Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Radical Fluoroalkylation Reactions of (Hetero)arenes and Sulfides under Red Light Photocatalysis

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Abstract

Fluoroalkylation reactions of (hetero)aromatics have been accomplished through low-power illumination from red LEDs with commercially available phthalocyanine zinc salt as photocatalyst in the presence of perfluoroalkyl iodides R_F-I in MeCN : DMF solvent mixtures. This methodology has been extended to the fluoroalkylation of sulfides

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Experimental Procedures

I.-General Considerations

All reactions were carried out in an argon atmosphere under anhydrous conditions. Reaction solvents such as *N,N´*-dimethylformamide (DMF), acetonitrile (MeCN), methanol (MeOH), were chromatography quality and were not further purified. Chromatography and extraction solvents dichloromethane, chloroform, *iso*octane, *n*-hexane, *n*-heptane, ethyl acetate, acetone, dichloromethane (DCM), and ethanol were purchased from commercial suppliers. Ascorbic acid was 99% pure and used as received from the supplier. 2,4,6-trimethylcollidine, and sodium acetate were used as received from the suppliers. Fluorinated reagents 1-iodo1,1,2,2,3,3,4,4,4-nonafluorobutane (perfluorobutyl iodide), was a commercial reagent and used without further purification, except when the Stern Volmer experiment was conducted, in which case it was filtered through a small neutral alumina column to remove traces of iodine dissolved. Heteroaromatic compounds (2-methyl-indole, Gramine, 2-amino-5-methylpyridine, 2-amio-5-bromopyridine, 2,4,6-triaminopyrimidine, 2-methoxy-9-methylcarbazole, 2-mercaptobenzothiazole, 2-mercaptobenzoimidazole, 5-mercaptopurine) and aromatic substrates (aniline, *N*-methylaniline, *N,N*-dimethylaniline, N,N-dimethylamino-α-naphthalene, 2-methylaniline, 2,5-dimethoxyaniline and anisole) were vacuum-distilled before use. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and 1,4-dinitrobenzene were ultra-pure-grade reagents. Dye Eosin Y (2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3 3*H*-xanthen-9- yl)benzoate), was 99.9% pure and used as received from the supplier. Methylene Blue (3,7-bis(dimethylamino)phenothiazin-5-ium),

29*H*,31*H*-phthalocyanine **1** , and the zinc salt of phthalocyanine **2** were commercially available and used as received from the supplier. Photocatalyst 2,9(10),16(17),23(24)-tetrakis-(1-adamantylsulfanyl) phthalocyaninatozinc(II) **3**, was synthesized according to literature procedures (see section V.-). Photocatalyst [Ir(dF(CF_3)ppy)$_2$(dtbbpy))PF_6 , (dF = 2-(2.4-difluorophenyl)-5-(trifluoromethyl)pyridine, dtbbpy = 4,4´-di-tert-butyl-2,2´-bipyridine) was used as received from the supplier. Zinc acetate was reagent grade. Yields were referred to as isolated yields of analytically pure materials unless otherwise noted, as the case of yields calculated from ^{19}F NMR and ^{1}H NMR spectral integration through the use of internal standard (benzotrifluoride). Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Silica gel 60 F254 pre-coated plates (0.25 mm, Merck), and revealed by UV-light. Purification of the reaction products was carried out by column chromatography using Ultra-Pure Silica Gel (230–400 mesh), standard silica-gel for column chromatography (60 mesh) or silica-gel for thin layer preparative chromatography with fluorescent indicator (rhodamine).

The light sources were commercially available LEDs (red light, 4 x 5 Watt each, total 20 Watt), household 60-watt fluorescent light bulb (CFL), a 5 -Watt blue LED, and green LED (5 Watt). ^{1}H NMR spectra were recorded on a Bruker Avance 500 (500 MHz), or a Bruker Avance 600 (600 MHz) spectrometers, and are reported in ppm using the solvent residual peak resonance as the internal standard ($CDCl_3$ at 7.28 ppm). ^{1}H NMR data are reported as follows: chemical shift; number of hydrogens; multiplicity; coupling constants (Hz). Multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, br = broad. Proton-decoupled ^{13}C NMR spectra were recorded on

a Bruker Avance 500 (at 125.758 MHz), or on a Bruker Avance 600 (at 150.903 MHz) spectrometers and are reported in ppm using the C resonance signal from the solvent as the internal standard ($CDCl_3$ at 77.00 ppm). ^{19}F NMR spectra were recorded on a Bruker Avance 500 (at 470.592 MHz), or a Bruker Avance 600 (at 564.686 MHz) spectrometers and are reported in ppm using the internal standard signal from the spectrometer. High-resolution mass spectra (HRMS) were obtained using JEOL-DX 700 mass spectrometer. UV spectra were recorded on a Jeol double-beam spectrometer.

Separations and purifications were carried out employing silica-gel column chromatography, and the eluants employed are described under compound spectral characterization.

II.-Photocatalytic Reactions. General Procedures

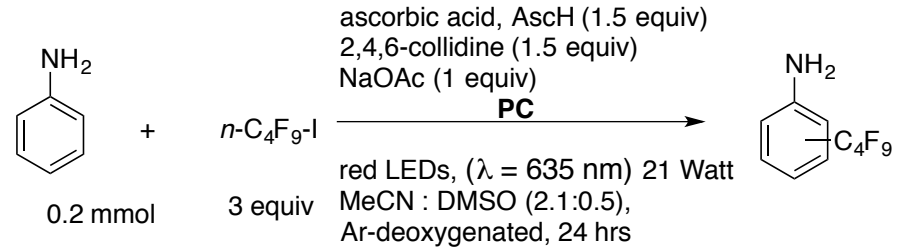
In a 3 mL-reaction vial provided with screw-cap septum and micro stir bar, 0.6 mmol (or 0.2 mmol when noted, as in Table 2) of (hetero)aromatic substrate, 0.36 mol% of photocatalysts (or otherwise used), and 1.5 equivalents (0.3 mmol, 52.8 mg) of ascorbic acid, 2,4,6-collidine (1.5 equivalents, 0.3 mmol, 30 μL) are placed. Solvent MeCN : DMSO (2.1 : 0.5, 2.6 mL total) or DMF : MeCN (1 : 1.3 mL total) mixture (for compounds in Tables 2 & 3) were added and the mixture is de-oxygenated with a stream of dry Ar for 15 minutes. 3 equivalents (103.3 μL) of *n*-C_4F_9-I are then introduced through the septum with microliter syringe. A brief deoxygenation with a slight stream of Ar is passed through for 3 additional minutes. The vessel is placed on a stir plate and stirred vigorously for 24 hrs. (at 22 °C) under constant illumination under 5-Watt-red LEDs (20-Watt total, distance from the lamp: 5 cm, or 1 cm from a blue LED). After the reaction

time elapsed, the mixture was extracted thrice with brine/DCM, and the DCM/DMF extracts evaporated in vacuo. The photoreaction mixtures carried out in DMF : MeCN were extracted with ethyl ether thrice, the organic layers washed with water/brine (thrice), dried over Mg_2SO_4, and evaporated under vacuo. TLC analyses were performed employing dichloromethane:*iso*octane (7 : 3) mobile phase (or otherwise noted). The crude residues were analyzed by ^{1}H NMR, and an ^{19}F NMR integration of the product area is measured. Other runs contain internal standard benzotrifluoride. The crude mixture was placed on a silica-gel preparative thin layer glass support and eluted with $CHCl_3$: MeOH or else by column chromatography which was carried out instead of thin layer preparative chromatography. The products reveal intensely under 254 nm-light (except for 2-((4,4,4,4,4,4,4,4,4-Nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)ethan-1-ol and methyl *N*-acetyl-S-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-L-cysteinate which reveal under ceric ammonium sulfate solution or the Hanessian's Stain. The eluants were gathered, evaporated under vacuo, yields calculated by weight and characterized by standard spectroscopic techniques (section VI). NMR integration yields reflect the % of product(s) calculated with the aid of an internal standard (benzotrifluoride for ^{19}F NMR spectra, and 1,3,5-trimethoxybenzene for ^{1} H NMR spectra). For perfluoroalkylthio ether products, a CAN (ceric ammonium nitrate) solution was employed to follow up the reactions by TLC.

Picture of the irradiation set-up illustrating the red LEDs employed in the perfluoroalkylation reactions

III.-Tables

Table S1. Optimization of reaction conditions for photocatalysts (**1-3**) absorbing at ca. 650 nm. Reactions of aniline (0.2 mmol) with *n*-C_4F_9I (3 equiv.) in solvent (3 mL, Ar-deoxygenated) under photocatalysis (PC, 0.01 equiv./ 0.36 mol% or otherwise noted), with vigorous constant stirring, under irradiation for 24 h. Substitution product: 2-perfluorobutylaniline and 4-perfluorobutylaniline isomers



entry	PC (mol%)	Base (equiv.)	Electron donor (equiv.)	Solvent (mL)	Yield,[a] %
1	**3** (0.36)	TMEDA (1.5)	$Na_2C_2O_4$ (1.5)	MeCN : DMSO (2.1 : 0.5)	-
2	**3** (0.36)	TMEDA	Ascorbic acid (1.5)	MeCN : DMSO (2.1 : 0.5)	27
3	**3** (0.36)	2,4,6-collidine (1.5)	Ascorbic acid (1.5)	MeCN : DMF (2.1 : 0.5)	< 30
4	**3** (0.36)	2,4,6-collidine (1.5)	Ascorbic acid (1.5)	DMF (3)	< 60

5	**3** (0.36)	2,4,6-collidine (1.5)	Ascorbic acid (1.5)	MeCN : DMSO (2.1 : 0.5)	90
6	**1**, (0.36)	2,4,6-collidine (1.5)	Ascorbic acid (1.5)	THF (3)	30
7	**1**, (0.36)[b]	1.5	1.5	THF (3)	-
8	**2,** (0.36)	2,4,6-collidine 1.5	Ascorbic acid (1.5)	MeCN : DMF (1.5 : 1.5)	93

a.- ^{19}F NMR and ^{1}H NMR yields (benzotrifluoride as internal standard) of combined *o*-perfluorobutylaniline and *p*-perfluorobutylaniline
b .-Addition of $Zn(OAc)_2$, 2 mg

Given the failed reaction of aniline reported in Table 1, entry 2, where Eosin Y is employed as PC under red-light irradiation, we undertook a Eosin-Y-photocatalyzed (0.2 mol% PC) reaction of aniline (0.2 mmol) with n-C_4F_9-I (6 equiv), in MeCN as solvent (3 mL, Ar-deoxygenated) in the presence of Cs_2CO_3 (1.5 equiv) as base, this time irradiating with two 5- Watt green LEDs (λ_{max} (Eosin Y) = 520 nm, $\lambda_{emission}$ green LED = 535 nm, see Figure S1B). The reaction afforded an excellent yield (96% conversion) of 4- and 2-perfluorobutylaniline derivatives.

This simple experiment shows the role of the excited PC in the production of C_4F_9 radicals.

Table S2. Reactions probing the mechanism for the red-light-(or otherwise noted)-photocatalyzed perfluoroalkylation of aniline (0.2 mmol) with *n*-C_4F_9-I (3 equiv.), in the presence of ascorbic acid (1.5 equiv.), 2,4,6-collidine (1.5 equiv.) in Ar-deoxygenated (or otherwise noted) MeCN : DMF (1 : 1) as solvent, for 24 hrs. with 15-Watt red LEDs (or otherwise noted). Photocatalyst **2** (0.36 mol%) employed.

entry	**additive**	**Irradiation source (Watt)**	**PC (mol%)**	**Yield,[a] %**
1	TEMPO[b]	Red LED (21)	**2** (0.36)	-
2	*p*-DNB[c]	Red LED (21)	**2** (0.36)	30
3	-	Red LED (21)[d]	**2** (0.36)	70
4	-	-[e]	**2** (0.36)	-
5	-	White light (40)	**2** (0.36)	30
6	-	Red LED (21)	**-**	< 5

a.- ^{19}F NMR and ^{1}H NMR yields (benzotrifluoride as internal standard) of combined *o*-perfluorobutylaniline
b.- 2,2,6,6-Tetramethyl-1-piperidinyloxy, 0.3 equiv.
c.-1,4-dinitrobenzene, 0.3 equiv.
d.-air-saturated MeCN : DMF
e.-24-h reaction conducted in the absence of light, with reaction vial wrapped up in aluminum foil.

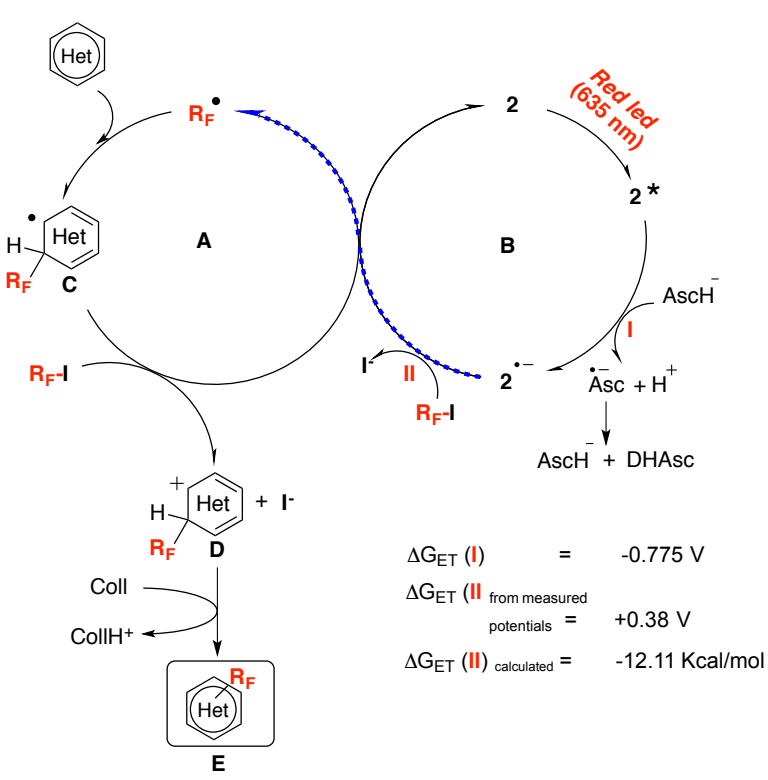
Table S3. Redox Potentials and Rehm Weller Parameters

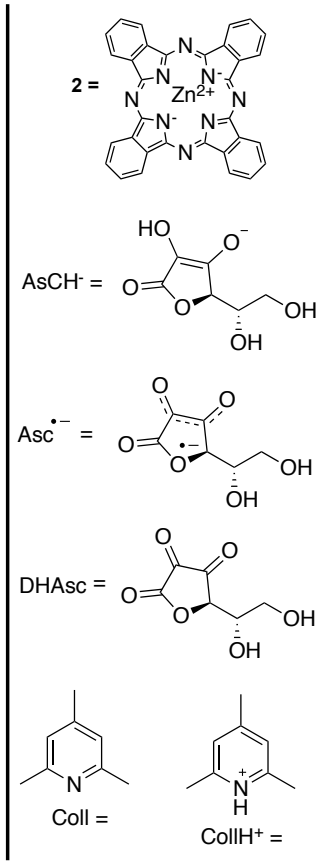
entry	compound	E_{red}(V)	E_{ox}(V)	E*ox (V)	E*red (V)	E*S[j] (eV)	λmax (nm)[k]	ΔG_{ET}[a] (eV)	ΔG_{ET}[a] (Kcal/ mol)
1	Eosin Y	+0.74[b,c]	-1.10[b,c]	-1.60	+1.18[d]	2.31[b]	539	-1.53	-3.5
2	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$			- +0.89[e]	+1.21[e]		380		
3	Zn-phthalocyanine	-0.89[f]				1.91	650		
4	Potassium oxalate		+0.21						
5	collidinium ascorbate		+0.295[h]					-0.32	-0.732
6	$n\text{-}C_4F_9I$	-1.27[i]					260		

a.- From the Rehm Weller equation

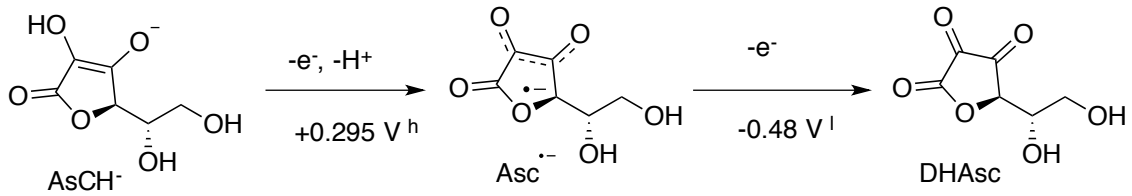
$$\Delta G^{o} = E_{(D/D+)} - E_{(A/A-)} - E^{*} + \frac{Z_1 Z_2}{\varepsilon r_{12}} \qquad (1)$$

Coulombic term taken as -0.05 eV



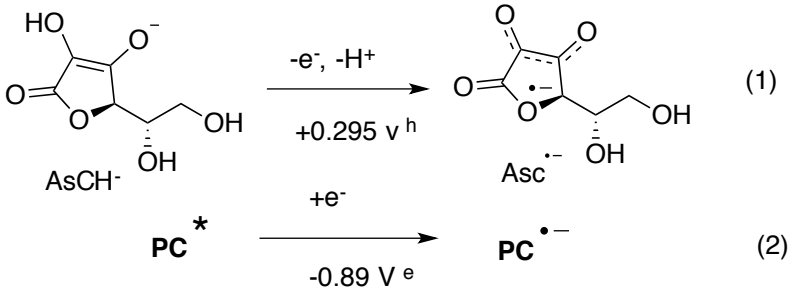


Scheme S1. Proposed reaction mechanism



Scheme S2. Reduction of ascorbate ($ASCH^-$) to ascorbate radical anion ($Asc^{\cdot -}$) and reduction of $Asc^{\cdot -}$ to dehydroascorbic acid (DHAsc)

Calculation of ΔG_{ET} between ascorbate anion ($AsCH^-$) and photoexcited PC **2***, process which renders ascorbate radical anion ($Asc^{\cdot -}$) and the radical anion of PC $\mathbf{2}^{\cdot -}$, according to step **I**, Scheme S1):

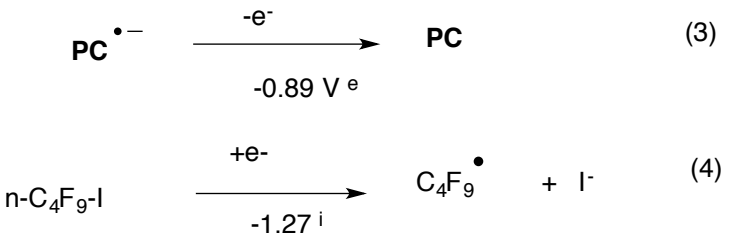


Scheme S3. Redox couple for the production of C_4F_9 radicals

$$\Delta \mathbf{G_{ET}}\ (Asc^- + PC^* \longrightarrow Asc\cdot + PC^{-}\cdot)$$

$$\Delta G_{ET} = +0.295\ V - (-0.89\ V)\ -1.91eV\ -0.05\ eV = -0.775\ V$$

Calculation of ΔG_{ET} between the radical anion of PC **2** ($\mathbf{2}^{-}\cdot$) and perfluorobutyl iodide *n*-C_4F_9-I (process which regenerates the ground state of PC **2** and perfluorobutyl radicals $C_4F_9\cdot$, according to step **II**, Scheme S1.

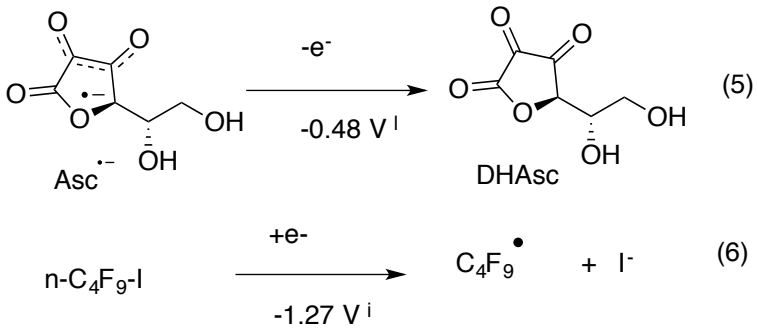


Scheme S4. Redox couple for the production of C_4F_9 radicals and regeneration of PC

$$\Delta \mathbf{G_{ET}}\ (PC\ \mathbf{2}^{-}\cdot + n\text{-}C_4F_9\text{-}I \longrightarrow PC\ \mathbf{2} + C_4F_9\cdot)$$

$$\mathbf{\Delta G_{ET} = -0.89\ V + 1.27\ V = +0.38\ V}$$

Calculation of ΔG_{ET} between the radical anion of ascorbate ($Asc^{-}\cdot$) and perfluorobutyl iodide *n*-C_4F_9-I (process which regenerates the ground state of dehydroascorbic acid (DHAsc, vide supra) and perfluorobutyl radicals $C_4F_9\cdot$(Scheme S1).



Scheme S5. Redox couple for the production of C_4F_9 radicals and dehydroascorbic acid DHAsc from $Asc^{\bar{}}\cdot$ and *n*-C_4F_9-I

$$\Delta G_{ET}\ (Asc^{\bar{}}\cdot + n\text{-}C_4F_9\text{-}I \longrightarrow DHAsc + C_4F_9\cdot)$$

$$\mathbf{\Delta G_{ET} = -0.48V - (-1.27V) = + 0.79\ V}$$

Propagation of the chain by ET between $Asc^{\bullet\bar{}}$ and PC **2** is precluded as the fate of $Asc^{\bar{}}\cdot$ is likely to be disproportionation to dehydroascorbic acid and ascorbate monoanion and not a chain carrier (D. D. M. Wayner, A. Houmam, Acta. Chem. Scand. 1998, 52, 377 –384).

b.- T. Shen, Z.-G. Zhao, Q. Yu, H.-J. Xu, *J.Photochem. Photobiol.*, *A* 1989, **47**, 203.
c.- X.-F. Zhang, I. Zhang, L. Liu, *Photochem. Photobiol*. 2010, **86**, 492.
d .-D. Ravelli, M. Fagnoni, A. Albini, *Chem. Soc. Rev.,* 2013,**42**, 97-113.
e.- (a) C. K. Prier,.D. A Rankic, D. W. C. MacMillan, *Chem. Rev*. 2013, **113**, 5322. (b) J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem*. 2012, **77**, 1617
f.- D. W. Clarck, N. S. Hush and I. S. Woolsey, *Inorganica Chim. Acta,* 1976, **19**, 129-132.
g.- E. Jacobsen, D. T. Sawyer, *J. Electroanal. Chem*. **16**(3), 361–374.
h.- +0.295 ± 0.05 V was measured in DMF as solvent against SCE using the technique reported by Allen J. Bard, *THE ELECTROCHEMISTRY OF ORGANIC COMPOUNDS IN APROTIC SOLVENTS—METHODS AND APPLICATIONS*. The literature oxidation potential of E ox = +0.33 V was reported from T. Iyanagi, I. Yamazaki and K. F. Anan, *Biochimica et Biophysica Acta* 1985, **806**, 255-261. The reported value is +0.33 V is also found: E. J. Nanni, Jr., M. D. Stallings, and D. T. Sawyer, *J. Am. Chem. Soc*. 1980, **102**, 4481.
i.- measured in DMF: C.P. Andrieux, L.G. Clis, M. Medebielle, P. Pinson, J.M. Saveant, *J. Am. Chem. Soc*.1990, **112**, 3509.
j.-The singlet excited state energies were obtained spectroscopically from the 0,0 overlap of the excitation (absorption) and emission (fluorescence) spectra. Singlet energies can also be easily calculated (see below for theoretical calculations)
k.-λ_{max} of absorption
l.- (a) S. Ono, M. Takagi, and T. Wasa, *J. Am. Chem. Soc*., 1953, **75**, 4369–4370. (b) H. Sapper, Sa-Ouk Kang, H. H. Paul, and W. Lohmann, *Z. Naturforsch*. 1982, **37**, 942.

IV.-Figures

Figure S1. UV-vis spectra of Phthalocyanines 2 and 3

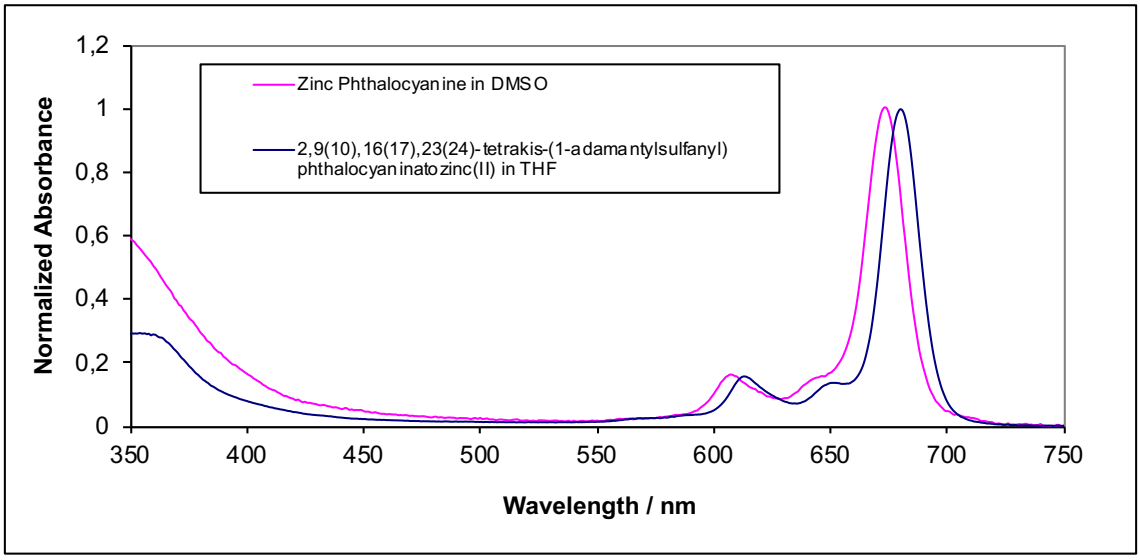


Figure S2. Peak emission wavelengths and spectra of blue LED, green LED and red LED used

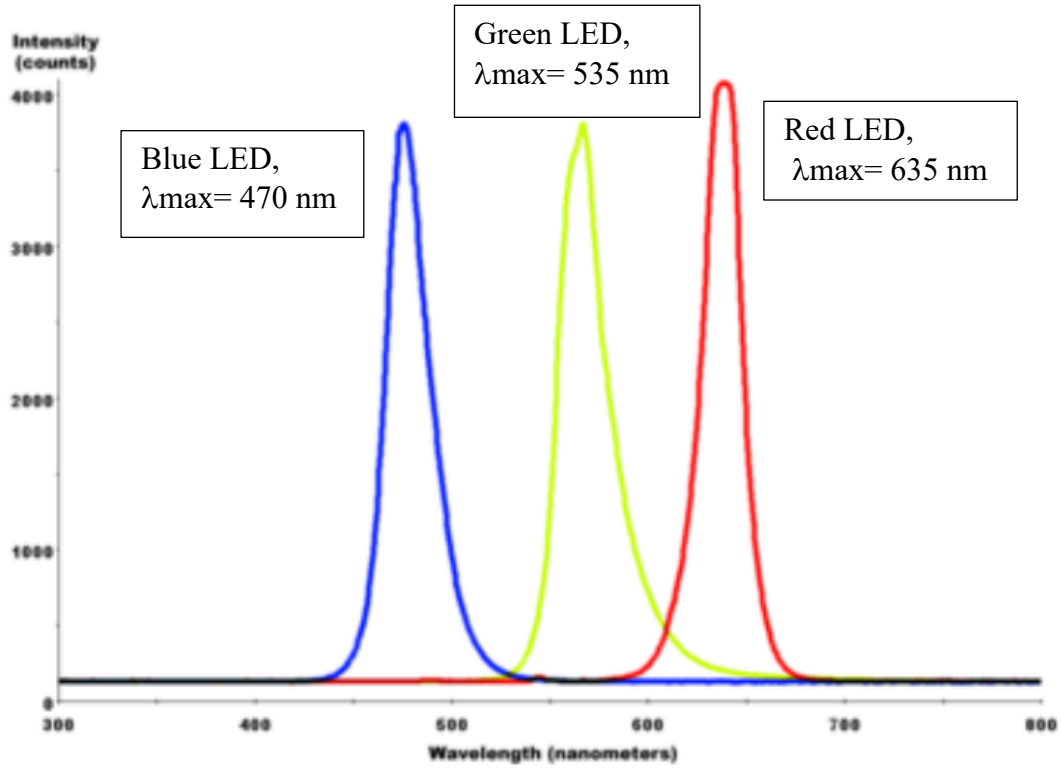


Figure S3. Peak emission wavelengths and spectrum of Compact Fluorescent Lamp, 20 Watt

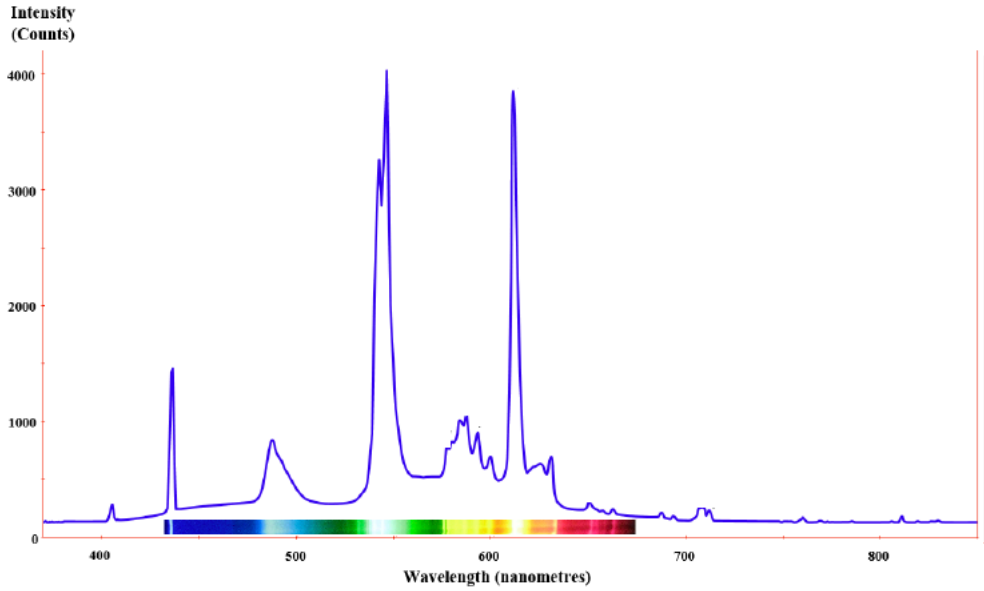
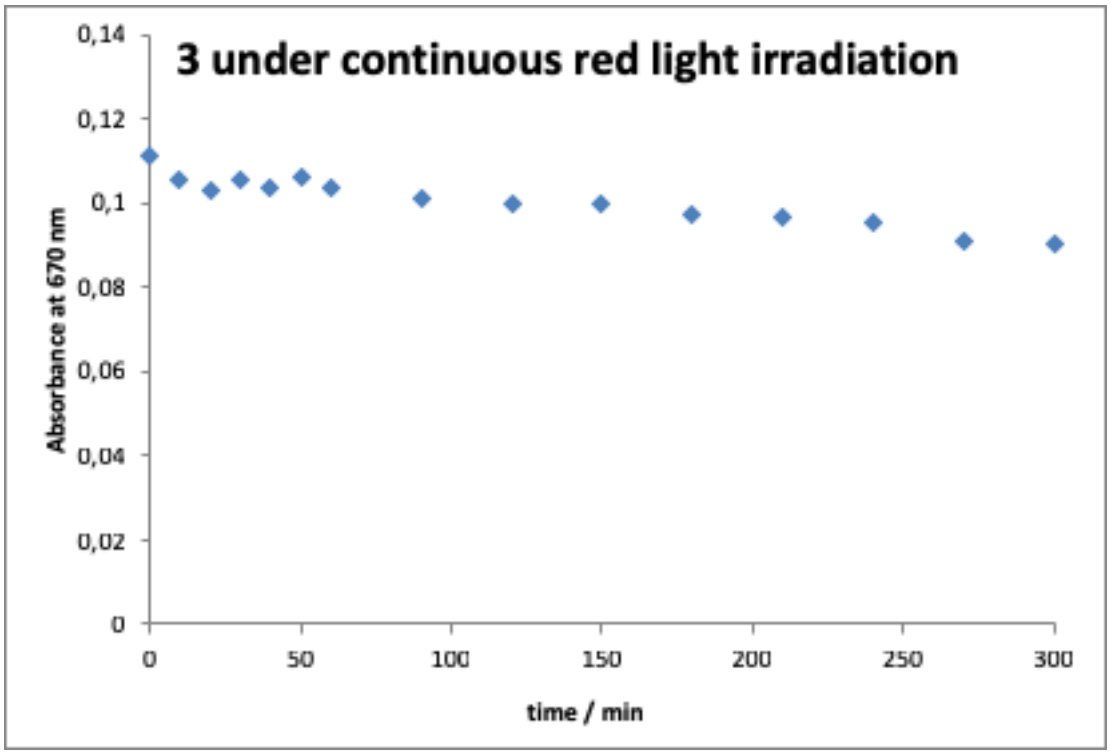


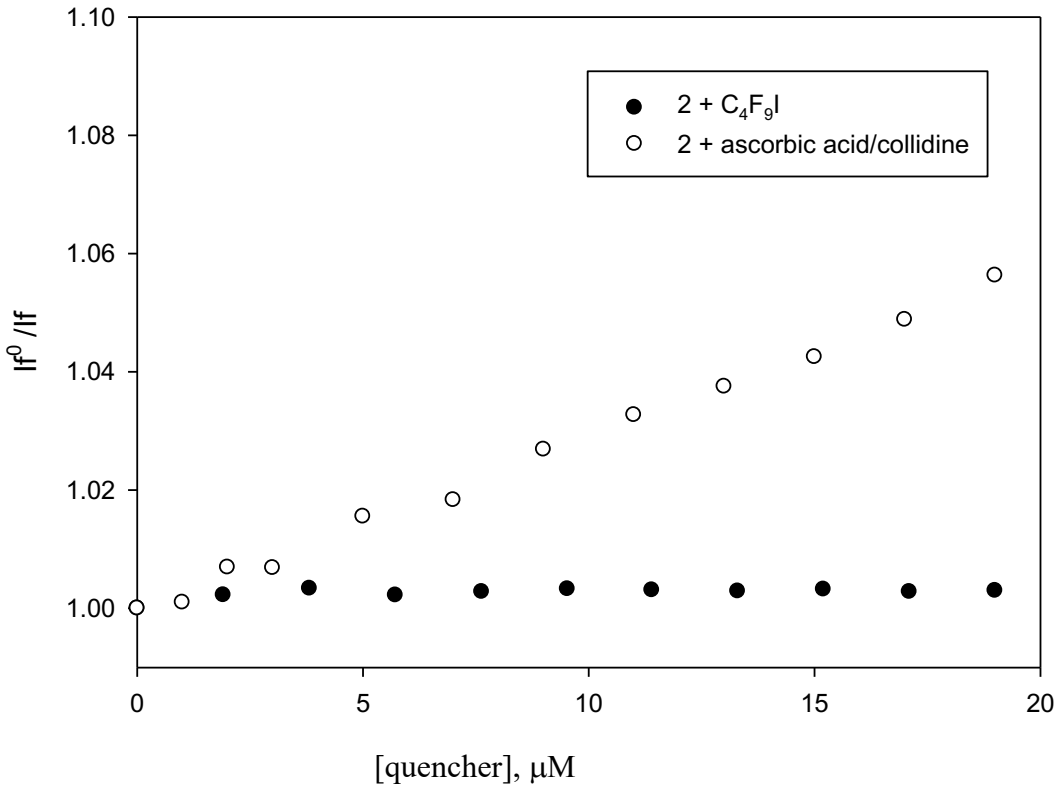
Figure S4. Photostability of 3 under continuous red-light irradiation (21 Watt)



The photostability of photocatalyst **3** (0.36 mol%) under red light (20 Watt red LEDs, λ_{max} = 635 nm) has also been measured after 5h-, 10h-, and 15 h-

irradiation of the mixture of aniline (0.2 mmol), ascorbic acid (1.5 equiv), 2,4,6-collidine, (1.5 equiv) in the presence of n-C_4F_9-I (3 equiv) in Ar-deoxygenated MeCN:DMF (3 mL) solvent mixture by checking the UV-vis absorption at 680 nm (λ_{max} of PC **3**). For the photocatalyzed reaction of aniline, the absorption at 15-hr irradiation decreases only 15% of the solution with respect to time = 0, purporting that the PC **3** is stable under the reaction conditions. Notwithstanding, for other substrates this result varies.

Figure S5. Stern Volmer plots of the quenching of fluorescence of 2 with ascorbic acid / 2,4,6-collidine (A) and perfluorobutyl iodide *n*-C_4F_9-I

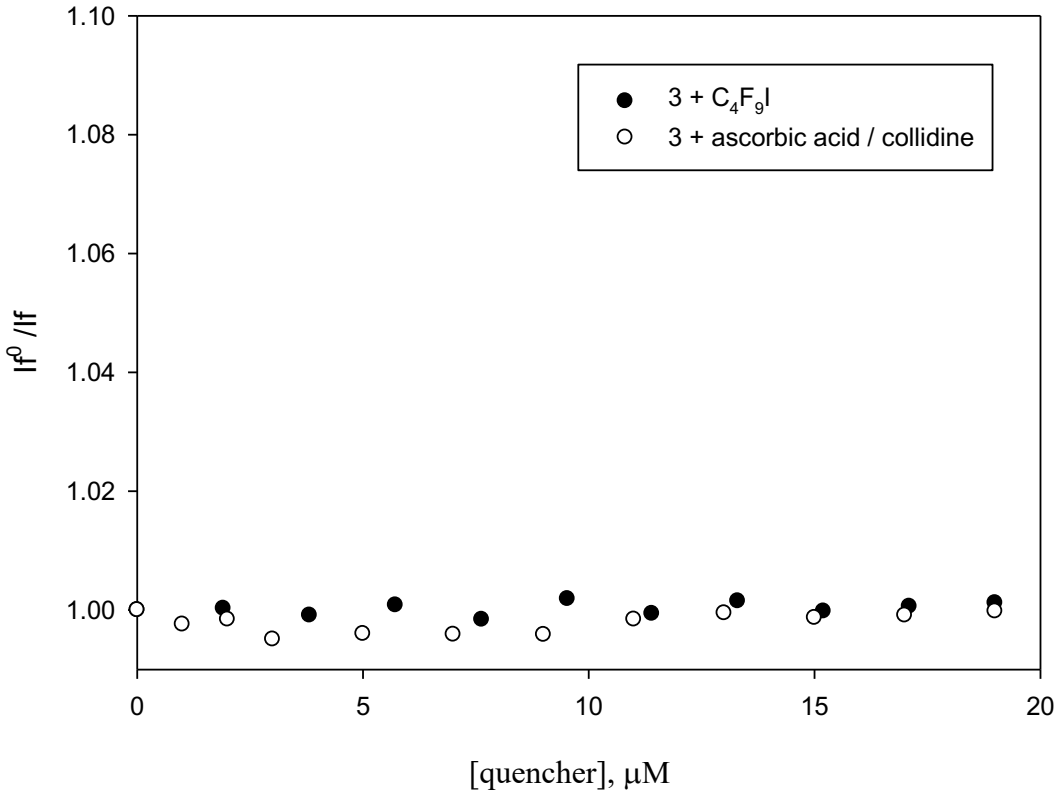


Y(**2*** + C_4H_9I) = 0.0003X + 1.0011

Y(**2*** + Ascorbic acid/collidine) =0.0029x + 0.9994

$K_{Stern\ Volmer} = 0.0029\ \mu M^{-1}$

Figure S6. Stern Volmer plots of the quenching of fluorescence of 3* with ascorbic acid / 2,4,6-collidine (A) and perfluorobutyl iodide *n*-C_4F_9-I



$Y(3+C_4H_9I) = 0.00006X + 0.9997$
$Y(3 + \text{Ascorbic acid/collidine}) = 0.0001x + 0.997$

$K_{\text{Stern Volmer}} = 6 \times 10^{-5}\ \mu M^{-1}$

Discussion of the plots:

Phthalocyanine solutions (5.0 μM) were excited at 600 nm and their fluorescence emission was recorded in the range of 640-750 nm. The fluorescence quenching data obtained were analyzed by Stern-Volmer formalism: $F^0/F = 1 + K_{SV}[Q]$, which relates the decrease in fluorescence intensity (F^0/F) to quencher concentration [Q]; K_{SV} is the Stern-Volmer quenching constant.

The quenching of the fluorescence of **2*** ($\lambda_{max}^{emission}$ = 673 nm, in DMF) is effected by the addition of incremental quantities of mixtures of ascorbic acid / 2,4,6-collidine (1 : 1), according to Figure S5. The Stern Volmer constant obtained is 0.0029 μM^{-1}. This result is in agreement with the transfer of an electron from the collidinium ascorbate anion to **2*** , generating the radical anion of $\mathbf{2}^{\bullet -}$ and ascorbate radical, as indicated in the proposed reaction mechanism (Scheme 4, path **I**), and also supported by calculations (Scheme 5, section VI, this ESI).

On the other hand, no quenching of the fluorescence of **2*** takes place upon addition of n-C_4F_9 which is also consistent with the mechanism proposed. We surmise that the radical anion of $\mathbf{2}^{\bullet -}$ transfer instead an electron to n-C_4F_9, to generate C_4F_9 radicals (path **II**, Scheme 4).

Surprisingly, no quenching of the fluorescence of **2*** takes place upon addition of a mixture of ascorbic acid / 2,4,6-collidine (1 : 1) neither upon addition of n-C_4F_9 (Figure S6).

V.-Synthesis of Photocatalyst 2,9(10),16(17),23(24)-tetrakis-(1-adamantylsulfanyl)phthalocyaninatozinc(II) *3*

This was reported in one of our previous publications [1]

VI.-Theoretical calculations

The energetic profile of the proposed reductive photoredox cycle of **2** is depicted in **Figure S7**. Following the absorption of light, a single electron transfer takes place from the anion ascorbate ($\mathbf{Asc}^-$) to the excited state of the photocatalyst (**2***), forming the radical anion of the photocatalyst ($\mathbf{2}^{\bullet -}$) and ascorbate radical anion ($\mathbf{Asc}^{\bullet -}$) (and proton, see Scheme S2 & S3). This latter step is highly exothermic (-67.39 Kcal/mol). Afterwards, an electron is transferred from $\mathbf{2}^{\bullet -}$ to C_4F_9I, generating the $C_4F_9^{\bullet}$ radical (and iodide anion) and the reconstitution of **2**

(this step is also exothermic by -12.11 Kcal/mol). Once the excitation of the photocatalyst takes place, the photoredox cycle is energetically favorable, corroborating that excitation of the photocatalyst is responsible for the production of the radical $C_4F_9^{\bullet}$ (Figure S7).

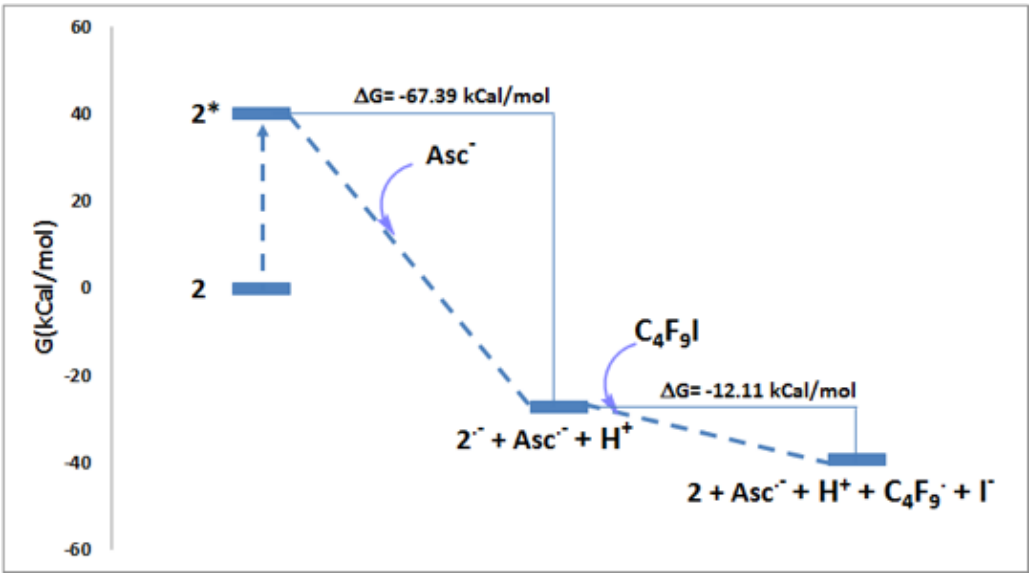


Figure S7. Free energies (Kcal/mol) of the reductive photoredox cycle of Zn-phthalocyanine

In **Figure S8**, the calculated reaction pathway between aniline and radical $C_4F_9^{\bullet}$ is presented. The rate determining step is the formation of the intermediate C_4F_9-substituted cyclohexadienyl radical adduct **C (A→C)**. From this point forward, a reductive quenching of the excited state of the photocatalyst (2*) to render $2^{\bullet-}$ and the Wheland intermediate **G** takes place, being this pathway (**C→G**, blue) the most thermodynamically favorable, as opposed to reduction of *n*-C_4F_9-I by radical adduct **C (C→D)** to afford Wheland intermediate and $C_4F_9^{\bullet}$. After the Wheland intermediate **G** is formed, a proton is abstracted by 2,4,6-collidine to yield the re-aromatized perfluoroalkylated product and protonated 2,4,6-trimethylcollidine.

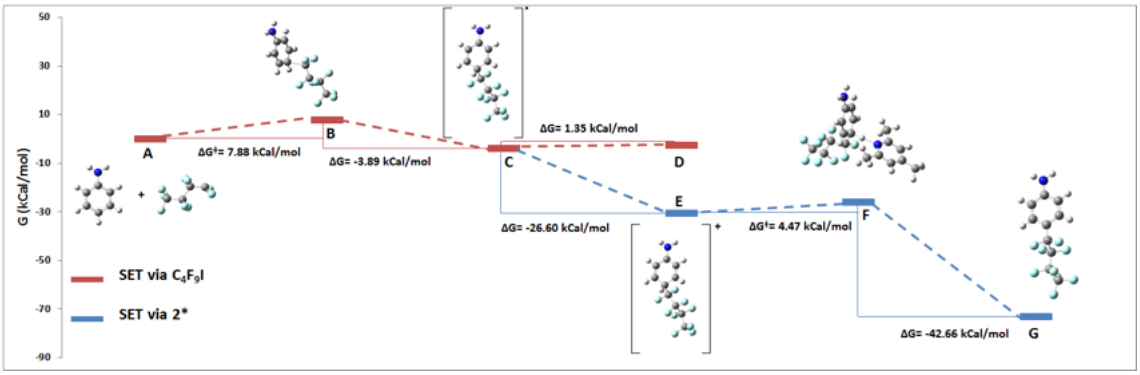


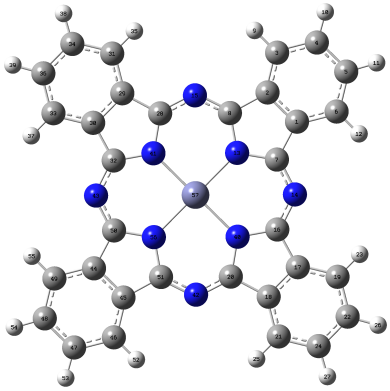
Figure S8. Energy reaction pathways of aniline with $C_4F_9^{\bullet}$ radical via SET to C_4F_9I (red) and SET to 2* (blue).

Computational methods

All the reactants, products, intermediates and transition states of the proposed mechanism in *N,N*-dimethylformamide (DMF) were optimized at the density

functional theory (DFT) level using Gaussian 09 program.[7] The B3LYP[8] method was used in combination with the LanL2DZ basis set. The gradient threshold for geometry optimization was taken as $4{,}5.10^{-4}$ Hartree/Bohr. The polarizable conductor calculation model (CPCM) of solvatation was employed in all calculations.[9,10] The excited state properties of Zn-phthalocyanine were obtained with the time-dependent density functional (TD-DFT) formalism.[11,12,13]
Geometry Coordinates and thermochemistry information:
Zn-Phthalocyanine Ground State

Geometry Coordinates and thermochemistry information:
Zn-Phthalocyanine Ground State



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3	6	0	-0.231981	5.625676	0.000004
4	6	0	0.737209	6.648512	0.000004
5	6	0	2.123032	6.343810	0.000004
6	6	0	2.573890	5.008735	0.000003
7	6	0	1.718554	2.521186	0.000001
8	6	0	-0.499327	3.009413	0.000002
9	1	0	-1.292664	5.857916	0.000004
10	1	0	0.422514	7.688769	0.000005
11	1	0	2.845083	7.156094	0.000005
12	1	0	3.634265	4.775176	0.000003
13	7	0	0.438335	1.986417	0.000001
14	7	0	2.880038	1.839797	0.000001
15	7	0	-1.839797	2.880038	0.000002
16	6	0	3.009413	0.499327	0.000001
17	6	0	4.295227	-0.216960	0.000001
18	6	0	3.989113	-1.608408	0.000000
19	6	0	5.625676	0.231981	0.000002
20	6	0	2.521186	-1.718554	-0.000001
21	6	0	5.008735	-2.573890	0.000001
22	6	0	6.648512	-0.737209	0.000003
23	1	0	5.857916	1.292664	0.000003
24	6	0	6.343810	-2.123032	0.000002
25	1	0	4.775176	-3.634265	-0.000000
26	1	0	7.688769	-0.422514	0.000004
27	1	0	7.156094	-2.845083	0.000002
28	6	0	-2.521186	1.718554	0.000001
29	6	0	-3.989113	1.608408	0.000002
30	6	0	-4.295227	0.216960	0.000001
31	6	0	-5.008735	2.573890	0.000003
32	6	0	-3.009413	-0.499327	-0.000001
33	6	0	-5.625676	-0.231981	0.000001
34	6	0	-6.343810	2.123032	0.000003
35	1	0	-4.775176	3.634265	0.000004
36	6	0	-6.648512	0.737209	0.000002
37	1	0	-5.857916	-1.292664	0.000000
38	1	0	-7.156094	2.845083	0.000004
39	1	0	-7.688769	0.422514	0.000003
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41	7	0	-1.986417	0.438335	-0.000000
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43	7	0	-2.880038	-1.839797	-0.000002
44	6	0	-1.608408	-3.989113	-0.000004
45	6	0	-0.216960	-4.295227	-0.000004
46	6	0	0.231981	-5.625676	-0.000005
47	6	0	-0.737209	-6.648512	-0.000007
48	6	0	-2.123032	-6.343810	-0.000007
49	6	0	-2.573890	-5.008735	-0.000005
50	6	0	-1.718554	-2.521186	-0.000002
51	6	0	0.499327	-3.009413	-0.000002
52	1	0	1.292664	-5.857916	-0.000005
53	1	0	-0.422514	-7.688769	-0.000008
54	1	0	-2.845083	-7.156094	-0.000008
55	1	0	-3.634265	-4.775176	-0.000005

```
     56          7           0       -0.438335   -1.986417   -0.000001
     57         30           0        0.000000    0.000000   -0.000001
 -------------------------------------------------------------------
 Zero-point correction=                           0.414781 (Hartree/Particle)
 Thermal correction to Energy=                    0.442551
 Thermal correction to Enthalpy=                  0.443495
 Thermal correction to Gibbs Free Energy=         0.357637
 Sum of electronic and zero-point Energies=          -1732.129019
 Sum of electronic and thermal Energies=             -1732.101249
 Sum of electronic and thermal Enthalpies=           -1732.100305
 Sum of electronic and thermal Free Energies=        -1732.186163
Excitation energies and oscillator strengths:

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    138A ->139A        0.62636
    138A ->140A       -0.33070
    138B ->139B       -0.62636
    138B ->140B        0.33070
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-KS) =  -1732.50049165
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   2:  3.000-A      1.1785 eV 1052.07 nm  f=0.0000  <S**2>=2.000
    138A ->139A        0.33070
    138A ->140A        0.62636
    138B ->139B       -0.33070
    138B ->140B       -0.62636

 Excited State   3:  1.000-A      2.0028 eV  619.04 nm  f=0.5963  <S**2>=0.000
    136A ->140A       -0.13991
    138A ->139A        0.58089
    138A ->140A        0.37326
    136B ->140B       -0.13991
    138B ->139B        0.58089
    138B ->140B        0.37326

 Excited State   4:  1.000-A      2.0028 eV  619.04 nm  f=0.5963  <S**2>=0.000
    136A ->139A        0.13991
    138A ->139A       -0.37326
    138A ->140A        0.58089
    136B ->139B        0.13991
    138B ->139B       -0.37326
    138B ->140B        0.58089

 Excited State   5:  3.000-A      2.6894 eV  461.00 nm  f=0.0000  <S**2>=2.000
    136A ->139A        0.47673
    136A ->140A        0.42620
    137A ->139A       -0.18691
    137A ->140A       -0.14104
    136B ->139B       -0.47673
    136B ->140B       -0.42620
    137B ->139B        0.18691
    137B ->140B        0.14104

 Excited State   6:  3.000-A      2.6894 eV  461.00 nm  f=0.0000  <S**2>=2.000
    136A ->139A       -0.42620
    136A ->140A        0.47673
    137A ->139A       -0.14104
    137A ->140A        0.18690
    136B ->139B        0.42620
    136B ->140B       -0.47673
    137B ->139B        0.14104
    137B ->140B       -0.18690

 Excited State   7:  3.000-A      2.8430 eV  436.10 nm  f=0.0000  <S**2>=2.000
    132A ->141A       -0.14939
    134A ->139A        0.33948
    134A ->140A        0.27874
    135A ->139A        0.27874
    135A ->140A       -0.33948
    138A ->142A        0.20918
    132B ->141B        0.14939
    134B ->139B       -0.33948
    134B ->140B       -0.27874
    135B ->139B       -0.27874
    135B ->140B        0.33948
    138B ->142B       -0.20918

 Excited State   8:  3.000-A      2.8802 eV  430.47 nm  f=0.0000  <S**2>=2.000
    130A ->140A       -0.13298
    131A ->139A       -0.13298
    134A ->139A        0.33588
    134A ->140A        0.27853
    135A ->139A       -0.27852
    135A ->140A        0.33588
    137A ->141A        0.17794
    138A ->143A       -0.11363
    130B ->140B        0.13298
    131B ->139B        0.13298
    134B ->139B       -0.33588
    134B ->140B       -0.27853
    135B ->139B        0.27852
    135B ->140B       -0.33588
    137B ->141B       -0.17794
    138B ->143B        0.11363

 Excited State   9:  3.000-A      2.9089 eV  426.23 nm  f=0.0000  <S**2>=2.000
    132A ->139A        0.21496
    132A ->140A       -0.28315
    135A ->141A       -0.15795
    136A ->139A       -0.10771
    136A ->140A        0.14239
    137A ->139A        0.34564
```

```
   137A ->140A       -0.38788
   132B ->139B       -0.21496
   132B ->140B        0.28315
   135B ->141B        0.15795
   136B ->139B        0.10771
   136B ->140B       -0.14239
   137B ->139B       -0.34564
   137B ->140B        0.38788

 Excited State  10:  3.000-A      2.9089 eV  426.23 nm  f=0.0000  <S**2>=2.000
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   132A ->140A       -0.21496
   134A ->141A        0.15795
   136A ->139A        0.14240
   136A ->140A        0.10771
   137A ->139A        0.38788
   137A ->140A        0.34564
   132B ->139B        0.28315
   132B ->140B        0.21496
   134B ->141B       -0.15795
   136B ->139B       -0.14240
   136B ->140B       -0.10771
   137B ->139B       -0.38788
   137B ->140B       -0.34564
```
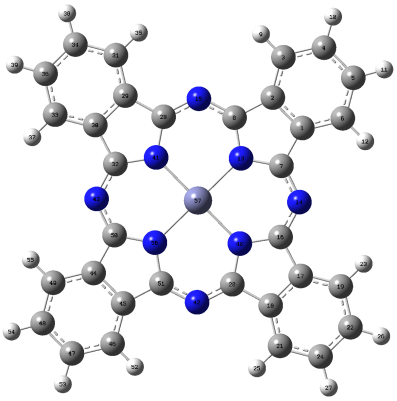

Zn-Phthalocyanine Excited State



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5	6	0	0.821161	6.638225	-0.000406
6	6	0	1.528271	5.417775	-0.000295
7	6	0	1.183111	2.817462	-0.000080
8	6	0	-1.087882	2.855480	-0.000097
9	1	0	-2.432152	5.484969	-0.000352
10	1	0	-1.114319	7.618741	-0.000514
11	1	0	1.368162	7.577450	-0.000472
12	1	0	2.614347	5.401342	-0.000269
13	7	0	0.034293	2.035628	-0.000013
14	7	0	2.474194	2.376194	-0.000002
15	7	0	-2.393192	2.458117	-0.000018
16	6	0	2.851407	1.092715	0.000041
17	6	0	4.259073	0.639331	0.000240
18	6	0	4.235614	-0.781717	0.000129
19	6	0	5.468362	1.343812	0.000489
20	6	0	2.813530	-1.188161	-0.000045
21	6	0	5.421307	-1.525326	0.000251
22	6	0	6.670307	0.595695	0.000622
23	1	0	5.484548	2.429424	0.000591
24	6	0	6.647117	-0.816920	0.000496
25	1	0	5.402437	-2.610876	0.000169
26	1	0	7.625468	1.113650	0.000825
27	1	0	7.584769	-1.365933	0.000597
28	6	0	-2.813531	1.188161	0.000011
29	6	0	-4.235615	0.781717	0.000189
30	6	0	-4.259072	-0.639331	0.000179
31	6	0	-5.421309	1.525325	0.000379
32	6	0	-2.851407	-1.092715	-0.000002
33	6	0	-5.468361	-1.343813	0.000373
34	6	0	-6.647117	0.816918	0.000568
35	1	0	-5.402440	2.610875	0.000390
36	6	0	-6.670306	-0.595698	0.000565
37	1	0	-5.484546	-2.429425	0.000386
38	1	0	-7.584770	1.365930	0.000728
39	1	0	-7.625467	-1.113653	0.000722
40	7	0	2.027838	-0.034377	-0.000090
41	7	0	-2.027838	0.034378	-0.000104
42	7	0	2.393192	-2.458116	-0.000095
43	7	0	-2.474193	-2.376193	-0.000046
44	6	0	-0.787343	-4.222435	-0.000219
45	6	0	0.645318	-4.246331	-0.000223
46	6	0	1.346128	-5.465587	-0.000310
47	6	0	0.598852	-6.661841	-0.000396
48	6	0	-0.821161	-6.638225	-0.000397

49	6	0	-1.528270	-5.417775	-0.000306
50	6	0	-1.183111	-2.817462	-0.000124
51	6	0	1.087882	-2.855480	-0.000133
52	1	0	2.432153	-5.484968	-0.000315
53	1	0	1.114319	-7.618740	-0.000465
54	1	0	-1.368162	-7.577450	-0.000466
55	1	0	-2.614346	-5.401341	-0.000302
56	7	0	-0.034293	-2.035627	-0.000075
57	30	0	-0.000001	-0.000000	0.000003

Zero-point correction=	0.411799	(Hartree/Particle)
Thermal correction to Energy=	0.439966	
Thermal correction to Enthalpy=	0.440910	
Thermal correction to Gibbs Free Energy=	0.354049	
Sum of electronic and zero-point Energies=	-1732.064580	
Sum of electronic and thermal Energies=	-1732.036413	
Sum of electronic and thermal Enthalpies=	-1732.035469	
Sum of electronic and thermal Free Energies=	-1732.122330	

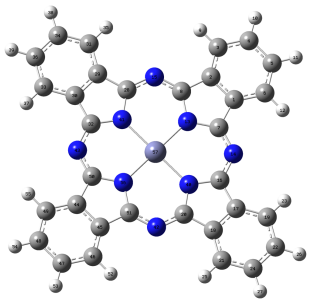
Energy of the excited state with solvatation correction:

After PCM corrections, the energy is -1732.46849464 a.u.

Energy of the ground state with the excited state geometry:
SCF Done: E(UB3LYP) = -1732.54129673 A.U. after 9 cycles

$E^{vert\text{-}abso}$= 619 nm $E^{vert\text{-}fluo}$= 626 nm

Zn-Phthalocyanine Radical Anion



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5	6	0	-6.627448	0.989742	0.000006
6	6	0	-5.387876	1.663020	0.000004
7	6	0	-2.784096	1.263557	0.000002
8	6	0	-2.880678	-1.021980	0.000002
9	1	0	-5.551446	-2.286738	0.000004
10	1	0	-7.656227	-0.919146	0.000006
11	1	0	-7.552136	1.561585	0.000007
12	1	0	-5.341050	2.748209	0.000005
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14	7	0	-2.334277	2.518728	0.000002
15	7	0	-2.539285	-2.310891	0.000001
16	6	0	-1.014906	2.889200	0.000000
17	6	0	-0.537872	4.261990	0.000001
18	6	0	0.897873	4.200992	-0.000001
19	6	0	-1.204029	5.508071	0.000002
20	6	0	1.256437	2.792559	-0.000001
21	6	0	1.667336	5.386144	-0.000001
22	6	0	-0.430411	6.678851	0.000001
23	1	0	-2.289663	5.556002	0.000002
24	6	0	0.995770	6.618329	0.000000
25	1	0	2.753171	5.342169	-0.000001
26	1	0	-0.919086	7.650511	0.000002
27	1	0	1.565028	7.545077	0.000000
28	6	0	-1.256437	-2.792559	0.000001
29	6	0	-0.897873	-4.200992	0.000001
30	6	0	0.537872	-4.261990	0.000000
31	6	0	-1.667337	-5.386144	0.000002
32	6	0	1.014905	-2.889200	-0.000001
33	6	0	1.204028	-5.508072	0.000000
34	6	0	-0.995772	-6.618329	0.000002
35	1	0	-2.753172	-5.342169	0.000002
36	6	0	0.430410	-6.678852	0.000001
37	1	0	2.289662	-5.556004	-0.000000
38	1	0	-1.565030	-7.545077	0.000003
39	1	0	0.919085	-7.650511	0.000001
40	7	0	0.086881	2.041047	-0.000001
41	7	0	-0.086881	-2.041047	-0.000001
42	7	0	2.539285	2.310891	-0.000002
43	7	0	2.334279	-2.518728	-0.000001
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46	6	0	5.508038	1.201385	-0.000005
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48	6	0	6.627449	-0.989741	-0.000006
49	6	0	5.387877	-1.663019	-0.000004
50	6	0	2.784096	-1.263557	-0.000002
51	6	0	2.880678	1.021980	-0.000002
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53	1	0	7.656227	0.919148	-0.000007

54	1	0	7.552137	-1.561583	-0.000006
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57	30	0	0.000000	-0.000000	-0.000001

Zero-point correction= 0.411908 (Hartree/Particle)
Thermal correction to Energy= 0.439903
Thermal correction to Enthalpy= 0.440847
Thermal correction to Gibbs Free Energy= 0.354053
Sum of electronic and zero-point Energies= -1732.259004
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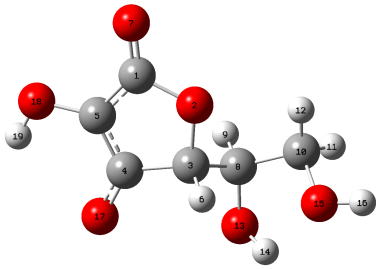
Sum of electronic and thermal Free Energies= -1732.316859

Ascorbate Anion



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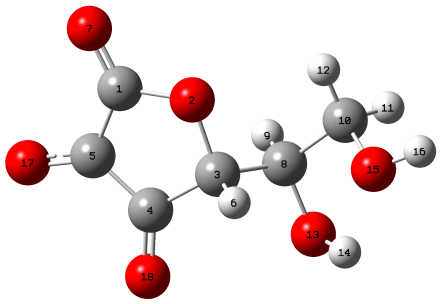
3	6	0	0.003468	0.092965	-0.446658
4	6	0	-1.097363	1.162405	-0.306526
5	6	0	-2.282608	0.469676	-0.011113
6	1	0	0.438571	0.094249	-1.452641
7	8	0	-2.878073	-1.905930	0.236552
8	6	0	1.133952	0.146739	0.611899
9	1	0	0.689081	0.201848	1.610395
10	6	0	2.060161	-1.073694	0.527518
11	1	0	2.751931	-1.065734	1.379537
12	1	0	1.481132	-2.002278	0.521190
13	8	0	1.935940	1.357338	0.450418
14	1	0	2.592858	1.172612	-0.260080
15	8	0	2.805580	-0.910805	-0.733695
16	1	0	3.575476	-1.513671	-0.766365
17	8	0	-0.951500	2.438053	-0.445988
18	8	0	-3.533512	1.086073	0.219835
19	1	0	-3.411955	2.057278	0.129803

Zero-point correction= 0.134470 (Hartree/Particle)
Thermal correction to Energy= 0.146513
Thermal correction to Enthalpy= 0.147457
Thermal correction to Gibbs Free Energy= 0.095848
Sum of electronic and zero-point Energies= -684.111207
Sum of electronic and thermal Energies= -684.099165
Sum of electronic and thermal Enthalpies= -684.098220
Sum of electronic and thermal Free Energies= -684.149829

Ascorbate Radical Anion



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.696901	-1.106906	-0.021462
2	8	0	-0.321386	-1.247191	-0.325733
3	6	0	0.318454	0.098003	-0.434025
4	6	0	-0.841420	1.091926	-0.275186
5	6	0	-2.045490	0.329119	0.019348
6	1	0	0.776062	0.162713	-1.426875
7	8	0	-2.404922	-2.121280	0.152721
8	6	0	1.422032	0.166892	0.655057
9	1	0	0.958779	0.104306	1.644446
10	6	0	2.449213	-0.961156	0.490894
11	1	0	3.128936	-0.961044	1.352212

12	1	0	1.953636	-1.933360	0.404030
13	8	0	2.111033	1.450473	0.601866
14	1	0	2.790716	1.385596	-0.108348
15	8	0	3.185746	-0.633688	-0.741654
16	1	0	4.000459	-1.169937	-0.817953
17	8	0	-3.240949	0.784936	0.262792
18	8	0	-0.735011	2.354807	-0.406900

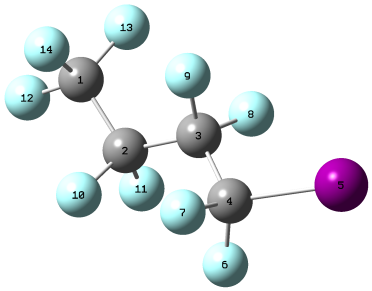
Zero-point correction=	0.123215 (Hartree/Particle)
Thermal correction to Energy=	0.134553
Thermal correction to Enthalpy=	0.135497
Thermal correction to Gibbs Free Energy=	0.084548
Sum of electronic and zero-point Energies=	-683.514461
Sum of electronic and thermal Energies=	-683.503124
Sum of electronic and thermal Enthalpies=	-683.502180
Sum of electronic and thermal Free Energies=	-683.553129

H^+ proton

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

Zero-point correction=	0.000000 (Hartree/Particle)
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.010654
Sum of electronic and zero-point Energies=	-0.498916
Sum of electronic and thermal Energies=	-0.497500
Sum of electronic and thermal Enthalpies=	-0.496555
Sum of electronic and thermal Free Energies=	-0.509570

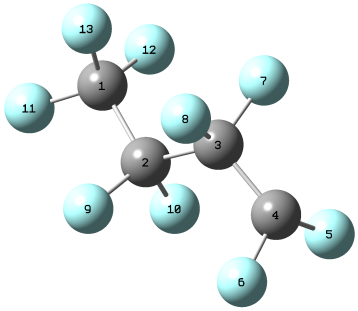
C4F9I



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.034411	-0.417897	0.103297
2	6	0	1.790176	0.487898	-0.210446
3	6	0	0.398724	-0.227432	-0.051353
4	6	0	-0.839110	0.708564	0.150635
5	53	0	-2.751037	-0.288026	-0.051285
6	9	0	-0.729330	1.760191	-0.785116
7	9	0	-0.736467	1.291682	1.427752
8	9	0	0.201633	-1.010727	-1.198265
9	9	0	0.470424	-1.101756	1.046992
10	9	0	1.858043	1.601068	0.637680
11	9	0	1.912053	0.945014	-1.527361
12	9	0	4.186380	0.200606	-0.356934
13	9	0	2.919536	-1.651452	-0.524549
14	9	0	3.171276	-0.624766	1.466571

Zero-point correction=	0.046176 (Hartree/Particle)
Thermal correction to Energy=	0.060179
Thermal correction to Enthalpy=	0.061123
Thermal correction to Gibbs Free Energy=	0.002893
Sum of electronic and zero-point Energies=	-1062.310468
Sum of electronic and thermal Energies=	-1062.296465
Sum of electronic and thermal Enthalpies=	-1062.295521
Sum of electronic and thermal Free Energies=	-1062.353751

C4F9 radical



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.974777	-0.182457	-0.092804
2	6	0	-2.296722	0.431897	1.181084
3	6	0	-2.711366	-0.207826	2.556443
4	6	0	-2.394260	0.590008	3.814772
5	9	0	-3.200005	1.662812	4.075144
6	9	0	-1.069632	0.865007	4.027272
7	9	0	-4.099368	-0.436221	2.526032
8	9	0	-2.064693	-1.452866	2.659726
9	9	0	-0.908682	0.320338	1.042748
10	9	0	-2.616168	1.799371	1.217604
11	9	0	-2.307701	0.241717	-1.231339
12	9	0	-4.297889	0.218212	-0.191541
13	9	0	-2.934438	-1.570192	-0.054142

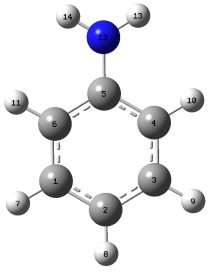
Zero-point correction=	0.044599	(Hartree/Particle)
Thermal correction to Energy=	0.057113	
Thermal correction to Enthalpy=	0.058057	
Thermal correction to Gibbs Free Energy=	0.003857	
Sum of electronic and zero-point Energies=	-1050.874848	
Sum of electronic and thermal Energies=	-1050.862334	
Sum of electronic and thermal Enthalpies=	-1050.861390	
Sum of electronic and thermal Free Energies=	-1050.915590	

I^- anion

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	53	0	0.709746	0.466102	0.000000

Zero-point correction=	0.000000	(Hartree/Particle)
Thermal correction to Energy=	0.001416	
Thermal correction to Enthalpy=	0.002360	
Thermal correction to Gibbs Free Energy=	-0.016848	
Sum of electronic and zero-point Energies=	-11.571310	
Sum of electronic and thermal Energies=	-11.569894	
Sum of electronic and thermal Enthalpies=	-11.568950	
Sum of electronic and thermal Free Energies=	-11.588158	

Aniline

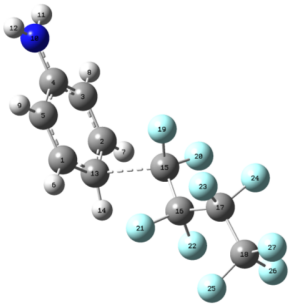


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.769028	-1.832578	-0.113091
2	6	0	4.173495	-1.906597	0.005919
3	6	0	4.908938	-0.707307	0.119927
4	6	0	4.262651	0.541082	0.115879
5	6	0	2.847118	0.617833	-0.004105
6	6	0	2.107633	-0.592132	-0.118867
7	1	0	2.183778	-2.745705	-0.202077
8	1	0	4.678903	-2.868507	0.009721
9	1	0	5.992621	-0.742821	0.212694
10	1	0	4.843684	1.457186	0.204702
11	1	0	1.023886	-0.551445	-0.211420
12	7	0	2.199664	1.850266	-0.009015
13	1	0	2.719592	2.711969	0.071560

14	1	0	1.195506	1.910827	-0.094688

Zero-point correction=	0.117274 (Hartree/Particle)
Thermal correction to Energy=	0.123315
Thermal correction to Enthalpy=	0.124259
Thermal correction to Gibbs Free Energy=	0.087850
Sum of electronic and zero-point Energies=	-287.455693
Sum of electronic and thermal Energies=	-287.449652
Sum of electronic and thermal Enthalpies=	-287.448708
Sum of electronic and thermal Free Energies=	-287.485116

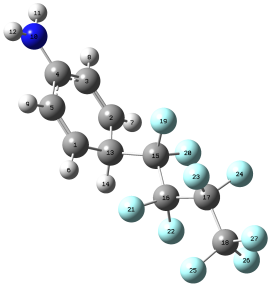
TS aniline C4F9



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.606343	-0.796289	-1.298503
2	6	0	-3.062818	1.486227	-0.491831
3	6	0	-4.174346	1.017876	0.212096
4	6	0	-4.515905	-0.374628	0.188167
5	6	0	-3.718602	-1.269109	-0.599939
6	1	0	-2.020679	-1.481034	-1.905329
7	1	0	-2.828240	2.546704	-0.484328
8	1	0	-4.802183	1.709001	0.769564
9	1	0	-3.999228	-2.318051	-0.659285
10	7	0	-5.603669	-0.840856	0.888590
11	1	0	-6.178372	-0.218075	1.440751
12	1	0	-5.856427	-1.820197	0.873785
13	6	0	-2.197936	0.580877	-1.201866
14	1	0	-1.515063	0.980784	-1.945764
15	6	0	-0.457764	0.466681	0.250489
16	6	0	0.899967	0.165583	-0.389835
17	6	0	2.098221	-0.288779	0.518720
18	6	0	3.533269	-0.134702	-0.091389
19	9	0	-0.756702	-0.536559	1.205718
20	9	0	-0.395665	1.692867	0.951373
21	9	0	0.716864	-0.864834	-1.346882
22	9	0	1.317711	1.316609	-1.097623
23	9	0	1.923777	-1.636688	0.863612
24	9	0	2.076616	0.458738	1.710652
25	9	0	3.585100	-0.645069	-1.383086
26	9	0	3.925016	1.195492	-0.128453
27	9	0	4.456109	-0.828953	0.681780

Zero-point correction=	0.162787 (Hartree/Particle)
Thermal correction to Energy=	0.181992
Thermal correction to Enthalpy=	0.182936
Thermal correction to Gibbs Free Energy=	0.112528
Sum of electronic and zero-point Energies=	-1338.337886
Sum of electronic and thermal Energies=	-1338.318681
Sum of electronic and thermal Enthalpies=	-1338.317737
Sum of electronic and thermal Free Energies=	-1338.388145

Intermediary aniline C4F9 radical adduct

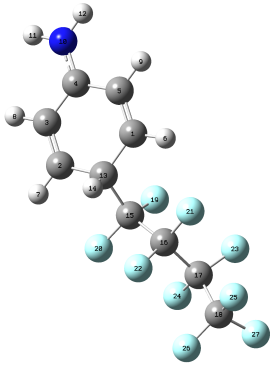


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.306632	-1.108981	-0.751865
2	6	0	-2.861553	1.349133	-0.595231
3	6	0	-4.081005	1.009840	-0.055769
4	6	0	-4.452840	-0.354789	0.192455
5	6	0	-3.541590	-1.387921	-0.213082
6	1	0	-1.672166	-1.920355	-1.091565

7	1	0	-2.630510	2.387604	-0.810611
8	1	0	-4.800217	1.797662	0.163357
9	1	0	-3.850757	-2.427451	-0.114561
10	7	0	-5.681101	-0.668008	0.757921
11	1	0	-6.331942	0.056467	1.028234
12	1	0	-5.953002	-1.628047	0.919023
13	6	0	-1.791448	0.314263	-0.911577
14	1	0	-1.417740	0.472941	-1.937834
15	6	0	-0.537806	0.590529	-0.008609
16	6	0	0.815810	-0.051310	-0.459479
17	6	0	1.983811	-0.059255	0.589883
18	6	0	3.422572	-0.224555	-0.016975
19	9	0	-0.766273	0.184354	1.332992
20	9	0	-0.283180	1.990523	0.053297
21	9	0	0.611253	-1.388802	-0.847197
22	9	0	1.262802	0.634747	-1.608760
23	9	0	1.775598	-1.115123	1.487600
24	9	0	1.985356	1.132802	1.327289
25	9	0	3.459032	-1.255743	-0.947393
26	9	0	3.843454	0.942698	-0.635671
27	9	0	4.324073	-0.521942	0.995231

Zero-point correction=	0.164356 (Hartree/Particle)
Thermal correction to Energy=	0.183465
Thermal correction to Enthalpy=	0.184409
Thermal correction to Gibbs Free Energy=	0.115246
Sum of electronic and zero-point Energies=	-1338.357799
Sum of electronic and thermal Energies=	-1338.338690
Sum of electronic and thermal Enthalpies=	-1338.337746
Sum of electronic and thermal Free Energies=	-1338.406910

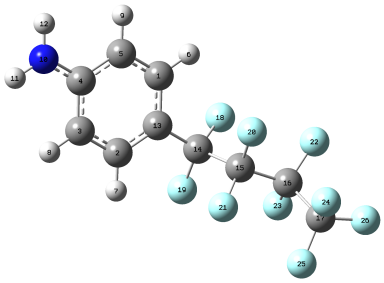
Intermediary aniline C4F9 cation adduct (Wheland intermediary)



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.680736	-1.278842	-1.192703
2	6	0	3.687739	-1.040886	1.333152
3	6	0	3.102948	0.176385	1.213111
4	6	0	2.781959	0.715995	-0.101141
5	6	0	3.093672	-0.060651	-1.293811
6	1	0	3.908213	-1.837937	-2.092832
7	1	0	3.920290	-1.437102	2.315838
8	1	0	2.860821	0.761748	2.094488
9	1	0	2.842726	0.348674	-2.267293
10	7	0	2.203667	1.905508	-0.210314
11	1	0	1.971586	2.464934	0.606826
12	1	0	1.967569	2.306371	-1.114612
13	6	0	4.099795	-1.869080	0.135911
14	1	0	5.205816	-1.889383	0.146058
15	6	0	3.643294	-3.341158	0.315065
16	6	0	4.430258	-4.420821	-0.506184
17	6	0	3.775552	-5.847620	-0.579200
18	6	0	4.775277	-7.013240	-0.908893
19	9	0	2.269380	-3.478227	-0.000833
20	9	0	3.777066	-3.719212	1.672463
21	9	0	4.607515	-3.975785	-1.828164
22	9	0	5.713282	-4.538097	0.058258
23	9	0	2.786584	-5.833468	-1.569880
24	9	0	3.157931	-6.159753	0.638101
25	9	0	5.592788	-6.674854	-1.979965
26	9	0	5.574591	-7.308867	0.183647
27	9	0	4.063382	-8.153711	-1.244786

Zero-point correction=	0.168970 (Hartree/Particle)
Thermal correction to Energy=	0.187351
Thermal correction to Enthalpy=	0.188295
Thermal correction to Gibbs Free Energy=	0.121309
Sum of electronic and zero-point Energies=	-1338.207107
Sum of electronic and thermal Energies=	-1338.188726
Sum of electronic and thermal Enthalpies=	-1338.187782
Sum of electronic and thermal Free Energies=	-1338.254768

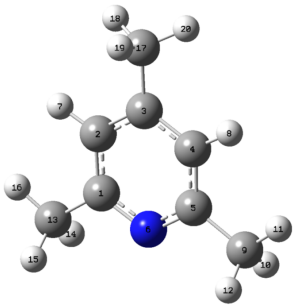
Aniline C4F9 product



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.512415	0.831730	0.894213
2	6	0	-2.519616	-0.468388	-1.174205
3	6	0	-3.833340	-0.868763	-0.922514
4	6	0	-4.515598	-0.424397	0.247959
5	6	0	-3.826534	0.437679	1.151374
6	1	0	-2.008883	1.491124	1.594960
7	1	0	-2.022212	-0.814279	-2.075444
8	1	0	-4.343339	-1.522833	-1.624856
9	1	0	-4.331308	0.790067	2.047032
10	7	0	-5.812703	-0.817482	0.500211
11	1	0	-6.306885	-1.428118	-0.135411
12	1	0	-6.301497	-0.507294	1.328475
13	6	0	-1.845086	0.387133	-0.271603
14	6	0	-0.440066	0.797112	-0.536633
15	6	0	0.677922	-0.122938	0.080181
16	6	0	2.148275	0.424503	0.085600
17	6	0	3.267835	-0.669364	0.203192
18	9	0	-0.161080	2.105572	-0.025663
19	9	0	-0.165267	0.849392	-1.934655
20	9	0	0.340555	-0.406418	1.416389
21	9	0	0.667975	-1.349626	-0.615659
22	9	0	2.301642	1.304351	1.166230
23	9	0	2.406541	1.146730	-1.088311
24	9	0	2.981041	-1.571779	1.220420
25	9	0	3.410998	-1.372427	-0.983272
26	9	0	4.483681	-0.064922	0.491007

Zero-point correction=	0.155200 (Hartree/Particle)
Thermal correction to Energy=	0.173726
Thermal correction to Enthalpy=	0.174671
Thermal correction to Gibbs Free Energy=	0.107247
Sum of electronic and zero-point Energies=	-1337.828149
Sum of electronic and thermal Energies=	-1337.809623
Sum of electronic and thermal Enthalpies=	-1337.808679
Sum of electronic and thermal Free Energies=	-1337.876103

Collidine

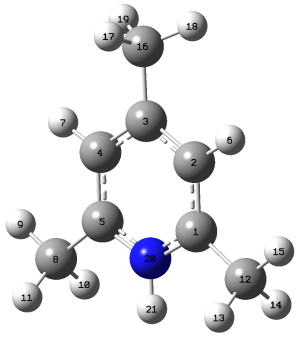


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.712825	1.174401	0.000503
2	6	0	0.697397	1.207743	-0.009047
3	6	0	1.433357	0.002926	-0.011506
4	6	0	0.701980	-1.204927	-0.009863
5	6	0	-0.708122	-1.177059	-0.000292
6	7	0	-1.401015	-0.002590	0.005360
7	1	0	1.212041	2.164582	-0.016639
8	1	0	1.220409	-2.159746	-0.018139
9	6	0	-1.528419	-2.449322	0.001370
10	1	0	-2.184448	-2.486413	-0.877737
11	1	0	-0.889460	-3.338175	-0.004578
12	1	0	-2.173486	-2.490661	0.888393
13	6	0	-1.537863	2.443619	0.003059
14	1	0	-2.194346	2.478703	-0.875782
15	1	0	-2.182719	2.482191	0.890357
16	1	0	-0.902190	3.334824	-0.002712
17	6	0	2.948211	0.005263	0.008154

18	1	0	3.353605	0.907623	-0.463203
19	1	0	3.319964	-0.020688	1.042278
20	1	0	3.356592	-0.871200	-0.507744

Zero-point correction=	0.171769 (Hartree/Particle)
Thermal correction to Energy=	0.181444
Thermal correction to Enthalpy=	0.182388
Thermal correction to Gibbs Free Energy=	0.135400
Sum of electronic and zero-point Energies=	-366.017149
Sum of electronic and thermal Energies=	-366.007474
Sum of electronic and thermal Enthalpies=	-366.006529
Sum of electronic and thermal Free Energies=	-366.053518

Collidine-H^+



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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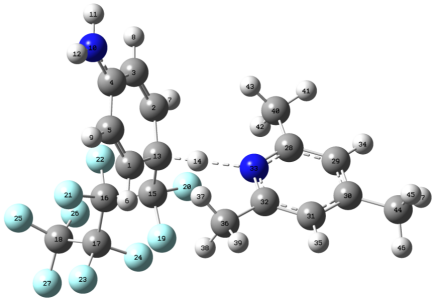
3	6	0	1.460262	0.000460	0.011602
4	6	0	0.735220	-1.214552	0.009462
5	6	0	-0.661325	-1.214749	0.000488
6	1	0	1.255160	2.165480	0.015321
7	1	0	1.256592	-2.164691	0.016156
8	6	0	-1.513732	-2.454066	-0.001928
9	1	0	-0.887127	-3.347768	0.002322
10	1	0	-2.164263	-2.485129	0.881057
11	1	0	-2.155397	-2.487484	-0.891297
12	6	0	-1.515346	2.453016	-0.002813
13	1	0	-2.157195	2.485594	-0.892078
14	1	0	-2.165737	2.484062	0.880277
15	1	0	-0.889329	3.347131	0.000907
16	6	0	2.967909	0.000948	-0.006758
17	1	0	3.326976	0.000688	-1.045689
18	1	0	3.374770	0.892467	0.480520
19	1	0	3.375348	-0.889960	0.481157
20	7	0	-1.301373	-0.000453	-0.004259
21	1	0	-2.321218	-0.000783	-0.008693

Zero-point correction=	0.186690 (Hartree/Particle)
Thermal correction to Energy=	0.196291
Thermal correction to Enthalpy=	0.197235
Thermal correction to Gibbs Free Energy=	0.151352
Sum of electronic and zero-point Energies=	-366.464832
Sum of electronic and thermal Energies=	-366.455231
Sum of electronic and thermal Enthalpies=	-366.454287
Sum of electronic and thermal Free Energies=	-366.500170

Transition state Wheland intermediary and collidine



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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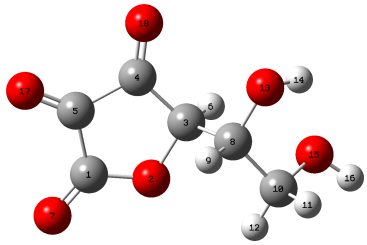
3	6	0	-0.317326	3.211548	1.244561
4	6	0	-0.414071	3.939332	-0.006142
5	6	0	-0.365727	3.211087	-1.258354
6	1	0	-0.219799	1.319257	-2.205736
7	1	0	-0.138149	1.320408	2.187383
8	1	0	-0.302379	3.766264	2.177472
9	1	0	-0.384116	3.765283	-2.191495
10	7	0	-0.520503	5.271825	-0.003717

11	1	0	-0.545229	5.802567	0.861460
12	1	0	-0.586777	5.802505	-0.866727
13	6	0	-0.331158	1.053661	-0.006512
14	1	0	-1.429031	0.560520	0.011514
15	6	0	0.546451	-0.198305	-0.019495
16	6	0	2.101898	-0.002265	0.017521
17	6	0	2.977071	-1.257498	-0.335617
18	6	0	4.450330	-1.209249	0.205143
19	9	0	0.264664	-0.969480	-1.180061
20	9	0	0.216482	-1.015428	1.092914
21	9	0	2.453327	1.020688	-0.879568
22	9	0	2.457197	0.439801	1.306777
23	9	0	3.035823	-1.387629	-1.728623
24	9	0	2.384081	-2.418376	0.178528
25	9	0	5.038886	0.018874	-0.071059
26	9	0	4.488482	-1.420746	1.574151
27	9	0	5.203171	-2.200599	-0.405068
28	6	0	-3.527705	-0.540979	1.216615
29	6	0	-4.667701	-1.367498	1.235261
30	6	0	-5.265817	-1.788050	0.030010
31	6	0	-4.677833	-1.343373	-1.174043
32	6	0	-3.537960	-0.520887	-1.148598
33	7	0	-2.974455	-0.133314	0.036291
34	1	0	-5.081929	-1.675475	2.190334
35	1	0	-5.101128	-1.633358	-2.131071
36	6	0	-2.890969	-0.041317	-2.428657
37	1	0	-2.650429	1.025785	-2.371547
38	1	0	-1.960526	-0.590390	-2.626802
39	1	0	-3.557620	-0.195618	-3.281838
40	6	0	-2.874196	-0.088355	2.502635
41	1	0	-3.541741	-0.247425	3.354310
42	1	0	-1.949659	-0.650460	2.690580
43	1	0	-2.621165	0.976137	2.461038
44	6	0	-6.509957	-2.648564	0.022234
45	1	0	-7.390022	-2.040503	-0.232038
46	1	0	-6.440621	-3.443225	-0.729362
47	1	0	-6.692255	-3.103449	1.000792

Zero-point correction=	0.340299	(Hartree/Particle)
Thermal correction to Energy=	0.368943	
Thermal correction to Enthalpy=	0.369888	
Thermal correction to Gibbs Free Energy=	0.277020	
Sum of electronic and zero-point Energies=	-1704.237876	
Sum of electronic and thermal Energies=	-1704.209232	
Sum of electronic and thermal Enthalpies=	-1704.208288	
Sum of electronic and thermal Free Energies=	-1704.301155	

Dehydroascorbate



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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2	8	0	-0.371966	-1.249442	-0.301185
3	6	0	0.335556	0.076251	-0.418389
4	6	0	-0.765649	1.117136	-0.287073
5	6	0	-2.067491	0.362405	0.024562
6	1	0	0.806635	0.097152	-1.405456
7	8	0	-2.470879	-2.091749	0.144830
8	6	0	1.435773	0.133855	0.684863
9	1	0	0.978484	0.051639	1.673786
10	6	0	2.462096	-0.985977	0.478681
11	1	0	3.163506	-0.987902	1.321611
12	1	0	1.973478	-1.962815	0.398476
13	8	0	2.086824	1.428113	0.624654
14	1	0	2.781582	1.383522	-0.073400
15	8	0	3.148090	-0.628432	-0.769189
16	1	0	3.941305	-1.182358	-0.913376
17	8	0	-3.179440	0.844038	0.251856
18	8	0	-0.678479	2.343288	-0.422827

Zero-point correction=	0.124281	(Hartree/Particle)
Thermal correction to Energy=	0.135701	
Thermal correction to Enthalpy=	0.136645	
Thermal correction to Gibbs Free Energy=	0.086119	
Sum of electronic and zero-point Energies=	-683.337998	
Sum of electronic and thermal Energies=	-683.326578	
Sum of electronic and thermal Enthalpies=	-683.325634	
Sum of electronic and thermal Free Energies=	-683.376160	

This work used TUPAC Cluster from the Computational Simulation Center of CONICET located in Buenos Aires, Argentina

VII.-Spectral Characterization of Compounds

4-(Perfluorobutyl)aniline, **4-*para*** [2,3], pale yellow oil, 65%. Isolated and purified mass obtained: 40 mg. TLC (CH_2Cl_2/iso-octane 1:1 v/v): Rf = 0.6; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.34 (d, J = 10 Hz, 2 H), 6.71 (d, J = 10 Hz, 2 H), 3.97 (b s, 2 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ:149.6, 128.2, 117.9, 114.2. ^{19}F NMR (564.603 MHz $CDCl_3$) δ: -81.11 (t, 3F), -109.72 (t, 2F), -122.93 (m, 2F), -125.65 (m, 2 F).

2-Perfluorobutylaniline, **4-*ortho*** [3], pale yellow oil, 27%, Isolated and purified mass obtained 17 mg: ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.33 (m, 2H), 6.82 (t, 1H, J = 5 Hz, J = 10 Hz, 1H), 6.74 (d, 1H, J = 10 Hz, 1H), 4.28 (b s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.7, 145.8, 133.0, 131, 129.1, 128.9 (t, CF_2), 122.8, 117.7. ^{19}F NMR (564.603 MHz $CDCl_3$) δ: -80.95 (t, 3F), -108.72 (t, 2F), -122.79 (m, 2F), - 125.85 (m, 2F).

2-methyl-4-(perfluorobutyl)aniline **5** [3], TLC (CH_2Cl_2/*iso*-octane 1:1 v/v): Rf = 0.6; 63%, 41 mg. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.22 (m, 2H), 6.70 (d, J =)Hz, 1H), 3.92 (b s, 2H), 2.19 (s, 3H). ^{13}C NMR (125.721 MHz, $CDCl_3$) δ: 128.8, 125.9, 113.9, 17.3. ^{19}F NMR (470.585 MHz CDCl3) δ: -81.06 (t, 3F), -109.51 (t, 2F), -122.78 (m, 2F), - 125.62 (m, 2F).

2,5-dimethoxy-4-(perfluorobutyl)aniline, **6** [7], yellow oil. Yield= 99%, Isolated and purified mass obtained: 74 mg. TLC (CH_2Cl_2: iso-octane 7:3 v/v): Rf= 0.69 ^{1}H NMR (600 MHz, CDCl3) δ: 6.82 (s, 1H), 6.35 (s, 1H), 4.15 (b s, 2H), 3.83 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ: 154.1, 141.2, 140.6, 116.8 (CF_2), 110.9, 104.9, 99.8, 56.7, 56.3. ^{19}F NMR (564.63

MHz, $CDCl_3$) δ: -81.00 (t, 3F), -106.20 (t, 2F), -122.25 (m, 2F), -126.06 (m, 2F).

N,N-Dimethyl-4-(perfluorobutyl)aniline, **7**, [3]: yellow oil, 85% yield. Isolated and purified mass obtained: 58 mg. TLC CH_2Cl_2/iso-octane 1:1 v/v): Rf = 0.75; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.40 (d, 2H, J = 10Hz), 6.71 (d, 2H, J = 9Hz), 3.02 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 152.8, 128.3, 115.6, 111.5, 40.4 ^{19}F NMR (564.603 MHz $CDCl_3$) δ: -81.08 (t, 3F), -109.44 (t, 2F), -122.91 (m, 2F), -125.65 (m, 2F).

N,N-Dimethyl-4-(1,1,2,2,3,3,4,4,4-nonafluorobutyl)naphthalene-1- amine **8,** [4]: Yield 56 mg isolated (72% GC yield); yellowish oil. ^{1} HNMR (600.1 MHz, $CDCl_3$): δ = 2.95 (s, 6 H, Me), 7.05 (d, 1 H, J = 8.1 Hz), 7.41 (t, 1 H, J = 8.06, 7.97 Hz), 7.54 (m, 3 H), 7.70 (d, 1 H, J = 8.25 Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.2 (Me), 112.4 (C), 118.3 (CH), 123.3 (CH), 124.5 (CH), 125.6 (CH), 126.1 (CH), 129.2 (C), 132.2 (C), 155.6 (C) ppm. ^{19}F NMR (564.603 MHz, $CDCl_3$): δ = –81.32 (CF_3), –111.64 (CF_2), –123.3 (CF_2), –126.17 (CF_2) ppm.

5-Methyl-4-(perfuorobutyl)pyridin-2-amine **9**, [7]. Yield 35%. Isolated and purified mass obtained: 23 mg. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.07 (s, 1H), 7.47 (s, 1H), 6.07 (broad s, 2H), 3.33 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: 154.6, 152.9, 142.3, 137.7, 120.6, 16.4. ^{19}F NMR (564.63 MHz, DMSO-d_6) δ: -80.5 (t, 3F), -108.86 (m, 2F), -122.23 (m, 2F), -125.34 (m, 2F).

5-Bromo-3-(perfluorobutyl)pyridin-2-amine **10**, [7]. Yield 33%. Isolated and purified mass obtained: 26 mg. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 8.31 (s, 1H), 7.79 (s, H), 6.65 (broad s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ: 155.2, 153.3, 139.2, 104.1, 99.5. ^{19}F NMR (564.63 MHz, DMSO-d_6) δ: -80.49 (t, 3F), -109.39 (m, 2F), -122.21 (m, 2F), -125.27 (m, 2F).

5-(Perfluorobutyl)pyrimidine-2,4,6-triamine **11**, [7]. Pale yellow oil. Yield 45%. Isolated and purified mass obtained: 31 mg. ^{1}H NMR (600 MHz, DMSO-d_6) δ: – ^{13}C NMR (151 MHz, DMSO-d_6) δ: 162.4, 162.5. ^{19}F NMR (564.63 MHz, DMSO-d_6) δ: -80.41 (t, 3F), -101.47 (m, 2F), -122.77 (m, 2F), -125.35 (m, 2F).

2-Methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-1H-indole **12** [6]: Yield 67mg isolated (99% yield); yellowish oil. ^{1} HNMR (600 MHz, $CDCl_3$): δ = 2.53 (t, 3H), 7.20 (ddt, 2 H, J = 6, 12 Hz), 7,32 (d, 1H, J = 6Hz), 7.66 (d, 1H, J = 12Hz), 8.20 (broad s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): 13.1, 110.7, 114.0, 119.8, 120.3, 121.5, 122.6, 126.5 (**C**F_3), 134.7, 136.8, 137.6 (**C**F_2). ^{19}F NMR (564.603 MHz, $CDCl_3$) δ: -81.03 (C**F**$_3$), -104.86 (CF_2), -123.1 (CF_2), -125.9 (CF_2).

3-(Dimethylaminomethyl)indole **13** .Yield 66mg isolated (85% yield) yellowish oil. ^{1} HNMR (600.1 MHz, $CDCl_3$): δ = 2.27 (s, 6H), 3.67 (s, 2 H), 7.19 (t, 1H, J = 8 Hz), 7.33 (t, 1H, J = 8 Hz), 7.40 (d, 1H, J = 8 Hz), 7.98 (d, 1H, J = 7.8 Hz), 8.27 (broad s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 45.6 (Me), 45.7 (Me), 63.6 (CH_2), 111.4, 111.5, 120.5, 122.3, 125.2, 128.2, 136.2. ^{19}F NMR (564.603 MHz,

$CDCl_3$) δ = -80.94 (CF_3), -107.34 (CF_2), -122.53 (CF_2), -125.89 (CF_2). HRMS-EI+ (M+1): Calcd. For $C_{15}H_{13}F_9N_2$ = 393,09350, found for M+1, 393,09361.

2-Methoxy-9-methylcarbazole **14** [14]: ^{1} HNMR (600.1 MHz, $CDCl_3$): δ = 3.80 (s, 3H), 3.99 (s, 3H), 6.85 (broad d, 1 H), 6.86 (s, 1H), 7.21 (t, 1H, J = 7.36 Hz), 7.35 (d, 1H, J = 7.36Hz), 7.40 (t, 1H, J = 7.36 Hz), 7.96 (d, 1H, J= 6.87Hz), 8 (s, 1H, J=7.36Hz). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 28.9 (CH3), 55.8 (CH3), 92.8, 107.2, 108.2, 118.9, 119.5, 120.6, 124.3.

2-Methoxy-9-methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-9H-carbazole **15**. Yield 42 % isolated 36 mg; yellowish oil. ^{1} HNMR (600 MHz, $CDCl_3$): δ = 3.85 (s, 3 H), 3.99 (s, 3H), 6.90 (s, 1H), 7.28 (t, 1H, J = 6Hz), 7.39 (d, 1H, J = 6Hz), 7.46 (t, 1H, J = 6Hz), 8.02 (d, 1H, J = 6Hz), 8.18 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 29.5, 56.5, 92.2, 108.8, 116.0, 119.9, 120.1, 121.8, 122.9, 125.5, 127.7, 141.6, 144.3, 157.9. ^{19}F NMR (564.603 MHz, $CDCl_3$) δ = -80.91 (CF_3), -105.71 (CF_2), -121.65 (CF_2), -125.99 (CF_2). HRMS-EI+ (M+1): Calcd. For $C_{18}H_{13}F_9NO$ =430.0775, found for M+1, 430.0779.

2-((4,4,4,4,4,4,4,4,4-Nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)ethan-1-ol **16** [5]. Yield 38 mg (65%), yellowish oil. ^{1}H-NMR (600 MHz, Cl_3CD) δ : 3.89 (t, 2H, J = 6.1 Hz), 3.14 (t, 2H, J = 6.1 Hz), 1.97 (bs, 1H). ^{13}C NMR (150 MHz, Cl_3CD) δ : 61.6, 31.7. ^{19}F NMR (564.603 MHz, Cl_3CD) δ : -81.0 (t, 3F), -87.0 (m, 2F), -120.7 (m, 2F), -125.5 (m, 2F).

N-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17**. Yield 52 mg (60%) yellowish oil. ^{1}H-NMR (600 MHz, Cl_3CD) δ : 3.84 (s, 2 H), 7.45 (m, 3 H), 7.79 (dd, 3 H, J = 7.5 Hz), 8.15 (broad s, 1 H). ^{13}C NMR (150 MHz, Cl_3CD) δ : 32.6 (CH_2), 117.4, 119.7, 125.5, 126.7, 127.6, 127.7, 129.1, 131.1, 135.6, 134.2, 164.1. ^{19}F NMR (564.603 MHz, Cl_3CD) δ : -80.89 (CF_3), -87.74 (CF_2), -120.51 (CF_2), -125.43 (CF_2). HRMS-EI+ (M+1): Calcd. For $C_{16}H_{10}F_9NOS$ = 436,03394. Found for M+1, 426.03401.

Methyl *N*-acetyl-S-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-L-cysteinate **18**. Yield 43 mg (55%) yellowish oil. ^{1}H-NMR (600 MHz, Cl_3CD) δ : 2.06 (s, 3H), 3.40 (dd, 1H, J = 18, 6Hz), 3.57 (1H, dd, J = 18, 6 Hz), 3.81 (s, 3H), 4.91 (m, 1H), 6.32 (d, 1H, J = 6Hz). ^{13}C NMR (150 MHz, $CDCl_3$): 23.1, 30.6, 51.9, 53.3, 170.0, 170.2. δ =, ^{19}F NMR (564.603 MHz, $CDCl_3$): -80.95 (CF_3), -86.47 (m, CF_2), -120.49 (CF_2), -125.47 (CF_2). HRMS-EI+ (M+1): Calcd. For $C_{10}H_{11}F_9NO_3S$: 396,02377. Found for M+1, 396,02388.

2-((4,4,4,4,4,4,4,4,4-Nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)pyrimidin-4-amine **19** [5]. Yield 52 mg (75%) yellowish oil. TLC (AcOEt: MeOH + Acetic Acid 9:1 v/v): Rf = 0.8. ^{1}H-NMR (600 MHz, DMSO-d_6) δ : 8.00 (d, 1H, J = 5.9 Hz), 7.34 (bs, 2H), 6.37 (d, 1H, J = 5.9 Hz). ^{13}C NMR (150 MHz, DMSO-d_6) δ : 163.7, 161.8, 155.6, 104.4. ^{19}F NMR (564.603 MHz, DMSO-d_6) δ : - 80.7 (t, 3F), -87.6 (t, 2F), -120.1 (m, 2F), -125.3 (m, 2F).

6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20.** Yield 25%, isolated mass 18.5 mg, yellowish oil. ^{1}H-NMR (600 MHz, Cl_3CD) δ :

8.39 (s, 1H), 8.98 (s, 1H), 12.47 (broad s, 1H). ^{13}C NMR (150 MHz, Cl_3CD) δ :152.3 (CH), 151.4 (C), 150.4 (CH), 143.4 (CH), 133.7 (C). ^{19}F NMR (564.603 MHz, Cl_3CD) δ : -80.88 (CF_3), -84.51 (S-CF_2), -119.80 (CF_2), -125.45 (CF_2). Calcd. For $C_9H_4F_9N_4S$: 370,9935. Found for M+1, 370.9961.

2-((Perfluorobutyl)thio)benzo[*d*]thiazole **21** [5]**.** Yield: 47%. Isolated and purified mass obtained: 36.2 mg. TLC ($CHCl_3$: iso-octane : MeOH, 0.8 : 1 : 0.2 v/v): Rf = 0.85. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.17 (cplx d, 1H, J = 8.2 Hz, 0.7 Hz), 7.92 (cplx d, 1H, J = 8.1 Hz, 0.7 Hz), 7.58 (m, 1H, J = 8.3 Hz, 1.2 Hz), 7.52 (m, 1H, J = 7.2 Hz, 1.3 Hz). ^{13}C NMR (125.721 MHz, $CDCl_3$) δ: 153.4, 150.0, 138.7, 127.2, 127.1, 124.6, 121.5. ^{19}F NMR (470.585 MHz, $CDCl_3$) δ: −80.9 (t, 3F), −85.2 (t, 2F), −119.8 (m, 2F), −125.5 (m, 2F).

((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23**, Yield 95 mg (99%). ^{1}H-NMR (600 MHz, Cl_3CD) δ : 2.53 (octet, 1H, J = 12 Hz, 6 Hz), 3.21 (m, 1H, J = 12 Hz, 6 Hz), 4.20 (dd, 1H, J = 12 Hz, 6 Hz), 4.31 (dd, 1H, J = 12 Hz, 6 Hz), 4.54 (m, 1H), 6.93 (d, 2H, J = 6Hz), 7.01 (t, 1H, 6 Hz), 7.31 (t, 2H, J = 6Hz). ^{19}F NMR (564.603 MHz, Cl_3CD) δ : -81.09 (t, 3F), -113.80 (dd, 2F), -124.50 (m, 2F), -125.95 (m, 2F). HRMS-EI+ (M+1): Calcd. For $C_{13}H_{10}F_9IO$ = 480,96326. Found for M+1, 480.96340.

VIII.-References from the ESI

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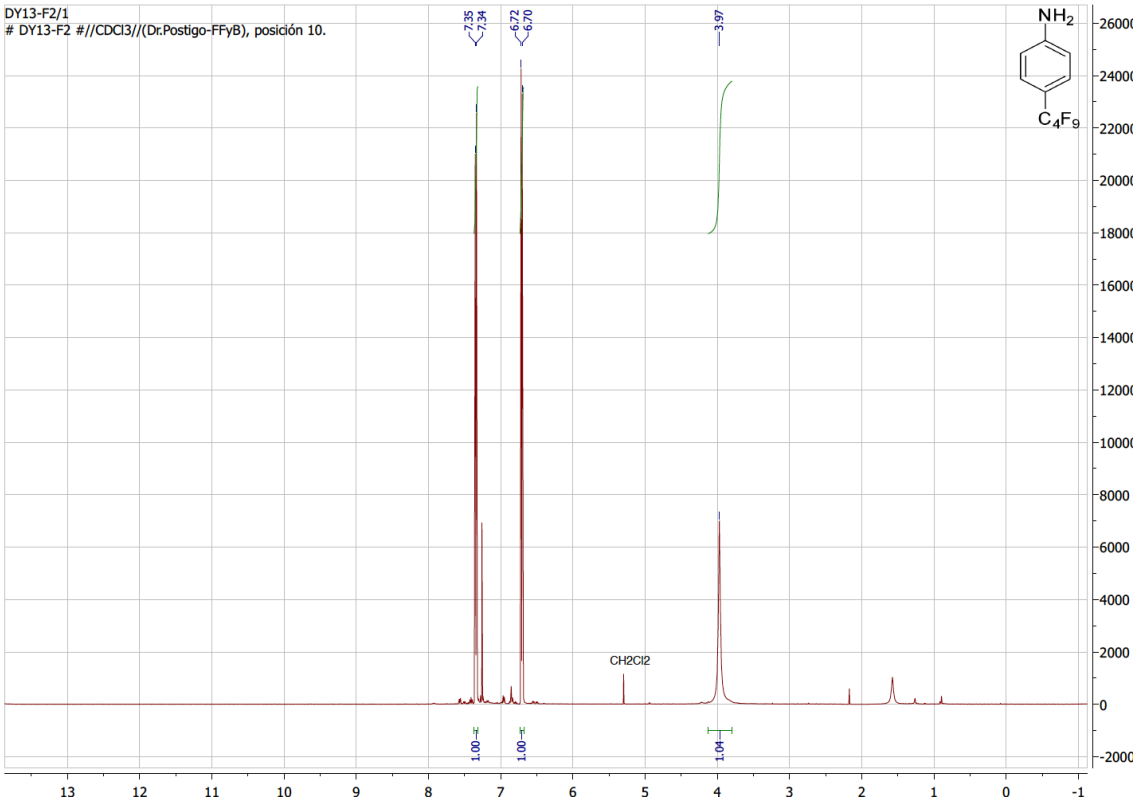
IX.-Copies of NMR spectra

^{1}H NMR spectrum of 4-(nonafluorobutyl)aniline **4** in $CDCl_3$



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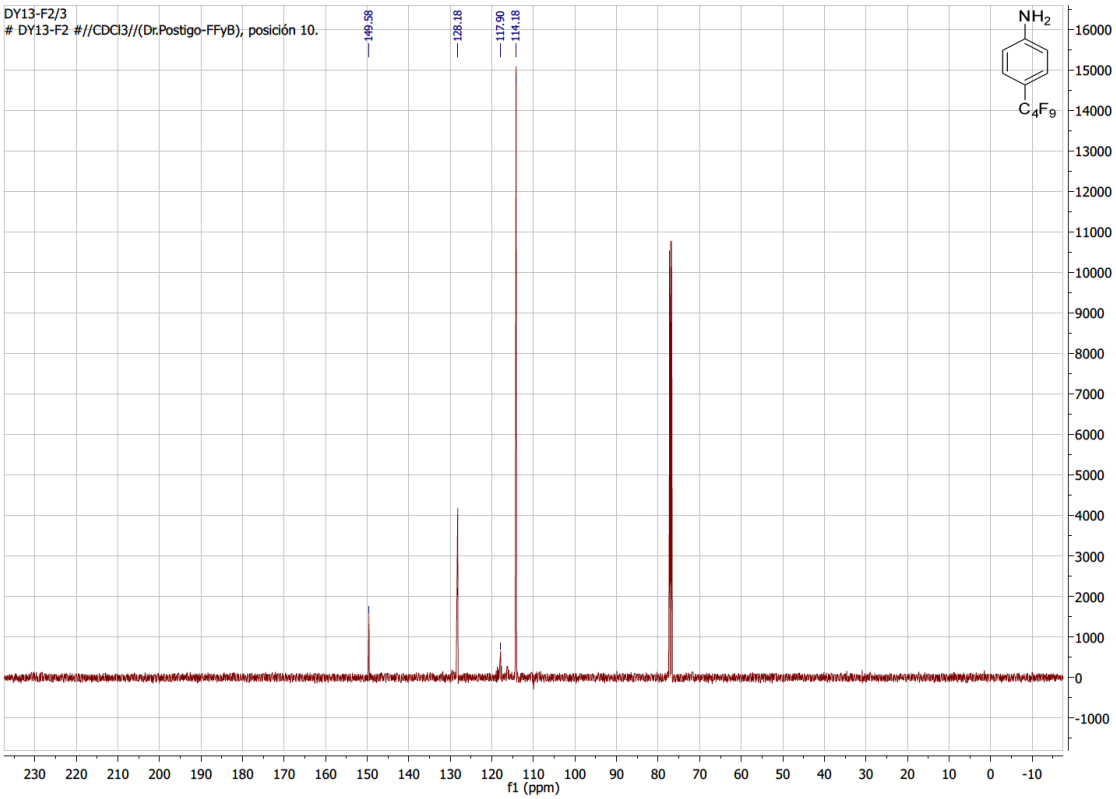

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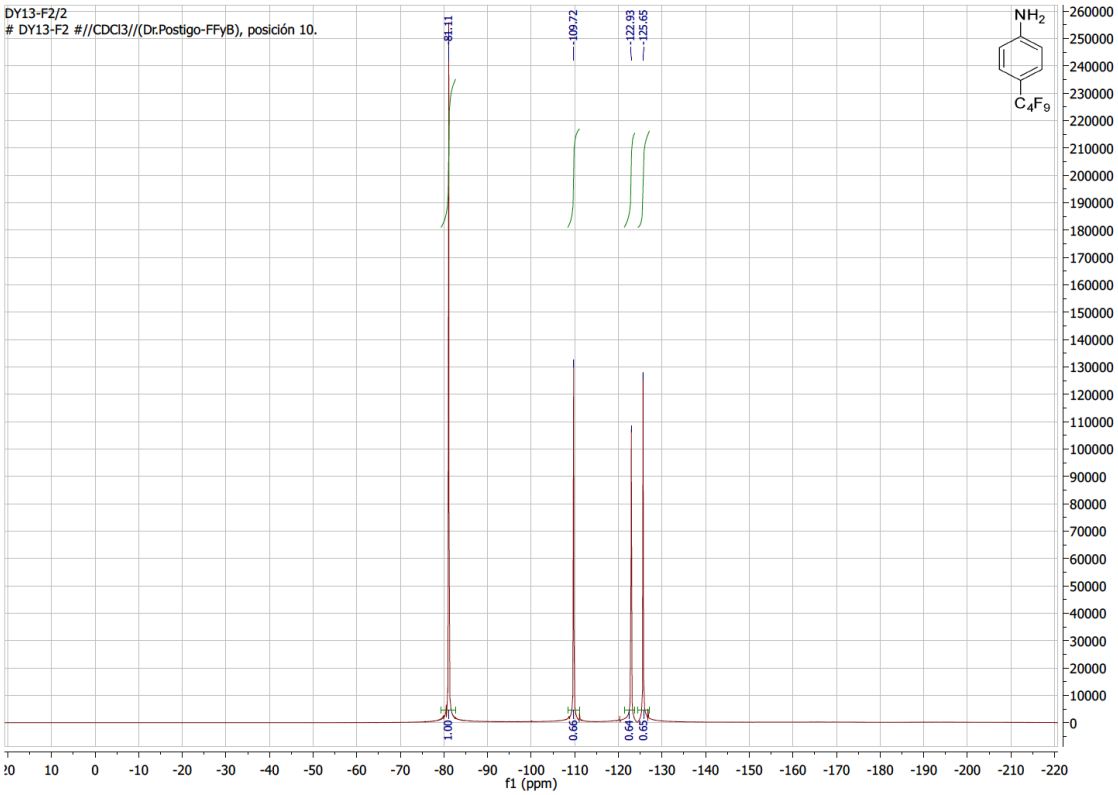

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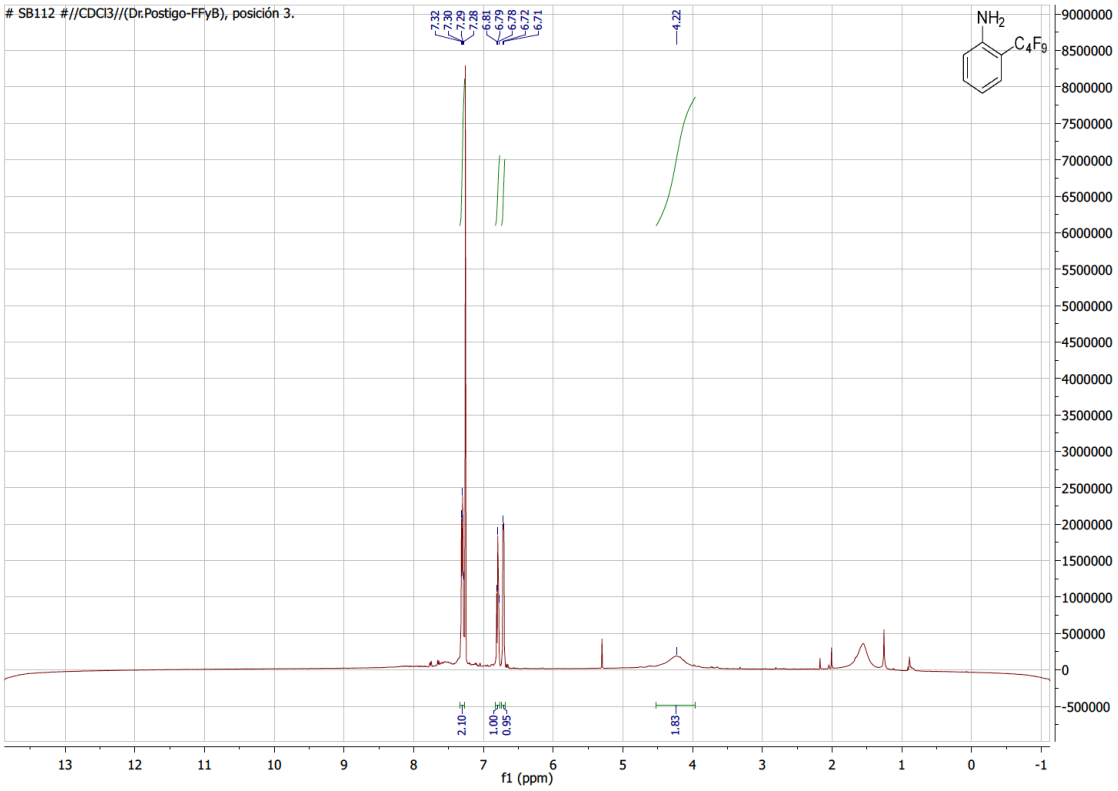

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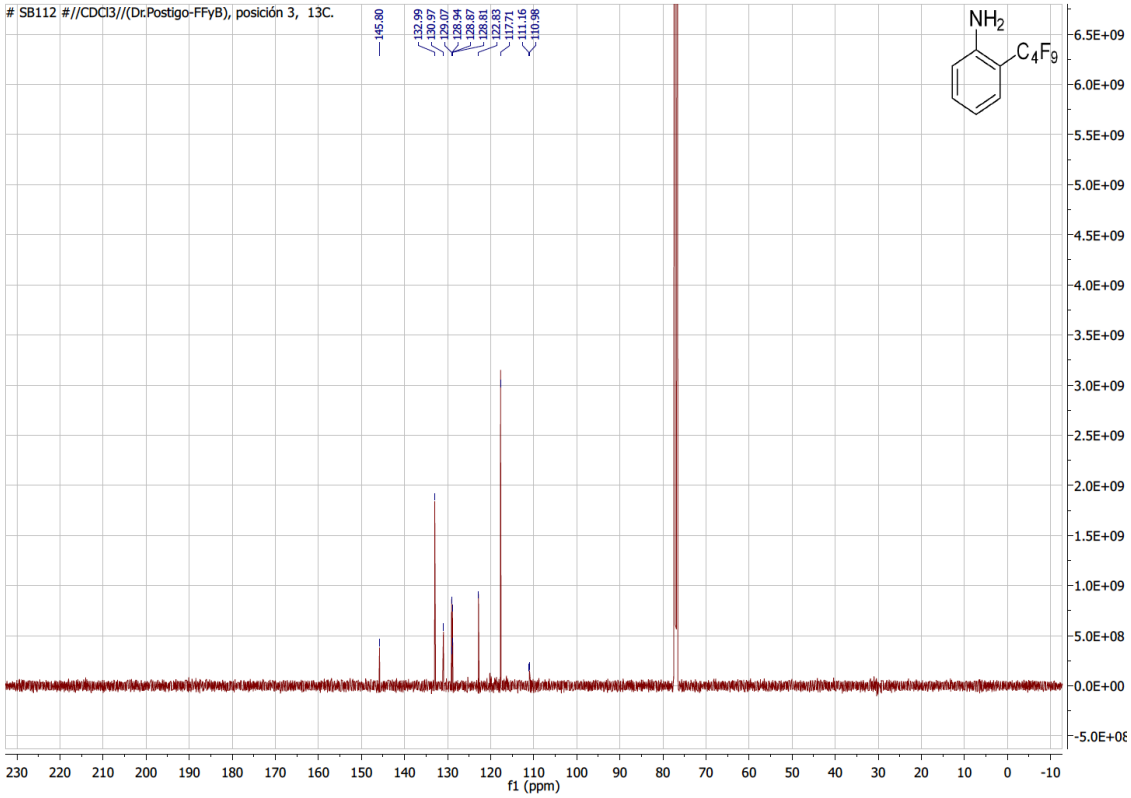

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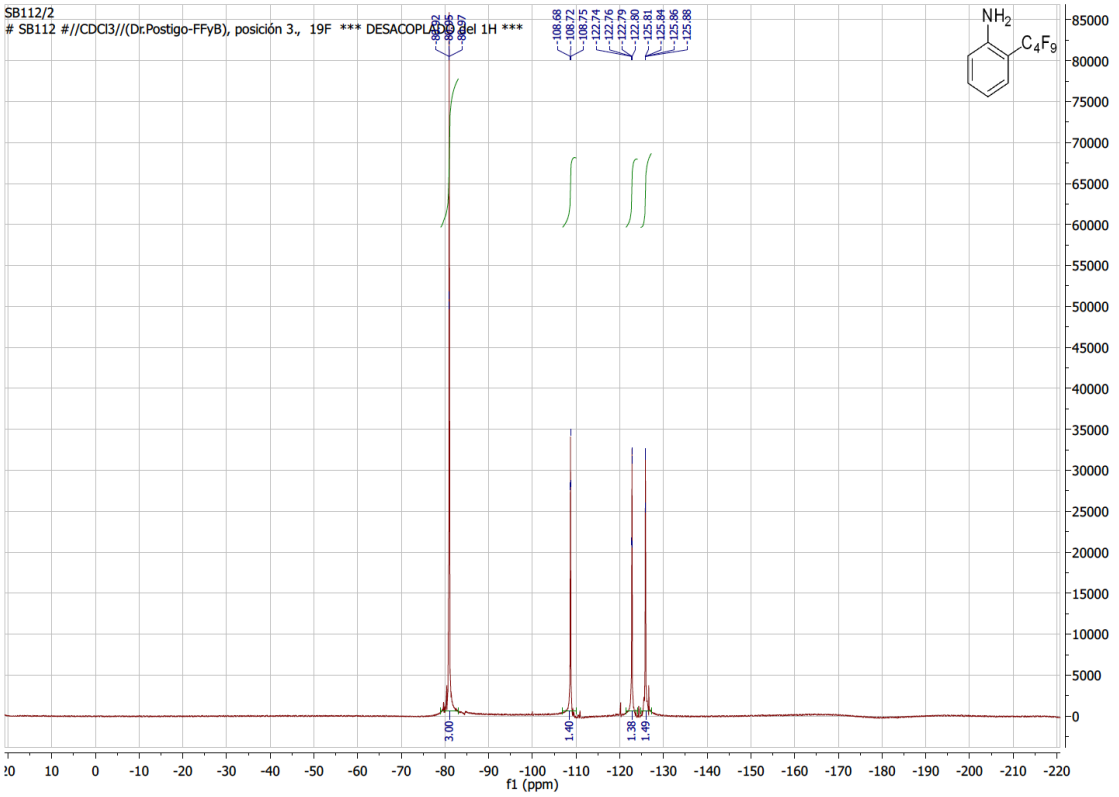
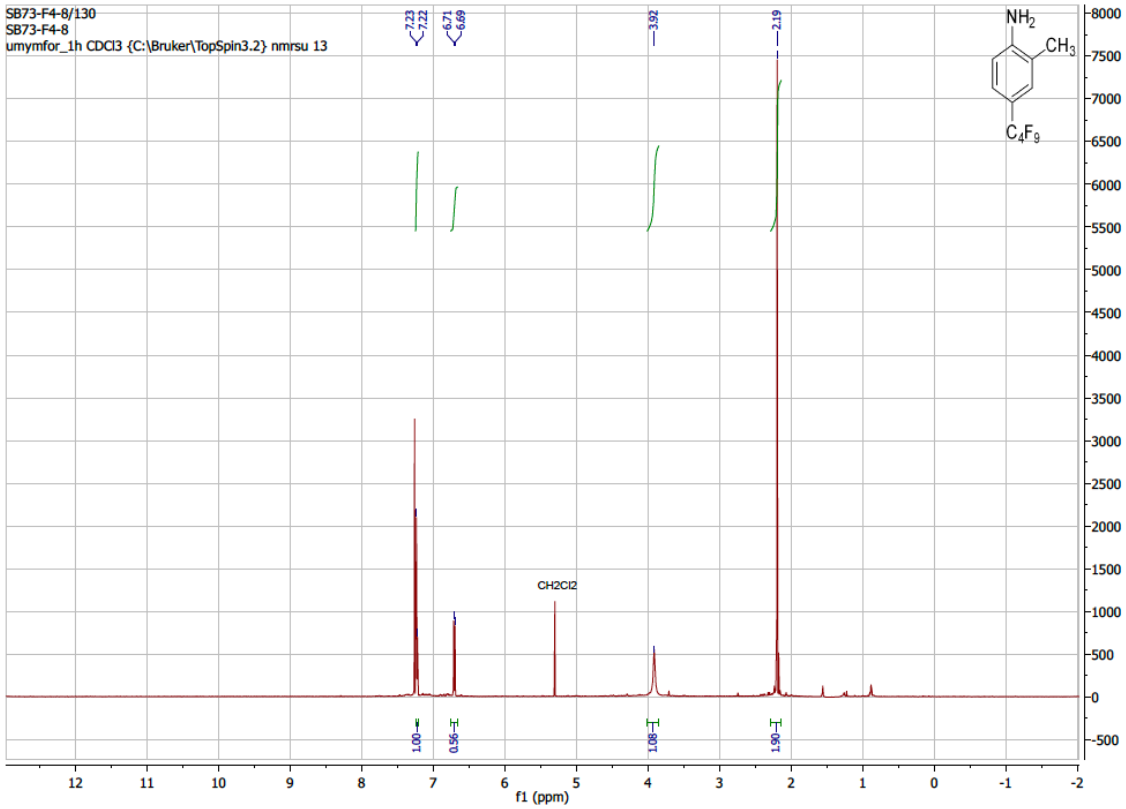
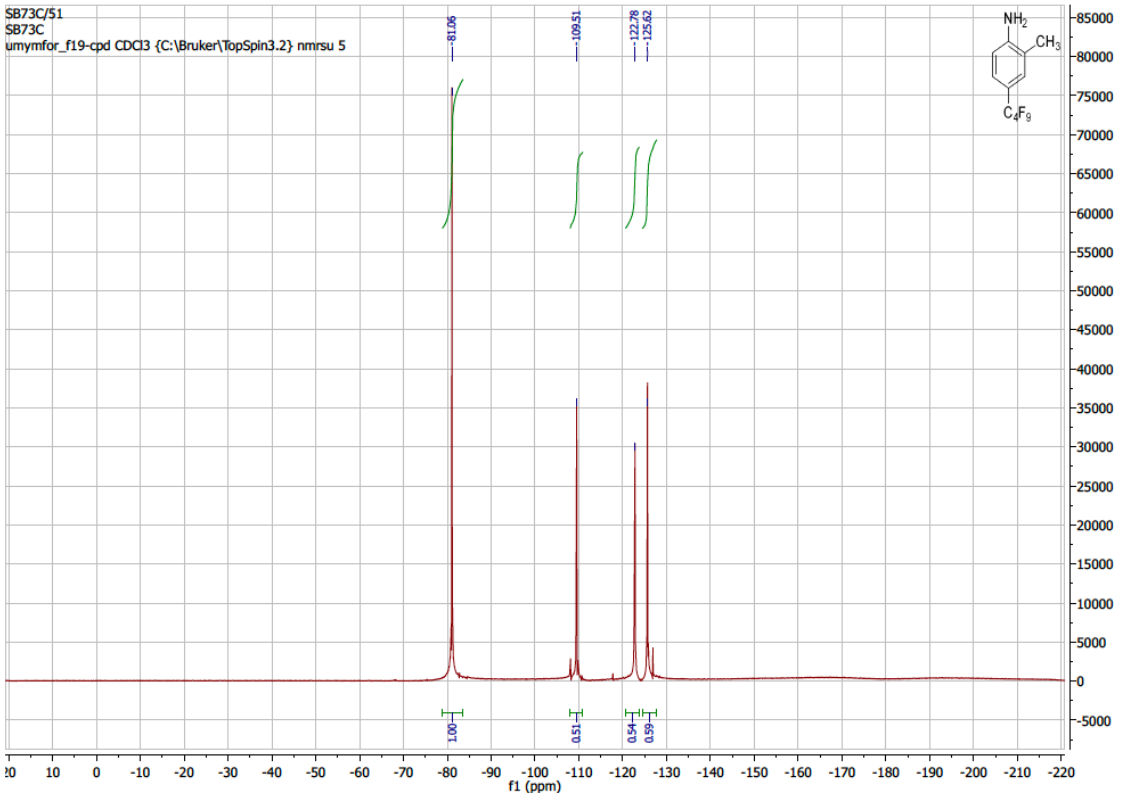


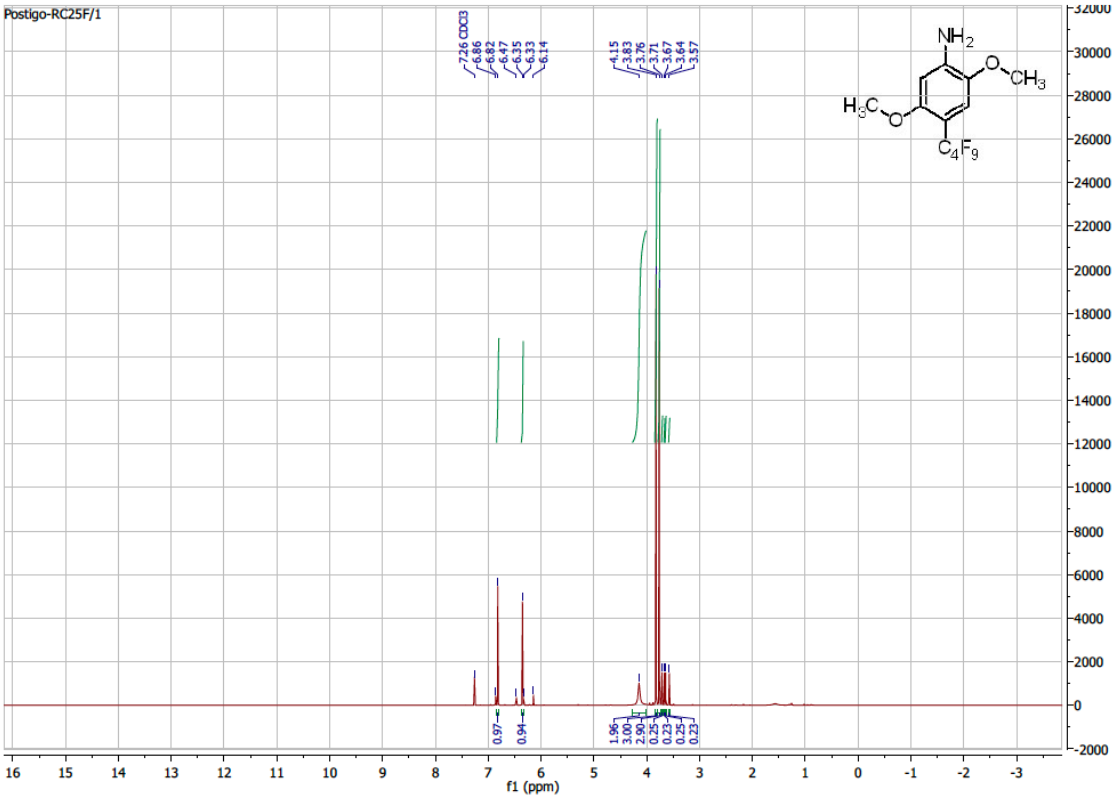
^{1}H NMR spectrum of *2*-methyl-4-(nonafluorobutyl)aniline **5** in $CDCl_3$



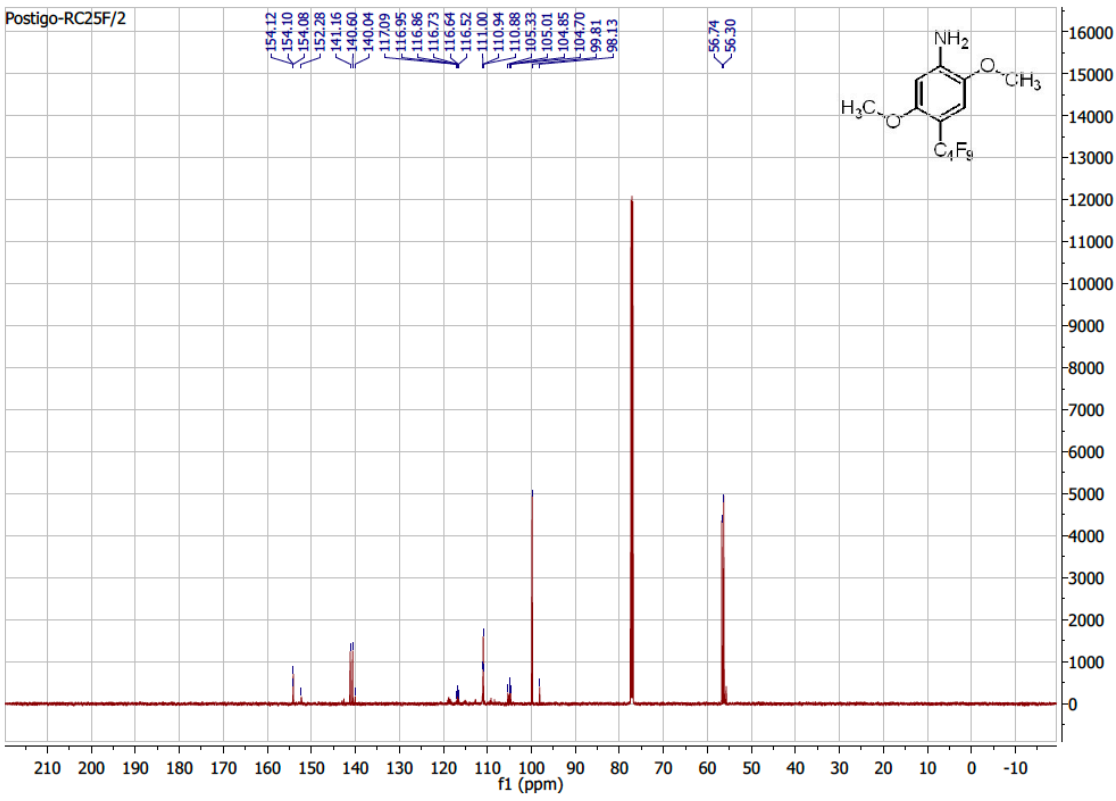
^{19}F NMR spectrum of *2*-methyl-4-(nonafluorobutyl)aniline **5** in $CDCl_3$



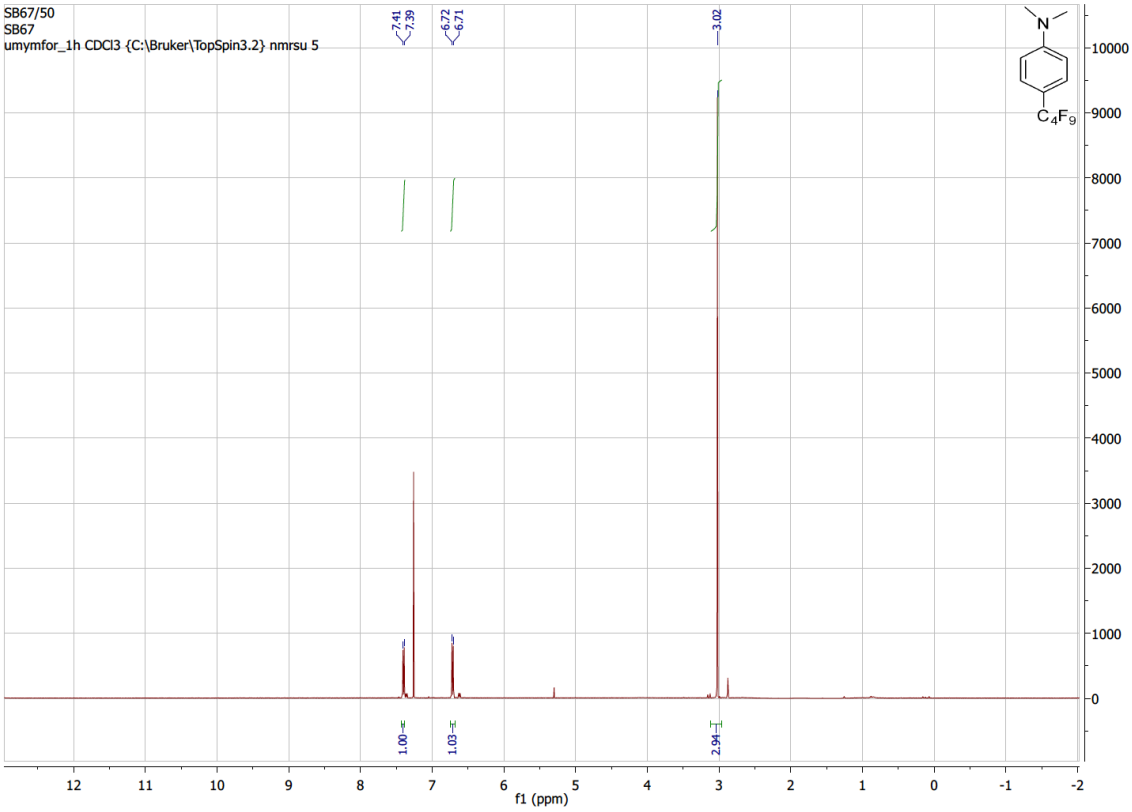
^{1}H NMR spectrum of *2,5*-dimethoxy-4-(nonafluorobutyl)aniline **6** in $CDCl_3$



^{13}C NMR spectrum of *2,5*-dimethoxy-4-(nonafluorobutyl)aniline **6** in $CDCl_3$

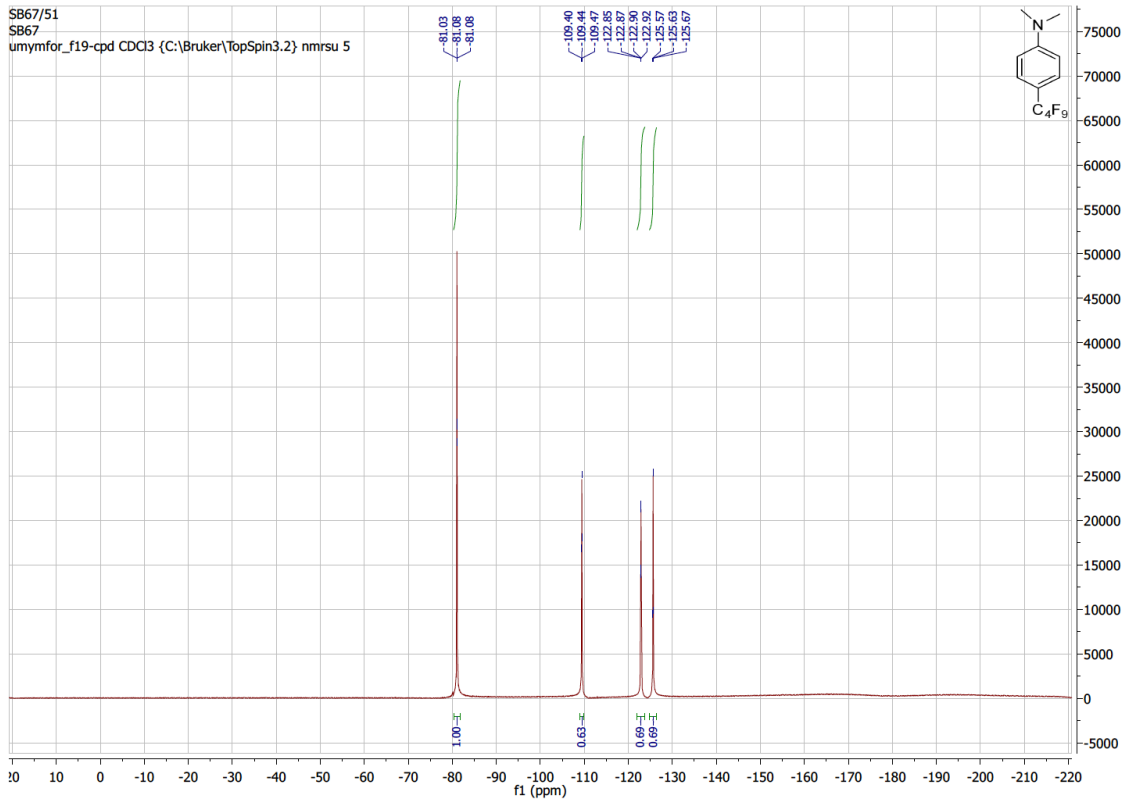


^{1}H NMR spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)aniline **7** in $CDCl_3$

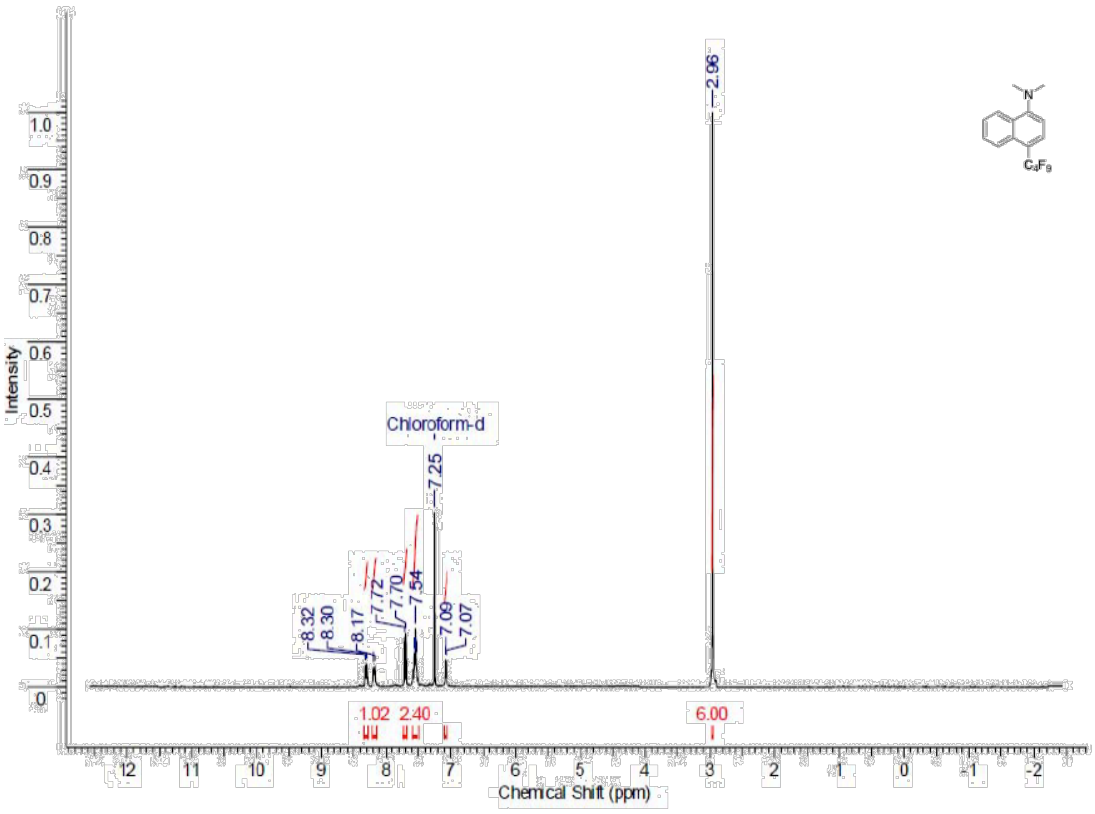


HSQC spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)aniline **7** in $CDCl_3$

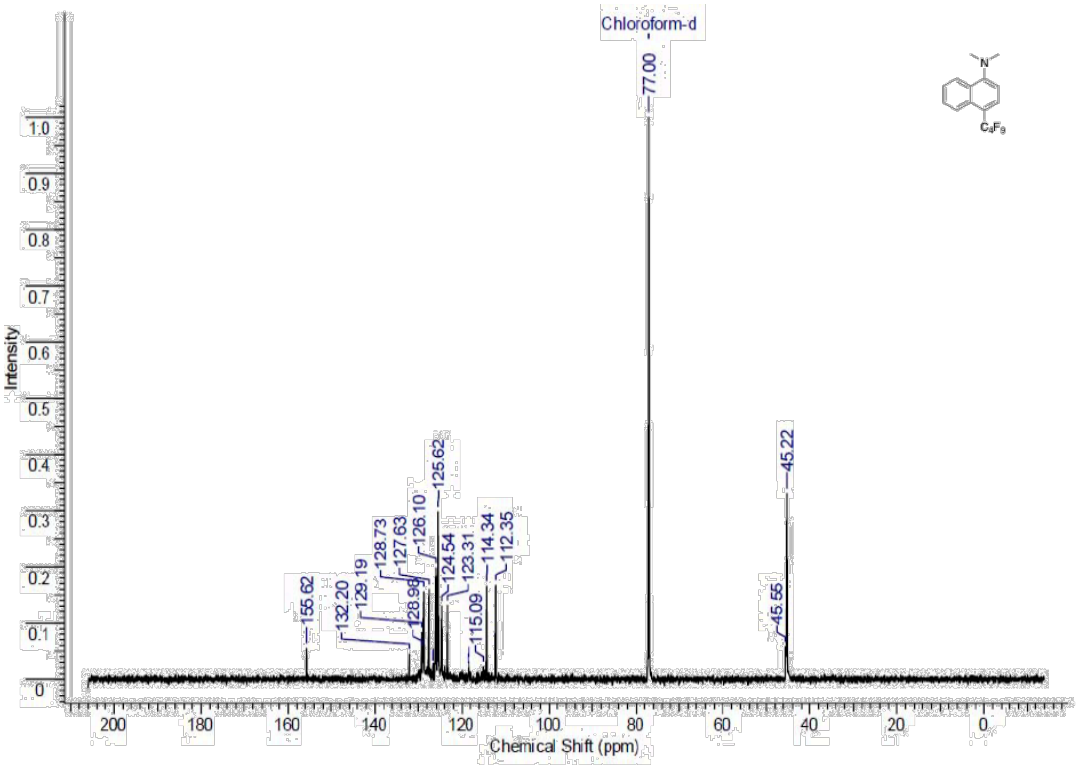
^{19}F NMR spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)aniline **7** in $CDCl_3$



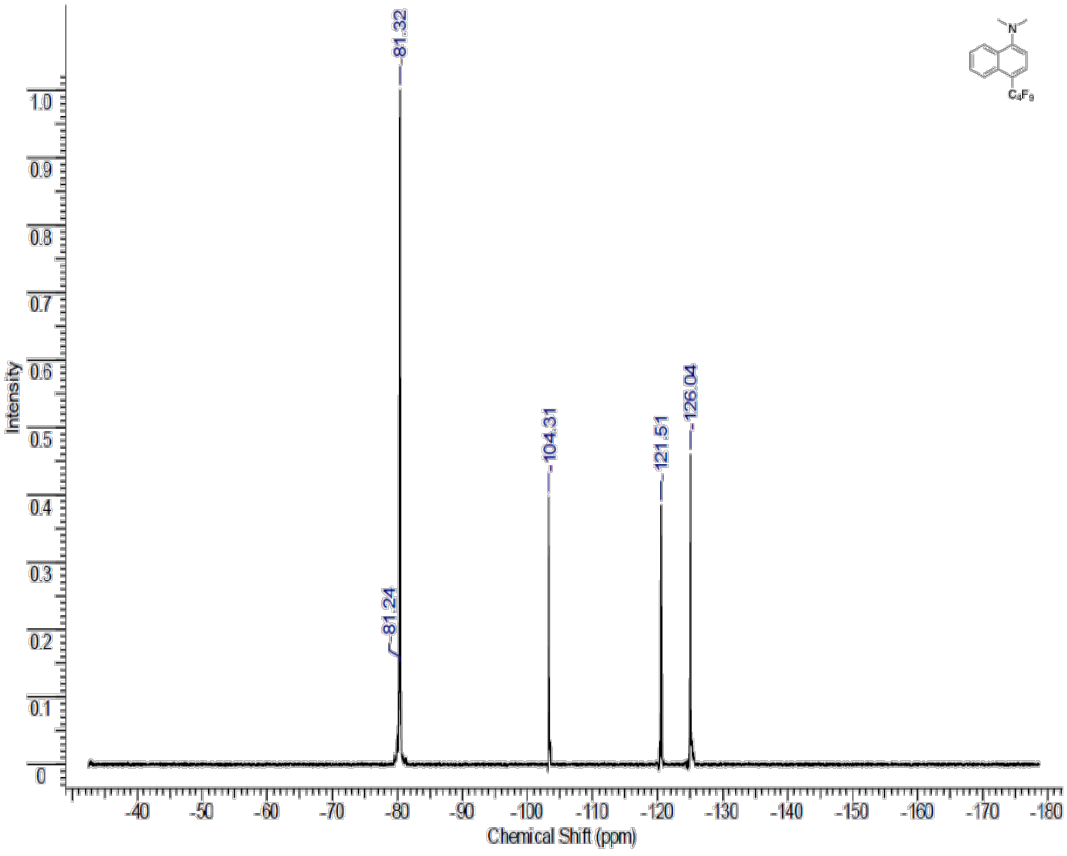
^{1}H NMR spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)naphthalen-1-amine **8** in $CDCl_3$



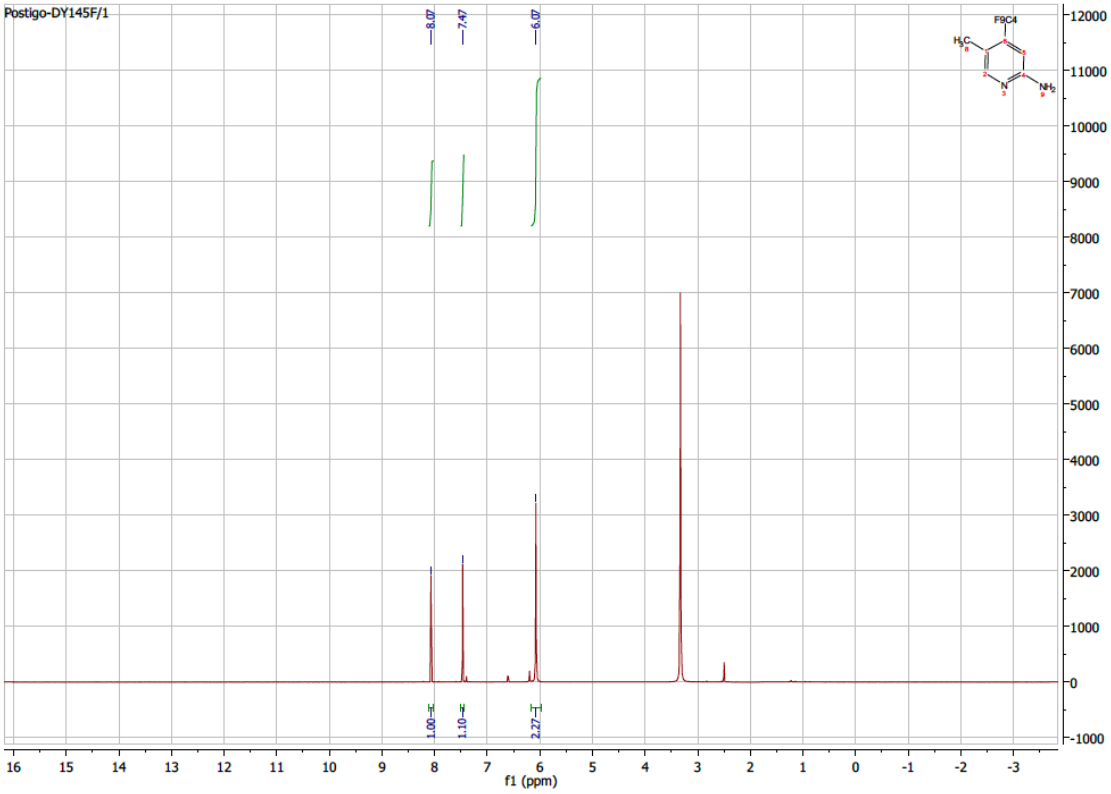
^{13}C NMR spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)naphthalen-1-amine **8** in $CDCl_3$



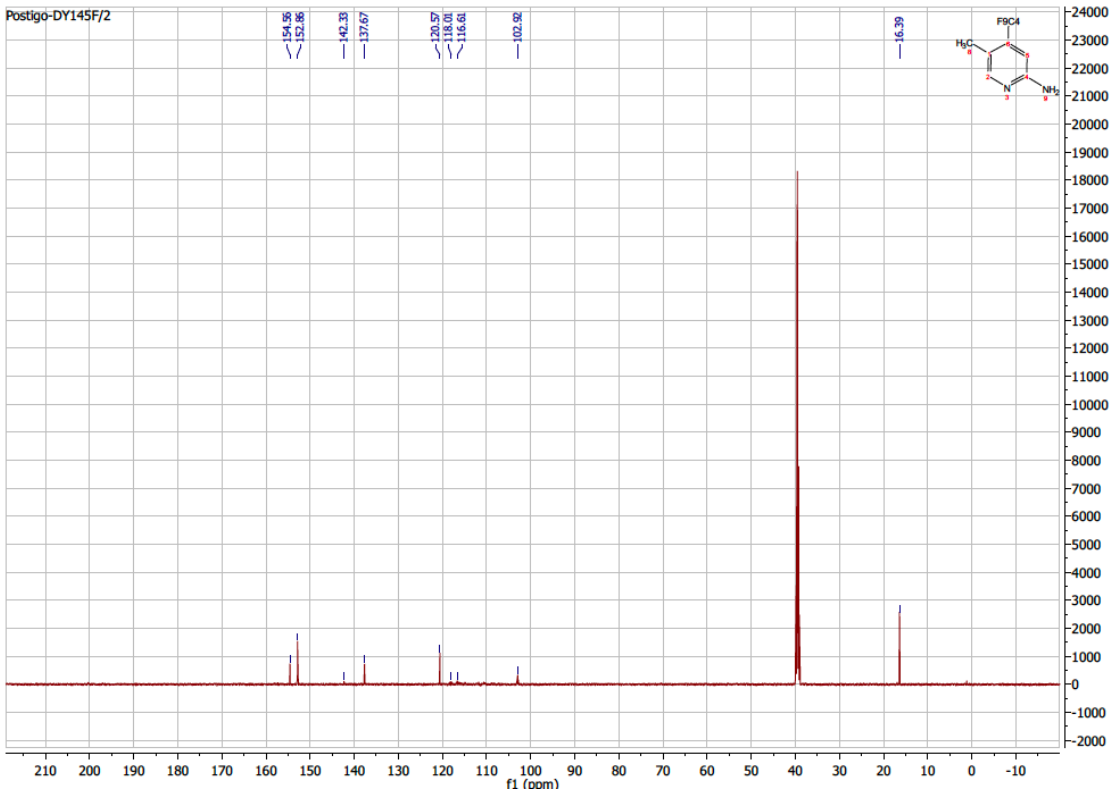
^{19} F NMR spectrum of *N,N*-dimethyl-4-(nonafluorobutyl)naphthalen-1-amine **8** in $CDCl_3$



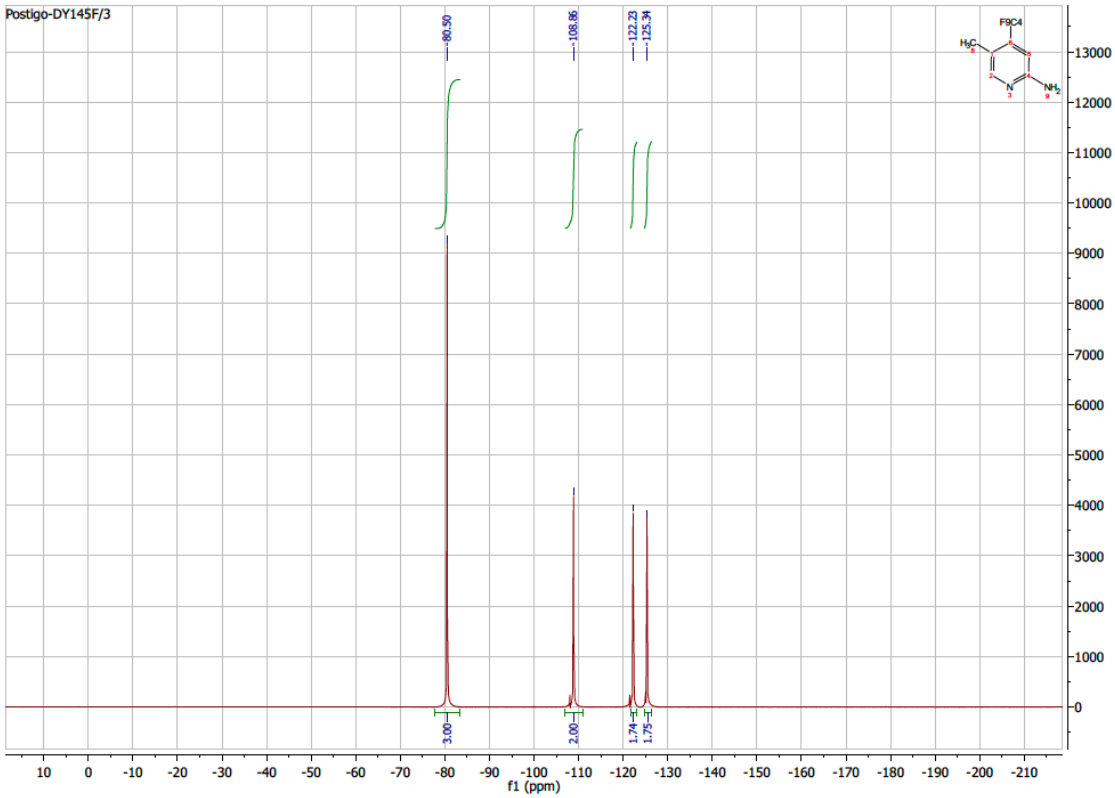
^{1}H NMR spectrum of 2-amino-5-methylpyridine **9** in in DMSO-d_6



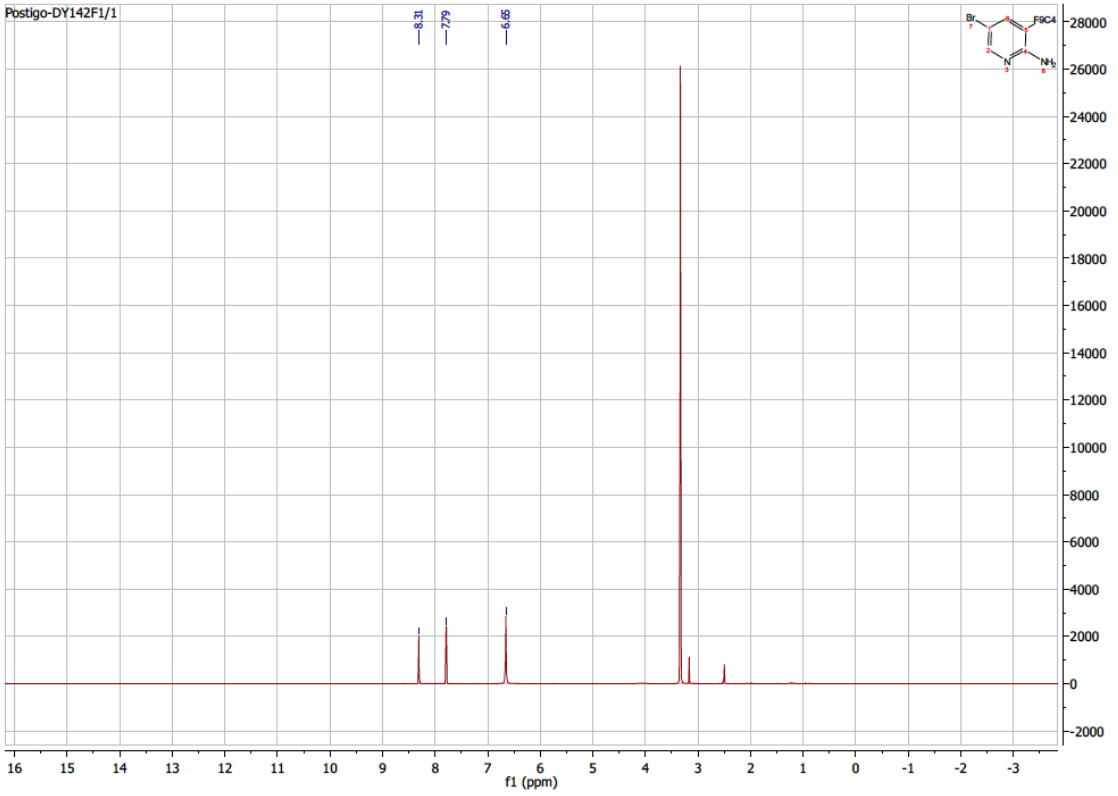
^{13}C NMR spectrum of 2-amino-5-methylpyridine **9** in DMSO-d_6



^{19}F NMR spectrum of 2-amino-5-methylpyridine **9** in DMSO-d_6



^{1}H NMR spectrum of 2-amino-5-bromopyridine **10** in DMSO-d_6



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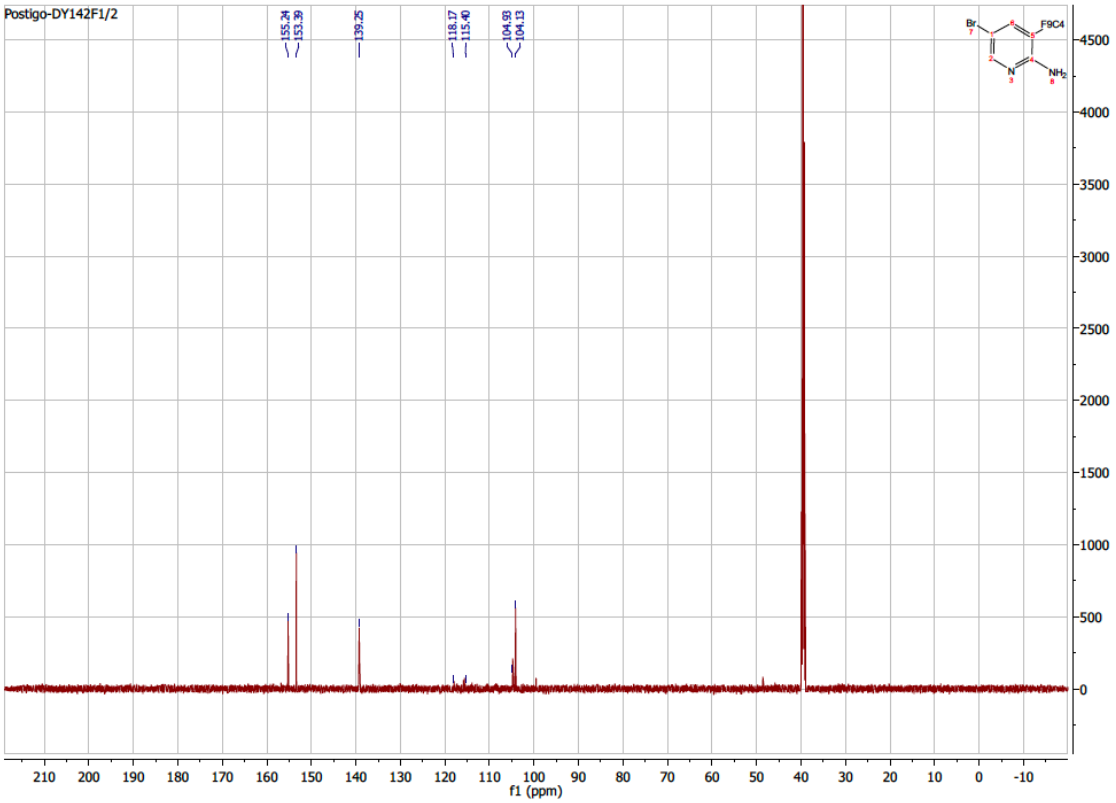
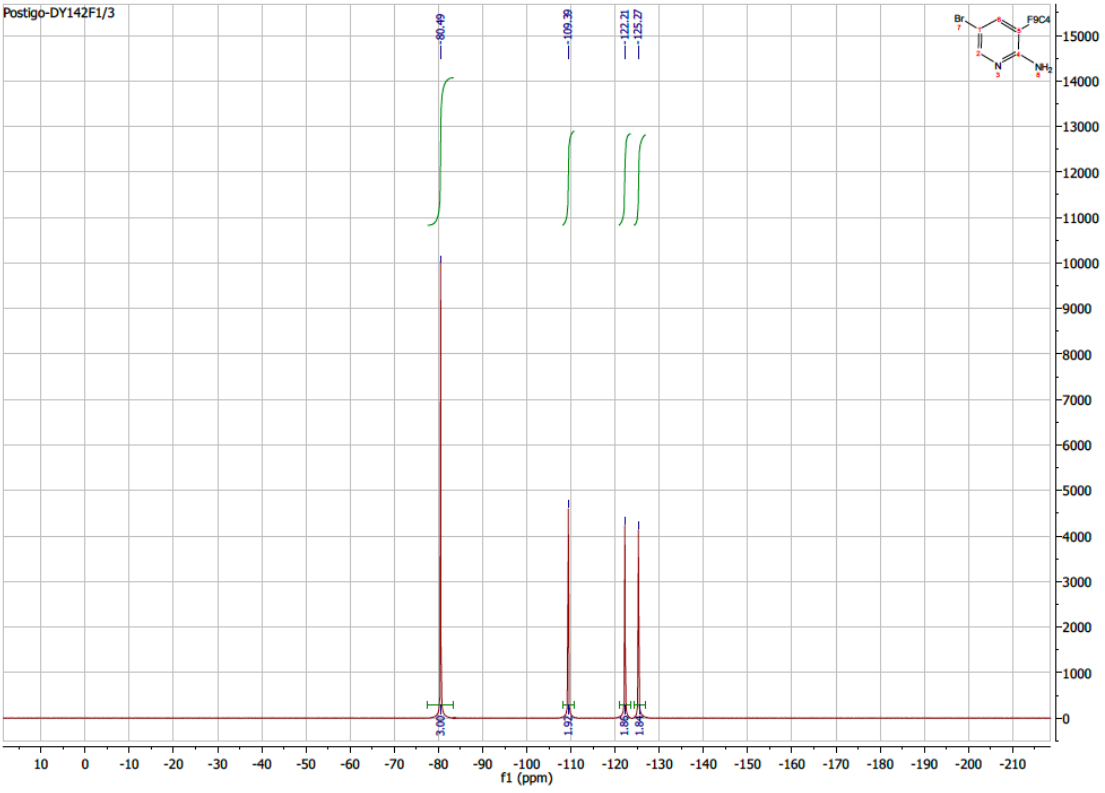
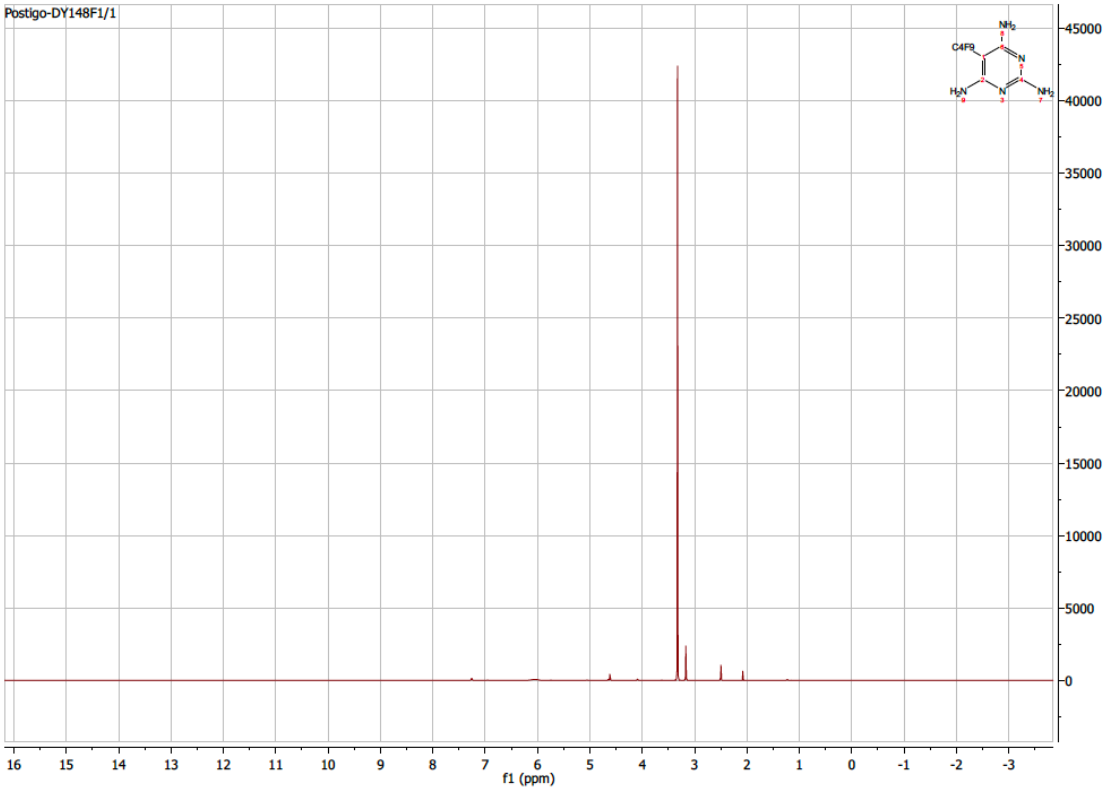


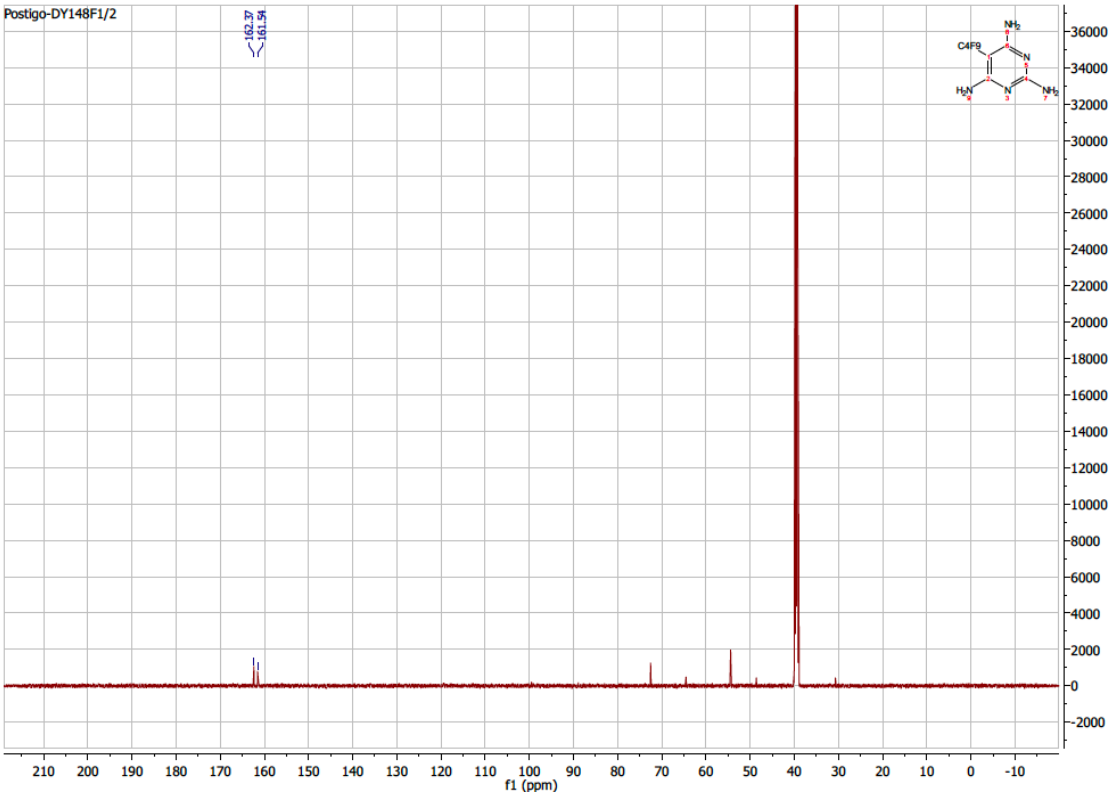
^{19} F NMR spectrum of 2-amino-5-bromopyridine **10** in DMSO-d_6



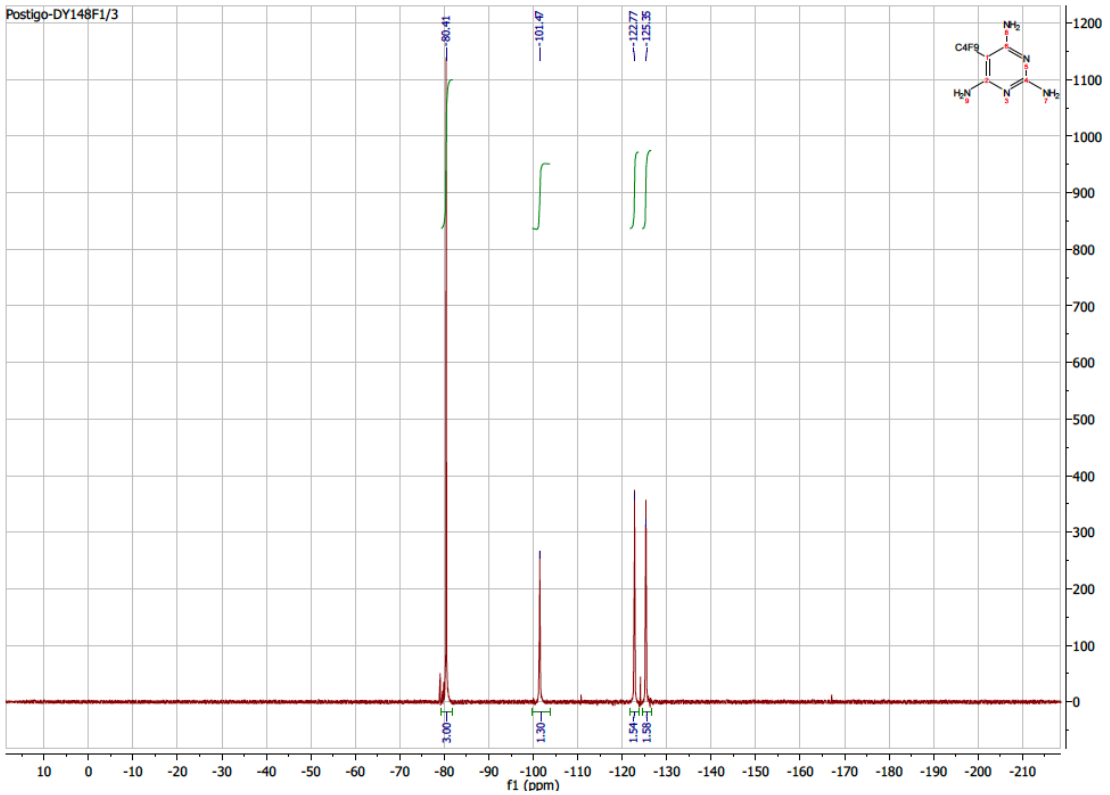
^{1}H NMR spectrum of 2,4,6-triamino-5-perfluorobutylpyrimidine **11** in DMSO-d_6



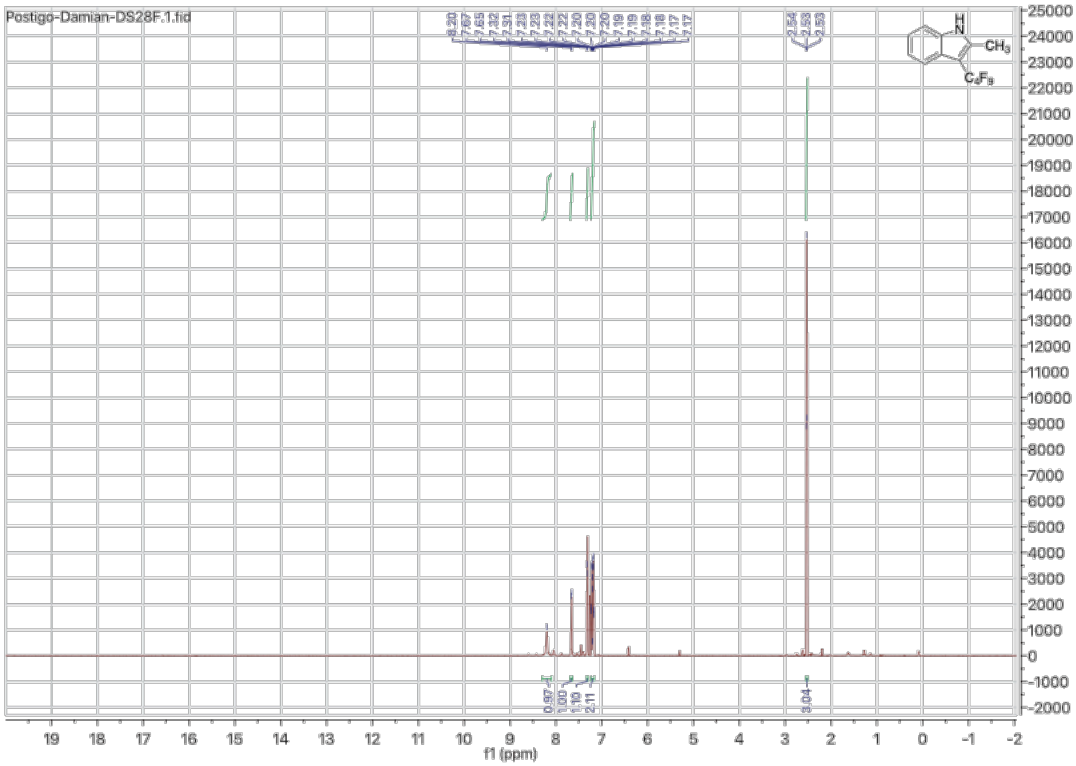
^{13}C NMR spectrum of 2,4,6-triamino-5-perfluorobutylpyrimidine **11** in DMSO-d_6



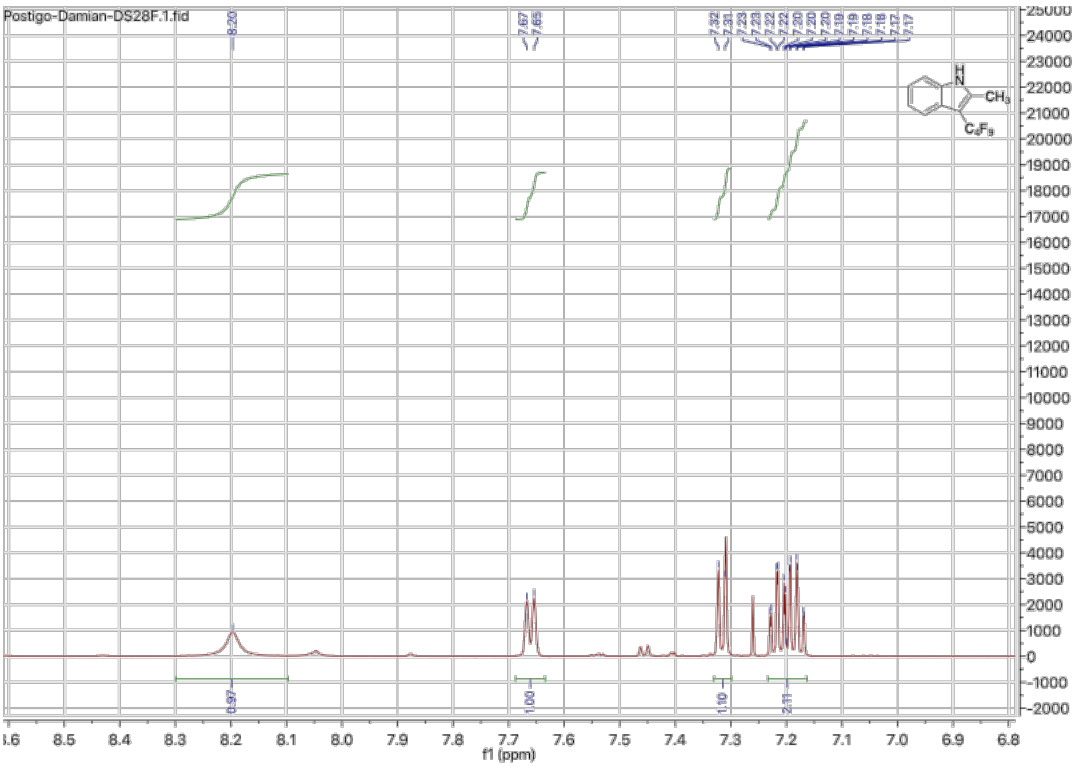
^{19}F NMR spectrum of 2,4,6-triamino-5-perfluorobutylpyrimidine **11** in DMSO-d_6



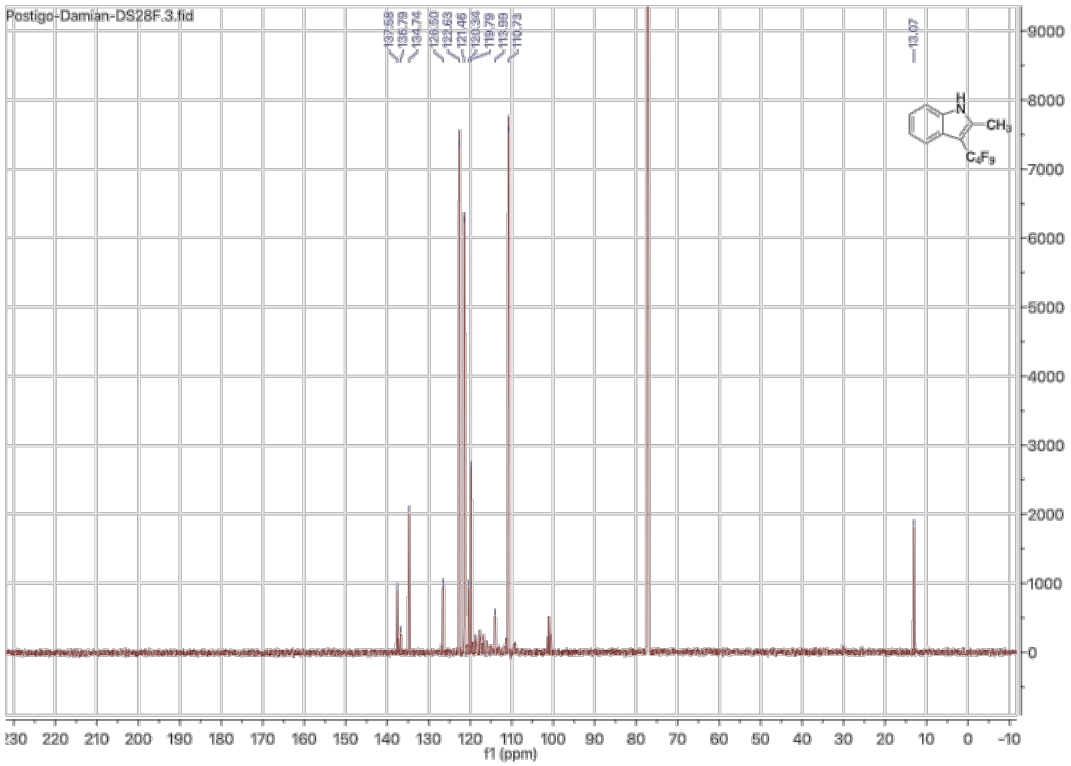
^{1}H NMR spectrum of 2-Methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-1H-indole **12** in $CDCl_3$



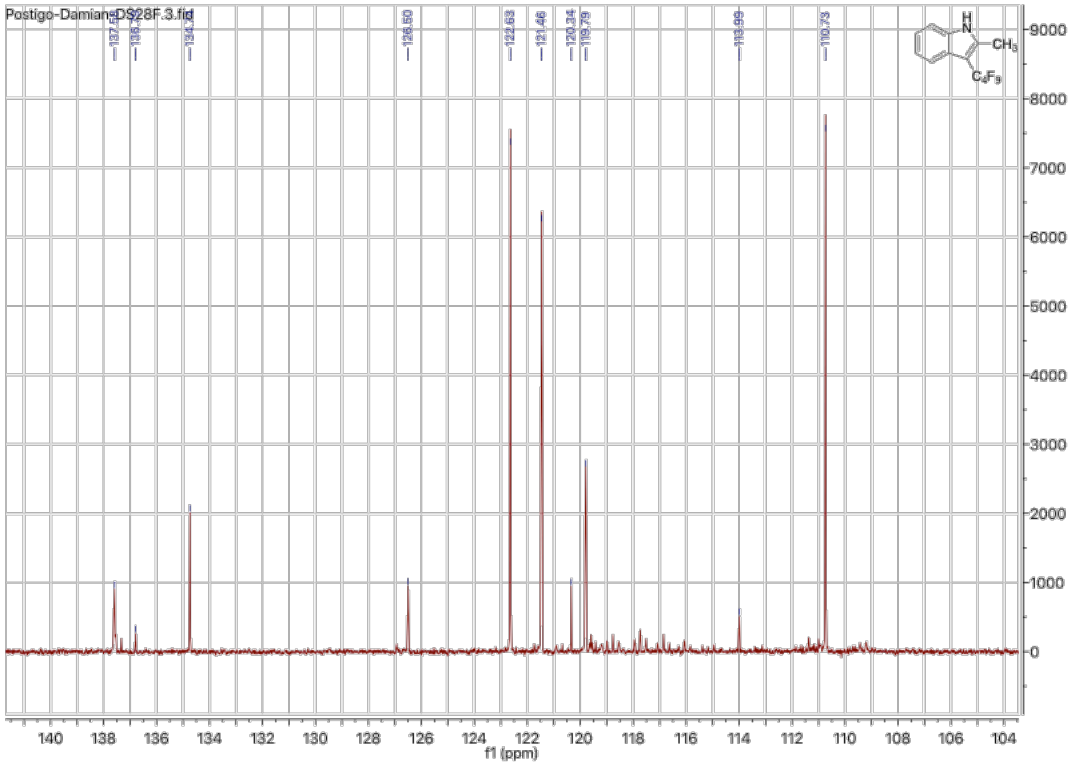
^{1}H NMR spectrum of 2-Methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-1H-indole **12.** Aromatic region in $CDCl_3$



^{13}C NMR spectrum of 2-Methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-1H-indole **12** in $CDCl_3$



^{13}C NMR spectrum of 2-Methyl-3-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-1H-indole **12.** Aromatic region in $CDCl_3$



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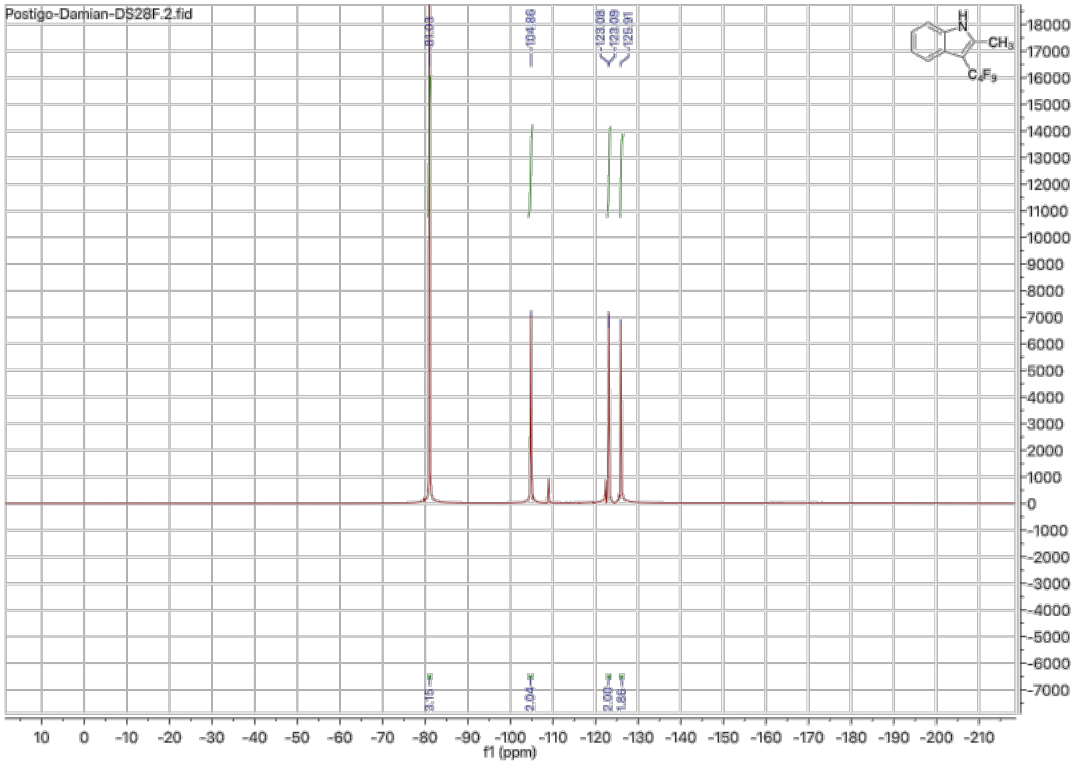
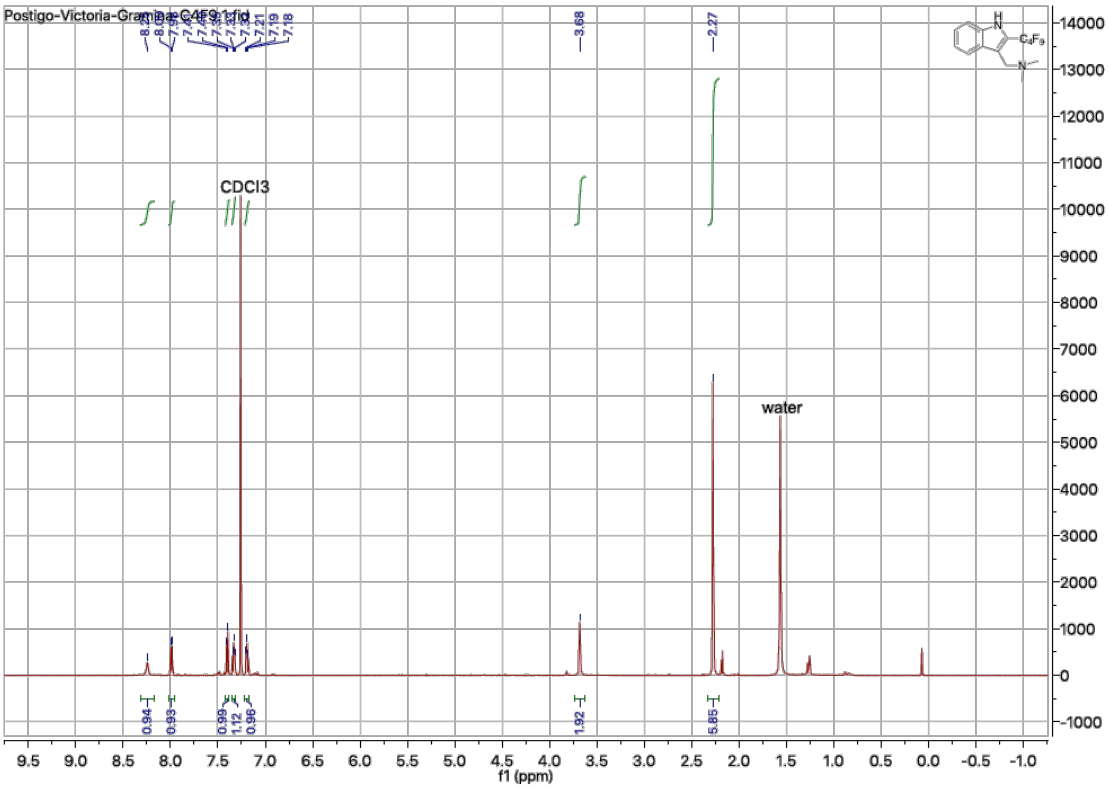


^{1}H NMR spectrum of 2-perfluorobutyl-3-(Dimethylaminomethyl)indole **13** in $CDCl_3$



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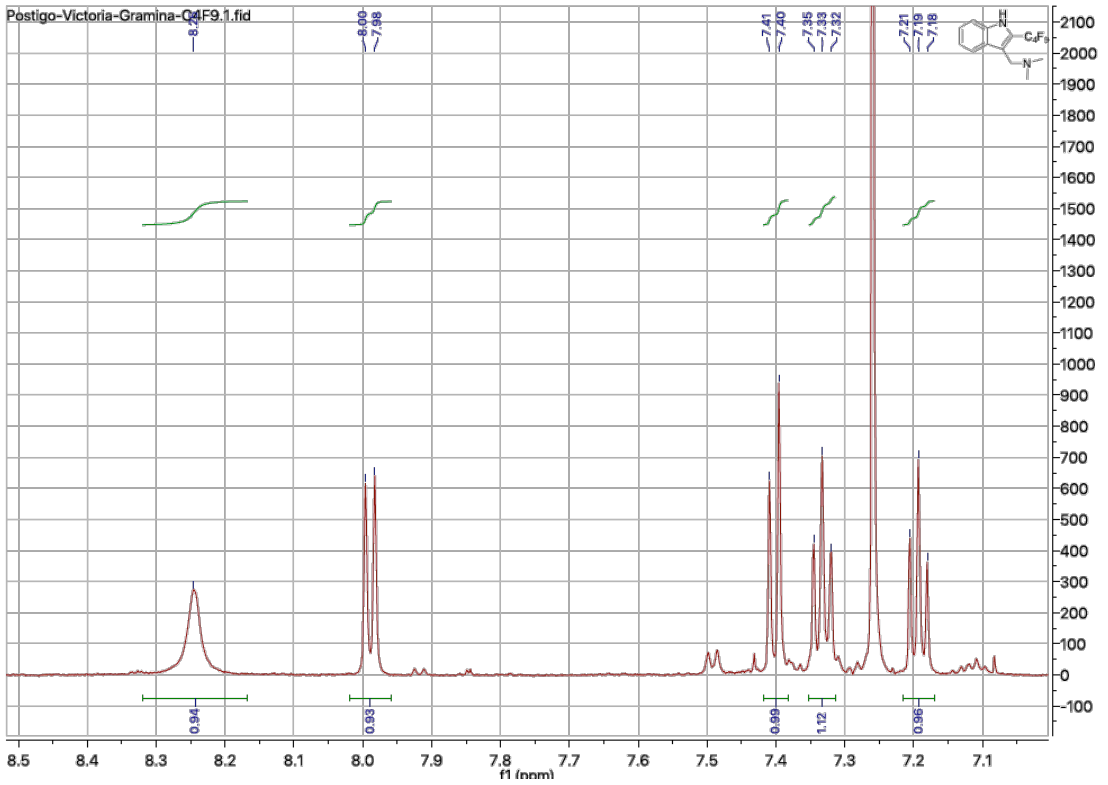
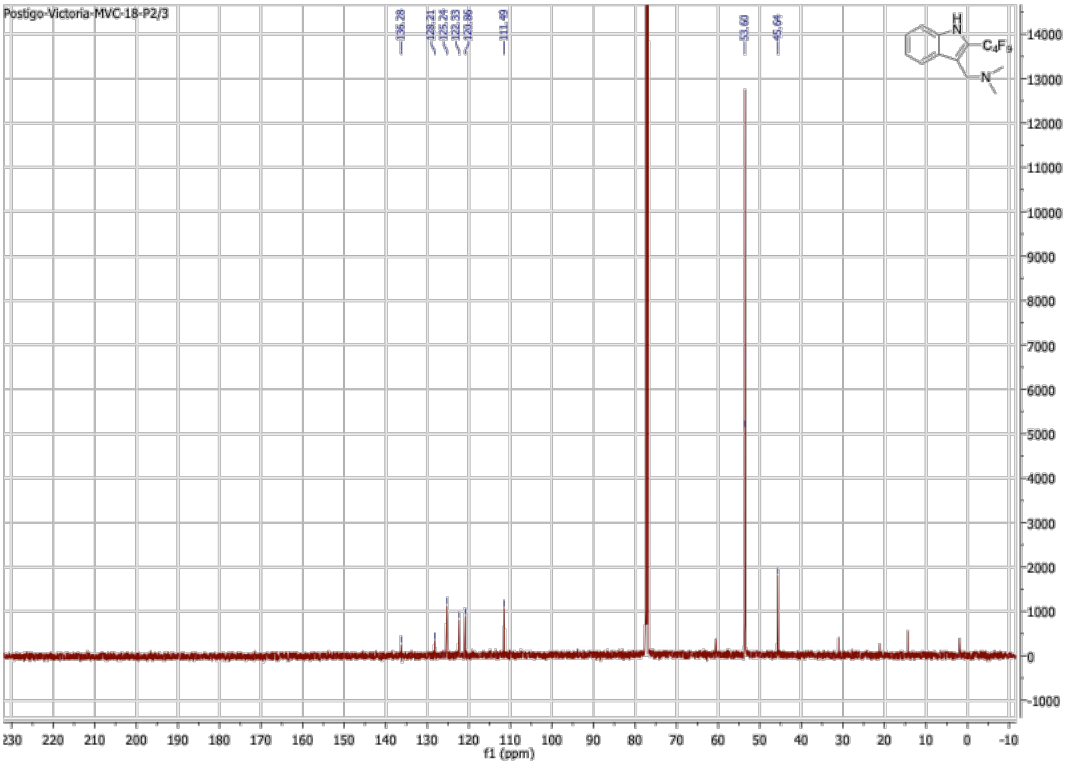
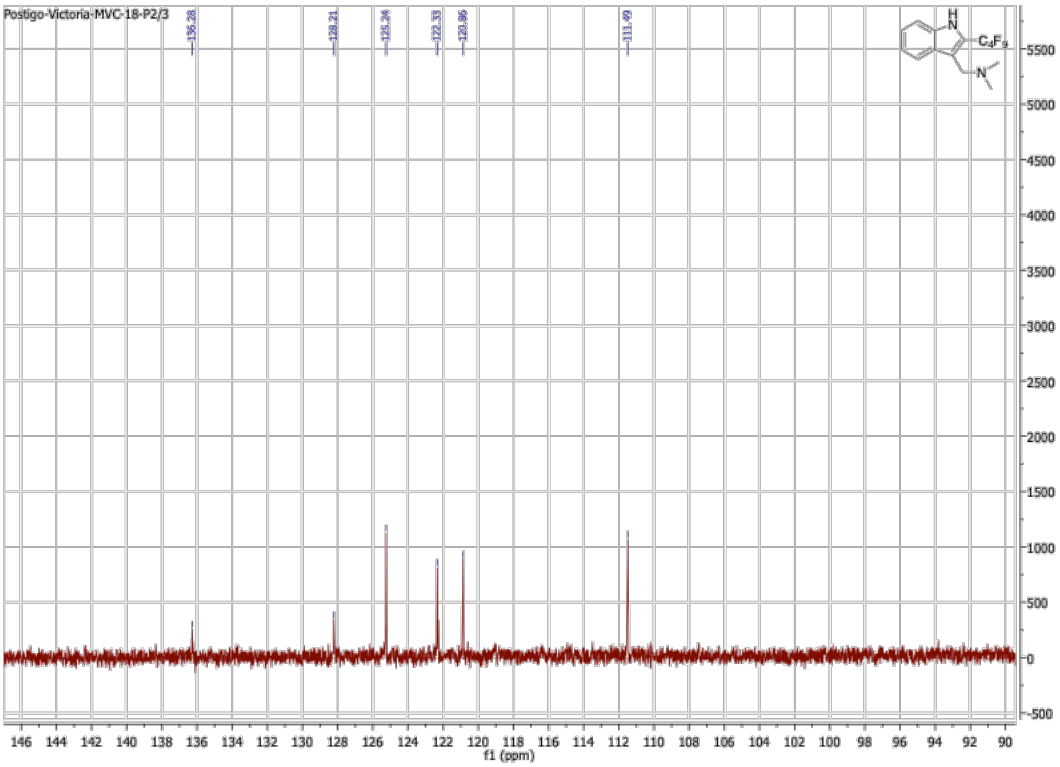


^{13}C NMR spectrum of 2-perfluorobutyl-3-(Dimethylaminomethyl)indole **13** in $CDCl_3$



^{13}C NMR spectrum of 2-perfluorobutyl-3-(Dimethylaminomethyl)indole **13**. Aromatic expansion in $CDCl_3$



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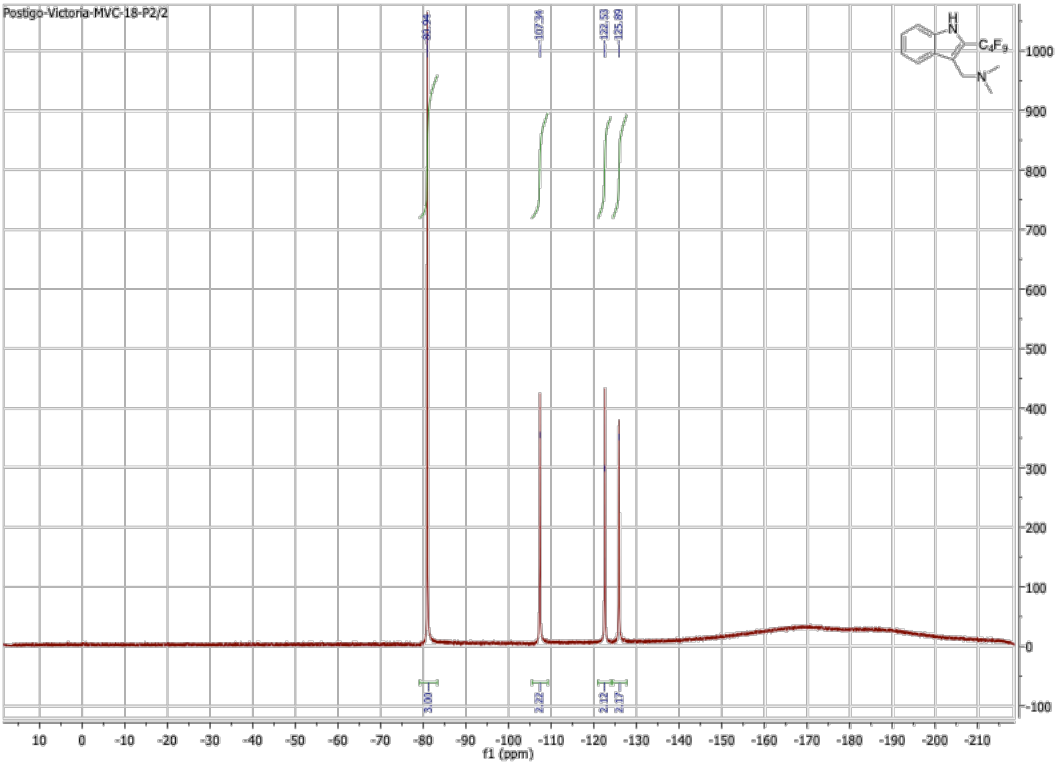
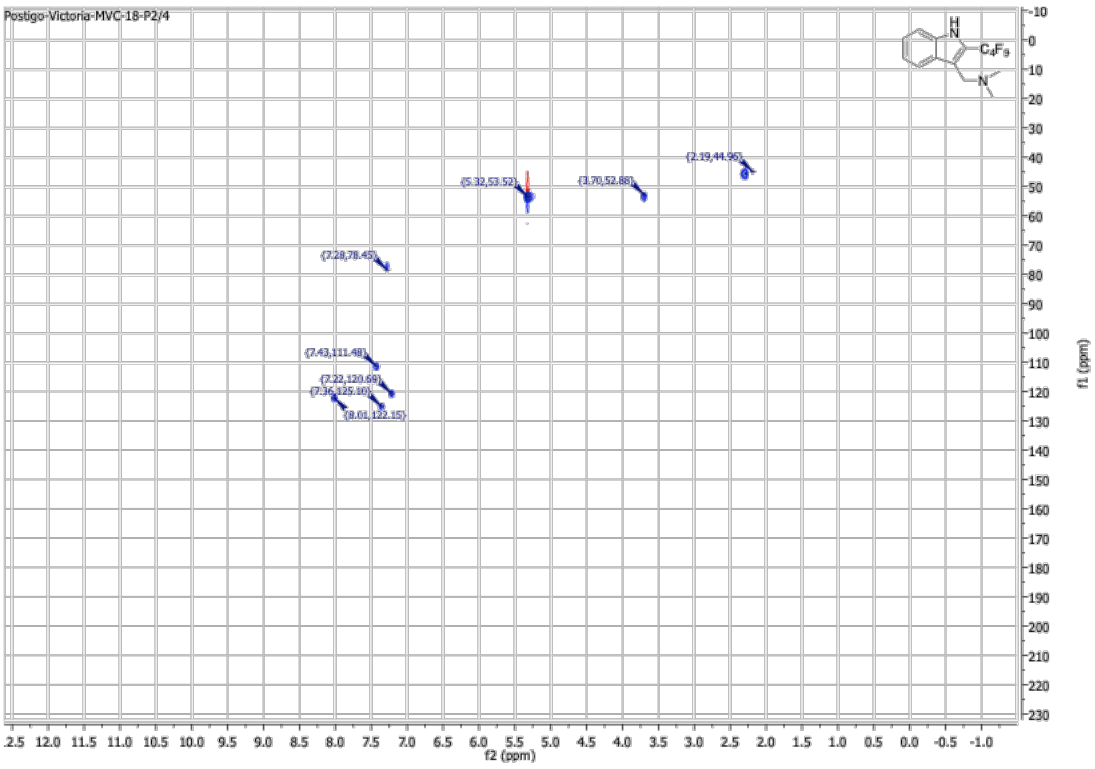
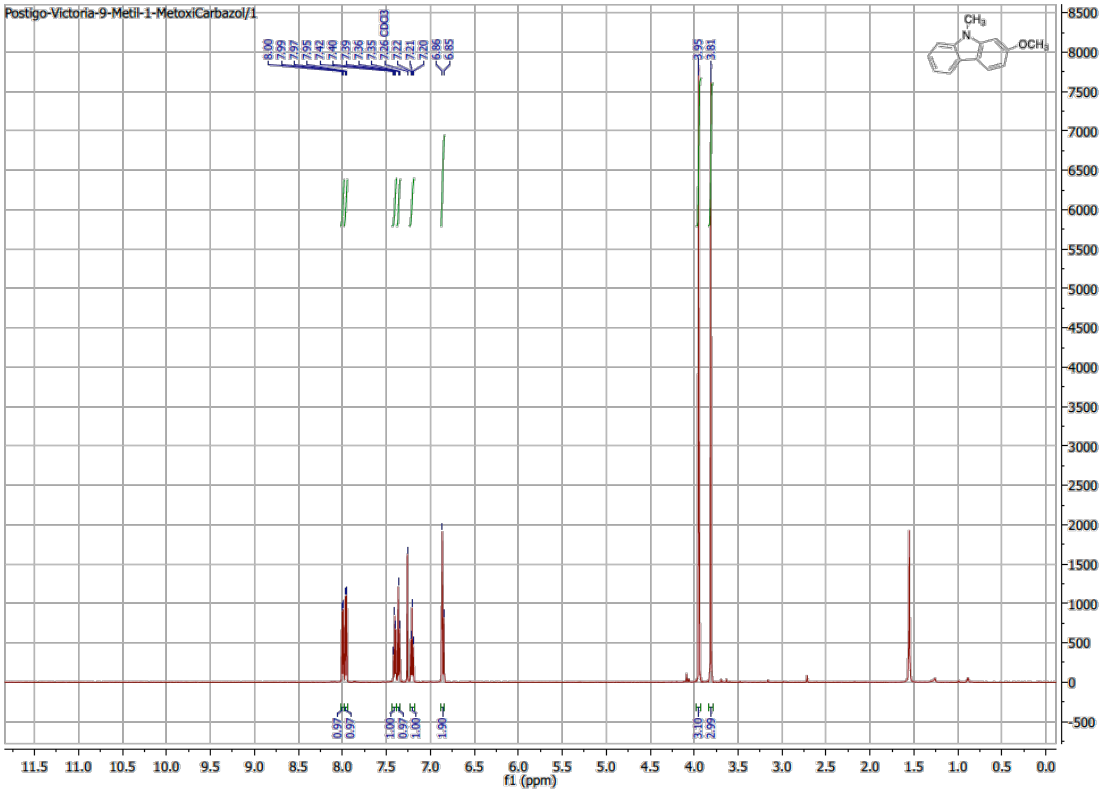


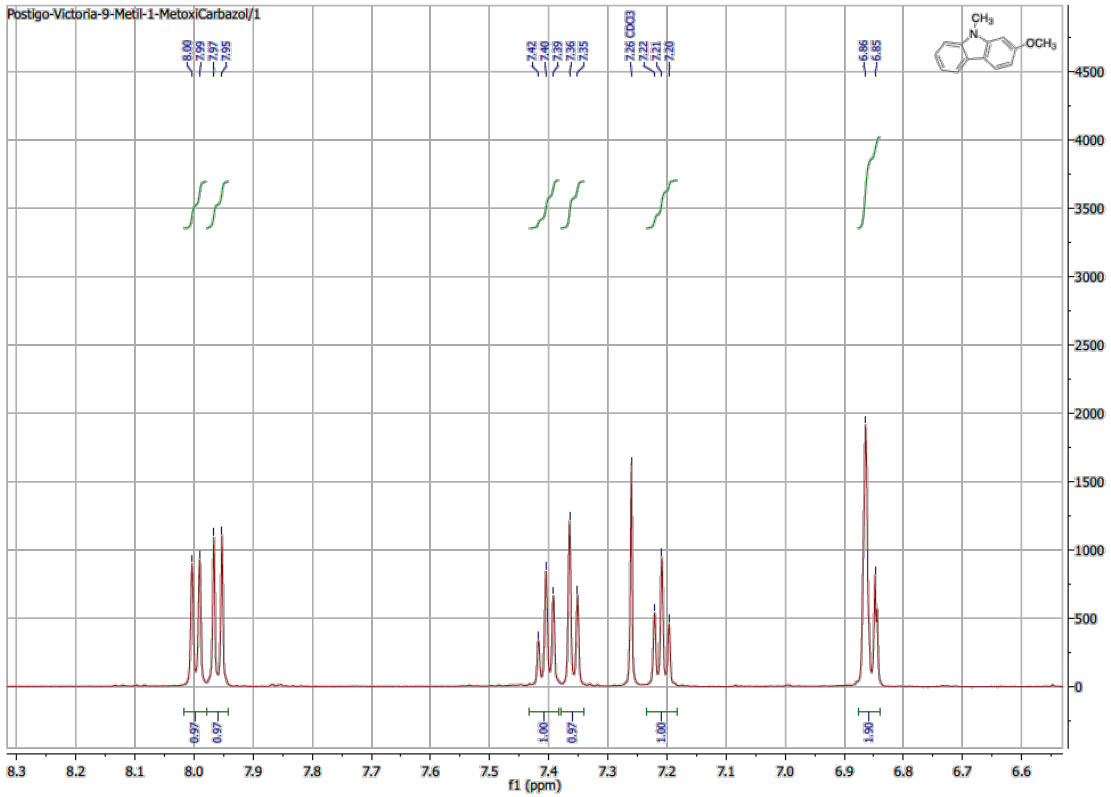
HSQC spectrum of 2-perfluorobutyl-3-(Dimethylaminomethyl)indole **13** in $CDCl_3$



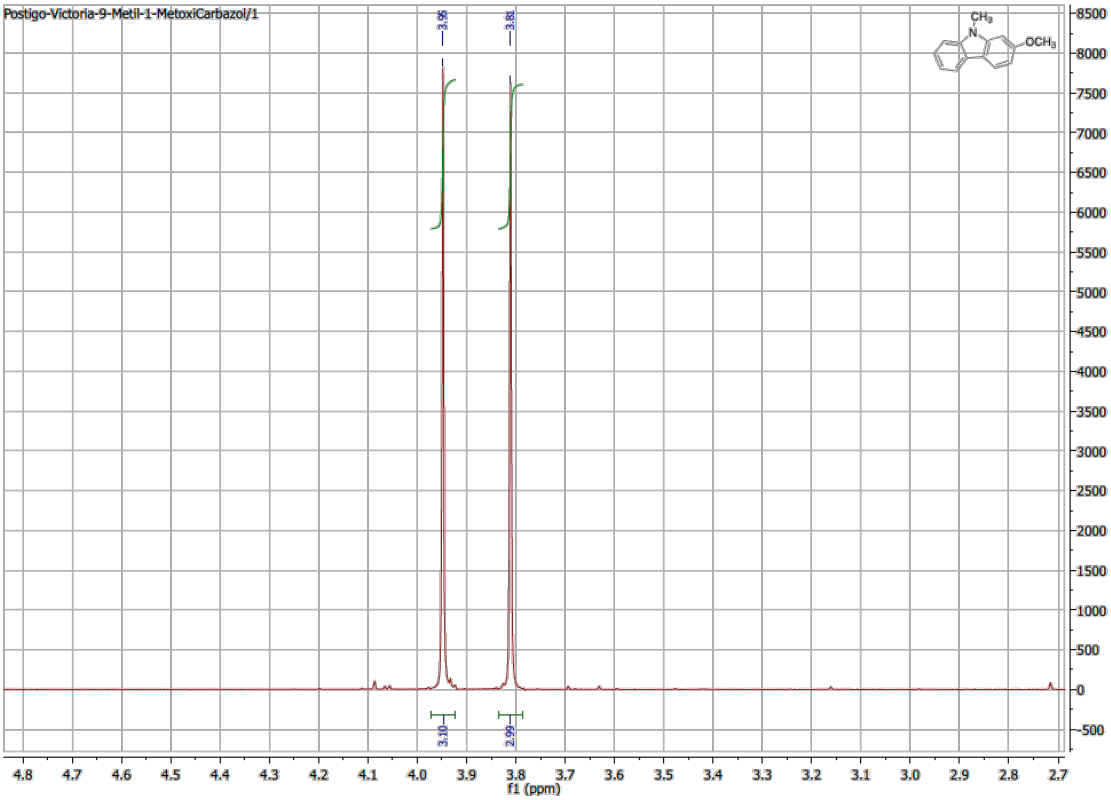
^{1}H NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**



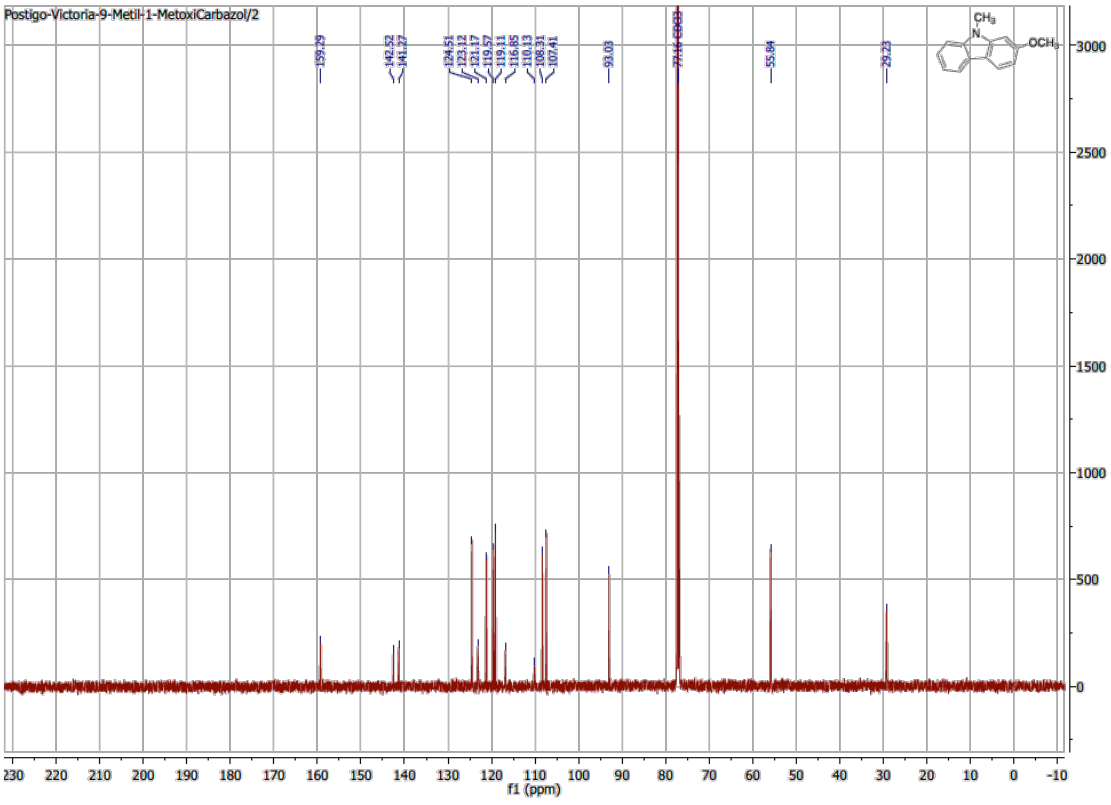
^{1}H NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**. Aromatic region.



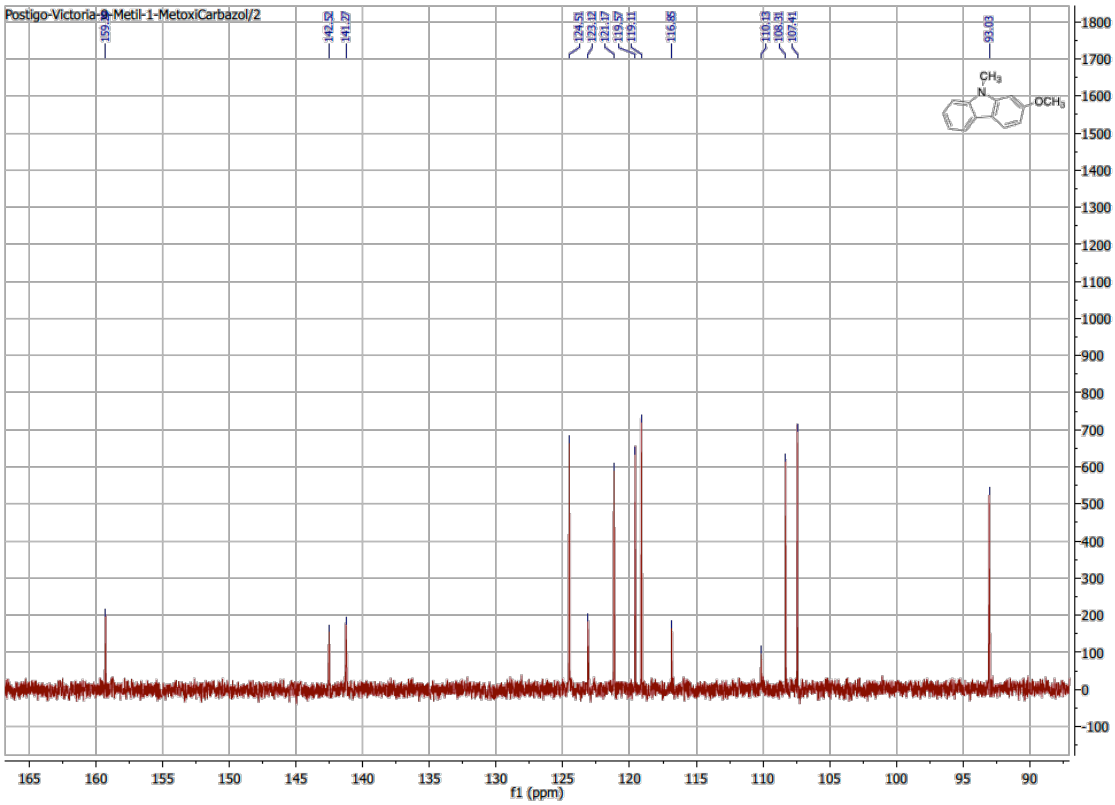
^{1}H NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**. Aliphatic region



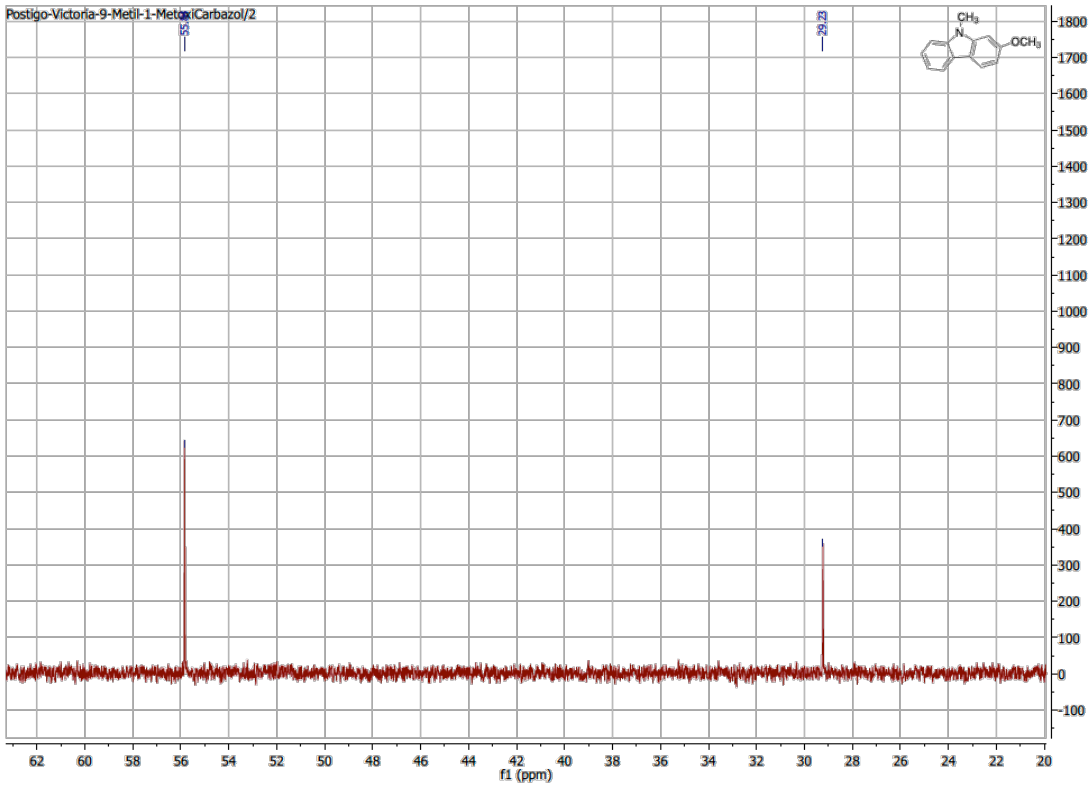
^{13}C NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**



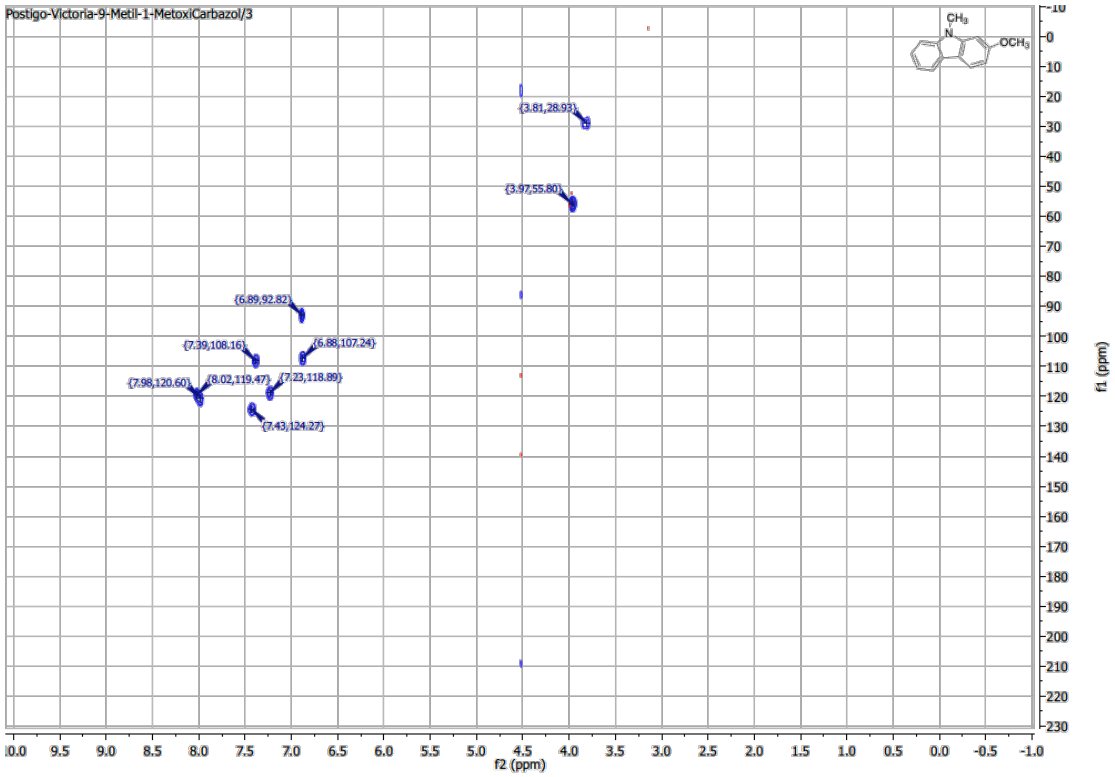
^{13}C NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**. Aromatic region



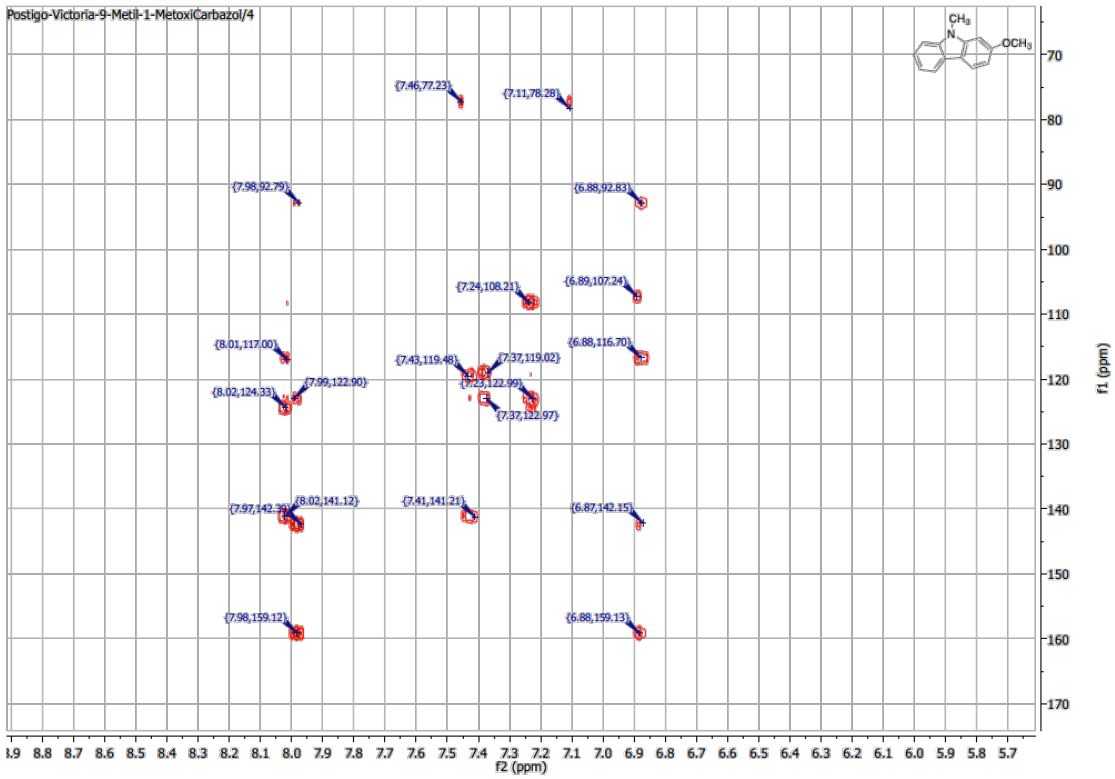
^{13}C NMR spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**. Aliphatic region



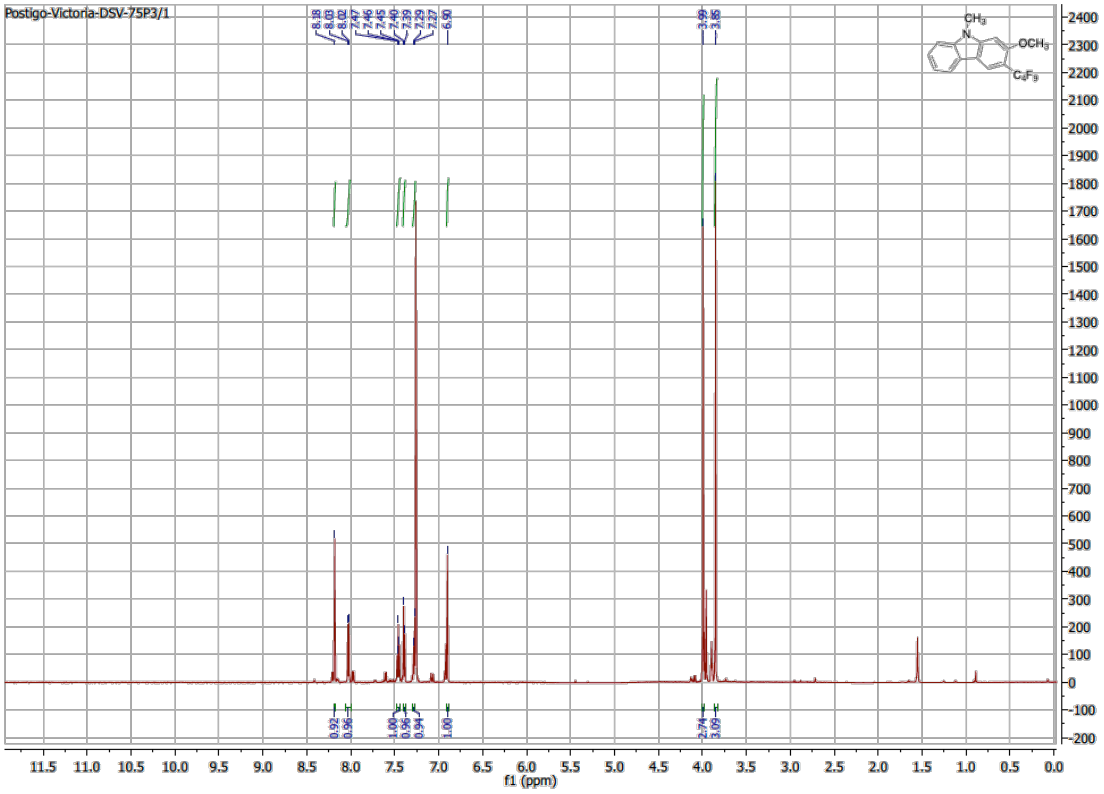
HSQC spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**



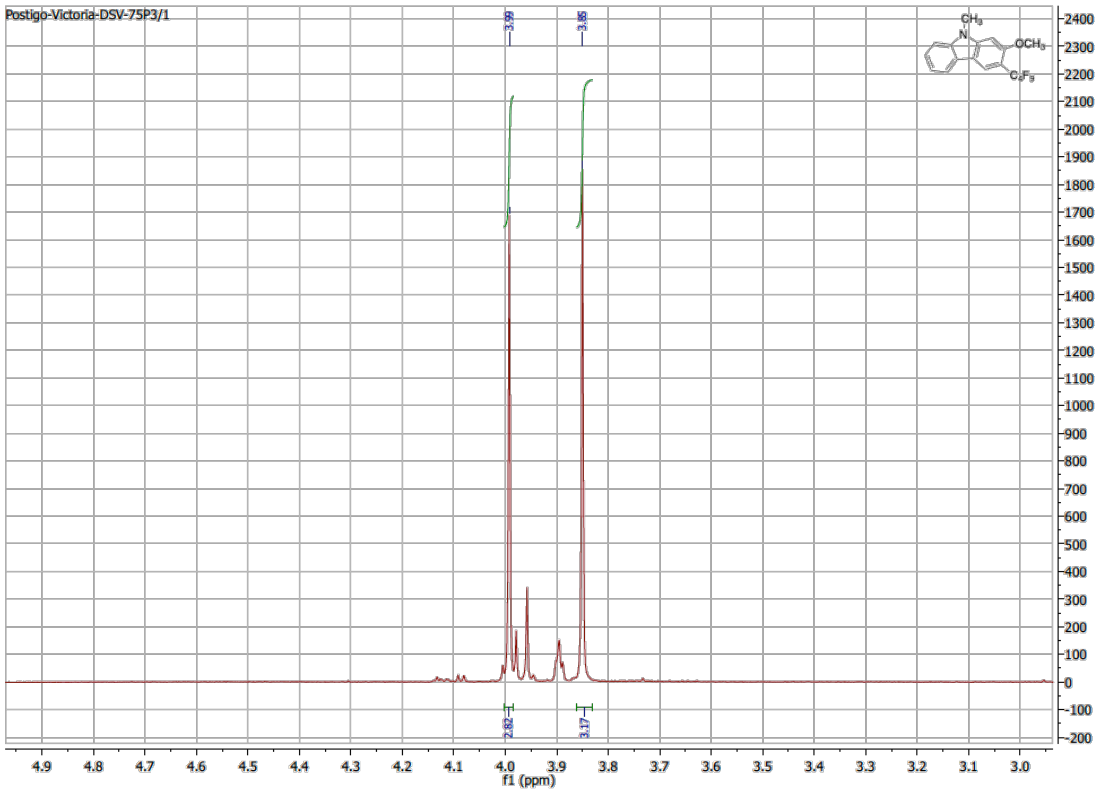
HMBC spectrum of 2-methoxy-9-methylcarbazole in $CDCl_3$ **14**



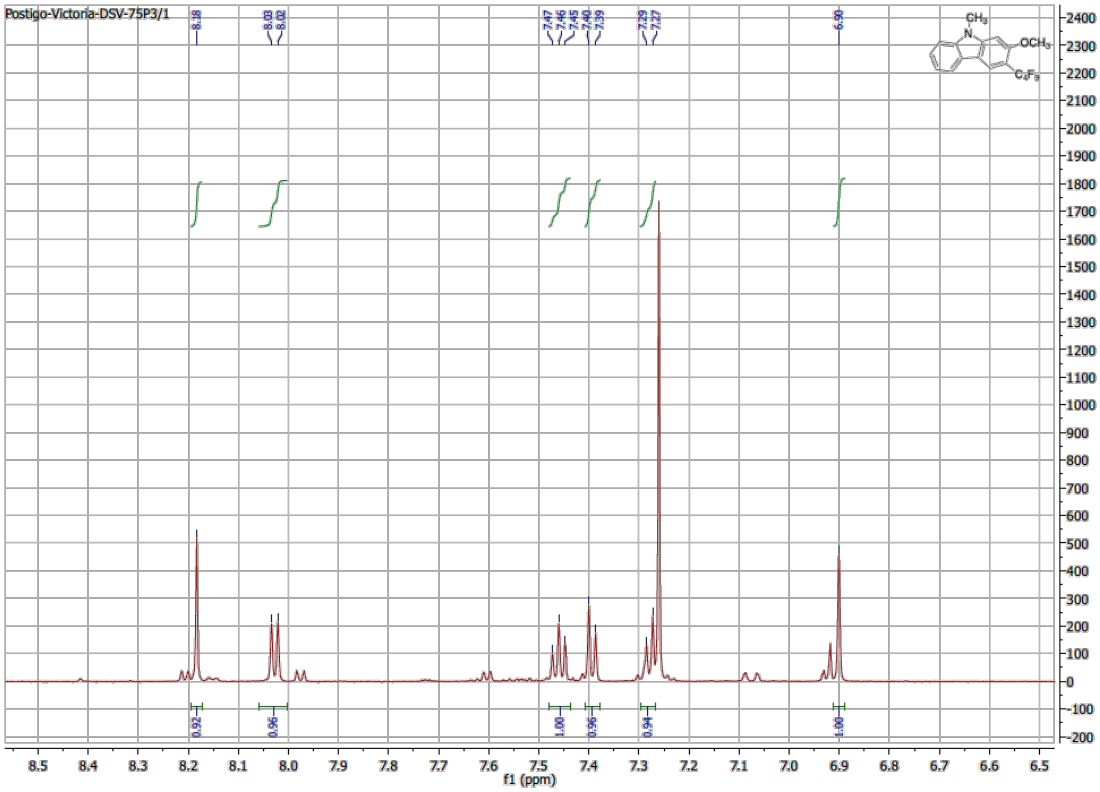
^{1}H NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$



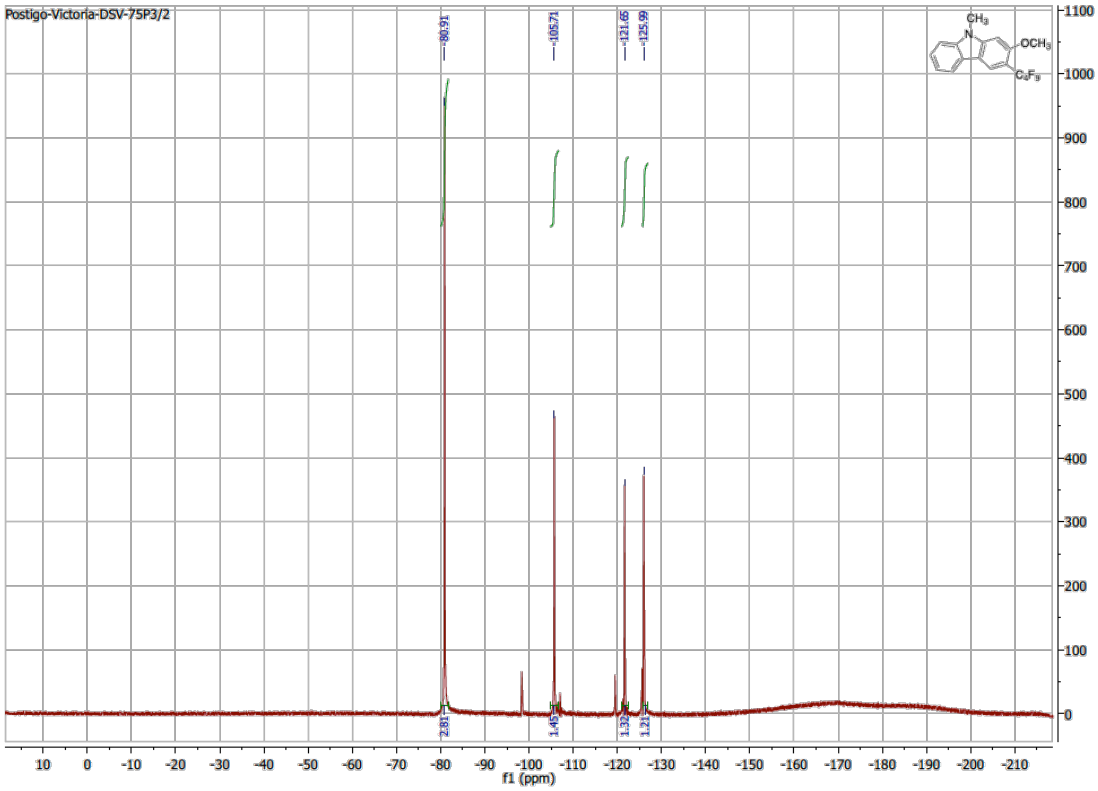
^{1}H NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15.** Expansion aliphatic region in $CDCl_3$



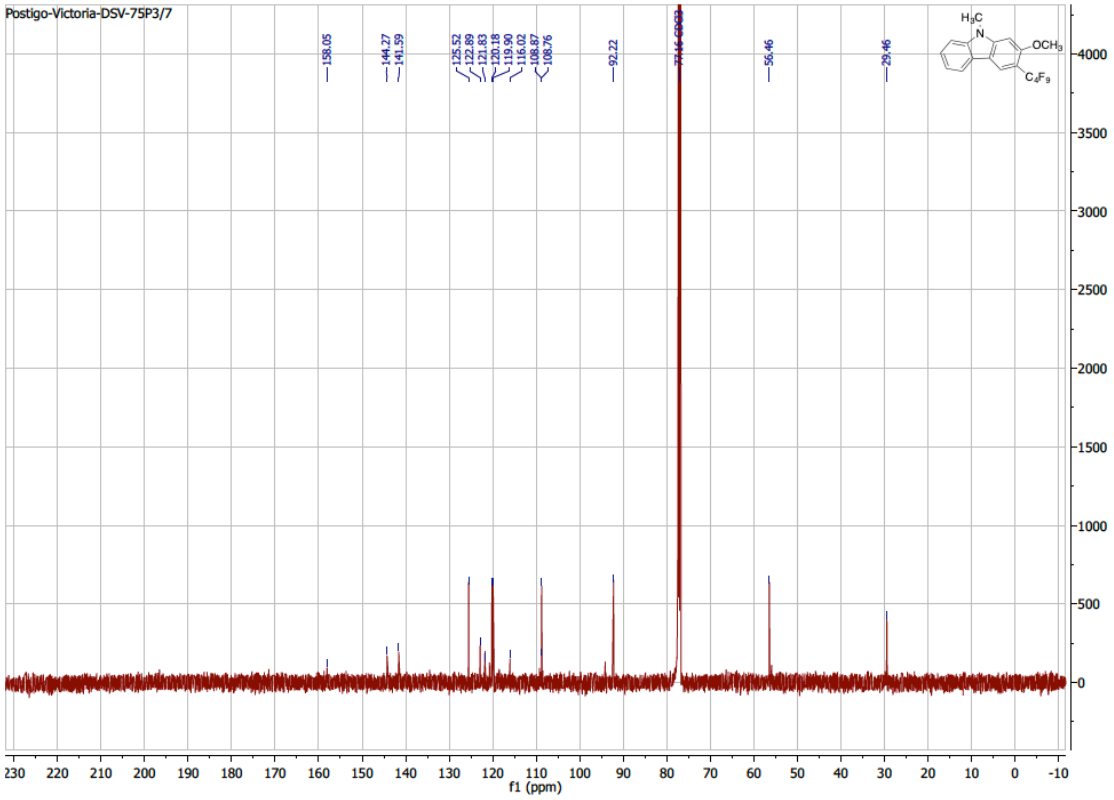
^{1}H NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15.** Expansion aromatic region in $CDCl_3$



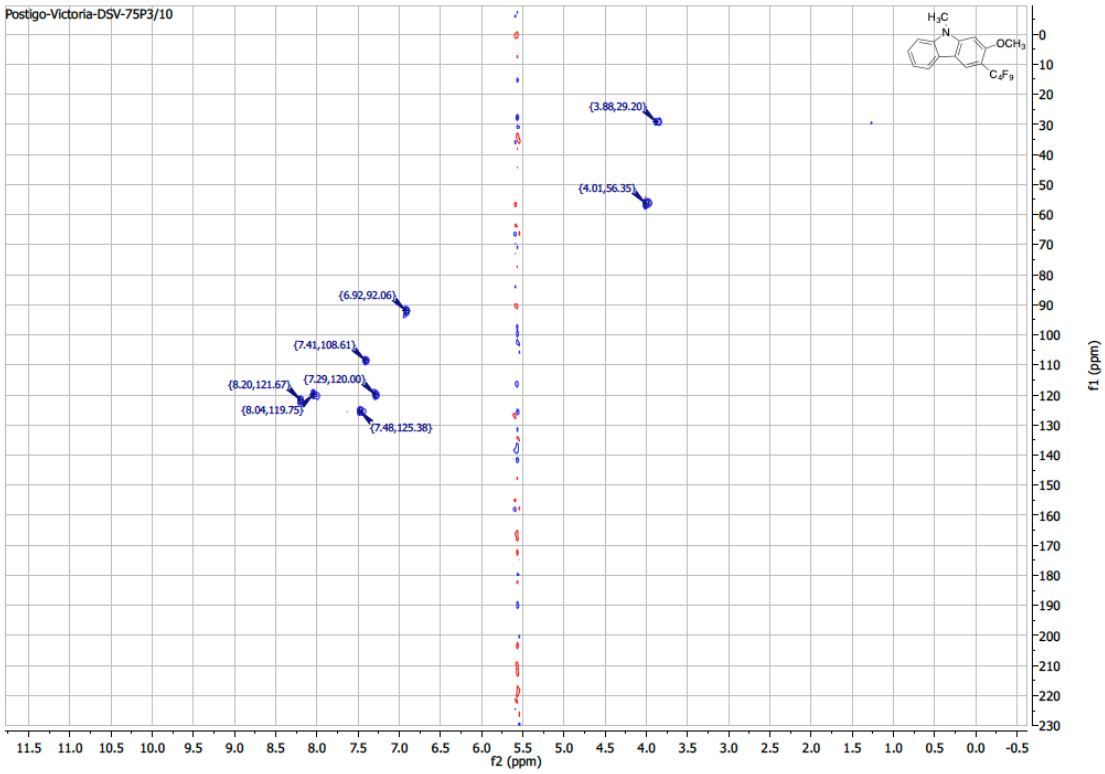
^{19} F NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$



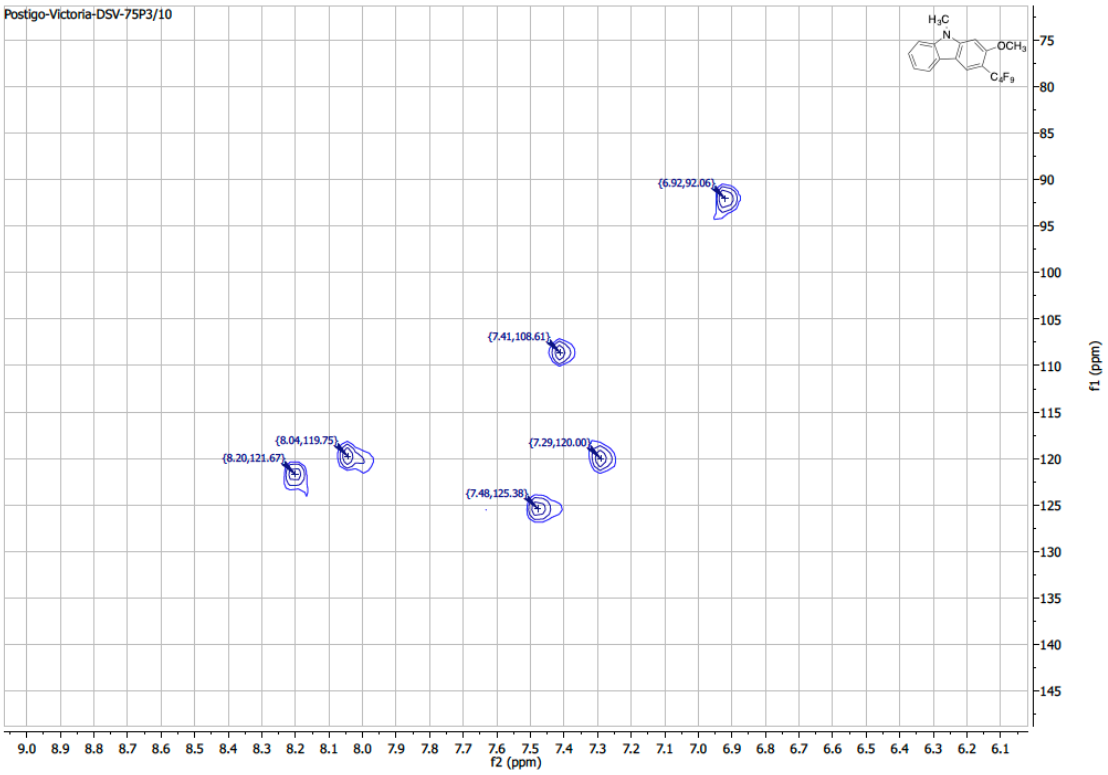
^{13}C NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$



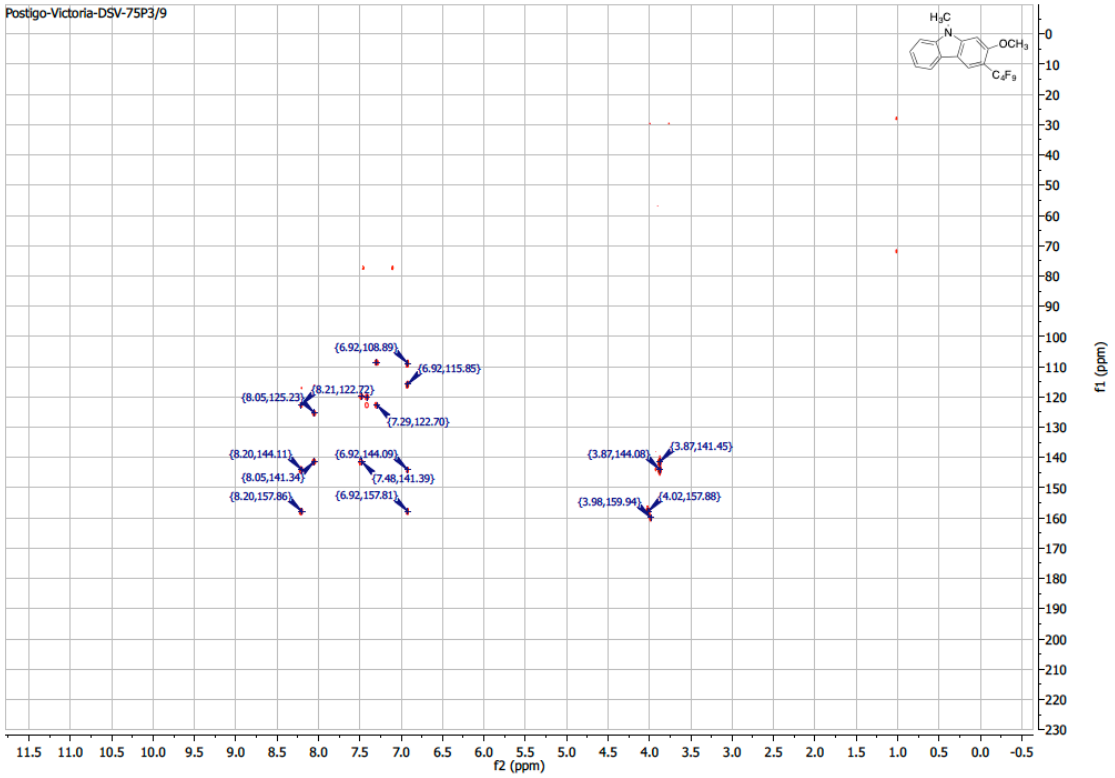
HSQC NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$



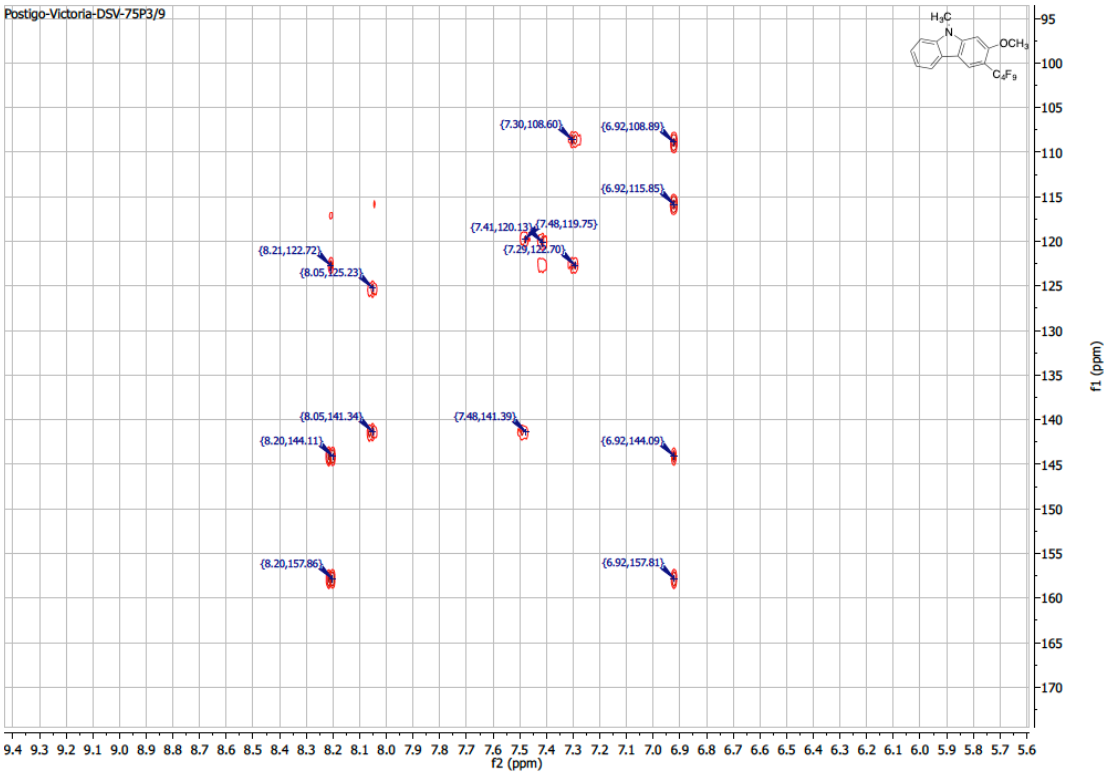
HSQC NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$. Aromatic region



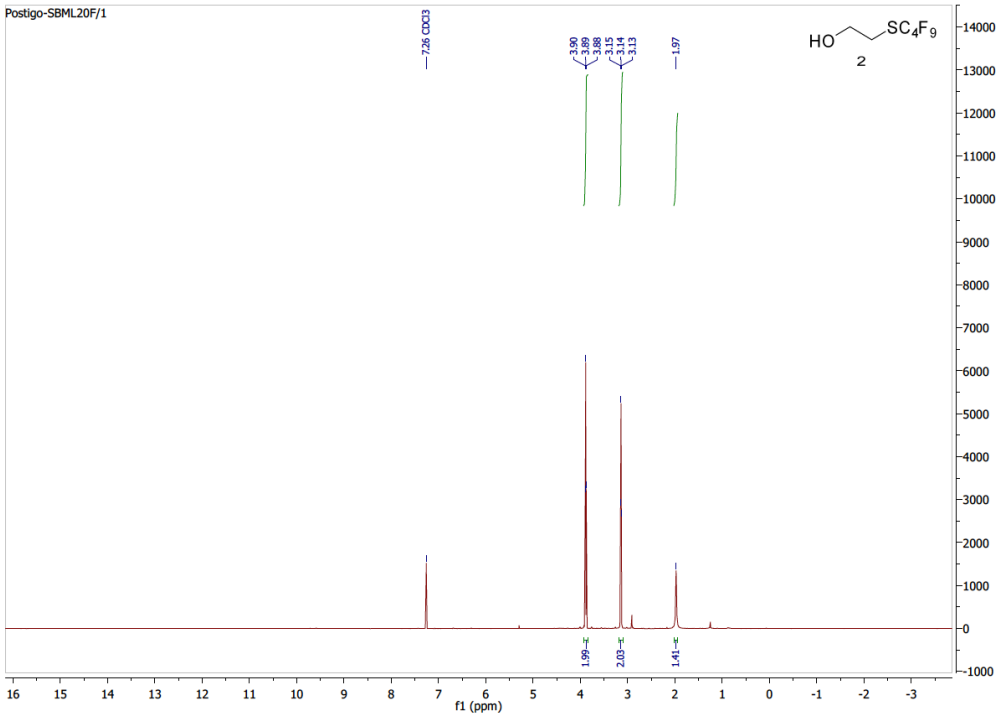
HMBC NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$



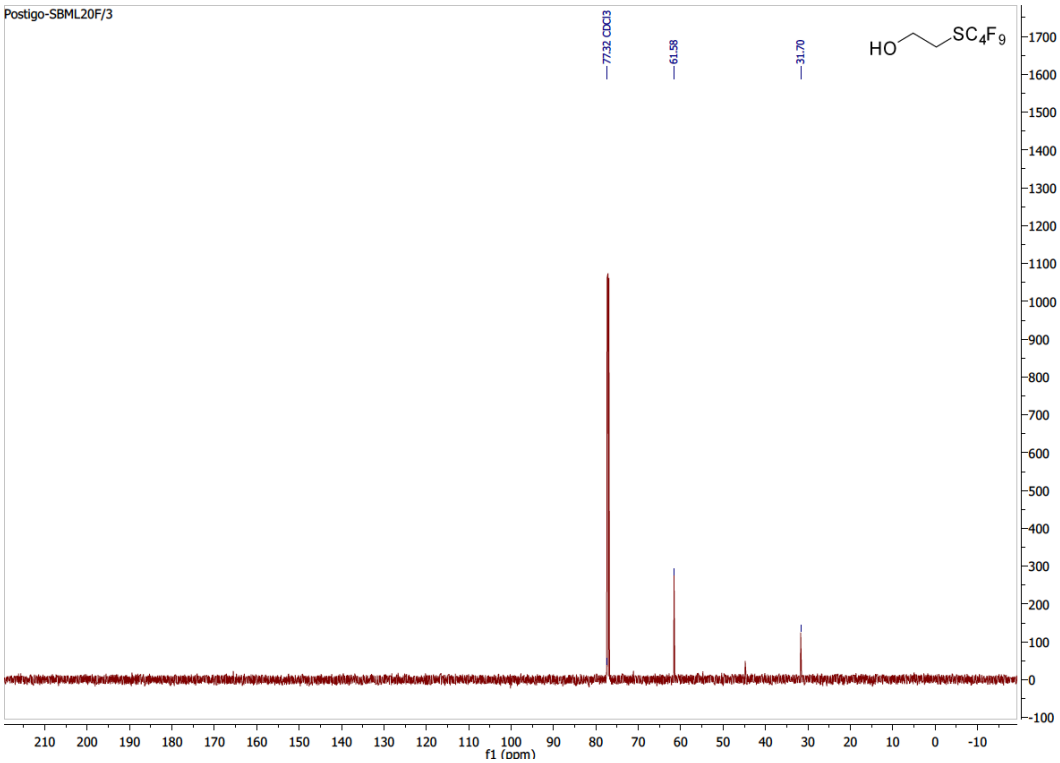
HMBC NMR spectrum of 2-methoxy-3-perfluorobutyl-9-methylcarbazole **15** in $CDCl_3$. Aromatic region



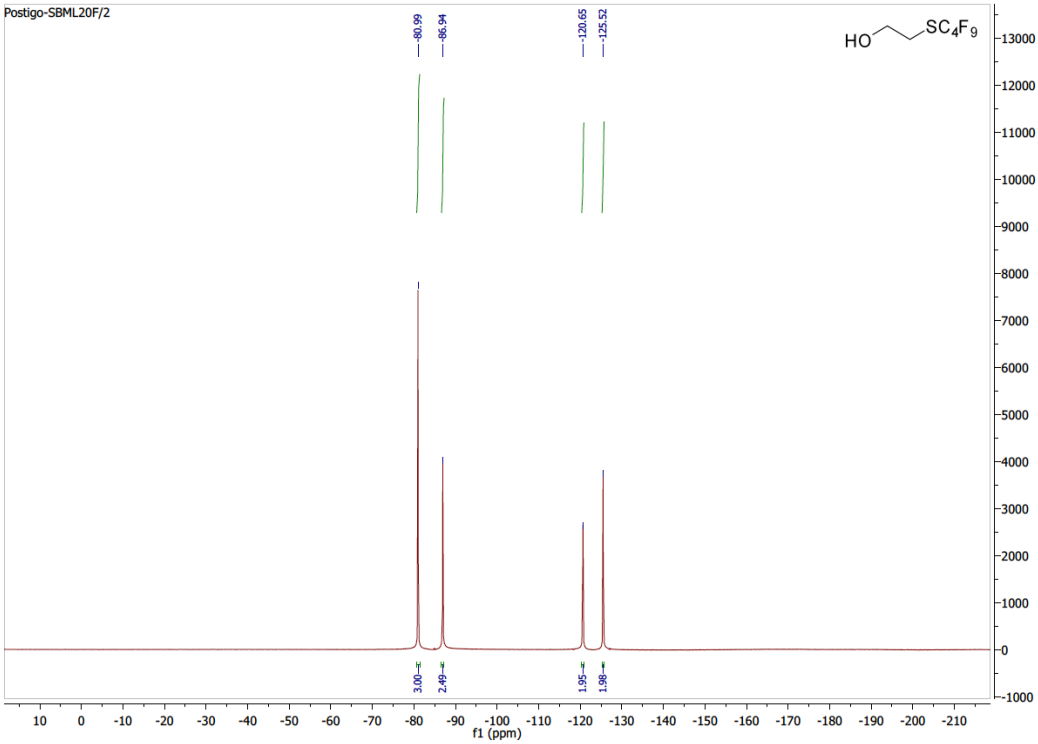
^{1}H NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)ethan-1-ol **16** in $CDCl_3$



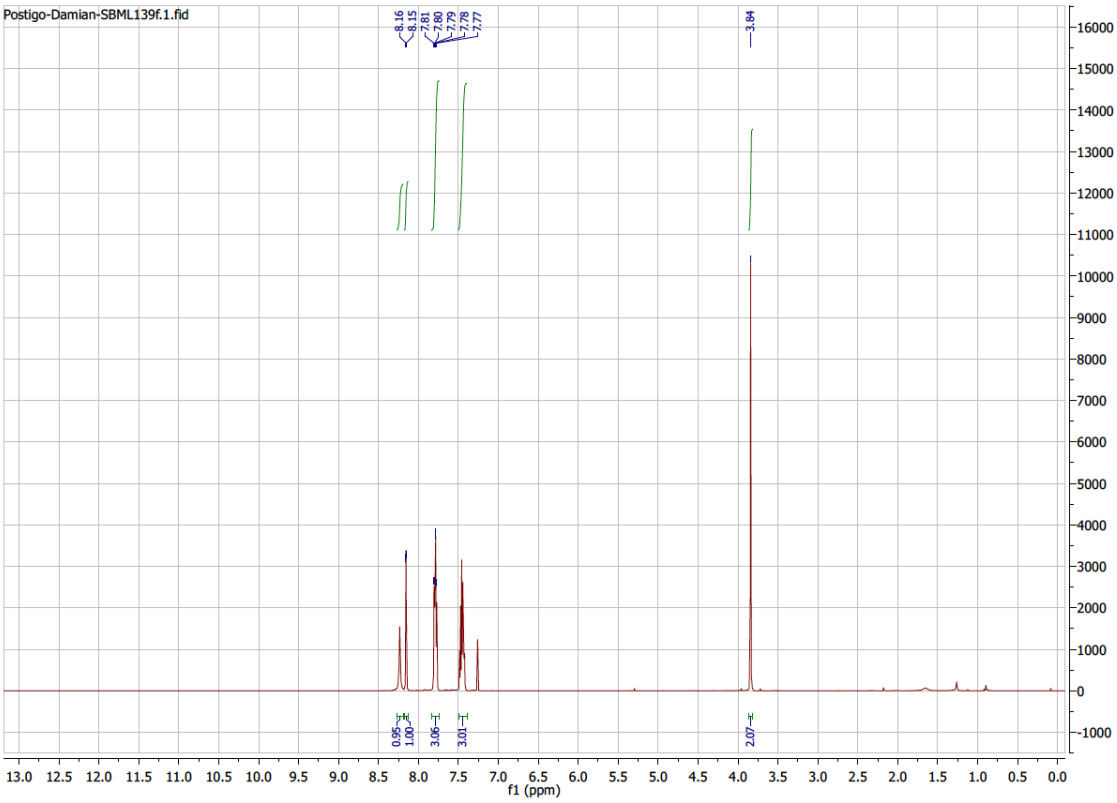
^{13}C NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)ethan-1-ol **16** in $CDCl_3$



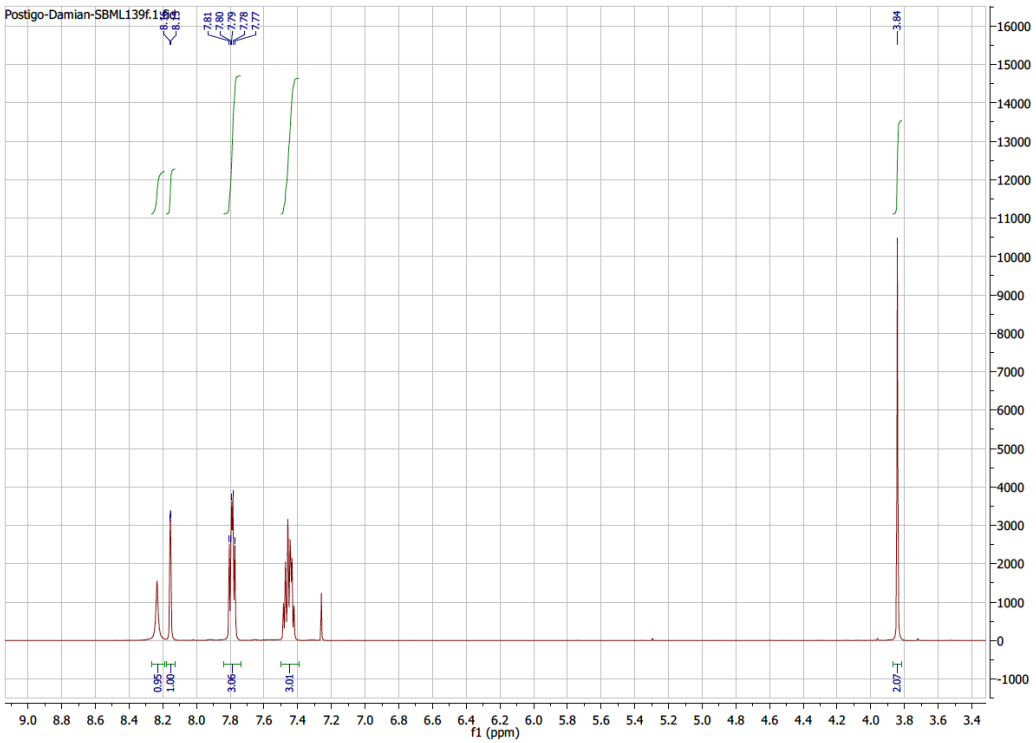
^{19}F NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)ethan-1-ol **16** in $CDCl_3$



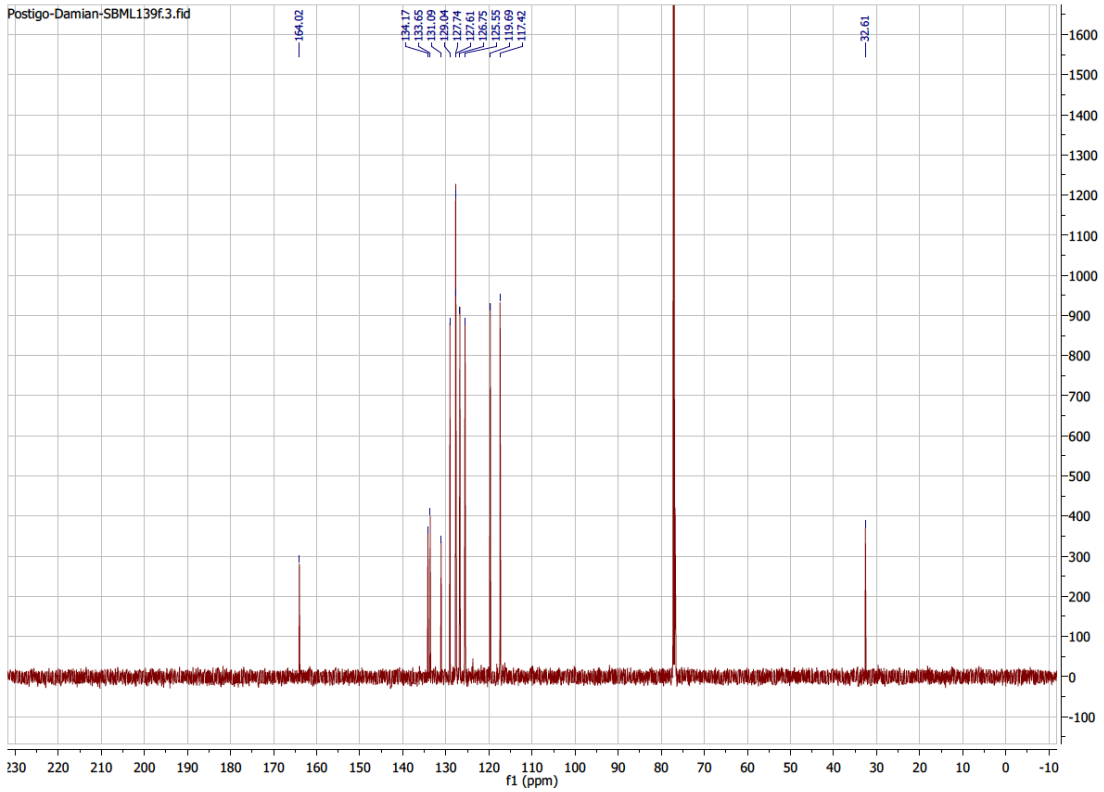
^{1}H NMR spectrum of *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17** in $CDCl_3$



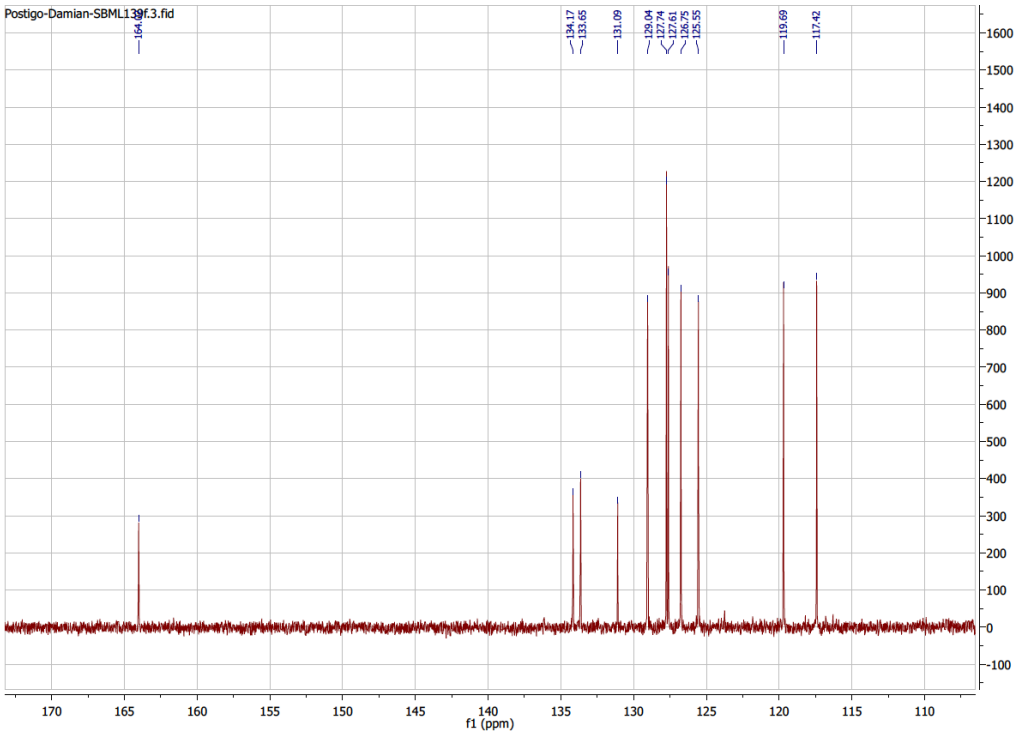
^{1}H NMR spectrum of *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17**. Region 9 – 3.5 ppm, in $CDCl_3$



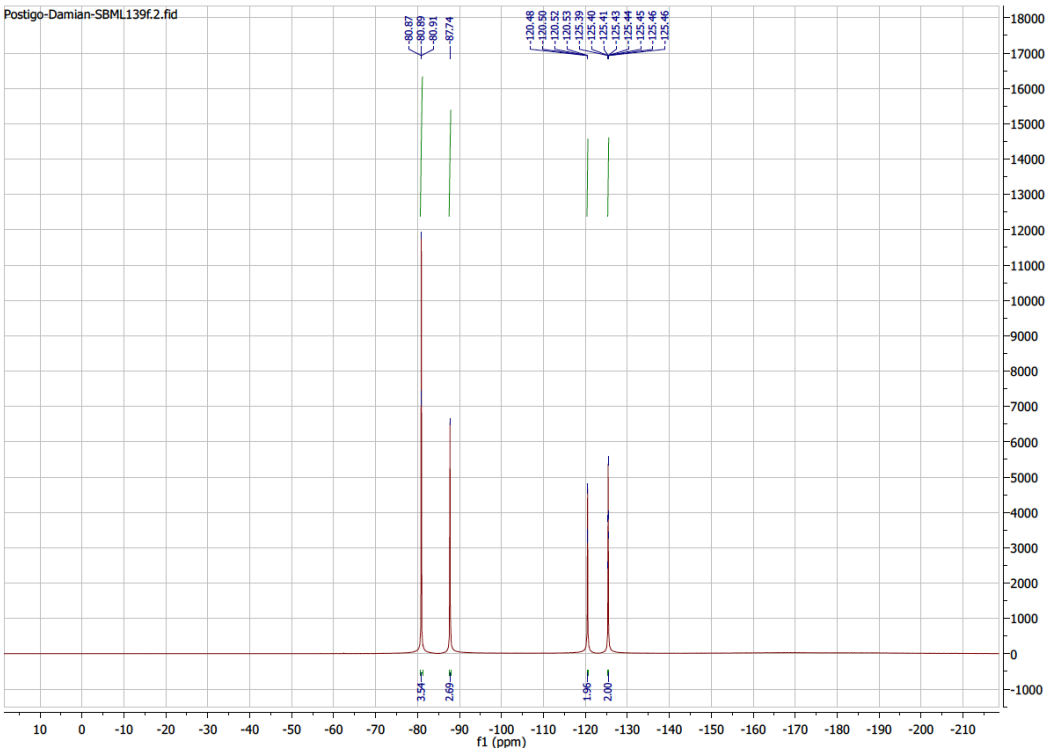
^{13}C NMR spectrum of *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17** in $CDCl_3$



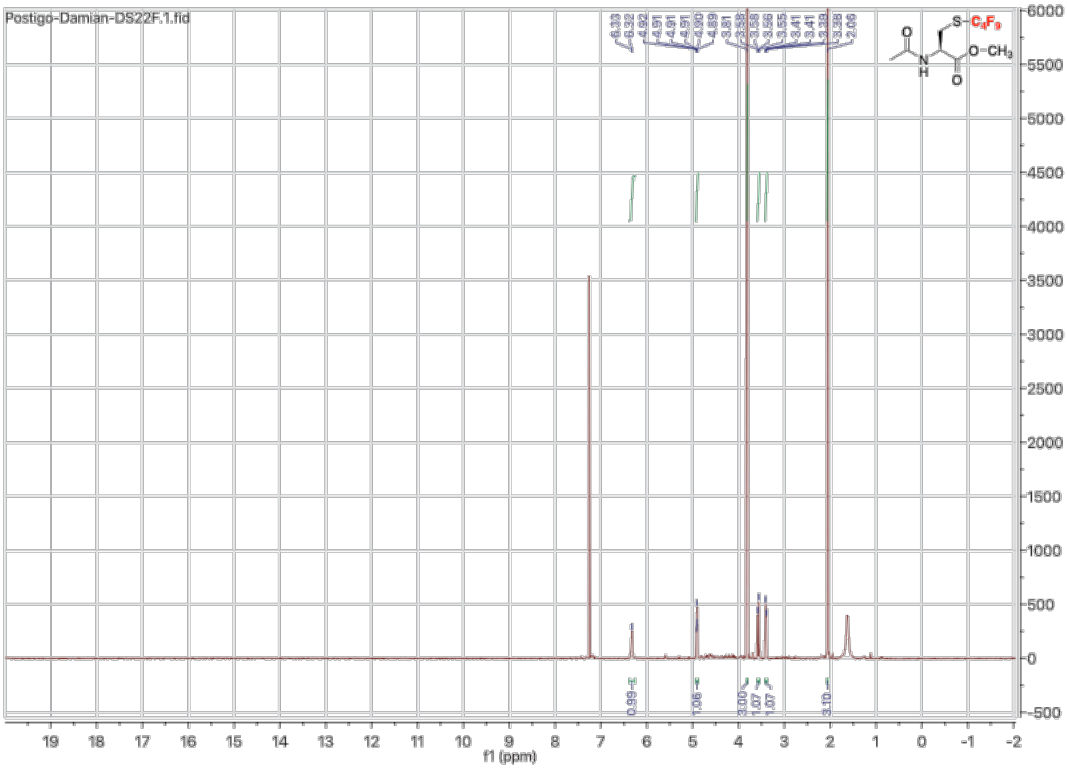
^{13}C NMR spectrum of *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17**. Aromatic region in $CDCl_3$



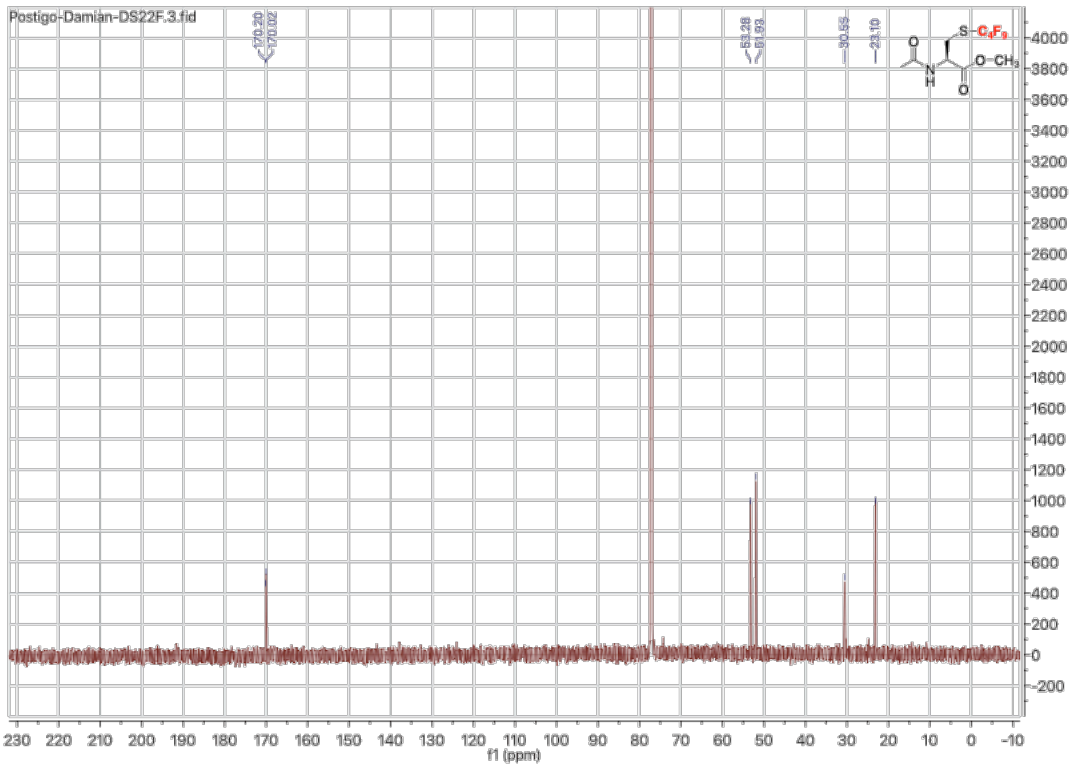
^{19}F NMR spectrum of *N*-(naphthalen-2-yl)-2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)acetamide **17** in $CDCl_3$



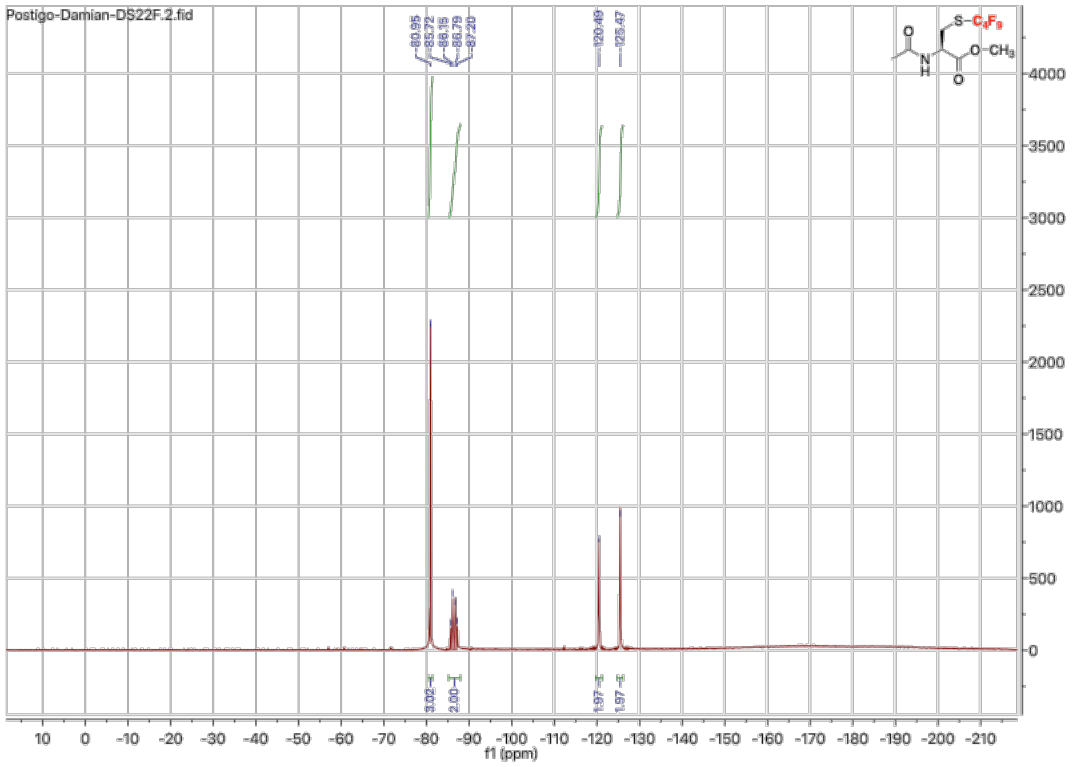
^{1}H NMR spectrum Methyl *N*-acetyl-S-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-L-cysteinate **18** in $CDCl_3$



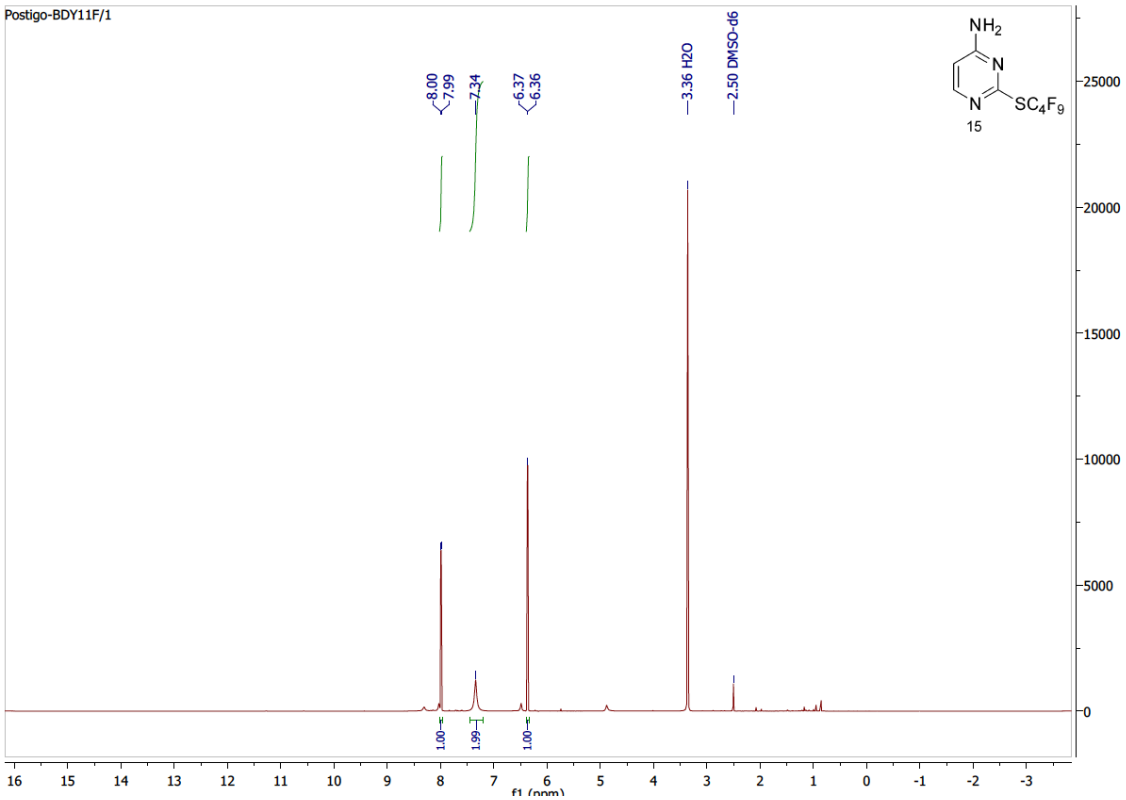
^{13}C NMR spectrum Methyl *N*-acetyl-S-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-L-cysteinate **18** in $CDCl_3$



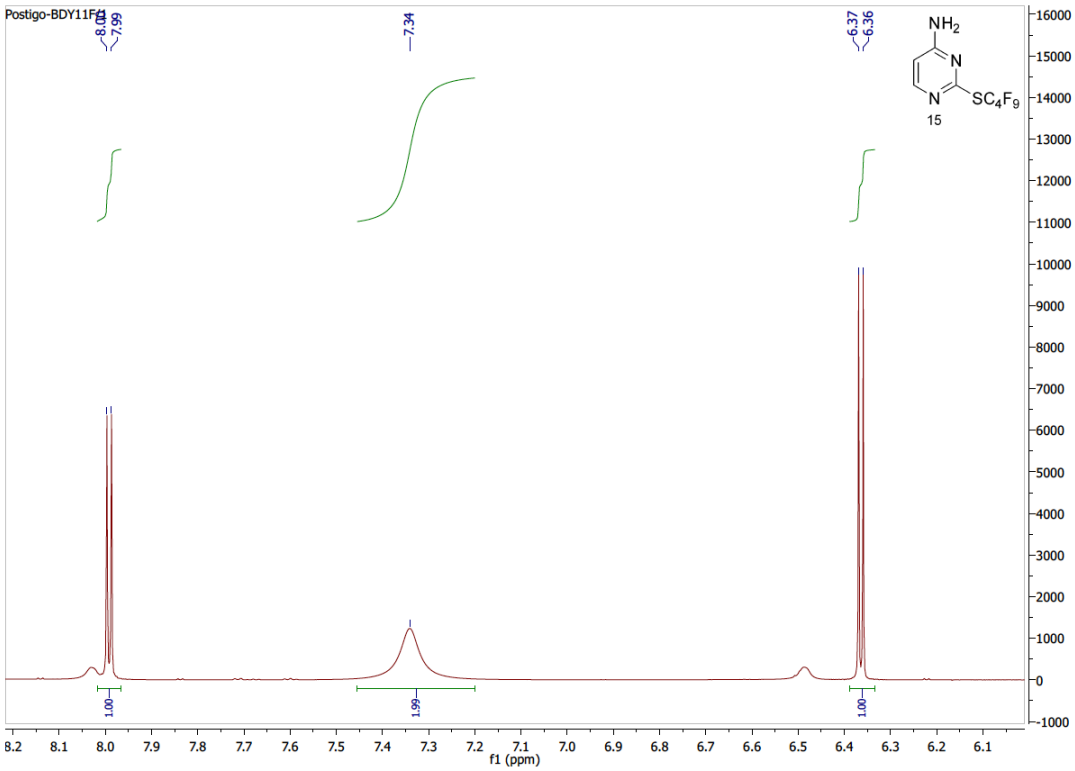
^{19}F NMR spectrum Methyl *N*-acetyl-S-(4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)-L-cysteinate **18** in $CDCl_3$



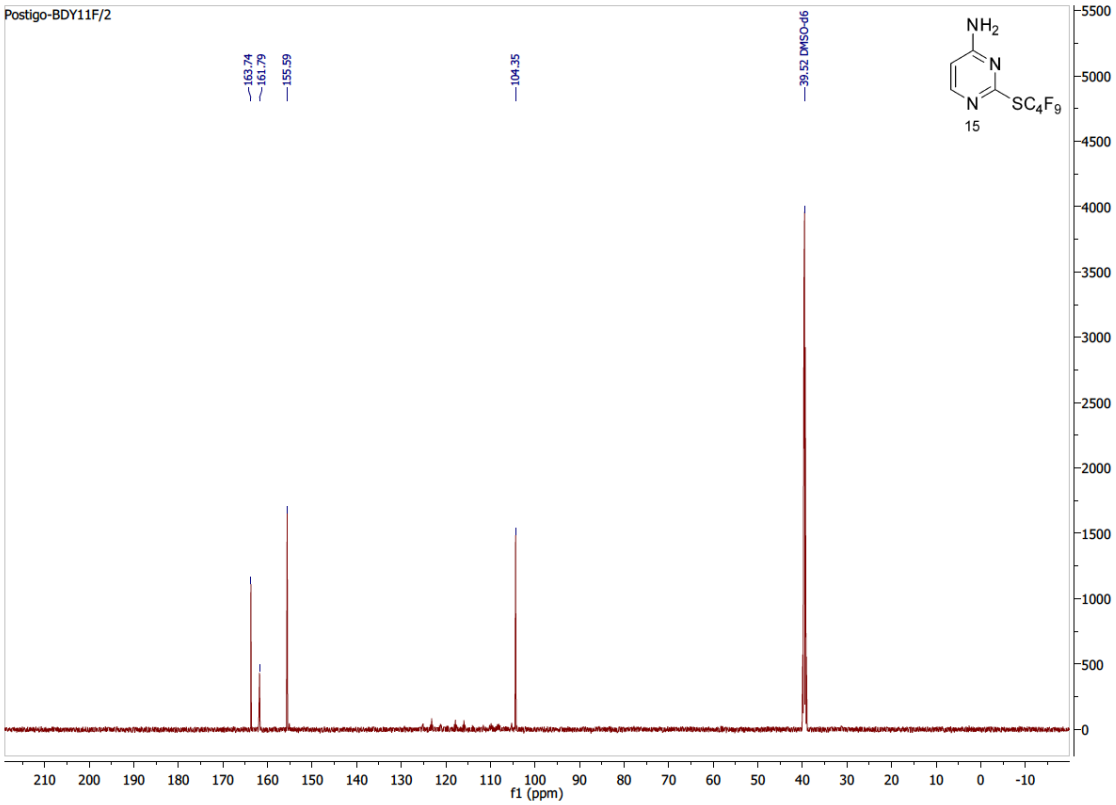
^{1}H NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)pyrimidin-4-amine **19** in DMSO-d_6



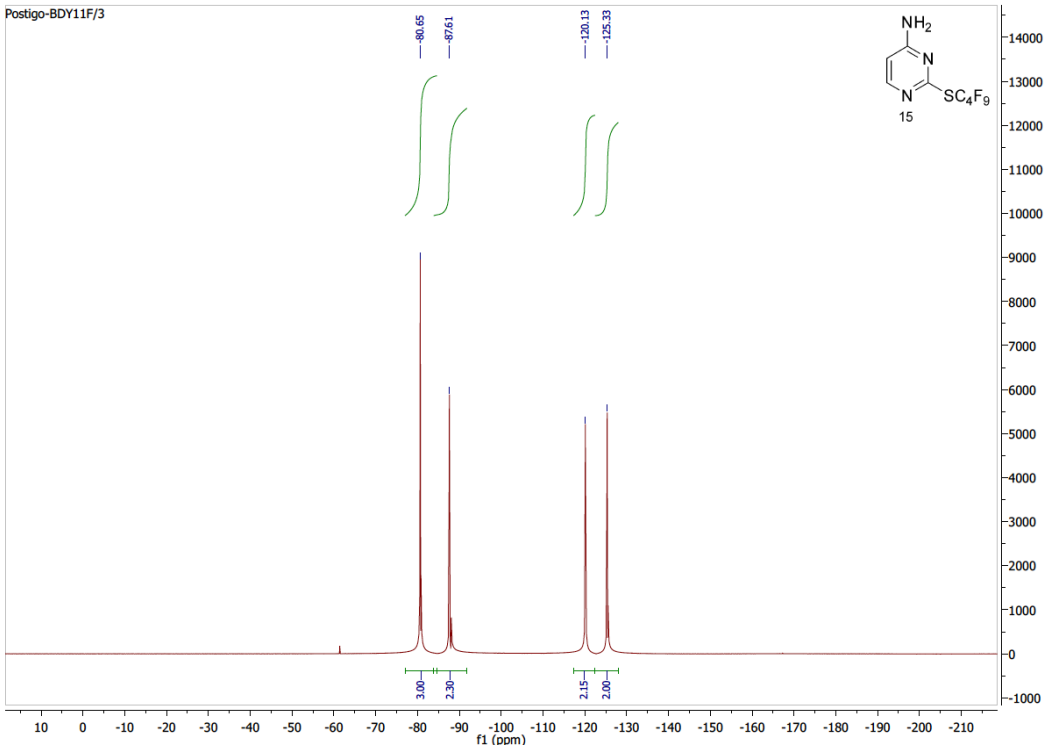
^{1}H NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)pyrimidin-4-amine **19.** Aromatic region in DMSO-d_6



^{13}C NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)pyrimidin-4-amine **19** in DMSO-d_6

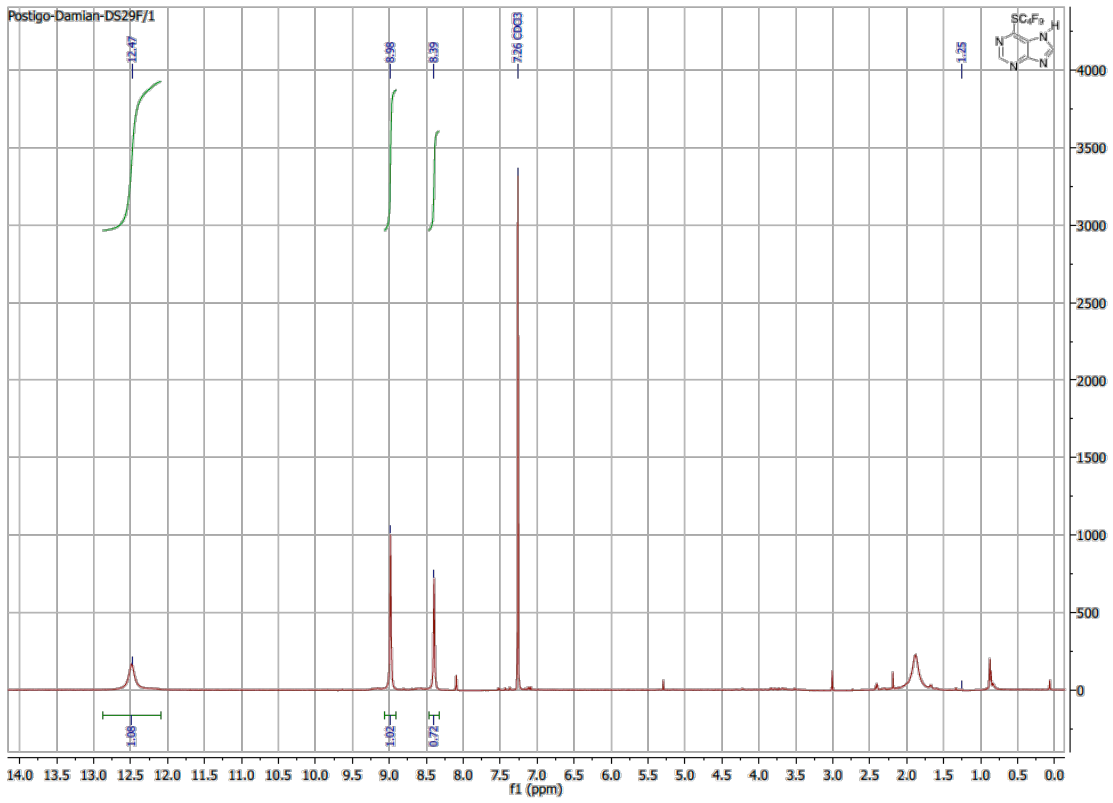


^{19}F NMR spectrum of 2-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)pyrimidin-4-amine **19** in DMSO-d_6



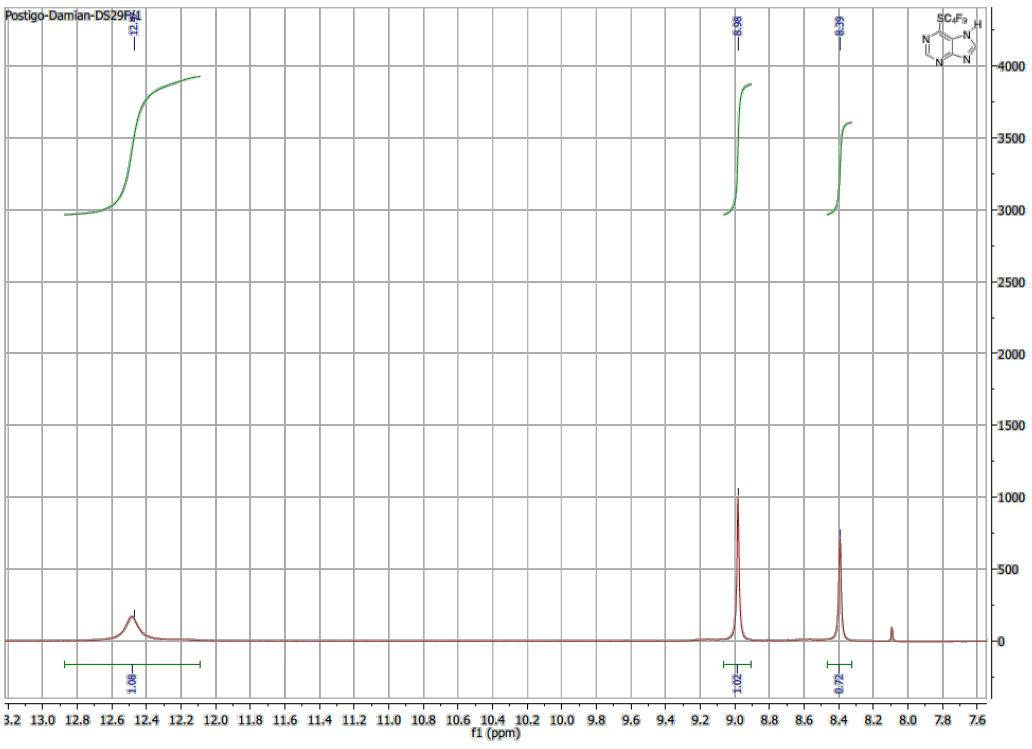
^{1}H NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**

in $CDCl_3$

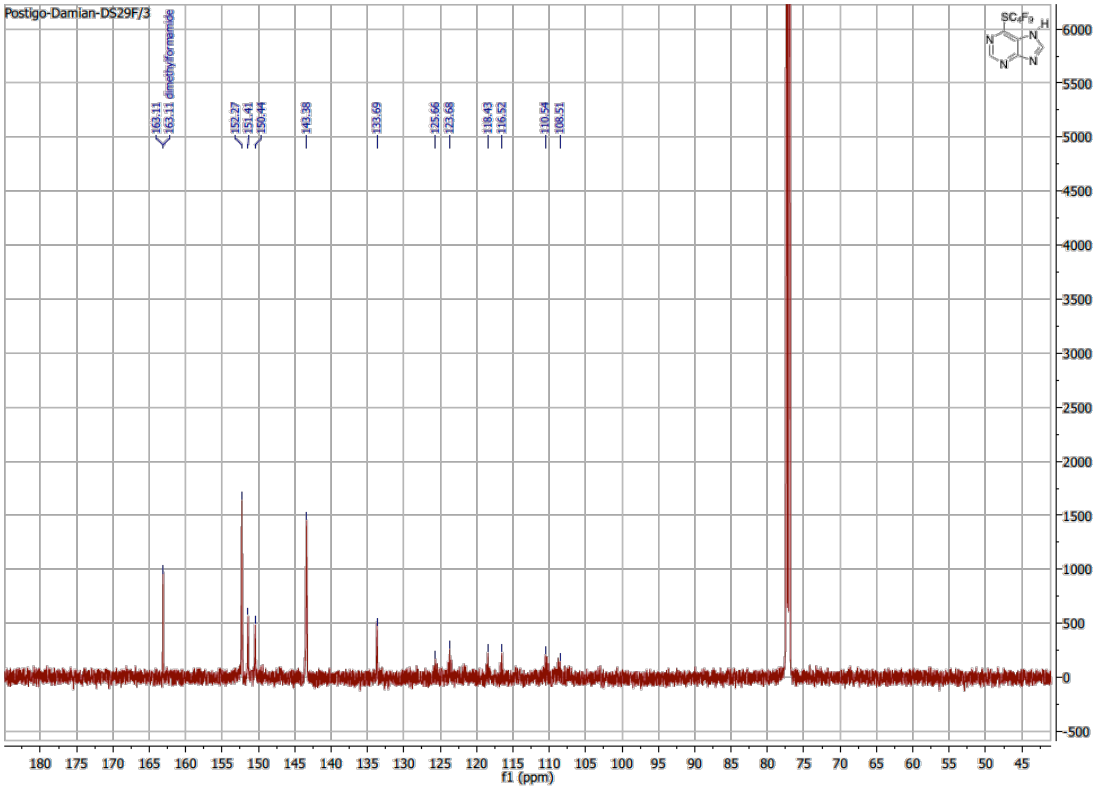


^{1}H NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**

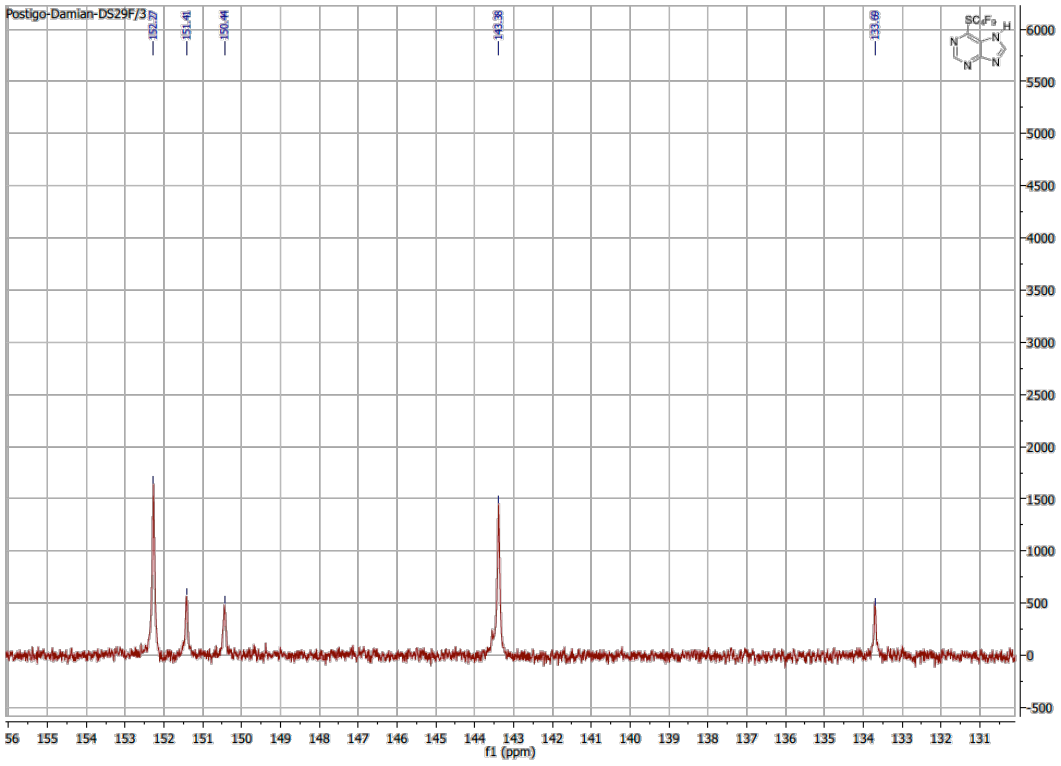
Aromatic region expanded in $CDCl_3$



^{13}C NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20** in $CDCl_3$

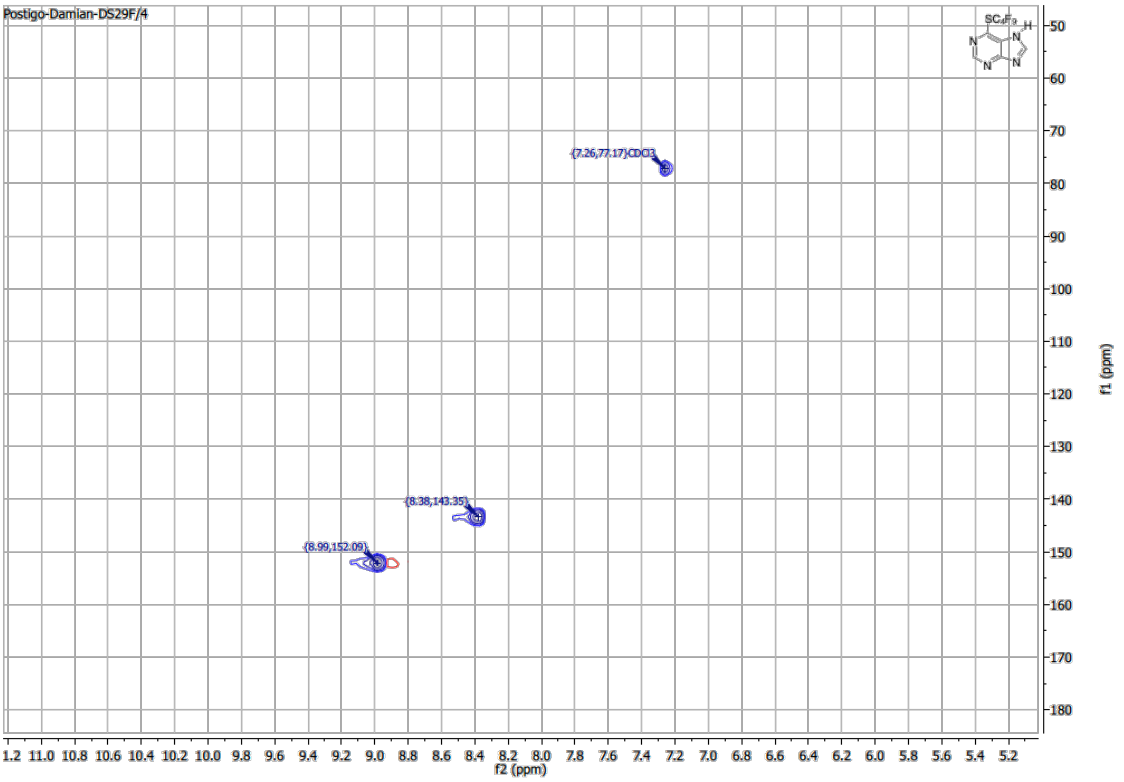


^{13}C NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**. Expansion aromatic region in $CDCl_3$



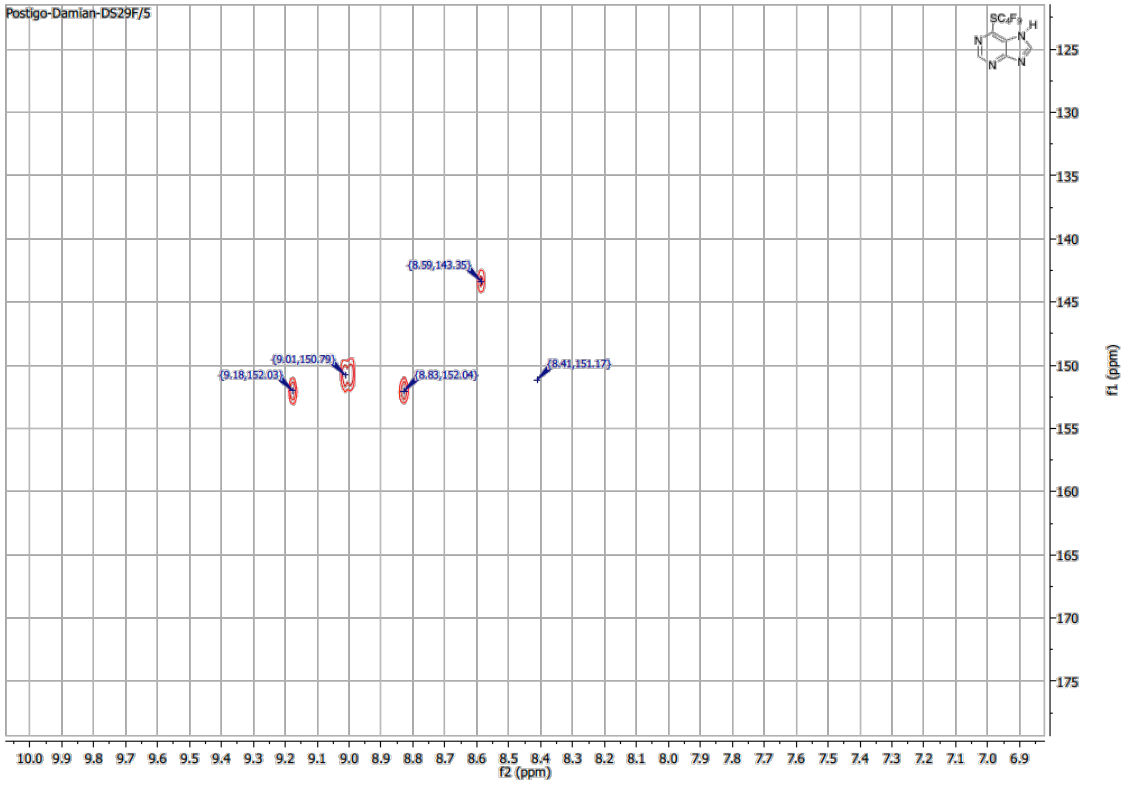
HSQC spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**

in $CDCl_3$

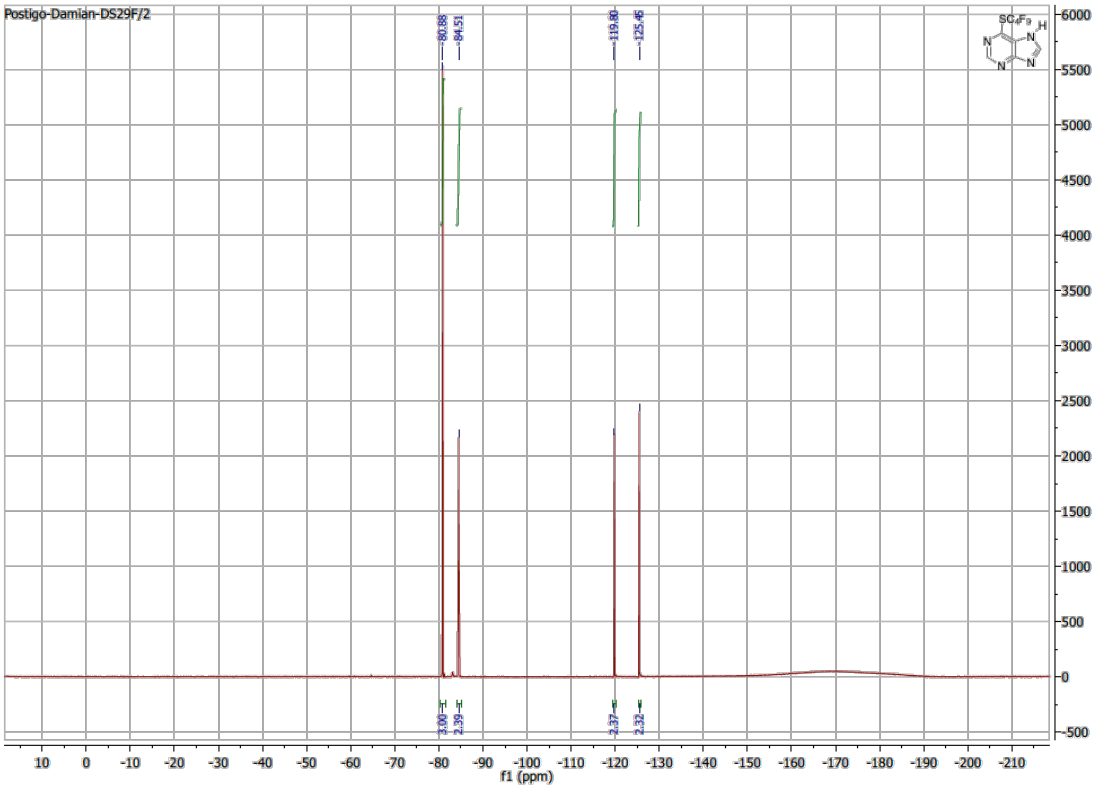


HMBC spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**

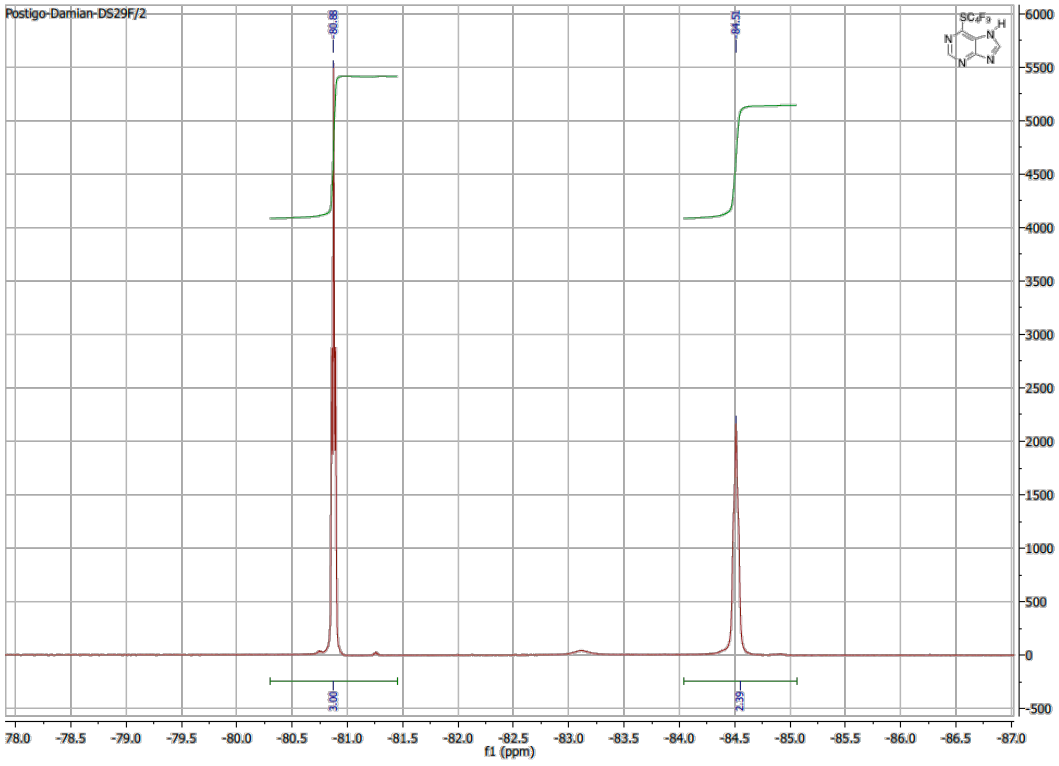
in $CDCl_3$



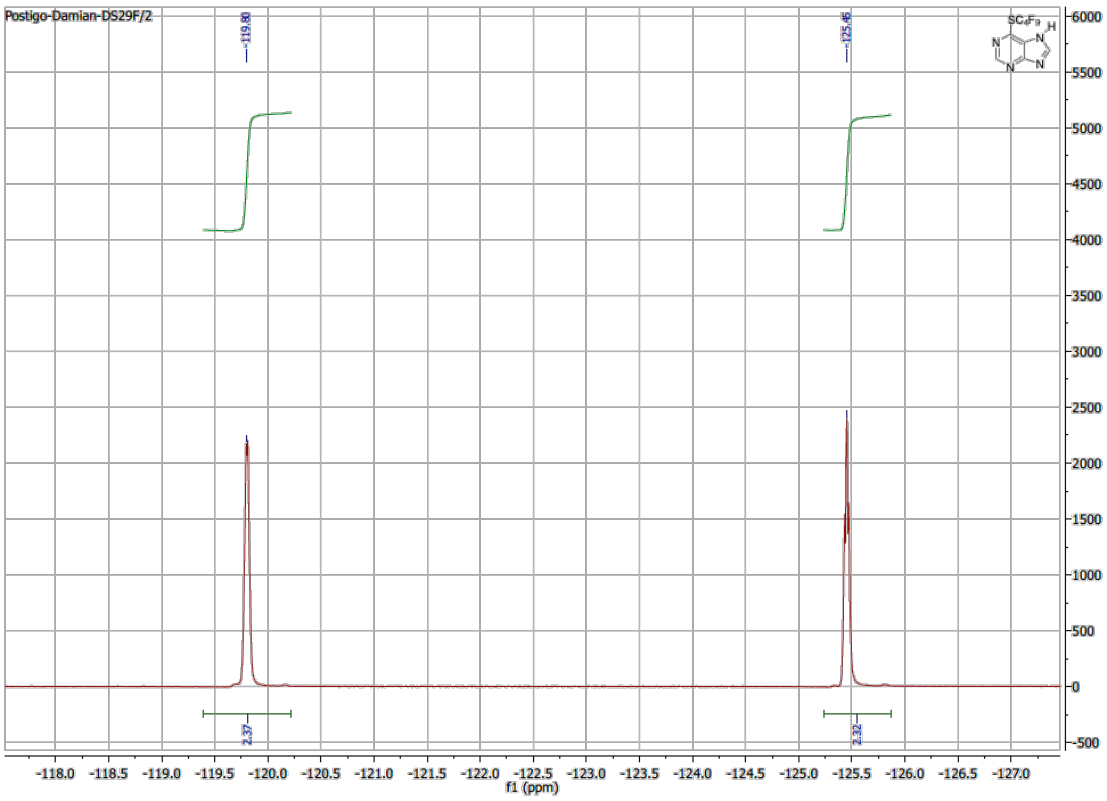
^{19} F NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20** in $CDCl_3$



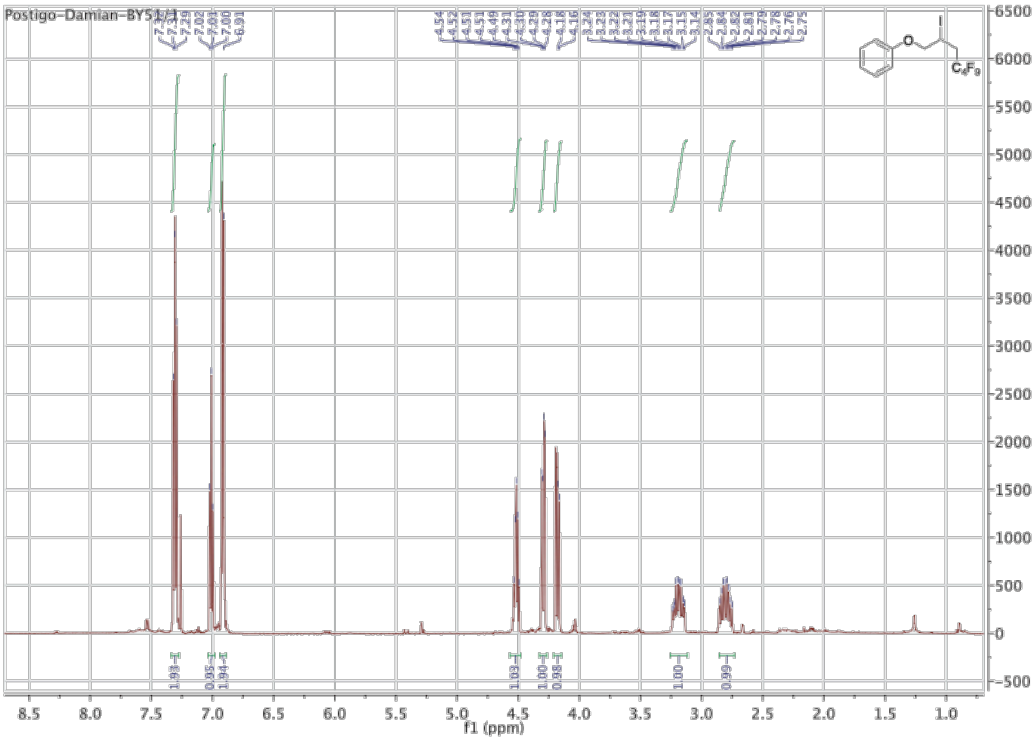
^{19} F NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**. Expansion -78 - -87 ppm in $CDCl_3$



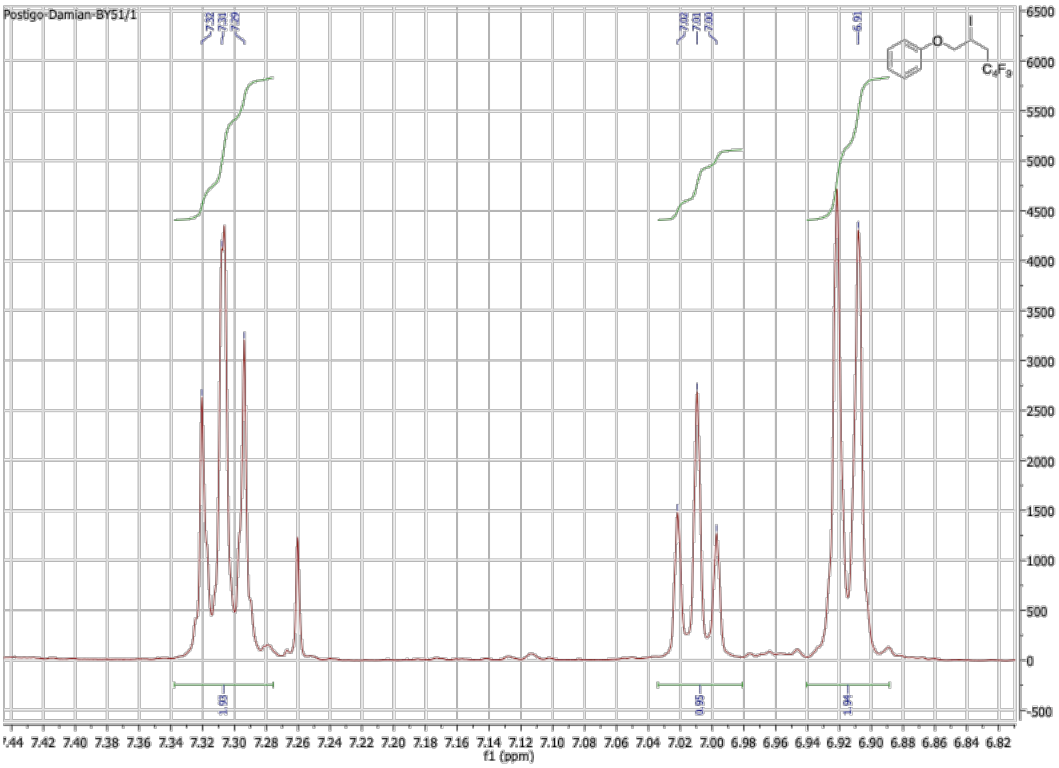
^{19} F NMR spectrum of 6-((4,4,4,4,4,4,4,4,4-nonafluoro-4λ12-buta-1,3-diyn-1-yl)thio)-7H-purine **20**. Expansion -118 - -127 ppm in $CDCl_3$



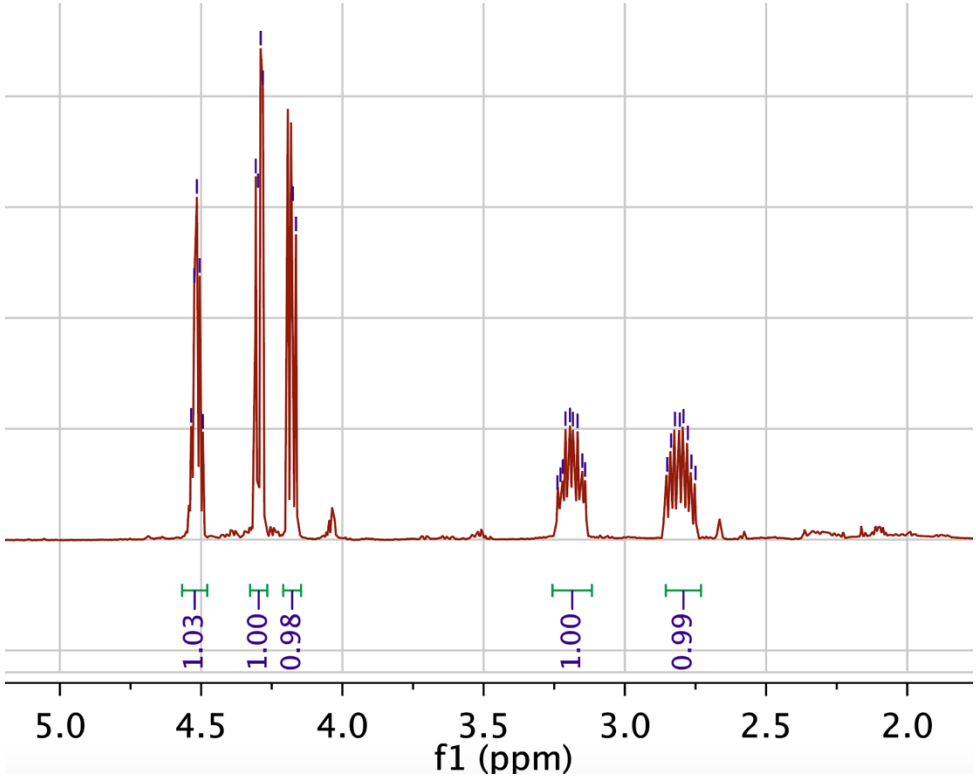
^{1}H NMR spectrum of ((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **22** in $CDCl_3$



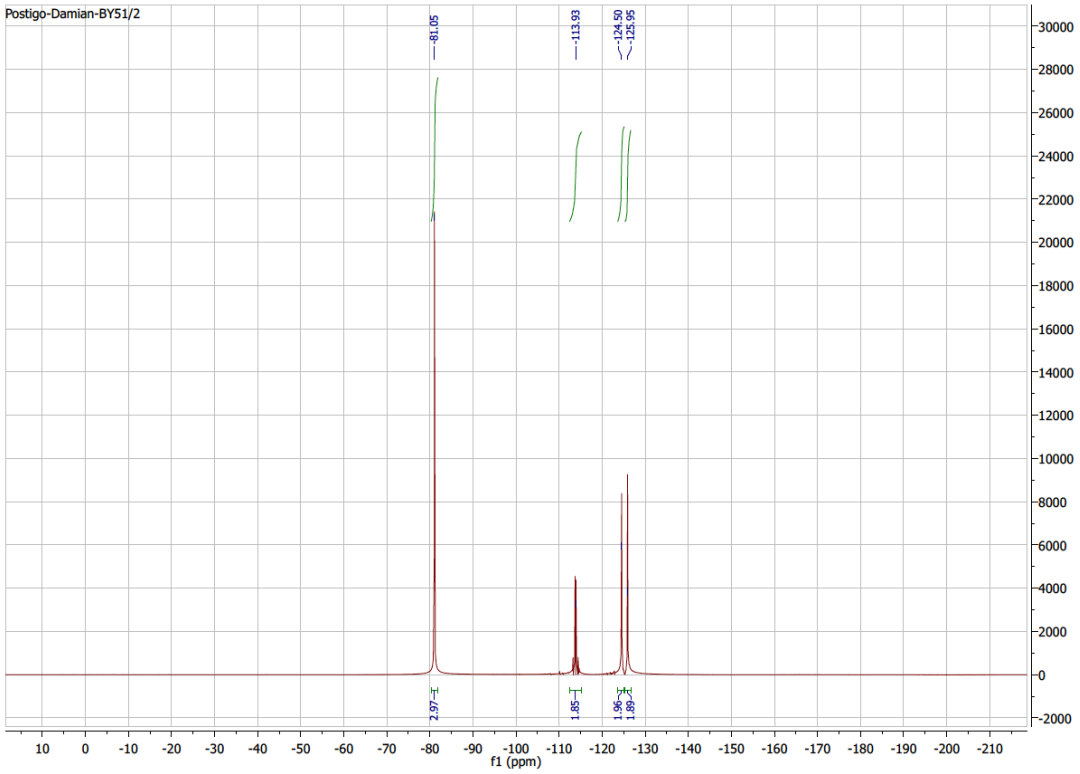
^{1}H NMR spectrum of ((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23.** Aromatic region in $CDCl_3$



^{1}H NMR spectrum of ((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23.** Aliphatic region in $CDCl_3$



^{19}F NMR spectrum of ((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23** in $CDCl_3$



^{19}F NMR spectrum of ((7,7,7,7,7,7,7,7,7-Nonafluoro-2-iodo-7λ12-hepta-4,6-diyn-1-yl)oxy)benzene **23. -**140 - -70 ppm region in $CDCl_3$