Supplementary Material

Unveiling the impact of a CF_2 motif in the isothiourea catalyst skeleton: Evaluating C(3)-F_2-HBTM and its catalytic activity

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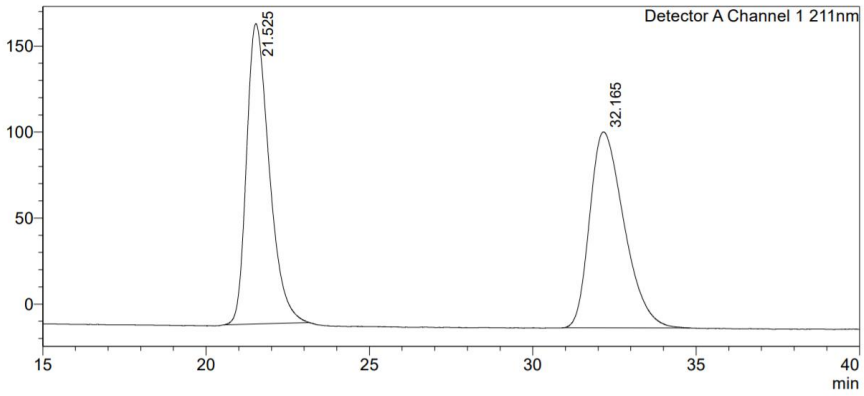
1. General Experimental

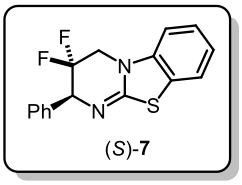
An Applied Photophysics SX.20 stopped-flow spectrophotometer system was used for monitoring the kinetics of the reactions of benzhydrylium ions with isothioureas. The temperature of drive syringes, the flow circuit, and the observation cell was maintained constant at 20 °C (± 0.2 °C) by use of a circulating bath cryostat. All solutions were prepared in flame-dried Schlenk tubes under an atmosphere of dry argon. The kinetic runs were initiated by mixing equal volumes of dichloromethane solutions of the nucleophile and the benzhydrylium salt. Nucleophile concentrations at least four times higher than the benzhydryl cation concentrations were employed, resulting in pseudo-first-order kinetics with an exponential decay of the benzhydryl cation concentration. First-order rate constants k_{obs} [s^{-1}] were obtained by least-squares fitting of the absorbance data (average from at least 5 runs at each nucleophile concentration) to the single-exponential $A = A_0 \cdot e^{-k_{obs} \cdot t} + C$. Second-order rate constants k_1 [$M^{-1} \cdot s^{-1}$] were then calculated from $k_{obs} = k_1[Nuc]_0$.

Cyclic voltammetry measurements on a CH Instruments, Inc., CHI6330E Electrochemical Workstation were performed in deaerated acetonitrile solutions containing 0.1 M Bu_4NClO_4 by using a 2 mm diameter platinum working electrode, a platinum wire counter electrode and an Ag/Ag^+ pseudo-reference electrode. Ferrocene was used as an internal standard for calibration vs. SCE (Fc/Fc^+ = +0.382 V vs. SCE in MeCN, Aranzaes, J. R., Daniel, M.-C., Astruc, D., *Can. J. Chem*., **2006**, *84*, 288-299.). The instrument parameters were: Scan rate 0.1V/s, sample interval 1 mV, quiet time 2 s and sensitivity 0.00001 A/V.

2. Chiral HPLC Analysis of (*S*)-7

Chiral HPLC analysis of (*S*)-**7**, Chiralcel OD-H (90:10 hexane : IPA, flow rate 1.0 $mLmin^{-1}$, 211 nm, 30 °C) t_R (*S*): 21.5 min, t_R (*R*) 32.2 min, >99:1 er

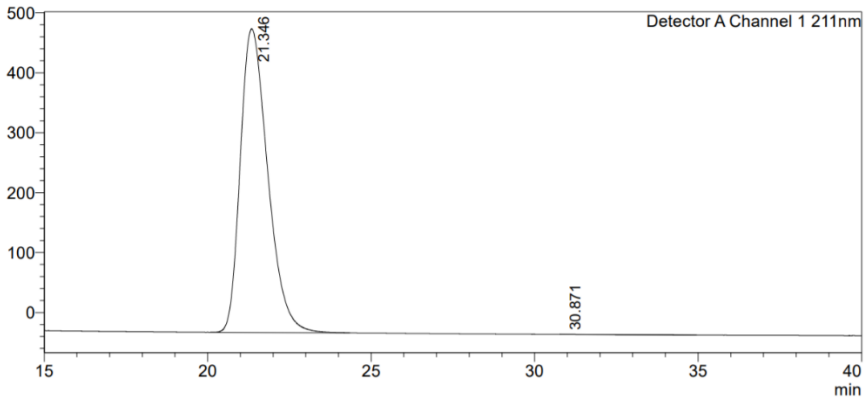




(*S*)-**7**

Detector A Channel 1 211nm

Peak#	Ret. Time	Area%
1	21.525	50.253
2	32.165	49.747
Total		100.000

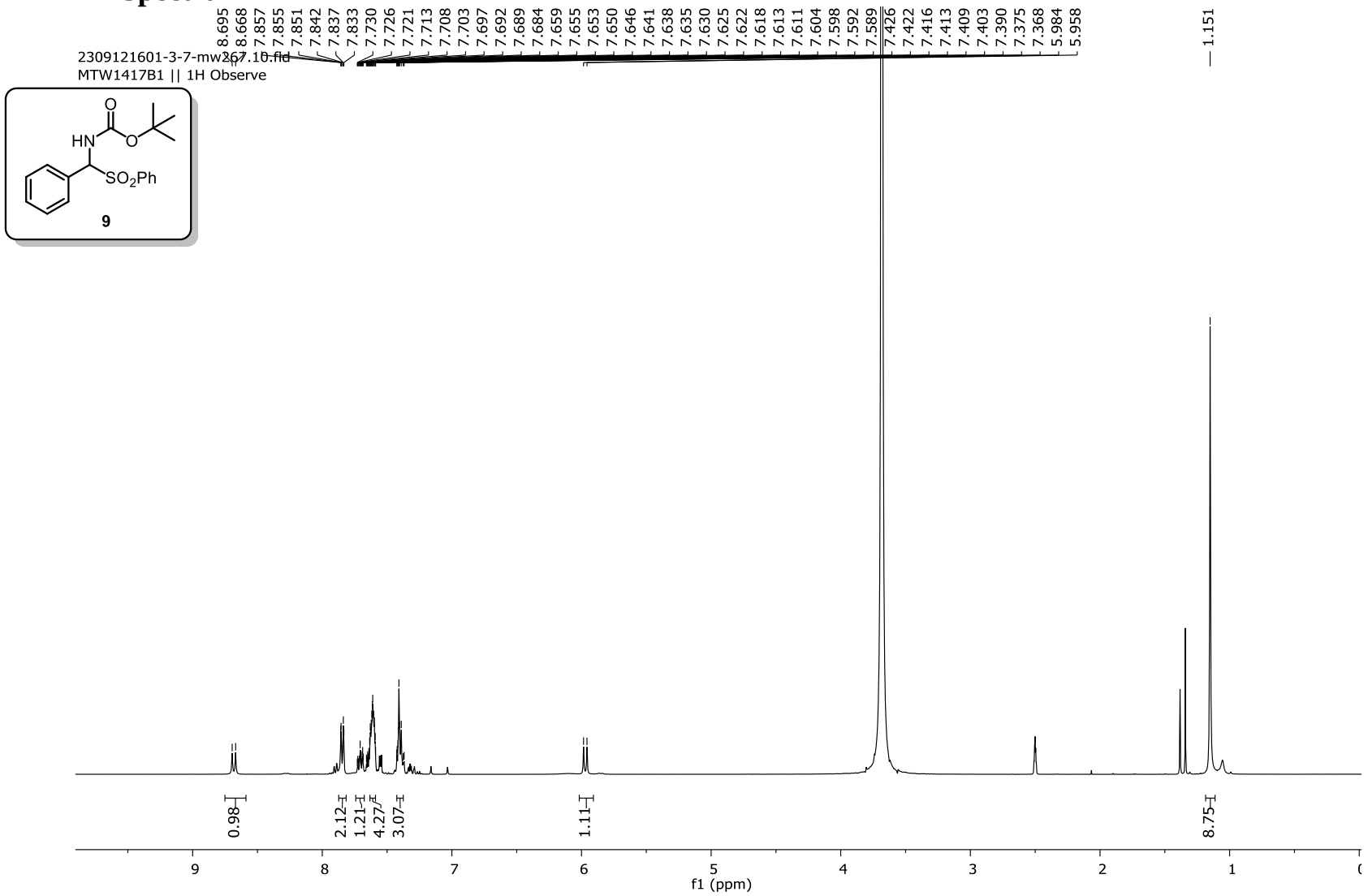


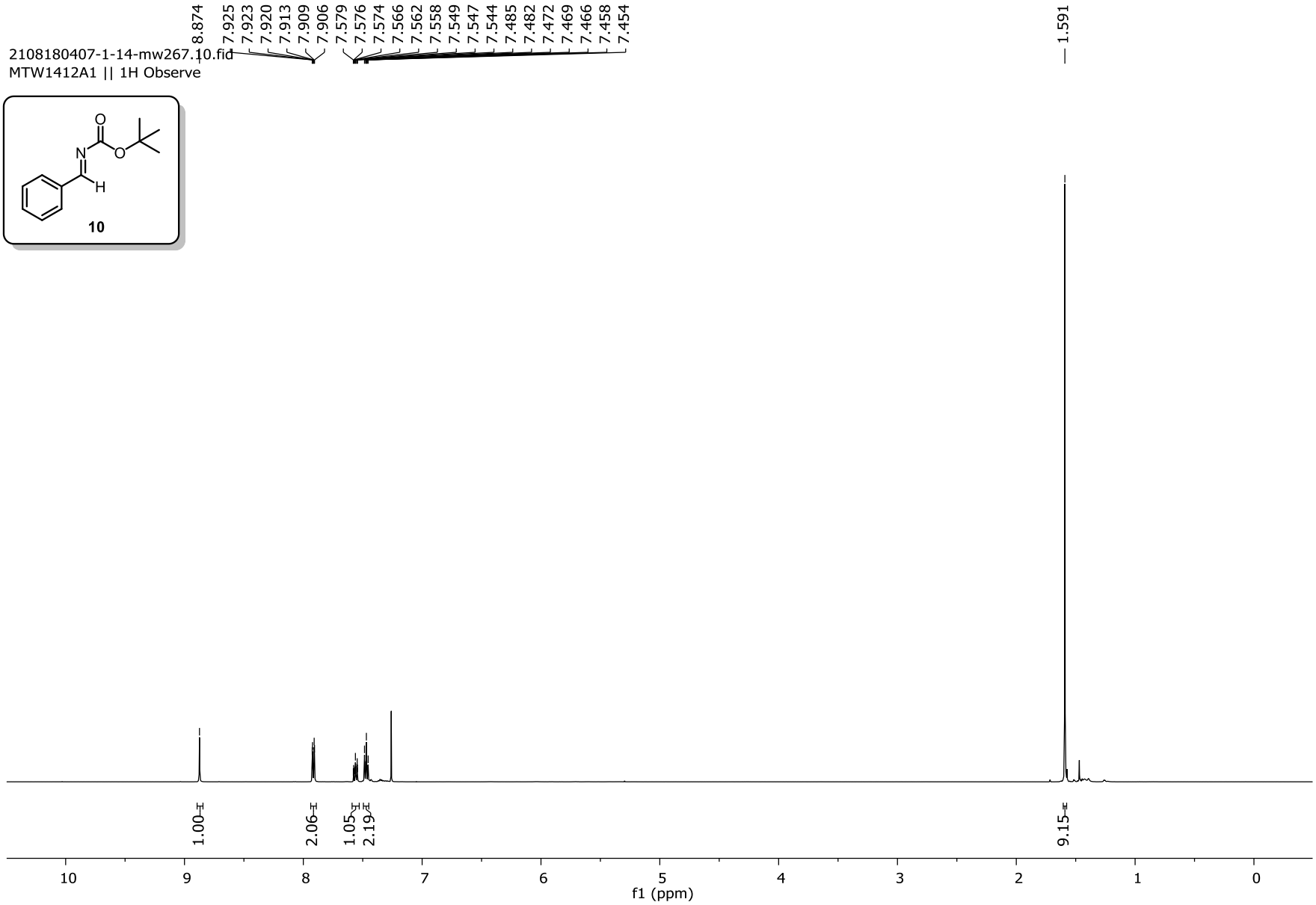
Detector A Channel 1 211nm

Peak#	Ret. Time	Area%
1	21.346	100.039
2	30.871	-0.039
Total		100.000

*Figure S1 HPLC Analysis on a chiral stationary phase of (S)-C(3)-F_2-HBTM **7***

3. NMR Spectra

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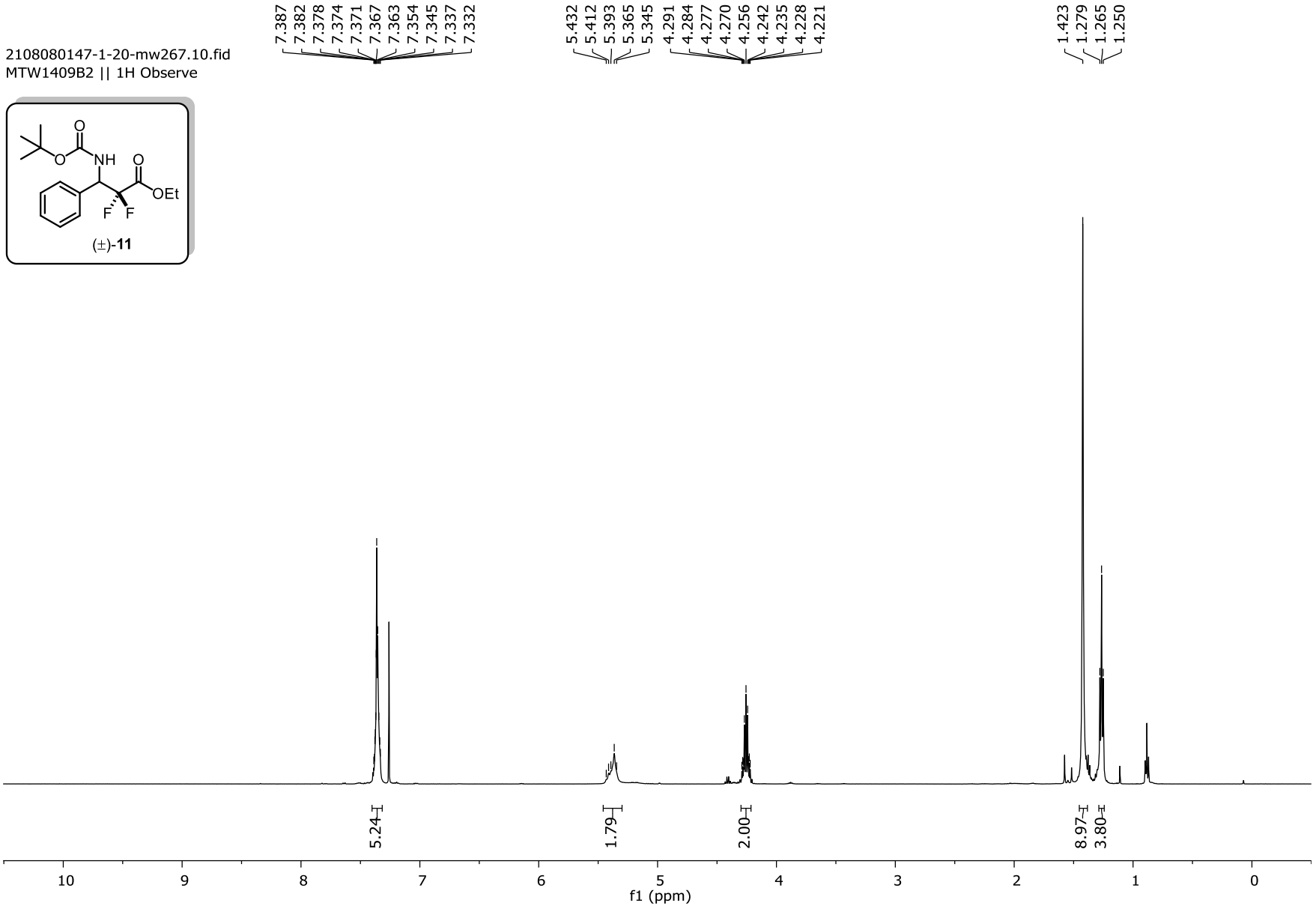
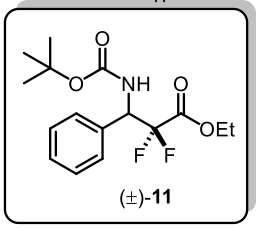
7.925
7.923
7.920
7.913
7.909
7.906
7.579
7.576
7.574
7.566
7.562
7.558
7.549
7.547
7.544
7.485
7.482
7.472
7.469
7.466
7.458
7.454
1.591
2108180407-1-14-mw267.10.fid
MTW1412A1 || 1H Observe
O
N
O
H
10
1.00
2.06
1.05
2.19
9.15
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

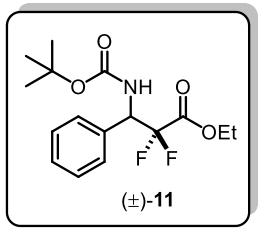

7.387
7.382
7.378
7.374
7.371
7.367
7.363
7.354
7.345
7.337
7.332
5.432
5.412
5.393
5.365
5.345
4.291
4.284
4.277
4.270
4.256
4.242
4.235
4.228
4.221
1.423
1.279
1.265
1.250
2108080147-1-20-mw267.10.fid
MTW1409B2 || 1H Observe
O
O
NH
O
OEt
F
F
(±)-11
5.24
1.79
2.00
8.97
3.80
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

2108080147-1-20-mw267.11.fid
MTW1409B2 || 19F Observe with 1H decoupling - Full Range SW

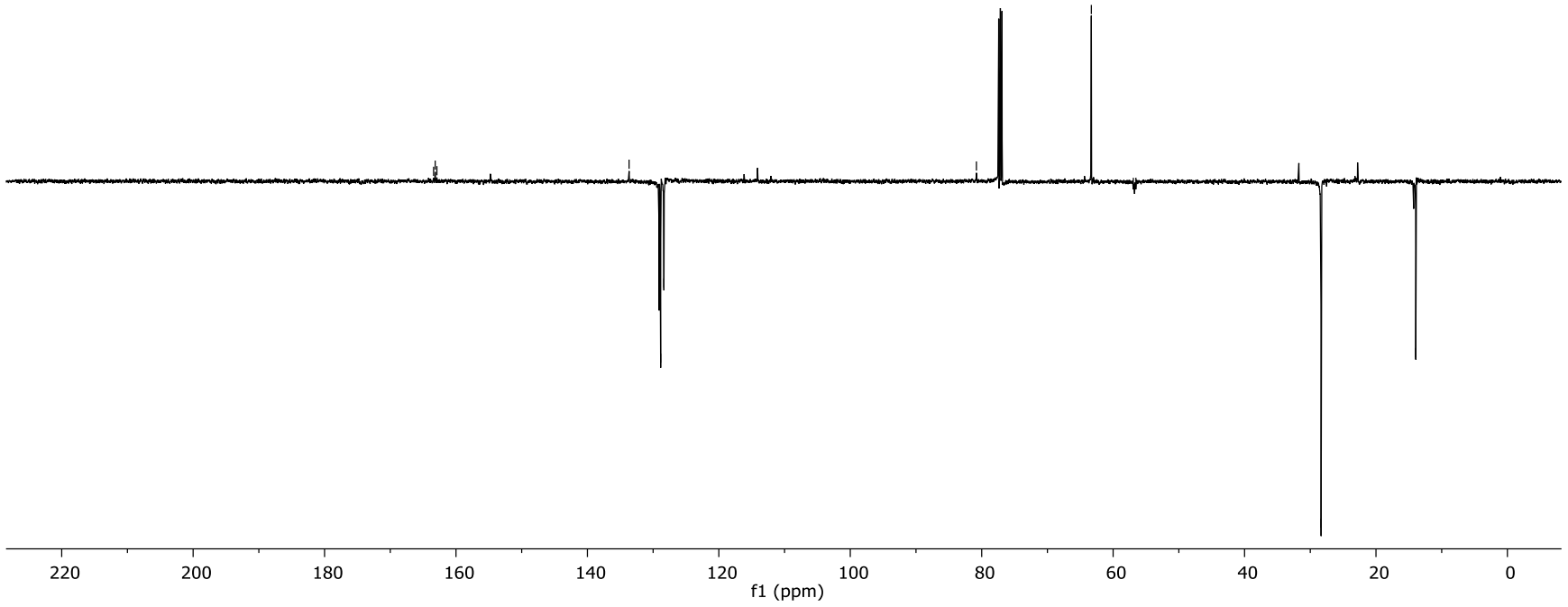


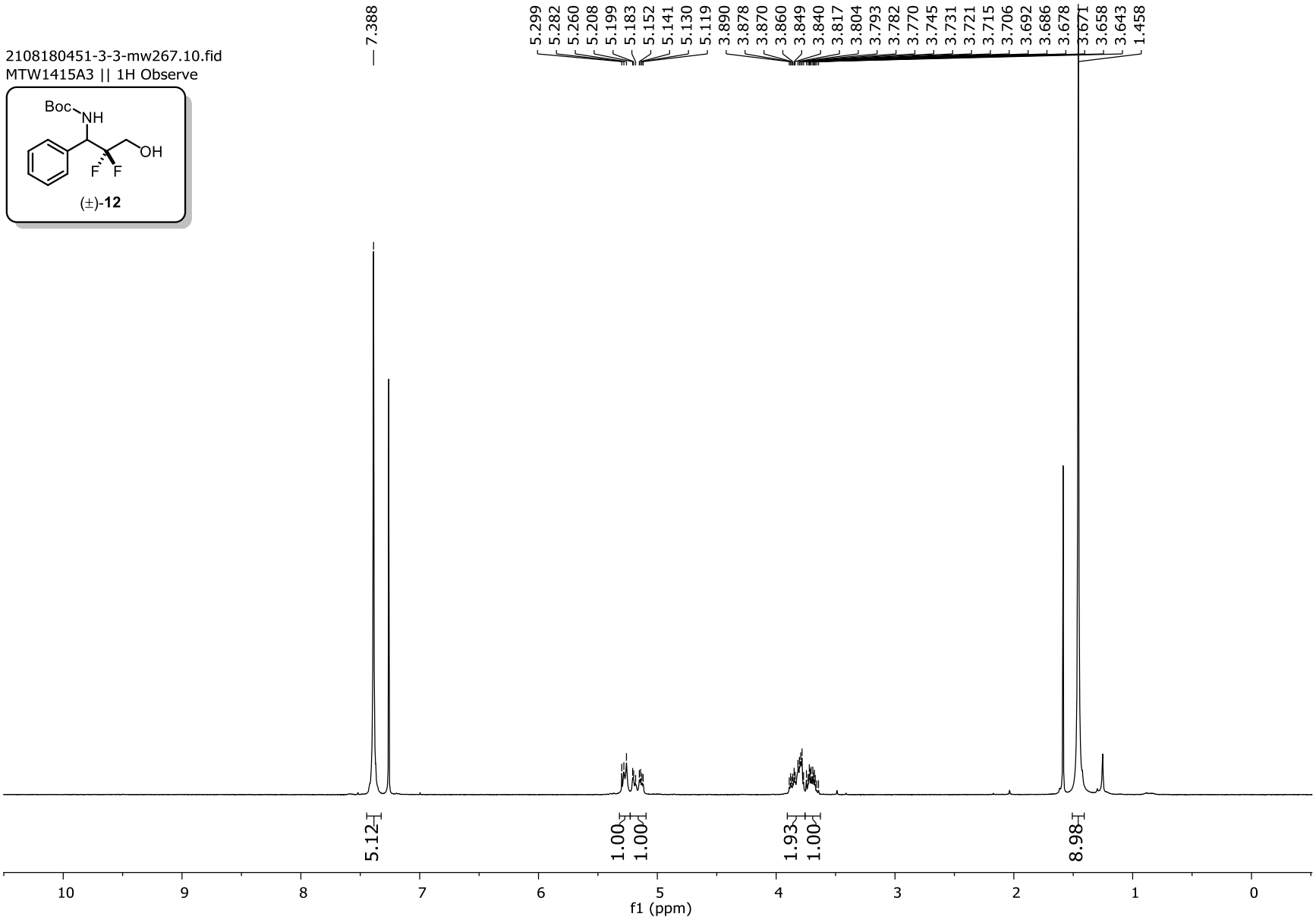
(±)-**11**

2108080147-1-20-mw267.12.fid
MTW1409B2 || 13C Observe with multiplicity editing - DEPTQ



(±)-**11**

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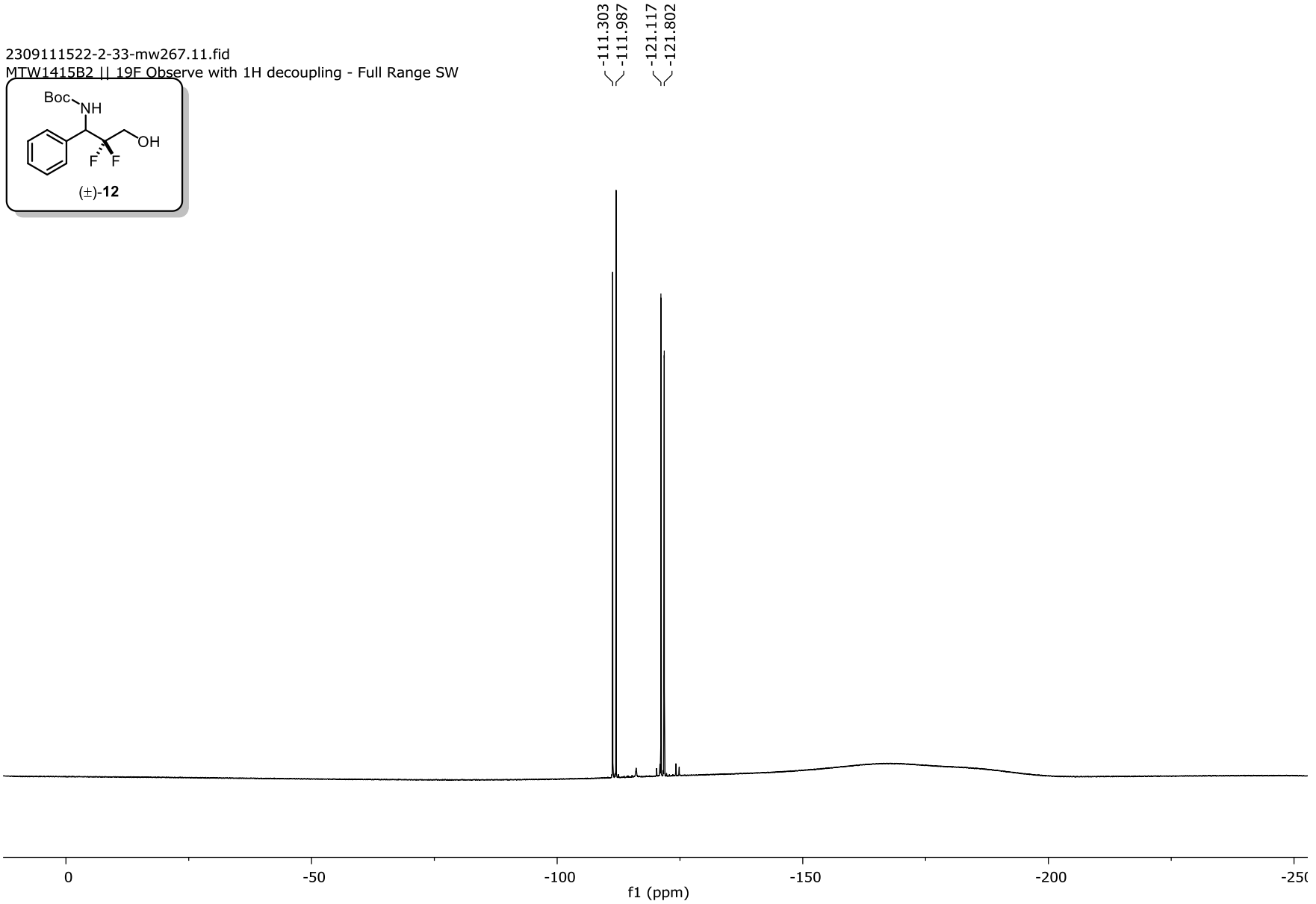
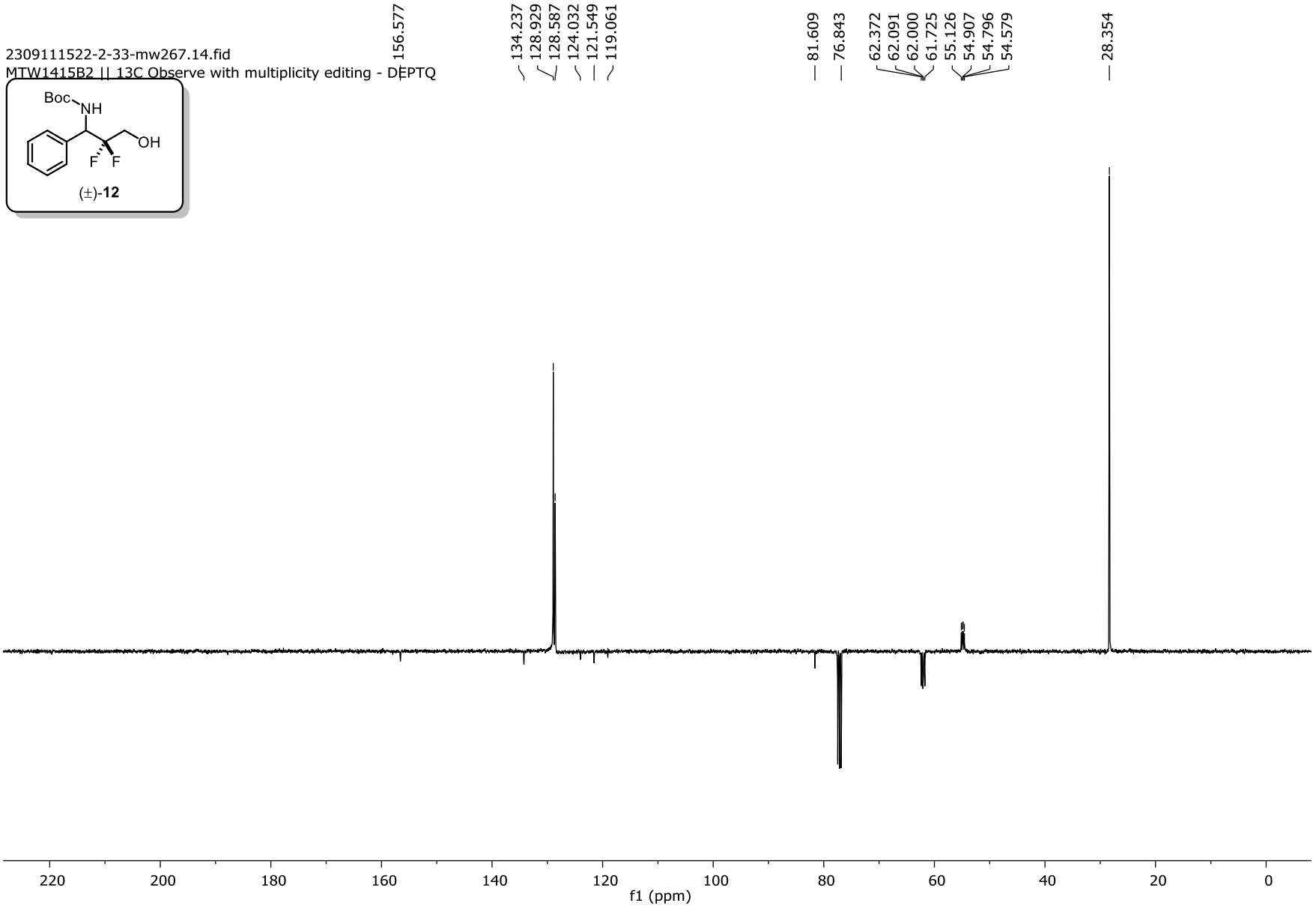
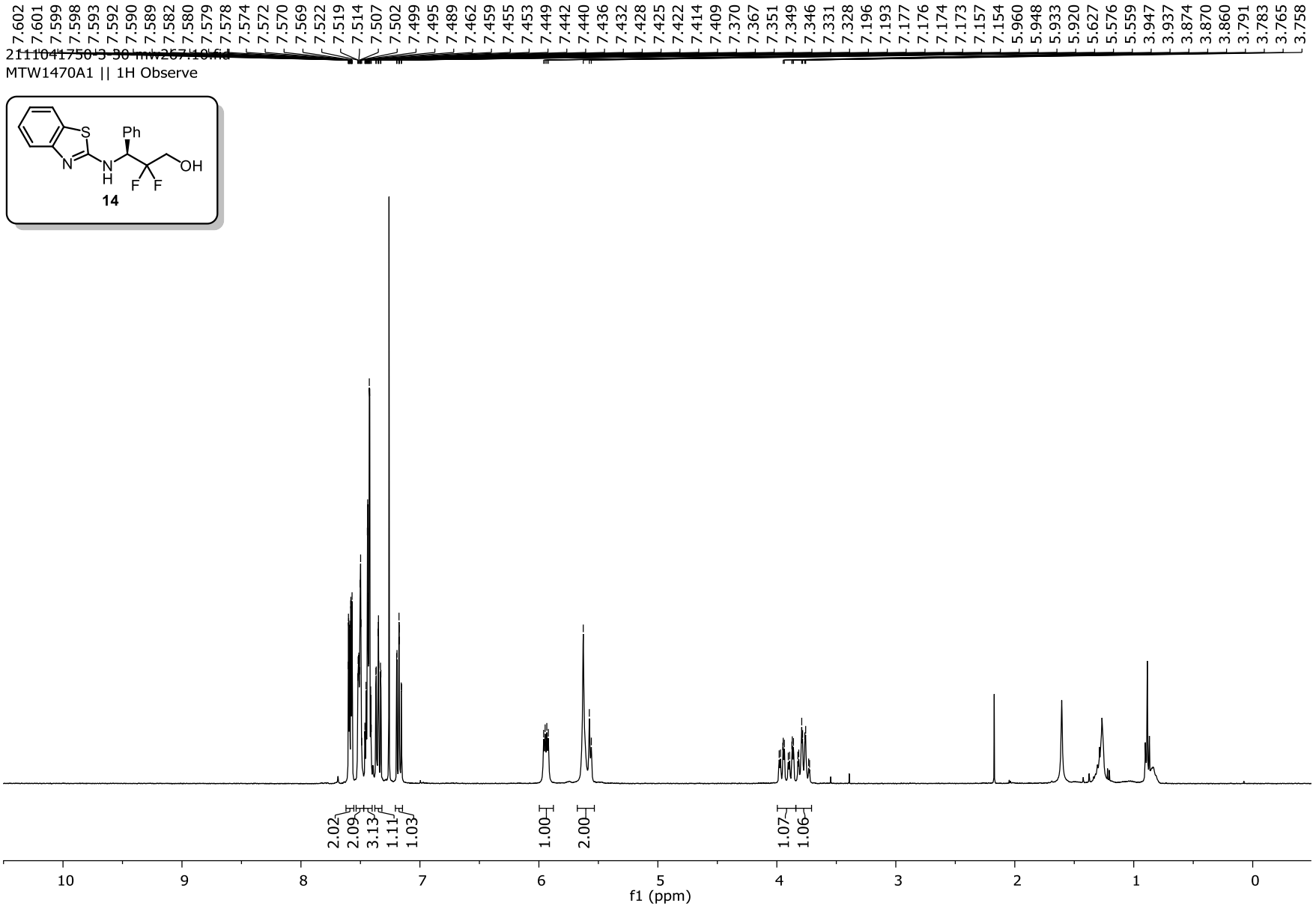
Boc
NH
OH
F
F
(±)-12
7.388
5.299
5.282
5.260
5.208
5.199
5.183
5.152
5.141
5.130
5.119
3.890
3.878
3.870
3.860
3.849
3.840
3.817
3.804
3.793
3.782
3.770
3.745
3.731
3.721
3.715
3.706
3.692
3.686
3.678
3.671
3.658
3.643
1.458
5.12
1.00
1.00
1.93
1.00
8.98
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


2309111522-2-33-mw267.11.fid
MTW1415B2 || 19F Observe with 1H decoupling - Full Range SW
-111.303
-111.987
-121.117
-121.802
Boc
NH
OH
F
F
(±)-12
0
-50
-100
-150
-200
f1 (ppm)


156.577
134.237
128.929
128.587
124.032
121.549
119.061
81.609
76.843
62.372
62.091
62.000
61.725
55.126
54.907
54.796
54.579
28.354
2309111522-2-33-mw267.14.fid
MTW1415B2 || 13C Observe with multiplicity editing - DEPTQ
Boc
NH
OH
F
F
(±)-12
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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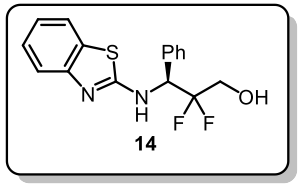
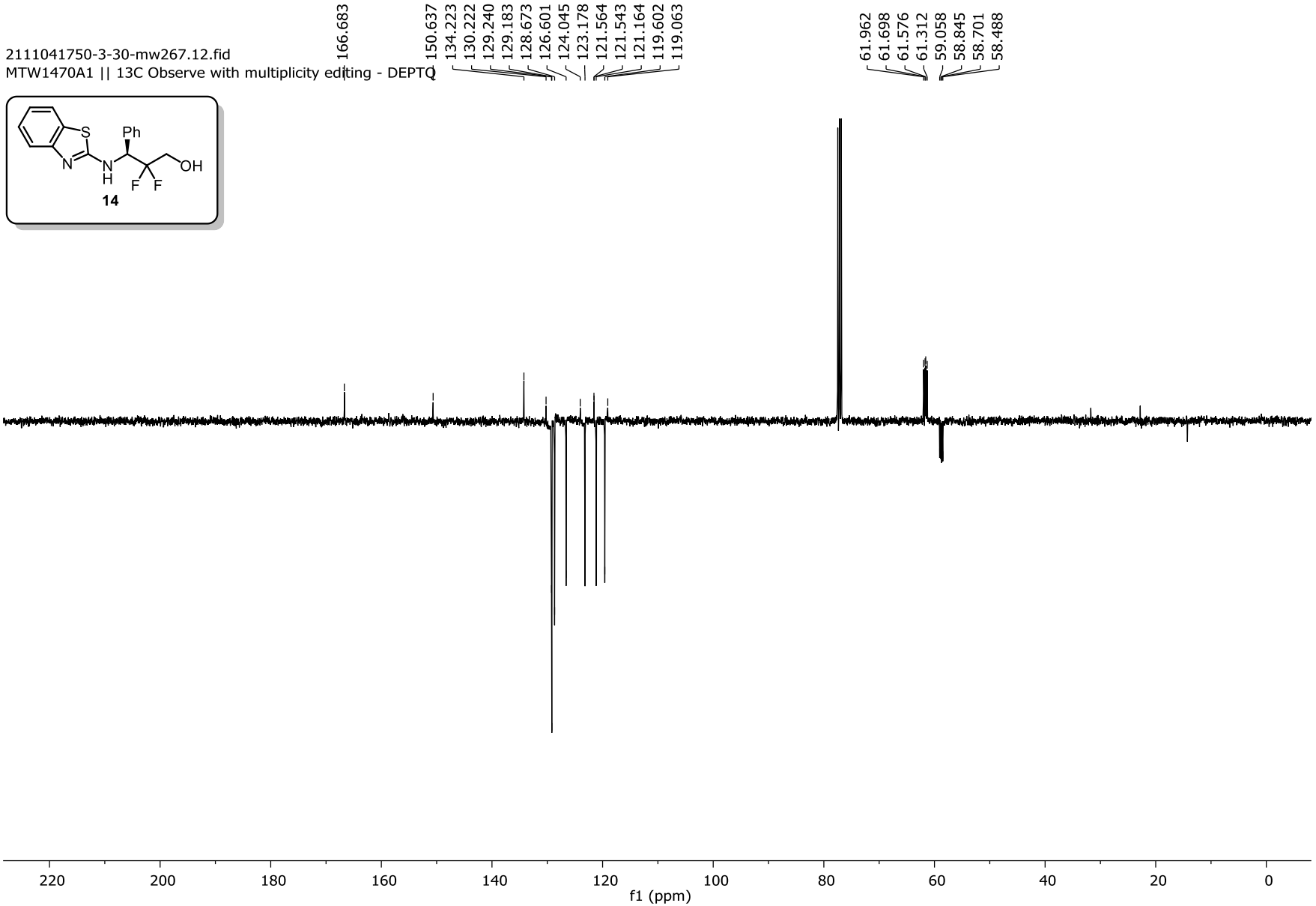
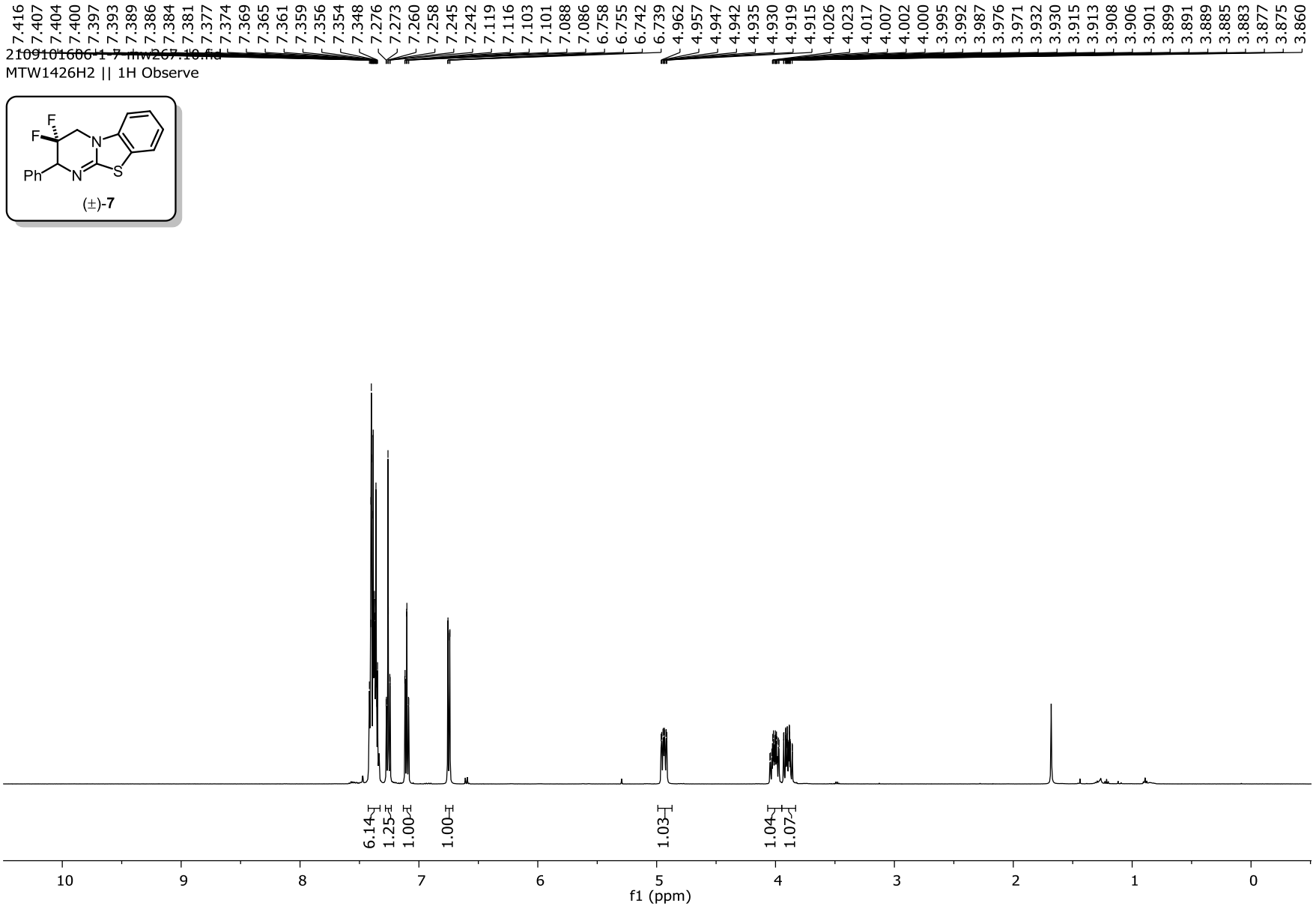
7.601
7.599
7.598
7.593
7.592
7.590
7.589
7.582
7.580
7.579
7.578
7.574
7.572
7.570
7.569
7.522
7.519
7.514
7.507
7.502
7.499
7.495
7.489
7.462
7.459
7.455
7.453
7.449
7.442
7.440
7.436
7.432
7.428
7.425
7.422
7.414
7.409
7.370
7.367
7.351
7.349
7.346
7.331
7.328
7.196
7.193
7.177
7.176
7.174
7.173
7.157
7.154
5.960
5.948
5.933
5.920
5.627
5.576
5.559
3.947
3.937
3.874
3.870
3.860
3.791
3.783
3.765
3.758
2111041750-3-30-mlv267.10.fid
MTW1470A1 || 1H Observe
S
Ph
N
N
H
F
F
OH
14
2.02
2.09
3.13
1.11
1.03
1.00
2.00
1.07
1.06
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)

2111041750-3-30-mw267.11.fid
MTW1470A1 || 19F Observe with 1H decoupling - Full Range SW



14


166.683
150.637
134.223
130.222
129.240
129.183
128.673
126.601
124.045
123.178
121.564
121.543
121.164
119.602
119.063
61.962
61.698
61.576
61.312
59.058
58.845
58.701
58.488
2111041750-3-30-mw267.12.fid
MTW1470A1 || 13C Observe with multiplicity editing - DEPTQ
S
Ph
N
N
H
F
F
OH
14
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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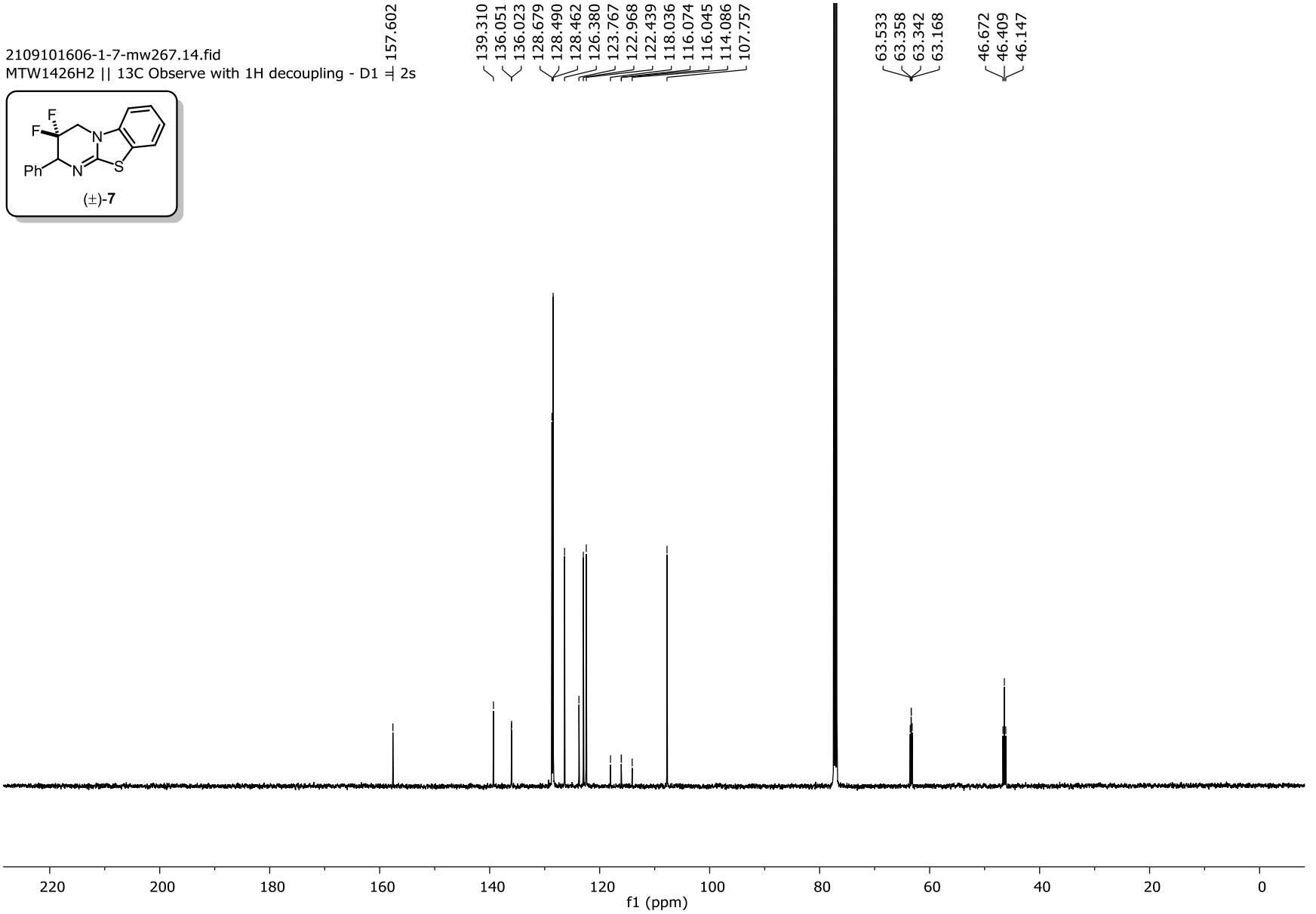
7.407
7.404
7.400
7.397
7.393
7.389
7.386
7.384
7.381
7.377
7.374
7.369
7.365
7.361
7.359
7.356
7.354
7.348
7.276
7.273
7.260
7.258
7.245
7.242
7.119
7.116
7.103
7.101
7.088
7.086
6.758
6.755
6.742
6.739
4.962
4.957
4.947
4.942
4.935
4.930
4.919
4.915
4.026
4.023
4.017
4.007
4.002
4.000
3.995
3.992
3.987
3.976
3.971
3.932
3.930
3.915
3.913
3.908
3.906
3.901
3.899
3.891
3.889
3.885
3.883
3.877
3.875
3.860
MTW1426H2 || 1H Observe
F
F
N
Ph
N
S
(±)-7
6.14
1.25
1.00
1.00
1.03
1.04
1.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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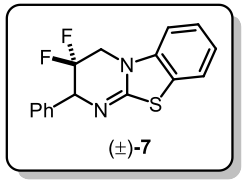
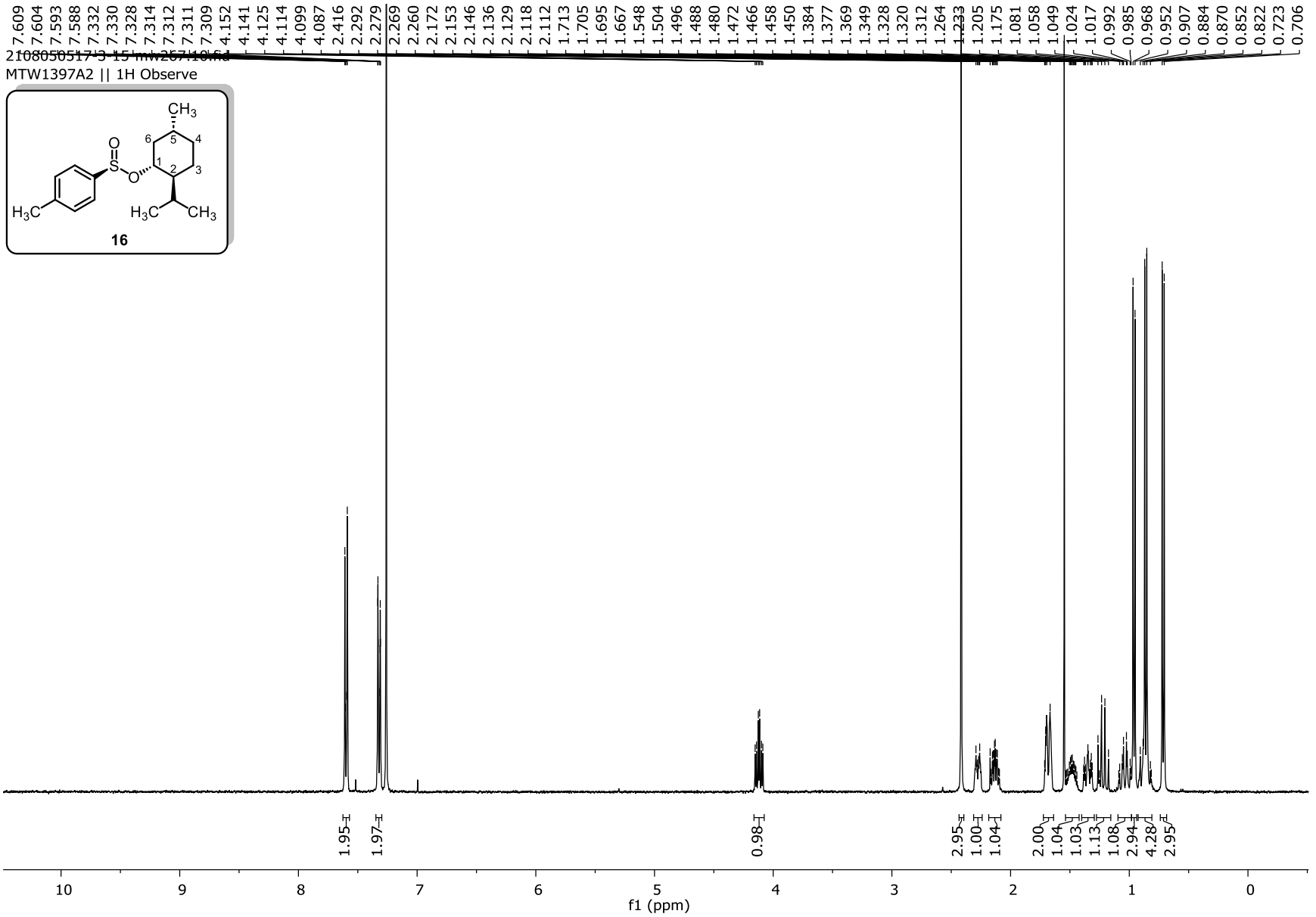
MTW1426H2 || 13C Observe with 1H decoupling - D1 = 2s
157.602
139.310
136.051
136.023
128.679
128.490
128.462
126.380
123.767
122.968
122.439
118.036
116.074
116.045
114.086
107.757
63.533
63.358
63.342
63.168
46.672
46.409
46.147
F
F
N
Ph
N
S
(±)-7
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

2109101606-1-7-mw267.11.fid
MTW1426H2 || 19F Observe with 1H decoupling - Full Range SW



(±)-**7**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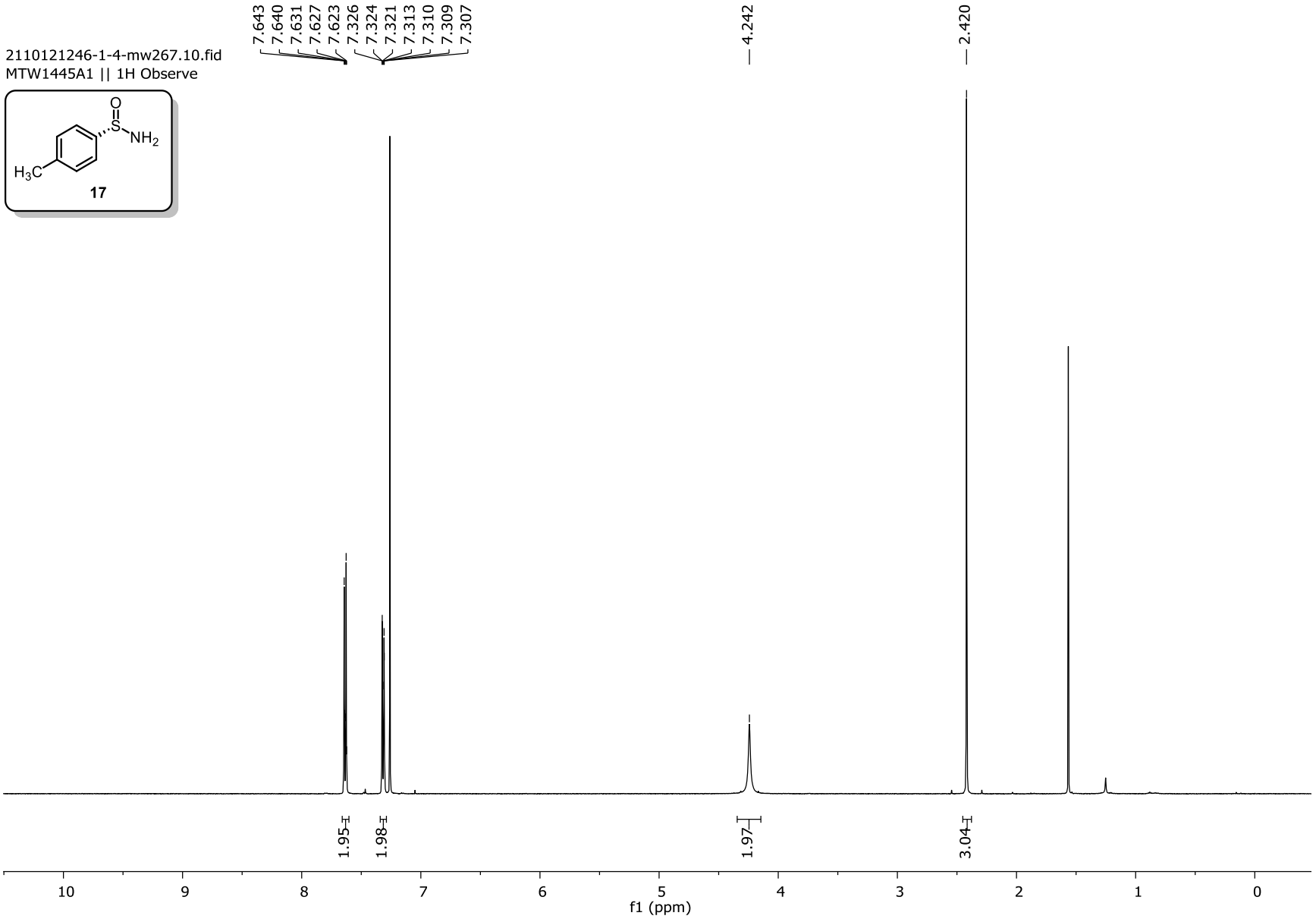
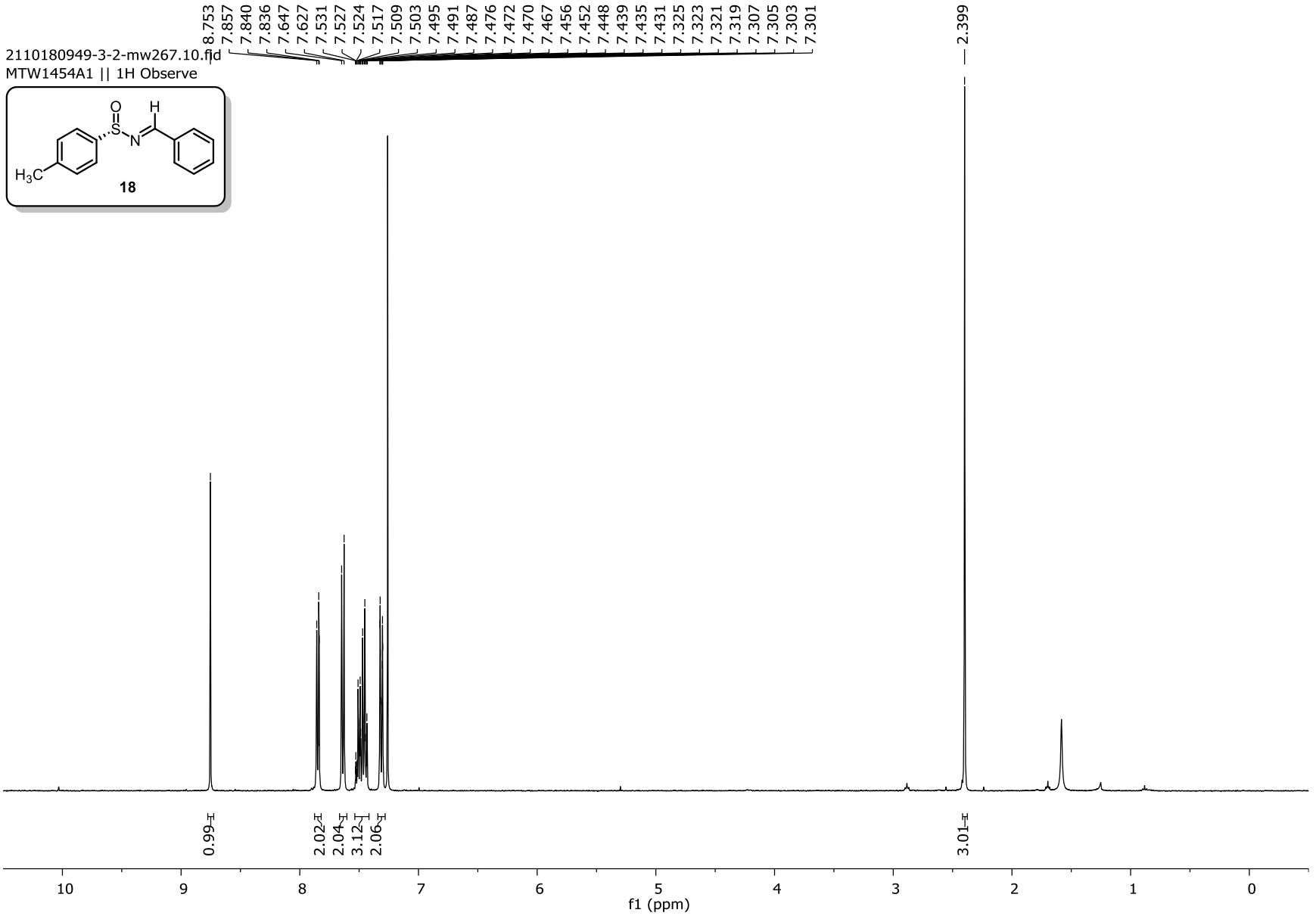
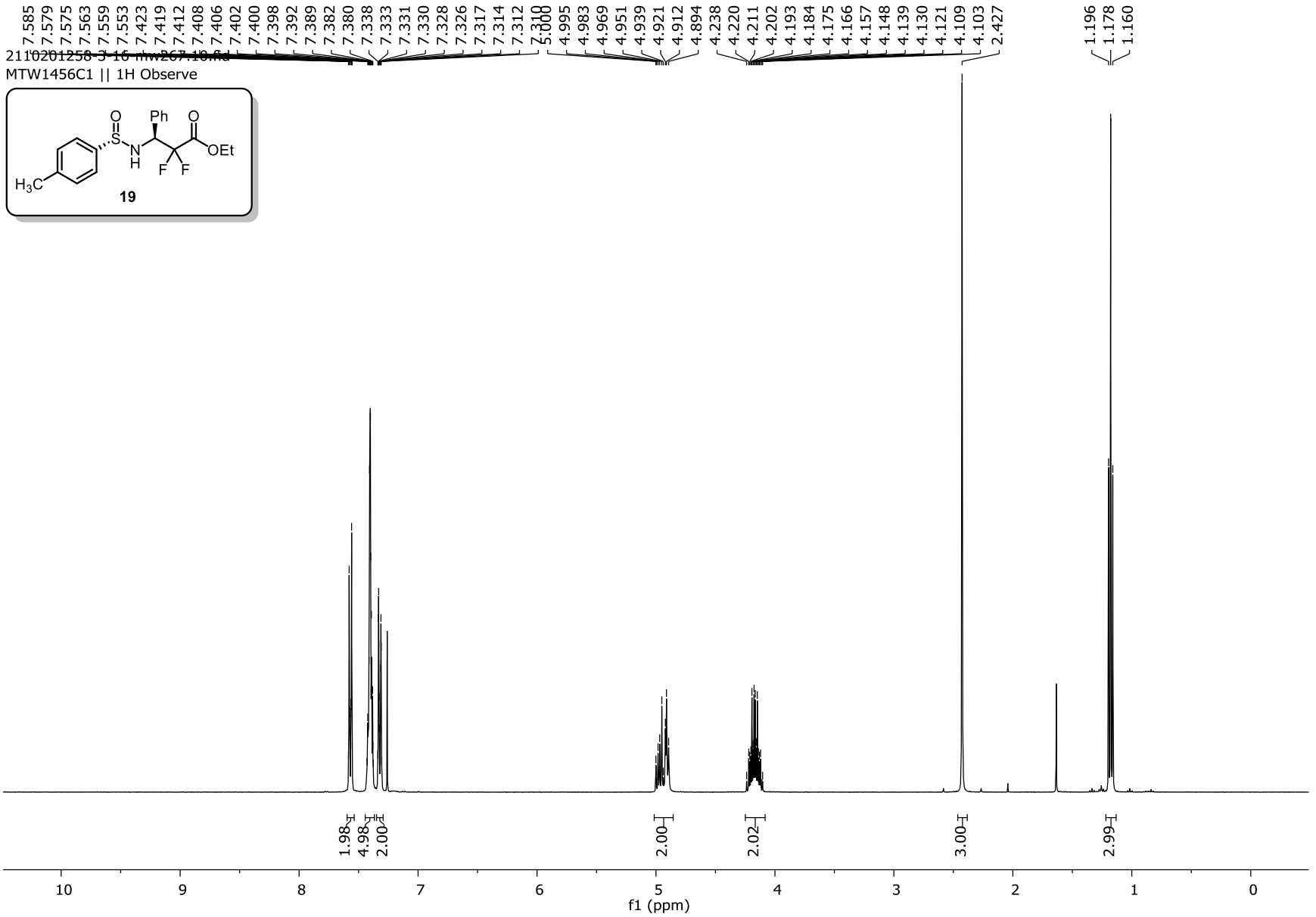
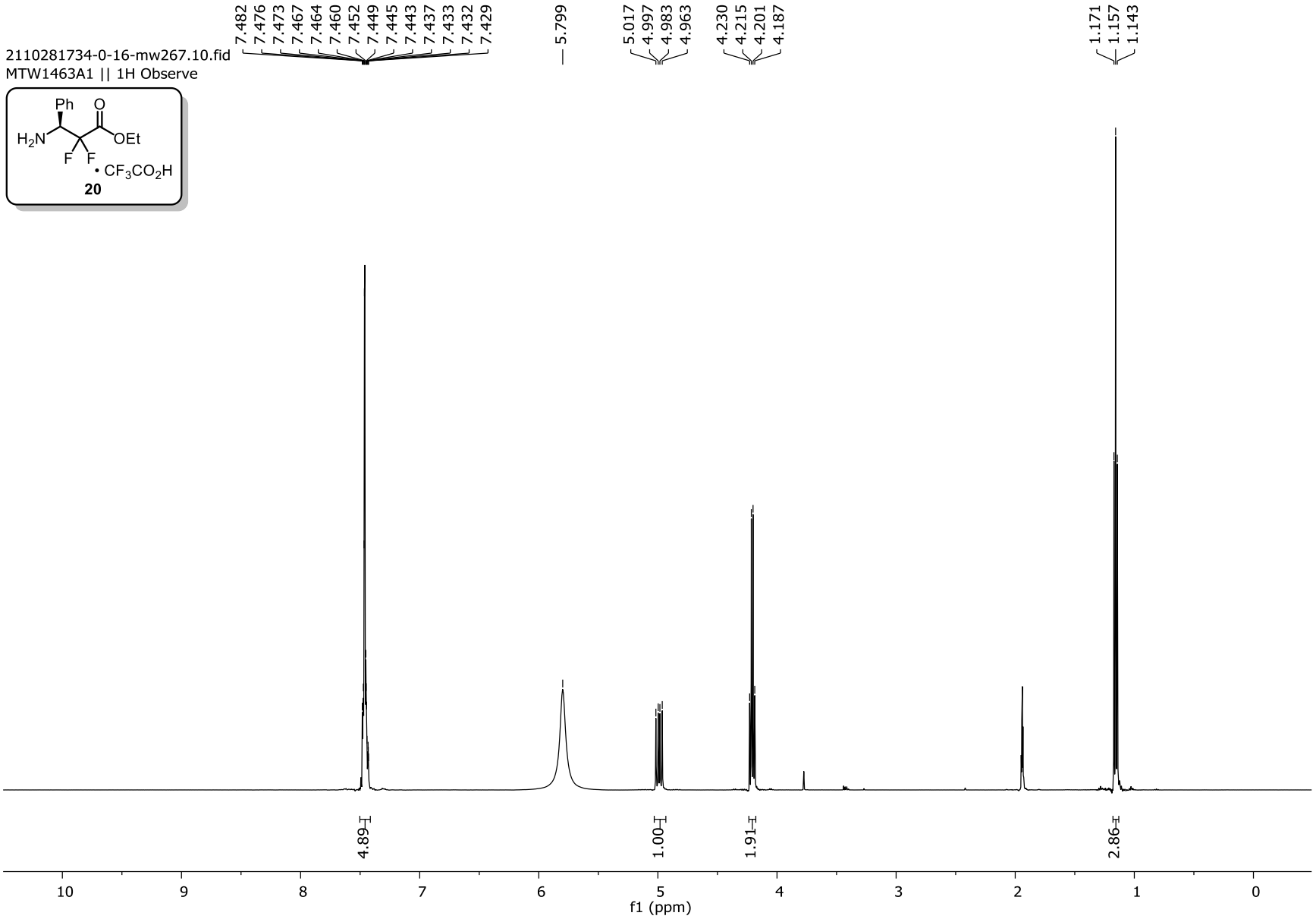
MTW1397A2 || 1H Observe
16
1.95 1.97 0.98 2.95 1.00 1.04 2.00 1.04 1.03 1.13 1.08 2.94 4.28 2.95
10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)


7.643
7.640
7.631
7.627
7.623
7.326
7.324
7.321
7.313
7.310
7.309
7.307
4.242
2.420
2110121246-1-4-mw267.10.fid
MTW1445A1 || 1H Observe
O
S
NH2
H3C
17
1.95
1.98
1.97
3.04
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


8.753
7.857
7.840
7.836
7.647
7.627
7.531
7.527
7.524
7.517
7.509
7.503
7.495
7.491
7.487
7.476
7.472
7.470
7.467
7.456
7.452
7.448
7.439
7.435
7.431
7.325
7.323
7.321
7.319
7.307
7.305
7.303
7.301
2.399
2110180949-3-2-mw267.10.fid
MTW1454A1 || 1H Observe
O
H
S
N
H3C
18
0.99
2.02
2.04
3.12
2.06
3.01
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


7.585
7.579
7.575
7.563
7.559
7.553
7.423
7.419
7.412
7.408
7.406
7.402
7.400
7.398
7.392
7.389
7.382
7.380
7.338
7.333
7.331
7.330
7.328
7.326
7.317
7.314
7.312
7.310
5.000
4.995
4.983
4.969
4.951
4.939
4.921
4.912
4.894
4.238
4.220
4.211
4.202
4.193
4.184
4.175
4.166
4.157
4.148
4.139
4.130
4.121
4.109
4.103
2.427
1.196
1.178
1.160
211\0201258-3-16-nhw267.10.fid
MTW1456C1 || 1H Observe
O
Ph
O
S
N
H
OEt
F
F
H3C
19
1.98
4.98
2.00
2.00
2.02
3.00
2.99
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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7.476
7.473
7.467
7.464
7.460
7.452
7.449
7.445
7.443
7.437
7.433
7.432
7.429
5.799
5.017
4.997
4.983
4.963
4.230
4.215
4.201
4.187
1.171
1.157
1.143
2110281734-0-16-mw267.10.fid
MTW1463A1 || 1H Observe
Ph
O
H2N
OEt
F
F
• CF3CO2H
20
4.89
1.00
1.91
2.86
10
9
8
7
6
5
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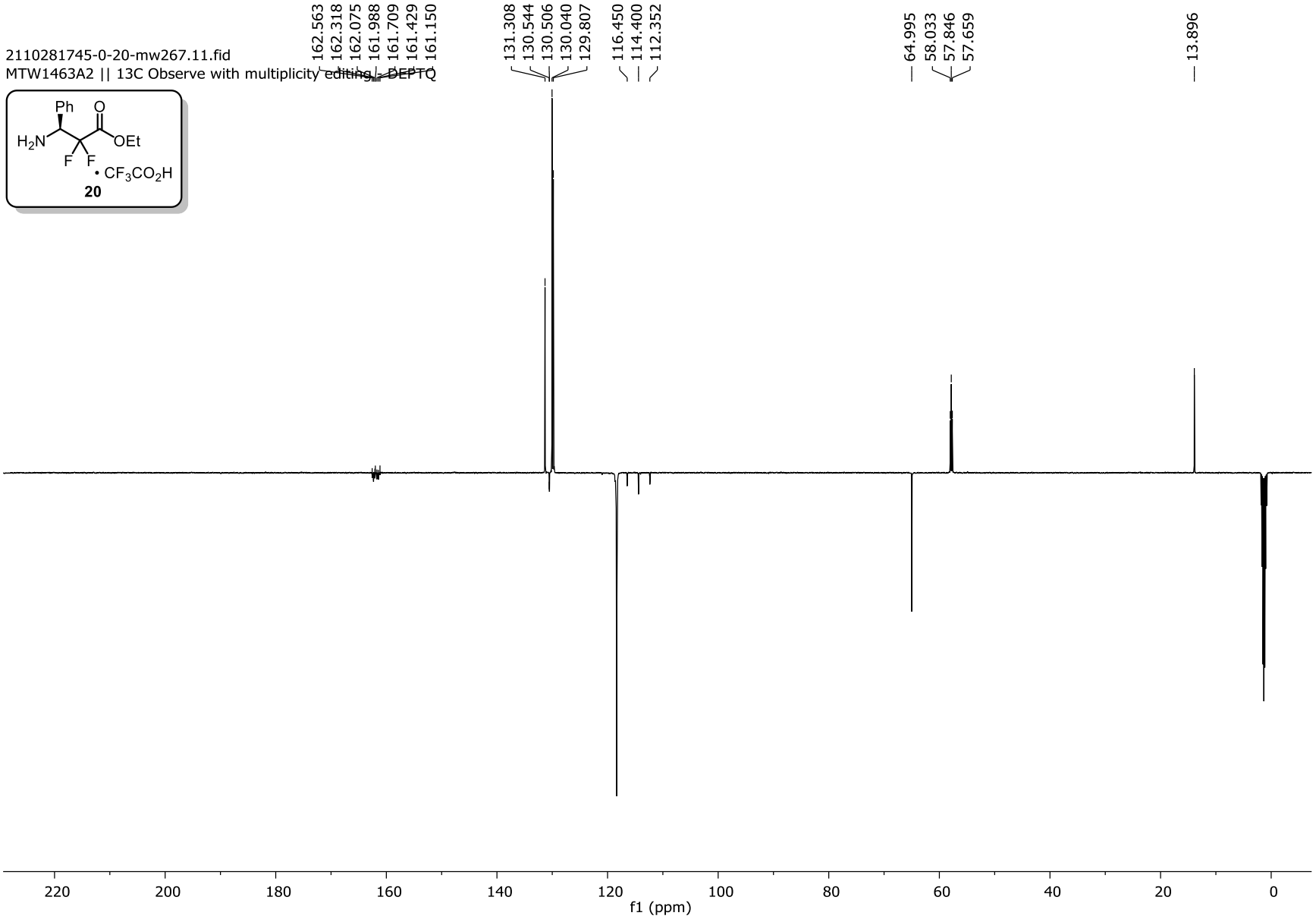
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H2N
OEt
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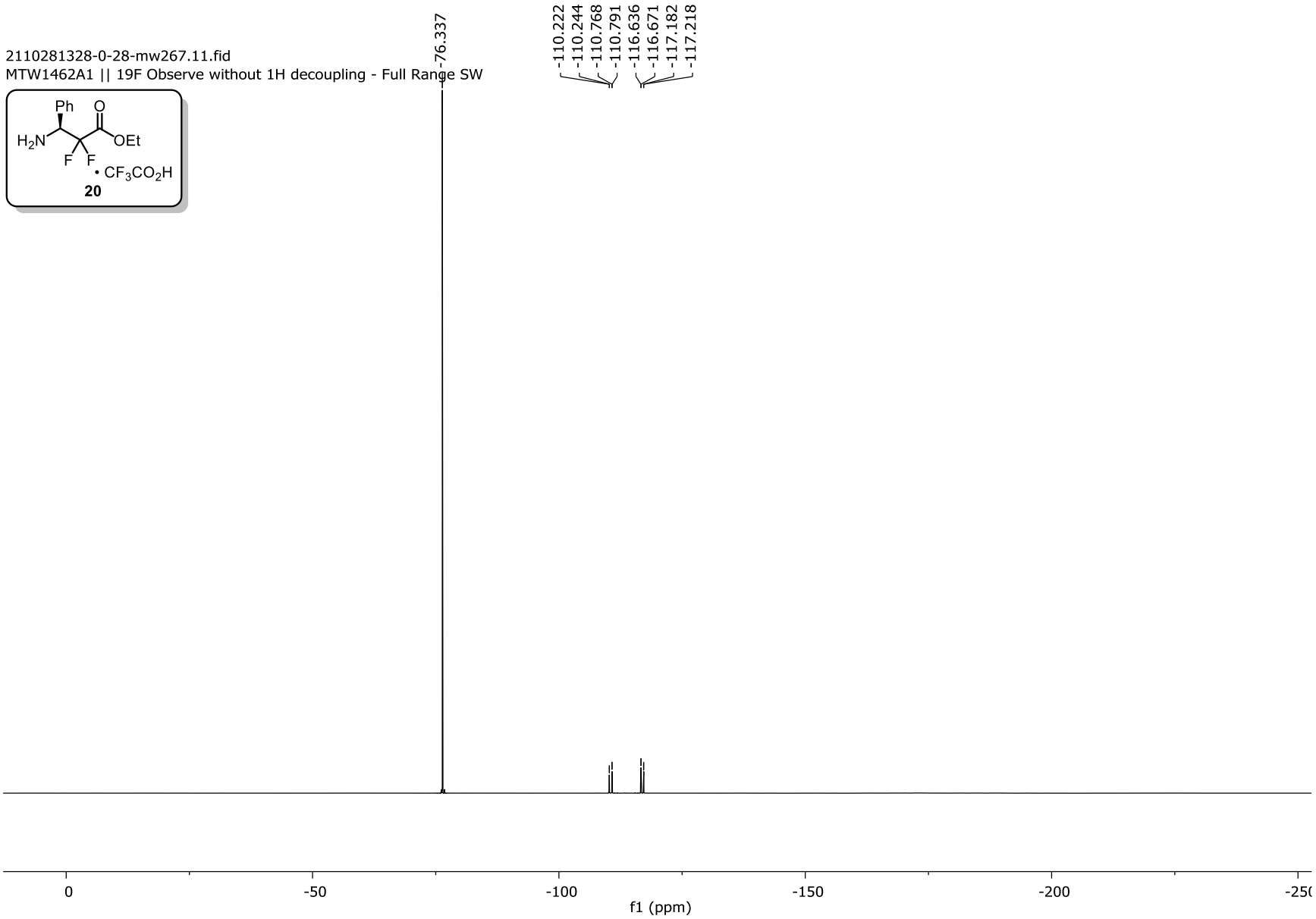
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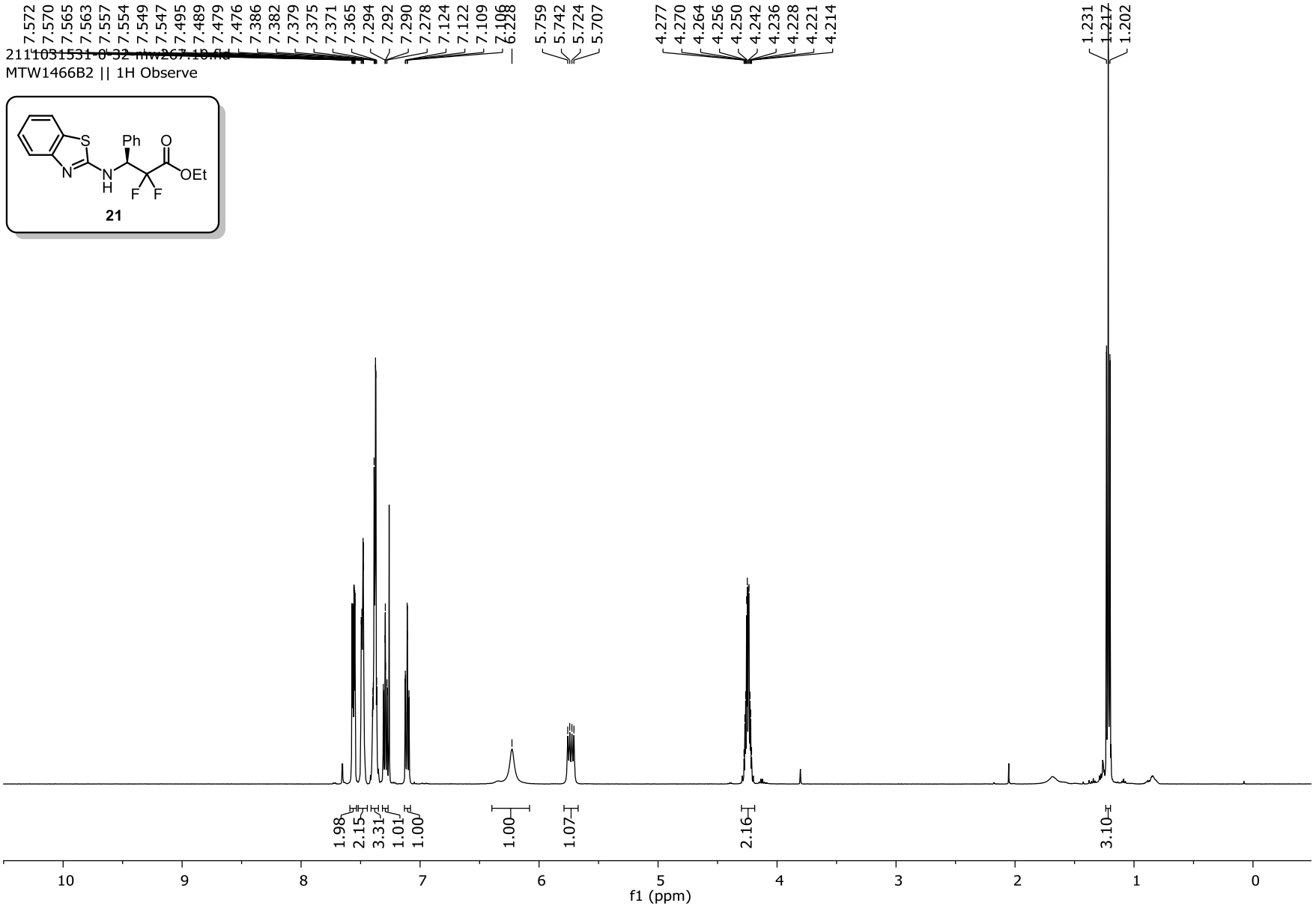
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H
F
F
OEt
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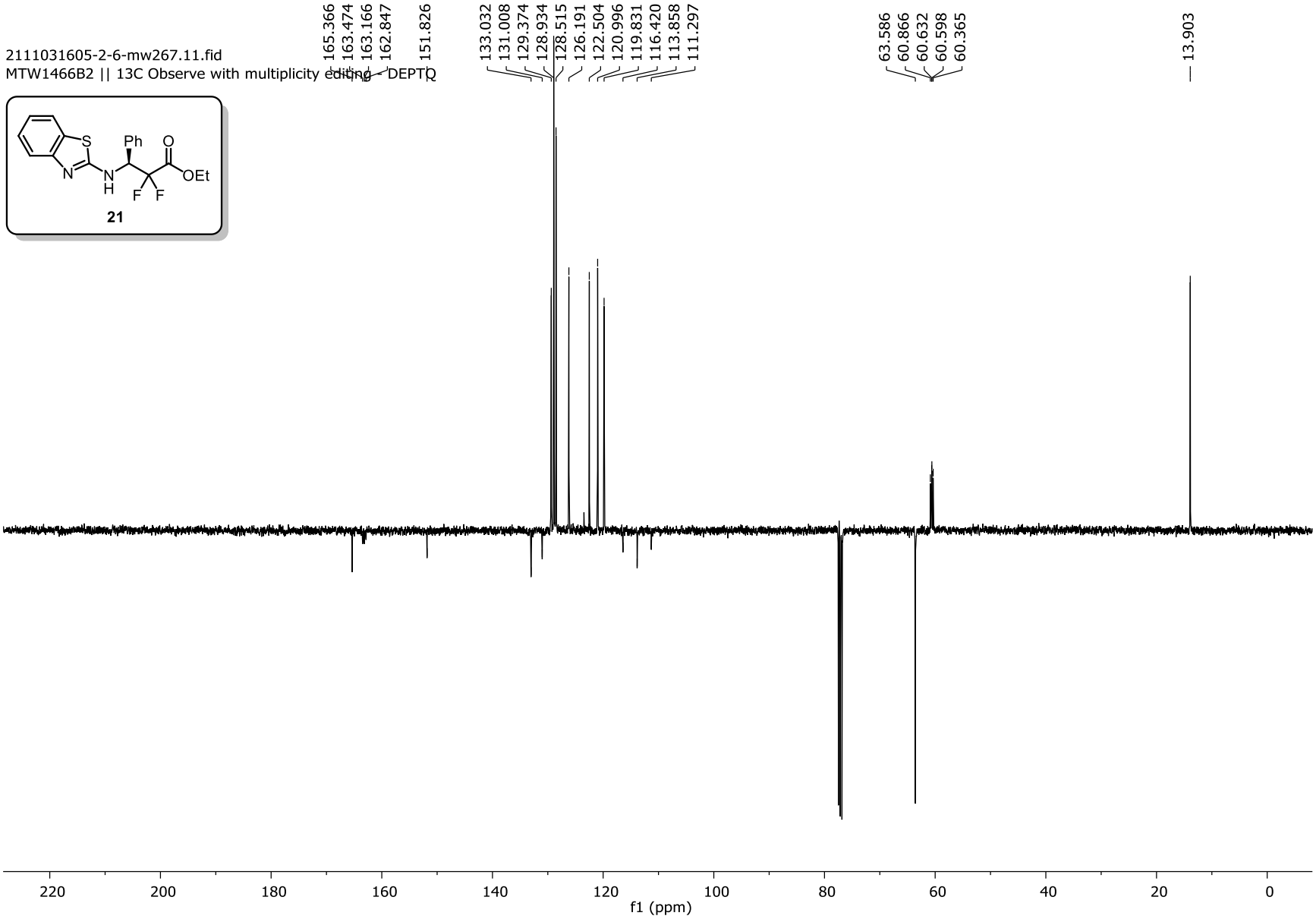
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Ph
O
N
N
H
F
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OEt
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200
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140
120
100
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60
40
20
0
f1 (ppm)

4. X-Ray Crystallography

Data Collection

A colorless platelet crystal of $C_{16}H_{12}F_2N_2S$ having approximate dimensions of 0.120 x 0.030 x 0.010 mm was mounted in a loop. All measurements were made on a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Mo-Ka radiation.

Cell constants and an orientation matrix for data collection corresponded to a primitive orthorhombic cell with dimensions:

a = 6.807(3) Å
b = 9.898(4) Å
c = 19.960(7) Å
V = 1344.8(9) $Å^3$

For Z = 4 and F.W. = 302.34, the calculated density is 1.493 g/cm^3. The reflection conditions of:

h00: h = 2n
0k0: k = 2n
00l: l = 2n

uniquely determine the space group to be:

$P2_12_12_1$ (#19)

The data were collected at a temperature of -180 ± 1°C to a maximum 2q value of 50.8°.

Data Reduction

Of the 6101 reflections were collected, where 2448 were unique (R_{int} = 0.0284); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku). [1]

The linear absorption coefficient, m, for Mo-Ka radiation is 2.573 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.734 to 0.997. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods[2] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement[3] on F^2 was based on 2448 observed reflections and 190 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = S \; ||Fo| - |Fc|| \; / \; S \; |Fo| = 0.0241$$

$$wR2 = [S (w (Fo^2 - Fc^2)^2)/ S \; w(Fo^2)^2]^{1/2} = 0.0678$$

The goodness of fit[4] was 0.88. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.29 and -0.18 $e^-/Å^3$, respectively. The final Flack parameter [5] was 0.00(3), indicating that the present absolute structure is correct. [6]

Neutral atom scattering factors were taken from International Tables for Crystallography (IT), Vol. C, Table 6.1.1.4 [7]. Anomalous dispersion effects were included in Fcalc[8]; the values for Df' and Df'' were those of Creagh and McAuley[9]. The values for the mass attenuation coefficients are those of Creagh and Hubbell[10]. All calculations were performed using the CrystalStructure[11] crystallographic software package except for refinement, which was performed using SHELXL Version 2018/3[12].

References

1. CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2015). Tokyo 196-8666, Japan.
2. SHELXT Version 2018/2: Sheldrick, G. M. (2014). Acta Cryst. A70, C1437.
3. Least Squares function minimized: (SHELXL Version 2018/3)
   i. $Sw(F_O^2-F_C^2)^2$ where w = Least Squares weights.
4. Goodness of fit is defined as:
   i. $[Sw(F_O^2-F_C^2)^2/(N_O-N_V)]^{1/2}$
   ii. where: N_O = number of observations
   a. N_V = number of variables
5. Parsons, S., Flack, H.D. and Wagner, T. Acta Cryst. B69 (2013) 249-259.
6. Flack, H.D. and Bernardinelli (2000), J. Appl. Cryst. 33, 114-1148.
7. International Tables for Crystallography, Vol.C (1992). Ed. A.J.C. Wilson, Kluwer Academic Publishers, Dordrecht, Netherlands, Table 6.1.1.4, pp. 572.
8. Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).
9. Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).
10. Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).
11. CrystalStructure 4.3: Crystal Structure Analysis Package, Rigaku Corporation (2000-2019). Tokyo 196-8666, Japan.
12. SHELXL Version 2018/3: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

EXPERIMENTAL DETAILS

Table S1. Crystal Data

Empirical Formula	$C_{16}H_{12}F_2N_2S$
Formula Weight	302.34
Crystal Color, Habit	colorless, platelet
Crystal Dimensions	0.120 X 0.030 X 0.010 mm
Crystal System	orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 6.807(3) Å b = 9.898(4) Å c = 19.960(7) Å V = 1344.8(9) $Å^3$
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.493 g/cm^3
F_{000}	624.00
m(MoKa)	2.573 cm^{-1}

Table S2. Intensity Measurements

Diffractometer	XtaLAB P200
Radiation	MoKa (l = 0.71075 Å) multi-layer mirror monochromated
Voltage, Current	45kV, 66mA
Temperature	-180.0^{o}C
Detector Aperture	83.8 x 70.0 mm
Data Images	451 exposures
Pixel Size	0.172 mm
$2q_{max}$	50.8^{o}
No. of Reflections Measured	Total: 6101 Unique: 2448 (R_{int} = 0.0284) Parsons quotients (Flack x parameter): 927
Corrections	Lorentz-polarization Absorption (trans. factors: 0.734 - 0.997)

Table S3. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXT Version 2018/2)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$S\ w\ (Fo^2 - Fc^2)^2$
Least Squares Weights	$w = 1/ [\ s^2(Fo^2) + (0.0577 \cdot P)^2 + 0.0000 \cdot P\ ]$ where $P = (Max(Fo^2,0) + 2Fc^2)/3$
$2q_{max}$ cutoff	50.8^o
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	2448
No. Variables	190
Reflection/Parameter Ratio	12.88
Residuals: R1 (I>2.00s(I))	0.0241
Residuals: R (All reflections)	0.0255
Residuals: wR2 (All reflections)	0.0678
Goodness of Fit Indicator	0.880
Flack parameter (Parsons' quotients = 927)	0.00(3)
Max Shift/Error in Final Cycle	0.001
Maximum peak in Final Diff. Map	$0.29\ e^-/Å^3$
Minimum peak in Final Diff. Map	$-0.18\ e^-/Å^3$

Table S4. Atomic coordinates and B_{iso}/B_{eq}

atom	x	y	z	B_{eq}
S1	0.60708(8)	0.46858(5)	0.62977(2)	1.543(12)
F1	0.28639(19)	0.36746(12)	0.82374(6)	1.91(2)
F2	0.32238(18)	0.52530(13)	0.89983(6)	1.80(2)
N8	0.3795(3)	0.56571(16)	0.72202(8)	1.28(3)
N12	0.6567(3)	0.43730(17)	0.76201(9)	1.49(3)
C2	0.3985(3)	0.56198(19)	0.60565(10)	1.36(3)
C3	0.3337(3)	0.5902(2)	0.54125(10)	1.57(4)
C4	0.1602(3)	0.6646(2)	0.53361(11)	1.70(4)
C5	0.0552(3)	0.7080(2)	0.58951(10)	1.58(4)
C6	0.1197(3)	0.67978(19)	0.65441(10)	1.41(3)
C7	0.2937(3)	0.6063(2)	0.66175(10)	1.29(3)
C9	0.2978(3)	0.5943(2)	0.78818(9)	1.48(4)
C10	0.3778(3)	0.49081(19)	0.83610(10)	1.50(3)
C11	0.5992(3)	0.4679(2)	0.83183(10)	1.45(3)
C13	0.5491(3)	0.4893(2)	0.71600(10)	1.41(3)
C14	0.7148(3)	0.5867(2)	0.86034(10)	1.44(3)
C15	0.7859(3)	0.6896(2)	0.81894(10)	1.54(4)
C16	0.8949(3)	0.7963(2)	0.84558(11)	1.69(3)
C17	0.9296(3)	0.8027(2)	0.91417(11)	1.79(4)
C18	0.8580(3)	0.7017(2)	0.95562(11)	2.04(4)
C19	0.7524(3)	0.5934(2)	0.92908(11)	1.75(4)

$B_{eq} = 8/3\ p^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos g + 2U_{13}(aa^*cc^*)\cos b + 2U_{23}(bb^*cc^*)\cos a)$

Table S5. Atomic coordinates and B_{iso} involving hydrogen atoms

atom	x	y	z	B_{iso}
H3	0.40531	0.55981	0.50328	1.887
H4	0.11375	0.68555	0.48996	2.036
H5	-0.06266	0.75790	0.58334	1.893
H6	0.04755	0.70957	0.69238	1.689
H9A	0.15262	0.58915	0.78679	1.771
H9B	0.33584	0.68626	0.80277	1.771
H11	0.63093	0.38675	0.85964	1.744
H15	0.75978	0.68691	0.77221	1.843
H16	0.94521	0.86461	0.81687	2.023
H17	1.00220	0.87587	0.93252	2.146
H18	0.88092	0.70638	1.00251	2.449
H19	0.70605	0.52388	0.95784	2.104

Table S6. Anisotropic displacement parameters

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	0.0194(3)	0.0226(3)	0.0166(2)	0.0049(2)	0.0024(2)	-0.0010(2)
F1	0.0257(7)	0.0203(6)	0.0267(7)	-0.0061(5)	0.0005(5)	0.0020(5)
F2	0.0241(6)	0.0287(7)	0.0156(6)	0.0017(6)	0.0041(5)	0.0016(5)
N8	0.0161(8)	0.0169(8)	0.0157(8)	0.0025(7)	0.0021(7)	-0.0000(7)
N12	0.0202(9)	0.0184(9)	0.0180(8)	0.0033(7)	0.0006(7)	0.0001(7)
C2	0.0169(9)	0.0142(9)	0.0207(9)	-0.0008(8)	0.0016(8)	-0.0004(8)
C3	0.0220(11)	0.0195(10)	0.0183(10)	-0.0010(9)	0.0020(9)	0.0012(9)
C4	0.0245(12)	0.0203(11)	0.0197(10)	-0.0017(9)	-0.0014(9)	0.0022(9)
C5	0.0186(11)	0.0169(10)	0.0245(11)	-0.0012(9)	-0.0008(9)	0.0021(9)
C6	0.0179(10)	0.0163(9)	0.0193(9)	-0.0004(9)	0.0026(9)	0.0002(8)
C7	0.0184(10)	0.0125(9)	0.0180(10)	-0.0034(8)	0.0000(9)	0.0000(8)
C9	0.0175(10)	0.0210(10)	0.0176(10)	0.0011(9)	0.0036(9)	-0.0008(9)
C10	0.0222(11)	0.0180(10)	0.0169(10)	-0.0032(9)	0.0039(9)	-0.0011(8)
C11	0.0214(10)	0.0165(9)	0.0174(10)	0.0017(9)	0.0018(9)	0.0022(8)
C13	0.0190(10)	0.0153(10)	0.0193(10)	-0.0014(8)	0.0029(8)	-0.0025(8)
C14	0.0150(10)	0.0176(10)	0.0221(11)	0.0057(8)	0.0015(8)	-0.0008(9)
C15	0.0182(10)	0.0201(10)	0.0201(10)	0.0038(9)	0.0021(9)	0.0020(9)
C16	0.0194(10)	0.0173(9)	0.0274(10)	0.0036(9)	0.0048(10)	0.0024(9)
C17	0.0172(11)	0.0207(10)	0.0301(11)	0.0004(9)	-0.0000(9)	-0.0051(9)
C18	0.0282(12)	0.0289(11)	0.0205(10)	0.0019(10)	-0.0003(10)	-0.0010(10)
C19	0.0235(11)	0.0227(11)	0.0204(11)	0.0008(9)	0.0012(9)	0.0032(9)

The general temperature factor expression: $\exp(-2p^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S7. Bond lengths (Å)

atom	atom	distance	atom	atom	distance
S1	C2	1.762(2)	S1	C13	1.778(2)
F1	C10	1.392(2)	F2	C10	1.370(2)
N8	C7	1.396(3)	N8	C9	1.460(3)
N8	C13	1.386(3)	N12	C11	1.479(3)
N12	C13	1.282(3)	C2	C3	1.387(3)
C2	C7	1.398(3)	C3	C4	1.400(3)
C4	C5	1.393(3)	C5	C6	1.396(3)
C6	C7	1.398(3)	C9	C10	1.504(3)
C10	C11	1.526(3)	C11	C14	1.525(3)
C14	C15	1.398(3)	C14	C19	1.397(3)
C15	C16	1.396(3)	C16	C17	1.391(3)
C17	C18	1.386(3)	C18	C19	1.396(3)

Table S8. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
C3	H3	0.950	C4	H4	0.950
C5	H5	0.950	C6	H6	0.950
C9	H9A	0.990	C9	H9B	0.990
C11	H11	1.000	C15	H15	0.950
C16	H16	0.950	C17	H17	0.950
C18	H18	0.950	C19	H19	0.950

Table S9. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C2	S1	C13	91.44(10)	C7	N8	C9	124.34(17)
C7	N8	C13	115.52(16)	C9	N8	C13	120.09(16)
C11	N12	C13	116.20(17)	S1	C2	C3	127.95(16)
S1	C2	C7	110.91(15)	C3	C2	C7	121.12(19)
C2	C3	C4	118.35(19)	C3	C4	C5	120.5(2)
C4	C5	C6	121.33(19)	C5	C6	C7	117.90(19)
N8	C7	C2	112.74(18)	N8	C7	C6	126.47(18)
C2	C7	C6	120.77(19)	N8	C9	C10	107.77(17)
F1	C10	F2	105.06(15)	F1	C10	C9	108.83(16)
F1	C10	C11	107.54(15)	F2	C10	C9	108.72(16)
F2	C10	C11	111.15(16)	C9	C10	C11	115.04(17)
N12	C11	C10	110.13(16)	N12	C11	C14	111.92(16)
C10	C11	C14	111.96(16)	S1	C13	N8	109.39(14)
S1	C13	N12	121.35(16)	N8	C13	N12	129.26(19)
C11	C14	C15	121.32(18)	C11	C14	C19	119.83(18)
C15	C14	C19	118.85(19)	C14	C15	C16	120.67(19)
C15	C16	C17	120.0(2)	C16	C17	C18	119.7(2)
C17	C18	C19	120.6(2)	C14	C19	C18	120.2(2)

Table S10. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C2	C3	H3	120.8	C4	C3	H3	120.8
C3	C4	H4	119.7	C5	C4	H4	119.7
C4	C5	H5	119.3	C6	C5	H5	119.3
C5	C6	H6	121.0	C7	C6	H6	121.1
N8	C9	H9A	110.2	N8	C9	H9B	110.2
C10	C9	H9A	110.1	C10	C9	H9B	110.1
H9A	C9	H9B	108.5	N12	C11	H11	107.5
C10	C11	H11	107.5	C14	C11	H11	107.5
C14	C15	H15	119.7	C16	C15	H15	119.7
C15	C16	H16	120.0	C17	C16	H16	120.0
C16	C17	H17	120.2	C18	C17	H17	120.2
C17	C18	H18	119.7	C19	C18	H18	119.7
C14	C19	H19	119.9	C18	C19	H19	119.9

Table S11. Torsion Angles(O)

(Those having bond angles > 160 or < 20 degrees are excluded.)

atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C2	S1	C13	N8	-0.69(13)	C2	S1	C13	N12	179.15(16)
C13	S1	C2	C3	-178.27(17)	C13	S1	C2	C7	0.44(13)
C7	N8	C9	C10	156.91(16)	C9	N8	C7	C2	-178.02(15)
C9	N8	C7	C6	0.2(3)	C7	N8	C13	S1	0.8(2)
C7	N8	C13	N12	-179.02(18)	C13	N8	C7	C2	-0.5(2)
C13	N8	C7	C6	177.78(16)	C9	N8	C13	S1	178.45(14)
C9	N8	C13	N12	-1.4(3)	C13	N8	C9	C10	-20.5(2)
C11	N12	C13	S1	176.77(14)	C11	N12	C13	N8	-3.4(3)
C13	N12	C11	C10	29.2(2)	C13	N12	C11	C14	-96.0(2)
S1	C2	C3	C4	178.67(13)	S1	C2	C7	N8	-0.1(2)
S1	C2	C7	C6	-178.45(13)	C3	C2	C7	N8	178.74(17)
C3	C2	C7	C6	0.4(3)	C7	C2	C3	C4	0.1(3)
C2	C3	C4	C5	-0.4(3)	C3	C4	C5	C6	0.4(3)
C4	C5	C6	C7	0.0(3)	C5	C6	C7	N8	-178.54(17)
C5	C6	C7	C2	-0.4(3)	N8	C9	C10	F1	-73.33(19)
N8	C9	C10	F2	172.75(14)	N8	C9	C10	C11	47.4(2)
F1	C10	C11	N12	68.22(18)	F1	C10	C11	C14	-166.57(13)
F2	C10	C11	N12	-177.29(13)	F2	C10	C11	C14	-52.09(19)
C9	C10	C11	N12	-53.2(2)	C9	C10	C11	C14	72.0(2)
N12	C11	C14	C15	29.0(2)	N12	C11	C14	C19	-150.54(16)
C10	C11	C14	C15	-95.2(2)	C10	C11	C14	C19	85.2(2)
C11	C14	C15	C16	-178.69(16)	C11	C14	C19	C18	-179.98(16)
C15	C14	C19	C18	0.5(3)	C19	C14	C15	C16	0.8(3)
C14	C15	C16	C17	-1.5(3)	C15	C16	C17	C18	0.9(3)
C16	C17	C18	C19	0.4(3)	C17	C18	C19	C14	-1.1(3)

Table S12. Intramolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
F1	N8	2.894(2)	F1	N12	2.890(2)
F1	C13	3.046(2)	F2	N8	3.593(2)
F2	C14	2.850(3)	F2	C19	3.060(3)
N8	C11	2.825(3)	N8	C14	3.588(3)
N8	C15	3.592(3)	N12	C7	3.593(3)
N12	C9	2.942(3)	N12	C15	2.881(3)
C2	C5	2.766(3)	C3	C6	2.830(3)
C4	C7	2.775(3)	C6	C9	3.052(3)
C9	C14	3.184(3)	C9	C15	3.508(3)
C10	C13	2.666(3)	C10	C15	3.421(3)
C10	C19	3.313(3)	C13	C14	3.241(3)
C13	C15	3.279(3)	C14	C17	2.804(3)
C15	C18	2.775(3)	C16	C19	2.785(3)

Table S13. Intramolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H3	3.013	F1	H9A	2.488
F1	H9B	3.201	F1	H11	2.460
F2	H9A	2.613	F2	H9B	2.510
F2	H11	2.634	F2	H19	2.857
N8	H6	2.735	N8	H15	3.024
N12	H9B	3.392	N12	H15	2.576
C2	H4	3.253	C2	H6	3.292
C3	H5	3.277	C4	H6	3.291
C5	H3	3.285	C6	H4	3.283
C6	H9A	2.799	C6	H9B	3.307
C7	H3	3.285	C7	H5	3.253
C7	H9A	2.679	C7	H9B	2.938
C9	H6	2.804	C9	H11	3.376
C9	H15	3.291	C10	H15	3.486
C10	H19	3.317	C11	H9A	3.390
C11	H9B	2.867	C11	H15	2.703
C11	H19	2.676	C13	H9A	3.203
C13	H9B	2.985	C13	H11	3.092
C13	H15	2.672	C14	H9B	2.991
C14	H16	3.283	C14	H18	3.276
C15	H9B	3.081	C15	H11	3.280
C15	H17	3.272	C15	H19	3.267
C16	H18	3.258	C17	H15	3.268
C17	H19	3.270	C18	H16	3.259
C19	H11	2.605	C19	H15	3.266
C19	H17	3.273	H3	H4	2.358
H4	H5	2.330	H5	H6	2.351
H6	H9A	2.342	H6	H9B	2.960
H9B	H15	2.950	H11	H15	3.555
H11	H19	2.438	H15	H16	2.341
H16	H17	2.343	H17	H18	2.334
H18	H19	2.340			

Table S14. Intermolecular contacts less than 3.60 Å

atom	atom	distance	atom	atom	distance
F1	C5[1]	3.301(3)	F1	C6[1]	3.359(3)
F1	C15[2]	3.384(3)	F2	C3[3]	3.225(3)
F2	C4[3]	3.267(3)	N8	C16[2]	3.524(3)
N12	C6[2]	3.406(3)	N12	C9[2]	3.553(3)
C2	C16[2]	3.442(3)	C2	C17[2]	3.425(3)
C3	F2[4]	3.225(3)	C3	C17[2]	3.479(3)
C4	F2[4]	3.267(3)	C5	F1[5]	3.301(3)
C6	F1[5]	3.359(3)	C6	N12[6]	3.406(3)
C6	C11[6]	3.445(3)	C7	C16[2]	3.328(3)
C9	N12[6]	3.553(3)	C9	C16[7]	3.583(3)
C11	C6[2]	3.445(3)	C15	F1[6]	3.384(3)
C16	N8[6]	3.524(3)	C16	C2[6]	3.442(3)
C16	C7[6]	3.328(3)	C16	C9[8]	3.583(3)
C17	C2[6]	3.425(3)	C17	C3[6]	3.479(3)

Symmetry Operators:

(1) -X,Y+1/2-1,-Z+1/2+1 (2) -X+1,Y+1/2-1,-Z+1/2+1
(3) -X+1/2,-Y+1,Z+1/2 (4) -X+1/2,-Y+1,Z+1/2-1
(5) -X,Y+1/2,-Z+1/2+1 (6) -X+1,Y+1/2,-Z+1/2+1
(7) X-1,Y,Z (8) X+1,Y,Z

Table S15. Intermolecular contacts less than 3.60 Å involving hydrogens

atom	atom	distance	atom	atom	distance
S1	H9B[1]	3.126	S1	H16[2]	3.388
S1	H17[2]	3.076	S1	H18[3]	3.075
F1	H4[4]	3.427	F1	H5[5]	2.633
F1	H6[5]	2.777	F1	H15[1]	2.638
F1	H16[1]	3.219	F2	H3[4]	2.716
F2	H4[4]	2.789	F2	H5[5]	3.201
F2	H18[6]	3.318	N8	H11[7]	3.572
N8	H16[1]	3.074	N12	H6[1]	3.156
N12	H9B[1]	2.802	N12	H16[2]	3.216
C2	H4[8]	3.469	C2	H11[7]	3.294
C2	H16[1]	3.418	C2	H17[1]	3.378
C3	H4[8]	2.991	C3	H5[8]	2.990
C3	H11[7]	3.548	C3	H17[1]	3.163
C4	H3[9]	3.316	C4	H4[8]	3.457
C4	H5[8]	3.098	C4	H11[7]	3.376
C4	H17[1]	3.138	C4	H19[10]	3.462
C5	H3[9]	3.123	C5	H4[9]	3.557
C5	H11[7]	2.954	C5	H17[1]	3.340
C6	H11[7]	2.675	C6	H15[11]	3.396
C6	H16[1]	3.202	C6	H17[1]	3.570
C7	H11[7]	2.855	C7	H16[1]	2.924
C7	H17[1]	3.577	C9	H16[1]	3.507
C10	H4[4]	3.533	C10	H5[5]	3.536
C11	H6[1]	3.543	C13	H9B[1]	3.123
C14	H9A[12]	3.322	C15	H6[12]	3.097
C15	H9A[12]	2.763	C16	H6[12]	3.34
C16	H9A[12]	2.943	C16	H9B[12]	3.306
C17	H18[13]	3.494	C18	H3[14]	3.194
C18	H17[6]	3.382	C18	H18[6]	3.474
C19	H3[14]	3.150	C19	H17[6]	3.260
C19	H18[6]	3.491	H3	F2[10]	2.716
H3	C4[8]	3.316	H3	C5[8]	3.123
H3	C18[3]	3.194	H3	C19[3]	3.150
H3	H4[8]	2.895	H3	H5[8]	2.508
H3	H17[1]	3.557	H3	H18[3]	3.010
H3	H19[3]	2.917	H4	F1[10]	3.427
H4	F2[10]	2.789	H4	C2[9]	3.469

Table S16. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H4	C3^{9}	2.991	H4	C4^{9}	3.457
H4	C5^{8}	3.557	H4	C10^{10}	3.533
H4	H3^{9}	2.895	H4	H5^{8}	2.703
H4	H11^{10}	3.171	H4	H17^{1}	3.523
H4	H19^{10}	3.074	H5	F1^{15}	2.633
H5	F2^{15}	3.201	H5	C3^{9}	2.990
H5	C4^{9}	3.098	H5	C10^{15}	3.536
H5	H3^{9}	2.508	H5	H4^{9}	2.703
H5	H11^{7}	3.400	H6	F1^{15}	2.777
H6	N12^{7}	3.156	H6	C11^{7}	3.543
H6	C15^{11}	3.097	H6	C16^{11}	3.342
H6	H11^{7}	2.991	H6	H15^{11}	2.535
H6	H16^{11}	3.002	H6	H16^{1}	3.420
H9A	C14^{11}	3.322	H9A	C15^{11}	2.763
H9A	C16^{11}	2.943	H9A	H15^{11}	2.859
H9A	H16^{11}	3.129	H9A	H16^{1}	3.109
H9B	S1^{7}	3.126	H9B	N12^{7}	2.802
H9B	C13^{7}	3.123	H9B	C16^{11}	3.306
H9B	H16^{11}	3.204	H11	N8^{1}	3.572
H11	C2^{1}	3.294	H11	C3^{1}	3.548
H11	C4^{1}	3.376	H11	C5^{1}	2.954
H11	C6^{1}	2.675	H11	C7^{1}	2.855
H11	H4^{4}	3.171	H11	H5^{1}	3.400
H11	H6^{1}	2.991	H15	F1^{7}	2.638
H15	C6^{12}	3.396	H15	H6^{12}	2.535
H15	H9A^{12}	2.859	H16	S1^{16}	3.388
H16	F1^{7}	3.219	H16	N8^{7}	3.074
H16	N12^{16}	3.216	H16	C2^{7}	3.418
H16	C6^{7}	3.202	H16	C7^{7}	2.924
H16	C9^{7}	3.507	H16	H6^{12}	3.002
H16	H6^{7}	3.420	H16	H9A^{12}	3.129
H16	H9A^{7}	3.109	H16	H9B^{12}	3.204
H17	S1^{16}	3.076	H17	C2^{7}	3.378
H17	C3^{7}	3.163	H17	C4^{7}	3.138
H17	C5^{7}	3.340	H17	C6^{7}	3.570
H17	C7^{7}	3.577	H17	C18^{13}	3.382
H17	C19^{13}	3.260	H17	H3^{7}	3.557

Table S17. Intermolecular contacts less than 3.60 Å involving hydrogens (continued)

atom	atom	distance	atom	atom	distance
H17	H4[7]	3.523	H17	H18[13]	2.998
H17	H19[13]	2.775	H18	S1[14]	3.075
H18	F2[13]	3.318	H18	C17[6]	3.494
H18	C18[13]	3.474	H18	C19[13]	3.491
H18	H3[14]	3.010	H18	H17[6]	2.998
H18	H18[6]	3.513	H18	H18[13]	3.513
H18	H19[13]	3.557	H19	C4[4]	3.462
H19	H3[14]	2.917	H19	H4[4]	3.074
H19	H17[6]	2.775	H19	H18[6]	3.557

Symmetry Operators:

(1) -X+1,Y+1/2-1,-Z+1/2+1 (2) -X+2,Y+1/2-1,-Z+1/2+1
(3) -X+1/2+1,-Y+1,Z+1/2-1 (4) -X+1/2,-Y+1,Z+1/2
(5) -X,Y+1/2-1,-Z+1/2+1 (6) X+1/2-1,-Y+1/2+1,-Z+2
(7) -X+1,Y+1/2,-Z+1/2+1 (8) X+1/2,-Y+1/2+1,-Z+1
(9) X+1/2-1,-Y+1/2+1,-Z+1 (10) -X+1/2,-Y+1,Z+1/2-1
(11) X-1,Y,Z (12) X+1,Y,Z
(13) X+1/2,-Y+1/2+1,-Z+2 (14) -X+1/2+1,-Y+1,Z+1/2
(15) -X,Y+1/2,-Z+1/2+1 (16) -X+2,Y+1/2,-Z+1/2+1

