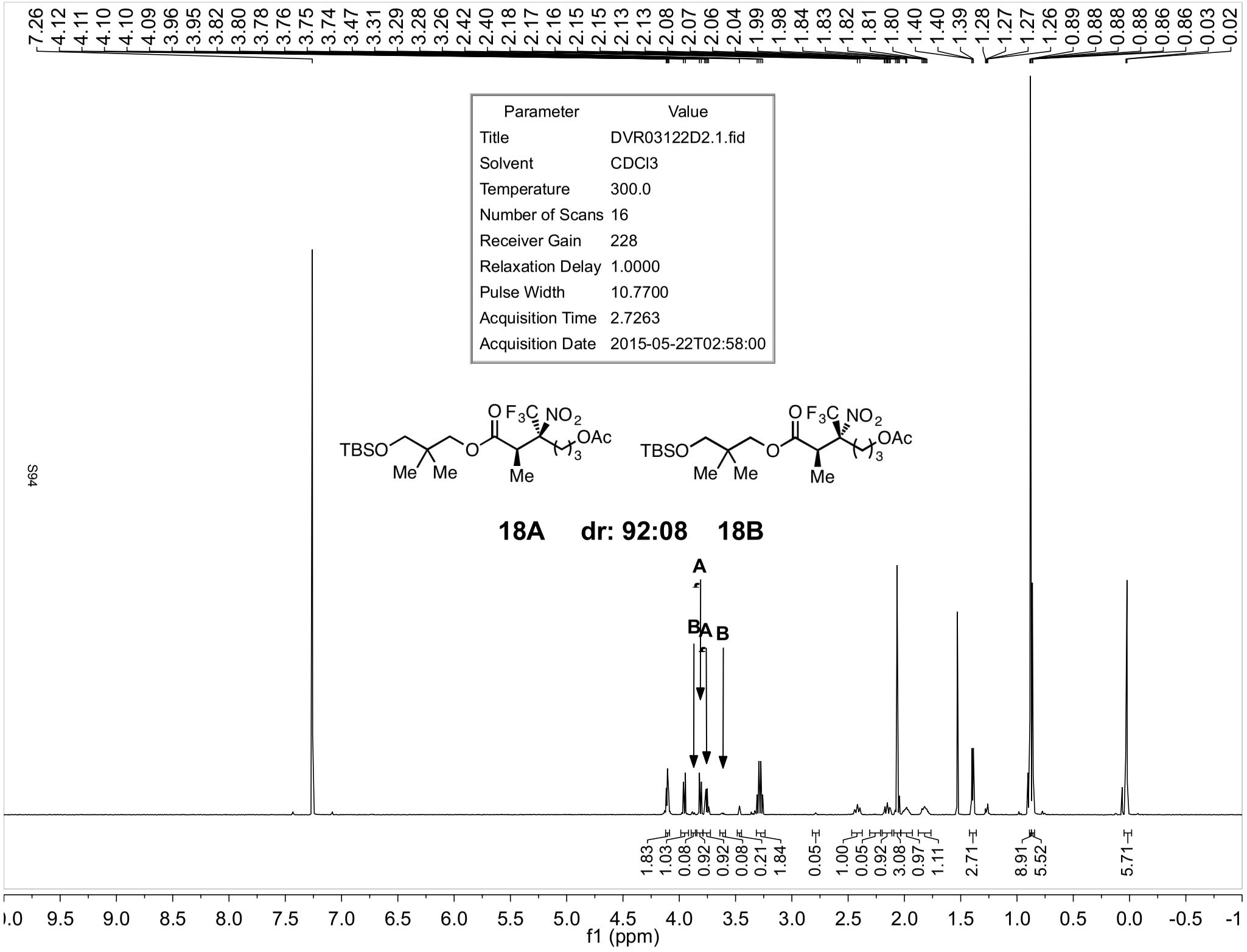


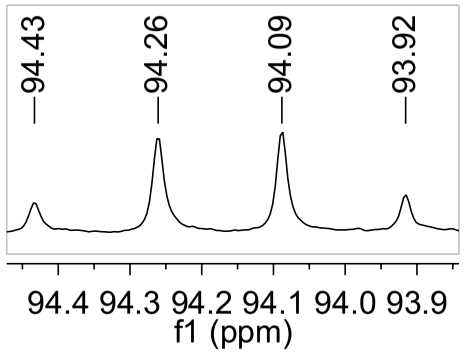


Crude

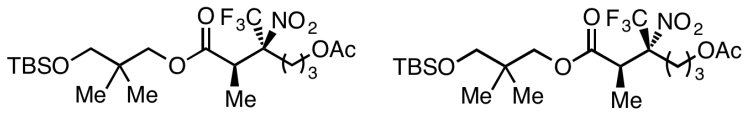
18A dr: 85:15 18B




7.26 4.12 4.11 4.10 4.10 4.09 3.96 3.95 3.82 3.80 3.78 3.76 3.75 3.74 3.47 3.31 3.29 3.28 3.26 2.42 2.40 2.18 2.17 2.16 2.15 2.15 2.13 2.13 2.08 2.07 2.06 2.04 1.99 1.98 1.84 1.83 1.82 1.81 1.80 1.40 1.40 1.39 1.28 1.27 1.27 1.26 0.89 0.88 0.88 0.88 0.86 0.86 0.03 0.02
Parameter Value
Title DVR03122D2.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 228
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-05-22T02:58:00
S94
18A dr: 92:08 18B
A
B A B
1.83 1.03 0.08 0.92 0.92 0.08 0.21 1.84 0.05 1.00 0.05 0.92 3.08 0.97 1.11 2.71 8.91 5.52 5.71
f1 (ppm)



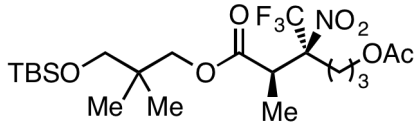
Parameter	Value
Title	DVR03122DS2C13.1.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	1024
Receiver Gain	2050
Relaxation Delay	5.0000
Pulse Width	10.6300
Acquisition Time	0.9437
Acquisition Date	2015-06-02T03:22:00

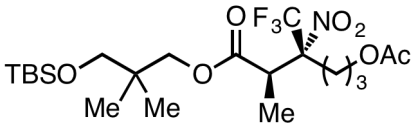


18A dr: 92:08 18B

-67.22
-67.46

Parameter	Value
Title	DVR03122D2.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-05-22T03:22:00



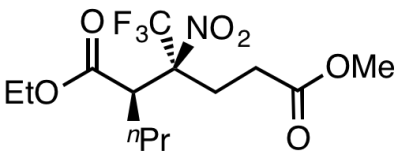


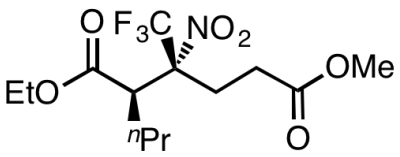
18A dr: 92:08 18B

-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -10

f1 (ppm)

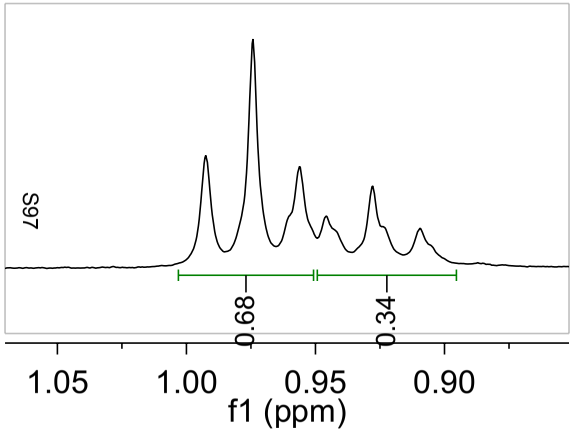
Parameter	Value
1 Title	DVR03108CRD.1.fid
2 Solvent	CDCl3
3 Temperature	298.2
4 Number of Scans	16
5 Receiver Gain	10
6 Relaxation Delay	1.0000
7 Pulse Width	15.0000
8 Spectrometer Frequency	400.13
9 Nucleus	1H

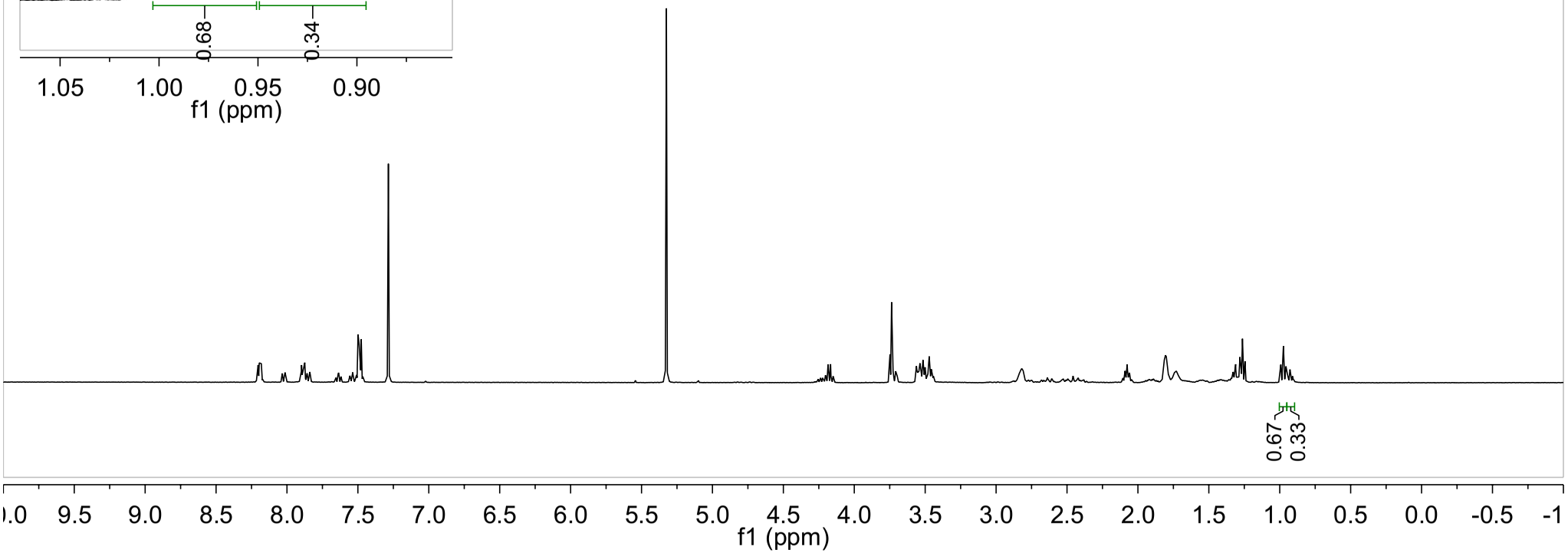


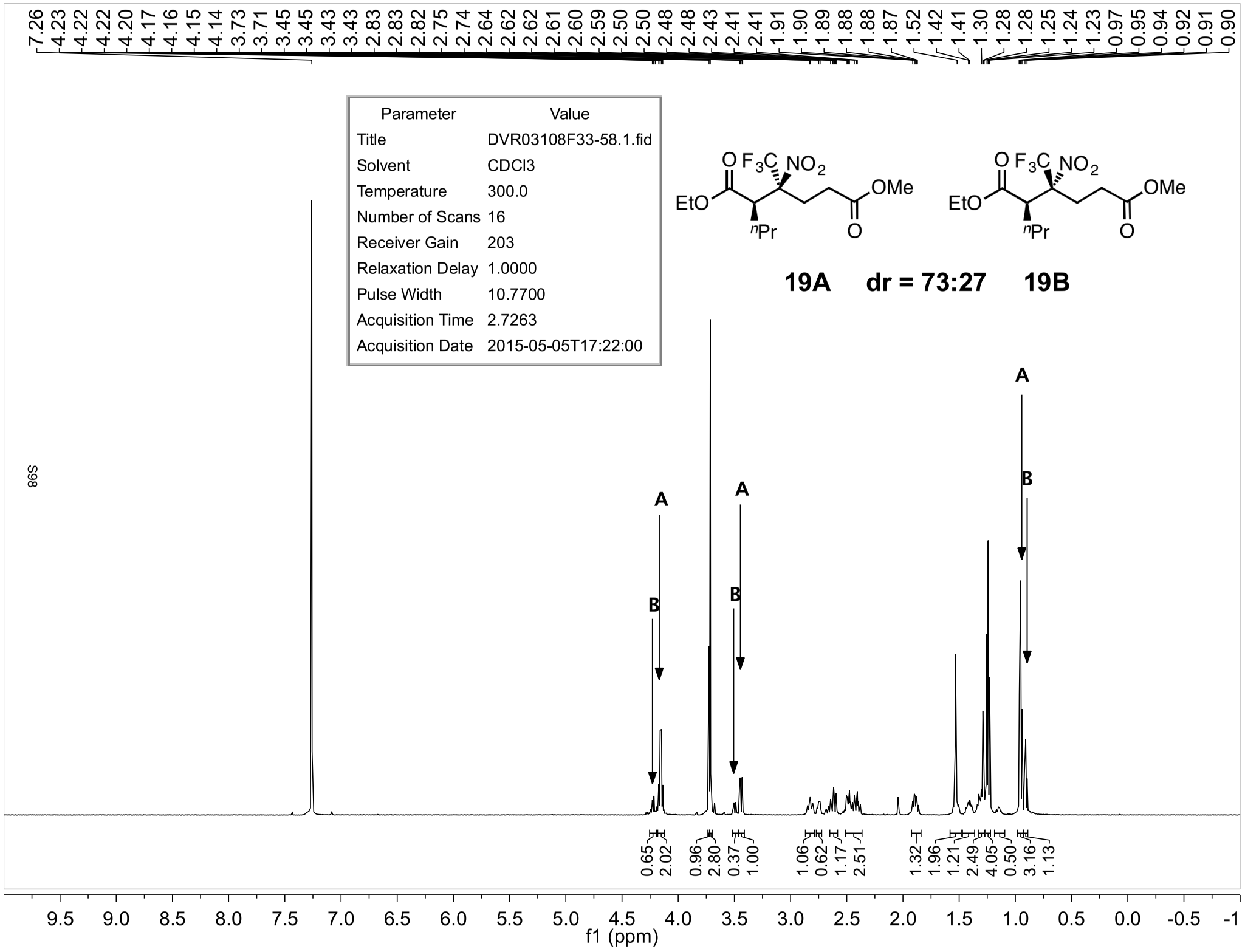


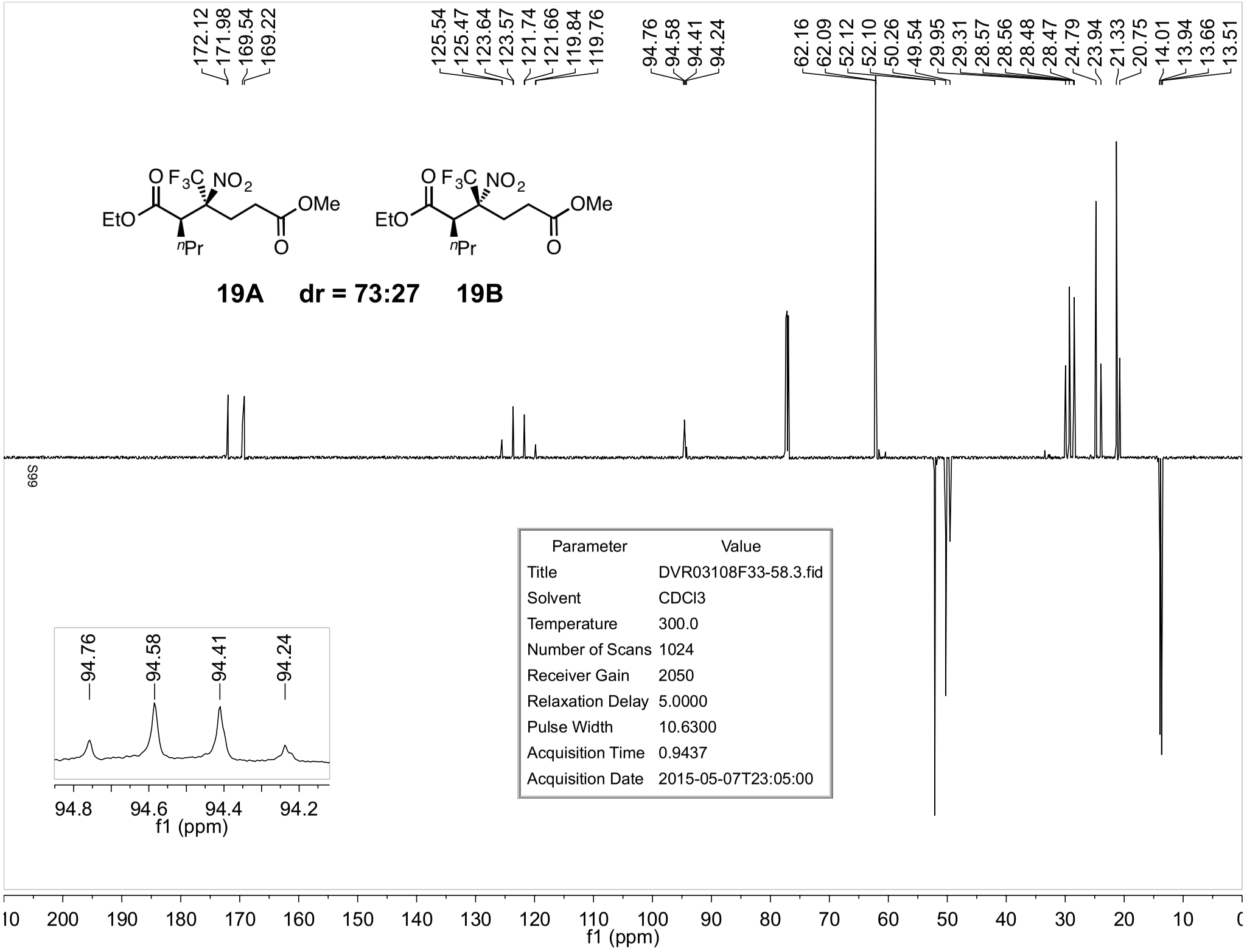
Crude

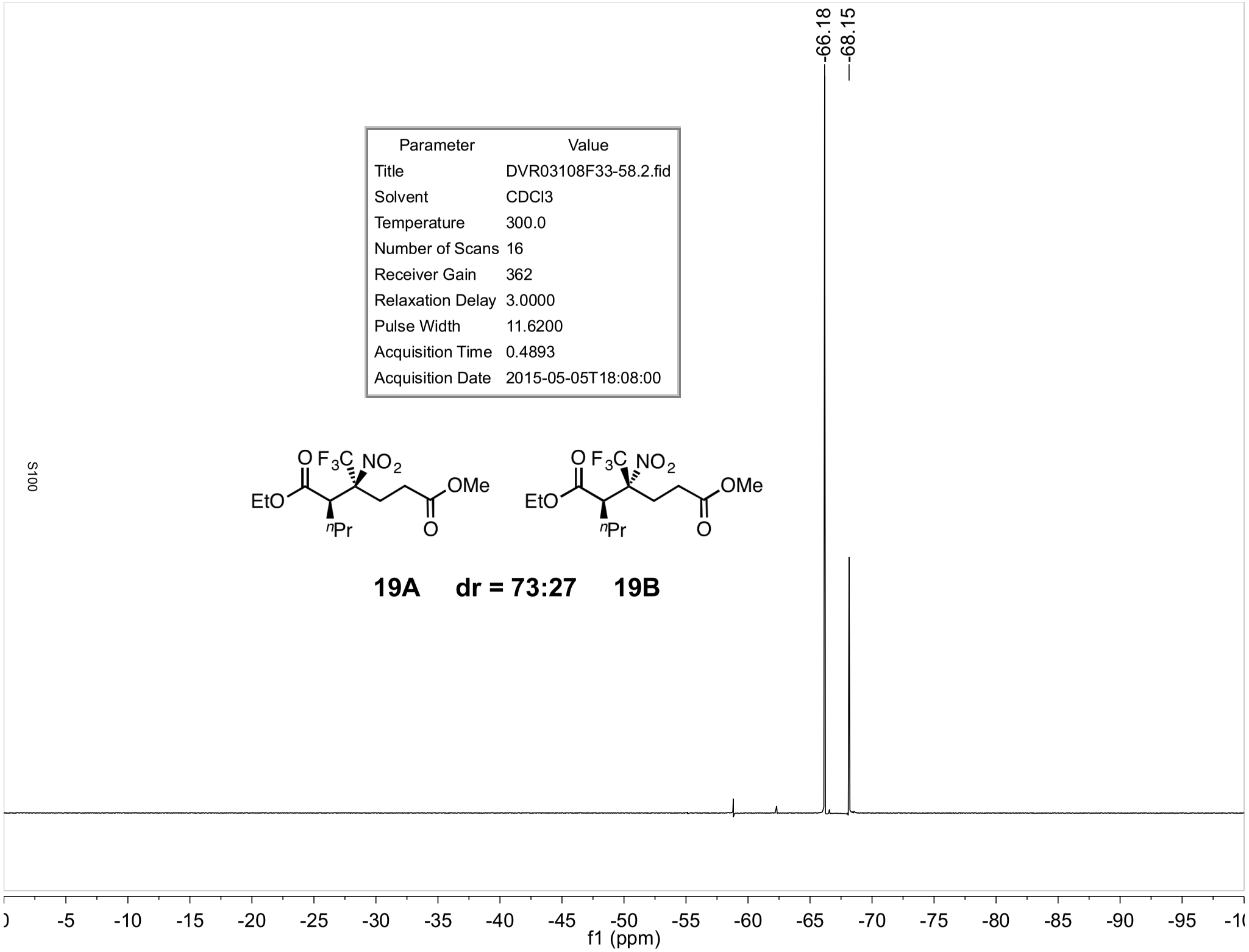
19A dr = 67:33 19B



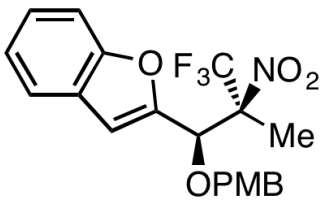


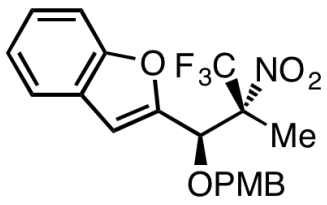

7.26 4.23 4.22 4.22 4.20 4.17 4.16 4.15 4.14 3.73 3.71 3.45 3.45 3.43 3.43 2.83 2.83 2.82 2.75 2.74 2.64 2.62 2.62 2.61 2.60 2.59 2.50 2.50 2.48 2.48 2.43 2.41 2.41 1.91 1.90 1.89 1.88 1.88 1.87 1.52 1.42 1.41 1.30 1.28 1.28 1.25 1.24 1.23 0.97 0.95 0.94 0.92 0.91 0.90
Parameter Value
Title DVR03108F33-58.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-05-05T17:22:00
O F3C NO2 EtO OMe nPr O
O F3C NO2 EtO OMe nPr O
19A dr = 73:27 19B
S98
A B A B A B
0.65 2.02 0.96 2.80 0.37 1.00 1.06 0.62 1.17 2.51 1.32 1.96 1.21 2.49 4.05 0.50 3.16 1.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


172.12
171.98
169.54
169.22
125.54
125.47
123.64
123.57
121.74
121.66
119.84
119.76
94.76
94.58
94.41
94.24
62.16
62.09
52.12
52.10
50.26
49.54
29.95
29.31
28.57
28.56
28.48
28.47
24.79
23.94
21.33
20.75
14.01
13.94
13.66
13.51
O F3C NO2
EtO
OMe
nPr
O
19A dr = 73:27 19B
66S
Parameter Value
Title DVR03108F33-58.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-05-07T23:05:00
94.8
94.6
94.4
94.2
f1 (ppm)
f1 (ppm)


-66.18
-68.15
Parameter Value
Title DVR03108F33-58.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 362
Relaxation Delay 3.0000
Pulse Width 11.6200
Acquisition Time 0.4893
Acquisition Date 2015-05-05T18:08:00
S100
EtO
OMe
^{n}Pr
F_3C
NO_2
19A dr = 73:27 19B
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)

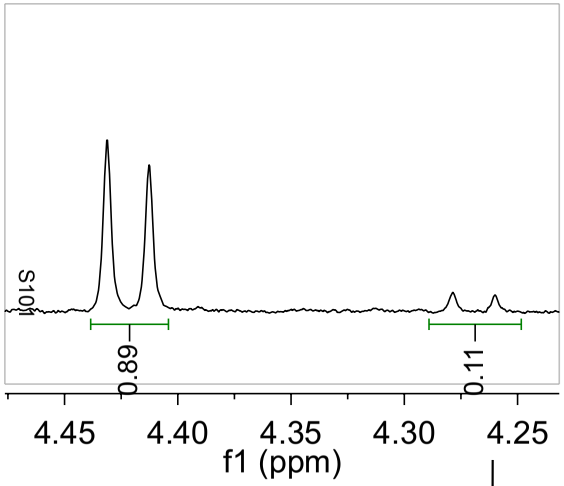
Parameter	Value
1 Title	DVR03127CRD.1.fid
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	228
6 Relaxation Delay	1.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

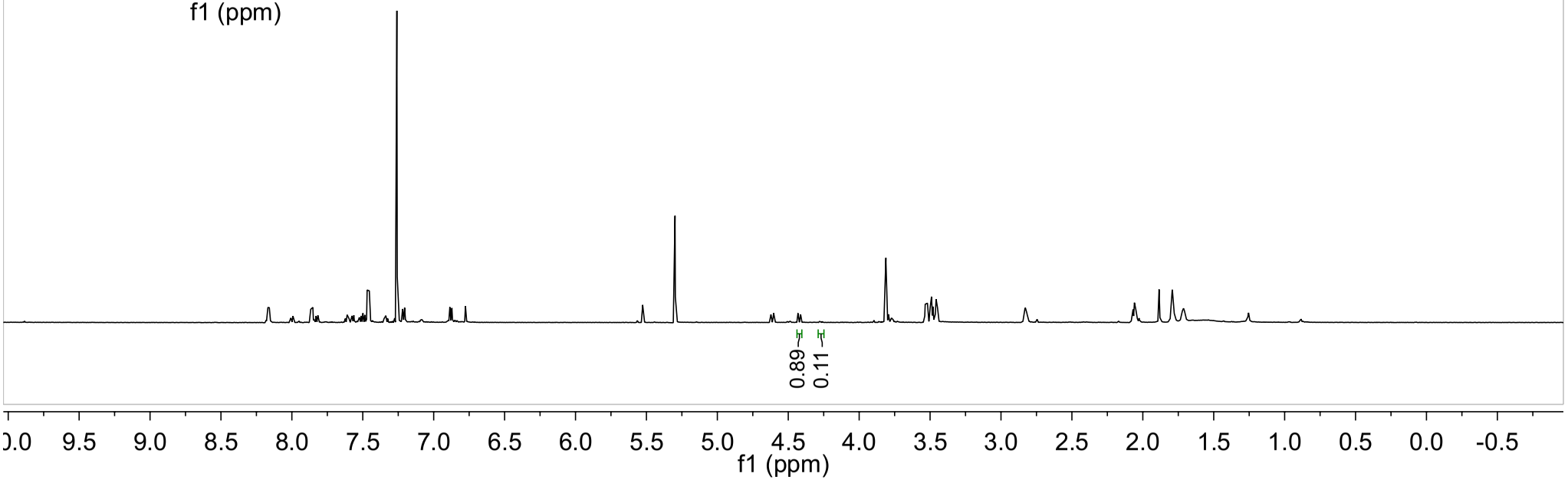


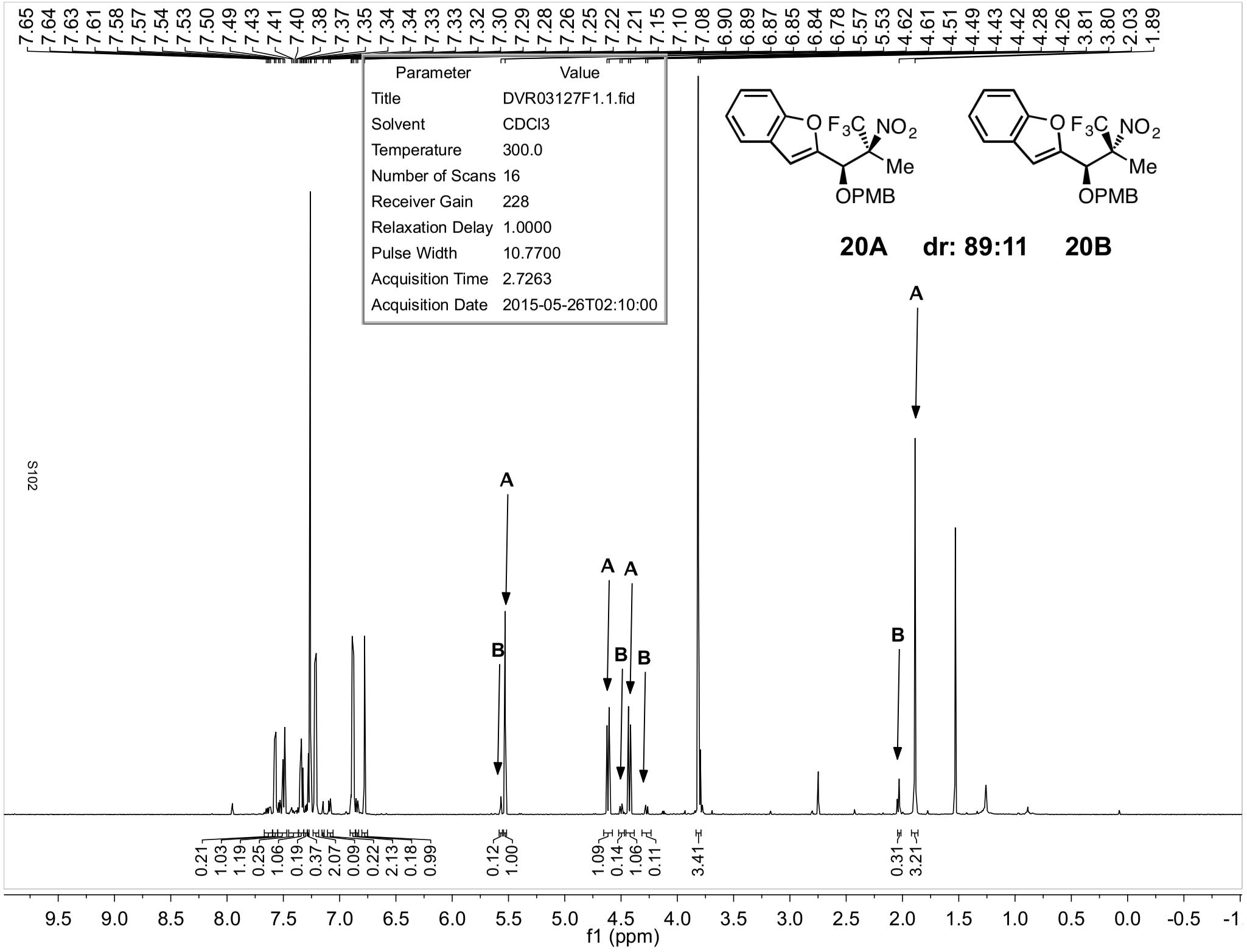


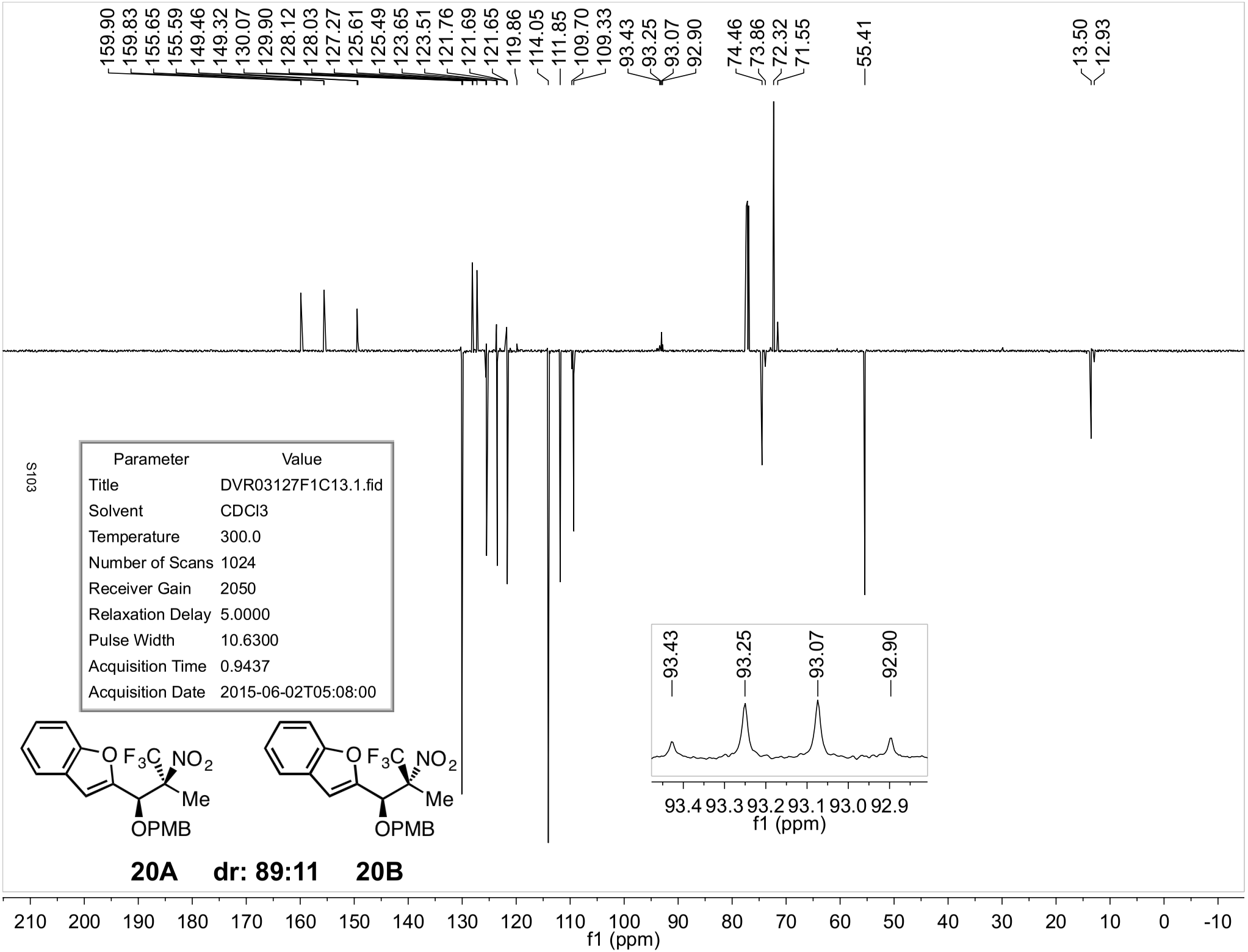
Crude

20A dr: 89:11 20B

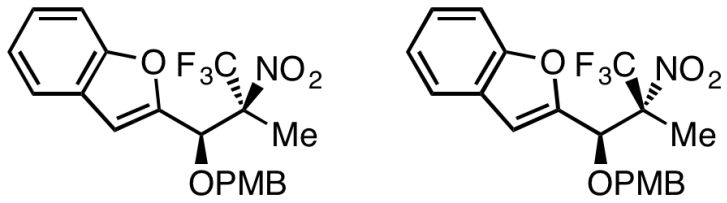




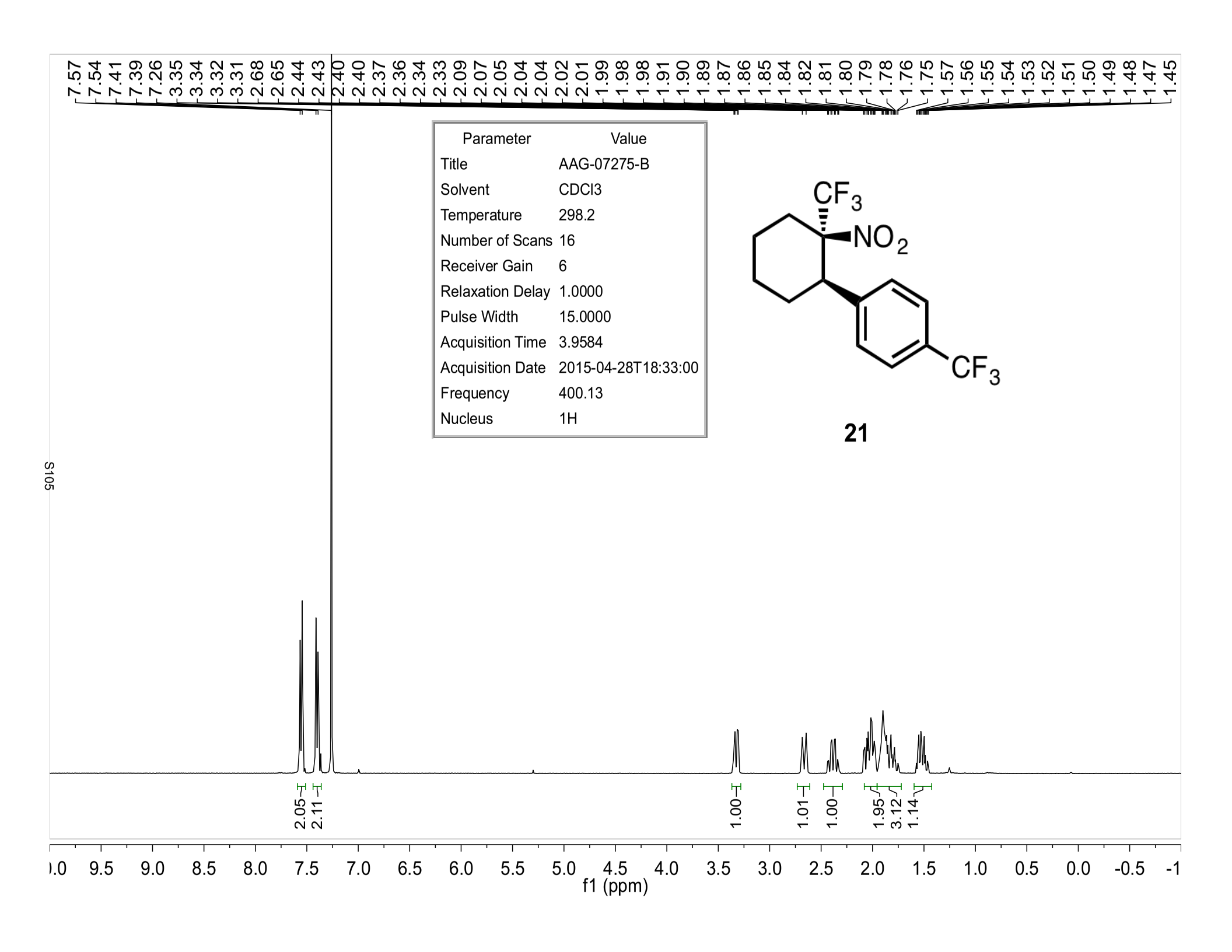

7.65 7.64 7.63 7.61 7.58 7.57 7.54 7.53 7.50 7.49 7.43 7.41 7.40 7.38 7.37 7.35 7.34 7.34 7.33 7.33 7.32 7.30 7.29 7.28 7.26 7.25 7.22 7.21 7.15 7.10 7.08 6.90 6.89 6.87 6.85 6.84 6.78 5.57 5.53 4.62 4.61 4.51 4.49 4.43 4.42 4.28 4.26 3.81 3.80 2.03 1.89
Parameter Value
Title DVR03127F1.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 228
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-05-26T02:10:00
O F3C NO2 Me OPMB
O F3C NO2 Me OPMB
20A dr: 89:11 20B
S102
A
B
A A
B B
B
0.21 1.03 1.19 0.25 1.06 0.19 0.37 2.07 0.09 0.22 2.13 0.18 0.99
0.12 1.00
1.09 0.14 1.06 0.11
3.41
0.31 3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

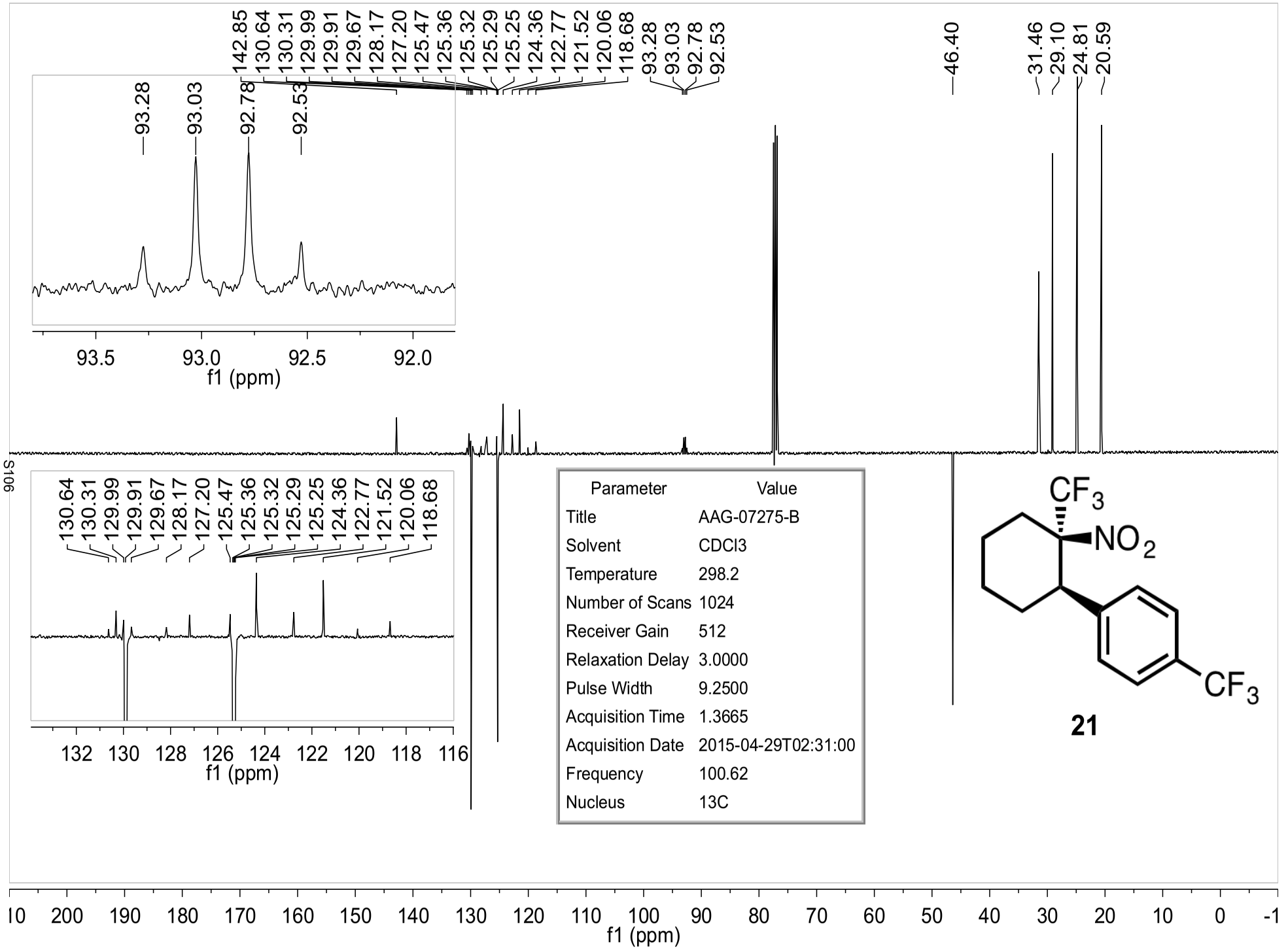

159.90
159.83
155.65
155.59
149.46
149.32
130.07
129.90
128.12
128.03
127.27
125.61
125.49
123.65
123.51
121.76
121.69
121.65
119.86
114.05
111.85
109.70
109.33
93.43
93.25
93.07
92.90
74.46
73.86
72.32
71.55
55.41
13.50
12.93
S103
Parameter Value
Title DVR03127F1C13.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-02T05:08:00
93.43
93.25
93.07
92.90
93.4 93.3 93.2 93.1 93.0 92.9
f1 (ppm)
O F3C NO2 Me OPMB
O F3C NO2 Me OPMB
20A dr: 89:11 20B
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
Title	DVR03127F1.3.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-05-26T02:12:00

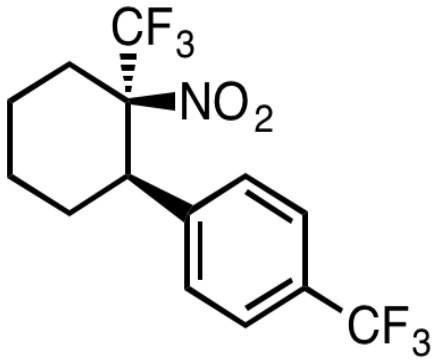


20A dr: 89:11 20B

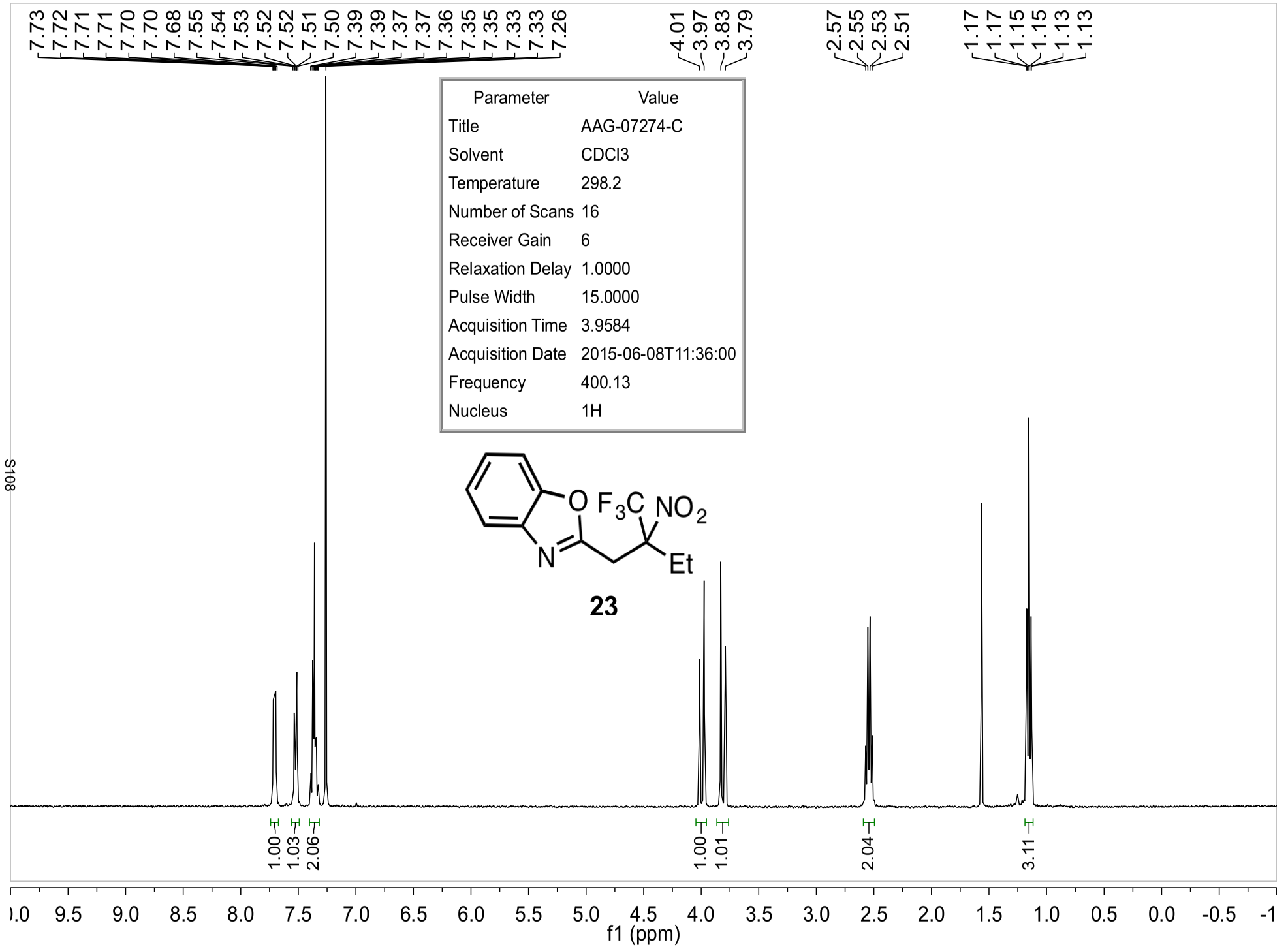

7.57 7.54 7.41 7.39 7.26 3.35 3.34 3.32 3.31 2.68 2.65 2.44 2.43 2.40 2.40 2.37 2.36 2.34 2.33 2.09 2.07 2.05 2.04 2.04 2.02 2.01 1.99 1.98 1.98 1.91 1.90 1.89 1.87 1.86 1.85 1.84 1.82 1.81 1.80 1.79 1.78 1.76 1.75 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.50 1.49 1.48 1.47 1.45
Parameter Value
Title AAG-07275-B
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 6
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-04-28T18:33:00
Frequency 400.13
Nucleus 1H
CF3
NO2
CF3
21
S105
2.05
2.11
1.00
1.01
1.00
1.95
3.12
1.14
f1 (ppm)

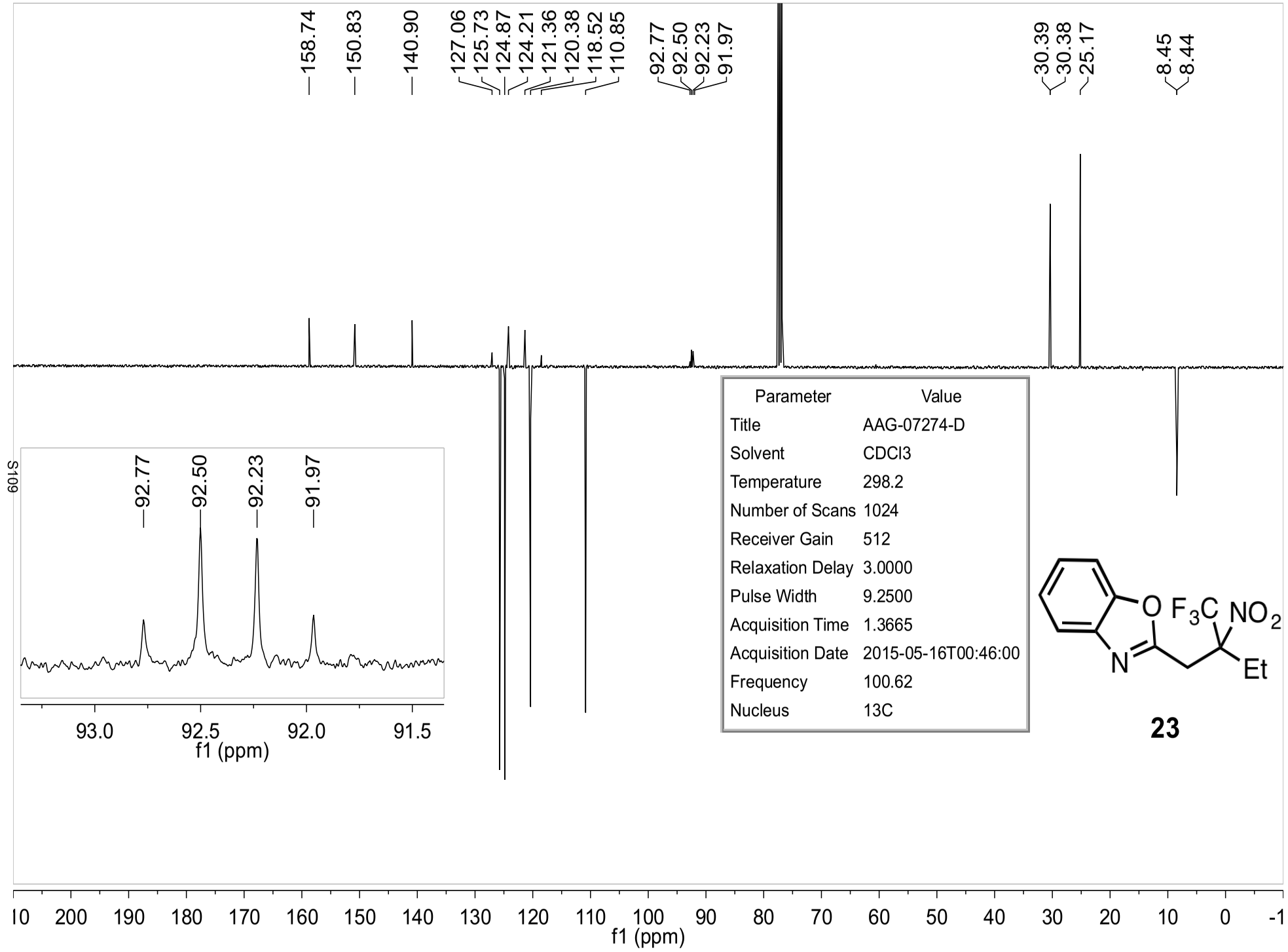

142.85 130.64 130.31 129.99 129.91 129.67 128.17 127.20 125.47 125.36 125.32 125.29 125.25 124.36 122.77 121.52 120.06 118.68 93.28 93.03 92.78 92.53
46.40
31.46 29.10 24.81 20.59
93.28 93.03 92.78 92.53
93.5 93.0 92.5 92.0
f1 (ppm)
S106
130.64 130.31 129.99 129.91 129.67 128.17 127.20 125.47 125.36 125.32 125.29 125.25 124.36 122.77 121.52 120.06 118.68
132 130 128 126 124 122 120 118 116
f1 (ppm)
Parameter Value
Title AAG-07275-B
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-04-29T02:31:00
Frequency 100.62
Nucleus 13C
CF3
NO2
CF3
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Parameter	Value
Title	AAG-07275-B
Solvent	CDCl3
Temperature	298.2
Number of Scans	16
Receiver Gain	575
Relaxation Delay	2.0000
Pulse Width	15.0300
Acquisition Time	0.8717
Acquisition Date	2015-04-29T03:04:00
Frequency	376.46
Nucleus	19F

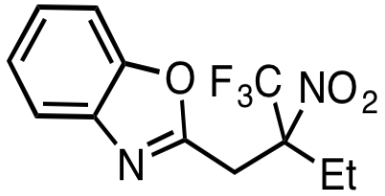


21

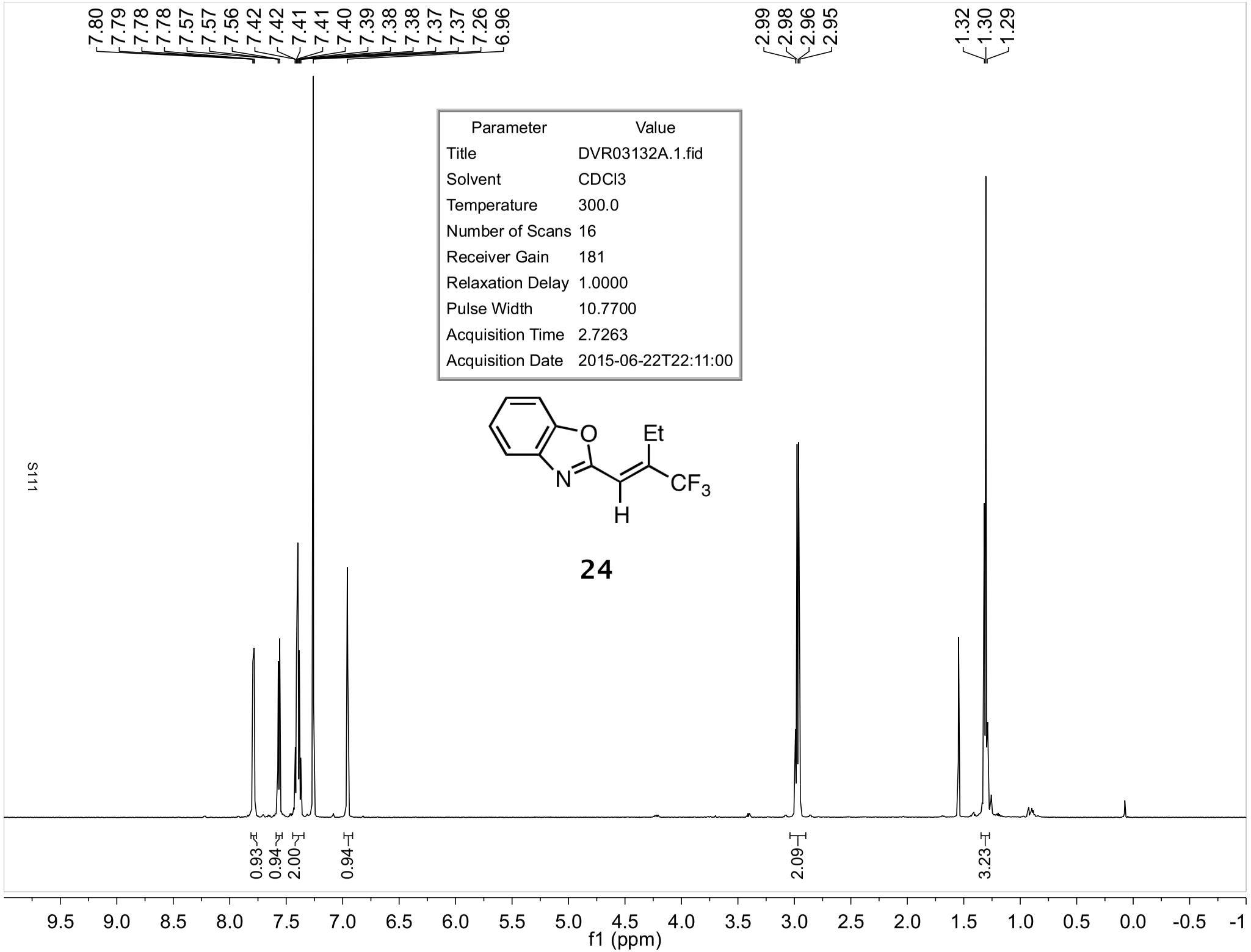

7.73 7.72 7.71 7.71 7.70 7.70 7.68 7.55 7.54 7.53 7.52 7.52 7.51 7.50 7.39 7.39 7.37 7.37 7.36 7.35 7.35 7.33 7.33 7.26
4.01 3.97 3.83 3.79
2.57 2.55 2.53 2.51
1.17 1.17 1.15 1.15 1.13 1.13
Parameter Value
Title AAG-07274-C
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 6
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-06-08T11:36:00
Frequency 400.13
Nucleus 1H
O F3C NO2
N
Et
23
S108
1.00 1.03 2.06 1.00 1.01 2.04 3.11
f1 (ppm)

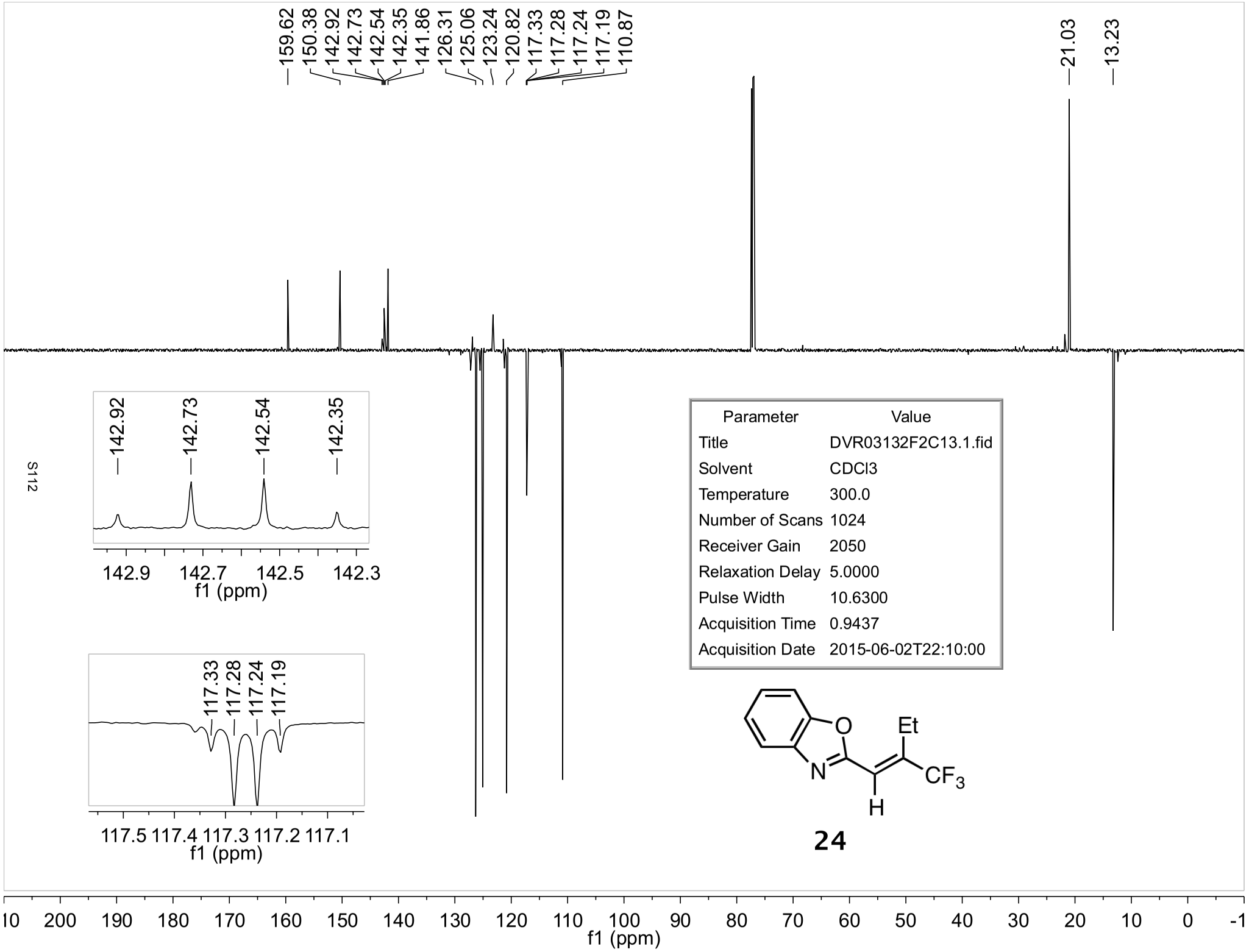

158.74
150.83
140.90
127.06
125.73
124.87
124.21
121.36
120.38
118.52
110.85
92.77
92.50
92.23
91.97
30.39
30.38
25.17
8.45
8.44
S109
92.77
92.50
92.23
91.97
93.0
92.5
92.0
91.5
f1 (ppm)
Parameter Value
Title AAG-07274-D
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-05-16T00:46:00
Frequency 100.62
Nucleus 13C
O
F3C
NO2
N
Et
23
f1 (ppm)

Parameter	Value
Title	AAG-07274-D
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Receiver Gain	1024
Relaxation Delay	2.0000
Pulse Width	15.0300
Acquisition Time	0.8717
Acquisition Date	2015-05-14T19:01:00
Frequency	376.46
Nucleus	19F

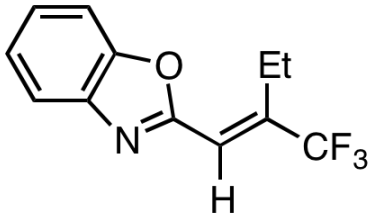


23

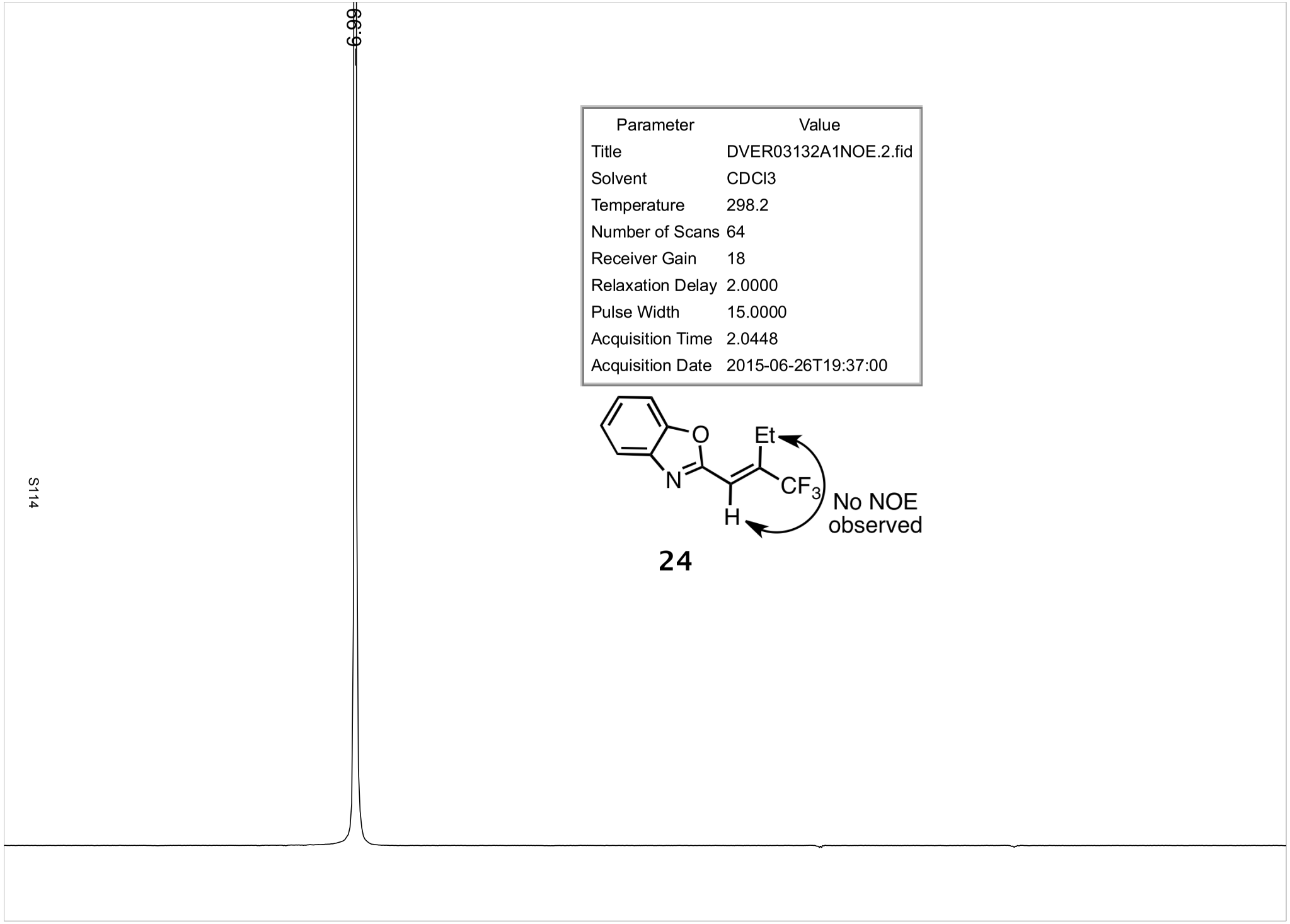

7.80
7.79
7.78
7.78
7.57
7.57
7.56
7.42
7.42
7.41
7.41
7.40
7.39
7.38
7.38
7.37
7.37
7.26
6.96
2.99
2.98
2.96
2.95
1.32
1.30
1.29
Parameter Value
Title DVR03132A.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-22T22:11:00
O
Et
N
CF3
H
24
S111
0.93
0.94
2.00
0.94
2.09
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

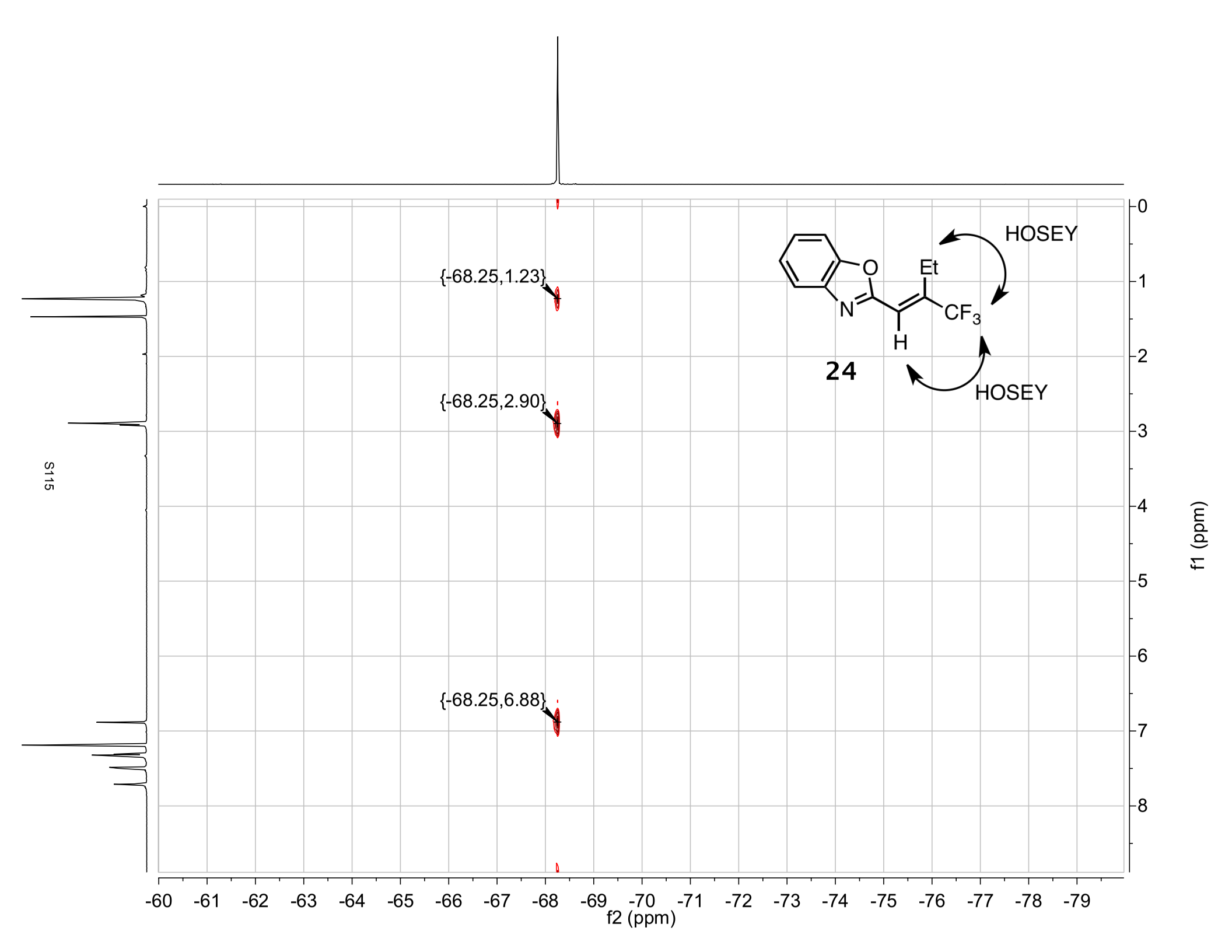

159.62
150.38
142.92
142.73
142.54
142.35
141.86
126.31
125.06
123.24
120.82
117.33
117.28
117.24
117.19
110.87
21.03
13.23
S112
142.92
142.73
142.54
142.35
142.9
142.7
142.5
142.3
f1 (ppm)
117.33
117.28
117.24
117.19
117.5 117.4 117.3 117.2 117.1
f1 (ppm)
Parameter Value
Title DVR03132F2C13.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-02T22:10:00
O
Et
N
CF3
H
24
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

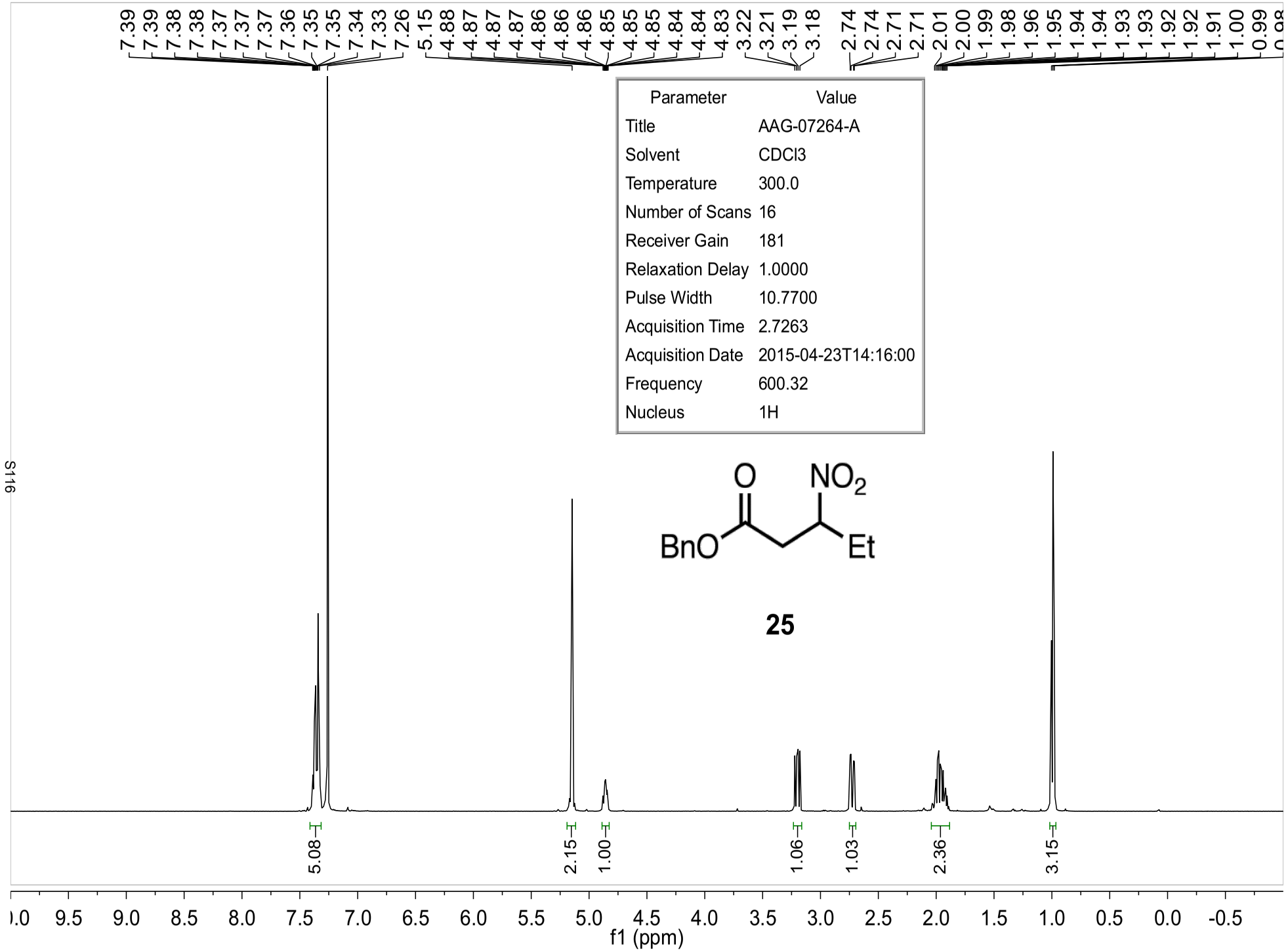
Parameter	Value
Title	DVR03132F2.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-06-02T16:25:00

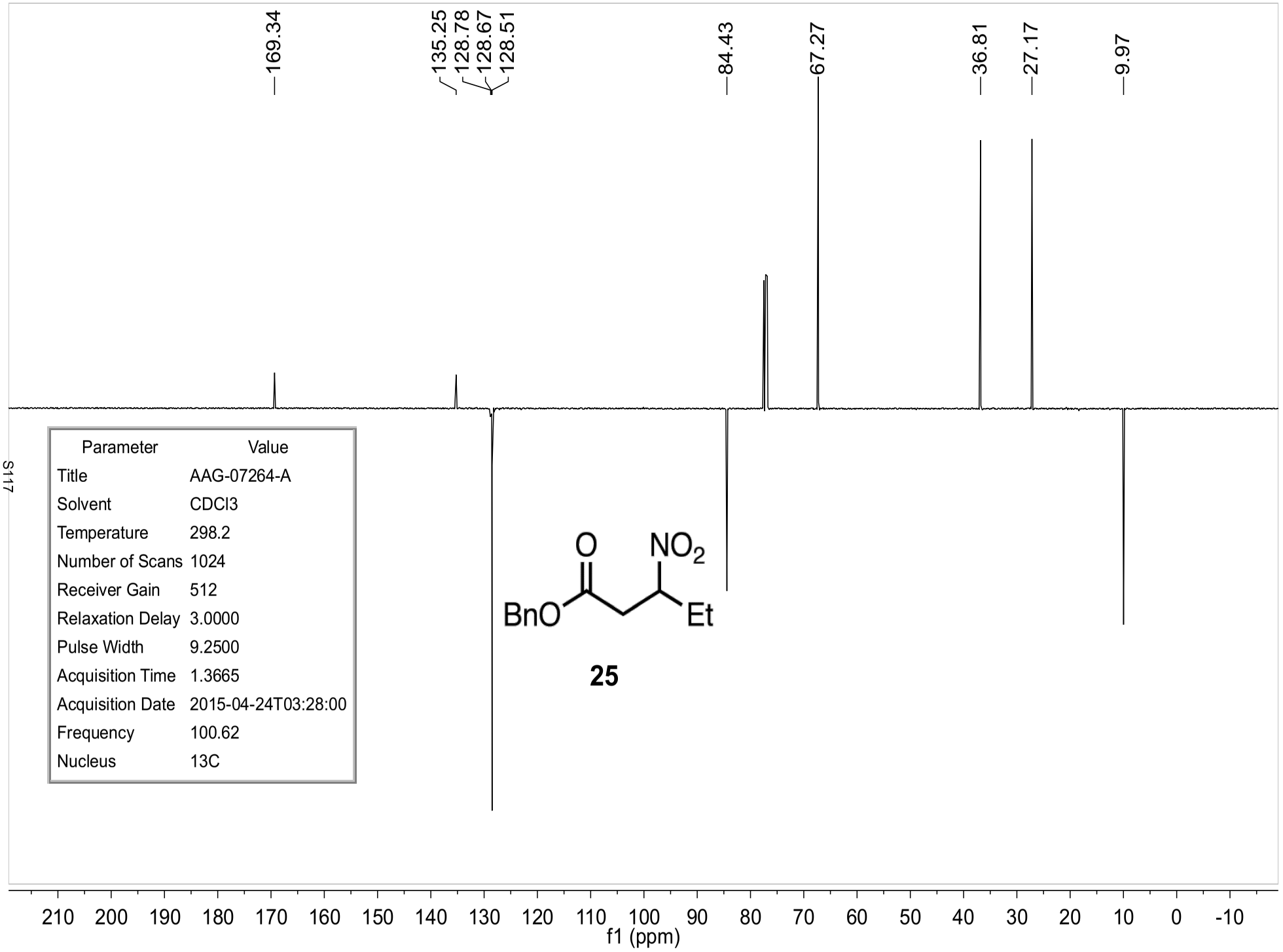


24

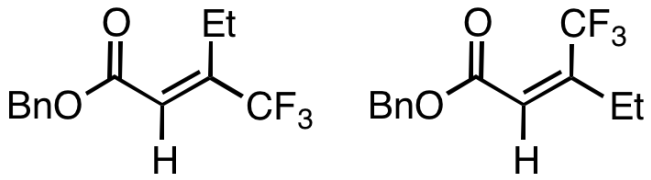

6.99
Parameter Value
Title DVER03132A1NOE.2.fid
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 18
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-26T19:37:00
O
N
Et
CF3
H
No NOE observed
24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


{-68.25,1.23}
{-68.25,2.90}
{-68.25,6.88}
HOSEY
HOSEY
Et
CF3
O
N
H
24
S115
f2 (ppm)
f1 (ppm)
-60 -61 -62 -63 -64 -65 -66 -67 -68 -69 -70 -71 -72 -73 -74 -75 -76 -77 -78 -79
0 1 2 3 4 5 6 7 8


7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.35 7.35 7.34 7.33 7.26
5.15 4.88 4.87 4.87 4.87 4.86 4.86 4.86 4.85 4.85 4.85 4.84 4.84 4.83
3.22 3.21 3.19 3.18
2.74 2.74 2.71 2.71
2.01 2.00 1.99 1.98 1.96 1.95 1.94 1.94 1.93 1.93 1.92 1.92 1.91 1.00 0.99
Parameter Value
Title AAG-07264-A
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-04-23T14:16:00
Frequency 600.32
Nucleus 1H
O
NO2
BnO
Et
25
S116
5.08
2.15
1.00
1.06
1.03
2.36
3.15
f1 (ppm)

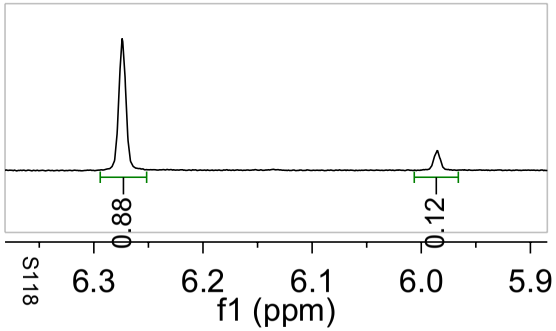

169.34
135.25
128.78
128.67
128.51
84.43
67.27
36.81
27.17
9.97
Parameter Value
Title AAG-07264-A
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-04-24T03:28:00
Frequency 100.62
Nucleus 13C
O
NO2
BnO
Et
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

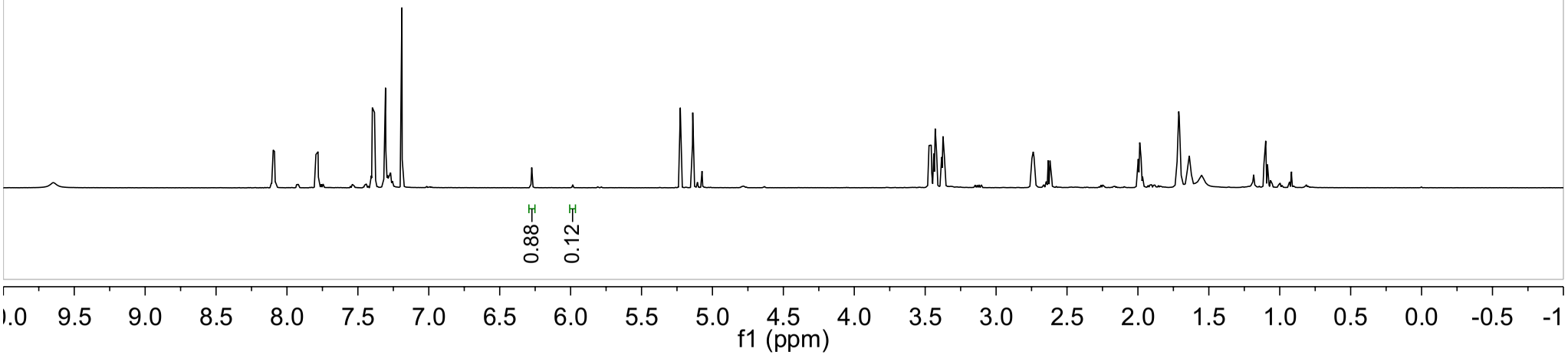
Parameter	Value
1 Title	DVR03134CRD.1.fid
2 Solvent	CDCl3
3 Temperature	300.0
4 Number of Scans	16
5 Receiver Gain	161
6 Relaxation Delay	1.0000
7 Pulse Width	10.7700
8 Spectrometer Frequency	600.32
9 Nucleus	1H

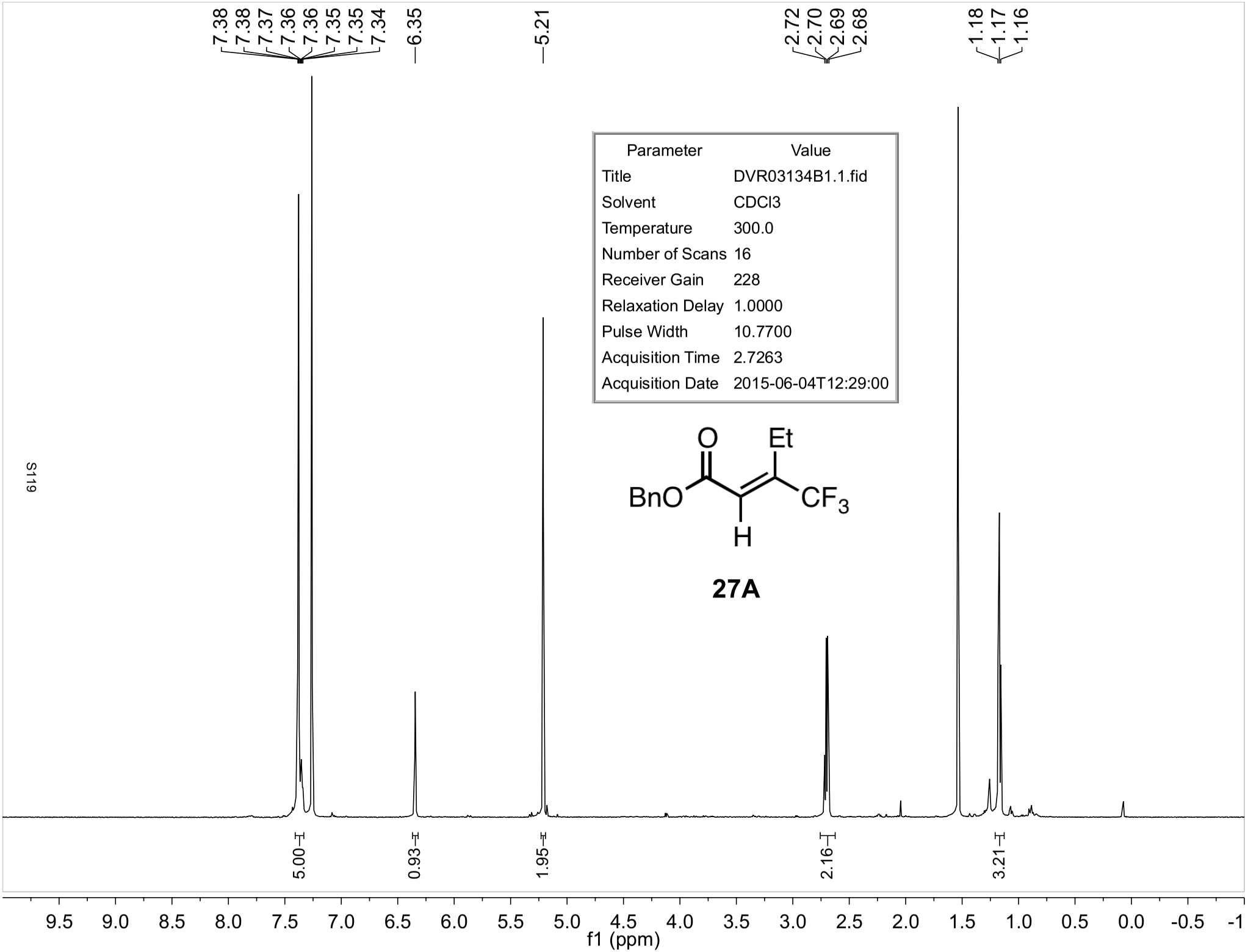


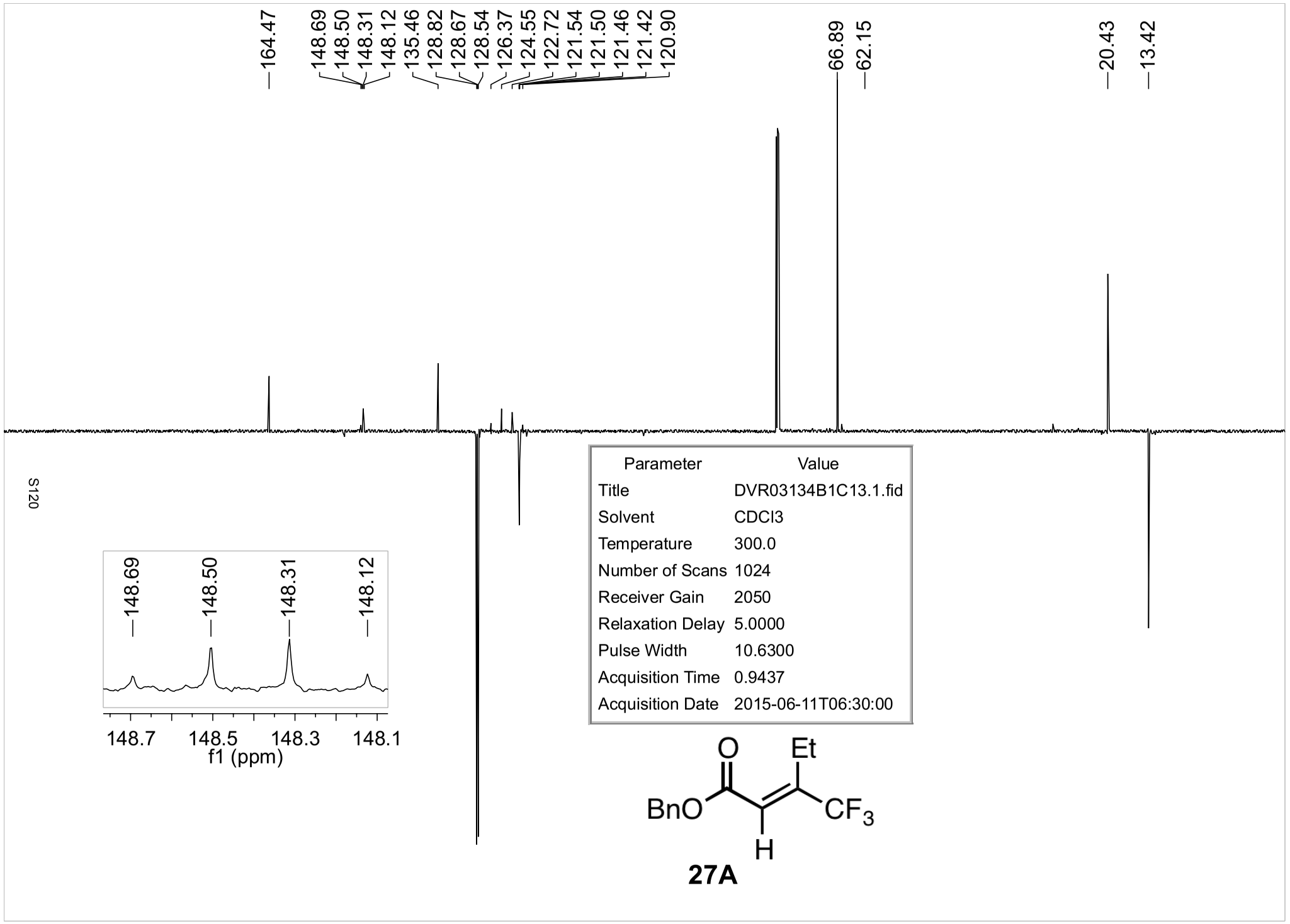
Crude

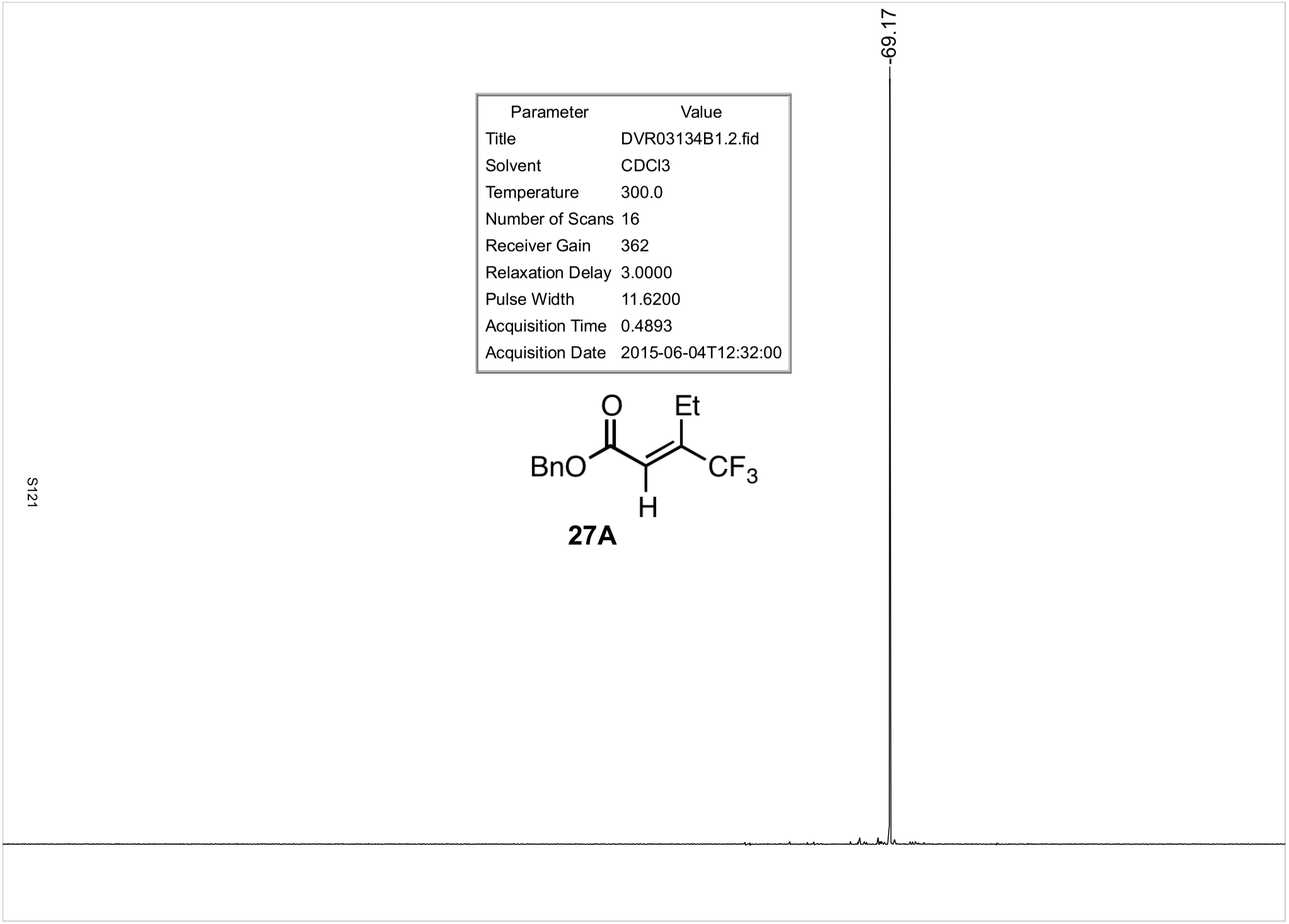
27A E:Z = 88:12 27B

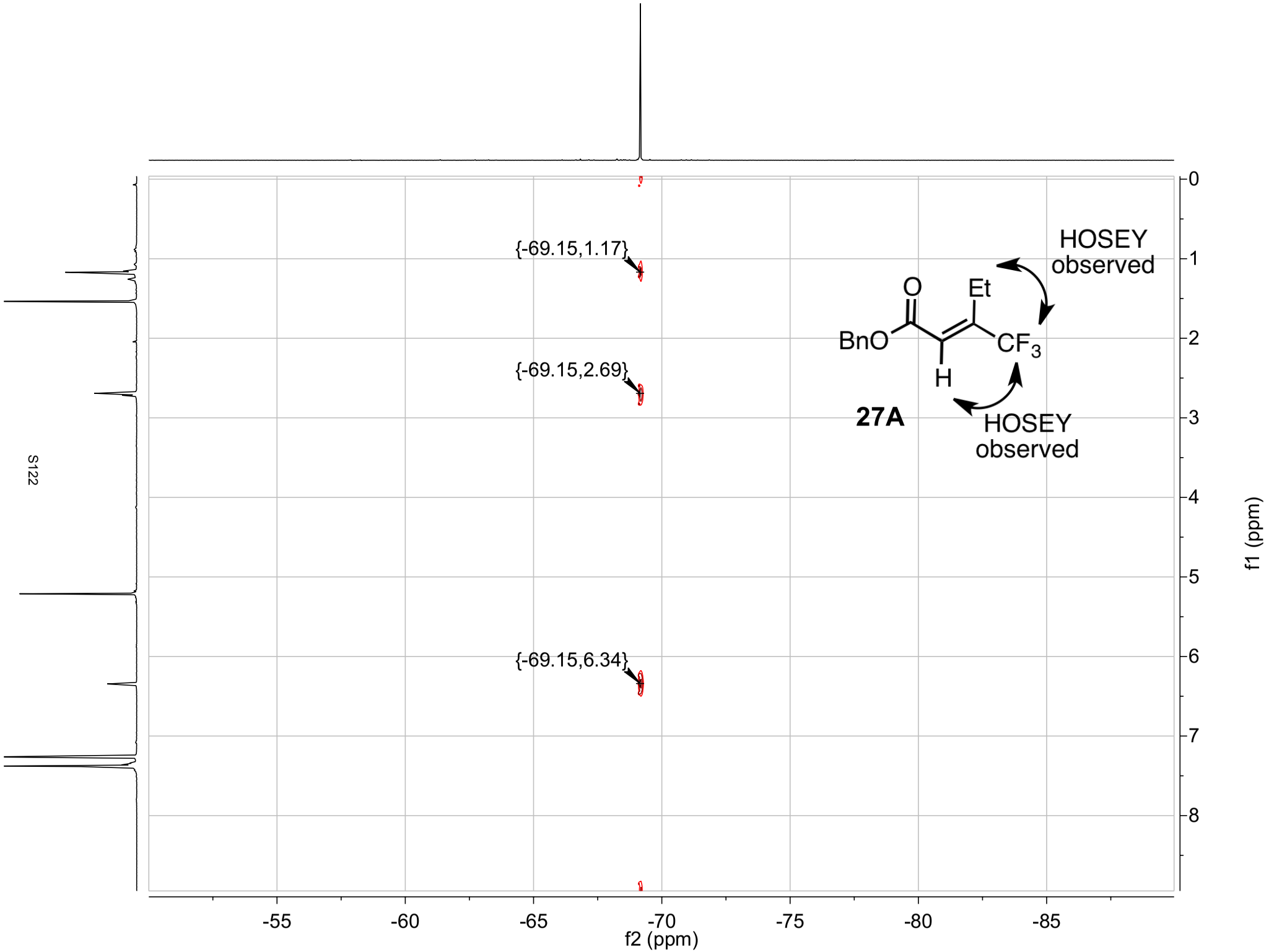


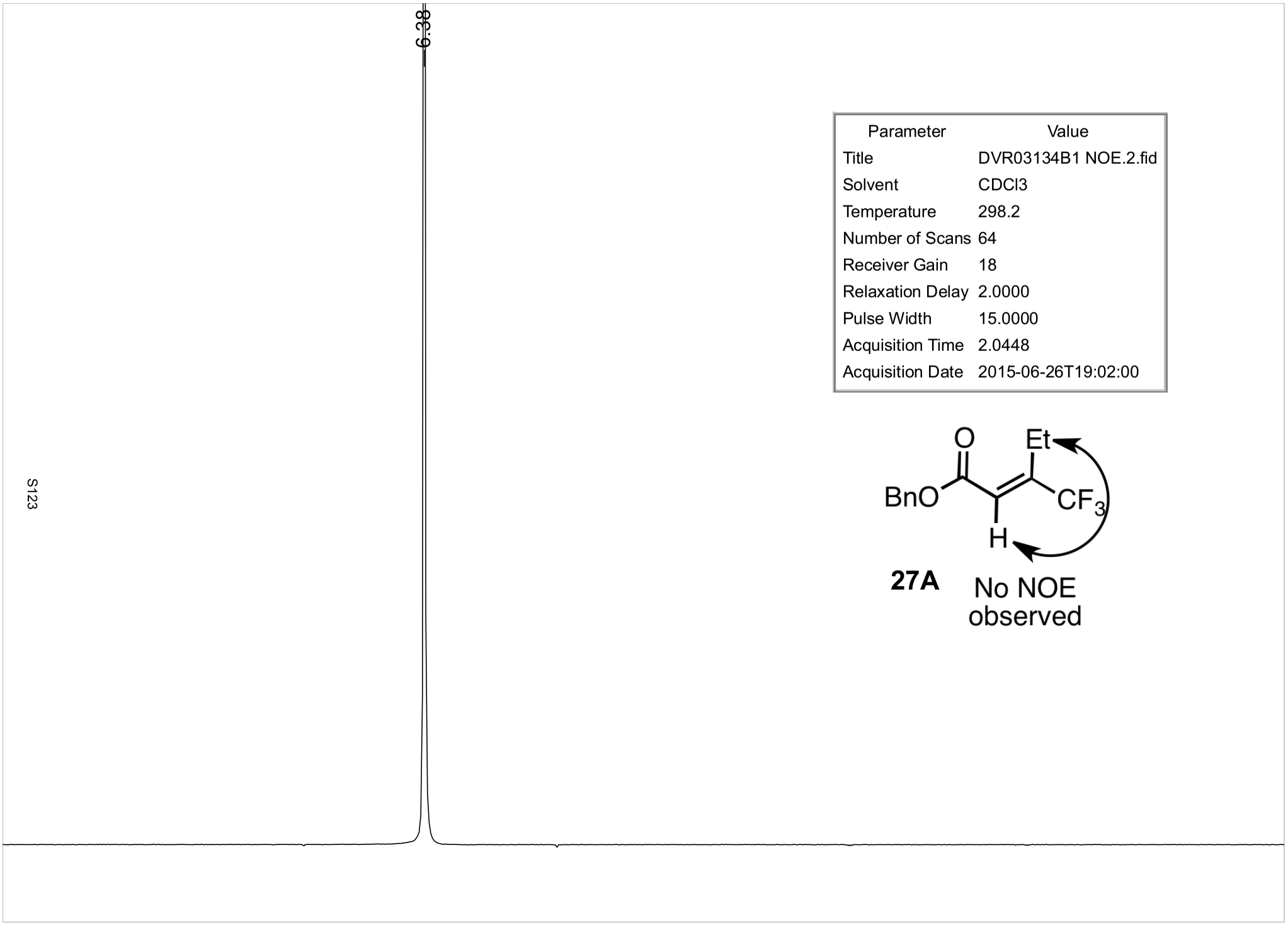


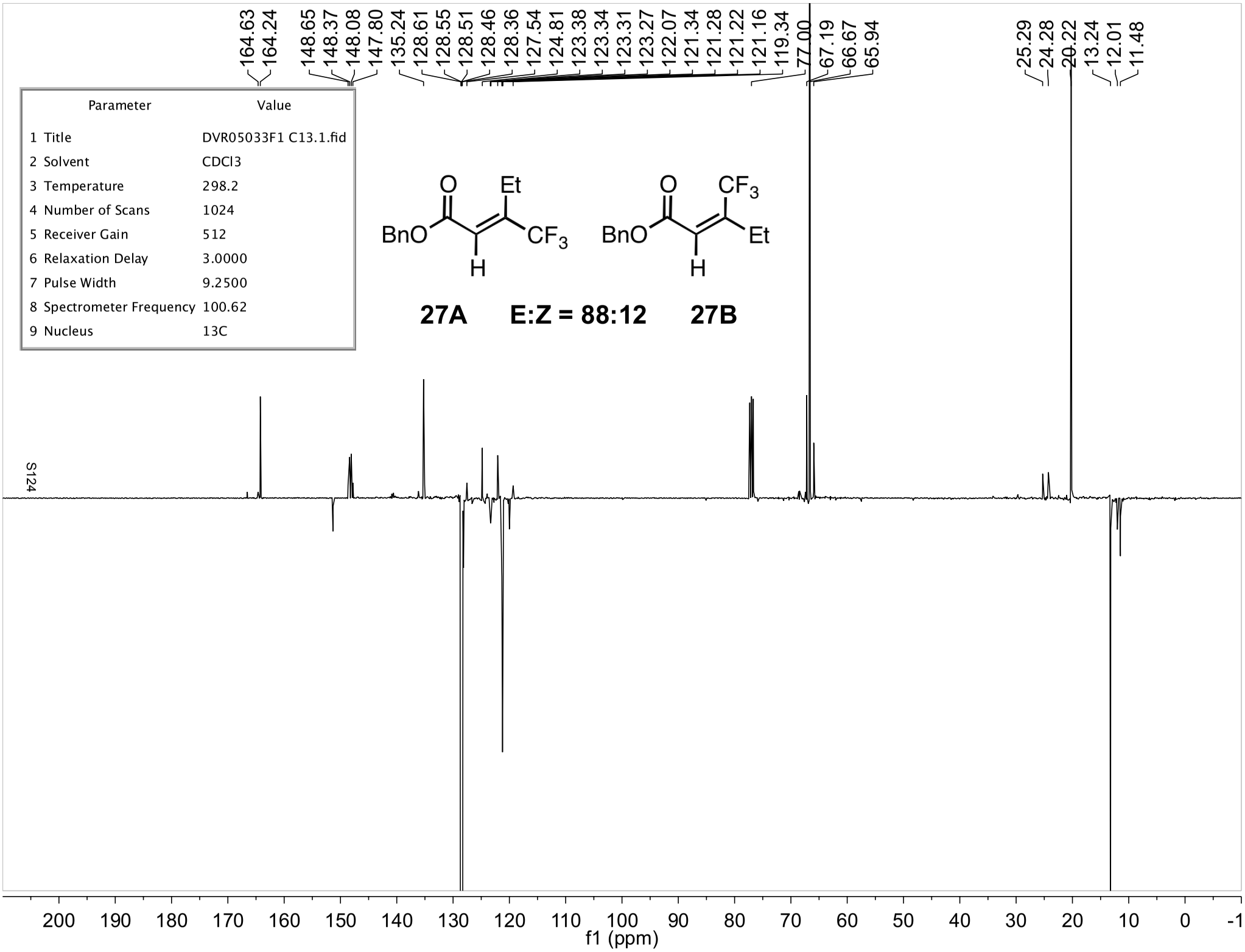

7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
6.35
5.21
2.72
2.70
2.69
2.68
1.18
1.17
1.16
Parameter Value
Title DVR03134B1.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 228
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-04T12:29:00
O
Et
BnO
CF3
H
27A
S119
5.00
0.93
1.95
2.16
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

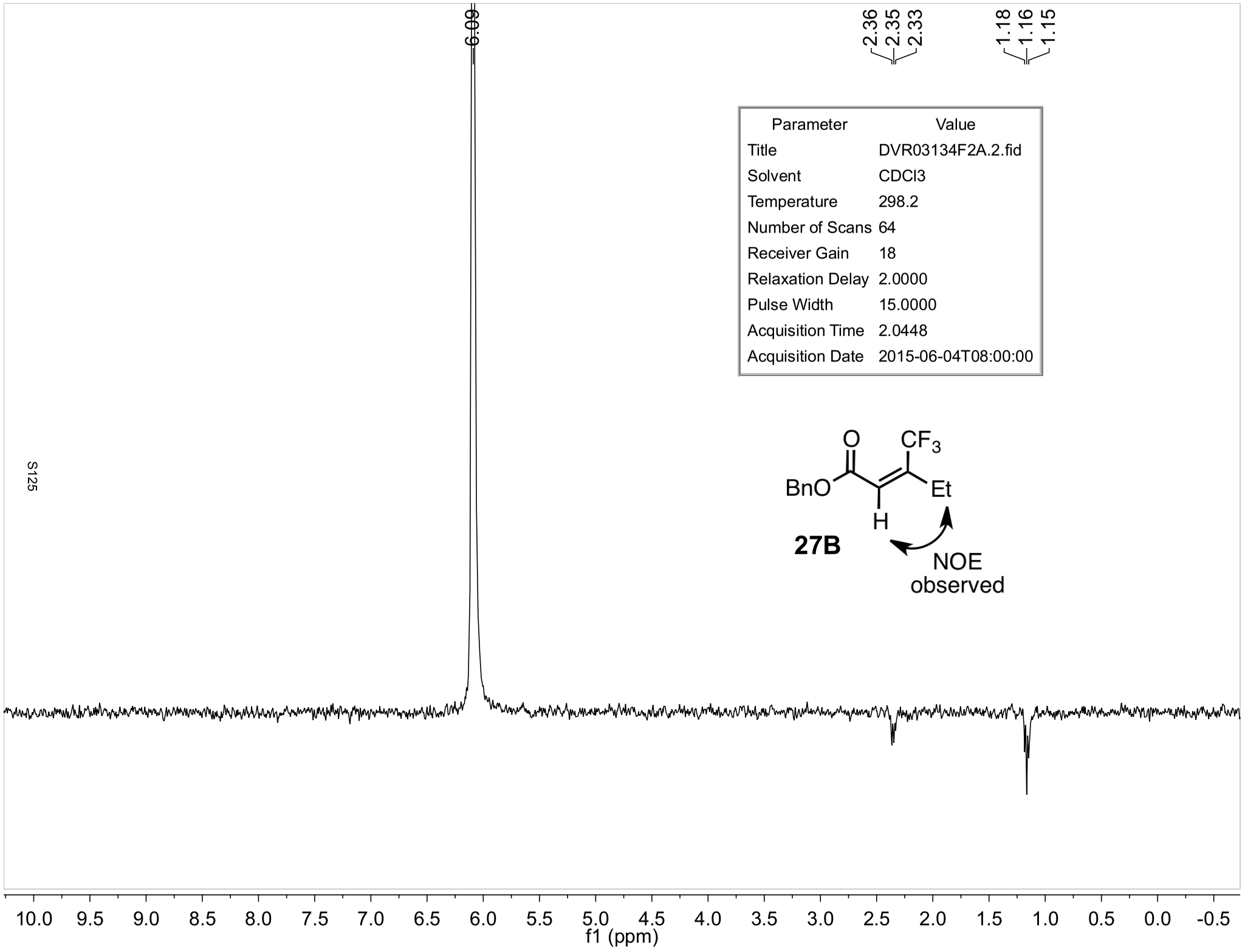

164.47
148.69
148.50
148.31
148.12
135.46
128.82
128.67
128.54
126.37
124.55
122.72
121.54
121.50
121.46
121.42
120.90
66.89
62.15
20.43
13.42
S120
148.69
148.50
148.31
148.12
148.7
148.5
148.3
148.1
f1 (ppm)
Parameter Value
Title DVR03134B1C13.1.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-11T06:30:00
O
Et
BnO
CF3
H
27A
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

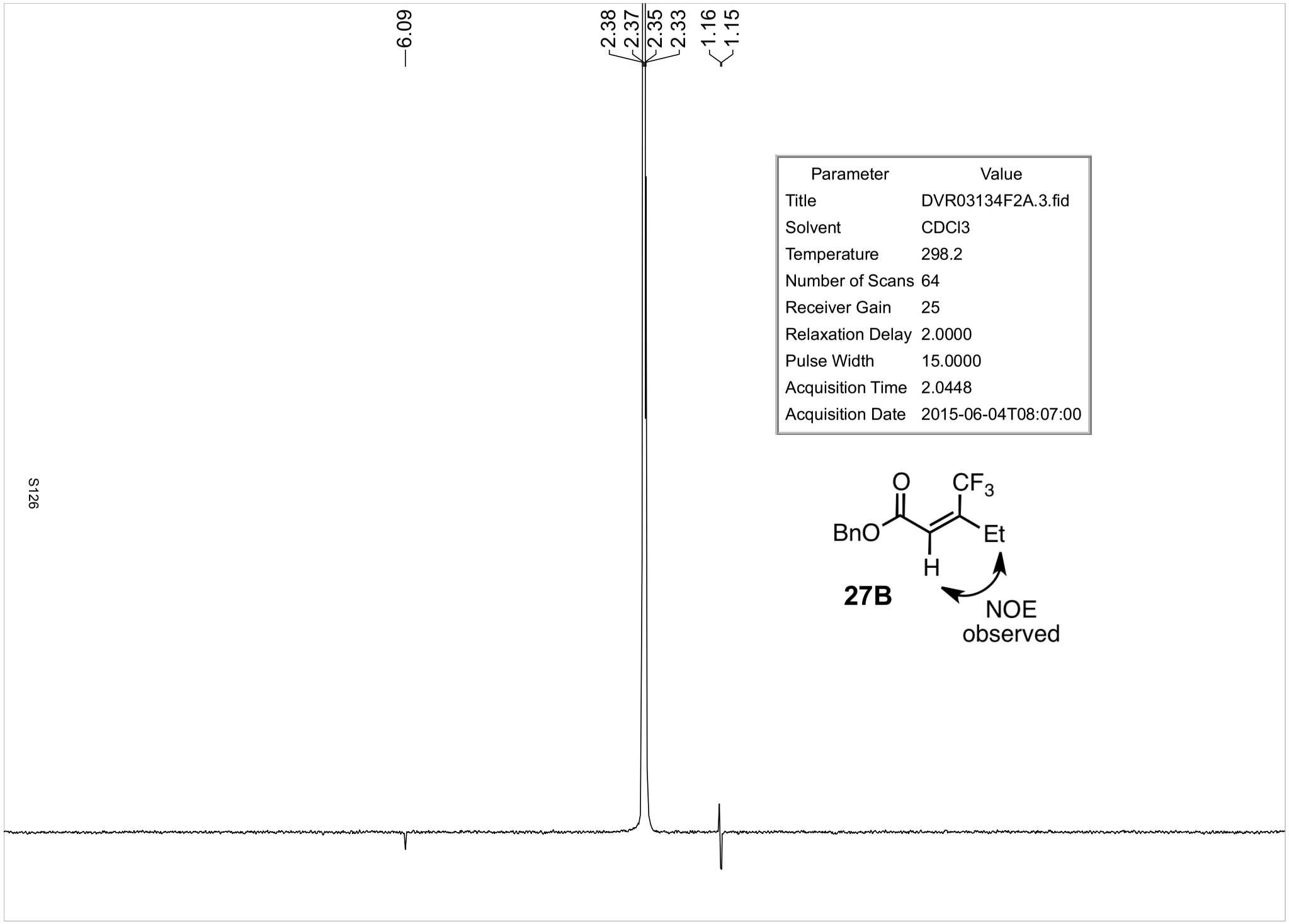

-69.17
Parameter Value
Title DVR03134B1.2.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 362
Relaxation Delay 3.0000
Pulse Width 11.6200
Acquisition Time 0.4893
Acquisition Date 2015-06-04T12:32:00
O
Et
BnO
CF3
H
27A
-5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95
f1 (ppm)


{-69.15,1.17}
{-69.15,2.69}
{-69.15,6.34}
HOSEY observed
O
Et
BnO
CF3
H
27A
HOSEY observed
S122
-55
-60
-65
-70
-75
-80
-85
f2 (ppm)
0
1
2
3
4
5
6
7
8
f1 (ppm)


6.38
S123
Parameter Value
Title DVR03134B1 NOE.2.fid
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 18
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-26T19:02:00
O
Et
BnO
CF3
H
27A
No NOE observed
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


164.63
164.24
148.65
148.37
148.08
147.80
135.24
128.61
128.55
128.51
128.46
128.36
127.54
124.81
123.38
123.34
123.31
123.27
122.07
121.34
121.28
121.22
121.16
119.34
77.00
67.19
66.67
65.94
25.29
24.28
20.22
13.24
12.01
11.48
Parameter Value
1 Title DVR05033F1 C13.1.fid
2 Solvent CDCl3
3 Temperature 298.2
4 Number of Scans 1024
5 Receiver Gain 512
6 Relaxation Delay 3.0000
7 Pulse Width 9.2500
8 Spectrometer Frequency 100.62
9 Nucleus 13C
O
Et
BnO
CF3
H
O
CF3
BnO
Et
H
27A E:Z = 88:12 27B
S124
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

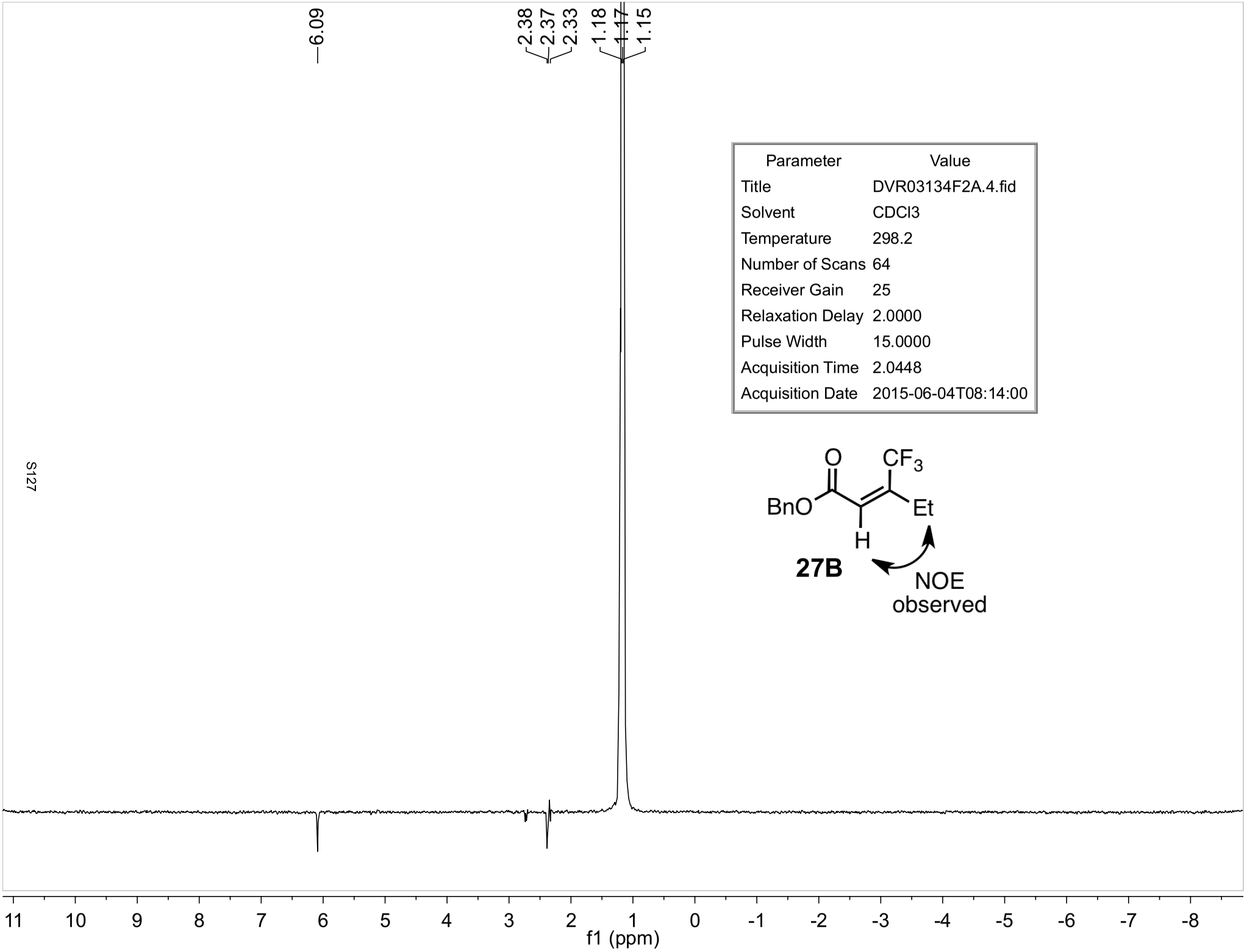

6.09
2.36
2.35
2.33
1.18
1.16
1.15
Parameter Value
Title DVR03134F2A.2.fid
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 18
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-04T08:00:00
O
CF3
BnO
Et
H
27B
NOE
observed
S125
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

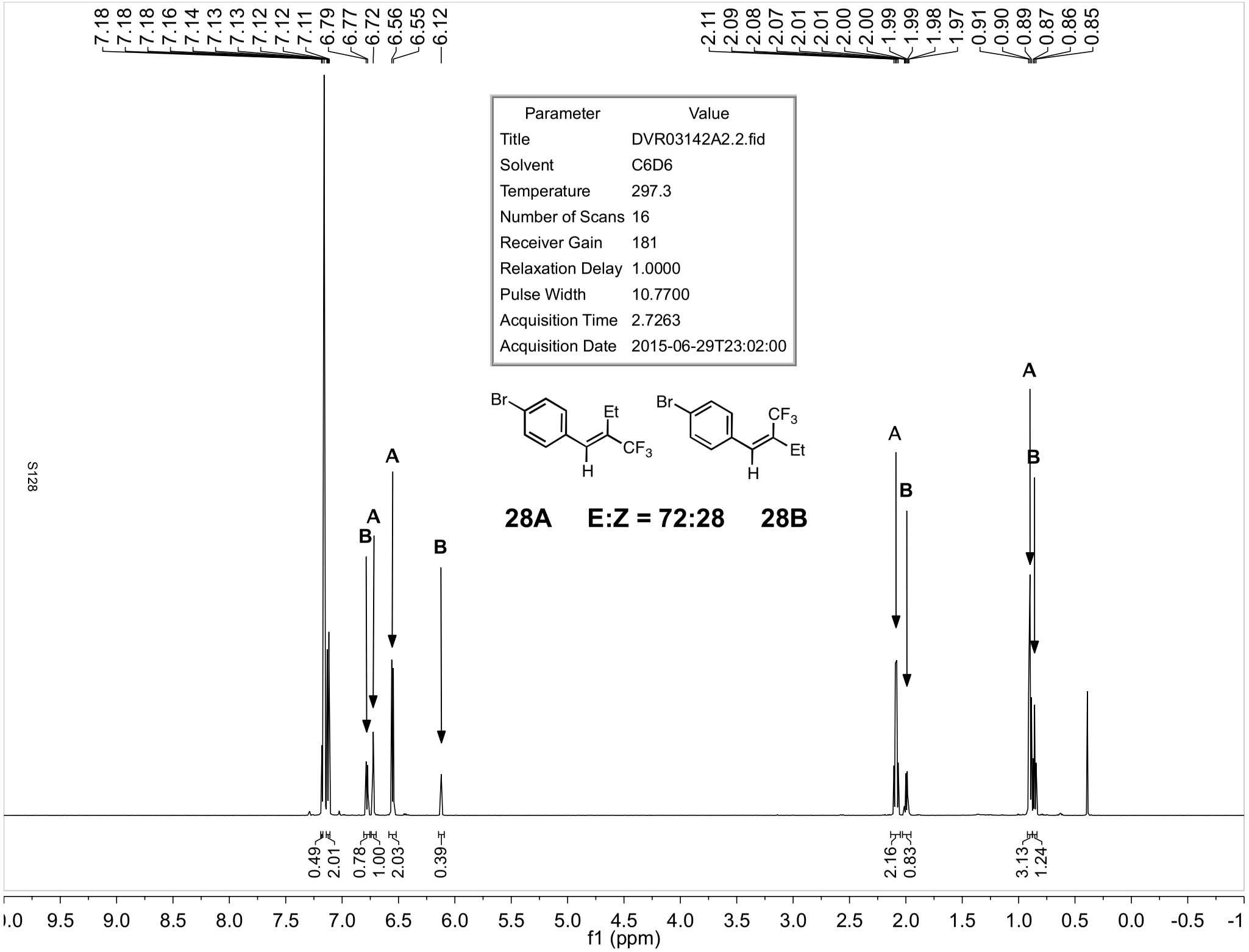


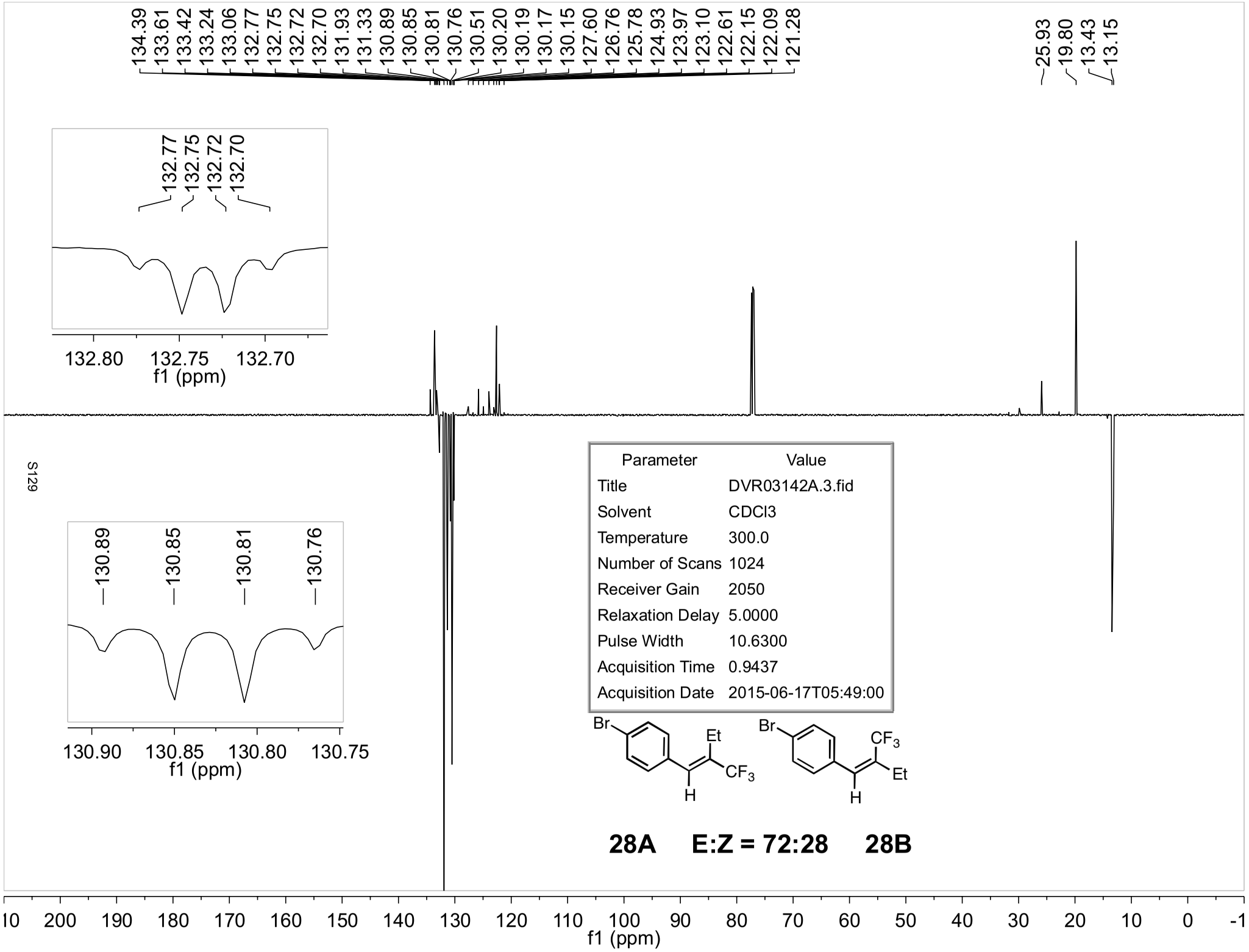
Parameter	Value
Title	DVR03134F2A.3.fid
Solvent	CDCl3
Temperature	298.2
Number of Scans	64
Receiver Gain	25
Relaxation Delay	2.0000
Pulse Width	15.0000
Acquisition Time	2.0448
Acquisition Date	2015-06-04T08:07:00

27B

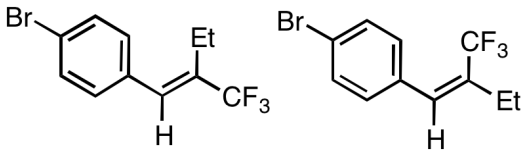
NOE observed


6.09
2.38
2.37
2.33
1.18
1.17
1.15
S127
Parameter Value
Title DVR03134F2A.4.fid
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 25
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-04T08:14:00
O
CF3
BnO
Et
H
27B
NOE
observed
11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8
f1 (ppm)

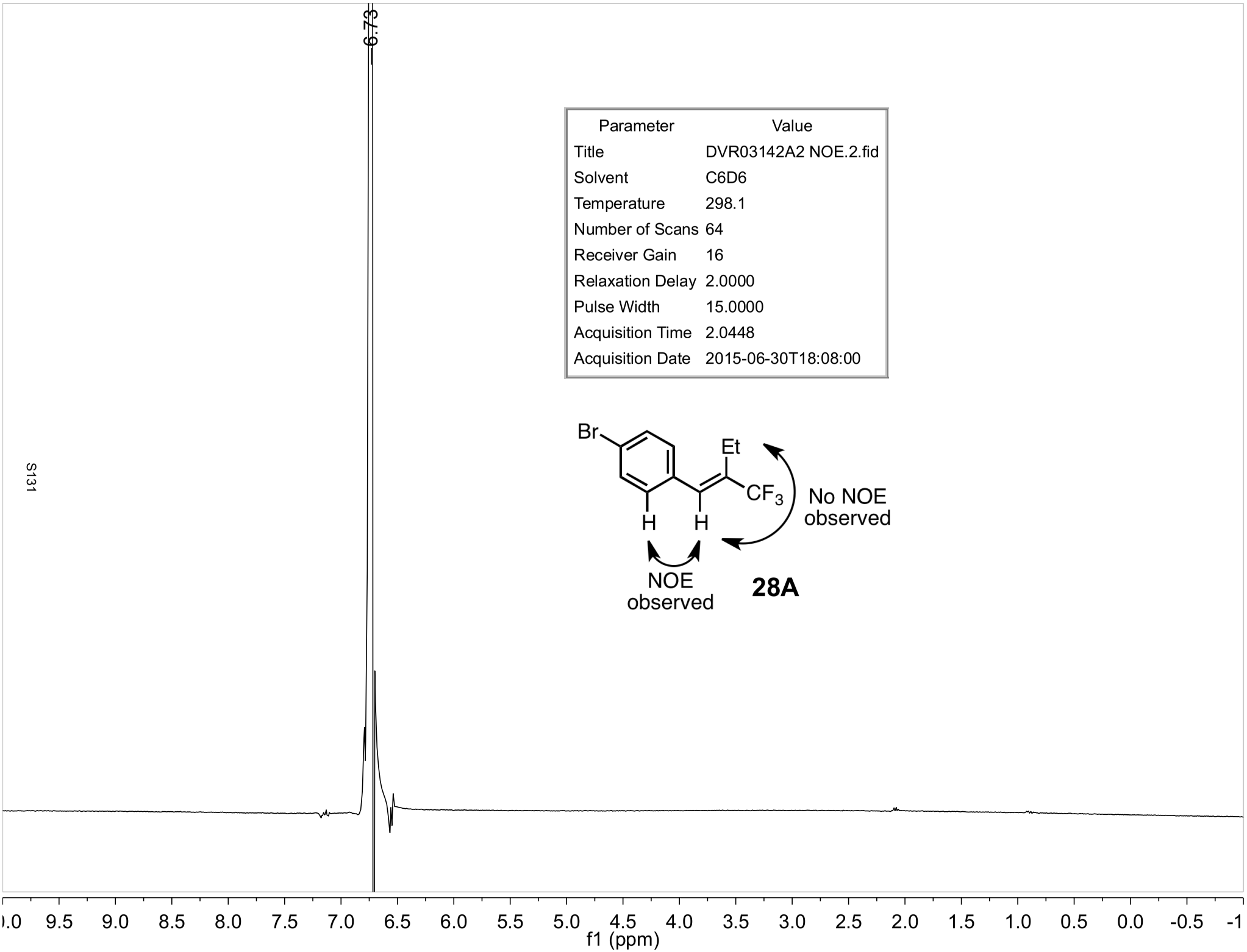

7.18 7.18 7.18 7.16 7.14 7.13 7.13 7.12 7.12 7.11 6.79 6.77 6.72 6.56 6.55 6.12
2.11 2.09 2.08 2.07 2.01 2.01 2.00 2.00 1.99 1.99 1.98 1.97 0.91 0.90 0.89 0.87 0.86 0.85
Parameter Value
Title DVR03142A2.2.fid
Solvent C6D6
Temperature 297.3
Number of Scans 16
Receiver Gain 181
Relaxation Delay 1.0000
Pulse Width 10.7700
Acquisition Time 2.7263
Acquisition Date 2015-06-29T23:02:00
Br Et CF3 H
Br CF3 Et H
28A E:Z = 72:28 28B
A B A B A B A B
0.49 2.01 0.78 1.00 2.03 0.39 2.16 0.83 3.13 1.24
S128
f1 (ppm)

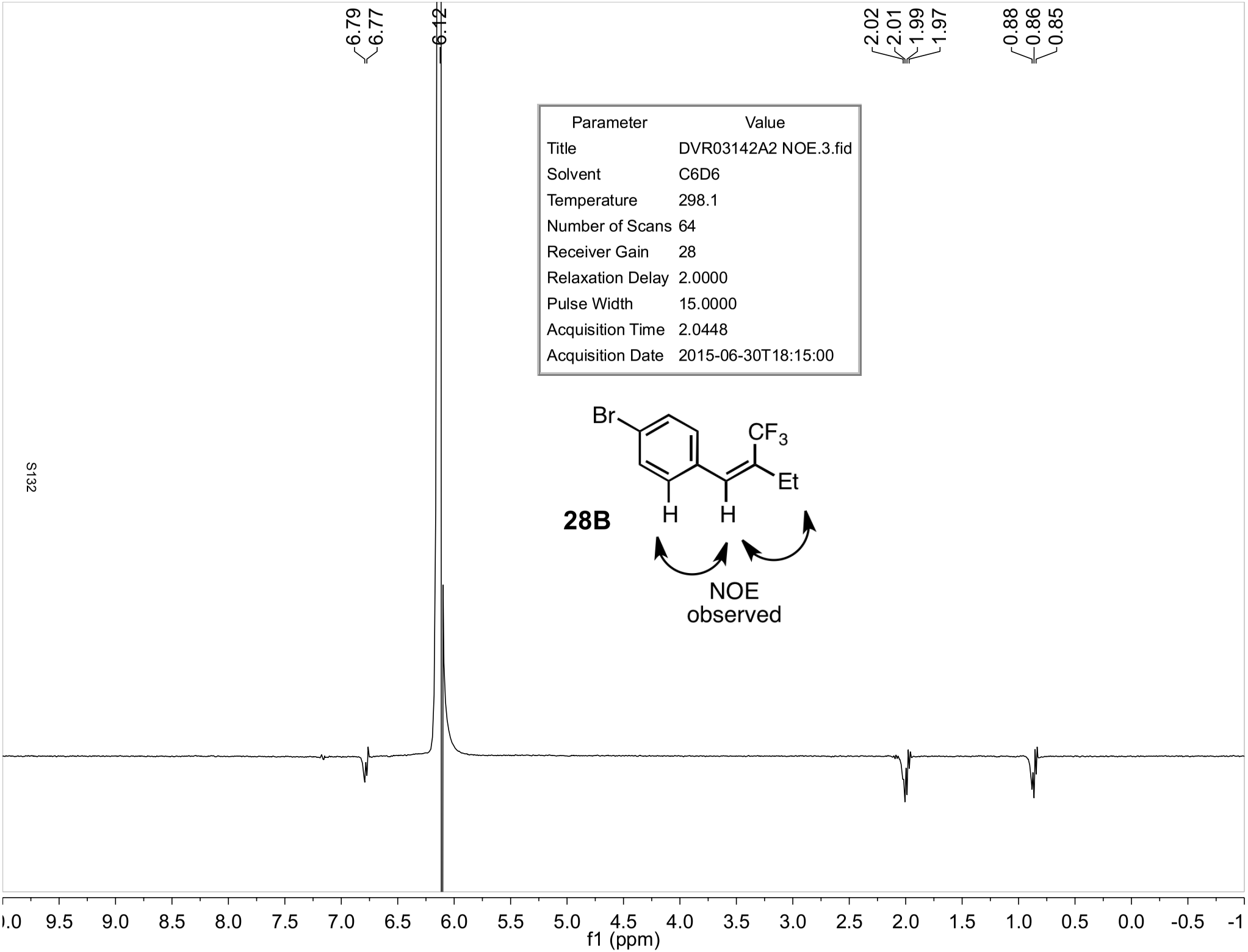

134.39
133.61
133.42
133.24
133.06
132.77
132.75
132.72
132.70
131.93
131.33
130.89
130.85
130.81
130.76
130.51
130.20
130.19
130.17
130.15
127.60
126.76
125.78
124.93
123.97
123.10
122.61
122.15
122.09
121.28
25.93
19.80
13.43
13.15
132.77
132.75
132.72
132.70
132.80
132.75
132.70
f1 (ppm)
S129
130.89
130.85
130.81
130.76
130.90
130.85
130.80
130.75
f1 (ppm)
Parameter Value
Title DVR03142A.3.fid
Solvent CDCl3
Temperature 300.0
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Acquisition Time 0.9437
Acquisition Date 2015-06-17T05:49:00
Br
Et
CF3
H
Br
CF3
Et
H
28A E:Z = 72:28 28B
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

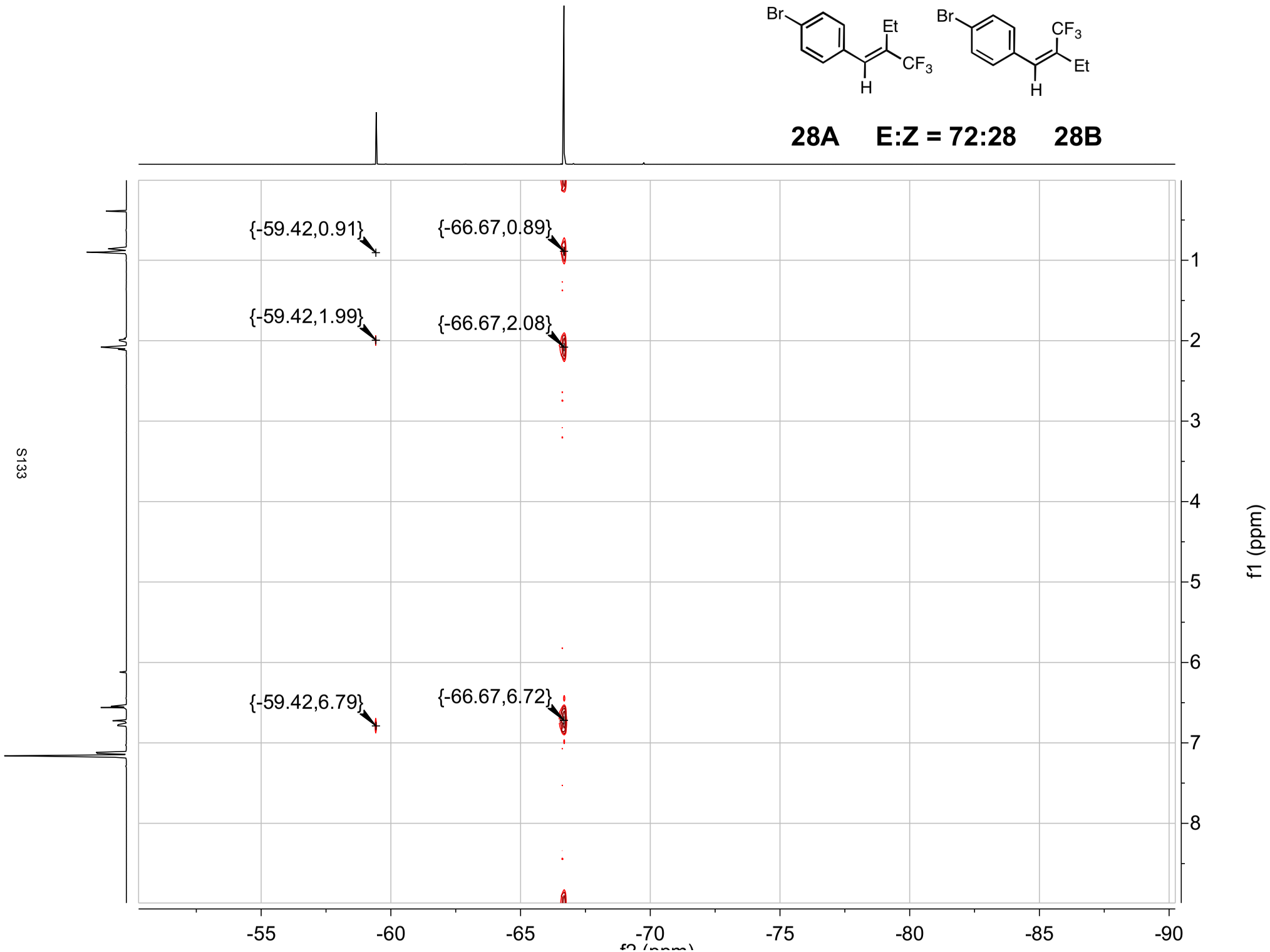
Parameter	Value
Title	DVR03142A.2.fid
Solvent	CDCl3
Temperature	300.0
Number of Scans	16
Receiver Gain	181
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-06-16T16:16:00

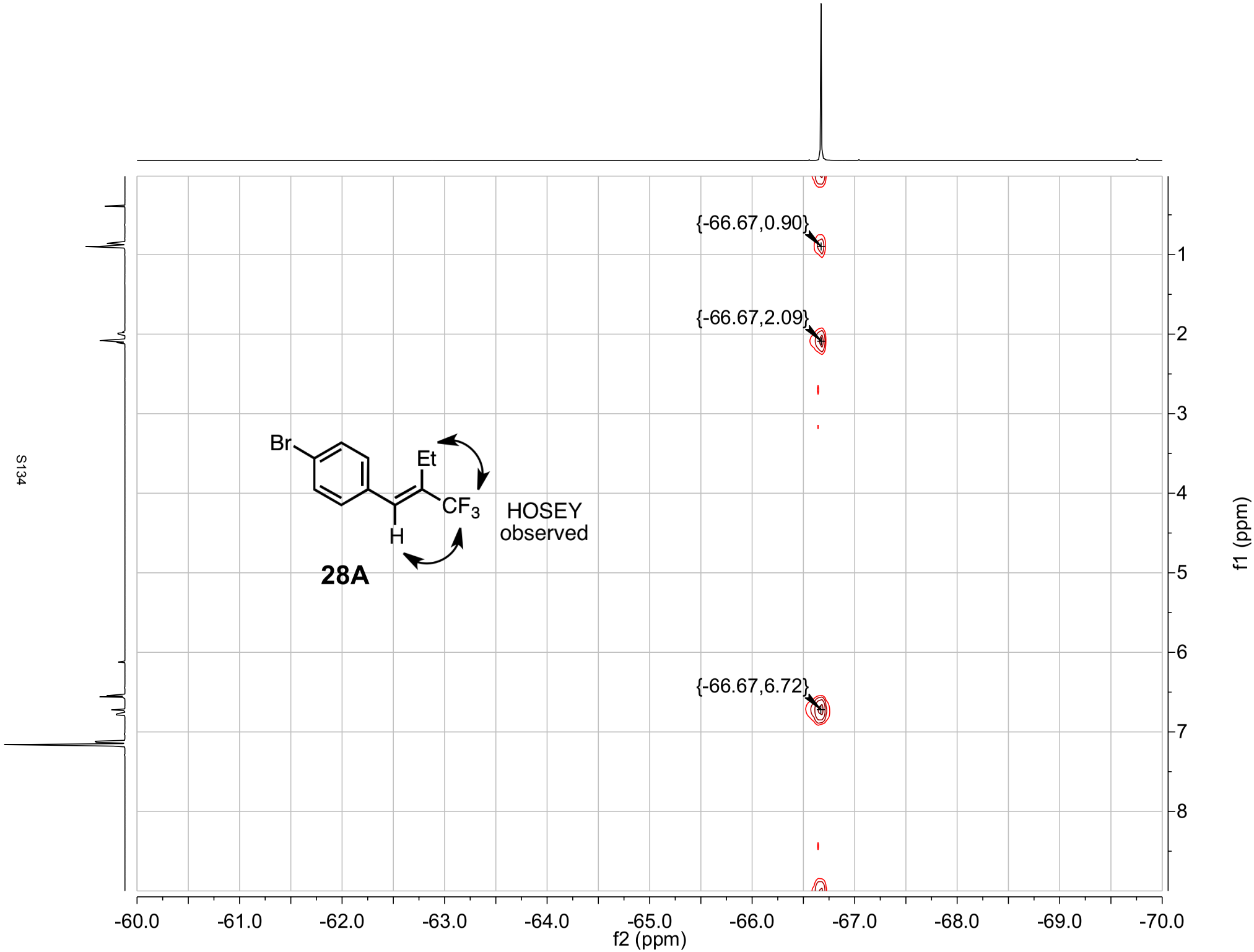


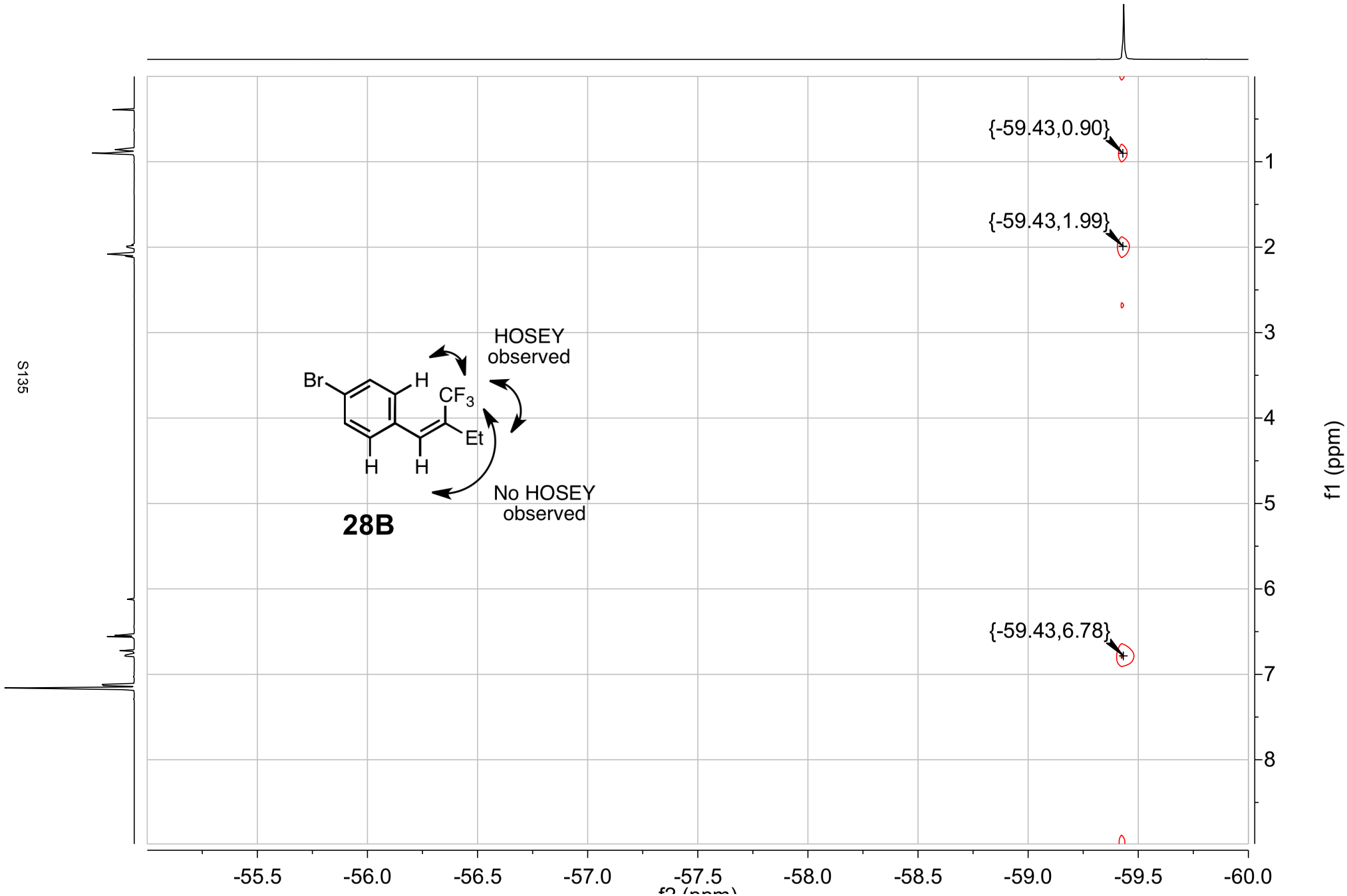
28A E:Z = 72:28 28B

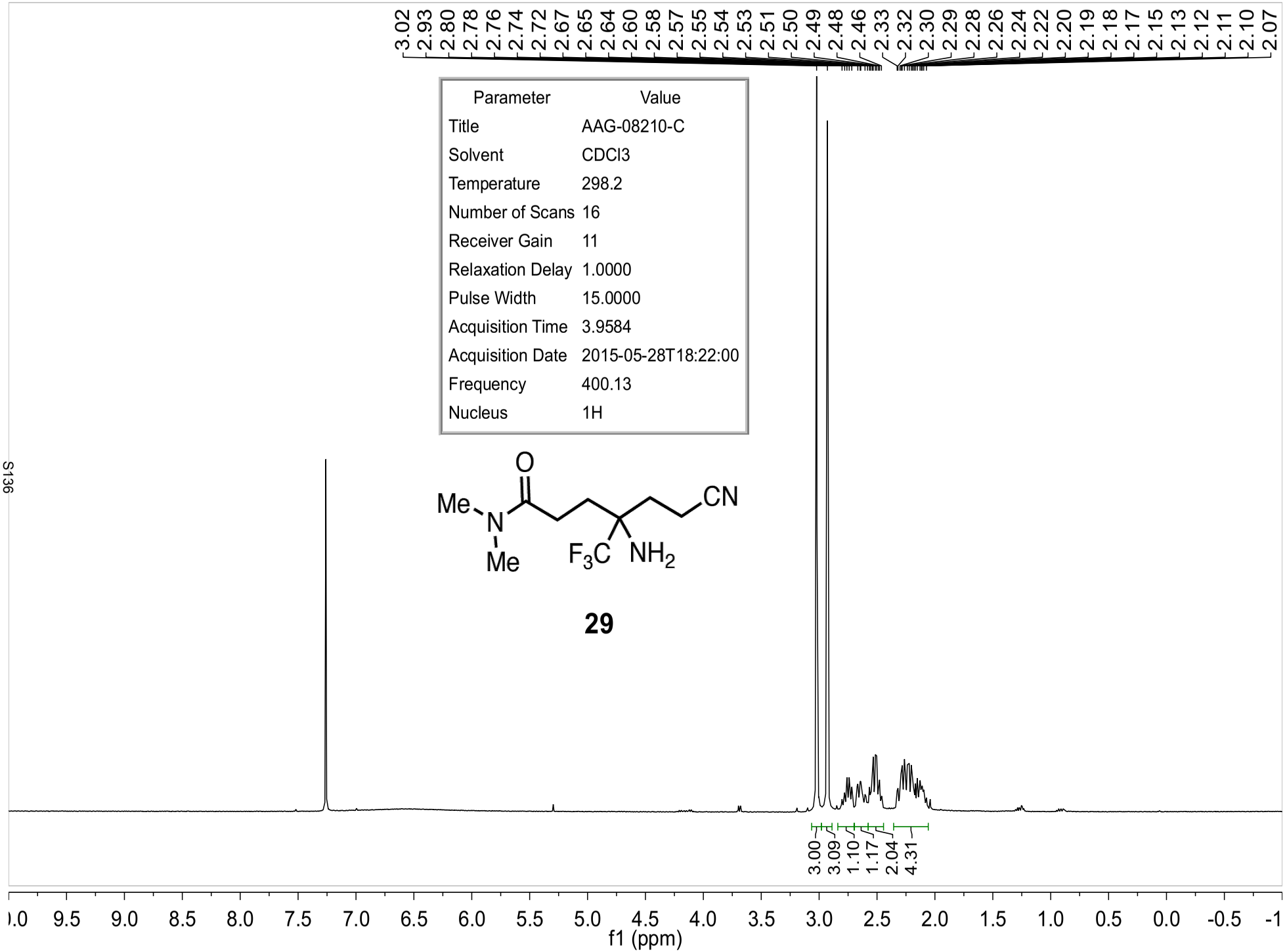

6.73
S131
Parameter Value
Title DVR03142A2 NOE.2.fid
Solvent C6D6
Temperature 298.1
Number of Scans 64
Receiver Gain 16
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-30T18:08:00
Br
Et
CF3
H
H
No NOE observed
NOE observed
28A
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

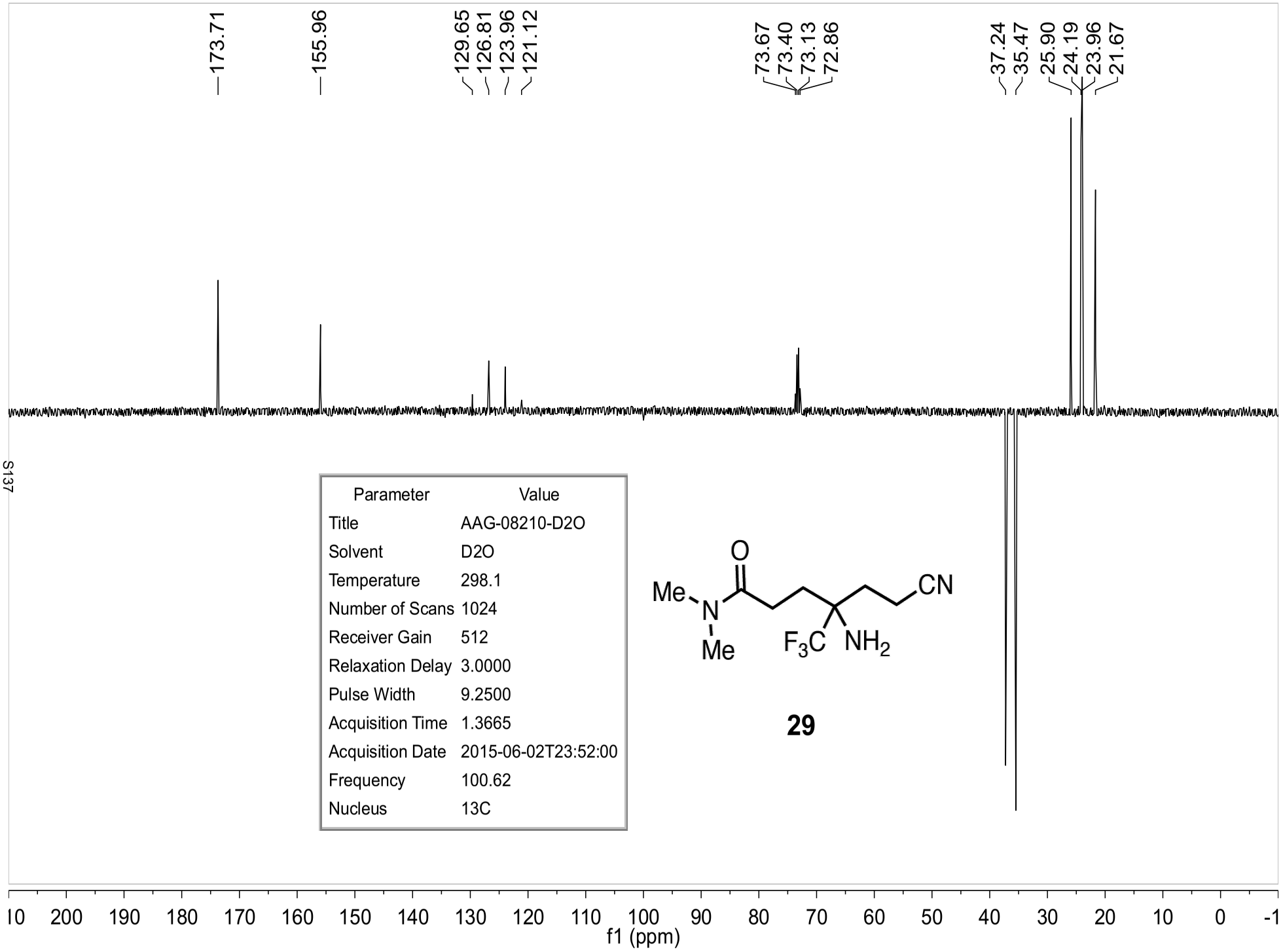

6.79
6.77
6.12
2.02
2.01
1.99
1.97
0.88
0.86
0.85
Parameter Value
Title DVR03142A2 NOE.3.fid
Solvent C6D6
Temperature 298.1
Number of Scans 64
Receiver Gain 28
Relaxation Delay 2.0000
Pulse Width 15.0000
Acquisition Time 2.0448
Acquisition Date 2015-06-30T18:15:00
Br
CF3
Et
H
H
28B
NOE
observed
S132
f1 (ppm)


Br
Et
CF3
H
Br
CF3
Et
H
28A E:Z = 72:28 28B
{-59.42,0.91}
{-66.67,0.89}
{-59.42,1.99}
{-66.67,2.08}
{-59.42,6.79}
{-66.67,6.72}
-55
-60
-65
-70
-75
-80
-85
-90
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

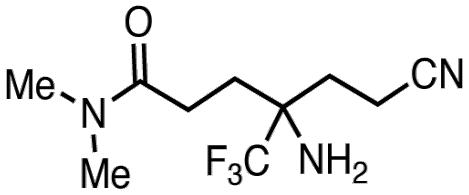

{-66.67,0.90}
{-66.67,2.09}
{-66.67,6.72}
Br
Et
CF3
H
HOSEY
observed
28A
-60.0
-61.0
-62.0
-63.0
-64.0
-65.0
-66.0
-67.0
-68.0
-69.0
-70.0
f2 (ppm)
f1 (ppm)
1
2
3
4
5
6
7
8


{-59.43,0.90}
{-59.43,1.99}
{-59.43,6.78}
HOSEY
observed
No HOSEY
observed
Br
H
CF3
Et
H
H
28B
-55.5
-56.0
-56.5
-57.0
-57.5
-58.0
-58.5
-59.0
-59.5
-60.0
f2 (ppm)
1
2
3
4
5
6
7
8
f1 (ppm)

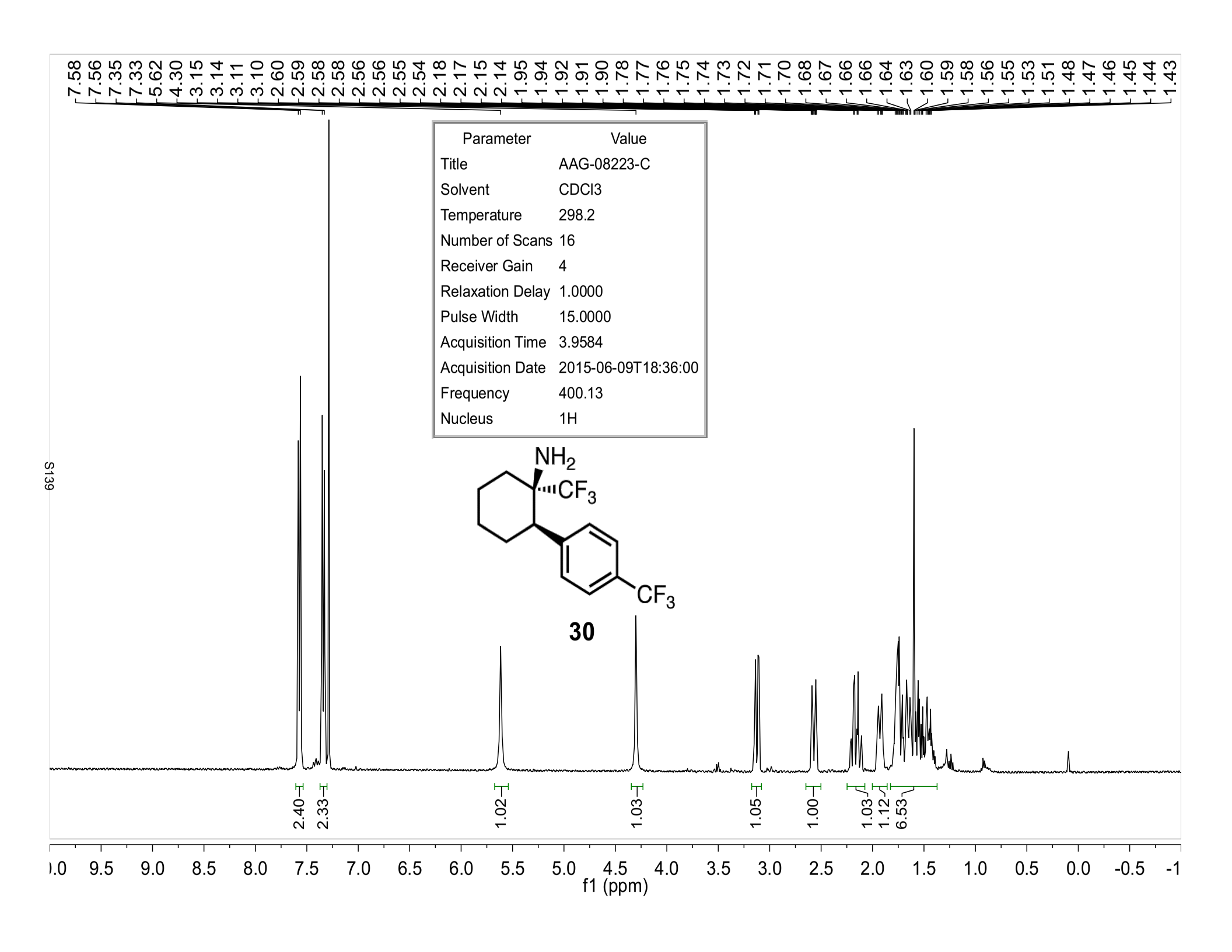

3.02 2.93 2.80 2.78 2.76 2.74 2.72 2.67 2.65 2.64 2.60 2.58 2.57 2.55 2.54 2.53 2.51 2.50 2.49 2.48 2.46 2.33 2.32 2.30 2.29 2.28 2.26 2.24 2.22 2.20 2.19 2.18 2.17 2.15 2.13 2.12 2.11 2.10 2.07
Parameter Value
Title AAG-08210-C
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-05-28T18:22:00
Frequency 400.13
Nucleus 1H
O
Me
N
Me
CN
F3C
NH2
29
3.00 3.09 1.10 1.17 2.04 4.31
f1 (ppm)

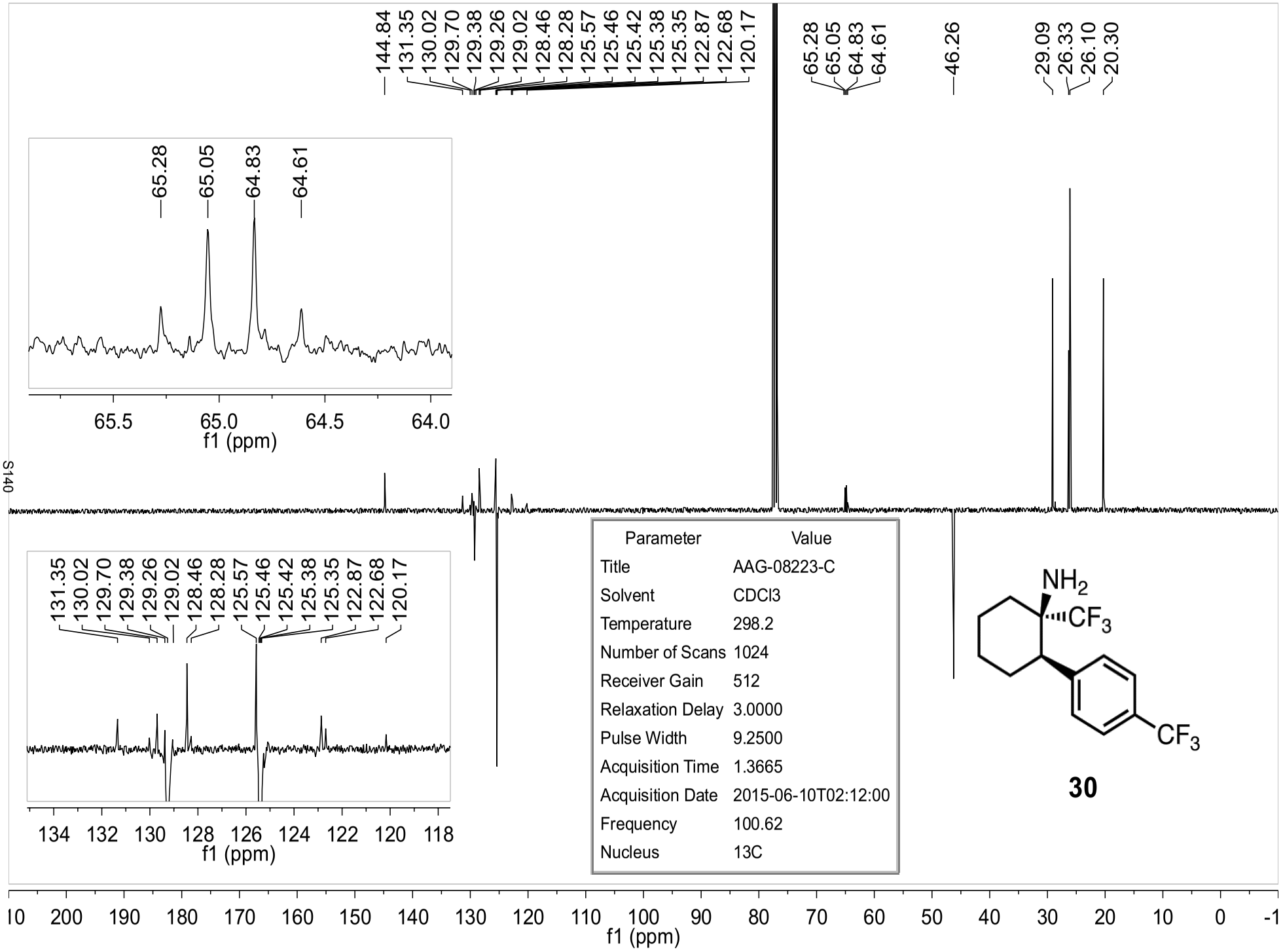

173.71
155.96
129.65
126.81
123.96
121.12
73.67
73.40
73.13
72.86
37.24
35.47
25.90
24.19
23.96
21.67
S137
Parameter Value
Title AAG-08210-D2O
Solvent D2O
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-06-02T23:52:00
Frequency 100.62
Nucleus 13C
O
Me
N
Me
F3C
NH2
CN
29
f1 (ppm)

Parameter	Value
Title	AAG-08210-C
Solvent	CDCl3
Temperature	298.2
Number of Scans	16
Receiver Gain	1626
Relaxation Delay	2.0000
Pulse Width	15.0300
Acquisition Time	0.8717
Acquisition Date	2015-05-28T18:25:00
Frequency	376.46
Nucleus	19F

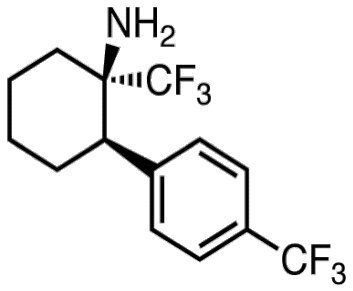


29

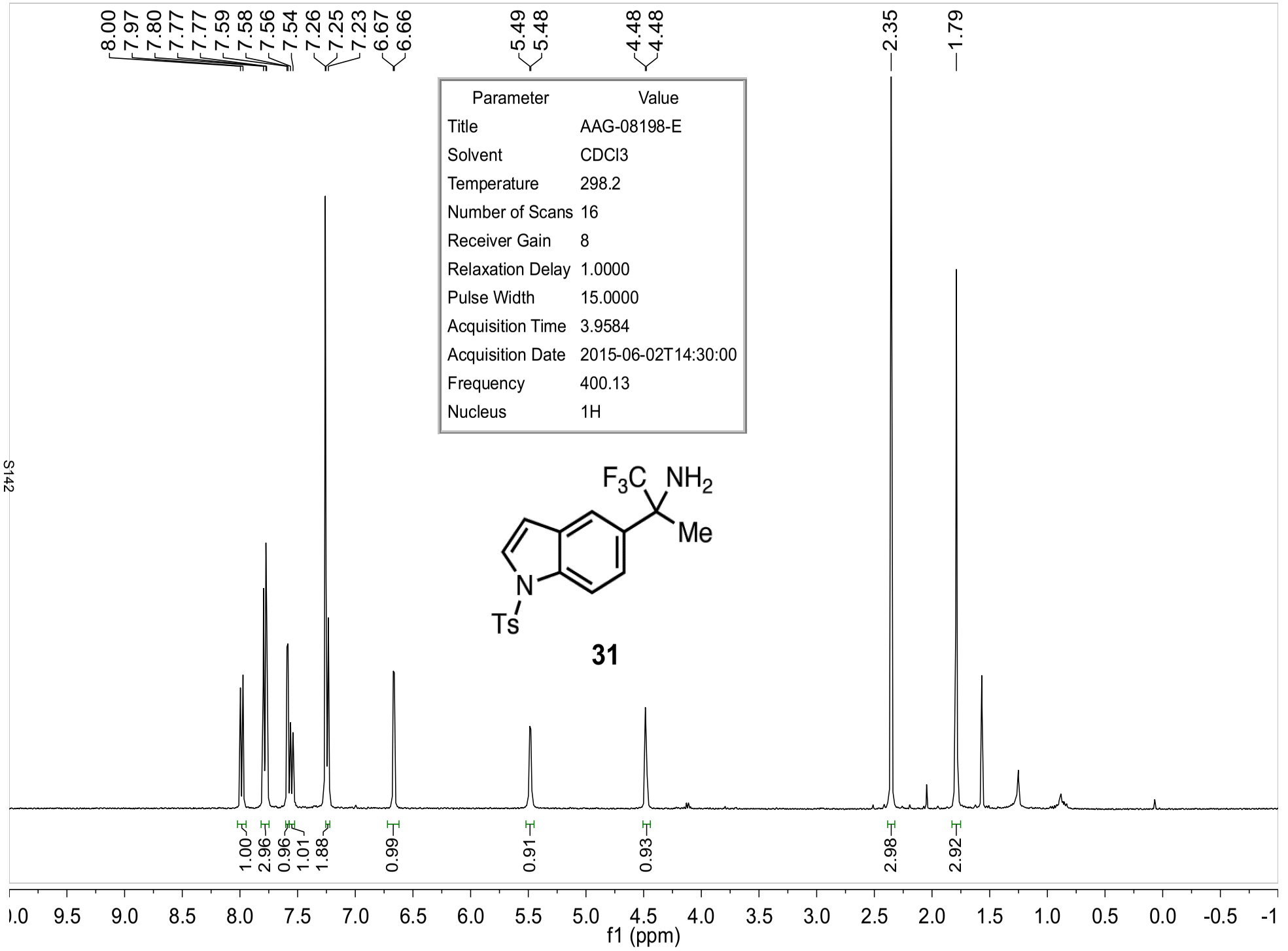

7.58 7.56 7.35 7.33 5.62 4.30 3.15 3.14 3.11 3.10 2.60 2.59 2.58 2.58 2.56 2.56 2.55 2.54 2.18 2.17 2.15 2.14 1.95 1.94 1.92 1.91 1.90 1.78 1.77 1.76 1.75 1.74 1.73 1.72 1.71 1.70 1.68 1.67 1.66 1.66 1.64 1.63 1.60 1.59 1.58 1.56 1.55 1.53 1.51 1.48 1.47 1.46 1.45 1.44 1.43
Parameter Value
Title AAG-08223-C
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 4
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-06-09T18:36:00
Frequency 400.13
Nucleus 1H
NH2
CF3
CF3
30
S139
2.40
2.33
1.02
1.03
1.05
1.00
1.03
1.12
6.53
f1 (ppm)

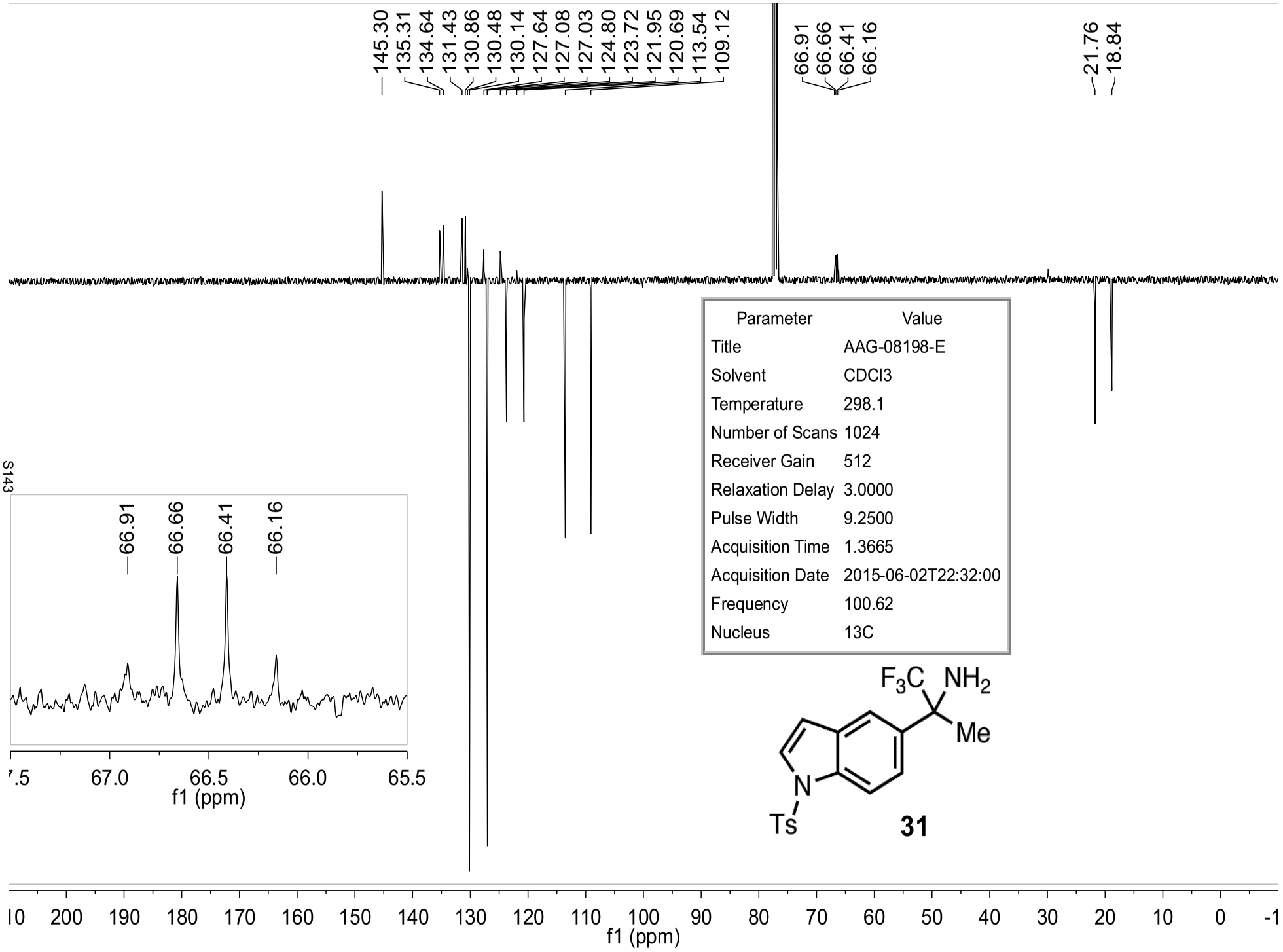

144.84
131.35
130.02
129.70
129.38
129.26
129.02
128.46
128.28
125.57
125.46
125.42
125.38
125.35
122.87
122.68
120.17
65.28
65.05
64.83
64.61
46.26
29.09
26.33
26.10
20.30
65.28
65.05
64.83
64.61
65.5
65.0
64.5
64.0
f1 (ppm)
131.35
130.02
129.70
129.38
129.26
129.02
128.46
128.28
125.57
125.46
125.42
125.38
125.35
122.87
122.68
120.17
134 132 130 128 126 124 122 120 118
f1 (ppm)
Parameter Value
Title AAG-08223-C
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-06-10T02:12:00
Frequency 100.62
Nucleus 13C
NH2
CF3
CF3
30
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

Parameter	Value
Title	AAG-07223-B
Solvent	CDCl3
Temperature	298.0
Number of Scans	16
Receiver Gain	362
Relaxation Delay	3.0000
Pulse Width	11.6200
Acquisition Time	0.4893
Acquisition Date	2015-03-18T19:13:00
Frequency	564.81
Nucleus	19F

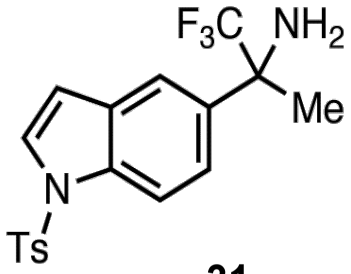


30


8.00
7.97
7.80
7.77
7.77
7.59
7.58
7.56
7.54
7.26
7.25
7.23
6.67
6.66
5.49
5.48
4.48
4.48
2.35
1.79
Parameter Value
Title AAG-08198-E
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Acquisition Time 3.9584
Acquisition Date 2015-06-02T14:30:00
Frequency 400.13
Nucleus 1H
F3C NH2
Me
N
Ts
31
S142
1.00
2.96
0.96
1.01
1.88
0.99
0.91
0.93
2.98
2.92
f1 (ppm)


145.30
135.31
134.64
131.43
130.86
130.48
130.14
127.64
127.08
127.03
124.80
123.72
121.95
120.69
113.54
109.12
66.91
66.66
66.41
66.16
21.76
18.84
Parameter Value
Title AAG-08198-E
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Acquisition Time 1.3665
Acquisition Date 2015-06-02T22:32:00
Frequency 100.62
Nucleus 13C
f1 (ppm)
F3C NH2
Me
N
Ts
31

Parameter	Value
Title	AAG-08198-E
Solvent	CDCl3
Temperature	298.1
Number of Scans	16
Receiver Gain	1626
Relaxation Delay	2.0000
Pulse Width	15.0300
Acquisition Time	0.8717
Acquisition Date	2015-06-02T14:33:00
Frequency	376.46
Nucleus	19F



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