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Organic Dye-photocatalyzed Fluoroalkylation of Heteroarene-*N*-Oxide Derivatives

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Abstract: The first direct CHet-H perfluoroalkylation reaction of heteroaromatic-N-oxides has been achieved through a visible light-photocatalyzed reaction in the presence of commercially available perfluoroalkyl iodides R_F-I and base in DMF as solvent. The reactions proceed in the absence of transition metals and can be scaled up. This protocol is applied to the direct perfluoroalkylation of bioactive heteroaromatic-N-oxide derivatives. Through an acid-catalyzed transformation of the perfluoroalkylated-N-oxides thus obtained, the first direct syntheses of 2-(perfluoroalkyl)benzo[f][1,3]oxazepines are achieved. De-oxygenation of the resulting perfluoroalkylated heteroaromatic-N-oxides leads to high yielding and regioselective radical perfluoroalkylation protocols of heteroaromatic compounds. To the best of our knowledge, this is the first report on a direct and direct method for perfluoroalkylation of pyridine-, quinoline-, and diazine- N-oxide derivatives

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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, methanol, were chromatography quality and were not further purified. Chromatography and extraction solvents dichloromethane, chloroform, *iso*-octane, *n*-hexane, *n*-heptane, ethyl acetate, acetone, dichloromethane, and ethanol were purchased from commercial suppliers.

Cesium carbonate was 99% pure and used as received from the supplier. *N,N,N´,N´*-tetramethylethylene diamine (TMEDA) and potassium oxalate were used as received from the supplier. Fluorinated reagents 1-iodo-1,1,2,2,3,3,4,4,4-nonafluorobutane (perfluorobutyl iodide), 1-iodo-1,1,2,2,3,3,4,4,5,5,6,6,6-tridecafluorohexane (perfluorohexyl iodide) and 1-iodo-1,1,2,2,3,3,3-heptafluoropropane (perfluoropropyl iodide) were commercial reagents and used without further purification. Heteroaromatic-*N*-oxides were commercially available. Quindoxin was prepared according to literature procedures (section V.b.-). 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and 1,4-dinitrobenzene were Ultra pure grade reagents. Dyes Rose Bengal (4,5,6,7-Tetrachloro-3',6'-dihydroxy-2',4',5',7'-tetraiodo-3*H*-spiro[isobenzofuran-1,9'-xanthen]-3-one), Eosin Y (2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3*H*-xanthen-9-yl)benzoate), and anthraquinone-2-sulfonic acid were 99.9% pure and used as received from the supplier. Photocatalyst $[Ir(dF(CF_3)ppy)_2(dtbbpy))PF_6$ photocatalyst (dF = 2-(2.4-difluorophenyl)-5-(trifluoromethyl)pyridine, dtbbpy = 4,4´-di-tert-butyl-2,2´-bipyridine) was used as received from the supplier. Yields

were referred to as isolated yields of analytically pure material unless otherwise noted, as the case of yields calculated from ^{19}F NMR and ^{1}H NMR spectral integration. Reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using Silica gel 60 F254 pre-coated plates (0.25 mm, Merk), 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 source was a commercially available household 60-watt fluorescent light bulb (CFL). Other light sources consisted of two-8W 254 nm Hg lamp (germicide lamps), or a 5 -Watt blue LED.

^{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.

II.-Photocatalyzed reactions. General procedures.

In a 3 mL-reaction vial provided with screw-cap septum and micro stir bar, 0.6 mmol of heteroaromatic-*N*-oxide substrate, 0.05 equivalents of photocatalysts (Rose Bengal or otherwise used), and 1.5 equivalents of Cs_2CO_3 are placed. Solvent DMF, 3 mL, is added and the mixture is de-oxygenated with a stream of dry Ar for 15 minutes. 3 equivalents of R_F-I (*n*-C_4F_9-I, *n*-C_6F_{13}-I, or C_3F_7-I) are then introduced through the septum with microliter syringe. A brief deoxygenation with a slight stream of Ar is passed through for additional 3 minutes. The vessel is placed on a stir plate, and stirred vigourously for 24 hrs (at 22 °C) under constant illumination with a 60 Watt CFL (distance from the lamp: 3 cm, or 1 cm from a blue LED). After the reaction time elapsed, the mixture was extracted thrice with brine/$CHCl_3$, and the chloroform/DMF extracts evaporated in vacuo. The crude residues were analyzed by ^{1}H NMR, and an NMR integration of the product area is measured. The crude mixture was placed on a silica-gel preparative thin layer glass support, and eluted with $CHCl_3$: MeOH. In some cases, column chromatography was carried out instead of thin layer preparative chromatography. The products reveal intensely under 254 nm-light. The eluants were gathered, evaporated under vacuo, and characterized by standard spectroscopic techniques (section VI). Part of the product is de-oxygenated inside the column or on the preparative thin layer chromatographic glass plate, as revealed by gathering the MeOH eluants, evaporated and characterized by ^{1}H NMR spectra. Isolated yields are based on

mass obtained after purification protocols. NMR integration yields reflect the % of product(s) calculated with the aid of an external standard (benzotrifluoride for ^{19}F NMR spectra, and 1,3,5-trimethoxybenzene for ^{1}H NMR spectra).

III Tables

Table 1. Optimization of reaction conditions. Reactions of isoquinoline-*N*-oxide **1** (0.6 mmol) with *n*-C_4F_9I (3 equiv.) in DMF as solvent (3 mL, Ar-deoxygenated), with vigorous constant stirring, under irradiation for 24 h. Substitution product: 1-perfluorobutyl-isoquinoline-*N*-oxide **2a**

entry	Reaction conditions	Substitution Yield (% **2**)
1	LPL [a]	- [a1] < 5% [a2]
2	TMEDA, CFL [b]	< 5%
3	Cs_2CO_3, CFL [c]	< 5%
4	Blue LED [d]	77%
5	CFL [e]	74%
6	CFL [f]	98%
7	*p*-DNB [g]	< 50 %
8	TEMPO [h]	< 5%
9	[i]	-

a1.-Low pressure Hg lamp, LPL (20 Watt, $\lambda_{max.}$=254 nm). Quartz vessel used. The reaction is carried out in H_2O for 2 hours. No additive. Absorbance ratio of substrate / C_4F_9I equals 80:1. **a2**.-Idem but ratio substrate / C_4F_9I is 1:20. **b**.- Commercial fluorescent lamp (CFL), 20 Watt, is used, and TMEDA (1.5 equiv), **c**.-CFL, 20 Watt, Cs_2CO_3 1.5 equiv. **d.**-Blue LED (5 Watt), (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 , 0.01 equiv, Cs_2CO_3 (1.5 equiv), 24 h. [Susbtrate]= 0.2 mmol. **e.-** CFL (40 Watt), Eosin Y (0.01 equiv), Cs_2CO_3 (1.5 equiv), 24 h. **f**.- Rose Benga (0.05 equiv)l as PC. *p*-dinitrobenzene.**g.-** *p*-DNB (0.3 equiv). **h.-**TEMPO (0.1 equiv). **i**.-dark reaction

The first photochemical studies of pyridine-*N*-oxides consisted of short-wavelength direct irradiations.[1,2] Thermal[3] and photoinduced[4a] electron transfer ET reactions between Py-NO and acceptors have been reported before generating the radical cations of Py-NO and the respective radical anions of acceptors. We therefore commenced our investigation by exploring the possibility of a high-energy photoinduced ET between *iso*quinoline-*N*-oxide[4b] and *n*-C_4F_9I,[5] in order to produce C_4F_9 radicals from the process. Under reaction conditions of entry 1, Table 1, an unidentified mixture of polymeric material is obtained. When the concentration of *n*-C_4F_9I is increased (conditions a2.-[6]) a mixture of C_4F_9-substituted products is obtained in very low yield together with polymeric material. The reported visible light-activation of the electron donor acceptor (EDA) complex formed between R_F-I and an *N,N´*-tetramethylethylenediamine TMEDA, was also explored in order to produce R_F radicals that could effect ring substitution.[6b,c] Under these conditions (entry 2, Table 1), no substitution product is encountered. When TMEDA was changed to Cs_2CO_3[7,8a] (entry 3, Table 1), the yield of substitution product is also very low.

When an organometallic photocatalyst PC is employed (i.e.: [Ir(dF(CF_3)ppy)$_2$(dtbbpy))PF_6) under blue light irradiation, a 77% yield of 1-

perfluorobutyl-isoquinoline-*N*-oxide **2a** is obtained (entry 4, Table 1). Replacing the organometallic photocatalyst by organic dye Eosin Y, a similar substitution yield (74% yield, entry 5 Table 1) of **2a** is observed (see table S1 for redox potentials). Employing Rose Bengal (RB) as photocatalyst, the visible light irradiation reaction of **1** in the presence of Cs_2CO_3 affords almost a quantitative yield of **2a** (98%, entry 6, Table 1). When Cs_2CO_3 is replaced by TMEDA, the RB-photocatyalyzed reaction does not afford substitution product. The reaction of **1** (entry 7, Table 1) with 1,4-dinitrobenzene (a radical anion scavenger) affords 50% yield of substitution product. When TEMPO (a radical scavenger, entry 8, Table 1) is added to the reaction mixture, very little product is encountered. This latter experiment seems to support the presence of radicals in the mechanism. Absence of light does not afford any product, with almost quantitative substrate recovery (entry 9, Table 1).

With the best reaction conditions in our hands (entry 6, Table S1), we have next examined a series of heteroaromatic-*N*-oxide derivatives and subjected them to the visible light-RB-photocatalyzed perfluoroalkylation reaction in order to study the scope, regioselectivity and electron demand/requirements of the substrates to undergo substitution with the R_F groups, according to Table 1 (manuscript).

Table S2. Redox Potentials and Rehm Weller Parameters

entry	compound	E_{ox} (V)	E_{red} (V)	E^*_{ox} (V)	E^*_{red} (V)	E^*_T (eV)	E^*_S (eV)	λ_{max} (nm)	$\Delta G_{ET}{}^a$ (eV)	$\Delta G_{ET}{}^a$ (Kcal/mol)
1	Rose Bengal, RB	+0.74[9]	-1.03[9]	-0.68	+0.99[10]	1.8[11]	2.17[11]	559	-1.53	-3.5
2	Eosin Y, EO-Y	+0.74[16,17]	-1.10[16,17]	-1.60	+1.18[10]	1.91[16]	2.31[17]	539		
3	$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$			-0.89[12]	+1.21[12]			380		
	Anthraquinone-2-sulfonic acid		-0.883[15]		+ 1.50 [15]			326		
4	CO_3^{2-}	+1.23[13]								
5	*n*-C_4F_9I		-1.27[14]					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

Table S3. Changes in Free Energy of ET in the couples (CO_3^{2-}/$RB^{\cdot-}$) and (RB*/*n*-C_4F_9I)

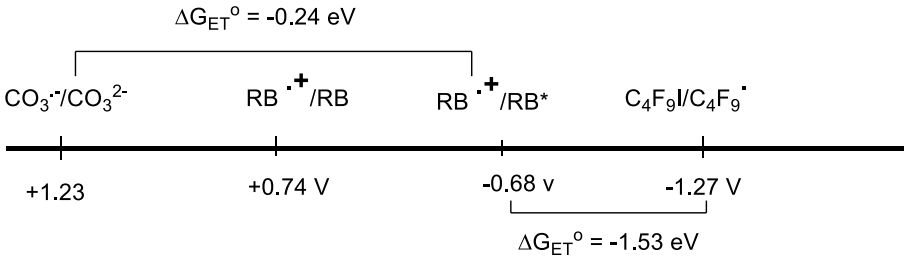


Figure S1. Concentration of **9** (■), **10** (●), **11** (▲) and **12** (▼) *vs.* irradiation time for the photolysis (CFL, 40 W) of 6 mL Ar_2-saturated 8-Isopropylquinoline-*N*-oxide (**9**) DMF solution (0.2 M) containing n-C_4F_9I (3.6 mmol), Cs_2CO_3 (1.8 mmol) and Rose Bengal (0.06 mmol).

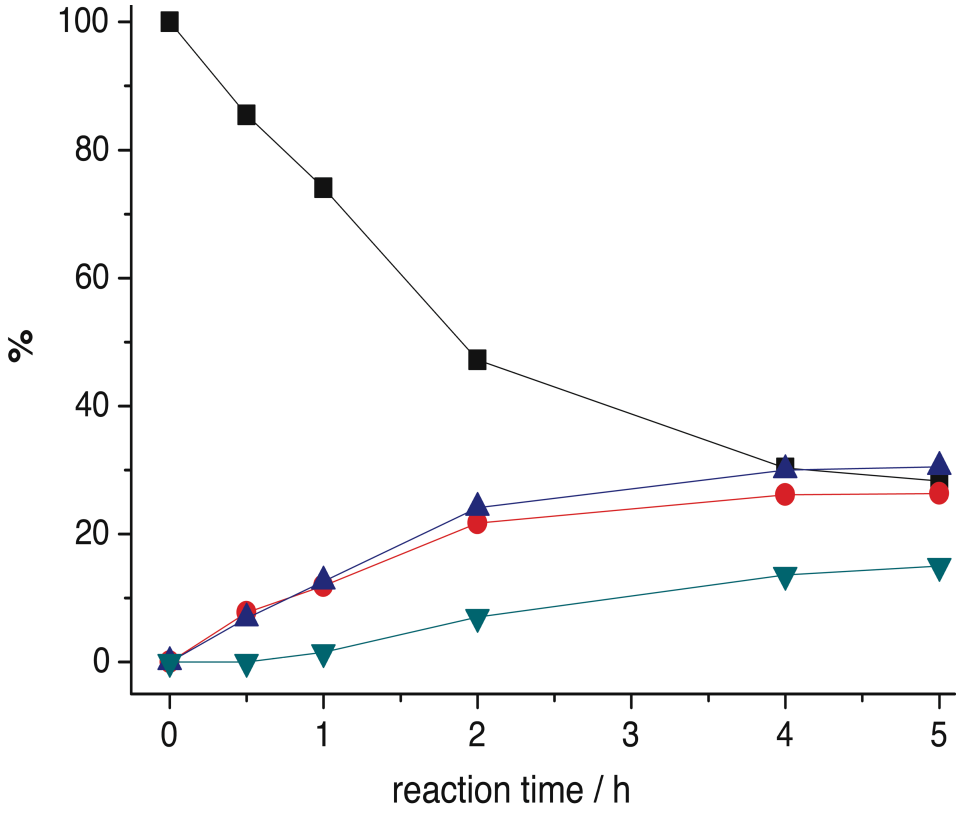
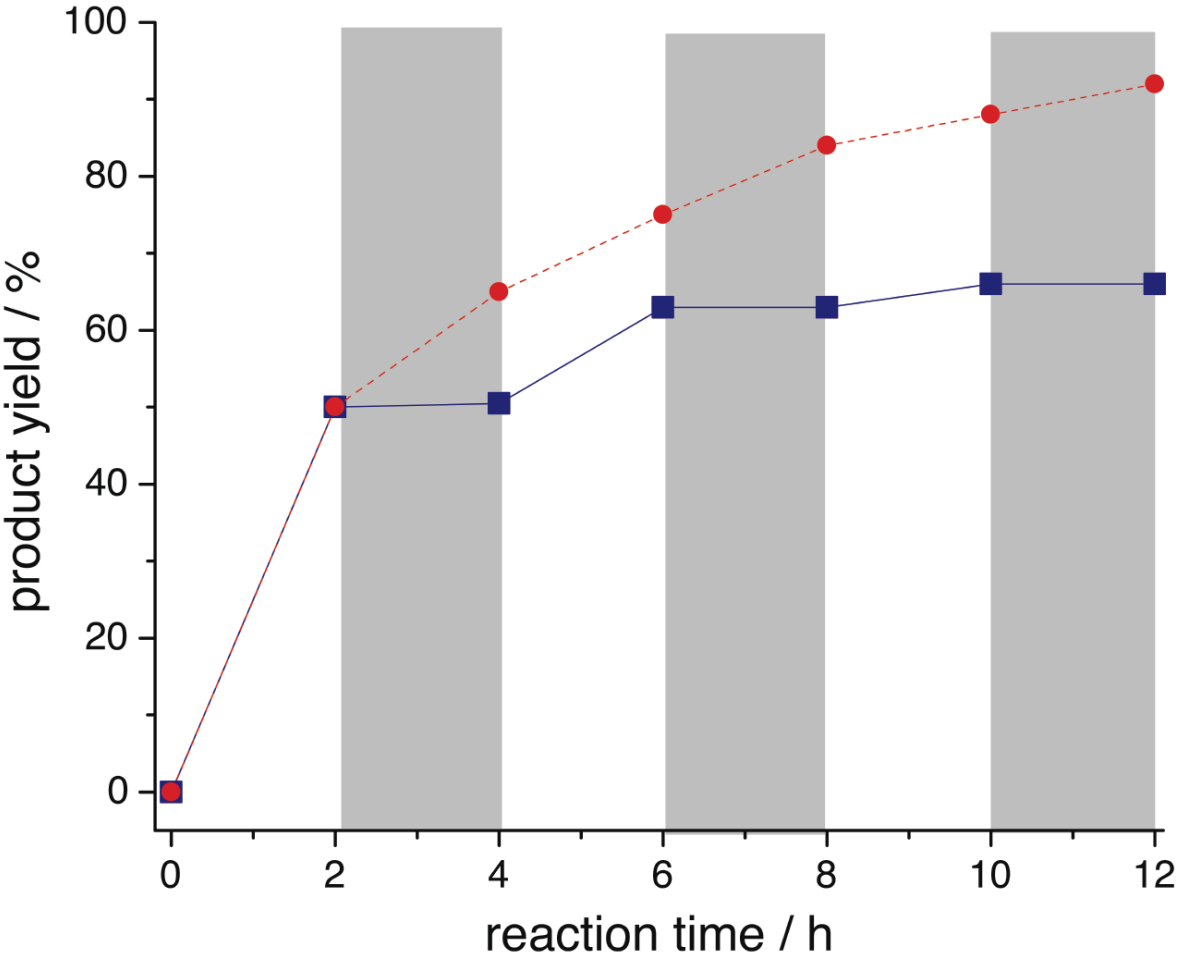


Figure S2. Concentration of **2a** *vs.* irradiation time for the photolysis (CFL, 40 W) of 6 mL Ar_2-saturated Isoquinoline-*N*-oxide (**1a**) DMF solution (0.2 M) containing n-C_4F_9I (3.6 mmol), Cs_2CO_3 (1.8 mmol) and Rose Bengal (0.06 mmol). The blue solid line represents the concentration of **2a** (■) under continuous irradiation (white areas) and interrupted illumination (shaded areas.) The red dashed line is a control experiment under continuous irradiation throughout.



IV.-Photocatalyzed Large Scale Reaction of Isoquinoline-*N*-oxide **1**

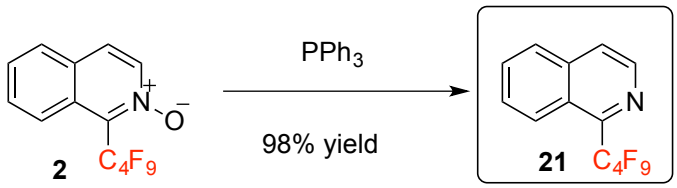
Procedure

In a 30 mL-reaction vessel provided with a screw-cap septum and a stir bar, 2 mmol of isoquinoline-*N*-oxide 1, 0.05 equivalents of photocatalysts Rose Bengal, and 3 equivalents of Cs_2CO_3 are placed. Solvent DMF, 30 mL, is added, and the mixture is de-oxygenated with a stream of dry Ar for 30 minutes. 3 equivalents of *n*-C_4F_9I are then introduced through the septum with syringe, and an Ar-deoxygenation stream is passed for 3 additional minutes. The vessel is placed on a stir plate, and stirred vigourously with a vortex for 24 hrs under constant illumination with a 60 Watt CFL (distance from the lamp: 3 cm). After the reaction time is elapsed, the mixture is extracted thrice with brine/$CHCl_3$, and the chloroform/DMF extracts evaporated in vacuo. The crude residue is analyzed by ^1H NMR (integration yield 50%), and silica-gel column-chromatographed, with DCM / MeOH mixture of eluants. The purified isolated yield of product 1-perfluorobutyl-isoquinoline-2-oxide is 50% (NMR yield), purified yield 0.137 g (13%). Part of the product is de-oxygenated inside the column, as revealed by gathering the MeOH eluants, evaporated and characterized by ^1H NMR spectra (confronted with sectra of compound 21, see sections VI, VII)

V.a.- Deoxygenation Reaction of 1-Perfluorobutyl-isoquinoline-*N*-oxide **2a** into 1-Perfluorobutylisoquinoline **21**

The deoxygenation reaction of 1-perfluorobutyl-isoquinoline-*N*-oxide **2** (0.135 mmol, 49 mg) was carried out in the absence of solvent and presence of Ph_3P

(1 equiv) at 280 ºC in a 5 mL Whetton vial provided with a screw-cap septum inmmersed in a sand bath for two hours. After the reaction time elapsed, the crude black oil was extracted into $CHCl_3$ / water thrice, the organic layers dried over Na_2SO_4 and evaporated, and a portion of the crude reaction mixture was taken for ^1H NMR analysis. The ^1H NMR spectrum of the crude reaction mixture revealed a quantitative conversion to deoxygenated product 1-perfluorobutyl-isoquinoline **21**. The crude reaction mixture was column-chromatographed with $CHCl_3$ as eluant, the fractions collected, evaporated under vacuo, and 25 mg (53% purified yield) was recovered as an isolated colerless oil which was characterized by standard spectroscopic techniques (see spectral characterization of compounds, section VI, and copies of spectra, section VII) as compound **21**.



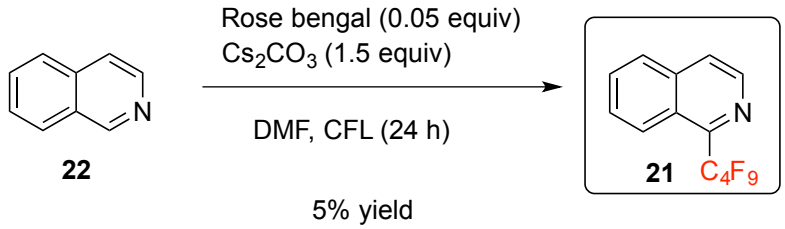
V.b.- Rose Bengal-photocatalyzed perfluoroalkylation of isoquinoline **22**

The Rose Bengal-photocatalyzed perfluoroalkylation of isoquinoline **22** was carried out under standard reaction conditions: In a 3 mL-reaction vial provided with screw-cap septum and micro stir bar, 0.6 mmol of **22**, 0.05 equivalents of photocatalysts (Rose Bengal or otherwise used), and 1.5 equivalents of Cs_2CO_3 are placed. Solvent DMF, 3 mL, is added and the mixture is de-oxygenated with a stream of dry Ar for 15 minutes. 3 equivalents 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 additional 3 minutes. The vessel is placed on

a stir plate, and stirred vigourously for 24 hrs (at 22 °C) under constant illumination with a 60 Watt CFL (distance from the lamp: 3 cm, or 1 cm from a blue LED). After the reaction time elapsed, the mixture was extracted thrice with brine/$CHCl_3$, and the chloroform/DMF extracts evaporated in vacuo. The crude residues were analyzed by ^{1}H NMR, and an NMR integration of the product area is measured. The crude mixture was placed on a silica-gel preparative thin layer glass support, and eluted with $CHCl_3$: MeOH. In some cases, column chromatography was carried out instead of thin layer preparative chromatography. The products reveal intensely under 254 nm-light. The eluants were gathered, evaporated under vacuo, and characterized by standard spectroscopic techniques (section VI). Part of the product is de-oxygenated inside the column or on the preparative thin layer chromatographic glass plate, as revealed by gathering the MeOH eluants, evaporated and characterized by ^{1}H NMR spectra. Isolated yields are based on mass obtained after purification protocols. NMR integration yields reflect the % of product(s) calculated with the aid of an external standard (benzotrifluoride for ^{19}F NMR spectra, and 1,3,5-trimethoxybenzene for ^{1} H NMR spectra).

the yield of **21** was exceedingly low (5%) giving rise to a mixture of perfluoroalkylated products at different ring positions (24 hour-reaction) with total lack of regioselectivity. The 2-hour reaction of **22** to yield 21 under the same reaction conditions (Scheme 6) affords the same distribution of products as the 24-hour reaction, revealing that even at low substrate conversion, the RB-photocatalyzed perfluoroalkylation of **22** is non-regioselective, unlike that of 1. Perfluoroalkylation of **1a** is a highly regioselective reaction towards the

synthesis of **2a** that can easily be chemically-transformed into **21** in a very high yield.



V.c.-Rearrangements of 1-Perfluoroalkyl-*iso*quinoline-*N*-oxides into 2-(Perfluoroalkyl)benzo[*f*][1,3]oxazepines **17**

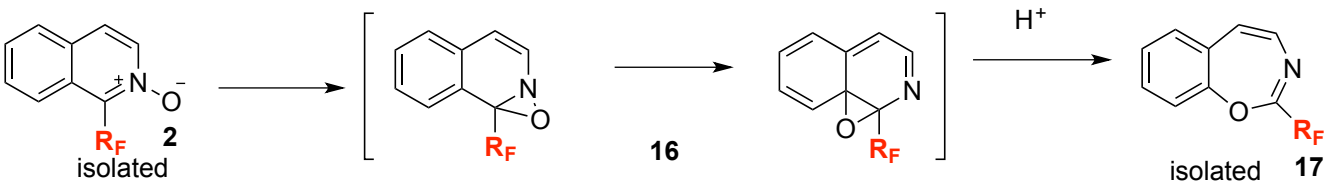
The 1-perfluoroalkyl-substituted -*iso*quinoline-*N*-oxides were isolated from the reaction mixtures, extracted thrice into $CHCl_3$ / water, the organic layers gathered, dried over Na_2SO_4, and evaporated under vacuo. The crude reaction mixtures were mixed with powdered silica-gel (60-Mesh), added chloroform, and the solvent evaporated under vacuo. The 1-perfluoroalkyl-substituted -*iso*quinoline-*N*-oxides absorbed in the dried silica-gel were left for 48 hrs at room temperature in round bottom flasks. When time elapsed, the mixtures were solvent-extracted from the silica-mixture, concentrated and were chromatographed over preparative thin layer chromatographic glass plates employing $CHCl_3$ / methanol as eluants. The fluorescent bands were scratched from the glass plates, collected, and filtered off from chloroform, evaporated under vacuo and characterized by spectroscopic techniques (sections **VI** and **VII**). The rearrangement reactions take place when products **2a-4** are left absorbed on silica-gel and do not arise from secondary photochemical reaction (irradiation under prolonged reaction times) of products **2a-4** (as confirmed by

36-hour visible- light irradiation), purporting that formation of products **18-20** involve a dark (thermal acid-catalyzed) rearrangement.

From 1-perfluorobutyl-*iso*quinoline-*N*-oxide **2a**, *2-(perfluorobutyl)benzo[f][1,3]oxazepine* **18**, 152 mg isolated, 70% yield is obtained.

From 1-perfluorohexyl-*iso*quinoline-*N*-oxide **3**, *2-(perfluorohexyl)benzo[f][1,3]oxazepine* **19**, 26 mg isolated, 9% yield is obtained.

From 1-perfluoropropyl-*iso*quinoline-*N*-oxide **4**, *2-(perfluoropropyl)benzo[f][1,3]oxazepine* **20**, 28 mg isolated, 15% yield is obtained.



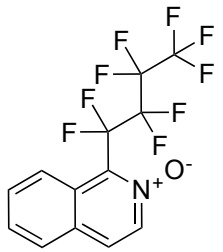
V.d.-Syntheses of 5-nitro-isoquinoline-*N*-oxide 1b and 8-nitro-isoquinoline-N-oxide 1c

Nitration of isoquinoline *N*-oxide gives 5-nitro and 8-nitro compounds from which it was seen that the effect of *N*-oxide group does not extend to the benzene ring.[19] The preparation followed the reported procedure.[19] Starting from 100 mg (0.69 mmol) in a mixture of H_2SO_4/HNO_3 at 50 °C for 24 h afforded 118 mg of a mixture of 5-nitro-isoquinoline-*N*-oxide and 8-nitro-isoquinoline-*N*-

oxide (90% yield). The mixture of nitro-compounds was not separated but subjected to the photocatalyzed perfluoroalkylation reaction as indicated in Section I.

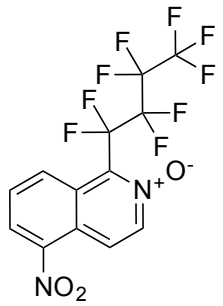
VI.-Spectral Characterization of Compounds

1-perfluorobutyl-isoquinoline-2-oxide **2a***,* 49 mg isolated, 40% (^{1}H NMR integrated yield: 98%).



^{1}H NMR: δ (ppm): 8.18 (1H, d, J=8.7 Hz), 8.16 (1H, d, J=7.1 Hz), 7.84 (1H, dd, J= 1.3, 8.1 Hz), 7.80 (1H, d, J= 7.0 Hz), 7.71 (1H, dt, J= 1.4, 7.0, 8.6 Hz), 7.64 (1H, t, J= 7.5 Hz). ^{13}C NMR: δ (ppm): 138.5, 133.8, 130.8, 129.2, 128.9, 128.5, 127.9, 127.2, 123.0. ^{19}F NMR: δ (ppm): -80.65, -105.14, -119.52, -126.37. HRMS (ESI (+)): Mass calc. for $C_{13}H_6F_9NNaO$: 386,02034, found: 386,01979.

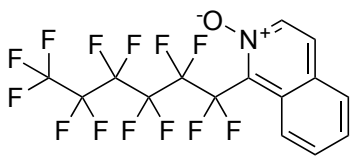
5-nitro-*1-perfluorobutyl-isoquinoline-2-oxide* **2b**, 56 mg, 23% isolated



^{1}H NMR: δ (ppm): 8.58 (1H, d, *J*= 7.6 Hz), 8.42 (1H, d, *J*= 9.0 Hz), 8.31 (1H, d, *J*= 7.8 Hz), 8.29 (1H, d, *J*= 7.7 Hz), 7.82 (1H, dd, *J*= 7.6, 9.0 Hz). ^{13}C NMR: δ (ppm): 146.51, 141.27, 133.95 (t, J= 25.9 Hz), 130.30, 129.56, 128.27, 125.00, 121.83, 120.61. ^{19}F NMR: δ (ppm): -80.53, -105.13,-119.61, -126.30.

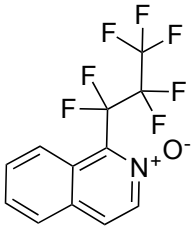
HRMS (ESI (+)): Mass calc. for $C_{13}H_6F_9N_2O_3$: 409.0156. Found: 409.0170. Mass cal. For $C_{13}H_5F_9N_2NaO_3$: 431.0156. Found: 431.0167. A selective H-H decoupling experiment was performed in the ^{1}H NMR experiment so as to irrevocably identify the position of the nitro group in relation to the R_F group. Irradiating the triplet at 7.82 ppm it was possible to identify the doublets coupled to the triplet signal. A selective NOE experiment was also carried out in order to irrevocably identify the position of the nitro group irradiating the doublet at 8.58 ppm (assigned to H*4*) an NOE was confirmed only with the signal at resonance 8.29 ppm (assigned to H*3*), supporting the *5*-position of the nitro group in the ring.

1-perfluorohexyl-isoquinoline-2-oxide **3**, 139 mg isolated, 50% (^{1}H NMR integrated yield: 87%).



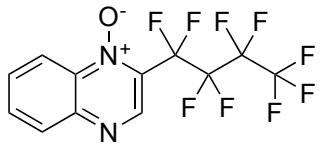
^{1}H NMR: δ (ppm): 8.15 (1H, d, *J*= 9.5 Hz), 8.14 (1H, d, *J*= 7.8 Hz), 7.81 (1H, d, *J*= 8.1 Hz), 7.77 (1H, d, *J*= 7.2 Hz), 7.68 (1H, t, *J*= 7.5 Hz), 7.60 (1H, t, *J*= 7.7 Hz). ^{13}C NMR: δ (ppm): 138.5, 133.7 (t, *J*= 24.0 Hz), 130.7, 128.8, 128.6, 128.4, 127.8, 127.2, 122.9 (t, *J*= 11.6 Hz). ^{19}F NMR: δ (ppm): -80.99, -105.09, -118.75, -122.30, -122.53, -126.26. HRMS (ESI (+)): Mass calc. for $C_{15}H_7F_{13}NO$: 464,03201, found: 464,03146, for: $C_{15}H_6F_{13}NNaO$: 486,01395, found:486,01340.

1-perfluoropropyl-isoquinoline-2-oxide **4**, 87 mg isolated, 45% (^{1}H NMR integrated yield: 97%).



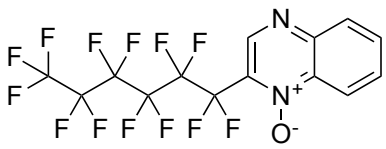
^{1}H NMR: δ (ppm): 8.17 (1H, d, *J*= 8.8 Hz), 8.15 (1H, d, *J*= 7.1 Hz), 7.84 (1H, d, *J*= 8.1 Hz), 7.79 (1H, d, *J*= 7.1 Hz), 7.71 (1H, td, *J*= 1.4, 8.6 Hz), 7.63 (1H, t, *J*= 7.5 Hz). ^{13}C NMR: δ (ppm): 138.4, 133.6 (t, *J*= 23.3 Hz), 130.8 (t, *J*= 1.9 Hz), 128.8, 128.6, 128.5, 127.9, 127.2, 122,9 (t, J= 11.5 Hz). ^{19}F NMR: δ (ppm): -80.74, -105.81, -123.01. HRMS (ESI (+)): Mass calc. for $C_{12}H_7F_7NO$: 314,04159, found:314,04104, for $C_{12}H_6F_7NNaO$: 336,02353, found: 336,02298.

2-perfluorobutyl-quinoxaline-1-oxide **6***,* 100.7 mg isolated, 50% (^{1}H NMR integrated yield: 50%).



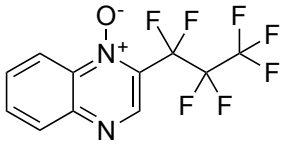
^{1}H NMR: δ (ppm): 8.92 (1H, s), 8.61 (1H, dd, *J*= 1.3, 8.7 Hz), 8.22 (1H, dd, *J*= 1.2, 8.4 Hz), 7.97 (1H, m, *J*= 1.4, 6.9, 8.7 Hz), 7.86 (1H, m, *J*= 1.3, 6.9, 8.5 Hz). ^{13}C NMR: δ (ppm): 146.4, 144.3 (t, J= 30 Hz), 138.0, 133.5, 131.2, 130.5, 129.6, 119.1. ^{19}F NMR: δ (ppm): -80.67, -112.35, -120.30, -126.30. HRMS (ESI (+)): Mass calc. for $C_{12}H_6F_9N_2O$:365,03364, found: 365.03309.

2-perfluorohexyl-quinoxaline-1-oxide **7***,* 80 mg isolated, 28%. (^{1}H NMR yield: 30%).



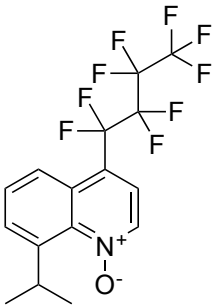
^{1}H NMR: δ (ppm): 8.92 (1H, s), 8.60 (1H, dd, *J*= 1.3, 8.7 Hz), 8.22 (1H, dd, *J*= 1.2, 8.5 Hz), 7.96 (1H, m, *J*= 1.4, 6.9, 8.4 Hz), 7.85 (1H, m, *J*= 1.3, 7.0, 8.6 Hz). ^{13}C NMR: δ (ppm): 146.3, 144.3 (t, *J*= 8.0 Hz), 138.0, 133.5, 131.2, 130.4, 129.6 (t, *J*= 25.1 Hz), 119.1. ^{19}F NMR: δ (ppm): -80.83, -112.19, -119.48,-122.16, -122.56, -126.18. HRMS (ESI (+)): Mass calc. for $C_{14}H_6F_{13}N_2O$: 465,02725 found:465,02725, for: $C_{14}H_5F_{13}N_2NaO$: 487,00920 found:487,00865.

2-perfluoropropyl-quinoxaline-1-oxide **8***,* 26 mg isolated, 50% (^{1}H NMR yield: 41%).



^{1}H NMR: δ (ppm): 8.92 (1H, s), 8.61 (1H, dd, *J*= 1.3, 7.4 Hz), 8.22 (1H, dd, *J*= 1.2, 8.5 Hz), 7.97 (1H, m, *J*= 1.4, 6.9, 8.4 Hz), 7.85 (1H, m, *J*= 1.3, 6.9, 8.5 Hz). ^{13}C NMR: δ (ppm): 146.4, 144.2, 137.9, 133.5, 131.2, 130.4, 129.4, 119.1. ^{19}F NMR: δ (ppm): -80.83, -112.97, -123.70. HRMS (ESI (+)): Mass calc. for $C_{11}H_6F_7N_2O$: 315,03684, found:315,03629.

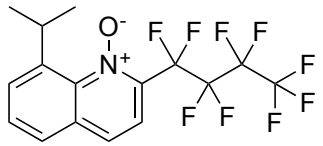
4-perfluorobutyl-8-isopropylquinoline-1-oxide **10**, 33.5 mg isolated, 15% (^{1}H NMR yield: 12%).



^{1}H NMR: δ (ppm): 8.48 (1H, d, *J*= 6.6 Hz), 8.05 (1H, d, *J*= 8.7 Hz), 7.79 (1H, d, *J*= 7.4 Hz), 7.66 (1H, t, *J*= 8.1 Hz), 7.51 (1H, d, *J*= 6.7 Hz), 5.13 (1H, m, *J*= 6.8 Hz), 1.39 (6H, d, *J*= 6.8 Hz). ^{13}C NMR: δ (ppm): 145.2, 141.5, 136.3, 129.4, 129.3, 128.5, 123.2 (m, *J*= 4.2 Hz), 121.7 (t, *J*= 10.8 Hz), 121.2 (t, *J*= 23.2 Hz),

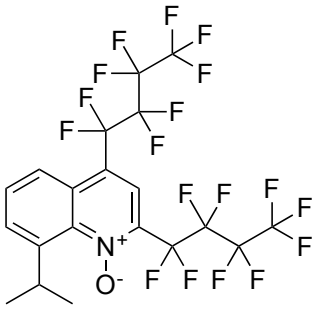
30.3, 24.8. ^{19}F NMR: δ (ppm): -80.84, -105.32, -120.88, -125.58. HRMS (ESI (+)): Mass calc. for $C_{16}H_{13}F_9NO$: 406,08534, found:406,08479, for $C_{16}H_{12}F_9NNaO$: 428,06729, found: 428,06674.

2-perfluorobutyl-8-isopropylquinoline-1-oxide **11**, 48 mg isolated, 20% (^{1}H NMR yield: 23%).



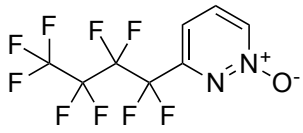
^{1}H NMR: δ (ppm): 7.75 (1H, dd, *J*= 1.5, 7.3 Hz), 7.72 (1H, dd, *J*= 1.5, 8.0 Hz), 7.70 (1H, d, *J*= 8.8 Hz), 7.64 (1H, t, *J*= 7.7 Hz), 7.54 (1H, d, *J*= 8.8 Hz), 5.07 (1H, h, *J*= 6.8 Hz), 1.37 (6H, d, *J*= 6.8 Hz). ^{13}C NMR: δ (ppm): 145.3, 143.6, 141.8, 133.2, 129.9, 128.6, 126.7, 124.6, 119.5 (t, *J*= 7.9 Hz), 30.1, 24.6. ^{19}F NMR: δ (ppm): -80.53, -110.16, -118.12, -126.46. HRMS (ESI (+)): Mass calc. for $C_{16}H_{13}F_9NO$: 406,08534, found:406,08492, for $C_{16}H_{12}F_9NNaO$: 428,06729, found: 428,06704.

2,4-bis(perfluorobutyl)-8-isopropylquinoline-1-oxide **12**, 88 mg isolated, 24% (^{1}H NMR yield: 25%).



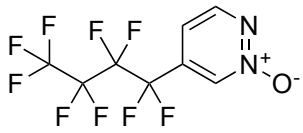
^{1}H NMR: δ (ppm): 8.08 (1H, d, *J*= 8.6 Hz), 7.85 (1H, d, *J*= 7.4 Hz), 7.79 (1H, s), 7.75 (1H, t, *J*= 8.1 Hz), 4.83 (1H, h, *J*= 6.7 Hz), 1.38 (6H, d, *J*= 6.8 Hz). ^{13}C NMR: δ (ppm): 146.0, 143.1, 131.1, 129.7, 129.4, 123.3, 121.0, 120.3, 116.5, 30.5, 24.6. ^{19}F NMR: δ (ppm): -80.55, -80.81, -105.41, -110.78, -118.70, -120.88, -125.54, -126.45. HRMS (ESI (+)): Mass calc. for $C_{20}H_{12}F_{18}NO$: 624,06315, found: 624,06260.

3-perfluorobutylpyridazine-1-oxide **14***,* 30 mg isolated, 15% (^{1}H NMR yield: 20%).



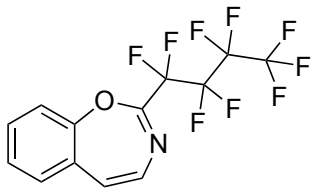
^{1}H NMR: δ (ppm): 8.63 (1H, dd, *J*= 2.4, 4.5 Hz), 7.98 (1H, dd, *J*= 2.4, 8.2 Hz), 7.19 (1H, dd, *J*= 5.4, 8.2 Hz). ^{13}C NMR: δ (ppm): 152.8, 134.6 (t, *J*= 6.8 Hz), 114.6, 112.9, (t, *J*= 33.9 Hz). ^{19}F NMR: δ (ppm): -80.64, -112.96, -119.62, -126.36. HRMS (ESI (+)): Mass calc. for $C_8H_3F_9N_2NaO$: 336,99994, found: 336,99978.

5-perfluorobutylpyridazine-1-oxide **15***,* 32 mg isolated, 16% (^{1}H NMR yield: 20%).



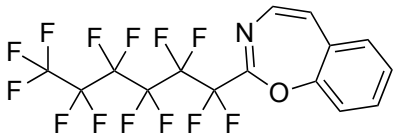
^{1}H NMR: δ (ppm): 8.64 (1H, d, *J*= 3.1 Hz), 8.20 (1H, d, *J*= 6.7 Hz), 7.79 (1H, dd, *J*= 3.1, 6.9 Hz). ^{13}C NMR: δ (ppm): 148.4 (t, *J*= 7.1 Hz), 134.0, 132.1 (t, *J*= 7.1 Hz), 116.3 (t, *J*= 28.0 Hz). ^{19}F NMR: δ (ppm): -80.90, -112.48, -122.62,-125.39. HRMS (ESI (+)): Mass calc. for $C_8H_3F_9N_2NaO$: 336,99994, found: 336,99939.

2-(perfluorobutyl)benzo[f][1,3]oxazepane **18**, 152 mg isolated, 70%.



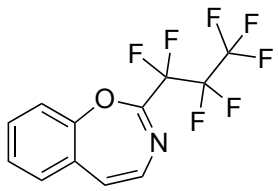
^{1}H NMR: δ (ppm): 6.55 (1H, d, *J*= 8.3 Hz), 6.77 (1H, d, *J*= 8.3 Hz), 7.05 (1H, d, *J*= 8.2 Hz), 7.20 (1H, dd, *J*= 1.8, 7.6 Hz), 7.24 (1H, dt, *J*= 1.1, 7.5 Hz), 7.44 (1H, dt, *J*= 1.8, 7.4 Hz). ^{13}C NMR: δ (ppm): 153.0,143.3, 134.2, 132.0, 129.2, 128.1, 126.5, 125.0, 120.9. ^{19}F NMR: δ (ppm): -80.91, -113.90, -122.17, -125.75. HRMS (ESI (+)): Mass calc. for $C_{13}H_6F_9NNaO$: 386,02034, found: 386,01982.

2-(perfluorohexyl)benzo[f][1,3]oxazepine **19**, 104 mg isolated, 36% (^{1}H NMR yield: 58%).



^{1}H NMR: δ (ppm): 7.44 (1H, td, *J*= 1.8, 7.2, 8.2 Hz), 7.24 (1H, td, *J*= 1.1, 7.5, 8.6 Hz), 7.20 (1H, dd, *J*= 1.8, 7.6 Hz), 7.04 (1H, d, *J*= 8.2 Hz), 6.77 (1H, d, *J*= 8.3 Hz), 6.55 (1H, d, *J*= 8.3 Hz). ^{13}C NMR: δ (ppm): 153.0, 141.4, 134.2, 132.0, 129.3, 129.2, 126.5, 125.0, 120.9. ^{19}F NMR: δ (ppm): -80.85, -105.06, -118.71, -122.14, -122.46, -127.17. HRMS (ESI (+)): Mass calc. for $C_{15}H_7F_{13}NO$: 464,03201, found: 464,03146, for: $C_{15}H_6F_{13}NNaO$: 486,01395, found:486,01340.

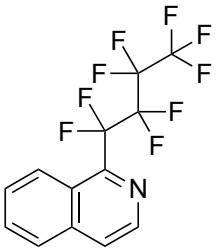
2-(perfluoropropyl)benzo[f][1,3]oxazepine **20**, 112 mg isolated, 60% (^{1}H NMR yield: 77%).



^{1}H NMR: δ (ppm): 7.45 (1H, td, *J*= 1.8, 7.2, 8.2 Hz), 7.25 (1H, td, *J*= 1.2, 7.5, 8.7 Hz), 7.22 (1H, dd, *J*= 1.8, 7.7 Hz), 7.05 (1H, d, *J*= 8.3 Hz), 6.78 (1H, d, *J*= 8.3 Hz), 6.55 (1H, d, *J*= 8.3 Hz). ^{13}C NMR: δ (ppm): 153.9, 144.3, 134.3, 132.0, 129.5, 129.2, 126.5, 125.0, 121.0. ^{19}F NMR: δ (ppm): -80.47, -114.62, -125.70.

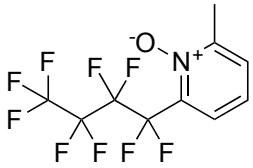
HRMS (ESI (+)): HRMS (ESI (+)): Mass calc. for $C_{12}H_7F_7NO$: 314,04159, found: 314,04104, for $C_{12}H_6F_7NNaO$: 336,02353, found: 336,02298.

1-perfluorobutyl-isoquinoline **21**, 25 mg isolated, 53% purified yield (^{1}H NMR yield: 99%).[18]



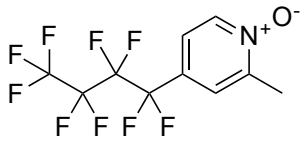
^{1}H NMR: δ (ppm): 8.70 (1H, d, J=5.5 Hz), 8.40 (1H, d, J=8.7 Hz), 7.97 (1H, dd, J= 1.2, 8.2 Hz), 7.90 (1H, d, J= 5.5 Hz), 7.80 (1H, dt, J= 1.0, 7.0, 8.1 Hz), 7.74 (1H, dt, J= 1.4, 8.6 Hz). ^{13}C NMR: δ (ppm): 146.1(t, J= 24Hz), 141.0, 137.3, 130.6, 128.8, 127.7, 126.4, 124.9 (m, J= 4.5Hz), 124.6. ^{19}F NMR: δ (ppm): -80.91, -106.27, -121.02, -125.04.

6-perfluorobutyl-2-methyl-pyridine-1-oxide **24**, 21 mg isolated, 21% (^{1}H NMR yield: 22%).



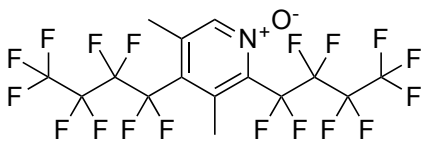
^{1}H NMR: δ (ppm): 7.59 (1H, dd, J=2.0, 8.1 Hz), 7.48 (1H, dd, J=1.9, 7.8 Hz), 7.29 (1H, t, J=7.8 Hz), 2.56 (3H, s). ^{13}C NMR: δ (ppm): 151.7, 139.0, 129.1, 124.3, 123.7, 17.6. ^{19}F NMR: δ (ppm): -80.59, -110.52, -118.61, -126.48. HRMS (ESI (+)): Mass calc. for: $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,01979.

4-perfluorobutyl-2-methylpyridine-1-oxide **25**, 56 mg isolated, 30% (^{1}H NMR yield: 32%).



^{1}H NMR: δ (ppm): 8.36 (1H, d, J=6.8 Hz), 7.48 (1H, d, J=2.6 Hz), 7.36 (1H, dd, J=2.6, 6.9 Hz), 2.58 (3H, s). ^{13}C NMR: δ (ppm): 150.0, 139.7, 124.5, 121.6, 121.5, 17.9. ^{19}F NMR: δ (ppm): -80.96, -112.12,-122.69, -125.49. HRMS (ESI (+)): Mass calc. for $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,01994.

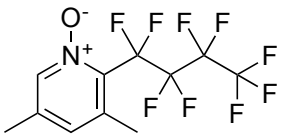
(2,4-diperfluorobutyl)-3,5-dimethylpyridine-1-oxide **27**, 44 mg isolated, 30% (^{1}H NMR yield: 37%).



^{1}H NMR: δ (ppm): 8.06 (1H, s), 2.51 (3H, q, J= 4.5 Hz), 2.46 (3H, t, J= 4.8 Hz). ^{13}C NMR: δ (ppm): 141.4, 141.0, 139.4, 134.0, 124.5, 19.4, 16.5. ^{19}F NMR: δ

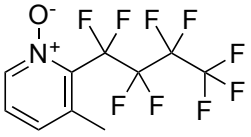
(ppm): -80.56, -80.75, -98.06, -103.43, -118.15,-119.84, -125.89, -126.32. HRMS (ESI (+)): Mass calc. for $C_{15}H_8F_{18}NO$: 560,03185, Mass found:560.03179.

2-perfluorobutyl-3,5-dimethylpyridine-1-oxide **28**, 13.4 mg isolated, 7% (^{1}H NMR yield: 11%).



^{1}H NMR: δ (ppm): 8.03 (1H, s), 6.96 (1H, s), 2.48 (3H, t, J = 5.6 Hz), 2.32 (3H, s). ^{13}C NMR: δ (ppm): 141.5, 139.5, 138.4, 138.5, 130.4, 20.5 (t, *J*= 8.7 Hz), 18.0. ^{19}F NMR: δ (ppm): -80.57, -105.02, -118.90,-126.52. HRMS (ESI (+)): Mass calc. for $C_{11}H_9F_9NO$: 342,05404, Mass found:342,05349.

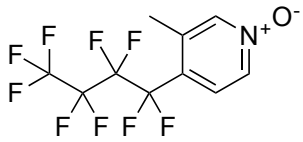
2-perfluorobutyl-3-methylpyridine-1-oxide **30**, 6 mg isolated, 3%.



^{1}H NMR: δ (ppm): 8.19 (1H, bs); 7.29 (1H, t, *J*= 8.3 Hz); 7.15 (1H, d, *J*= 8.0 Hz); 2.53 (3H, t, *J*= 2.9 Hz). ^{13}C NMR: δ (ppm): 139.6, 139.5, 129.0, 127.2, 125.3, 20.3 (t, *J*= 0.06 Hz). ^{19}F NMR: δ (ppm): -80.57, -105.34, -118.81, -126.51.

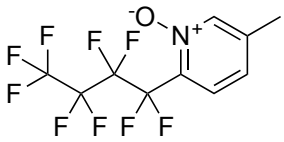
HRMS (ESI (+)): Mass calc. for $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,01999.

4-perfluorobutyl-3-methylpyridine-1-oxide **31**, 36 mg isolated, 18%.



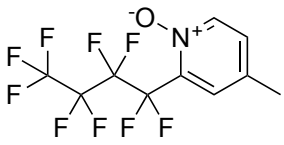
^{1}H NMR: δ (ppm): 8.18 (2H, bs), 8.17 (2H, bs), 7.40 (1H, d, *J*= 7.3 Hz), 2.44 (3H, t, *J*= 2.9 Hz). ^{13}C NMR: δ (ppm): 141.3, 137.0, 136.7, 125.3, 124.4, 17.3. ^{19}F NMR: δ (ppm): -80.91, -108.15, -121.90, -125.71. HRMS (ESI (+)): Mass calc. for $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,02001.

6-perfluorobutyl-3-methylpyridine-1-oxide **32**, 10 mg isolated, 5%.



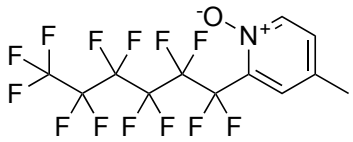
^{1}H NMR: δ (ppm): 8.16 (1H, s), 7.56 (1H, d, *J*= 8.3 Hz), 7.18 (1H, d, *J*= 8.3 Hz), 2.39 (3H, s). ^{13}C NMR: δ (ppm): 141.6, 140.2, 125.9, 125.6, 18.2. ^{19}F NMR: δ (ppm): -80.64, -110.97, -119.31,-126.43. HRMS (ESI (+)): Mass calc. for $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,01996.

2-perfluorobutyl-4-methylpyridine-1-oxide **34**, 60 mg isolated, 30% (^{1}H NMR yield: 30%).



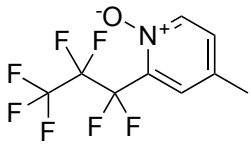
^{1}H NMR: δ (ppm): 8.20 (1H, d, J= 6.6 Hz), 7.47 (1H, d, J= 1.9 Hz), 7.26 (1H, dd, J= 2.4, 6.6 Hz), 2.44 (3H, s). ^{13}C NMR: δ (ppm): 145.8, 141.1, 136.4, 129.4, 127.1 (d, J= 7.4 Hz), 20.4. ^{19}F NMR: δ (ppm): -80.62, -111.11, -119.09, -126.37. HRMS (ESI (+)): Mass calc. for $C_{10}H_6F_9NNaO$: 350,02034. Mass found: 350,01989.

2-perfluorohexyl-4-methylpyridine-1-oxide **35**, 92 mg isolated, 32 % (^{1}H NMR yield: 46%).



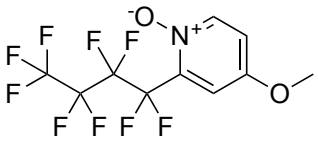
^{1}H NMR: δ (ppm): 8.19 (1H, d, *J*= 6.6 Hz), 7.47 (1H, d, *J*= 2.5 Hz), 7.27 (1H, dd, *J*= 2.6, 6.8 Hz), 2.44 (3H, s). ^{13}C NMR: δ (ppm): 147.8, 141.1, 136.2, 129.5, 127.0 (t, *J*= 7.4 Hz), 20.4. ^{19}F NMR: δ (ppm): -80.78, -110.90, -118.23, -122.14, -122.45, -126.17. HRMS (ESI (+)): Mass calc. for $C_{12}H_7F_{13}NO$: 428.03201. Mass found: 428,03146. Mass calc. for $C_{12}H_6F_{13}NNaO$: 450,01395. Mass found: 450,01340.

2-perfluoropropyl-4-methylpyridine-1-oxide **36**, 126 mg isolated, 72% (^{1}H NMR yield: 76%).



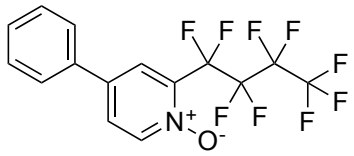
^{1}H NMR: δ (ppm): 8.18 (1H, d, *J*= 6.6 Hz), 7.46 (1H, d, *J*= 2.5 Hz), 7.26 (1H, dd, *J*= 2.5, 6.8 Hz), 2.43 (3H, s). ^{13}C NMR: δ (ppm): 140.9, 138.0 (t, *J*= 27.9 Hz), 136.0, 129.4, 126.8, 20.3. ^{19}F NMR: δ (ppm): -81.03, -111.66, -122.45. HRMS (ESI (+)): Mass calc. for $C_9H_7F_7NO$: 278,04159. Mass found: 278,04104.

2-perfluorobutyl-4-methoxypyridine-1-oxide **38**, 20 mg isolated, 10% (^{1}H NMR yield: 16%).



^{1}H NMR: δ (ppm): 8.22 (1H, d, J=7.3 Hz), 7.18 (1H, d, J=3.5 Hz), 7.00 (1H, dd, J=3.4, 7.2 Hz), 394 (3H, s). ^{13}C NMR: δ (ppm): 156.7, 142.6, 114.8, 112.1, 56.5. ^{19}F NMR: δ (ppm): -80.60, -110.86,-118.77, -126.34. HRMS (ESI (+)): Mass calc. for $C_{10}H_7F_9NO_2$: 344,03331, found:344.03276.

2-perfluorobutyl-4-phenyl-pyridine-1-oxide **40a**, 8.9 mg isolated, 4%.

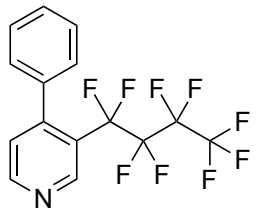


^{1}H NMR: δ (ppm): 8.34 (1H, d, *J*= 6.8 Hz), 7.87 (1H, d, *J*= 2.7 Hz), 7.68 (1H, dd, *J*= 2.7, 6.7 Hz), 7.62 (2H, d, *J*= 7.3 Hz), 7.55 (2H, t, *J*= 7.0 Hz), 7.51 (1H, t, *J*= 7.3 Hz).

^{13}C NMR: δ (ppm): 141.8, 137. 7, 135.4, 129.7, 129.5, 126.4, 126.2, 124.2 (t, *J*= 7.3 Hz), 114.0.

^{19}F NMR: δ (ppm): -80.60, -111.01, -119.10, -126.30. HRMS (ESI (+)): Mass calc. for $C_{15}H_9F_9NO$: 390,05404. Mass found: 390,05398.

3-perfluorobutyl-4-phenyl-pyridine **40b**, 2 mg isolated, 1%.

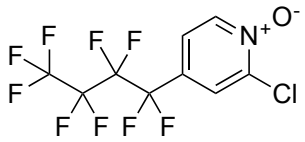


^{1}H NMR: δ (ppm): 8.83 (1H, d, *J*= 5.0 Hz), 7.92 (1H, bs), 7.73 (1H, dd, *J*= 1.7, 5.1 Hz), 7.69 (2H, dd, *J*= 1.7, 6.7 Hz), 7.55 (2H, t, *J*= 6.9 Hz), 7.54 (1H, t, *J*= 6.9 Hz).

^{13}C NMR: δ (ppm): 150.5, 150.1, 136.9, 129.9, 129.4, 127.1, 124.2, 124.1, 120.3.

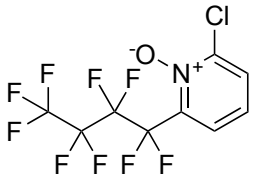
^{19}F NMR: δ (ppm): -80.91, -114.08, -122.58, -125.62. HRMS (ESI (+)): Mass calc. for $C_{15}H_9F_9N$: 374,05913. Mass found: 374,05858.

4-perfluorobutyl-2-chloropyridine-1-oxide **42**, 12 mg isolated, 6% (^{1}H NMR yield: 10%).



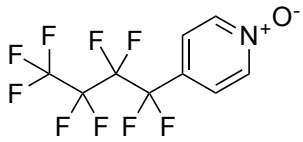
^{1}H NMR: δ (ppm): 8.44 (1H, d, *J*= 6.9 Hz), 7.73 (1H, *J*= 2.6 Hz), 7.41 (1H, dd, *J*= 2.6, 6.9 Hz). ^{13}C NMR: δ (ppm): 147.9, 140.8, 140.4, 125.4, 121.8. ^{19}F NMR: δ (ppm): -80.90, -112.07, -122.51, -125.42. HRMS (ESI (+)): Mass calc. for $C_9H_4ClF_9NO$: 347,98377. Mass found:347,98364.

6-perfluorobutyl-2-chloropyridine-1-oxide **43**, 22 mg isolated, 10% (^{1}H NMR yield: 10%).



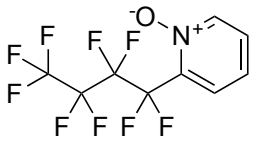
^{1}H NMR: δ (ppm): 7.70 (1H, dd, *J*= 2.6, 8.1 Hz), 7.62 (1H, dd, *J*= 2.0, 8.1 Hz), 7.31 (1H, t, *J*= 8.1 Hz).

4-perfluorobutyl-pyridine-1-oxide **45**, 10 mg isolated, 10% (^{1}H NMR yield: 20%).



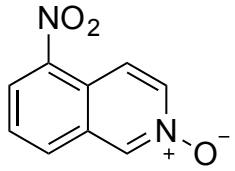
^{1}H NMR: δ (ppm): 8.31 (2H, d, *J*= 6.9 Hz), 7.49 (2H, d, *J*= 7.1 Hz). ^{13}C NMR: δ (ppm): 139.7, 124.3. ^{19}F NMR: δ (ppm): -80.63, -11.30, -119.19, -126.38. HRMS (ESI (+)): Mass calc. for $C_9H_5F_9NO$: 314,02274. Mass found: 314.02221.

2-perfluorobutyl-pyridine-1-oxide **46**, 10 mg isolated, 10% (^{1}H NMR yield: 20%).



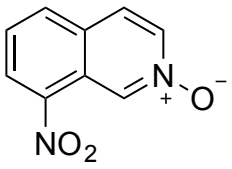
^{1}H NMR: δ (ppm): 8.29 (1H, d, *J*= 6.6 Hz), 7.68 (1H, dd, *J*= 2.1, 8.1 Hz), 7.47 (1H, ddd, *J*= 2.0, 6.6, 8.1 Hz), 7.36 (1H, t, *J*= 7.9 Hz). ^{13}C NMR: δ (ppm): 141.8, 139.2, 128.7, 128.6, 121.1. ^{19}F NMR: δ (ppm): -80.94, -122.20, -122.71, -125.43. HRMS (ESI (+)): Mass calc. for $C_9H_5F_9NO$: 314,02274. Mass found: 314.02219.

5-nitro-isoquinoline-N-oxide **1b**, 59 mg, 50% [19].



^{1}H NMR: δ (ppm): 8.86 (1H, s), 8.62 (1H, d, *J*=7.6 Hz), 8.42 (1H, d, *J*= 7.6 Hz), 8.32 (1H, dd, *J*= 1.7, 7.1 Hz), 8.03 (1H, d, *J*= 8.2 Hz), 7.76 (1H, t, *J*= 8.0 Hz).

8-nitro-isoquinoline-N-oxide **1c**, 47 mg, 40% [19].



^{1}H NMR: δ (ppm): 9.79 (1H, s), 8.55 (1H, d, *J*=7.6 Hz), 8.26 (1H, dd, *J*= 1.8, 7.6 Hz), 8.11 (1H, d, *J*= 8.1 Hz), 7.82 (1H, d, *J*= 7.1 Hz), 7.69 (1H, t, *J*= 8.0 Hz).

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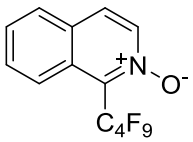
Author Contributions

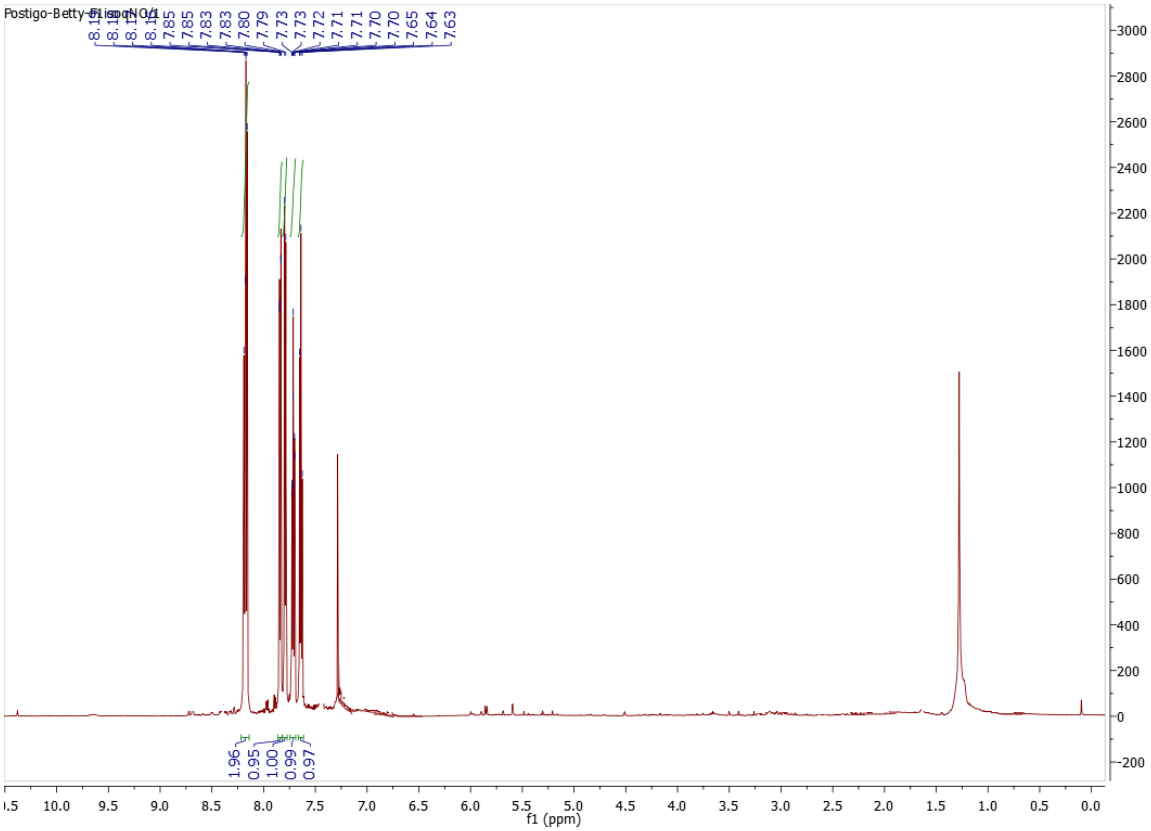
Dr. Beatriz Lantaño: responsible for the reaction protocols, the synthesis and purification of products. Structural elucidation of products and spectroscopic assignment.

Dr. Sebastian Barata-Vallejo: responsible for the reaction protocols, the synthesis and purification of products, collaboration in the mechanism proposal.

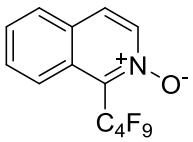
Professor Dr. Al Postigo: funding acquisition, formal analysis and design, investigation, project administration, validation, writing of original draft.

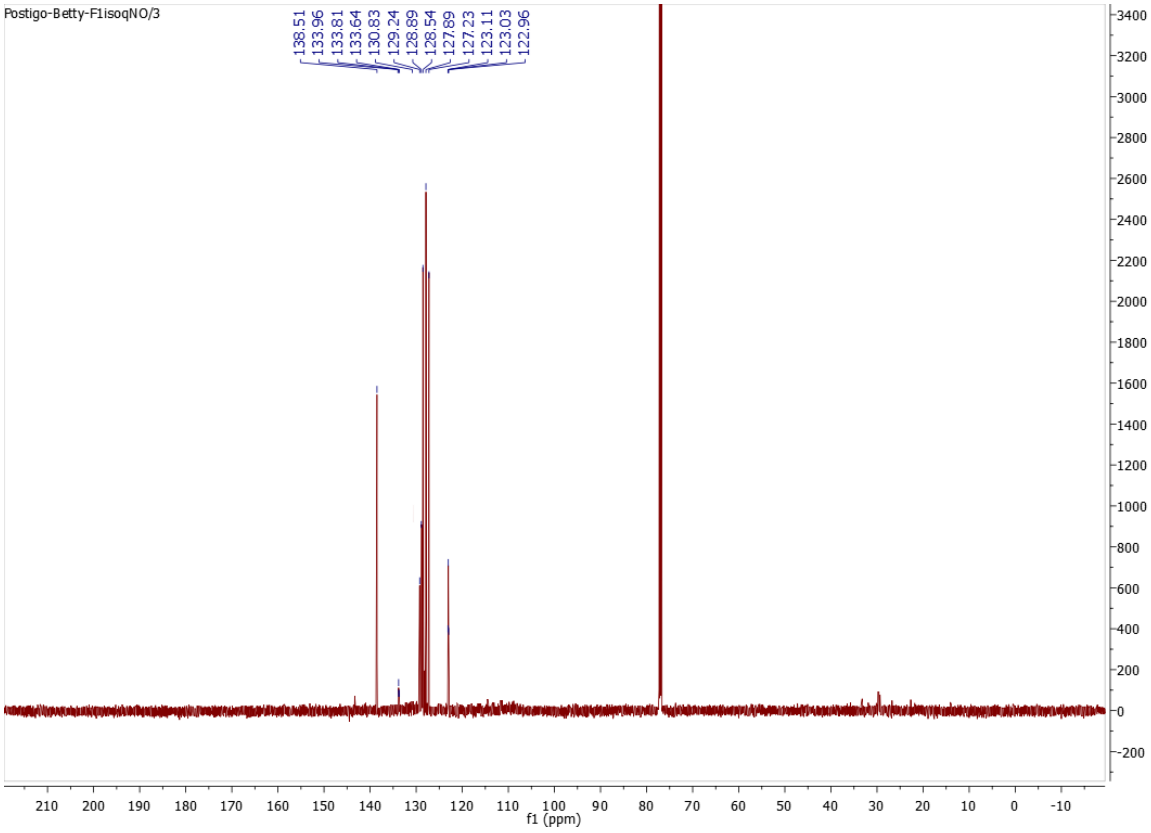
1H NMR spectrum
0f 2 in CDCl3



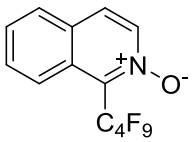


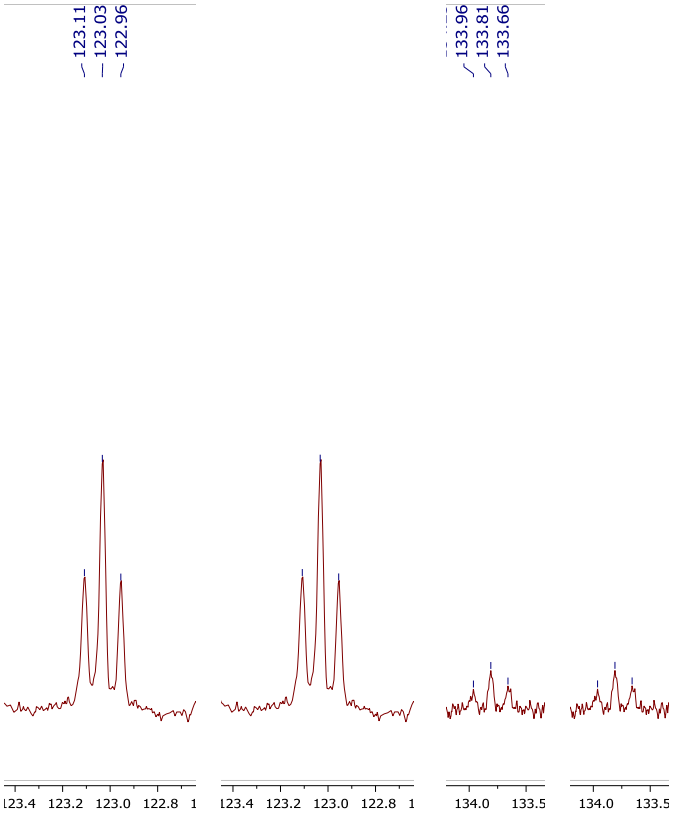
13C NMR spectrum 0f 2 in CDCl3



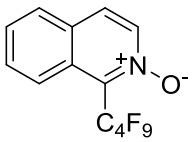


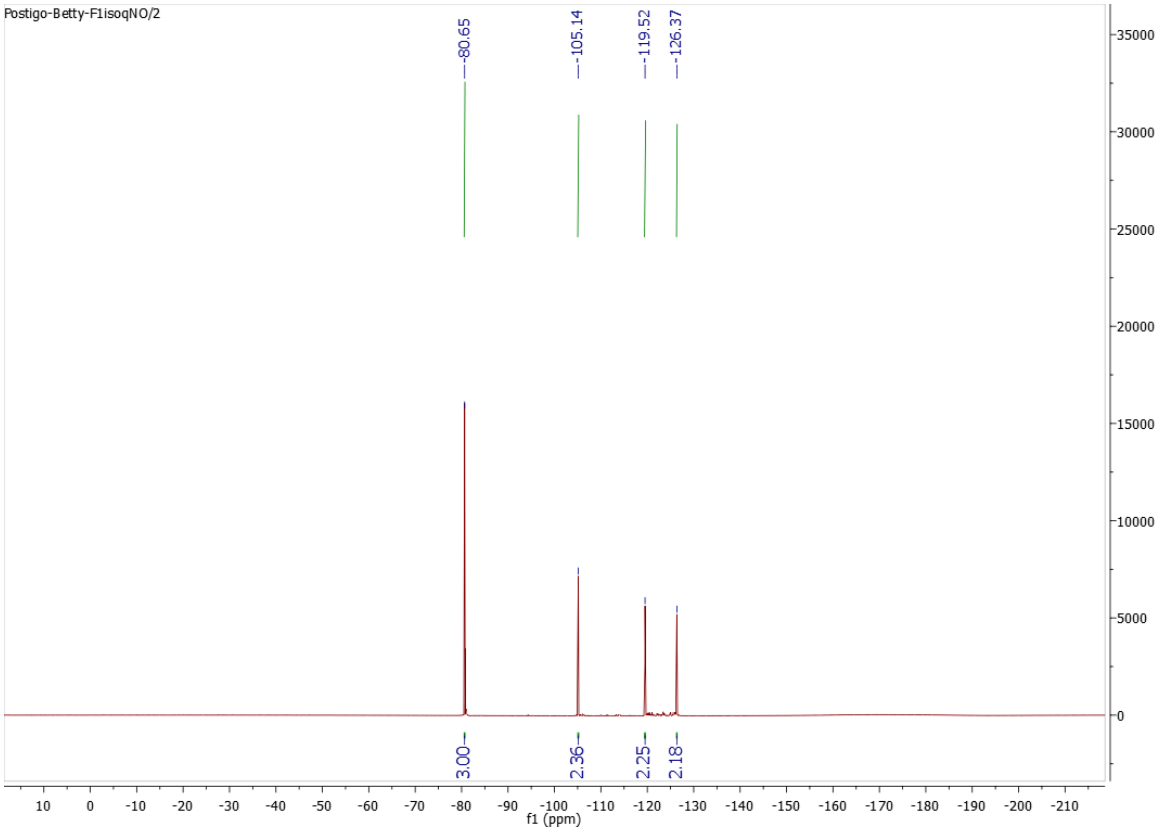
13C NMR spectrum 0f 2 in CDCl3, enlargement



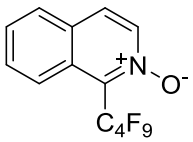


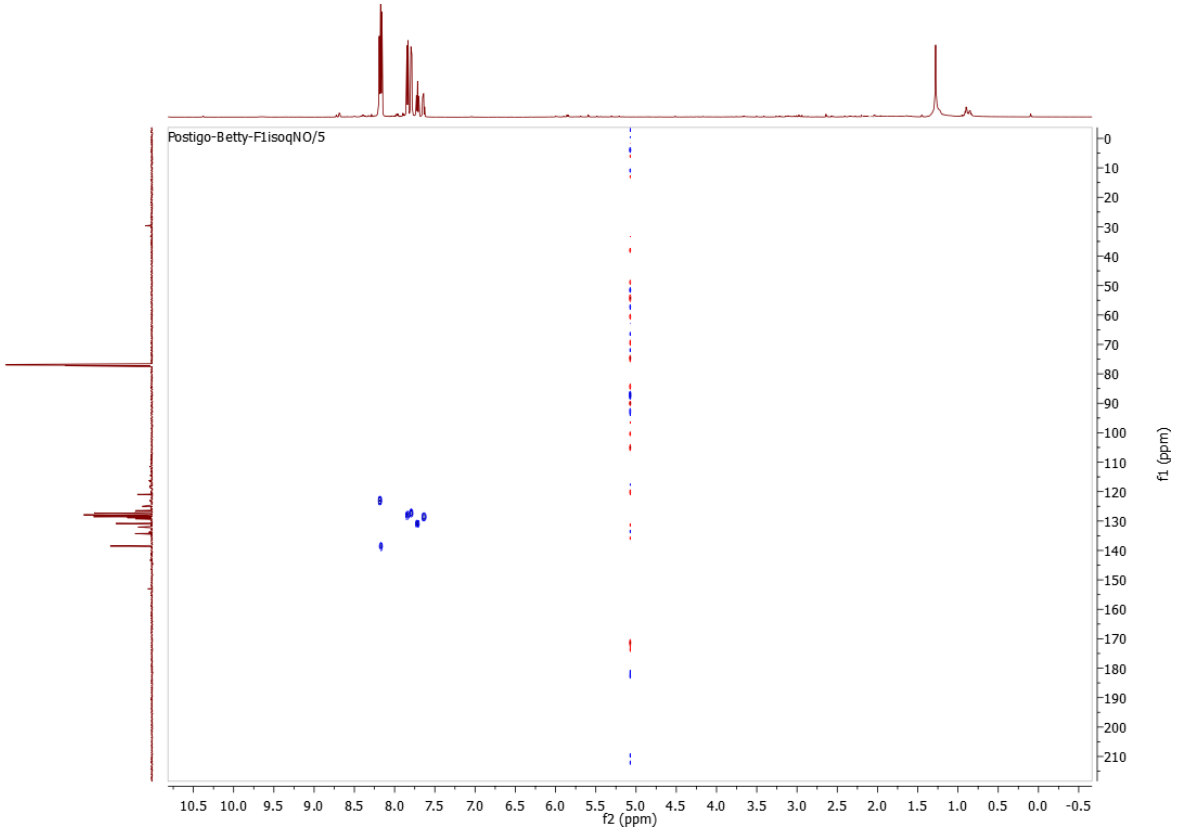
19F NMR spectrum 0f 2 in CDCl3



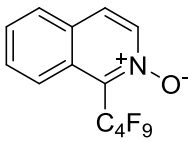


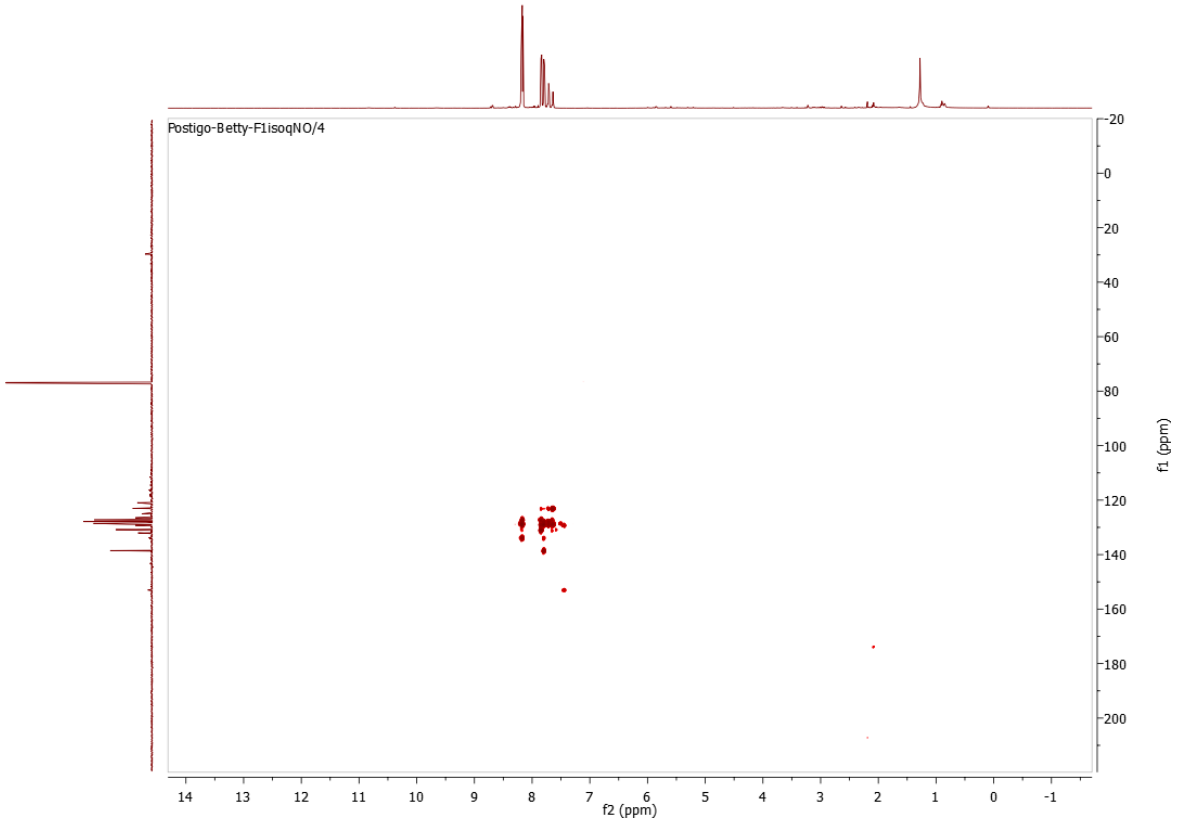
HSQC spectrum of 2 in CDCl3



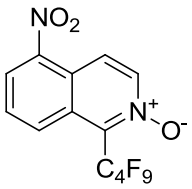


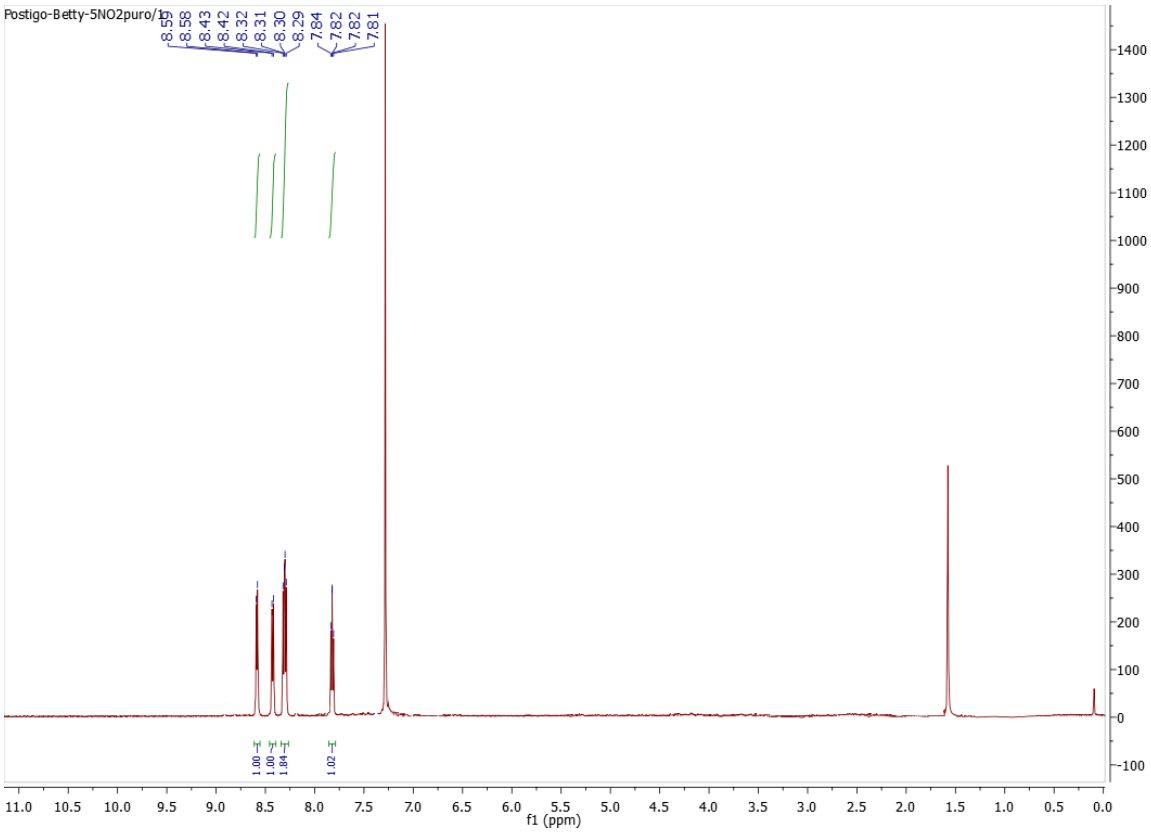
HMBC spectrum of 2a in CDCl3



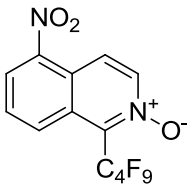


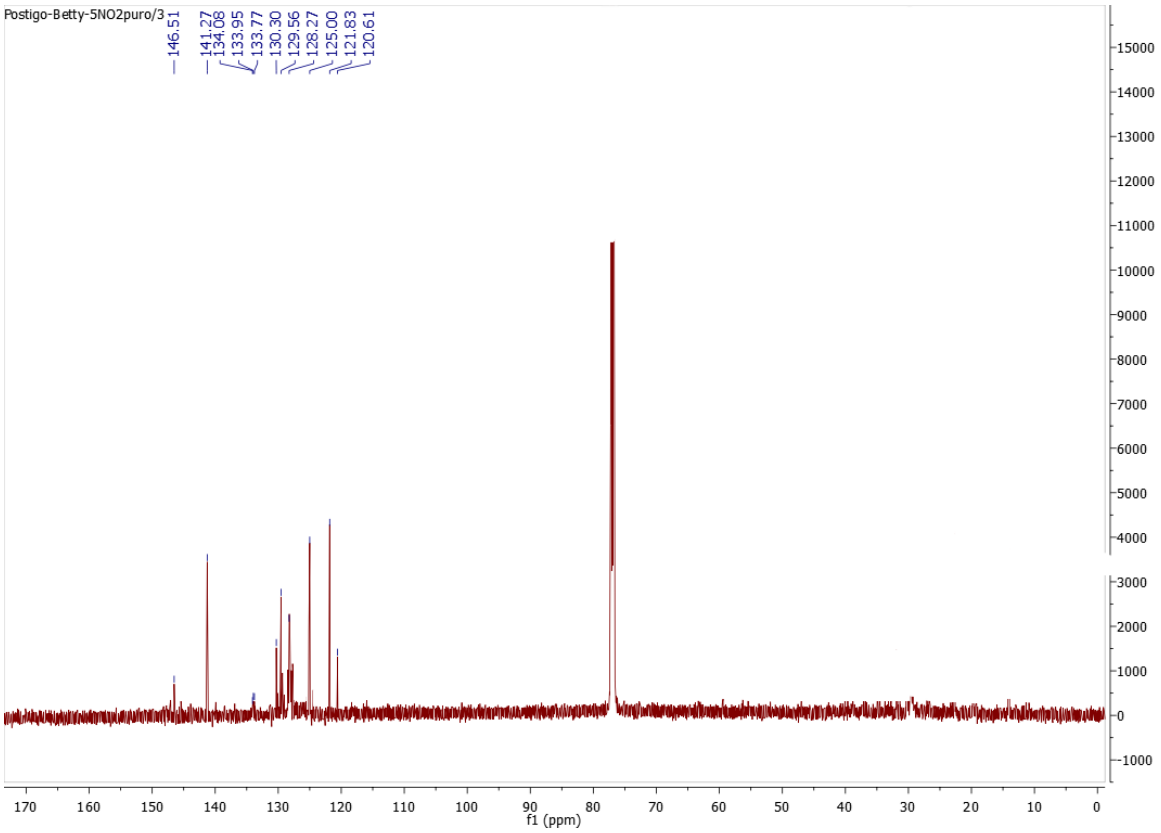
1H NMR spectrum 0f 2b
in CDCl3



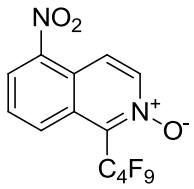


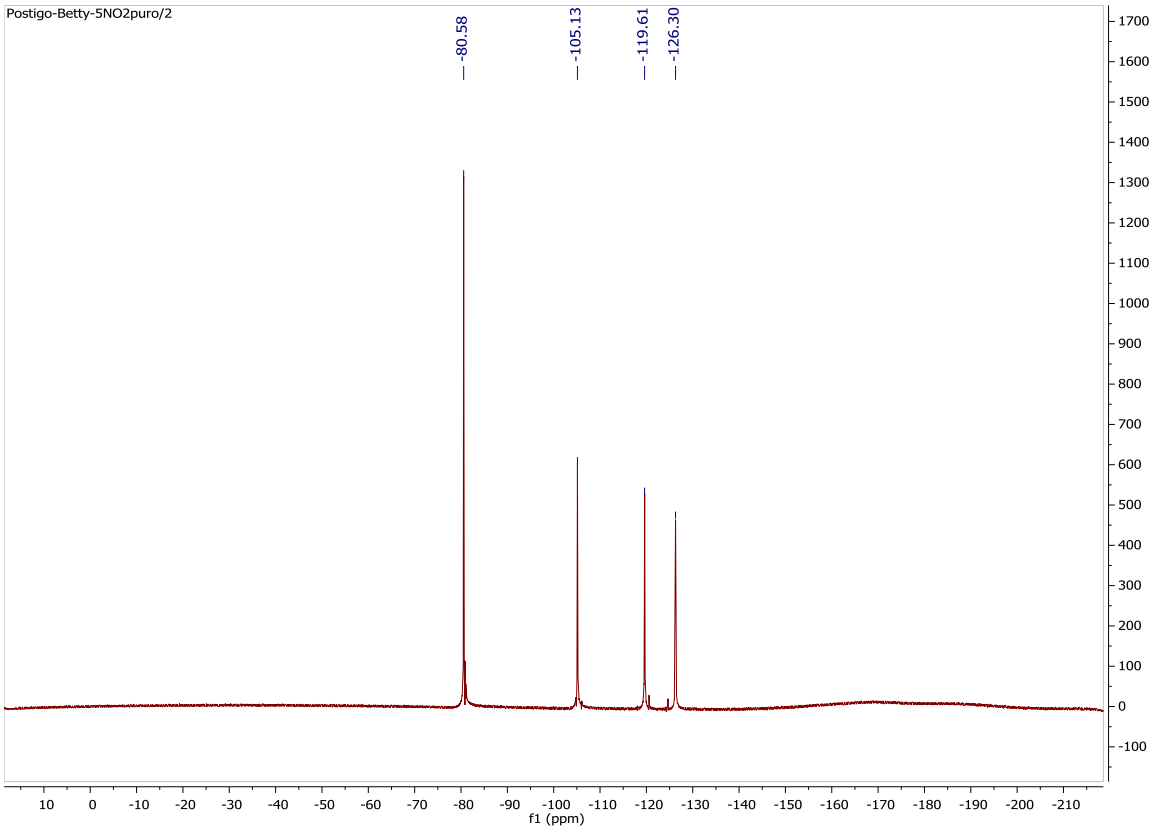
13C NMR spectrum 0f 2b
in CDCl3



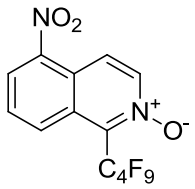


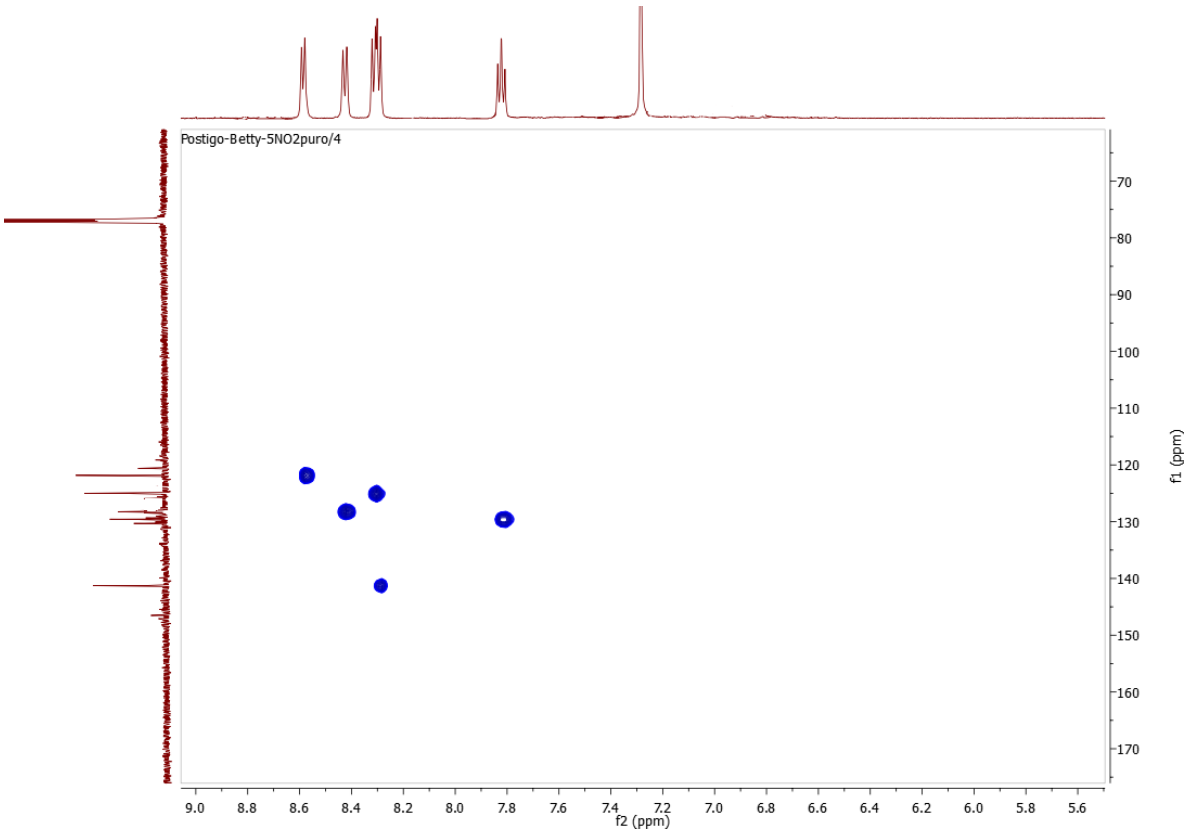
19F NMR spectrum 0f 2b
in CDCl3



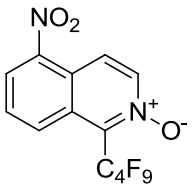


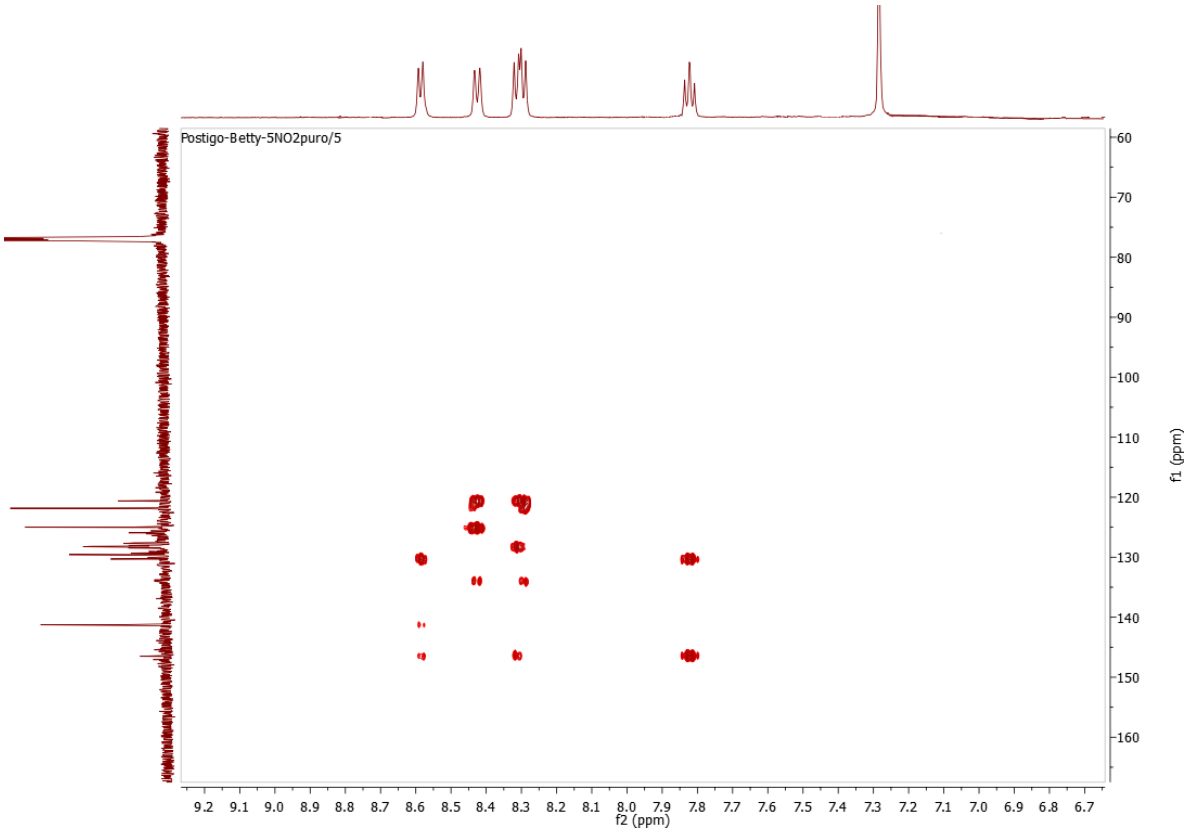
HSQC NMR spectrum 0f
2b in CDCl3



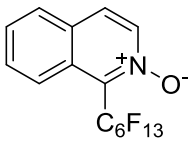


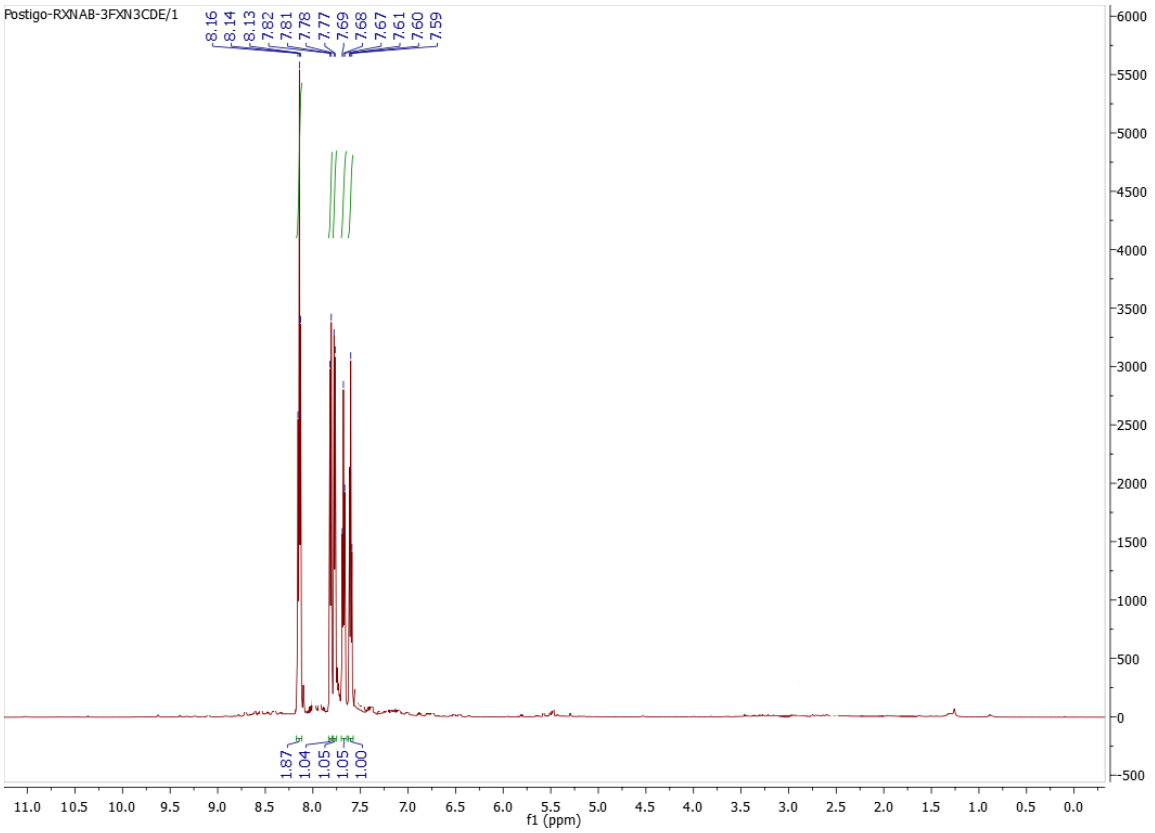
HMBC NMR spectrum 0f
2b in CDCl3



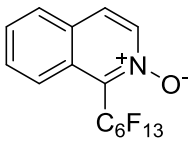


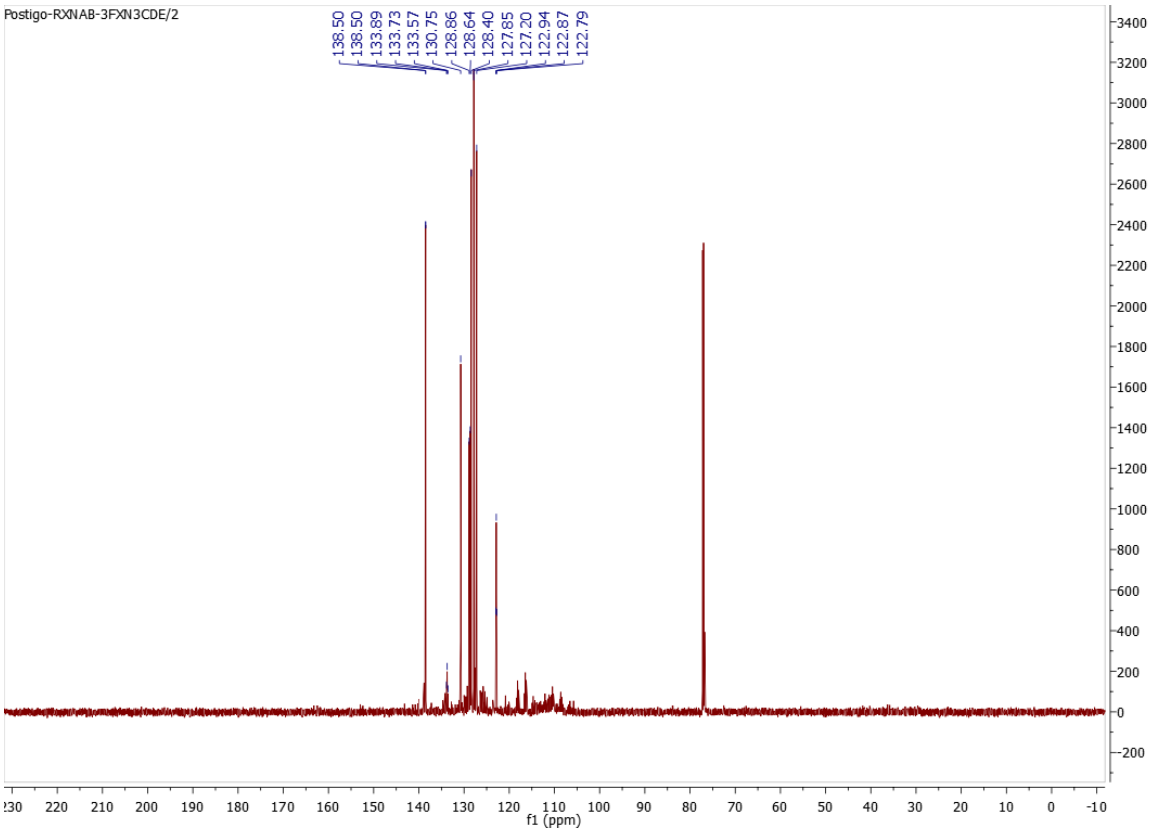
1H NMR spectrum
0f 3 in CDCl3



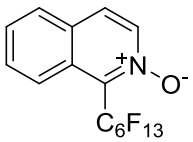


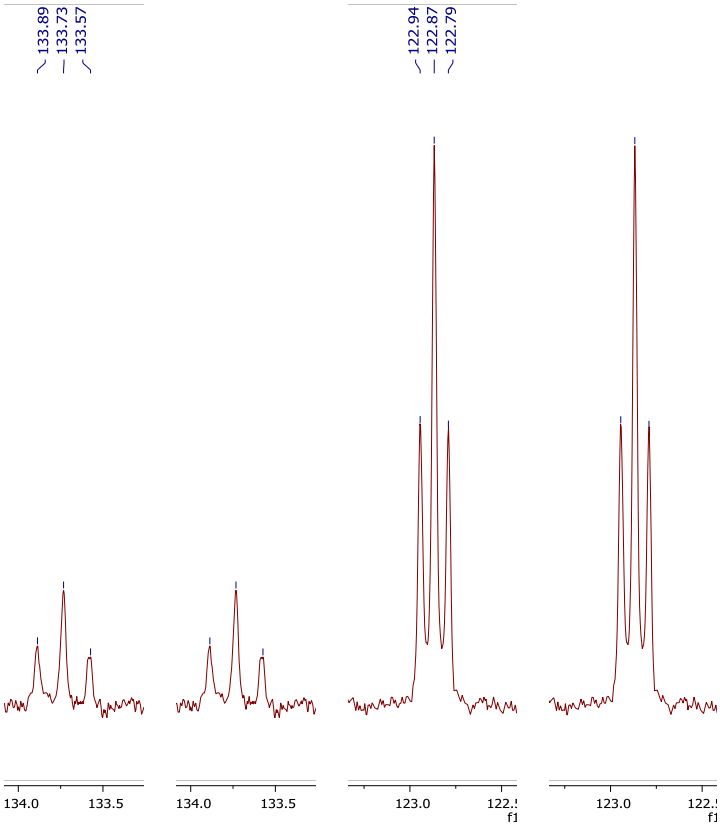
13C NMR spectrum 0f 3 in CDCl3



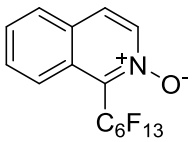


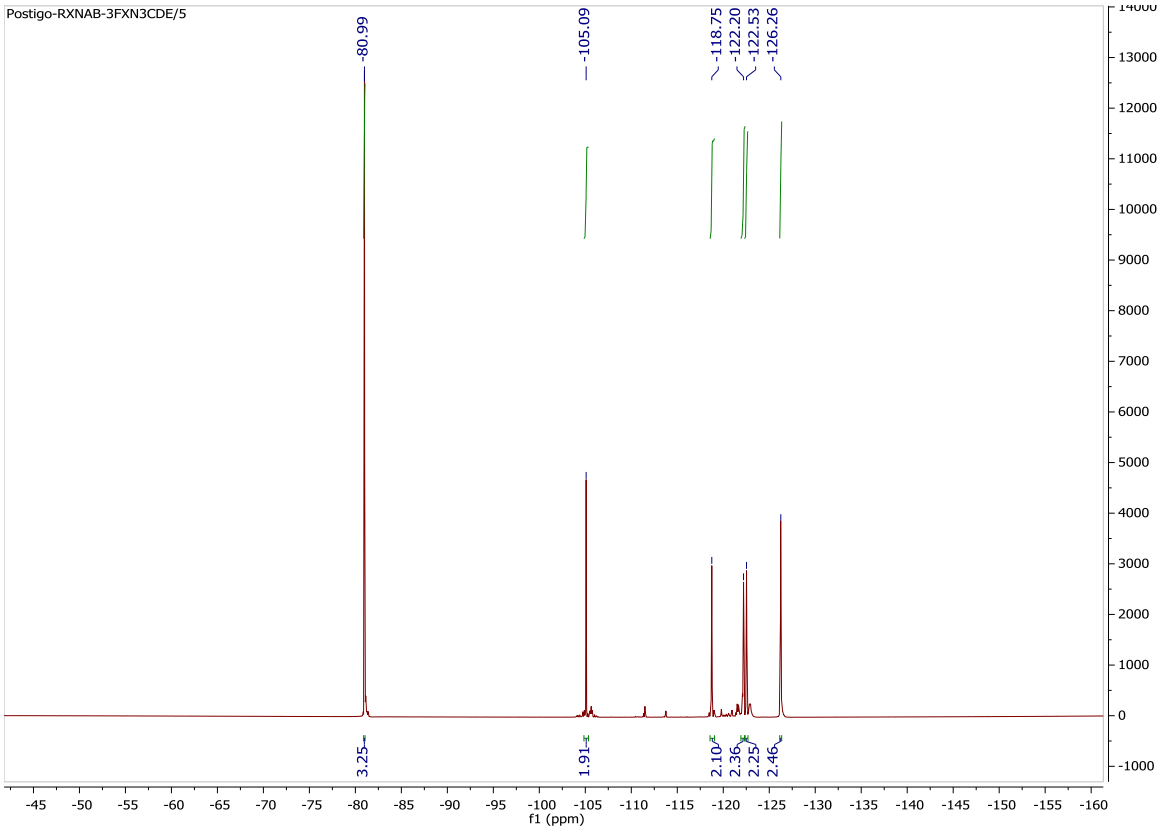
13C NMR spectrum 0f 3 in CDCl3, enlargement



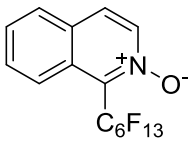


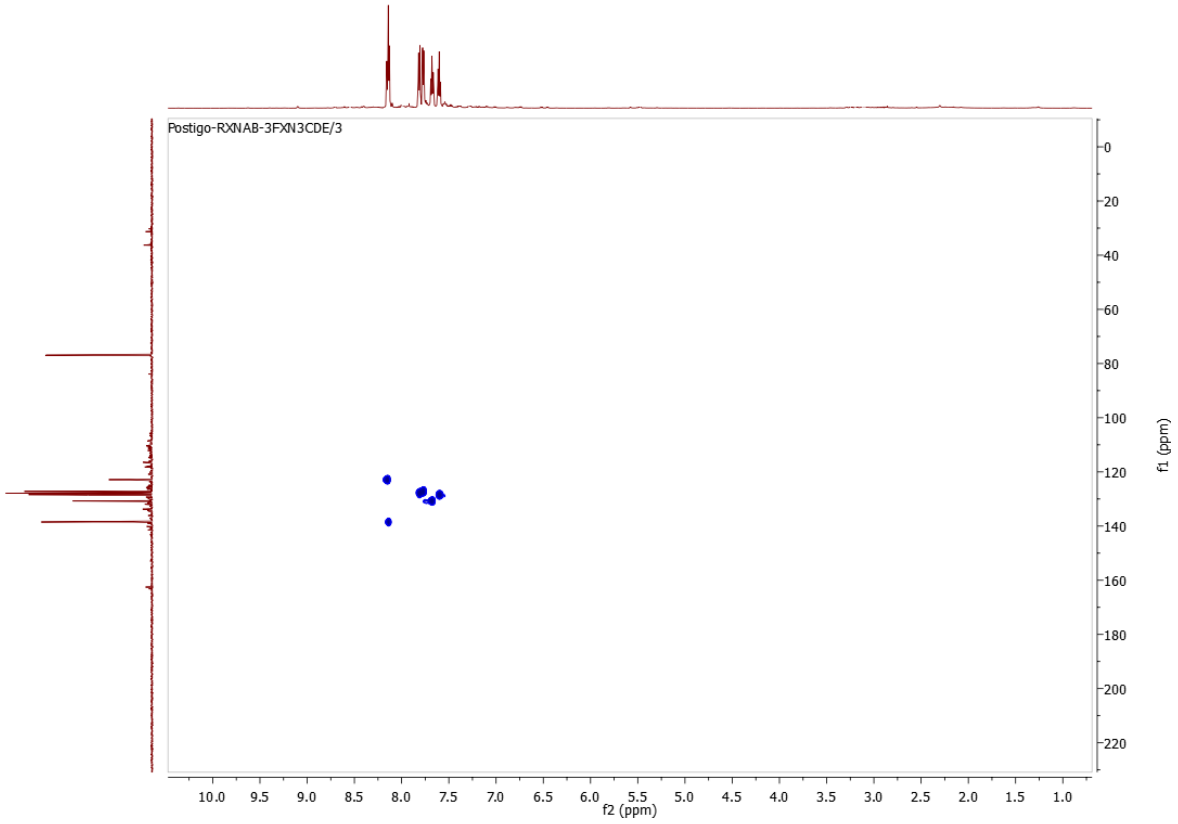
19F NMR spectrum 0f 3 in CDCl3



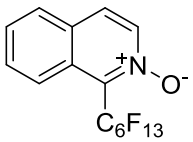


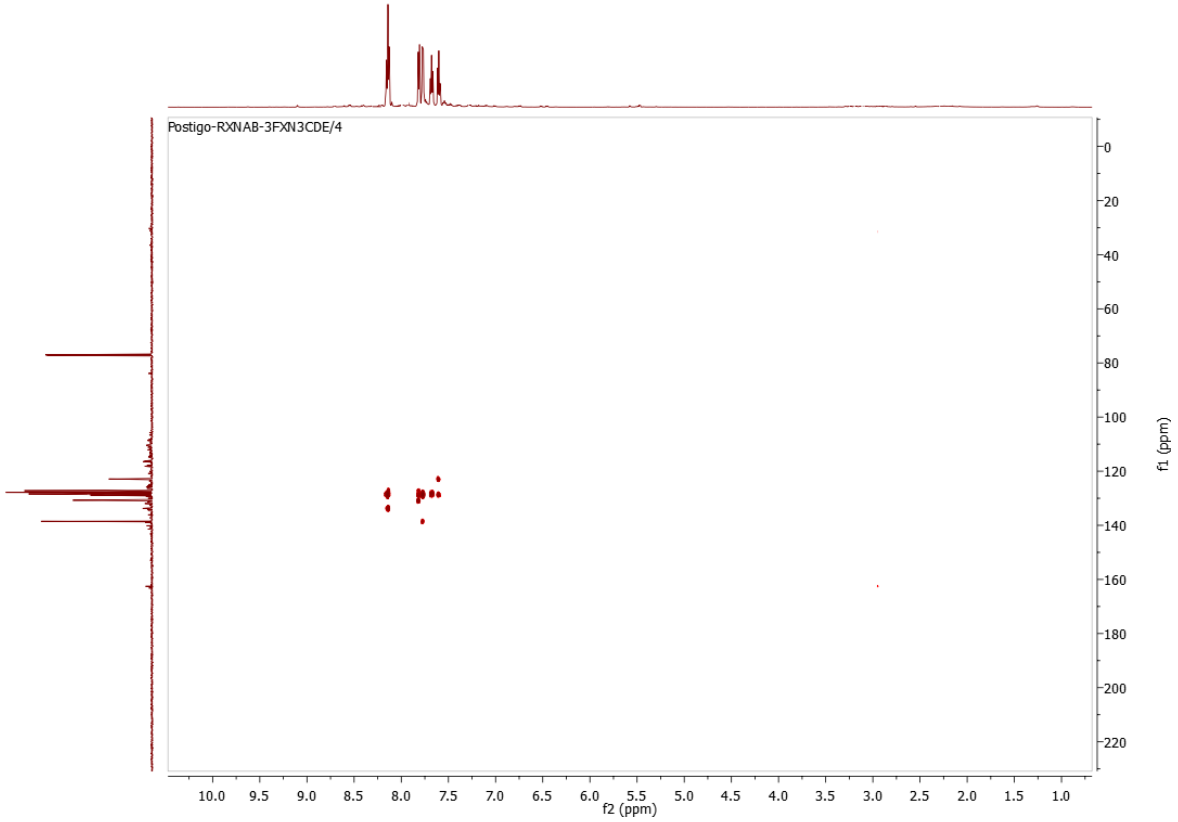
HSQC NMR spectrum 0f 3 in CDCl3



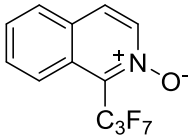


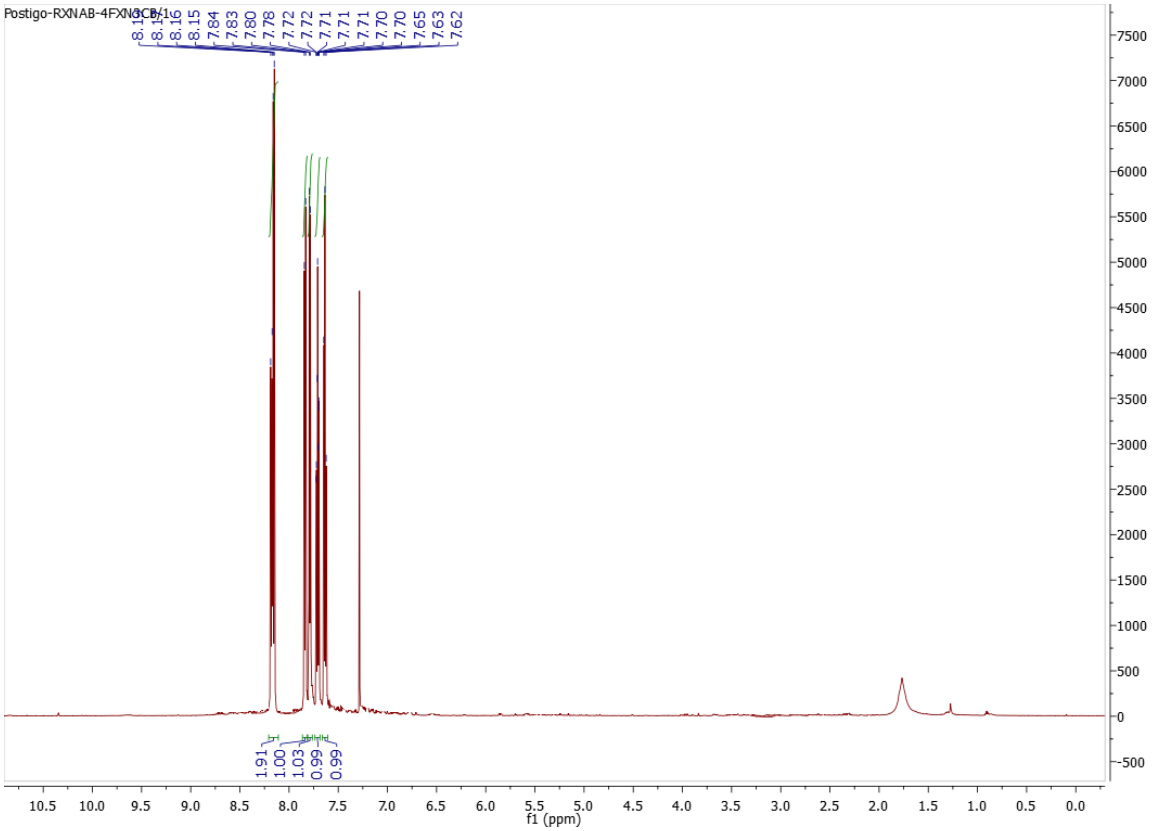
HMBC NMR spectrum 0f 3 in CDCl3



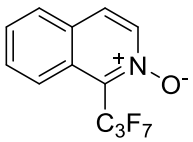


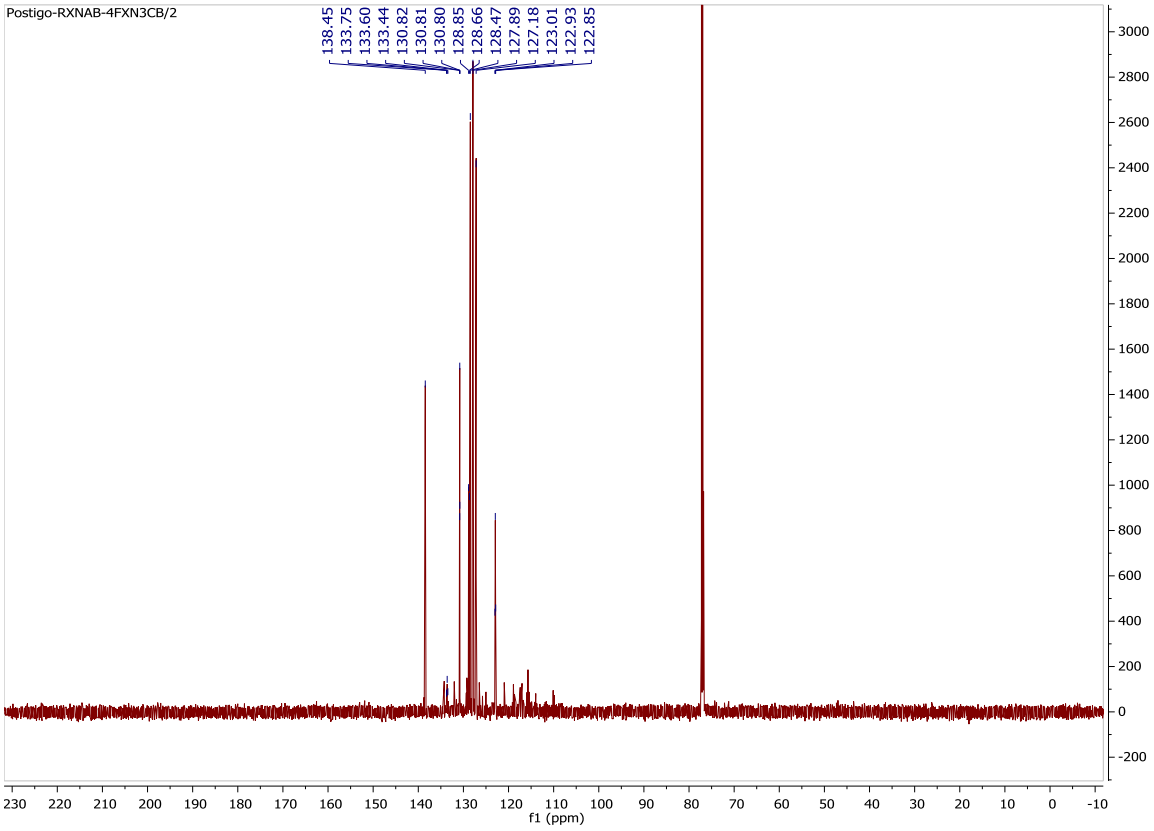
1H NMR spectrum
0f 4 in CDCl3



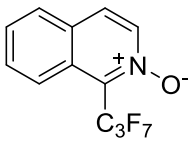


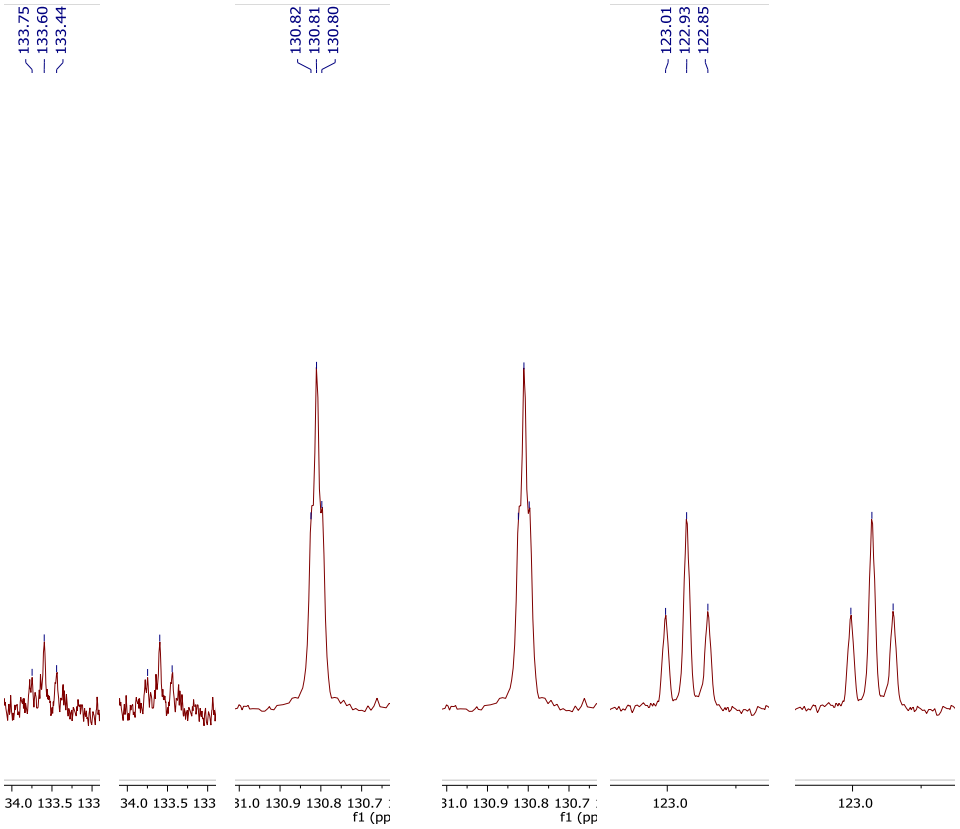
13C NMR spectrum 0f 4 in CDCl3



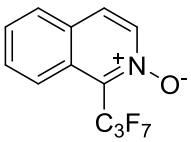


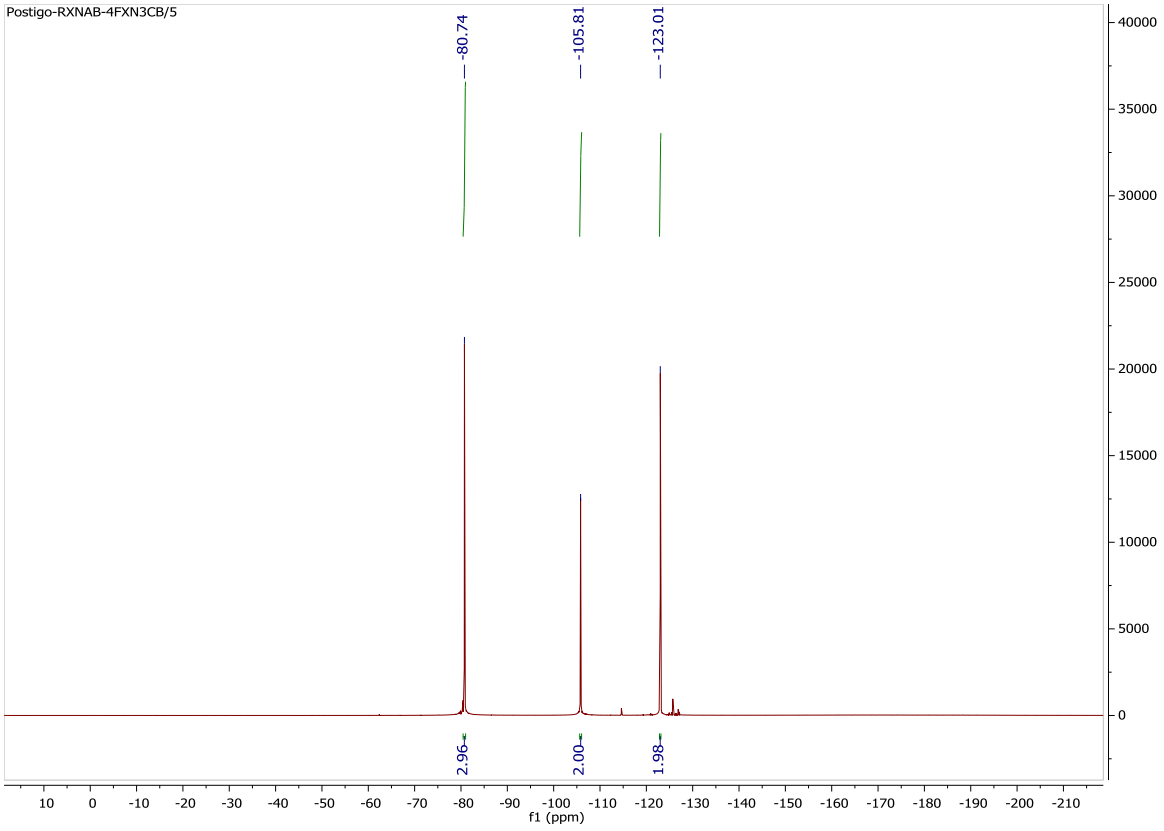
13C NMR spectrum 0f 4 in CDCl3, enlargement



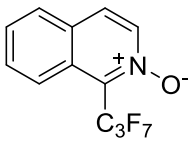


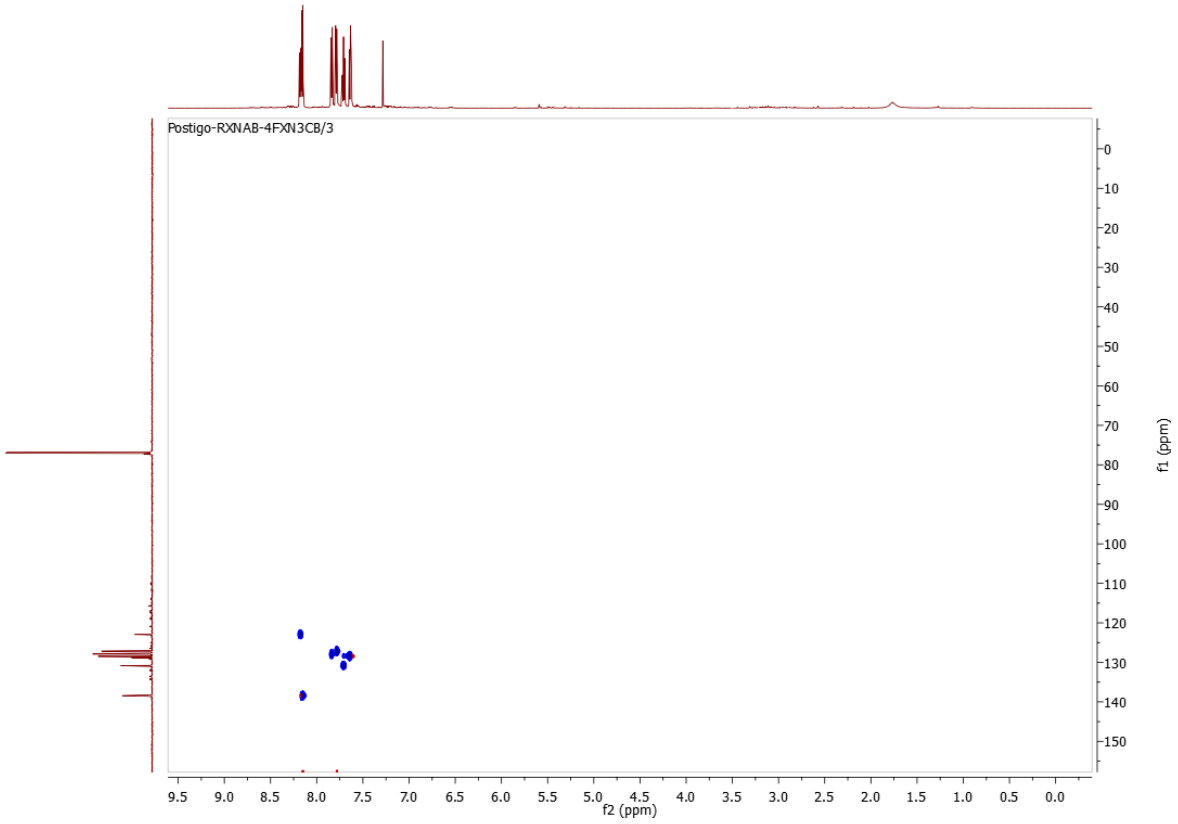
19F NMR spectrum 0f 4 in CDCl3



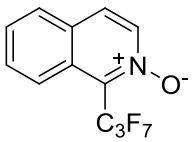


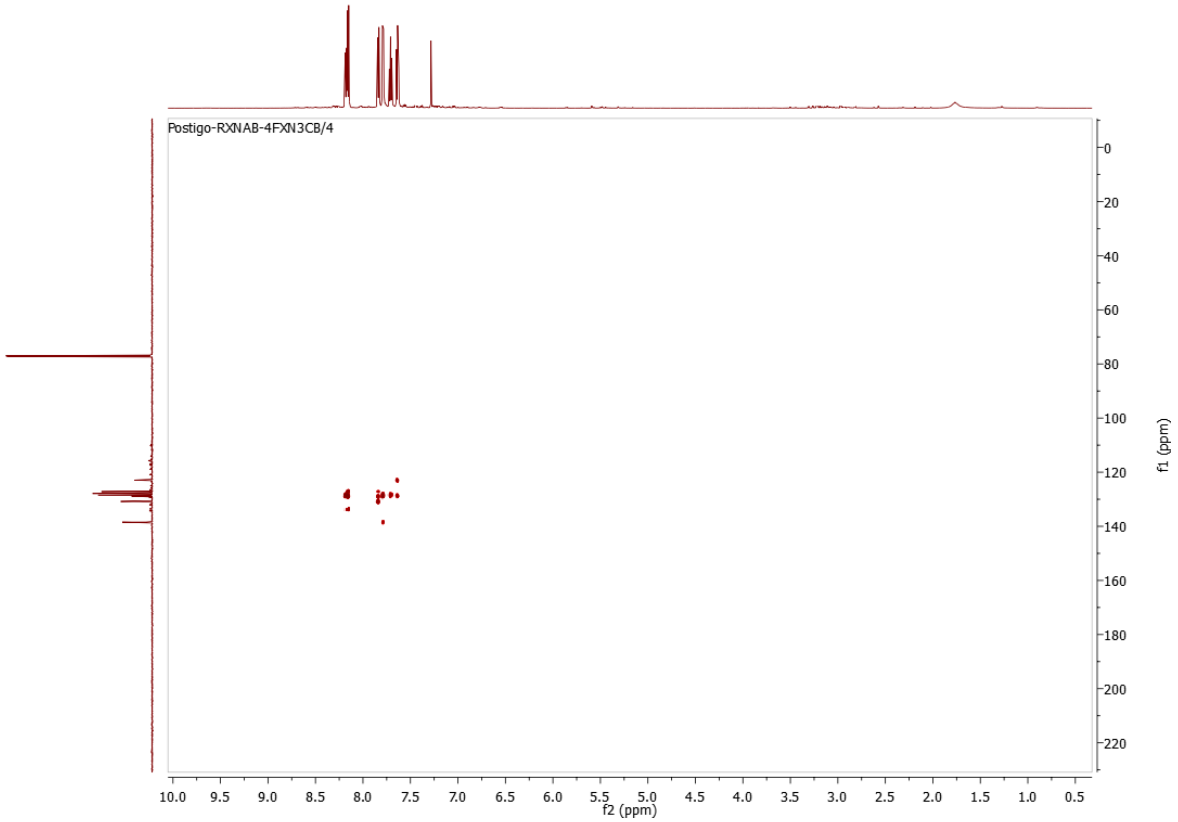
HSQC NMR spectrum 0f 4 in CDCl3



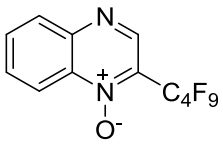


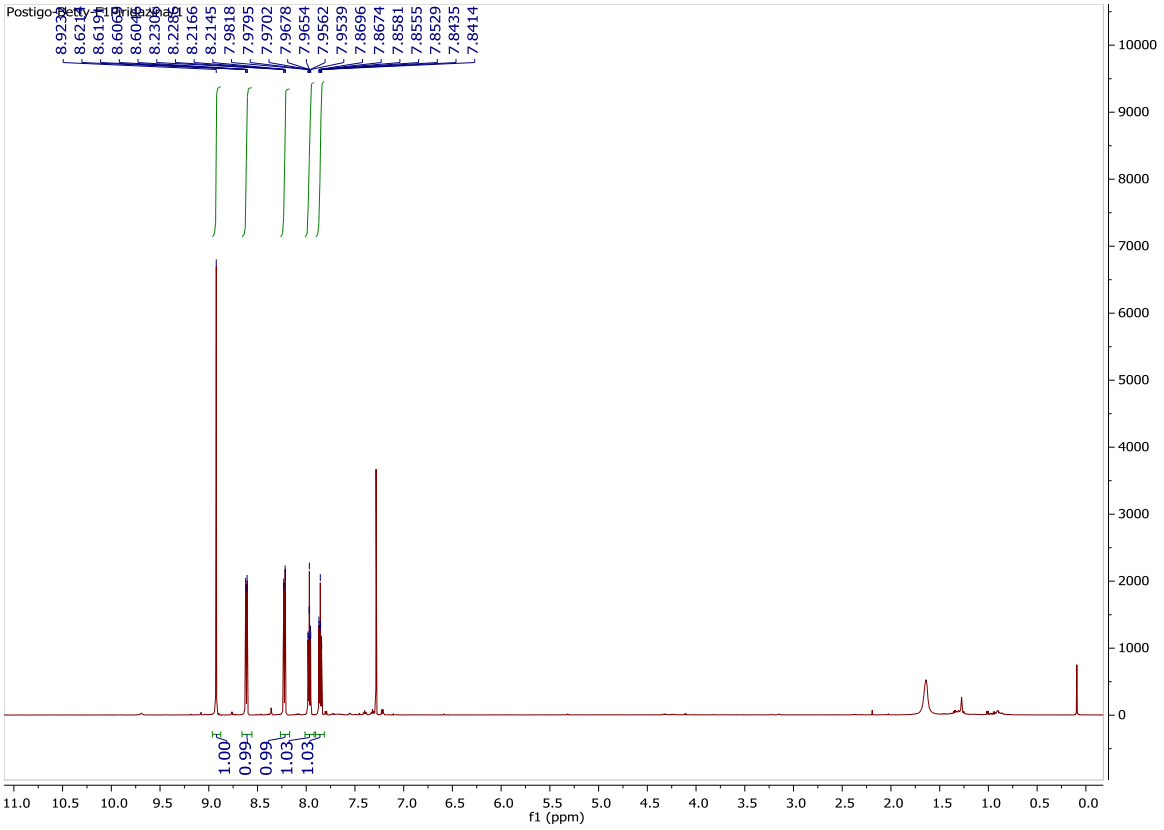
HMBC NMR spectrum 0f 4 in CDCl3



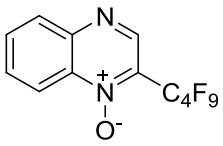


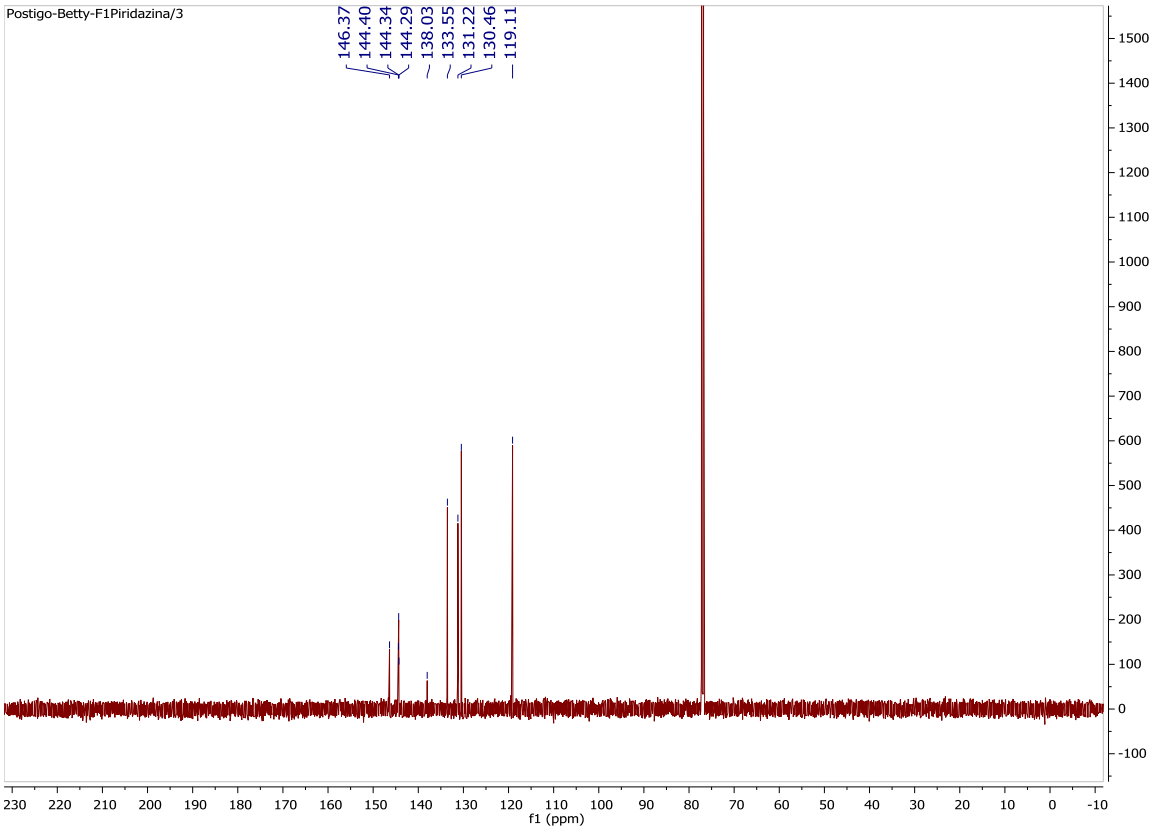
1H NMR spectrum 0f 6 in CDCl3



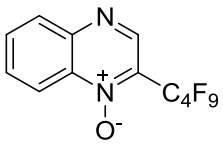


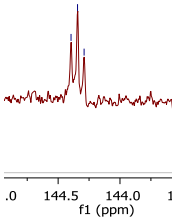
13C NMR spectrum 0f 6 in CDCl3

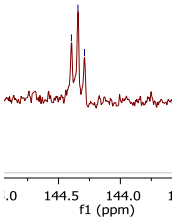




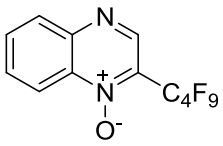
13C NMR spectrum 0f 6 in CDCl3, enlargement

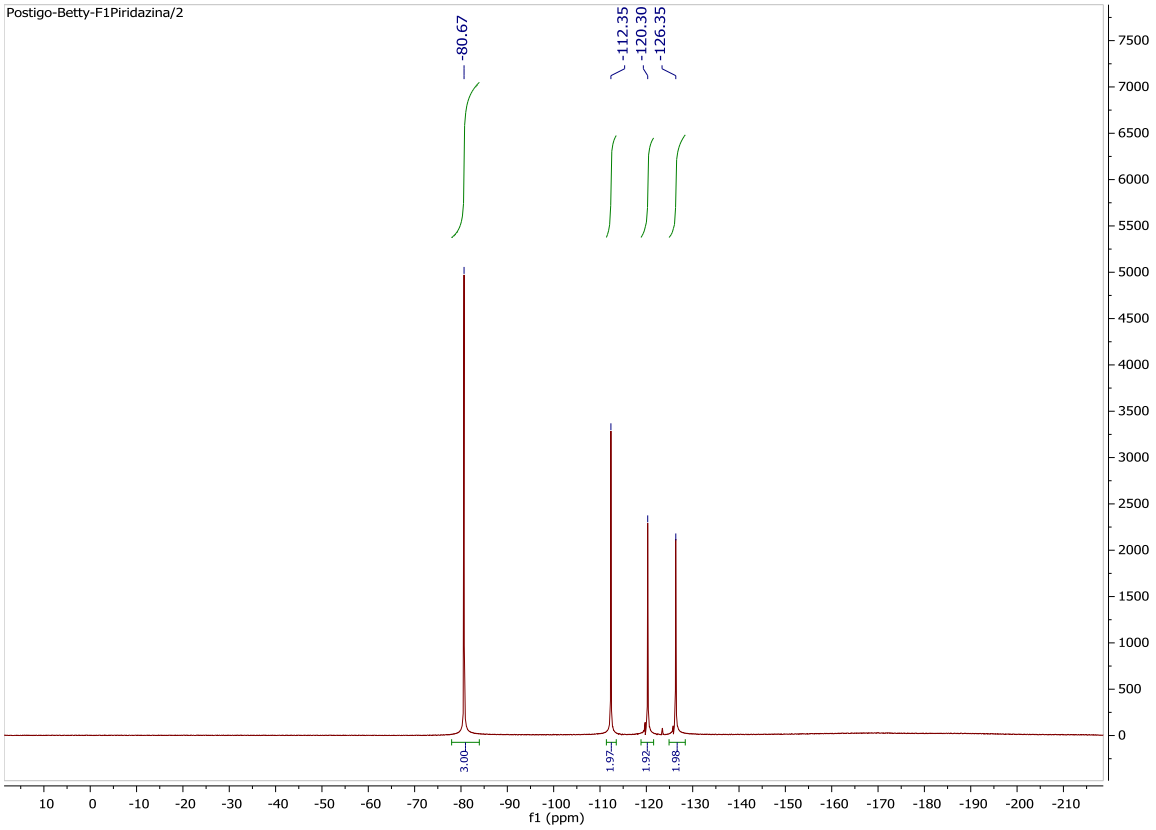




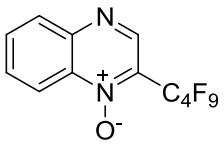


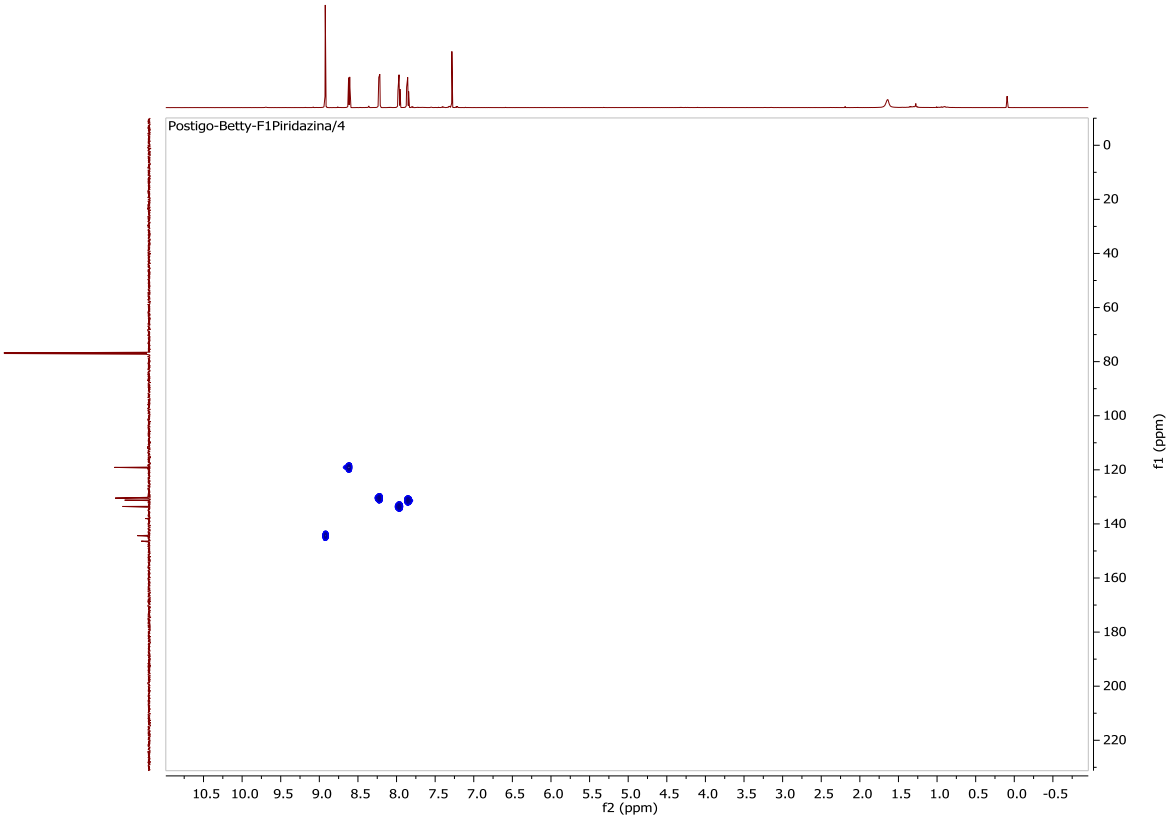
19F NMR spectrum 0f 6 in CDCl3



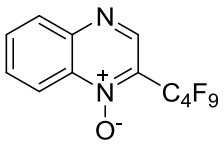


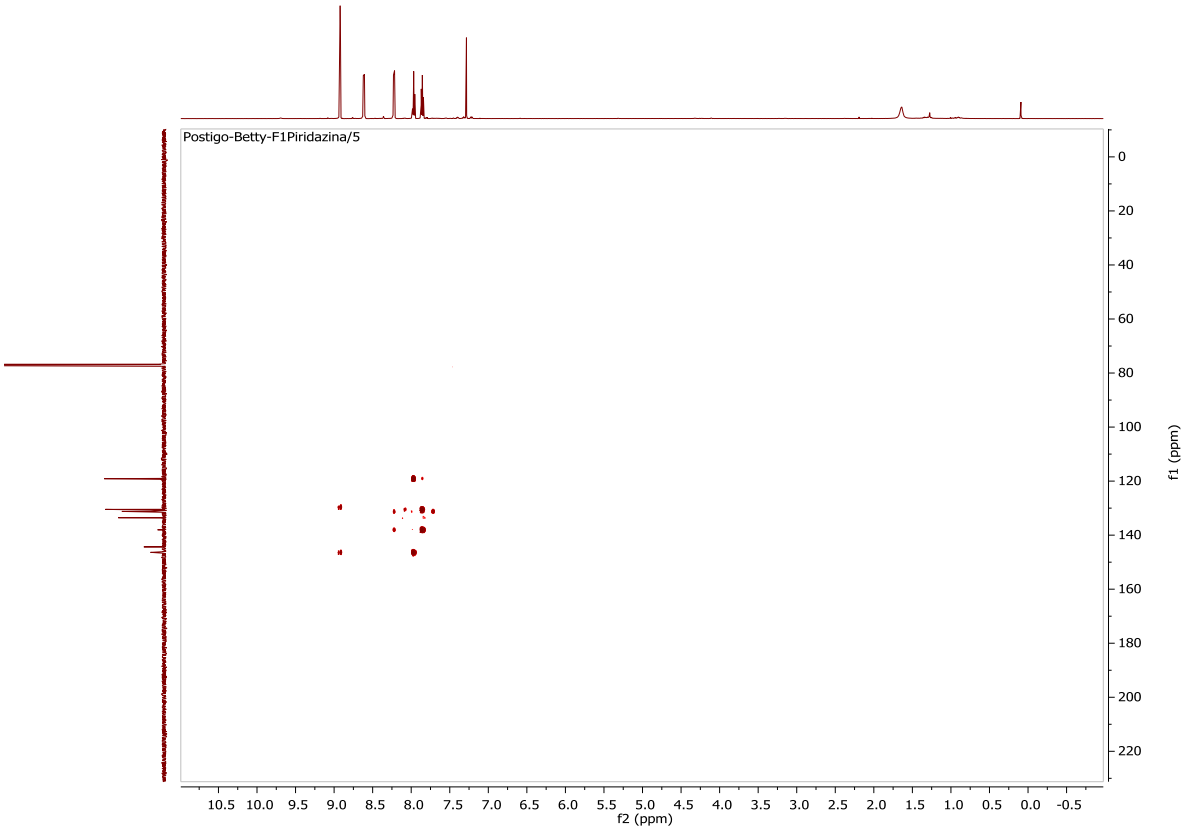
HSQC NMR spectrum 0f 6 in CDCl3



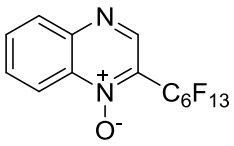


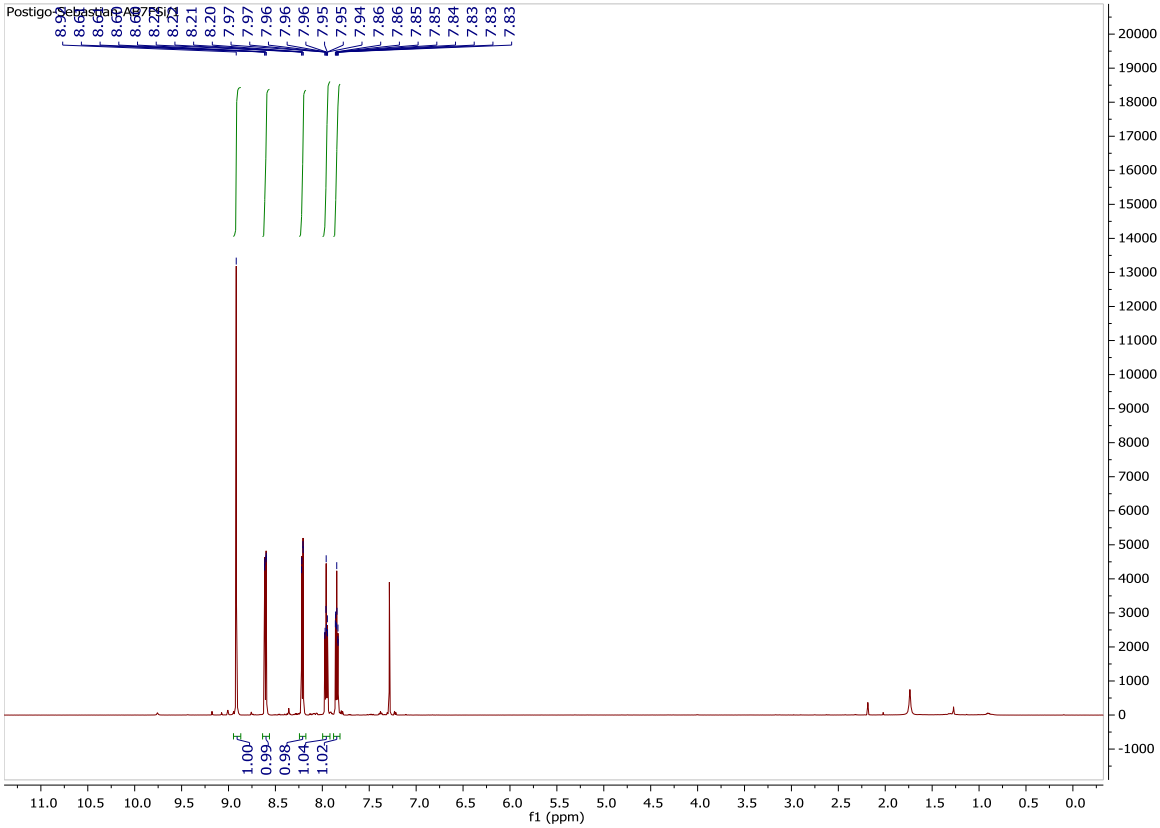
HMBC NMR spectrum 0f 6 in CDCl3



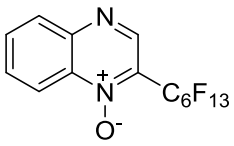


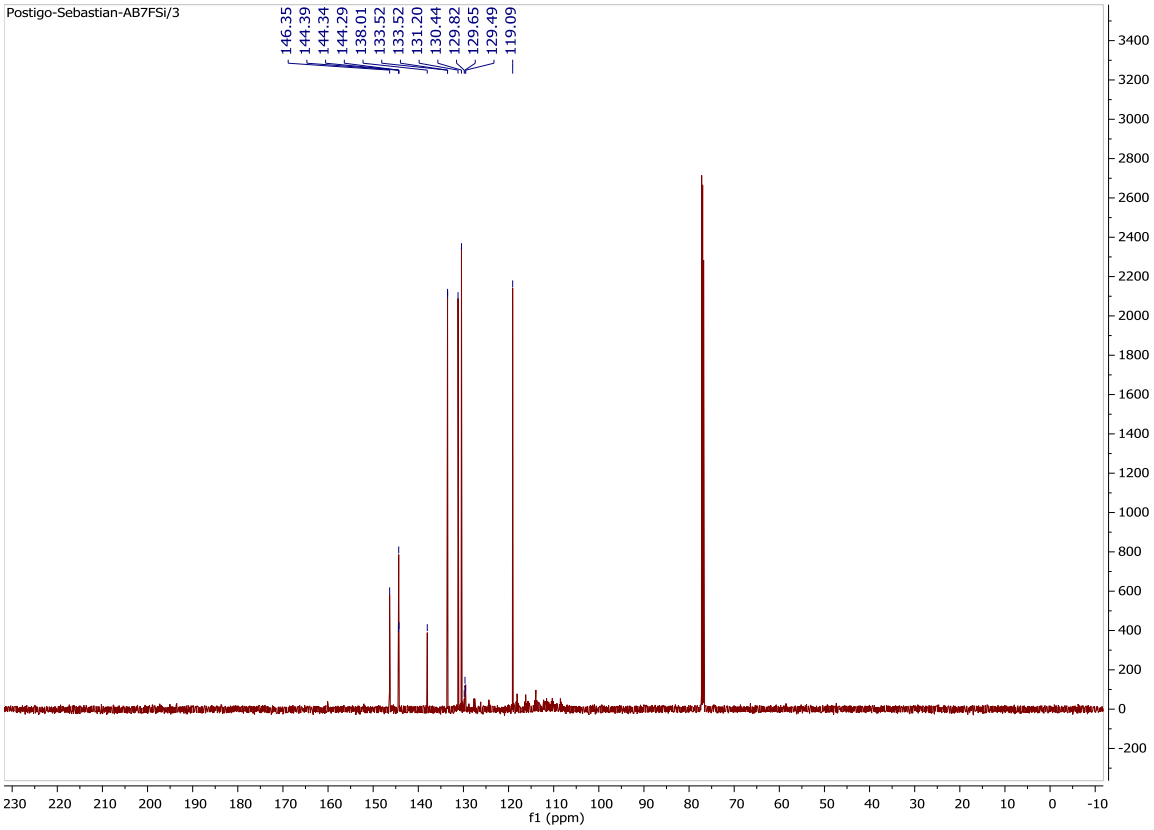
1H NMR spectrum
0f 7 in CDCl3



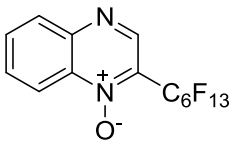


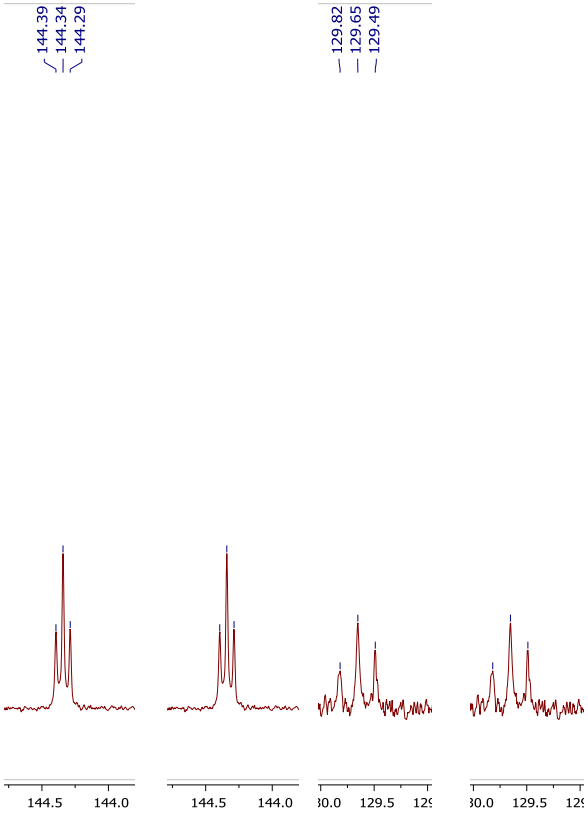
13C NMR spectrum 0f 7 in CDCl3



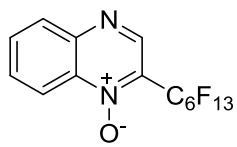


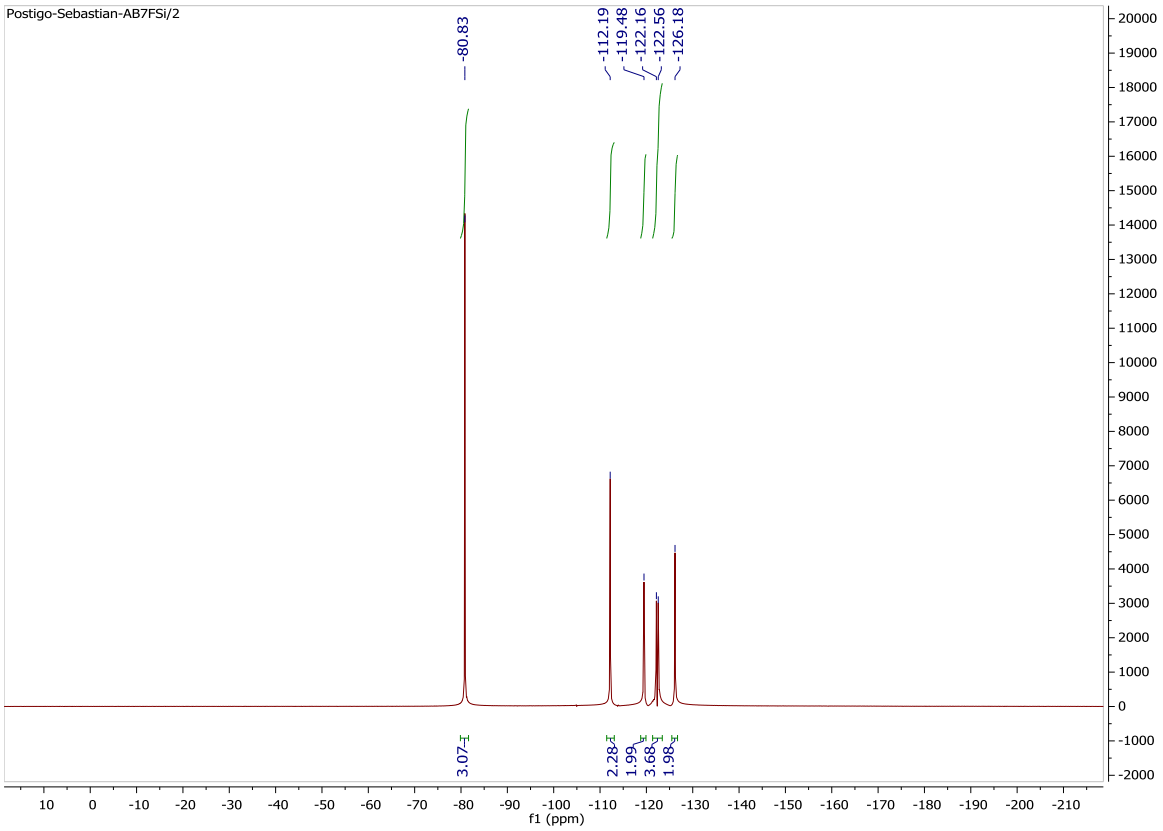
13C NMR spectrum 0f 7 in CDCl3, enlargement



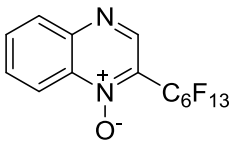


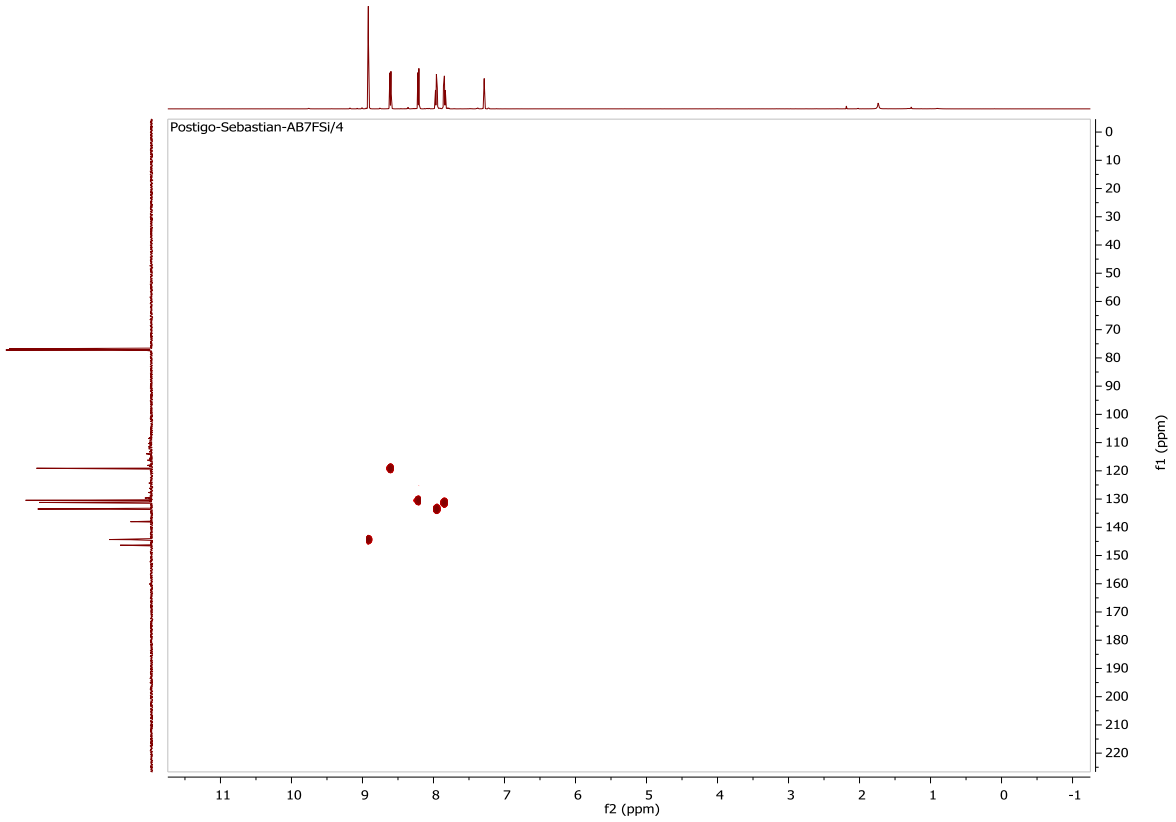
19F NMR spectrum 0f 7 in CDCl3



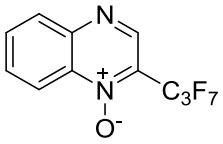


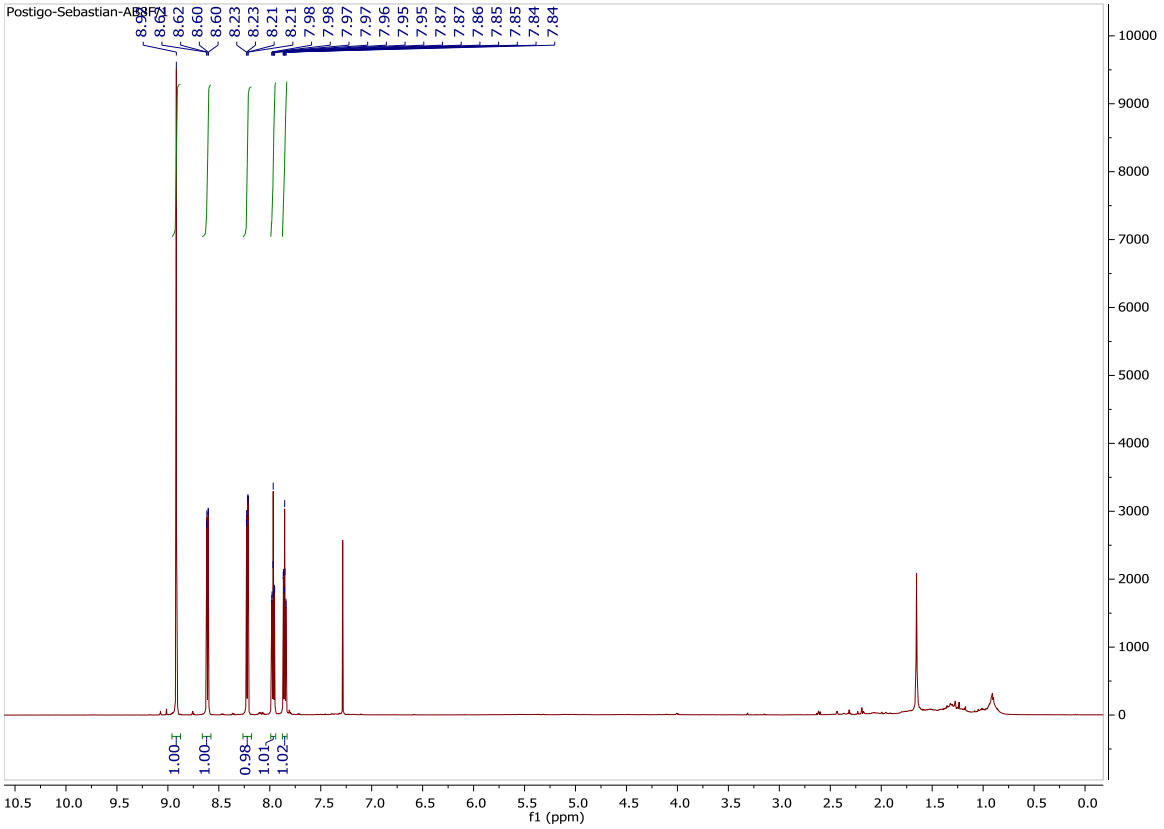
HSQC NMR spectrum 0f 7 in CDCl3



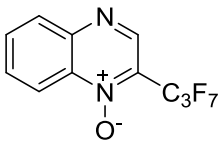


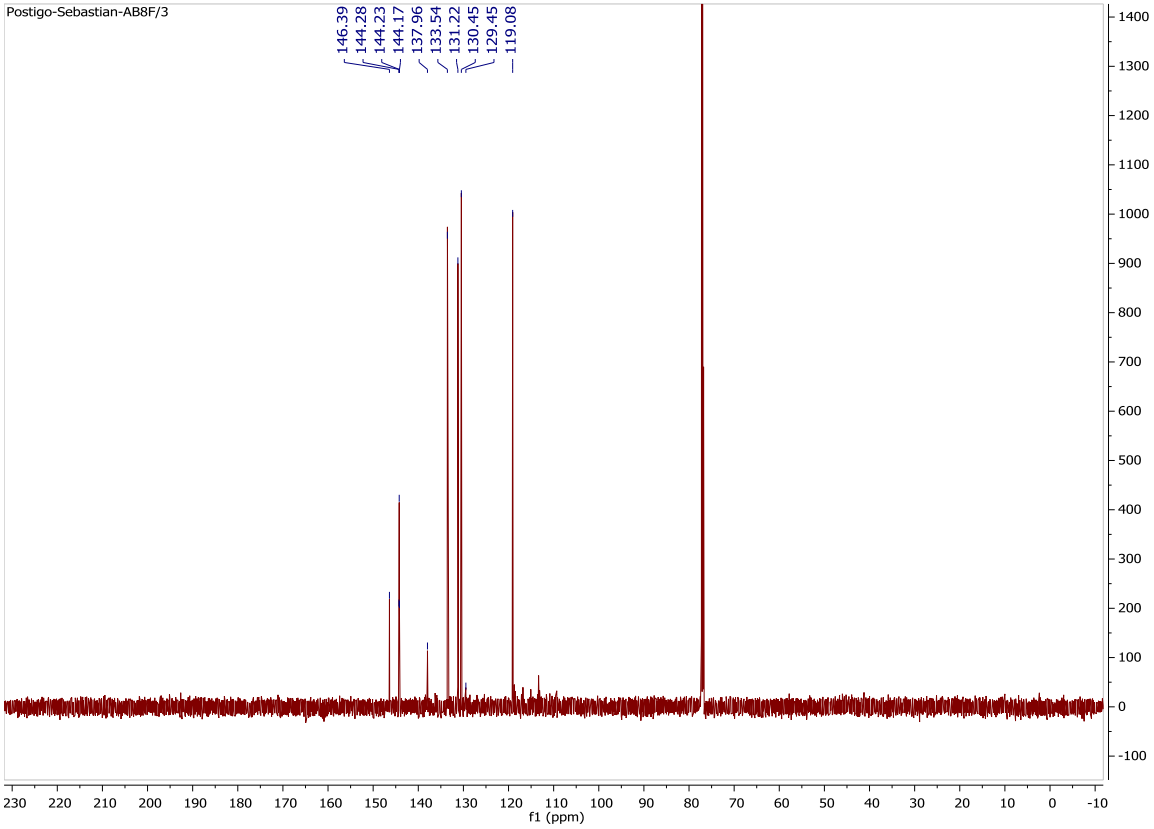
1H NMR spectrum 0f 8 in CDCl3



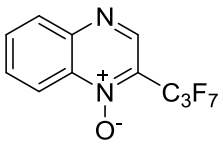


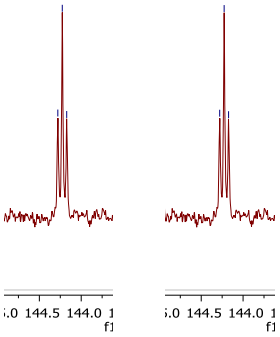
13C NMR spectrum 0f 8 in CDCl3



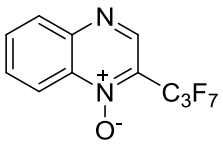


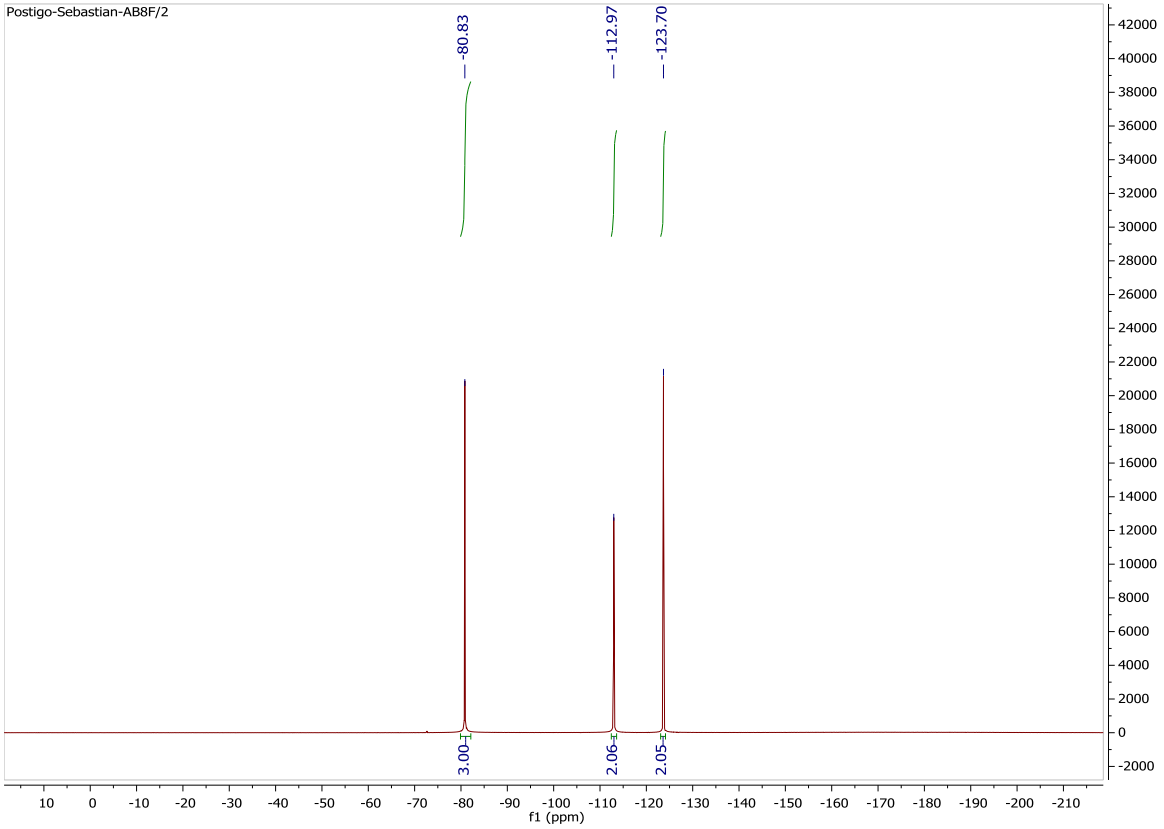
13C NMR spectrum 0f 8 in CDCl3, enlargement



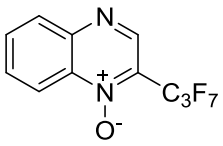


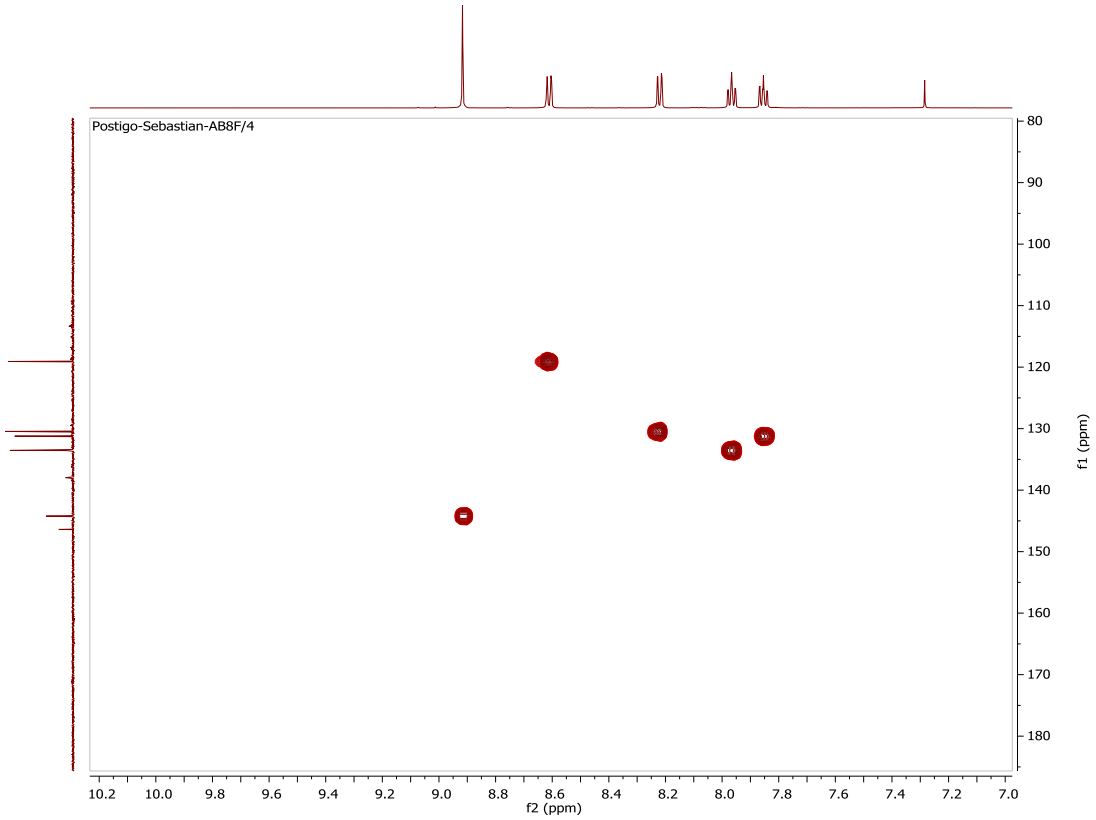
19F NMR spectrum 0f 8 in CDCl3



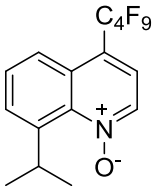


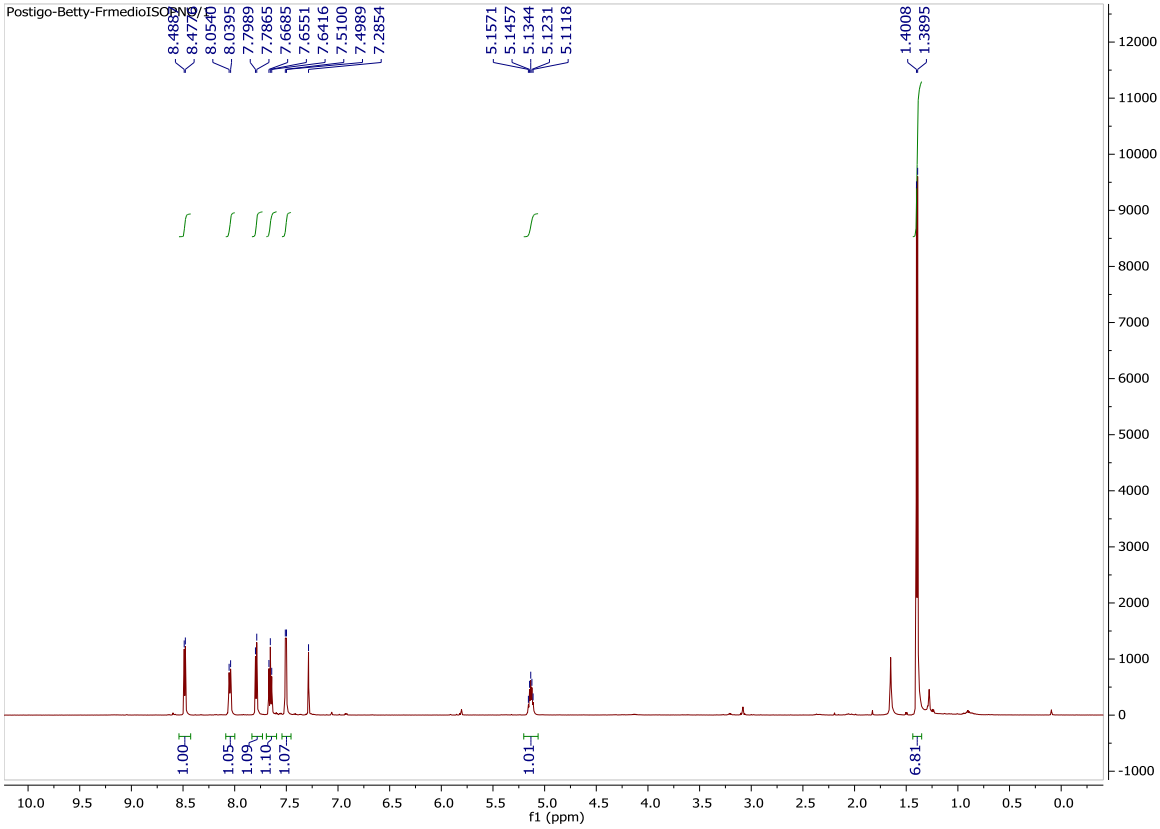
HSQC NMR spectrum 0f 8 in CDCl3



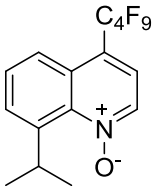


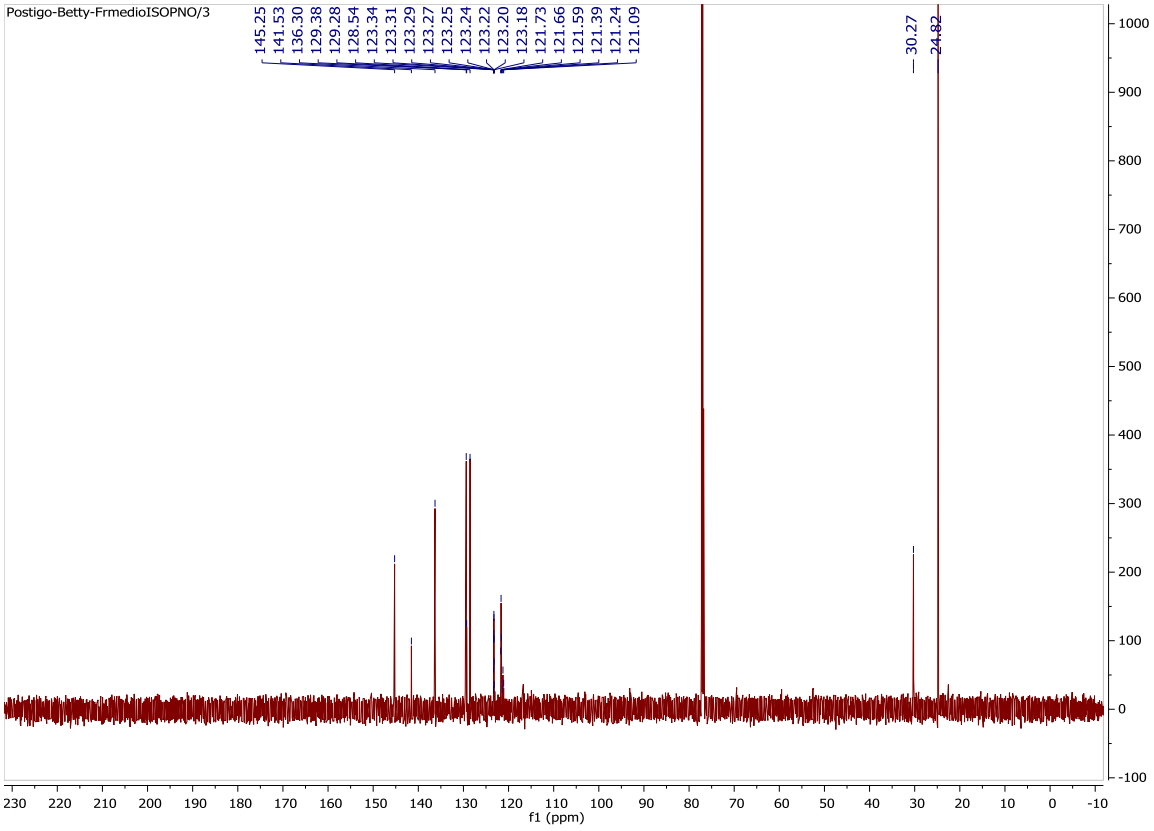
1H NMR spectrum of 10 in CDCl3



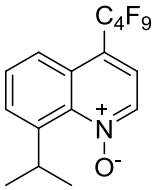


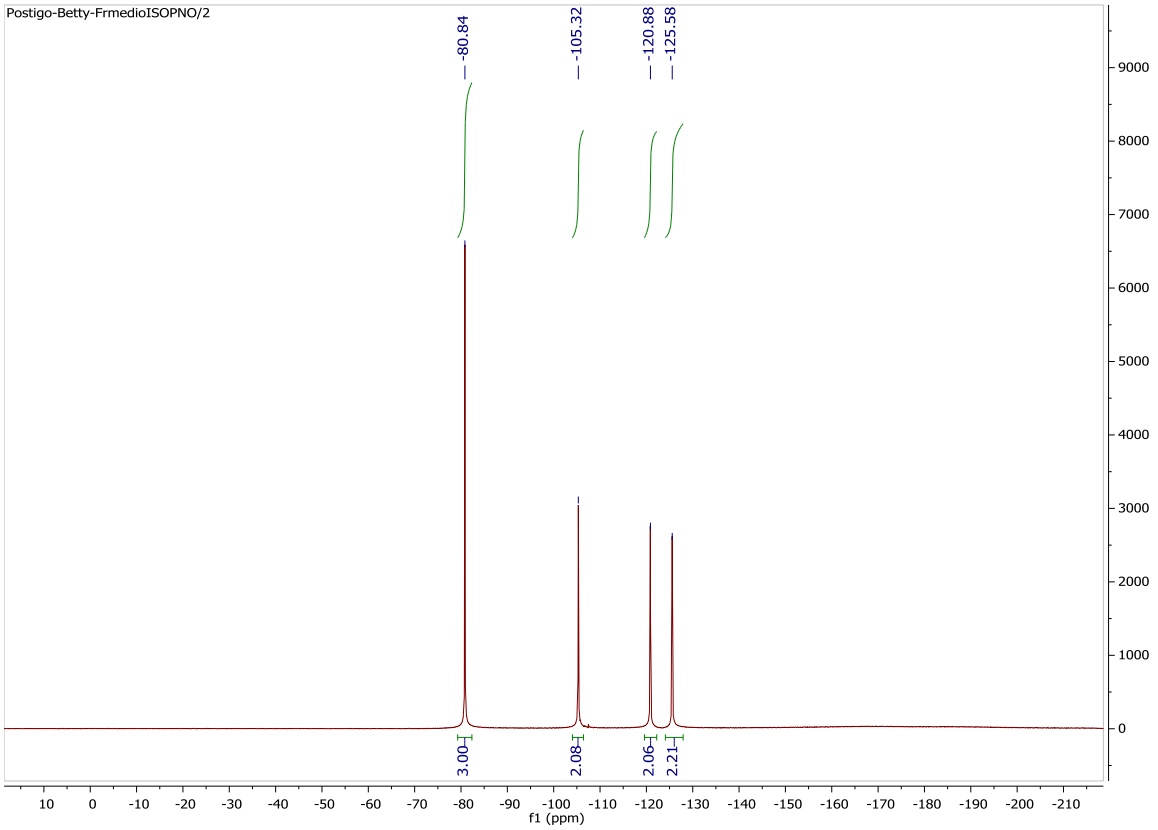
13C NMR spectrum of 10 in CDCl3



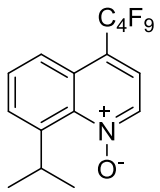


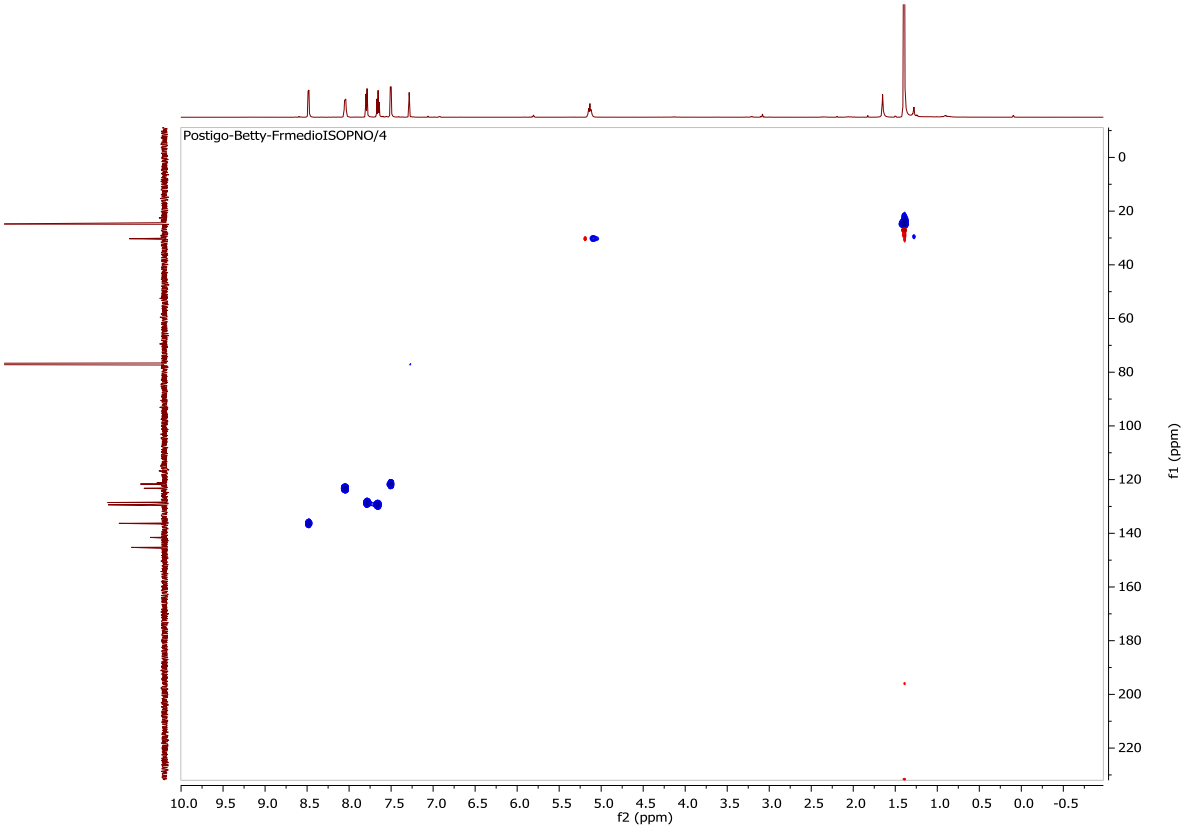
19F NMR spectrum of 10 in CDCl3



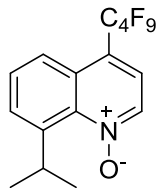


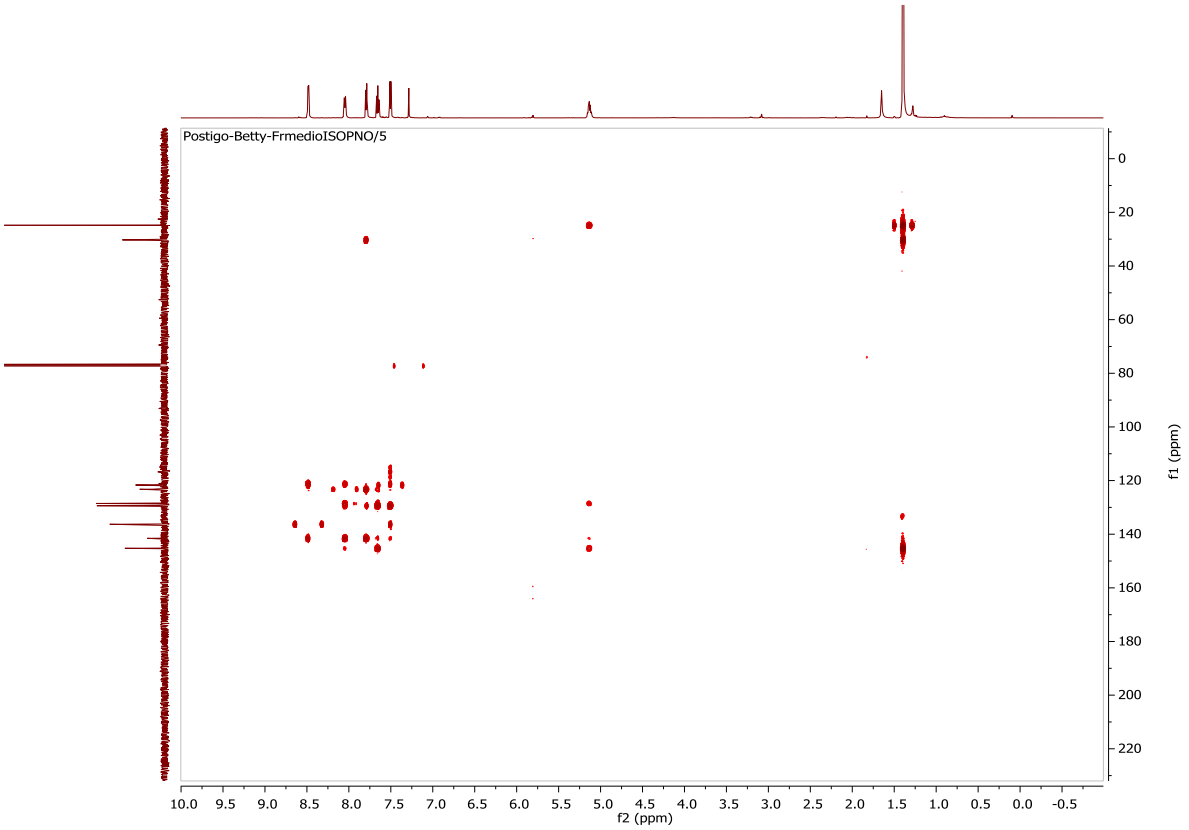
HSQC NMR spectrum of 10 in CDCl3



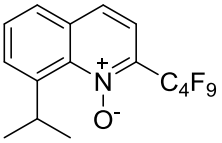


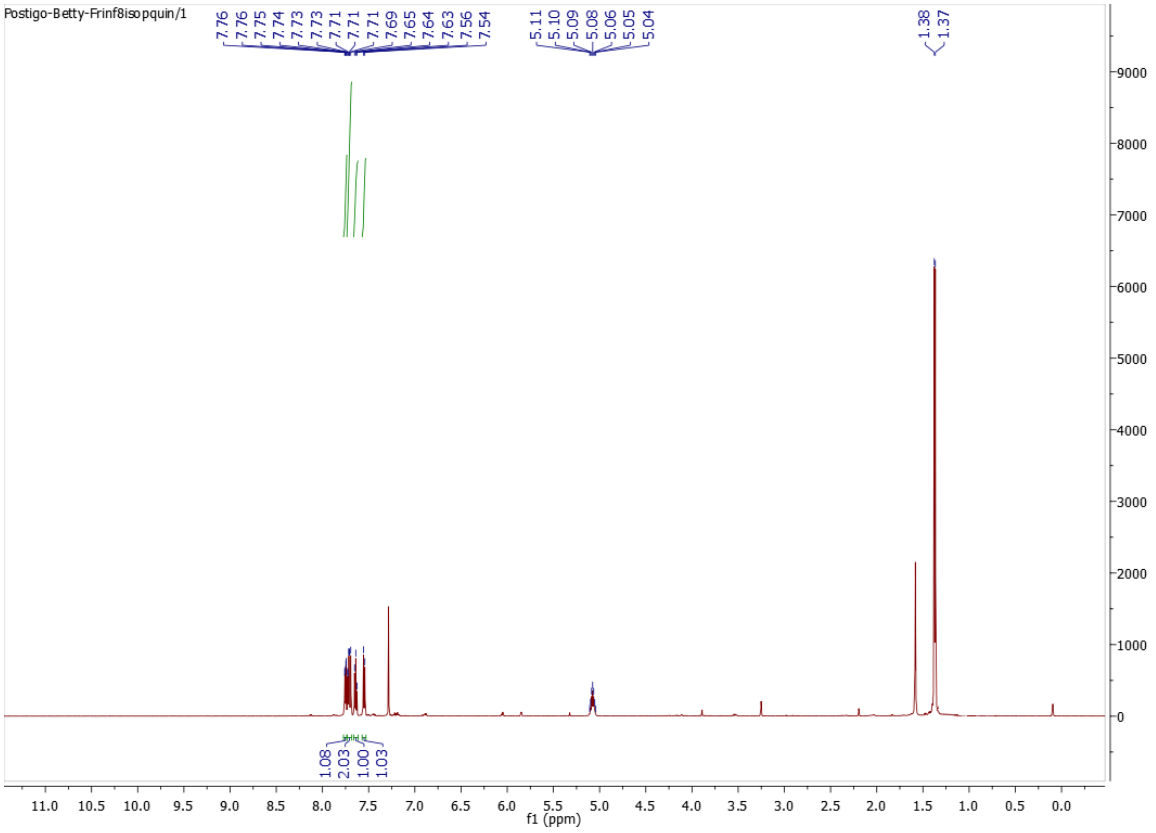
HMBC NMR spectrum of 10 in CDCl3



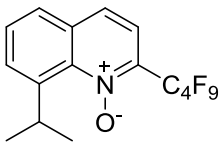


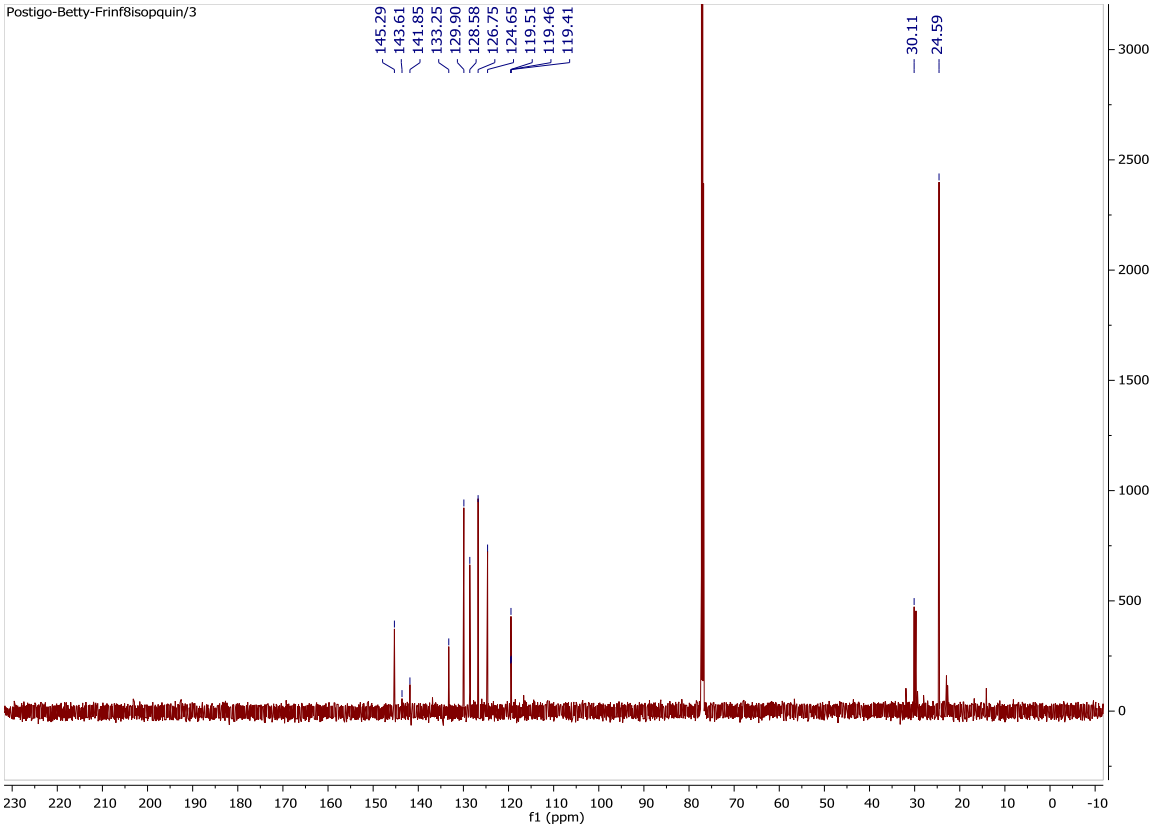
1H NMR spectrum 0f 11 in CDCl3



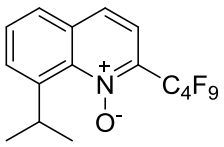


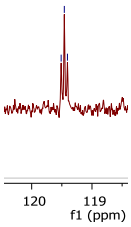
13C NMR spectrum 0f 11 in CDCl3

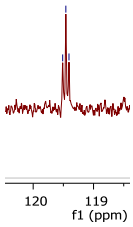




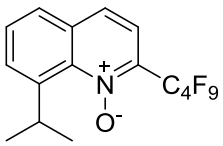
13C NMR spectrum 0f 11 in CDCl3, enlargement

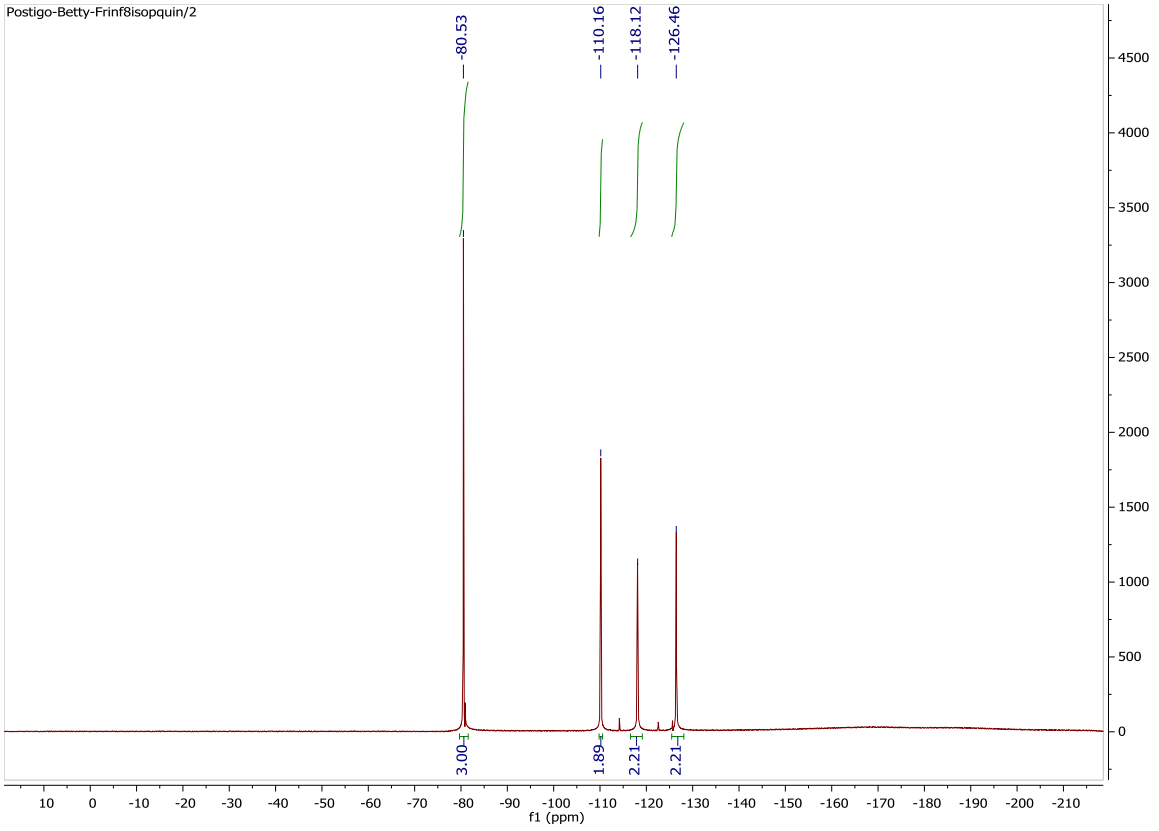




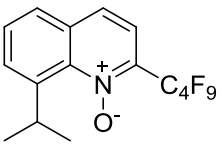


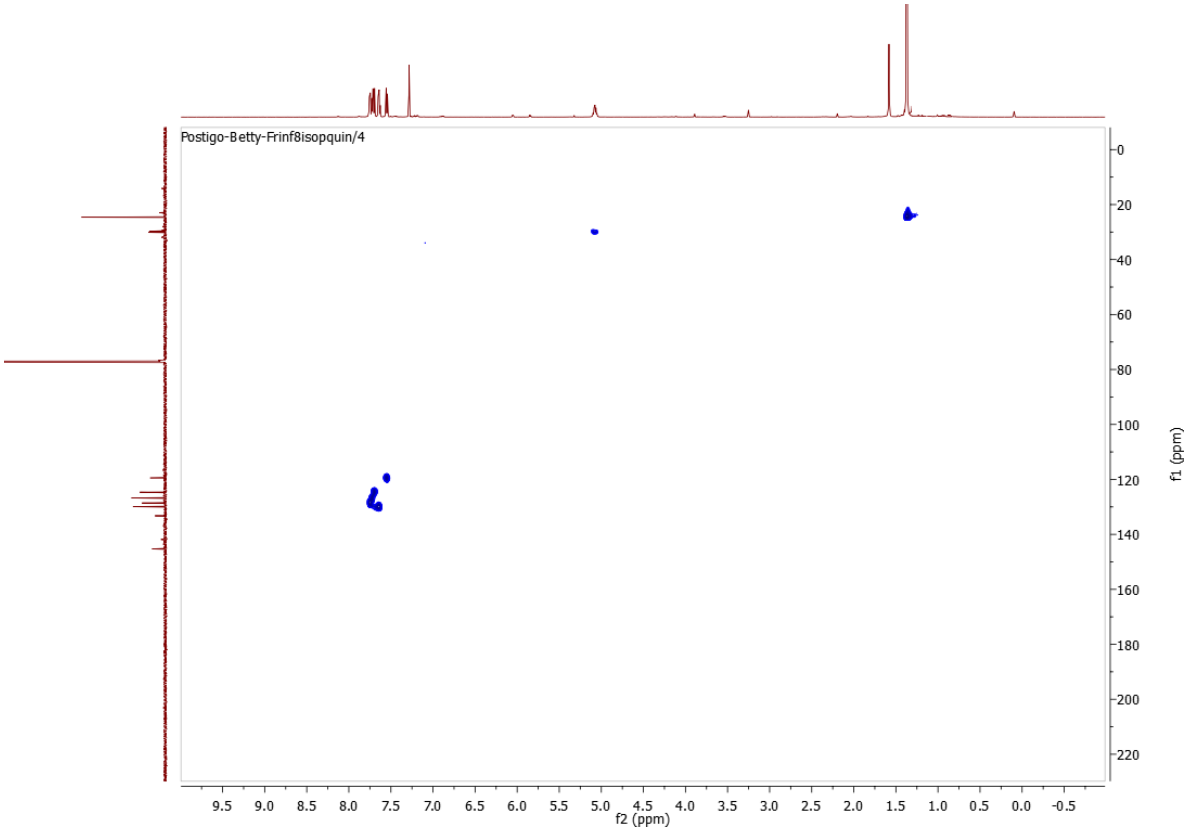
19F NMR spectrum 0f 11 in CDCl3



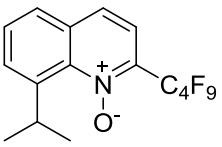


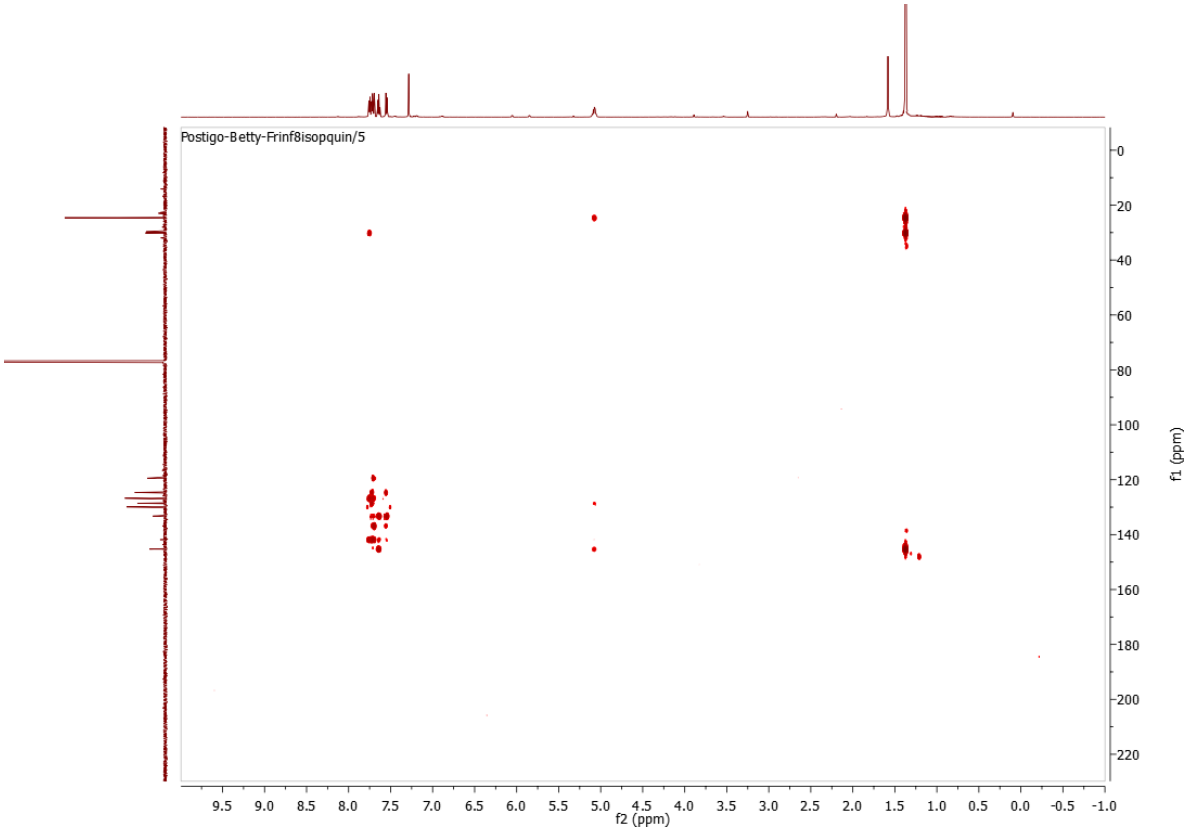
HSQC NMR spectrum 0f 11 in CDCl3



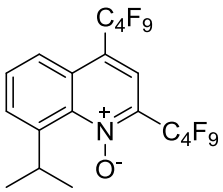


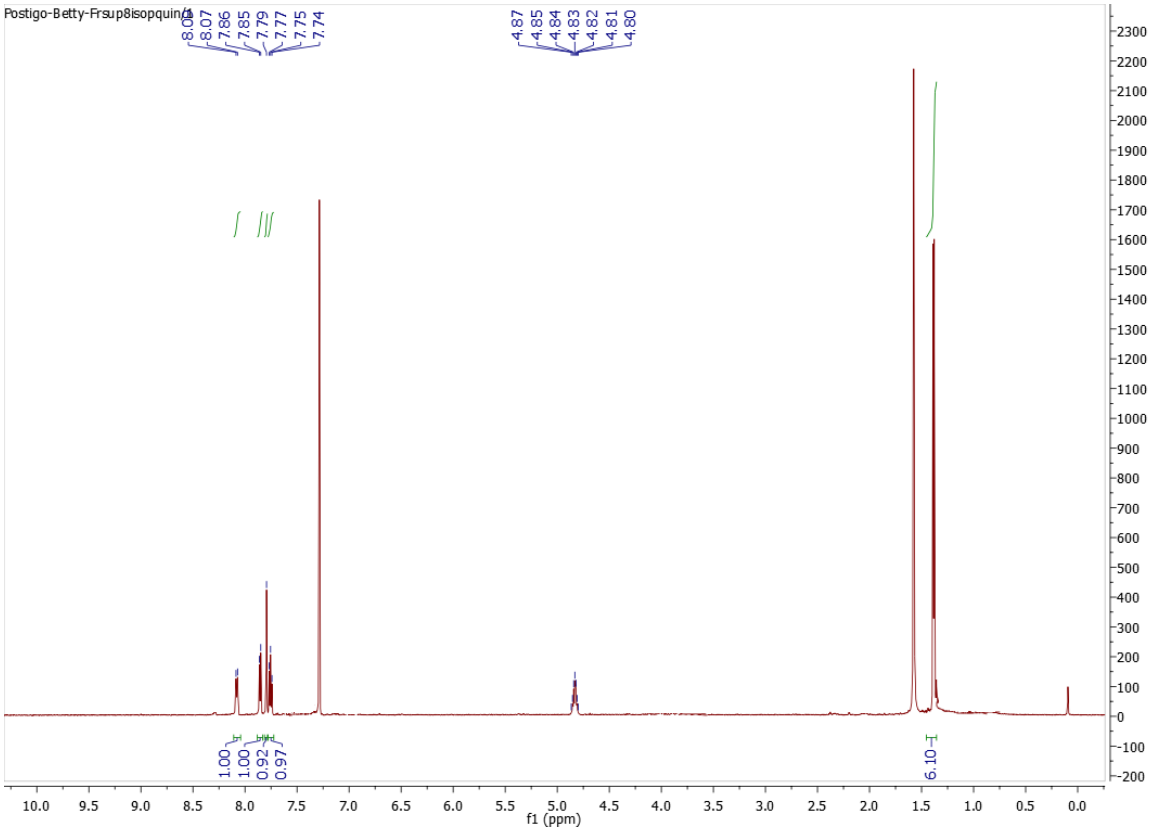
HMBC NMR spectrum 0f 11 in CDCl3



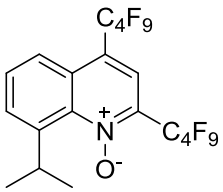


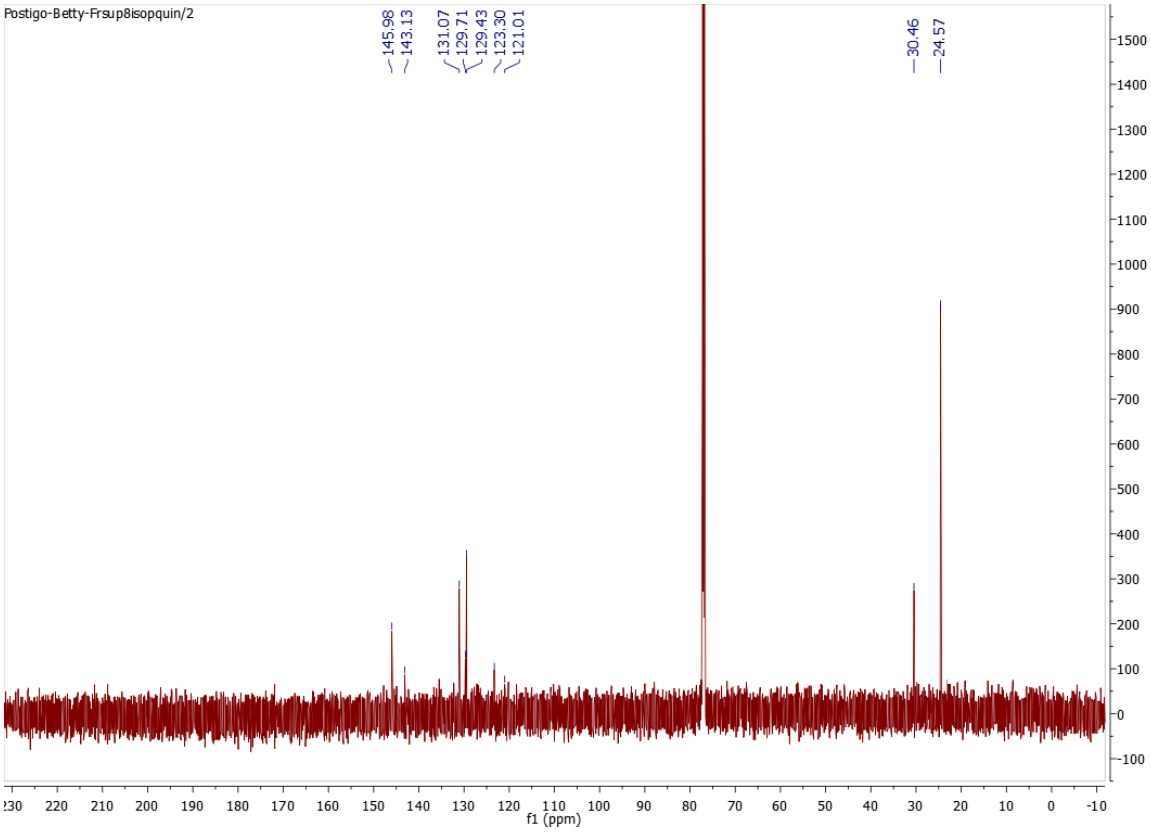
1H NMR spectrum 0f 12 in CDCl3



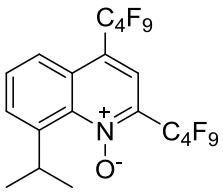


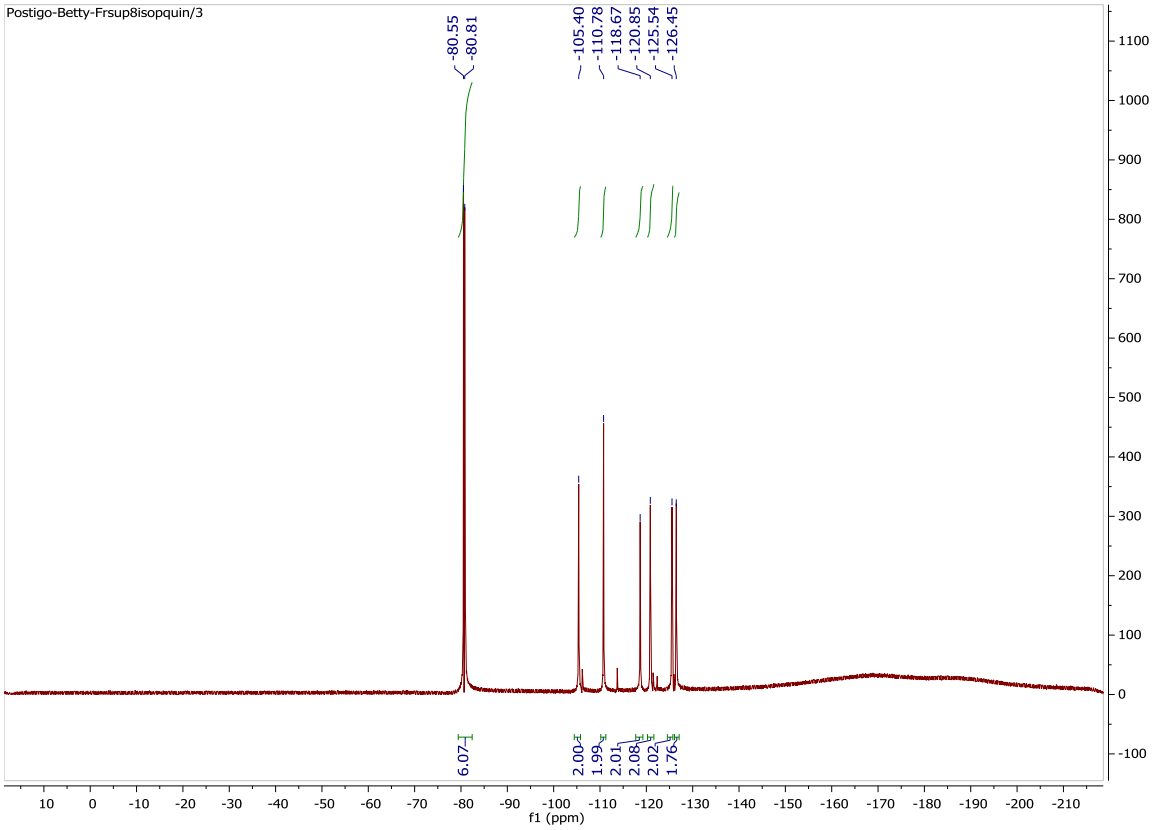
13C NMR spectrum 0f 12 in CDCl3



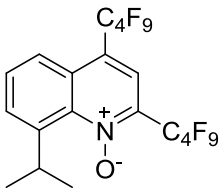


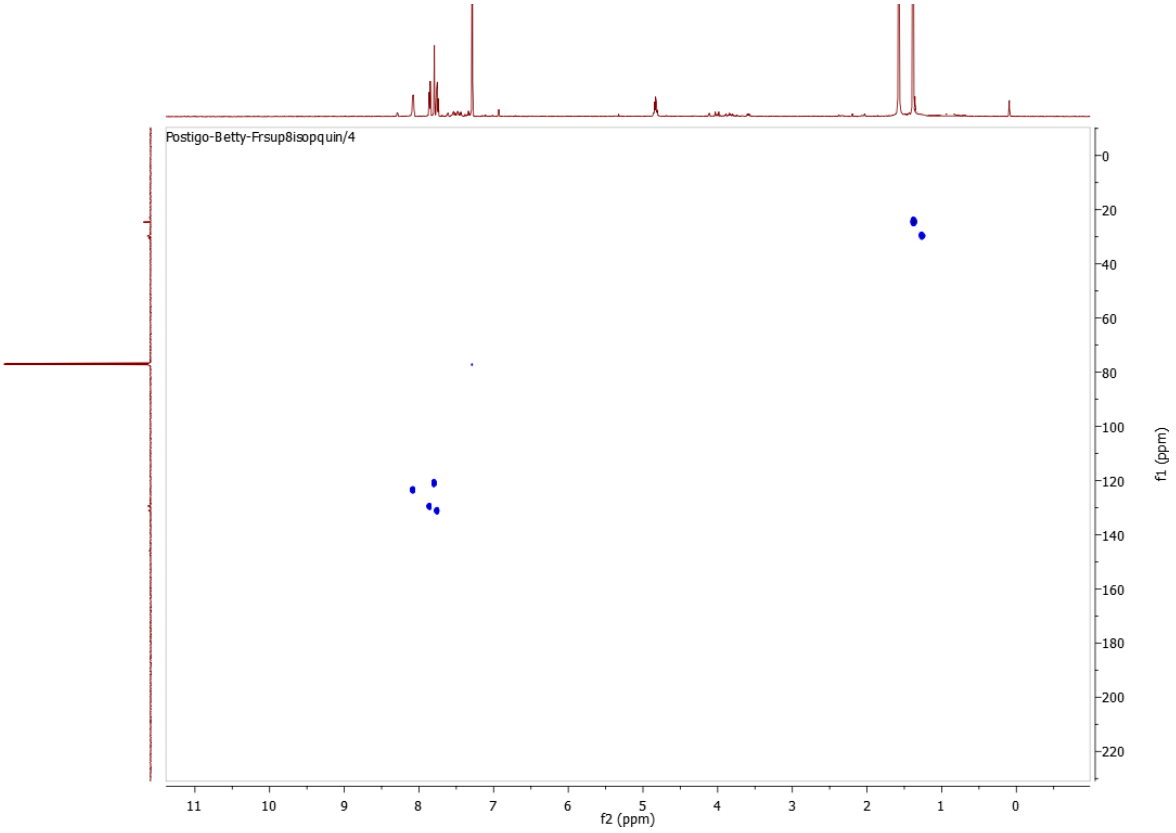
19F NMR spectrum 0f 12 in CDCl3



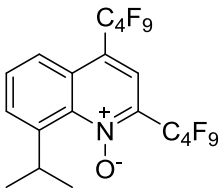


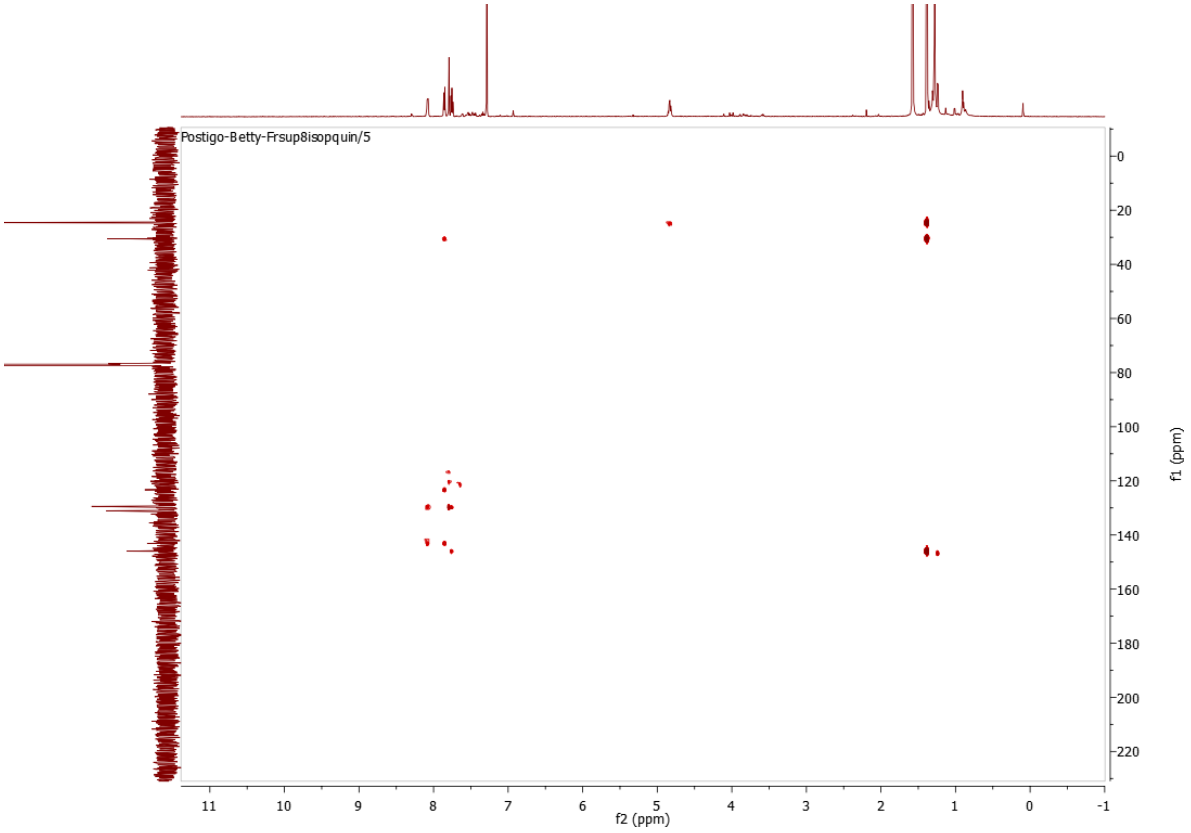
HSQC NMR spectrum 0f 12 in CDCl3



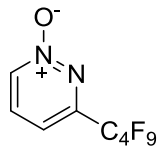


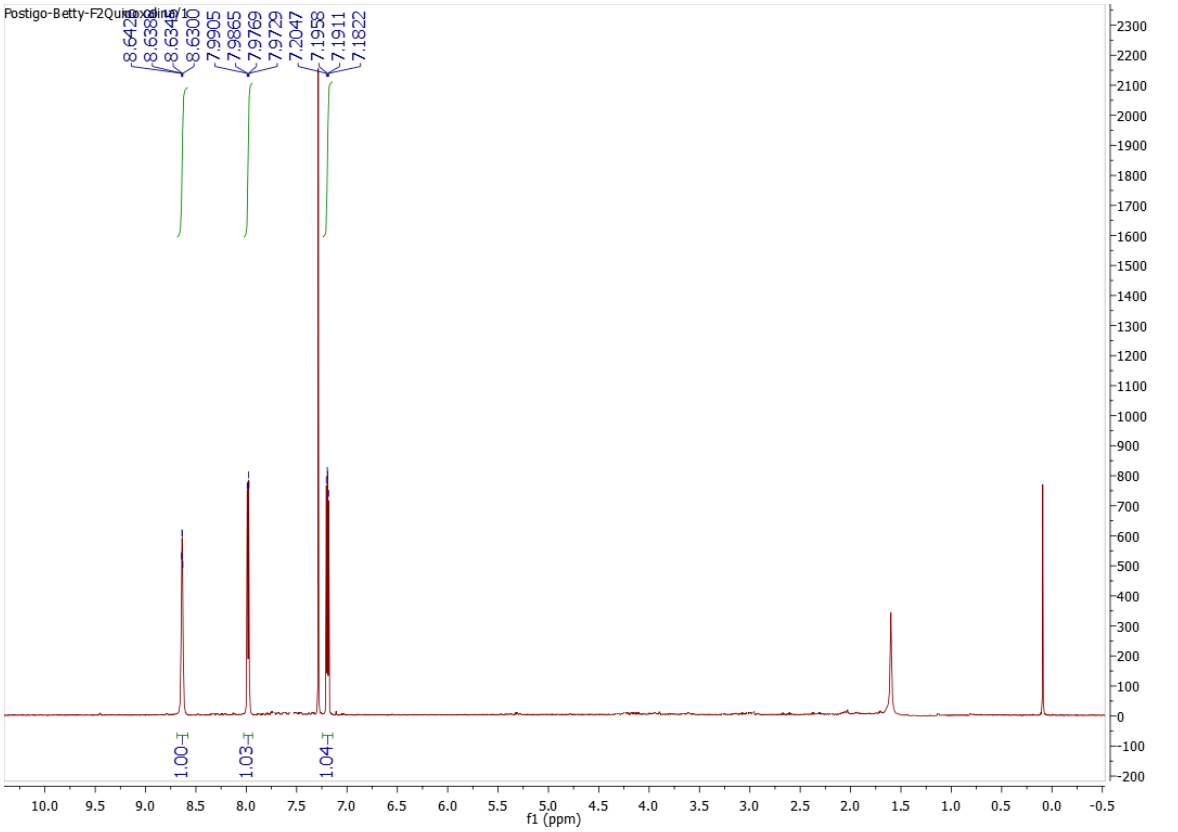
HMBC NMR spectrum 0f 12 in CDCl3



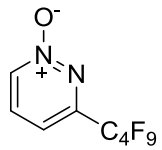


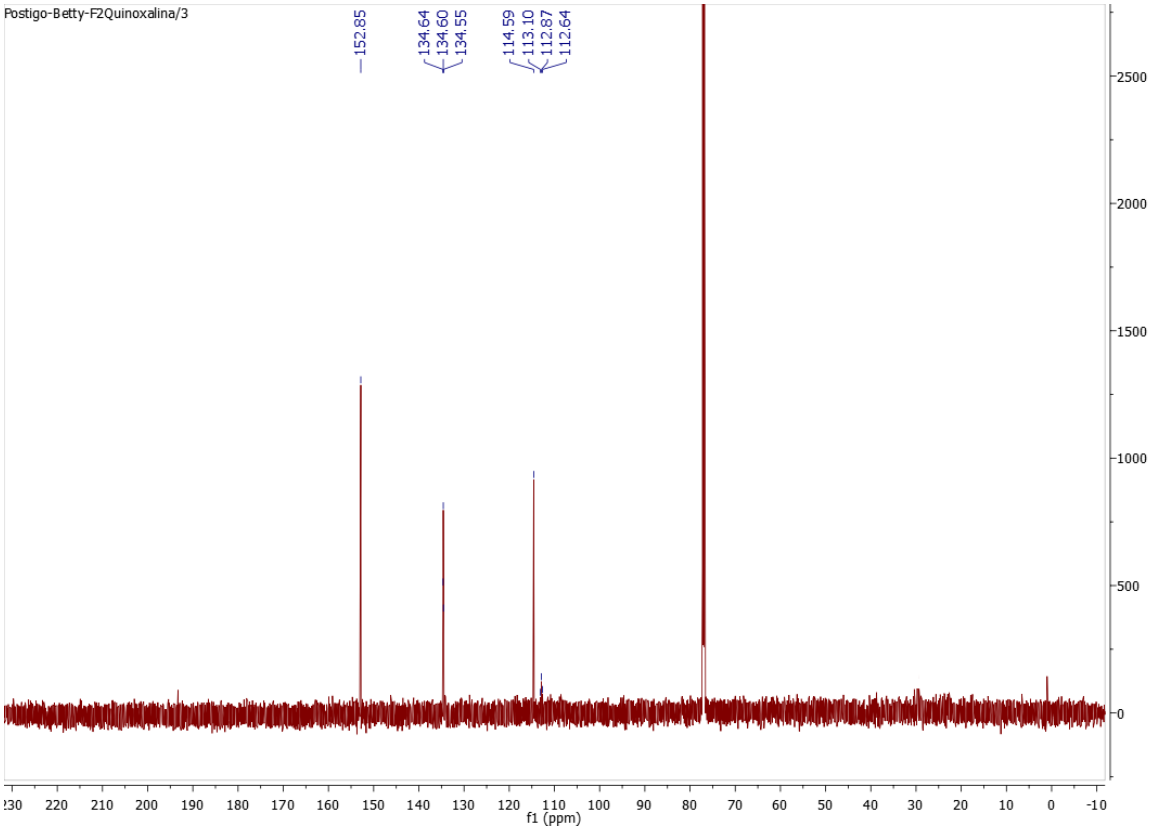
1H NMR spectrum
0f 14 in CDCl3



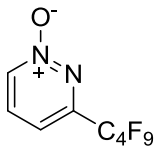


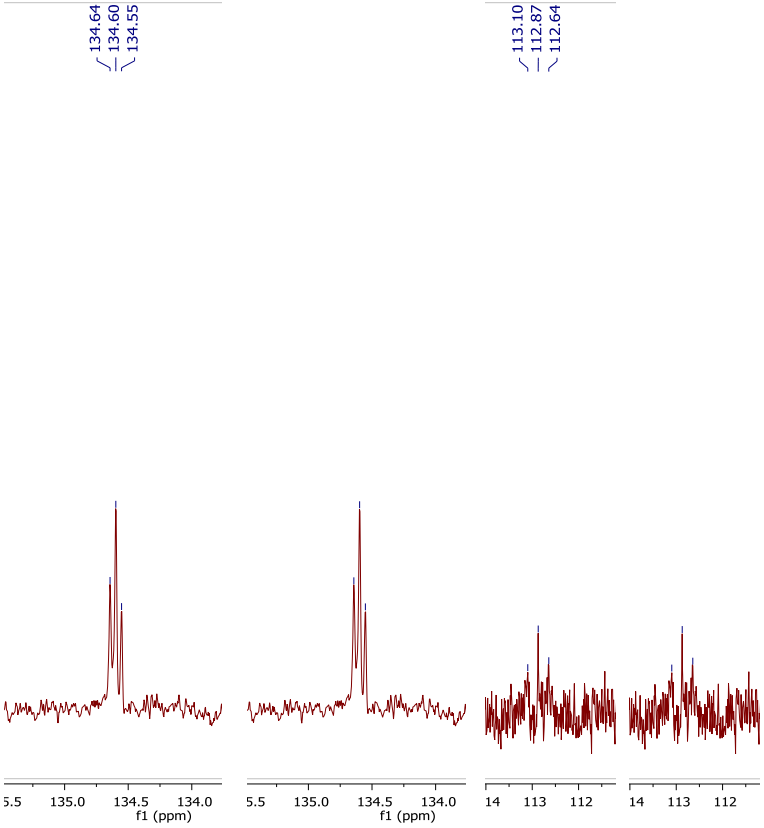
13C NMR spectrum 0f 14 in CDCl3



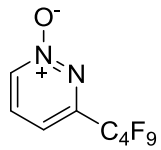


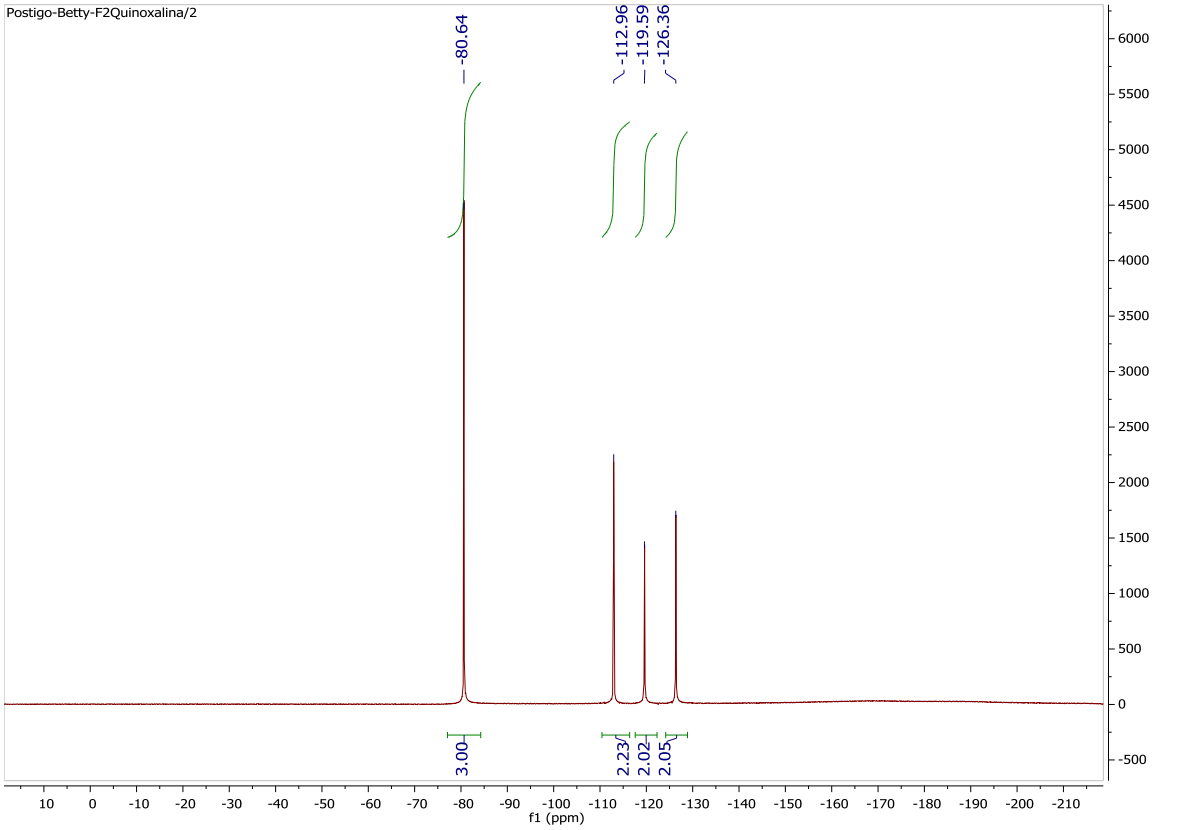
13C NMR spectrum 0f 14 in CDCl3, enlargement



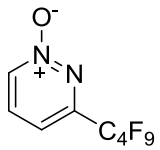


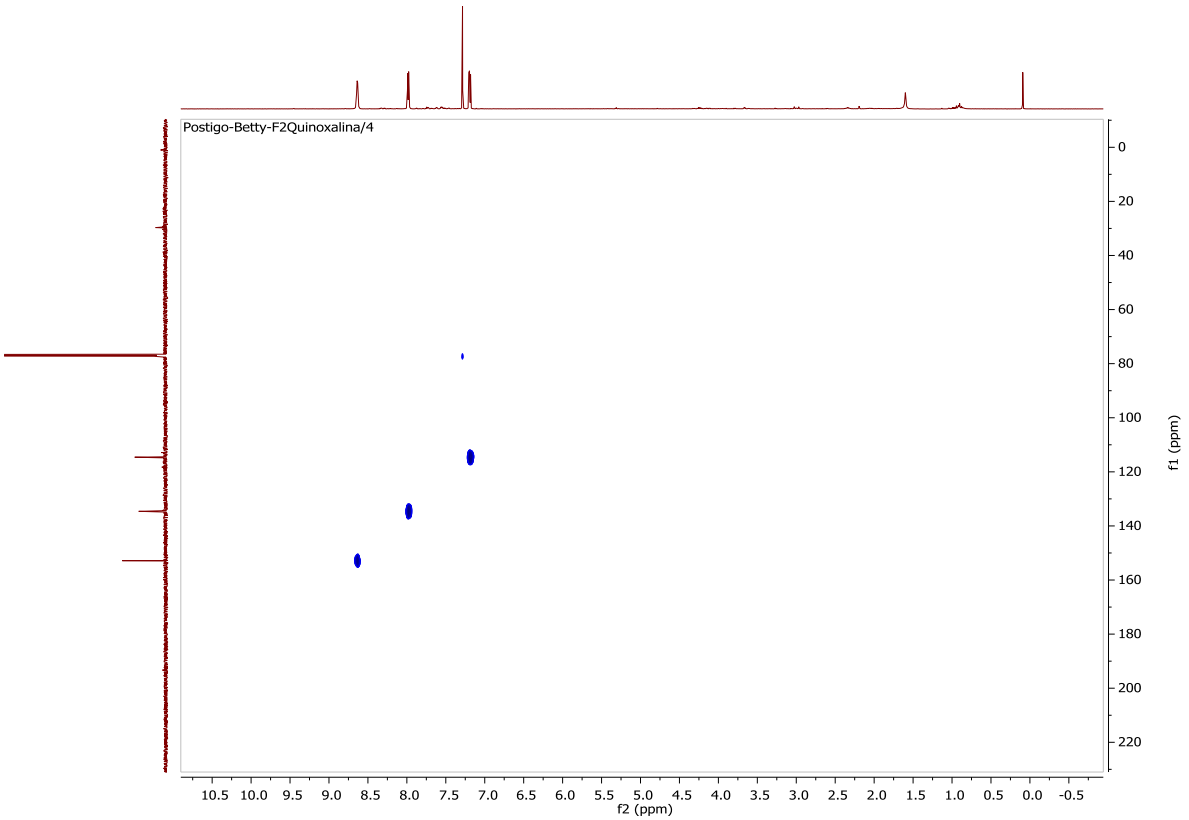
19F NMR spectrum 0f 14 in CDCl3



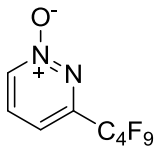


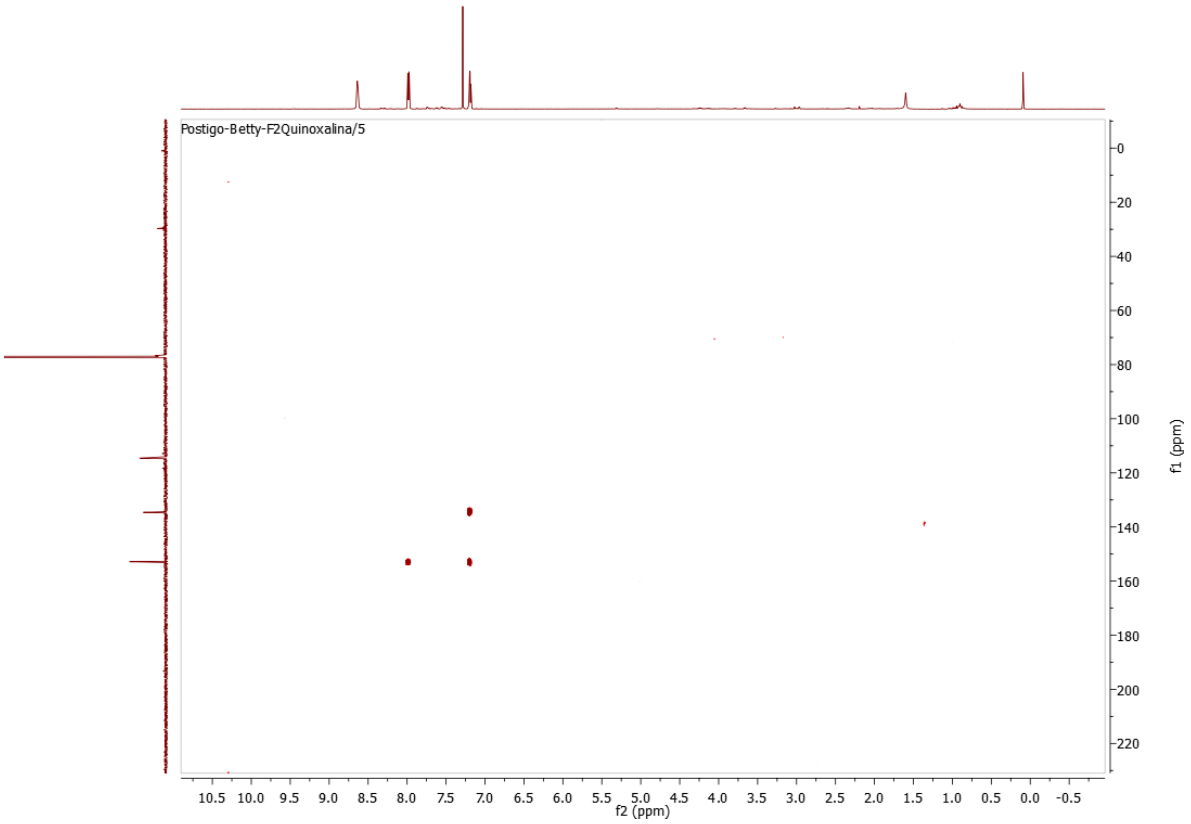
HSQC NMR spectrum 0f 14 in CDCl3



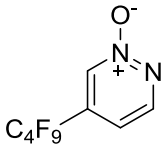


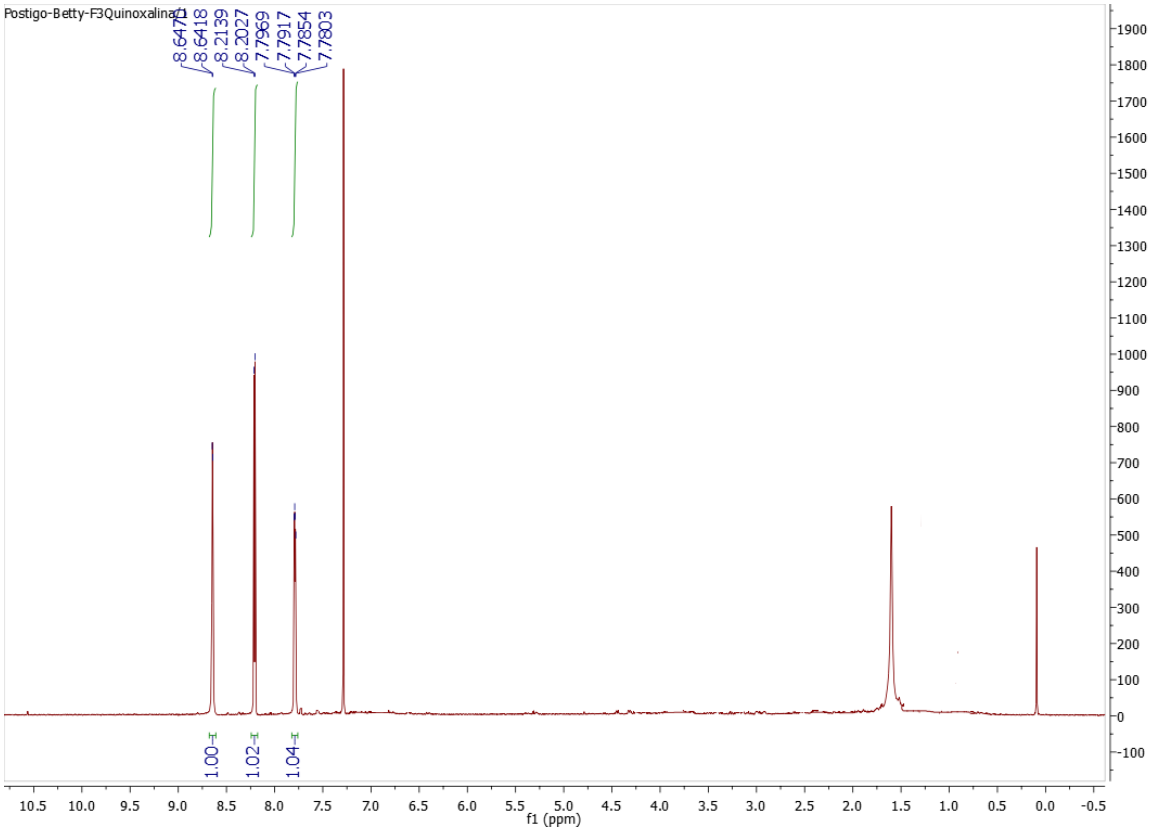
HMBC NMR spectrum 0f 14 in CDCl3



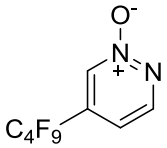


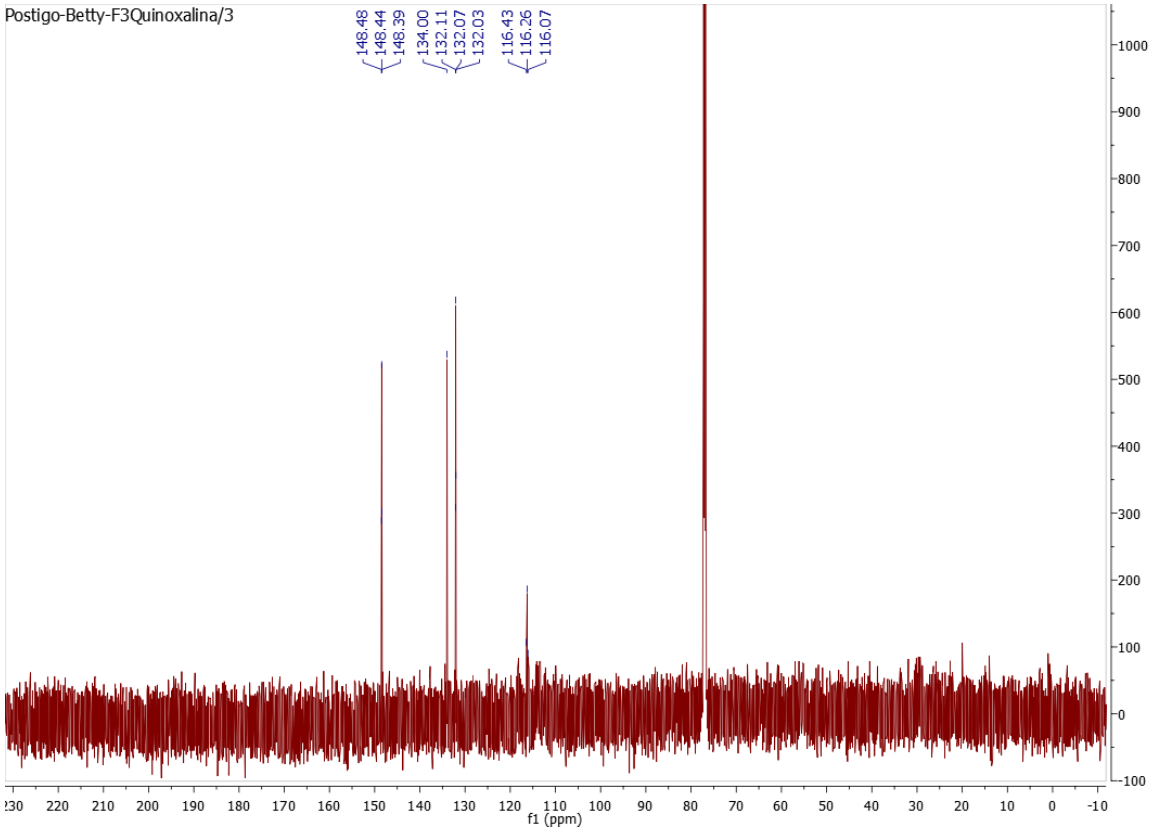
1H NMR spectrum
0f 15 in CDCl3



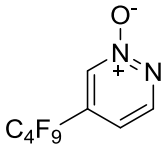


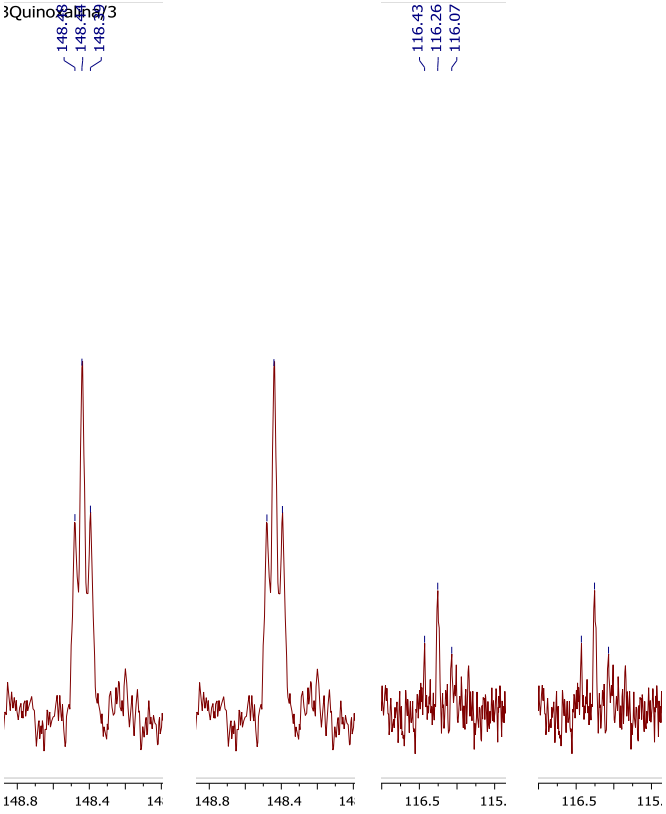
13C NMR spectrum 0f 15 in CDCl3



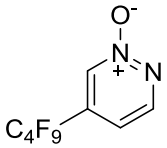


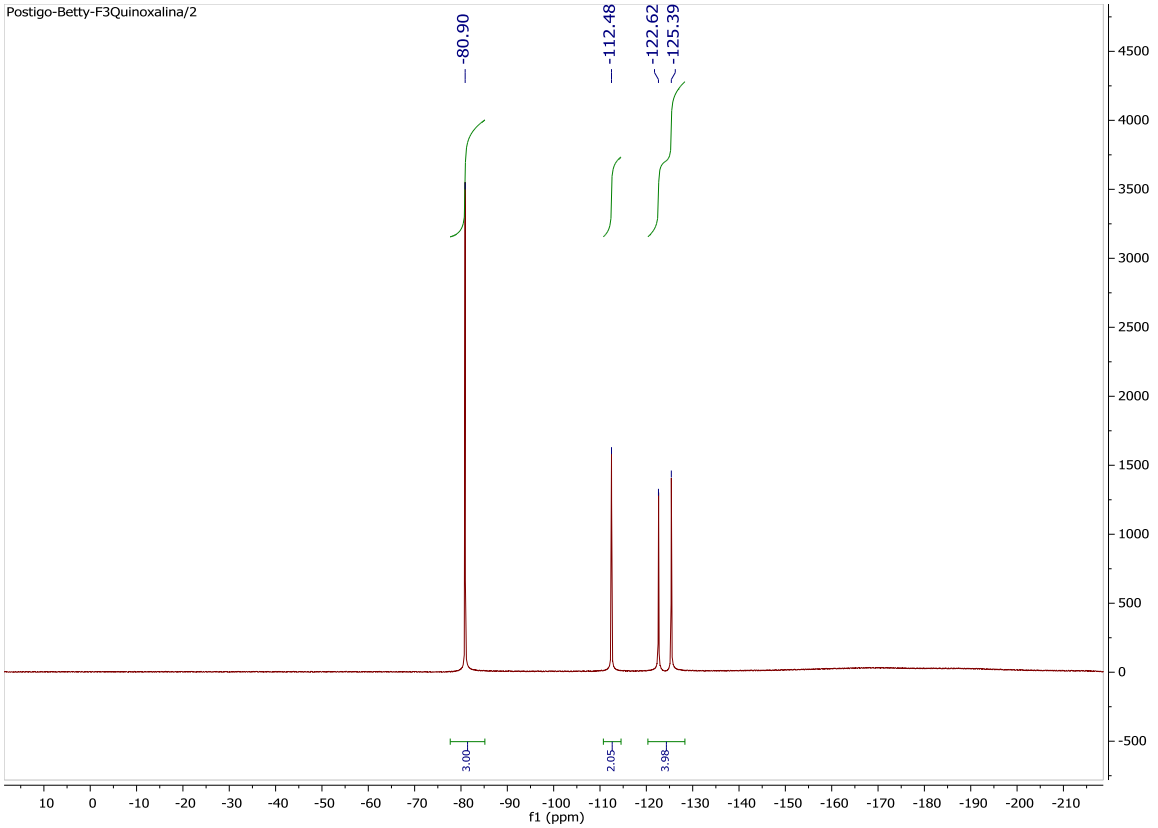
13C NMR spectrum 0f 15 in CDCl3, enlargement



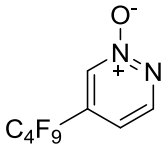


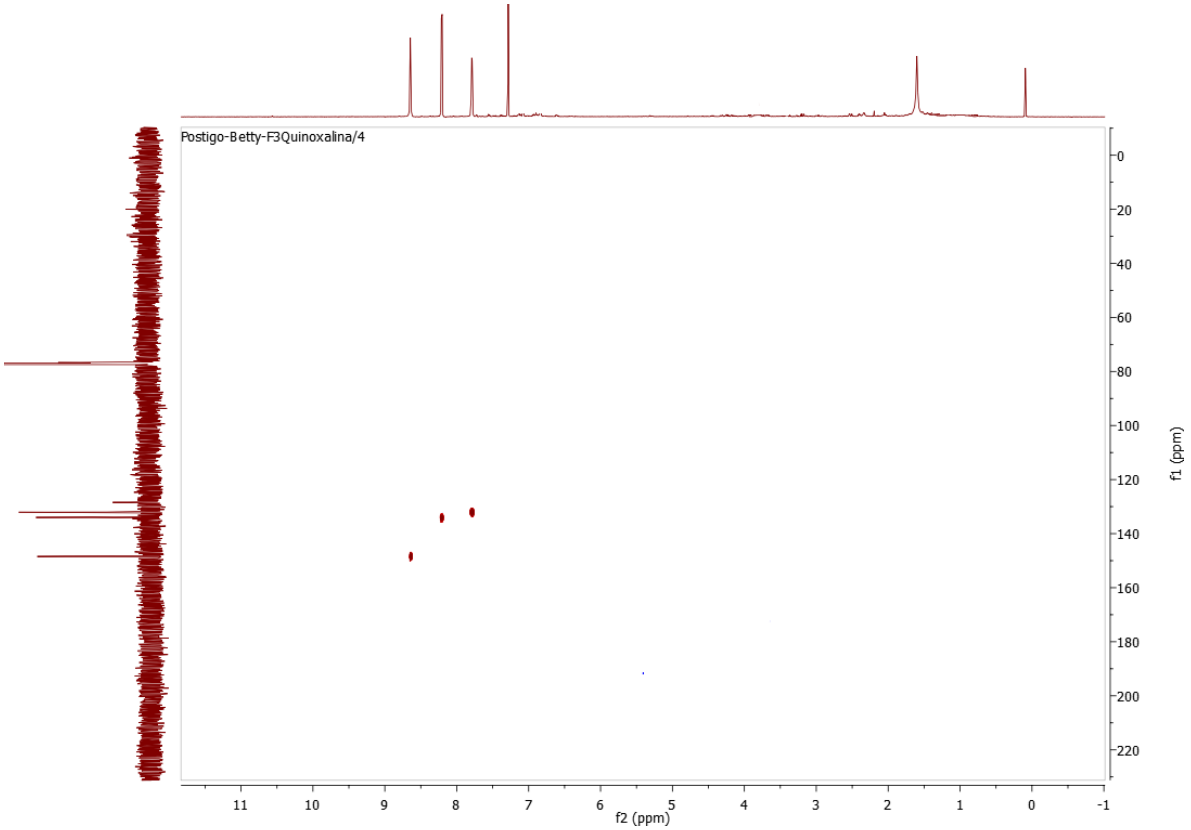
19F NMR spectrum 0f 15 in CDCl3



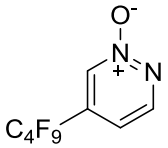


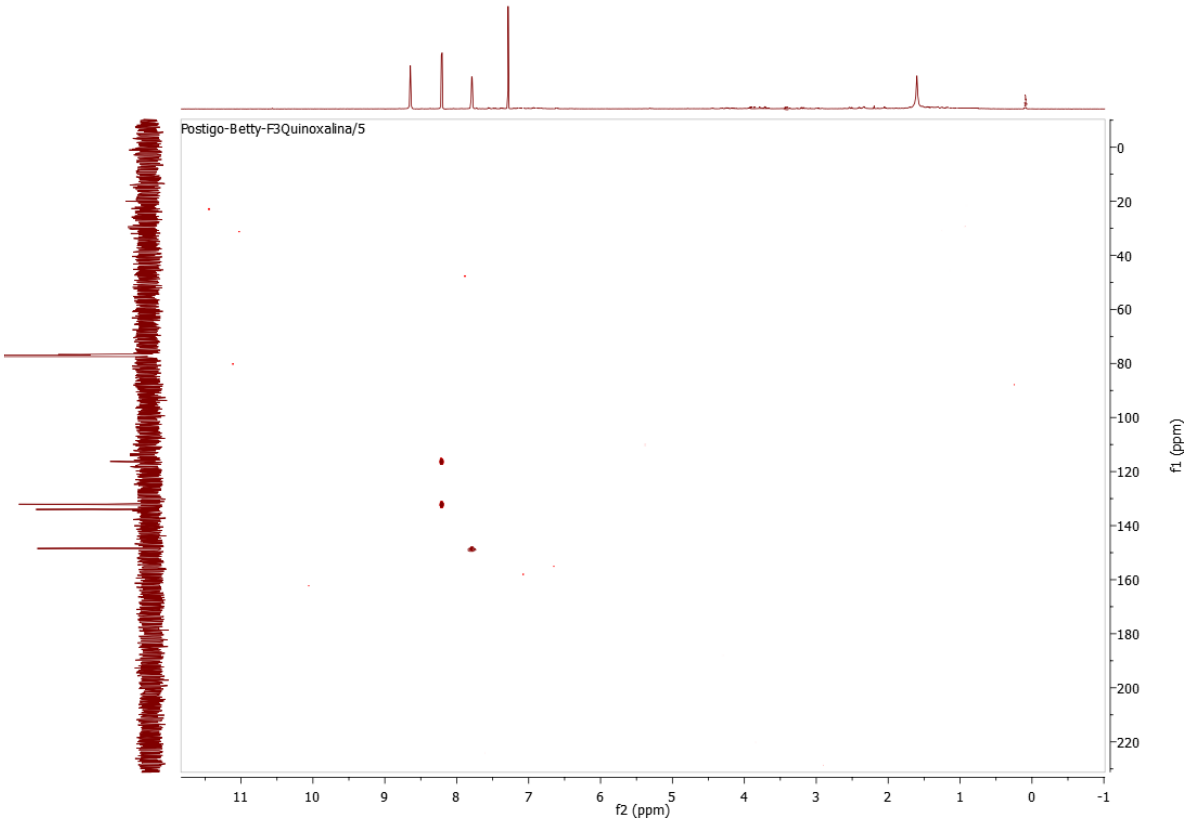
HSQC NMR spectrum 0f 15 in CDCl3



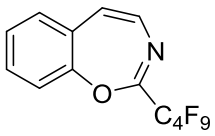


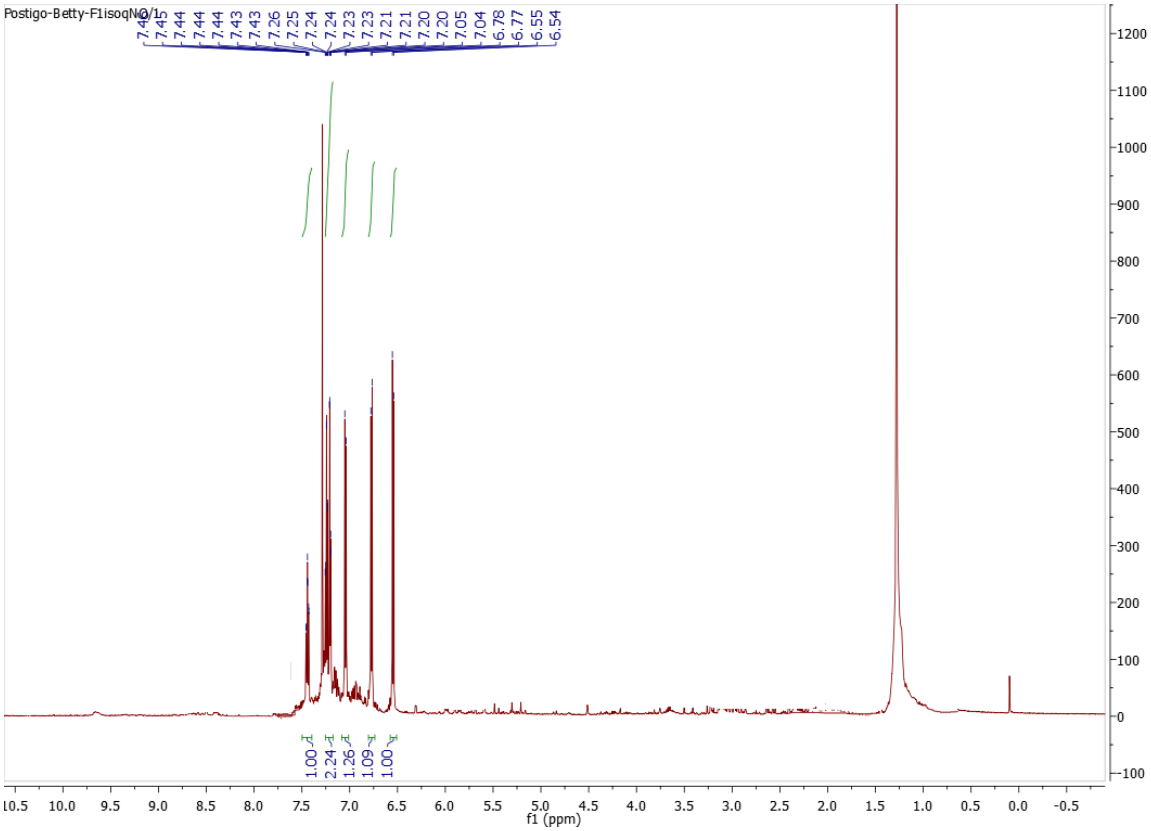
HMBC NMR spectrum 0f 15 in CDCl3



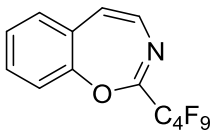


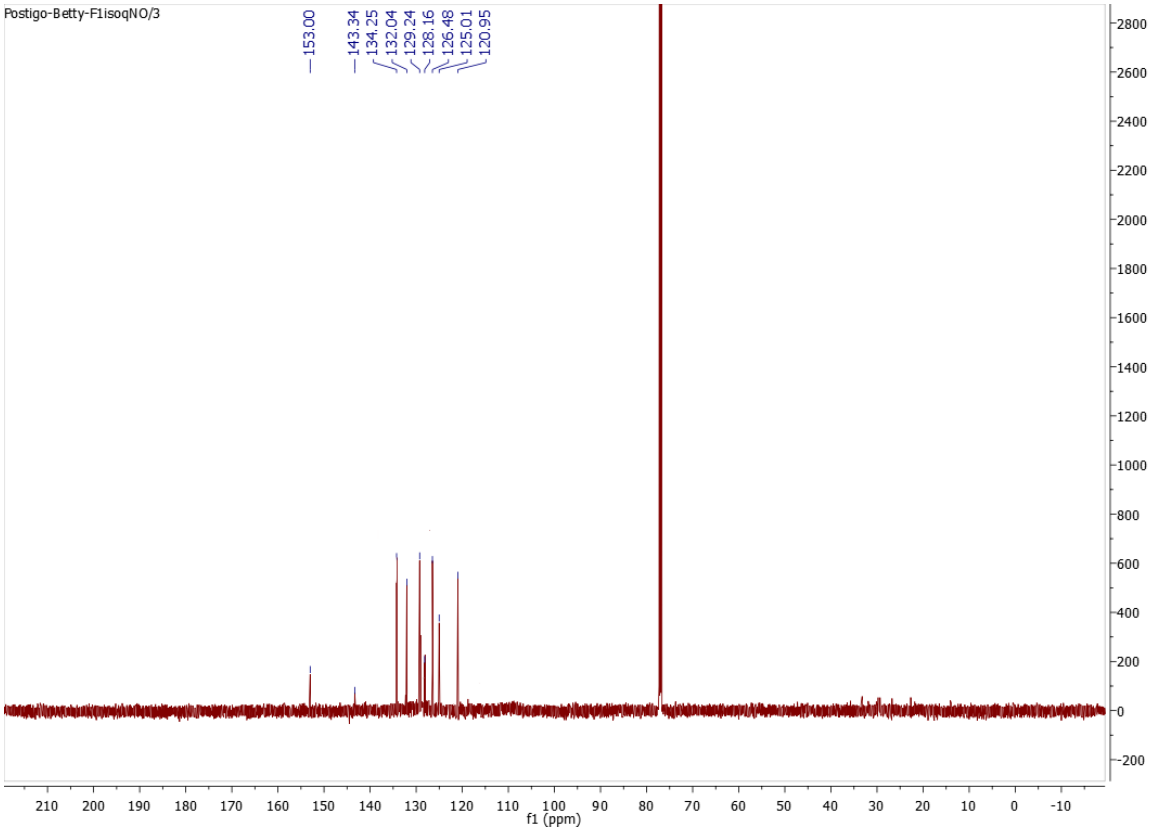
1H NMR spectrum
0f 18 in CDCl3



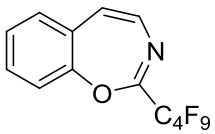


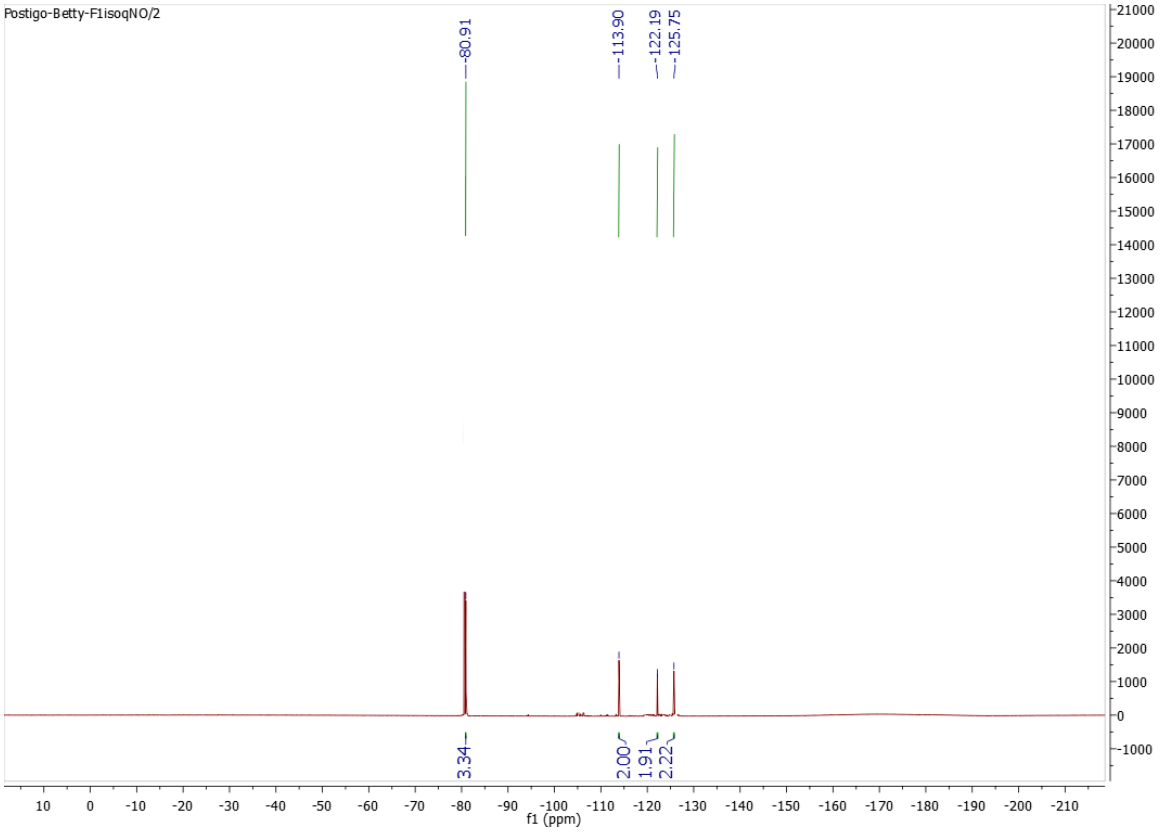
13C NMR spectrum 0f 18 in CDCl3



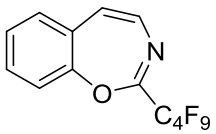


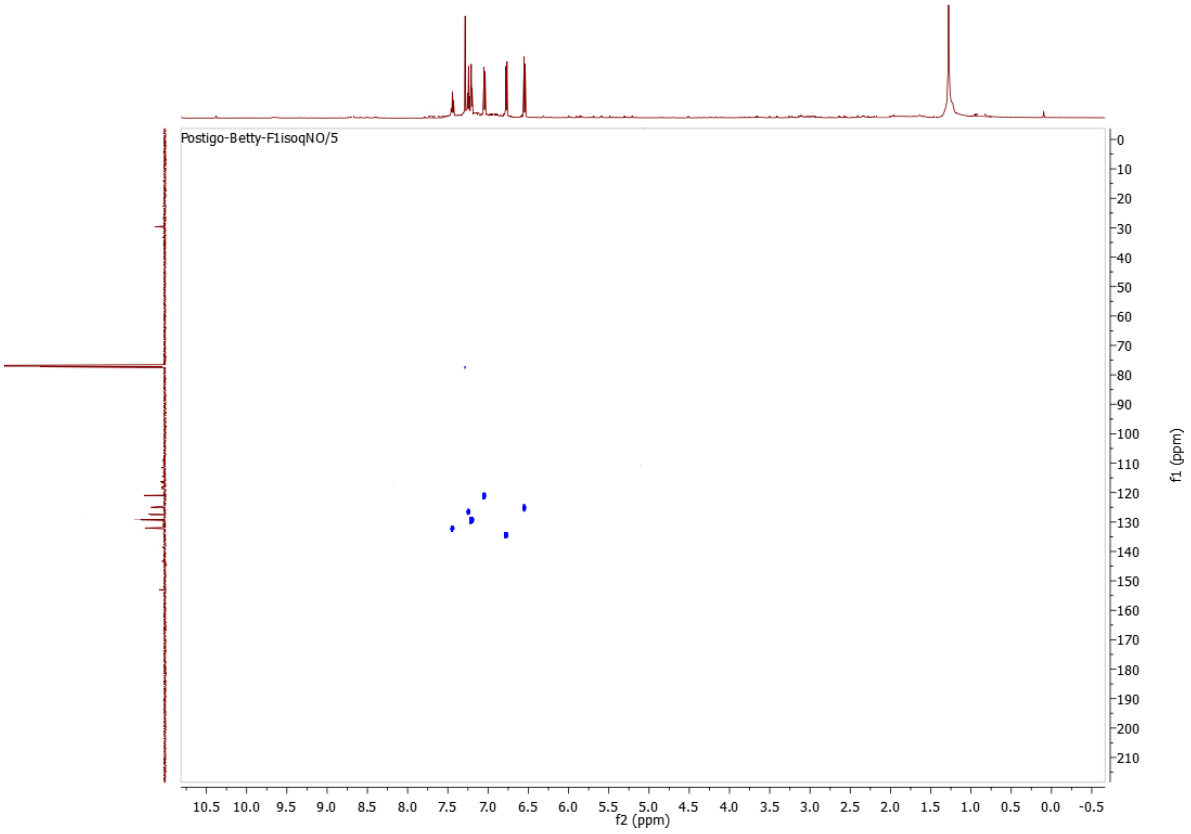
19F NMR spectrum 0f 18 in CDCl3



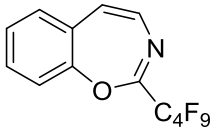


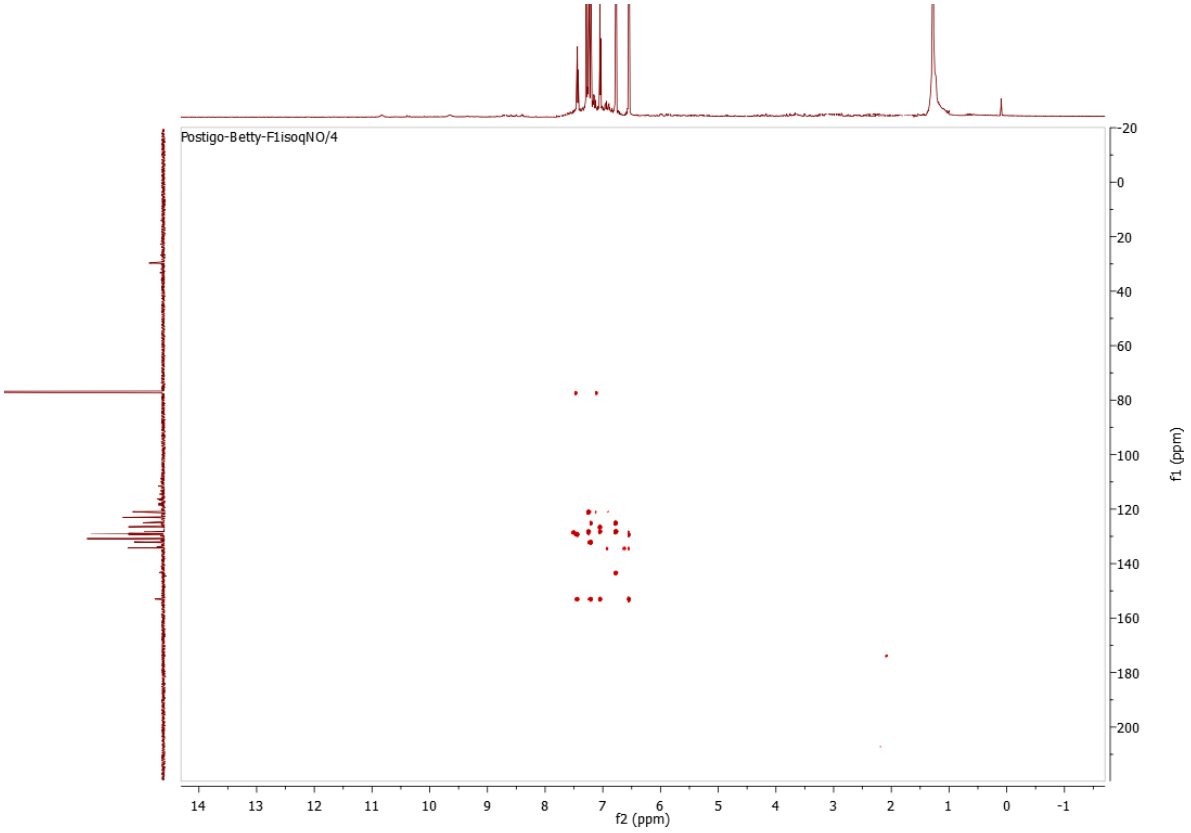
HSQC NMR spectrum 0f 18 in CDCl3



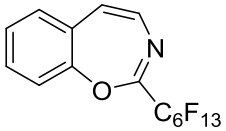


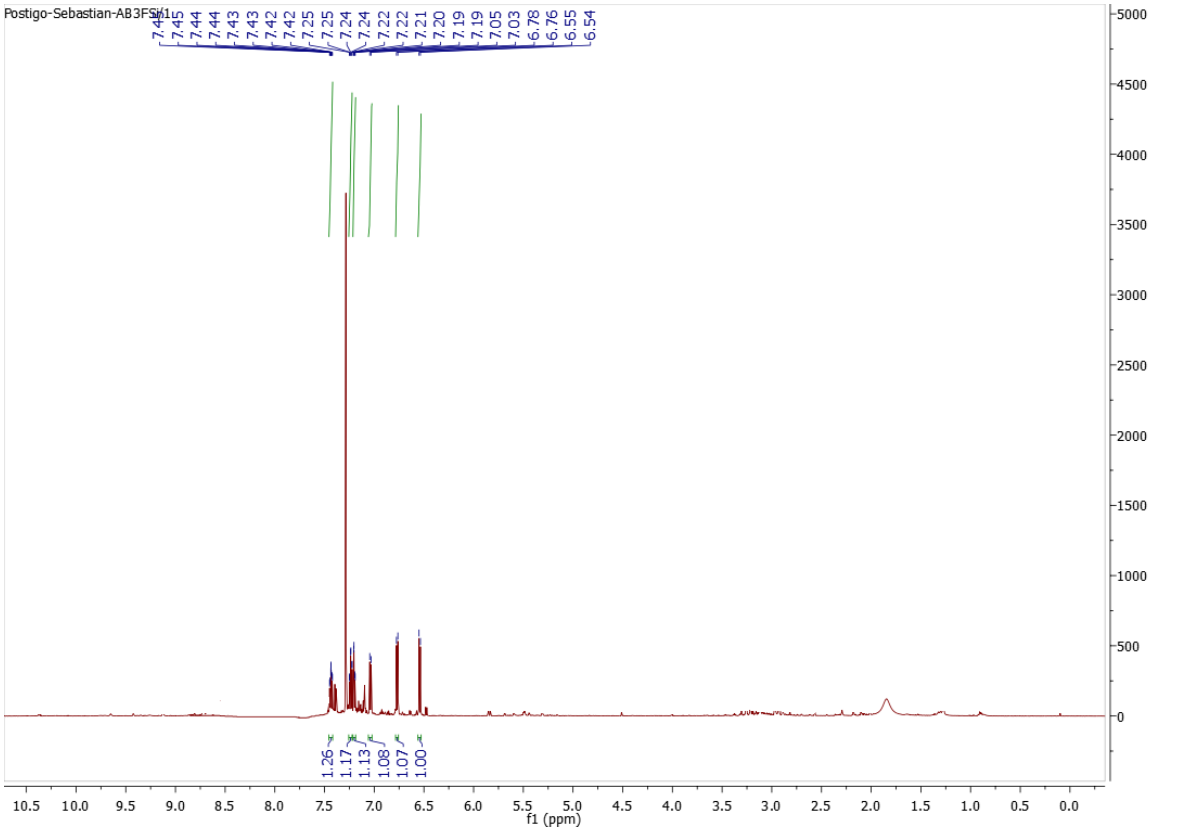
HMBC NMR spectrum 0f 18 in CDCl3



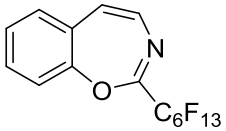


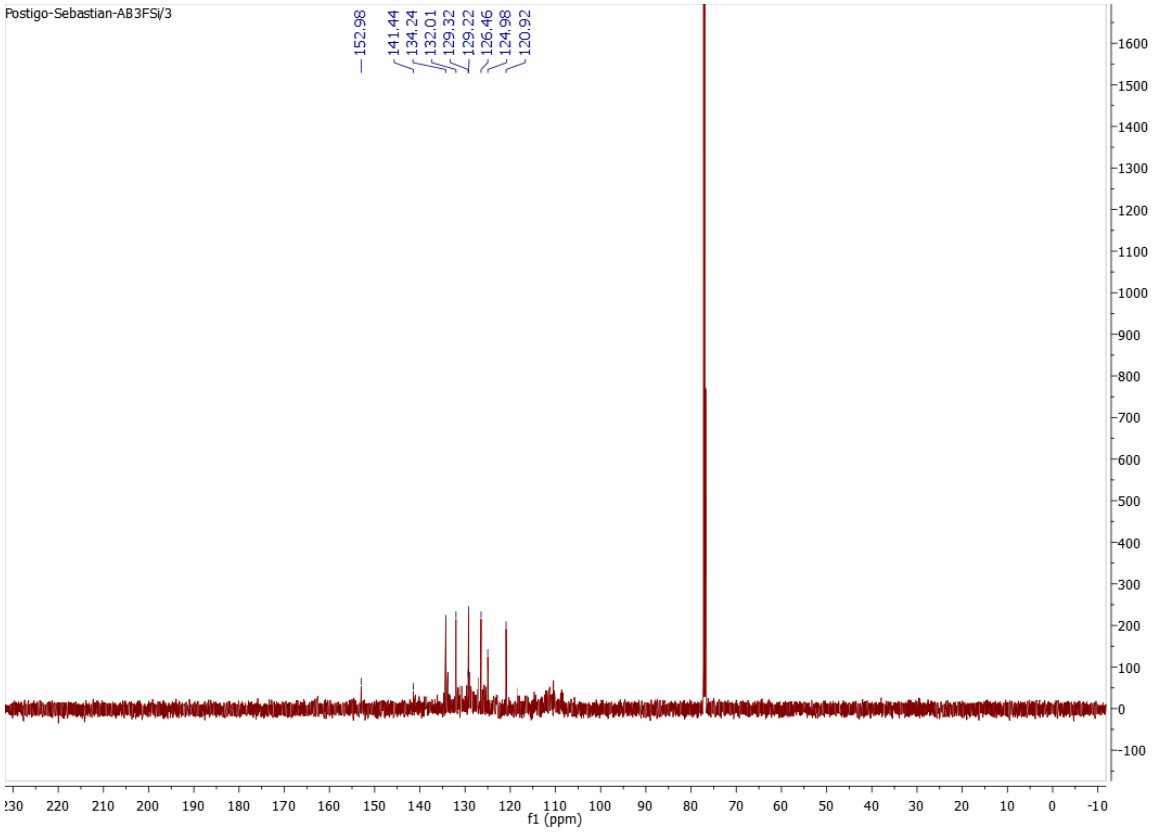
1H NMR spectrum 0f 19 in CDCl3



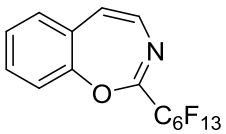


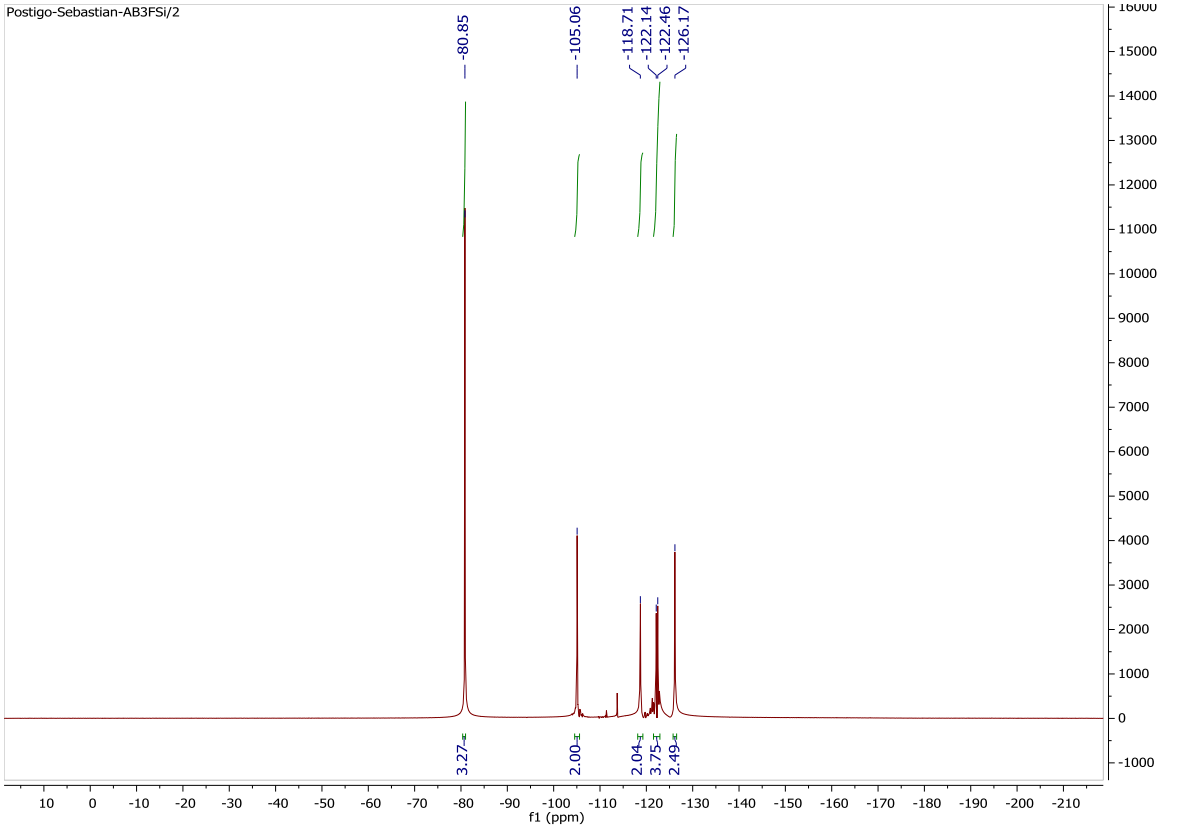
13C NMR spectrum 0f 19 in CDCl3



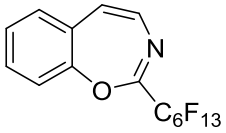


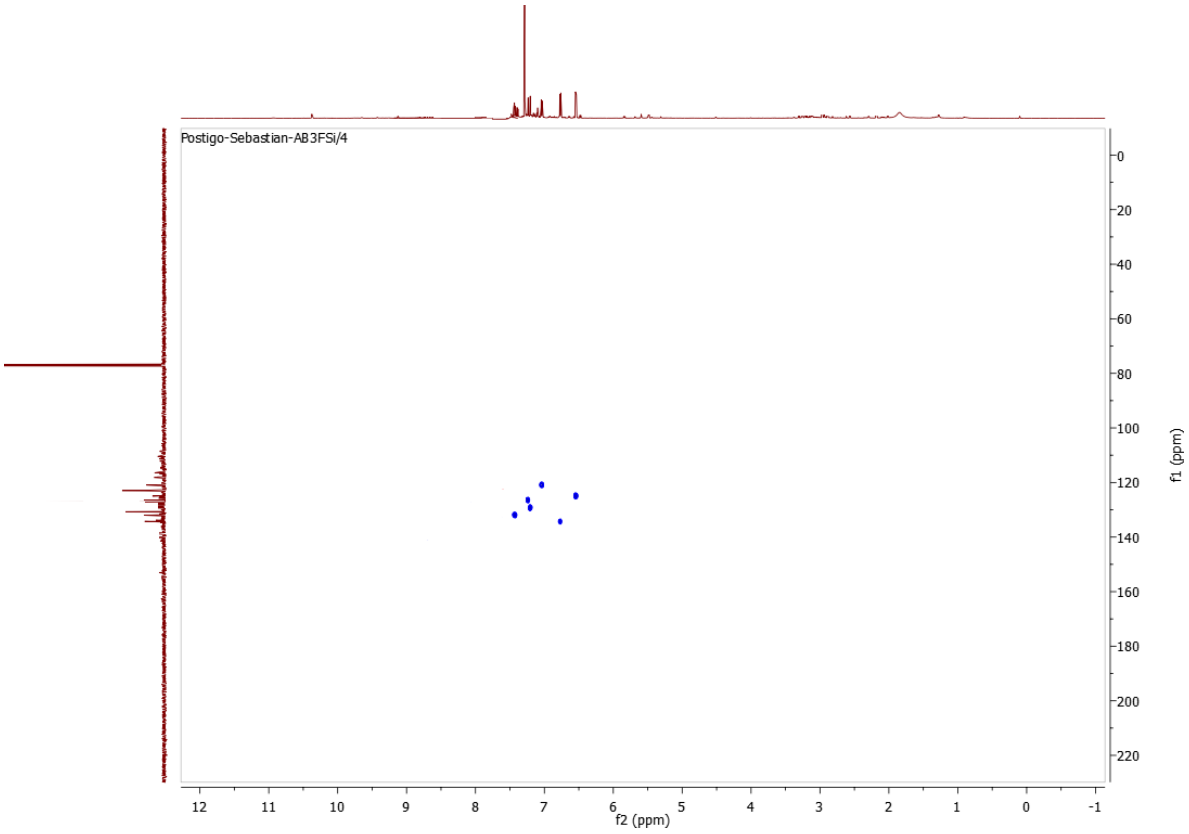
19F NMR spectrum 0f 19 in CDCl3



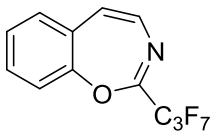


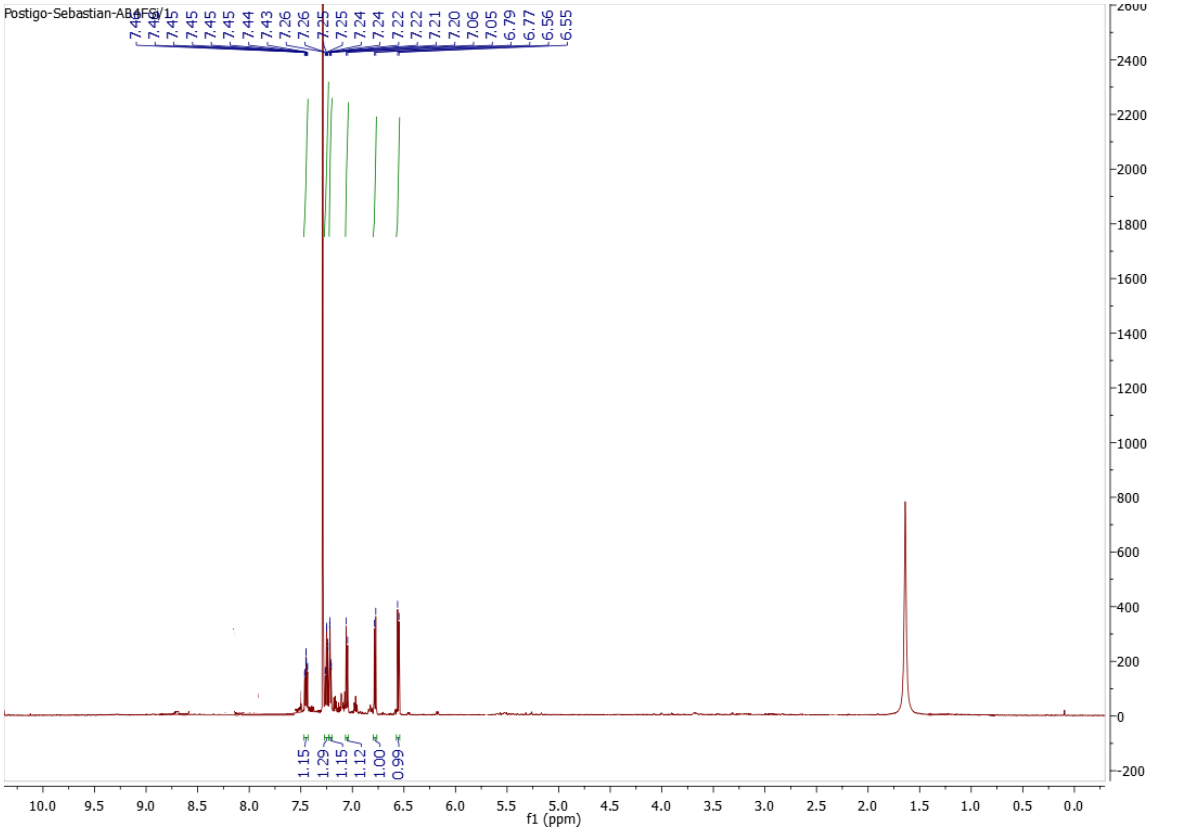
HSQC NMR spectrum 0f 19 in CDCl3



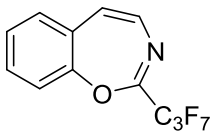


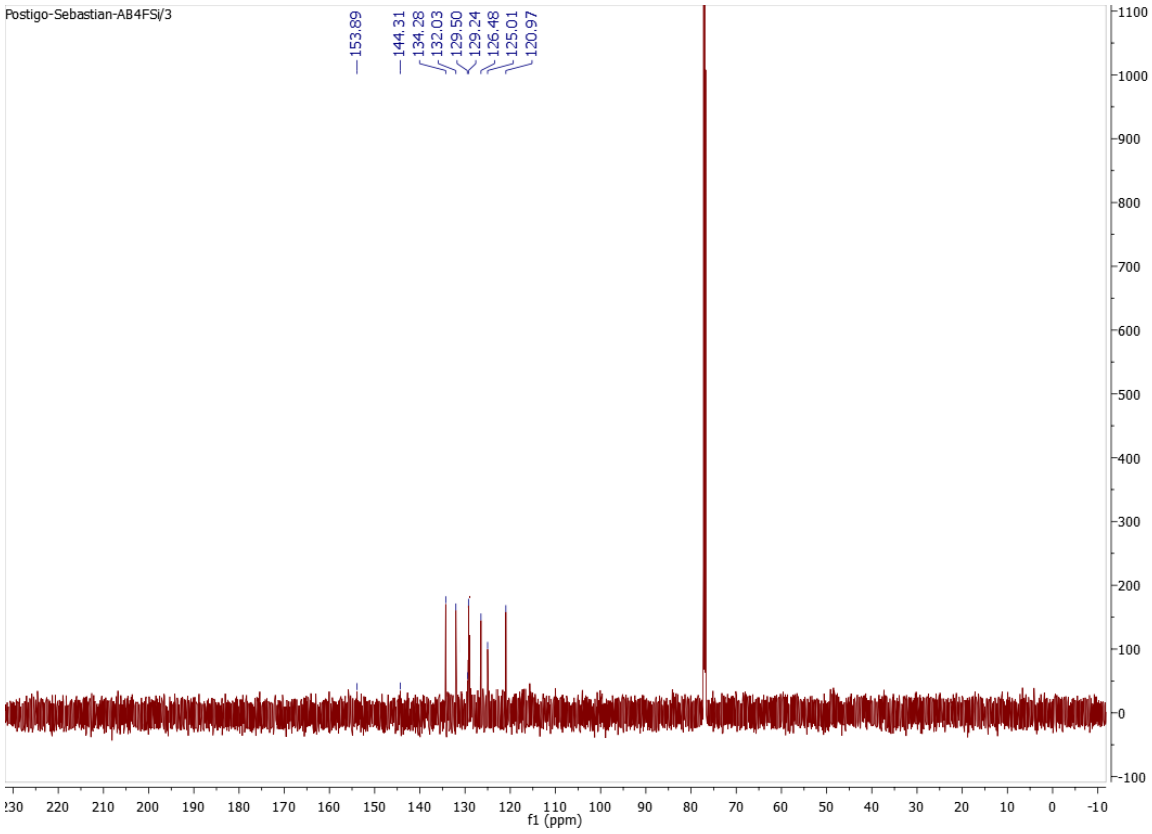
1H NMR spectrum 0f 20 in CDCl3



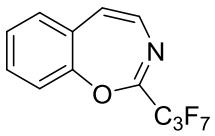


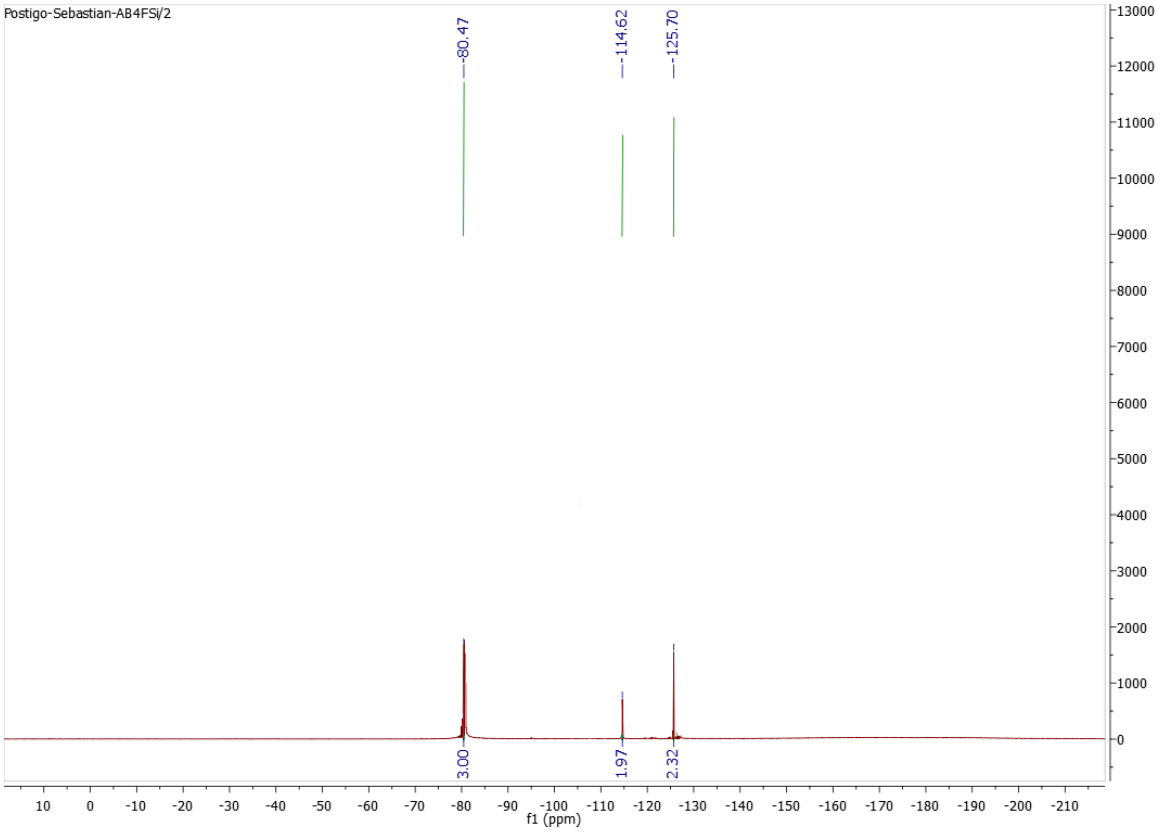
13C NMR spectrum 0f 20 in CDCl3



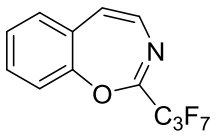


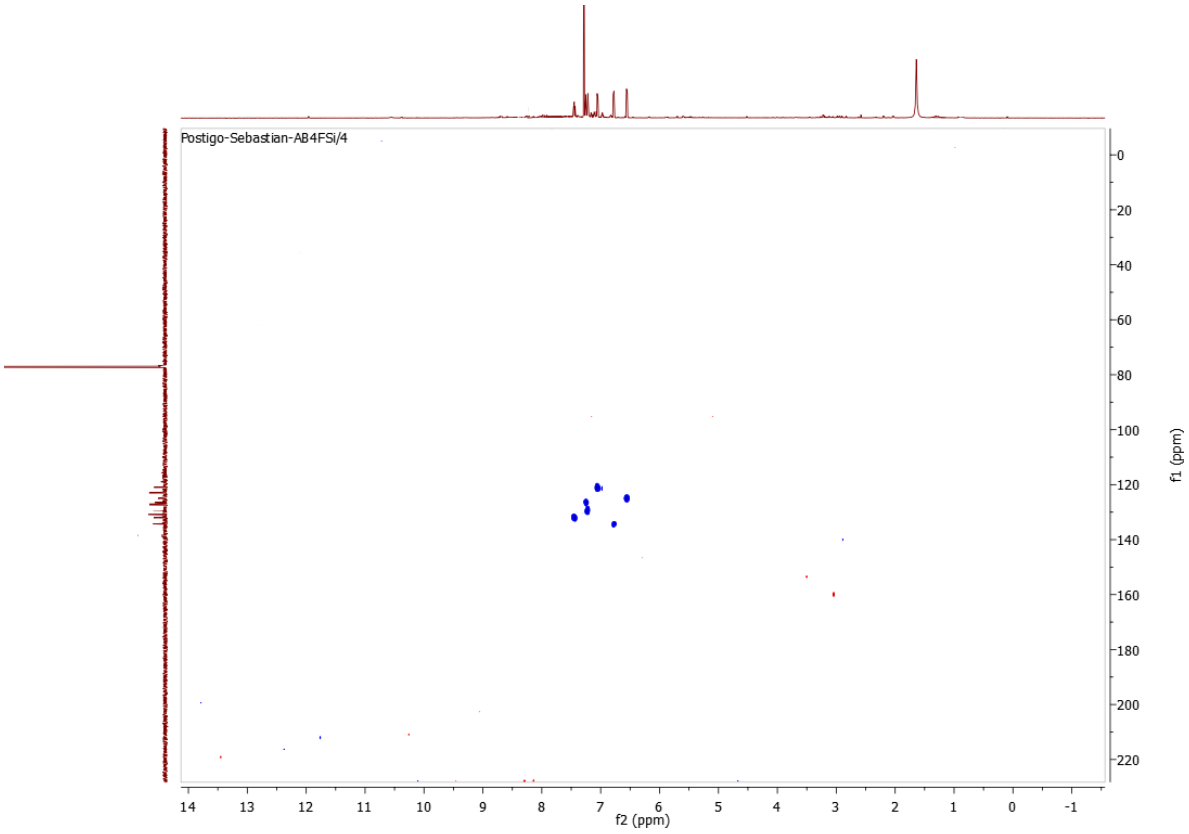
19F NMR spectrum 0f 20 in CDCl3



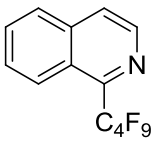


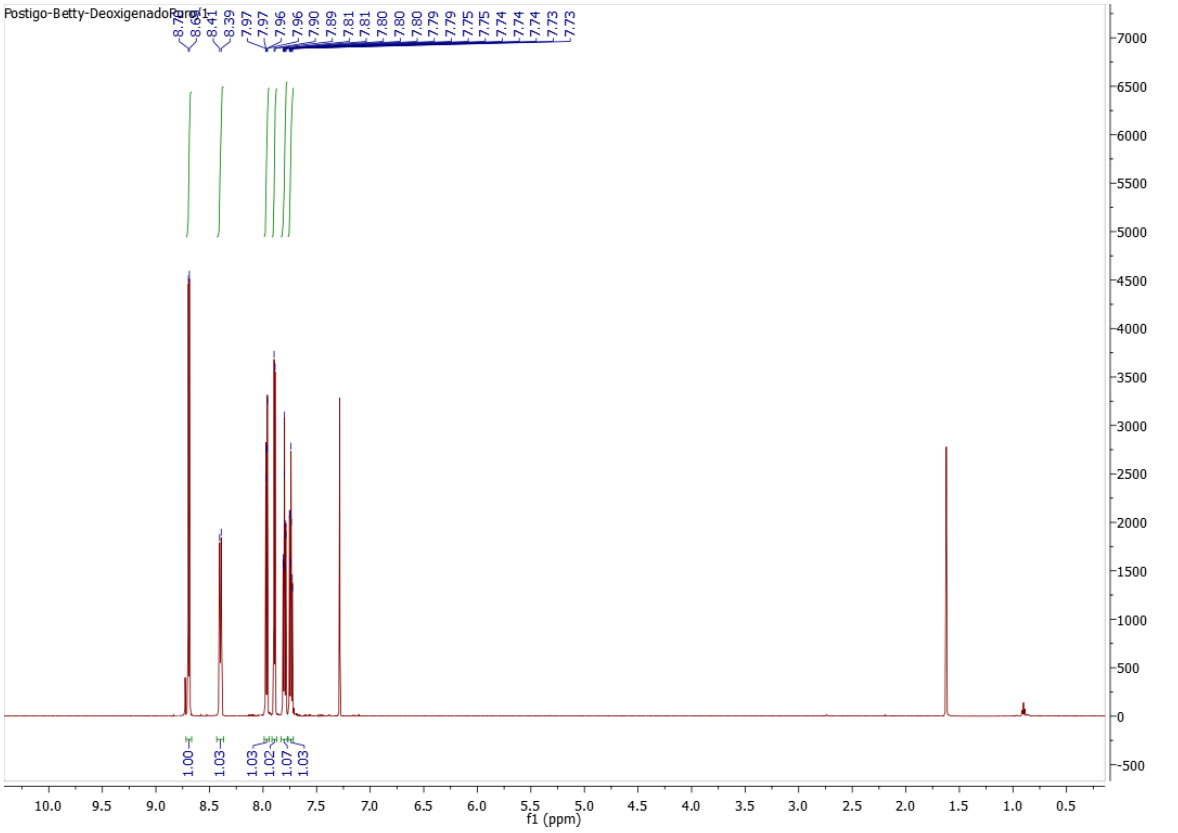
HSQC NMR spectrum 0f 20 in CDCl3



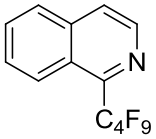


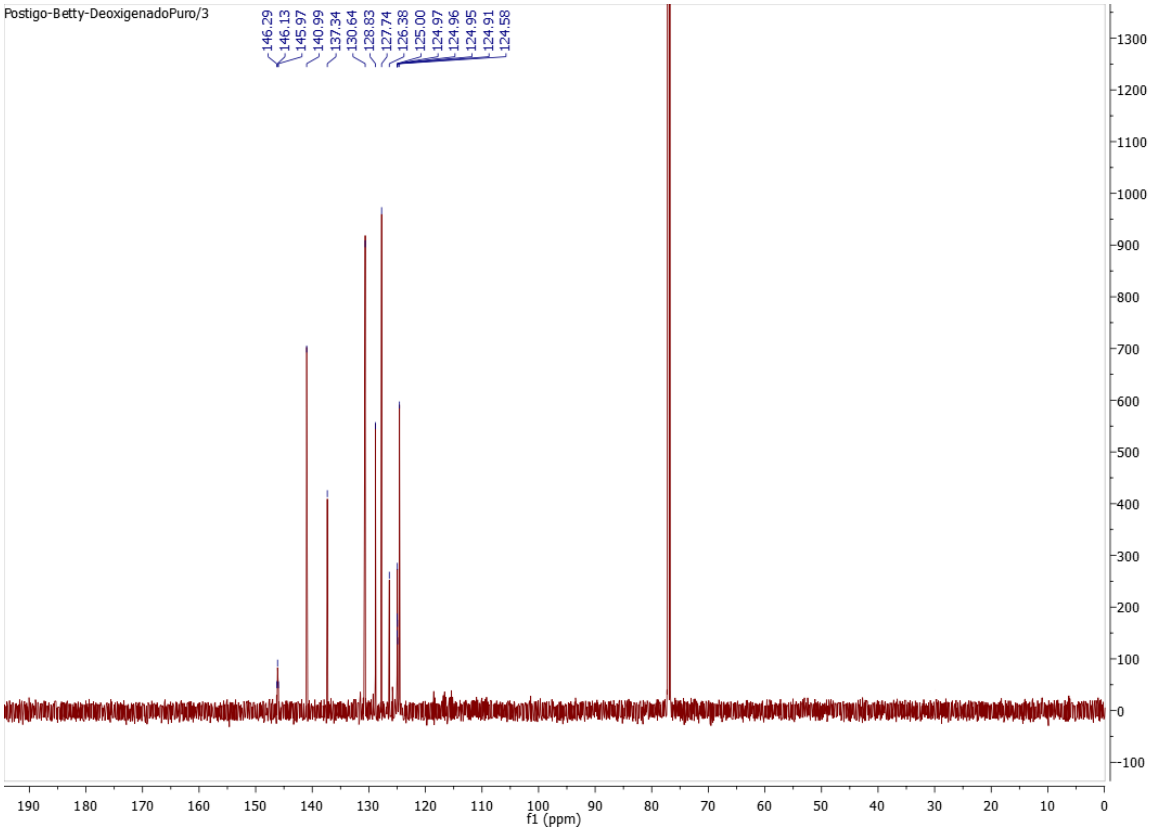
1H NMR spectrum 0f 21 in CDCl3



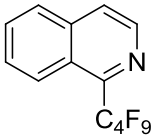


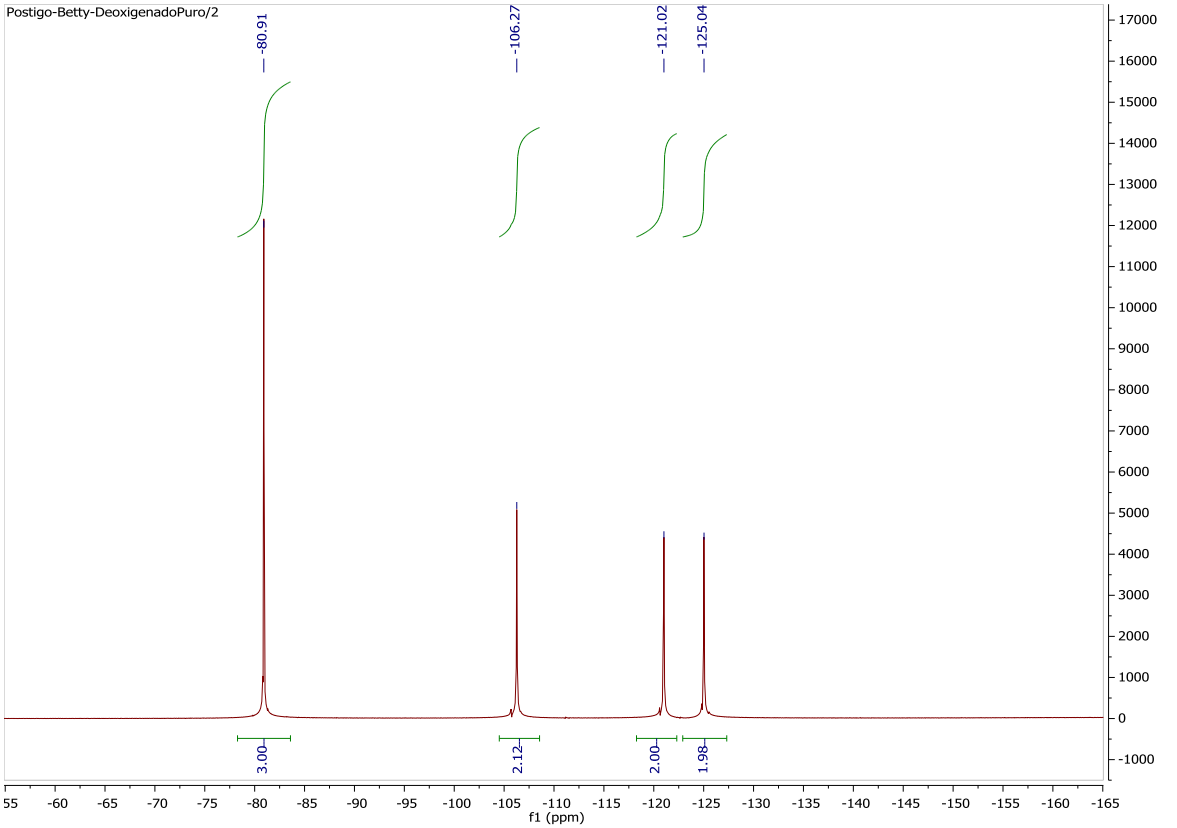
13C NMR spectrum 0f 21 in CDCl3



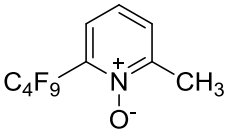


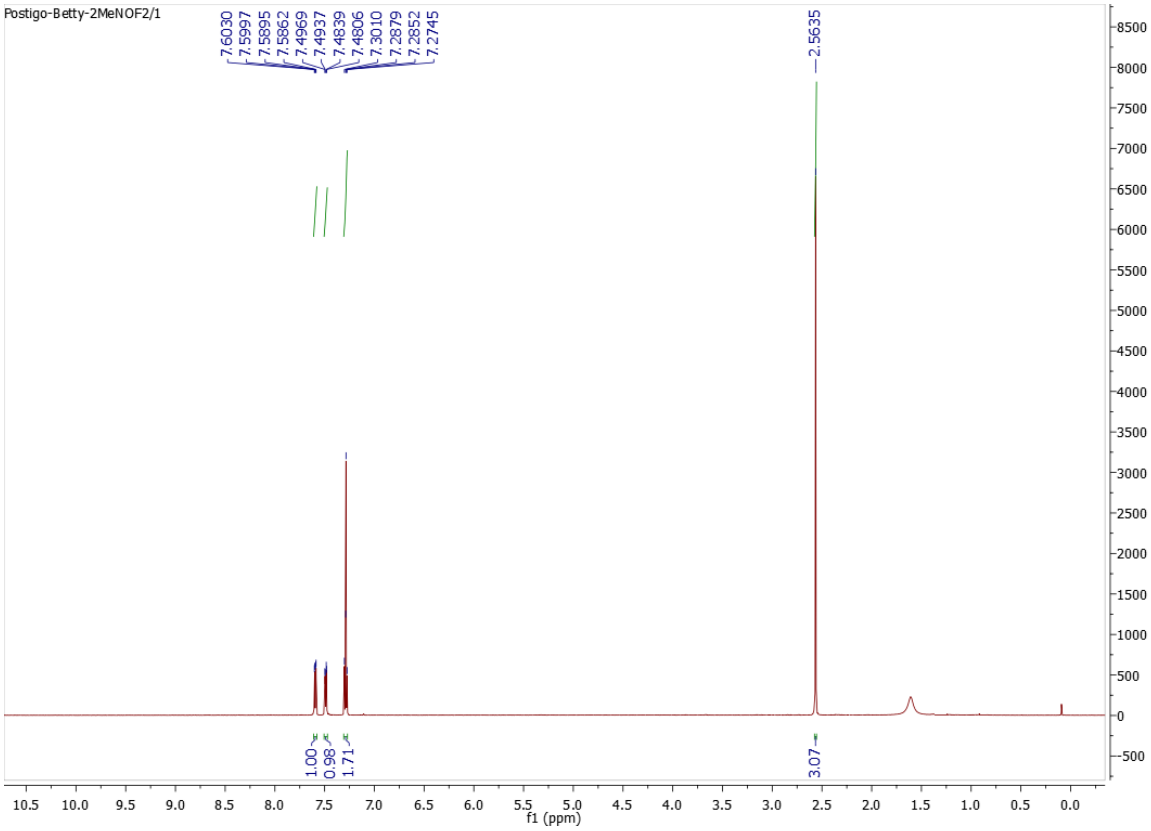
19F NMR spectrum 0f 21 in CDCl3



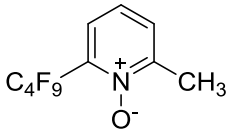


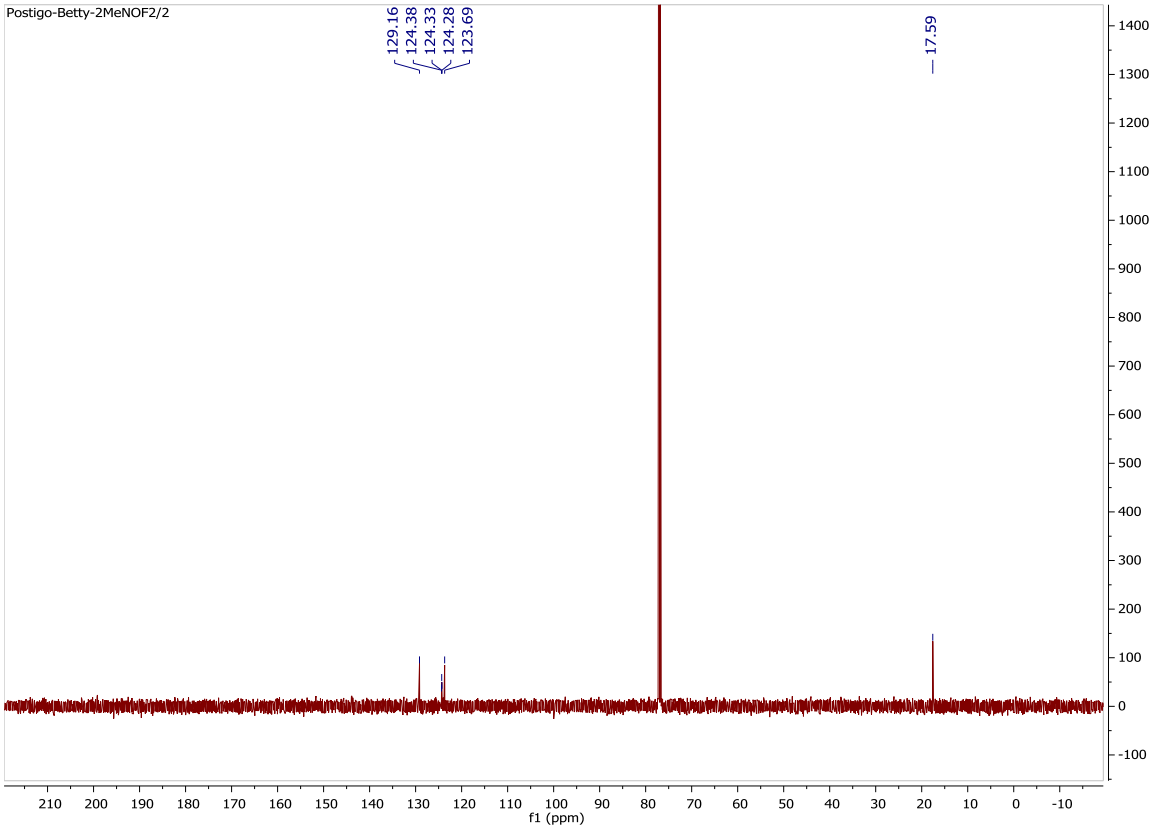
1H NMR spectrum 0f 24 in CDCl3



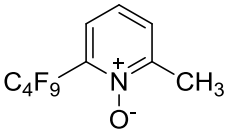


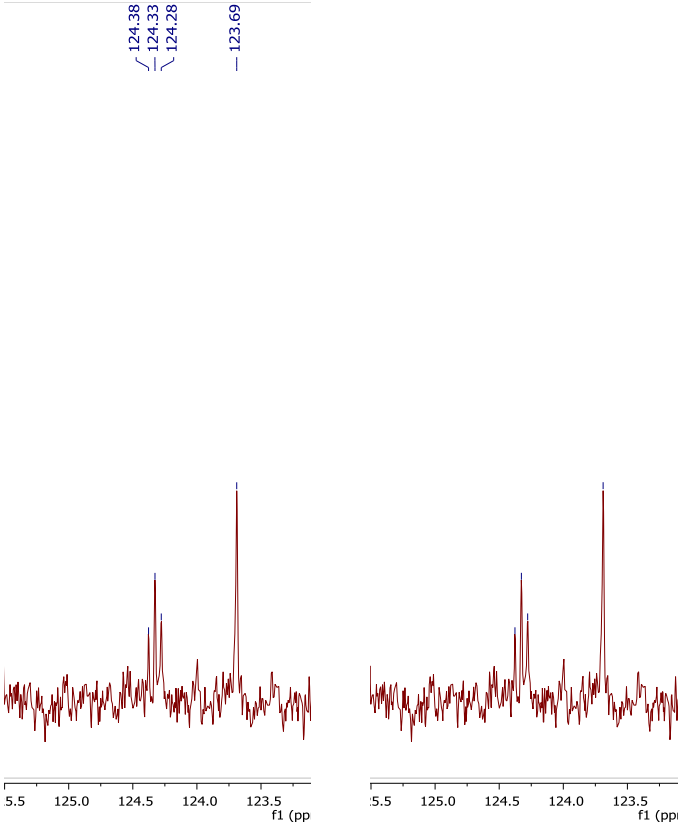
13C NMR spectrum 0f 24 in CDCl3



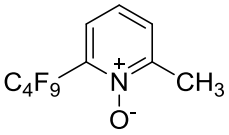


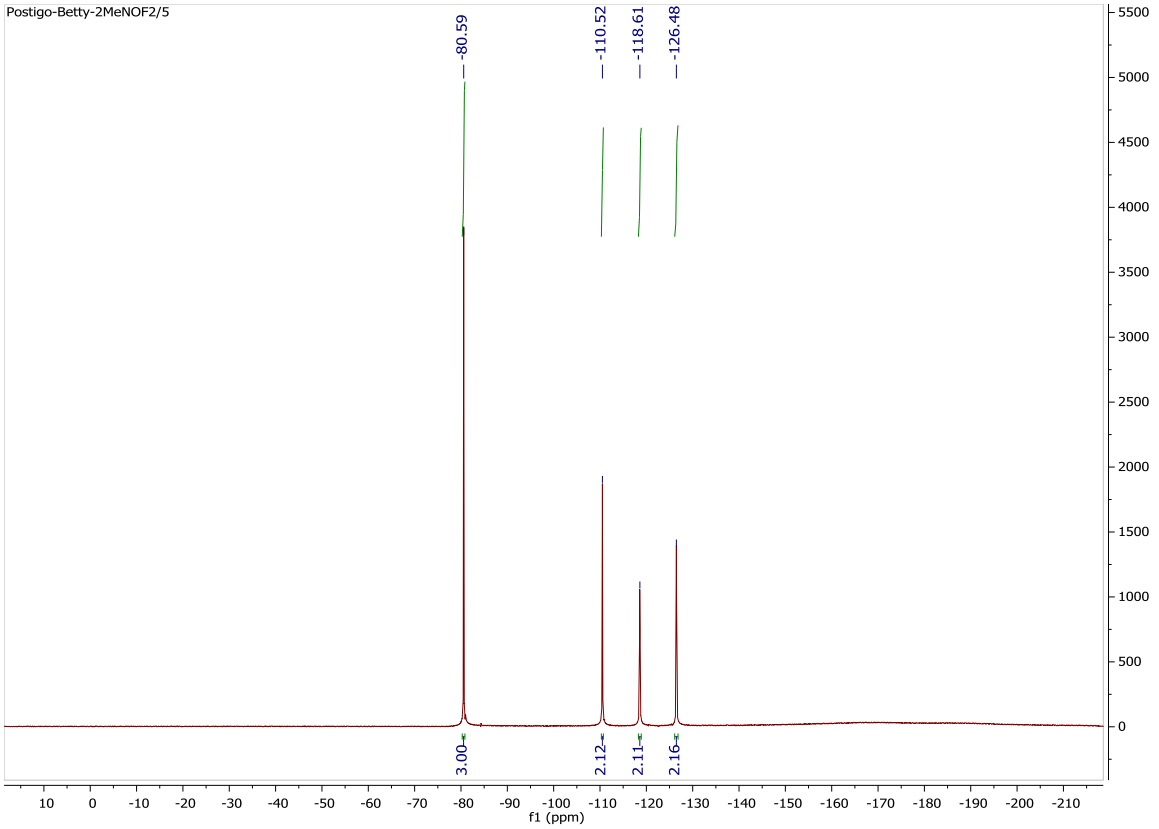
13C NMR spectrum 0f 24 in CDCl3, enlargement



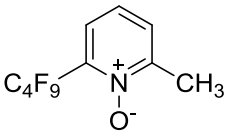


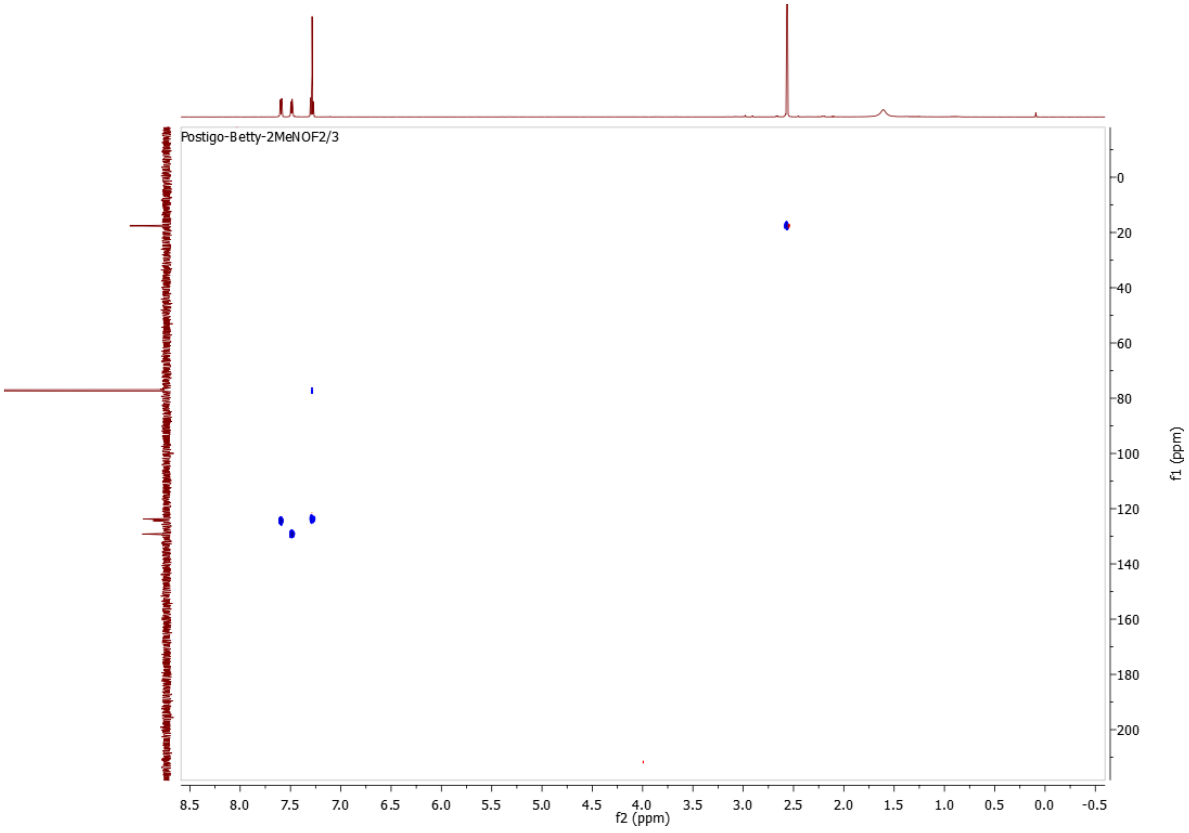
19F NMR spectrum 0f 24 in CDCl3



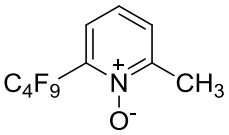


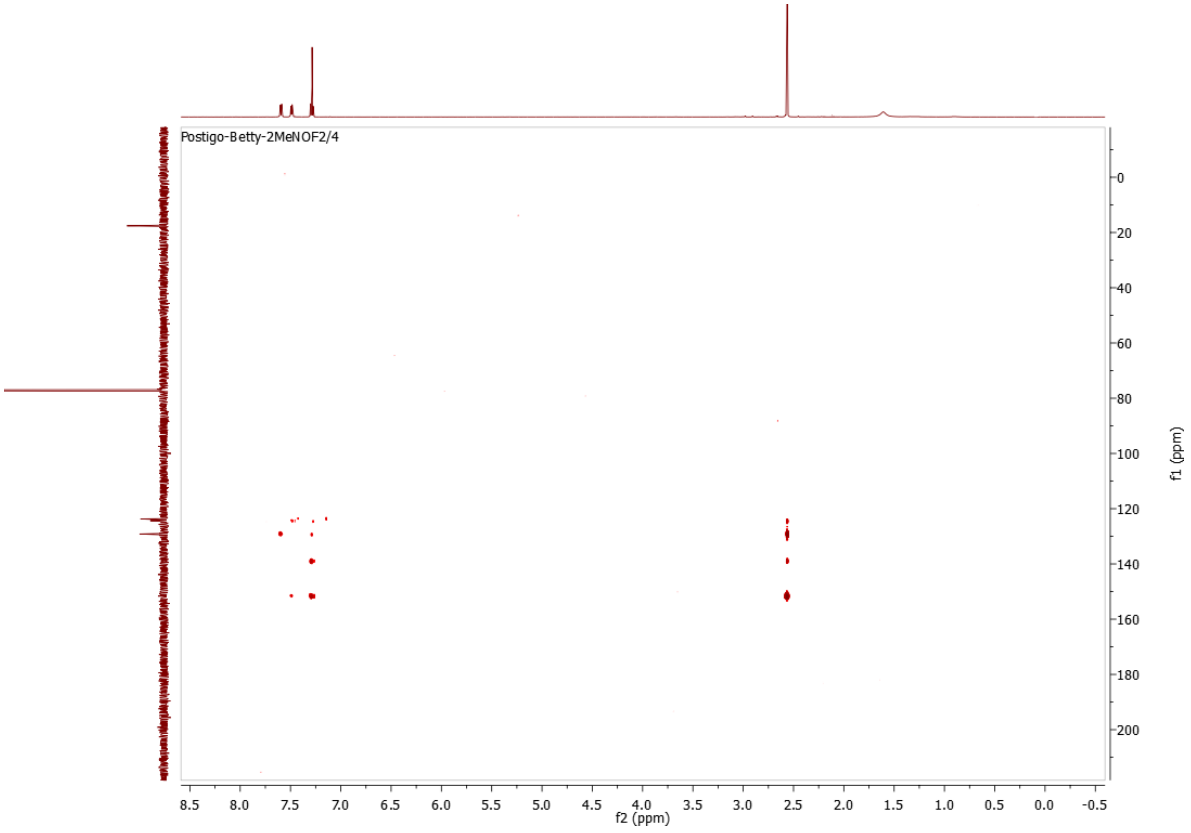
HSQC
NMR spectrum 0f 24 in CDCl3



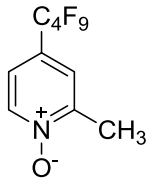


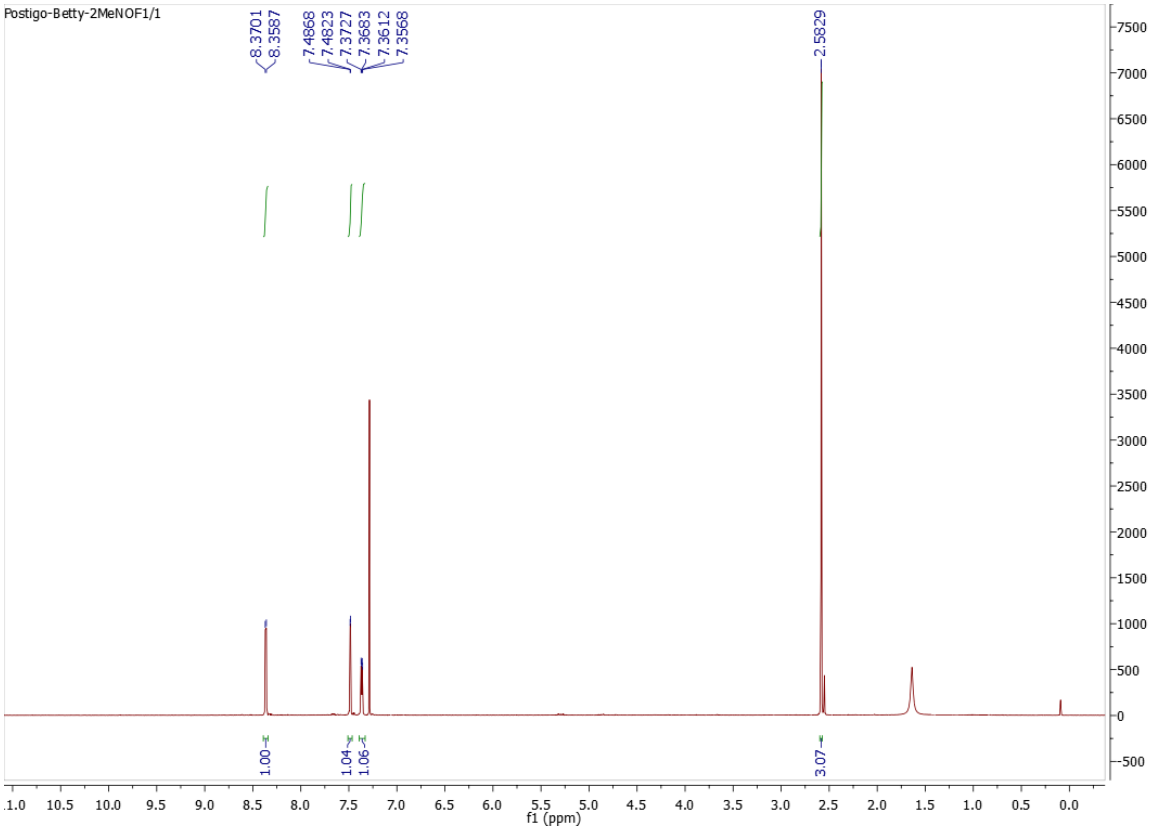
HMBC
NMR spectrum 0f 24 in CDCl3



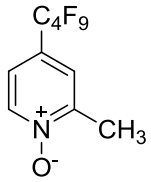


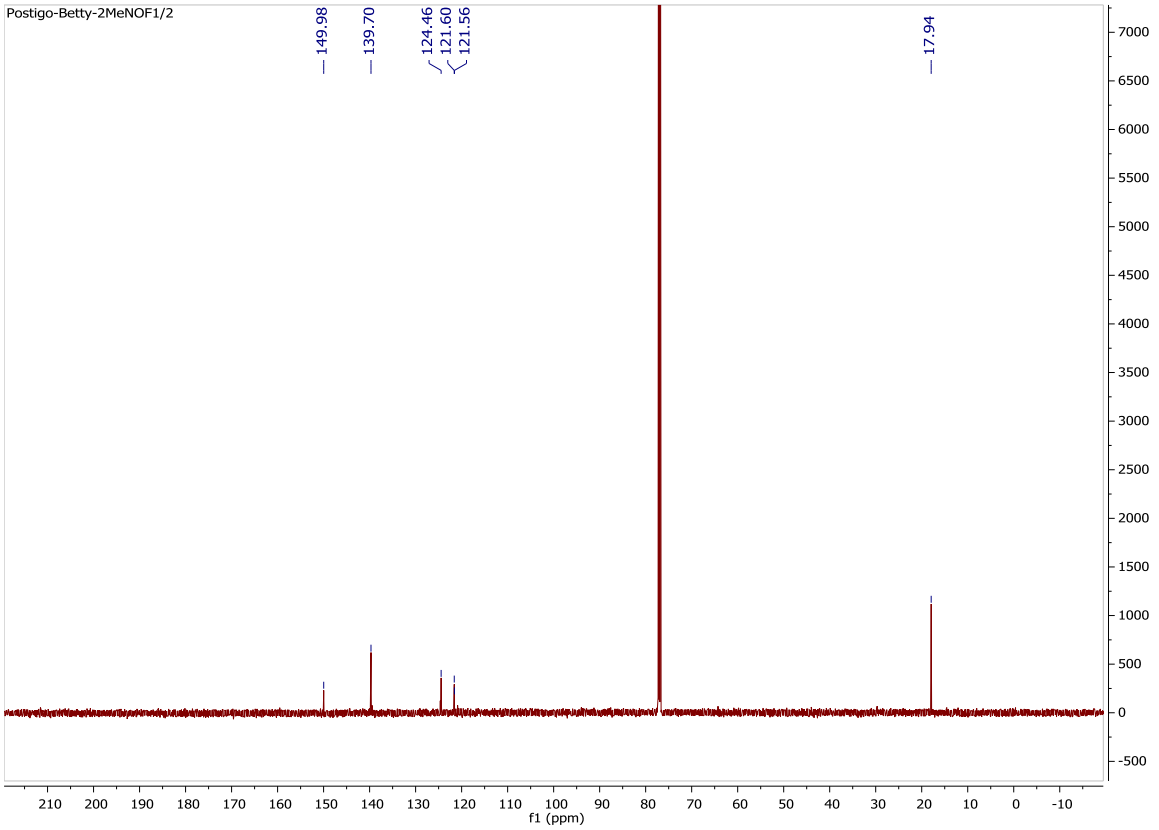
1H NMR spectrum
0f 25 in CDCl3



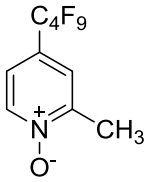


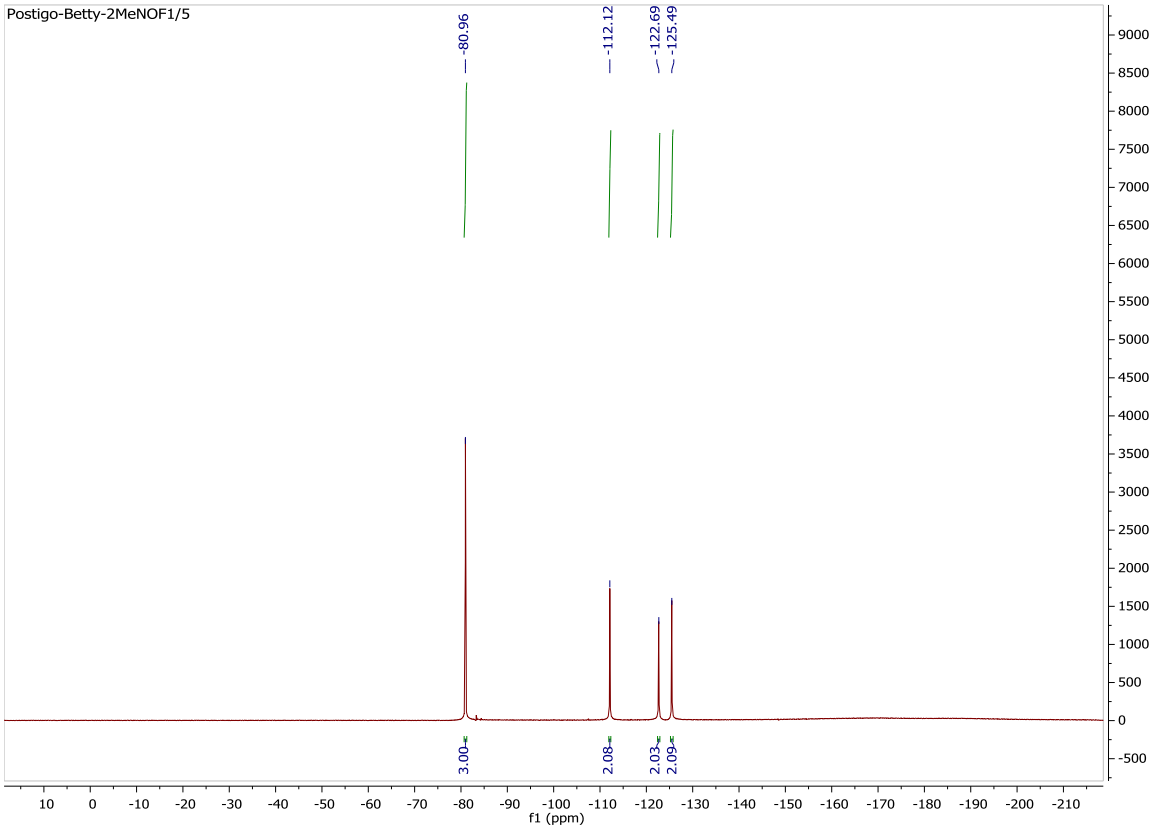
13C NMR spectrum 0f 25 in CDCl3



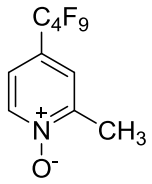


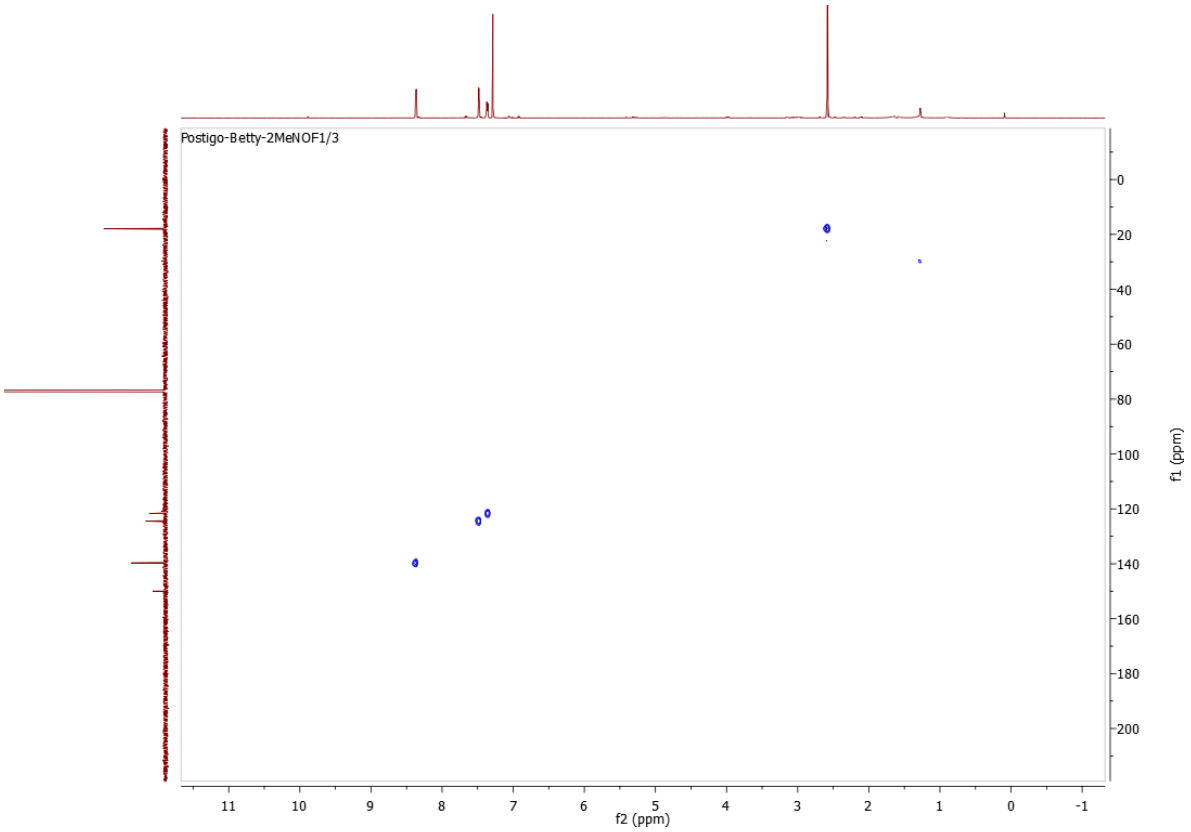
19F NMR spectrum 0f 25 in CDCl3



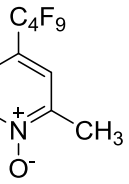


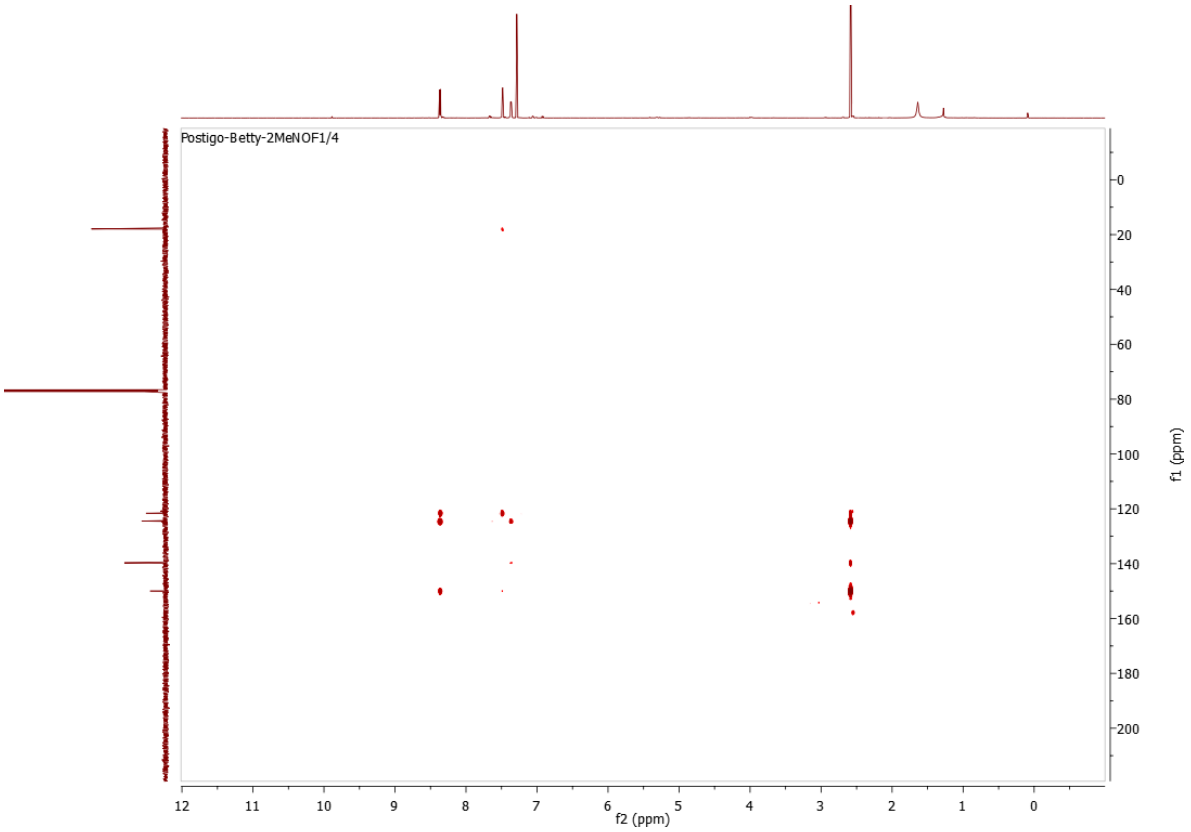
HSQC NMR spectrum 0f 25 in CDCl3



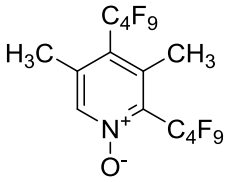


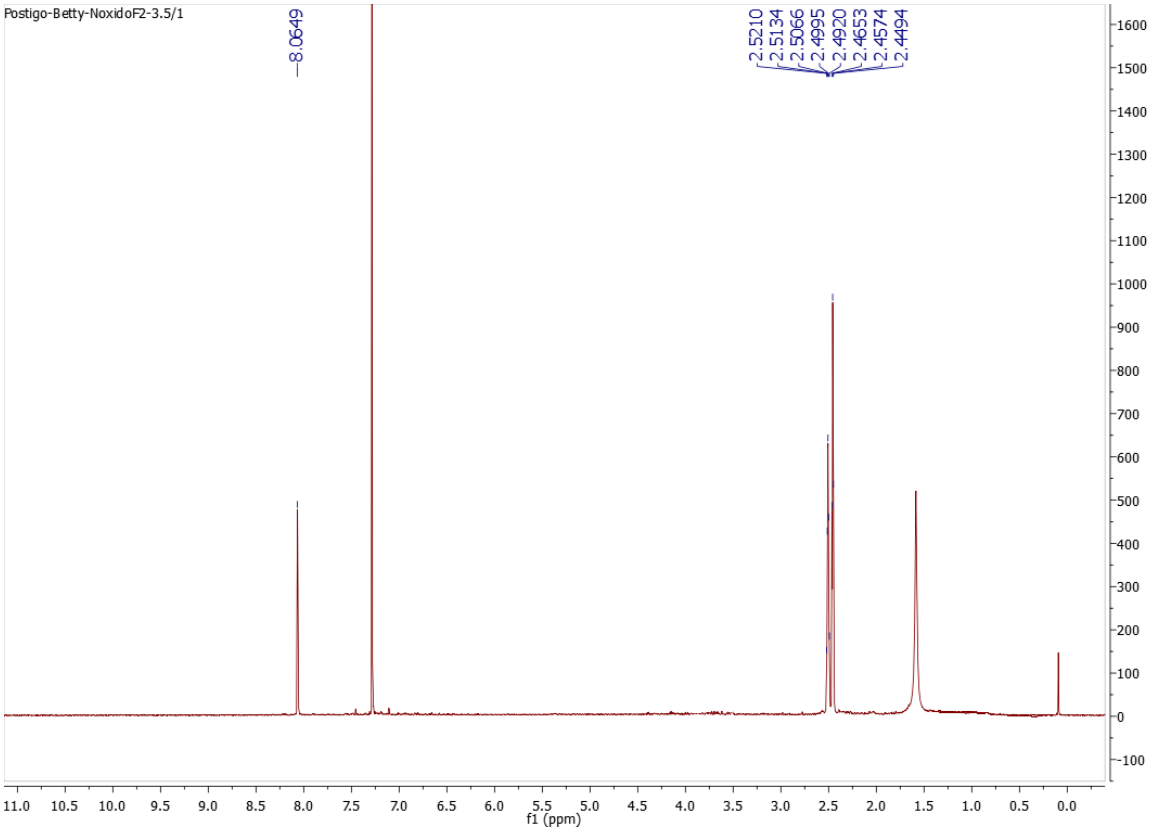
HMBC NMR spectrum 0f 25 in CDCl3



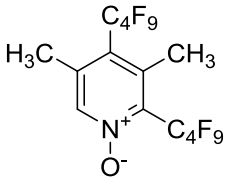


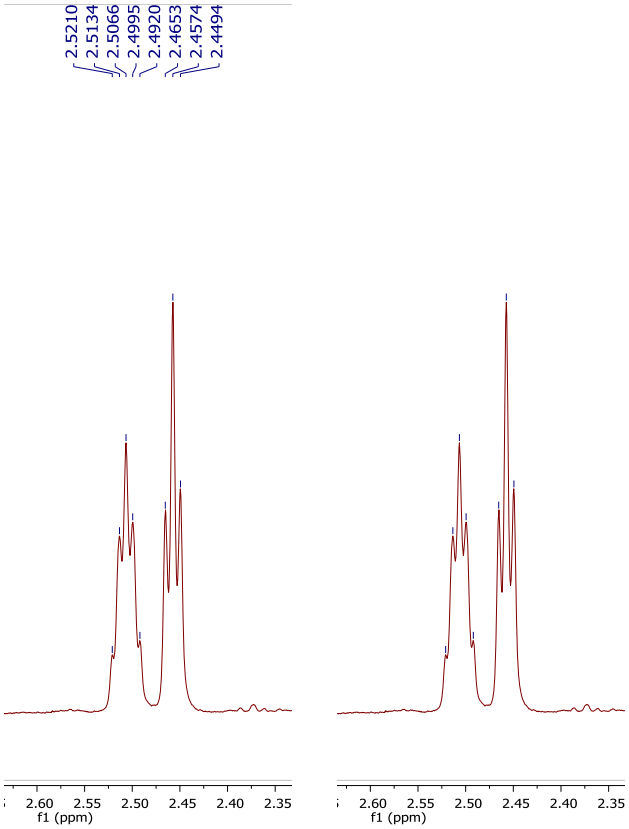
1H NMR spectrum
0f 27 in CDCl3



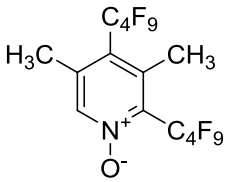


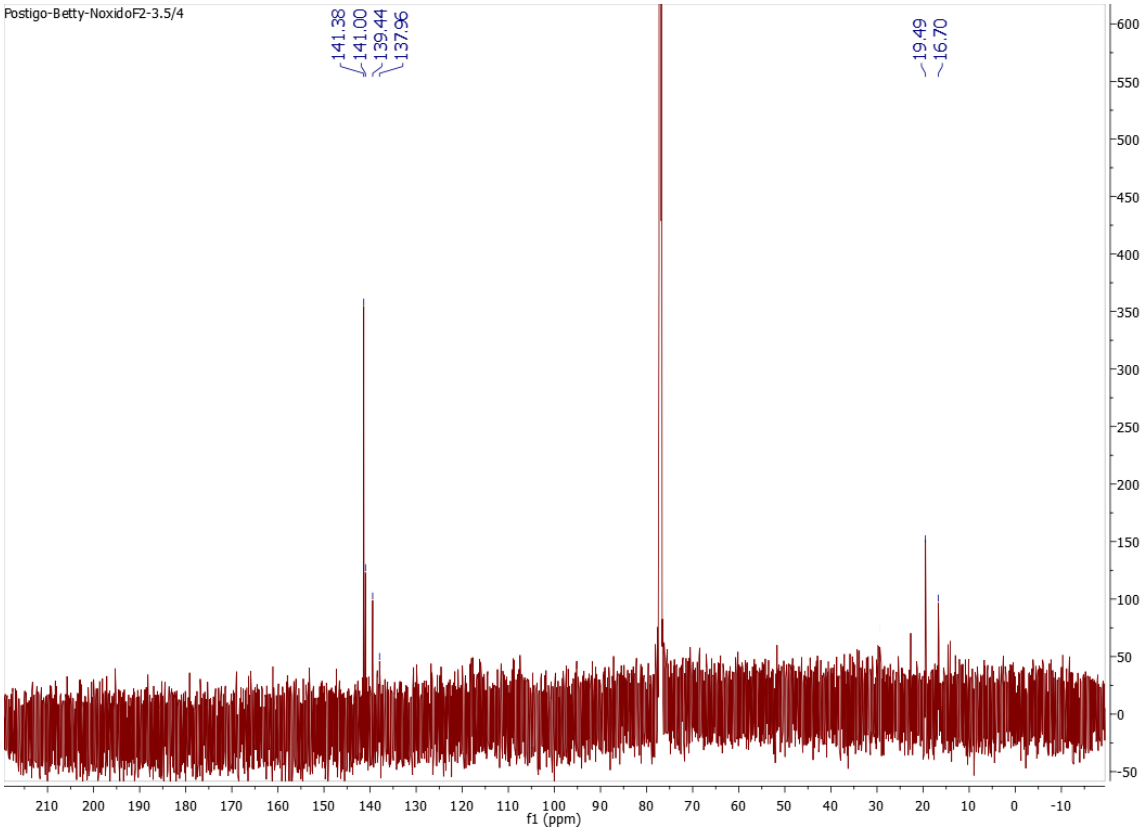
1H NMR spectrum 0f 27 in CDCl3, enlargement



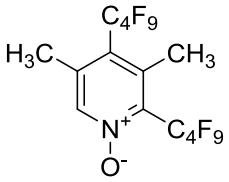


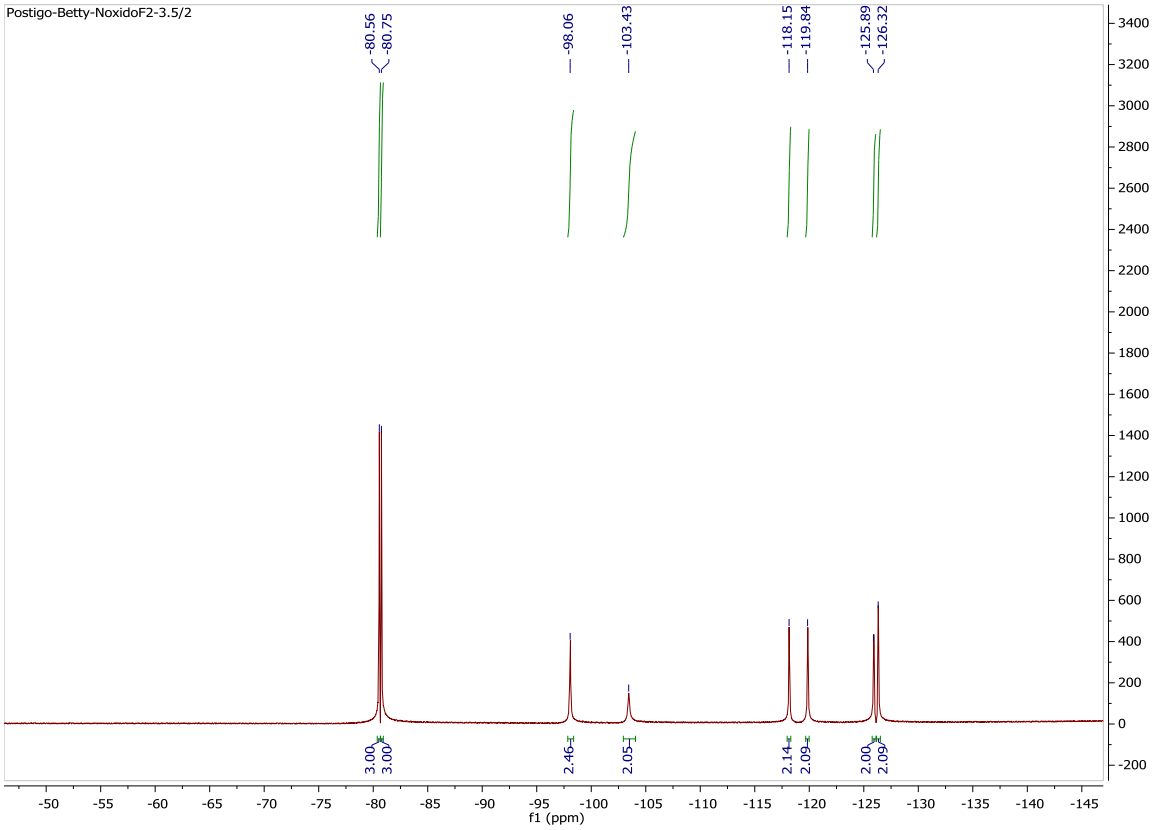
13C NMR spectrum 0f 27 in CDCl3



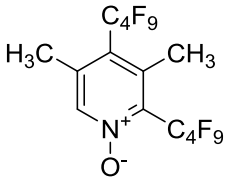


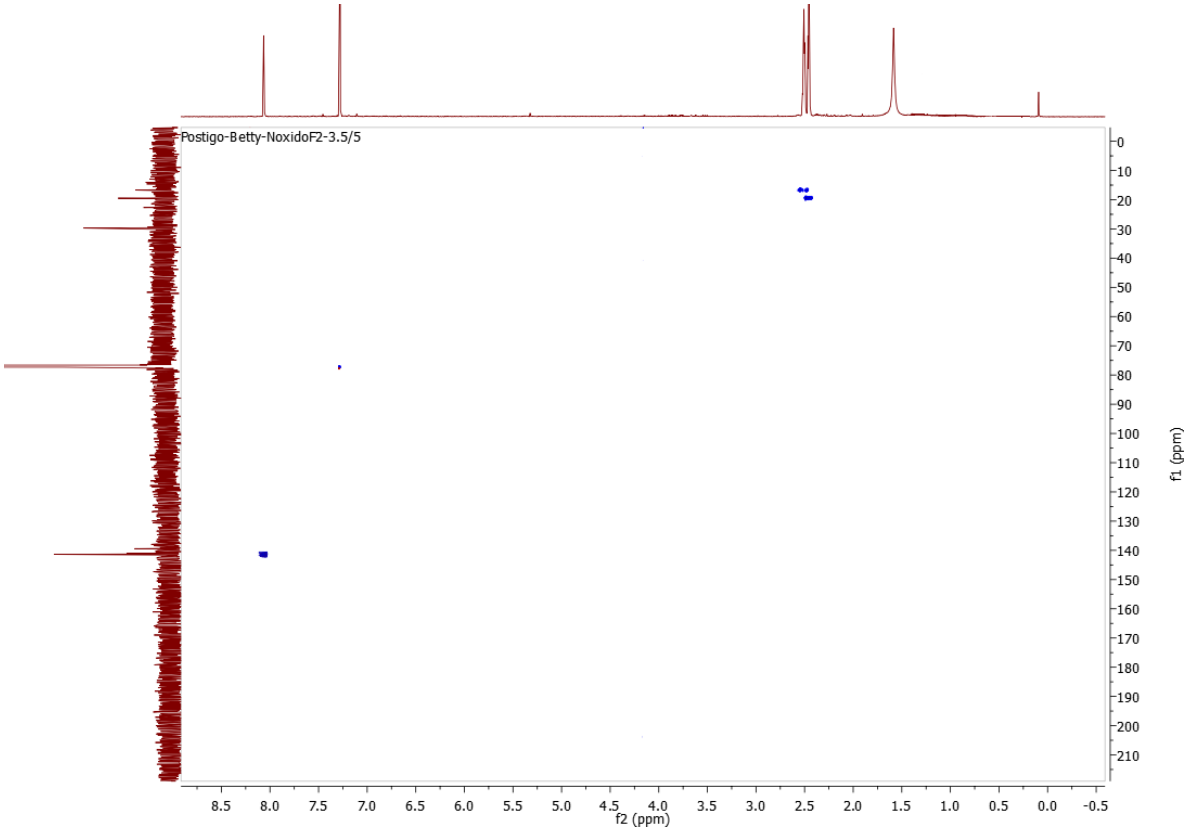
19F NMR spectrum 0f 27 in CDCl3



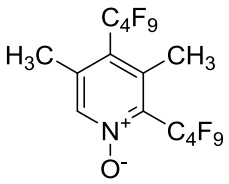


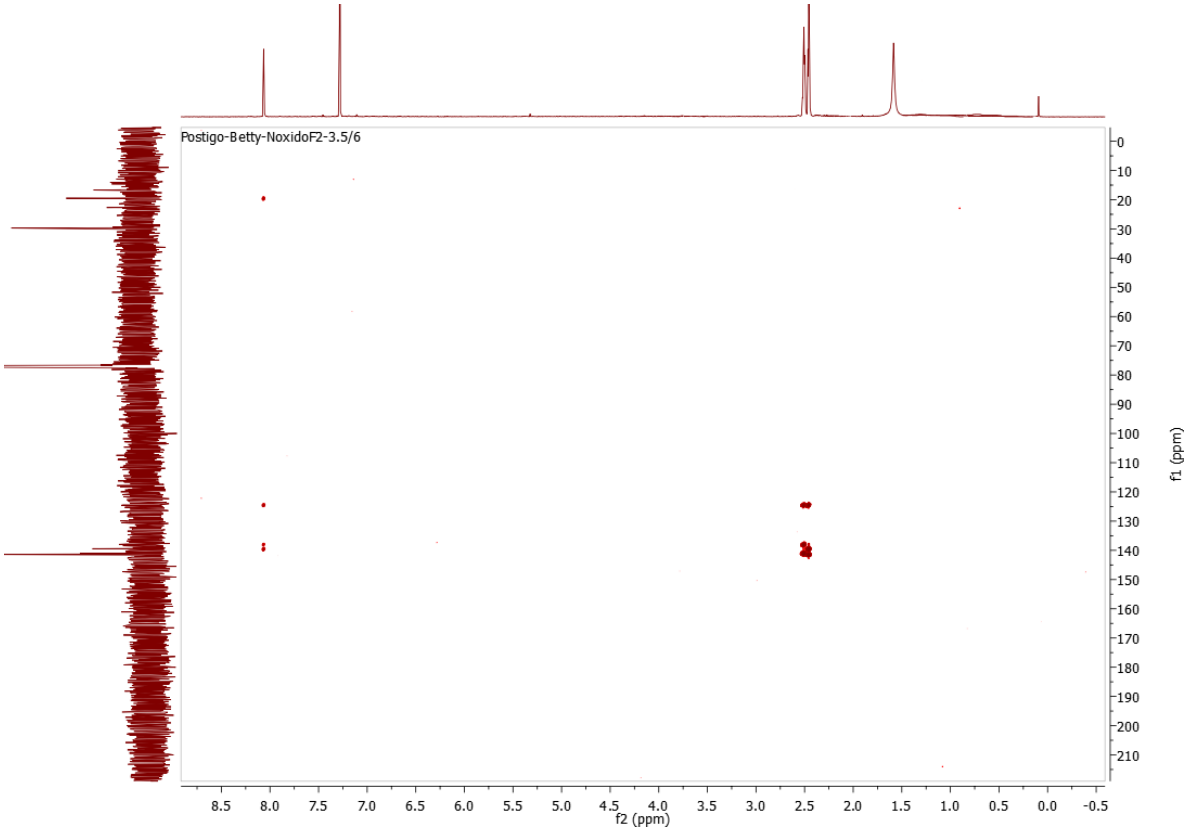
HSQC NMR spectrum 0f 27 in CDCl3



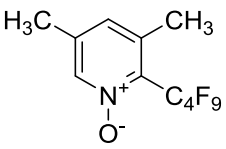


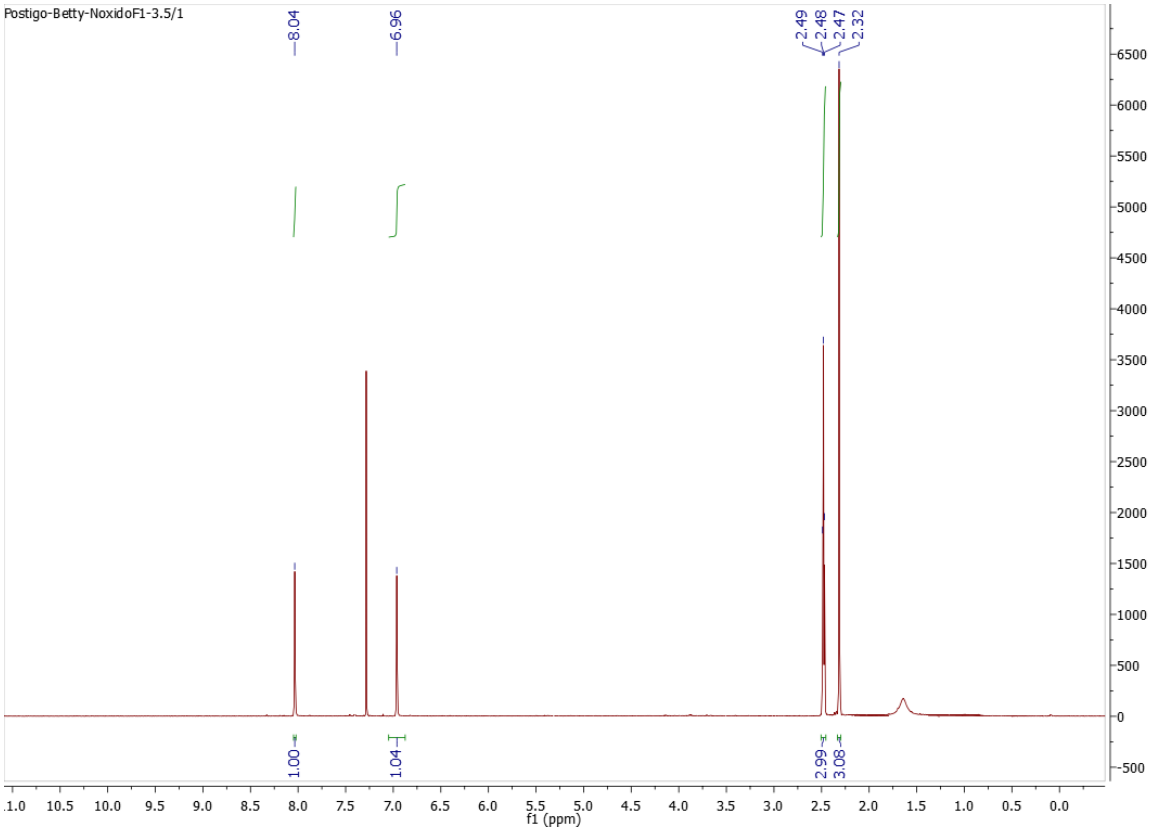
HMBC NMR spectrum 0f 27 in CDCl3



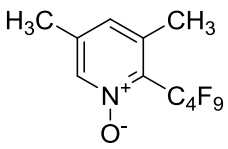


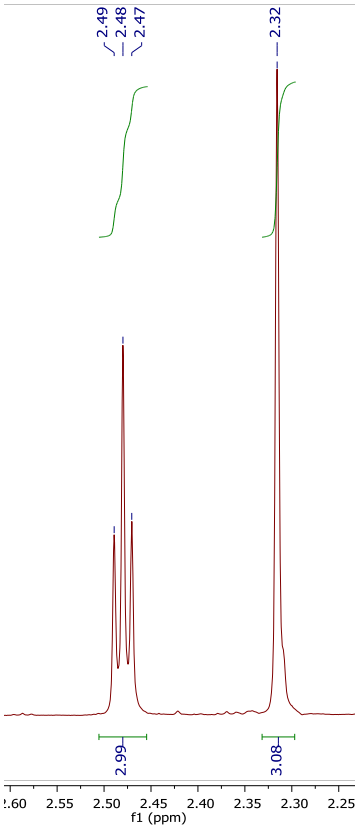
1H NMR spectrum 0f 28 in CDCl3

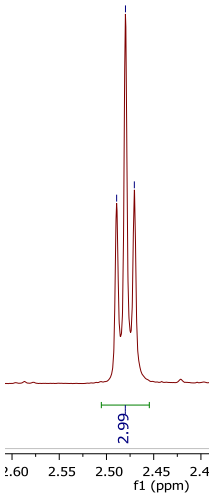




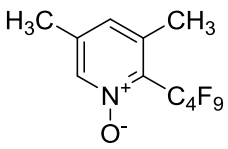
1H NMR spectrum 0f 28 in CDCl3, enlargement

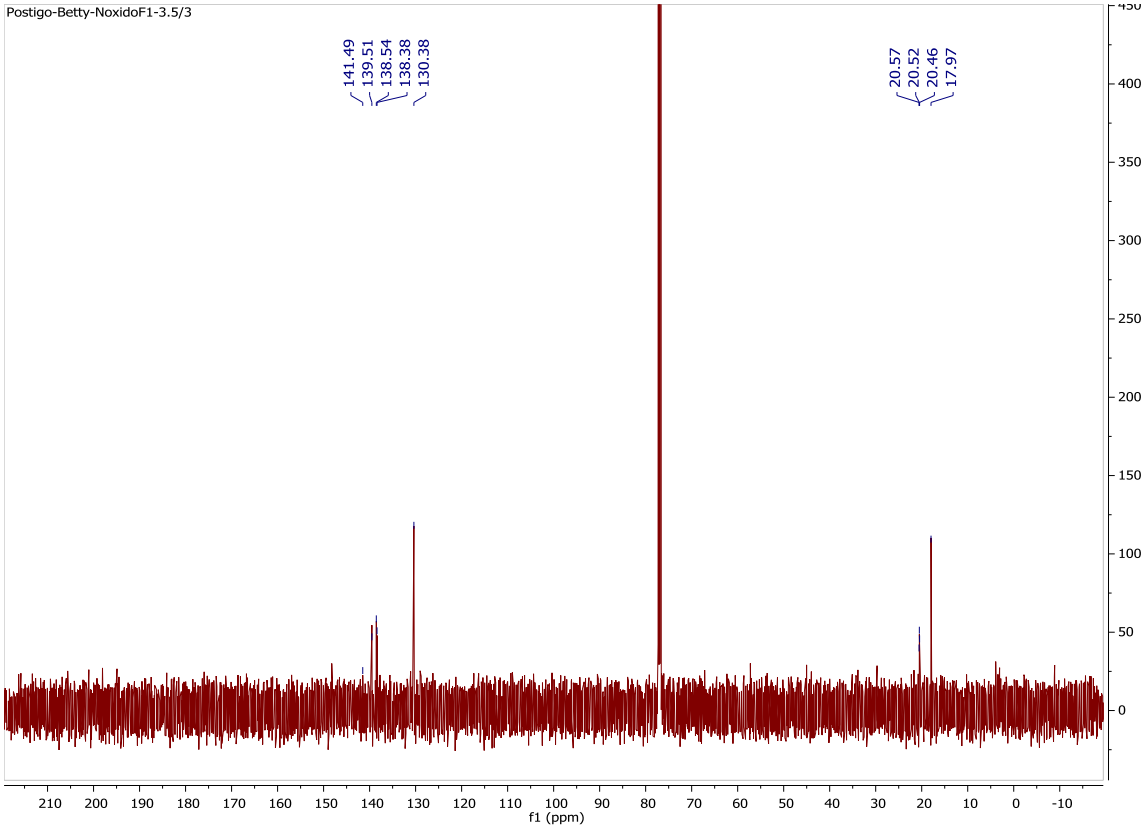




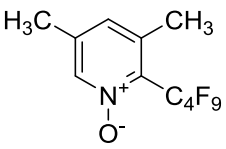


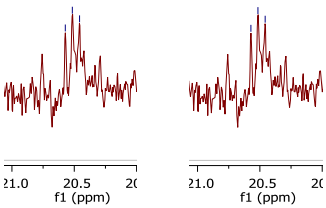
13C NMR spectrum 0f 28 in CDCl3



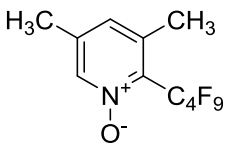


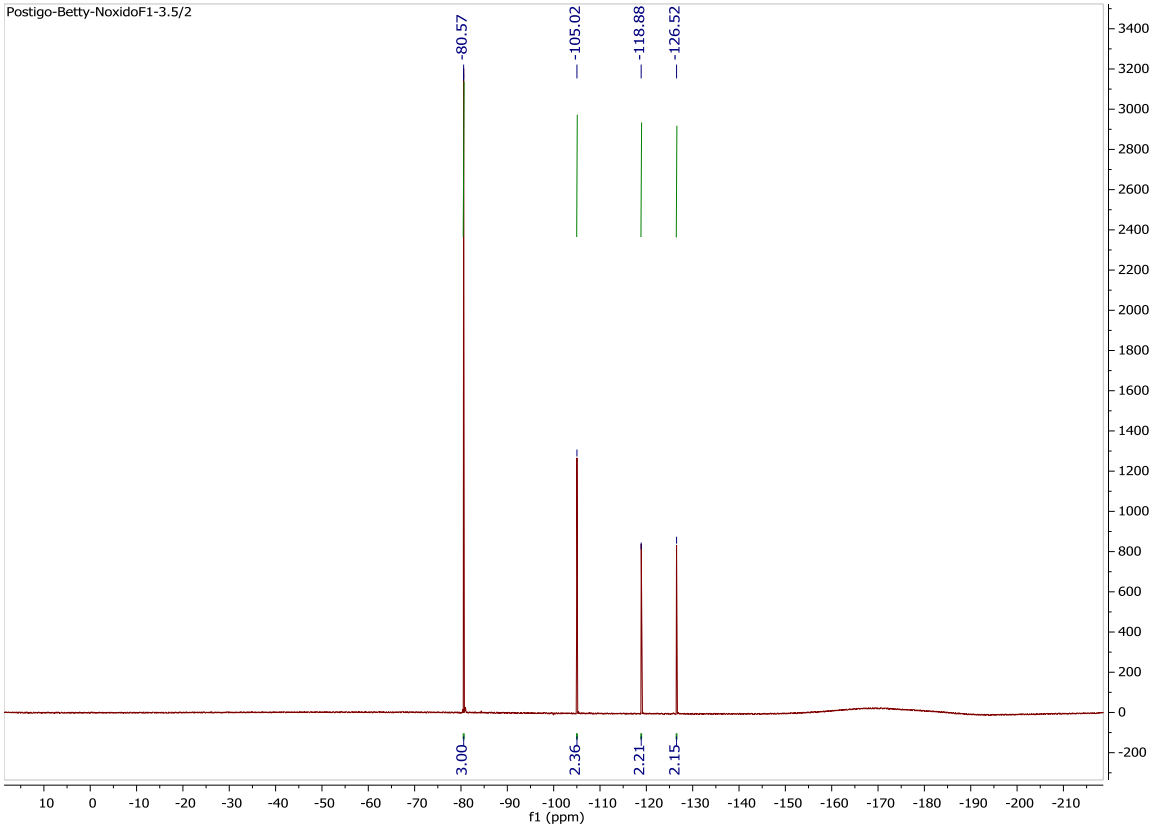
13C NMR spectrum 0f 28 in CDCl3, enlargement



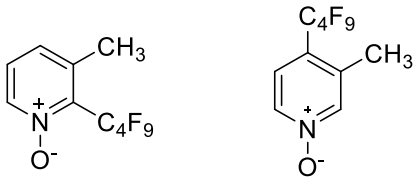


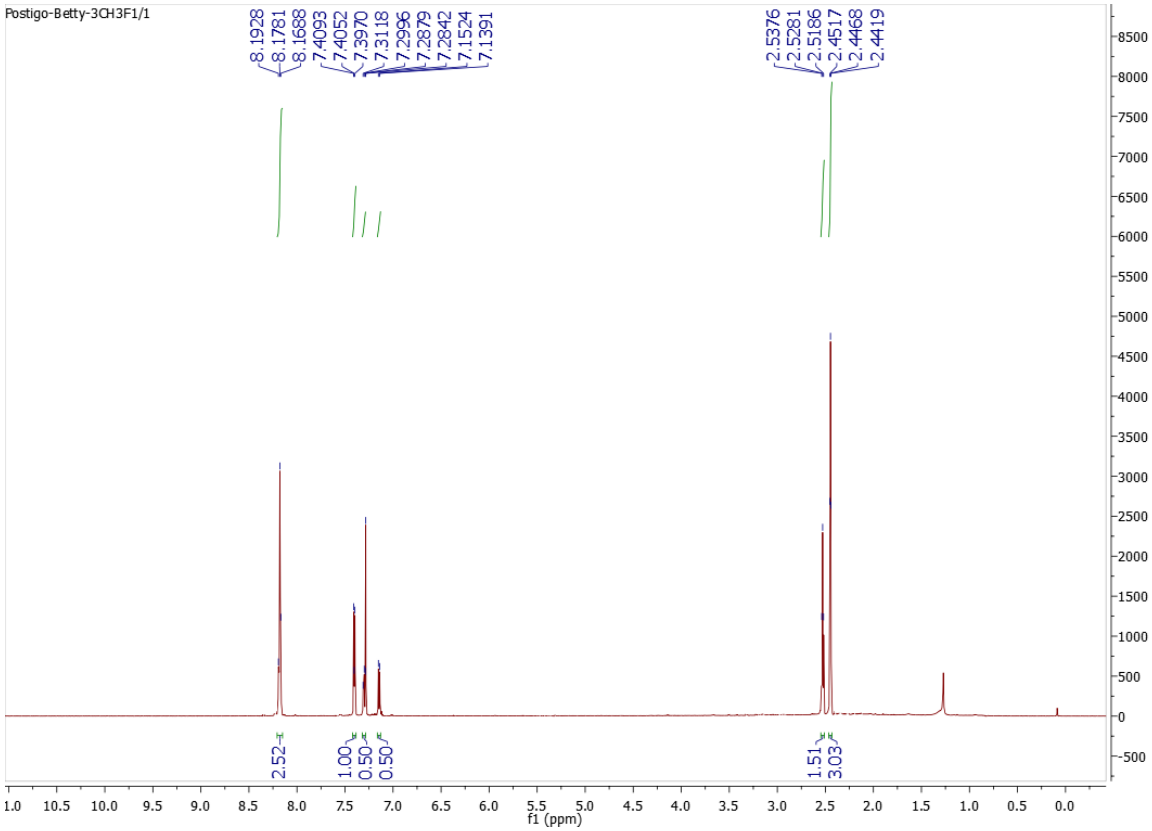
19F NMR spectrum 0f 28 in CDCl3



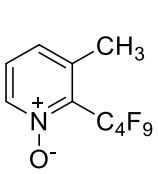


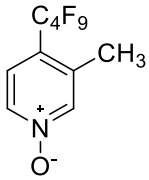
1H NMR spectrum of 30 and 31 in CDCl3

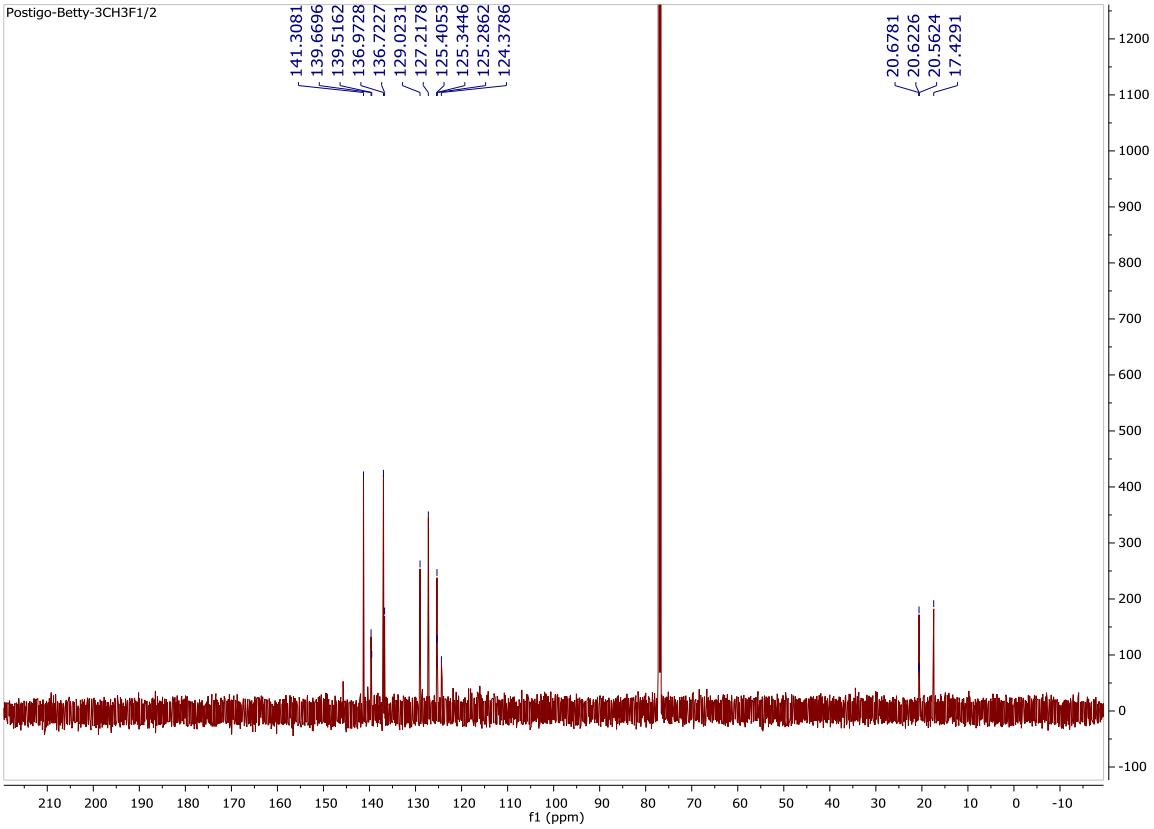




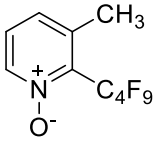
13C NMR spectrum of 30 and 31 in CDCl3

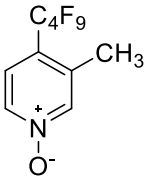


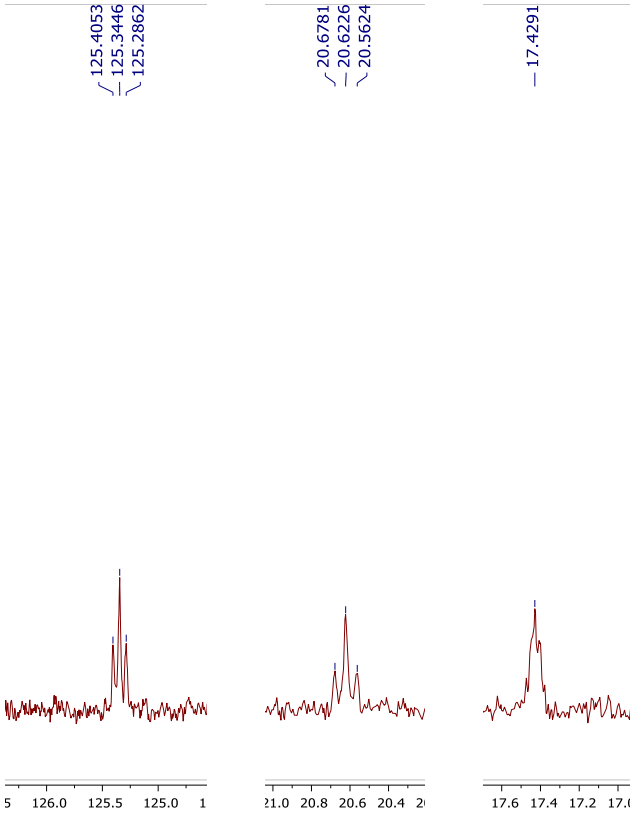




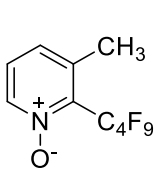
13C NMR spectrum of 30 and 31 in CDCl3, enlargement

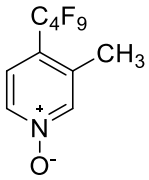


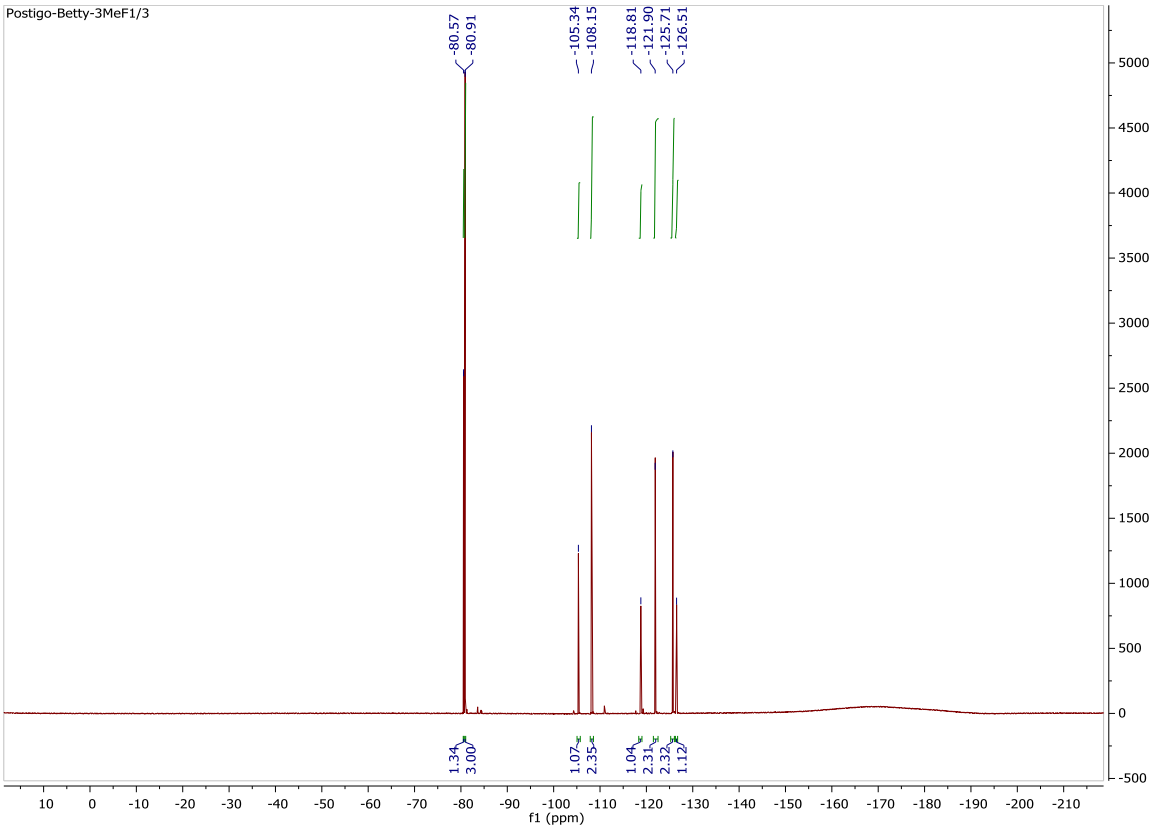




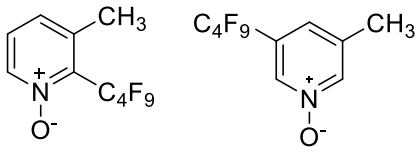
19F NMR spectrum of 30 and 31 in CDCl3

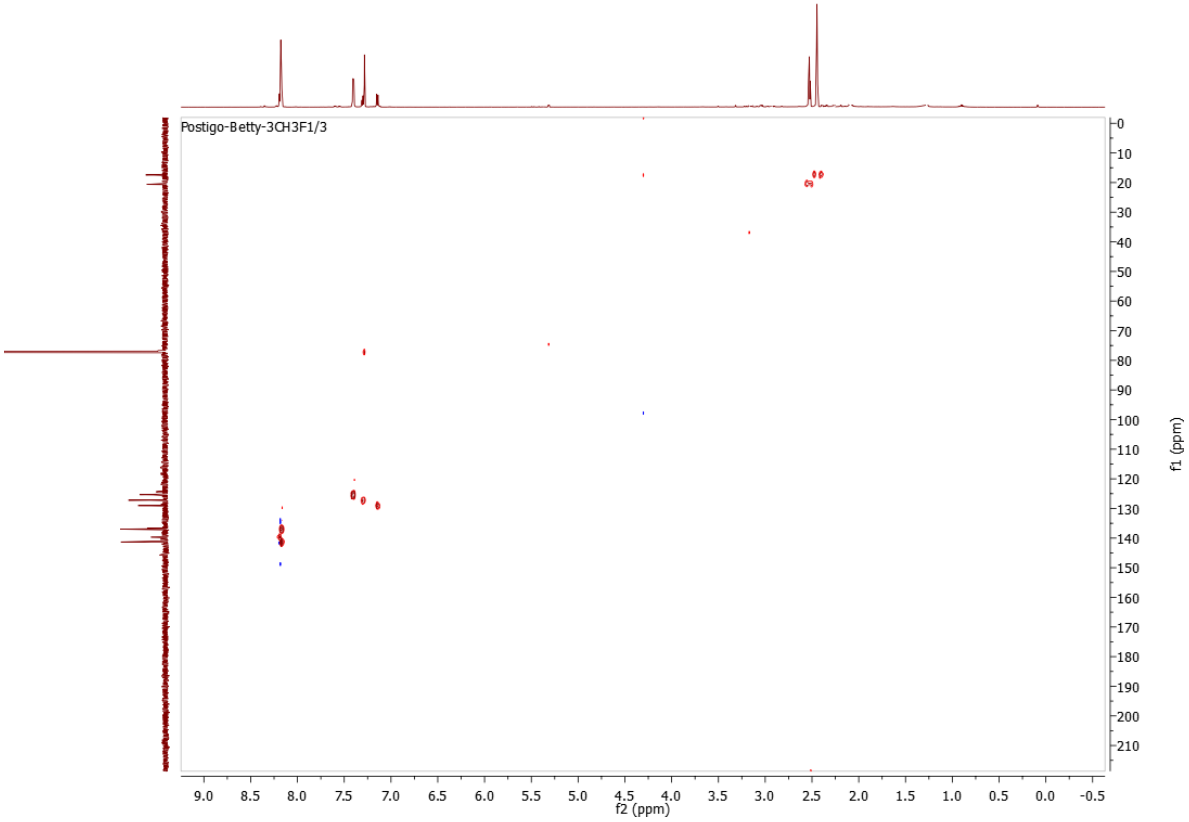




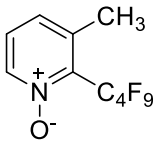


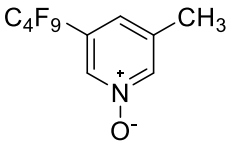
HSQC NMR spectrum of 30 and 31 in CDCl3

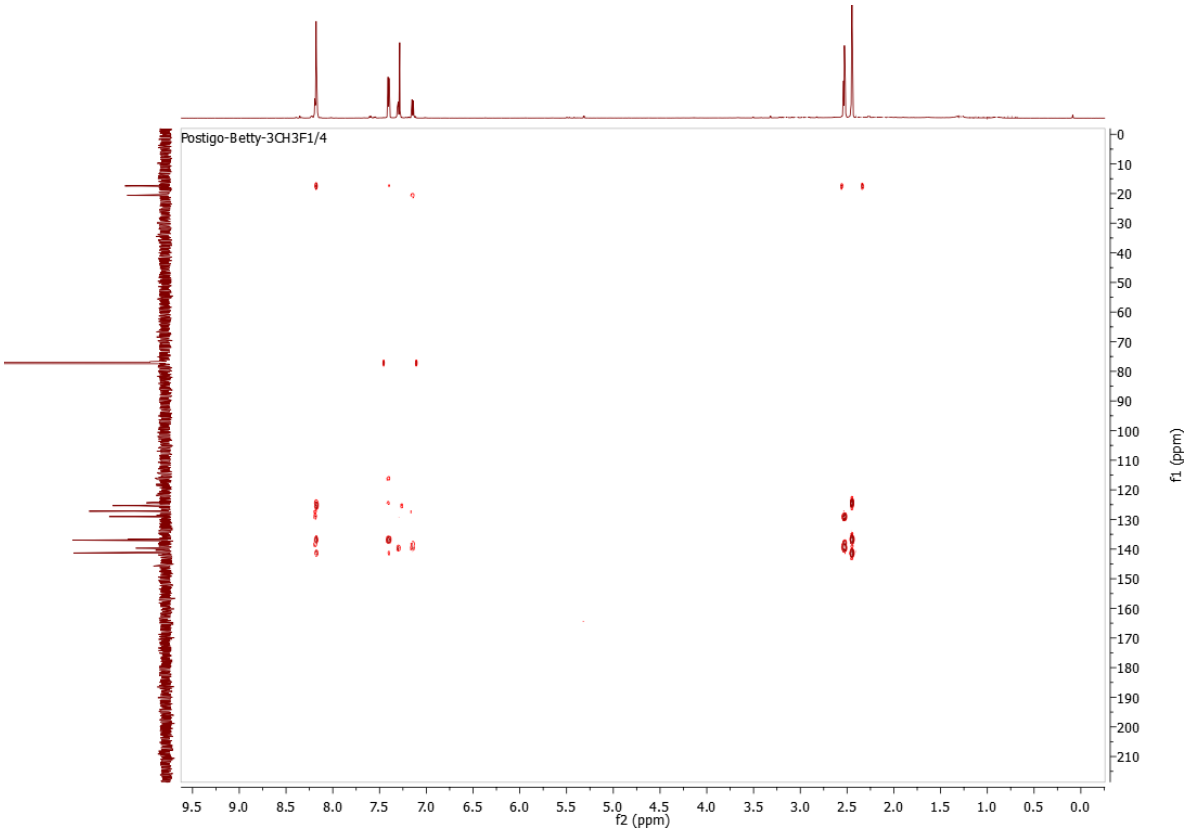




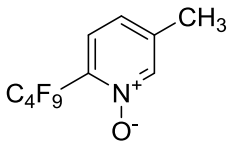
HMBC NMR spectrum of 30 and 31 in CDCl3

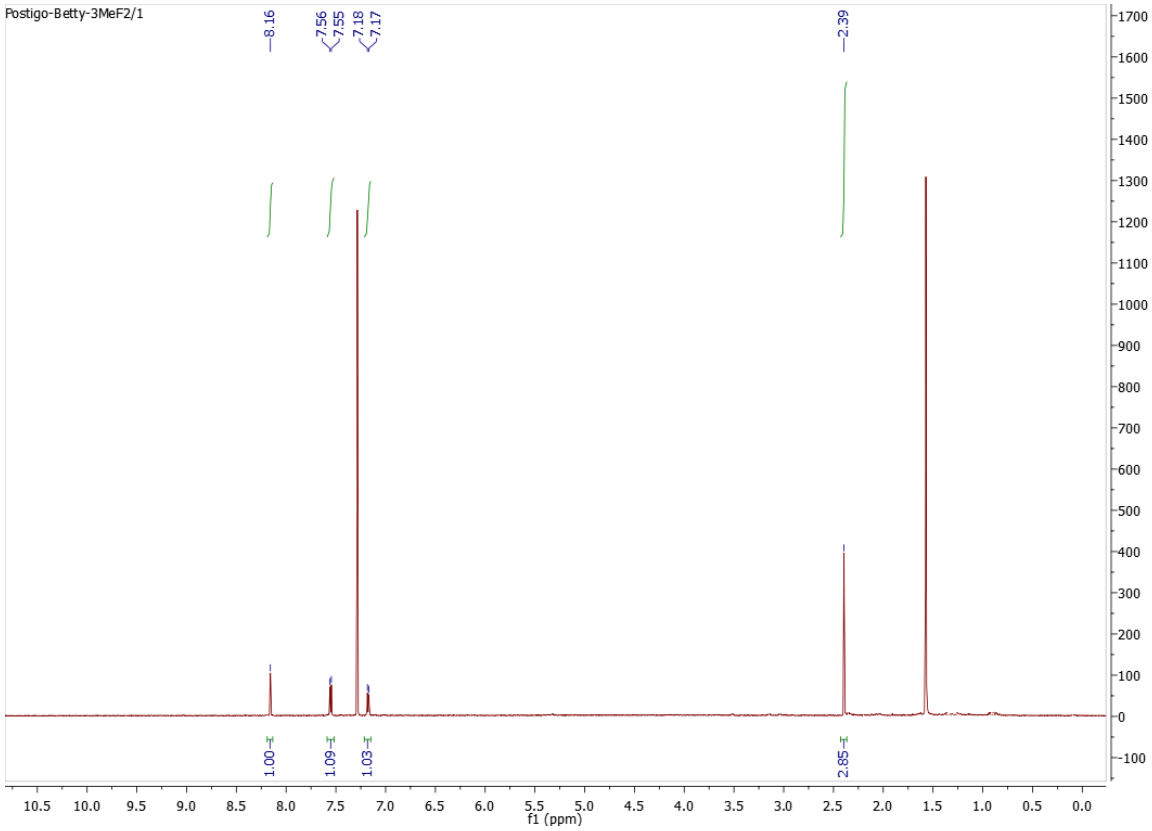




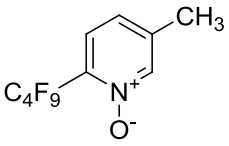


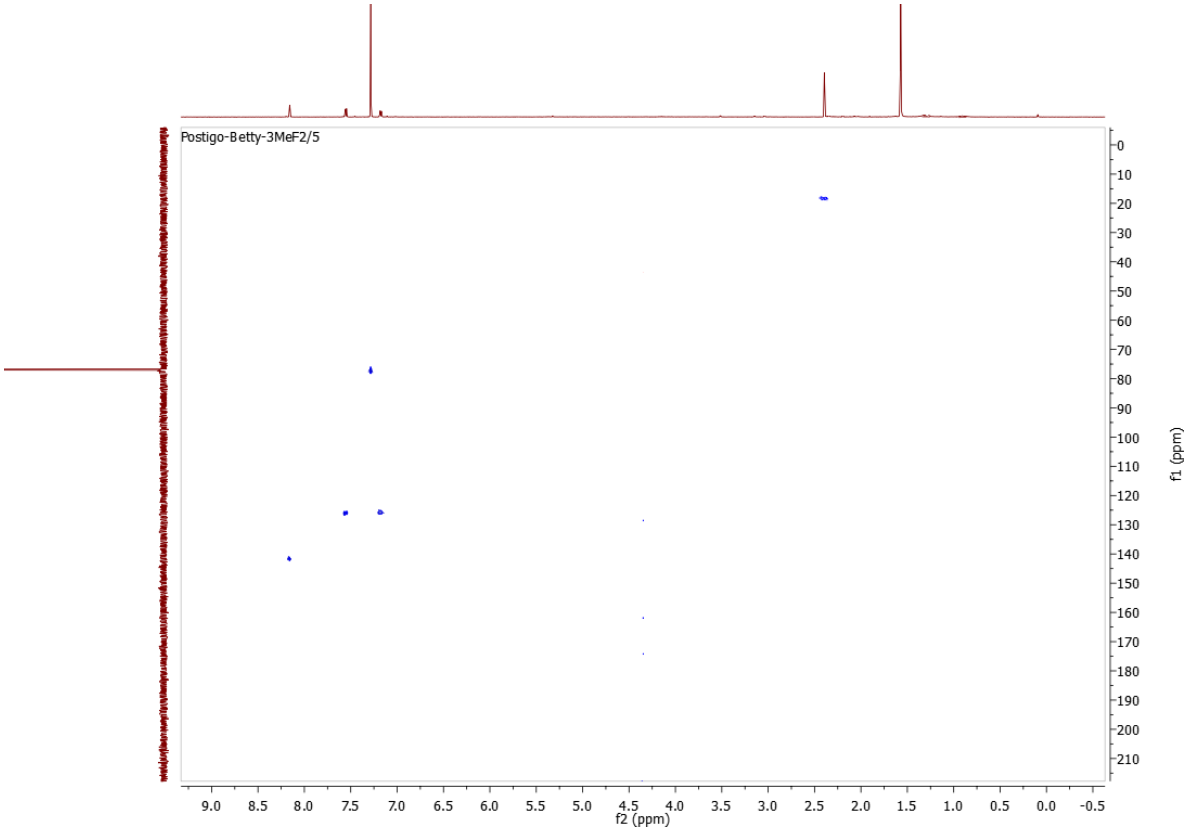
1H NMR spectrum 0f 32 in CDCl3



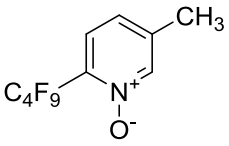


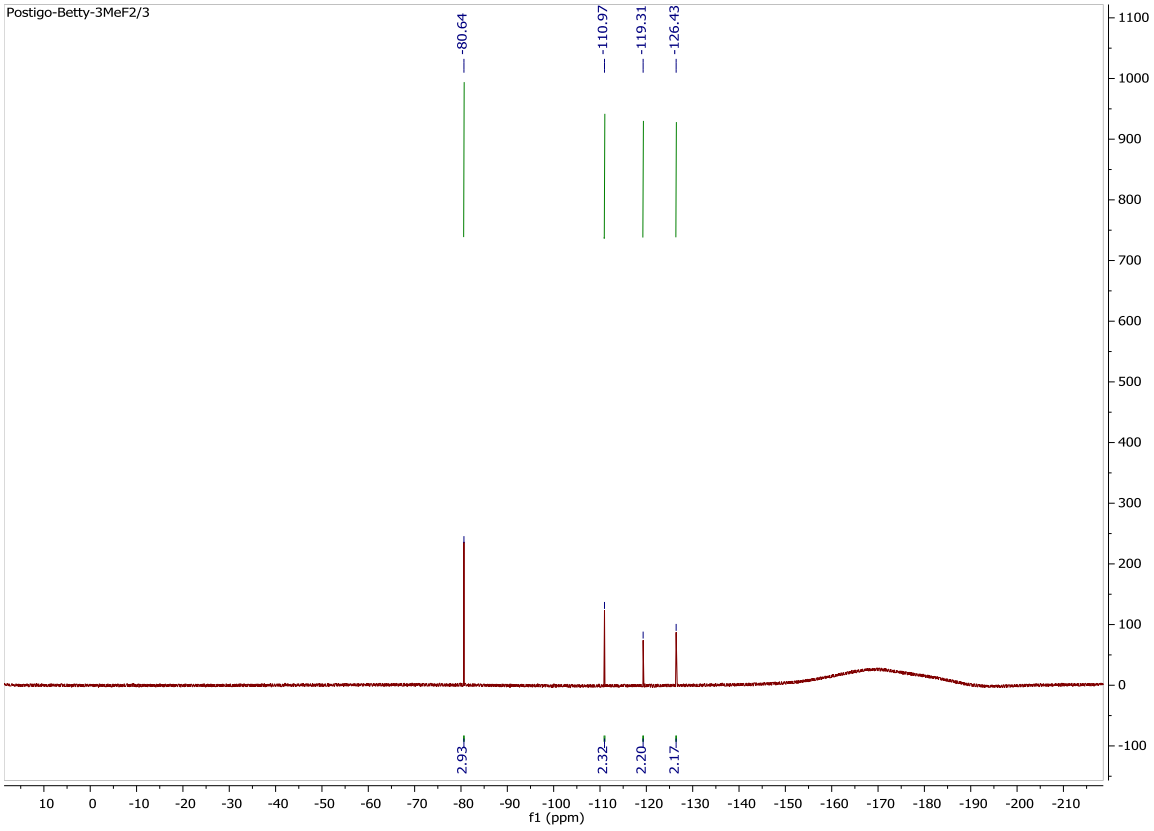
13C NMR spectrum 0f 32 in CDCl3



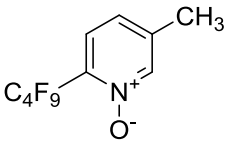


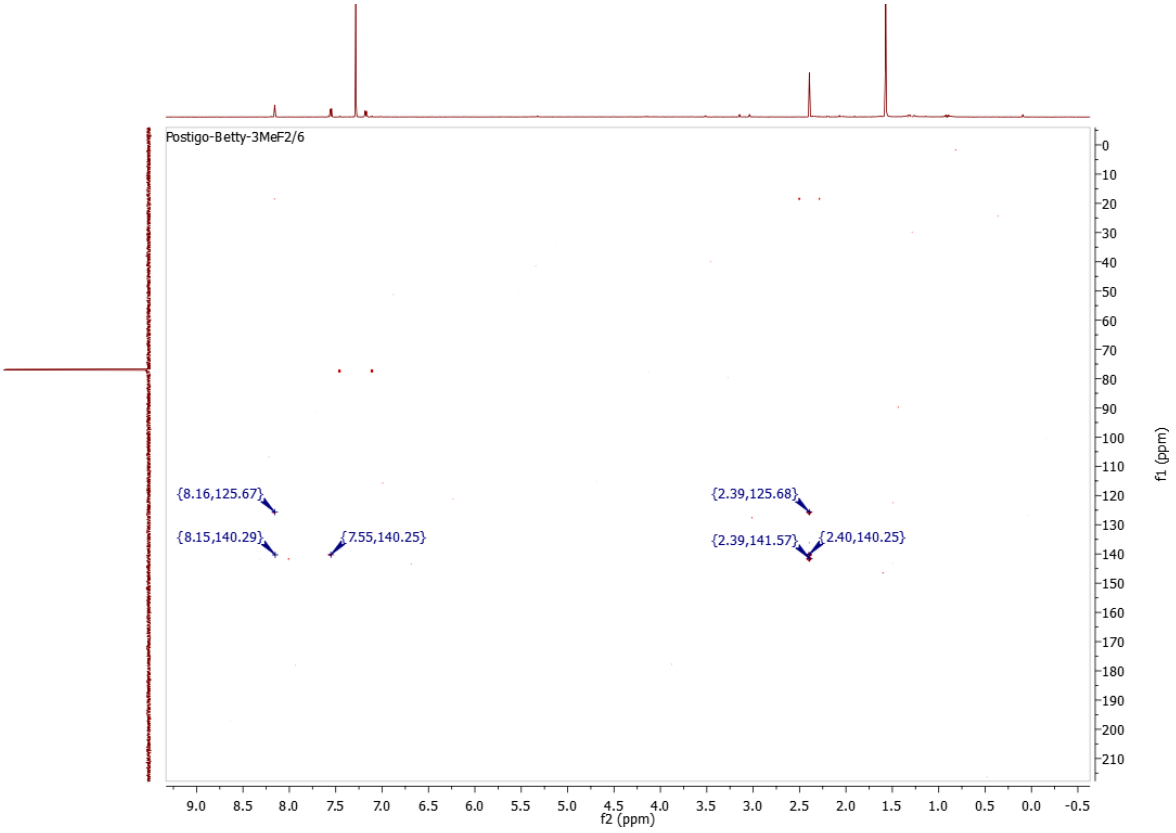
19F NMR spectrum 0f 32 in CDCl3



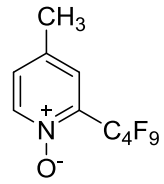


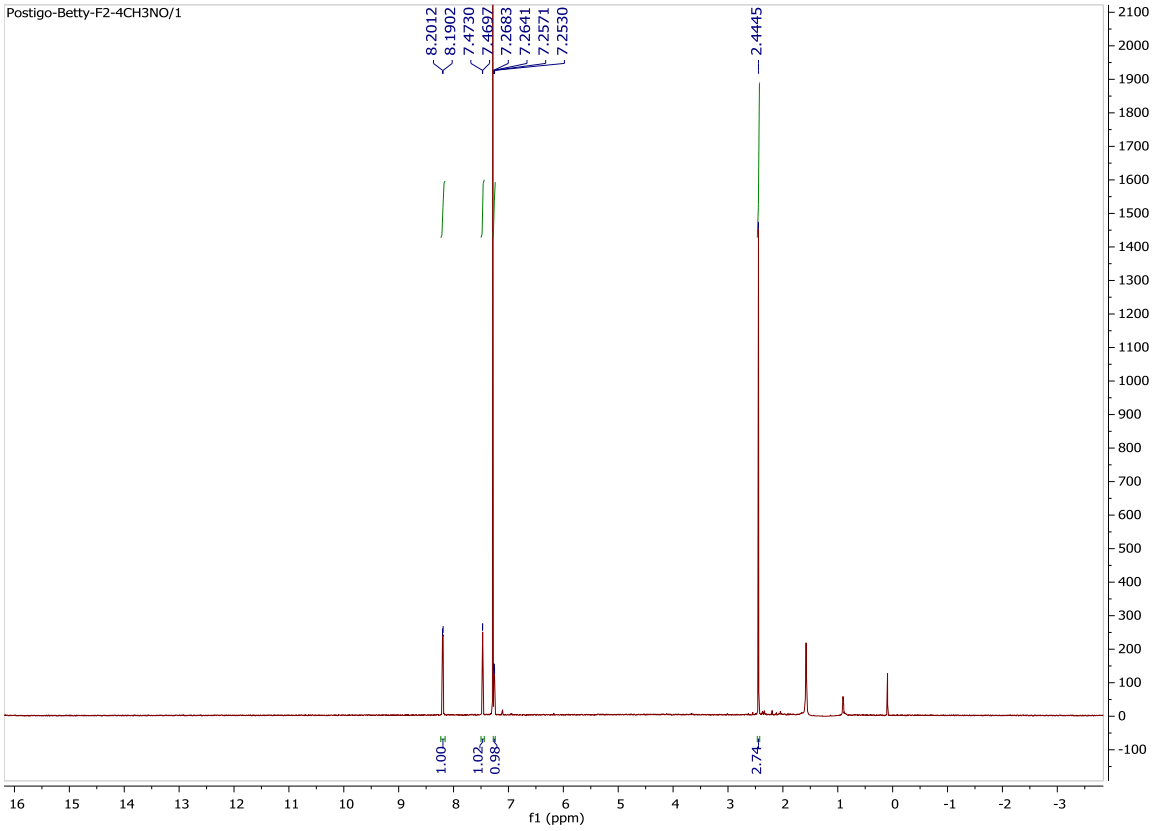
HMBC NMR spectrum 0f 32 in CDCl3



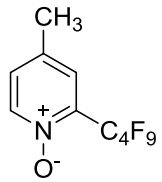


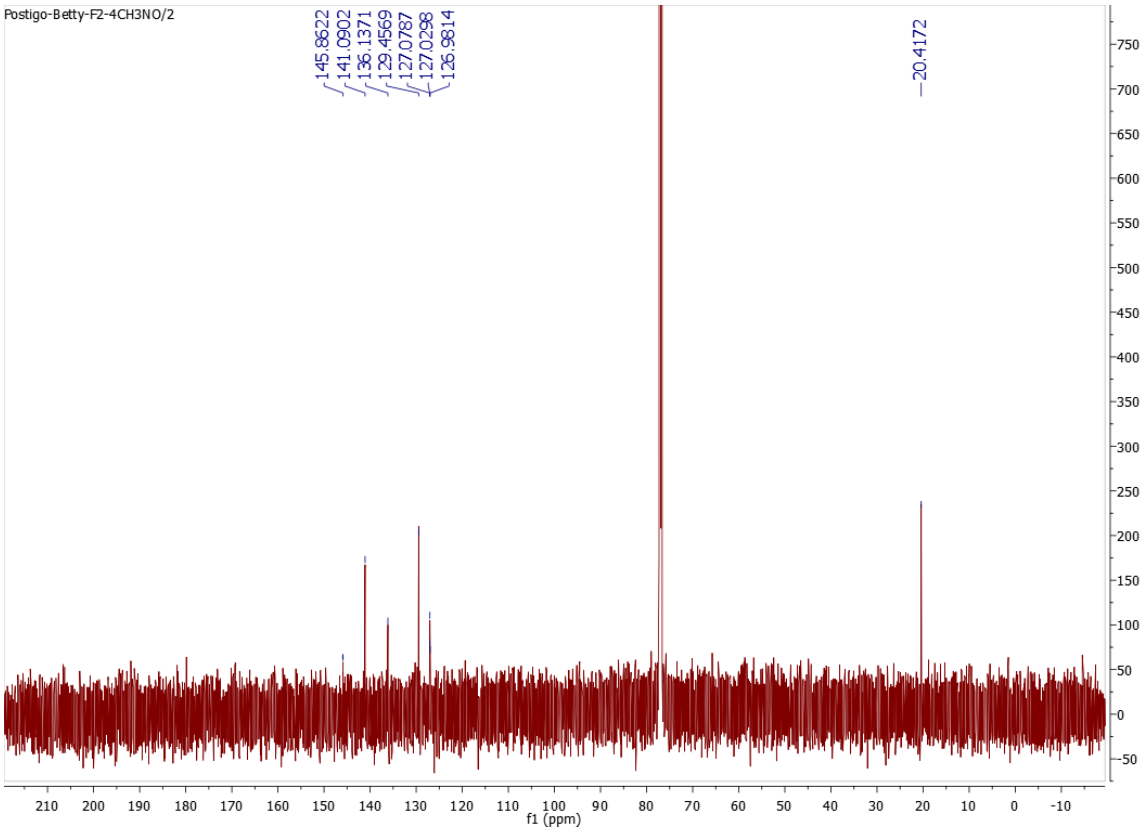
1H NMR spectrum
0f 34 in CDCl3



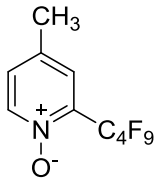


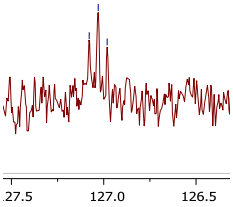
13C NMR spectrum 0f 34 in CDCl3

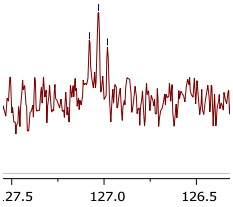




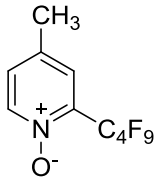
13C NMR spectrum 0f 34 in CDCl3, enlargement

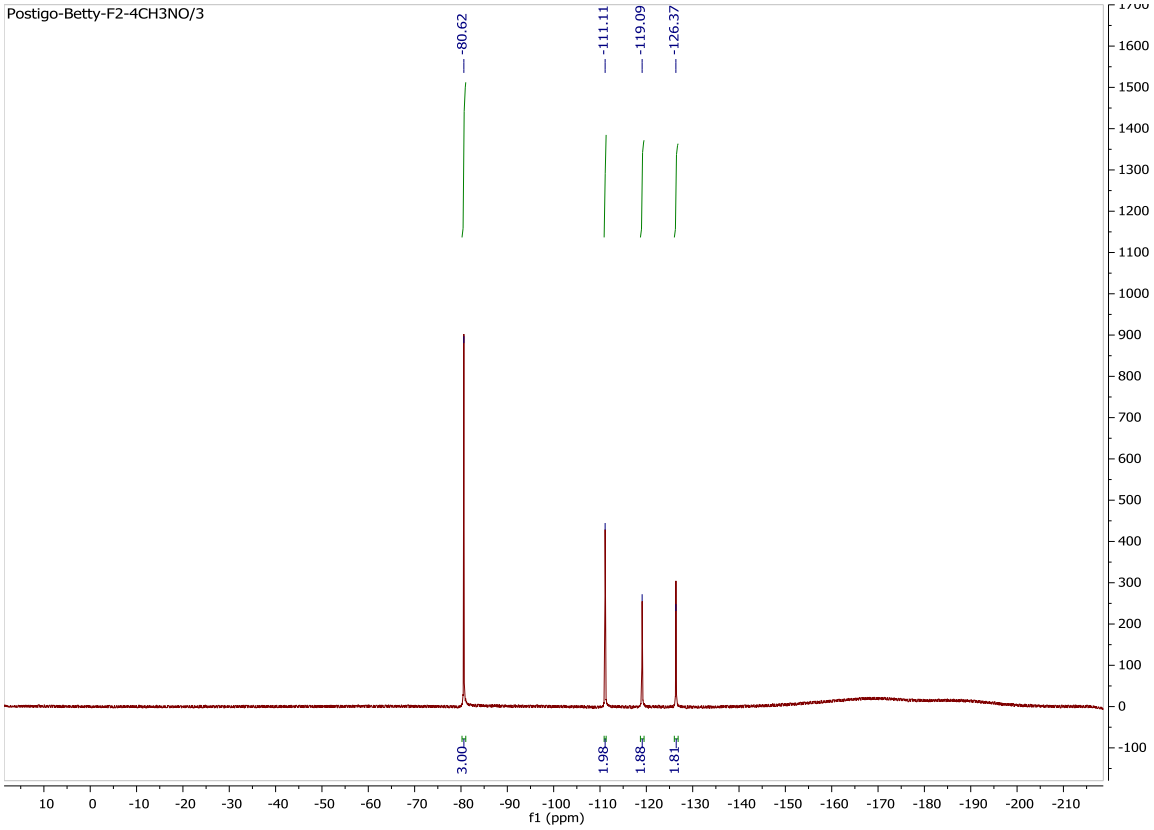




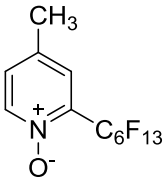


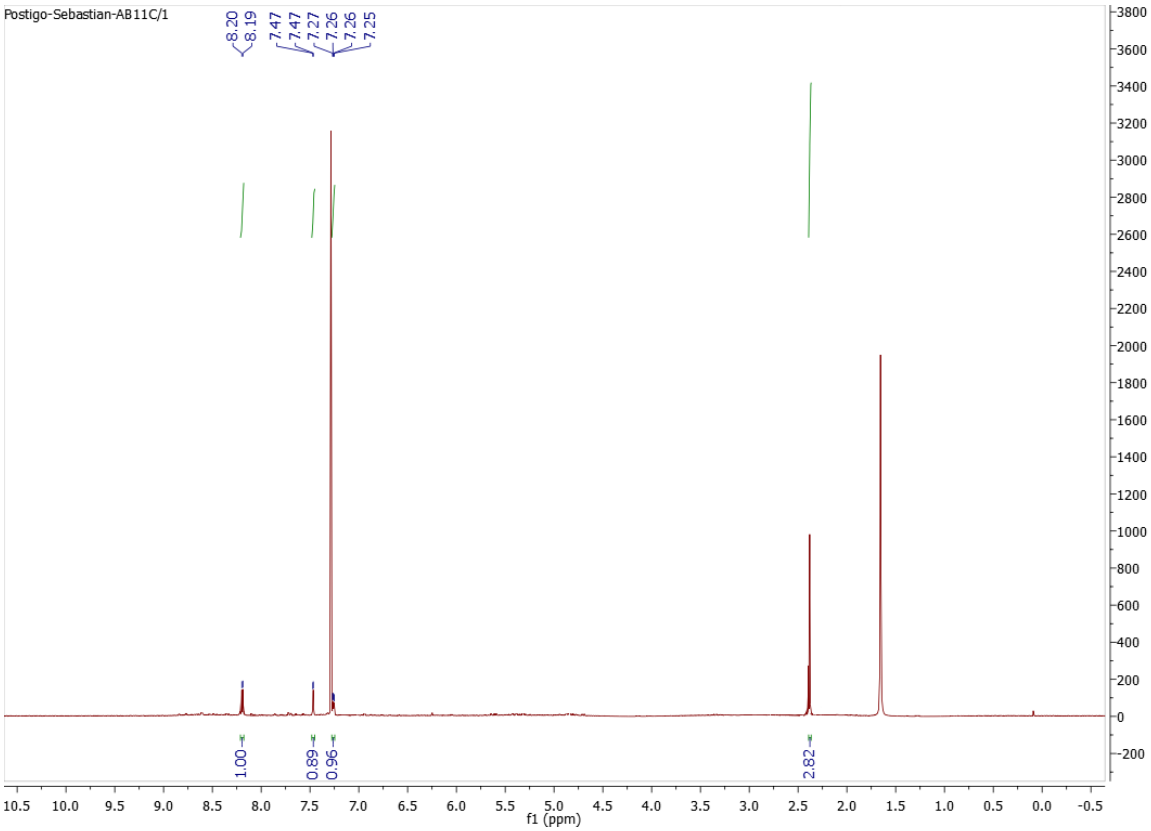
19F NMR spectrum 0f 34 in CDCl3



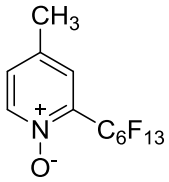


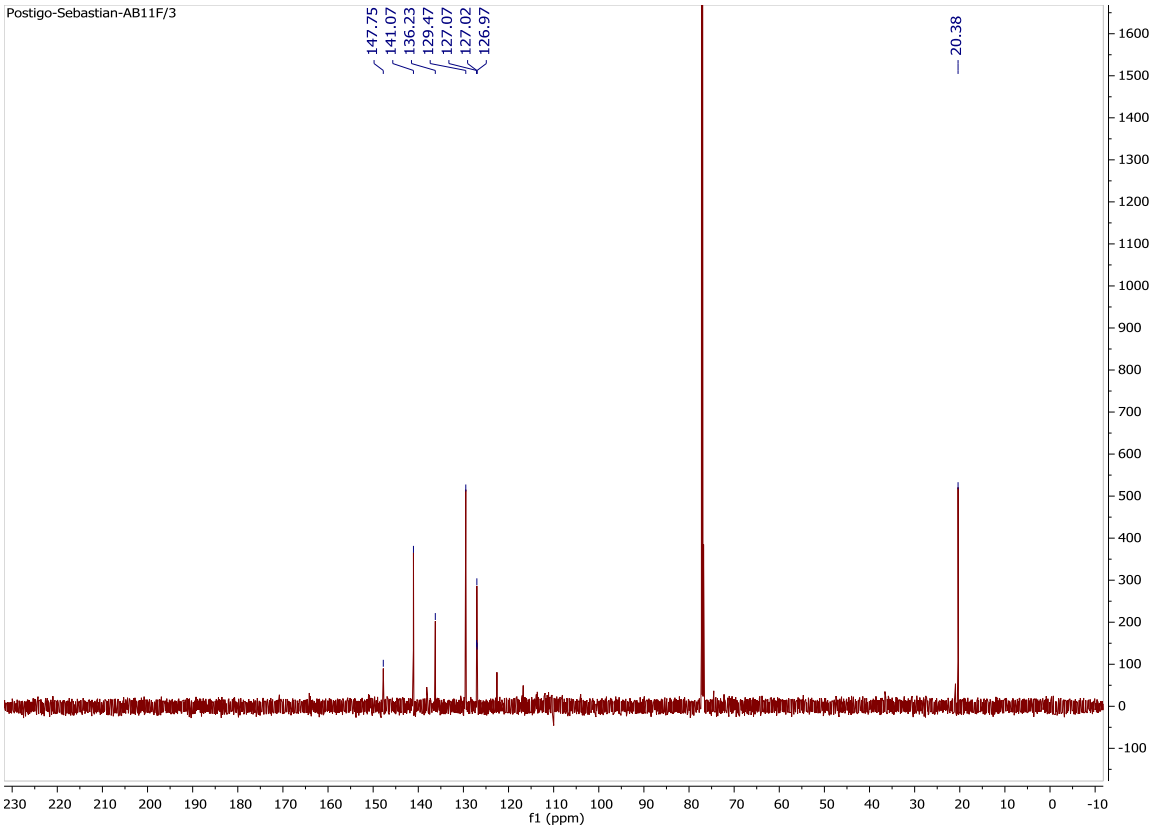
1H NMR spectrum
0f 35 in CDCl3



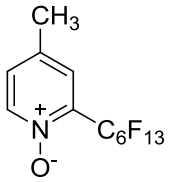


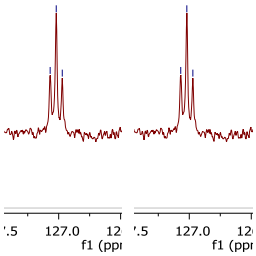
13C NMR spectrum 0f 35 in CDCl3



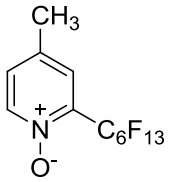


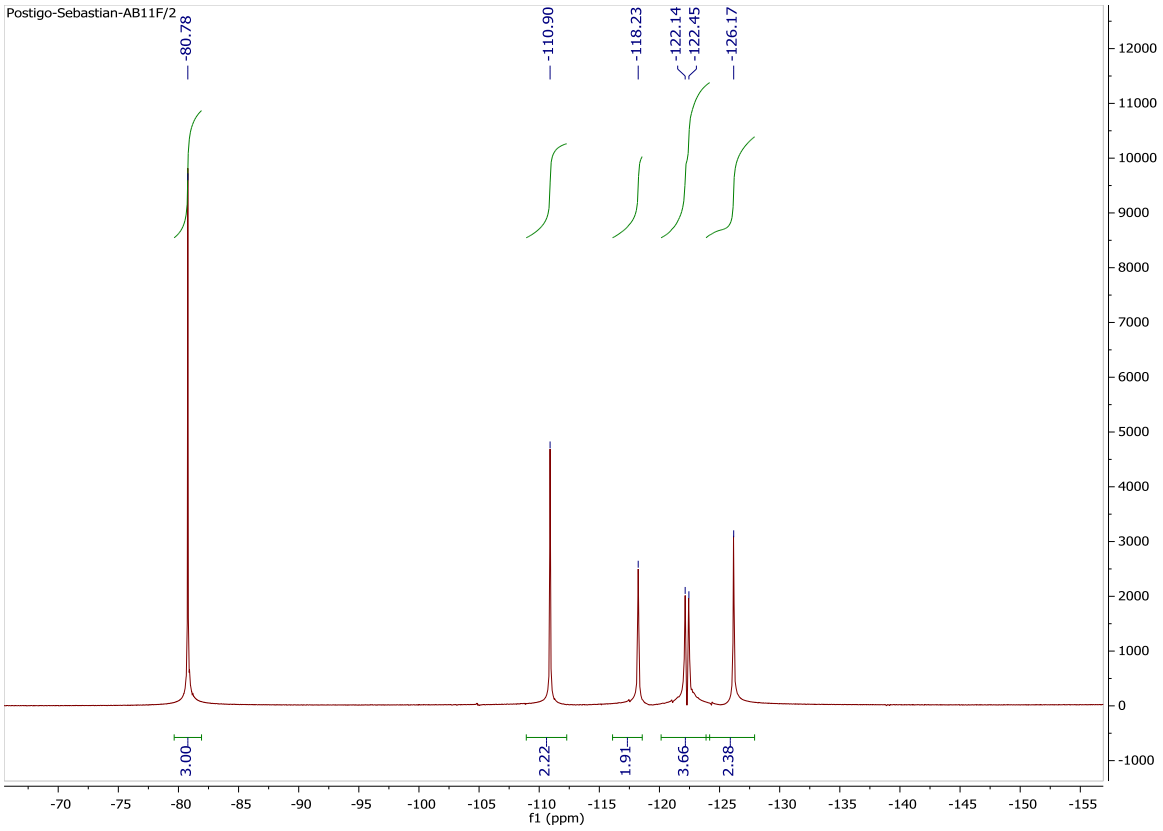
13C NMR spectrum 0f 35 in CDCl3, enlargement



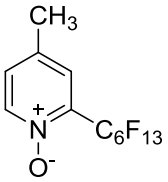


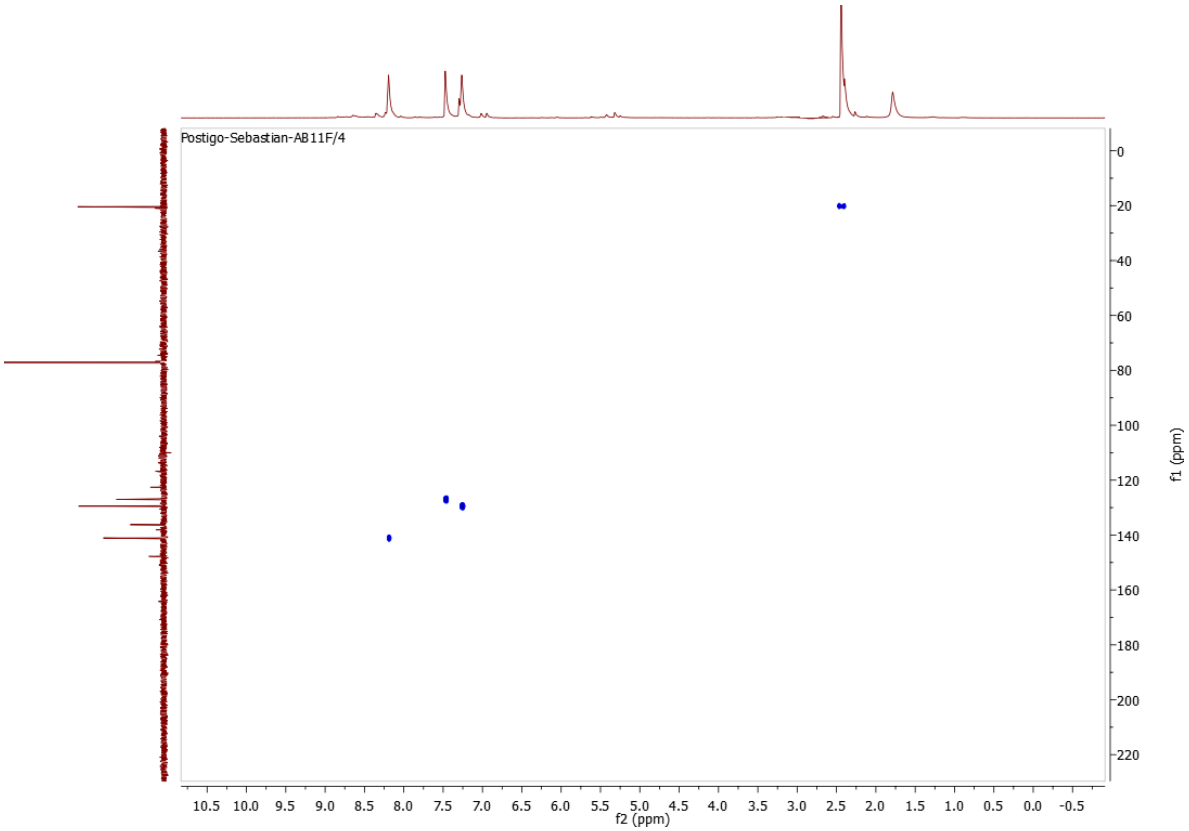
19F NMR spectrum 0f 35 in CDCl3



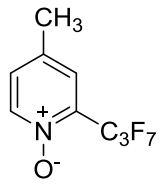


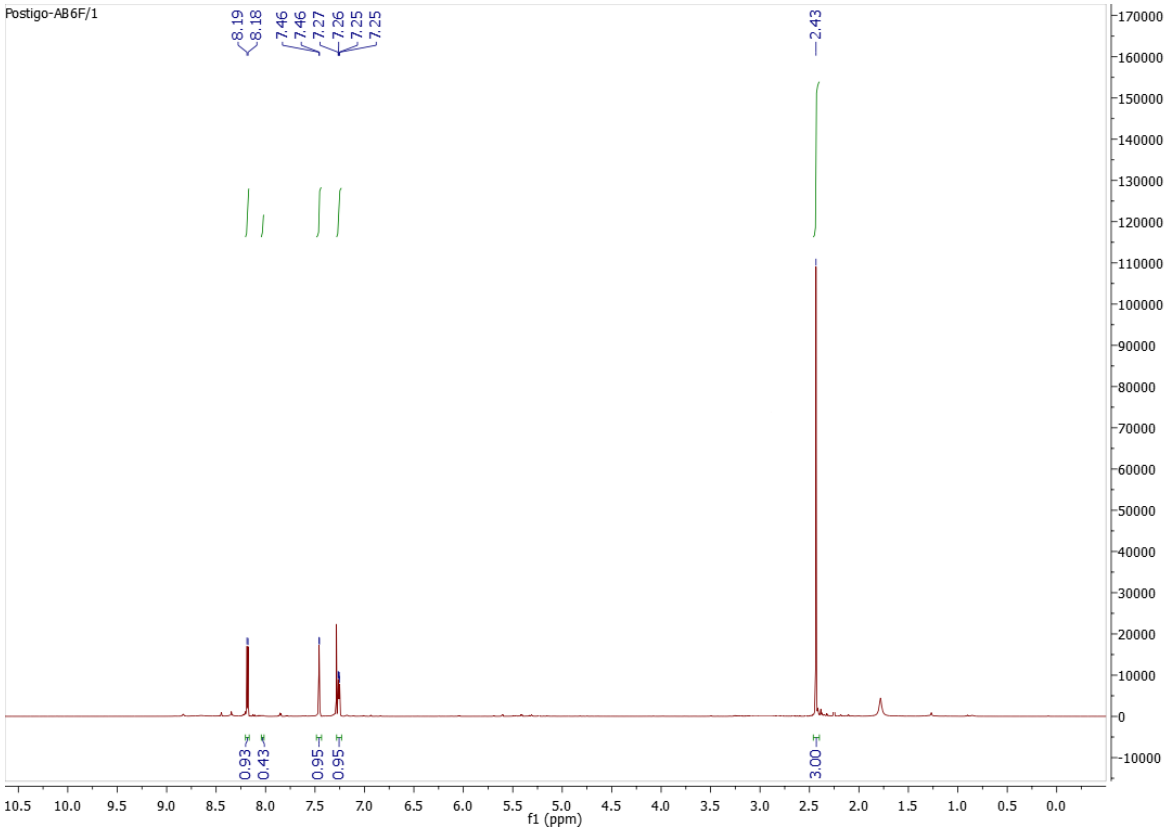
HSQC NMR spectrum 0f 35 in CDCl3



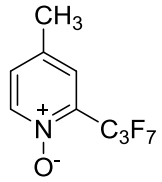


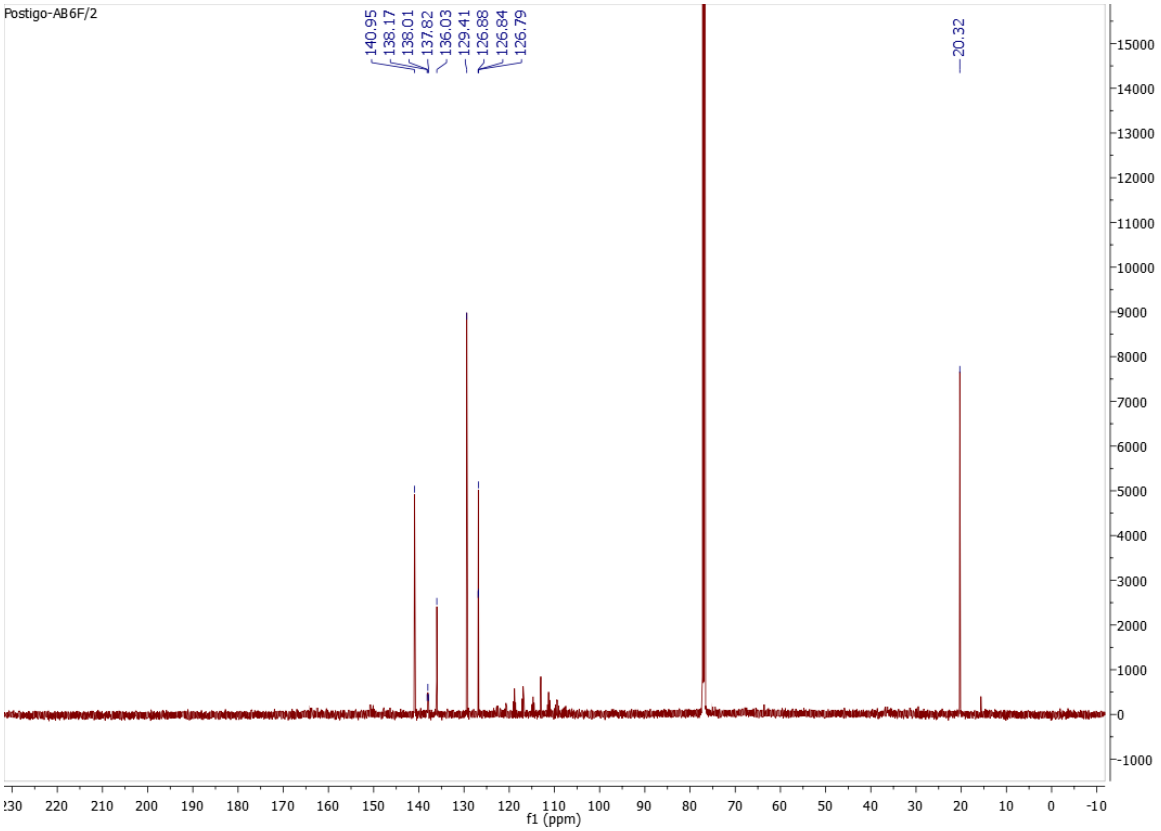
1H NMR spectrum
0f 36 in CDCl3



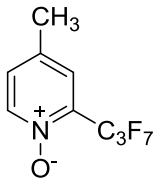


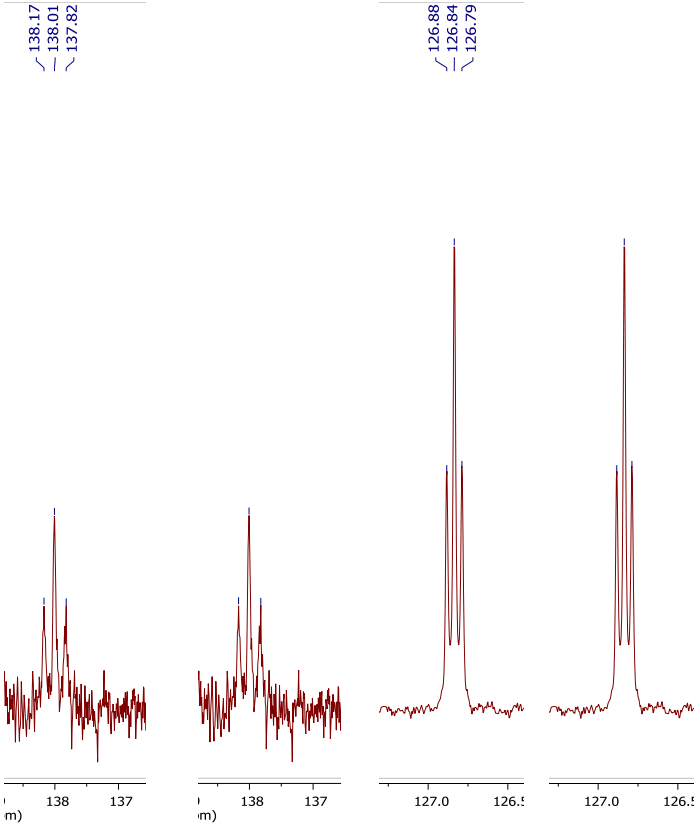
13C NMR spectrum 0f 36 in CDCl3



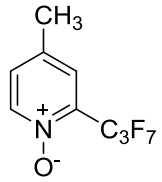


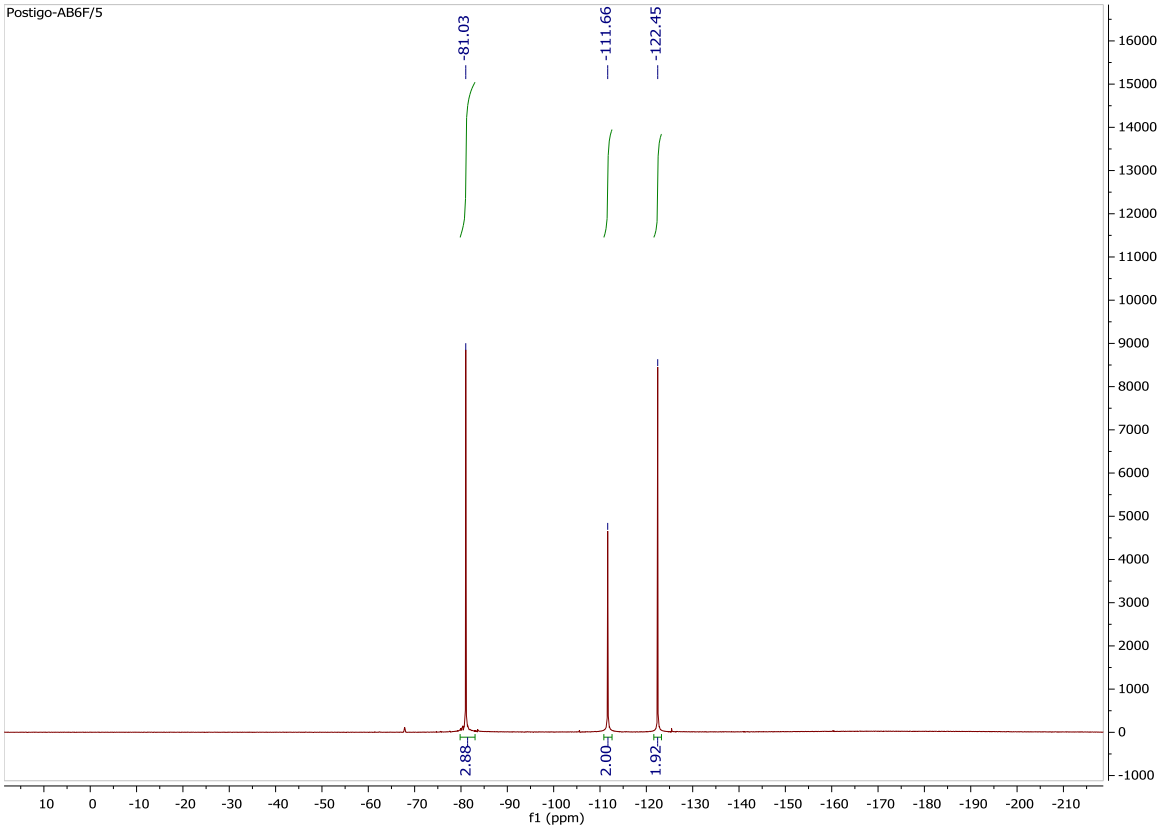
13C NMR spectrum 0f 36 in CDCl3, enlargement



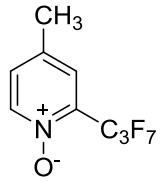


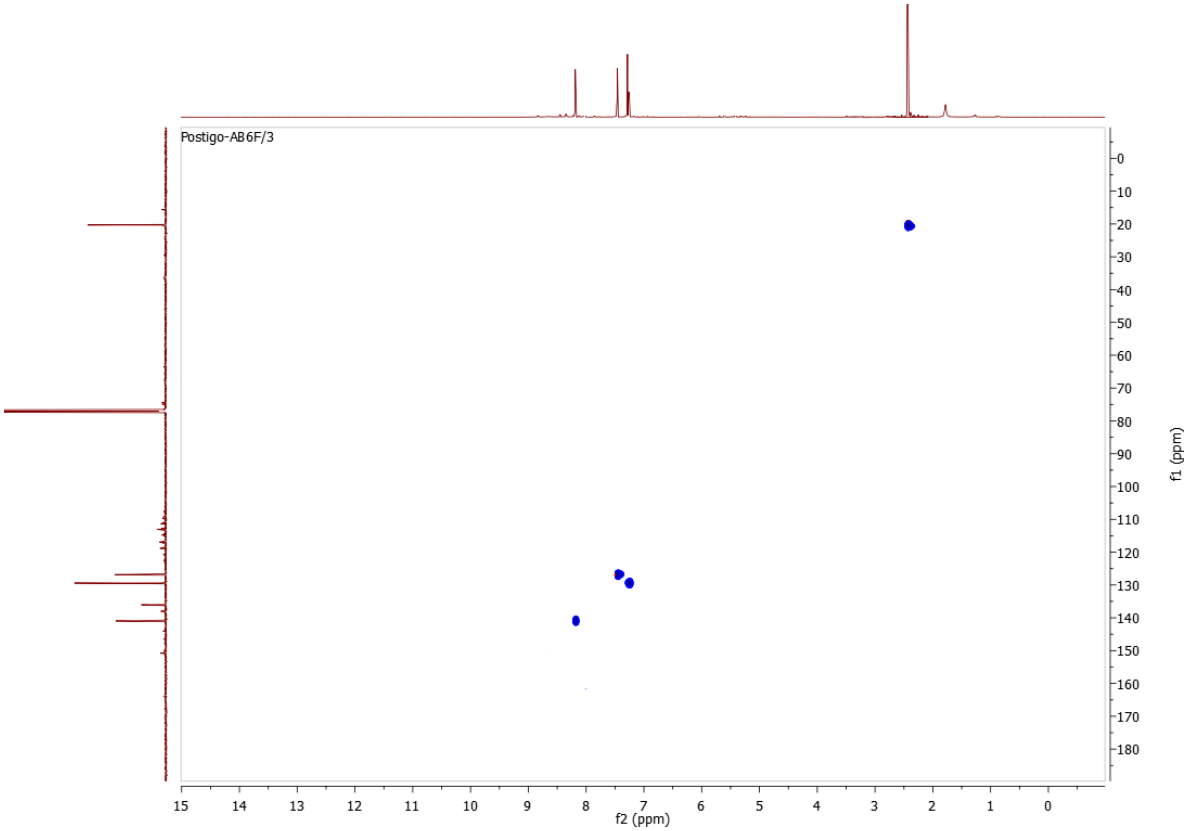
19F NMR spectrum 0f 36 in CDCl3



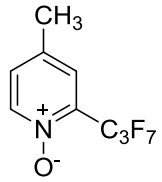


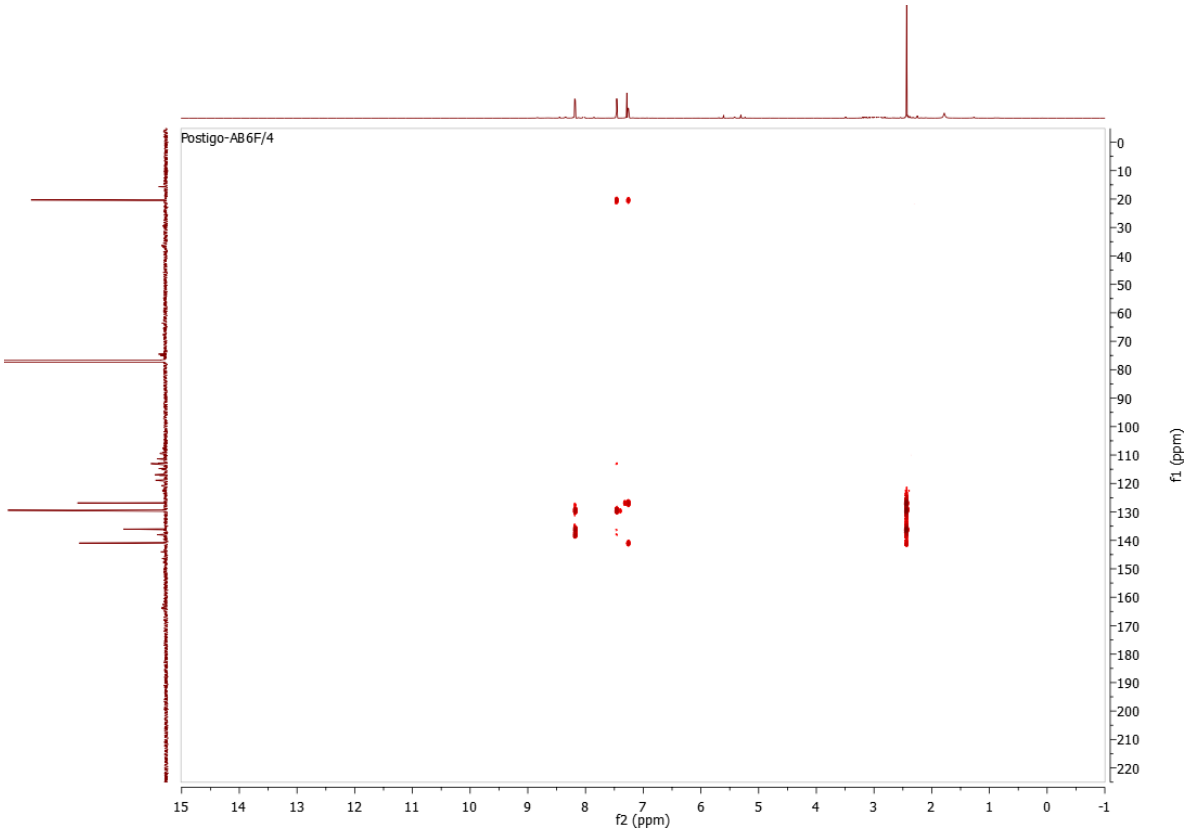
HSQC NMR spectrum 0f 36 in CDCl3



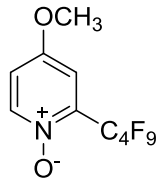


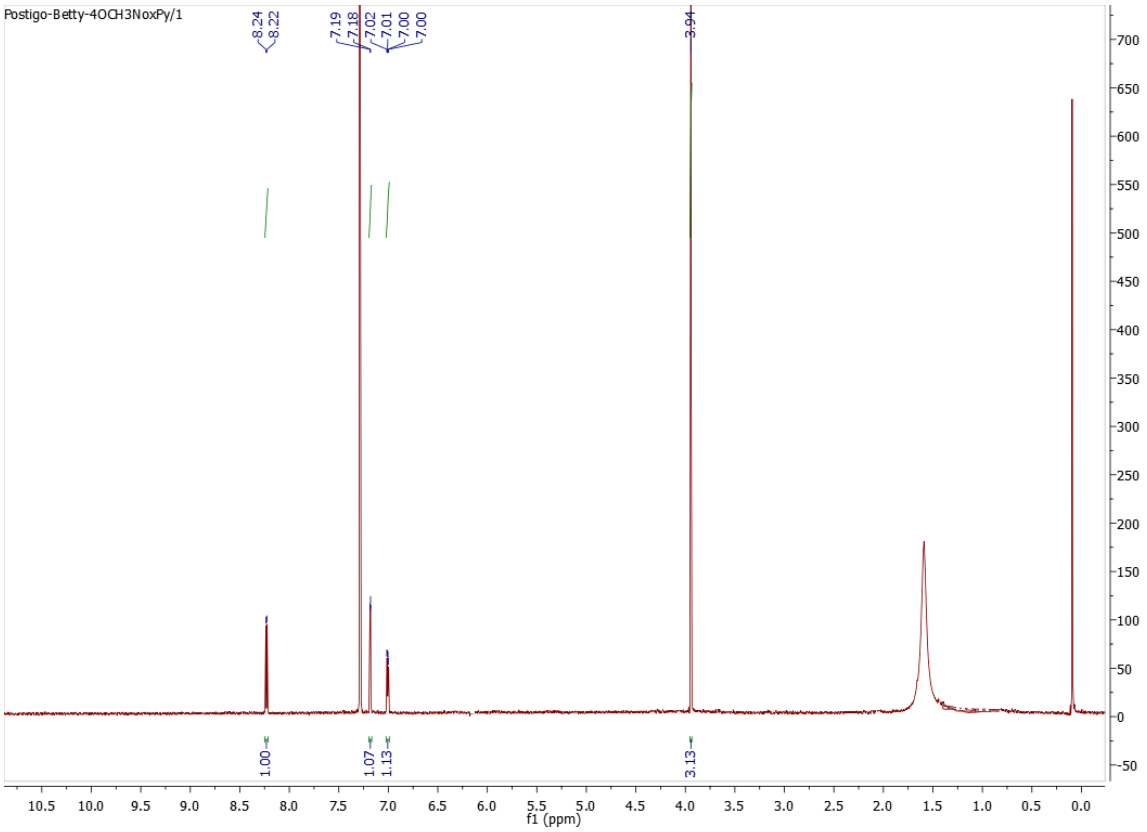
HMBC NMR spectrum 0f 36 in CDCl3



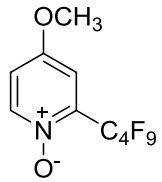


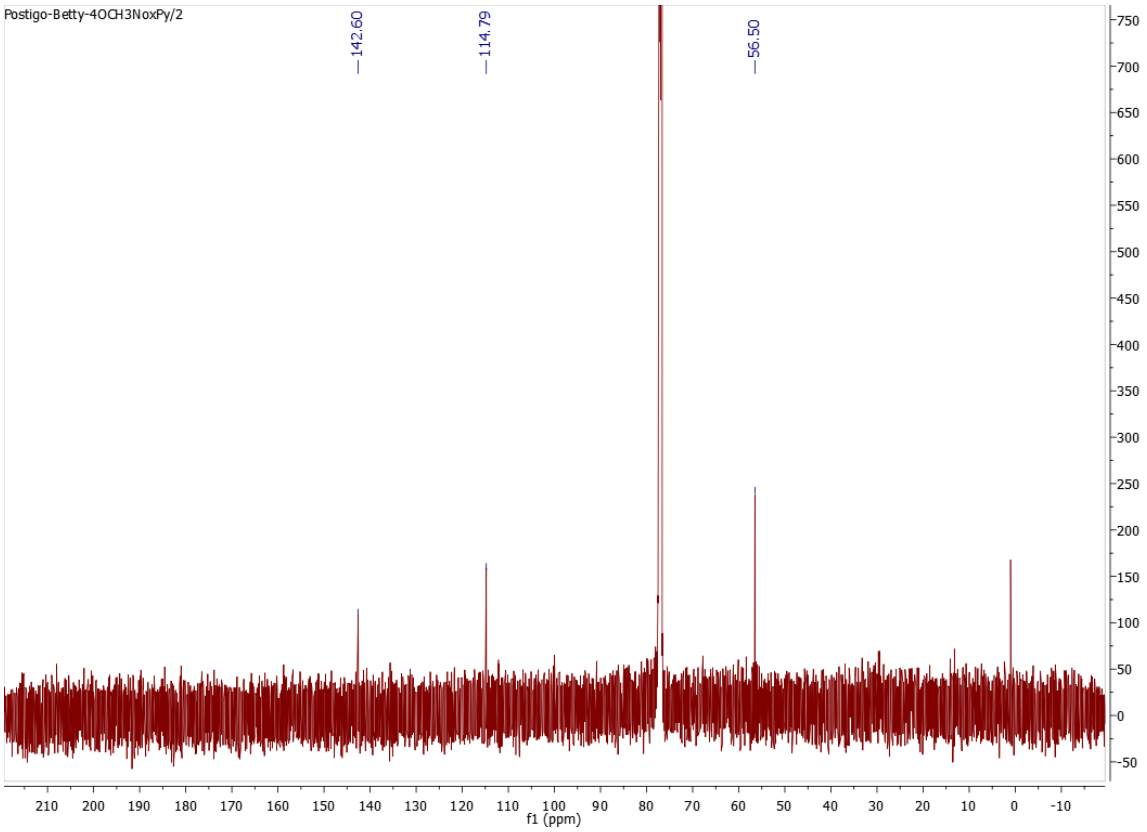
1H NMR spectrum
0f 38 in CDCl3



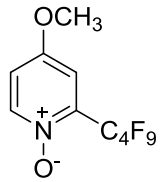


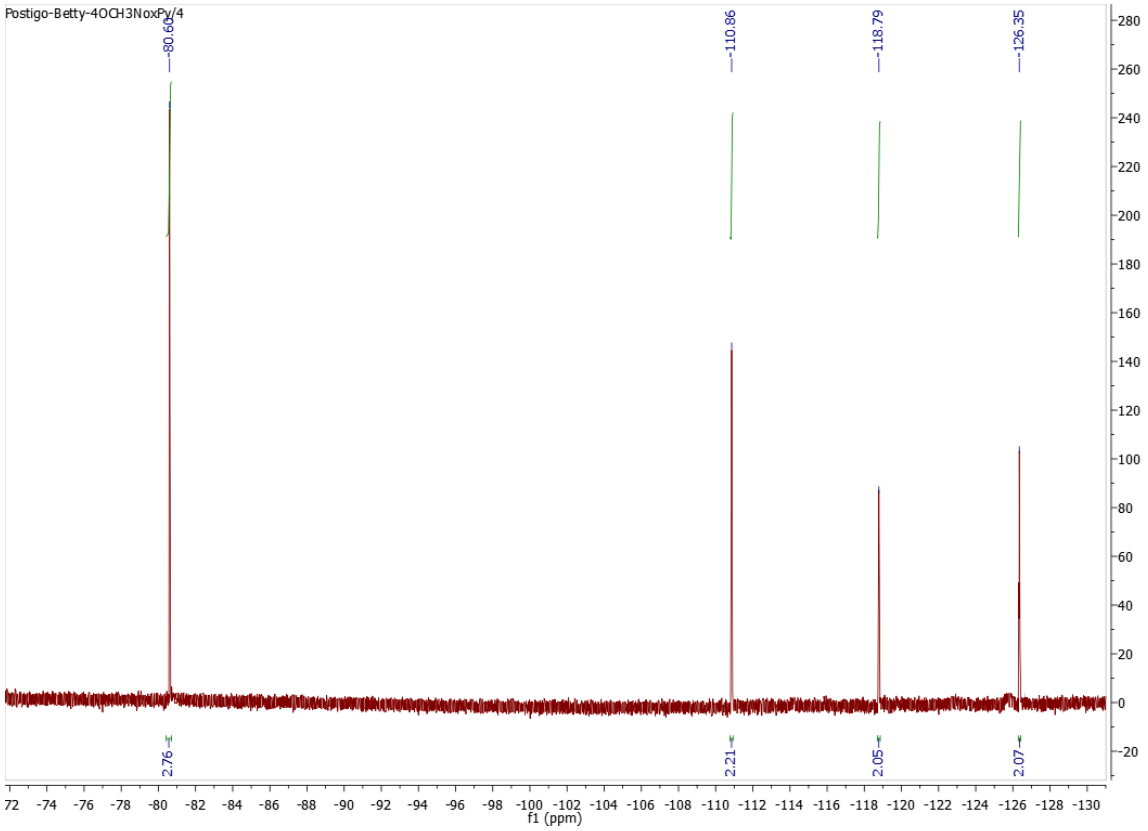
13C NMR spectrum 0f 38 in CDCl3



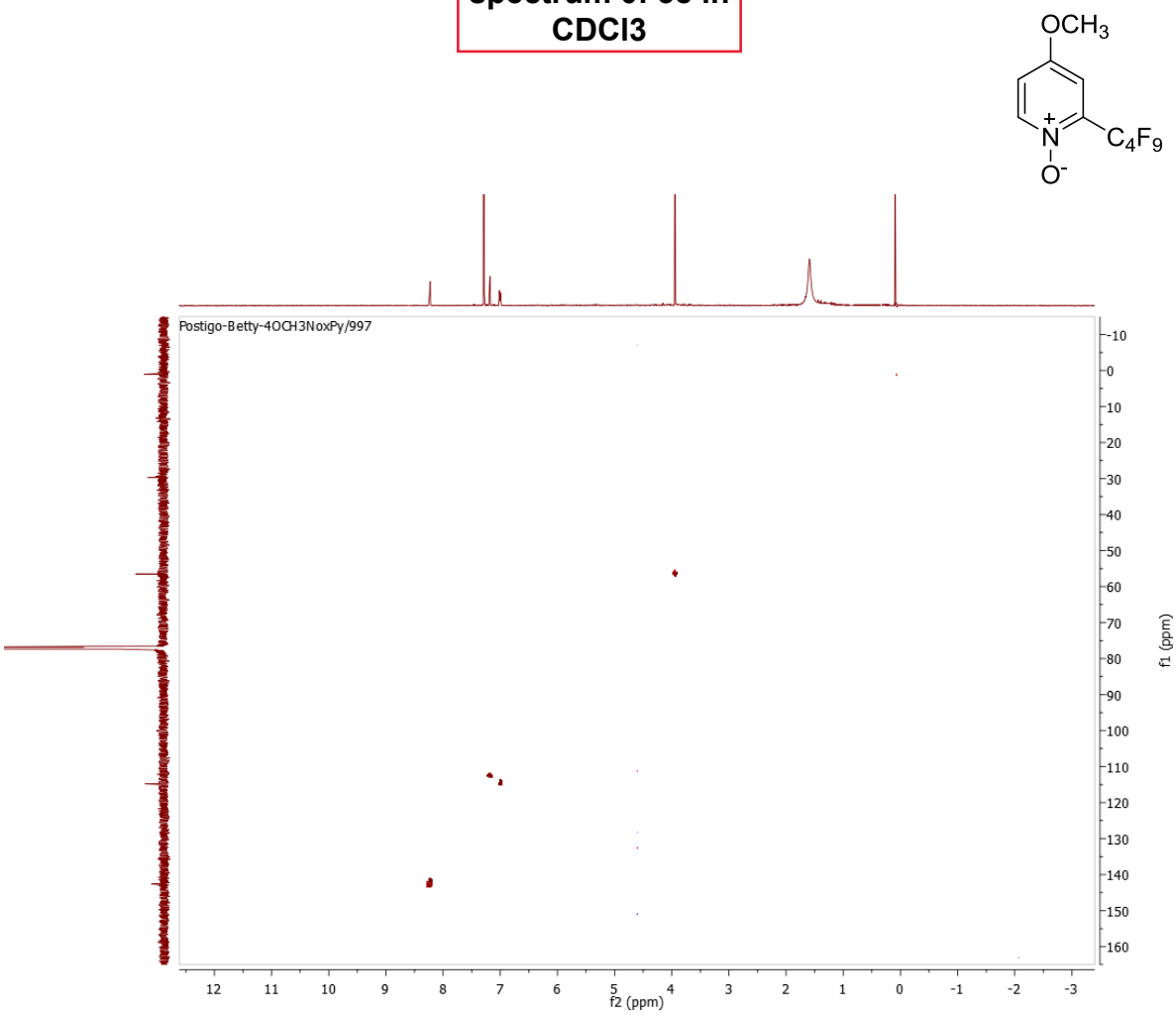


19F NMR spectrum 0f 38 in CDCl3

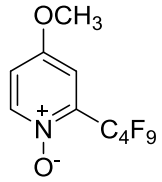


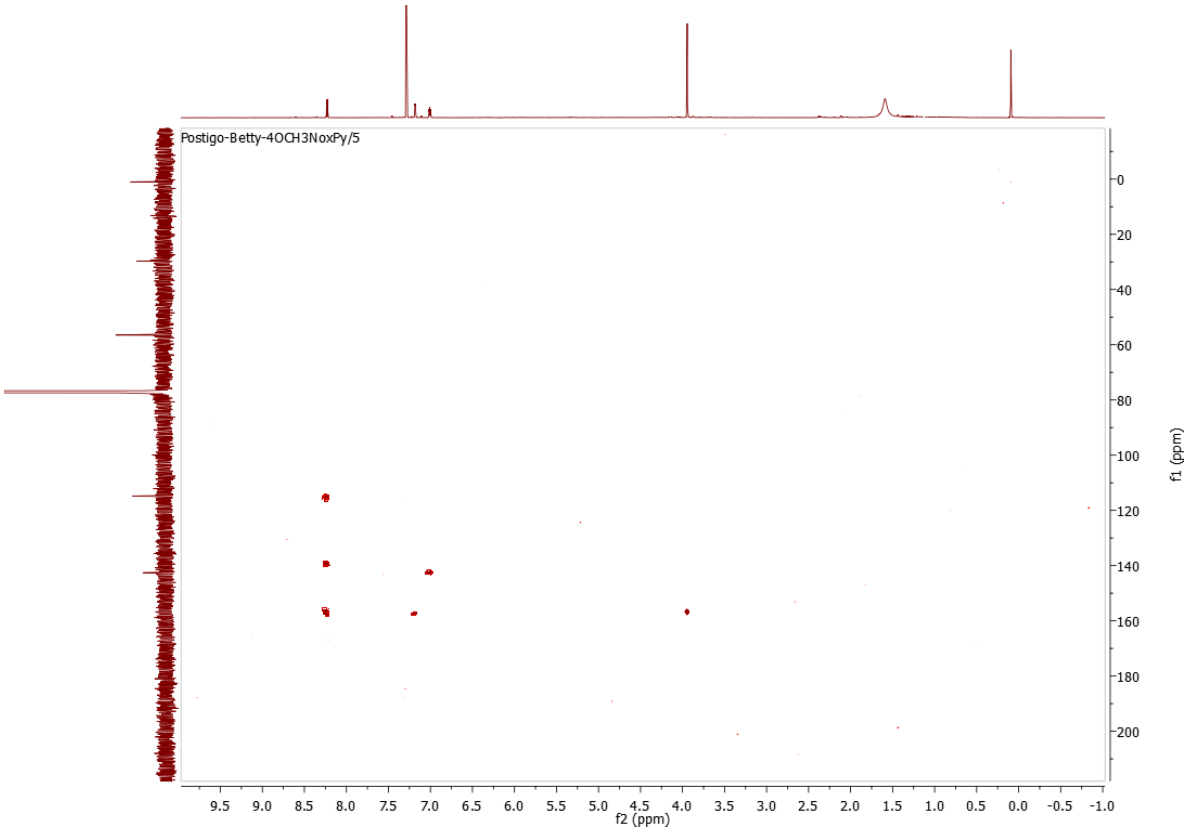


HSQC NMR spectrum 0f 38 in CDCl3

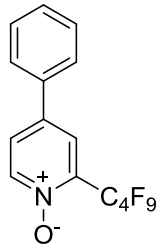


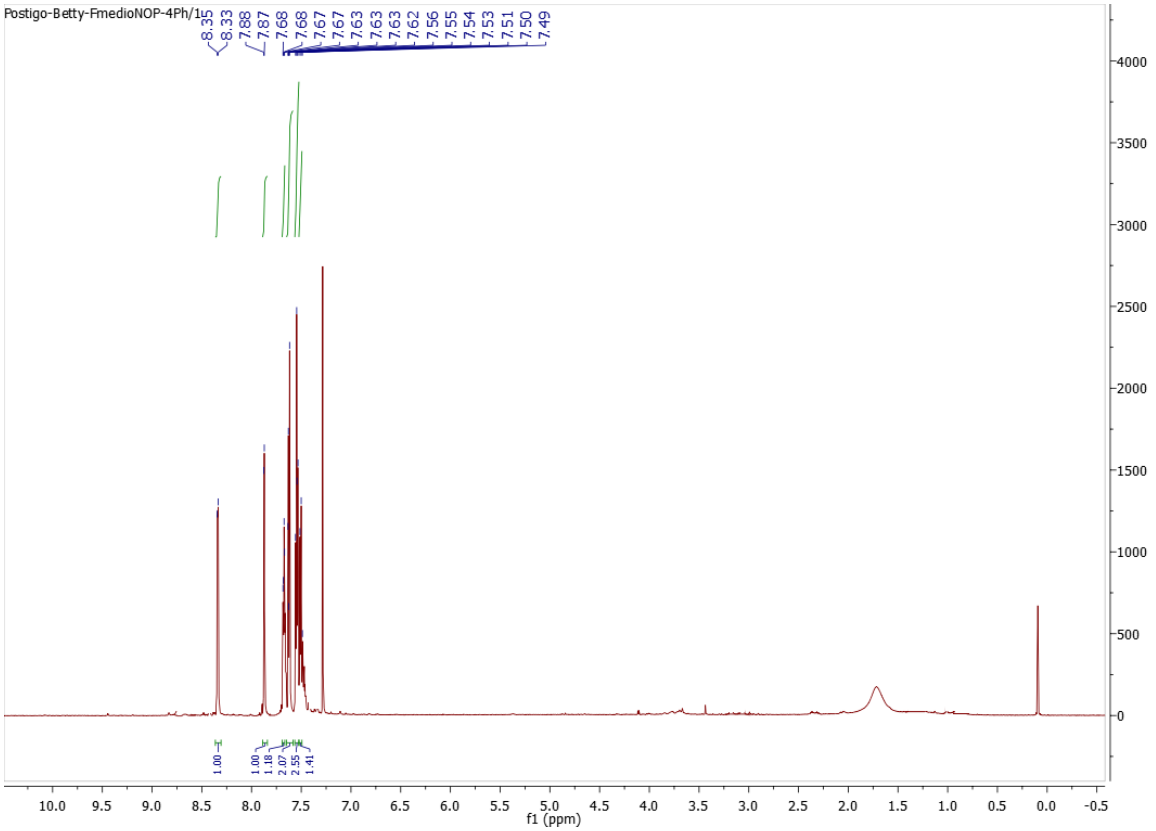
HMBC NMR spectrum 0f 38 in CDCl3



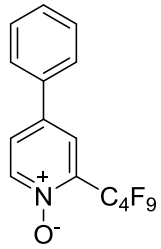


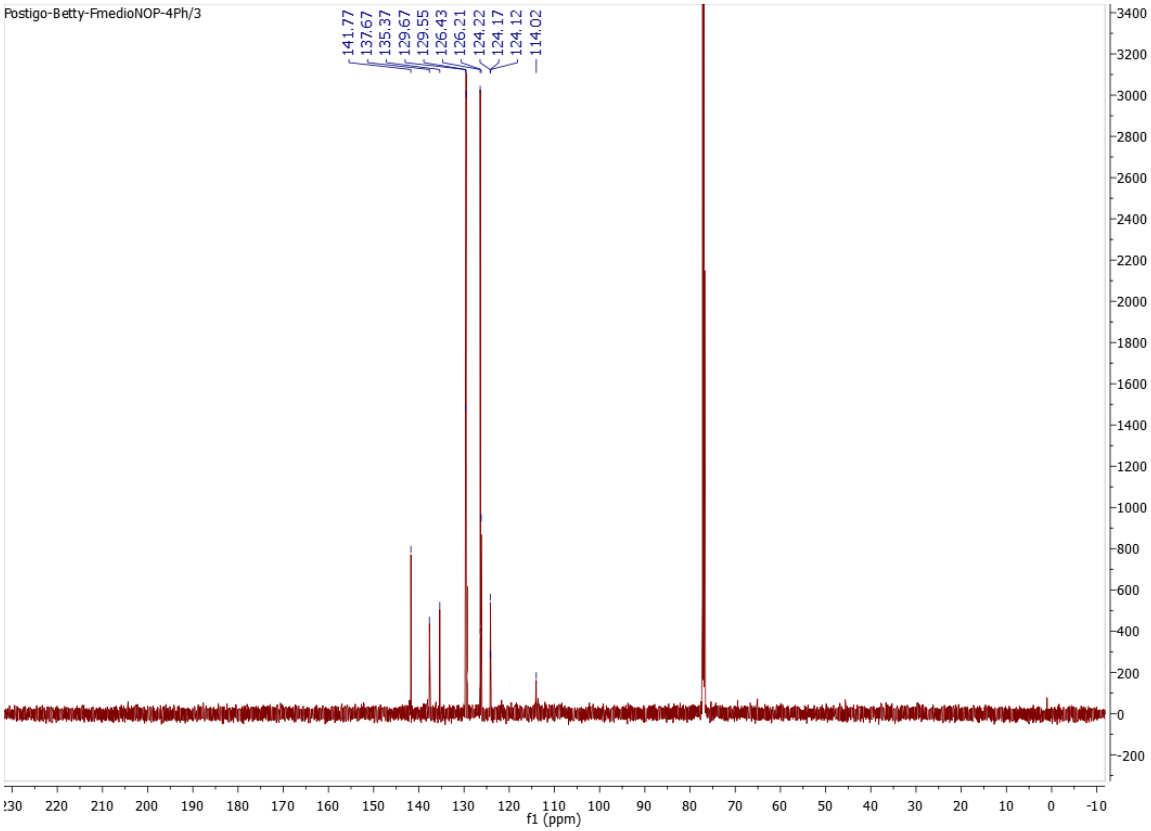
1H NMR spectrum 0f 40a in CDCl3



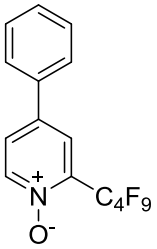


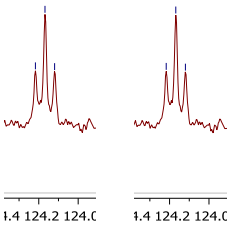
13C NMR spectrum 0f 40a in CDCl3



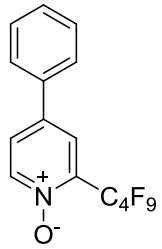


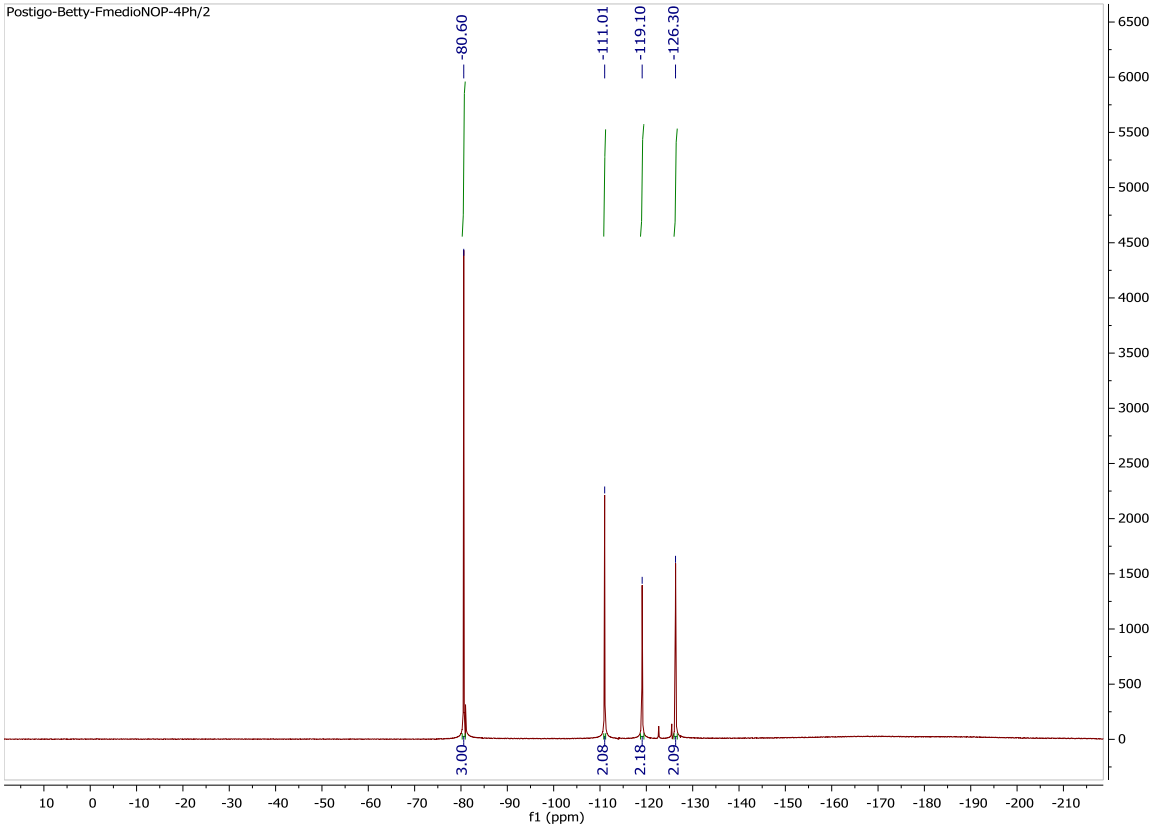
13C NMR spectrum 0f 40a in CDCl3, enlargement



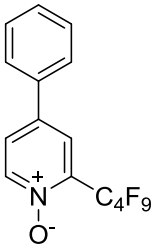


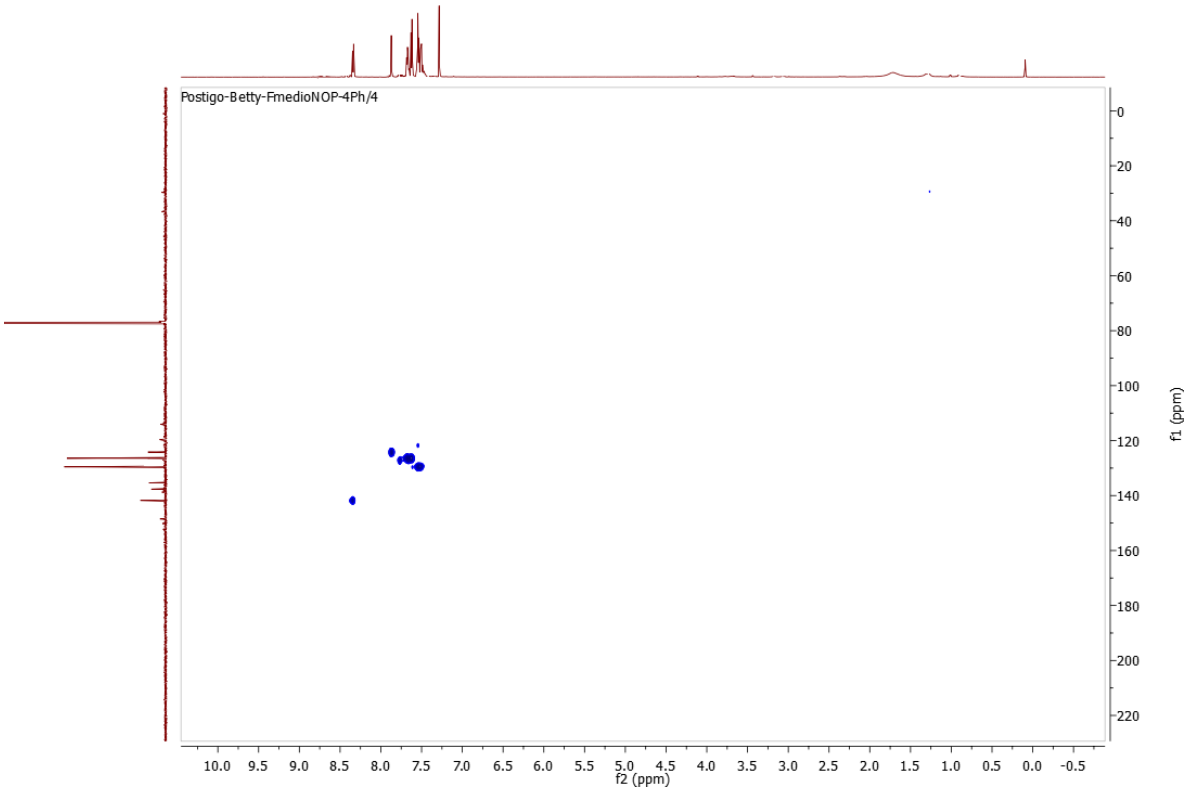
19F NMR spectrum 0f 40a in CDCl3



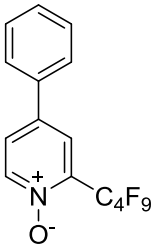


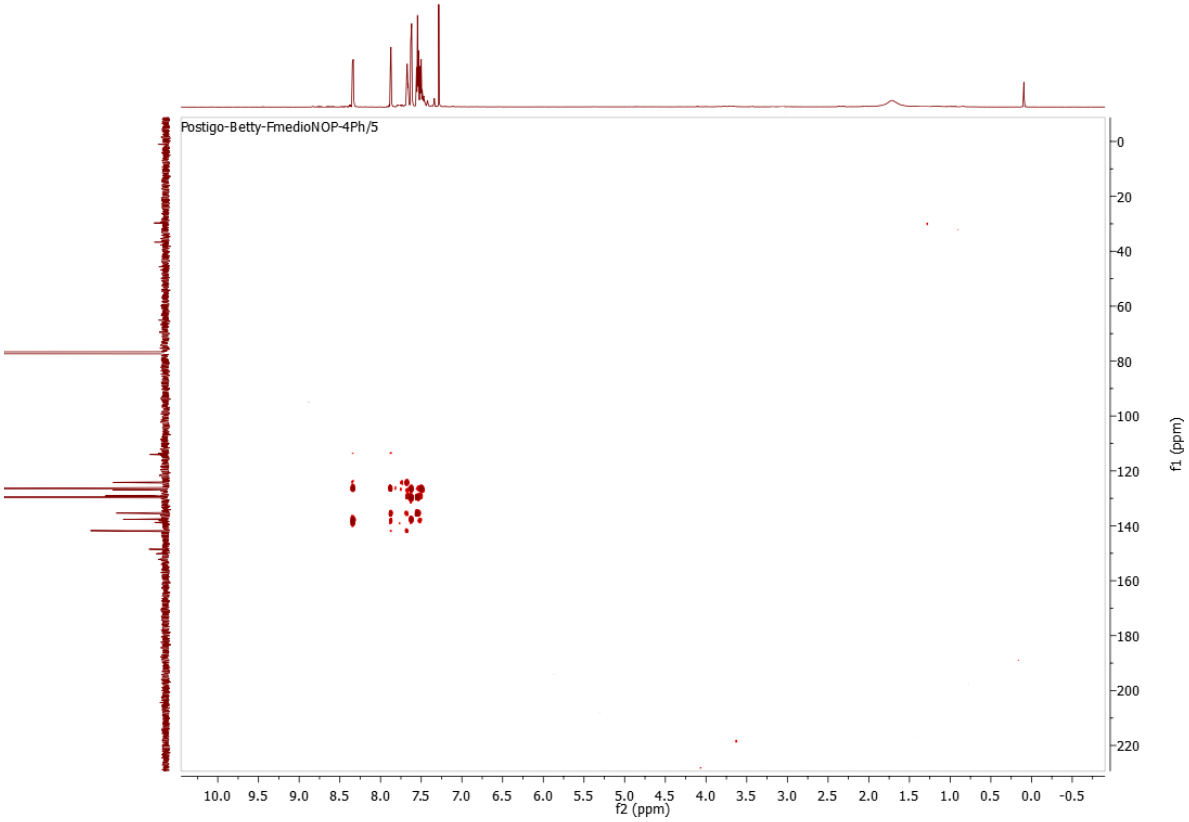
HSQC NMR spectrum 0f 40a in CDCl3



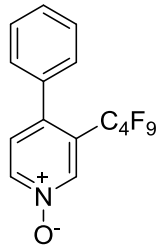


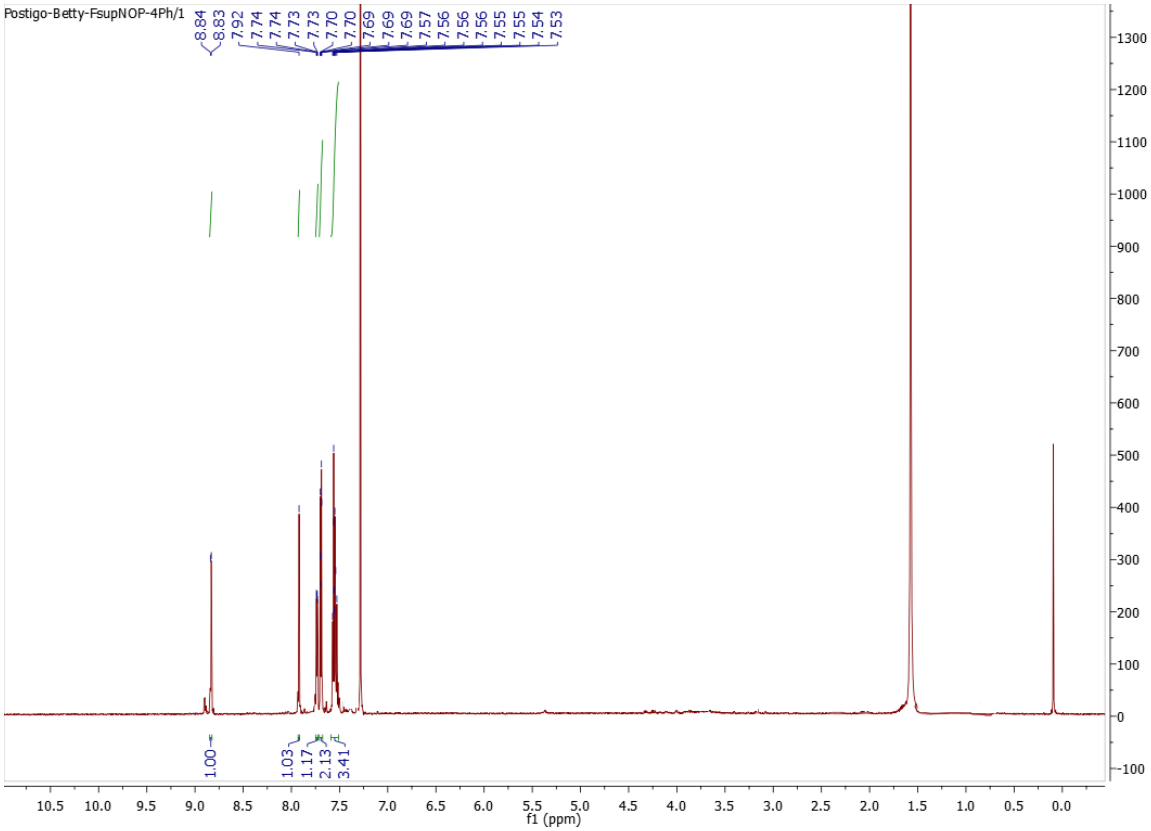
HMBC NMR spectrum 0f 40a in CDCl3



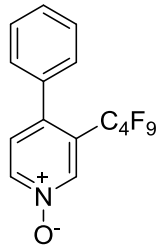


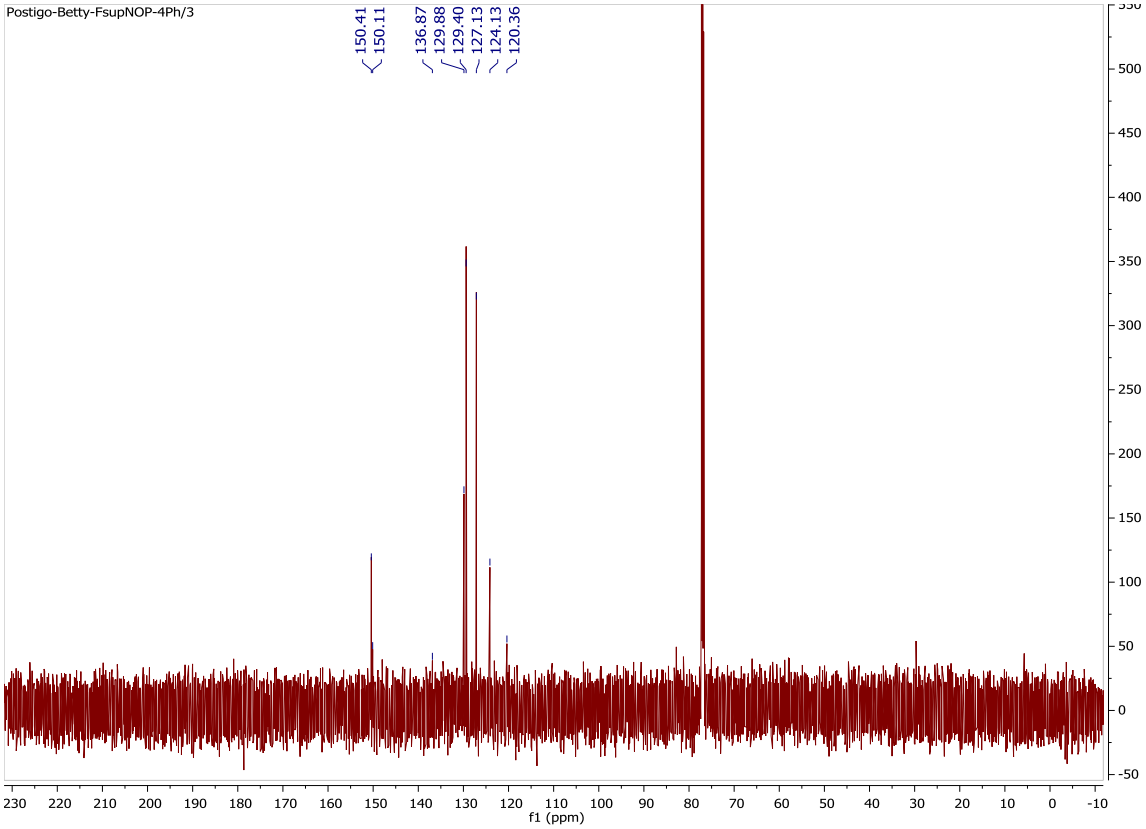
1H NMR spectrum 0f 40b in CDCl3



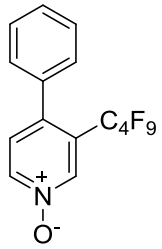


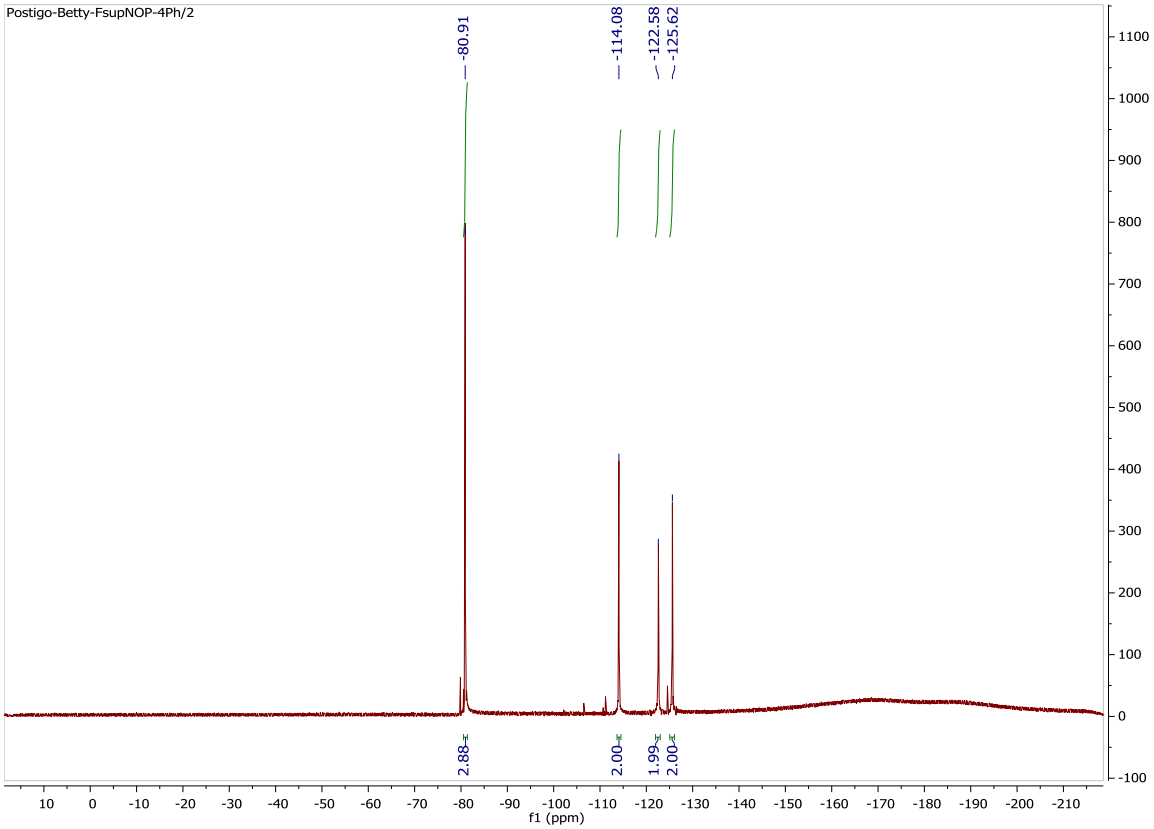
13C NMR spectrum 0f 40b in CDCl3



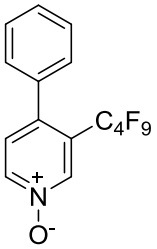


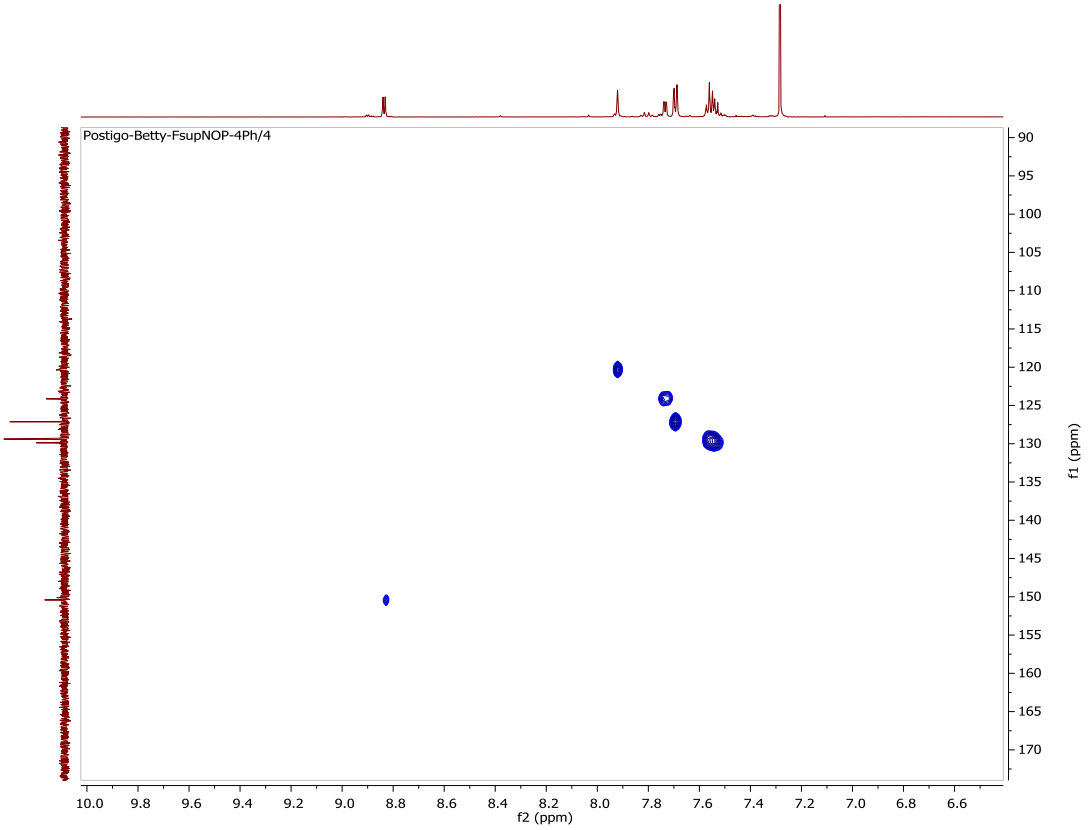
19F NMR spectrum 0f 40b in CDCl3



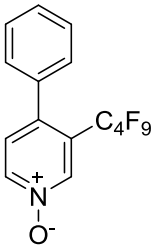


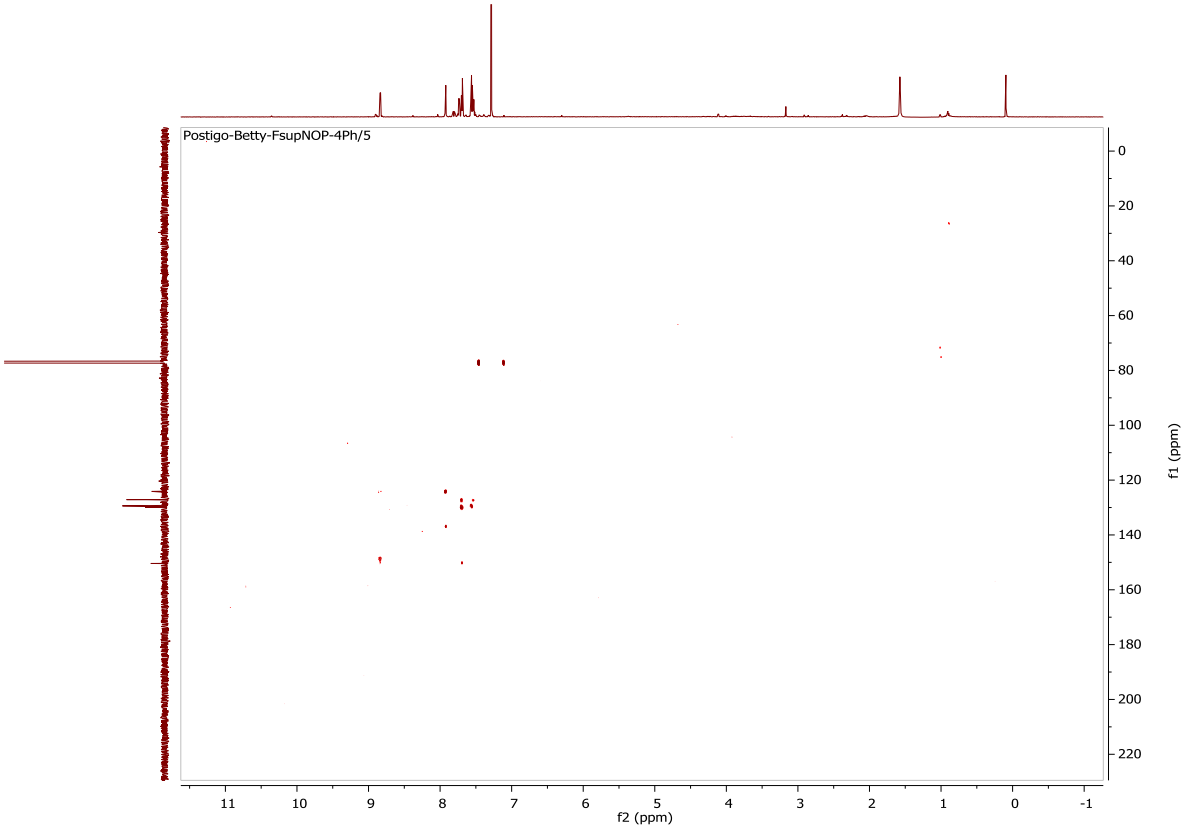
HSQC NMR spectrum 0f 40b in CDCl3



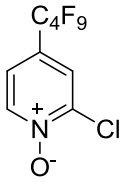


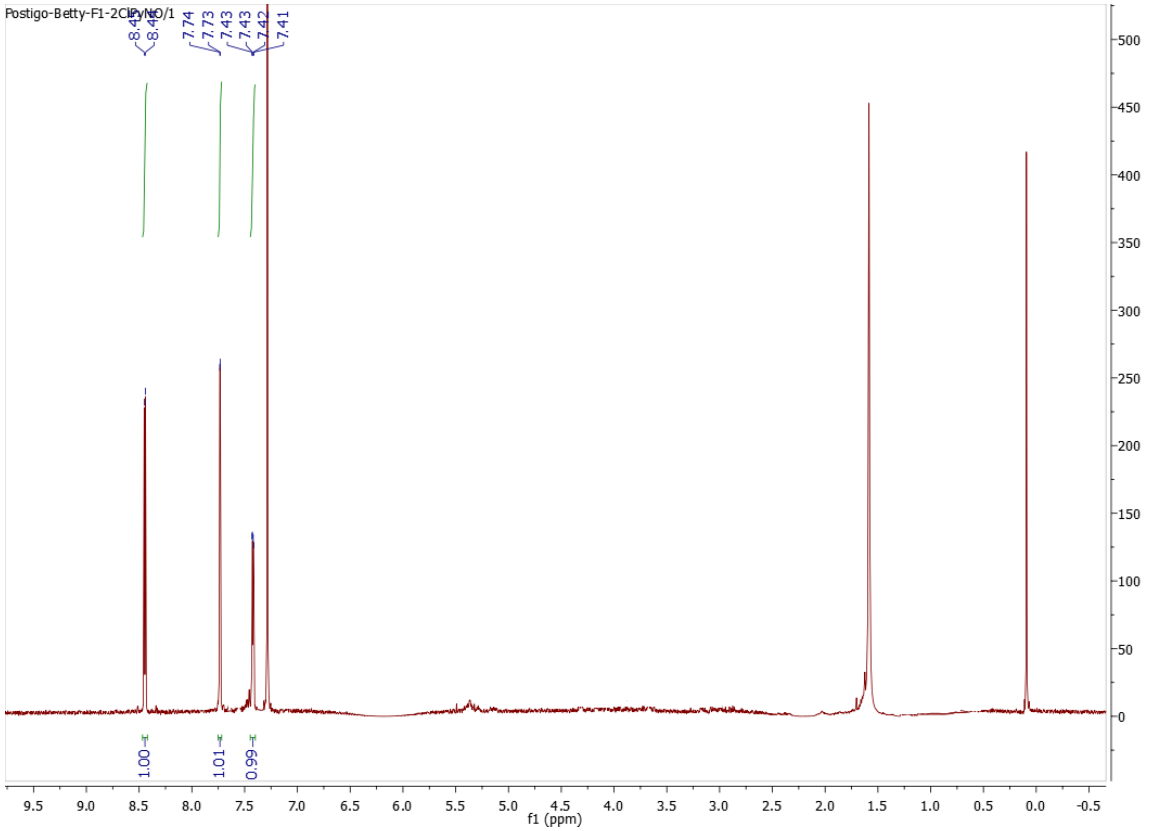
HMBC NMR spectrum 0f 40b in CDCl3



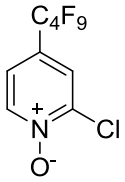


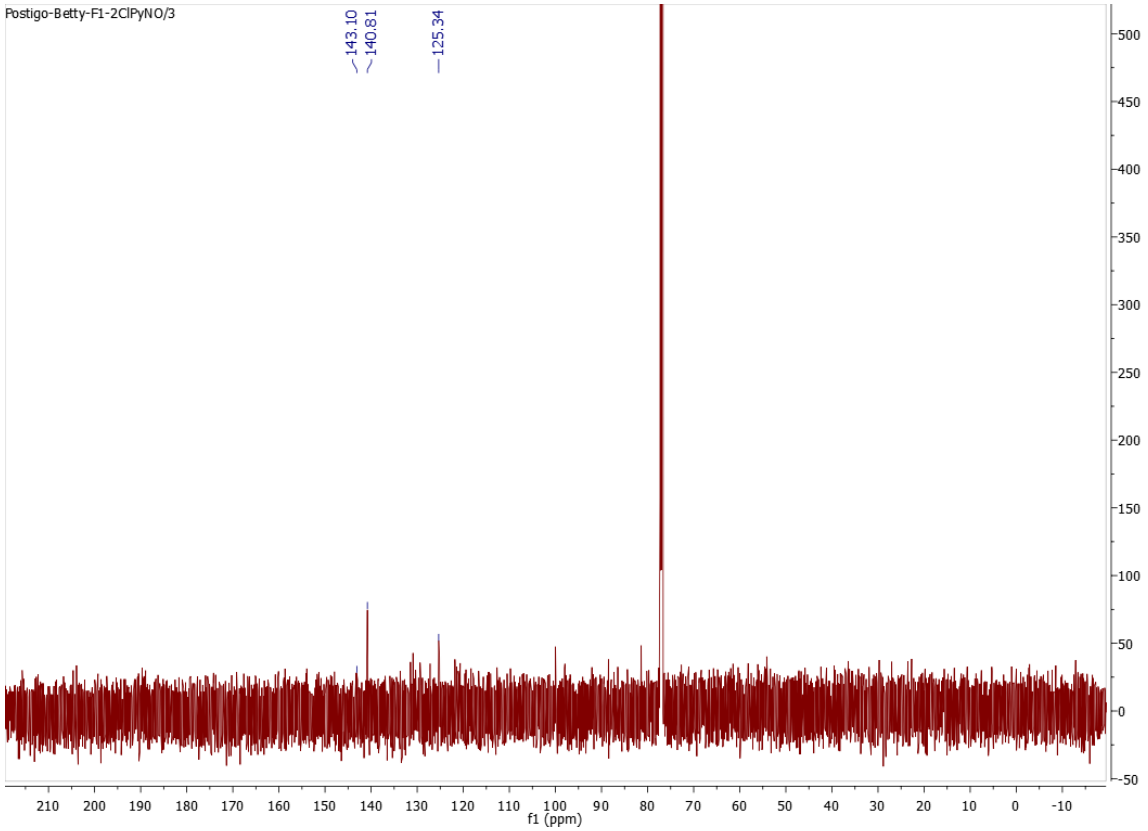
1H NMR spectrum
0f 42 in CDCl3



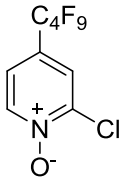


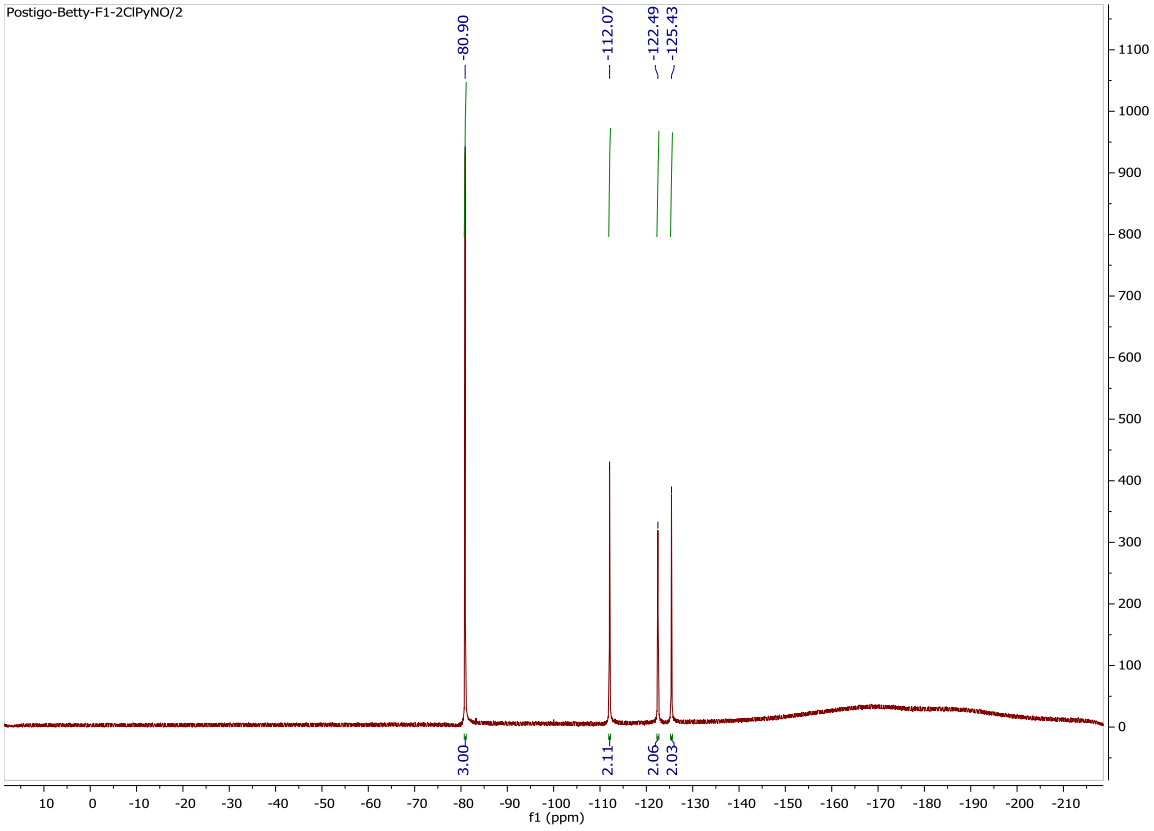
13C NMR spectrum 0f 42 in CDCl3



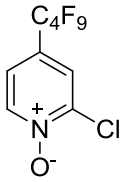


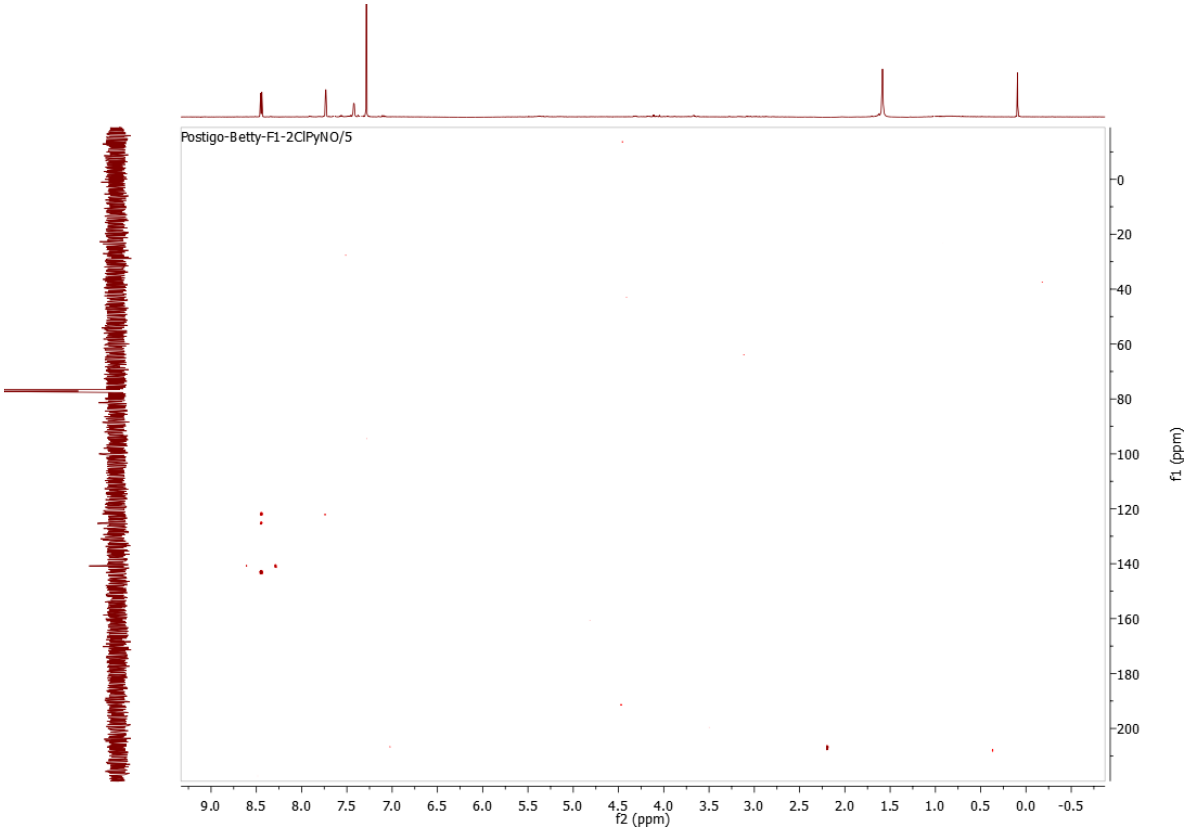
19F NMR spectrum 0f 42 in CDCl3



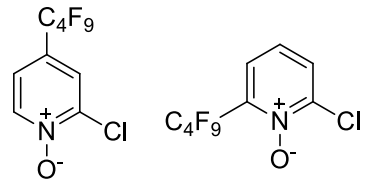


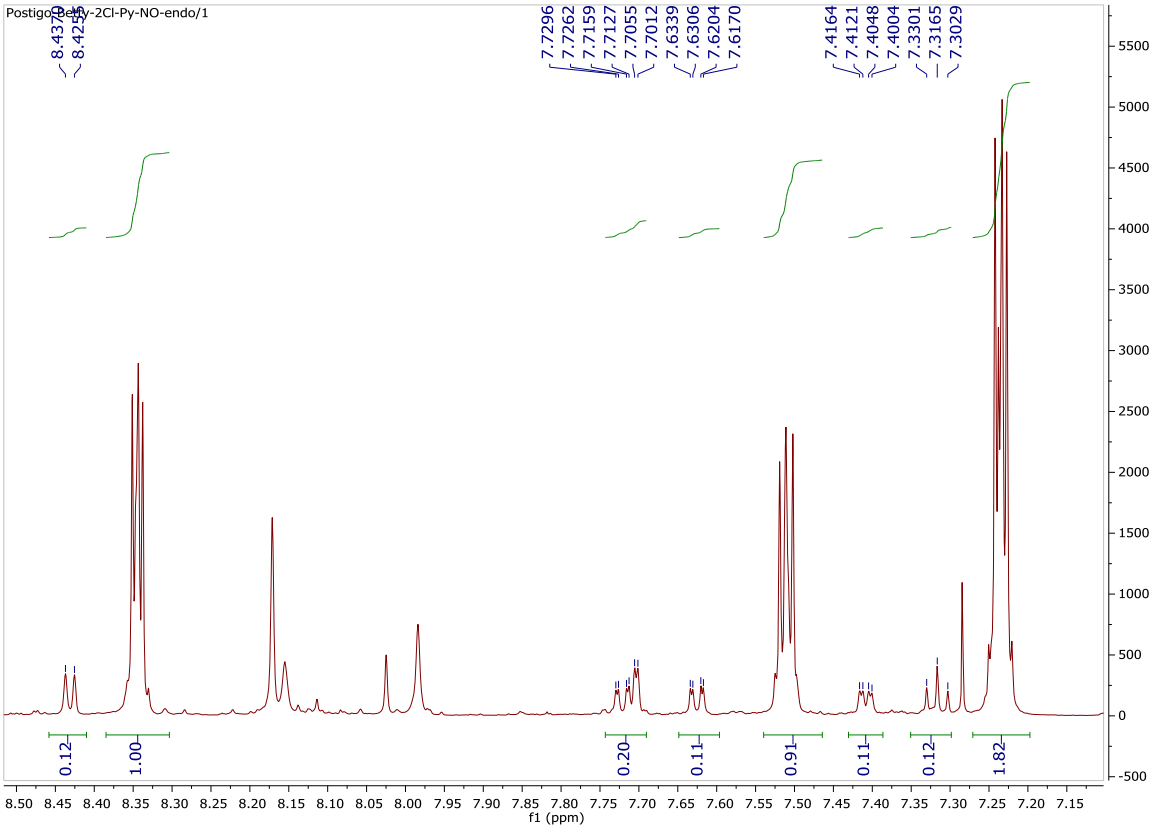
HSQC NMR spectrum 0f 42 in CDCl3



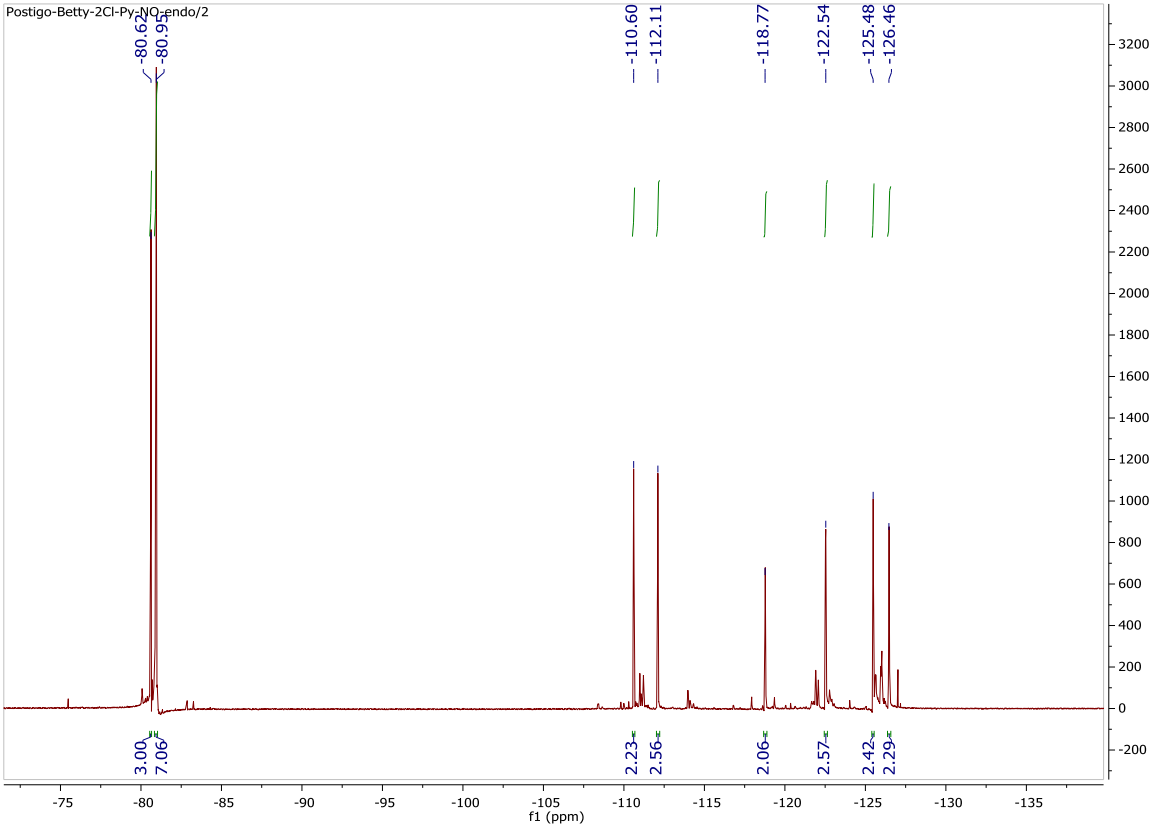


1H NMR spectrum 0f 42 and 43 in CDCl3

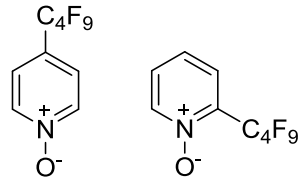


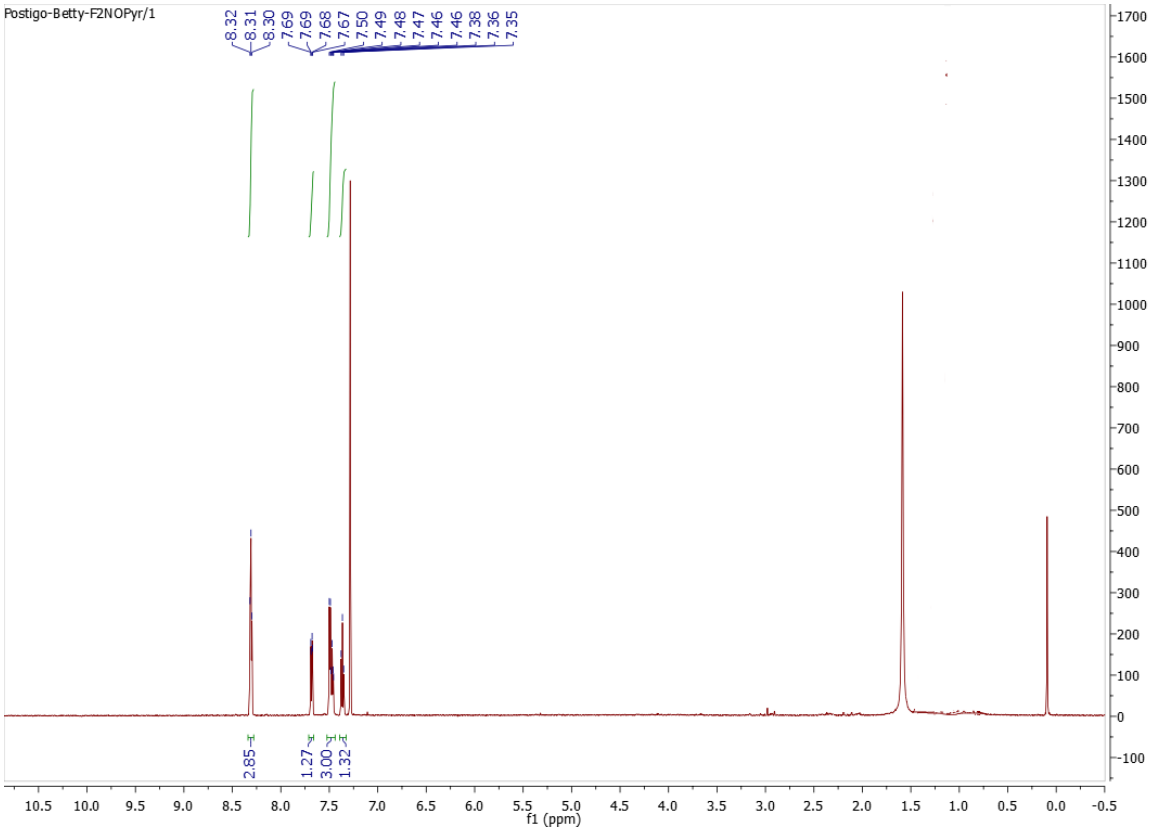


13C NMR spectrum 0f 42 and 43 in CDCl3

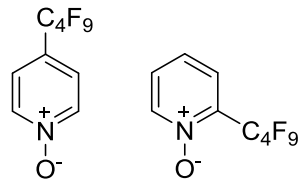


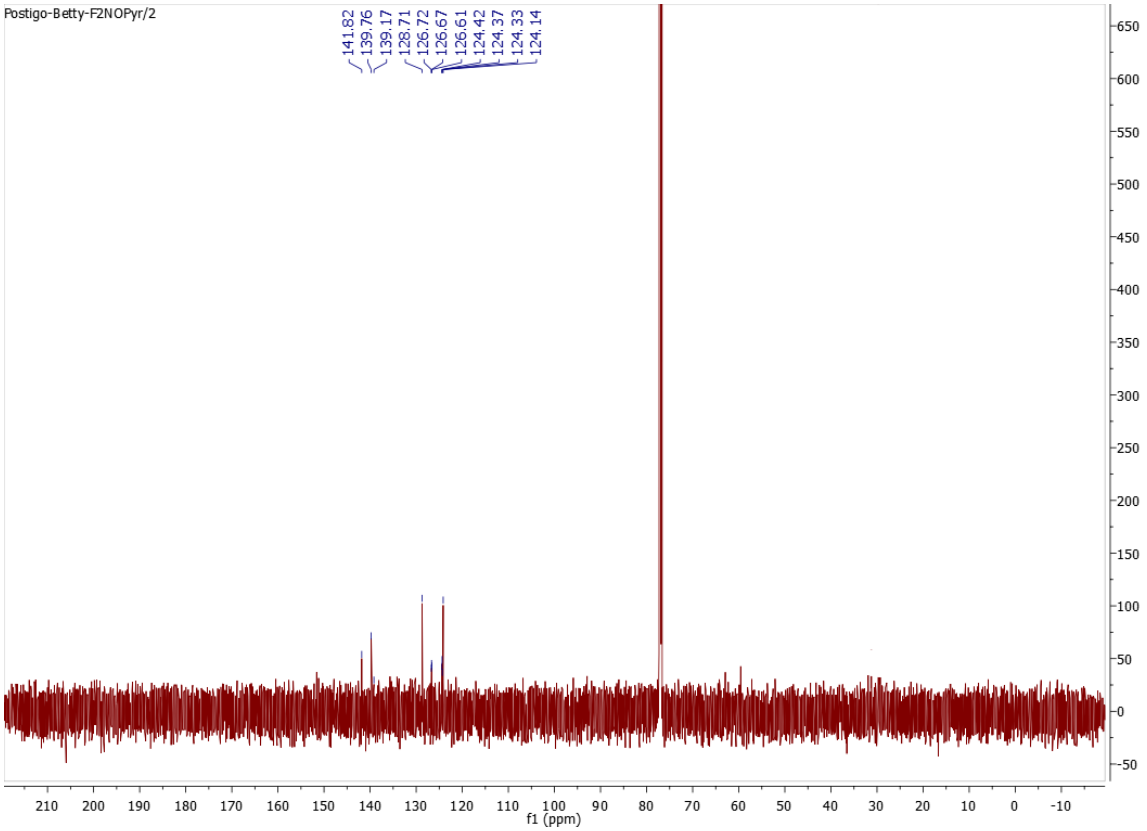
1H NMR spectrum 0f 45 and 46 in CDCl3

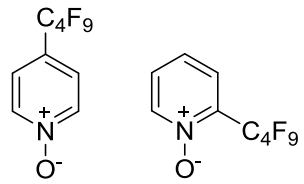




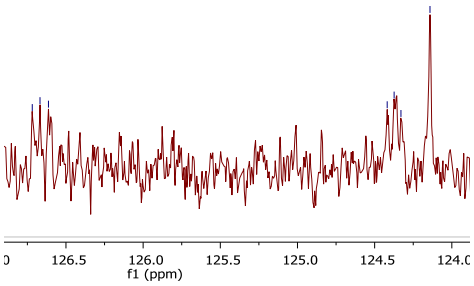
13C NMR spectrum 0f 45 and 46 in CDCl3

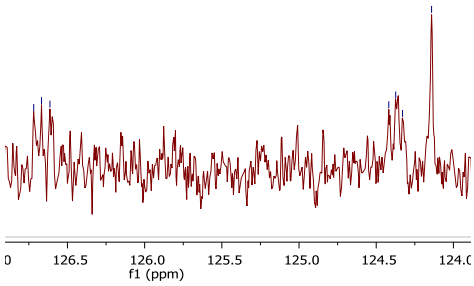




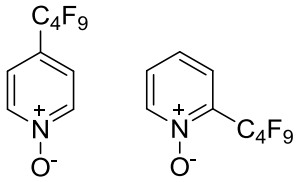

C4F9
N
O-
N
O-
C4F9

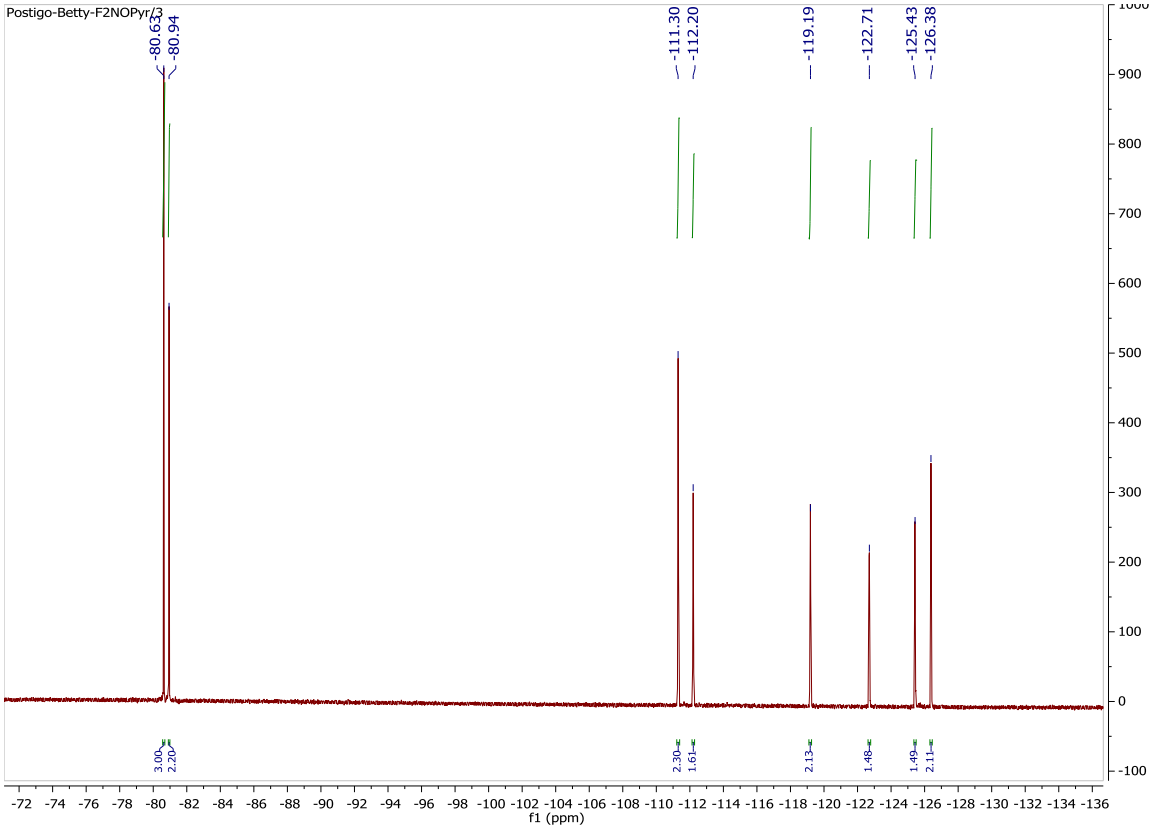

126.72
126.67
126.61
124.42
124.37
124.33
124.14


126.5
126.0
125.5
125.0
124.5
f1 (ppm)

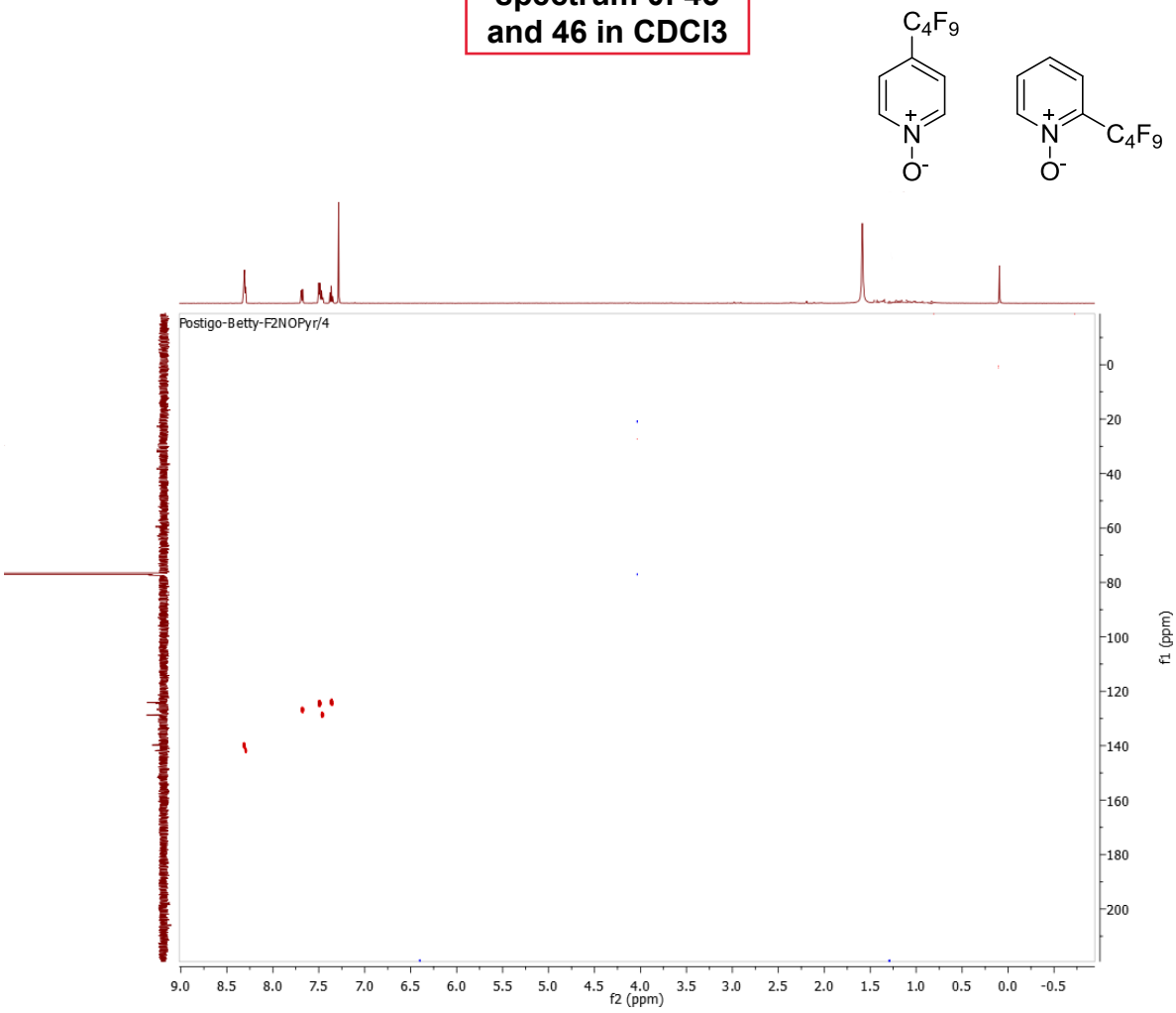

126.5
126.0
125.5
125.0
124.5
f1 (ppm)

19F NMR spectrum 0f 45 and 46 in CDCl3

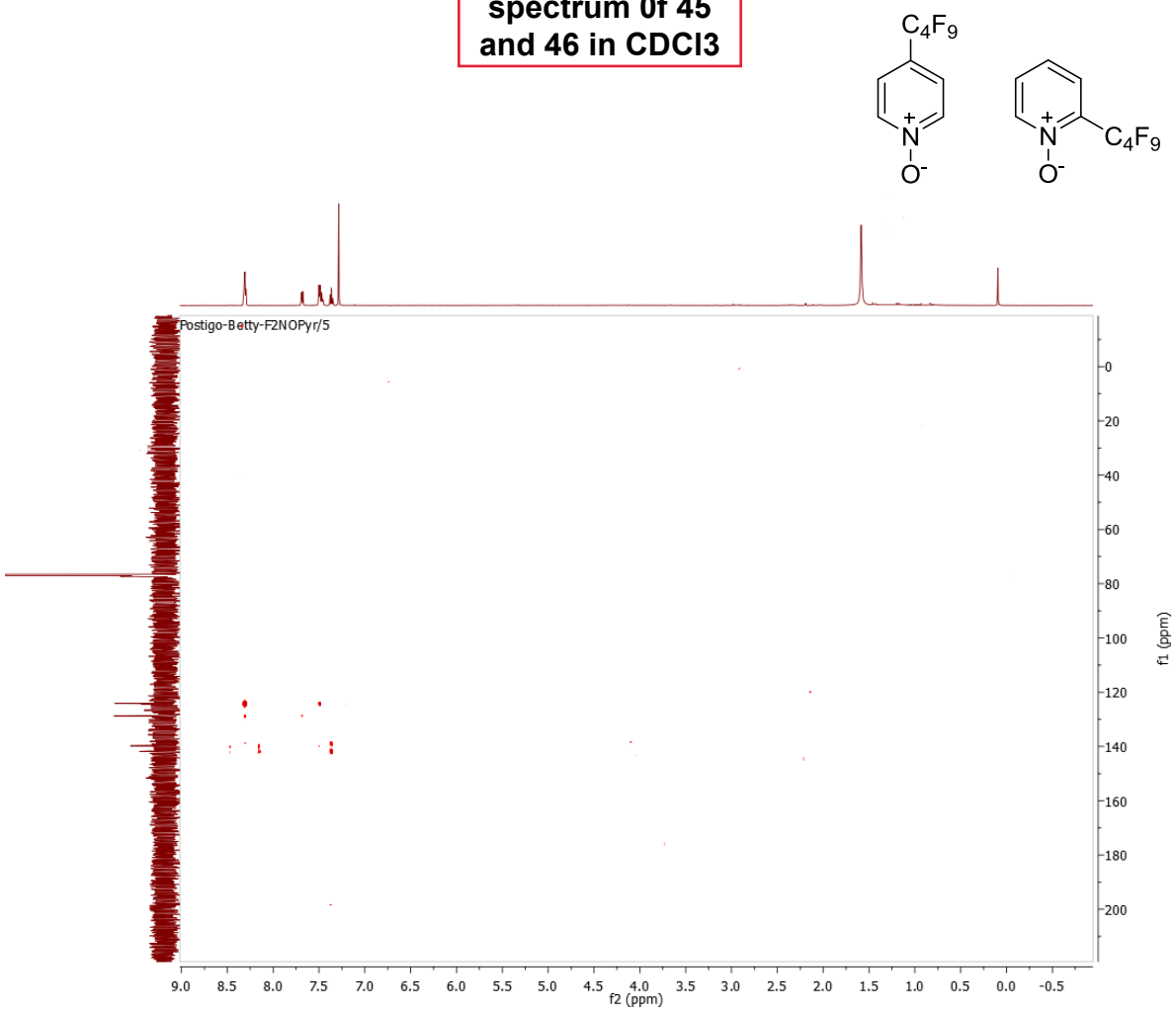




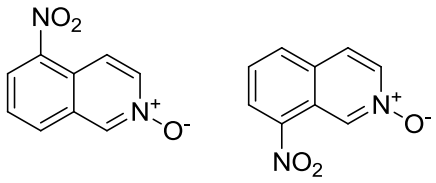
HSQC NMR spectrum 0f 45 and 46 in CDCl3

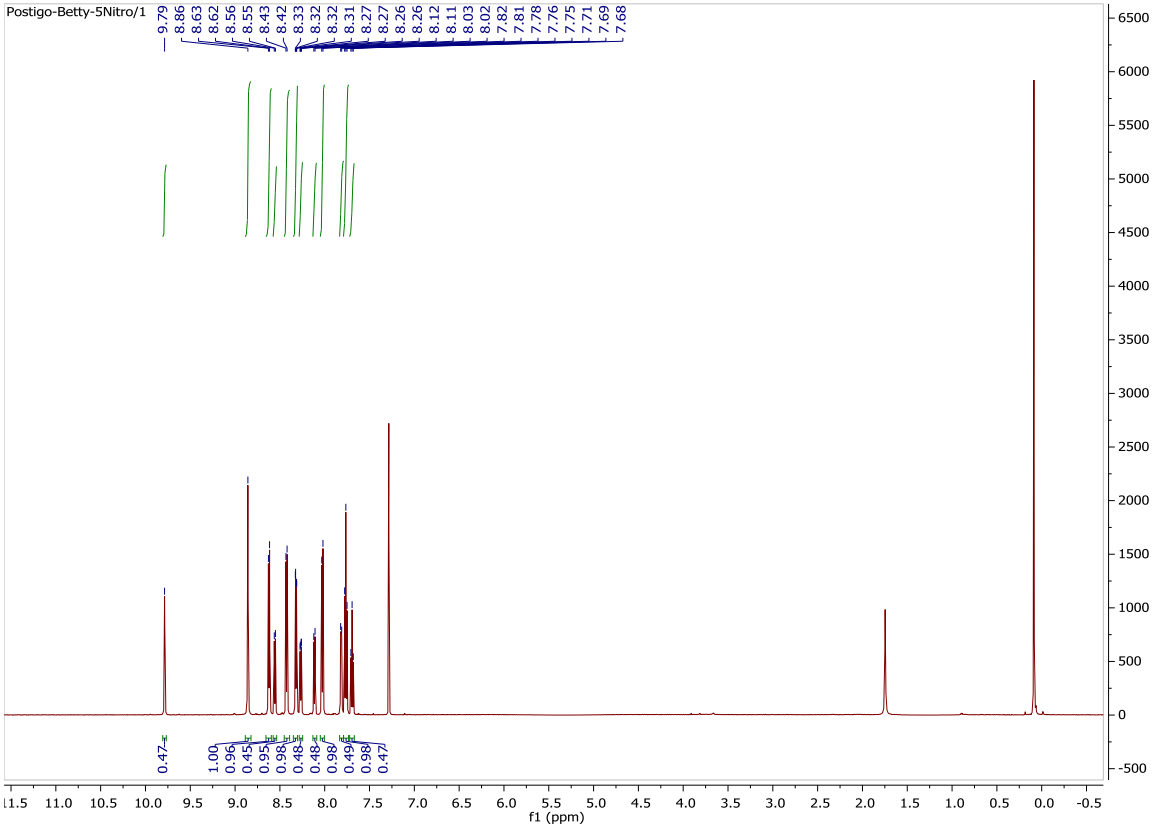


HMBC NMR spectrum 0f 45 and 46 in CDCl3



1H NMR spectrum 0f 1b and 1c in CDCl3





1H NMR spectrum 0f 1b and 1c in CDCl3