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Supplementary Information

Dual-State Emission versus no emission by manipulating molecular structures of cyanovinyl – benzofuran derivatives

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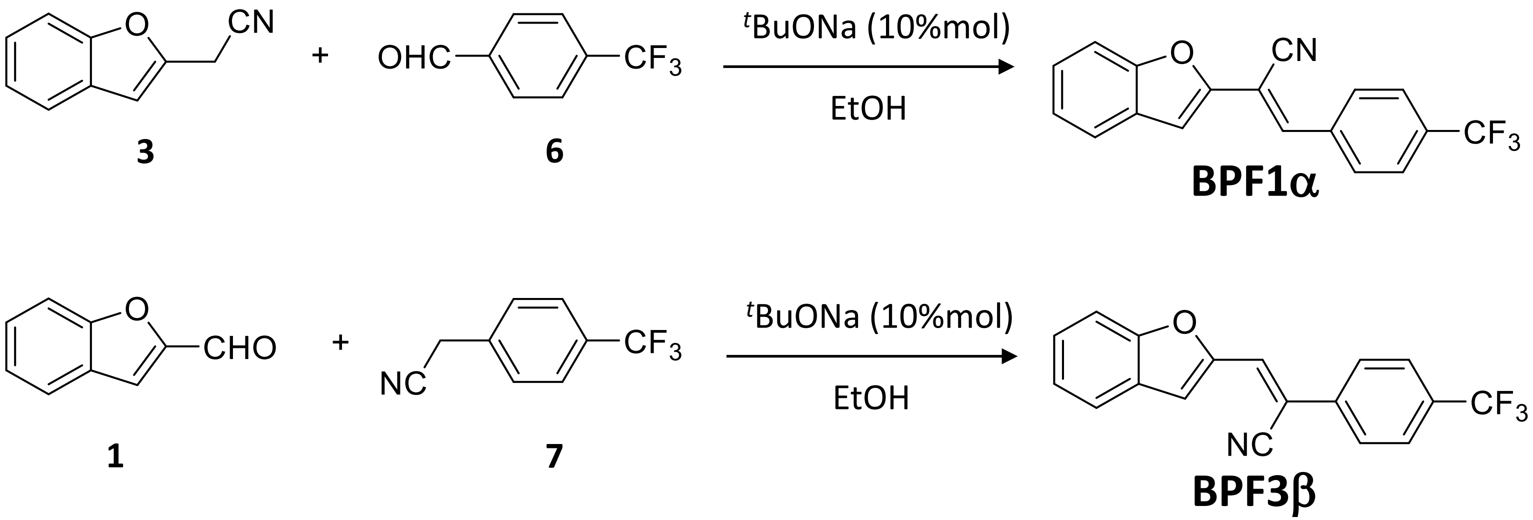
Contents

Synthesis of **BPF3α** and **BPF3β**

The compounds were prepared by Knoevenagel condensation in EtOH according to the general procedure

General procedure for the Knoevenagel reactions

A mixture of aldehyde (4 mmol), carbonitrile derivative (1.1 equiv.) and a catalytic amount of NaO^{t}Bu (10% mol.) was let in ethanol (10 mL) for 2 h at room temperature in dark. The resulting precipitate was filtered, washed with cold ethanol. Afterwards, it was dried in high vacuo to give the as-synthetized powders.



Scheme S1: Synthesis of **BPF3α–β** by Knoevenagel condensation

Table S1: X-ray crystallographic data of single crystals of series **BPF1α–β and Cy-BPF1**

	BPF1α	**BPF1β**	**Cy-BPF1**	
Formula	C17 H6 F5 N O	C17 H6 F5 N O	C36.25 H16.5 F10 N2 O2.75	
M	335.23	335.23	714.01	
T (K)	200	200	200	
Crystal system	Orthorhombic,	Monoclinic,	Triclinic,	
Space group	P 2_1 2_1 2_1	P 2_1/n	P -1	
Unit cell.: a (Å)	6.2934(2)	6.8261(4)	11.7298(6)	
b (Å)	7.4260(2)	28.701(2)	12.3008(7)	
c (Å)	28.4033(8)	6.9455(5)	12.8705(9)	
a (°)	90	90	64.625(6)	
b (°)	90	101.958(7)	88.736(5)	
g (°)	90	90	72.512(5)	
Volume (Å^3)	1327.42(7)	1331.21(15)	1588.00(18)	
Z	4	4	2	
Calculated density	1.677	1.673	1.493	
F(000)	672	672	720	
θ range (°)	3.11 to 71.949	6.17 to 76.21	3.831 to 71.847	
Limiting indices	-7≤h≤7, -8≤k≤7, -35≤l≤33	-8≤h≤6 -35≤k≤34 -8≤l≤8	-14≤h≤14 -15≤k≤15 -15≤l≤15	
Reflection coll.	3348	5905	12415	
Unique	2179	2695	6071	
R (int)	0.0103	0.0296	0.0295	
Final R indices, [I>2sigma(I)],				
R1	0.0286	0.0535	0.0547	
wR2	0.0757	0.1453	0.1554	
R indices (all data),				
R1	0.0288	0.0630	0.0604	
wR2	0.0760	0.1546	0.1631	
Largest diff.	0.199	0.317	0.484	
Peak and hole (e A^{-3})	-0.192	-0.278	-0.356	
CCDC number	2163090	2164115	2163092	

Table S2: X-ray crystallographic data of single crystals of series **BPF2α** and **BPF3α–β**

	BPF2α	**BPF3α**	**BPF3β**
Formula	C17 H6 Br F4 N O	C18 H10 F3 N O	C18 H10 F3 N O
M	396.14	313.27	313.27
T (K)	293	220	293
Crystal system	Monoclinic,	Triclinic,	Triclinic,
Space group	P 2_1/c	P -1	P -1
Unit cell.: a (Å)	6.292(2)	6.4098(3)	6.7868(5)
b (Å)	7.628(2)	7.2975(5)	8.5364(8)
c (Å)	30.394(2)	15.8052(8)	13.0400(10)
a (°)	90	84.237(5)	86.970(7)
b (°)	92.960(10)	81.645(4)	86.932(7)
g (°)	90	79.261(5)	78.760(7)
Volume (Å^3)	1456.8(6)	716.59(7)	739.22(10)
Z	4	2	2
Calculated density	1.806	1.452	1.407
F(000)	776	320	320
θ range (°)	3.79 to 28.00	2.83 to 83.88	3.76 to 27.50
Limiting indices	-8≤h≤5, -9≤k≤9, -39≤l≤39	-7≤h≤5 -8≤k≤8 -19≤l≤19	-8≤h≤8 -10≤k≤11 -16≤l≤16
Reflection coll.	12588	4815	18618
Unique	3321	2682	3347
R (int)	0.0410	0.0287	0.0498
Final R indices, [I>2sigma(I)],			
R1	0.0449	0.0522	0.0764
wR2	0.0957	0.1405	0.2139
R indices (all data),			
R1	0.0862	0.0624	0.1066
wR2	0.1124	0.1625	0.2478
Largest diff.	0.349	0.396	0.761
Peak and hole (e A^{-3})	-0.605	-0.281	-0.405
CCDC number	2164116	2163091	2164117

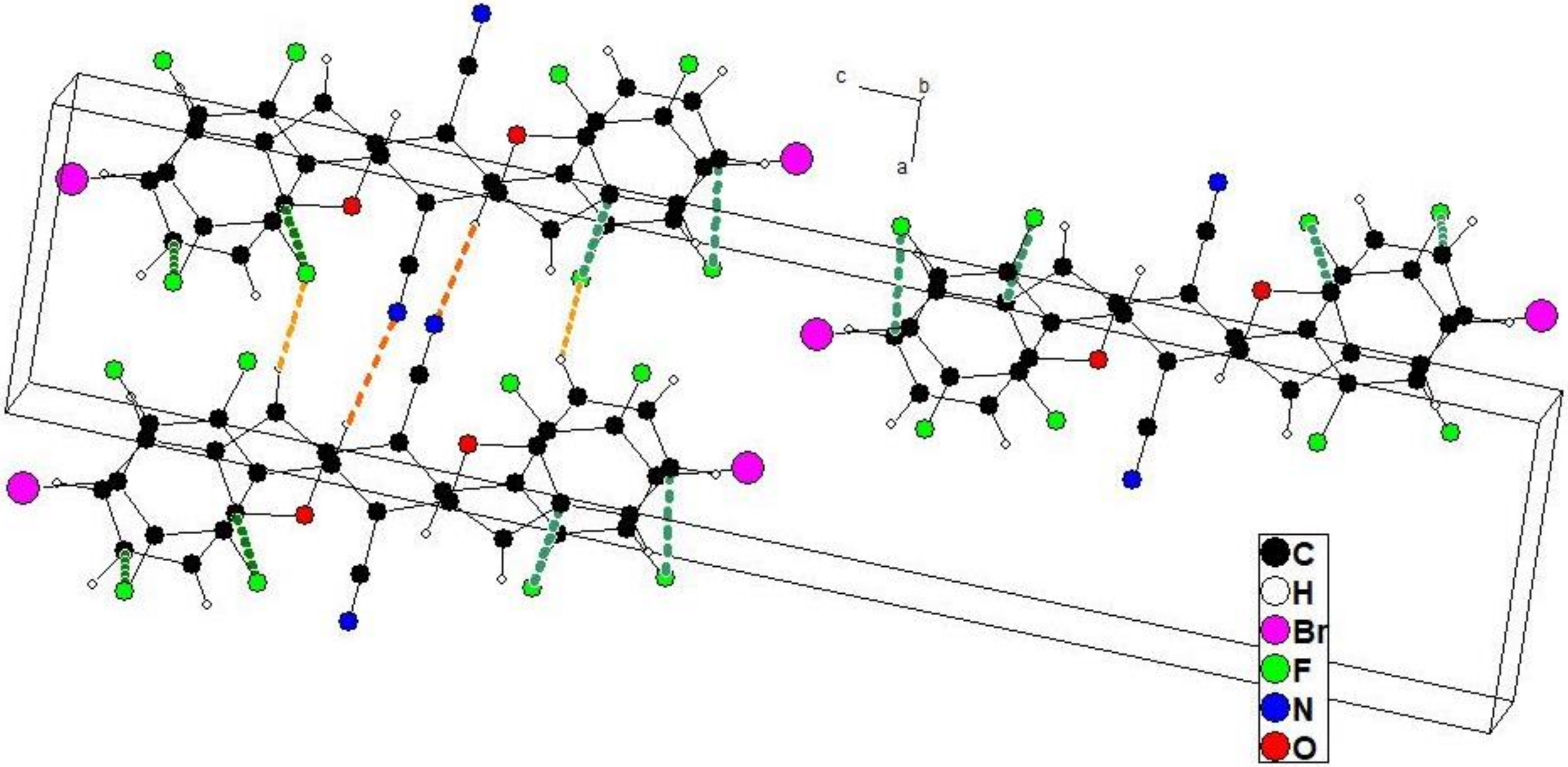
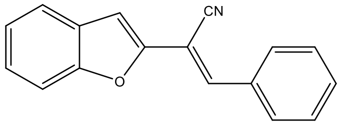
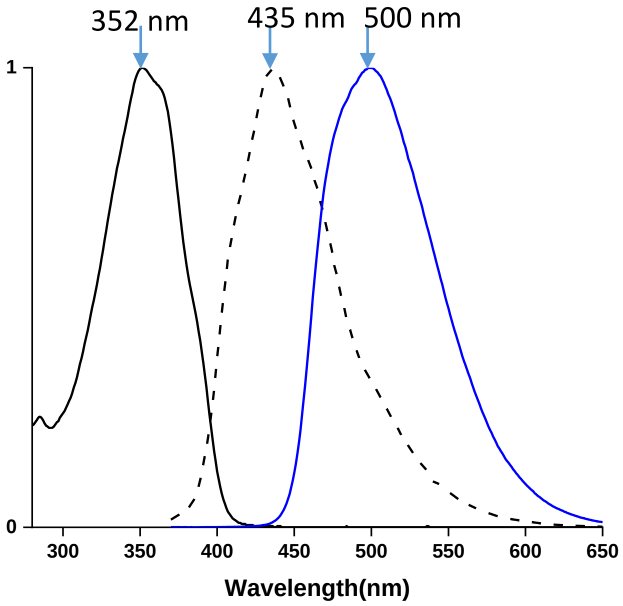


Figure S1: Stacking modes and intermolecular contacts identified from the single crystals X-ray data of **BPF2α**



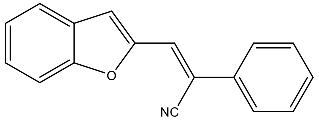
BF2α



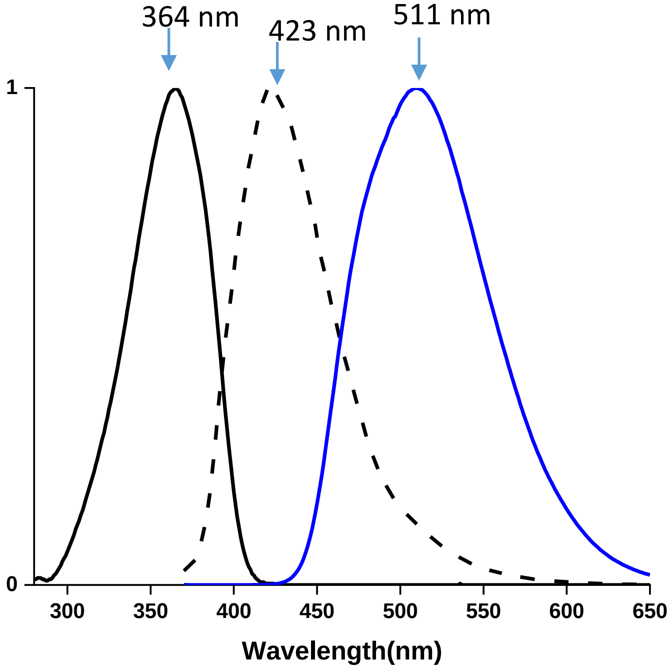
ε = 25400 L.mol^{-1}.cm^{-1}

Φ_{solu} = 9 %

Φ_{solid}= 40%



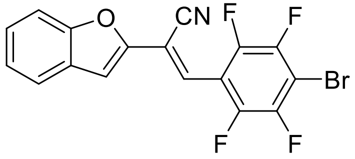
BF2β



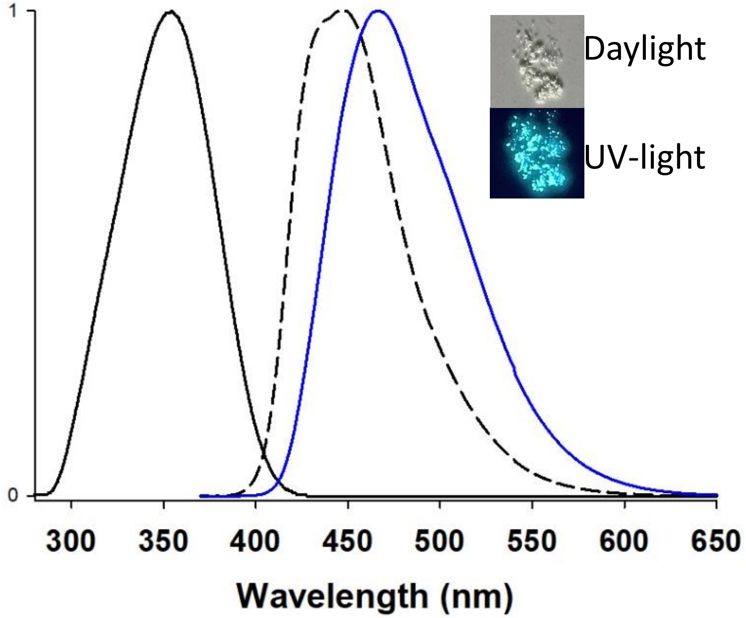
ε = 27800 L.mol^{-1}.cm^{-1}

Φ_{solu}= 2%

Φ_{solid}= 35%



BPF2α



ε = 29300 L.mol^{-1}.cm^{-1}

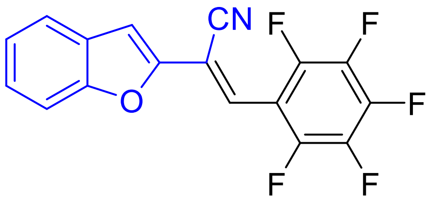
Φ_{solu}= 80%

Φ_{solid}= 42%

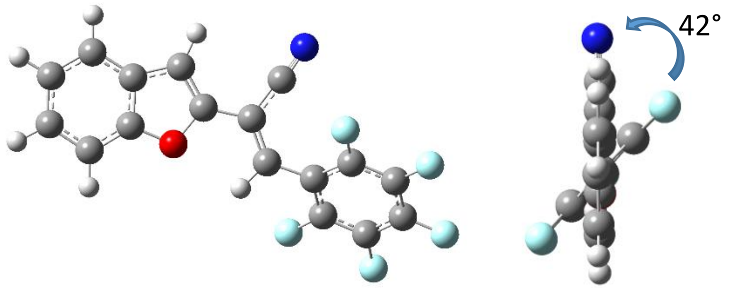
Figure S2: Normalized absorption spectra 10^{-5} M in $CHCl_3$ (black line), fluorescence under excitation at 350 nm spectra 10^{-5} M in $CHCl_3$ (dashed black line) and in the solid state (blue line). In red, values of molar extinction coefficient and absolute emission quantum yield in solution (chloroform solution) and in the solid state.

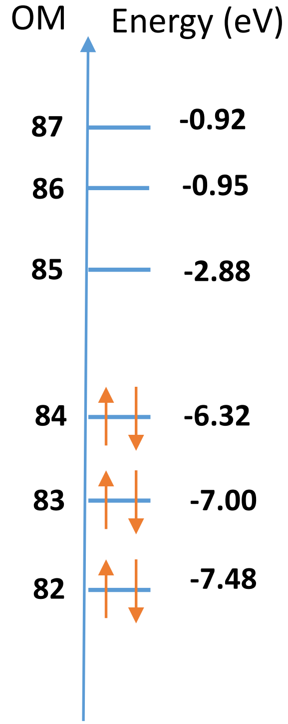
Theoretical calculations

BPF1α

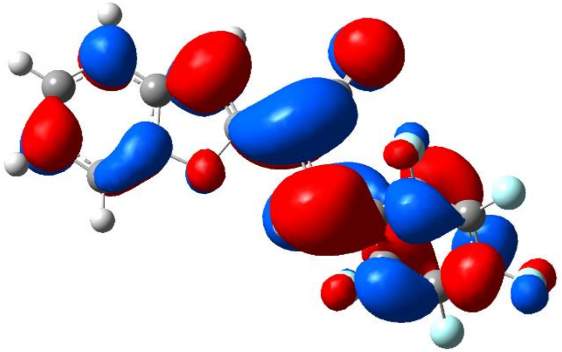


Ground state

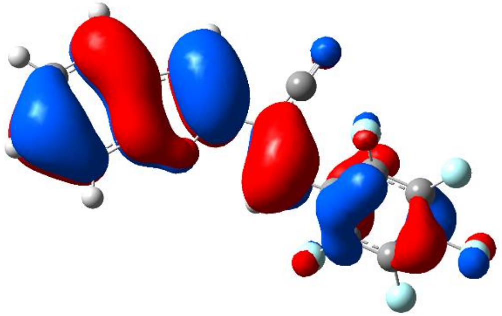




LUMO (OM 85)



HOMO (OM 84)



B3LYP/6.31g(d,p) in $CHCl_3$ using PCM model

UV-Vis theoretical

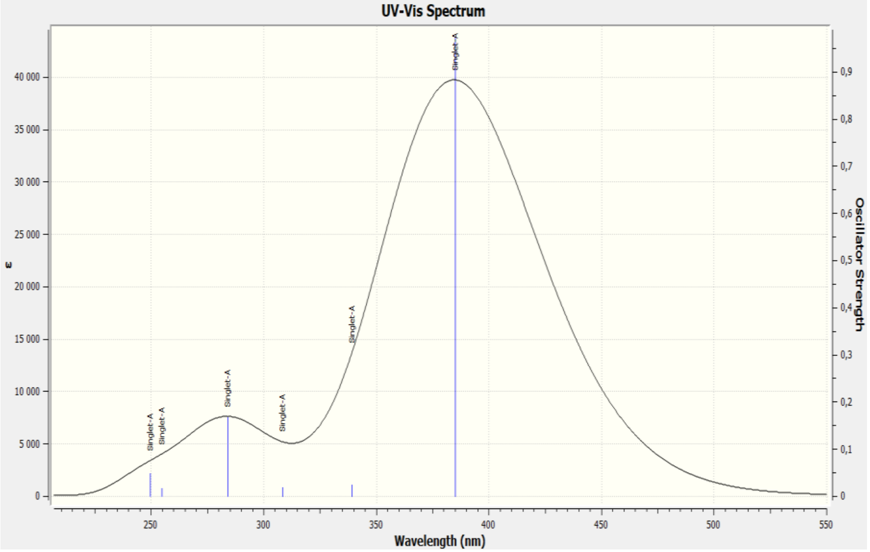


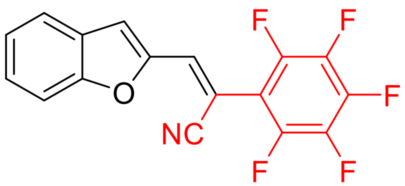
Figure S3 : Theoritical UV-Vis of **BPF1α**

```
Excitation energies (singlet) and oscillator strengths:
Excited State   1:      Singlet-A      3.2194 eV  385.11 nm  f=0.9716  <S**2>=0.000
84 -> 85         0.70544
Excited State   2:      Singlet-A      3.6543 eV  339.28 nm  f=0.0239  <S**2>=0.000
83 -> 85         0.70144
Excited State   3:      Singlet-A      4.0226 eV  308.22 nm  f=0.0184  <S**2>=0.000
82 -> 85         0.68684
Excited State   4:      Singlet-A      4.3650 eV  284.04 nm  f=0.1681  <S**2>=0.000
81 -> 85         0.67056
84 -> 86        -0.13105
84 -> 87        -0.14313
Excited State   5:      Singlet-A      4.8669 eV  254.75 nm  f=0.0172  <S**2>=0.000
82 -> 85        -0.12609
84 -> 86         0.54988
84 -> 87        -0.39658
```

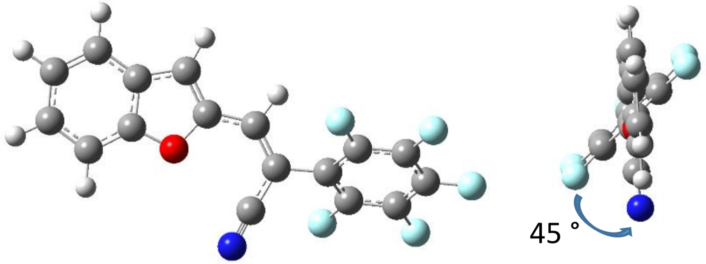
TD-SCF, B3LYP/6.31g(d,p) in $CHCl_3$ using PCM model

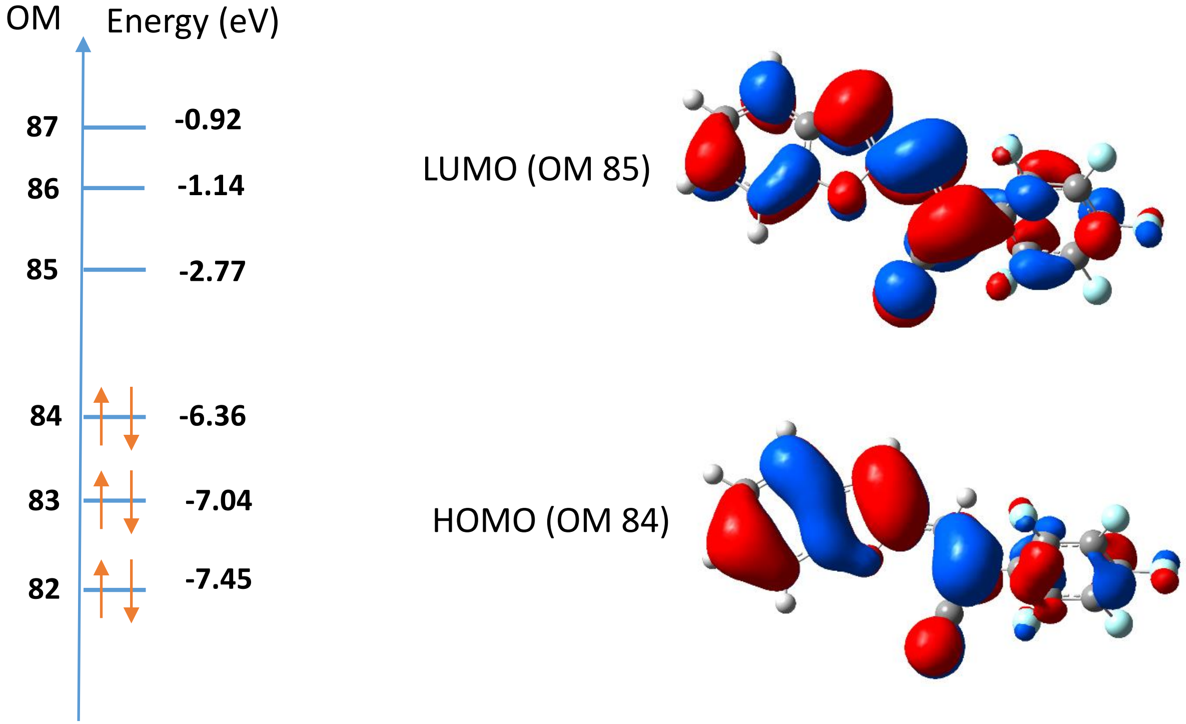
Theoretical calculations

BPF1β



Ground state





OM	Energy (eV)
87	**-0.92**
86	**-1.14**
85	**-2.77**
84	**-6.36**
83	**-7.04**
82	**-7.45**

LUMO (OM 85)

HOMO (OM 84)

B3LYP/6.31g(d,p) in $CHCl_3$ using PCM model

UV-Vis theoretical

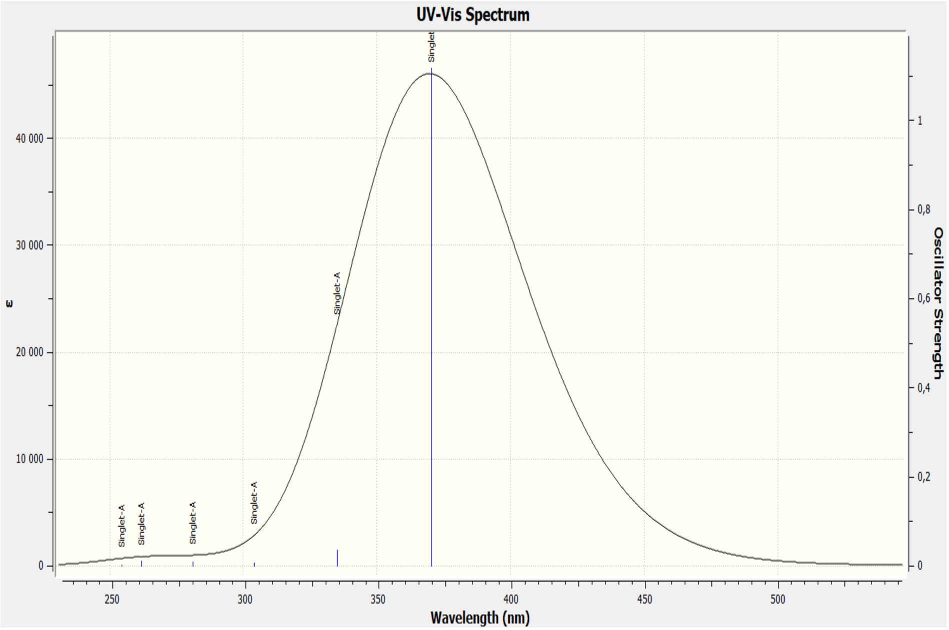


Figure S4 : Theoritical UV-Vis of **BPF1β**

```
Excitation energies (singlet) and oscillator strengths:
Excited State   1:    Singlet-A     3.3473 eV  370.40 nm  f=1.1180  <S**2>=0.000
84 -> 85        0.70466
Excited State   2:    Singlet-A     3.7004 eV  335.06 nm  f=0.0356  <S**2>=0.000
83 -> 85        0.69946
Excited State   3:    Singlet-A     4.0775 eV  304.07 nm  f=0.0078  <S**2>=0.000
82 -> 85        0.69818
Excited State   4:    Singlet-A     4.4088 eV  281.22 nm  f=0.0099  <S**2>=0.000
81 -> 85        0.65147     84 -> 86       -0.23749
Excited State   5:    Singlet-A     4.7349 eV  261.85 nm  f=0.0117  <S**2>=0.000
81 -> 85        0.23140
84 -> 86        0.63801
```

TD-SCF, B3LYP/6.31g(d,p) in $CHCl_3$ using PCM model

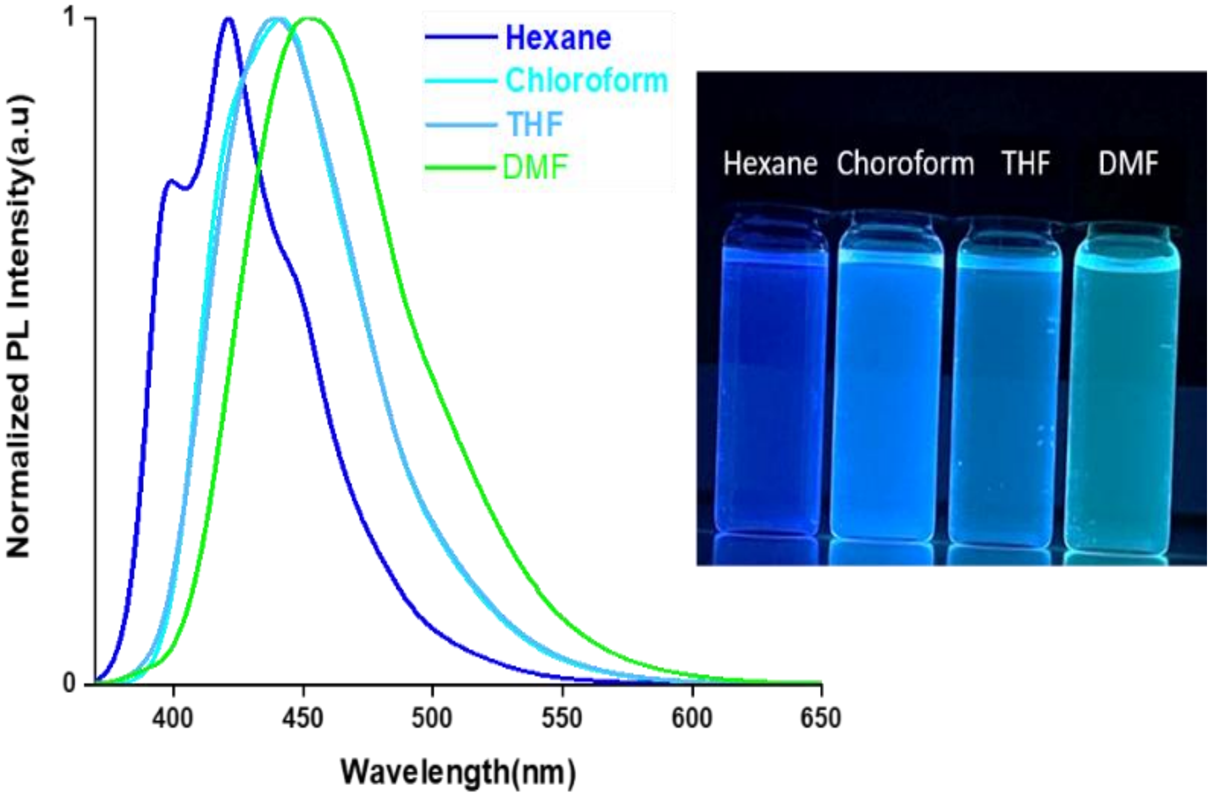


Figure S5: Emission spectra of **BPF1α** in different solvents and photographs of emission under excitation at 350 nm.

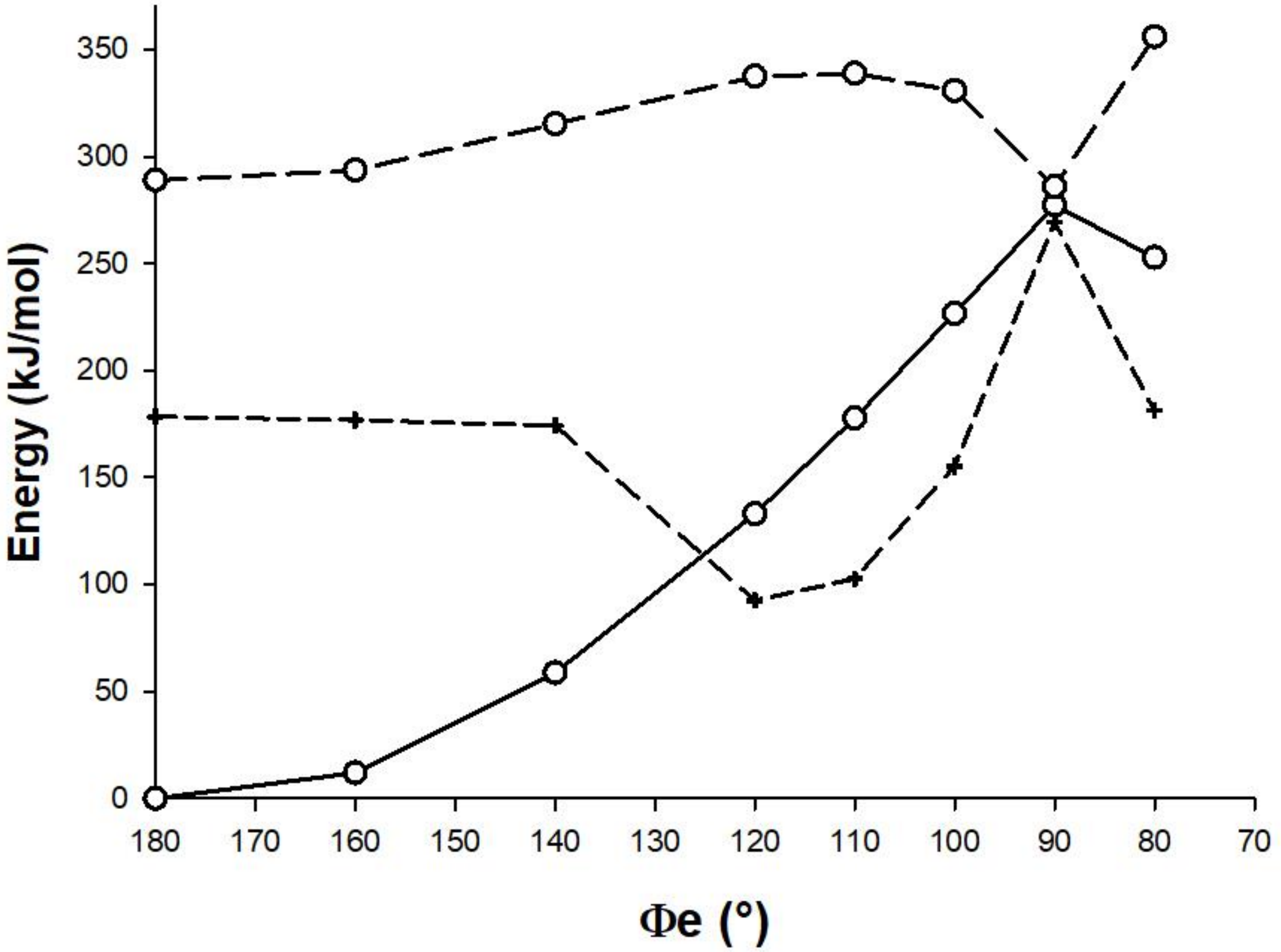


Figure S6: TD-DFT torsional scans of double bond Φe for **BPF2α** using the optimized S0 state at the TD-B3LYP/6-31G(d,p) level , S0, S1 and T1 energies were computed for each data point.

Determination of the lifetime

The instrument response function (IRF) measured with a scattering solution at the excitation wavelength (i.e. 375nm) is very different from the one that would be measured at the wavelength of emission of the fluorophore. This is mainly due to the time response of the avalanche photodiode (APD).

Consequently, the instrument response function was measured differently. More precisely, a dye known for its single 5.0ns decay in water, namely Atto 390, was measured with the apparatus. It was then fitted with a 5.0 ns decay convoluted with a IRF modelized as [A] :

$$IRF(t;\tau_{IRF}) = \frac{t}{\tau_{IRF}} exp\left(-\frac{t}{\tau_{IRF}}\right)$$

where τ_{IRF} is the characteristic time of the IRF corresponding to the convolution of the response time of the APD and the pulse shape of the exciting laser. It is the only free parameters during this fitting procedure.

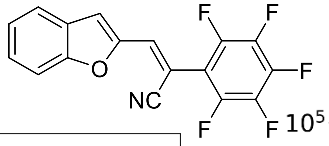
This modelized profile with the corresponding value of τ_{IRF} (with here $\tau_{IRF} = 0.1ns$) was then used for reconvolution during the fitting of the fluorescence decays.

NB: The bump at 15ns is an artifact due to a sub-laser pulse that is artificially magnified by the use of the log scale and only marginally affects the fit of the data.

[A] : W. Becker. *The bh TCSPC handbook. 8th edition*. Becker et Hickl, 2019

Lifetime delay

BPF1α



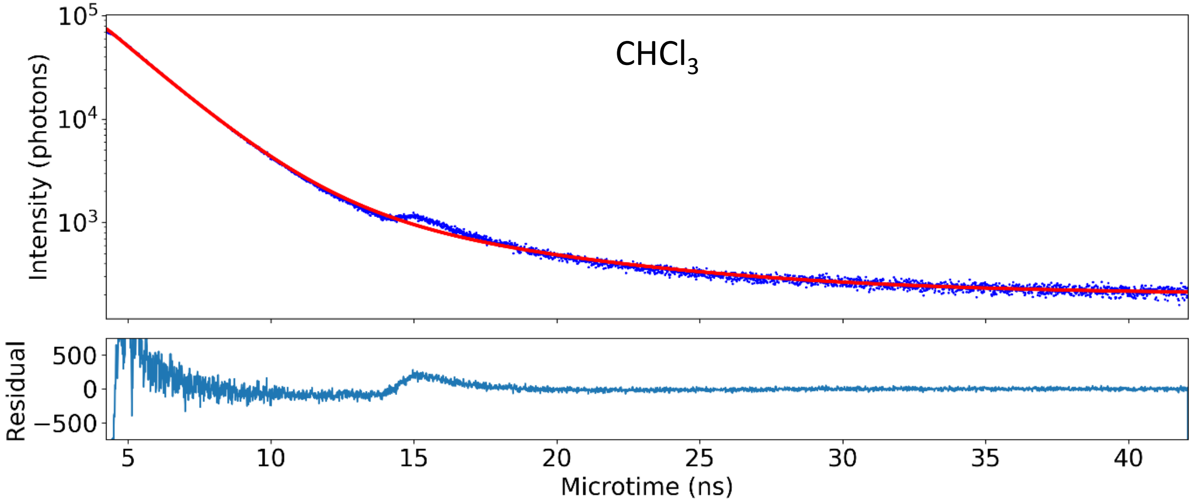


Figure S7 : Lifetime decay of **BPF1α** in CHCl$_3$. Two components : 2ns (95%) and 4.5 (4.5%).

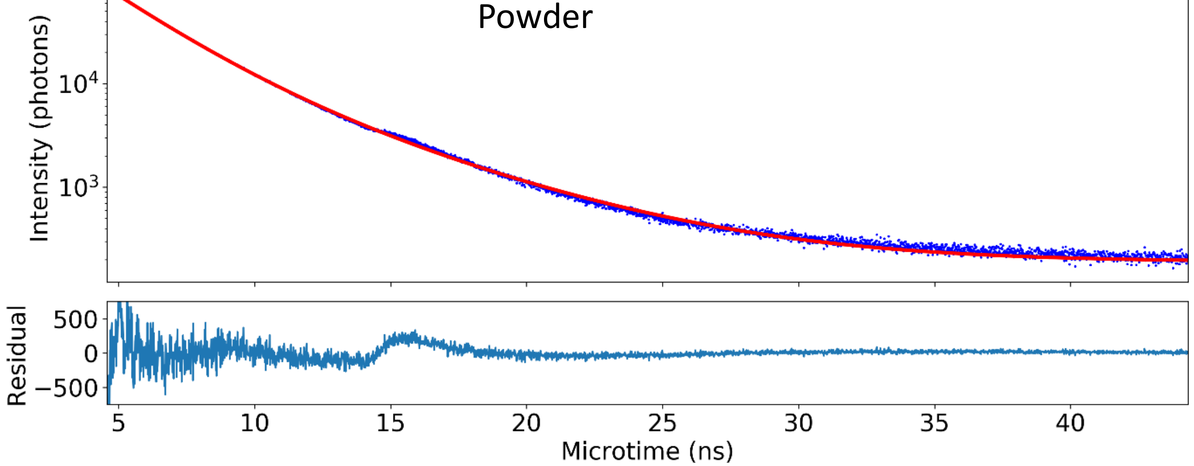
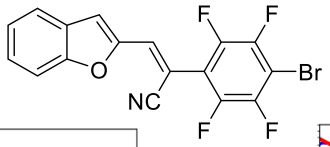


Figure S8 : Lifetime decay of **BPF1α** as a powder. Two components : 2.8ns (50 %) and 6.4ns (50%)

BPF2α

Lifetime delay



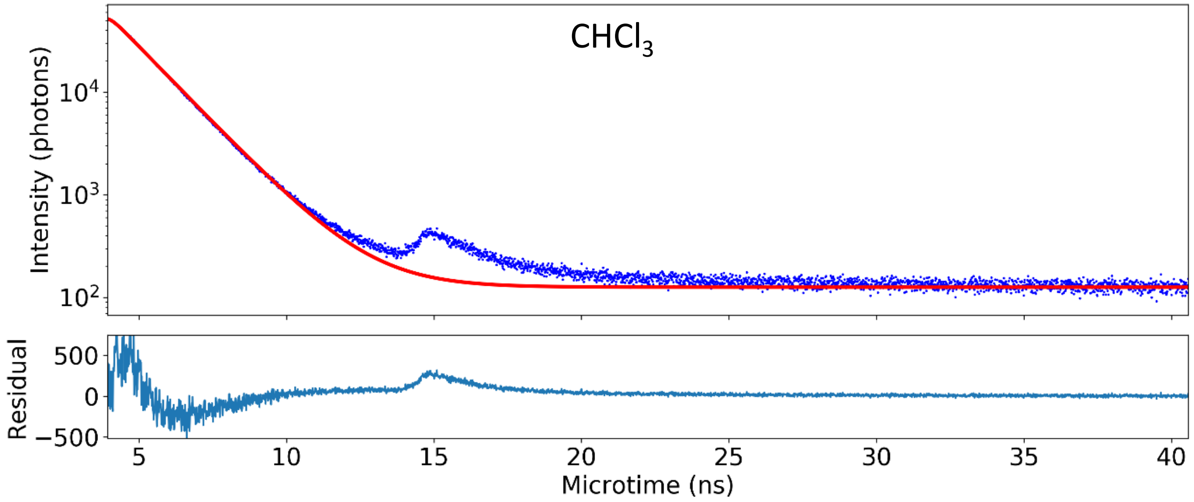


Figure S9 : Lifetime decay of **BPF2α** in CHCl$_3$. One component : 1.45ns

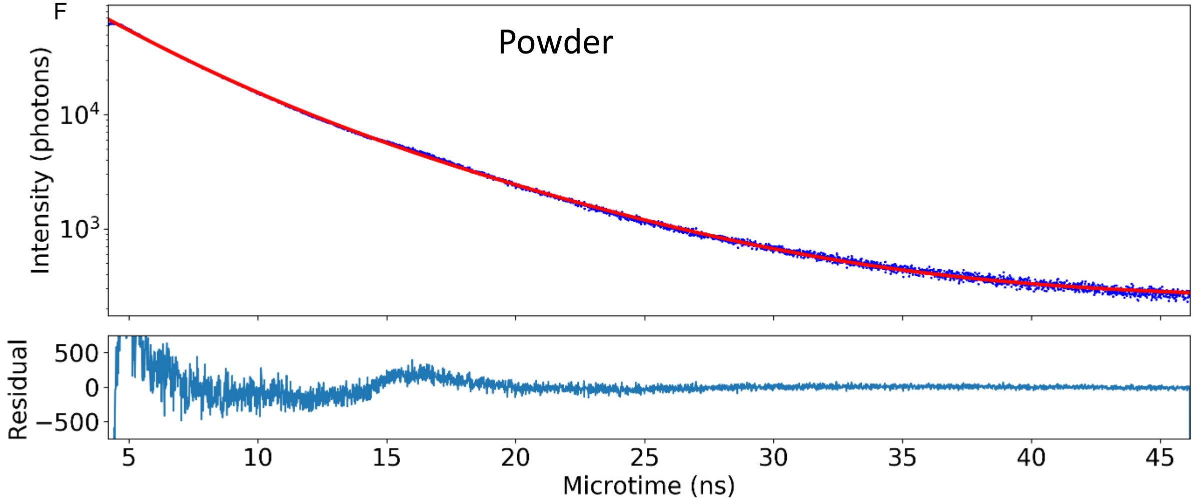


Figure S10 : Lifetime decay of **BPF2α** as a powder. Two components : 2.25 (71%) 5.1 (29%)

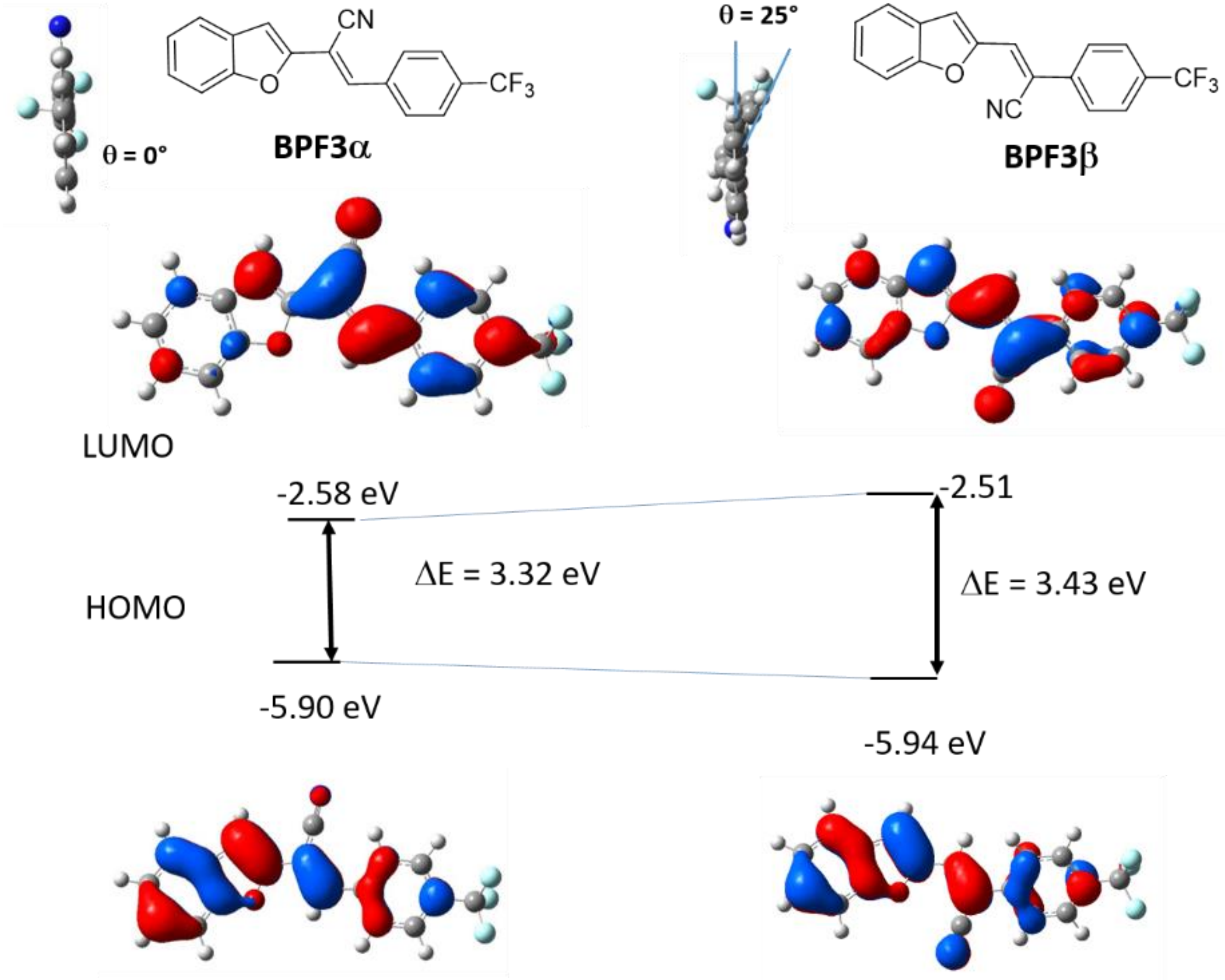


Figure S11 HOMO and LUMO frontier orbitals along with their corresponding energy levels calculated gas-phase by DFT at the B3LYP/6-31G(d,p) level.

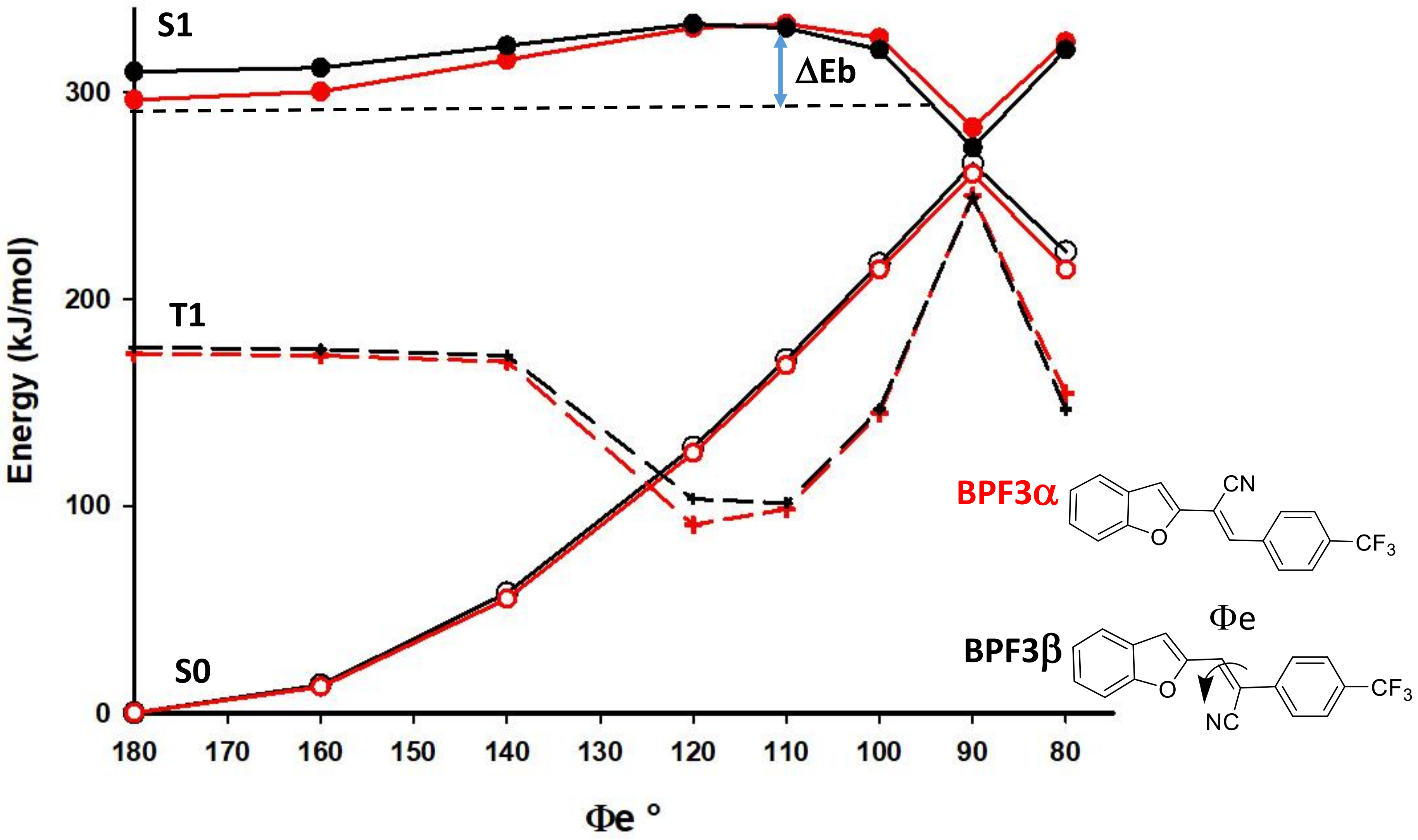


Figure S12: TD-DFT torsional scans of double bond Φe for **BPF3α** (red) and **BPF3β** (black) using the optimized S0 state at the TD-B3LYP/6-31G(d,p) level , S0, S1 and T1 energies were computed for each data point

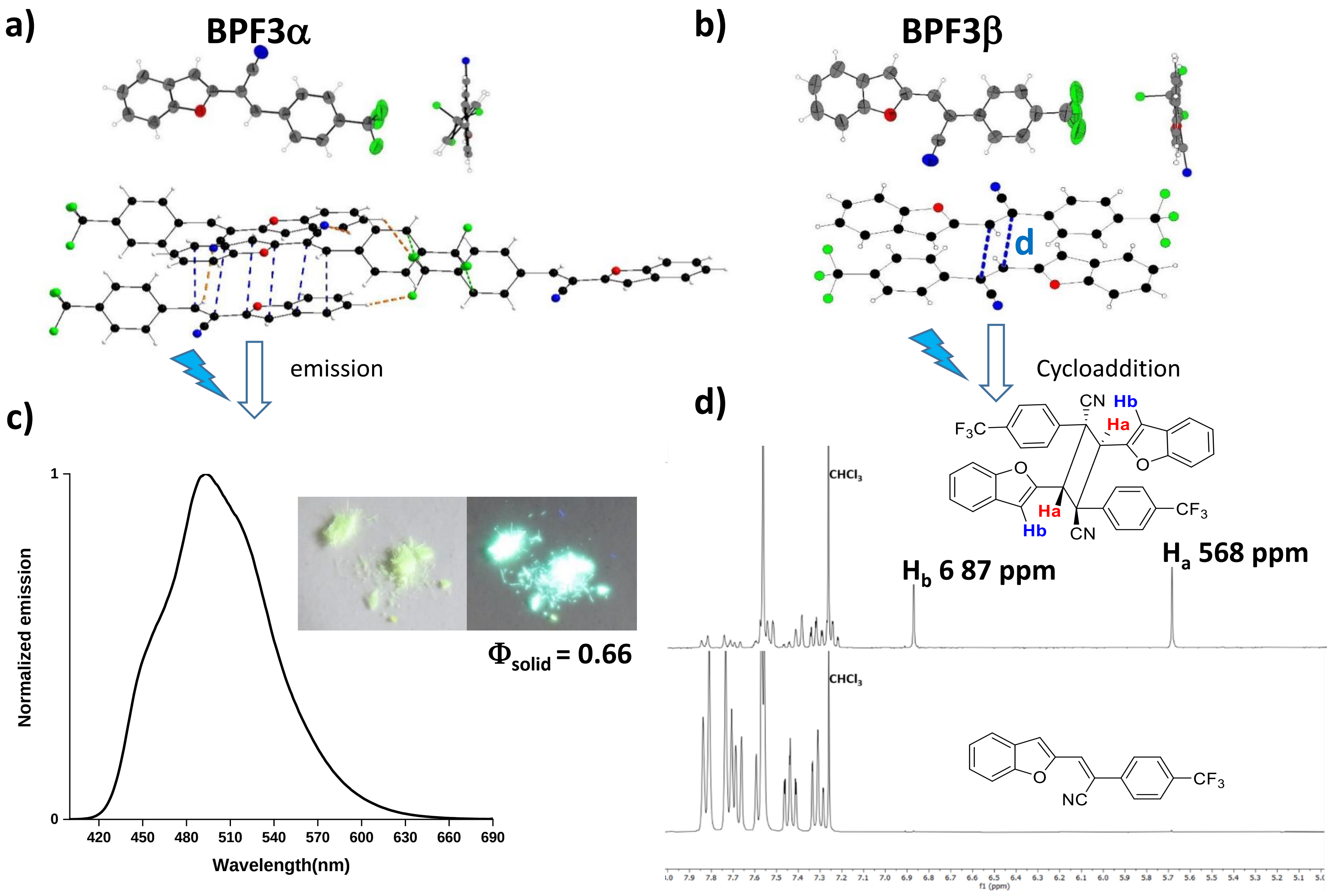
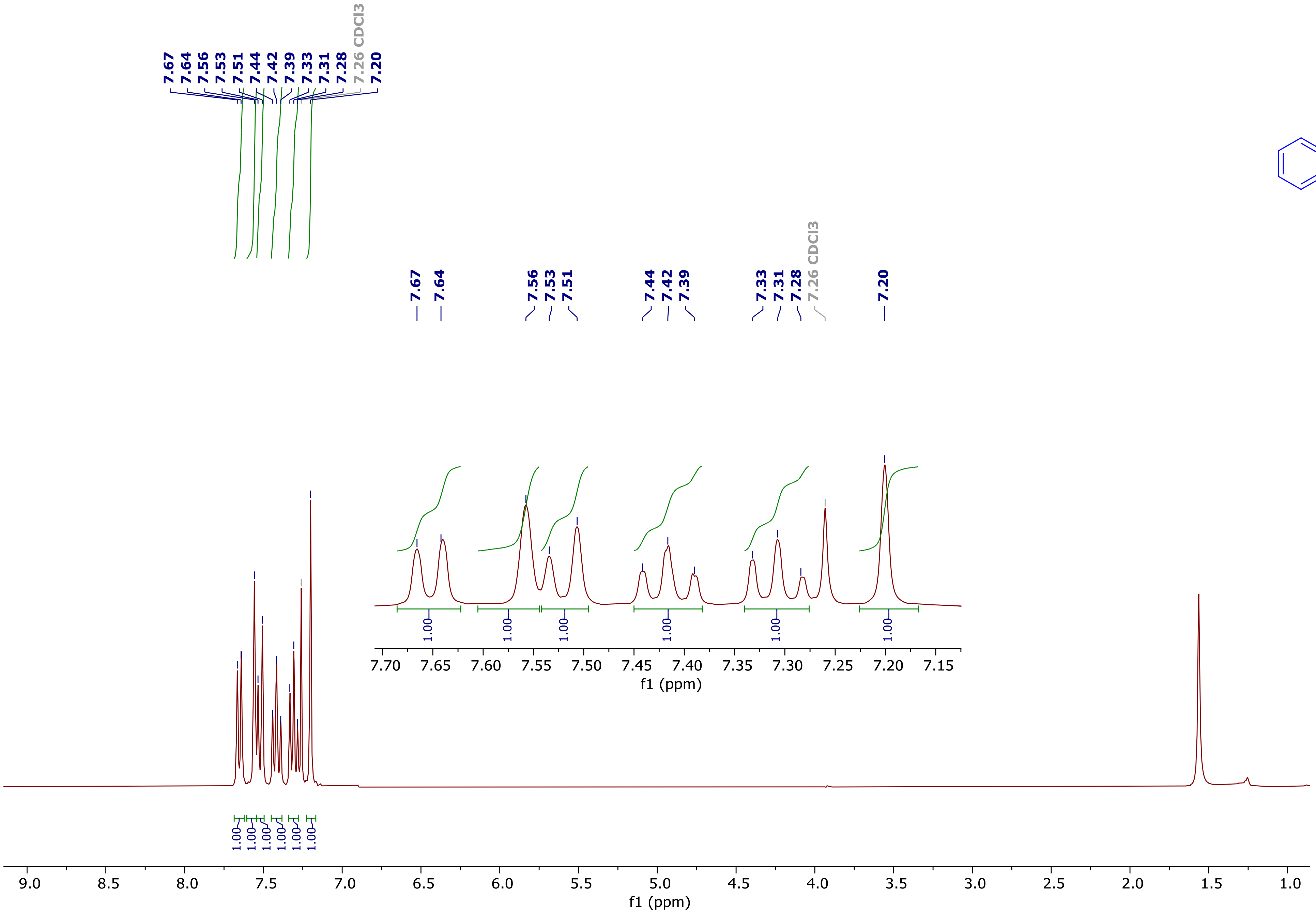
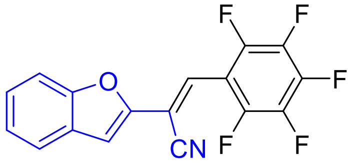
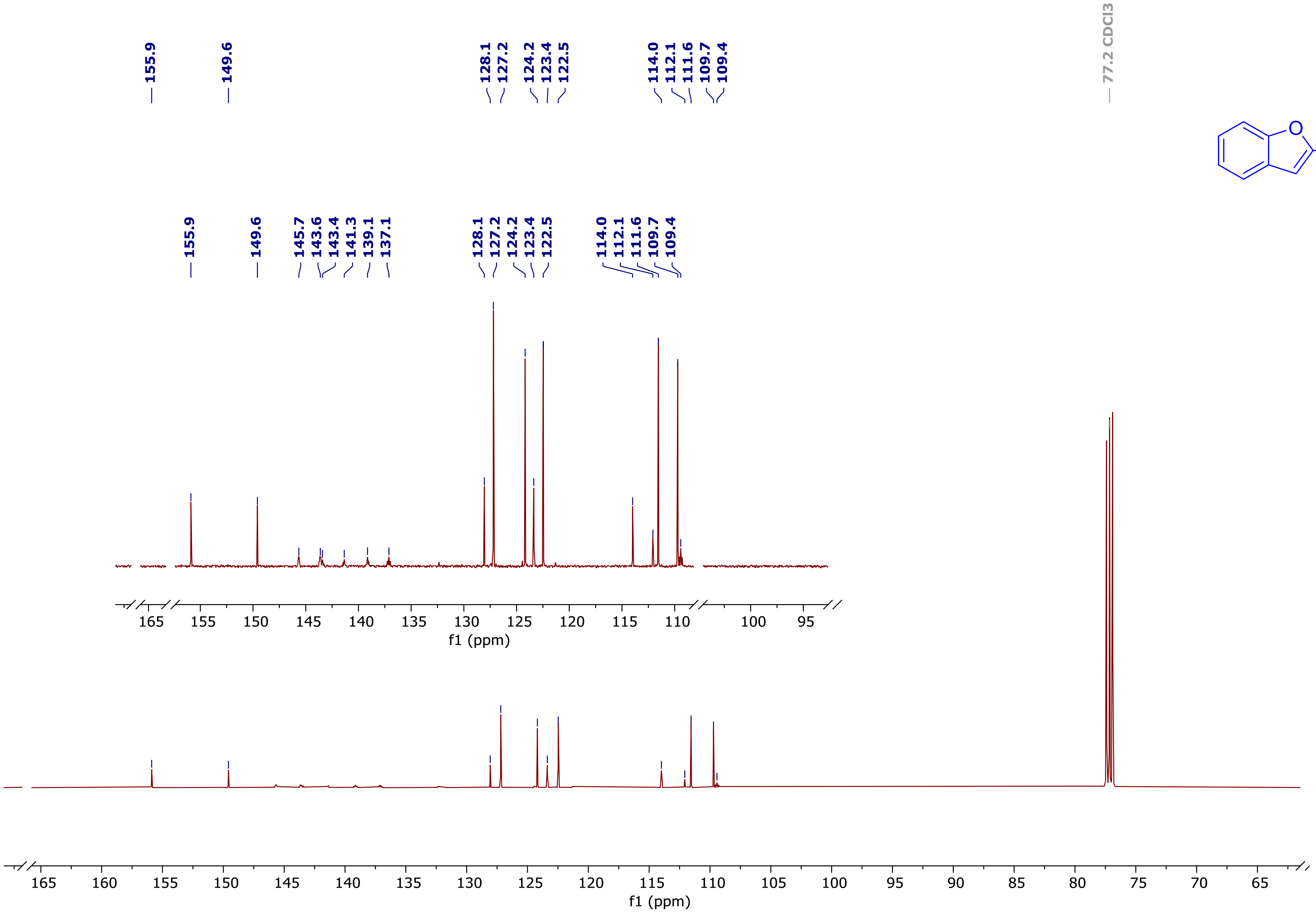


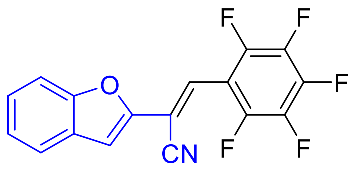
Figure S13: a) Stacking mode and intermolecular contacts in the X-Ray structure of **BPF3α.** b) Dimer of **BPF3β** showing the distances d = 3.76 Å between the centroids of the cyanovinyl bonds. c) Emission spectrum of **BPF3α** solid under excitation at 350 nm and photographs of crystals under daylight and UV light (350 nm). d) ^{1}H NMR in $CDCl_3$ of **BPF3β**(bottom) and irradiated **BPF3β** with UV light (365 nm) for 12 h



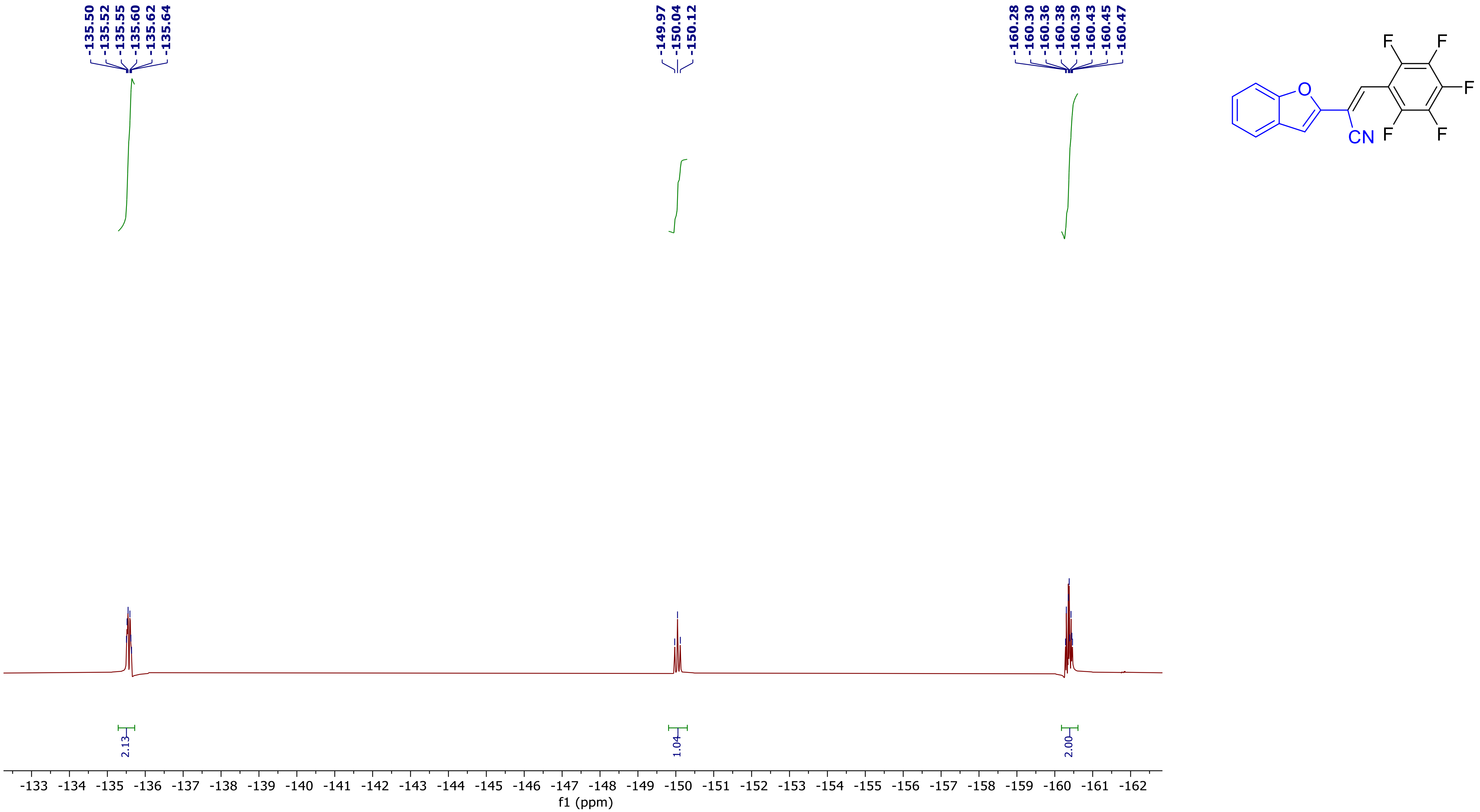


^{1}H NMR of **BPF1α** compound in $CDCl_3$

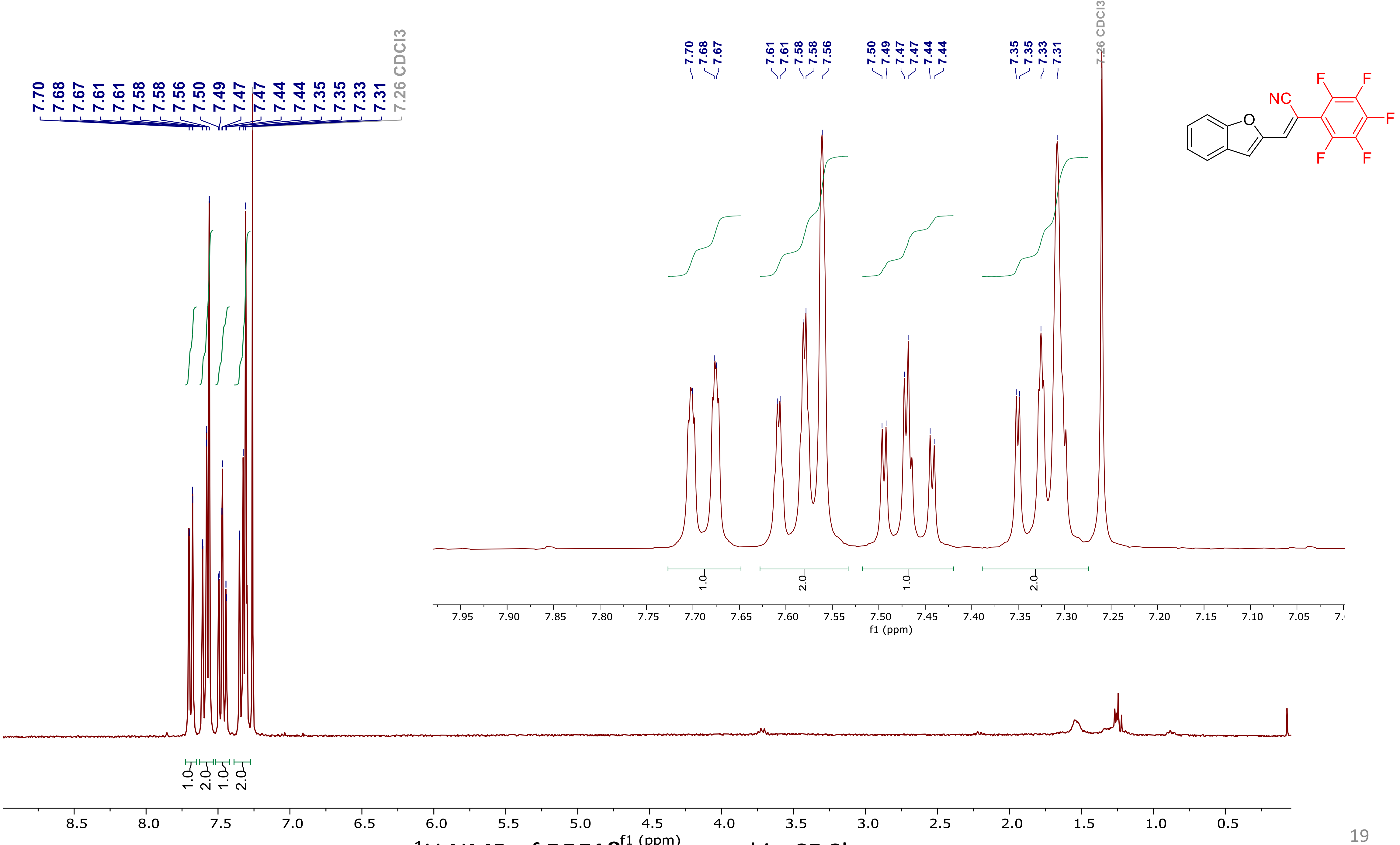




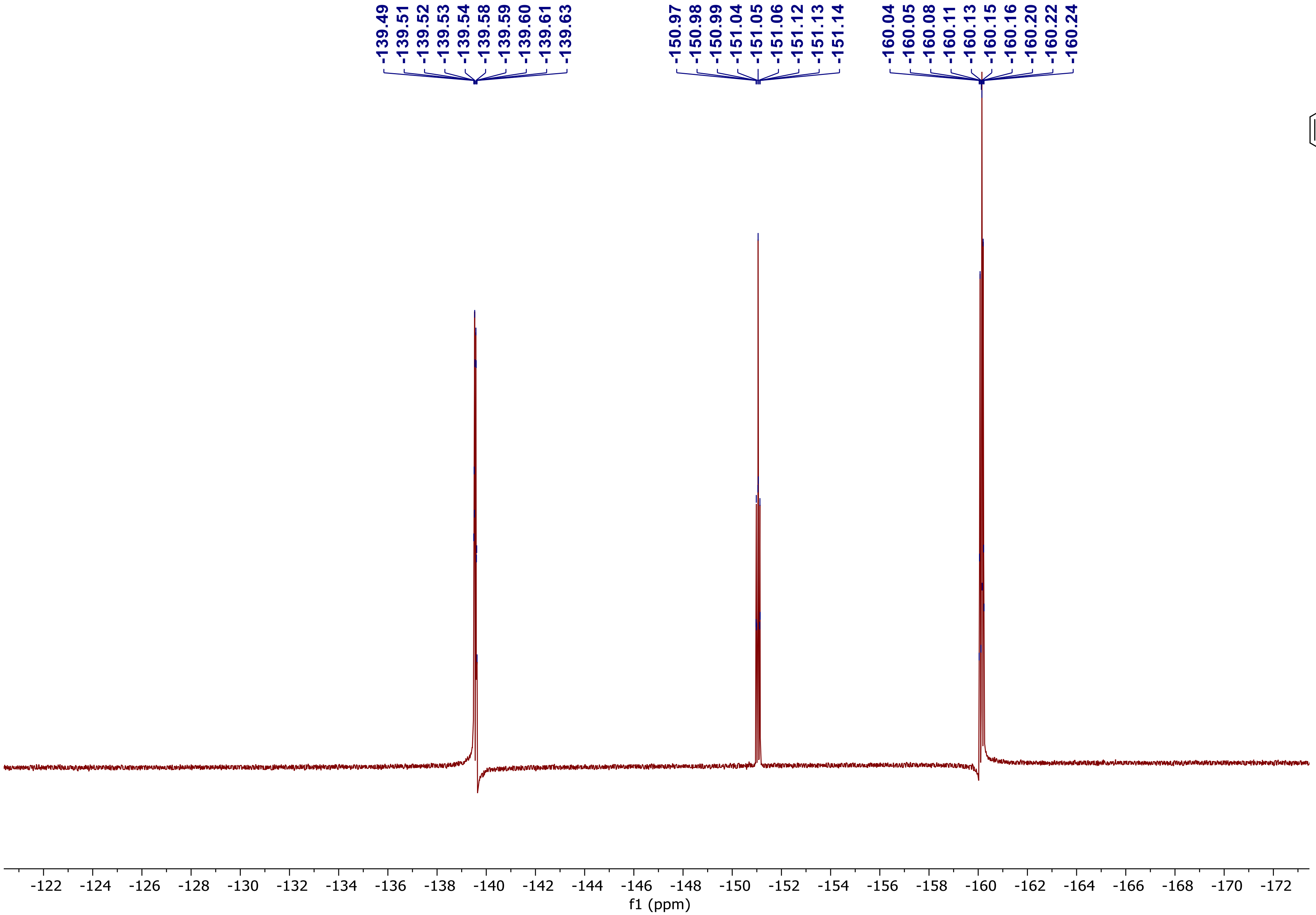
^{13}C NMR of **BPF1α** compound in $CDCl_3$

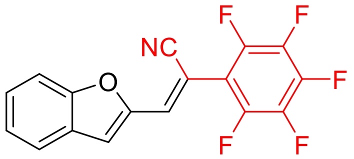


^{19}F NMR of **BPF1α** compound in $CDCl_3$

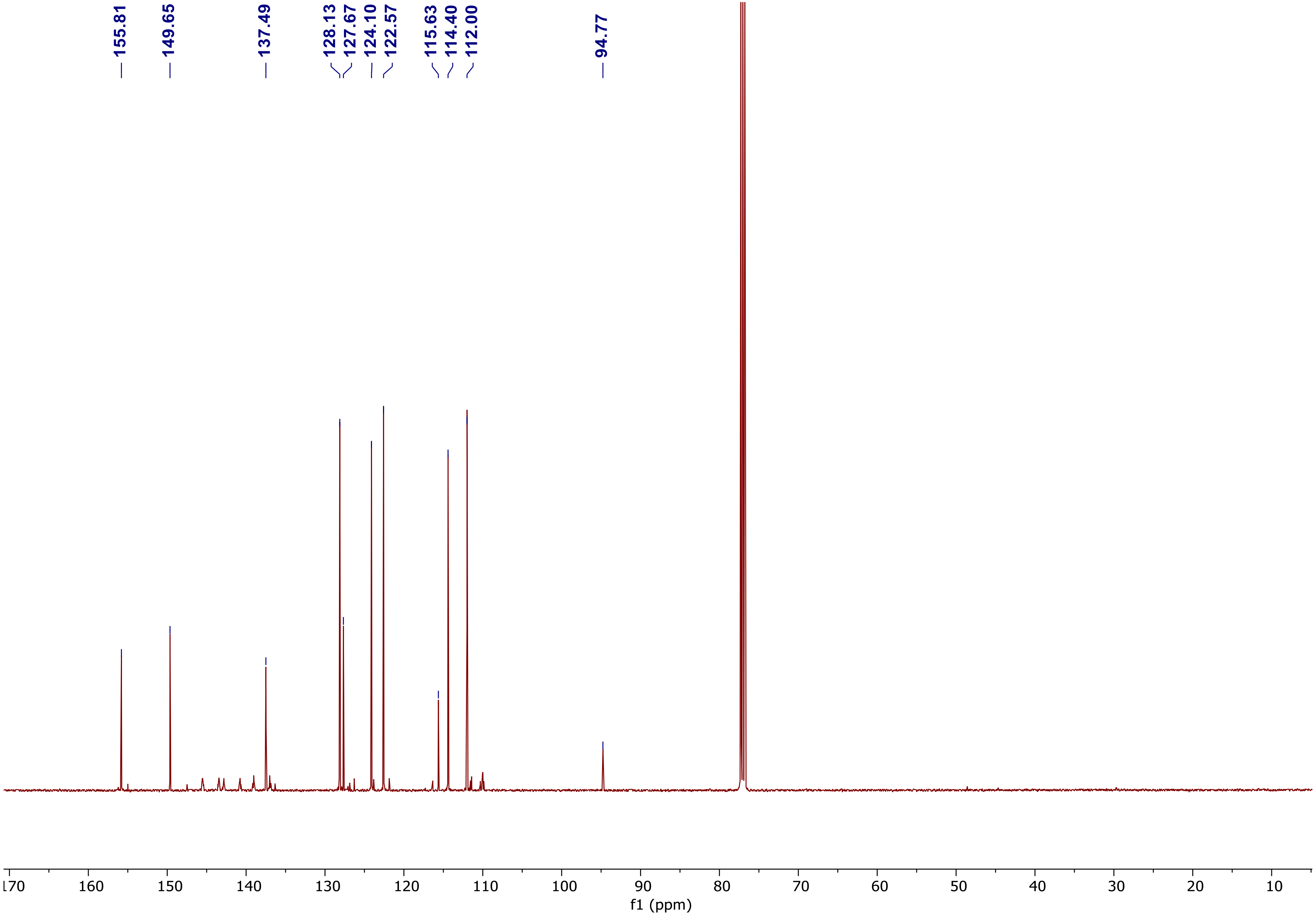


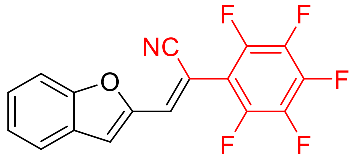
^{1}H NMR of **BPF1β** compound in $CDCl_3$





^{19}F NMR of **BPF1β** compound in $CDCl_3$





^{13}C NMR of **BPF1β** compound in $CDCl_3$

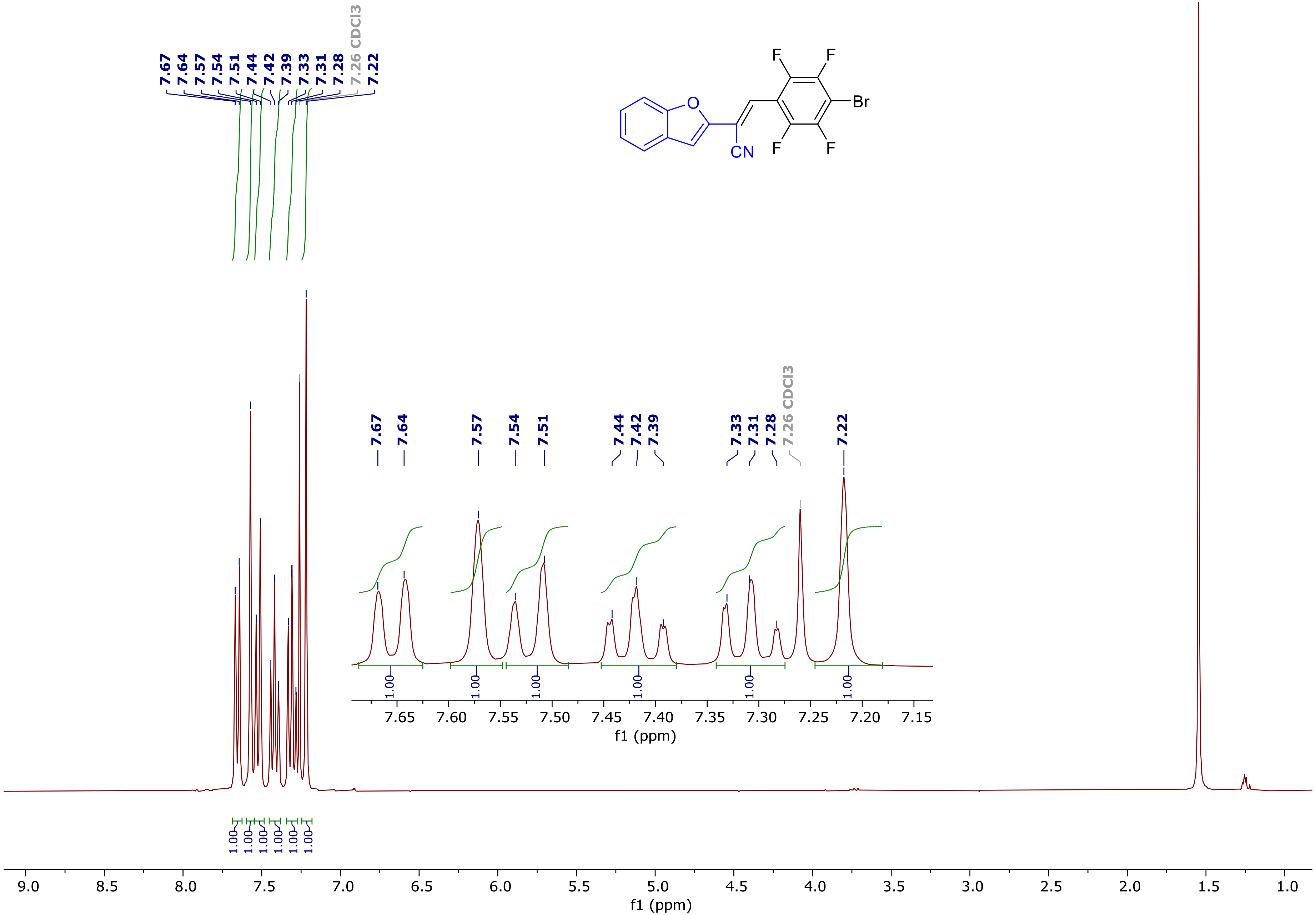


Figure: ^{1}H NMR of **BPF2α** compound in $CDCl_3$

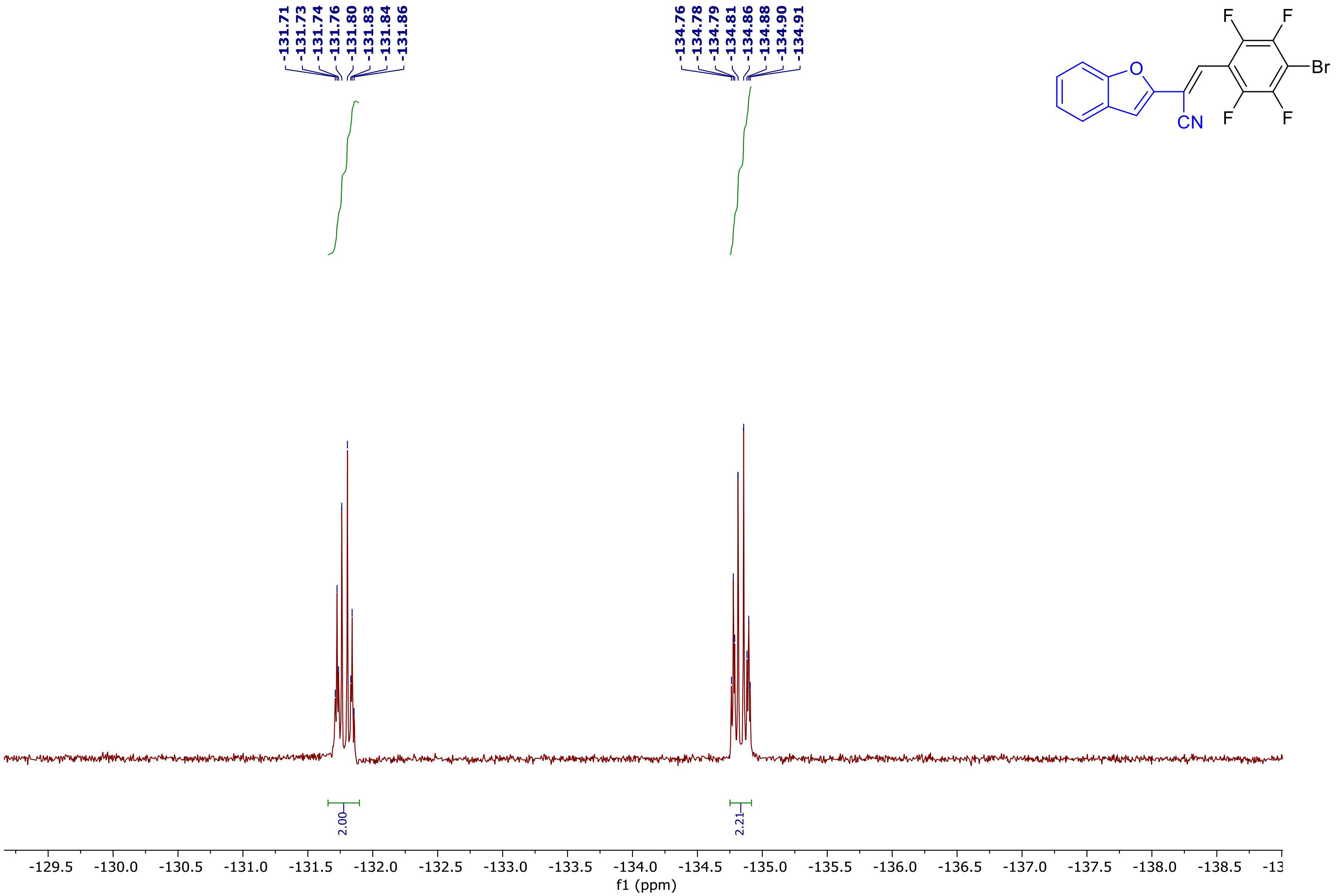


Figure: ^{19}F NMR of **BPF2α** compound in $CDCl_3$

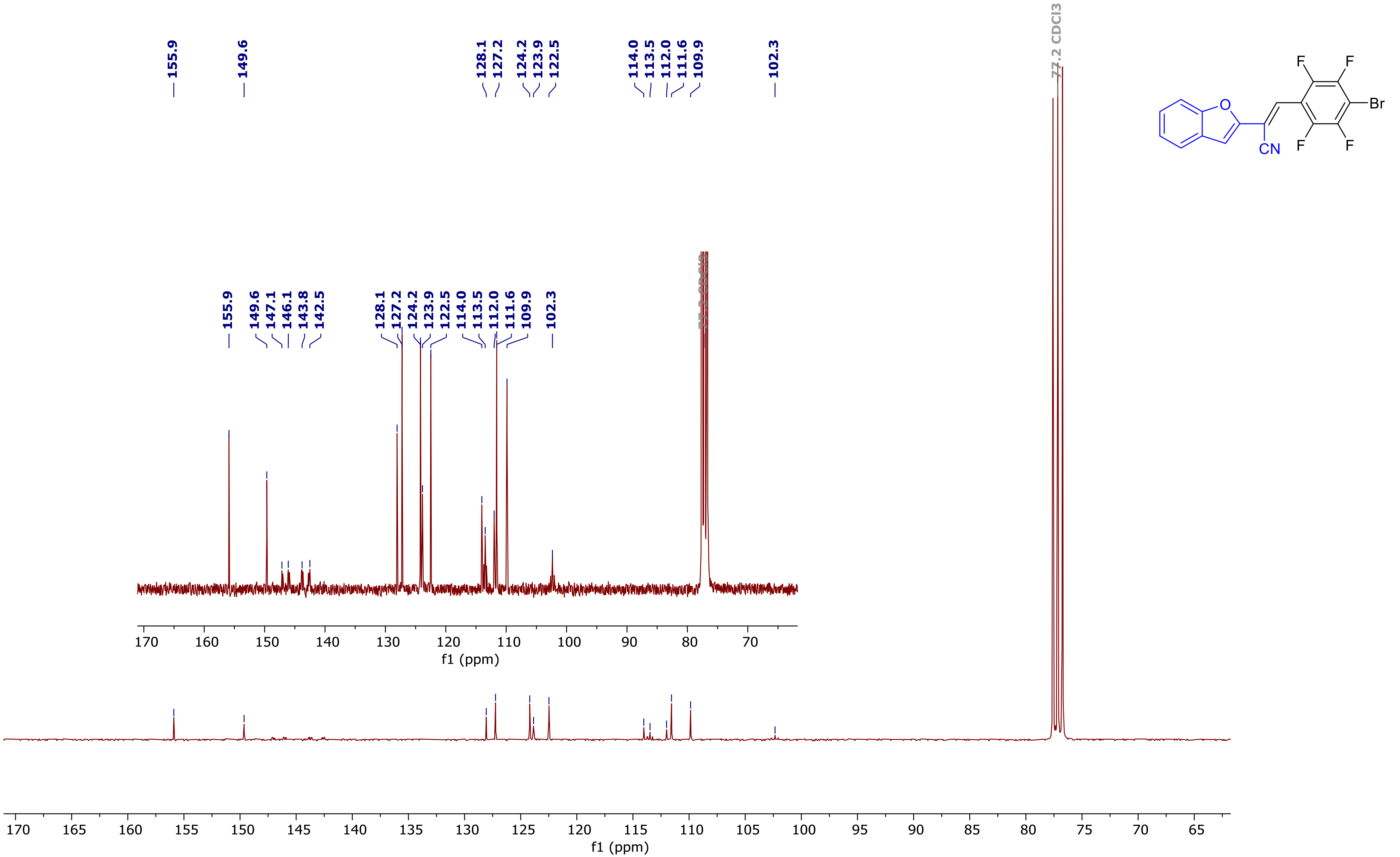


Figure: ^{13}C NMR of **BPF2α** compound in $CDCl_3$

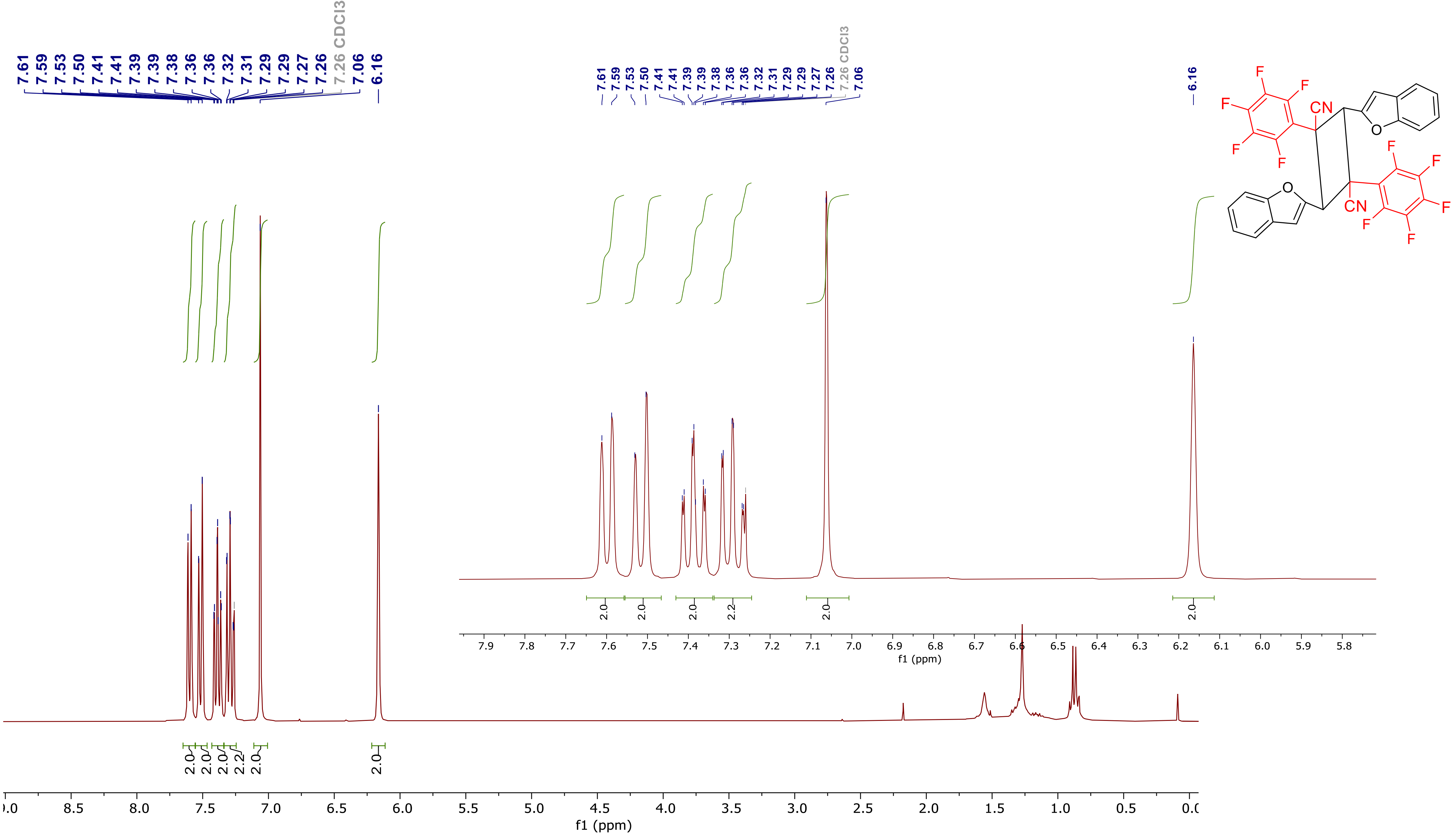


Figure: ^{1}H NMR of **Cy-BPF1** compound in $CDCl_3$

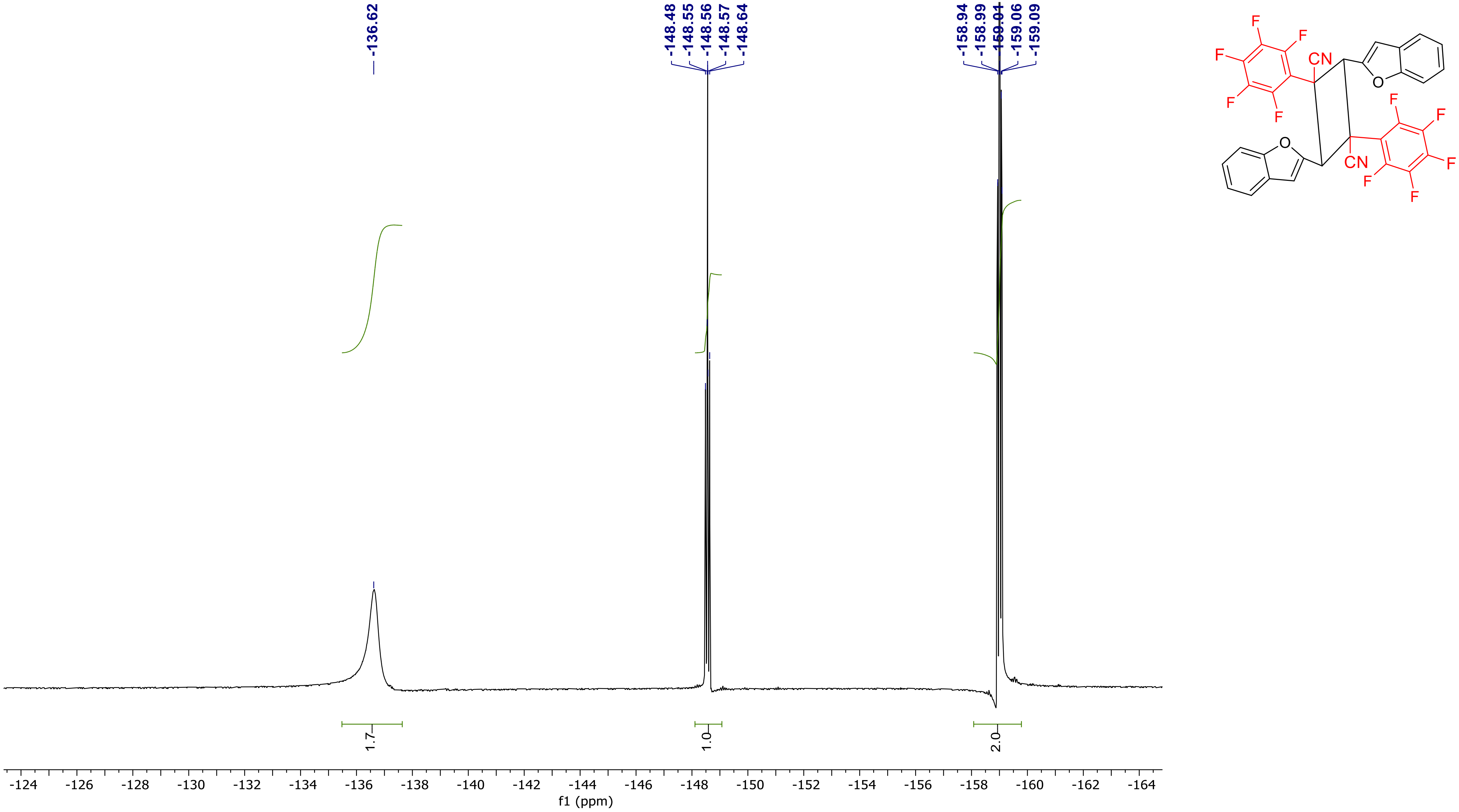


Figure: ^{19}F NMR of **Cy-BPF1** compound in $CDCl_3$

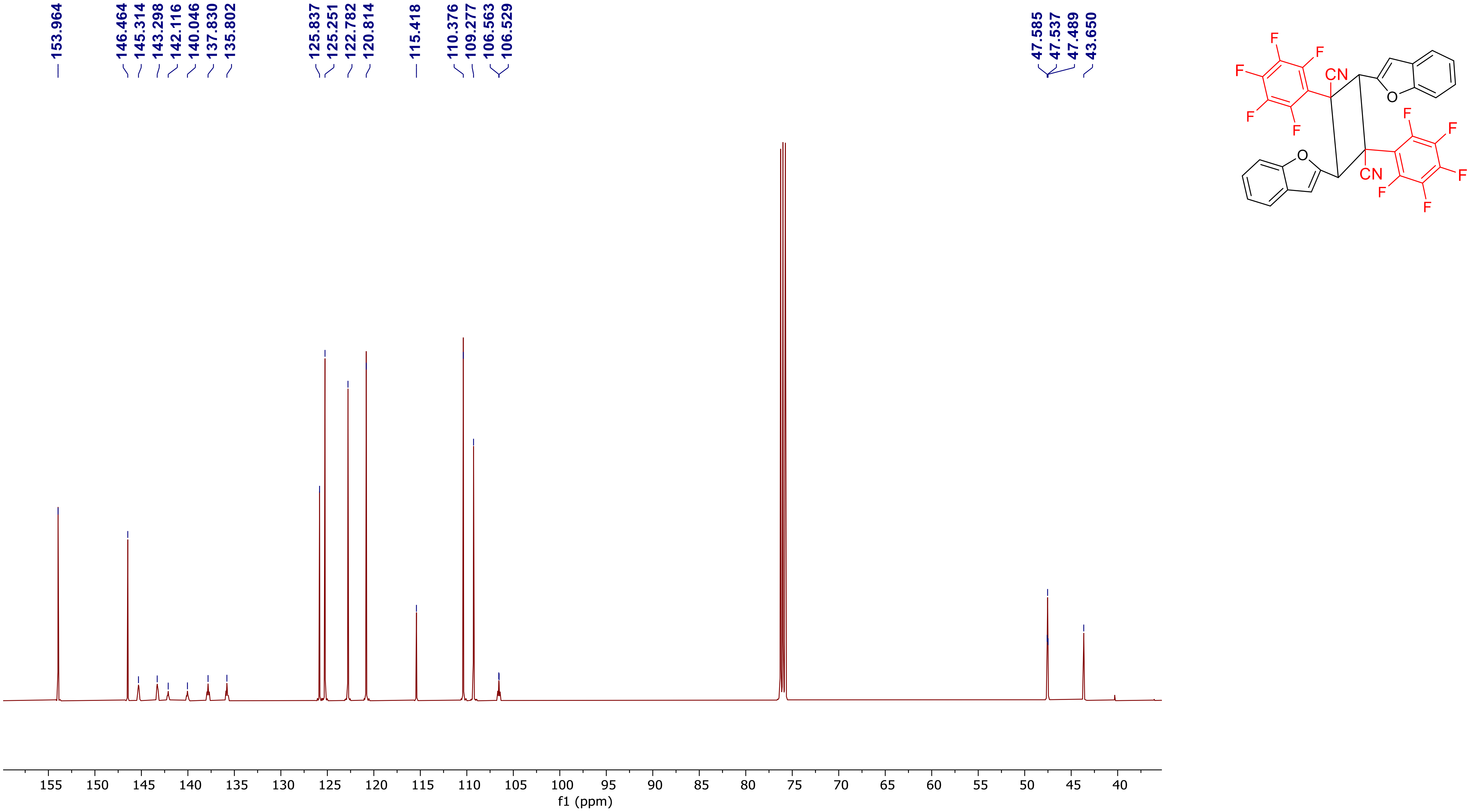
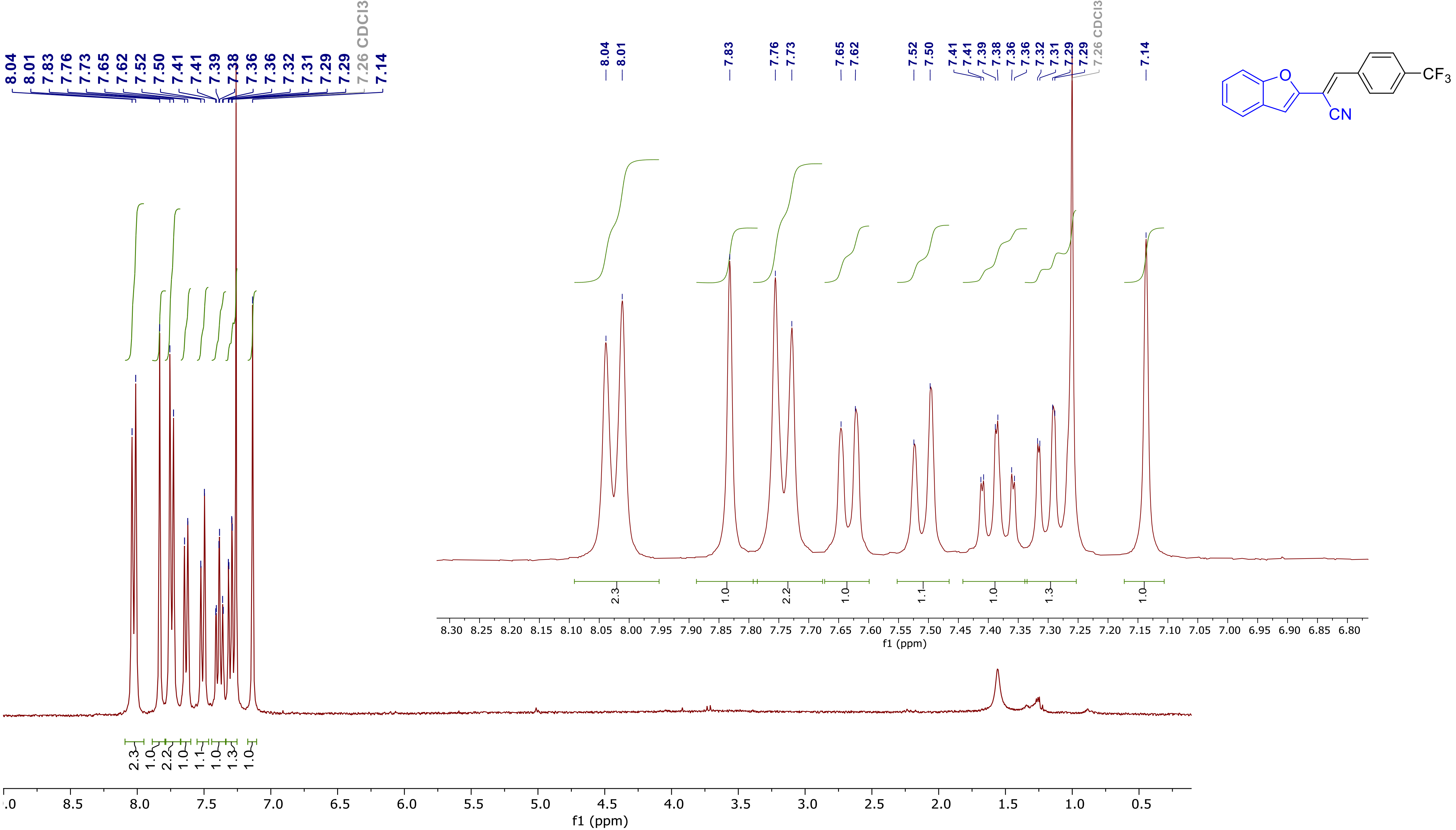
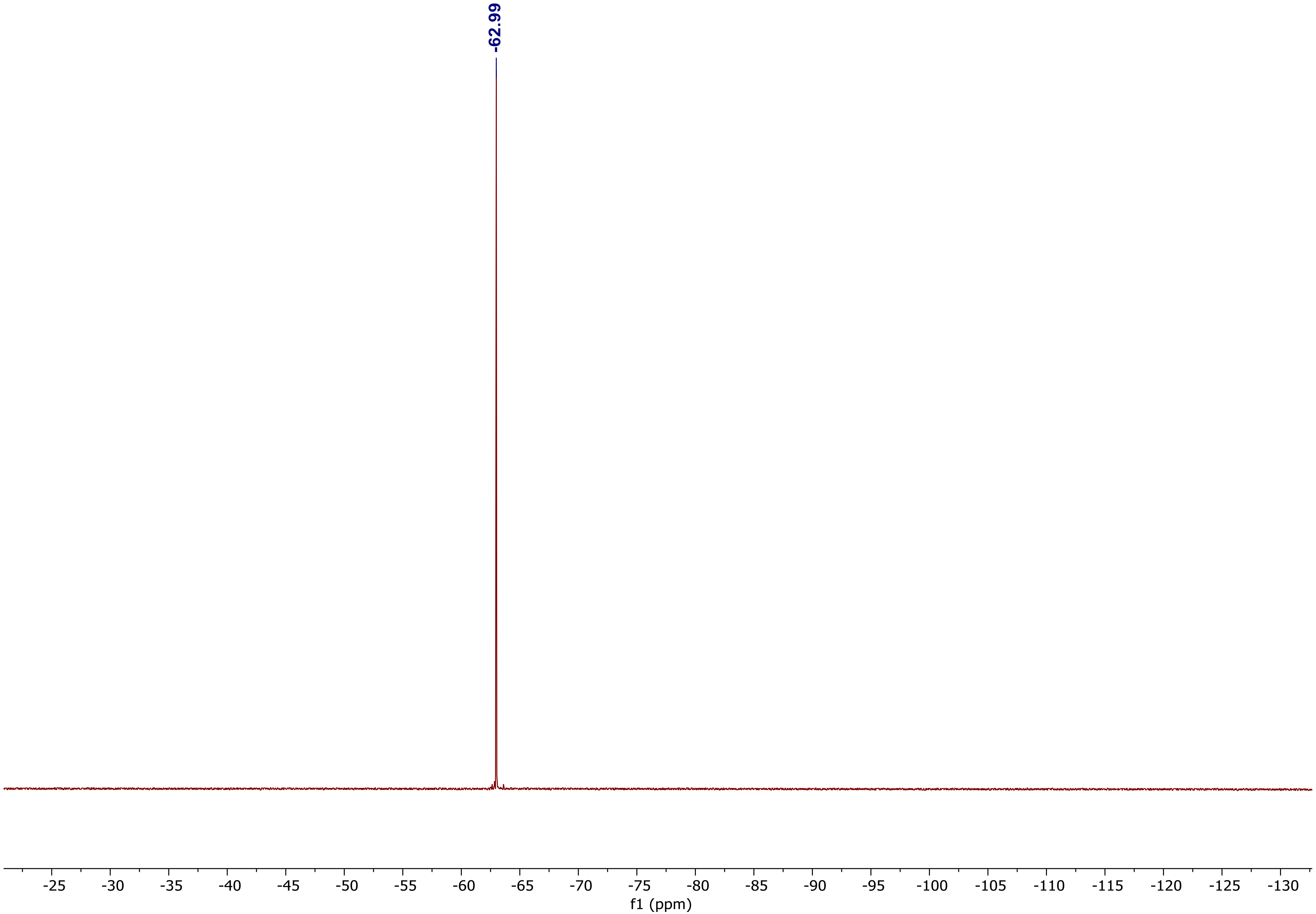
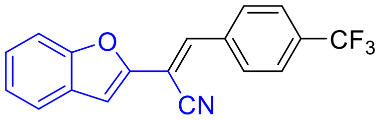


Figure: ^{13}C NMR of **Cy-BPF1** compound in $CDCl_3$

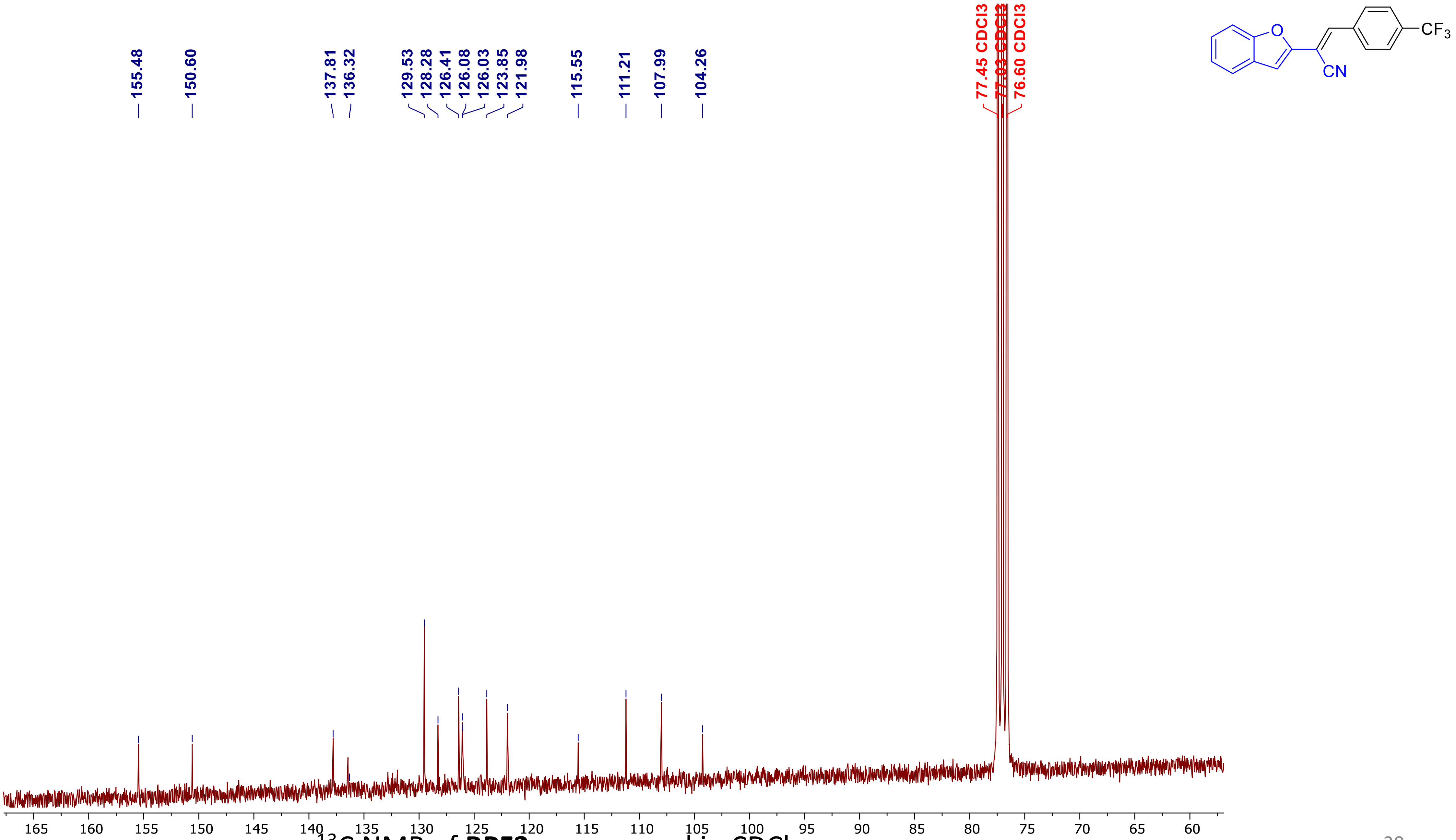


^{1}H NMR of **BPF3α** compound in $CDCl_3$

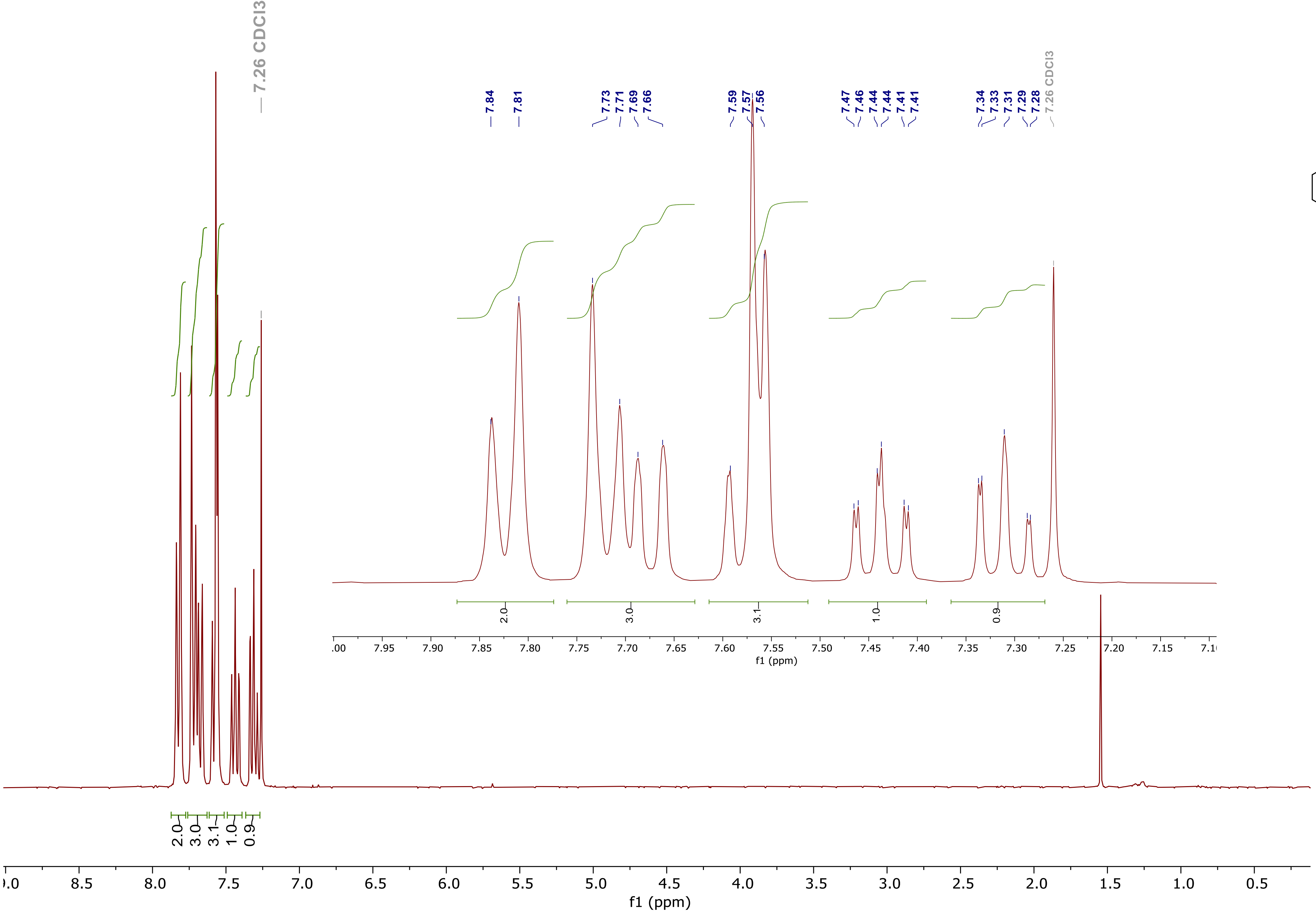


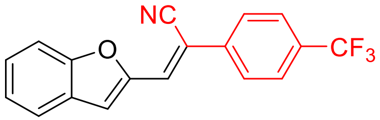


^{19}F NMR of **BPF3α** compound in $CDCl_3$

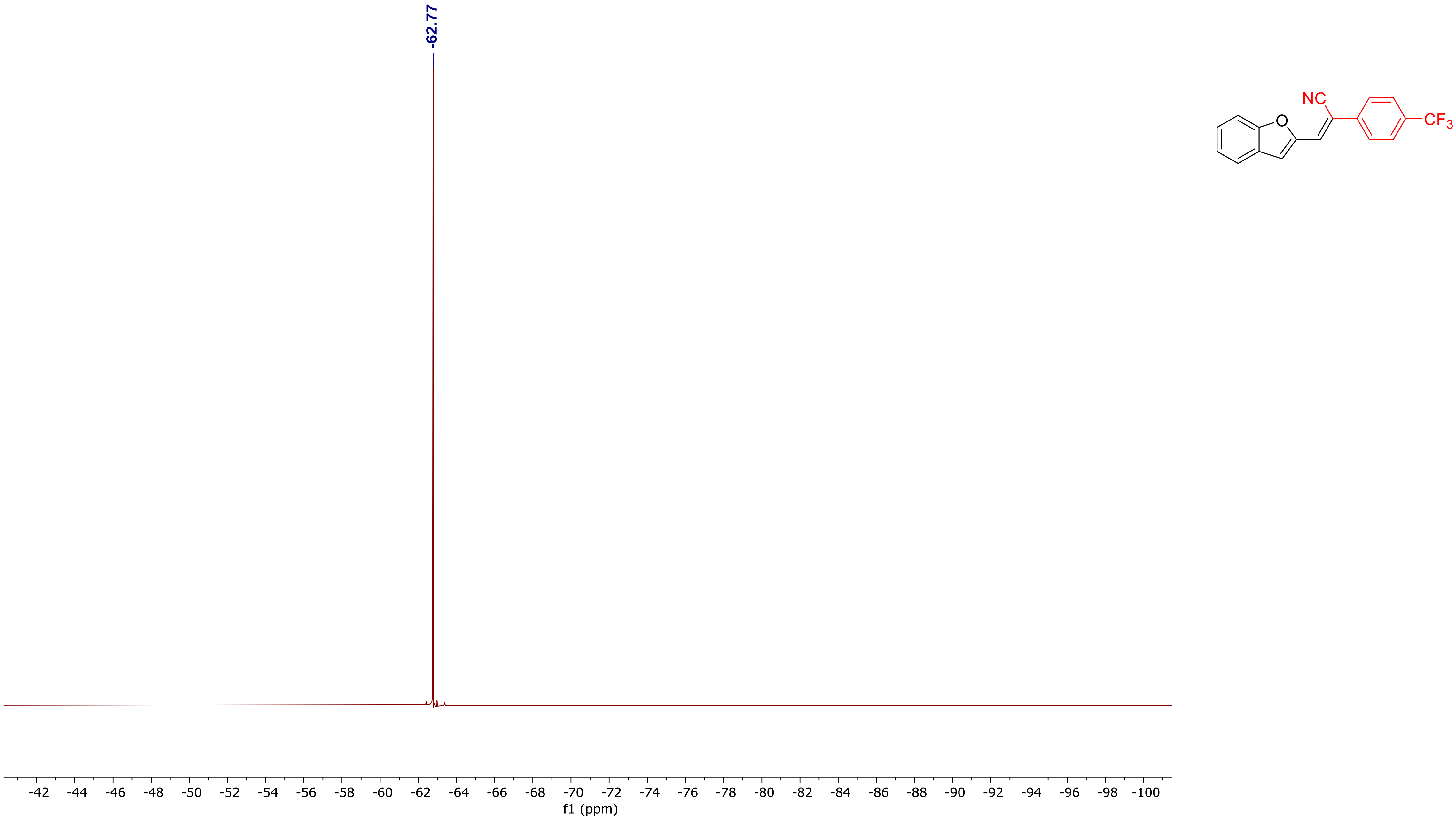


^{13}C NMR of **BPF3α** compound in $CDCl_3$

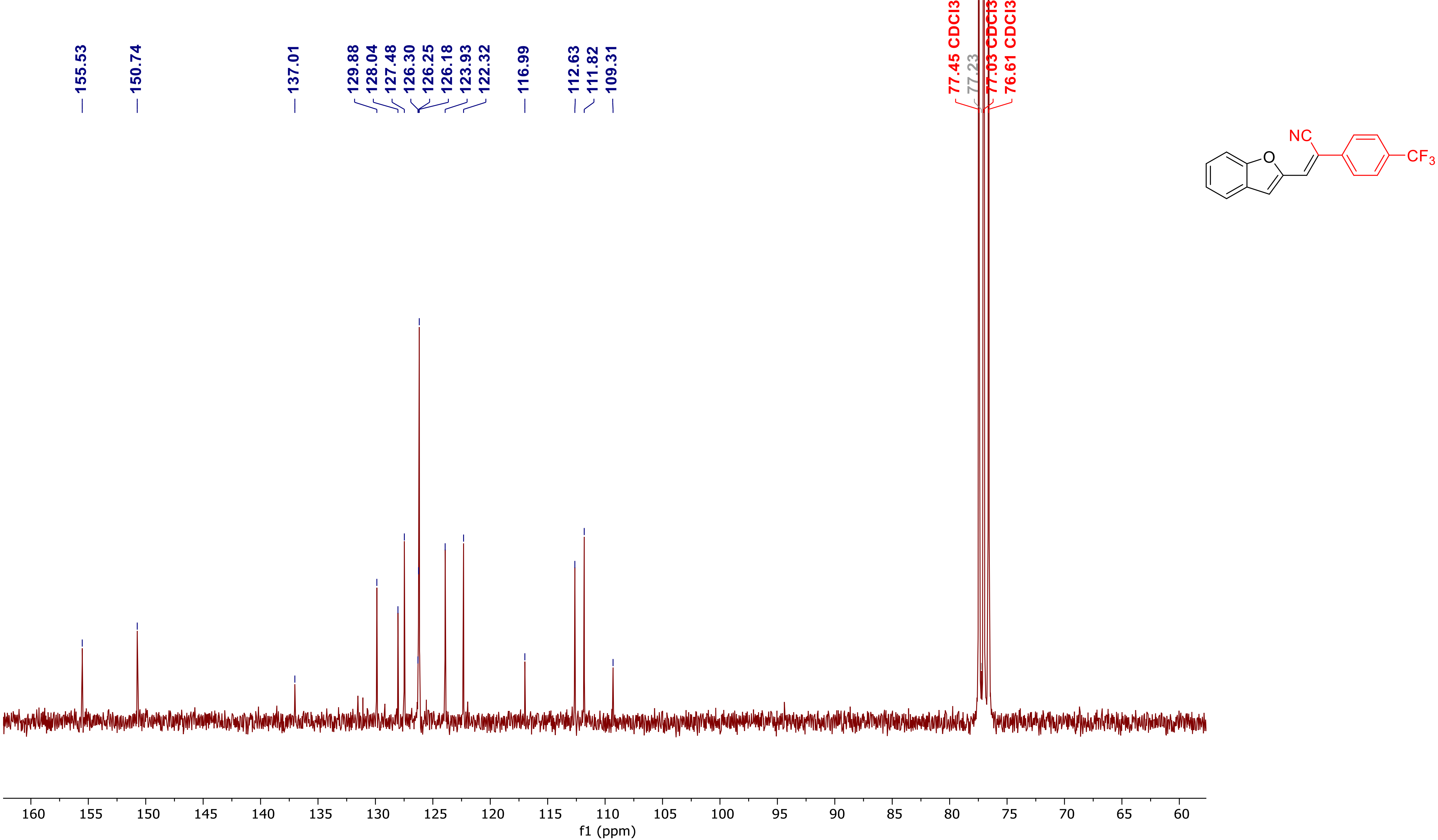




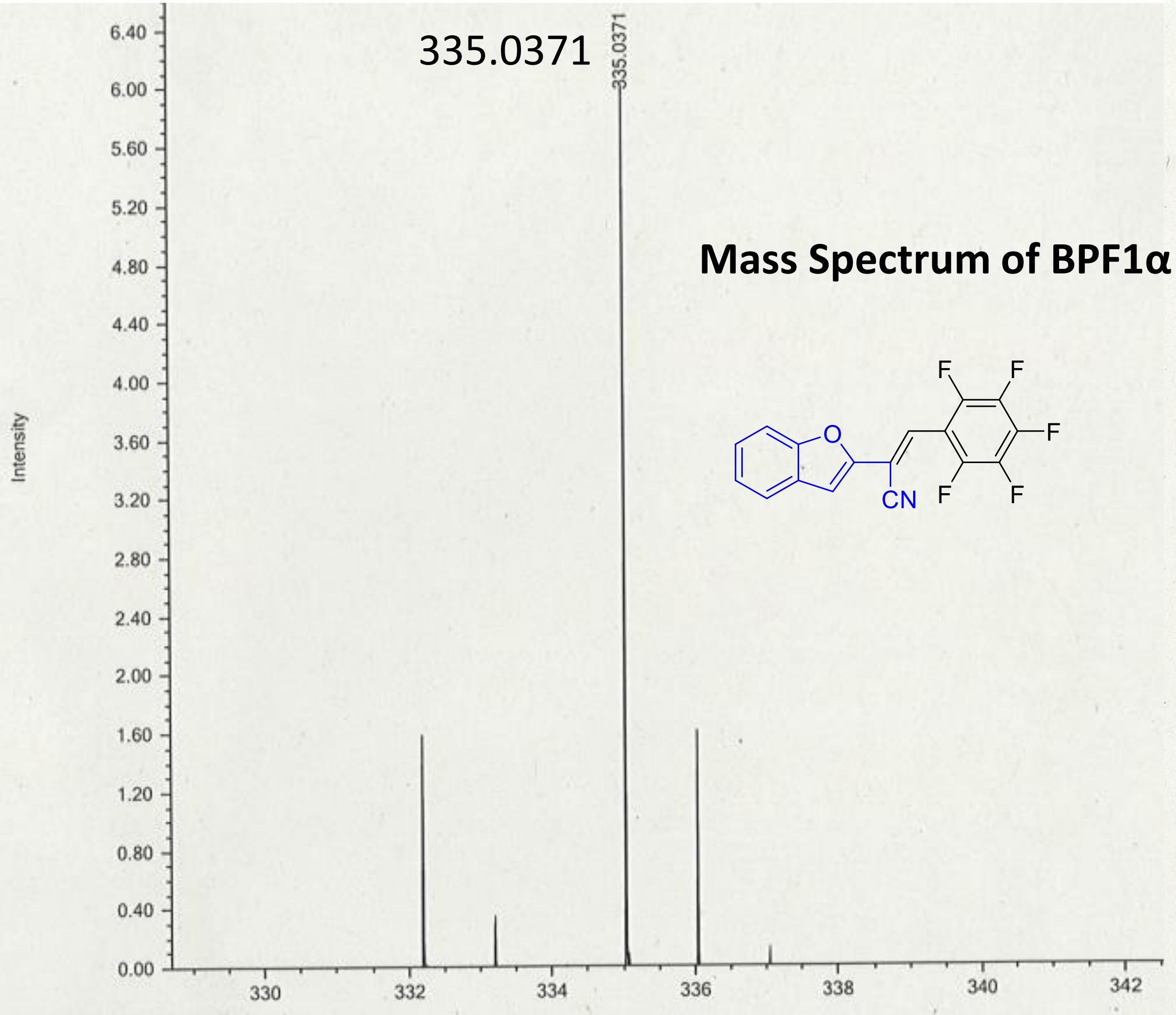
^{1}H NMR of **BPF3β** compound in CDCl$_3$



^{19}F NMR of **BPF3β** compound in $CDCl_3$



^{13}C NMR of **BPF3β** compound in $CDCl_3$



Mass Spectrum of BPF1α

335.0371

Elemental Composition Estimation

Parameters:

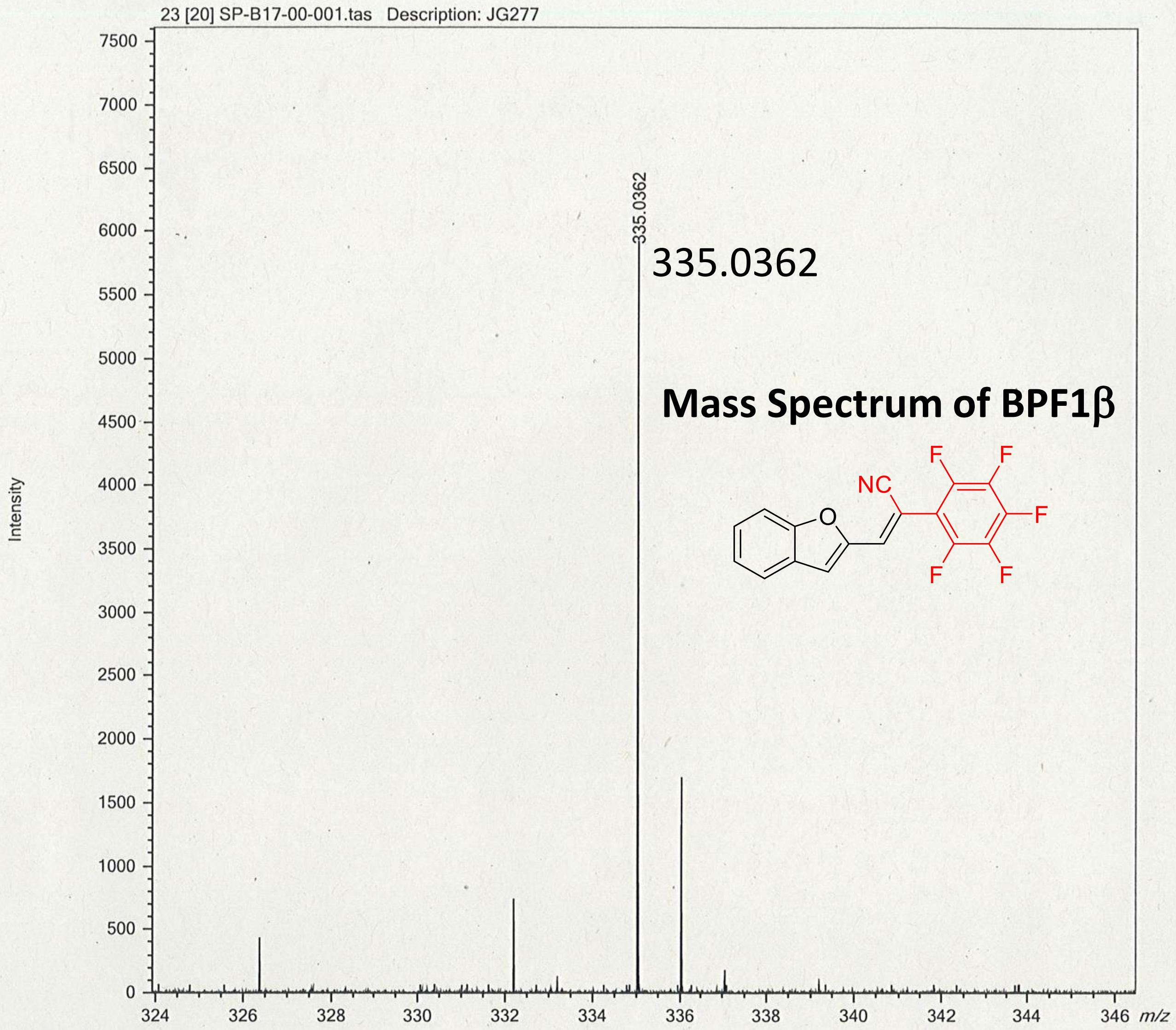
Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
335.03714 ± 0.00101	3.0 ppm	Odd	+1	-0.5 - 200.0	100

Elements

C	0 - 20	H	0 - 100	F	0 - 5	O	0 - 2	N	0 - 2	Br	0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C17 H6 N O F5	335.03641	13.0	0.00073	0.00073	2.19



Mass Spectrum of BPF1β

335.0362

Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
335.03615 ± 0.00034	1.0 ppm	Odd	+1	-0.5 - 200.0	100

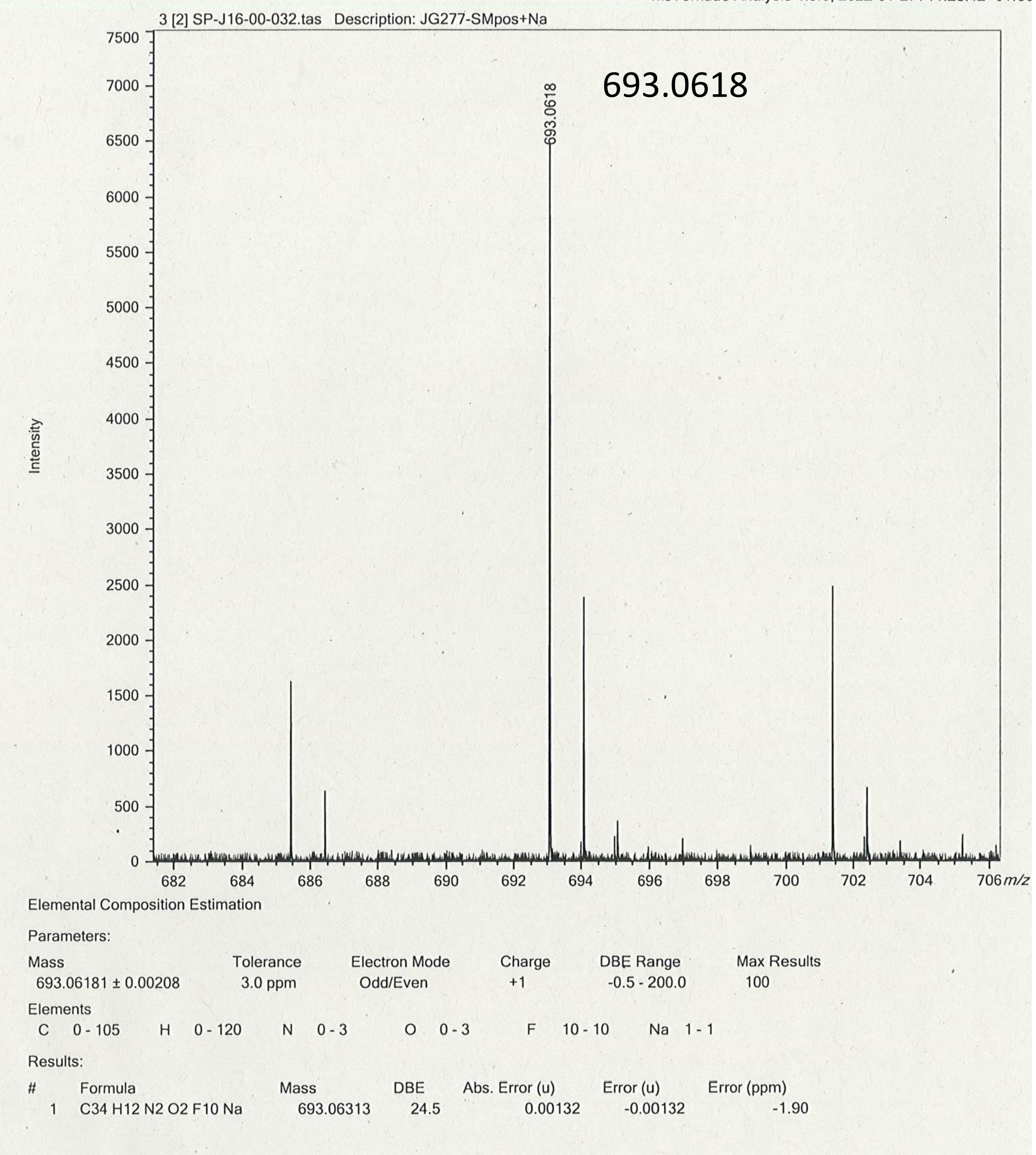
Elements

C	0 - 20	H	0 - 100	F	0 - 5	O	0 - 2	N	0 - 2	Br	0 - 0

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C17 H6 N O F5	335.03641	13.0	0.00025	-0.00025	-0.76

Mass Spectrum of Cy-BPF1, Na



3 [2] SP-J16-00-032.tas Description: JG277-SMpos+Na

Elemental Composition Estimation

Parameters:

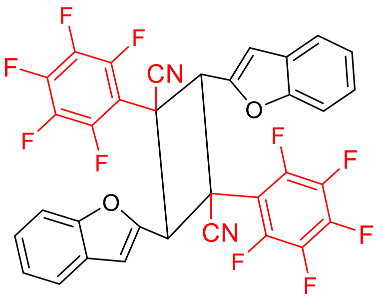
Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
693.06181 ± 0.00208	3.0 ppm	Odd/Even	+1	-0.5 - 200.0	100

Elements

C	H	N	O	F	Na
0 - 105	0 - 120	0 - 3	0 - 3	10 - 10	1 - 1

Results:

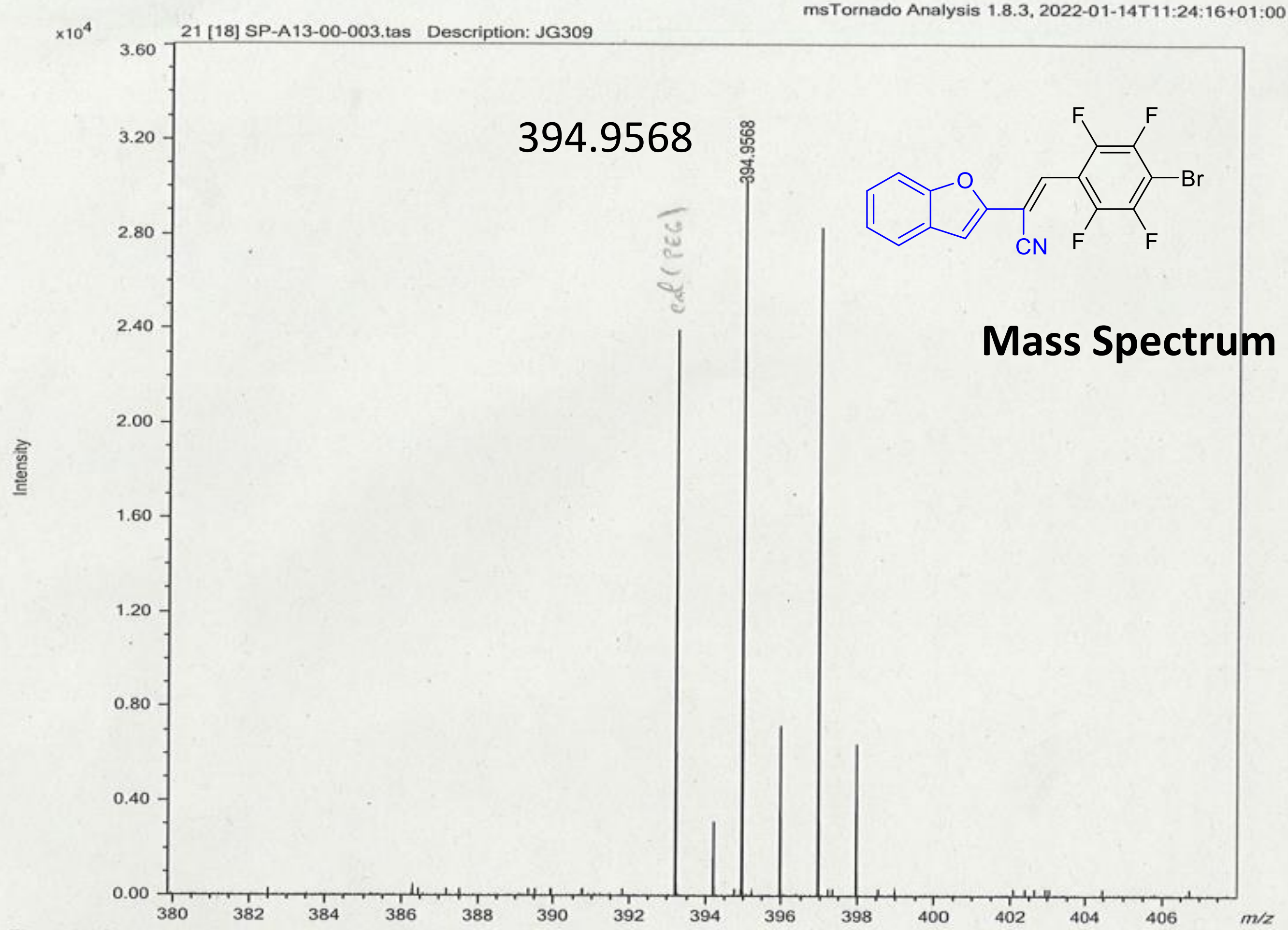
#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C34 H12 N2 O2 F10 Na	693.06313	24.5	0.00132	-0.00132	-1.90



Mass Spectrum of BPF2

msTornado Analysis 1.8.3, 2022-01-14T11:24:16+01:00

21 [18] SP-A13-00-003.tas Description: JG309



Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
394.95679 ± 0.00059	1.5 ppm	Odd	+1	-0.5 - 200.0	100

Elements

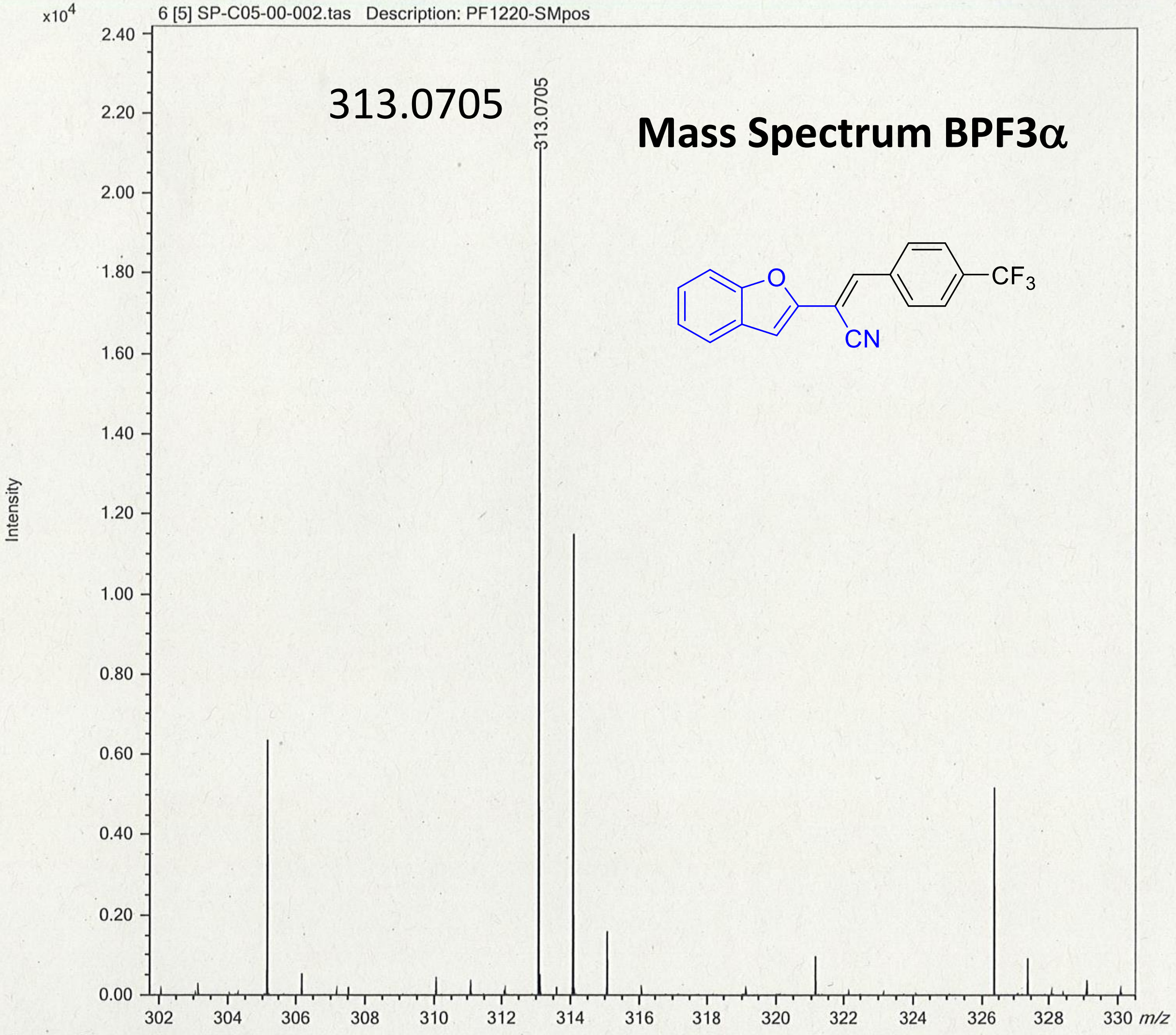
C 0 - 100 H 0 - 100 F 0 - 5 O 0 - 2 N 0 - 2 Br 1 - 1

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C17 H6 N O F4 Br	394.95634	13.0	0.00045	0.00045	1.13

msTornado Analysis 1.8.3, 2022-03-03T09:45:47+01:00

6 [5] SP-C05-00-002.tas Description: PF1220-SMpos



Mass Spectrum BPF3α

Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
313.07050 ± 0.00125	4.0 ppm	Odd	+1	-0.5 - 200.0	100

Elements

C 0 - 20 H 0 - 200 N 0 - 5 O 0 - 5 F 3 - 3

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C18 H10 N O F3	313.07090	13.0	0.00040	-0.00040	-1.29

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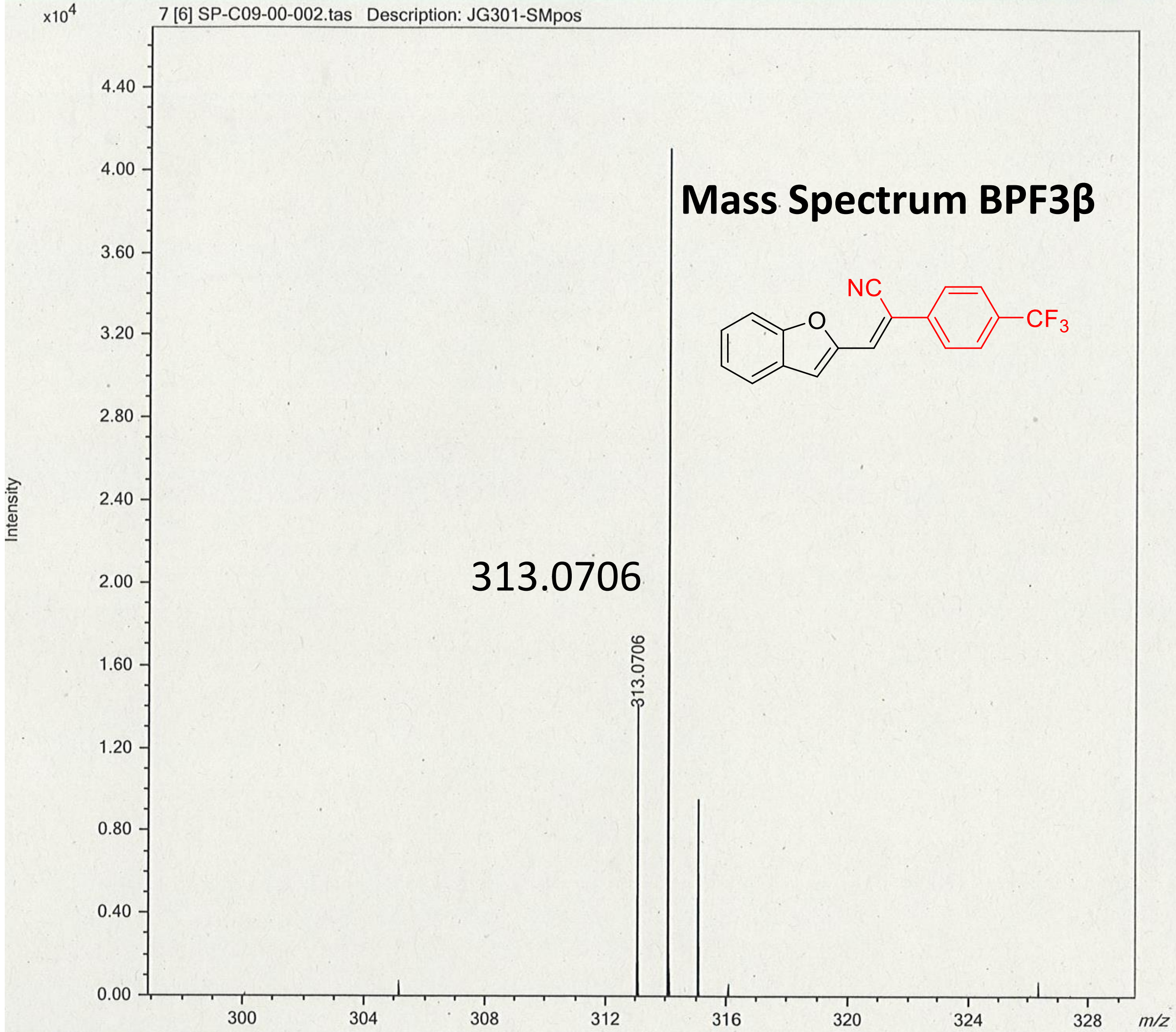
msTornado Analysis 1.8.3, 2022-03-03T09:51:45+01:00

7 [6] SP-C09-00-002.tas Description: JG301-SMpos



Mass Spectrum BPF3β

Elemental Composition Estimation

Parameters:

Mass	Tolerance	Electron Mode	Charge	DBE Range	Max Results
313.07061 ± 0.00125	4.0 ppm	Odd	+1	-0.5 - 200.0	100

Elements

C 0 - 20 H 0 - 200 N 0 - 5 O 0 - 5 F 3 - 3

Results:

#	Formula	Mass	DBE	Abs. Error (u)	Error (u)	Error (ppm)
1	C18 H10 N O F3	313.07090	13.0	0.00029	-0.00029	-0.94