

# Synthesis and characterisation of an open-cage fullerene encapsulating hydrogen fluoride

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## Supplementary Information

Experimental procedures, compound characterization data and details of calculations.

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## **General:**

All reactions were executed under nitrogen atmosphere. All additions were performed using regular air-free techniques. Reactions involving hydrogen fluoride pyridine were carried out in polytetrafluoroethylene (PTFE) or polyethylene (PE) tubes fitted with screw caps. Hydrogen fluoride pyridine was handled using PE or PTFE containers and tubing. The reaction course was monitored by TLC using Merck silica gel 60 F254 plates detecting the spots using an UV lamp or by HPLC performed on a Cosmosyl Bukyprep analytical column with detection at 326nm. Flash column chromatography was run using Merck silica gel Geduran Si60 (40-63  $\mu\text{m}$ ) as stationary phase. FT-IR spectra were recorded on a Bruker Alpha-T instrument. UV-Vis spectra were recorded on an Ocean Optics USB2000+ UV/Vis spectrometer. Electrospray mass spectra were recorded in the positive ion mode. The expected peaks due to natural abundance of  $^{13}\text{C}$  were present but not reported. Note that, due to the noise reducing threshold used in processing, relative intensities of weak peaks are reduced.

## **Materials:**

Compound **1** was synthesised according to the reported procedure.<sup>1</sup> Dichloromethane was distilled over calcium hydride under nitrogen atmosphere. 70% w/w hydrogen fluoride in pyridine was purchased from Sigma-Aldrich Company Ltd. and directly used as supplied.

## **Solution NMR:**

Spectra were recorded on Bruker, DPX400 or 500 spectrometers. Chemical shifts are reported in ppm and referenced to the residual solvent peak for  $^1\text{H}$  and  $^{13}\text{C}$  or  $\text{CFCl}_3$  for  $^{19}\text{F}$  spectra.

## **Solid-State NMR:**

$^1\text{H}$  NMR Experiments were performed at 20 T (850 MHz) at the National High field facility at the University Of Warwick on a Bruker AVANCE III console. A Hahn echo experiment with a 92 KHz amplitude pulse was used to generate the transverse magnetization and a dead time of 5  $\mu\text{s}$  was left before recording the free induction decay. The spectrum is the average of 8 transients, with 4 seconds between scans. The

experiments were performed using magic angle spinning at variable spinning speeds to remove anisotropic interactions and increase resolution.  $^1\text{H}$  proton NMR spectra were referenced to adamantane at 1.8 ppm.<sup>2</sup>

$^{19}\text{F}$  experiments were also performed at 20 T, the spectra are the result of 256 scans with a 2 second pulse delay.  $^{19}\text{F}$  spectra were referenced to  $\beta$ -Polyvinylidene fluoride (PVDF) as an indirect reference for the accepted 0 ppm IUPAC standard  $\text{CFCl}_3(\text{aq})$ , with a chemical shift of -98 ppm.<sup>2</sup> To protect the sample against heat generated from high spinning speeds, a nitrogen gas stream was used for cooling at speeds of 20 KHz and above. Processing of spectra was done using matNMR.

### **Simulations:**

In order to extract NMR interaction parameters, we used SPINACH<sup>3,4</sup> for global minimization with multiple experimental datasets. Then we verified error margins with SIMPSON<sup>5</sup> by simulating a matrix of various interaction magnitudes and monitoring RMS between experiment and simulations centered around the best fit values.

### **DFT calculations:**

Density Function Theory calculations on the formation of  $\text{H}_2@2\text{B}$ ,  $\text{H}_2\text{O}@2\text{B}$  and  $\text{HF}@2\text{B}$ , where 2B is a model for **2** in which the 5-tert-butyl-pyridyl substituents were replaced by methyl groups, were carried out using Guassian 09<sup>6</sup> and the results are shown in Table 1. Minimum energy and transition state structures were obtained using the B3LYP functional<sup>7</sup> with 6-31G(d) basis set.<sup>8</sup> Frequency calculations were carried out to confirm the nature of the structures (single imaginary frequency for transitions states) and to provide a zero point energy correction. Energies were obtained by single point calculations using Truhlar's M062X hybrid functional (which copes well with dispersion-like interactions)<sup>9</sup> with Dunning's cc-pVDZ correlation consistent double-zeta basis set<sup>10</sup> correcting for Basis Set Superposition Errors using counterpoise.<sup>11</sup> Note that B3LYP gives poor results as would be expected for a functional which neglects dispersion-like interactions.

**Table 1.** Calculations on activation energy for entry / exit and binding energy for H<sub>2</sub>, H<sub>2</sub>O and HF into **2B**.

Energies / Hatree										
H <sub>2</sub>	2B	zpe	H <sub>2</sub>	zpe	H <sub>2</sub> @2B	cp	zpe	TS	cp	zpe
B3LYP/631d	-2820.49974	0.50264	-1.17548	0.00995	-2821.67281	0.00145	0.51438	-2821.65049	0.00227	0.51773
m062x/vdz@B3LYP/631d	-2819.91343	0.50264	-1.16332	0.00995	-2821.08748	0.00093	0.51438	-2821.05963	0.00223	0.51773
H <sub>2</sub> O	2B	zpe	H <sub>2</sub> O	zpe	H <sub>2</sub> O@2B	cp	zpe	TS	cp	zpe
B3LYP/631d	-2820.49974	0.50264	-76.40895	0.02075	-2896.91201	0.00966	0.52392	-2896.88673	0.01692	0.52672
m062x/vdz@B3LYP/631d	-2819.91343	0.50264	-76.38876	0.02075	-2896.32793	0.01003	0.52392	-2896.30337	0.01774	0.52672
HF	2B	zpe	HF	zpe	HF@2B	cp	zpe	TS	cp	zpe
B3LYP/631d	-2820.49974	0.50264	-100.42017	0.00888	-2920.93013	0.01228	0.51284	-2920.91479	0.02082	0.51388
m062x/vdz@B3LYP/631d	-2819.91343	0.50264	-100.40277	0.00888	-2920.33845	0.01106	0.51284	-2920.32459	0.01739	0.51388

H <sub>2</sub>	Energies / Hartree			Energies / kJ/mol		
	E(H <sub>2</sub> @2B-(H <sub>2</sub> +2B))	Ea (entry)	Ea (exit)	E(H <sub>2</sub> @2B-(H <sub>2</sub> +2B))	Ea (entry)	Ea (exit)
B3LYP/631d	0.00566	0.03214	0.02648	14.87	84.38	69.51
m062x/vdz@B3LYP/631d	-0.00800	0.02450	0.03250	-21.01	64.32	85.33
H <sub>2</sub> O	E(H <sub>2</sub> O@2B-(H <sub>2</sub> O+2B))	Ea (entry)	Ea (exit)	E(H <sub>2</sub> O@2B-(H <sub>2</sub> O+2B))	Ea (entry)	Ea (exit)
B3LYP/631d	0.00687	0.04221	0.03534	18.04	110.81	92.77
m062x/vdz@B3LYP/631d	-0.01519	0.01989	0.03508	-39.89	52.22	92.11
HF	E(HF@2B-(HF+2B))	Ea (entry)	Ea (exit)	E(HF@2B-(HF+2B))	Ea (entry)	Ea (exit)
B3LYP/631d	0.00339	0.02831	0.02492	8.89	74.33	65.44
m062x/vdz@B3LYP/631d	-0.00987	0.01137	0.02123	-25.91	29.84	55.75

cp - Counterpoise correction for Basis Set Superposition Error

zpe - zero point energy correction (taken from B3LYP/631d frequency calculation).

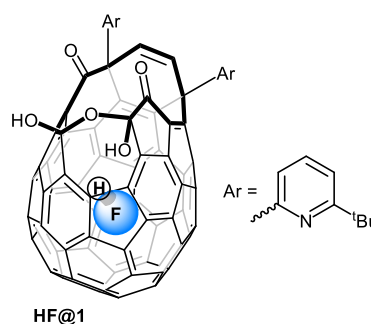
TS – Transition state of entry/exit of the endohedral molecule.

## Optimised procedure for the synthesis of HF@1:

Compound **1** (316 mg, 0.282 mmol) was placed inside an oven dried polytetrafluoroethylene (PTFE) tube equipped with a screw cap. The tube was flushed with nitrogen gas and distilled dichloromethane (16 mL) was added under nitrogen gas. 70% w/w hydrogen fluoride in pyridine (1.5 mL, 205 eq of HF) was added and the tube was closed. The mixture was stirred at room temperature for 23 hours. The reaction was quenched by dropping it, via PTFE tubing, inside a round bottom flask containing Na<sub>2</sub>CO<sub>3</sub> saturated solution (50 mL) and toluene (50 mL) under stirring. After the evolution of gas had stopped the organic layer was collected, washed with brine, dried over MgSO<sub>4</sub>, filtered and evaporated to dryness to afford a black solid. This material was purified by flash column chromatography over silica gel (eluent gradient 5% to 15% ethyl acetate in toluene). The fractions containing the spot located at R<sub>f</sub> = 0.31 (eluent 15% ethyl acetate in toluene) were collected and evaporated to yield 50% filled **HF@1** as a black solid (283 mg, 89%).

### HF@1 characterisation data and spectra:

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.64 (t, *J* = 7.8 Hz, 1H, H-4 of pyridyl), 7.57 (t, *J* = 7.8 Hz, 1H, H-4 of pyridyl), 7.49 (dd, *J* = 7.5, 2.2 Hz, 1H, H-3 or H-5 of pyridyl), 7.23 (d, *J* = 7.8 Hz, 1H, H-3 or H-5 of pyridyl), 7.22 (d, *J* = 7.8 Hz, 1H, H-3 or H-5 of pyridyl), 7.17 (d, *J* = 7.7 Hz, 1H, H-3 or H-5 of pyridyl), 7.12 (d, *J* = 10.2 Hz, 1H, alkenyl), 7.02 (d, *J* = 10.1 Hz, 1H, alkenyl), 6.28 (s broad, 1H, hydroxyl), 6.00 (s broad, 1H, hydroxyl), 1.24 (s, 9H, t-butyl), 1.18 (s, 9H, t-butyl), -6.55 (d, *J* = 508 Hz, 0.5 H, endohedral HF).



Note: the signals of the H-3 or H-5 protons of the pyridyl groups falling between 7.25 and 7.15 ppm overlapped with the aromatic CH signals from residual toluene present in the sample. Prolonged exposure of the sample to high vacuum (>0.1 mmHg) to achieve complete removal of residual toluene led to a substantial loss (-50%) of the endohedral HF.

<sup>13</sup>C NMR: (125 MHz, odcb-d<sub>4</sub>, δ): 198.77, 193.96, 168.71, 168.29, 164.42, 162.84, 153.56, 164.42, 162.84, 153.56, 149.94, 149.56, 149.5, 148.47, 148.39, 147.78, 147.63, 147.13, 147.04, 146.69, 146.15, 145.21, 145.16, 144.96, 144.42, 143.61, 143.48, 142.96,

142.57, 142.19, 141.19, 141.04, 140.64, 140.43, 140.17, 140, 139.82, 138.93, 138.2, 137.5, 137.32, 137.23, 137.11, 136.44, 135.77, 135.24, 134.73, 134.53, 134.3, 133.59, 133.54, 131.98, 131.45, 131.3, 129.02, 119.99, 119.86, 117.45, 117.42, 116.86, 116.83, 110.52, 96.97, 59.75, 59.72, 54.87, 37.65, 37.46, 29.94, 29.8.

Note: the solvent signals overlapped between 132.3 and 128.8 ppm. The signals of compound **1** are present but not listed.

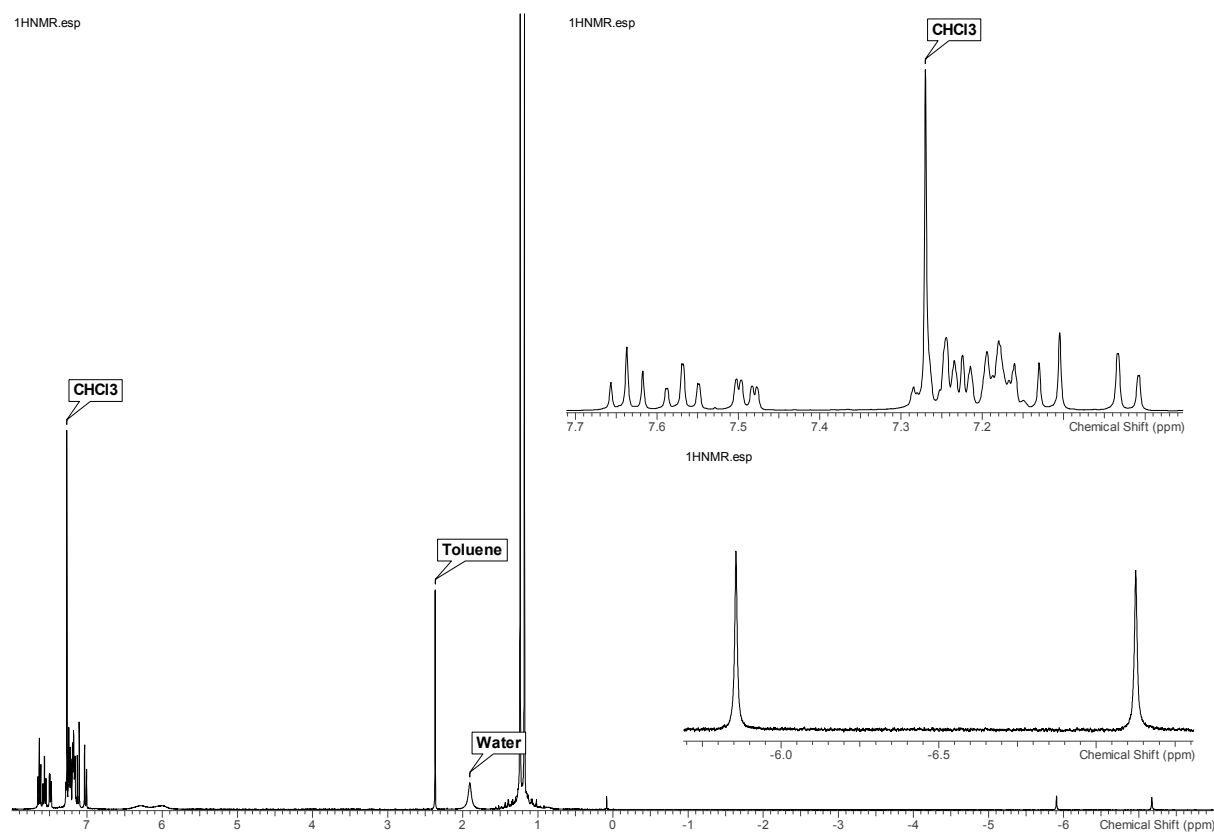
**$^{19}\text{F}$  NMR:** (376 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -223.91 (d,  $J = 508$  Hz).

**$\{^1\text{H}\}^{19}\text{F}$  NMR:** (376 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): -223.91 (s).

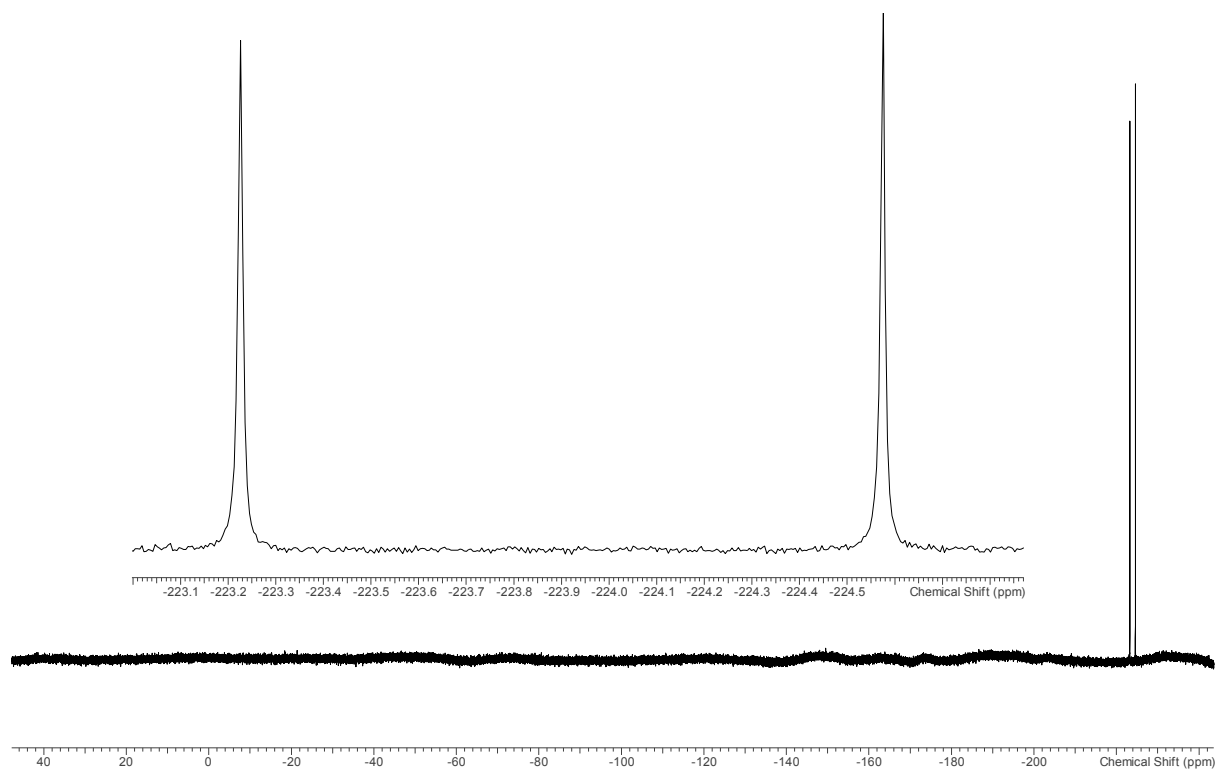
**IR:** ( $\nu$ ,  $\text{cm}^{-1}$ ): 3445, 2958, 1761, 1694, 1571, 1515, 1444, 1145, 1080.

**UV:**  $\text{CH}_2\text{Cl}_2$   $\lambda_{\text{max}}$  ( $\epsilon$ ): 258.60 (92550), 327.93 (36421).

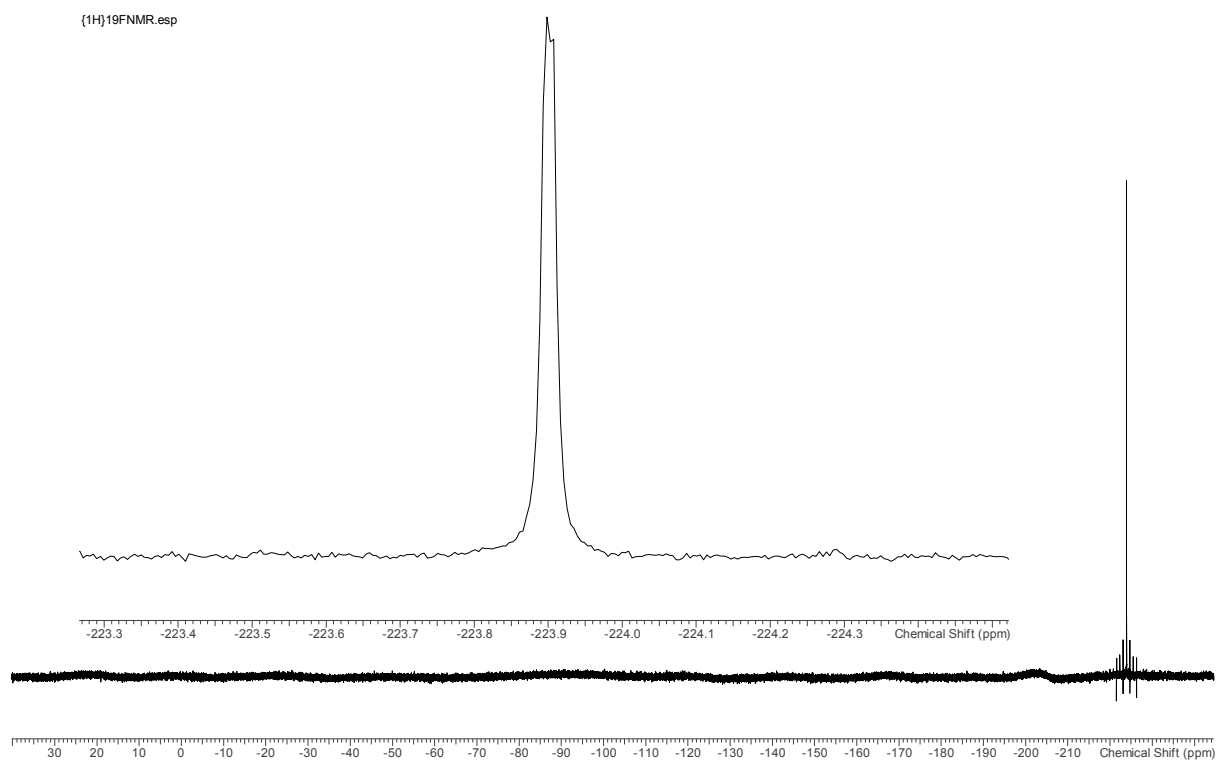
**MS-ESI:**  $m/z$  (relative intensity, ion): 1141 (100%,  $[\text{M}+\text{H}]^+$ , **HF@1**), 1121 (53%,  $[\text{M}+\text{H}]^+$ , empty **1**)



**$^1\text{H}$  NMR spectrum of compound HF@1.**

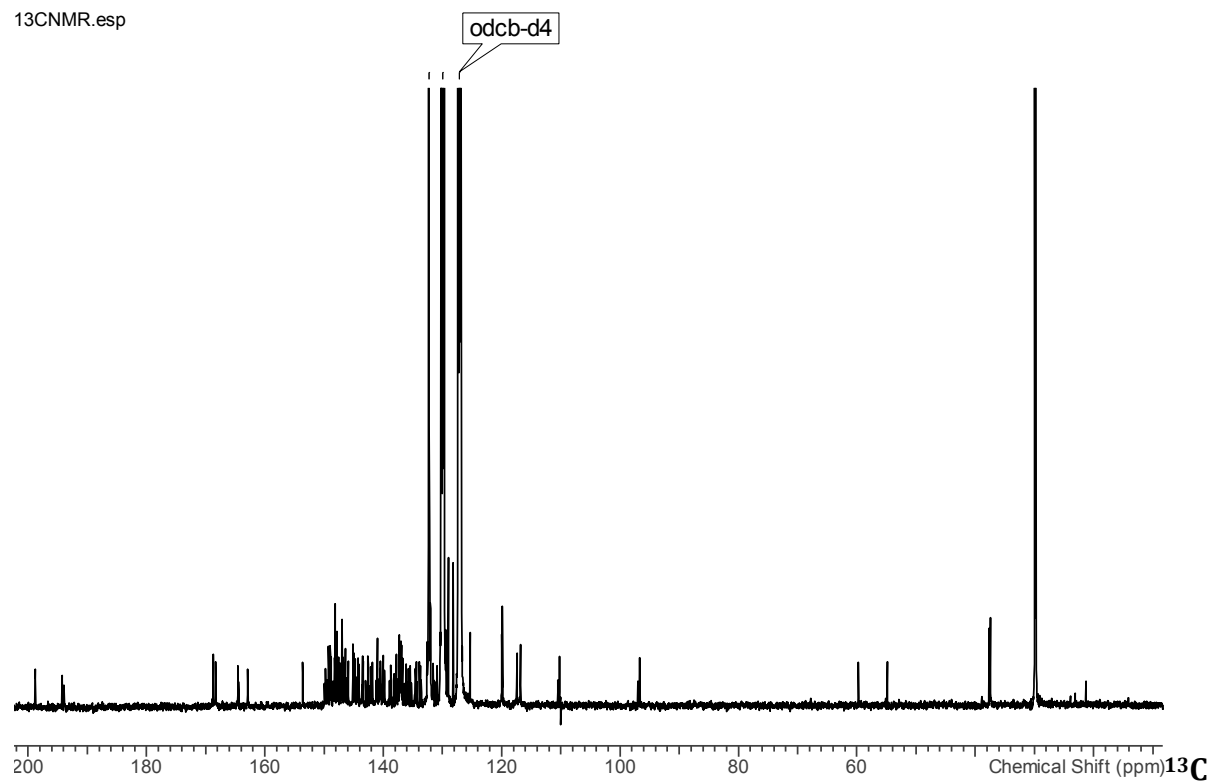


**$^{19}\text{F}$  NMR spectrum of compound HF@1.**

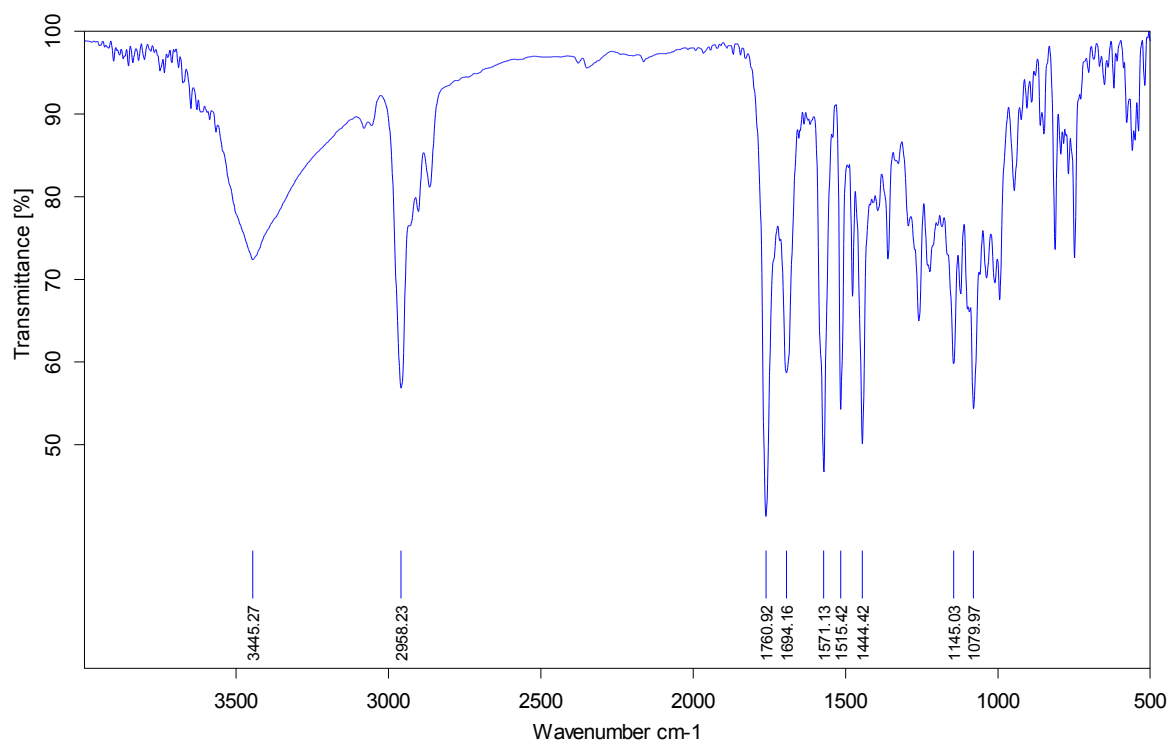


**$\{^1\text{H}\}^{19}\text{F}$  NMR spectrum of compound HF@1.**

13CNMR.esp

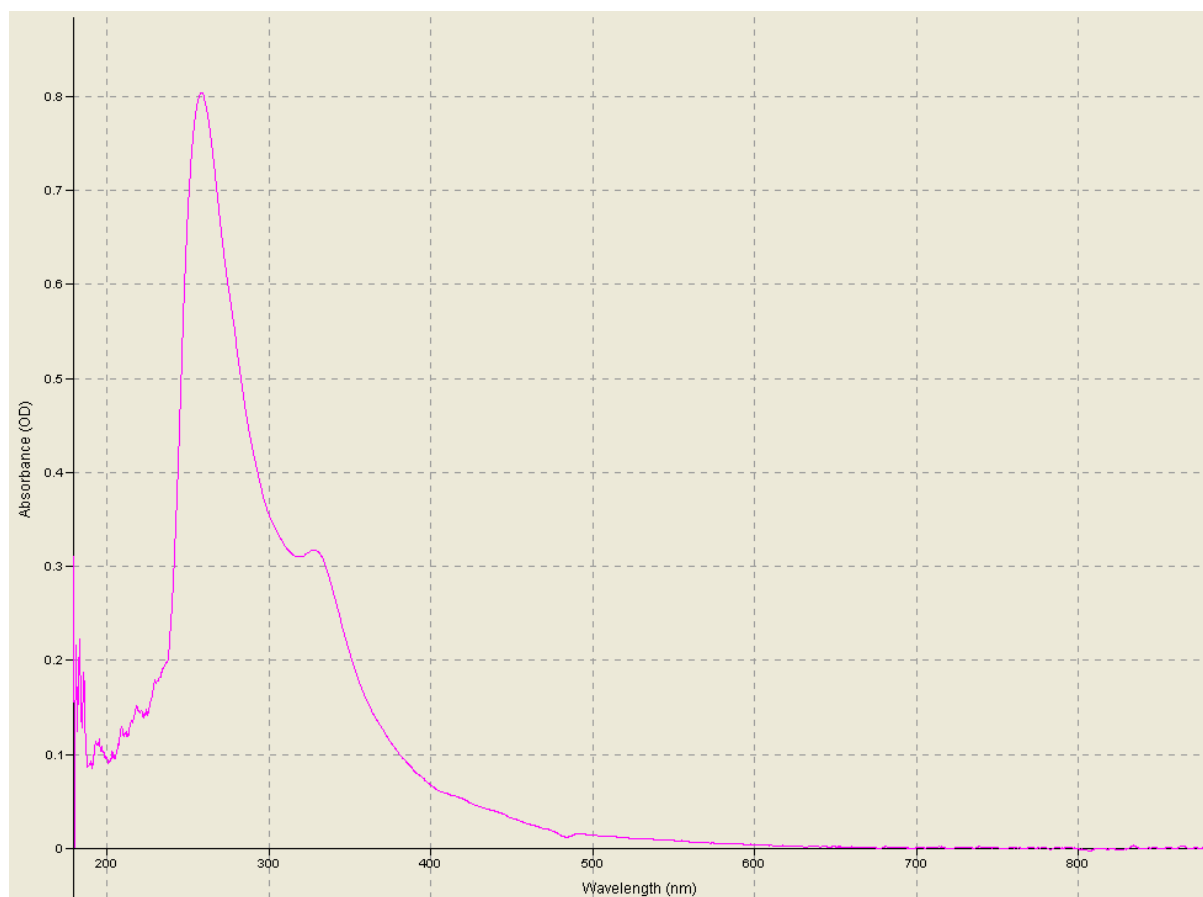


**NMR spectrum of compound HF@1.**



**IR spectrum of compound HF@1.**





**UV spectrum of compound HF@1.**

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