Supporting Information

Diastereoselective synthesis of CF3-oxazinoquinolines in water

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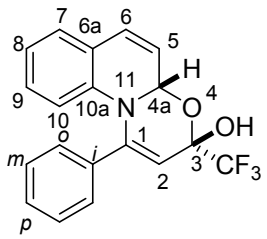
General remarks. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer in CD_3CN and $CDCl_3$ at 400, 100 and 376 MHz respectively. Chemical shifts (δ) in ppm are reported with the use of the residual CHD_2CN and chloroform signals (1.94 and 7.25 for ^{1}H and 77.0 for ^{13}C) as internal reference. The ^{19}F chemical shifts were referenced to C_6F_6, (-162.9 ppm). HRMS (ESI-TOF) spectra were measured with an Orbitrap Elite instrument. TLC analysis was performed on "Merck 60 F_{254}" plates. All reagents were of reagent grade and were used as such or distilled prior to use. CF_3-ynones **2** were prepared as reported previously[1]. Melting points were determined on an Electrothermal 9100 apparatus. The NMR and m.p. data of compounds **3** (with the exception of **3i,j,k,n**, which is a new compound) are in agreement with those in the literature[2].

Reaction of CF_3-ynones and quinolines in water (general procedure): A 4 mL vial with a screw cap was charged with water (0.5 mL), quinoline **1** (0.475 mmol, 0.95 equiv.) and then CF_3-ynone **2** (0.5 mmol, 1 equiv.) was added at vigorous stirring. The reaction mixture was stirred at room temperature for 1-2 h (TLC or ^{19}F NMR control; 24 h for quinoline **1c** and for ketone **2i**). Excess water was decanted; the residue was dissolved in ethyl acetate (0.5 mL) and dried over Na_2SO_4 (directly in the reaction vial). The solution was transferred into a round bottomed flask and the product crystallized by addition of appropriate amount of heptane (2-3 mL). The mother liquor was decanted, the crude product was dried under reduced pressure to give pure (3*R**,4a*R**)-isomer of **3**.

(3*R,4a*R**)-1-Phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]-quinolin-3-ol (3a).** Obtained from



quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). White powder, m.p. 154-156 °C (heptane), yield 0.153 g (93%). For multi gram scale reaction (60 equivalents of water): compound **3a** was obtained from quinoline **1a** (0.613 g, 4.75 mmol), water (5 mL) and acetylene **2a** (0.995 g, 5 mmol). Ethyl acetate (2.5 mL) and heptane (8 mL) were used for isolation of **3a**. White powder, m.p. 154-156 °C (heptane), yield 1.480 g (90%). Calculation of E-factor for multi gram scale reaction (60 equiv.): E=[m(EtOAc)+m(heptane)+m(water)+m(Na_2SO_4)+m(**1a**)+m(**2a**)]/m(**3a**)=(2.25+5.44+5+0.30+0.613+0.995)/1.480=9.86. For multi gram scale reaction (3 equivalents of water): compound **3a** was obtained from quinoline **1a** (1.612 g, 12.5 mmol), water (0.675 mL) and acetylene **2a** (2.612 g, 13.1 mmol). Ethyl acetate (6 mL) and heptane (20 mL) were used for first crystallization. For purification of material obtained from the mother liquor ethyl acetate (2.5 mL) and heptane (8 mL) were used. White powder, m.p. 154-156 °C (heptane), yield 3.878 g (90%). Calculation of E-factor for multi gram scale reaction (3 equiv.):

[1] V. M. Muzalevskiy, A. Yu. Rulev, A. R. Romanov, E. V. Kondrashov, I. A. Ushakov, V. A. Chertkov and V. G. Nenajdenko, *J. Org. Chem*., 2017, **82**, 7200.

[2] B. A. Trofimov, K. V. Belyaeva, L. P. Nikitina, A. V. Afonin, A. V. Vashchenko, V. M. Muzalevskiy and V. G. Nenajdenko, *Chem. Commun*., 2018, **54**, 2268.

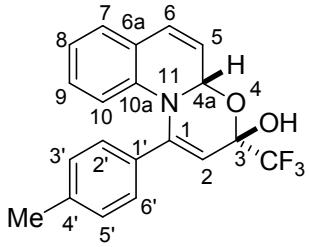
E=[m(EtOAc)+m(heptane)+m(water)+m(Na_2SO_4)+m(**1a**)+m(**2a**)]/m(**3a**)=(7.667+19.152+0.675+0.70+1.613+2.612)/3.878=8.36. Calculation of E-factor (approximate value) for the reaction in MeCN[2]: E=[m(MeCN)+m(water)+m(**1a**)+m(**2a**)+m(Sicagel)+m(eluents)]/m(**3a**)=(2.37+0.009+0.061+0.099+25.0+266…399 (~200-300 mL of eluents was used))/0.148=1983…2867~ 2000-3000.

^{1}H NMR (400.13 MHz, CD_3CN): δ 7.56-7.54 (m, 2H, H_o from Ph), 7.47-7.39 (m, 3H, $H_{m,p}$ from Ph), 7.25 (dd, ^3J = 7.1 Hz, ^4J = 1.9 Hz, 1H, H-7), 7.01 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.90 (td, ^3J = 7.4 Hz, ^4J = 1.8 Hz, 1H, H-9), 6.85 (td, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, H-8), 6.31 (d, ^3J = 7.8 Hz, 1H, H-10), 6.12 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.03 (s, 1H, H-2), 5.66 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.55 (s, 1H, OH) ppm.

^{19}F NMR (376.50 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H, H_o from Ph), 7.43-7.35 (m, 3H, $H_{m,p}$ from Ph), 7.18 (dd, ^3J = 7.2 Hz, ^4J = 0.8 Hz, 1H, H-7), 6.95 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.90 (td, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 1H, H-9), 6.84 (t, ^3J = 7.2 Hz, 1H, H-8), 6.33 (d, ^3J = 8.1 Hz, 1H, H-10), 6.04 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.97 (s, 1H, H-2), 5.68 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 3.19 (s, 1H, OH) ppm.

(3*R,4a*R**)-1-(4-Methylphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3b)**

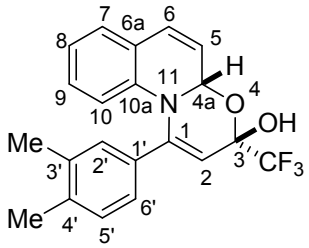


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2b** (0.106 g, 0.5 mmol). Light-brown powder, m.p. 132-134 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.27, yield 0.163 g (96%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.43 (d, ^3J = 8.1 Hz, 2H, H-2',6'), 7.24 (dd, ^3J = 7.1 Hz, ^4J = 1.6 Hz, 1H, H-7), 7.22 (d, ^3J = 8.1 Hz, 2H, H-3',5'), 6.99 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.91-6.83 (m, 2H, H-9, H-8), 6.33 (d, ^3J = 8.0 Hz, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.97 (s, 1H, H-2), 5.63 (d, ^3J = 4.7 Hz, 1H, H-4a), 5.54 (br s, 1H, OH), 2.35 (s, 3H, Me) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

(3*R,4a*R**)-1-(3,4-Dimethylphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3c).**

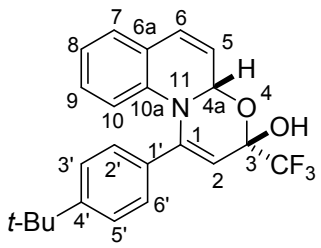


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2c** (0.113 g, 0.5 mmol). Light-brown powder, m.p. 95-97 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.30, yield 0.169 g (95%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.34 (s, 1H, H-2'), 7.24-7.22 (m, 2H, H-7, H-6'), 7.16 (d, ^3J = 7.8 Hz, 1H, H-5'), 6.99 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.92-6.83 (m, 2H, H-9, H-8), 6.34 (d, ^3J = 7.9 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.5 Hz, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-5), 5.93 (s, 1H, H-2), 5.61 (d, $^3J_{4a,5}$ = 4.5 Hz, 1H, H-4a), 5.47 (br s, 1H, OH), 2.27 (s, 3H, Me), 2.24 (s, 3H, Me) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

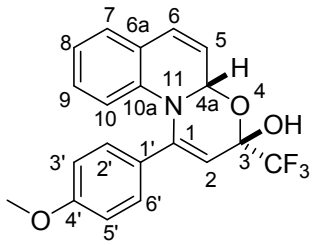
(3*R,4a*R**)-1-(4-(*tert*-Butyl)phenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3d).**



Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2d** (0.127 g, 0.5 mmol). Light-brown powder, m.p. 104-106 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.27, yield 0.182 g (96%). ^{1}H NMR (400.1 MHz, CD_3CN): δ 7.42-7.48 (m, 4H, H-2',3',5',6'), 7.24 (dd, ^3J = 7.2 Hz, ^4J = 1.6 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.90-6.83 (m, 2H, H-9, H-8), 6.32 (d, ^3J = 7.8 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.98 (s, 1H, H-2), 5.63 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.51 (s, 1H, OH), 1.31 (s, 9H, 3Me from *t*-Bu) ppm.

^{19}F NMR (376.3 Hz, CD_3CN): δ -82.0 (CF_3) ppm.

(3*R,4a*R**)-1-(4-Methoxyphenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3e).**

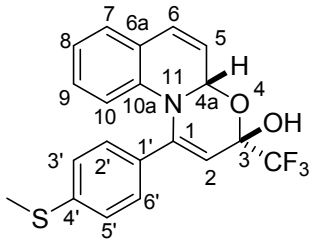


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2e** (0.114 g, 0.5 mmol). Light-brown powder, m.p. 95-97 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.43, yield 0.176 g (99%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.46 (d, ^3J = 8.9 Hz, 2H, H-2',6'), 7.24 (dd, ^3J = 7.3 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.93 (d, ^3J = 8.9 Hz, 2H, H-3',5'), 6.90-6.83 (m, 2H, H-9, H-8), 6.35 (d, ^3J = 8.0 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.9 Hz, 1H, H-5), 5.92 (s, 1H, H-2), 5.63 (d, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-4a), 5.58 (br s, 1H, OH), 3.79 (s, 3H, OMe) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

(3*R,4a*R**)-1-[4-(Methylthio)phenyl]-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3f).**

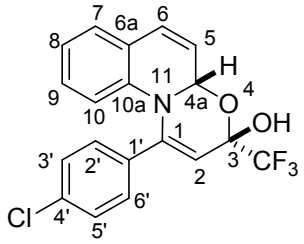


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2f** (0.122 g, 0.5 mmol). Light-brown powder, m.p. 98-100 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.20, yield 0.178 g (96%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.45 (d, ^3J = 8.4 Hz, 2H, H-2',6'), 7.26-7.21 (m, 3H, H-7, H-3',5'), 6.99 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.94-6.84 (m, 2H, H-9, H-8), 6.33 (d, ^3J = 8.1 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.6 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.98 (s, 1H, H-2), 5.61 (d, $^3J_{4a,5}$ = 4.3 Hz, 1H, H-4a), 5.54 (br s, 1H, OH), 2.47 (s, 3H, MeS) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

(3*R,4a*R**)-1-(4-Chlorophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3g).**

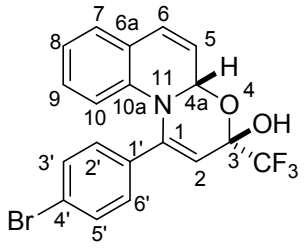


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2g** (0.116 g, 0.5 mmol). Light-brown powder, m.p. 91-93 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.70, yield 0.159 g (88%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.53 (d, ^3J = 8.7 Hz, 2H, H-2',6'), 7.42 (d, ^3J = 8.7 Hz, 2H, H-3',5'), 7.25 (dd, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1H, H-7), 6.99 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.95-6.85 (m, 2H, H-9, H-8), 6.27 (d, ^3J = 8.0 Hz, 1H, H-10), 6.11 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.03 (s, 1H, H-2), 5.62 (d, ^3J = 4.8 Hz, 1H, H-4a), 5.55 (br s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

(3*R,4a*R**)-1-(4-Bromophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3h).**

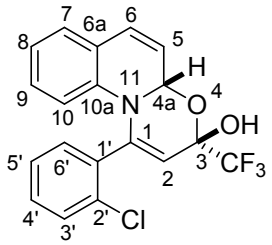


Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2h** (0.138 g, 0.5 mmol). Light-brown powder, m.p. 128-130 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.73, yield 0.192 g (95%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.57 (d, ^3J = 8.6 Hz, 2H, H-3',5'), 7.45 (d, ^3J = 8.6 Hz, 2H, H-2',6'), 7.25 (dd, ^3J = 7.3 Hz, ^4J = 1.2 Hz, 1H, H-7), 7.00 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.95-6.85 (m, 2H, H-9, H-8), 6.27 (d, ^3J = 8.0 Hz, 1H, H-10), 6.10 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.04 (s, 1H, H-2), 5.61 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.56 (s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.9 (CF_3) ppm.

(3*R,4a*R**)-1-(2-Chlorophenyl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3i).**



Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2i** (0.116 g, 0.5 mmol). Light-brown powder, m.p. 100-102 °C (heptane), yield 0.165 g (91%).

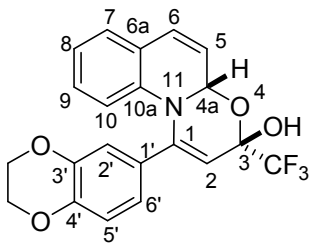
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.54-7.49 (m, 2H), 7.41 (td, ^3J = 7.7 Hz, ^4J = 1.8 Hz, 1H), 7.35 (td, ^3J = 7.4 Hz, ^4J = 1.4 Hz, 1H), 7.23 (dd, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 1H, H-7), 6.97 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.94-6.90 (m, 1H, H-9), 6.86-6.81 (m, 1H, H-8), 6.36 (d, ^3J = 8.1 Hz, 1H, H-10), 6.09 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.6 Hz, 1H, H-5), 5.94 (s, 1H, H-2), 5.71 (d, ^3J = 4.3 Hz, 1H, H-4a), 5.53 (br s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -81.8 (CF_3) ppm.

^{13}C NMR (100.6 Hz, CD_3CN): δ 145.0 (C-1), 137.4, 134.4, 133.0, 131.79, 131.77, 131.5, 130.2, 129.9, 129.1, 128.6, 123.6 (q, $^1J_{CF}$ = 285.3 Hz, CF_3), 122.1, 121.9, 121.6, 119.1, 116.4, 116.0, 92.7 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.8 (C-4a) ppm.

HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{19}H_{12}ClF_3NO^+$: 362.0554; found: 362.0554; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}ClF_3NO_2^+$: 380.066; found: 380.0658.

(3*R,4a*R**)-1-(2,3-Dihydrobenzo[b][1,4]dioxin-7-yl)-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3j).** Obtained from quinoline **1a** (0.061 g, 0.475 mmol) and acetylene **2j** (0.114 g, 0.5 mmol). Yellow-brown powder, m.p. 114-116 °C (heptane), yield 0.190 g (99%).



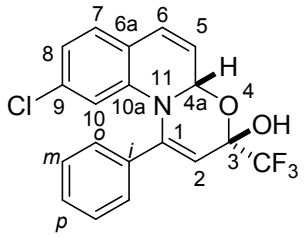
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.24 (dd, ^3J = 7.5 Hz, ^4J = 1.5 Hz, 1H, H-7), 7.03-6.92 (m, 4H, H-6, H-9, H-5',6'), 6.88-6.84 (m, 2H, H-8, H-2'), 6.36 (d, ^3J = 8.2 Hz, 1H, H-10), 6.08 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 5.89 (s, 1H, H-2), 5.58 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.34 (br s, 1H, OH), 4.27-4.21 (m, 4H, OCH_2CH_2O) ppm.

^{13}C NMR (100.6 Hz, CD_3CN): δ 148.0, 146.2, 144.9 (C-1), 138.3, 130.4, 129.5, 128.8, 128.7, 123.5 (q, $^1J_{CF}$ = 285.5 Hz, CF_3), 122.5, 121.4, 120.3, 119.2, 118.6, 118.0, 116.0, 111.2, 93.0 (q, $^2J_{CF}$ = 32.8 Hz, C-3), 78.3 (C-4a), 65.3 (CH_2), 65.0 (CH_2) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.2 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{21}H_{15}F_3NO_3^+$: 386.0999; found: 386.0999; m/z $[M+H]^+$ Calcd for $C_{21}H_{17}F_3NO_4^+$: 404.1104; found: 404.1108.

(3*R,4a*R**)-9-Chloro-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3k).**



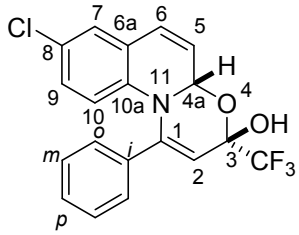
Obtained from quinoline **1b** (0.078 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). Pale yellow powder, m.p. 146-148 °C (heptane), yield 0.169 g (94%). ^{1}H NMR (400.13 MHz, CD_3CN): δ 7.59-7.54 (m, 2H, H_o from Ph), 7.49-7.41 (m, 3H, $H_{m,p}$ from Ph), 7.22 (d, $^3J_{7,8}$ = 8.1 Hz, 1H, H-7), 6.99 (d, $^3J_{5,6}$ = 9.8 Hz, 1H, H-6), 6.85 (dd, $^3J_{7,8}$ = 8.1 Hz, $^4J_{8,10}$ = 1.9 Hz, 1H, H-8), 6.28 (d, $^4J_{8,10}$ = 1.5 Hz, 1H, H-10), 6.13 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.07 (s, 1H, H-2), 5.67 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.49 (s, 1H, OH) ppm.

^{13}C NMR (100.6 Hz, CD_3CN): δ 148.0 (C-1), 139.2, 135.0, 134.2, 131.1, 130.2, 130.1, 129.5, 127.3, 123.5 (q, $^1J_{CF}$ = 285.1 Hz, CF_3), 121.4, 121.3, 119.7, 117.6, 113.3, 93.0 (q, $^2J_{CF}$ = 33.0 Hz, C-3), 78.2 (C-4a) ppm.

^{19}F NMR (376.50 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

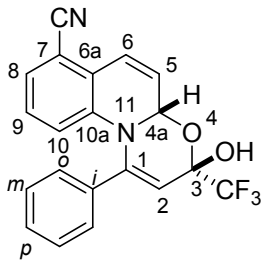
HRMS (ESI-TOF): m/z $[M-OH]^+$ Calcd for $C_{19}H_{12}ClF_3NO^+$: 362.0554; found: 362.0555; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}ClF_3NO_2^+$: 380.066; found: 380.0655.

(3*R,4a*R**)-8-Chloro-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3l).**



Obtained from quinoline **1c** (0.078 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). White powder, m.p. 138-140 °C (heptane), yield 0.175 g (97%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.53-7.50 (m, 2H, H_o from Ph), 7.44-7.36 (m, 3H, $H_{m,p}$ from Ph), 7.16 (d, $^4J_{7,9}$ = 2.4 Hz, 1H, H-7), 6.86 (d, $^3J_{5,6}$ = 8.9 Hz, 1H, H-6), 6.85 (d, $^3J_{9,10}$ = 8.8 Hz, 1H, H-9), 6.28 (d, $^3J_{9,10}$ = 8.8 Hz, 1H, H-10), 6.08 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.00 (s, 1H, H-2), 5.67 (d, $^3J_{4a,5}$ = 4.5 Hz, 1H, H-4a), 3.22 (s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, $CDCl_3$): δ -84.2 (CF_3) ppm.



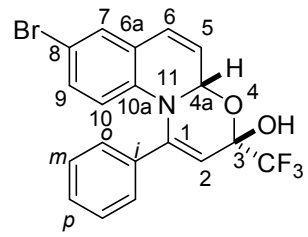
(3*R,4a*R**)-3-Hydroxy-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinoline-6-carbonitrile (3m).** Obtained from quinoline **1f** (0.073 g, 0.475 mmol)

and acetylene **2a** (0.099 g, 0.5 mmol). Light-brown powder, m.p. 107-110 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.30, yield 0.170 g (97%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.56-7.52 (m, 2H, H_o from Ph), 7.46-7.39 (m, 3H, $H_{m,p}$ from Ph), 7.31 (d, $^3J_{5,6}$ = 10.0 Hz, 1H, H-6), 7.21 (dd, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1H, H-8), 7.00 (pseudo-t, ^3J ~ 8 Hz, 1H, H-9), 6.59 (pseudo-d, ^3J ~ 8 Hz, 1H, H-10), 6.38 (dd, $^3J_{5,6}$ = 9.9 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.10 (s, 1H, H-2), 5.72 (d, $^3J_{4a,5}$ = 5.0 Hz, 1H, H-4a), 5.72 (br. s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.2 (CF_3) ppm.

(3*R,4a*R**)-8-Bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3n).**



Obtained from quinoline **1d** (0.098 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). White powder, m.p. 136-138 °C (heptane), yield 0.195 g (97%).

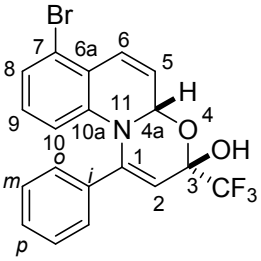
^{1}H NMR (400.1 MHz, CD_3CN): δ 7.55-7.53 (m, 2H, H_o from Ph), 7.45-7.39 (m, 4H, $H_{m,p}$ from Ph, H-7), 7.00 (dd, $^3J_{9,10}$ = 8.8 Hz, ^4J = 2.4 Hz, 1H, H-9), 6.95 (d, $^3J_{5,6}$ = 9.9 Hz, 1H, H-6), 6.21 (d, $^3J_{9,10}$ = 8.8 Hz, 1H, H-10), 6.16 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-5), 6.02 (s, 1H, H-2), 5.64 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 5.59 (s, 1H, OH) ppm.

^{13}C NMR (100.16 Hz, CD_3CN): δ 148.2 (C-1), 137.3 (C-10a), 135.1 (C_i from Ph), 131.9 (C-6), 131.00 and 130.98 (C_p from Ph, C-6), 130.1 (C_m from Ph), 129.3 (C-9), 127.3 (C_o from Ph), 127.3 (C-7), 124.5 (C-8), 123.5 (q, $^1J_{CF}$ = 284.9 Hz, CF_3), 120.8 (C-5), 119.7 (C-10), 113.3 (C-6a), 113.0 (C-2), 93.0 (q, $^2J_{CF}$ = 33.2 Hz, C-3), 78.2 (C-4a) ppm.

^{19}F NMR (376.50 Hz, CD_3CN): δ -82.1 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M\text{-}OH]^+$ Calcd for $C_{19}H_{12}BrF_3NO^+$: 406.0049; found: 406.0052; m/z $[M+H]^+$ Calcd for $C_{19}H_{14}BrF_3NO_2^+$: 424.0155; found: 424.0157.

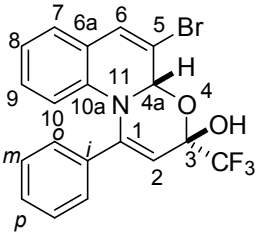
(3*R,4a*R**)-6-Bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3o).**



Obtained from quinoline **1e** (0.099 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). Light-brown powder, m.p. 115-117 °C (heptane), R_F(CH_2Cl_2-MeOH 100:1) = 0.71, yield 0.199 g (99%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.55-7.53 (m, 2H, H_o from Ph), 7.45-7.36 (m, 4H, H-6, $H_{m,p}$ from Ph), 7.10 (d, ^3J = 8.1 Hz, 1H, H-8), 6.77 (t, ^3J = 8.1 Hz, 1H, H-9), 6.33 (d, ^3J = 8.1 Hz, 1H, H-10), 6.25 (dd, $^3J_{5,6}$ = 9.8 Hz, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-5), 6.08 (s, 1H, H-2), 5.65 (d, ^3J = 4.7 Hz, 1H, H-4a), 5.61 (br. s, 1H, OH) ppm.

^{19}F NMR (376.3 MHz, CD_3CN): δ -82.1 (CF_3) ppm.



(3*R,4a*R**)-5-Bromo-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]-oxazino[3,2-*a*]quinolin-3-ol (3p).** Obtained from quinoline **1g** (0.099 g, 0.475 mmol) and acetylene

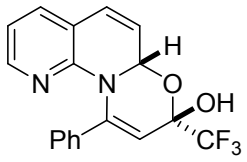
2a (0.099 g, 0.5 mmol). Light-yellow powder, m.p. 68-70 °C (heptane), yield 0.186 g (92%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.58-7.55 (m, 2H, H_o from Ph), 7.48-7.38 (m, 4H, H_m and H_p from Ph, H-6), 7.22 (dd, ^3J = 7.2 Hz, ^4J = 1.7 Hz, 1H, H-7), 6.96-6.86 (m, 2H, H-9, H-8), 6.32 (d, $^3J_{9,10}$ = 8.1 Hz, 1H, H-10), 6.06 (s, 1H, H-2), 5.74 (s, 1H, H-4a), 5.67 (br. s, 1H, OH) ppm.

^{13}C NMR (100.16 Hz, CD_3CN): δ 148.0 (C-2), 136.9 (C-11a), 135.1 (C_i from Ph), 132.6 (C-6), 131.1 (C_p from Ph), 130.1 (C_m from Ph), 130.0 (C-9), 128.4 (C-7), 127.4 (C_o from Ph), 123.3 (q, $^1J_{CF}$ = 282.9 Hz, CF_3), 122.1 (C-6a), 122.0 (C-8), 118.9 (C-10), 113.0 (C-5), 112.4 (C-2), 93.4 (q, $^2J_{CF}$ = 33.2 Hz, C-3), 83.3 (C-4a) ppm.

^{19}F NMR (376.5 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

(6a*R,8*R**)-10-Phenyl-8-(trifluoromethyl)-6a*H*,8*H*-[1,3]oxazino[3,2-*a*][1,8]naphthyridin-8-ol (3q).**

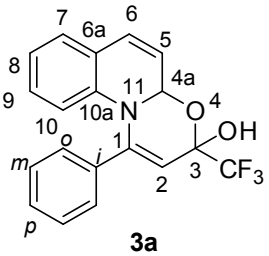


Obtained from 1,8-naphthyridine **1h** (0.062 g, 0.475 mmol) and acetylene **2a** (0.099 g, 0.5 mmol). Pale brown crystals, m.p. 145-147 °C (heptane), yield 0.155 g (94%).

^{1}H NMR (400.1 MHz, CD_3CN): δ 7.73 (dd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, 1H), 7.55 (dd, ^3J = 7.4 Hz, ^4J = 1.5 Hz, 1H), 7.49-7.45 (m, 2H, H_o from Ph), 7.37-7.32 (m, 3H, $H_{m,p}$ from Ph), 7.00 (d, ^3J = 9.7 Hz, 1H), 6.82 (dd, ^3J = 7.4 Hz, ^3J = 5.0 Hz, 1H), 6.16 (dd, ^3J = 9.7 Hz, ^3J = 4.7 Hz, 1H), 5.96 (s, 1H), 5.81 (d, ^3J = 4.6 Hz, 1H), 5.65 (s, 1H, OH) ppm.

^{19}F NMR (376.5 MHz, CD_3CN): δ -82.0 (CF_3) ppm.

Epimerization of (3*R,4a*R*)-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3a).**



3a

Oxazine **3a** (0.050 g, 0.145 mmol) was dissolved in t-BuOH (1 mL) and H_2O (0.5 mL) was added. The solution formed was left overnight. The volatiles were evaporated in vacuo to give mixture of **3a ((3*R**,4a*R*)**-isomer) and **3a' ((3*S**,4a*R*)**-isomer) (0.050 g, ~100%) as light brown powder, m.p. 142-144 °C. (3*R**, 4a*R**):(3*S**, 4a*R**)-isomers ratio is 87:13.

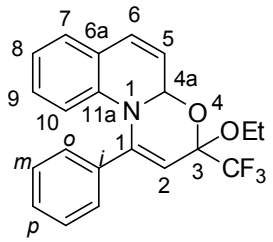
^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.54-7.52 (m, 2H, H_o from Ph), 7.43-7.35 (m, 3H, $H_{m,p}$ from Ph), 7.0 (d, ^3J = 7.2 Hz, 1H, H-7), 6.97-6.81 (m, 3H, H-6, H-9, H-8), 6.33 (d, ^3J = 7.8 Hz, 1H, H-10), 6.04 (dd, $^3J_{5,6}$ = 9.3 Hz, $^3J_{4a,5}$ = 4.4 Hz, 1H, H-5), 5.97 (s, 1H, H-2), 5.68 (br s, 1H, H-4a), 3.19 (s, 1H, OH) ppm.

^{19}F NMR (376.50 Hz, $CDCl_3$): δ -84.3 (CF_3) ppm;

(4*S**, 5a*R**)-**3a'**: ^{1}H NMR (400.13 MHz, $CDCl_3$): 6.09 (dd, $^3J_{5a,6}$ = 4.7 Hz, $^3J_{6,7}$ = 9.8 Hz, 1H, H-6), 5.62 (d, $^3J_{5a,6}$ = 4.7 Hz, 1H, H-5a) ppm. The other signals are identical to those of major isomer.

^{19}F NMR (376.50 Hz, $CDCl_3$): δ -81.1 (CF_3) ppm.

(3*R,4a*R**)-3-Ethoxy-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinoline (4).**



Oxazine **3a** (0.100 g, 0.29 mmol) was dissolved in absolute EtOH (1 mL) and the solution formed was left for 1 day. The volatiles were evaporated in vacuo to give **4** (0.106 g, 98%) as light yellow powder, m.p. 130-132 °C.

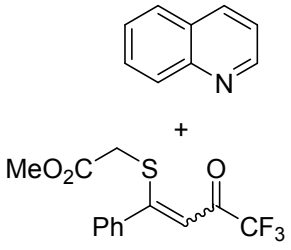
^{1}H NMR (400.13 MHz, CD_3CN): δ 7.56-7.54 (m, 2H, H_o from Ph), 7.47-7.38 (m, 3H, $H_{m,p}$ from Ph), 7.25 (dd, ^3J = 7.1 Hz, ^4J = 1.8 Hz, 1H, H-7), 7.01 (d, $^3J_{5,6}$ = 9.7 Hz, 1H, H-6), 6.91-6.83 (m, 2H, H-9, H-8), 6.32 (d, ^3J = 7.8 Hz, 1H, H-10), 6.20 (dd, $^3J_{5,6}$ = 9.7 Hz, $^3J_{4a,5}$ = 4.7 Hz, 1H, H-5), 6.07 (s, 1H, H-2), 5.69 (d, $^3J_{4a,5}$ = 4.8 Hz, 1H, H-4a), 3.91-3.78 (m, 2H, CH_2), 1.24 (t, 3H, ^3J = 7.0 Hz, CH_3) ppm.

^{19}F NMR (376.50 MHz, CD_3CN): δ -80.1 (CF_3) ppm.

^{13}C NMR (100.6 Hz, CD_3CN): δ 150.5, 138.1, 135.4, 131.1, 130.4, 130.1, 129.6, 128.9, 127.42, 127.36, 123.2 (q, $^1J_{CF}$ = 286.2 Hz, CF_3), 121.6, 119.0, 117.9, 112.8, 95.6 (q, $^2J_{CF}$ = 31.7 Hz), 80.3, 60.0, 15.8 ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{21}H_{18}F_3NO_2^+$: 374.1362; found: 374.1369.

Reaction of oxazine (3a) with methyl 2-mercaptoacetate. A 4 mL vial with a screw cup was charged with

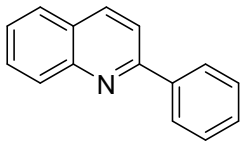


with oxazine **3a** (0.071 g, 0.2 mmol), solution of methyl 2-mercaptoacetate in MeOH (1 mL, 0.5 M, 0.5 mmol) and left at room temperature for 72 h. MeOH was evaporated to give 0.093 g of light brown oil, consisting of quinoline, methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (85:15 mixture of isomers) and dimethyl 2,2'-disulfanediyldiacetate ($MeCO_2$-CH_2-S-S-CH_2CO_2Me appeared due to oxidation of methyl 2-mercaptoacetate by oxygen) in molar ratio 1:1:0.22. Compound **5**, major isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.40-7.42 (m, 2H, Ar), 7.21-7.25 (m, 3H, Ar), 6.57 (s, 1H, C=C<u>H</u>), 3.52 (s, 3H, OC<u>H</u>$_3$), 3.31 (s, 2H, SC<u>H</u>$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 177.3 (q, <u>C</u>-CF_3, J = 35.0), 171.3, 168.3, 136.7, 129.9, 128.8, 127.6, 116.1 (q, CF_3, J = 290.4), 114.8, 52.5, 35.0. ^{19}F NMR (376.50 Hz, $CDCl_3$): δ -78.7. Minor isomer: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.41-7.44 (m, 2H, Ar), 7.30-7.32 (m, 3H, Ar), 6.47 (s, 1H, C=C<u>H</u>), 3.78 (s, 3H, OC<u>H</u>$_3$), 3.66 (s, 2H, SC<u>H</u>$_2$). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 130.2, 128.4, 127.9, 109.3, 52.9, other signals are identical to those of major isomer. ^{19}F NMR (376.50 Hz, $CDCl_3$): δ -79.6. Quinoline: ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.88 (dd, ^3J = 4.3 Hz, ^4J = 1.7 Hz, 1H), 8.14 (dd, ^3J = 8.3 Hz, ^4J = 1.1 Hz, 1H), 8.09 (d, ^3J = 8.5 Hz, 1H), 7.78 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1H), 7.70-7.66 (m, 1H), 7.53-7.49 (m, 1H), 7.38-7.34 (m, 1H). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 150.0, 147.7, 136.3, 129.5, 128.9, 128.2, 127.7, 126.6, 121.0. The NMR data of 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5**[3] and quinoline[4] are in agreement with those in the literature.

Transformation of oxazine (3a) into 2-phenylquinoline (6). A 4 mL vial with a screw cap was charged with oxazine **3a** (0.030 g, 0.087 mmol), water (0.5 mL) and NaOH (0.0104 g, 0.261 mmol). The reaction mixture was heated at 80 °C at stirring for 2 h. After cooling down to room temperature, the reaction mixture was extracted with EtOAc (2x0.5 mL), combined organic phase was passed through a short silica gel pad

[3] V. M. Muzalevskiy, A. A. Iskandarov, V. G. Nenajdenko, *J. Fluorine Chem*. **2018**, 214, 13-16.
[4] T. Kaiya, N. Shiraiy, Y. Kawazoe, *Chem. Pharm. Bull*., 1986, **34**, 881-885.

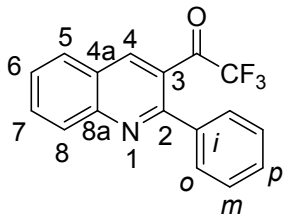
using heptane followed by heptane-EtOAc (15:1) as an eluents. Evaporation of volatiles afforded **6** as light brown powder, m.p. 81-83 °C (Lit. data: 82-84 °C[5]), yield 0.016 g (90%).



^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.22 (d, ^3J = 8.6 Hz, 1H), 8.19-8.15 (m, 3H), 7.87 (d, ^3J = 8.6 Hz, 1H), 7.83 (dd, ^3J = 8.1 Hz, ^4J = 0.7 Hz, 1H), 7.75-7.70 (m, 1H), 7.54-7.51 (m, 3H), 7.48-7.44 (m, 1H) ppm.

^{13}C NMR (100.6 MHz, $CDCl_3$): δ 157.3, 148.2, 139.6, 136.7, 129.63, 129.61, 129.3, 128.8, 127.5, 127.4, 127.1, 126.2, 119.0 ppm. The NMR data are in agreement with those in the literature[4].

Transformation of oxazine (3a) into 2,2,2-trifluoro-1-(2-phenylquinolin-3-yl)ethanone (7). A 4 mL vial with a screw cap was charged with oxazine **3a** (0.030 g, 0.087 mmol), MeCN (0.5 mL) and morpholine (0.0075 g, 0.087 mmol). The reaction mixture was heated at 80 °C for 6 h and then volatiles were evaporated in vacuo. The residue was passed through a short silica gel pad using heptane followed by heptane-EtOAc (10:1) as an eluents. Evaporation of volatiles afforded **7** as a pale yellow powder, m.p. 86-87 °C, yield 0.023 g (88%).



^{1}H NMR (400.1 MHz, CD_3CN): δ 8.77 (s, 1H, H-4), 8.09 (m, 1H, H-8), 8.07 (m, 1H, H-5), 7.91 (m, 1H, H-7), 7.68 (m, 1H, H-6), 7.56 (m, 2H, H_o from Ph), 7.49 (m, 3H, $H_{m,p}$ from Ph) ppm.

^{13}C NMR (100.6 MHz, CD_3CN): δ 185.4 (q, $^2J_{CF}$ = 36.0 Hz, C=O), 158.4 (C-2), 149.6 (C-8a), 140.8 (C_i from Ph), 140.7 (q, $^4J_{CF}$ = 3.0 Hz, C-4), 134.3 (C-8), 130.3 (C-6), 130.2 (C_p from Ph, C-7), 130.1 (C_o from Ph), 129.6 (C_m from Ph), 129.1 (C-5), 126.4 (C-4a), 126.0 (C-3), 117.1 (q, $^1J_{CF}$ = 291.7 Hz, CF_3) ppm.

^{19}F NMR (376.5 MHz, CD_3CN): δ -72.4 (CF_3) ppm.

^{1}H NMR (400.1 MHz, $CDCl_3$): δ 8.59 (s, 1H, H-4), 8.21 (d, ^3J = 8.5 Hz, 1H, H-8), 7.97 (d, ^3J = 8.1 Hz, 1H, H-5), 7.91 (ptd, ^3J ~ 8 Hz, ^4J ~ 1 Hz, 1H, H-7), 7.68 (ptd, ^3J ~ 8 Hz, ^4J ~ 1 Hz, 1H, H-6), 7.59-7.57 (m, 2H, H_o from Ph), 7.52-7.48 (m, 3H, $H_{m,p}$ from Ph) ppm.

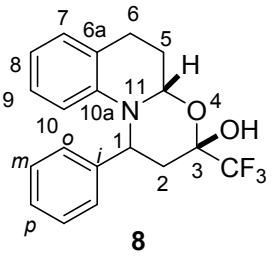
^{13}C NMR (100.6 MHz, $CDCl_3$): δ 184.6 (q, $^2J_{CF}$ = 36.0 Hz, C=O), 157.7 (C-2), 148.7 (C-8a), 139.3 (C_i from Ph), 139.0 (q, $^4J_{CF}$ = 3.0 Hz, C-4), 133.0 (C-8), 129.3 (C-6), 128.9 (C_o from Ph), 128.8 (C_m from Ph), 128.7 (C_p from Ph, C-7), 127.9 (C-5), 125.9 (C-4a), 124.9 (C-3), 115.9 (q, $^1J_{CF}$ = 292.1 Hz, CF_3) ppm.

^{19}F NMR (376.5 MHz, $CDCl_3$): δ -73.7 (CF_3) ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{17}H_{11}F_3NO^+$: 302.0793; found: 302.0790.

[5] N. Sudhapriya, A. Nandakumar, P. T. Perumal, *RSC Advances*, 2014, **4**, 58476-58480.

Hydrogenation of (3*R,4a*R*)-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3a) to form 8 and 9.** Three-necked round bottomed flask was charged with oxazine **3a** (0.105 g, 0.304 mmol), 10% Pd on carbon (0.032 g, 0.03 mmol, 10 mol%) and THF (5 mL). The flask was evacuated and flushed with H_2 from a balloon. The solution formed was stirred 36 h and filtered off. The filter cake was washed with EtOAc (3*3 mL), the volatiles were evaporated in vacuo. The residue was passed through a short silica gel pad using heptane followed by heptane-EtOAc (10:1) as an eluents. Evaporation of the volatiles afforded a mixture **8** and **9** (75:25) as a colorless oil, yield 0.077 g (72%).



8

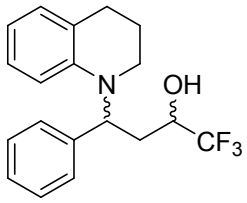
(3R*,4aR*)-1-Phenyl-3-(trifluoromethyl)-2,3,4a,5-tetrahydro-1H,6H-[1,3]oxazino[3,2-a]quinolin-3-ol (8). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.44-7.29 (m, 5H, Ph), 7.08 (d, ^3J = 7.3 Hz, 1H, H-7), 7.01 (pseudo-t, ^3J ~ 8 Hz, 1H, H-9), 6.76 (pseudo-t, ^3J ~ 7 Hz, 1H, H-8), 6.40 (d, ^3J = 8.1 Hz, 1H, H-10), 5.53 (br s, 1H, H-4a), 4.98 (dd, ^3J = 11.8 Hz, ^3J = 7.0 Hz, 1H, H-1), 3.10-2.93 (m, 1H), 2.79-2.67 (m, 3H), 2.37-2.30 (m, 1H), 2.33 (dd, ^3J = 14.4 Hz, ^3J = 11.8 Hz, 1H, H-2), 2.11-2.02 (m, 1H) ppm.

^{19}F NMR (376.50 Hz, $CDCl_3$): δ -88.0 (CF_3) ppm;

^{13}C NMR (100.16 Hz, $CDCl_3$): δ 143.4 (C_q), 142.2 (C_q), 129.1 (C_m from Ph), 128.5, 128.3, 127.5, 127.4, 127.0, 125.1 (C_o from Ph), 123.2 (C_q), 122.3 (q, $^1J_{CF}$ = 285.5 Hz, CF_3), 118.5, 112.9, 94.4 (q, $^2J_{CF}$ = 31.5 Hz, C-3), 79.2 (C-4a), 55.5 (C-1), 33.4 (CH_2), 25.9 (CH_2), 21.6 (CH_2) ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{19}H_{18}F_3NO_2^+$: 350.1362; found: 350.1351.

4-(3,4-diHydroquinolin-1(2H)-yl)-1,1,1-trifluoro-4-phenylbutan-2-ol (9). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.44-7.29 (m, 5H, Ph), 6.64 (pseudo-t, ^3J ~ 7 Hz, 1H, H-8), 6.47 (d, ^3J = 8.1 Hz, 1H, H-10), 5.61-5.37 (m, 1H), 4.14-4.10 (m, 1H), 3.10-2.93 (m, 2H), 2.79-2.67 (m, 1H), 2.50-2.43 (m, 1H), 2.37-2.30 (m, 2H), 2.29-2.22 (m, 1H), 1.87-1.84 (m, 2H) ppm.



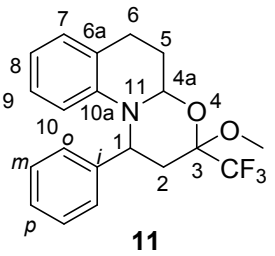
9

^{19}F NMR (376.50 Hz, $CDCl_3$): δ -80.8 (d, $^3J_{HF}$ = 6.8 Hz CF_3) ppm;

^{13}C NMR (100.16 Hz, $CDCl_3$): δ 145.8 (C_q), 140.0 (C_q), 129.7 (C_m from Ph), 129.0, 127.4, 127.3, 125.5 (C_o from Ph), 122.8 (C_q), 125.4 (q, $^1J_{CF}$ = 281.7 Hz, CF_3), 116.2, 111.0, 67.7 (q, $^2J_{CF}$ = 31.5 Hz, C-3), 54.3 (C-1), 42.1, 29.9 (CH_2), 28.5 (CH_2), 21.7 (CH_2) ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{19}H_{20}F_3NO^+$: 336.1570; found: 336.1560.

Hydrogenation of (3*R,4a*R*)-1-phenyl-3-(trifluoromethyl)-3*H*,4a*H*-[1,3]oxazino[3,2-*a*]quinolin-3-ol (3a) to form 11.** Three-necked round bottomed flask was charged with oxazine **3a** (0.105 g, 0.304 mmol), 10% Pd on carbon (0.034 g, 0.03 mmol, 10 mol%) and MeOH (5 mL). The flask was evacuated and flushed with H_2 from a balloon. The solution formed was stirred 36 h and filtered off. The filter cake was washed with EtOAc (3*3 mL), the volatiles were evaporated in vacuo. The residue was passed



11

through a short silica gel pad using heptane followed by heptane-EtOAc (10:1) as an eluents. Compounds **10** and **11** were isolated as a separate fractions.

3-Methoxy-1-phenyl-3-(trifluoromethyl)-4a,5-dihydro-3H,6H-[1,3]oxazino[3,2-a]quinoline (10). Colorless oil, yield 0.011 g (10%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H, Ph), 7.11-7.09 (m, 1H), 6.84-6.78 (m, 2H), 6.22-6.20 (m, 1H), 5.60 (br s, 1H, H-4a), 5.33 (t, ^{3}J = 7.7 Hz, 1H), 3.52 (s, 1H, MeO), 2.81-2.63 (m, 3H), 1.92-1.82 (m, 1H) ppm.

^{19}F NMR (376.50 Hz, $CDCl_3$): δ -81.5 (CF_3) ppm;

^{13}C NMR (100.16 Hz, $CDCl_3$): δ 149.3, 138.8, 134.7, 130.3, 129.6 128.6, 127.1, 126.8, 122.4 (q, $^{1}J_{CF}$ = 286.9 Hz, CF_3), 121.5, 120.2, 105.6, 95.7 (q, $^{2}J_{CF}$ = 31.8 Hz, C-3), 83.0 (C-4a), 50.8 (MeO), 29.4(CH_2), 24.7 (CH_2) ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{20}H_{19}F_3NO_2^+$: 362.1362; found: 362.1357.

3-Methoxy-1-phenyl-3-(trifluoromethyl)-2,3,4a,5-tetrahydro-1H,6H-[1,3]oxazino[3,2-a]quinoline (11). A colorless oil solidifies at standing, m.p. 142-143 °C, yield 0.093 g (84%). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 7.41-7.29 (m, 5H, Ph), 7.05 (d, ^{3}J = 7.3 Hz, 1H, H-7), 6.99 (pseudo-t, ^{3}J ~ 8 Hz, 1H, H-9), 6.73 (pseudo-t, ^{3}J ~ 7 Hz, 1H, H-8), 6.39 (d, ^{3}J = 8.1 Hz, 1H, H-10), 5.52 (br s, 1H, H-4a), 4.90 (dd, ^{3}J = 11.9 Hz, ^{3}J = 7.0 Hz, 1H, H-1), 3.29 (s, 1H, MeO), 3.14-3.06 (m, 1H), 2.78-2.68 (m, 1H), 2.59 (dd, ^{3}J = 14.3 Hz, ^{3}J = 7.0 Hz, 1H, H-2), 2.45-2.39 (m, 1H), 2.33 (dd, ^{3}J = 14.3 Hz, ^{3}J = 11.9 Hz, 1H, H-2), 2.12-2.03 (m, 1H) ppm.

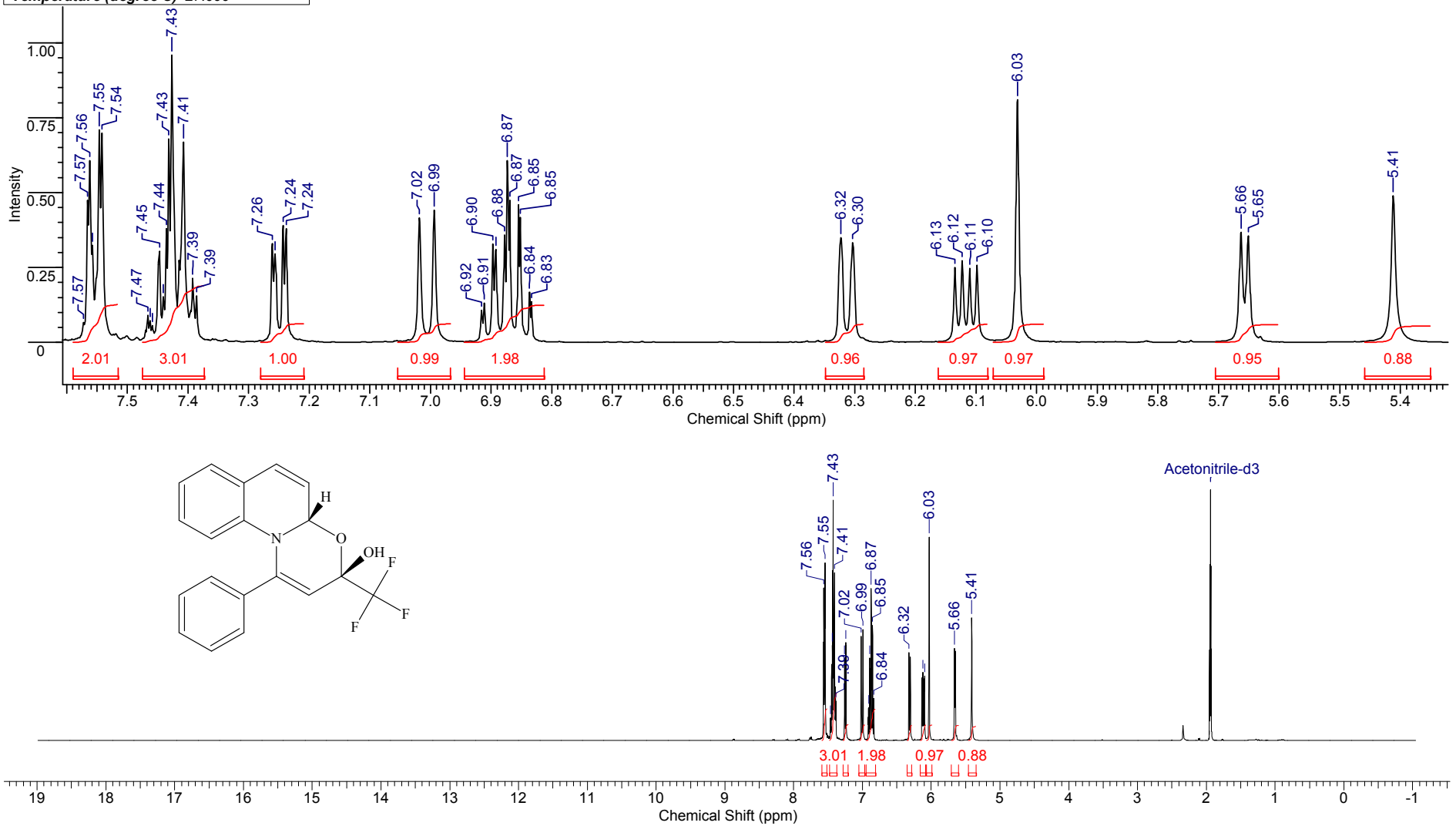
^{19}F NMR (376.50 Hz, $CDCl_3$): δ -83.1 (CF_3) ppm;

^{13}C NMR (100.16 Hz, $CDCl_3$): δ 143.5 (C_q), 142.3 (C_q), 129.1 (C_m from Ph), 128.3, 127.5, 127.4, 125.2 (C_o from Ph), 122.8 (C_q), 122.7 (q, $^{1}J_{CF}$ = 289.3 Hz, CF_3), 118.3, 112.8, 95.8 (q, $^{2}J_{CF}$ = 31.5 Hz, C-3), 79.0 (C-4a), 55.8 (MeO), 50.5 (C-1), 34.6 (CH_2), 26.3(CH_2), 22.3 (CH_2) ppm.

HRMS (ESI-TOF): m/z $[M+H]^+$ Calcd for $C_{20}H_{21}F_3NO_2^+$: 364.1519; found: 364.1522.

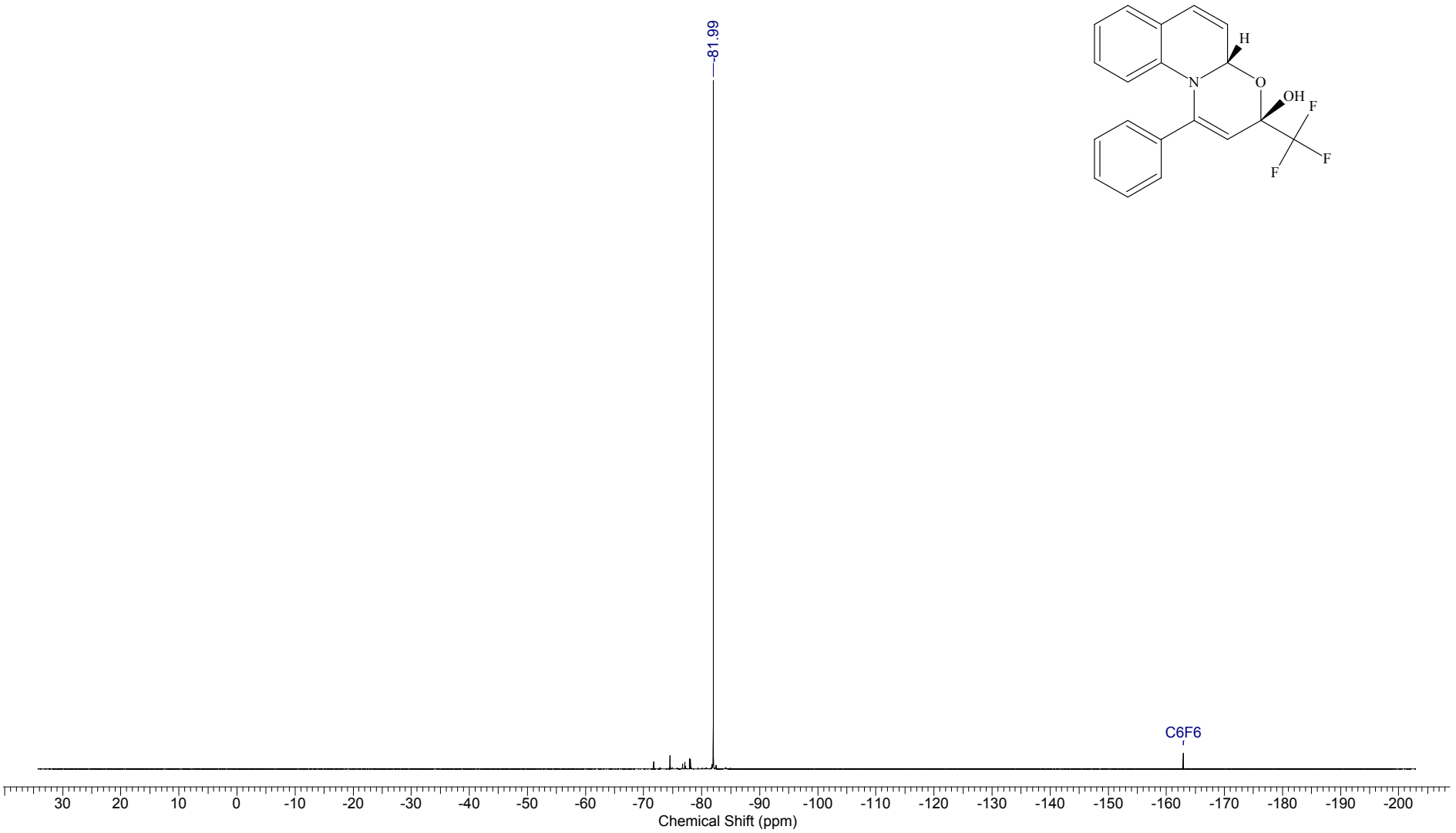
FW	345.3152	***Formula***	$C_{19}H_{14}F_3NO_2$

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	22 Feb 2019 23:06:50
File Name	C:\BM_DATA\DOCS\Manuscr_Ultra\BM_2018\bm190222\BM-1499_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



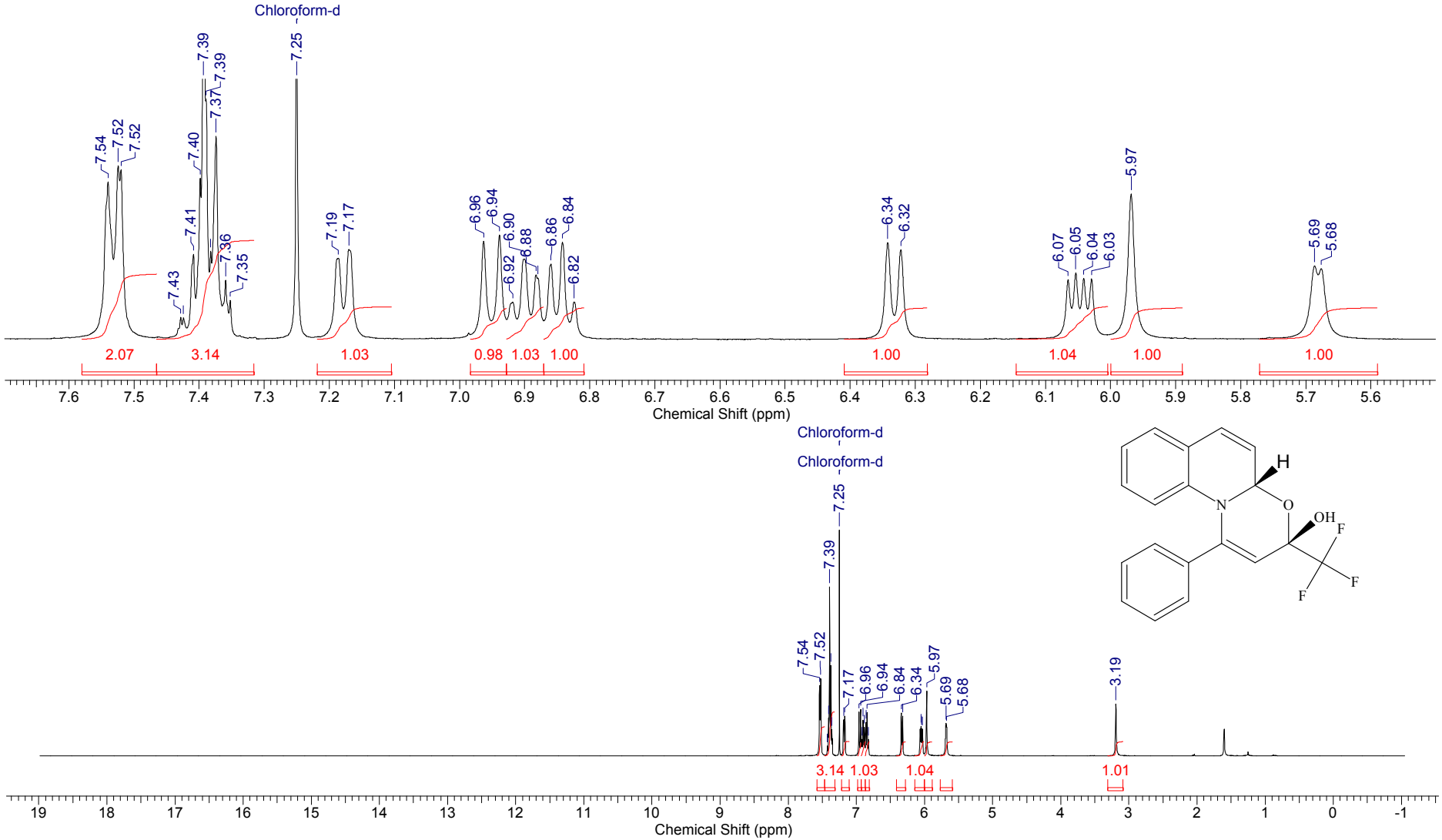
^{1}H NMR spectrum of **3a** (400.1 MHz, CD_3CN)

FW	345.3152	***Formula***	$C_{19}H_{14}F_3NO_2$				
Acquisition Time (sec)	1.9000	***Date***	Oct 1 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.01\BM-1371_20181001_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	169643
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	89285.71
Temperature (degree C)	22.000						



^{19}F NMR spectrum of **3a** (376.5 MHz, CD_3CN)

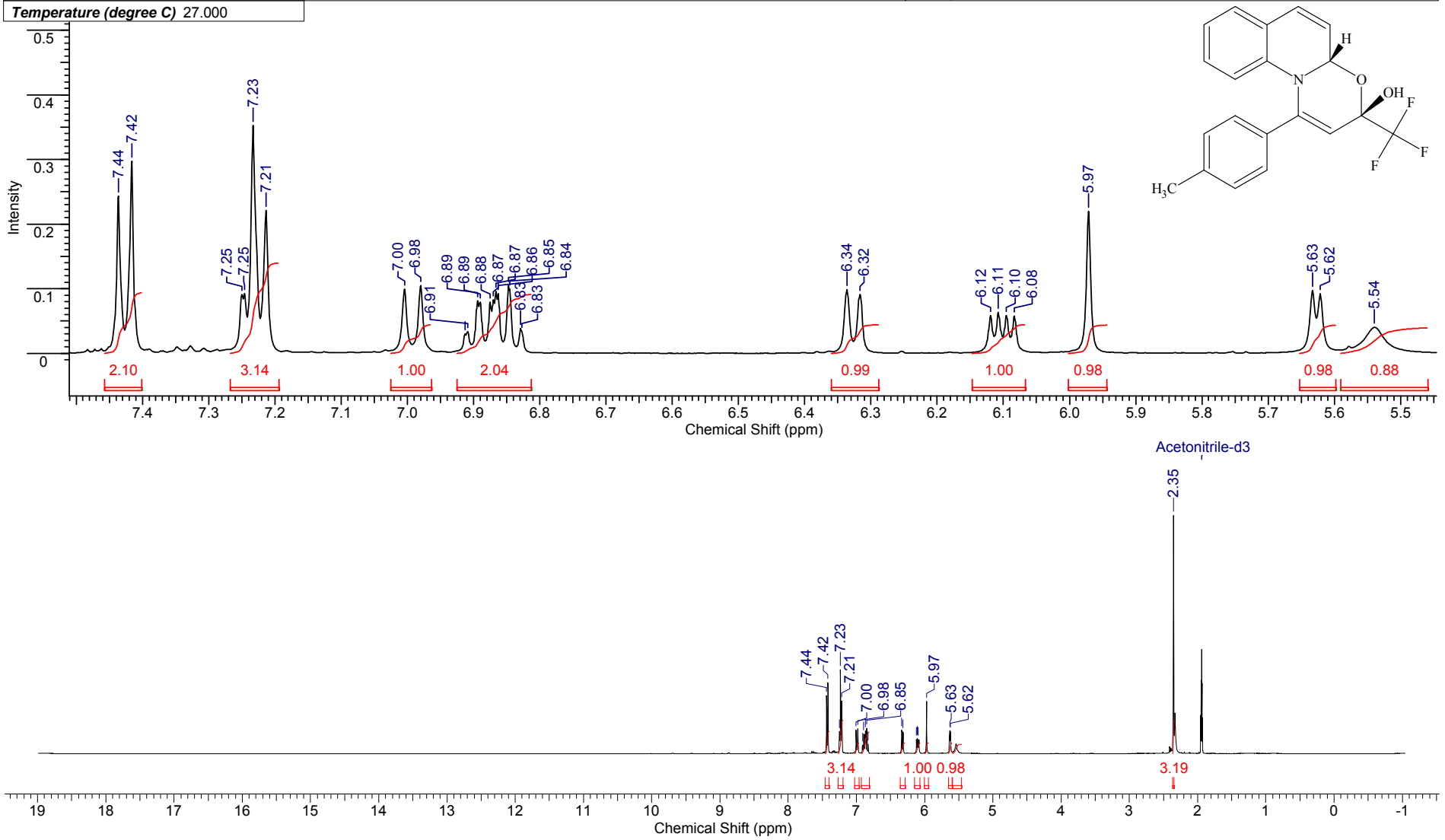
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	24 Jul 2019 17:34:04
File Name	C:\DOCS\OUTPUT_301\2019\07.èþ ëü\190724\BM-1659-1_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3a** in multi gram scale synthesis (400.1 MHz, $CDCl_3$)

FW	359.3418	***Formula***	$C_{20}H_{16}F_3NO_2$

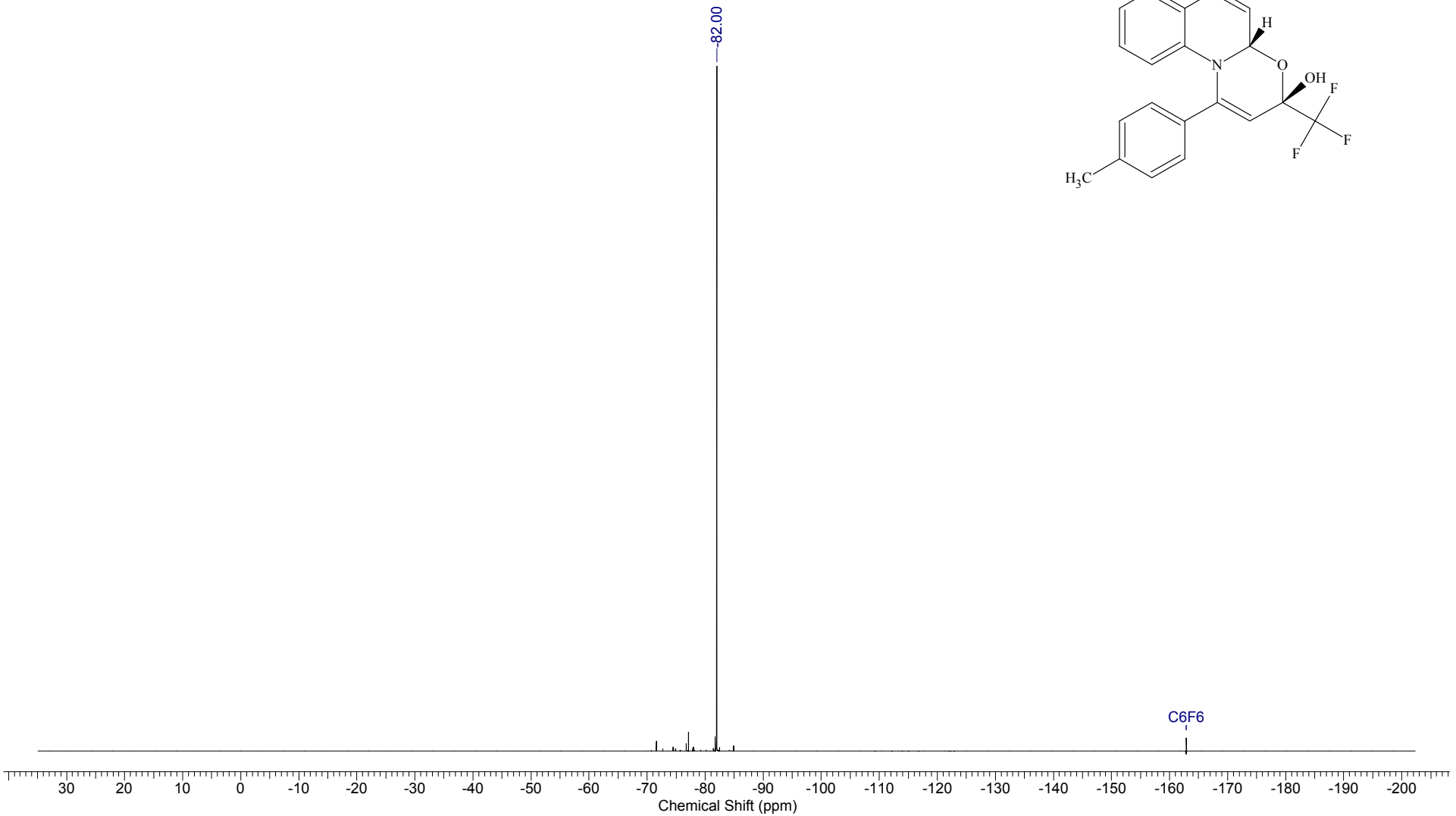
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	27 Sep 2018 19:18:46
File Name	C:\DOCS\OUTPUT_301\2018\09.ñåí òÿáðü\BM-1372\BM-1372_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3b** (400.1 MHz, CD_3CN)

FW	359.3418	***Formula***	$C_{20}H_{16}F_3NO_2$

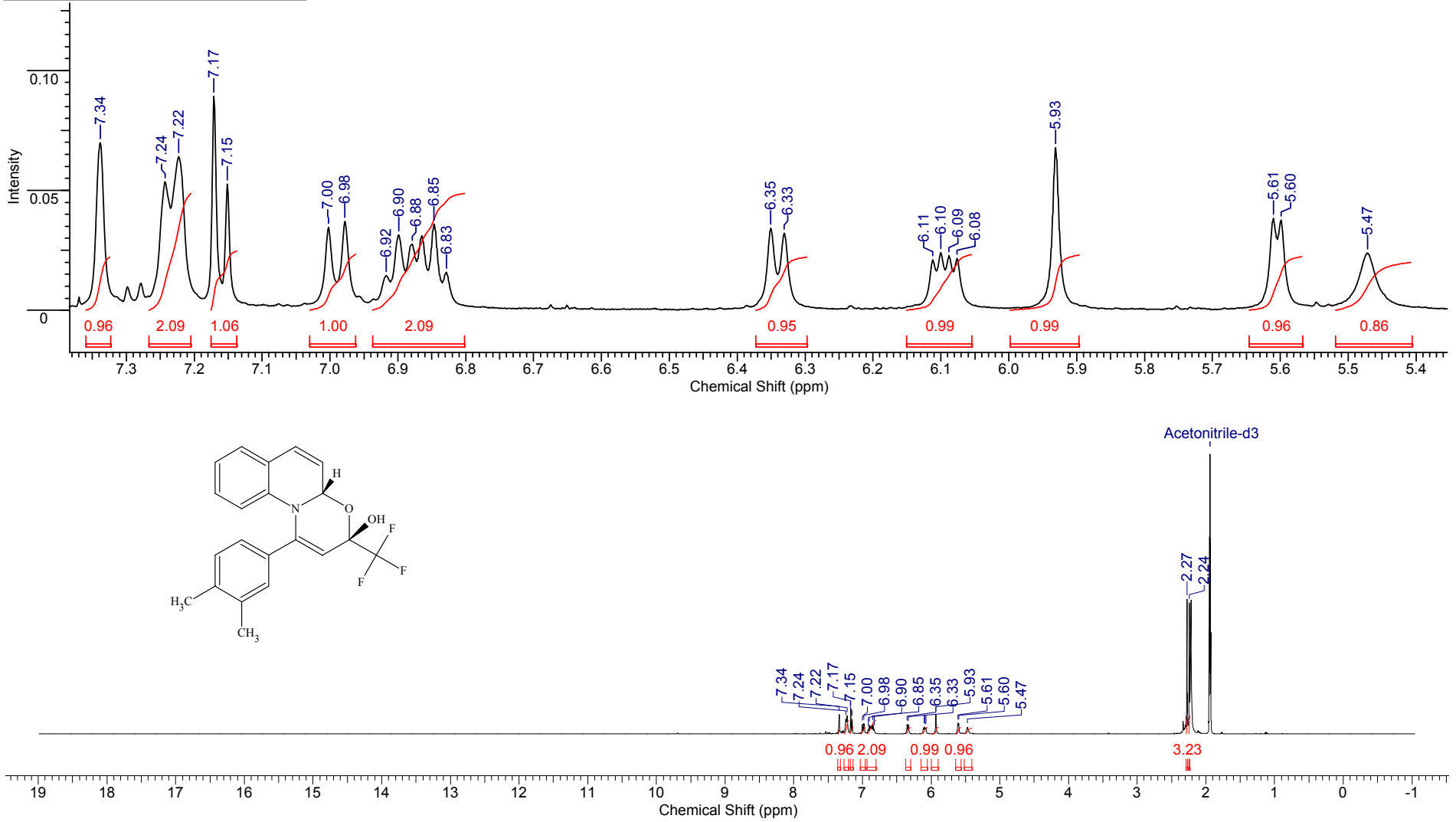
Acquisition Time (sec)	1.0000	***Date***	Sep 28 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.09.28\BM-1372_20180928_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3b** (376.5 MHz, CD_3CN)

FW	373.3684	***Formula***	$C_{21}H_{18}F_3NO_2$

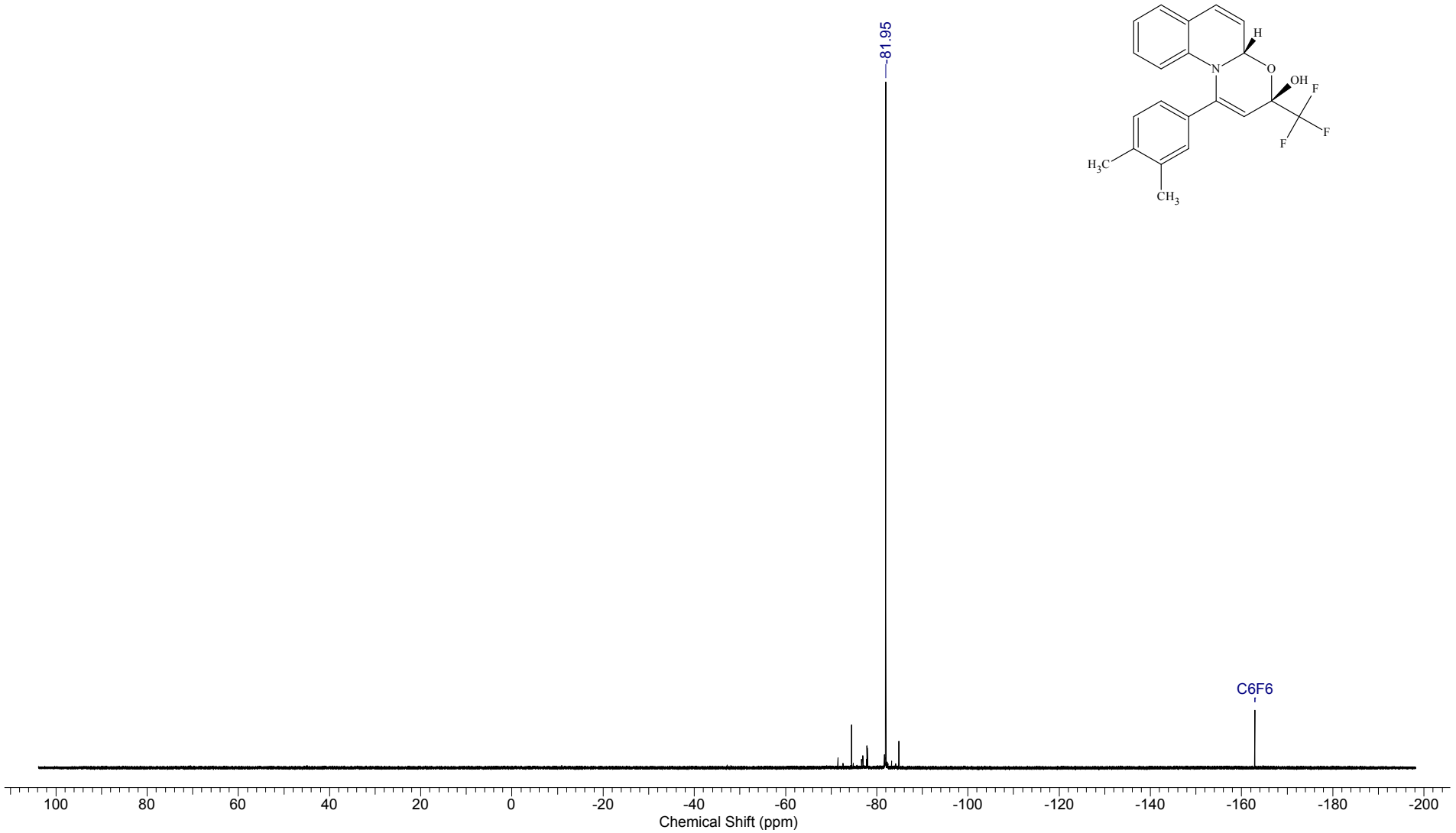
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	17 Oct 2018 23:19:18
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181017\BM-1397d_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3c** (400.1 MHz, CD_3CN)

FW	373.3684	***Formula***	$C_{21}H_{18}F_3NO_2$

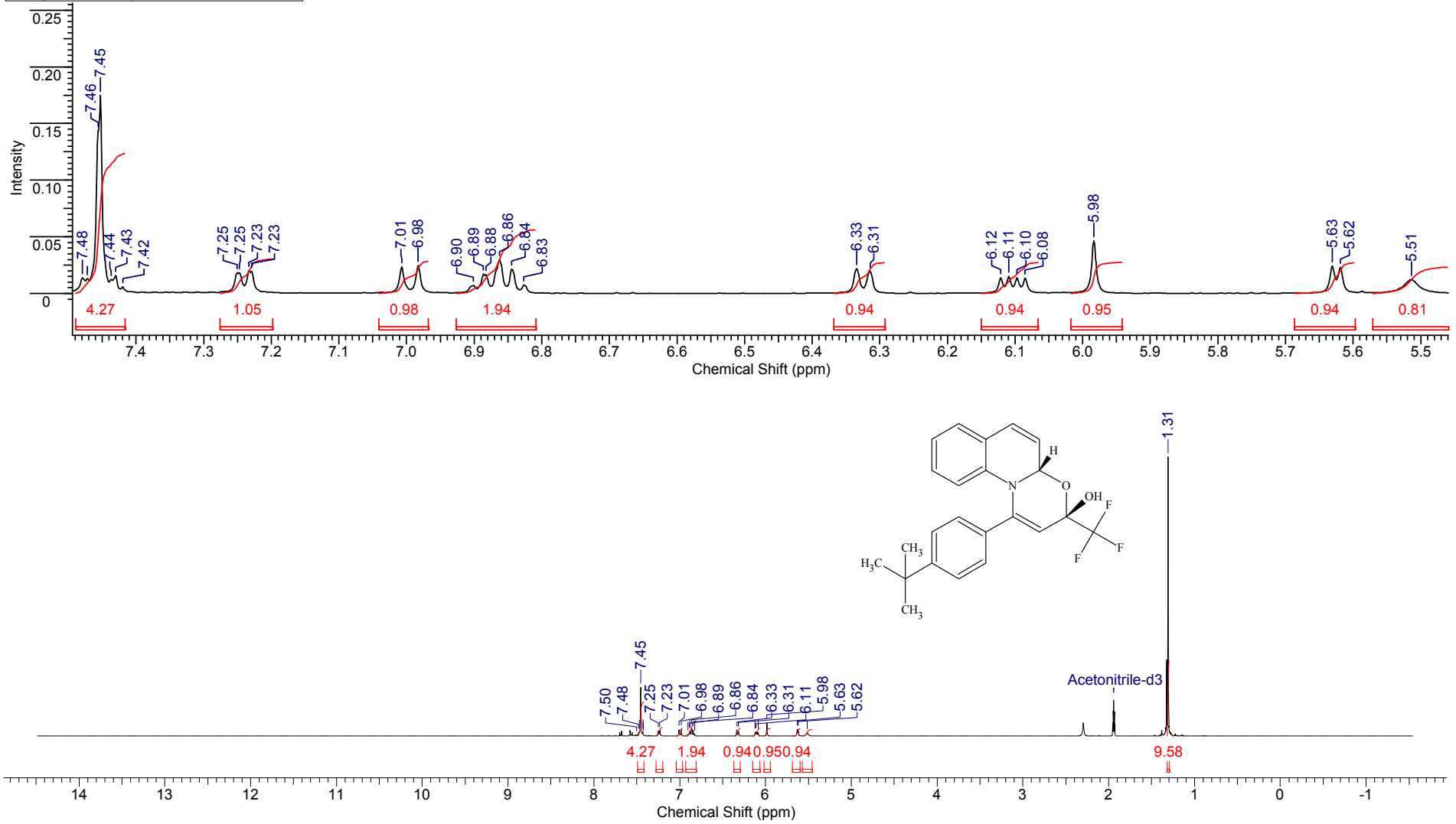
Acquisition Time (sec)	2.3069	***Date***	Oct 18 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.18\BM-1397d-F_20181018_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3c** (376.5 MHz, CD_3CN)

FW	401.4215	Formula	$C_{23}H_{22}F_3NO_2$

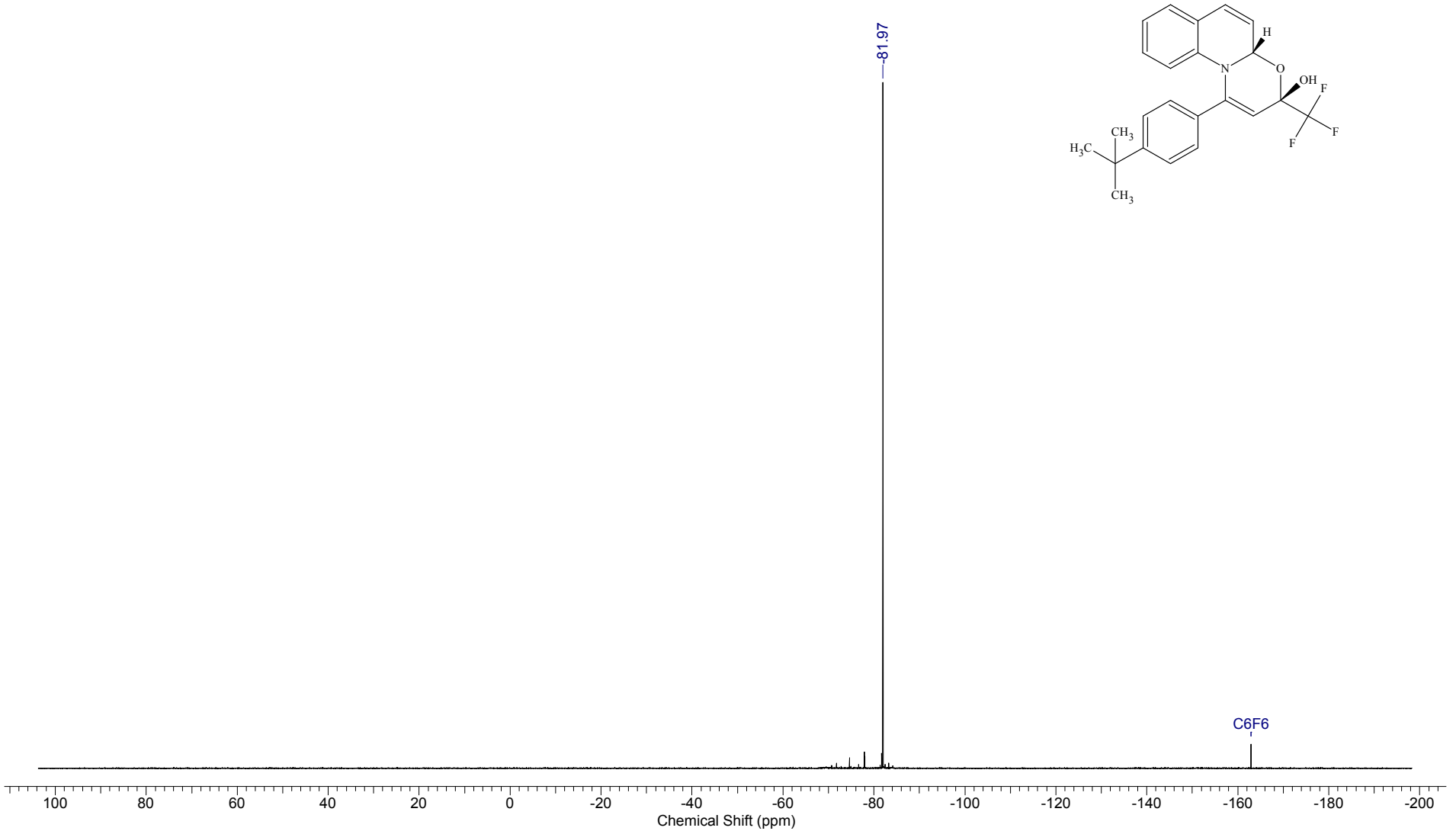
Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	02 Oct 2018 15:32:08
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòýáðü\BM-1377-2.H_001001r					**Frequency (MHz)**	400.13
Nucleus	1H	**Number of Transients**	4	**Original Points Count**	16384	**Points Count**	65536
Pulse Sequence	zg30	**Solvent**	ACETONITRILE-D3			**Sweep Width (Hz)**	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3d** (400.1 MHz, CD_3CN)

FW 401.4215	***Formula*** $C_{23}H_{22}F_3NO_2$

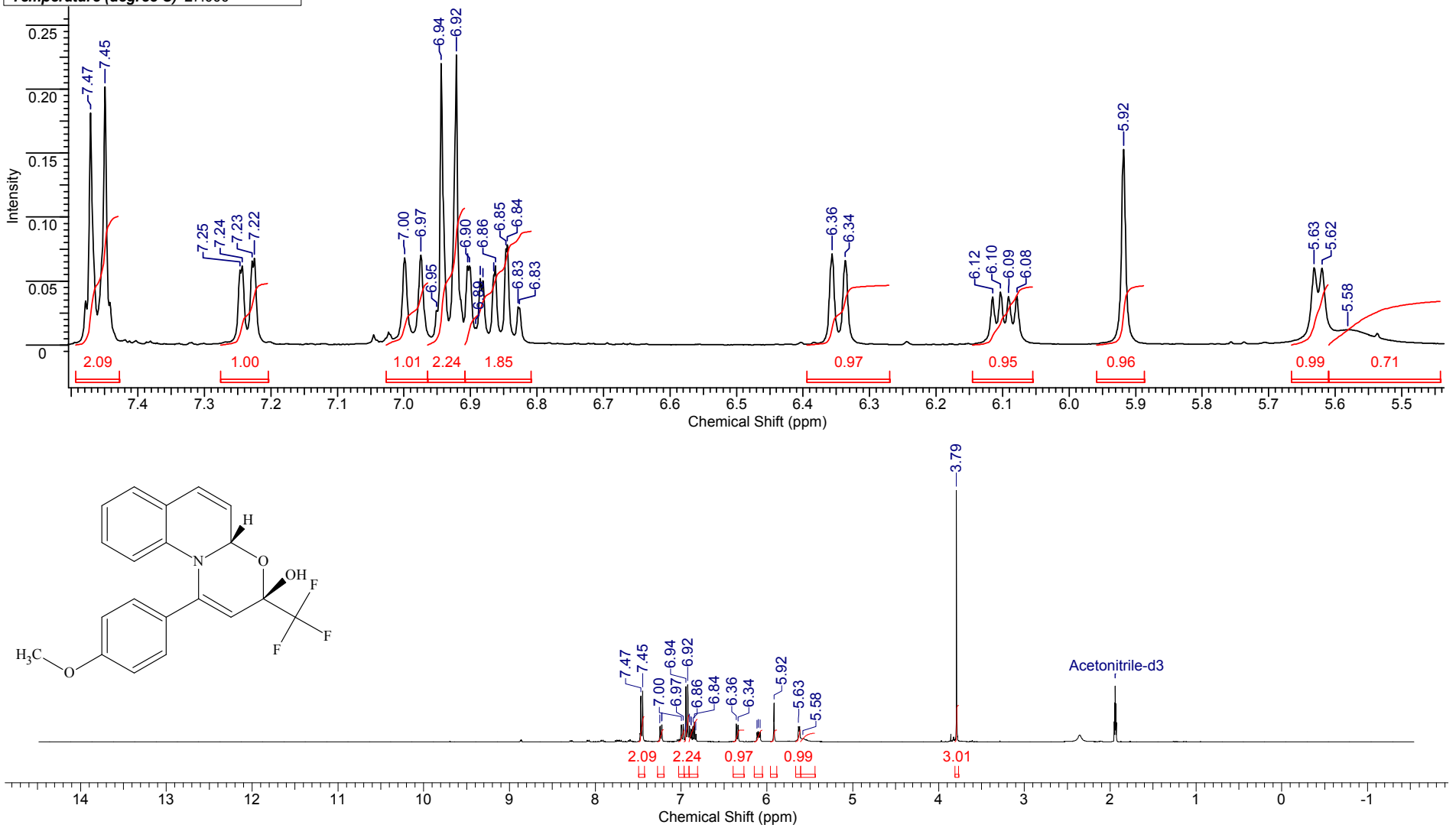
Acquisition Time (sec)	2.3069	***Date***	Oct 4 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.04\BM-1377-F_20181004_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3d** (376.5 MHz, CD_3CN)

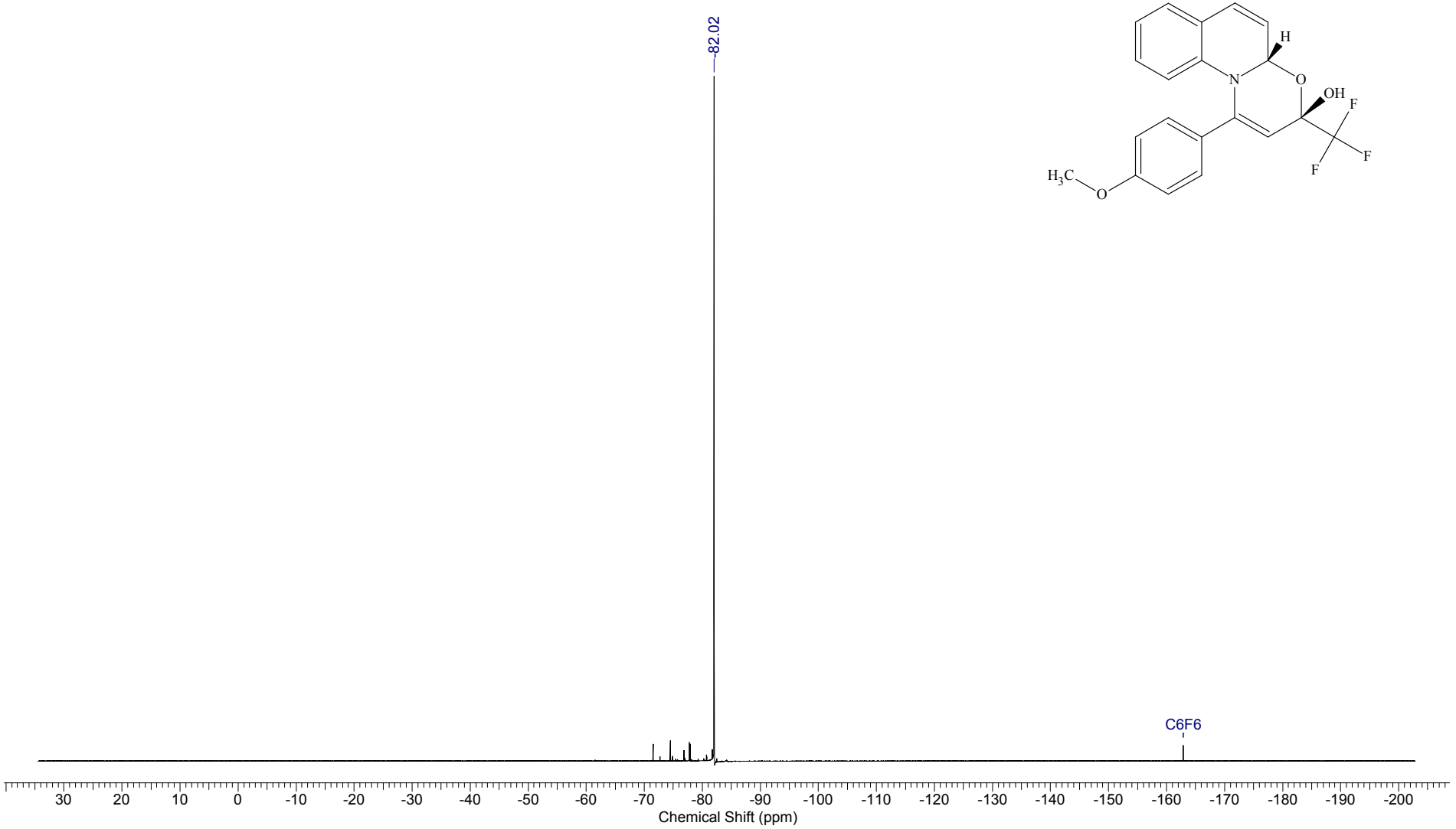
FW	375.3412	Formula	$C_{20}H_{16}F_3NO_3$

Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	29 Sep 2018 14:08:28
File Name	C:\DOCS\OUTPUT_301\2018\09.ñåí òÿáðü\BM-1373.H_001001r					Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	4	Original Points Count	16384	Points Count	65536
Pulse Sequence	zg30	Solvent	ACETONITRILE-D3			Sweep Width (Hz)	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3e** (400.1 MHz, CD_3CN)

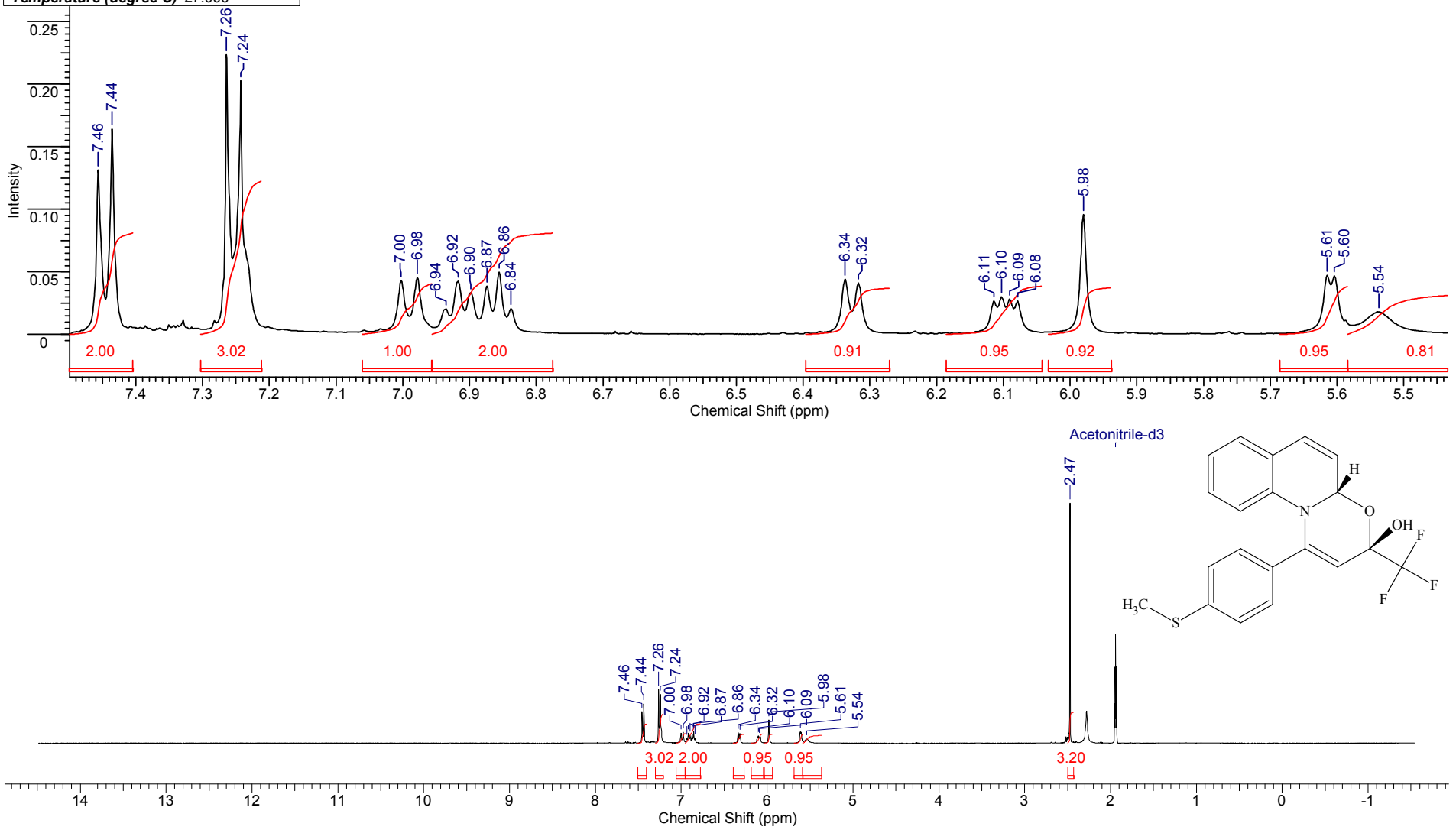
FW	375.3412	***Formula***	$C_{20}H_{16}F_3NO_3$				
Acquisition Time (sec)	1.9000	***Date***	Oct 1 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.01\BM-1373_20181001_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	169643
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	89285.71
Temperature (degree C)	22.000						



^{19}F NMR spectrum of **3e** (376.5 MHz, CD_3CN)

FW	391.4078	**Formula**	$C_{20}H_{16}F_3NO_2S$

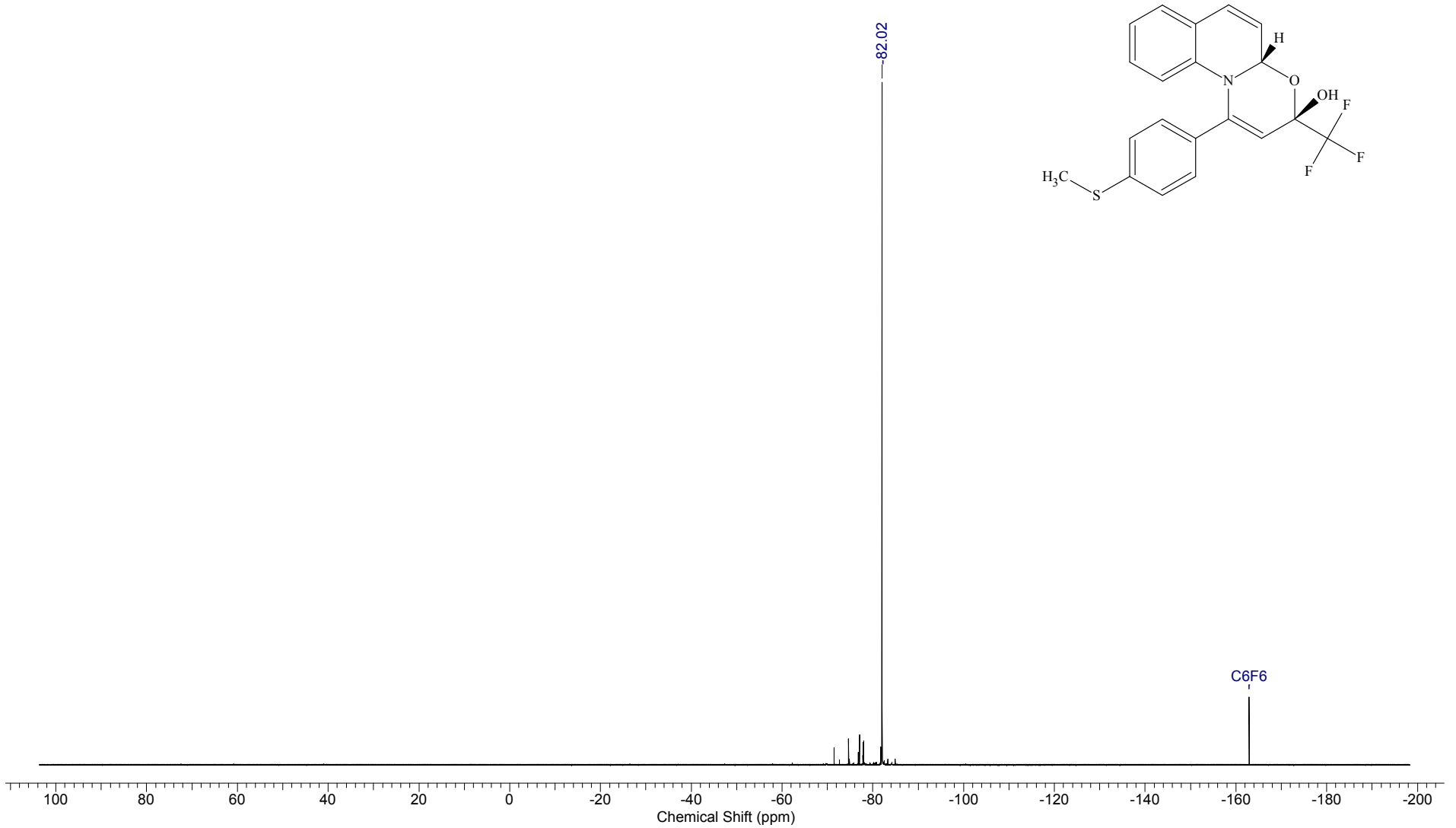
Acquisition Time (sec)	2.5559	**Comment**	Imported from UXNMR.			**Date**	02 Oct 2018 15:34:56
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1378.H_001001r					**Frequency (MHz)**	400.13
Nucleus	1H	**Number of Transients**	4	**Original Points Count**	16384	**Points Count**	65536
Pulse Sequence	zg30	**Solvent**	ACETONITRILE-D3			**Sweep Width (Hz)**	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3f** (400.1 MHz, CD_3CN)

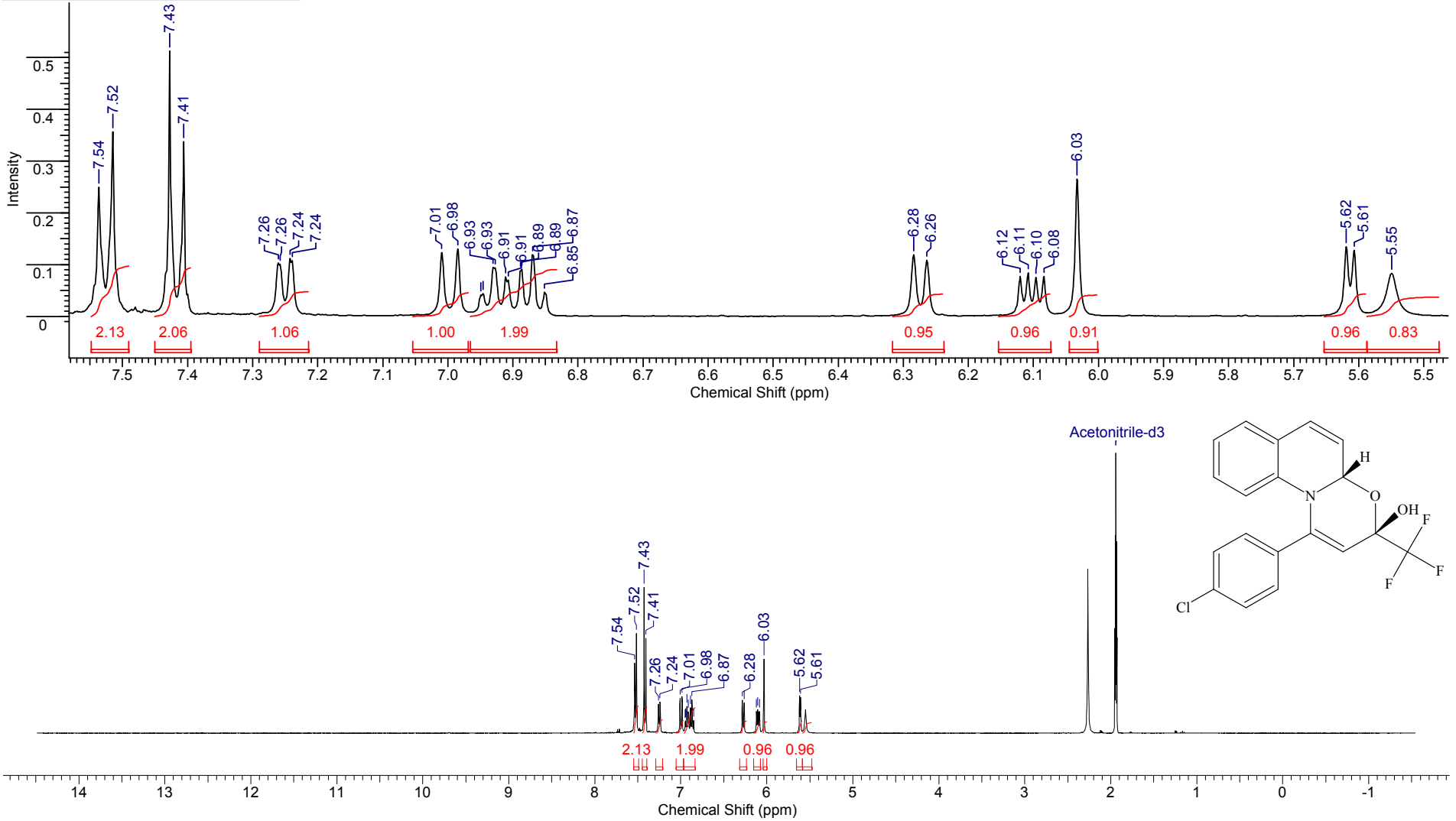
FW	391.4078	***Formula***	$C_{20}H_{16}F_3NO_2S$

Acquisition Time (sec)	2.3069	***Date***	Oct 4 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.04\BM-1378-F_20181004_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3f** (376.5 MHz, CD_3CN)

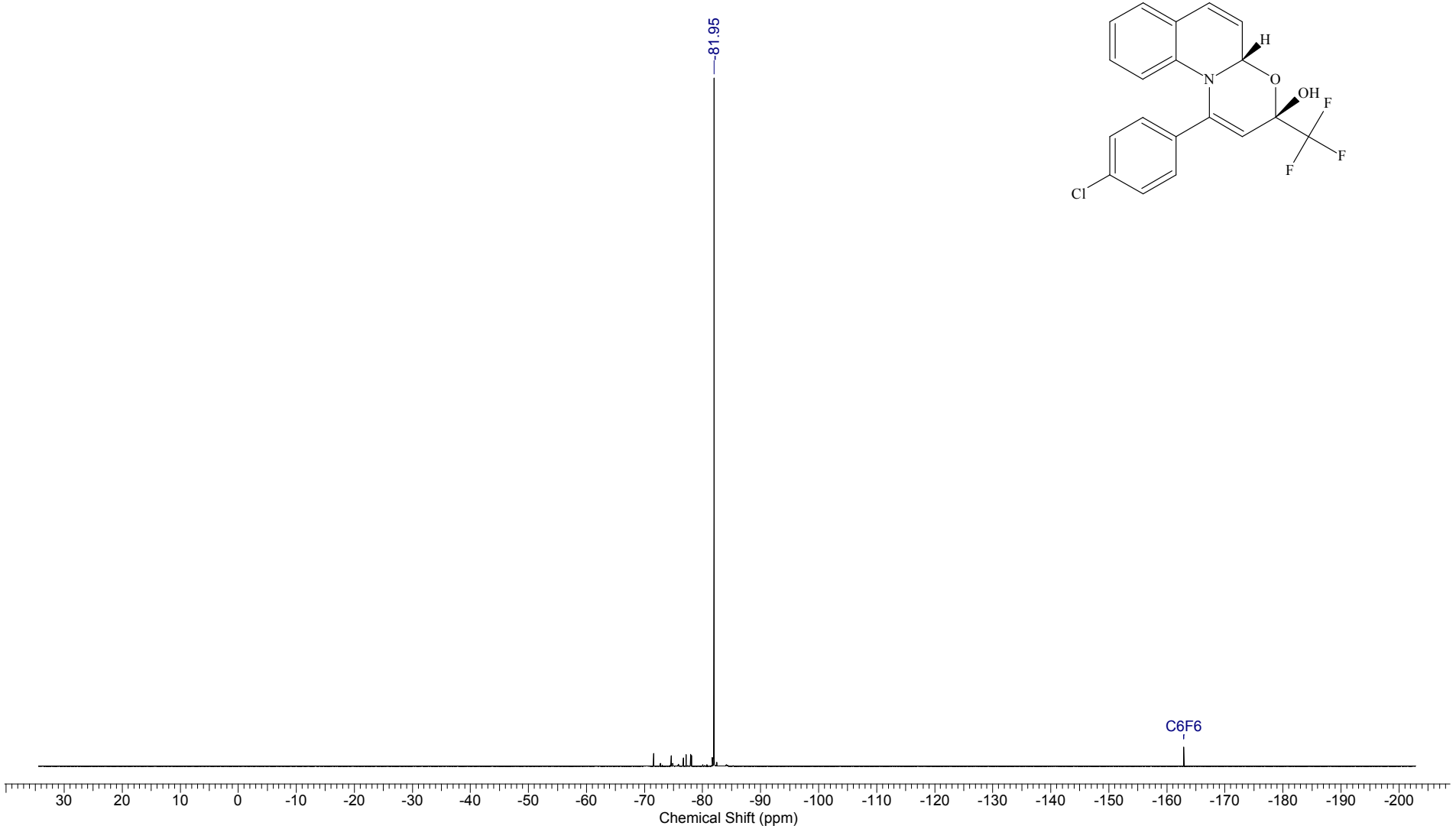
FW	379.7600	***Formula***	$C_{19}H_{13}ClF_3NO_2$				
Acquisition Time (sec)	2.5559	***Comment***	Imported from UXNMR.			***Date***	16 Oct 2018 16:12:24
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1399-2.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	16384	***Points Count***	65536
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3g** (400.1 MHz, CD_3CN)

FW	379.7600	***Formula***	$C_{19}H_{13}ClF_3NO_2$

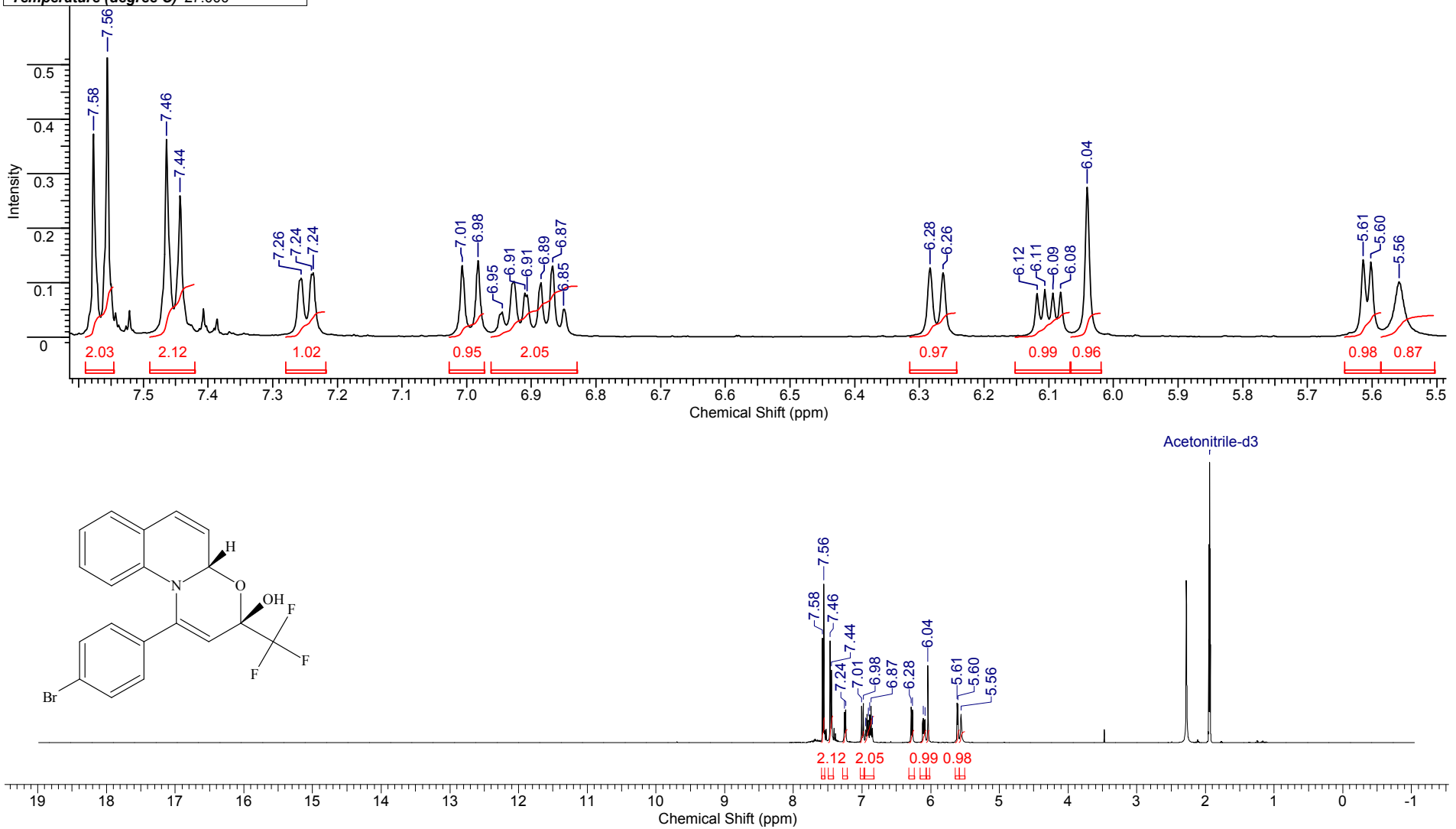
Acquisition Time (sec)	1.9000	***Comment***	STANDARD FLUORINE PARAMETERS			***Date***	Oct 1 2018
File Name	C:\DOCS\OUTPUT_301\F19\2018.10.01\BM1375_20181001_01\FLUORINE_01					***Frequency (MHz)***	376.31
Nucleus	19F	***Number of Transients***	16	***Original Points Count***	169643	***Points Count***	262144
Pulse Sequence	s2pul	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	89285.71	***Temperature (degree C)***	22.000



^{19}F NMR spectrum of **3g** (376.5 MHz, CD_3CN)

FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$

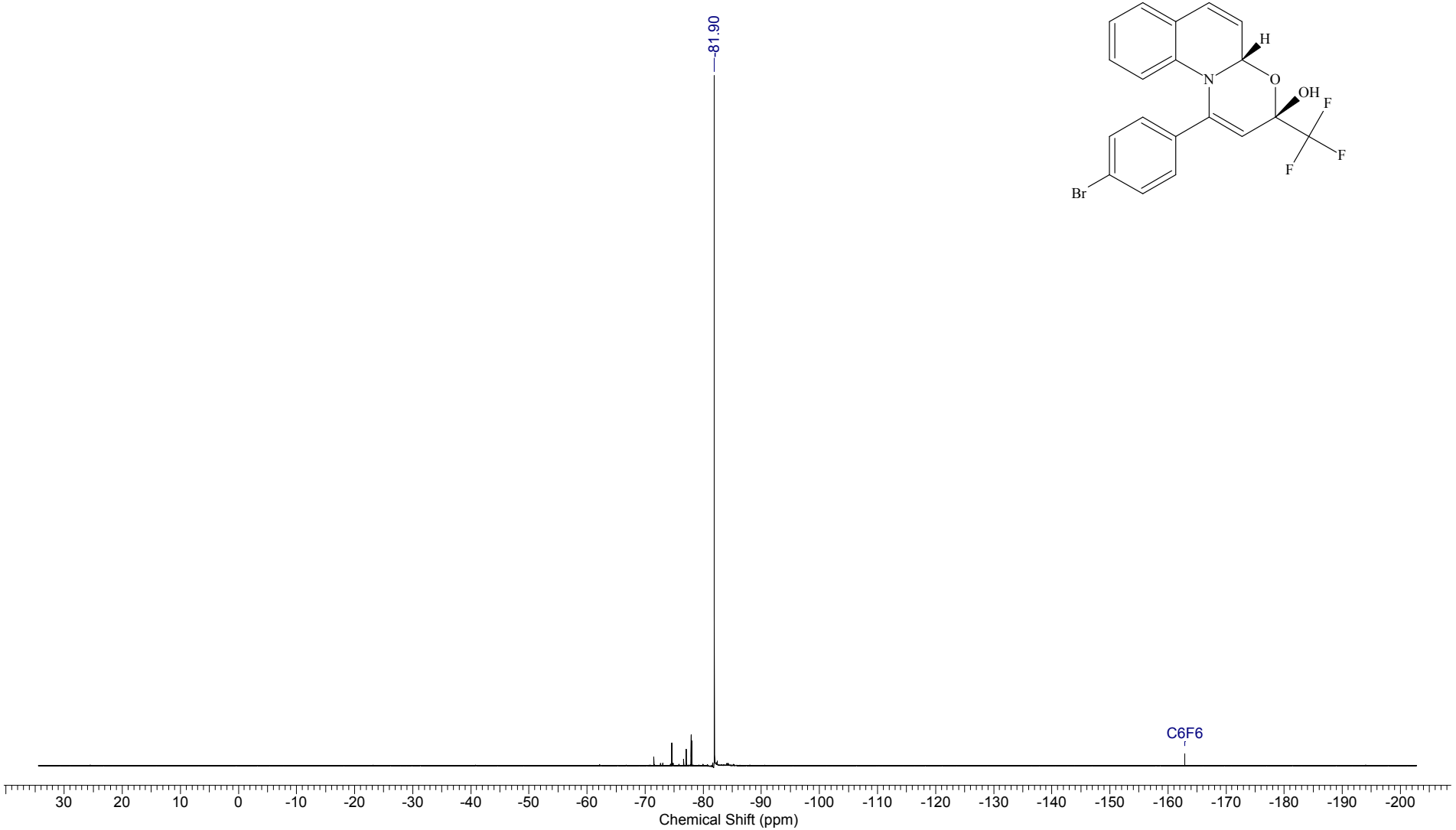
Acquisition Time (sec)	4.0894	**Comment**	Imported from UXNMR.			**Date**	16 Oct 2018 20:47:00
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181016\BM-1398-2_001001r					**Frequency (MHz)**	400.13
Nucleus	1H	**Number of Transients**	8	**Original Points Count**	32768	**Points Count**	131072
Pulse Sequence	zg30	**Solvent**	ACETONITRILE-D3			**Sweep Width (Hz)**	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3h** (400.1 MHz, CD_3CN)

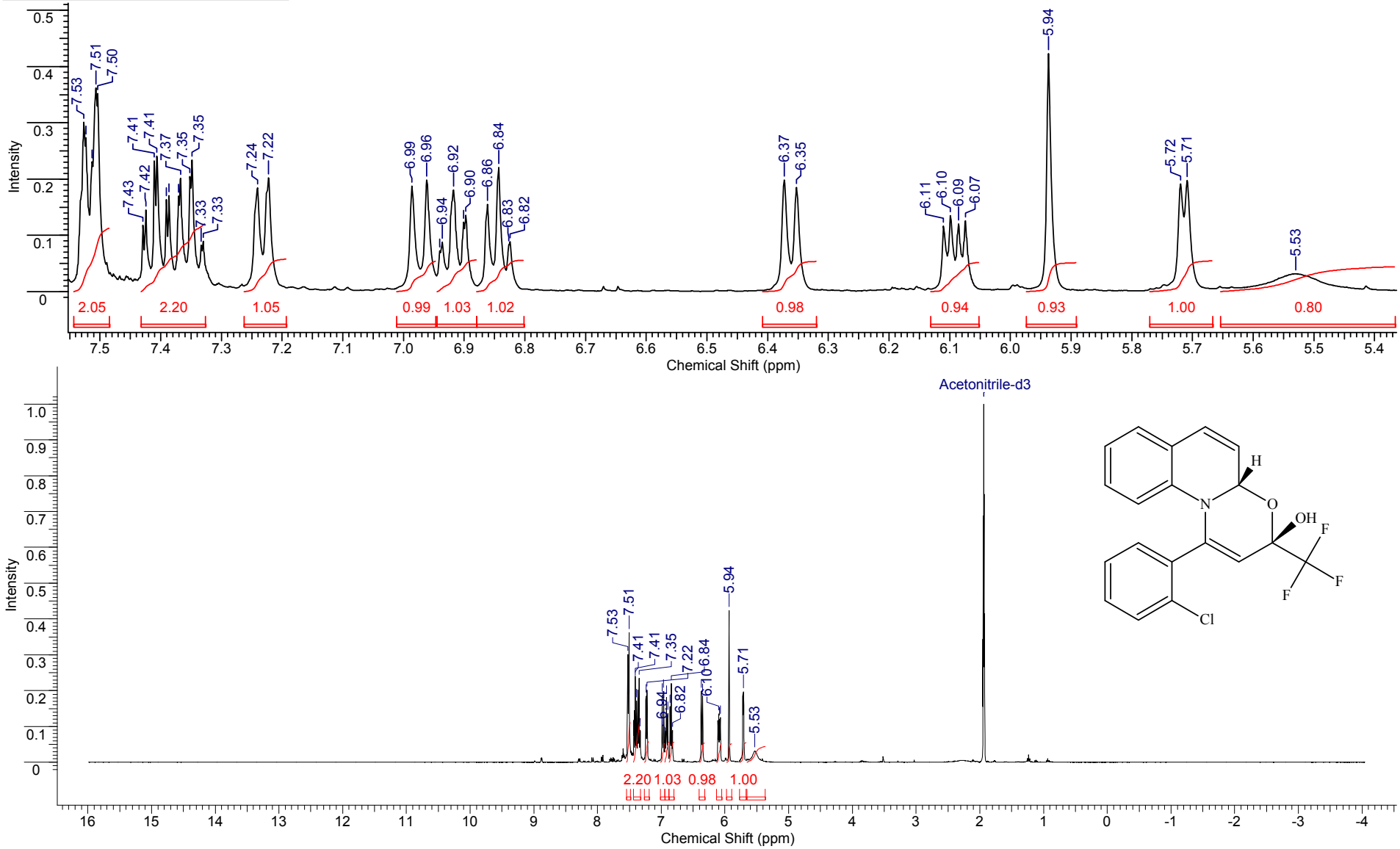
FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$

Acquisition Time (sec)	1.9000	***Date***	Oct 1 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.01\BM1376_20181001_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	169643
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	89285.71
Temperature (degree C)	22.000						



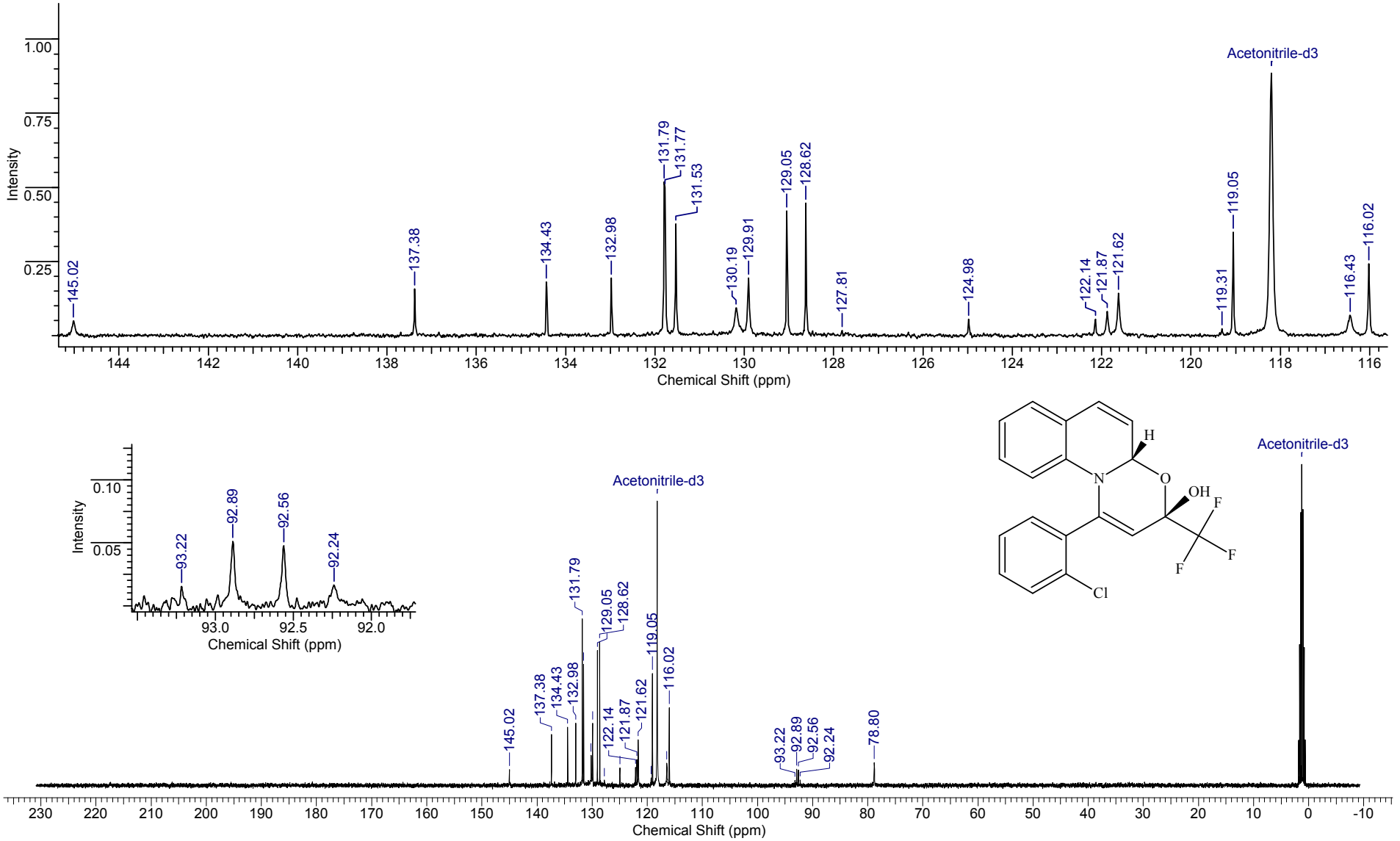
^{19}F NMR spectrum of **3h** (376.5 MHz, CD_3CN)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	18 Mar 2019 15:56:38
File Name	C:\DOCS\OUTPUT_301\2019\03.ì àðò\BM-1520-2.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



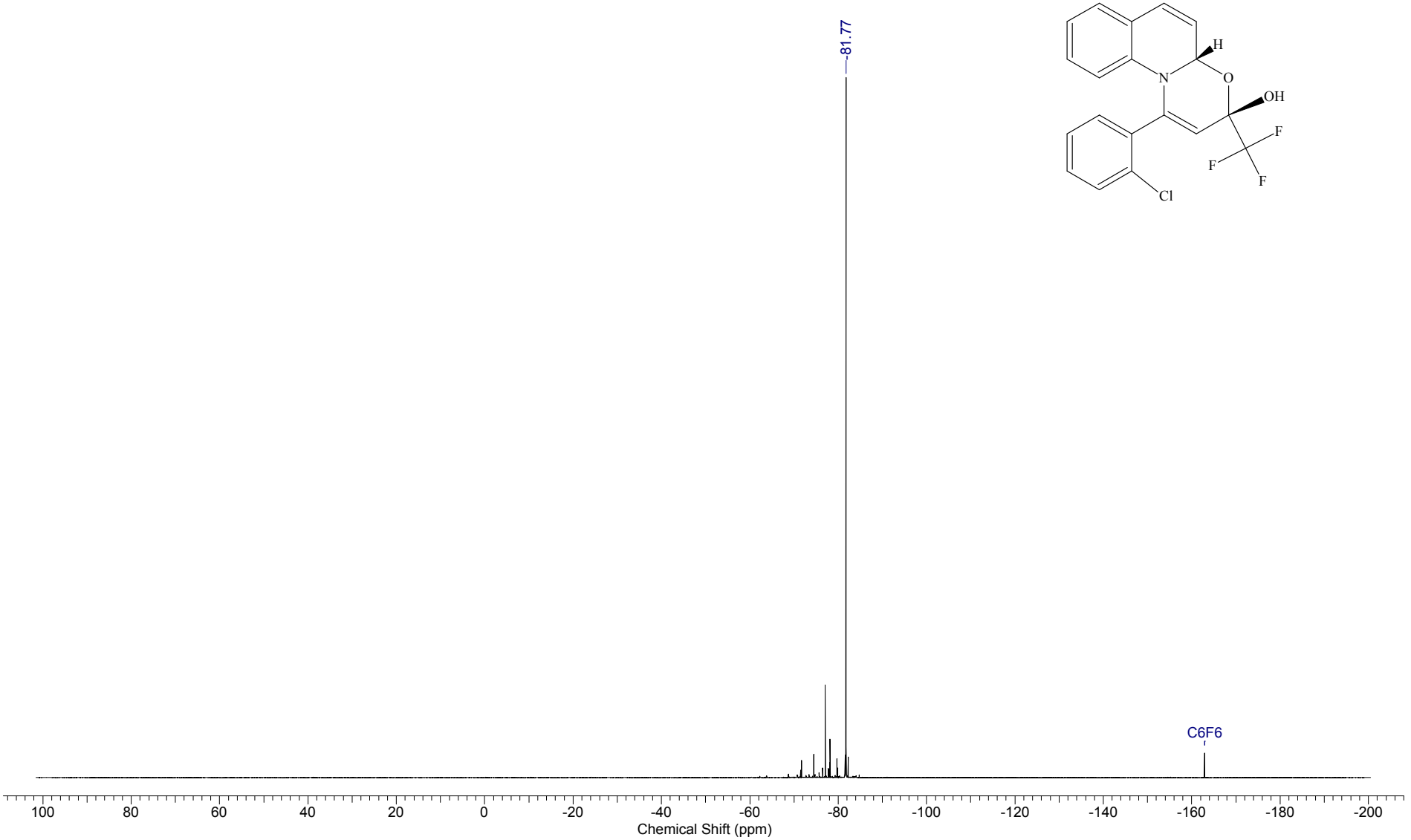
^{1}H NMR spectrum of **3i** (400.1 MHz, CD_3CN)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	16 Mar 2019 14:04:18
File Name	C:\DOCS\OUTPUT_301\2019\03.ì àðò\BM-1520.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	106	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



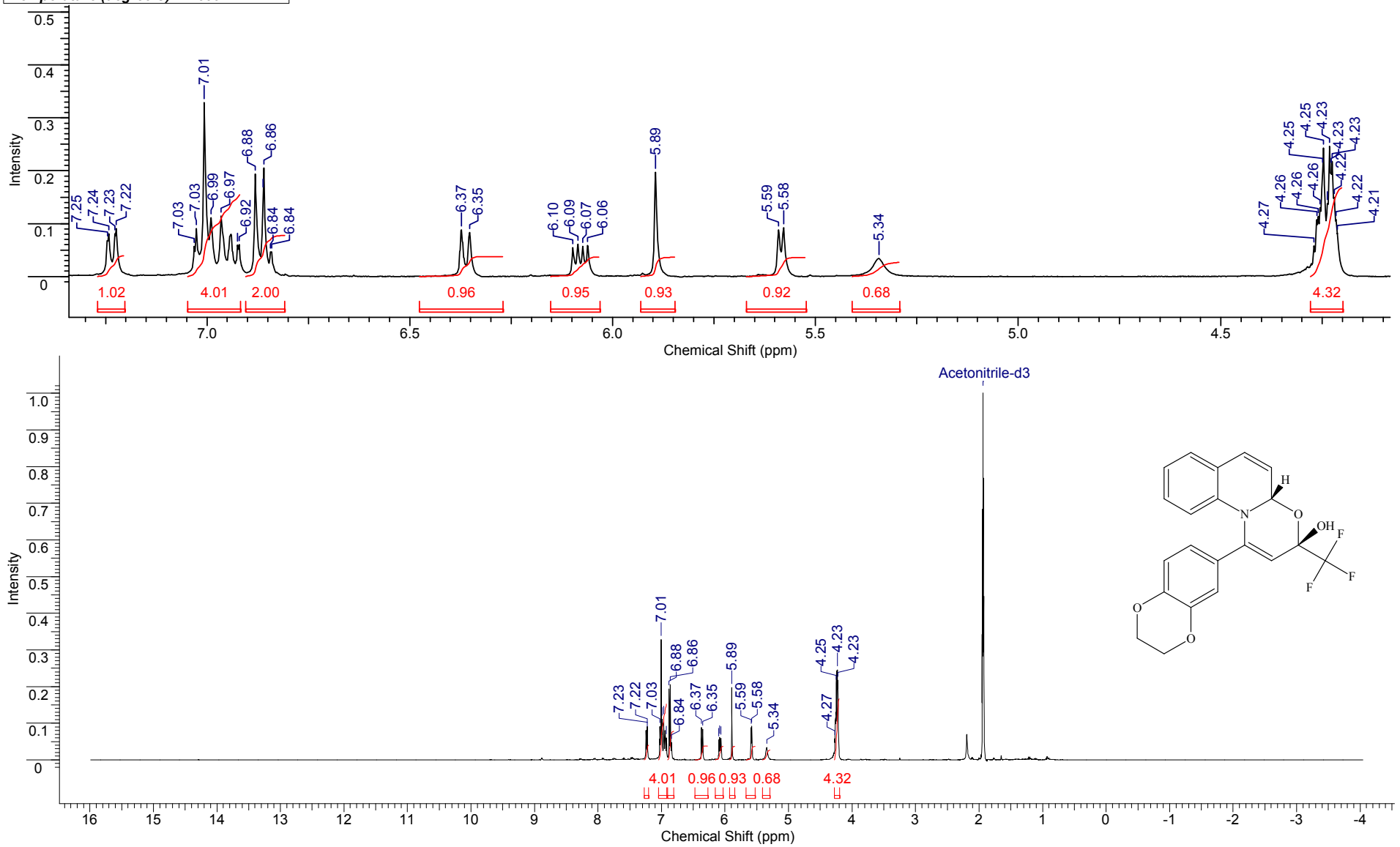
^{13}C NMR spectrum of **3i** (100.6 MHz, CD_3CN)

Acquisition Time (sec)	2.3069	***Date***	Mar 14 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.03.14\BM-1511-A-F_20190314_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



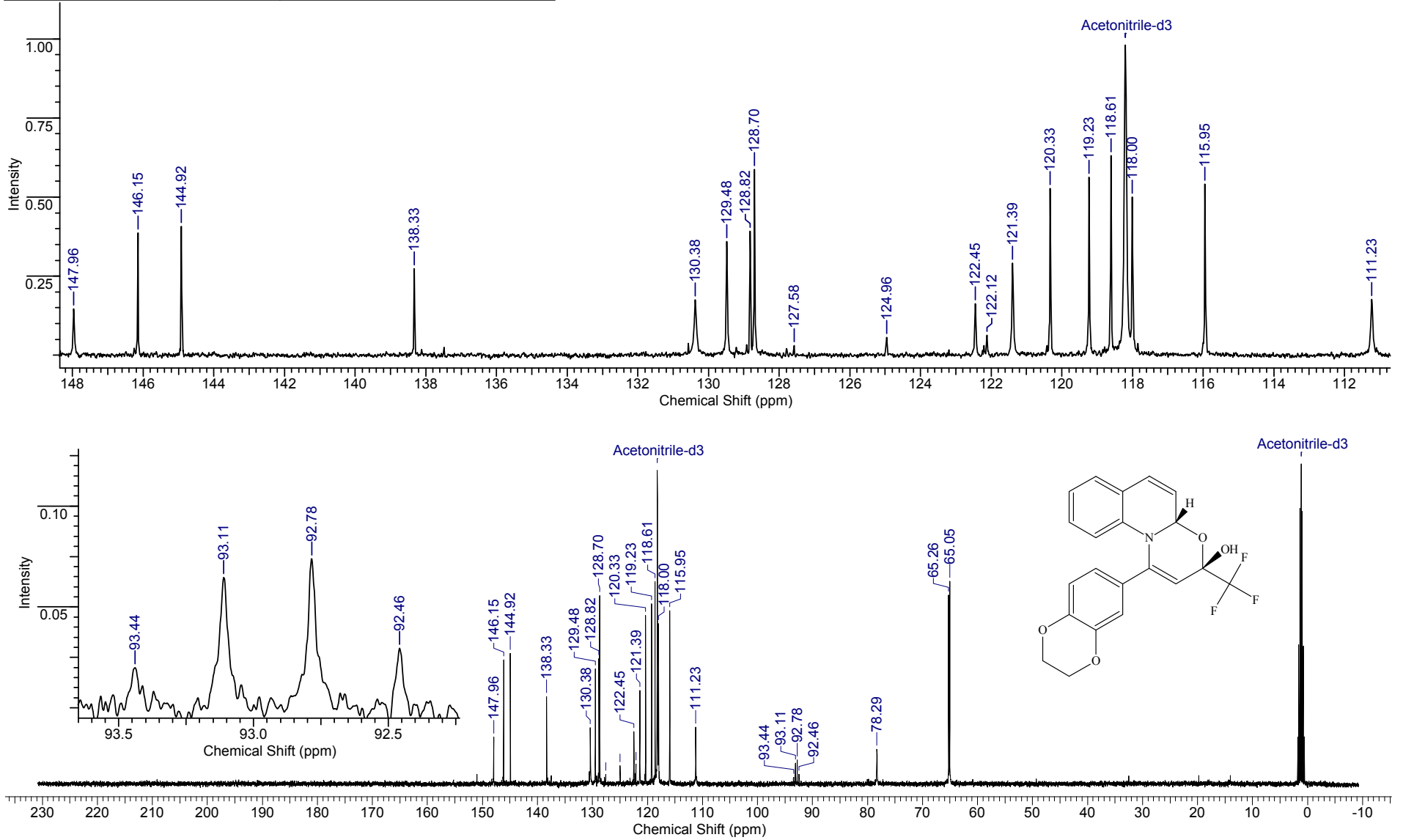
^{19}F NMR spectrum of **3i** (376.5 MHz, CD_3CN)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	18 Mar 2019 16:02:18
File Name	C:\DOCS\OUTPUT_301\2019\03.ì àðò\BM-1521-2.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3j** (400.1 MHz, CD_3CN)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	16 Mar 2019 21:35:50
File Name	C:\DOCS\BM\190316\BM-1521_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C	***Number of Transients***	128
Original Points Count	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	24154.59	***Temperature (degree C)***	27.000						

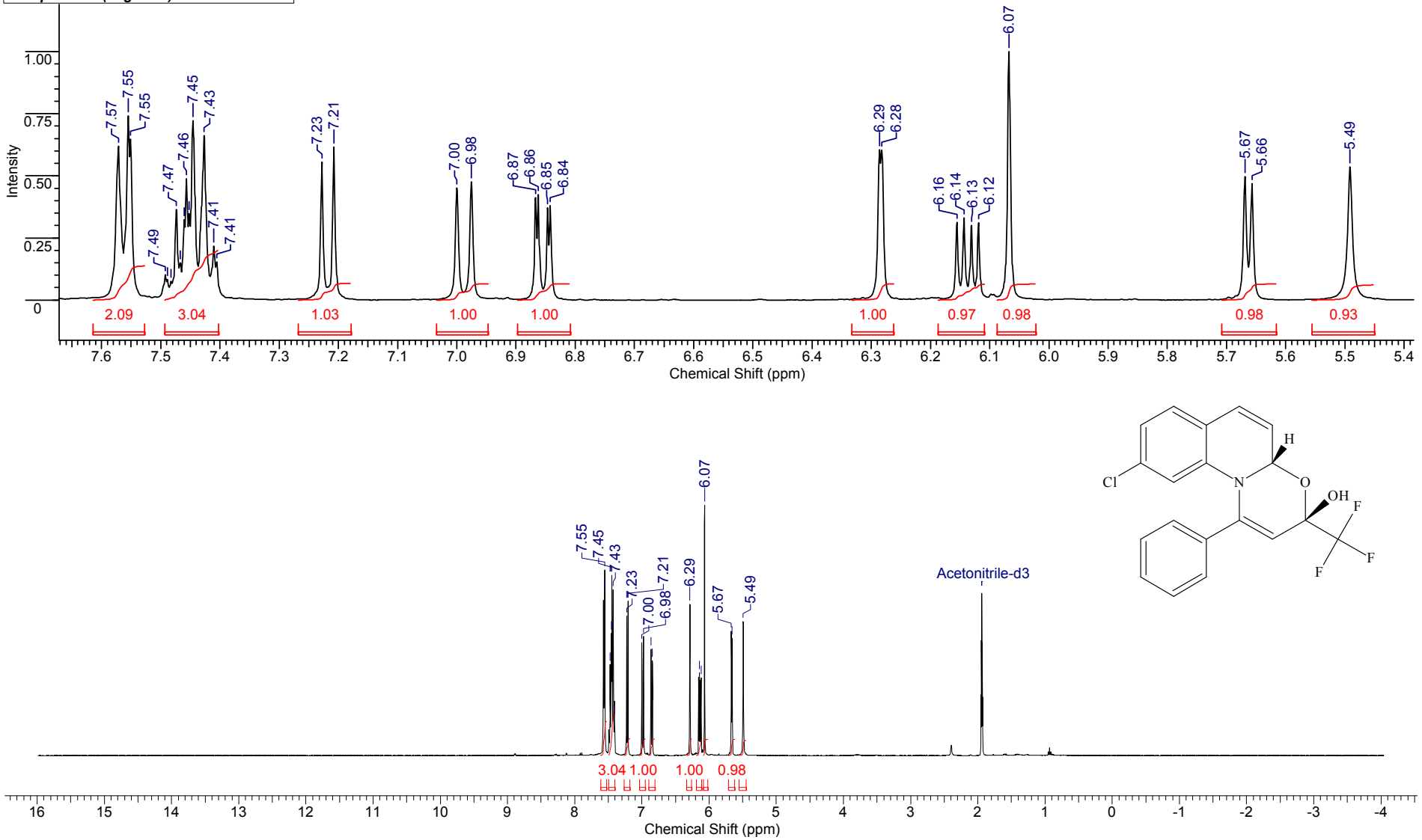


^{13}C NMR spectrum of **3j** (100.6 MHz, CD_3CN)

Acquisition Time (sec)	0.7340	***Date***	Mar 19 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.03.19\bm1521-2-f_20190319_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	1000	***Original Points Count***	65536
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				

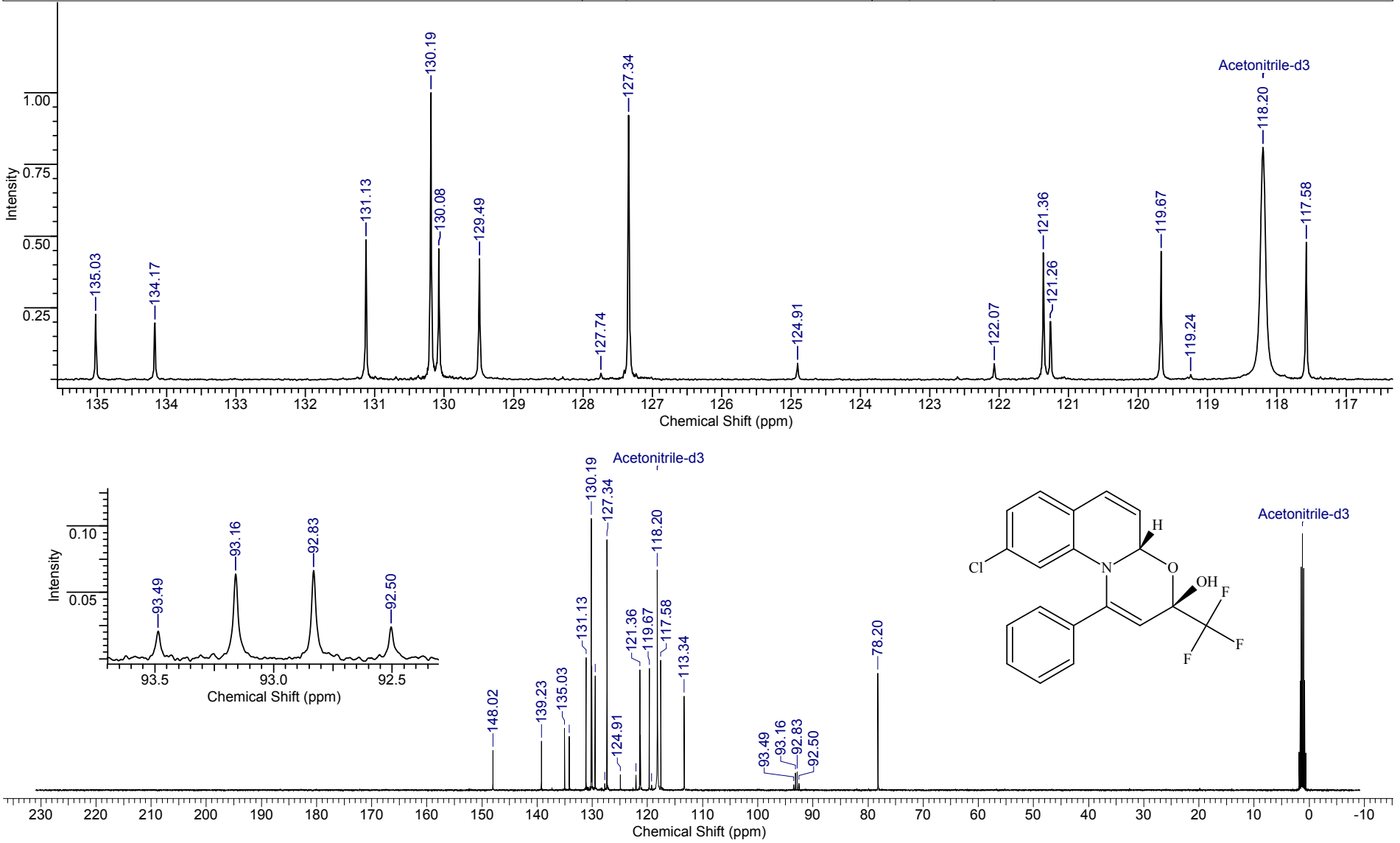
^{19}F NMR spectrum of **3j** (376.5 MHz, CD_3CN)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	12 Mar 2019 14:47:30
File Name	C:\DOCS\OUTPUT_301\2019\03.ì àðò\BM-1512-P.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



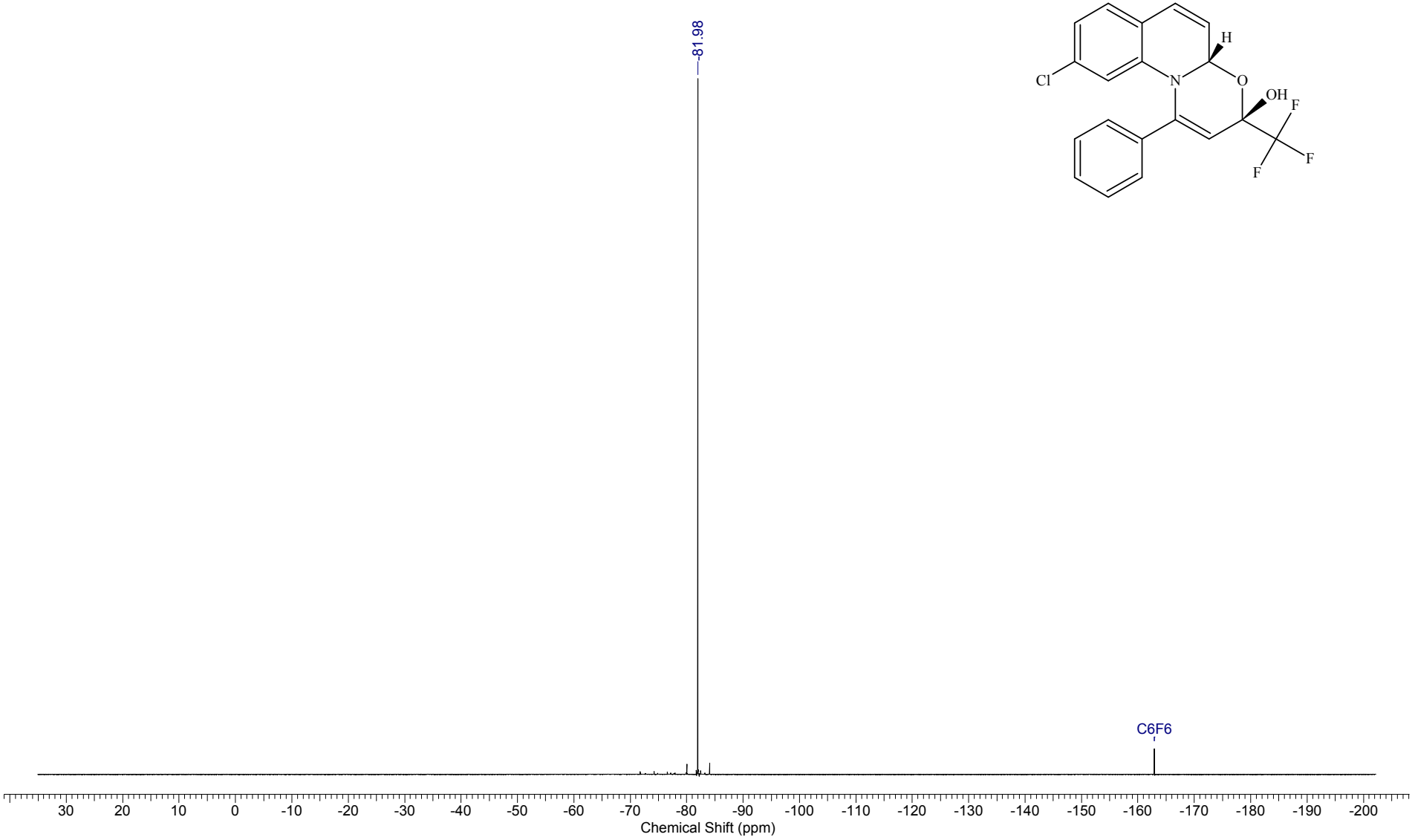
^{1}H NMR spectrum of **3k** (400.1 MHz, CD_3CN)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	12 Mar 2019 15:31:56
File Name	C:\DOCS\OUTPUT_301\2019\03.ì àðò\BM-1512-P.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	1116	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



^{13}C NMR spectrum of **3k** (100.6 MHz, CD_3CN)

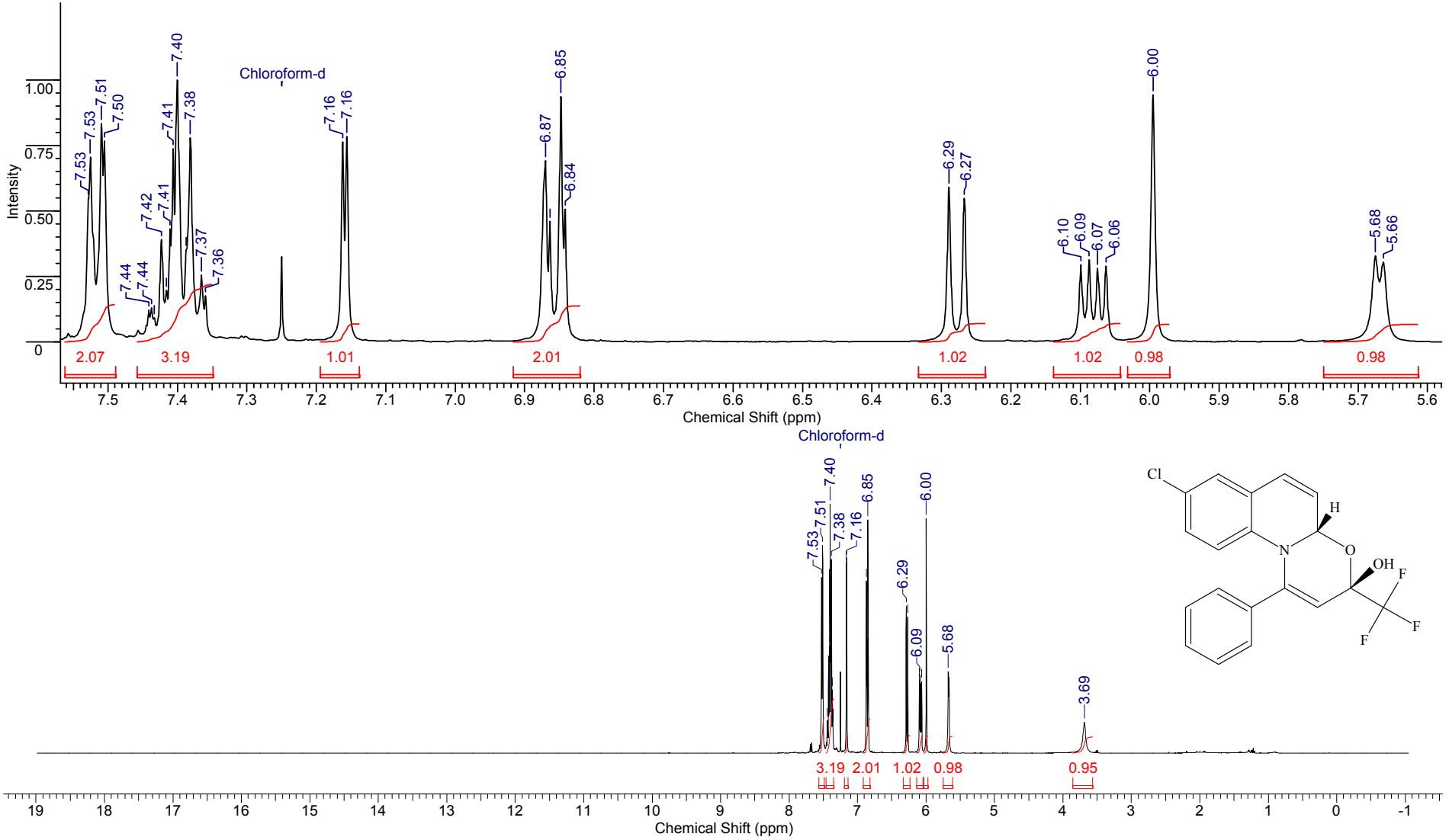
Acquisition Time (sec)	0.7340	***Date***	Mar 12 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.03.12\bm1512-f_20190312_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	100	***Original Points Count***	65536
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3k** (376.5 MHz, CD_3CN)

FW	379.7600	***Formula***	$C_{19}H_{13}ClF_3NO_2$

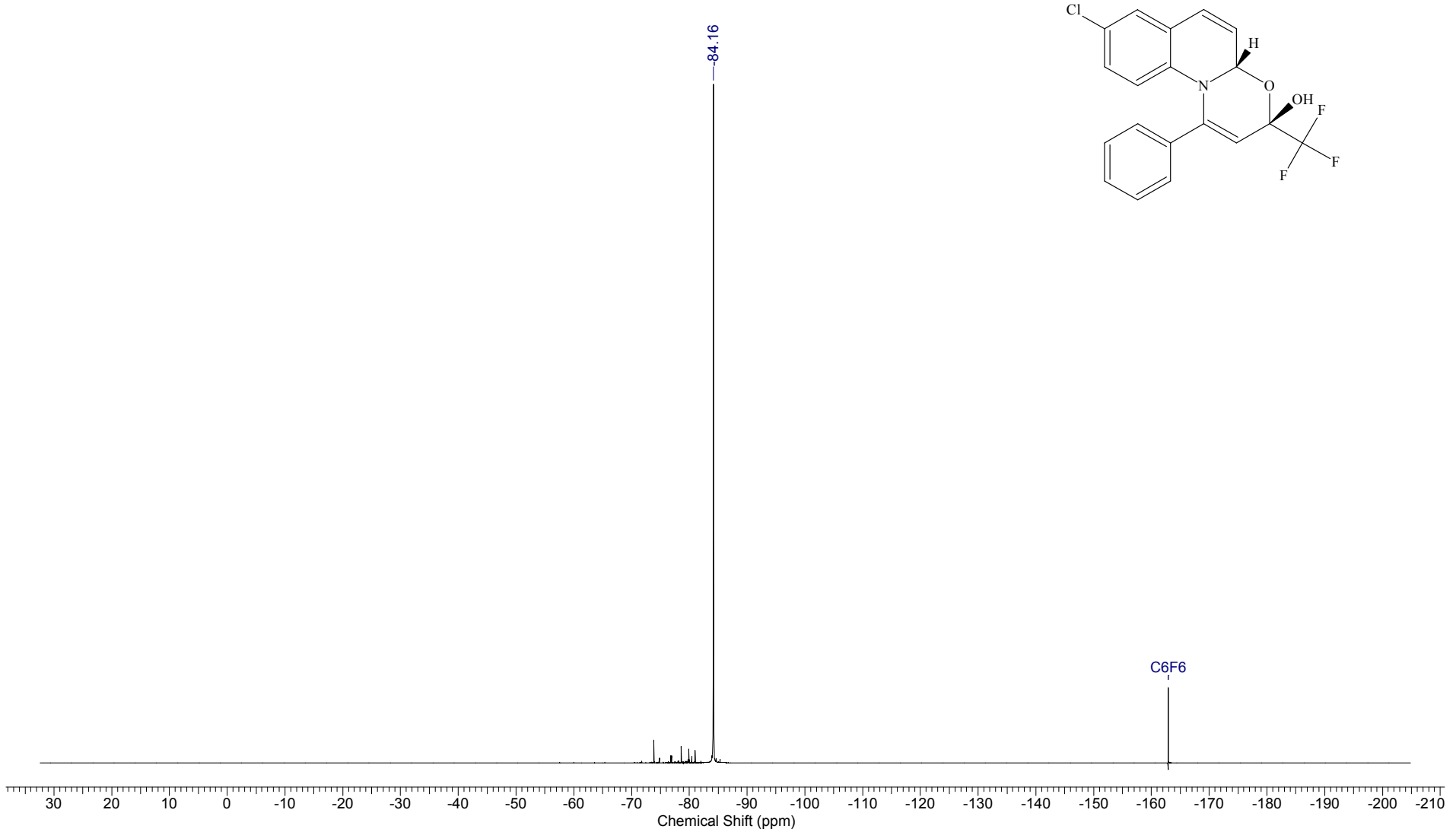
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	18 Oct 2018 22:21:32
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181018\BM-1404_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	Tol	***Sweep Width (Hz)***	8012.82	***Temperature (degree C)***	27.000



^{1}H NMR spectrum of **3l** (400.1 MHz, $CDCl_3$)

FW	379.7600	***Formula***	$C_{19}H_{13}ClF_3NO_2$

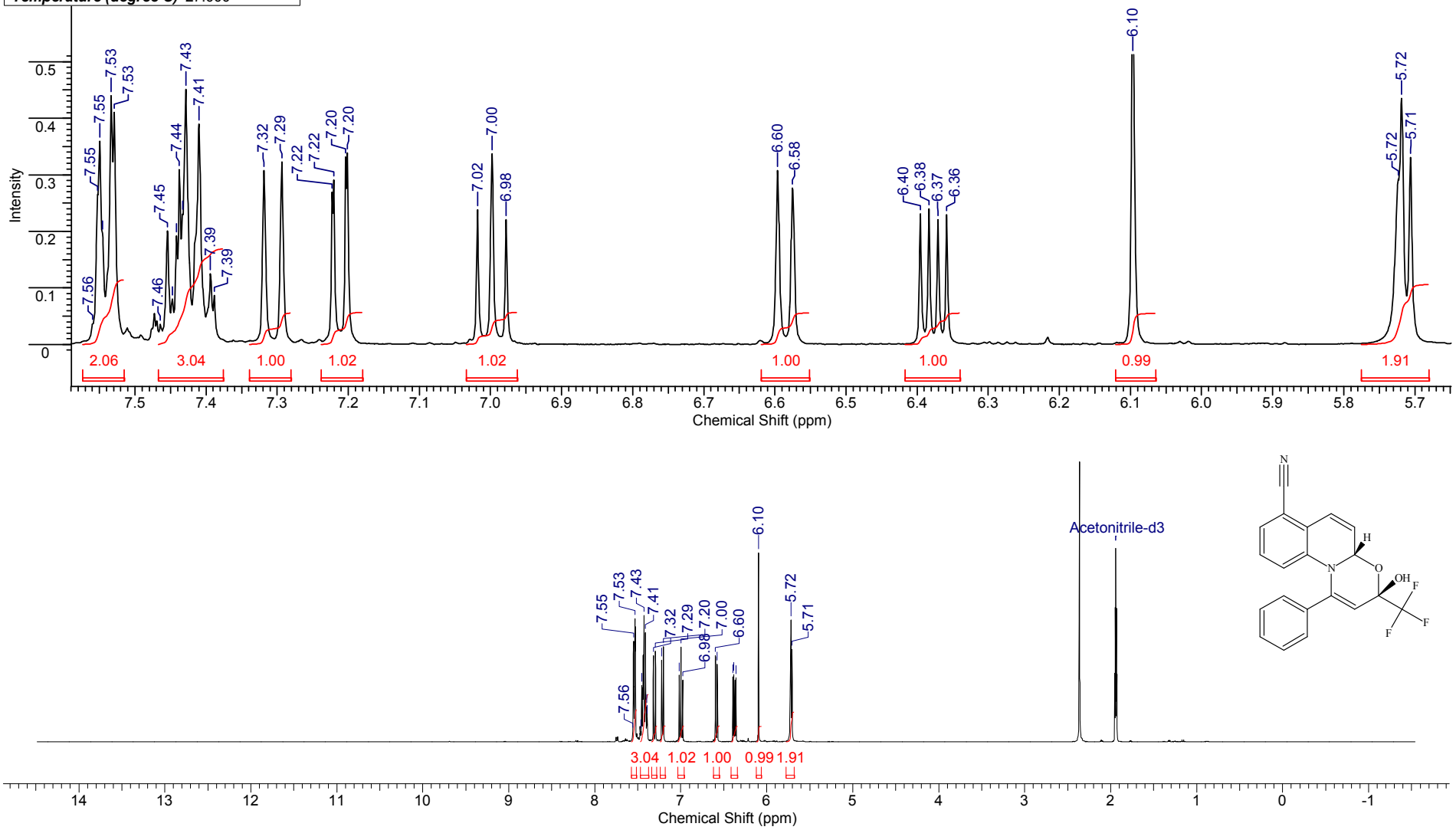
Acquisition Time (sec)	1.0000	***Date***	Oct 19 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.19\BM-1404_20181019_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	32	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3l** (376.5 MHz, $CDCl_3$)

FW	370.3247	Formula	$C_{20}H_{13}F_3N_2O_2$

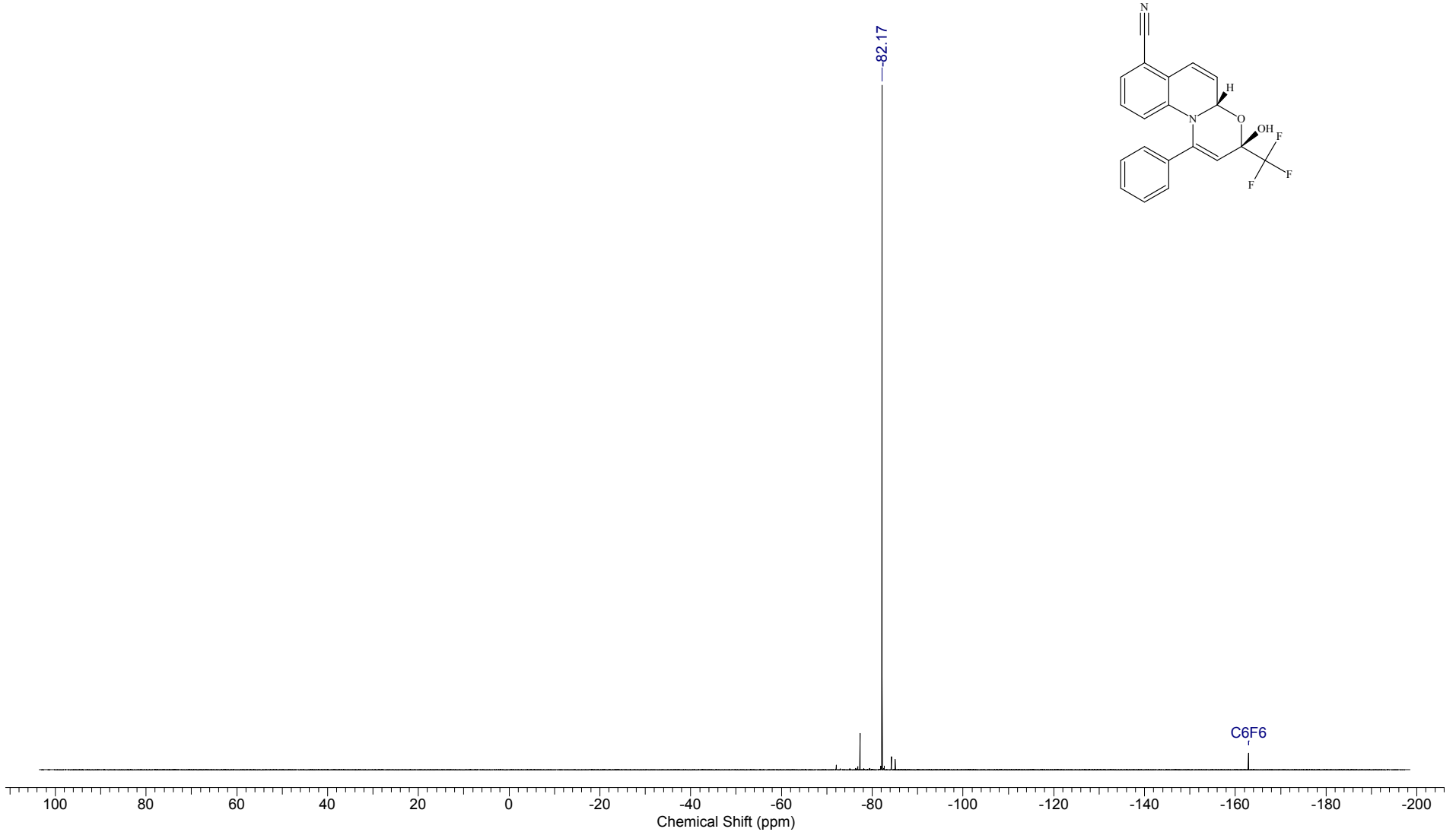
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	03 Oct 2018 17:50:24
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1380.H_001001r					Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	4	Original Points Count	16384	Points Count	65536
Pulse Sequence	zg30	Solvent	CHLOROFORM-D			Sweep Width (Hz)	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3m** (400.1 MHz, CD_3CN)

FW	370.3247	***Formula***	$C_{20}H_{13}F_3N_2O_2$

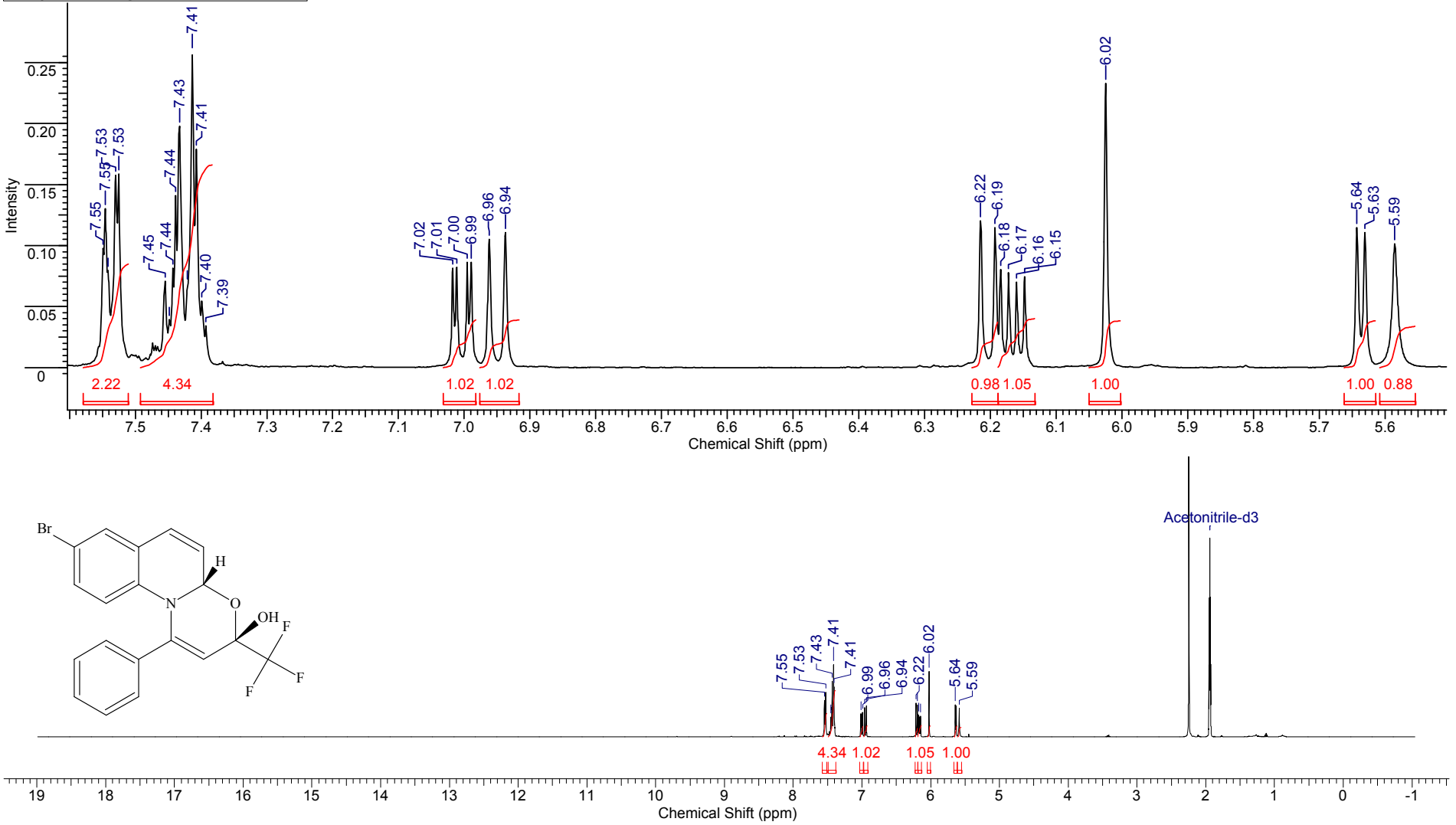
Acquisition Time (sec)	2.3069	***Date***	Oct 4 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.04\BM-1380-F_20181004_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3m** (376.5 MHz, CD_3CN)

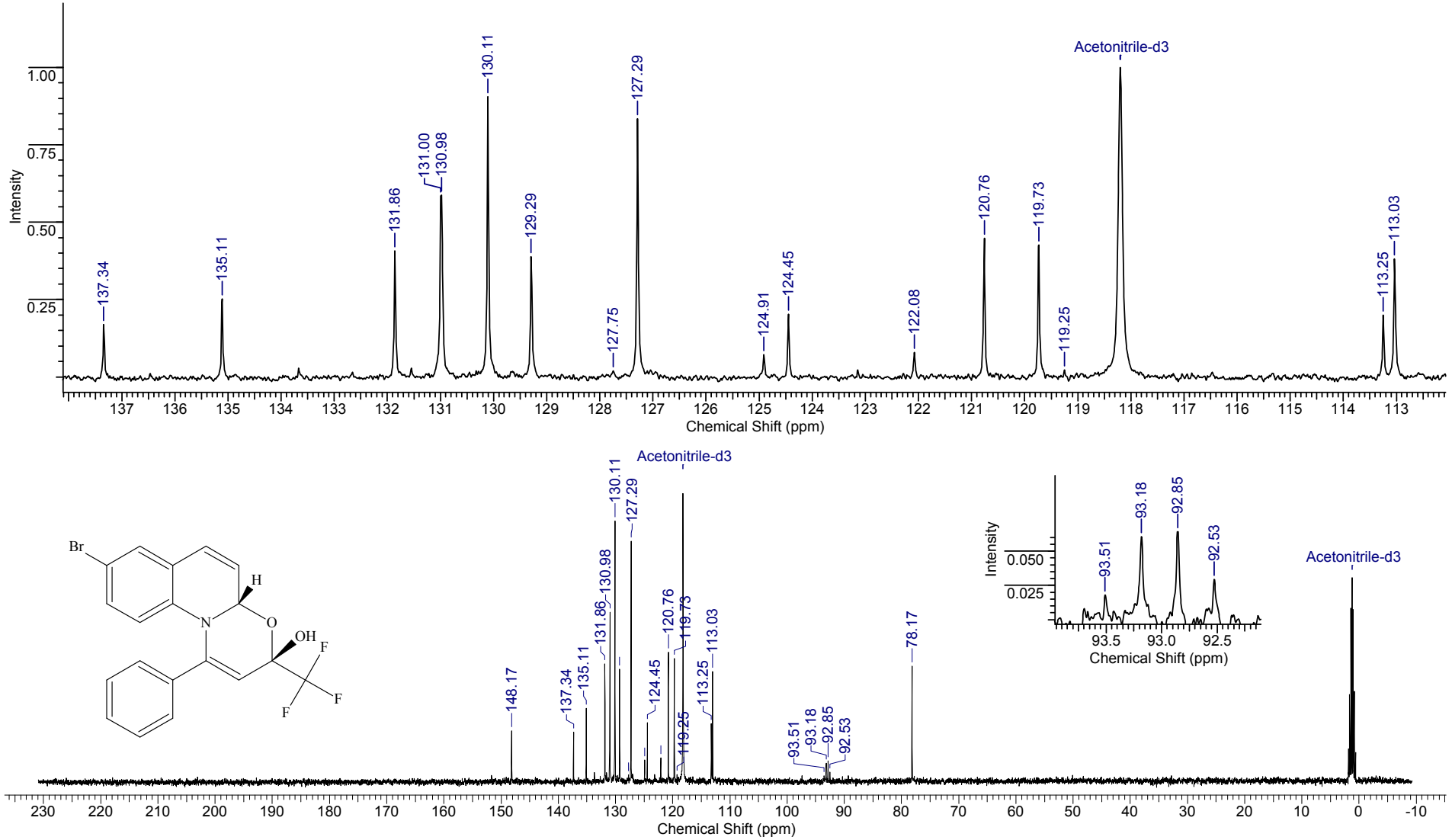
FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$

Acquisition Time (sec)	4.0894	**Comment**	Imported from UXNMR.			**Date**	17 Oct 2018 23:22:50
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181017\BM-1402-2_001001r					**Frequency (MHz)**	400.13
Nucleus	1H	**Number of Transients**	8	**Original Points Count**	32768	**Points Count**	131072
Pulse Sequence	zg30	**Solvent**	ACETONITRILE-D3			**Sweep Width (Hz)**	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3n** (400.1 MHz, CD_3CN)

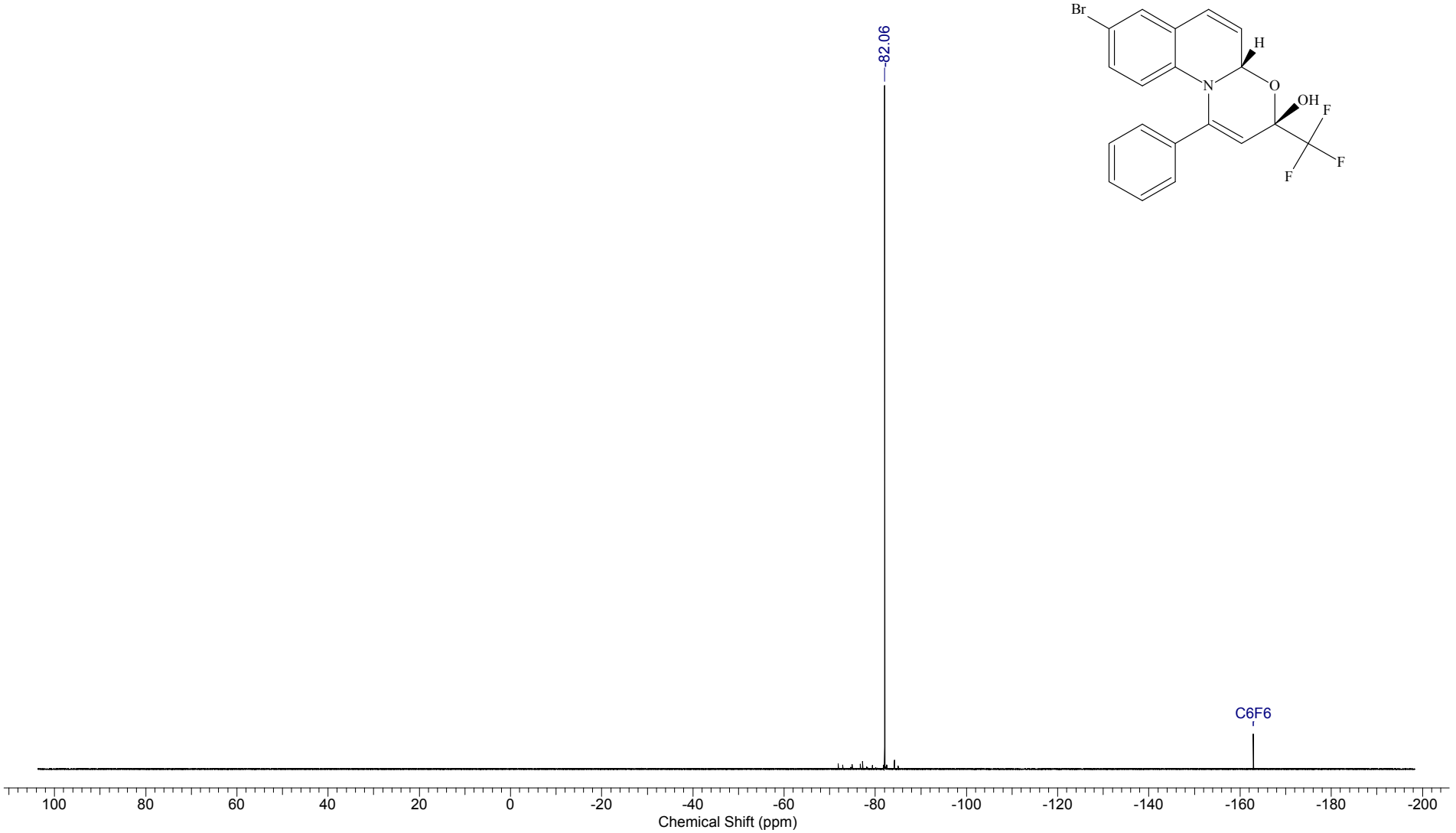
FW	424.2113	Formula	$C_{19}H_{13}BrF_3NO_2$				
Acquisition Time (sec)	0.4999	Comment	Imported from UXNMR.			Date	17 Oct 2018 17:16:02
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1402.C_002001r					Frequency (MHz)	100.61
Nucleus	13C	Number of Transients	128	Original Points Count	12076	Points Count	65536
Pulse Sequence	zgpg30	Solvent	DMSO-D6	Sweep Width (Hz)	24154.59	Temperature (degree C)	27.000



^{13}C NMR spectrum of **3n** (100.6 MHz, CD_3CN)

FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$

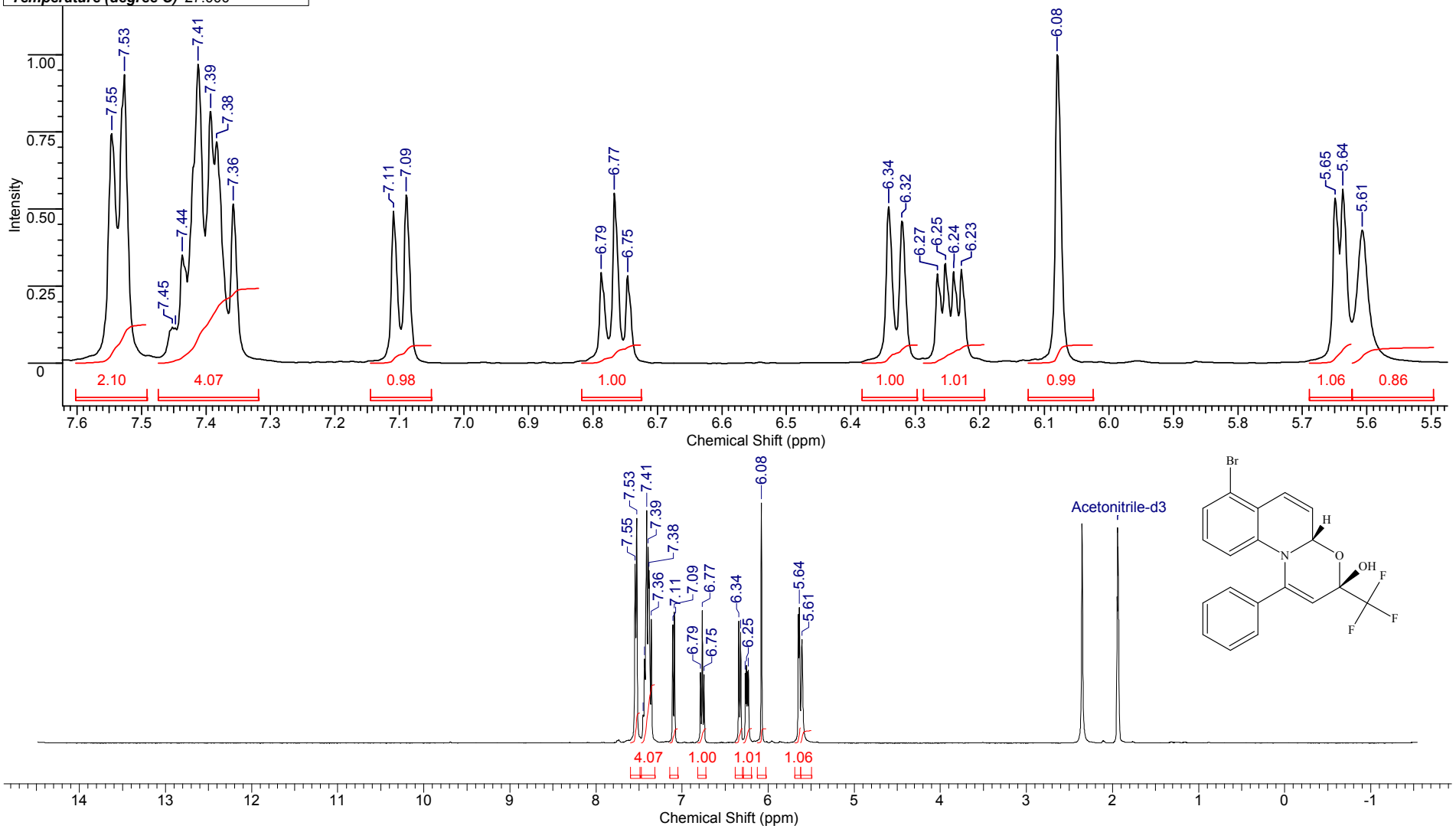
Acquisition Time (sec)	2.3069	***Date***	Oct 18 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.18\BM-1402-2-F_20181018_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3n** (376.5 MHz, CD_3CN)

FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$

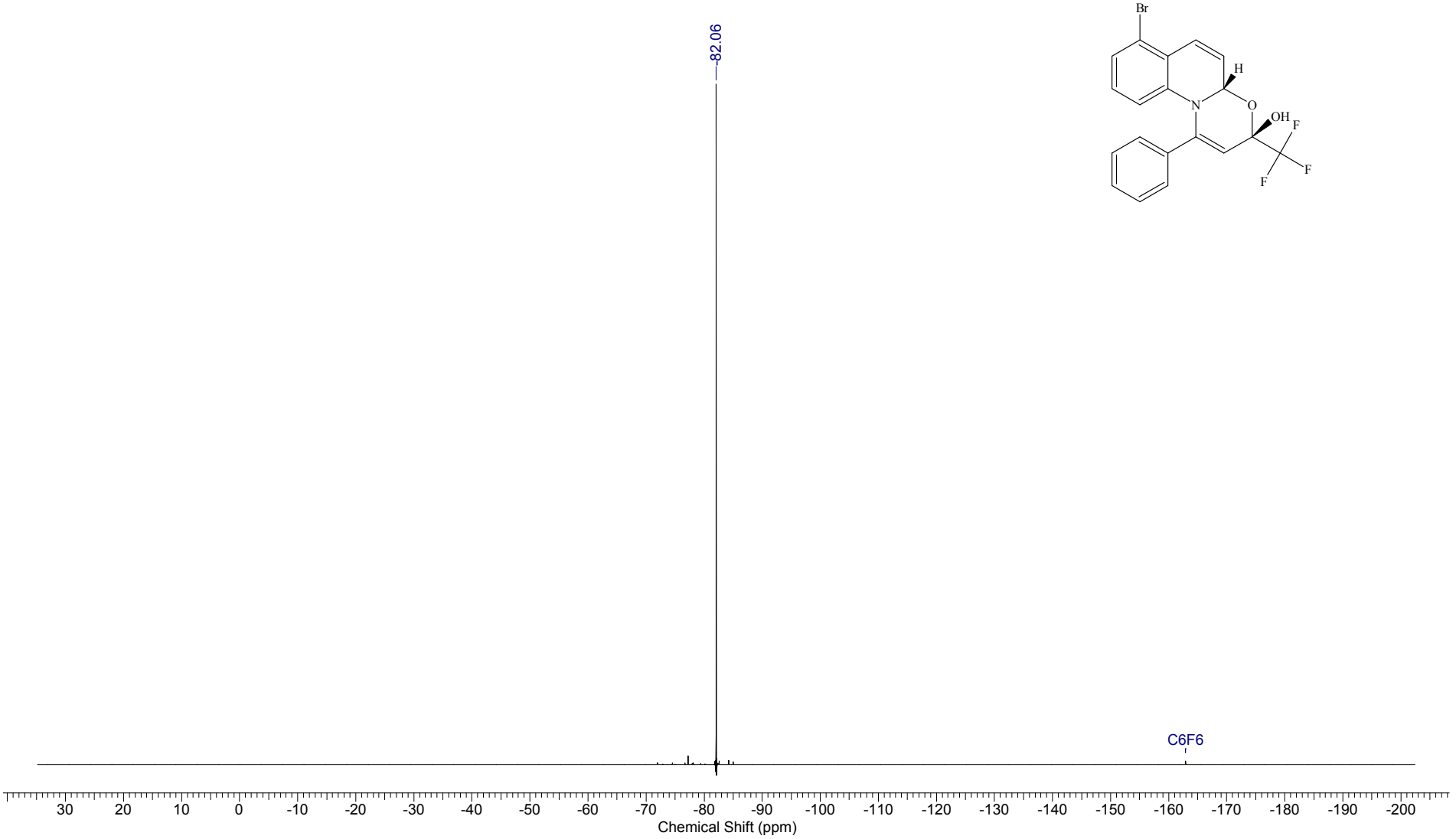
Acquisition Time (sec)	2.5559	***Comment***	Imported from UXNMR.			***Date***	04 Oct 2018 08:19:12
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1381.H\BM-1381.H_001000fid					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	16384	***Points Count***	16384
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3o** (400.1 MHz, CD_3CN)

FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$

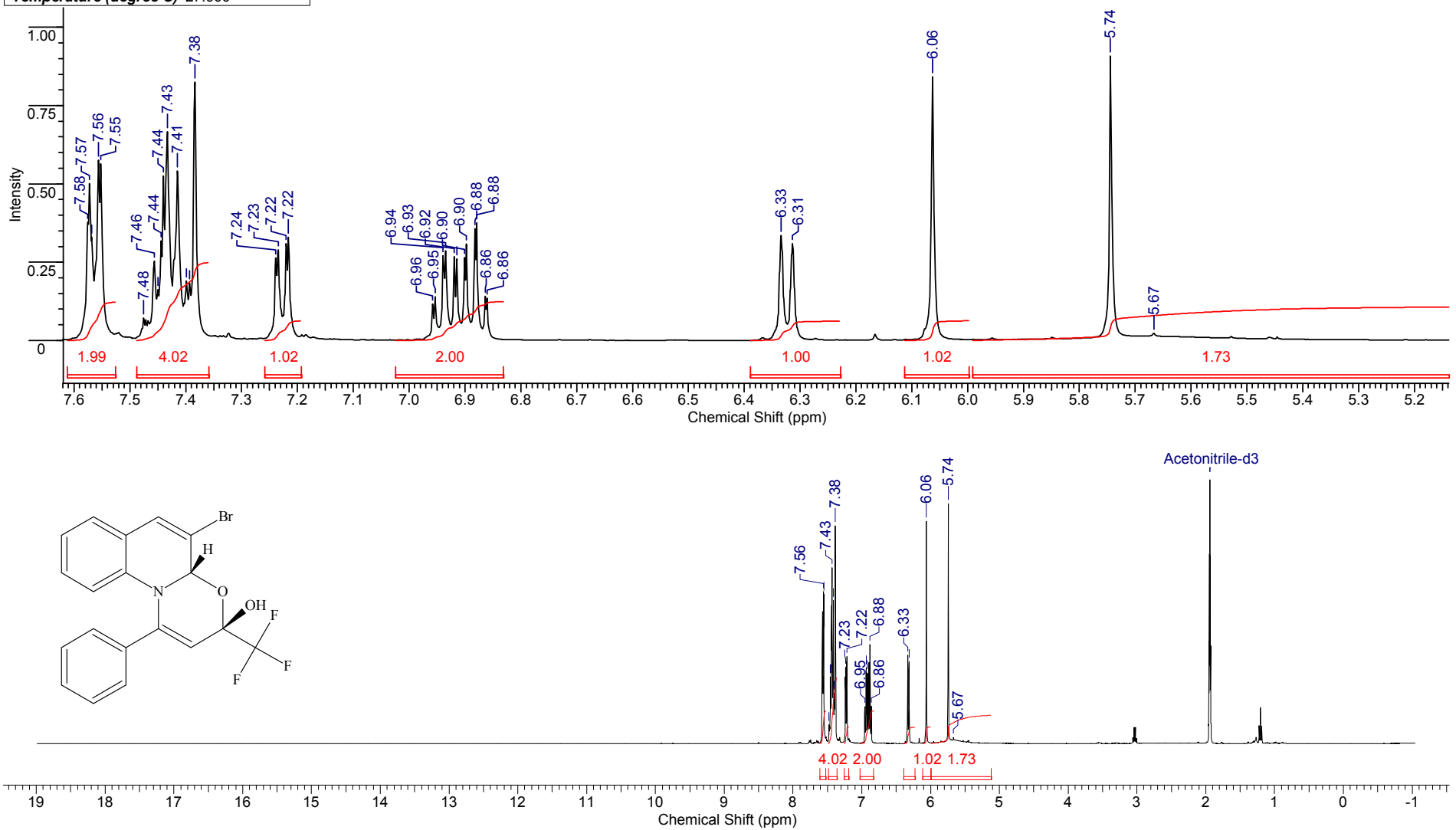
Acquisition Time (sec)	1.0000	***Date***	Oct 5 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.05\BM-1381_20181005_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	32	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3o** (376.5 MHz, CD_3CN)

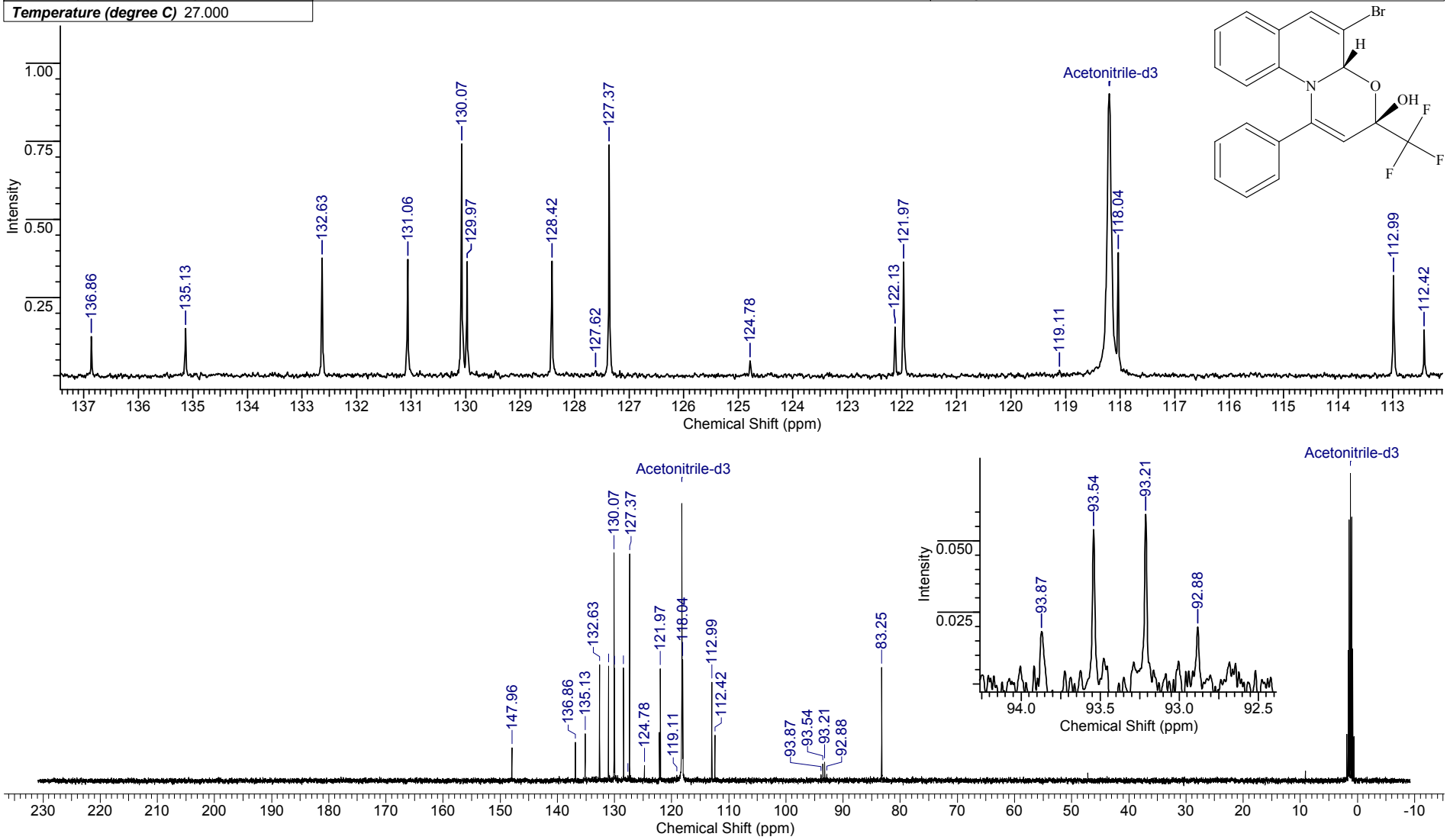
FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	27 Oct 2018 22:02:24
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181027-2\BM-1392-2f_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	8	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3p** (400.1 MHz, CD_3CN)

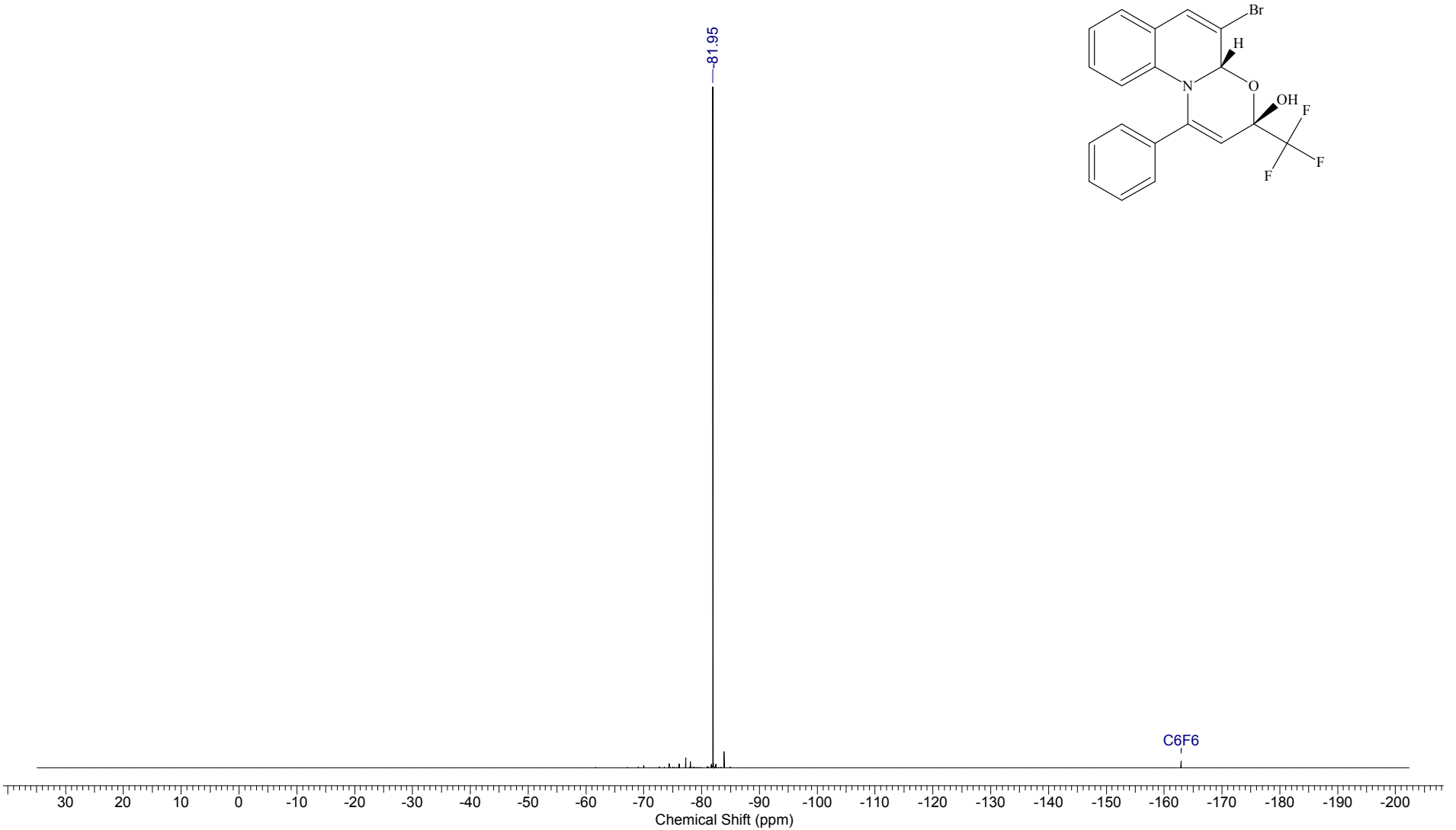
FW	424.2113	***Formula***	$C_{19}H_{13}BrF_3NO_2$				
Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	27 Oct 2018 22:12:02
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\bm181027-2\BM-1392-2f_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	240	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	24154.59
Temperature (degree C)	27.000						



^{13}C NMR spectrum of **3p** (100.6 MHz, CD_3CN)

FW	424.2113	**Formula**	$C_{19}H_{13}BrF_3NO_2$

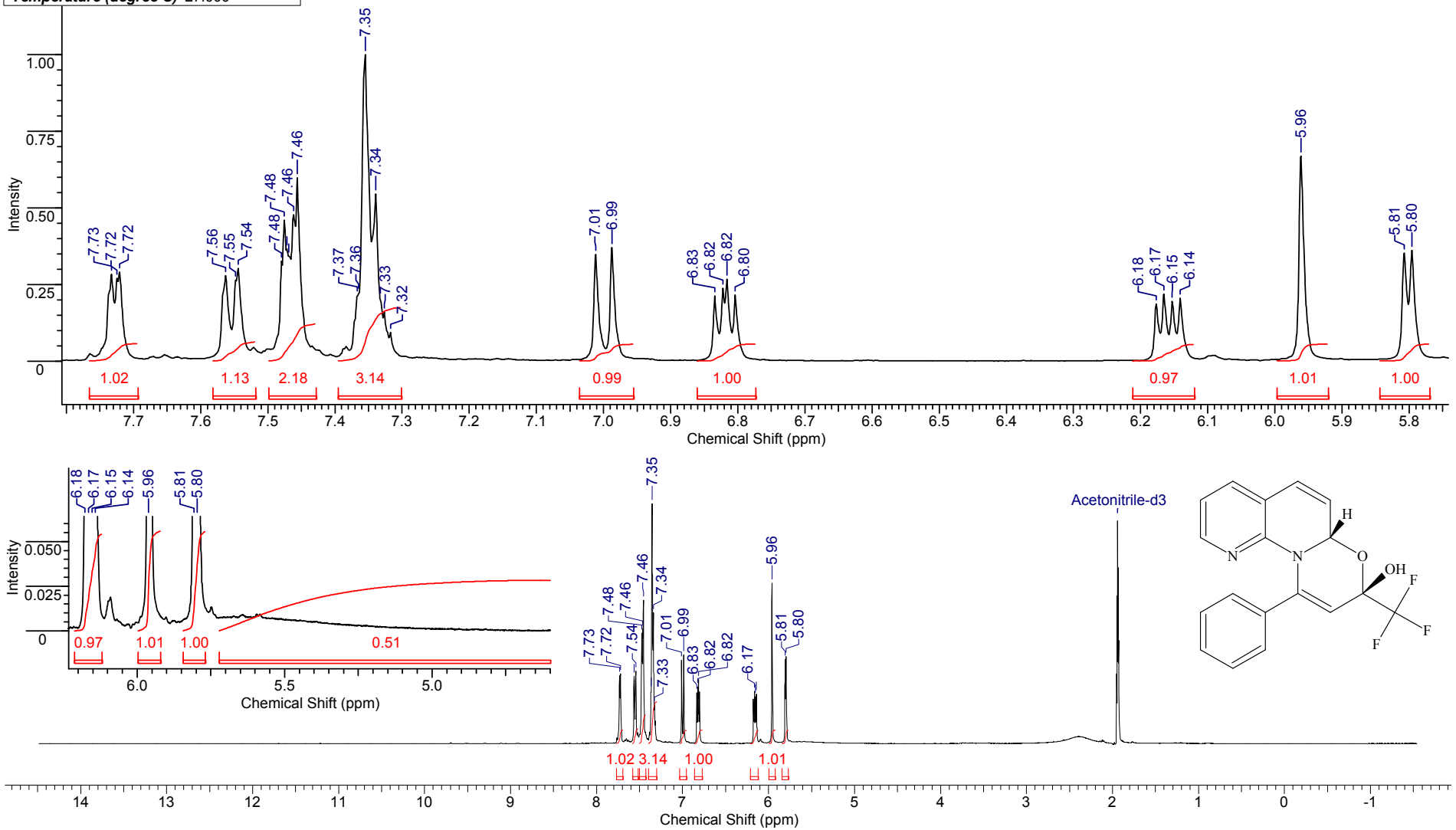
Acquisition Time (sec)	2.0000	***Date***	Oct 29 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.29\BM-1392-2f_20181029_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	178571
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	22.000				



^{19}F NMR spectrum of **3p** (376.5 MHz, CD_3CN)

FW	346.3033	Formula	$C_{18}H_{13}F_3N_2O_2$

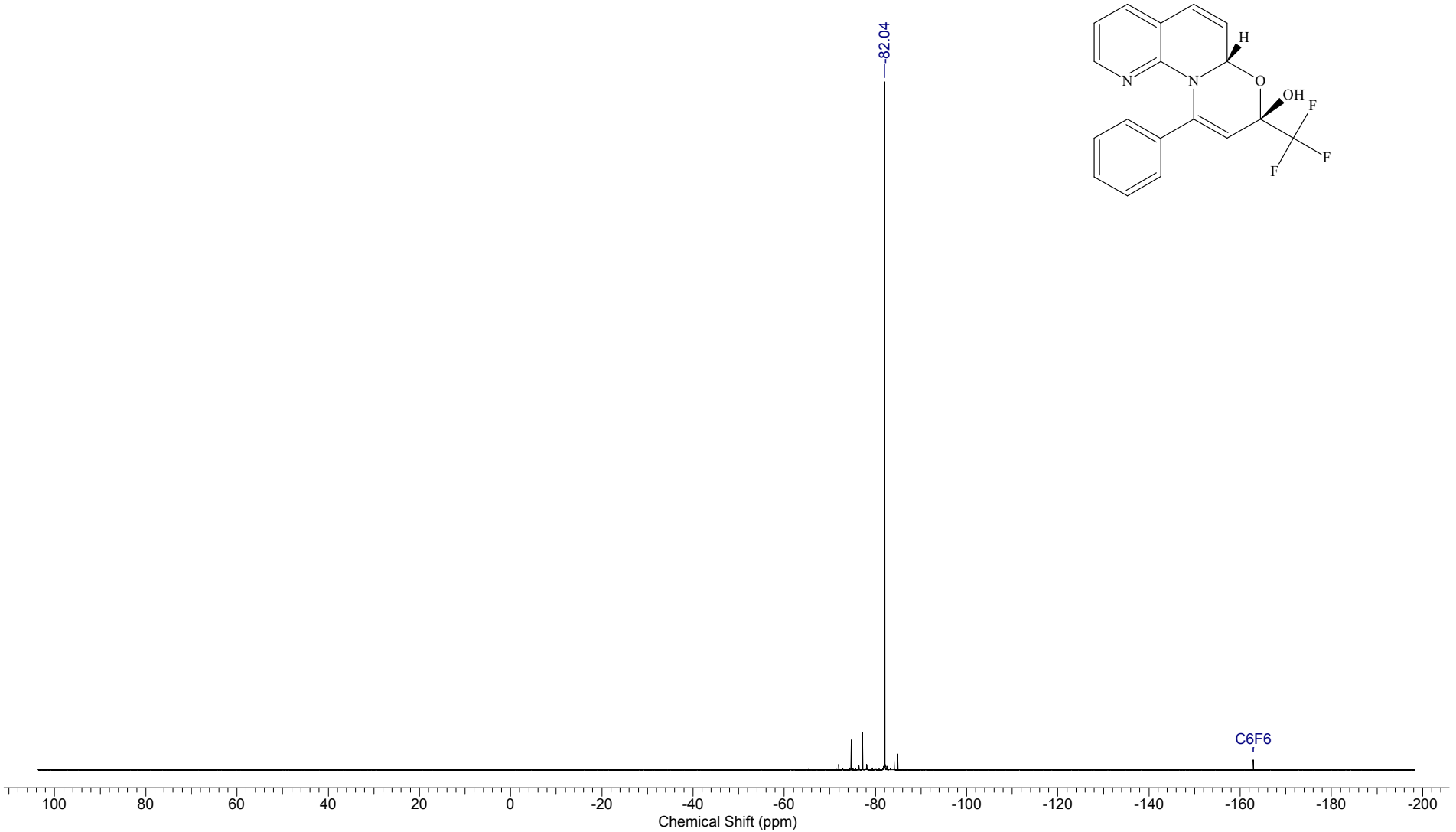
Acquisition Time (sec)	2.5559	Comment	Imported from UXNMR.			Date	17 Oct 2018 17:28:12
File Name	C:\DOCS\OUTPUT_301\2018\10.î êòÿáðü\BM-1394.H_001001r					Frequency (MHz)	400.13
Nucleus	1H	Number of Transients	6	Original Points Count	16384	Points Count	65536
Pulse Sequence	zg30	Solvent	ACETONITRILE-D3			Sweep Width (Hz)	6410.26
Temperature (degree C)	27.000						



^{1}H NMR spectrum of **3q** (400.1 MHz, CD_3CN)

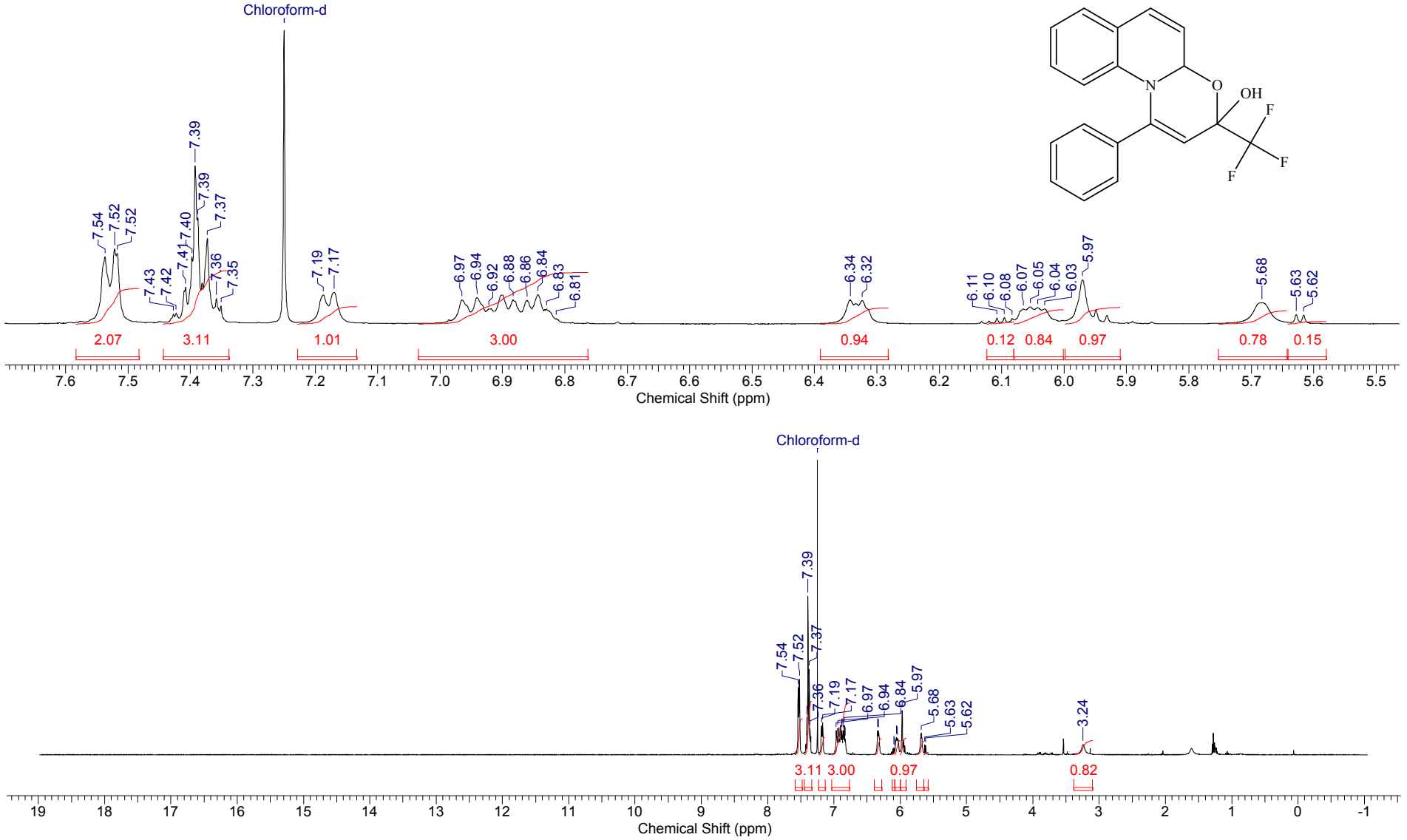
FW	346.3033	***Formula***	$C_{18}H_{13}F_3N_2O_2$

Acquisition Time (sec)	2.3069	***Date***	Oct 18 2018	***File Name***	C:\DOCS\OUTPUT_301\F19\2018.10.18\BM-1394-F_20181018_01\FLUORINE_01		
Frequency (MHz)	376.32	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	262144
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	ACETONITRILE-D3		
Sweep Width (Hz)	113636.37	***Temperature (degree C)***	22.000				



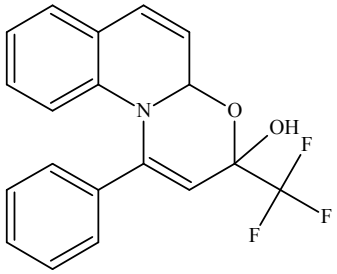
^{19}F NMR spectrum of **3q** (376.5 MHz, CD_3CN)

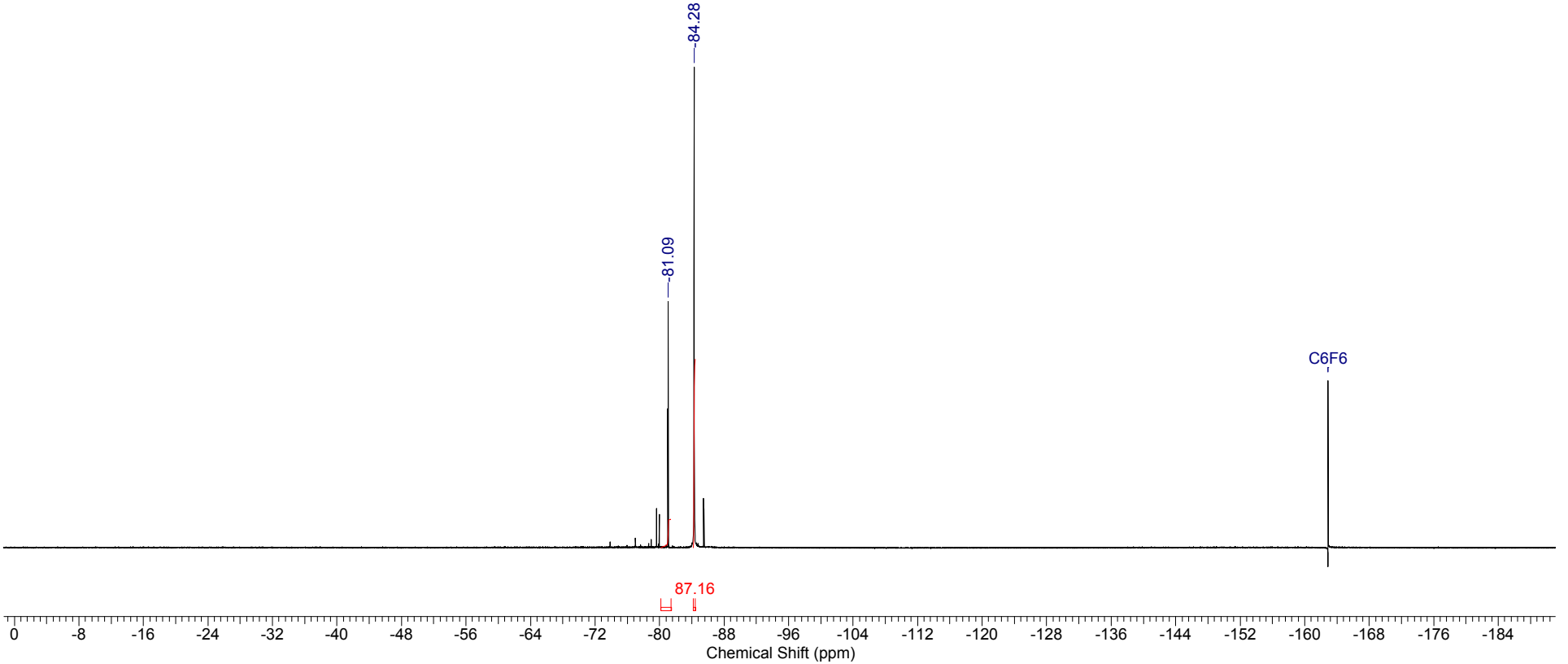
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	06 Jun 2019 19:17:06
File Name	I:\SPEC_2019_H,C\06.èþ í ü\BM-1604-a_001001r			***Frequency (MHz)***	400.13	***Nucleus***	1H	***Number of Transients***	8
Original Points Count	32768	***Points Count***	131072	***Pulse Sequence***	zg30	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	8012.82	***Temperature (degree C)***	27.000						



^{1}H NMR spectrum of diastereomeric mixture of **3a** and **3a'** (400.1 MHz, $CDCl_3$)

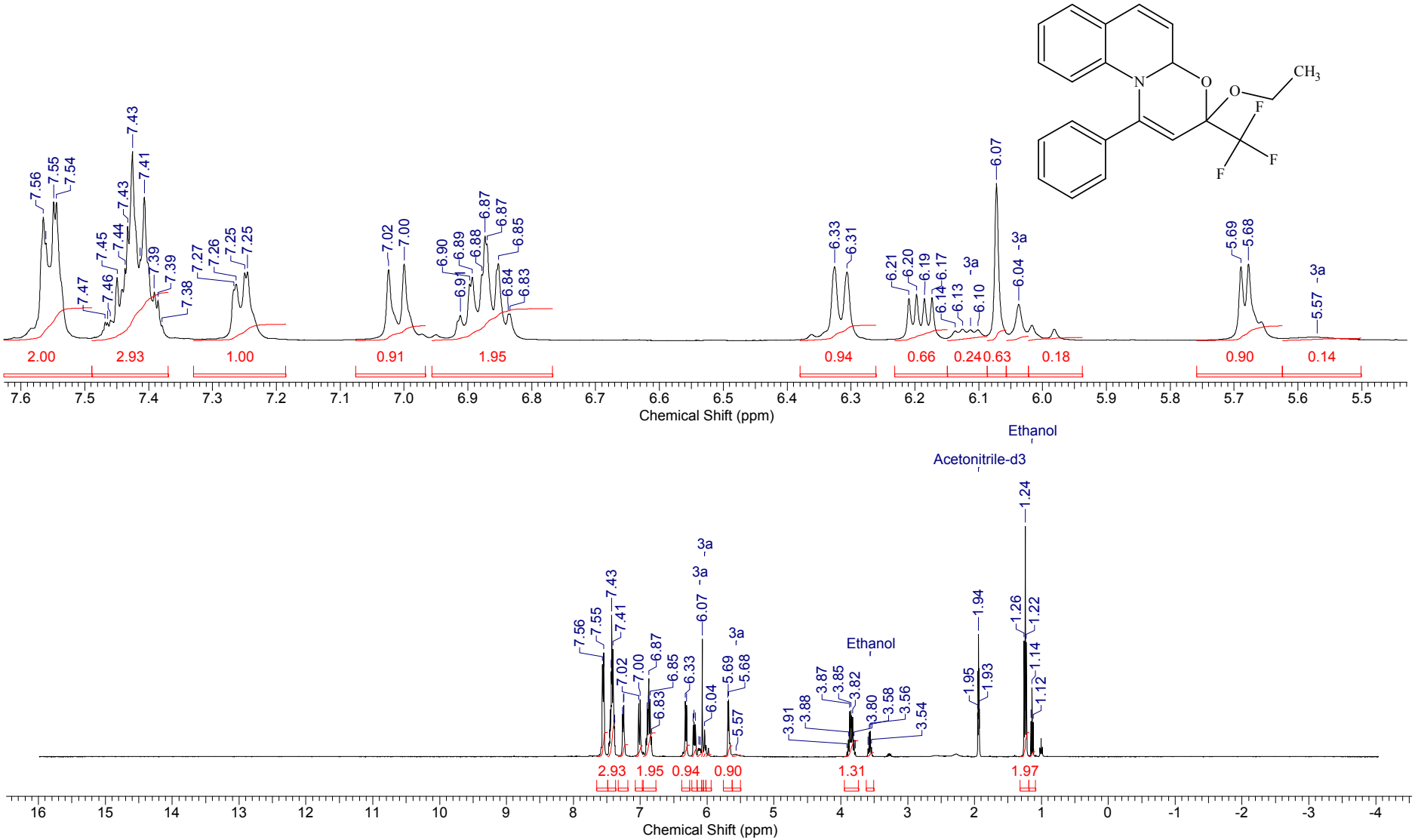
Acquisition Time (sec)	1.0000	***Date***	Jun 7 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.06.07\BM-1604-a_20190607_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	21.000				





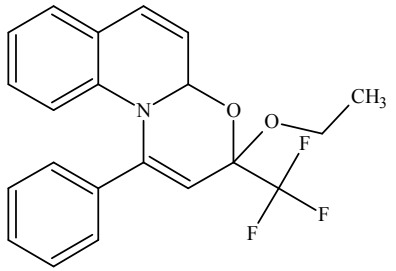
^{19}F NMR spectrum of diastereomeric mixture of **3a** and **3a'** (376.5 MHz, $CDCl_3$)

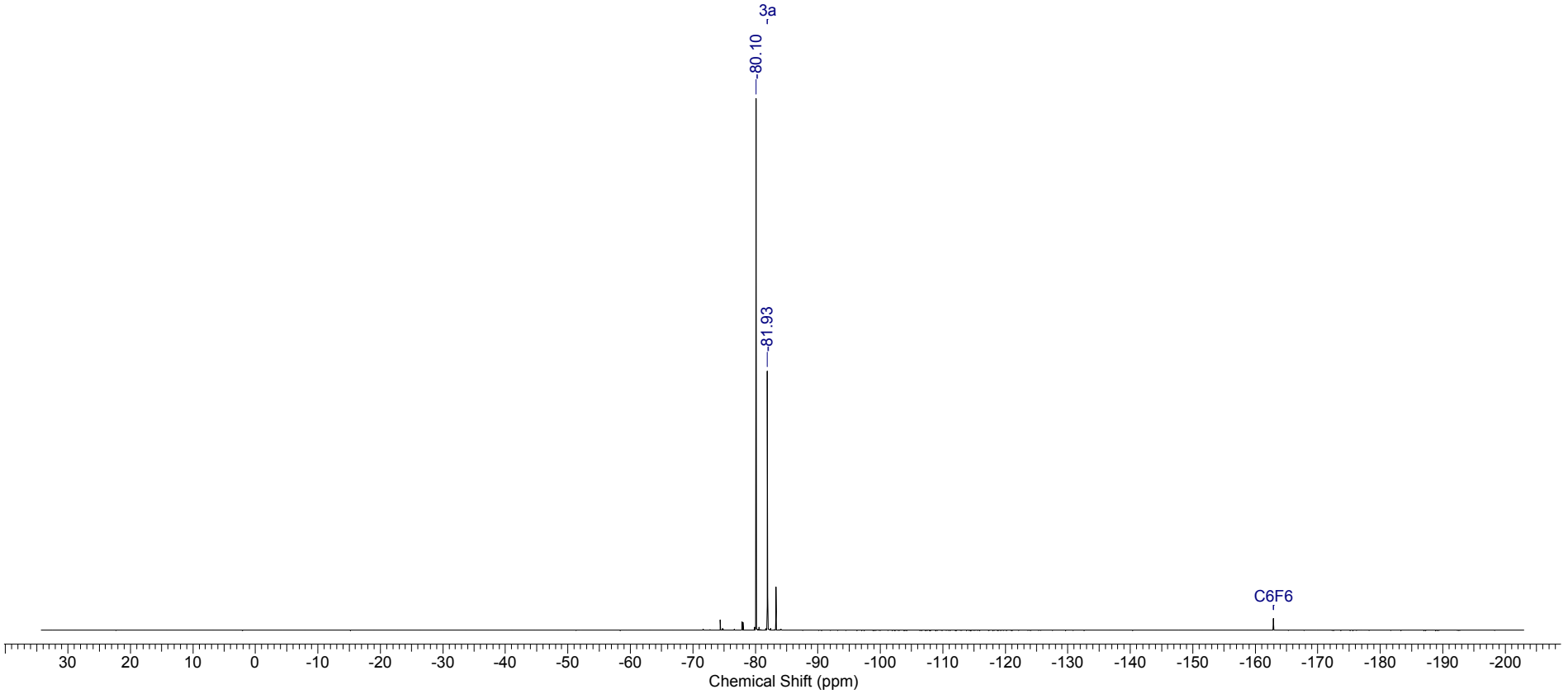
Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	31 May 2019 15:12:08
File Name	C:\DOCS\OUTPUT_301\2019\05.ì àé\BM-1588.H_001001r			***Frequency (MHz)***	400.13	***Nucleus***	1H
Number of Transients	4	***Original Points Count***	32768	***Points Count***	131072	***Pulse Sequence***	zg30
Solvent	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82	***Temperature (degree C)***	27.000



^{1}H NMR spectrum of **4** (400.1 MHz, CD_3CN). Signals of **3a** are the result of hydrolysis of **4** during preparation and storing of the NMR sample.

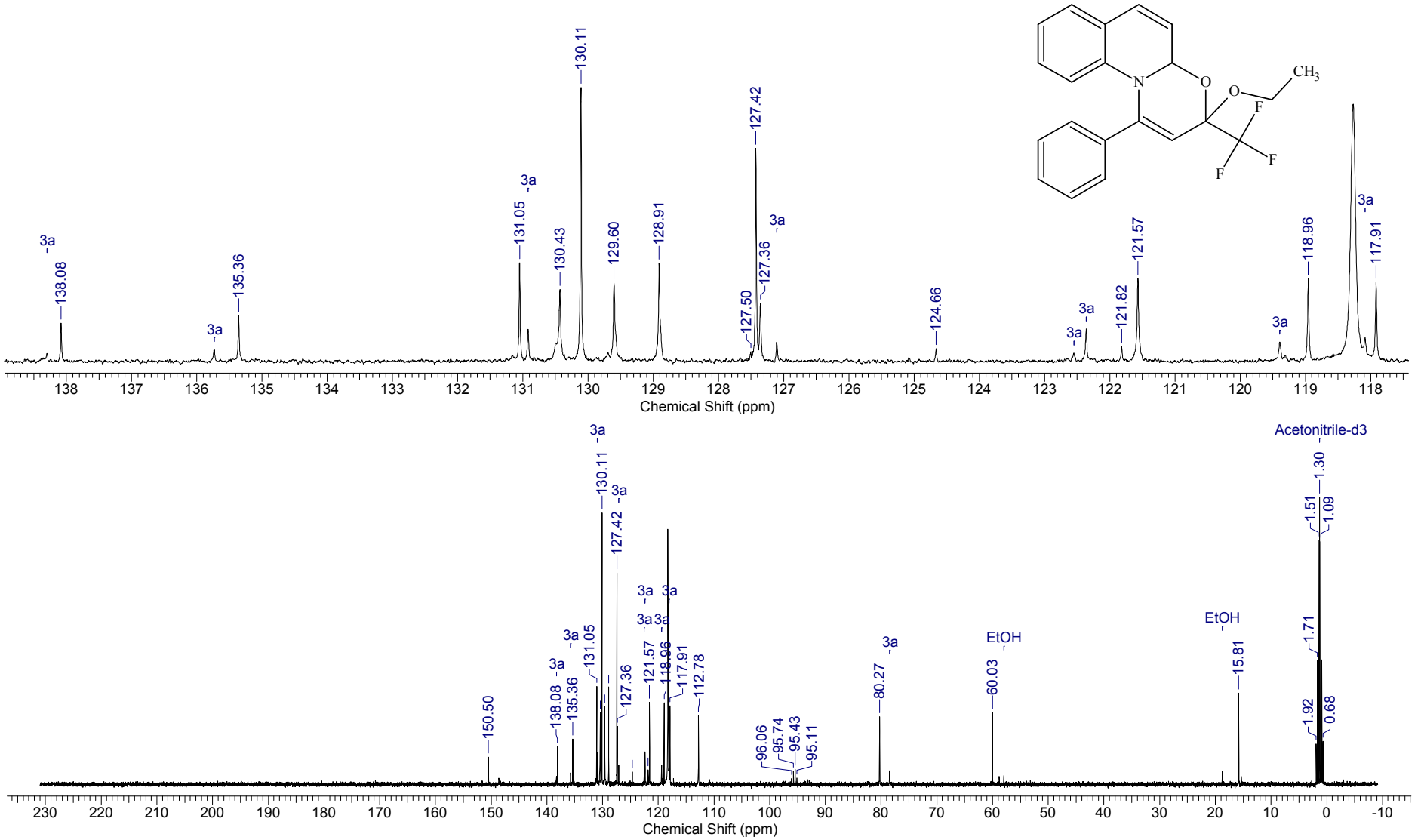
Acquisition Time (sec)	1.0000	***Date***	Jun 3 2019	***File Name***	I:\SPEC_F_2019\2019.06.03\BM-1588_20190603_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	21.000				





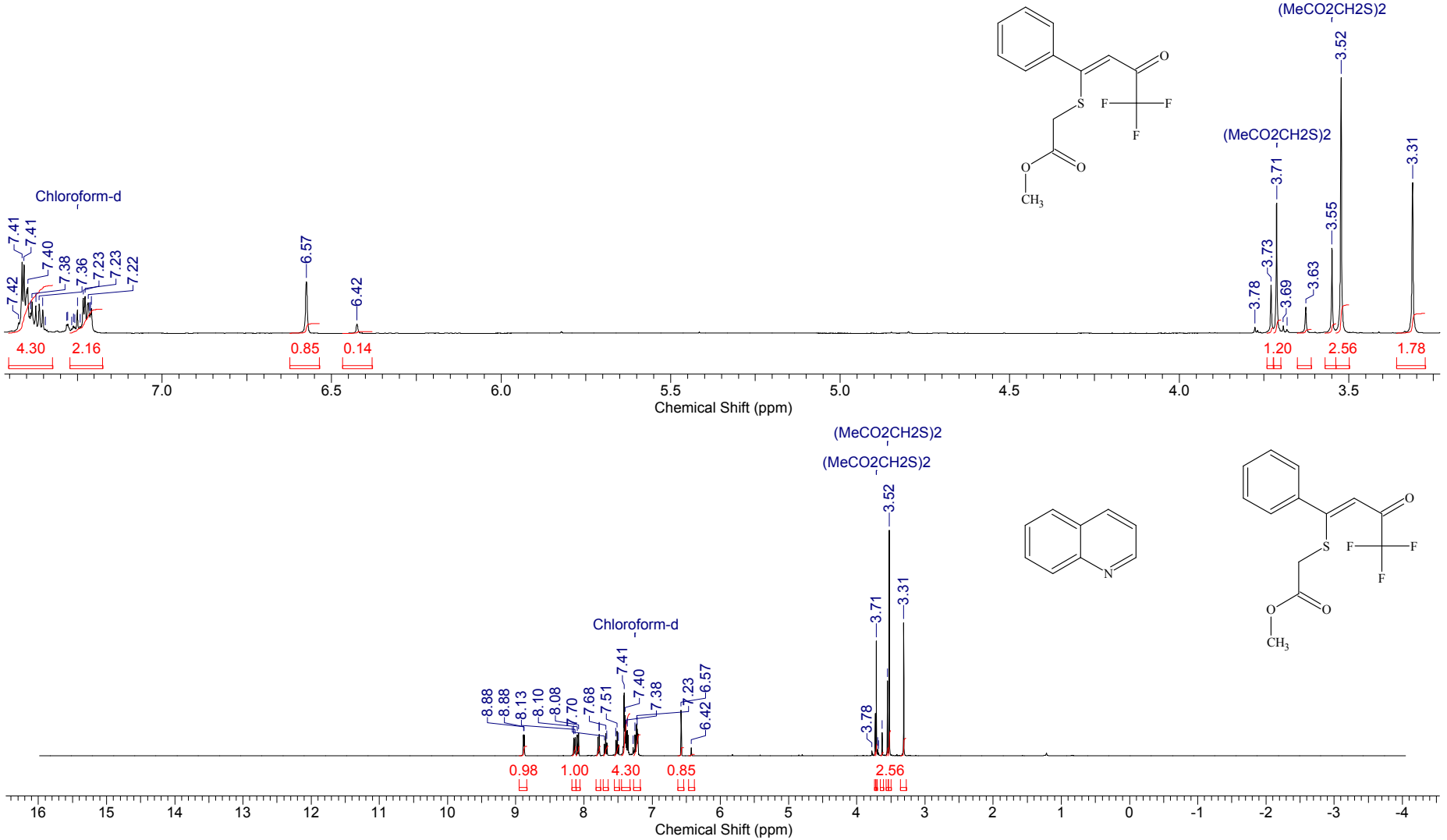
^{19}F NMR spectrum of **4** (376.5 MHz, CD_3CN). Signals of **3a** are the result of hydrolysis of **4** during preparation and storing of the NMR sample.

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	31 May 2019 15:20:20
File Name	C:\DOCS\OUTPUT_301\2019\05.ì àé\BM-1588.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	161	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



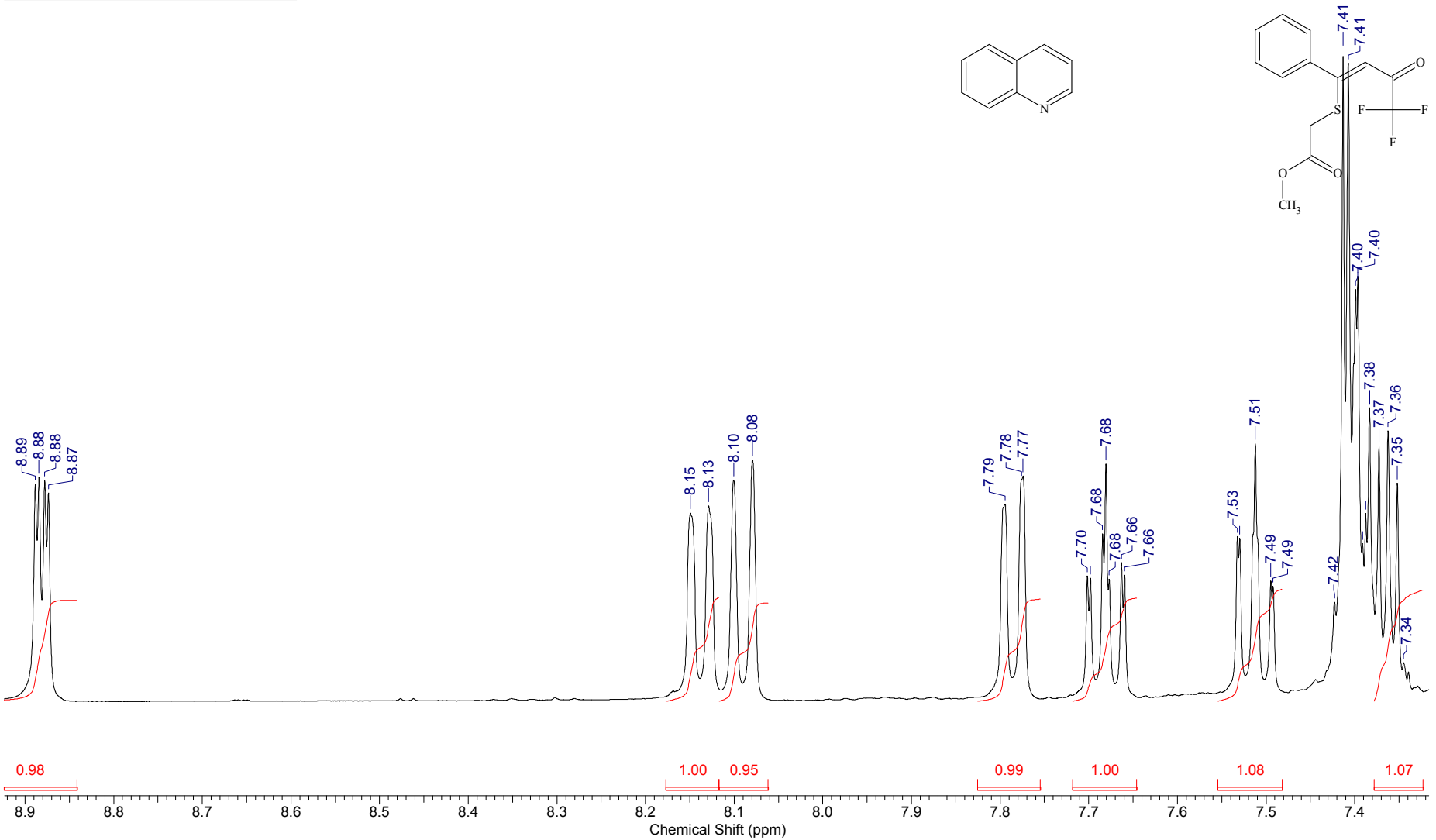
^{13}C NMR spectrum of **4** (100.6 MHz, CD_3CN). Signals of **3a** are the result of hydrolysis of **4** during preparation and storing of the NMR sample.

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	05 Jun 2019 17:26:50
File Name	C:\DOCS\OUTPUT_301\2019\06.èþ í ü\BM-1591-a.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



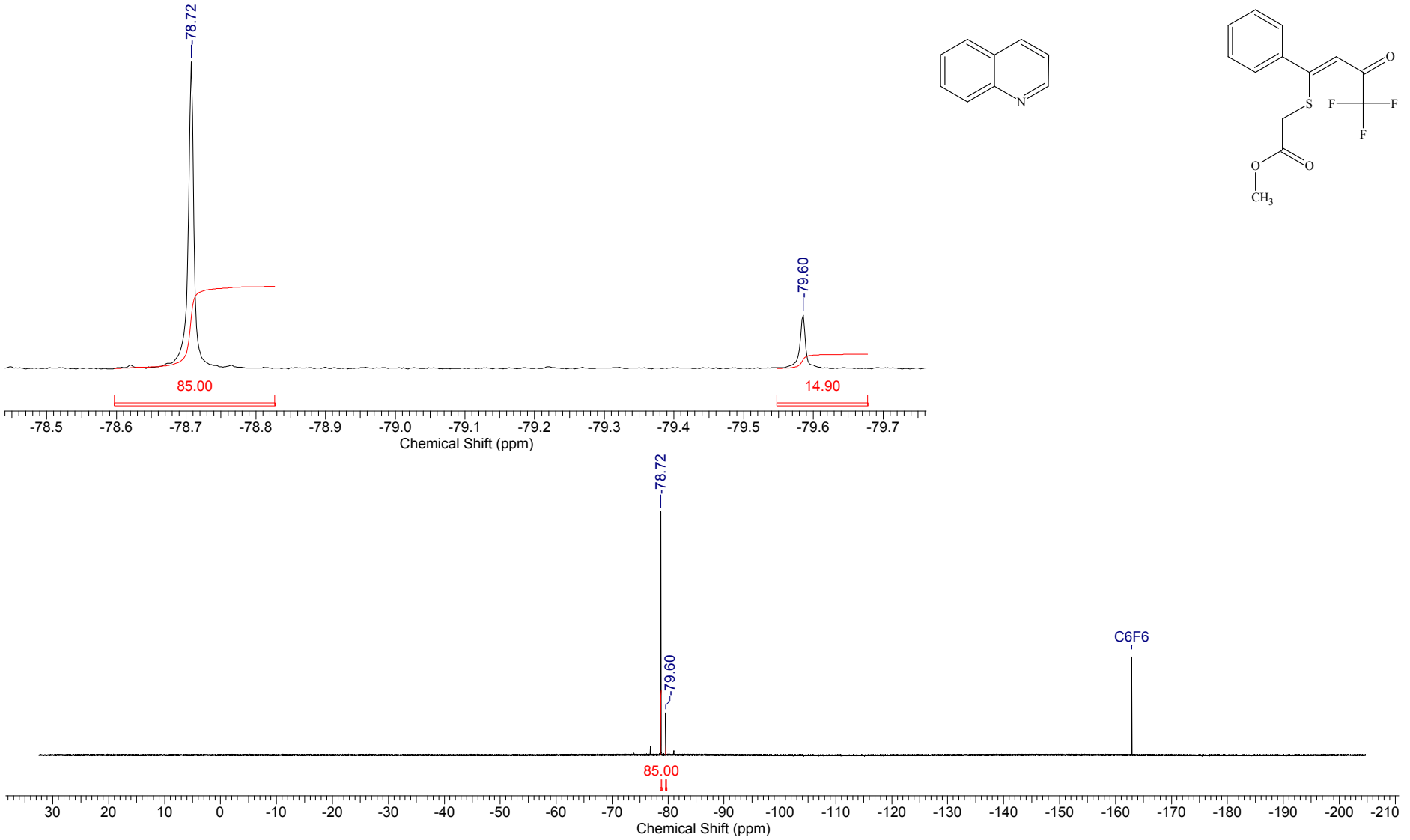
^{1}H NMR spectrum of mixture of quinoline and methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (400.1 MHz, $CDCl_3$). The region with signals of compound **5** are highlighted.

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	05 Jun 2019 17:26:50
File Name	C:\DOCS\OUTPUT_301\2019\06.èþ í ü\BM-1591-a.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



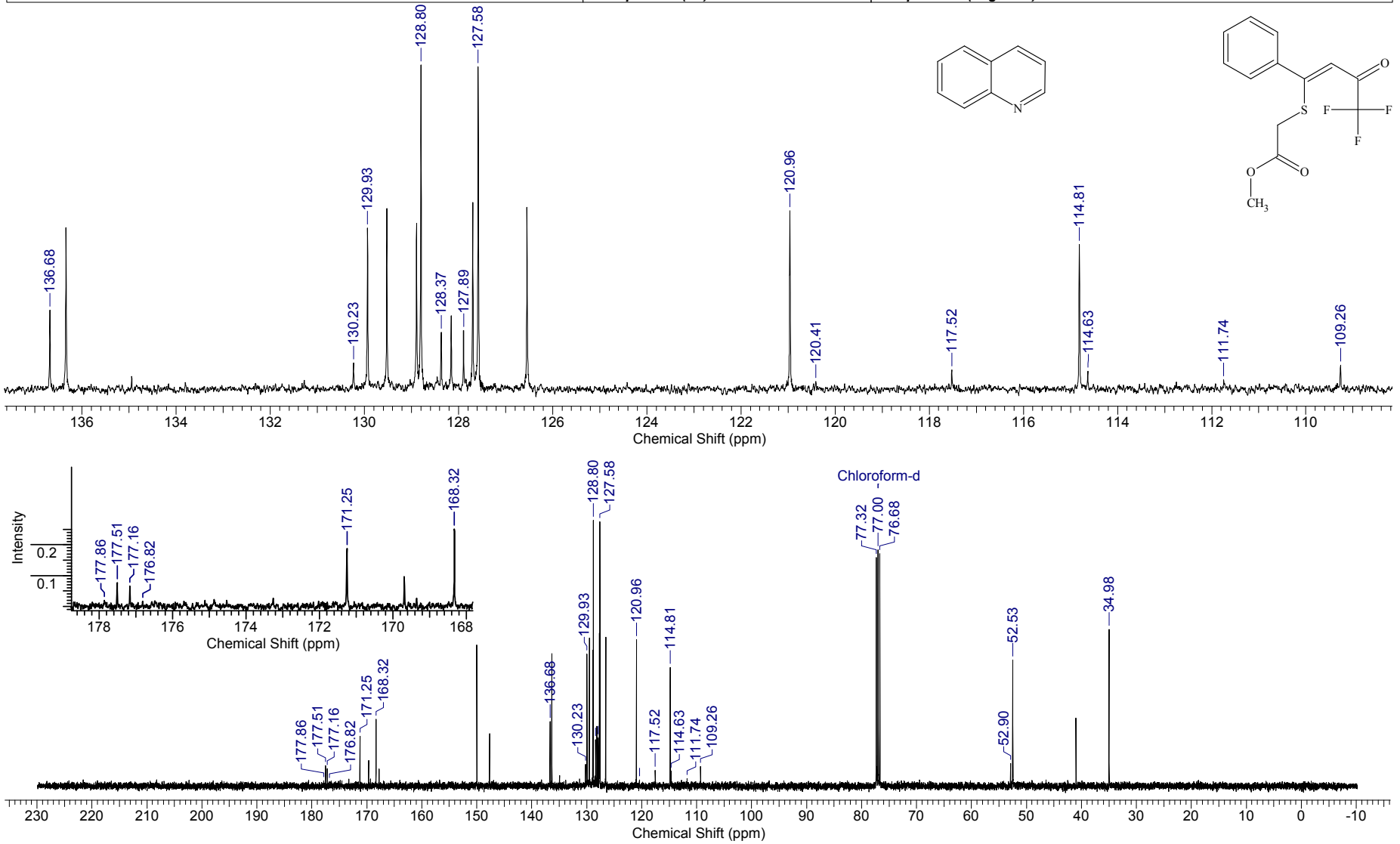
^{1}H NMR spectrum of mixture of quinoline and methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (400.1 MHz, $CDCl_3$). The region with signals of quinoline are highlighted.

Acquisition Time (sec)	1.0000	***Date***	Jun 3 2019	***File Name***	I:\SPEC_F_2019\2019.06.03\BM-1591_20190603_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	21.000				



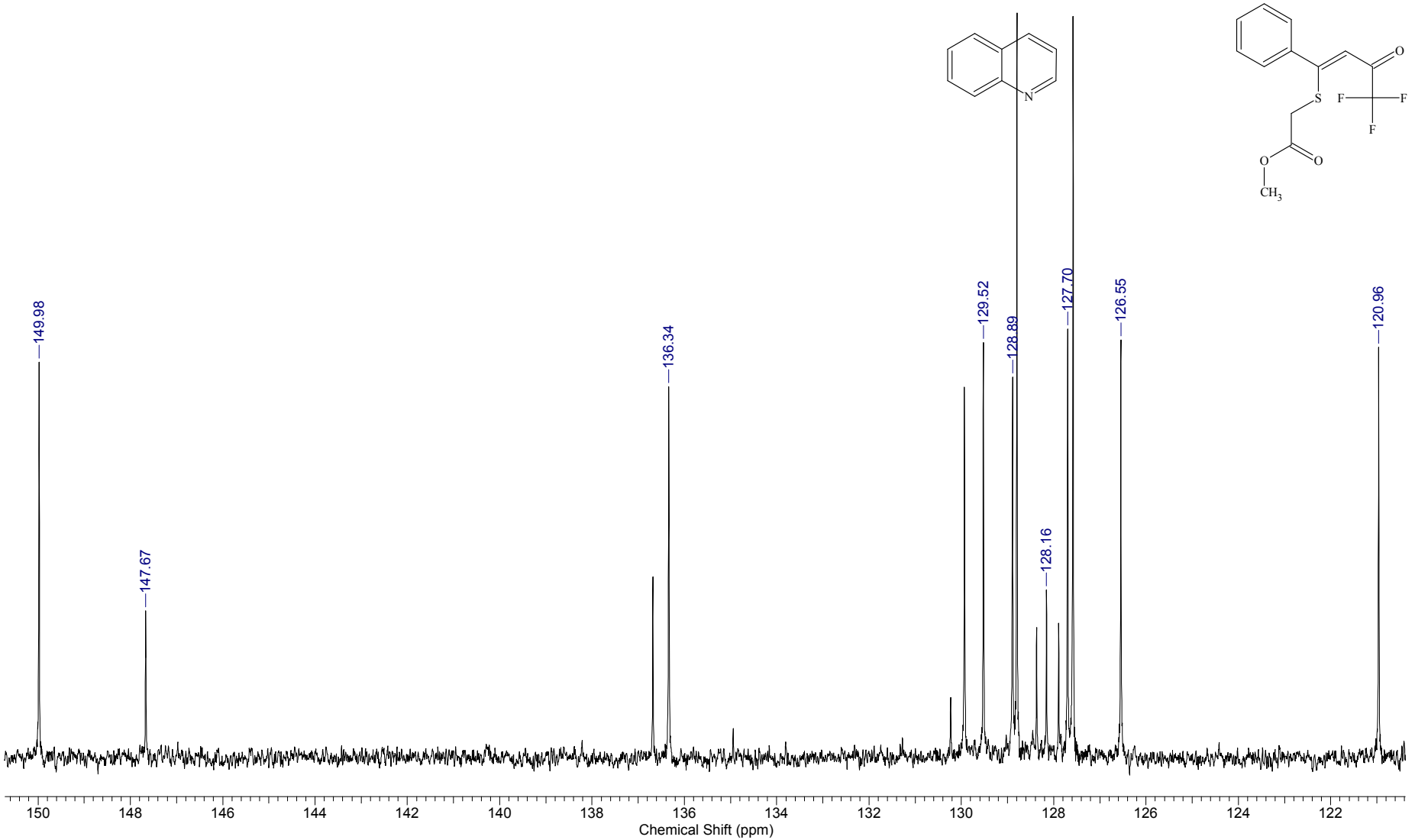
^{19}F NMR spectrum of mixture of quinoline and methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (376.5 MHz, $CDCl_3$)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	05 Jun 2019 17:41:04
File Name	C:\DOCS\OUTPUT_301\2019\06.èþ í ü\BM-1591-a.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	361	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



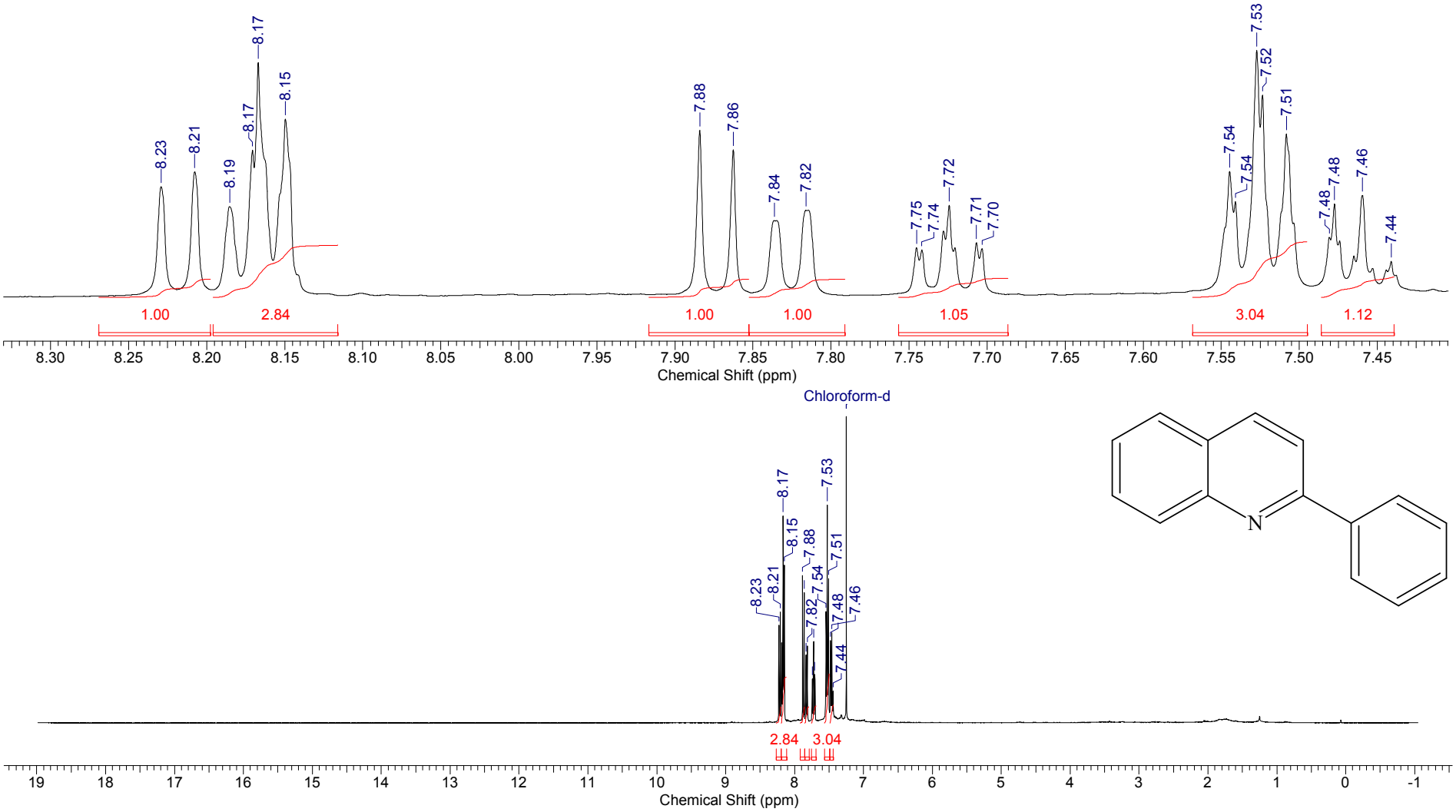
^{13}C NMR spectrum of mixture of quinoline and methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (100.6 MHz, $CDCl_3$). The signals of compound **5** are highlighted.

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.	***Date***	05 Jun 2019 17:41:04
File Name	C:\DOCS\OUTPUT_301\2019\06.èþ í ü\BM-1591-a.C_002001r	***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	361	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



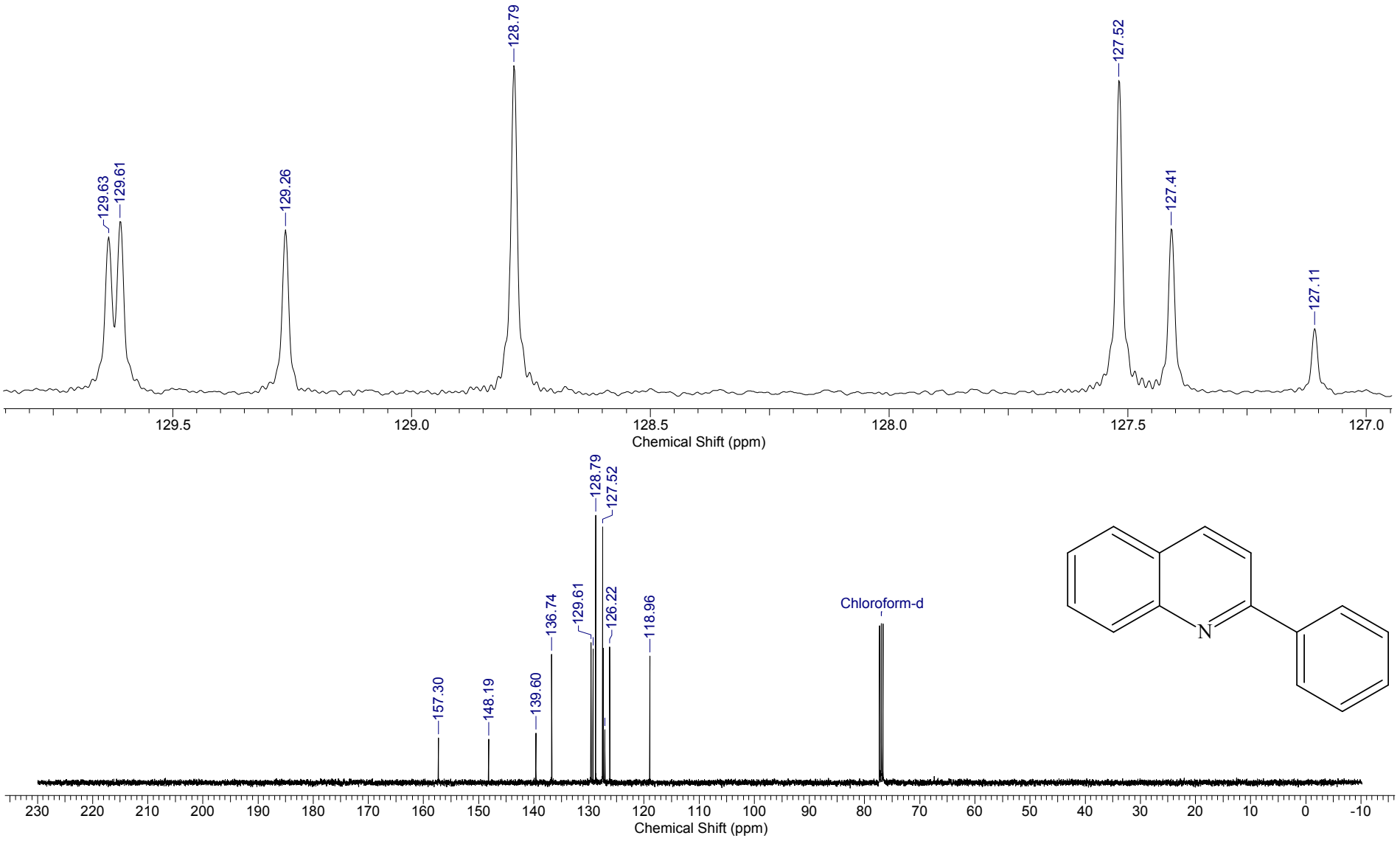
^{13}C NMR spectrum of mixture of quinoline and methyl 2-((4,4,4-trifluoro-3-oxo-1-phenylbut-1-en-1-yl)thio)acetate **5** (100.6 MHz, $CDCl_3$). The signals of quinoline are highlighted.

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	20 Jun 2019 19:27:10
File Name	C:\Users\BM-1\Downloads\BM-1607\BM-1607_001001r			***Frequency (MHz)***	400.13	***Nucleus***	1H
Number of Transients	8	***Original Points Count***	32768	***Points Count***	131072	***Pulse Sequence***	zg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	8012.82	***Temperature (degree C)***	27.000



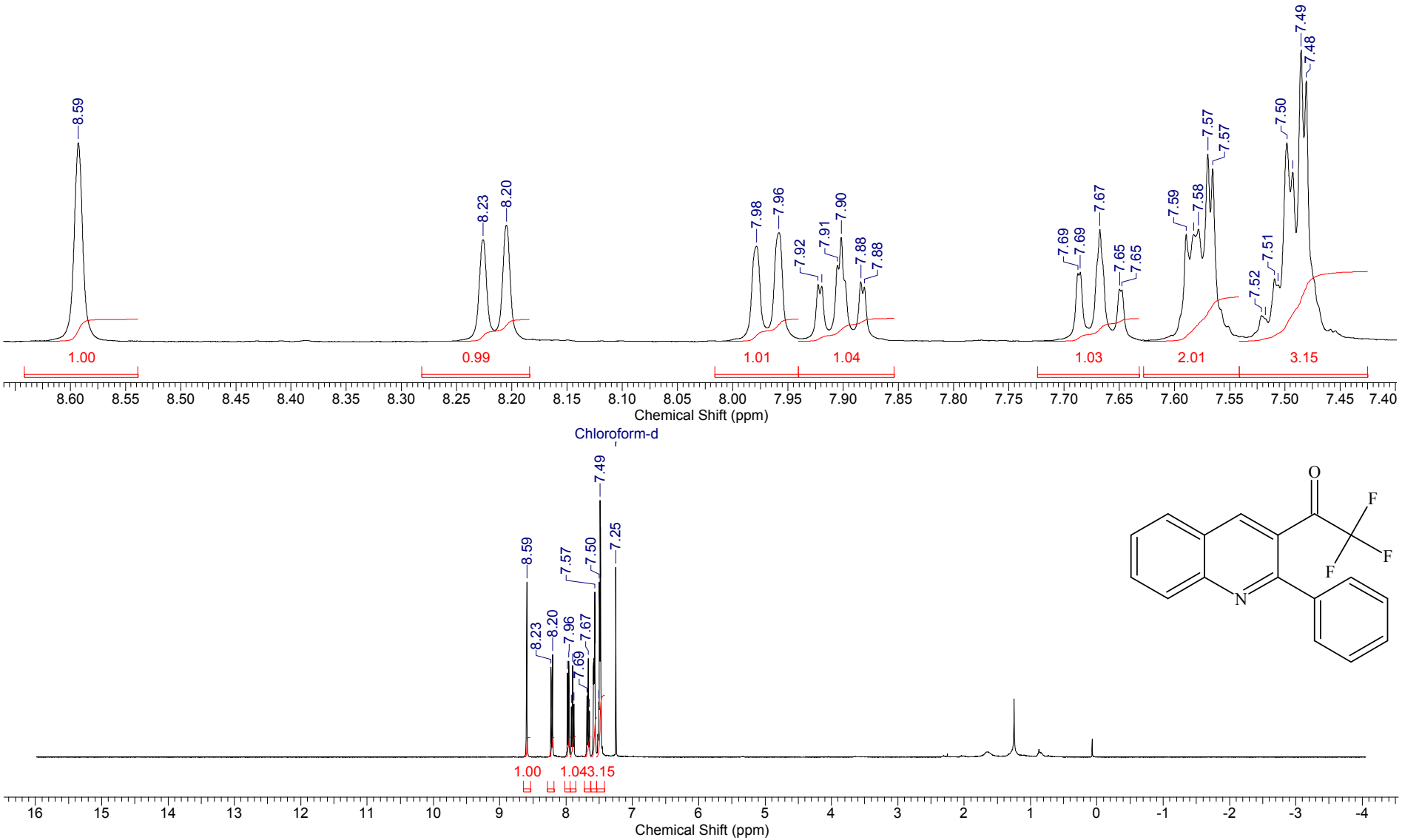
^{1}H NMR spectrum of **6** (400.1 MHz, $CDCl_3$).

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	01 Jun 2019 14:15:34
File Name	C:\DOCS\OUTPUT_301\2019\06.èþ í ü\BM-1595.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	146	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	ACETONITRILE-D3			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



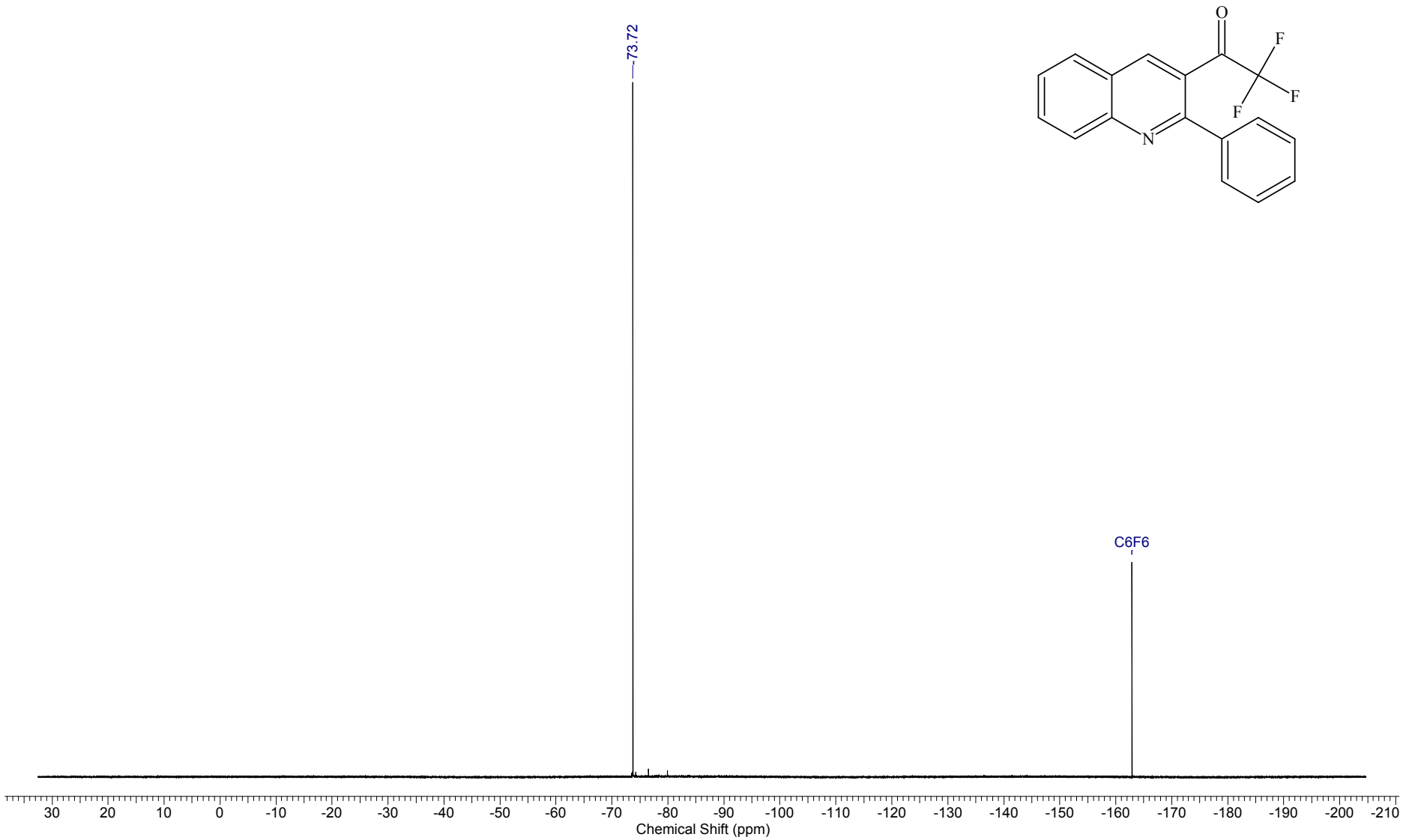
^{13}C NMR spectrum of **6** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	08 Jul 2019 15:50:32
File Name	C:\DOCS\OUTPUT_301\2019\07.èþ ëü\BM-1623-1.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	8012.82	***Temperature (degree C)***	27.000



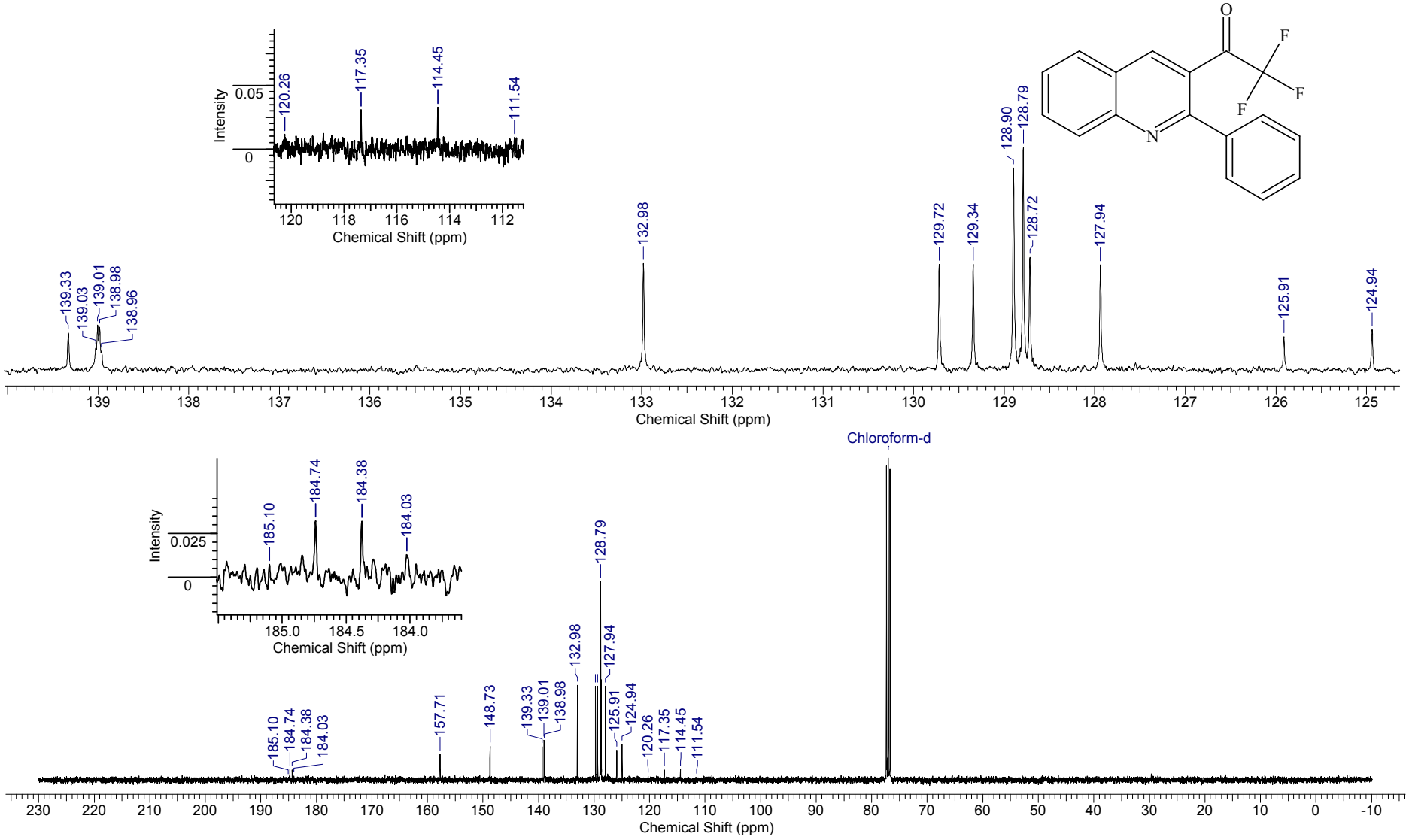
^{1}H NMR spectrum of **7** (400.1 MHz, $CDCl_3$)

Acquisition Time (sec)	0.7340	***Date***	Jul 5 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.07.05\BM-1623-R_20190705_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	65536
Points Count	65536	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	25.000				

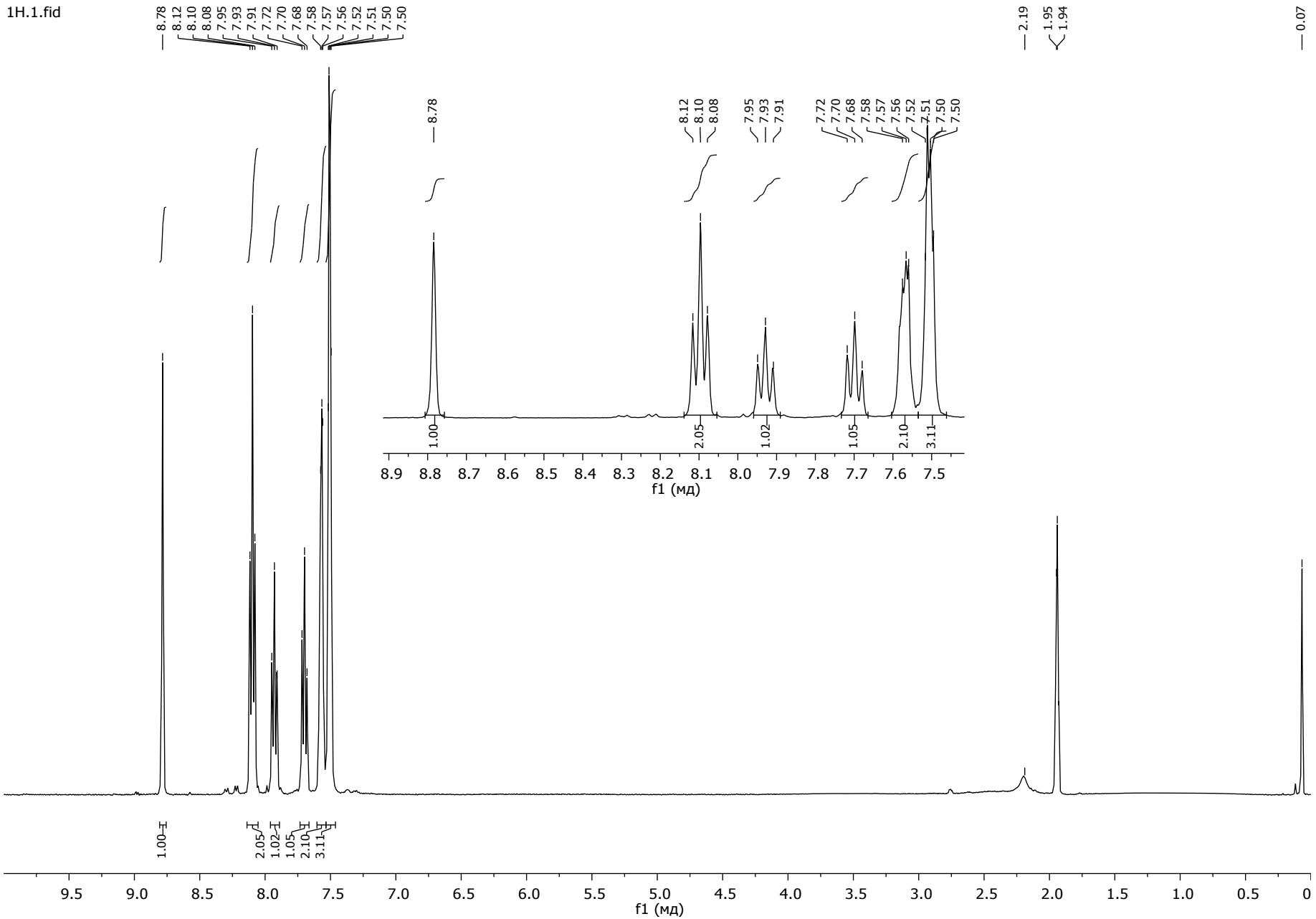


^{19}F NMR spectrum of **7** (376.5 MHz $CDCl_3$)

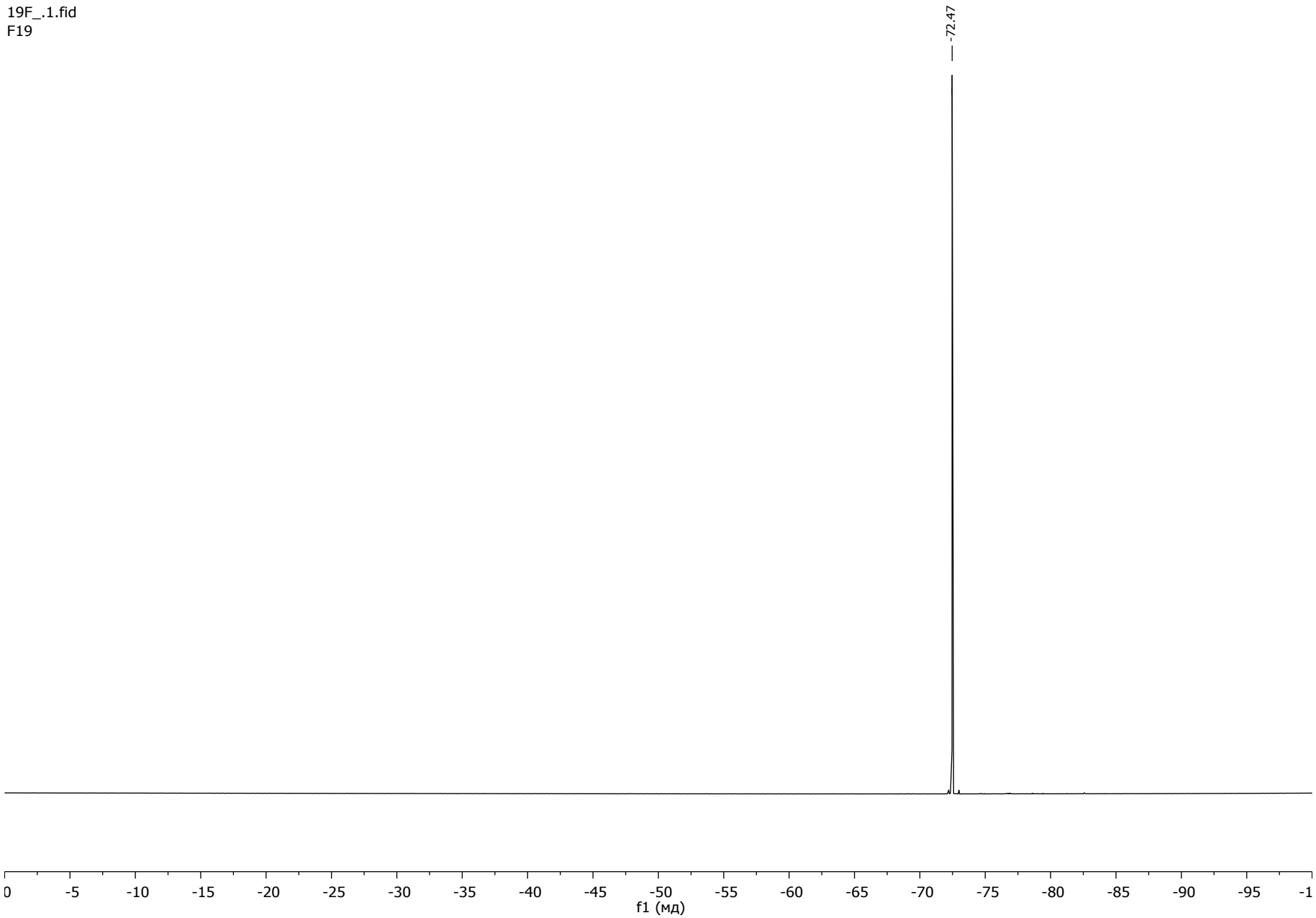
Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	08 Jul 2019 16:10:16
File Name	C:\DOCS\OUTPUT_301\2019\07.èþ ëü\BM-1623-1.C_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	505	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	DMSO-D6	***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



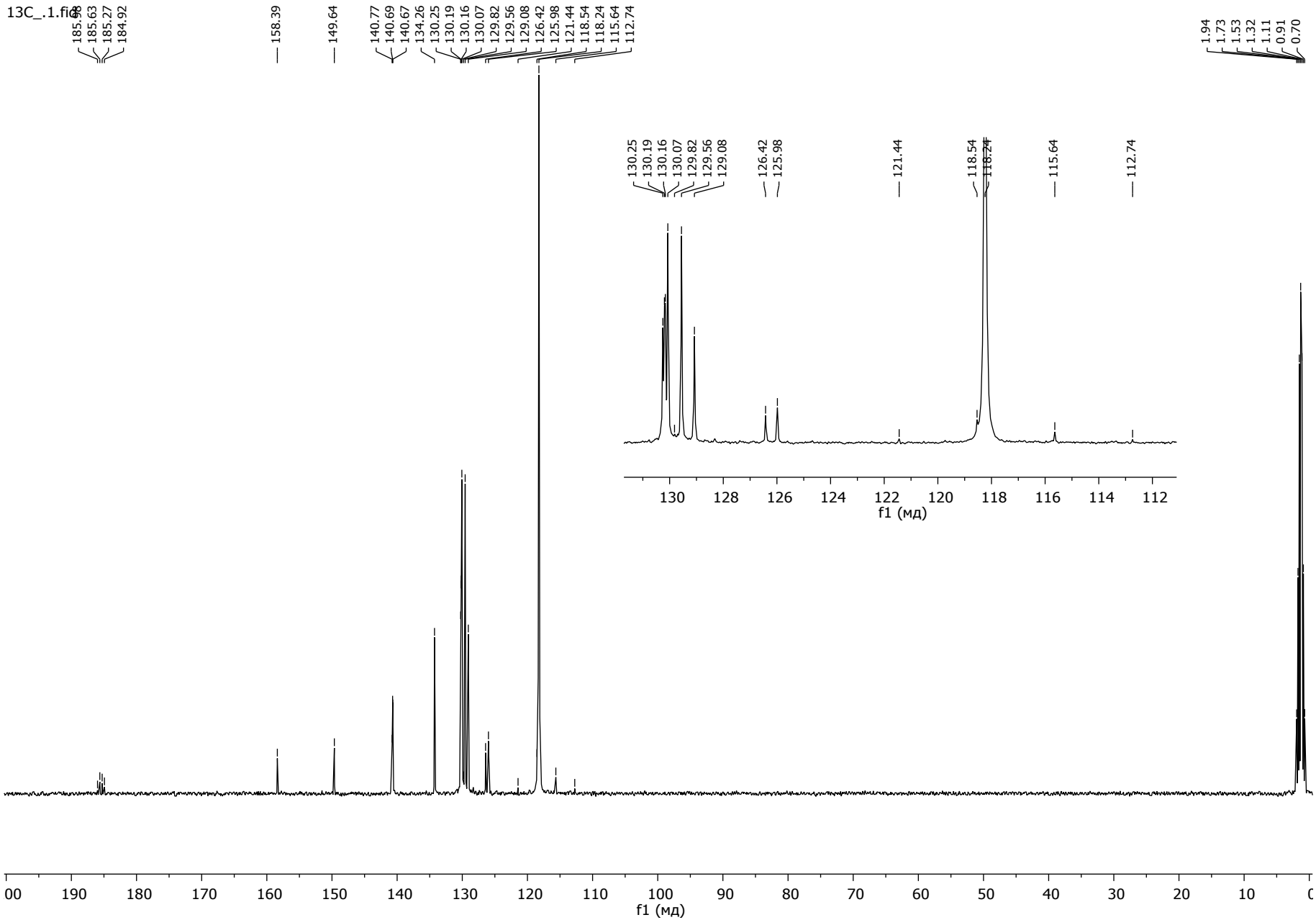
^{13}C NMR spectrum of **7** (100.6 MHz, $CDCl_3$)



^{1}H NMR spectrum of **7** (400.1 MHz, CD_3CN)

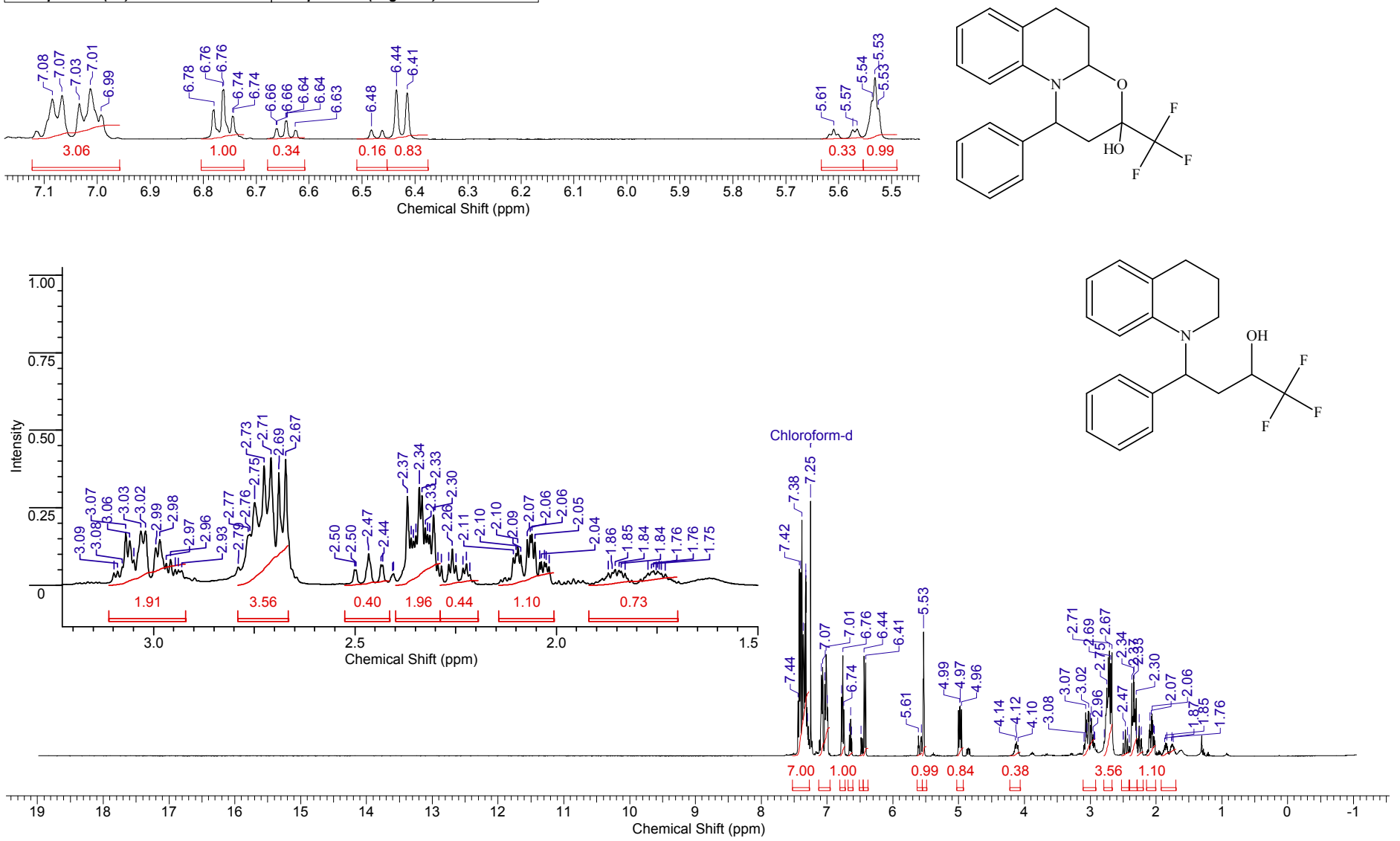


^{19}F NMR spectrum of **7** (376.5 MHz, CD_3CN)



^{13}C NMR spectrum of **7** (100.6 MHz, CD_3CN)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	28 Sep 2019 10:32:32	
File Name	I:\BM-1716-2\BM-1716-2_001001r			***Frequency (MHz)***	400.13	***Nucleus***	1H	***Number of Transients*** 8
Original Points Count	32768	***Points Count***	131072	***Pulse Sequence***	zg30	***Solvent***	CHLOROFORM-D	
Sweep Width (Hz)	8012.82	***Temperature (degree C)***	27.000					

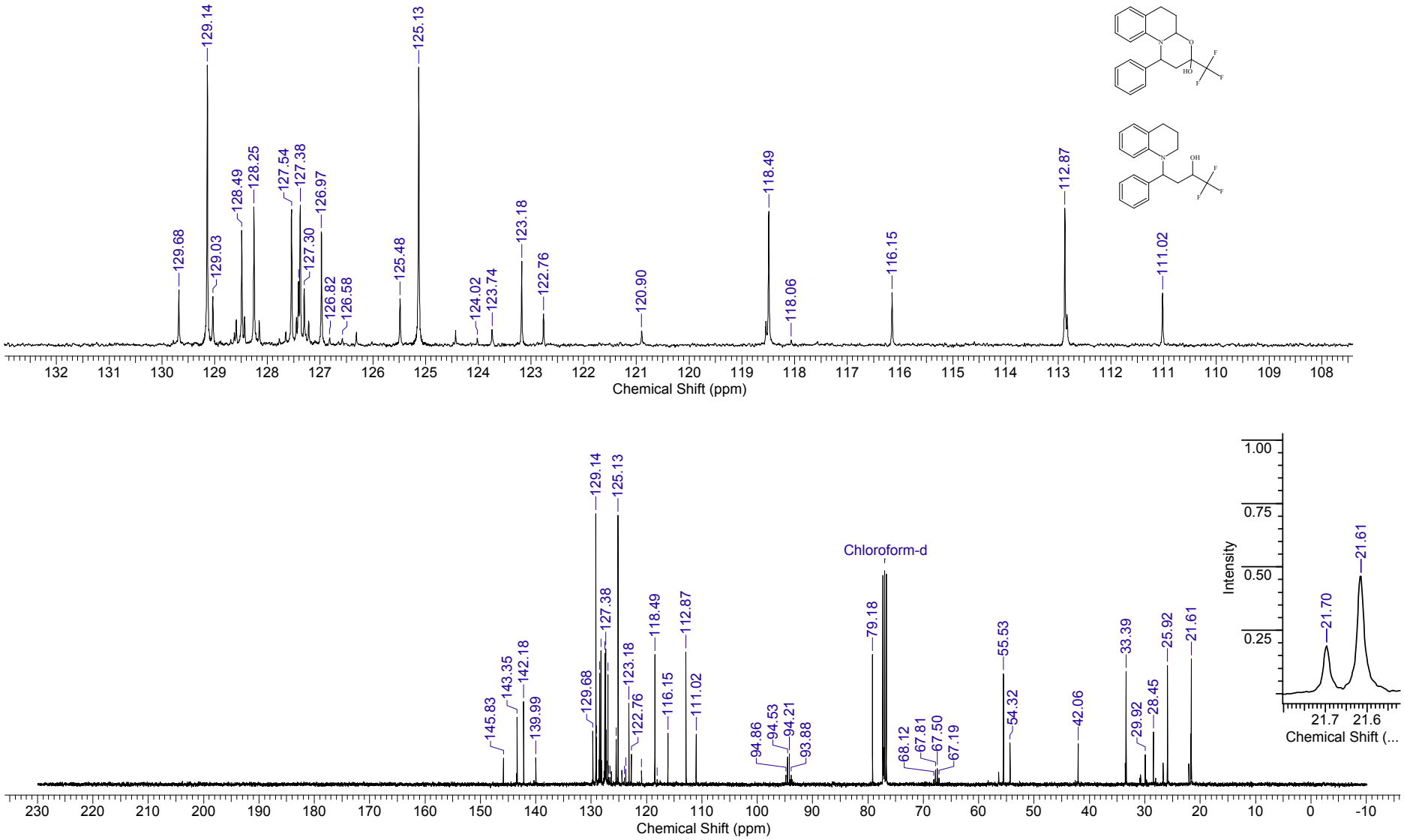


^{1}H NMR spectrum of **8** and **9** (400.1 MHz, $CDCl_3$)

Acquisition Time (sec)	2.0000	***Date***	Sep 30 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.09.30\BM-1716-2_20190930_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	178571
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	20.000				

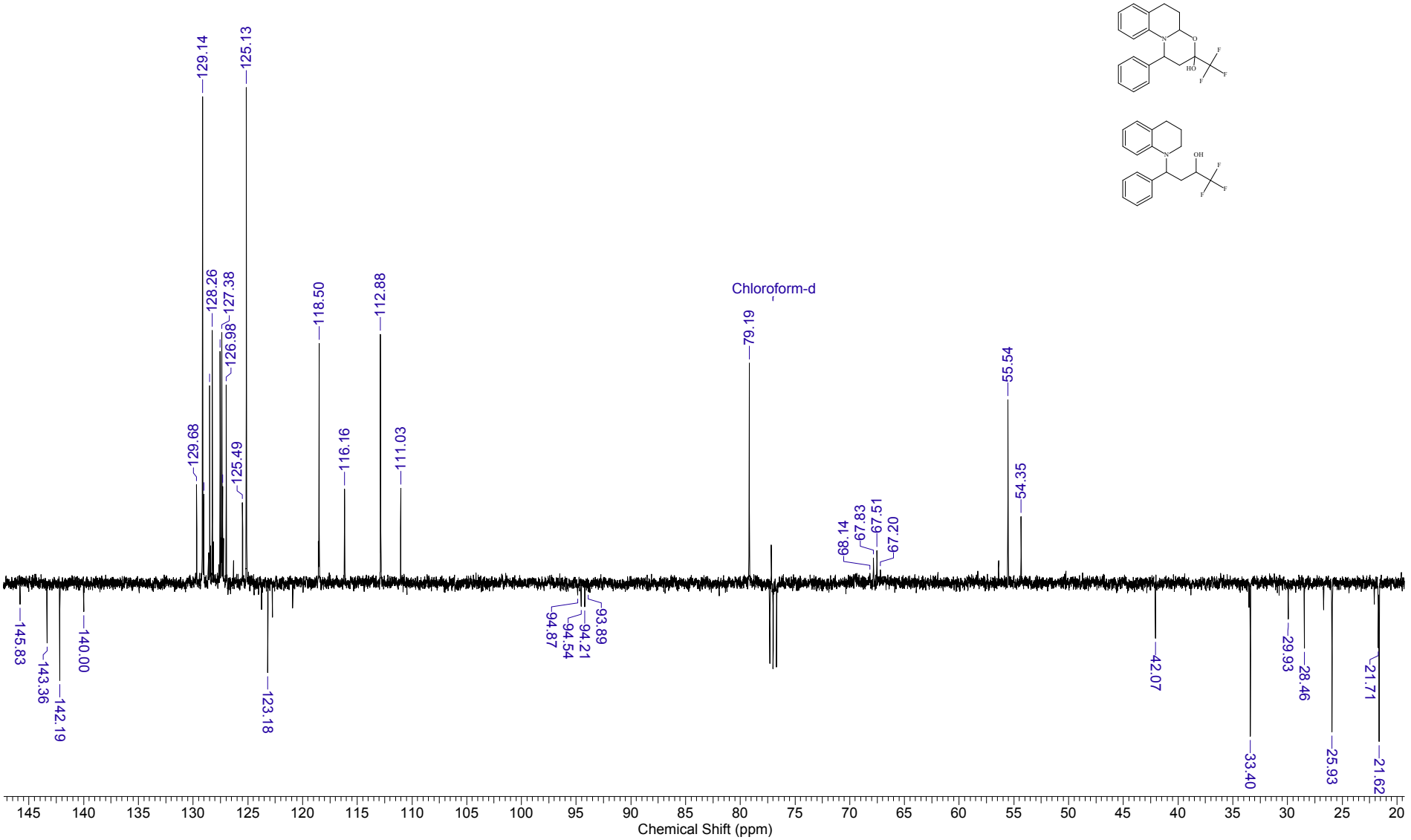
^{19}F NMR spectrum of **8** and **9** (376.5 MHz $CDCl_3$)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	28 Sep 2019 11:10:38	
File Name	I:\BM-1716-2\BM-1716-2_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C	***Number of Transients*** 904
Original Points Count	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30	***Solvent***	CHLOROFORM-D	
Sweep Width (Hz)	24154.59	***Temperature (degree C)***	27.000					



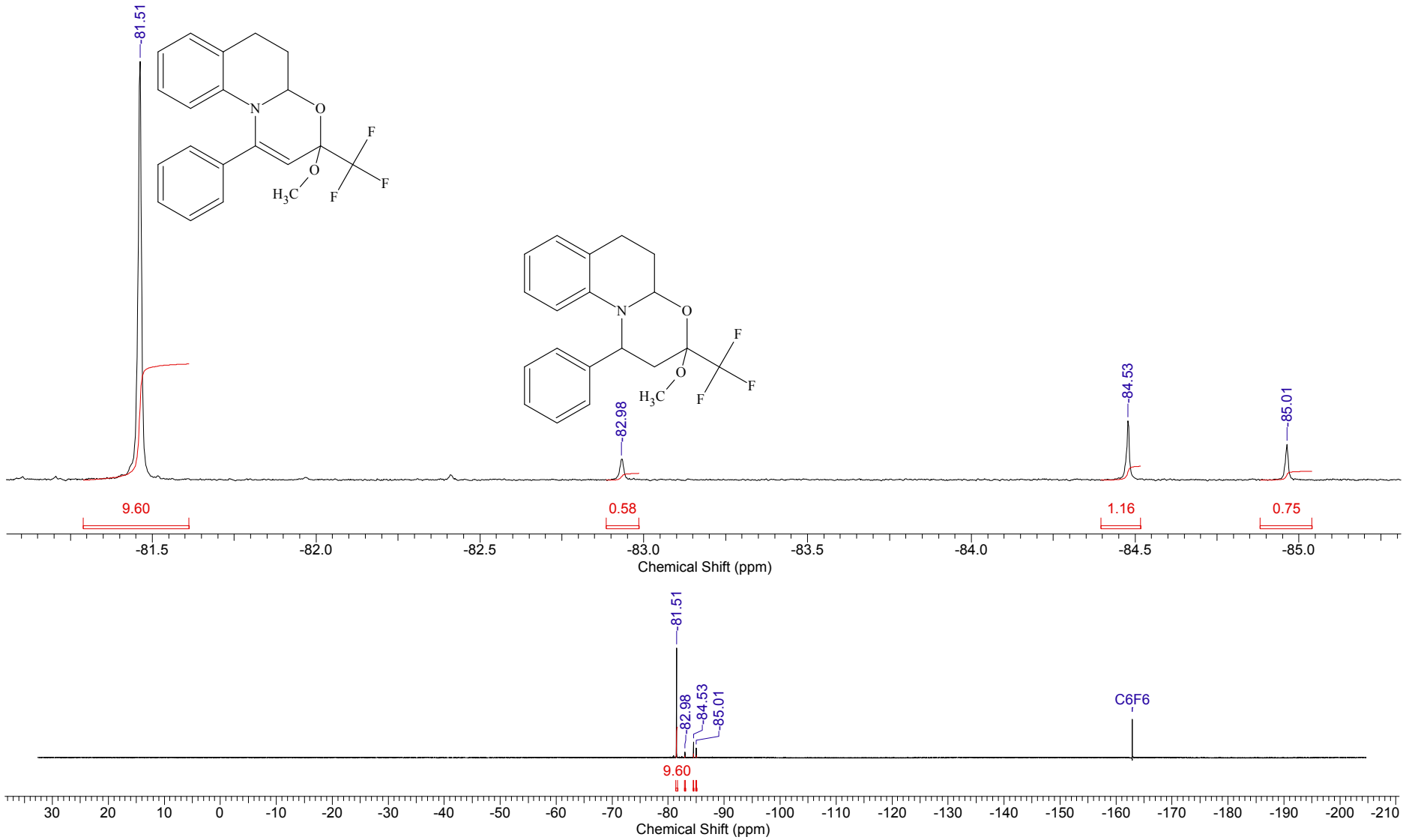
^{13}C NMR spectrum of **8** and **9** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	1.3664	***Comment***	Imported from UXNMR.			***Date***	30 Sep 2019 16:01:36
File Name	I:\SPEC_2019_H,C\09.ñåí òÿáðü\BM-1716-2.APT_004001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	49	***Original Points Count***	32768	***Points Count***	131072	***Pulse Sequence***	jmod
Solvent	ACETONITRILE-D3			***Sweep Width (Hz)***	23980.81	***Temperature (degree C)***	27.000



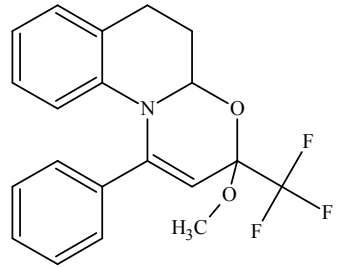
^{13}C APT NMR spectrum of **8** and **9** (100.6 MHz, $CDCl_3$)

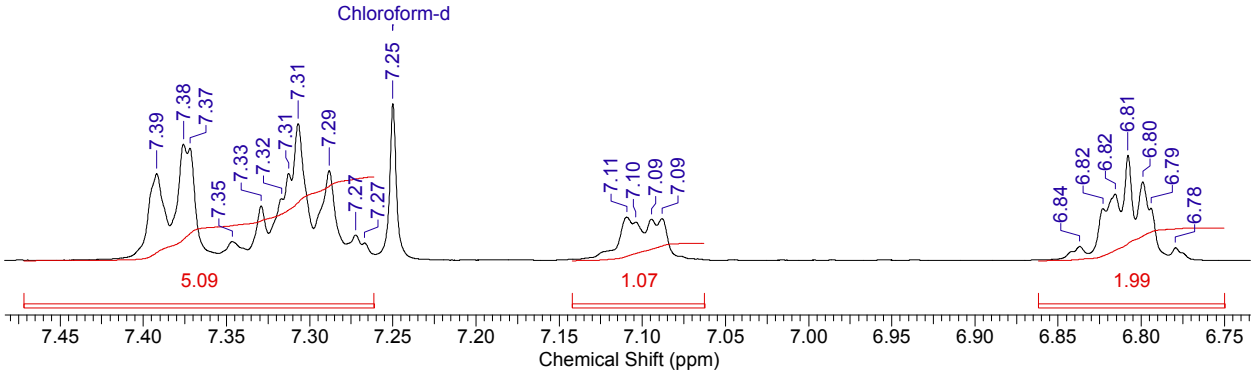
Acquisition Time (sec)	1.0000	***Date***	Sep 20 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.09.20\BM-1709-R_20190920_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	8	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	20.000				

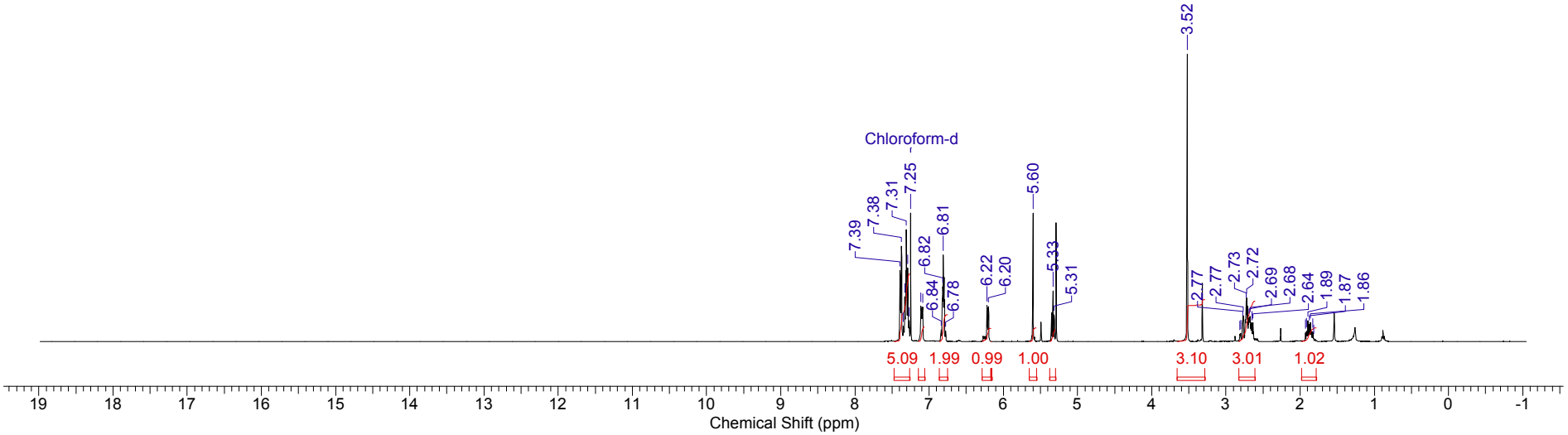


^{19}F NMR monitoring of hydrogenation of 3a in MeOH.Spectrum of the reaction mixture after first 14 h (376.5 MHz $CDCl_3$)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	28 Sep 2019 16:54:48
File Name	C:\DOCS\BM\BM-1709-f\BM-1709-f_001001r			***Frequency (MHz)***	400.13	***Nucleus***	1H	***Number of Transients***	8
Original Points Count	32768	***Points Count***	131072	***Pulse Sequence***	zg30	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	8012.82	***Temperature (degree C)***	27.000						

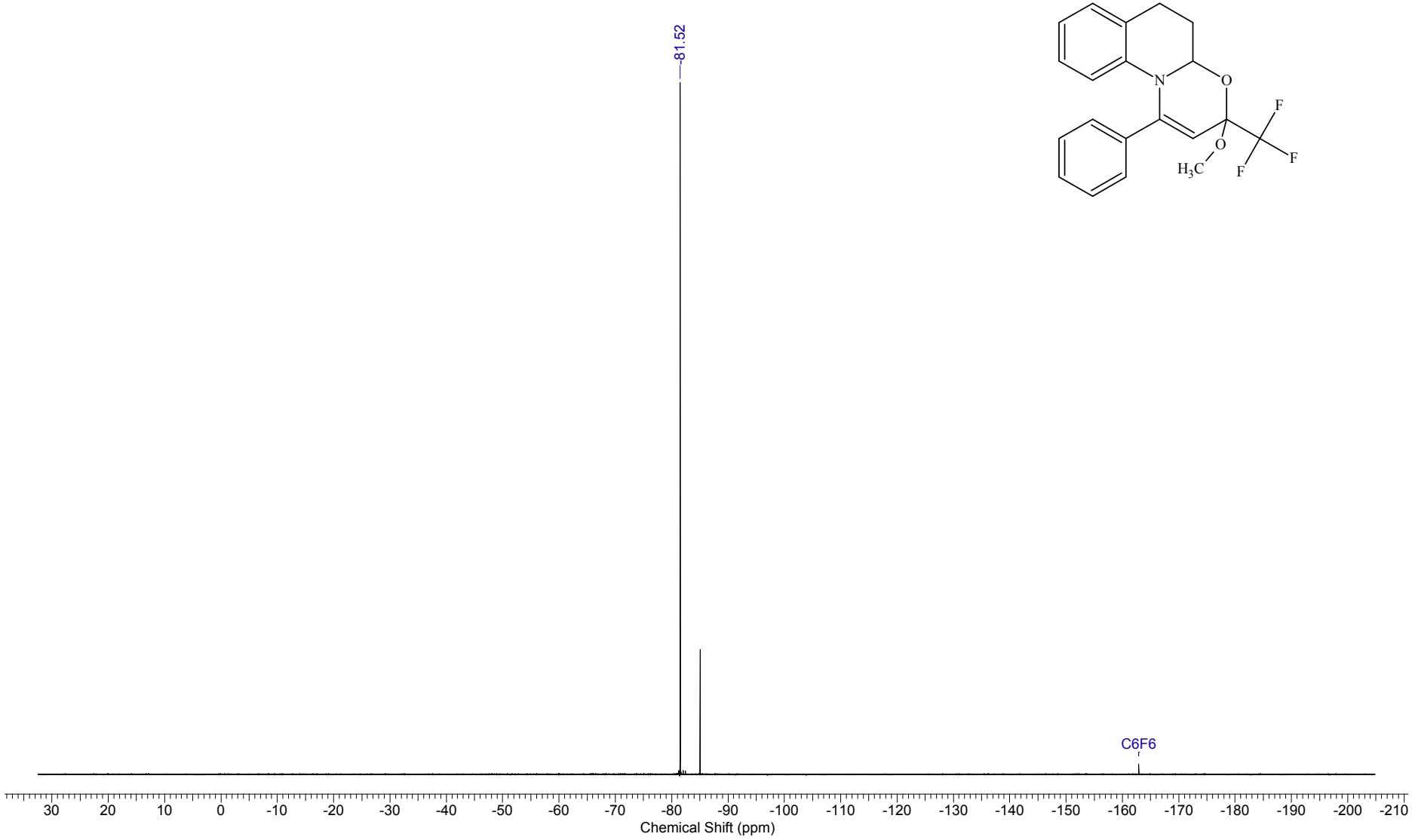






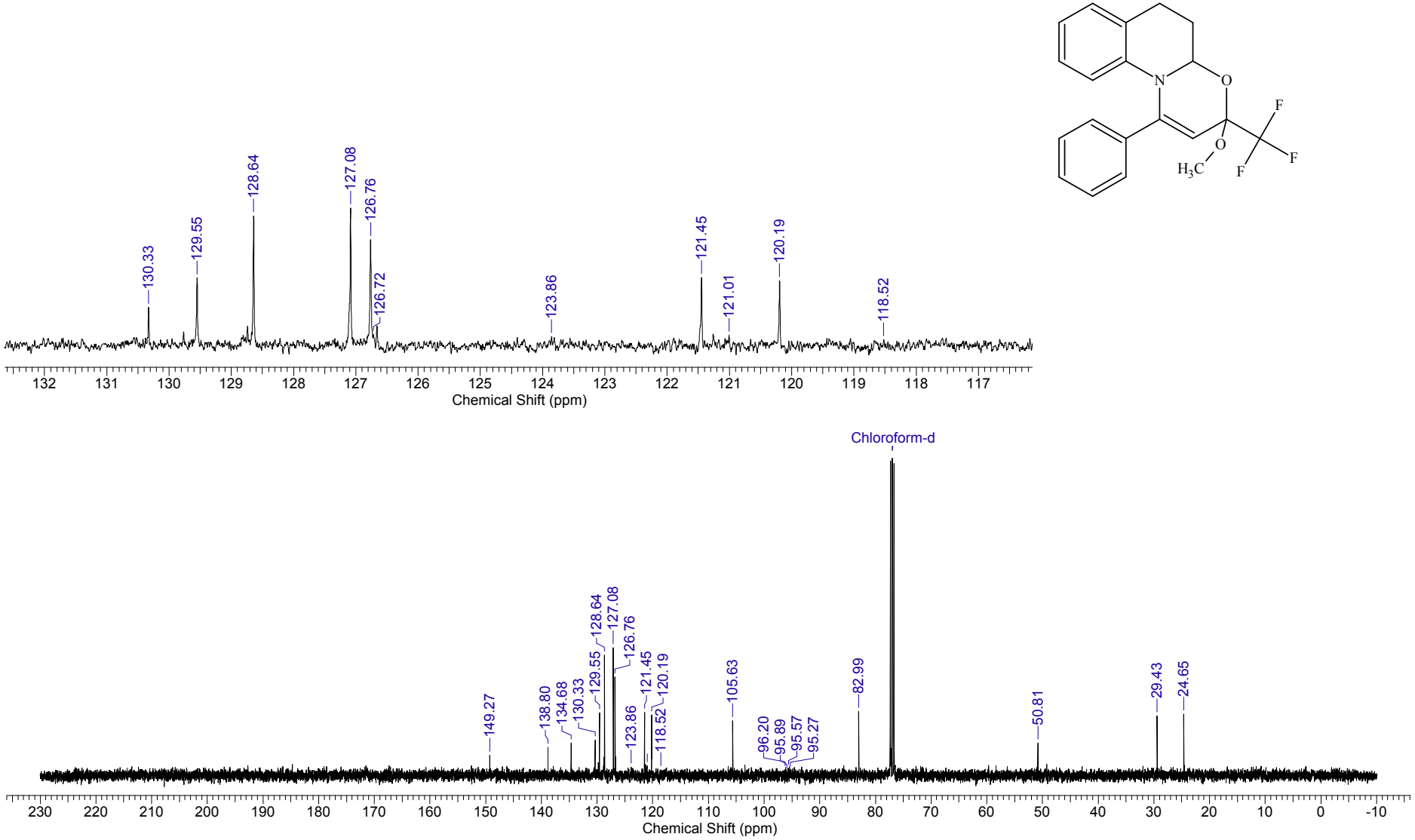
^{1}H NMR spectrum of **10** (400.1 MHz, $CDCl_3$)

Acquisition Time (sec)	2.0000	***Date***	Sep 30 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.09.30\BM-1709-F_20190930_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	16	***Original Points Count***	178571
Points Count	262144	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	20.000				



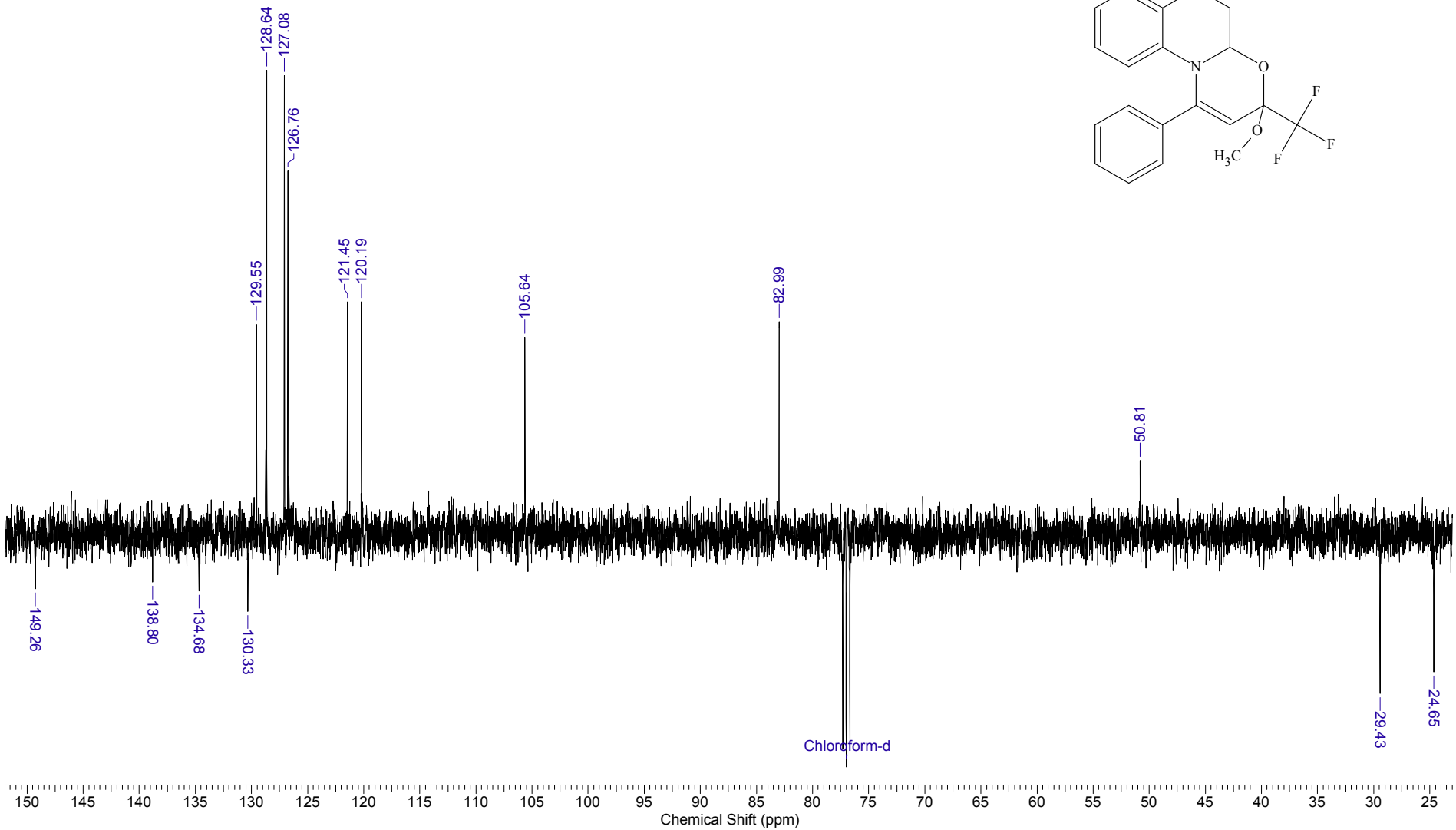
^{19}F NMR spectrum of **10** (376.5 MHz $CDCl_3$)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	30 Sep 2019 15:45:06
File Name	I:\SPEC_2019_H,C\09.ñãí òÿáðü\BM-1709-F.C_002001r			***Frequency (MHz)***	100.61	***Nucleus***	13C
Number of Transients	161	***Original Points Count***	16384	***Points Count***	131072	***Pulse Sequence***	zgpg30
Solvent	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59	***Temperature (degree C)***	27.000



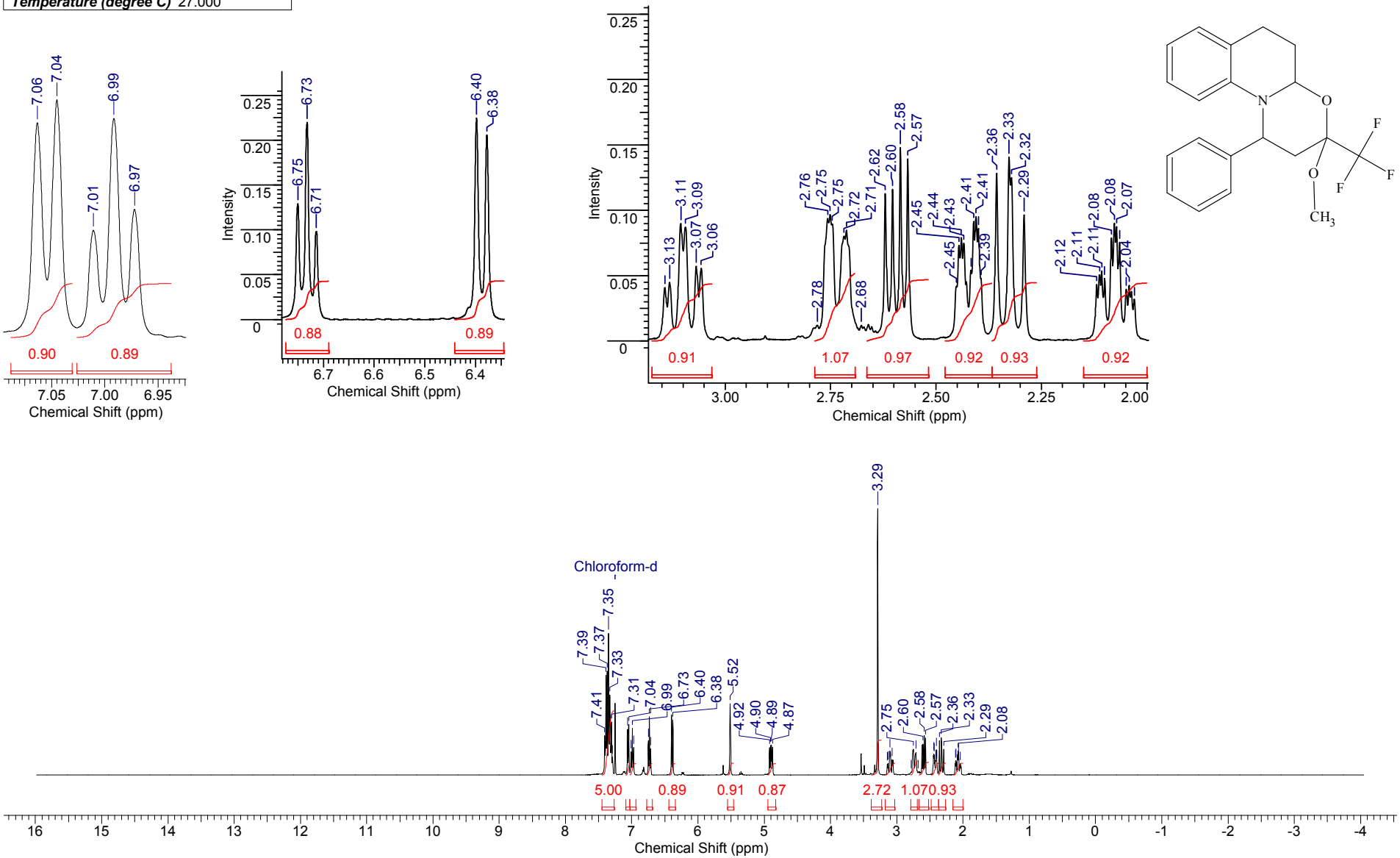
^{13}C NMR spectrum of **10** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	1.3664	***Comment***	Imported from UXNMR.			***Date***	30 Sep 2019 15:49:36
File Name	C:\DOCS\OUTPUT_301\2019\09.ñåí òÿáðü\BM-1709-F.APT_004001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	33	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	jmod	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	23980.81
Temperature (degree C)	27.000						



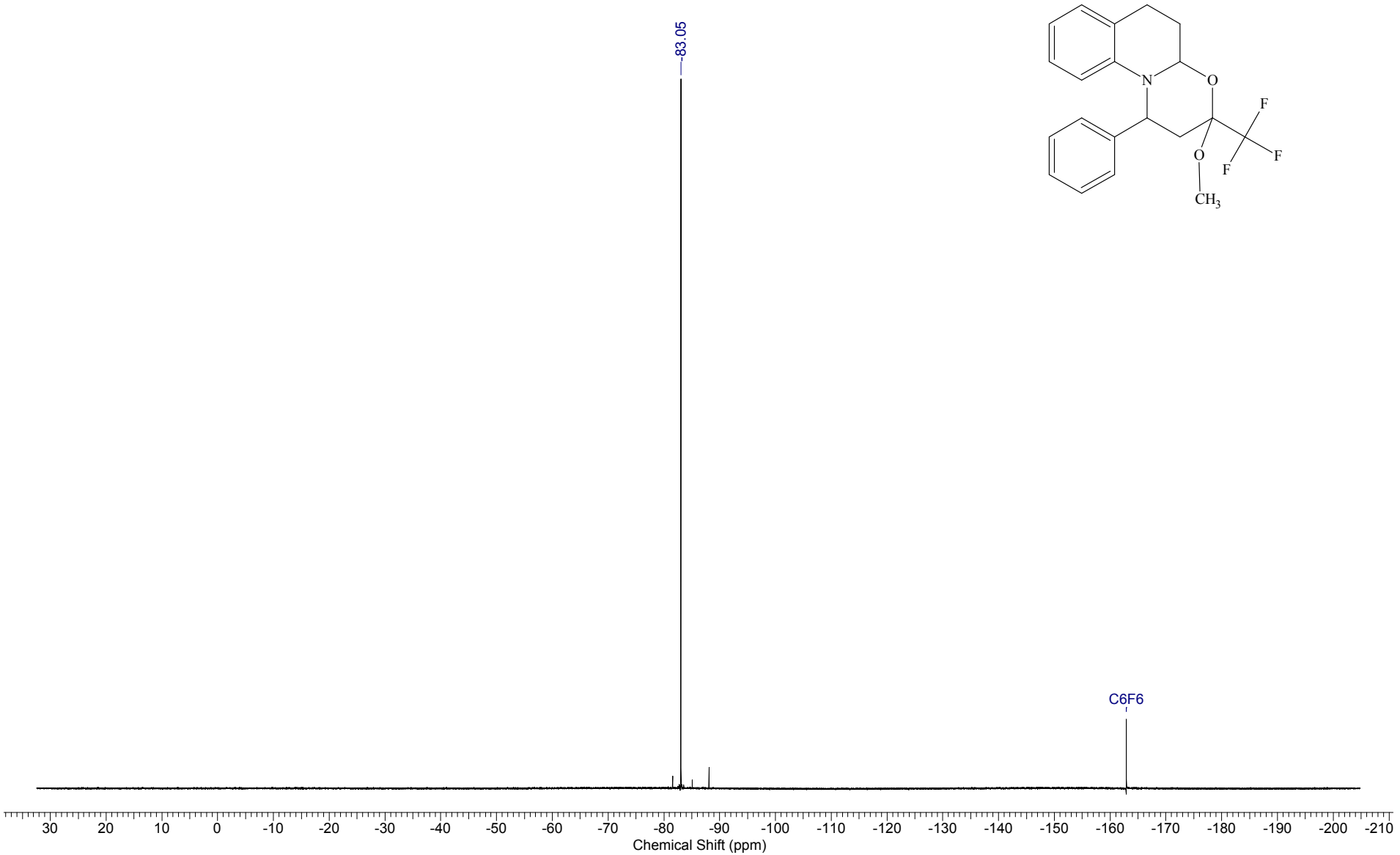
^{13}C APT NMR spectrum of **10** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	4.0894	***Comment***	Imported from UXNMR.			***Date***	27 Sep 2019 15:28:36
File Name	C:\DOCS\OUTPUT_301\2019\09.ñåí òÿáðü\BM-1709-K.H_001001r					***Frequency (MHz)***	400.13
Nucleus	1H	***Number of Transients***	4	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	zg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	8012.82
Temperature (degree C)	27.000						



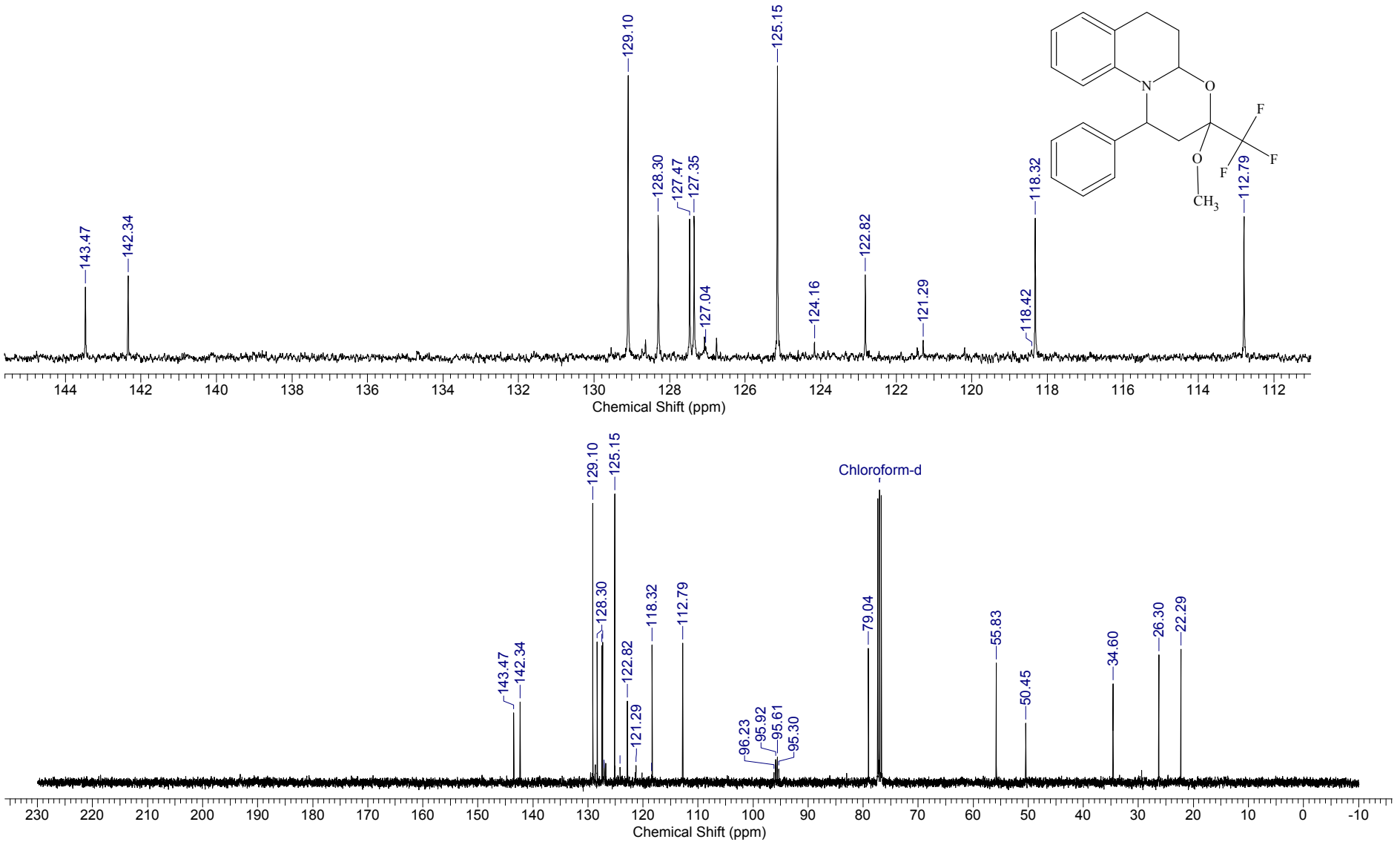
^{1}H NMR spectrum of **11** (400.1 MHz, $CDCl_3$)

Acquisition Time (sec)	1.0000	***Date***	Sep 27 2019	***File Name***	C:\DOCS\OUTPUT_301\F19\2019.09.27\BM-1709-K_20190927_01\FLUORINE_01		
Frequency (MHz)	376.31	***Nucleus***	19F	***Number of Transients***	4	***Original Points Count***	89286
Points Count	131072	***Pulse Sequence***	s2pul	***Solvent***	CHLOROFORM-D		
Sweep Width (Hz)	89285.71	***Temperature (degree C)***	20.000				



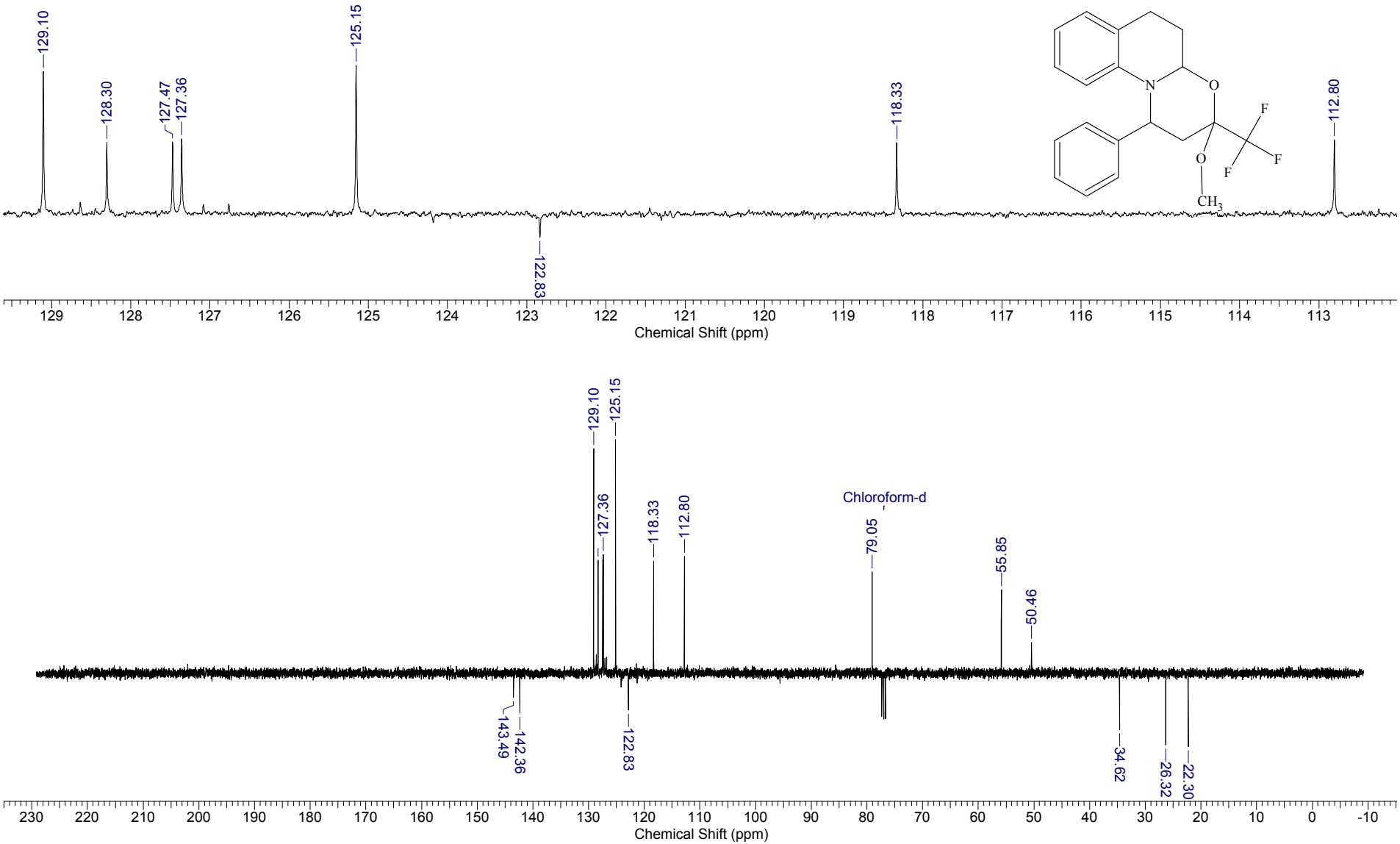
^{19}F NMR spectrum of **11** (376.5 MHz $CDCl_3$)

Acquisition Time (sec)	0.6783	***Comment***	Imported from UXNMR.			***Date***	27 Sep 2019 15:38:00
File Name	C:\DOCS\OUTPUT_301\2019\09.ñåí òÿáðü\BM-1709-K.C_002001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	233	***Original Points Count***	16384	***Points Count***	131072
Pulse Sequence	zgpg30	***Solvent***	CHLOROFORM-D			***Sweep Width (Hz)***	24154.59
Temperature (degree C)	27.000						



^{13}C NMR spectrum of **11** (100.6 MHz, $CDCl_3$)

Acquisition Time (sec)	1.3664	***Comment***	Imported from UXNMR.			***Date***	30 Sep 2019 15:55:04
File Name	C:\DOCS\OUTPUT_301\2019\09.ñåí òÿáðü\BM-1709-R.APT_004001r					***Frequency (MHz)***	100.61
Nucleus	13C	***Number of Transients***	34	***Original Points Count***	32768	***Points Count***	131072
Pulse Sequence	jmod	***Solvent***	ACETONITRILE-D3			***Sweep Width (Hz)***	23980.81
Temperature (degree C)	27.000						



^{13}C APT NMR spectrum of **11** (100.6 MHz, $CDCl_3$)