Supporting Information

H-Bond Mediated Photocatalyzed Oxidation of Oximes under visible light and Air. A General Route toward Dioxazoles, Oxadiazoles and Isoxazoles.

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1. General Information

Reagents: All reagent-grade chemicals were obtained from commercial suppliers and were used as received unless otherwise noted. CH_2Cl_2 and THF were dried over activated alumina columns on MBraun Solvent Purification System (SPS-800). DCE, and MeCN were distilled from CaH_2 and anhydrous dimethylformamide, triethylamine (reagent grade, ≥98%) and dimethylsulfoxide (anhydrous, ≥99.9%) were purchased from Sigma Aldrich. EtOAc (water ≤ 0.05%) and petroleum ether were purchased from Fisher scientific and were used as it is.

Reactions: All reactions for the Visible-Light Photocatalyzed Oxidation of Oximes were set up on bench-top in the open air and carried out in re-sealable Schlenk tubes with a balloon of normal air atmosphere. Photochemical reactions were performed using Kessil PR160L lamps- 456 nm (10 W) blue LEDs (λ = 456 nm (± 15nm), 12 V, 500 mA). Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light, ceric Ammonium molybdate, ninhydrin and $KMnO_4$. Flash chromatography was performed on silica gel (0.043-0.063 mm). Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials, unless otherwise stated.

Instruments: ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR were recorded on a Brüker Avance 300 (^{1}H: 300 MHz, ^{13}C: 75.46 MHz, ^{19}F-NMR: 282 MHz), using $CDCl_3$ as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: bs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplets. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 using a diamond NEAT accessory. HRMS were recorded with a Waters Q-TOF 2 spectrometer in the electrospray ionization (ESI) and CI^+ mode.

X-ray were recorded using four-circle diffractometer (Kappa geometry) of a double source (a microsource type IμS with Cu anticathode /45kV and a microsource type IμS with Mo anticathode /50kV) along with APEX II 2-dimensional CCD detector of a Cryostream 700 Oxford Cryosystems liquid nitrogen low temperature measuring device allowing measurements in a range varying from 80K to 400K.

Fluorescence lifetimes were measured using time-correlated single photon counting (TC-SPC). Decay parameters were extracted from reconvolution of the time-resolved emission decay profiles collected using a home-built TC-SPC instrument equipped with a Picoquant 450 nm pulsed

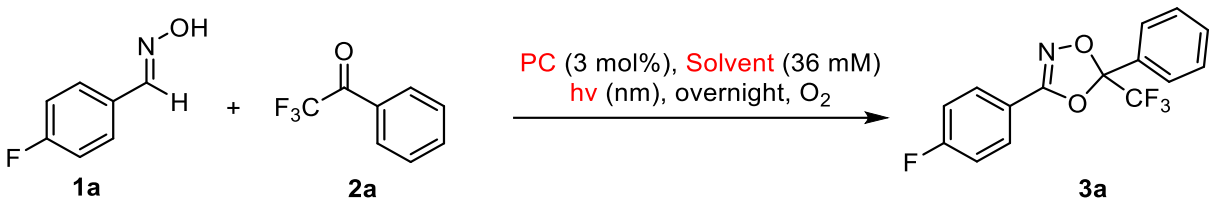
excitation source and a Hamamatsu R6427 photomultiplier and Timeharp 260 collection electronics. A monochromator was used to isolate the emission from the sample at 520 nm.

Fluorescence quenching experiments were recorded using Fluoromax (Horiba) with excitation wavelength at 450 nm and emission wavelength at 520 nm.

Electron Paramagnetic Resonance (EPR) experiments were performed with a Bruker X-band (9.54 GHz) ESP300E spectrometer equipped with a rectangular resonant cavity (TE104 mode). The spectra were recorded at room temperature (293 K) with the following parameters: microwave power of 50 mW, magnetic field modulation with 100 kHz frequency and 0.05 mT amplitude, conversion time of 20.48 ms, time constant of 2.56 ms and a spectral resolution of 0.008 mT/pt. DPPH (g = 2.0036) was used as external reference for magnetic field scale calibration. Analysis of experimental data and spectrum simulation were performed with Bruker WinEPR and WinSimfonia softwares.

2. Tables of optimization and quenchers

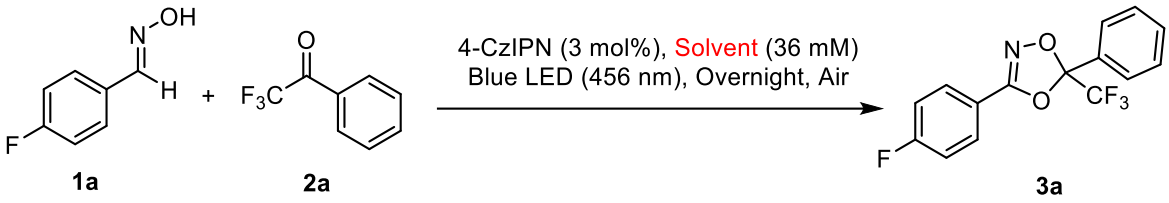
Table ESI-1: Screening of the photocatalyst part (I)



Entry	PC	λ (nm)	Solvent	%Yield[a]
1[b]	------	------	EtOAc	0
2[b]	------	456	EtOAc	0
3[b]	Porphyrin	660	EtOAc	0
4[b]	Porphyrin	660	DCE	0
5[b]	Phthalocyanines	660	EtOAc	0
6[b]	Phthalocyanines	660	DCE	0
7[b]	Rose Bengal	660	EtOAc	0
8[b]	Rose Bengal	660	DCE	0
9[b]	Rose Bengal	525	EtOAc	0
10[b]	Rose Bengal	525	DCE	0
11[b]	Methylene Blue	660	EtOAc	0
12[b]	Methylene Blue	660	DCE	0
13	Fluorenone	370	DCM	0
14	Fluorenone	370	DCE	0
15	Fluorenone	370	CH_3CN	0
16	Phenanthrene	370	DCE	0
17	Carbazole	370	DCE	0
18	Pyrene	370	DCM	2
19	TiO_2	370	EtOAc	0
20	4-CzIPN	456	DCE	8

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (10.0 mmol), photocatalyst (3 mol%). [a] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets. [b]: No reaction at all and starting material recovered.

Table ESI-2: Screening of the solvent

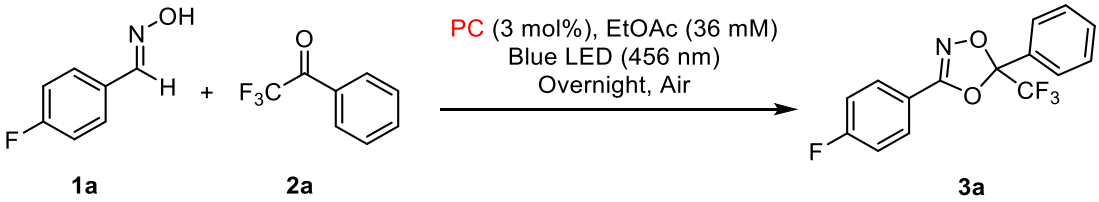


1a **2a** **3a**

Entry	Solvent	%Yield
1	EtOH	0
2	DCE	8
3	t-butanol	0
4	DCM	0
5	CH_3CN	22
6	EtOAc	(31)

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (10.0 mmol), photocatalyst (3 mol%). [a] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets.

Table ESI-3: Screening of the photocatalyst part (II)

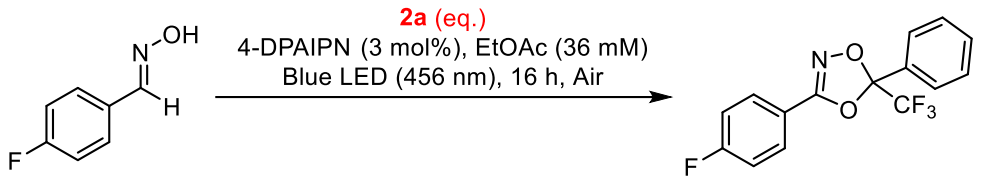


1a **2a** **3a**

Entry	PC	%Yield[a]
1	4-DPATPN	Trace
2	4-CzTPN	12
3	4-*t*ButCzTPN	Trace
4	3-DPAFIPN	21
5	3-CzFIPN	17
6	4-CzIPN	31
7	4-MeOCzIPN	26
8	4-*t*ButCzIPN	35
9	4-BrCzIPN	5
10	4-DPAIPN	(57)

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (3.0 mmol), photocatalyst (3 mol%). [a] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets.

Table ESI-4: Screening the additive quantity

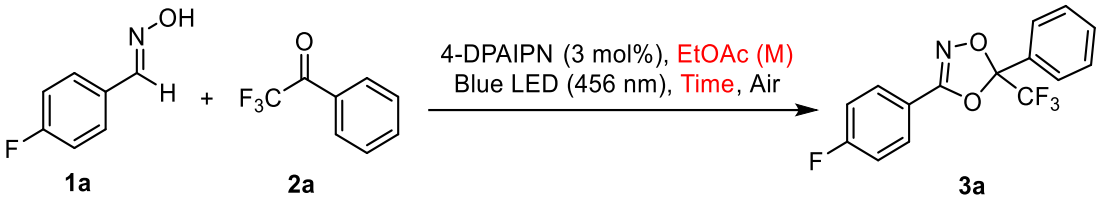


1a **3a**

Entry	2a (eq.)	%Yield[a]
1	10	58
2	5	56
3	3	(57)
4	1.5	33

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (x eq.), 4-DPAIPN (3 mol%) in solution of EtOAc. [a] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets.

Table ESI-5: Screening the concentration

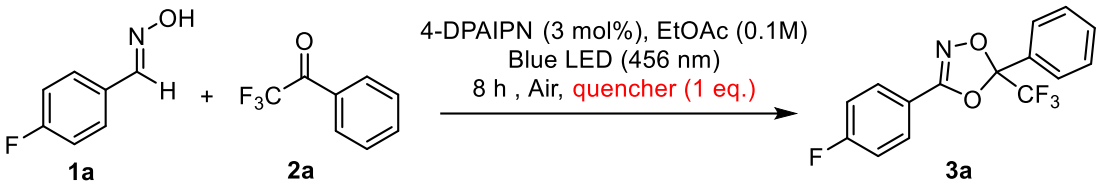


1a **2a** **3a**

Entry	EtOAc (M)	Time (h)[a]	%Yield[b]
1	0.009 M	16	51
2	0.012 M	16	54
3	0.018 M	16	49
4	0.036 M	16	(57)
5	0.1 M	8	(81)
6	0.2 M	3	(69)

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (3.0 mmol), 4-DPAIPN (3 mol%) in solution of EtOAc at given molar concentration. [a] Reaction time were monitored by TLC upon the consumption of the starting material. [b] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets.

Table ESI-6: Table of quenchers

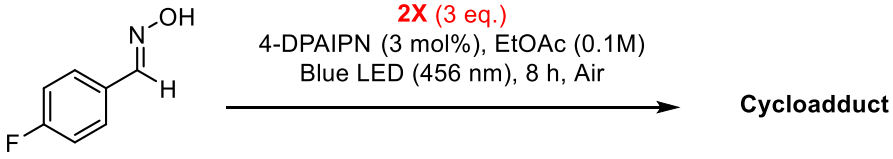


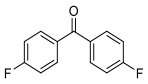
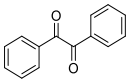
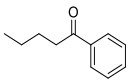
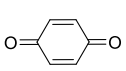
1a + **2a** → **3a**

Entry	Quencher	%Yield[a]
1	DABCO[b]	0
2	NaN_3[c]	0
3	TEMP	Traces
4	TEMPO[d]	(18)
5	4-F-MPBA	(29)
6	*p*-Benzoquinone	0

Reaction conditions were set up as follows: **1a** (1.0 mmol) and **2a** (3.0 mmol), photocatalyst (3 mol%) in solution of EtOAc (0.1 M) and quencher (1.0 mmol, 1 eq). [a] Yields were calculated by ^{19}F NMR using 1,4-bis-(trifluoromethyl)benzene as an internal standard with isolated yield under brackets. [b] Oxime recovered in 77% with only by-product aldehyde obtained in12%. [c] Oxime recovered in 74% with only by-product aldehyde obtained in 19%. [d] Oxime has been totally consumed with by-products aldehyde and acid obtained in 62% and 16%, respectively.

Table ESI-7: List of tested carbonyl compounds

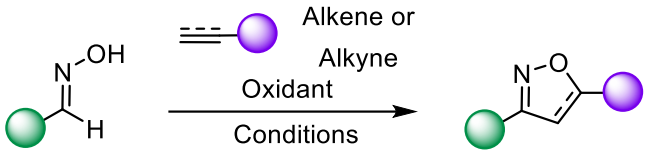


Entry	Carbonyl additive (2X)	Comments
2c[a]		No product
2d[a]		No product
2e		Traces
2f[a]		No product
2g		No product, starting material recovered in (93%)

([a]): only the corresponding by-products (aldehyde + acid).

3. Oxidation of oximes and [3+2]-cycloaddition with alkenes and alkynes. A comparison with literature protocols

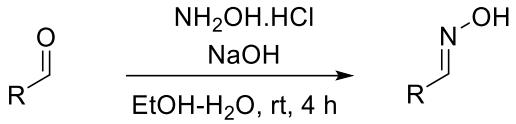
In order to compare the advantages and limitations of our methodology, the table below lists a non-exhaustive number of processes for the oxidation of oximes in the presence of alkenes or alkynes, developed over time, focusing on the number of steps, yields and also the waste generated.



Oxidant	Number of steps	Conditions	Yields	Waste generation	Reference
t-BuONO	1	Oxime (1.0 eq.), alkyne (1.1 eq.), *t*-BuONO (1.1 eq.) in ethyl methyl ketone, 65 °C, 3h	80-90%	Excess *t*-BuONO	K. S. Kadama *et al. Synthesis* **2016**, *48*, 3996-4008
t-BuOCl	2	1. Oxime, Bu_3SnH, Et_3N 2. Alkene or alkyne (1 to 20 eq.), *t*-BuOCl (1 eq.), CH_2Cl_2, RT, 5h	35-82%	Tin derivatives Excess alkene and alkyne	O. Moriya *et al. J. C. S. Chem. Commun.* **1991**, 1671-1672
N-Chlorosuccinimide	2	1. Oxime (1 eq.), NCS (1.3 eq.), in DMF, 0°C 2. Alkyne (1 eq.), Et_3N (1.2 eq.), oxime (1.3 eq.)	34%	NEt_3HCl, DMF	A.R. Sekirnik, *et al.* *Angew. Chem. Int. Ed.* **2016**, *55*, 8353-8357
1 - chlorobenzotriazole	1	Oxime (1 eq.), 1 - chlorobenzotriazole (1 eq.) in CH_2Cl_2, RT, 0.5 h	62-63%, one example of intramolecular 3+2 with alkene)	1 H-benzotriazole hydrochloride	J. N. Kim *et al. Synth. Comm* **1990**, *20*, 1373-1377
$ArI(OAc)_2$ (PIDA)	1	Oxime (1.0 eq.), alkene (1.1 eq.) in MeOH containing TFA, PIDA (1.1 eq.), RT	50-95%	PhI, AcOH	M.A. Ciufolini *et al. Org. Lett.* **2009**, *11*, 1539–1542
$ArI(OCOCF_3)_2$ (PIFA)	1	Oxime (1.5 eq.), alkyne (1 eq.), PIFA (1.5 eq.) in MeOH-H_2O, RT, 7h	10-90%	PhI, CF_3CO_2H	A.M. Jawalekar *et al. Chem. Comm.* **2011**, *47*, 3198-3200

NaClO	1	5% NaOCl, oxime (1 eq.) alkyne (6 eq.), Et_3N (1 eq.) in $CHCl_3$, RT, 45 min.	64%	H_2O, NaCl Excess alkyne	S. Al-Busafi *et al.* *Synth. Comm.* **2010**, *40*, 1088-1092
Chloramine-T		Oxime (1 eq.), alkene (1 eq.), Chloramine-T (1 eq.) in EtOH, reflux, 3h	65-93%	Tosylamide	A. Hassner, *et al.* *Synthesis* **1989**, 57-58
$Pb(OAc)_4$	1	Oxime (1 eq.), Pb(OAc)4 (1.2 eq.), alkene (large excess), in CH_2Cl_2, then Et3N (2 eq.), -78°C to RT	81%	Lead salts Excess alkene	G. Just et al. Tetrahedron 1968, 24, 5251-5269
MnO_2	1	Oxime (1 eq.), alkene (3 eq.) MnO_2 (18 eq.) in CH_2Cl_2, RT, 3h	41-92%	Mn salts Excess alkene	J. Kiegiel *et al.* *Tetrahedron Lett.* **1999**, *40*, 5605-5608
CrO_2	1	Oxime (1 eq.), alkyne (3 eq.), CrO_2 (10 eq) in MeCN, 80°C, 2h	63-87%	Cr salts, excess alkyne	S. Bhosale *et al.* *Tetrahedron Lett.* **2009**, 50, 3948–3951
NaCl/oxone	1	Oxime (1 eq.), alkyne (1.3 eq.), NaCl, oxone (1.1 eq.) in CH_3CN-H_2O, RT, 12h	14-95%	Oxone salts	G. Zhao *et al* *Org. Lett.* **2019**, *21*, 315-319
H_2O_2 - triscetylpyridinium tetrakis (oxodiperoxotungsto) (PCWP) catalyst	1	Oxime (1 eq.), alkyne (3 eq.), H_2O_2 (8 eq.), PCWP (1 mol%) in $CHCl_3$, 40°C, 12h	Mixture of regioisomers 33-55%	Excess alkyne, catalyst	F. P. Ballistreri *et al.* *Molecules* **2008**, *13*, 1230-1237
Electrochemistry	1	Oxime (1 eq.) Alkene or alkyne (3 eq.), tributylmethylammonium methylsulfate (MTBS, 10 mg/mL) in acetonitrile + 15 vol% H_2O + 5 vol% HFIP. 31 °C, ,current density of 5 mA/cm^2	20-81%	Electrolyte (MTBS)	S. Hofmann *et al.* *ChemElectroChem* **2023**, *10*, e202300434
Cl_2	2	1. Dry Cl_2 (excess), oxime (1 eq.) in CH_2Cl_2, 0°C, 3h 2. Chlorooxime (1 eq.), Et_3N (2 eq.), alkyne (5 eq.) in EtOH	11-97%	NEt_3HCl Excess alkyne	O. V. Demina *et al.* *Russ.Chem.Bull., Int. Ed.* **2014,** *63*, 2092-2113

4. General procedure and characterization of prepared Oximes.



Following a reported procedure,[1] hydroxylamine hydrochloride (1.2 equiv.) was dissolved in water (0.67 M aqueous solution) and neutralized with an aqueous sodium hydroxide solution (1.2 eq., 10 % by weight). A solution of benzaldehyde (1.0 eq.) in ethanol (1.0 M) was added slowly to this mixture with stirring in an ice bath. The reaction mixture was stirred at room temperature and the reaction progress was monitored by TLC. Upon completion of the reaction (~4h) the ethanol was evaporated to give the crude oxime. When the oxime was a solid, the desired product was obtained through a simple filtration. With oily oxime, the ethanol was evaporated and the residue dissolved in CH_2Cl_2. The organic layer was then washed with brine, and dried with anhydrous Na_2SO_4. Evaporation of the solvent afforded the required oxime.

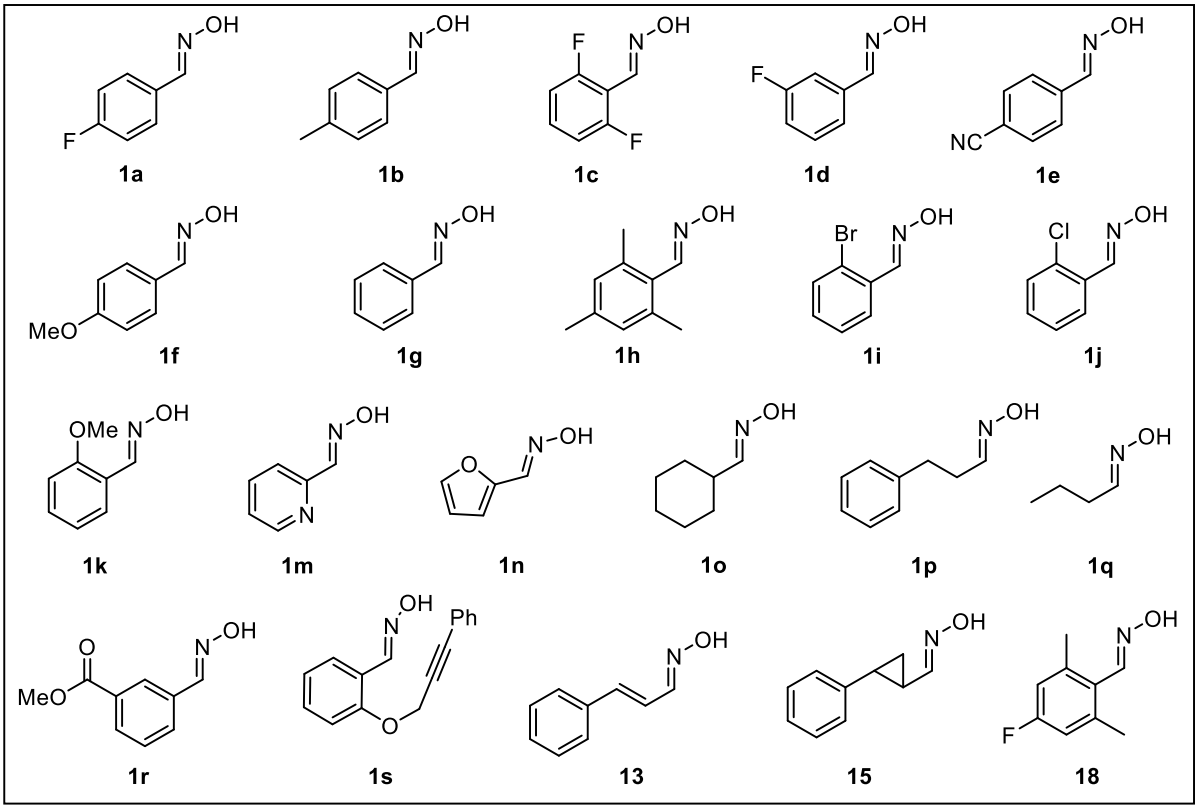
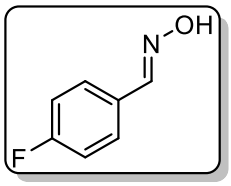


Figure ESI-1. Prepared Oximes

[1] Schwarz, L.; Girreser, U.; Clement, B., Synthesis and characterization of para-Substituted *N*,*N*′-Dihydroxybenzamidines and their derivatives as model compounds for a class of prodrugs. *Eur. J. Org. Chem.* **2014,** 9, 1961-1975.

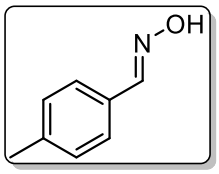
Characterizations of the synthesized starting material (Oximes)

4-Fluorobenzaldehyde oxime (1a). Was obtained through the general procedure as a white solid



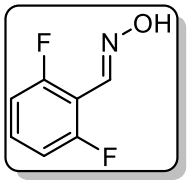
(5.33 g, 95%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.56 (s, 1H), 8.14 (s, 1H), 7.62 – 7.52 (m, 2H), 7.14 – 7.02 (m, 2H). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -110.2 (tt, *J* = 8.5, 5.1 Hz). Spectroscopic data were in good agreement with literature.[2]

4-Methylbenzaldehyde oxime (1b). Was obtained through the general procedure as a white solid



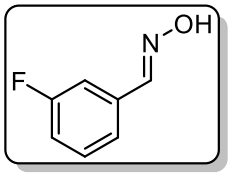
(5.35 g, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.14 (s, 1H), 7.52 – 7.43 (m, 2H), 7.20 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 3H). Spectroscopic data were in good agreement with literature.[1]

2,6-Difluorobenzaldehyde oxime (1c). Was obtained through the general procedure as a white solid



(6.22 g, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.51 (s, 1H), 8.34 (s, 1H), 7.39 – 7.24 (m, 1H), 7.02 – 6.90 (m, 2H)·. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -111.4 (dd, *J* = 8.9, 6.3 Hz). Spectroscopic data were in good agreement with literature.[3]

3-Fluorobenzaldehyde oxime (1d). Was obtained through the general procedure as a white solid



(5.557 mg, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.13 (s, 1H), 7.41 – 7.29 (m, 3H), 7.13 – 7.04 (m, 1H). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -112.4 (td, *J* = 9.0, 8.6, 4.8 Hz). Spectroscopic data were in good agreement with literature.[4]

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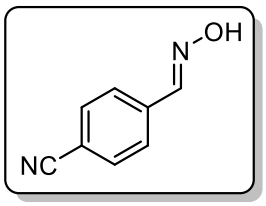
2 Sanders, B. C.; Friscourt, F.; Ledin, P. A.; Mbua, N. E.; Arumugam, S.; Guo, J.; Boltje, T. J.; Popik, V. V.; Boons, G.-J., Metal-free sequential [3+ 2]-dipolar cycloadditions using cyclooctynes and 1, 3-dipoles of different reactivity. *J. Am. Chem. Soc.* **2011,** *4*, 949-957.

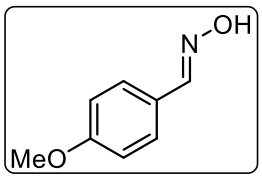
3 Ni, T.; Chi, X.; Xie, F.; Li, L.; Wu, H.; Hao, Y.; Wang, X.; Zhang, D.; Jiang, Y., Design, synthesis, and evaluation of novel tetrazoles featuring isoxazole moiety as highly selective antifungal agents. *Eur. J. Med. Chem.* **2023,** *246*, 115007.

4 Hou, Y.; Lu, S.; Liu, G., Iodine (III)-mediated [3+ 2] cyclization for one-pot synthesis of benzo [d] isoxazole-4, 7-diols in aqueous medium. *J. Org. Chem.* **2013,** *17*, 8386-8395.

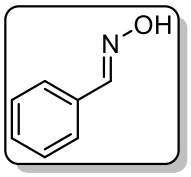
4-((Hydroxyimino)methyl)benzonitrile (1e). Was obtained through the general procedure as a white solid (5.72 g, 98%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.14 (s, 1H), 7.68 (s, 4H). Spectroscopic data were in good agreement with literature.[1]



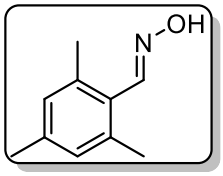
4-Methoxybenzaldehyde oxime (1f). Was obtained through the general procedure as a white solid (6.0 g, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.41 (s, 1H), 8.11 (s, 1H), 7.55 – 7.49 (m, 2H), 6.97 – 6.87 (m, 2H), 3.83 (s, 3H). Spectroscopic data were in good agreement with literature.[2]



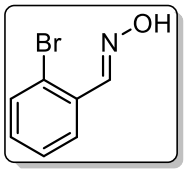
Benzaldehyde oxime (1g). Was obtained through the general procedure as a colourless liquid (7.064 g, 97%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.13 (s, 1H), 8.21 (s, 1H), 7.66 – 7.56 (m, 2H), 7.44 – 7.37 (m, 3H). Spectroscopic data were in good agreement with literature.[2]



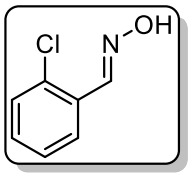
2,4,6-Trimethylbenzaldehyde oxime (1h). Was obtained through the general procedure as white solid (5.121 g, 93%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.42 (s, 1H), 6.88 (s, 2H), 2.37 (s, 6H), 2.28 (s, 3H). Spectroscopic data were in good agreement with literature.[5]



2-Bromobenzaldehyde oxime (1i). Was obtained through the general procedure as a white solid (7.49 g, 94%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.54 (s, 1H), 7.81 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.36 – 7.20 (m, 2H). Spectroscopic data were in good agreement with literature.[5]



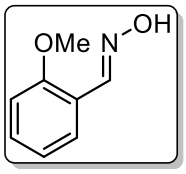
2-Chlorobenzaldehyde oxime (1j). Was obtained through the general procedure as a white solid (6.209g, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.58 (s, 1H), 7.82 (ddd, *J* = 7.3, 1.6, 1.0 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.36 – 7.23 (m, 2H). Spectroscopic data were in good agreement with literature.[6]



[5] Xue, Y.; Wang, S., Generation of Carbonyl Compounds from Oximes through Electrooxidative Deoximation. *J. Org. Chem.* **2024,** *6*, 4199-4204.

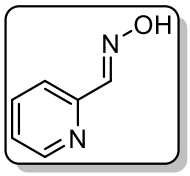
[6] Ramon, R. S.; Bosson, J.; Diez-Gonzalez, S.; Marion, N.; Nolan, S. P., Au/Ag-cocatalyzed aldoximes to amides rearrangement under solvent-and acid-free conditions. *J. Org. Chem.* **2010,** *4*, 1197-1202.

2-Methoxybenzaldehyde oxime (1k). Was obtained through the general procedure as a white solid



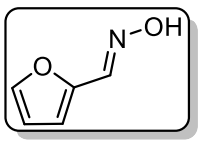
(5.958 g, 99%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.48 (s, 1H), 7.66 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.4, 1.8 Hz, 1H), 7.02 – 6.87 (m, 2H), 3.87 (s, 3H). Spectroscopic data were in good agreement with literature.[4]

2-Pyridinecarbaldehyde oxime (1m). Was obtained through the general procedure as a white



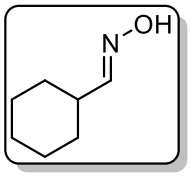
solid (3.52 g, 72%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 10.04 (s, 1H), 8.63 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 8.35 (s, 1H), 7.84 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.72 (td, *J* = 7.7, 1.7 Hz, 1H), 7.29 (ddd, *J* = 7.5, 4.9, 1.3 Hz, 1H). Spectroscopic data were in good agreement with literature.[4]

2-Furaldehyde oxime (1n). Was obtained through the general procedure as a off-white solid (5.14



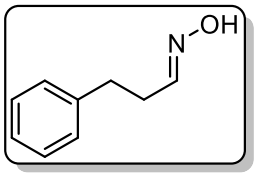
g, 89%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.22 (s, 1H), 8.02 (s, 1H), 7.48 (ddd, *J* = 2.7, 1.8, 0.7 Hz, 1H), 6.66 – 6.62 (m, 1H), 6.46 (dd, *J* = 3.4, 1.8 Hz, 1H). Spectroscopic data were in good agreement with literature.[7]

Cyclohexanecarbaldehyde oxime (1o). Was obtained through the general procedure as colourless



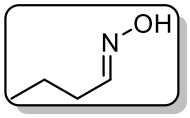
liquid; (major and minor isomers) **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.33 (d, *J* = 6.0 Hz, 1H, major), 6.53 (d, *J* = 7.4 Hz, 1H, minor), 2.97 (dtd, *J* = 11.1, 7.4, 3.7 Hz, 1H minor), 2.31 – 2.12 (m, 1H, major), 1.93 – 1.56 (m, 6H), 1.45 – 1.01 (m, 8H). Spectroscopic data were in good agreement with literature.[7]

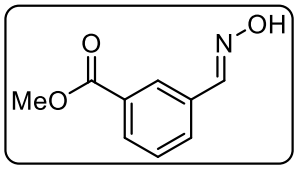
3-Phenylpropanal oxime (1p). Was obtained through the general procedure as a white solid (3.41

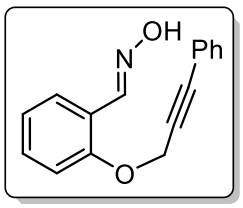


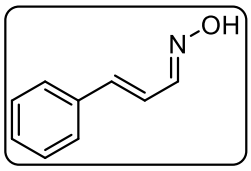
g, 61%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.07 (s, 1H), 8.58 (s, 1H), 7.48 (t, *J* = 5.9 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.27 – 7.18 (m, 5H), 6.78 (t, *J* = 5.2 Hz, 1H), 2.84 (tt, *J* = 8.6, 2.2 Hz, 3H), 2.78 – 2.69 (m, 2H), 2.60 – 2.50 (m, 1H). Spectroscopic data were in good agreement with literature.[4]

[7] Wang, L.; Geng, Y.; Liu, L.; Wang, J.; Chen, J.; Li, Y.; Wang, J.; Song, L.; Sun, K.; Yan, Y., Synthesis, anti-allergic rhinitis evaluation and mechanism investigation of novel 1, 2, 4-triazole-enamides as CB1 R antagonist. *Eur. J. Med. Chem.* **2025,** *289*, 117461.

Butyraldehyde oxime (1q). Was obtained through the general procedure as pale purple liquid  (2.03 g, 34%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.42 (t, *J* = 6.1 Hz, 1H), 6.72 (t, *J* = 5.4 Hz, 1H), 2.36 (td, *J* = 7.5, 5.4 Hz, 2H), 2.18 (td, *J* = 7.4, 6.1 Hz, 2H), 1.52 (h, *J* = 7.4 Hz, 4H), 0.96 (td, *J* = 7.4, 5.2 Hz, 6H). Spectroscopic data were in good agreement with literature.[7]

Methyl 3-((hydroxyimino)methyl)benzoate (1r). Was obtained through the general procedure as white solid  (1.047 g, 96%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.53 (s, 1H), 8.24 – 8.17 (m, 2H), 8.05 (ddd, *J* = 7.8, 1.7, 1.2 Hz, 1H), 7.80 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 166.8, 149.6, 132.6, 131.1, 131.0, 130.9, 129.0, 128.6, 52.5. **HRMS (ESI):** Calculated for $C_9H_8NO_3^-$ $[M-H]^-$ 178.05097, found 178.05110. Spectroscopic data were in good agreement with literature.[8]

2-((3-Phenylprop-2-yn-1-yl)oxy)benzaldehyde oxime (1s). Was obtained through the general procedure as off-white solid  (2.045 g, 96%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.60 (s, 1H), 8.62 (s, 1H), 7.77 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 (ddd, *J* = 8.8, 7.3, 1.7 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.15 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 4.99 (s, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 155.9, 146.6, 131.9, 131.2, 128.8, 128.4, 127.3, 122.2, 121.7, 121.4, 113.2, 87.7, 83.6, 57.3. **HRMS (ESI):** Calculated for $C_{16}H_{13}NO_2Na^+$ $[M+Na]^+$ 274.08385, found 274.08386. Spectroscopic data were in good agreement with literature.[9]

Cinnamaldehyde oxime (13). Was obtained through the general procedure as off-white solid (5.17  g, 93%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 9.16 (s, 1H), 7.98 (dd, *J* = 6.0, 3.1 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.6 Hz, 2H), 7.43 – 7.26 (m, 3H), 6.89 – 6.83 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 152.2, 139.2, 135.9, 129.0, 128.9, 127.1, 121.7. Spectroscopic data were in good agreement with literature.[5,6]

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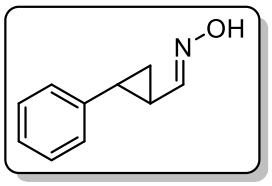
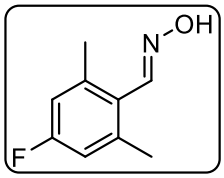
8 Tambara, K.; Pantoş, G. D., Conversion of aldoximes into nitriles and amides under mild conditions. *Org. & Biomol. Chem.* **2013,** *15*, 2466-2472.

9 Mironova, I. A.; Nenajdenko, V. G.; Postnikov, P. S.; Saito, A.; Yusubov, M. S.; Yoshimura, A., Efficient Catalytic Synthesis of Condensed Isoxazole Derivatives via Intramolecular Oxidative Cycloaddition of Aldoximes. *Molecules* **2022,** *12*, 3860.

2-Phenylcyclopropane-1-carbaldehyde oxime (15). Was obtained through the general procedure as off-white solid (0.736 g, 67%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.62 (s, 1H), 7.32 – 7.24 (m, 2H), 7.23 – 7.16 (m, 1H), 7.15 – 7.09 (m, 2H), 6.23 (d, *J* = 8.6 Hz, 1H), 2.59 (tdd, *J* = 8.6, 5.5, 4.3 Hz, 1H), 2.19 (ddd, *J* = 9.0, 6.1, 4.3 Hz, 1H), 1.41 (ddd, *J* = 8.7, 6.1, 5.2 Hz, 1H), 1.26 (dt, *J* = 9.0, 5.4 Hz, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 153.7, 140.4, 128.6, 126.4, 126.2, 24.2, 18.9, 15.6. **HRMS (ESI):** Calculated for $C_{10}H_{12}NO^+$ $[M+H]^+$ 162.09134, found 162.09115. Spectroscopic data were in good agreement with literature.[10]

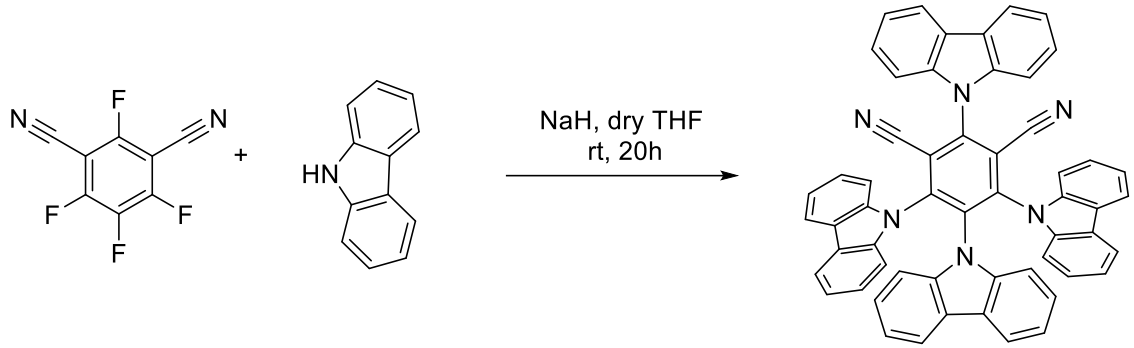


4-Fluoro-2,6-dimethylbenzaldehyde oxime (18). Was obtained through the general procedure as white solid (1.046 g, 95%); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.36 (s, 1H), 8.25 (s, 1H), 6.78 (d, *J* = 9.3 Hz, 2H), 2.39 (s, 6H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 162.5 (d, *J* = 248.4 Hz), 149.2, 140.4 (d, *J* = 8.6 Hz), 125.5 (d, *J* = 3.1 Hz), 115.3 (d, *J* = 21.2 Hz), 21.3 (d, *J* = 1.7 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -113.2 (t, *J* = 9.3 Hz). Spectroscopic data were in good agreement with literature.[5]



[10] Wasylenko, W. A.; Kebede, N.; Showalter, B. M.; Matsunaga, N.; Miceli, A. P.; Liu, Y.; Ryzhkov, L. R.; Hadad, C. M.; Toscano, J. P., Generation of oxynitrenes and confirmation of their triplet ground states. *J. Am. Chem. Soc.* **2006,** *40*, 13142-13150.

5. General procedure and characterizations of synthesized photocatalysts



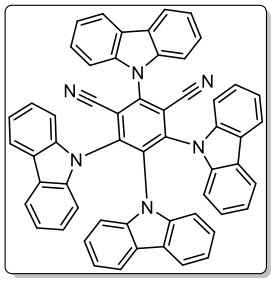
4-CzIPN and 4-CzTPN family were synthesized according to the following reported procedure.[11] NaH (60% in oil, 7.5 mmol) was added slowly to a stirred solution of carbazole, or 3,6-dimethoxy-9H-carbazole, or 3,6-di-tert-butyl-9H-carbazole, or 3,6-dibromo-9H-carbazole or diphenylamine (5 mmol) in dry THF (40 mL) under a nitrogen atmosphere at room temperature. After 30 min, 2,4,5,6-tetrafluoroisophthalonitrile or 2,3,5,6-tetrafluoroterephthalonitrile (1.0 mmol), were added. After stirring at room temperature for 16 h, 3 mL of water were added to the reaction mixture to quench the excess NaH. The resulting mixture was then concentrated under reduced pressure, filtered and successively washed by water and EtOH to yield the crude solid. The crude product was purified with flash column chromatography using (EtOAc or DCM in petroleum ether 10% to 100%) to afford the pure product as yellow, red or orange solids.

3-DPAFIPN and 3-CzFIPN were synthesized according to the same procedure, except that the NaH (60% in oil, 5 mmol) and (diphenylamine or carbazole) (3.75 mmol) were added to the 2,4,5,6-tetrafluoroisophthalonitrile (1.0 mmol).

[11] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C., Highly efficient organic light-emitting diodes from delayed fluorescence. *Nature* **2012,** *492*, 234-238.

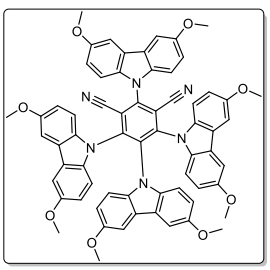
Characterization of the synthesized Organophotocatalysts

2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile (4-CzIPN). 4-CzIPN was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (800.4 mg, 4.0 mmol) and carbazole (3.3442 g, 20.0 mmol), as a yellow solid (3.02 g, 96%); Rf (PE/EA 10:1) = 0.25; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.23 (dt, *J* = 7.8, 1.0 Hz, 2H), 7.75 – 7.66 (m, 8H), 7.49 (ddd, *J* = 8.1, 6.2, 2.0 Hz, 2H), 7.33 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.25 – 7.19 (m, 4H), 7.14 – 7.04 (m, 8H), 6.83 (td, *J* = 8.3, 1.5 Hz, 4H), 6.68 – 6.59 (m, 2H). **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 145.2, 144.6, 140.0, 138.2, 137.0, 134.8, 127.0, 125.8, 125.0, 124.8, 124.6, 123.9, 122.4, 122.0, 121.4, 121.0, 120.5, 119.7, 116.4, 111.7, 110.0, 109.5, 109.4. **HRMS (FD+):** For $C_{56}H_{32}N_6^{\bullet+}$ $[M]^{\bullet+}$ Calculated 788.26884, found 788.26788. Spectroscopic data were in good agreement with literature.[11,,12]



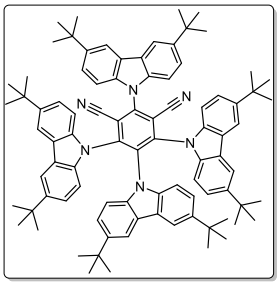
2,4,5,6-Tetrakis(3,6-dimethoxy-9H-carbazol-9-yl)isophthalonitrile (4-MeOCzIPN).

4-MeOCzIPN was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and 3,6-dimethoxy-9H-carbazole (1.136 g, 5.0 mmol), as a red solid (946 mg, 92%); Rf (PE/EA 10:4) = 0.32; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.59 (d, *J* = 2.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 2.5 Hz, 2H), 7.15 (d, *J* = 2.5 Hz, 4H), 7.04 (d, *J* = 8.9 Hz, 4H), 6.82 (d, *J* = 2.5 Hz, 2H), 6.72 – 6.64 (m, 6H), 6.30 (dd, *J* = 8.9, 2.5 Hz, 2H), 3.99 (s, 6H), 3.79 (s, 12H), 3.69 (s, 6H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 155.6, 155.1, 154.4, 135.3, 133.6, 132.5, 125.7, 125.3, 124.6, 114.5, 112.0, 110.8, 104.1, 103.5, 56.1, 55.9, 55.8. **HRMS (ESI):** Calcd. For $C_{64}H_{48}N_6O_8Na^+$ $[M+Na]^+$ 1051.34233, found 1051.34258. Spectroscopic data were in good agreement with literature.[13]



2,4,5,6-Tetrakis(3,6-di-tbutyl-9H-carbazol-9-yl)isophthalonitrile (4-*t*ButCzIPN).

(4-*t*ButCzIPN) was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and 3,6-di-tert-butyl-9H-carbazole (1.397 g, 5.0 mmol), as a greenish yellow solid (1.2 g, 97%); Rf (PE/EA 10:0.5) = 0.66; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.22 (d, *J* = 1.3 Hz, 2H), 7.76 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.65 – 7.58 (m, 6H), 7.19 (d, *J* = 1.3 Hz, 2H), 7.04 (t, *J* = 1.3 Hz, 8H), 6.55 – 6.43 (m, 4H),

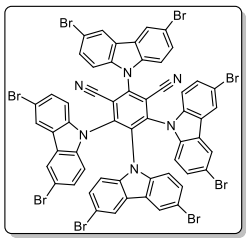


[12] Leitch, J. A.; Smallman, H. R.; Browne, D. L., Solvent-minimized synthesis of 4CzIPN and related organic fluorophores via ball milling. *J. Org. Chem.* **2021,** 20, 14095-14101.

[13] Speckmeier, E.; Fischer, T. G.; Zeitler, K., A toolbox approach to construct broadly applicable metal-free catalysts for photoredox chemistry: deliberate tuning of redox potentials and importance of halogens in donor–acceptor cyanoarenes. *J. Am. Chem. Soc.* **2018,** *45*, 15353-15365.

1.55 (s, 18H), 1.31 (s, 36H), 1.23 (s, 18H). **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 146.0, 145.1, 144.8, 144.5, 143.5, 138.7, 137.2, 135.7, 134.1, 125.1, 124.6, 124.2, 123.4, 122.2, 117.6, 116.2, 115.5, 115.1, 112.4, 109.9, 109.1, 109.1, 35.1, 34.7, 34.4, 32.1, 31.9, 31.9, 22.8, 14.3. **MS (FD+):** Calculated. For $C_{88}H_{96}N_6^{\bullet+}$ $[M]^{\bullet+}$ 1236.76, found 1236.7. Spectroscopic data were in good agreement with literature.[12]

2,4,5,6-Tetrakis(3,6-dibromo-9H-carbazol-9-yl)isophthalonitrile (4-DBCzIPN).

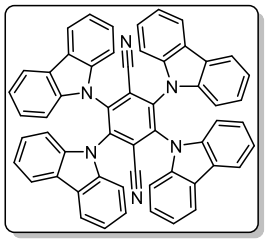


(4-DBrCzIPN) was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and 3,6-dibromo-9H-carbazole (1.625 g, 5.0 mmol), as a yellow solid (1.26 g, 89%); Rf (PE/EA 10:1) = 0.45; **^{1}H NMR (300 MHz, DMSO) δ (ppm):** 8.73 (d, *J* = 1.9 Hz, 2H), 8.29 (d, *J* = 2.0 Hz, 4H), 8.06 – 7.97 (m, 4H), 7.94 (d, *J* = 2.0 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 4H), 7.43 (dd, *J* = 8.8, 2.5 Hz, 6H), 7.05 (dd, *J* = 8.6, 2.0 Hz, 2H). **HRMS (ESI negative):** Calculated. For $C_{56}H_{24}{}^{79}Br_4{}^{81}Br_4N_6Cl$ $[M+Cl]^-$ 1454.51416, found 1454.51392. Spectroscopic data were in good agreement with literature.[12]

2,4,5,6-Tetrakis(diphenylamino)isophthalonitrile (4-DPAIPN). (4-DPAIPN) was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and diphenylamine (846.1 mg, 5.0 mmol), as a yellow solid (740 mg, 93%); Rf (PE/EA 10:1) = 0.27; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.32 – 7.23 (m, 4H), 7.13 – 6.99 (m, 14H), 6.95 – 6.84 (m, 8H), 6.73 – 6.66 (m, 10H), 6.59 – 6.53 (m, 4H). **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 154.2, 151.8, 145.6, 144.7, 143.2, 140.3, 129.4, 128.6, 127.6, 124.2, 124.0, 123.0, 122.6, 121.1, 113.2, 113.0. **HRMS (ESI):** Calculated For $C_{56}H_{40}N_6Na^+$ $[M+Na]^+$ 819.32067, found 819.31961. Spectroscopic data were in good agreement with literature.[14]

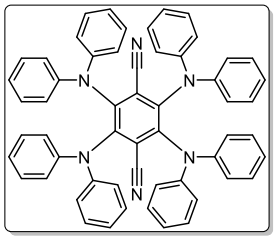
[14] Sahari, A.; Puumi, J.; Mannisto, J. K.; Repo, T., Dual nickel photocatalysis for O-aryl carbamate synthesis from carbon dioxide. *J. Org. Chem.* **2023,** *6*, 3822-3829.

2,3,5,6-Tetra(9H-carbazol-9-yl)terephthalonitrile (4-CzTPN). (4-CzTPN) was obtained



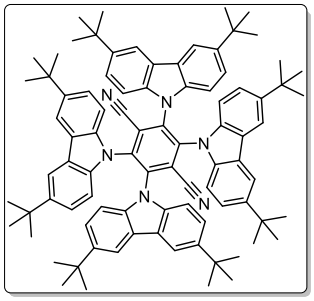
following the general procedure, starting from 2,3,5,6-tetrafluoroterephthalonitrile (400.2 mg, 2.0 mmol) and carbazole (1.672 g, 10.0 mmol), as an orange solid (1.47 g, 94%); Rf (PE/EA 10:4) = 0.15; **^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm):** 7.85 – 7.78 (m, 8H), 7.35 – 7.30 (m, 8H), 7.26 – 7.16 (m, 16H). **HRMS (ESI):** Calculated for $C_{56}H_{32}N_6Na^+$ $[M+Na]^+$ 811.25807, found 811.2569. Spectroscopic data were in good agreement with literature.[11,12]

2,3,5,6-Tetrakis(diphenylamino)terephthalonitrile (4-DPATPN). (4-DPATPN) was obtained



following the general procedure, starting from 2,3,5,6-tetrafluoroterephthalonitrile (400.2 mg, 2.0 mmol) and diphenylamine (1.692 g, 10.0 mmol), as a pink-red solid (1.412 g, 89%); Rf (PE:EA 10:4) = 0.05; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.16 – 7.07 (m, 16H), 6.92 – 6.84 (m, 8H), 6.83 – 6.74 (m, 16H). **HRMS (ESI):** Calculated for $C_{56}H_{40}N_6K^+$ $[M+K]^+$ 835.29460, found 835.29382. Spectroscopic data were in good agreement with literature.[14]

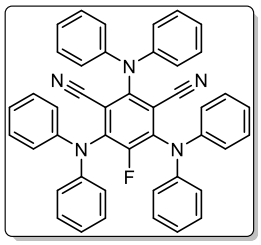
2,3,5,6-Tetrakis(3,6-di-tert-butyl-9H-carbazol-9-yl)terephthalonitrile (4-*t*ButCzTPN).



(4-*t*ButCzTPN) was obtained following the general procedure, starting from 2,3,5,6-tetrafluoroterephthalonitrile (200.1 mg, 1.0 mmol) and 3,6-di-*tert*-butyl-9H-carbazole (1.397 g, 5.0 mmol), as an orange solid (1.11 g, 90%); Rf (PE/EA 10:1) = 0.89; **^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm):** 7.67 (s, 8H), 7.18 – 6.97 (m, 16H), 1.40 (s, 72H). **MS (FD+):** Calculated. For $C_{88}H_{96}N_6^{\bullet+}$ $[M]^{\bullet+}$ 1236.76, found 1236.8. Spectroscopic data were in good agreement with literature.[15]

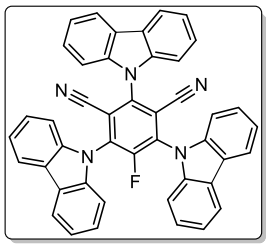
[15] Etherington, M. K.; Kukhta, N. A.; Higginbotham, H. F.; Danos, A.; Bismillah, A. N.; Graves, D. R.; McGonigal, P. R.; Haase, N.; Morherr, A.; Batsanov, A. S., Persistent dimer emission in thermally activated delayed fluorescence materials. *J. Phys. Chem. C* **2019,** *17*, 11109-11117.

2,4,6-Tris(diphenylamino)-5-fluoroisophthalonitrile (3-DPAFIPN):



(3-DPAFIPN) was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and diphenylamine (635 mg, 3.75 mmol), as a yellow solid (0.575 g, 89%); Rf (PE/EA 10:1) = 0.29; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.30 – 7.22 (m, 12H), 7.10 – 7.03 (m, 6H), 7.02 – 6.96 (m, 12H). **^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm):** 152.4 (d, J = 259.7), 151.8, 145.5, 145.3 (d, *J* = 0.9 Hz), 143.1 (d, *J* = 11.2 Hz), 129.5, 129.4, 124.6, 124.0, 122.8, 122.7, 112.7, 109.0 (d, *J* = 3.4 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -121.3. **HRMS (ESI):** Calculated For $C_{44}H_{30}FN_5K^+$ $[M+K]^+$ 686.21168, found 686.20913. Spectroscopic data were in good agreement with literature.[13]

2,4,6-Tris(9H-carbazol-9-yl)-5-fluoroisophthalonitrile (3-CzFIPN).



(3-CzFIPN) was obtained following the general procedure, starting from 2,4,5,6-tetrafluoroisophthalonitrile (200.1 mg, 1.0 mmol) and carbazole (627 mg, 3.75 mmol), as a yellow solid (0.455 g, 71%); Rf (PE/EA 10:1) = 0.19; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.22 – 8.11 (m, 6H), 7.65 – 7.52 (m, 6H), 7.48 – 7.30 (m, 12H). **^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm):** 140.1, 139.8, 139.7, 139.2, 127.0, 126.9, 126.8, 126.7, 124.9, 124.8, 124.6, 124.5, 122.6, 122.3, 121.93, 121.4, 121.2, 121.1, 120.9, 110.0, 109.8, 109.2. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -111.1 (d, *J* = 2.8 Hz). **HRMS (FD+):** For $C_{44}H_{24}FN_5^{\bullet+}$ $[M]^{\bullet+}$ Calculated 641.20157, found 641.20207. Spectroscopic data were in good agreement with literature.[15]

6. General procedures for the oxidation of Oximes into cycloadduct.

6.1. Experimental Setup

Photochemical reactions were performed using a 456 nm blue LEDs (λ = 456 nm, 10 W, 12 V, 500 mA). The temperature was controlled through a ventilation system (35 +/- 2°C). Visible-Light Photocatalyzed Oxidations of Oximes were set up on bench-top in the open air and carried out in re-sealable Schlenk tubes with a balloon of air at ~3 cm distance from the two Kessil PR160L lamps (40 W, at 10% intensity, λ = 456 nm (± 15nm), 12 V, 500 mA) **(Figure ESI-2)**.

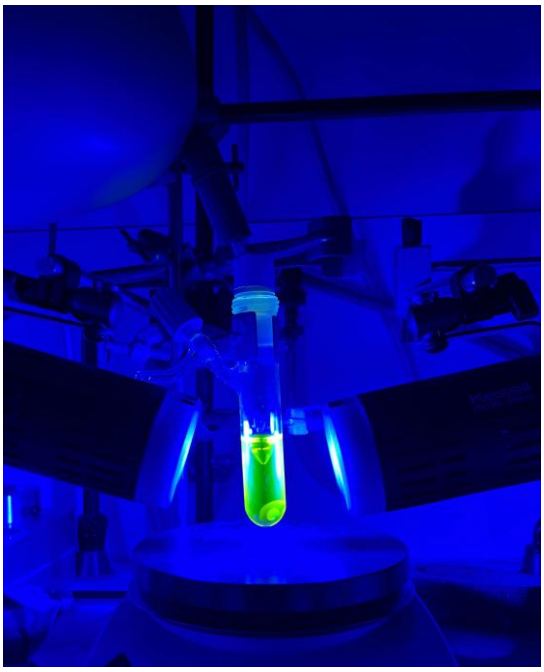
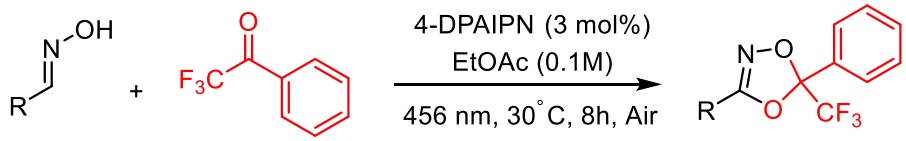


Figure ESI-2. Experimental Setup.

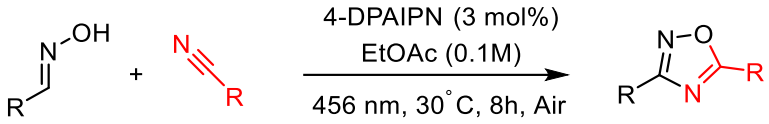
6.2. Synthesis of 1,4,2-dioxazole



The Oxime (1.00 mmol, 1 eq) and 4-DPAIPN (3% mole) were placed into a 20 mL re-sealable Schlenk tube equipped with a magnetic stirring bar and a Teflon septum, then 2,2,2-trifluoroacetophenone **2a** or ethyl glyoxylate **2b** (3.0 mmol, 3.0 eq) were placed into the tube. EtOAc (0.1M) was then added. An air balloon was then connected to the reactor septum via a needle (see Figure ESI-2 above). The reaction mixture was stirred vigorously for 5 minutes (sonicated if needed) then left under blue LED (456 nm) irradiation at 35°C (+/- 2°C). A fan was installed near the reactor to maintain the temperature inside the tube around this temperature. The reaction was monitored by TLC. Upon completion (8h), the reaction mixture was transferred to a round bottom flask and the solvent evaporated under reduced pressure. The residue was purified

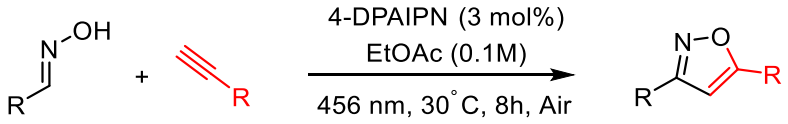
by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford the desired product as a colorless to pale yellow thick oil.

6.3. Synthesis of 1,2,4-oxadiazole



The Oxime (1.00 mmol, 1 eq) and 4-DPAIPN (3% mole) were placed into a 20 mL re-sealable Schlenk tube equipped with a magnetic stirring bar and a Teflon septum, then benzonitrile derivatives **4a-e** (3.0 mmol, 3.0 eq) were placed into the tube. EtOAc (0.1M) was then added. An air balloon was then connected to the reactor septum via a needle (see Figure ESI-2 above). The reaction mixture was stirred vigorously for 5 minutes (sonicated if needed) then left under blue LED (456 nm) irradiation at 35°C (+/- 2°C). A fan was installed near the reactor to maintain the temperature inside the tube around this temperature. The reaction was monitored by TLC. Upon completion (8h), the reaction mixture was transferred to a round bottom flask and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford the desired product as white solid. Recrystallization from petroleum ether if needed.

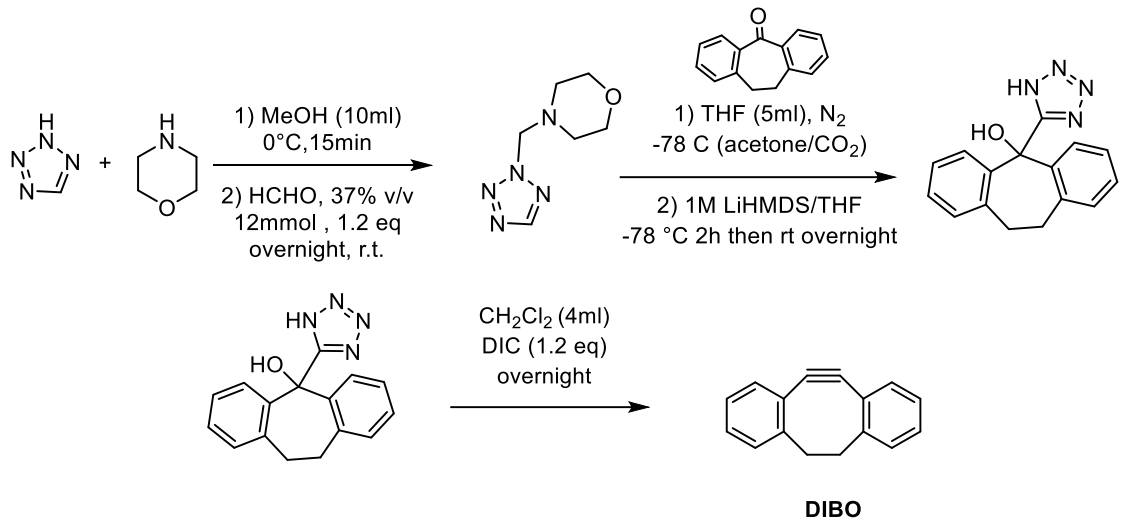
6.4. Synthesis of 1,2-Isoxazole



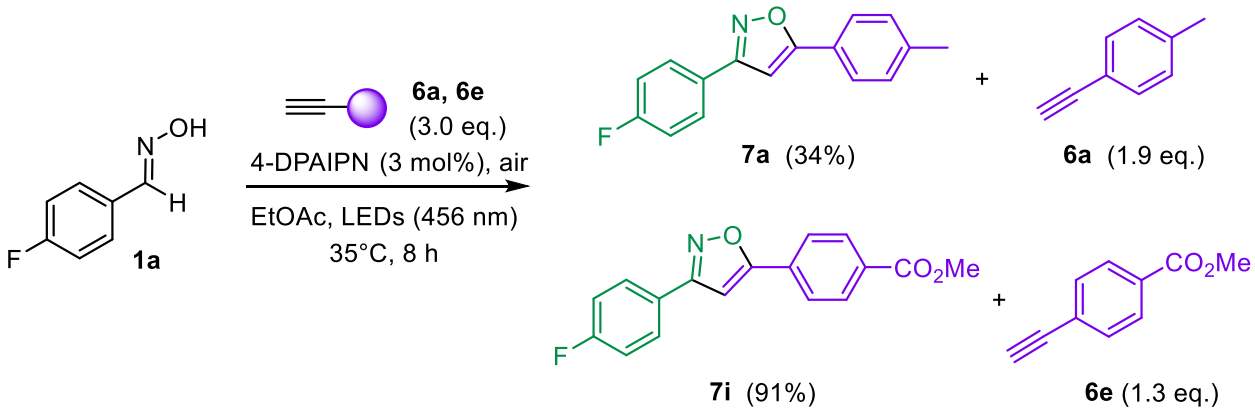
The Oxime (1.00 mmol, 1 eq) and 4-DPAIPN (3% mole) were placed into a 20 mL re-sealable Schlenk tube equipped with a magnetic stirring bar and a Teflon septum, then phenyl acetylene or alkyne derivatives **6a-h** (3.0 mmol, 3.0 eq) were placed into the tube. EtOAc (0.1M) was then added. An air balloon was then connected to the reactor septum via a needle (see Figure ESI-2 above). The reaction mixture was stirred vigorously for 5 minutes (sonicated if needed) then left under blue LED (456 nm) irradiation at 35°C (+/- 2°C). A fan was installed near the reactor to maintain the temperature inside the tube around this temperature. The reaction was monitored by TLC. Upon completion (8h), the reaction mixture was transferred to a round bottom flask and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford the desired product as white solid. Recrystallization from petroleum ether if needed.

6.5. Synthesis of DIBO (6h) as dipolarophile

Dibenzocyclooctyne (DIBO) were prepared starting from tetrazole and morpholine then by adding dibenzosuberone according to reported literature.[16] The final product was obtained in 54% (47% over 3 steps), mp = 86°C.



6.6. Tentative recovery of excess alkyne

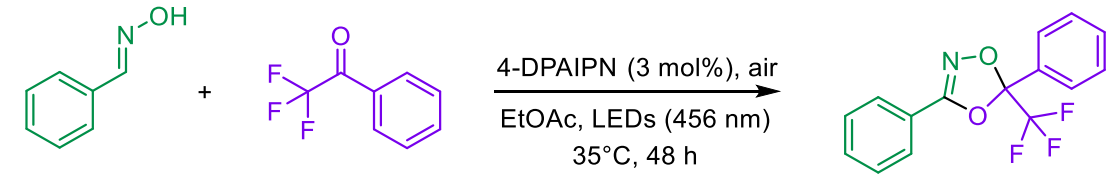


Alkynes **6a** and **6e** were recovered from the photocatalyzed oxidation of oxime **1a** during synthesis of **7a** and **7i**, respectively, as follows: following the general procedure, starting from oxime **1a** (139.13 mg, 1.0 mmol, 1 eq), 4-DPAIPN (3 mol%) and alkyne **6a** or **6e** (3.0 mmol, 3.0 eq) in EtOAc (0.1 M). After completion of the reaction, the mixture was transferred to a round bottom flask. Solvent were distilled off and the residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford the desired products as white solids in reliable

[16] Dones, J. M.; Abularrage, N. S.; Khanal, N.; Gold, B.; Raines, R. T., Acceleration of 1, 3-dipolar cycloadditions by integration of strain and electronic tuning. *J. Am. Chem. Soc.* **2021,** *143*, 9489-9497.

yields (see Scheme 3). Excess alkyne was recovered in each case, respectively **6a** (223 mg, 64%, 1.9 eq.) as a pale-yellow liquid; Rf (PE:EA / 10:1) = 0.89), and **6e** (215 mg, 45%, 1.3 eq.) as pale-yellow solid; Rf (PE:EA / 10:1) = 0.73. Both were obtained in purity allowing their reuse without further purifications.

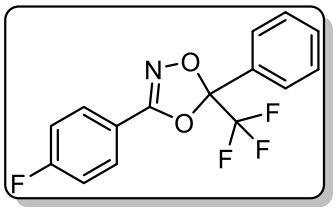
6.7. Large scale synthesis and recovery of the solvent



1g (10 mmol) **2a** (3.0 eq.) **3g** (72%)

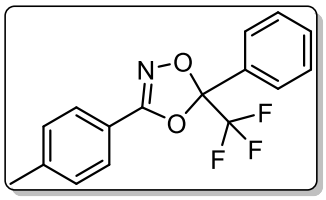
3,5-Diphenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3g). 3g was obtained following the general procedure after 48h, from oxime **1g** (1.211 g, 10.0 mmol) and ketone **2a** (5.224 g, 30.0 mmol, 3.0 eq.). The Oxime **1g** (1.211 g, 10.0 mmol, 1.0 eq.) and 4-DPAIPN (3 mol%) were placed into a 100 mL re-sealable Schlenk tube equipped with a magnetic stirring bar and a Teflon septum, then 2,2,2-trifluoroacetophenone **2a** (5.224 g, 30.0 mmol, 3.0 eq.) and EtOAc (100 mL, 0.1 M) were then added into the tube. An air balloon was then connected to the reactor septum via a needle. The reaction mixture was sonicated and stirred vigorously for 5 minutes then left under blue LED (456 nm) irradiation at 35°C (+/- 2°C). A fan was installed near the reactor to maintain the temperature inside the tube around this temperature. The reaction was monitored by TLC. Upon completion (48h), the reaction mixture was transferred to a round bottom flask. EtOAc was distilled off using simple distillation apparatus and collected (84 mL, 84% recovery by volume). The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford **3g** as a pale yellow thick oil (2.097 g, 72%). Spectroscopic data were in good agreement with those obtained on 1 mmol scale.

6.8. Characterization of the synthesized Heterocycles



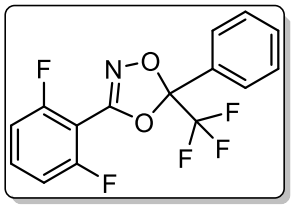
3-(4-Fluorophenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3a). 3a was obtained following the general procedure, from oxime **1a** (139.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a pale yellow thick oil (252 mg, 81%); Rf (PE/EA 10:1) = 0.42; **IR (neat)** υ_{max} **(cm^{-1})**: 3073, 1905, 1638, 1607, 1514, 1350, 1241, 1196, 1085, 959.8, 842.5, 724.6, 695.7, 667.1, 509.5. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 7.91 – 7.83 (m, 2H), 7.73 – 7.67 (m, 2H), 7.53 – 7.44 (m, 3H), 7.21 – 7.12 (m, 2H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 165.2 (d, J = 254.2 Hz),

158.1, 131.3, 131.0, 129.6, 128.7, 126.5 (d, J = 1.4 Hz), 121.4 (q, J = 288.9 Hz), 117.7 (d, J = 3.4 Hz), 116.4 (d, J = 22.5 Hz), 109.3 (q, J = 34.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2, -105.6. **HRMS (EI+):** Calculated for $C_{15}H_9F_4NO_2^{\bullet+}$ $[M]^{\bullet+}$ 311.05639, found 311.05626.



5-Phenyl-3-(p-tolyl)-5-(trifluoromethyl)-1,4,2-dioxazole (3b). 3b was obtained following the general procedure, from oxime **1b** (135.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a pale yellow thick oil (237 mg, 77%); Rf (PE/EA 10:1) = 0.84; **IR (neat) υ_{max} (cm^{-1}):** 2925, 1740, 1633, 1453, 1349, 1275, 1194, 1085, 1033, 959.2, 821.5, 724.1, 695.8, 667.8, 491.9. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.81 – 7.68 (m, 4H), 7.53 – 7.45 (m, 3H), 7.31 – 7.24 (m, 2H), 2.42 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 158.9, 143.1, 131.6, 130.9, 129.7, 128.7, 127.2, 126.5 (d, J = 1.4 Hz), 121.5 (q, J = 288.9 Hz), 118.5, 109.2 (q, J = 34.3 Hz), 21.8. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2. **HRMS (EI+):** Calculated for $C_{16}H_{12}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 307.08146, found 307.08104.

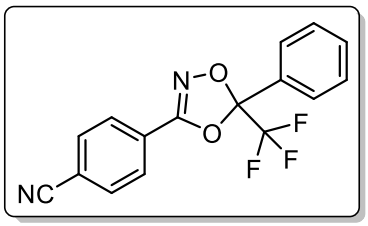
3-(2,6-Difluorophenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3c). 3c was obtained following the general procedure, from oxime **1c** (157.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a pale yellow thick oil (240 mg, 73%); Rf (PE/EA 10:1) = 0.51; **IR (neat) υ_{max} (cm^{-1}):** 3074, 2927, 1621, 1589, 1488, 1472, 1337, 1302, 1243, 1196, 1086, 1014, 959.8, 857, 790.7, 723.4, 584. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.74 – 7.65 (m, 2H), 7.58 – 7.44 (m, 4H), 7.11 – 6.99 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 161.1 (dd, J = 260.1, 4.9 Hz), 152.0, 134.4 (t, J = 10.4 Hz), 131.1, 131.0, 128.7, 126.5, 121.4 (q, J = 288.9 Hz), 112.5 (dd, J = 21.2, 3.5 Hz), 109.2 (q, J = 34.7 Hz), 100.3 (t, J = 16.8 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.4, -105.6. **HRMS (EI+):** Calculated for $C_{15}H_8F_5NO_2^{\bullet+}$ $[M]^{\bullet+}$ 329.04752, found 329.04772.



3-(3-Fluorophenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3d). 3d was obtained following the general procedure, from oxime **1d** (139.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a pale yellow thick oil (261 mg, 84%); Rf (PE/EA 10:1) = 0.45; **IR (neat) υ_{max} (cm^{-1}):** 3701, 3076, 1884, 1587, 1495, 1457, 1344, 1198, 1082, 961.2, 839.1, 724.8, 691.7, 603.8, 529.5. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.74 – 7.64 (m, 3H), 7.59 – 7.42 (m, 5H), 7.25 (tdd, J = 8.4, 2.6, 1.0 Hz, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 162.7 (d, J = 248.0 Hz),

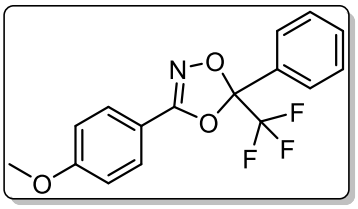
158.0 (d, *J* = 3.1 Hz), 131.2, 131.1, 130.9 (d, *J* = 8.0 Hz), 128.8, 126.5 (d, *J* = 1.4 Hz), 123.3 (d, *J* = 8.4 Hz), 123.0 (d, *J* = 3.2 Hz), 121.4 (q, *J* = 288.9 Hz), 119.5 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 24.3 Hz), 109.6 (q, *J* = 34.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.24, -110.92 (td, *J* = 8.7, 5.5 Hz). **HRMS (EI+):** Calculated for $C_{15}H_9F_4NO_2^{\bullet+}$ $[M]^{\bullet+}$ 311.05694, found 311.05705.

4-(5-Phenyl-5-(trifluoromethyl)-1,4,2-dioxazol-3-yl)benzonitrile (3e). 3e was obtained



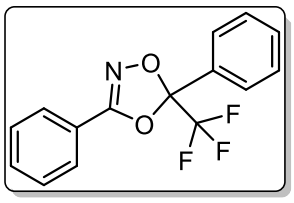
following the general procedure, from oxime **1e** (146.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a white solid (283 mg, 89%); mp = (93℃, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.56; **IR (neat) υ_{max} (cm^{-1}):** 3070, 2233, 1892, 1632, 1411, 1353, 1279, 1196, 1085, 1033, 959.2, 846.4, 724.7, 696.1, 666.8, 548.1. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.97 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.76 (dd, *J* = 8.4, 1.7 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.57 – 7.44 (m, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 157.6, 132.7, 131.2, 130.7, 128.8, 127.7, 126.4, 125.5, 121.2 (q, *J* = 288.5 Hz), 117.8, 115.9, 110.0 (q, *J* = 34.7 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.3. **HRMS (EI+):** Calculated for $C_{16}H_9F_3N_2O_2^{\bullet+}$ $[M]^{\bullet+}$ 318.06106, found 318.06055.

3-(4-Methoxyphenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3f). 3f was obtained



following the general procedure, from oxime **1f** (151.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as a brown thick oil (284 mg, 88%); Rf (PE/EA 10:1) = 0.64; **IR (neat) υ_{max} (cm^{-1}):** 3683, 2963, 2054, 1633, 1610, 1516, 1425, 1353, 1309, 1262, 1191, 1086, 1031, 959.3, 837.2, 724.4, 695.9, 667.8, 518.9. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.83 – 7.76 (m, 2H), 7.74 – 7.67 (m, 2H), 7.52 – 7.44 (m, 3H), 6.99 – 6.93 (m, 2H), 3.86 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 162.9, 158.7, 131.6, 130.9, 129.1, 128.7, 126.6 (d, *J* = 1.4 Hz), 121.5 (q, *J* = 288.7 Hz), 114.5, 113.5, 108.8 (q, *J* = 34.0 Hz), 55.6. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2. **HRMS (ESI):** Calculated for $C_{16}H_{13}F_3NO_3$ $[M+H]^+$ 324.08420, found 324.08367.

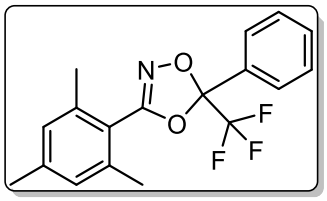
3,5-Diphenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3g). 3g was obtained following the general



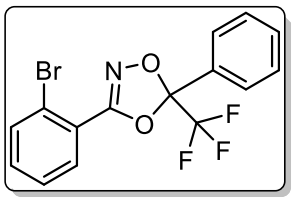
procedure, from oxime **1g** (121.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (270 mg, 92%); Rf (PE/EA 10:1) = 0.86; **IR (neat) υ_{max} (cm^{-1}):** 3068, 2928, 1893, 1635, 1498, 1452, 1353, 1195, 1085, 1032, 960.3, 860, 765.9, 725.6, 689.3, 666.3, 600, 499.4. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.92 – 7.85 (m, 2H), 7.74 (dd, *J* = 7.6, 2.2 Hz, 2H), 7.59 –

7.44 (m, 6H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 158.8, 132.4, 131.5, 131.0, 129.0, 128.7, 127.2, 126.5 (d, *J* = 1.4 Hz), 121.5 (q, *J* = 288.9 Hz), 121.4, 109.2 (q, *J* = 34.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2. **HRMS (EI+):** Calculated for $C_{15}H_{10}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 293.06581, found 293.06630.

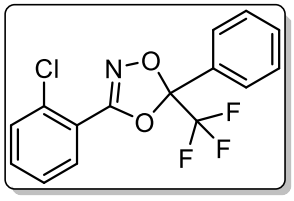
3-Mesityl-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3h). 3h was obtained following the general procedure, from oxime **1h** (163.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (248 mg, 74%); Rf (PE/EA 10:1) = 0.74; **IR (neat) υ_{max} (cm^{-1}):** 2923, 1639, 1612, 1452, 1314, 1186, 1075, 1030, 1019, 957, 909, 722, 694, 663. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.75 (dt, *J* = 7.7, 1.8 Hz, 2H), 7.60 – 7.46 (m, 3H), 6.98 (s, 2H), 2.36 (s, 9H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 157.7, 141.7, 139.0, 131.9, 130.9, 128.9, 128.7, 126.5 (d, *J* = 1.3 Hz), 121.6 (q, *J* = 288.2 Hz), 117.6, 108.7 (q, *J* = 34.3 Hz), 21.3, 19.8. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -82.8. **HRMS (EI+):** Calculated for $C_{18}H_{16}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 335.11331, found 335.11353.



3-(2-Bromophenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3i). 3i was obtained following the general procedure, from oxime **1i** (200.0 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (294 mg, 79%); Rf (PE/EA 10:1) = 0.67; **IR (neat) υ_{max} (cm^{-1}):** 3070, 1963, 1620, 1453, 1332, 1273, 1194, 1075, 958.9, 761.3, 727.2, 666.8, 501.3. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.78 – 7.70 (m, 4H), 7.53 – 7.45 (m, 3H), 7.45 – 7.33 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 158.0, 134.7, 133.1, 131.5, 131.2, 131.0, 128.7, 127.6, 126.6 (d, *J* = 1.3 Hz), 122.8, 122.2, 121.4 (q, *J* = 288.9 Hz), 109.2 (q, *J* = 34.5 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2. **HRMS (EI+):** Calculated for $C_{15}H_9BrF_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 370.97633, found 370.97519.

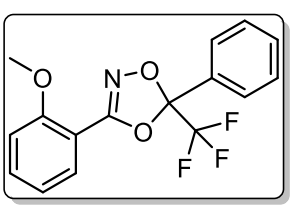


3-(2-Chlorophenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3j). 3j was obtained following the general procedure, from oxime **1j** (155.6 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (275 mg, 84%); Rf (PE/EA 10:1) = 0.68; **IR (neat) υ_{max} (cm^{-1}):** 3071, 1964, 1817, 1621, 1594, 1454, 1335, 1276, 1195, 1076, 959.5, 853.9, 761.5, 722.8, 695.4, 666.8, 601.1, 501.6. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.81 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.73 (dd, *J* = 7.7, 2.1 Hz, 2H), 7.56 – 7.43 (m, 5H), 7.38 (td, *J* = 7.4, 1.6 Hz, 1H). **^{13}C NMR (76 MHz,**

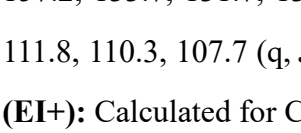


$CDCl_3$) δ (ppm): 157.5, 133.9, 133.0, 131.4, 131.2, 131.0, 128.7, 127.1, 126.6 (d, *J* = 1.0 Hz), 121.4 (q, *J* = 288.9 Hz), 120.7, 109.0 (q, *J* = 34.3 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.2. **HRMS (EI+):** Calculated for $C_{15}H_9ClF_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 327.02684, found 327.02699.

3-(2-Methoxyphenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3k). 3k was obtained following the general procedure, from oxime **1k** (151.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (268 mg, 83%); Rf (PE/EA 10:1) = 0.41; **IR (neat) υ_{max} (cm^{-1}):** 3072, 2943, 2842, 1602, 1499, 1284, 1192, 1083, 1024, 959.5, 758.6, 724.7, 696.3, 501. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.78 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.76 – 7.67 (m, 2H), 7.54 – 7.43 (m, 4H), 7.09 – 7.00 (m, 2H), 3.95 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 158.5, 157.2, 133.7, 131.7, 130.8, 130.1, 128.6, 126.6 (d, *J* = 1.4 Hz), 121.6 (q, *J* = 288.9 Hz), 120.6, 111.8, 110.3, 107.7 (q, *J* = 34.1 Hz), 56.1. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -83.1. **HRMS (EI+):** Calculated for $C_{16}H_{12}F_3NO_3^{\bullet+}$ $[M]^{\bullet+}$ 323.07638, found 323.07644.



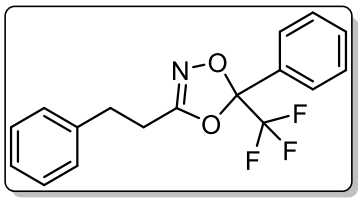
Ethyl 3-(4-fluorophenyl)-1,4,2-dioxazole-5-carboxylate (3l). 3l was obtained following the general procedure, from oxime **1a** (151.2 mg, 1.0 mmol) and ethyl glyoxylate **2b** (306.3 mg, 3.0 mmol), as pale yellow thick oil (170 mg, 71%); Rf (PE/EA 10:1) = 0.47; **IR (neat) υ_{max} (cm^{-1}):** 2987, 1746, 1604, 1510, 1416, 1356, 1220, 1157, 1089, 1012, 840, 609. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.87 – 7.79 (m, 2H), 7.17 – 7.09 (m, 2H), 6.25 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 165.4, 165.1 (d, *J* = 253.5 Hz), 158.4, 129.7 (d, *J* = 9.0 Hz), 118.1 (d, *J* = 3.4 Hz), 116.3 (d, *J* = 22.4 Hz), 101.0, 62.7, 14.1. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -106.1. **HRMS (EI+):** Calculated for $C_{11}H_{10}FNO_4^{\bullet+}$ $[M]^{\bullet+}$ 239.05884, found 239.05941.



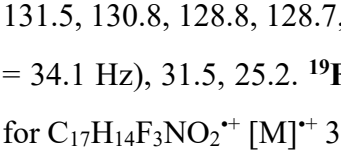
3-Cyclohexyl-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3o). 3o was obtained following the general procedure, from oxime **1o** (127.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (170 mg, 57%); Rf (PE/EA 10:1) = 0.78; **IR (neat) υ_{max} (cm^{-1}):** 2933, 2857, 1758, 1649, 1563, 1452, 1181, 1076, 959, 761, 721, 694, 664. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.63 – 7.56 (m, 2H), 7.51 – 7.40 (m, 3H), 2.53 (tt, *J* = 11.1, 3.6 Hz, 1H), 2.03 – 1.06 (m, 10H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 163.7, 131.7, 130.7, 128.6, 126.5 (d, *J* = 1.4 Hz),

121.5 (q, *J* = 289.2 Hz), 110.6, 108.1 (q, *J* = 33.9 Hz), 33.6, 29.1, 28.9, 25.6, 25.3. **^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm):** -83.6. **HRMS (EI+):** Calculated for $C_{15}H_{16}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 299.11276, found 299.11320.

3-Phenethyl-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (3p). 3p was obtained following the general procedure, from oxime **1p** (149.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (228 mg, 71%); Rf (PE/EA 10:1) = 0.74; **IR (neat) υ_{max} (cm^{-1}):** 3066.3, 3030.6, 1653.7, 1497.5, 1454.1, 1180.2, 1076.1, 1053.9, 959.4, 724.1, 695.2. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 7.65 – 7.58 (m, 2H), 7.55 – 7.43 (m, 3H), 7.35 – 7.16 (m, 5H), 3.05 – 2.97 (m, 2H), 2.82 – 2.74 (m, 2H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 160.2, 139.2, 131.5, 130.8, 128.8, 128.7, 128.4, 126.9, 126.5 (d, *J* = 1.4 Hz), 121.4 (q, *J* = 288.9 Hz), 108.6 (q, *J* = 34.1 Hz), 31.5, 25.2. **^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm):** -83.4. **HRMS (EI+):** Calculated for $C_{17}H_{14}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 321.09711, found 321.09870.



5-Phenyl-3-propyl-5-(trifluoromethyl)-1,4,2-dioxazole (3q). 3q was obtained following the general procedure, from oxime **1q** (87.1 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as pale yellow thick oil (171 mg, 66%); Rf (PE/EA 10:1) = 0.83; **IR (neat) υ_{max} (cm^{-1}):** 2970, 2879, 1749, 1654, 1563, 1454, 1296, 1265, 1182, 1076, 959, 762, 723, 695, 664. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 7.63 – 7.57 (m, 2H), 7.50 – 7.41 (m, 3H), 2.43 (td, *J* = 7.3, 1.1 Hz, 2H), 1.72 (h, *J* = 7.3 Hz, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 160.7, 131.7, 130.8, 128.6, 126.5 (d, *J* = 1.4 Hz), 121.5 (q, *J* = 289.0 Hz), 108.3 (q, *J* = 34.0 Hz), 25.1, 18.9, 13.4. **^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm):** -83.6. **HRMS (EI+):** Calculated for $C_{12}H_{12}F_3NO_2^{\bullet+}$ $[M]^{\bullet+}$ 259.08146, found 259.08126.



3-(4-Fluoro-2,6-dimethylphenyl)-5-phenyl-5-(trifluoromethyl)-1,4,2-dioxazole (20). 20 was obtained following the general procedure, from oxime **18** (167.2 mg, 1.0 mmol) and ketone **2a** (522.4 mg, 3.0 mmol), as colorless thick oil (244 mg, 72%); Rf (PE/EA 10:1) = 0.86; **IR (neat) υ_{max} (cm^{-1}):** 3073, 2981, 2929, 1597, 1481, 1452, 1321, 1268, 1185, 1075, 1020, 957, 861, 761, 722, 664, 603. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 7.73 – 7.63 (m, 2H), 7.57 – 7.45 (m, 3H), 6.83 (d, *J* = 9.2 Hz, 2H), 2.33 (s, 6H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 164.2 (d, *J* = 251.4 Hz), 157.0, 142.3 (d, *J* = 9.1 Hz), 131.7, 131.0, 128.8, 126.5 (d, *J* = 1.2 Hz), 121.5 (q, *J* =

288.2 Hz), 116.7 (d, *J* = 2.9 Hz), 115.1 (d, *J* = 21.7 Hz), 109.0 (q, *J* = 34.3 Hz), 20.1 (d, *J* = 1.6 Hz). **^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm):** -82.87, -109.33 (t, *J* = 9.3 Hz). **HRMS (CI+):** Calculated for $C_{17}H_{14}F_4NO_2^+$ $[M+H]^+$ 340.09607, found 340.09670.

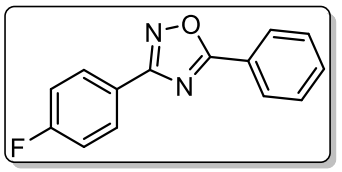
3-(2,6-Difluorophenyl)-5-phenyl-1,2,4-oxadiazole (5a). 5a was obtained following the general procedure, from oxime **1c** (157.1 mg, 1.0 mmol) and benzonitrile **4a** (309.4 mg, 3.0 mmol), as white solid (224 mg, 87%); mp = (91 – 92°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.58; **IR (neat) υ_{max} (cm^{-1}):** 3094, 3072, 1633, 1590, 1558, 1469, 1452, 1354, 1271, 1237, 1131, 1005, 923, 785, 716, 683, 583, 534, 509. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 8.26 – 8.16 (m, 2H), 7.65 – 7.43 (m, 4H), 7.12 – 7.02 (m, 2H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 176.1, 161.7 (t, *J* = 2.5 Hz), 161.2 (dd, *J* = 256.5, 5.9 Hz), 133.1, 132.8 (t, *J* = 10.4 Hz), 129.3, 128.4, 124.0, 112.2 (dd, *J* = 22.3, 2.9 Hz), 106.0 (t, *J* = 17.5 Hz). **^{19}F NMR (282 MHz, CDCl$_3$) δ (ppm):** -109.1 (t, *J* = 7.2 Hz). **HRMS (ESI):** Calculated for $C_{14}H_9F_2N_2O^+$ $[M+H]^+$ 259.06775, found 259.06744.

4-(5-Phenyl-1,2,4-oxadiazol-3-yl)benzonitrile (5b). 5b was obtained following the general procedure, from oxime **1e** (146.2 mg, 1.0 mmol) and benzonitrile **4a** (309.4 mg, 3.0 mmol), as pale yellow solid (192 mg, 78%); mp = (167°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.54; **IR (neat) υ_{max} (cm^{-1}):** 3062, 2227, 1608, 1553, 1490, 1448, 1412, 1355, 1275, 1134, 1068, 916, 844, 746, 715, 679, 547. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 8.33 – 8.28 (m, 2H), 8.25 – 8.19 (m, 2H), 7.84 – 7.78 (m, 2H), 7.68 – 7.54 (m, 3H). **^{13}C NMR (76 MHz, CDCl$_3$) δ (ppm):** 176.5, 167.8, 133.3, 132.8, 131.3, 129.4, 128.4, 128.2, 124.0, 118.4, 114.9. **HRMS (EI+):** Calculated for $C_{15}H_9N_3O^{\bullet+}$ $[M]^{\bullet+}$ 247.07401, found 247.07547.

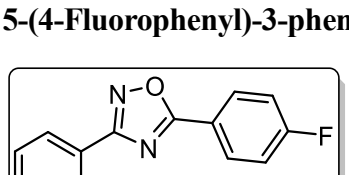
5-Phenyl-3-(p-tolyl)-1,2,4-oxadiazole (5c). 5c was obtained following the general procedure, from oxime **1b** (135.2 mg, 1.0 mmol) and benzonitrile **4a** (309.4 mg, 3.0 mmol), as white solid (170 mg, 72%); mp = (84 – 86°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.66; **IR (neat) υ_{max} (cm^{-1}):** 3030, 2919, 1681, 1608, 1559, 1490, 1447, 1410, 1354, 1275, 1179, 1132, 1067, 1022, 964, 904, 826, 737, 687, 476. **^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm):** 8.28 – 8.16 (m, 2H), 8.10 – 8.04 (m, 2H), 7.64 – 7.51 (m, 3H), 7.34 – 7.29 (m, 2H), 2.43 (s, 3H). **^{13}C NMR (76 MHz,**

$CDCl_3$) δ (ppm): 175.7, 169.1, 141.6, 132.8, 129.7, 129.2, 128.3, 127.6, 124.5, 124.3, 21.7. **HRMS (ESI):** Calculated for $C_{15}H_{13}N_2O^+$ $[M+H]^+$ 237.10224, found 237.10205.

3-(4-Fluorophenyl)-5-phenyl-1,2,4-oxadiazole (5d). 5d was obtained following the general procedure, from oxime **1a** (139.1 mg, 1.0 mmol) and benzonitrile **4a** (309.4 mg, 3.0 mmol), as white solid (182 mg, 76%); mp = (122 – 124°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.81; **IR (neat) υ_{max} (cm^{-1}):** 3061, 1604, 1560, 1491, 1449, 1416, 1354, 1280, 1217, 1157, 1134, 904, 839, 743, 685, 610, 514. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.25 – 8.14 (m, 4H), 7.66 – 7.48 (m, 3H), 7.25 – 7.15 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 175.9, 168.3, 164.7 (d, J = 251.4 Hz), 132.9, 129.8 (d, J = 8.7 Hz), 129.3, 128.3, 124.4, 123.4 (d, J = 3.1 Hz), 116.2 (d, J = 21.8 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -108.5 (ddd, J = 13.8, 8.8, 5.3 Hz). **HRMS (EI+):** Calculated for $C_{14}H_9FN_2O^{\bullet+}$ $[M]^{\bullet+}$ 240.06934, found 240.06968.



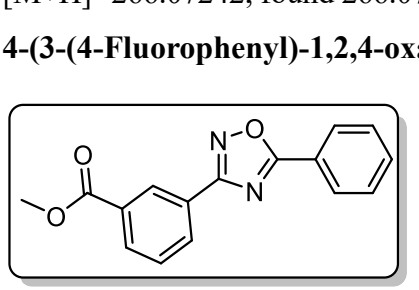
5-(4-Fluorophenyl)-3-phenyl-1,2,4-oxadiazole (5e). 5e was obtained following the general procedure, from oxime **1g** (121.1 mg, 1.0 mmol) and 4-fluorobenzonitrile **4b** (363.3 mg, 3.0 mmol), as white crystals **(**185 mg, 77%); mp = (110 – 111°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.59; **IR (neat) υ_{max} (cm^{-1}):** 1600, 1471, 1415, 1361, 1281, 1222, 1135, 1078, 897, 842, 746, 685, 615, 513. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.27 – 8.20 (m, 2H), 8.20 – 8.14 (m, 2H), 7.62 – 7.42 (m, 4H), 7.25 (t, J = 8.7 Hz, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 174.9, 169.1, 165.6 (d, J = 254.9 Hz), 131.4, 130.7 (d, J = 9.0 Hz), 129.0, 127.6, 127.0, 120.8 (d, J = 3.1 Hz), 116.6 (d, J = 22.2 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -105.1 (tt, J = 9.0, 5.4 Hz). **HRMS (EI+):** Calculated for $C_{14}H_9FN_2O^{\bullet+}$ $[M]^{\bullet+}$ 240.06934, found 240.06991.



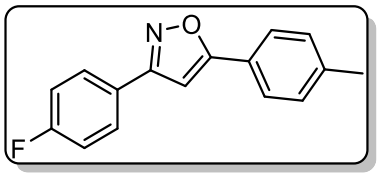
4-(3-(4-Fluorophenyl)-1,2,4-oxadiazol-5-yl)benzonitrile (5f). 5f was obtained following the general procedure, from oxime **1a** (139.1 mg, 1.0 mmol) and terephthalonitrile **4c** (384.4 mg, 3.0 mmol), as white crystals **(**177 mg, 67%); mp = (201 – 202°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.57; **IR (neat) υ_{max} (cm^{-1}):** 3094, 2962, 2233, 1605, 1554, 1497, 1410, 1350, 1222, 1157, 1019, 908, 839, 757, 625, 548, 512. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.33 (d, J = 8.0 Hz, 2H), 8.17 (dd, J = 8.6, 5.3 Hz, 2H), 7.86 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 8.6 Hz, 2H). **^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm):** 8.38 – 8.27 (m, 2H), 8.22 – 8.13 (m, 2H), 7.92 – 7.83 (m, 2H), 7.28 – 7.19 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 174.1, 168.6, 164.9 (d, J = 252.1 Hz), 133.1, 129.9 (d, J = 8.7 Hz), 128.8, 128.0, 122.8 (d, J = 3.1 Hz), 117.8, 116.4, 116.3 (d, J = 22.2 Hz). **^{13}C NMR (76 MHz, CD_2Cl_2) δ (ppm):** 174.6, 168.9, 165.2 (d, J = 251.4 Hz), 133.4, 133.2, 130.1 (d, J = 9.0 Hz), 129.0, 128.2, 123.3 (d, J = 3.5 Hz), 118.2,

116.5 (d, *J* = 22.2 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -107.74 (p, *J* = 7.1 Hz). **^{19}F NMR (282 MHz, CD_2Cl_2) δ (ppm):** -108.7 (td, *J* = 8.7, 4.6 Hz). **HRMS (CI^+):** Calculated for $C_{15}H_9FN_3O^+$ $[M+H]^+$ 266.07242, found 266.07319.

4-(3-(4-Fluorophenyl)-1,2,4-oxadiazol-5-yl)benzonitrile (5g). 5g was obtained following the general procedure, from oxime **1r** (179.2 mg, 1.0 mmol) and benzonitrile **4a** (309.4 mg, 3.0 mmol), as white crystals **(**205 mg, 73%); mp = (115℃, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.47; **IR (neat) υ_{max} (cm^{-1}):** 3071, 2958, 1726, 1609, 1562, 1434, 1369, 1288, 1257, 1143, 1105, 726, 682. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.84 (t, *J* = 1.8 Hz, 1H), 8.36 (dt, *J* = 7.8, 1.5 Hz, 1H), 8.21 (ddt, *J* = 10.7, 7.8, 1.5 Hz, 3H), 7.65 – 7.52 (m, 4H), 3.97 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 176.1, 168.4, 166.5, 133.0, 132.3, 131.8, 131.1, 129.3, 129.2, 128.8, 128.4, 127.6, 124.3, 52.5. **HRMS (ESI):** Calculated for $C_{16}H_{12}N_2O_3Na^+$ $[M+Na]^+$ 303.07456 found 303.07444.



3-(4-Fluorophenyl)-5-(p-tolyl)isoxazole (7a). 7a was obtained following the general procedure, from oxime **1a** (139.2 mg, 1.0 mmol) and 1-ethynyl-4-methylbenzene **6a** (348.5 mg, 3.0 mmol), as white solid **(**86 mg, 34%); mp = (171 – 172℃, recrystallized from petroleum ether); Rf (PE/EA 0:1) = 0.63; **IR (neat) υ_{max} (cm^{-1}):** 3108, 2922, 1603, 1505, 1433, 1382, 1217, 1157, 1099, 948, 917, 842, 807, 638, 585, 531, 478. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.91 – 7.79 (m, 2H), 7.75 – 7.70 (m, 2H), 7.32 – 7.28 (m, 2H), 7.21 – 7.13 (m, 2H), 6.74 (s, 1H), 2.42 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 170.9, 140.8, 129.9, 128.9, 128.8, 125.9, 124.8, 116.3, 116.0, 96.9, 21.7. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -110.7 (tt, *J* = 8.9, 5.3 Hz). **HRMS (ESI):** Calculated for $C_{16}H_{13}FNO^+$ $[M+H]^+$ 254.09757, found 254.09749.



3,5-Bis(4-fluorophenyl)isoxazole (7b). 7b was obtained following the general procedure, from oxime **1a** (139.2 mg, 1.0 mmol) and 1-ethynyl-4-fluorobenzene **6b** (360.4 mg, 3.0 mmol), as white crystals **(**211 mg, 82%); mp = (198℃, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.48; **IR (neat) υ_{max} (cm^{-1}):** 3110, 1598, 1501, 1432, 1383, 1229, 1159, 1098, 947, 919, 841, 808, 638, 533. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.89 – 7.78 (m, 4H), 7.23 – 7.13 (m, 4H), 6.74 (s, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.8, 165.7, 162.3, 128.9 (d, *J* = 8.3 Hz), 128.1 (d, *J* = 8.3 Hz), 125.4 (d, *J* = 3.5 Hz), 123.9 (d, *J* = 3.0 Hz), 116.5 (d,

J = 15.6 Hz), 116.2 (d, *J* = 15.6 Hz), 97.3. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -109.2 (tt, *J* = 9.2, 5.3 Hz), -110.4 (td, *J* = 9.2, 4.7 Hz). **HRMS (FI):** Calculated for $C_{15}H_9F_2NO^{\bullet+}$ $[M]^{\bullet+}$ 257.06467, found 257.06459.

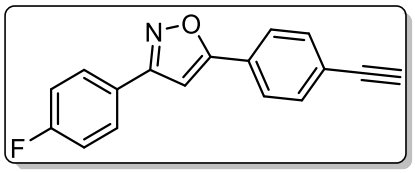
5-(4-Fluorophenyl)-3-(p-tolyl)isoxazole (7c). 7c was obtained following the general procedure, from oxime **1b** (135.2 mg, 1.0 mmol) and 1-ethynyl-4-fluorobenzene **6b** (360.4 mg, 3.0 mmol), as white crystals **(**206 mg, 81%); mp = (178 – 179°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.45; **IR (neat) υ_{max} (cm^{-1}):** 3110, 3022, 2925, 2866, 1614, 1599, 1501, 1217, 1157, 947, 913, 840, 807, 723, 636, 528. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.86 – 7.78 (m, 2H), 7.78 – 7.72 (m, 2H), 7.32 – 7.25 (m, 2H), 7.22 – 7.13 (m, 2H), 6.75 (s, 1H), 2.42 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.4, 163.9 (d, *J* = 251.2 Hz), 163.2, 140.4, 129.8, 128.0 (d, *J* = 8.6 Hz), 126.8, 126.3, 124.1 (d, *J* = 3.5 Hz), 116.3 (d, *J* = 22.2 Hz), 97.4, 21.6. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -109.6 (td, *J* = 8.5, 4.2 Hz). **HRMS (FI):** Calculated for $C_{16}H_{12}FNO^{\bullet+}$ $[M]^{\bullet+}$ 253.08974, found 253.09079.

4-(5-(4-Fluorophenyl)isoxazol-3-yl)benzonitrile (7d). 7d was obtained following the general procedure, from oxime **1e** (146.2 mg, 1.0 mmol) and 1-ethynyl-4-fluorobenzene **6b** (360.4 mg, 3.0 mmol), as white crystals **(**194 mg, 73%); mp = (176 – 179°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.38; **IR (neat) υ_{max} (cm^{-1}):** 3069, 2235, 1613, 1500, 1431, 1223, 1156, 948, 920, 838, 792, 621, 552, 517. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.00 – 7.94 (m, 2H), 7.86 – 7.80 (m, 2H), 7.80 – 7.74 (m, 2H), 7.24 – 7.14 (m, 2H), 6.81 (s, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 170.5, 164.1 (d, *J* = 252.1 Hz), 161.7, 133.4, 132.9, 128.1 (d, *J* = 8.3 Hz), 127.5, 123.5 (d, *J* = 3.5 Hz), 118.4, 116.5 (d, *J* = 22.2 Hz), 113.8, 97.3 (d, *J* = 1.4 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -108.58 (tt, *J* = 8.6, 4.9 Hz). **HRMS (FI):** Calculated for $C_{16}H_9FN_2O^{\bullet+}$ $[M]^{\bullet+}$ 264.06934, found 264.06962.

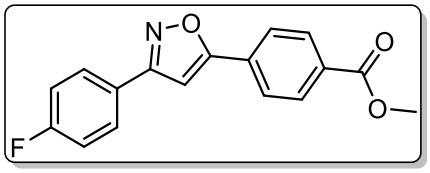
5-(4-Fluorophenyl)-3-phenylisoxazole (7e). 7e was obtained following the general procedure, from oxime **1g** (121.1 mg, 1.0 mmol) and 1-ethynyl-4-fluorobenzene **6b** (360.4 mg, 3.0 mmol), as white crystals **(**208 mg, 88%); mp = (173°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.52; **IR (neat) υ_{max} (cm^{-1}):** 3109, 3060, 1614, 1600, 1496, 1459, 1224, 1157, 1089, 948, 918, 841, 812, 767, 694, 529. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.89 – 7.79 (m, 4H), 7.53 – 7.44 (m, 3H), 7.22 – 7.14 (m, 2H), 6.78 (s, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.6, 163.9 (d, *J* = 251.3 Hz), 163.2, 130.2, 129.1, 129.1, 128.1 (d, *J* = 8.6 Hz), 126.9,

124.0 (d, *J* = 3.3 Hz), 116.4 (d, *J* = 22.2 Hz), 97.4 (d, *J* = 1.2 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -109.43 (tt, *J* = 8.7, 5.0 Hz). **HRMS (FI):** Calculated for $C_{15}H_{10}FNO^{\bullet+}$ $[M]^{\bullet+}$ 239.07409, found 239.07478.

5-(4-Ethynylphenyl)-3-(4-fluorophenyl)isoxazole (7f). 7f was obtained following the general procedure, from oxime **1a** (139.1 mg, 1.0 mmol) and 1,4-diethynylbenzene **6c** (378.5 mg, 3.0 mmol), as white crystals **(**195 mg, 74%); mp = (177 – 178°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.53; **IR (neat) υ_{max} (cm^{-1}):** 3298, 3111, 1607, 1528, 1496, 1433, 1237, 1160, 1100, 947, 917, 846, 812, 615, 542, 517. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.90 – 7.75 (m, 4H), 7.64 – 7.55 (m, 2H), 7.22 – 7.13 (m, 2H), 6.81 (s, 1H), 3.21 (s, 1H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.8, 164.0 (d, *J* = 250.0 Hz), 162.3, 132.9, 128.9 (d, *J* = 8.7 Hz), 127.5, 125.8, 125.3 (d, *J* = 3.1 Hz), 124.3, 116.3 (d, *J* = 21.8 Hz), 98.2, 83.0, 79.5. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -110.3 (tt, *J* = 9.2, 5.3 Hz). **HRMS (ESI):** Calculated for $C_{17}H_{11}FNO^+$ $[M+H]^+$ 264.08192, found 264.08165.



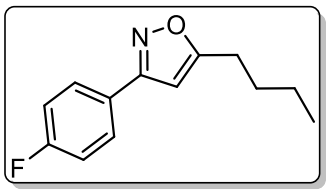
5-(4-Fluorophenyl)-3-phenylisoxazole (7g). 7g was obtained following the general procedure, from oxime **1f** (151.2 mg, 1.0 mmol) and 1-ethynyl-4-fluorobenzene **6b** (360.4 mg, 3.0 mmol), as white crystals **(**191 mg, 71%); mp = (154°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.45; **IR (neat) υ_{max} (cm^{-1}):** 3109, 3013, 2945, 2843, 1613, 1503, 1436, 1385, 1296, 1237, 1176, 1025, 947, 918, 841, 809, 637, 535. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.86 – 7.76 (m, 4H), 7.22 – 7.13 (m, 2H), 7.03 – 6.96 (m, 2H), 6.72 (s, 1H), 3.87 (s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.3, 163.9 (d, *J* = 251.1 Hz), 162.8, 161.2, 128.3, 128.0 (d, *J* = 8.3 Hz), 124.1 (d, *J* = 3.1 Hz), 121.7, 116.3 (d, *J* = 22.2 Hz), 114.5, 97.2, 55.5. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -109.6 (tt, *J* = 8.7, 5.1 Hz). **HRMS (ESI):** Calculated for $C_{16}H_{13}FNO_2^+$ $[M+H]^+$ 270.09248, found 270.09206.



Methyl 4-(3-(4-fluorophenyl)isoxazol-5-yl)benzoate (7i). 7i was obtained following the general procedure, from oxime **1a** (139.1 mg, 1.0 mmol) and methyl 4-ethynylbenzoate **6e** (480.5 mg, 3.0 mmol), as white crystals **(**270 mg, 91%); mp = (207 – 208°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.61; **IR (neat) υ_{max} (cm^{-1}):** 3109, 2964, 1717, 1605, 1528, 1506, 1434, 1273, 1104, 1018, 949, 814, 770, 701, 614. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 8.21 – 8.12 (m, 2H), 7.95 – 7.81 (m, 4H), 7.23 – 7.14 (m, 2H), 6.90 (s, 1H), 3.96

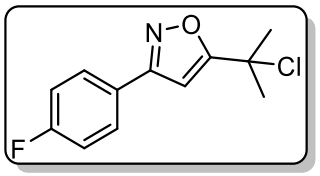
(s, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 169.5, 166.4, 162.4, 131.7, 131.2, 130.5, 128.9, 128.9, 125.9, 116.4, 116.2, 98.9, 52.6. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -110.2 (tt, *J* = 8.9, 4.9 Hz). **HRMS (ESI):** Calculated for $C_{17}H_{13}FNO_3^+$ $[M+H]^+$ 298.08740, found 298.08735.

5-Butyl-3-(4-fluorophenyl)isoxazole (7j). 7j was obtained following the general procedure, from



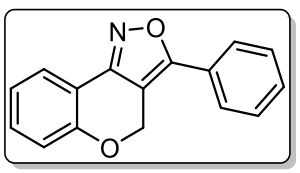
oxime **1a** (139.1 mg, 1.0 mmol) and hex-1-yne **6f** (246.5 mg, 3.0 mmol), as pale-yellow liquid **(**127 mg, 58%); Rf (PE/EA 10:1) = 0.56; **IR (neat) υ_{max} (cm^{-1}):** 2959, 2933, 2873, 1608, 1590, 1525, 1432, 1226, 1157, 840, 793, 594, 522. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.80 – 7.73 (m, 2H), 7.16 – 7.08 (m, 2H), 6.24 (t, *J* = 0.8 Hz, 1H), 2.82 – 2.75 (m, 2H), 1.79 – 1.65 (m, 2H), 1.50 – 1.35 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 174.6, 163.7 (d, *J* = 249.3 Hz), 161.4, 128.7 (d, *J* = 8.3 Hz), 125.8 (d, *J* = 3.5 Hz), 115.9 (d, *J* = 21.8 Hz), 98.7, 29.6, 26.5, 22.3, 13.7. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -111.1 (tt, *J* = 9.1, 5.3 Hz). **HRMS (ESI):** Calculated for $C_{13}H_{15}FNO^+$ $[M+H]^+$ 220.11322, found 220.11291.

5-(2-Chloropropan-2-yl)-3-(4-fluorophenyl)isoxazole (7k). 7k was obtained following the



general procedure after (24h), from oxime **1a** (139.1 mg, 1.0 mmol) and 3-chloro-3-methylbut-1-yne **6g** (307.7 mg, 3.0 mmol), as pale yellow solid (124 mg, 52%); mp = (133 – 135℃, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.75; **IR (neat) υ_{max} (cm^{-1}):** 2960, 1608, 1591, 1525, 1432, 1225, 1157, 807. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.85 – 7.73 (m, 2H), 7.18 – 7.11 (m, 2H), 6.53 (s, 1H), 2.02 (s, 6H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 175.8, 164.0 (d, *J* = 250.1 Hz), 161.6, 128.9 (d, *J* = 8.3 Hz), 125.2 (d, *J* = 3.3 Hz), 116.2 (d, *J* = 21.9 Hz), 98.9, 60.6, 31.9. **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -110.3 (td, *J* = 8.7, 4.6 Hz). **HRMS (ESI):** Calculated for $C_{12}H_{12}ClFNO$ $[M+H]^+$ 240.05860, found 240.05846.

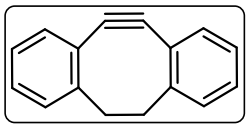
3-Phenyl-4H-chromeno[4,3-c]isoxazole (7m). 7m was obtained following the general procedure,



from oxime **1s** (251.3 mg, 1.0 mmol), as white solid (70 mg, 28%); m.p. = (168 – 170℃, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.43; **IR (neat) υ_{max} (cm^{-1}):** 3058, 1613, 1574, 1474, 1221, 1032, 993, 954, 819, 756, 743, 683. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.88 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.53 – 7.41 (m, 3H), 7.35 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 7.12 – 6.98 (m, 2H),

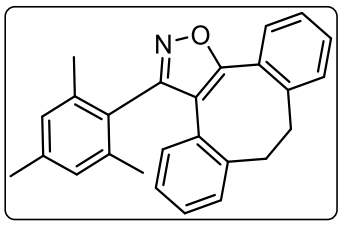
5.42 (s, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 161.6, 154.9, 154.7, 132.1, 130.2, 129.2, 127.4, 126.3, 124.5, 122.3, 117.7, 114.2, 106.6, 62.6. **HRMS (ESI):** Calculated for $C_{16}H_{12}NO_2$ $[M+H]^+$ 250.08626, found 250.08643.

Dibenzocyclooctyne (DIBO) (6h). 6h was obtained following literature protocol,[17] as off-white solid



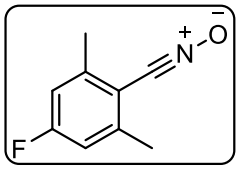
(159 mg, 54%); mp = (86°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.8; **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.37 (dddd, *J* = 21.7, 9.1, 6.6, 3.7 Hz, 8H), 3.44 – 3.29 (m, 2H), 2.58 – 2.43 (m, 2H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 153.6, 129.5, 127.7, 126.6, 126.2, 124.0, 111.7, 36.5. **HRMS (CI+):** Calculated for $C_{16}H_{13}^+$ $[M+H]^+$ 205.10173, found 205.10228.

3-Mesityl-8,9-dihydrodibenzo[3,4:7,8]cycloocta[1,2-d]isoxazole (7l). 7l was obtained through the



general procedure, from oxime **1h** (163 mg, 1.0 mmol) and DIBO **6h** (204 mg, 1.0 mmol), except that DIBO was added through a syringe pump over 8h. the product obtained as white solid **(**31 mg, 34%); mp = (177 – 178°C, recrystallized from petroleum ether); Rf (PE/EA 10:1) = 0.68; **IR (neat) υ_{max} (cm^{-1}):** 3726, 3060, 3019, 2945, 2899, 2360, 1614, 1450, 1423, 1394, 849, 754, 731. **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 7.67 – 7.55 (m, 1H), 7.32 – 7.21 (m, 4H), 7.15 (td, *J* = 7.5, 1.4 Hz, 1H), 6.93 (td, *J* = 7.6, 1.4 Hz, 1H), 6.86 (s, 2H), 6.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 3.51 – 3.37 (m, 2H), 3.18 (dd, *J* = 7.6, 5.7 Hz, 2H), 2.28 (s, 3H), 2.11 (s, 6H). **^{13}C NMR (76 MHz, $CDCl_3$) δ (ppm):** 167.1, 161.7, 140.6, 138.8, 138.4, 137.5, 131.6, 131.3, 129.5, 129.4, 129.3, 128.9, 128.4, 128.2, 127.0, 126.2, 126.1, 125.2, 116.9, 37.6, 32.1, 21.3, 20.2. **HRMS (ESI):** Calculated for $C_{26}H_{24}NO^+$ $[M+H]^+$ 366.18524, found 366.18569.

4-fluoro-2,6-dimethylbenonitrile oxide (19): The Oxime **18** (167 mg, 1.00 mmol, 1 eq) and 4-



DPAIPN (3% mole) were placed into a 20 mL Schlenk tube equipped with a magnetic stirring bar and a Teflon septum, then EtOAc (0.1M) was added. An air balloon was then connected to the reactor septum via a needle. The reaction mixture was stirred vigorously for 5 minutes then left under blue LED (456 nm) irradiation at 35°C (+/- 2°C). A fan was installed near the reactor to maintain the temperature inside the tube around this temperature. The reaction was monitored by TLC. Upon completion (8h), the reaction mixture was transferred to a round bottom flask and the solvent evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc 10:1), to afford the desired product as a white solid (68 mg, 41%); Rf (PE/EA 10:1) = 0.63; mp = 130-133°C, recrystallized from petroleum ether); **^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):** 6.82 (d, *J* = 9.0 Hz, 2H), 2.46 (s, 6H). **^{13}C**

NMR (76 MHz, $CDCl_3$) δ (ppm): 163.4 (d, *J* = 253.1 Hz), 144.9 (d, *J* = 9.3 Hz), 115.0 (d, *J* = 22.5 Hz), 110.4 (d, *J* = 3.3 Hz), 21.2 (d, *J* = 1.7 Hz). **^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm):** -107.8 (t, *J* = 8.9 Hz). **HRMS (CI^+):** Calculated for $C_9H_9FNO^+$ $[M+H]^+$ 166.06682 found 166.06622.

7. Experimental Investigations.

7.1. Quantum yield measurement

Quantum yields (Φ) were measured at low conversion (< 10 %) for the model reaction affording **3a** (Scheme 1) by irradiating a known volume of solution of EtOAc (3 mL) containing oxime **1a** (0.1 M), ketone **2a** (3.0 eq.) and 4-DPAIPN (3 mol%) in a 1-cm pathlength quartz cuvette. The solution was open to air and stirred during the course of the irradiation. At these concentrations, all of the incident light is absorbed by the solution. The energy of the incident light (456 nm Kessil lamp) held at a distance of 3 cm determined using a calibrated energy meter (Thorlabs S170C). Under these conditions, the amount of incident light energy was determined to be 1.03 W, corresponding to 3.92×10^{-6} Einstein s^{-1}. Following irradiation, the amount of product or by-product formed were determined using ^{19}F NMR with 1,4-bis(trifluoromethyl) benzene as an external standard. The quantum yield for each process (formation of aldehyde by-product or product) was calculated according to:

Φ = (Moles of product) / (Moles of photons absorbed)

Conversion at 466 nm[a]			
Time (min)	Photons absorbed (mol)	**3a** (mol)	Aldehyde (mol)
0	0	0	0
60	0.014112	6.571×10^{-6}	1.6144×10^{-5}
120	0.028224	2.672×10^{-5}	2.7325×10^{-5}

[a] In aerated EtOAc solution.

Plotting the conversion versus the moles of photons absorbed is expected to yield a line with a slope equal to the quantum yield. Analysis of the data above yields $\Phi = 9.5 \times 10^{-4}$ for **3a** and 1.9×10^{-3} for the aldehyde by-product at low conversion. The experimental error in the determination of photochemical quantum yields are generally assumed to be ± 20 %.

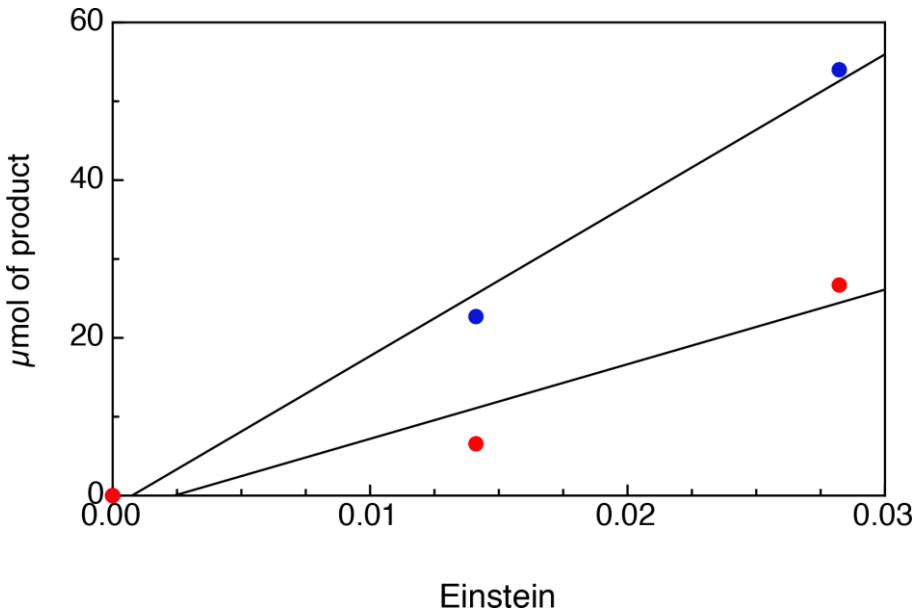


Figure ESI-3. Conversion of oxime into **3a** (red filled circles) or aldehyde by-product (blue filled circles) vs. absorbed photons at 466 nm. The black lines are linear best fit with a slope (Φ) of 9.5 × 10^{-4} (**3a**, r^2 = 0.960) and 1.9 × 10^{-3} (aldehyde, r^2 = 0.992)

7.2. Fluorescence quenching analysis of the photocatalyst

Fluorescence quenching analysis were carried out on samples of 4-DPAIPN (1×10^{-5} M) in EtOAc, with different concentrations of oxime (**1a**) (**Figure ESI-4**) or ketone (**2a**) (**Figure ESI-5**). For the quenching of 4-DPAIPN with oxygen, the samples were purged with argon for 30 min, equilibrated with air, or bubbled with pure oxygen for 30 min (**Figure ESI-6**). All fluorescence spectra were recorded at λ_{ex} = 450 nm and λ_{em} = 520 nm. The solubility of oxygen in EtOAc equilibrated with pure oxygen was calculated to be 8.89 mM.[17]

[17] Battino, R.; Rettich, T. R.; Tominaga, T., The solubility of oxygen and ozone in liquids. *J. Phys. Chem. & Chem. Data* **1983,** *12*, 163-178.

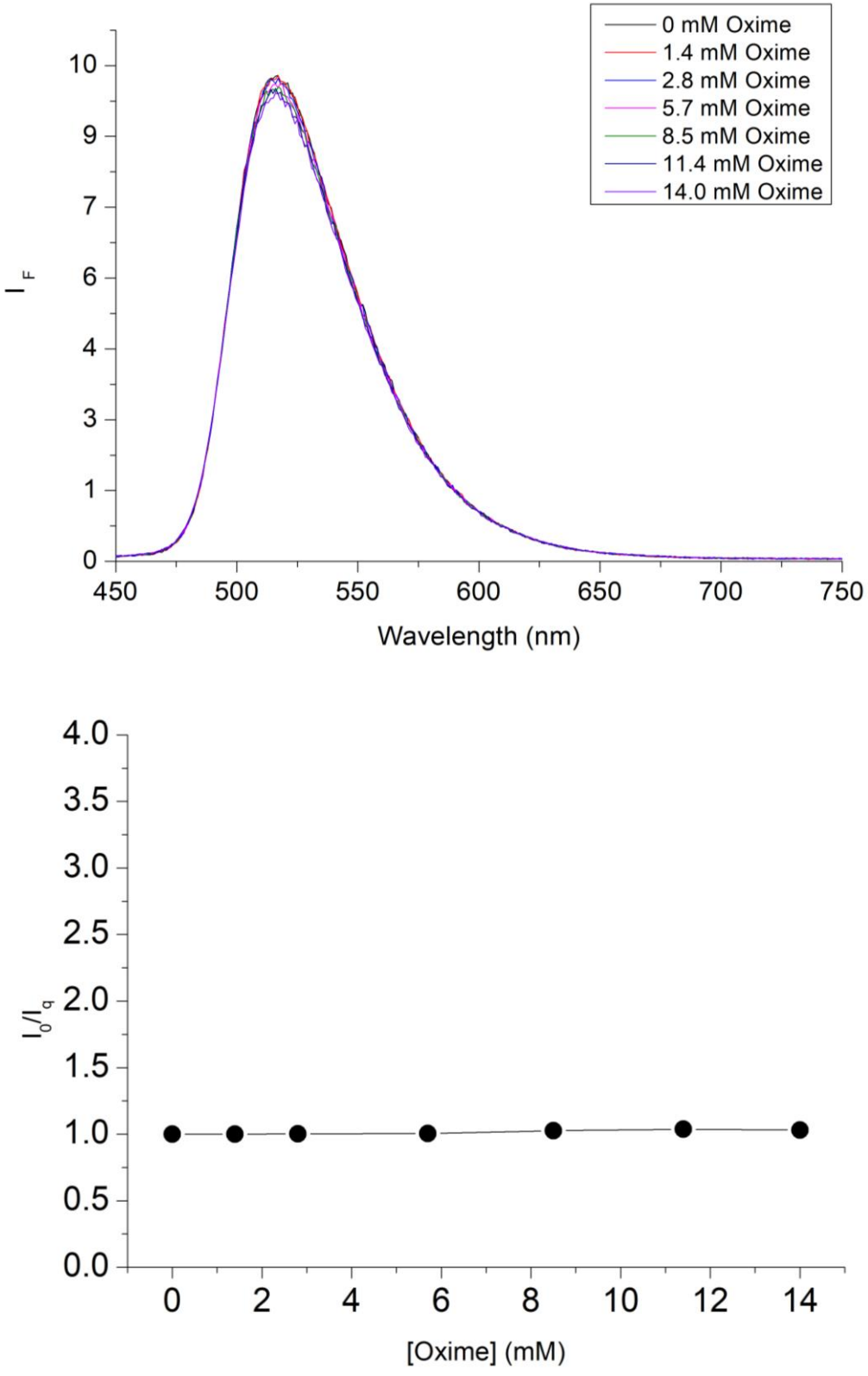


Figure ESI-4. Fluorescence quenching analysis (up) and Stern-Volmer graph (down) of 4-DPAIPN (1×10^{-5} M) in EtOAc, with different concentrations of oxime (**1a**), λ_{ex} = 450 nm, λ_{em} = 520 nm.

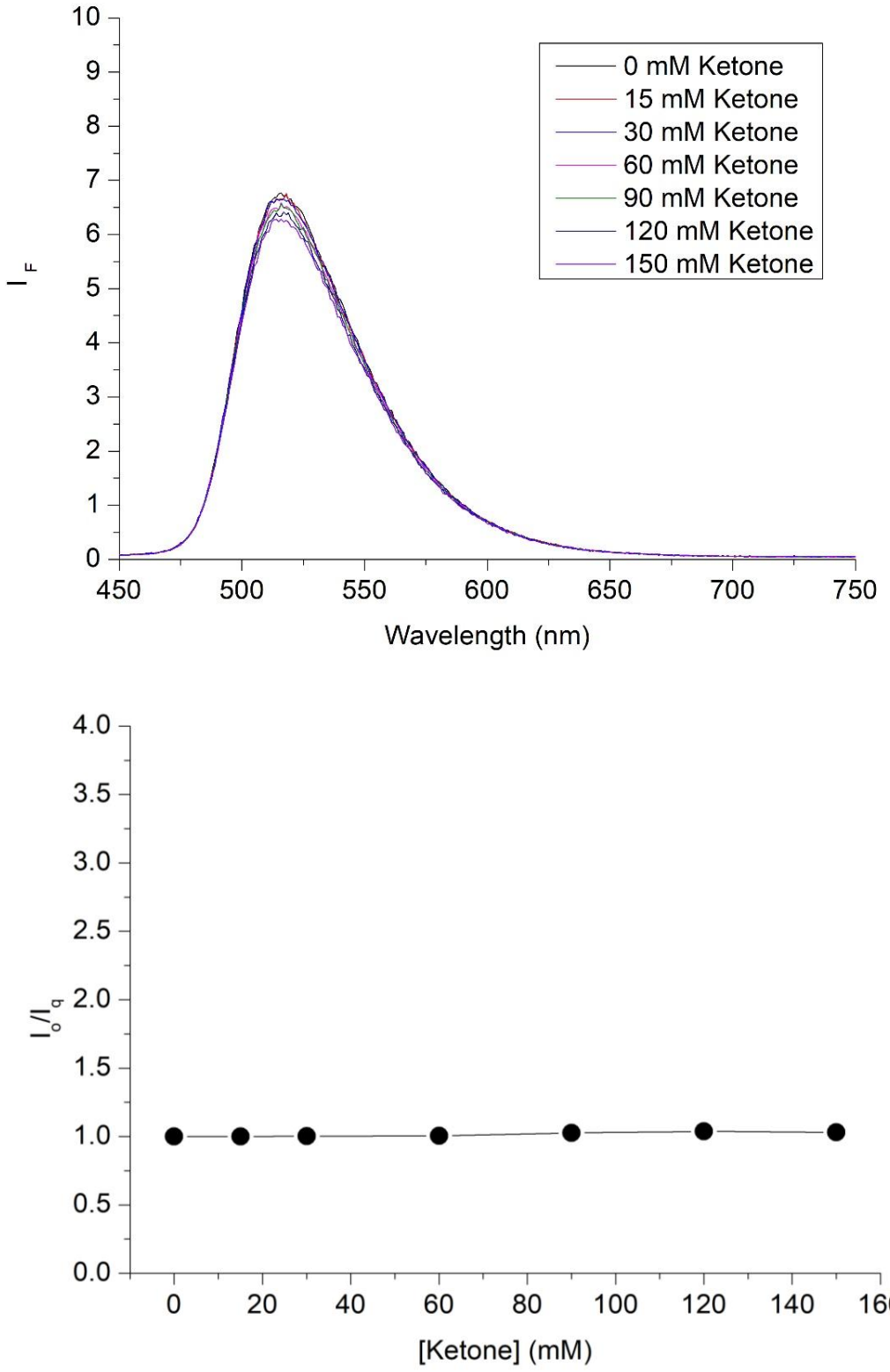


Figure ESI-5. Fluorescence quenching analysis (up) and Stern-Volmer graph (down) of 4-DPAIPN (1×10^{-5} M) in EtOAc, with different concentrations of ketone (**2a**), λ_{ex} = 450 nm, λ_{em} = 520 nm.

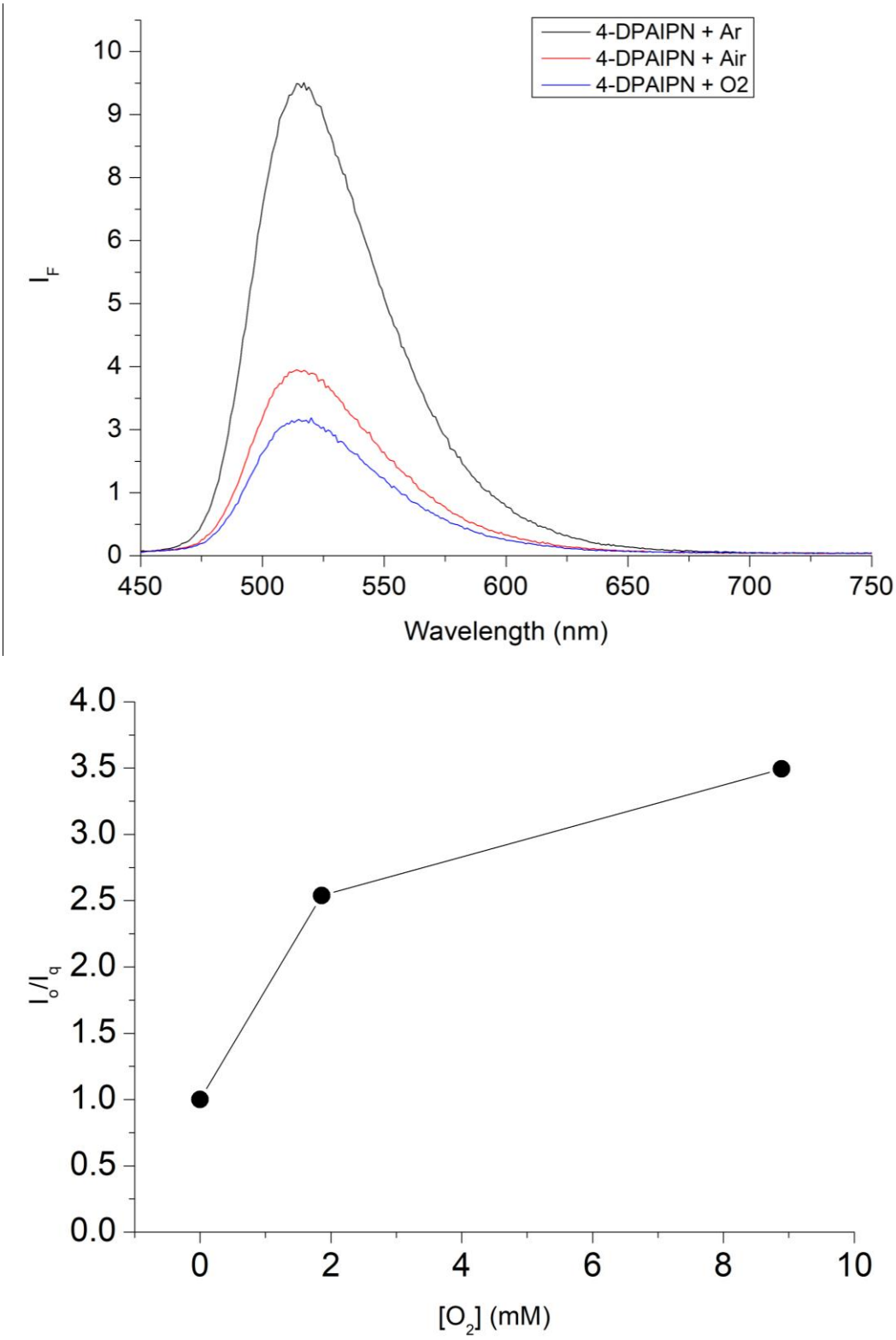
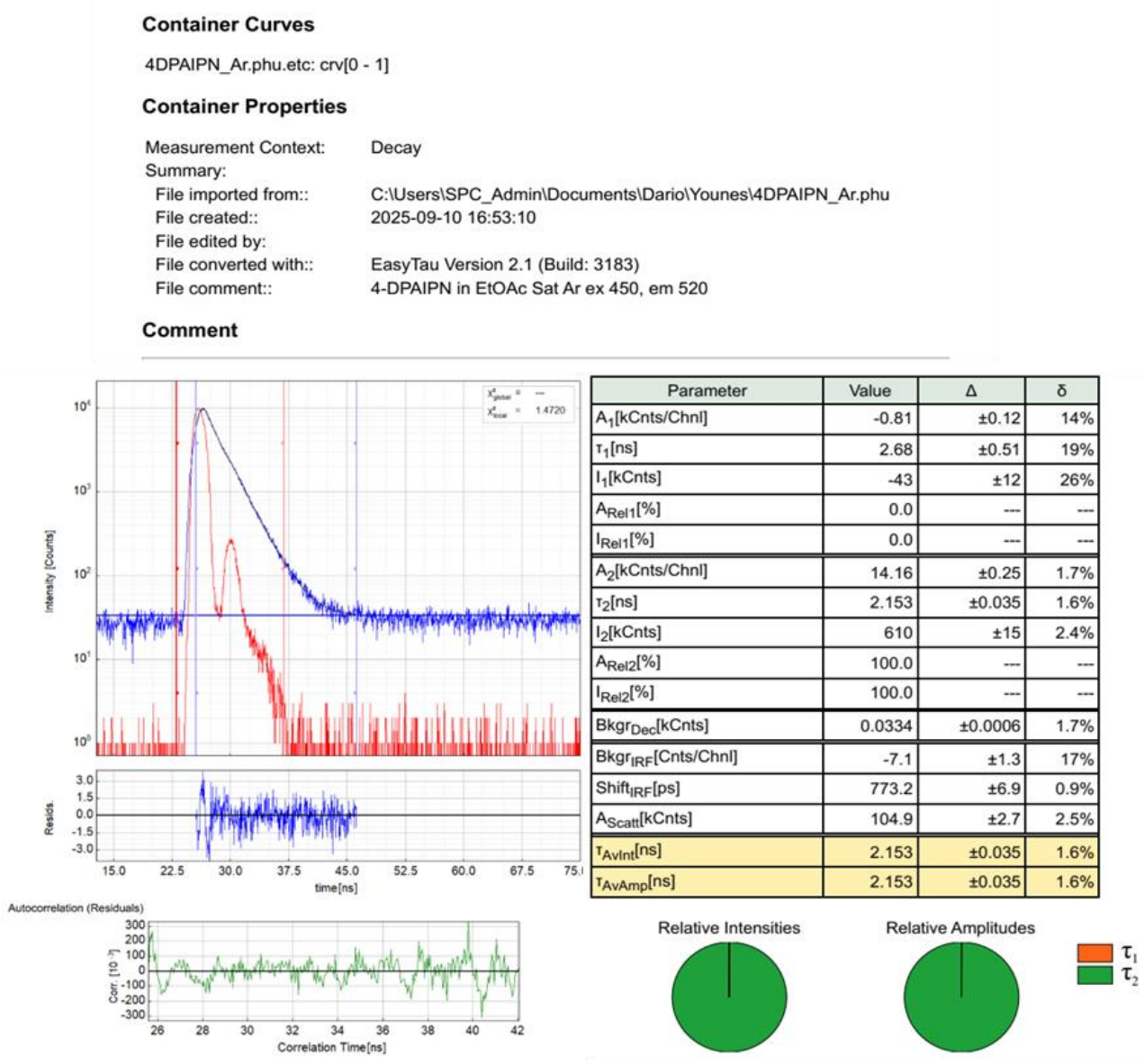


Figure ESI-6. Fluorescence quenching analysis (up) and Stern-Volmer graph (down) of 4-DPAIPN (1×10^{-5} M) in EtOAc, with argon for 30 min (black), equilibrated with air (red), or bubbled with pure oxygen for 30 min (blue), λ_{ex} = 450 nm, λ_{em} = 520 nm.

7.3. Fluorescence decay profiles of photocatalyst excited states lifetime

Fluorescence decay profiles using single photon counting technique for determination of the lifetime of the excited states of PC were collected using three samples, either purged with argon for 30 min **(Figure ESI-7)**, equilibrated with air **(Figure ESI-8)** or bubbled with pure oxygen for 30 min **(Figure ESI-9)**.



Parameter	Value	Δ	δ
A_1[kCnts/Chnl]	-0.81	±0.12	14%
τ_1[ns]	2.68	±0.51	19%
I_1[kCnts]	-43	±12	26%
A_{Rel1}[%]	0.0	---	---
I_{Rel1}[%]	0.0	---	---
A_2[kCnts/Chnl]	14.16	±0.25	1.7%
τ_2[ns]	2.153	±0.035	1.6%
I_2[kCnts]	610	±15	2.4%
A_{Rel2}[%]	100.0	---	---
I_{Rel2}[%]	100.0	---	---
$Bkgr_{Dec}$[kCnts]	0.0334	±0.0006	1.7%
$Bkgr_{IRF}$[Cnts/Chnl]	-7.1	±1.3	17%
$Shift_{IRF}$[ps]	773.2	±6.9	0.9%
A_{Scatt}[kCnts]	104.9	±2.7	2.5%
τ_{AvInt}[ns]	2.153	±0.035	1.6%
τ_{AvAmp}[ns]	2.153	±0.035	1.6%

Figure ESI-7. Fluorescence decay profiles using the single photon counting technique for the lifetime of the singlet state of 4-DPAIPN (1×10^{-5} M) in EtOAc purged with argon for 30 min, λ_{ex} = 450 nm, λ_{em} = 520 nm.

Container Curves

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Container Properties

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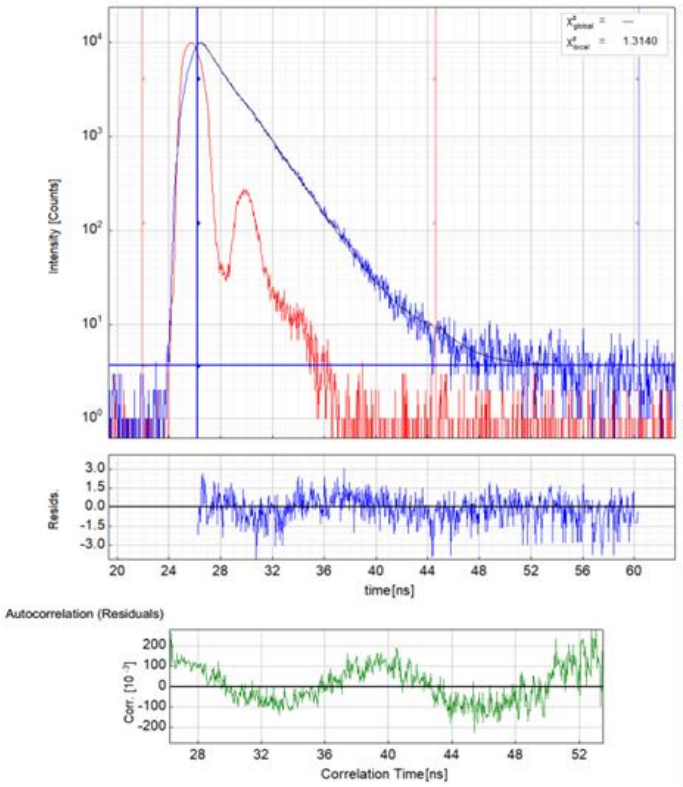
File edited by:	
File converted with::	EasyTau Version 2.1 (Build: 3183)
File comment::	4-DPAIPN in EtOAc Sat Air ex 450, em 520

Comment



Parameter	Value	Δ	δ
A_1[kCnts/Chnl]	14.98	±0.14	0.9%
τ_1[ns]	2.0636	±0.0042	0.2%
I_1[kCnts]	618.0	±4.4	0.7%
A_{Rel1}[%]	100.0	---	---
I_{Rel1}[%]	100.0	---	---
$Bkgr_{Dec}$[kCnts]	0.0038	±0.0002	3.6%
$Bkgr_{IRF}$[Cnts/Chnl]	-1.10	±0.16	14%
$Shift_{IRF}$[ps]	563	±16	2.8%
A_{Scatt}[kCnts]	79.8	±4.4	5.4%
τ_{AvInt}[ns]	2.0636	±0.0042	0.2%
τ_{AvAmp}[ns]	2.0636	±0.0042	0.2%

Figure ESI-8. Fluorescence decay profiles using the single photon counting technique for the lifetime of the singlet state of 4-DPAIPN (1×10^{-5} M) in EtOAc equilibrated with air, λ_{ex} = 450 nm, λ_{em} = 520 nm.

Container Curves

4DPAIPN_O2.phu.etc: crv[0 - 1]

Container Properties

Measurement Context:	Decay
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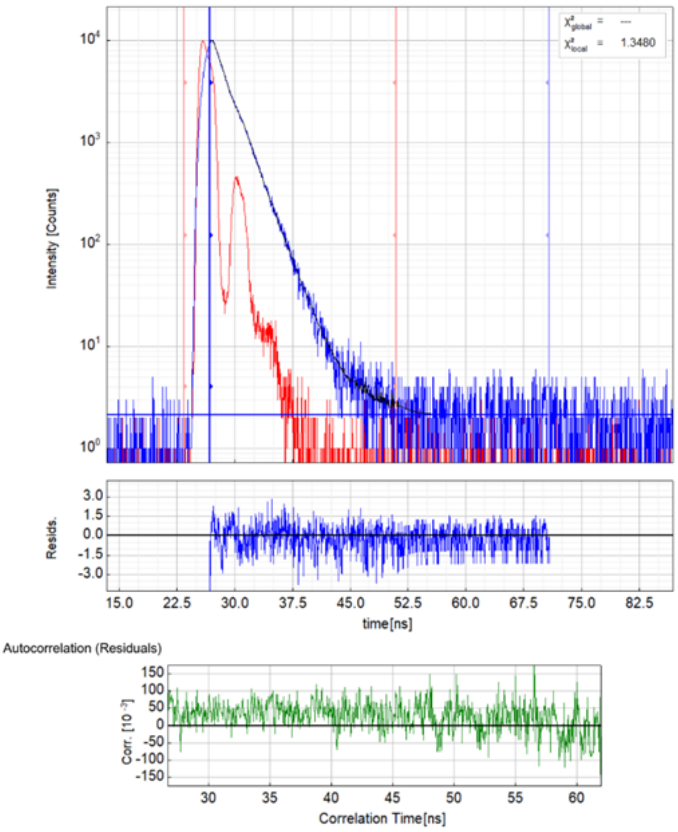
File edited by:	
File converted with::	EasyTau Version 2.1 (Build: 3183)
File comment::	4-DPAIPN in EtOAc Sat O2 ex 450, em 520

Comment



Parameter	Value	Δ	δ
A_1[kCnts/Chnl]	7.70	±0.77	10.0%
τ_1[ns]	2.172	±0.037	1.7%
I_1[kCnts]	335	±29	8.6%
A_{Rel1}[%]	7.6	±1.4	19%
I_{Rel1}[%]	16.1	±2.9	18%
A_2[kCnts/Chnl]	94.9	±6.7	7.0%
τ_2[ns]	0.925	±0.061	6.6%
I_2[kCnts]	1 760	±190	10%
A_{Rel2}[%]	92.5	±1.4	1.5%
I_{Rel2}[%]	84.0	±2.9	3.4%
A_3[kCnts/Chnl]	-92.6	±5.2	5.5%
τ_3[ns]	0.816	±0.057	6.9%
I_3[kCnts]	-1 500	±150	9.6%
A_{Rel3}[%]	0.0	---	---
I_{Rel3}[%]	0.0	---	---
$Bkgr_{Dec}$[kCnts]	0.0022	±0.0001	2.9%
$Bkgr_{IRF}$[Cnts/Chnl]	0.32	±0.13	40%
$Shift_{IRF}$[ps]	443	±23	5.2%
A_{Scatt}[kCnts]	123	±21	17%
τ_{AvInt}[ns]	1.124	±0.048	4.2%
τ_{AvAmp}[ns]	1.018	±0.042	4.1%

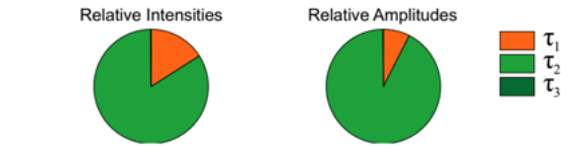


Figure ESI-9. Fluorescence decay profiles using the single photon counting technique for the lifetime of the singlet state of 4-DPAIPN (1×10^{-5} M) in EtOAc bubbled with pure oxygen for 30 min, λ_{ex} = 450 nm, λ_{em} = 520 nm.

7.4. EPR spectrum of DMPO and TEMP (detection of $O_2^{\bullet-}$ and $^1O_2$)

The EPR spectroscopy of DMPO for detecting the presence of superoxide radical anion ($O_2^{\bullet-}$) and TEMP for detecting singlet oxygen ($^1O_2$), were performed in EtOAc at room temperature.

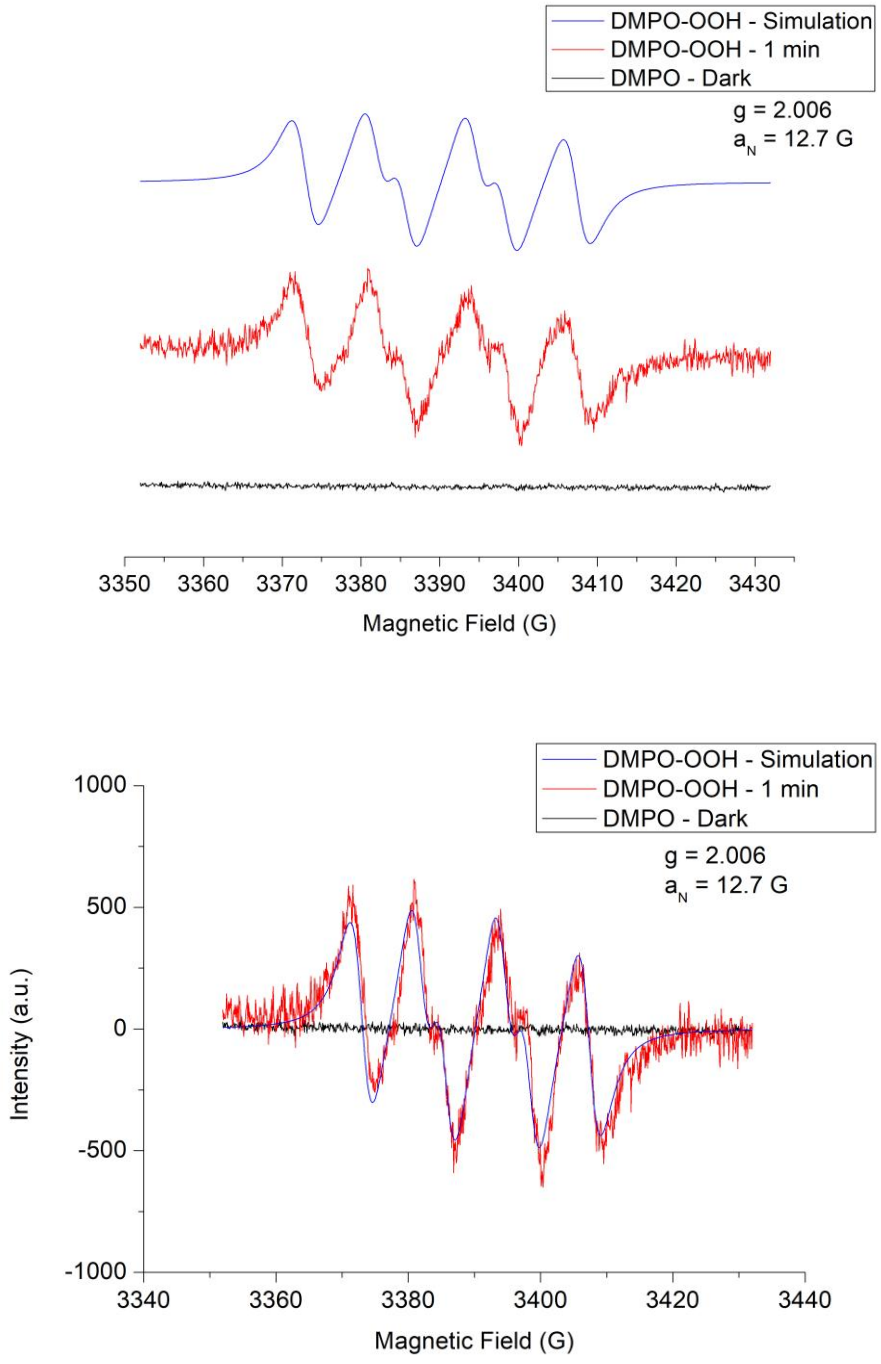


Figure ESI-10. EPR spectrum after 1 minute of a mixture of DMPO (0.1 M) in EtOAc (1 equiv.), 4-fluorobenzaldehyde oxime **1a** (1 equiv.) and 2,2,2-trifluoroacetophenone **2a** (3.0 equiv.), 4-DPAIPN (0.5 mol%), irradiated at 456 nm LEDs *in situ*. DMPO-Dark (in black), and simulation (in blue).

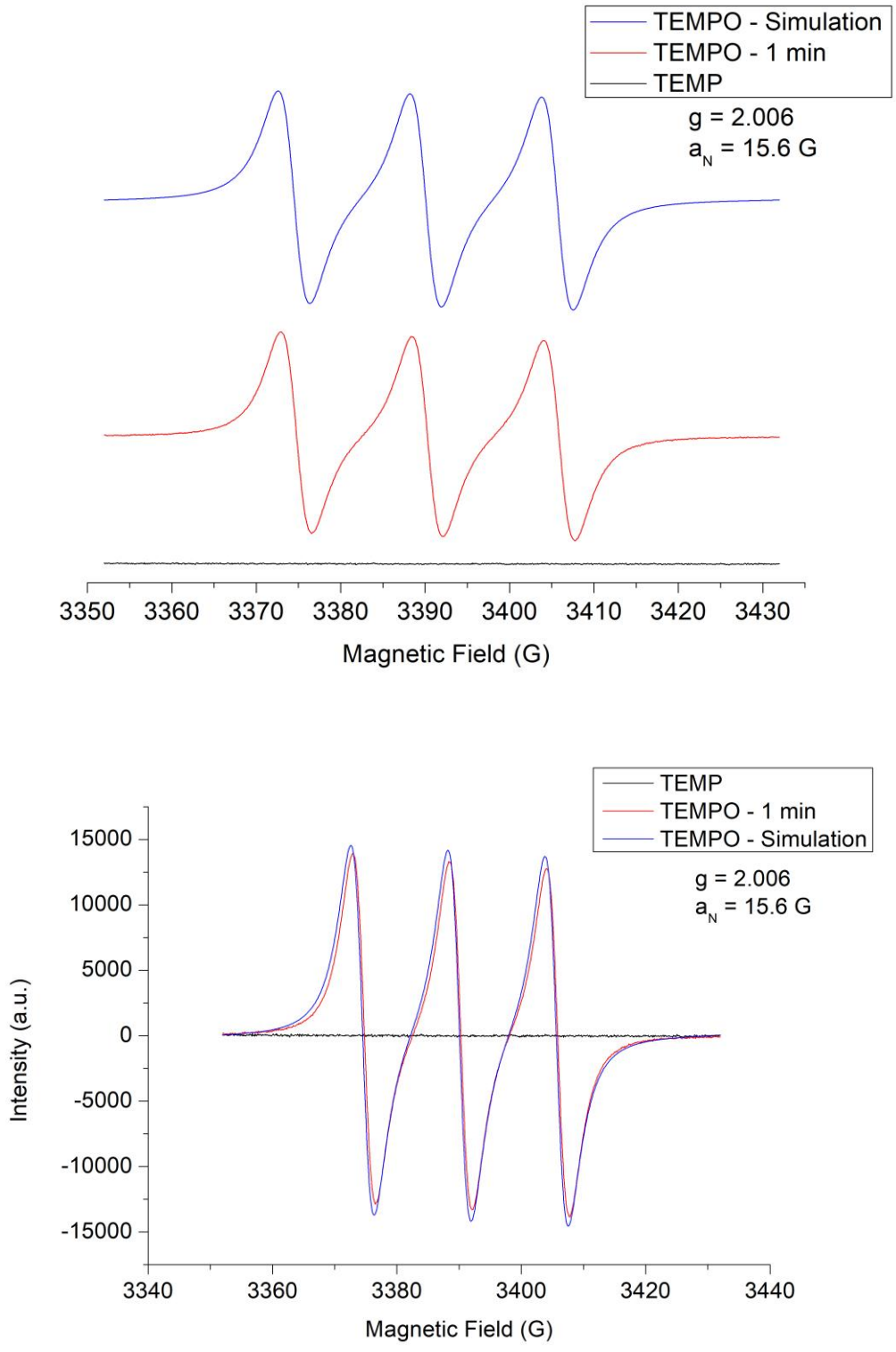


Figure ESI-11. EPR spectrum of a mixture of TEMP (0.1 M) in EtOAc, 4-fluorobenzaldehyde oxime **1a** (1 equiv.) and 2,2,2-trifluoroacetophenone **2a** (3.0 equiv.) with 4-DPAIPN (0.5 mol%), irradiated at 456 nm LEDs *in situ*, and the formation of TEMPO after 1 min (in red), with simulation (in blue).

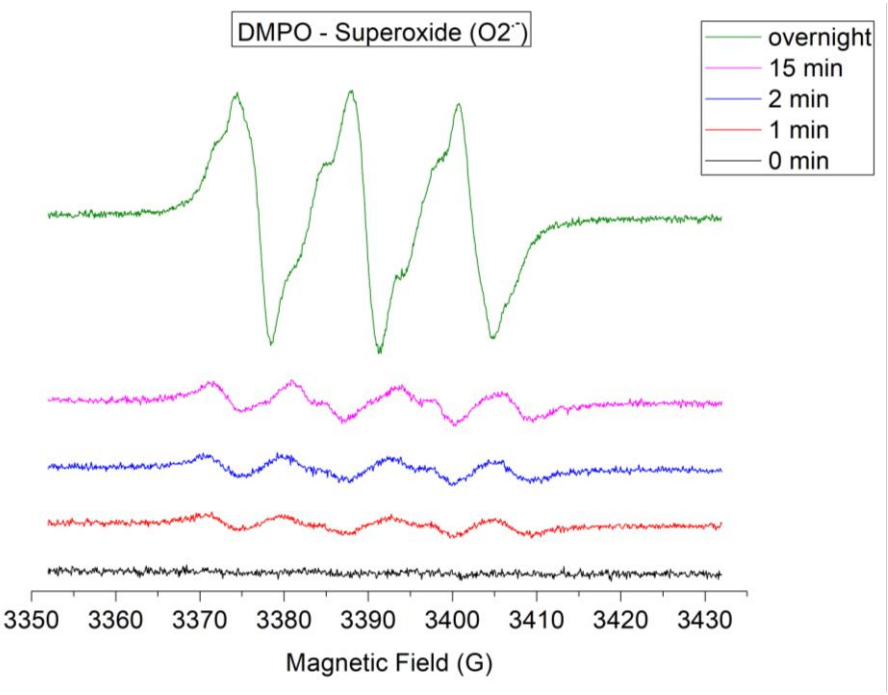


Figure ESI-12. EPR spectrum over time of a mixture of DMPO 0.1M in EtOAc (1 equiv.) with 4-fluorobenzaldehyde oxime **1a** (1 equiv.), 2,2,2-trifluoroacetophenone **2a** (3.0 equiv.) and 4-DPAIPN (0.5%), irradiated at 456 nm LEDs *in situ*, at different times.

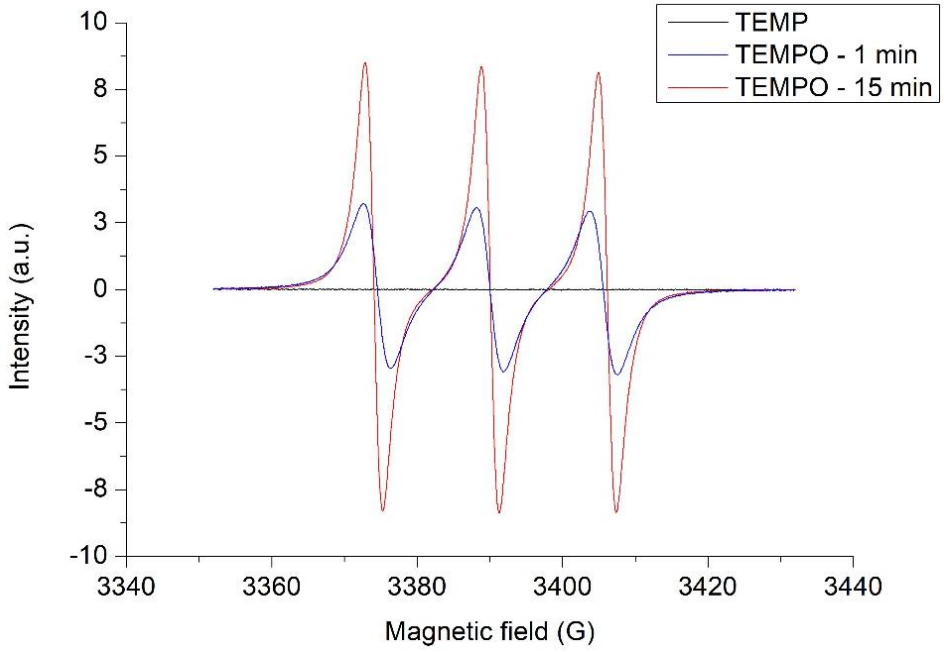


Figure ESI-13. EPR spectrum of TEMP (0.1 M) in EtOAc with 4-fluorobenzaldehyde oxime **1a** (1 equiv.) and 2,2,2-trifluoroacetophenone **2a** (3.0 equiv.) with 4-DPAIPN (0.5 mol%), irradiated at 456 nm LEDs *in situ*, and the formation of TEMPO after 1 min in blue and (15 min) in red.

7.5. Laser flash photolysis studies

Transient absorption spectra were acquired from solutions of 4-DPAIPN in EtOAc adjusted to an optical density of 2 at 355 nm in quartz fluorescence cuvettes of 1 cm path length. Samples were excited at right angle geometry using a frequency-tripled Nd-YAG laser (Expla NL300, 5.5 ns pulse width, 10 or 50 mJ/pulse, 355 nm excitation wavelength). Transient absorption spectra were probed with a Xe lamp and recorded with an Andor iStar ICCD camera coupled with an Oriel Multispec spectrograph. The lifetime measurements were performed by following the decay of the transient signal at 484 nm, and the data was recorded on a RTM3002 oscilloscope.

The raw transient absorption spectra obtained at Δt = 200 ns for nitrogen-purged or aerated solutions (with and without 0.1 M **1a**) are shown in Fig. ESI-14. The large negative signal at 550 nm corresponds to the delayed component of the emission from the chromophore. The latter needs to be subtracted from the raw data to extract the absorption spectrum of the transient intermediates. Based on the quenching data, we may expect that ca. 40% of the initial emission of the nitrogen-purged solutions remains upon saturation with air. However, this represents a lower estimate since a greater proportion of the global emission will be collected by the temporal window of the ICCD (50 ns) corresponding to the emission close to t = 0. Experimentally, we find that a value of 60% allows the correction of the emission without visibly distorting the resulting spectra.

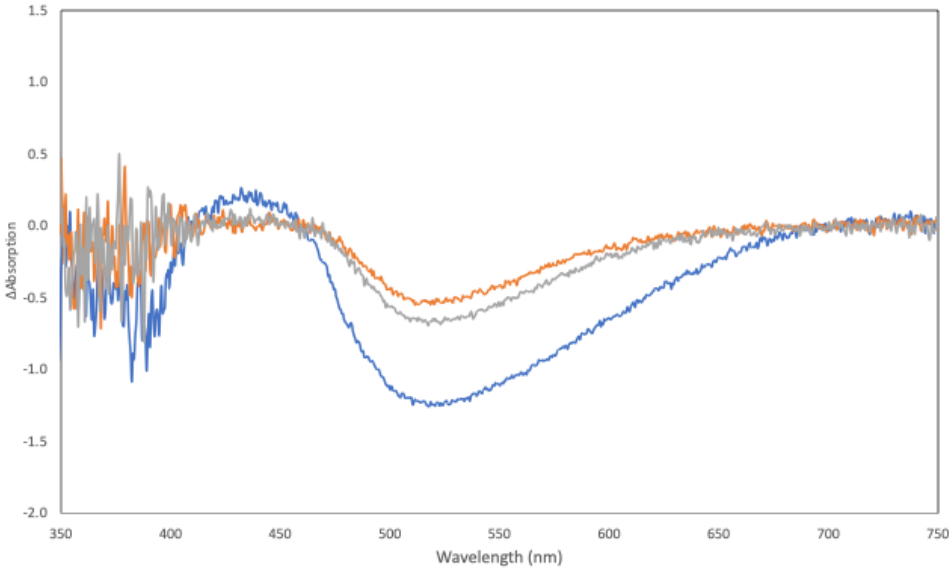


Figure ESI-14. Raw transient absorption spectra collected 200 ns (50 ns window) following laser excitation (50 mJ/pulse) in EtOAc solutions of 4-DPAIPN in nitrogen-purged solution (blue line), aerated solution (orange line) or in the presence of 0.1 M **1a** (aerated solution, gray line).

7.6. ^{1}H NMR titration (oxime 1a vs PC)

[PC] (mM)	δ OH (**1a**)$_{exp}$	δ OH (**1a**)$_{corr}$
0	7.3447	7.3478
1.2	7.3516	7.3526
2.4	7.3578	7.3573
3.5	7.3635	7.3614
4.5	7.3678	7.3651
5.6	7.3716	7.3690
6.5	7.3739	7.3721
8.3	7.3793	7.3780
10	7.3844	7.3834
13.6	7.3908	7.3940
16.7	7.3981	7.4024
21.4	7.4082	7.4140
27.8	7.4228	7.4277
31.8	7.4362	7.4354
34.6	7.4441	7.4404
36.7	7.4501	7.4439

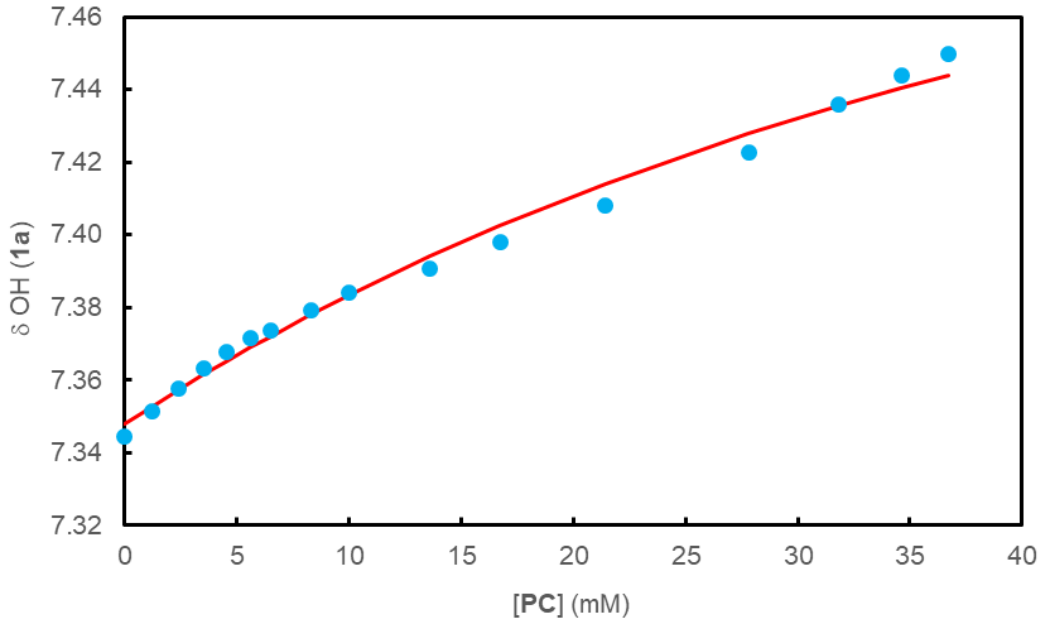


Figure ESI-15. Binding isotherm between **1a** (5 mM) and PC in CD_2Cl_2 derived from the chemical shift of the OH proton in **1a**. Red line is best fit through the points with a binding constant of 18 M^{-1}.

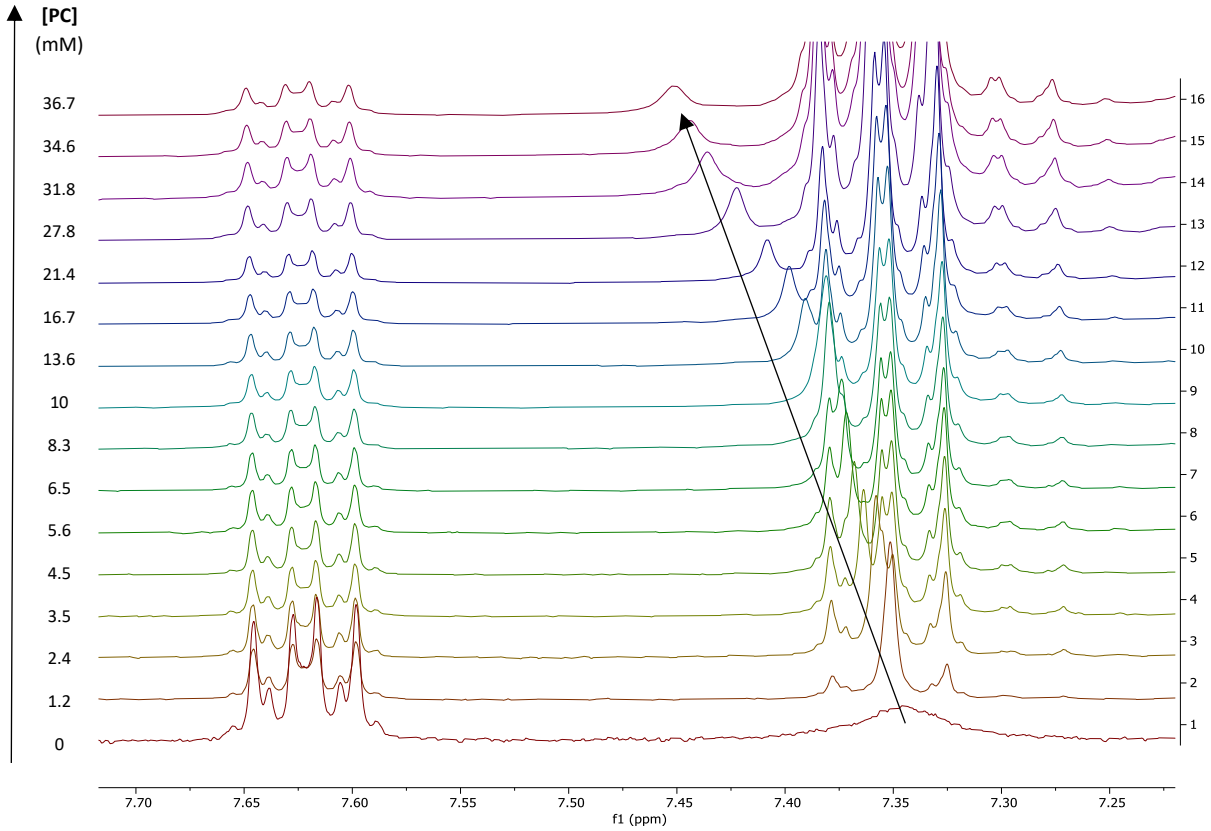
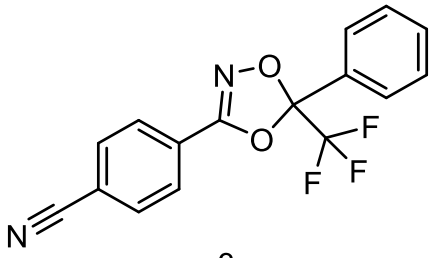
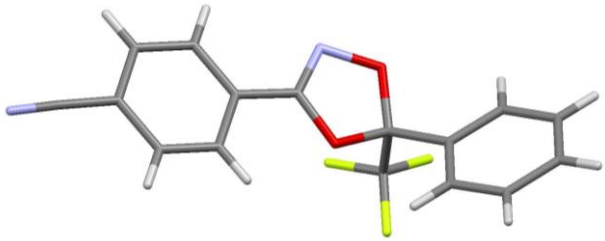
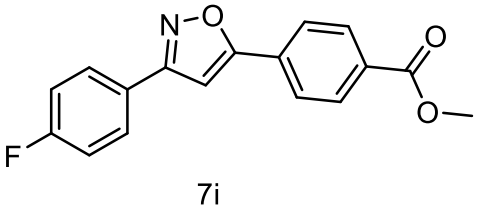
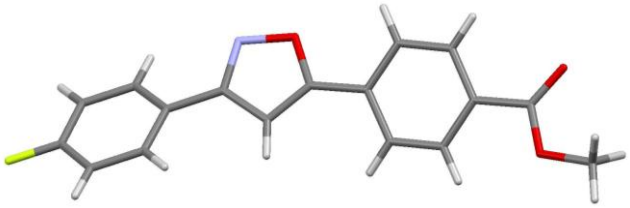


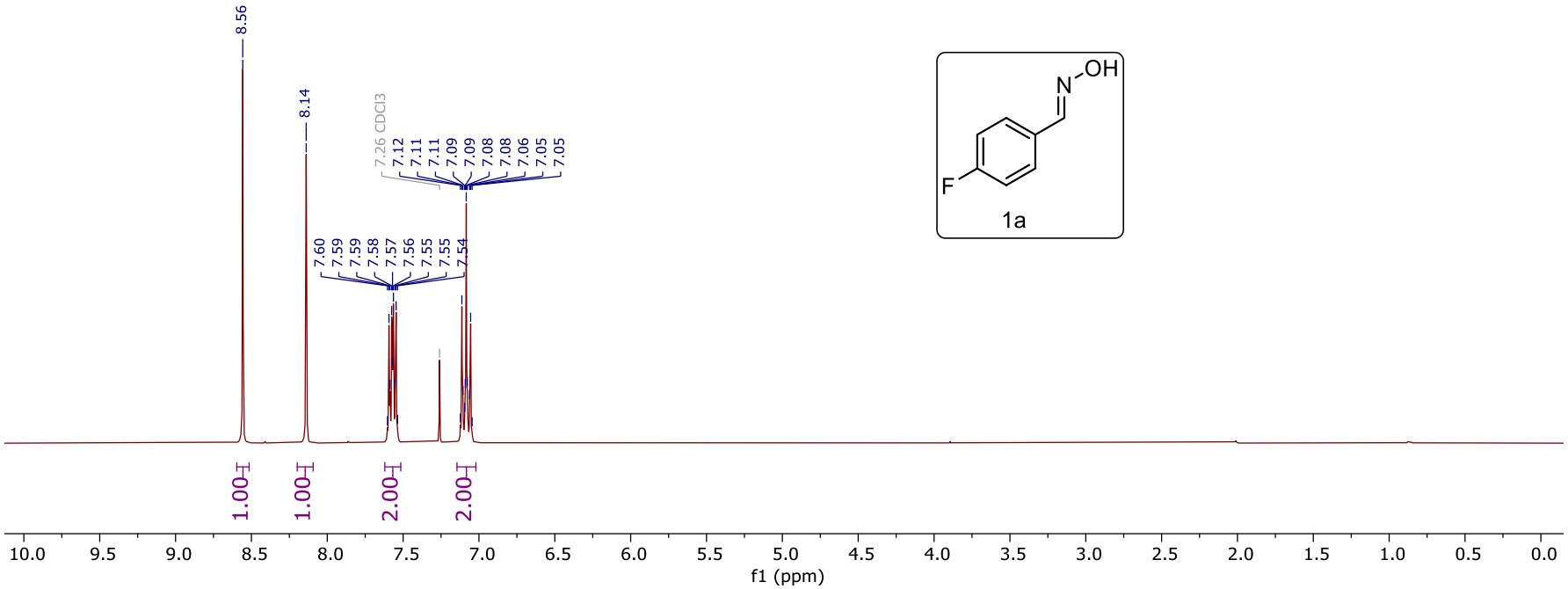
Figure ESI-16. ^{1}H NMR of the PC-Oxime in CD_2Cl_2 between **1a** (5 mM) and different concentrations of PC (see Figure ESI-14 above) showing the chemical shift of the OH proton.

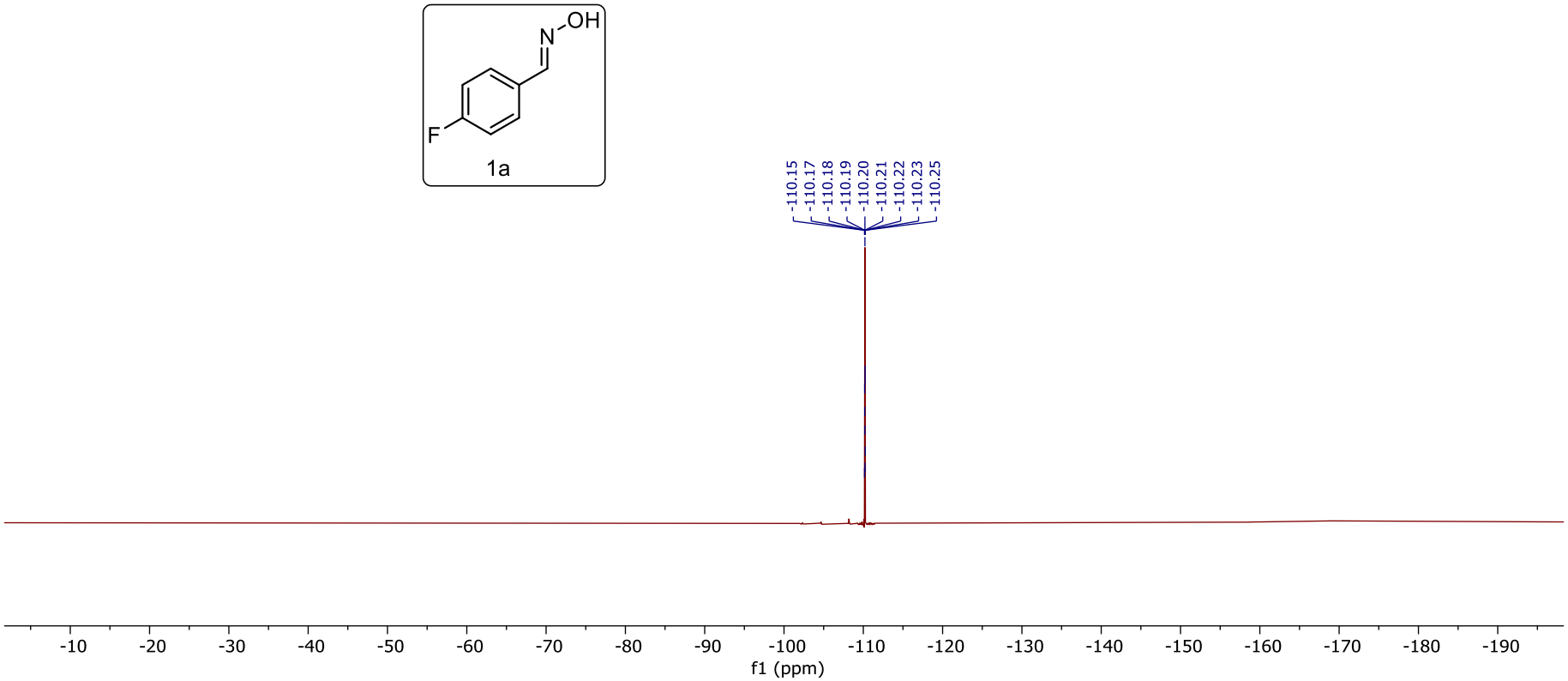
8. Crystallographic Data

4-(5-Phenyl-5-(trifluoromethyl)-1,4,2-dioxazol-3-yl)benzonitrile (3e):		
 3e 		
Empirical Formula	$C_{16}H_9F_3N_2O_2$	
Formula Weight	318.25 g.mol^{-1}	
Temperature	150(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	a = 7.7206(5) A	alpha = 92.407(2) deg.
	b = 9.3225(6) A	beta = 99.423(2) deg.
	c = 10.2659(7) A	gamma = 91.424(2) deg.
Volume	1914.8(4) A^3	
Z, Calculated density	2, 1.452 Mg/m^3	
Absorption coefficient	0.123 mm^-1	
F(000)	324	
Crystal size	0.150 x 0.050 x 0.040 mm	
Theta range for data collection	2.013 to 26.406 deg.	
Limiting indices	$-9 \le h \le 9$, $-11 \le k \le 11$, $-12 \le l \le 12$	
Reflections collected / unique	20696 / 2991 [R(int) = 0.0315]	
Completeness to theta = 25.242	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.7258	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2991 / 0 / 208	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0746	
R indices (all data)	R1 = 0.0502, wR2 = 0.0847	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.225 and -0.192 e.A^-3	
CCDC number	***CCDC 2489790***	

Methyl 4-(3-(4-fluorophenyl)isoxazol-5-yl)benzoate (7i):		
 7i		
Empirical Formula	$C_{17}H_{12}FNO_3$	
Formula Weight	297.28 $g.mol^{-1}$	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Monoclinic, P 21/c	
Unit cell dimensions	a = 32.317(2) A	alpha = 90 deg.
	b = 5.8385(4) A	beta = 90.826(3) deg.
	c = 7.1851(5) A	gamma = 90 deg.
Volume	1355.57(16) A^3	
Z, Calculated density	4, 1.457 Mg/m^3	
Absorption coefficient	0.110 mm^-1	
F(000)	616	
Crystal size	0.050 x 0.050 x 0.020 mm	
Theta range for data collection	0.630 to 26.421 deg.	
Limiting indices	$-40 \leq h \leq 40, -7 \leq k \leq 7, -8 \leq 1 \leq 8$	
Reflections collected / unique	43454 / 2775 [R(int) = 0.0792]	
Completeness to theta = 25.242	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.7070	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2775 / 0 / 201	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1543	
R indices (all data)	R1 = 0.1055, wR2 = 0.1856	
Extinction coefficient	0.0041(14)	
Largest diff. peak and hole	0.196 and -0.189 e.A^-3	
CCDC number	***CCDC 2489789***	

9. Copies of ^{1}H and ^{13}C NMR and ^{19}F NMR Spectra.

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-110.21
-110.22
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-10
-20
-30
-40
-50
-60
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-110
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-160
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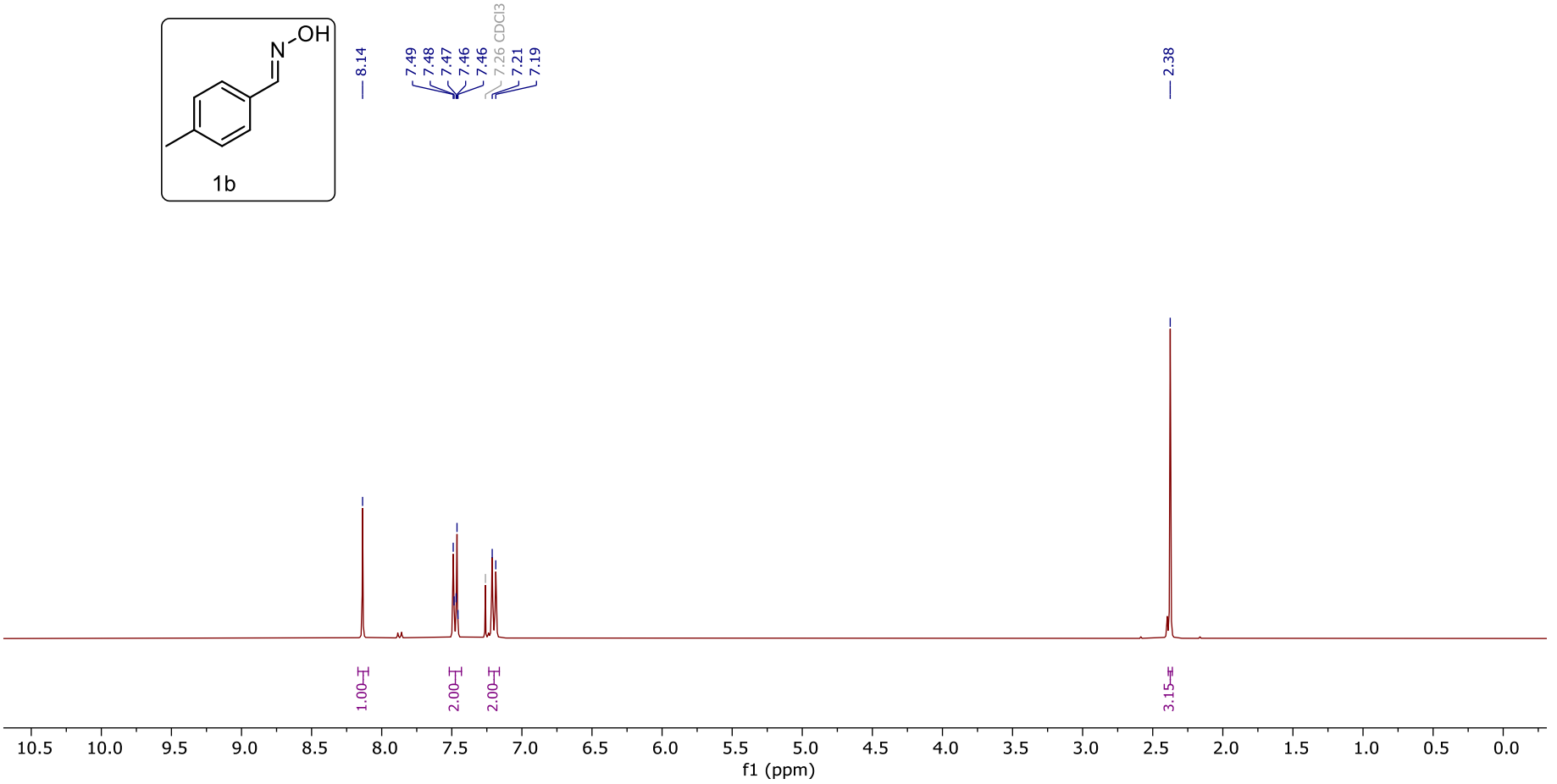
-190
f1 (ppm)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2.00
2.00
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9.5
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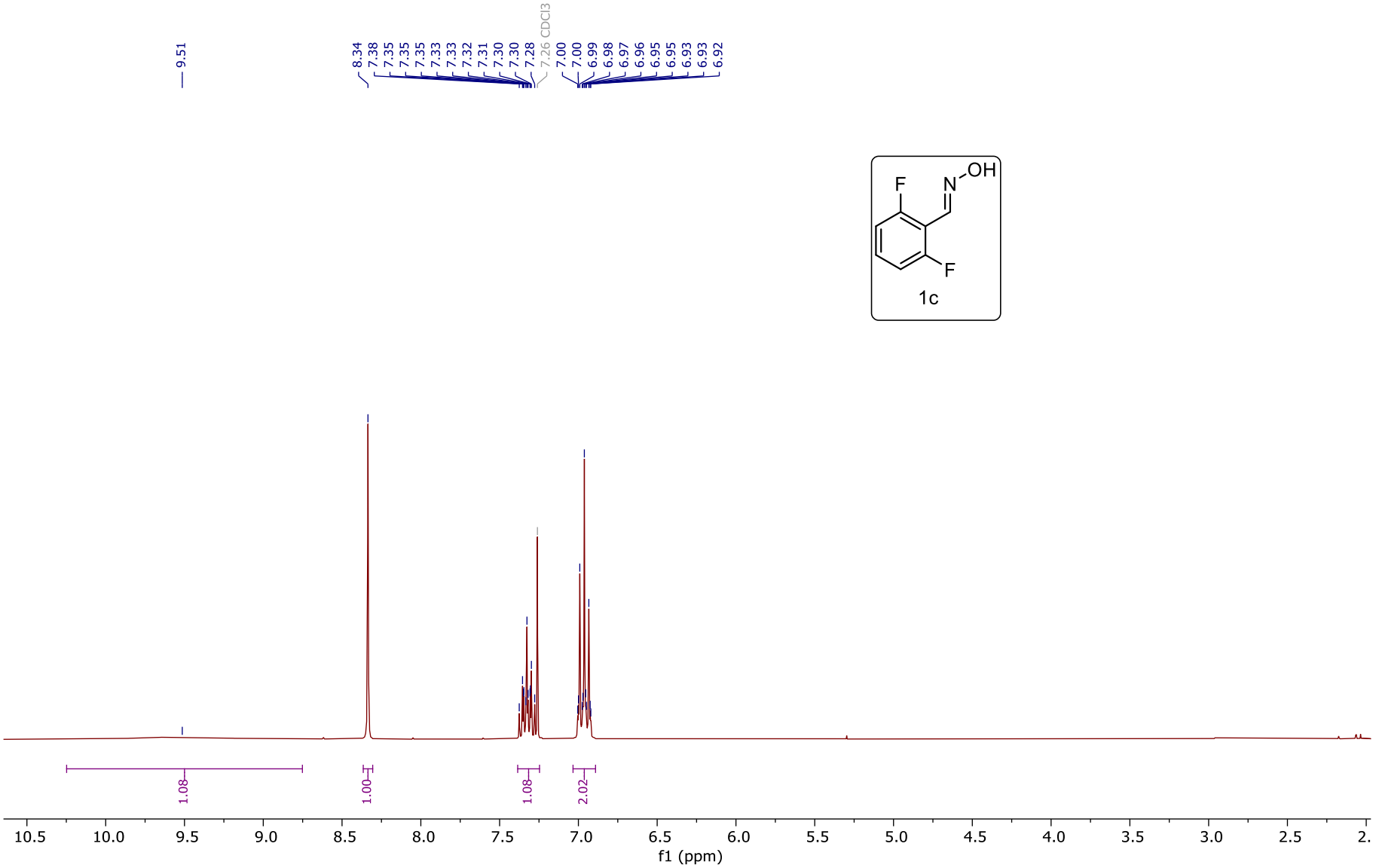
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7.00
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6.96
6.95
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6.92
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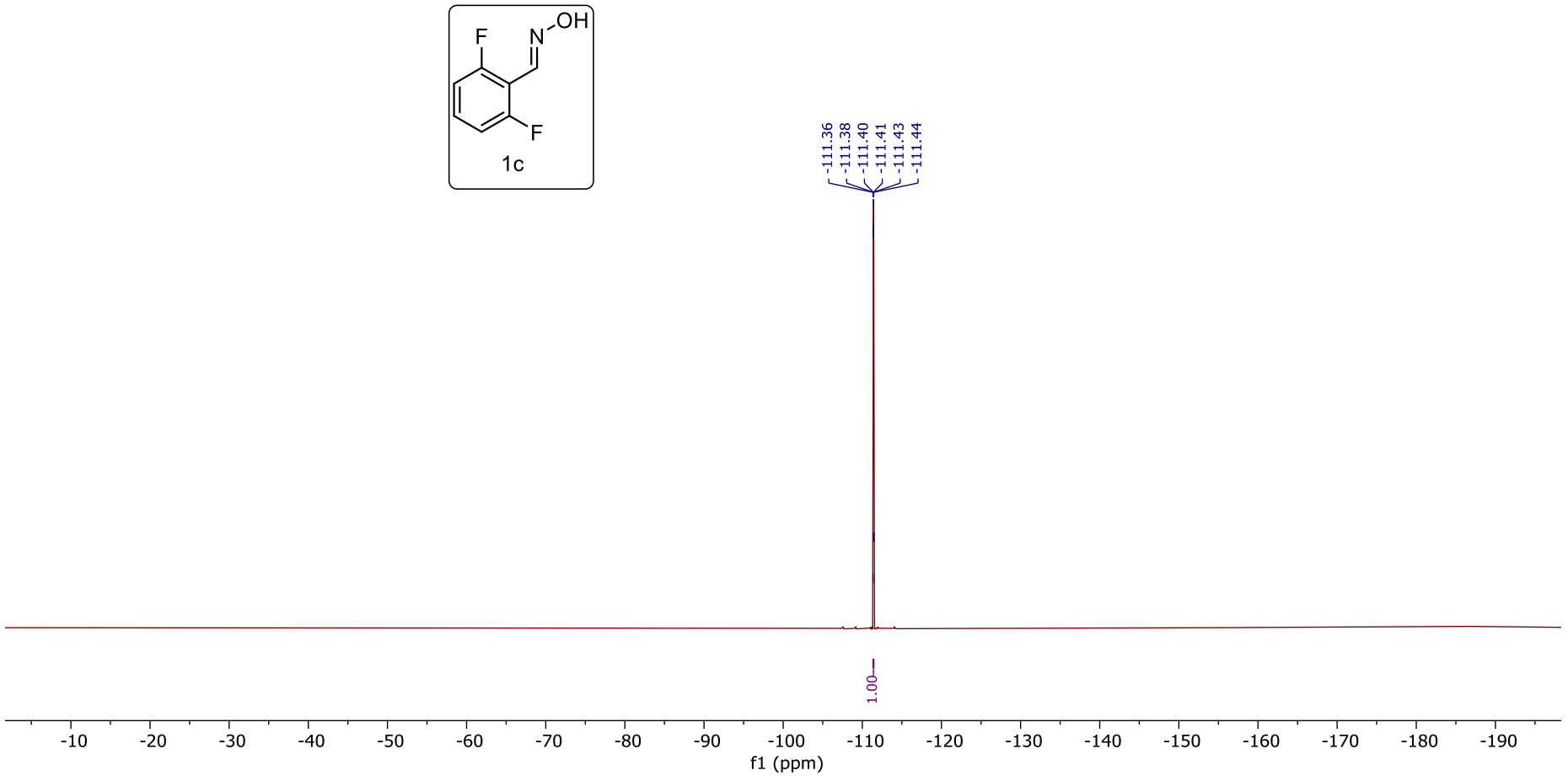
2.
f1 (ppm)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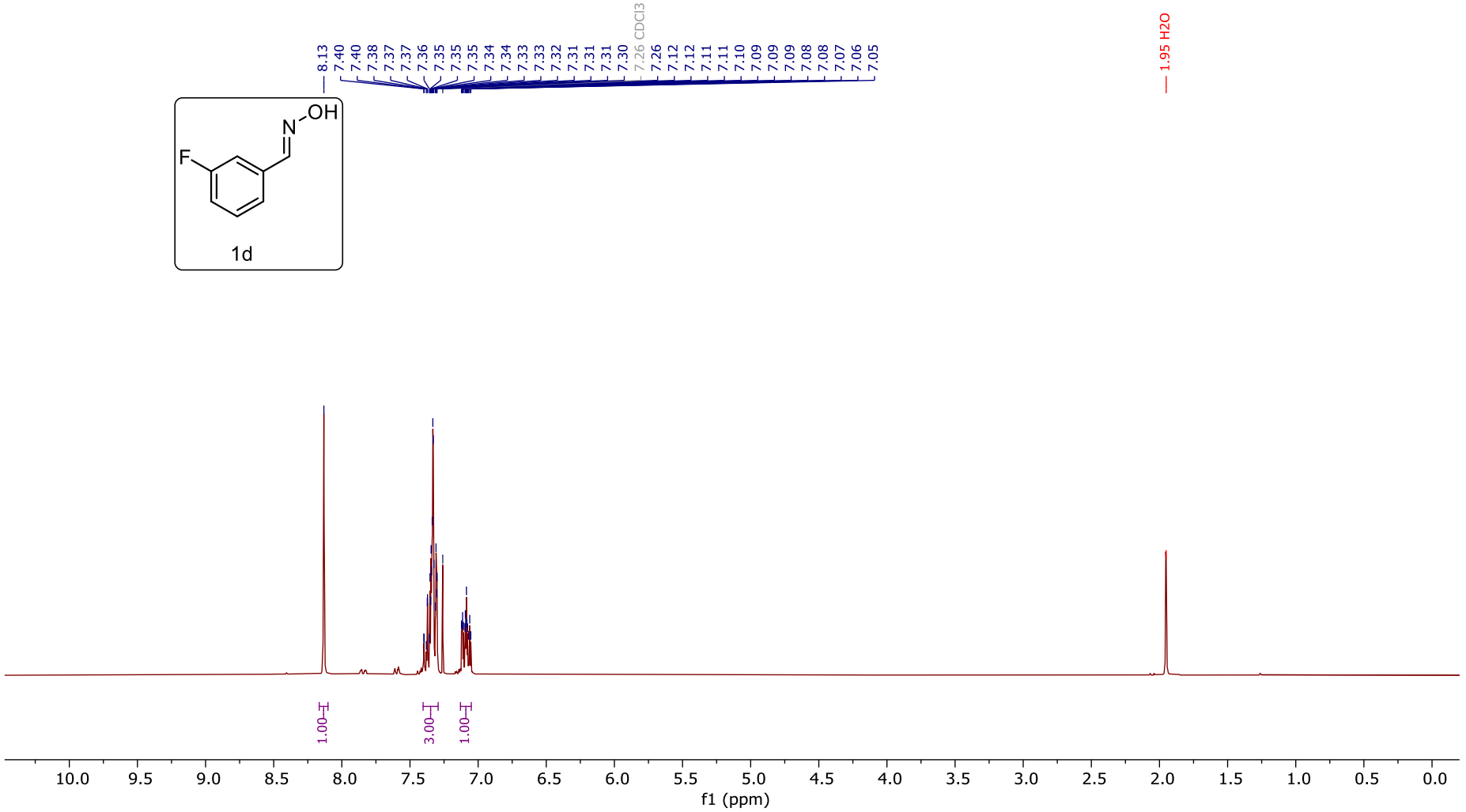
f1 (ppm)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7.06
7.05
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N
OH
F
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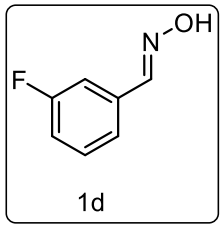
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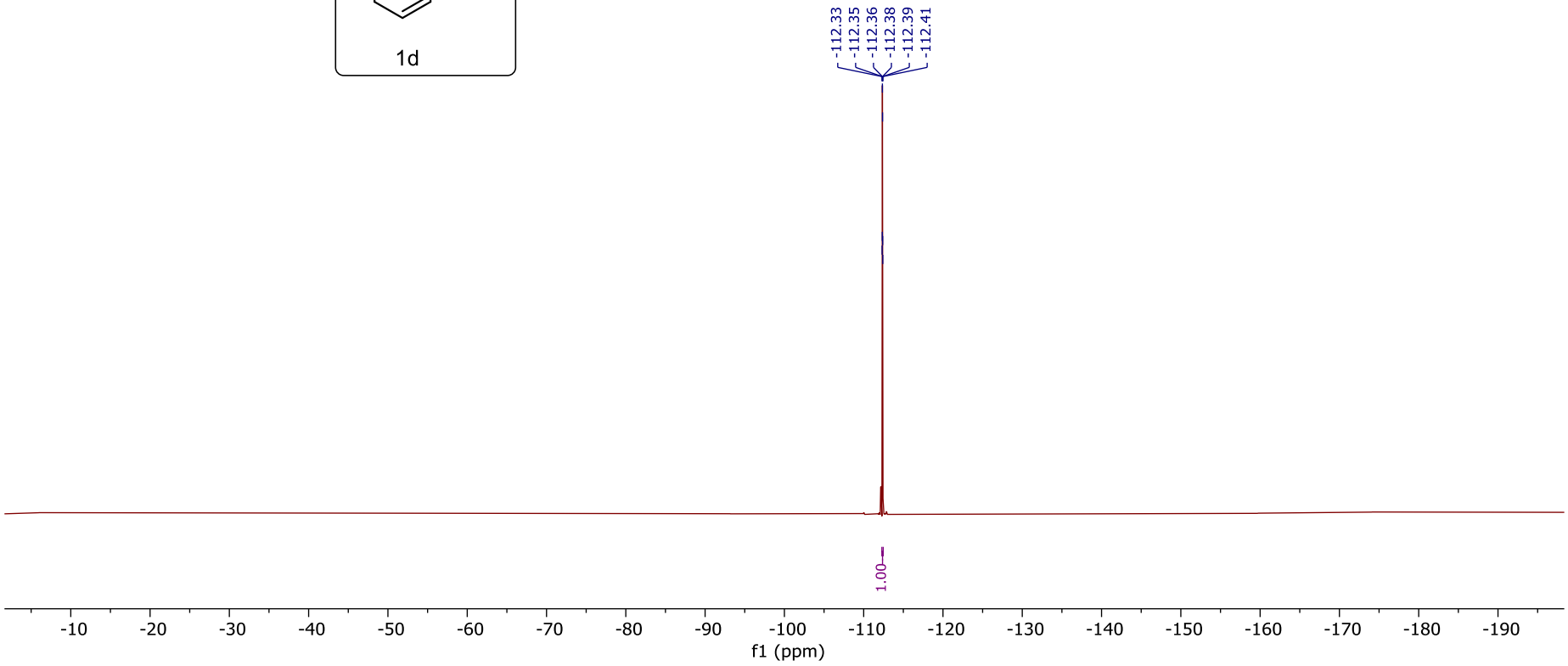
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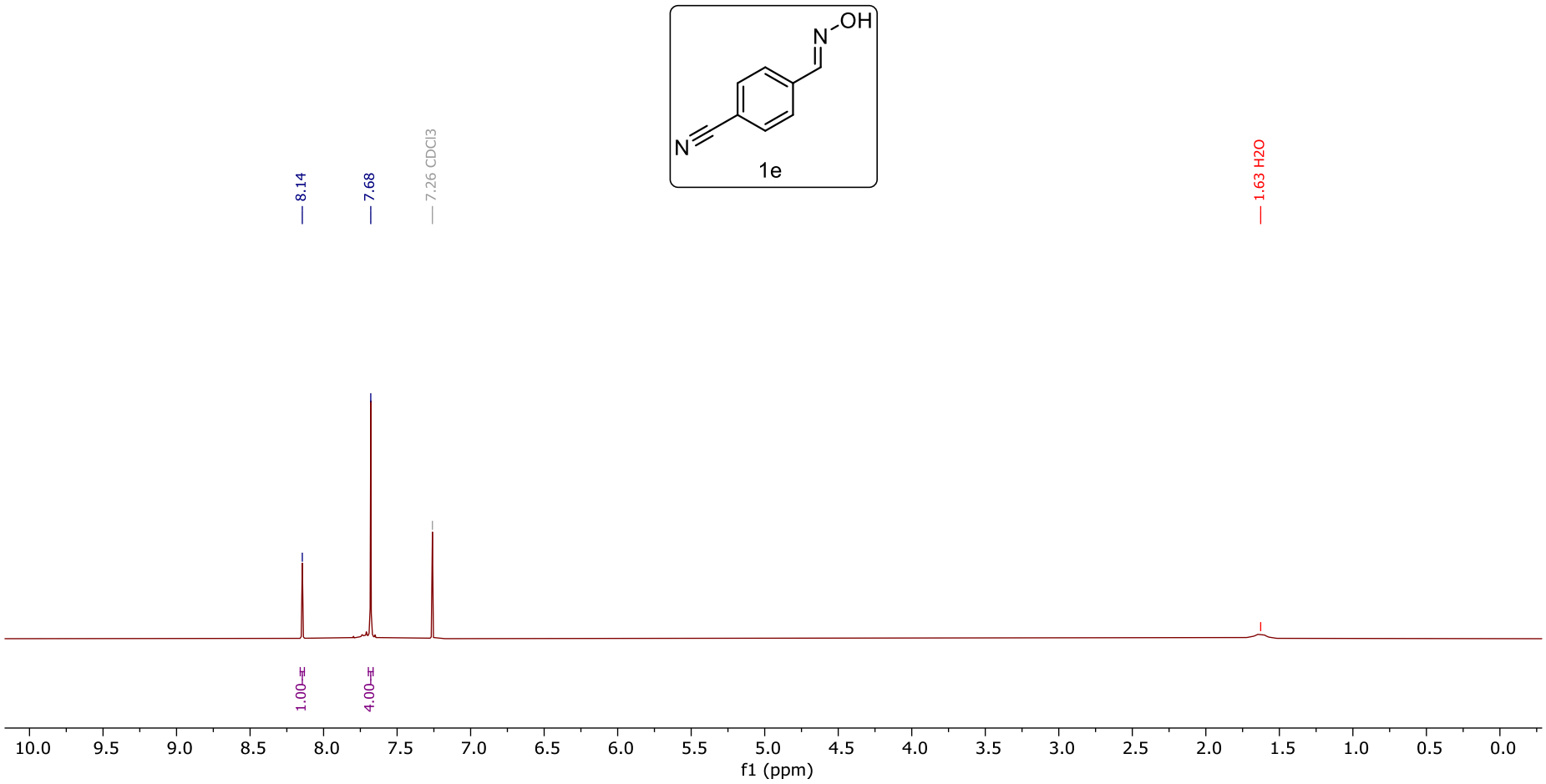
f1 (ppm)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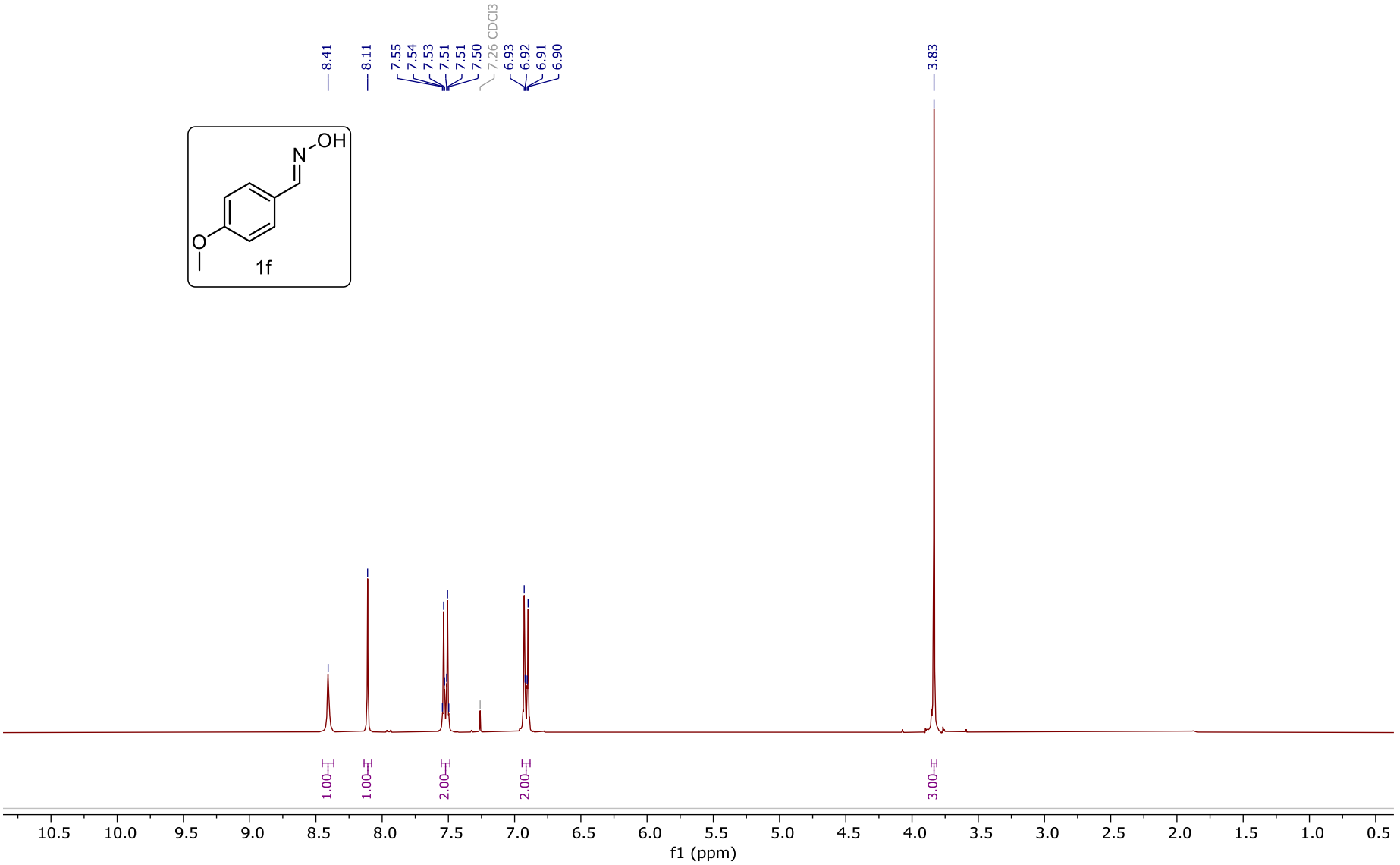
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3.00
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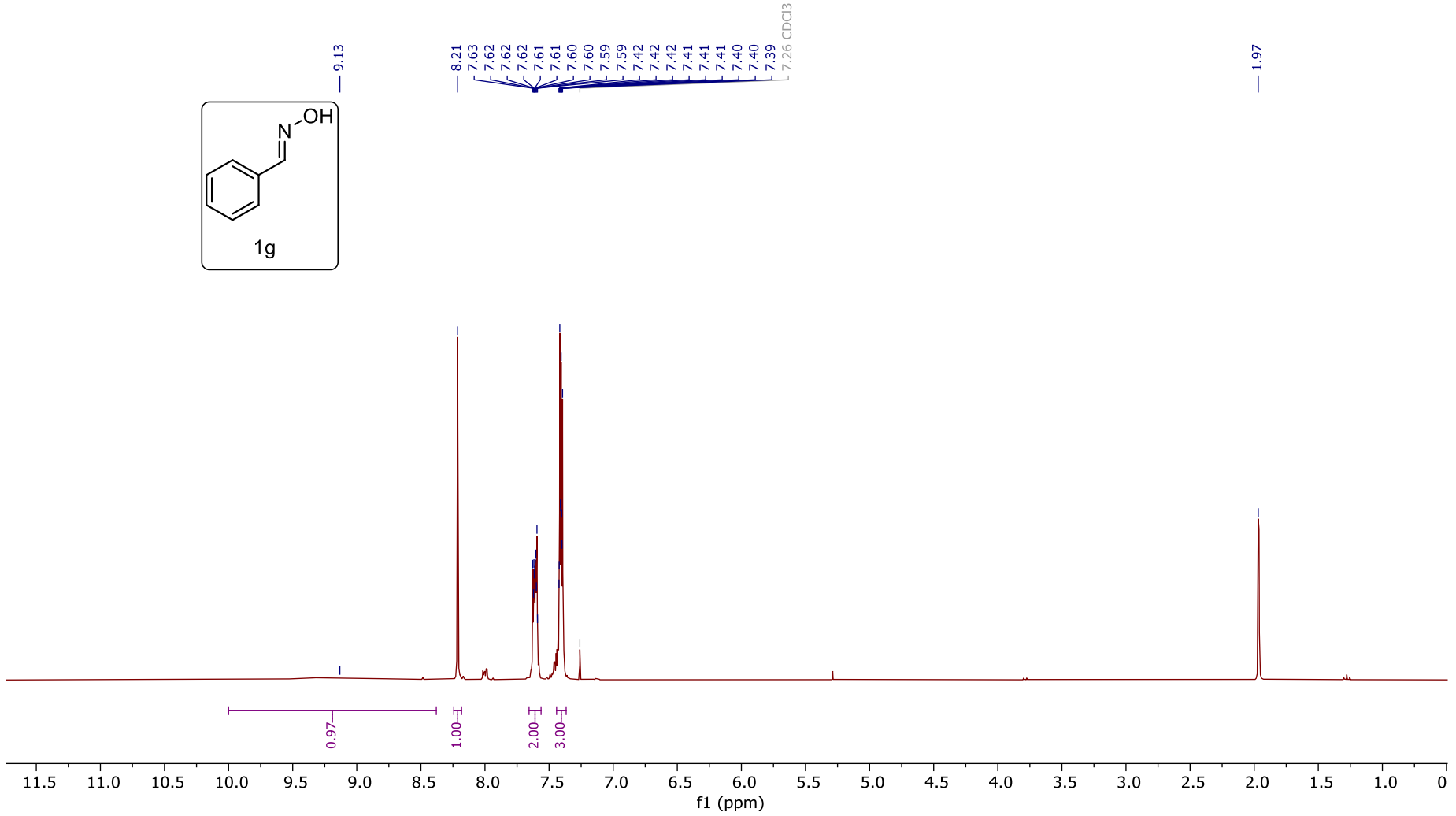
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7.41
7.41
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7.40
7.39
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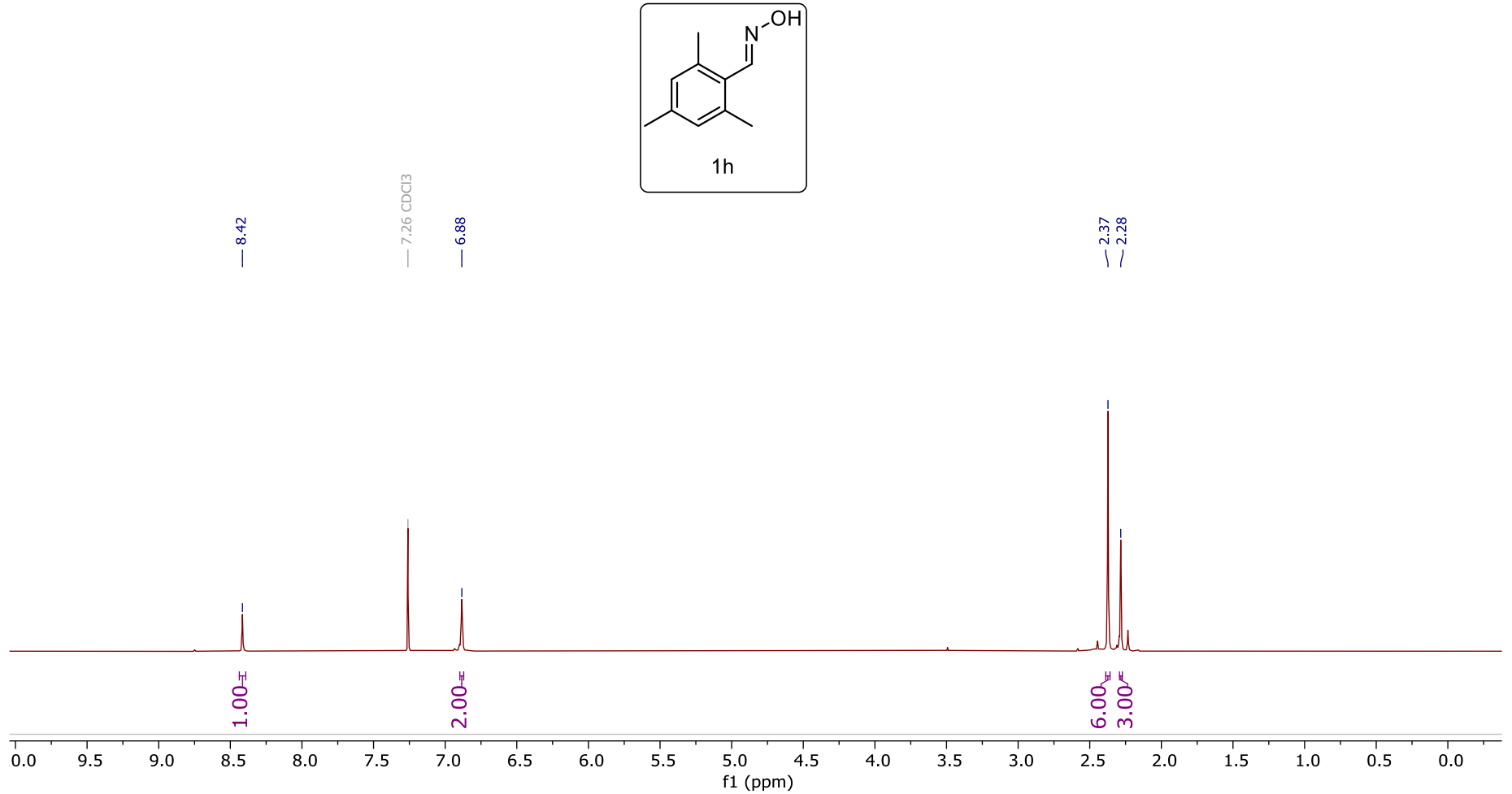
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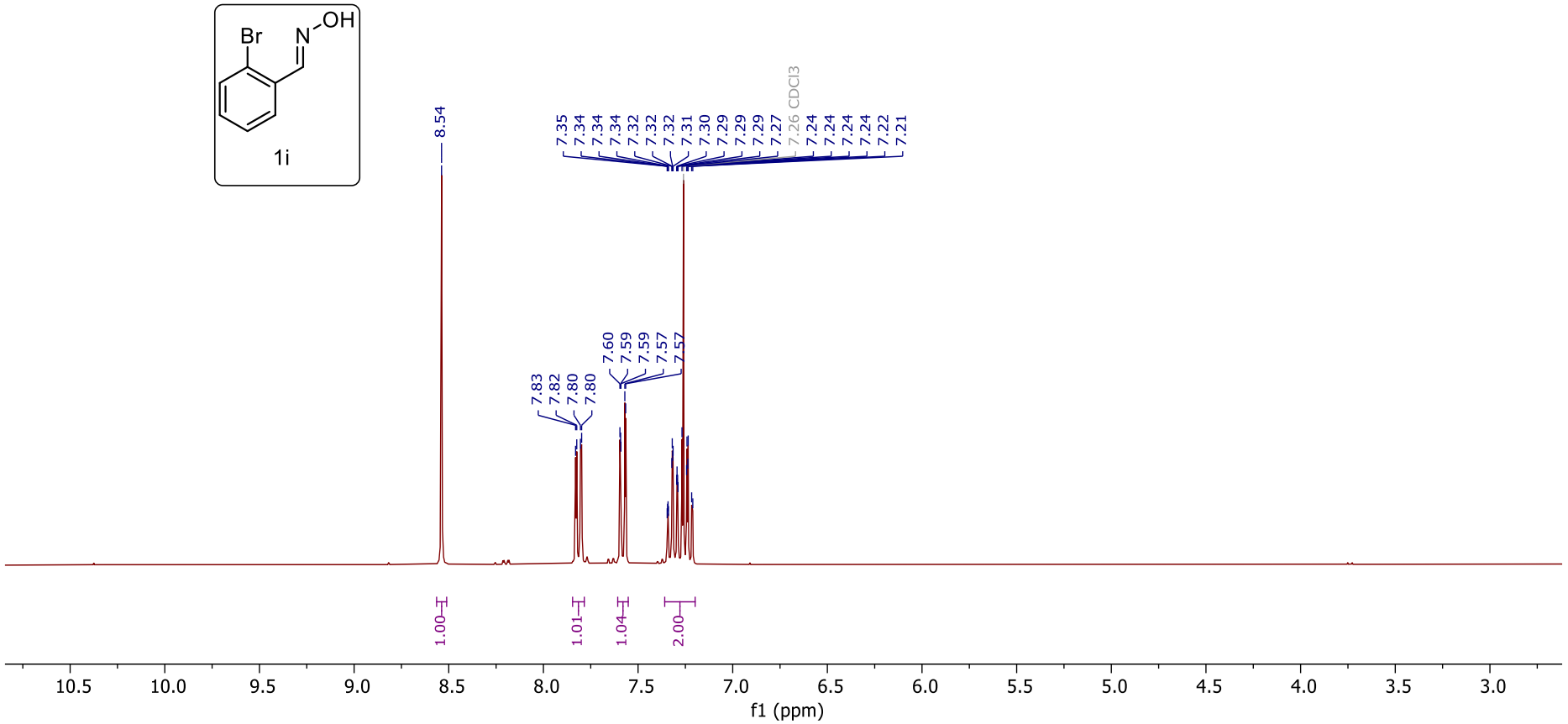
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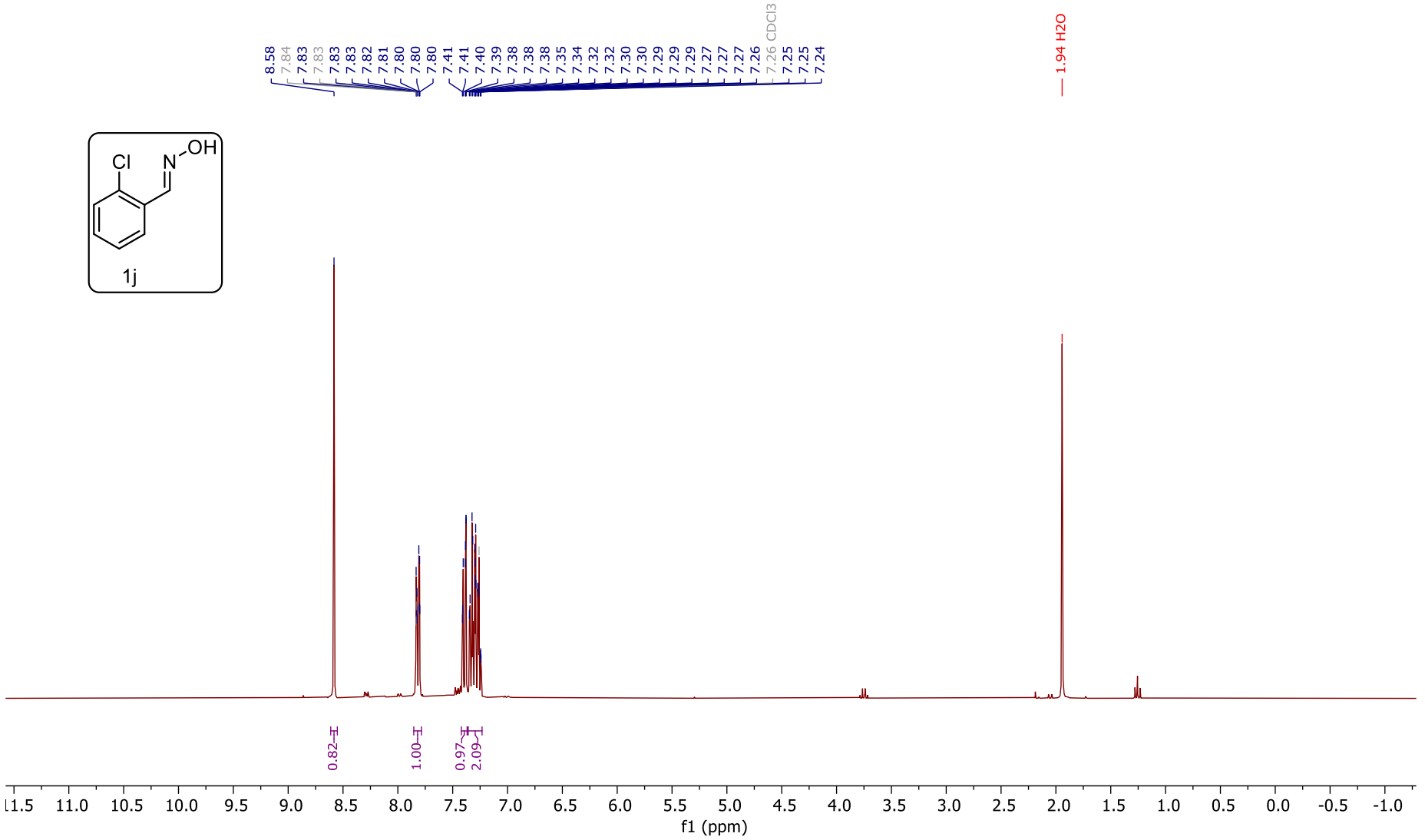
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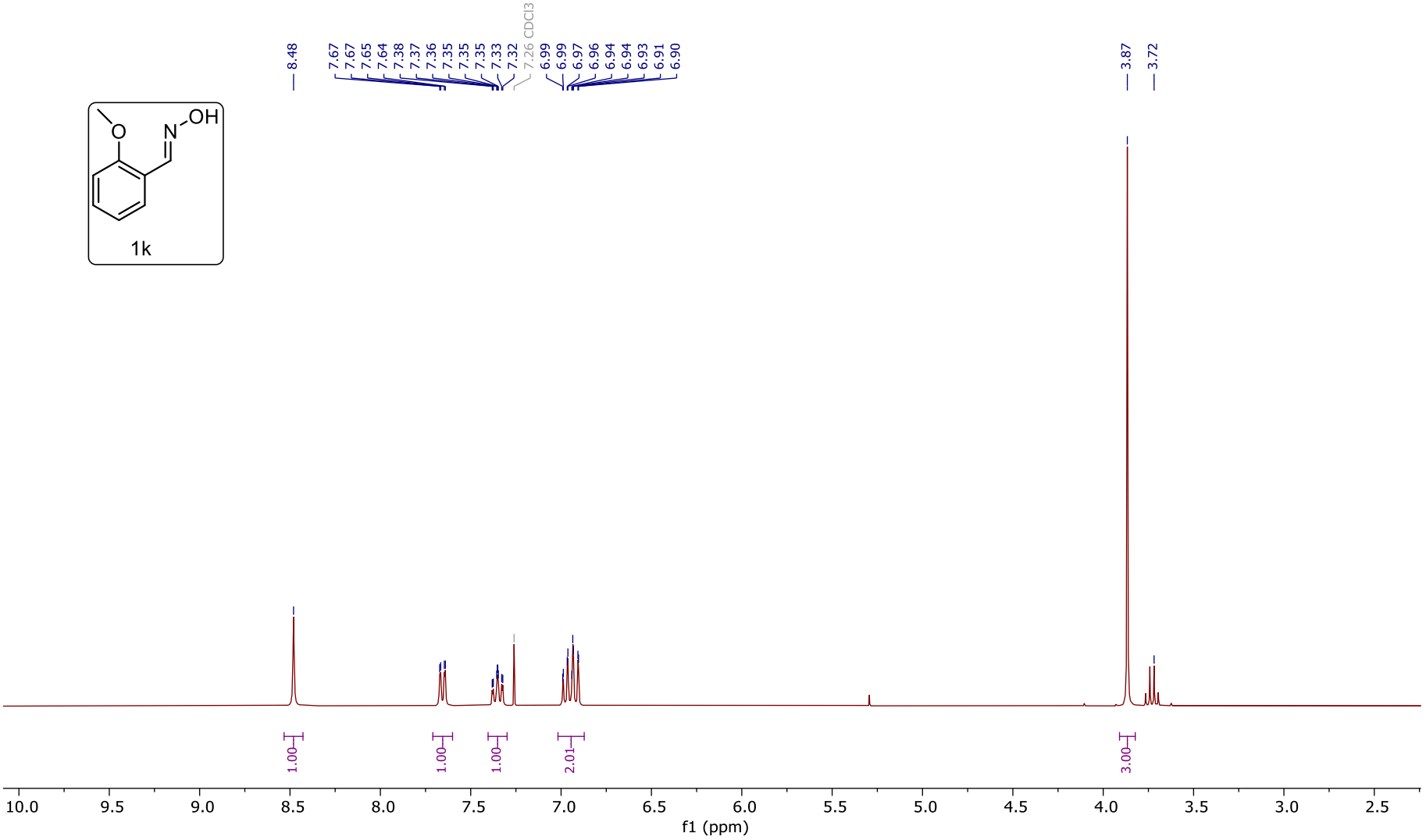
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OH
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1.00
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2.5
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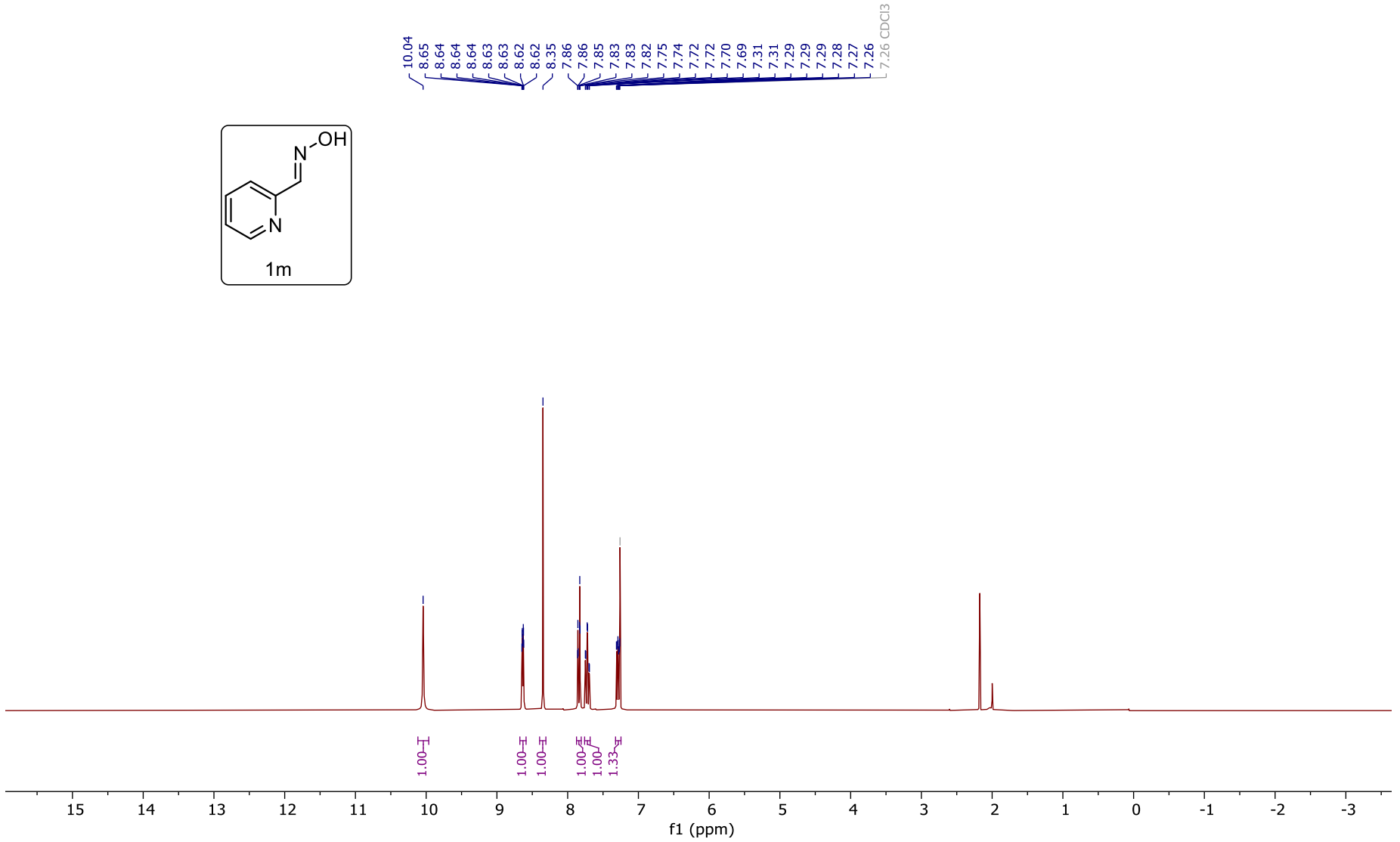
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7.26 CDCl3
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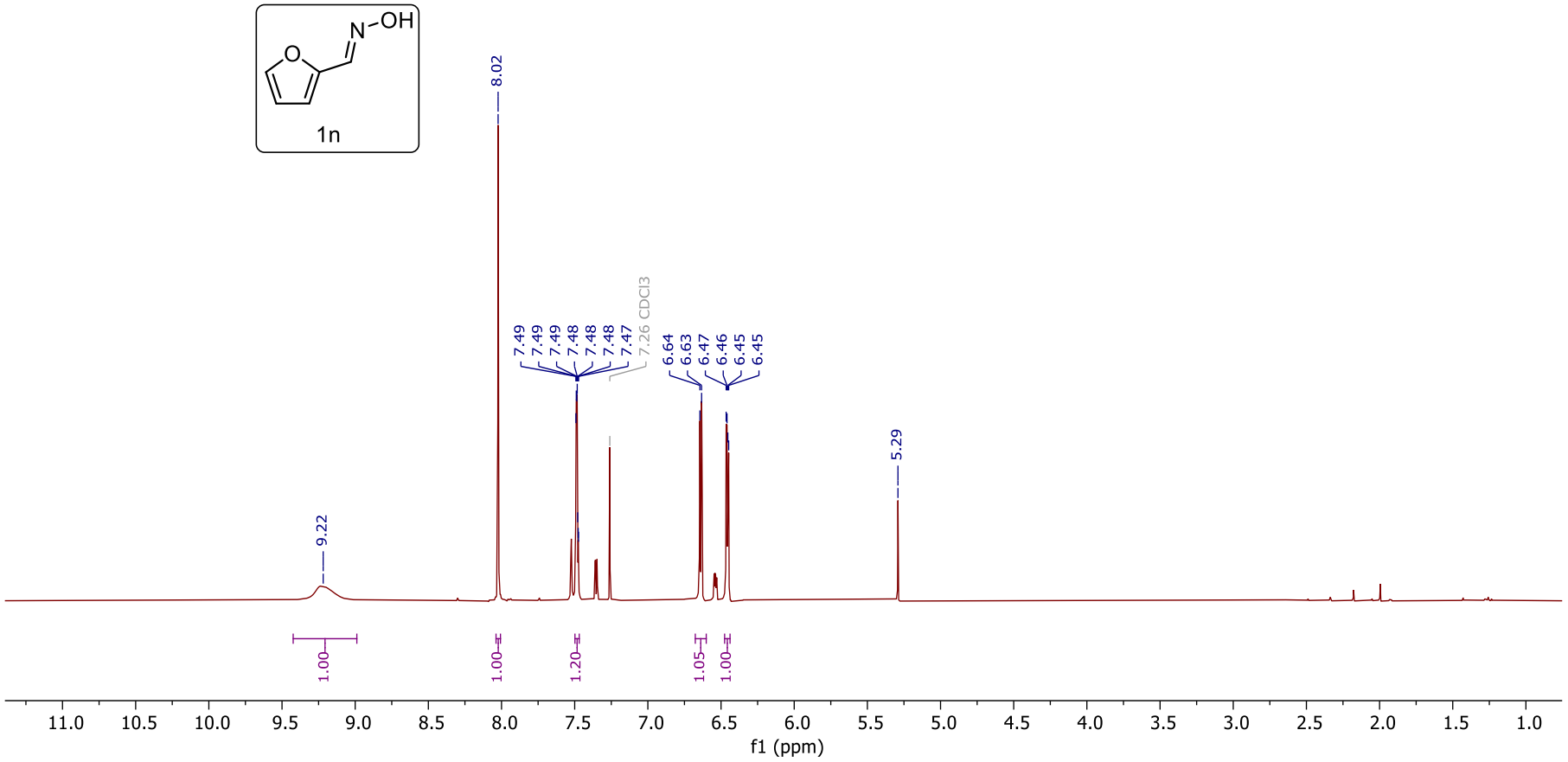
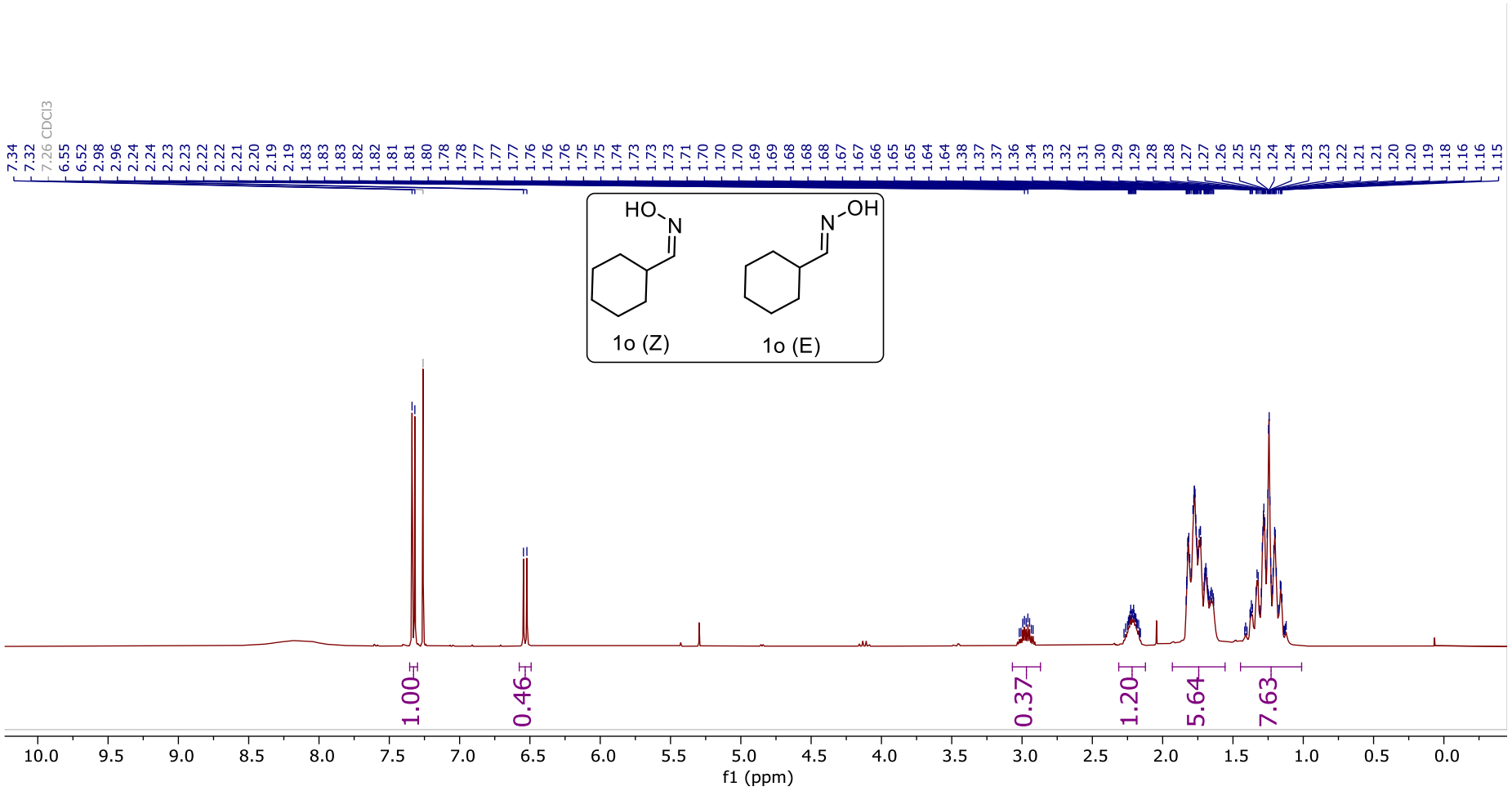
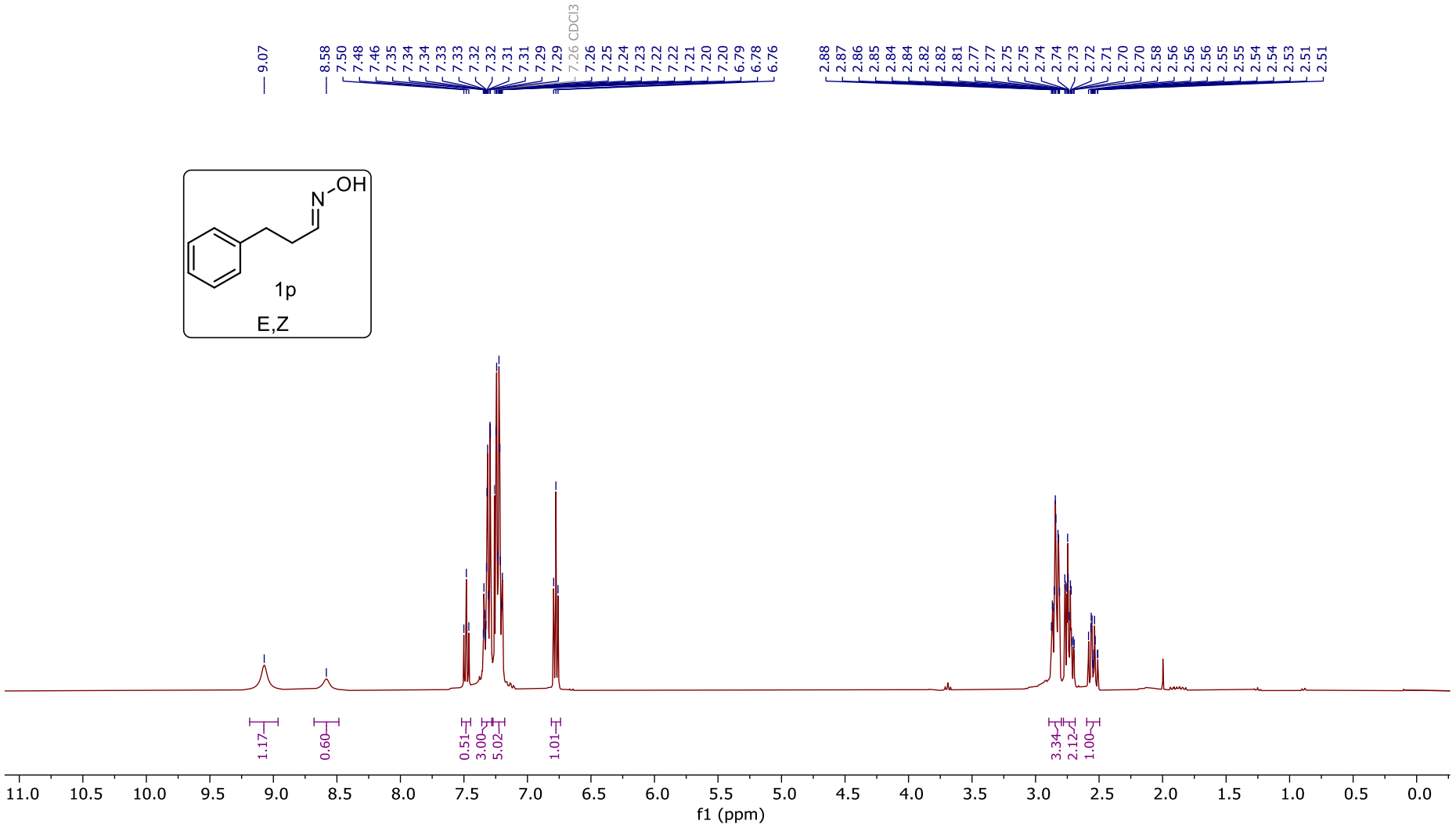
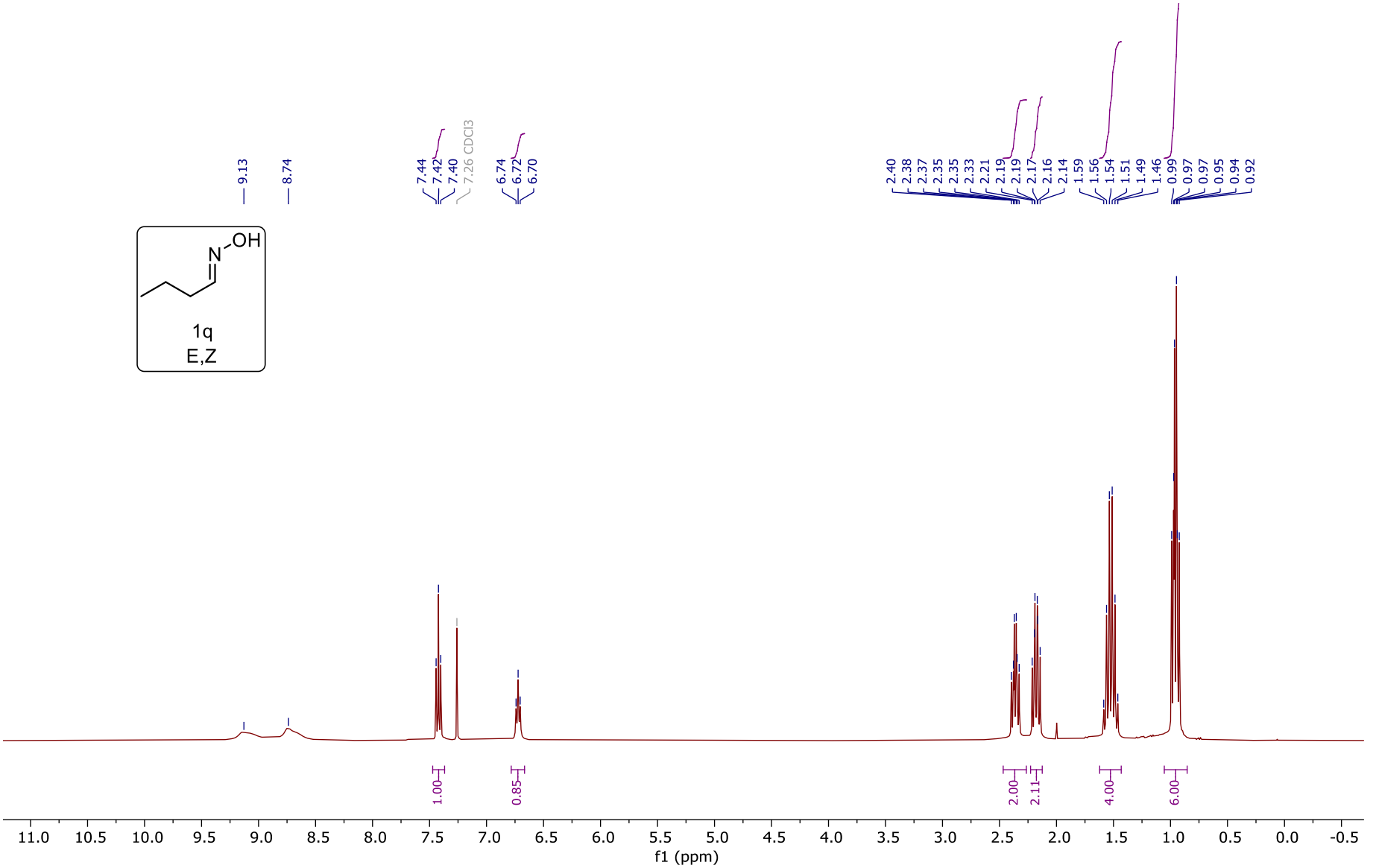
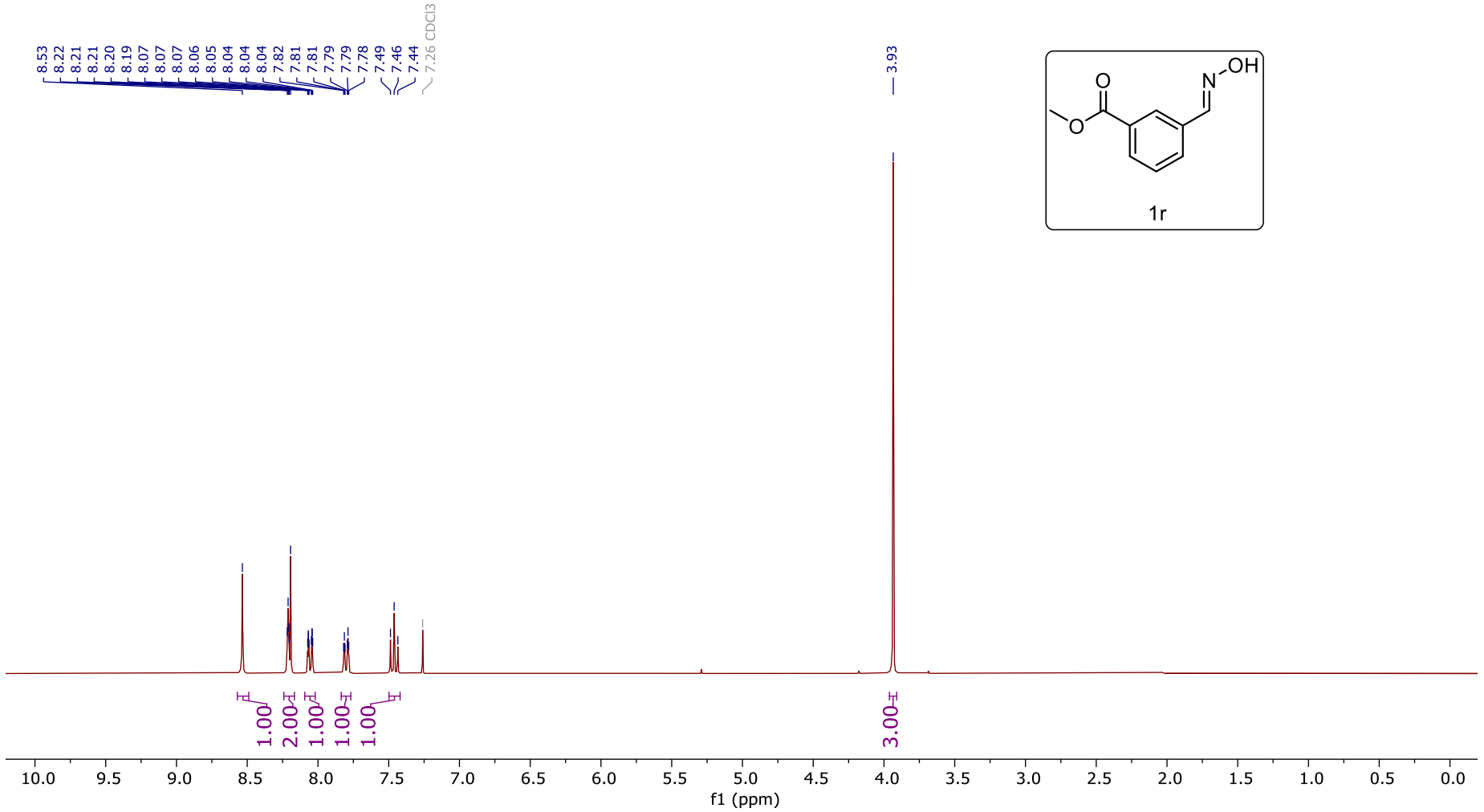
1m
1.00
1.00
1.00
1.00
1.00
1.33
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

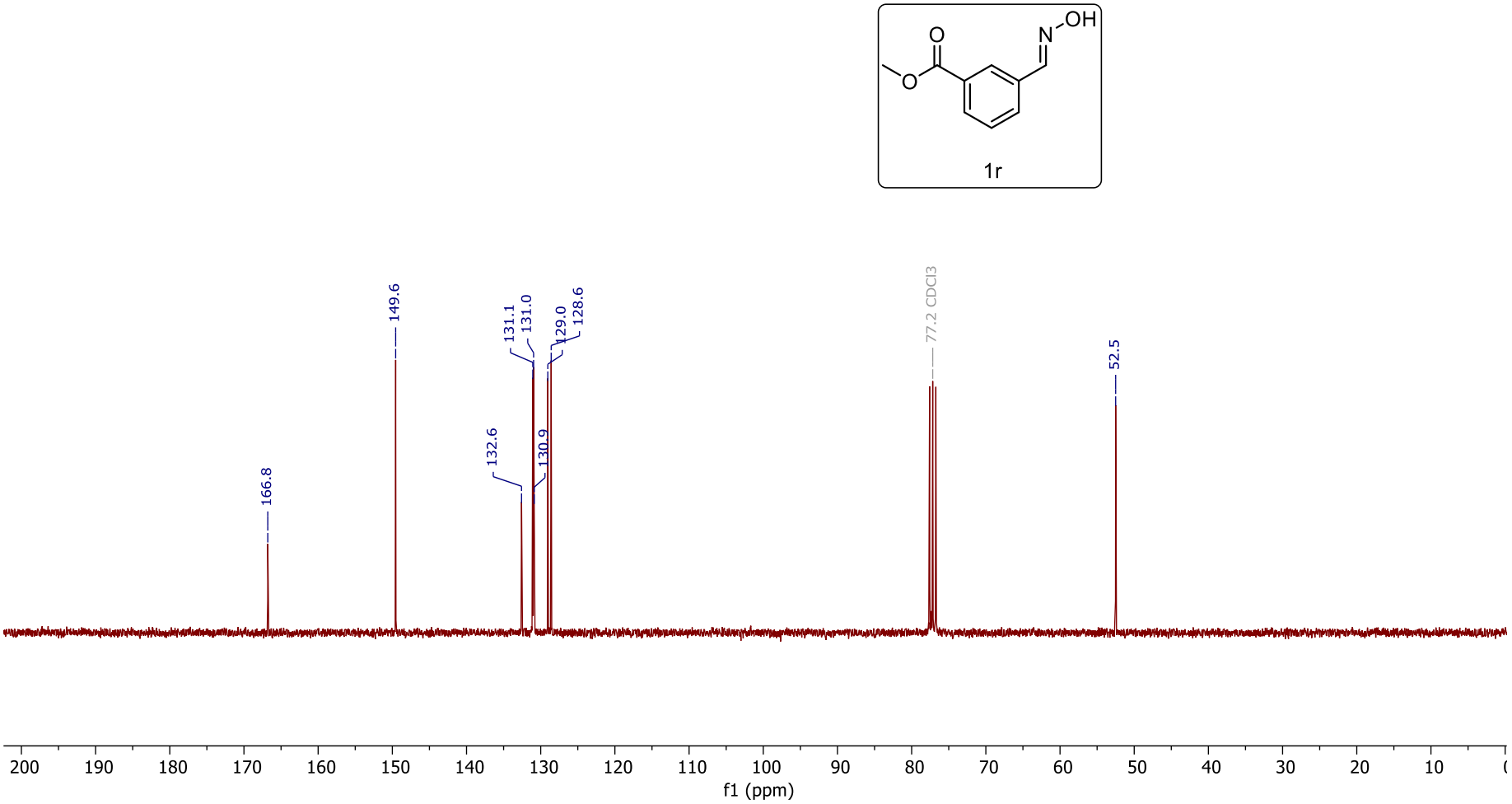

N-OH
O
1n
8.02
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.26 CDCl3
6.64
6.63
6.47
6.46
6.45
6.45
5.29
9.22
1.00
1.00
1.20
1.05
1.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

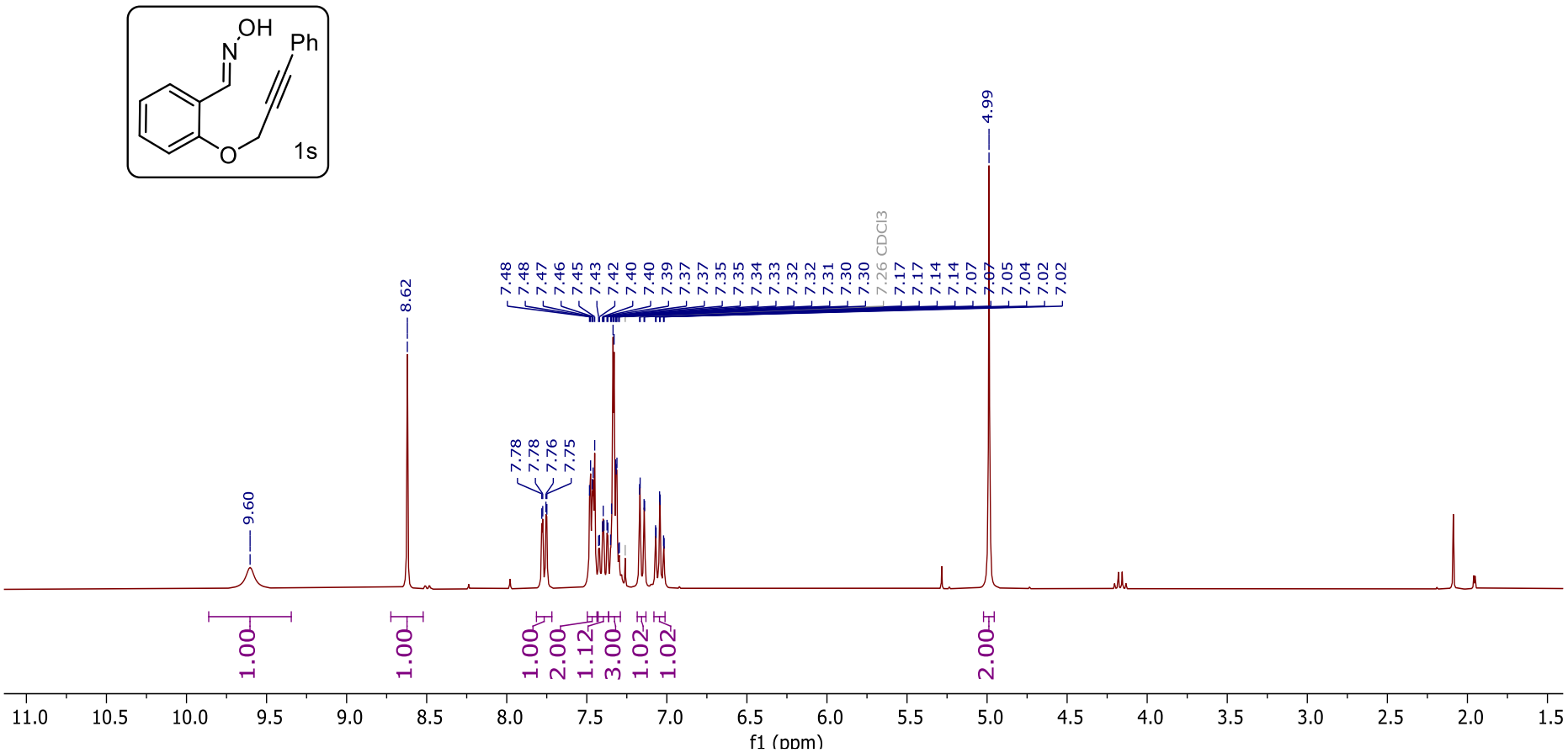

7.34
7.32
7.26 CDCl3
6.55
6.52
2.98
2.96
2.24
2.24
2.23
2.23
2.22
2.22
2.21
2.20
2.19
2.19
1.83
1.83
1.83
1.82
1.82
1.81
1.81
1.80
1.78
1.78
1.77
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.73
1.73
1.73
1.71
1.70
1.70
1.70
1.69
1.69
1.68
1.68
1.68
1.67
1.67
1.66
1.65
1.65
1.64
1.64
1.38
1.37
1.37
1.36
1.34
1.33
1.32
1.31
1.30
1.29
1.29
1.28
1.28
1.27
1.27
1.26
1.25
1.25
1.24
1.24
1.23
1.23
1.22
1.21
1.21
1.20
1.20
1.19
1.18
1.16
1.16
1.15
HO
N
N
OH
1o (Z)
1o (E)
1.00
0.46
0.37
1.20
5.64
7.63
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)

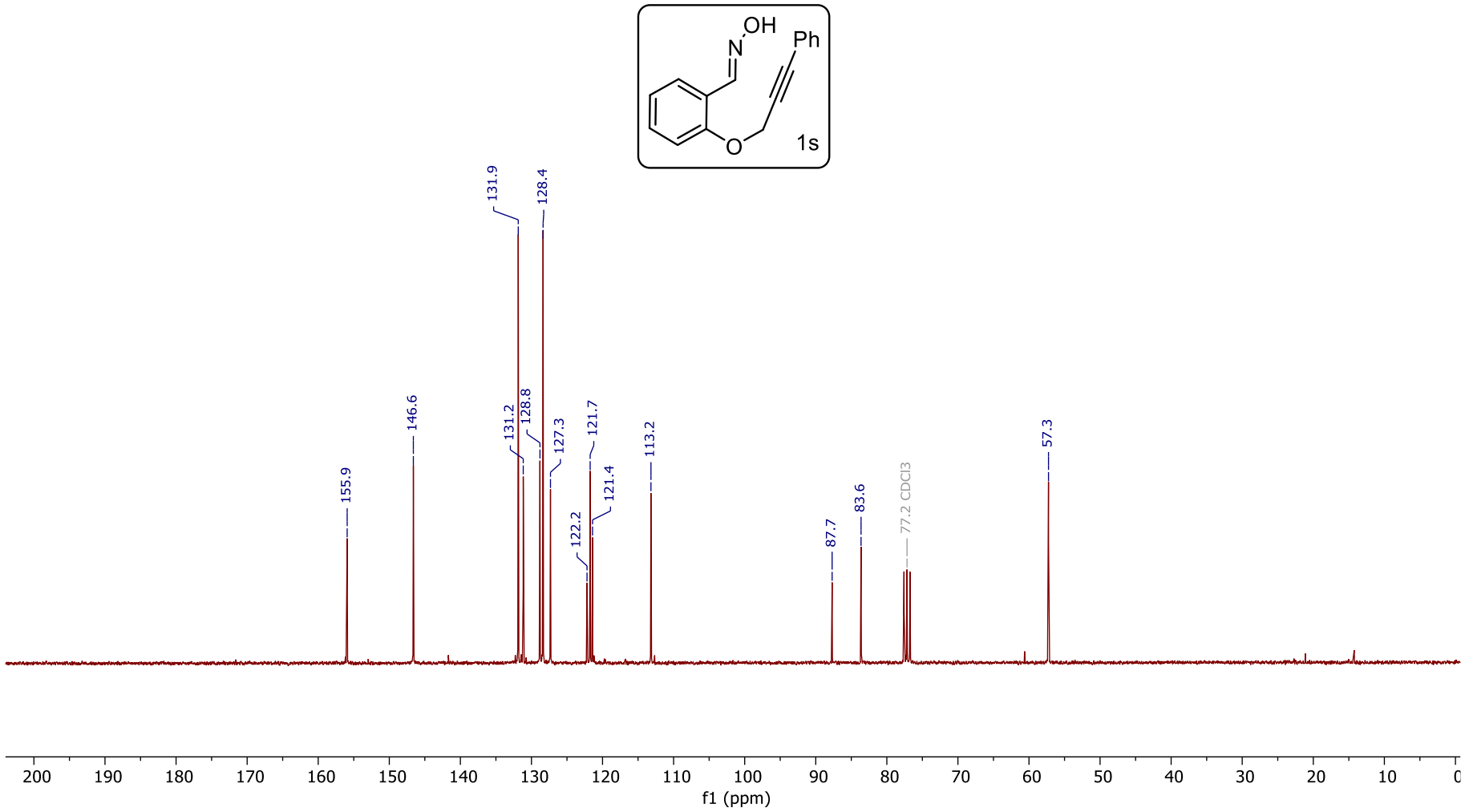

9.07
8.58
7.50
7.48
7.46
7.35
7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.29
7.29
7.26 CDCl3
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.20
6.79
6.78
6.76
2.88
2.87
2.86
2.85
2.84
2.84
2.82
2.82
2.81
2.77
2.77
2.75
2.75
2.74
2.74
2.73
2.72
2.71
2.70
2.70
2.58
2.56
2.56
2.56
2.55
2.55
2.54
2.54
2.53
2.51
2.51
N
OH
1p
E,Z
1.17
0.60
0.51
3.00
5.02
1.01
3.34
2.12
1.00
11.0
10.5
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)

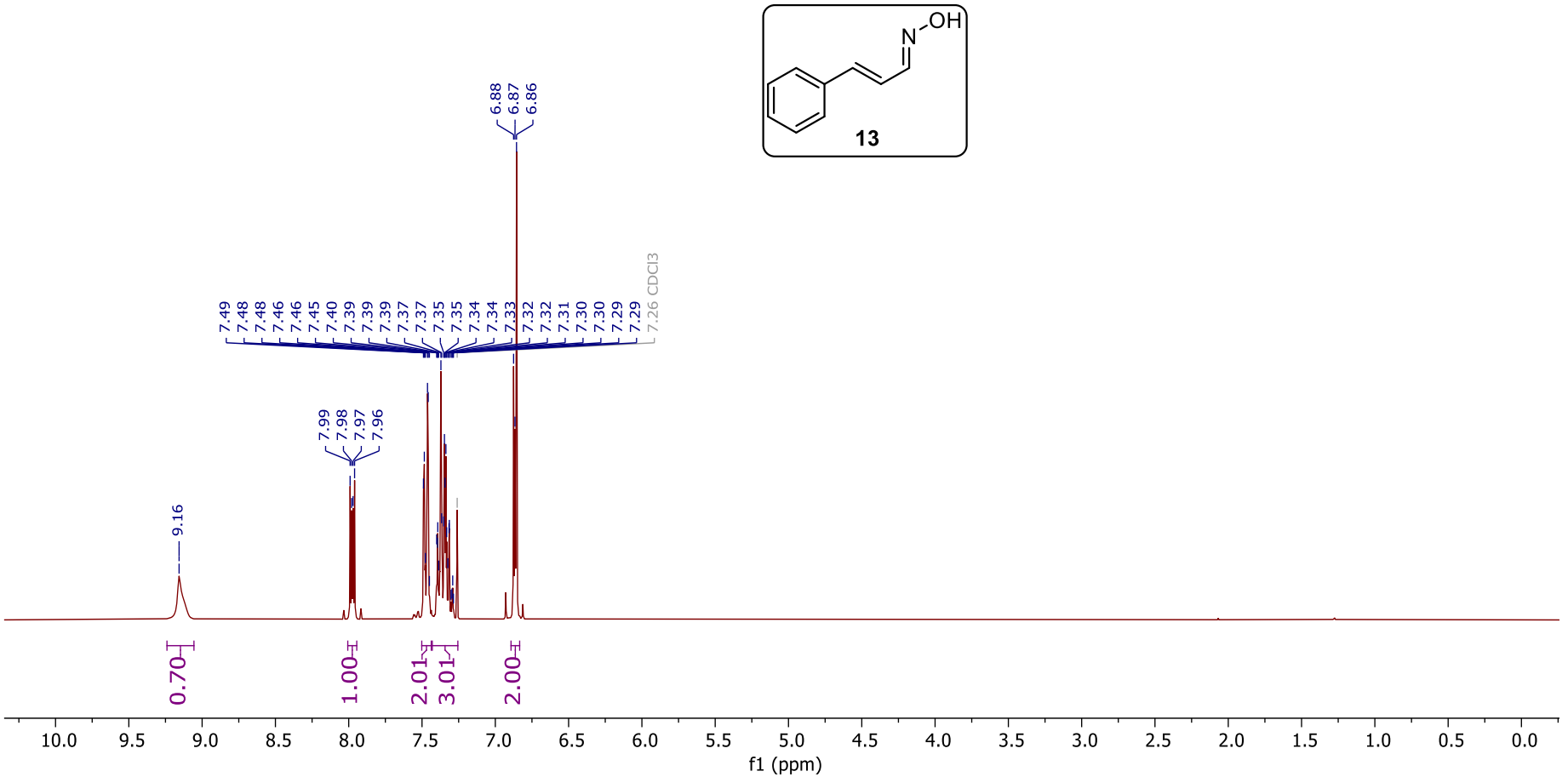

9.13
8.74
7.44
7.42
7.40
7.26 CDCl3
6.74
6.72
6.70
2.40
2.38
2.37
2.35
2.35
2.33
2.21
2.19
2.19
2.17
2.16
2.14
1.59
1.56
1.54
1.51
1.49
1.46
0.99
0.97
0.97
0.95
0.94
0.92
OH
N
1q
E,Z
1.00
0.85
2.00
2.11
4.00
6.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

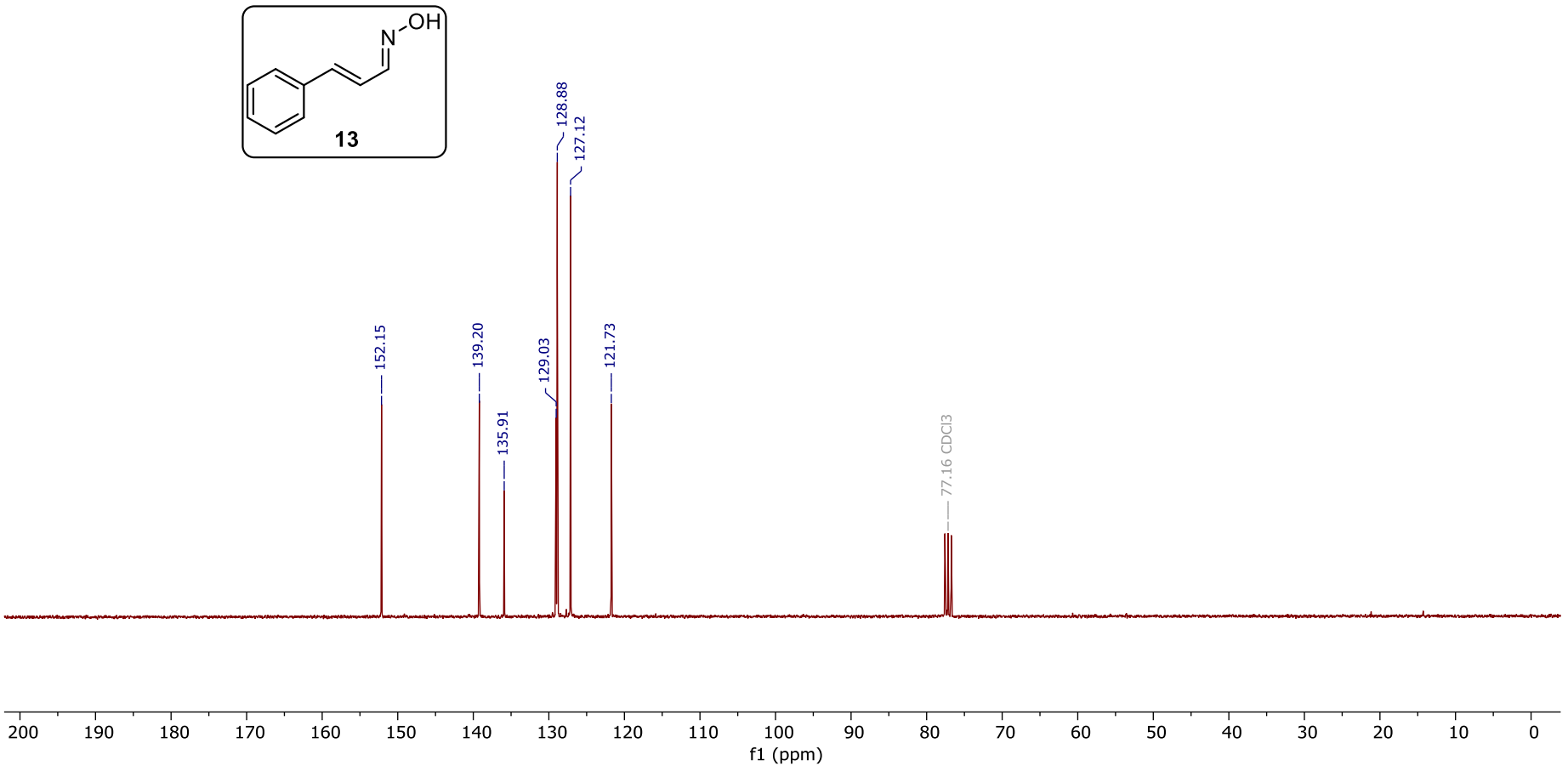

8.53
8.22
8.21
8.21
8.20
8.19
8.07
8.07
8.07
8.06
8.05
8.04
8.04
8.04
7.82
7.81
7.81
7.79
7.79
7.78
7.49
7.46
7.44
7.26 CDCl3
3.93
O
N
OH
O
1r
1.00
2.00
1.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

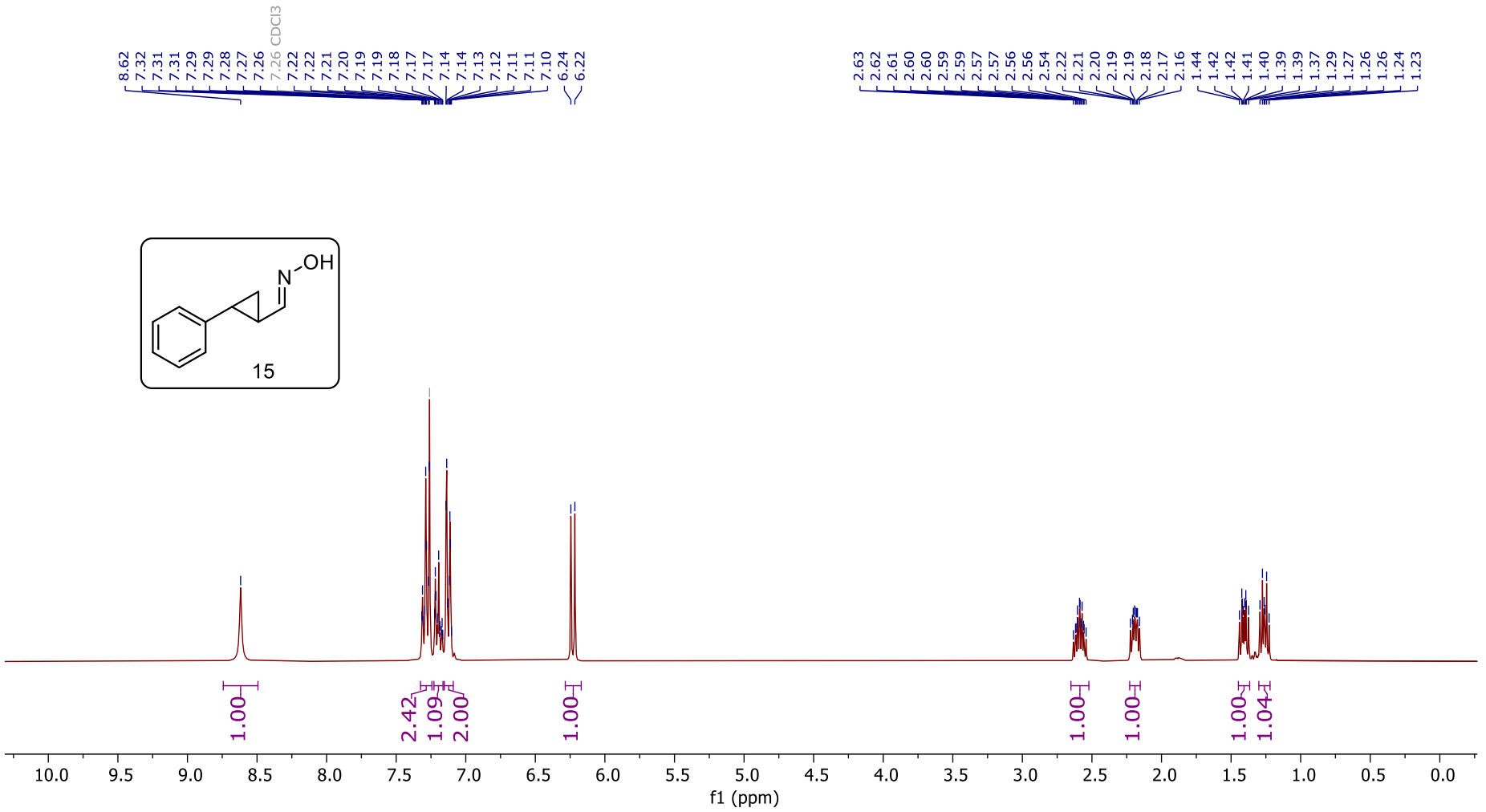

1r
166.8
149.6
132.6
131.1
131.0
130.9
129.0
128.6
77.2 CDCl3
52.5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

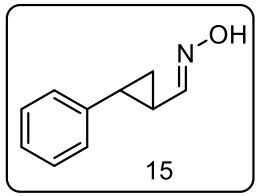

OH
N
Ph
O
1s
9.60
8.62
7.78
7.78
7.76
7.75
7.48
7.48
7.47
7.46
7.45
7.43
7.42
7.40
7.40
7.39
7.37
7.37
7.35
7.35
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.26 CDCl3
7.17
7.17
7.14
7.14
7.07
7.07
7.05
7.04
7.02
7.02
4.99
1.00
1.00
1.00
2.00
1.12
3.00
1.02
1.02
2.00
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

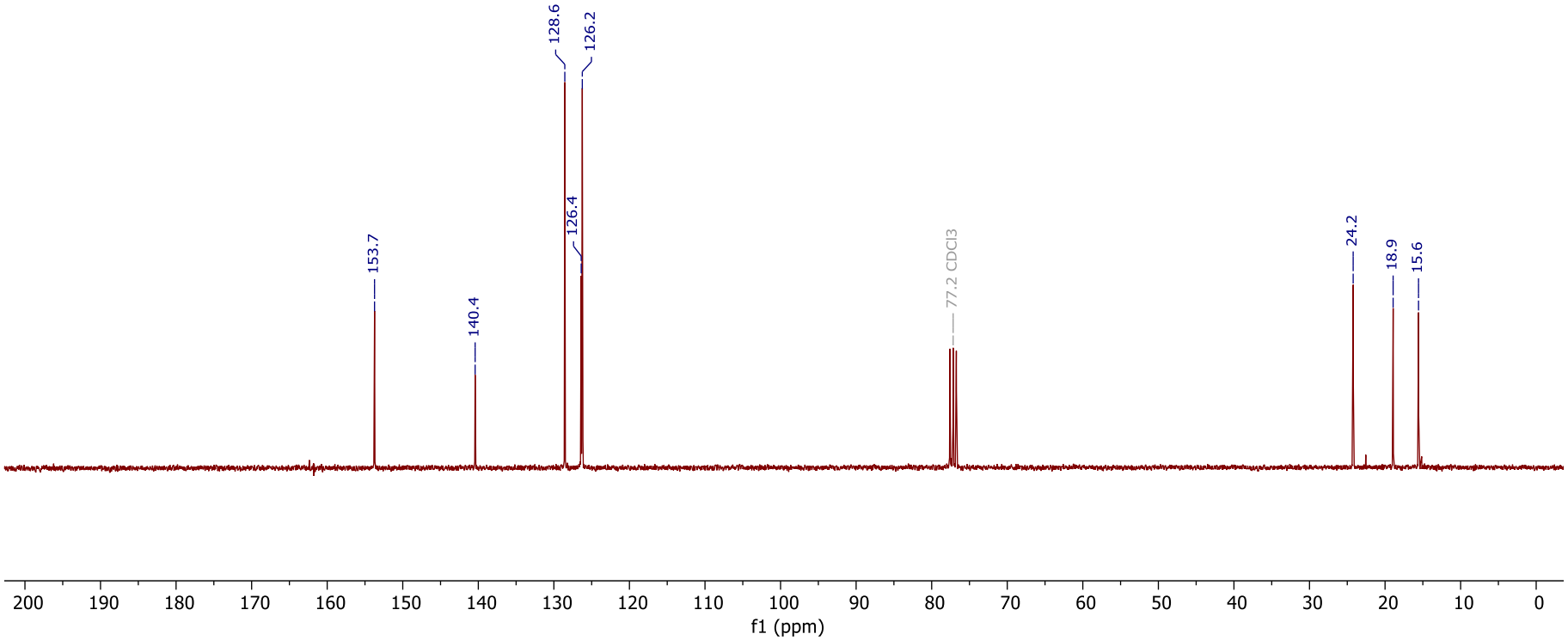

OH
N
Ph
O
1s
155.9
146.6
131.9
131.2
128.8
128.4
127.3
122.2
121.7
121.4
113.2
87.7
83.6
77.2 CDCl3
57.3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

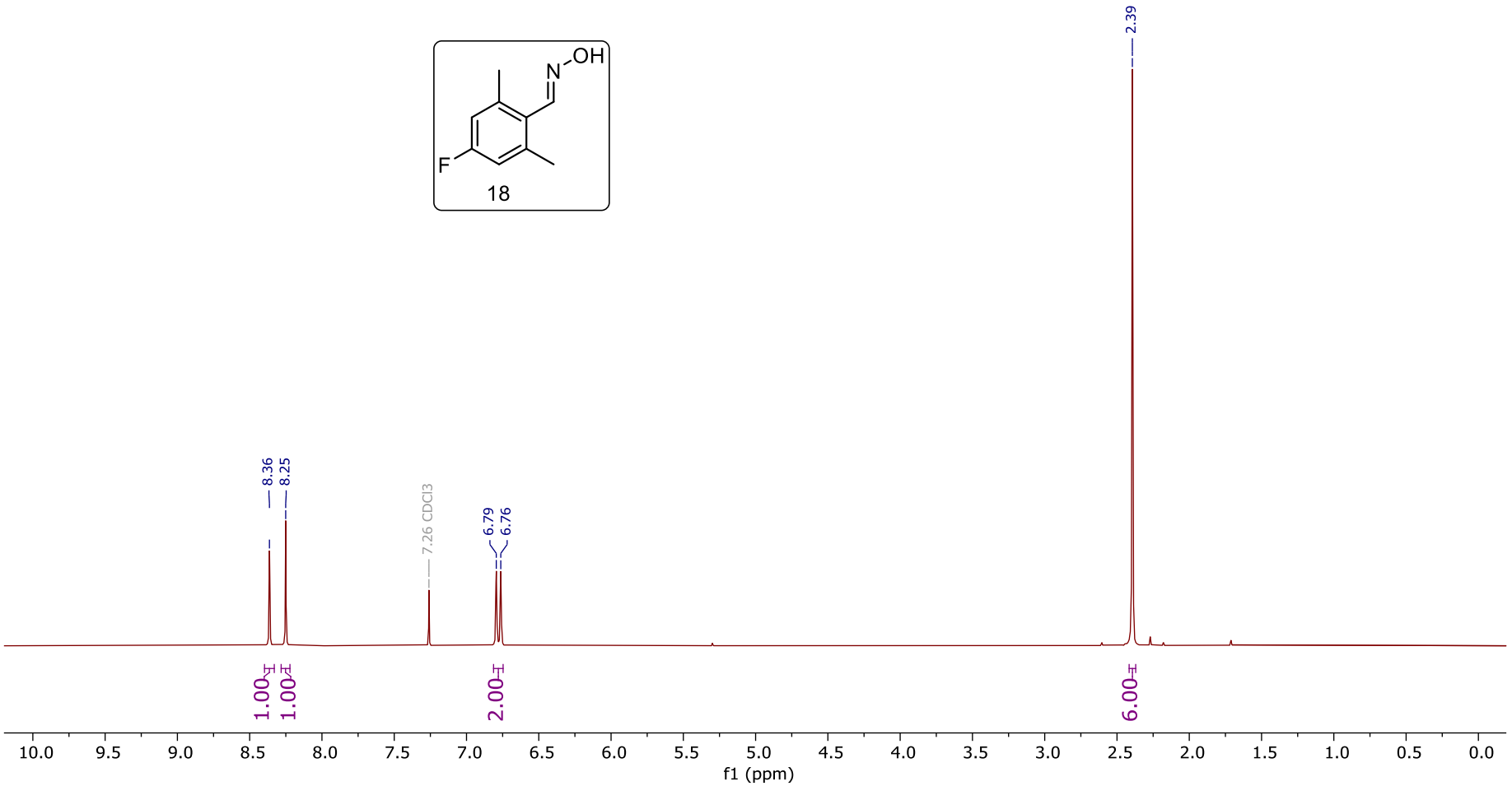

OH
N
13
6.88
6.87
6.86
7.49
7.48
7.48
7.46
7.46
7.45
7.40
7.39
7.39
7.39
7.37
7.37
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.26 CDCl3
7.99
7.98
7.97
7.96
9.16
0.70
1.00
2.01
3.01
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

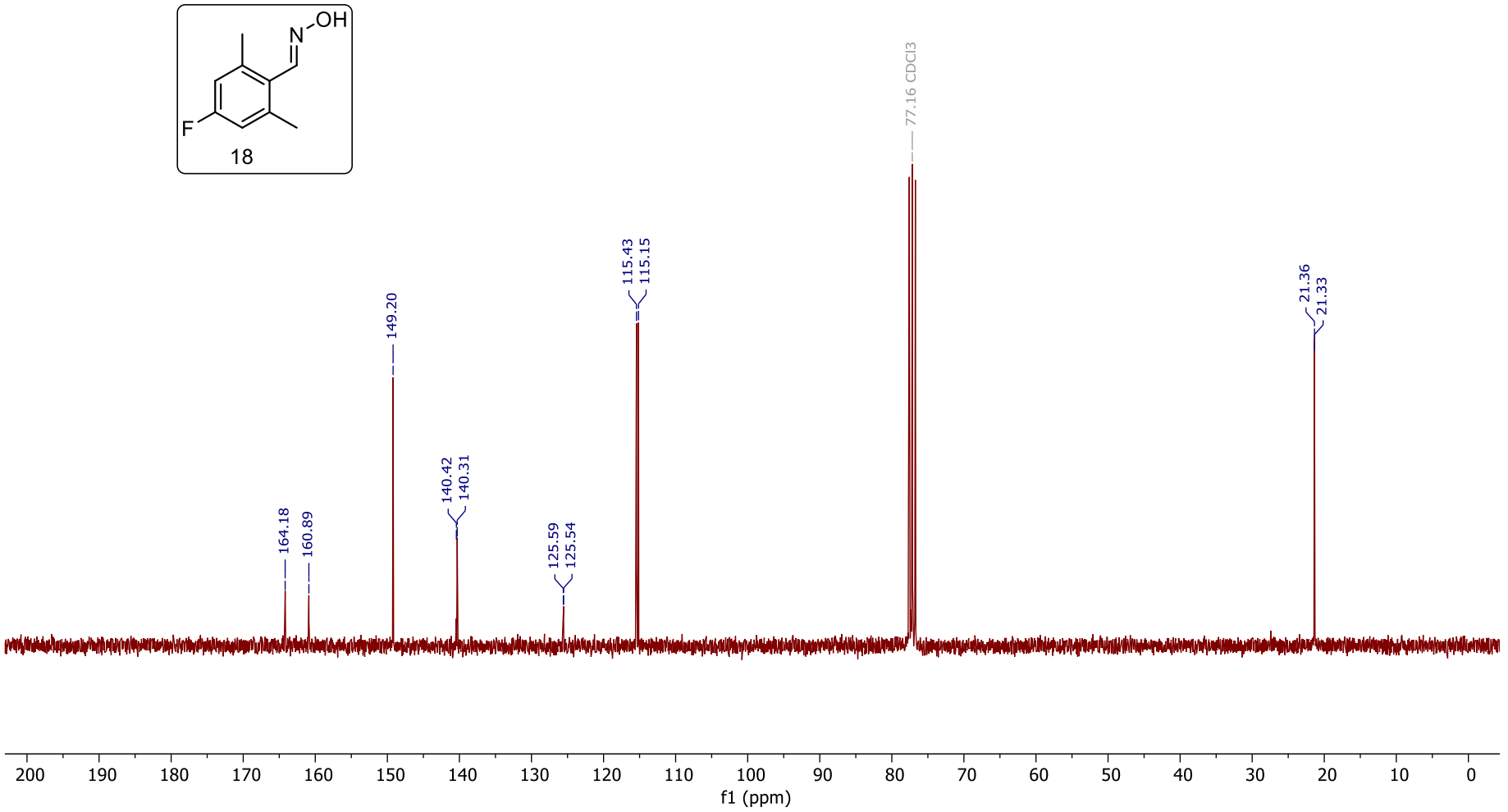

OH
N
13
152.15
139.20
135.91
129.03
128.88
127.12
121.73
77.16 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

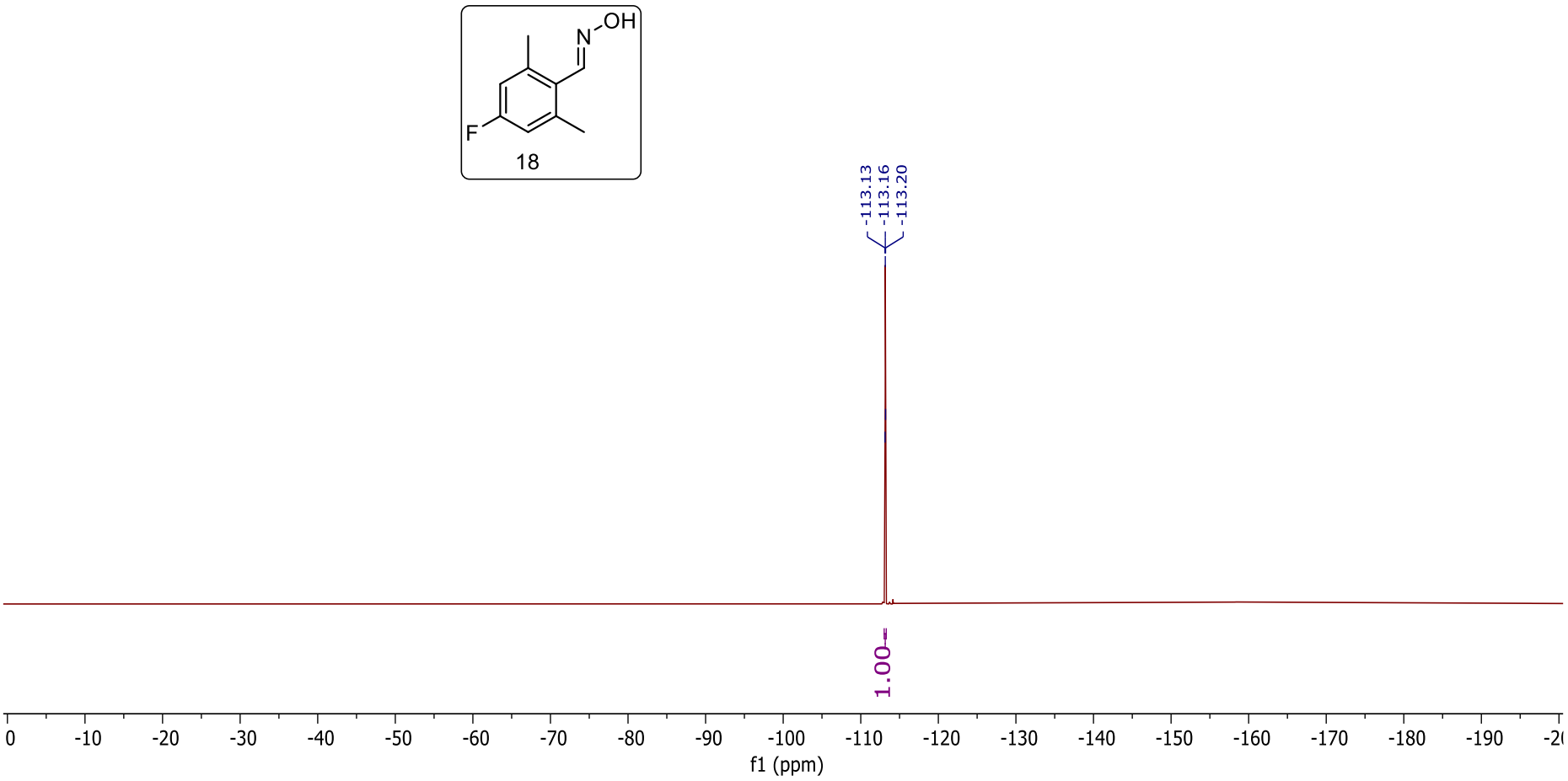

8.62
7.32
7.31
7.31
7.29
7.29
7.28
7.27
7.26
7.26 CDCl3
7.22
7.22
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.14
7.14
7.13
7.12
7.11
7.11
7.10
6.24
6.22
2.63
2.62
2.61
2.60
2.60
2.59
2.59
2.57
2.57
2.56
2.56
2.54
2.22
2.21
2.20
2.19
2.19
2.18
2.17
2.16
1.44
1.42
1.42
1.41
1.40
1.39
1.39
1.37
1.29
1.27
1.26
1.26
1.24
1.23
N
OH
15
1.00
2.42
1.09
2.00
1.00
1.00
1.00
1.00
1.04
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)

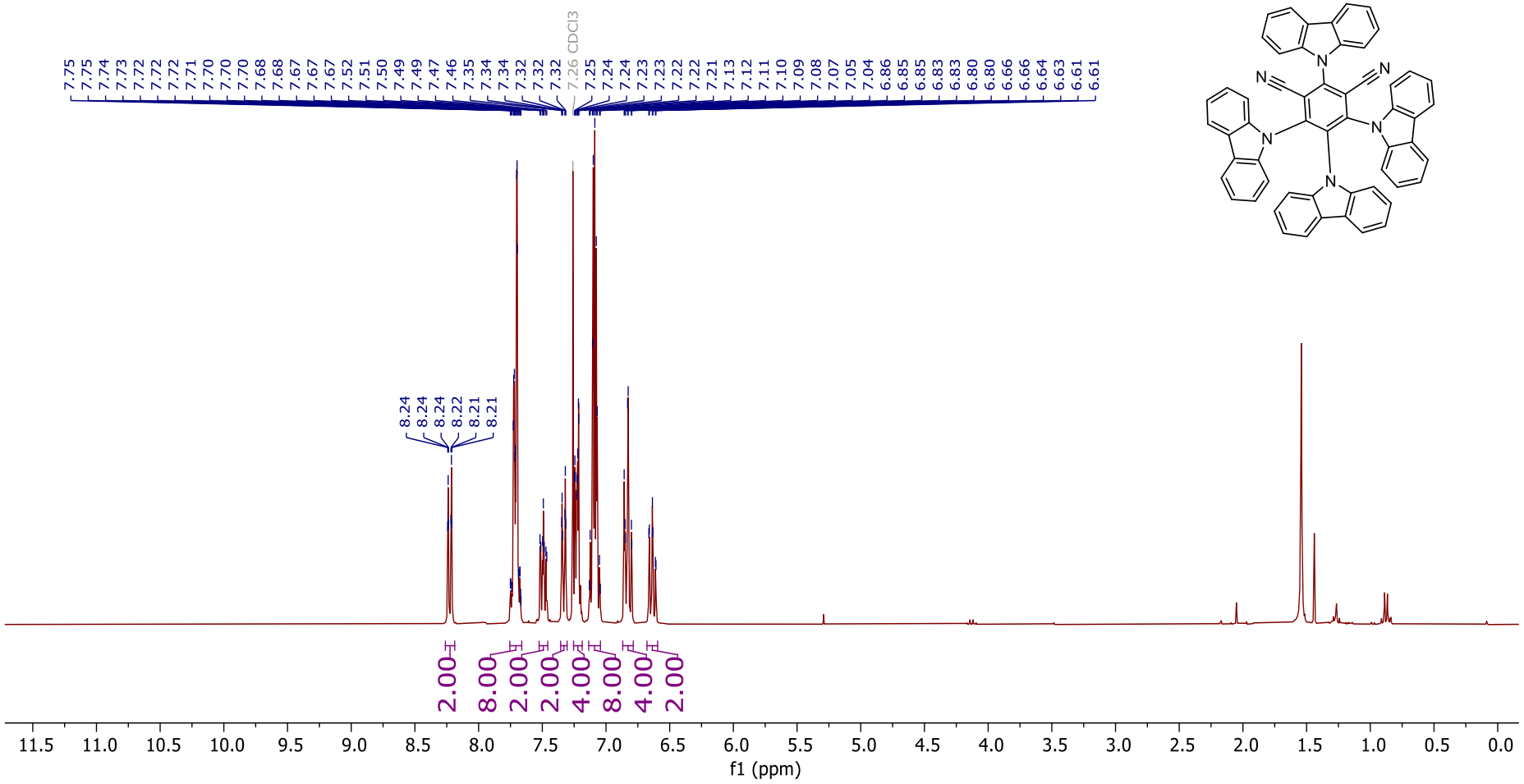

N
OH
15

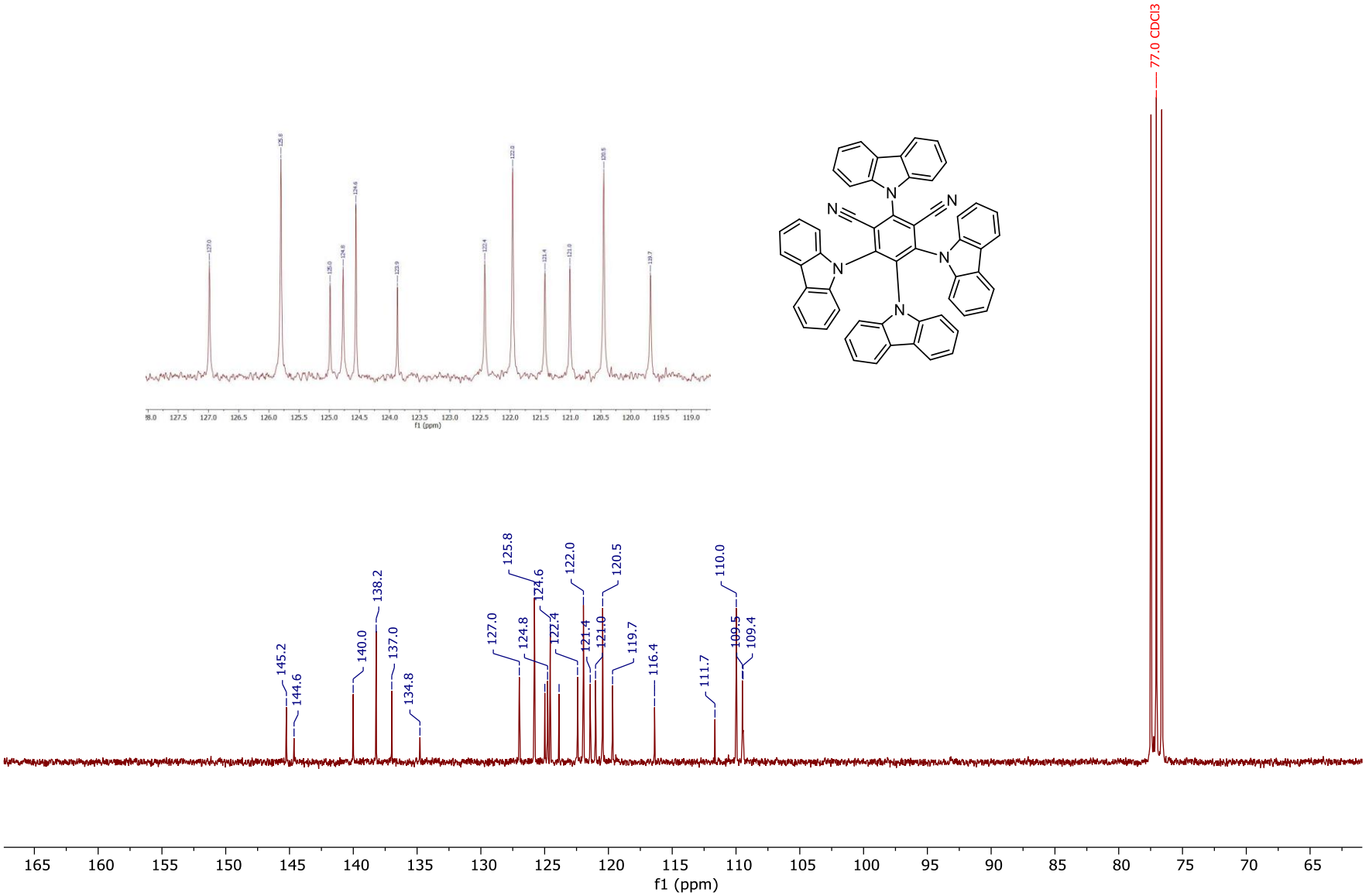

153.7
140.4
128.6
126.4
126.2
77.2 CDCl3
24.2
18.9
15.6
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

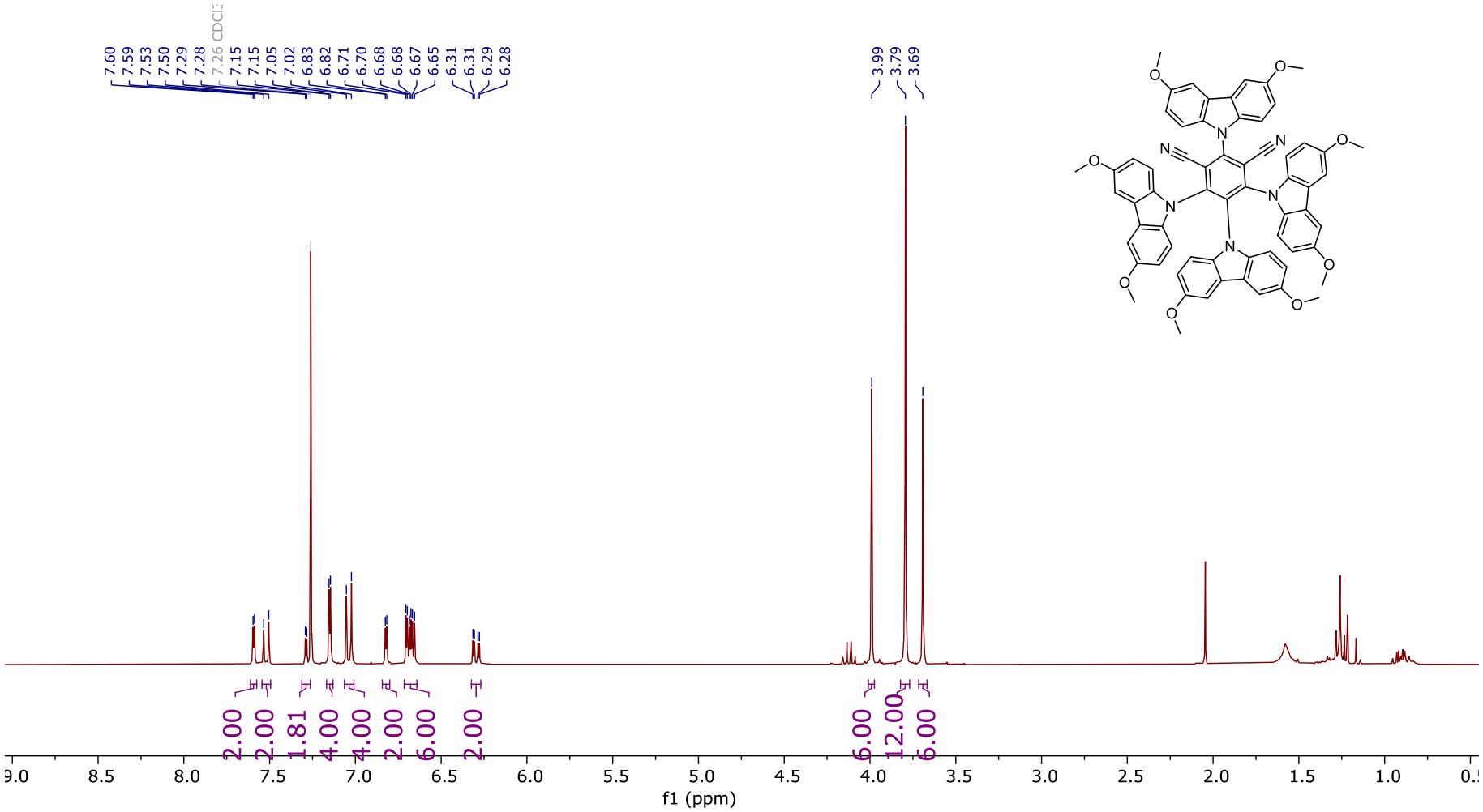

N
OH
F
18
2.39
8.36
8.25
7.26 CDCl3
6.79
6.76
1.00
1.00
2.00
6.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

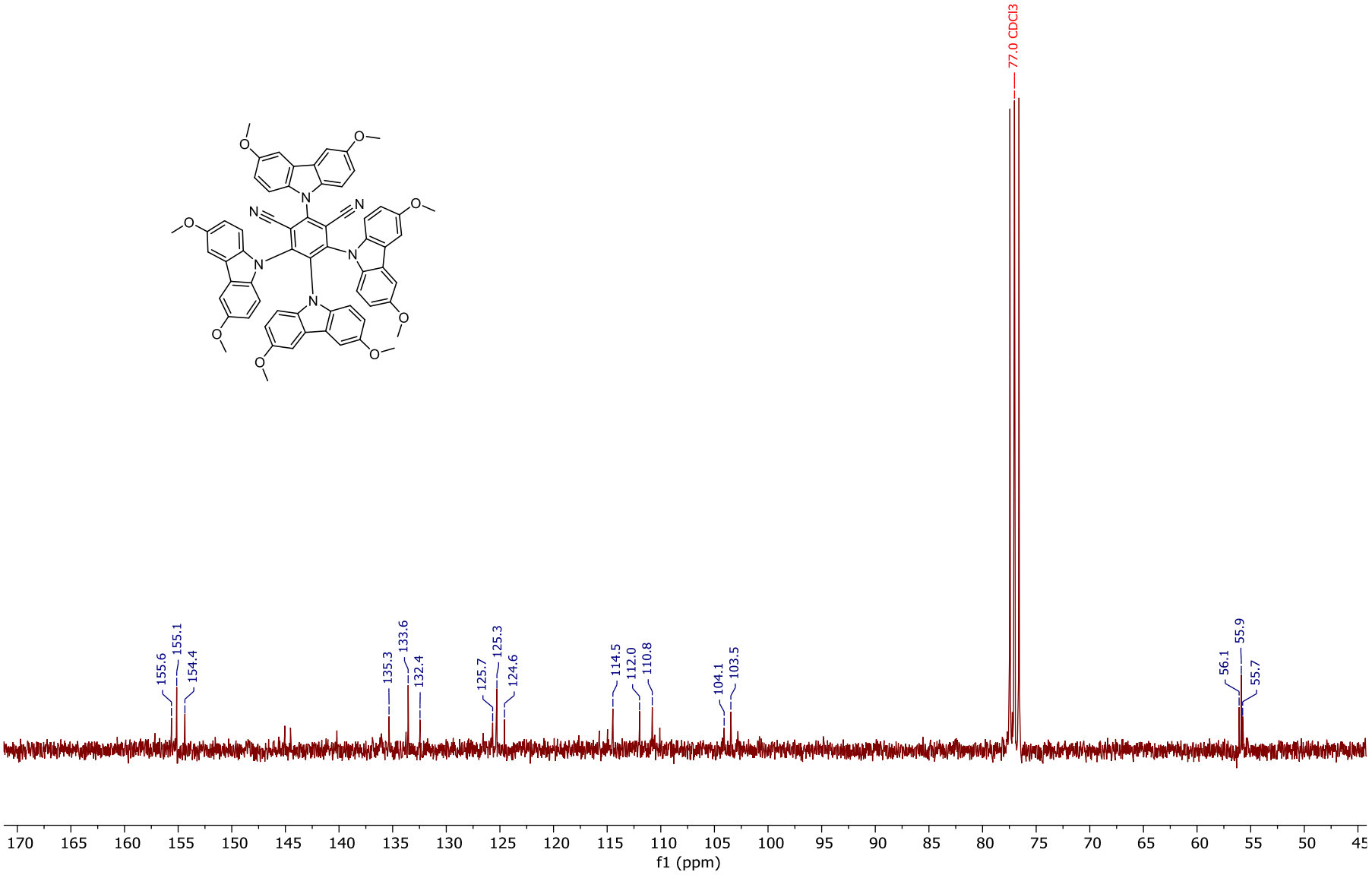

N
OH
F
18
164.18
160.89
149.20
140.42
140.31
125.59
125.54
115.43
115.15
77.16 CDCl3
21.36
21.33
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

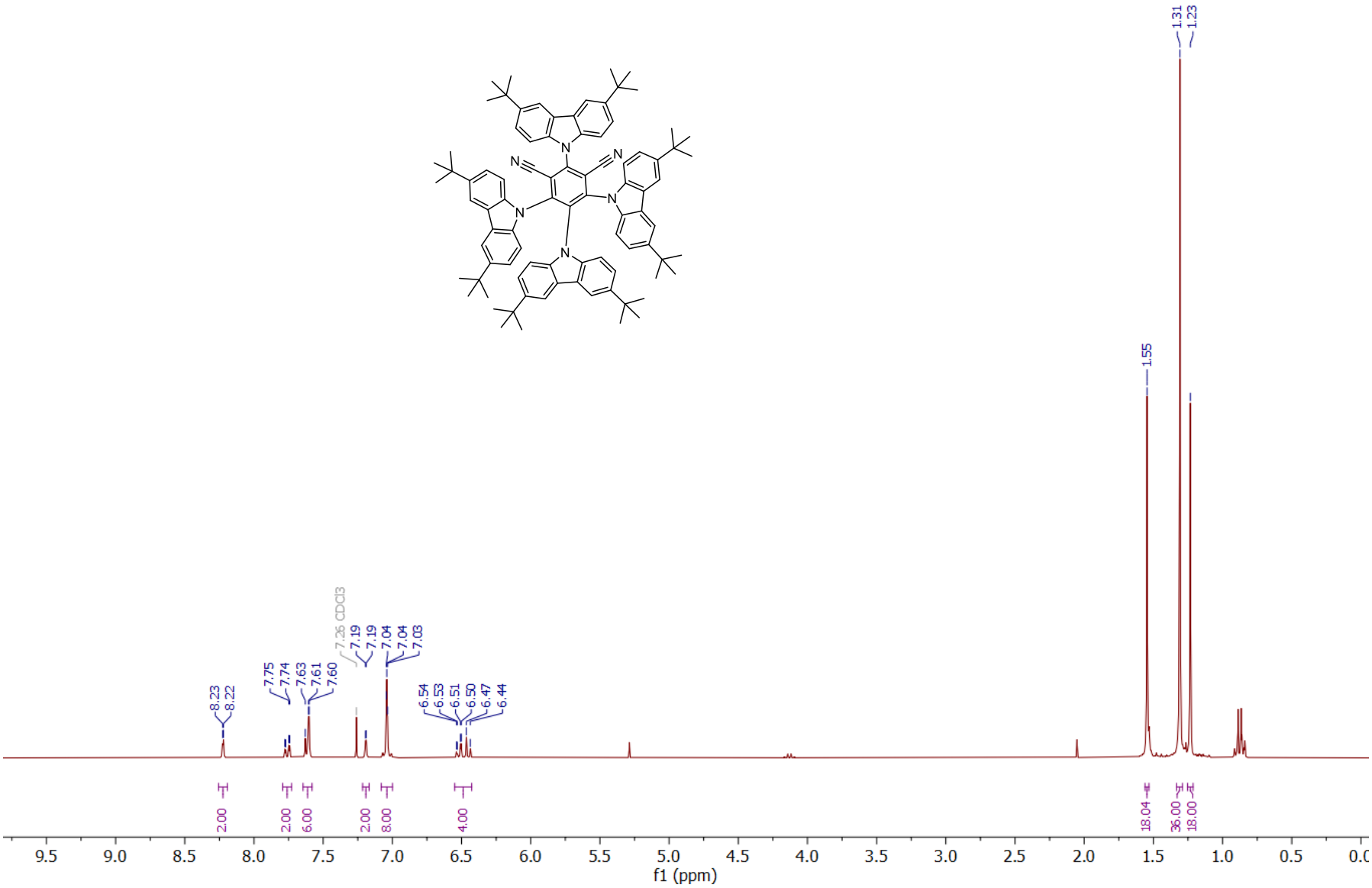

N
OH
F
18
-113.13
-113.16
-113.20
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

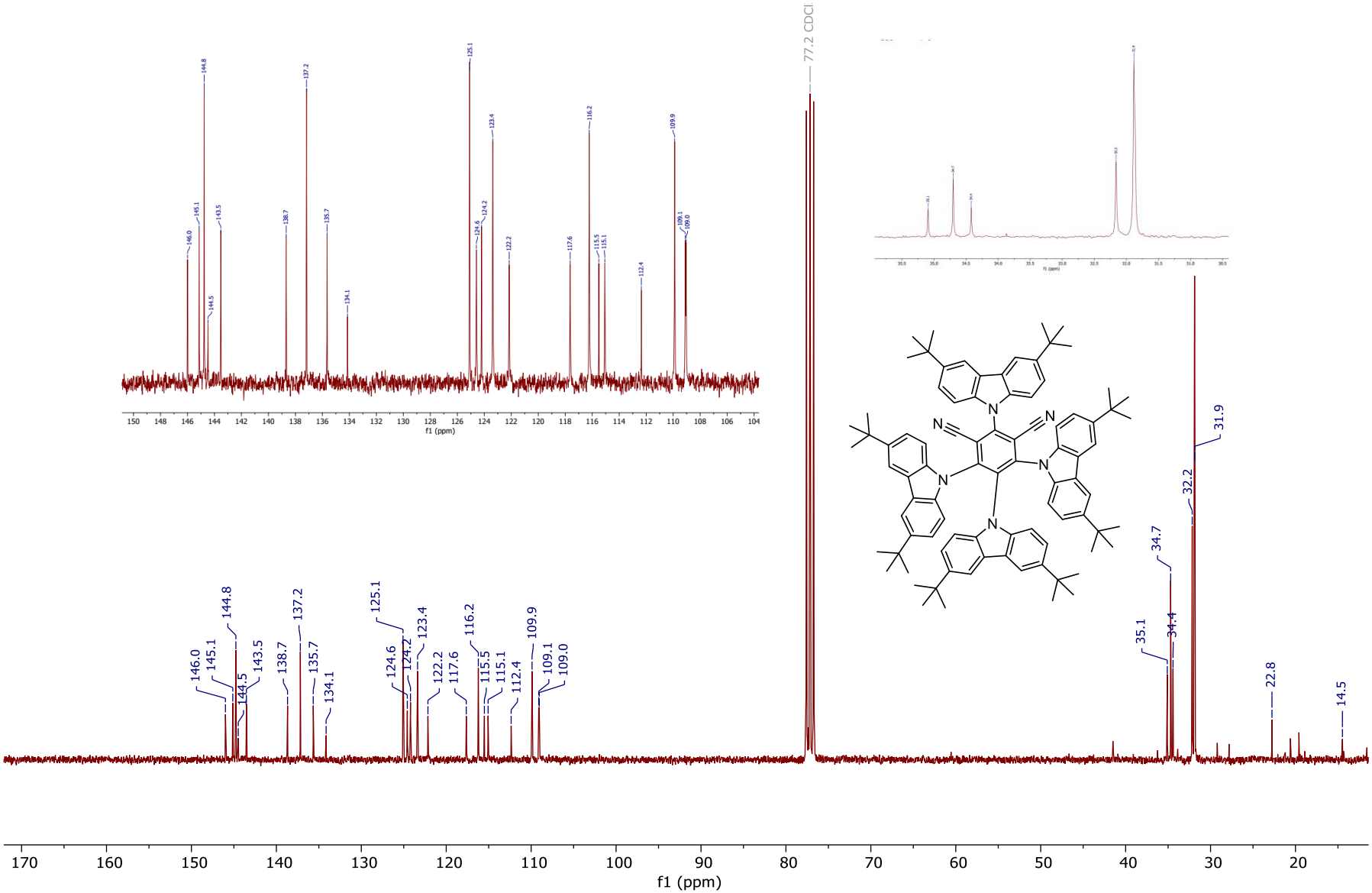

7.75 7.75 7.74 7.73 7.72 7.72 7.72 7.71 7.70 7.70 7.70 7.68 7.67 7.67 7.67 7.52 7.51 7.50 7.49 7.49 7.47 7.46 7.35 7.34 7.34 7.32 7.32 7.32 CDCl3 7.25 7.24 7.24 7.23 7.23 7.22 7.22 7.21 7.13 7.12 7.11 7.10 7.09 7.08 7.07 7.05 7.04 6.86 6.85 6.85 6.83 6.83 6.80 6.80 6.66 6.66 6.64 6.63 6.61 6.61
8.24 8.24 8.24 8.22 8.21 8.21
2.00 8.00 2.00 2.00 4.00 8.00 4.00 2.00
11.5 11.0 10.5 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)

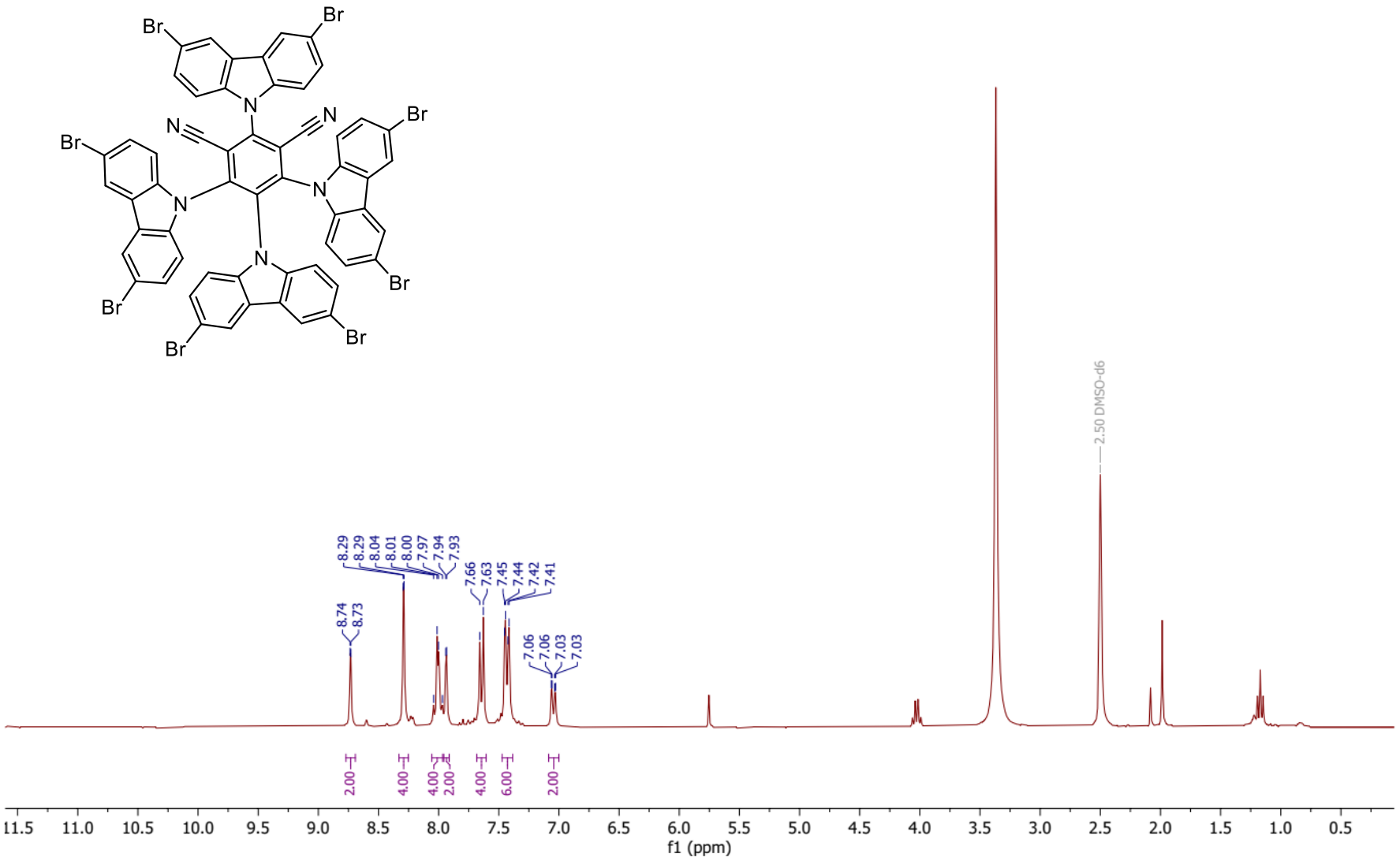

77.0 CDCl3
145.2
144.6
140.0
138.2
137.0
134.8
127.0
125.8
124.8
124.6
122.4
122.0
121.4
121.0
120.5
119.7
116.4
111.7
110.0
109.5
109.4
f1 (ppm)

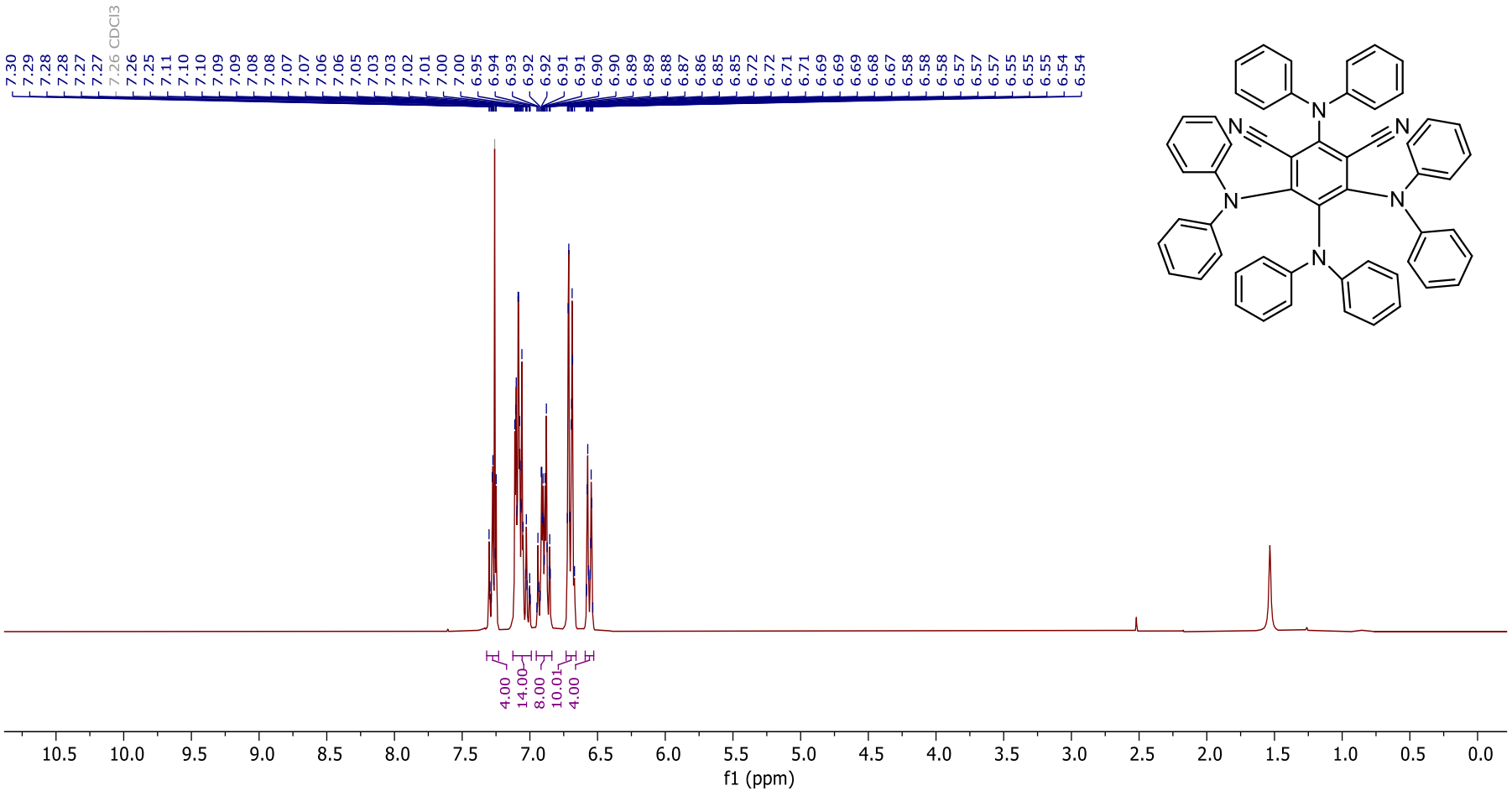

7.60
7.59
7.53
7.50
7.29
7.28
7.26 CDCl3
7.15
7.15
7.05
7.02
6.83
6.82
6.71
6.70
6.68
6.68
6.67
6.65
6.31
6.31
6.29
6.28
3.99
3.79
3.69
2.00
2.00
1.81
4.00
4.00
2.00
6.00
2.00
6.00
12.00
6.00
f1 (ppm)

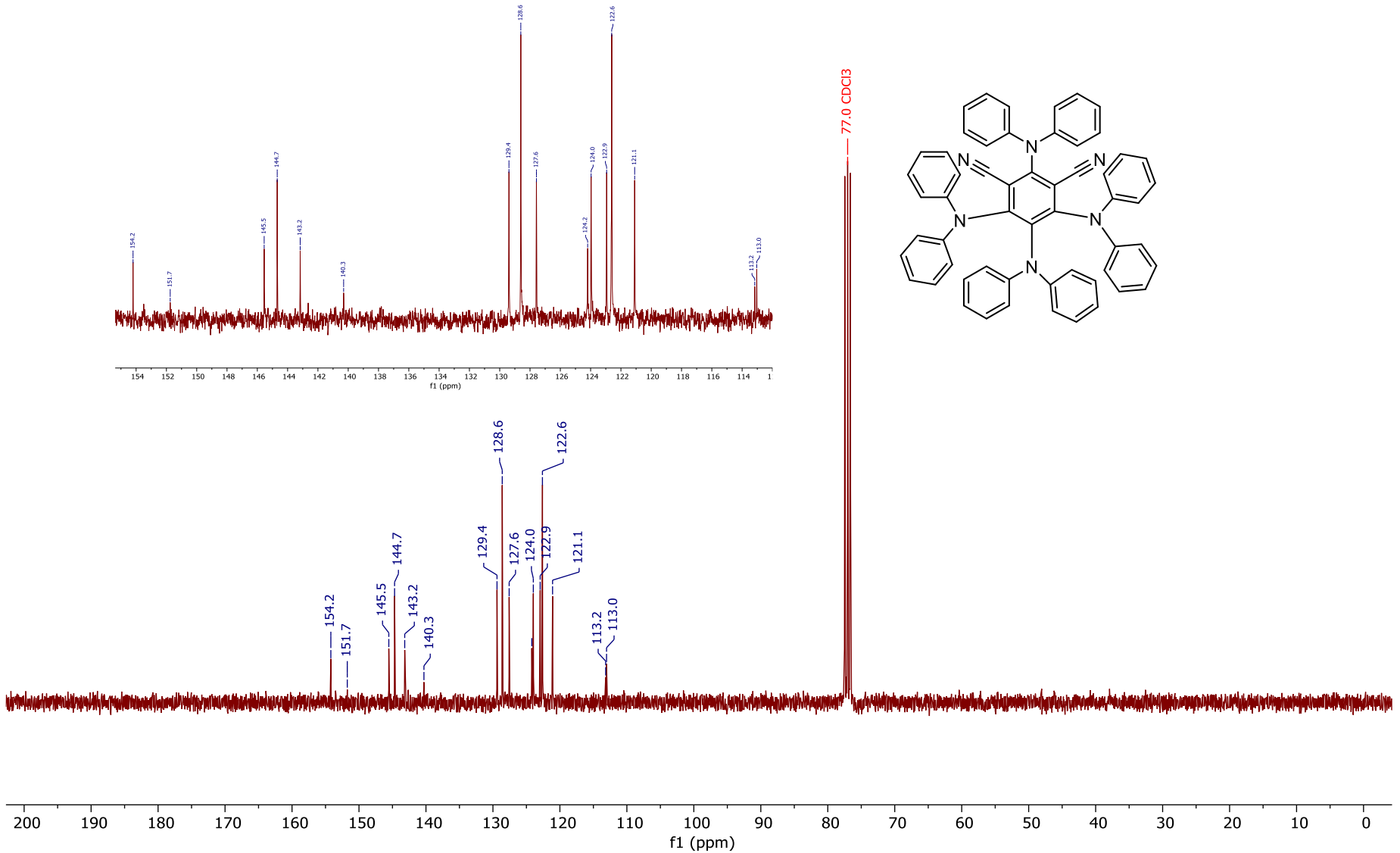

77.0 CDCl3
155.6
155.1
154.4
135.3
133.6
132.4
125.7
125.3
124.6
114.5
112.0
110.8
104.1
103.5
56.1
55.9
55.7
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)

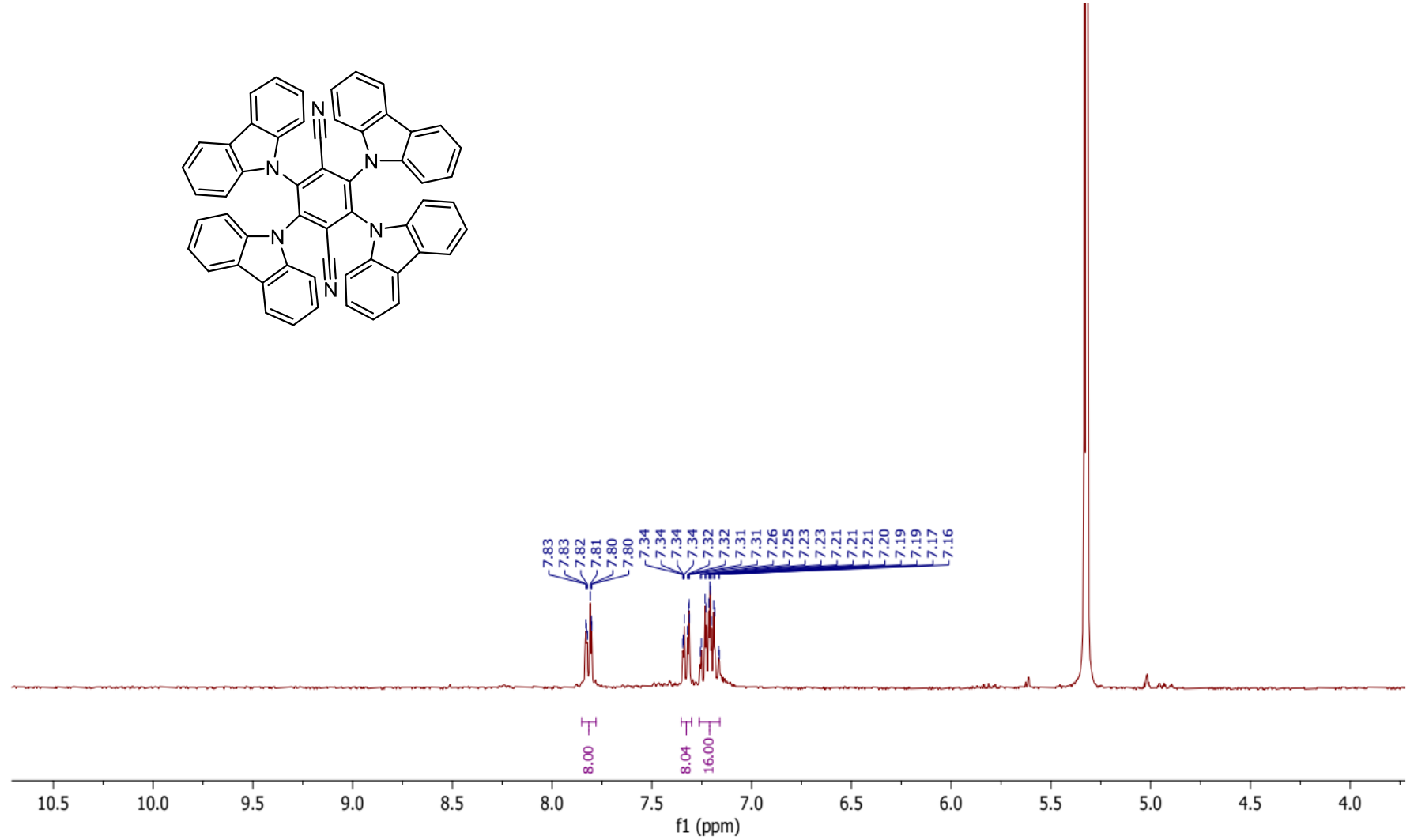

1.31
1.23
1.55
7.26 CDCl3
8.23
8.22
7.75
7.74
7.63
7.61
7.60
7.19
7.19
7.04
7.04
7.03
6.54
6.53
6.51
6.50
6.47
6.44
2.00
2.00
6.00
2.00
8.00
4.00
18.04
36.00
18.00
f1 (ppm)

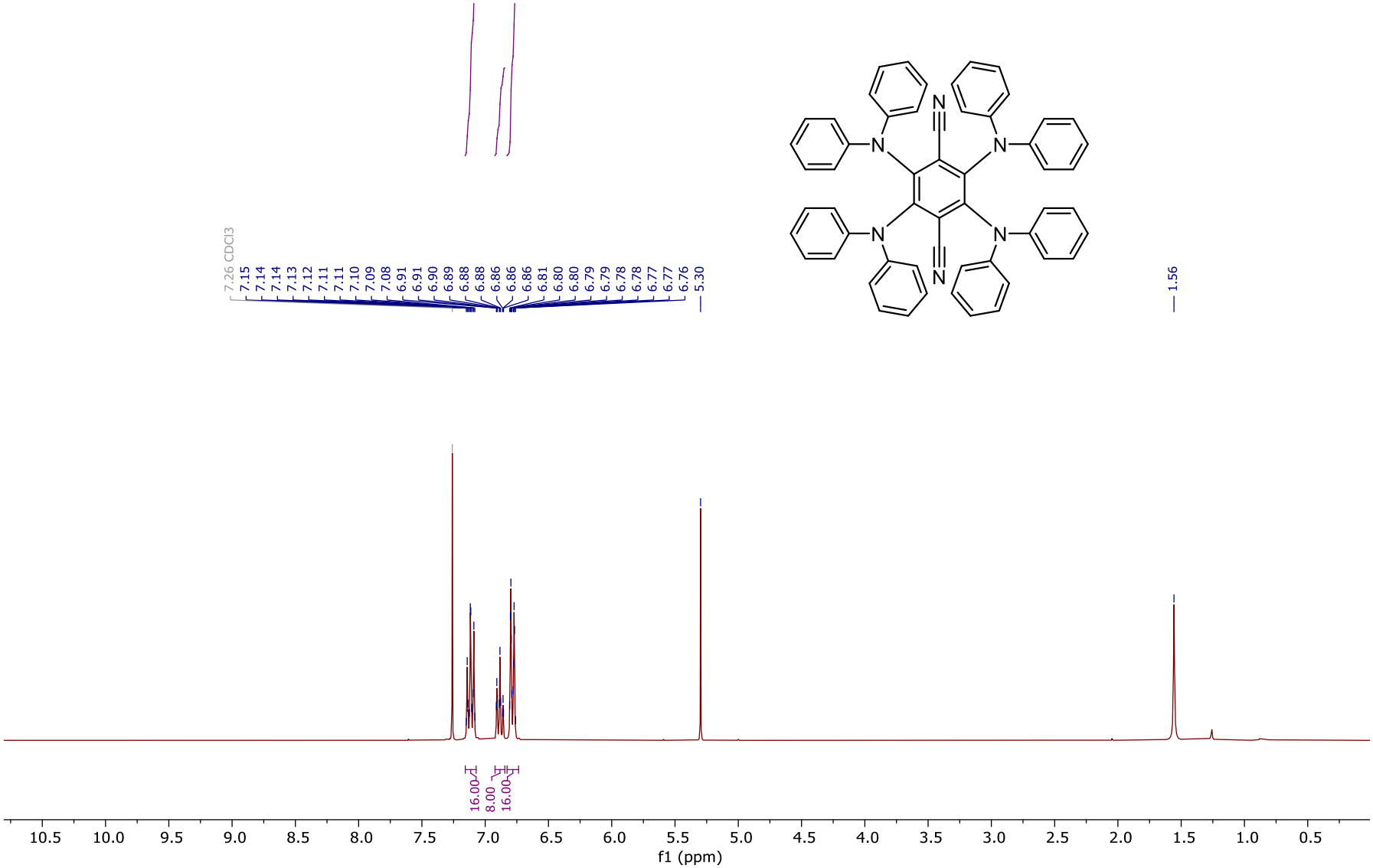

77.2 CDCl
146.0
145.1
144.8
144.5
143.5
138.7
137.2
135.7
134.1
125.1
124.6
124.2
123.4
122.2
117.6
116.2
115.5
115.1
112.4
109.9
109.1
109.0
35.1
34.7
34.4
32.2
31.9
22.8
14.5
f1 (ppm)

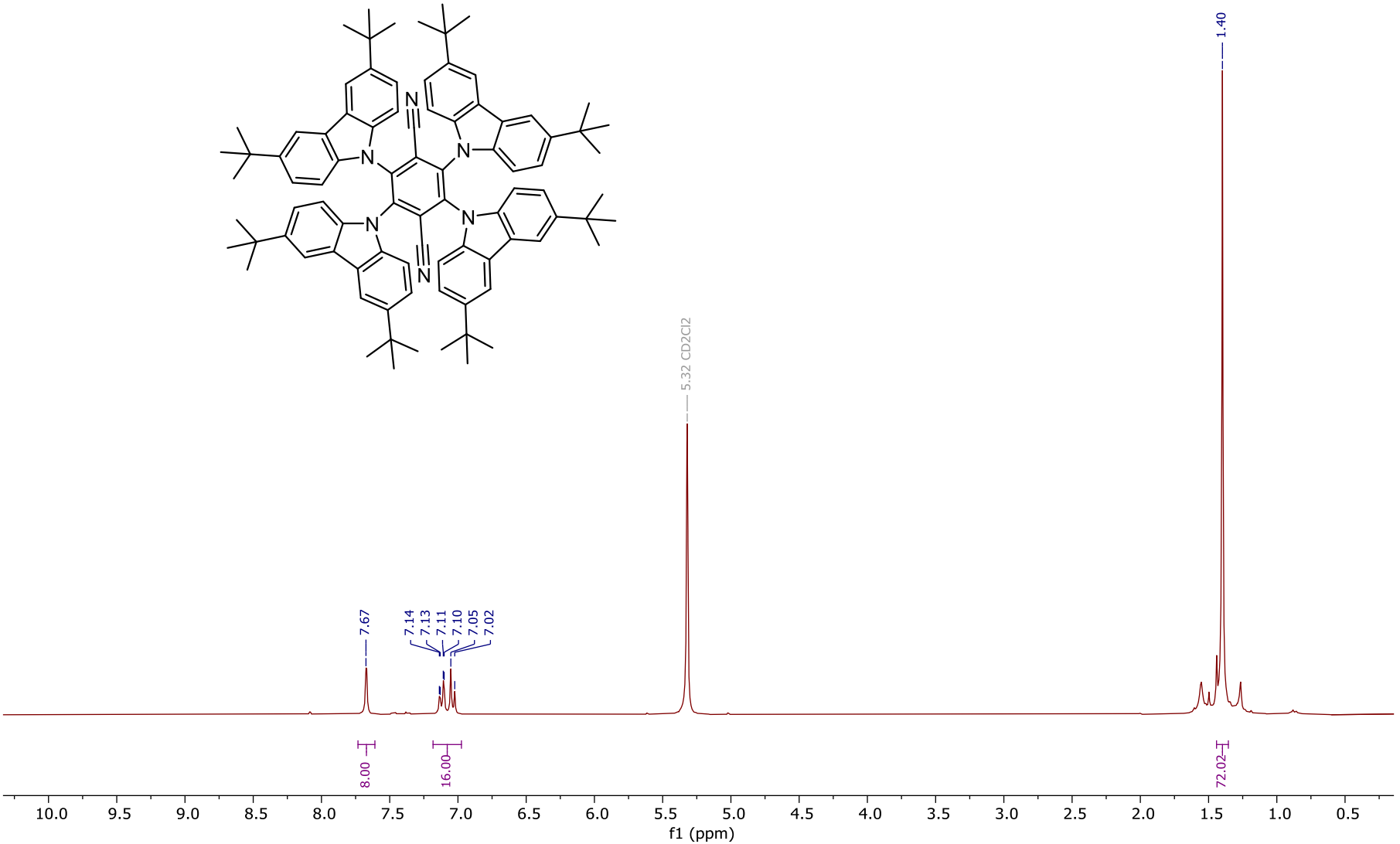

Br
Br
N
N
Br
Br
N
N
Br
Br
N
Br
Br
Br
8.74
8.73
8.29
8.29
8.04
8.01
8.00
7.97
7.94
7.93
7.66
7.63
7.45
7.44
7.42
7.41
7.06
7.06
7.03
7.03
2.50 DMSO-d6
2.00
4.00
4.00
2.00
4.00
6.00
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

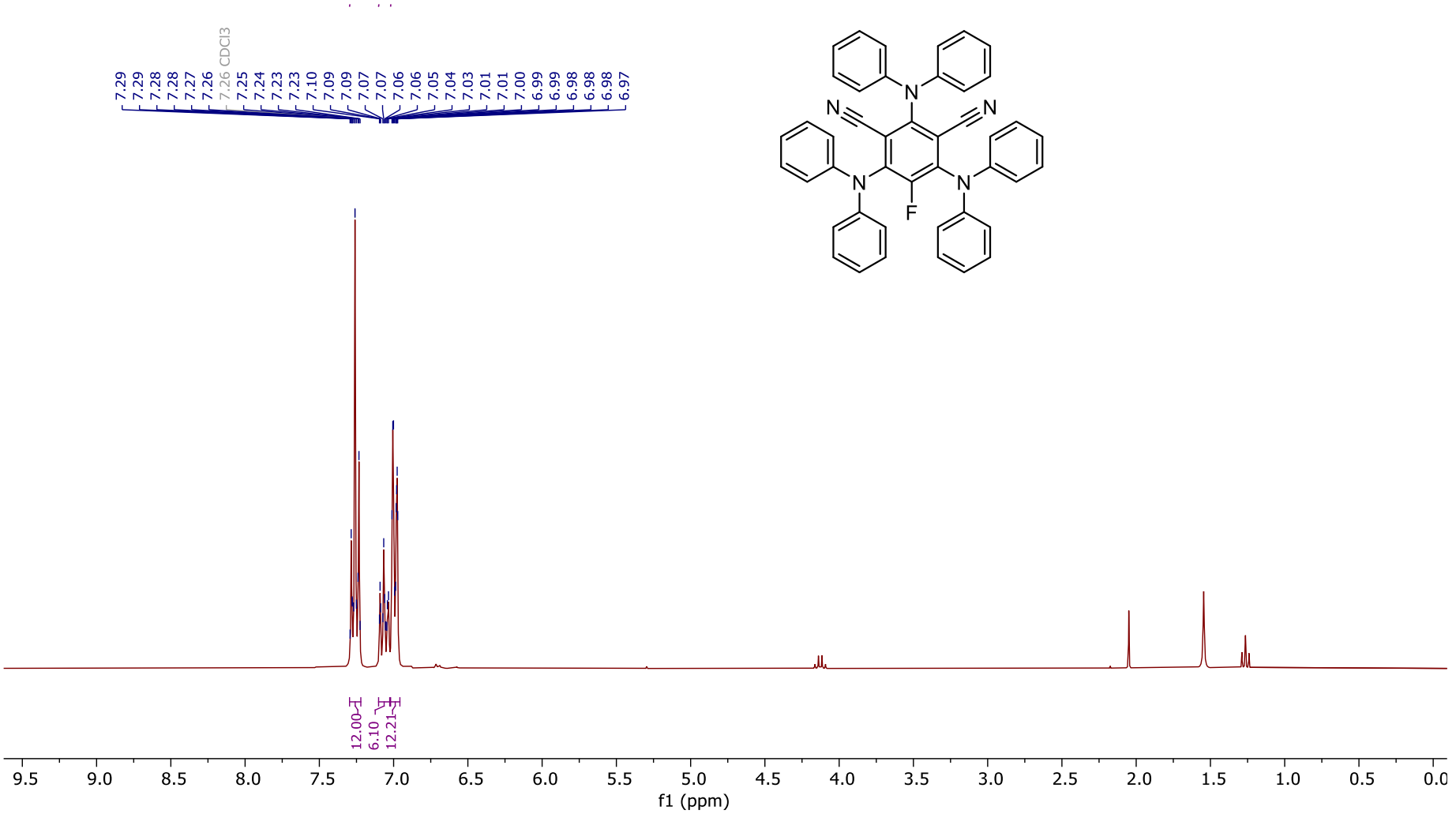

7.30 7.29 7.28 7.28 7.27 7.27 7.26 CDCl3 7.26 7.25 7.11 7.10 7.10 7.09 7.09 7.08 7.08 7.07 7.07 7.06 7.06 7.05 7.03 7.03 7.02 7.01 7.00 7.00 6.95 6.94 6.93 6.92 6.92 6.91 6.91 6.90 6.90 6.89 6.89 6.88 6.87 6.86 6.85 6.85 6.72 6.72 6.71 6.69 6.69 6.68 6.67 6.58 6.58 6.58 6.57 6.57 6.55 6.55 6.55 6.54 6.54
4.00 14.00 8.00 10.01 4.00
10.5 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)

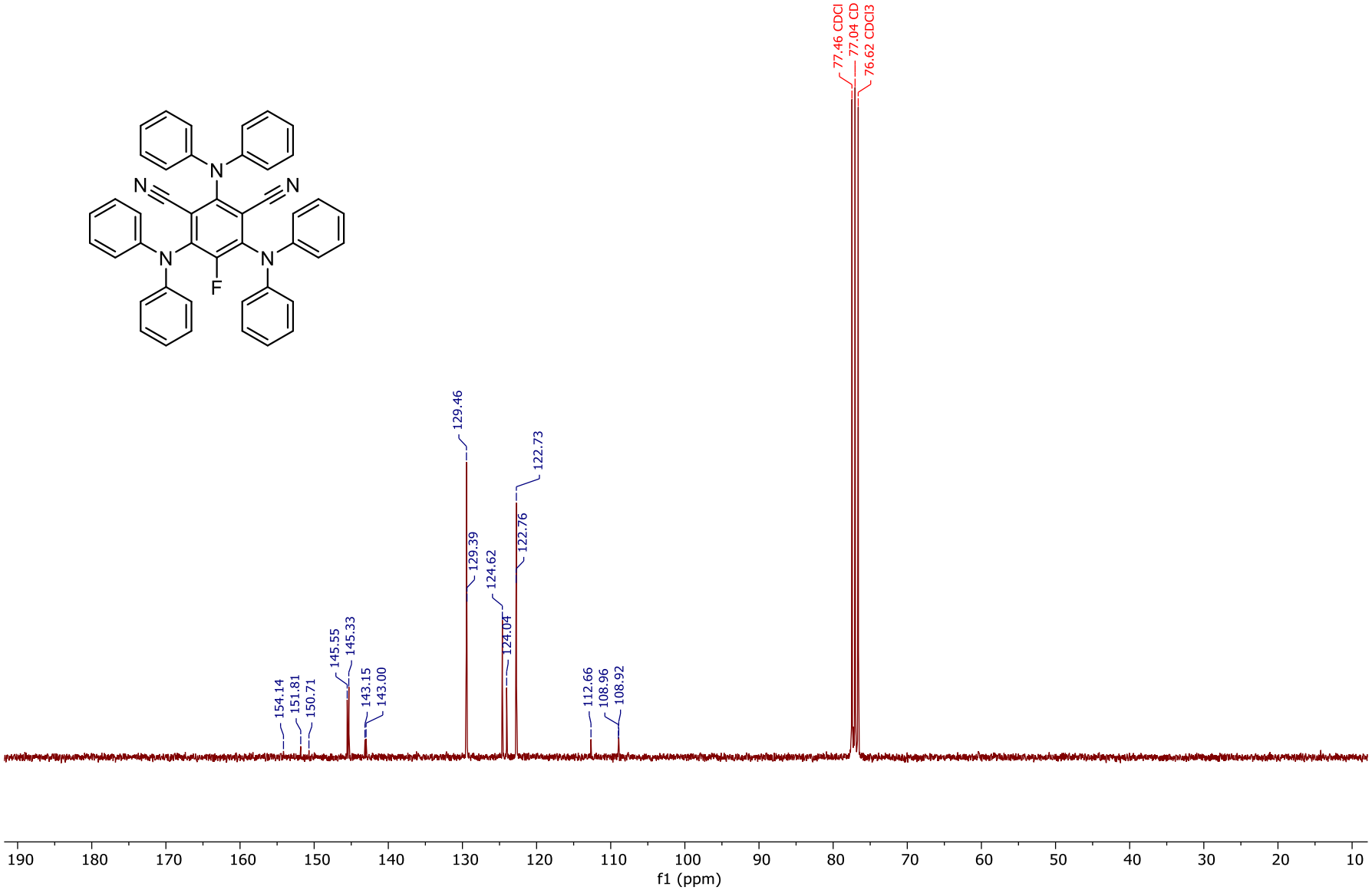

154.2
151.7
145.5
144.7
143.2
140.3
129.4
128.6
127.6
124.2
124.0
122.9
122.6
121.1
113.2
113.0
77.0 CDCl3
f1 (ppm)

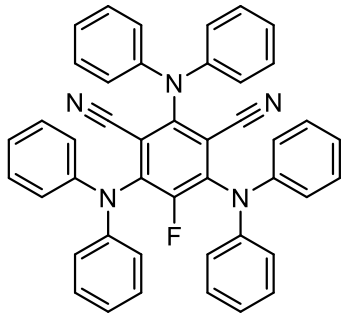

N
N
N
N
N
N
7.83
7.83
7.82
7.81
7.80
7.80
7.34
7.34
7.34
7.34
7.32
7.32
7.31
7.31
7.26
7.25
7.23
7.23
7.21
7.21
7.21
7.20
7.19
7.19
7.17
7.16
8.00
8.04
16.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
f1 (ppm)


7.26 CDCl3
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.10
7.09
7.08
6.91
6.91
6.90
6.89
6.88
6.88
6.86
6.86
6.86
6.81
6.80
6.80
6.79
6.79
6.78
6.78
6.77
6.77
6.76
5.30
1.56
16.00
8.00
16.00
10.5
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
f1 (ppm)

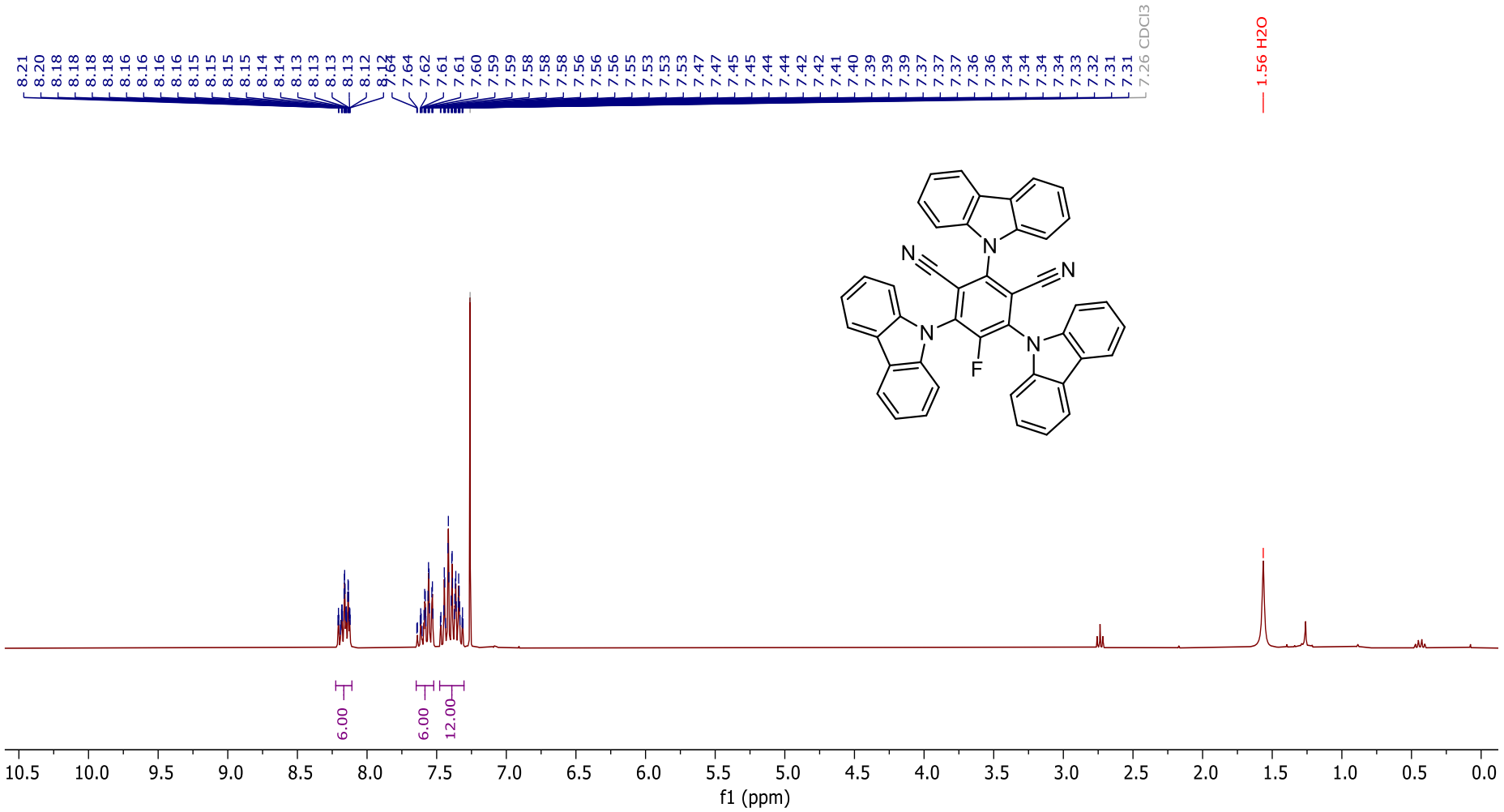

1.40
5.32 CD2Cl2
7.67
7.14
7.13
7.11
7.10
7.05
7.02
8.00
16.00
72.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

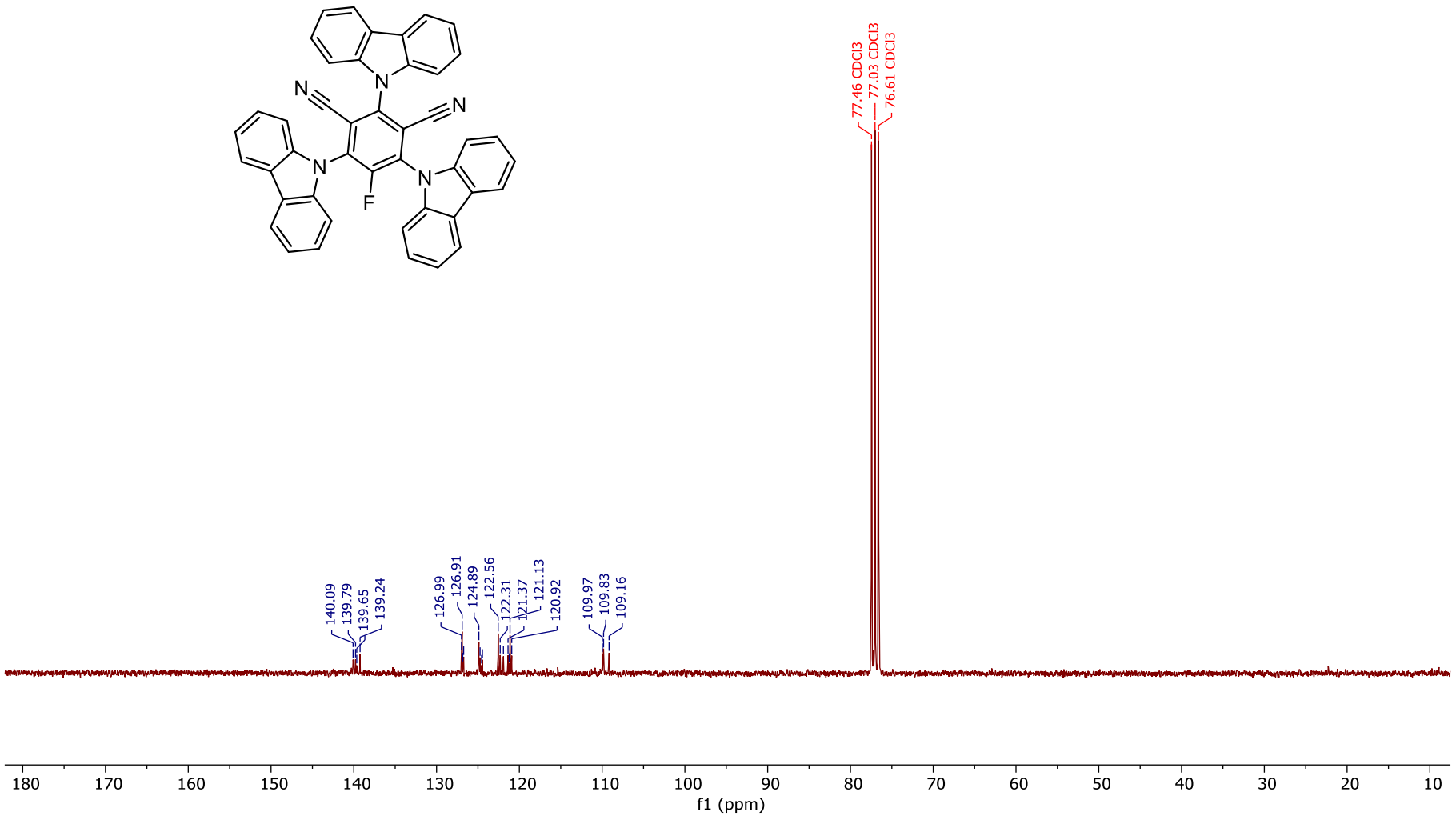

7.29
7.29
7.28
7.28
7.27
7.26
7.26 CDCl3
7.25
7.24
7.23
7.23
7.10
7.09
7.09
7.07
7.07
7.06
7.06
7.05
7.04
7.03
7.01
7.01
7.00
6.99
6.99
6.98
6.98
6.98
6.97
N
N
N
N
N
F
12.00
6.10
12.21
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

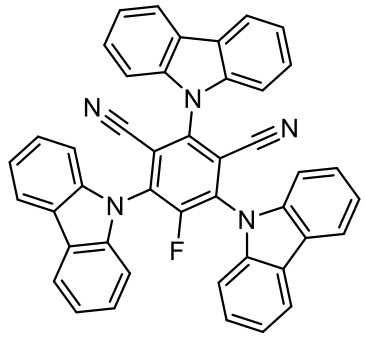

77.46 CDCl
77.04 CD
76.62 CDCl3
129.46
129.39
124.62
124.04
122.73
122.76
154.14
151.81
150.71
145.55
145.33
143.15
143.00
112.66
108.96
108.92
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

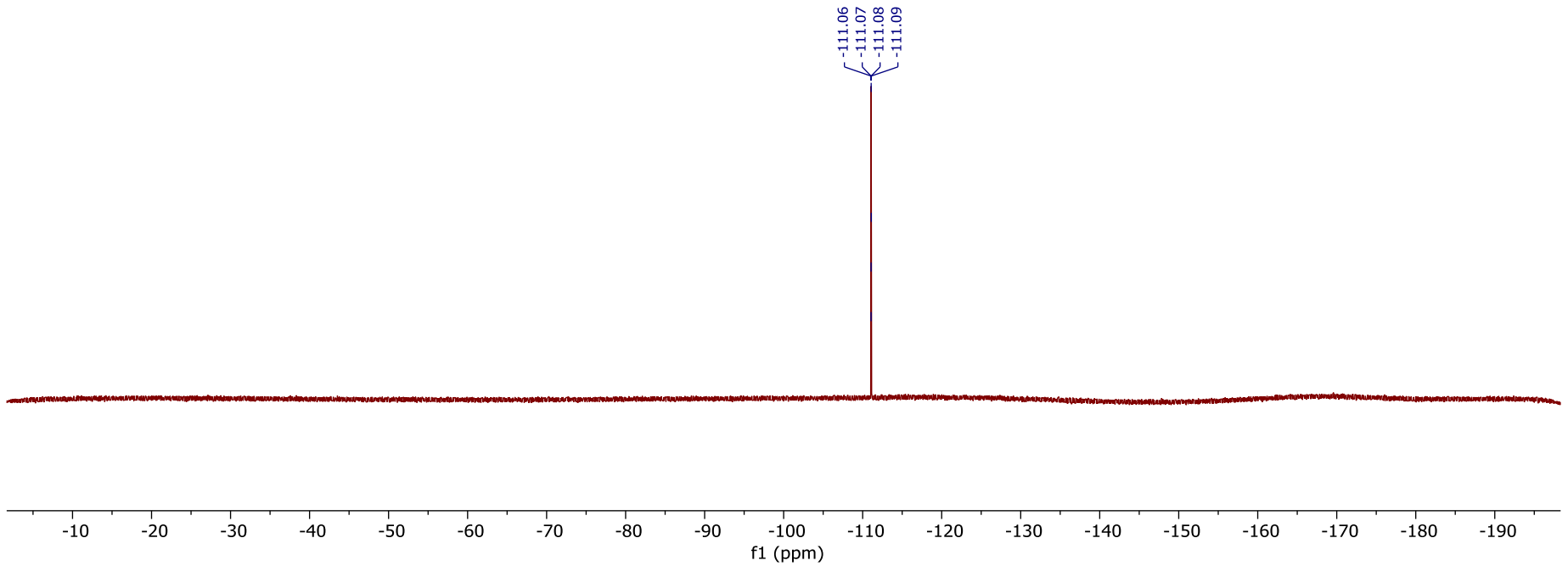

N
N
N
N
F

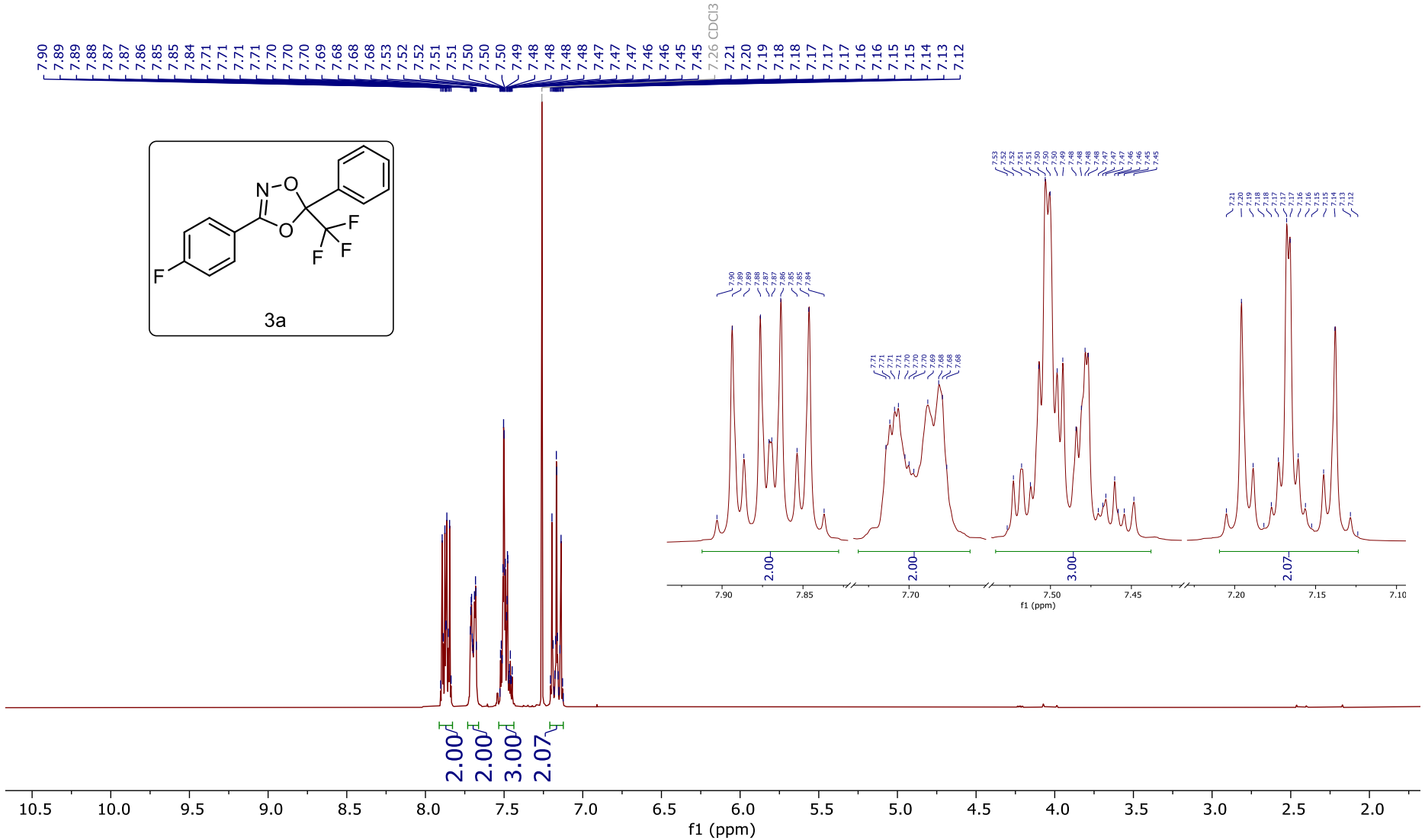
-121.30
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

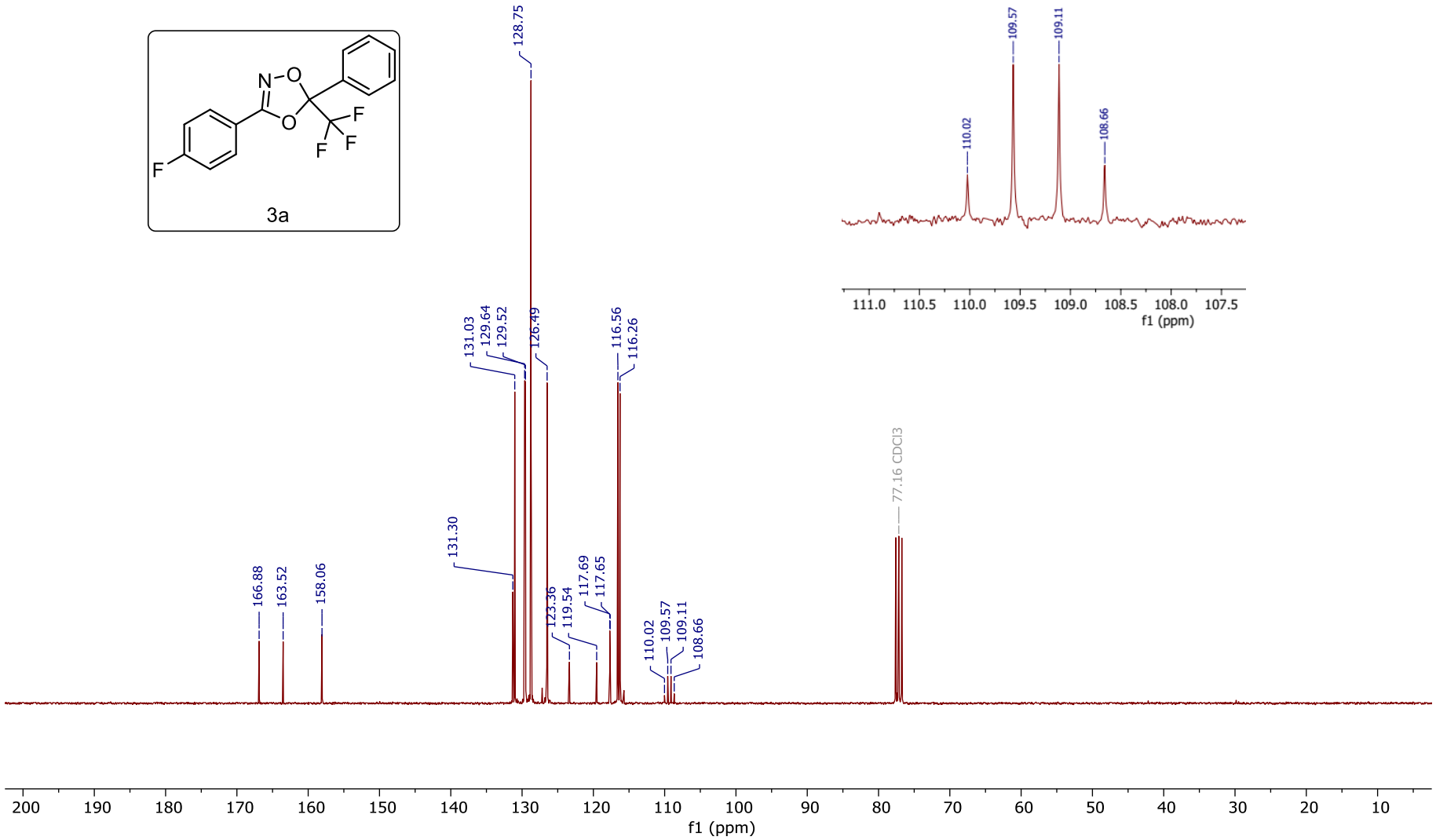

8.21 8.20 8.18 8.18 8.18 8.16 8.16 8.16 8.15 8.15 8.15 8.14 8.14 8.13 8.13 8.13 8.13 8.12 8.12 7.64 7.64 7.62 7.61 7.61 7.60 7.59 7.59 7.58 7.58 7.58 7.56 7.56 7.56 7.55 7.53 7.53 7.53 7.47 7.47 7.45 7.45 7.44 7.44 7.42 7.42 7.41 7.40 7.39 7.39 7.39 7.37 7.37 7.37 7.36 7.36 7.34 7.34 7.34 7.34 7.33 7.32 7.31 7.31
7.26 CDCl3
1.56 H2O
N
N
N
N
N
F
6.00
6.00
12.00
10.5 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)

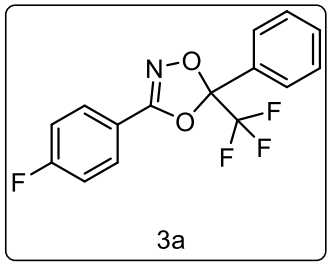

N
N
N
F
N
77.46 CDCl3
77.03 CDCl3
76.61 CDCl3
140.09
139.79
139.65
139.24
126.99
126.91
124.89
122.56
122.31
121.37
121.13
120.92
109.97
109.83
109.16
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

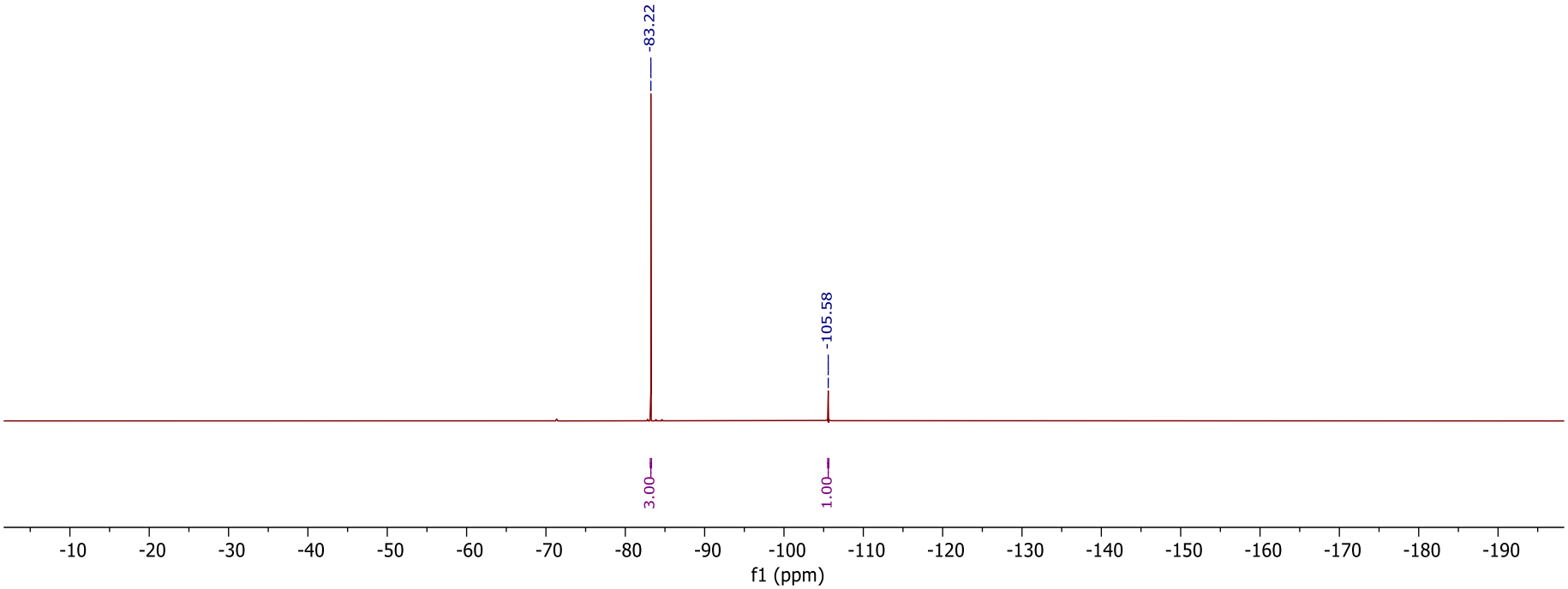

N
N
N
N
F

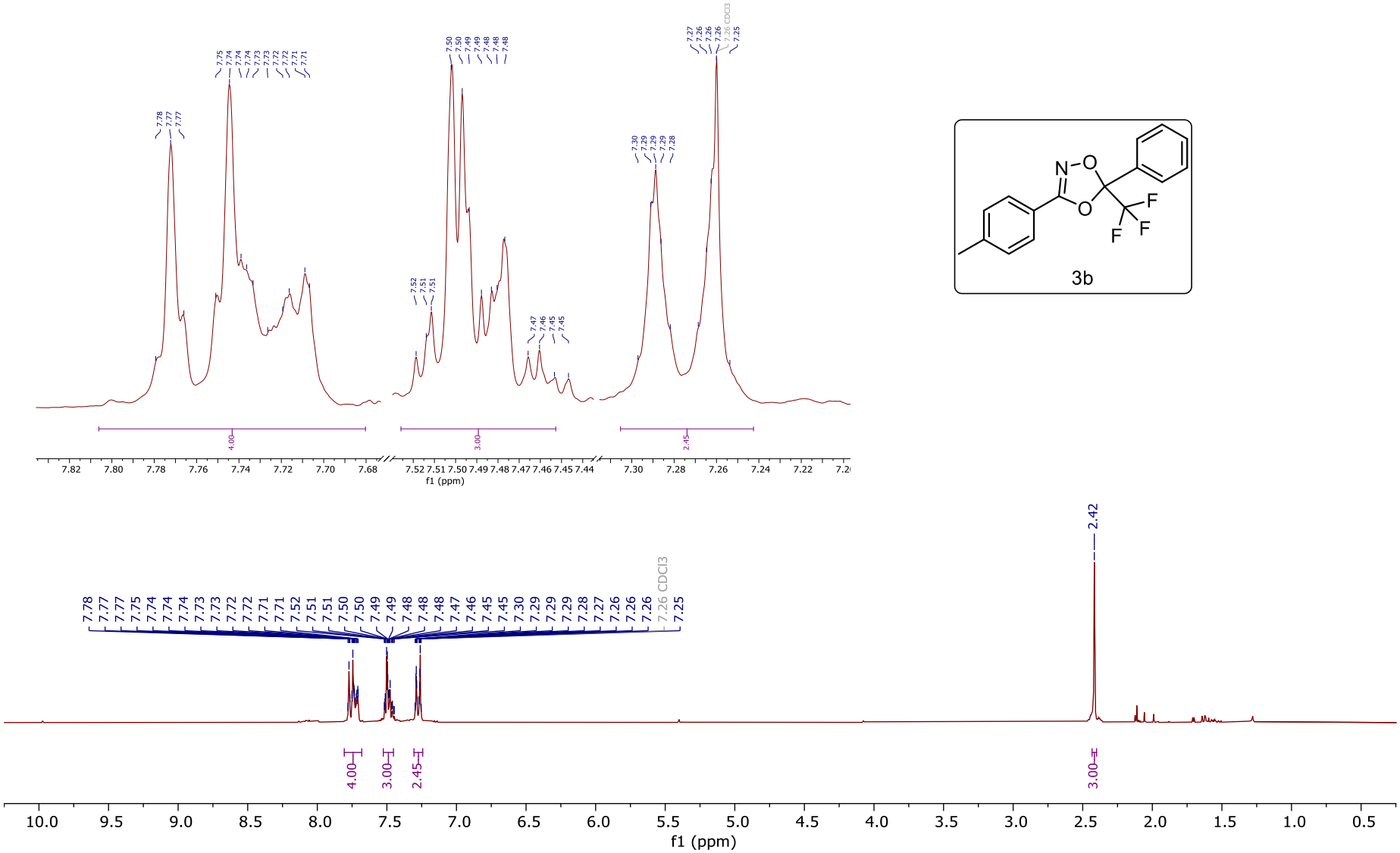

-111.06
-111.07
-111.08
-111.09
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

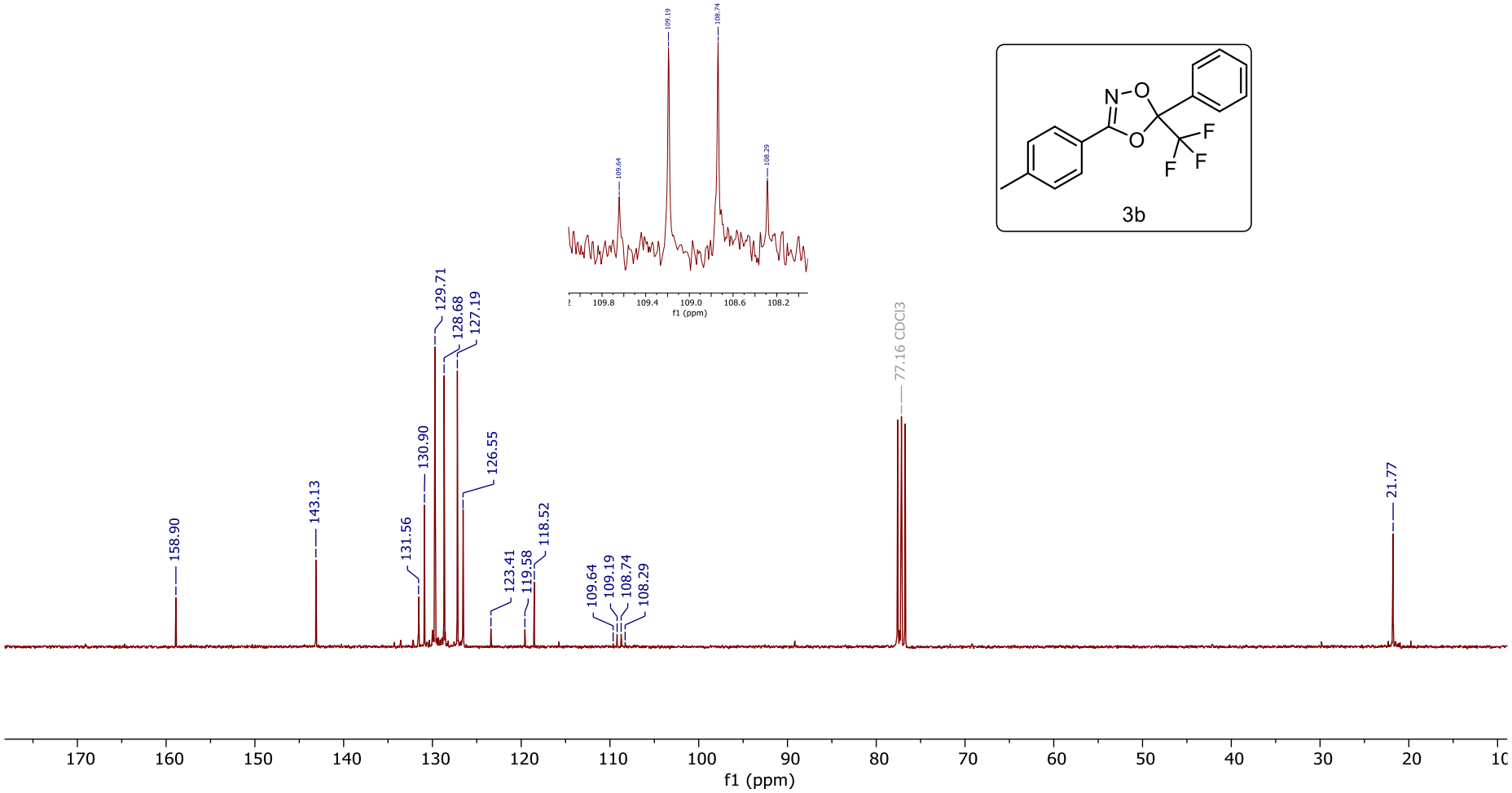

7.26 CDCl3
3a
2.00
2.00
3.00
2.07
f1 (ppm)

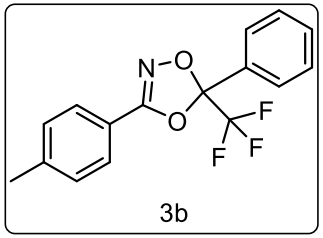

3a
128.75
131.03
129.64
129.52
126.49
116.56
116.26
131.30
166.88
163.52
158.06
123.36
119.54
117.69
117.65
110.02
109.57
109.11
108.66
77.16 CDCl3
f1 (ppm)


N
O
O
F
F
F
F
3a

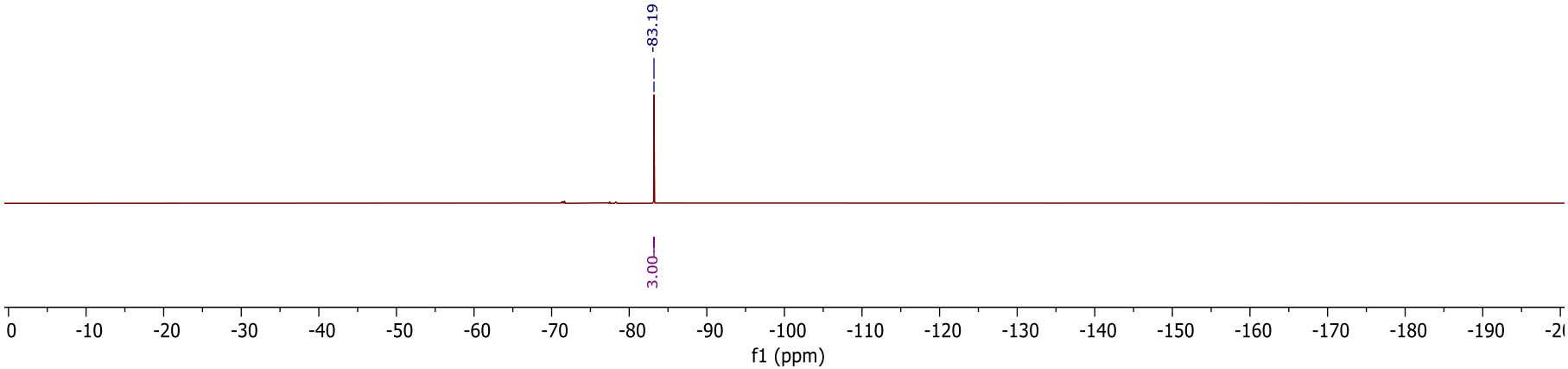

-83.22
-105.58
3.00
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

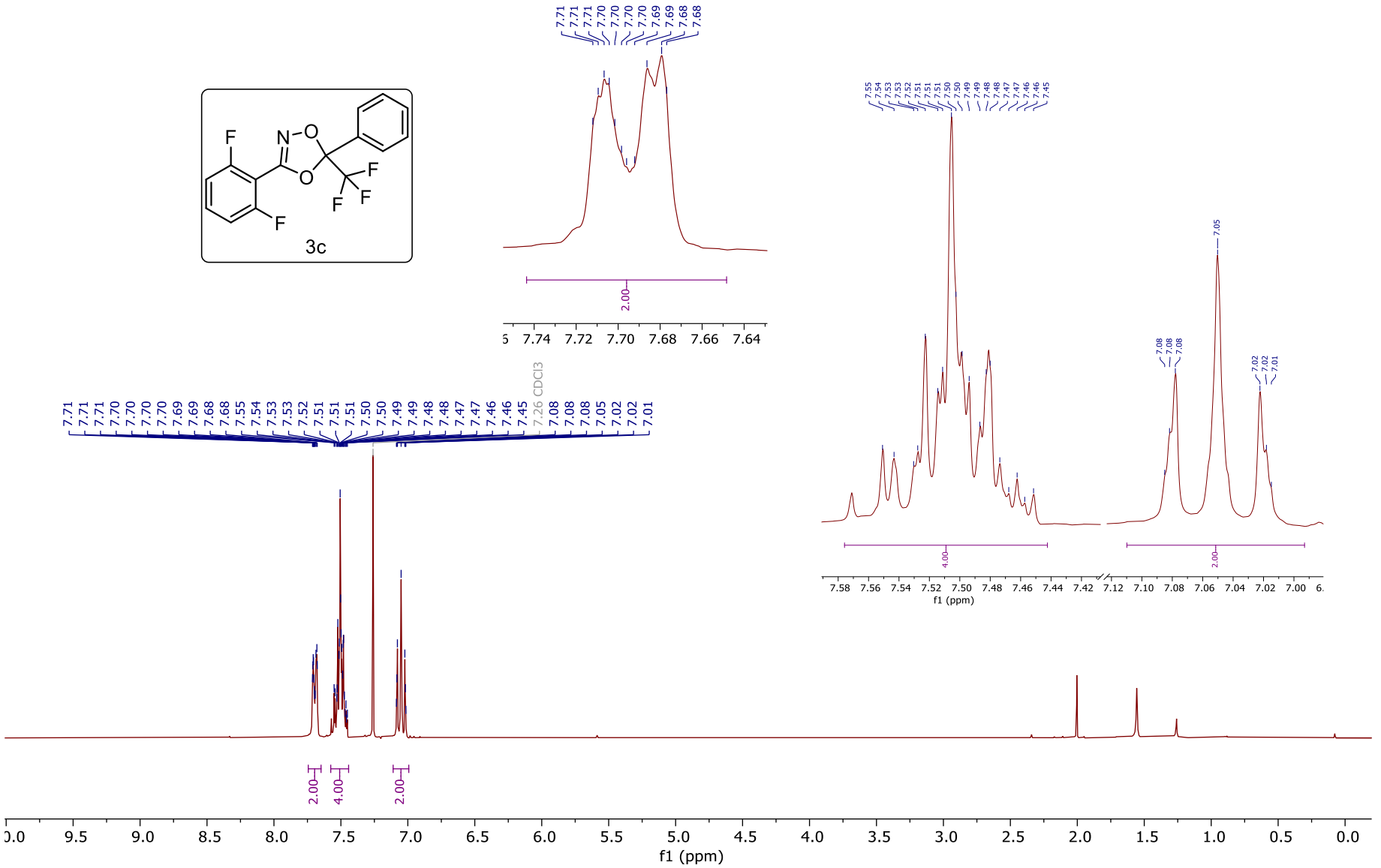

3b
f1 (ppm)

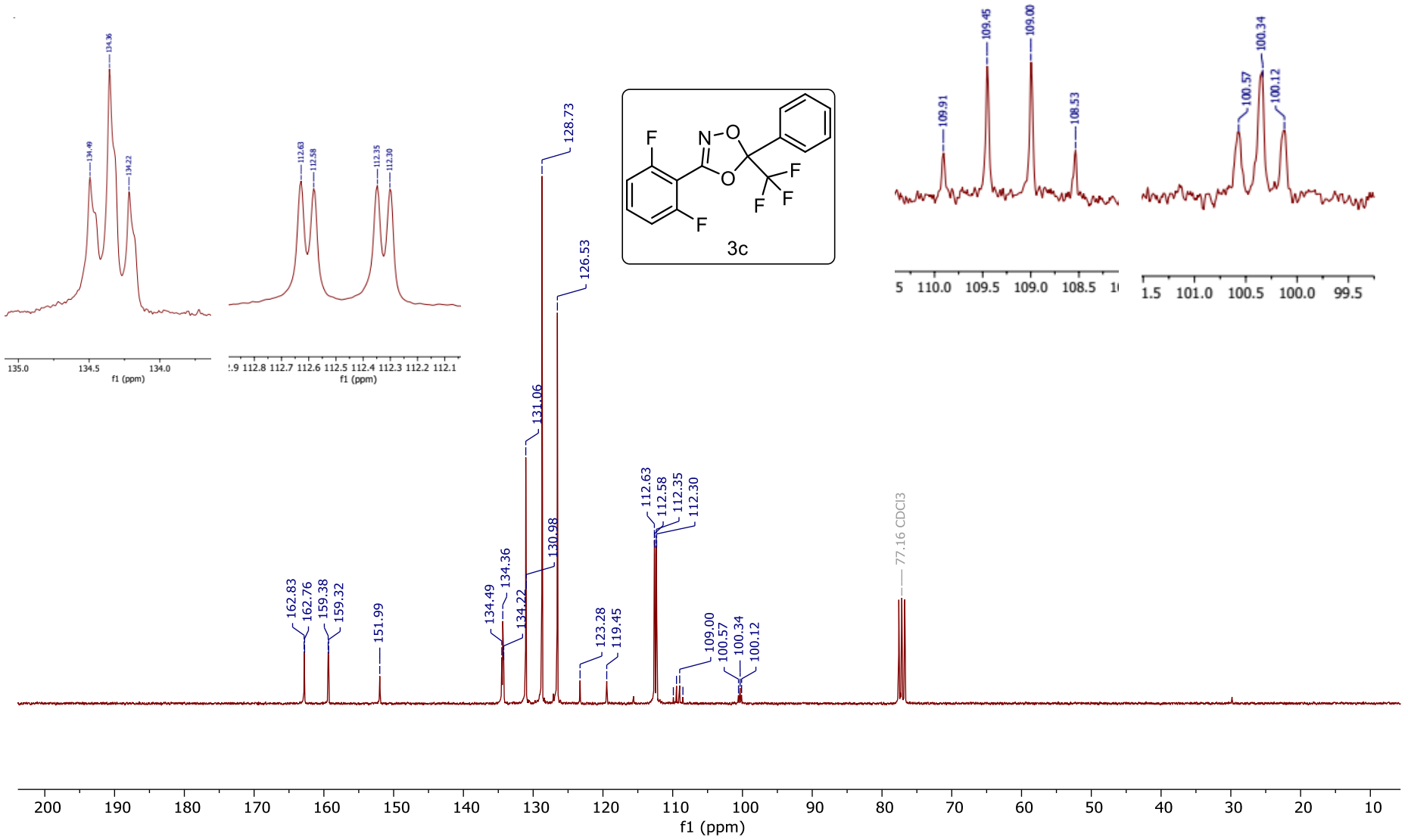

3b
158.90
143.13
131.56
130.90
129.71
128.68
127.19
126.55
123.41
119.58
118.52
109.64
109.19
108.74
108.29
77.16 CDCl3
21.77
f1 (ppm)

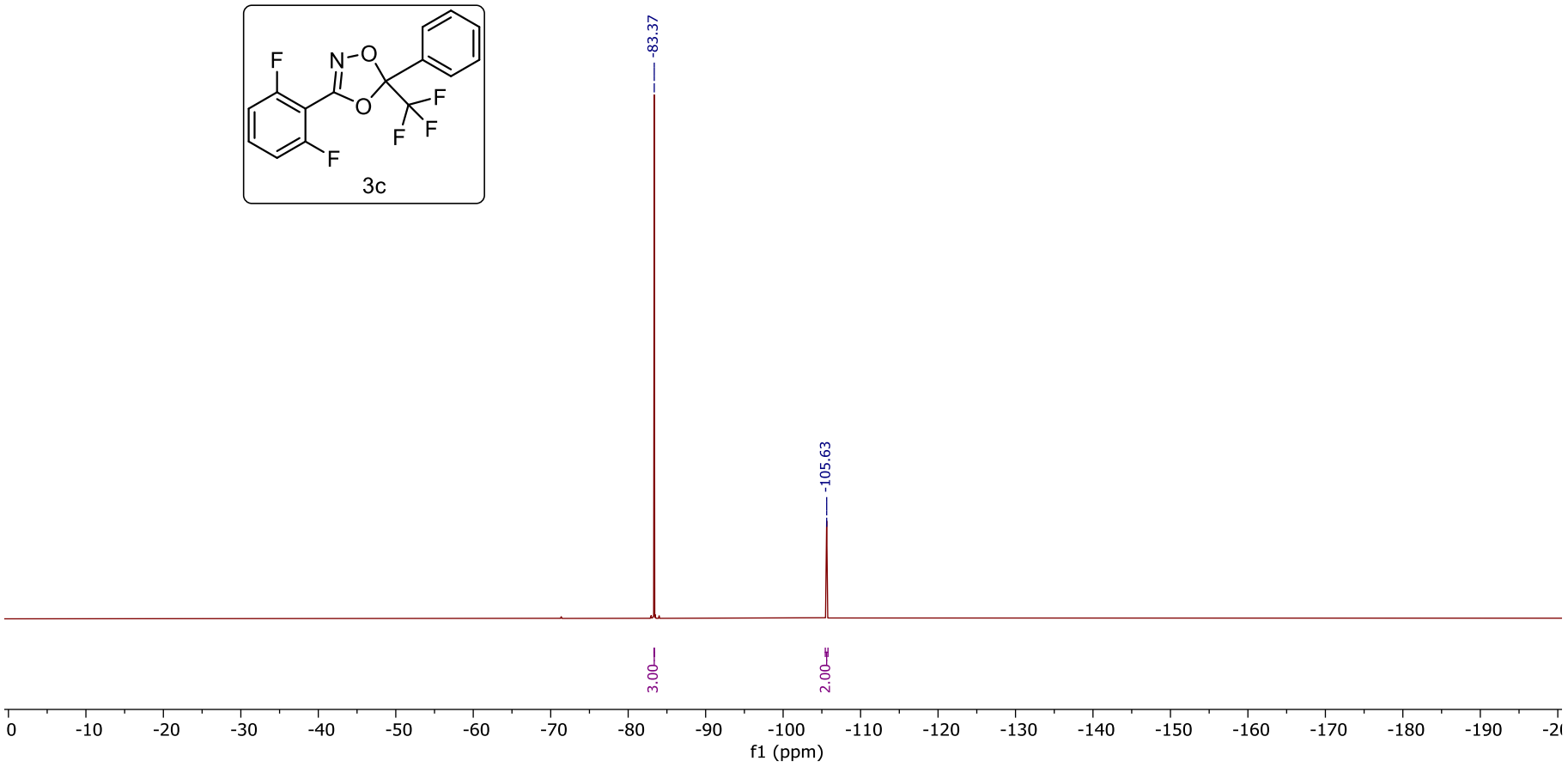

N
O
O
F
F
F

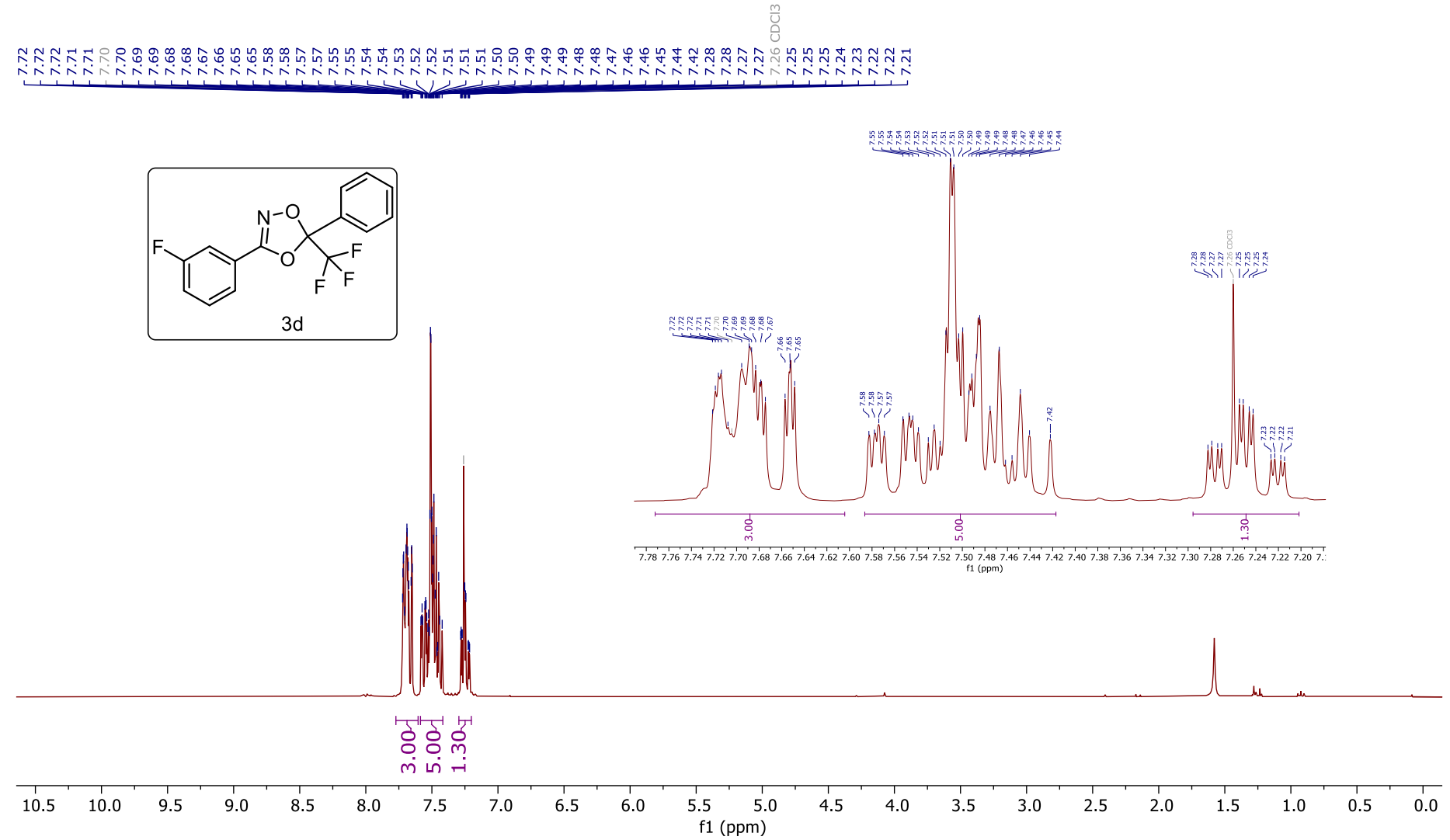
3b

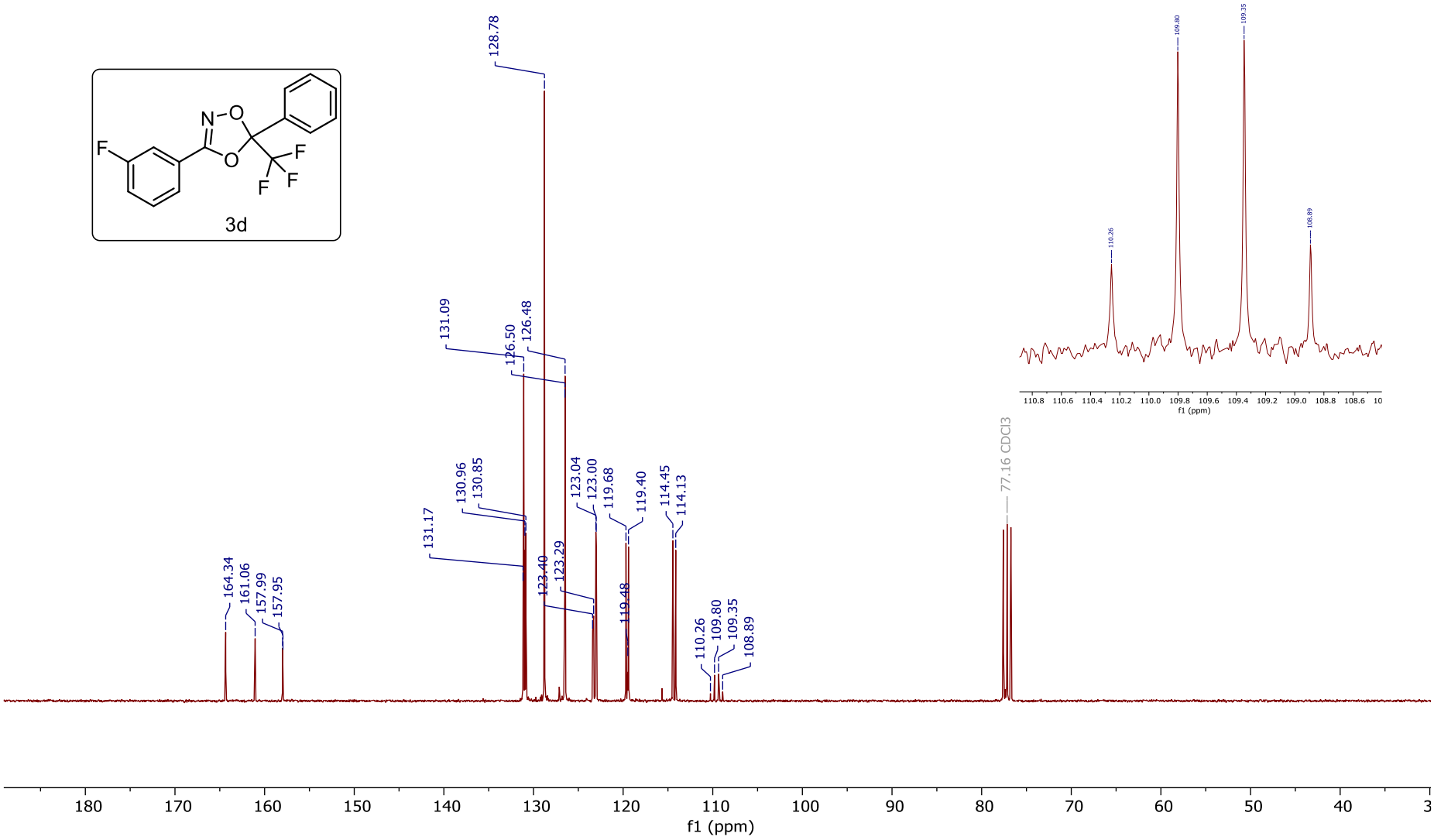

-83.19
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

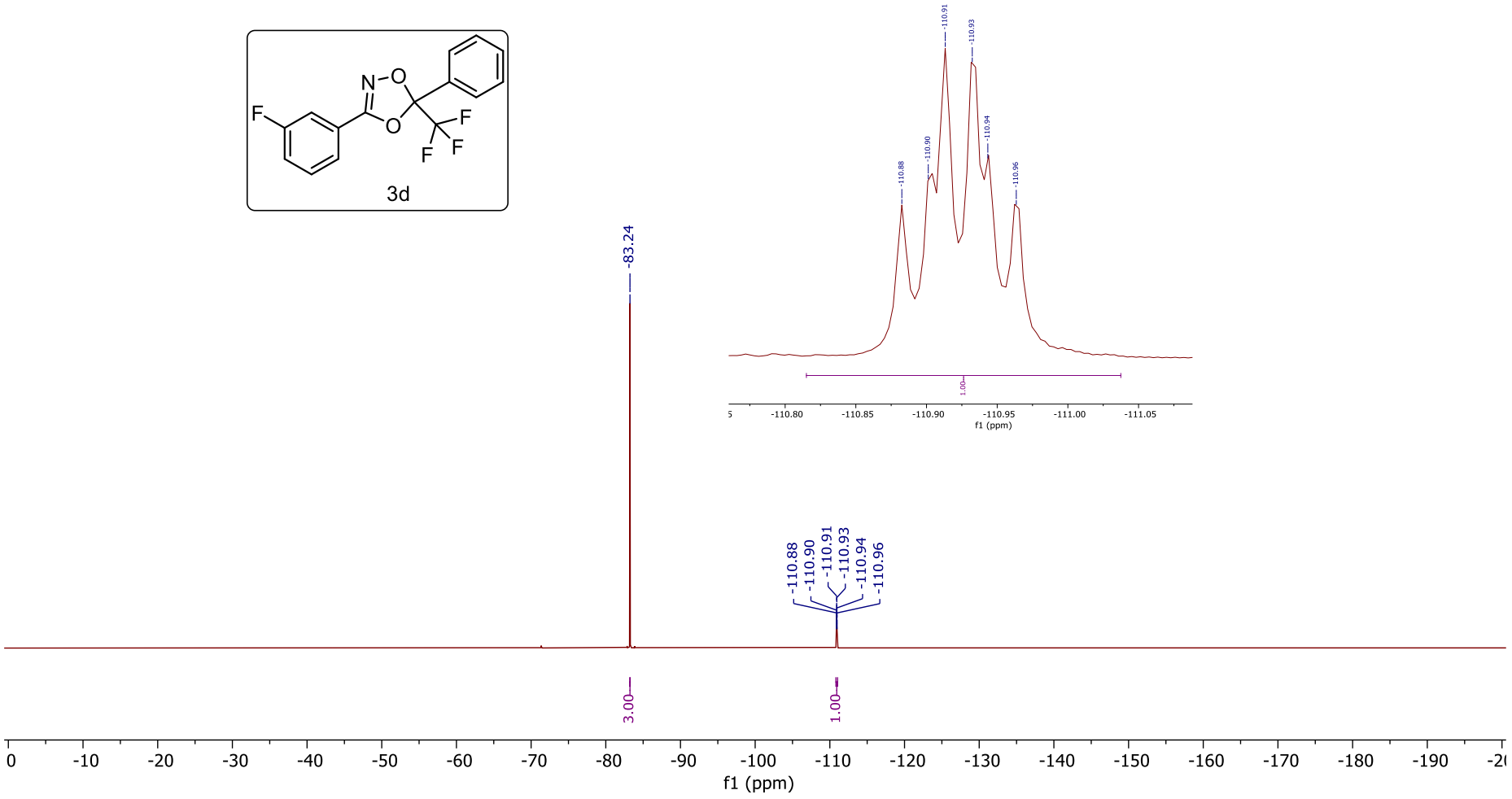

3c
F
N
O
O
F
F
F
F
7.71 7.71 7.71 7.70 7.70 7.70 7.70 7.69 7.69 7.68 7.68
2.00
7.74 7.72 7.70 7.68 7.66 7.64
7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45
7.05
7.08 7.08 7.08
7.02 7.02 7.01
4.00
2.00
7.58 7.56 7.54 7.52 7.50 7.48 7.46 7.44 7.42 7.12 7.10 7.08 7.06 7.04 7.02 7.00
f1 (ppm)
7.71 7.71 7.71 7.70 7.70 7.70 7.70 7.69 7.69 7.68 7.68 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.48 7.47 7.47 7.46 7.46 7.45
7.26 CDCl3
7.08 7.08 7.08 7.05 7.02 7.02 7.01
2.00
4.00
2.00
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)

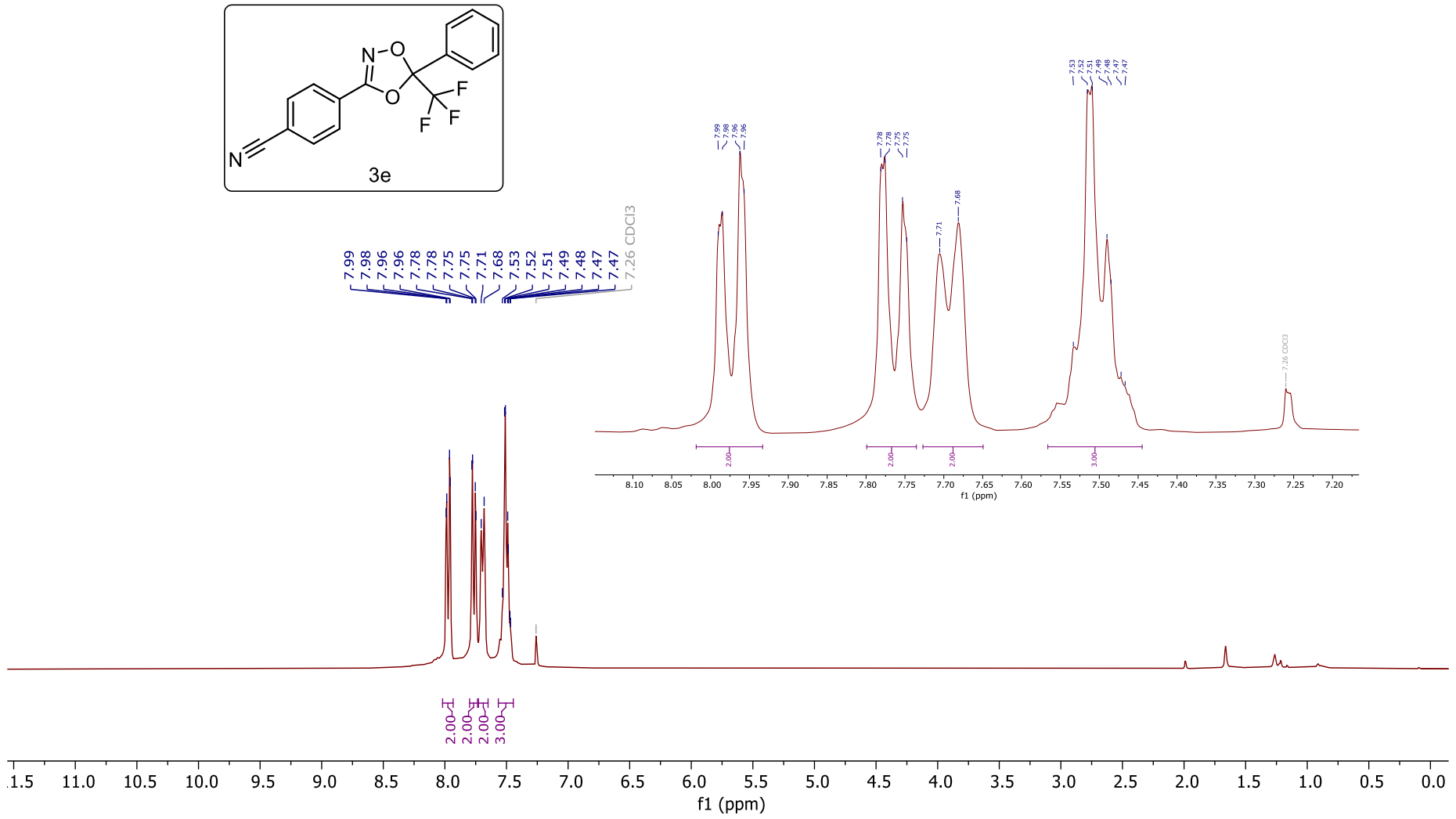

F
N
O
O
F
F
F
F
3c
162.83
162.76
159.38
159.32
151.99
134.49
134.36
134.22
131.06
128.73
130.98
126.53
123.28
119.45
112.63
112.58
112.35
112.30
109.00
100.57
100.34
100.12
77.16 CDCl3
f1 (ppm)

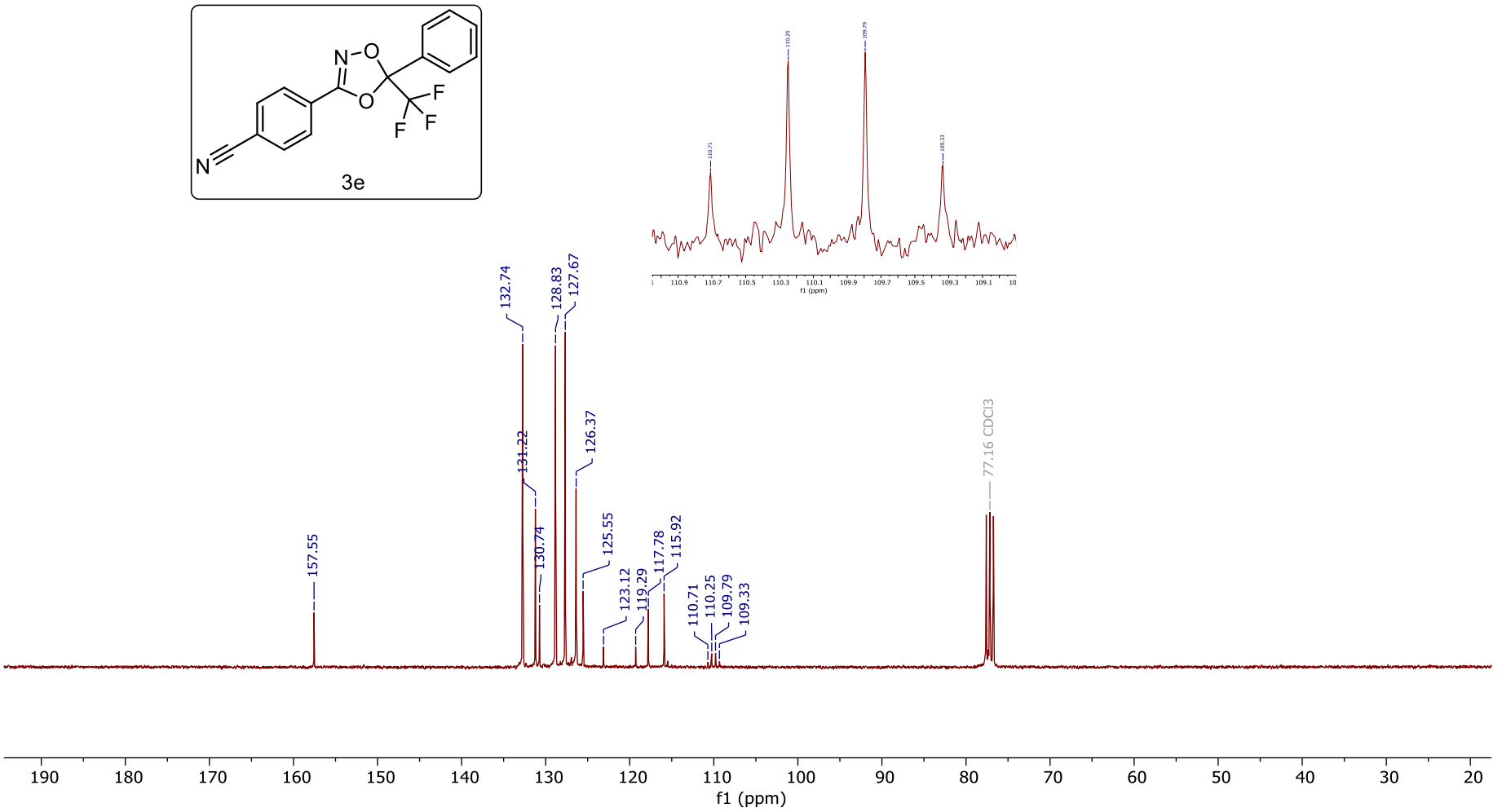

F
N
O
O
F
F
F
F
3c
-83.37
-105.63
3.00
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

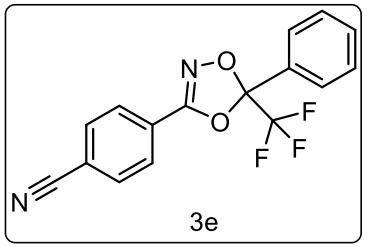

7.72 7.72 7.72 7.71 7.71 7.70 7.70 7.69 7.69 7.68 7.68 7.67 7.66 7.65 7.65 7.58 7.58 7.57 7.57 7.55 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.51 7.51 7.50 7.50 7.49 7.49 7.49 7.48 7.48 7.47 7.46 7.46 7.45 7.44 7.42 7.28 7.28 7.27 7.27 7.26 CDCl3 7.25 7.25 7.25 7.24 7.23 7.22 7.22 7.21
3d
3.00
5.00
1.30
f1 (ppm)

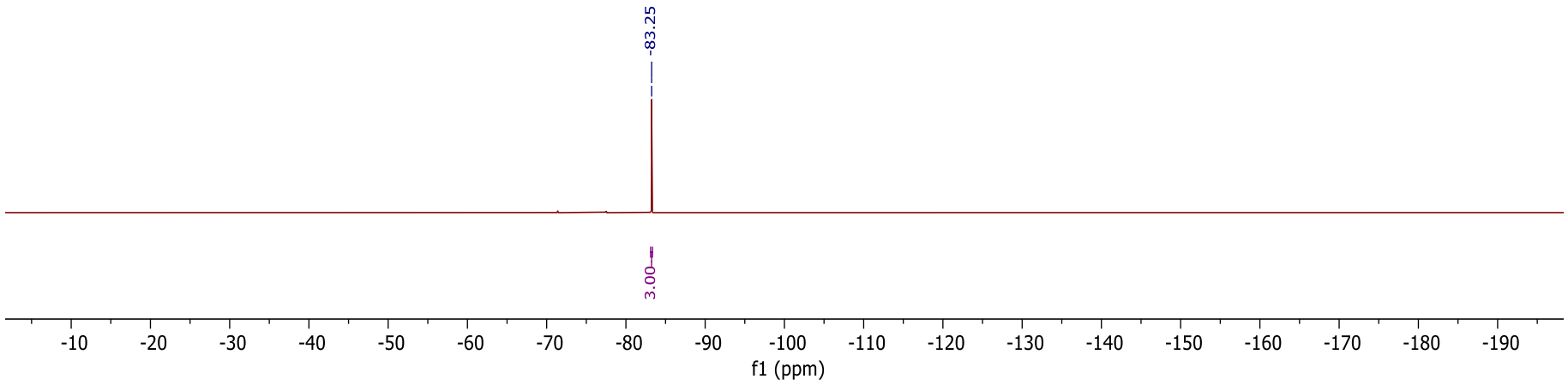

3d
128.78
131.09
126.50
126.48
130.96
130.85
131.17
123.04
123.00
119.68
119.40
114.45
114.13
123.40
123.29
119.48
164.34
161.06
157.99
157.95
110.26
109.80
109.35
108.89
77.16 CDCl3
f1 (ppm)

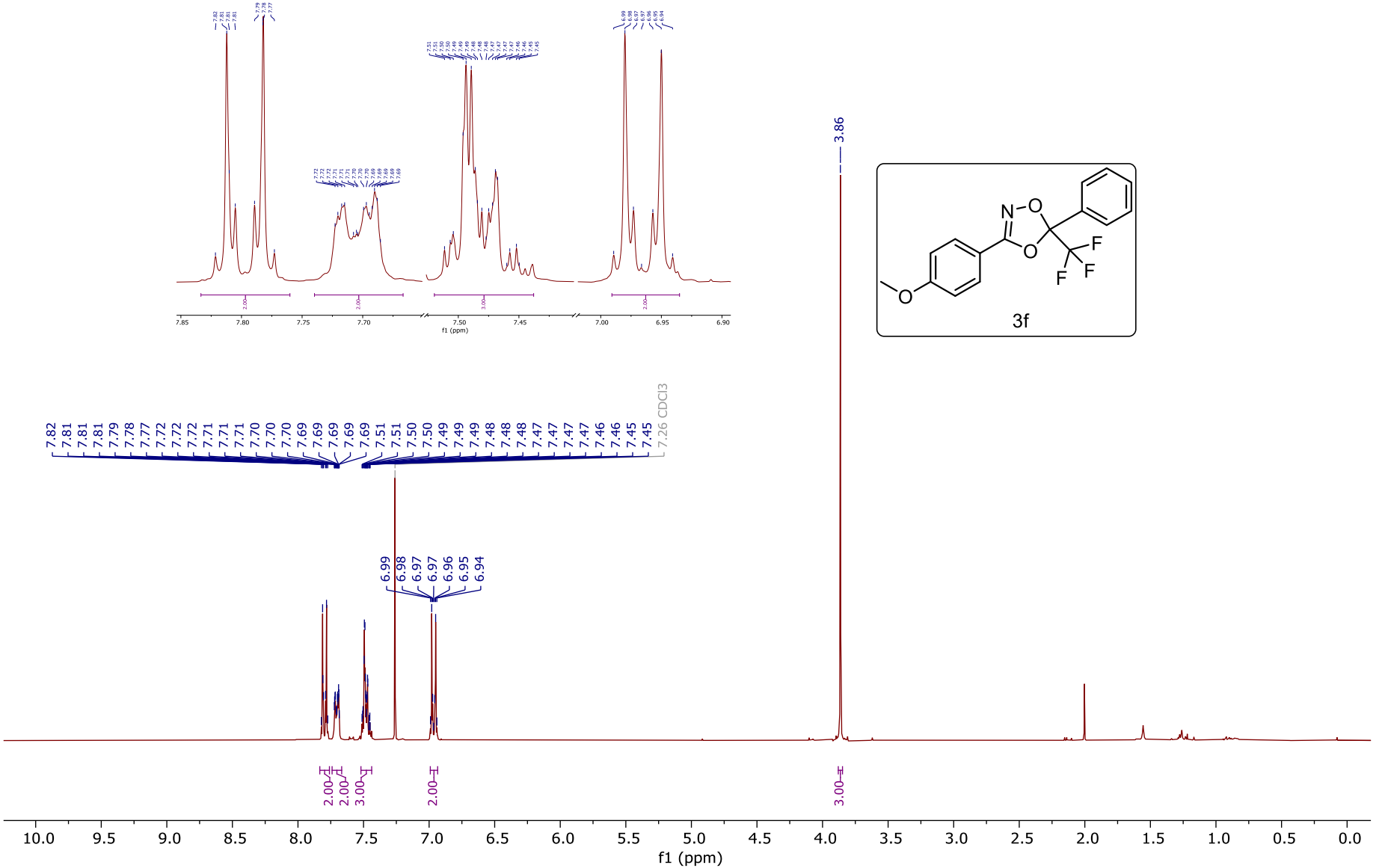

3d
-83.24
-110.88
-110.90
-110.91
-110.93
-110.94
-110.96
3.00
1.00
f1 (ppm)

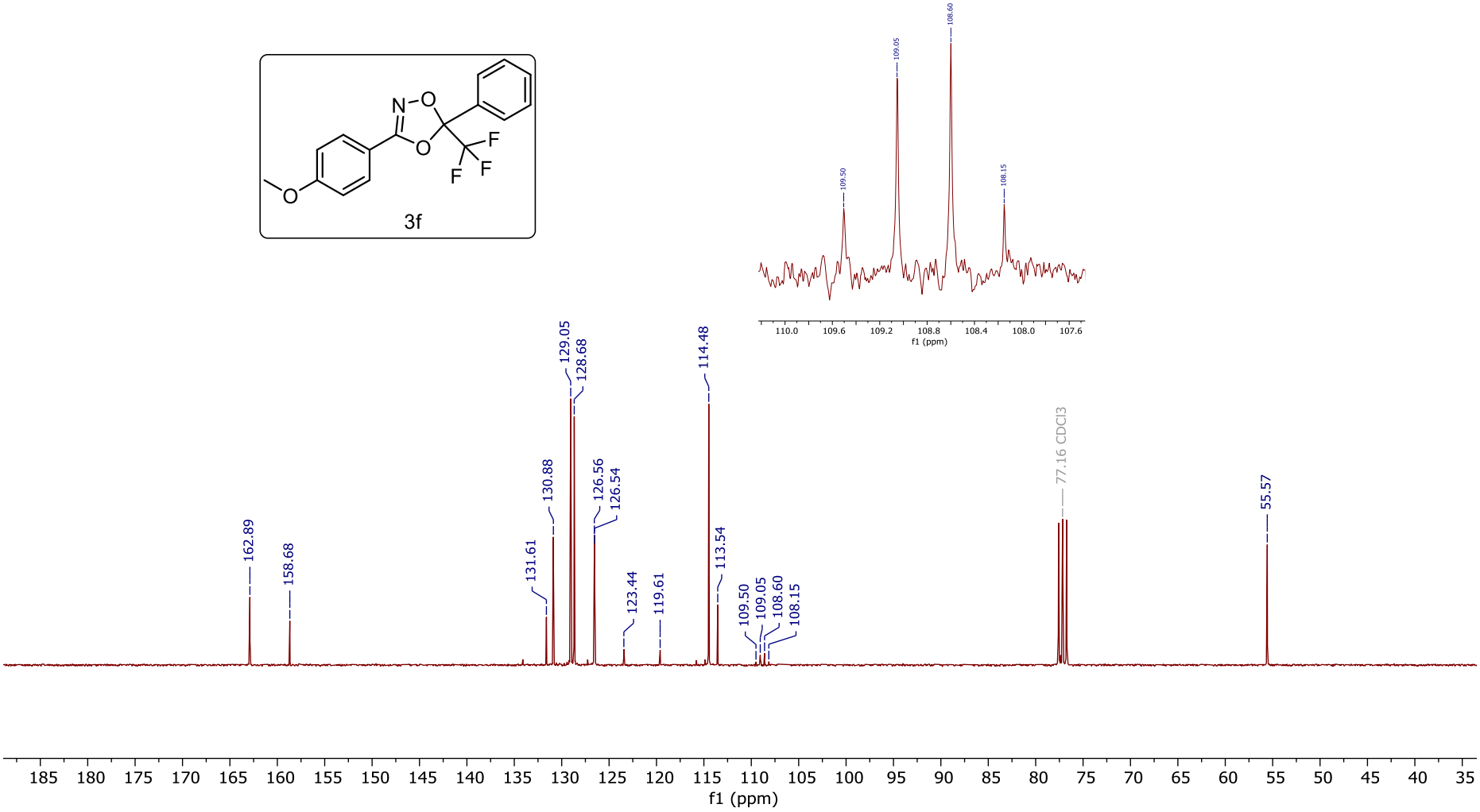

3e
7.99
7.98
7.96
7.96
7.78
7.78
7.75
7.75
7.71
7.68
7.53
7.52
7.51
7.49
7.48
7.47
7.47
7.26 CDCl3
2.00
2.00
2.00
3.00
f1 (ppm)

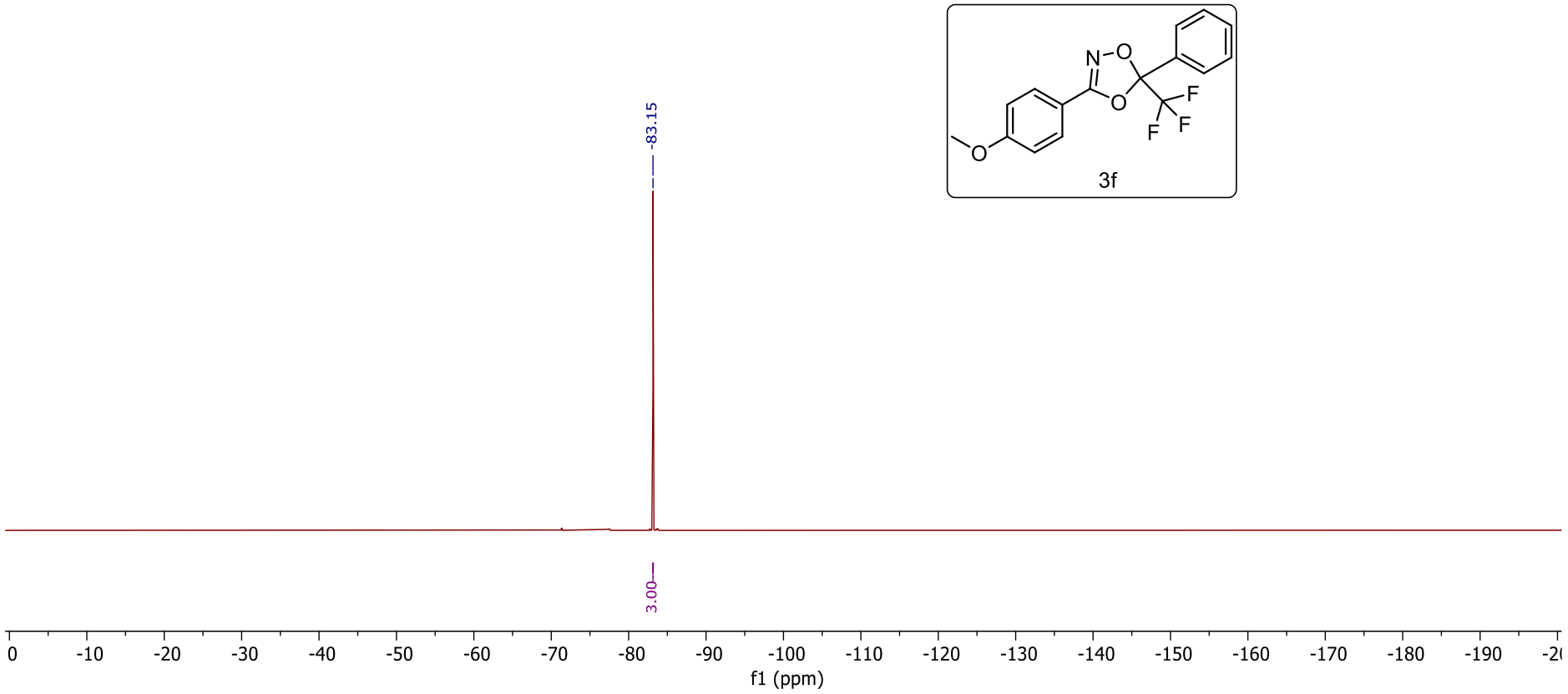

3e
157.55
132.74
131.22
130.74
128.83
127.67
126.37
125.55
123.12
119.29
117.78
115.92
110.71
110.25
109.79
109.33
77.16 CDCl3
f1 (ppm)

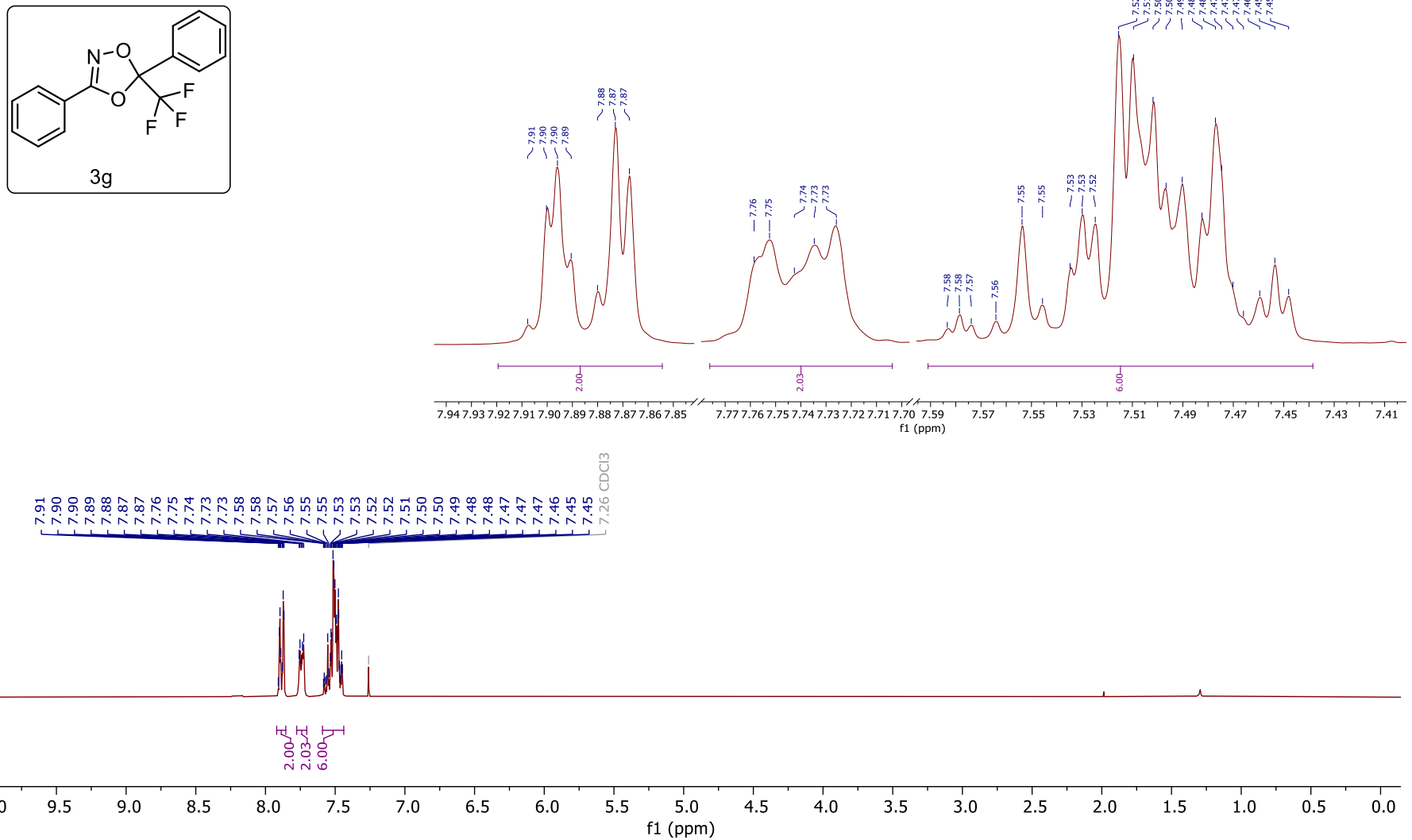

N
O
O
F
F
F
N
3e

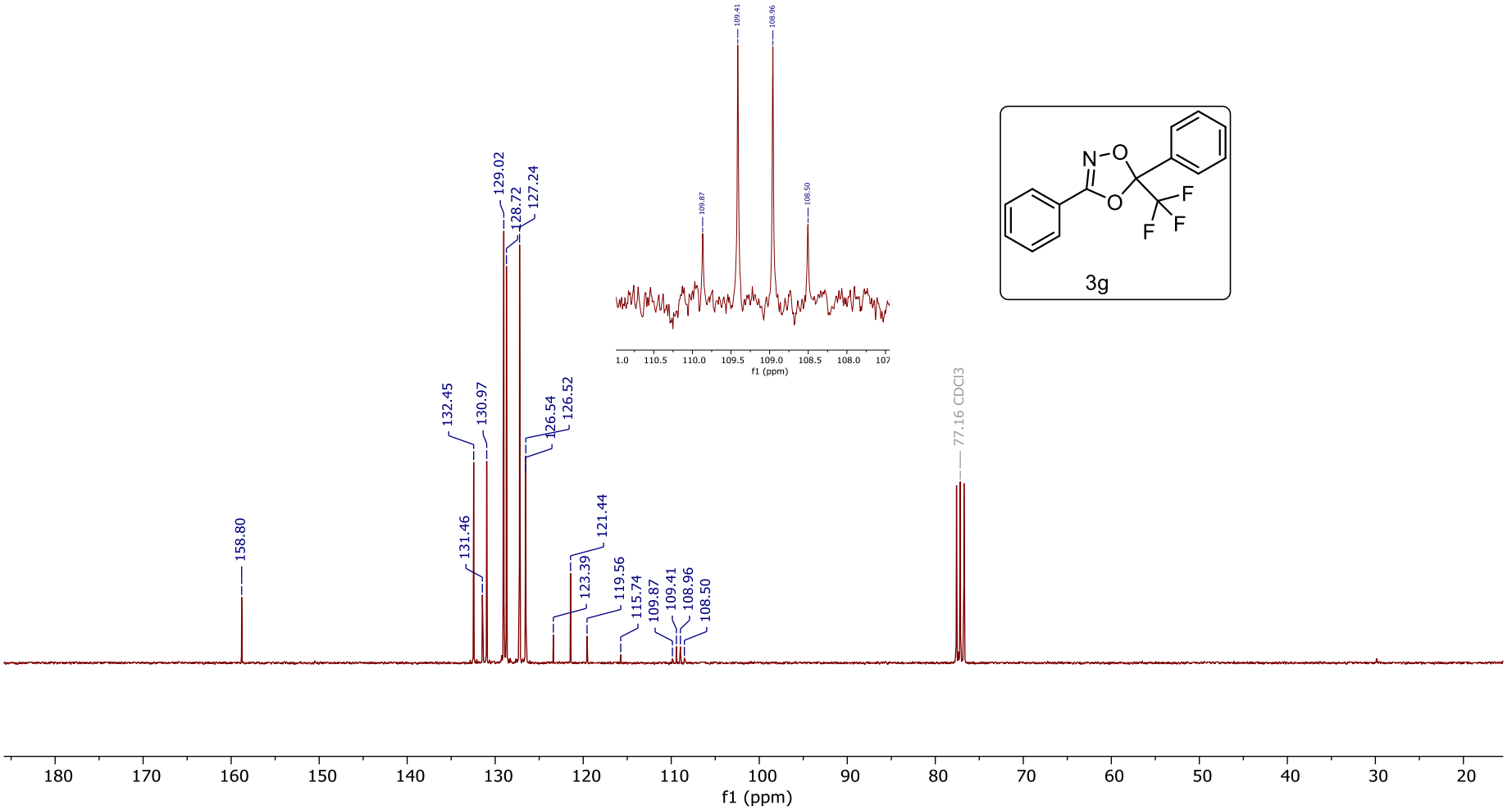

-83.25
3.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

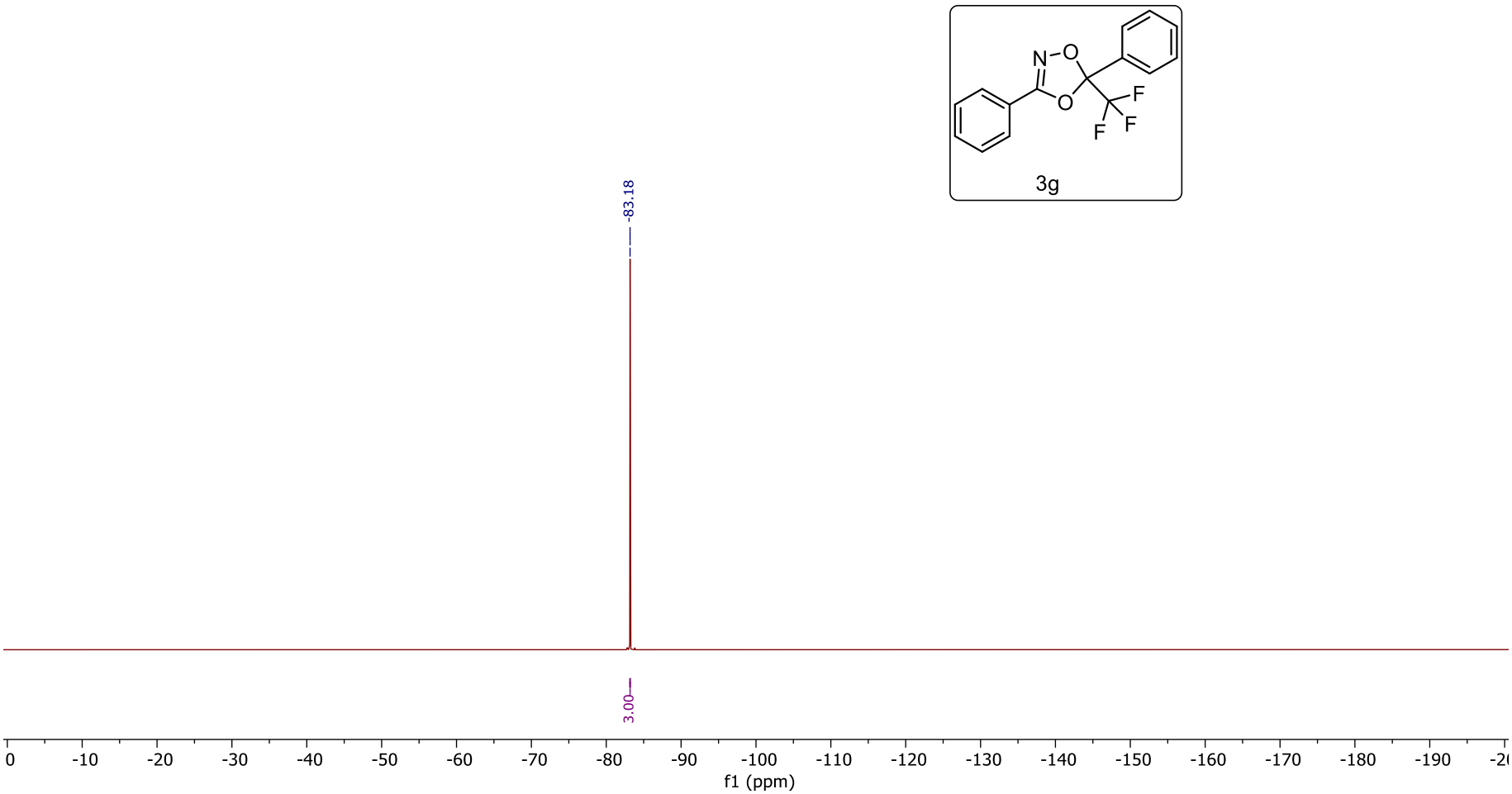

3.86
7.82
7.81
7.81
7.81
7.79
7.78
7.77
7.72
7.72
7.72
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.69
7.69
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.47
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.26 CDCl3
6.99
6.98
6.97
6.97
6.96
6.95
6.94
2.00
2.00
3.00
2.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
N
O
O
F
F
F
O
3f

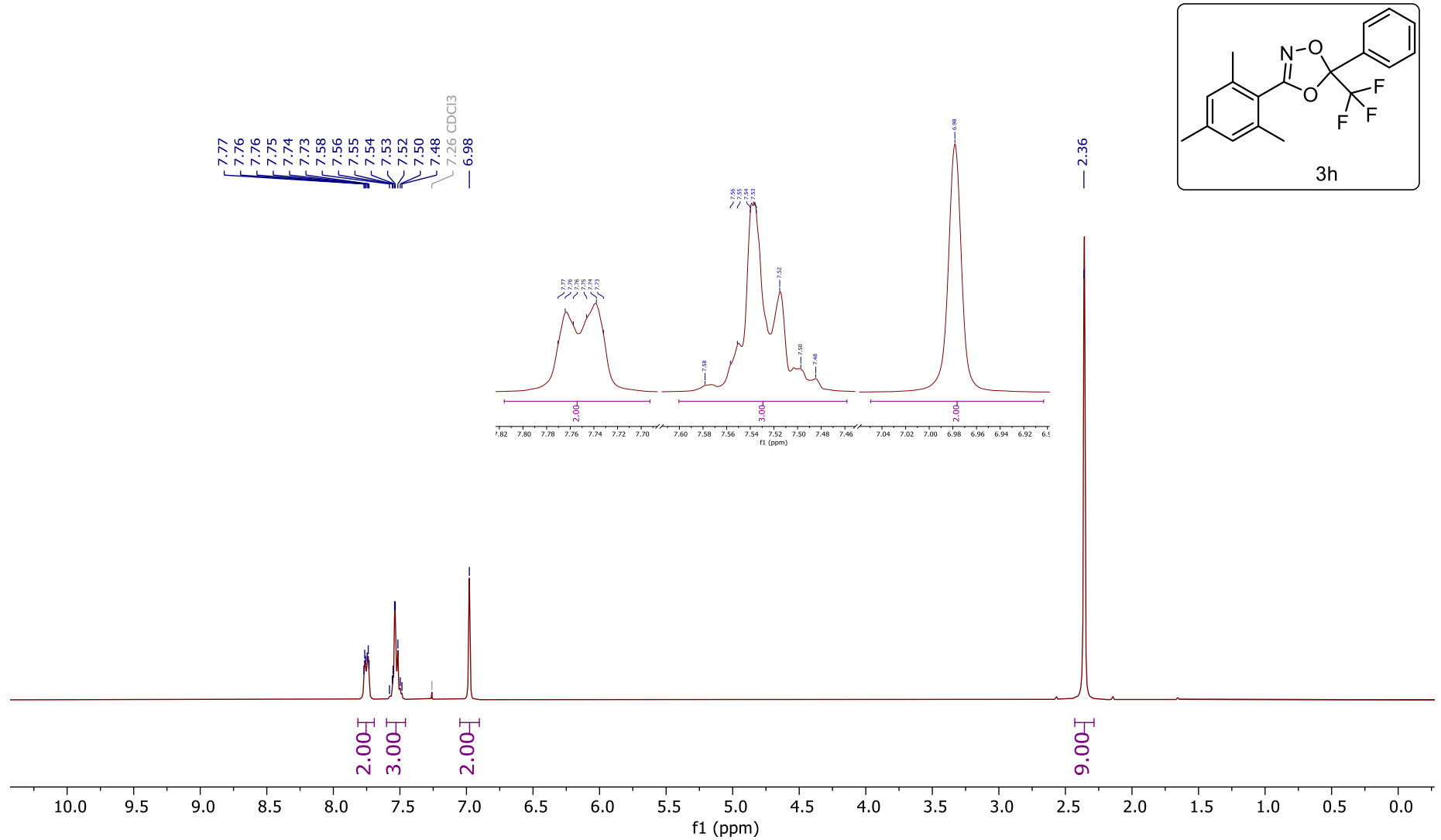

3f
162.89
158.68
131.61
130.88
129.05
128.68
126.56
126.54
123.44
119.61
114.48
113.54
109.50
109.05
108.60
108.15
77.16 CDCl3
55.57
f1 (ppm)

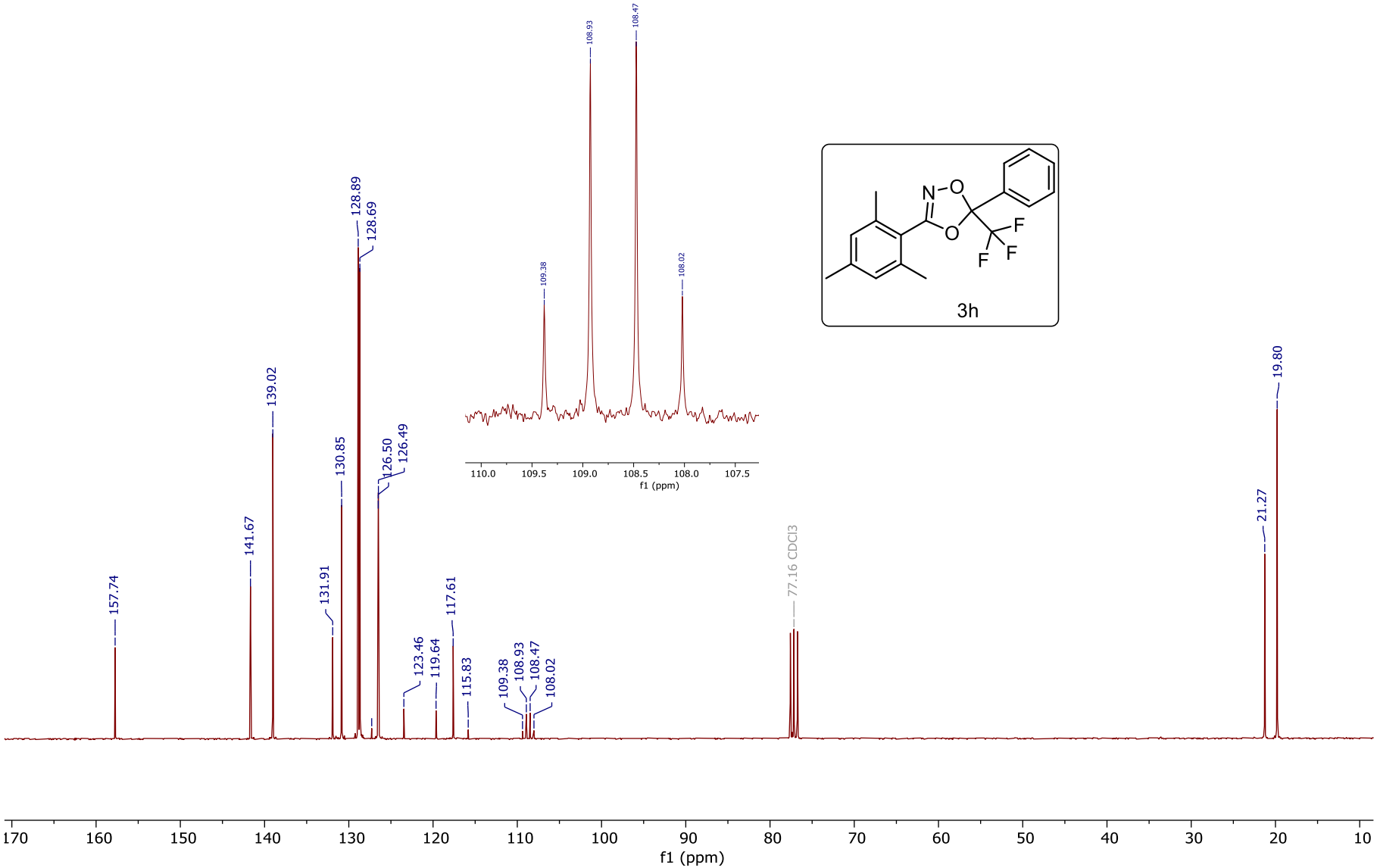

-83.15
3.00
3f
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

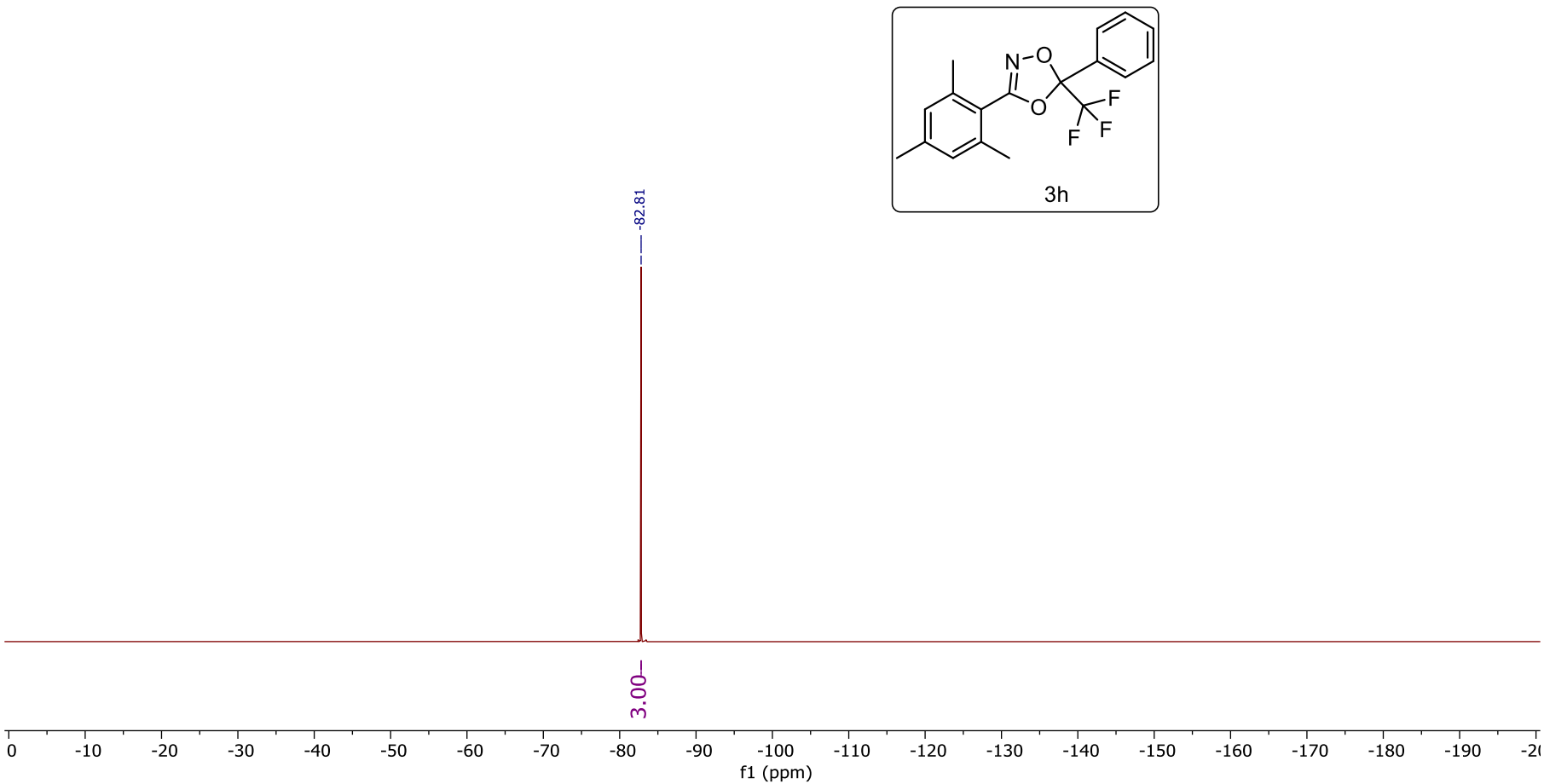

3g
7.91 7.90 7.90 7.89
7.88 7.87 7.87
7.76 7.75
7.74 7.73 7.73
7.58 7.58 7.57
7.56
7.55 7.55
7.53 7.53 7.52
7.52 7.51 7.50 7.50 7.49 7.48 7.48 7.47 7.47 7.47 7.46 7.45 7.45
2.00
2.03
6.00
f1 (ppm)
7.26 CDCl3
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

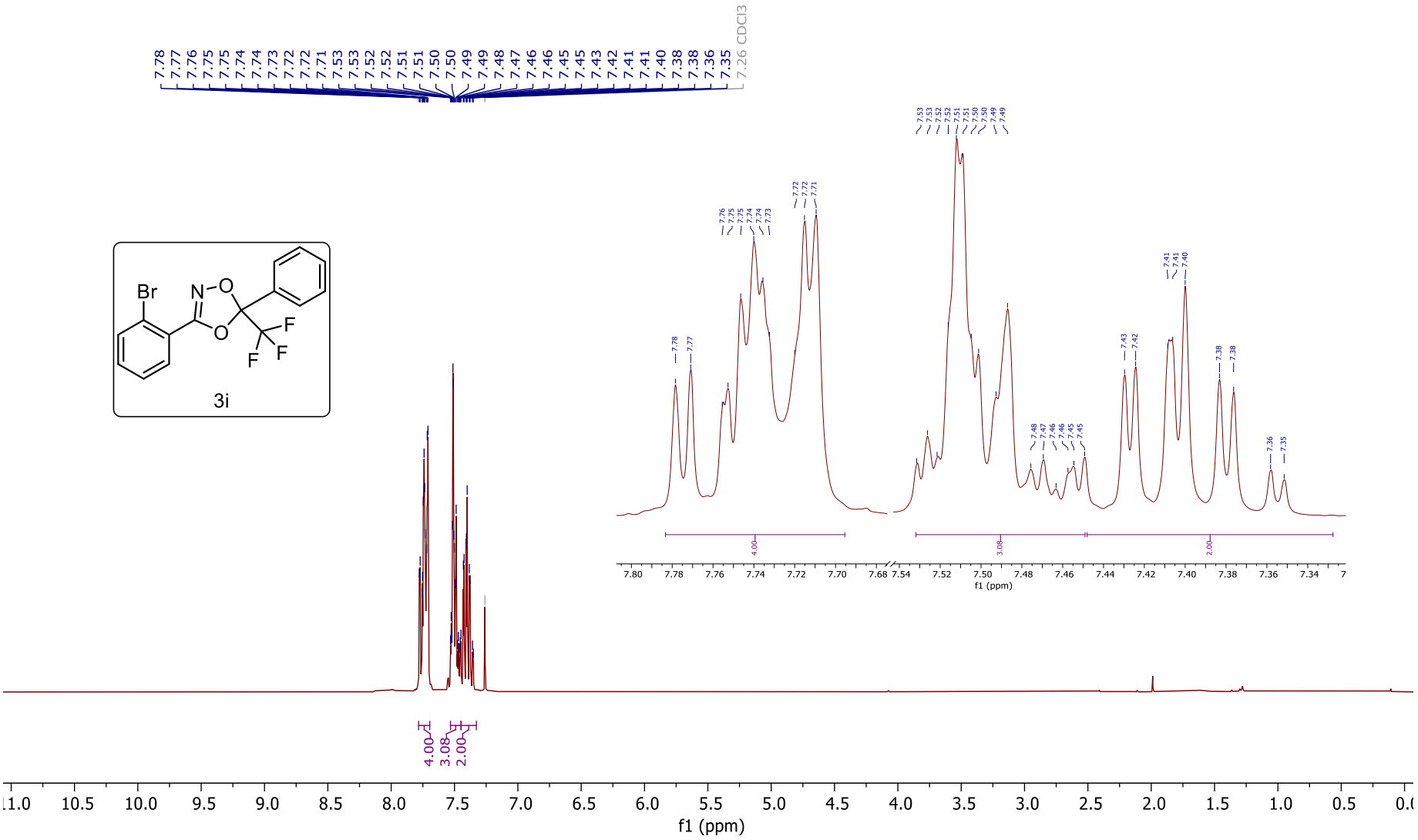

158.80
132.45
131.46
130.97
129.02
128.72
127.24
126.54
126.52
123.39
121.44
119.56
115.74
109.87
109.41
108.96
108.50
77.16 CDCl3
f1 (ppm)
3g

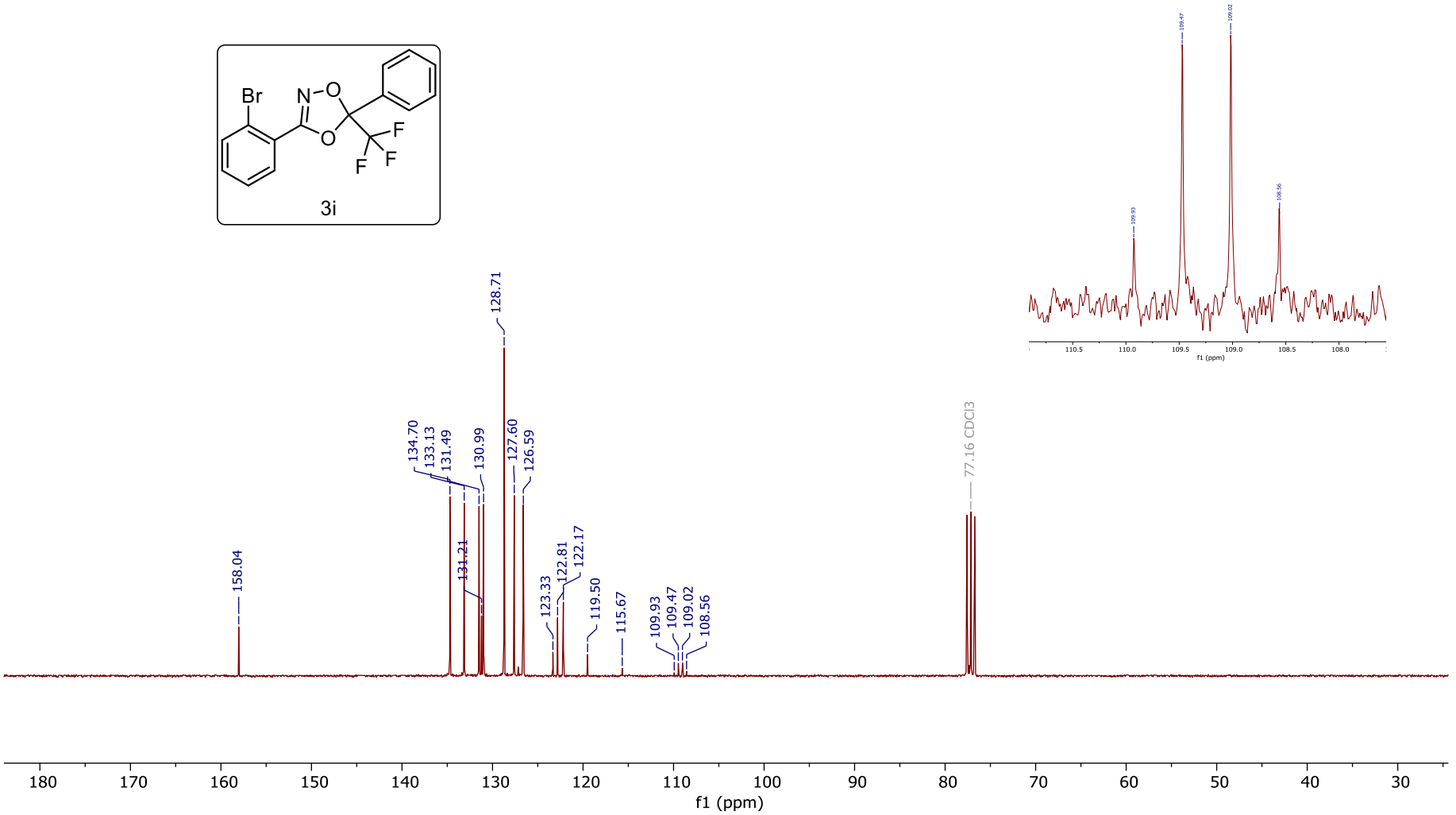

3g
-83.18
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

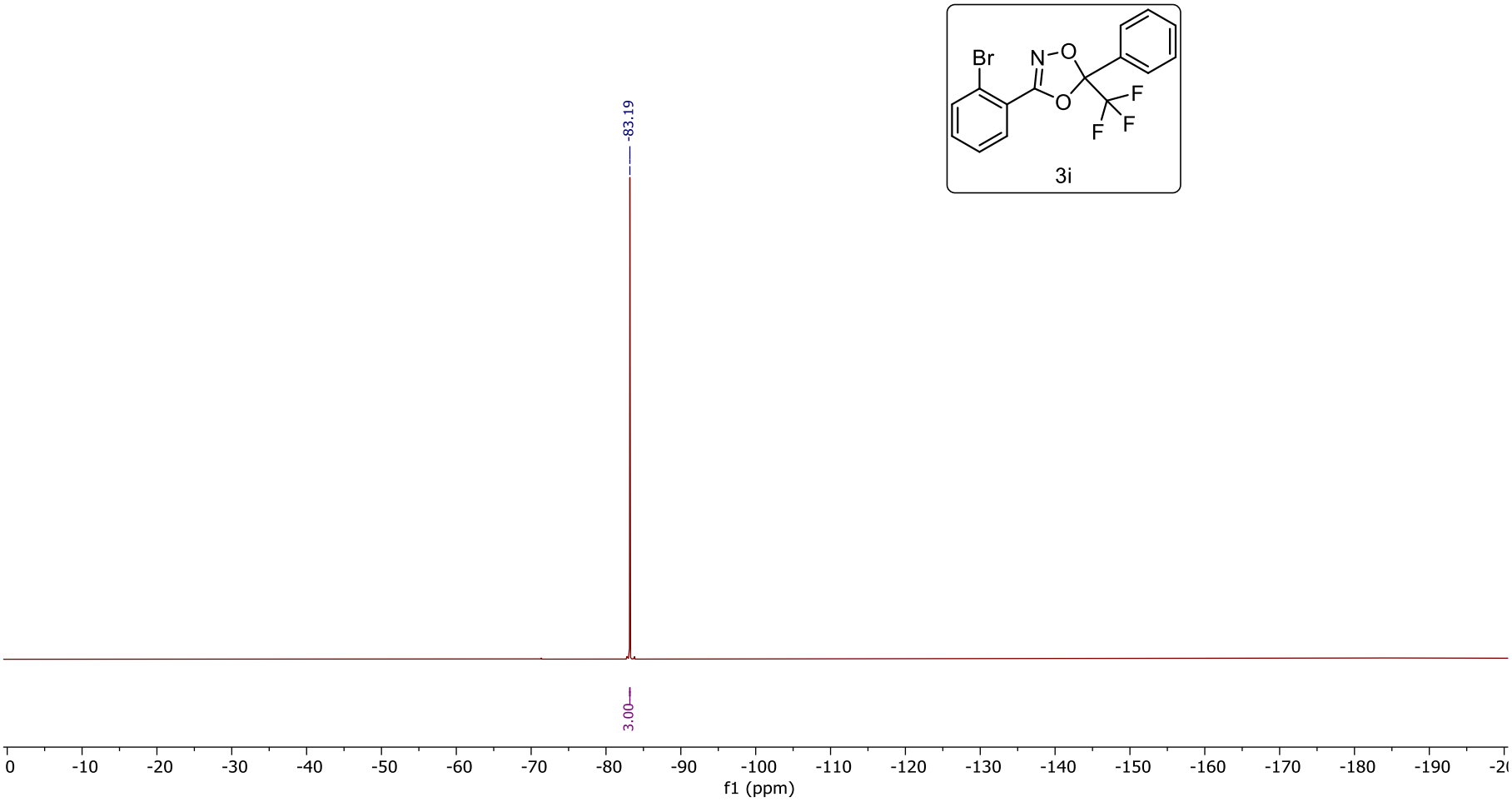

7.77
7.76
7.76
7.75
7.74
7.73
7.58
7.56
7.55
7.54
7.53
7.52
7.50
7.48
7.26 CDCl3
6.98
2.36
3h
2.00
3.00
2.00
9.00
f1 (ppm)

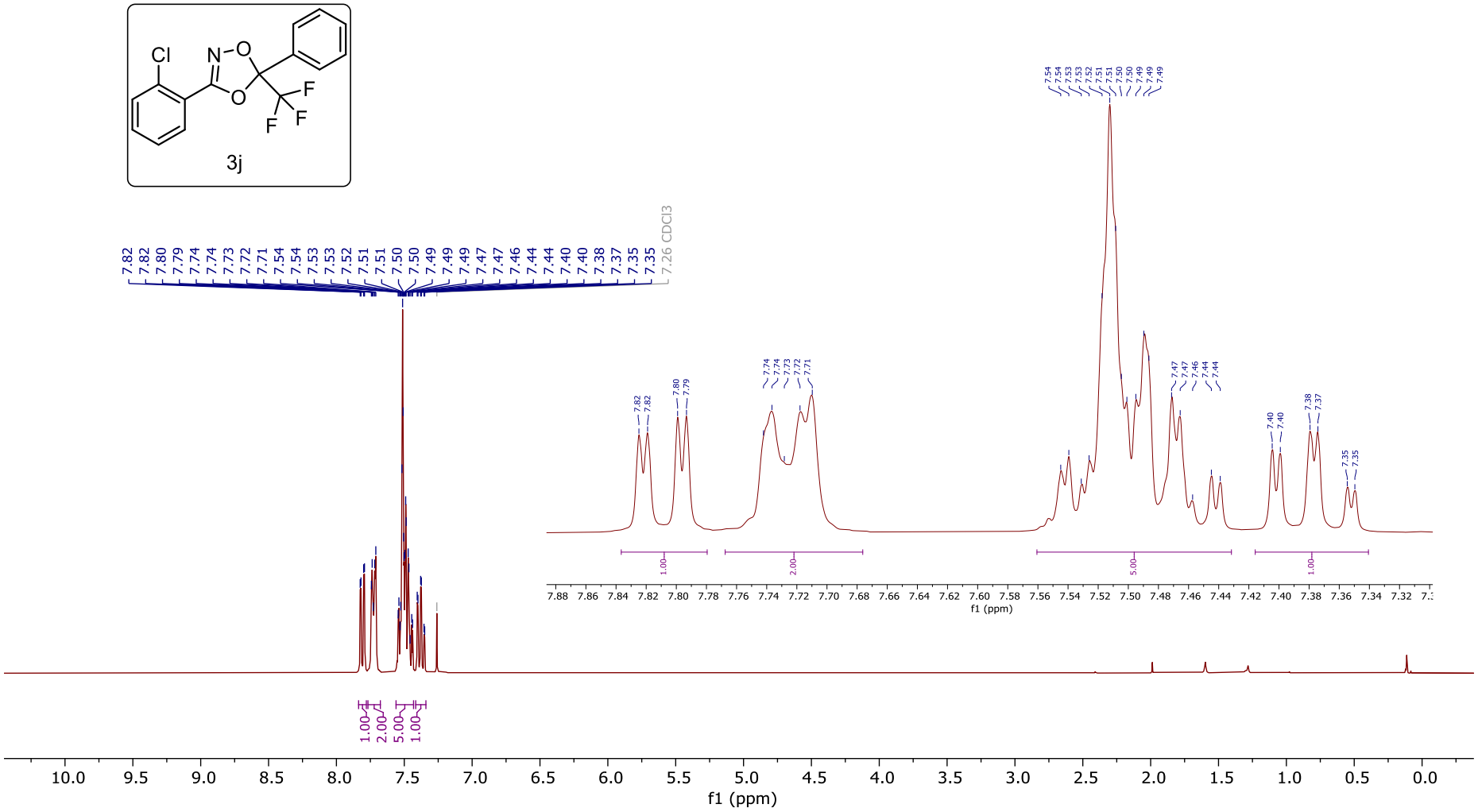

157.74
141.67
139.02
131.91
130.85
128.89
128.69
126.50
126.49
123.46
119.64
117.61
115.83
109.38
108.93
108.47
108.02
77.16 CDCl3
21.27
19.80
f1 (ppm)
3h
F
F
F
N
O
O

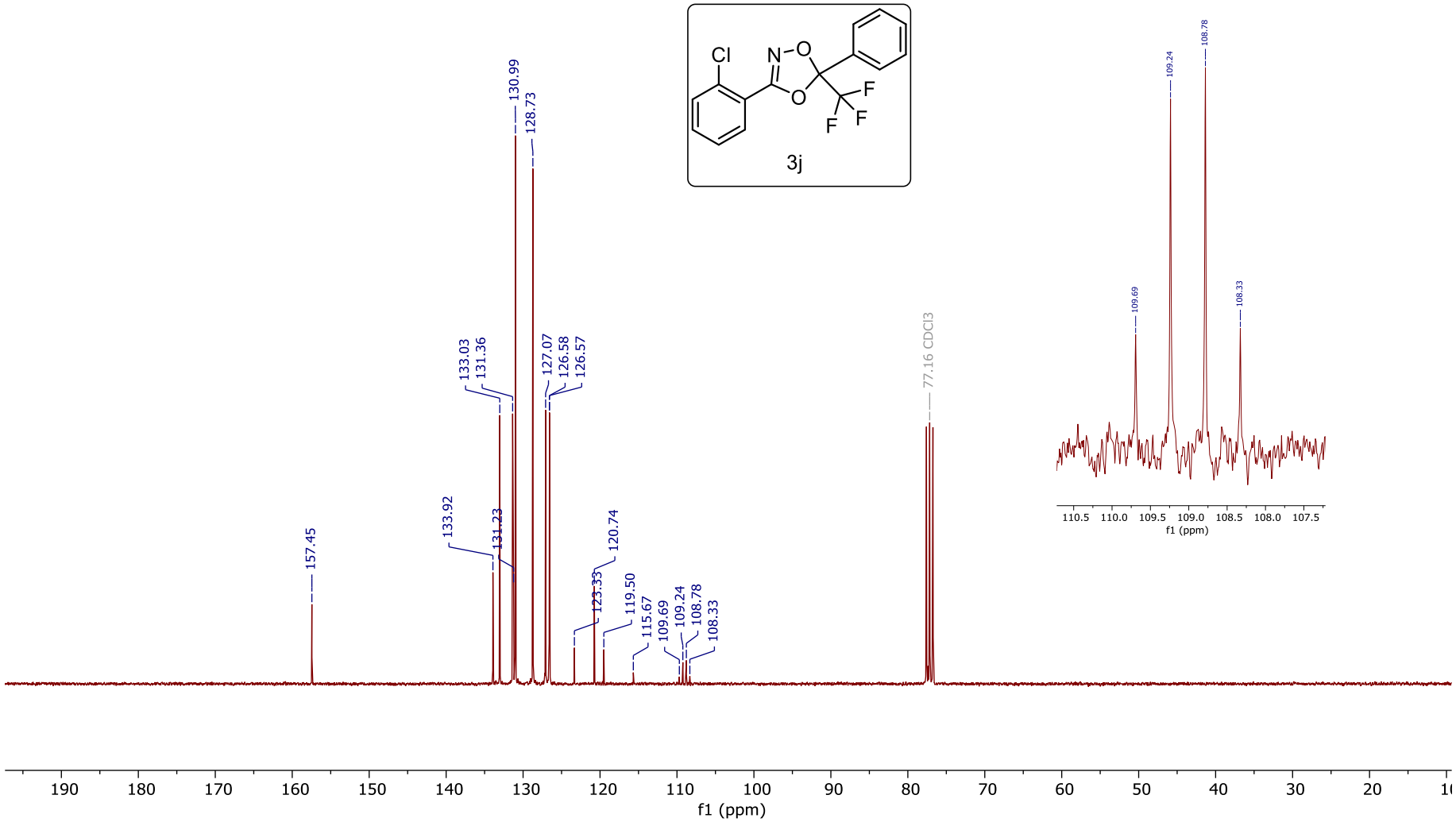

3h
-82.81
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

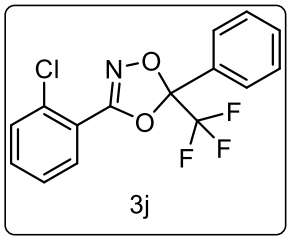

7.78 7.77 7.76 7.75 7.75 7.74 7.74 7.73 7.72 7.72 7.71 7.53 7.53 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.48 7.47 7.46 7.46 7.45 7.43 7.42 7.41 7.40 7.38 7.38 7.36 7.35 7.26 CDCl3
Br
N
O
O
F
F
F
3i
4.00
3.08
2.00
f1 (ppm)


Br
N
O
O
F
F
F
3i
158.04
134.70
133.13
131.49
131.21
130.99
128.71
127.60
126.59
123.33
122.81
122.17
119.50
115.67
109.93
109.47
109.02
108.56
77.16 CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

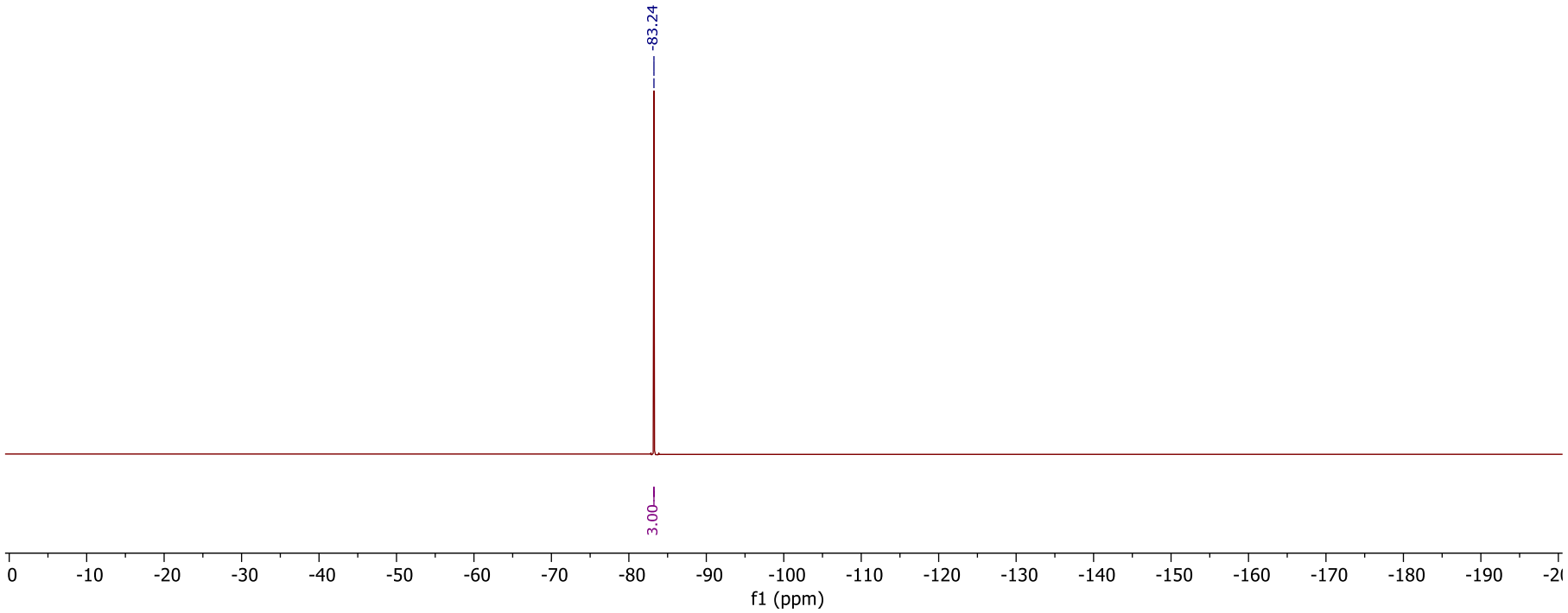

-83.19
3.00
Br
N
O
O
F
F
F
3i
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

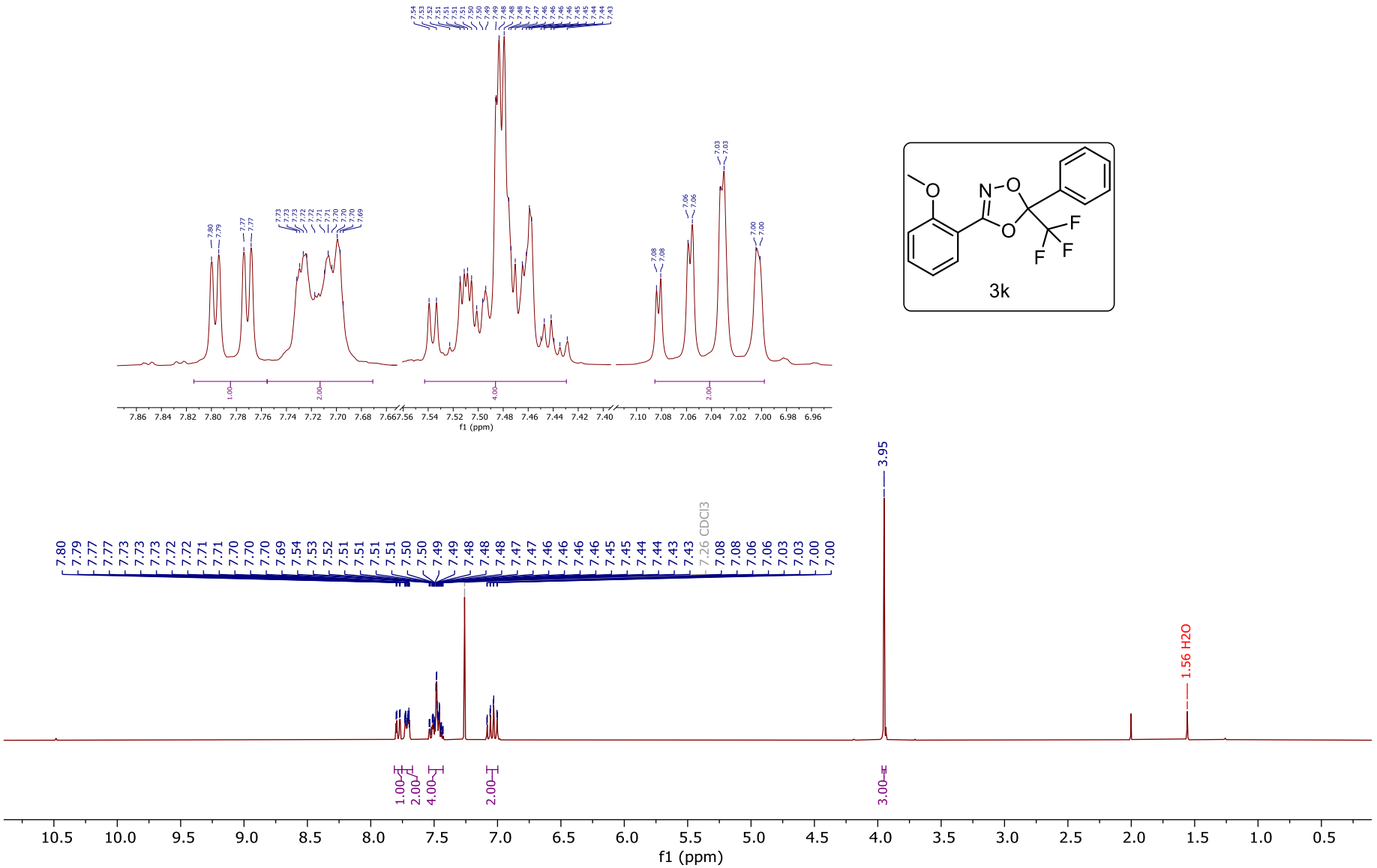

Cl
N
O
O
F
F
F
3j
7.82
7.82
7.80
7.79
7.74
7.74
7.73
7.72
7.71
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.46
7.44
7.44
7.40
7.38
7.37
7.35
7.35
7.26 CDCl3
1.00
2.00
5.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
7.88 7.86 7.84 7.82 7.80 7.78 7.76 7.74 7.72 7.70 7.68 7.66 7.64 7.62 7.60 7.58 7.56 7.54 7.52 7.50 7.48 7.46 7.44 7.42 7.40 7.38 7.36 7.34 7.32
f1 (ppm)

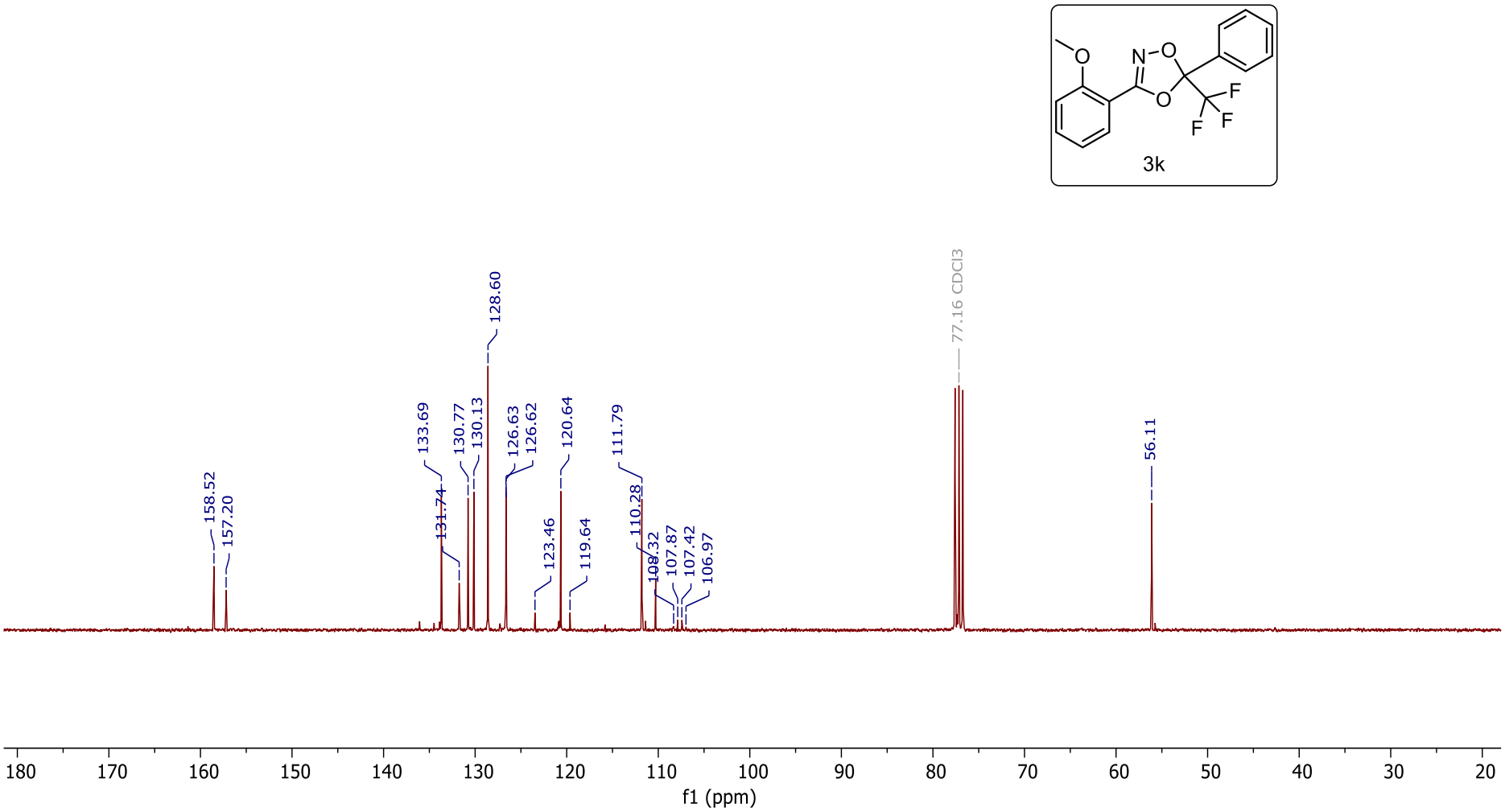

Cl
N
O
O
F
F
F
3j
130.99
128.73
133.03
131.36
127.07
126.58
126.57
133.92
131.23
120.74
123.33
119.50
115.67
109.69
109.24
108.78
108.33
157.45
77.16 CDCl3
109.69
109.24
108.78
108.33
110.5 110.0 109.5 109.0 108.5 108.0 107.5
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

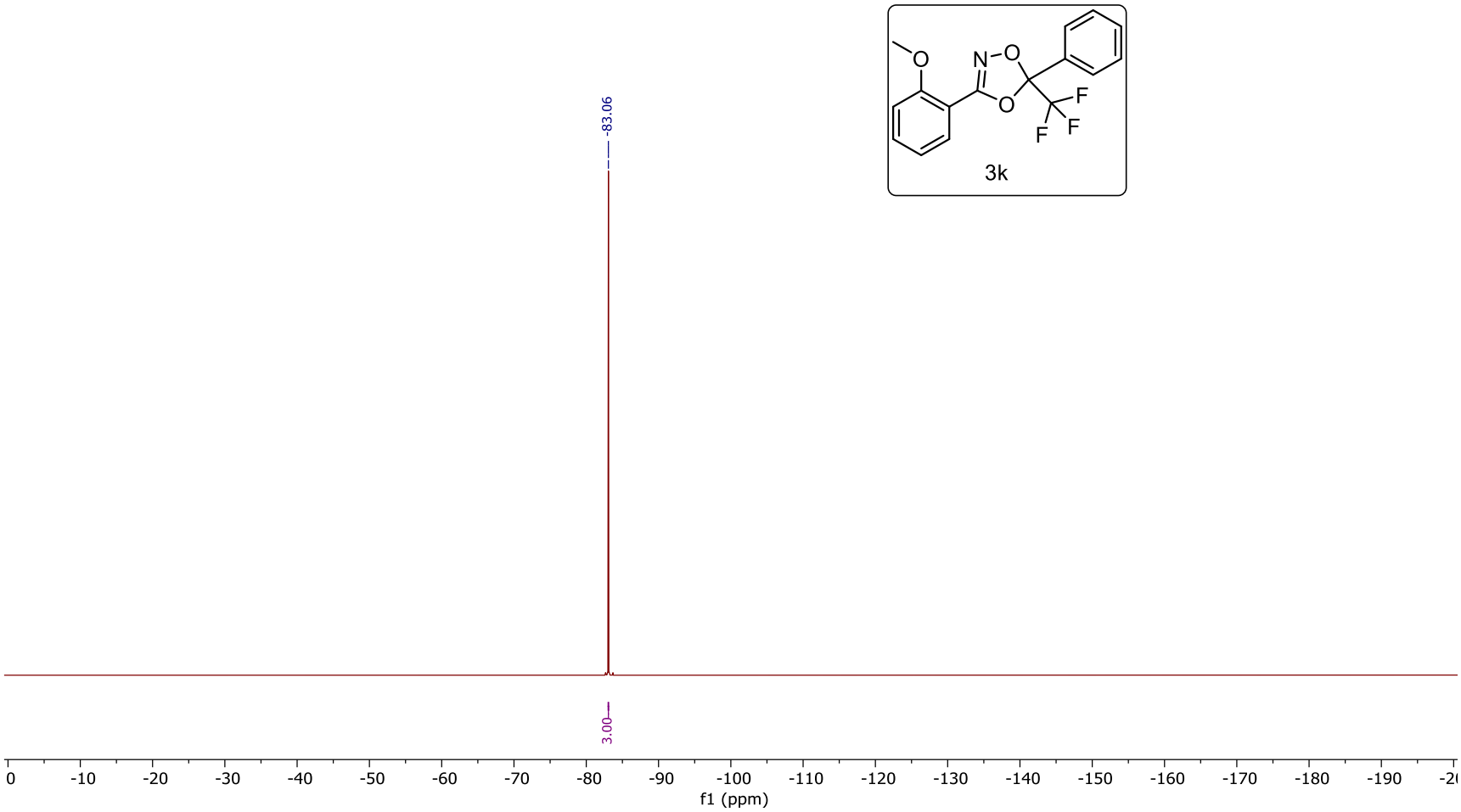

Cl
N
O
O
F
F
F

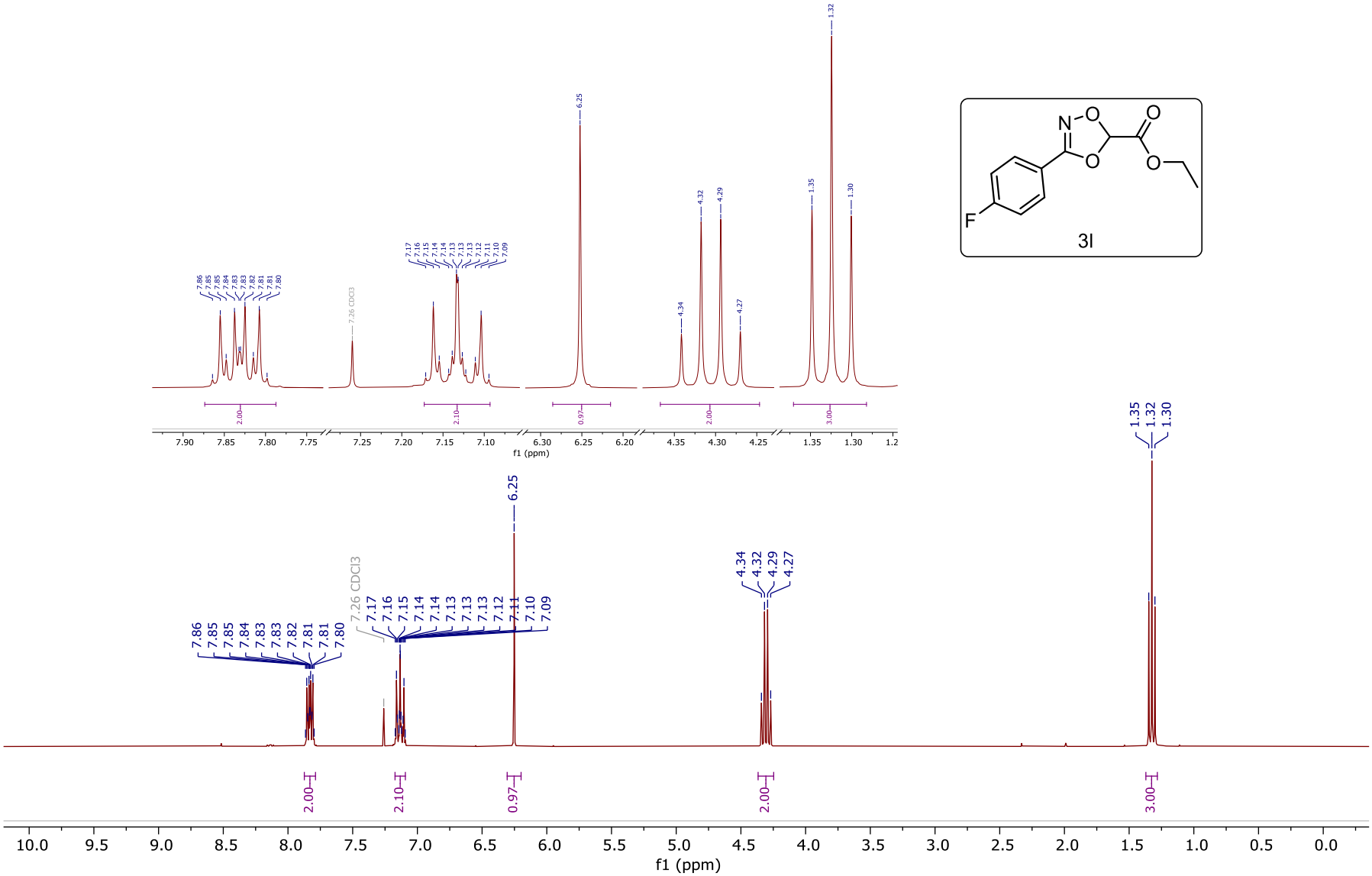
3j

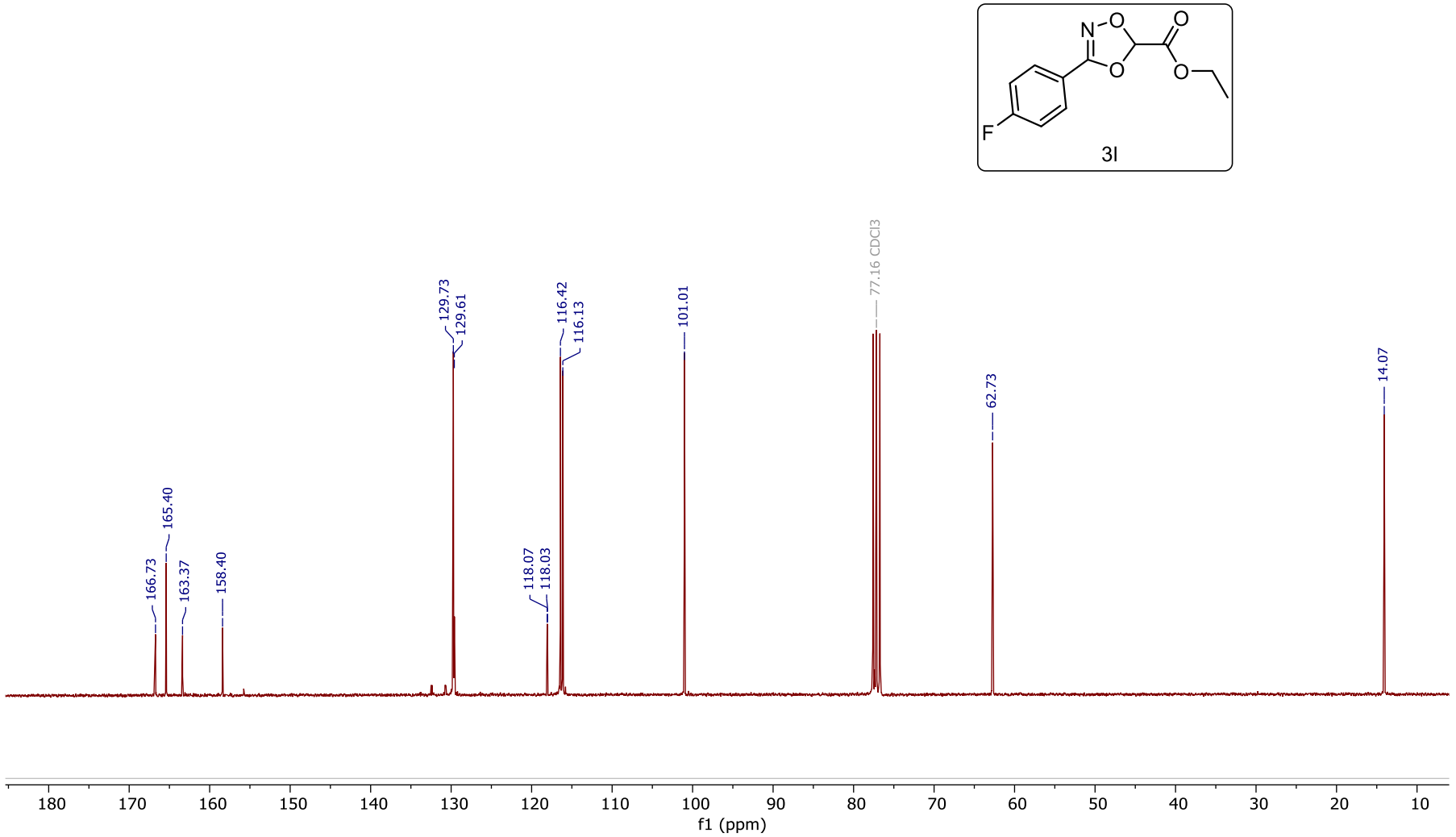

-83.24
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

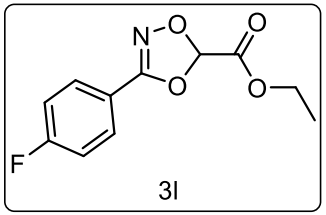

3k
f1 (ppm)
CDCl3
1.56 H2O
3.95


3k
158.52
157.20
133.69
131.74
130.77
130.13
128.60
126.63
126.62
123.46
120.64
119.64
111.79
110.28
109.32
107.87
107.42
106.97
77.16 CDCl3
56.11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

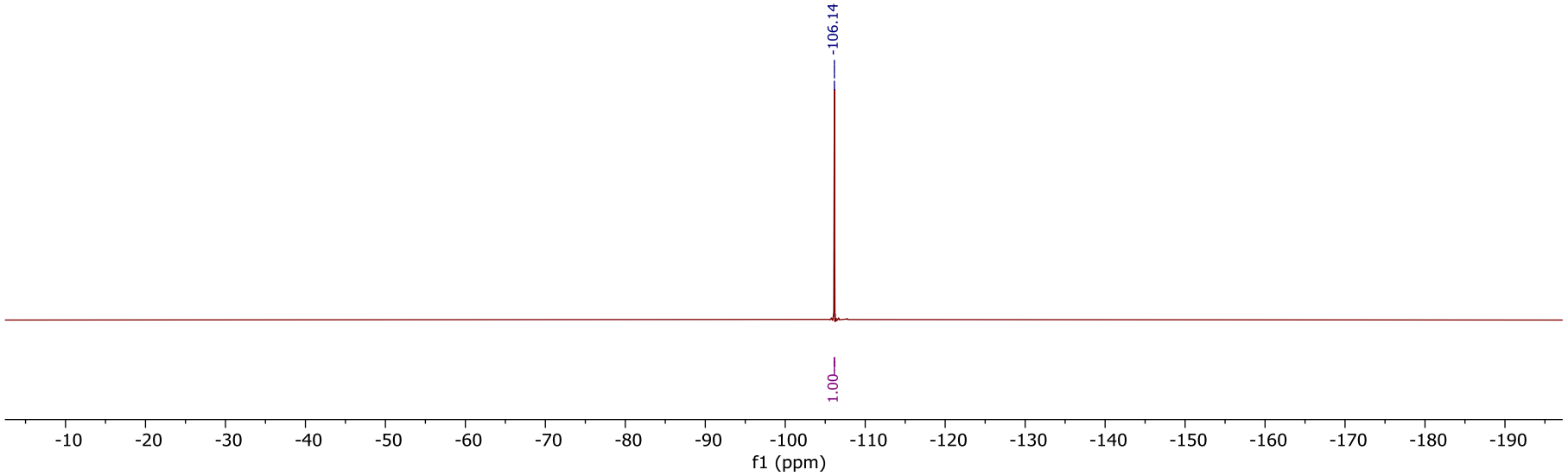

-83.06
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)
O
N
O
O
F
F
F
3k

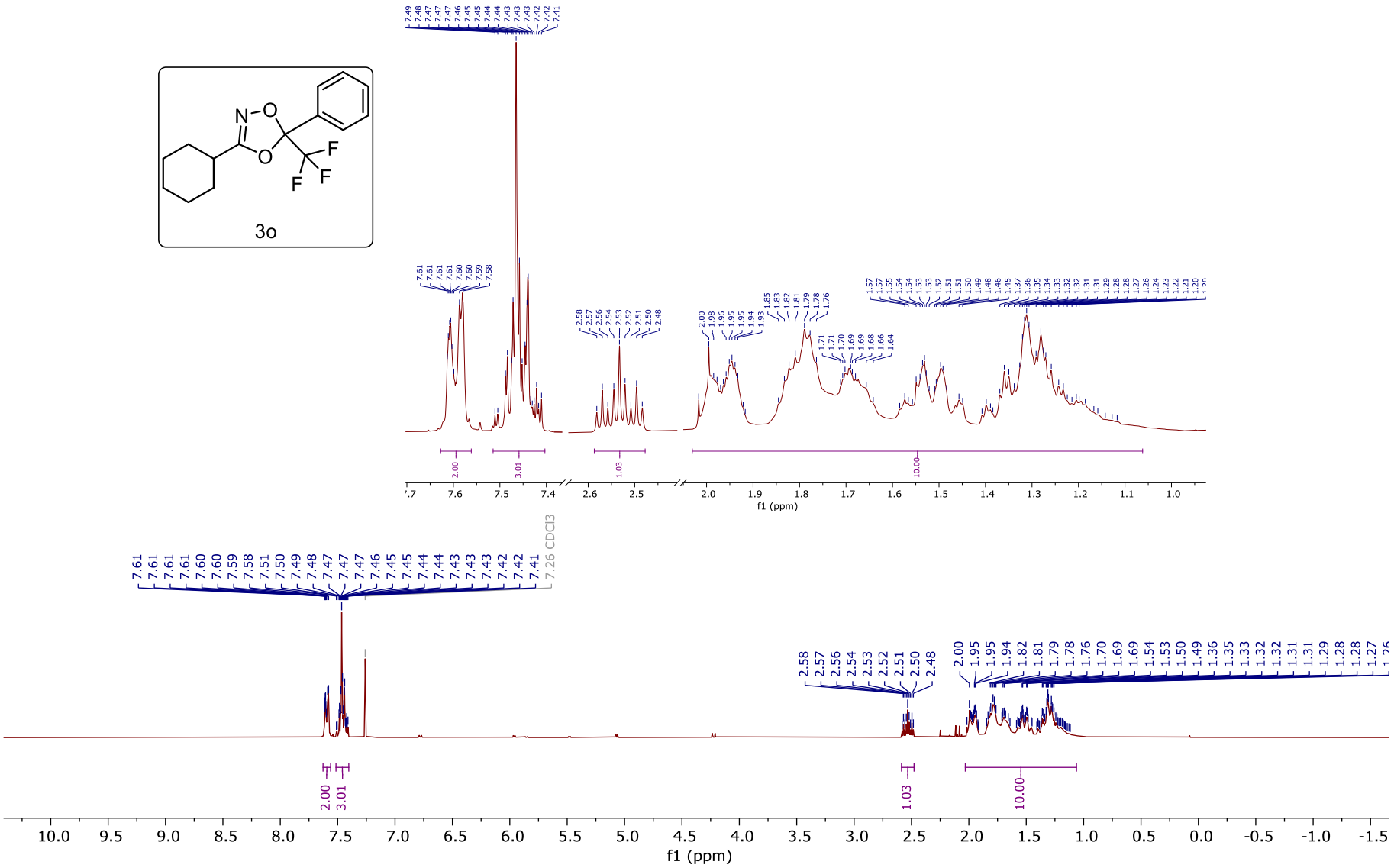

3l
F
N
O
O
O
O
7.86
7.85
7.85
7.84
7.83
7.83
7.82
7.81
7.81
7.80
7.26 CDCl3
7.17
7.16
7.15
7.14
7.14
7.13
7.13
7.13
7.12
7.11
7.10
7.09
6.25
4.34
4.32
4.29
4.27
1.35
1.32
1.30
2.00
2.10
0.97
2.00
3.00
f1 (ppm)

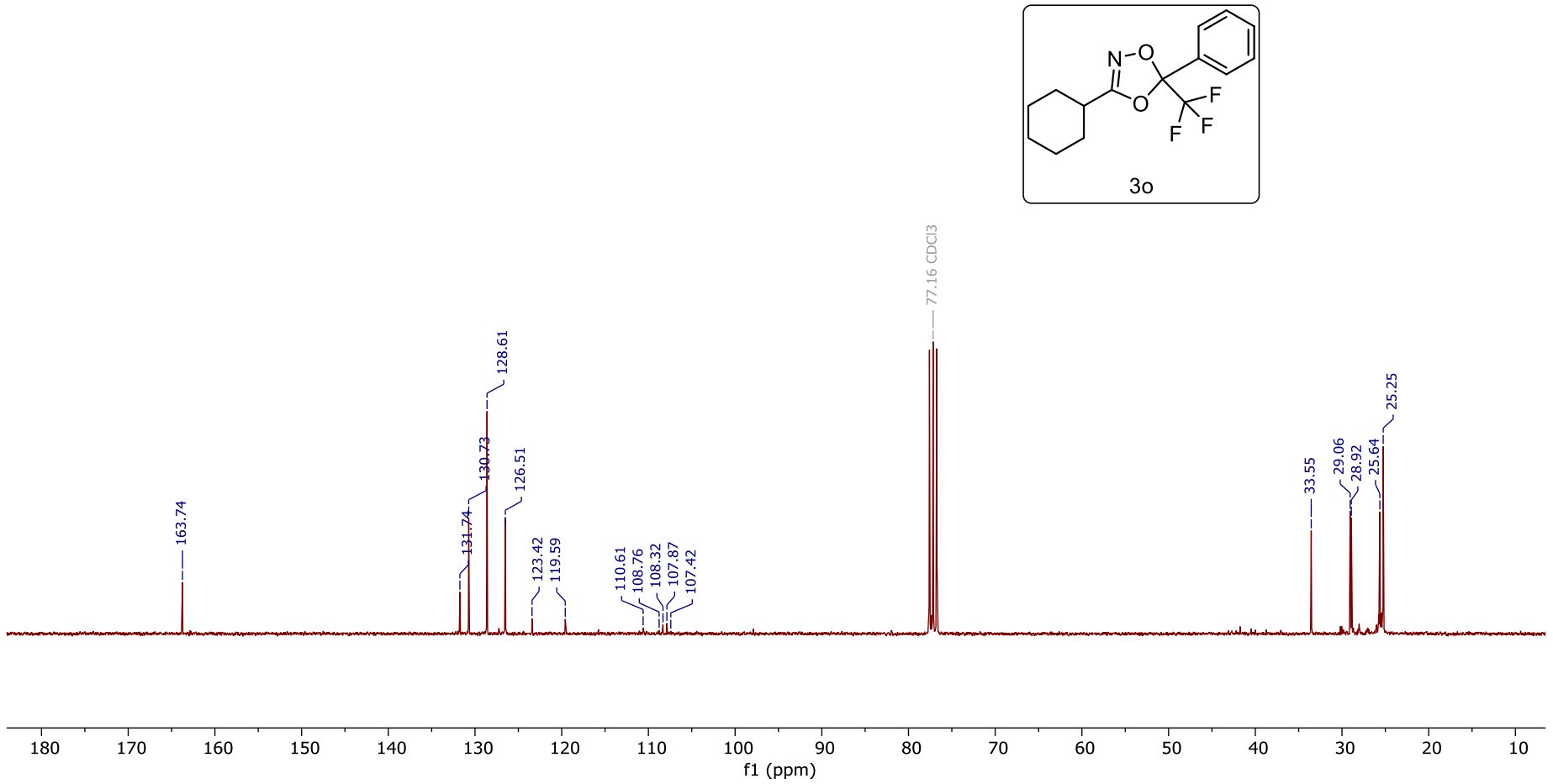

3l
166.73
165.40
163.37
158.40
129.73
129.61
118.07
118.03
116.42
116.13
101.01
77.16 CDCl3
62.73
14.07
f1 (ppm)

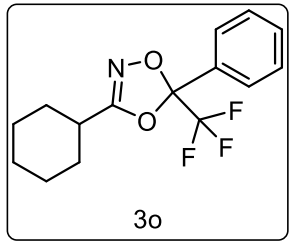

N
O
O
O
O
F

3l

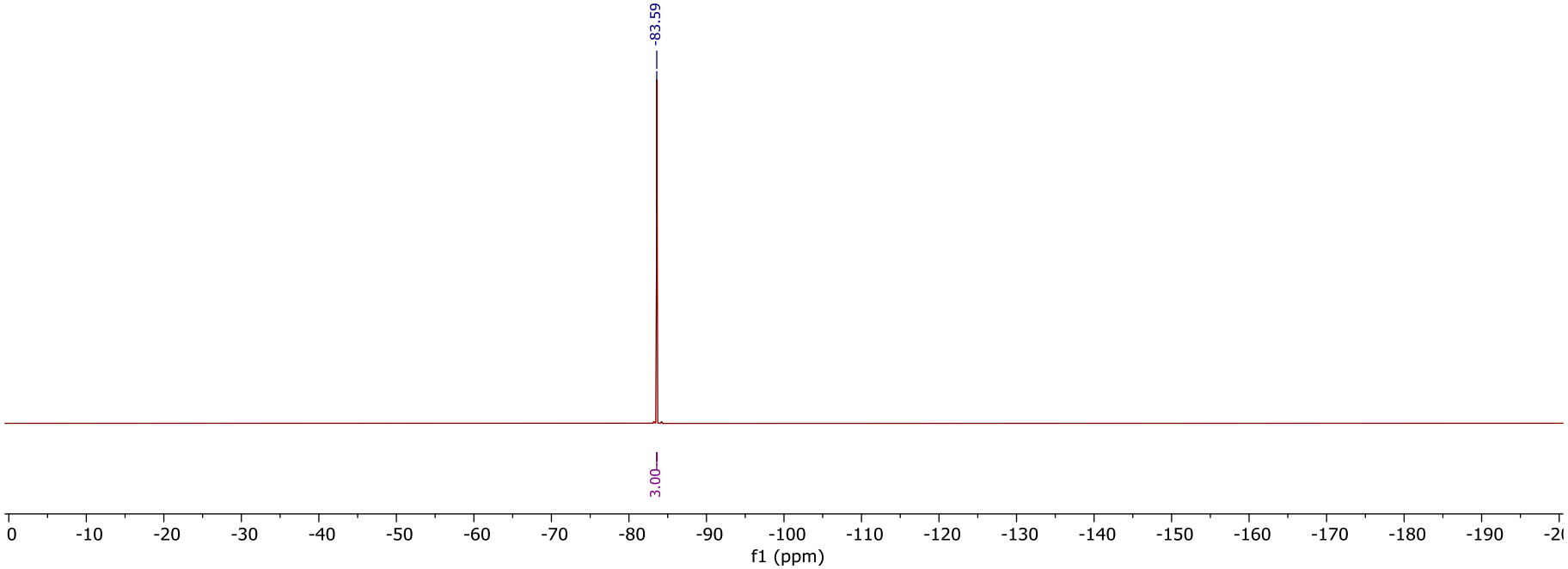

-106.14
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

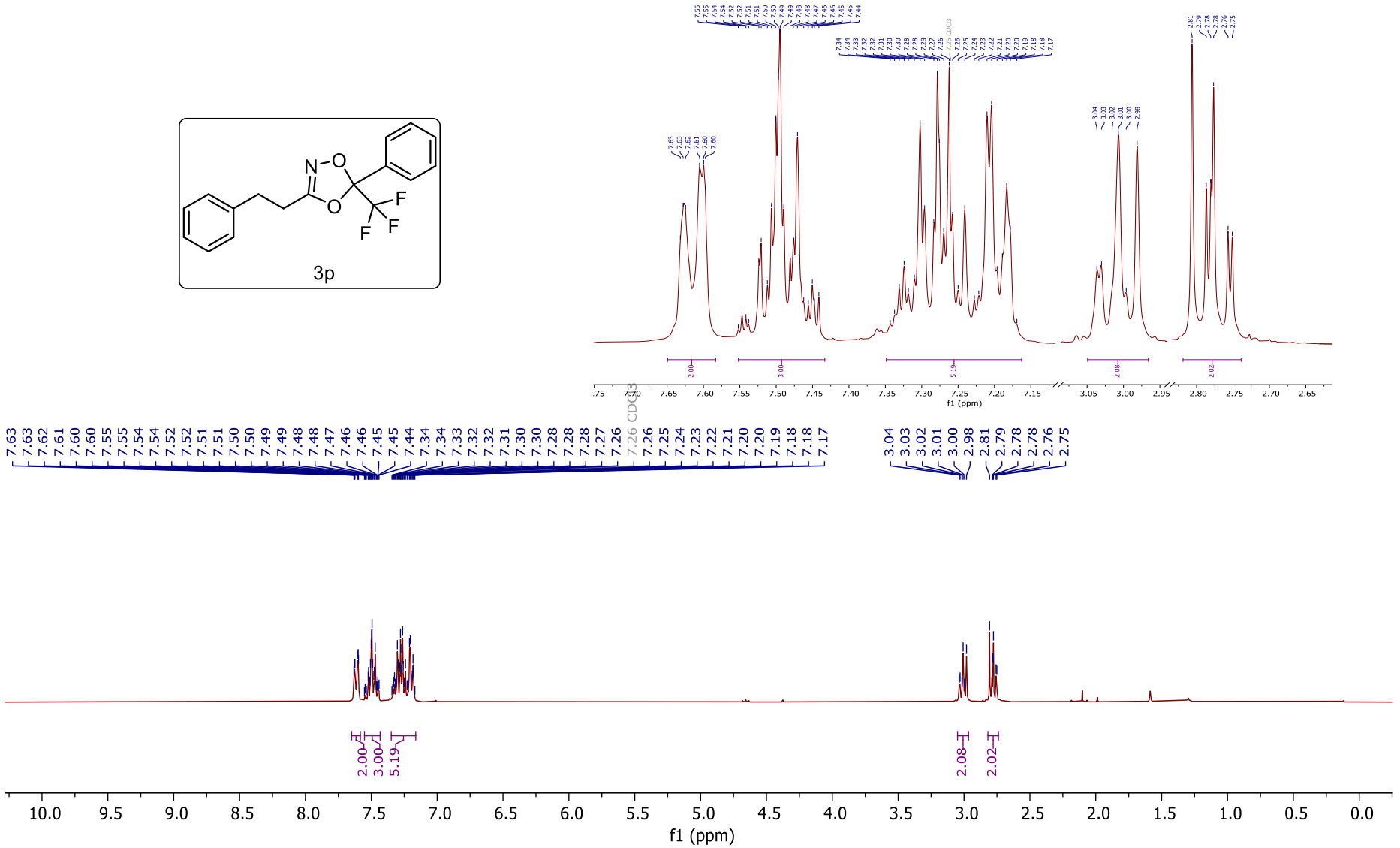

3o
f1 (ppm)
f1 (ppm)

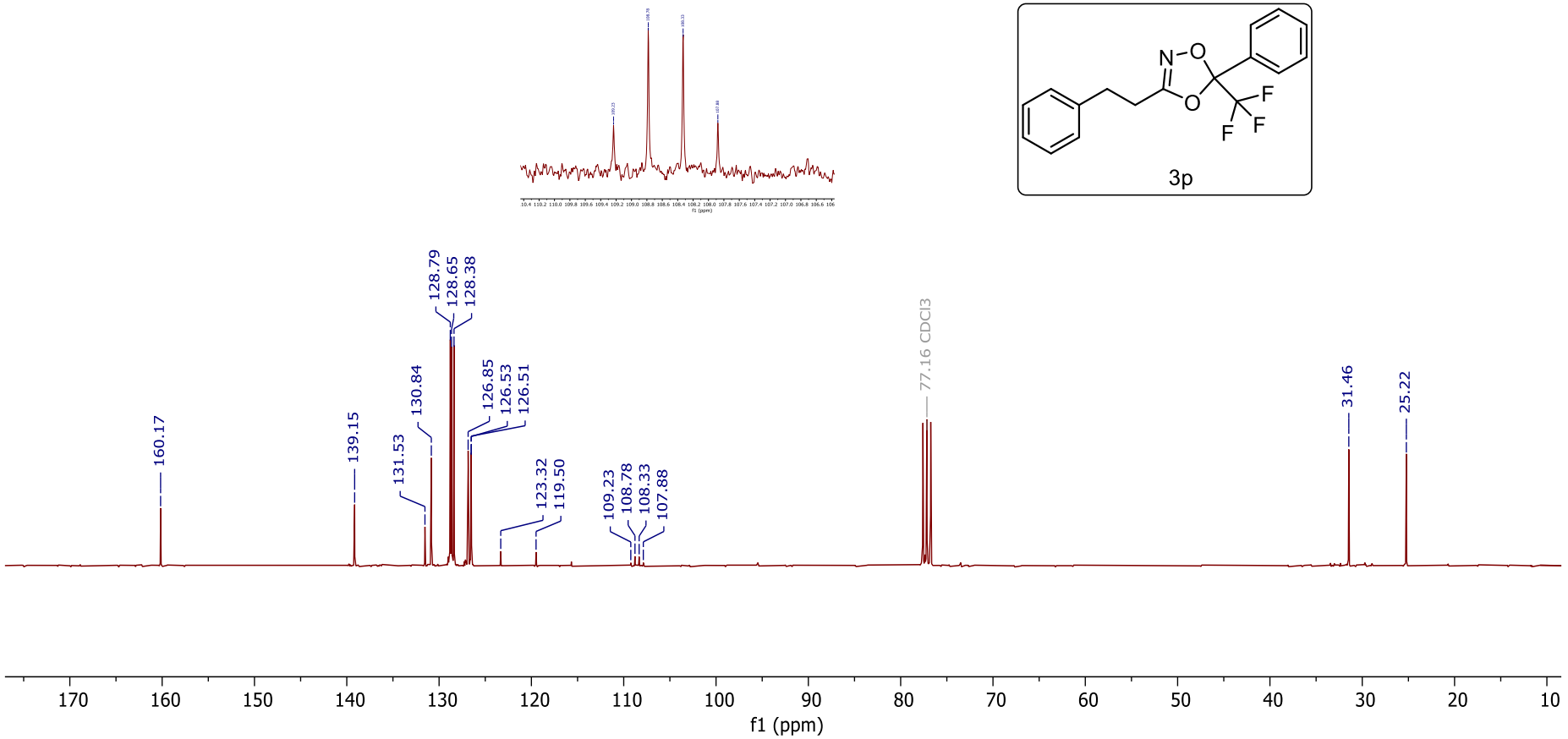

3o
163.74
131.74
130.73
128.61
126.51
123.42
119.59
110.61
108.76
108.32
107.87
107.42
77.16 CDCl3
33.55
29.06
28.92
25.64
25.25
f1 (ppm)

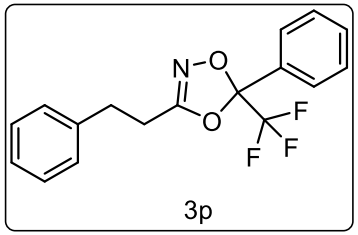

N
O
O
F
F
F

3o

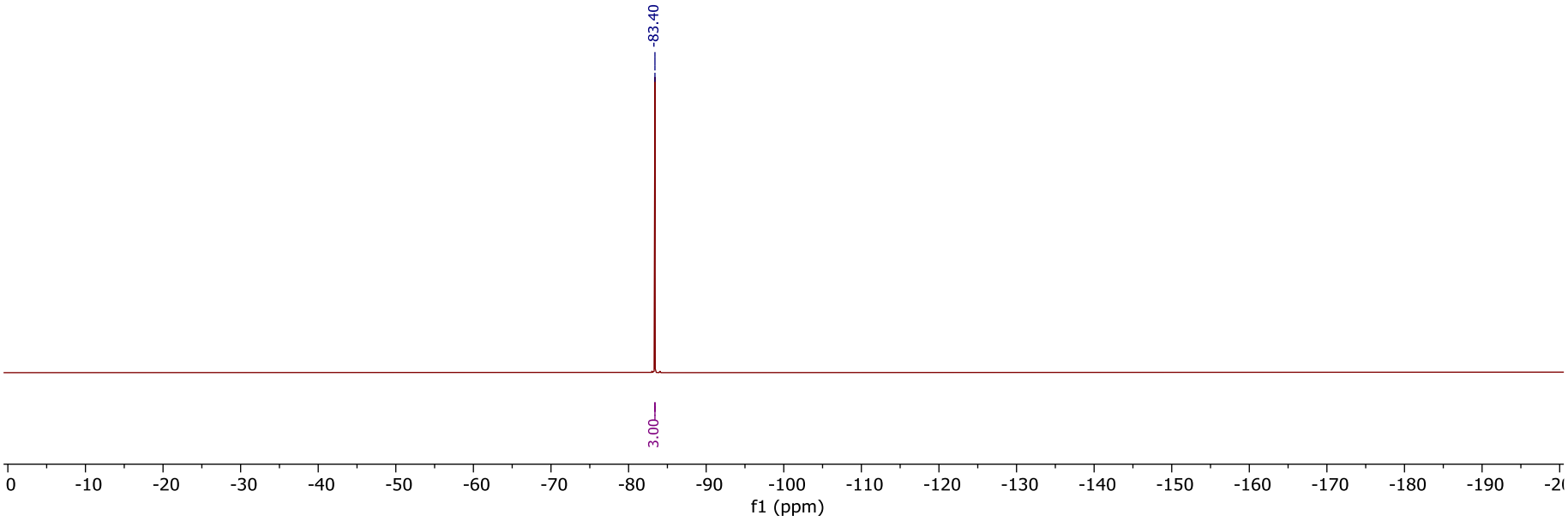

-83.59
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

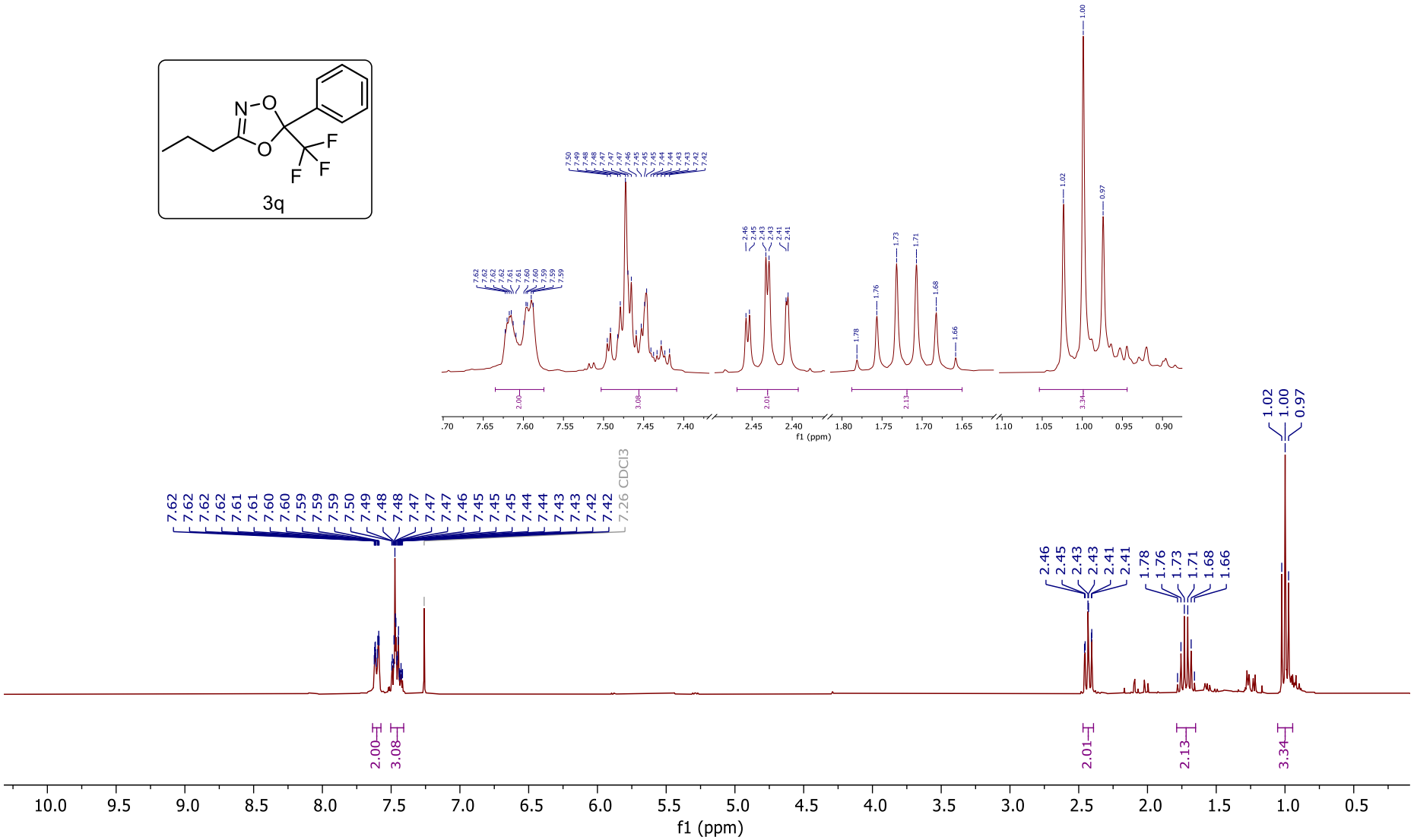

3p
f1 (ppm)

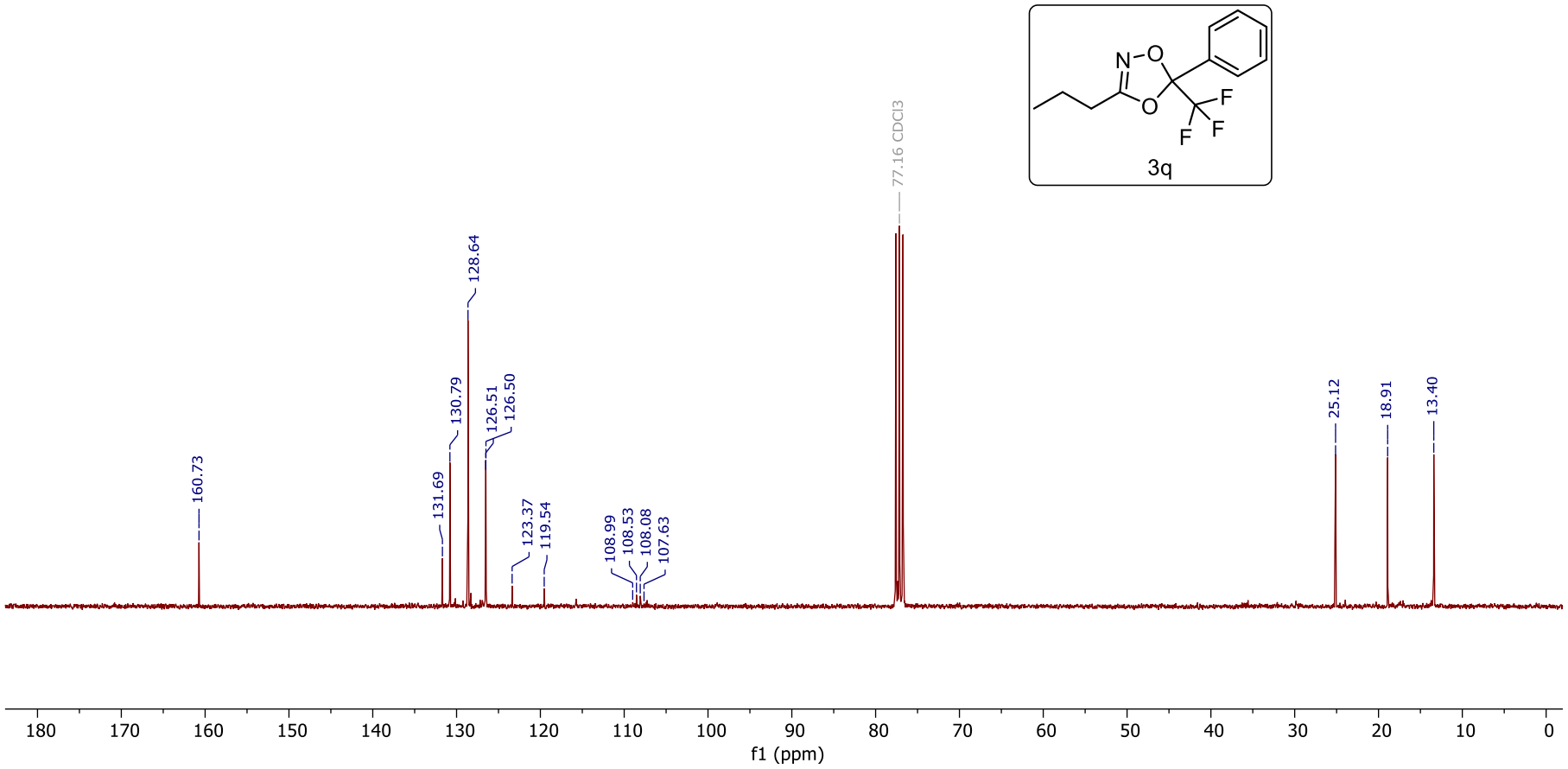

3p
160.17
139.15
131.53
130.84
128.79
128.65
128.38
126.85
126.53
126.51
123.32
119.50
109.23
108.78
108.33
107.88
77.16 CDCl3
31.46
25.22
f1 (ppm)

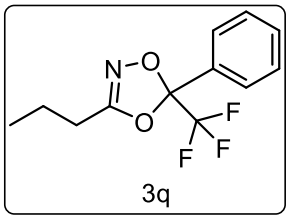

N
O
O
F
F
F

3p

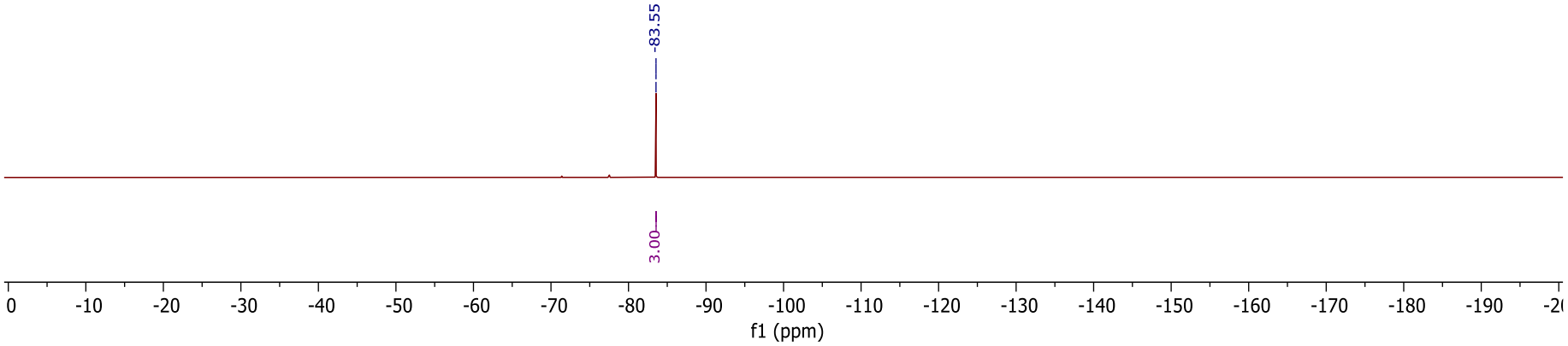

-83.40
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

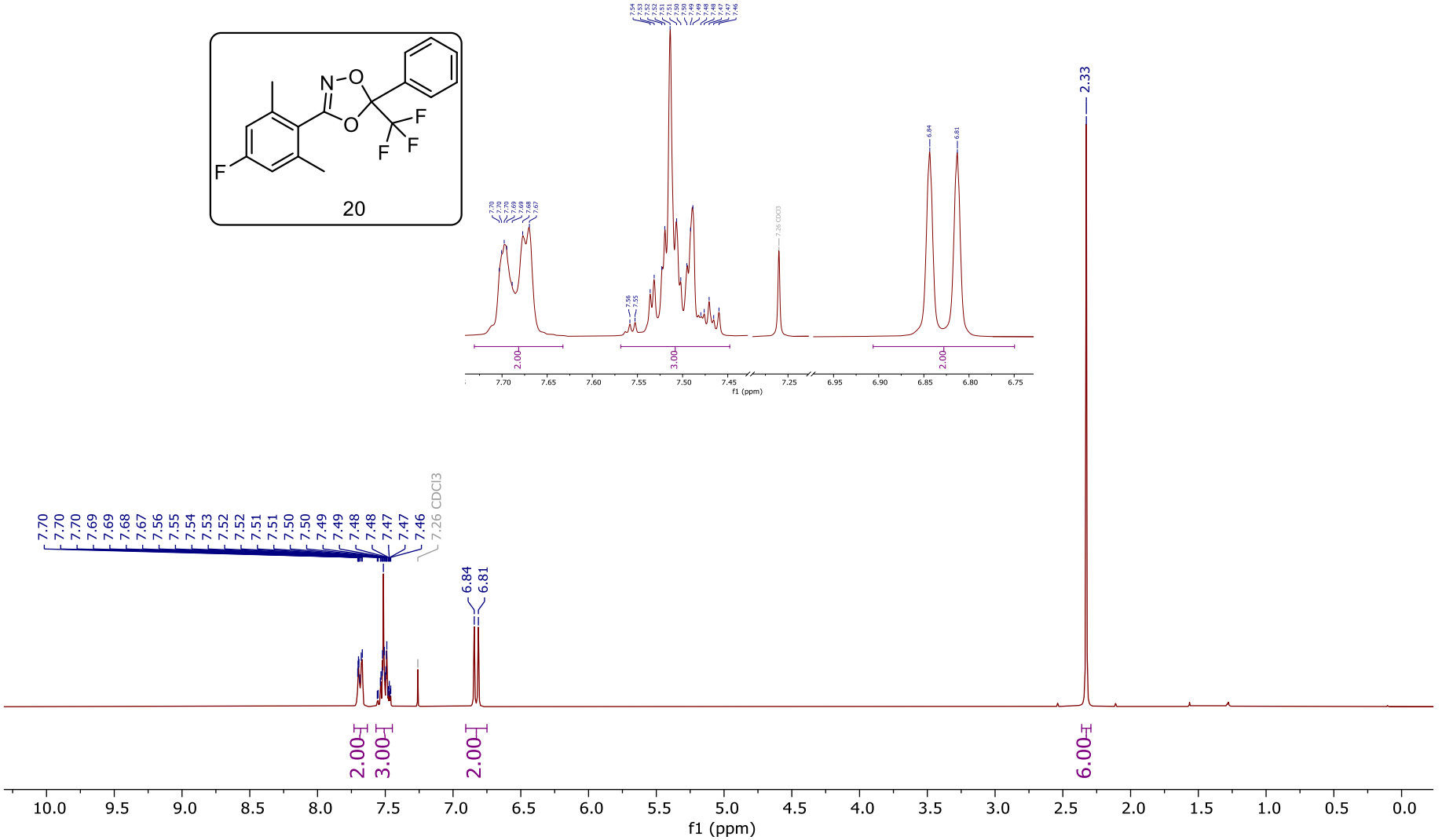

3q
f1 (ppm)
CDCl3

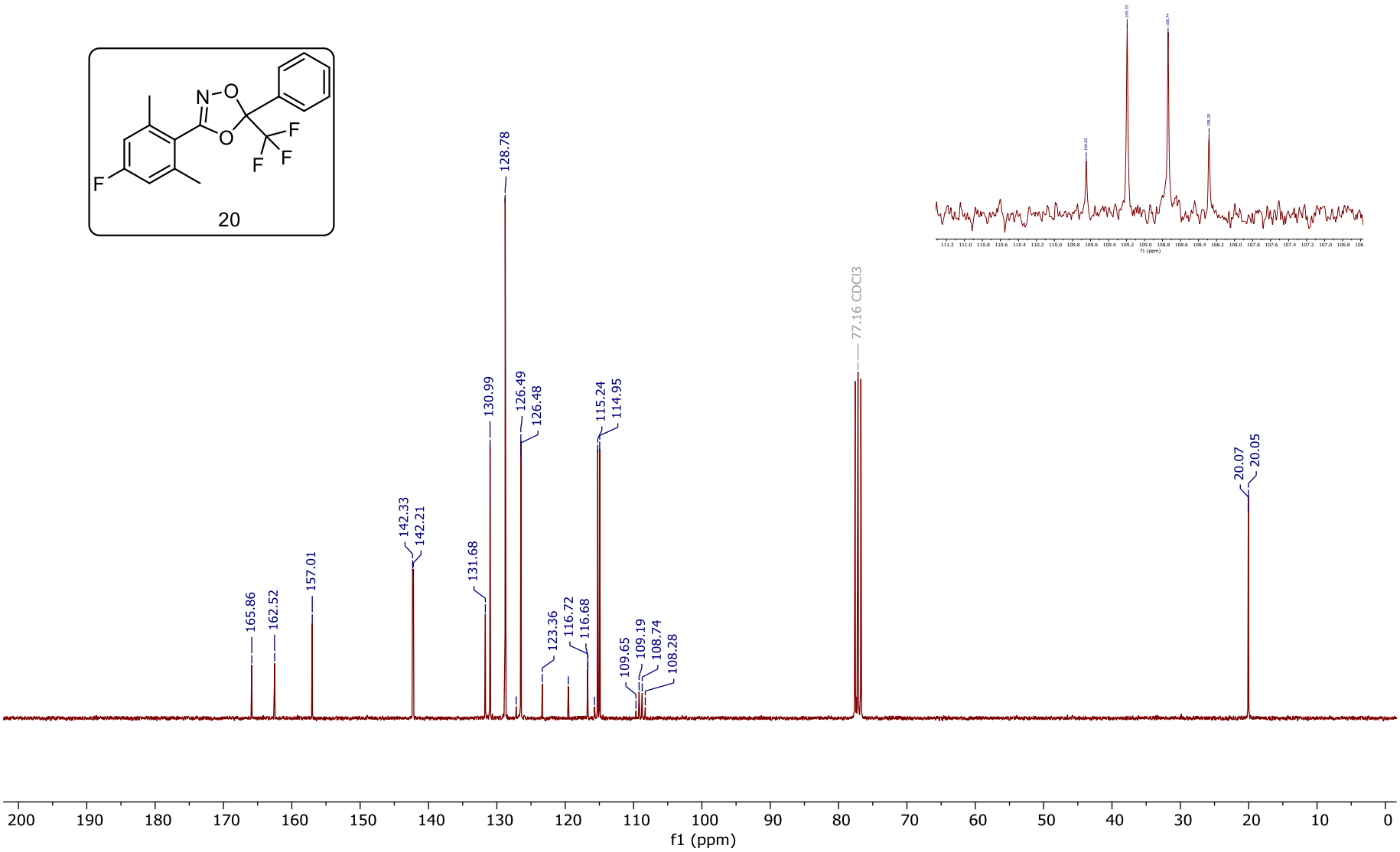

3q
77.16 CDCl3
160.73
131.69
130.79
128.64
126.51
126.50
123.37
119.54
108.99
108.53
108.08
107.63
25.12
18.91
13.40
f1 (ppm)

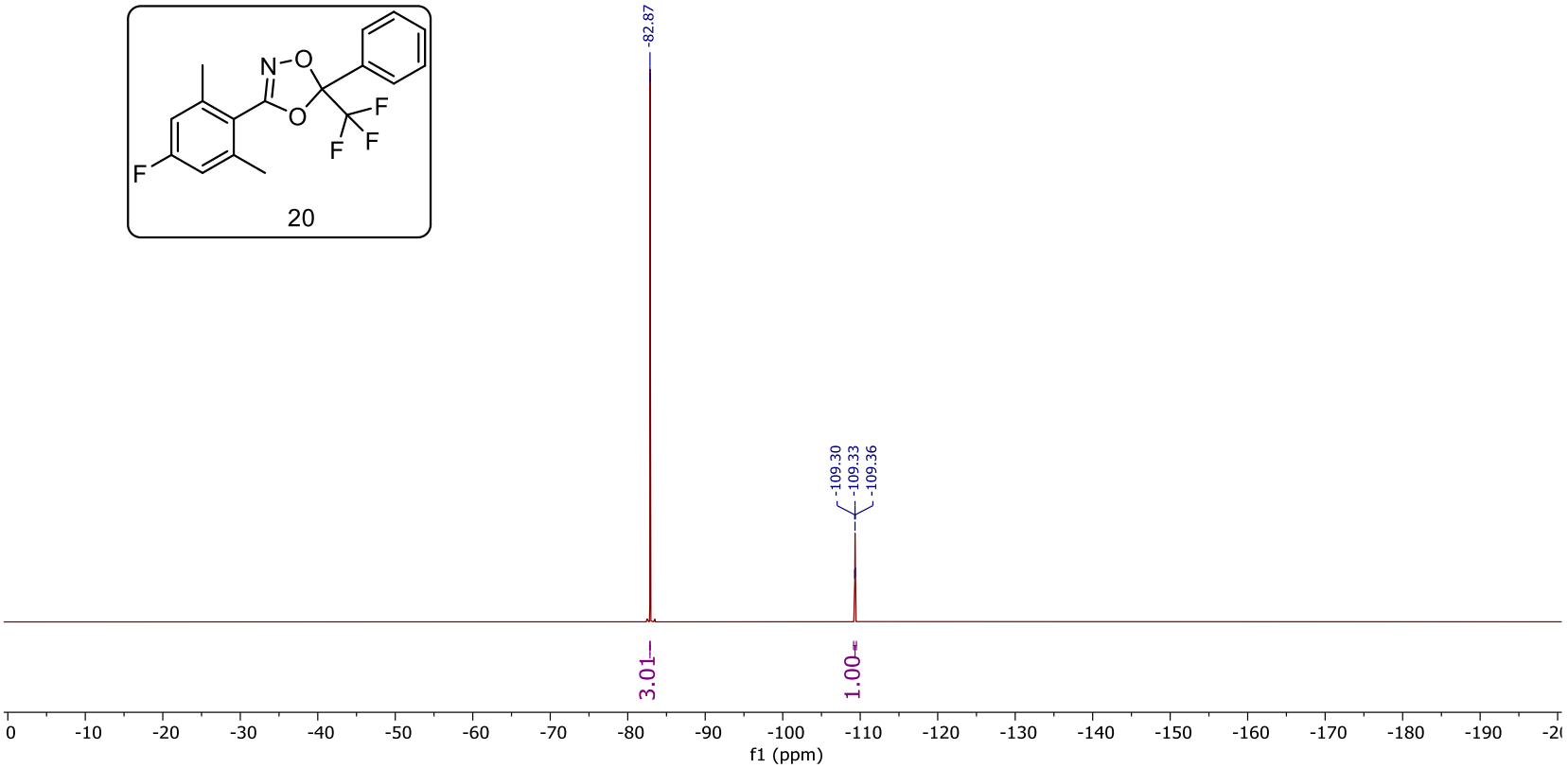

N
O
O
F
F
F

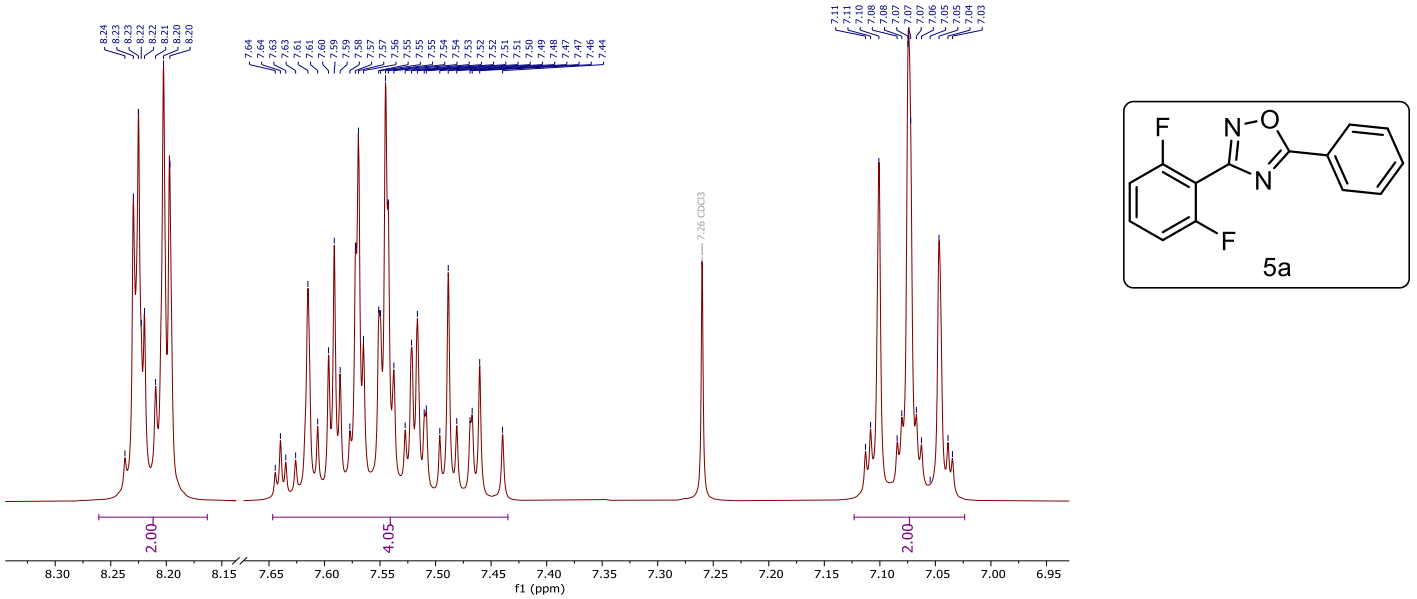
3q

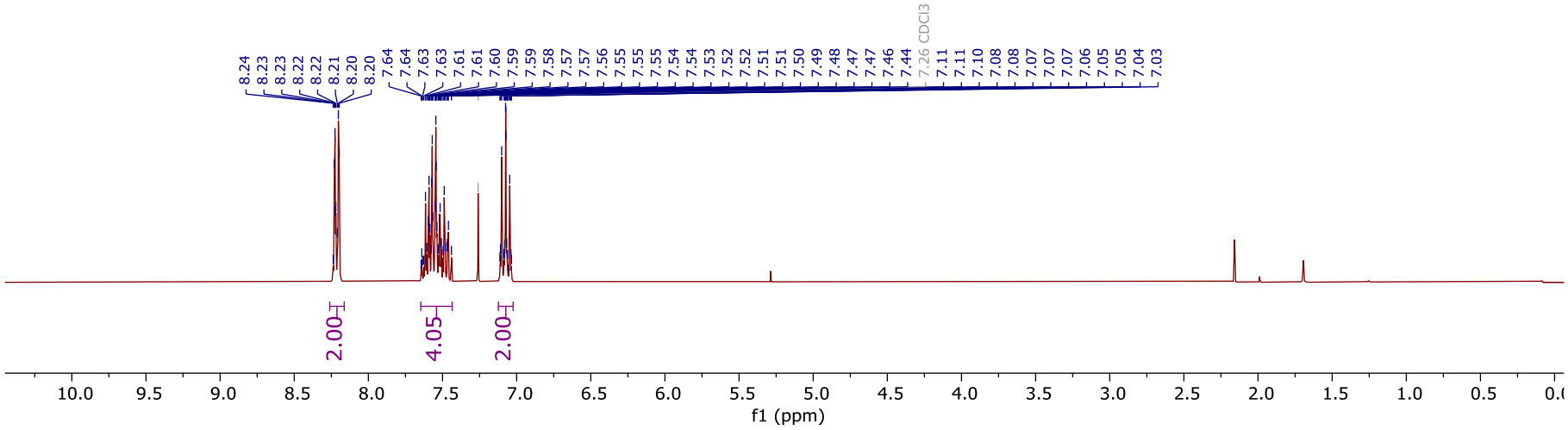

-83.55
3.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

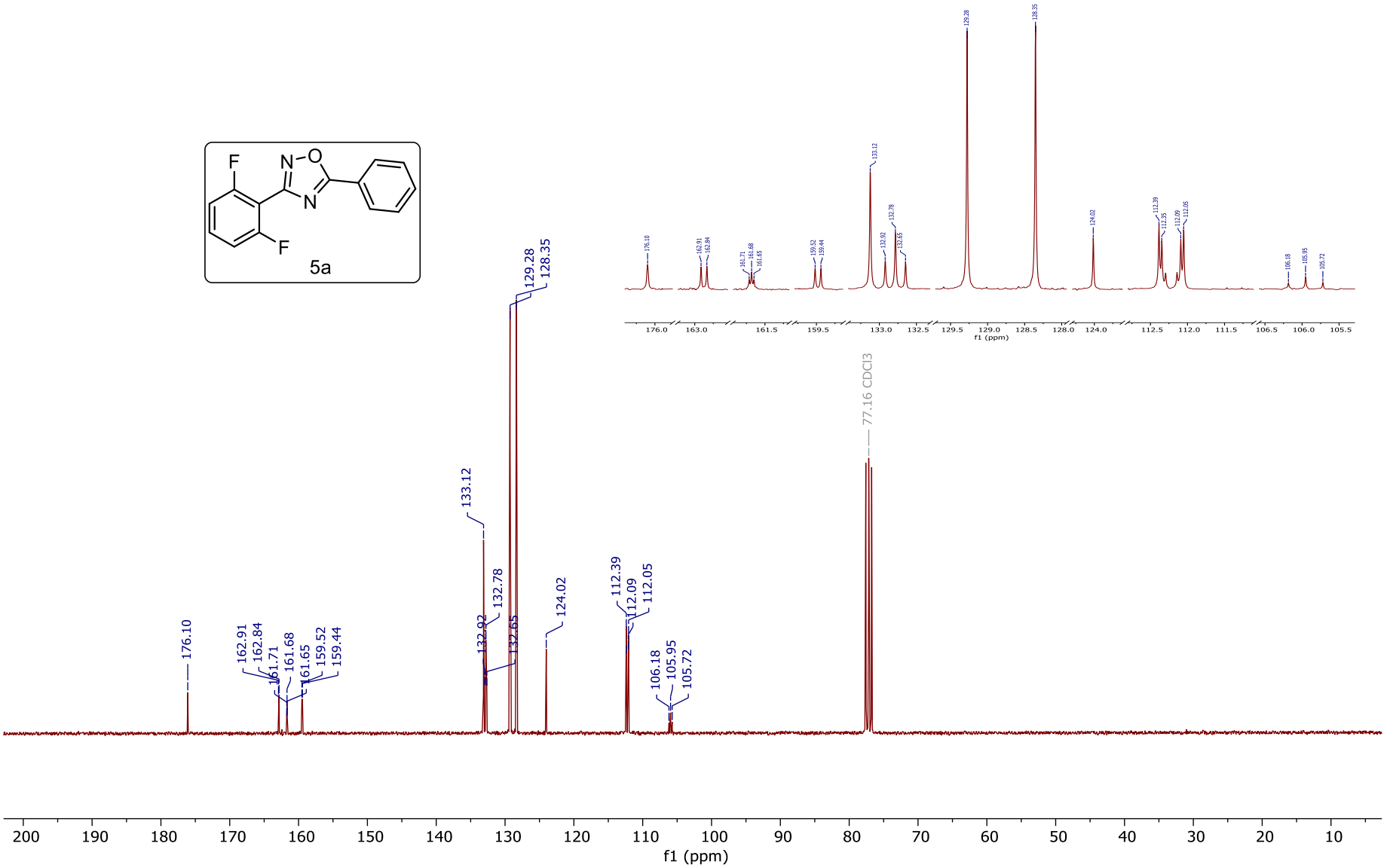

20
7.70
7.70
7.70
7.69
7.69
7.68
7.67
7.56
7.55
7.54
7.53
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.26 CDCl3
6.84
6.81
2.33
2.00
3.00
2.00
6.00
f1 (ppm)

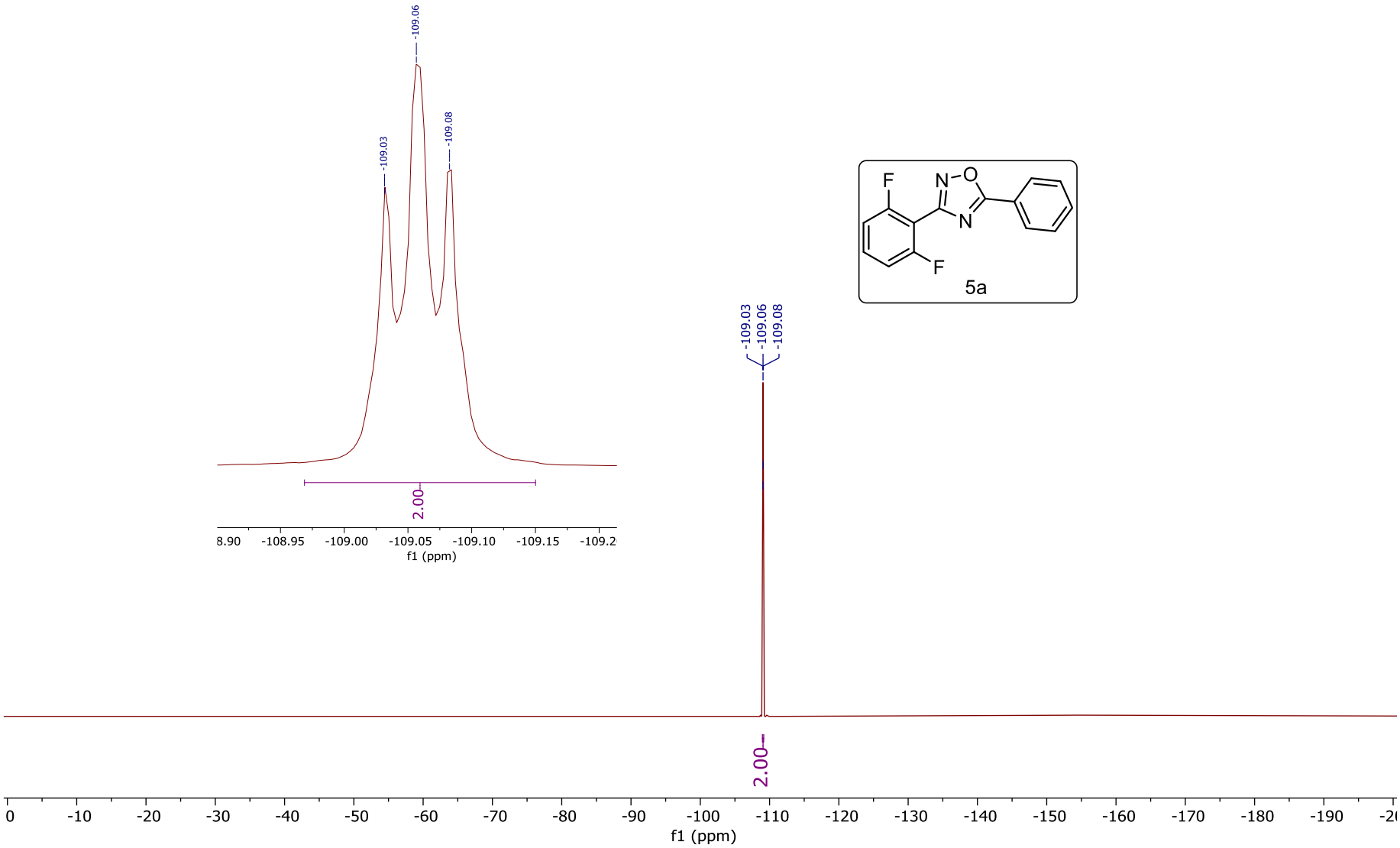

20
165.86
162.52
157.01
142.33
142.21
131.68
130.99
128.78
126.49
126.48
123.36
116.72
116.68
115.24
114.95
109.65
109.19
108.74
108.28
77.16 CDCl3
20.07
20.05
f1 (ppm)

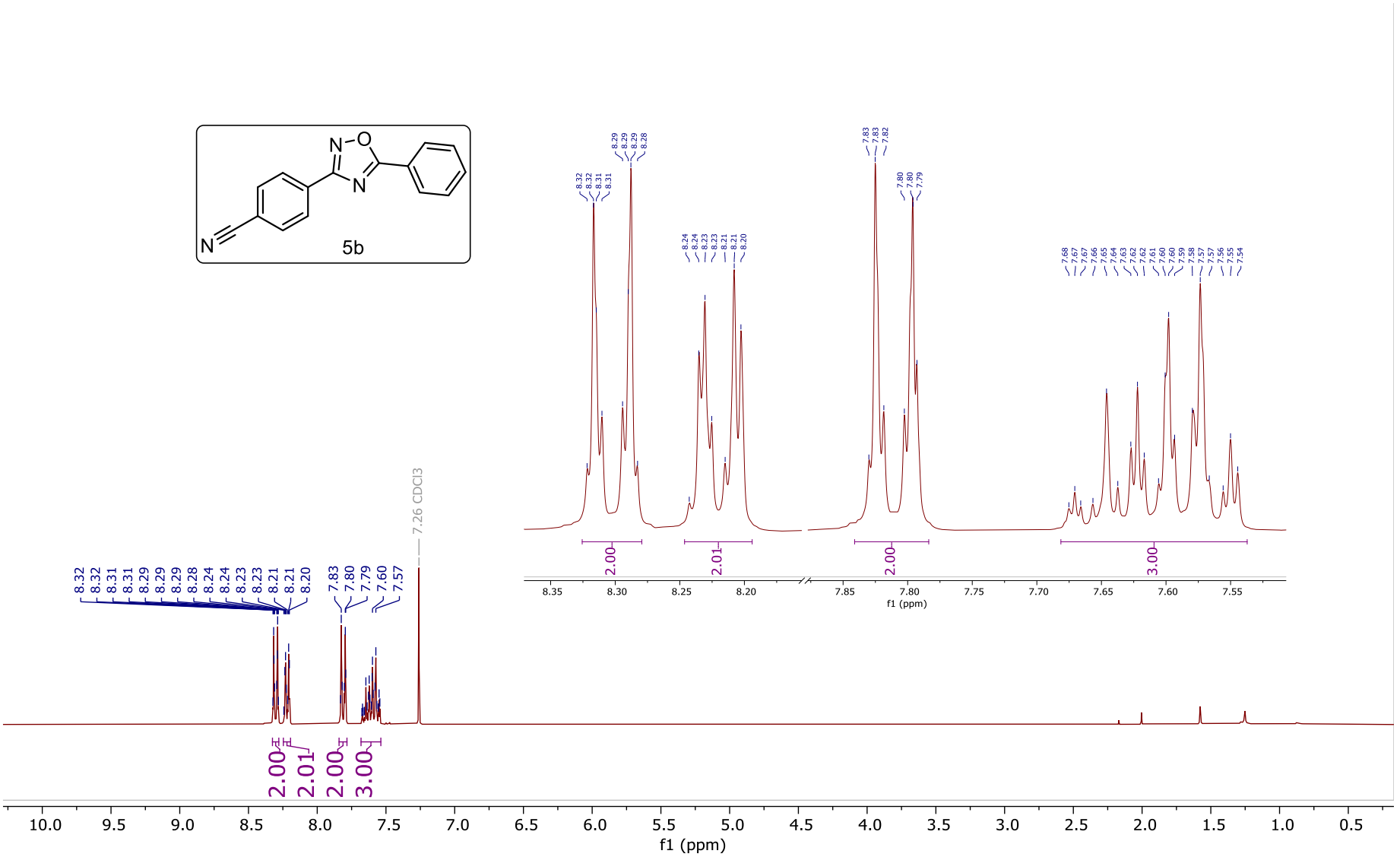

N
O
O
F
F
F
F
20
-82.87
-109.30
-109.33
-109.36
3.01
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

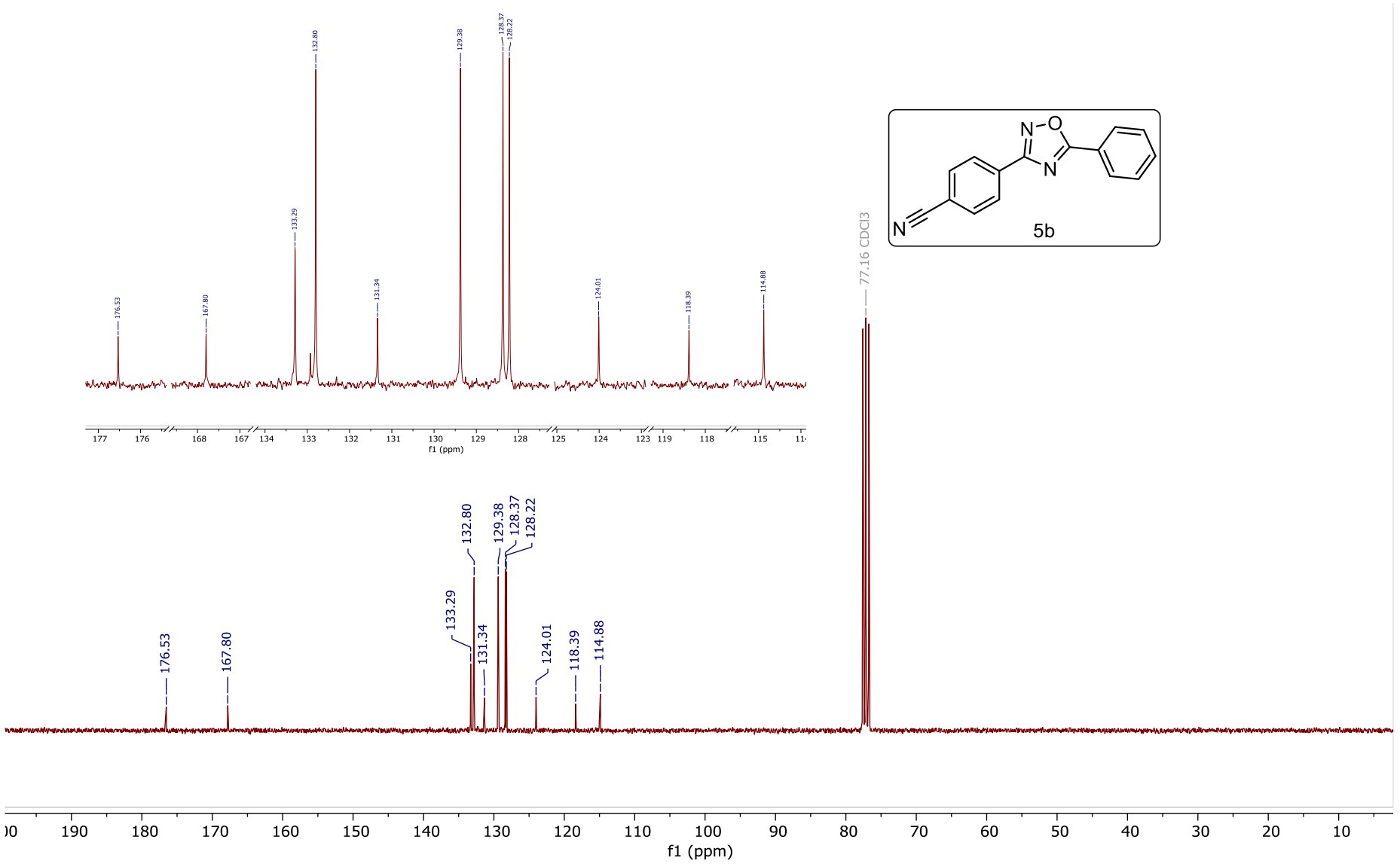

F
N
O
N
F
5a
7.26 CDCl3
2.00
4.05
2.00
f1 (ppm)

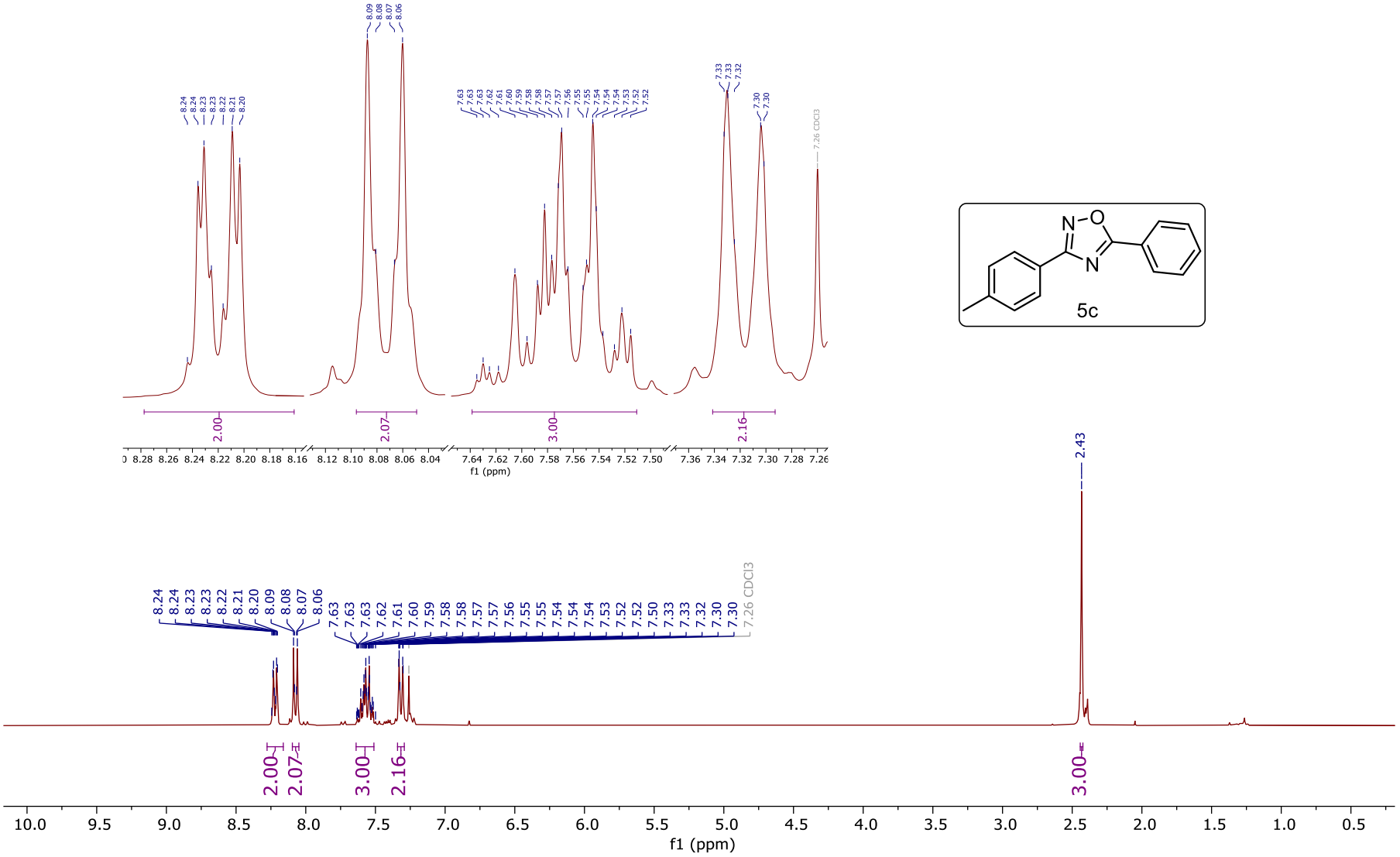

7.26 CDCl3
2.00
4.05
2.00
f1 (ppm)

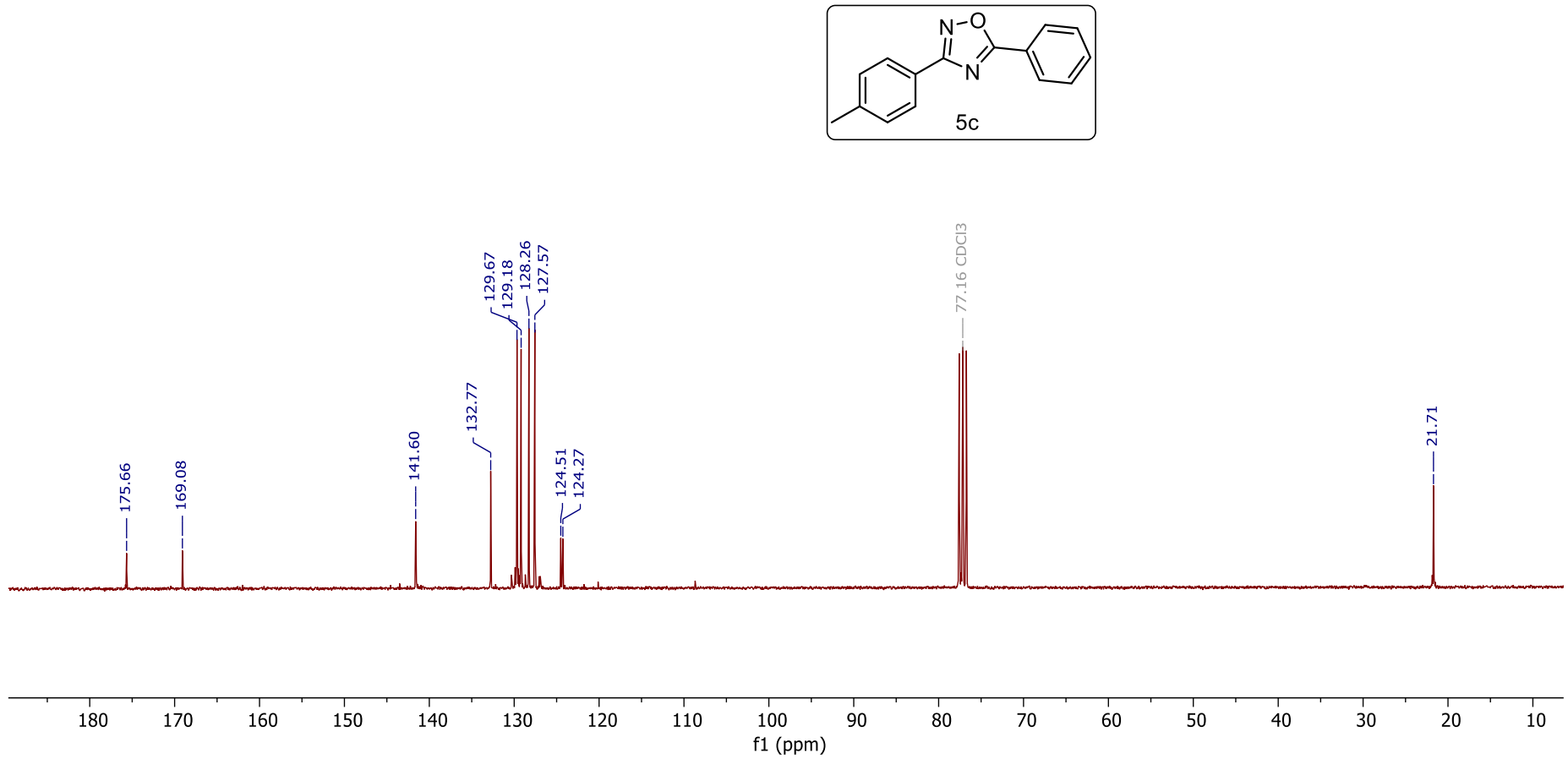

F
N
O
N
F
5a
176.10
162.91
162.84
161.71
161.68
161.65
159.52
159.44
133.12
132.92
132.78
132.65
129.28
128.35
124.02
112.39
112.09
112.05
106.18
105.95
105.72
77.16 CDCl3
f1 (ppm)

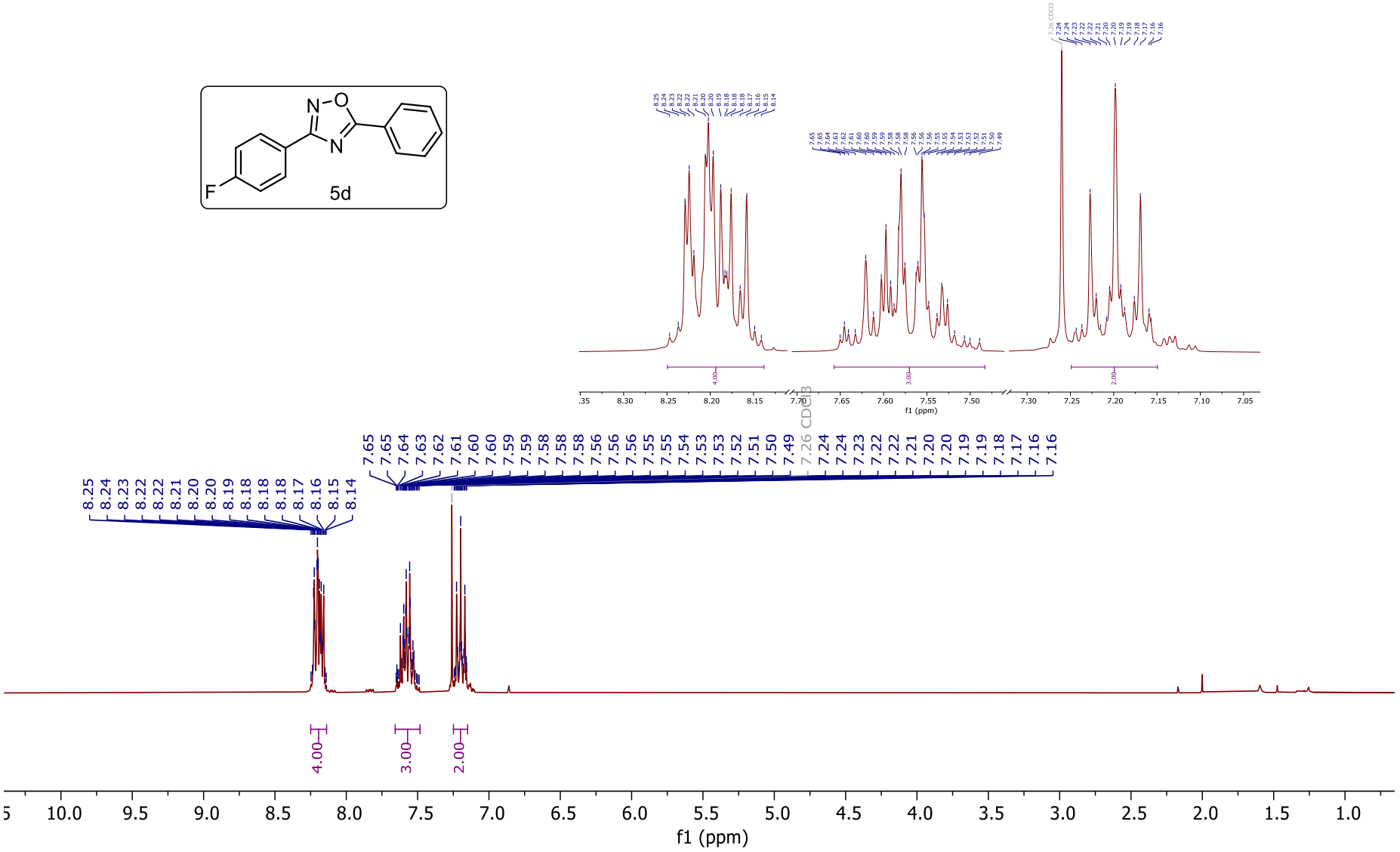

-109.06
-109.03
-109.08
2.00
8.90
-108.95
-109.00
-109.05
-109.10
-109.15
-109.2
f1 (ppm)
F
N
O
N
F
5a
-109.03
-109.06
-109.08
2.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

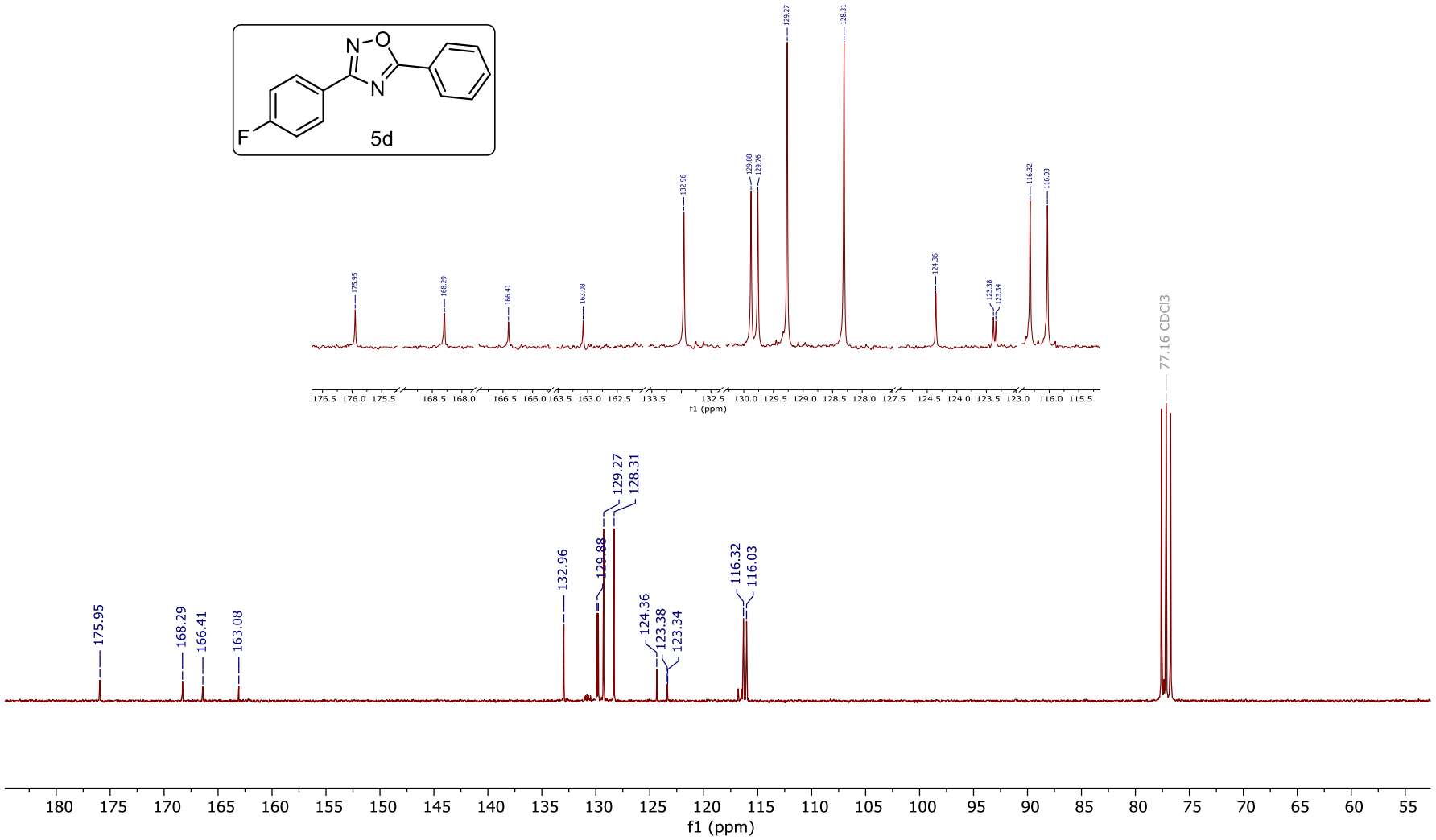

5b
8.32
8.32
8.31
8.31
8.29
8.29
8.29
8.28
8.24
8.24
8.23
8.23
8.21
8.21
8.20
7.83
7.80
7.79
7.60
7.57
7.26 CDCl3
2.00
2.01
2.00
3.00
f1 (ppm)

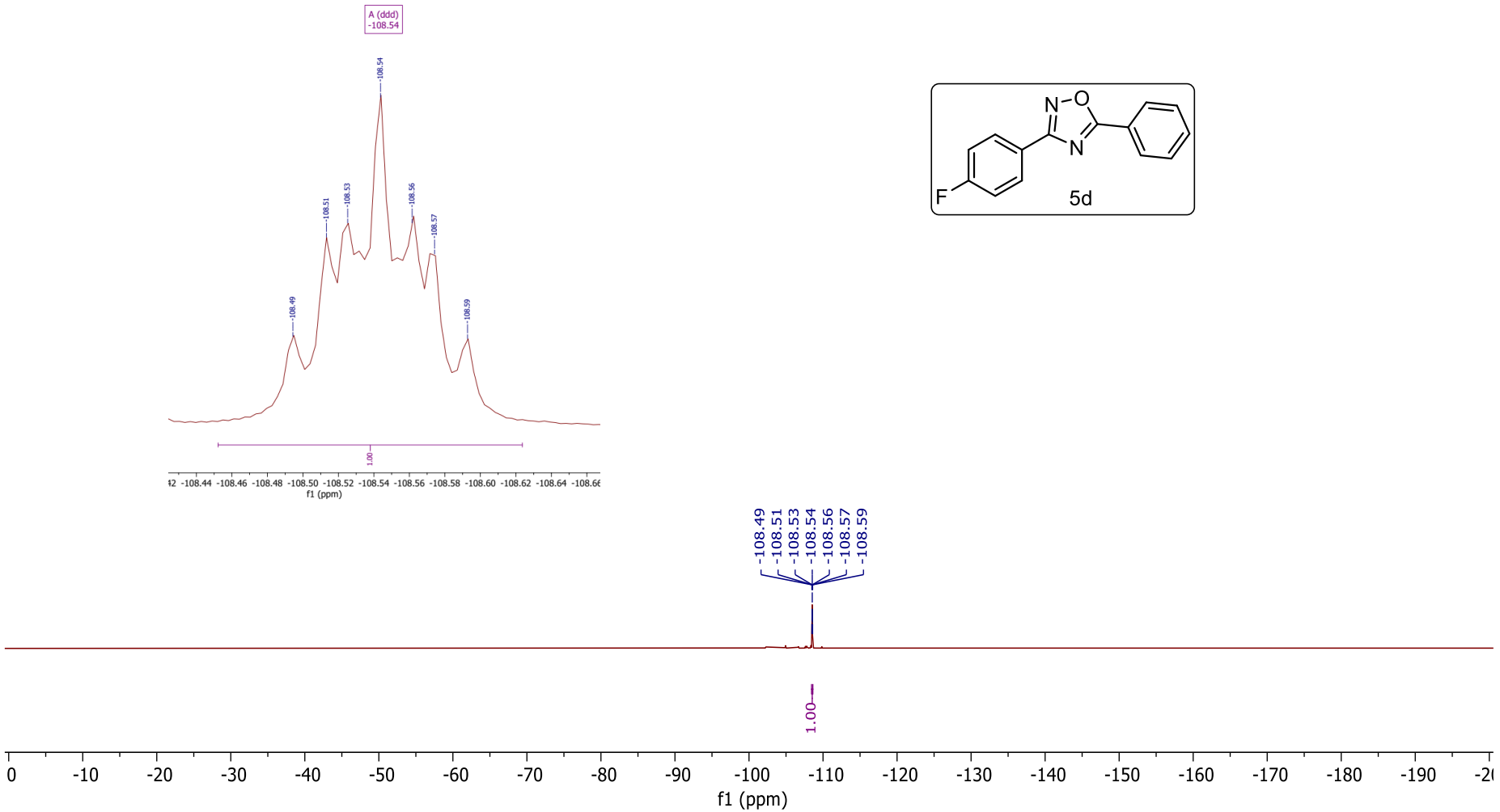

5b
176.53
167.80
133.29
132.80
131.34
129.38
128.37
128.22
124.01
118.39
114.88
77.16 CDCl3
f1 (ppm)

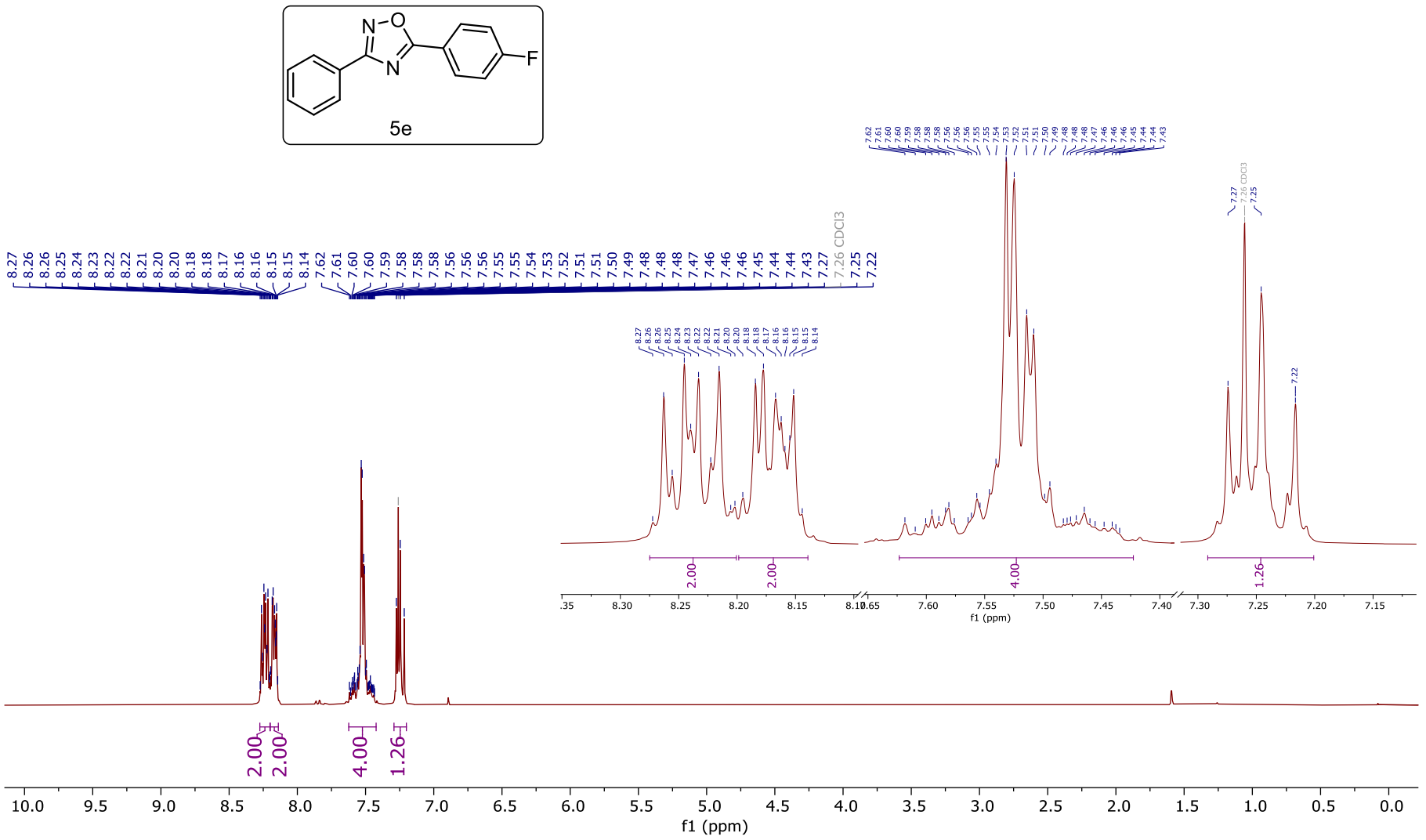

5c
f1 (ppm)

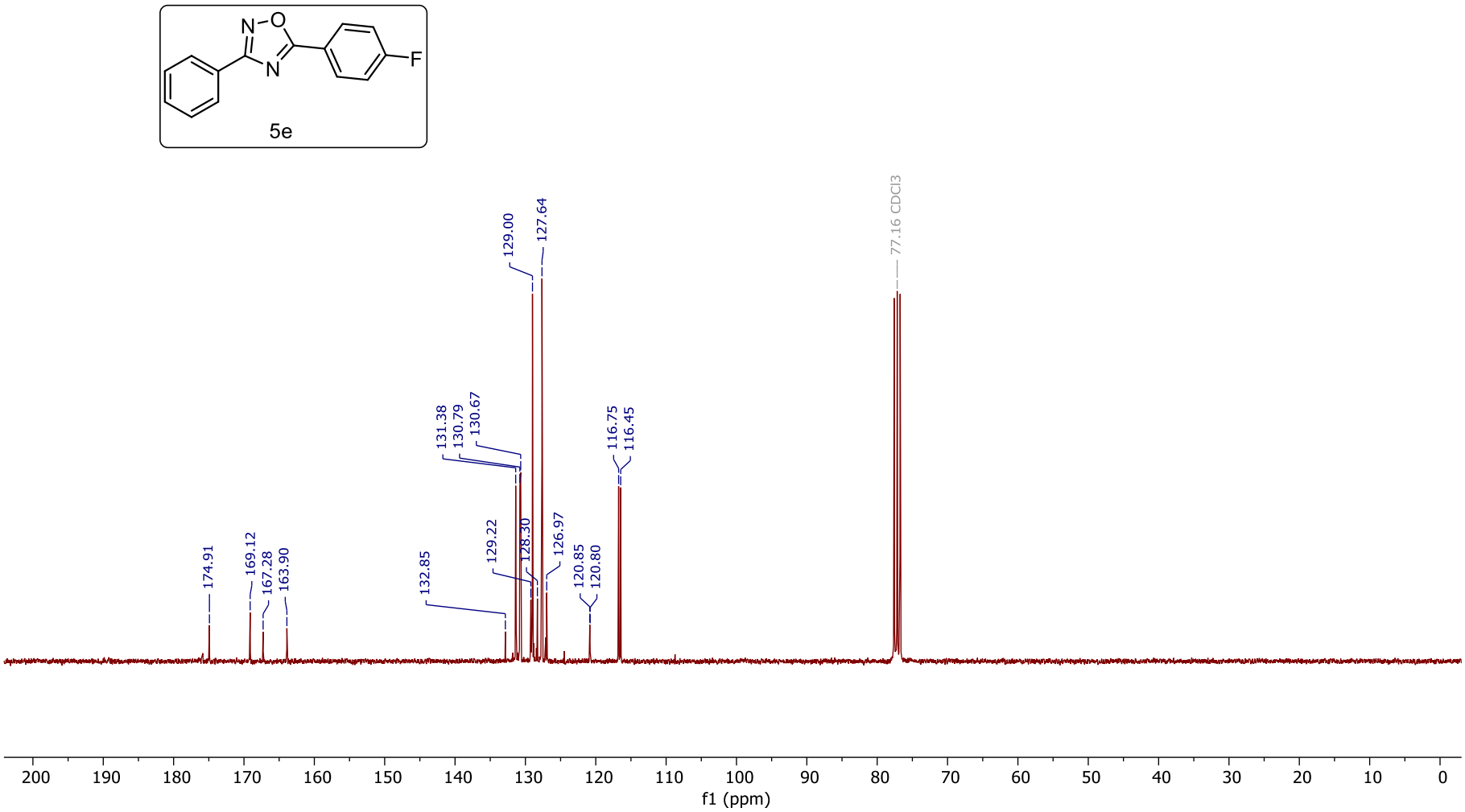

5c
175.66
169.08
141.60
132.77
129.67
129.18
128.26
127.57
124.51
124.27
77.16 CDCl3
21.71
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

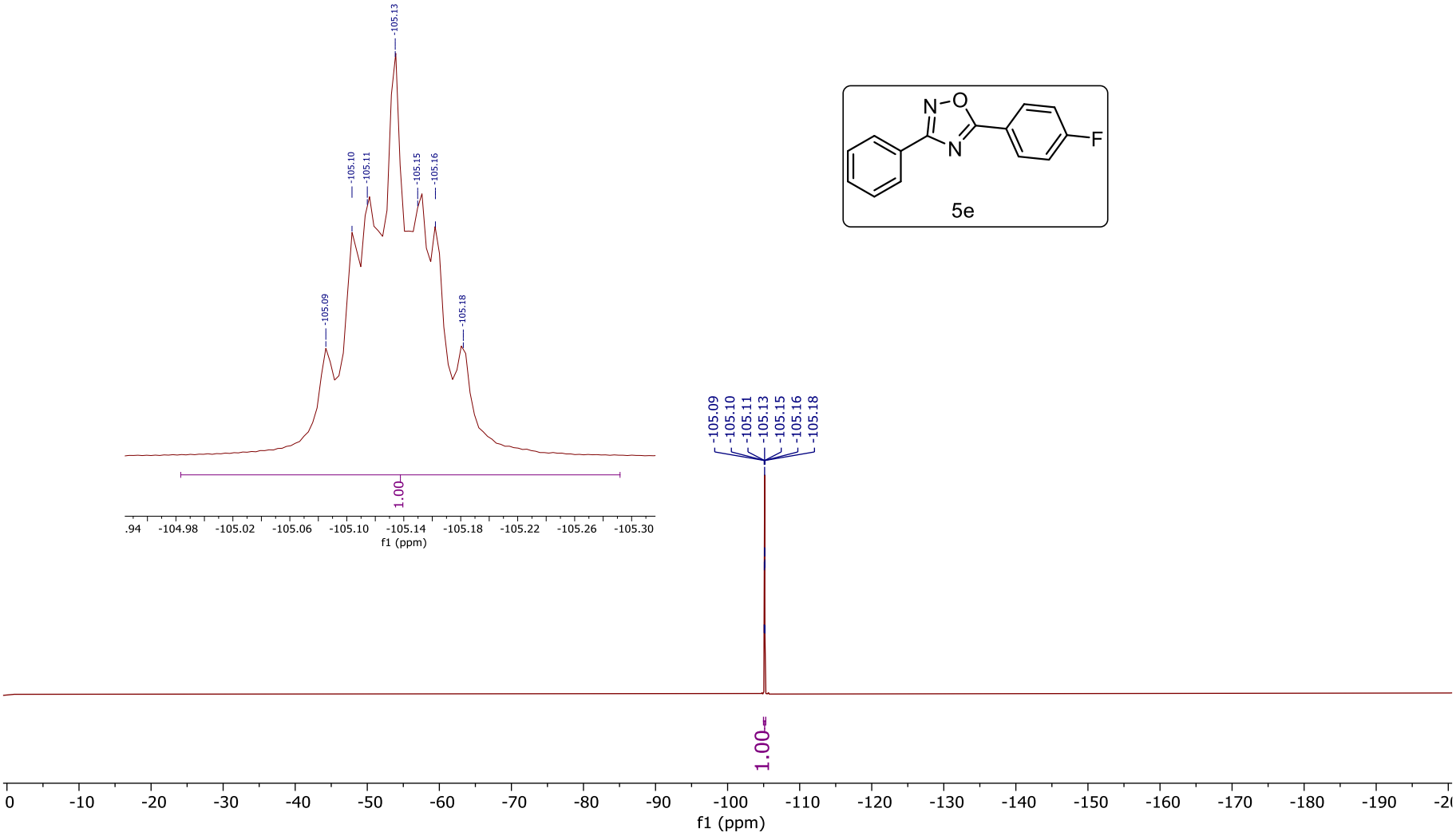

F
5d
7.26 CDCl3
f1 (ppm)
4.00
3.00
2.00

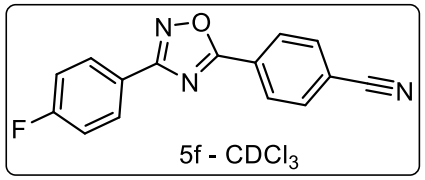

F
5d
175.95
168.29
166.41
163.08
132.96
129.88
129.76
129.27
128.31
124.36
123.38
123.34
116.32
116.03
77.16 CDCl3
f1 (ppm)


A (ddd)
-108.54
-108.49
-108.51
-108.53
-108.54
-108.56
-108.57
-108.59
1.00
f1 (ppm)
N
O
N
F
5d
-108.49
-108.51
-108.53
-108.54
-108.56
-108.57
-108.59
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

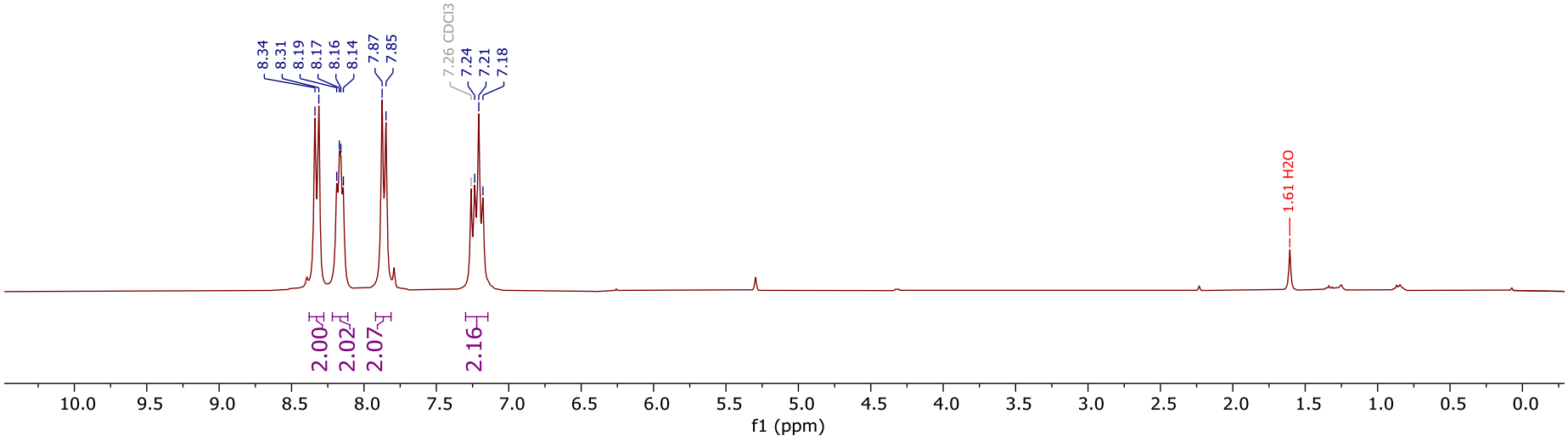

5e
F
N
O
N
2.00
2.00
4.00
1.26
f1 (ppm)
CDCl3

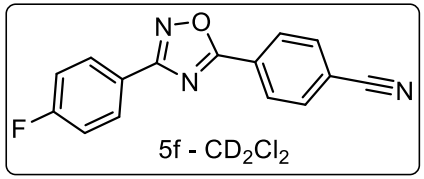

5e
174.91
169.12
167.28
163.90
132.85
131.38
130.79
130.67
129.22
129.00
128.30
127.64
126.97
120.85
120.80
116.75
116.45
77.16 CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

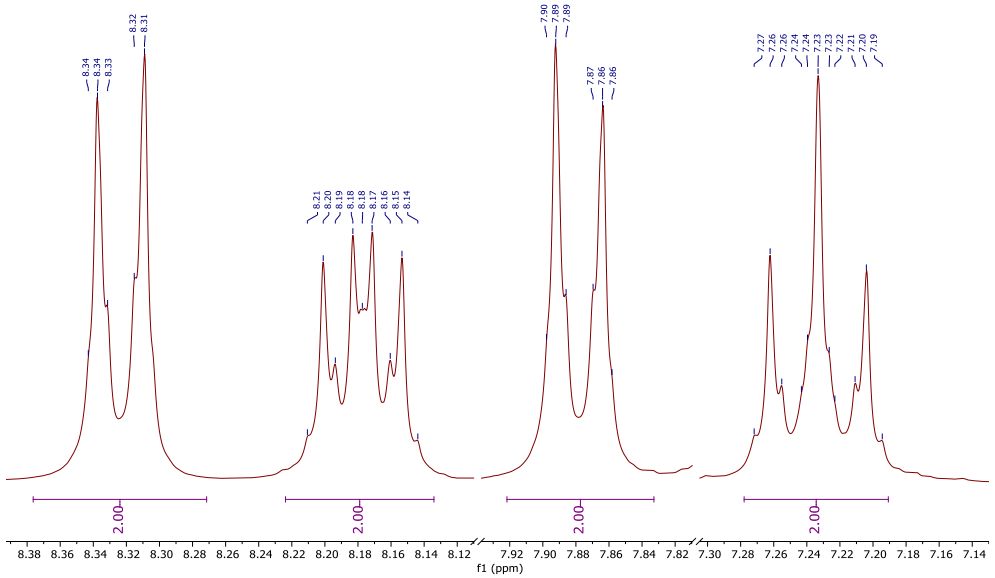

-105.13
-105.10
-105.11
-105.15
-105.16
-105.09
-105.18
1.00
.94 -104.98 -105.02 -105.06 -105.10 -105.14 -105.18 -105.22 -105.26 -105.30
f1 (ppm)
N
O
N
F
5e
-105.09
-105.10
-105.11
-105.13
-105.15
-105.16
-105.18
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

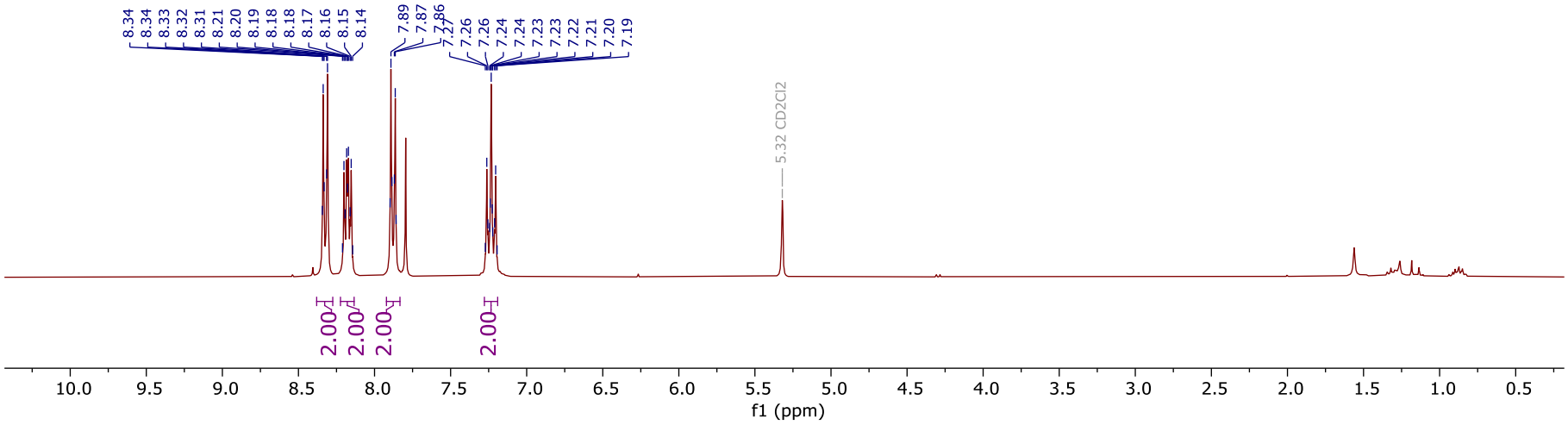

N
O
N
F
N

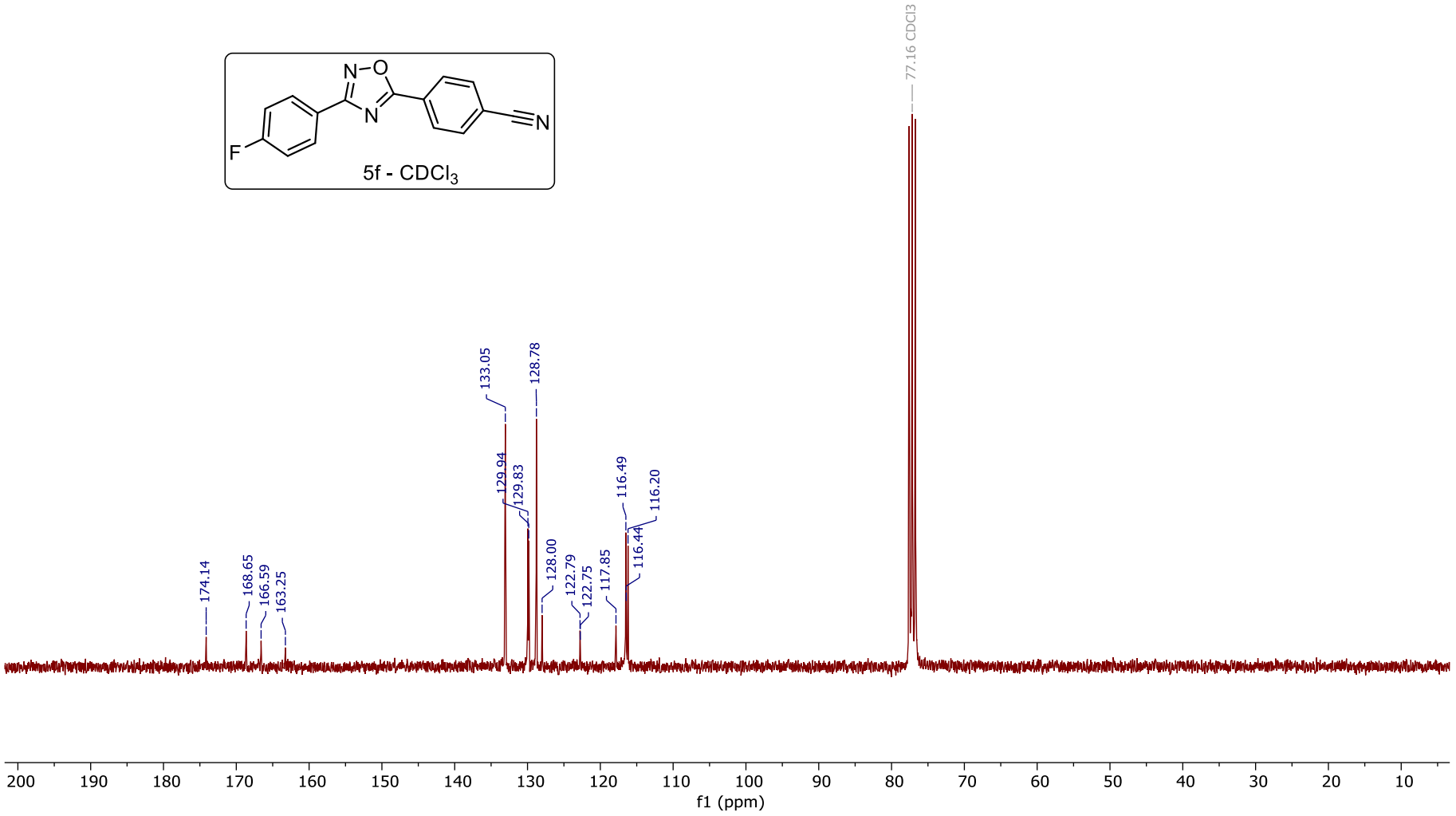
5f - $CDCl_3$

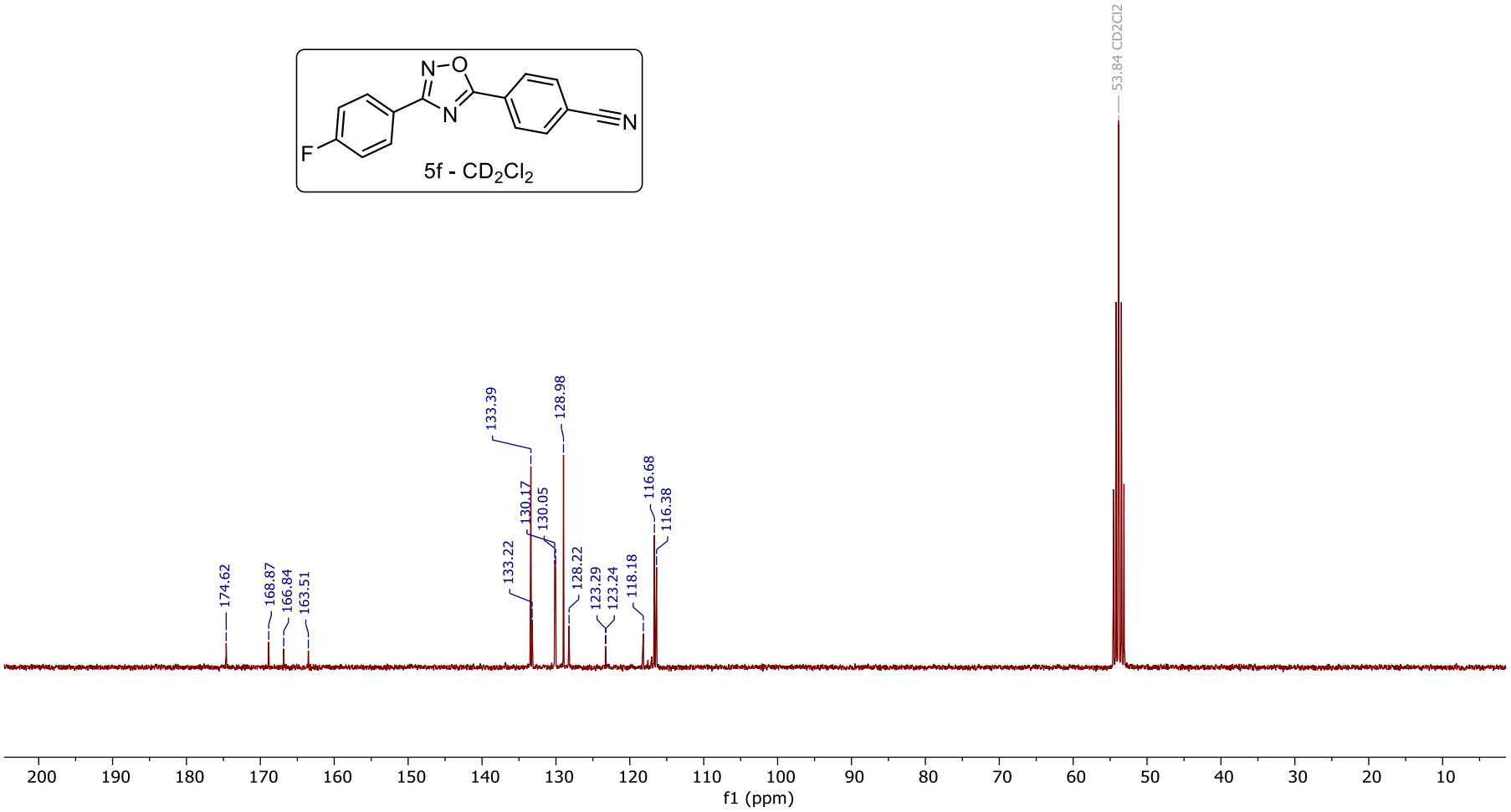

8.34
8.31
8.19
8.17
8.16
8.14
7.87
7.85
7.26 CDCl3
7.24
7.21
7.18
1.61 H2O
2.00
2.02
2.07
2.16
f1 (ppm)

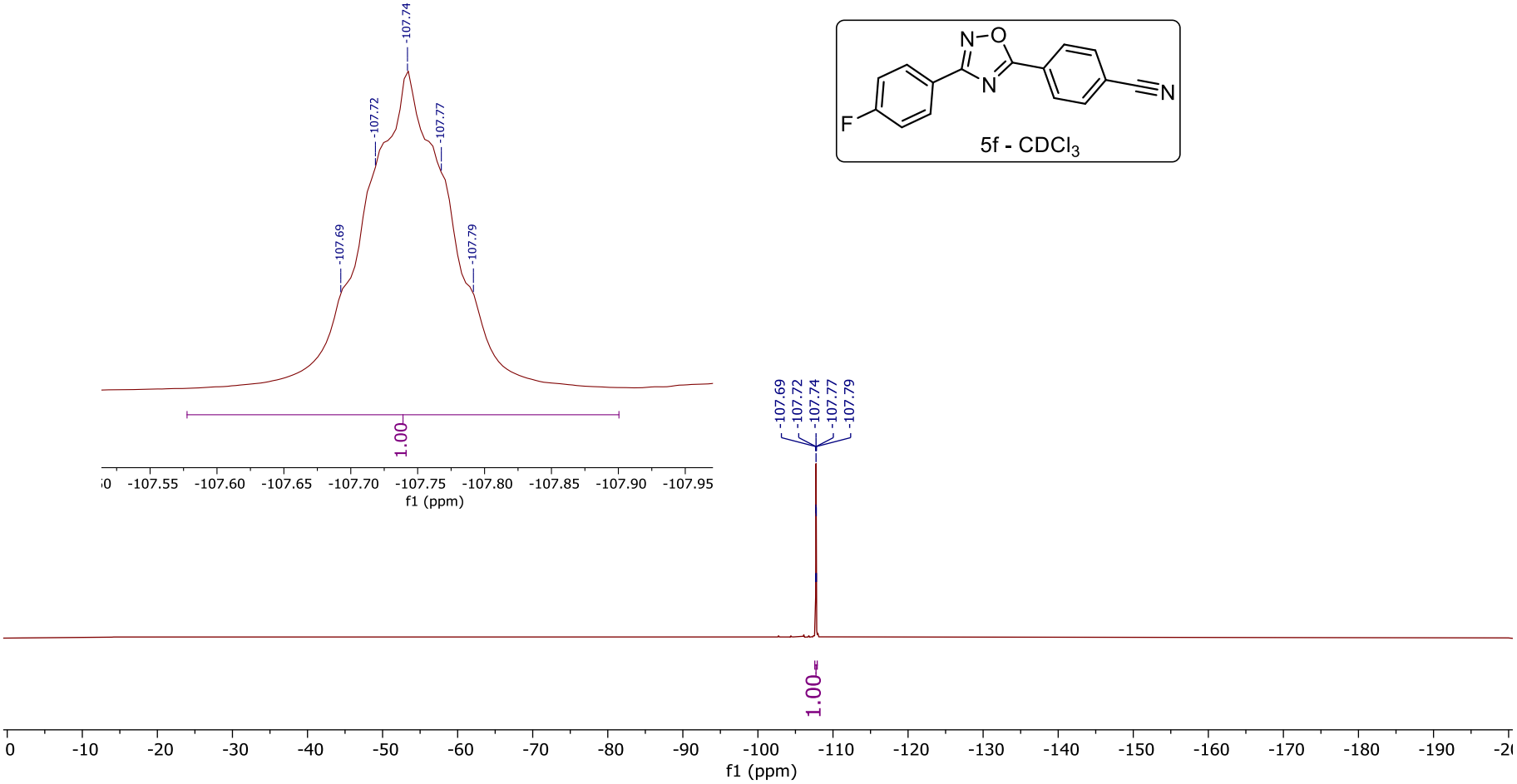

N
O
N
F
N
5f - CD_2Cl_2

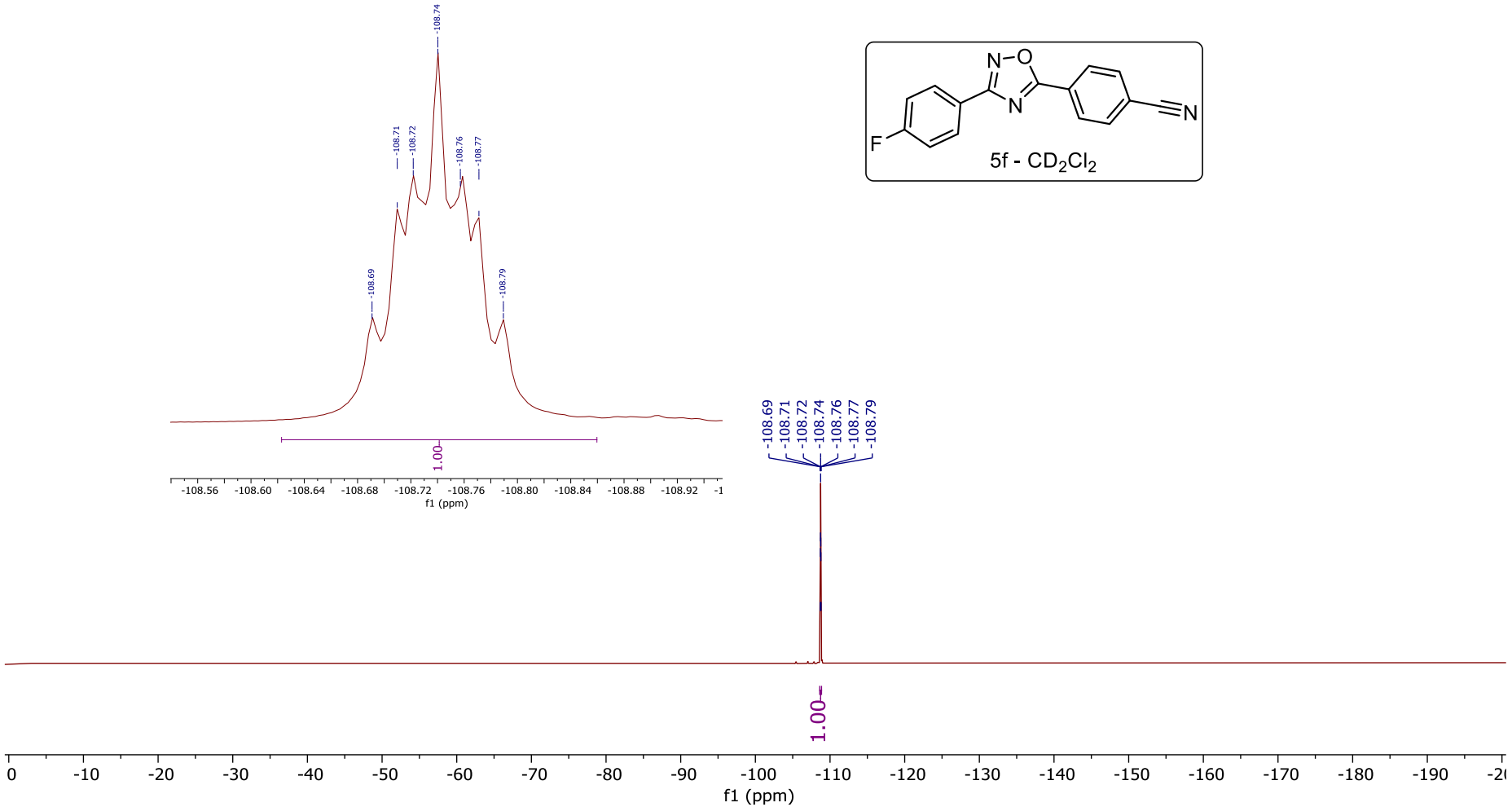

8.34
8.34
8.33
8.32
8.31
8.21
8.20
8.19
8.18
8.18
8.17
8.16
8.15
8.14
7.90
7.89
7.89
7.87
7.86
7.86
7.27
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.19
2.00
2.00
2.00
2.00
f1 (ppm)

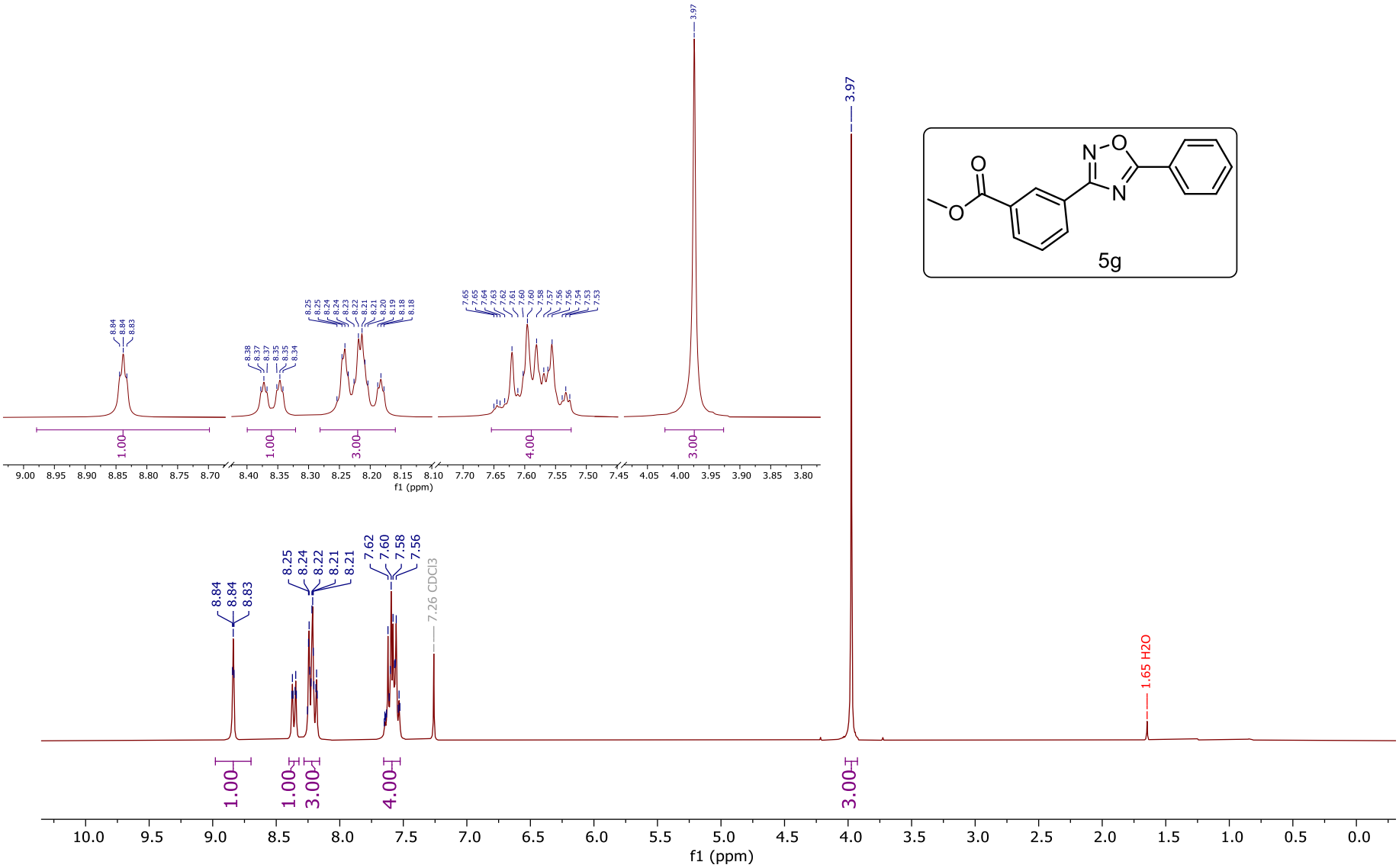

8.34
8.34
8.33
8.32
8.31
8.21
8.20
8.19
8.18
8.18
8.17
8.16
8.15
8.14
7.89
7.87
7.86
7.27
7.26
7.26
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.19
5.32 CD2Cl2
2.00
2.00
2.00
2.00
f1 (ppm)

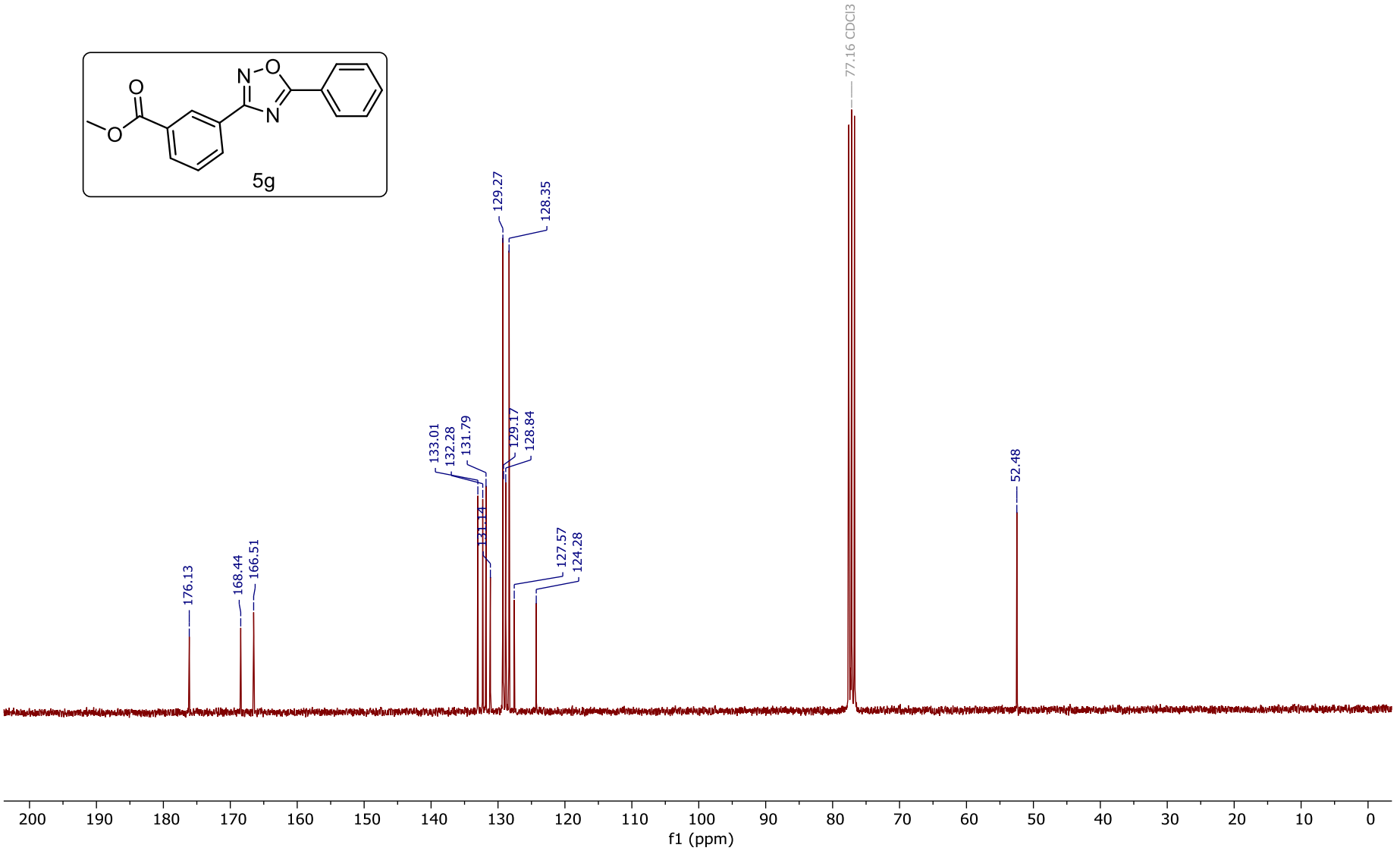

5f - CDCl3
F
N
O
N
N
77.16 CDCl3
174.14
168.65
166.59
163.25
133.05
129.94
129.83
128.78
128.00
122.79
122.75
117.85
116.49
116.44
116.20
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

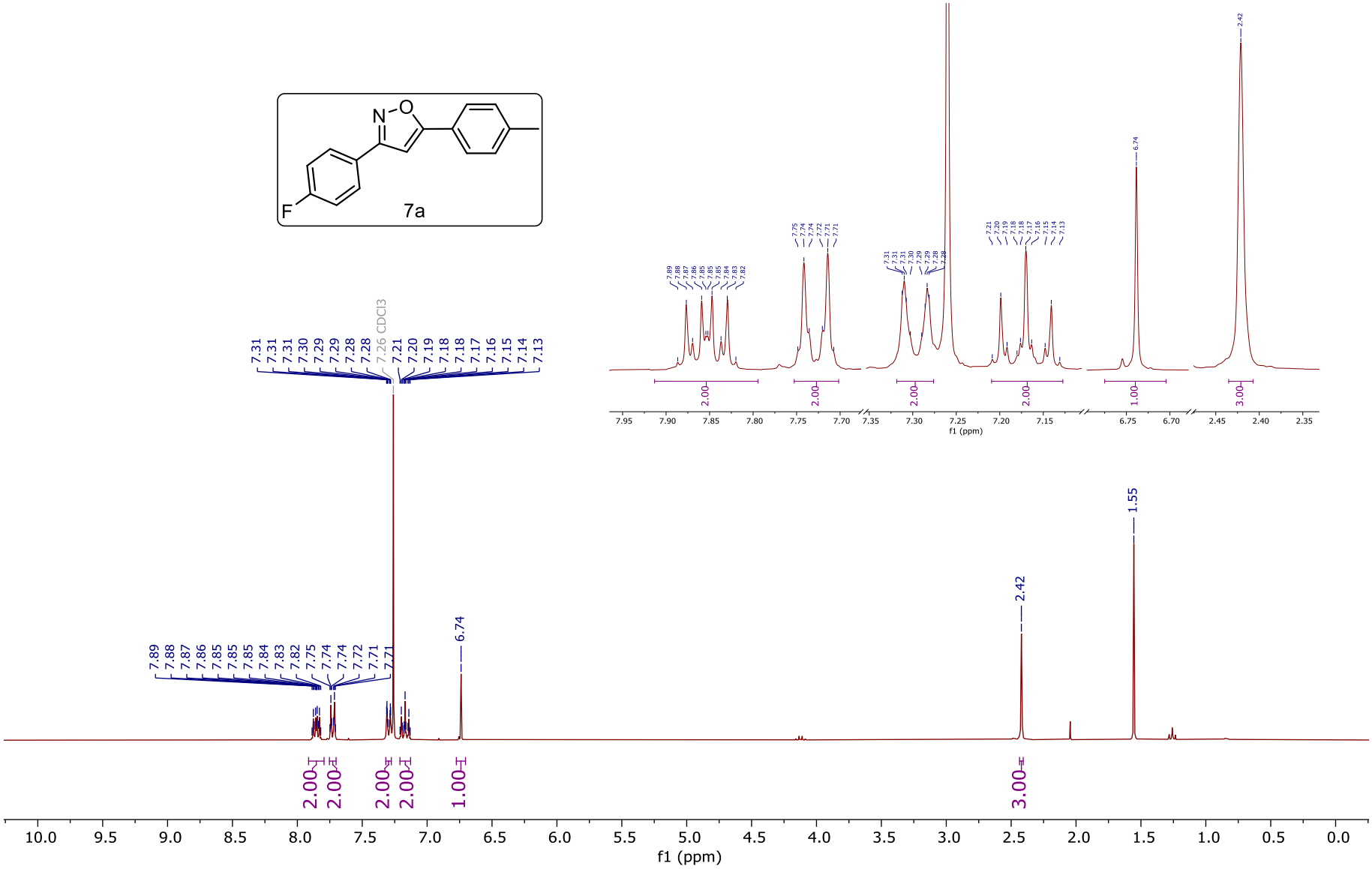

5f - CD_2Cl_2
53.84 CD2Cl2
174.62
168.87
166.84
163.51
133.39
133.22
130.17
130.05
128.98
128.22
123.29
123.24
118.18
116.68
116.38
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

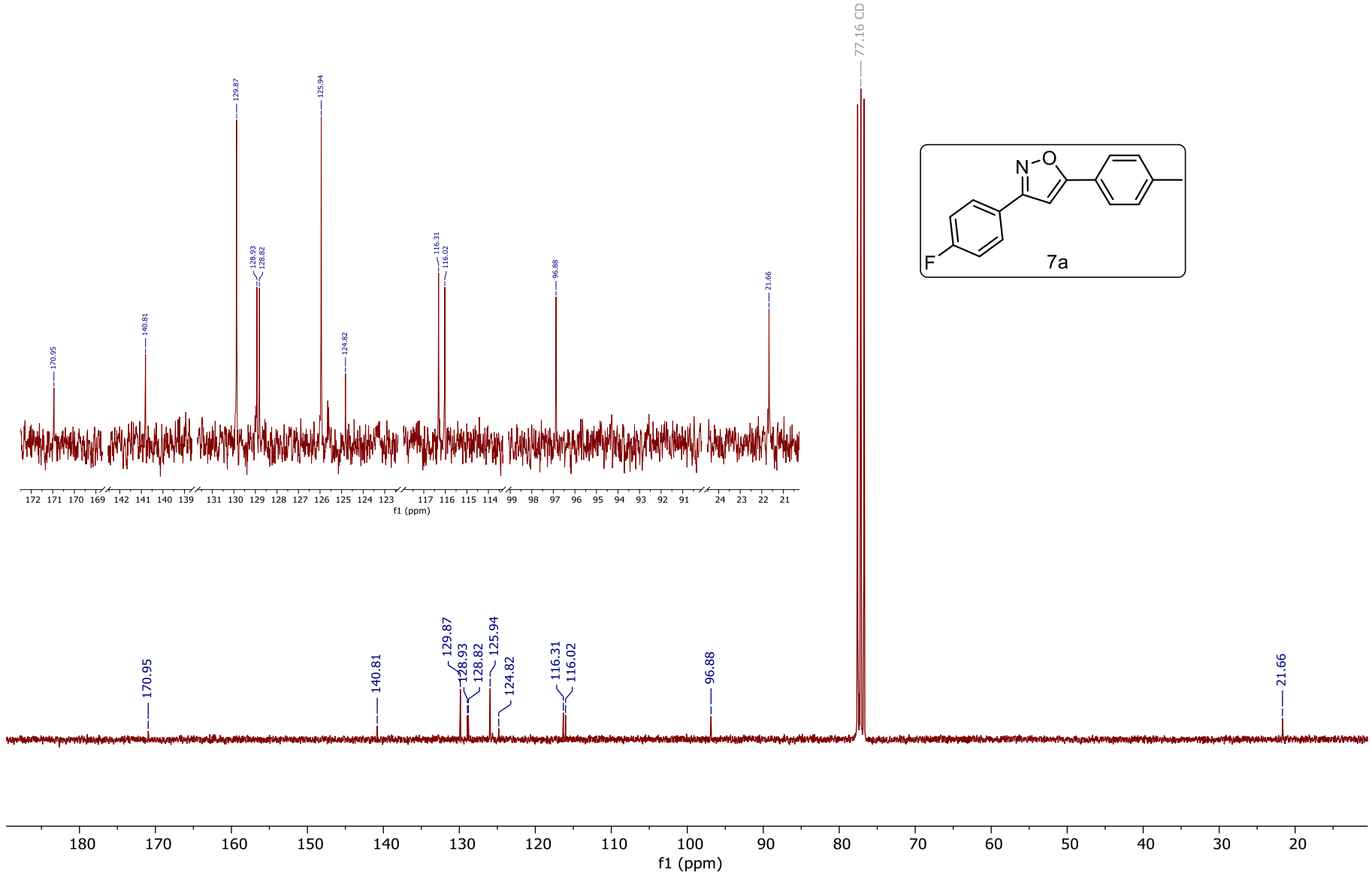

-107.74
-107.72
-107.77
-107.69
-107.79
1.00
-107.55 -107.60 -107.65 -107.70 -107.75 -107.80 -107.85 -107.90 -107.95
f1 (ppm)
N
O
N
F
N
5f - CDCl3
-107.69
-107.72
-107.74
-107.77
-107.79
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

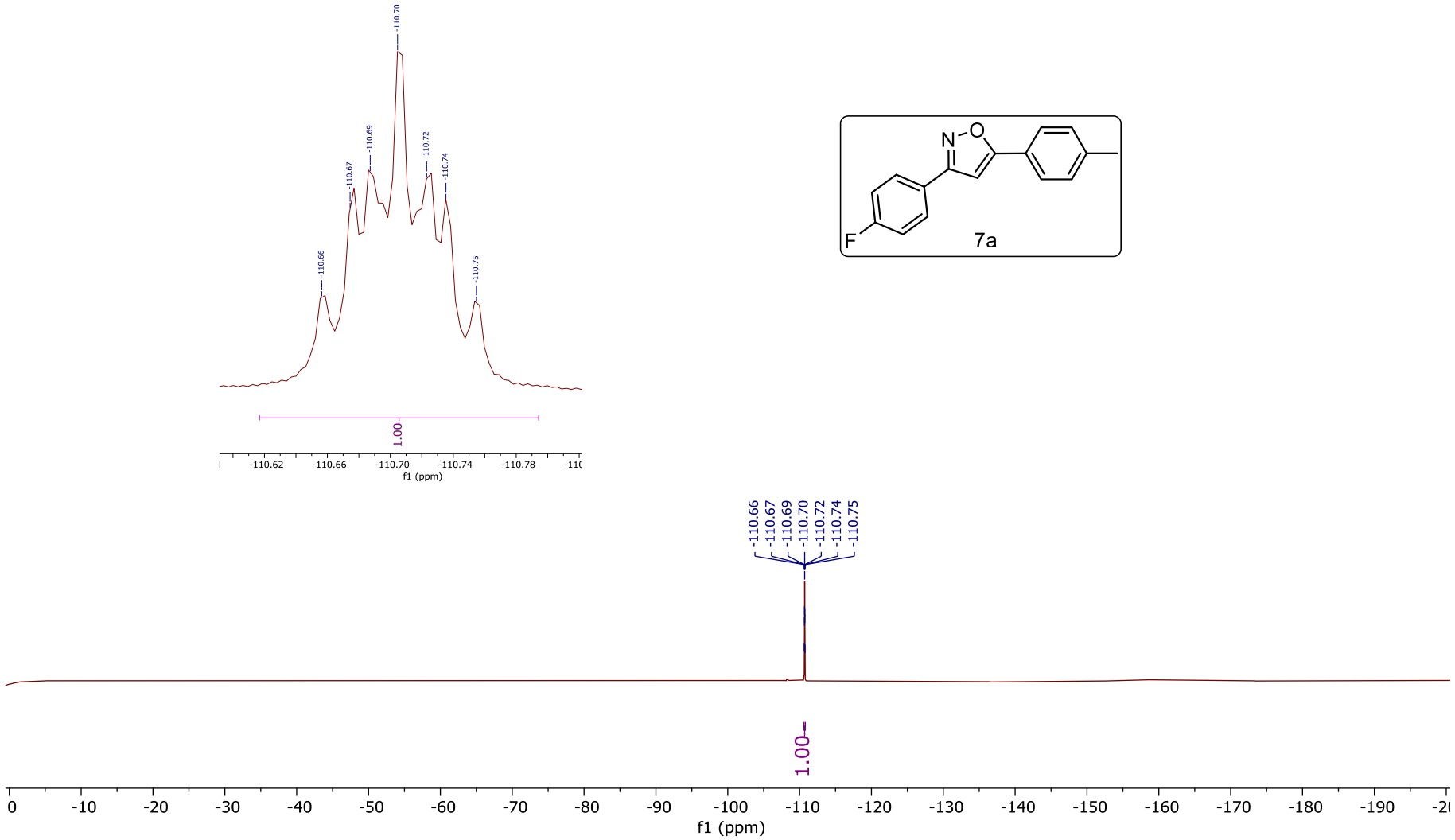

-108.74
-108.71
-108.72
-108.76
-108.77
-108.69
-108.79
1.00
-108.56 -108.60 -108.64 -108.68 -108.72 -108.76 -108.80 -108.84 -108.88 -108.92
f1 (ppm)
N
O
N
F
N
5f - CD2Cl2
-108.69
-108.71
-108.72
-108.74
-108.76
-108.77
-108.79
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

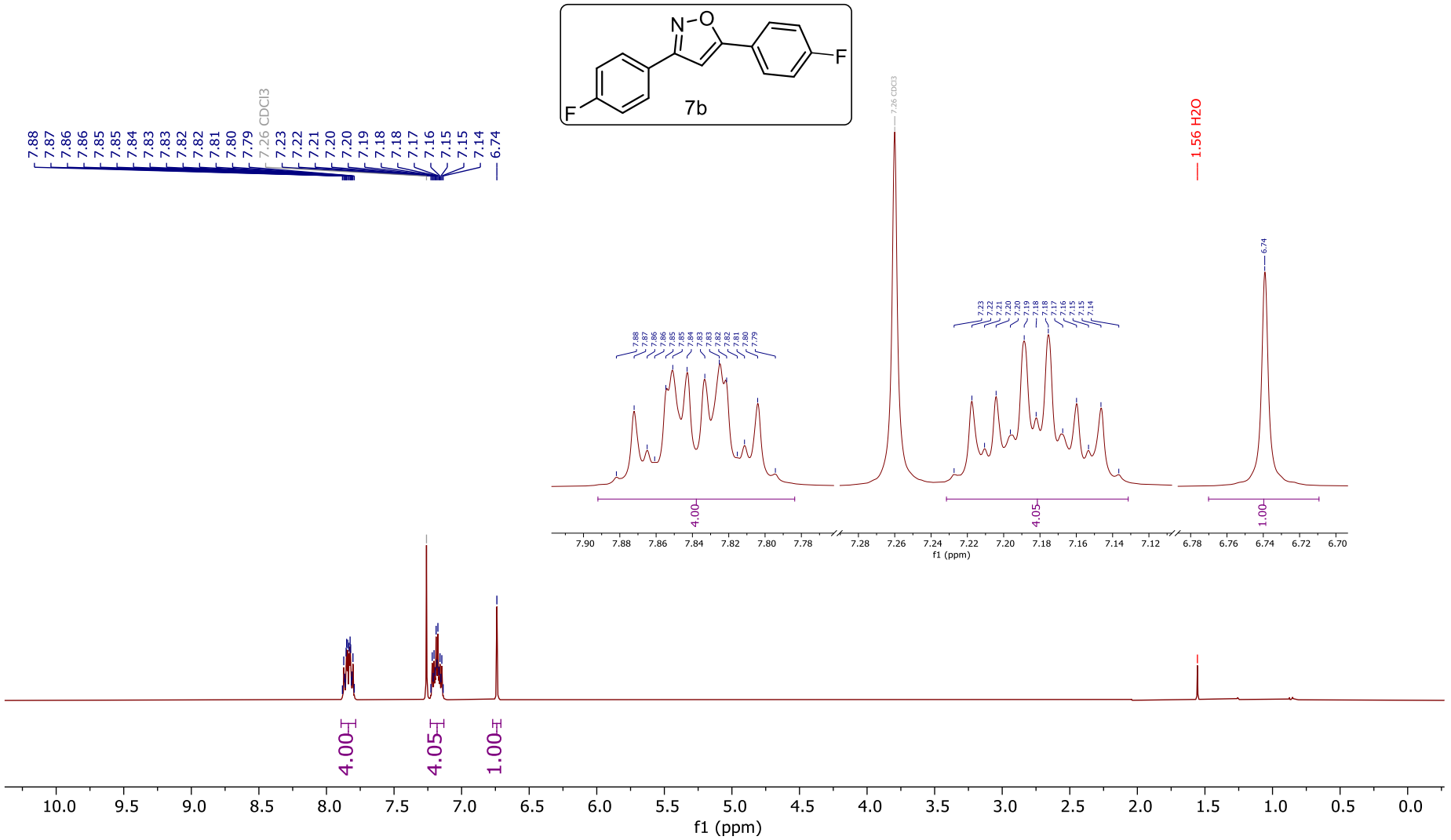

3.97
8.84
8.84
8.83
8.38
8.37
8.37
8.35
8.35
8.34
8.25
8.25
8.24
8.24
8.23
8.22
8.21
8.21
8.20
8.19
8.18
8.18
7.65
7.65
7.64
7.63
7.62
7.61
7.60
7.60
7.58
7.57
7.56
7.56
7.54
7.53
7.53
1.00
1.00
3.00
4.00
3.00
f1 (ppm)
8.84
8.84
8.83
8.25
8.24
8.22
8.21
8.21
7.62
7.60
7.58
7.56
7.26 CDCl3
1.65 H2O
1.00
1.00
3.00
4.00
3.00
f1 (ppm)
O
O
N
O
N
5g

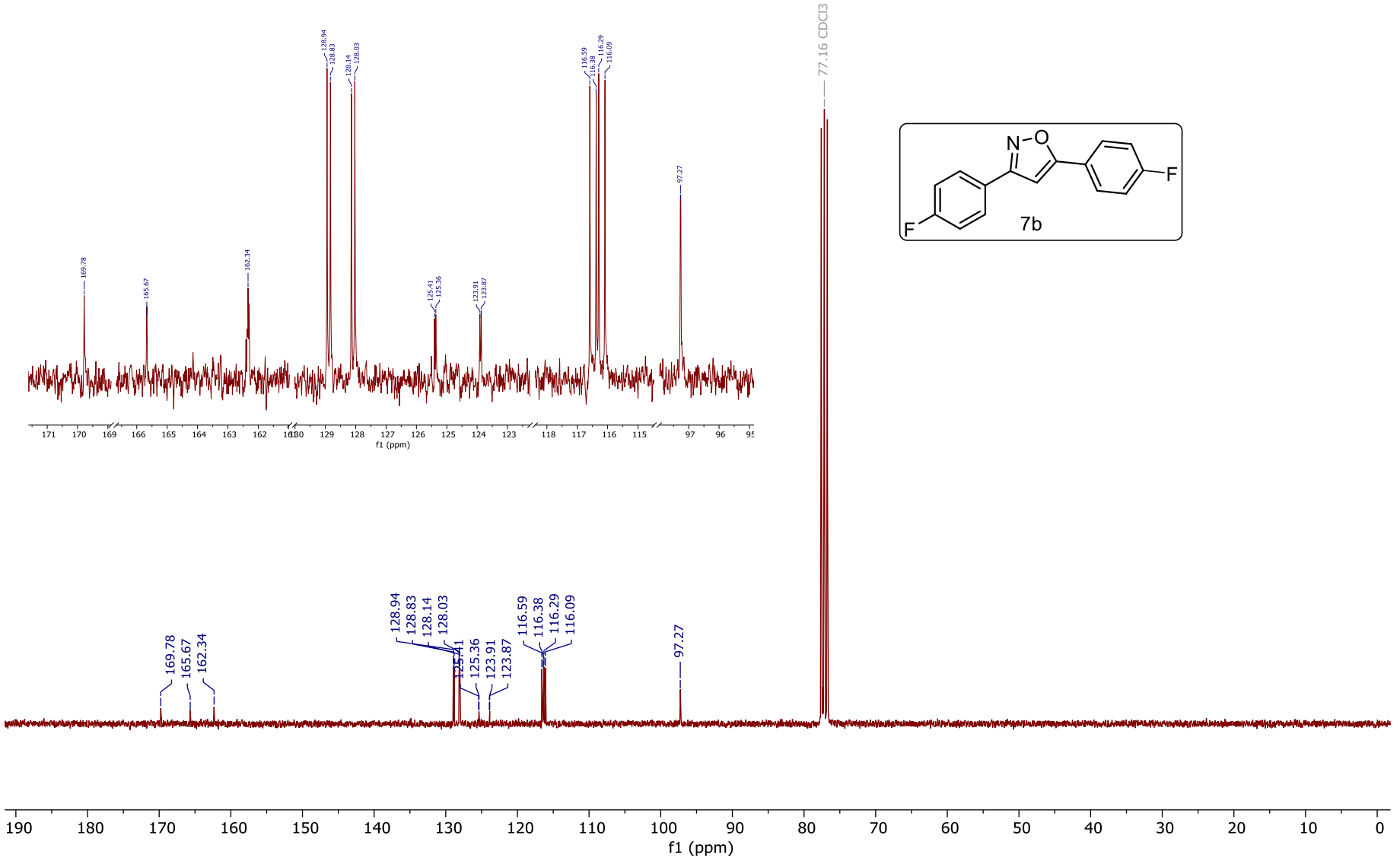

5g
176.13
168.44
166.51
133.01
132.28
131.79
131.14
129.27
129.17
128.84
128.35
127.57
124.28
77.16 CDCl3
52.48
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

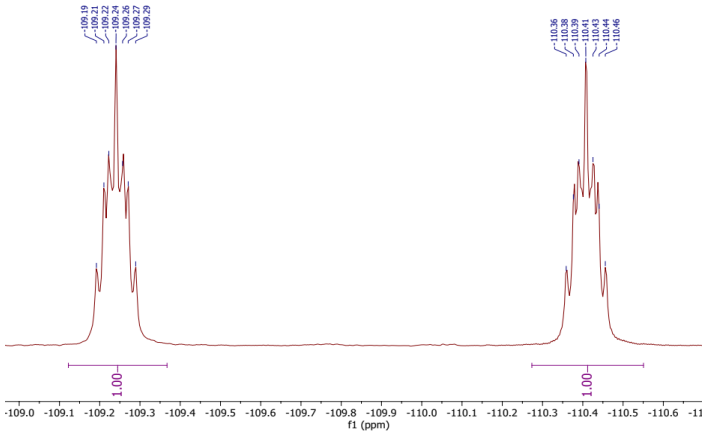

F
7a
7.89
7.88
7.87
7.86
7.85
7.85
7.84
7.83
7.82
7.75
7.74
7.74
7.72
7.71
7.71
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.26 CDCl3
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
7.13
6.74
2.42
1.55
2.00
2.00
2.00
2.00
1.00
3.00
f1 (ppm)

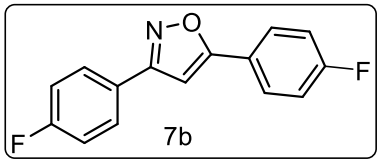

77.16 CD
129.87
125.94
128.93
128.82
116.31
116.02
96.88
21.66
170.95
140.81
124.82
f1 (ppm)
7a
F
N
O

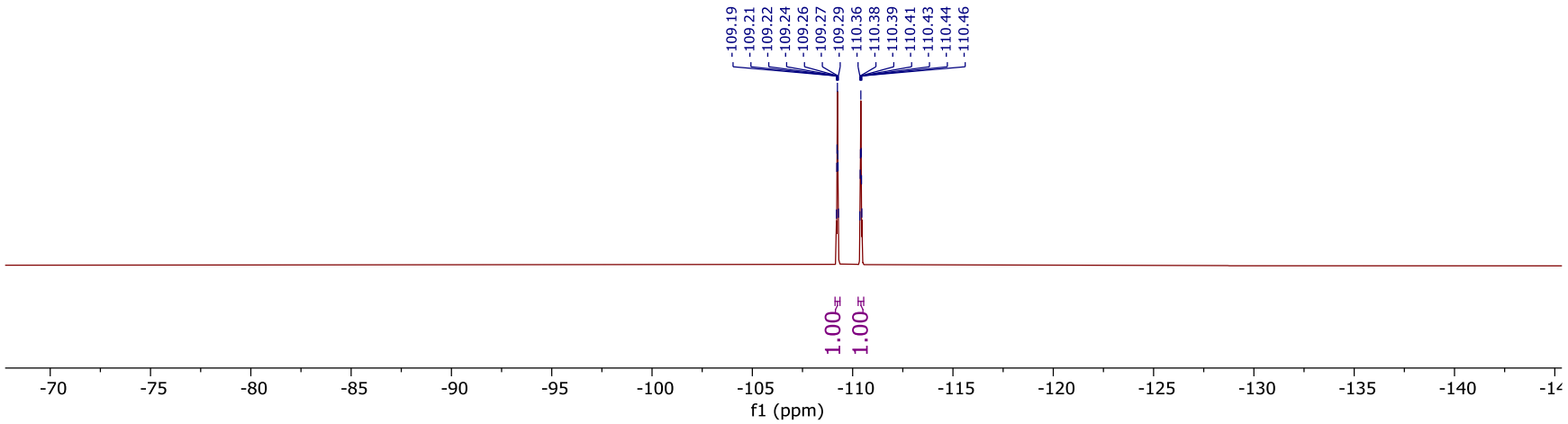

-110.66
-110.67
-110.69
-110.70
-110.72
-110.74
-110.75
1.00
-110.62
-110.66
-110.70
-110.74
-110.78
f1 (ppm)
N
O
F
7a
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

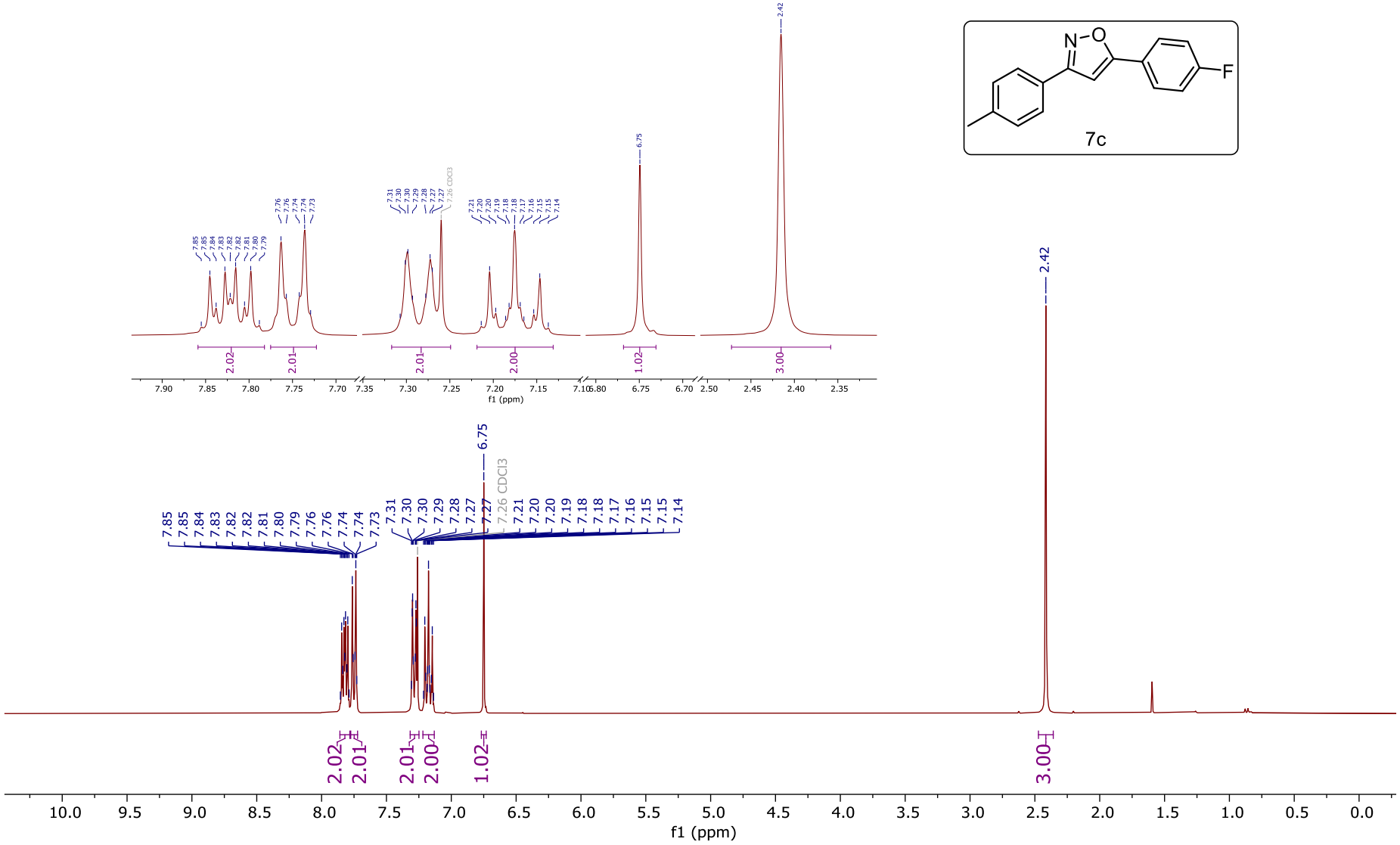

7b
F
F
N
O
7.88 7.87 7.86 7.86 7.85 7.85 7.84 7.83 7.83 7.82 7.82 7.81 7.80 7.79 7.26 CDCl3 7.23 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.16 7.15 7.15 7.14 6.74
1.56 H2O
4.00
4.05
1.00
f1 (ppm)

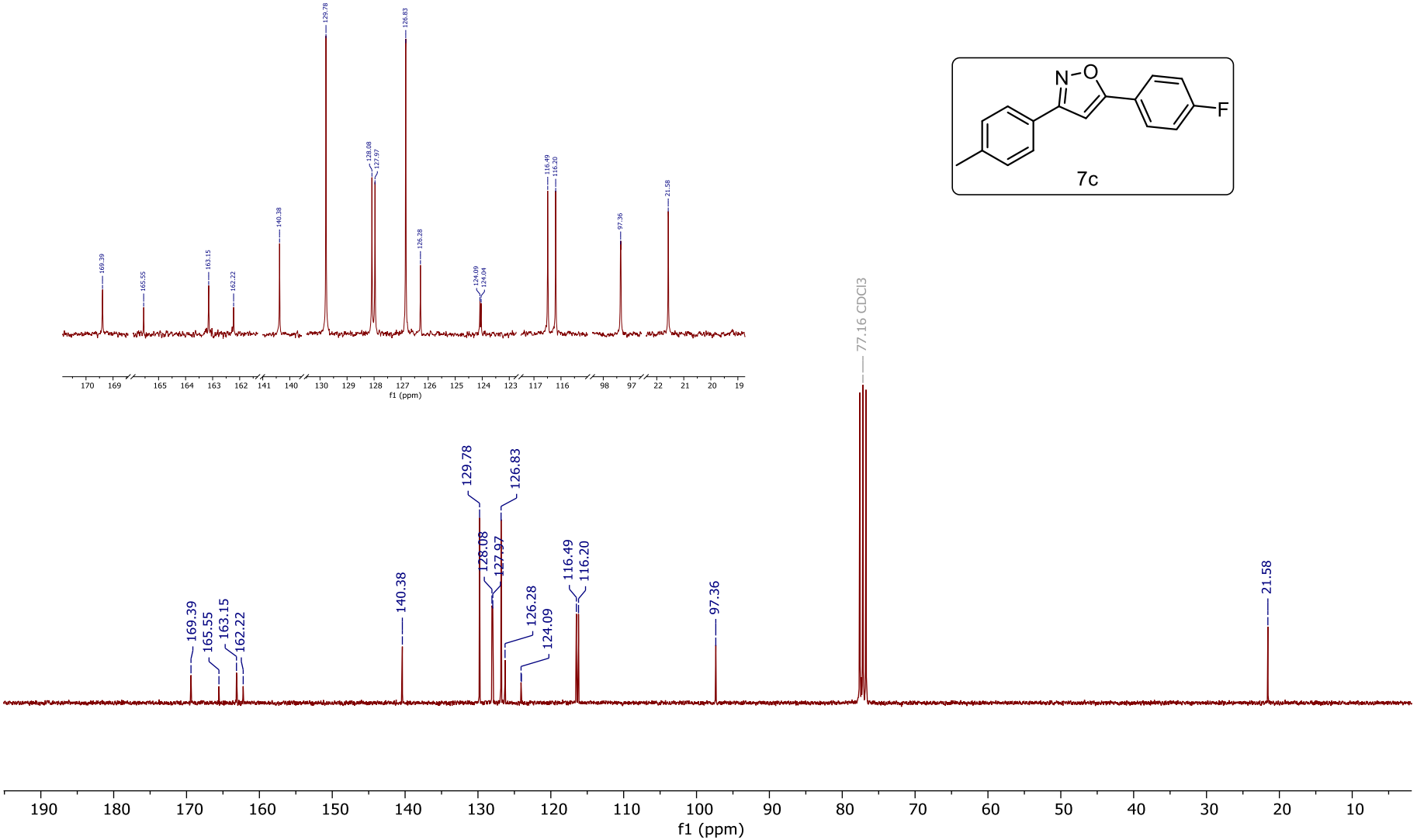

77.16 CDCl3
169.78
165.67
162.34
128.94
128.83
128.14
128.03
125.41
125.36
123.91
123.87
116.59
116.38
116.29
116.09
97.27
N
O
F
F
7b
f1 (ppm)

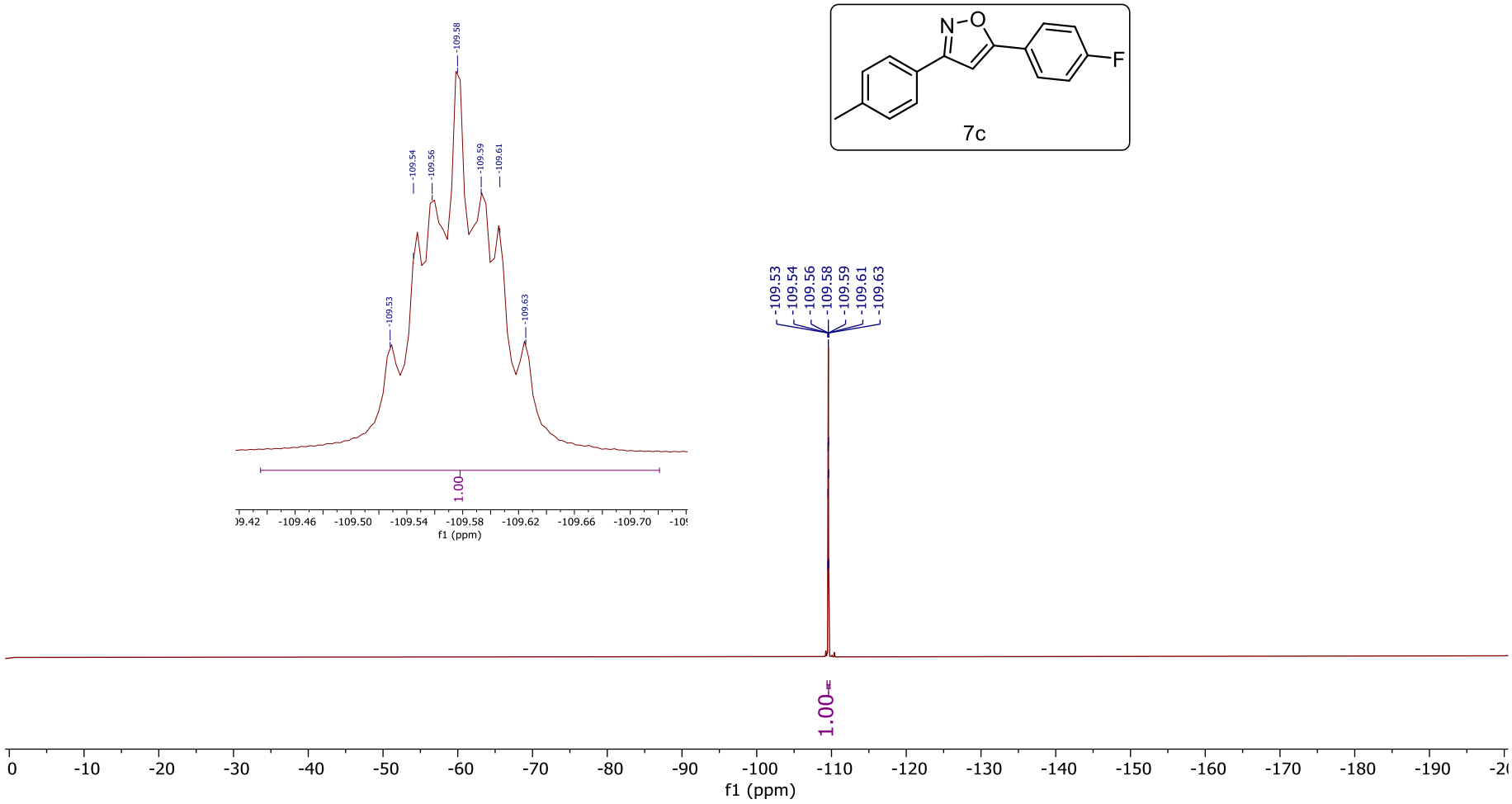

-109.19
-109.21
-109.22
-109.24
-109.26
-109.27
-109.29
-110.36
-110.38
-110.39
-110.41
-110.43
-110.44
-110.46
1.00
1.00
-109.0 -109.1 -109.2 -109.3 -109.4 -109.5 -109.6 -109.7 -109.8 -109.9 -110.0 -110.1 -110.2 -110.3 -110.4 -110.5 -110.6
f1 (ppm)

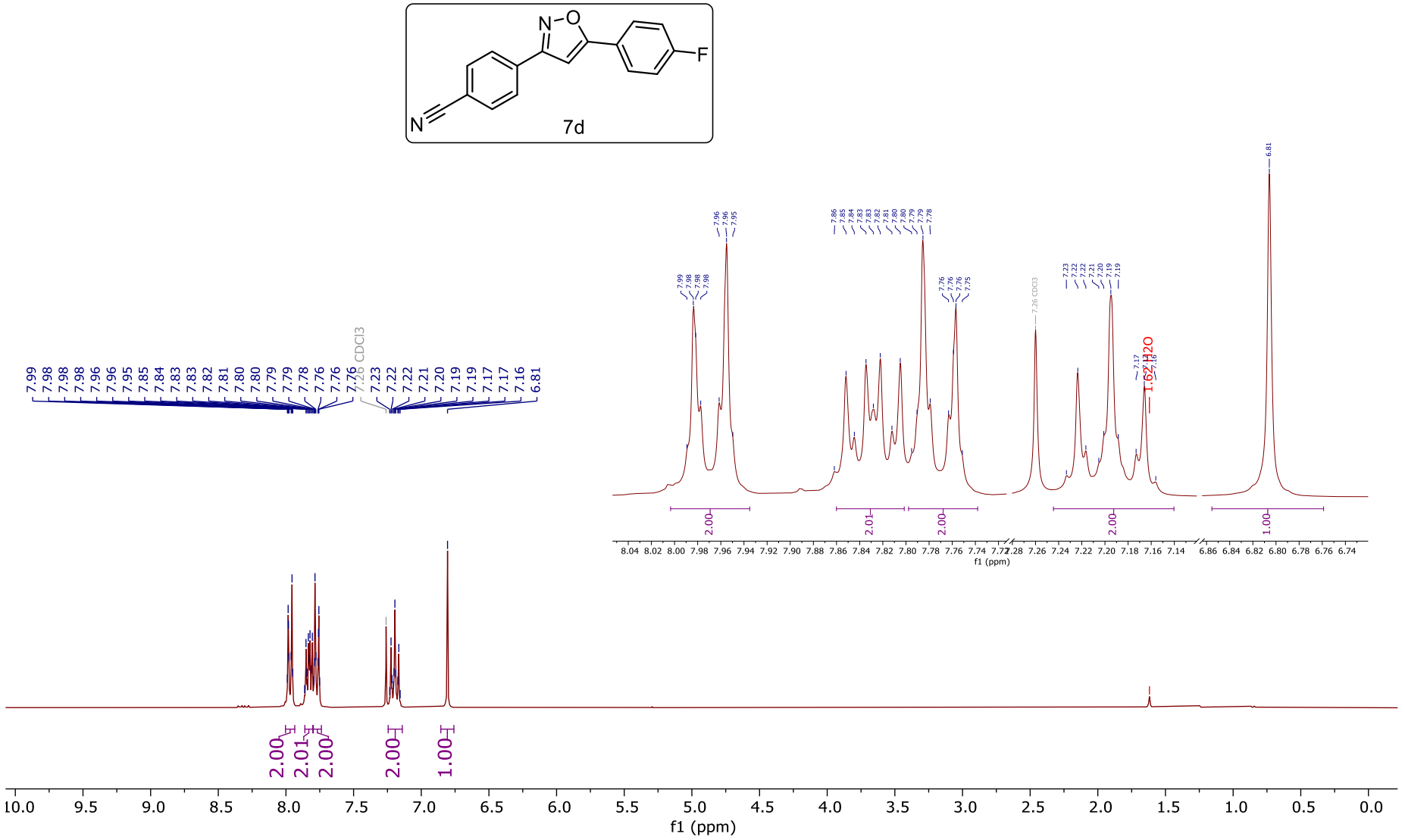

N
O
F
F
7b

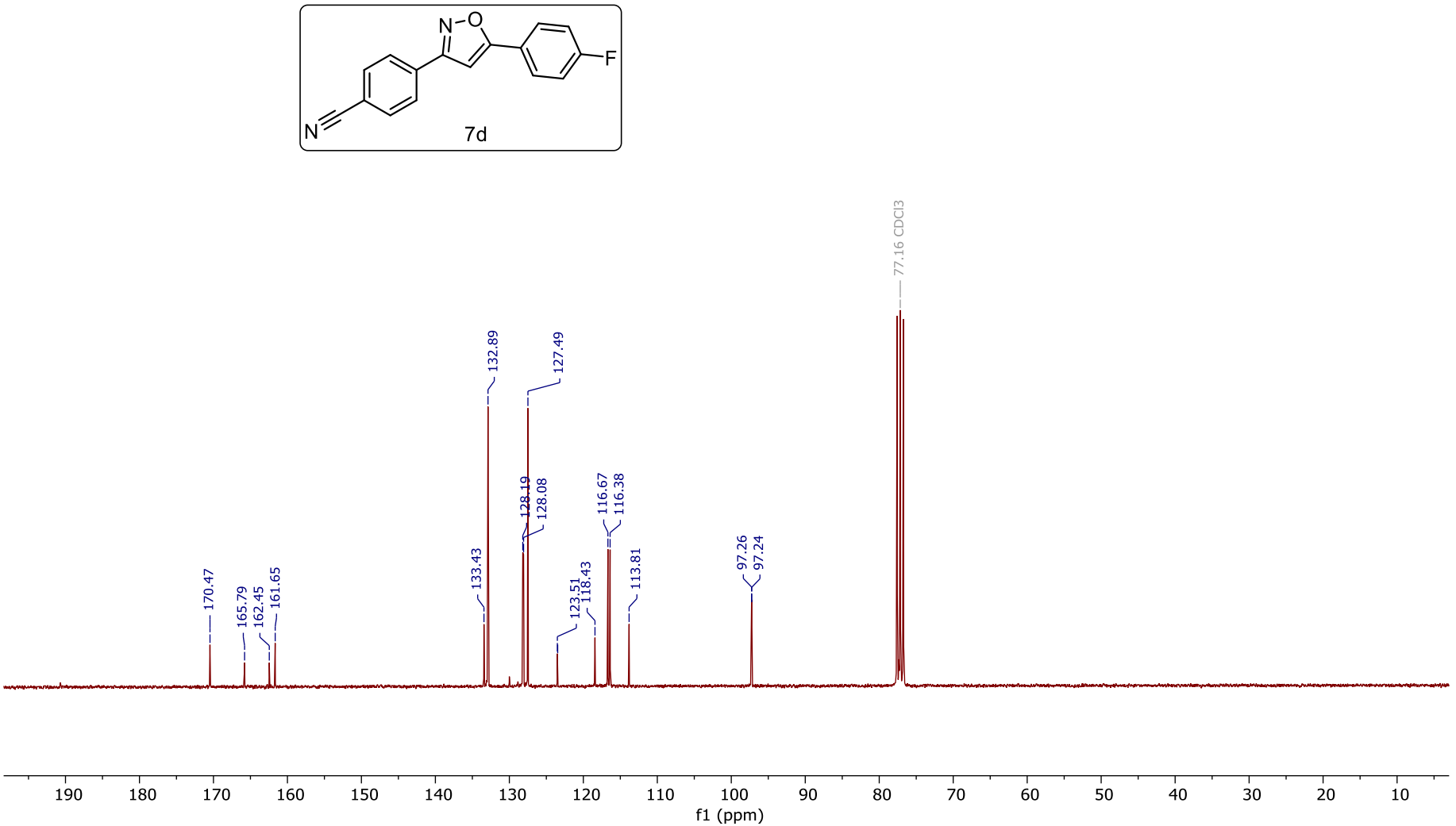

-109.19
-109.21
-109.22
-109.24
-109.26
-109.27
-109.29
-110.36
-110.38
-110.39
-110.41
-110.43
-110.44
-110.46
1.00
1.00
-70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
f1 (ppm)

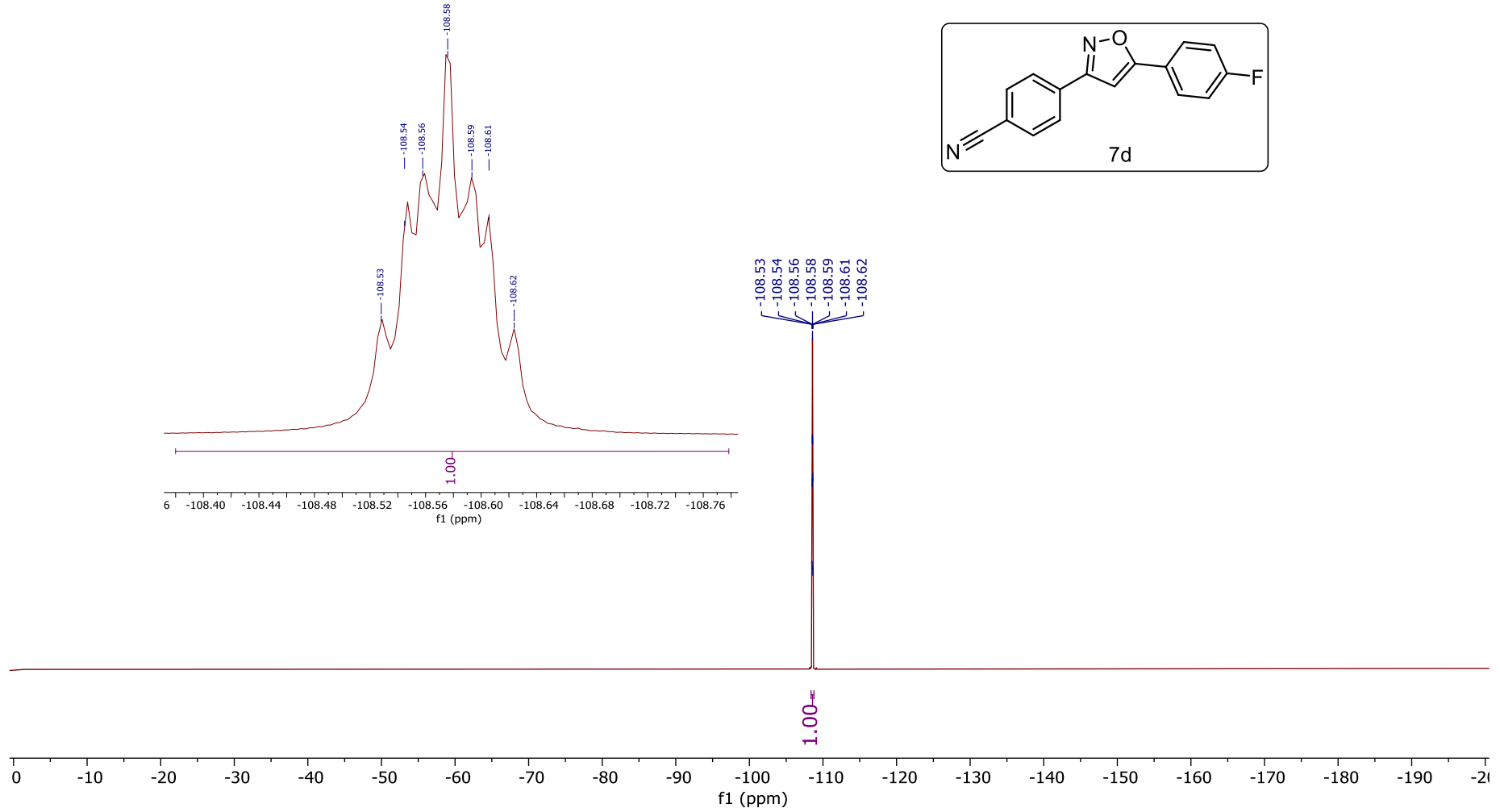

7c
N
O
F
2.42
6.75
7.26 CDCl3
f1 (ppm)

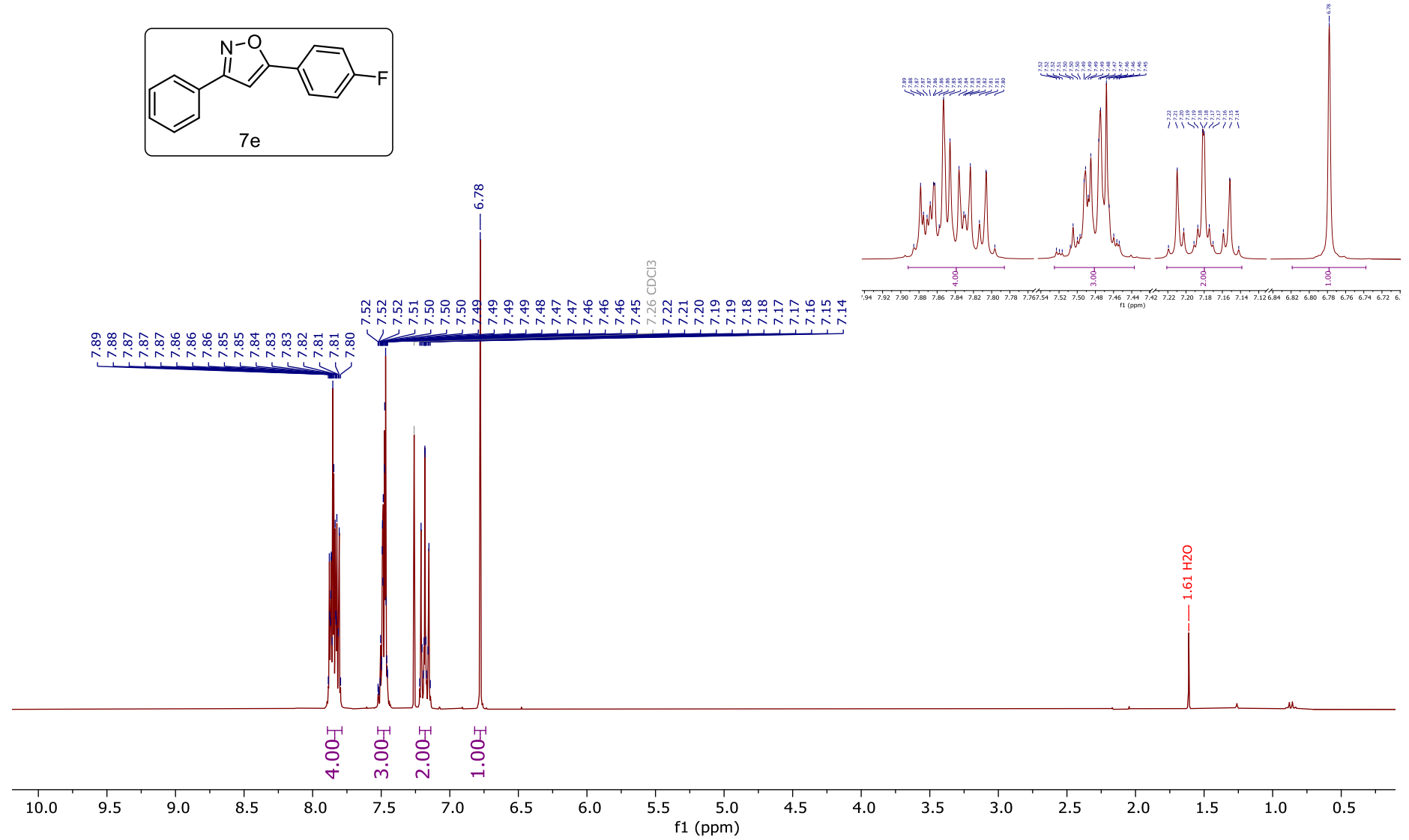

7c
F
N
O
77.16 CDCl3
169.39
165.55
163.15
162.22
140.38
129.78
128.08
127.97
126.83
126.28
124.09
116.49
116.20
97.36
21.58
f1 (ppm)

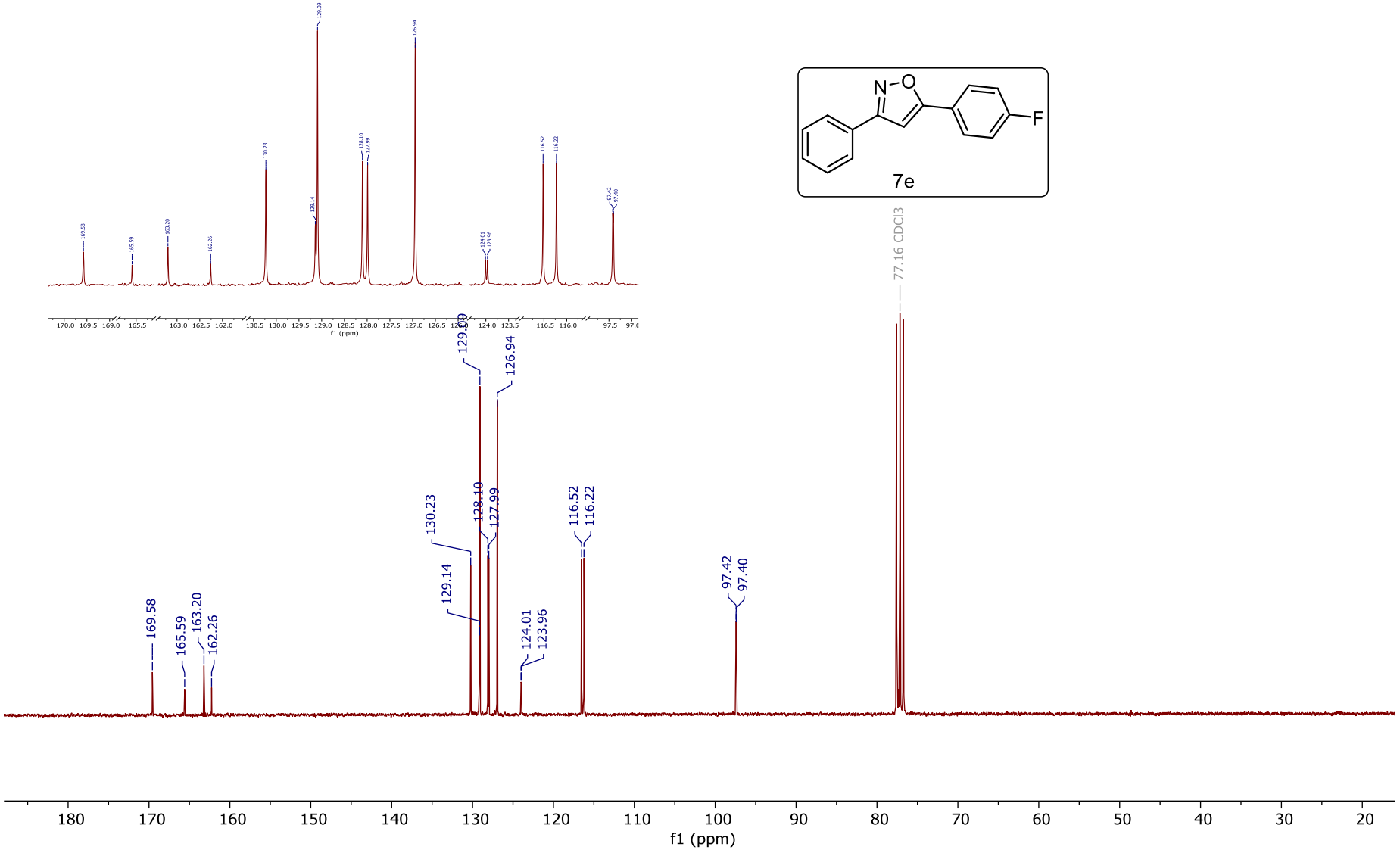

N
O
F
7c
-109.53
-109.54
-109.56
-109.58
-109.59
-109.61
-109.63
1.00
f1 (ppm)
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190

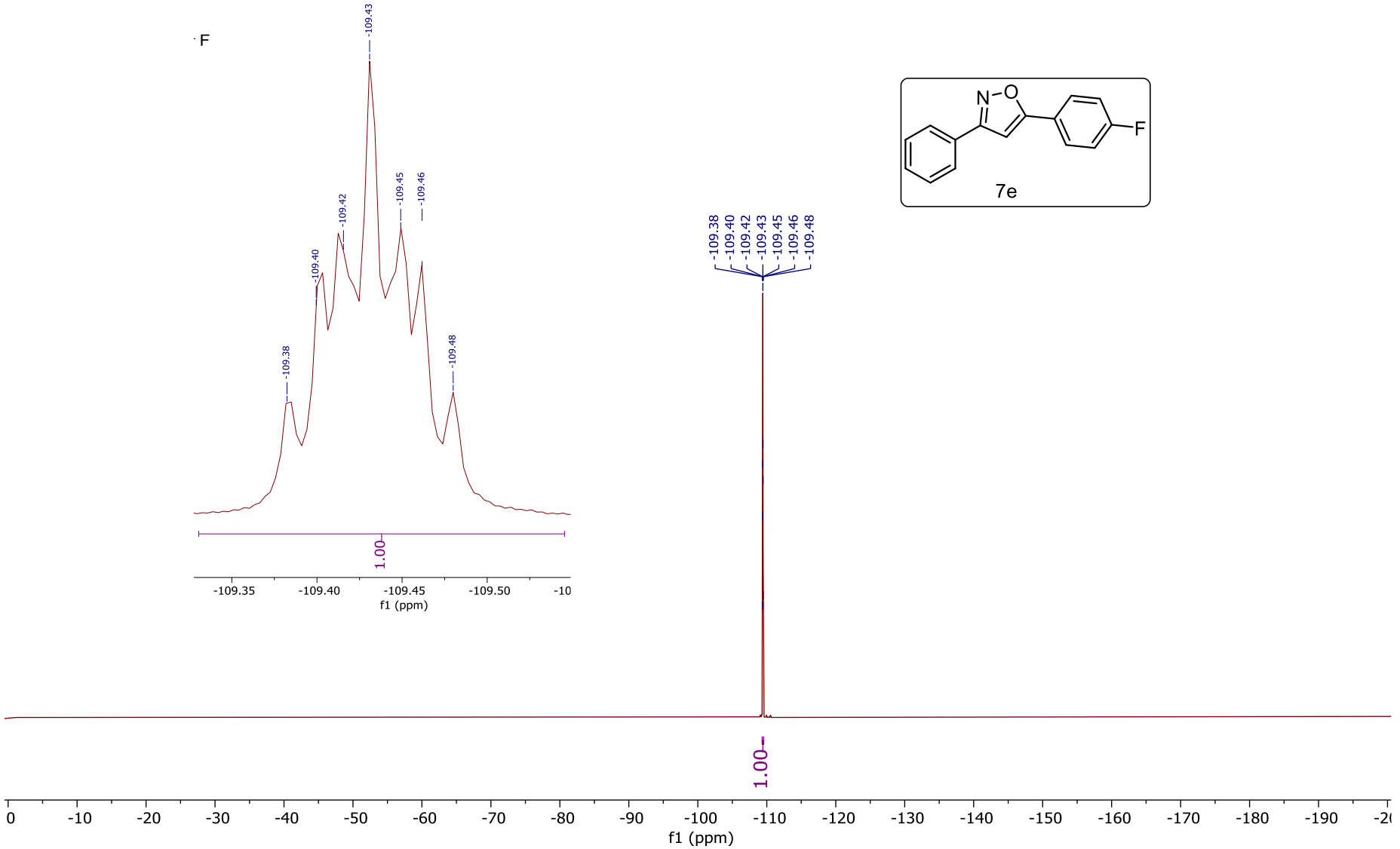

7d
N
O
F
N
CDCl3
1.62 H2O
f1 (ppm)

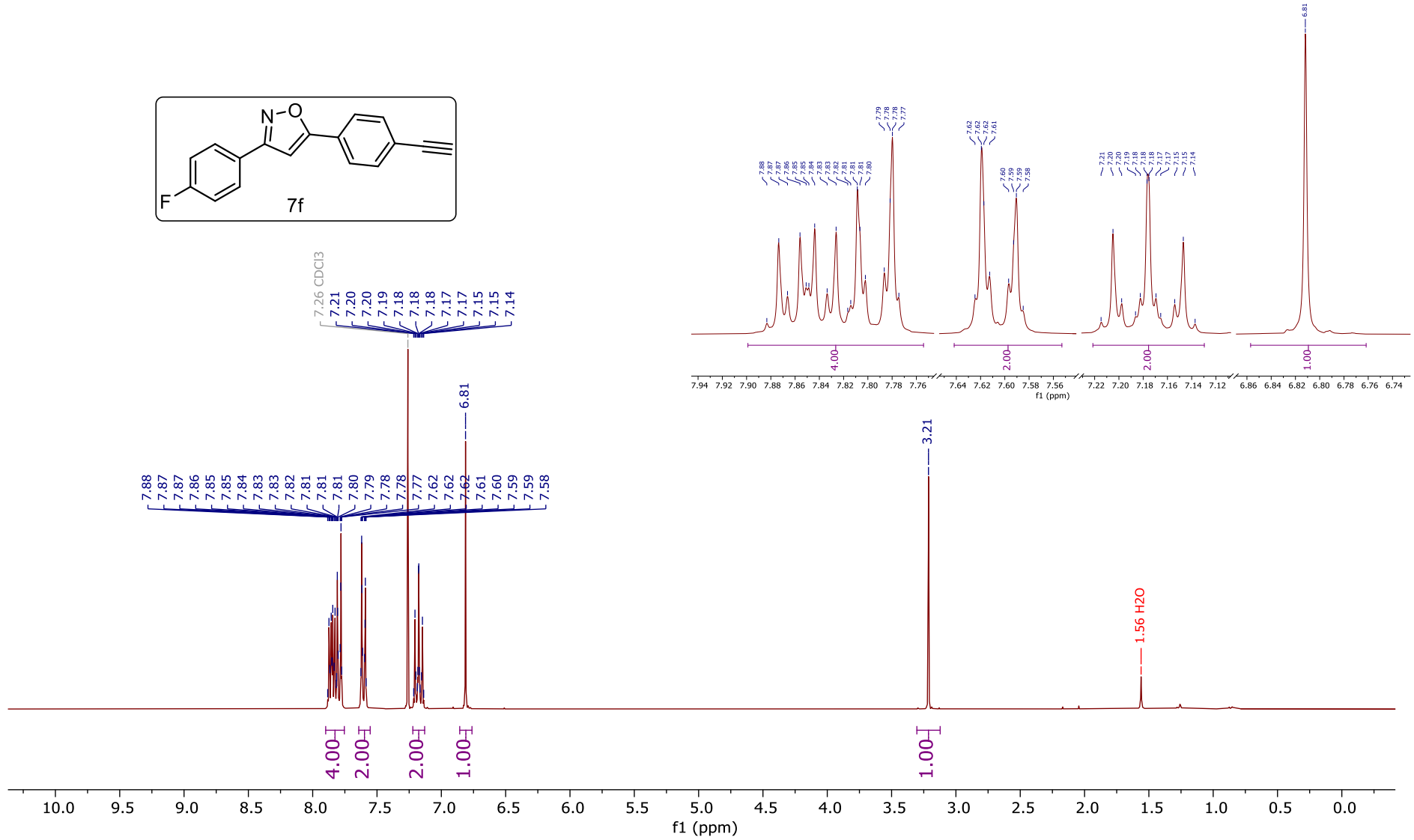

N
O
F
N
7d
77.16 CDCl3
132.89
127.49
128.19
128.08
116.67
116.38
133.43
123.51
118.43
113.81
97.26
97.24
170.47
165.79
162.45
161.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

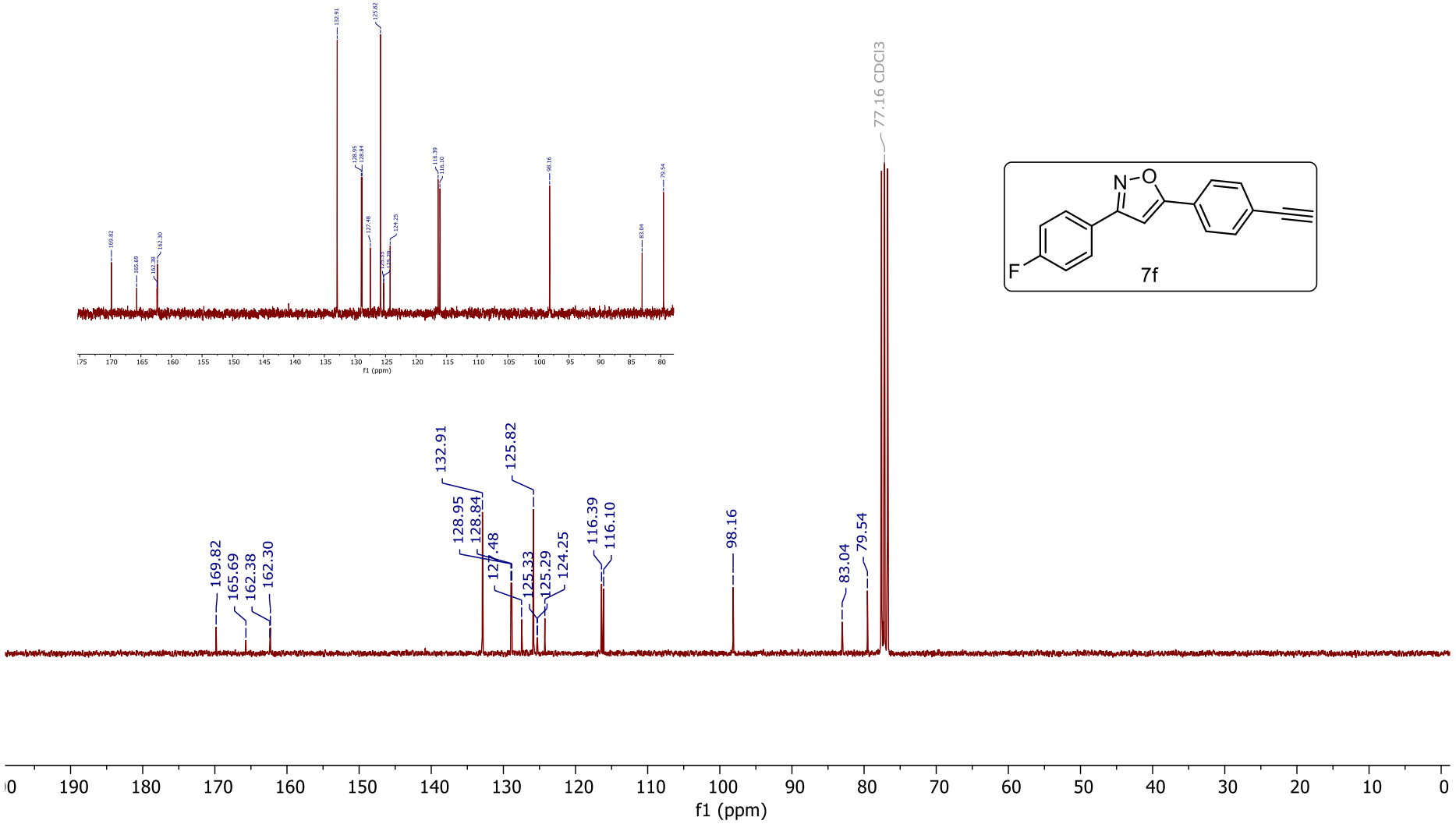

-108.58
-108.54
-108.56
-108.59
-108.61
-108.53
-108.62
1.00
6 -108.40 -108.44 -108.48 -108.52 -108.56 -108.60 -108.64 -108.68 -108.72 -108.76
f1 (ppm)
-108.53
-108.54
-108.56
-108.58
-108.59
-108.61
-108.62
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)
N
O
F
N
7d

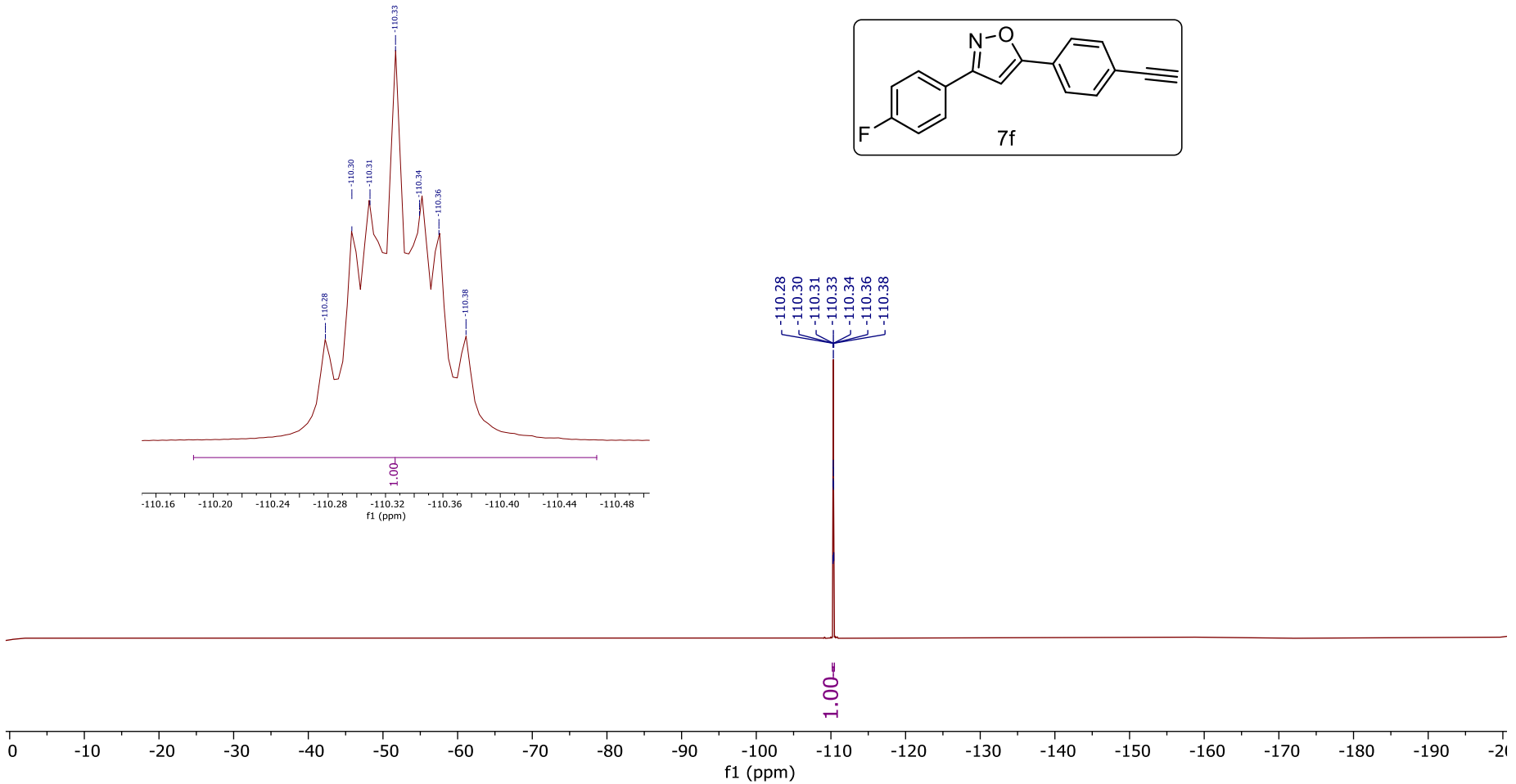

7e
7.89
7.88
7.87
7.87
7.87
7.86
7.86
7.86
7.85
7.85
7.84
7.83
7.83
7.82
7.81
7.81
7.80
7.52
7.52
7.52
7.51
7.50
7.50
7.50
7.49
7.49
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.46
7.45
7.26 CDCl3
7.22
7.21
7.20
7.19
7.19
7.18
7.18
7.17
7.17
7.16
7.15
7.14
6.78
1.61 H2O
4.00
3.00
2.00
1.00
f1 (ppm)

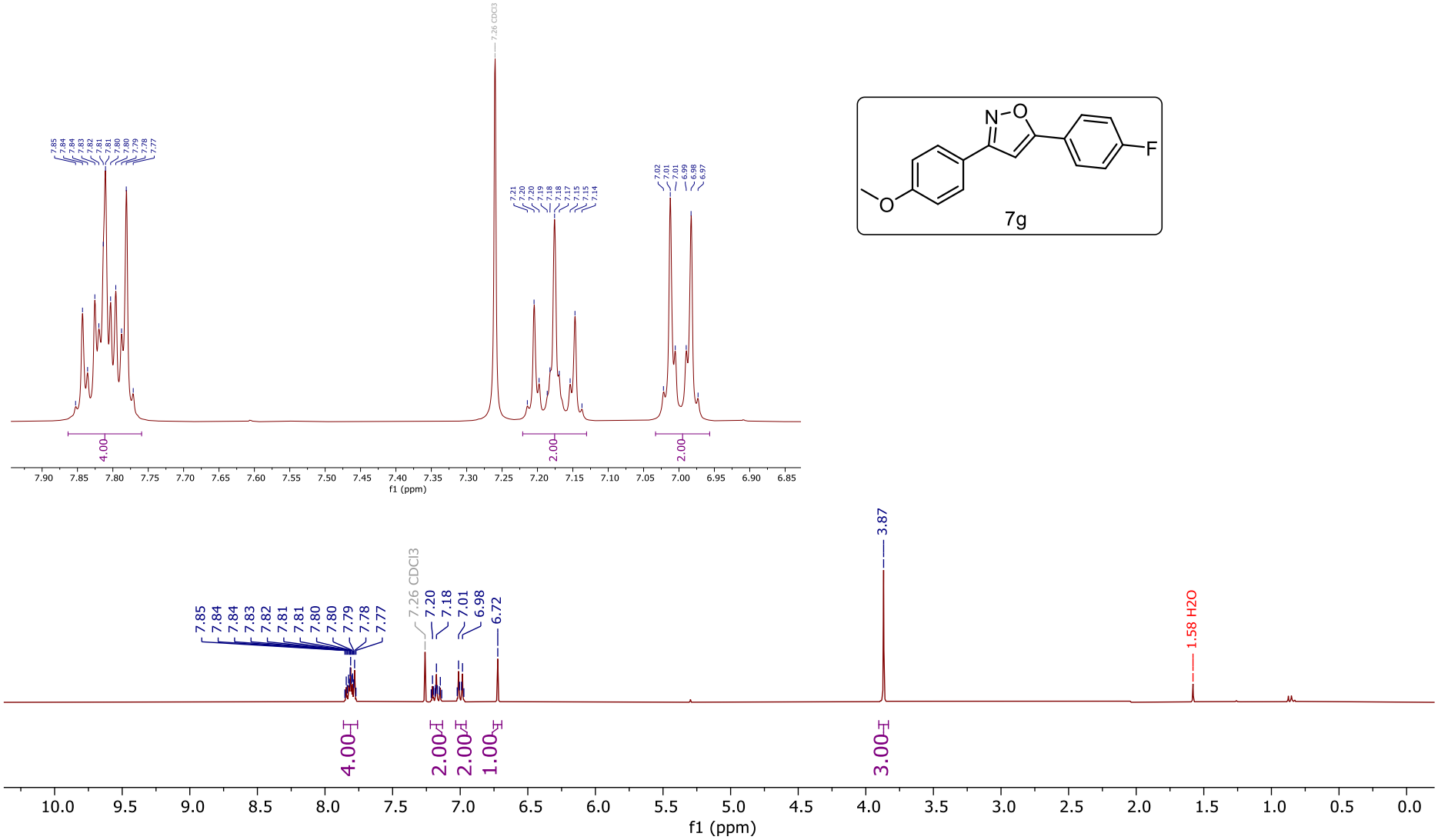

7e
F
N
O
77.16 CDCl3
169.58
165.59
163.20
162.26
130.23
129.14
129.09
128.10
127.99
126.94
124.01
123.96
116.52
116.22
97.42
97.40
f1 (ppm)

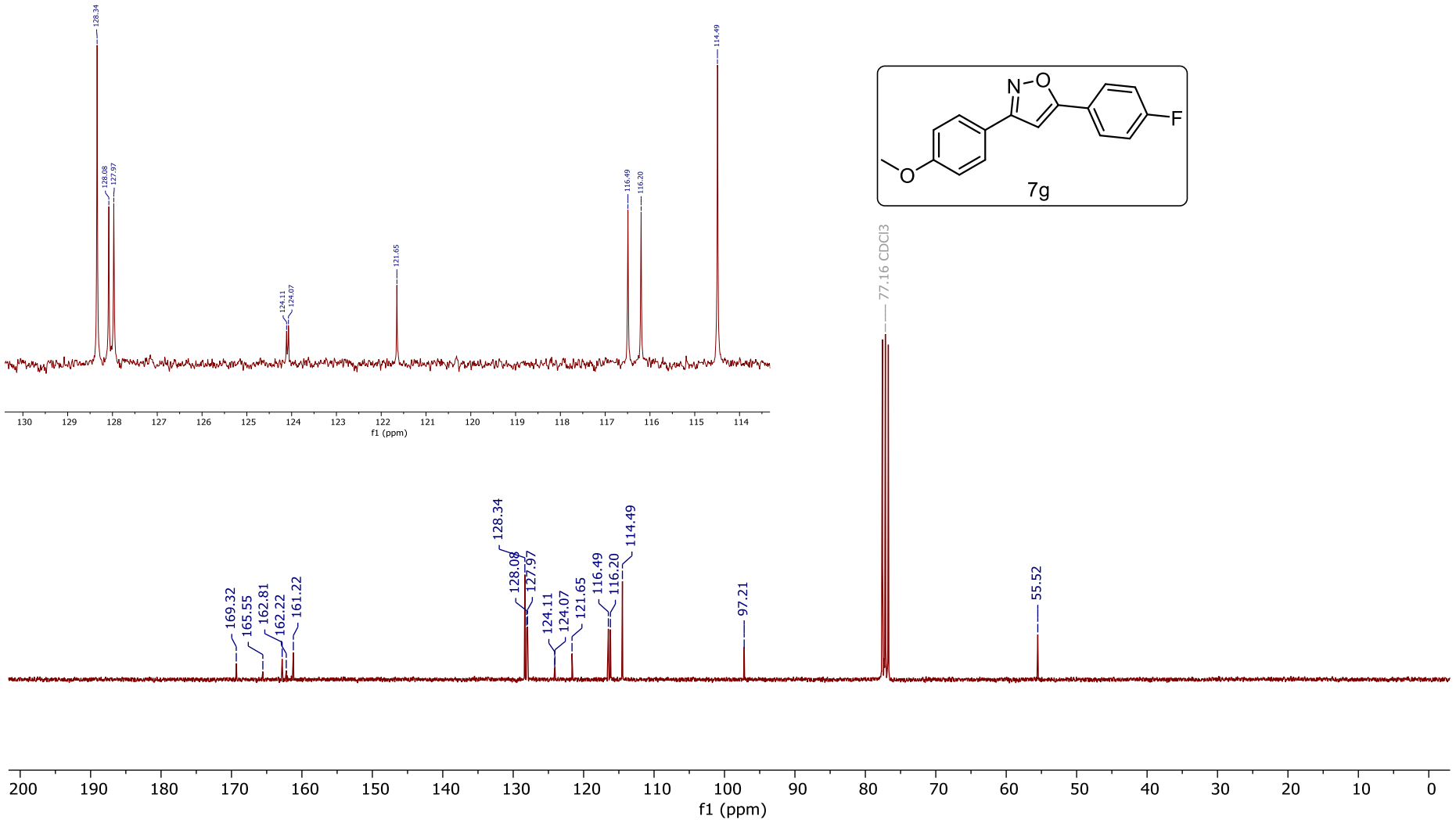

F
-109.43
-109.45
-109.46
-109.42
-109.40
-109.38
-109.48
1.00
-109.35
-109.40
-109.45
-109.50
-10
f1 (ppm)
N
O
F
7e
-109.38
-109.40
-109.42
-109.43
-109.45
-109.46
-109.48
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

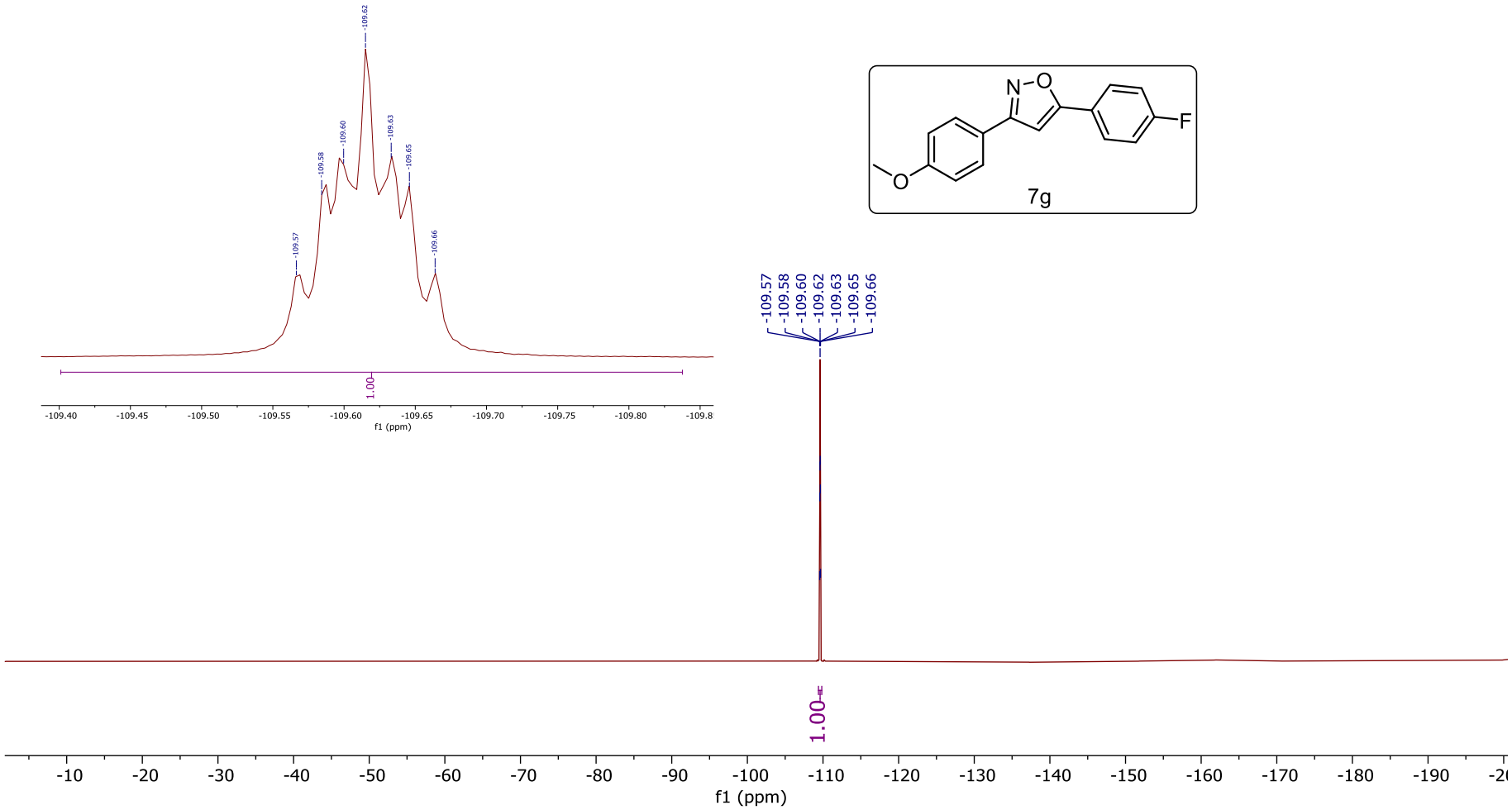

7f
F
N
O
7.26 CDCl3
6.81
3.21
1.56 H2O
4.00
2.00
2.00
1.00
1.00
f1 (ppm)

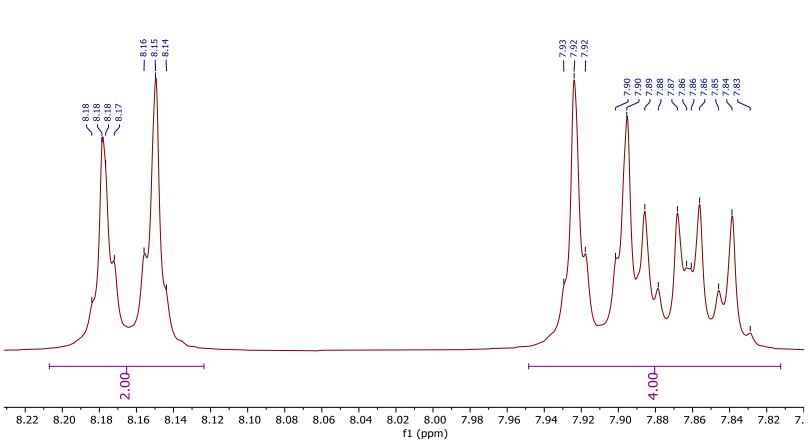

169.82
165.69
162.38
162.30
132.91
128.95
128.84
127.48
125.82
125.33
125.29
124.25
116.39
116.10
98.16
83.04
79.54
77.16 CDCl3
f1 (ppm)
N
O
F
7f

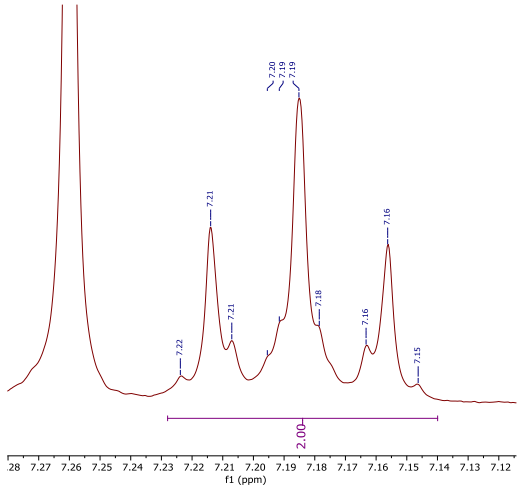

-110.33
-110.30
-110.31
-110.34
-110.36
-110.28
-110.38
1.00
-110.16
-110.20
-110.24
-110.28
-110.32
-110.36
-110.40
-110.44
-110.48
f1 (ppm)
N
O
F
7f
-110.28
-110.30
-110.31
-110.33
-110.34
-110.36
-110.38
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

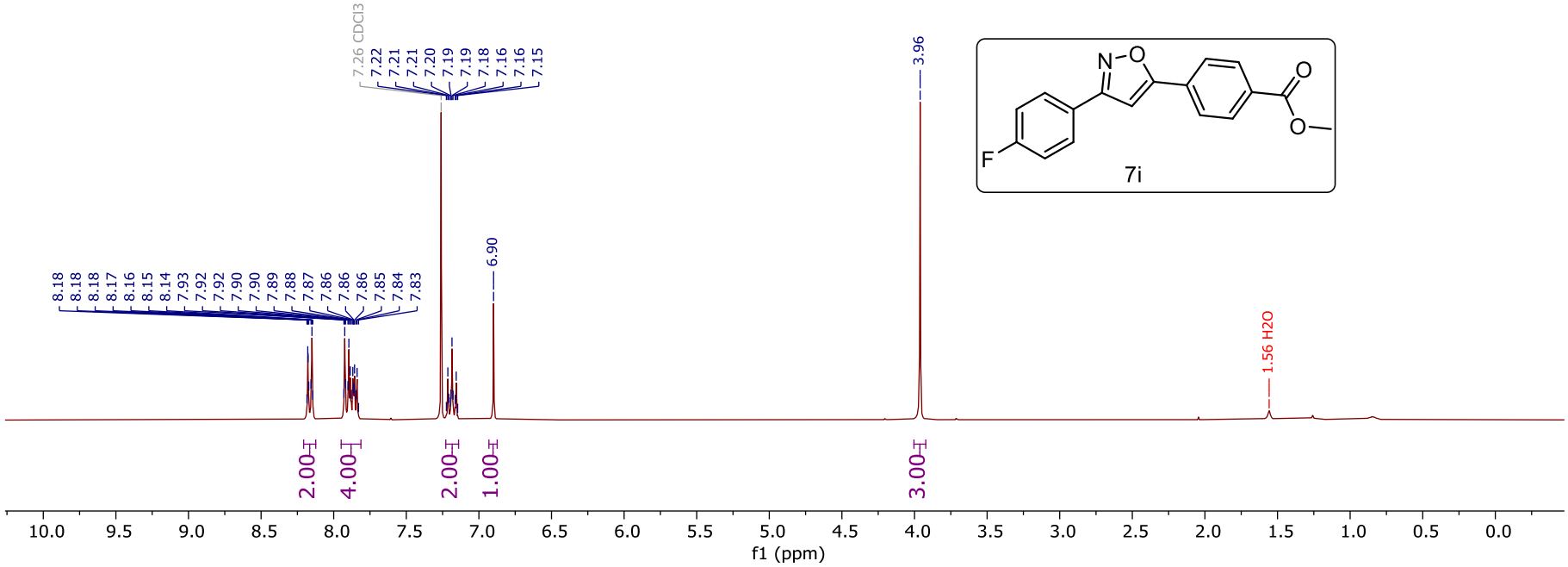

7.85
7.84
7.84
7.83
7.82
7.81
7.81
7.80
7.80
7.79
7.78
7.77
7.26 CDCl3
7.21
7.20
7.20
7.19
7.18
7.18
7.17
7.15
7.15
7.14
7.02
7.01
7.01
6.99
6.98
6.97
4.00
2.00
2.00
f1 (ppm)
N
O
F
O
7g
3.87
1.58 H2O
4.00
2.00
2.00
1.00
3.00


7g
77.16 CDCl3
169.32
165.55
162.81
162.22
161.22
128.34
128.08
127.97
124.11
124.07
121.65
116.49
116.20
114.49
97.21
55.52
f1 (ppm)

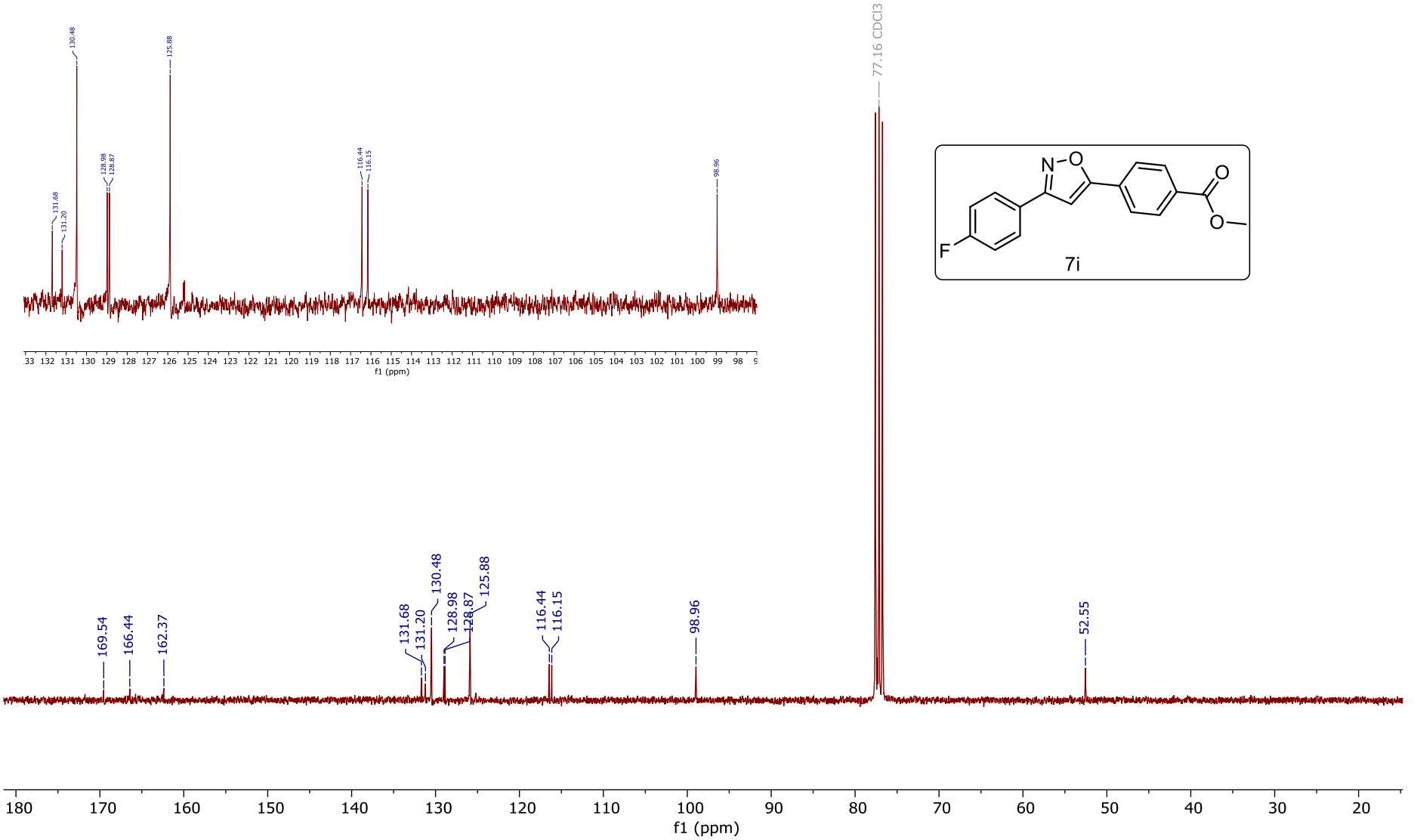

-109.57
-109.58
-109.60
-109.62
-109.63
-109.65
-109.66
1.00
-109.40
-109.45
-109.50
-109.55
-109.60
-109.65
-109.70
-109.75
-109.80
f1 (ppm)
N
O
F
O
7g
-109.57
-109.58
-109.60
-109.62
-109.63
-109.65
-109.66
1.00
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

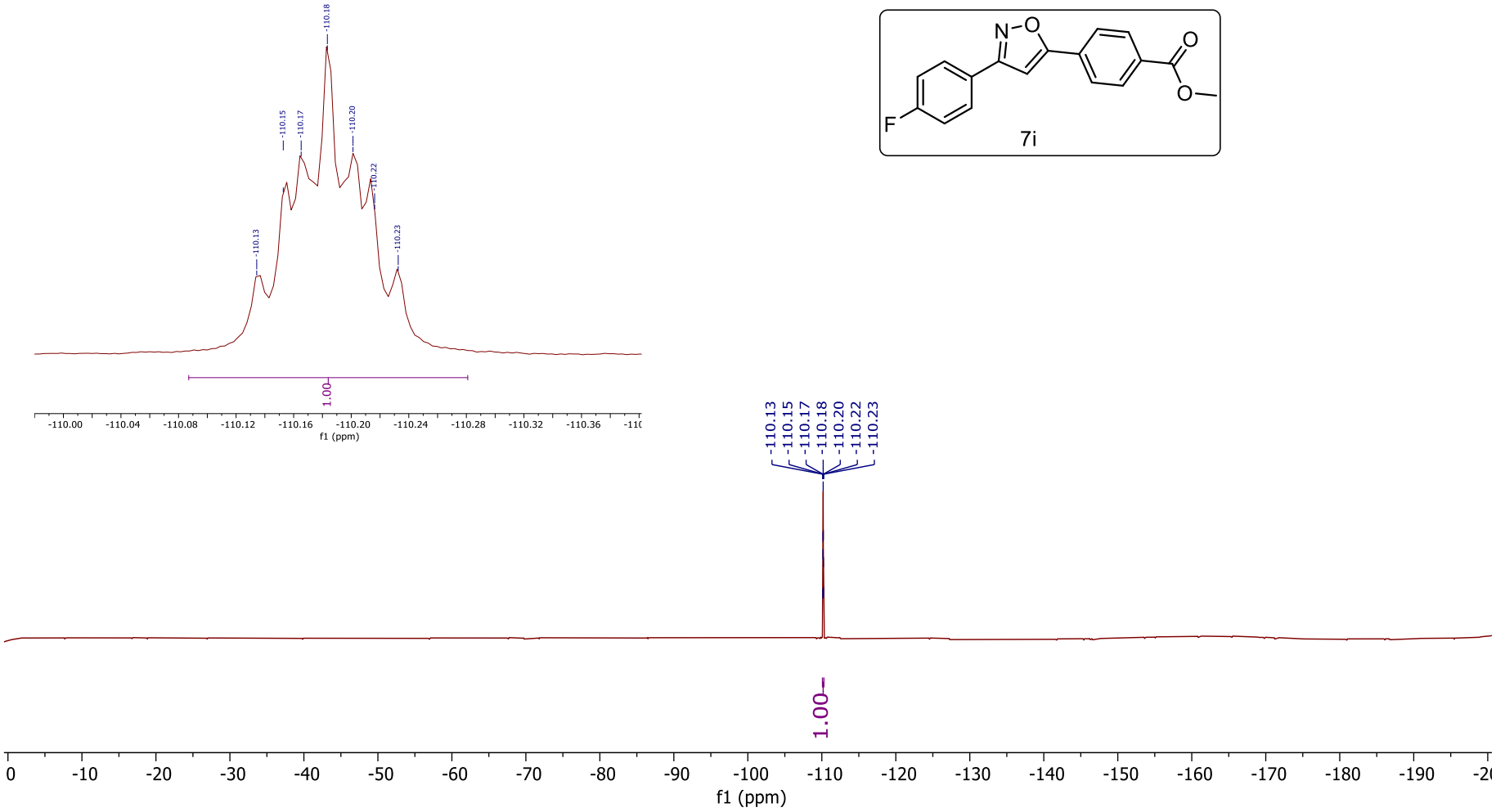

8.18
8.18
8.18
8.17
8.16
8.15
8.14
7.93
7.92
7.92
7.90
7.90
7.89
7.88
7.87
7.86
7.86
7.85
7.84
7.83
2.00
4.00
f1 (ppm)

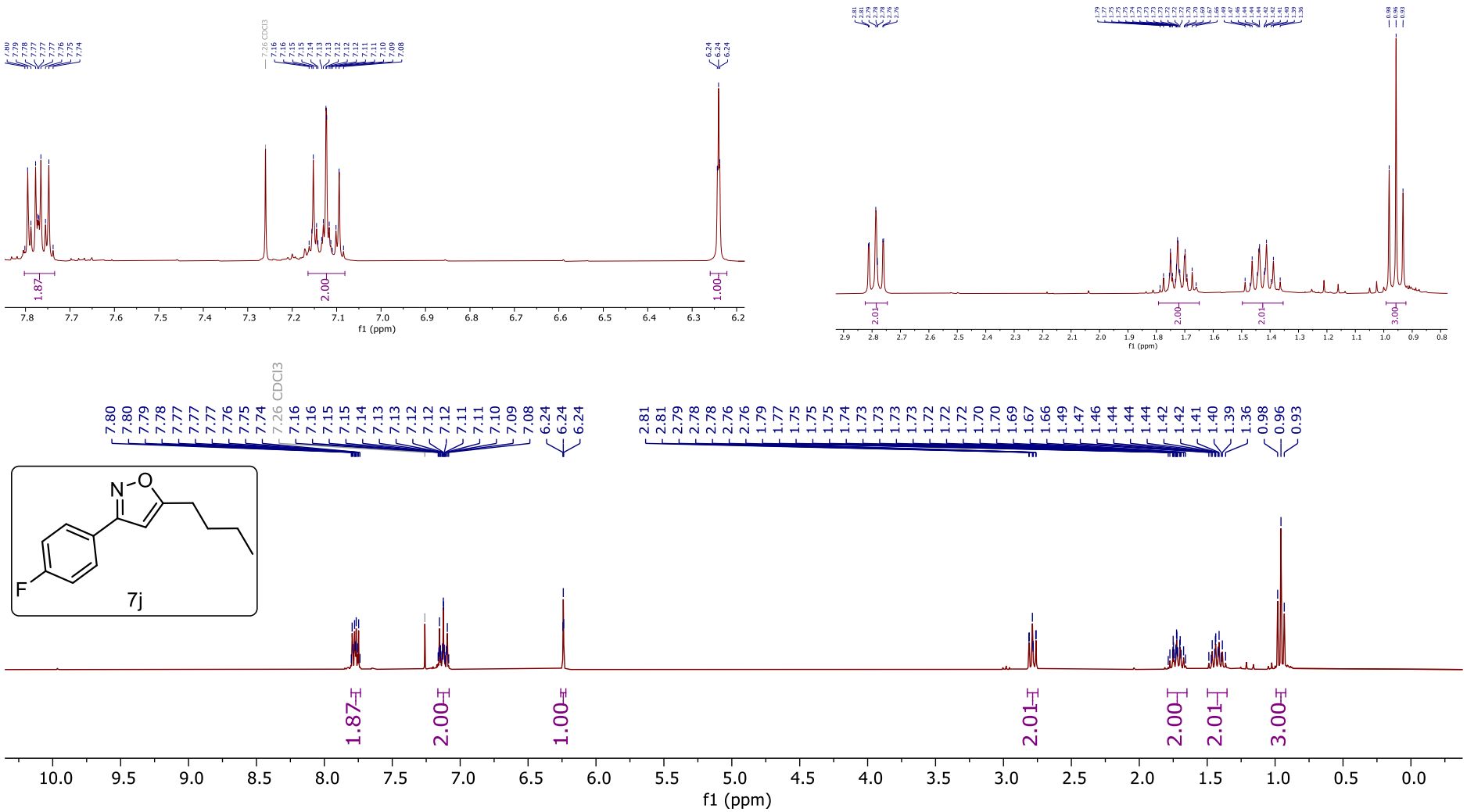

7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.16
7.16
7.15
2.00
f1 (ppm)

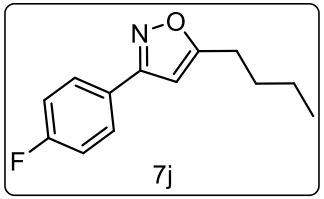

7.26 CDCl3
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.16
7.16
7.15
3.96
6.90
1.56 H2O
8.18
8.18
8.18
8.17
8.16
8.15
8.14
7.93
7.92
7.92
7.90
7.90
7.89
7.88
7.87
7.86
7.86
7.86
7.85
7.84
7.83
2.00
4.00
2.00
1.00
3.00
f1 (ppm)

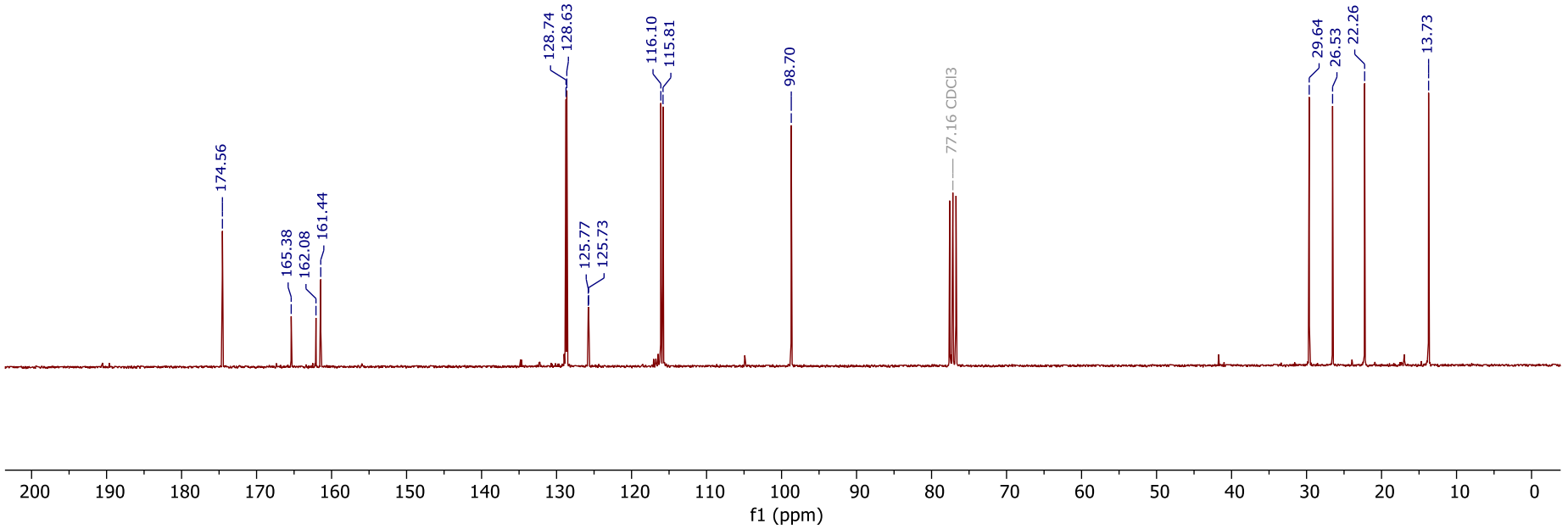
N
O
O
O
F
7i

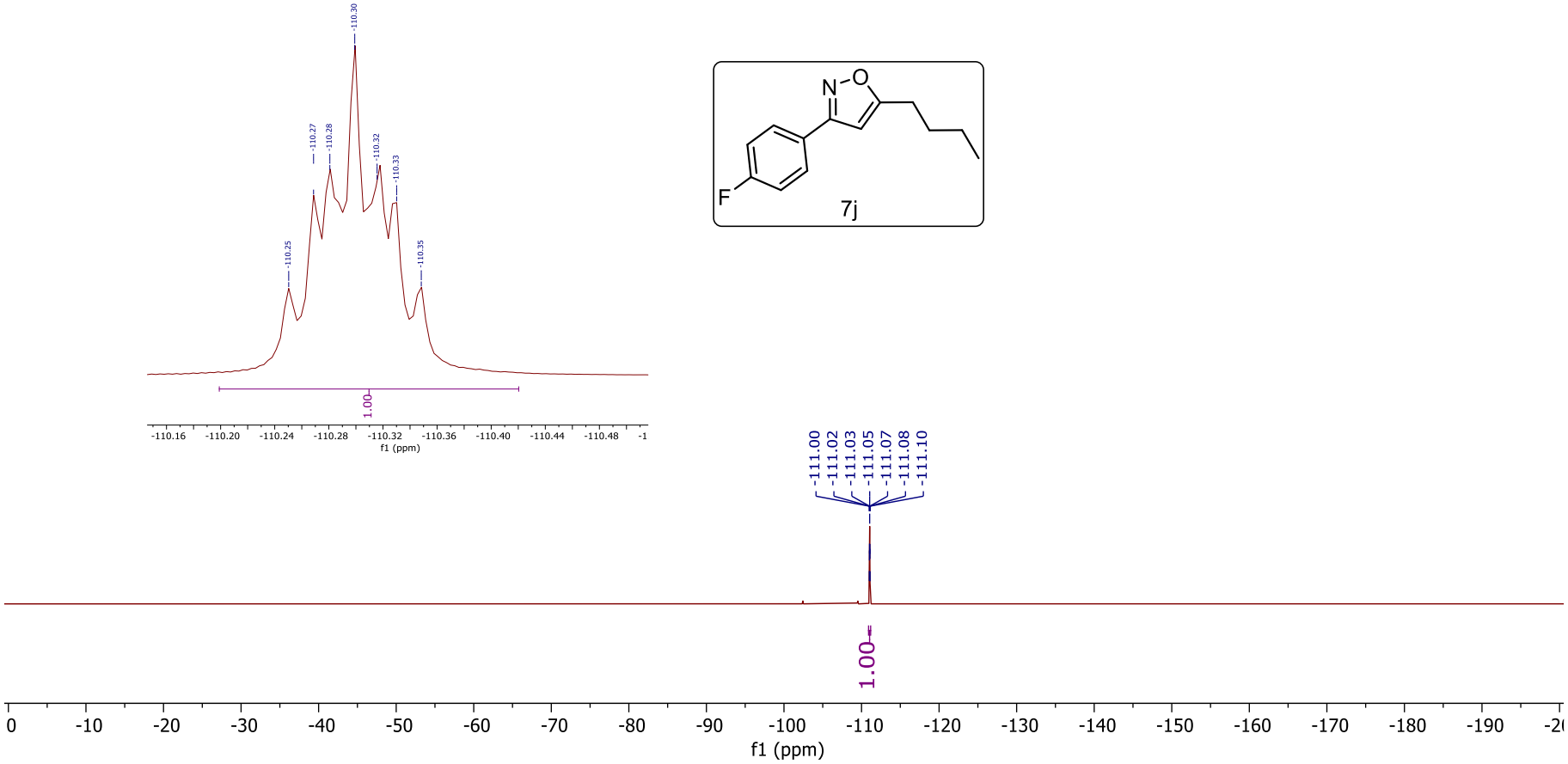

77.16 CDCl3
169.54
166.44
162.37
131.68
131.20
130.48
128.98
128.87
125.88
116.44
116.15
98.96
52.55
f1 (ppm)
7i

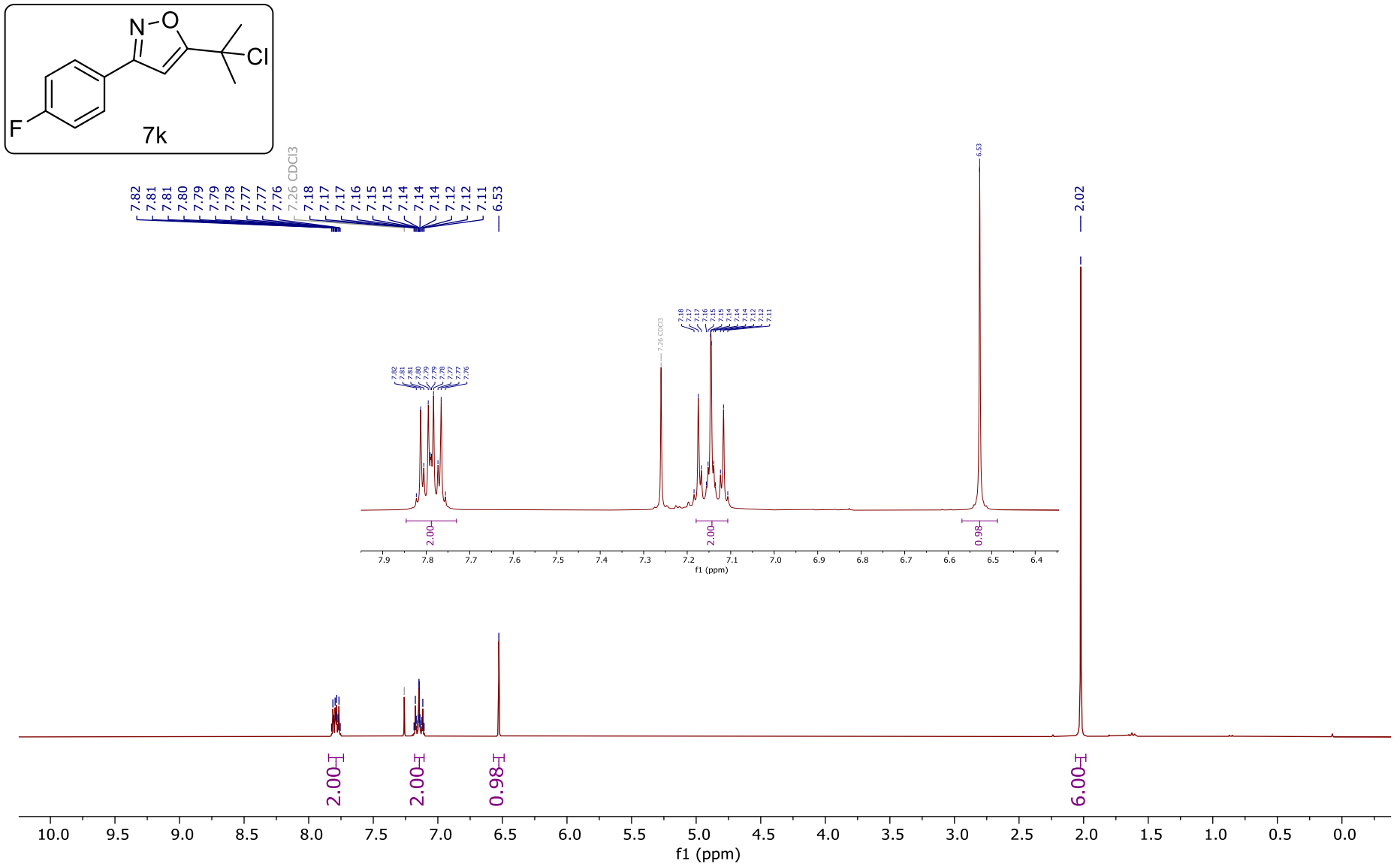

-110.13
-110.15
-110.17
-110.18
-110.20
-110.22
-110.23
1.00
-110.00 -110.04 -110.08 -110.12 -110.16 -110.20 -110.24 -110.28 -110.32 -110.36
f1 (ppm)
N
O
O
O
F
7i
-110.13
-110.15
-110.17
-110.18
-110.20
-110.22
-110.23
1.00
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

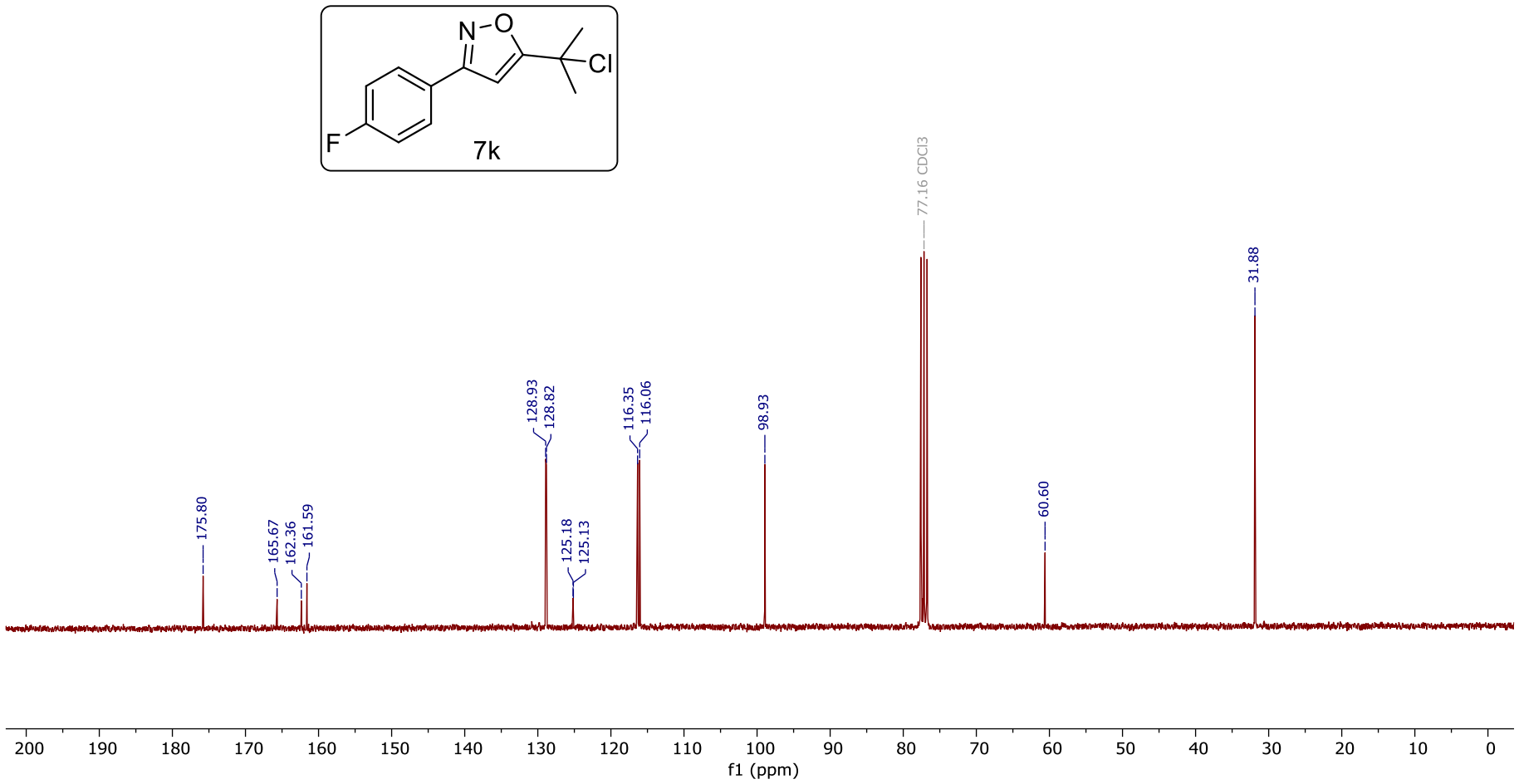

7.80 7.80 7.79 7.78 7.77 7.77 7.77 7.76 7.75 7.74
7.26 CDCl3
7.16 7.16 7.15 7.15 7.14 7.13 7.13 7.12 7.12 7.12 7.11 7.11 7.10 7.09 7.08
6.24 6.24 6.24
2.81 2.81 2.79 2.78 2.78 2.76 2.76 1.79 1.77 1.75 1.75 1.74 1.73 1.73 1.73 1.72 1.72 1.72 1.70 1.70 1.69 1.67 1.66 1.49 1.47 1.46 1.44 1.44 1.42 1.42 1.41 1.40 1.39 1.36 0.98 0.96 0.93
1.87 2.00 1.00 2.01 2.00 2.01 3.00
f1 (ppm)
N O F
7j

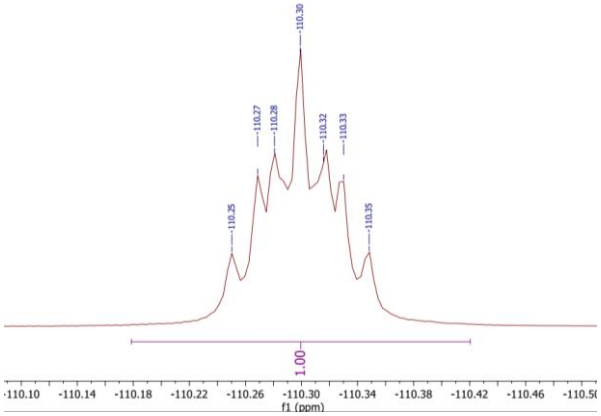

N
O
F
7j

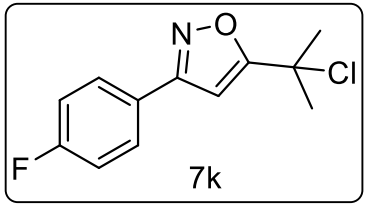

174.56
165.38
162.08
161.44
128.74
128.63
125.77
125.73
116.10
115.81
98.70
77.16 CDCl3
29.64
26.53
22.26
13.73
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

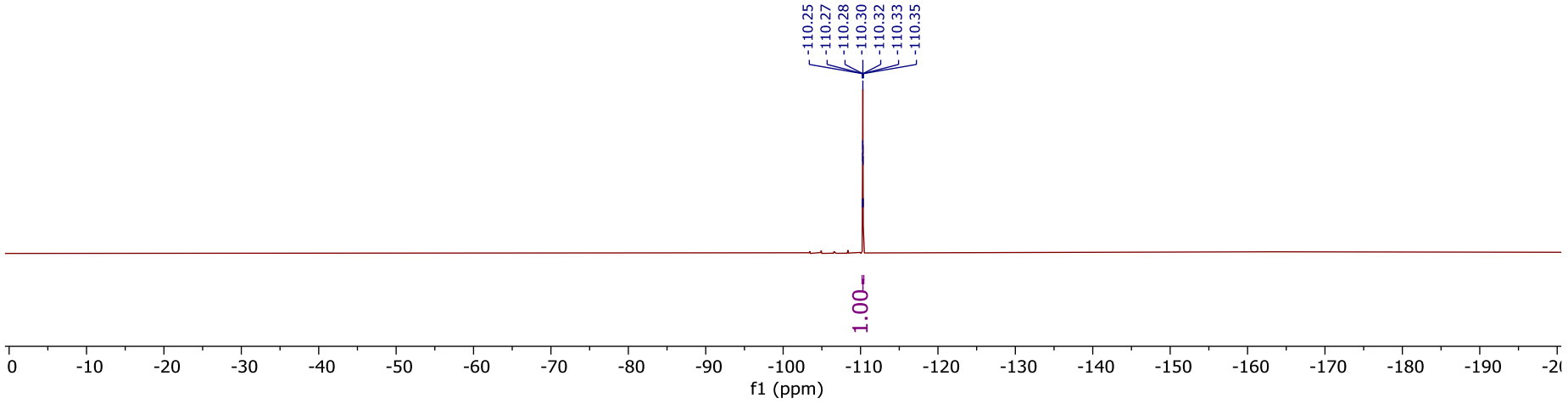

-110.25
-110.27
-110.28
-110.30
-110.32
-110.33
-110.35
1.00
-110.16
-110.20
-110.24
-110.28
-110.32
-110.36
-110.40
-110.44
-110.48
f1 (ppm)
N
O
F
7j
-111.00
-111.02
-111.03
-111.05
-111.07
-111.08
-111.10
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

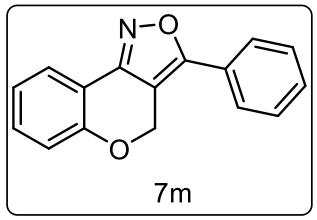

N
O
Cl
F
7k
7.26 CDCl3
6.53
2.02
2.00
2.00
0.98
6.00
f1 (ppm)


N
O
Cl
F
7k
175.80
165.67
162.36
161.59
128.93
128.82
125.18
125.13
116.35
116.06
98.93
77.16 CDCl3
60.60
31.88
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

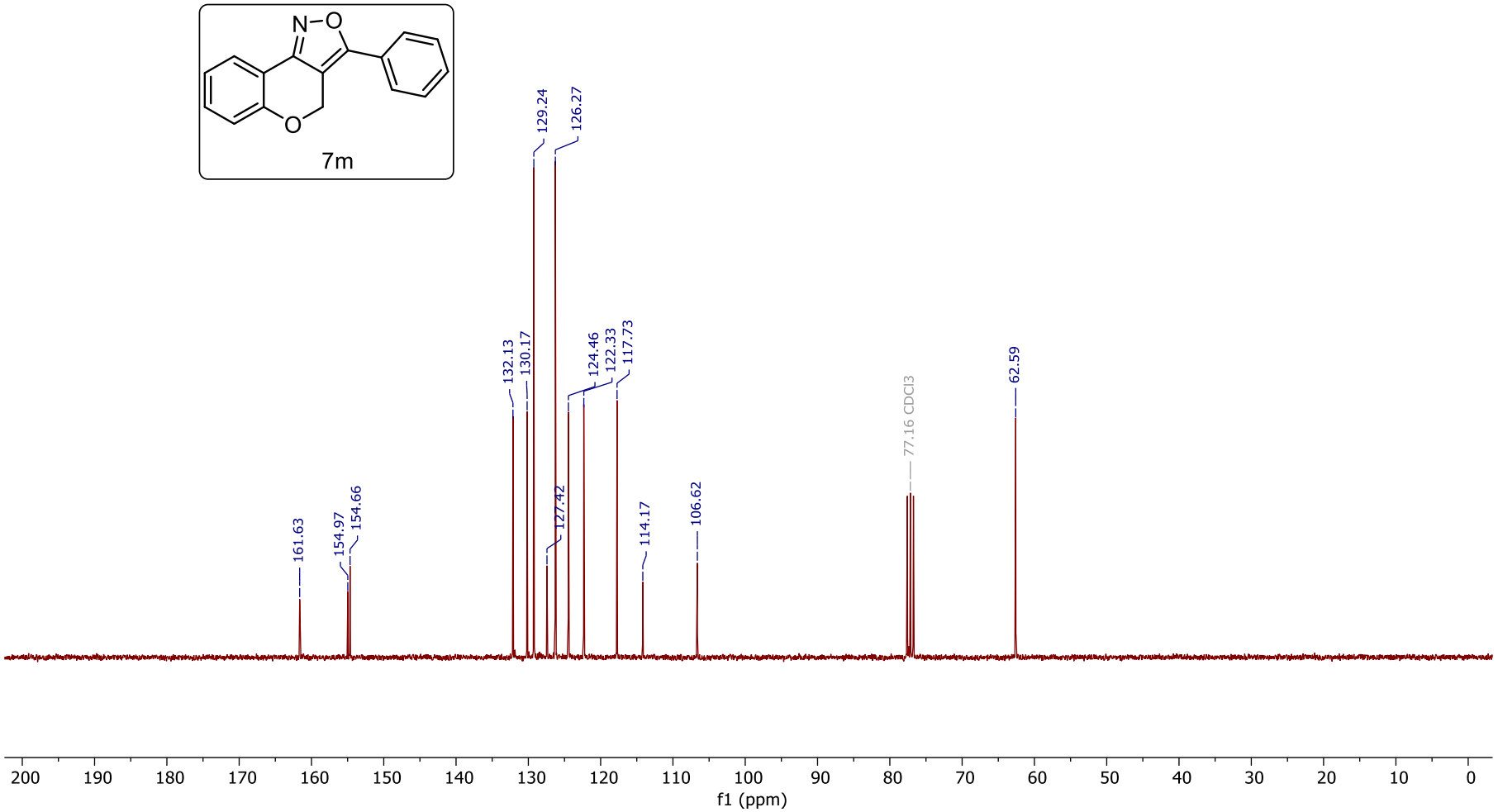

-110.25
-110.27
-110.28
-110.30
-110.32
-110.33
-110.35
1.00
-110.10
-110.14
-110.18
-110.22
-110.26
-110.30
-110.34
-110.38
-110.42
-110.46
f1 (ppm)

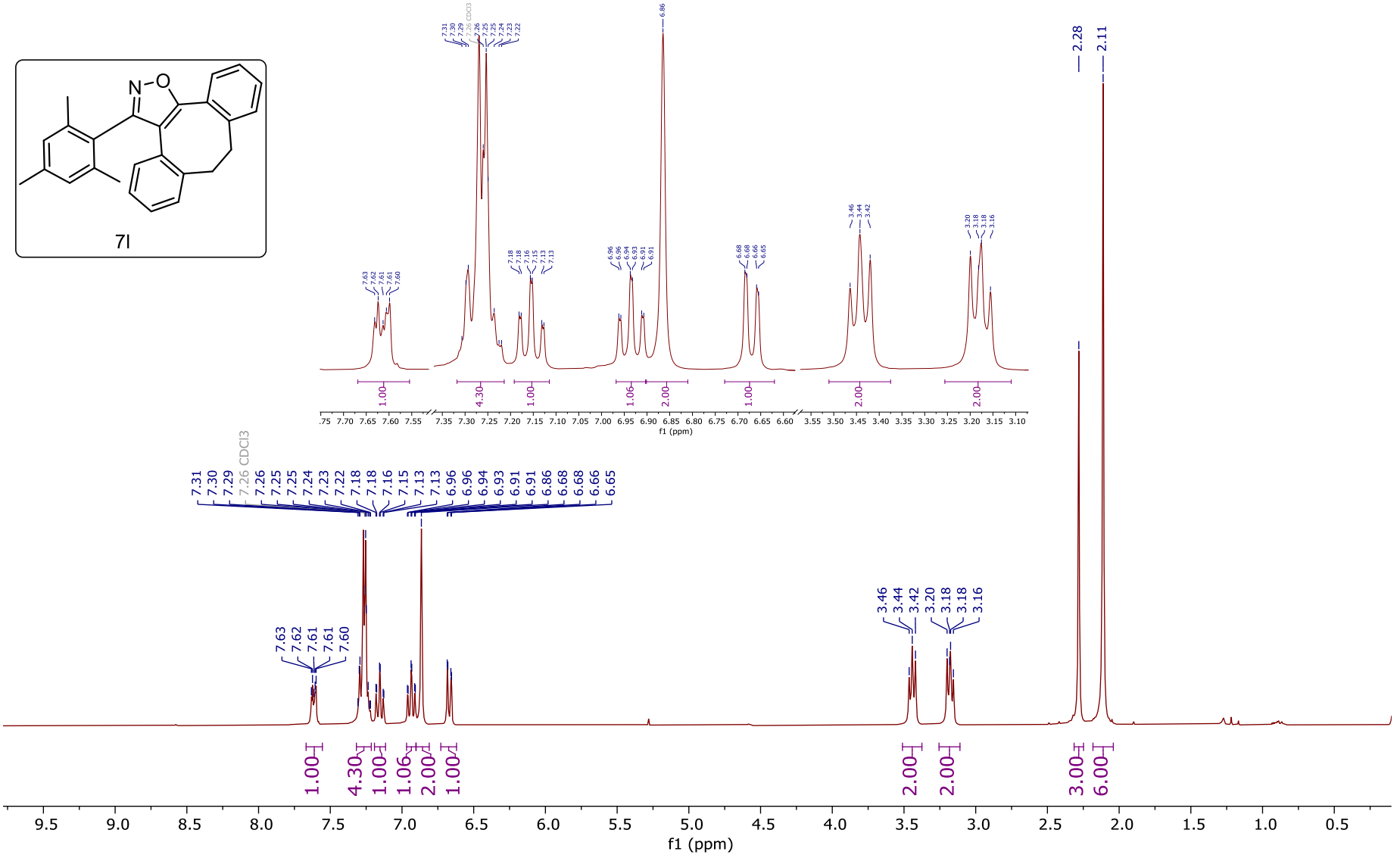

N
O
Cl
F
7k

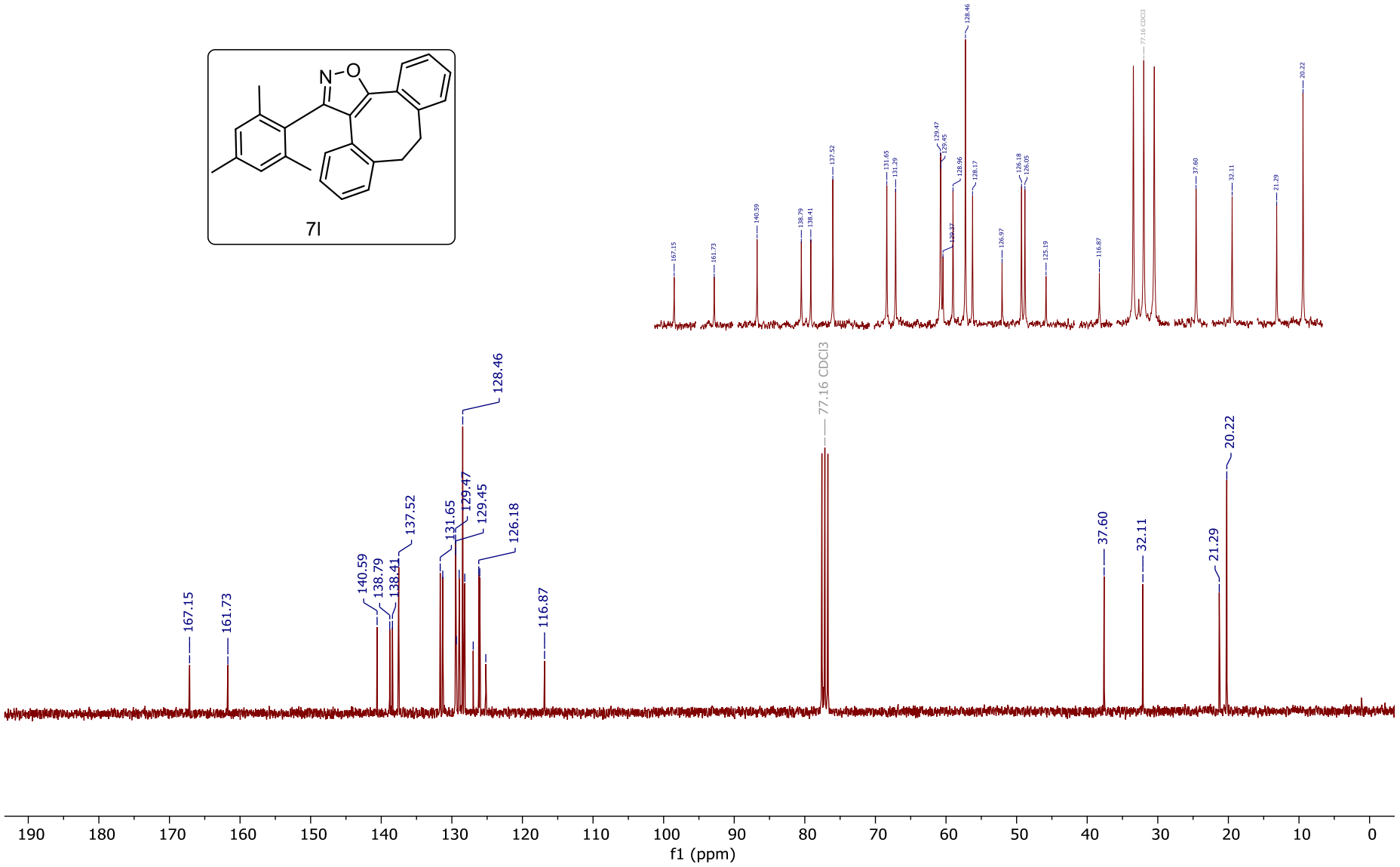

-110.25
-110.27
-110.28
-110.30
-110.32
-110.33
-110.35
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

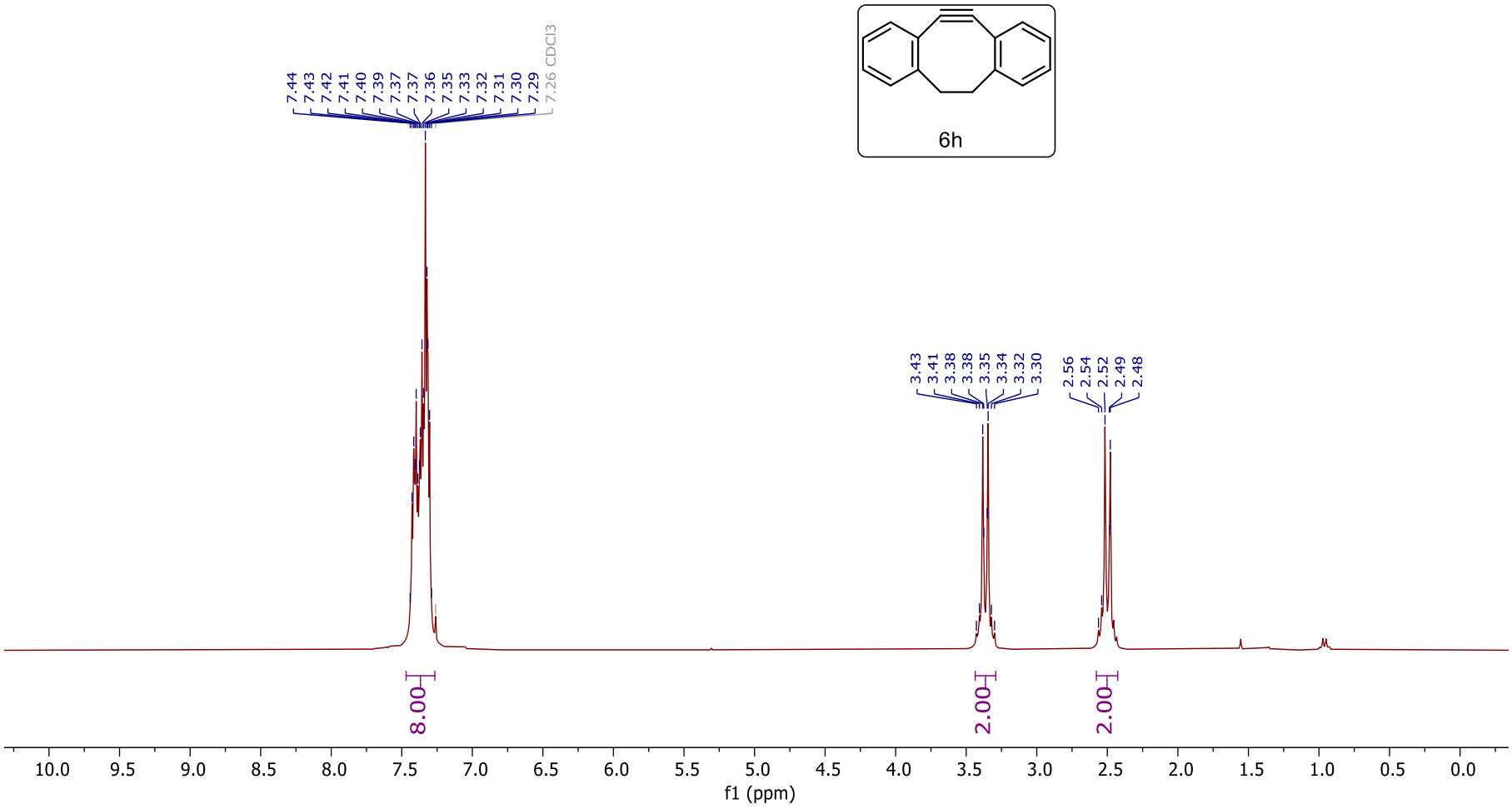

N
O
O
7m

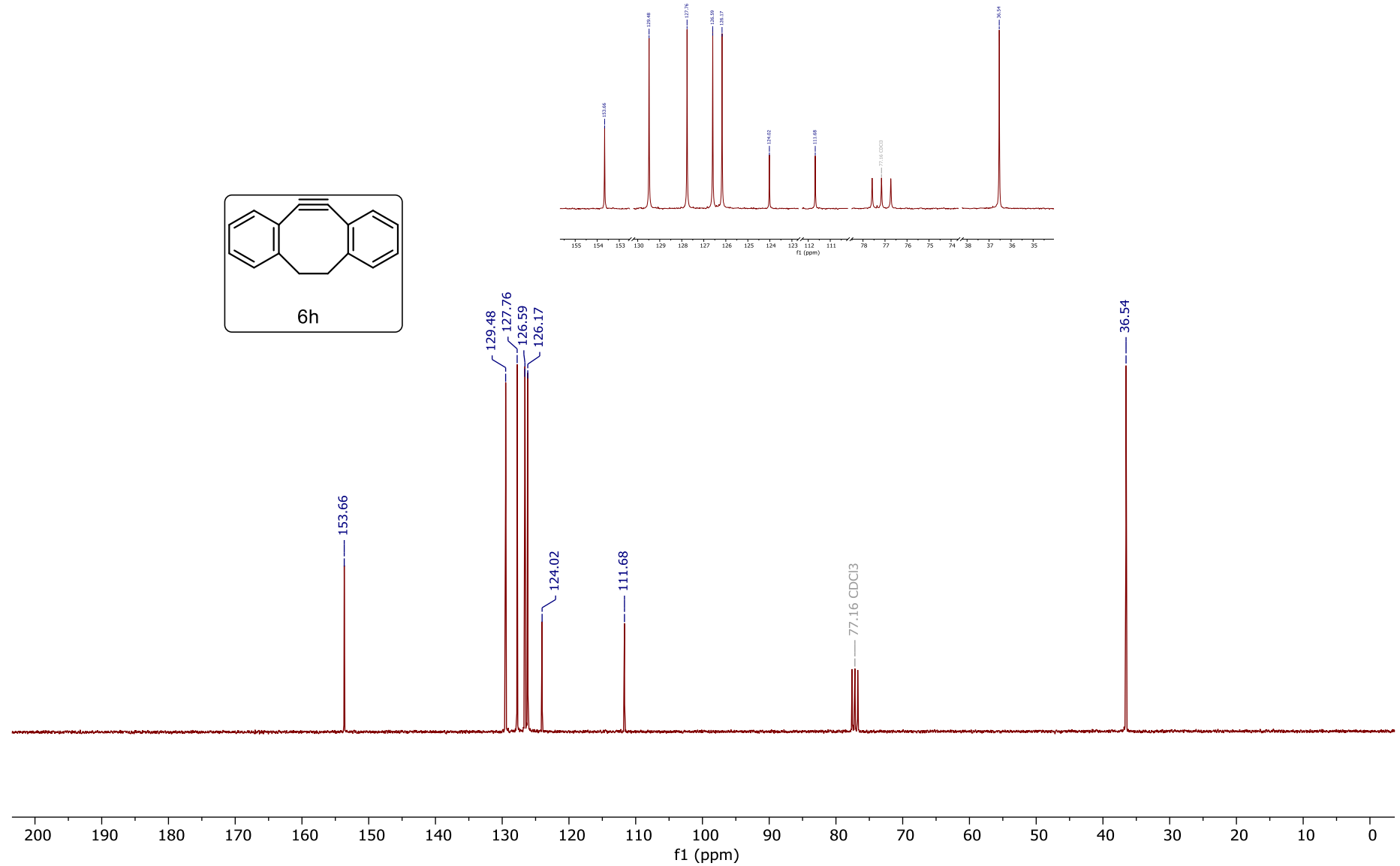
5.42
7.26 CDCl3
1.00
2.00
3.00
1.00
2.00
2.00
f1 (ppm)

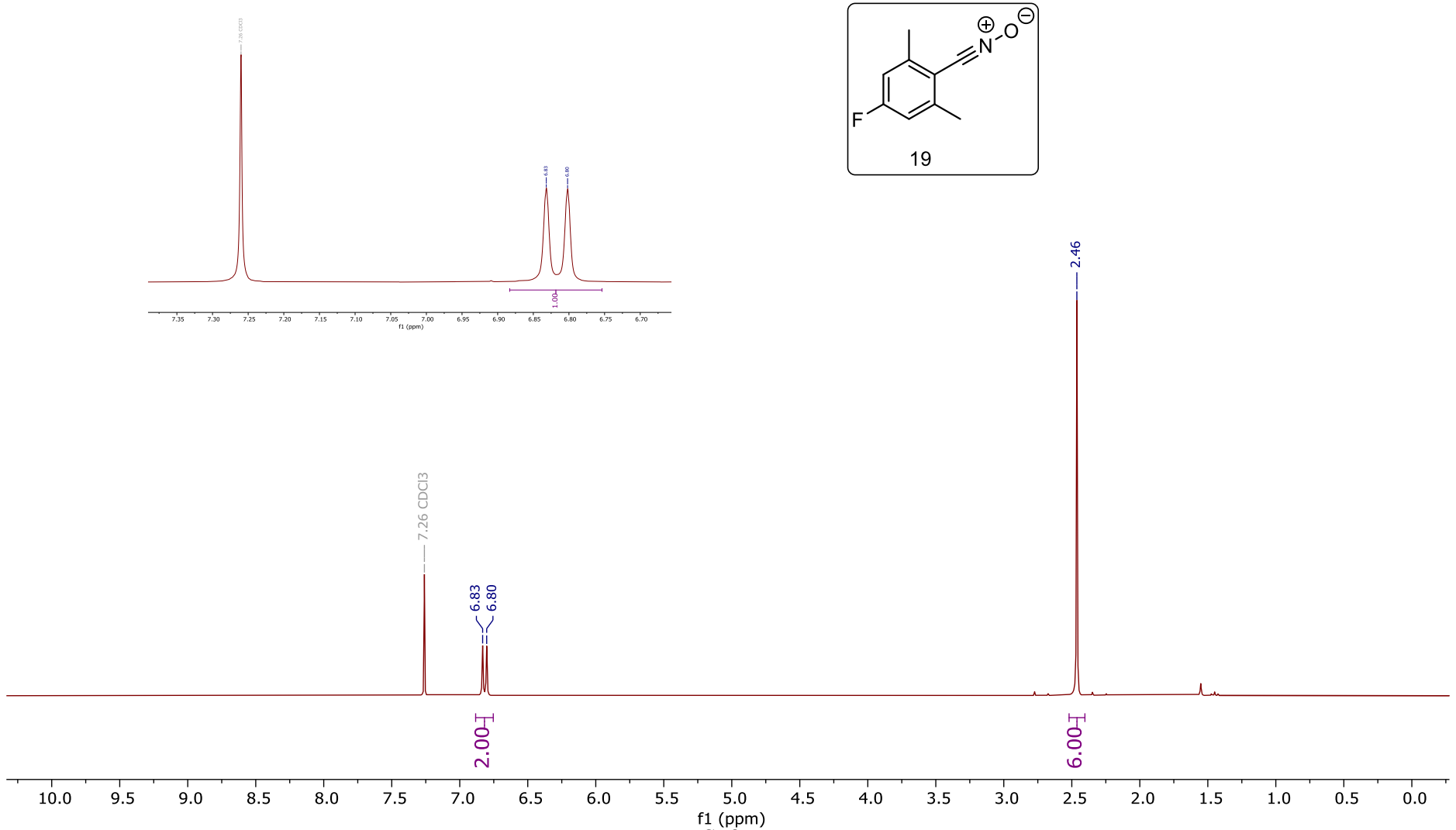

7m
161.63
154.97
154.66
132.13
130.17
129.24
127.42
126.27
124.46
122.33
117.73
114.17
106.62
77.16 CDCl3
62.59
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

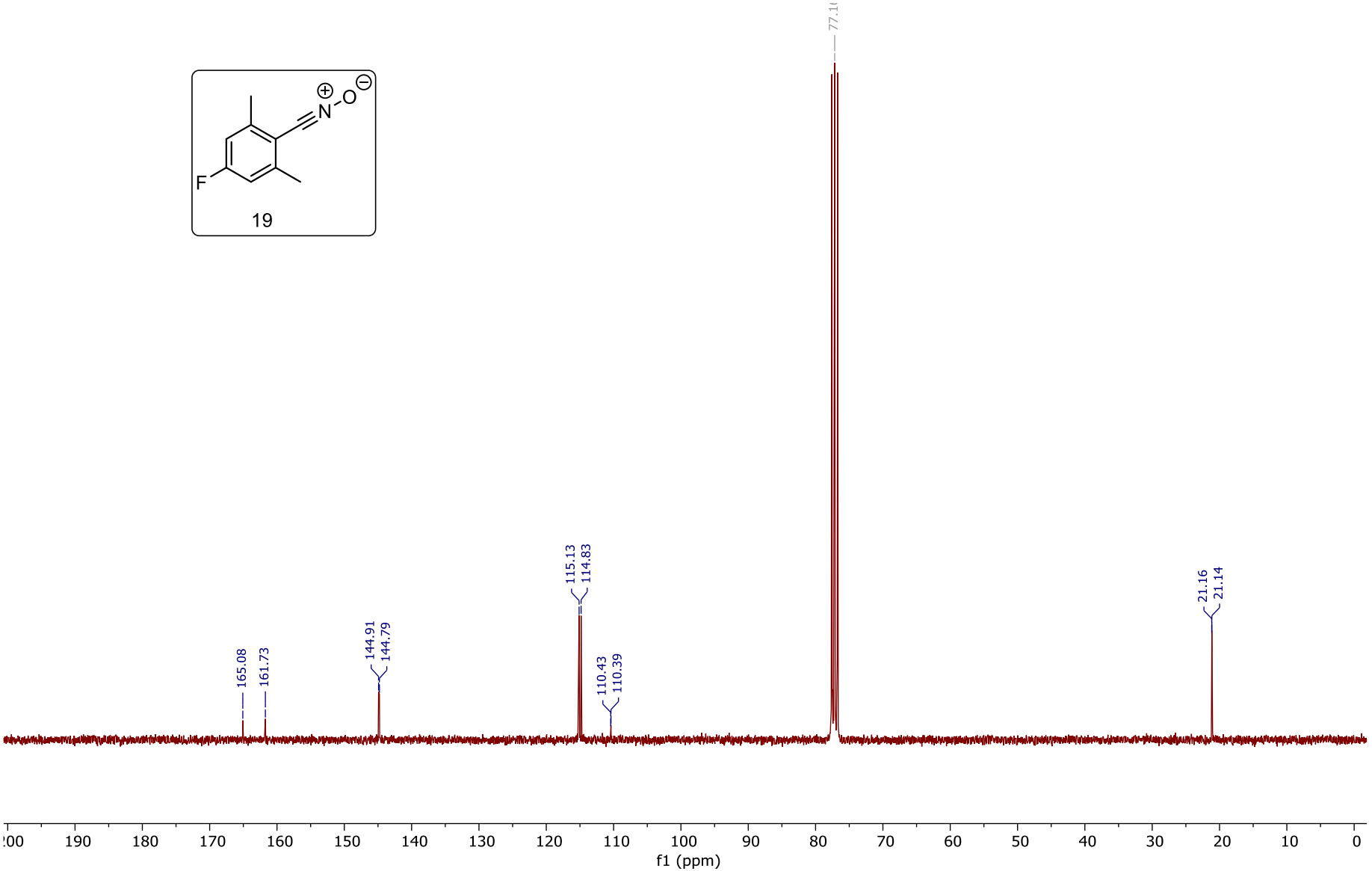

7l
f1 (ppm)

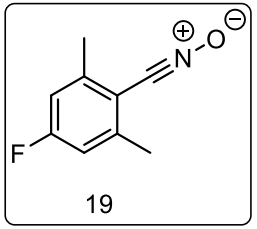

7l
167.15
161.73
140.59
138.79
138.41
137.52
131.65
129.47
129.45
128.46
126.18
116.87
77.16 CDCl3
37.60
32.11
21.29
20.22
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

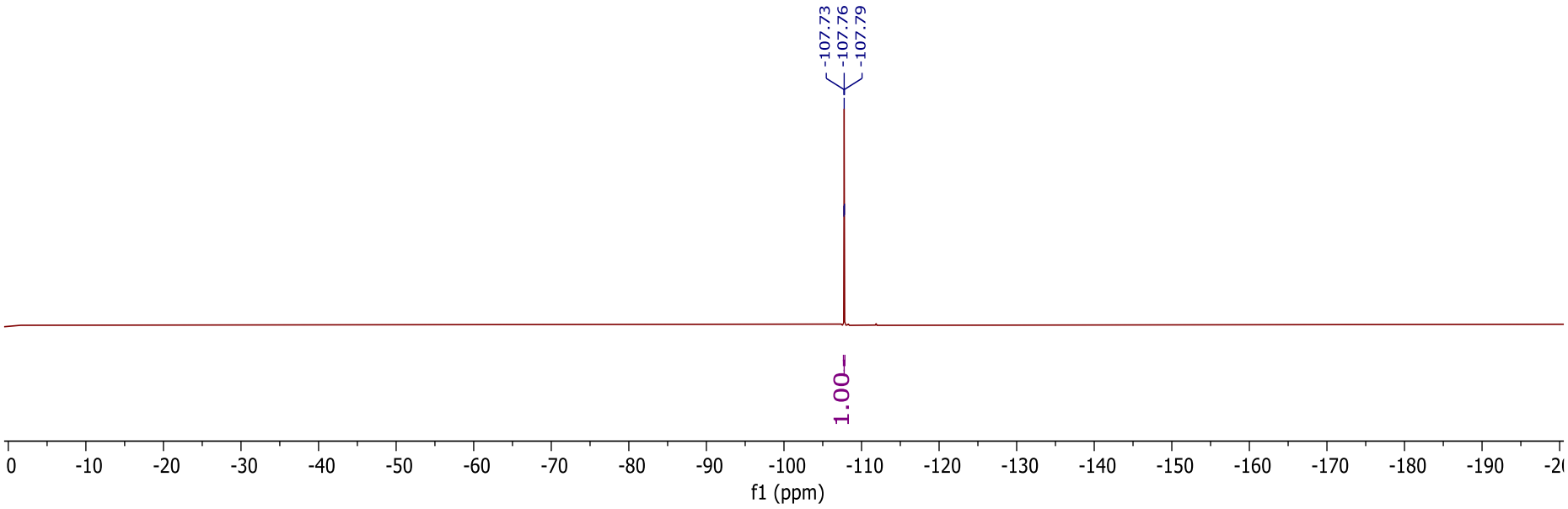

7.44
7.43
7.42
7.41
7.40
7.39
7.37
7.37
7.36
7.35
7.33
7.32
7.31
7.30
7.29
7.26 CDCl3
3.43
3.41
3.38
3.38
3.35
3.34
3.32
3.30
2.56
2.54
2.52
2.49
2.48
6h
8.00
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


6h
153.66
129.48
127.76
126.59
126.17
124.02
111.68
77.16 CDCl3
36.54
f1 (ppm)


F
19
2.46
7.26 CDCl3
6.83
6.80
2.00
6.00
f1 (ppm)


F
19
165.08
161.73
144.91
144.79
115.13
114.83
110.43
110.39
21.16
21.14
f1 (ppm)


F
19


-107.73
-107.76
-107.79
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

10. GCMS and HRMS of the intermediates:

1,4-dimethylnaphthalene trap experiment:

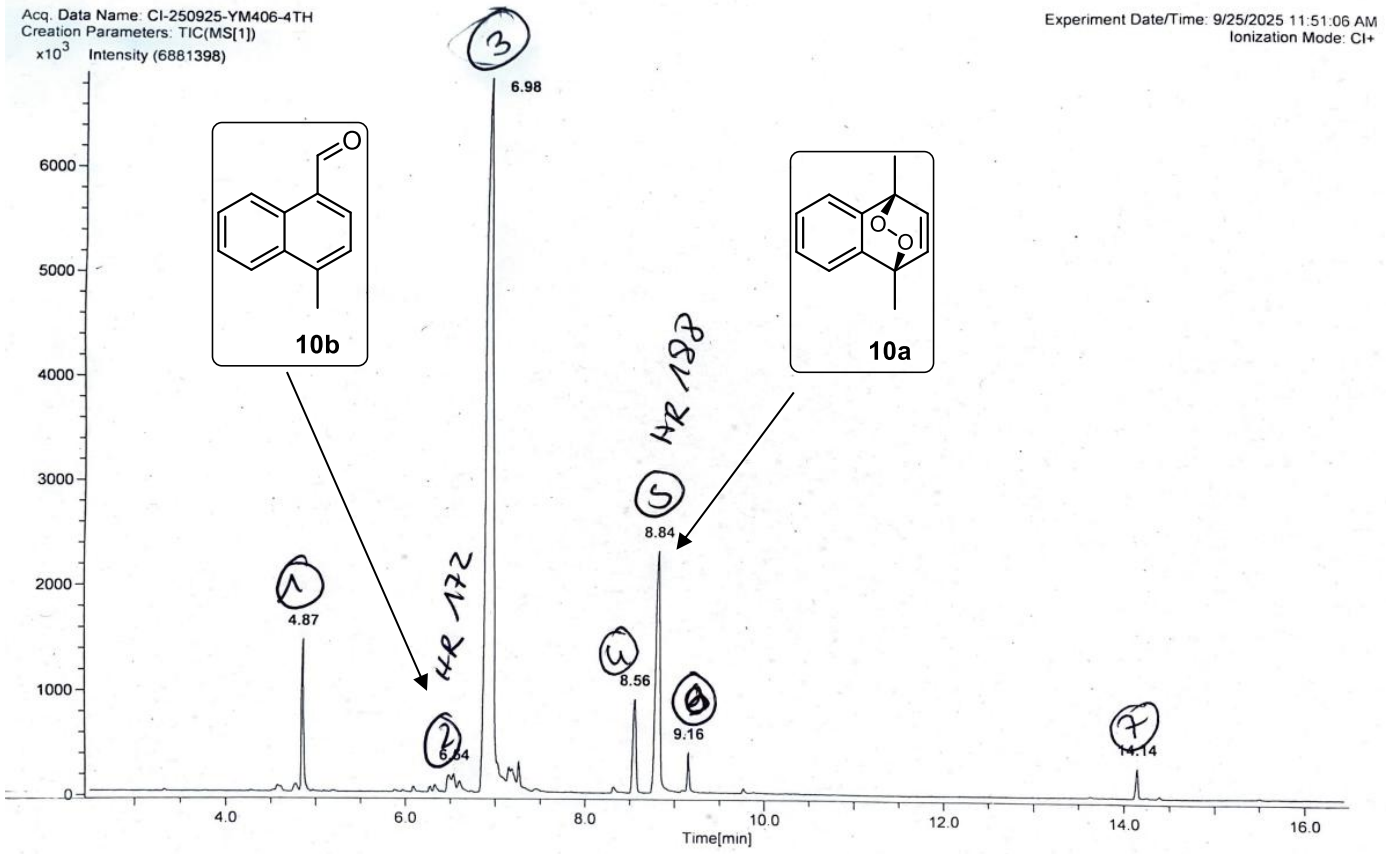
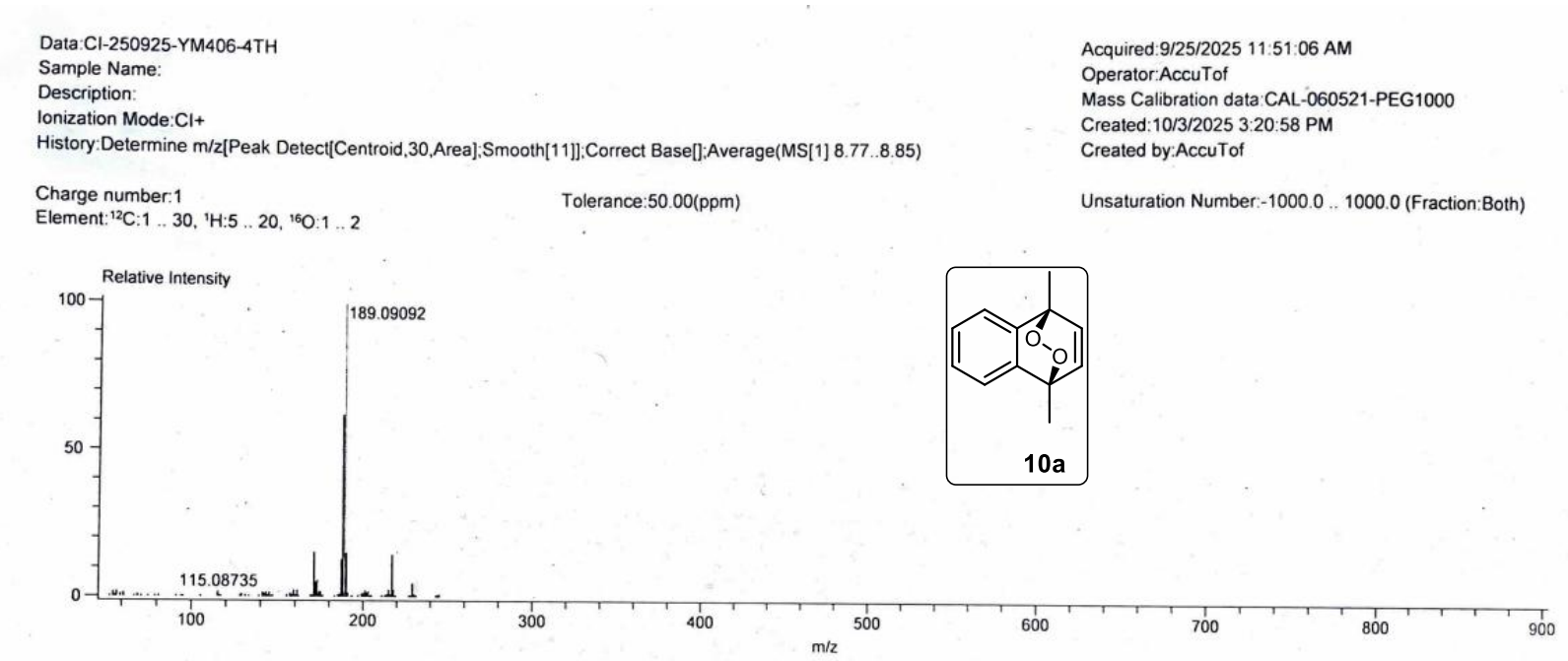
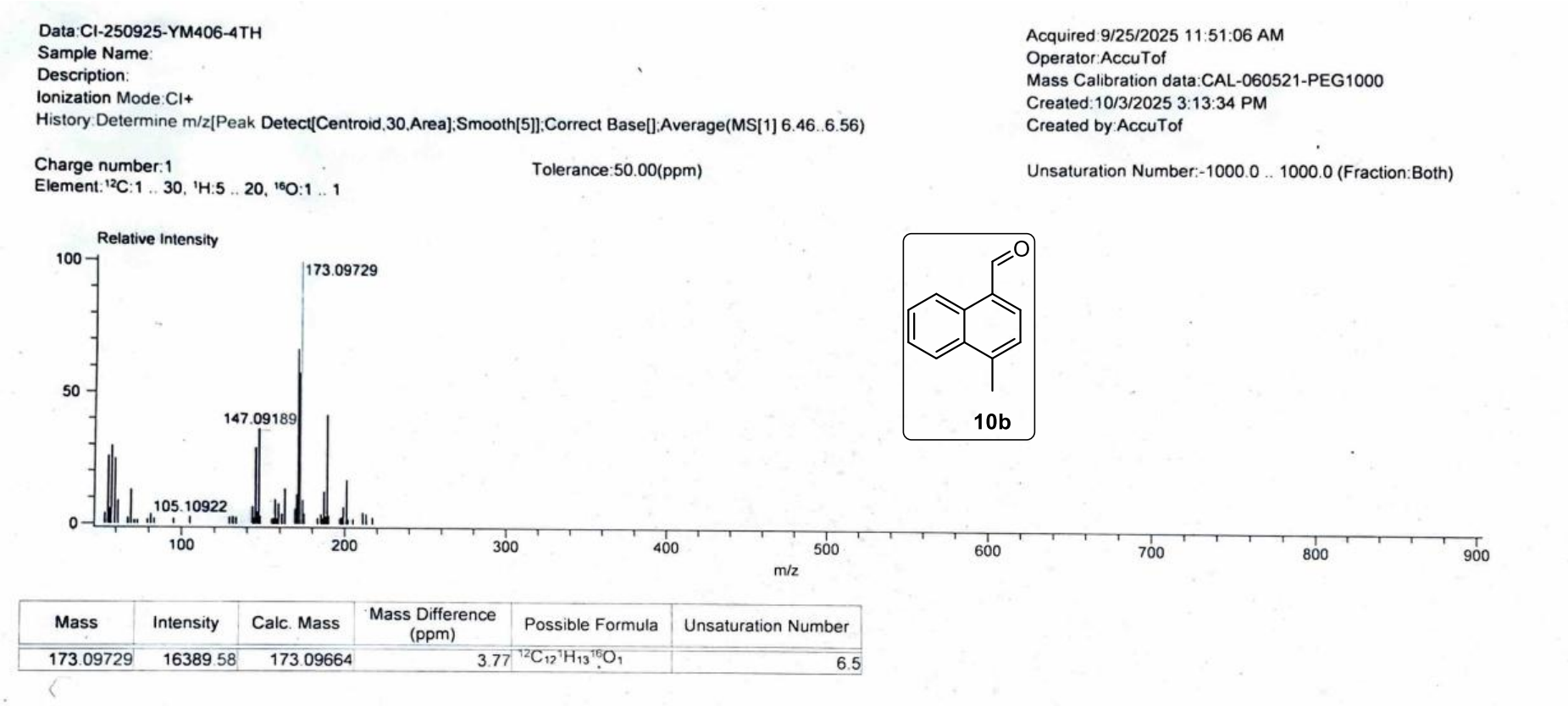


Figure ESI-17. GC-MS with (CI^+) mode of 1,4-dimethylnaphthalene trap experiment.



Mass	Intensity	Calc. Mass	Mass Difference (ppm)	Possible Formula	Unsaturation Number
189.09092	289337.95	189.09155	-3.33	$^{12}C_{12}{}^{1}H_{13}{}^{16}O_2$	6.5

Figure ESI-18: HRMS with (CI^+) mode of product (**10a**) of 1,4-dimethylnaphthalene trap experiment.



Mass	Intensity	Calc. Mass	Mass Difference (ppm)	Possible Formula	Unsaturation Number
173.09729	16389.58	173.09664	3.77	$^{12}C_{12}{}^{1}H_{13}{}^{16}O_1$	6.5

Figure ESI-19. HRMS with (CI^+) mode of product (**10b**) of 1,4-dimethylnaphthalene trap experiment.

(4-fluoro-3-methylphenyl)Boronic acid trap experiment (11):

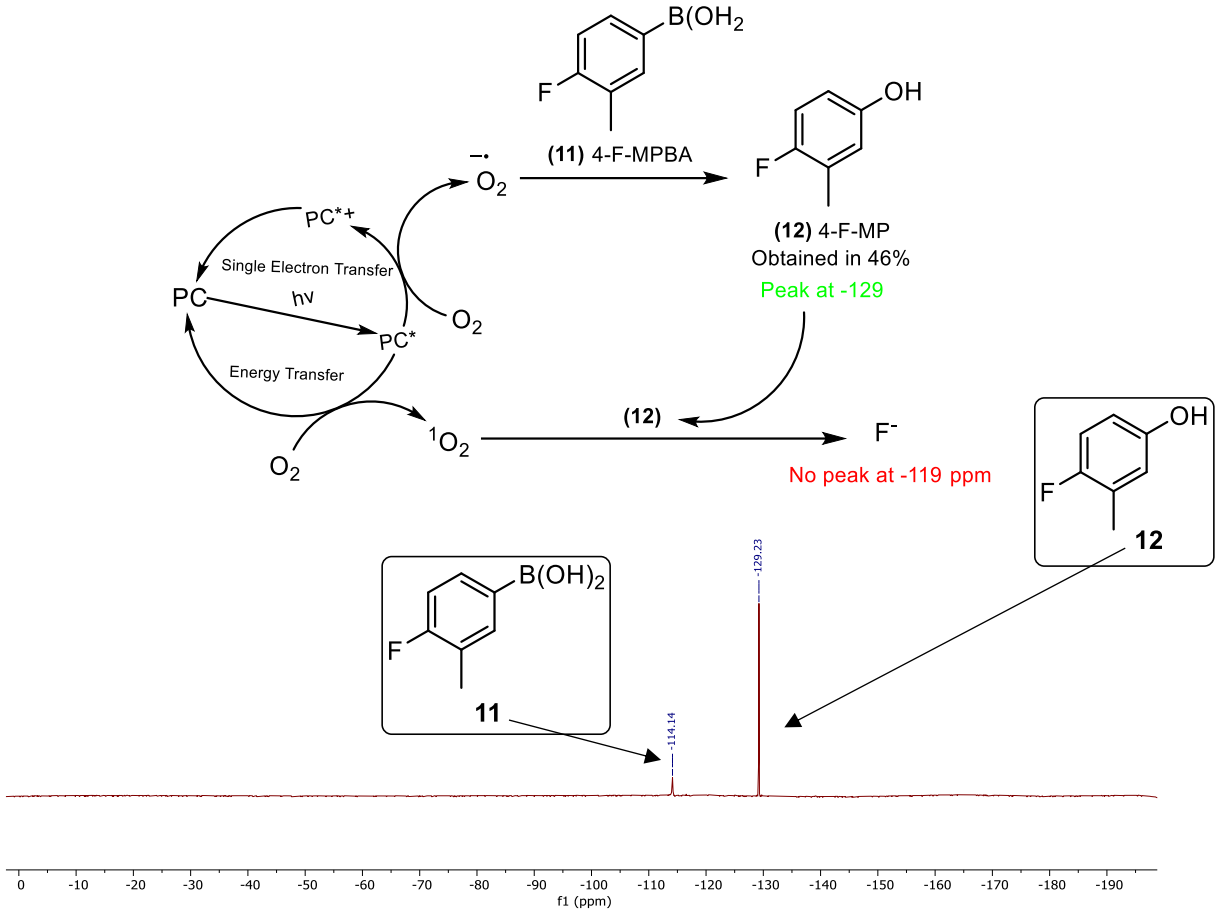
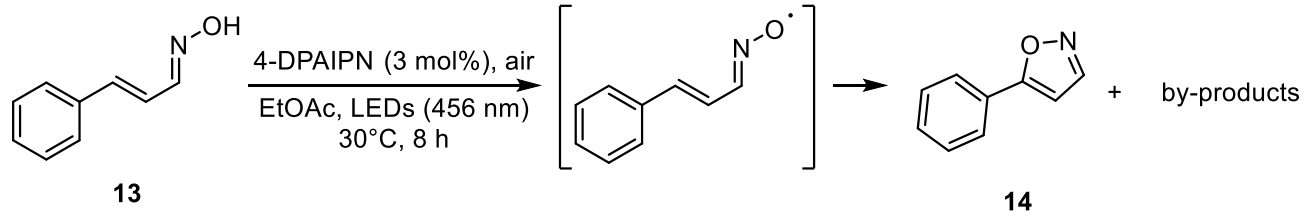


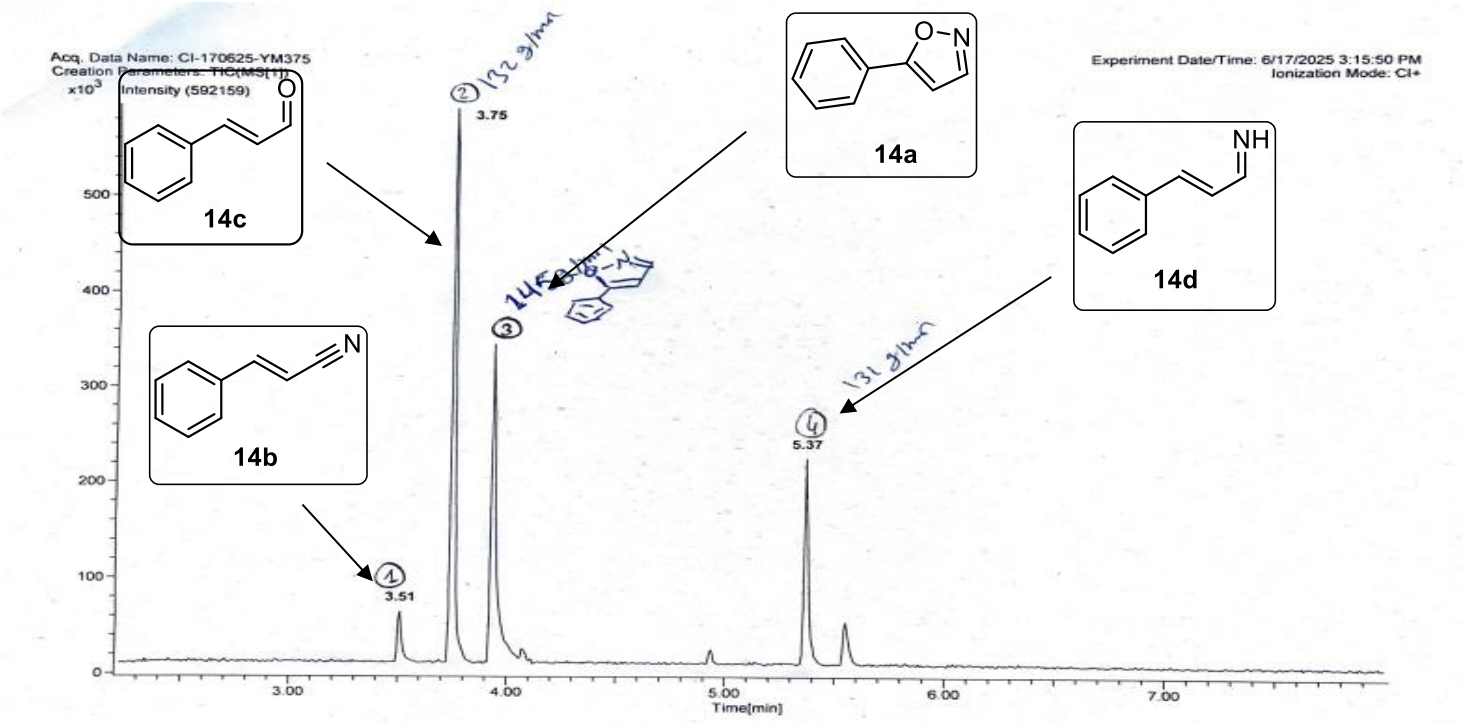
Figure ESI-20: ^{19}F-NMR of the Crude product of (4-fluoro-3-methylphenyl)Boronic acid trap **(11)**, (1.0 mmol) in EtOAc (0.1 M) with 4-DPAIPN (3 mol%).

Iminoxyl radical trap experiment of 5-phenylisoxazole (14):



13 14

Figure ESI-21. GC-MS with (CI^+) mode $[M+H]^+$ of 5-phenylisoxazole Intermediate.



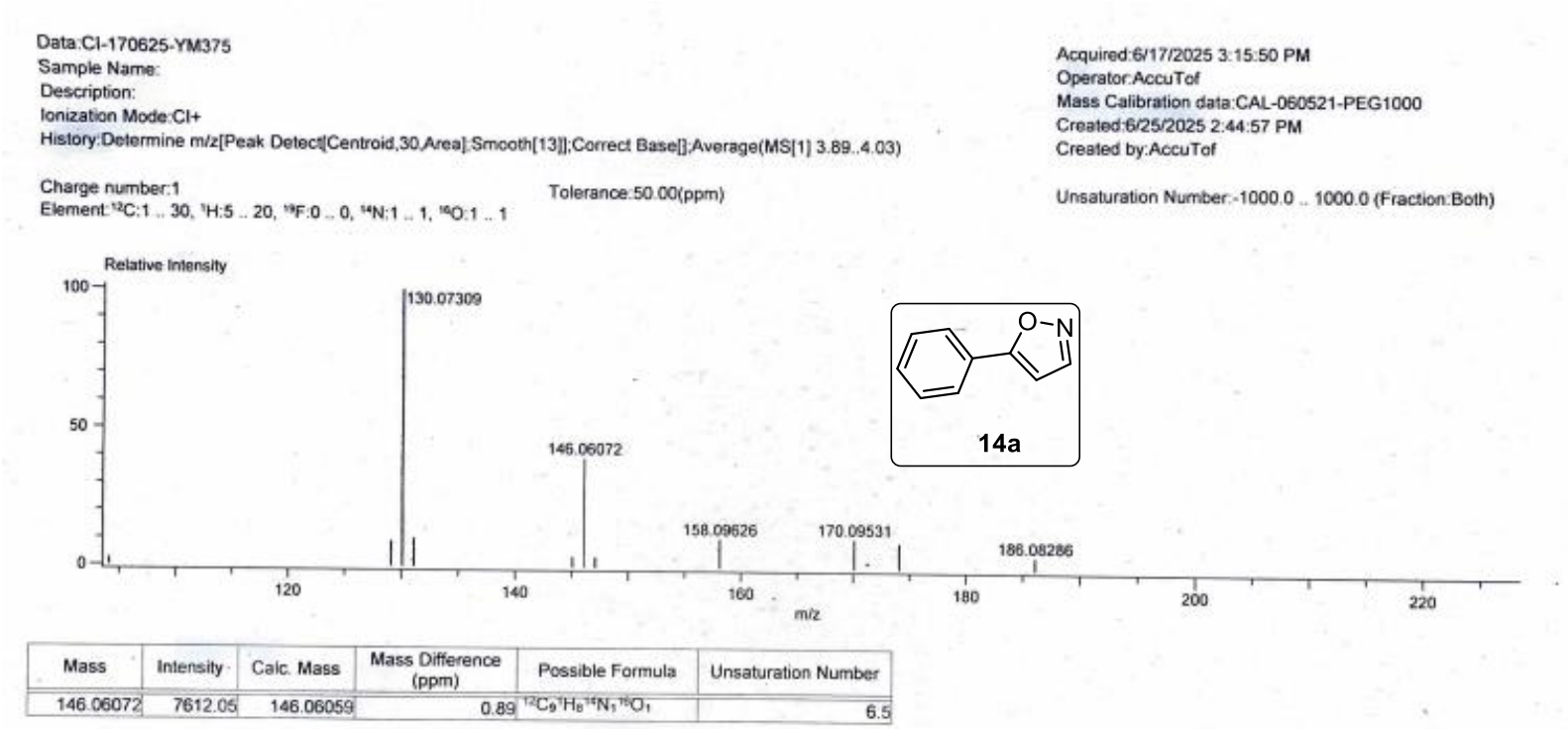


Figure ESI-22. HRMS with (CI^+) mode $[M+H]^+$ of 5-phenylisoxazole Intermediate.

Iminoyl or oxymidoyl radical trap experiment from 2-phenylcyclopropane-1-carbaldehyde oxime (15):

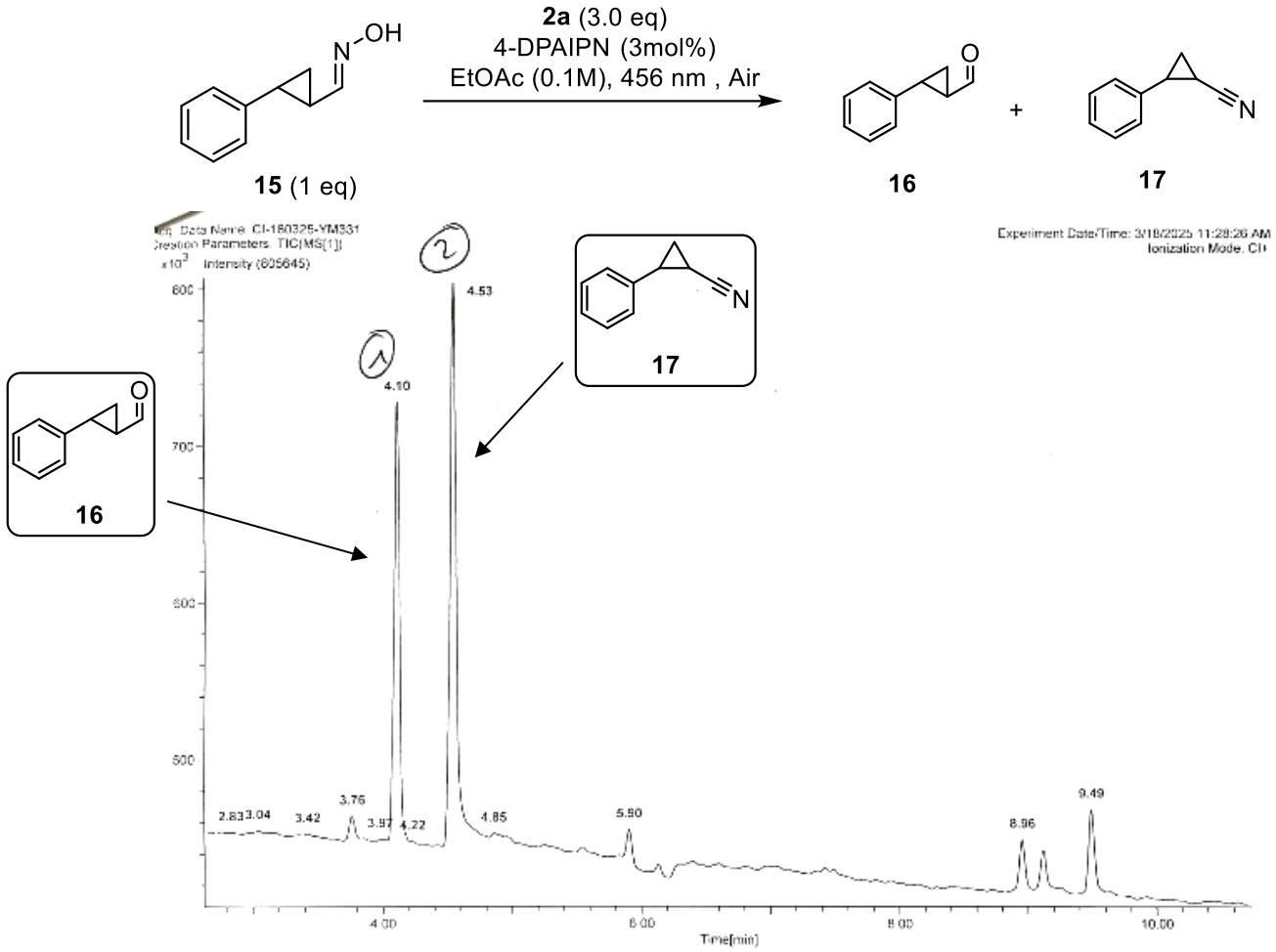


Figure ESI-23. GC-MS with (CI^+) mode $[M+H]^+$ of by-products obtained from 2-phenylcyclopropane-1-carbaldehyde oxime.

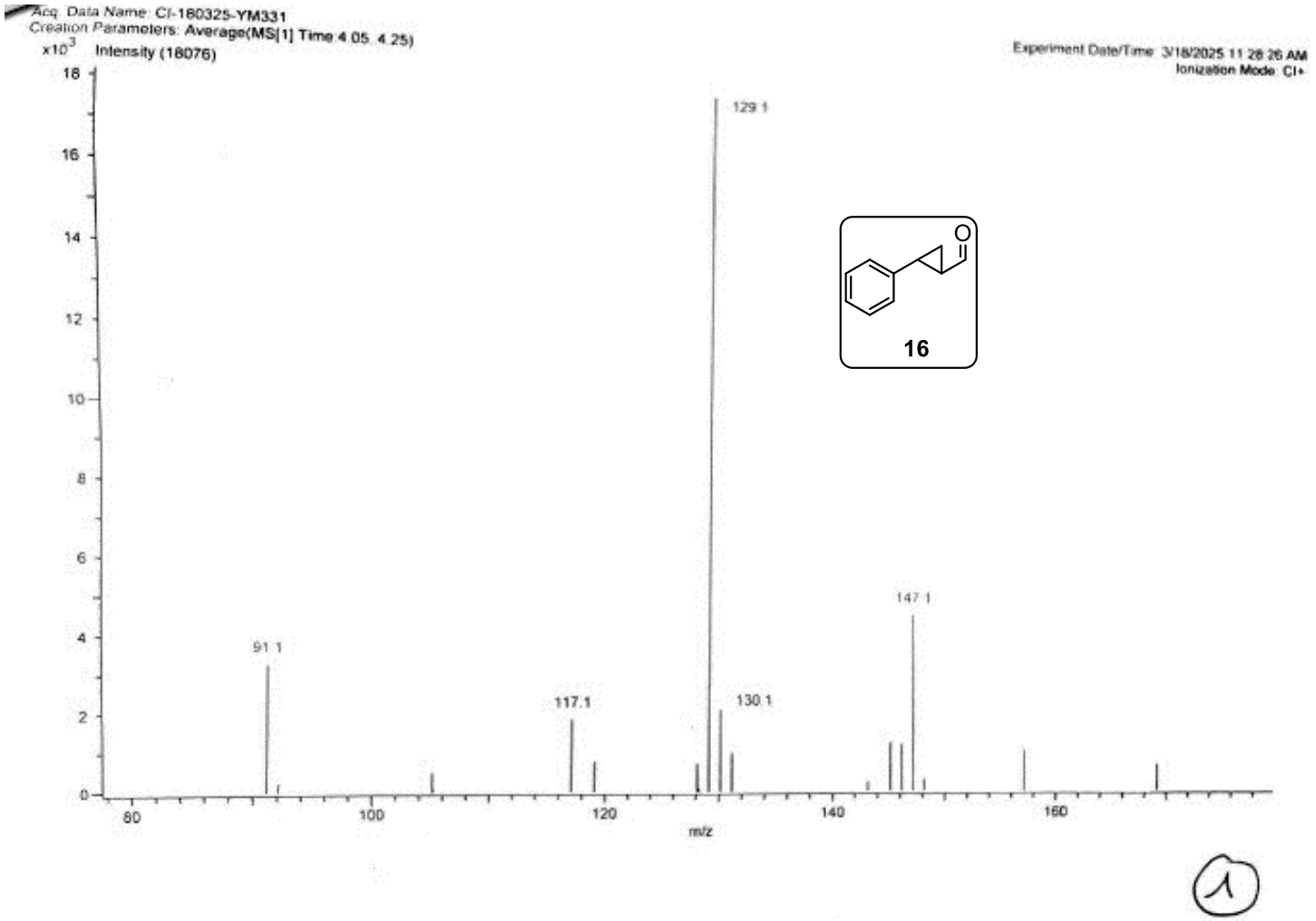


Figure ESI-24. GC-MS with (CI^+) mode $[M+H]^+$ of the first by-product (2-phenylcyclopropane-1-carbaldehyde).

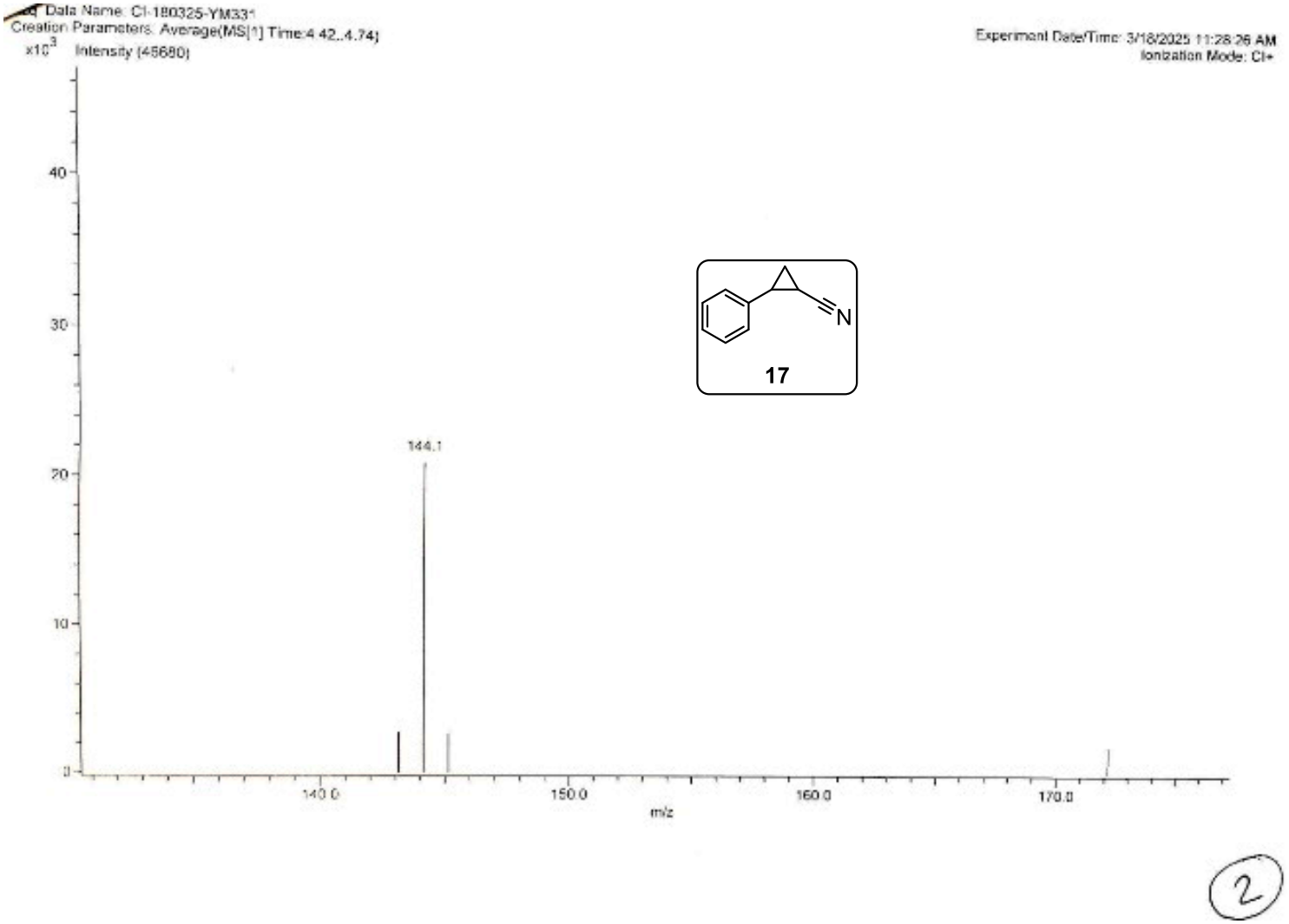
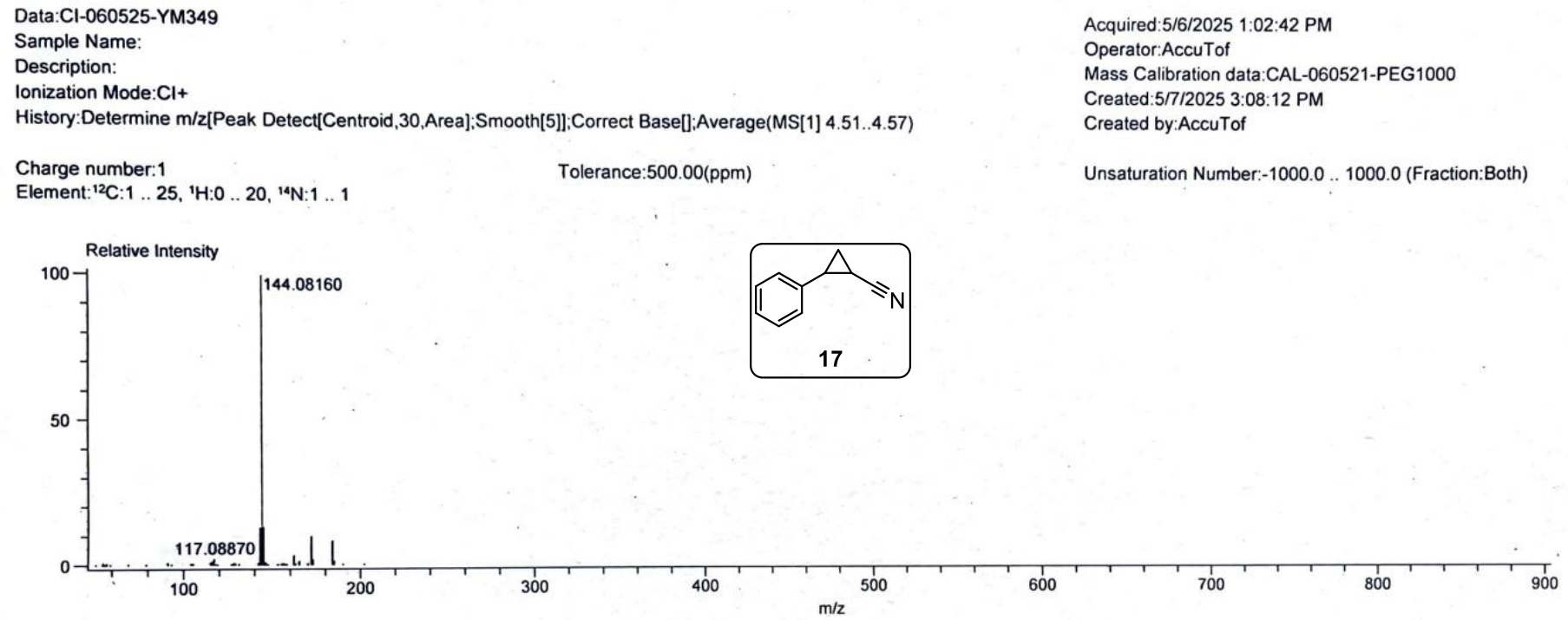


Figure ESI-25. GC-MS with (CI^+) mode $[M+H]^+$ of the second by-product (2-phenylcyclopropane-1-carbonitrile).



Mass	Intensity	Calc. Mass	Mass Difference (ppm)	Possible Formula	Unsaturation Number
144.08160	268089.54	144.08132	1.90	$^{12}C_{10}{}^{1}H_{10}{}^{14}N_{1}$	6.5

Figure ESI-26. HRMS with (CI^+) mode $[M+H]^+$ of the second by-product (2-phenylcyclopropane-1-carbonitrile).

Suggested side reaction followed by ^{19}F NMR.

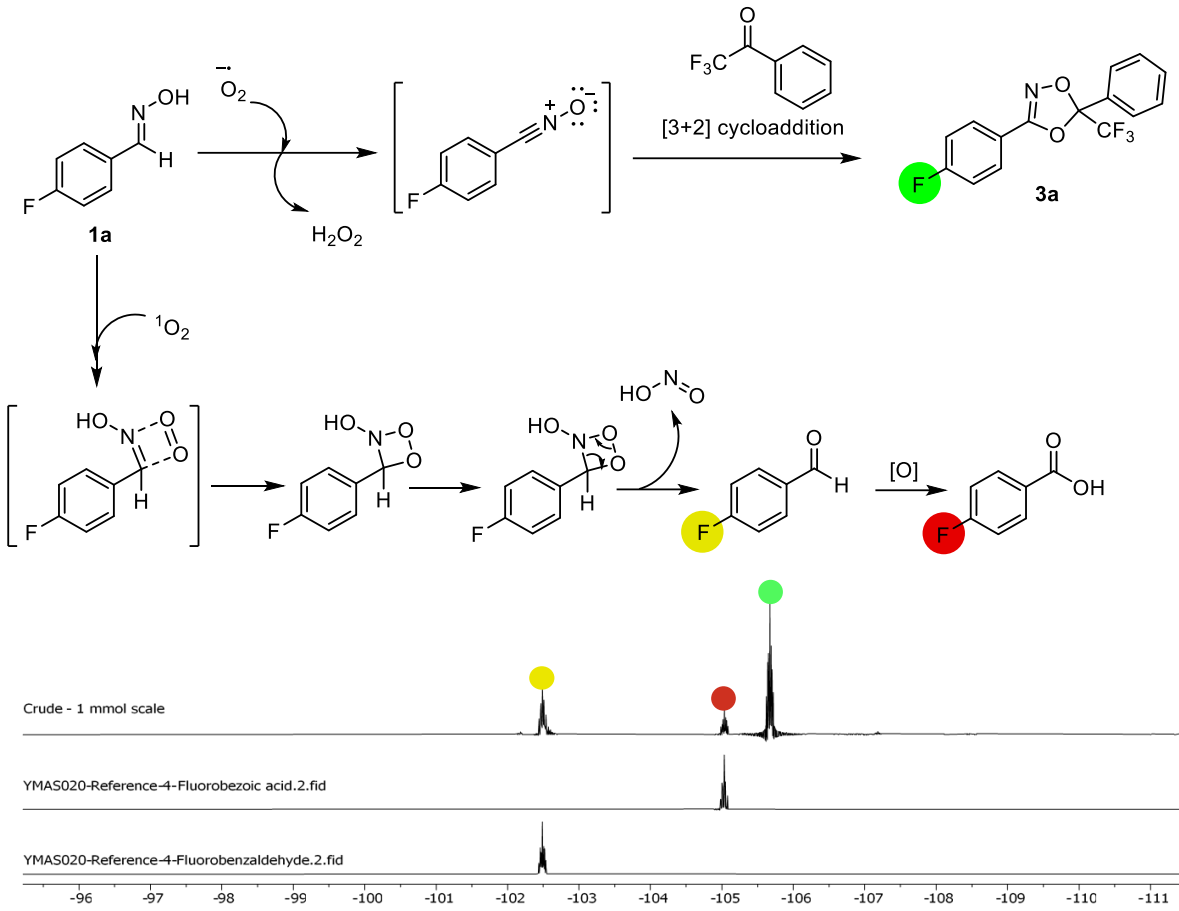


Figure ESI-27. ^{19}F NMR of the Crude mixture of a reaction of oxime **1a** (1 mmol) with ketone **2a** (3.0 mmol) in EtOAc (0.1 M) and 4-DPAIPN (3 mol%) under LEDs (456 nm) and Air, ahowing the formations of the target product and by-products (the corresponding aldehyde and acid).

Nitrile oxide intermediate:

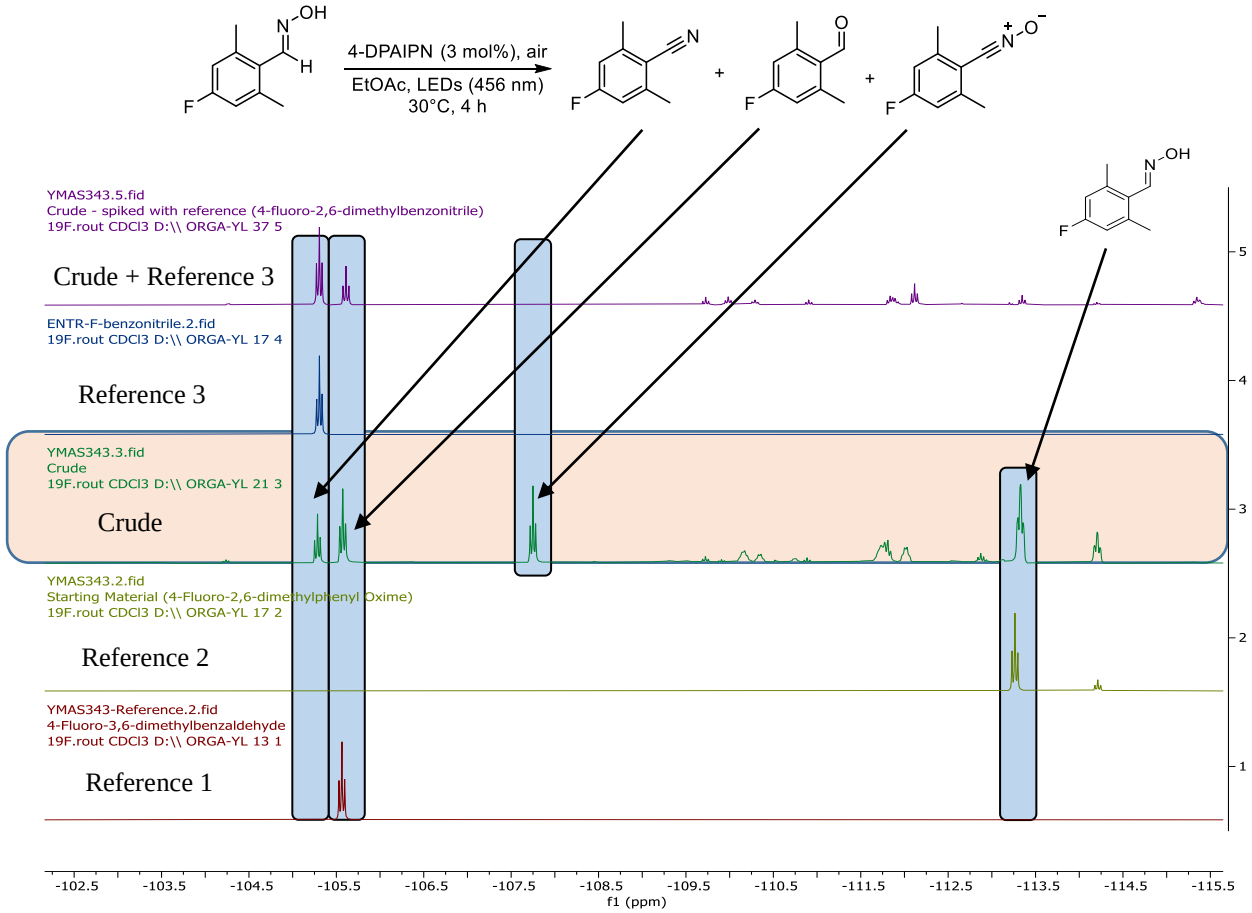
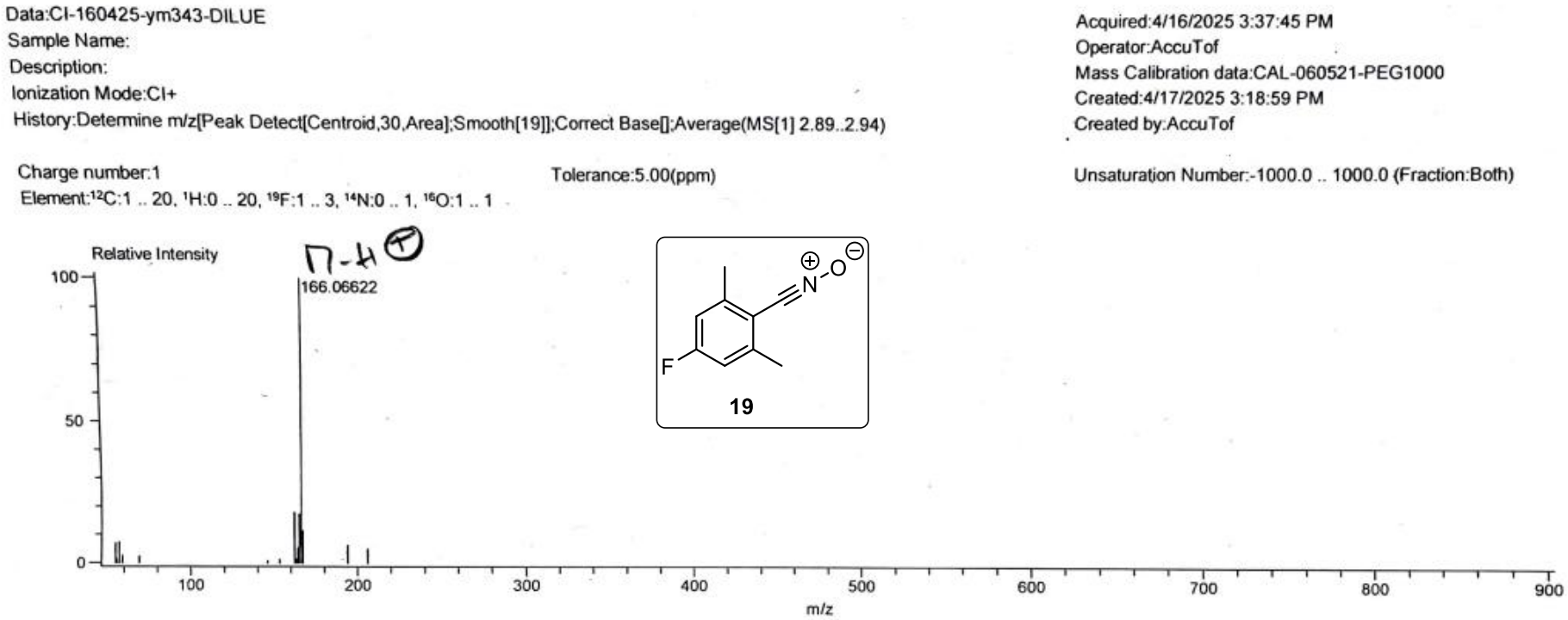


Figure ESI-28. ^{19}F-NMR of 4-fluoro-2,6-dimethylbenzonitrile oxide.



Mass	Intensity	Calc. Mass	Mass Difference (ppm)	Possible Formula	Unsaturation Number
166.06622	35037.41	166.06682	-3.60	$^{12}C_9{}^{1}H_9{}^{19}F_1{}^{14}N_1{}^{16}O_1$	5.5

Figure ESI-29. HRMS with (CI^+) mode $[M+H]^+$ of 4-fluoro-2,6-dimethylbenzonitrile oxide.