

Supporting Information

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**Photoredox-catalyzed three-component difluorobenzylation of
quinoxalin-2(1*H*)-ones with unactivated vinylarenes and
BrCF₂CO₂Et/HCF₂CO₂H**

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Contents

1 General information.....	S1
2 Screening the reaction conditions	S1
3 Copies of spectra of products	S2
4 Copies of HRMS and ¹⁹ F NMR spectra of compounds 7 and 8	S57

1 General information

All chemicals were commercially available and used as received. Column chromatography was performed using 300–400 mesh silica. Nuclear magnetic resonance spectra were recorded on Bruker Avance 400 MHz spectrometer. ^1H NMR spectra are recorded in parts per million (ppm; δ scale) 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 ppm from tetramethylsilane. ^{19}F NMR spectra were recorded in ppm with fluorobenzene as external standard. High resolution mass spectra (HRMS) was performed using a Thermo Scientific Q Exactive Hybrid Quadrupole-Orbitrap mass spectrometer equipped with an EASY Spray nanospray source operated in positive ion mode. 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

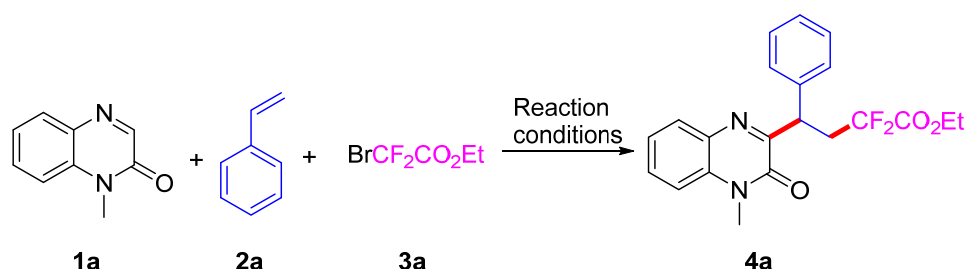


Table S1 Screening the molar ratio of **1a**, **2a** and **3a**^a

Entry	Molar ratio of 1a , 2a and 3a	Yields (%) ^b
1	1 : 1 : 1	<5
2	1 : 2 : 2	52
3	1 : 2 : 3	93
4	1 : 3 : 3	90

^a Reaction conditions: 1-methylquinoxalin-2(1H)-one **1a** (0.2 mmol, 32.0 mg), styrene **2a**, ethyl 2-bromo-2,2-difluoroacetate **3a**, *fac*-[Ir(ppy)] (0.002 mmol, 1.31 mg), K_2CO_3 (0.3 mmol, 41.4 mg) and CH_3CN (2.0 mL), 5 W blue LEDs at room temperature under N_2 atmosphere for 4.0 h. ^b Isolated yield.

3 Copies of spectra of products

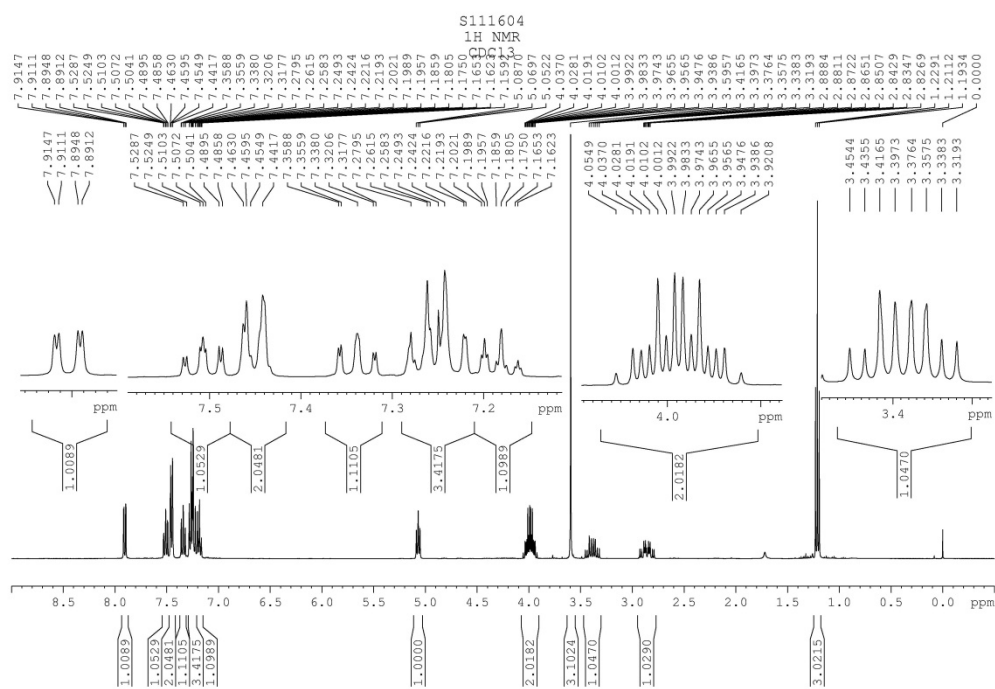


Fig. 1 ^1H NMR spectrum of compound **4a**

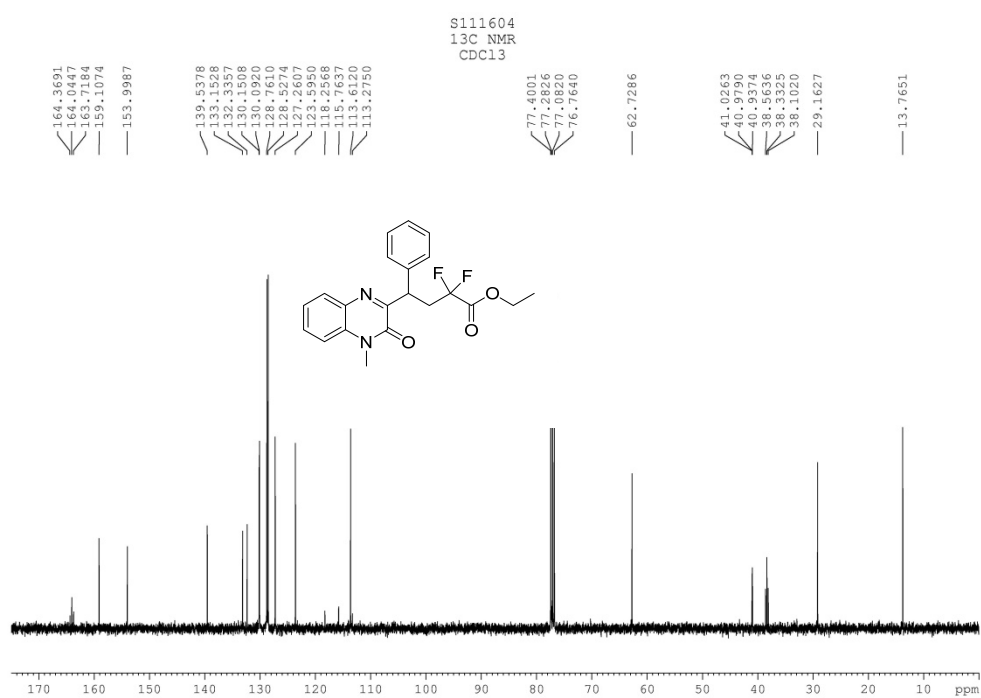


Fig. 2 ^{13}C NMR spectrum of compound **4a**

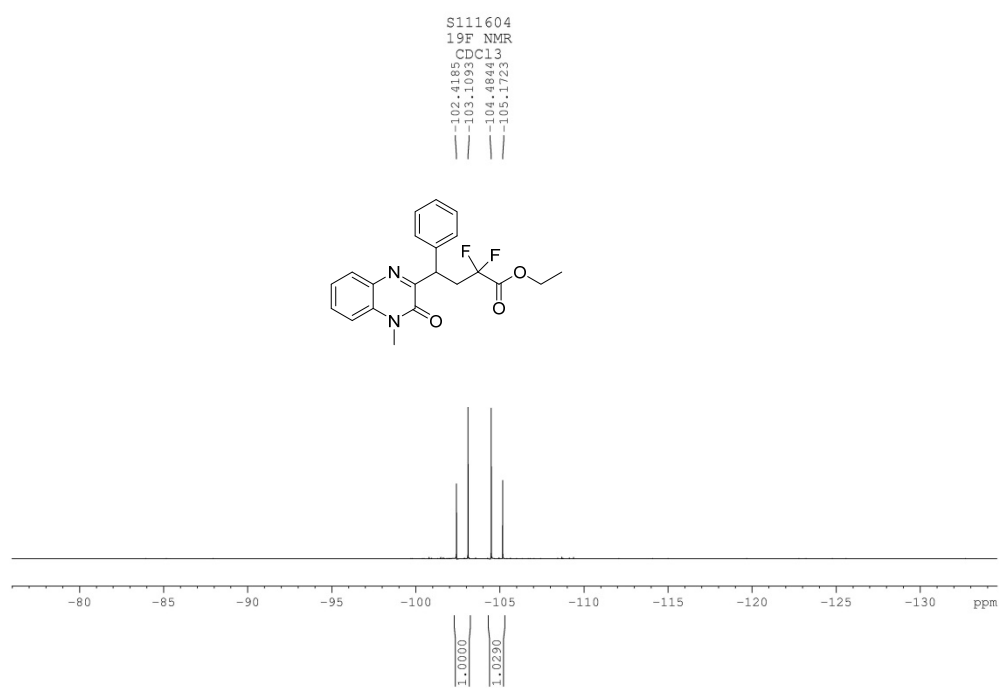


Fig. 3 ¹⁹F NMR spectrum of compound 4a

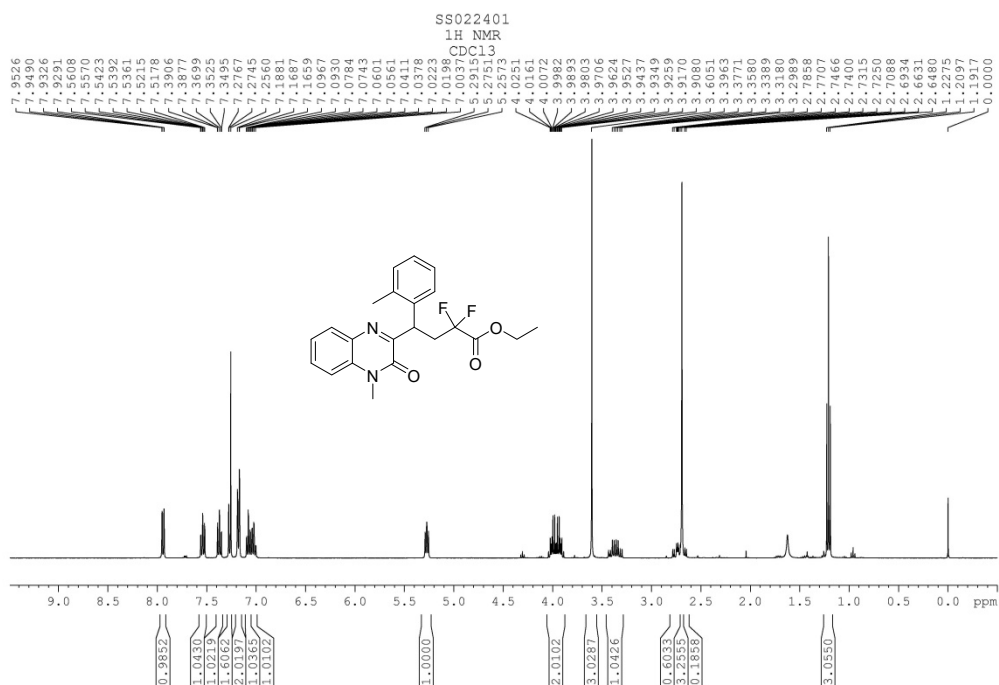


Fig. 4 ¹H NMR spectrum of compound 4b

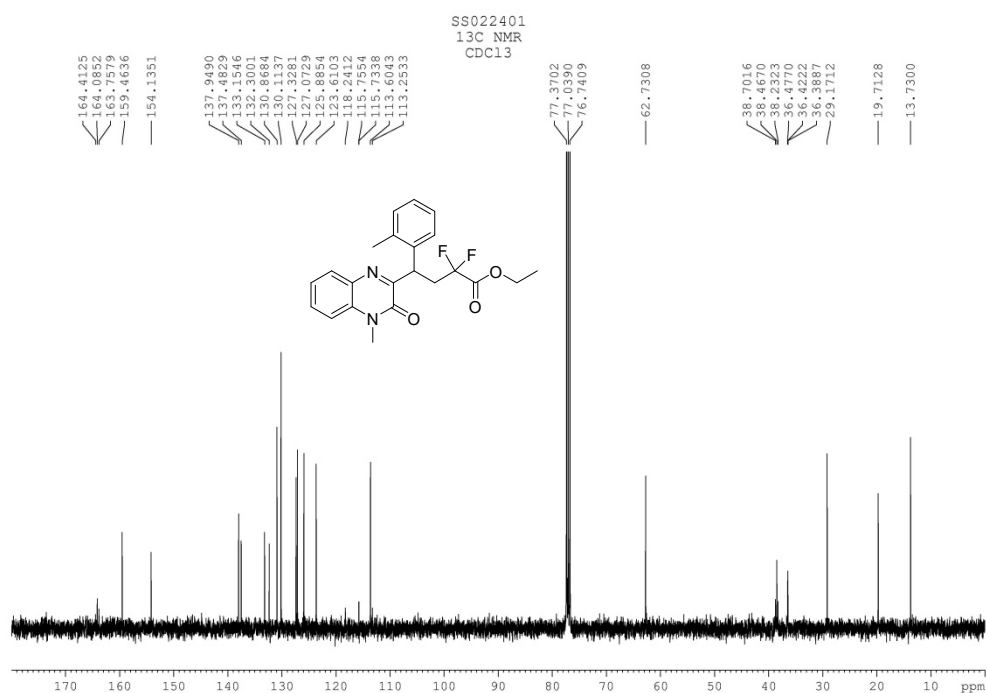


Fig. 5 ^{13}C NMR spectrum of compound 4b

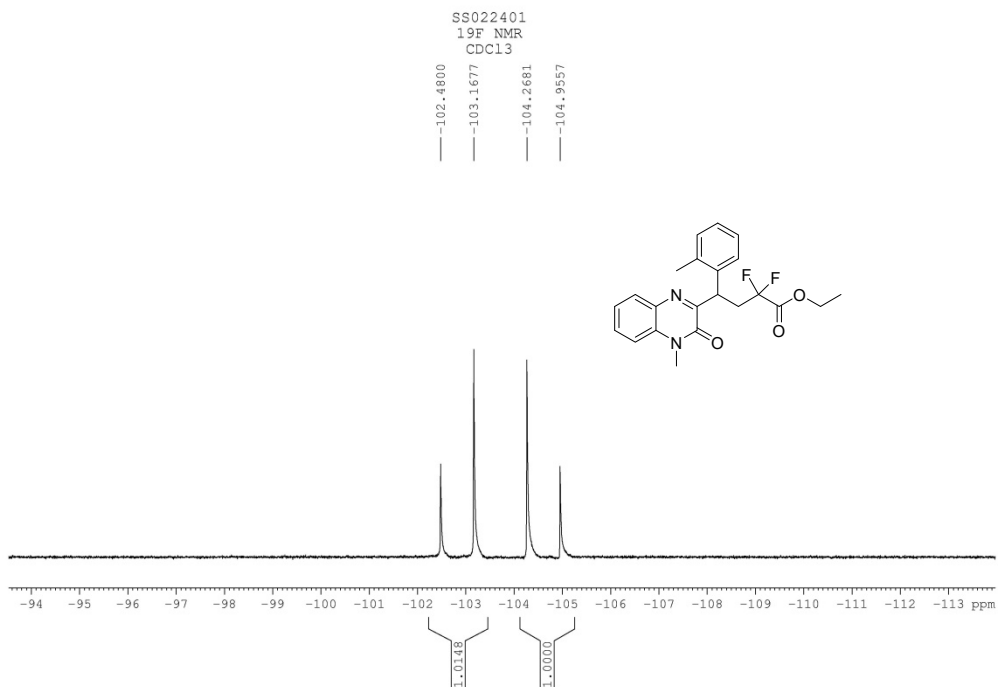


Fig. 6 ^{19}F NMR spectrum of compound 4b

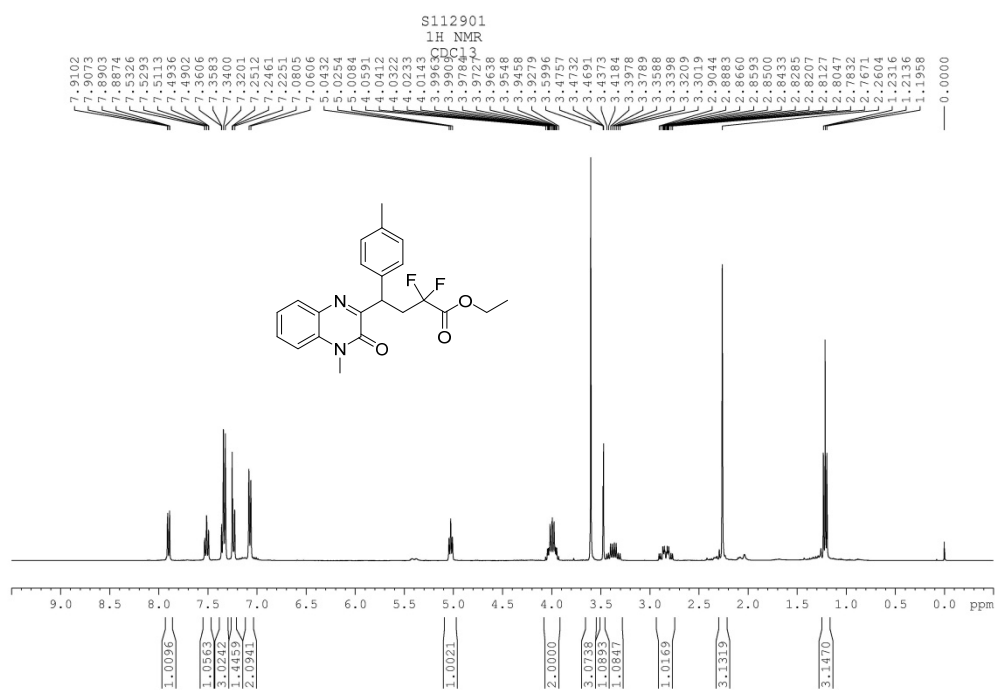


Fig. 7 ^1H NMR spectrum of compound 4c

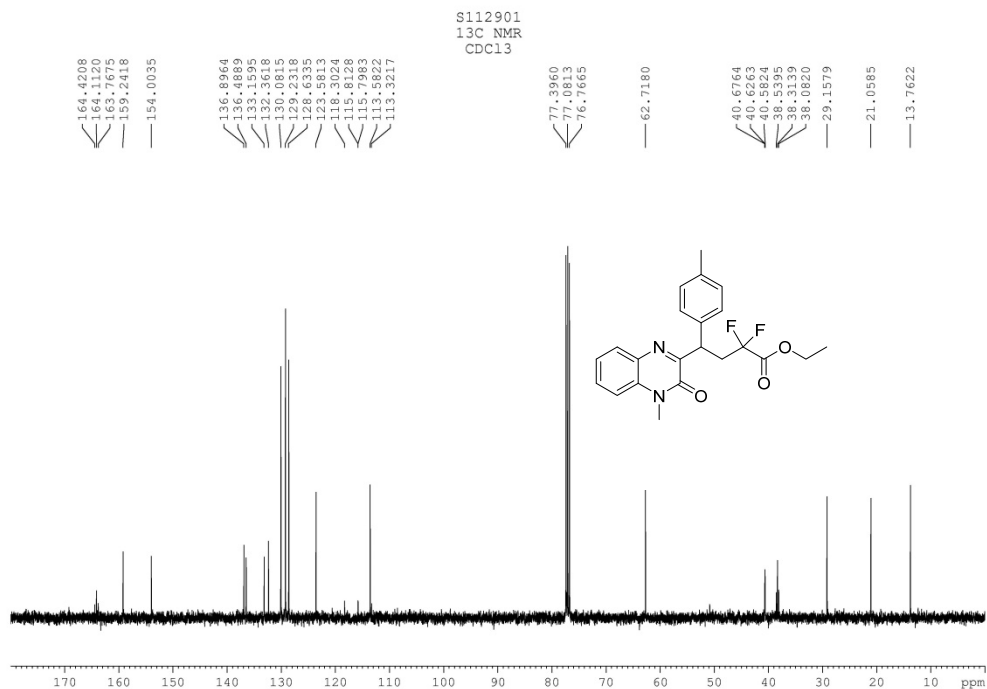


Fig. 8 ^{13}C NMR spectrum of compound 4c

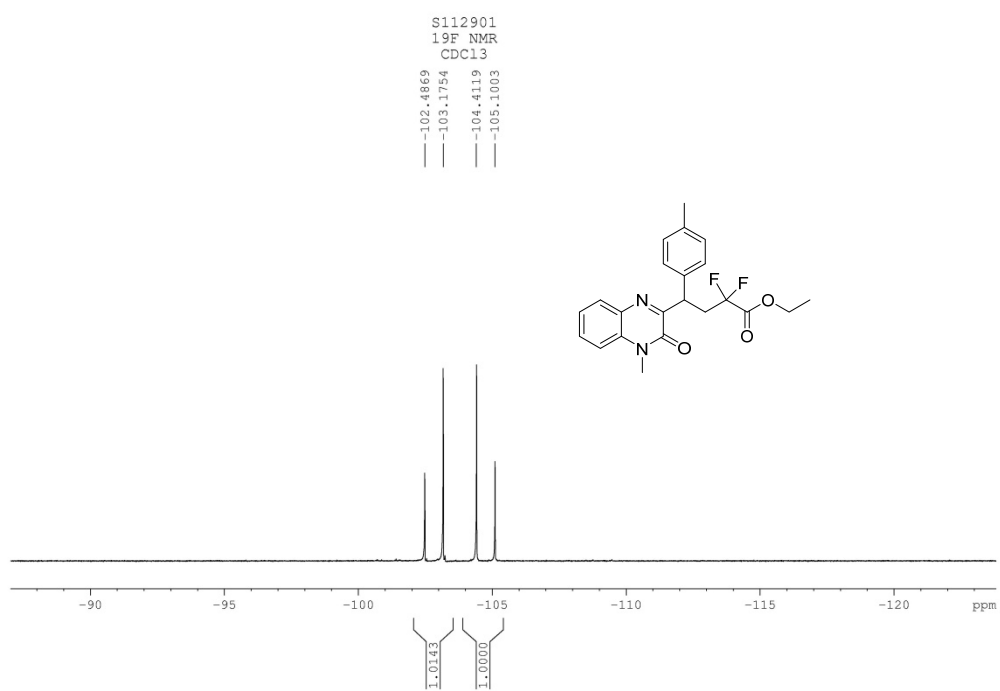


Fig. 9 ¹⁹F NMR spectrum of compound 4c

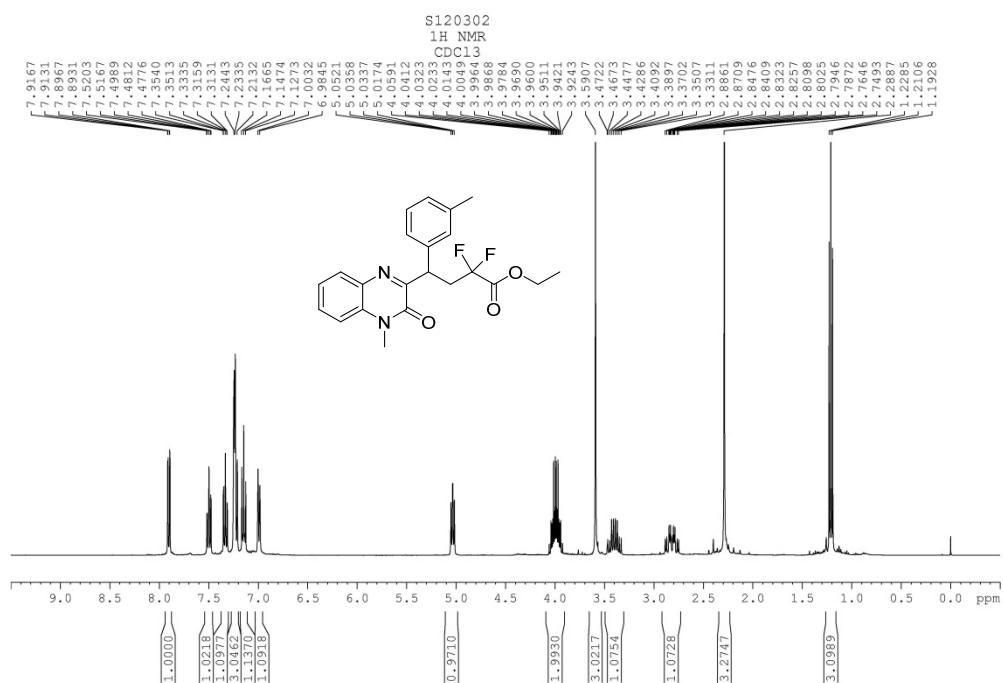


Fig. 10 ¹H NMR spectrum of compound 4d

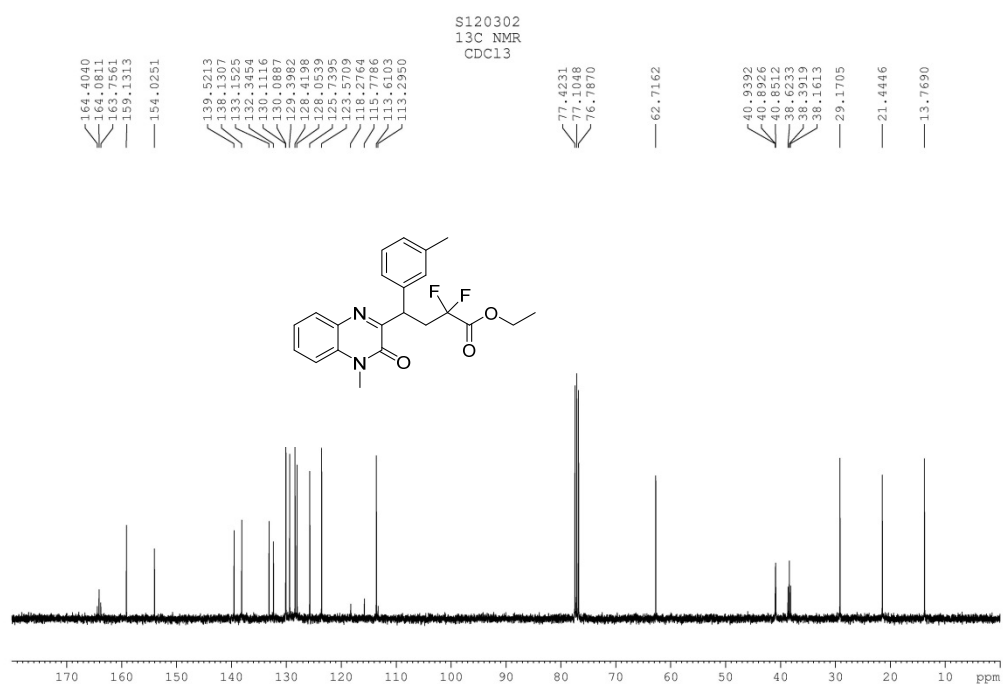


Fig. 11 ^{13}C NMR spectrum of compound 4d

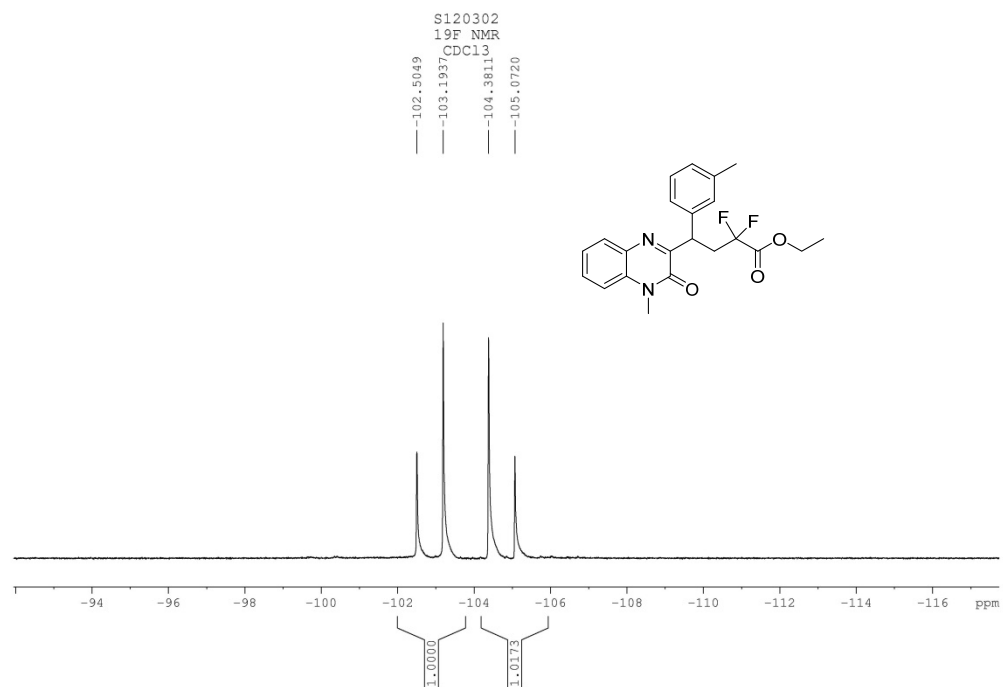


Fig. 12 ^{19}F NMR spectrum of compound 4d

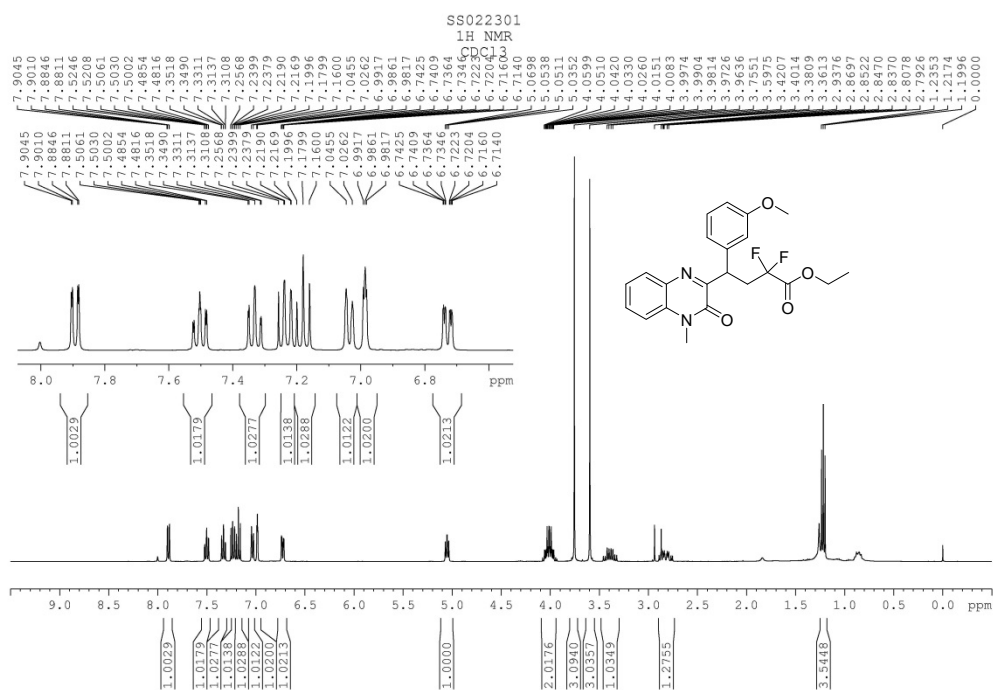


Fig. 13 ^1H NMR spectrum of compound 4e

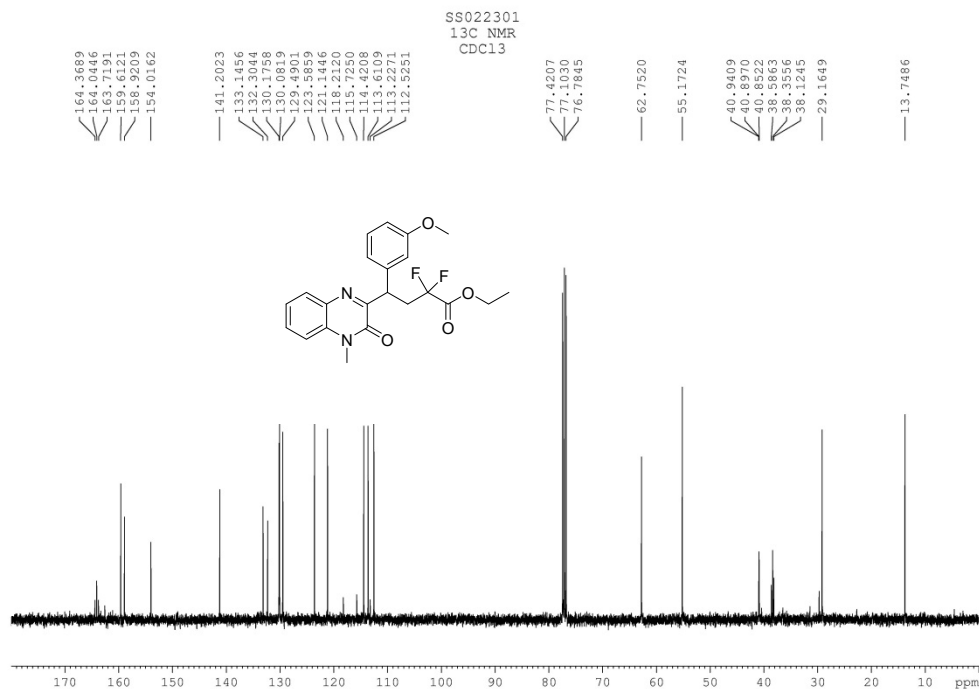


Fig. 14 ^{13}C NMR spectrum of compound 4e

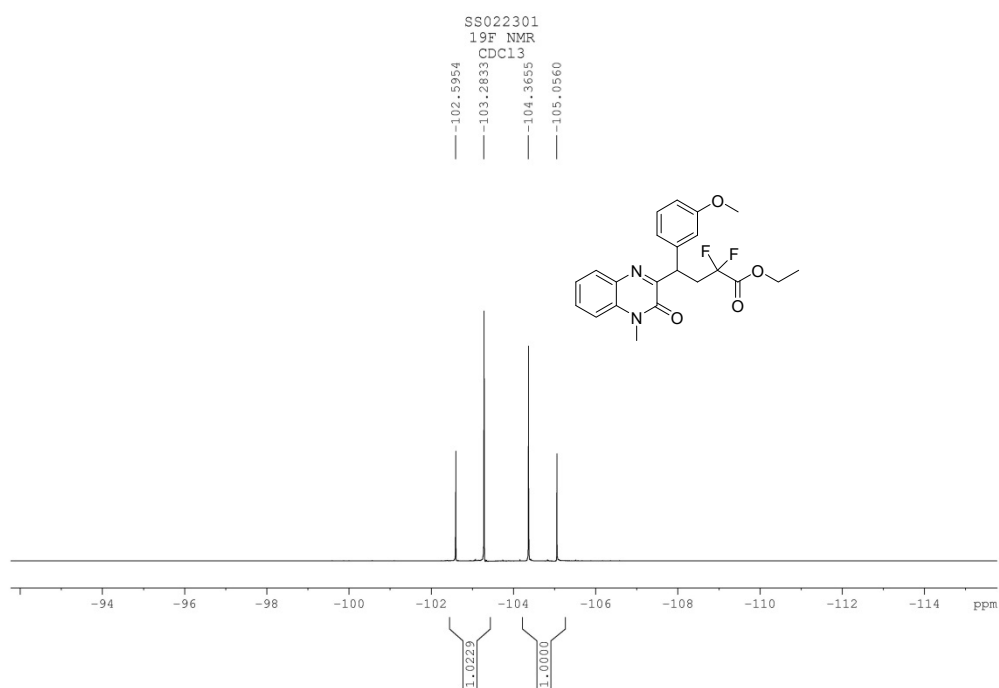


Fig. 15 ^{19}F NMR spectrum of compound 4e

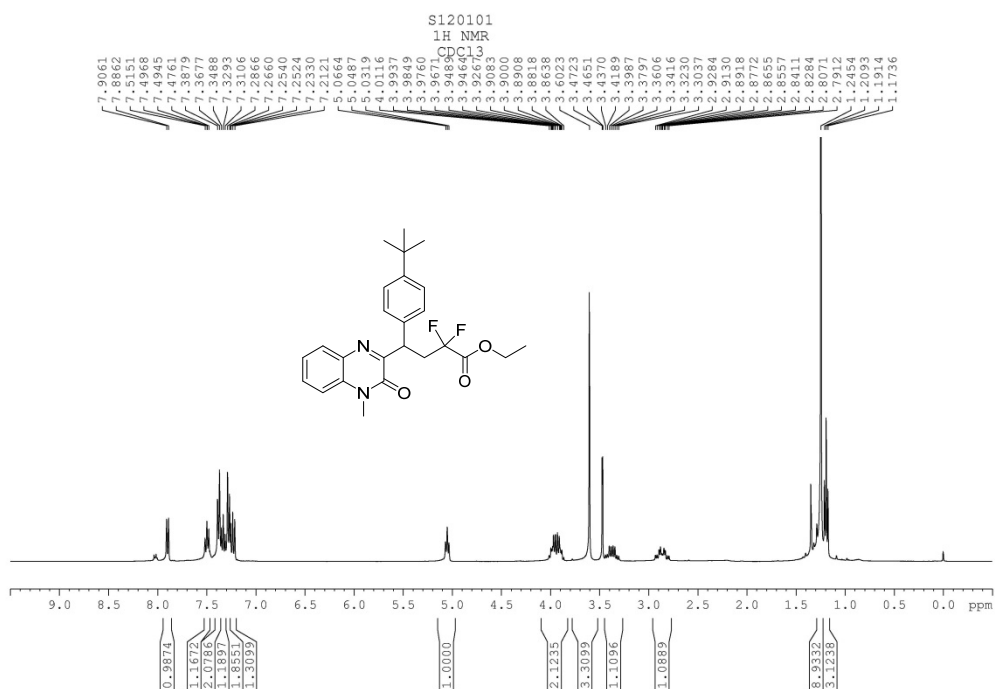


Fig. 16 ^1H NMR spectrum of compound 4f

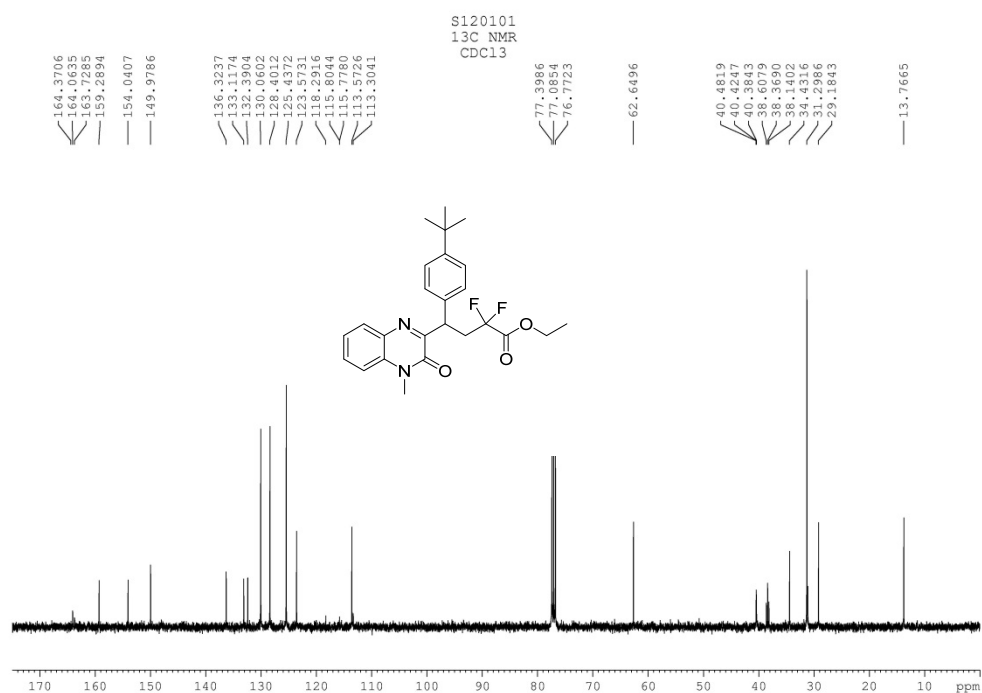


Fig. 17 ^{13}C NMR spectrum of compound 4f

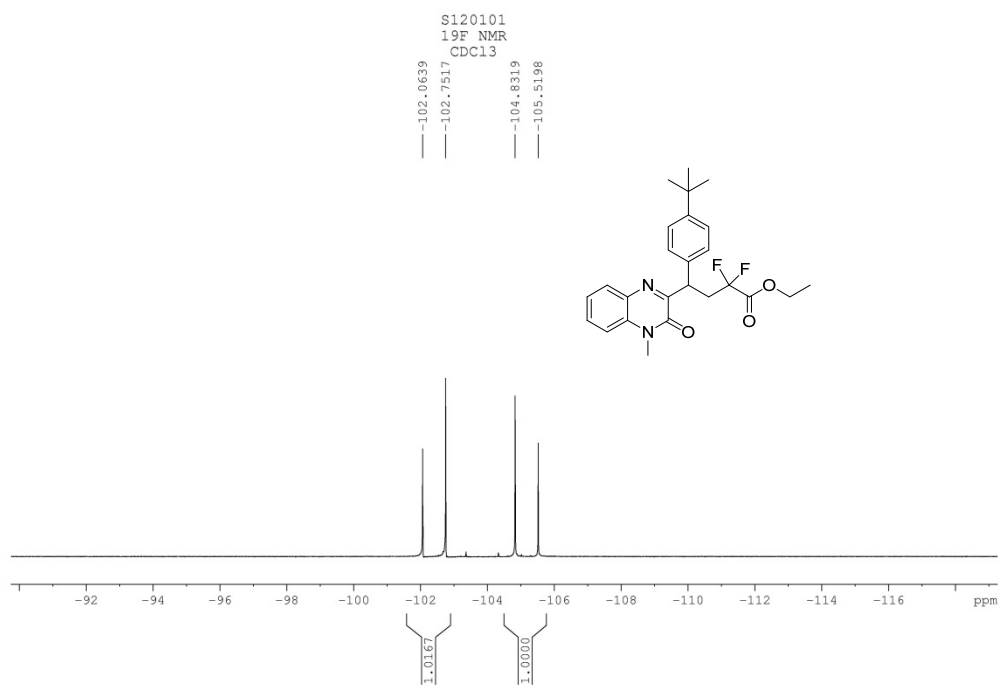


Fig. 18 ^{19}F NMR spectrum of compound 4f

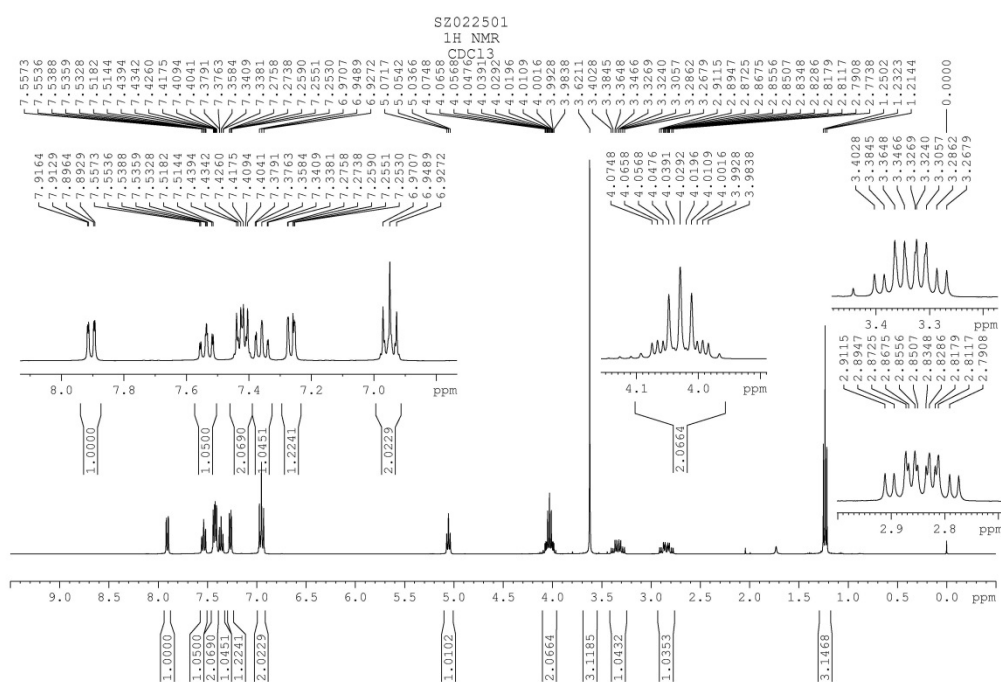


Fig. 19 ^1H NMR spectrum of compound **4g**

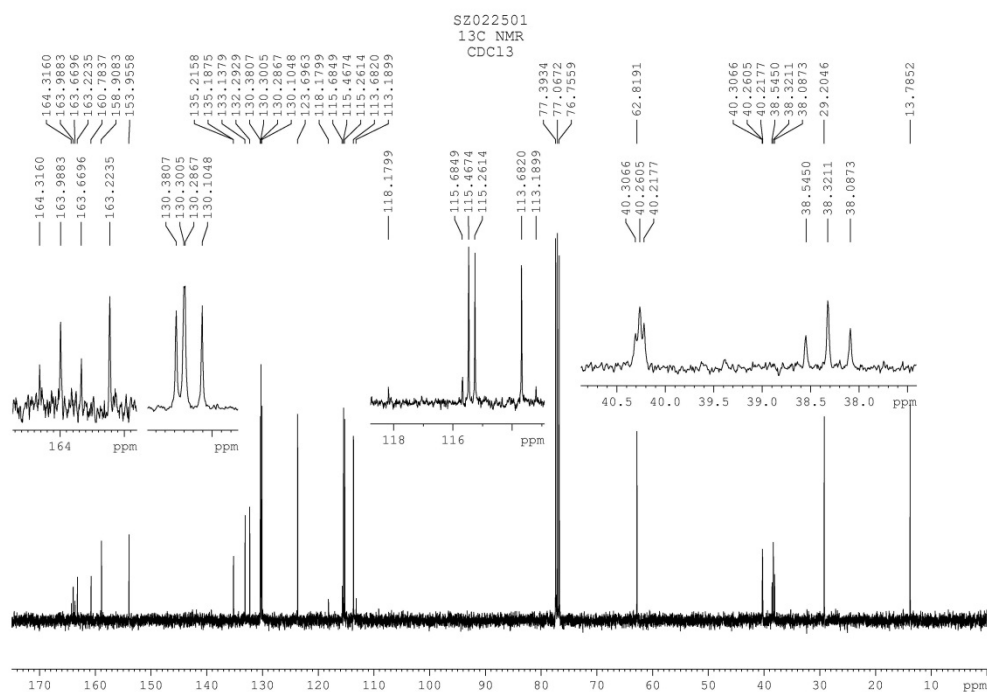


Fig. 20 ^{13}C NMR spectrum of compound **4g**

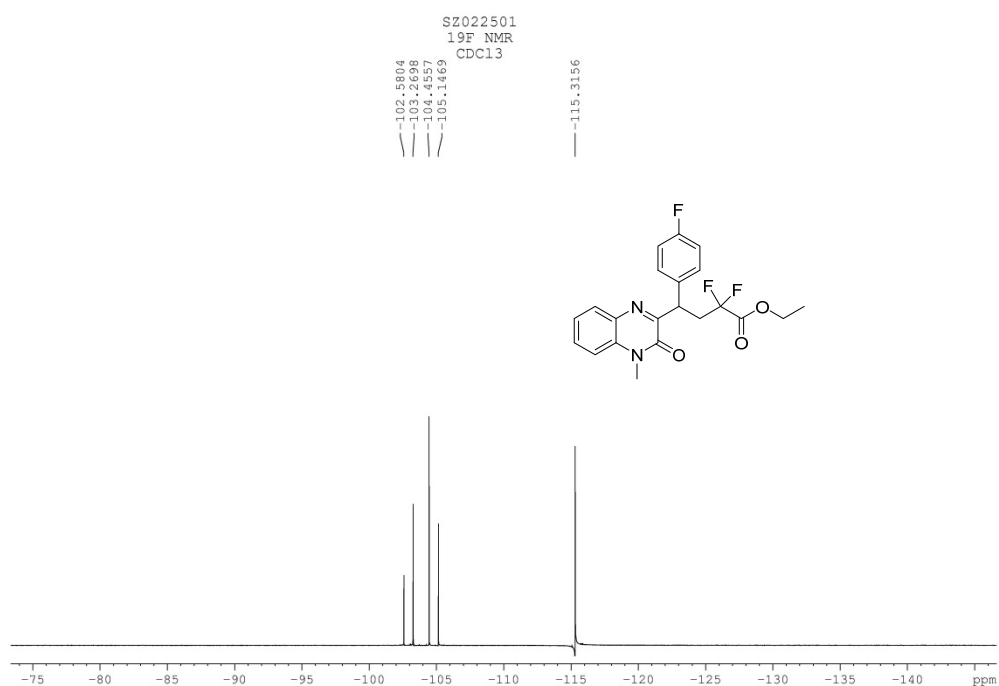


Fig. 21 ^{19}F NMR spectrum of compound 4g

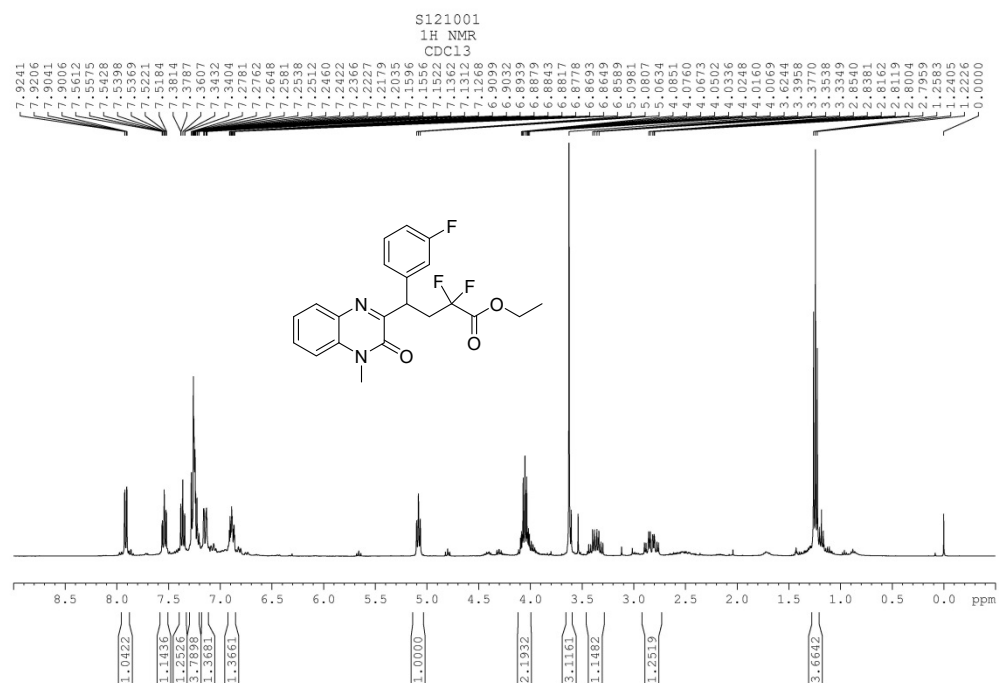


Fig. 22 ^1H NMR spectrum of compound 4h

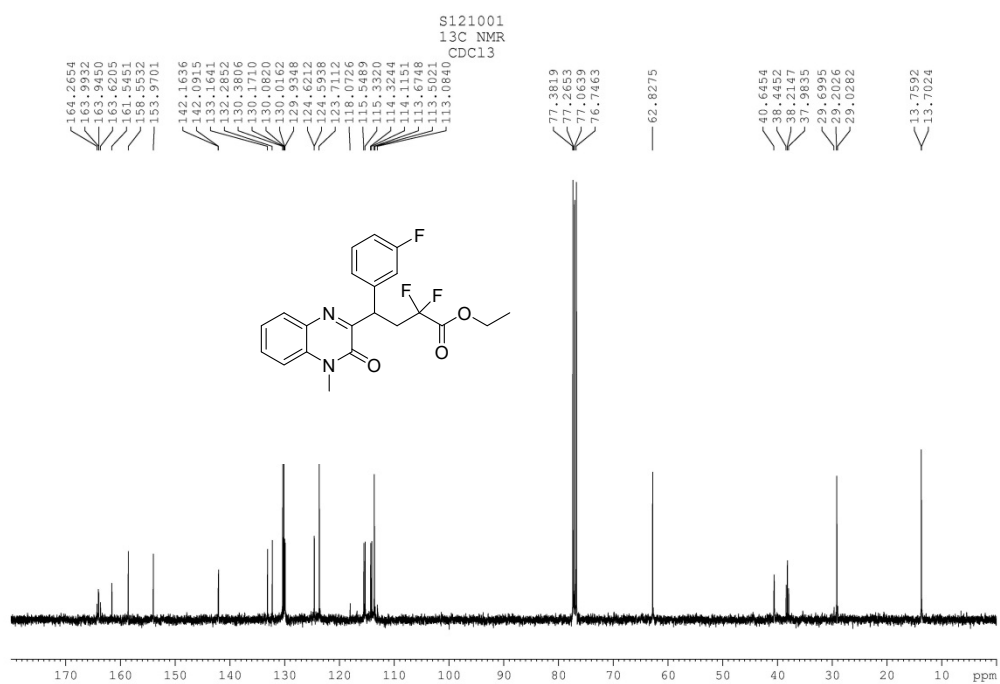


Fig. 23 ^{13}C NMR spectrum of compound 4h

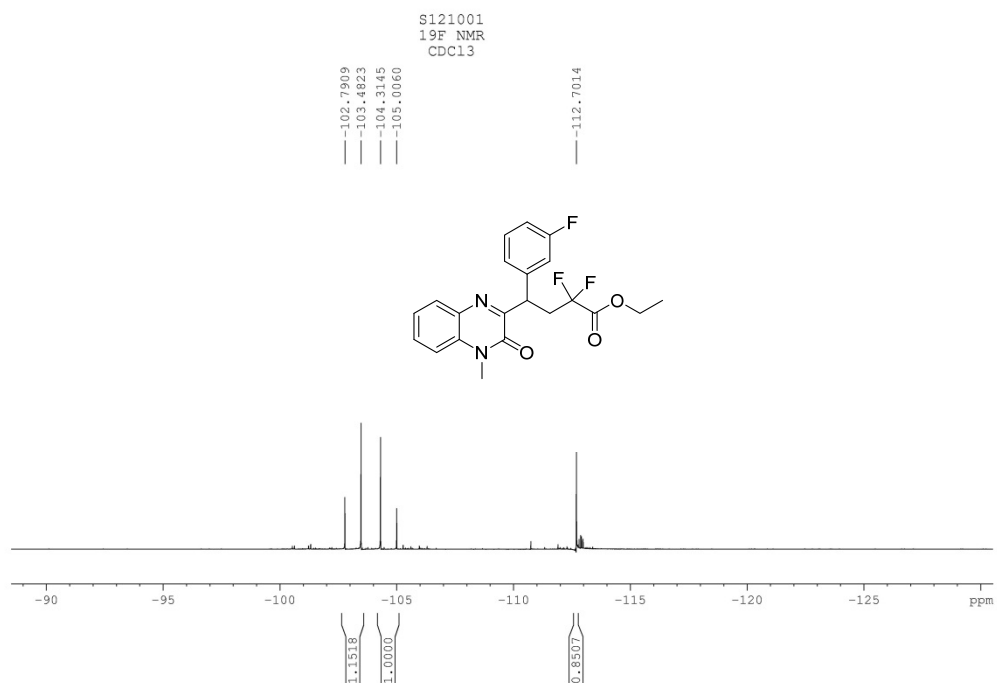


Fig. 24 ^{19}F NMR spectrum of compound 4h

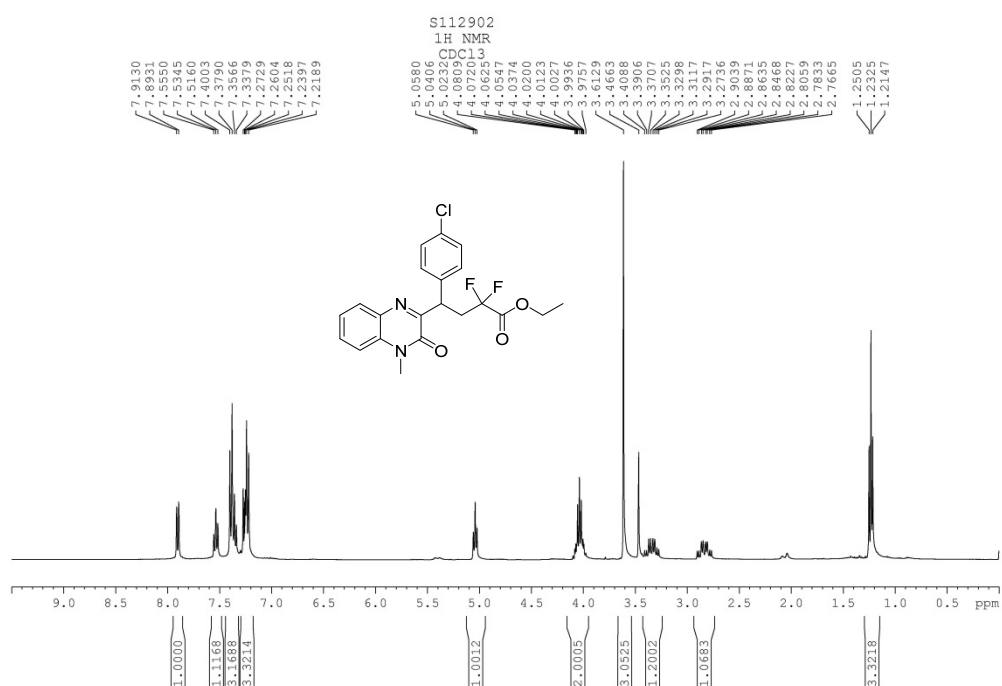


Fig. 25 ¹H NMR spectrum of compound 4i

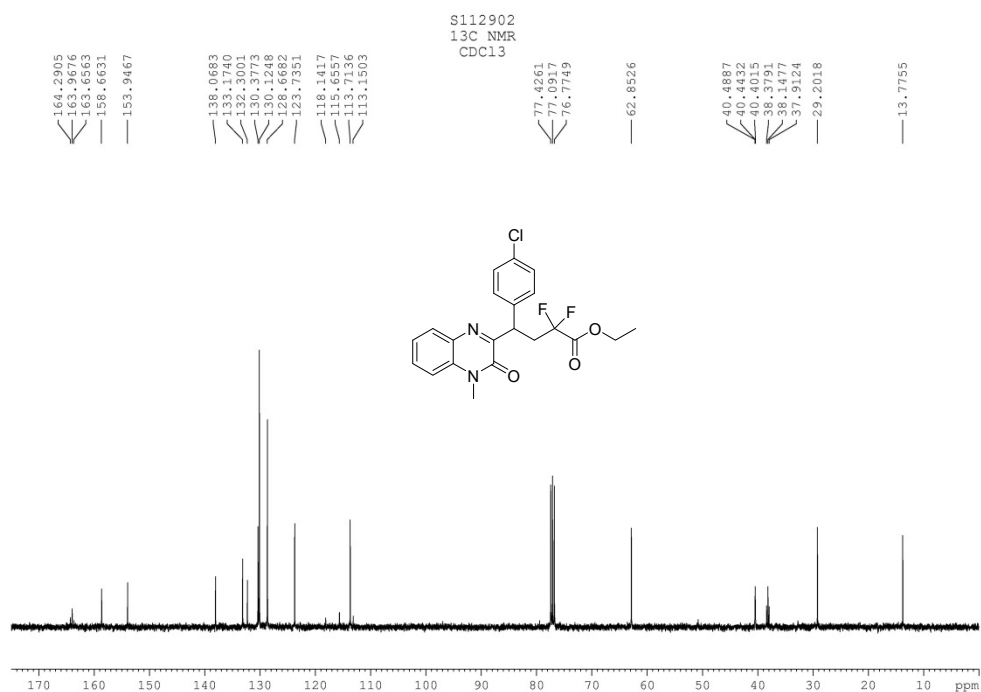


Fig. 26 ¹³C NMR spectrum of compound 4i

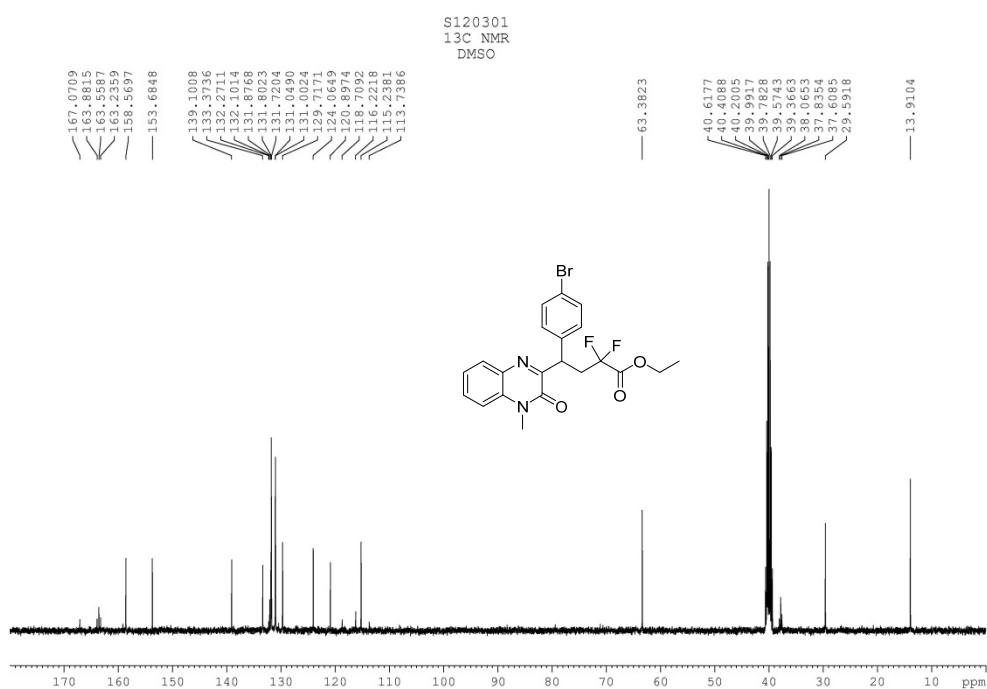


Fig. 29 ^{13}C NMR spectrum of compound 4j

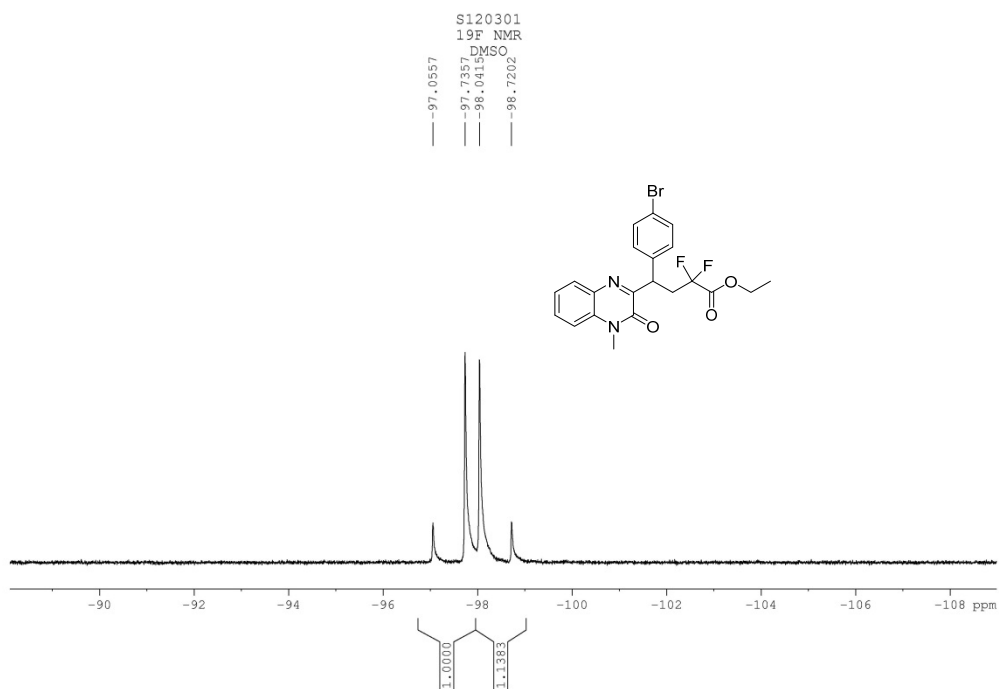


Fig. 30 ^{19}F NMR spectrum of compound 4j

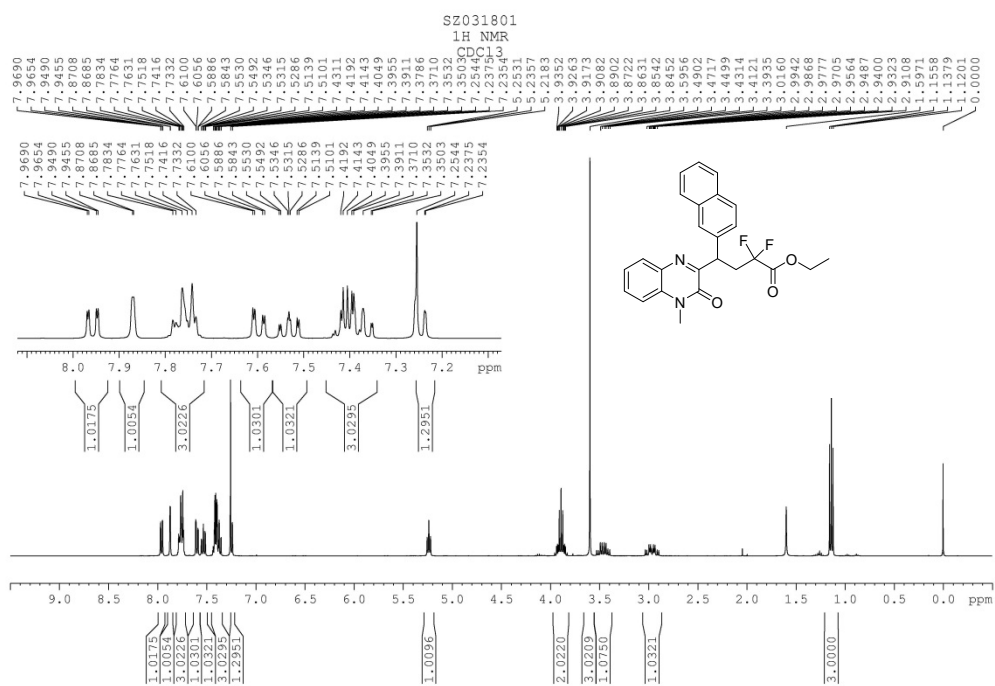


Fig. 31 ¹H NMR spectrum of compound 4k

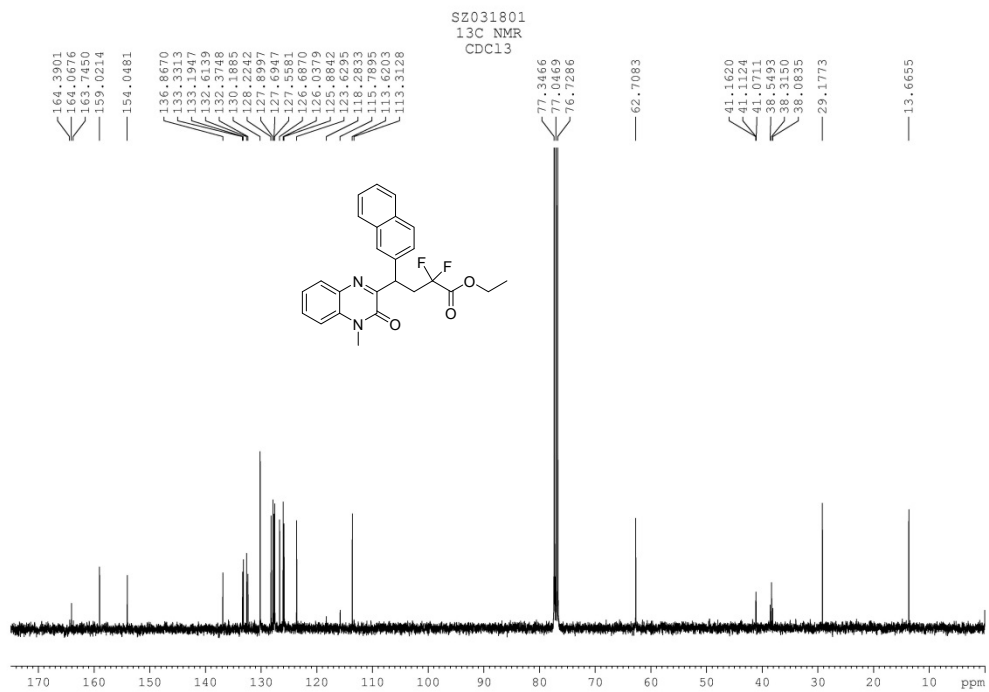


Fig. 32 ¹³C NMR spectrum of compound 4k

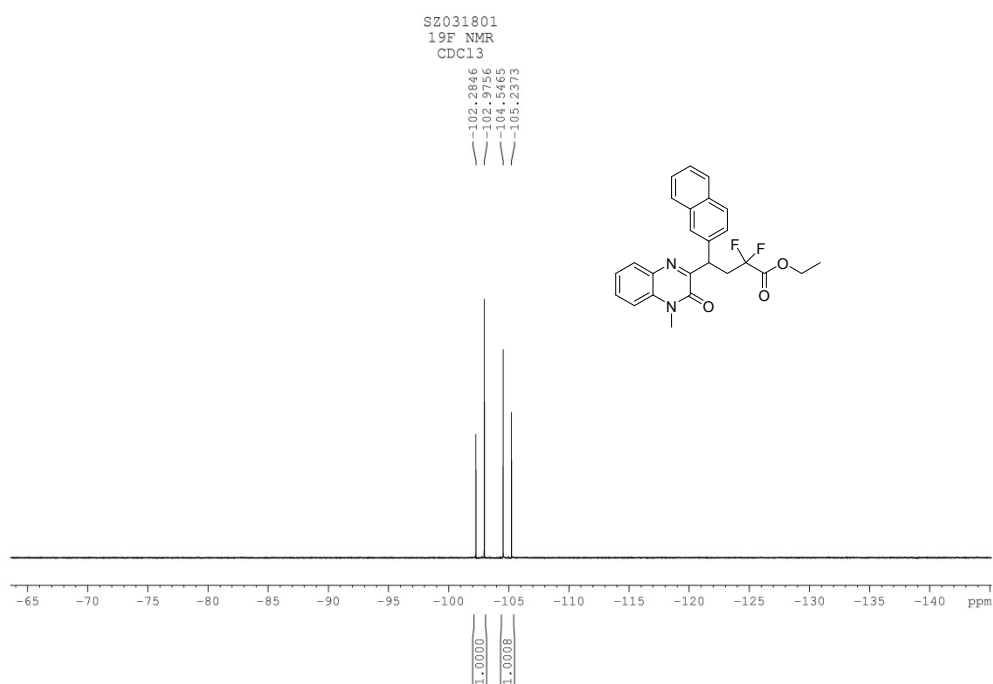


Fig. 33 ^{19}F NMR spectrum of compound 4k

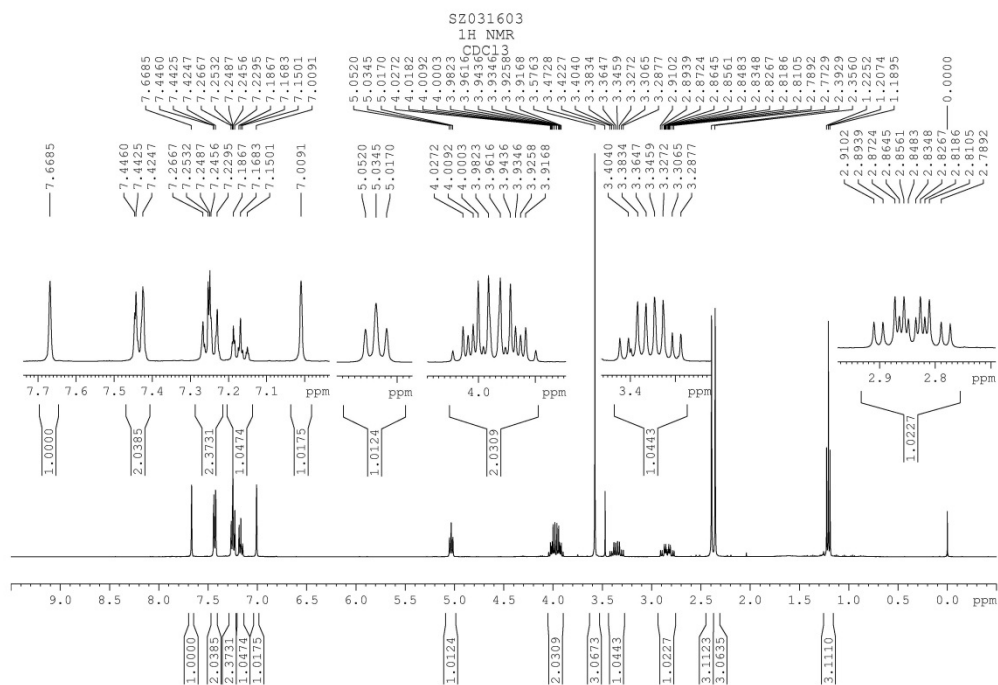


Fig. 34 ^1H NMR spectrum of compound 4m

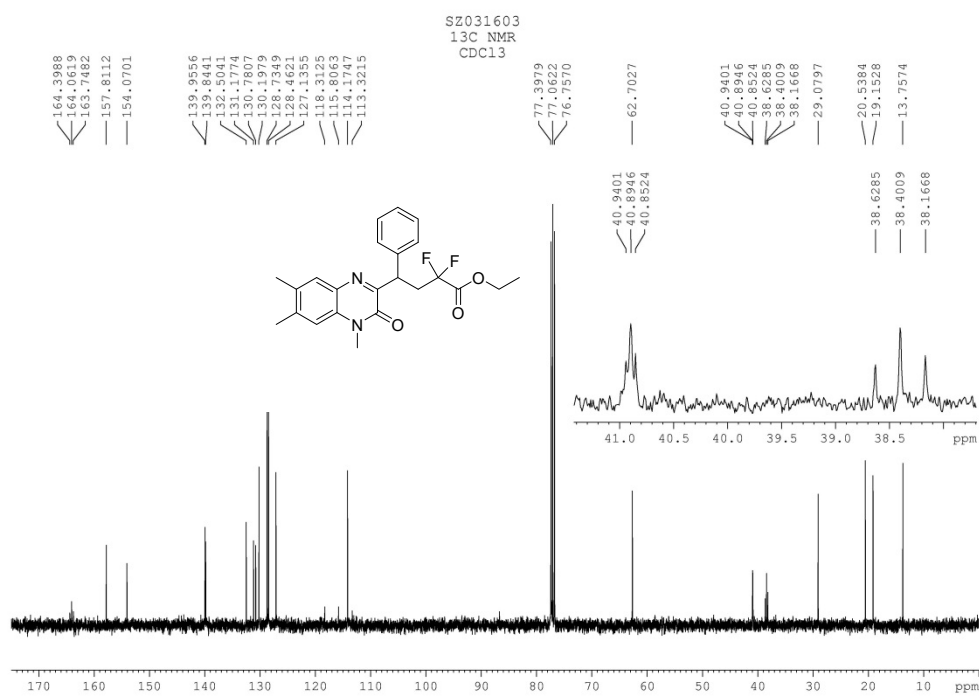


Fig. 35 ^{13}C NMR spectrum of compound 4m

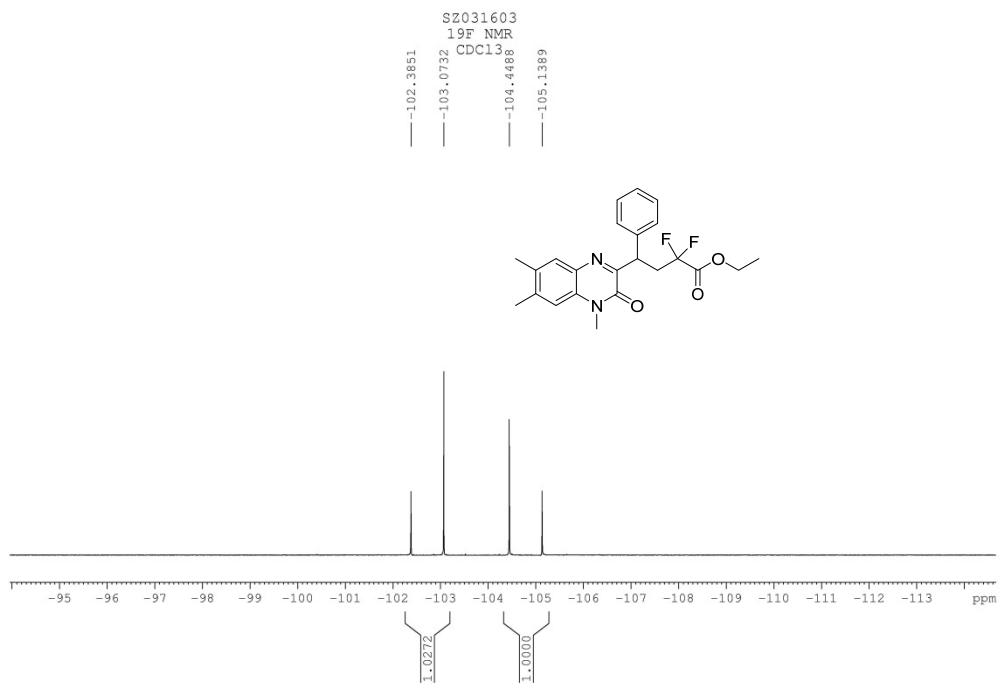


Fig. 36 ^{19}F NMR spectrum of compound 4m

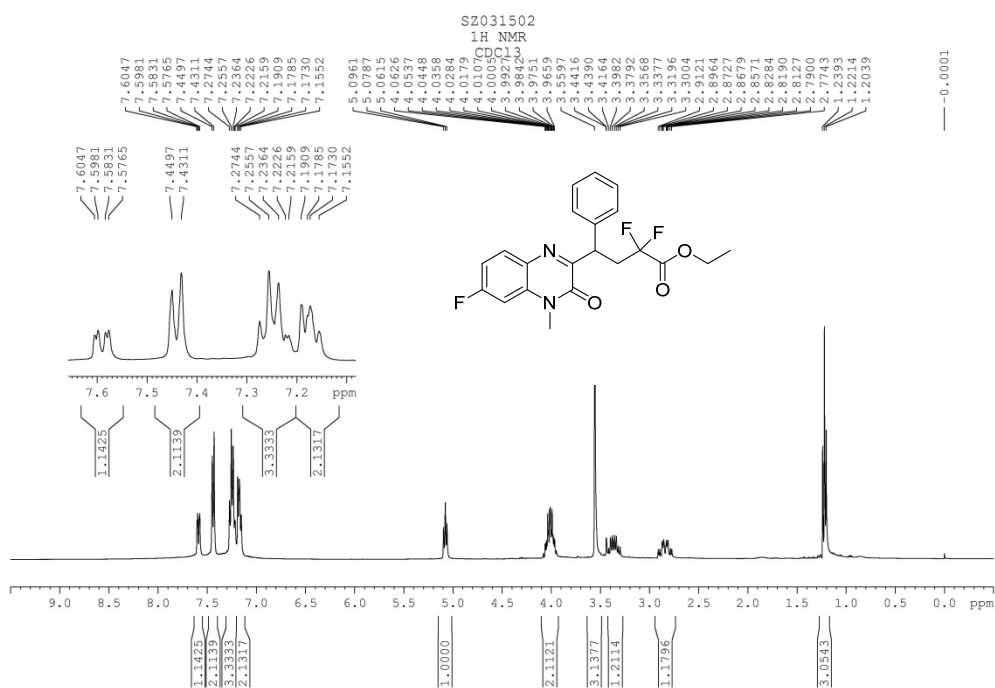


Fig. 37 ¹H NMR spectrum of compound 4n

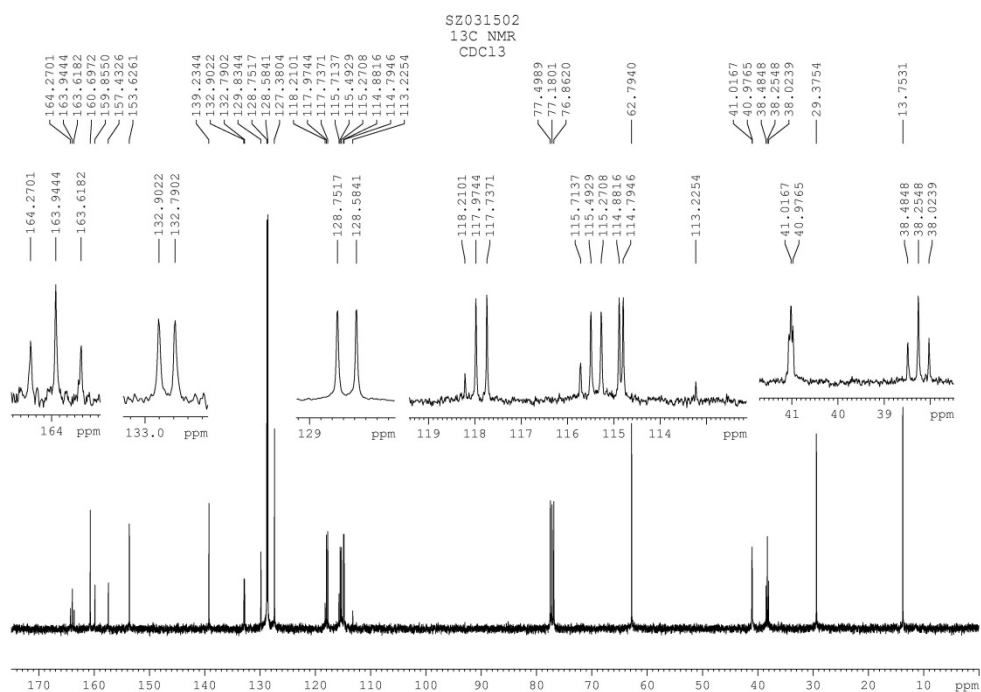


Fig. 38 ¹³C NMR spectrum of compound 4n



Fig. 39 ¹⁹F NMR spectrum of compound 4n

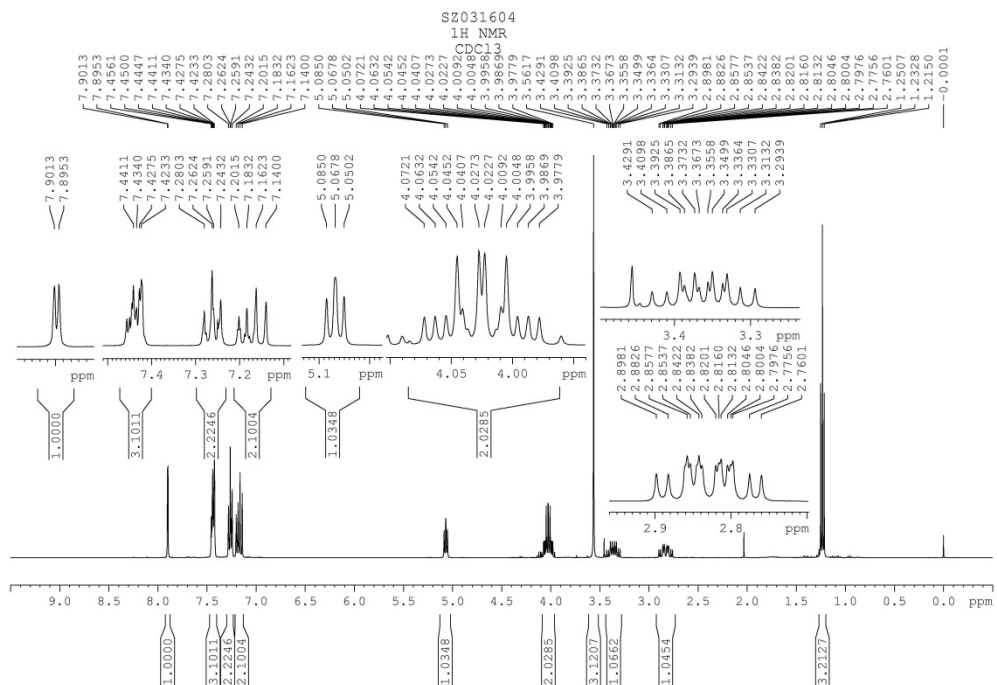


Fig. 40 ¹H NMR spectrum of compound 4o

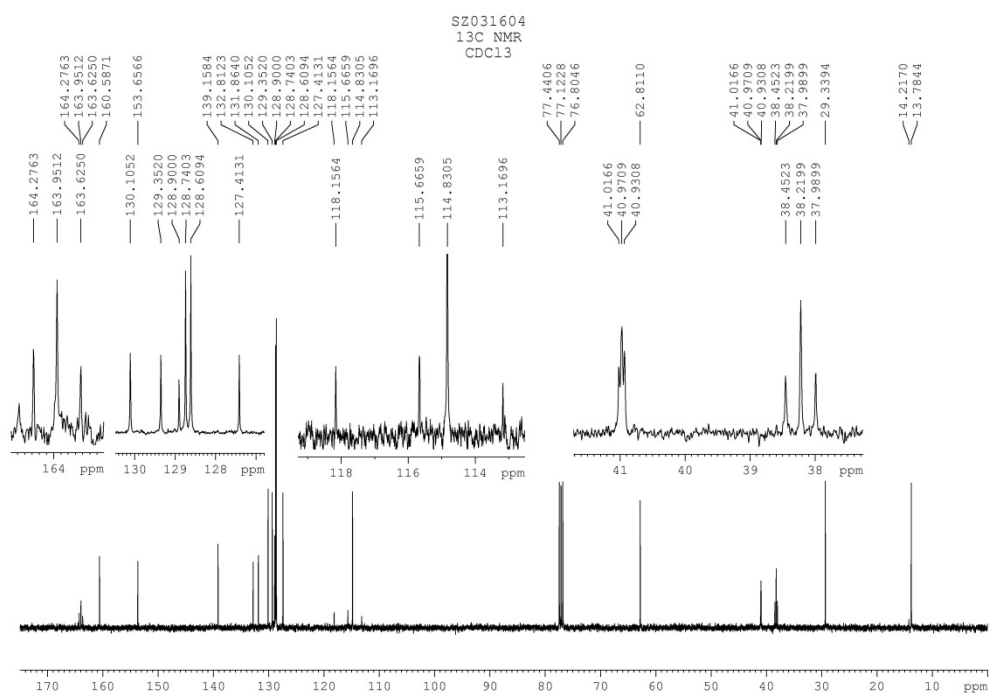


Fig. 41 ^{13}C NMR spectrum of compound **4o**

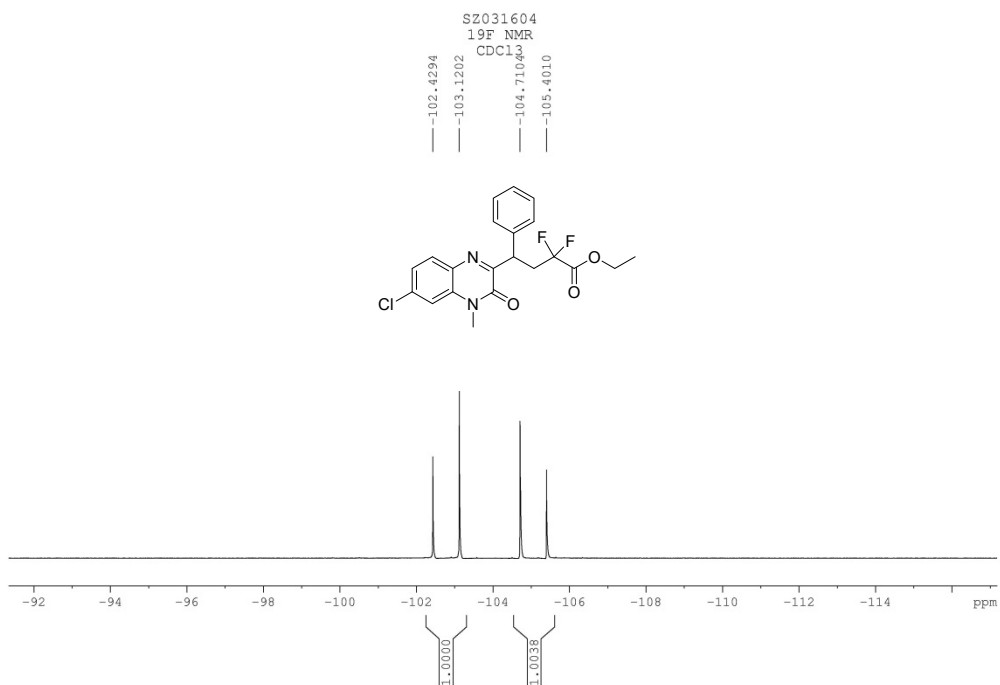
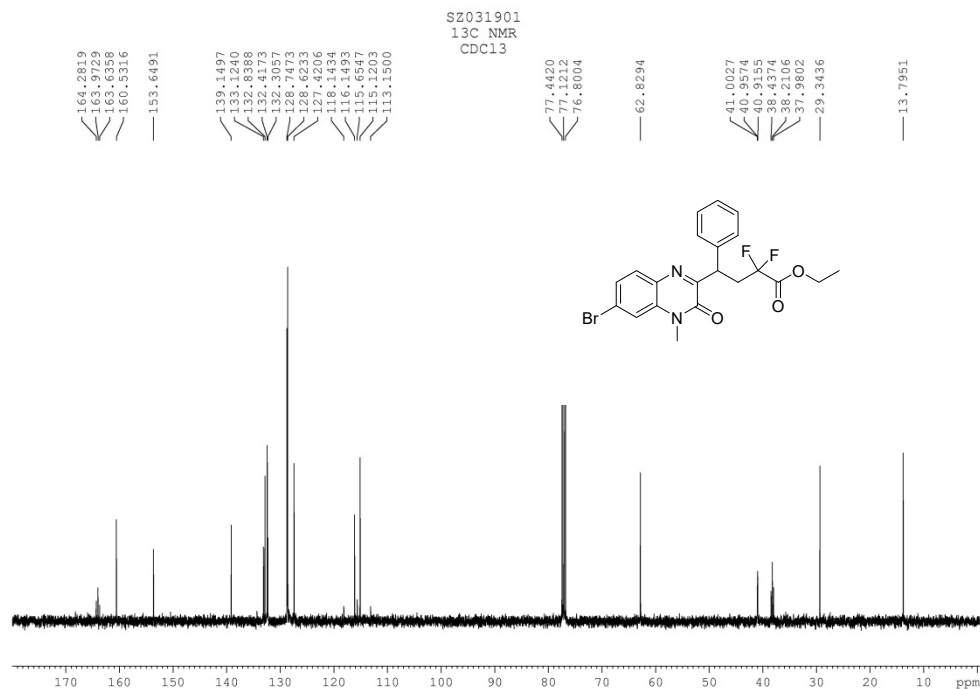
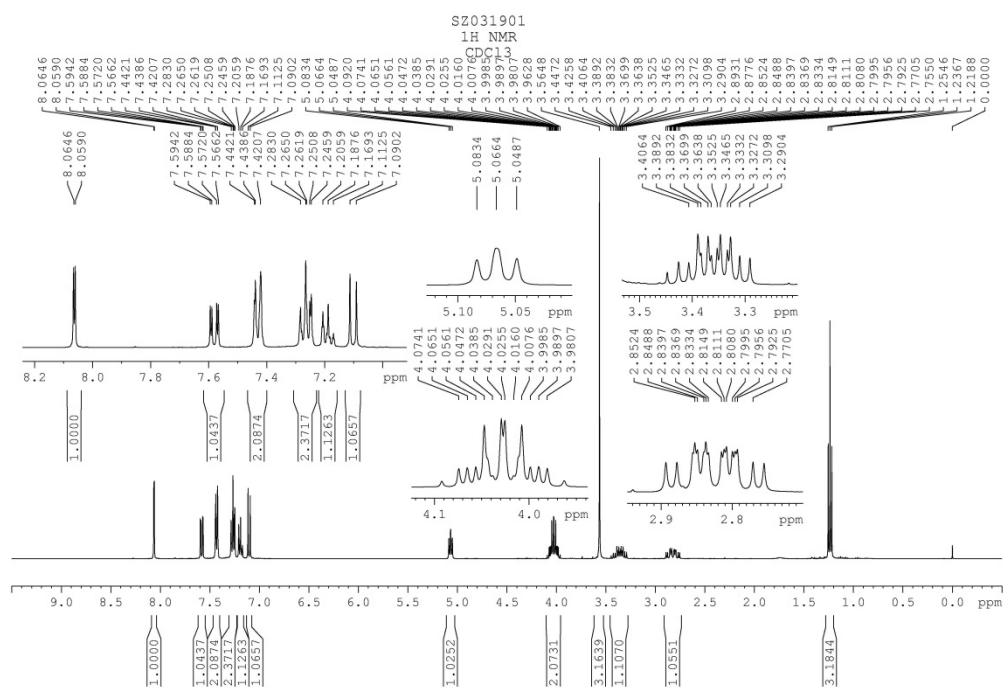


Fig. 42 ^{19}F NMR spectrum of compound **4o**



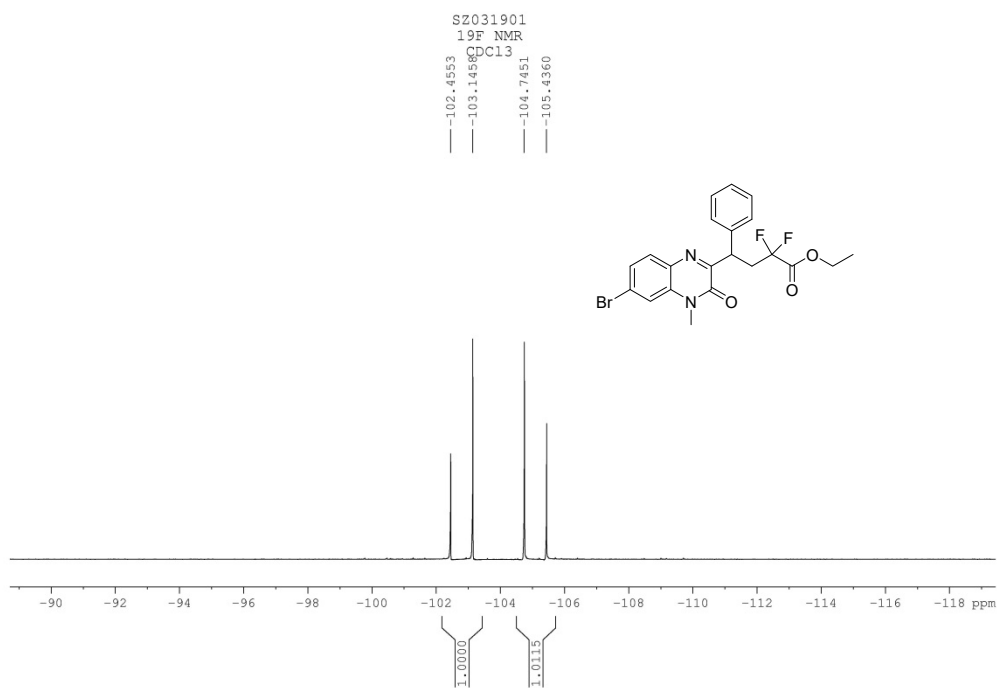


Fig. 45 ^{19}F NMR spectrum of compound 4p

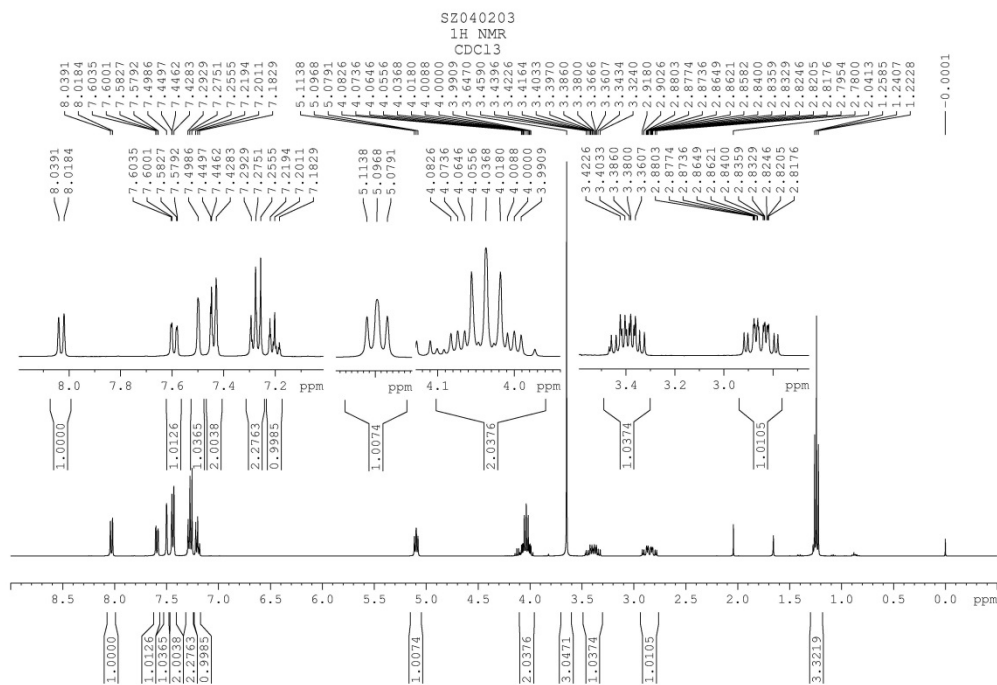


Fig. 46 ^1H NMR spectrum of compound 4q

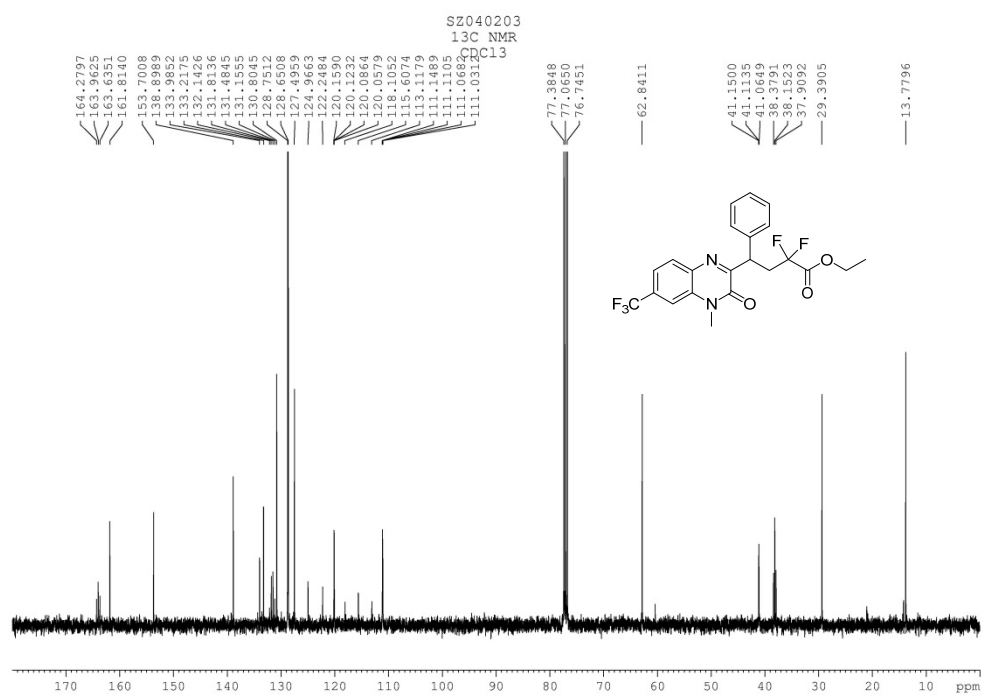


Fig. 47 ^{13}C NMR spectrum of compound 4q

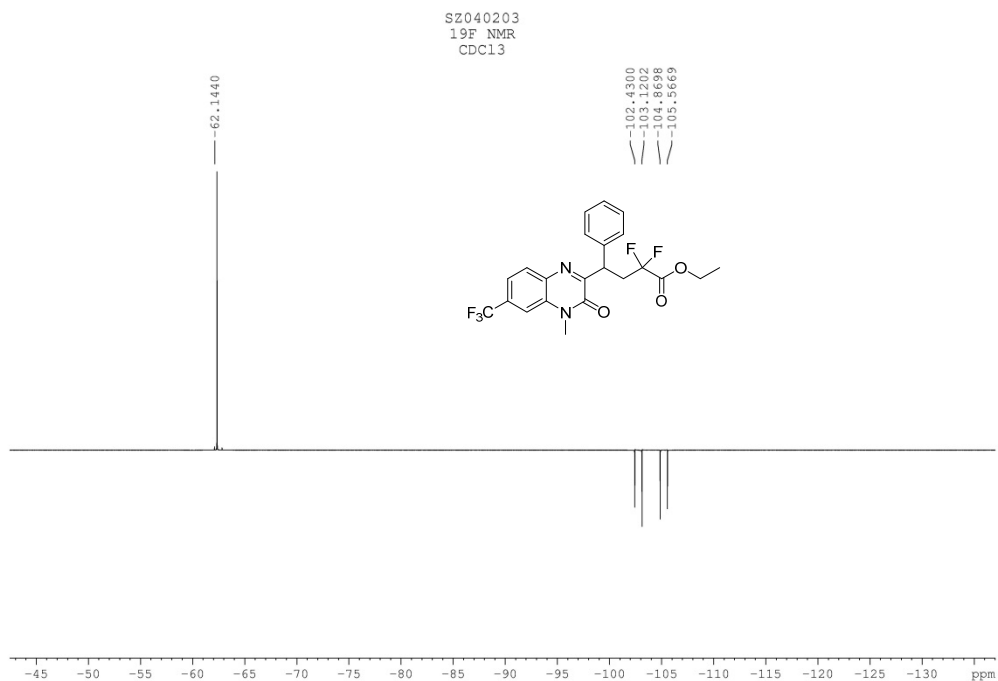


Fig. 48 ^{19}F NMR spectrum of compound 4q

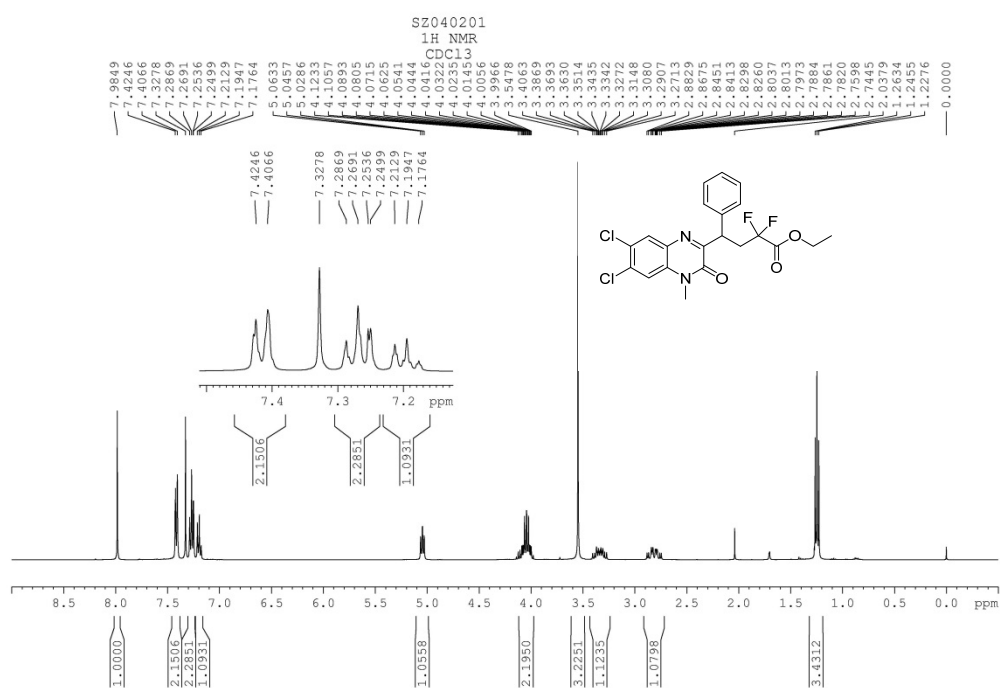


Fig. 49 ¹H NMR spectrum of compound 4r

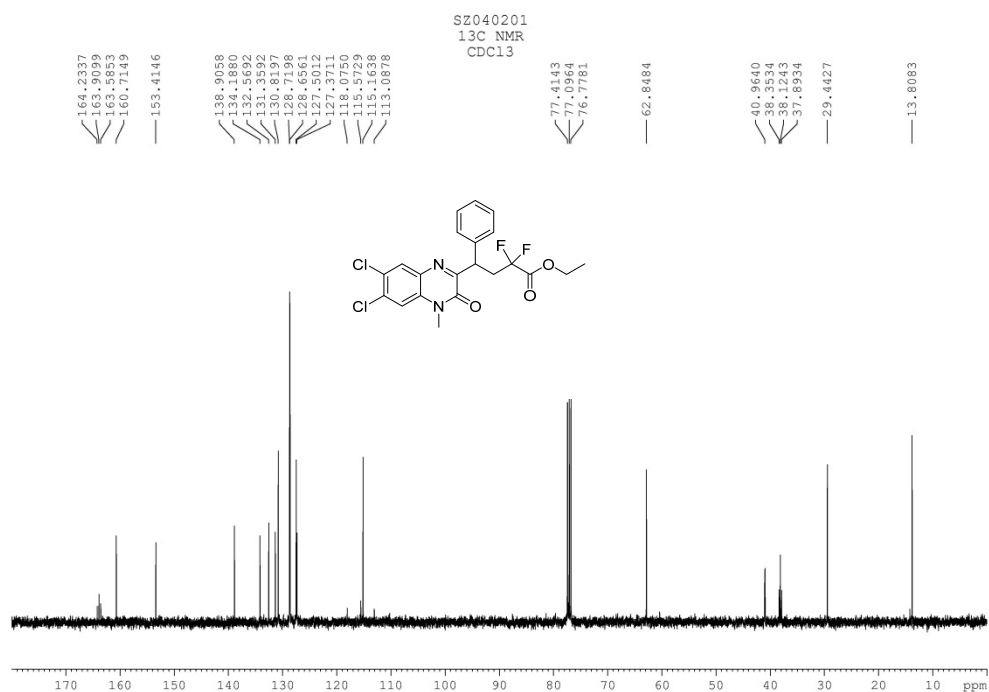


Fig. 50 ¹³C NMR spectrum of compound 4r

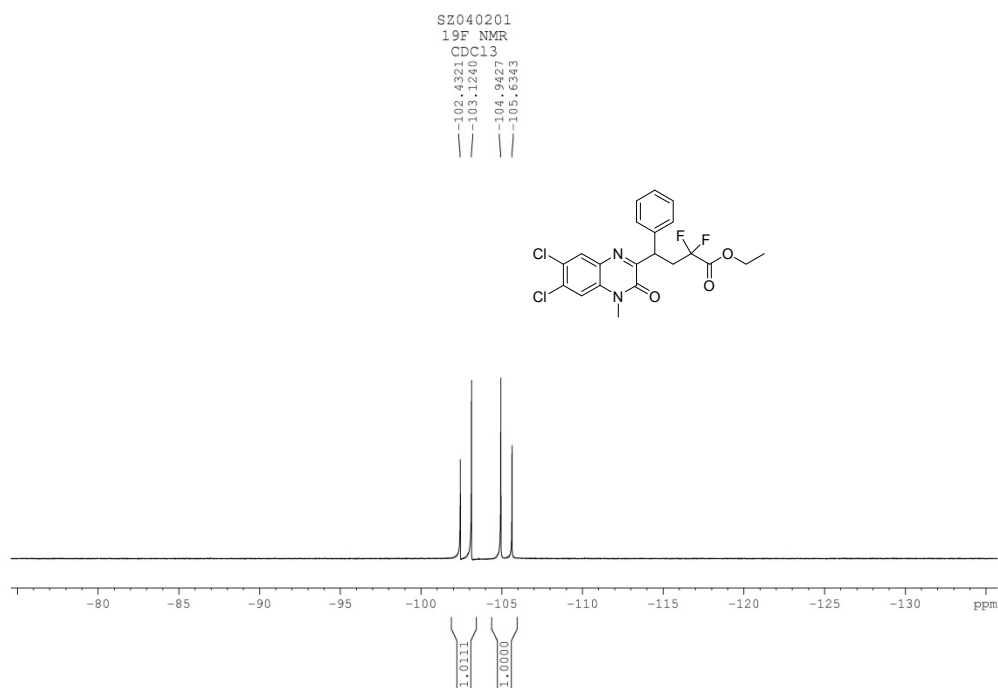


Fig. 51 ¹⁹F NMR spectrum of compound 4r

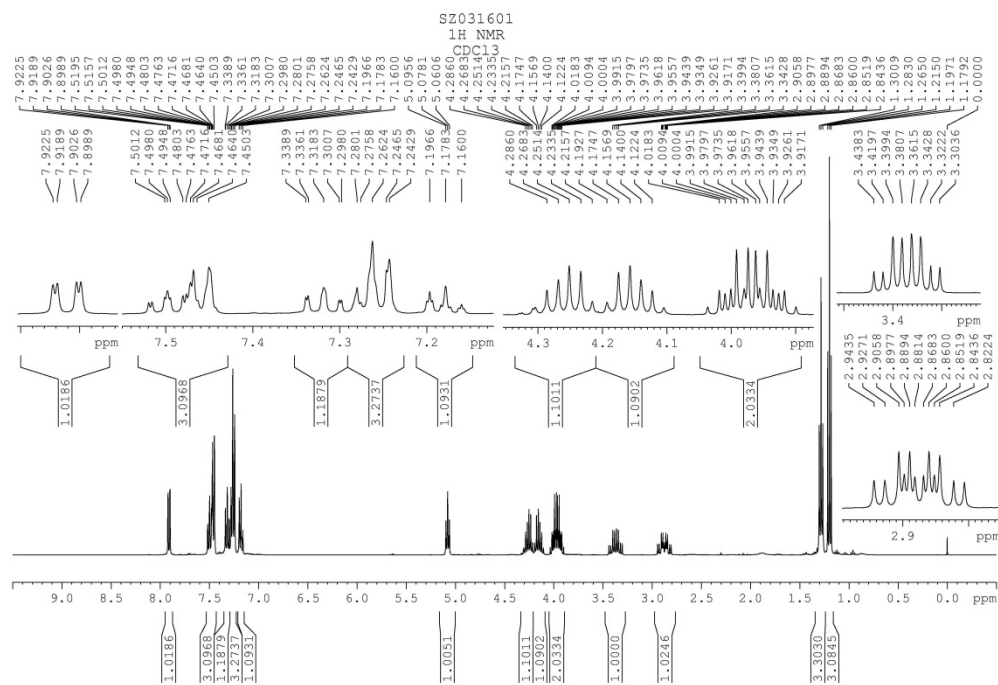


Fig. 52 ¹H NMR spectrum of compound 4s

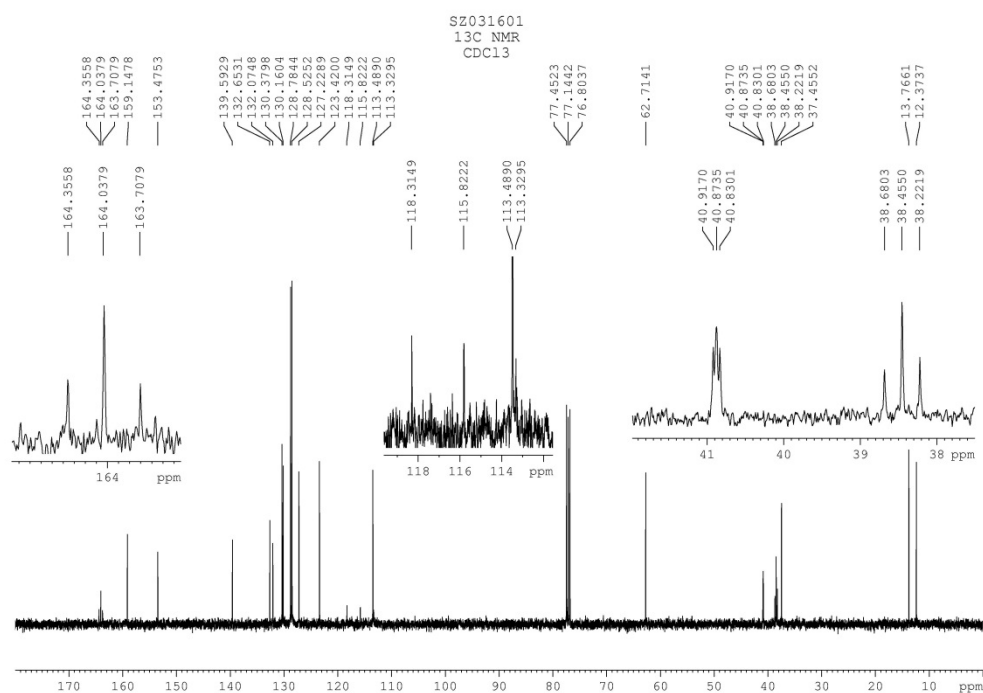


Fig. 53 ^{13}C NMR spectrum of compound 4s

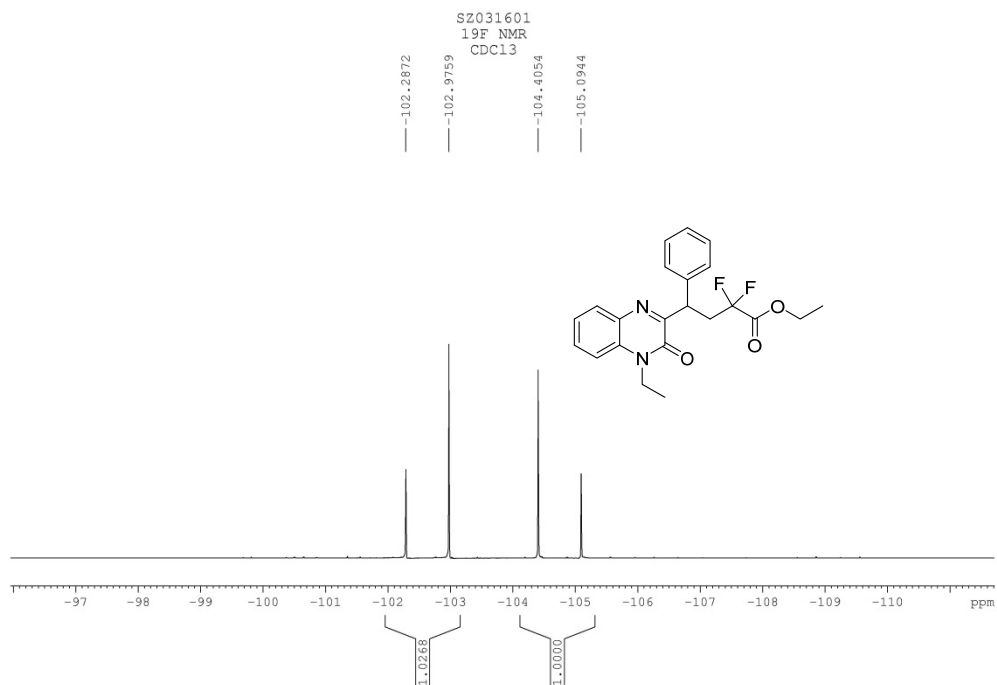


Fig. 54 ^{19}F NMR spectrum of compound 4s

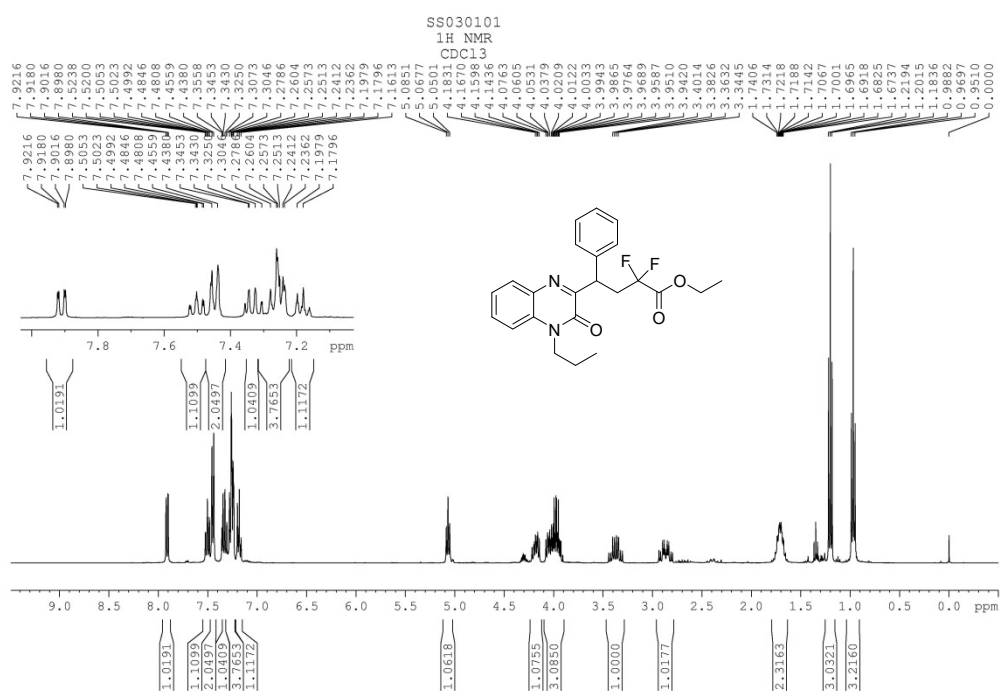


Fig. 55 ^1H NMR spectrum of compound 4t

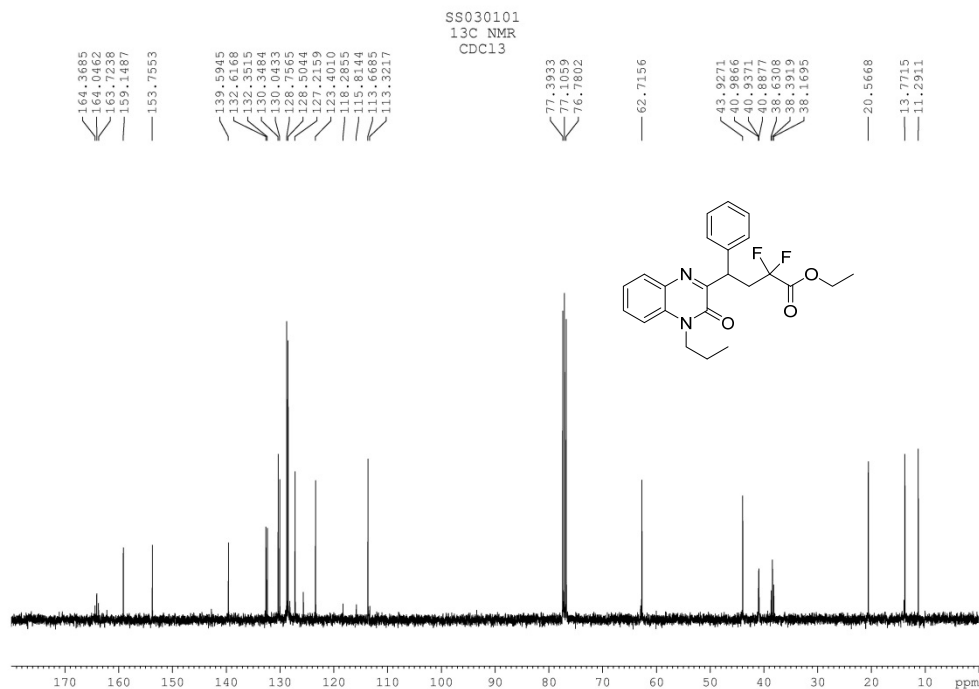


Fig. 56 ^{13}C NMR spectrum of compound 4t

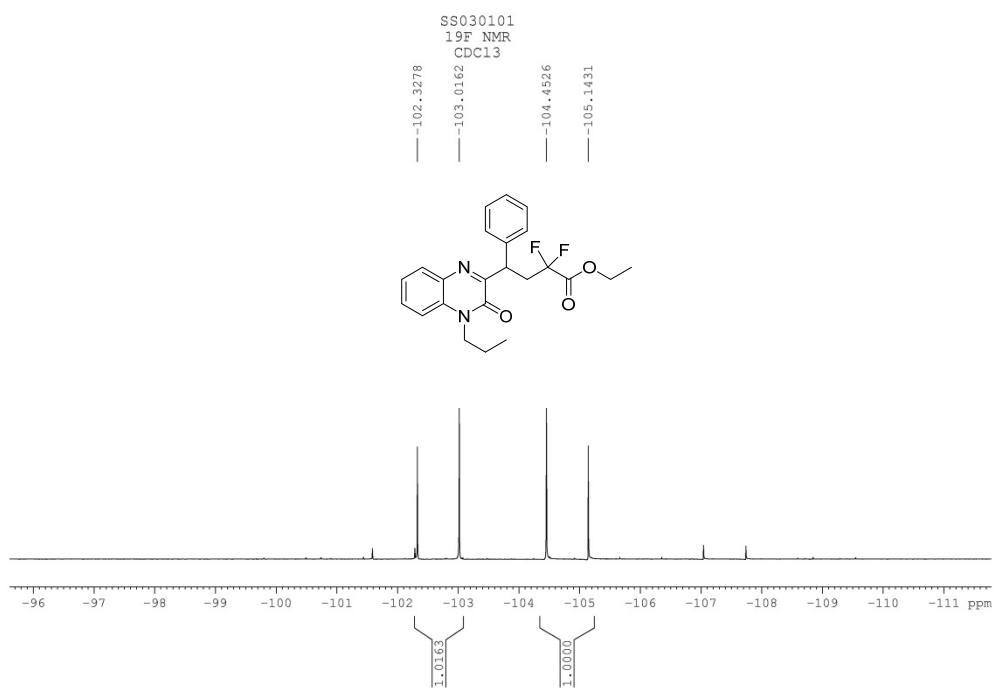


Fig. 57 ^{19}F NMR spectrum of compound 4t

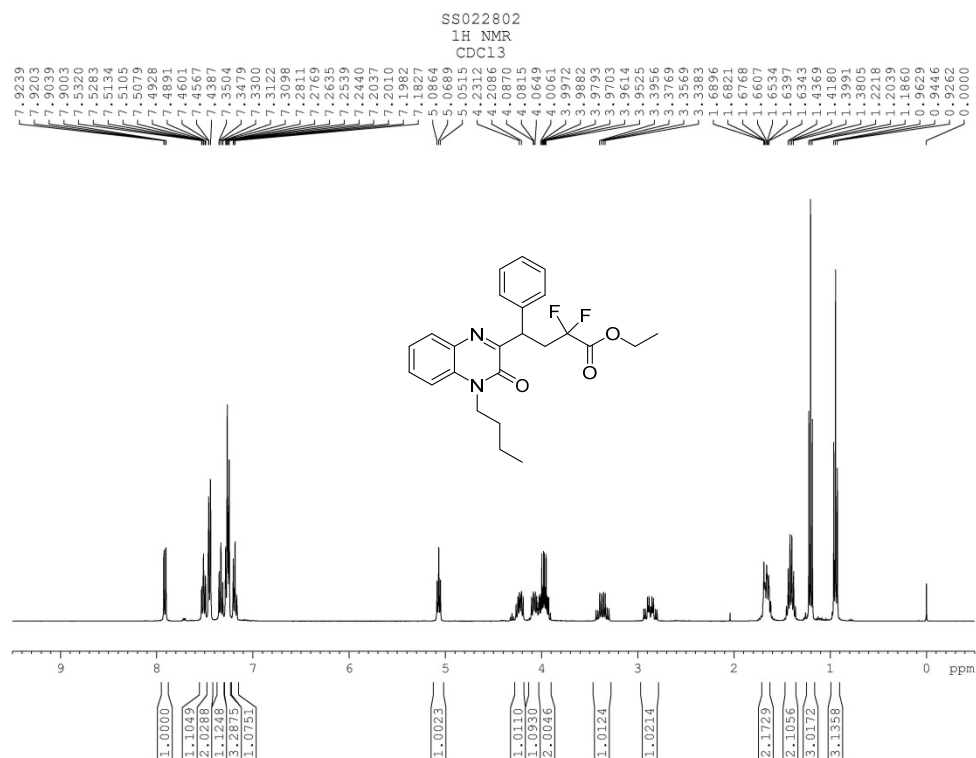


Fig. 58 ^1H NMR spectrum of compound 4u

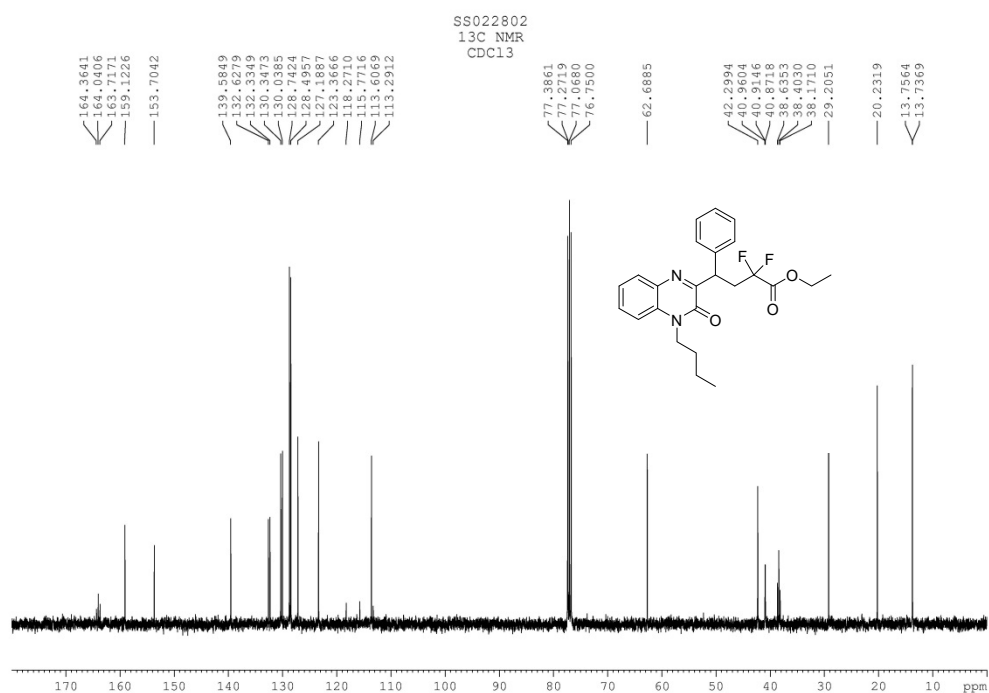


Fig. 59 ^{13}C NMR spectrum of compound 4u

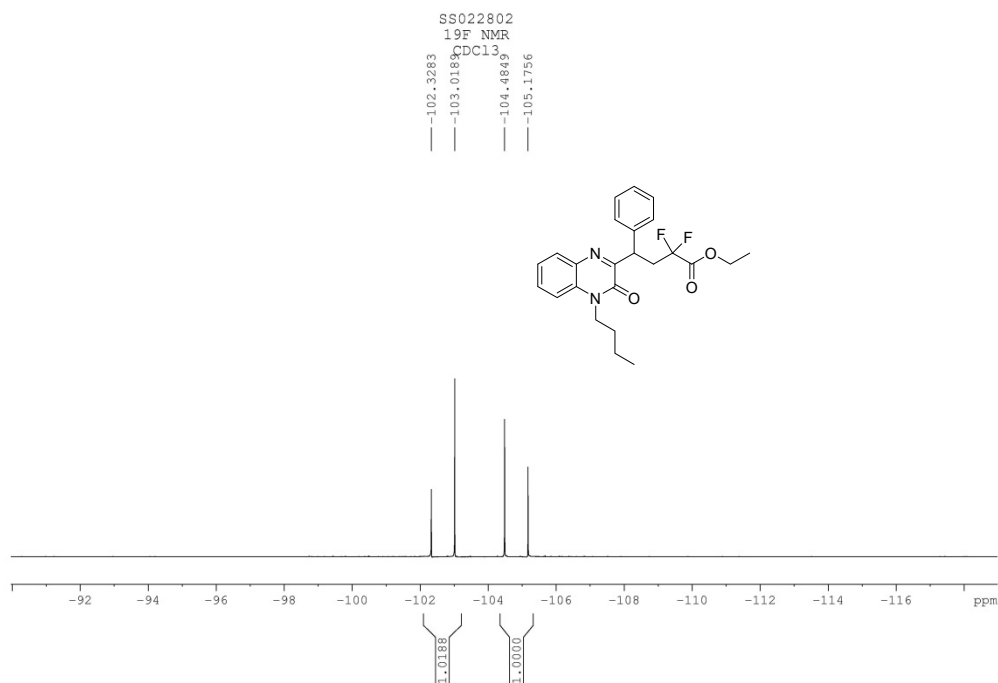


Fig. 60 ^{19}F NMR spectrum of compound 4u

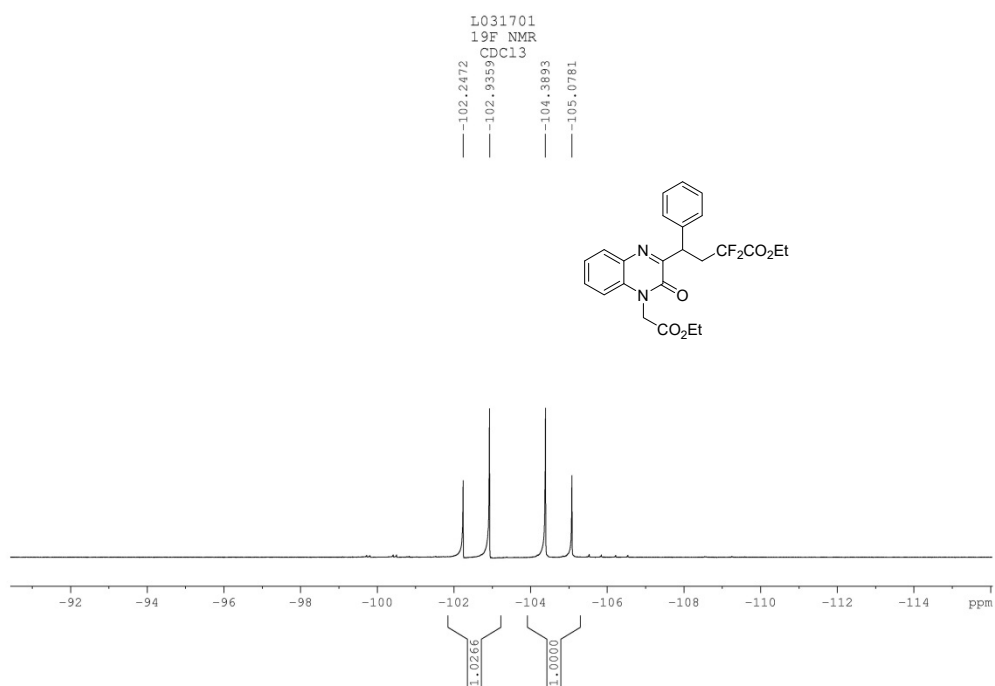
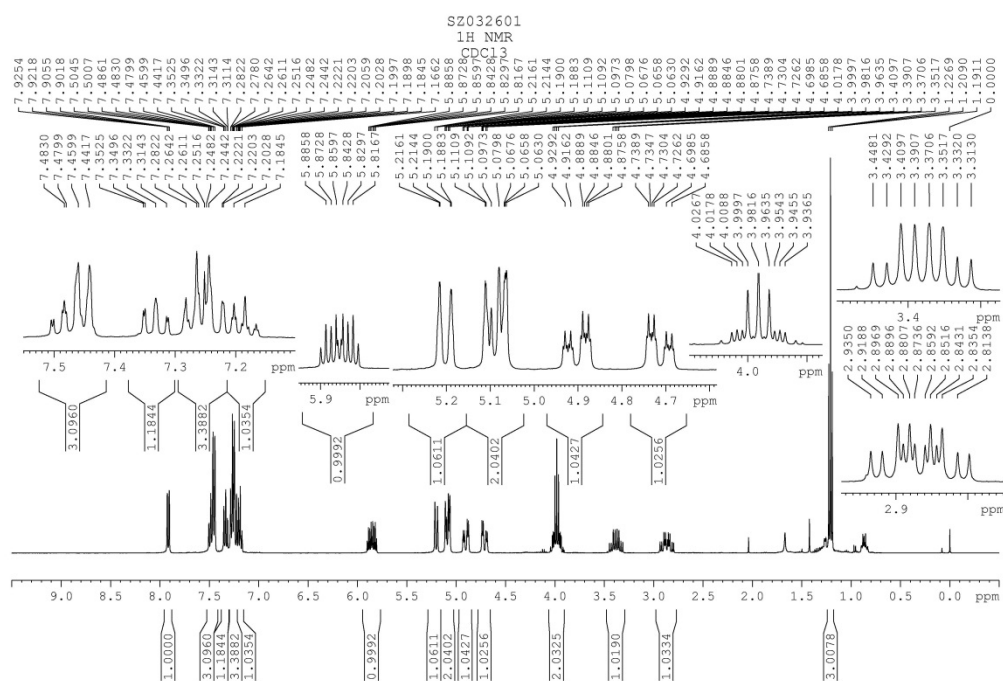


Fig. 63 ¹⁹F NMR spectrum of compound 4v



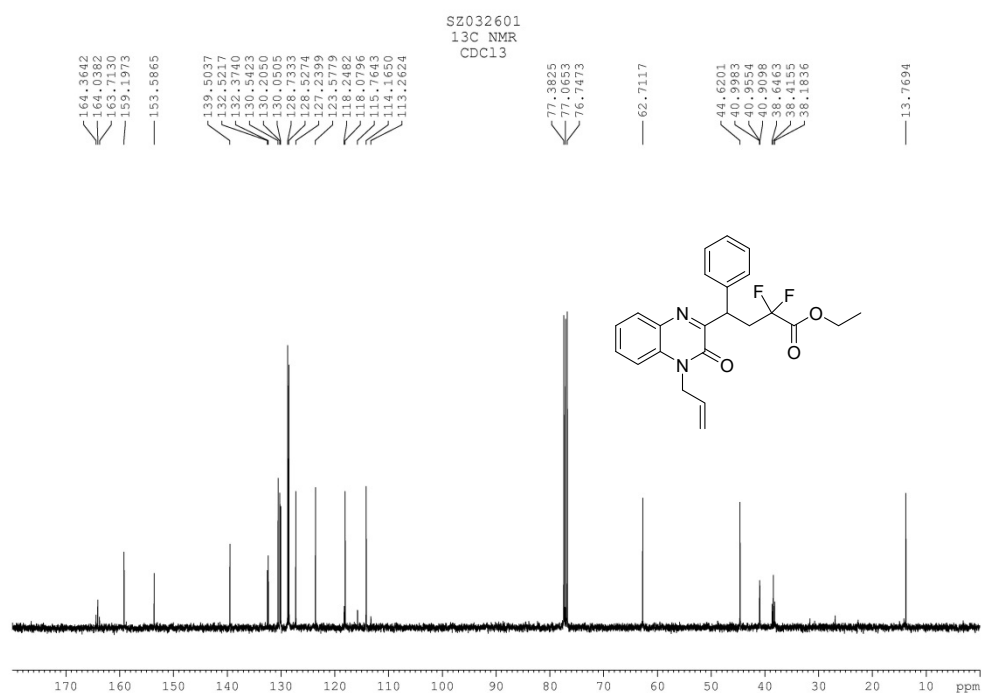


Fig. 65 ¹³C NMR spectrum of compound 4w

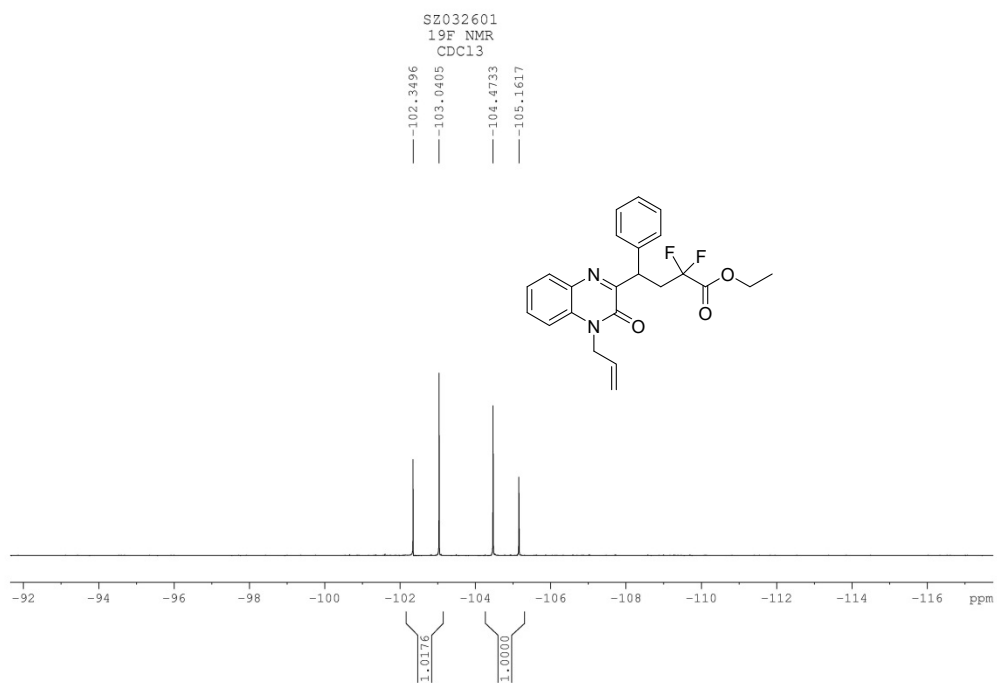
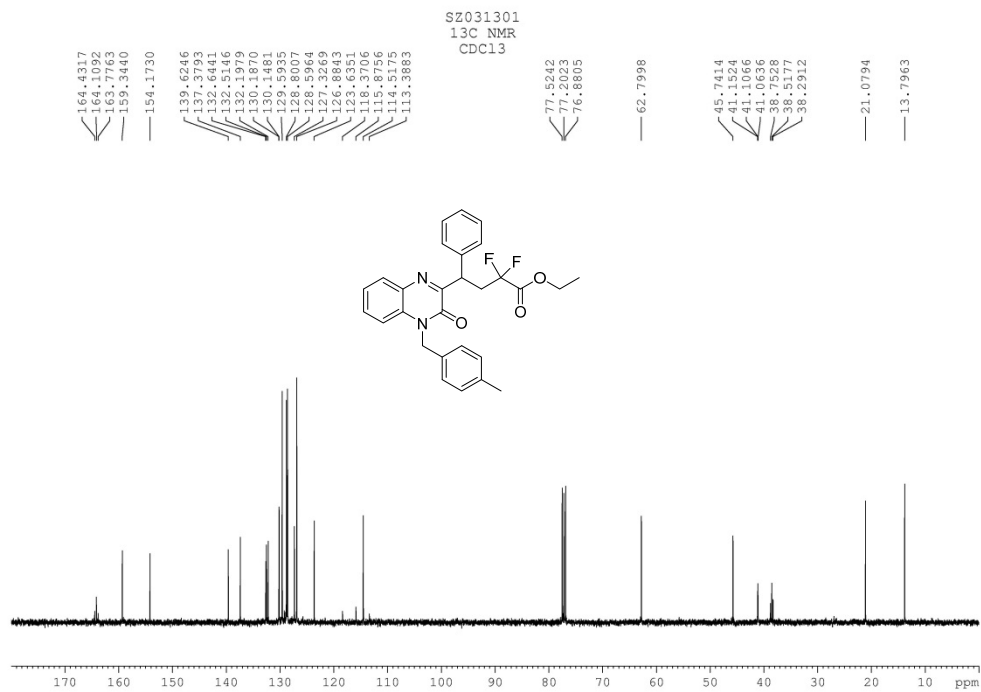
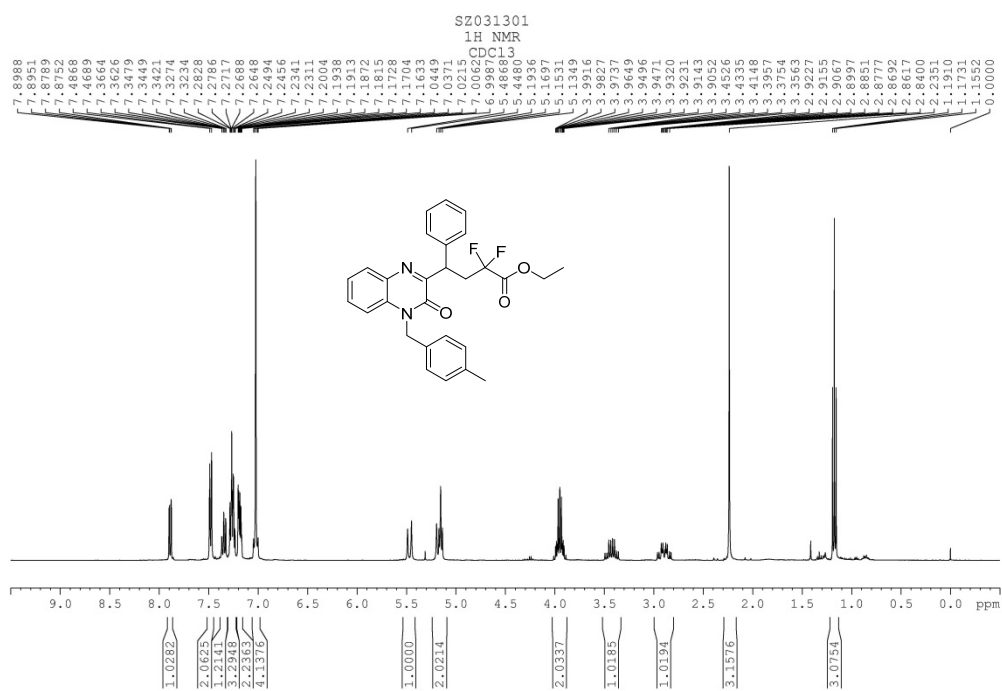


Fig. 66 ¹⁹F NMR spectrum of compound 4w



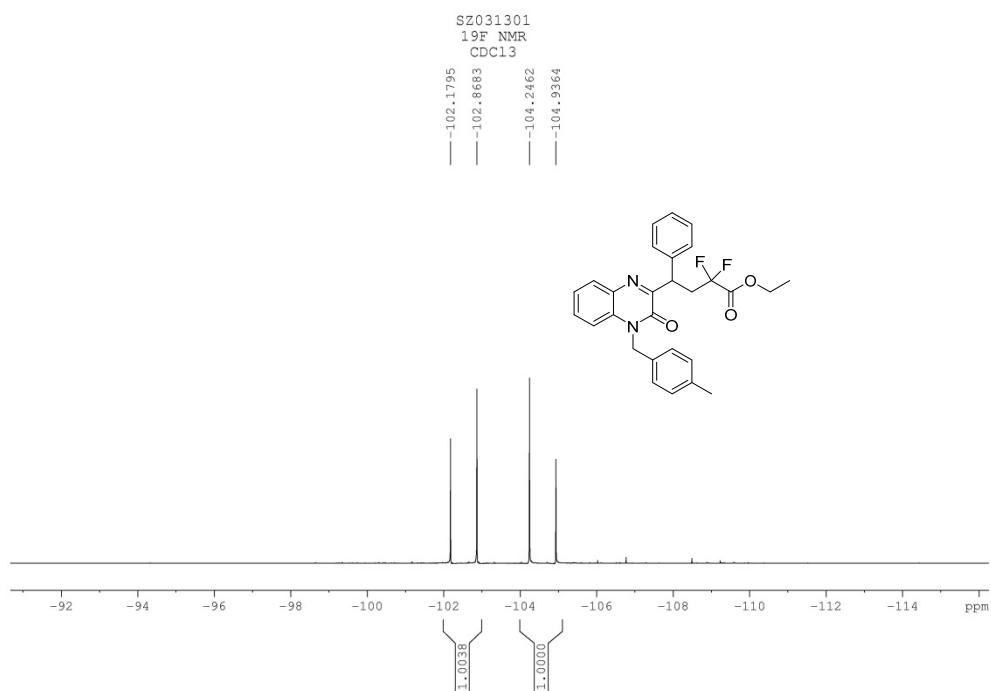


Fig. 69 ^{19}F NMR spectrum of compound 4x

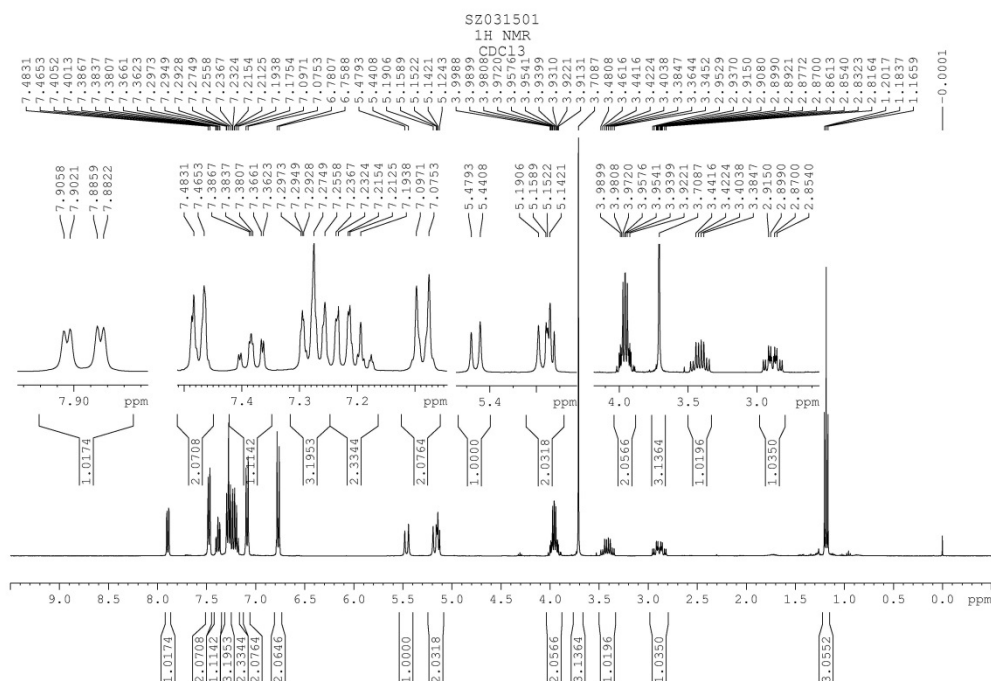


Fig. 70 ^1H NMR spectrum of compound 4y

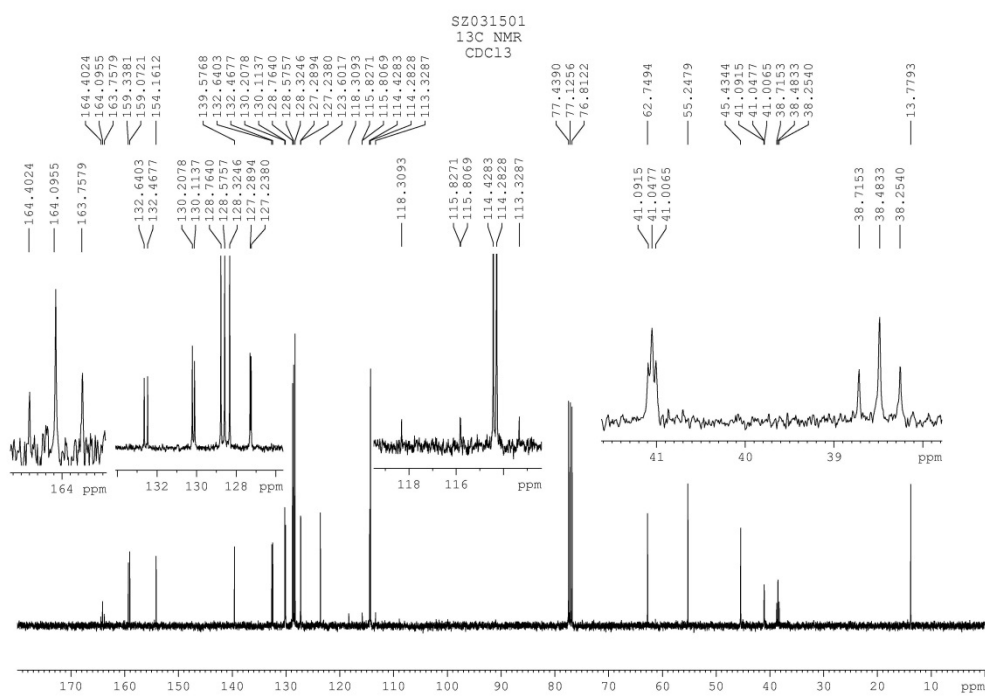


Fig. 71 ^{13}C NMR spectrum of compound 4y

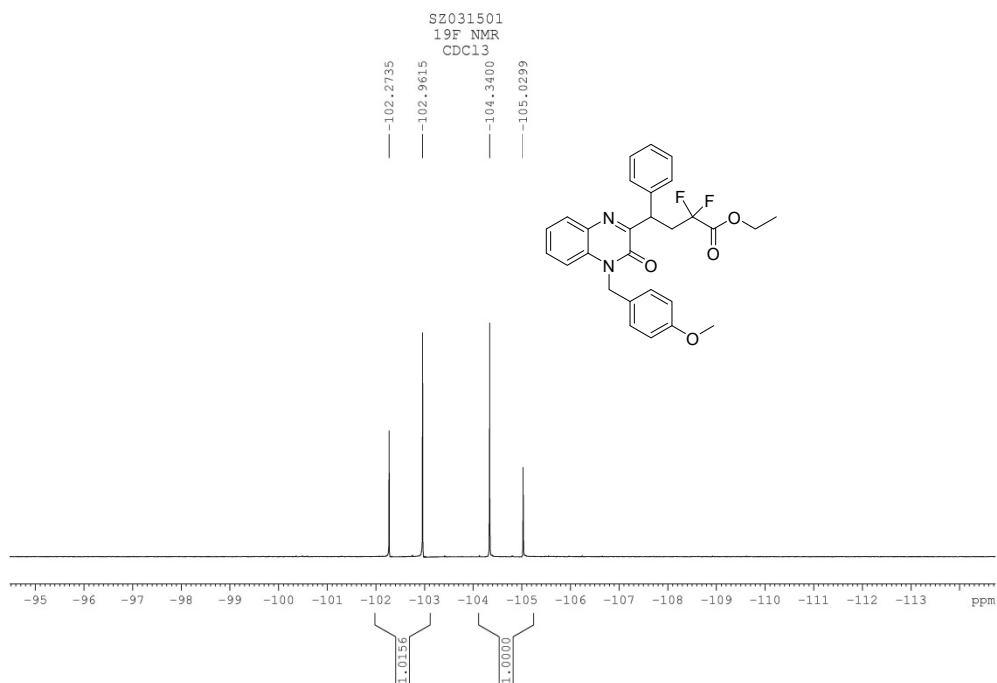


Fig. 72 ^{19}F NMR spectrum of compound 4y

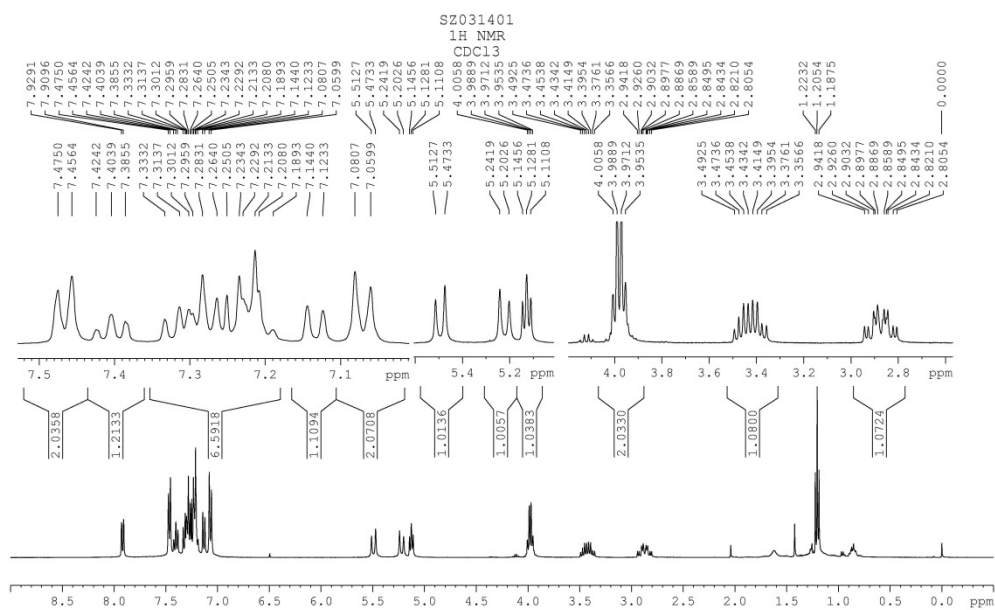


Fig. 73 ¹H NMR spectrum of compound 4z

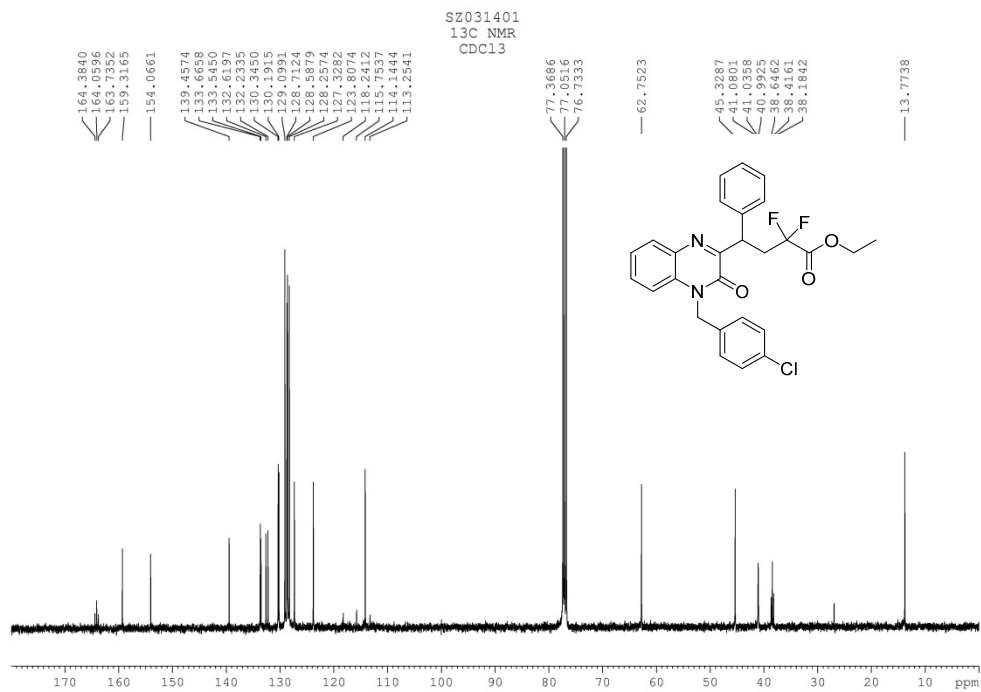


Fig. 74 ¹³C NMR spectrum of compound 4z

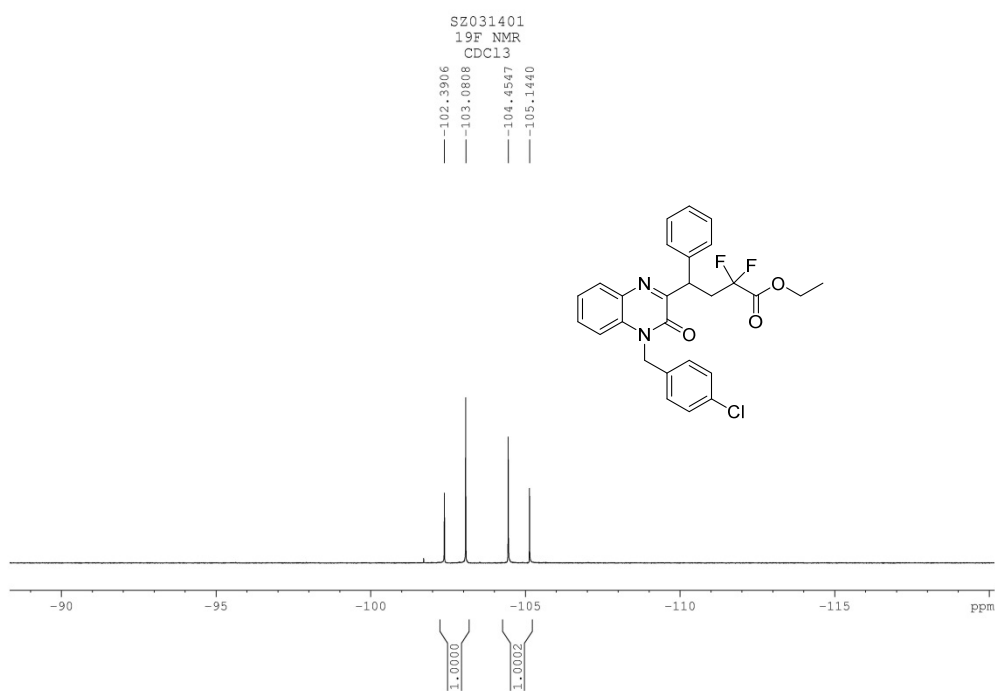


Fig. 75 ^{19}F NMR spectrum of compound **4z**

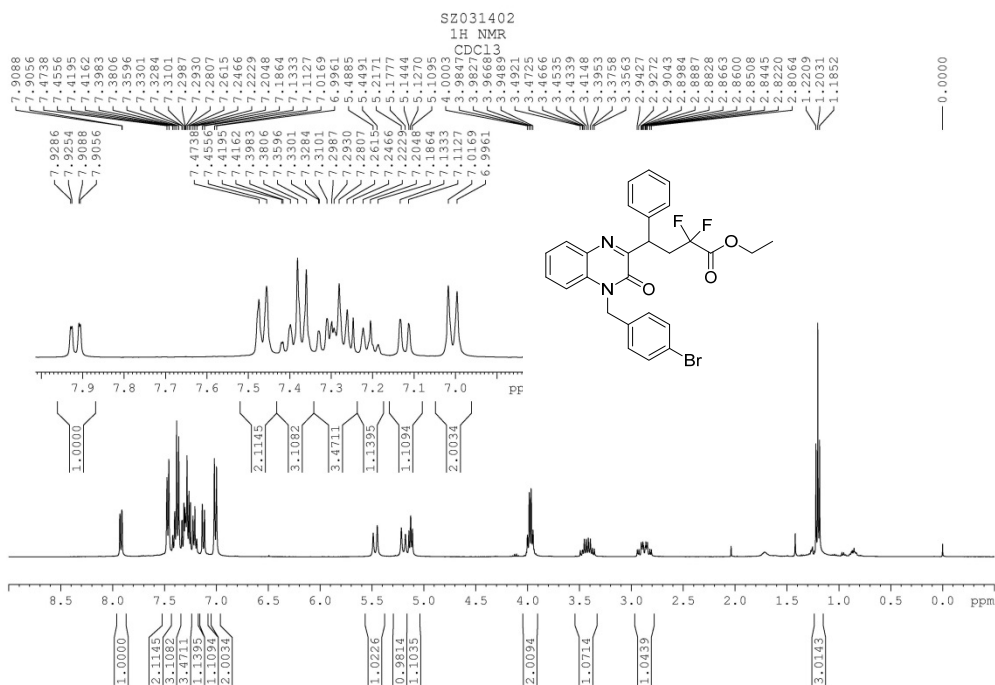


Fig. 76 ^1H NMR spectrum of compound **4aa**

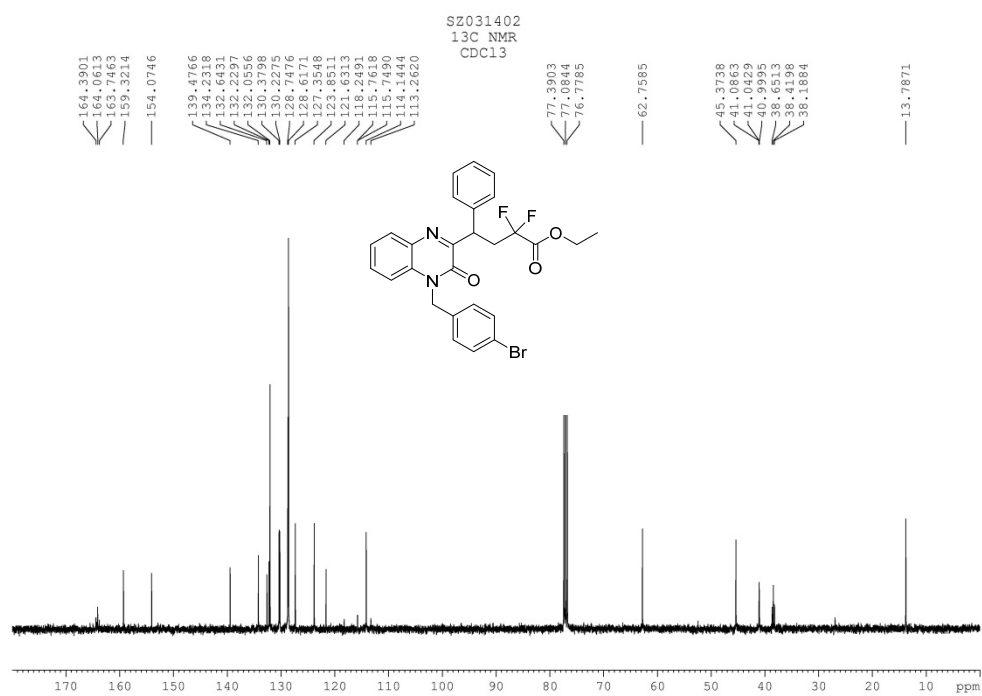


Fig. 77 ^{13}C NMR spectrum of compound 4aa

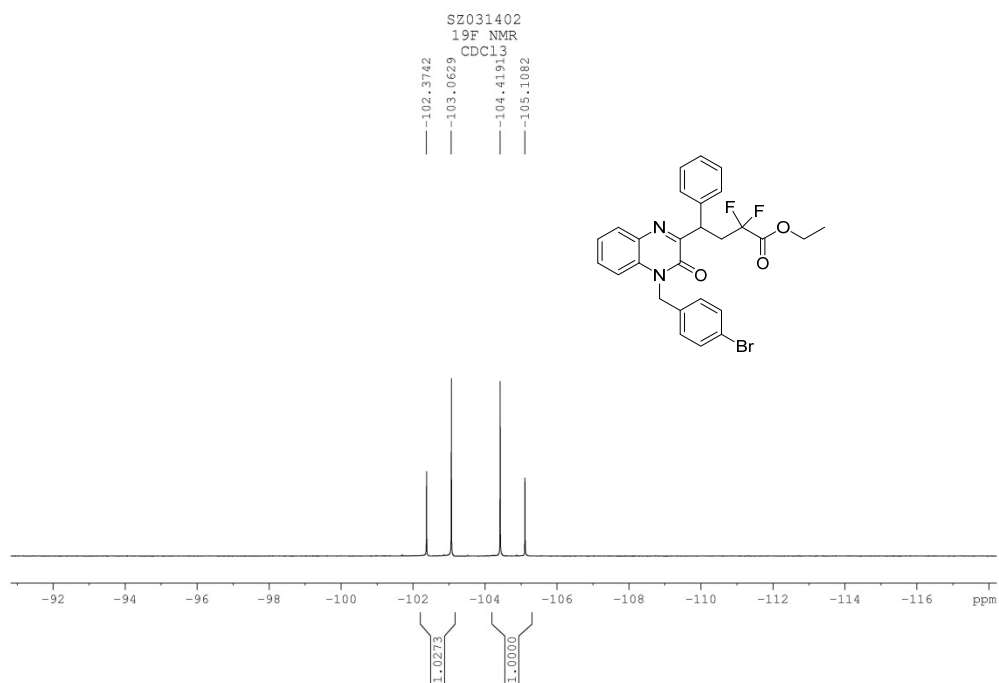


Fig. 78 ^{19}F NMR spectrum of compound 4aa

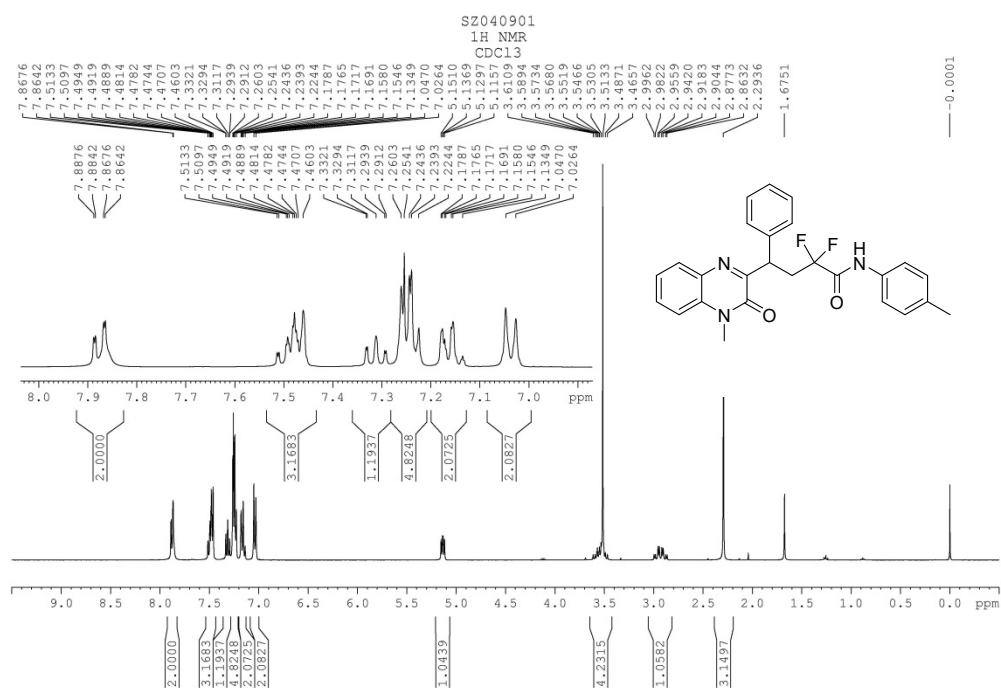


Fig. 79 ^1H NMR spectrum of compound 4ab

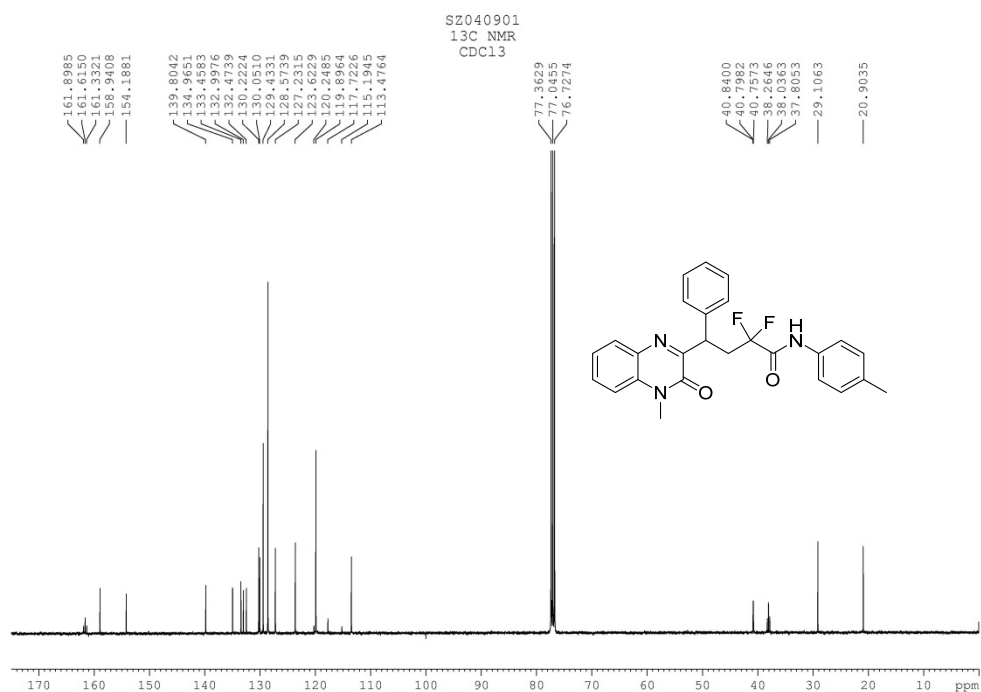


Fig. 80 ^{13}C NMR spectrum of compound 4ab

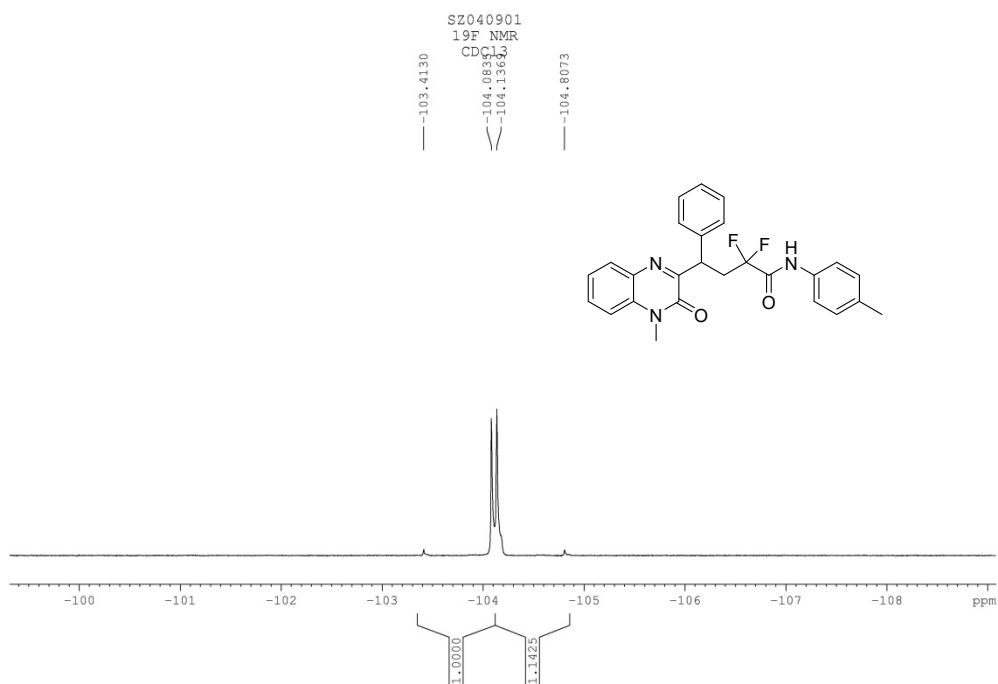


Fig. 81 ¹⁹F NMR spectrum of compound 4ab

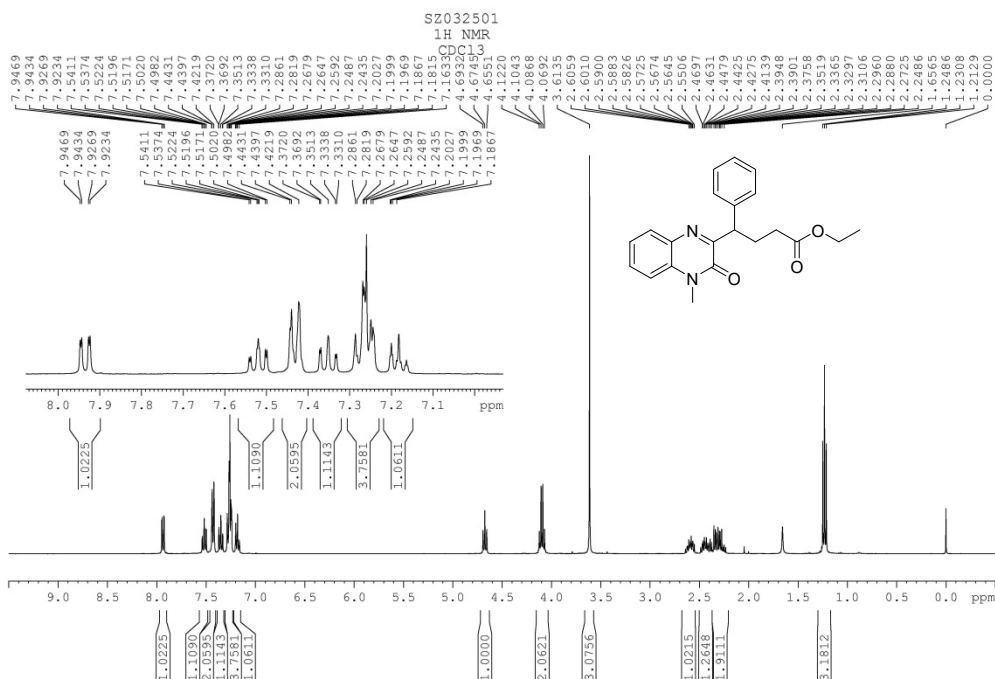


Fig. 82 ¹H NMR spectrum of compound 4ad

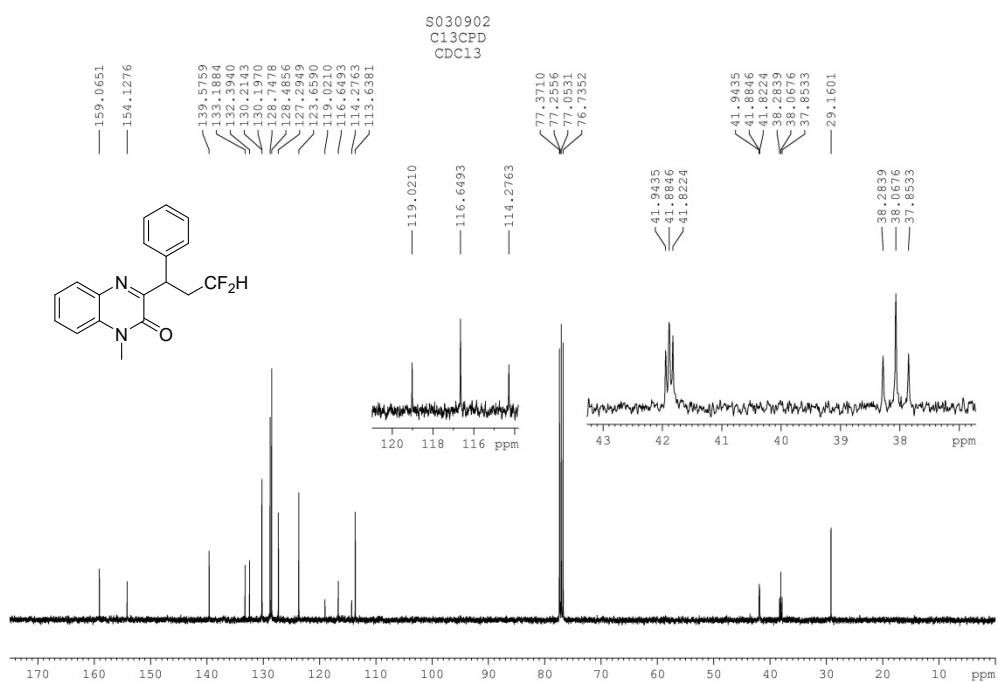


Fig. 85 ^{13}C NMR spectrum of compound **6a**

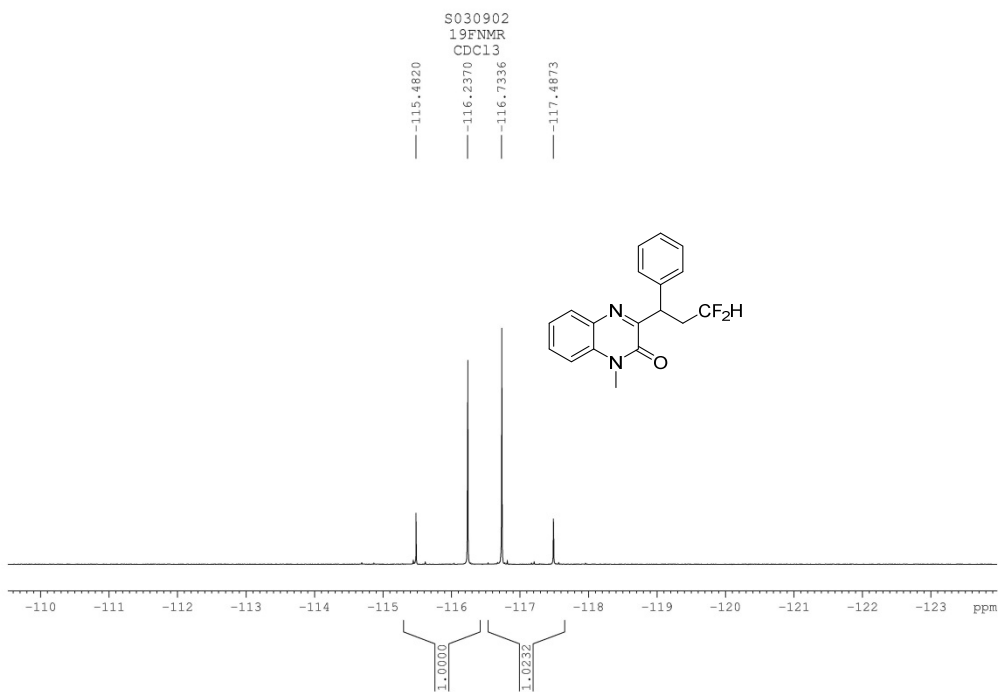


Fig. 86 ^{19}F NMR spectrum of compound **6a**

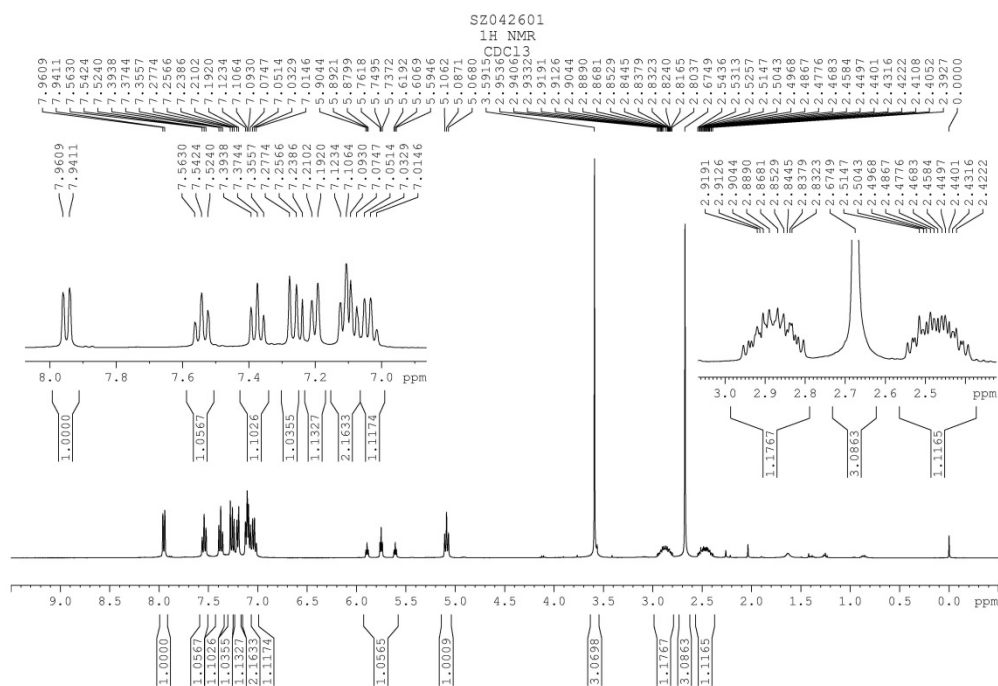


Fig. 87 ^1H NMR spectrum of compound 6b

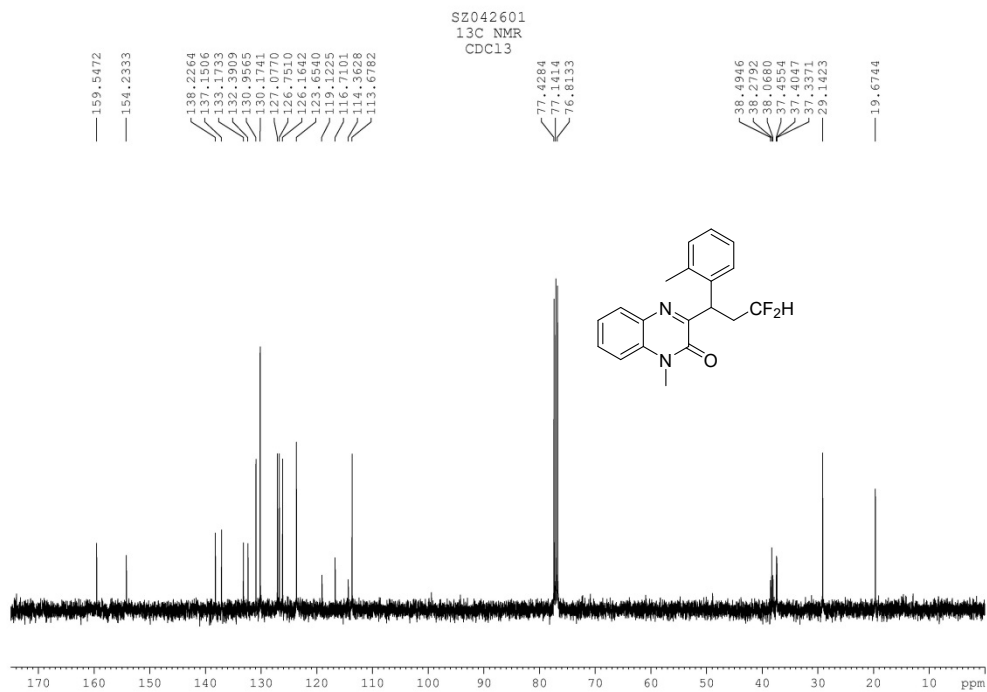


Fig. 88 ^{13}C NMR spectrum of compound 6b

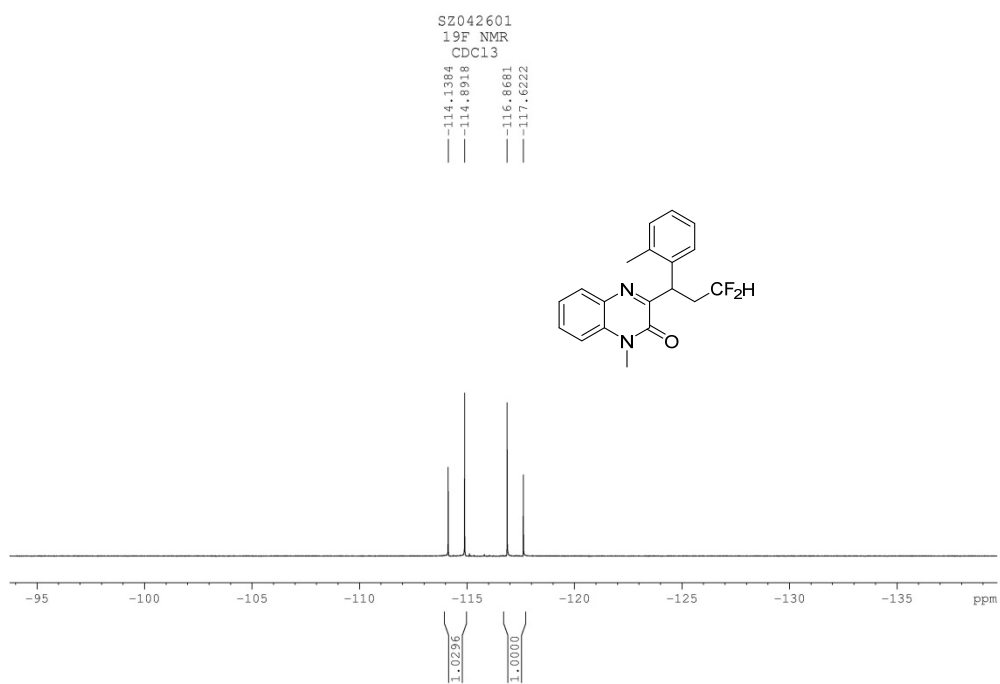


Fig. 89 ^{19}F NMR spectrum of compound 6b

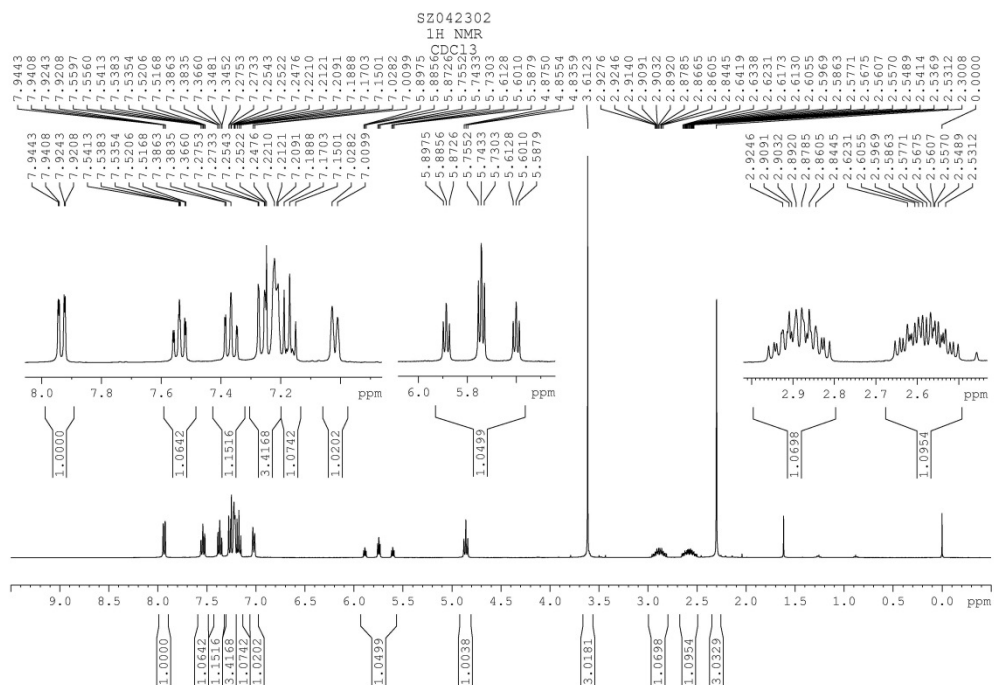


Fig. 90 ^1H NMR spectrum of compound 6c

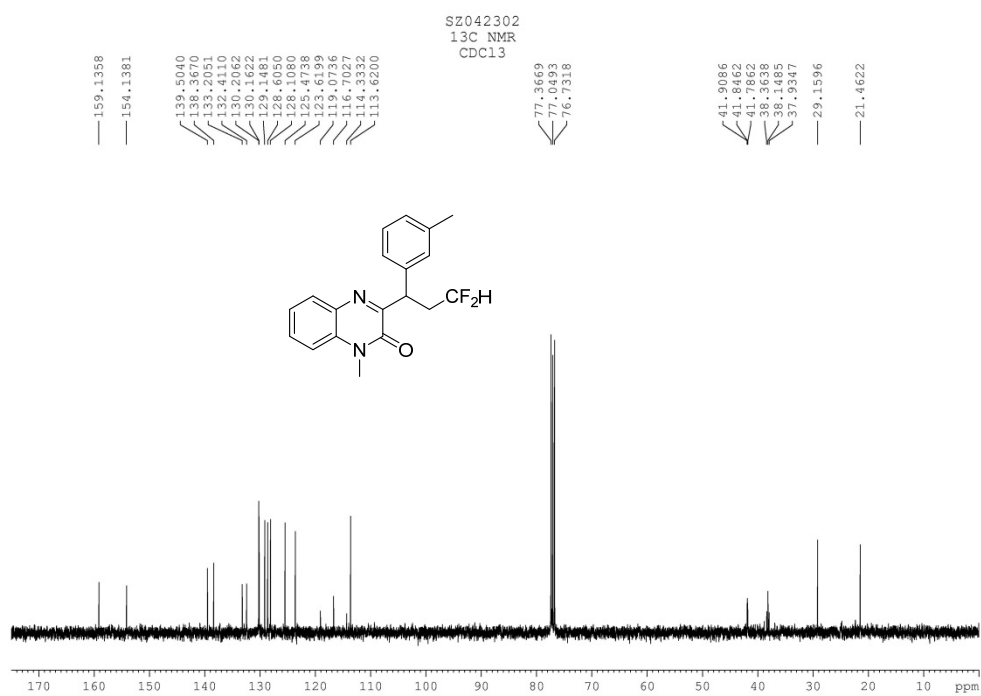


Fig. 91 ¹³C NMR spectrum of compound 6c

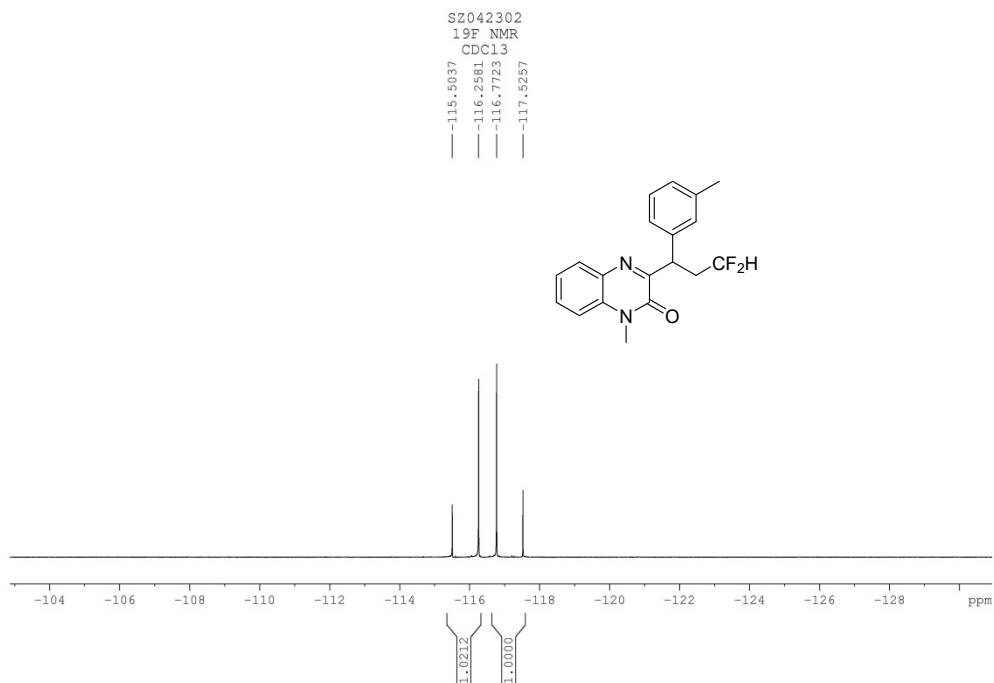


Fig. 92 ¹⁹F NMR spectrum of compound 6c

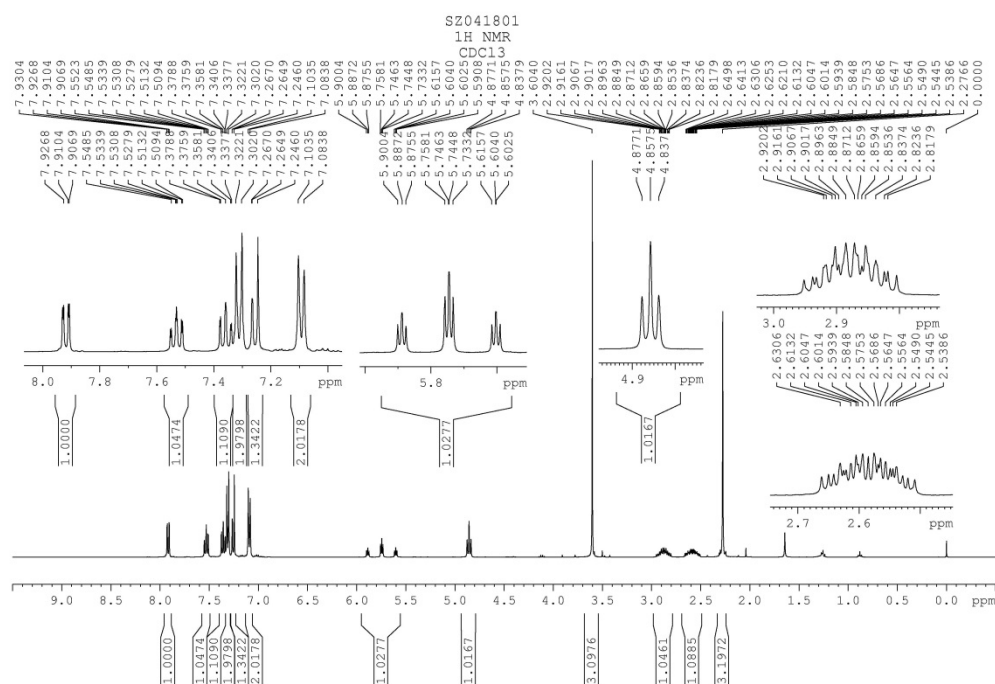


Fig. 93 ¹H NMR spectrum of compound 6d

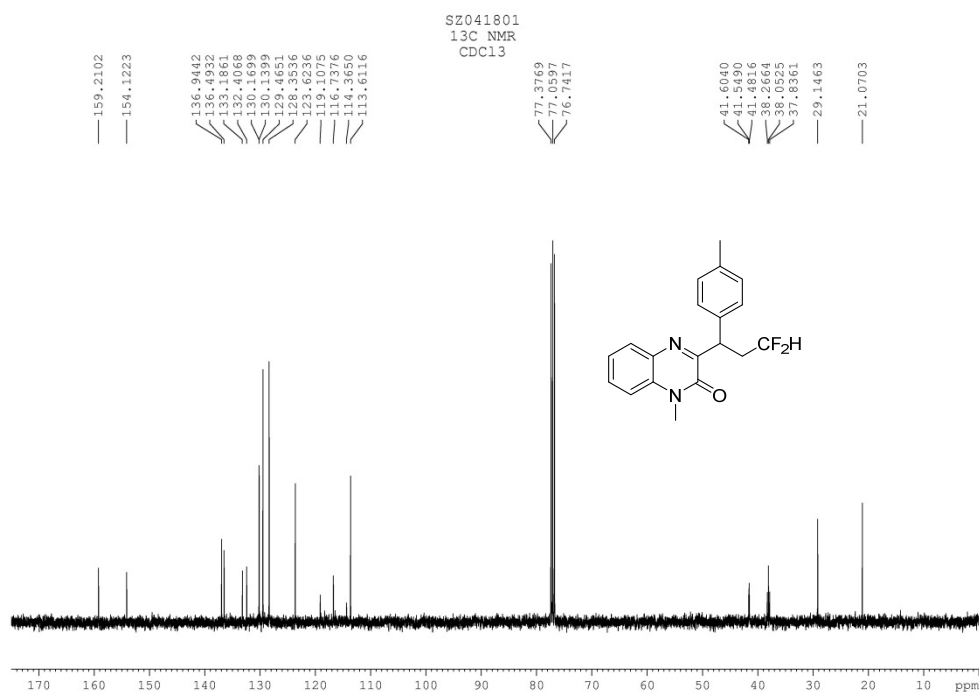


Fig. 94 ¹³C NMR spectrum of compound 6d

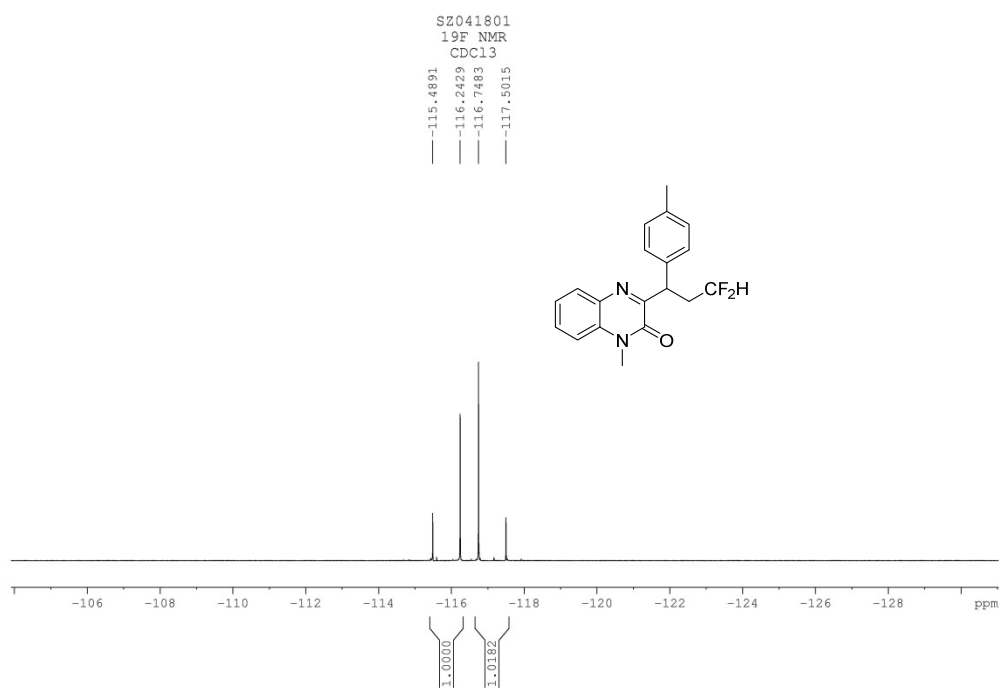


Fig. 95 ¹⁹F NMR spectrum of compound 6d

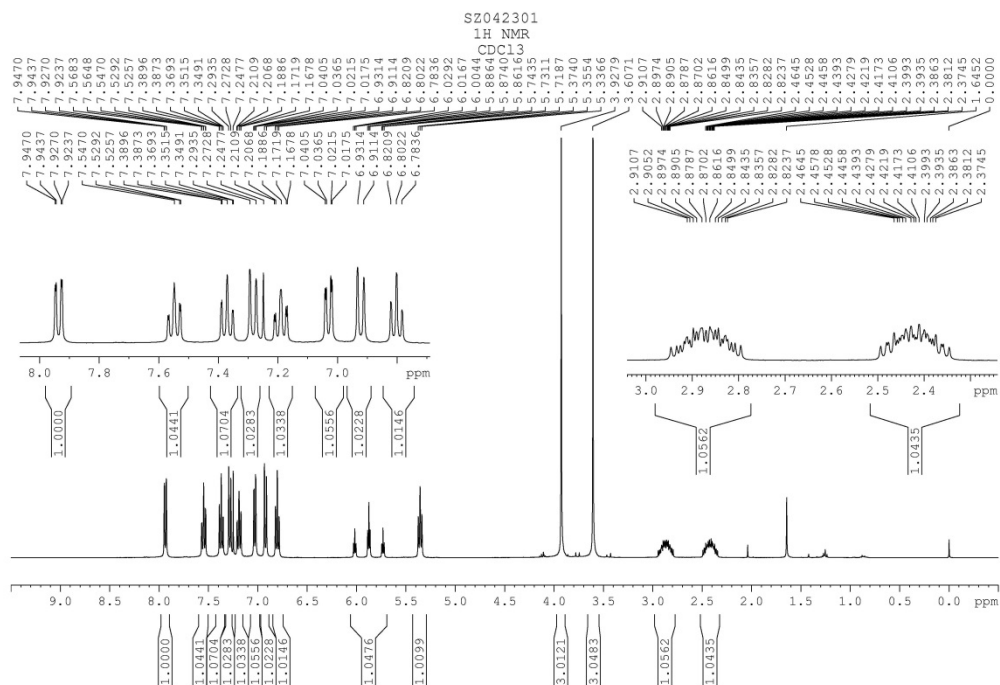


Fig. 96 ¹H NMR spectrum of compound 6e

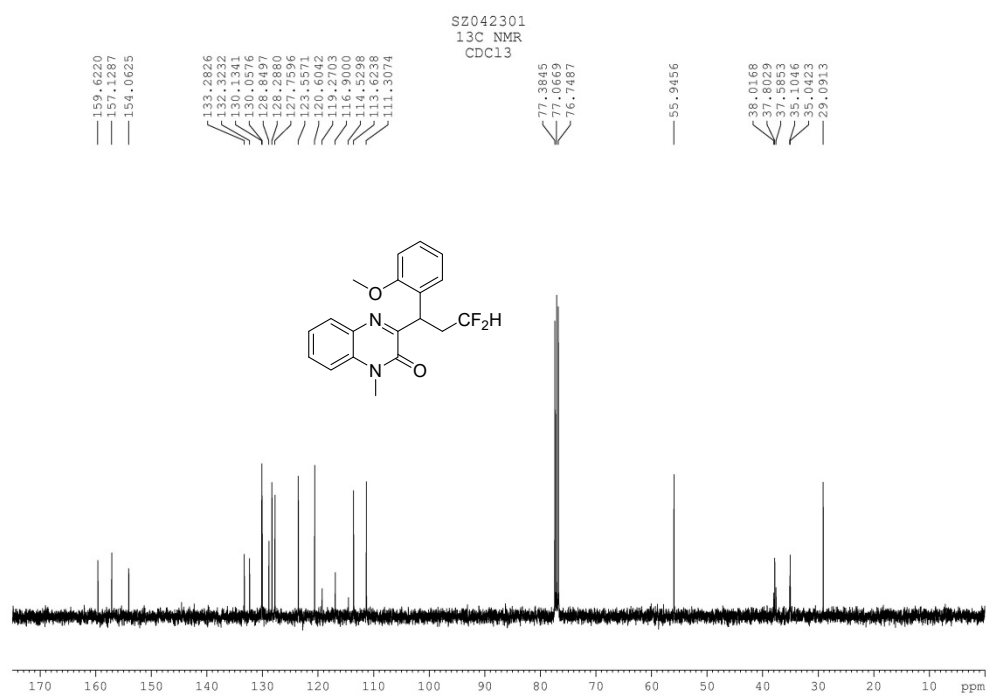


Fig. 96 ^{13}C NMR spectrum of compound 6e

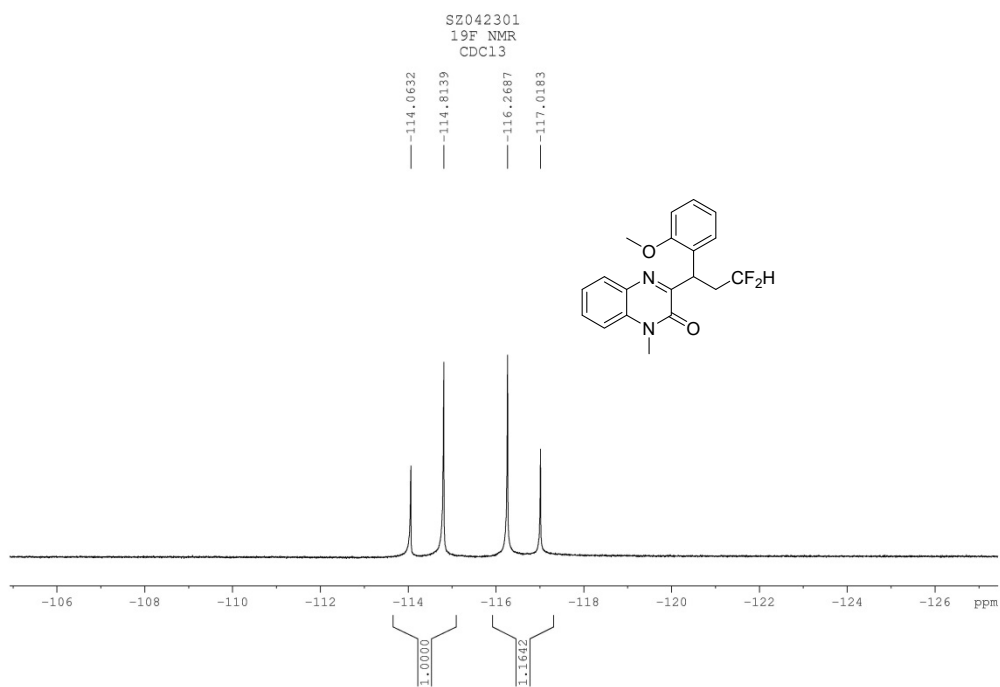


Fig. 98 ^{19}F NMR spectrum of compound 6e

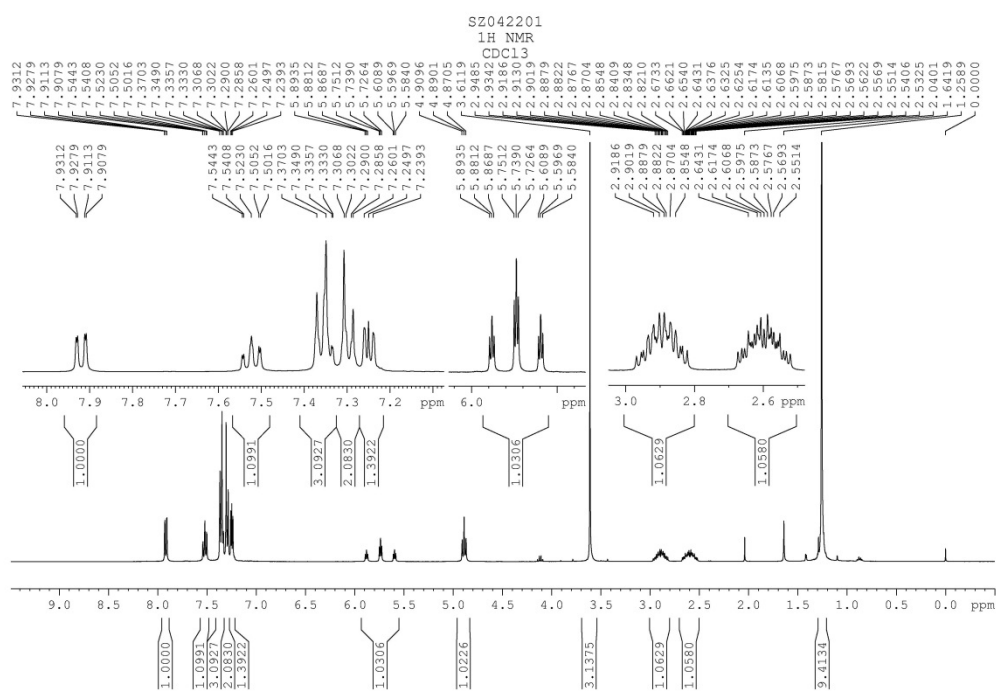


Fig. 99 ^1H NMR spectrum of compound 6f

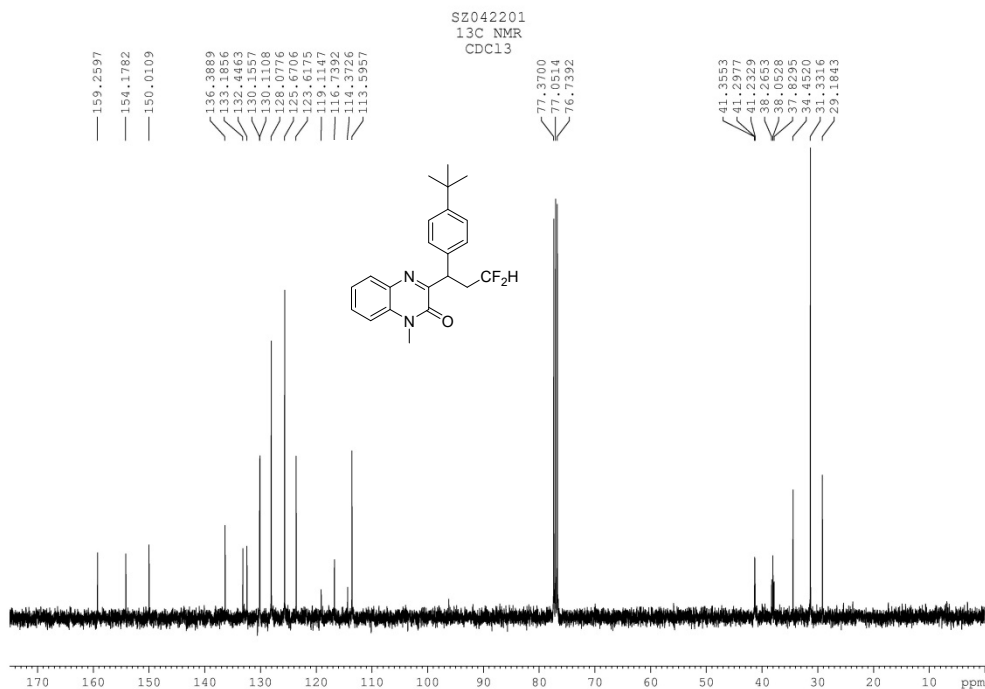


Fig. 100 ^{13}C NMR spectrum of compound 6f

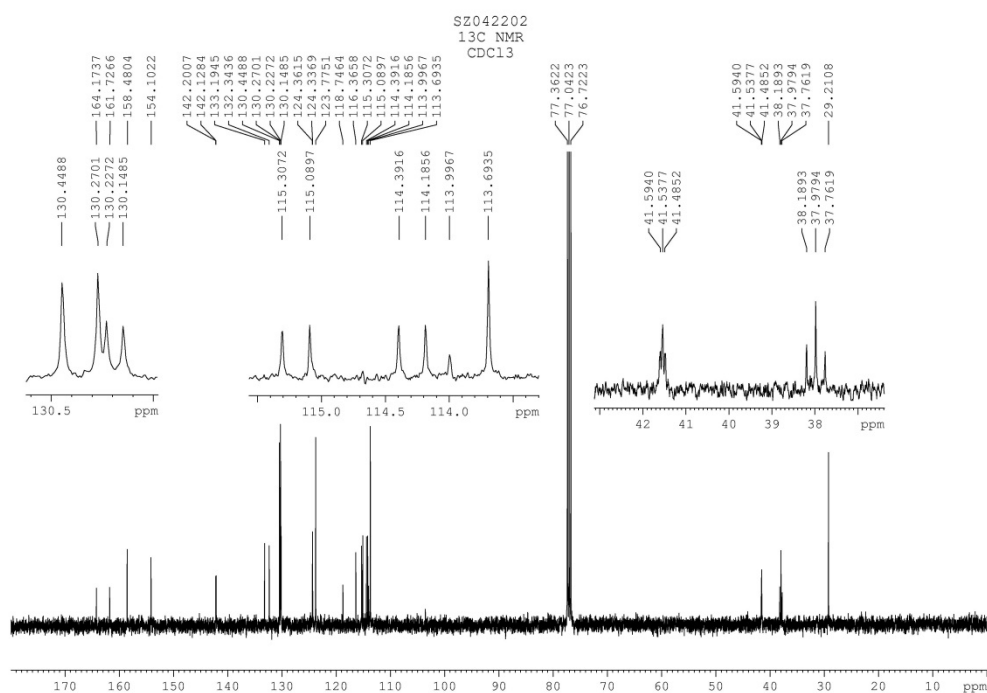


Fig. 103 ^{13}C NMR spectrum of compound 6g

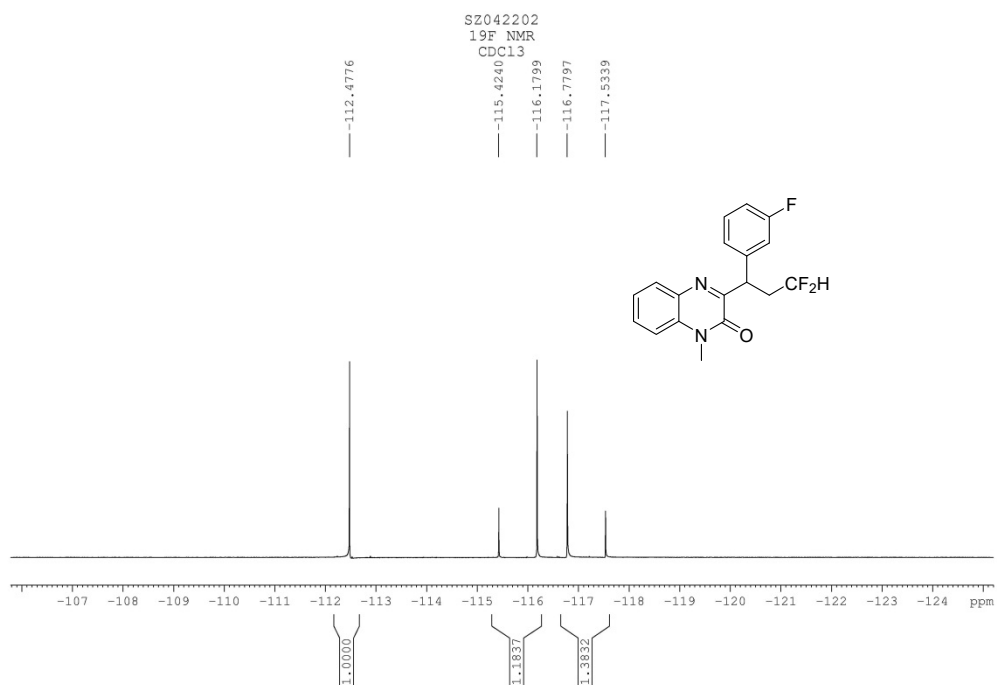


Fig. 104 ^{19}F NMR spectrum of compound 6g

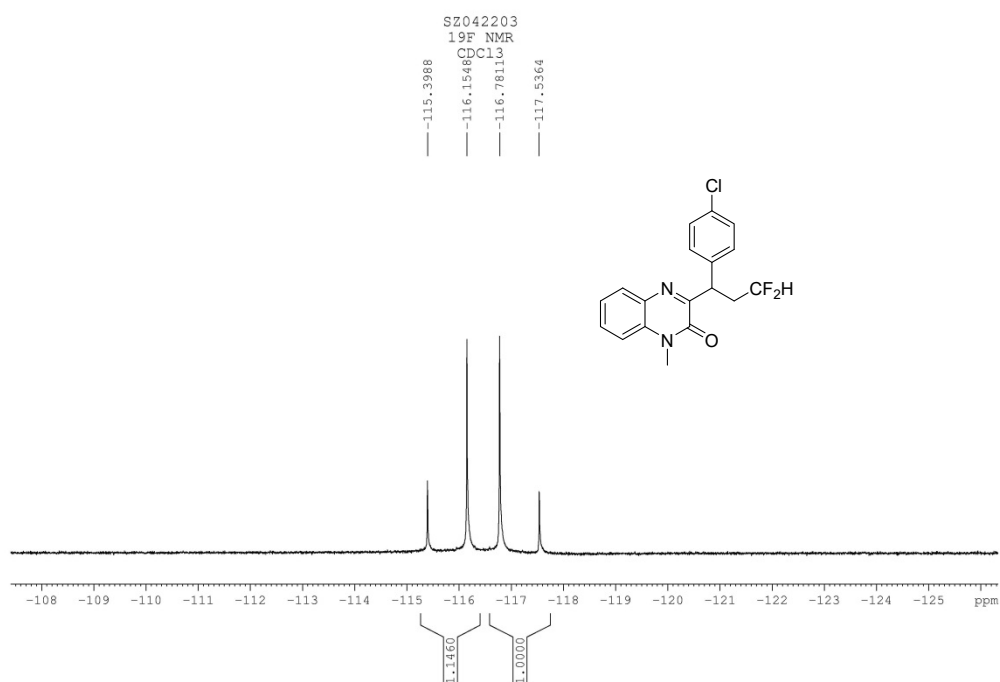


Fig. 107 ¹⁹F NMR spectrum of compound 6h

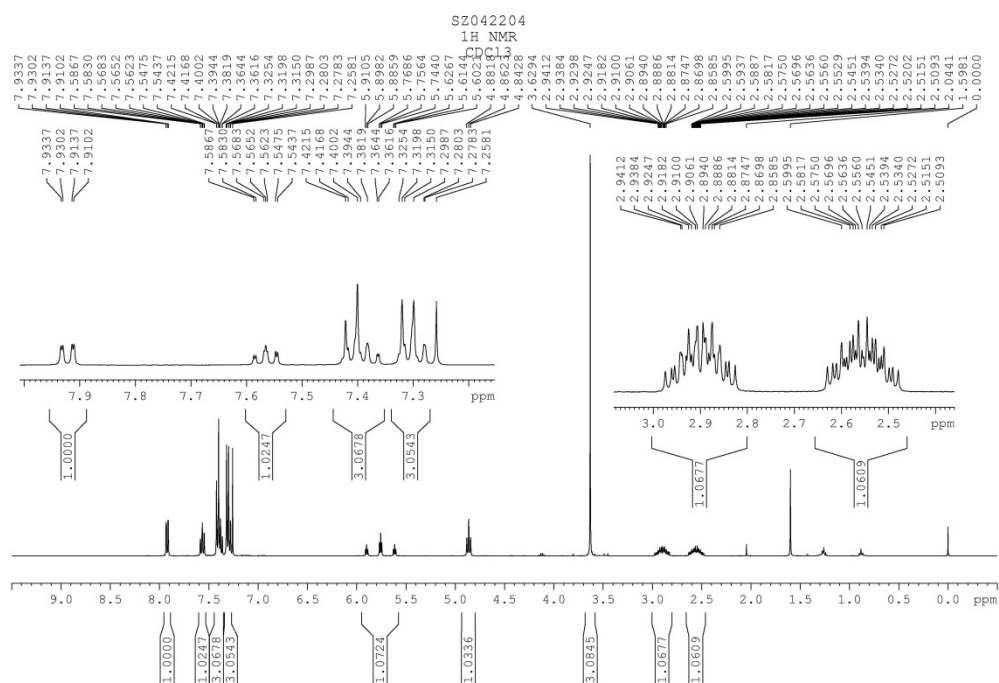


Fig. 108 ¹H NMR spectrum of compound 6i

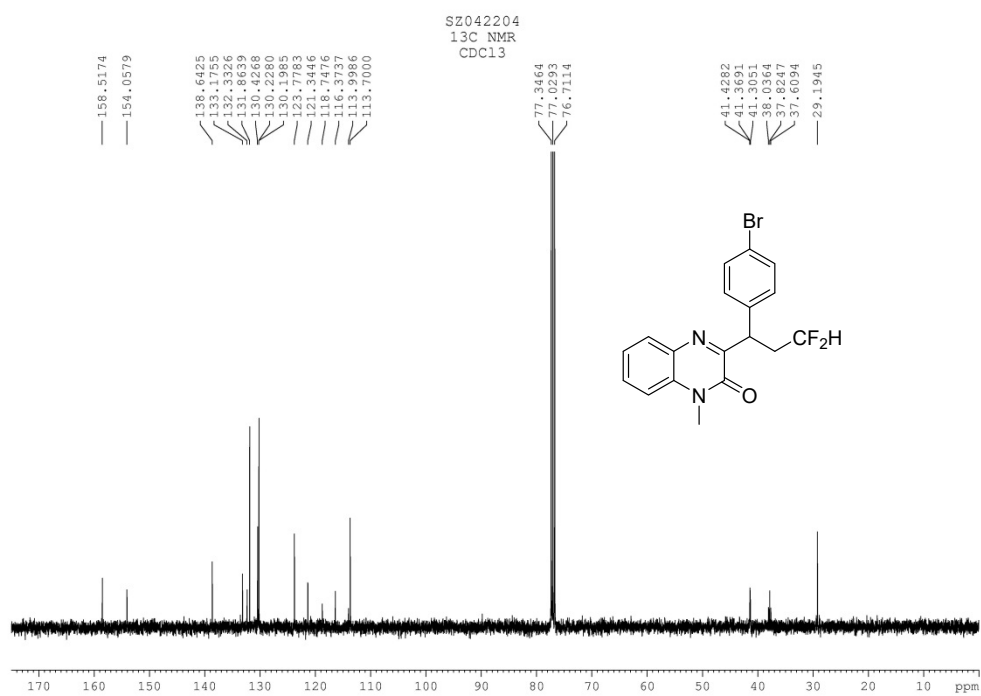


Fig. 109 ^{13}C NMR spectrum of compound 6i



Fig. 110 ^{19}F NMR spectrum of compound 6i

4 Copies of HRMS and ^{19}F NMR spectra of compounds 7 and 8

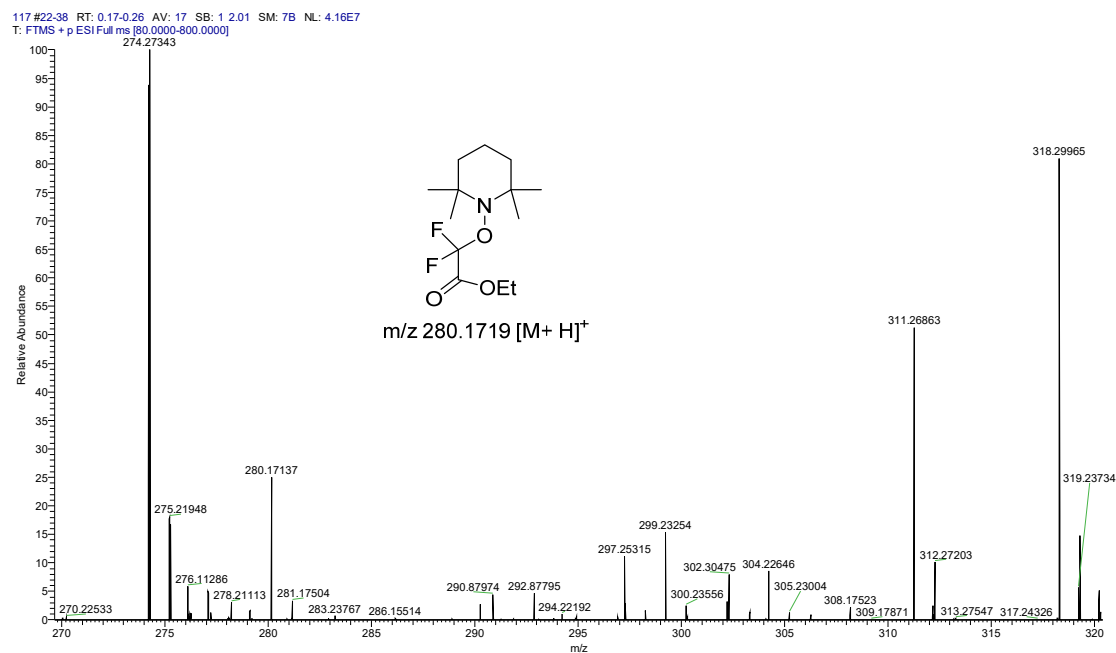


Fig. 111 HRMS spectrum of compound 7

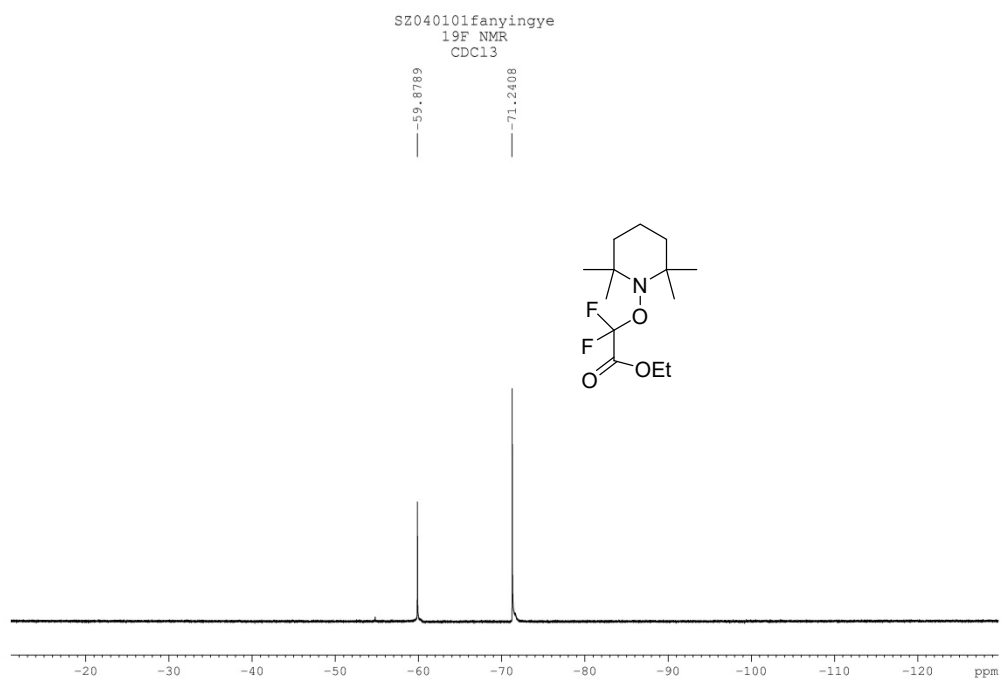


Fig. 112 ^{19}F NMR spectrum of compound 7

118 #30-42 RT: 0.17-0.23 AV: 13 SB: 1.2.01 SM: 7B NL: 1.24E6
T: FTMS +p ESI Full ms [80.0000-800.0000]

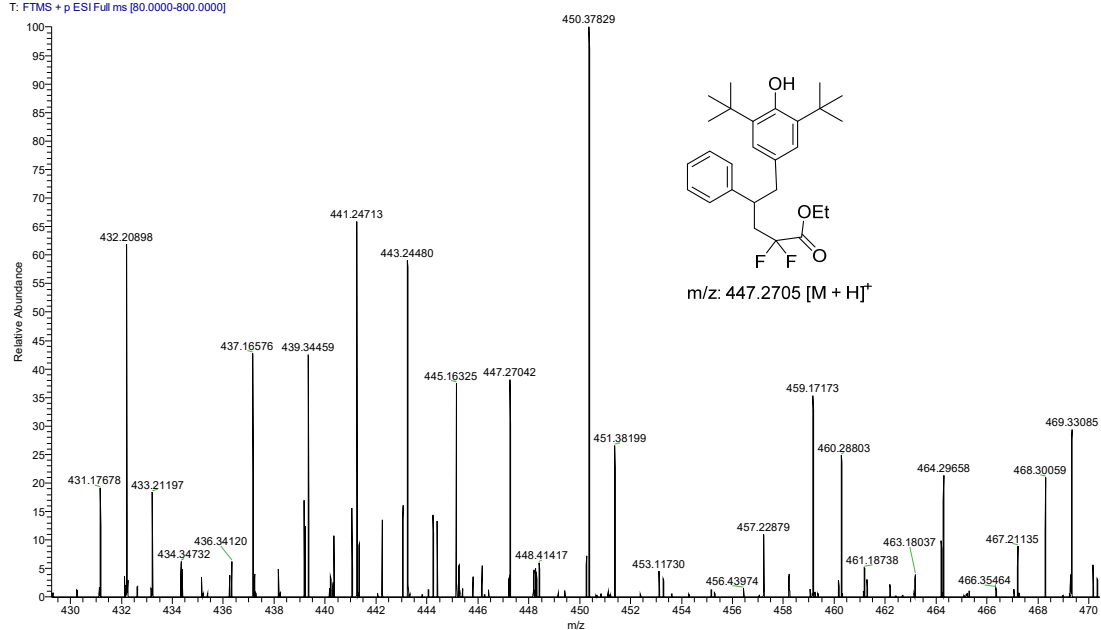


Fig. 113 HRMS spectrum of compound **8**