Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Visible-Light-Induced Tandem Difluoroalkylated Spirocyclization of *N*-arylpropiolamides: Access to C3-Difluoroacetylated Spiro[4,5]trienones

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Contents

1 General information

All chemicals were commercially available and used as received without further. Column chromatography was performed using 300-400 mesh silica. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. ^{1}H NMR spectra are recorded in parts per million from tetramethylsilane. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant in Hz and integration. ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane. ^{19}F NMR spectra were recorded in parts per million with fluorobenzene as external standard. High resolution mass spectra (HR MS) were obtained on Thermo Scientific LTQ Orbitrap XL instrument using the ESI technique. IR spectra were recorded on WQF-510 Fourier transform infrared spectrophotometer. Melting points were measured on an XT4A microscopic apparatus uncorrected.

2 Screening the reaction conditions

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

Table S1 Screening the molar ratio of **1a** and **2a**[a]

Entry	the molar ratio of **1a** and **2a**	Yields (%)[b]
1	1 : 1	22
2	1 : 1.5	37
3	1 : 2	44
4	1 : 2.5	50
5	1 : 3	56
6	1 : 3.5	55

[a] Reaction conditions: *N*-(4-methoxyphenyl)-*N*-methyl-3-phenylpropiolamide **1a** (0.2 mmol, 53.0 mg), ethyl 2-

bromo-2,2-difluoroacetate **2a**, *fac*-[Ir(ppy)] (0.002 mmol, 1.31 mg), K_3PO_4 (0.3 mmol, 63.6 mg) and DMF (2.0 mL), 5 W blue LEDs at room temperature under N_2 atmosphere for 4.5 h.

[b] Isolated yield.

3 Luminescence quenching study

Emission intensities were recorded using a F-7000 FL Spectrophotometer. First, the emission intensity of fluorescein solutions was observed at 369 nm. The solutions were irradiated at 510 nm (Maximum absorption wavelength of fluorescein) and fluorescence was measured from 450 nm to 650 nm. In a typical experiment, the emission spectrum of a 1×10^{-4} M solution of fluorescein with different concentration of **2a** in degassed anhydrous CH_2Cl_2 and the linear relationship between I_0/I and the increasing concentration of **2a** from 0 M to 5.0×10^{-2} M**.**

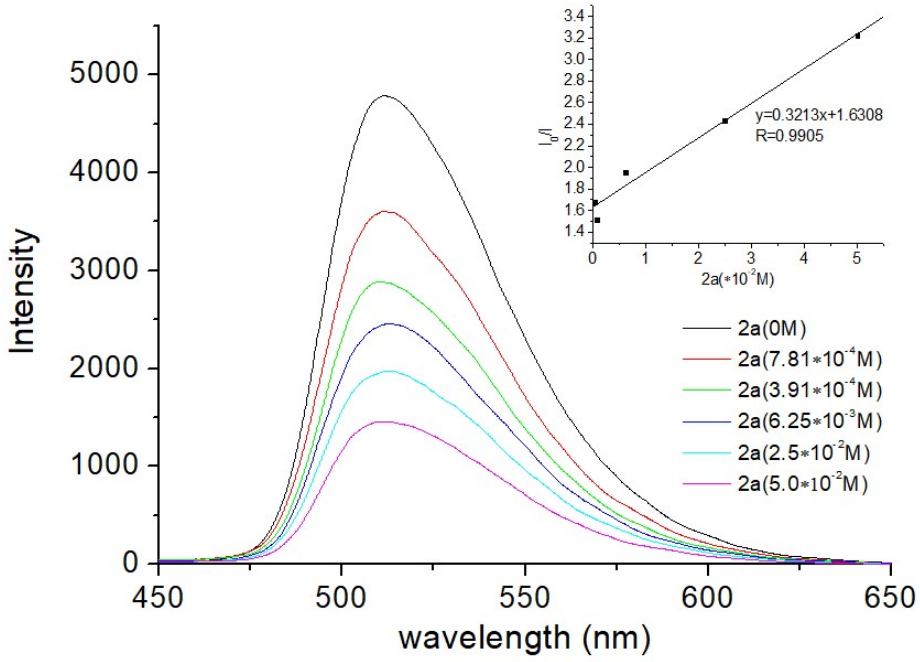

Figure 1 Luminescence quenching study

4 Copies of spectra of products

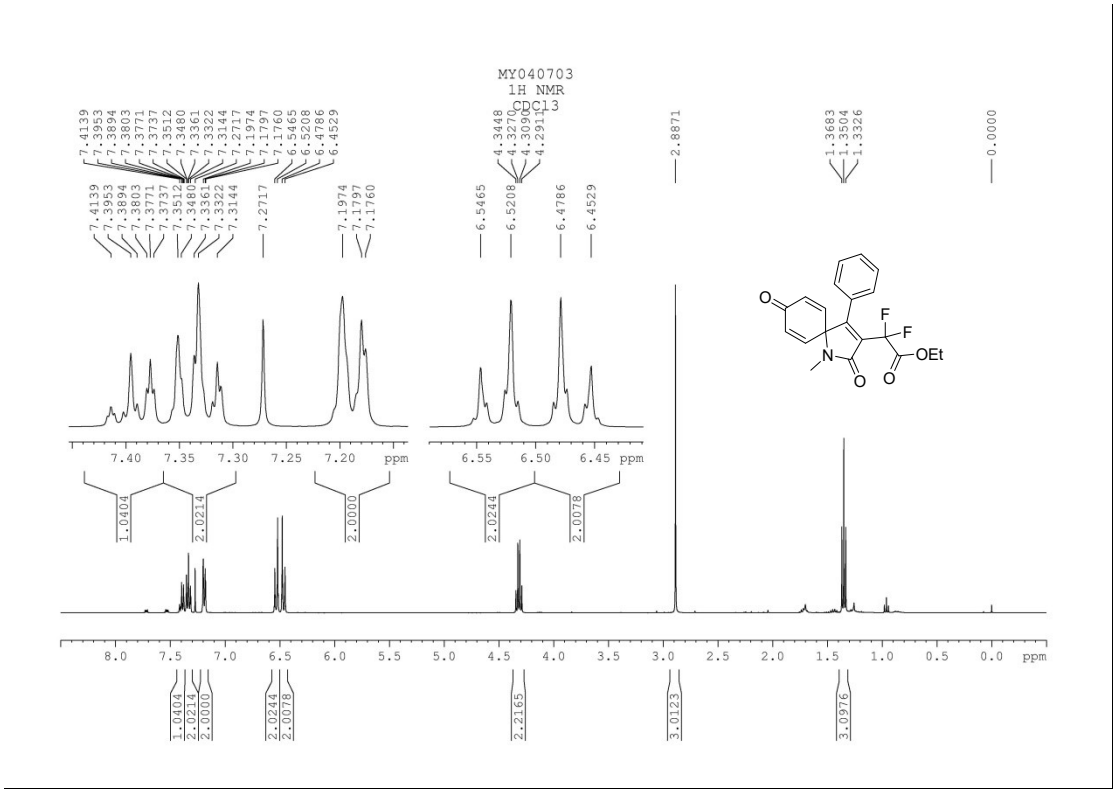

Fig. 2 ^{1}H NMR spectrum of compound **3a**

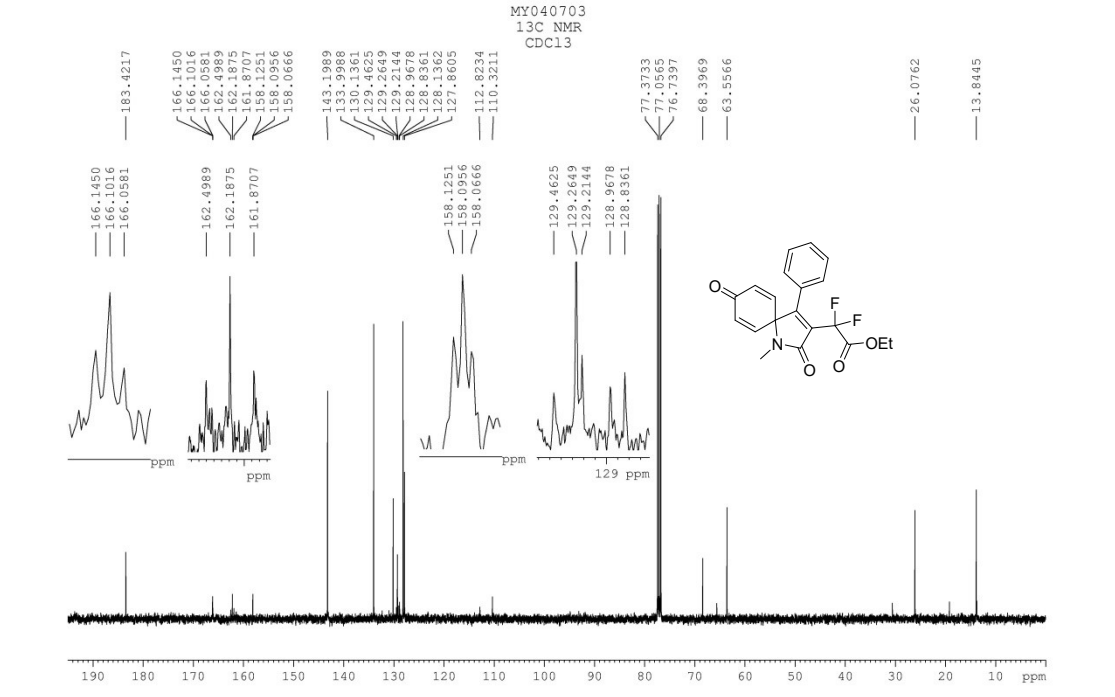

Fig. 3 ^{13}C NMR spectrum of compound **3a**

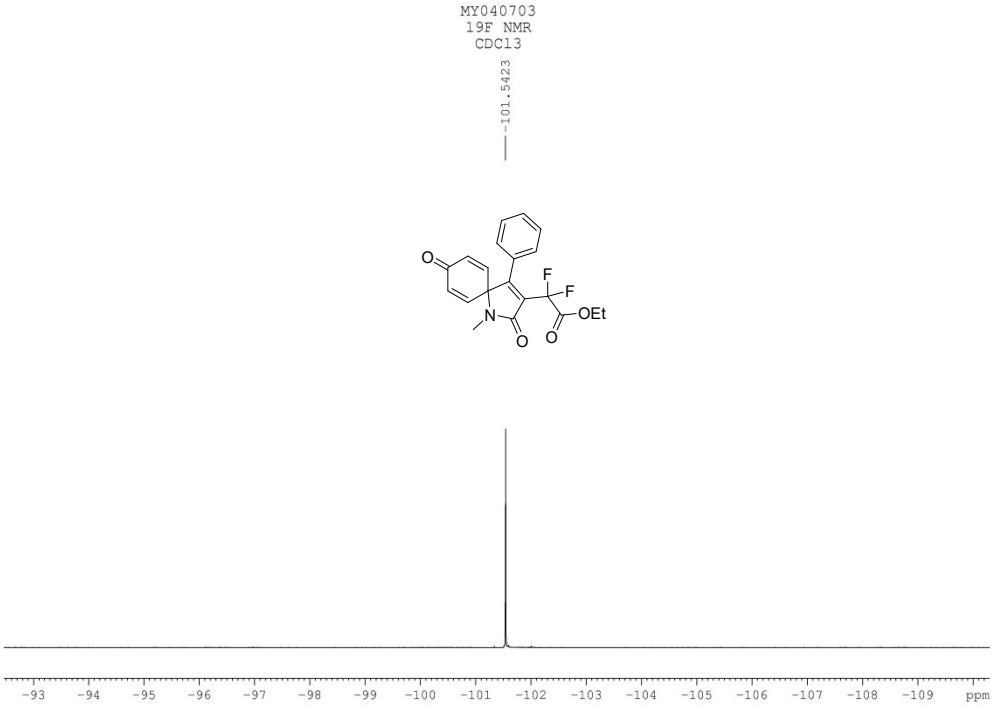

Fig. 4 ^{19}F NMR spectrum of compound **3a**

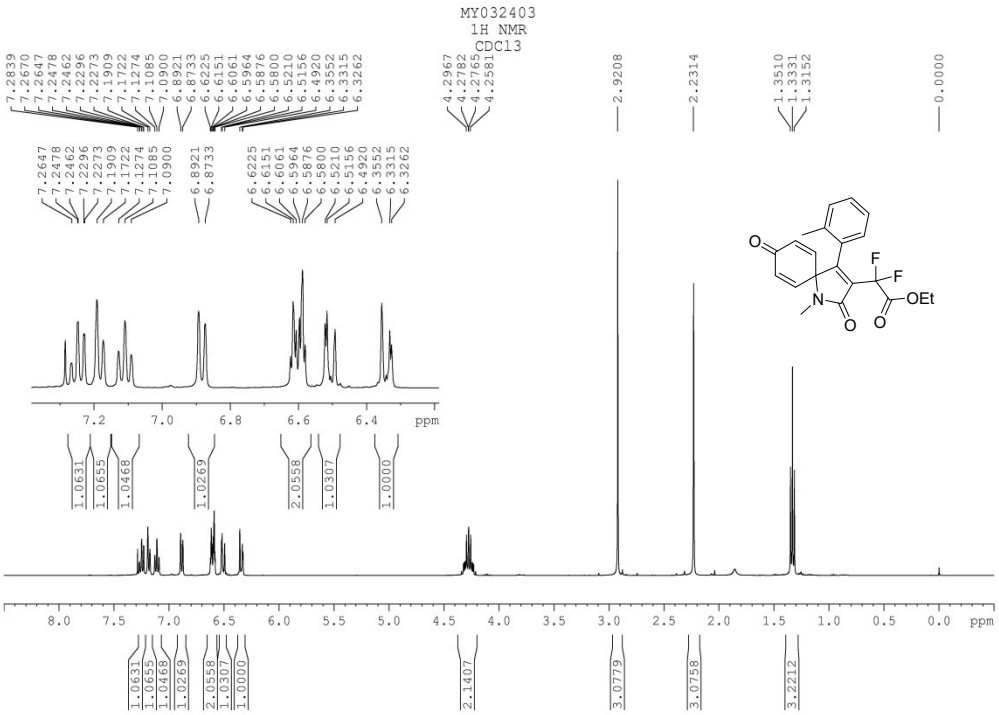

Fig. 5 ^{1}H NMR spectrum of compound **3b**

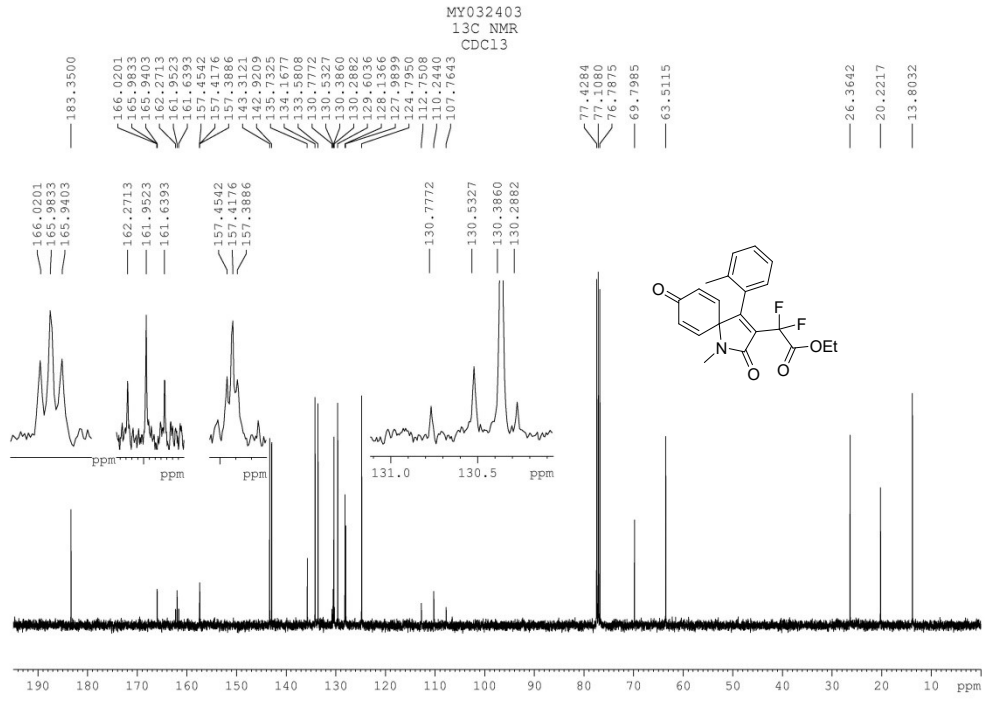

Fig. 6 ^{13}C NMR spectrum of compound **3b**

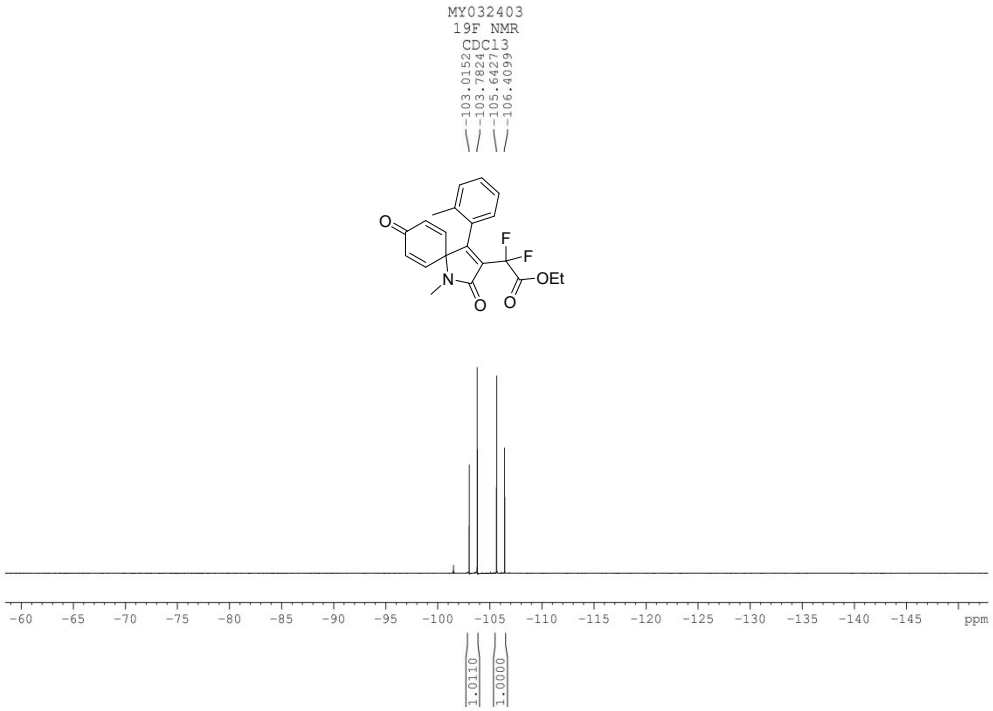

Fig. 7 ^{19}F NMR spectrum of compound **3b**

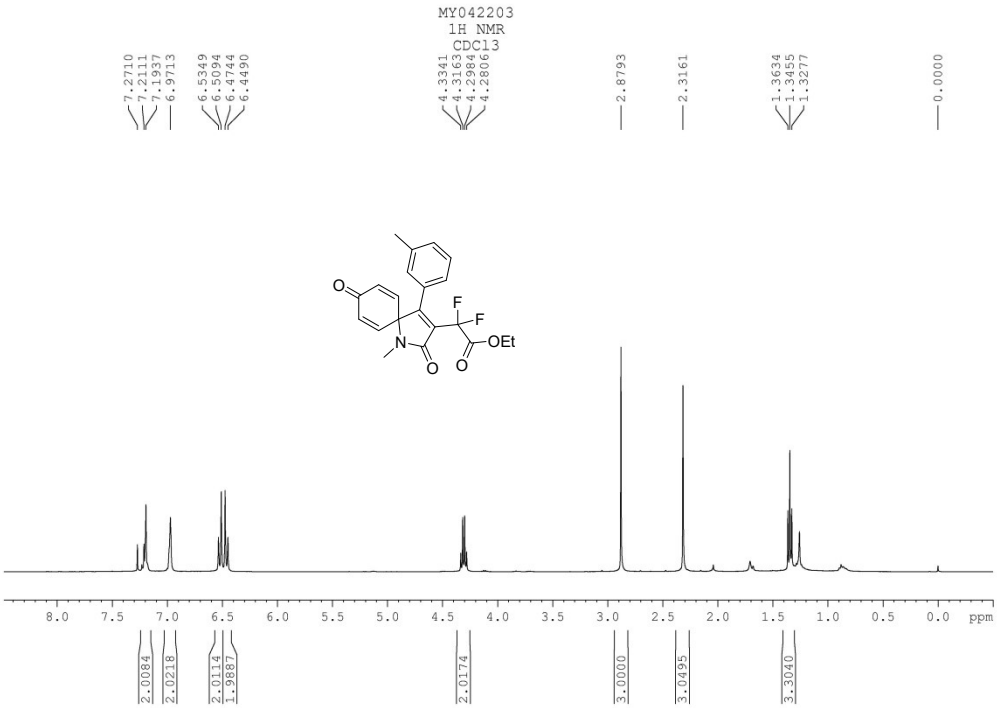

Fig. 8 ^{1}H NMR spectrum of compound **3c**

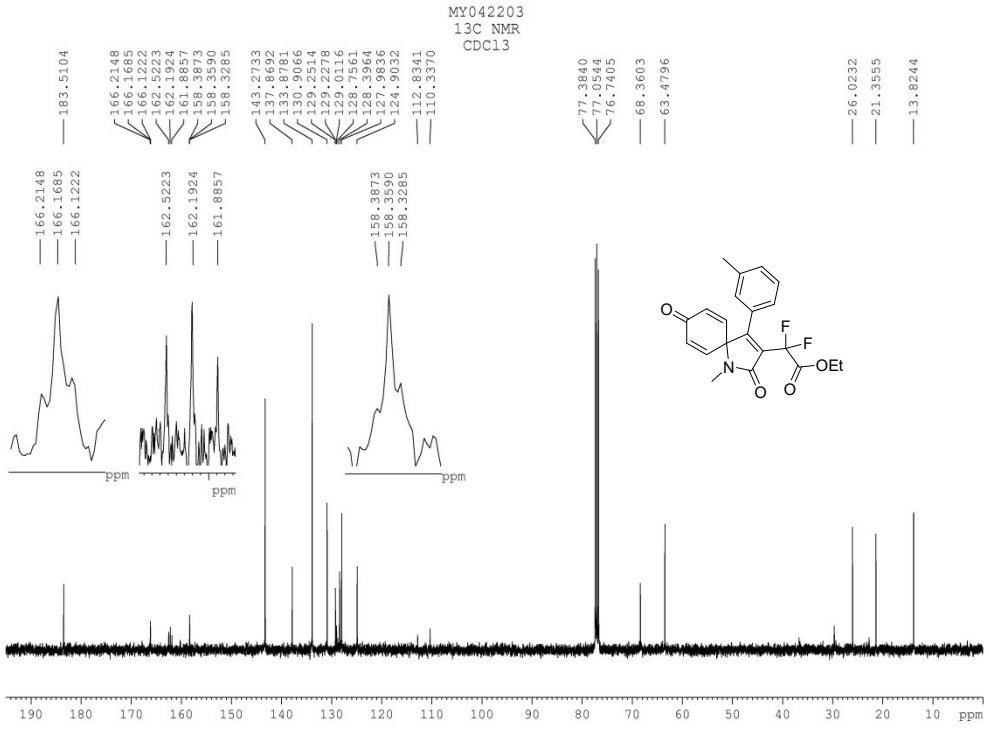

Fig. 9 ^{13}C NMR spectrum of compound **3c**

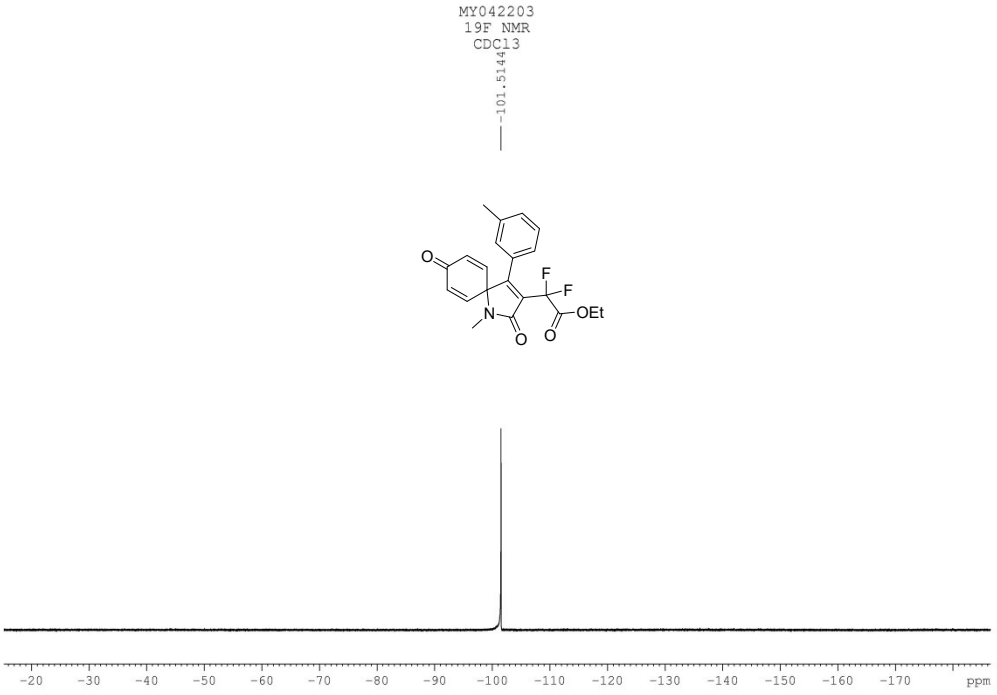

Fig. 10 ^{19}F NMR spectrum of compound **3c**

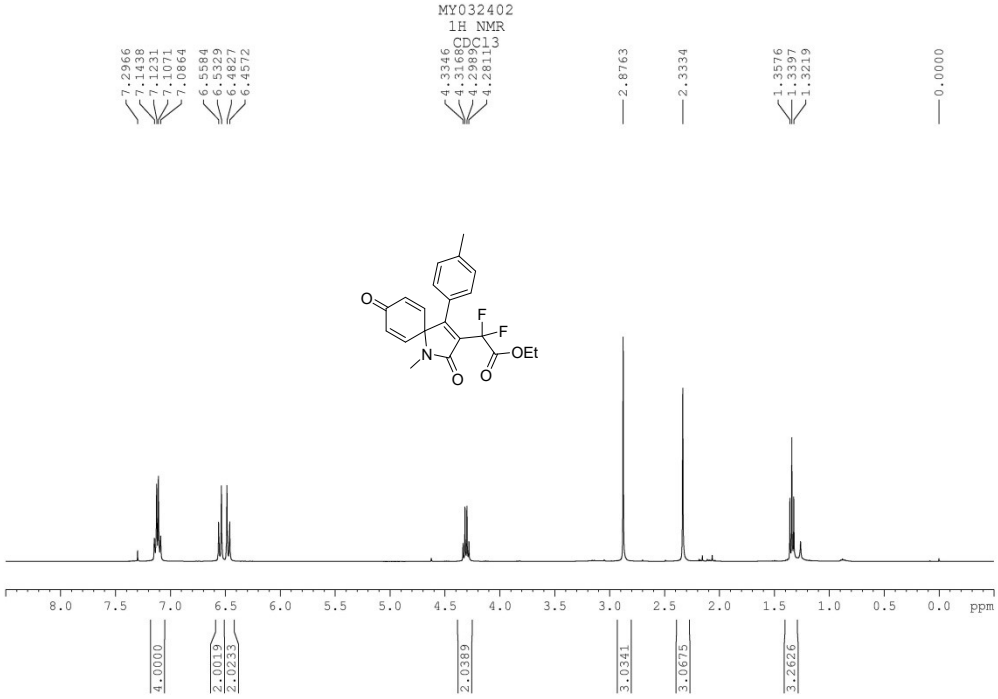

Fig. 11 ^{1}H NMR spectrum of compound **3d**

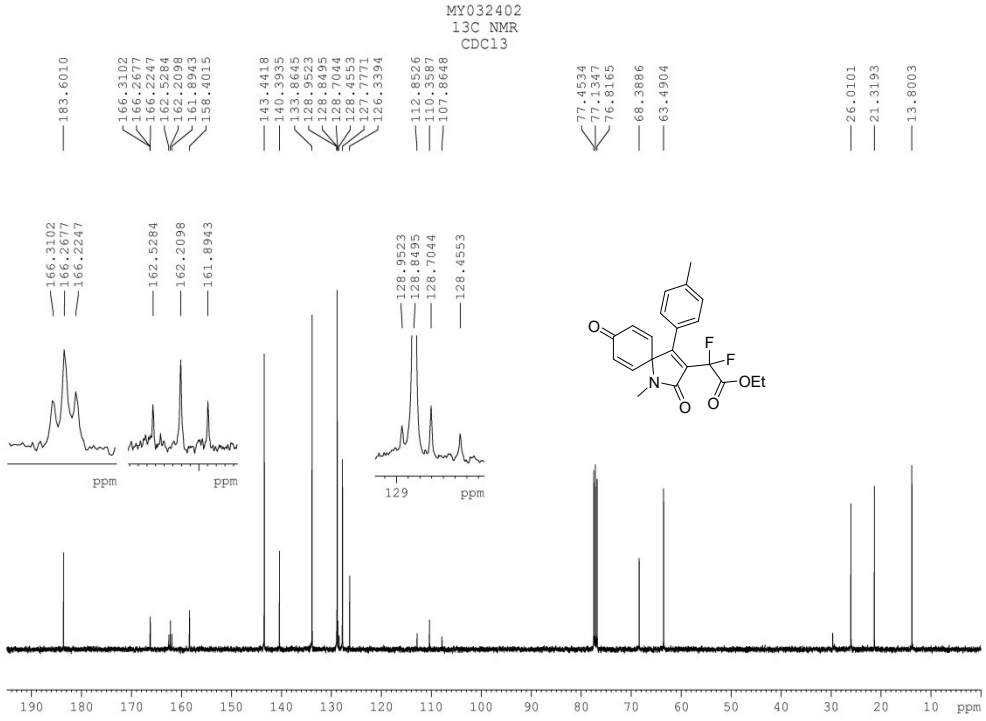

Fig. 12 ^{13}C NMR spectrum of compound **3d**

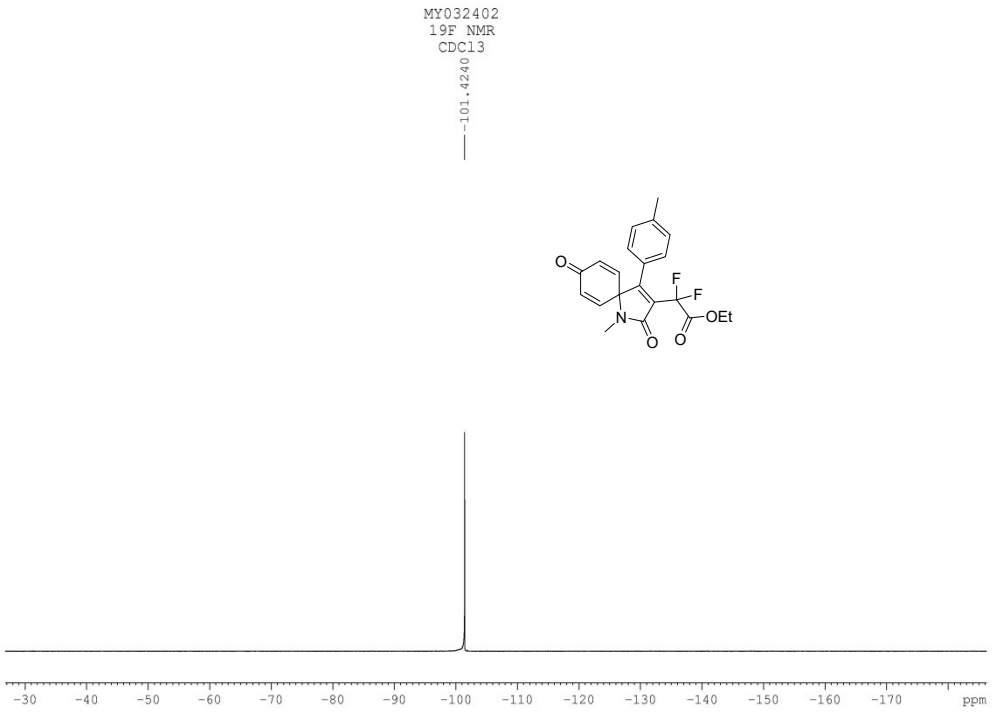

Fig. 13 ^{19}F NMR spectrum of compound **3d**

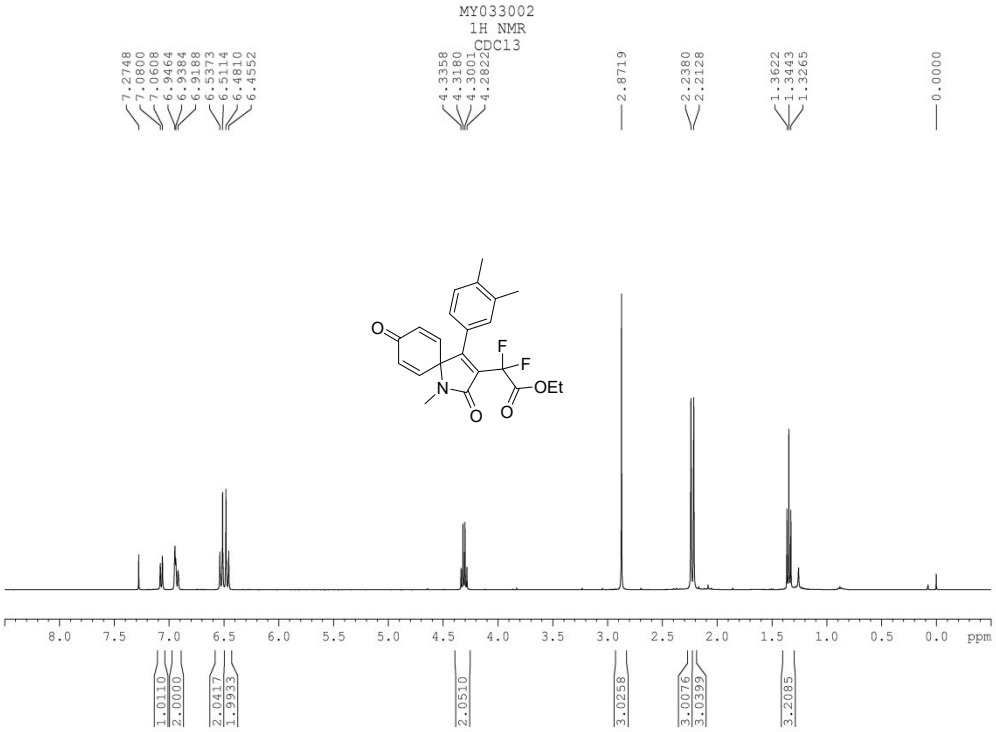

Fig. 14 ^{1}H NMR spectrum of compound **3e**

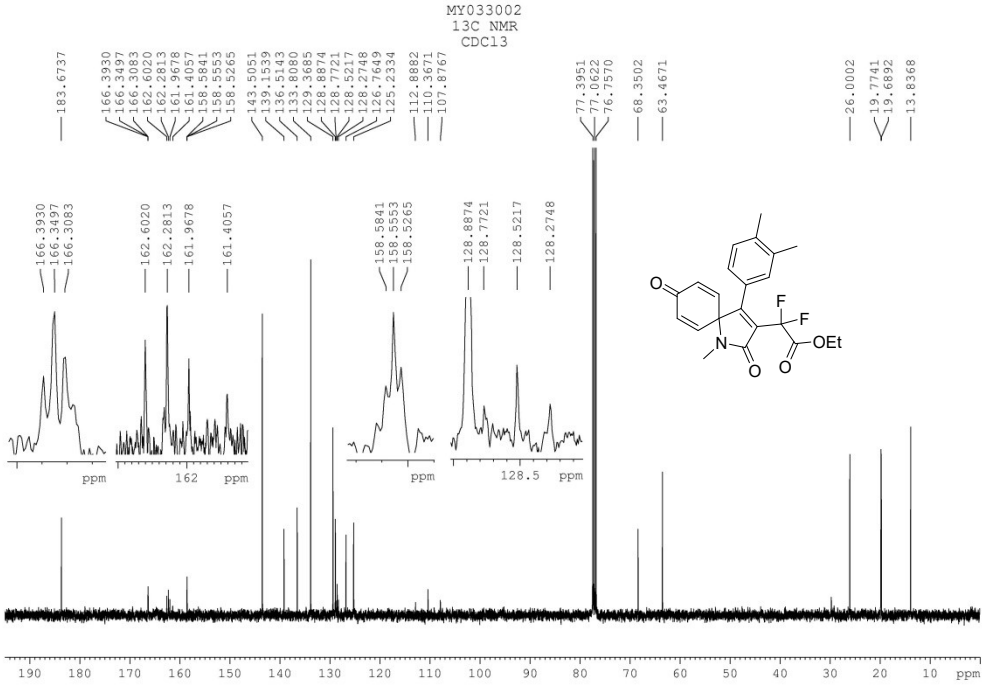

Fig. 15 ^{13}C NMR spectrum of compound **3e**

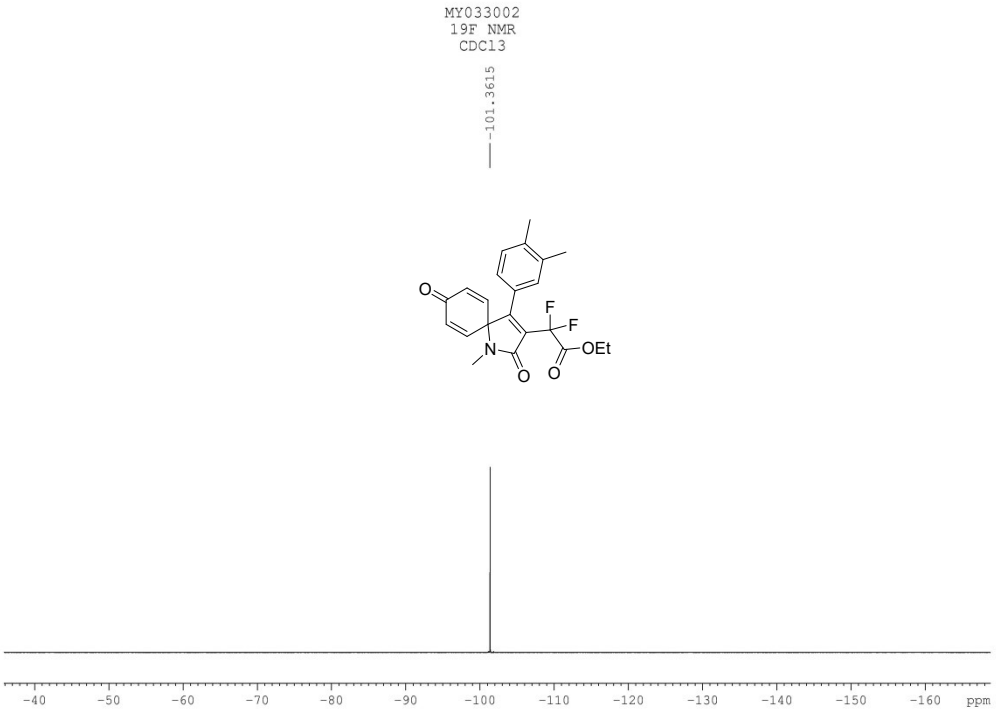

Fig. 16 ^{19}F NMR spectrum of compound **3e**

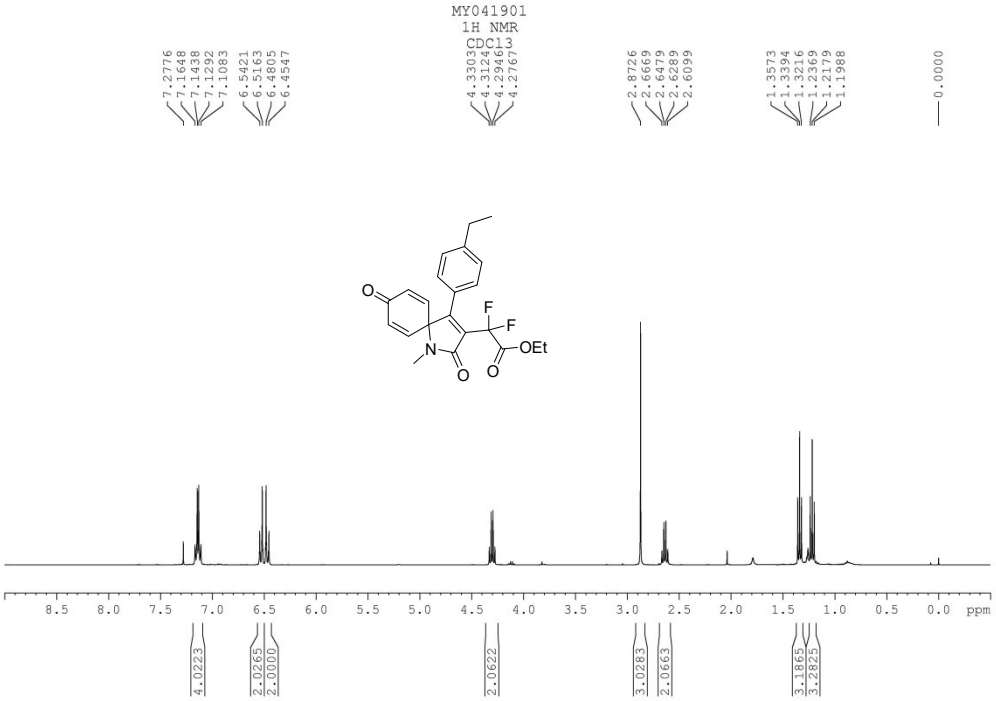

Fig. 17 ^{1}H NMR spectrum of compound **3f**

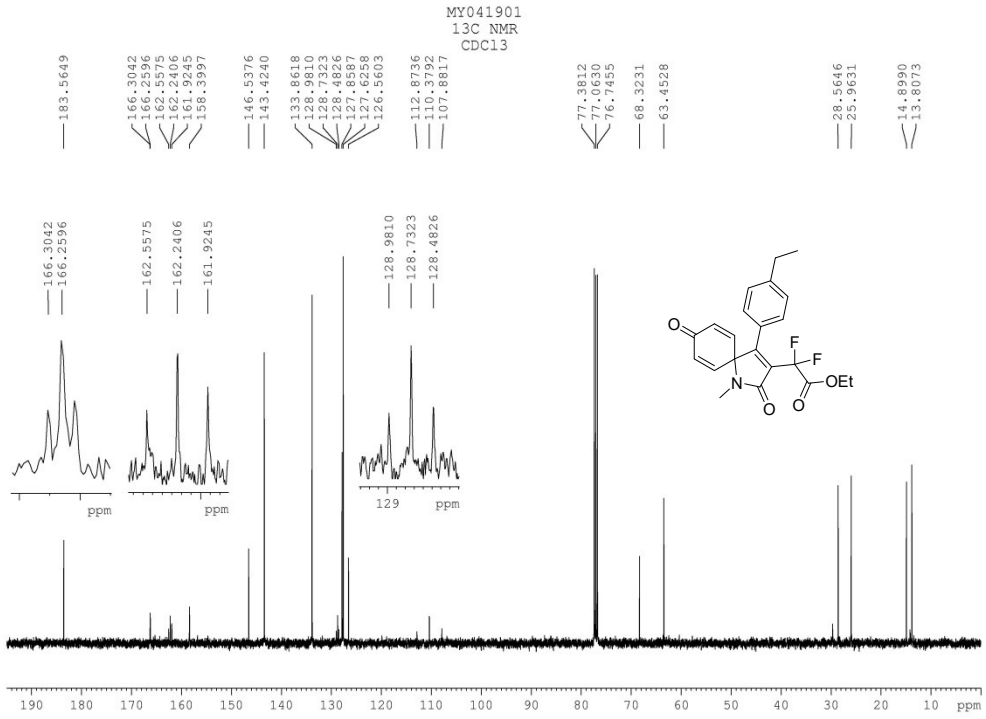

Fig. 18 ^{13}C NMR spectrum of compound **3f**

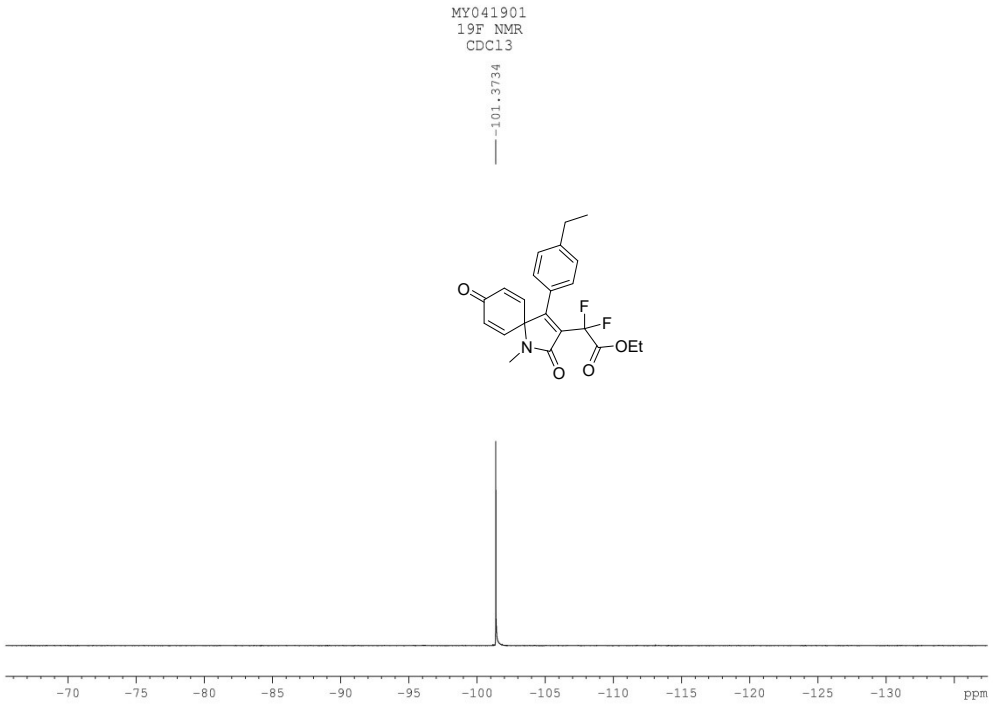

Fig. 19 ^{19}F NMR spectrum of compound **3f**

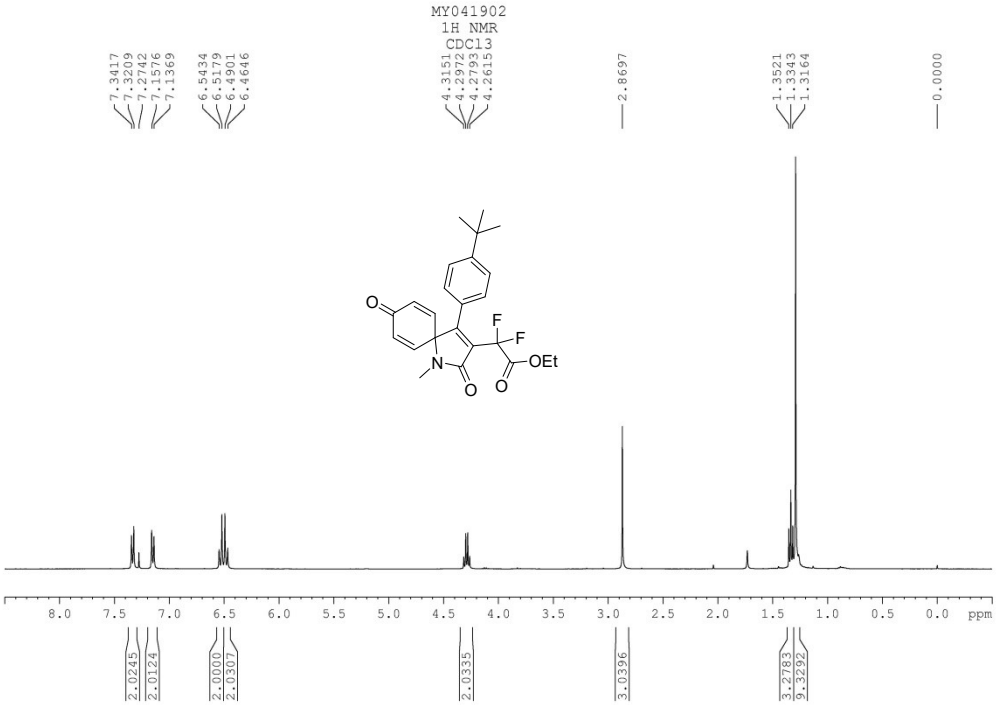

Fig. 20 ^{1}H NMR spectrum of compound **3g**

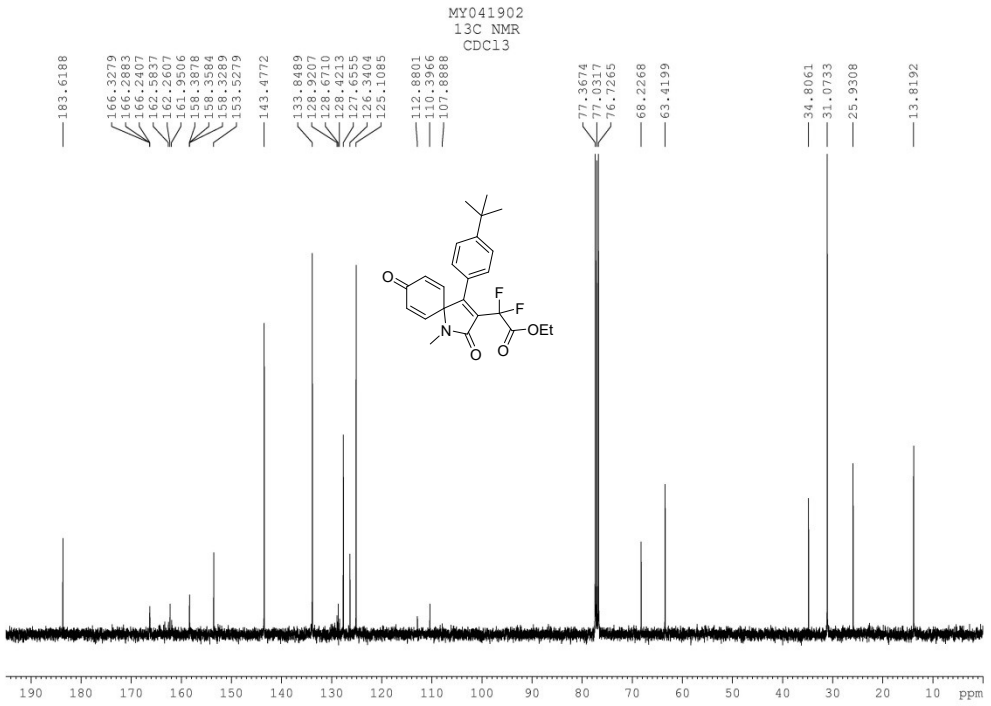

Fig. 21 ^{13}C NMR spectrum of compound **3g**

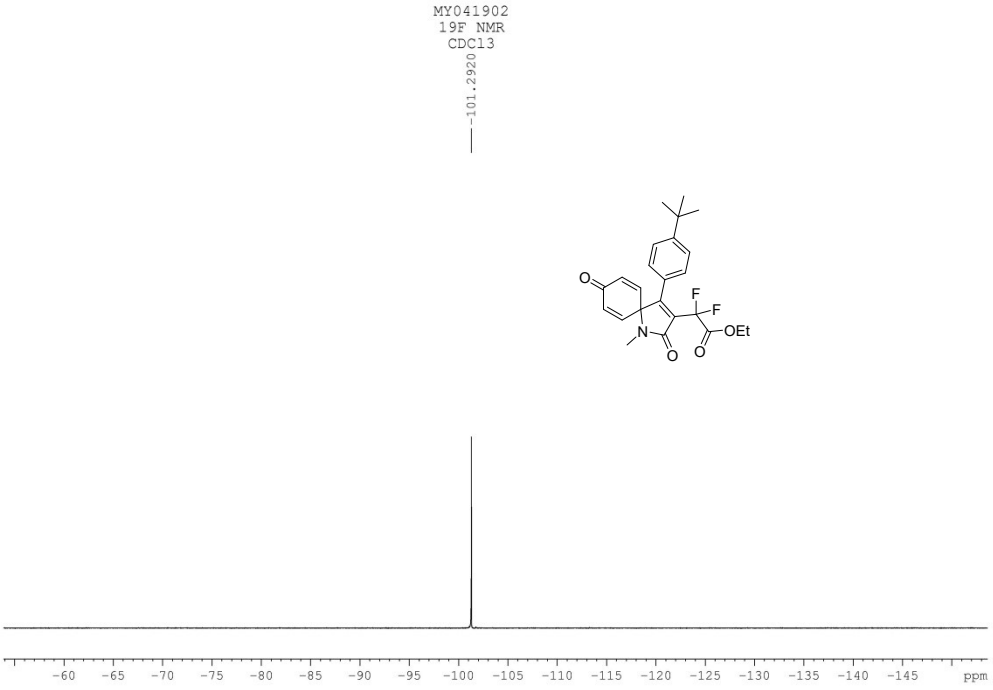

Fig. 22 ^{19}F NMR spectrum of compound **3g**

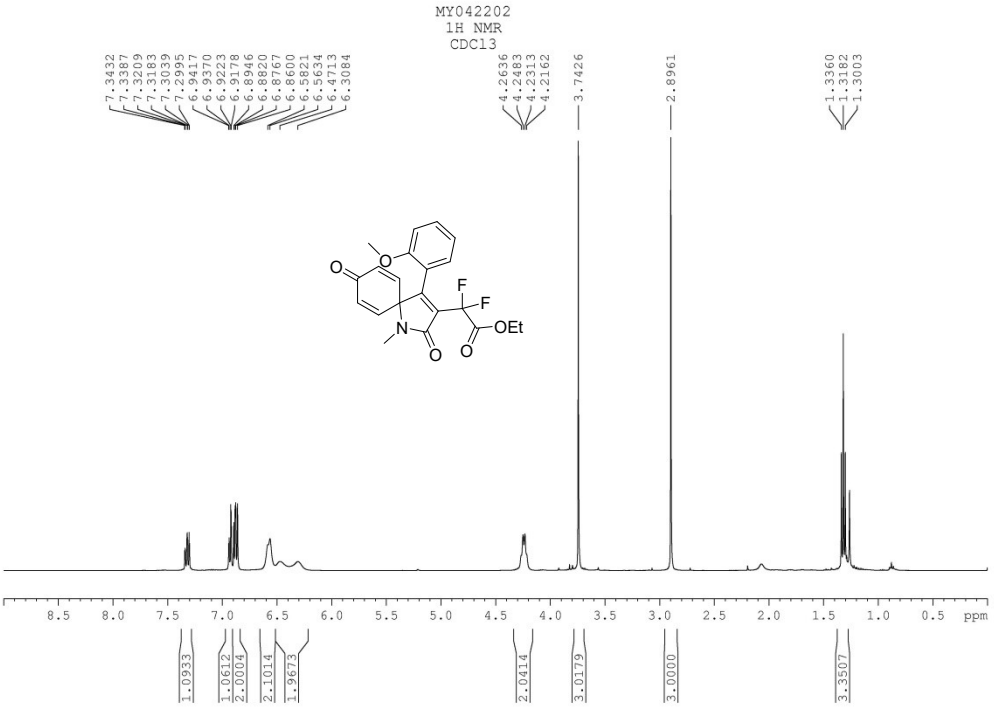

Fig. 23 ^{1}H NMR spectrum of compound **3h**

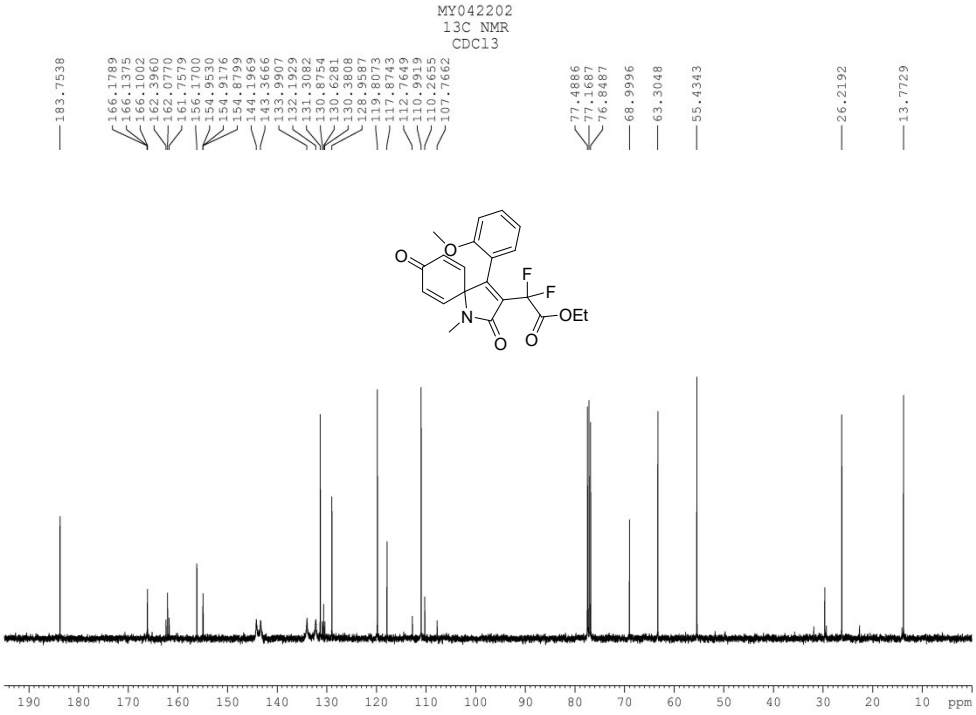

Fig. 24 ^{13}C NMR spectrum of compound **3h**

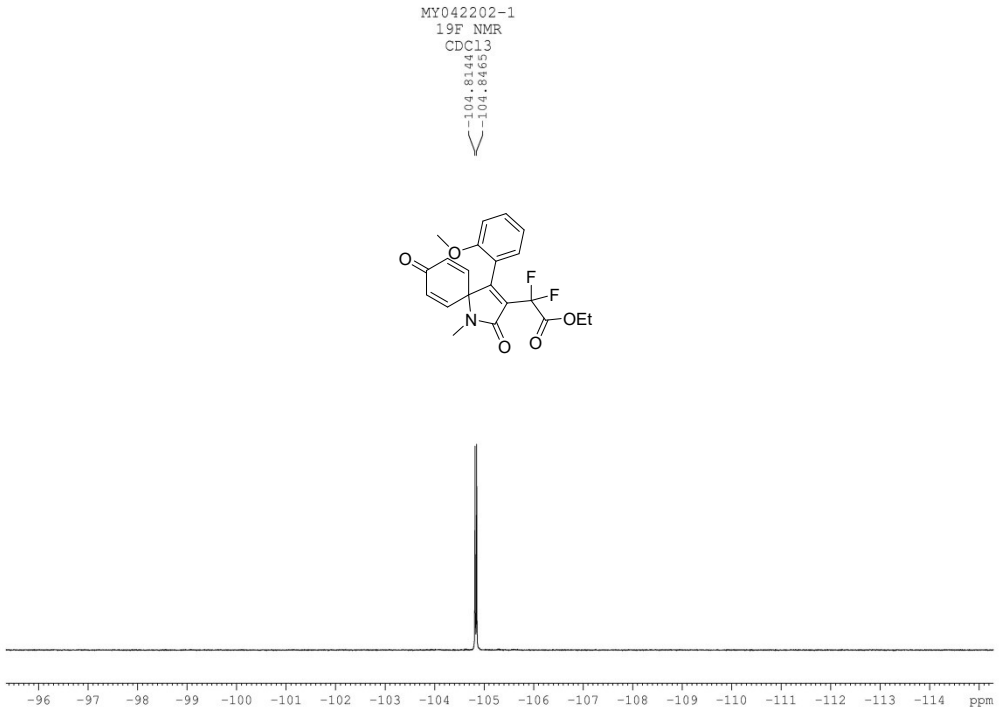

Fig. 25 ^{19}F NMR spectrum of compound **3h**

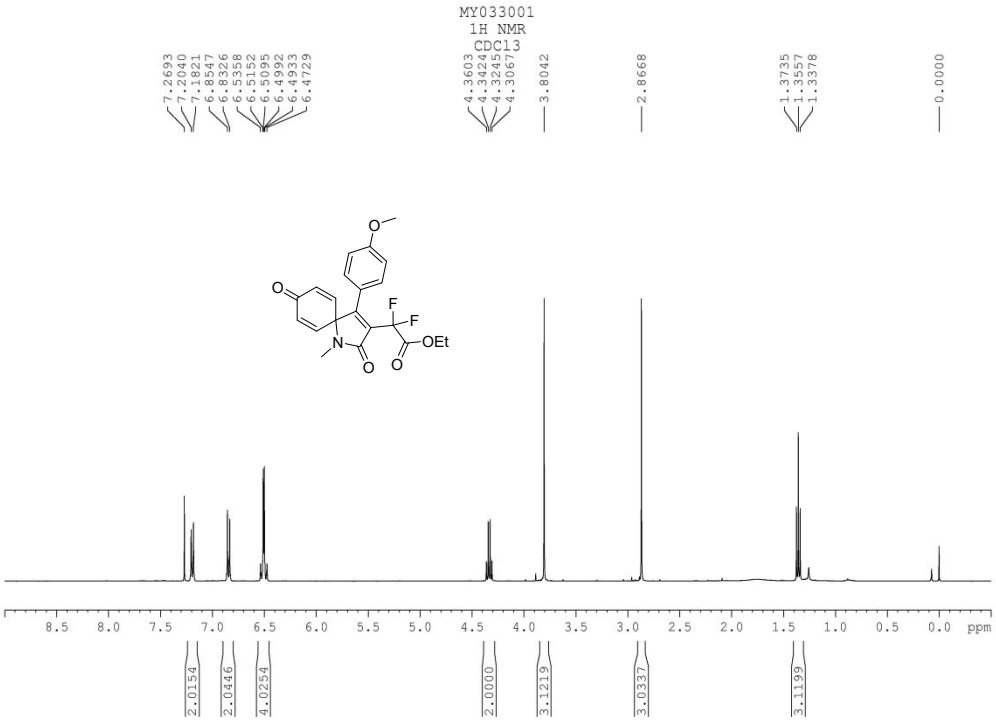

Fig. 26 ^{1}H NMR spectrum of compound **3i**

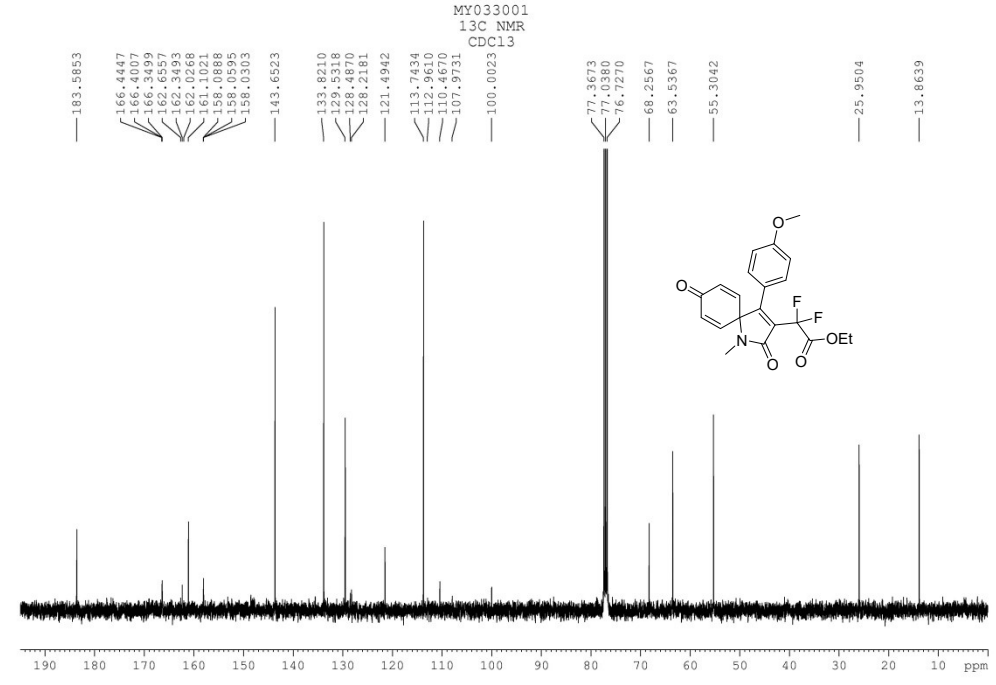

Fig. 27 ^{13}C NMR spectrum of compound **3i**

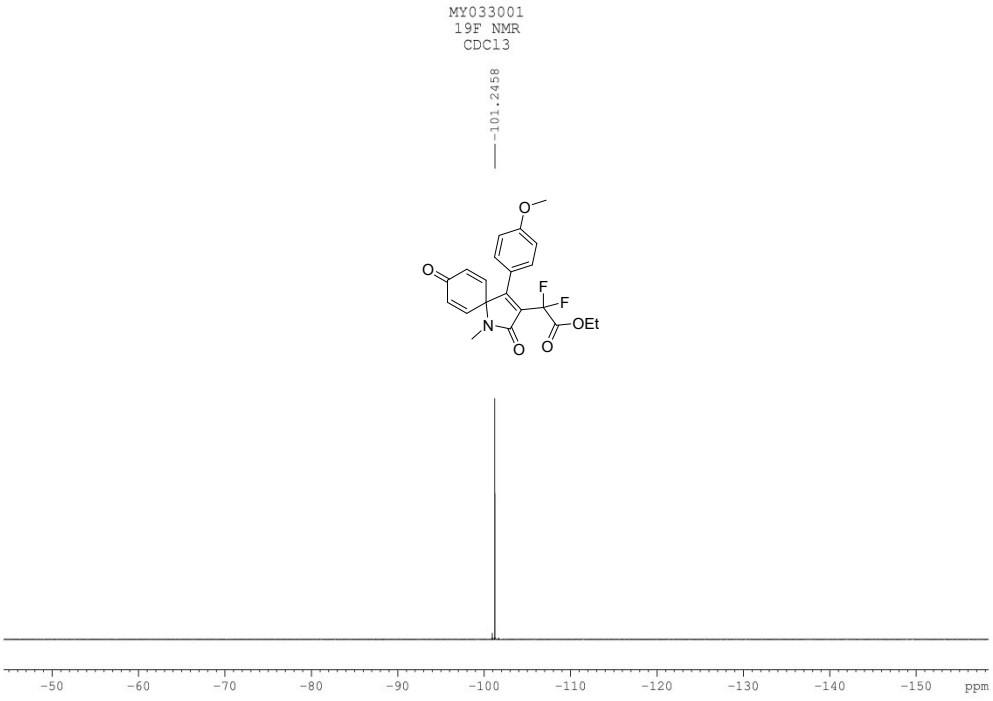

Fig. 28 ^{19}F NMR spectrum of compound **3i**

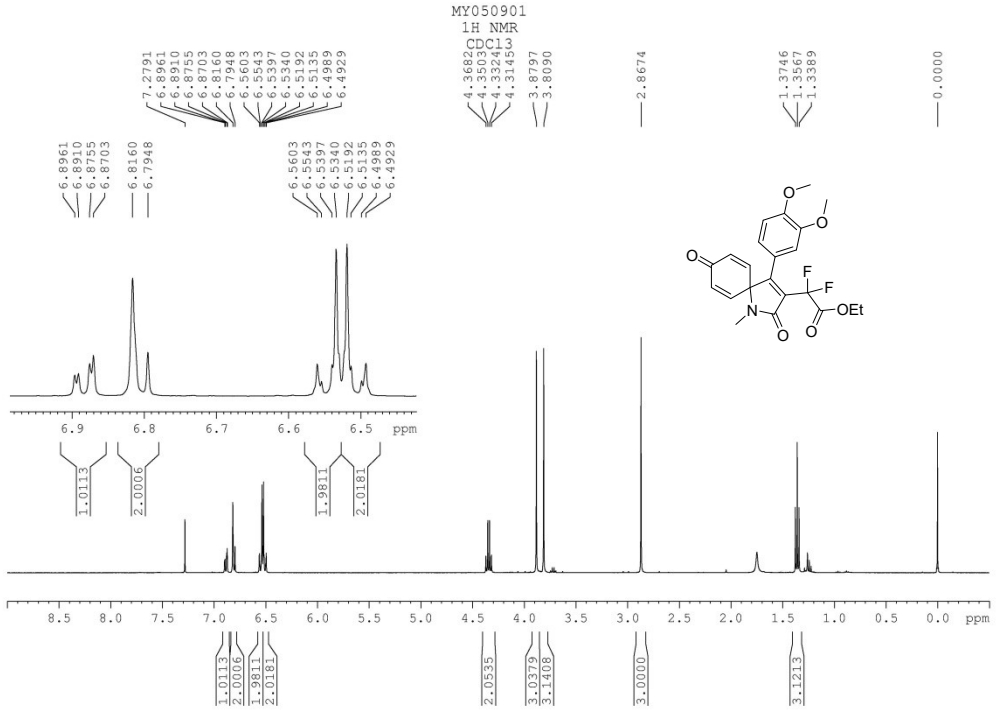

Fig. 29 ^{1}H NMR spectrum of compound **3j**

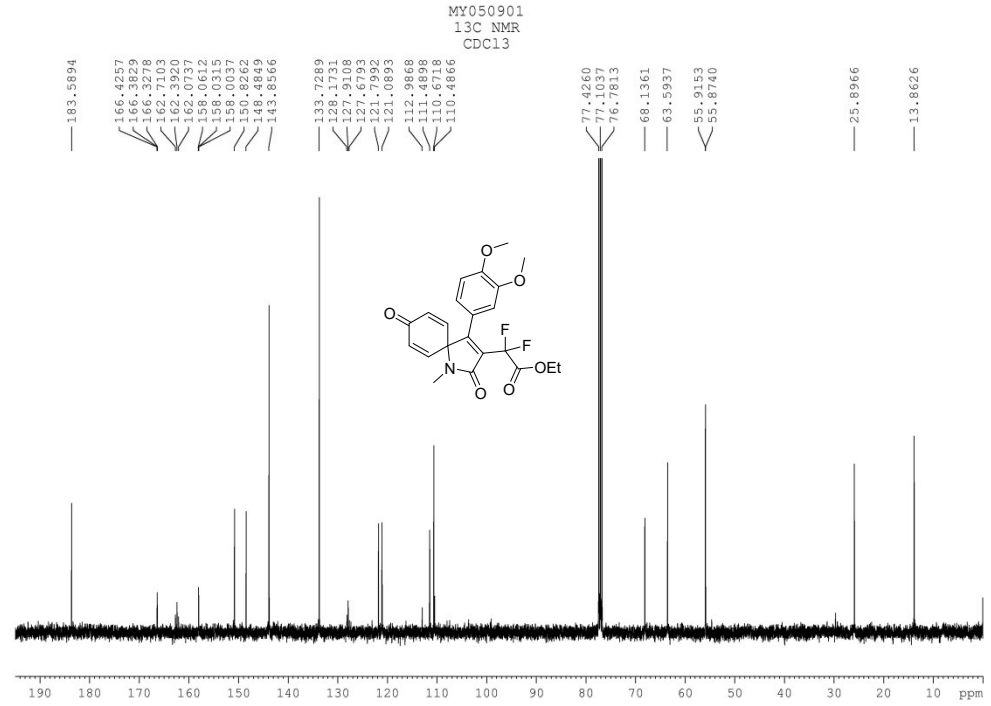

Fig. 30 ^{13}C NMR spectrum of compound **3j**

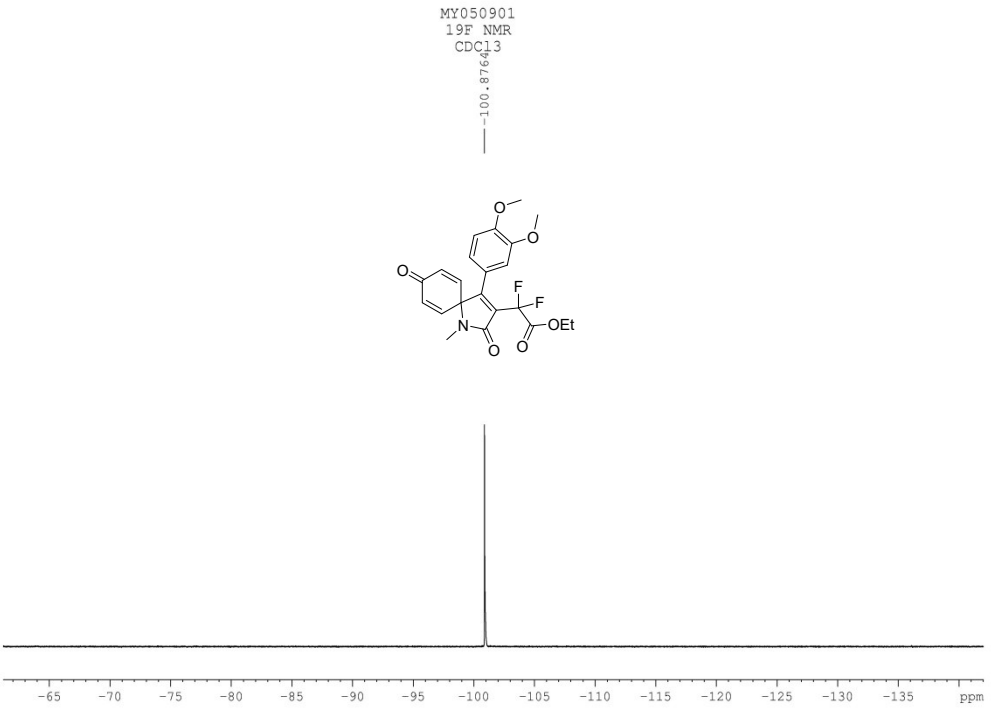

Fig. 31 ^{19}F NMR spectrum of compound **3j**

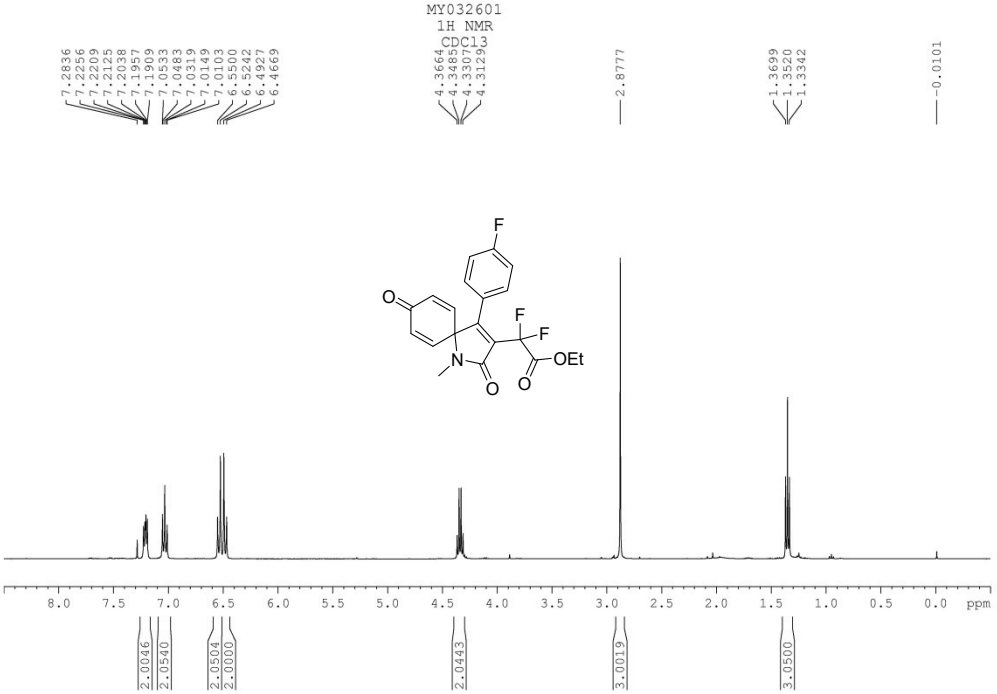

Fig. 32 ^{1}H NMR spectrum of compound **3k**

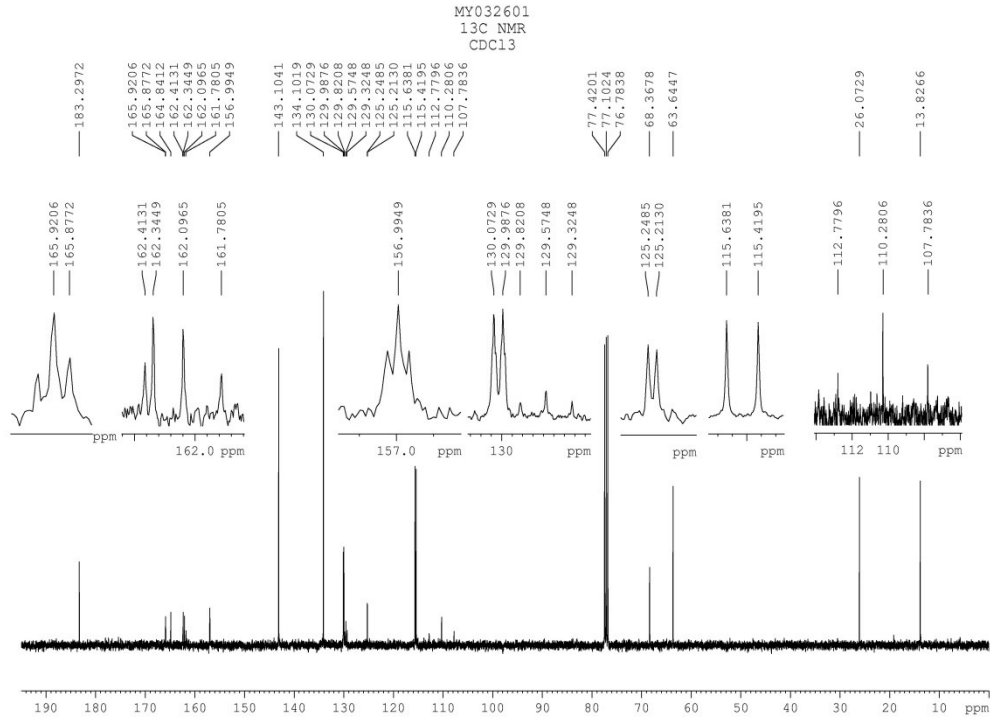

Fig. 33 ^{13}C NMR spectrum of compound **3k**

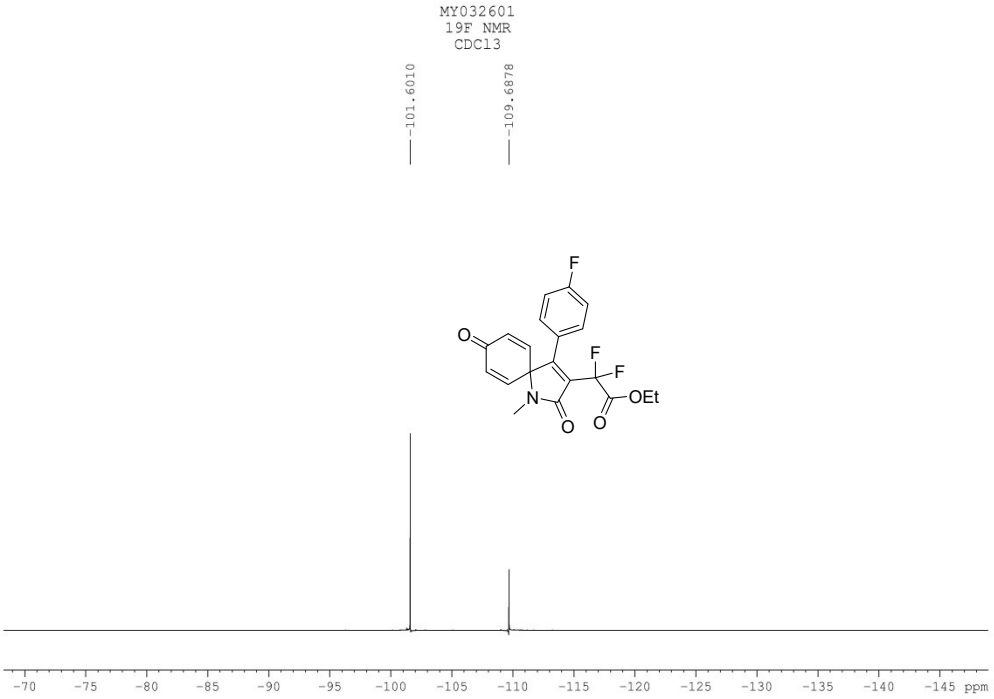

Fig. 34 ^{19}F NMR spectrum of compound **3k**

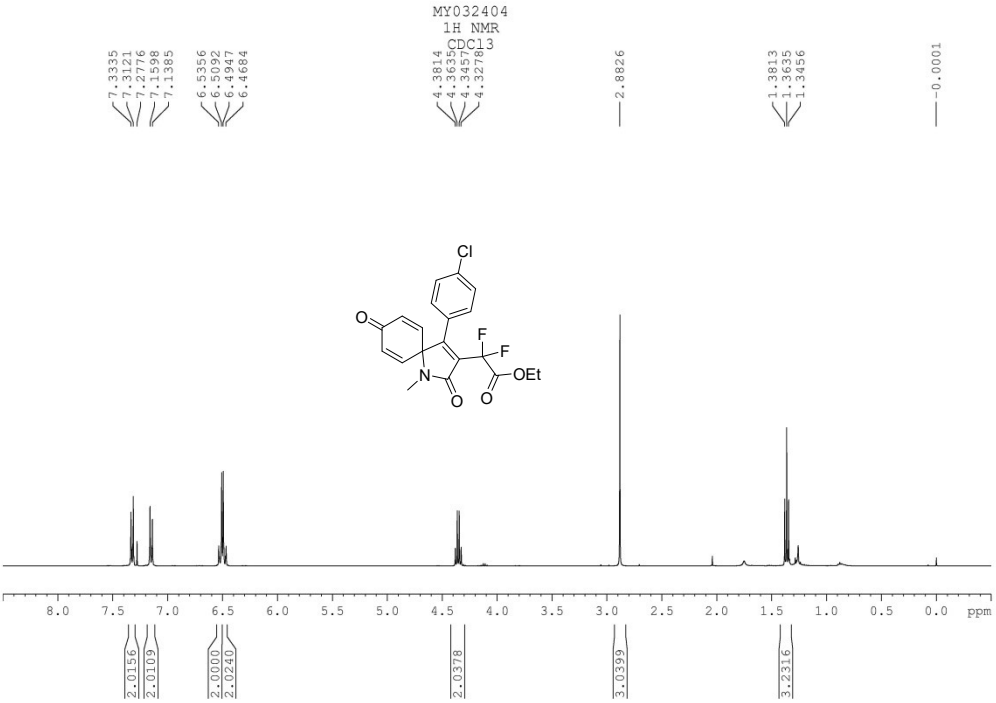

Fig. 35 ^{1}H NMR spectrum of compound **3l**

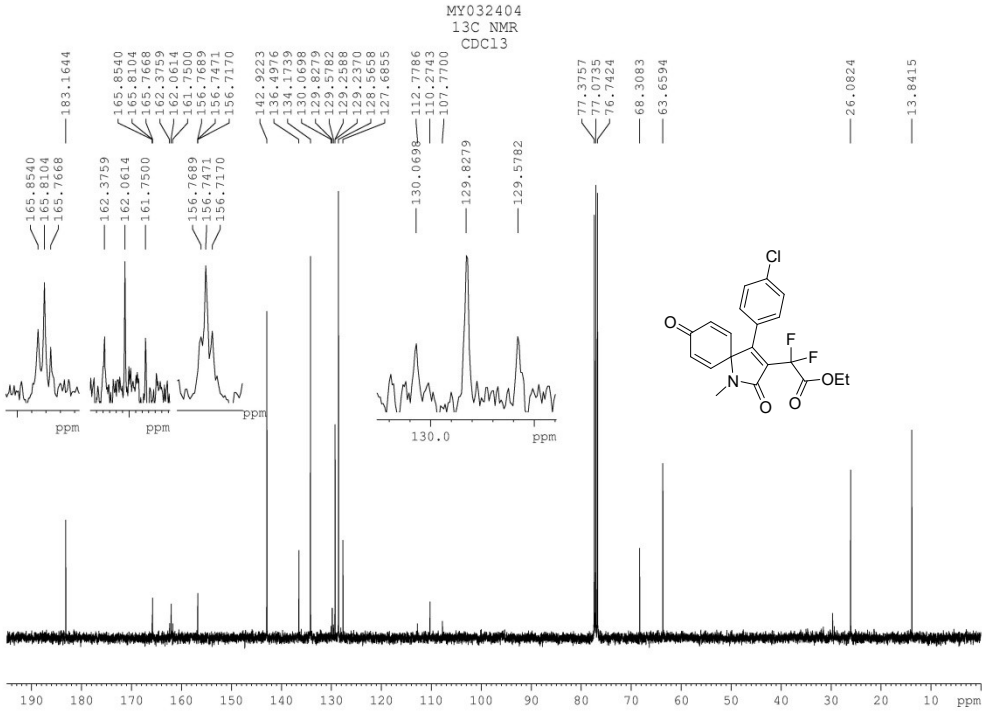

Fig. 36 ^{13}C NMR spectrum of compound **3l**

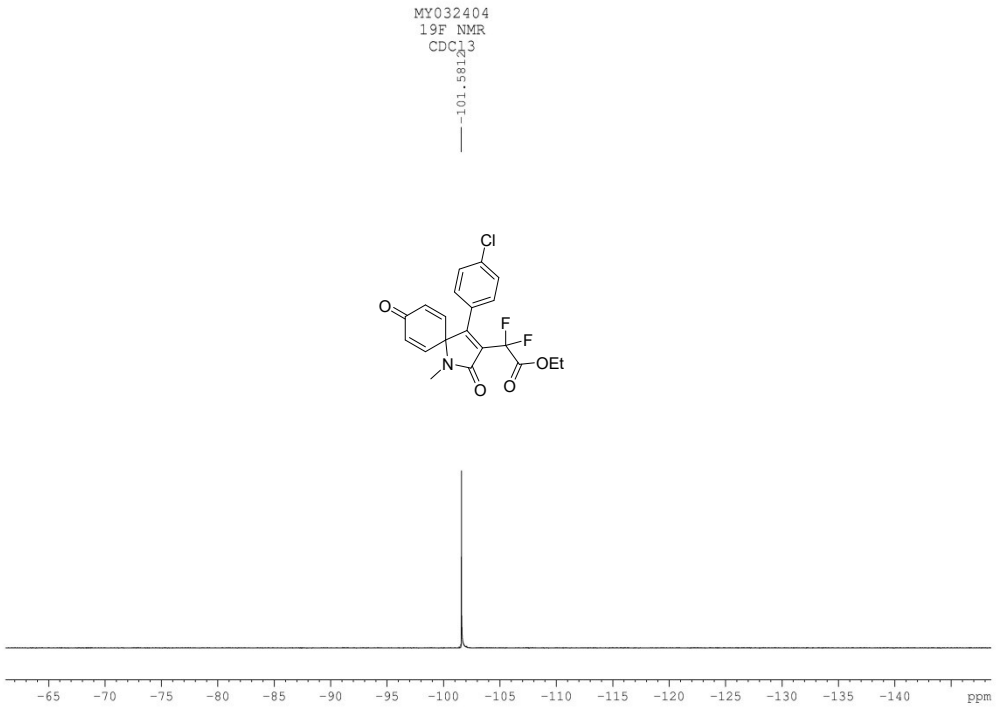

Fig. 37 ^{19}F NMR spectrum of compound **3l**

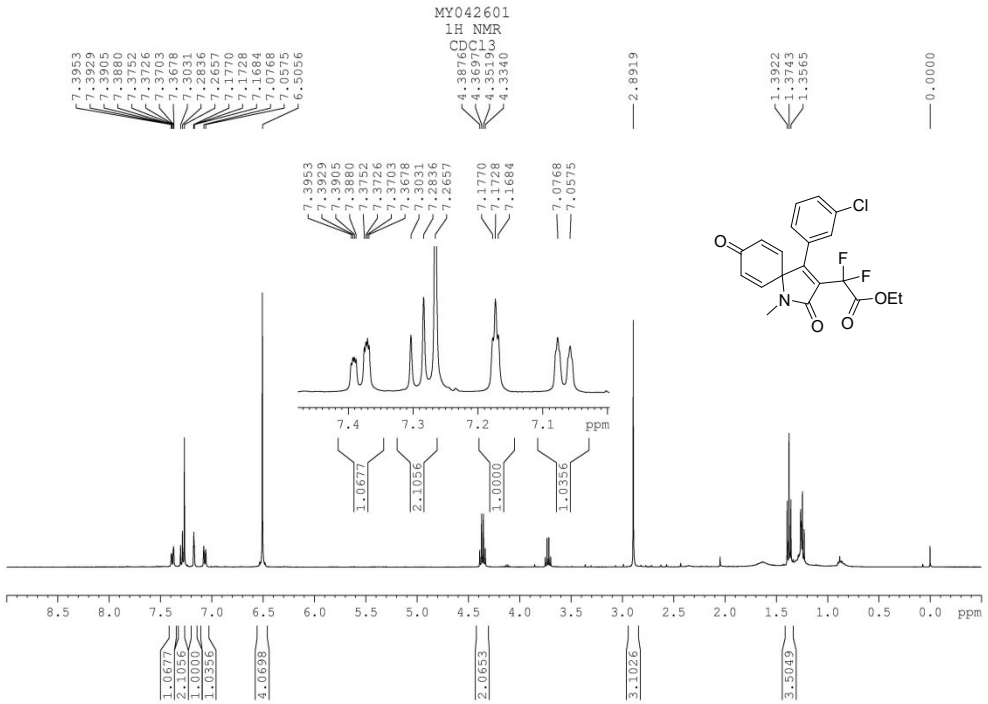

Fig. 38 ^{1}H NMR spectrum of compound **3m**

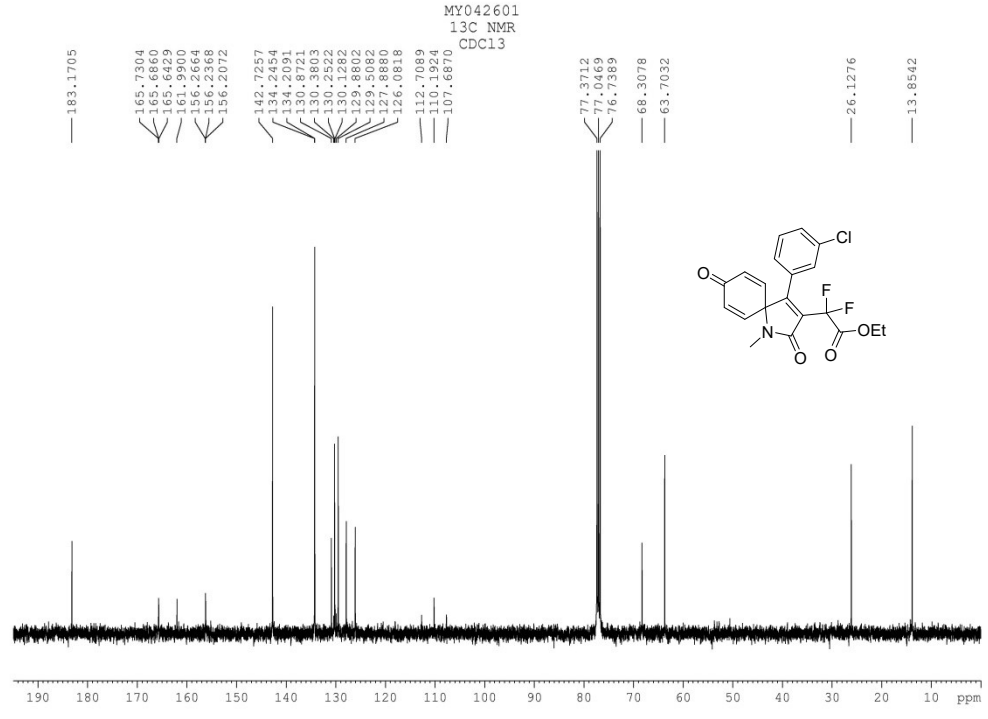

Fig. 39 ^{13}C NMR spectrum of compound **3m**

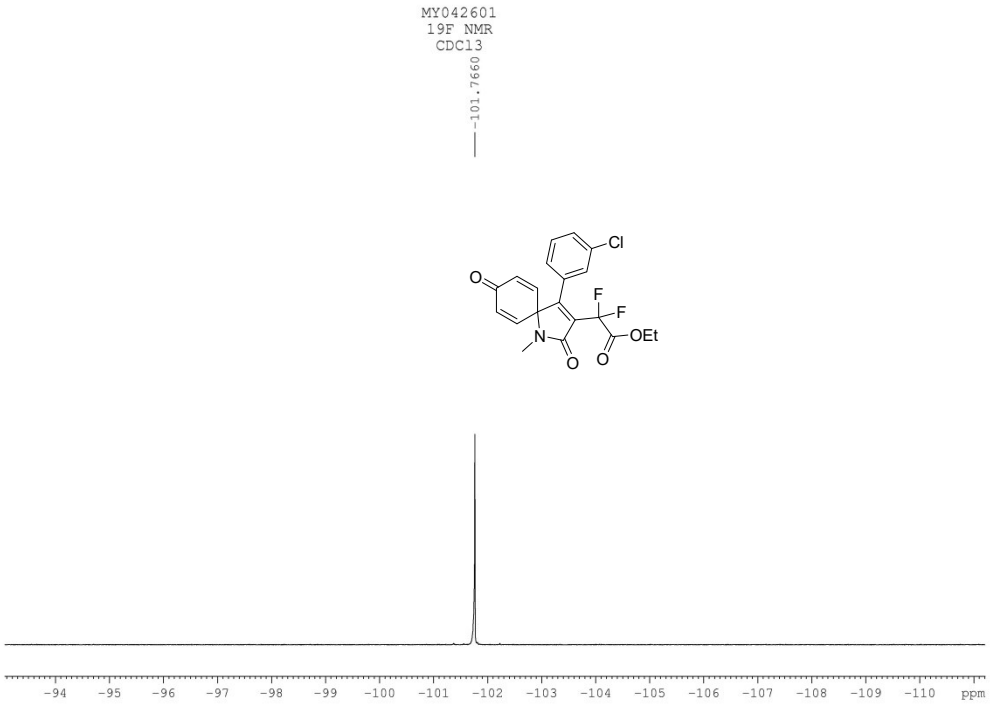

Fig. 40 ^{19}F NMR spectrum of compound **3m**

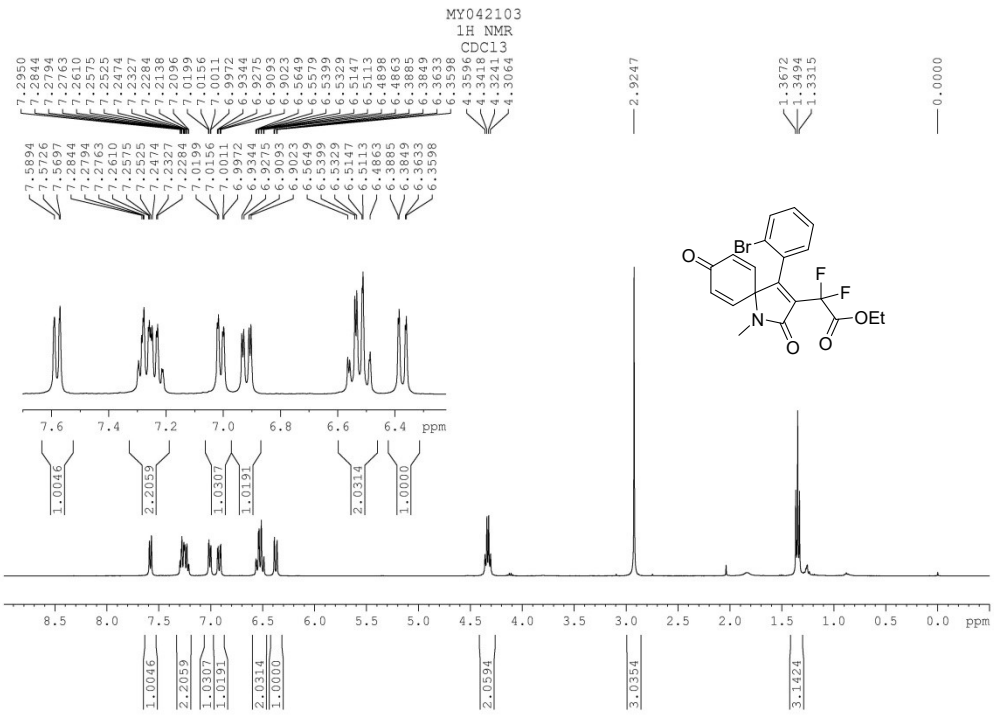

Fig. 41 ^{1}H NMR spectrum of compound **3n**

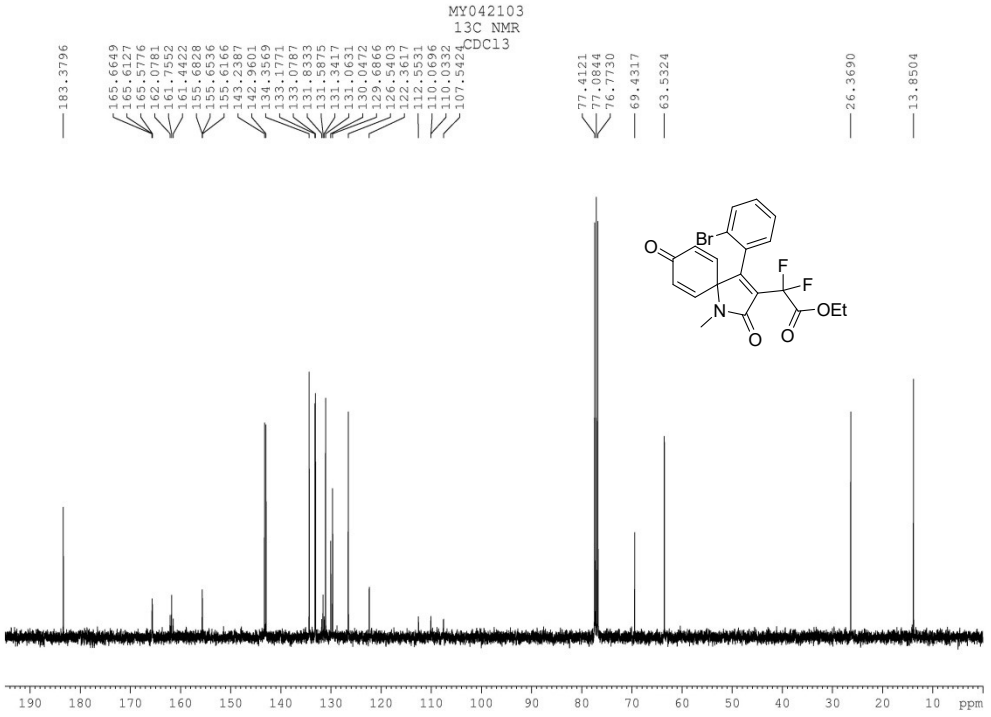

Fig. 42 ^{13}C NMR spectrum of compound **3n**

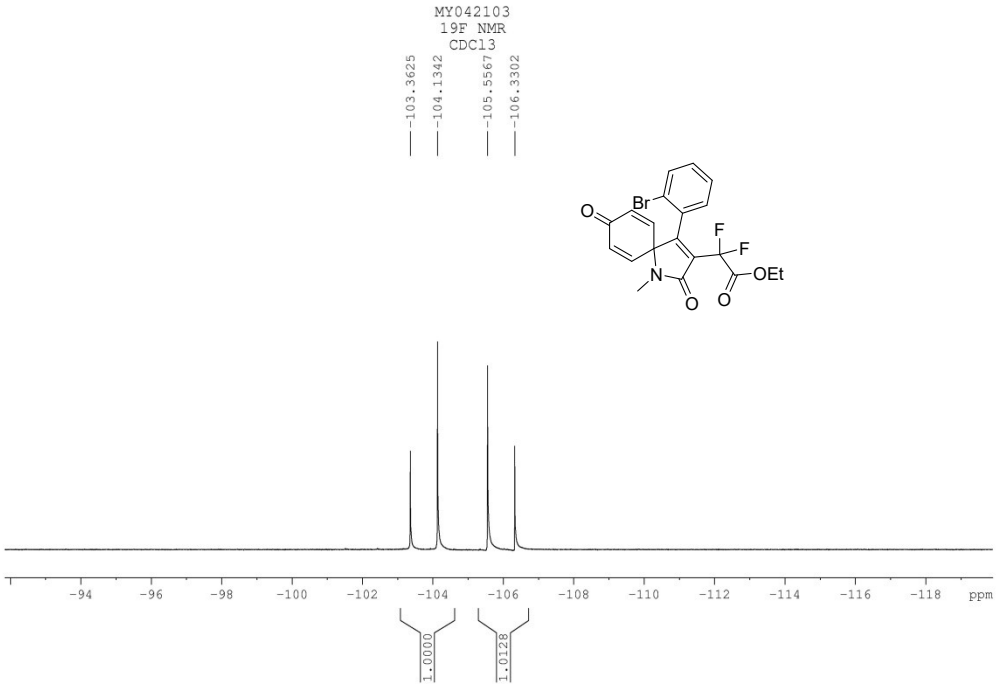

Fig. 43 ^{19}F NMR spectrum of compound **3n**

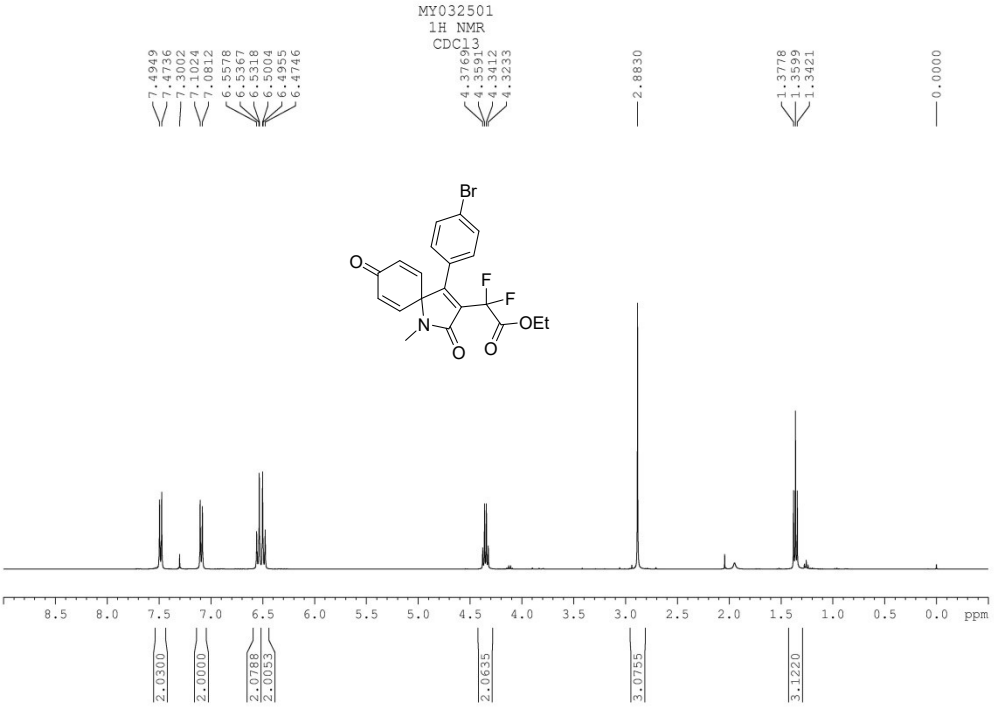

Fig. 44 ^{1}H NMR spectrum of compound **3o**

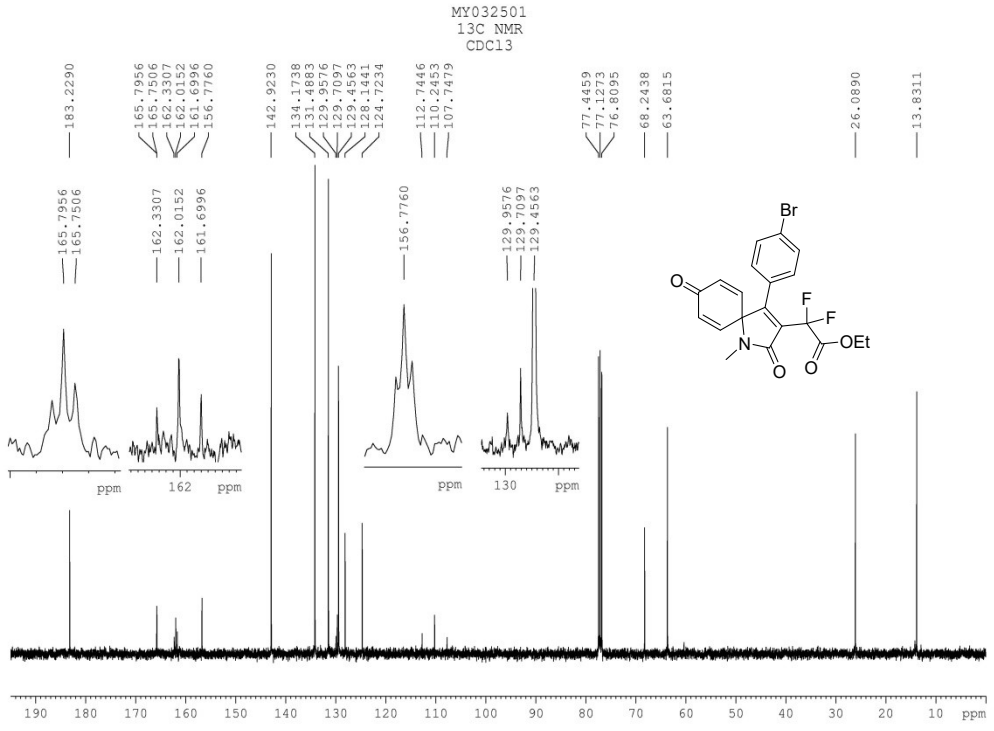

Fig. 45 ^{13}C NMR spectrum of compound **3o**

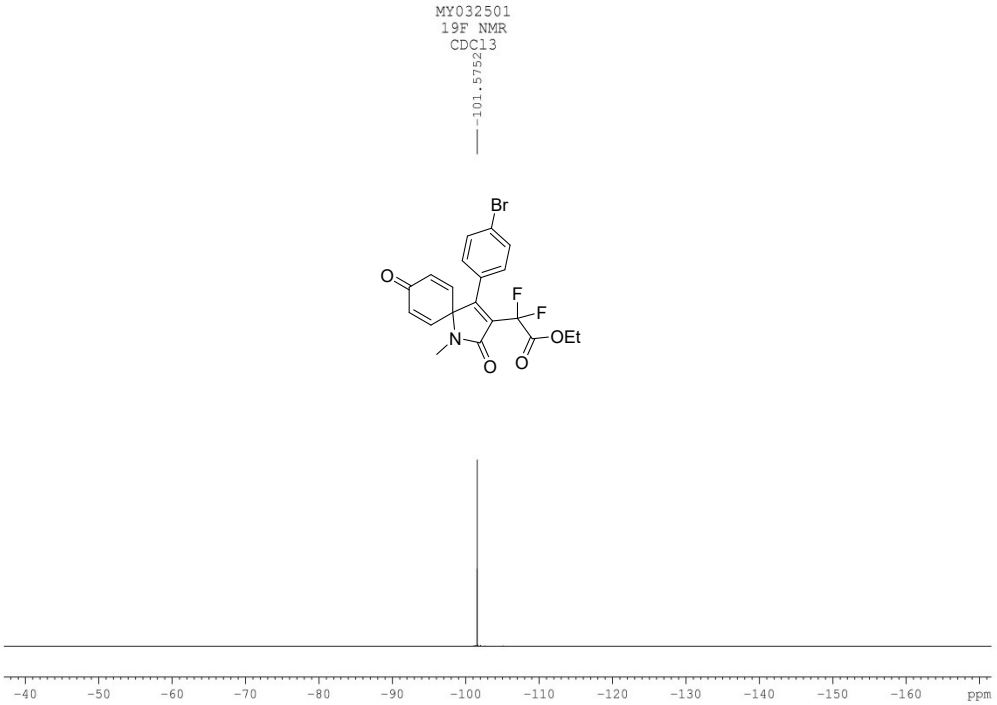

Fig. 46 ^{19}F NMR spectrum of compound **3o**

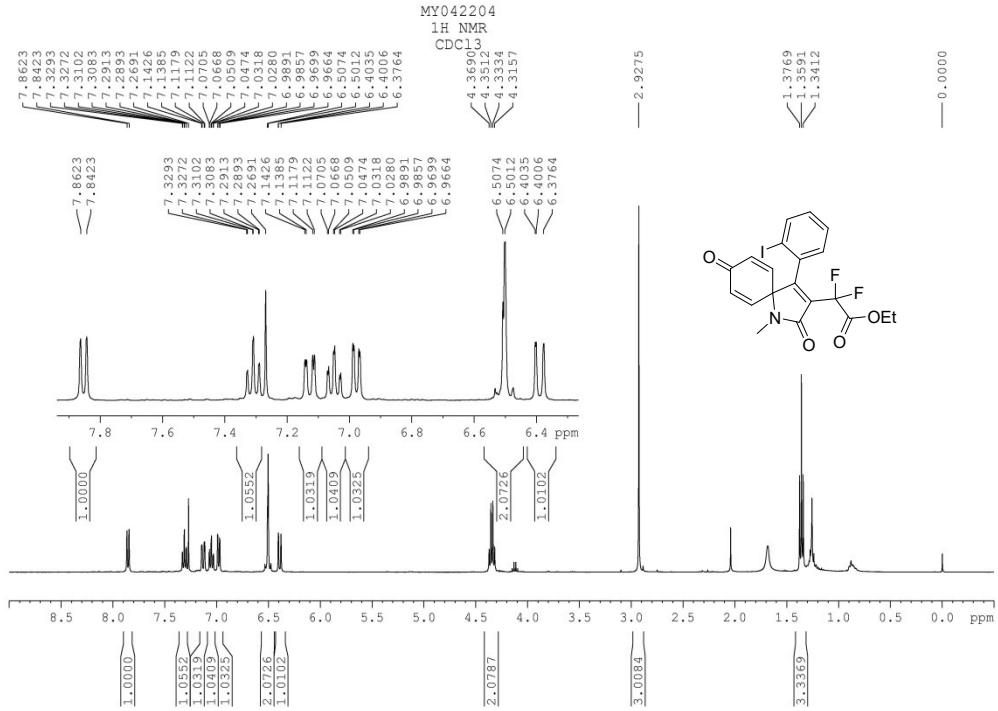

Fig. 47 ^{1}H NMR spectrum of compound **3p**

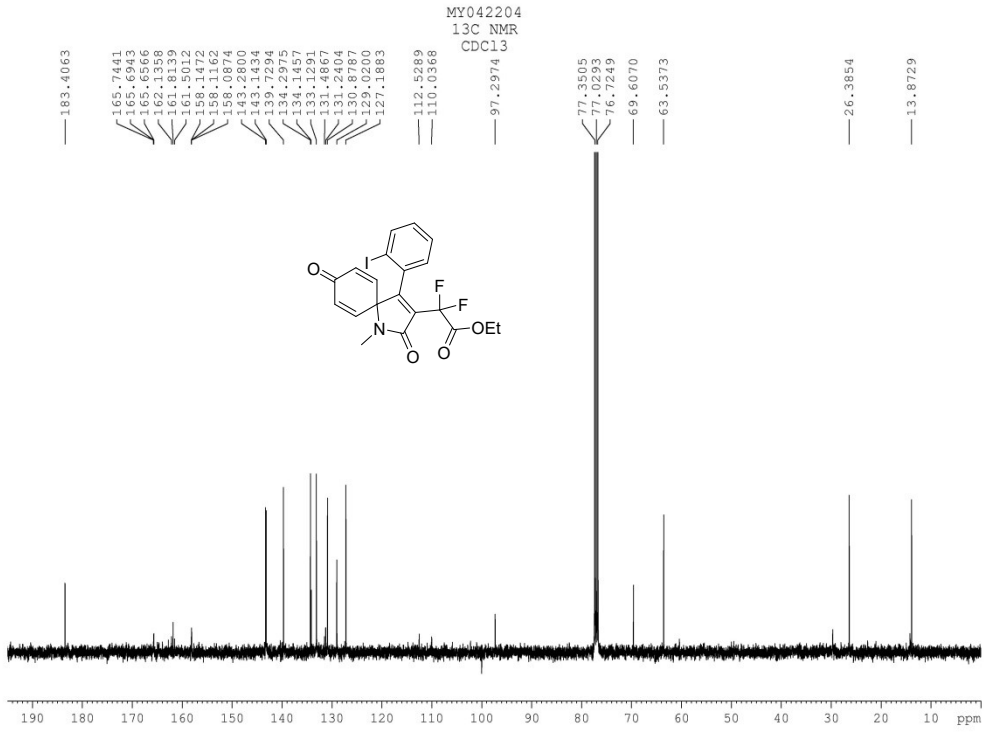

Fig. 48 ^{13}C NMR spectrum of compound **3p**

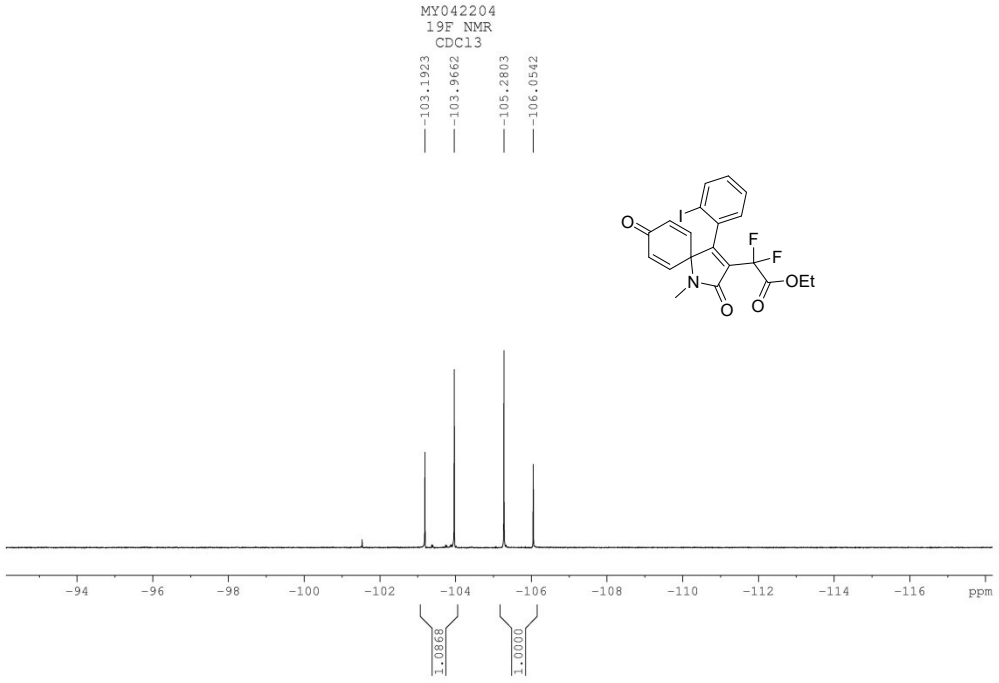

Fig. 49 ^{19}F NMR spectrum of compound **3p**

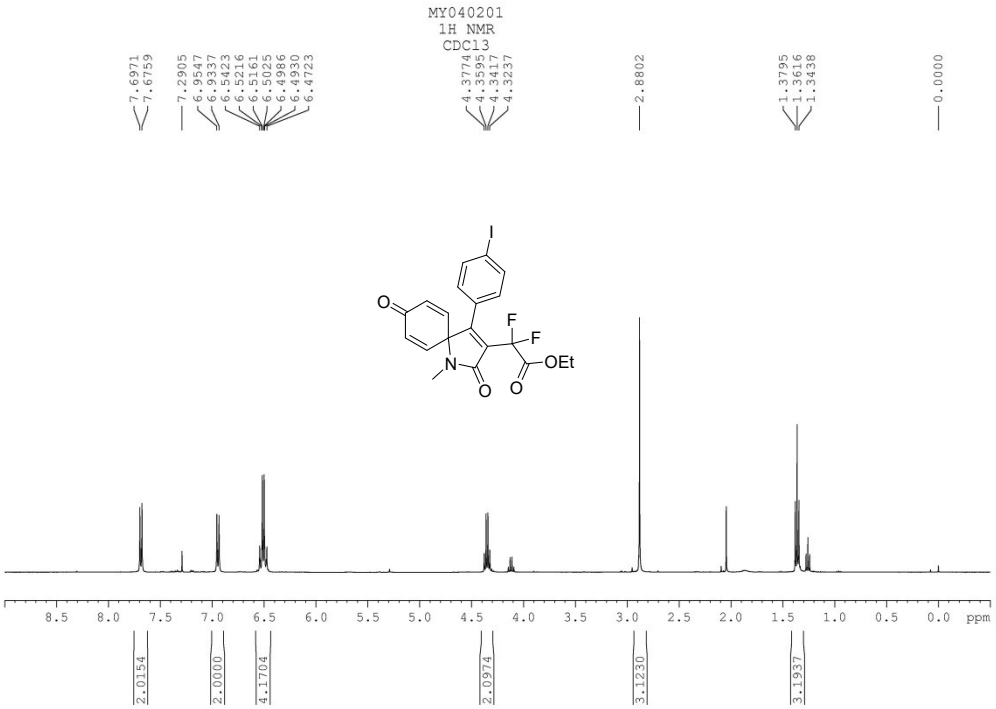

Fig. 50 ^{1}H NMR spectrum of compound **3q**

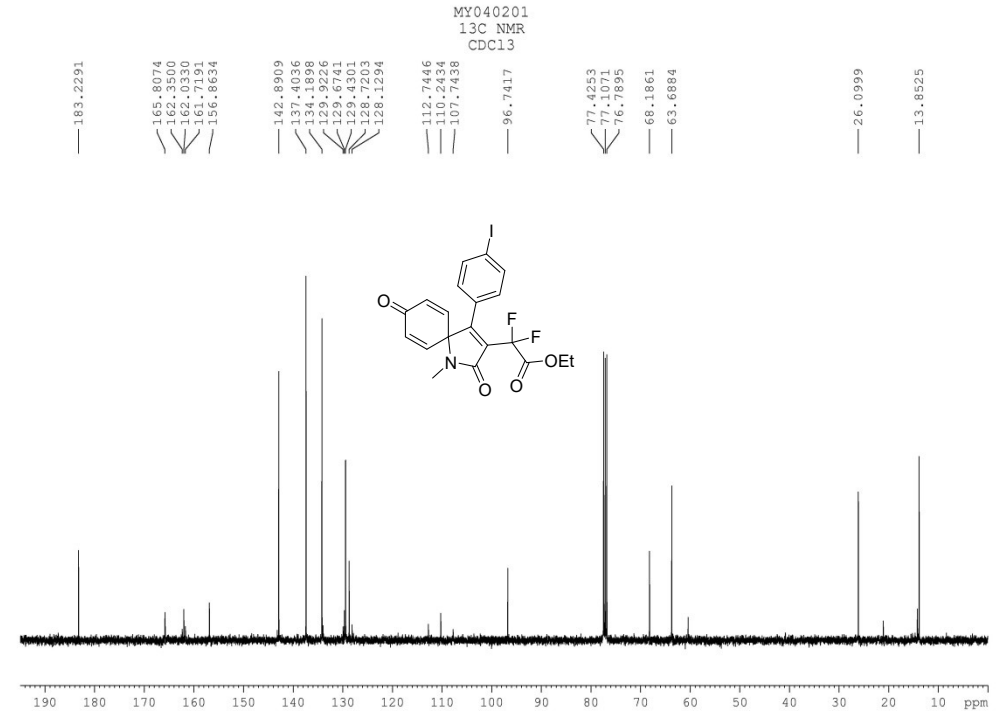

Fig. 51 ^{13}C NMR spectrum of compound **3q**

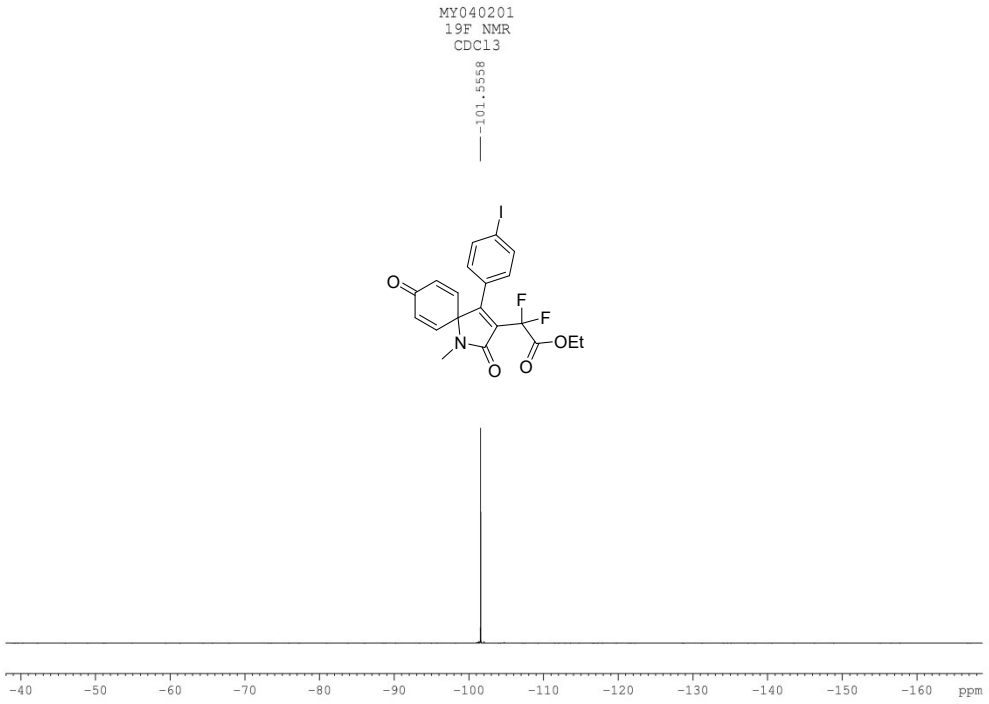

Fig. 52 ^{19}F NMR spectrum of compound **3q**

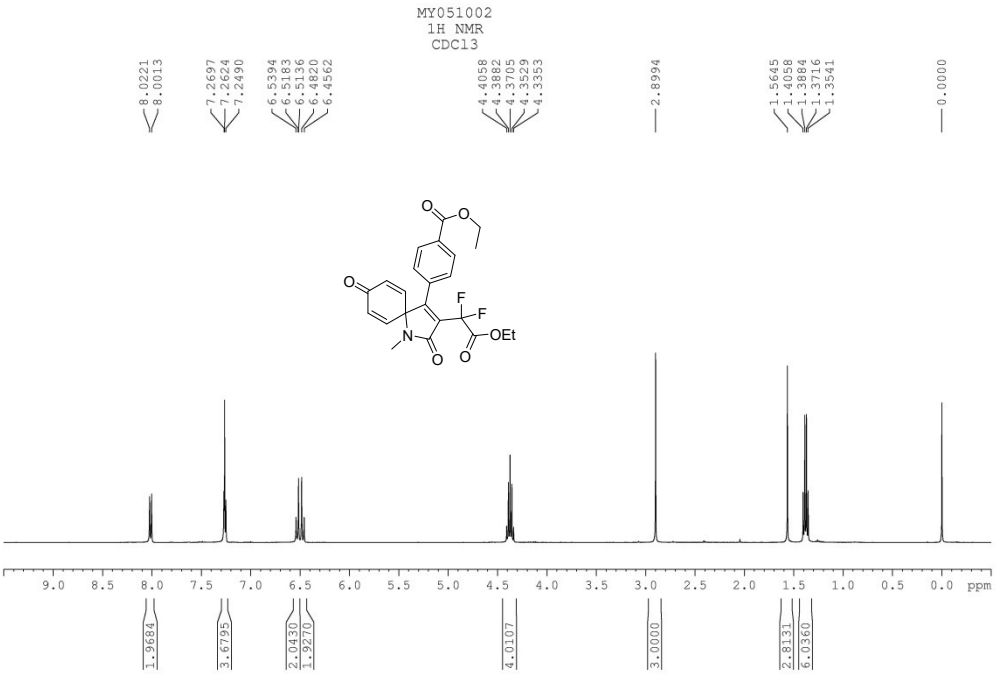

Fig. 53 ^{1}H NMR spectrum of compound **3r**

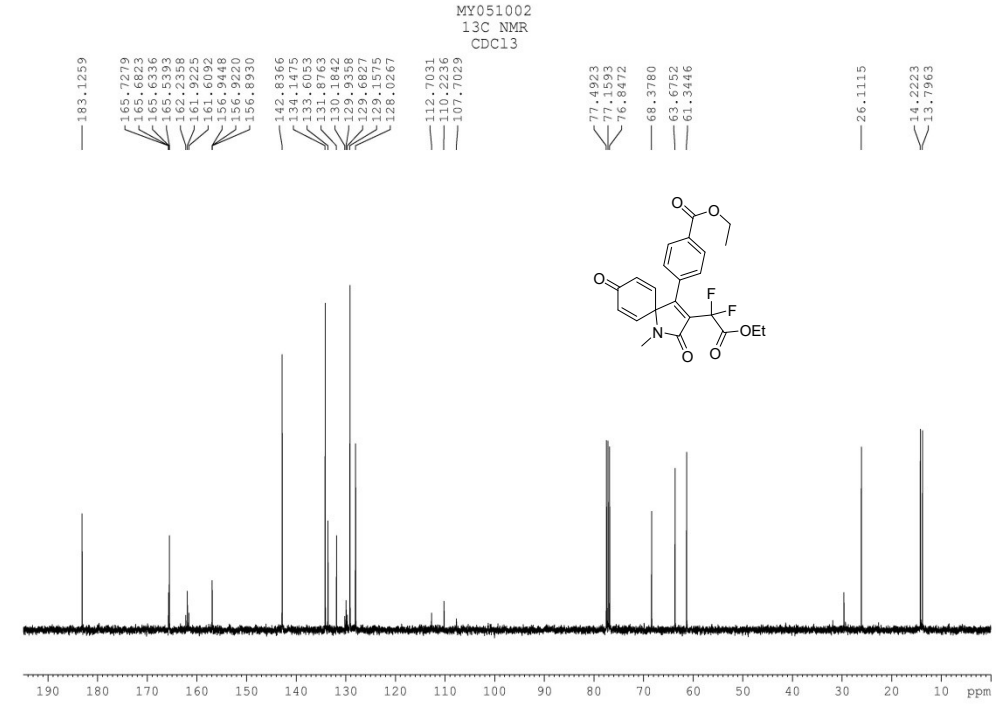

Fig. 54 ^{13}C NMR spectrum of compound **3r**

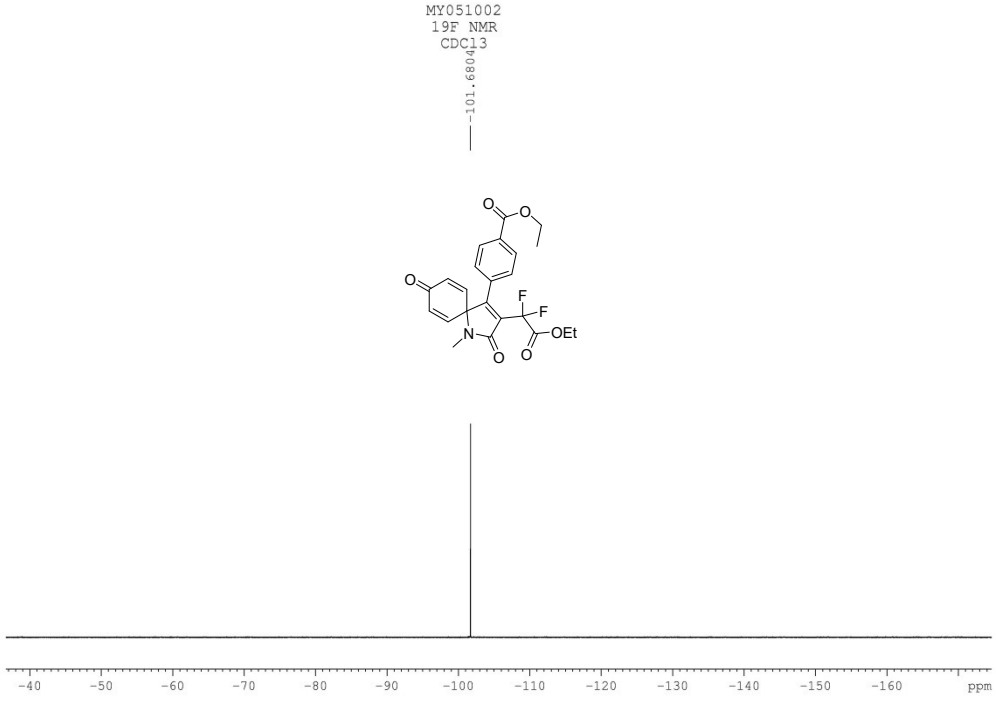

Fig. 55 ^{19}F NMR spectrum of compound **3r**

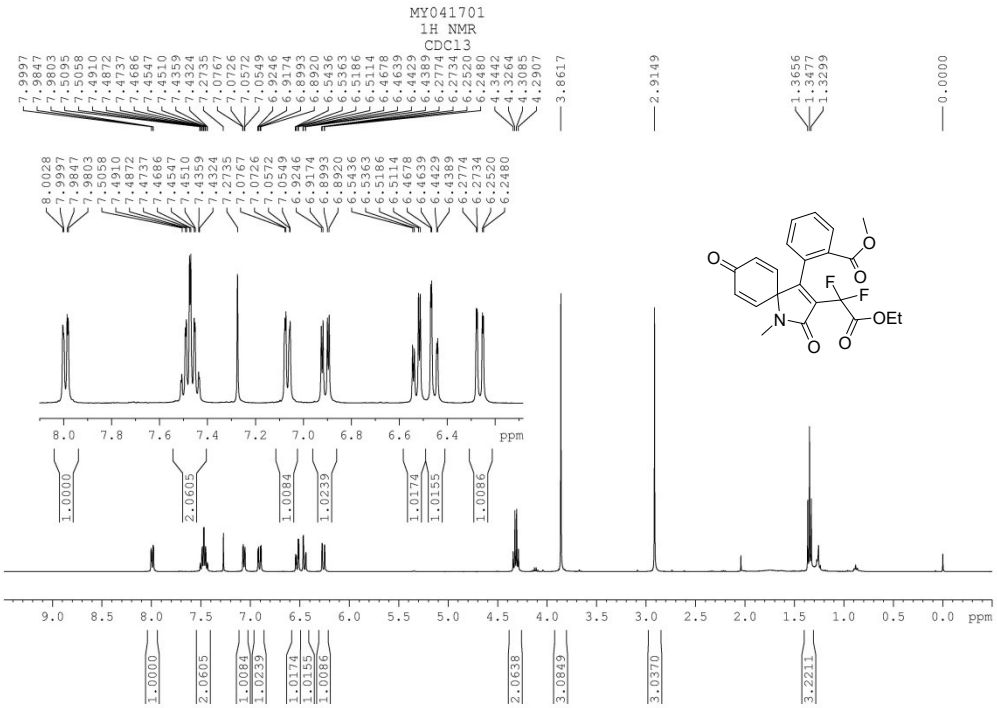

Fig. 56 ^{1}H NMR spectrum of compound **3s**

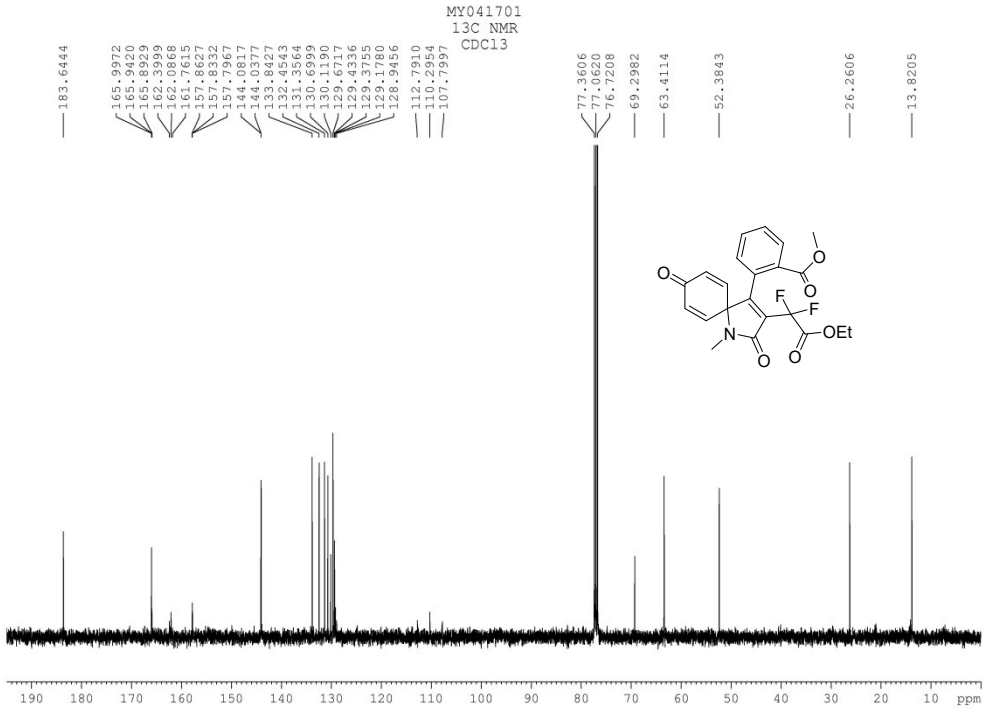

Fig. 57 ^{13}C NMR spectrum of compound **3s**

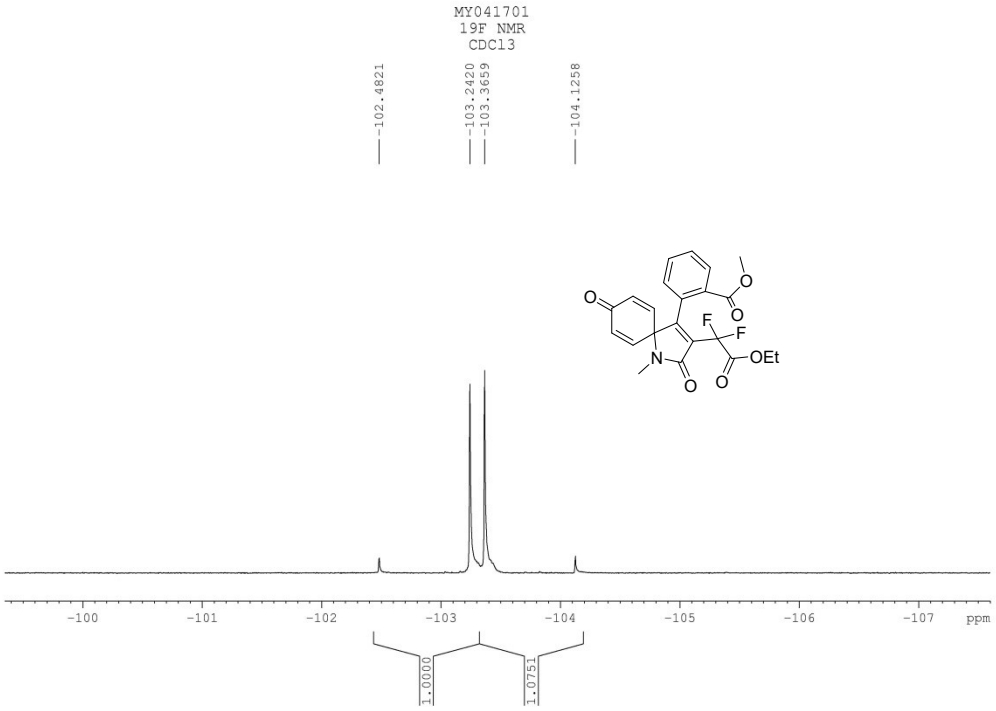

Fig. 58 ^{19}F NMR spectrum of compound **3s**

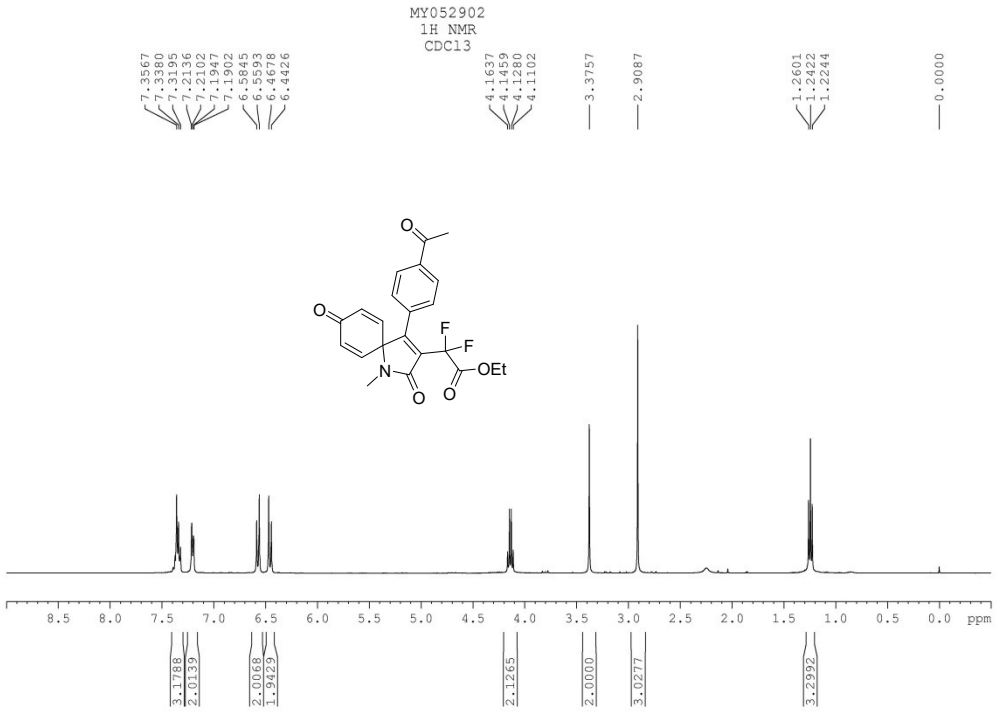

Fig. 59 ^{1}H NMR spectrum of compound **3t**

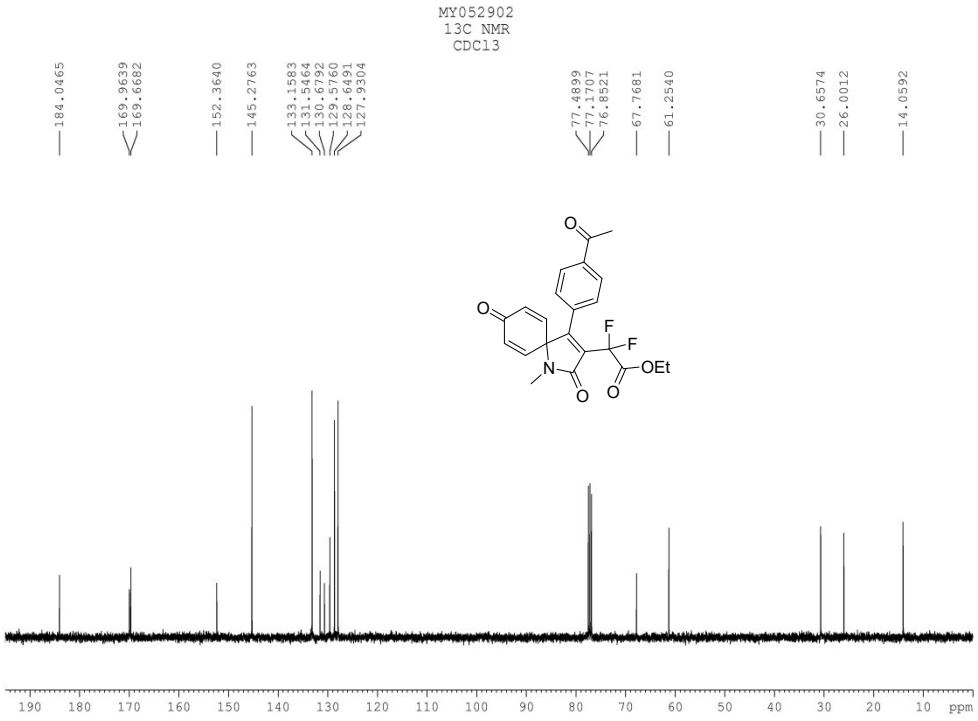

Fig. 60 ^{13}C NMR spectrum of compound **3t**

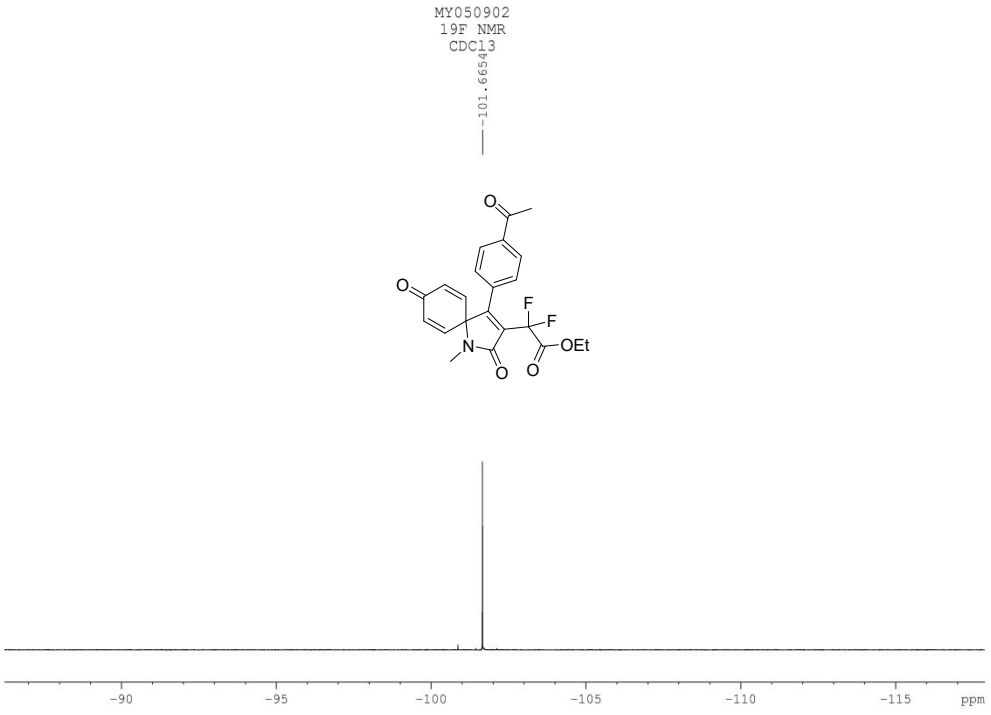

Fig. 61 ^{19}F NMR spectrum of compound **3t**

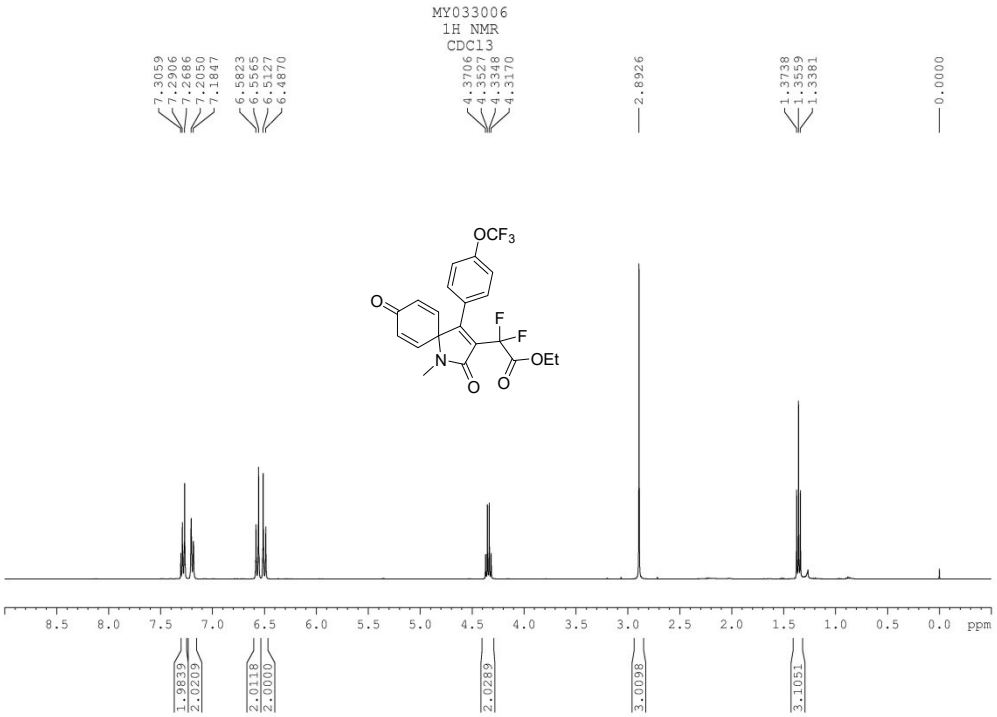

Fig. 62 ^{1}H NMR spectrum of compound **3u**

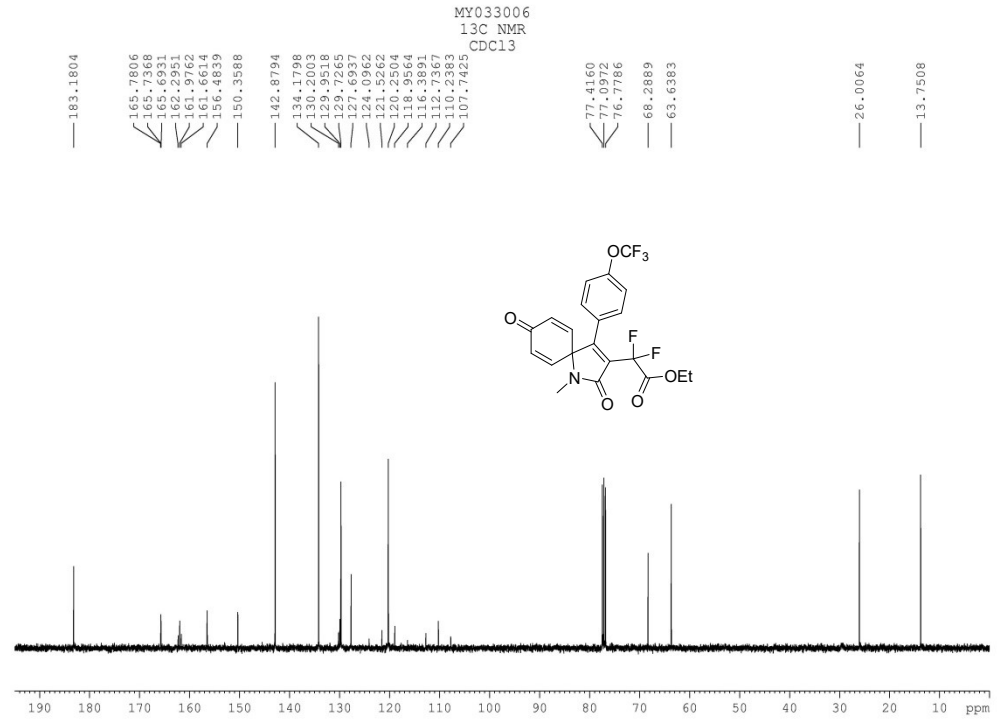

Fig. 63 ^{13}C NMR spectrum of compound **3u**

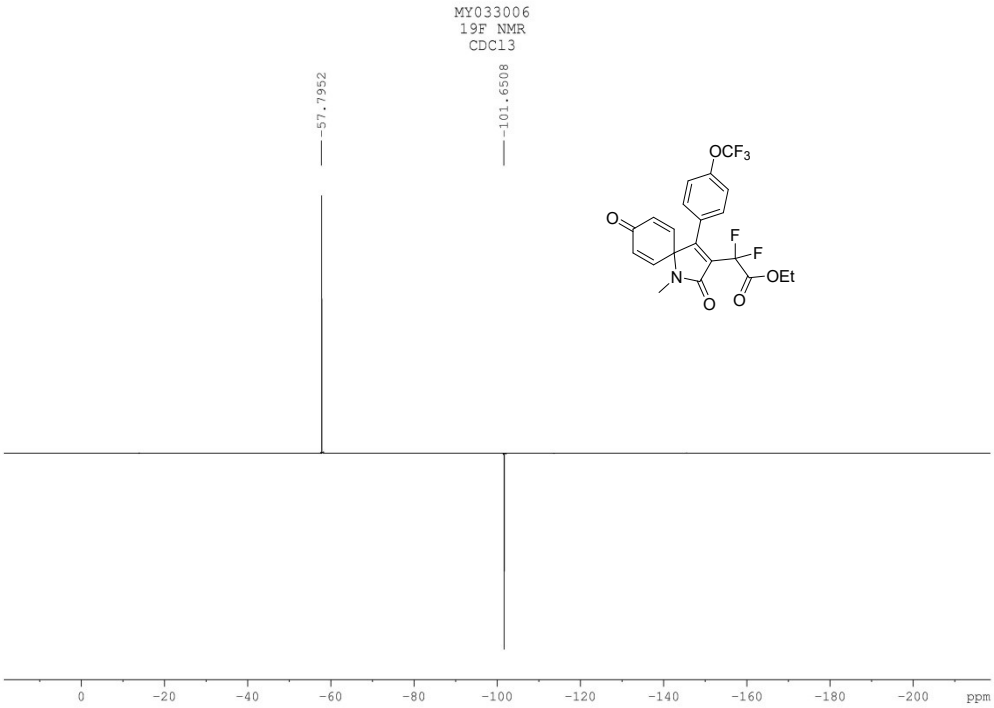

Fig. 64 ^{19}F NMR spectrum of compound **3u**

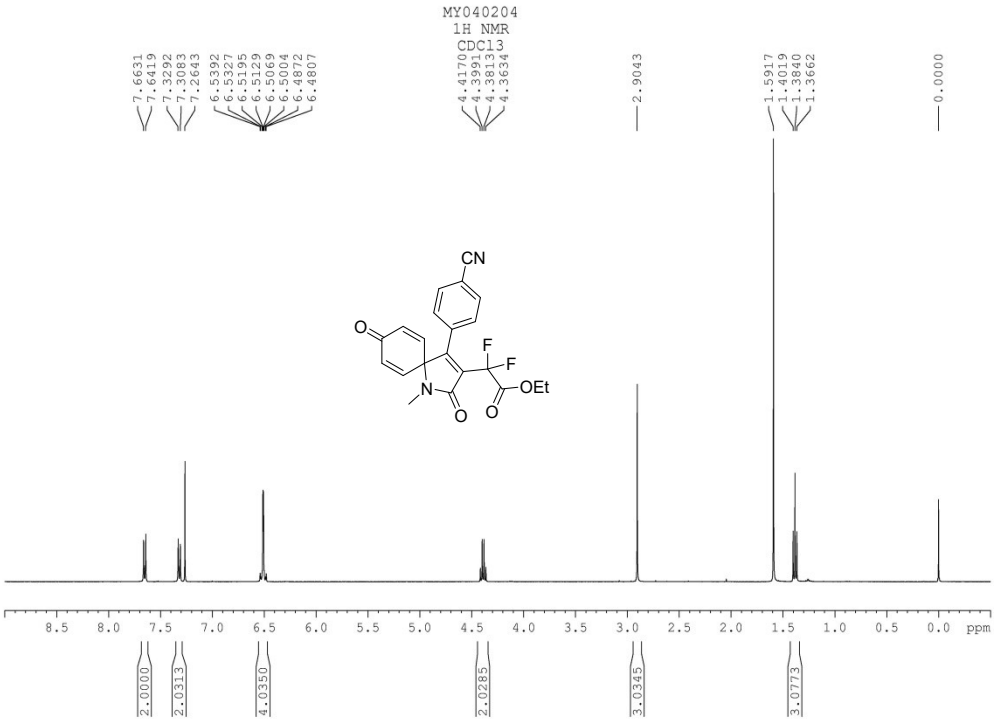

Fig. 65 ^{1}H NMR spectrum of compound **3v**

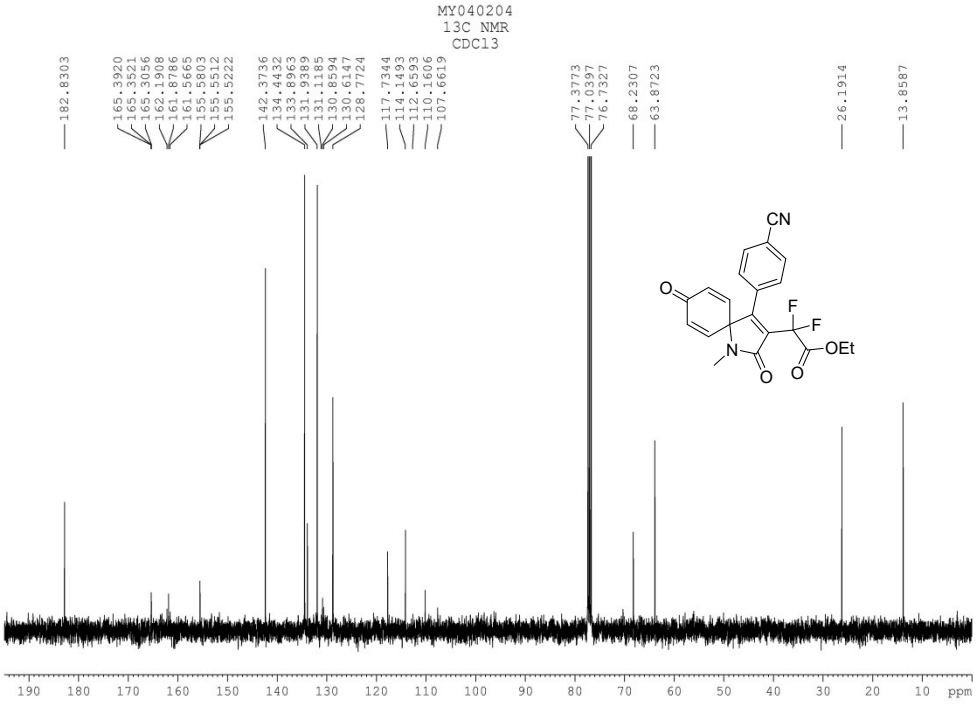

Fig. 66 ^{13}C NMR spectrum of compound **3v**

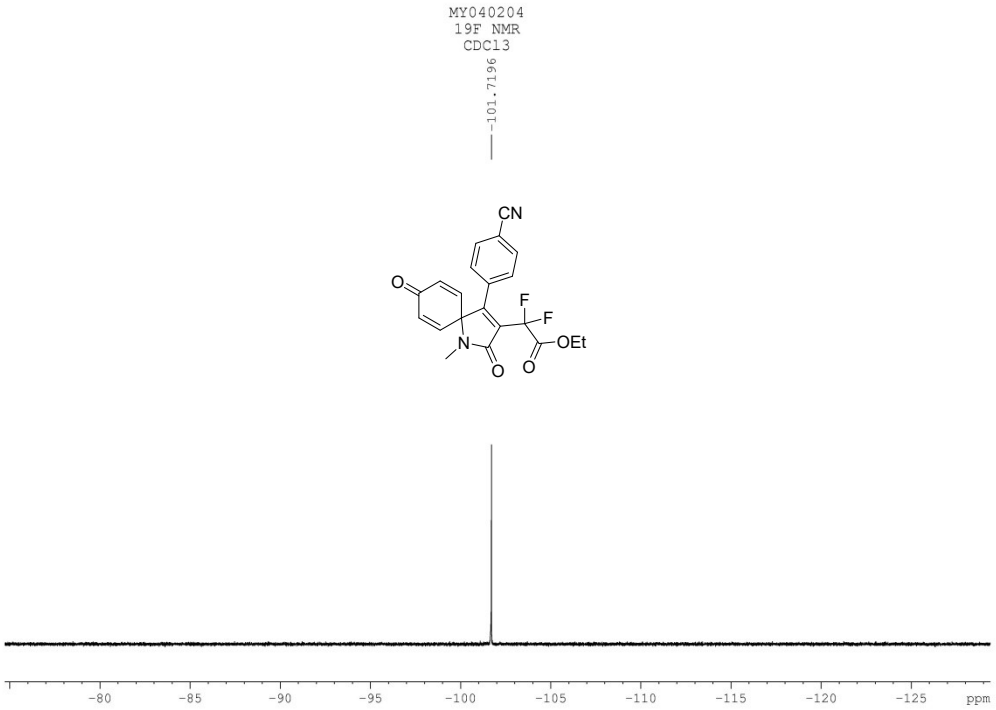

Fig. 67 ^{19}F NMR spectrum of compound **3v**

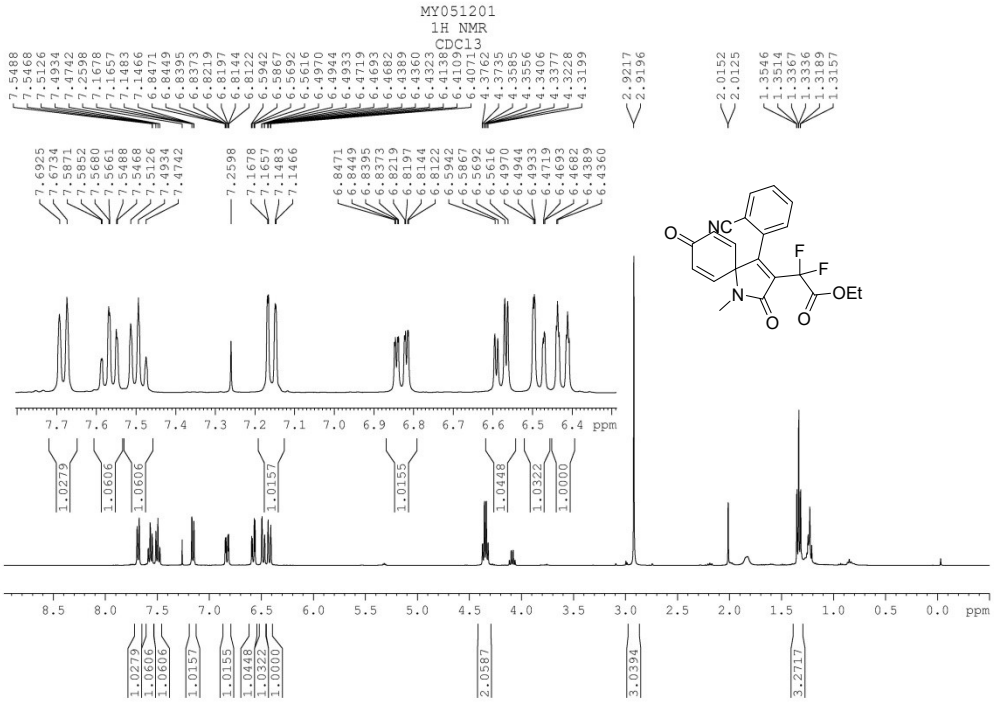

Fig. 68 ^{1}H NMR spectrum of compound **3w**

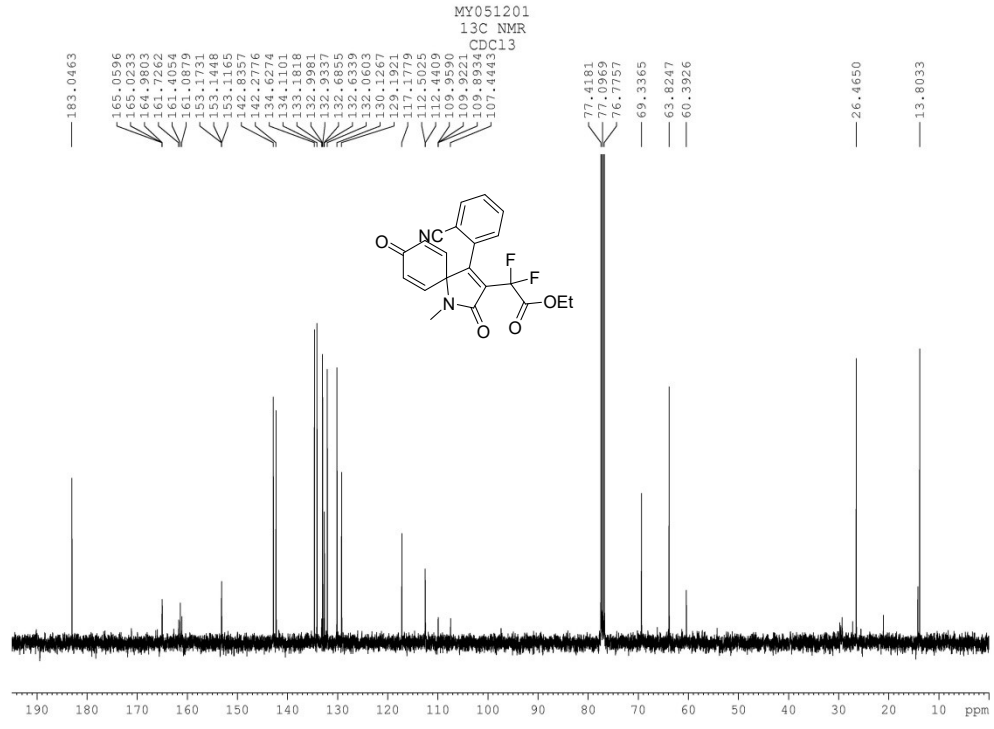

Fig. 69 ^{13}C NMR spectrum of compound **3w**

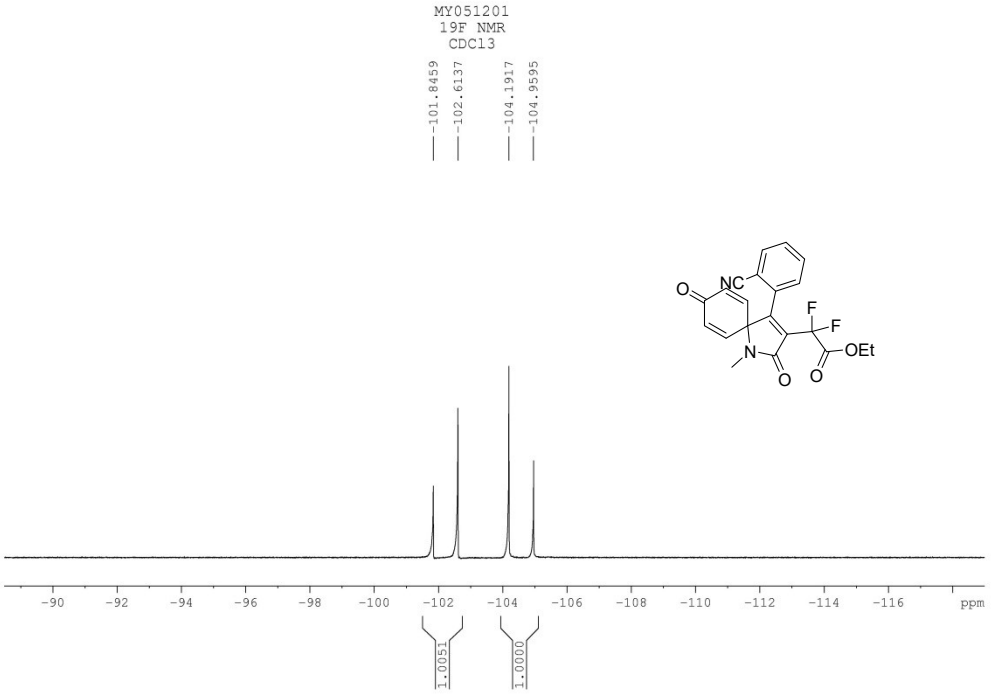

Fig. 70 ^{19}F NMR spectrum of compound **3w**

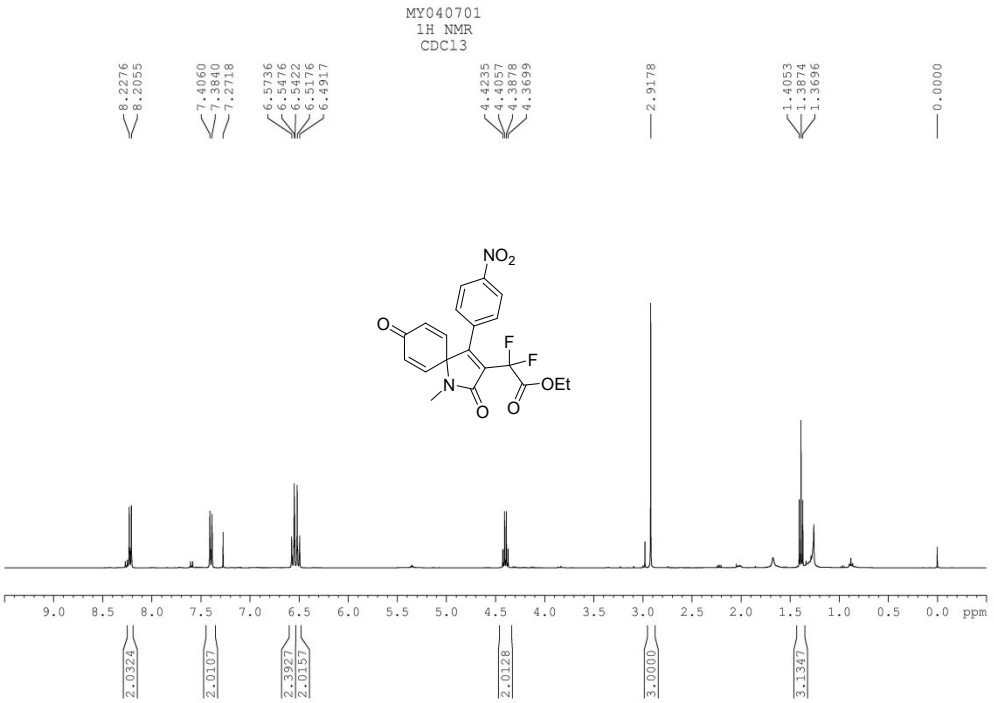

Fig. 71 ^{1}H NMR spectrum of compound **3x**

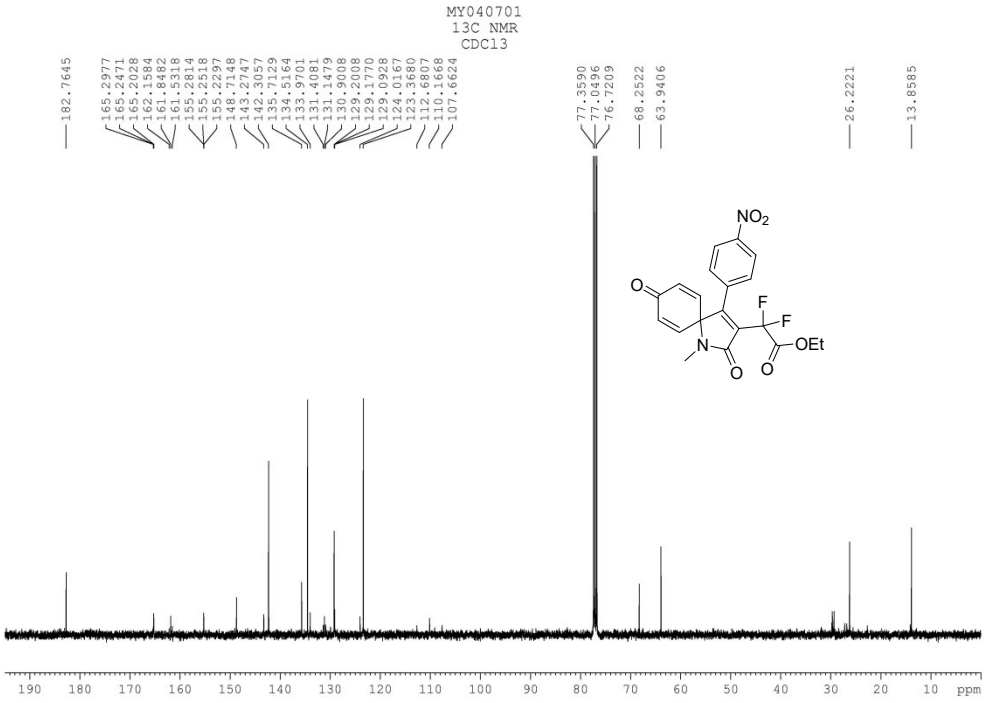

Fig. 72 ^{13}C NMR spectrum of compound **3x**

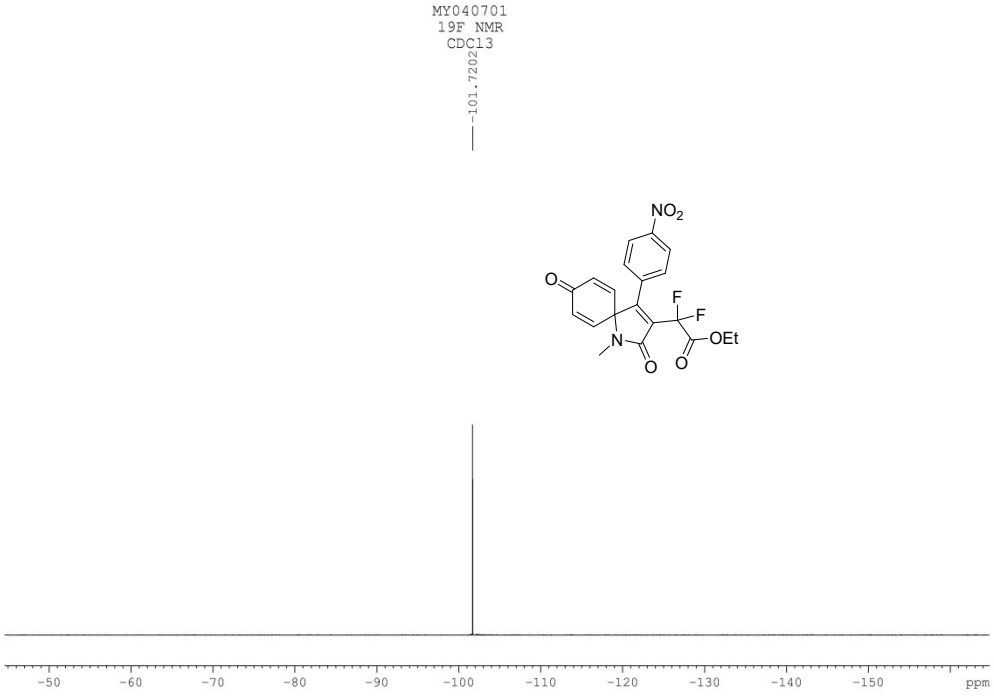

Fig. 73 ^{19}F NMR spectrum of compound **3x**

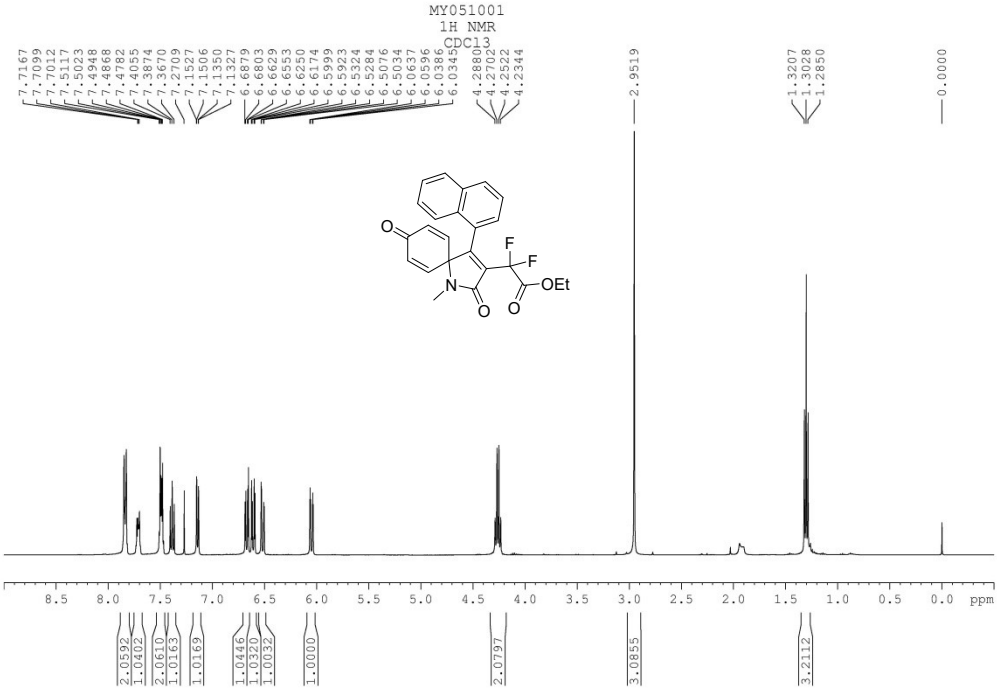

Fig. 74 ^{1}H NMR spectrum of compound **3y**

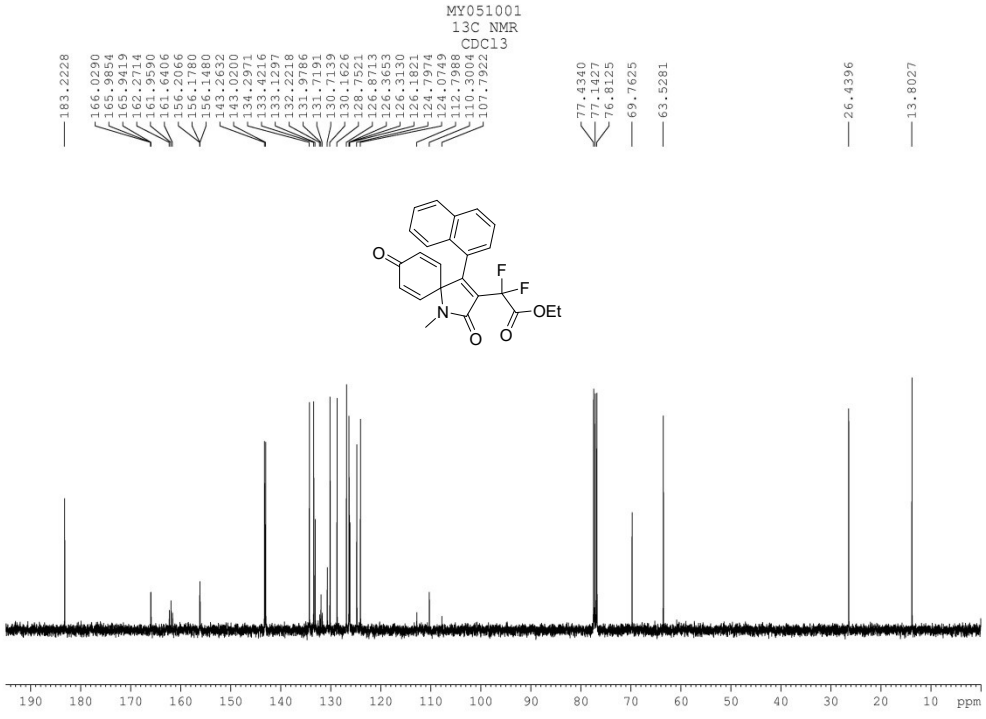

Fig. 75 ^{13}C NMR spectrum of compound **3y**

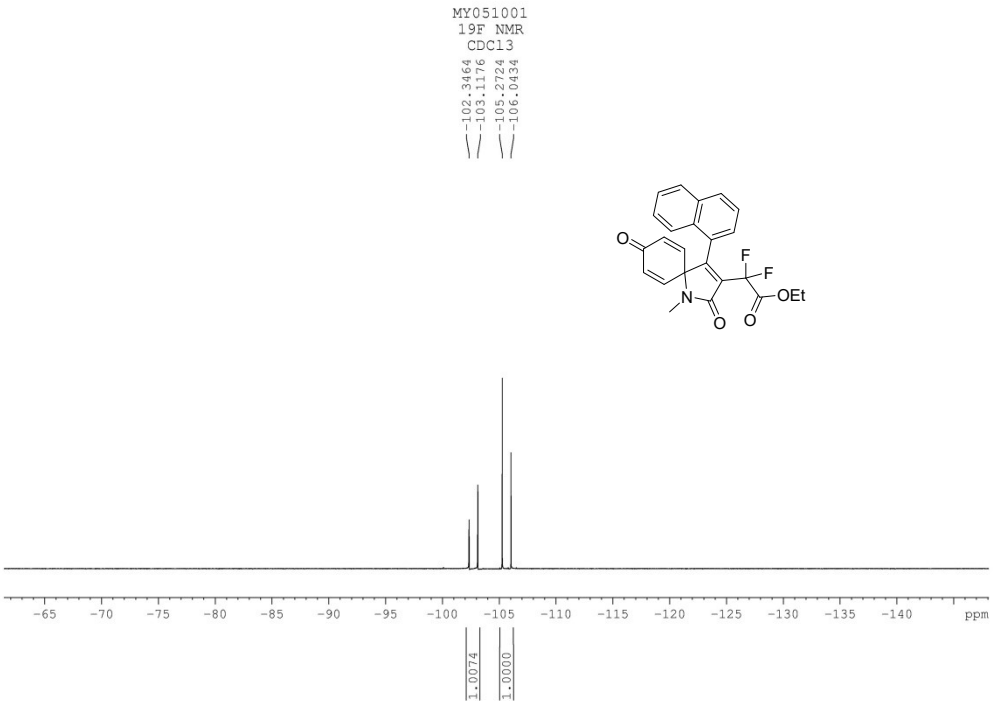

Fig. 76 ^{19}F NMR spectrum of compound **3y**

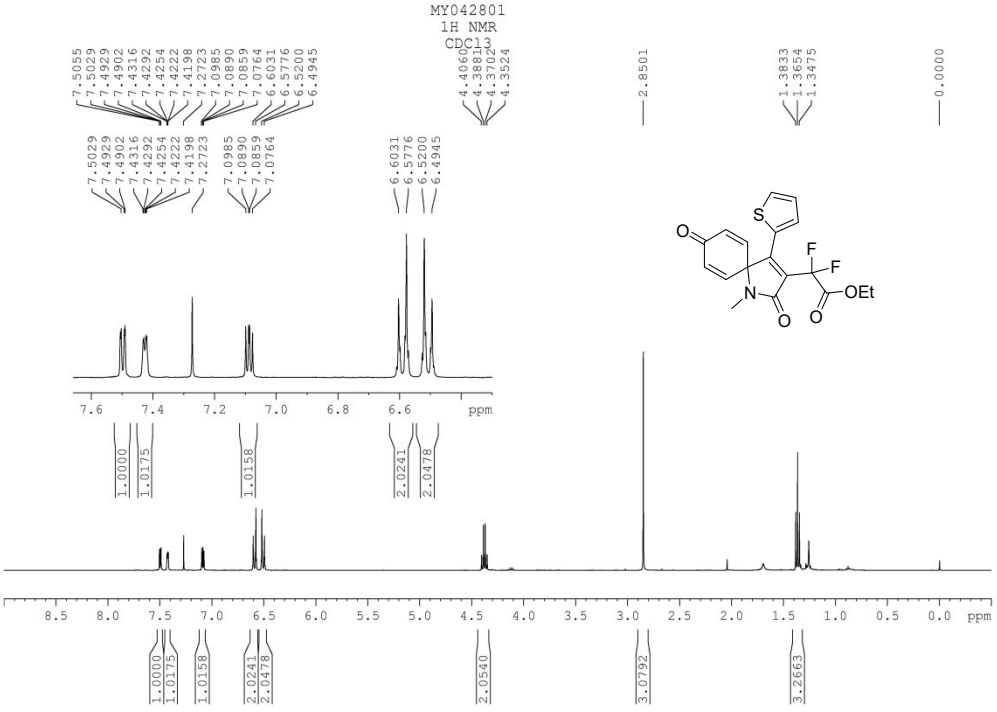

Fig. 77 ^{1}H NMR spectrum of compound **3z**

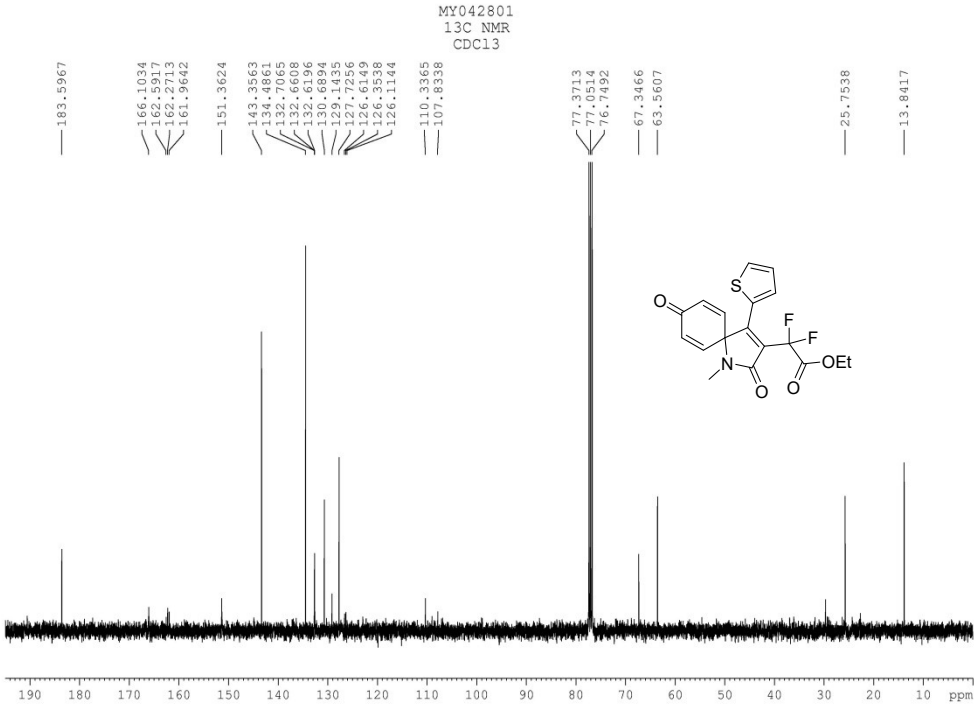

Fig. 78 ^{13}C NMR spectrum of compound **3z**

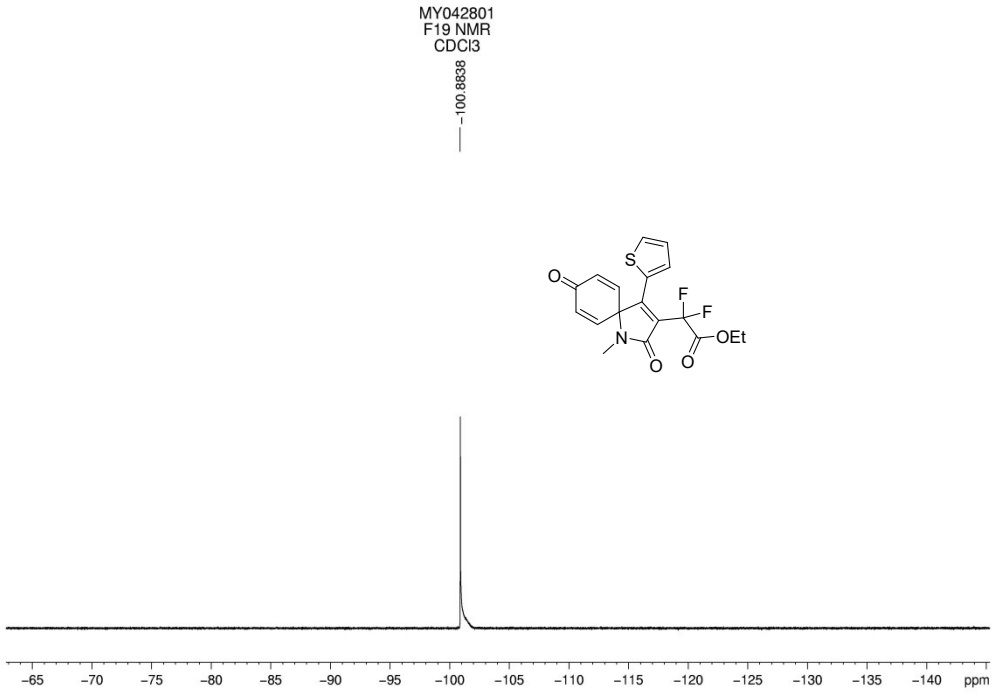

Fig. 79 ^{19}F NMR spectrum of compound **3z**

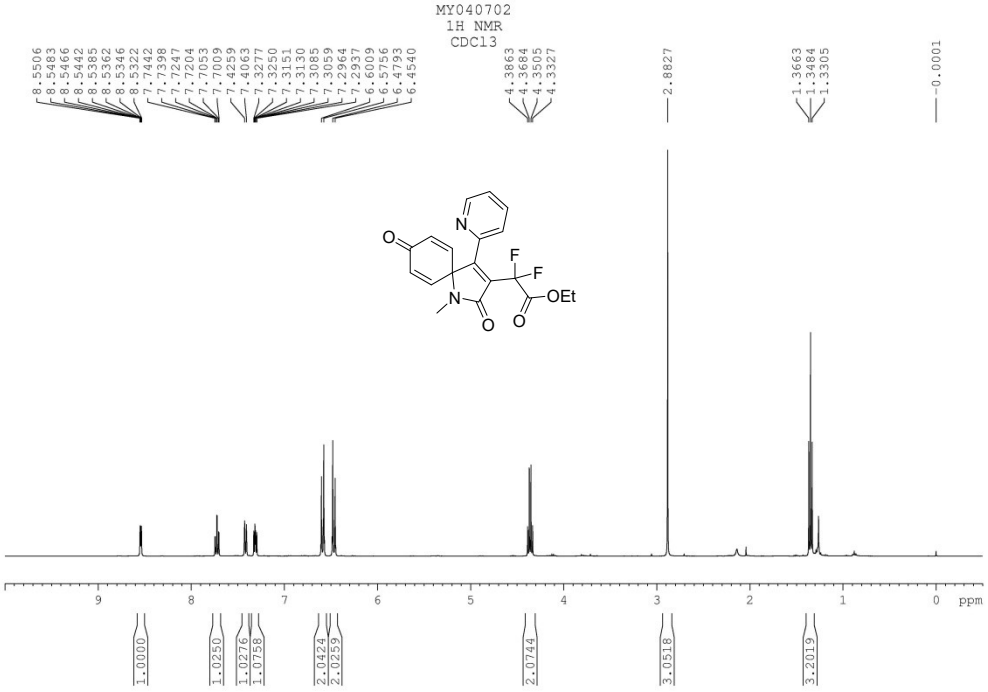

Fig. 80 ^{1}H NMR spectrum of compound **3ab**

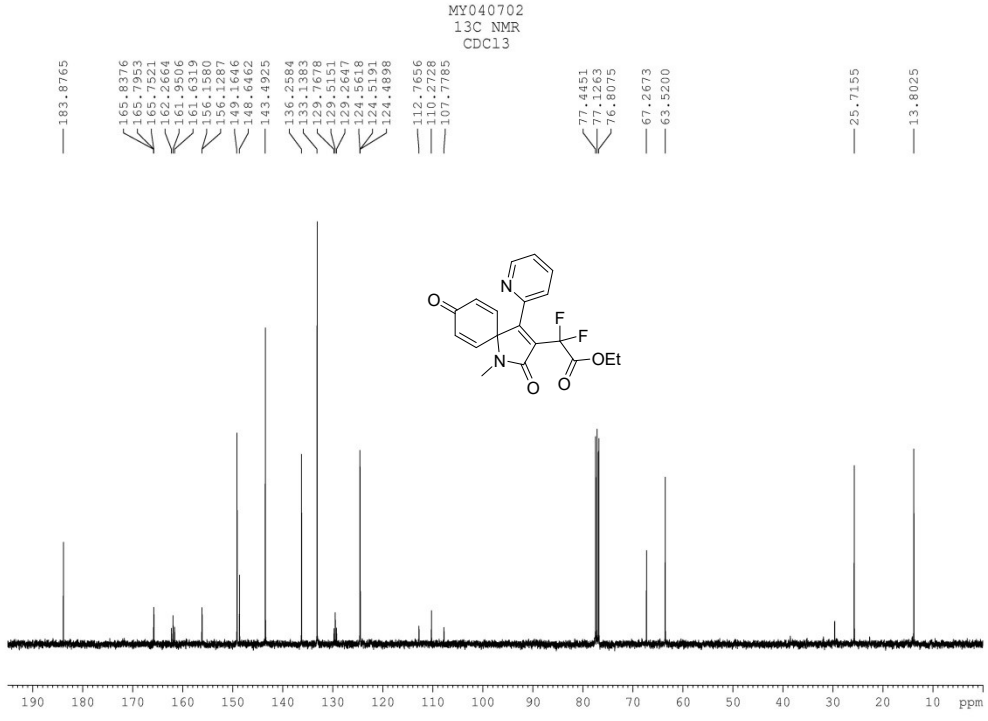

Fig. 81 ^{13}C NMR spectrum of compound **3ab**

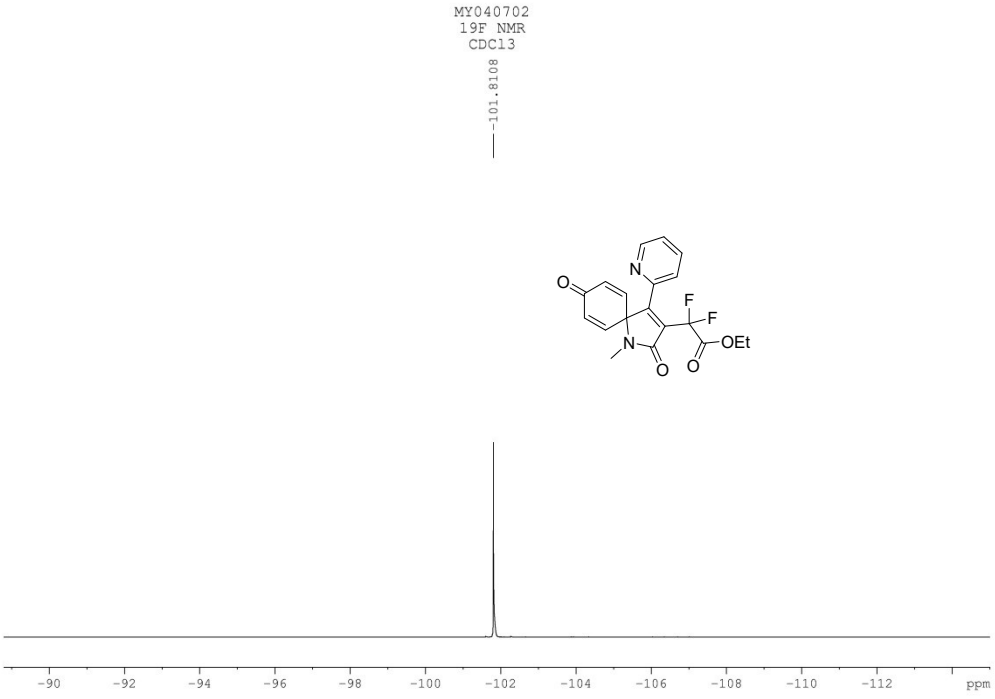

Fig. 82 ^{19}F NMR spectrum of compound **3ab**

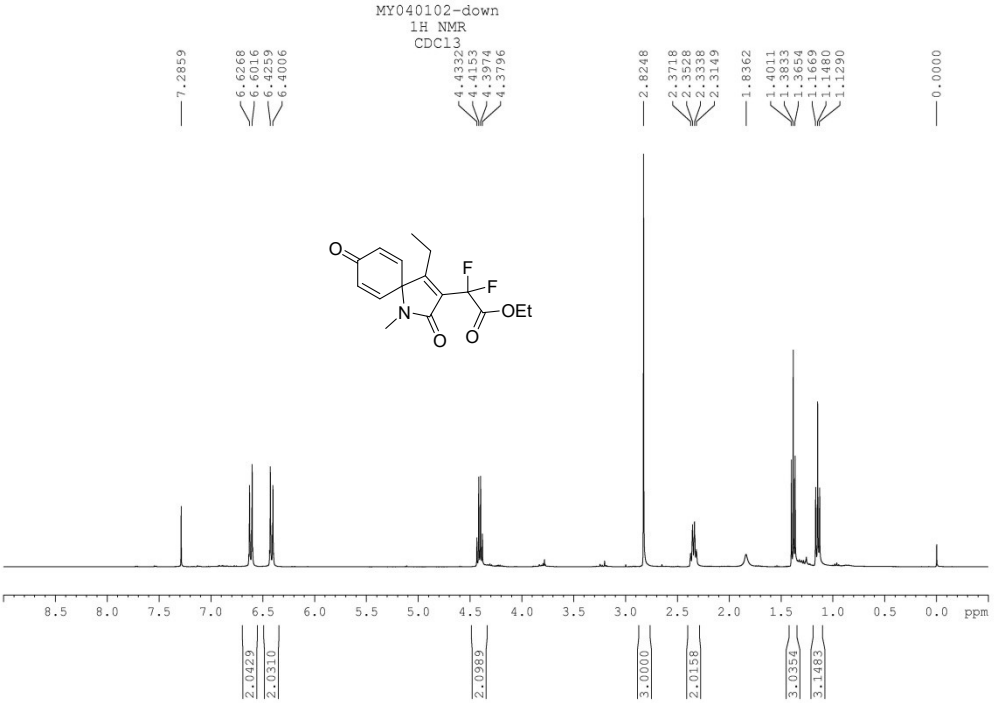

Fig. 83 ^{1}H NMR spectrum of compound **3ac**

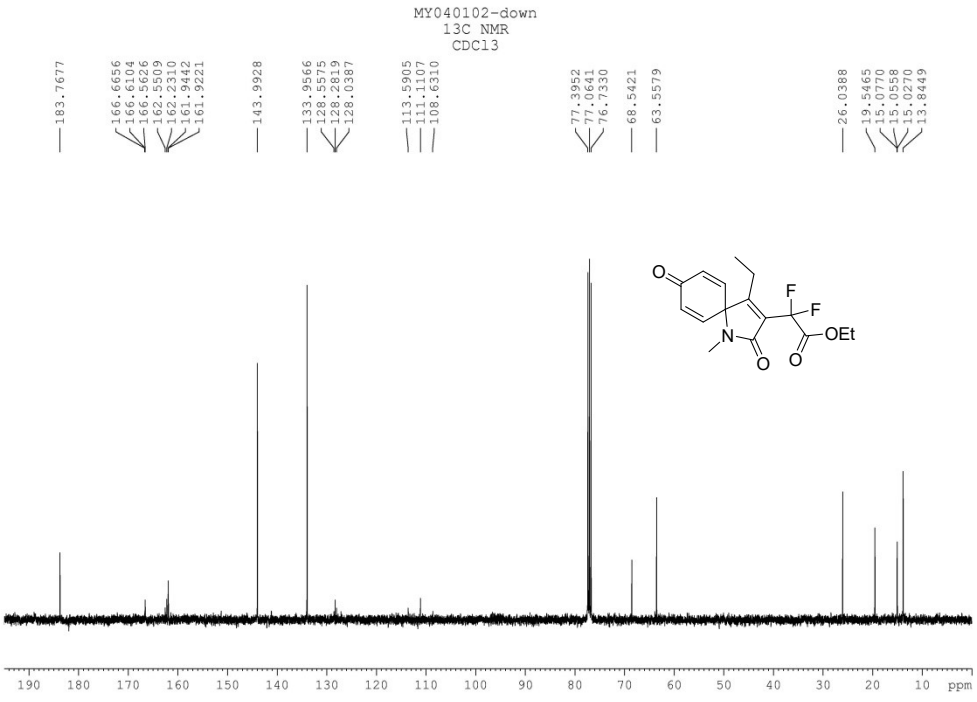

Fig. 84 ^{13}C NMR spectrum of compound **3ac**

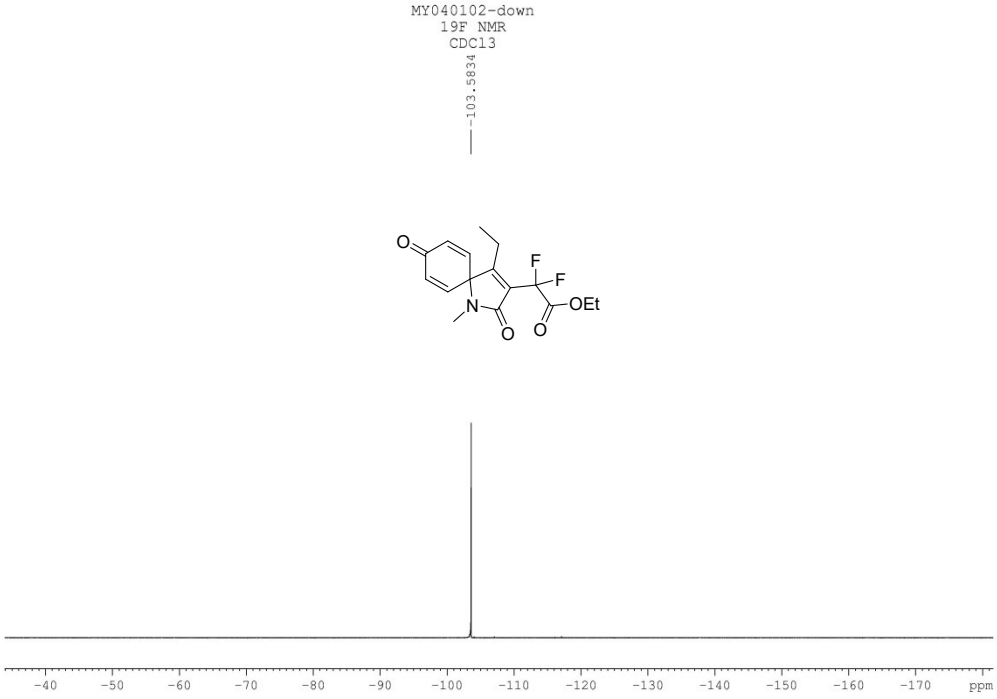

Fig. 85 ^{19}F NMR spectrum of compound **3ac**

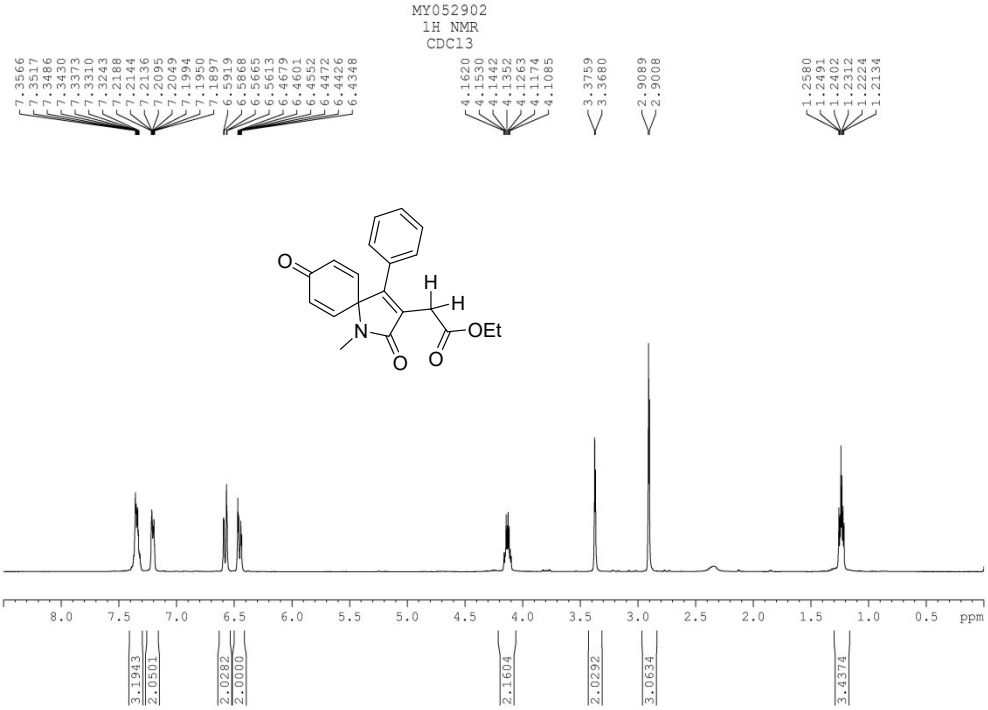

Fig. 86 ^{1}H NMR spectrum of compound **3ad**

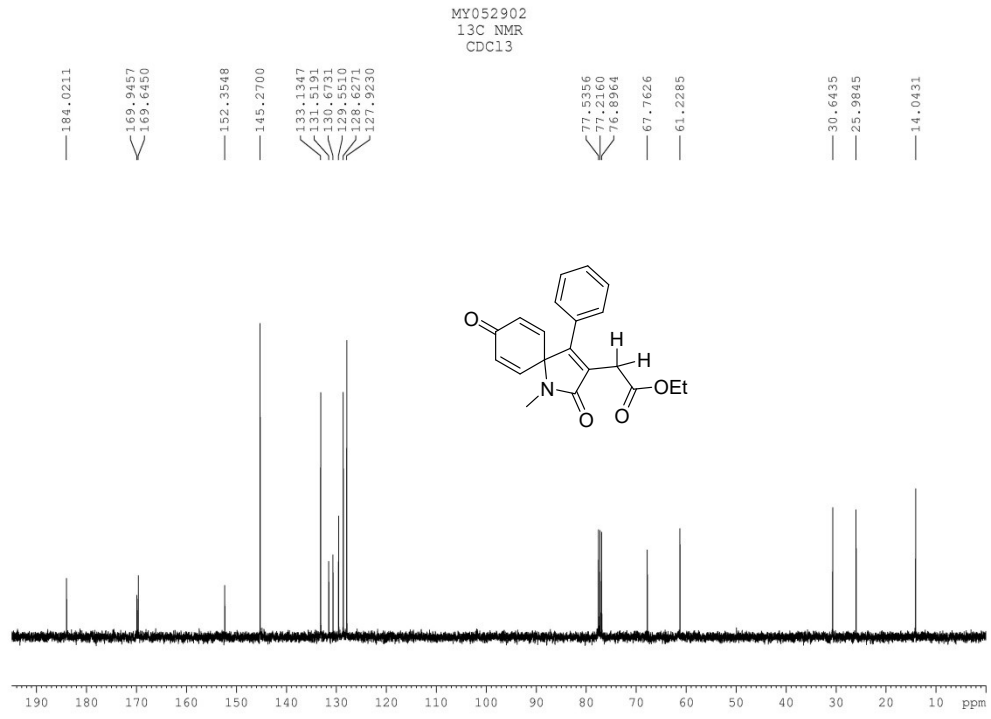

Fig. 87 ^{13}C NMR spectrum of compound **3ad**

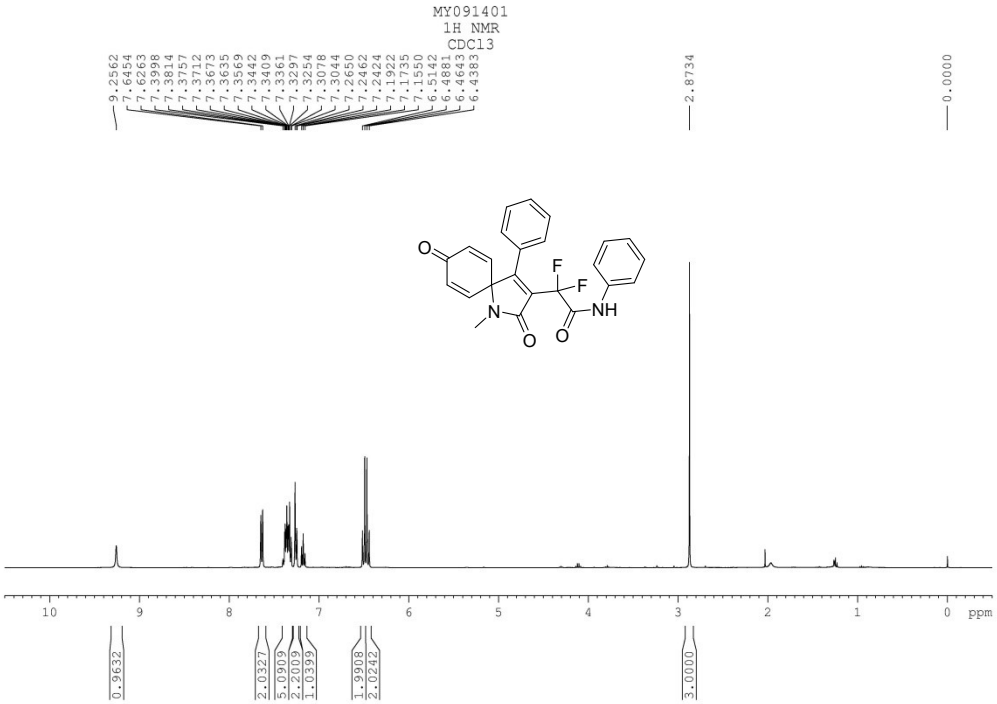

Fig. 88 ^{1}H NMR spectrum of compound **5a**

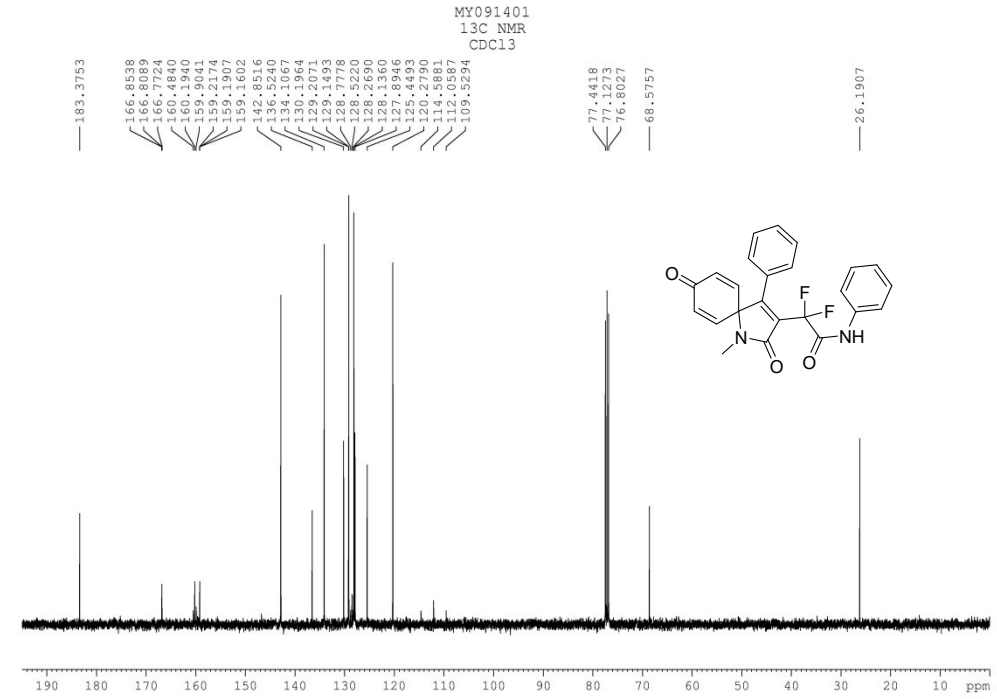

Fig. 89 ^{13}C NMR spectrum of compound **5a**

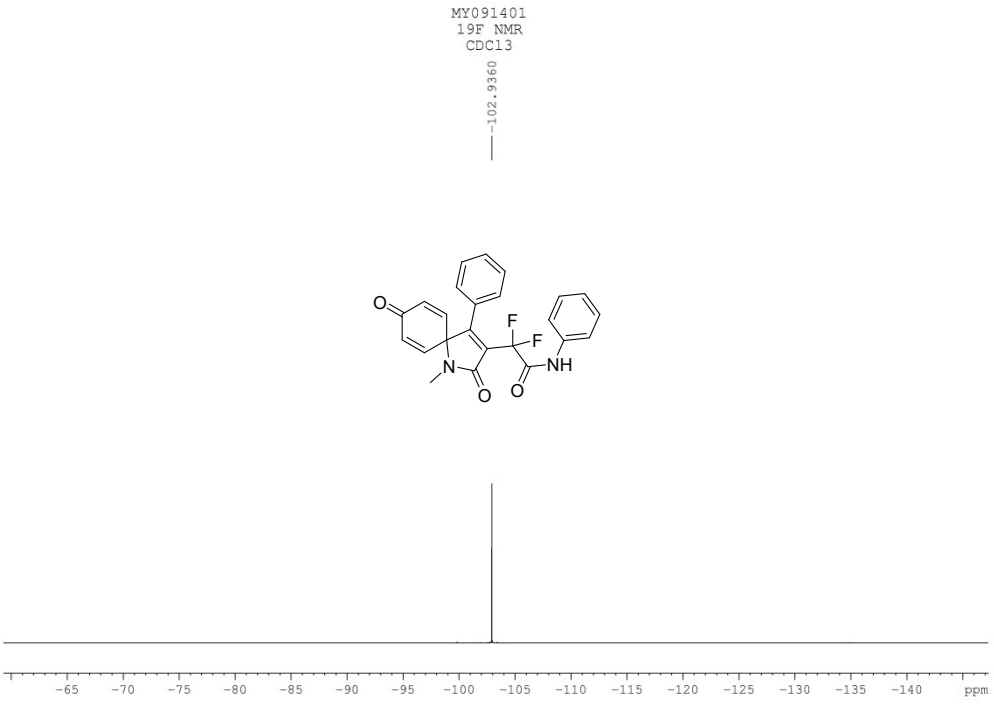

Fig. 90 ^{19}F NMR spectrum of compound **5a**

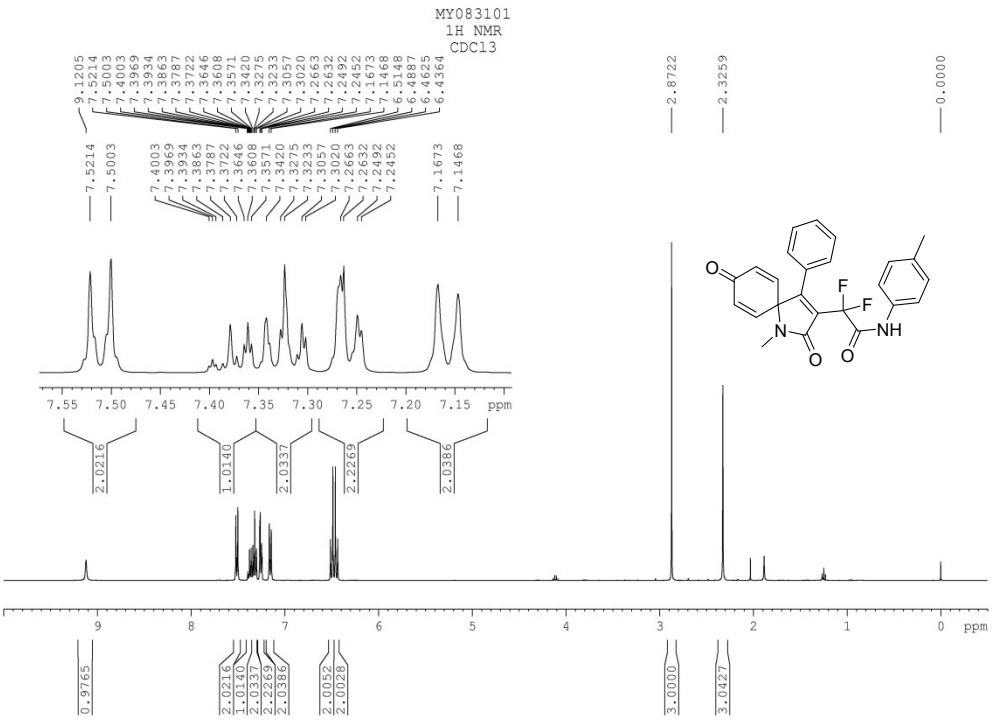

Fig. 91 ^{1}H NMR spectrum of compound **5b**

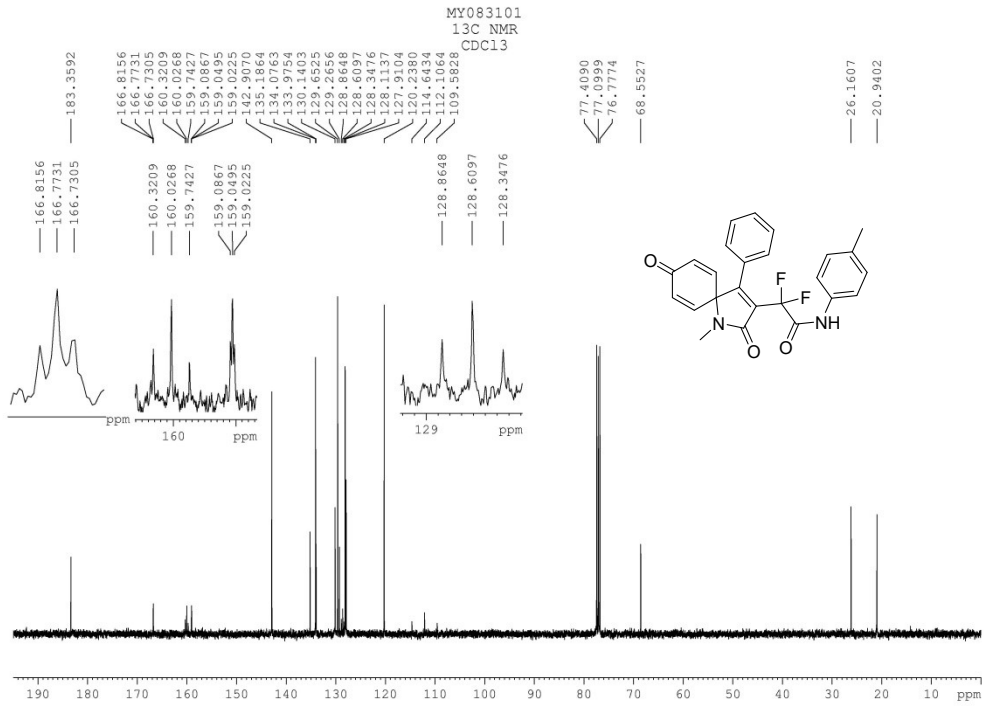

Fig. 92 ^{13}C NMR spectrum of compound **5b**

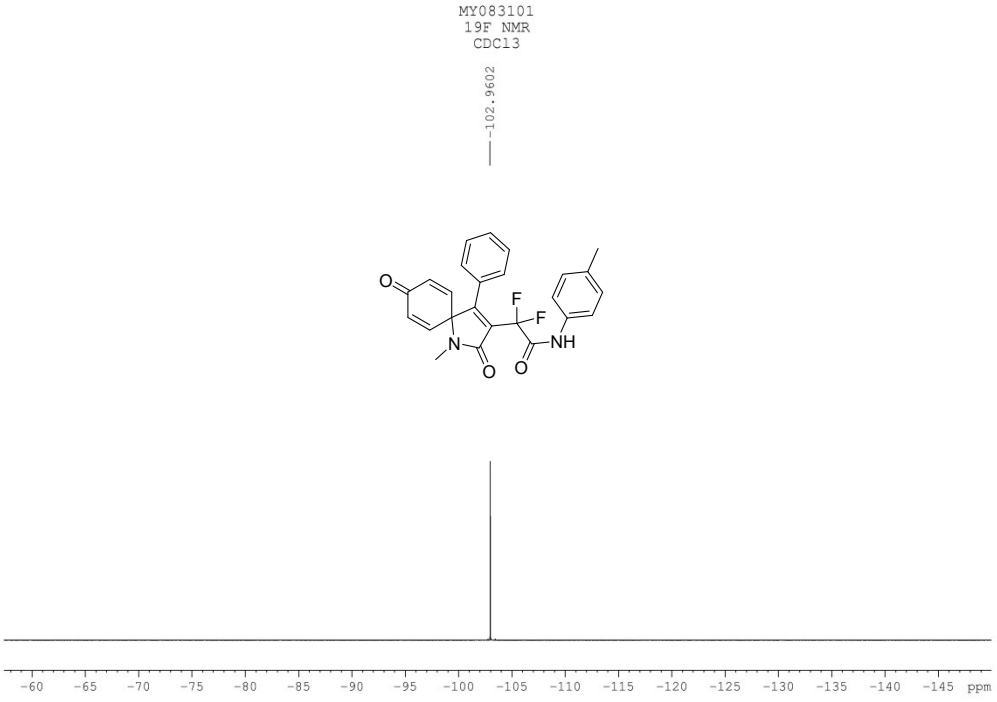

Fig. 93 ^{19}F NMR spectrum of compound **5b**

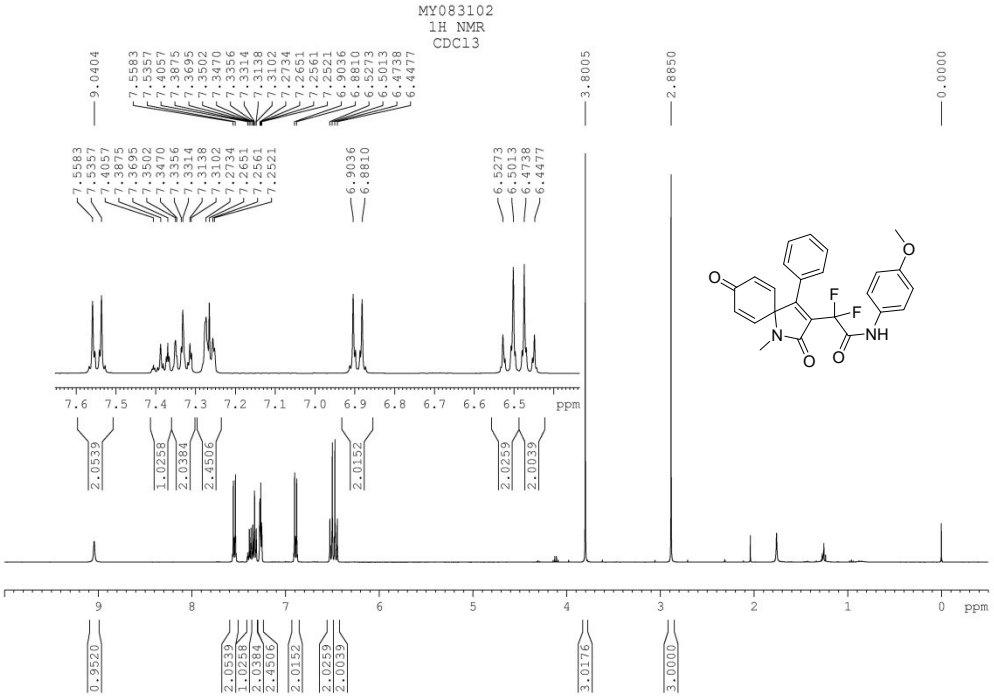

Fig. 94 ^{1}H NMR spectrum of compound **5c**

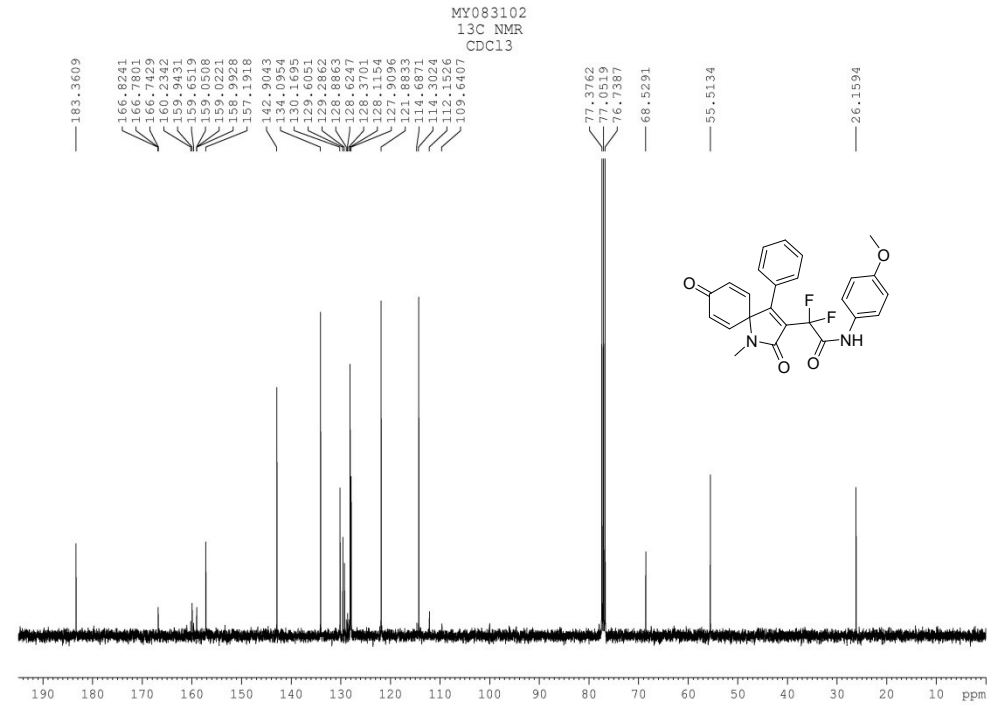

Fig. 95 ^{13}C NMR spectrum of compound **5c**

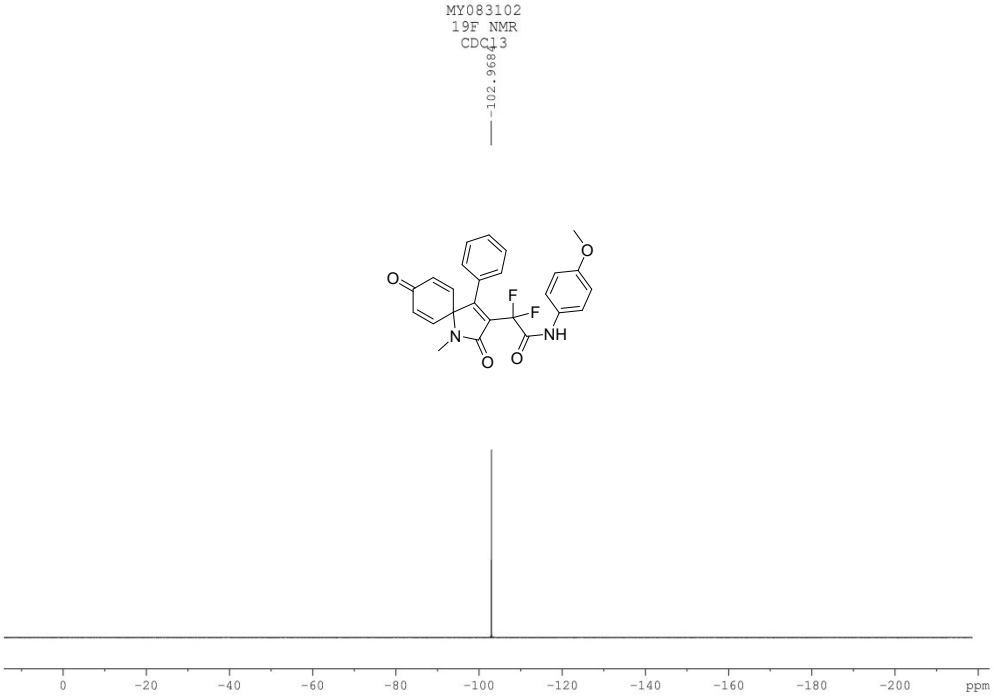

Fig. 96 ^{19}F NMR spectrum of compound **5c**

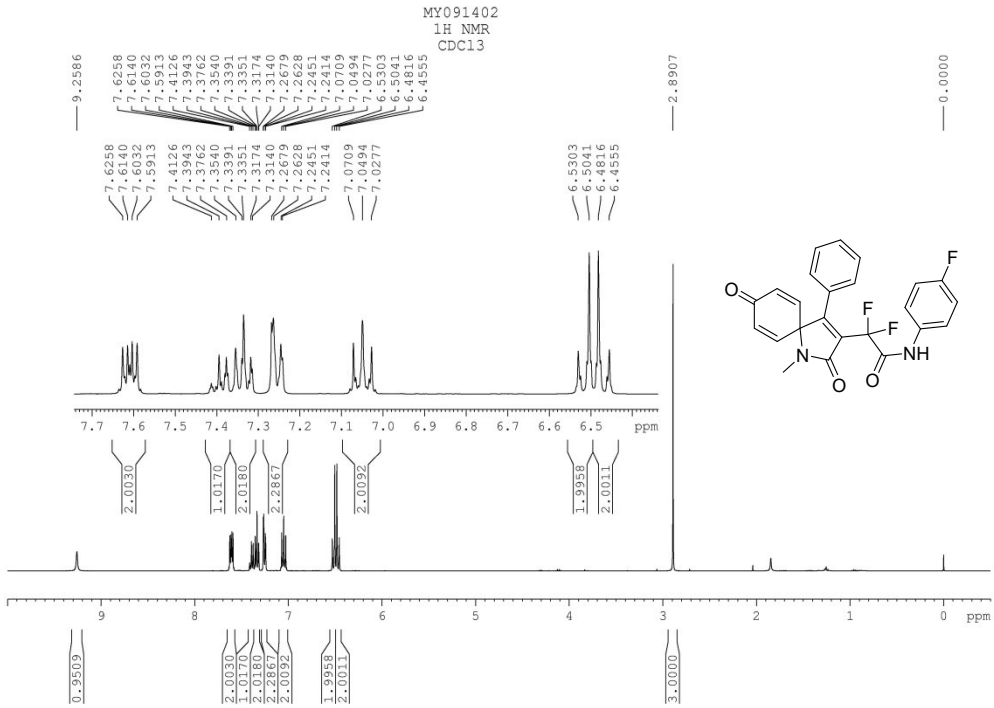

Fig. 97 ^{1}H NMR spectrum of compound **5d**

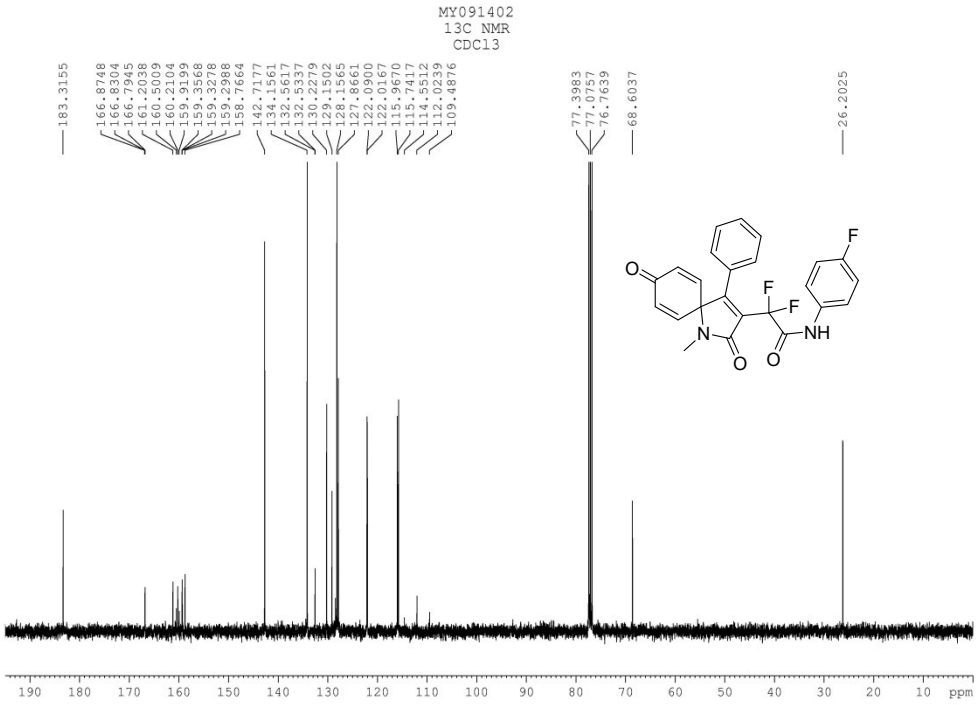

Fig. 98 ^{13}C NMR spectrum of compound **5d**

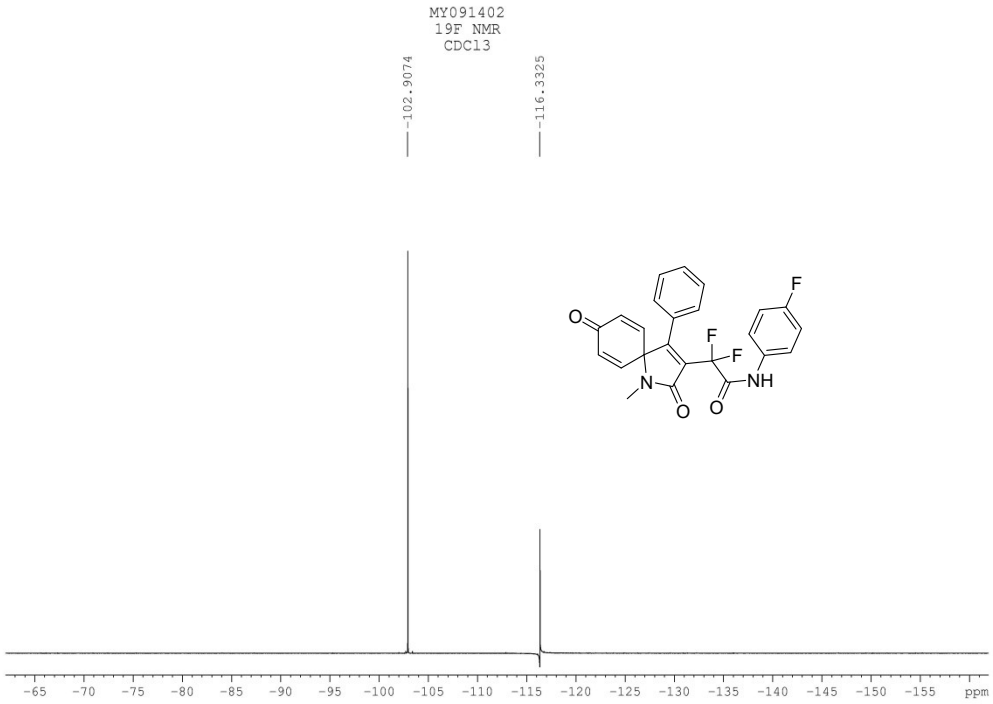

Fig. 99 ^{19}F NMR spectrum of compound **5d**

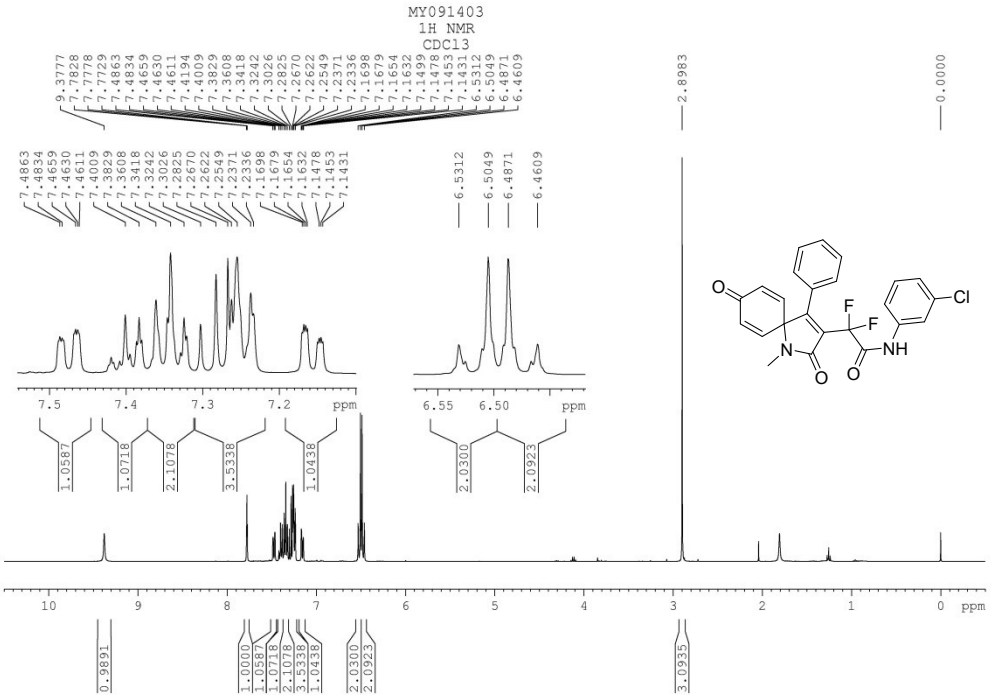

Fig. 100 ^{1}H NMR spectrum of compound **5e**

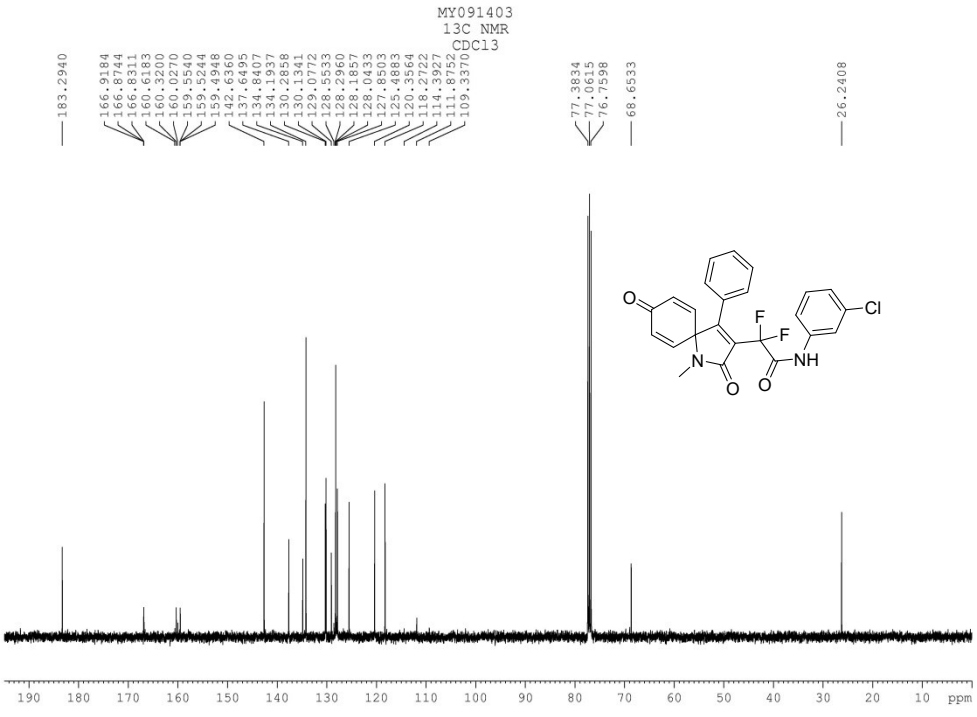

Fig. 101 ^{13}C NMR spectrum of compound **5e**

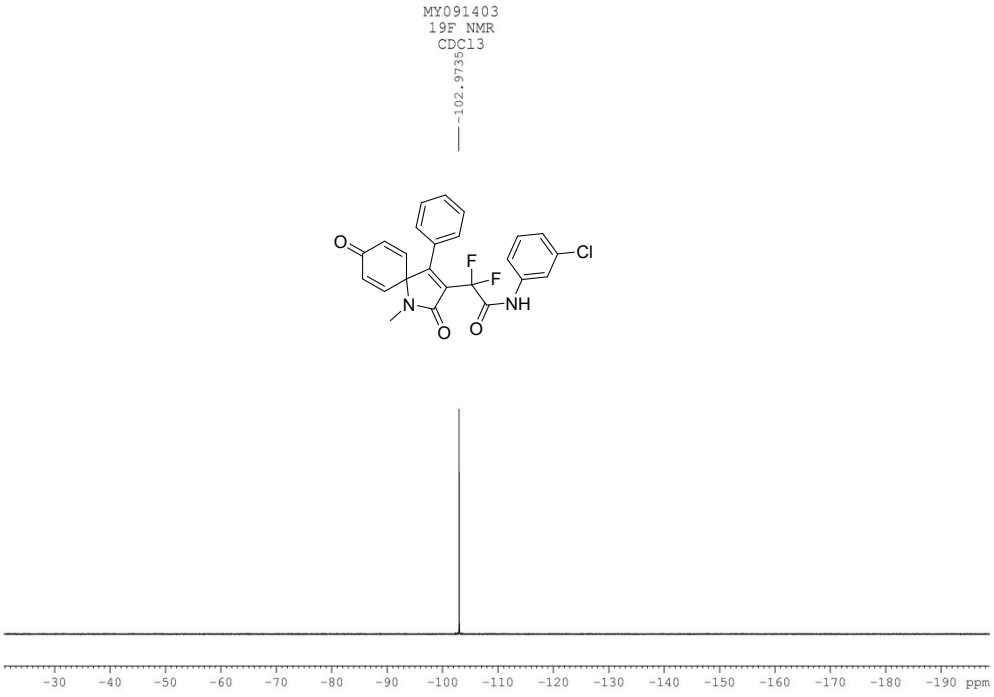

Fig. 102 ^{19}F NMR spectrum of compound **5e**

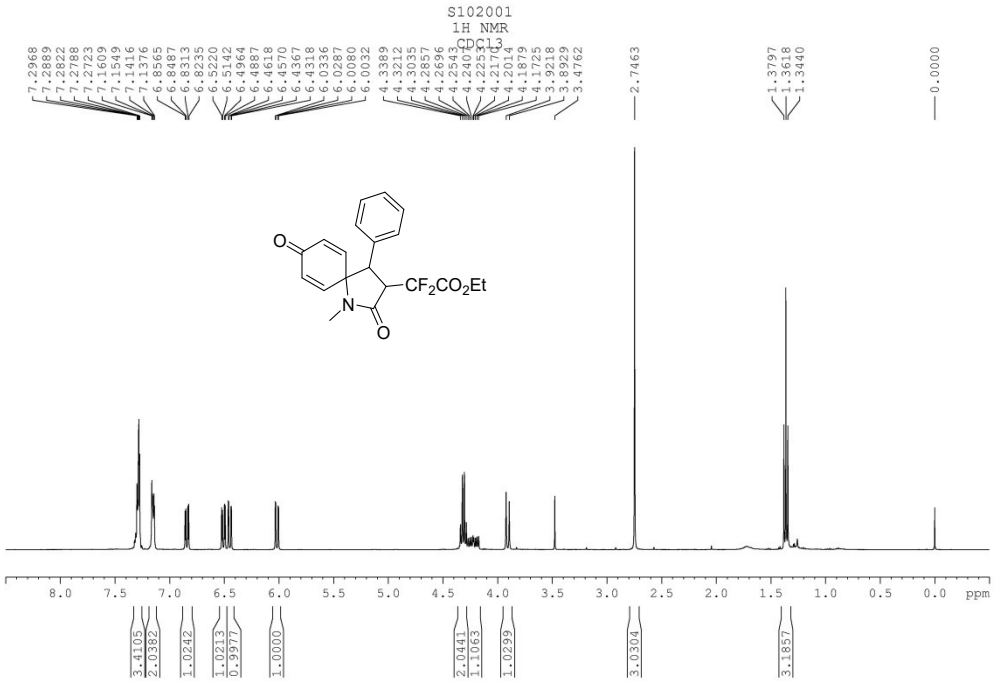

Fig. 103 ^{1}H NMR spectrum of compound **7**

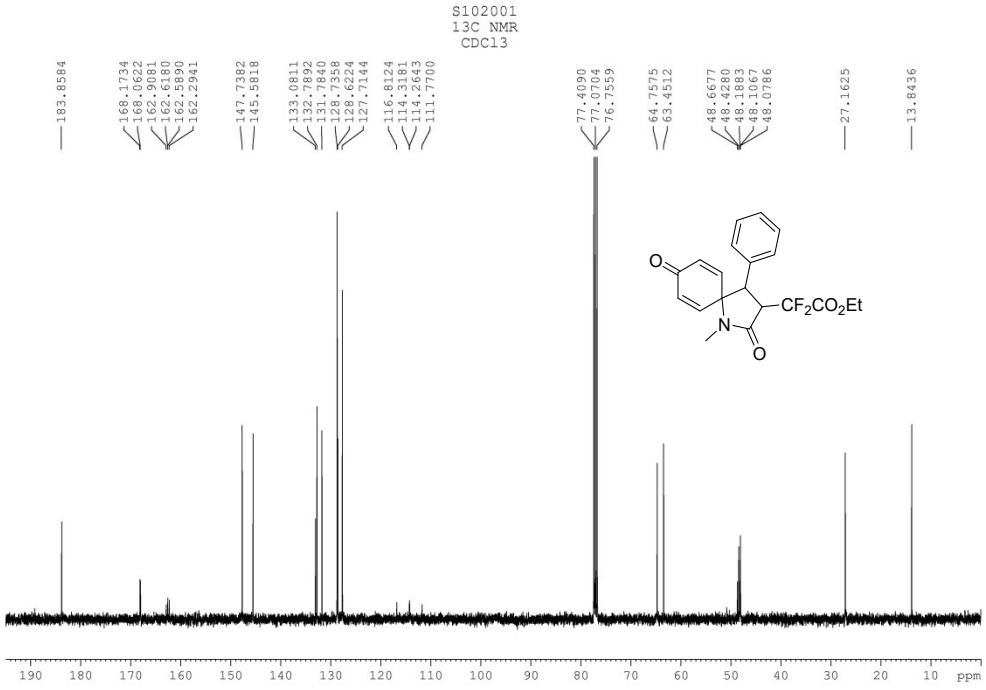

Fig. 104 ^{13}C NMR spectrum of compound **7**

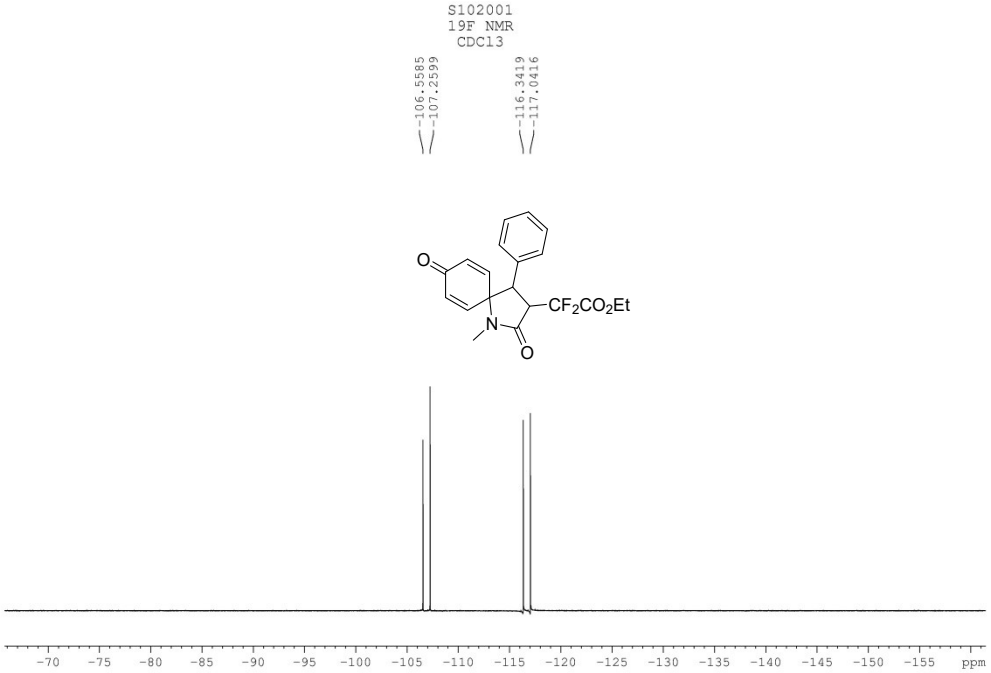

Fig. 105 ^{19}F NMR spectrum of compound **7**

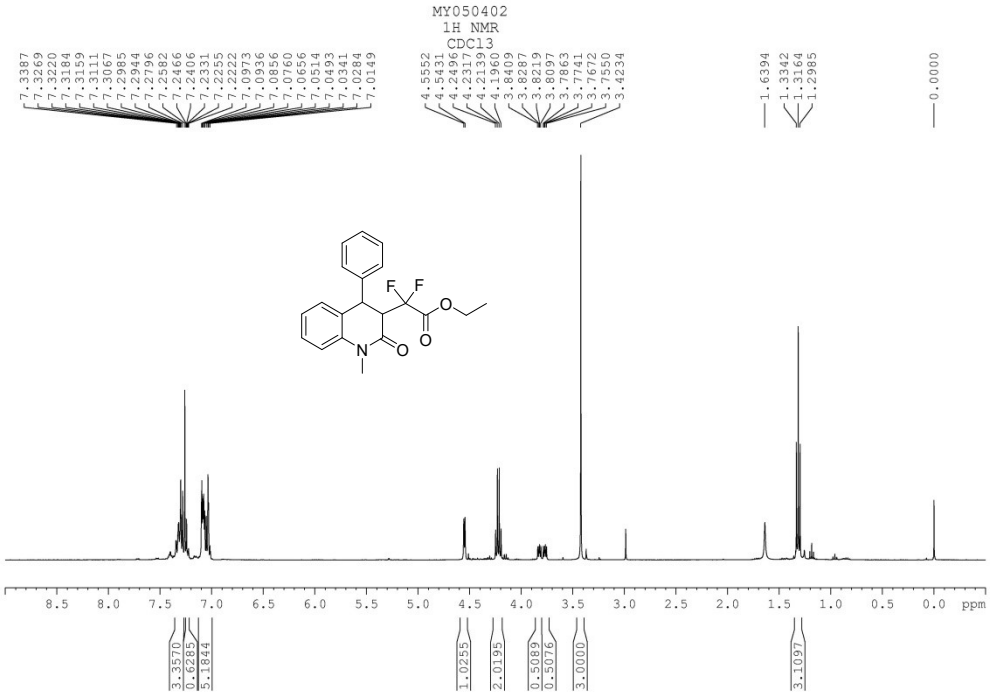

Fig. 106 ^{1}H NMR spectrum of compound **9**

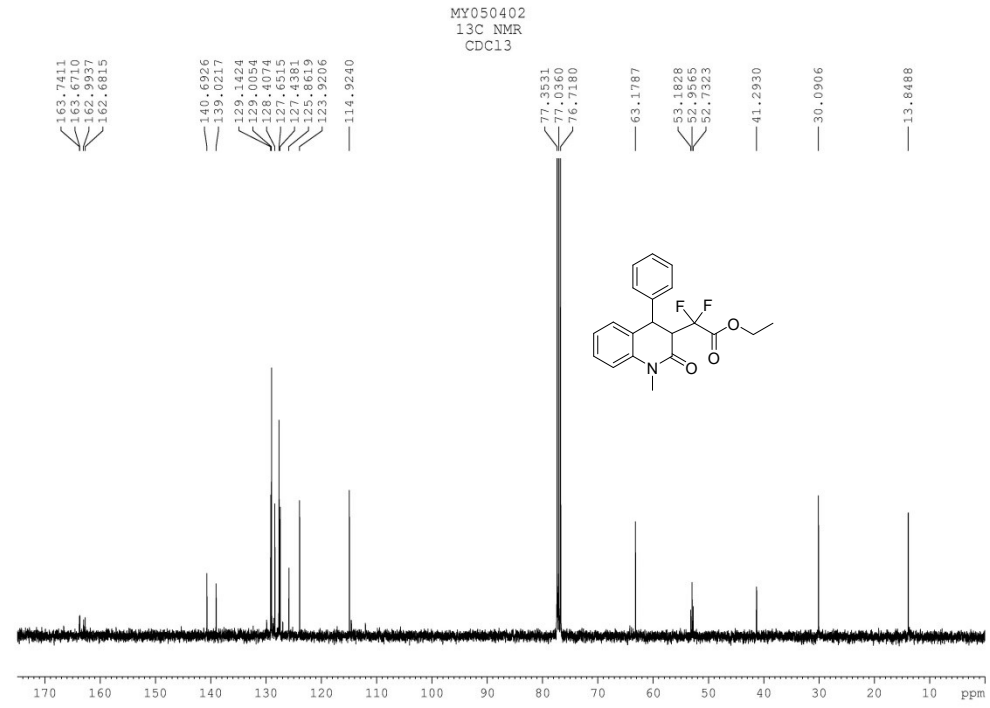

Fig. 107 ^{13}C NMR spectrum of compound **9**

Fig. 108 ^{19}F NMR spectrum of compound **9**

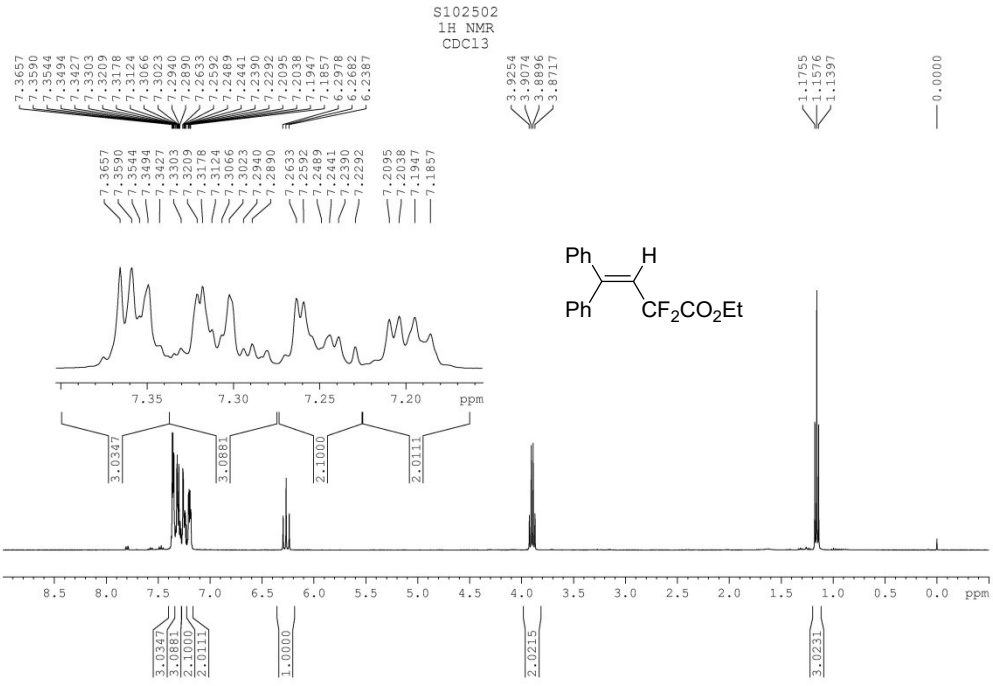

Fig. 109 ^{1}H NMR spectrum of compound **10**

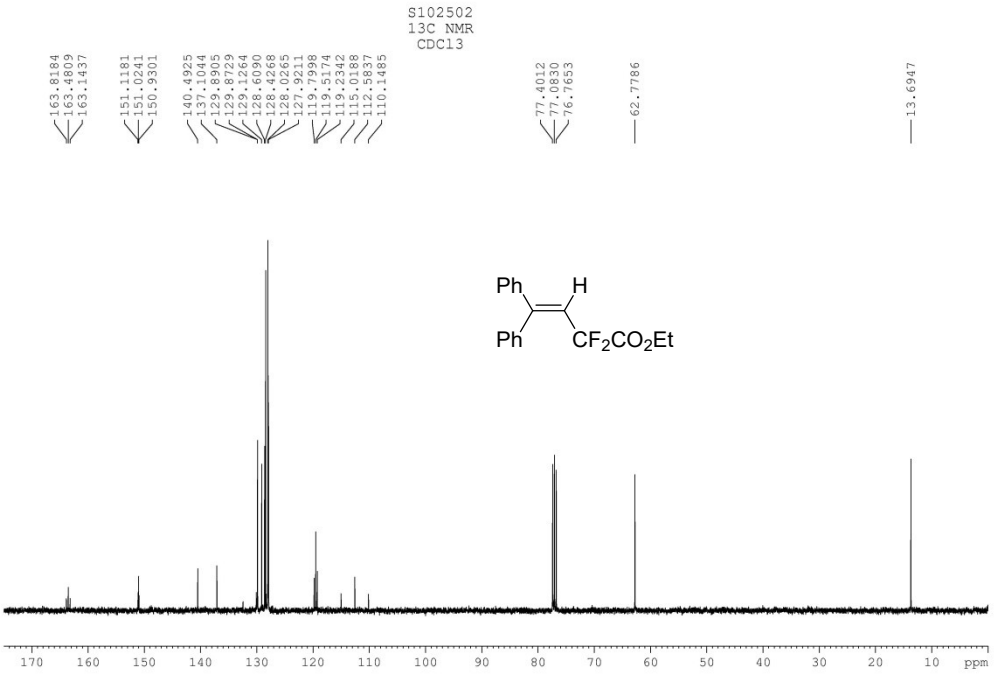

Fig. 110 ^{13}C NMR spectrum of compound **10**

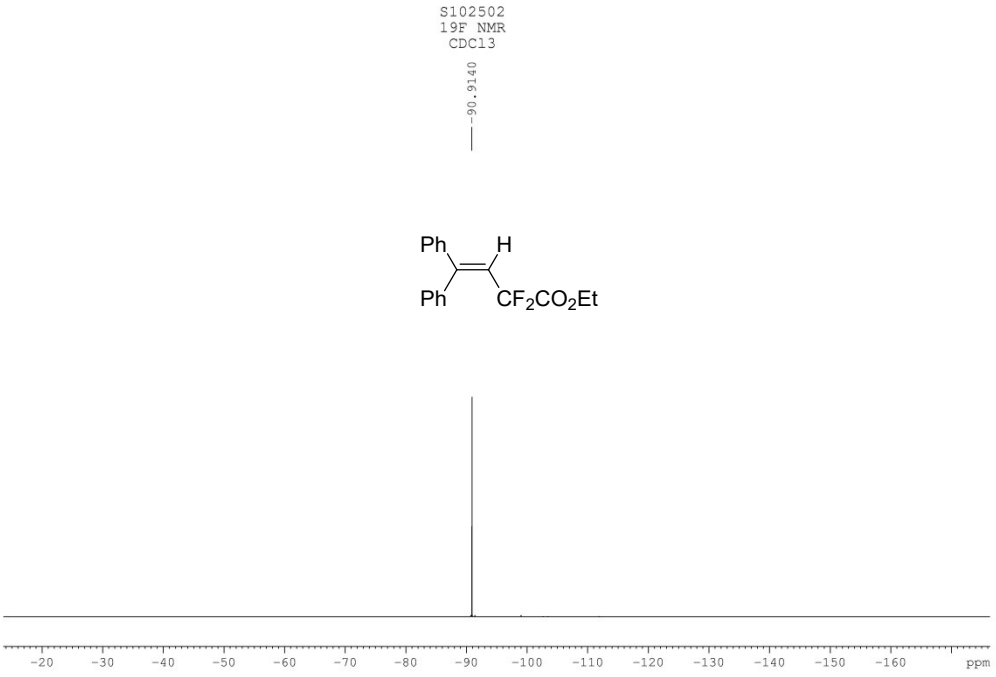

Fig. 111 ^{19}F NMR spectrum of compound **10**

5 ^{19}F NMR spectrum of TEMPO-CF_2CO_2Et adduct

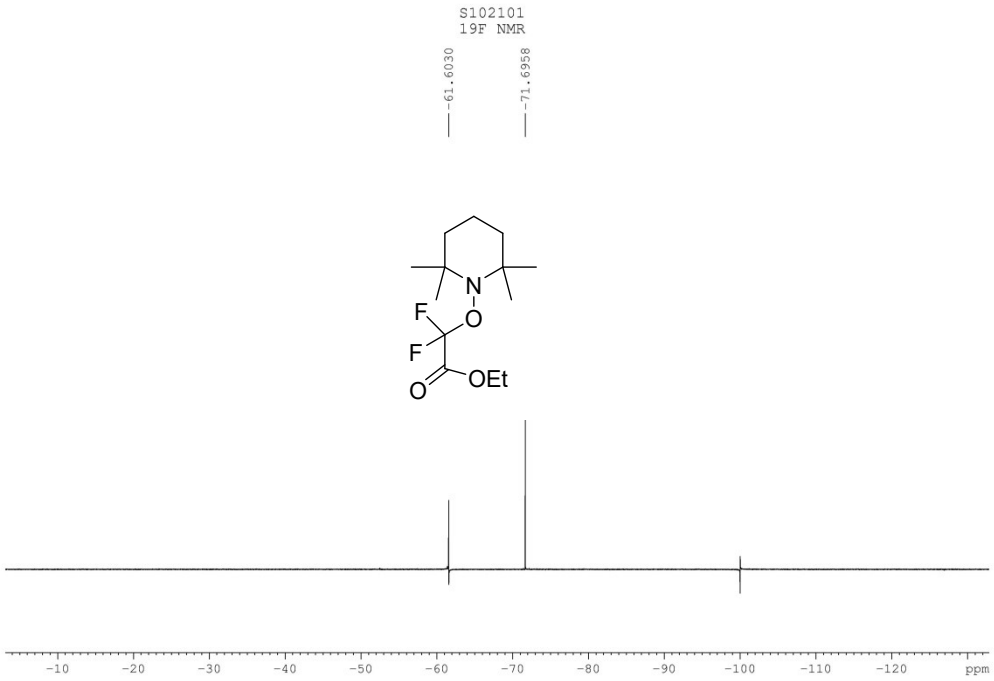

Fig. 112 ^{19}F NMR spectrum of TEMPO-CF_2CO_2Et adduct

6 HR MS of BHT-CF_2CO_2Et adduct

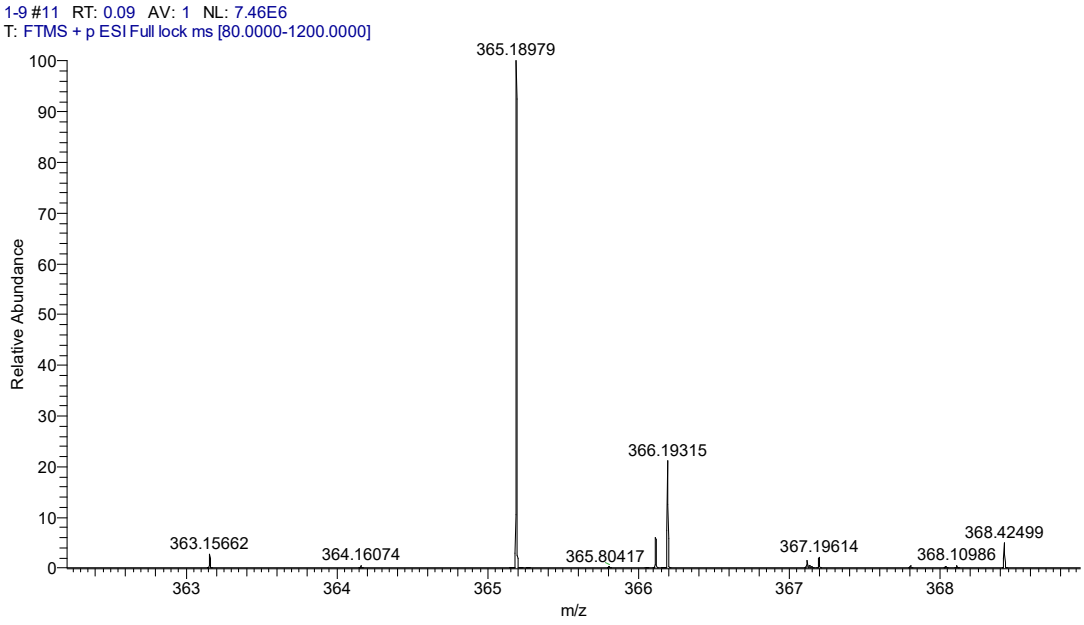

Fig. 113 HR MS of BHT-CF_2CO_2Et adduct