Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Fluorous Enzymatic Synthesis of Phosphatidylinositides

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This material contains Figures S1 and S2, Experimental protocols, and NMR spectra of key compounds (28 pages in total).

Fig. S1 Critical Micelle Concentration (CMC) of 1

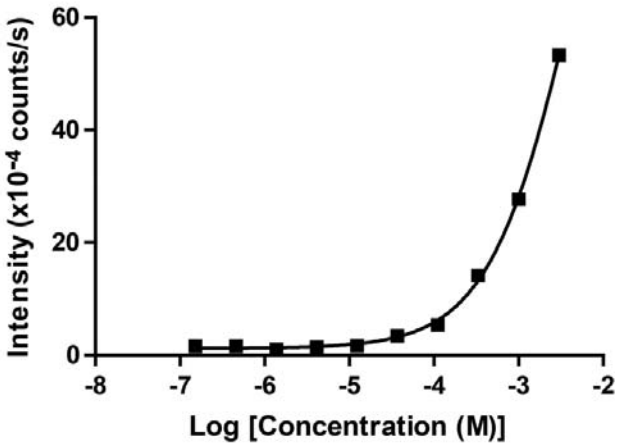
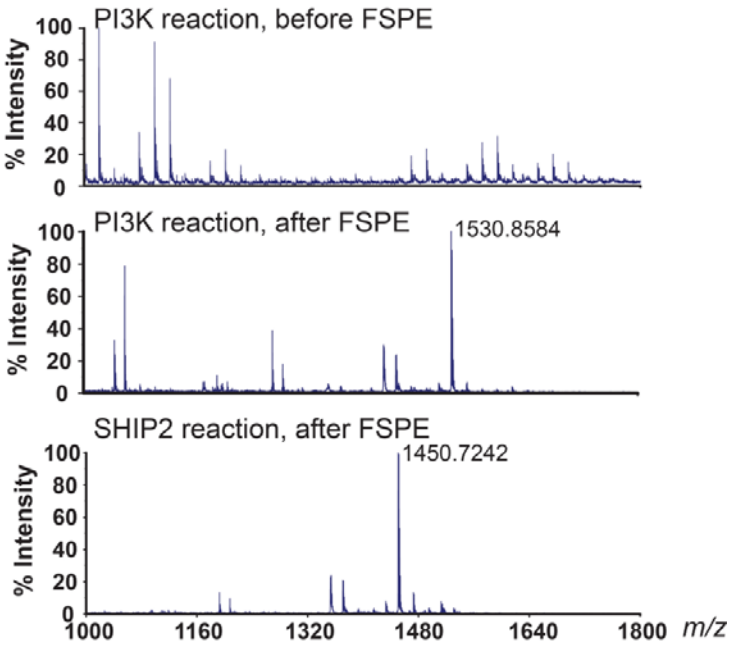


Fig. S2 Mass spectra of enzymatic products before and after FSPE



Experimental

General. Chemicals were purchased from Aldrich and Acros Chemical Corporation and used without further purification. Solvents were purchased from suppliers as anhydrous grade. The fluorous reversed-phase silica gel were purchased from Fluorous Technology or Sigma. NMR spectra were recorded at room temperature on Inova-400 MHz or Inova-500 MHz spectrometer. Chemical shifts are reported in ppm with TMS as the internal standard for ^{1}H NMR and 85% H_3PO_4 as the external standard for ^{31}P NMR spectra. Mass spectra were obtained on AB Sciex 4800 Plus MALDI-TOF, Agilent Technologies 6110 Quadrupole LC/MS or Shimadzu LCMS-IT/TOF (High Resolution Mass Spec). Purified PI3K (PIK3CA/PIK3R1) was obtained from Invitrogen. Dynamic light scattering data were recorded on a Wyatt DynaPro dynamic light scattering plate reader. Purified SHIP2 phosphatase, PTEN phosphatase, and biotinylated phosphoinositides antibody were purchased from Echelon Biosciences Inc. Phospholipase C was obtained as a gift from Dr. John Sondek (University of North Carolina).

Compound 4

A mixture of compound **3** (120 mg, 0.26 mmol), fluorous acid **2** (157 mg, 0.31 mmol), DCC (64 mg, 0.31 mmol) and DMAP (15 mg, 0.12 mmol) in anhydrous CH_2Cl_2 (3 mL) was stirred at room temperature overnight. After removal of the solvent, the resulting residue was re-suspended in ethyl acetate, filtered, and concentrated under vacuum. The solids were filtered, while the liquid fraction was concentrated and purified by column chromatography (hexane: ethyl acetate = 3:1) to give the coupled product (221 mg, 90%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.37 (m, 5H), 7.23 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 5.18-5.28 (m, 1H), 5.08 (s, 2H), 4.89 (brs, 1H), 4.46 (AB, J_{AB} = 11.7 Hz, 2H), 4.34 (dd, J = 11.9, 3.8 Hz, 1H), 4.16 (dd, J = 11.9, 6.4 Hz, 1H), 3.79 (s, 3H), 3.54 (d, J = 5.6 Hz, 2H), 3.18 (q, J = 6.6 Hz, 2H), 2.22-2.35 (m, 4H), 1.95-2.12 (m, 2H), 1.53-1.67 (m, 6H), 1.43-1.53 (m, 2H), 1.23-1.41 (m, 14H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 173.15, 173.12,

159.41, 156.48, 136.82, 129.86, 129.37, 128.55, 128.13, 128.10, 113.89, 105.0-125.0 (m, C_6F_{13}) 73.02, 70.14, 67.98, 66.60, 62.88, 55.26, 40.91, 34.36, 33.93, 30.94 (t, J_{CF} = 22.3 Hz), 29.69, 29.43, 29.41, 29.31, 29.29, 29.16, 29.12, 26.24, 25.00, 24.50, 20.17; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -80.70 (t, *J* = 10.1 Hz), -114.43, -122.01, -122.95, -123.60, -126.22.

DDQ (43 mg, 0.19 mmol) was added to the solution of the coupling product as described above (85 mg, 0.09 mmol) in wet CH_2Cl_2 (2.0 mL) and the resulting reaction mixture was stirred at room temperature for 4 h. Additional CH_2Cl_2 was added followed by washing with 10% $NaHCO_3$ and saturated NaCl. The layers were separated and the organic phase was dried over $MgSO_4$ and concentrated under vacuum. Column purification (hexane: ethyl acetate = 2:1) of the residue gave the product **4** (73 mg, 98%) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27-7.39 (m, 5H), 5.05-5.19 (m, 3H), 4.92 (brs, 1H), 4.34 (dd, *J* = 11.9, 4.4 Hz, 1H), 4.20 (dd, *J* = 11.9, 5.7 Hz, 1H), 3.71 (d, *J* = 5.1 Hz, 2H), 3.19 (q, *J* = 6.6 Hz, 2H), 2.28-2.38 (m, 4H), 1.95-2.15 (m, 2H), 1.45-1.70 (m, 8H), 1.23-1.43 (m, 14H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 173.94, 173.45, 156.55, 136.66, 128.55, 128.13, 105.0-125.0 (m, C_6F_{13}), 72.11, 66.68, 62.25, 61.42, 40.87, 34.30, 33.91, 30.92 (t, J_{CF} = 22.4 Hz), 29.66, 29.40, 29.36, 29.27, 29.25, 29.14, 29.11, 26.16, 24.95, 24.48, 20.04.

Compound 6

To the solution of 1-(benzyloxy)-*N*,*N*,*N*',*N*'-tetraisopropylphosphinediamine (0.13 mmol) and tetrazole (4.0 mg, 57 μmol) in anhydrous CH_2Cl_2 (0.5 mL) was added dropwise the solution of **4** (73 mg, 88 μmol) in anhydrous CH_2Cl_2 (1.0 mL) under Ar. The solution was stirred at room temperature for 2 h, concentrated and purified by flash column chromatography (hexane: ethyl acetate: triethyl amine = 100: 20: 3) to give the phosphoramidite intermediate (73 mg) as colorless oil. Such freshly prepared phosphoramidite (69 μmol) was added to the solution of compound **5** (48 mg, 58 μmol) and *1H*-tetrazole (20 mg, 0.29 mmol) in anhydrous CH_2Cl_2 under Ar. The reaction mixture was stirred at room temperature overnight, followed by the addition of 5.5 M *t*-BuOOH (64 μL, 0.35 mmol) at -40 ^{o}C. The reaction mixture was then

warmed to room temperature gradually, concentrated and purified by column chromatography (hexane: acetone= 2:1) to give the product **6** (89 mg, 56% from compound **4**) as colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18-7.50 (m, 30 H), 4.82-5.24 (m, 14 H), 4.60-4.80 (m, 4H), 4.55 (d, *J* = 6.9 Hz, 1H), 4.05-4.49 (m, 9H), 3.55 (dd, *J* = 9.7, 10.5 Hz, 1H), 3.39 (conformation 1) and 3.36 (conformation 2) (s, 3H), 3.33 (conformation 1) and 3.29 (conformation 2) (s, 3H), 3.24 (conformation 1) and 3.23 (conformation 2) (s, 3H), 3.18 (q, *J* = 6.4 Hz, 2H), 2.23-2.35 (m, 4H), 1.95-2.15 (m, 2H), 1.44-1.67 (m, 8H), 1.20-1.40 (m, 14H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 172.86, 172.78 and 172.73 (1C), 156.44, 136.71, 136.18, 136.14, 136.05, 136.01, 135.96, 135.88, 135.57, 128.75, 128.71, 128.49, 128.48, 128.42, 128.39, 128.33, 128.29, 128.24, 128.05, 128.03, 127.98, 127.93, 105.0-125.0 (m, C_6F_{13}), 98.87 and 98.80 (1C), 97.57, 96.92, 78.83, 77.26, 76.46, 75.83, 74.68, 74.58, 69.89, 69.75, 69.69, 69.58, 69.52, 69.46, 69.41, 69.26, 69.21, 66.54, 66.43, 61.55, 56.67 and 56.61 (1C), 55.89 and 55.87 (1C), 55.78, 40.84, 34.05, 33.74, 30.89 (t, J_{CF} = 22.7 Hz), 29.62, 29.37, 29.35, 29.25, 29.23, 29.11, 26.17, 24.77, 24.40, 20.11; ^{31}P NMR ($CDCl_3$, 162 MHz) δ -1.29 (2P), -1.66 and -1.69 (1P); ^{19}F NMR (CD_3OD, 376 MHz) δ -80.80 (t, *J* = 10.1 Hz), -114.38, -121.94, -122.89, -123.56, -126.14; ESI-HRMS for $[M + H]^+$ $C_{81}H_{100}F_{13}NO_{24}P_3$: calcd 1810.5641; found 1810.5603.

Compound 7

Compound **6** (30 mg, 17 μmol) was dissolved in MeOH (4.0 mL) and subjected to hydrogenolysis over 10% Pd/C (8 mg) for 6 h. After filtration, the filtrate was concentrated, and dried under vacuum for 2 h. The residue was dissolved in anhydrous CH_2Cl_2 (5 mL), and freshly distilled TMSBr (5 mL) was added at 0 ^{o}C under Ar. The reaction mixture was then warmed to room temperature gradually, and stirred for 1 h. The reaction mixture was concentrated, and the residue was dried under vacuum for 1 h. MeOH (20 mL) was subsequently added and the solution was stirred at room temperature for 1 h. After removal of the solvent by evaporation, the residue was dried under vacuum for 1 h to give the product **7** (15 mg, 81%) as white foamy solid. ^{1}H NMR (CD_3OD, 400 MHz) δ 5.10-5.20 (m, 1H), 4.41 (dd, *J* = 9.2,

18.4 Hz, 1H), 4.32 (dd, *J* = 11.9, 4.3 Hz, 1H), 3.96-4.18 (m, 6H), 3.89 (dd, *J* = 9.3, 9.3 Hz, 1H), 3.55 (d, *J* = 5.9 Hz, 1H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.22-2.38 (m, 4H), 1.98-2.15 (m, 2H), 1.43-1.67 (m, 8H), 1.16-1.41 (m, 14H); ^{13}C NMR (CD_3OD, 101 MHz) δ 174.64, 174.62, 105.0-125.0 (m, C_6F_{13}), 81.09, 79.92, 78.82 and 78.75 (1C), 72.40, 71.72, 71.52, 71.33 and 71.25 (1C), 66.08 and 66.02 (1C), 63.03, 40.60, 34.99, 34.42, 31.71 (t, J_{CF} = 22.5 Hz), 30.51, 30.48, 30.42, 30.39, 30.30, 30.13, 28.20, 26.82, 25.95, 25.29, 21.28; ^{31}P NMR (CD_3OD, 202 MHz) δ 0.84 (1P), 0.49 (1P), -1.02 (1P); ^{19}F NMR (CD_3OD, 376 MHz) δ -82.43 (t, *J* = 10.2 Hz), -115.37, -122.96, -123.92, -124.53, -127.33; ESI-HRMS for $[M + H]^+$ $C_{32}H_{52}F_{13}NO_{19}P_3$: calcd 1094.2139; found 1094.2131.

Compound 1

To the solution of compound **7** (10 mg, 9.1 μmol) in TEAB buffer (0.50 M, 4.3 mL) was added the solution of NHS ester **8** (8.6 mg, 18.2 μmol) in DMF (4.3 mL). The reaction mixture was stirred in the dark at room temperature overnight, and the solvents were removed under vacuum. The crude product was then re-dissolved in 30% MeOH and purified by HPLC on a Thermo Betasil C18 reverse Phase column (150 x 10 mm, 5 μm) to yield the product (10 mg, 75%) as yellow solid. The compound was immediately treated with 1.0 M TEAB buffer to form the triethyl amine salt, which was stable at -20 ^{o}C for 6 months. ^{1}H NMR (CD_3OD, 400 MHz) δ 6.5-8.50 (m, 9H), 5.10-5.25 (m, 1H), 4.41 (dd, *J* = 12.0, 3.4 Hz, 1H), 4.27-4.37 (m, H), 4.00-4.24 (m, 4H), 3.90-4.00 (m, 3H), 3.56 (dd, *J* = 9.6, 2.3 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 2.20-2.38 (m, 4H), 2.00-2.20 (m, 2H), 1.46-1.72 (m, 8H), 1.16-1.46 (m, 14H); ^{13}C NMR (CD_3OD, 125 MHz) δ 174.88, 174.73, 171.22, 168.54, 155.68, 137.74, 133.58, 131.08, 130.91, 130.00, 126.41, 112.43, 105.0-125.0 (m, C_6F_{13}), 103.77, 80.42, 78.29, 77.82 and 77.90 (1C), 72.81, 72.42, 72.08, 71.98, 64.93, 63.80, 41.03, 35.10, 34.78, 31.71 (t, J_{CF} = 22.4 Hz), 30.74, 30.53, 30.44, 30.41, 30.14, 30.05, 27.53, 26.00, 25.67, 25.57, 21.29; ^{31}P NMR (CD_3OD, 162 MHz) δ 2.45 (1P), 1.71 (1P), -0.45 (1P); ^{19}F NMR (CD_3OD, 376 MHz) δ -82.41 (t, *J* = 10.1 Hz), -115.35, -122.95, -123.91, -124.51, -127.31; ESI-HRMS for $[M + H]^+$ $C_{53}H_{62}F_{13}NO_{25}P_3$: calcd

1452.2616; found 1452.2575.

Fluorous Solid Phase Extraction (FSPE)

FSPE was performed on a 1.5 mL column packed with fluorous silica gel (perfluorooctane bonded phase, 5 mm particles, Fluorous Technology or Sigma). After equilibration with 10% MeOH in 50 mM TEAB (pH 8.5), the assay sample was treated with 0.5 M TEAB (pH 8.5) and loaded onto the column. The column was first washed with 10% and then 30% MeOH in 50 mM TEAB (10 column volume for each), before the fluorous tagged product was eluted using 60% and 80% MeOH in 50 mM TEAB (10 column volume for each).

PI3K Assay

The fluorous PtdIns(4,5)P_2 derivative **1** (40 μM, final concentration) was added to the assay buffer (600 μL, final volume) composed of MOPS (50 mM, pH 6.5), NaCl (100 mM), sodium cholate (0.5 mM), DTT (1 mM), $MgCl_2$ (10 mM), and ATP (4 mM). The reaction was initiated by the addition of purified PI3K (20 nM). The samples were incubated at 37 ^oC for indicated times, and the reaction progression was monitored by TLC as reported before.

SHIP2 Assay

The PtdIns(3,4,5)P_3 derivative (128 μM, final concentration) generated from the PI3K reaction was added to the assay buffer (720 μL, final volume) containing Hepes (50 mM, pH 7.2), NaCl (100 mM), $MgCl_2$ (1 mM), and EDTA (0.25 mM). The reaction was initiated by the addition of purified SHIP2 phosphatase (40 nM). The samples were incubated at 37 ^oC for indicated times, and the reaction progression was monitored by TLC as described above.

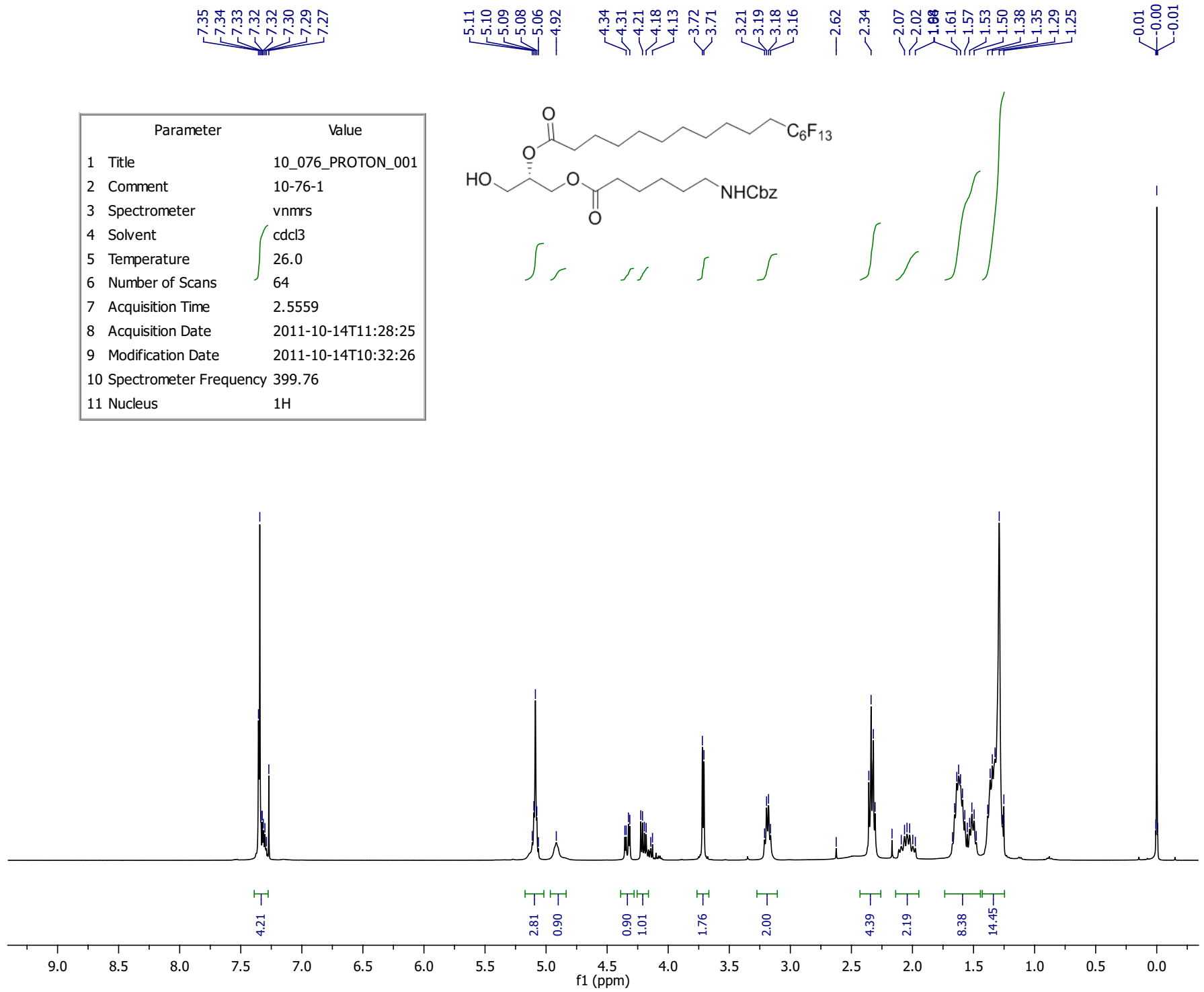
PTEN Assay

The fluorous PtdIns(3,4,5)P_3 derivative (20 μM, final concentration) generated from the PI3K reaction or PtdIns(3,4)P_2 product (40 μM, final concentration) generated from the SHIP2 reaction were added to the assay buffer (500 μL, final volume) containing Tris-HCl (25 mM, pH 7.4), NaCl (130 mM), KCl (2.7 mM), and DTT (1 mM). The reaction was initiated by the addition of purified PTEN (10 nM) and the

resulting mixture was incubated at 37 ^{o}C for indicated times and monitored by TLC as described above.

Fluorous microarray

Solutions of fluorous PtdIns(4,5)P_2, PtdIns(3,4,5)P_3, or PtdIns(3,4)P_2 in 90% MeOH (1 μM or 0.5 μM, 2 μL) were spotted onto a Teflon membrane, and dried in the dark. The membrane was then incubated with biotinylated antibody (2 ng/μL in 1 mg/mL BSA) for 30 min at room temperature, followed by washing with cold PBS 4 times. Subsequently, Cy®5-Streptavidin in PBS containing 1 mg/mL BSA was applied to the membrane and incubated at room temperature for 15 min. The membrane was washed with cold PBS buffer 4 times, and scanned on a Typhoon 9400 Variable Mode Imager ($\lambda_{ex}/\lambda_{em}$=488 nm/520 nm for fluorescein, and $\lambda_{ex}/\lambda_{em}$=633 nm/670 nm for Cy®5).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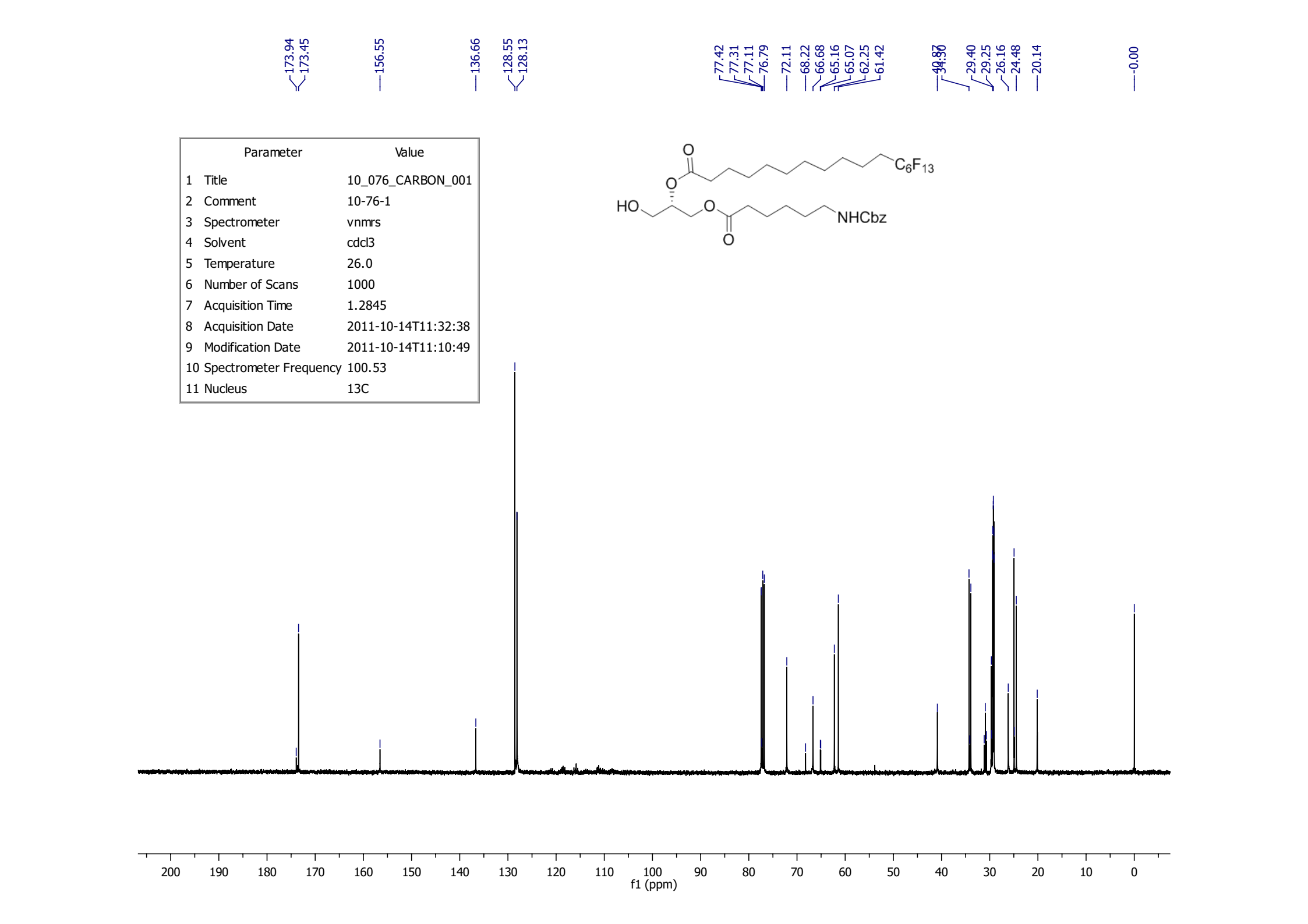
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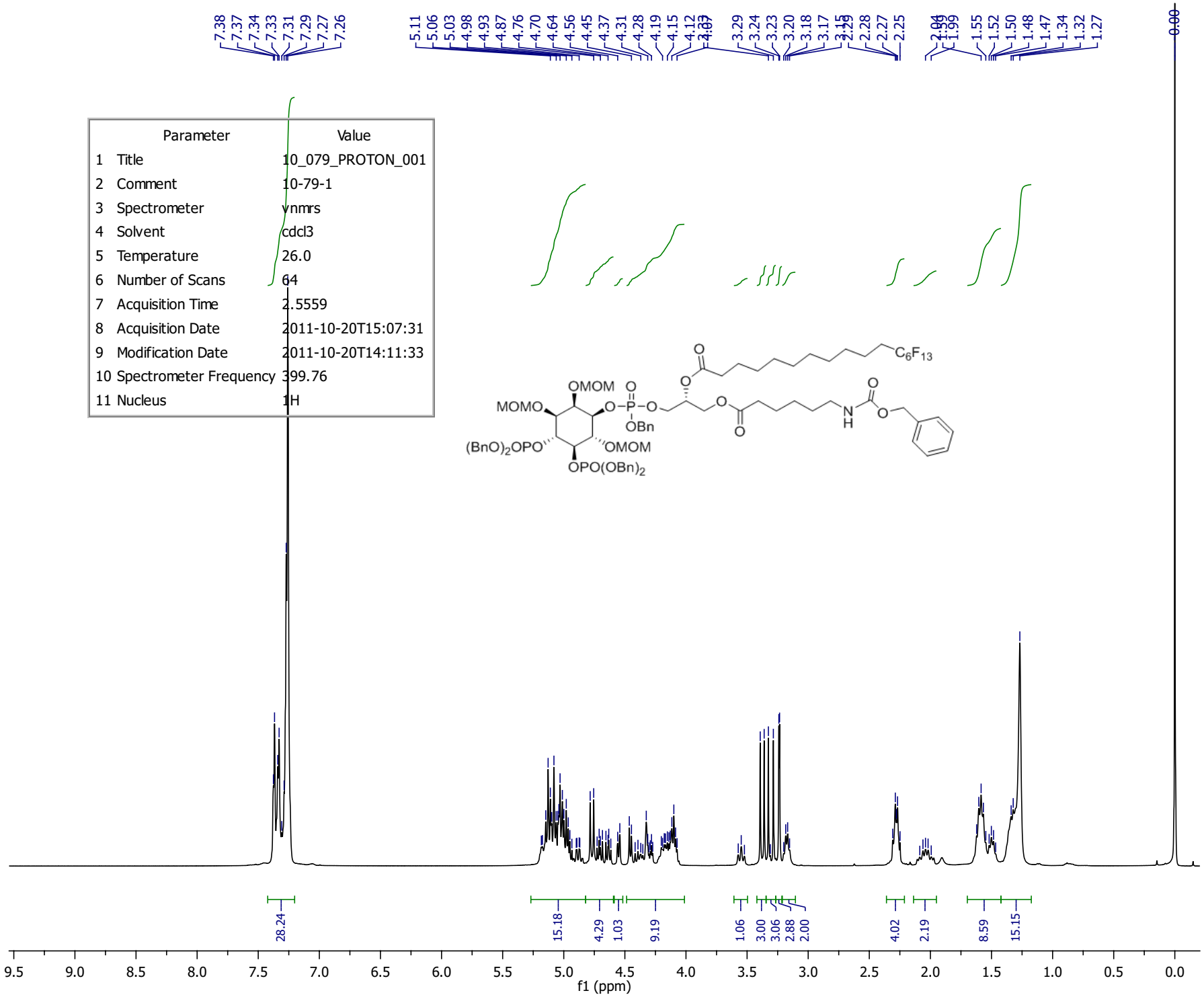
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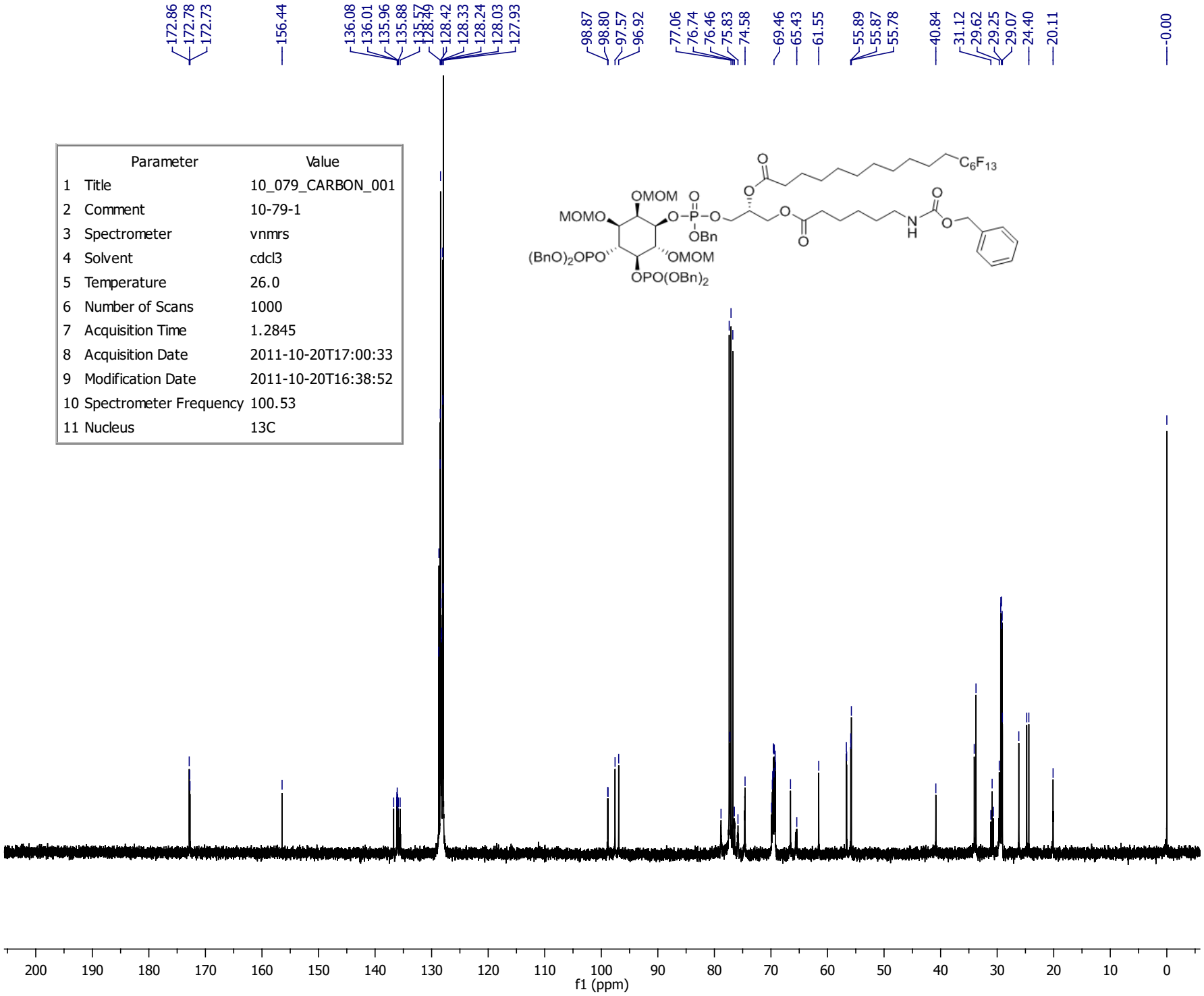
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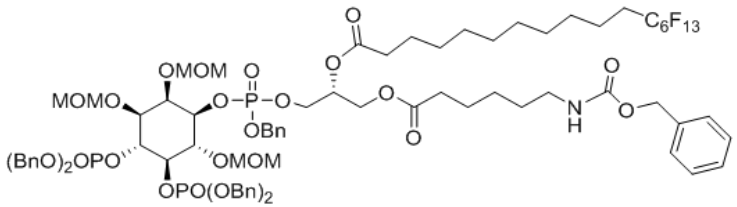

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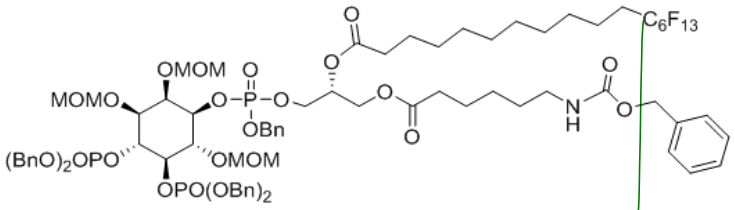

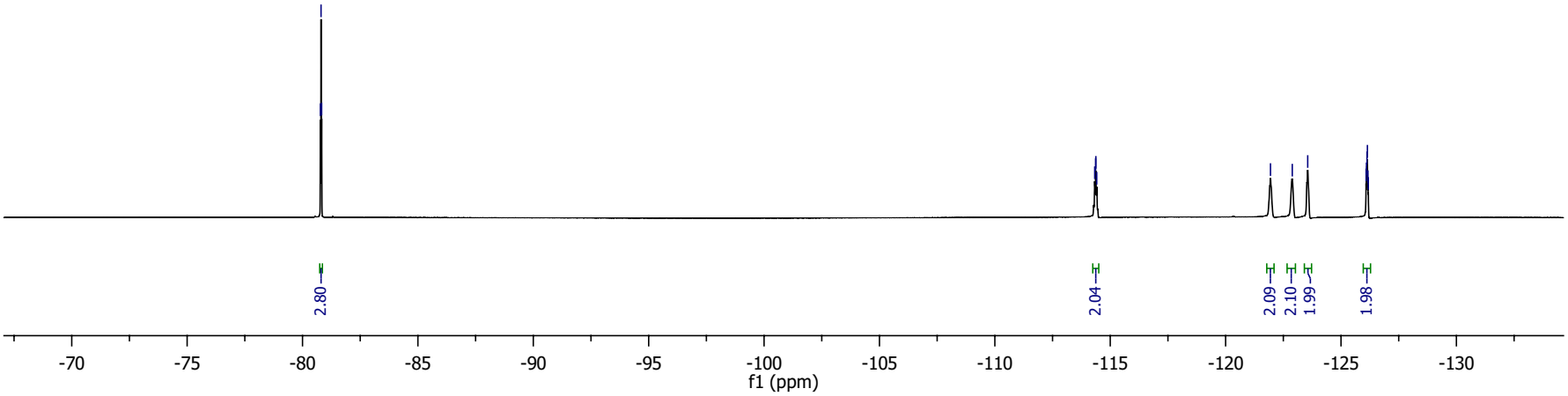

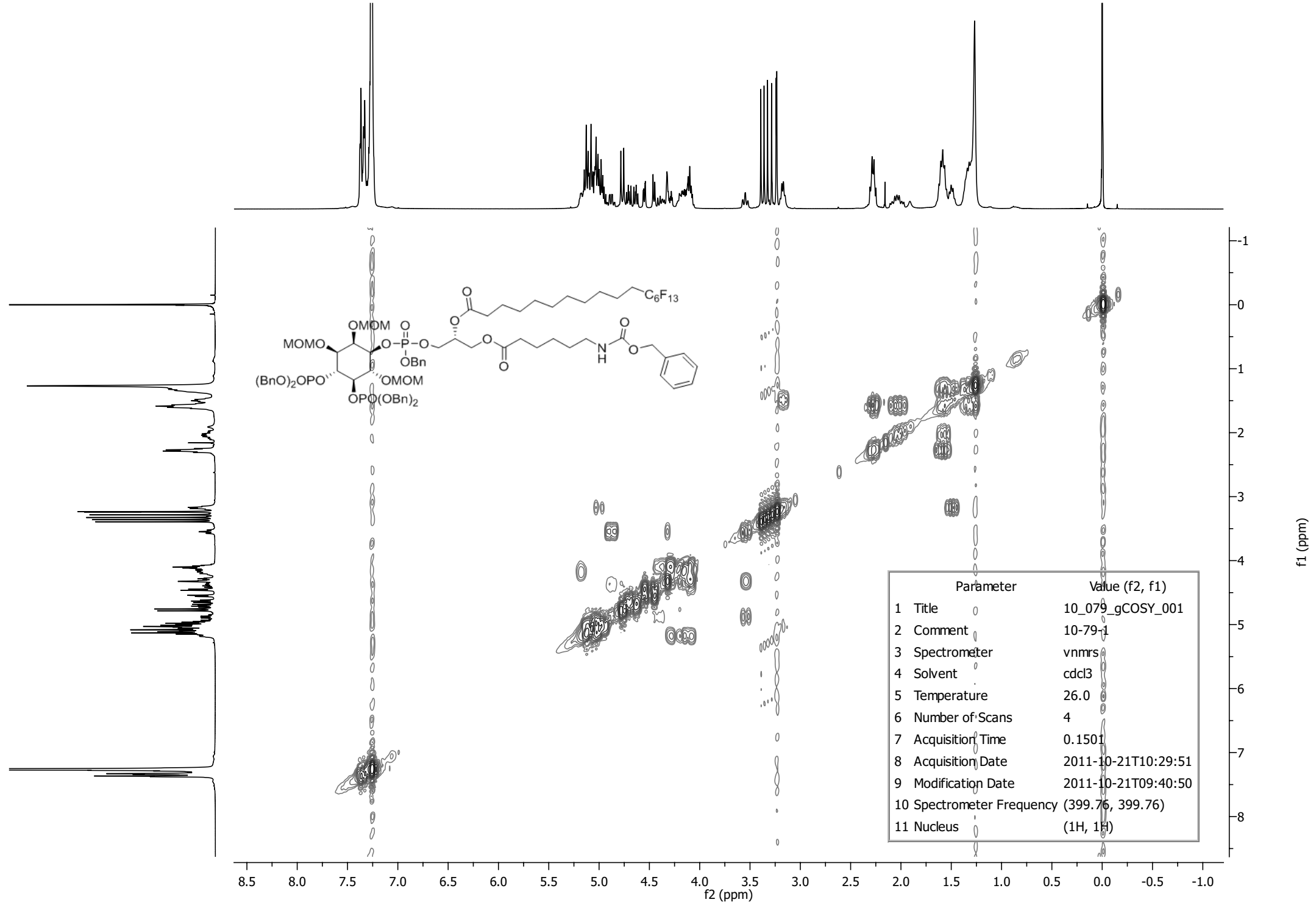
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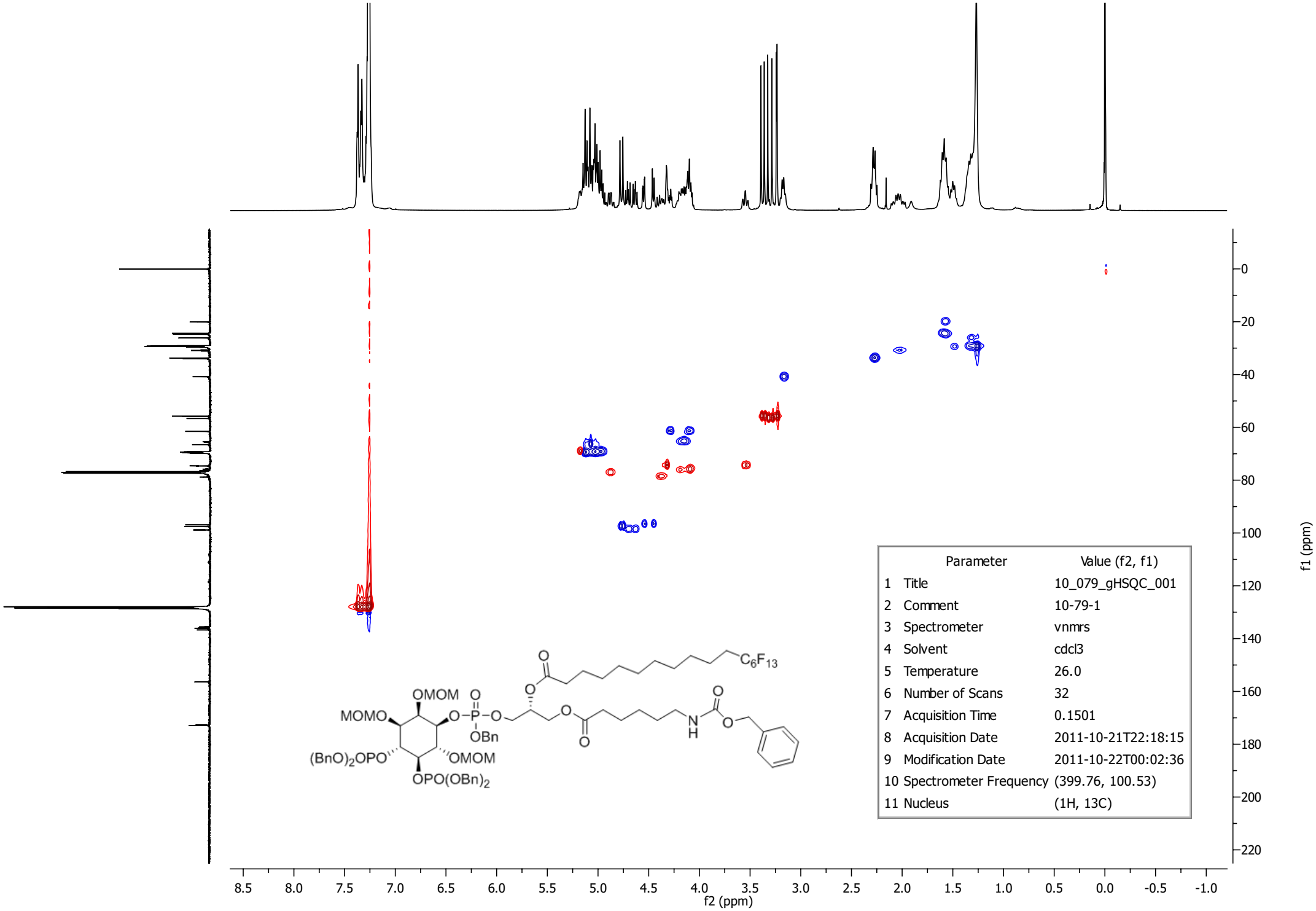
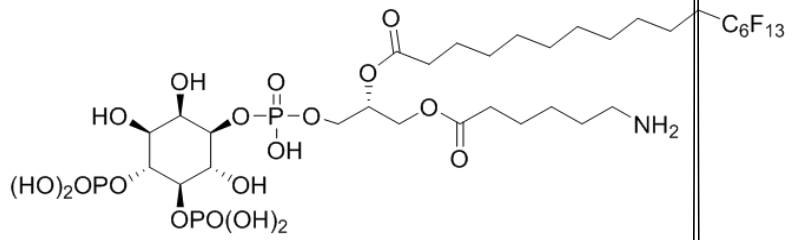
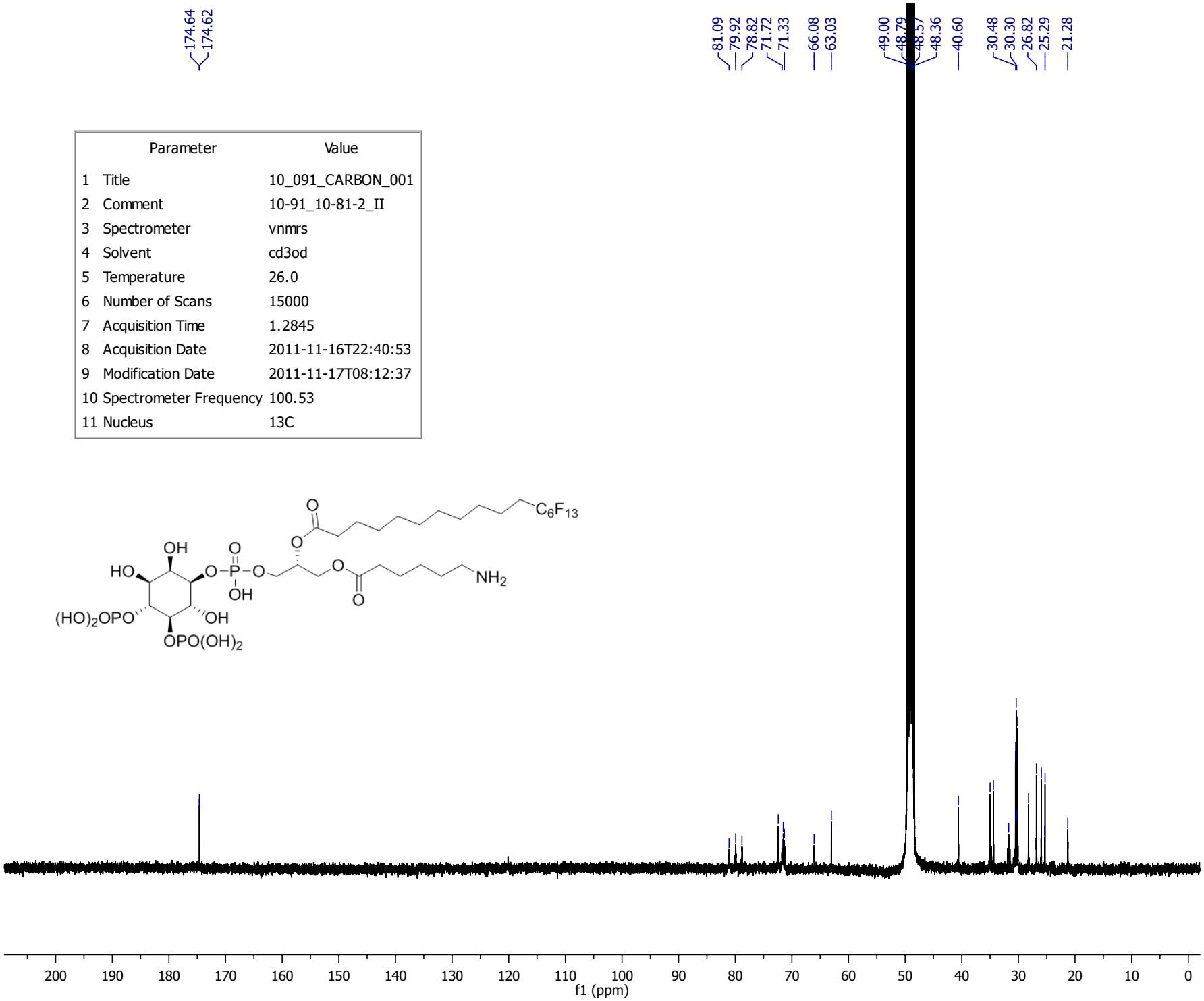
3 Spectrometer
vnmrs
4 Solvent
cdcl3
5 Temperature
26.0
6 Number of Scans
4
7 Acquisition Time
0.1501
8 Acquisition Date
2011-10-21T10:29:51
9 Modification Date
2011-10-21T09:40:50
10 Spectrometer Frequency
(399.76, 399.76)
11 Nucleus
(1H, 1H)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

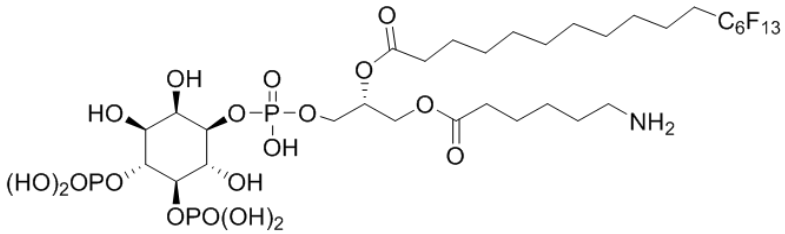

f2 (ppm)
f1 (ppm)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
0 20 40 60 80 100 120 140 160 180 200 220
OMOM
MOMO
O–P–O
OBn
(BnO)2OPO
OMOM
OPO(OBn)2
C6F13
O
N
H
Parameter Value (f2, f1)
1 Title 10_079_gHSQC_001
2 Comment 10-79-1
3 Spectrometer vnmrs
4 Solvent cdcl3
5 Temperature 26.0
6 Number of Scans 32
7 Acquisition Time 0.1501
8 Acquisition Date 2011-10-21T22:18:15
9 Modification Date 2011-10-22T00:02:36
10 Spectrometer Frequency (399.76, 100.53)
11 Nucleus (1H, 13C)

	Parameter	Value
1	Title	10_091_PROTON_002
2	Comment	10-91_10-81-2_II
3	Spectrometer	vnmrs
4	Solvent	cd3od
5	Temperature	26.0
6	Number of Scans	128
7	Acquisition Time	2.5559
8	Acquisition Date	2011-11-16T16:56:13
9	Modification Date	2011-11-16T17:04:03
10	Spectrometer Frequency	399.76
11	Nucleus	1H



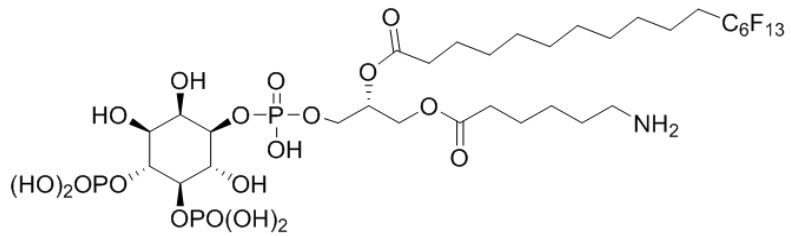

174.64
174.62
81.09
79.92
78.82
71.72
71.33
66.08
63.03
49.00
48.79
48.57
48.36
40.60
30.48
30.30
26.82
25.29
21.28
Parameter Value
1 Title 10_091_CARBON_001
2 Comment 10-91_10-81-2_II
3 Spectrometer vnmrs
4 Solvent cd3od
5 Temperature 26.0
6 Number of Scans 15000
7 Acquisition Time 1.2845
8 Acquisition Date 2011-11-16T22:40:53
9 Modification Date 2011-11-17T08:12:37
10 Spectrometer Frequency 100.53
11 Nucleus 13C
C6F13
NH2
OH
HO
(HO)2OPO
OPO(OH)2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

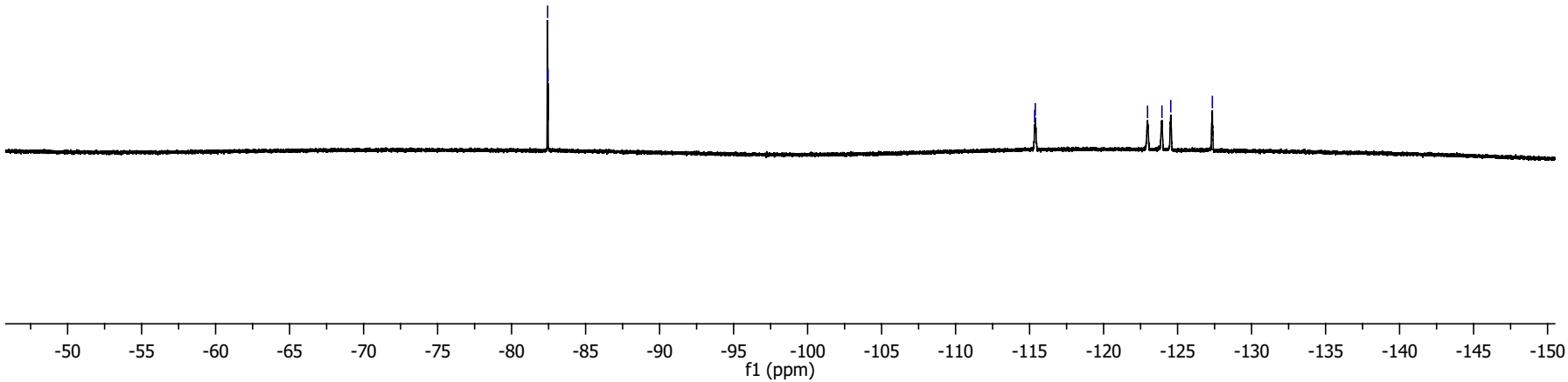
	Parameter	Value
1	Title	20111026_10-81-2_CD3OD_P31
2	Comment	20111026_10-81-2_CD3OD_P31
3	Spectrometer	inova
4	Solvent	cd3od
5	Temperature	25.3
6	Number of Scans	264
7	Acquisition Time	1.6000
8	Acquisition Date	2011-10-26T17:33:47
9	Modification Date	2011-10-26T16:45:40
10	Spectrometer Frequency	202.32
11	Nucleus	31P

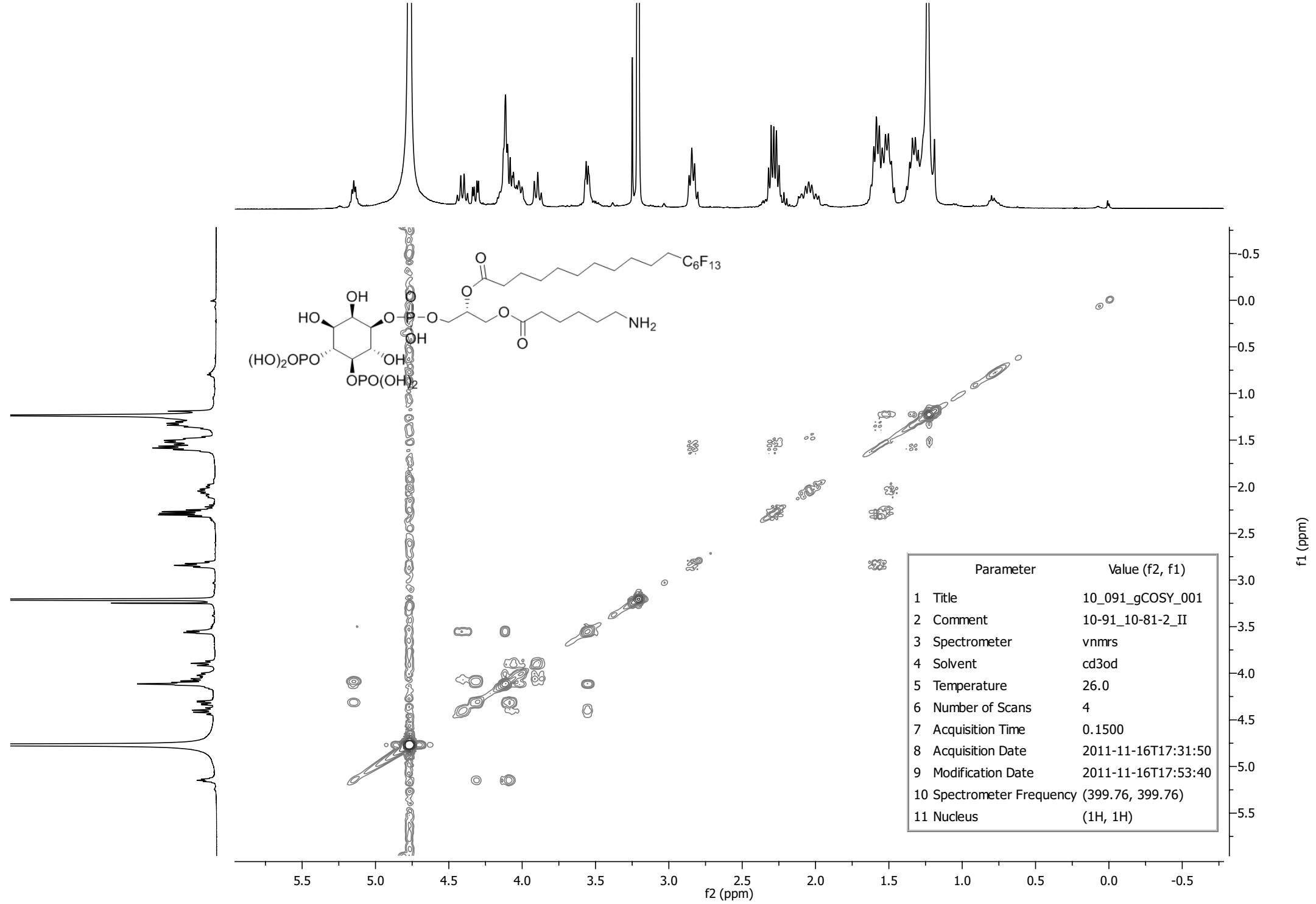


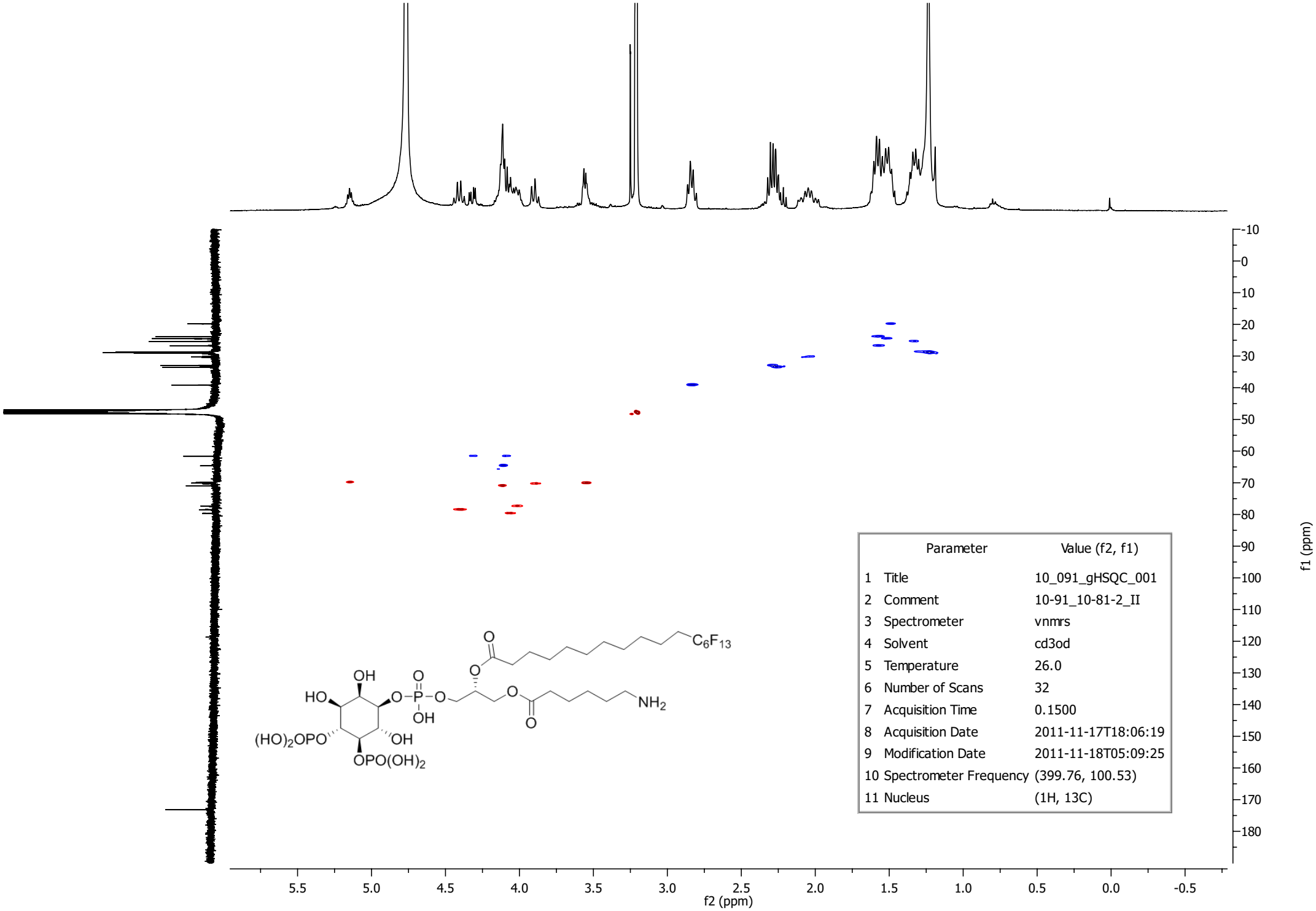
-82.41
-82.44
-82.46
-115.34
-115.39
-122.97
-123.94
-124.54
-127.35

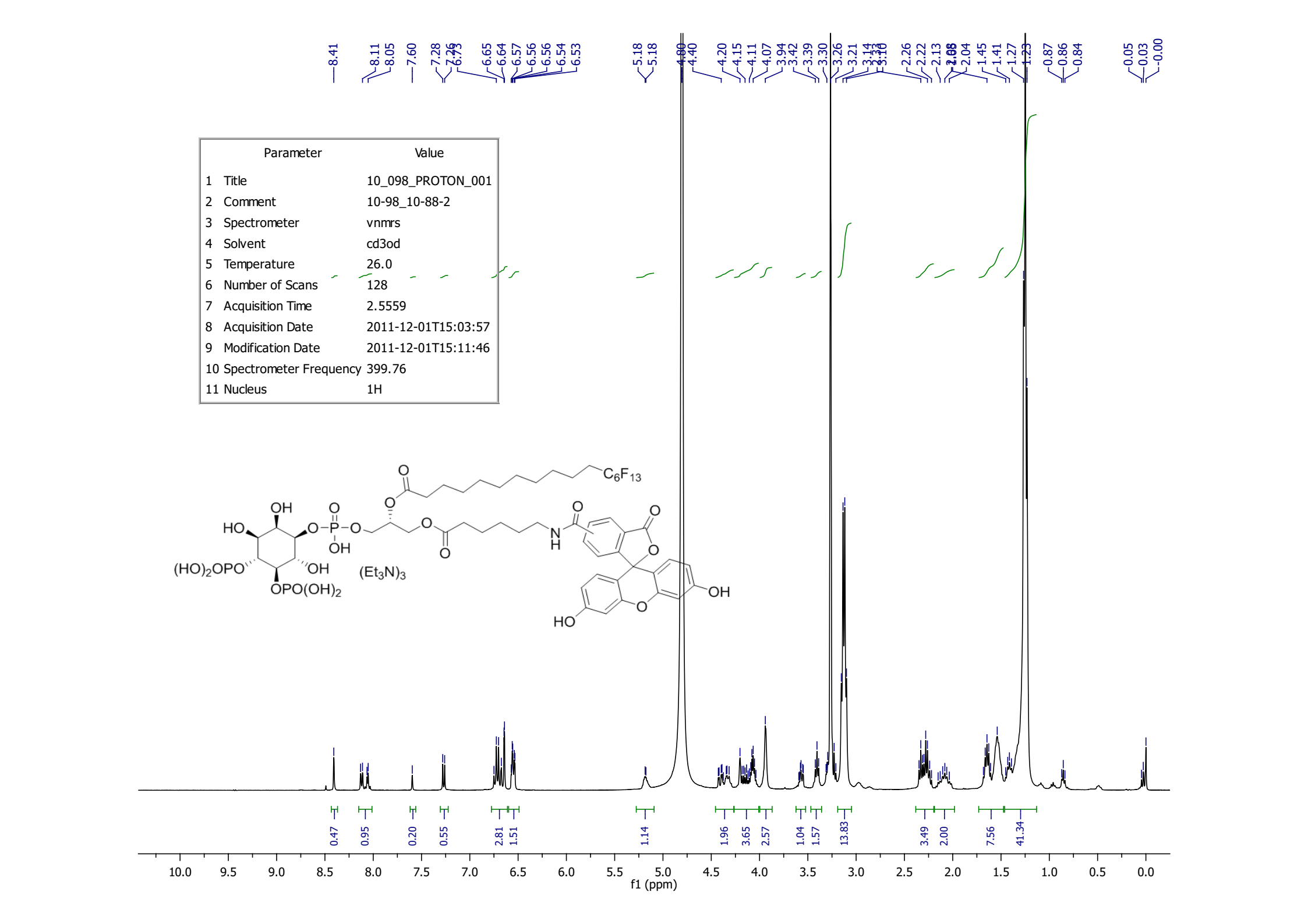
	Parameter	Value
1	Title	10_100_FLUORINE_002
2	Comment	10-100_10-81-2
3	Spectrometer	vnmrs
4	Solvent	cd3od
5	Temperature	26.0
6	Number of Scans	512
7	Acquisition Time	0.7340
8	Acquisition Date	2011-12-12T11:58:56
9	Modification Date	2011-12-12T12:13:49
10	Spectrometer Frequency	376.11
11	Nucleus	19F

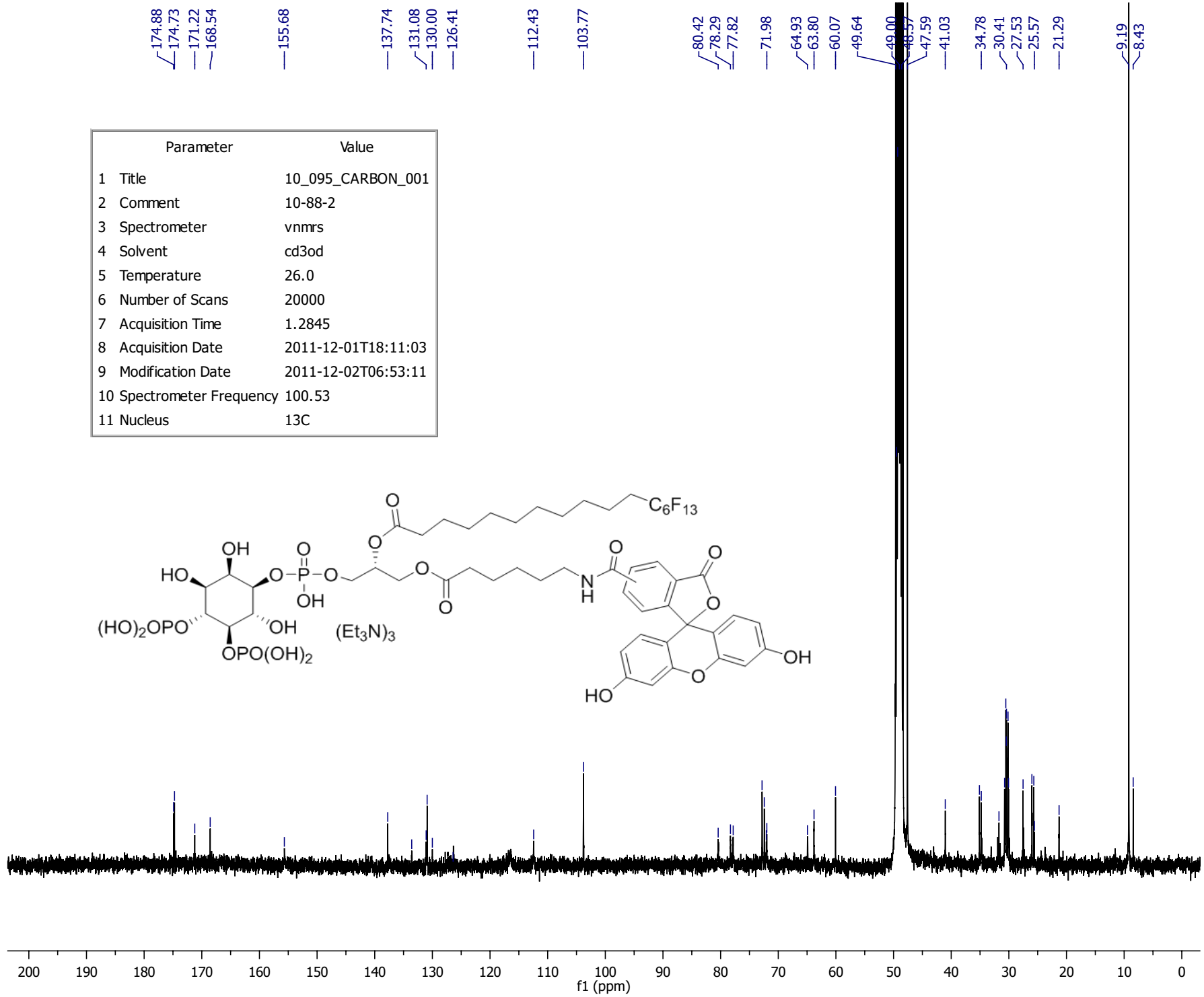




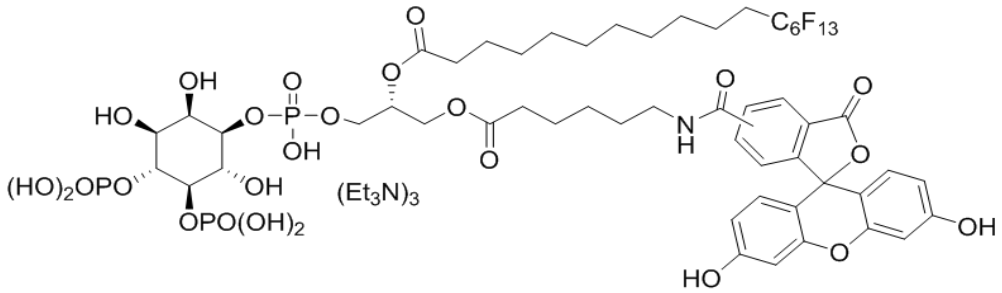

OH
HO
O
P
O
OH
(HO)2OPO
OH
OPO(OH)2
O
O
O
O
O
C6F13
NH2
Parameter
Value (f2, f1)
1 Title
10_091_gCOSY_001
2 Comment
10-91_10-81-2_II
3 Spectrometer
vnmrs
4 Solvent
cd3od
5 Temperature
26.0
6 Number of Scans
4
7 Acquisition Time
0.1500
8 Acquisition Date
2011-11-16T17:31:50
9 Modification Date
2011-11-16T17:53:40
10 Spectrometer Frequency
(399.76, 399.76)
11 Nucleus
(1H, 1H)
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
f2 (ppm)
f1 (ppm)

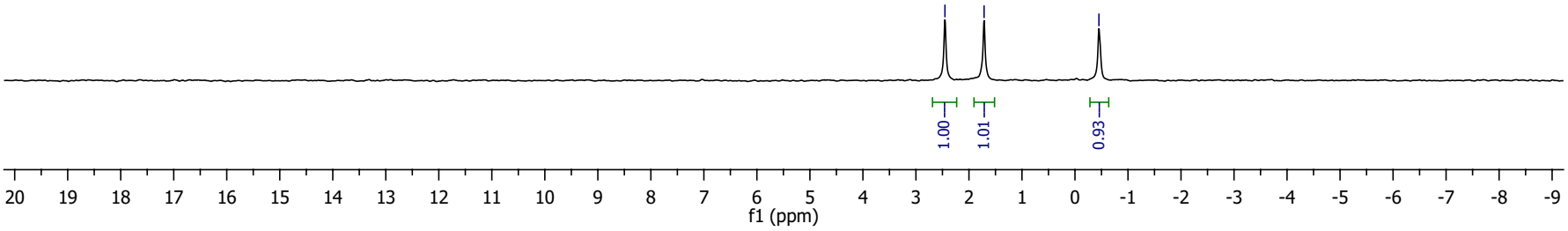

f2 (ppm)
f1 (ppm)
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
OH
HO
O
P
O
OH
(HO)2OPO
OH
OPO(OH)2
O
O
O
O
C6F13
NH2
Parameter
Value (f2, f1)
1 Title
10_091_gHSQC_001
2 Comment
10-91_10-81-2_II
3 Spectrometer
vnmrs
4 Solvent
cd3od
5 Temperature
26.0
6 Number of Scans
32
7 Acquisition Time
0.1500
8 Acquisition Date
2011-11-17T18:06:19
9 Modification Date
2011-11-18T05:09:25
10 Spectrometer Frequency
(399.76, 100.53)
11 Nucleus
(1H, 13C)

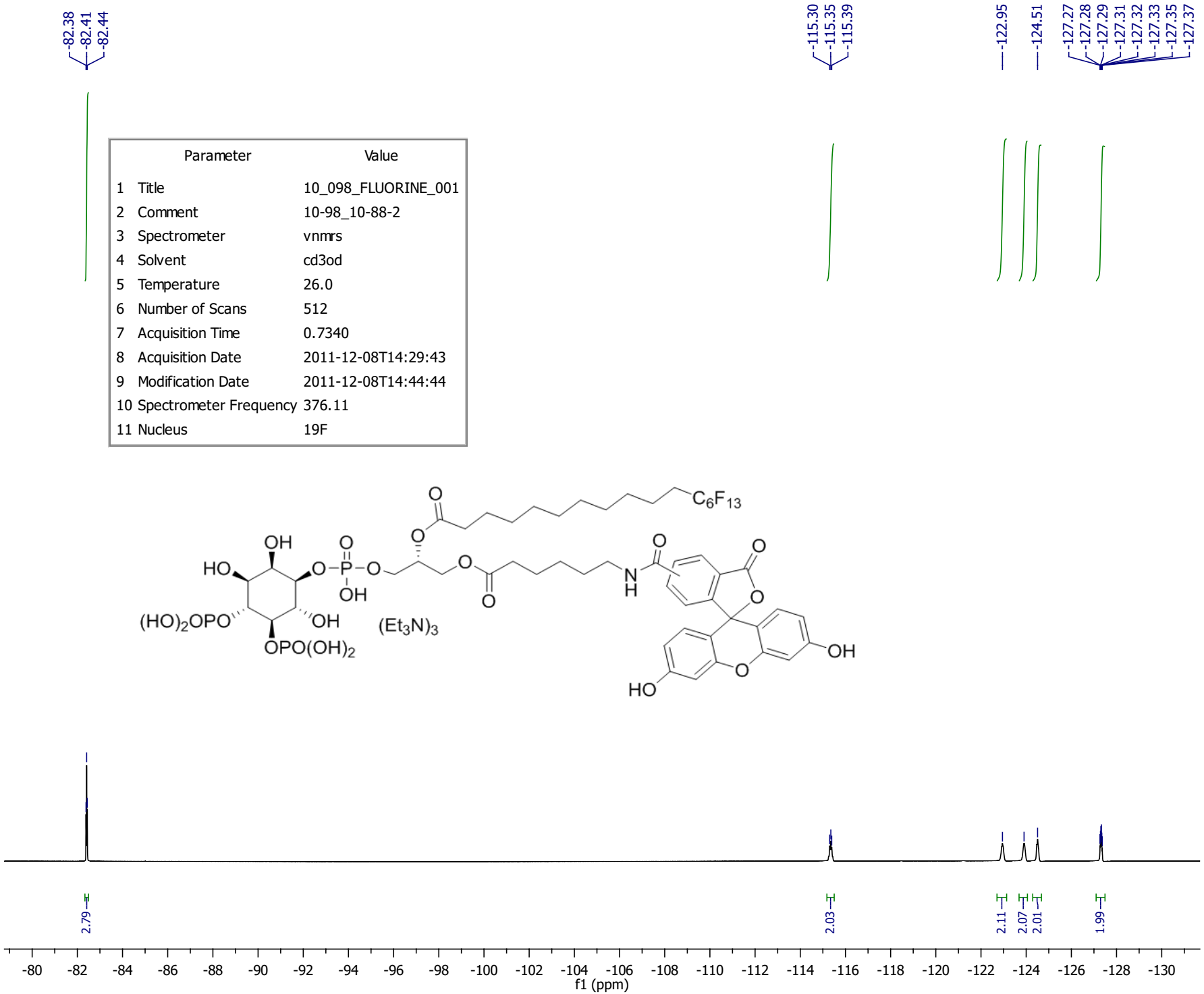

8.41
8.11
8.05
7.60
7.28
7.26
6.73
6.65
6.64
6.57
6.56
6.56
6.54
6.53
5.18
5.18
4.80
4.40
4.20
4.15
4.11
4.07
3.94
3.42
3.39
3.30
3.26
3.21
3.14
3.10
2.26
2.22
2.13
2.04
1.45
1.41
1.27
1.23
0.87
0.86
0.84
0.05
0.03
-0.00
Parameter Value
1 Title 10_098_PROTON_001
2 Comment 10-98_10-88-2
3 Spectrometer vnmrs
4 Solvent cd3od
5 Temperature 26.0
6 Number of Scans 128
7 Acquisition Time 2.5559
8 Acquisition Date 2011-12-01T15:03:57
9 Modification Date 2011-12-01T15:11:46
10 Spectrometer Frequency 399.76
11 Nucleus 1H
C6F13
OH
HO
(HO)2OPO
OPO(OH)2
(Et3N)3
0.47
0.95
0.20
0.55
2.81
1.51
1.14
1.96
3.65
2.57
1.04
1.57
13.83
3.49
2.00
7.56
41.34
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
f1 (ppm)

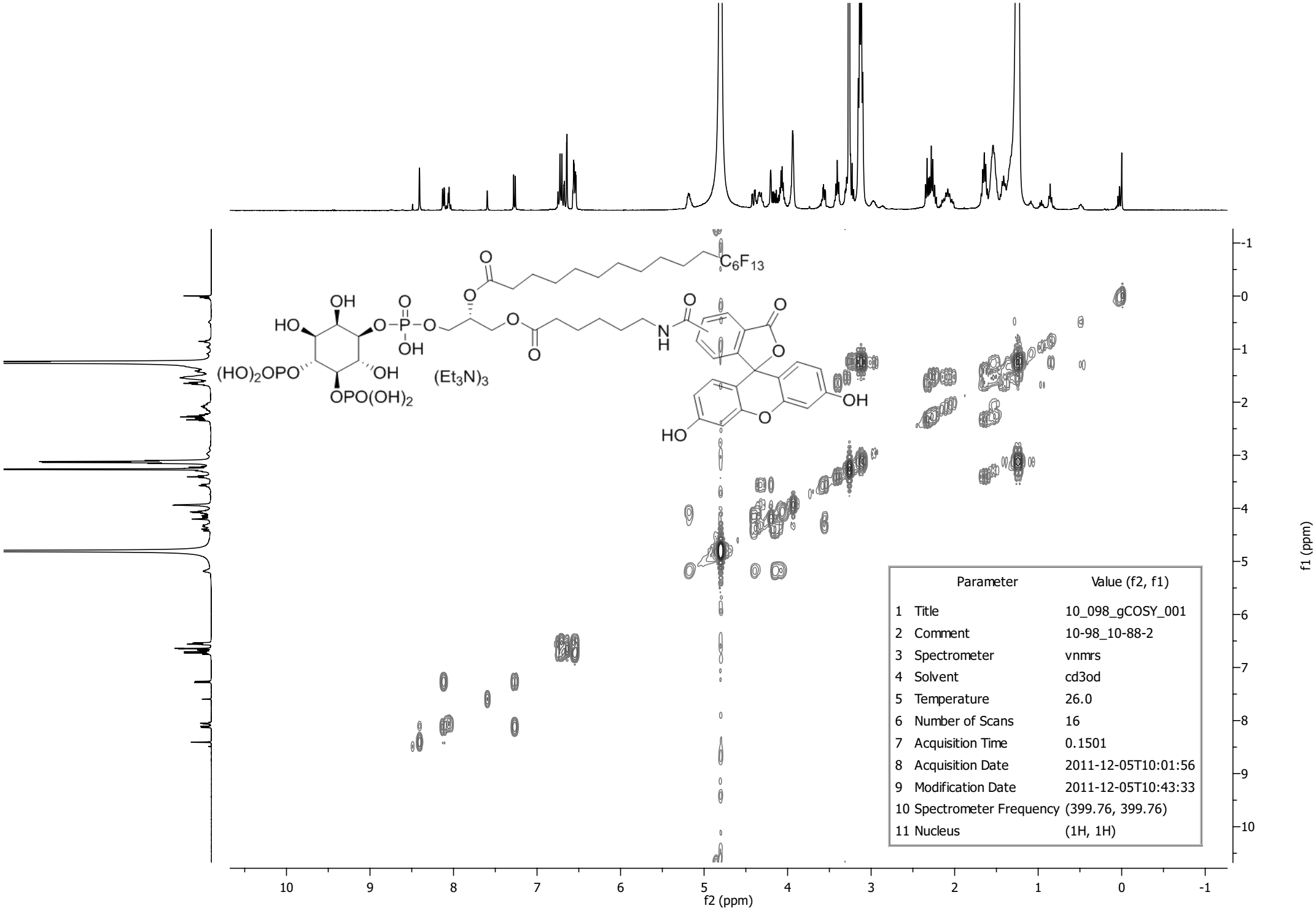

174.88
174.73
171.22
168.54
155.68
137.74
131.08
130.00
126.41
112.43
103.77
80.42
78.29
77.82
71.98
64.93
63.80
60.07
49.64
49.00
48.57
47.59
41.03
34.78
30.41
27.53
25.57
21.29
9.19
8.43
Parameter Value
1 Title 10_095_CARBON_001
2 Comment 10-88-2
3 Spectrometer vnmrs
4 Solvent cd3od
5 Temperature 26.0
6 Number of Scans 20000
7 Acquisition Time 1.2845
8 Acquisition Date 2011-12-01T18:11:03
9 Modification Date 2011-12-02T06:53:11
10 Spectrometer Frequency 100.53
11 Nucleus 13C
C6F13
OH
HO
O
P
(HO)2OPO
OPO(OH)2
(Et3N)3
N
H
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

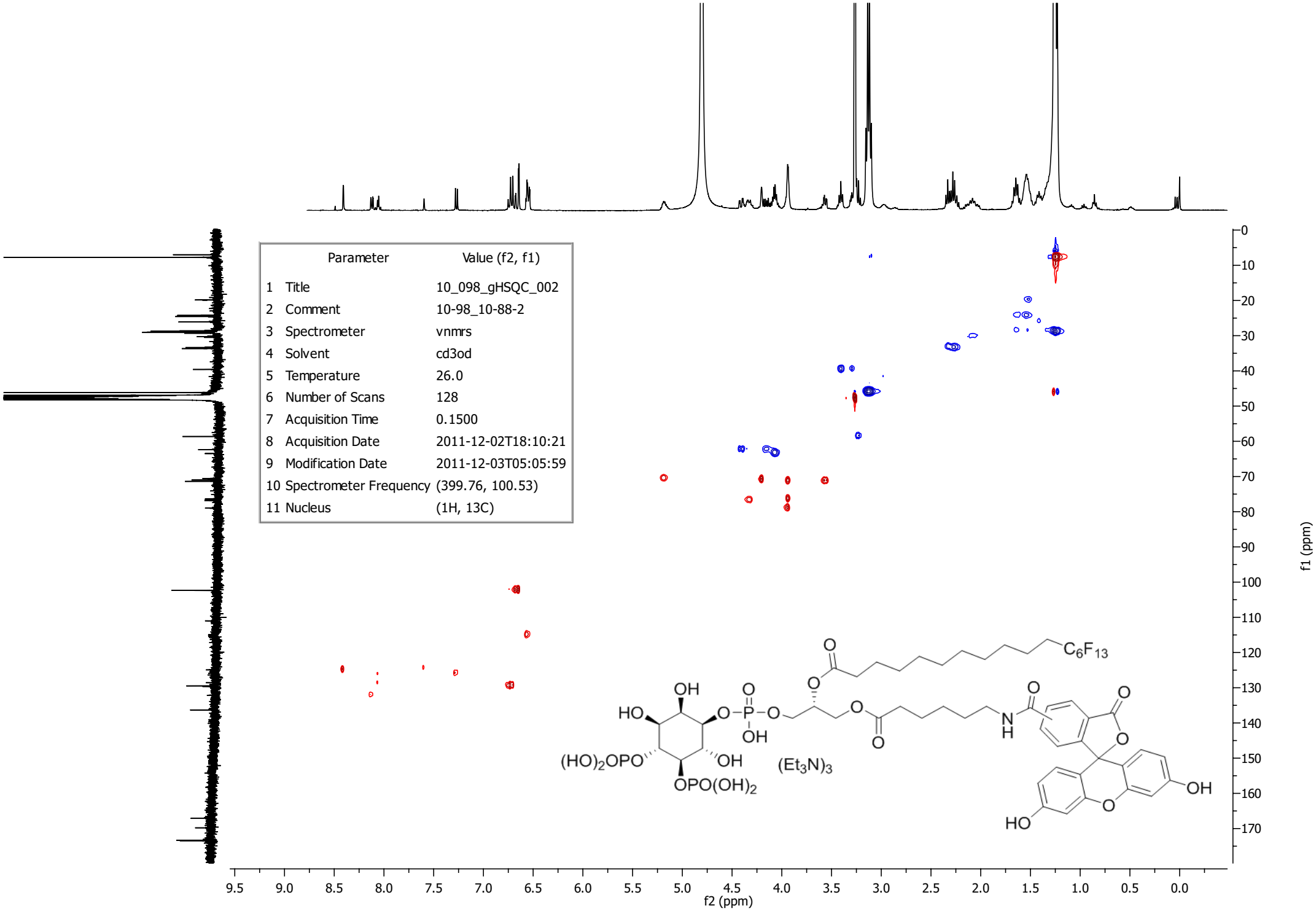
	Parameter	Value
1	Title	10_098_PHOSPHORUS_001
2	Comment	10-98_10-88-2
3	Spectrometer	vnmrs
4	Solvent	cd3od
5	Temperature	26.0
6	Number of Scans	128
7	Acquisition Time	0.7864
8	Acquisition Date	2011-12-01T15:13:16
9	Modification Date	2011-12-01T15:17:09
10	Spectrometer Frequency	161.84
11	Nucleus	31P






-82.38
-82.41
-82.44
-115.30
-115.35
-115.39
-122.95
-124.51
-127.27
-127.28
-127.29
-127.31
-127.32
-127.33
-127.35
-127.37
Parameter Value
1 Title 10_098_FLUORINE_001
2 Comment 10-98_10-88-2
3 Spectrometer vnmrs
4 Solvent cd3od
5 Temperature 26.0
6 Number of Scans 512
7 Acquisition Time 0.7340
8 Acquisition Date 2011-12-08T14:29:43
9 Modification Date 2011-12-08T14:44:44
10 Spectrometer Frequency 376.11
11 Nucleus 19F
C6F13
OH
HO
O
P
OH
(HO)2OPO
OH
OPO(OH)2
(Et3N)3
N
H
O
HO
2.79
2.03
2.11
2.07
2.01
1.99
-80 -82 -84 -86 -88 -90 -92 -94 -96 -98 -100 -102 -104 -106 -108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130
f1 (ppm)


C_6F_{13}
OH
HO
O
P
OH
$(HO)_2OPO$
OH
$OPO(OH)_2$
$(Et_3N)_3$
N
H
HO
OH
f2 (ppm)
f1 (ppm)
Parameter
Value (f2, f1)
1 Title
10_098_gCOSY_001
2 Comment
10-98_10-88-2
3 Spectrometer
vnmrs
4 Solvent
cd3od
5 Temperature
26.0
6 Number of Scans
16
7 Acquisition Time
0.1501
8 Acquisition Date
2011-12-05T10:01:56
9 Modification Date
2011-12-05T10:43:33
10 Spectrometer Frequency
(399.76, 399.76)
11 Nucleus
(1H, 1H)


Parameter Value (f2, f1)
1 Title 10_098_gHSQC_002
2 Comment 10-98_10-88-2
3 Spectrometer vnmrs
4 Solvent cd3od
5 Temperature 26.0
6 Number of Scans 128
7 Acquisition Time 0.1500
8 Acquisition Date 2011-12-02T18:10:21
9 Modification Date 2011-12-03T05:05:59
10 Spectrometer Frequency (399.76, 100.53)
11 Nucleus (1H, 13C)
f2 (ppm)
f1 (ppm)
(HO)2OPO
OPO(OH)2
(Et3N)3
C6F13