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

Supporting Information

Ag-catalyzed Minisci C-H difluoromethylarylation of N-heteroarenes

Contents

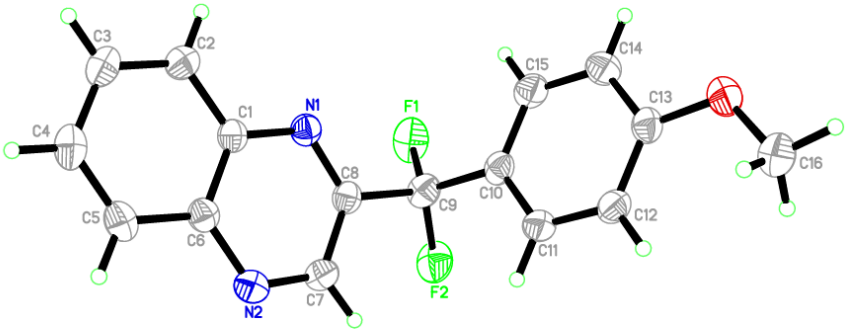
1. General information

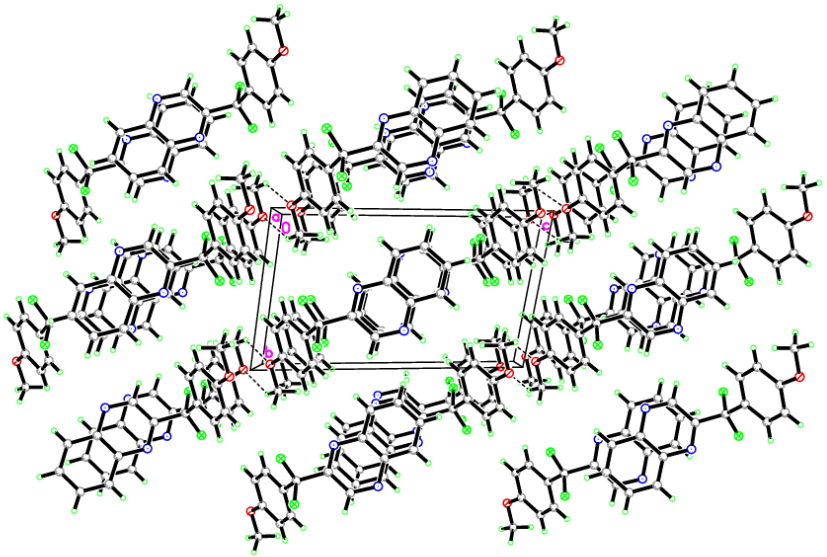
^{1}H-, ^{13}C- and ^{19}F- NMR spectra were recorded in $CDCl_3$ on a Bruker AV-500 and AV-600 spectrometer. Chemical shifts for ^{l}H NMR spectra are reported in ppm relative to residual $CHCl_3$ as internal reference (δ 7.26 ppm for ^{1}H) downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal $CDCl_3$ (δ77.16 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane ($CFCl_3$). Chemical shifts for ^{l}H NMR spectra are reported in ppm relative to residual DMSO as internal reference (δ 2.50 ppm for ^{1}H) downfield from TMS, chemical shifts for ^{13}C NMR spectra are reported in ppm relative to internal DMSO-d_6 (δ 39.52 ppm for ^{13}C), and chemical shifts for ^{19}F NMR spectra are reported in ppm downfield from internal fluorotrichloromethane ($CFCl_3$). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t, q refer to multiplet, singlet, doublet, triplet, quartlet, respectively; br refers to a broad signal. The structures were solved by direct method with SHELXS-97 program and refined by full matrix least-squares on F2 with SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated position. Infrared spectra (IR) were recorded on AVATAR 370 FT-IR spectrometer, absorbance frequencies are given at maximum of intensity in cm^{-1}. High resolution mass spectra (HRMS) and Mass spectra (MS) were recorded using an Electron impact (EI) or Electrospray ionization (ESI) techniques. High resolution mass spectra (HRMS) was recorded on Thermo Fisher Scientific LTQ FT Ultra.

2. General synthetic procedure for the synthesis of difluoromethylated derivatives

A mixture of Aryl difluoroacetic acid (0.40 mmol), N-hereroarene(0.02 mmol), $AgNO_3$ (0.02 mmol), and $(NH_4)S_2O_8$ (0.40 mmol) in 5 mL of DCM and H_2O (v:v, 1.5:1.0) under N_2 atmosphere in pressure flask was stirred at 50^oC for 24 h. Then the reaction mixture was extracted with ethyl acetate and water. The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to give the desired difluoromethylated derivatives. (**3aa-3al & 3ba-3sa**)

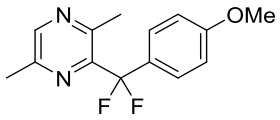
3. Single crystal X-ray analysis of 3ea





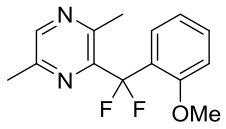
4. Characterization of the products

4.1 3-(difluoro(4-methoxyphenyl)methyl)-2,5-dimethylpyrazine (3aa)



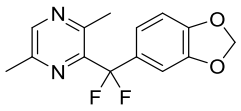
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.38 (s, 1H), 7.42 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H), 2.55 (s, 3H), 2.53 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -90.78 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.0, 149.8, 149.2, 147.6 (t, *J* = 29.7 Hz), 144.3, 128.1 (t, *J* = 27.3 Hz), 127.6 (t, *J* = 5.3 Hz), 119.3 (t, *J* = 241.4 Hz), 113.8, 55.4, 22.0, 21.1; **HRMS (ESI)** calcd. for $C_{14}H_{14}F_2N_2O$ $[M+H]^+$ 265.1147, found 265.1145.

4.2 3-(difluoro(2-methoxyphenyl)methyl)-2,5-dimethylpyrazine (3ab)



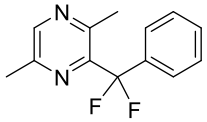
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.32 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 3.53 (s, 3H), 2.61 (s, 3H), 2.42 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.07 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 157.0 (t, *J* = 4.3 Hz), 149.2, 148.8, 147.8 (t, *J* = 29.7 Hz), 143.6, 131.8, 127.0 (t, *J* = 7.5 Hz), 124.6 (t, *J* = 25.4 Hz), 120.3, 119.3 (t, *J* = 241.2 Hz), 111.8, 55.6, 22.0, 20.9; **HRMS (ESI)** calcd. for $C_{14}H_{14}F_2N_2O$ $[M+H]^+$ 265.1147, found 265.1145.

4.3 3-(benzo[*d*][1,3]dioxol-5-yldifluoromethyl)-2,5-dimethylpyrazine (3ac)



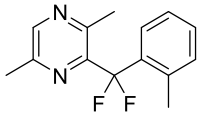
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.39 (s, 1H), 6.98 (s, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 5.99 (s, 2H), 2.55 (s, 3H), 2.54 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -90.55 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.3, 149.2, 147.9, 147.4 (t, *J* = 29.3 Hz), 144.4, 129.8 (t, *J* = 27.3 Hz), 120.3 (t, *J* = 6.3 Hz), 119.1 (t, *J* = 242.1 Hz), 108.1, 106.8 (t, *J* = 5.5 Hz), 101.7, 22.0, 21.1; **HRMS (ESI)** calcd. for $C_{14}H_{12}F_2N_2O_2$ $[M+H]^+$ 279.0940, found 279.0938.

4.4 3-(difluoro(phenyl)methyl)-2,5-dimethylpyrazine (3ad)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.39 (s, 1H), 7.52 (d, *J* = 6.6 Hz, 2H), 7.44 – 7.40 (m, 3H), 2.56 (s, 3H), 2.55 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -92.44 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.3, 147.4 (t, *J* = 29.4 Hz), 144.4, 135.9 (t, *J* = 26.6 Hz), 130.3, 128.5, 126.0 (t, *J* = 5.6 Hz), 119.3 (t, *J* = 241.9 Hz), 22.0, 21.1; **HRMS (ESI)** calcd. for $C_{13}H_{12}F_2N_2$ $[M+H]^+$ 235.1041, found 235.1039.

4.5 3-(difluoro(o-tolyl)methyl)-2,5-dimethylpyrazine (3ae)

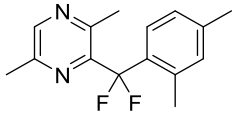


^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.22 (m, 2H), 2.62 (s, 3H), 2.48 (s, 3H), 2.22 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -90.79 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.9, 149.6, 144.3, 137.2, 134.1 (t, *J* = 24.3 Hz), 131.9, 130.3, 126.6 (t, *J* = 8.3 Hz), 125.7, 125.5, 121.0 (t, *J* = 240.8 Hz), 22.1, 21.1, 20.5; **HRMS (ESI)** calcd. for $C_{14}H_{14}F_2N_2$ $[M+H]^+$ 249.1198, found 249.1196.

4.6 3-((3,4-dimethylphenyl)difluoromethyl)-2,5-dimethylpyrazine (3af)

^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 7.27 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 2.58 (s, 3H), 2.53 (s, 3H), 2.27 (s, 3H), 2.26 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -91.90 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.2, 147.7 (t, *J* = 29.2 Hz), 144.3, 139.2, 137.0, 133.4 (t, *J* = 26.7 Hz), 129.7, 127.0 (t, *J* = 5.4 Hz), 123.4 (t, *J* = 5.8 Hz), 119.2 (t, *J* = 242.1 Hz), 22.1, 21.2, 20.0, 19.8; **HRMS (ESI)** calcd. for $C_{15}H_{16}F_2N_2$ $[M+H]^+$ 263.1354, found 263.1353.

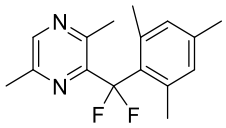
4.7 3-((2,4-dimethylphenyl)difluoromethyl)-2,5-dimethylpyrazine (3ag)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.04 – 7.02 (m, 2H), 2.59 (s, 3H), 2.50 (s, 3H), 2.35 (s, 3H), 2.20 (s, 3H); **^{19}F NMR** (471 MHz,

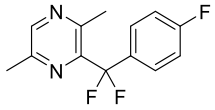
$CDCl_3$) δ ppm -90.32 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.6, 147.5 (t, *J* = 30.6 Hz), 144.2, 140.3, 137.0, 132.8, 131.2 (t, *J* = 24.5 Hz), 126.7 (t, *J* = 7.9 Hz), 126.1, 121.0 (t, *J* = 241.3 Hz), 22.2, 21.2, 21.1, 20.4; **HRMS (ESI)** calcd. for $C_{15}H_{16}F_2N_2$ $[M+H]^+$ 263.1354, found 263.1353.

4.8 3-(difluoro(mesityl)methyl)-2,5-dimethylpyrazine (3ah)



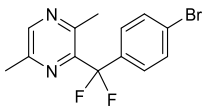
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.36 (s, 1H), 6.87 (s, 2H), 2.71 (s, 3H), 2.40 (s, 3H), 2.30 (s, 3H), 2.20 (s, 6H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -83.31 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.5, 147.9 (t, *J* = 32.3 Hz), 144.1, 139.0, 137.4 (t, *J* = 3.3 Hz), 130.7, 130.5, 124.0 (t, *J* = 241.7 Hz), 22.5, 22.0, 21.1, 21.0; **HRMS (ESI)** calcd. for $C_{16}H_{18}F_2N_2$ $[M+H]^+$ 277.1511, found 277.1514.

4.9 3-(difluoro(4-fluorophenyl)methyl)-2,5-dimethylpyrazine (3ai)



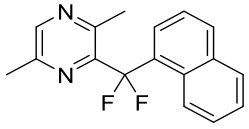
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.39 (s, 1H), 7.50 (t, *J* = 5.1 Hz, 2H), 7.10 (t, *J* = 8.9 Hz, 2H), 2.58 (s, 3H), 2.52 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -91.21 (s, CF_2), -110.37 - -110.44 (m, F); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 163.8(d, *J* = 248.7 Hz), 149.5 (d, *J* = 62.3Hz), 147.2 (t, *J* = 30.0 Hz), 144.5, 132.0 (td, *J* = 27.3, 3.2 Hz), 128.4, 119.3 (t, *J* = 242.1 Hz), 115.6, 115.5, 22.0, 21.1; **HRMS (ESI)** calcd. for $C_{13}H_{11}F_3N_2$ $[M+H]^+$ 253.0947, found 253.0949.

4.10 3-((4-bromophenyl)difluoromethyl)-2,5-dimethylpyrazine (3aj)



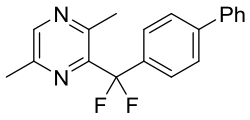
^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 2.60 (s, 3H), 2.52 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -92.28 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.9, 149.3, 147.0 (t, *J* = 29.9 Hz), 144.5, 135.0 (t, *J* = 27.2 Hz), 131.7, 127.9 (t, *J* = 5.8 Hz), 124.8, 119.4 (t, *J* = 242.1 Hz), 22.0, 21.1; **HRMS (ESI)** calcd. for $C_{13}H_{11}BrF_2N_2$ $[M+H]^+$ 313.0146, found 313.0145.

4.11 3-(difluoro(naphthalen-1-yl)methyl)-2,5-dimethylpyrazine (3ak)



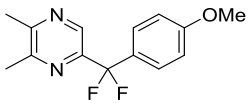
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.40 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.50 (q, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.1 Hz, 1H), 2.64 (s, 3H), 2.47 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -89.15 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.8, 149.7, 147.6 (t, *J* = 29.4 Hz), 144.5, 134.2, 131.6, 131.4, 130.2, 128.8, 126.8, 126.1, 125.8 (t, *J* = 2.7 Hz), 125.4 (t, *J* = 8.5 Hz), 124.3, 121.0 (t, *J* = 242.3 Hz), 22.3, 21.1; **HRMS (ESI)** calcd. for $C_{17}H_{14}F_2N_2$ $[M+H]^+$ 285.1198, found 285.1195.

4.12 3-([1,1'-biphenyl]-4-yldifluoromethyl)-2,5-dimethylpyrazine (3al)



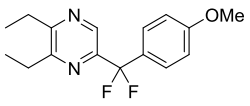
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.42 (s, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 4H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 2.61 (s, 3H), 2.58 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -92.15 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 149.9, 149.3, 147.5 (t, *J* = 29.6 Hz), 144.5, 143.3, 140.2, 134.8 (t, *J* = 26.9 Hz), 129.0, 128.0, 127.4, 127.3, 126.6 (t, *J* = 5.5 Hz), 119.4 (t, *J* = 242.2 Hz), 22.1, 21.2; **HRMS (ESI)** calcd. for $C_{19}H_{16}F_2N_2$ $[M+H]^+$ 311.1354, found 311.1355.

4.13 5-(difluoro(4-methoxyphenyl)methyl)-2,3-dimethylpyrazine (3ba)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.61 (s, 1H), 7.51 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.55 (s, 3H), 2.53 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.79 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.0, 154.0, 152.4, 147.6 (t, *J* = 31.2 Hz), 137.9 (t, *J* = 4.9 Hz), 128.5 (t, *J* = 27.8 Hz), 127.5 (t, *J* = 6.0 Hz), 118.7 (t, *J* = 241.3 Hz), 113.8, 55.4, 22.2, 22.1; **HRMS (ESI)** calcd. for $C_{14}H_{14}F_2N_2O$ $[M+H]^+$ 265.1147, found 265.1145.

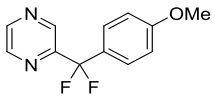
4.14 5-(difluoro(4-methoxyphenyl)methyl)-2,3-diethylpyrazine (3ca)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.66 (s, 1H), 7.56 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.90 – 2.83 (m, 4H), 1.31 (t, *J* = 7.5 Hz, 3H), 1.26 (t, *J* = 7.4 Hz, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -94.06 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.9, 157.6, 156.0, 147.5 (t, *J* = 31.2 Hz), 137.8 (t, *J* = 4.7 Hz), 128.7

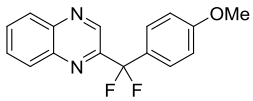
(t, *J* = 27.8 Hz), 127.5 (t, *J* = 5.6 Hz), 118.8 (t, *J* = 241.4 Hz), 113.7, 55.4, 27.5, 27.4, 12.6, 12.4; **HRMS (ESI)** calcd. for $C_{16}H_{18}F_2N_2O$ $[M+H]^+$ 293.1460, found 293.1463.

4.15 2-(difluoro(4-methoxyphenyl)methyl)pyrazine (3da)



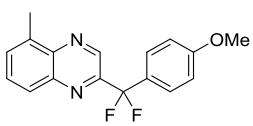
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.01 (s, 1H), 8.65 (s, 1H), 8.62 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -94.31 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.2, 151.5 (t, *J* = 32.0 Hz), 145.8, 144.2, 142.0 (t, *J* = 4.9 Hz), 127.9 (t, *J* = 27.3 Hz), 127.5 (t, *J* = 6.3 Hz), 118.6 (t, *J* = 242.0 Hz), 114.1, 55.5; **HRMS (ESI)** calcd. for $C_{12}H_{10}F_2N_2O$ $[M+H]^+$ 237.0834, found 237.0832.

4.16 2-(difluoro(4-methoxyphenyl)methyl)quinoxaline (3ea)



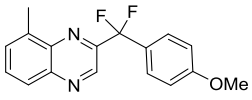
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.19 (s, 1H), 8.15 (d, *J* = 8.5 Hz, 2H), 7.83 - 7.78 (m, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.80 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.43 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.2, 150.4 (t, *J* = 31.8 Hz), 142.8, 142.0 (t, *J* = 3.9 Hz), 141.2, 131.3, 130.9, 130.0, 129.4, 127.9 (t, *J* = 27.3 Hz), 127.6 (t, *J* = 5.6 Hz), 118.8 (t, *J* = 242.9 Hz), 114.0, 55.4; **HRMS (ESI)** calcd. for $C_{16}H_{12}F_2N_2O$ $[M+H]^+$ 287.0990, found 287.0989.

4.17 2-(difluoro(4-methoxyphenyl)methyl)-5-methylquinoxaline (3fa)



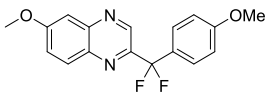
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.18 (s, 1H), 7.99 (d, *J* = 7.7 Hz, 1H), 7.70 -7.64 (m, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 2.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.52 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.2, 149.9 (t, *J* = 31.3 Hz), 142.0, 141.4, 140.8 (t, *J* = 3.9 Hz), 137.8, 131.2, 130.7, 128.1 (t, *J* = 27.4 Hz), 127.9, 127.6 (t, *J* = 5.8 Hz), 118.9 (t, *J* = 242.8 Hz), 114.0, 55.5, 17.4; **HRMS (ESI)** calcd. for $C_{17}H_{14}F_2N_2O$ $[M+H]^+$ 301.1147, found 301.1149.

4.18 2-(difluoro(4-methoxyphenyl)methyl)-8-methylquinoxaline（3f'a）



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.21 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.71 (t, *J* = 8.4 Hz, 1H), 7.64 (s, 1H), 7.63 (d, *J* = 6.7 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 2H), 3.83 (s, 3H), 2.74 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.37 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.1, 149.1 (t, *J* = 32.4 Hz), 142.9, 141.4 (t, *J* = 3.7 Hz), 140.5, 138.6, 131.1, 130.7, 128.3 (t, *J* = 27.3 Hz), 127.7 (t, *J* = 5.7 Hz), 127.1, 119.0 (t, *J* = 242.5 Hz), 113.9, 55.5, 17.0; **HRMS (ESI)** calcd. for $C_{17}H_{14}F_2N_2O$ $[M+H]^+$ 301.1147, found 301.1145.

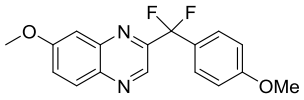
4.19 2-(difluoro(4-methoxyphenyl)methyl)-6-methoxyquinoxaline (3ga)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.02 (s, 1H), 8.01 (d, *J* = 9.2 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.46 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.41 (d, *J* = 2.8 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.95 (s, 3H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -

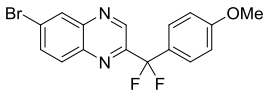
93.50 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.5, 161.2, 150.3 (t, *J* = 31.2 Hz), 143.1, 139.3 (t, *J* = 4.3 Hz), 139.2, 130.3, 128.2 (t, *J* = 27.4 Hz), 127.6 (t, *J* = 5.8 Hz), 125.0, 118.8 (t, *J* = 242.6 Hz), 114.0, 107.0, 56.0, 55.5; **HRMS (ESI)** calcd. for $C_{17}H_{14}F_2N_2O_2$ $[M+H]^+$ 317.1096, found 317.1094.

4.20 2-(difluoro(4-methoxyphenyl)methyl)-7-methoxyquinoxaline (3g'a)



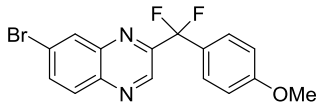
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.10 (s, 1H), 8.01 (d, *J* = 9.3 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.44 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.40 (d, *J* = 2.7 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.97 (s, 3H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -92.66 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.9, 161.1 (t, *J* = 1.5 Hz), 147.9 (t, *J* = 31.6 Hz), 144.6, 142.0 (t, *J* = 4.2 Hz), 137.5, 130.9, 128.3 (t, *J* = 27.8 Hz), 127.6 (t, *J* = 5.8 Hz), 124.5, 119.0 (t, *J* = 242.3 Hz), 114.0, 106.5, 56.0, 55.5; **HRMS (ESI)** calcd. for $C_{17}H_{14}F_2N_2O_2$ $[M+H]^+$ 317.1096, found 317.1097.

4.21 6-bromo-2-(difluoro(4-methoxyphenyl)methyl)quinoxaline (3ha)



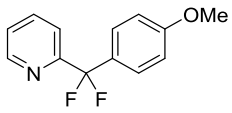
^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 9.18 (s, 1H), 8.34 (s, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.9 Hz, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 6.96 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -93.65 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.3, 150.7 (t, *J* = 32.3 Hz), 143.3, 142.9 (t, *J* = 4.0 Hz), 140.0, 134.6, 133.9, 131.8, 131.3, 127.6 (t, *J* = 7.0 Hz), 125.6, 118.7 (t, *J* = 242.4 Hz), 114.1, 55.5; **HRMS (ESI)** calcd. for $C_{16}H_{11}BrF_2N_2O$ $[M+H]^+$ 365.0096, found 365.0094.

4.22 7-bromo-2-(difluoro(4-methoxyphenyl)methyl)quinoxaline (3h'a)



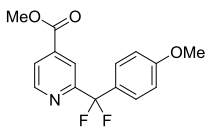
^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 9.20 (s, 1H), 8.35 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.9 Hz, 1H), 7.91 (dd, *J* = 8.9, 2.0 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -93.86 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.4, 151.3 (t, *J* = 32.3 Hz), 142.3 (t, *J* = 4.0 Hz), 141.8, 141.6, 134.9, 133.9, 132.3, 130.7, 127.6 (t, *J* = 6.0 Hz), 125.2, 118.7 (t, *J* = 242.9 Hz), 114.1, 55.5; **HRMS (ESI)** calcd. for $C_{16}H_{11}BrF_2N_2O$ $[M+H]^+$ 365.0096, found 365.0099.

423 2-(difluoro(4-methoxyphenyl)methyl)pyridine (3ia)



^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.67 (d, *J* = 4.4 Hz, 1H), 7.81 (t, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -93.27 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.9, 159.8, 155.9 (t, *J* = 31.0 Hz), 149.8, 137.2, 127.5 (t, *J* = 5.7 Hz), 124.5, 120.3 (t, *J* = 4.1 Hz), 119.0 (t, *J* = 241.2 Hz), 113.9, 55.5; **HRMS (ESI)** calcd. for $C_{13}H_{11}F_2NO$ $[M+H]^+$ 236.0881, found 236.0880.

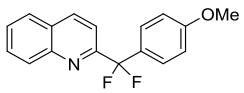
4.24 methyl 2-(difluoro(4-methoxyphenyl)methyl)isonicotinate (3ja)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.79 (d, *J* = 4.9 Hz, 1H), 8.25 (s, 1H), 7.87 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 3.96 (s,

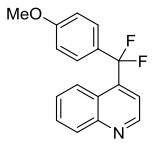
3H), 3.78 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -93.58 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 165.0, 160.9, 156.9 (t, *J* = 31.7 Hz), 150.6, 138.7, 128.4 (t, *J* = 27.8 Hz), 127.4 (t, *J* = 5.9 Hz), 123.7, 119.5 (t, *J* = 4.1 Hz), 118.7 (t, *J* = 241.8 Hz), 113.8, 55.3, 53.0; **HRMS (ESI)** calcd. for $C_{15}H_{13}F_2NO_3$ $[M+H]^+$ 294.0936, found 294.0934.

4.25 2-(difluoro(4-methoxyphenyl)methyl)quinoline (3ka)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.27 (d, *J* = 8.6 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.75 (t, *J* = 8.6 Hz, 2H), 7.61 – 7.58 (m, 3H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -92.92 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.0, 155.6 (t, *J* = 30.5 Hz), 147.5, 137.5, 130.2, 129.1 (t, *J* = 28.0 Hz), 128.1, 127.73, 127.68, 127.64, 119.1 (t, *J* = 242.0 Hz), 117.7 (t, *J* = 3.6 Hz), 113.8, 113.6, 55.5; **HRMS (ESI)** calcd. for $C_{17}H_{13}F_2NO$ $[M+H]^+$ 286.1038, found 286.1039.

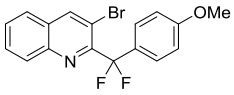
4.26 4-(difluoro(4-methoxyphenyl)methyl)quinoline (3k'a)



^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.03 (d, *J* = 4.2 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.46 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.78 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -84.42 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.3, 149.8, 149.1, 141.3 (t, *J* = 27.3 Hz), 130.3, 129.6, 128.7 (t, *J* = 27.2 Hz), 127.7 (t, *J* = 4.9 Hz), 127.3, 125.6, 124.4, 120.6 (t, *J* = 239.7 Hz), 118.8 (t, *J* = 7.4 Hz), 114.0, 55.4; **HRMS (ESI)** calcd.

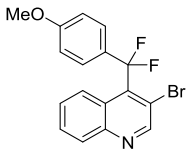
for $C_{17}H_{13}F_2NO$ $[M+H]^+$ 286.1038, found 286.1035.

4.27 3-bromo-2-(difluoro(4-methoxyphenyl)methyl)quinoline (3la)



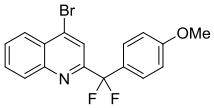
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.45 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.65 (td, *J* = 8.1, 1.0 Hz, 1H), 7.52 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -90.42 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.1, 151.4 (t, *J* = 28.3 Hz), 145.1, 142.1, 130.6, 130.3, 130.0, 129.3, 129.0, 128.0 (t, *J* = 5.4 Hz), 126.6, 118.9 (t, *J* = 243.5 Hz), 114.0, 113.7, 55.5; **HRMS (ESI)** calcd. for $C_{17}H_{12}BrF_2NO$ $[M+H]^+$ 364.0143, found 364.0145.

4.28 3-bromo-4-(difluoro(4-methoxyphenyl)methyl)quinoline (3l'a)



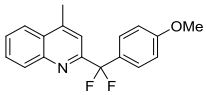
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 9.07 (s, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.73 (t, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -76.48 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.6, 154.2, 147.6, 139.5 (t, *J* = 25.5 Hz), 132.7, 130.5, 129.7, 128.2, 127.8 (t, *J* = 4.7 Hz), 126.7, 126.0 (t, *J* = 7.9 Hz), 121.3 (t, *J* = 242.4 Hz), 116.8, 114.3, 55.5; **HRMS (ESI)** calcd. for $C_{17}H_{12}BrF_2NO$ $[M+H]^+$ 364.0143, found 364.0140.

4.29 4-bromo-2-(difluoro(4-methoxyphenyl)methyl)quinoline (3ma)



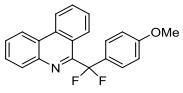
^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.20 – 8.16 (m, 2H), 8.05 (s, 1H), 7.78 (t, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -93.04 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.1, 155.4 (t, *J* = 31.3 Hz), 148.0, 135.4, 131.1, 130.6, 129.0, 128.4 (t, *J* = 27.8 Hz), 127.7, 127.6 (t, *J* = 5.8 Hz), 126.7, 121.7 (t, *J* = 3.8 Hz), 118.5 (t, *J* = 242.9 Hz), 113.9, 55.4; **HRMS (ESI)** calcd. for $C_{17}H_{12}BrF_2NO$ $[M+H]^+$ 364.0143, found 364.0141.

4.30 2-(difluoro(4-methoxyphenyl)methyl)-4-methylquinoline (3na)



^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 8.19 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.4 Hz, 1H), 7.61 - 7.57 (m, 4H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.74 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -93.15 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 160.9, 155.3 (t, *J* = 30.0 Hz), 147.2, 146.1, 130.8, 129.8, 128.1, 127.7 (t, *J* = 5.6 Hz), 127.5, 126.2, 123.8, 119.1 (t, *J* = 242.1 Hz), 118.3 (t, *J* = 3.4 Hz), 113.8, 55.4, 19.2; **HRMS (ESI)** calcd. for $C_{18}H_{15}F_2NO$ $[M+H]^+$ 300.1194, found 300.1193.

4.31 6-(difluoro(4-methoxyphenyl)methyl)phenanthridine (3oa)



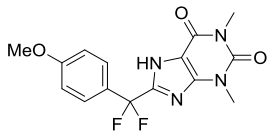
^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 8.69 (d, *J* = 8.4 Hz, 1H), 8.62 (d, *J* = 7.8 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.27 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.83 (t, *J* = 8.2 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.61 (t, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H); **^{19}F NMR** (471 MHz, $CDCl_3$) δ ppm -86.35 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 161.0, 153.4 (t, *J* = 27.9 Hz), 142.3, 134.1, 131.3, 130.8, 129.1, 128.5, 127.9 (t, *J* = 5.4 Hz), 127.6 (t, *J* = 5.2 Hz), 127.5, 124.8, 123.1, 122.5,

122.1 (t, *J* = 26.4 Hz), 129.0, 120.3 (t, *J* = 241.6 Hz), 113.9, 55.5; **HRMS (ESI)** calcd. for $C_{21}H_{15}F_2NO$ $[M+H]^+$ 336.1194, found 336.1198.

4.32 6-(difluoro(4-methoxyphenyl)methyl)-3-hydroxypyrazine-2-carboxamide （3pa）

^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 9.76 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 6.96 – 6.93 (m, 3H), 3.83 (s, 3H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -103.54 (s, CF_2); **^{13}C NMR** (125 MHz, $CDCl_3$) low solubility, only nine kinds of carbons were observed δ ppm 164.6, 161.9, 132.7, 127.3, 124.3 (t, *J* = 24.7 Hz), 120.9, 114.2, 114.0, 55.5; **IR (KBr)**: ν_{max} 3400, 2936, 2348, 1755, 1590, 1515, 1418, 1310, 1253, 1177, 1098, 993, 904, 836, 635, 503 cm^{-1}; **MS (ESI)** m/z = 296.1 $[M+H]^+$; **HRMS (ESI)** calcd. for $C_{13}H_{11}F_2N_3O_3$ $[M+H]^+$ 296.0841, found 296.0844.

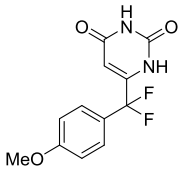
4.33 8-(difluoro(4-methoxyphenyl)methyl)theophylline (3qa)



^{1}H NMR (600 MHz, $CDCl_3$) δ ppm 7.57 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 3.31 (s, 6H); **^{19}F NMR** (565 MHz, $CDCl_3$) δ ppm -59.23 (s, CF_2) ; **^{13}C NMR** (125 MHz, $CDCl_3$) δ ppm 162.2, 161.9, 157.0, 150.3, 132.4, 127.6(t, *J* = 4.2 Hz), 124.8 (t, *J* = 32.0 Hz), 121.1 (t, *J* = 232.7 Hz), 113.8, 81.9, 55.5, 29.8, 29.7; **IR (KBr)**: ν_{max} 3436, 2923, 1701, 1614, 1445, 1378, 1306, 1257, 1179, 1092, 1023, 836, 749 cm^{-1}; **MS (ESI)** m/z = 337.1 $[M+H]^+$; **HRMS (ESI)** calcd. for $C_{15}H_{14}F_2N_4O_3$

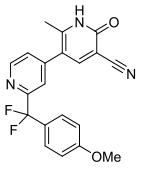
$[M+H]^+$ 337.1107, found 337.1105.

4.34 6-(difluoro(4-methoxyphenyl)methyl)uracil (3ra)



^{1}H NMR (600 MHz, DMSO-d_6) δ ppm 12.60 (s, 1H), 7.91 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H); **^{19}F NMR** (565 MHz, DMSO-d_6) δ ppm -95.30 (s, CF_2); **^{13}C NMR** (125 MHz, DMSO-d_6) low solubility, only eight kinds of carbons were observed δ ppm 167.7, 163.3, 131.9, 123.4, 114.6, 114.5, 114.2, 55.7; **IR (KBr)**: ν_{max} 3407, 1680, 1513, 1255, 1171, 1010, 825, 765, 614 cm^{-1}; **MS (ESI)** m/z = 269.1 $[M+H]^+$; **HRMS (ESI)** calcd. for $C_{12}H_{10}F_2N_2O_3$ $[M+H]^+$ 269.0732, found 269.0733.

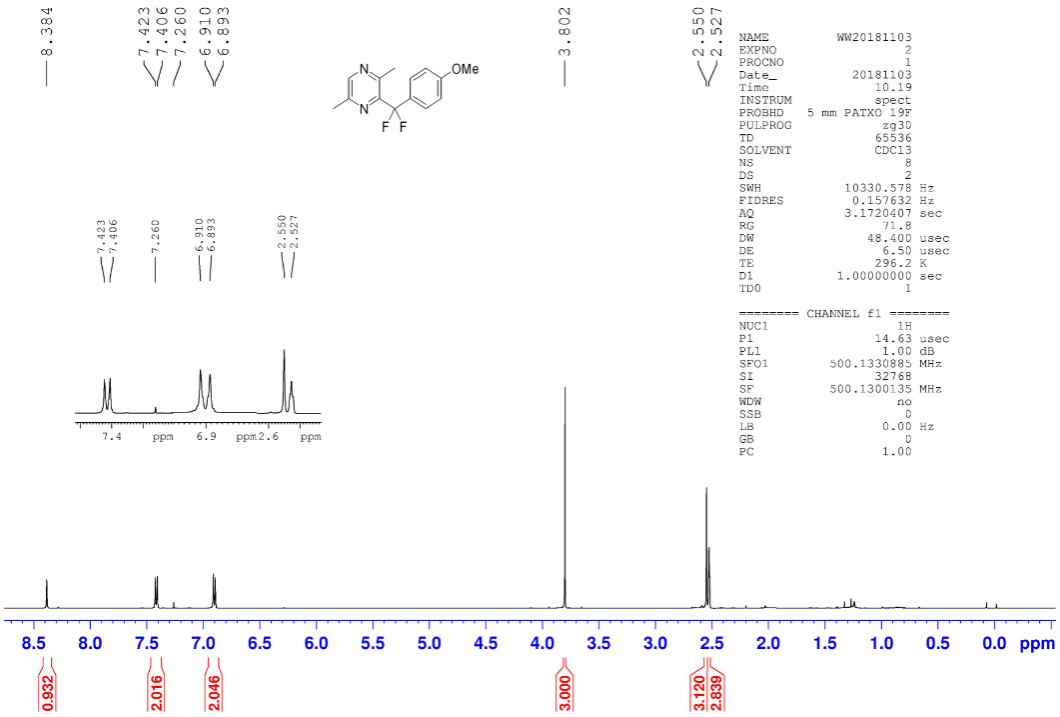
4.35 2-(difluoro(4-methoxyphenyl)methyl)milrinone (3sa)



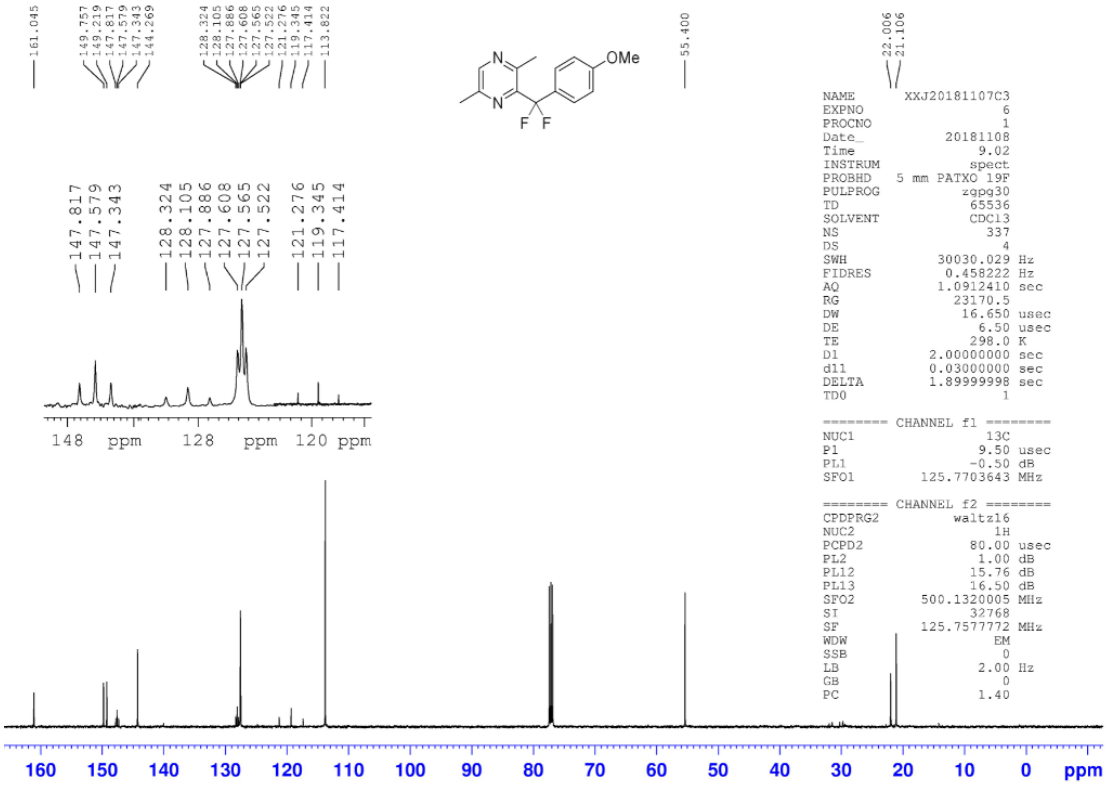
^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 12.86 (s, 1H), 8.66 (d, J = 4.9 Hz, 1H), 8.27 (s, 1H), 7.83 (s, 1H), 7.54 – 7.50 (m, 3H), 7.02 (d, J = 8.6 Hz, 2H), 3.77 (s, 3H), 2.33 (s, 3H); **^{19}F NMR** (471 MHz, DMSO-d_6) δ ppm -92.10 (s, CF_2); **^{13}C NMR** (125 MHz, DMSO-d_6) δ ppm 160.5, 160.1, 155.1 (t, J = 30.9 Hz), 152.0, 149.8, 149.7, 145.3, 128.3 (t, J = 27.9 Hz), 127.2 (t, J = 5.8 Hz), 125.2, 120.0 (t, J = 123.0 Hz), 116.3 (t, J = 121.2 Hz), 113.9, 100.5, 55.3, 18.3; **IR (KBr)**: ν_{max} 3410, 2253, 1659, 1378, 1007, 825, 763, 624 cm^{-1}; **MS (ESI)** m/z = 368.1 $[M+H]^+$; **HRMS (ESI)** calcd. for $C_{20}H_{15}F_2N_3O_2$ $[M+H]^+$ 368.1205, found 368.1204.

5. Copies of ^{1}H NMR, ^{19}F NMR, ^{13}C NMR spectra of the products

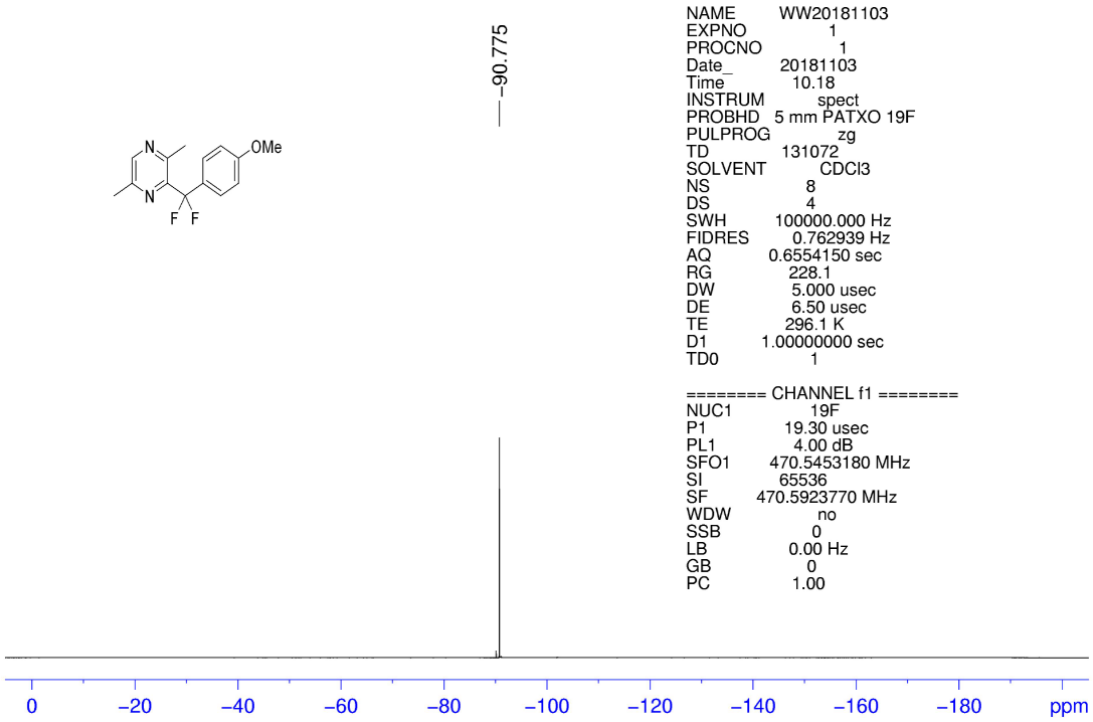
^{1}H NMR Spectra of **3aa**



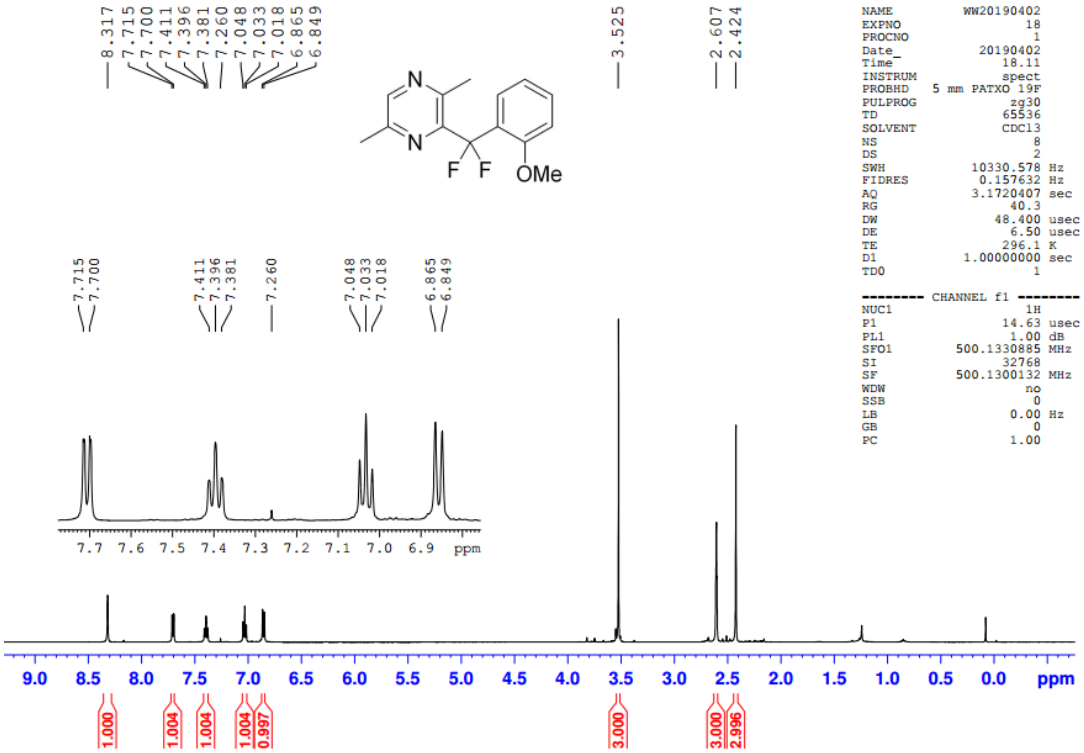
^{13}C NMR Spectra of **3aa**



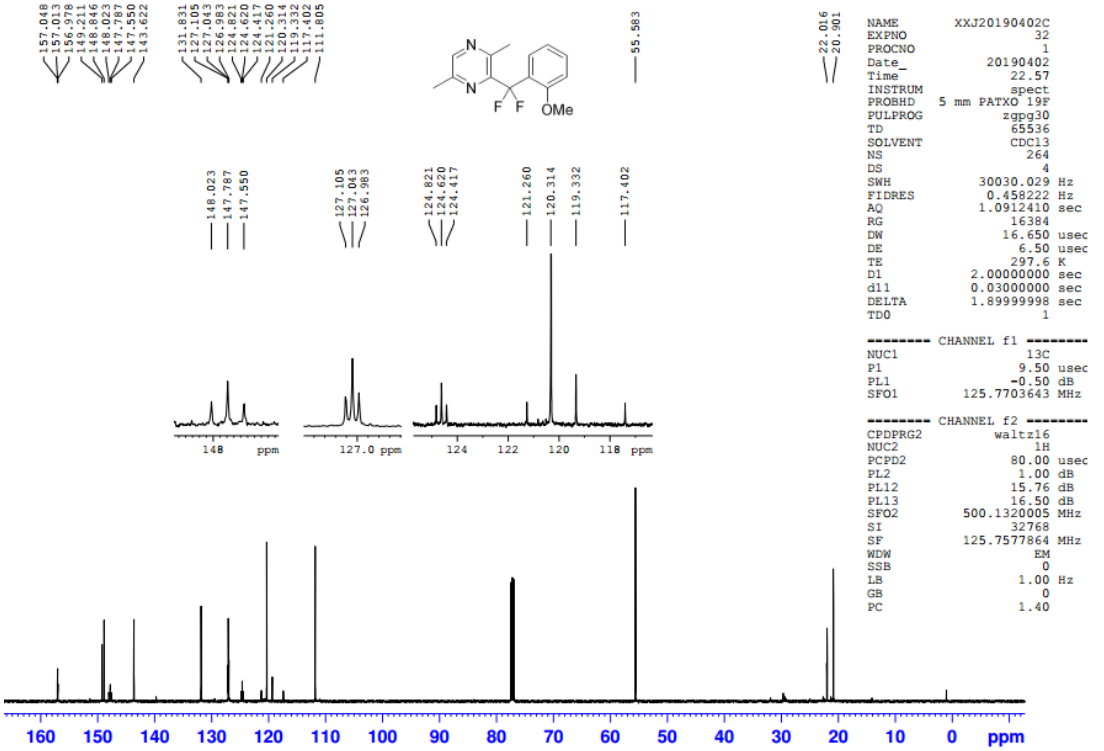
^{19}F NMR Spectra of **3aa**



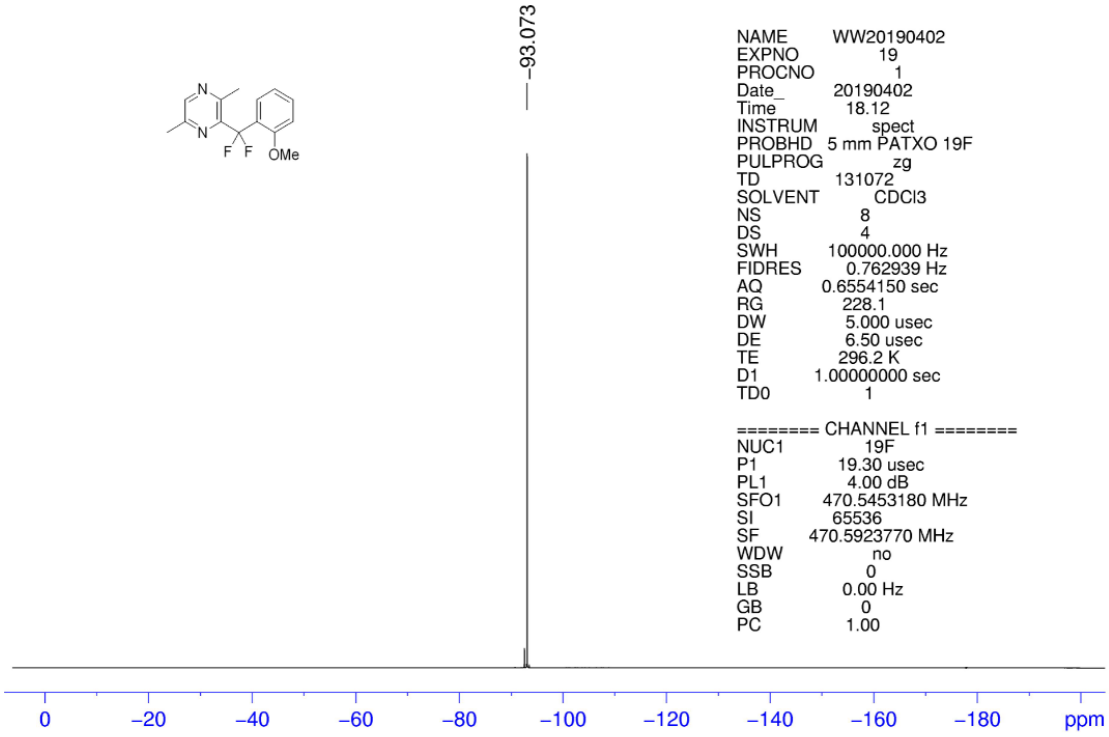
^{1}H NMR Spectra of **3ab**



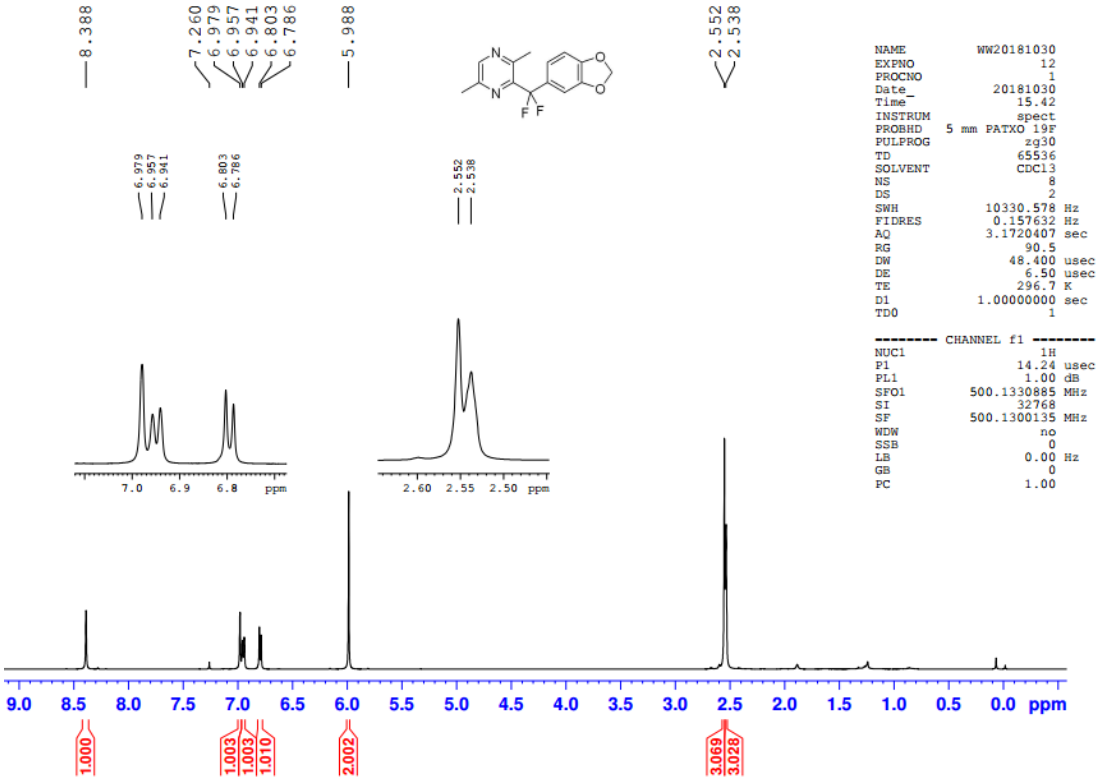
^{13}C NMR Spectra of **3ab**



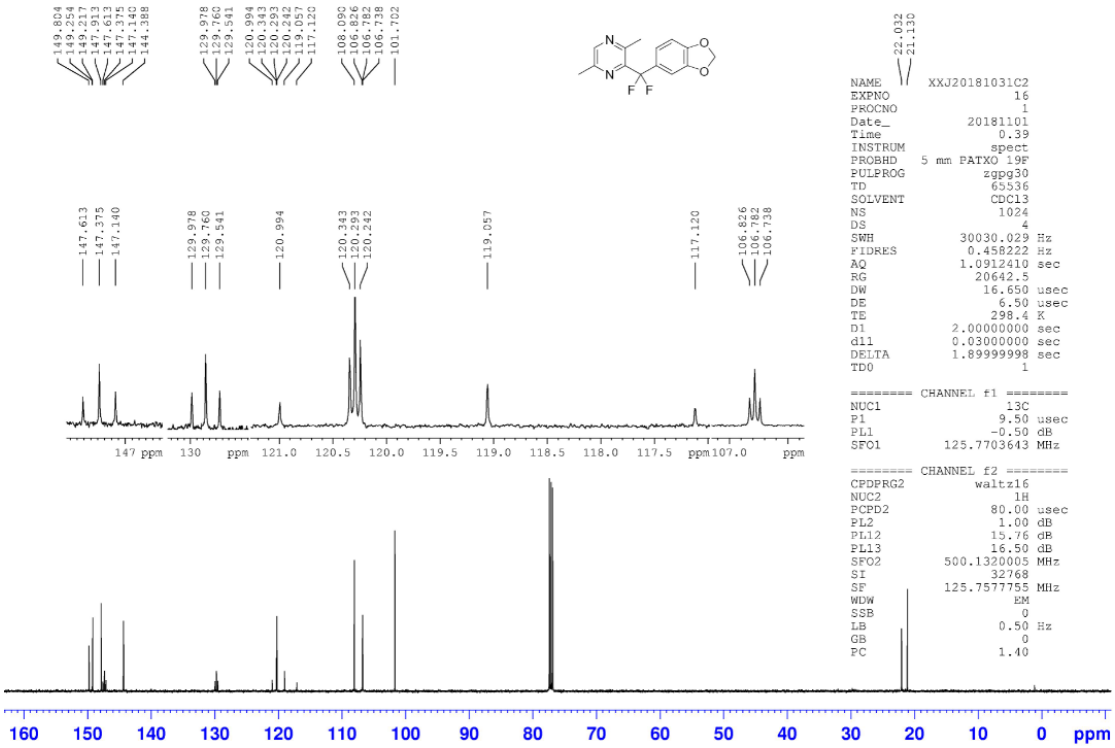
^{19}F NMR Spectra of **3ab**



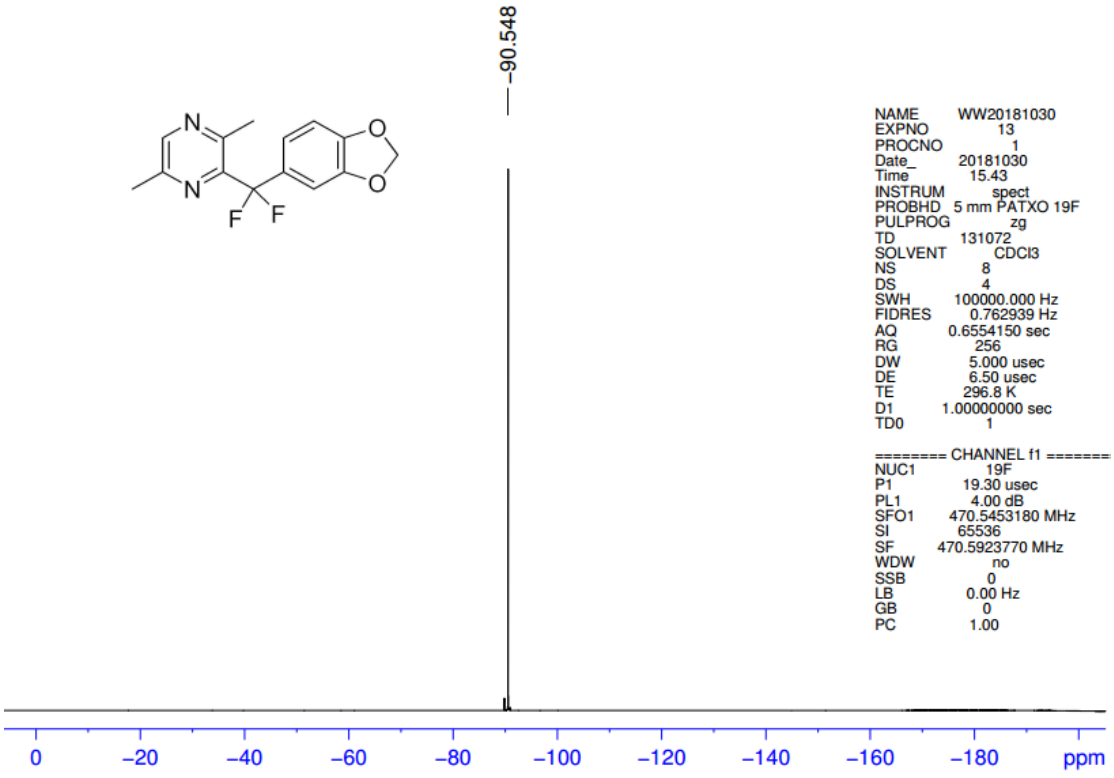
^{1}H NMR Spectra of **3ac**



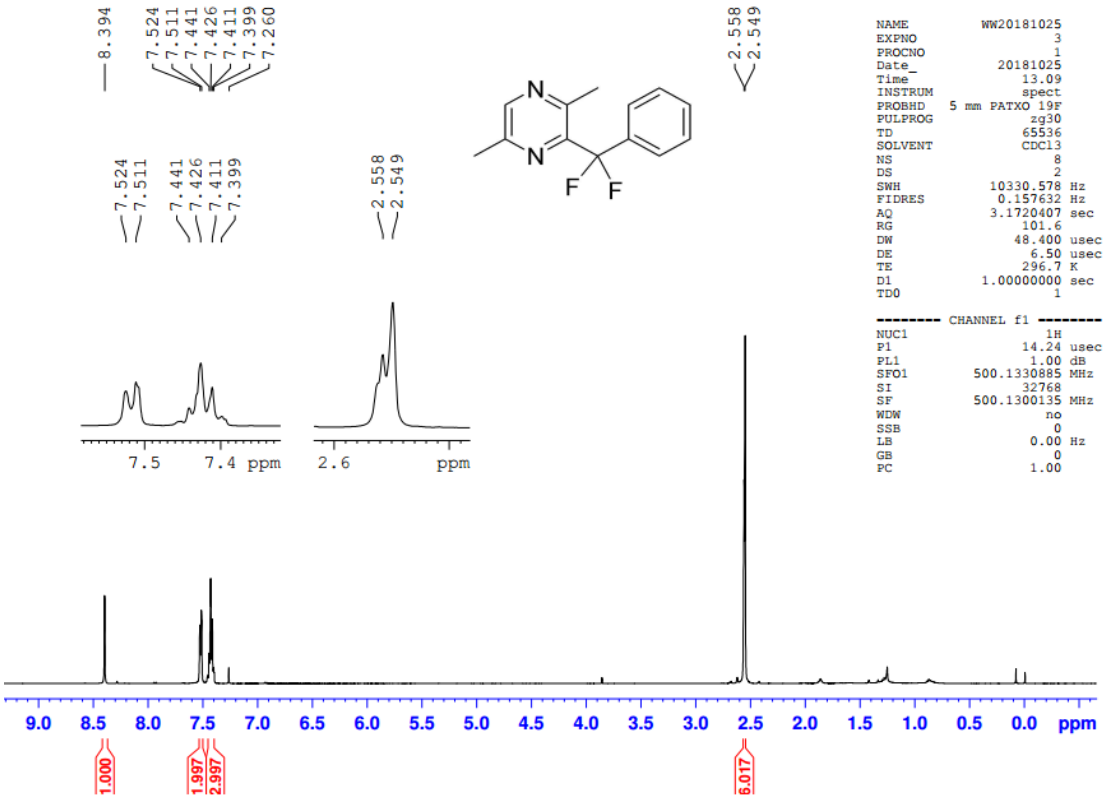
^{13}C NMR Spectra of **3ac**



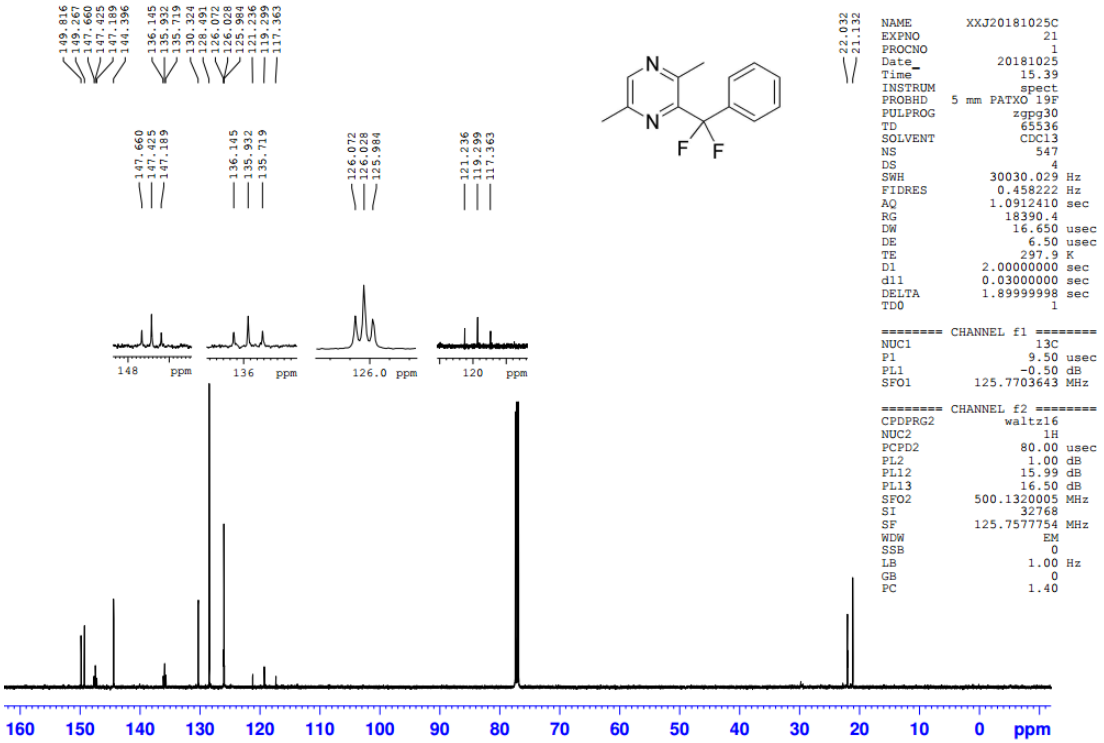
^{19}F NMR Spectra of **3ac**



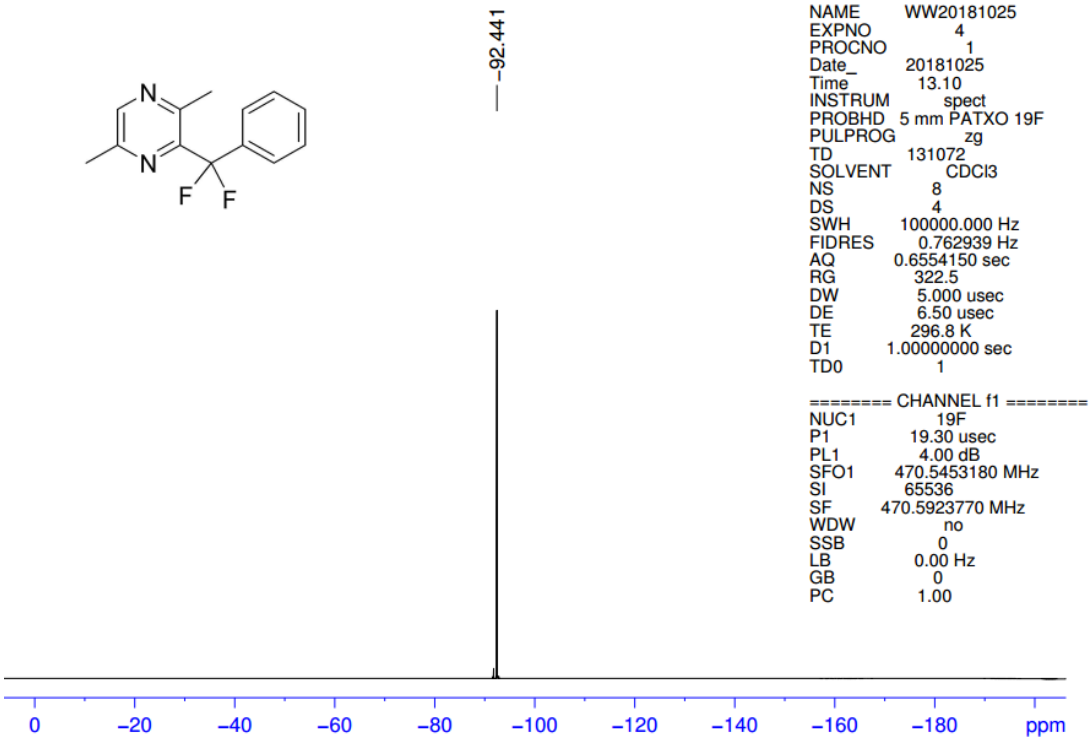
^{1}H NMR Spectra of **3ad**



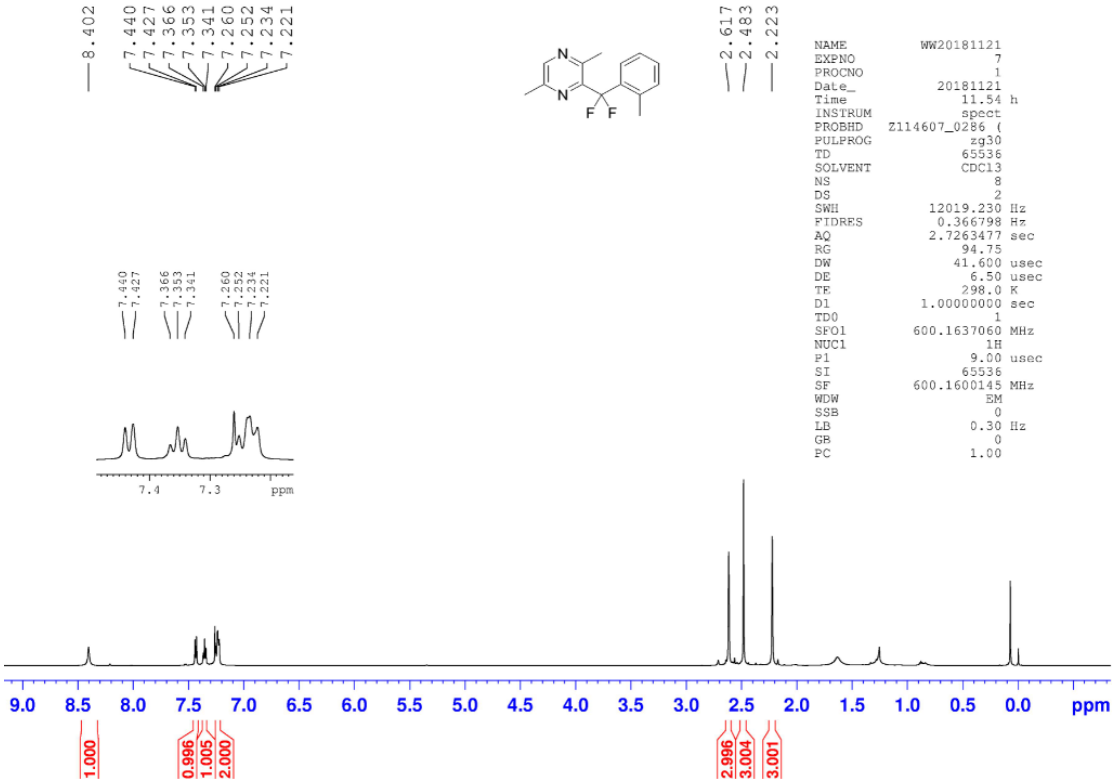
^{13}C NMR Spectra of **3ad**



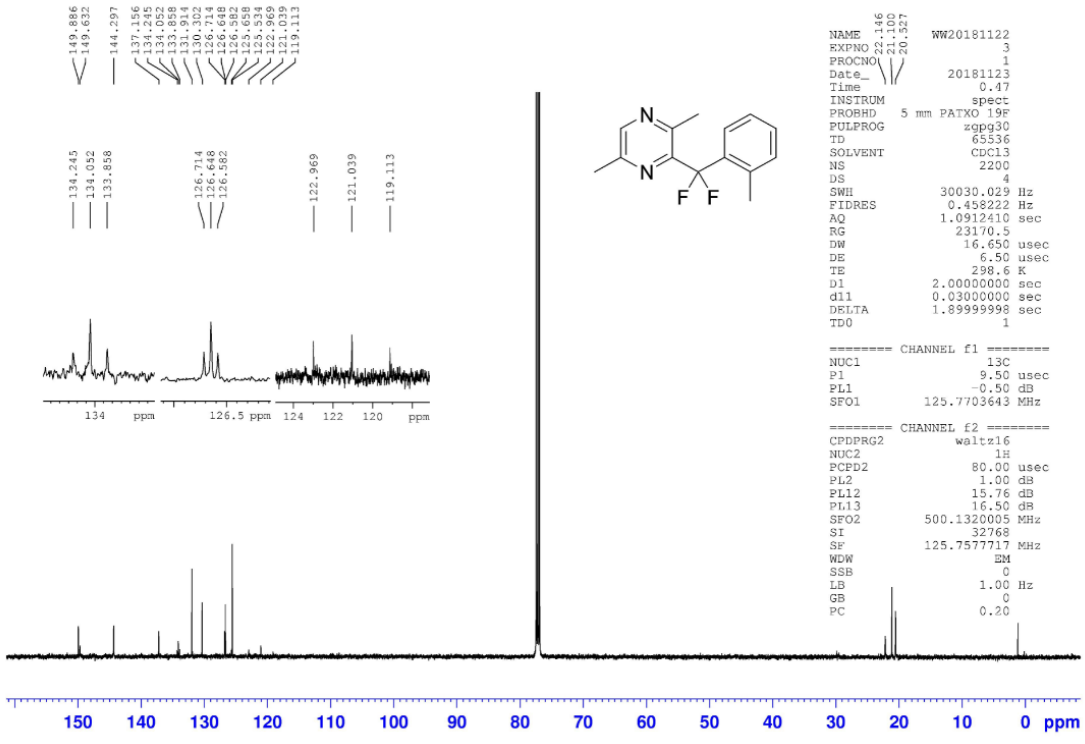
^{19}F NMR Spectra of **3ad**



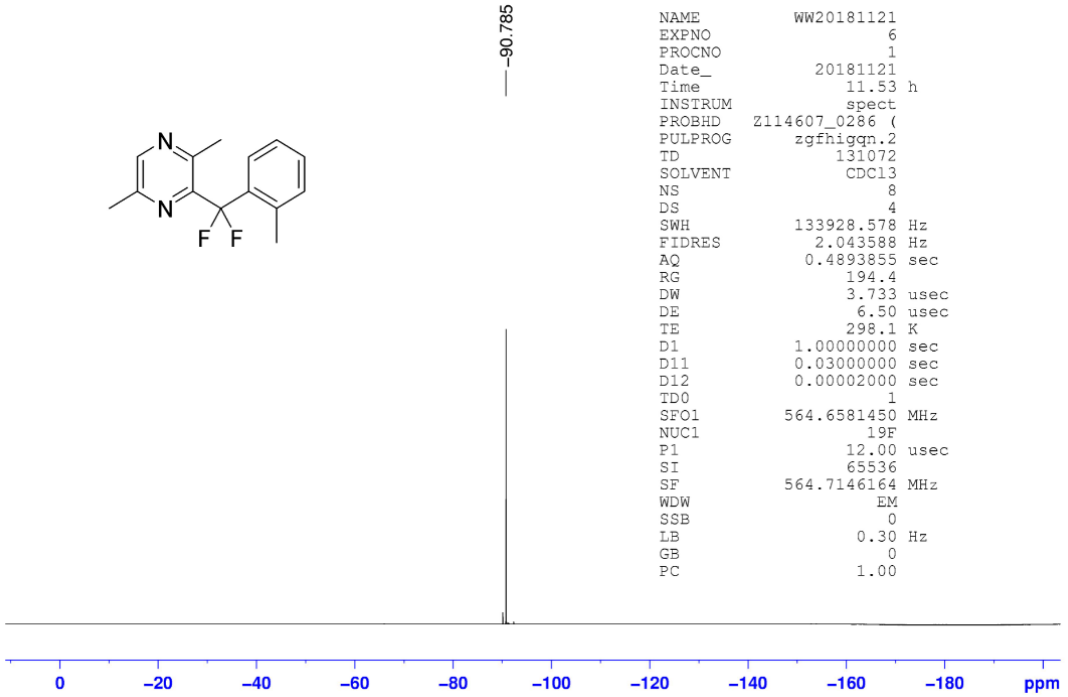
^{1}H NMR Spectra of **3ae**



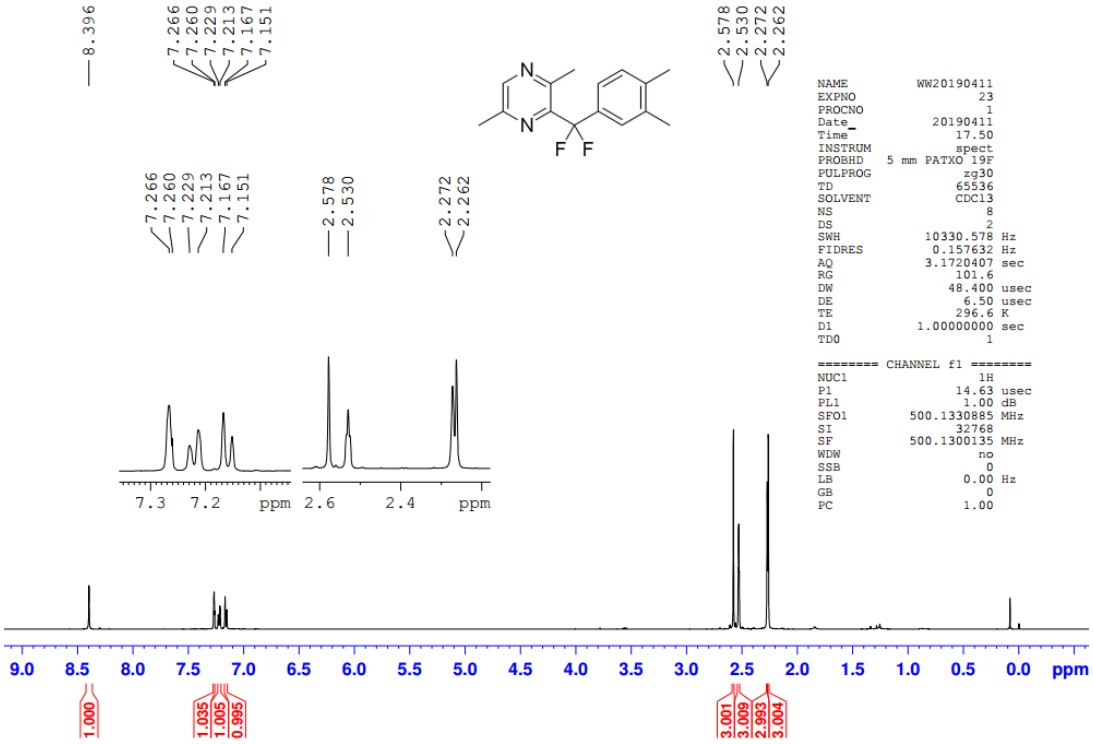
^{13}C NMR Spectra of **3ae**



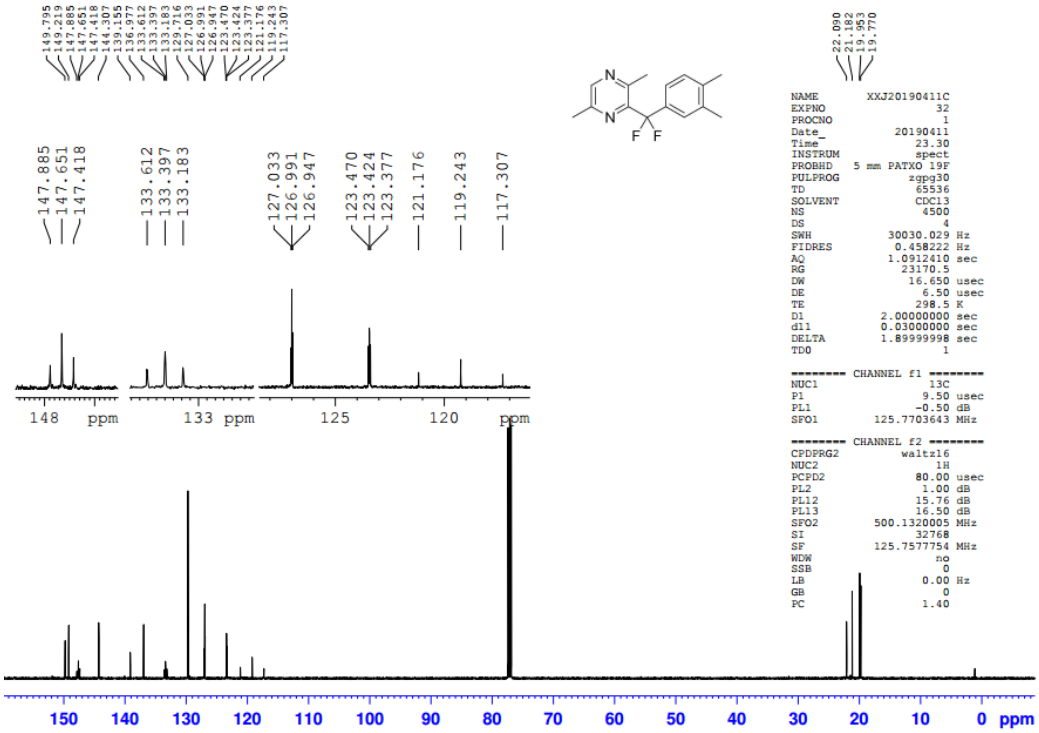
^{19}F NMR Spectra of **3ae**



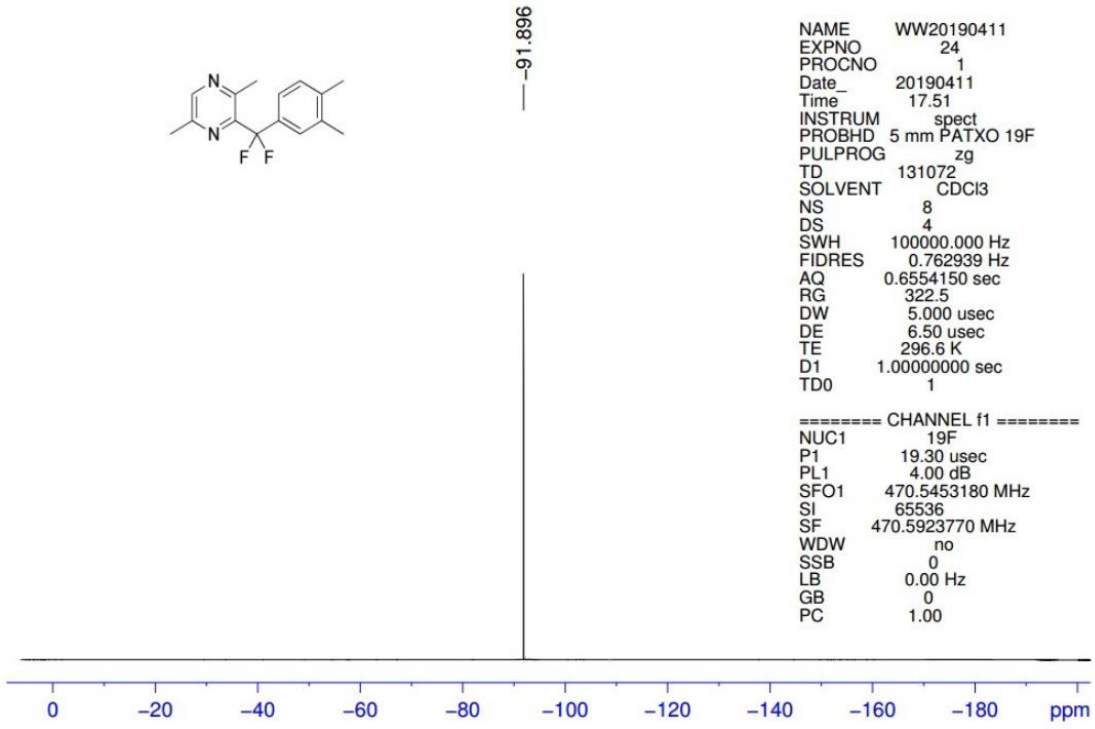
^{1}H NMR Spectra of **3af**



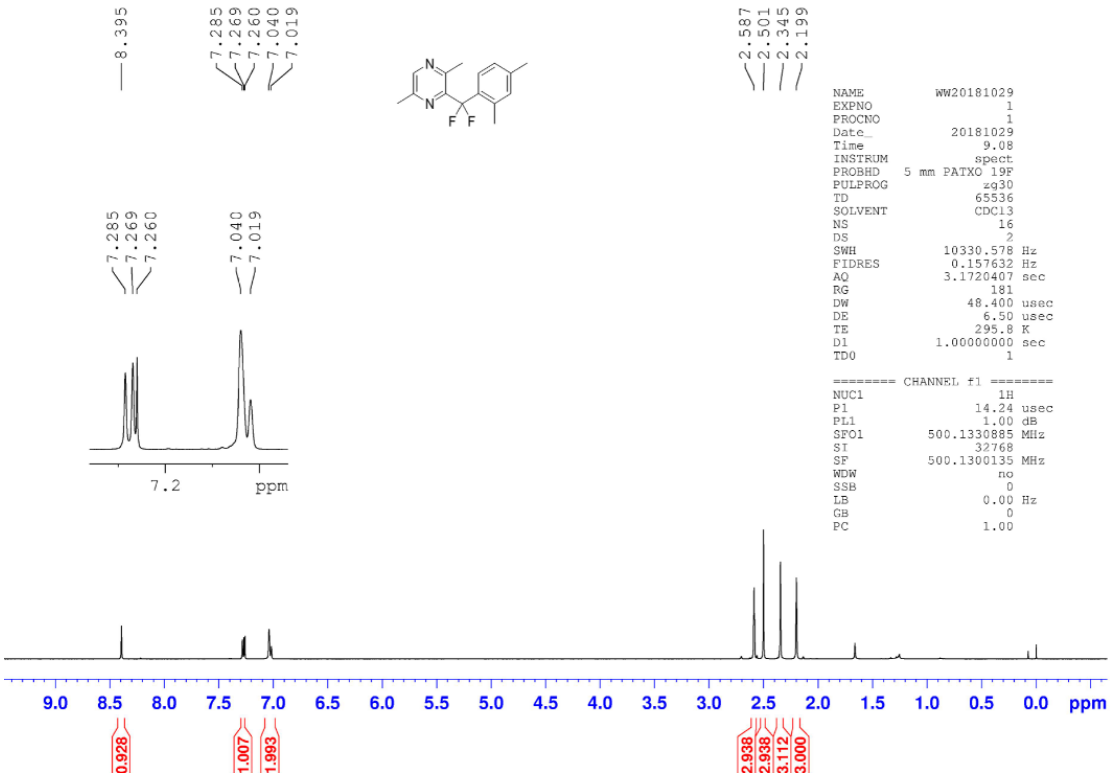
^{13}C NMR Spectra of **3af**



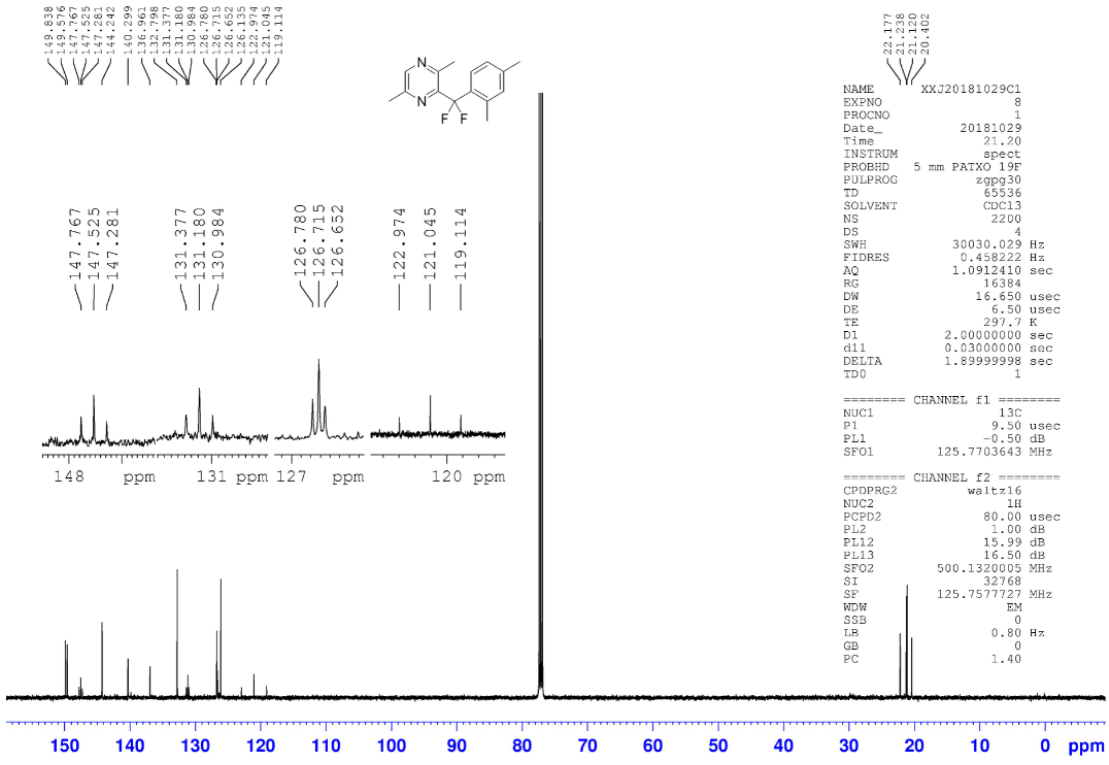
^{19}F NMR Spectra of **3af**



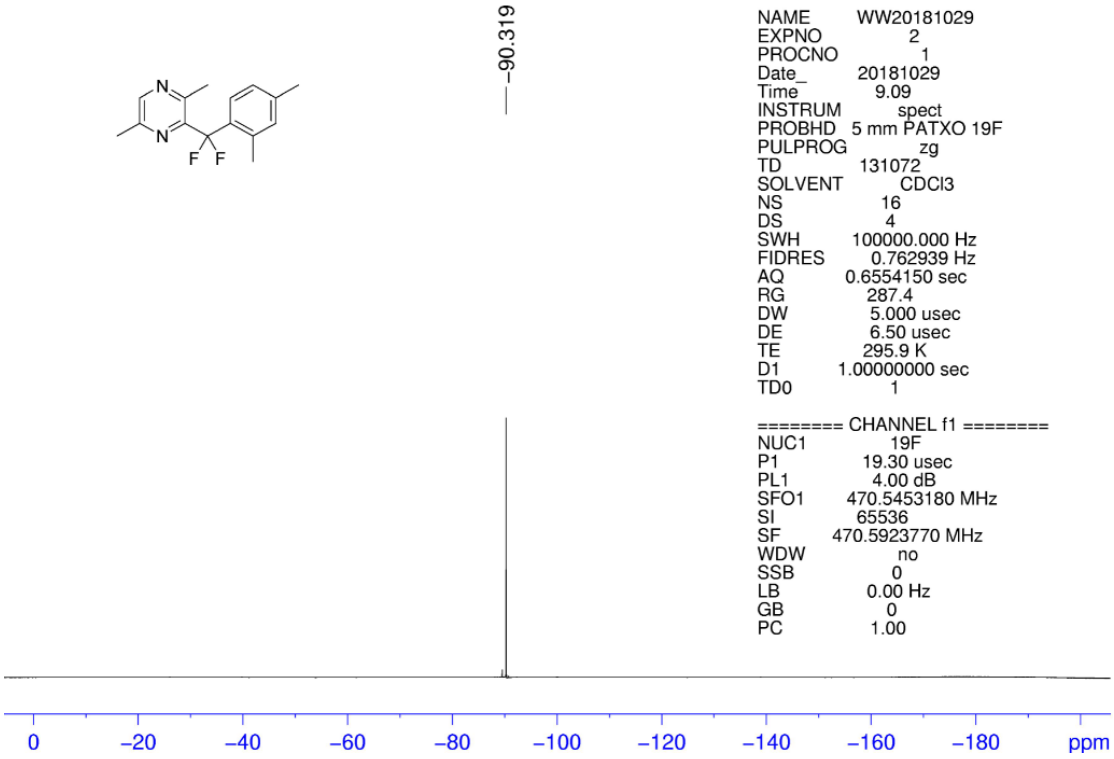
^{1}H NMR Spectra of **3ag**



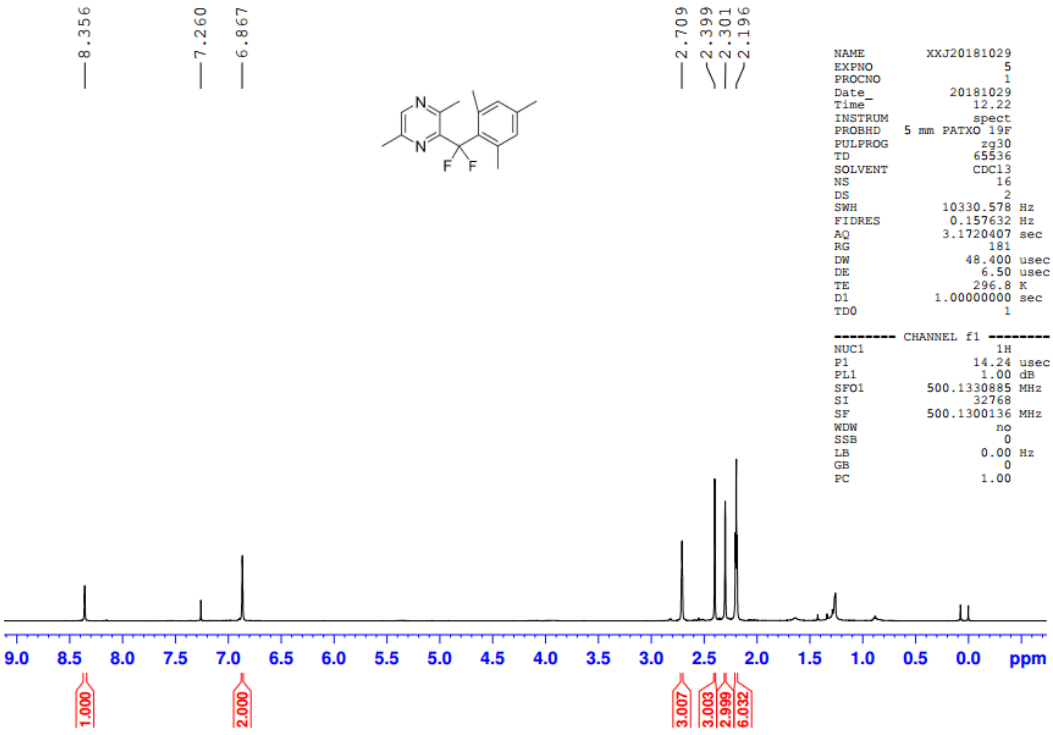
^{13}C NMR Spectra of **3ag**



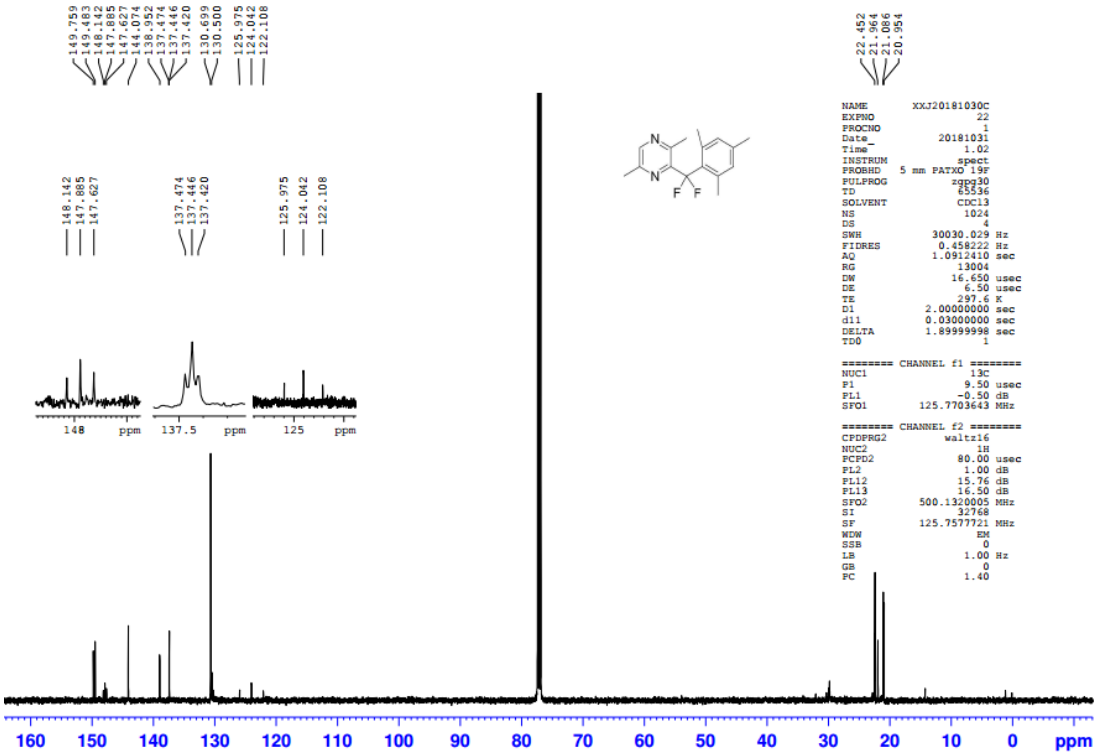
^{19}F NMR Spectra of **3ag**



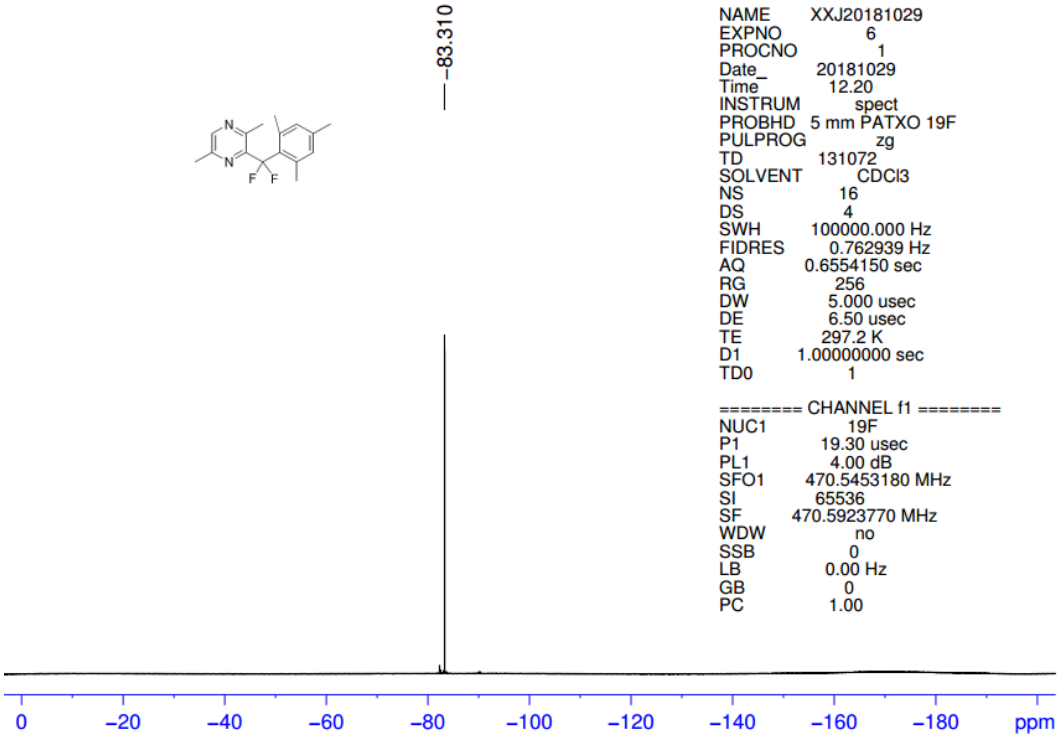
^{1}H NMR Spectra of **3ah**



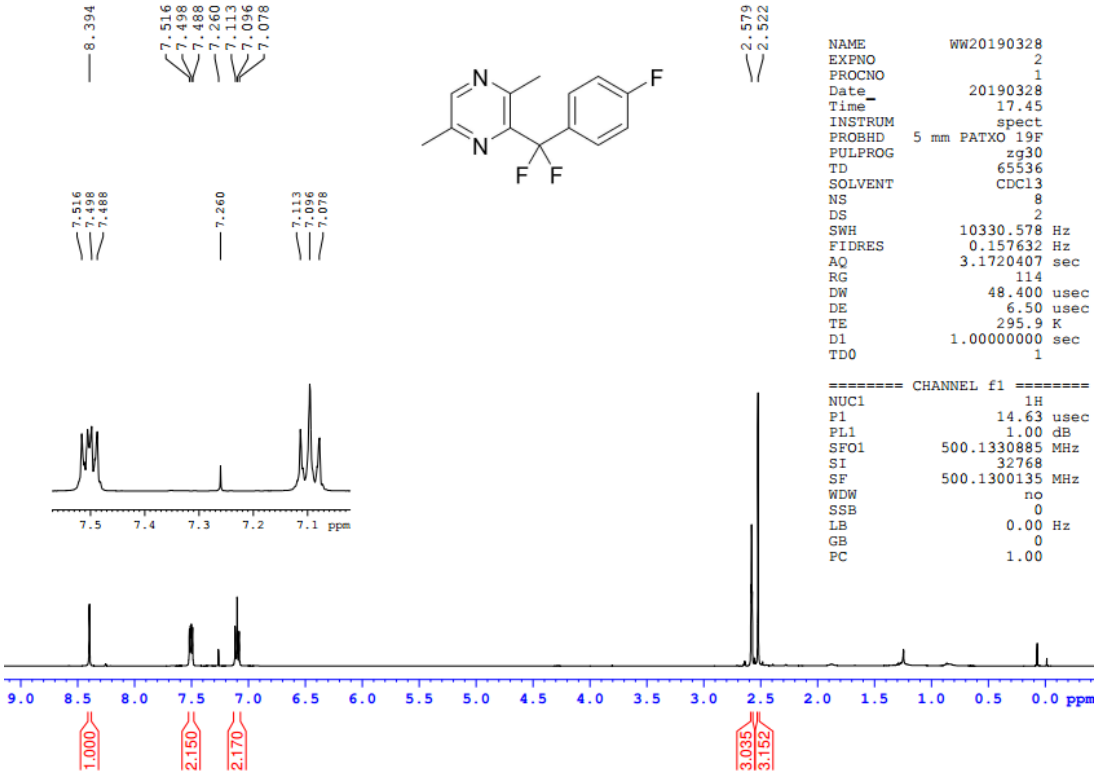
^{13}C NMR Spectra of **3ah**



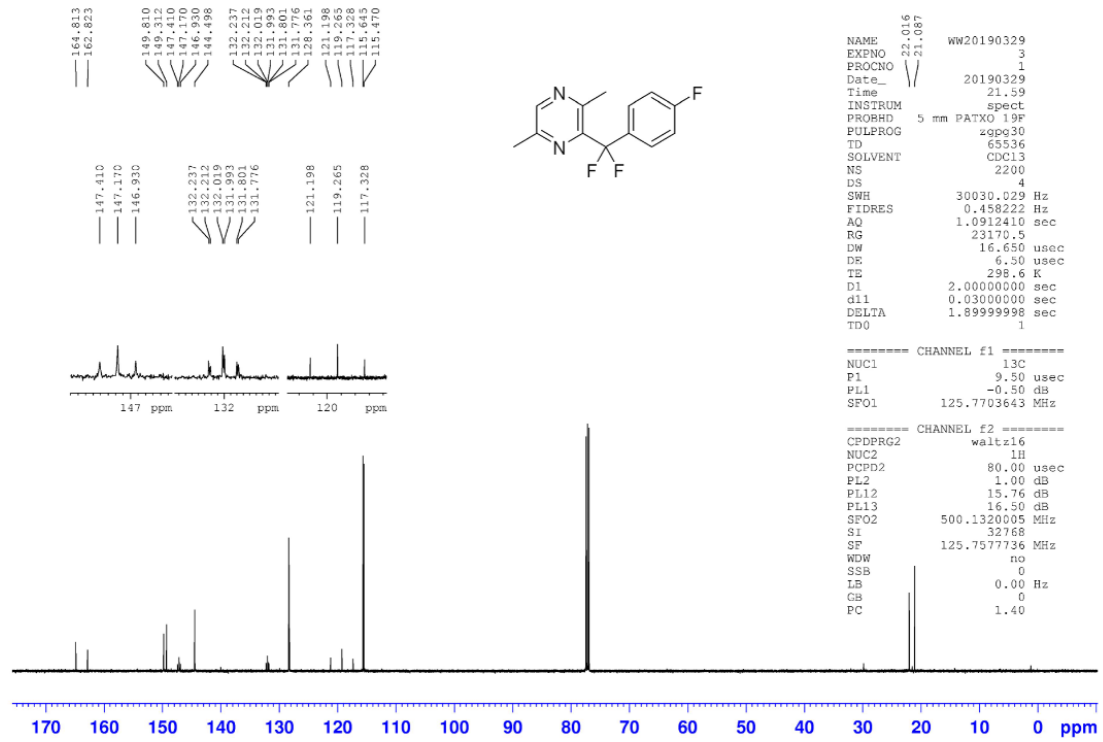
^{19}F NMR Spectra of **3ah**



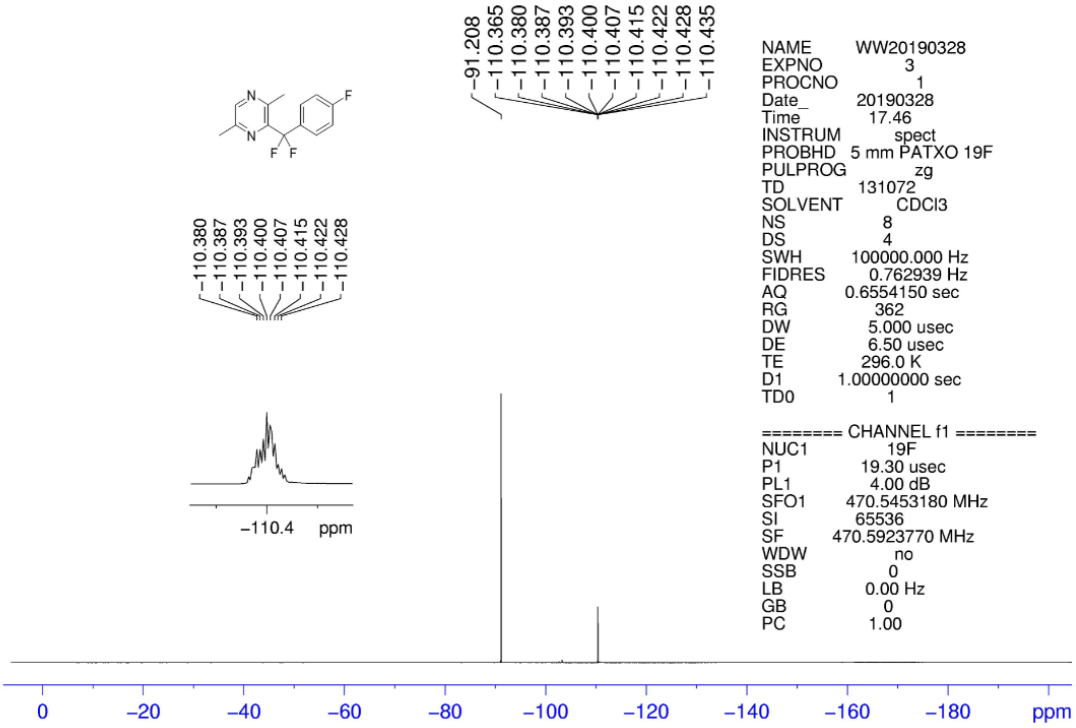
^{1}H NMR Spectra of **3ai**



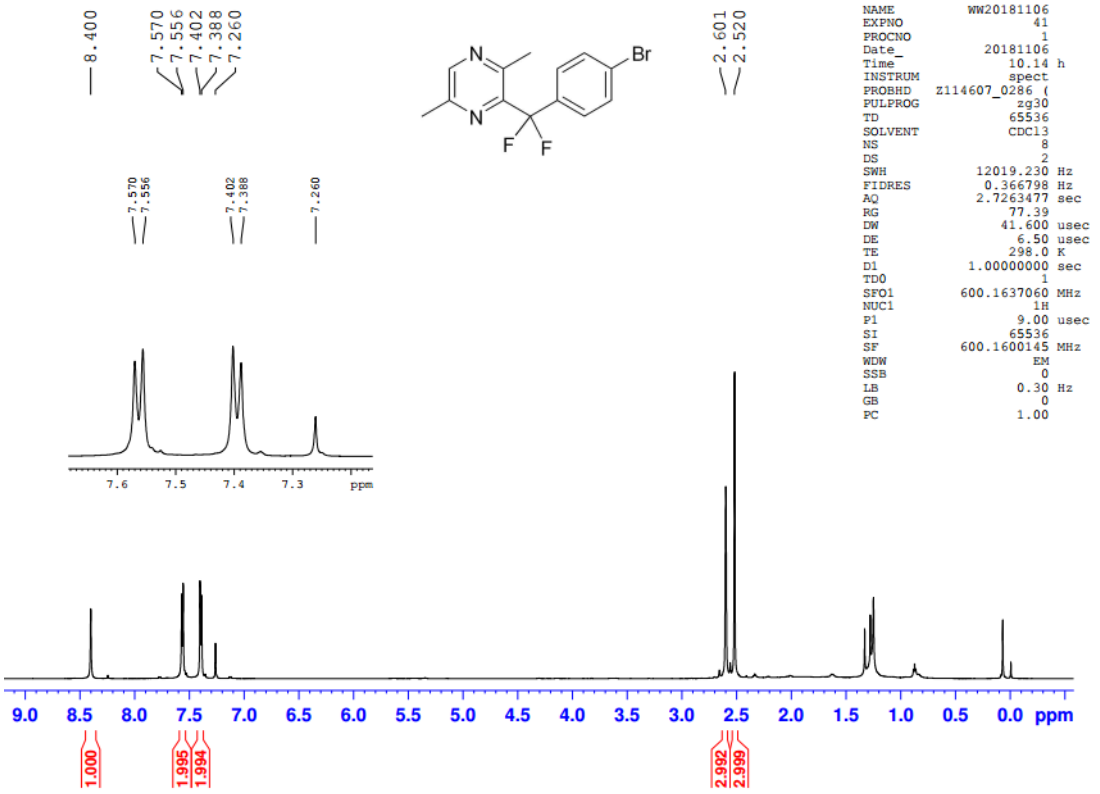
^{13}C NMR Spectra of **3ai**



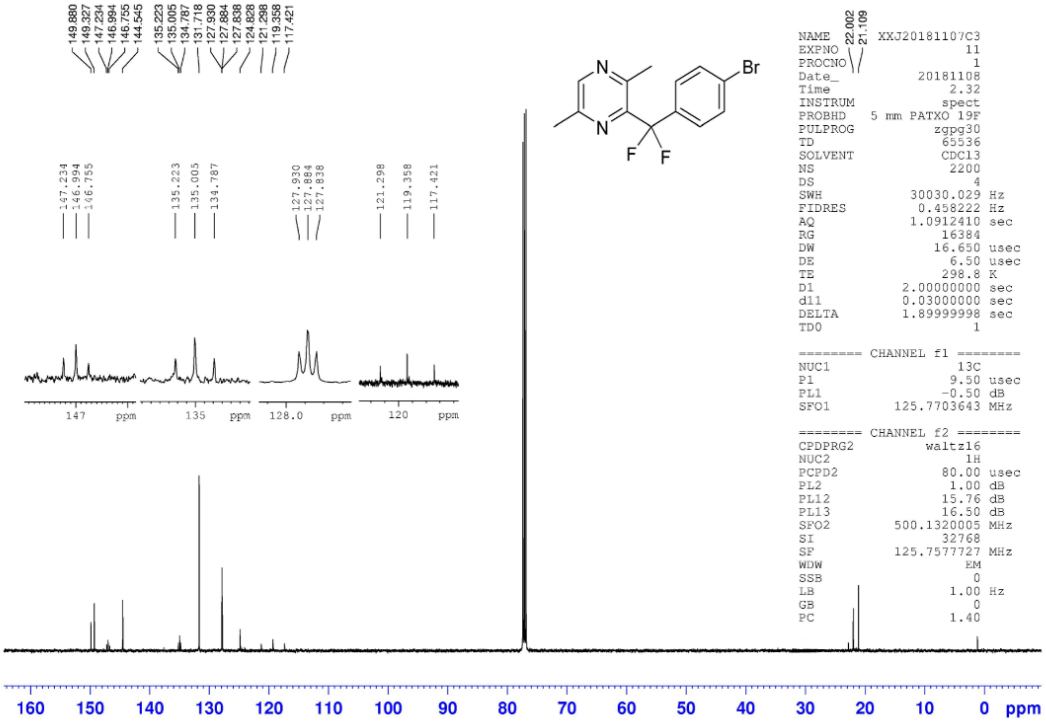
^{19}F NMR Spectra of **3ai**



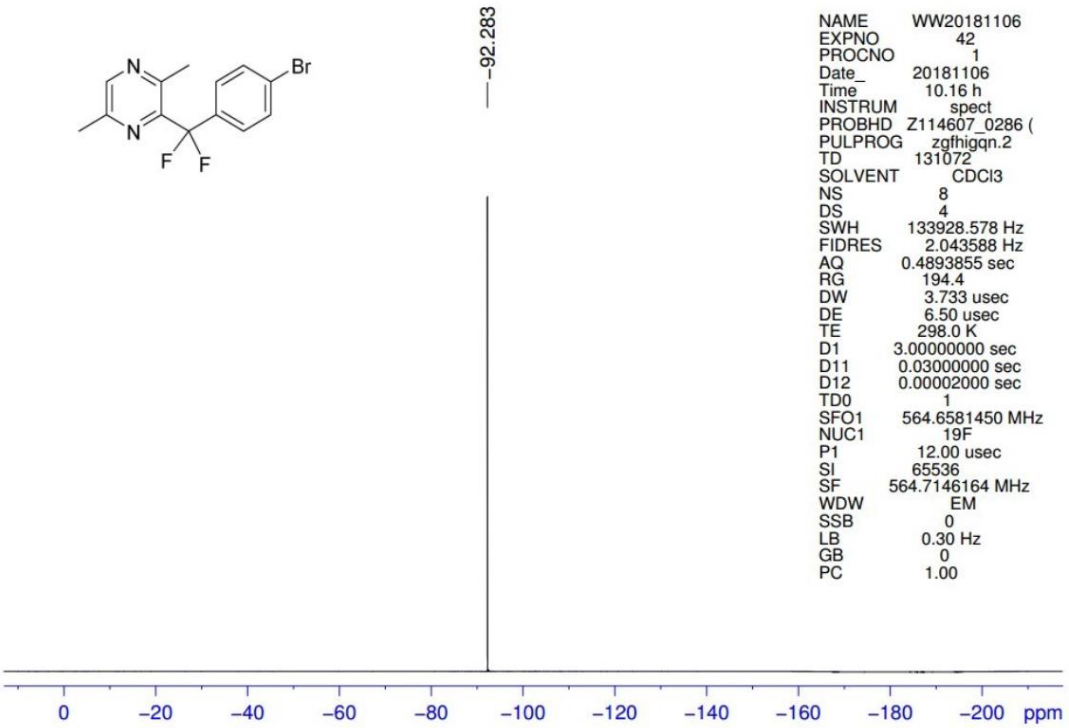
^{1}H NMR Spectra of **3aj**



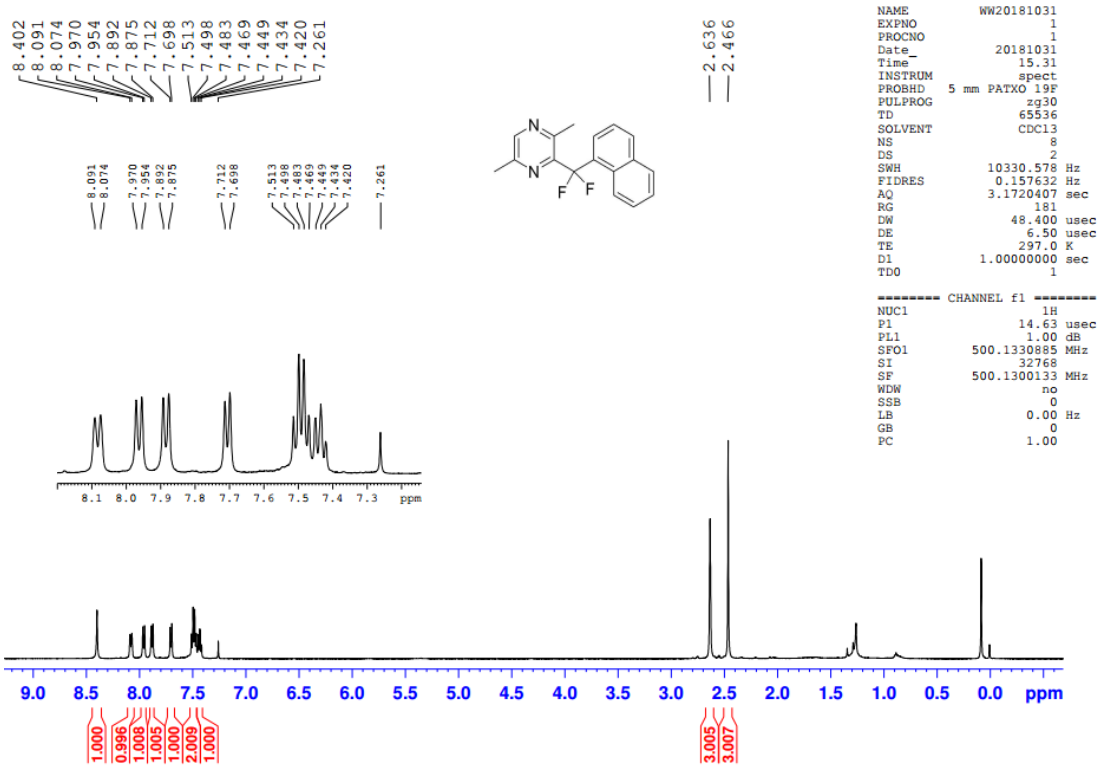
^{13}C NMR Spectra of **3aj**



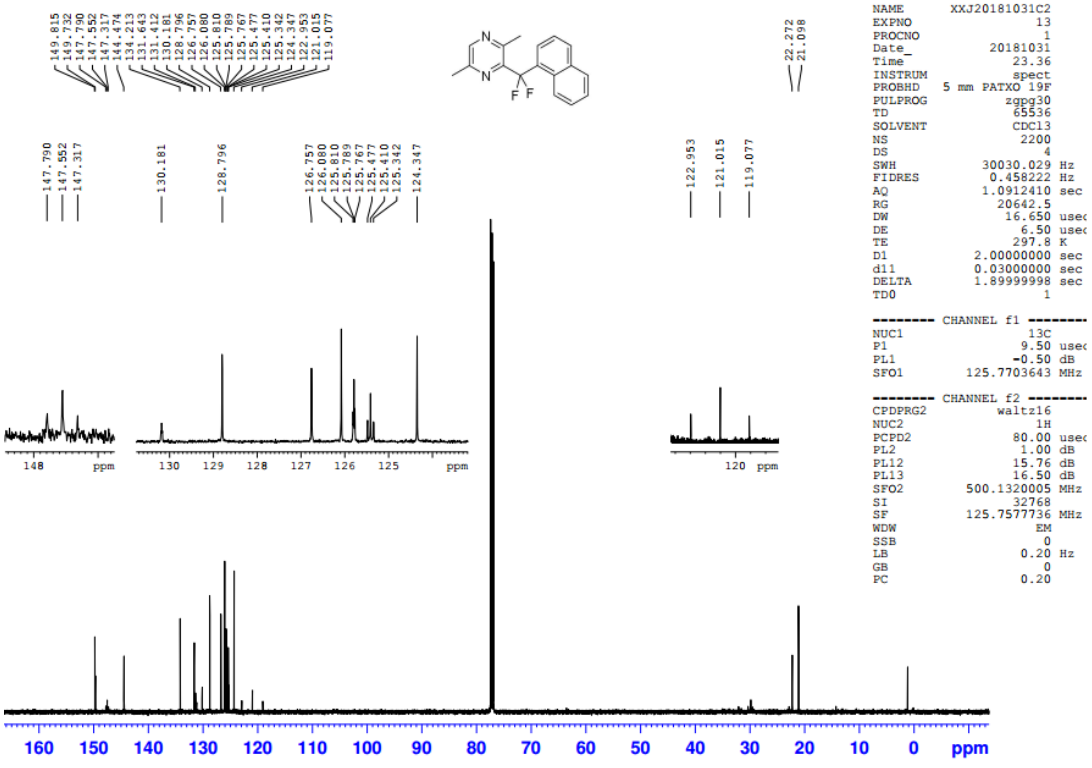
^{19}F NMR Spectra of **3aj**



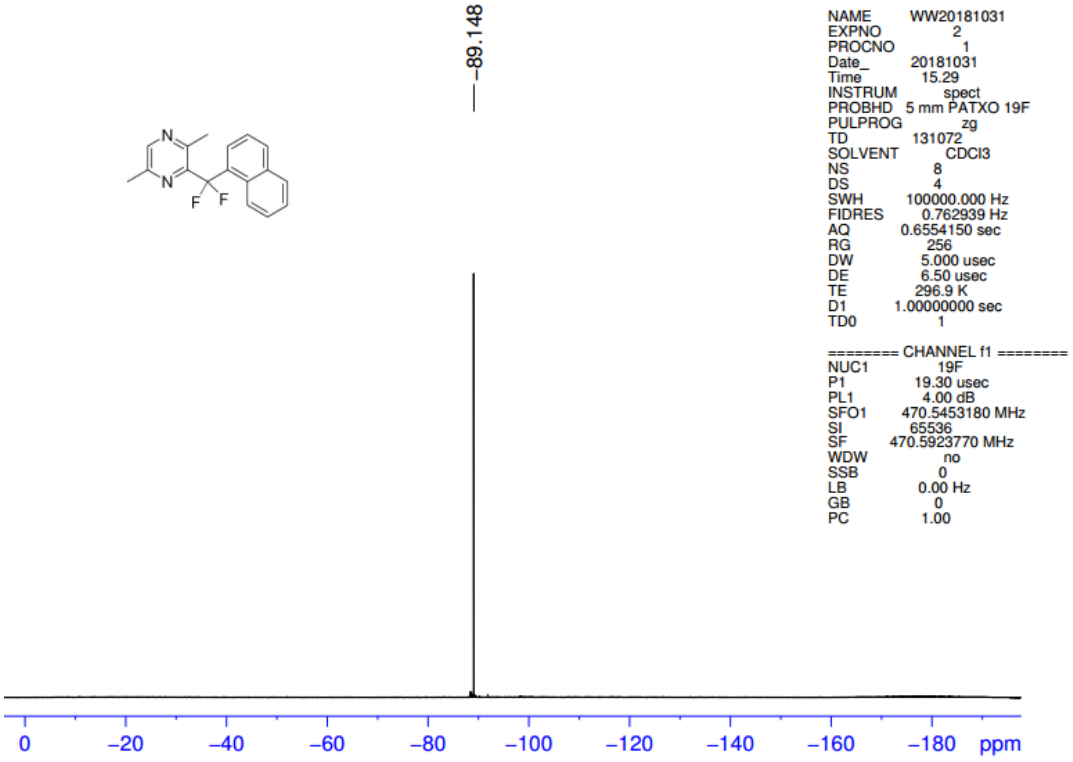
^{1}H NMR Spectra of **3ak**



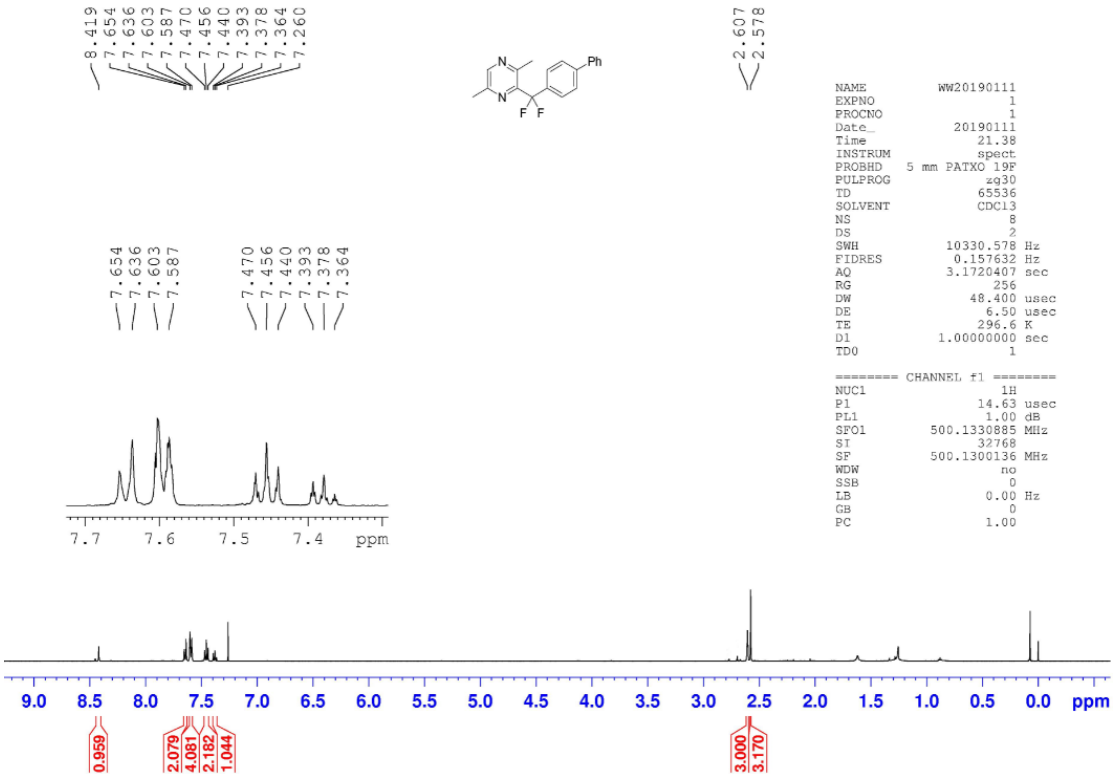
^{13}C NMR Spectra of **3ak**



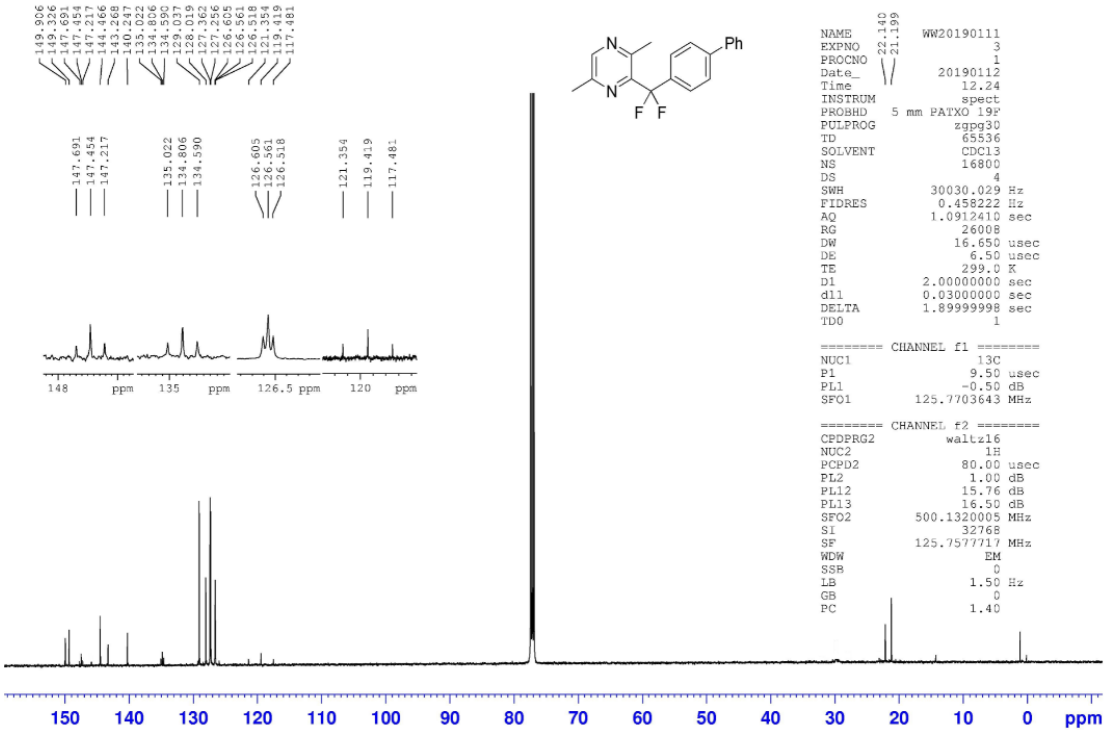
^{19}F NMR Spectra of **3ak**



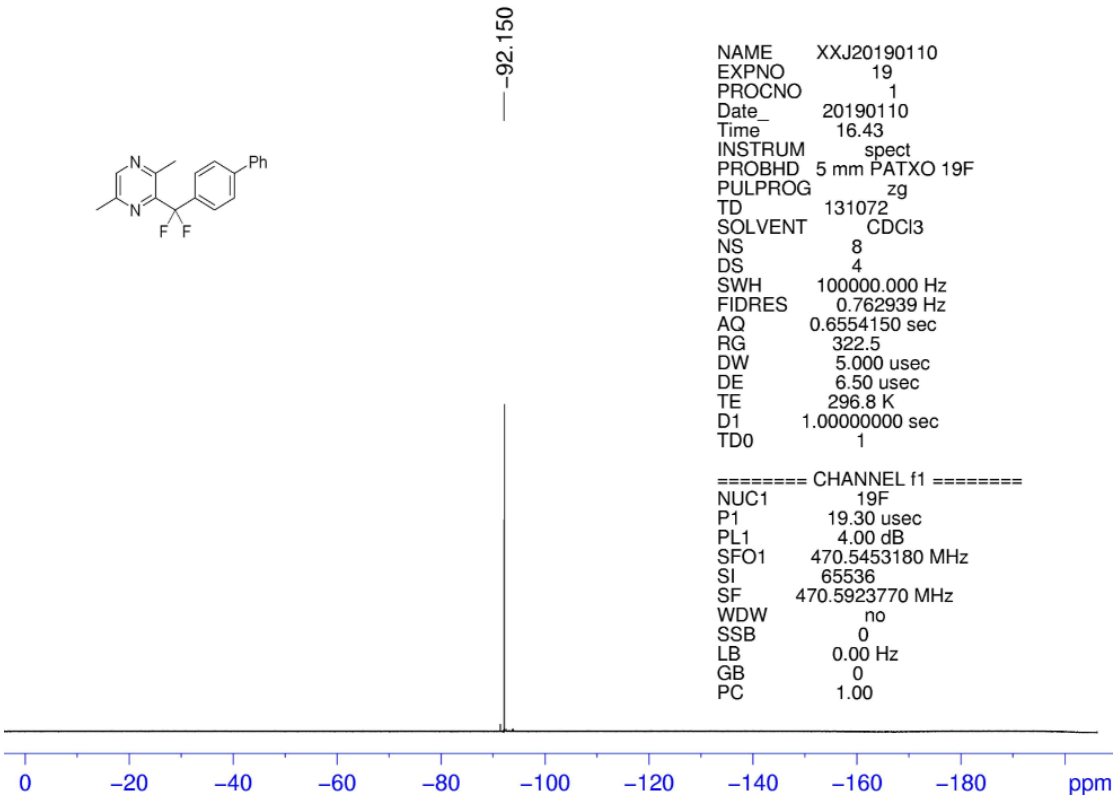
^{1}H NMR Spectra of **3al**



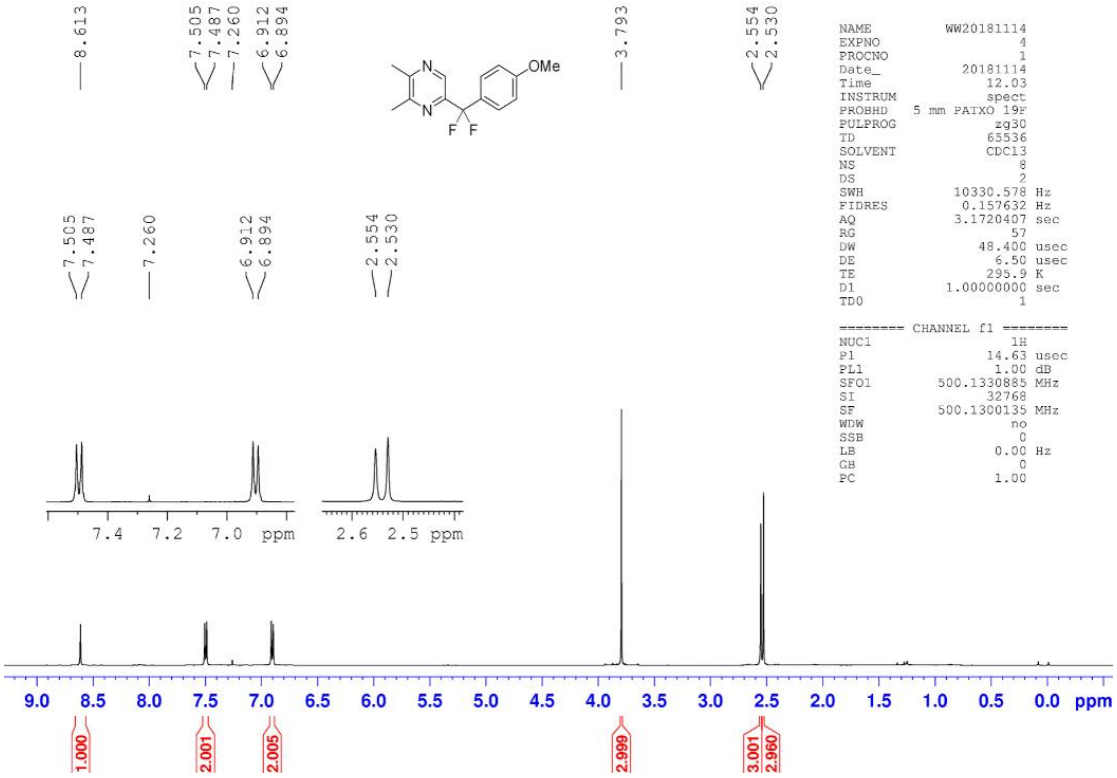
^{13}C NMR Spectra of **3al**



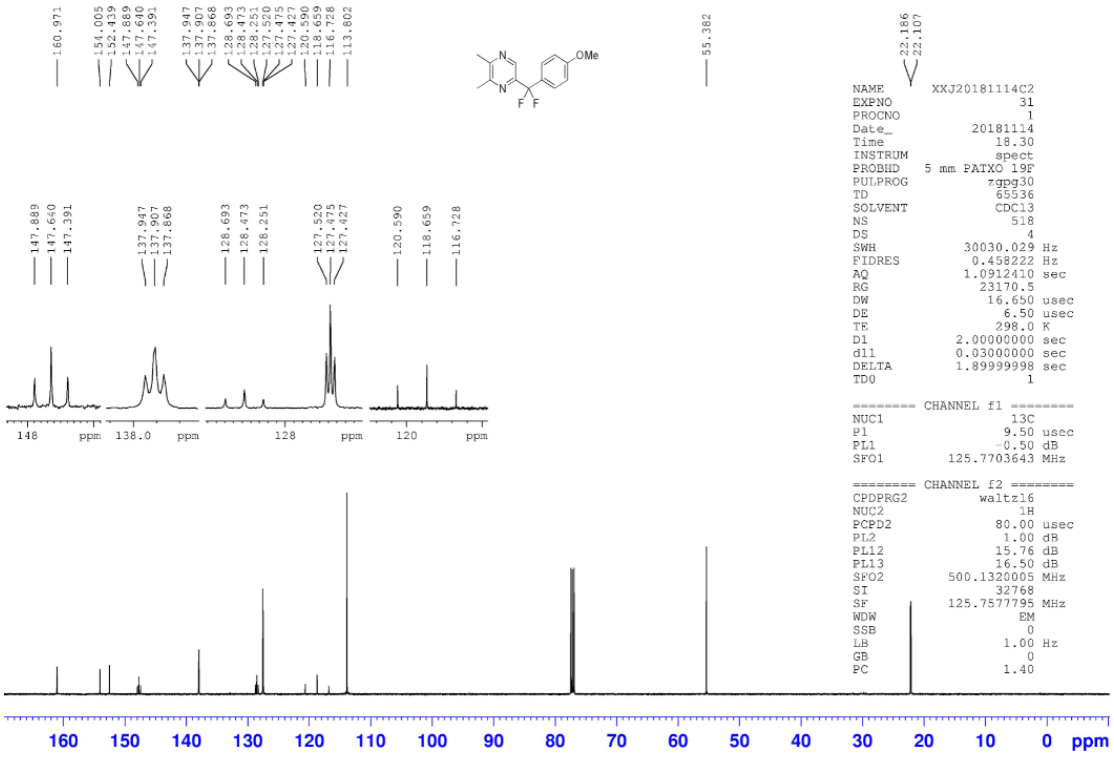
^{19}F NMR Spectra of **3al**



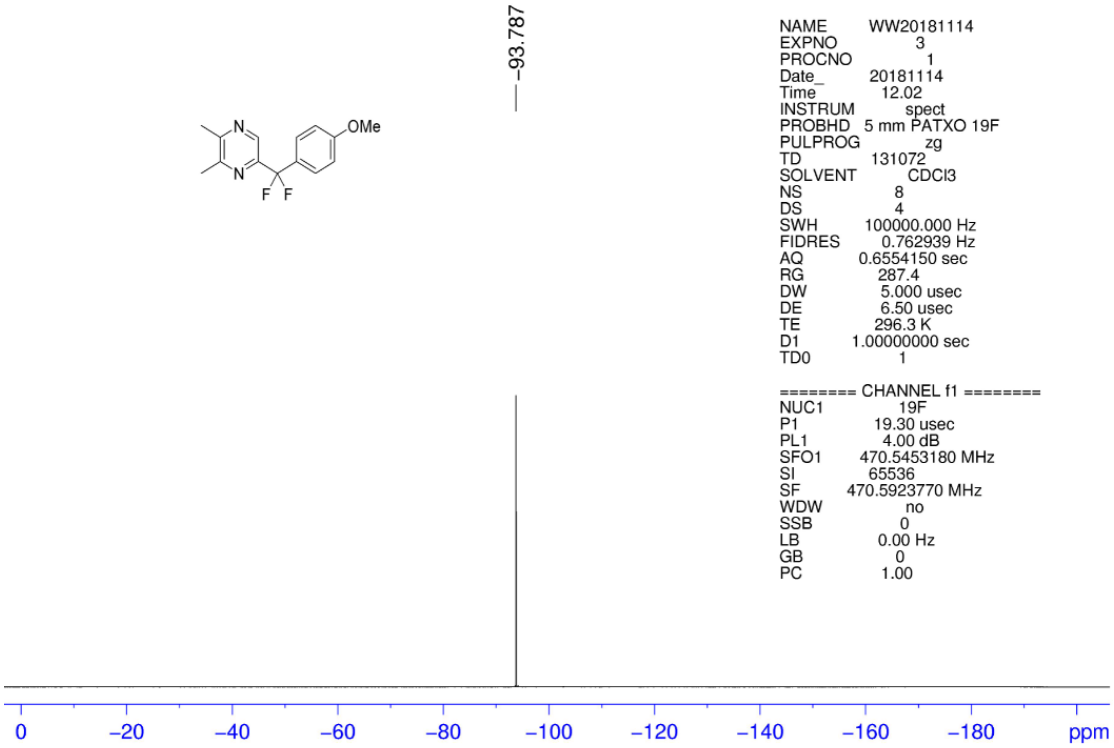
^{1}H NMR Spectra of **3ba**



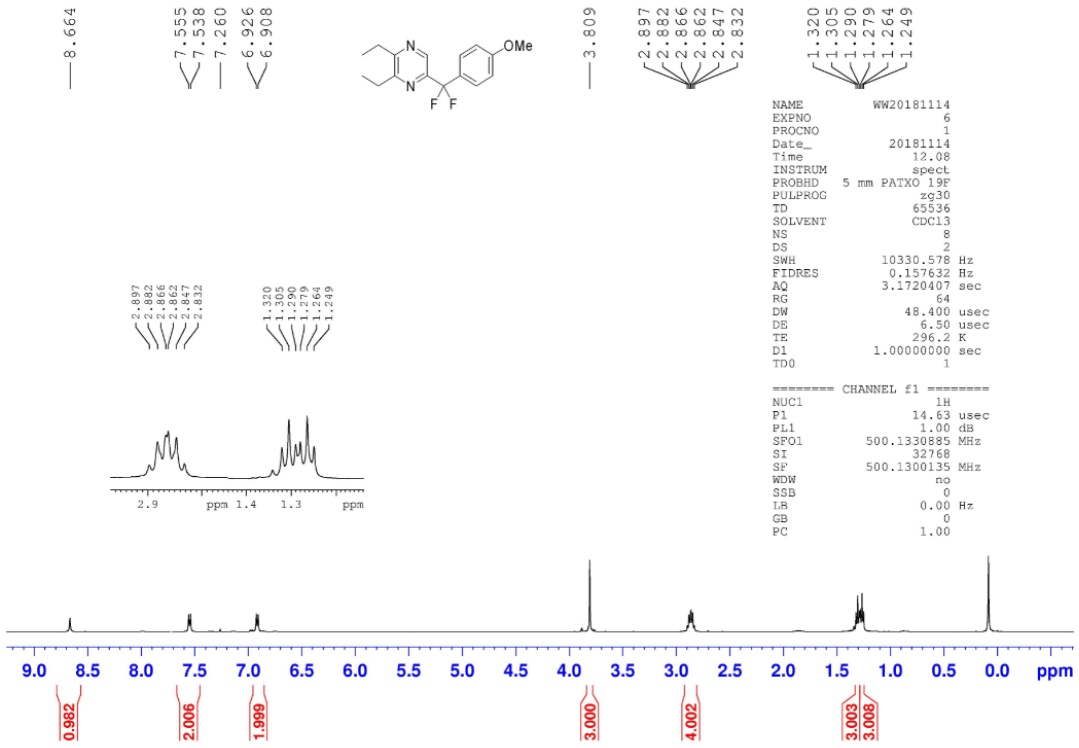
^{13}C NMR Spectra of **3ba**



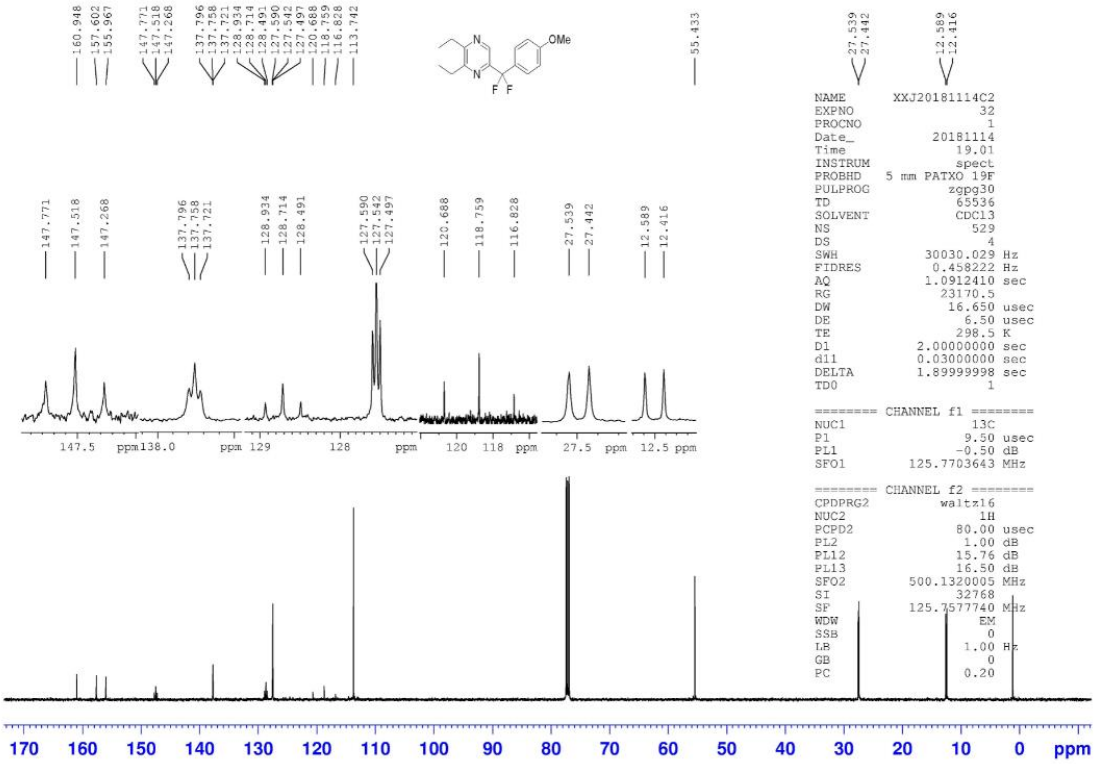
^{19}F NMR Spectra of **3ba**



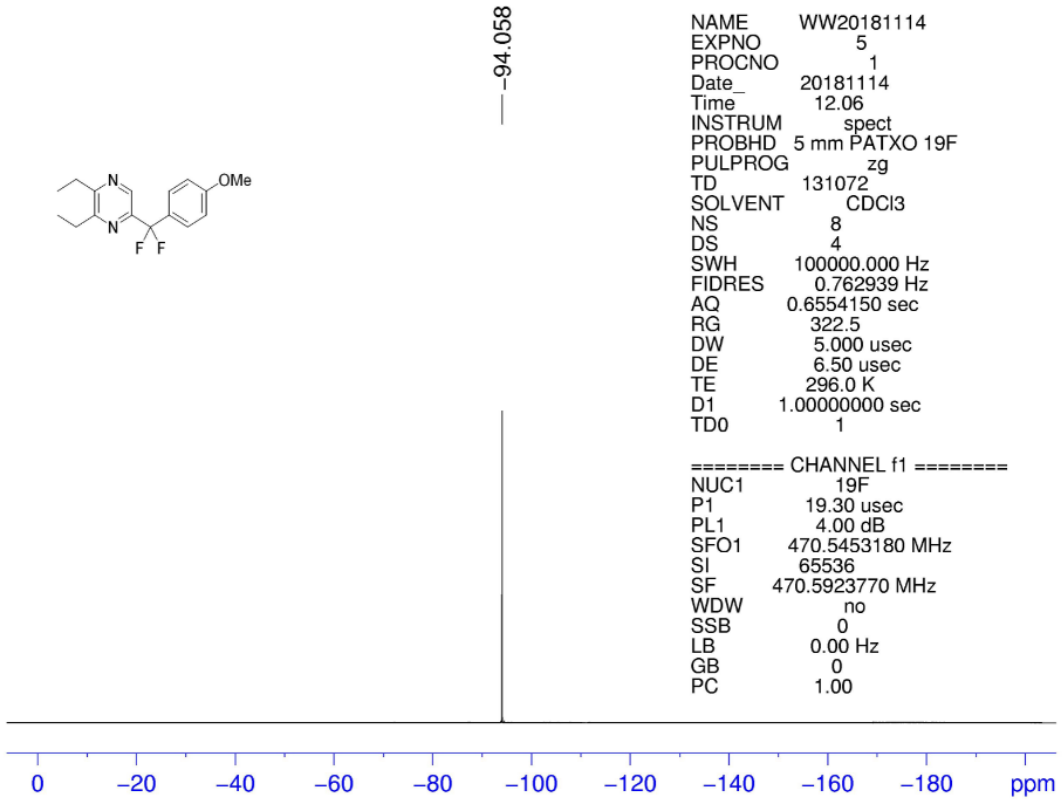
^{1}H NMR Spectra of **3ca**



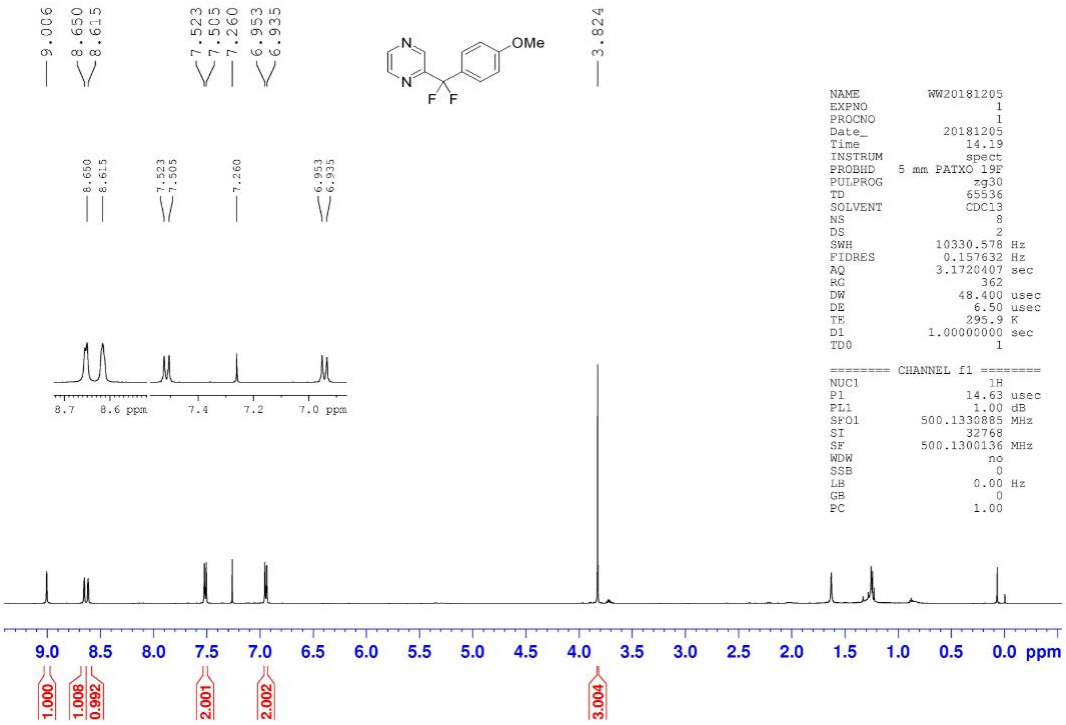
^{13}C NMR Spectra of **3ca**



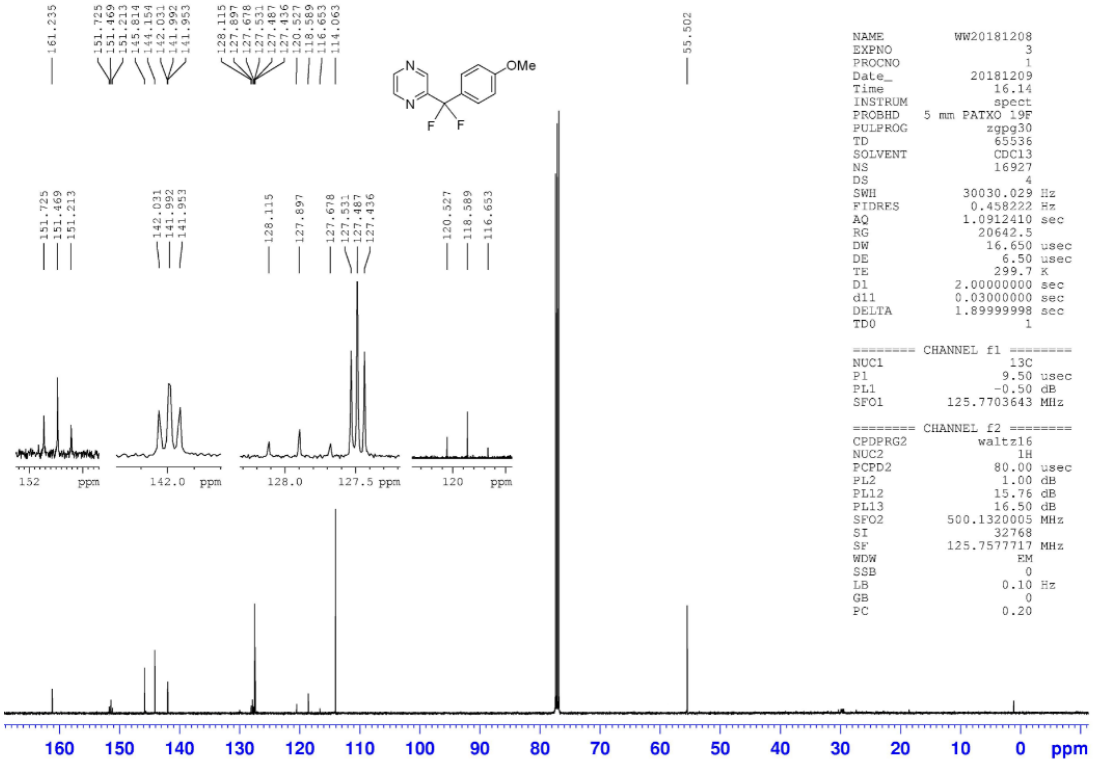
^{19}F NMR Spectra of **3ca**



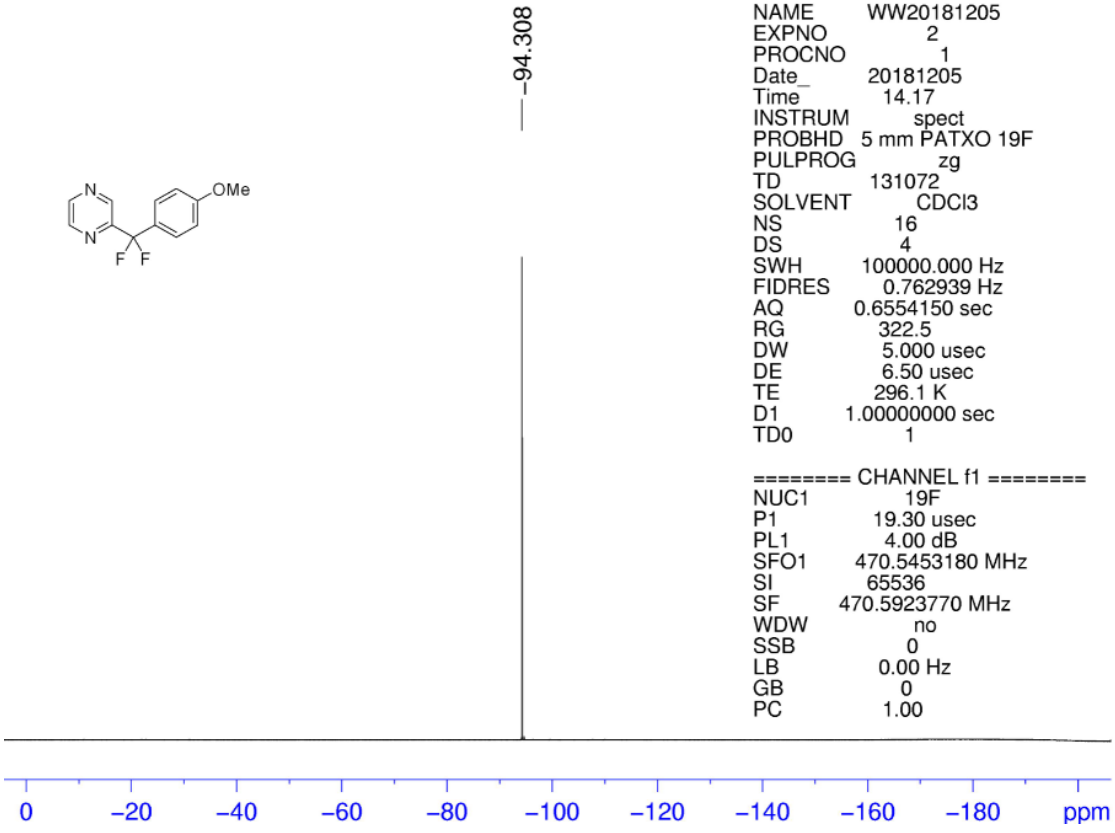
^{1}H NMR Spectra of **3da**



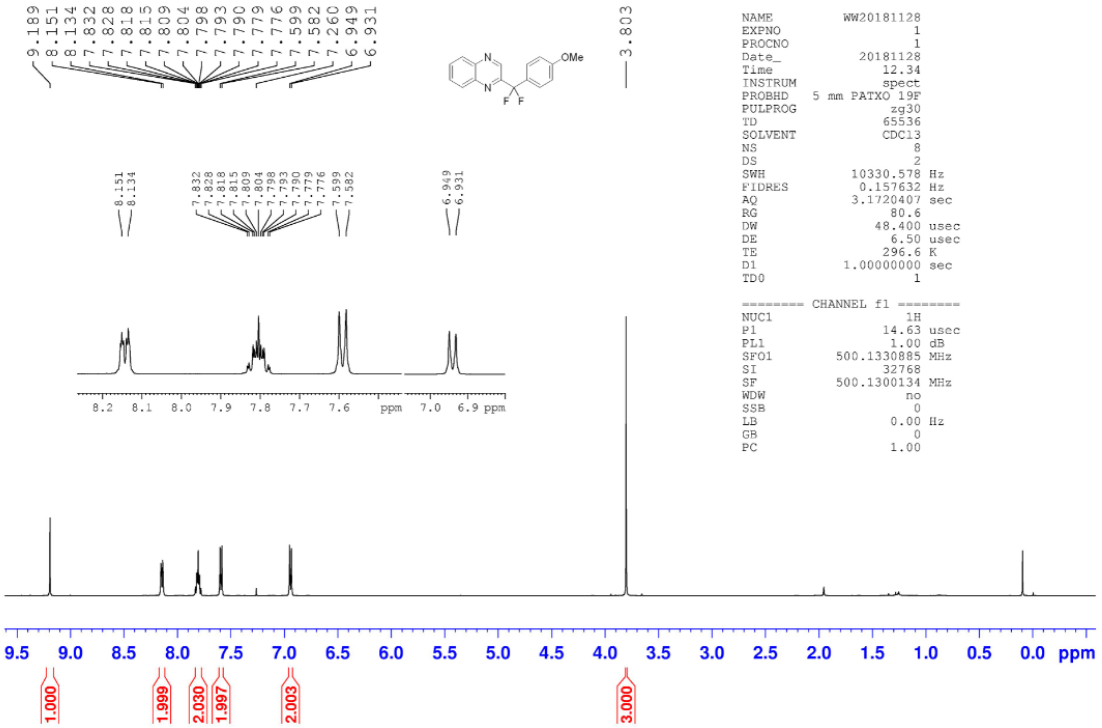
^{13}C NMR Spectra of **3da**



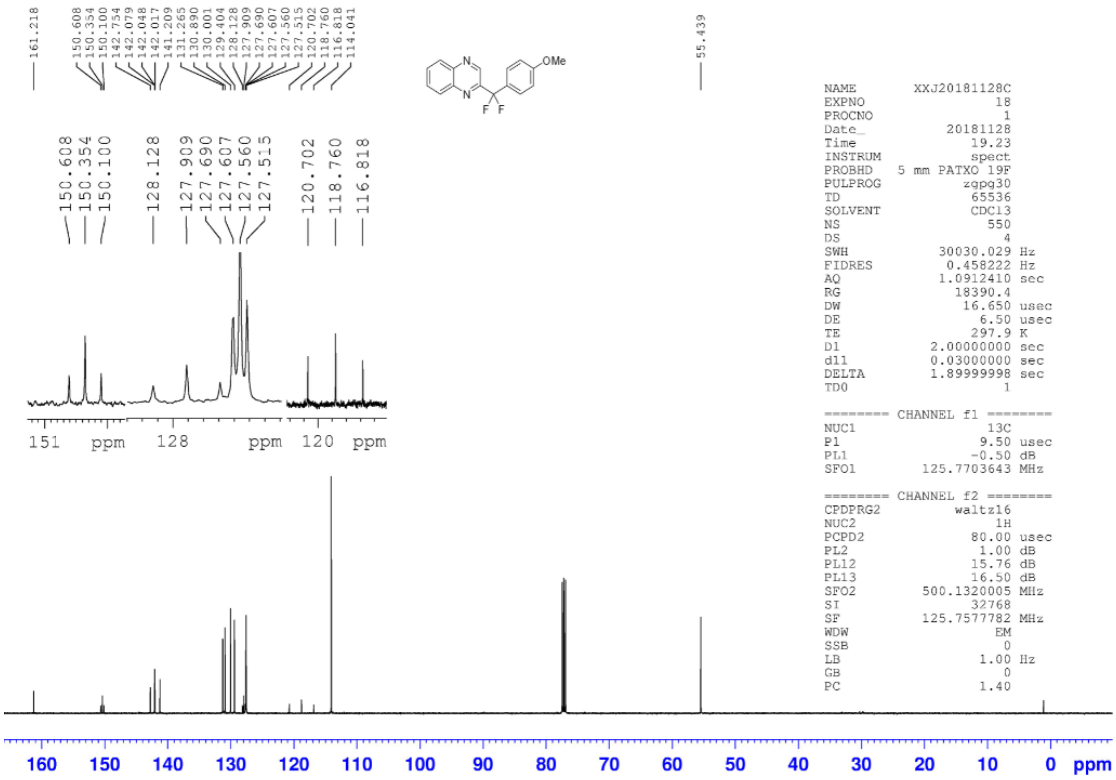
^{19}F NMR Spectra of **3da**



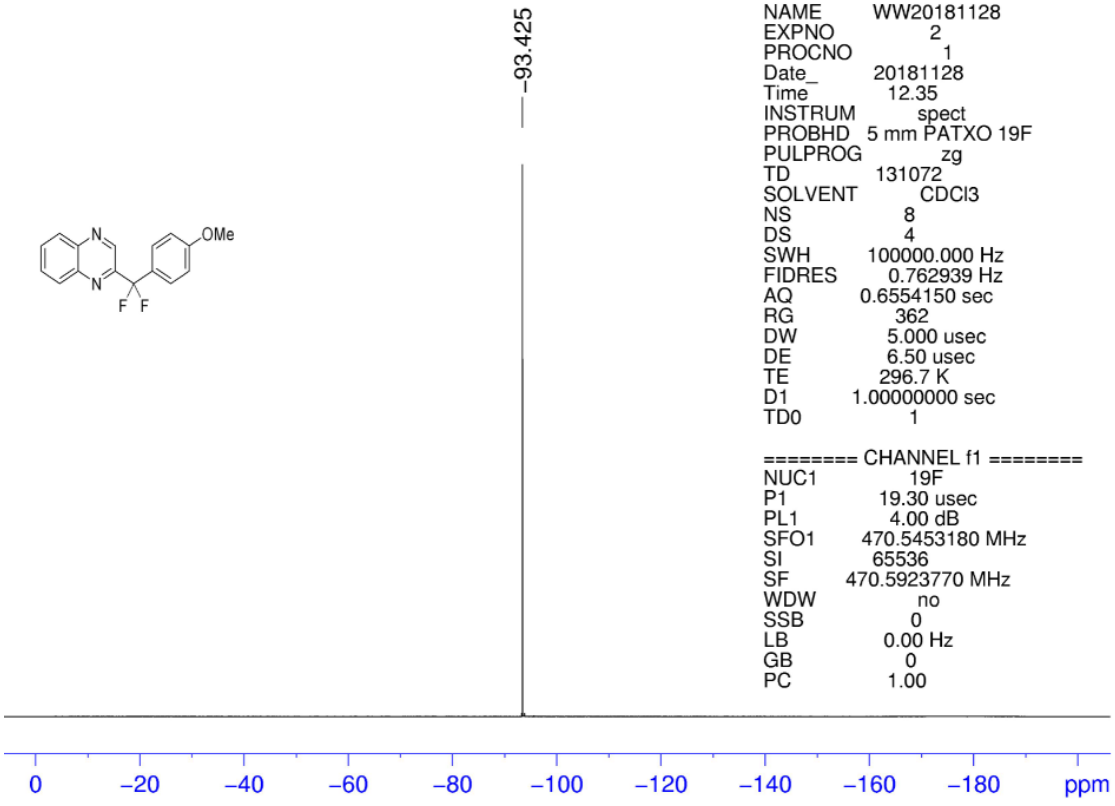
^{1}H NMR Spectra of **3ea**



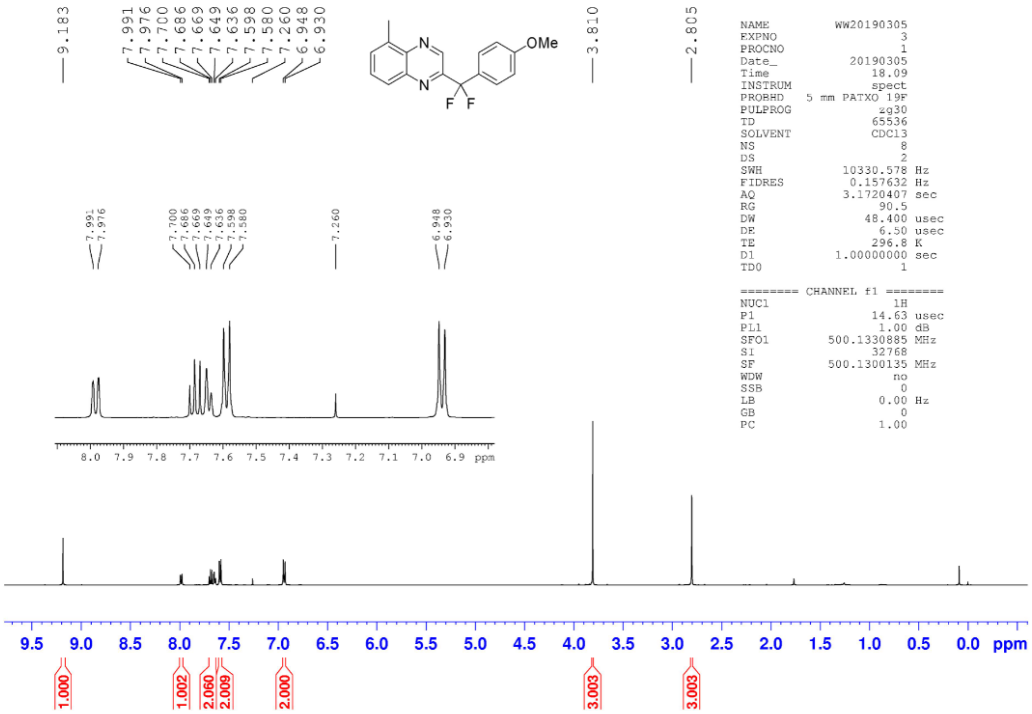
^{13}C NMR Spectra of **3ea**



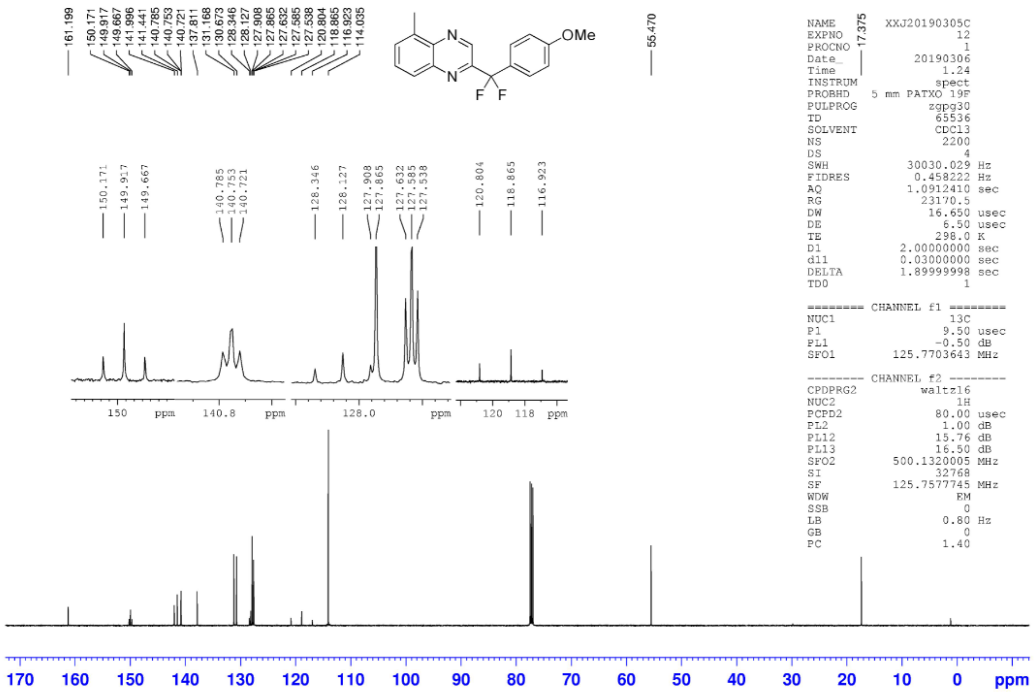
^{19}F NMR Spectra of **3ea**



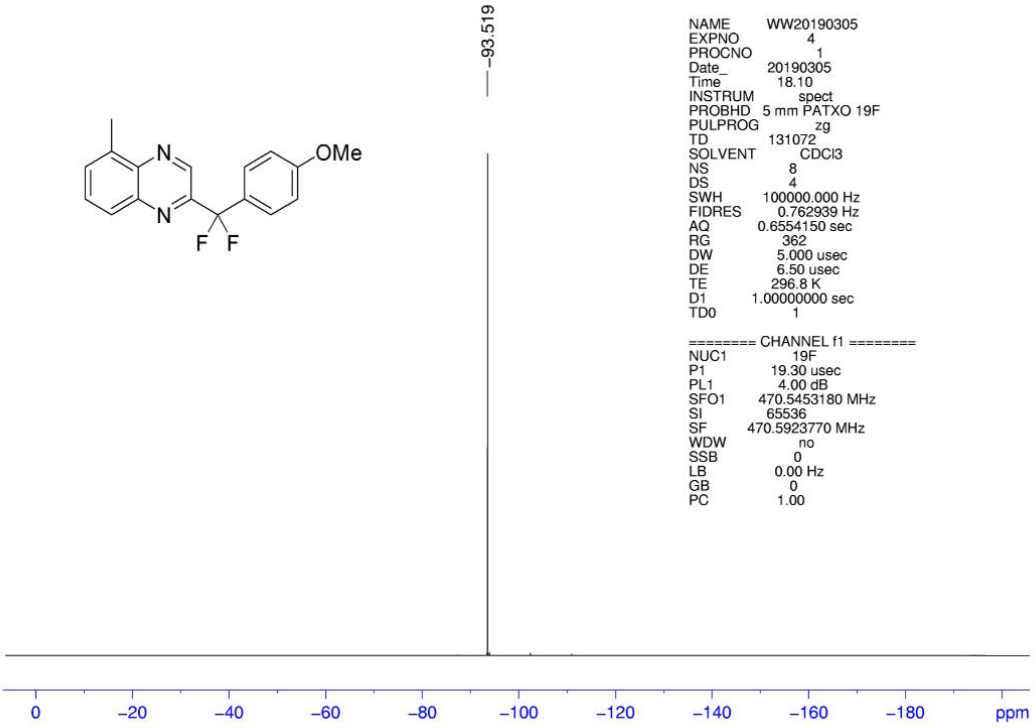
^{1}H NMR Spectra of **3fa**



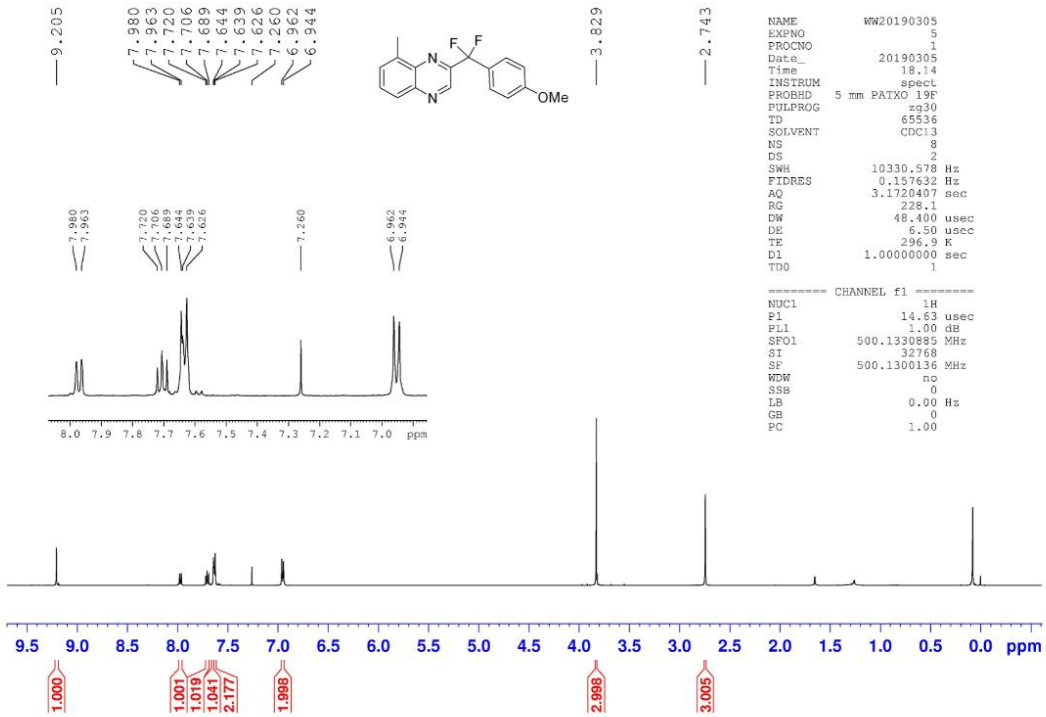
^{13}C NMR Spectra of **3fa**



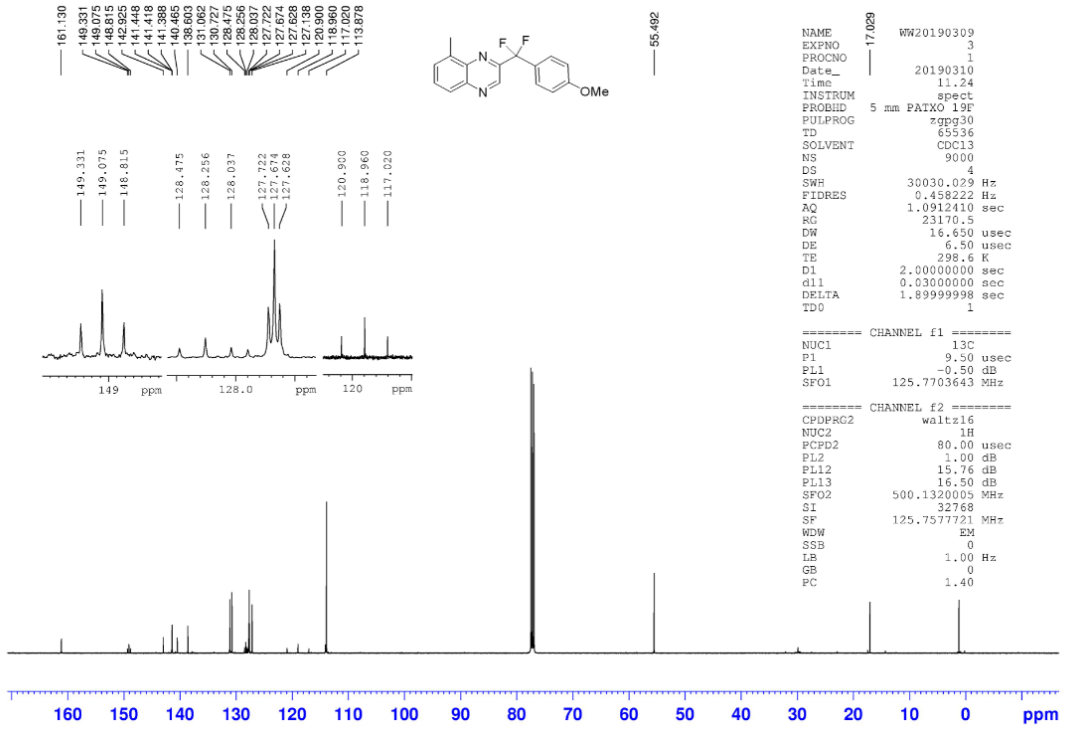
^{19}F NMR Spectra of **3fa**



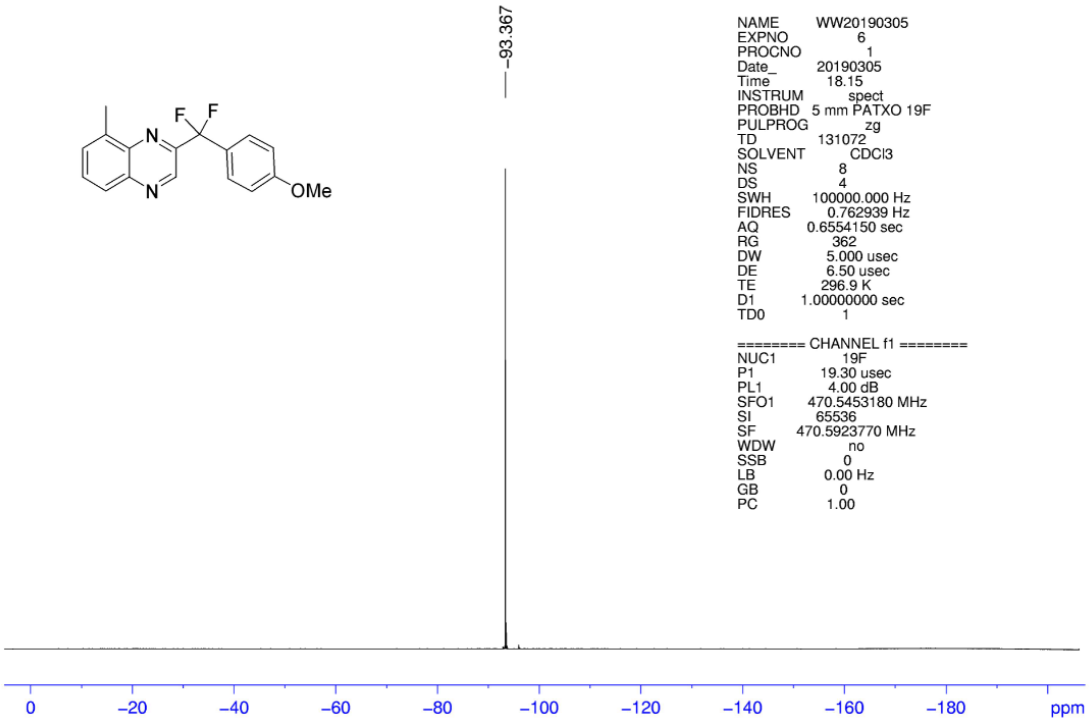
^{1}H NMR Spectra of **3f'a**



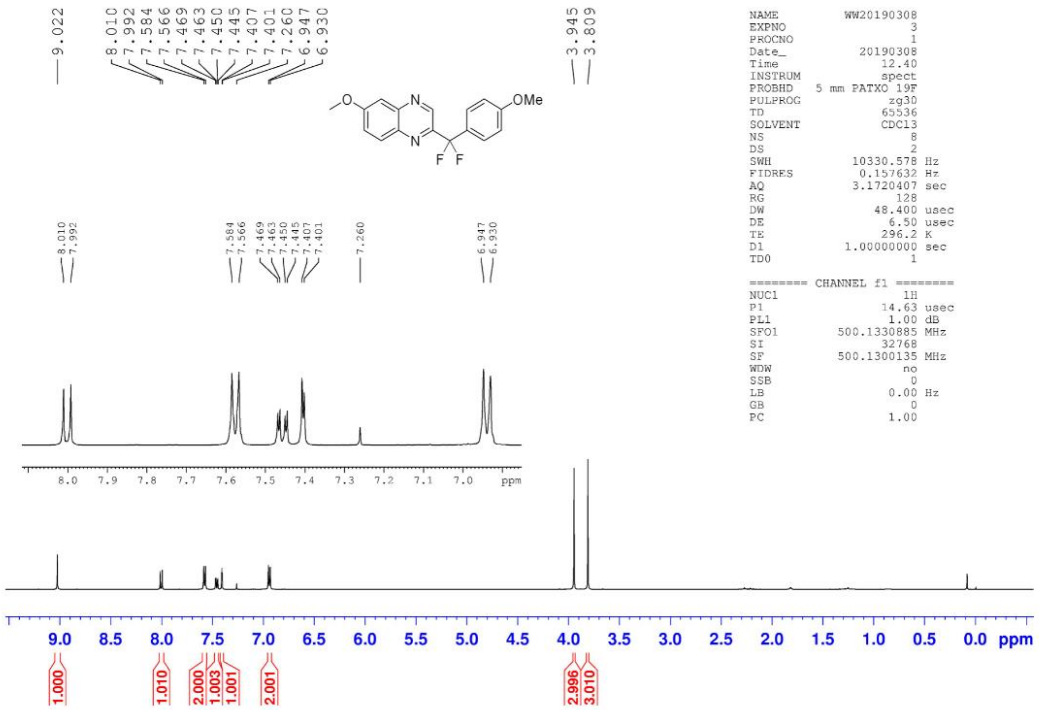
^{13}C NMR Spectra of **3f'a**



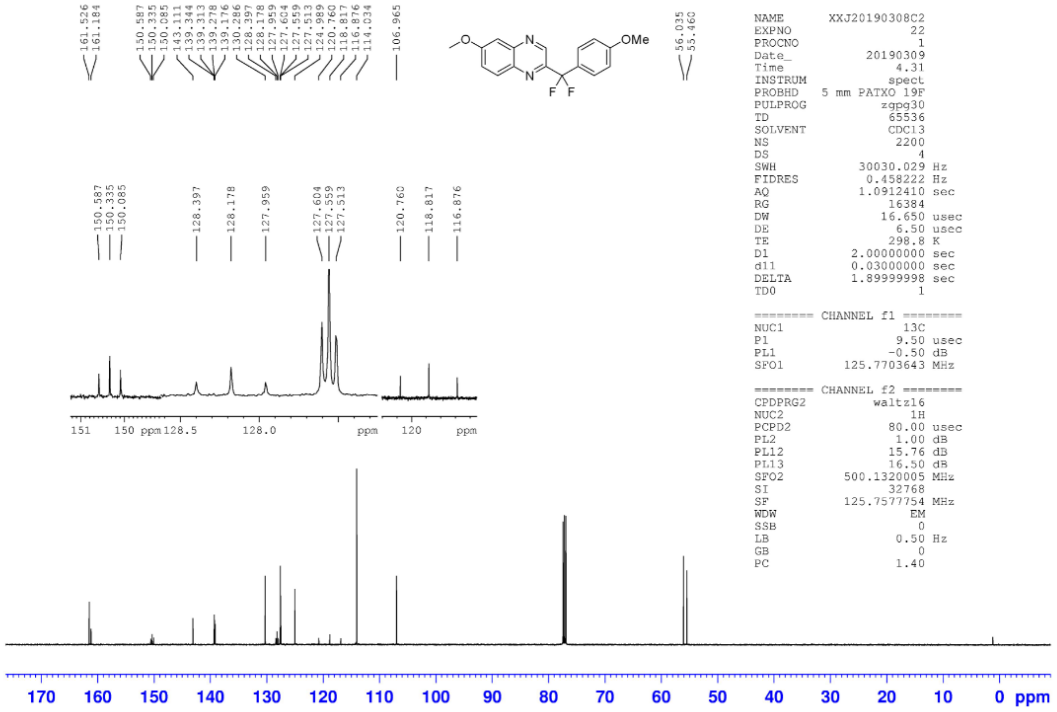
^{19}F NMR Spectra of **3f'a**



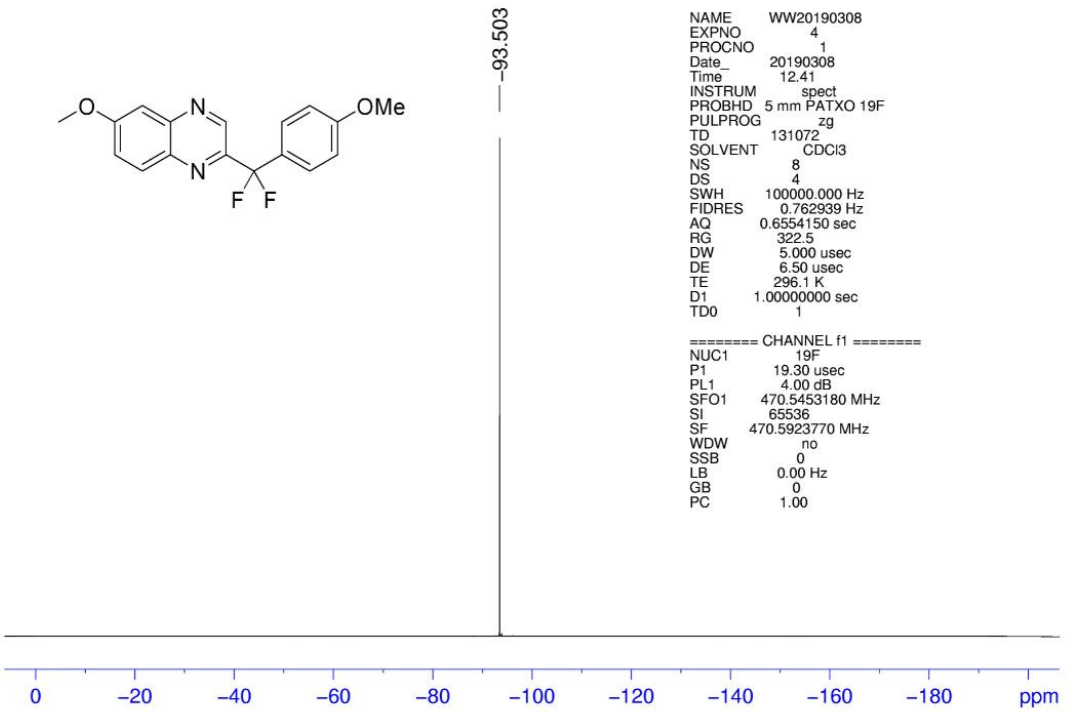
^{1}H NMR Spectra of **3ga**



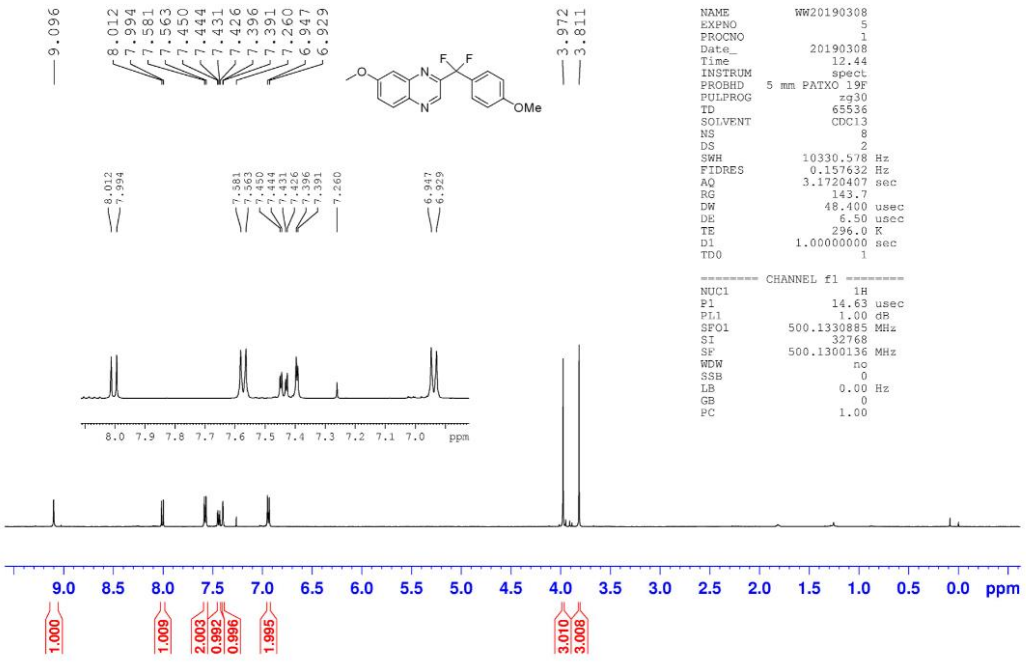
^{13}C NMR Spectra of **3ga**



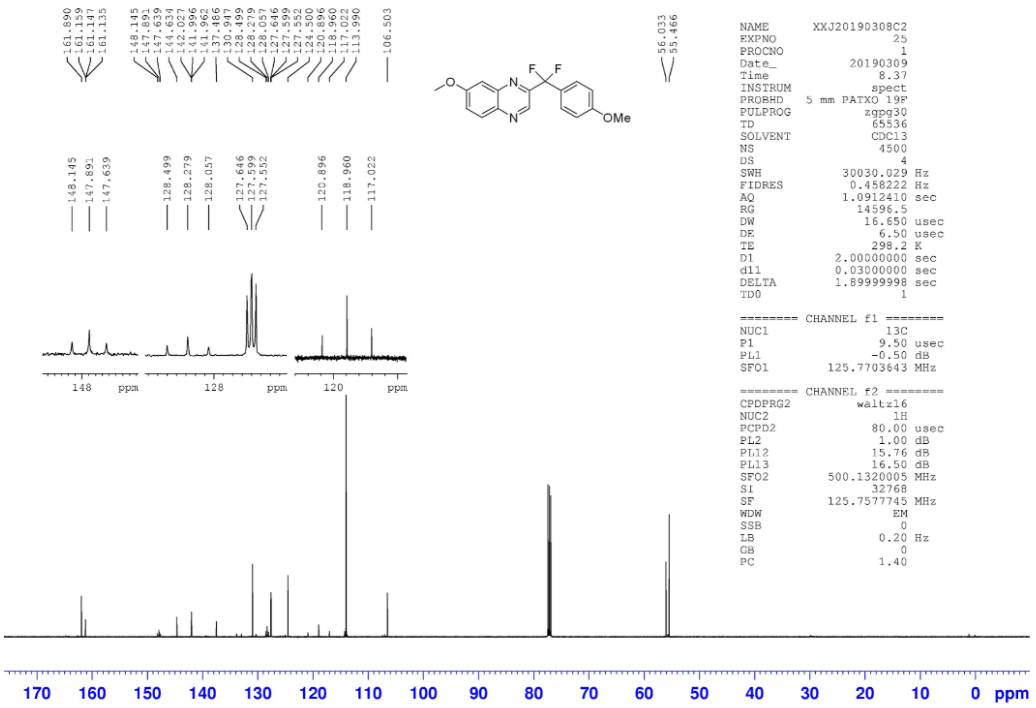
^{19}F NMR Spectra of **3ga**



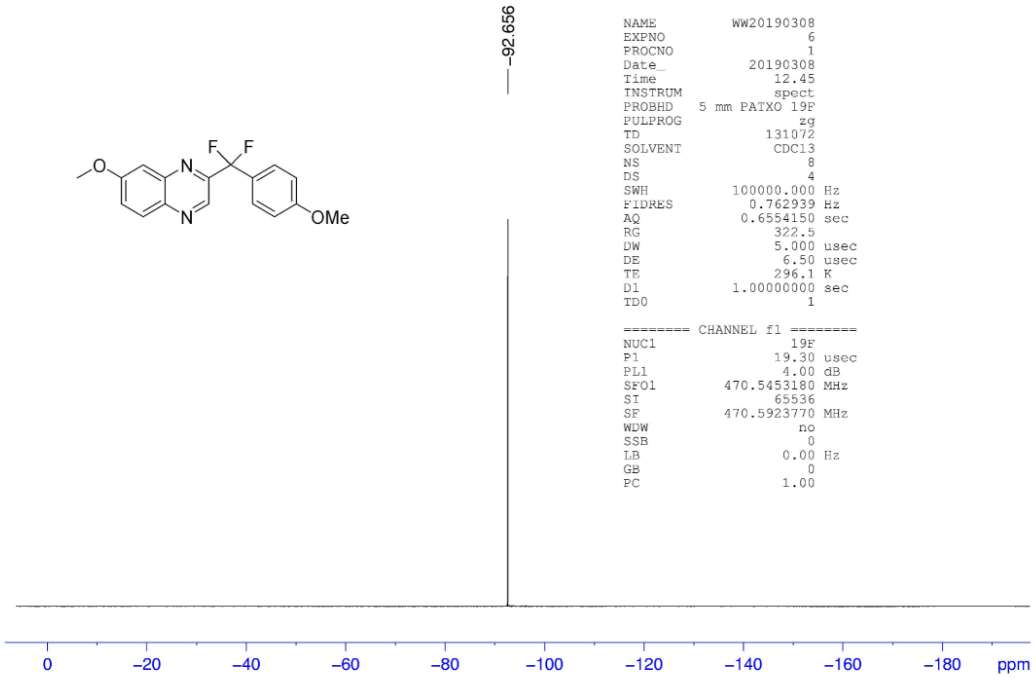
^{1}H NMR Spectra of **3g'a**



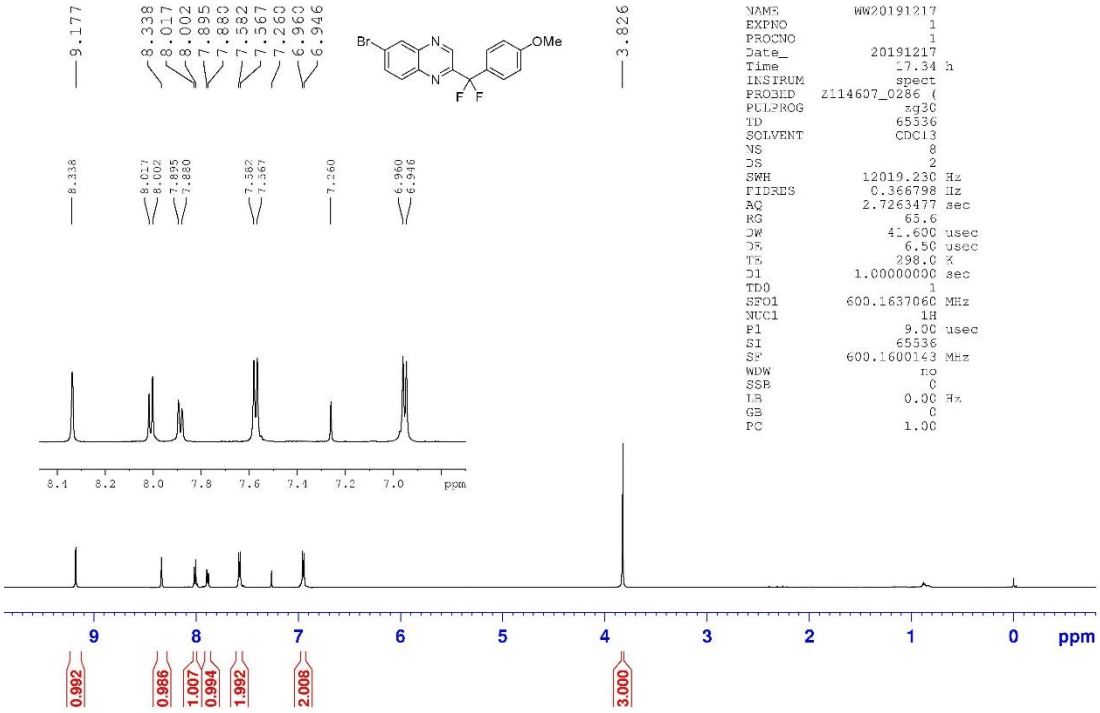
^{13}C NMR Spectra of **3g'a**



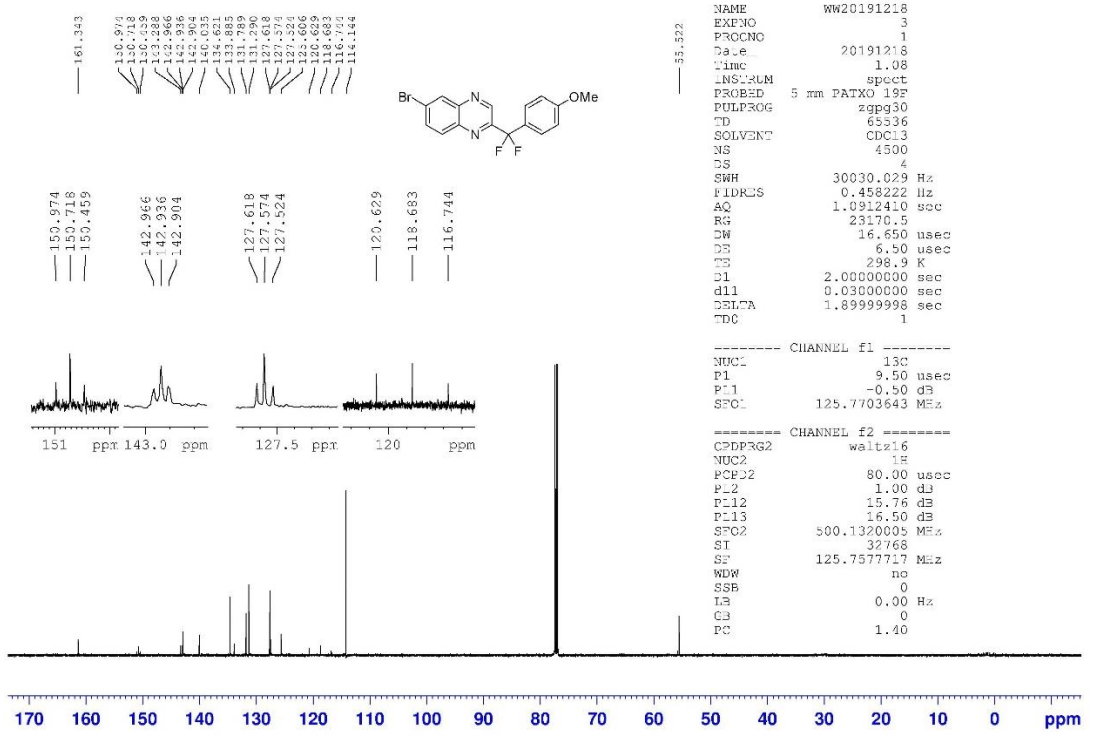
^{19}F NMR Spectra of **3g'a**



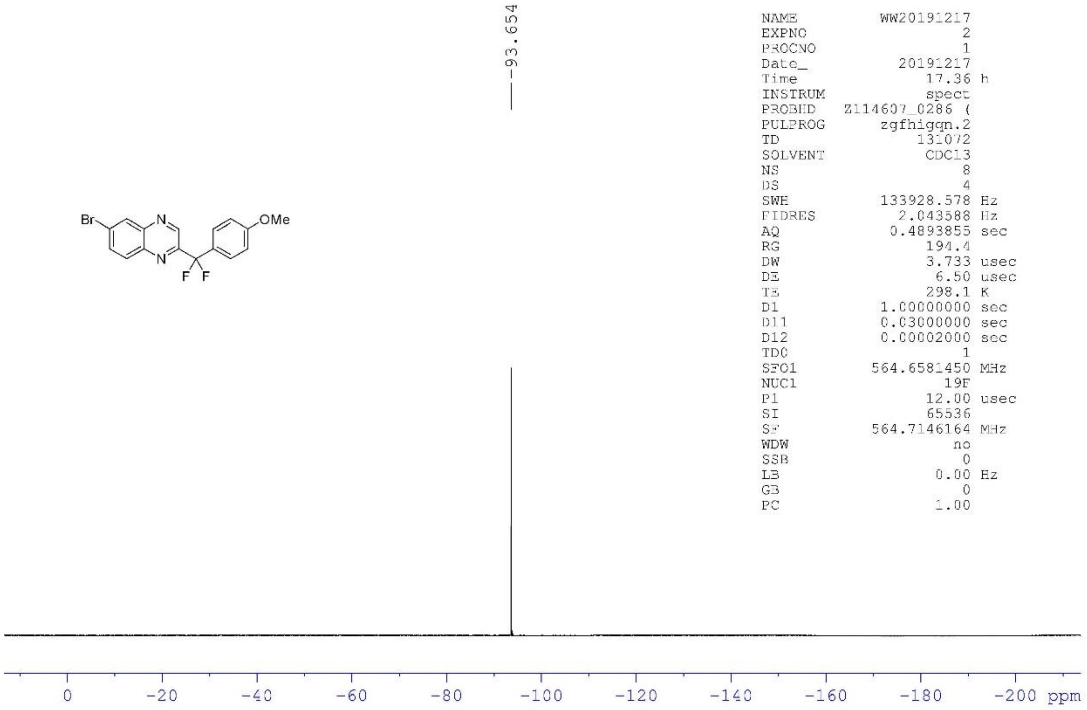
^{1}H NMR Spectra of **3ha**



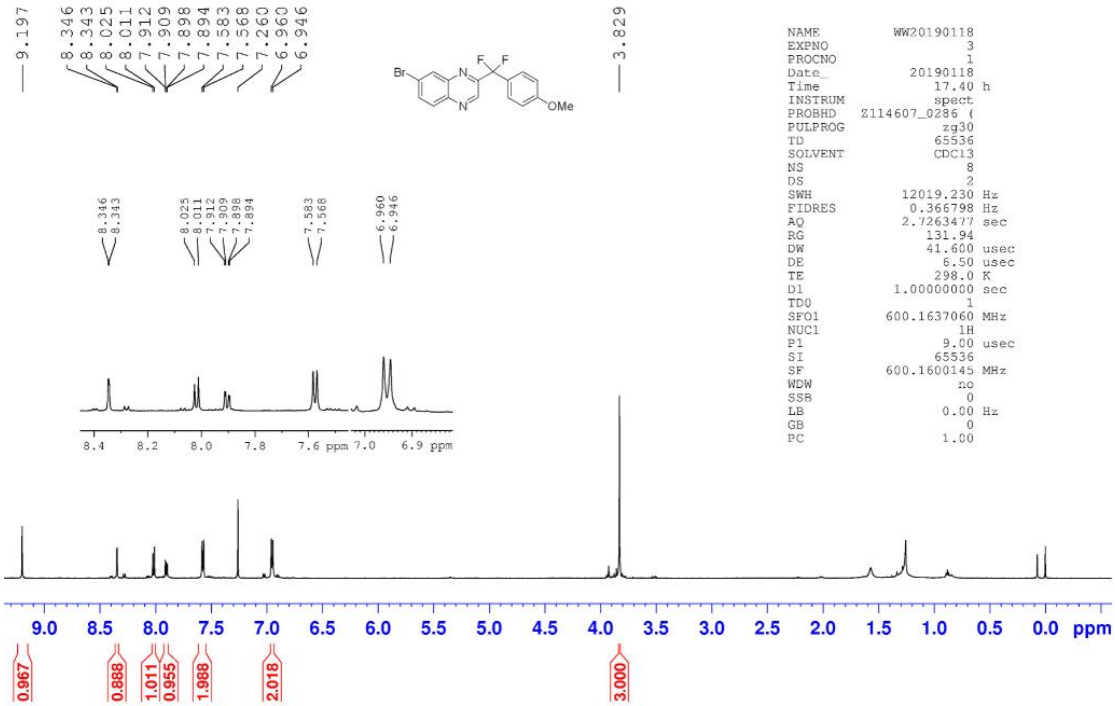
^{13}C NMR Spectra of **3ha**



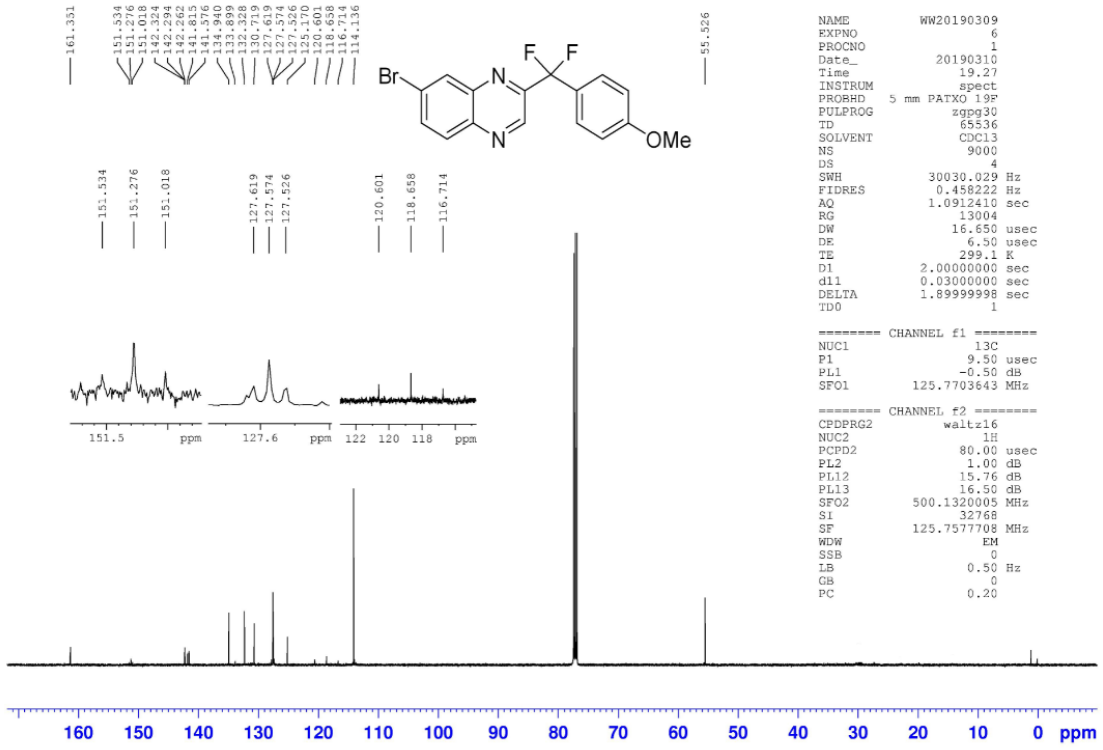
^{19}F NMR Spectra of **3ha**



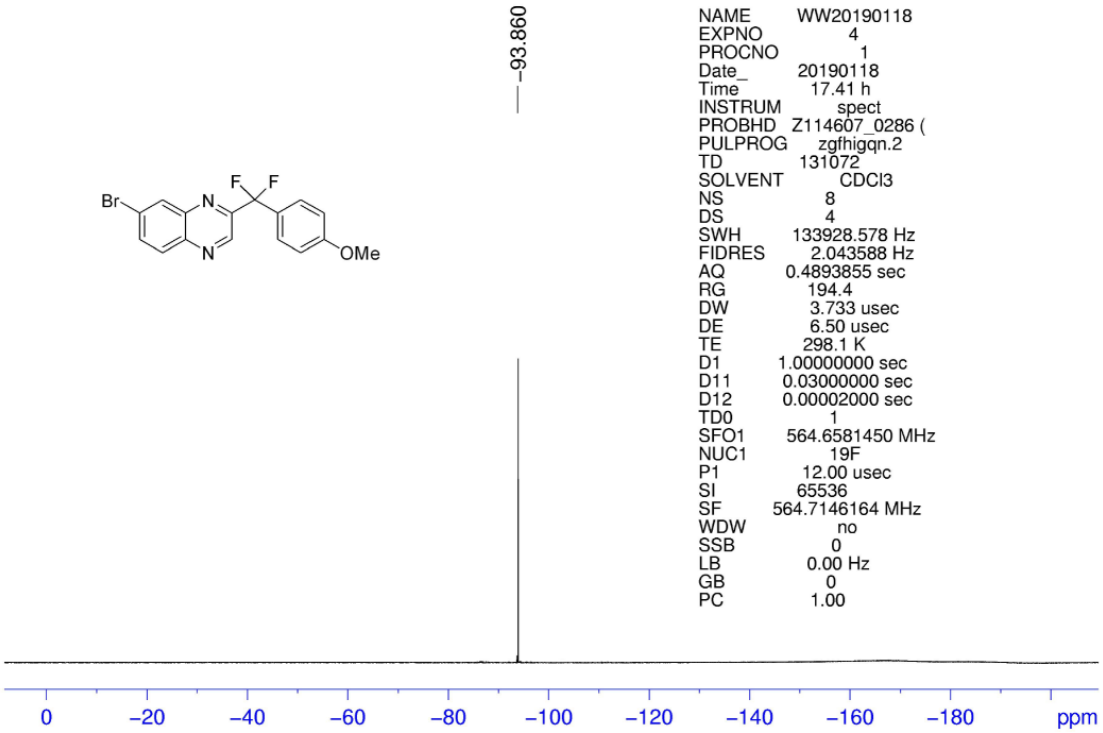
^{1}H NMR Spectra of **3h'a**



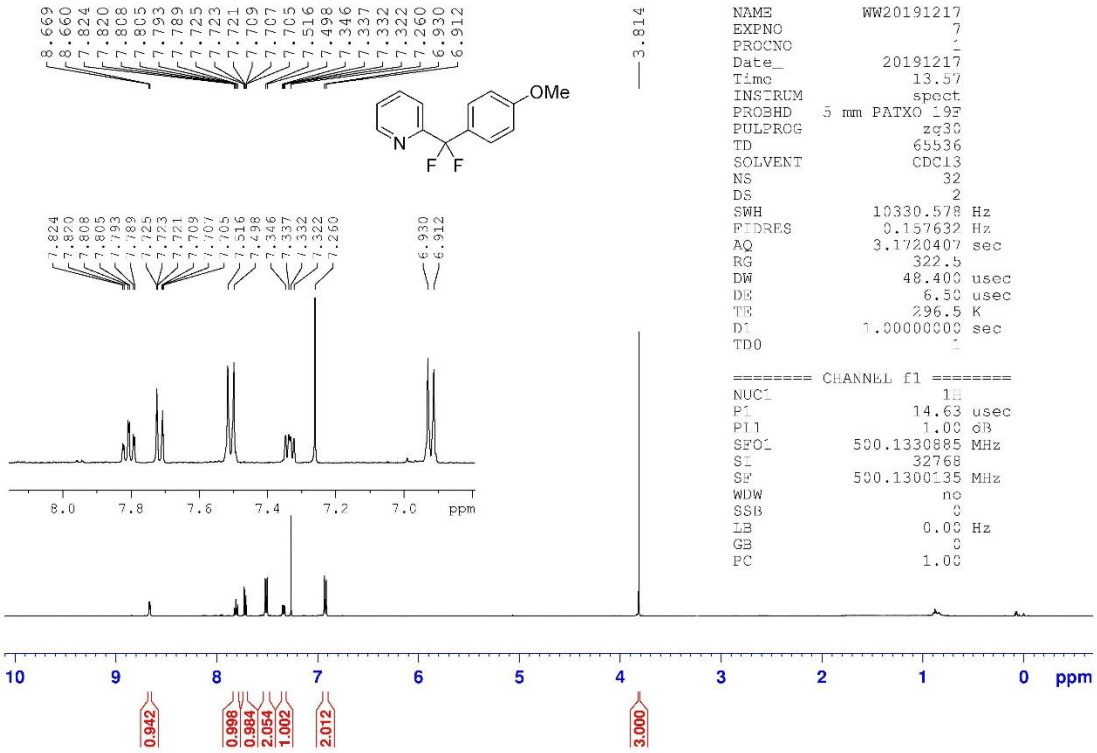
^{13}C NMR Spectra of **3h'a**



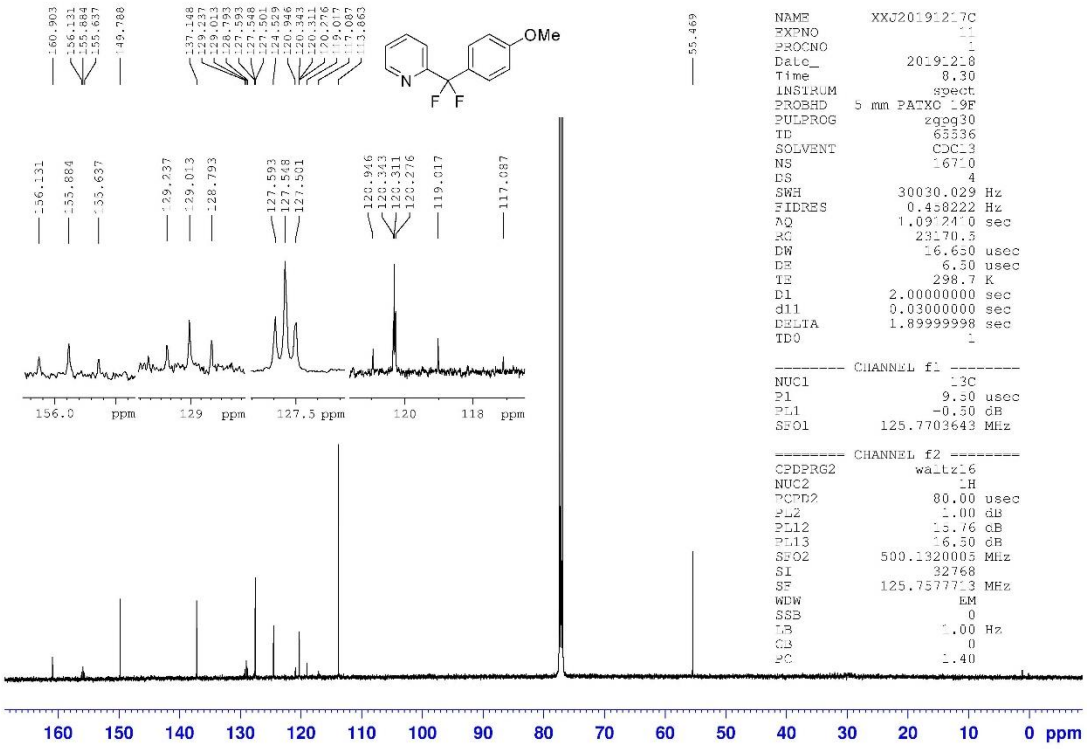
^{19}F NMR Spectra of **3h'a**



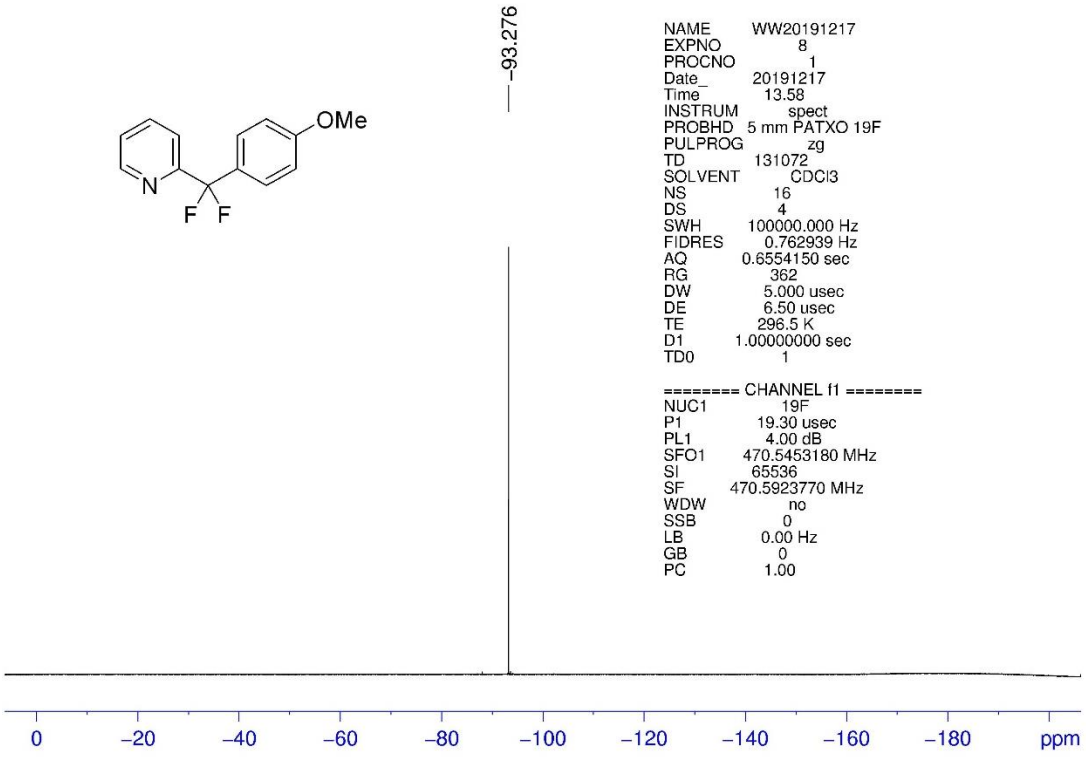
^{1}H NMR Spectra of **3ia**



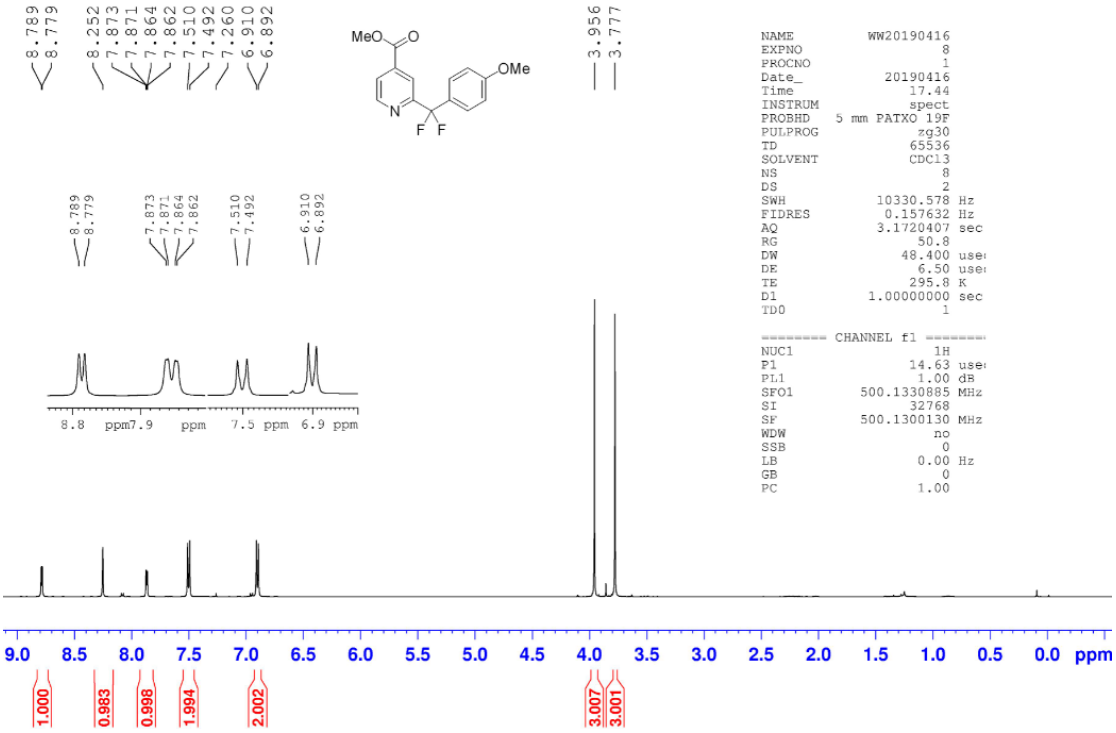
^{13}C NMR Spectra of **3ia**



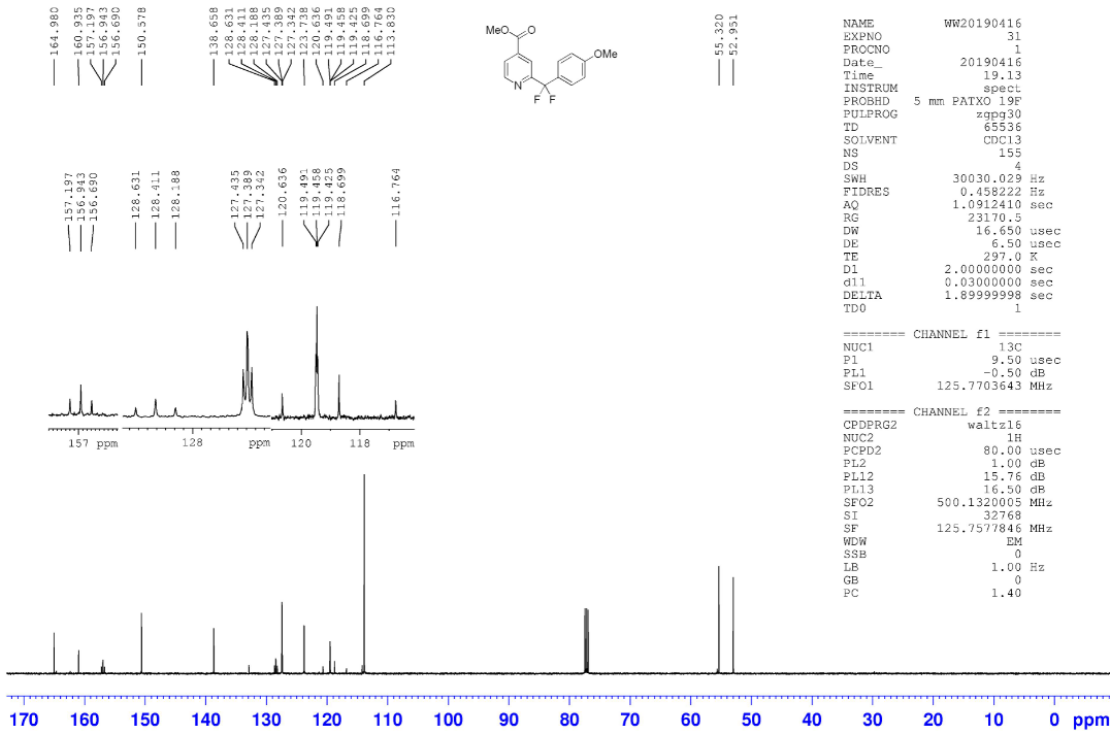
^{19}F NMR Spectra of **3ia**



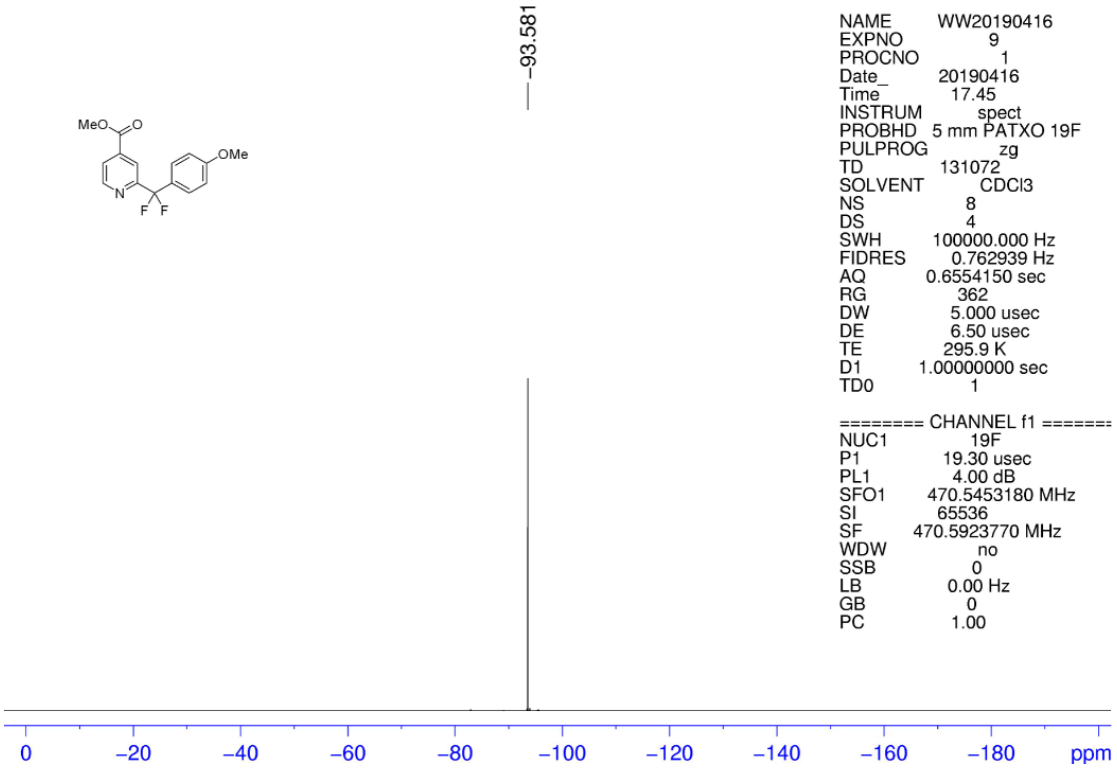
^{1}H NMR Spectra of **3ja**



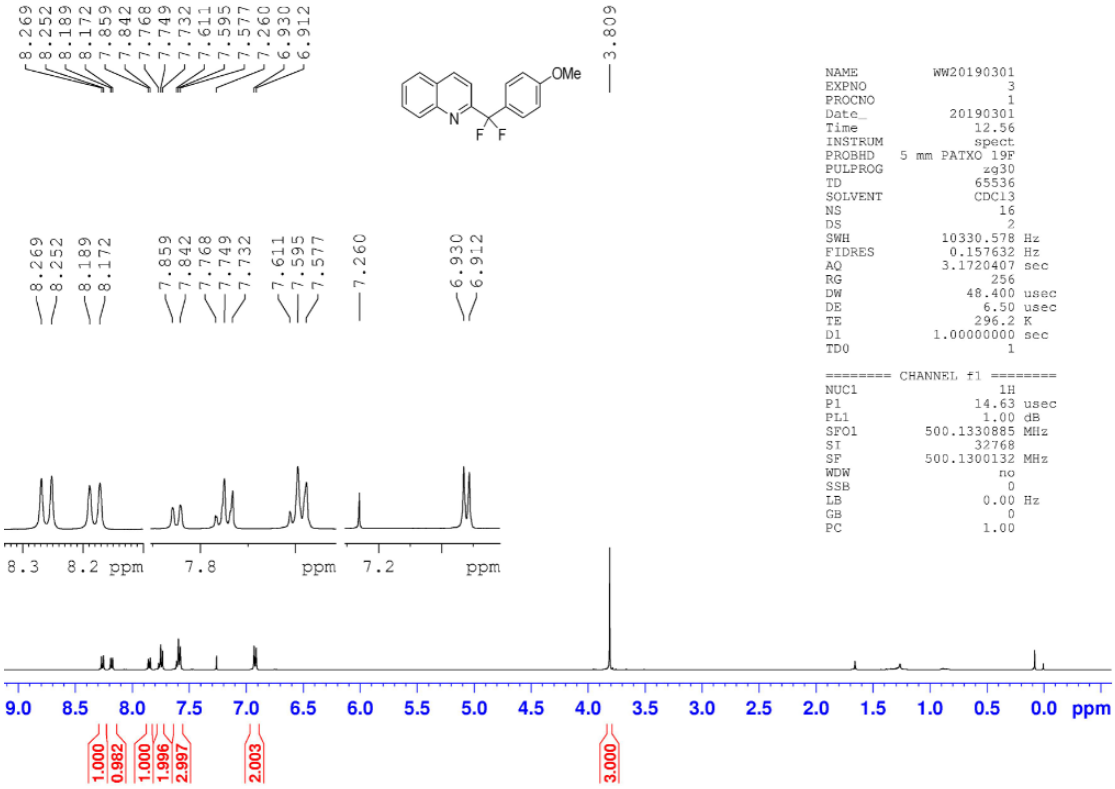
^{13}C NMR Spectra of **3ja**



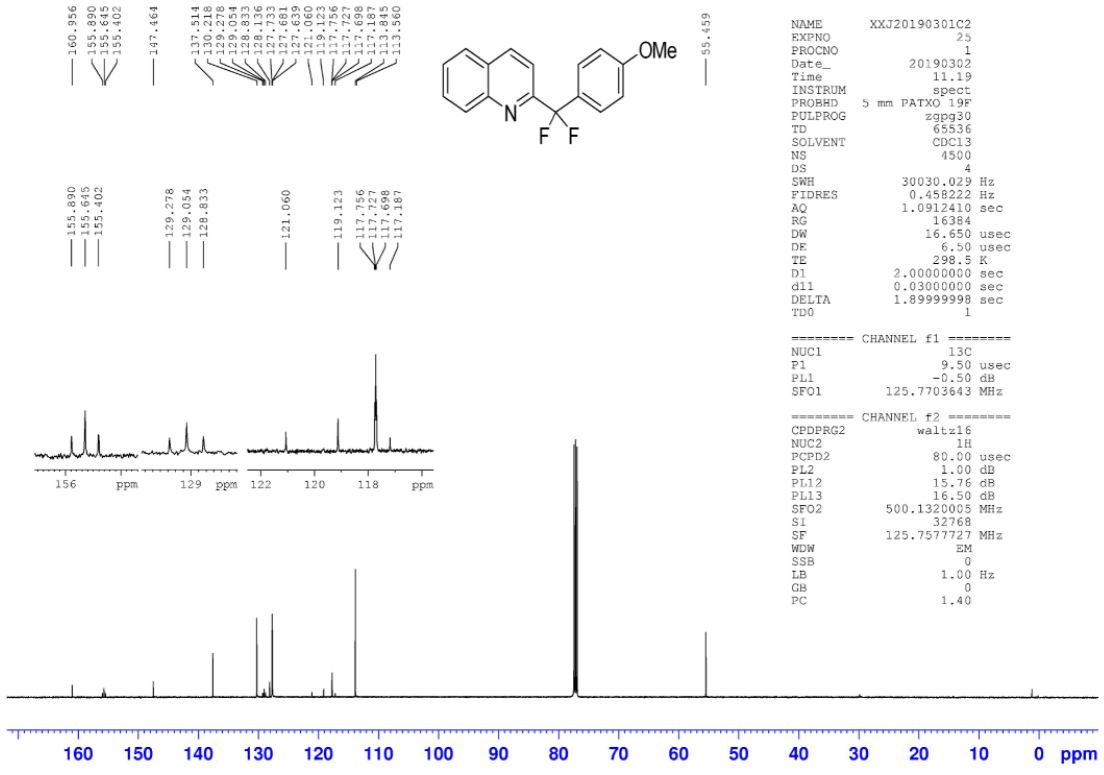
^{19}F NMR Spectra of **3ja**



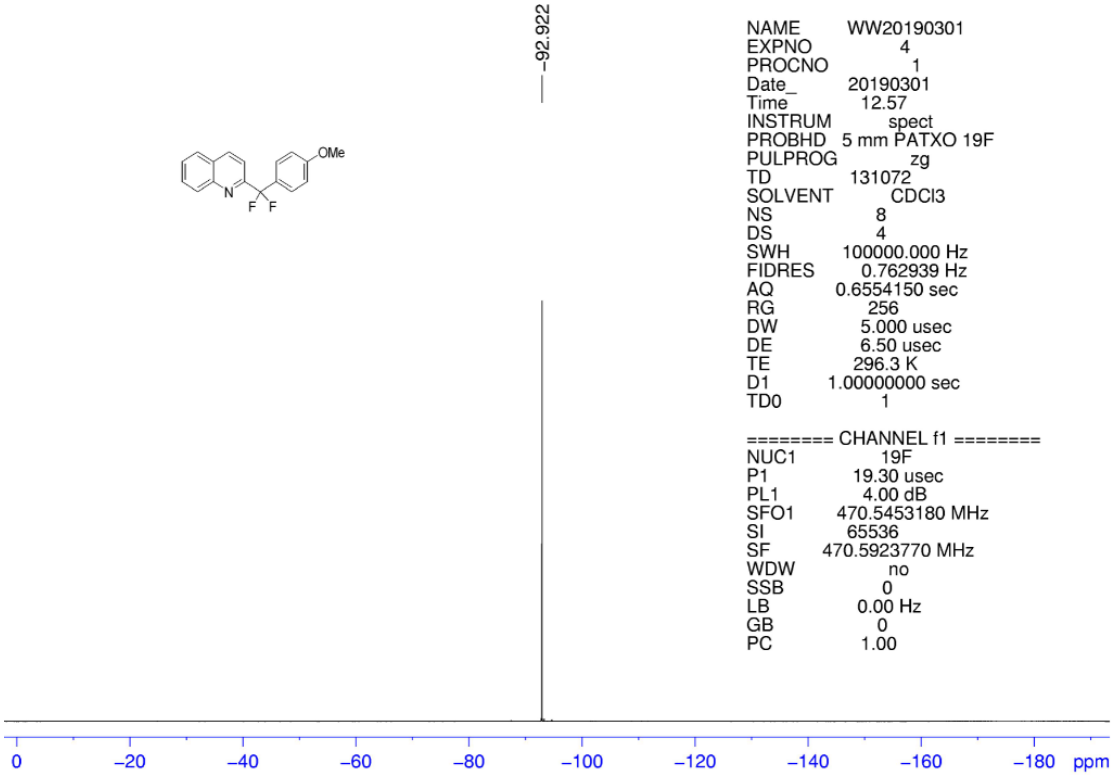
^{1}H NMR Spectra of **3ka**



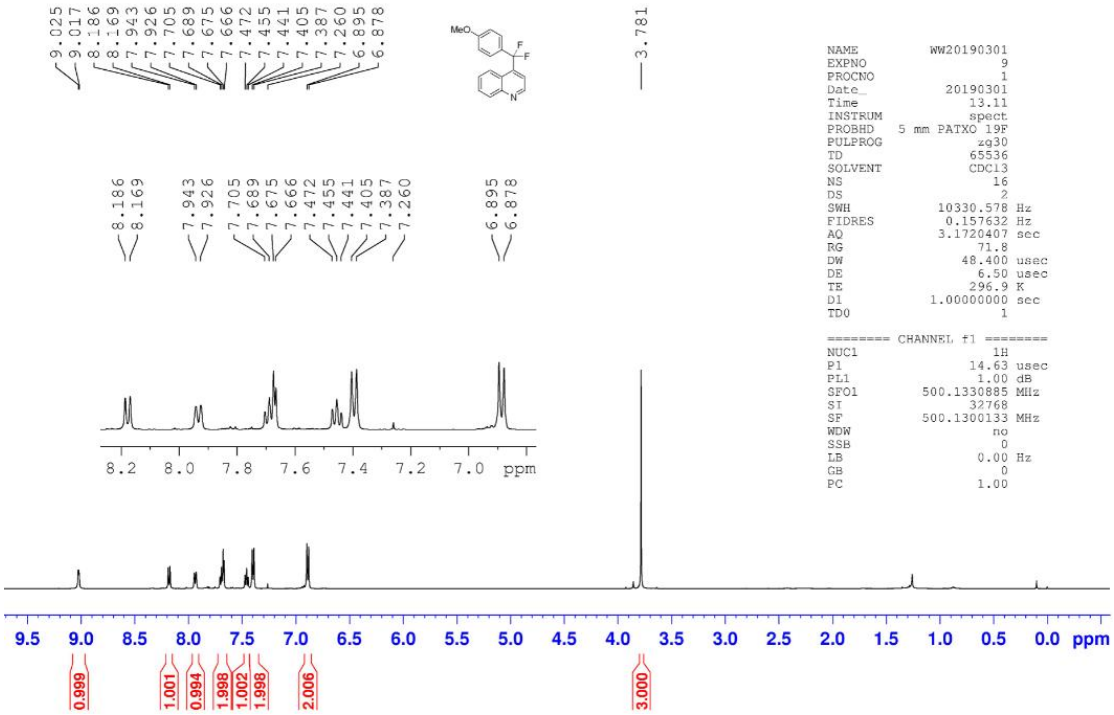
^{13}C NMR Spectra of **3ka**



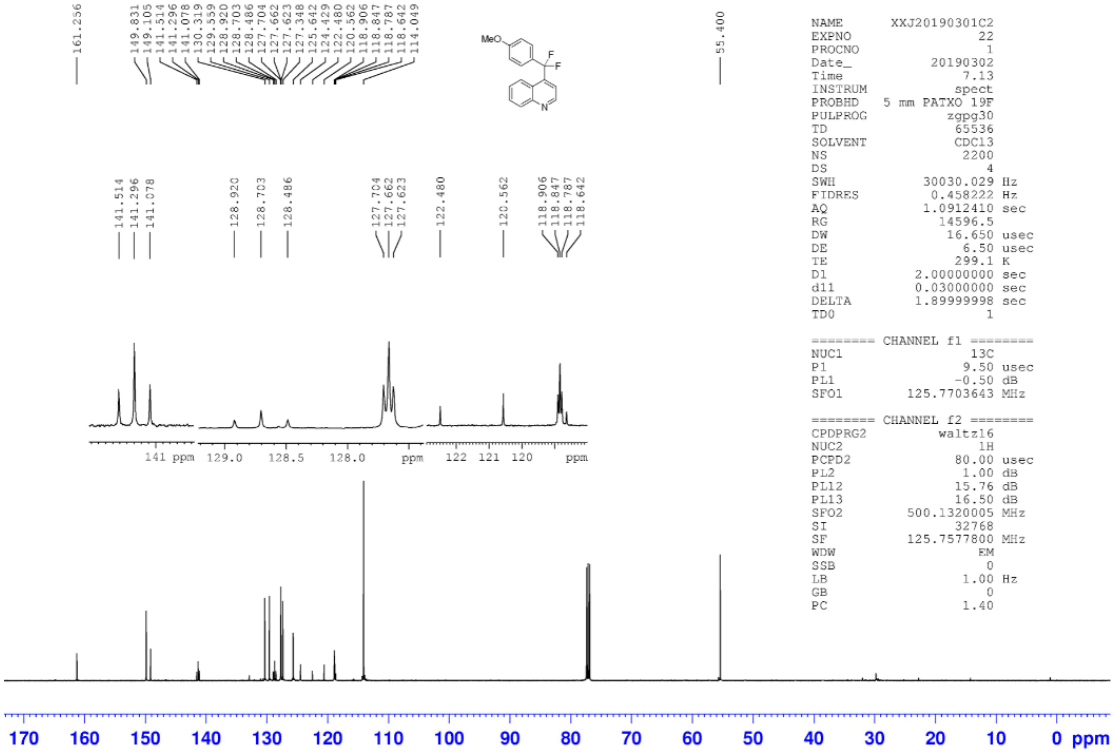
^{19}F NMR Spectra of **3ka**



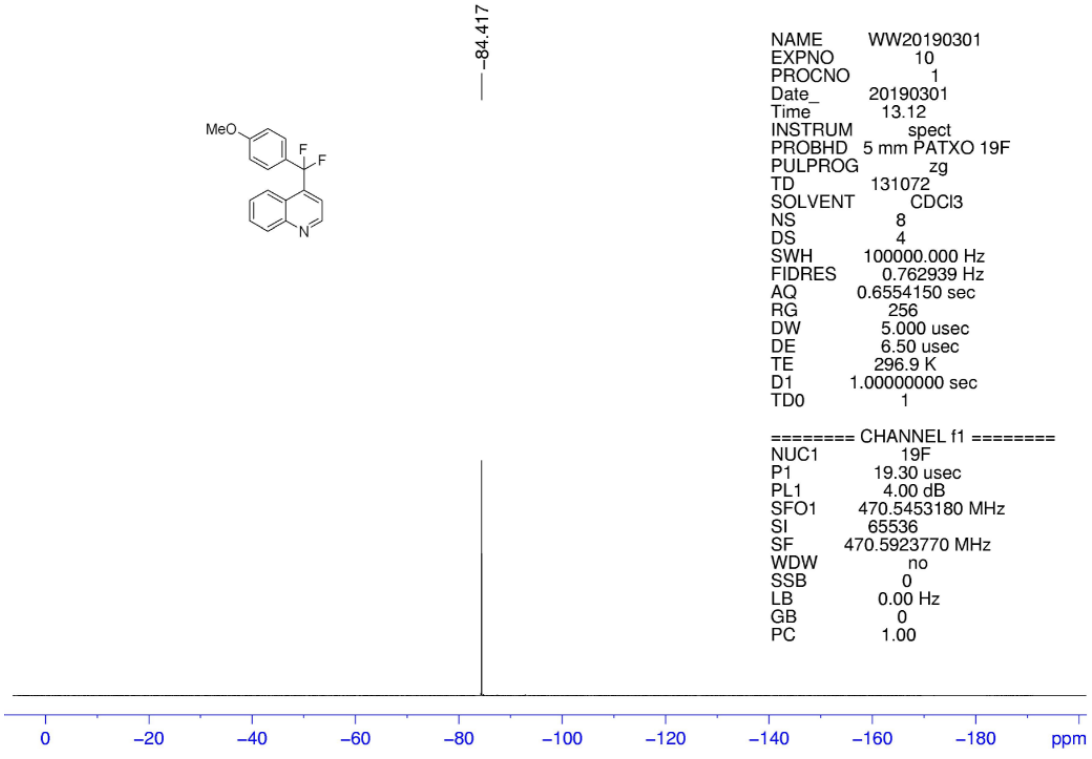
^{1}H NMR Spectra of **3k'a**



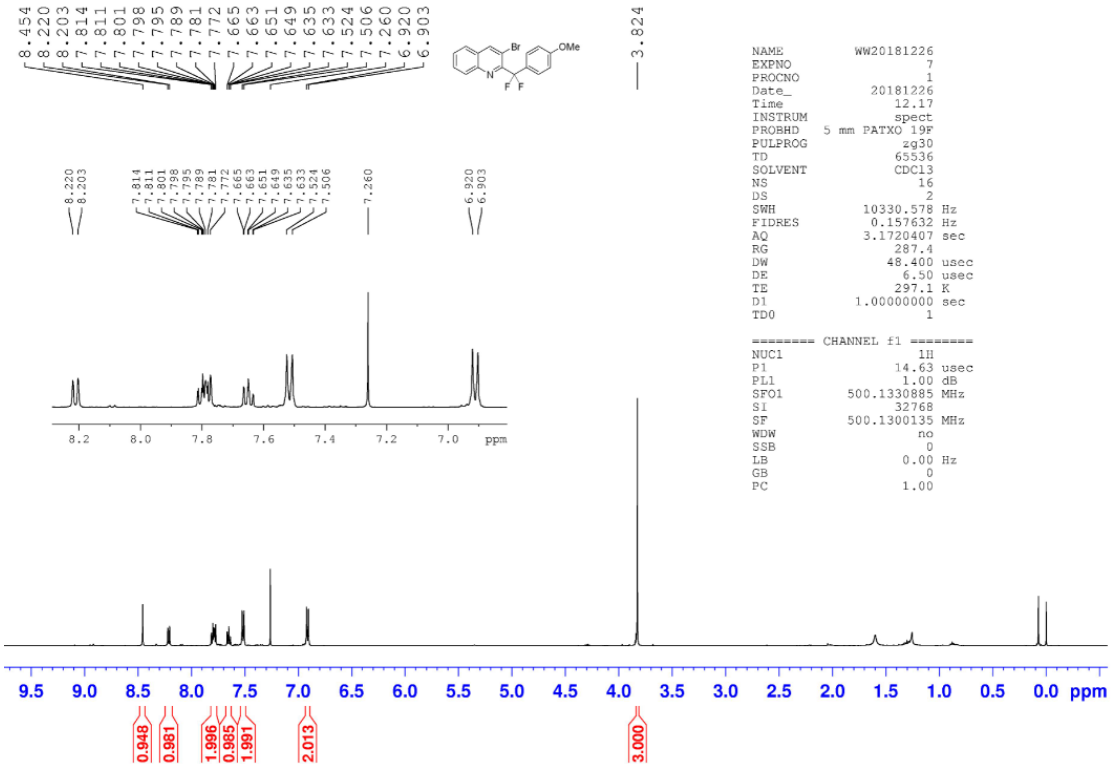
^{13}C NMR Spectra of **3k'a**



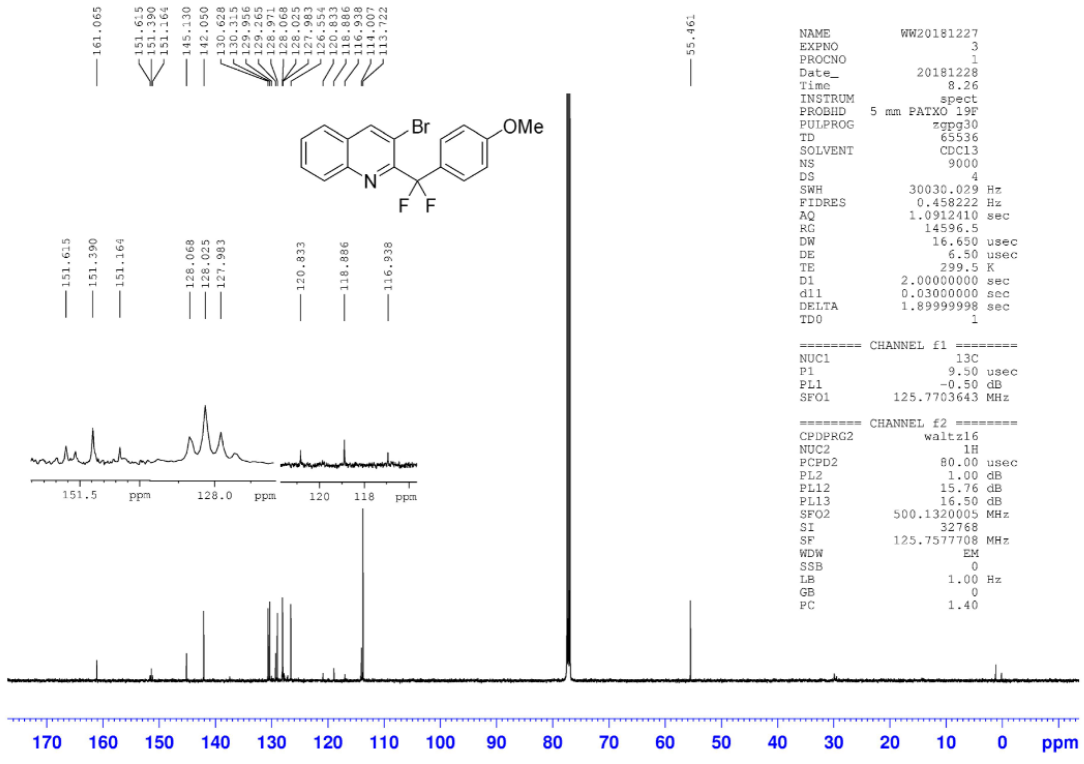
^{19}F NMR Spectra of **3k'a**



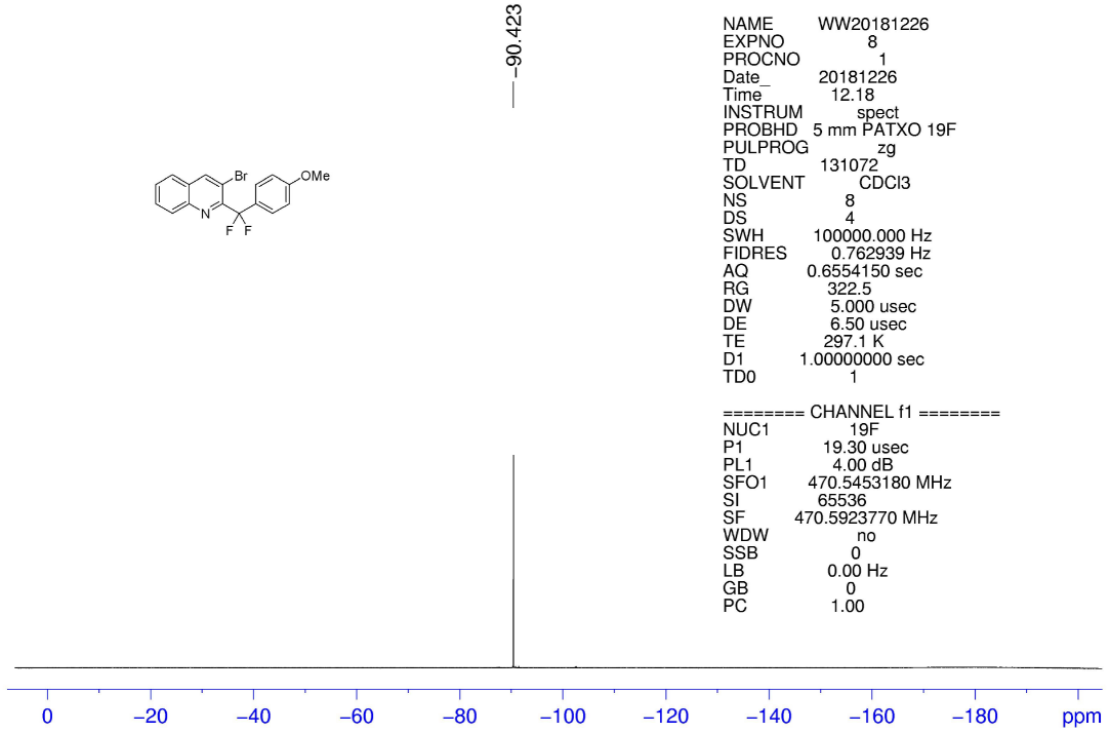
^{1}H NMR Spectra of **3la**



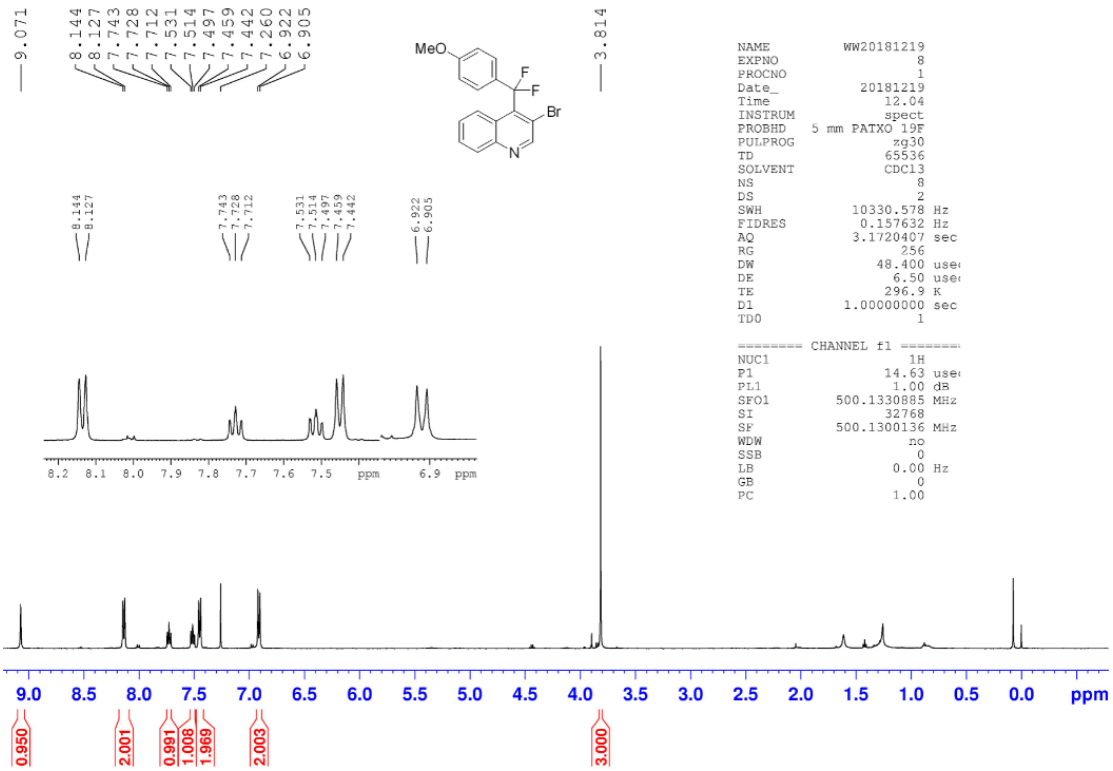
^{13}C NMR Spectra of **3la**



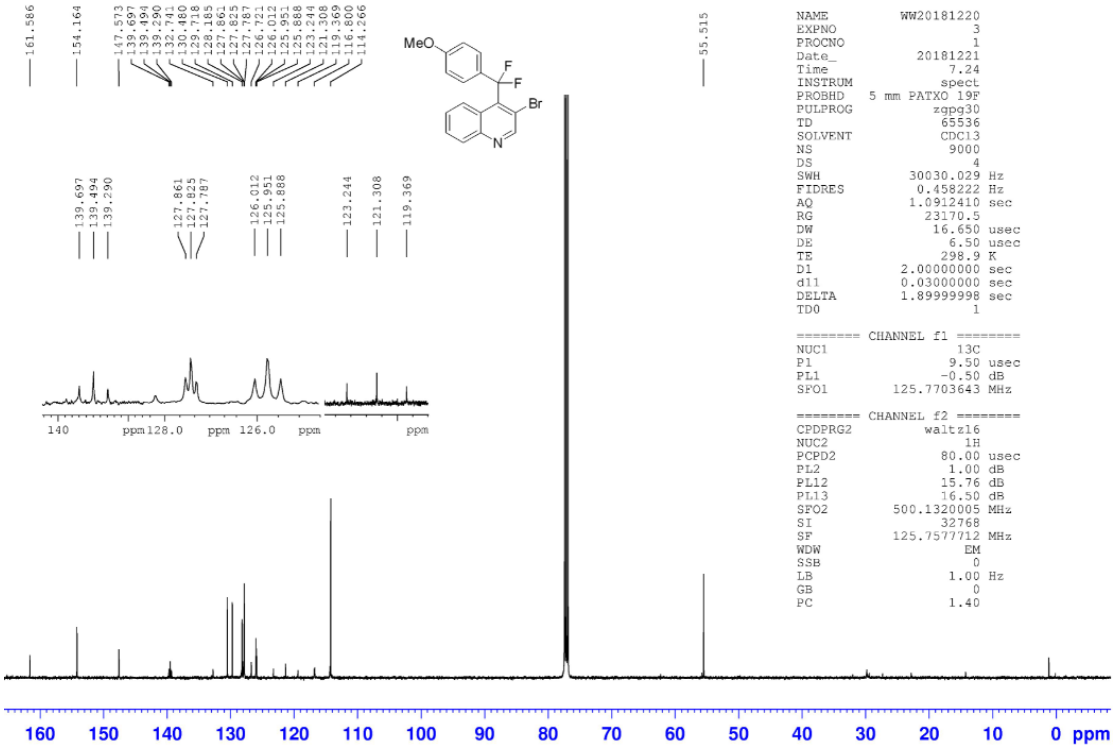
^{19}F NMR Spectra of **3la**



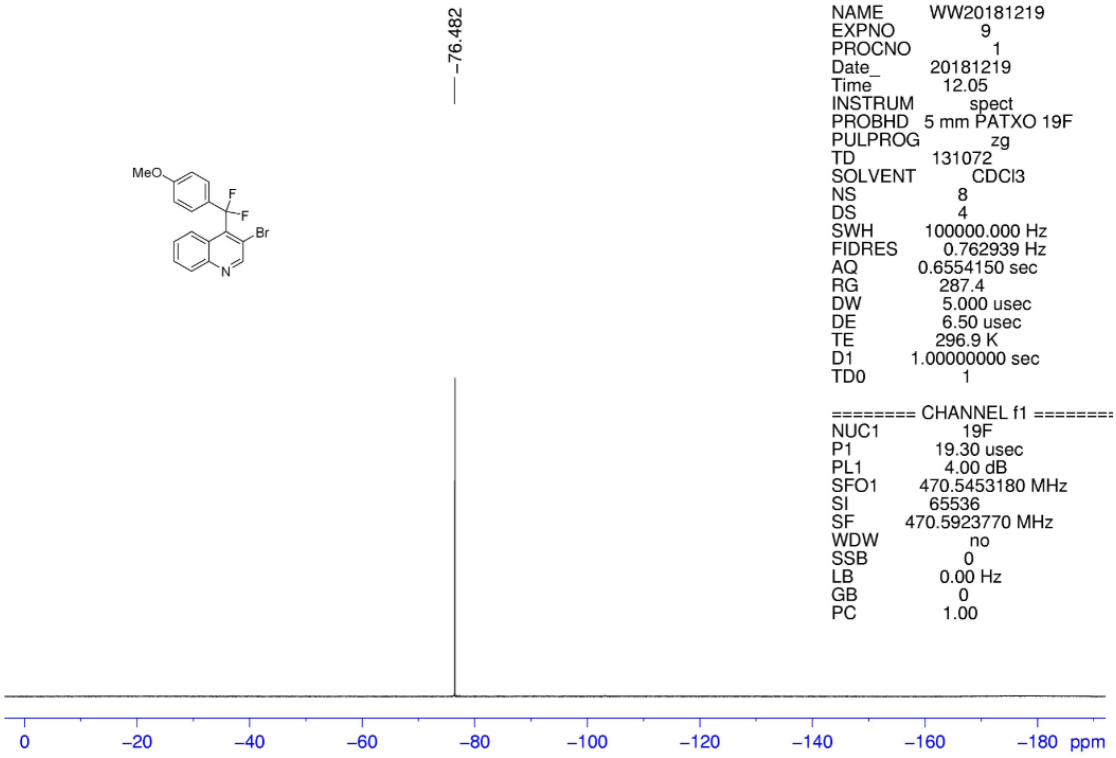
^{1}H NMR Spectra of **3l'a**



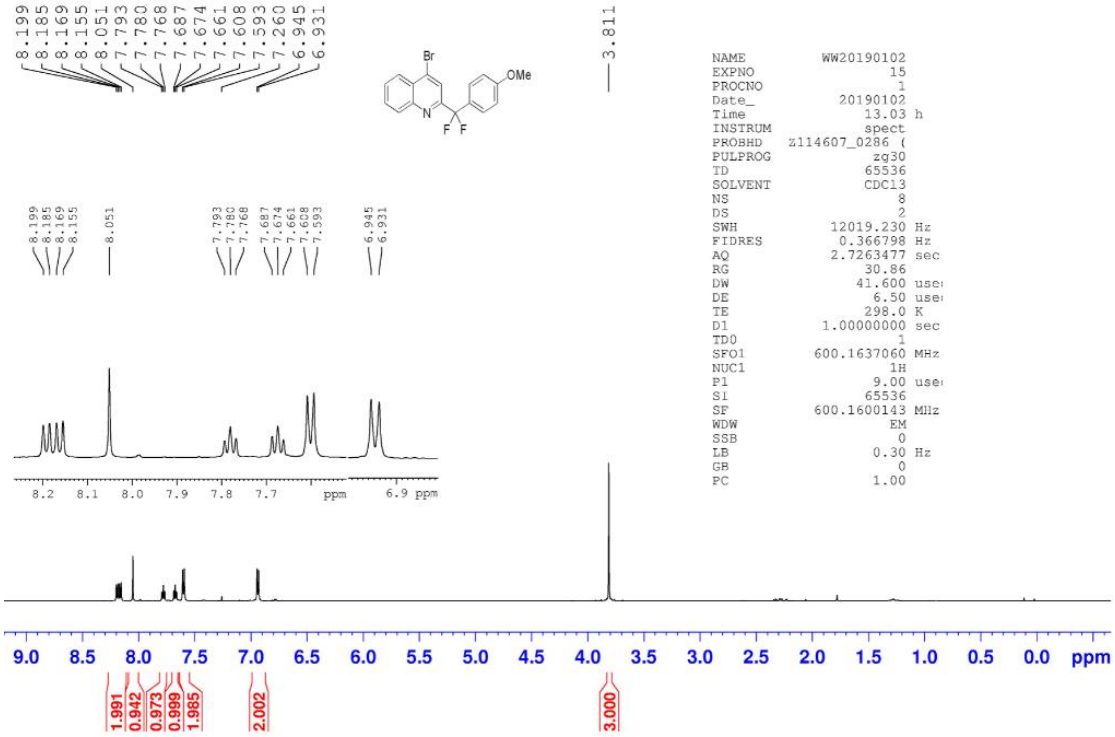
^{13}C NMR Spectra of **3l'a**



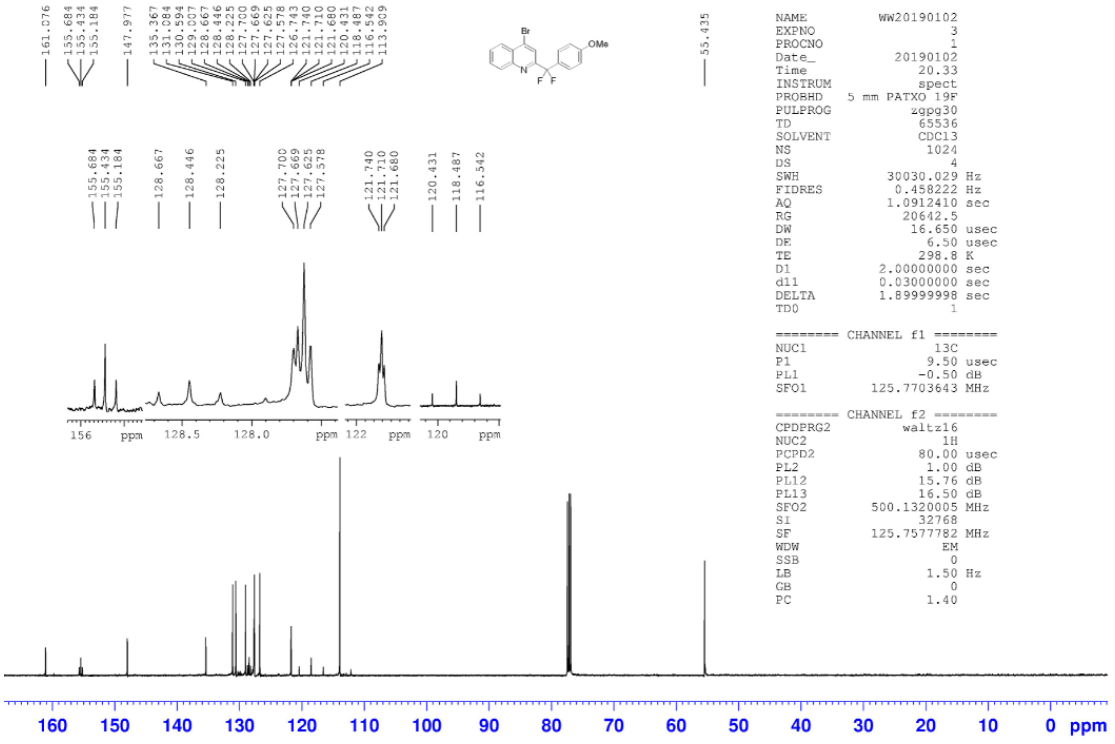
^{19}F NMR Spectra of **3l'a**



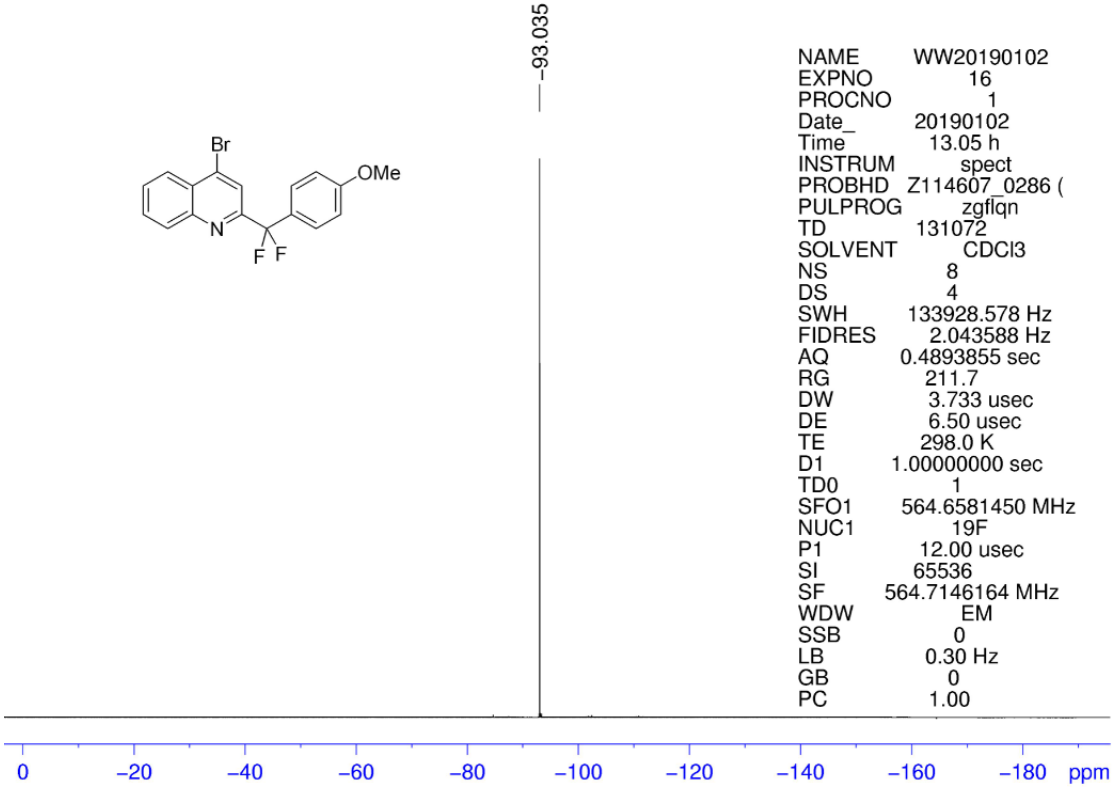
^{1}H NMR Spectra of **3ma**



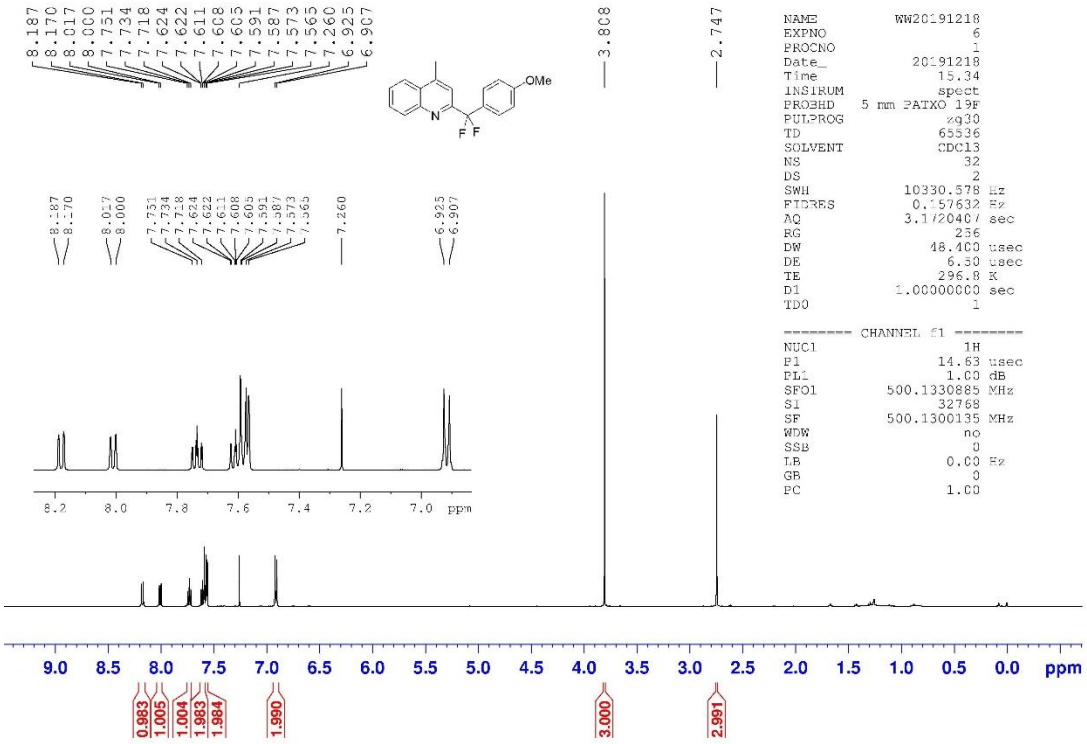
^{13}C NMR Spectra of **3ma**



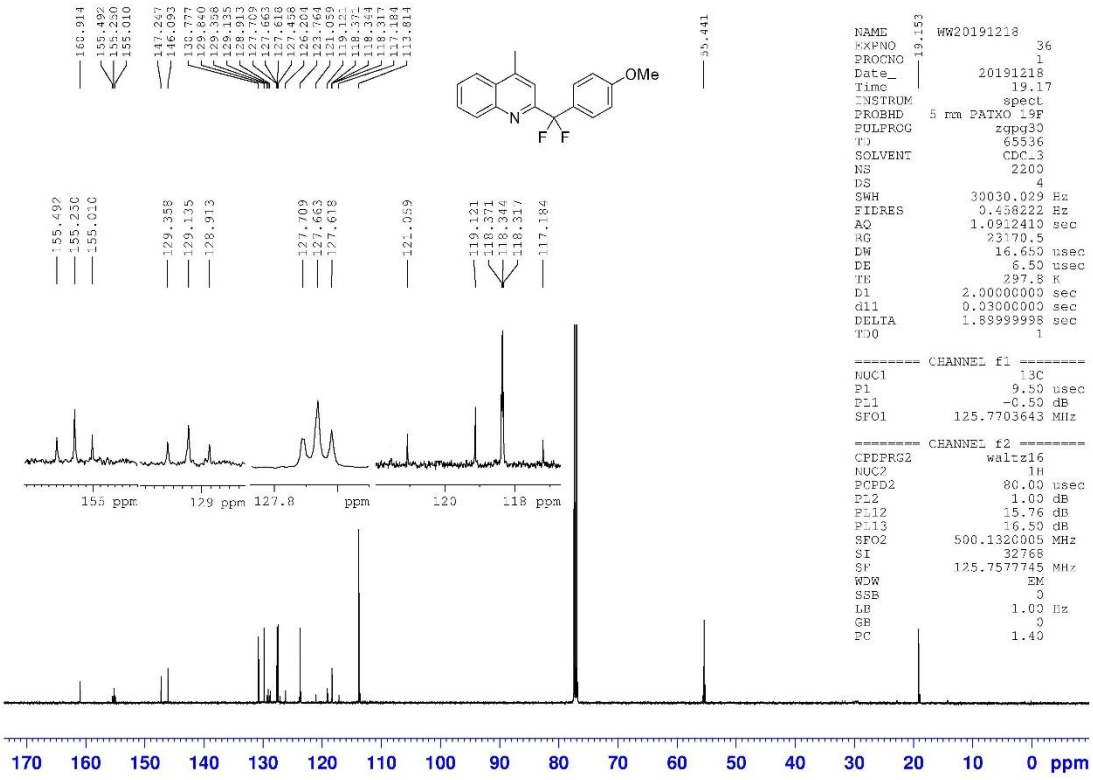
^{19}F NMR Spectra of **3ma**



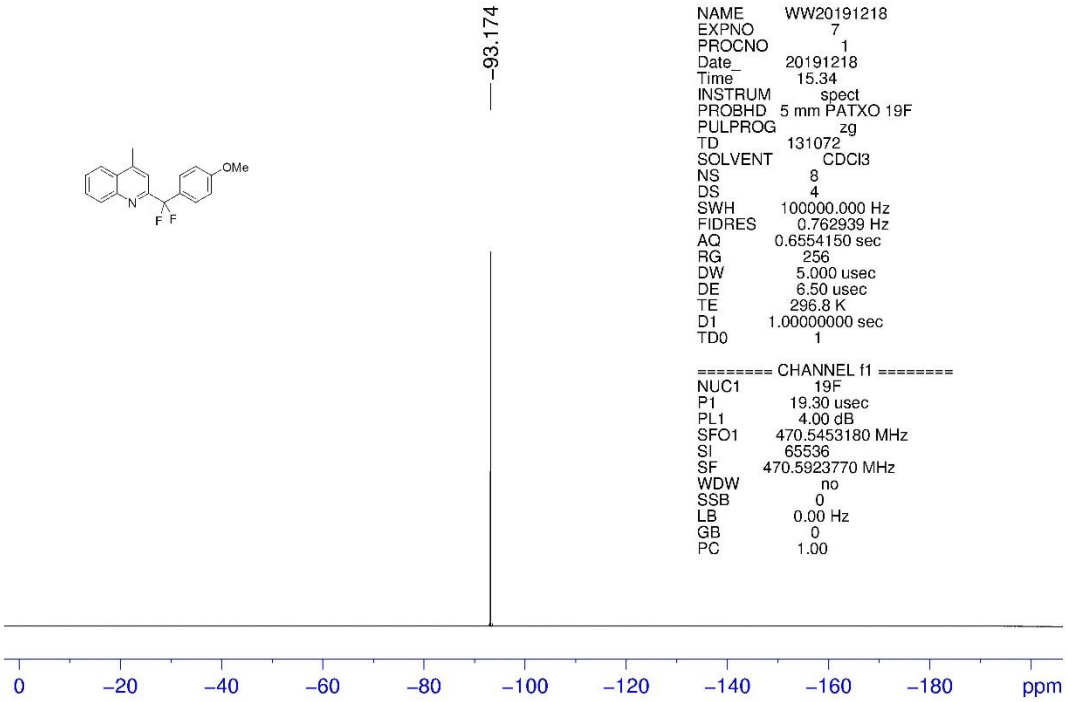
^{1}H NMR Spectra of **3na**



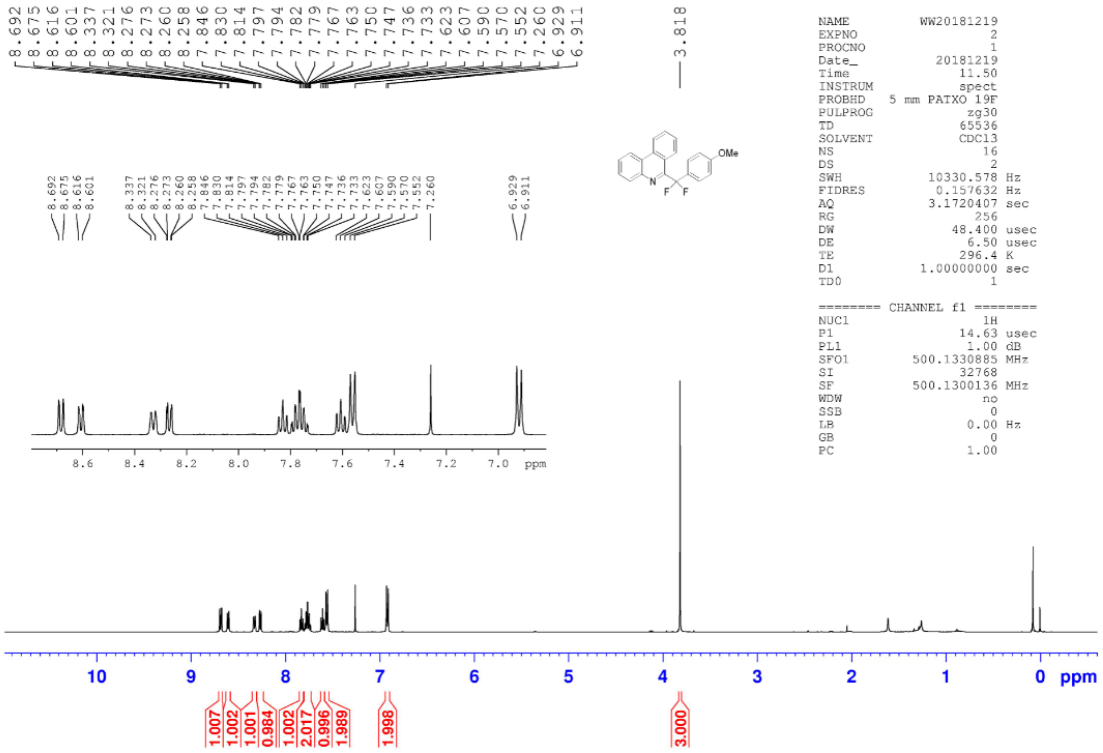
^{13}C NMR Spectra of **3na**



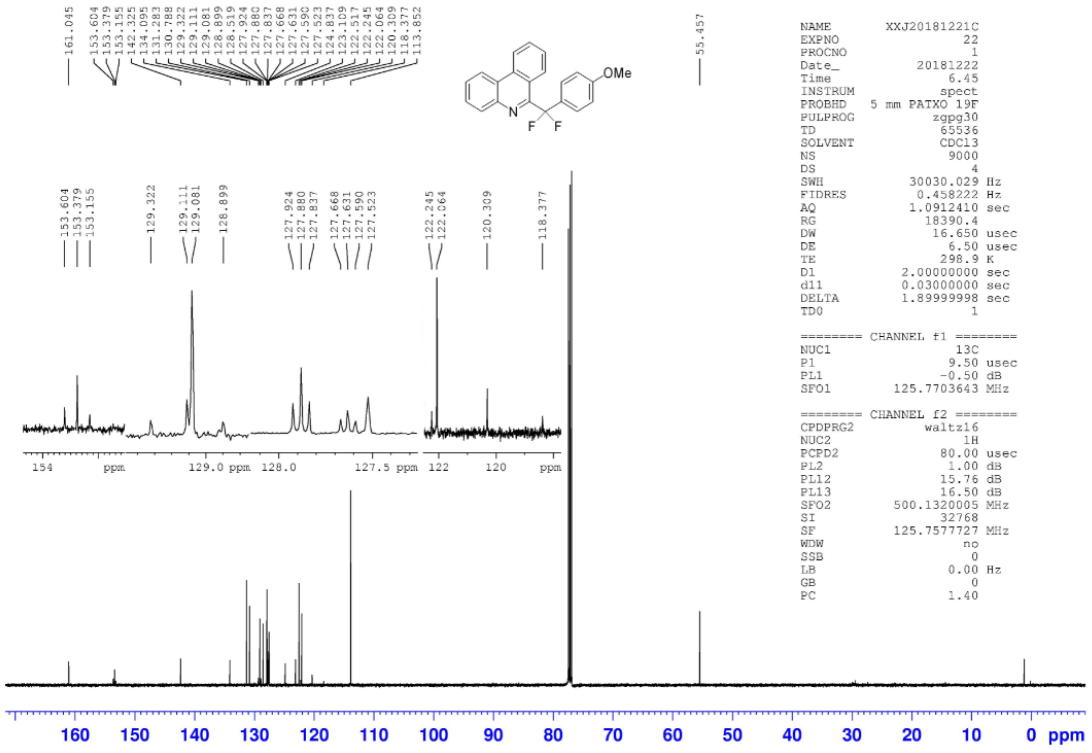
^{19}F NMR Spectra of **3na**



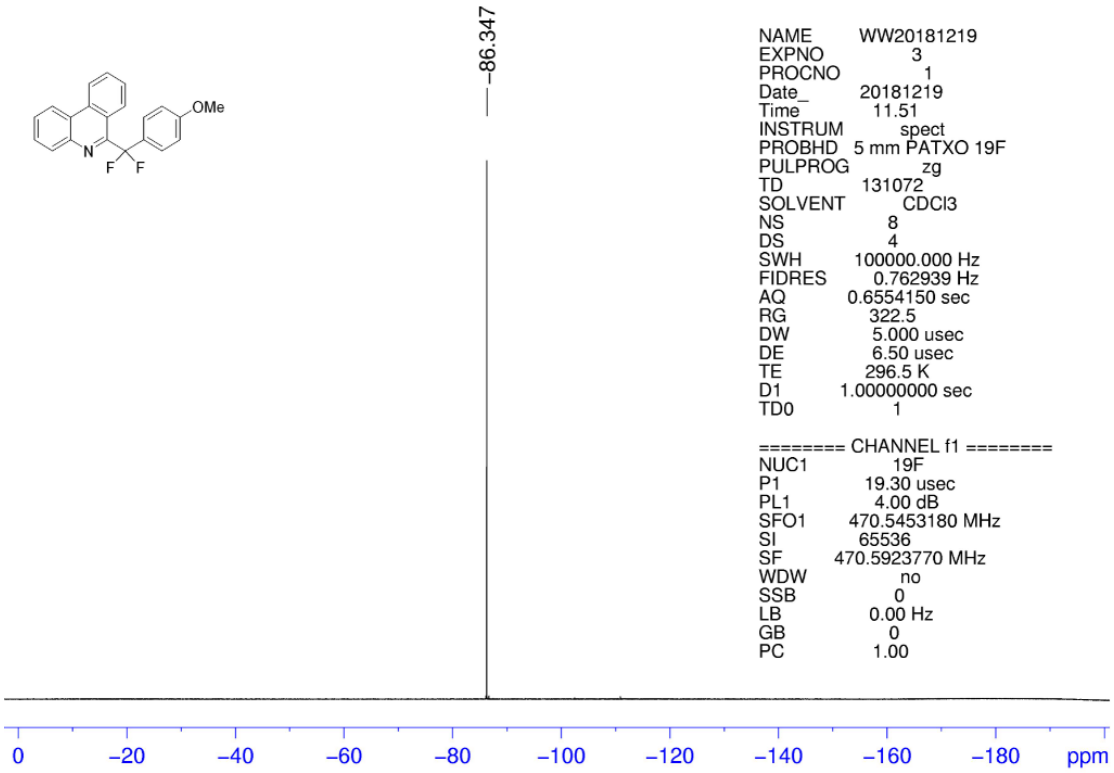
^{1}H NMR Spectra of **3oa**



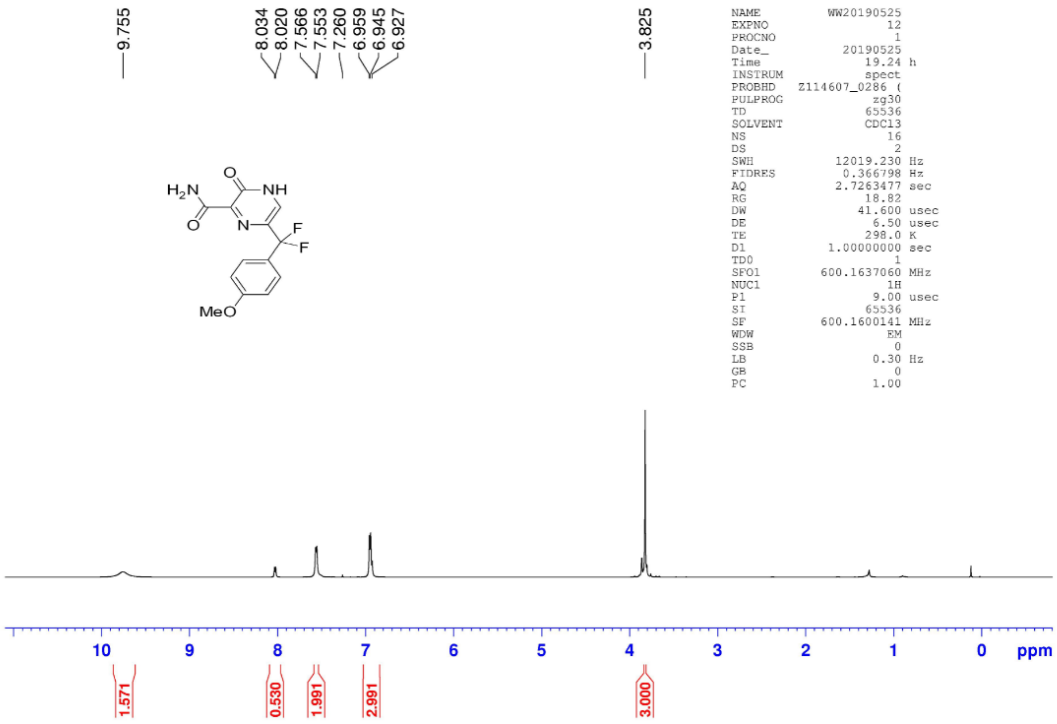
^{13}C NMR Spectra of **3oa**



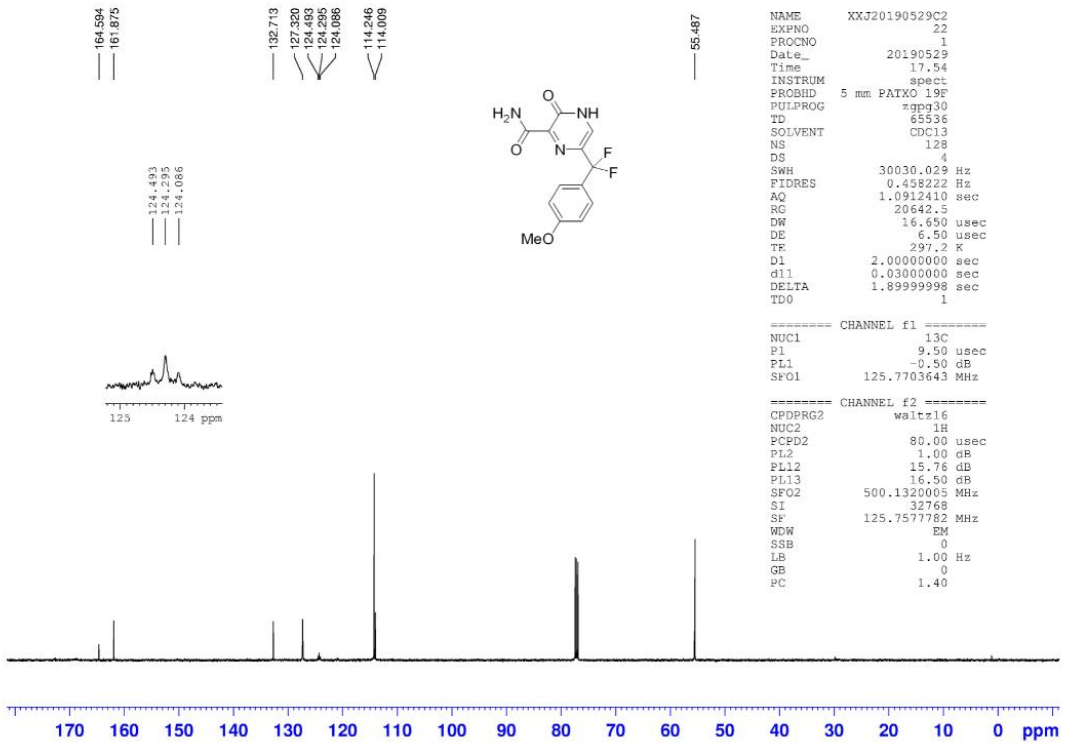
^{19}F NMR Spectra of **3oa**



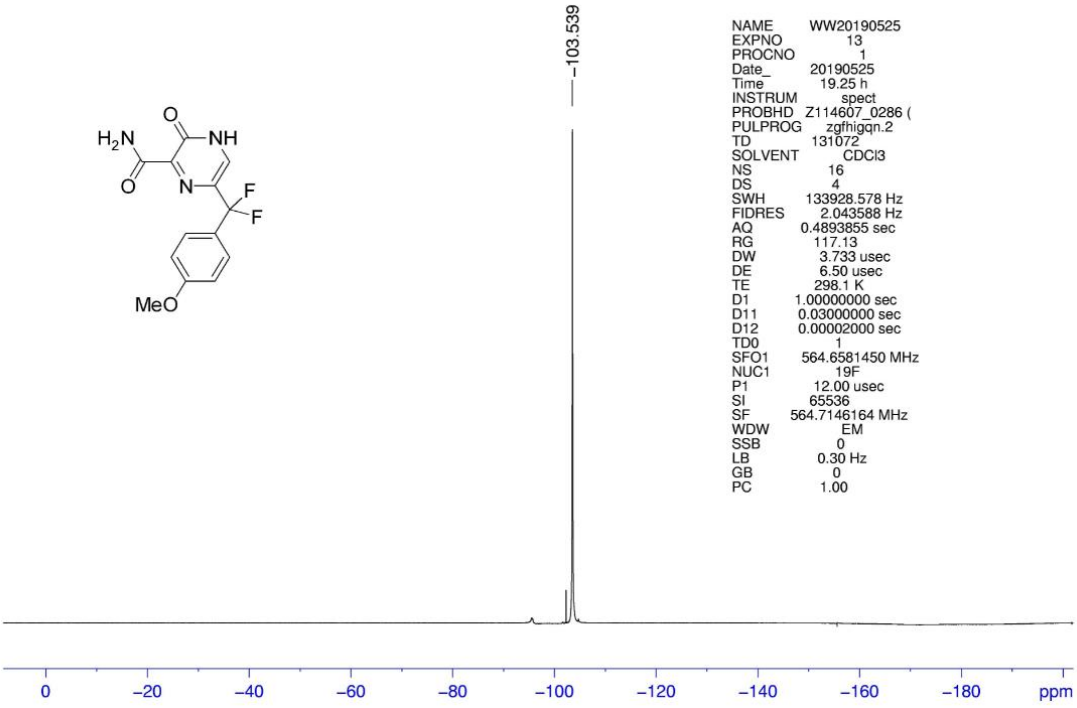
^{1}H NMR Spectra of **3pa**



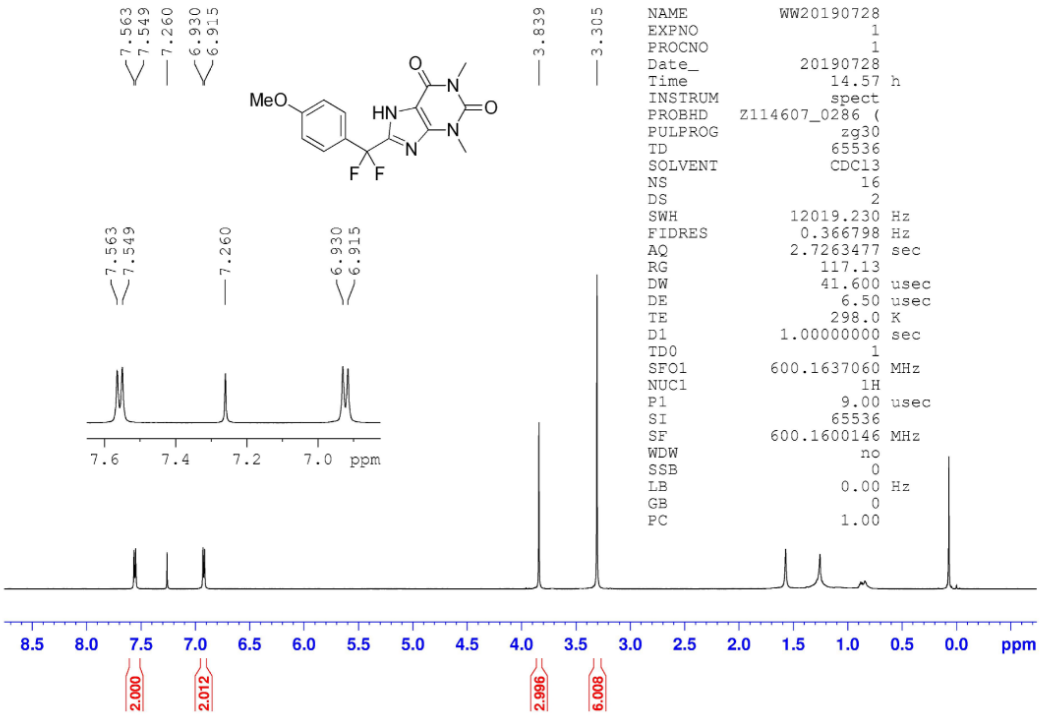
^{13}C NMR Spectra of **3pa**



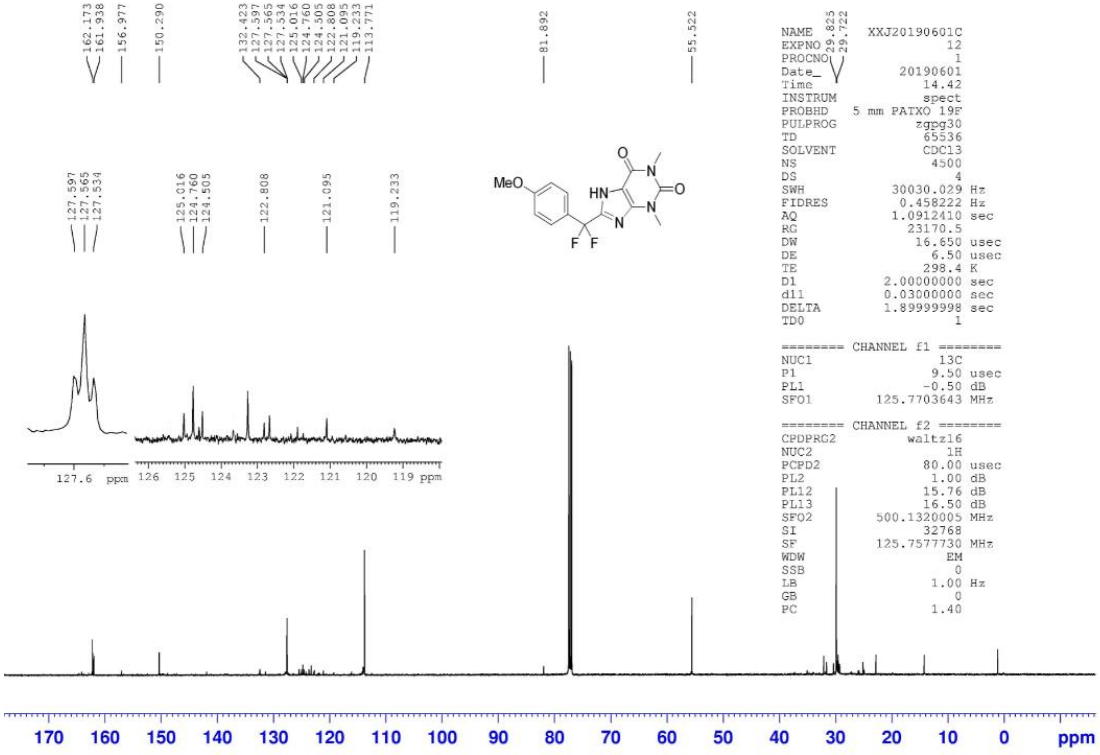
^{19}F NMR Spectra of **3pa**



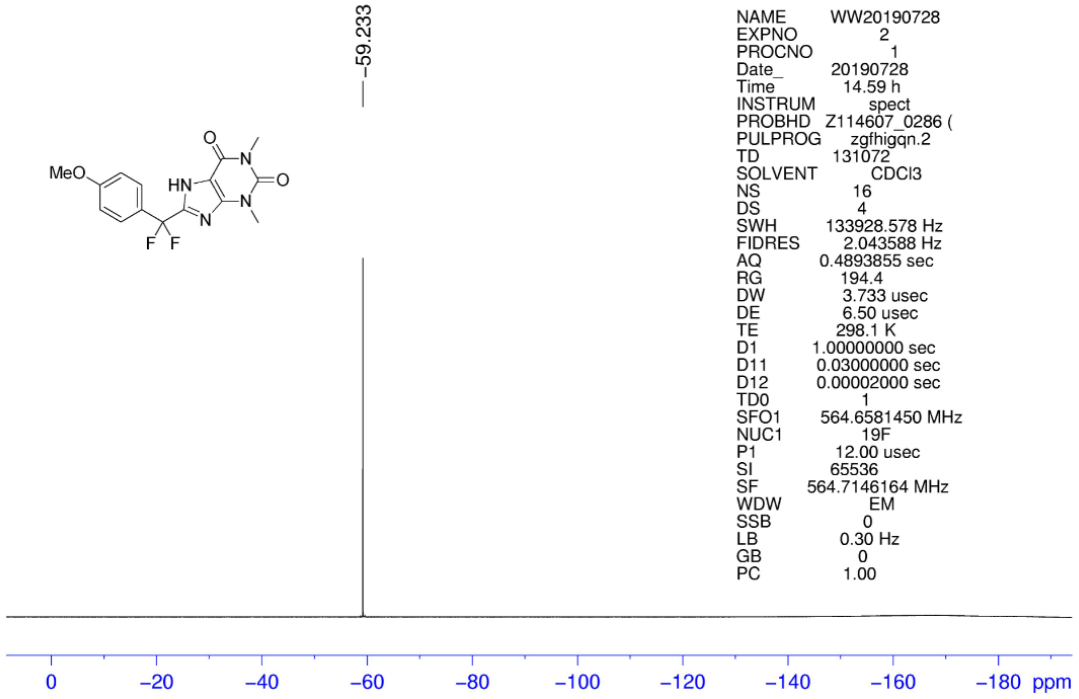
^{1}H NMR Spectra of **3qa**



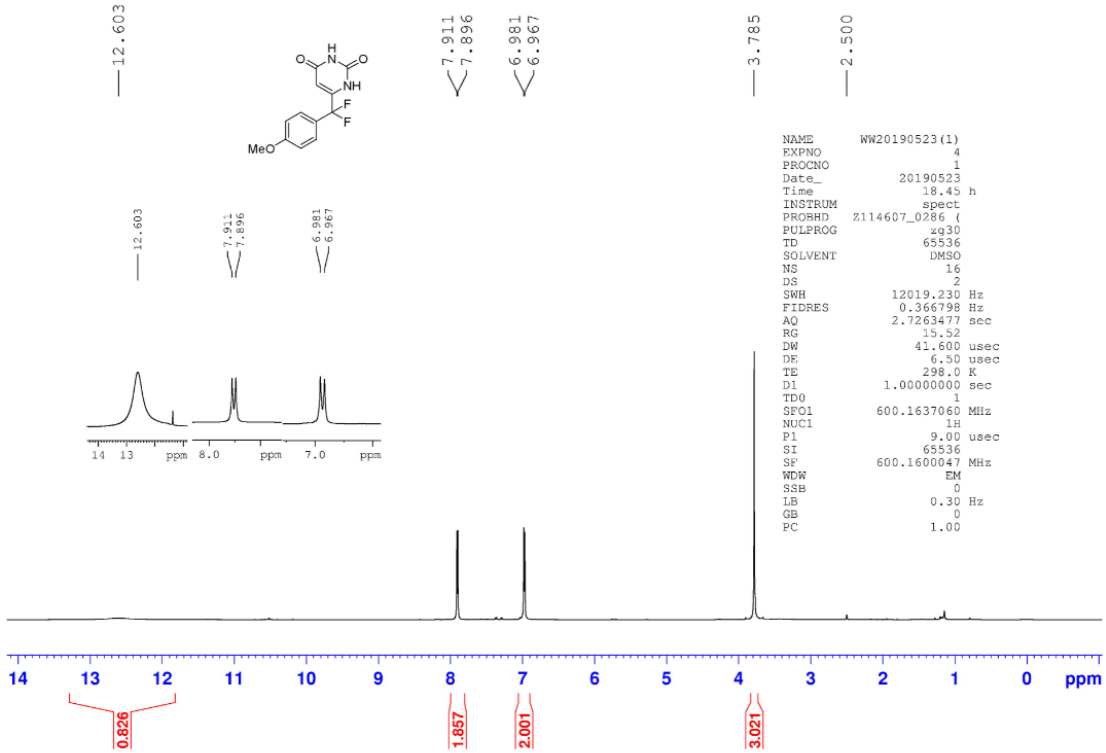
^{13}C NMR Spectra of **3qa**



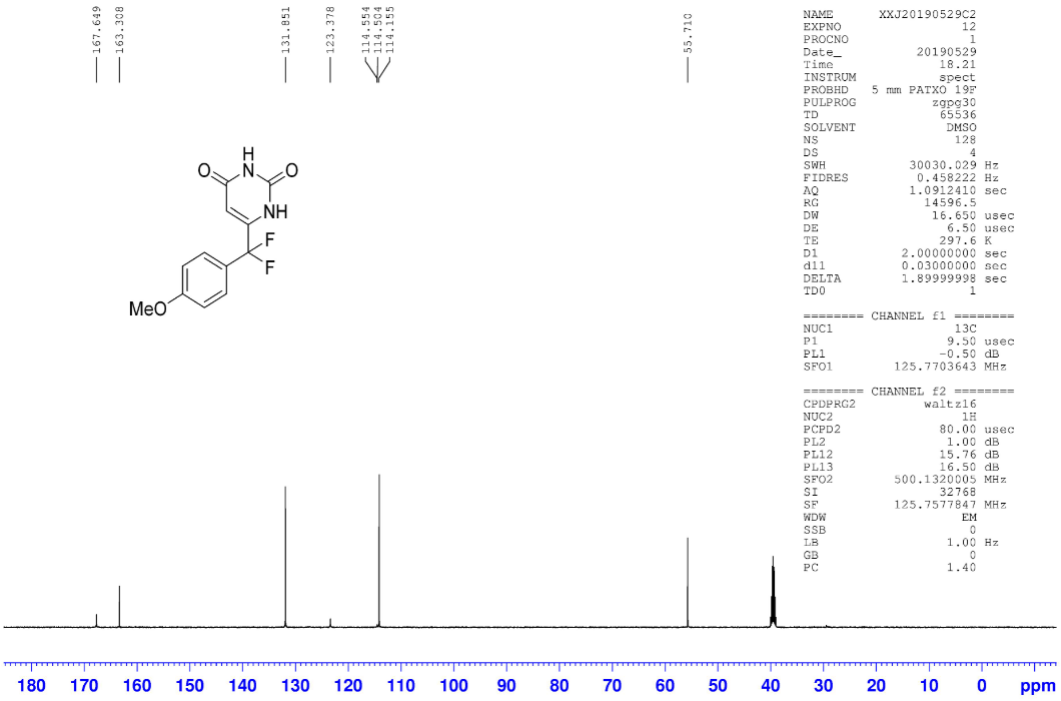
^{19}F NMR Spectra of **3qa**



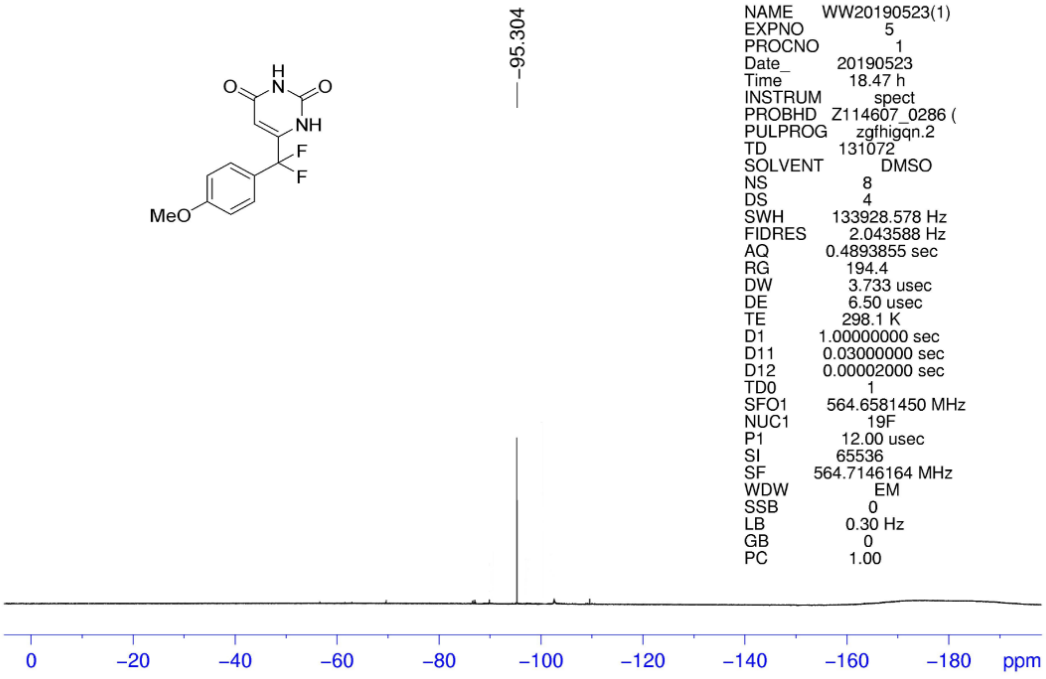
^{1}H NMR Spectra of **3ra**



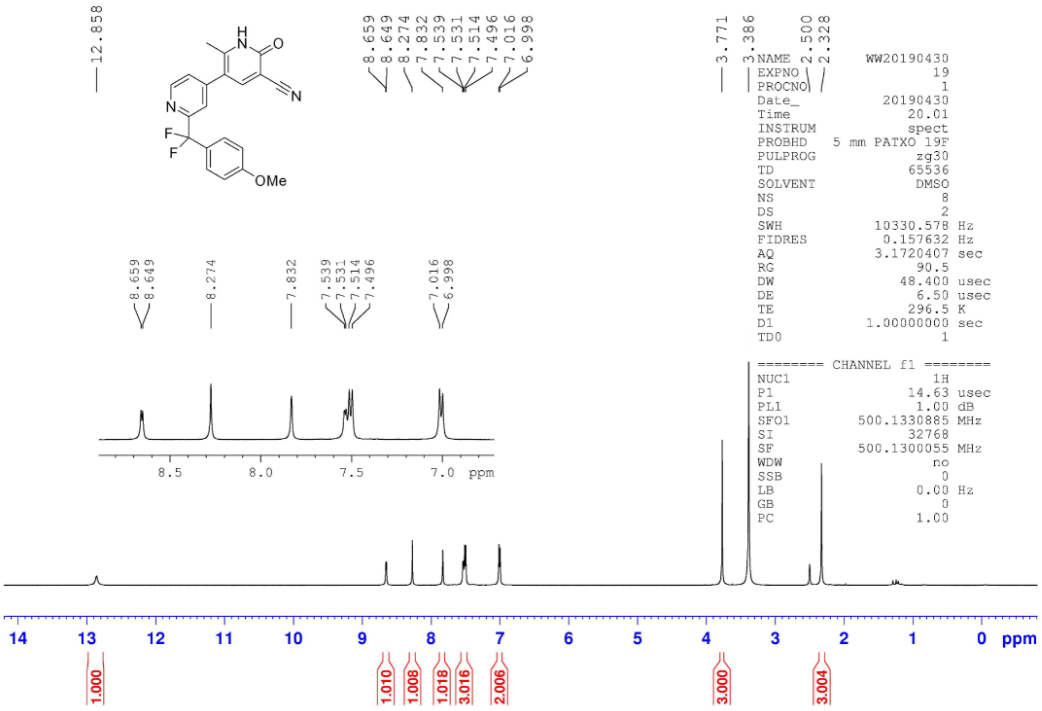
^{13}C NMR Spectra of **3ra**



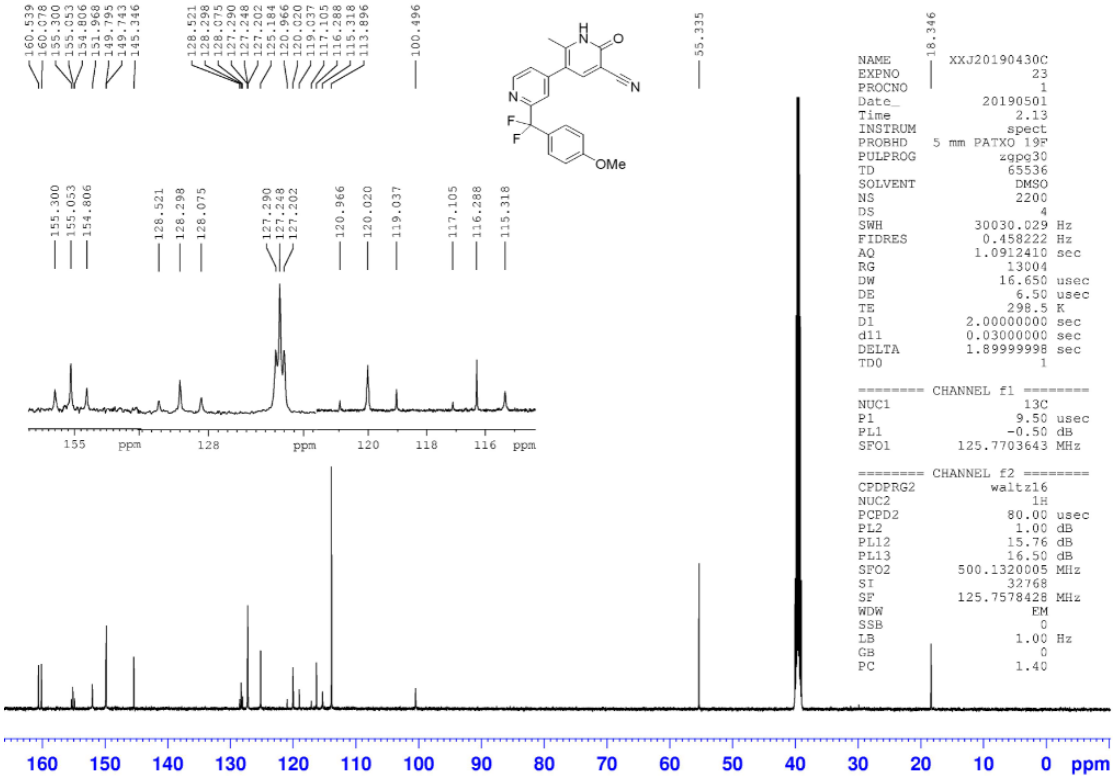
^{19}F NMR Spectra of **3ra**



^{1}H NMR Spectra of **3sa**



^{13}C NMR Spectra of **3sa**



^{19}F NMR Spectra of **3sa**