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Stereoselective epoxidation of 4-fluoro-4-nitrocyclohexenes

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Experimental part

All reagents were purchased from commercial sources and used without any further purification. Dichloromethane (DCM) was dried over CaH_2 before use by the standard procedures [D. B. G. Williams, M. Lawton, *J. Org. Chem.* 2010, **75**, 8351]. Melting points (Mp) were measured with a Büchi B-545 melting point apparatus. NMR (^{1}H, ^{13}C and ^{19}F) spectra were registered with Bruker Avance 400 spectrometer. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectroscopic data were referenced to the residual solvent resonance. Chemical shifts for ^{19}F NMR spectroscopic data were referenced to $PhCF_3$ (δ = -63.72 ppm) or C_6F_6 (δ = -164.9 ppm) added to the analyzed samples as a reference standard. Data are reported as follows: chemical shift, integration multiplicity (s = *singlet*, d = *doublet*, t = t*riplet*, q = *quadruplet*, qui = *quintet*, sext = *sextet*, sept = *septe*t, br = *broad*, m = multiplet, dd = *doublet of doublets*, ddd = *doublet of doublet of doublets*, dddd = *doublet of doublet of doublet of doublets*, dt = *doublet of triplet*s, td = *triplet of doublets*) and coupling constants (Hz). The starting (1*S**,2*S**)-2-fluoro-4,5-dimethyl-2-nitro-1,2,3,6-tetrahydro-1,1'-biphenyls **1a-k** were prepared according to the described procedure and all are known compounds [R.V. Larkovich, S. A. Ponomarev, A.S. Aldoshin, A. A. Tabolin, S. L. Ioffe and V. G. Nenajdenko, *Eur. J. Org. Chem.*, 2020, **2020**, 2479]

General procedure for epoxidation of cyclohexenes 1.

In a typical experiment a solution of a selected cyclohexene **1** (0.1 mmol, 1 mol. equiv.), *m*CPBA (0.15 mmol, 1.5 mol. equiv.) in DCM (1 ml) was stirred overnight at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction the reaction mixture was concentrated under vacuum. The pure product was isolated by column chromatography on silica with gradient elution.

(1*S,3*S**,4*S**,6*R**)-4-(4-Bromophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]-heptane** (**2a**). Eluent: Hex/DCM (6:1), Hex/DCM (4:1), Hex/DCM (3:1), Hex/DCM (2:1). 53.51 mg (89 %); colorless solid; Mp = 140-142 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{15}{}^{79}BrFNNaO_3{}^+$ $[M+Na]^+$ = 366.0112; found 366.0114. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, $^3J_{HH}$= 8.2 Hz, 2H), 7.08 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 3.67 (ddd, $^3J_{HF}$ = 31.7, $^3J_{HH}$ = 11.5, 6.1 Hz, 1H), 3.01 (dd, $^3J_{HF}$ = 37.2, $^2J_{HH}$ = 15.9 Hz, 1H), 2.46 – 2.22 (m, 3H), 1.43 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.7, 132.0, 130.6 (d, $^4J_{CF}$ = 1.8 Hz), 122.7, 119.1 (d, $^1J_{CF}$ = 242.5 Hz), 62.3, 59.5, 42.5 (d, $^2J_{CF}$ = 19.3 Hz), 40.8 (d, $^2J_{CF}$ = 24.5 Hz), 35.1 (d, $^3J_{CF}$ = 3.9 Hz), 20.9, 18.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -134.09 (ddd, $^3J_{HF}$ = 37.2, 31.7, 19.9 Hz) ppm.

(1*S,3*S**,4*S**,6R*)-4-(2,4-Dichlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]-heptane** (**2b**). Eluent: Hex/DCM (8:1), Hex/DCM (6:1), Hex/DCM (4:1), Hex/DCM (3:1), Hex/DCM (2:1), Hex/DCM (1:1). 38.47 mg (74 %); colorless oil. HRMS (ESI) m/z: calcd. for $C_{14}H_{15}{}^{35}Cl_2FNO_3{}^+$ $[M+H]^+$ = 334.0408; found 334.0398. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.36 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 7.19 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.2 Hz, 1H), 4.42 (ddd, $^3J_{HF}$ = 31.9, $^3J_{HH}$ =12.4, 5.0 Hz, 1H), 3.02 (dd, $^3J_{HF}$ = 38.4, $^2J_{HH}$ = 15.8 Hz, 1H), 2.40 (dd, $^3J_{HF}$ = 19.7, $^2J_{HH}$ = 15.8 Hz, 1H), 2.33 (dd, $^2J_{HH}$ = 15.3, $^3J_{HH}$ = 4.5 Hz, 1H), 2.14 (dd, $^2J_{HH}$ = 14.4, $^3J_{HH}$ = 12.9 Hz, 1H), 1.44 (s, 3H), 1.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.2, 134.7, 132.0 (d, $^3J_{CF}$ = 2.1 Hz), 130.0 (d, $^4J_{CF}$ = 6.6 Hz), 129.6, 127.7, 118.8 (d, $^1J_{CF}$ = 242.6 Hz), 62.2, 59.5, 41.3 (d, $^2J_{CF}$ = 24.8 Hz), 38.0 (d, $^2J_{CF}$ = 19.9 Hz), 35.5 (d, $^3J_{CF}$ = 4.0 Hz), 21.1, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -132.91 (ddd, $^3J_{HF}$ = 38.4, 31.9, 19.7 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-1,6-dimethyl-3-nitro-4-(*p*-tolyl)-7-oxabicyclo[4.1.0]heptane** (**2c**). Eluent: Hex/DCM (6:1), Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1). 49.74 mg (94 %); colorless oil. HRMS (ESI) m/z: calcd. for $[M+Na]^+$ $C_{15}H_{18}FNNaO_3{}^+$ = 302.1163; found 302.1162. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.12 – 7.05 (m, 4H), 3.66 (ddd, $^3J_{HF}$ = 32.2, $^3J_{HH}$ = 12.3, 5.4 Hz, 1H), 3.03 (dd, $^3J_{HF}$ = 37.2, $^2J_{HH}$ = 15.9 Hz, 1H), 2.29 (s, 3H), 2.43 – 2.27 (m, 3H), 1.43 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.2, 131.6, 129.5, 128.8 (d, $^4J_{CF}$ = 1.8 Hz), 119.6 (d, $^1J_{CF}$ = 242.4 Hz), 62.5, 59.5, 42.6 (d, $^2J_{CF}$ = 19.3 Hz), 40.9 (d, $^2J_{CF}$ = 24.8 Hz), 35.2 (d, $^3J_{CF}$ = 3.8 Hz), 21.2, 21.0, 18.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -134.05 (ddd, $^3J_{HF}$ = 37.2, 32.2, 19.7 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]-heptane** (**2d-**major isomer). Eluent: Hex/DCM (4:1), Hex/DCM (3:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2). 87.52 mg (72 %); colorless solid; Mp = 131-132 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{18}FNNaO_4^+$ $[M+Na]^+$ = 318.1112; found 318.1113. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.12 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 6.79 (d, $^3J_{HH}$ = 8.7 Hz, 2H), 3.74 (s, 3H), 3.64 (ddd, $^3J_{HF}$ = 32.2, $^3J_{HH}$ = 12.2, 5.4 Hz, 1H), 3.02 (dd, $^3J_{HF}$ = 37.1, $^2J_{HH}$ = 15.9 Hz, 1H), 2.44 – 2.24 (m, 3H), 1.42 (s, 3H), 1.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.6, 130.0, 126.5, 119.6 (d, $^1J_{CF}$ = 241.9 Hz), 114.1, 62.5, 59.5, 55.2, 42.2 (d, $^2J_{CF}$ = 20.0 Hz), 40.8 (d, $^2J_{CF}$ = 24.7 Hz), 35.2 (d, $^3J_{CF}$ = 3.7 Hz), 20.9, 18.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -134.29 (ddd, *J* = 37.1, 32.2, 19.8 Hz) ppm.

(1*R,3*S**,4*S**,6*S**)-3-Fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]-heptane** (**2d-**minor isomer). Eluent: Hex/DCM (4:1), Hex/DCM (3:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2). 10.58 mg (9 %); colorless solid; Mp = 141-143 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{18}FNNaO_4^+$ $[M+Na]^+$ = 318.1112; found 318.1113. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.11 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 1.1 Hz, 2H), 6.83 – 6.78 (m, 2H), 3.76 (s, 3H), 3.56 (ddd, $^3J_{HF}$ = 31.3, $^3J_{HH}$ = 13.1, 6.7 Hz, 1H), 2.87 (dd, $^3J_{HF}$ = 31.3, $^2J_{HH}$ = 15.6 Hz, 1H), 2.65 (dd, $^3J_{HH}$ = 15.6 Hz, $^3J_{HF}$ = 15.4 Hz, 1H), 2.52 (dd, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 13.1 Hz, 1H), 2.20 (dd, $^2J_{HH}$ = 15.5, $^3J_{HH}$ = 6.7 Hz, 1H), 1.44 (s, 3H), 1.44 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 130.0, 126.9, 121.1 (d, $^1J_{CF}$ = 251.3 Hz), 114.3, 61.5, 61.2, 55.3, 45.0 (d, $^2J_{CF}$ = 19.9 Hz), 40.1 (d, $^2J_{CF}$ = 19.9 Hz), 36.4, 21.0, 19.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -133.47 (td, $^3J_{HF}$ = 31.3, 15.4 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-1,6-dimethyl-3-nitro-4-(4-trifluoromethylphenyl)-7-oxabicyclo-[4.1.0]heptane** (**2e**). Eluent: Hex/DCM (6:1), Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1). 48.34 mg (94 %); colorless solid; Mp = 118-120 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{16}F_4NO_3^+$ $[M+H]^+$ = 334.1061; found 334.1063. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.35 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 3.79 (ddd, $^3J_{HF}$ = 31.5, $^3J_{HH}$ =12.0, 5.6 Hz, 1H), 3.03 (dd, $^3J_{HF}$ = 37.2, $^2J_{HH}$ = 15.9 Hz, 1H), 2.47 – 2.28 (m, 3H), 1.44 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 130.8 (q, $^2J_{CF}$ = 32.6 Hz), 129.4 (d, $^4J_{CF}$ = 2.1 Hz), 125.8 (q, $^3J_{CF}$ = 3.7 Hz), 124.0 (q, $^1J_{CF}$ = 272.1 Hz), 119.0 (d, $^1J_{CF}$ = 243.0 Hz), 62.3, 59.5, 42.9 (d, $^2J_{CF}$ = 19.3 Hz), 40.8 (d, $^2J_{CF}$ = 24.6 Hz), 35.2 (d, $^3J_{CF}$ = 3.6 Hz), 20.9, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -65.95 (s, 3F), -135.88 (ddd, $^3J_{HF}$ = 37.2, 31.5, 20.0 Hz, 1F) ppm.

Methyl 4-[(1*R,3*S**,4*S**,6*S**)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]hept-3-yl]benzoate** (**2f**). Eluent: Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2), Hex/DCM (1:3). 43.54 mg (87 %); colorless solid; Mp = 96-98 °C. HRMS (ESI) m/z: calcd. for $C_{16}H_{19}FNO_5^+$ $[M+H]^+$ = 324.1242; found 324.1244. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 – 7.89 (m, 2H), 7.29 (d, $^3J_{HH}$ = 7.5 Hz, 2H), 3.88 (s, 3H), 3.76 (ddd, $^3J_{HF}$ = 31.6, $^3J_{HH}$ =12.2, 5.4 Hz, 1H), 3.02 (dd, $^3J_{HF}$ = 37.2, $^2J_{HH}$ = 15.9 Hz, 1H), 2.49 – 2.26 (m, 3H), 1.43 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.7, 139.8, 130.3, 130.0, 129.0 (d, $^4J_{CF}$ = 1.6 Hz), 119.1 (d, $^1J_{CF}$ = 242.8 Hz), 62.3, 59.5, 52.3, 43.0 (d, $^2J_{CF}$ = 19.0 Hz), 40.8 (d, $^2J_{CF}$ = 24.6 Hz), 35.0 (d, $^3J_{CF}$ = 3.6 Hz), 20.9, 18.8 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -133.70 (ddd, $^3J_{HF}$ = 37.2, 31.6, 19.9 Hz) ppm.

4-[(1*R,3*S**,4*S**,6*S**)-4-Fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]hept-3-yl]-benzonitrile** (**2g**). Eluent: Hex/DCM (3:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2), Hex/DCM (1:3). 21.01 (89 %); colorless solid; Mp = 117-120 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{16}FN_2O_3^+$ $[M+H]^+$ = 291.1139; 291.1140. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.34 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 3.78 (ddd, $^3J_{HF}$ = 31.1, $^3J_{HH}$ =11.6, 6.0 Hz, 1H), 3.02 (dd, $^3J_{HF}$ = 37.3, $^2J_{HH}$ =16.0 Hz, 1H), 2.49 – 2.27 (m, 3H), 1.44 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.1, 132.6, 129.8 (d, $^4J_{CF}$ = 1.9 Hz), 118.8 (d, $^1J_{CF}$ = 243.1 Hz), 118.4, 112.7, 62.2, 59.5, 43.1 (d, $^2J_{CF}$ = 19.2 Hz), 40.8 (d, $^2J_{CF}$ = 24.6 Hz), 35.0 (d, $^3J_{CF}$ = 3.4 Hz), 20.9, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -133.65 (ddd, $^3J_{HF}$ = 37.4, 31.3, 20.2 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]-heptane** (major isomer) and **(1*R**,3*S**,4*S**,6*S**)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane** (minor isomer) (**2h**). Eluent: Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2). 51.16 mg (96 %); dr = 81:19; yellowish solid; Mp = 151-153 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{16}FN_2O_5^+$ $[M+H]^+$ = 311.1038; found 311.1042. **Major**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (dd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 1.3 Hz, 1H), 7.68 – 7.61 (m, 1H), 7.53 (td, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.1 Hz, 1H), 7.44 – 7.37 (m, 1H), 4.45 (ddd, $^3J_{HF}$ = 31.4, $^3J_{HH}$ = 12.3, 4.9 Hz, 1H), 2.89 (dd, $^3J_{HF}$ = 38.6, $^2J_{HH}$ = 15.7 Hz, 1H), 2.79 – 2.22 (m, 3H), 1.44 (s, 3H), 1.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.6, 132.9, 129.5 (d, $^3J_{CF}$ = 2.3 Hz), 129.4 (d, $^4J_{CF}$ = 7.4 Hz), 129.2, 124.9, 118.9 (d, $^1J_{CF}$ = 244.0 Hz), 62.1, 59.2, 41.5 (d, $^2J_{CF}$ = 24.8 Hz), 36.8 (d, $^2J_{CF}$ = 17.9 Hz), 35.7 (d, $^3J_{CF}$ = 3.8 Hz), 21.0, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -132.27 (ddd, *J* = 38.6, 31.4, 19.5 Hz) ppm. **Minor**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.72 (m, 1H), 7.68 – 7.61 (m, 1H), 7.58 – 7.52 (m, 1H), 7.44 – 7.37 (m, 1H), 4.47 –4.33 (m, 1H), 2.79 – 2.23 (m, 4H), 1.47 (s, 3H), 1.43 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 133.2, 129.9 (d, $^3J_{CF}$ = 2.3 Hz), 129.7 (d, $^4J_{CF}$ = 7.7 Hz), 129.2, 124.8, 120.2 (d,

$^{1}J_{CF}$ = 253.5 Hz), 61.7, 61.0, 40.7 (d, $^{2}J_{CF}$ = 20.0 Hz), 39.35 (d, $^{2}J_{CF}$ = 18.9 Hz), 36.5, 20.8, 19.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -130.78 – -131.07 (m) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-1,6-dimethyl-3-nitro-4-(3-nitrophenyl)-7-oxabicyclo[4.1.0]-heptane** (**2i**). Eluent: Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2). 40.43 mg (78 %); colorless solid; Mp = 168-170 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{14}FN_2O_5^-$ $[M-H]^-$ = 309.0892; found 309.0897. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 – 8.10 (m, 2H), 7.53 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.49 – 7.44 (m, 1H), 3.85 (ddd, $^{3}J_{HF}$ = 31.0, $^{3}J_{HH}$ =12.2, 5.4 Hz, 1H), 3.03 (dd, $^{3}J_{HF}$ = 37.2, $^{2}J_{HH}$ = 16.0 Hz, 1H), 2.49 – 2.32 (m, 3H), 1.45 (s, 3H), 1.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 136.8, 135.3 (d, $^{4}J_{CF}$ = 1.5 Hz), 129.9, 123.9 (d, $^{4}J_{CF}$ = 2.4 Hz), 123.7, 118.8 (d, $^{1}J_{CF}$ = 242.9 Hz), 62.2, 59.5, 42.8 (d, $^{2}J_{CF}$ = 19.5 Hz), 40.7 (d, $^{2}J_{CF}$ = 24.5 Hz), 35.0 (d, $^{3}J_{CF}$ = 3.5 Hz), 20.9, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -133.82 (ddd, $^{3}J_{HF}$ = 37.2, 31.0, 20.2 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-3-Fluoro-1,6-dimethyl-3-nitro-4-(4-nitrophenyl)-7-oxabicyclo[4.1.0]-heptane** (**2j**). Eluent: Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1), Hex/DCM (1:2). 44.57 mg (87 %); colorless solid; Mp = 129-131 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{14}FN_2O_5^-$ $[M-H]^-$ = 309.0892; found 309.0893. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H), 7.40 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H), 3.84 (ddd, $^{3}J_{HF}$ = 31.1, $^{3}J_{HH}$ =11.9, 5.7 Hz, 1H), 3.02 (dd, $^{3}J_{HF}$ = 37.3, $^{2}J_{HH}$ = 16.0 Hz, 1H), 2.51 – 2.26 (m, 3H), 1.45 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 142.1, 130.0 (d, $^{4}J_{CF}$ = 2.2 Hz), 124.0, 118.8 (d, $^{1}J_{CF}$ = 243.2 Hz), 62.1, 59.5, 42.9 (d, $^{2}J_{CF}$ = 19.3 Hz), 40.7 (d, $^{2}J_{CF}$ = 24.6 Hz), 35.0 (d, $^{3}J_{CF}$ = 3.7 Hz), 20.9, 18.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -133.61 (ddd, $^{3}J_{HF}$ = 37.3, 31.1, 20.2 Hz) ppm.

(1*S,3*S**,4*S**,6*R**)-4-(4-Chlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]-heptane** (**2k**). Eluent: Hex/DCM (6:1), Hex/DCM (4:1), Hex/DCM (2:1), Hex/DCM (1:1). 48.09 mg (91 %); colorless solid; Mp = 92 – 94 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{16}{}^{35}ClFNO_3^+$ $[M+H]^+$ = 300.0797; found 300.0796. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27 – 7.22 (m, 2H), 7.17 – 7.10 (m, 2H), 3.68 (ddd, $^{3}J_{HF}$ = 31.7, $^{3}J_{HH}$ = 11.7, 5.9 Hz, 1H), 3.01 (dd, $^{3}J_{HF}$ = 37.2, $^{2}J_{HH}$ = 15.9 Hz, 1H), 2.44 – 2.25 (m, 3H), 1.43 (s, 6H), ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.5, 133.2, 130.3 (d, $^{4}J_{CF}$ = 2.0 Hz), 129.1, 119.2 (d, $^{1}J_{CF}$ = 242.5 Hz), 62.3, 59.5, 42.5 (d, $^{2}J_{CF}$ = 19.4 Hz), 40.8 (d, $^{2}J_{CF}$ = 24.7 Hz), 35.1 (d, $^{3}J_{CF}$ = 3.7 Hz), 20.9, 18.8, ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ = -134.11 (ddd, $^{3}J_{HF}$ = 37.2, 31.7, 19.9 Hz) ppm.

General procedure for ring-opening hydrolysis of cyclohexane epoxides 2.

In a typical experiment a selected cyclohexane epoxide **2** (0.1 mmol, 1 mol. equiv.) was dissolved in 0.4 M solution of H_2SO_4 in dioxane/water 2:1 (2.12 mL) and stirred overnight at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction the reaction mixture was concentrated under vacuum. The pure product was isolated by column chromatography on silica with gradient elution.

(1*R,2*R**,4*S**,5*S**)-5-(4-Bromophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol** (**3a**). Eluent: DCM, DCM/EtOAc (10:1), DCM/EtOAc (5:1). 46.88 mg (69 %); colorless solid; Mp = 140-142 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{16}{}^{79}BrO_2^+$ [M-HNO_2-HF+H]$^+$ = 295.0328; found 295.0301.^{1}H NMR (400 MHz, DMSO-d6) δ = 7.50 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.11 (d, $^3J_{HH}$ = 7.9 Hz, 2H), 5.00 (s, 1H), 4.83 (s, 1H), 4.01 (ddd, $^3J_{HF}$ = 31.9, $^3J_{HH}$ = 13.4, 3.9 Hz, 1H), 2.72 (dd, $^3J_{HF}$ = 38.2, $^2J_{HH}$ = 14.2 Hz, 1H), 2.51 (pseudo-t, $^2J_{HH}$ = $^3J_{HH}$ = 14.4 Hz, 1H), 2.04 (dd, $^2J_{HH}$ = 13.9, $^3J_{HF}$ = 12.4 Hz, 1H), 1.54 (dd, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 4.0 Hz, 1H), 1.19 (s, 3H), 1.17 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ = 135.4, 131.5, 131.2, 122.3 (d, $^1J_{CF}$ = 251.1 Hz), 121.3, 72.5, 71.4, 43.3 (d, $^2J_{CF}$ = 19.2 Hz), 42.3 (d, $^2J_{CF}$ = 19.0 Hz), 38.0, 23.4, 22.9 ppm. ^{19}F NMR (376 MHz, DMSO-d6) δ = -134.36 (ddd, *J* = 38.2, 31.9, 12.4 Hz) ppm.

(1*R,2*R**,4*S**,5*S**)-5-(2,4-Dichlorophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol** (**3b**). Eluent: DCM, DCM/EtOAc (10:1), DCM/EtOAc (5:1). 33.94 mg (89 %); colorless solid; Mp = 168-169 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{15}{}^{35}Cl_2O_2^+$ [M-HNO_2-HF+H]$^+$ = 285.0444; found 285.0404. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.0 Hz, 1H), 7.36 (d, $^4J_{HH}$ = 2.2 Hz, 1H), 7.22 (dd, $^3J_{HH}$ = 8.5, $^4J_{HH}$ = 2.2 Hz, 1H), 4.85 (ddd, $^3J_{HF}$ = 32.8, $^3J_{HH}$ = 13.3, 4.1 Hz, 1H), 3.09 (dd, $^3J_{HF}$ = 38.5, $^2J_{HH}$ = 14.7 Hz, 1H), 2.45 (pseudo-t, $^2J_{HH}$ = $^3J_{HH}$ = 13.7 Hz, 1H), 2.13 (dd, $^2J_{HH}$ = 14.7, $^3J_{HF}$ = 12.1 Hz, 1H), 1.90 (d, *J* = 3.9 Hz, 1H), 1.71 (dd, $^2J_{HH}$ = 14.1, $^3J_{HH}$ = 4.1 Hz, 1H), 1.59 (s, 1H), 1.38 (s, 3H), 1.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 135.2, 134.6, 132.2, 130.9 (d, $^4J_{HF}$ = 8.0 Hz), 129.8, 127.7, 120.9 (d, $^1J_{CF}$ = 246.3 Hz), 74.1, 73.2, 43.1 (d, $^2J_{CF}$ = 19.0 Hz), 39.7, 39.3 (d, $^2J_{CF}$ = 18.2 Hz), 23.8, 23.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -134.50 (ddd, *J* = 38.5, 32.8, 12.1 Hz) ppm.

(1*R,2*R**,4*S**,5*S**)-4-Fluoro-1,2-dimethyl-4-nitro-5-(*p*-tolyl)cyclohexane-1,2-diol** (**3c**). Eluent: Hex/EtOAc (2:1), Hex/EtOAc (1:1). 30.62 mg (62 %); colorless solid; Mp = 156-157 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{19}O_2^+$ [M-HNO_2-HF+H]$^+$ = 231.1380; found 231.1379. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.10 (s, 4H), 4.08 (ddd, $^3J_{HF}$ = 32.5, $^3J_{HH}$ = 13.6, 4.2 Hz, 1H), 3.05 (dd, $^3J_{HF}$ = 38.1, $^2J_{HH}$ = 14.6 Hz, 1H), 2.61 (dd, $^2J_{HH}$ = 13.9 Hz, $^3J_{HH}$ = 13.9, 1H), 2.30 (s, 3H), 2.18

(s, 1H), 2.08 (br s, 1H), 2.10 (dd, $^2J_{HH}$ = 14.6, $^3J_{HF}$ = 11.6 Hz, 1H), 1.75 (dd, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 4.2 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H) ppm. ^{13}C = NMR (100 MHz, $CDCl_3$) δ = 138.1, 131.9, 129.5, 129.0, 121.9 (d, $^1J_{CF}$ = 244.2 Hz), 74.1, 73.3, 43.8 (d, $^2J_{CF}$ = 19.1 Hz), 42.8 (d, $^2J_{CF}$ = 18.8 Hz), 38.6, 23.7, 23.6, 21.2 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -134.66 (ddd, $^3J_{HF}$ = 38.1, 32.5, 11.6 Hz) ppm.

(1*R,2*R**,4*S**,5*S**)-4-Fluoro-5-(4-methoxyphenyl)-1,2-dimethyl-4-nitrocyclohexane-1,2-diol** (**3d**). Eluent: DCM, DCM/EtOAc (10:1), DCM/EtOAc (5:1). 32.06 mg (78 %); colorless solid; Mp = 168-169 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{21}FNO_5^+$ $[M+H]^+$ = 314.1398; found 314.1393. ^{1}H NMR (400 MHz, DMSO-d6) δ = 7.06 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 6.85 (d, $^3J_{HH}$ = 8.8 Hz, 2H), 4.95 (s, 1H), 4.78 (s, 1H), 3.96 (ddd, $^3J_{HF}$ = 32.2, $^3J_{HH}$ = 13.5, 4.0 Hz, 1H), 3.71 (s, 3H), 2.70 (dd, $^3J_{HF}$ = 38.0, $^2J_{HH}$ = 14.1 Hz, 1H), 2.50 (pseudo-t, $^2J_{HH}$ = $^3J_{HH}$ = 13.5 Hz, 1H), 2.01 (dd, $^2J_{HH}$ = 14.0, $^3J_{HF}$ = 12.2 Hz, 1H), 1.50 (dd, $^2J_{HH}$ = 13.4, $^3J_{HH}$ = 4.0 Hz, 1H), 1.18 (s, 3H), 1.16 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ = 158.8, 130.0, 127.8, 122.7 (d, $^1J_{CF}$ = 250.2 Hz), 113.9, 72.6, 71.5, 55.0, 43.0 (d, $^2J_{CF}$ = 19.4 Hz), 42.5 (d, $^2J_{CF}$ = 18.8 Hz), 38.4, 23.5, 22.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -134.69 (ddd, *J* = 38.0, 32.2, 12.2 Hz) ppm.

(1*R,2*R**,4*S**,5*S**)-4-Fluoro-1,2-dimethyl-4-nitro-5-(4-trifluoromethylphenyl)cyclohexane-1,2-diol** (**3e**). Eluent: DCM, DCM/EtOAc (20:1), DCM/EtOAc (10:1). 28.29 mg (70 %); colorless solid; Mp = 168-169 °C. HRMS (ESI) m/z: calcd. for $C_{15}H_{16}F_3O_2^+$ $[M-HNO_2-HF+H]^+$ = 285.1097; found 285.1097. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.36 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 4.22 (ddd, $^3J_{HF}$ = 31.8, $^3J_{HH}$ = 13.5, 4.1 Hz, 1H), 3.04 (dd, $^3J_{HF}$ = 38.1, $^2J_{HH}$ = 14.7 Hz, 1H), 2.65 (pseudo-t, $^2J_{HH}$ = $^3J_{HH}$ = 13.8 Hz, 1H), 2.13 (dd, $^2J_{HH}$ = 14.7, $^3J_{HF}$ = 11.9 Hz, 1H), 1.89 (d, *J* = 4.5 Hz, 1H), 1.76 (dd, $^2J_{HH}$ = 14.1, $^3J_{HH}$ = 4.2 Hz, 1H), 1.54 (s, 1H), 1.41 (s, 3H), 1.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.1, 130.6 (q, $^2J_{CF}$ = 32.8 Hz), 129.7, 125.7 (q, $^3J_{CF}$ = 3.6 Hz), 124.1 (q, $^1J_{CF}$ = 272.3 Hz), 121.3 (d, $^1J_{CF}$ = 246.0 Hz), 74.0, 73.2, 44.0 (d, $^2J_{CF}$ = 20.2 Hz), 42.8 (d, $^2J_{CF}$ = 18.9 Hz), 38.4, 23.8, 23.7 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -65.94 (s, 3F), -136.67 – -136.96 (m, 1F) ppm.

Methyl 4-[(1*S,2*S**,4*R**,5*R**)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl]-benzoate** (**3f**). Eluent: DCM, DCM/EtOAc (10:1), DCM/EtOAc (5:1), DCM/EtOAc (2:1). 28.86 mg (80 %); colorless solid; Mp = 239-240 °C. HRMS (ESI) m/z: calcd. for $C_{16}H_{21}FNO_6^+$ $[M+H]^+$ = 342.1347; found 342.1351. ^{1}H NMR (400 MHz, DMSO-d6) δ = 7.89 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.31 (d, $^3J_{HH}$ = 7.8 Hz, 2H), 5.03 (br s, 1H), 4.86 (br s, 1H), 4.10 (ddd, $^3J_{HF}$ = 31.6, $^3J_{HH}$ = 13.3, 3.8 Hz, 1H), 3.83 (s, 3H), 2.73 (dd, $^3J_{HF}$ = 38.3, $^2J_{HH}$ = 14.1 Hz, 1H),

2.57 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.4 Hz, 1H), 2.06 (dd, $^{2}J_{HH}$ = 14.3, $^{3}J_{HF}$ =12.4 Hz, 1H), 1.56 (dd, $^{2}J_{HH}$ = 13.4, $^{3}J_{HH}$ = 4.0 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H) ppm. ^{13}C NMR (100 MHz, DMSO-d6) δ = 166.0, 141.4, 129.5, 129.4, 129.3, 122.3 (d, $^{1}J_{CF}$ = 251.5 Hz), 72.6, 71.4, 52.3, 43.8 (d, $^{2}J_{CF}$ = 17.6 Hz), 42.3 (d, $^{2}J_{CF}$ = 17.6 Hz), 37.92, 23.5, 22.9 ppm. ^{19}F NMR (376 MHz, DMSO-d6) δ = -134.21 (ddd, $^{3}J_{HF}$ = 38.3, 31.6, 12.4 Hz) ppm.

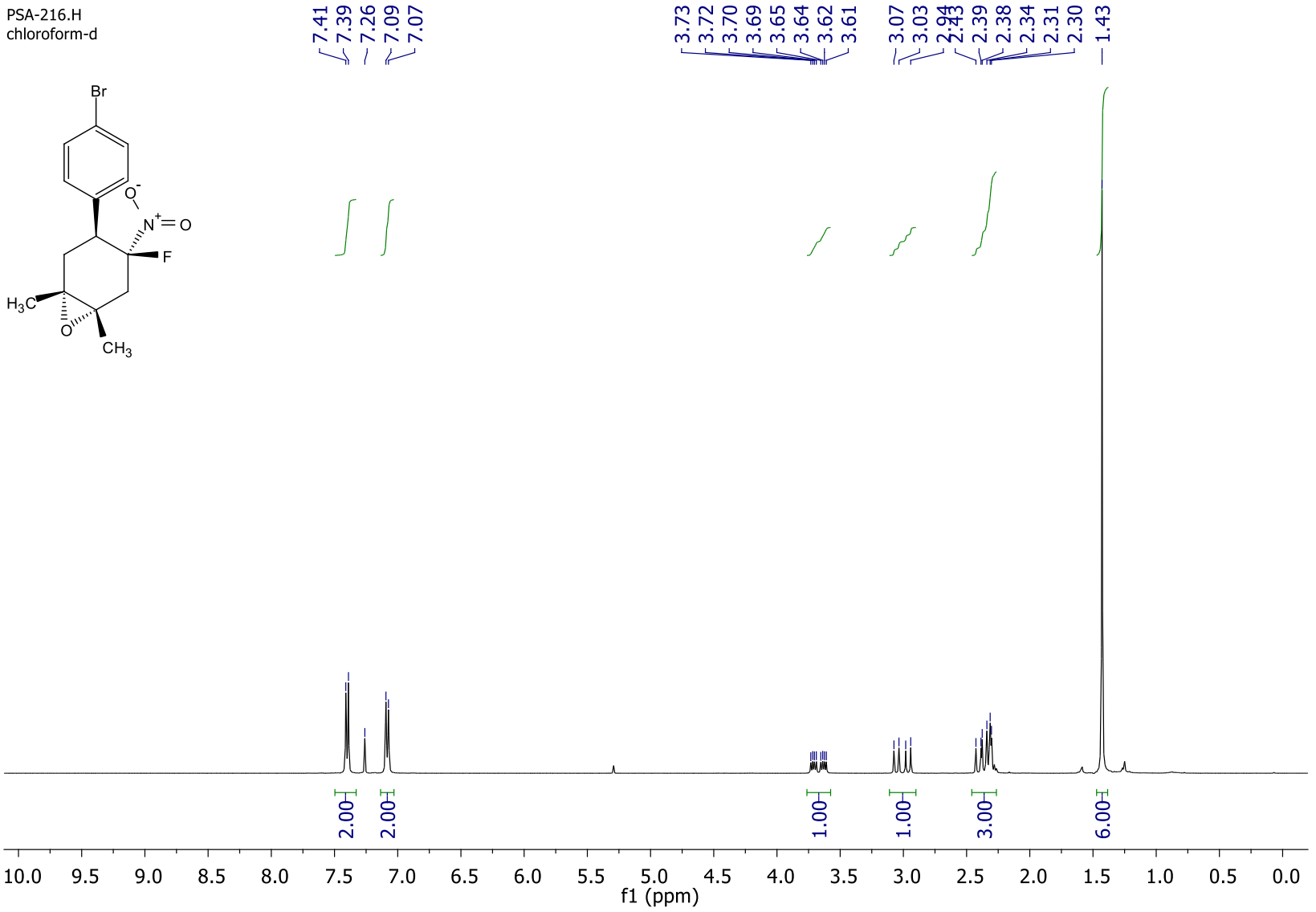
4-[(1*S,2*S**,4*R**,5*R**)-2-Fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl]benzonitrile** (**3g**). Eluent: Hex/EtOAc (2:1), Hex/EtOAc (1:1). 14.16 mg (76 %); yellowish solid; Mp = 187-188 °C (decomp.). HRMS (ESI) m/z: calcd. for $C_{15}H_{18}FN_2O_4^+$ $[M+H]^+$ = 309.1245; found 309.1247. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 7.36 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H), 4.22 (ddd, $^{3}J_{HF}$ = 31.5, $^{3}J_{HH}$ = 13.6, 3.8 Hz, 1H), 3.03 (dd, $^{3}J_{HF}$ = 38.1, $^{2}J_{HH}$ = 14.7 Hz, 1H), 2.64 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.7 Hz, 1H), 2.14 (dd, $^{2}J_{HH}$ = 14.4, $^{3}J_{HF}$ = 12.3 Hz, 1H), 1.91 (br s, 1H), 1.76 (dd, $^{2}J_{HH}$ = 14.0, $^{3}J_{HH}$ = 3.9 Hz, 1H), 1.64 (br s, 1H), 1.41 (s, 3H), 1.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.6, 132.5, 130.1, 121.1 (d, $^{1}J_{CF}$ = 246.9 Hz), 118.5, 112.4, 74.0, 73.1, 44.2 (d, $^{2}J_{CF}$ = 19.4 Hz), 42.8 (d, $^{2}J_{CF}$ = 19.3 Hz), 38.2, 23.8, 23.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -134.50 (ddd, $^{3}J_{HF}$ = 38.1, 31.5, 12.2 Hz) ppm.

(1*R,2*R**,4*S**,5*S**)-4-Fluoro-1,2-dimethyl-4-nitro-5-(2-nitrophenyl)cyclohexane-1,2-diol** (**3h**). Eluent: Hex/EtOAc (3:1), Hex/EtOAc (2:1), Hex/EtOAc (1:1). 38.08 mg (81 %); colorless solid; Mp = 122-124 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{18}FN_2O_6^+$ $[M+H]^+$ 329.1143; found 329.1145. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 – 7.69 (m, 2H), 7.55 (td, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.3 Hz, 1H), 7.41 (td, $^{3}J_{HH}$ = 8.0, $^{4}J_{HH}$ = 1.3 Hz, 1H), 4.94 (ddd, $^{3}J_{HF}$ = 32.4, $^{3}J_{HH}$ = 13.3, 4.0 Hz, 1H), 2.91 (dd, $^{3}J_{HF}$ = 38.6, $^{2}J_{HH}$ = 14.6 Hz, 1H), 2.60 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.6 Hz, 1H), 2.15 (dd, $^{2}J_{HH}$ = 14.6, $^{3}J_{HF}$ = 12.2 Hz, 1H), 1.94 (dd, $^{2}J_{HH}$ = 14.0, $^{3}J_{HH}$ = 4.0 Hz, 1H), 1.86 (br s, 2H), 1.39 (s, 3H), 1.36 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.7, 132.8, 130.6 (d, $^{4}J_{CF}$ = 8.4 Hz), 129.7 (d, $^{3}J_{CF}$ = 1.1 Hz), 129.0, 124.7, 121.1 (d, $^{1}J_{CF}$ = 247.8 Hz), 74.3, 73.1, 43.3 (d, $^{2}J_{CF}$ = 19.1 Hz), 39.7, 37.6 (d, $^{2}J_{CF}$ = 17.9 Hz), 23.9, 23.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = -132.66 (dddd, $^{3}J_{HF}$ = 38.6, 32.4, 12.2, $^{4}J_{HF}$ = 2.1 Hz) ppm.

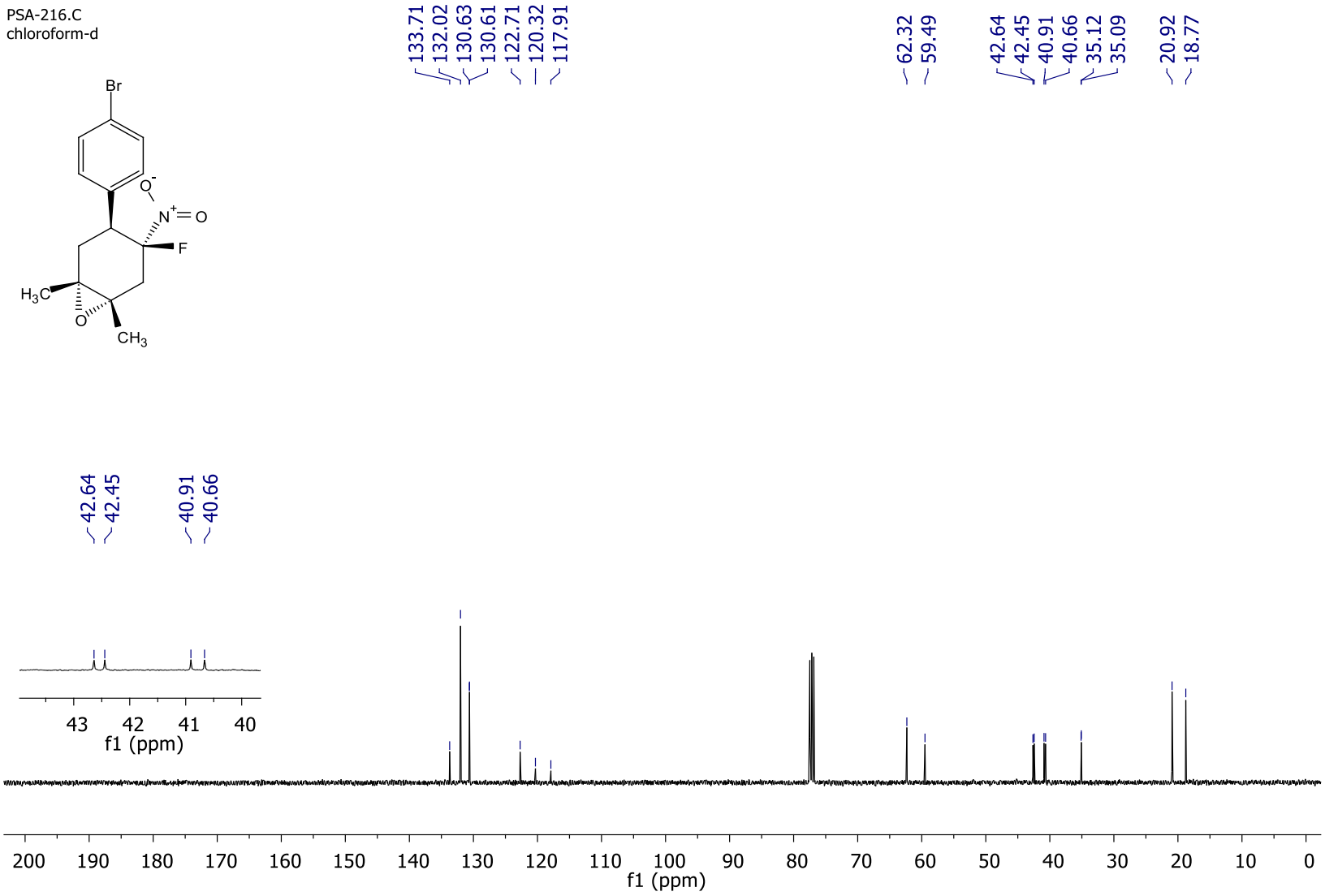
(1*R,2*R**,4*S**,5*S**)-4-Fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol** (**3i**). Eluent: Hex/EtOAc (3:1), Hex/EtOAc (1:1). 27.63 mg (74 %); yellowish solid; Mp = 164-165 °C. HRMS (ESI) m/z: calcd. for $C_{14}H_{17}FN_2NaO_6^+$ $[M+Na]^+$ 351.0963 found 351.0969. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 – 8.12 (m, 2H), 7.56 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H), 7.51 – 7.44 (m, 1H), 4.29 (ddd, $^{3}J_{HF}$ = 31.3, $^{3}J_{HH}$ = 13.5, 4.1 Hz, 1H), 3.05 (dd, $^{3}J_{HF}$ = 38.1, $^{2}J_{HH}$ = 14.7 Hz, 1H), 2.69 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.8, 1H), 2.16 (dd, $^{2}J_{HH}$ = 14.7, $^{3}J_{HF}$ = 12.0 Hz,

1H), 1.89 (br s, 1H), 1.79 (dd, $^{2}J_{HH}$ = 14.0, $^{3}J_{HH}$ = 4.1 Hz, 1H), 1.58 (br s, 1H), 1.43 (s, 3H), 1.38 (s, 3H) ppm.

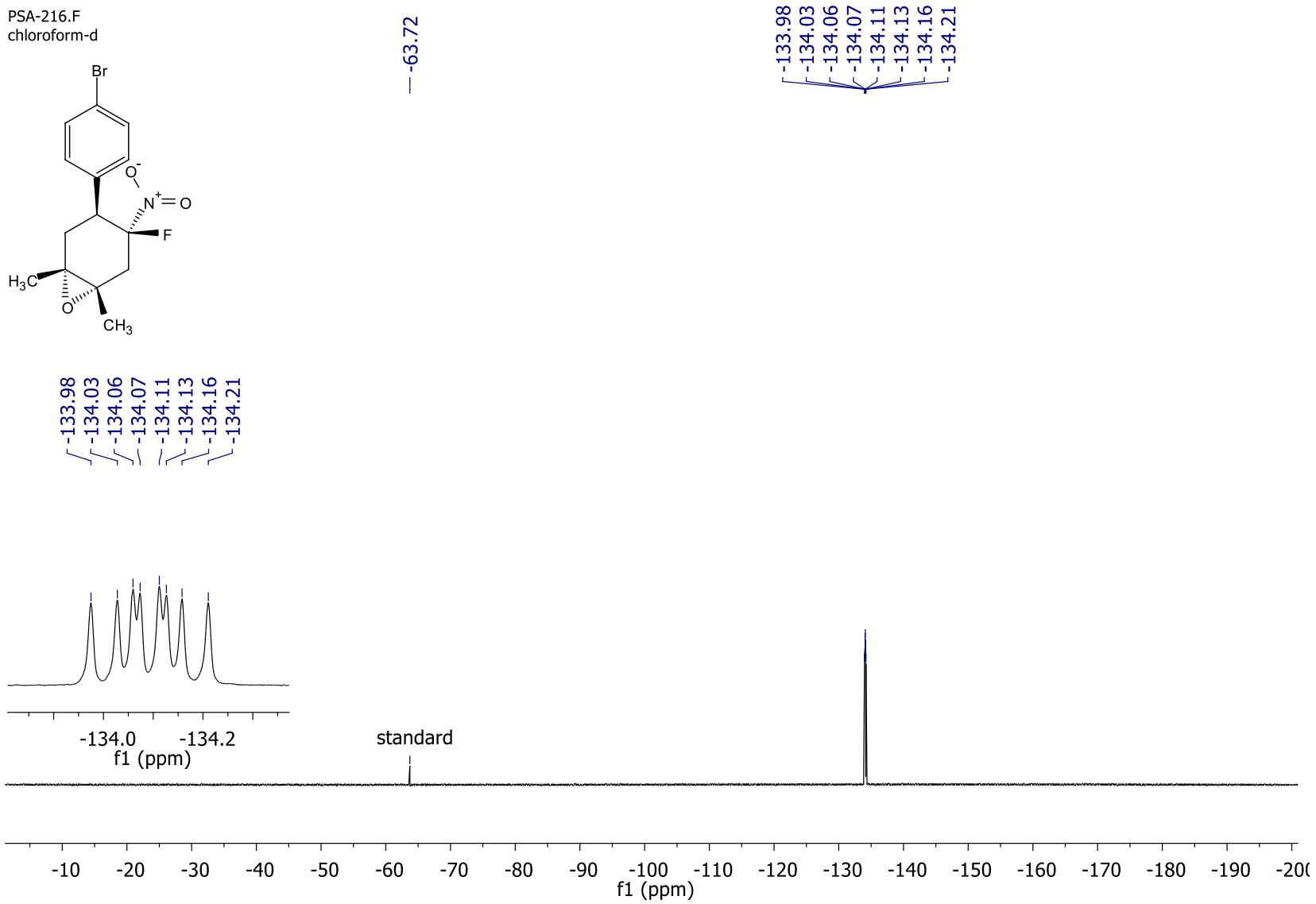
^{1}H NMR (400 MHz, acetone-d_6) δ = 8.22 – 8.15 (m, 1H), 8.12 (br s, 1H), 7.72 – 7.60 (m, 2H), 4.37 (ddd, $^{3}J_{HF}$ = 31.1, $^{3}J_{HH}$ = 13.4, 4.1 Hz, 1H), 3.03 (s, 1H), 3.00 (s, 1H), 2.96 (dd, $^{3}J_{HF}$ = 38.4, $^{3}J_{HH}$ = 15.2 Hz, 1H), 2.78 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.5 Hz, 1H), 2.18 (dd, $^{2}J_{HH}$ = 14.3, $^{3}J_{HF}$ = 12.5 Hz, 1H), 1.77 (dd, $^{2}J_{HH}$ = 13.5, $^{3}J_{HH}$ = 4.1 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, acetone-d6) δ 149.1, 139.4, 136.6, 130.8, 124.6 (d, $^{4}J_{CF}$ = 1.9 Hz), 123.8, 122.8 (d, $^{1}J_{CF}$ = 250.1 Hz), 73.9, 72.9, 44.8 (d, $^{2}J_{CF}$ = 18.2 Hz), 43.6 (d, $^{2}J_{CF}$ = 18.4 Hz), 39.2, 23.9, 23.2 ppm. ^{19}F NMR (376 MHz, acetone-d_6) δ = -133.69 (ddd, *J* = 38.4, 31.1, 12.5 Hz) ppm. ^{1}H NMR (400 MHz, DMSO-d6) δ = 8.21 – 8.13 (m, 1H), 7.99 (s, 1H), 7.67 – 7.59 (m, 2H), 5.08 (br s, 1H), 4.91 (br s, 1H), 4.20 (ddd, $^{3}J_{HF}$ = 31.6, 13.4, 3.9 Hz, 1H), 2.75 (dd, $^{3}J_{HF}$ = 38.6, $^{2}J_{HH}$ = 14.2 Hz, 1H), 2.58 (pseudo-t, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 13.4 Hz, 1H), 2.10 (dd, $^{2}J_{HH}$ = 14.4 Hz, $^{3}J_{HF}$ = 12.5 Hz, 1H), 1.62 (dd, $^{2}J_{HH}$ = 13.4, $^{3}J_{HH}$ = 4.0 Hz, 1H), 1.20 (s, 3H), 1.18 (s, 3H) ppm.^{13}C NMR (100 MHz, DMSO-d6) δ = 147.8, 138.1, 136.0, 130.4, 123.4, 123.2, 122.1 (d, $^{1}J_{CF}$ = 248.0 Hz), 72.6, 71.5, 43.5 (d, $^{2}J_{CF}$ = 18.9 Hz), 42.2 (d, $^{2}J_{CF}$ = 18.1 Hz), 38.0, 23.4, 22.8 ppm. ^{19}F NMR (376 MHz, DMSO-d6) δ = -134.51 (ddd, $^{3}J_{HF}$ = 38.6, 31.6, 12.5 Hz) ppm.



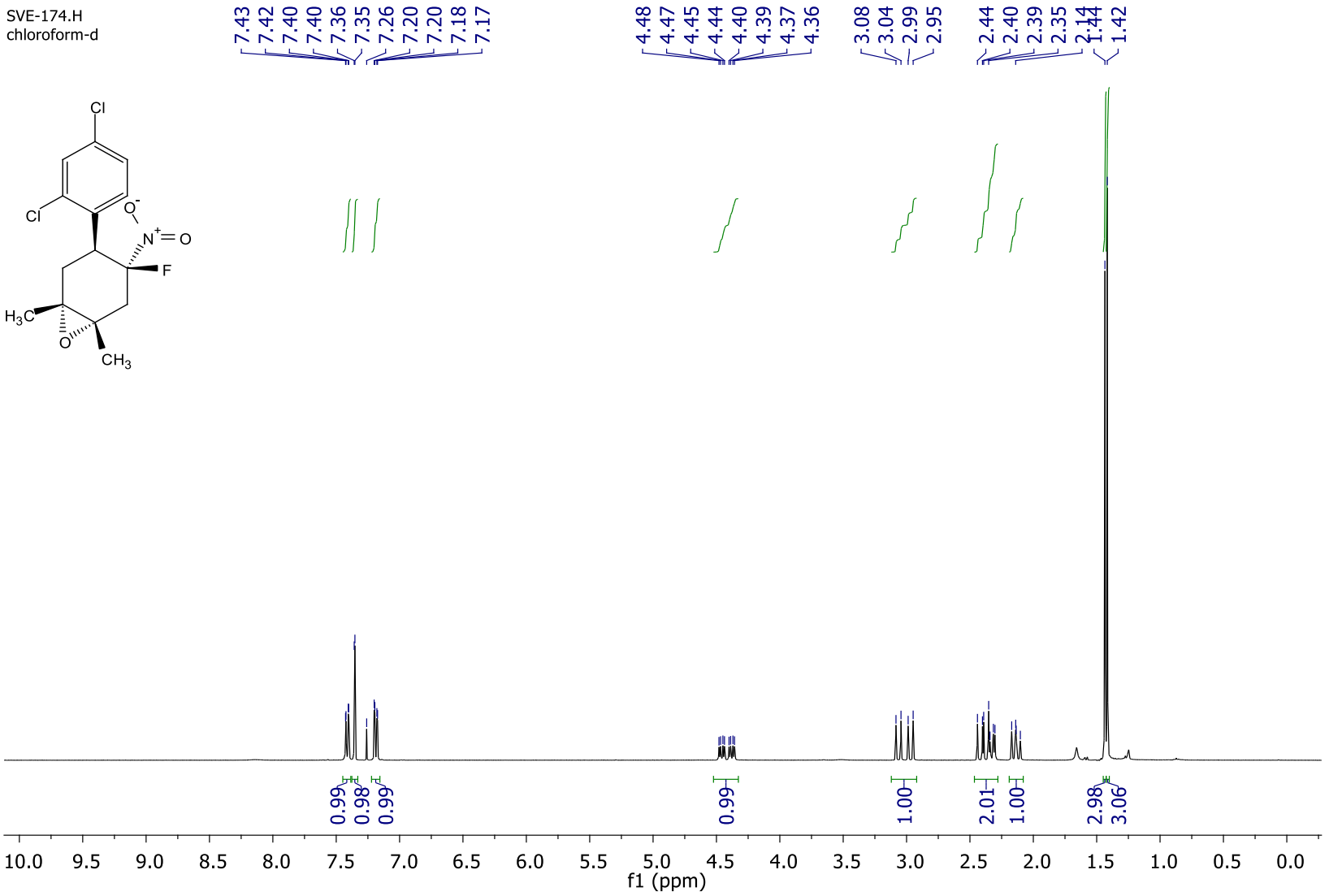
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-bromophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2a**)



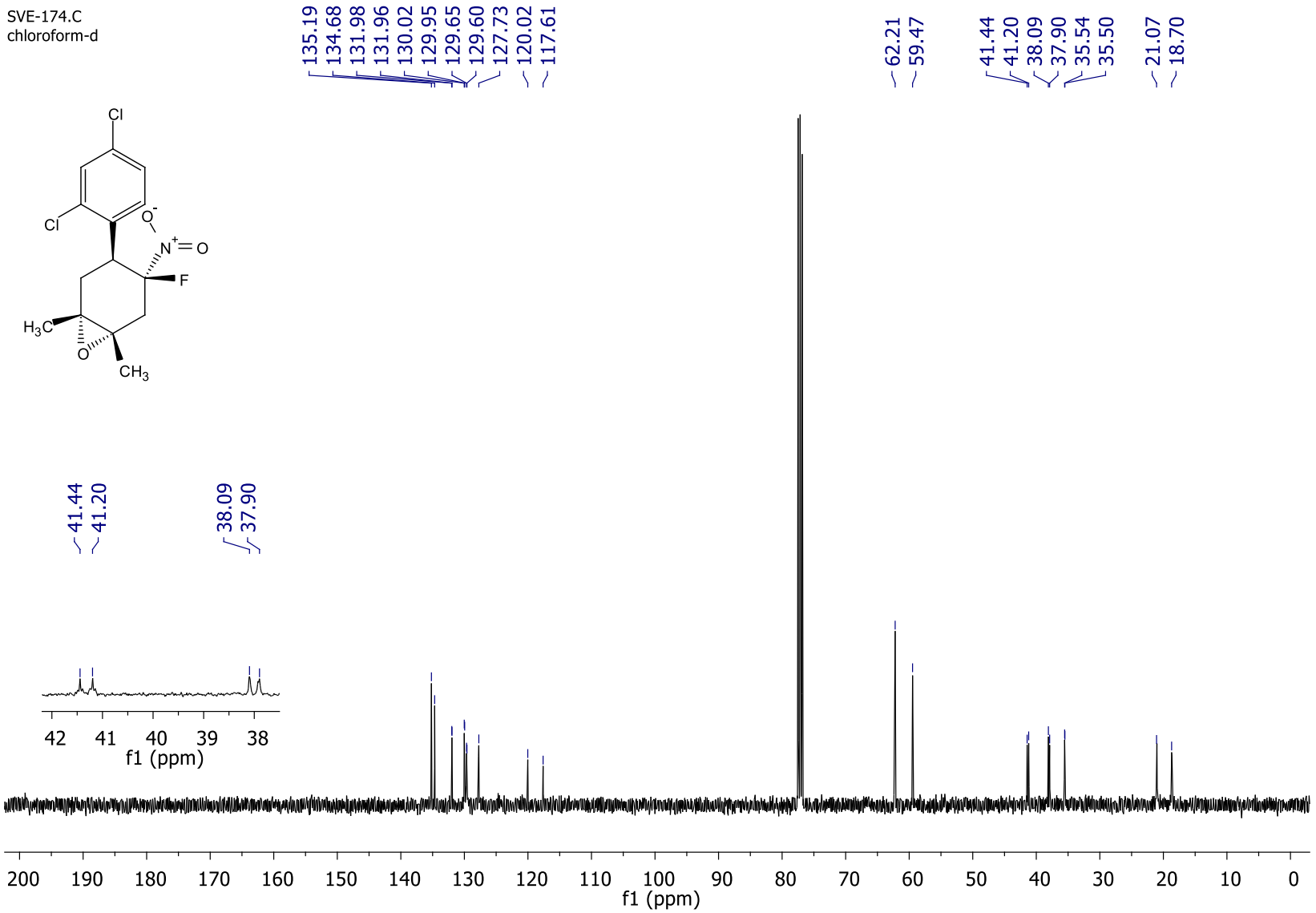
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-bromophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2a**)



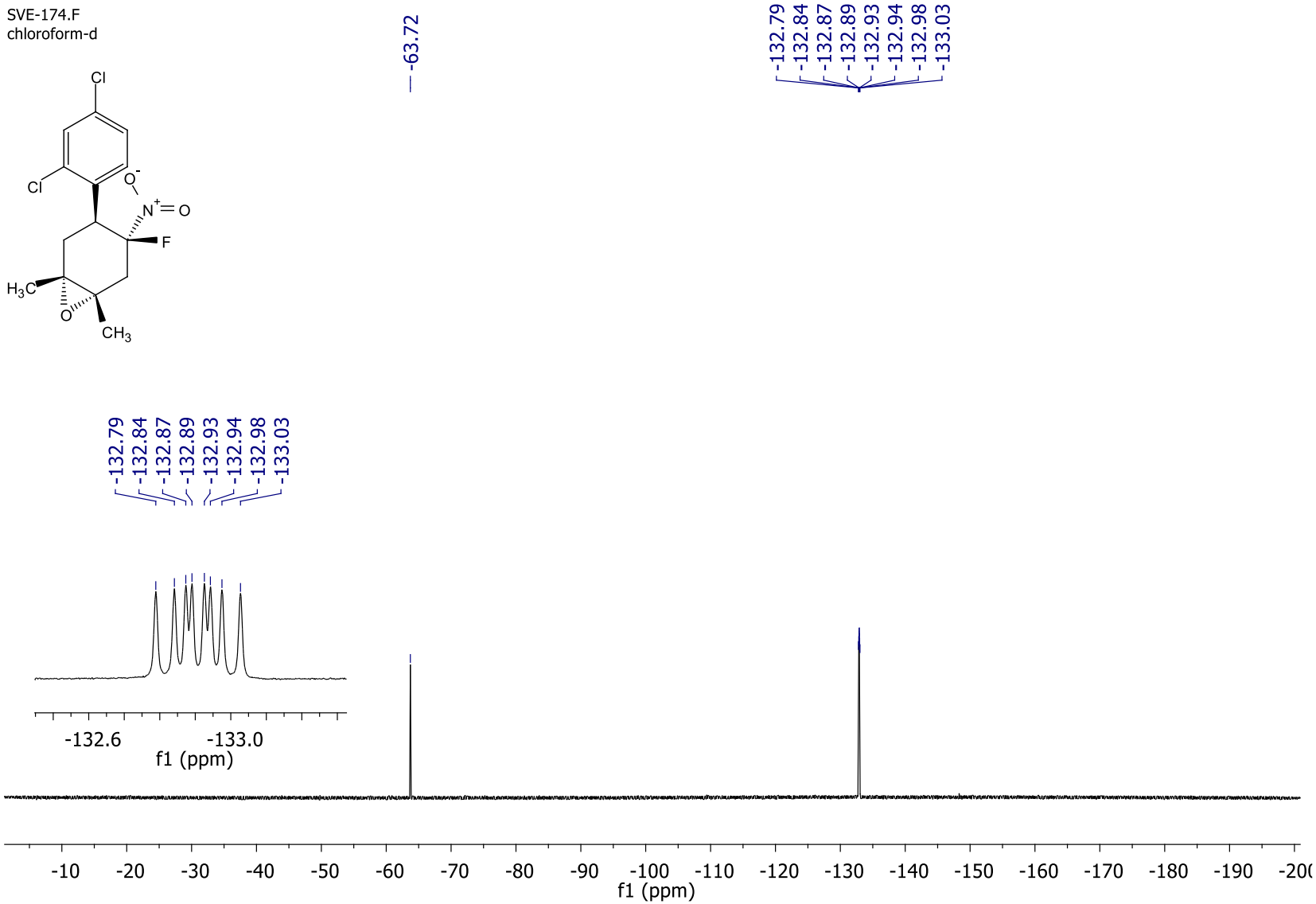
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-bromophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2a**)



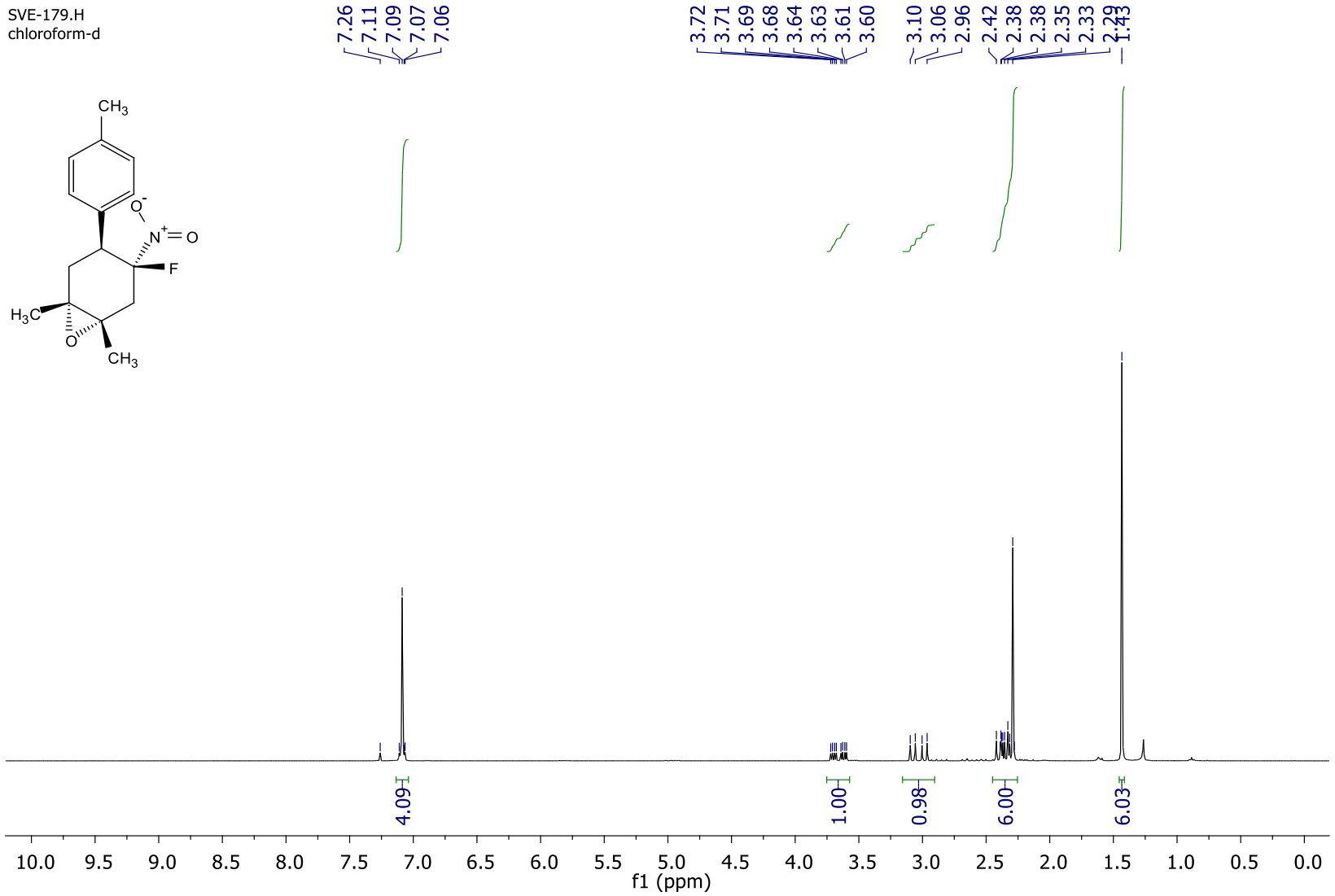
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-4-(2,4-dichlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2b**)



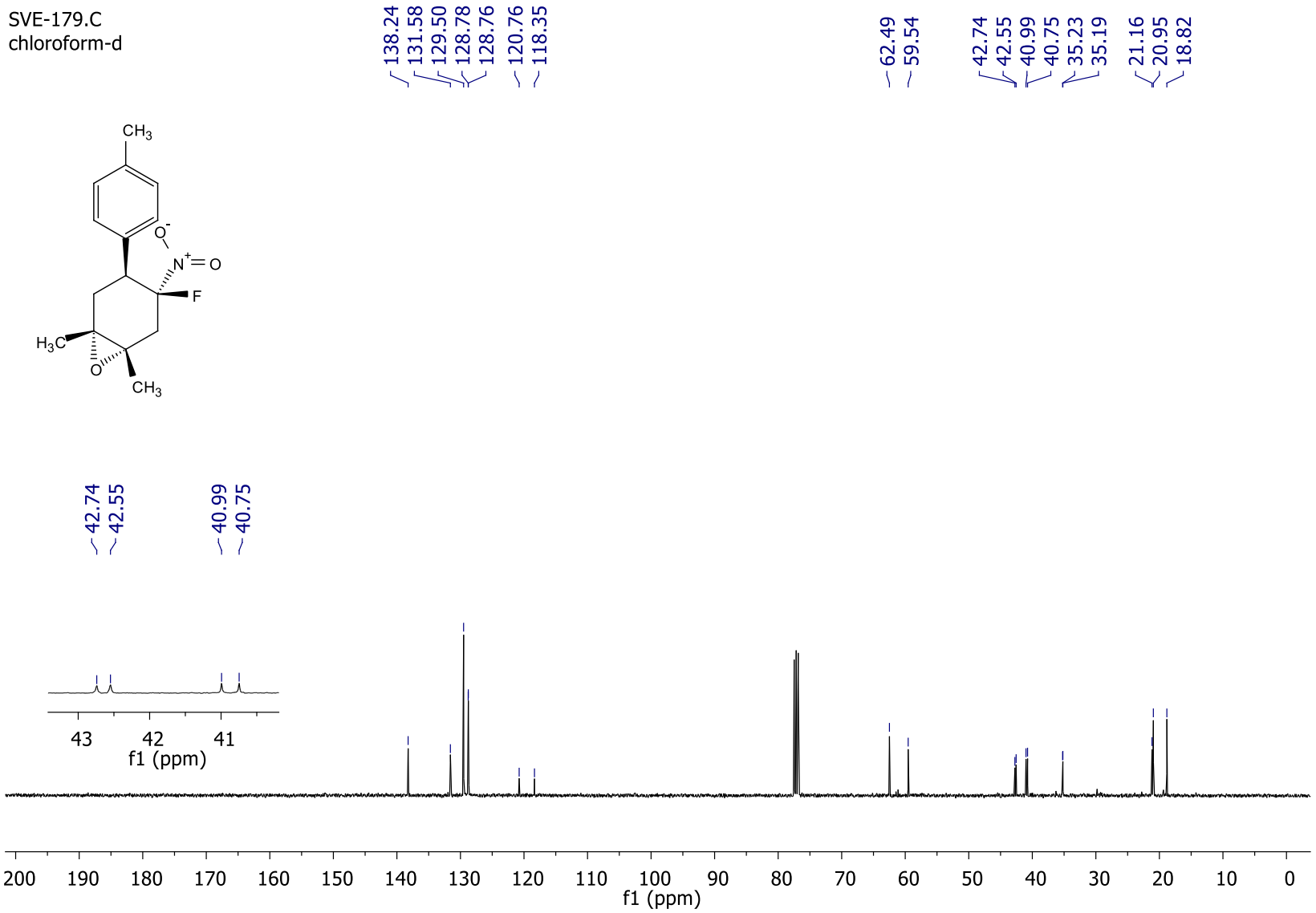
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-4-(2,4-dichlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2b**)



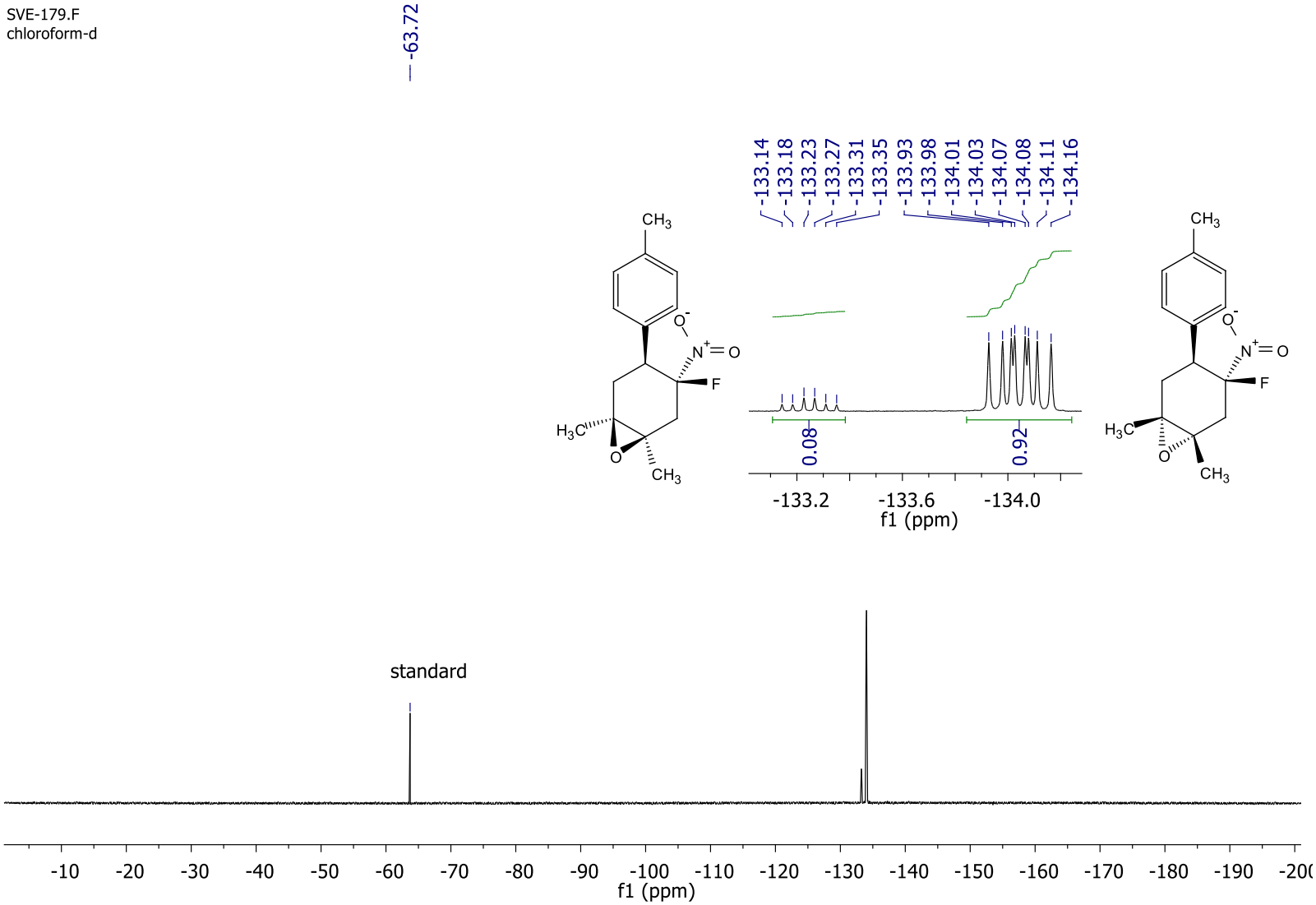
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-4-(2,4-dichlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2b**)



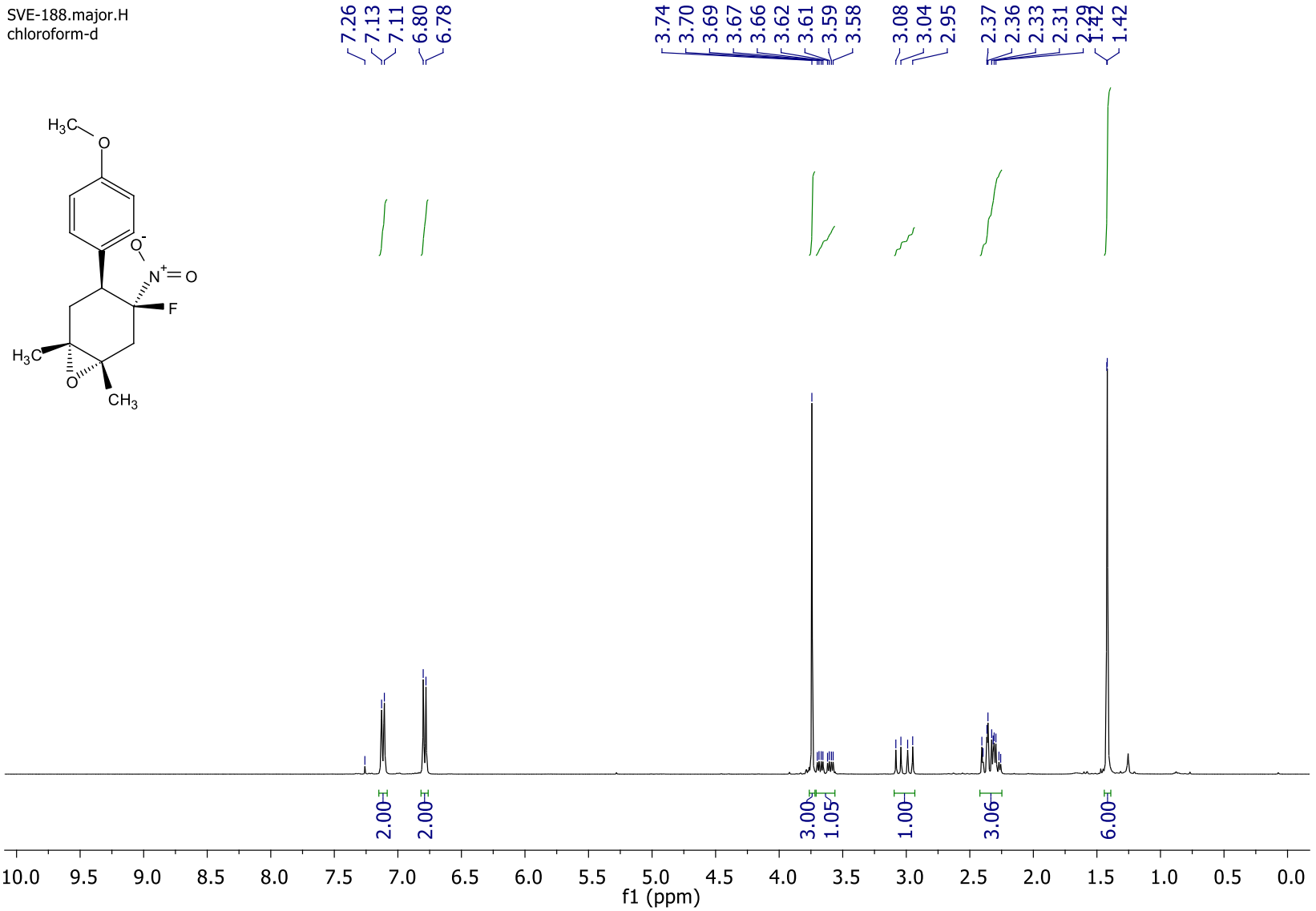
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(p-tolyl)-7-oxabicyclo[4.1.0]heptane (**2c**)



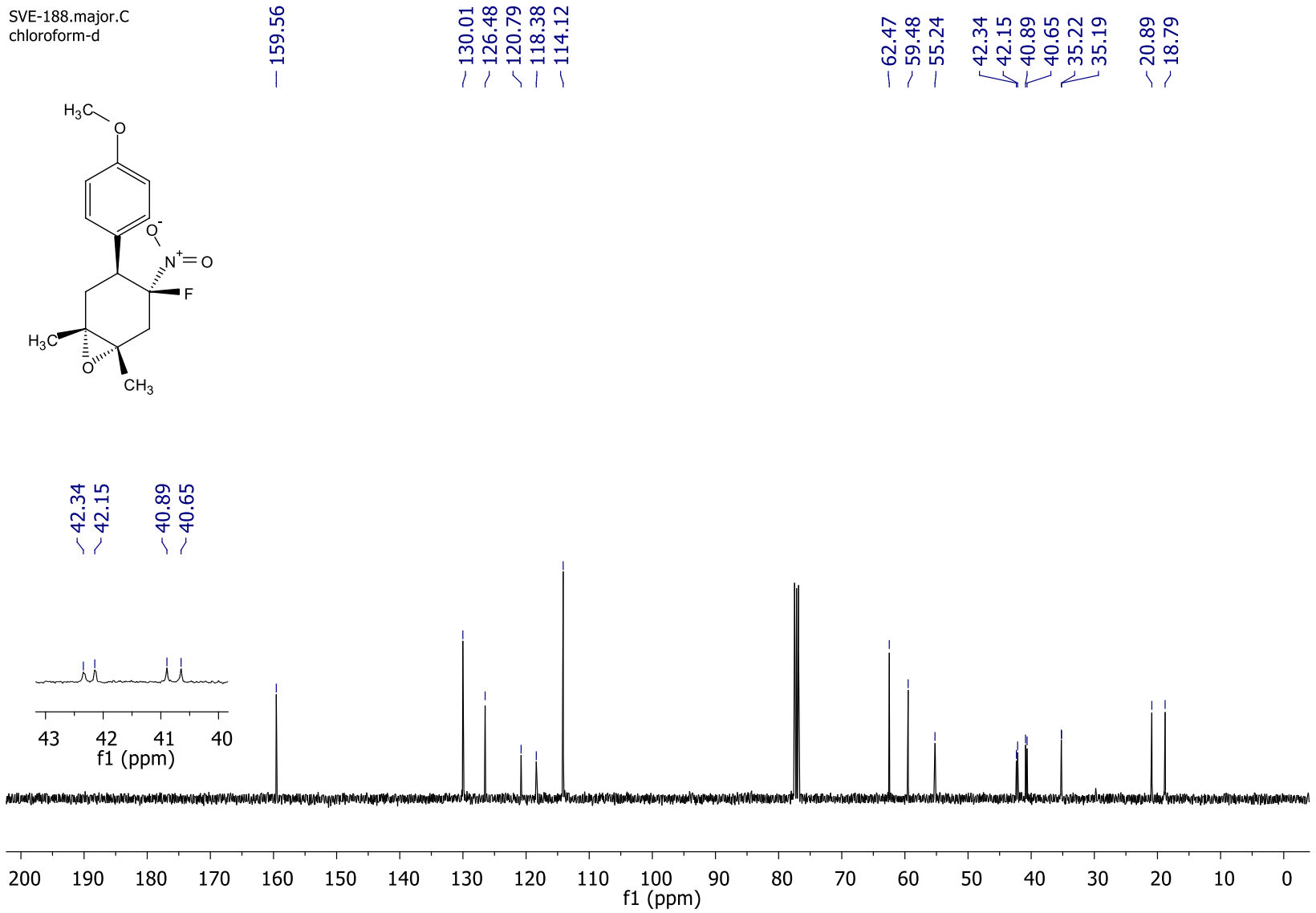
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(p-tolyl)-7-oxabicyclo[4.1.0]heptane (**2c**)



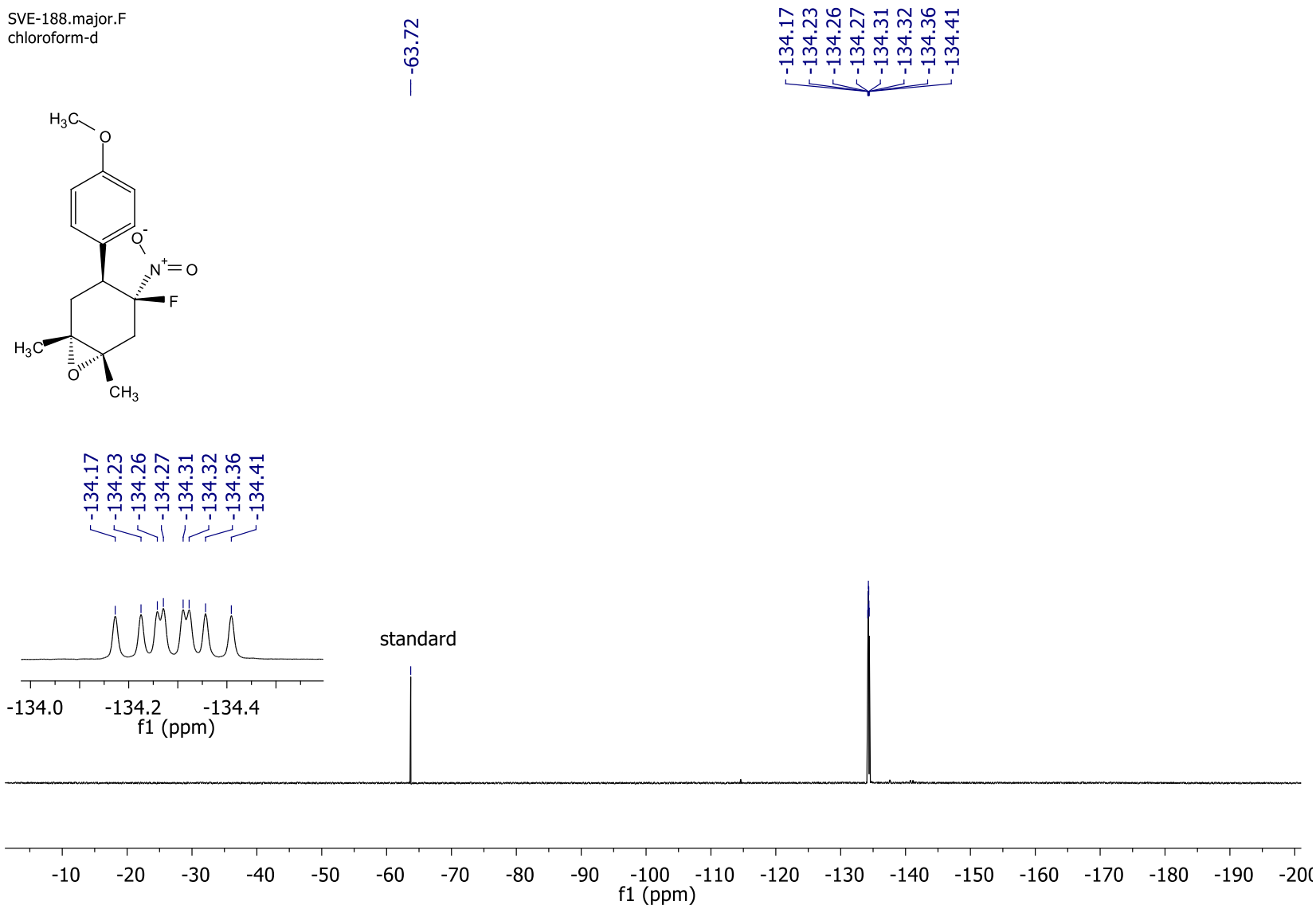
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(p-tolyl)-7-oxabicyclo[4.1.0]heptane (**2c**-major) with 8% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(p-tolyl)-7-oxabicyclo[4.1.0]heptane (**2c**-minor)



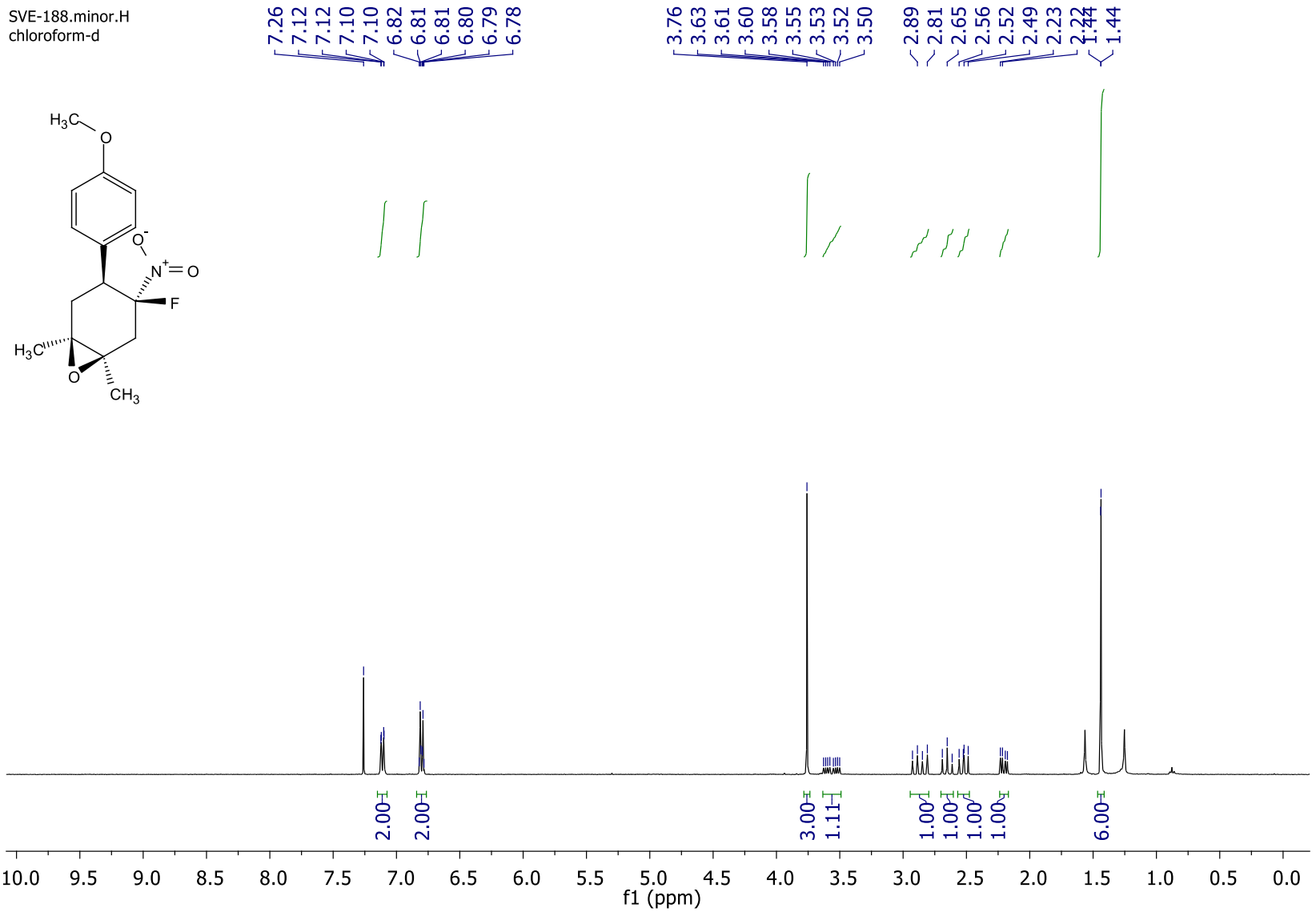
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-major isomer)



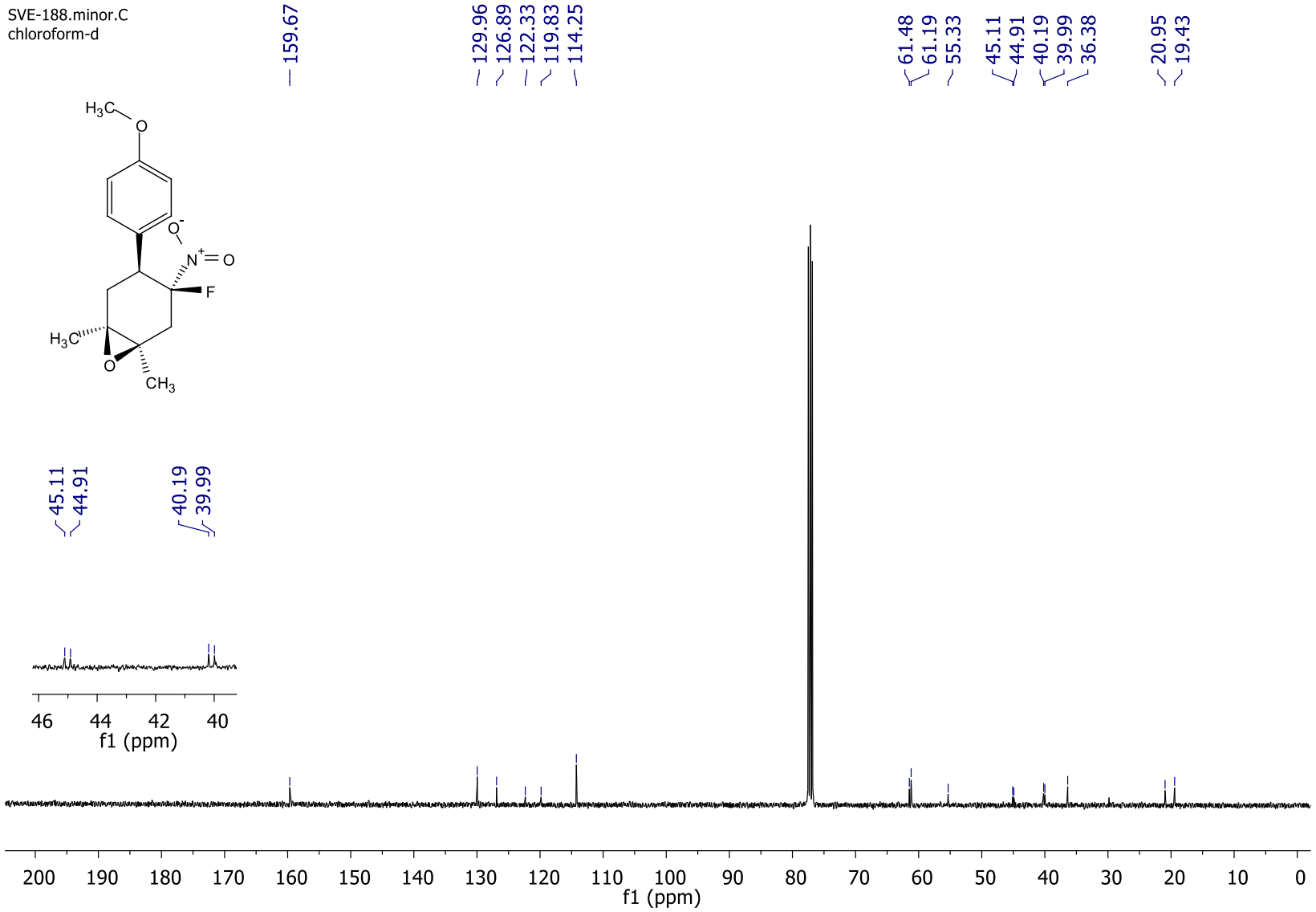
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-major isomer)



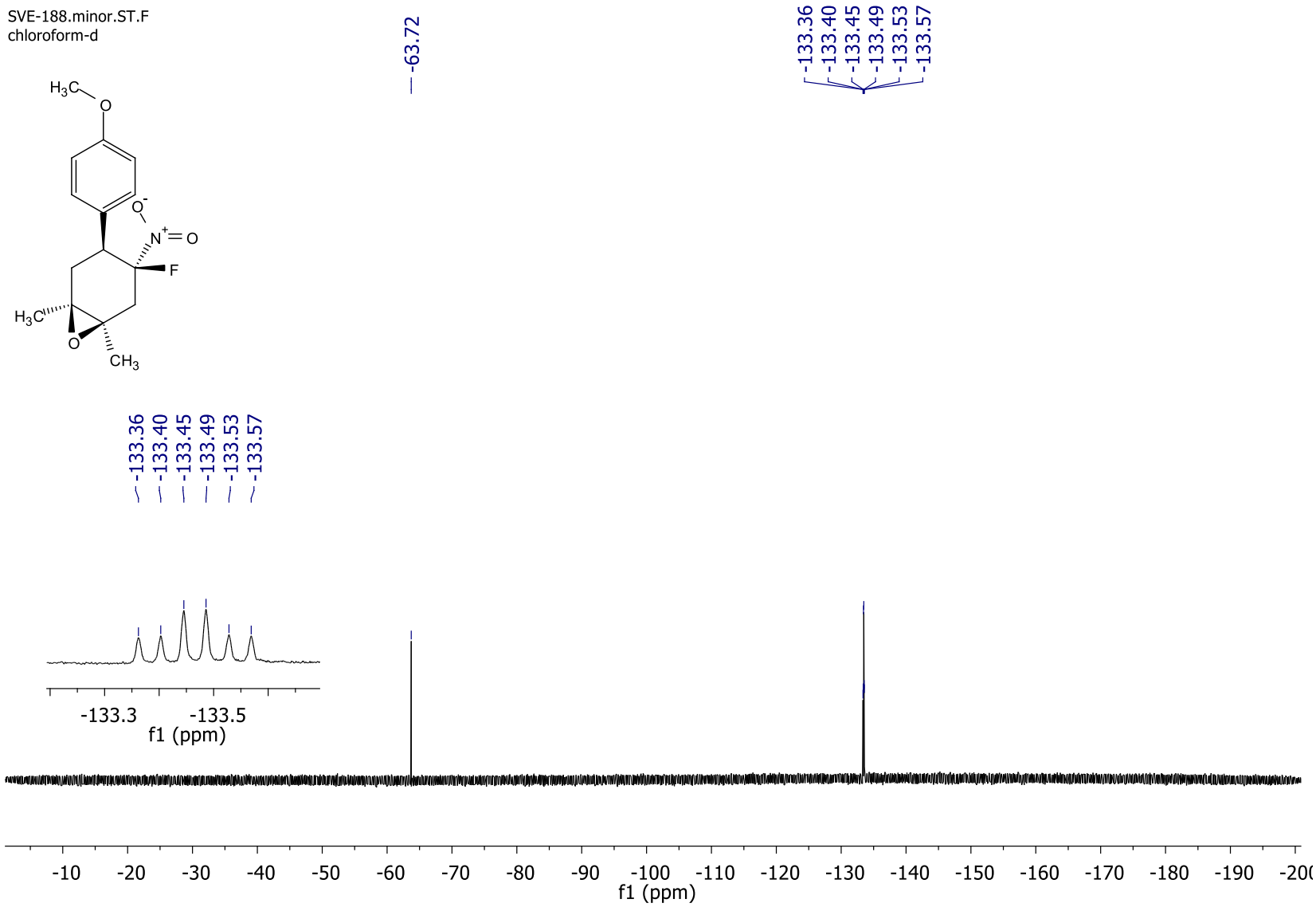
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-major isomer)



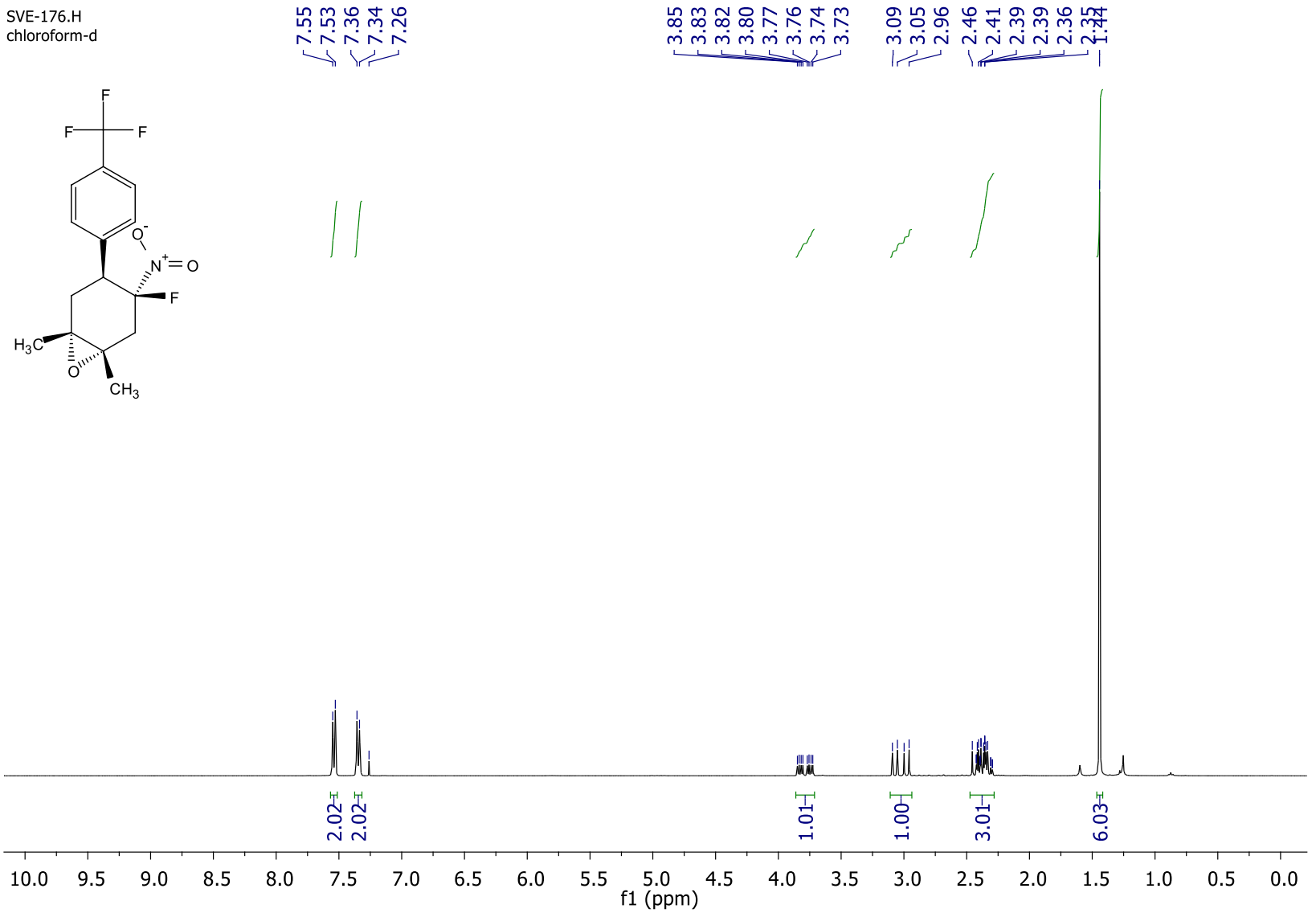
^{1}H NMR spectrum of (1R*,3S*,4S*,6S*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-minor isomer)



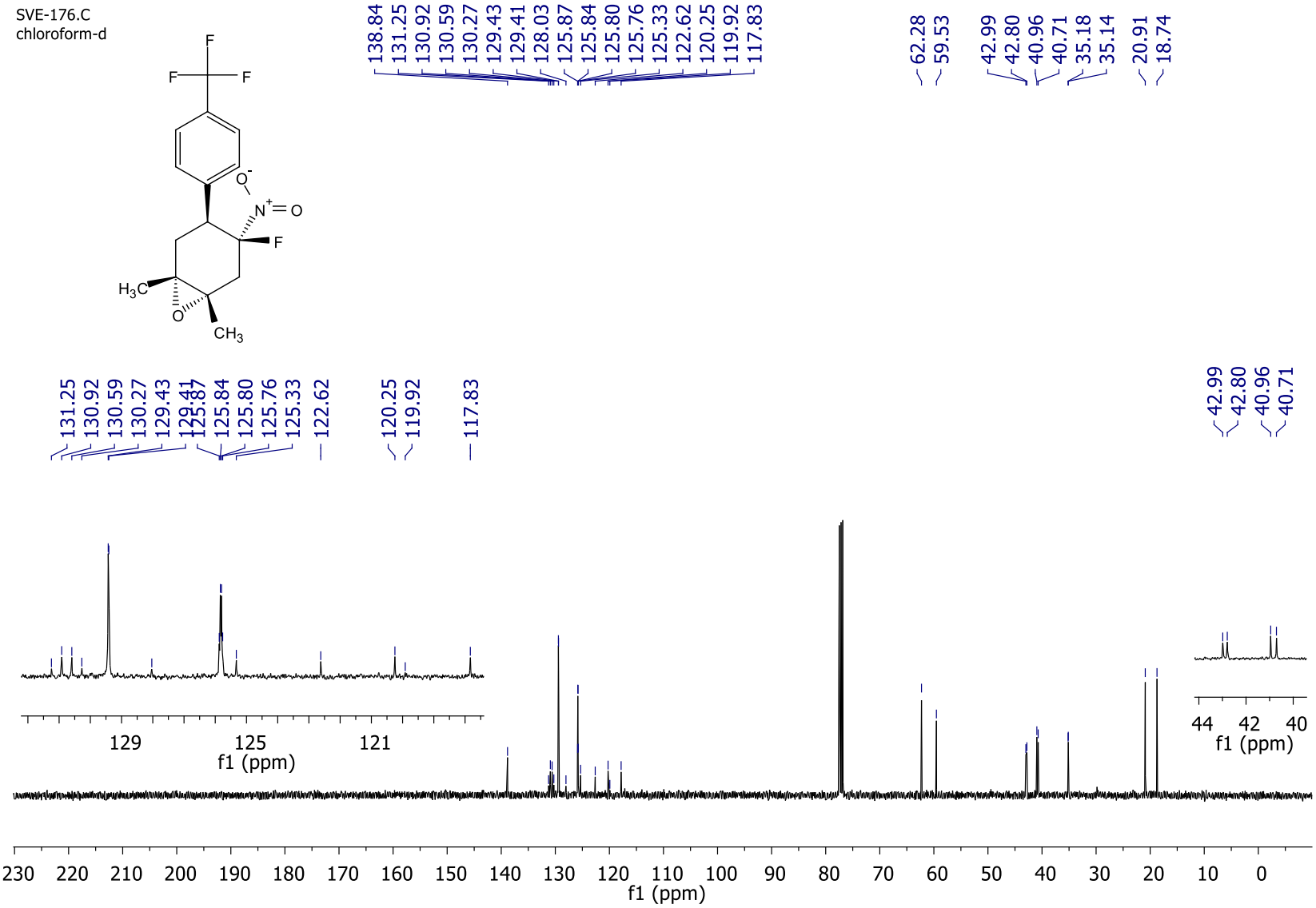
^{13}C NMR spectrum of (1R*,3S*,4S*,6S*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-minor isomer)



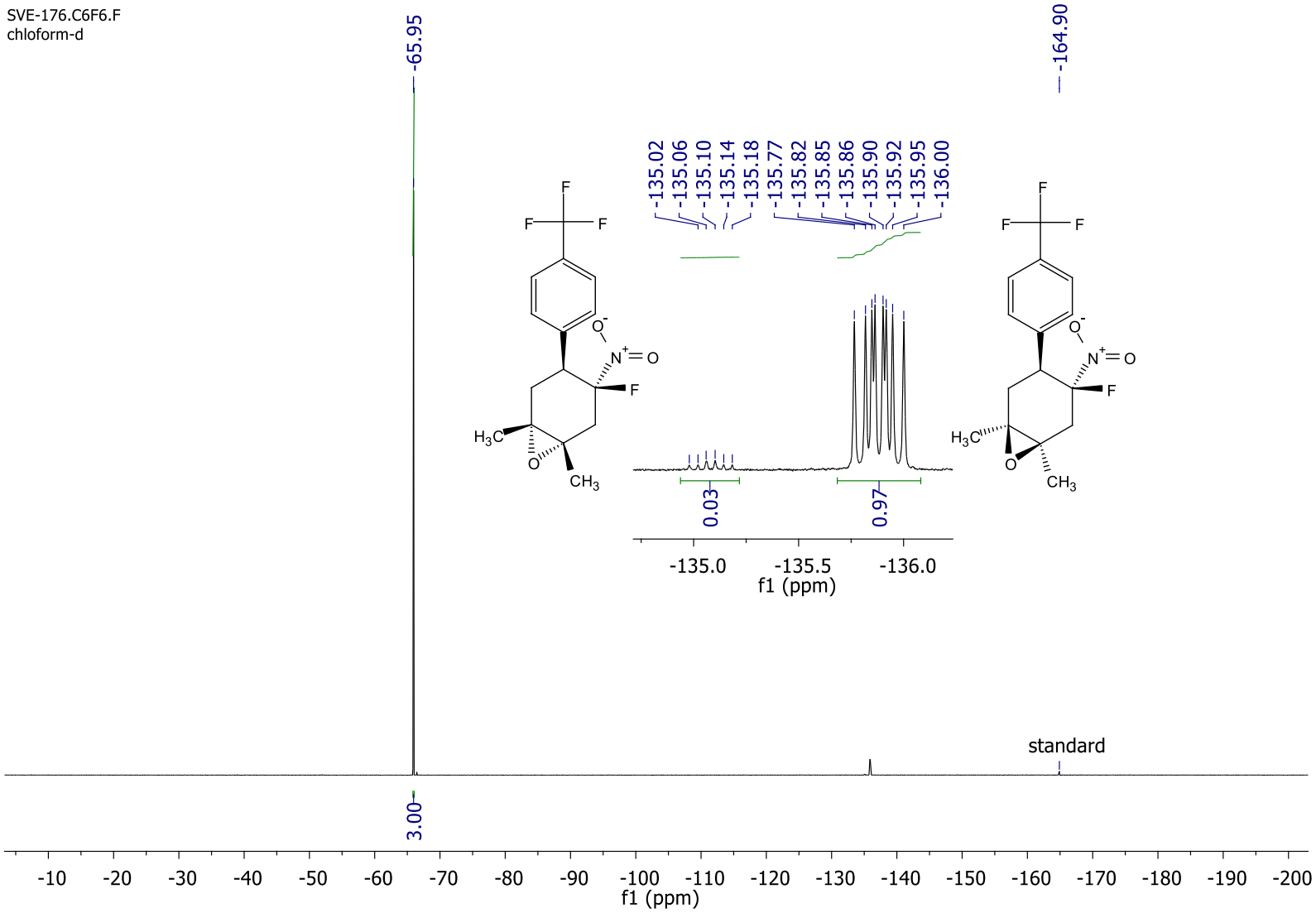
^{19}F NMR spectrum of (1R*,3S*,4S*,6S*)-3-fluoro-4-(4-methoxyphenyl)-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2d**-minor isomer)



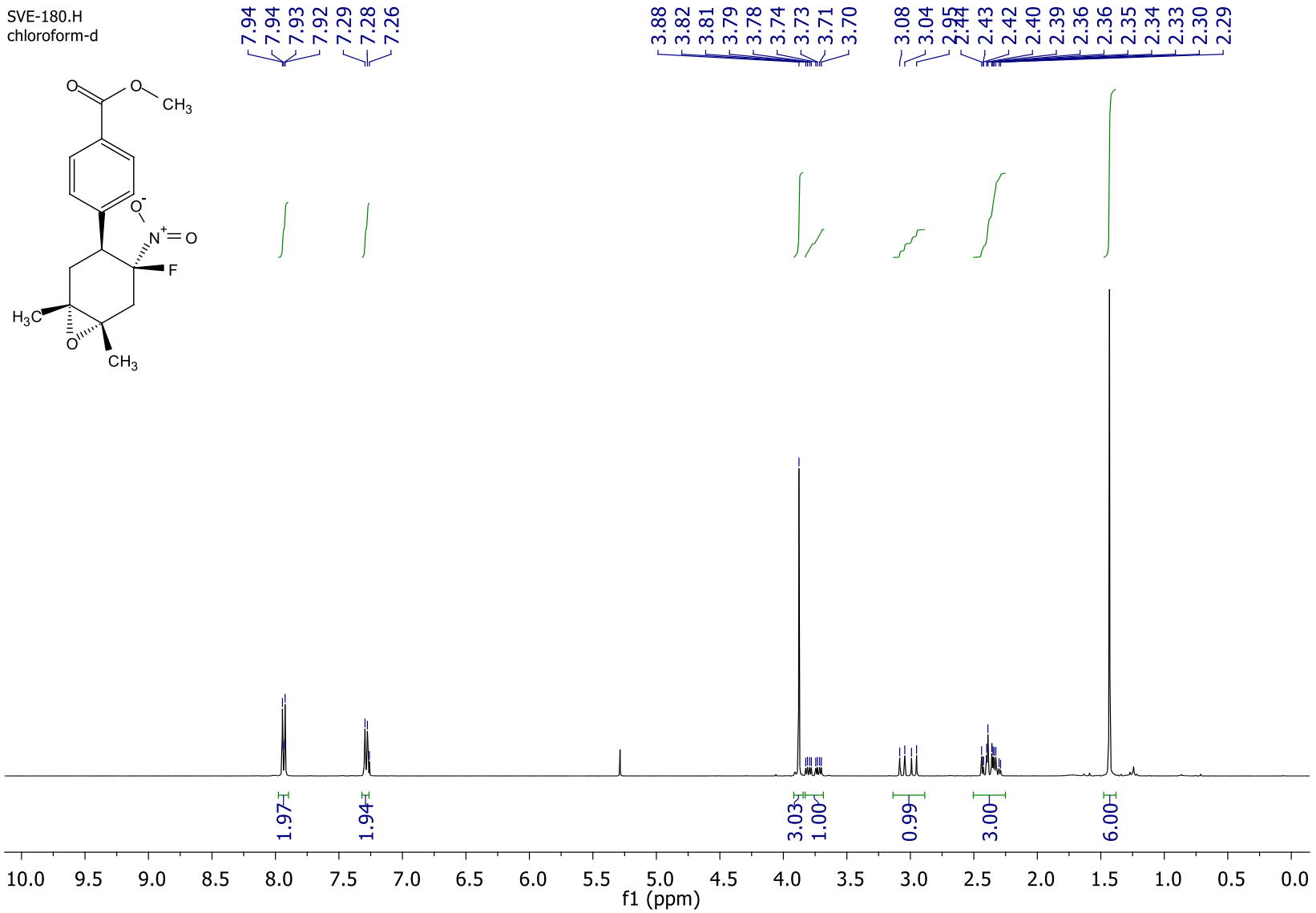
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-(trifluoromethyl)phenyl)-7-oxabicyclo[4.1.0]heptane (**2e**)



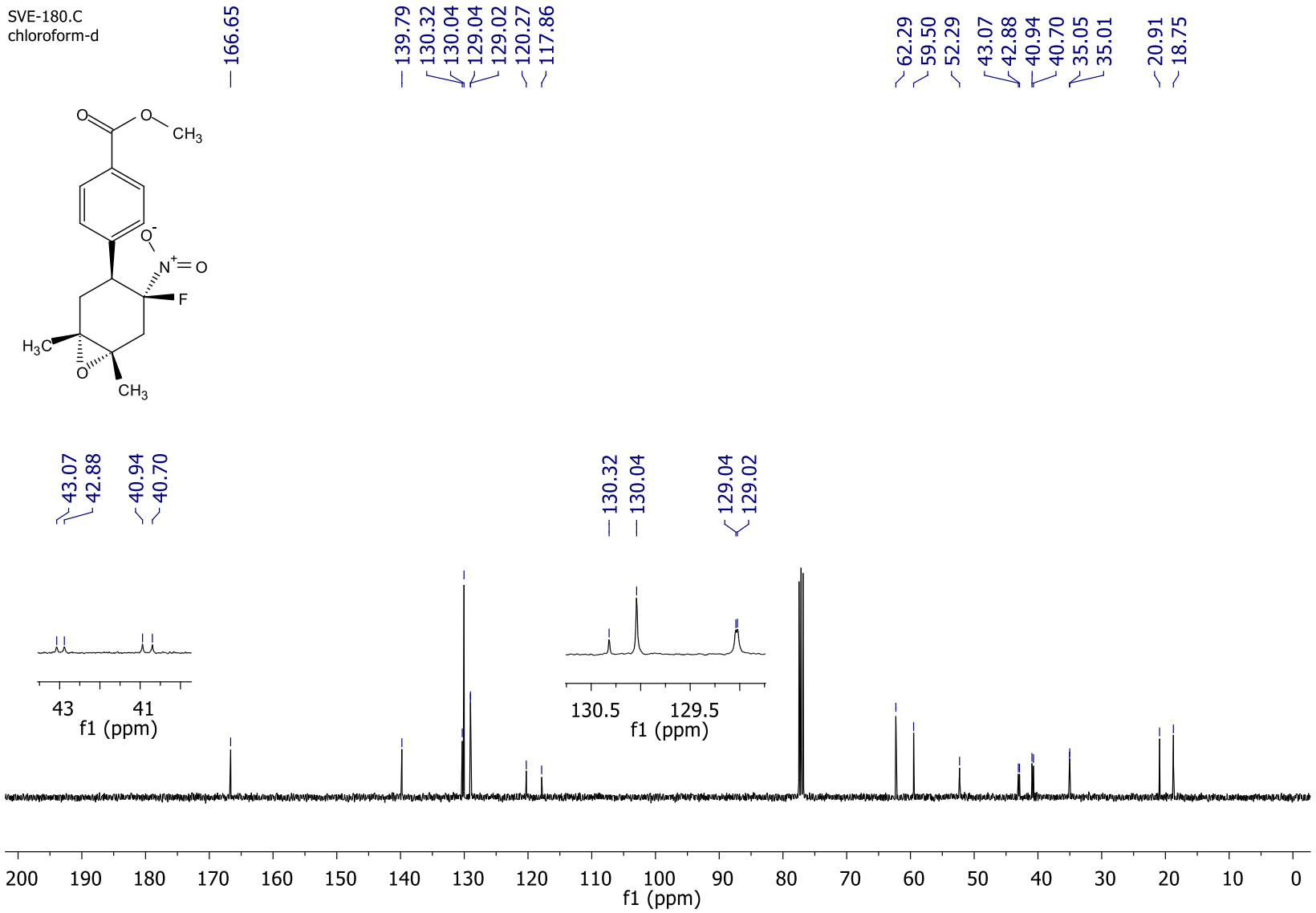
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-(trifluoromethyl)phenyl)-7-oxabicyclo[4.1.0]heptane (**2e**)



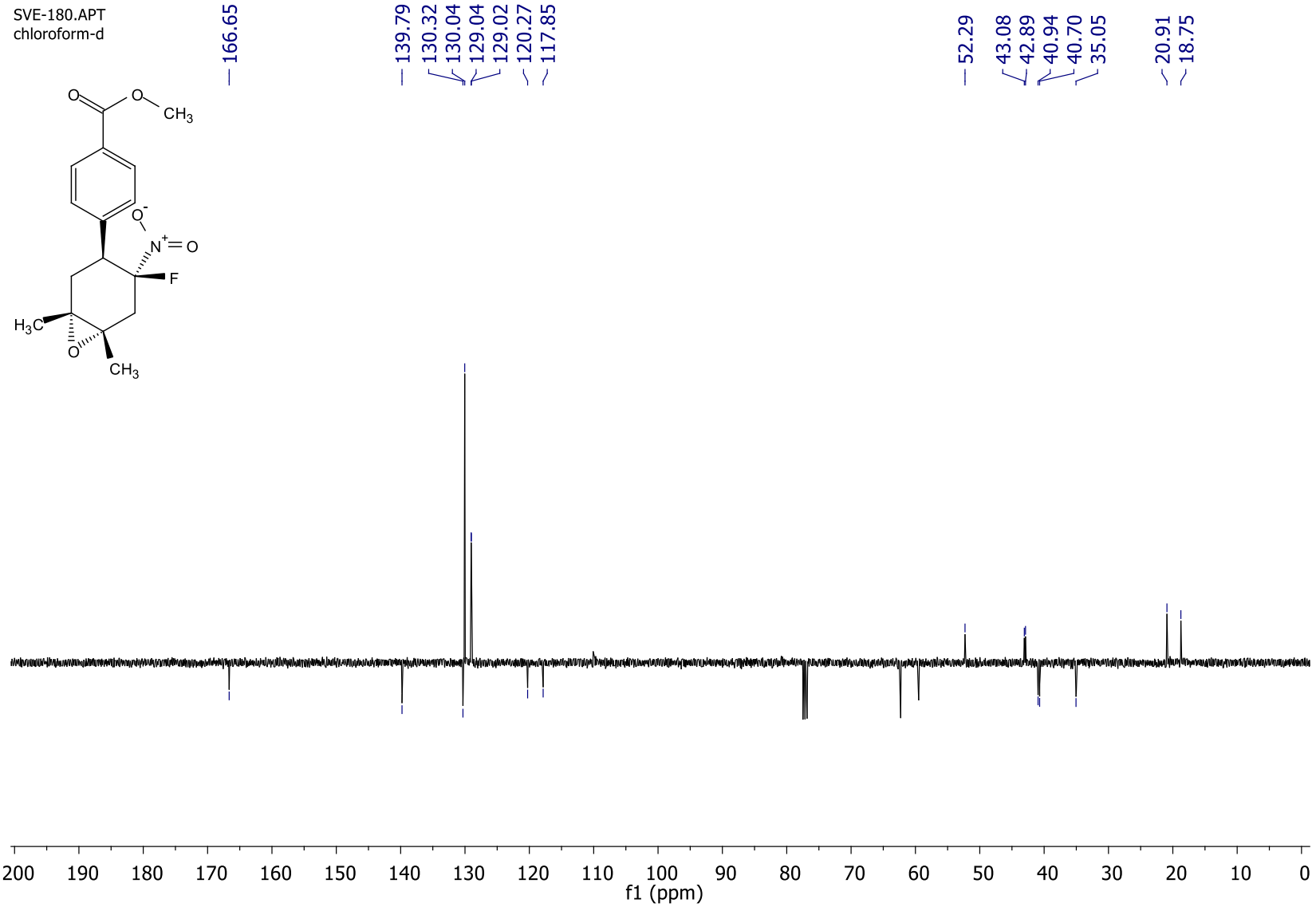
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-(trifluoromethyl)phenyl)-7-oxabicyclo[4.1.0]heptane (**2e**-major) with 3% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-(trifluoromethyl)phenyl)-7-oxabicyclo[4.1.0]heptane (**2e**-minor)



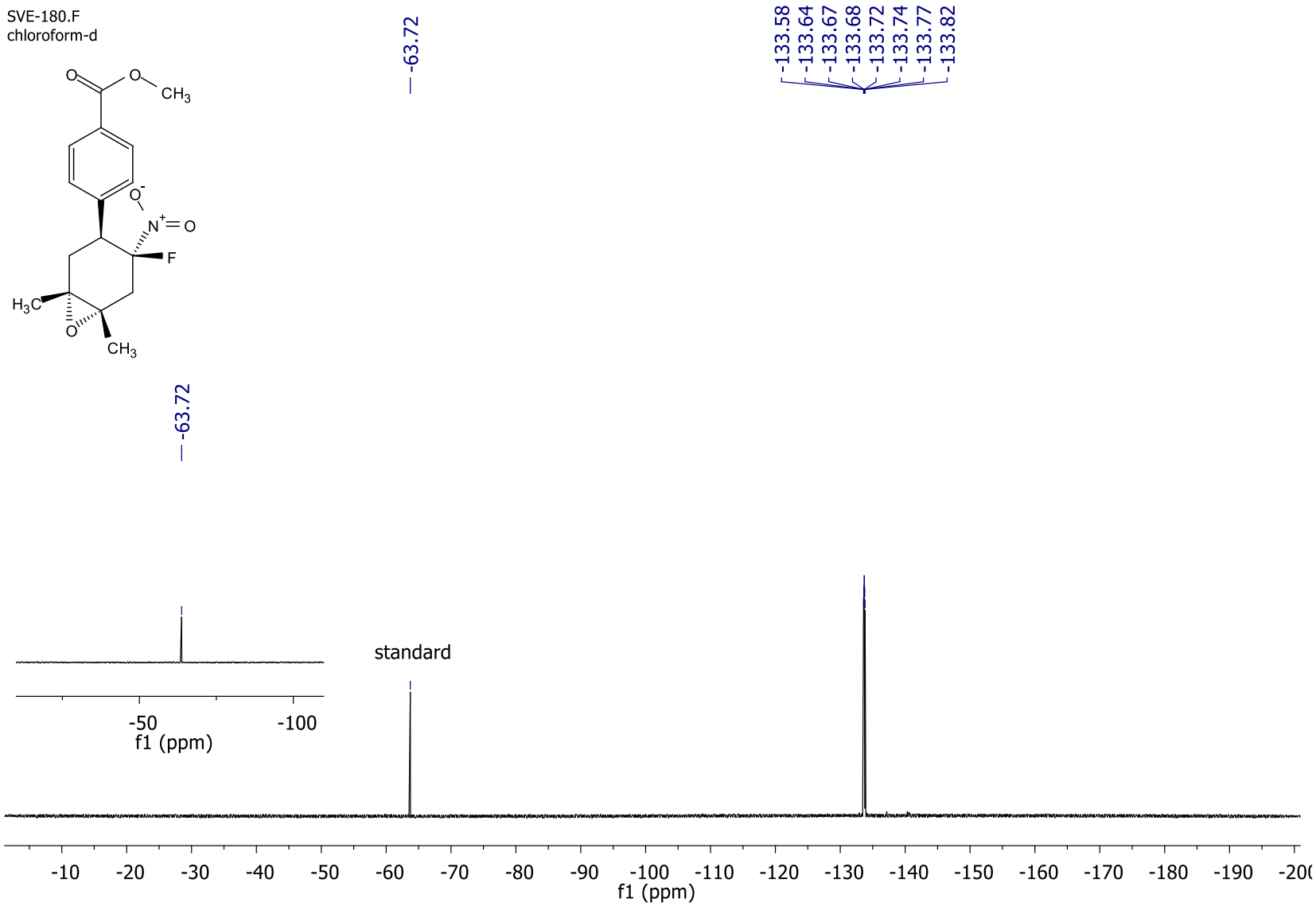
^{1}H NMR spectrum of methyl 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzoate (**2f**)



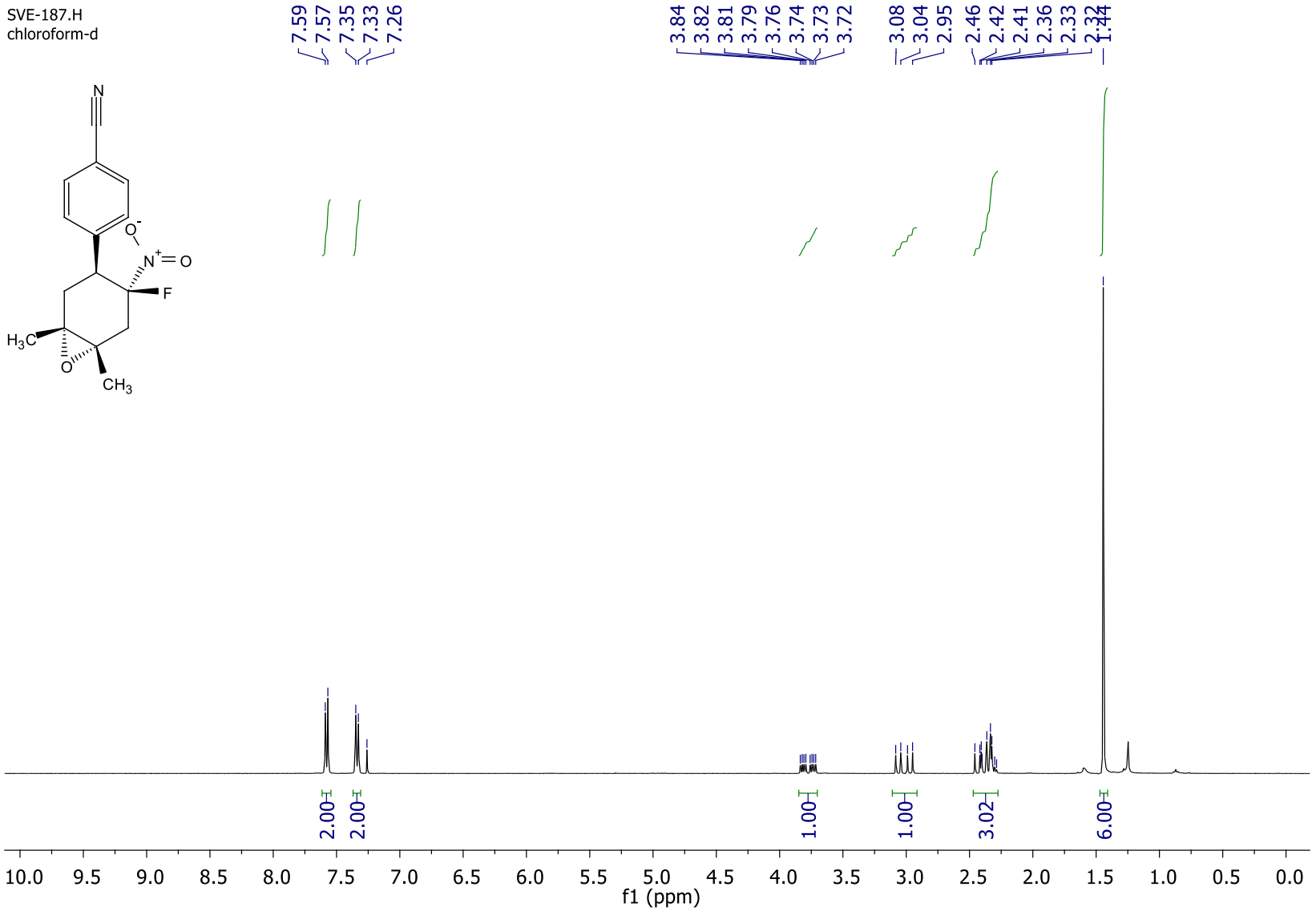
^{13}C NMR spectrum of methyl 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzoate (**2f**)



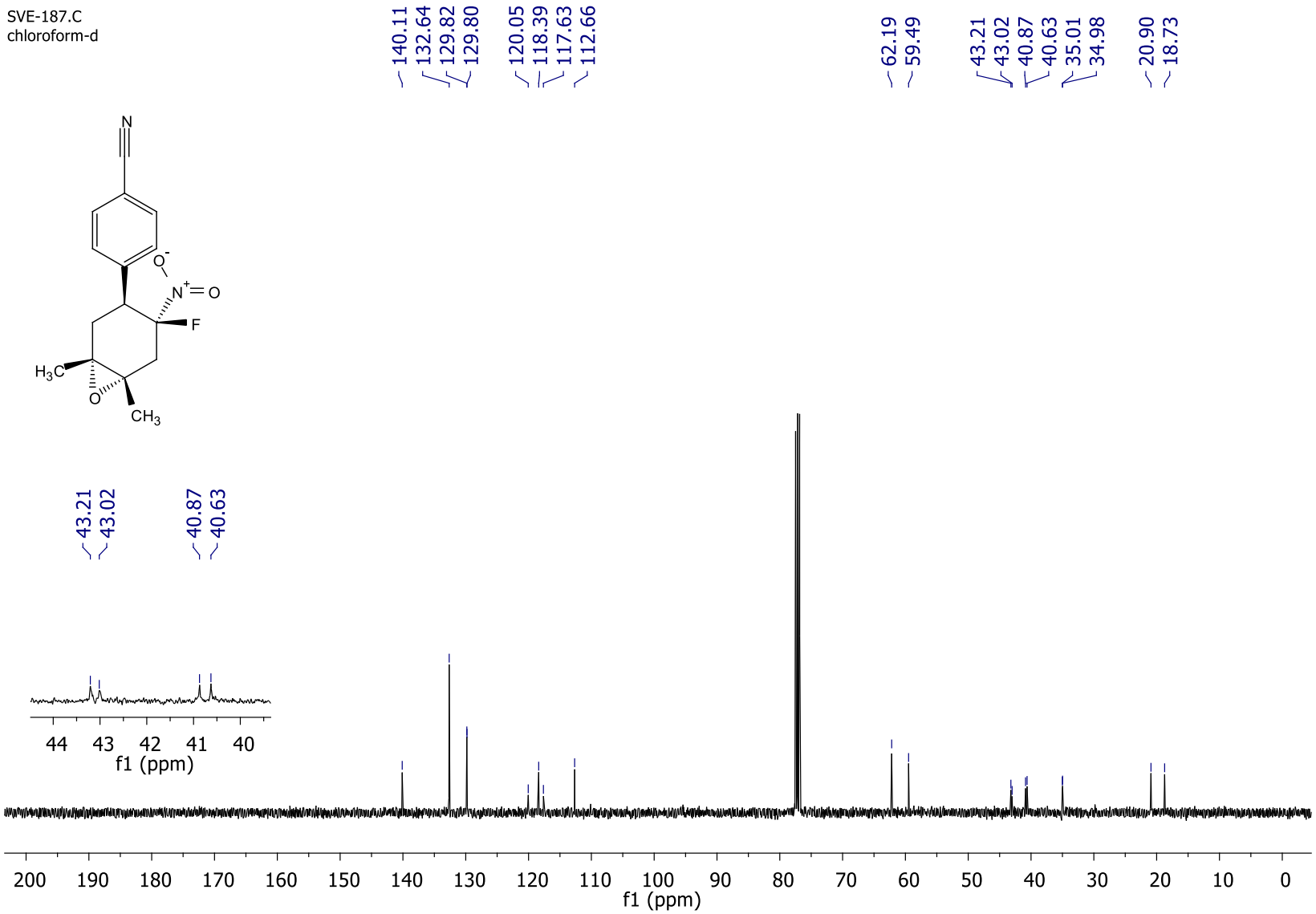
^{13}C APT NMR spectrum of methyl 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzoate (**2f**)



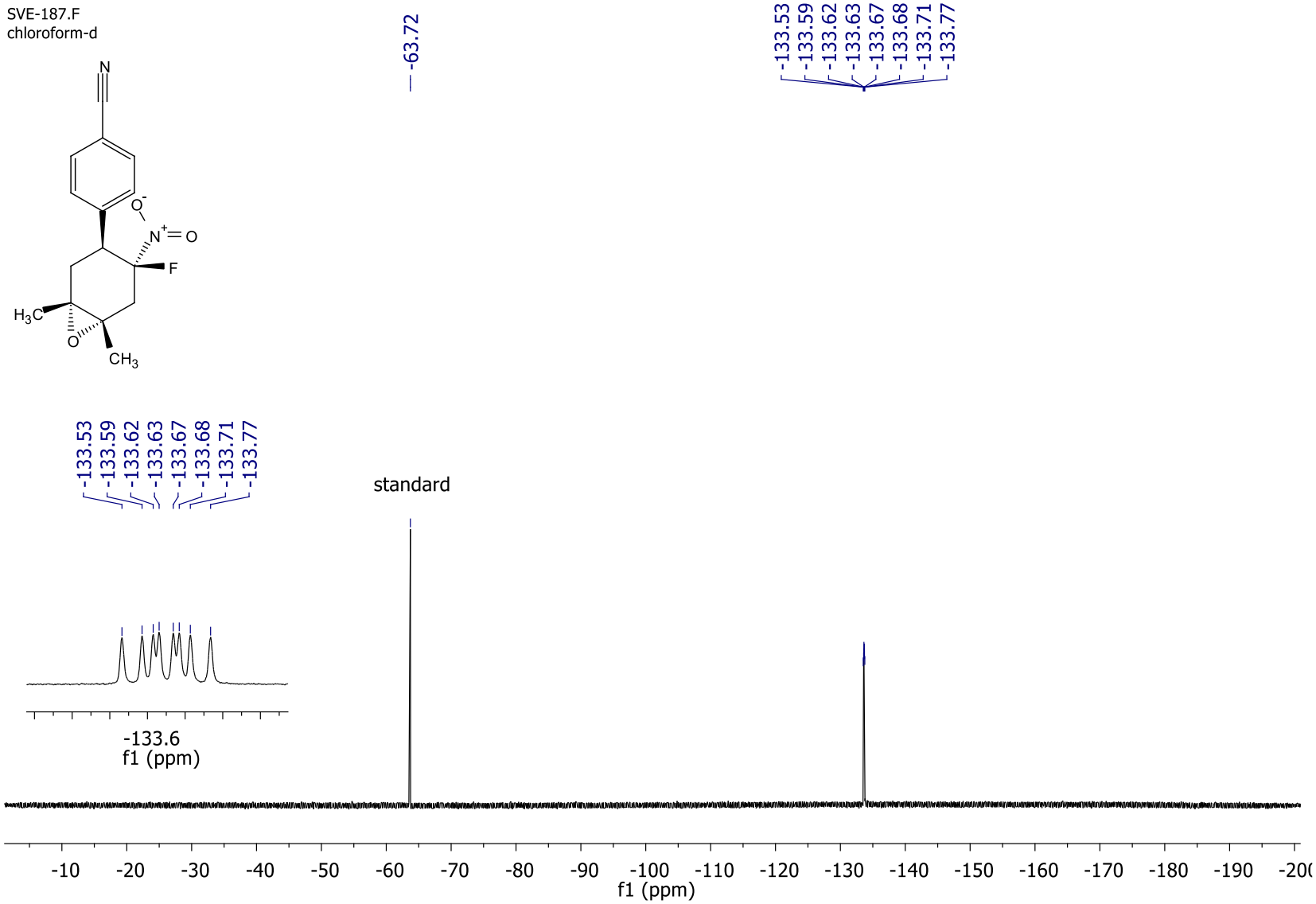
^{19}F NMR spectrum of methyl 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzoate (**2f**)



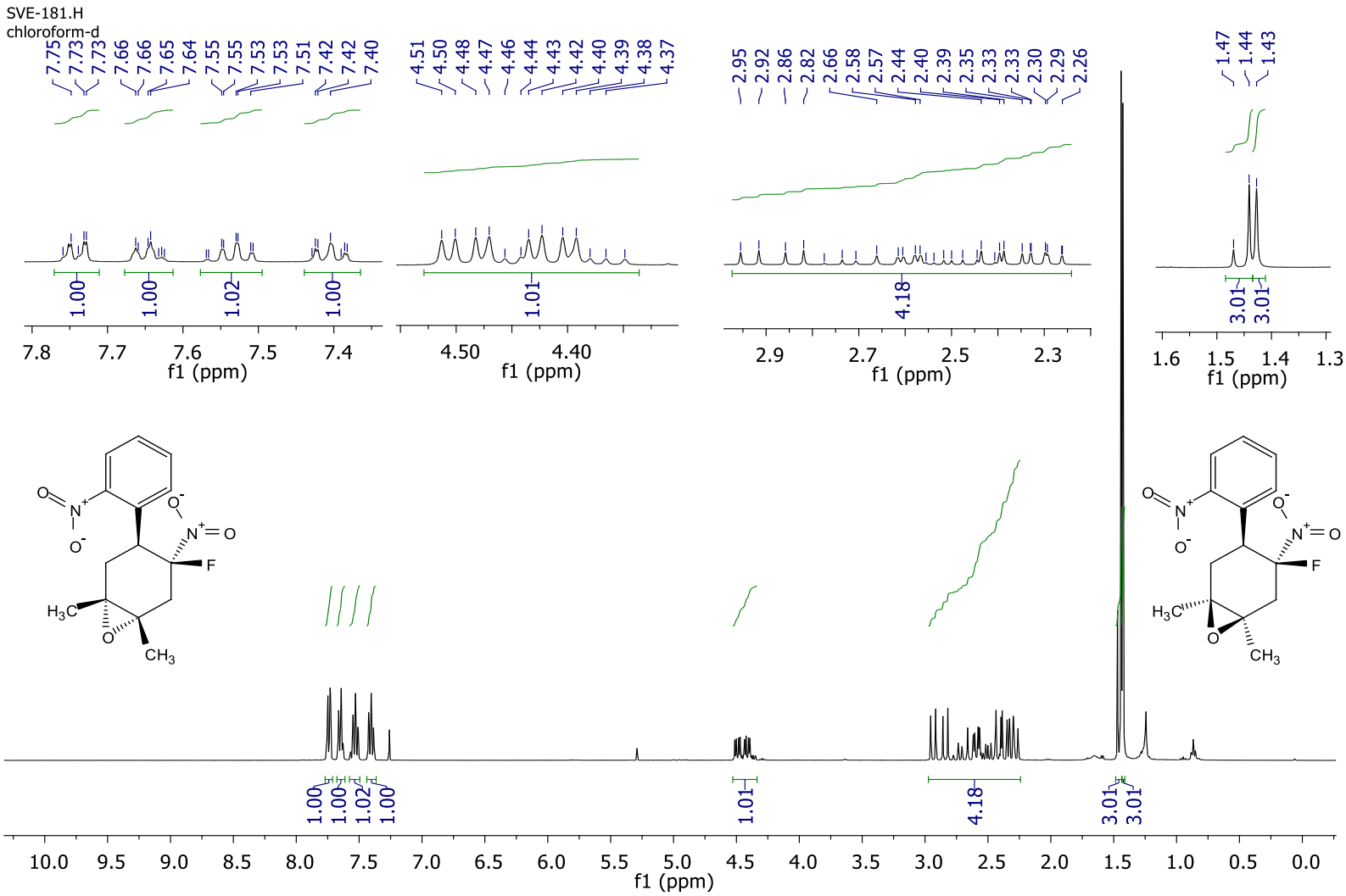
^{1}H NMR spectrum of 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzonitrile (**2g**)



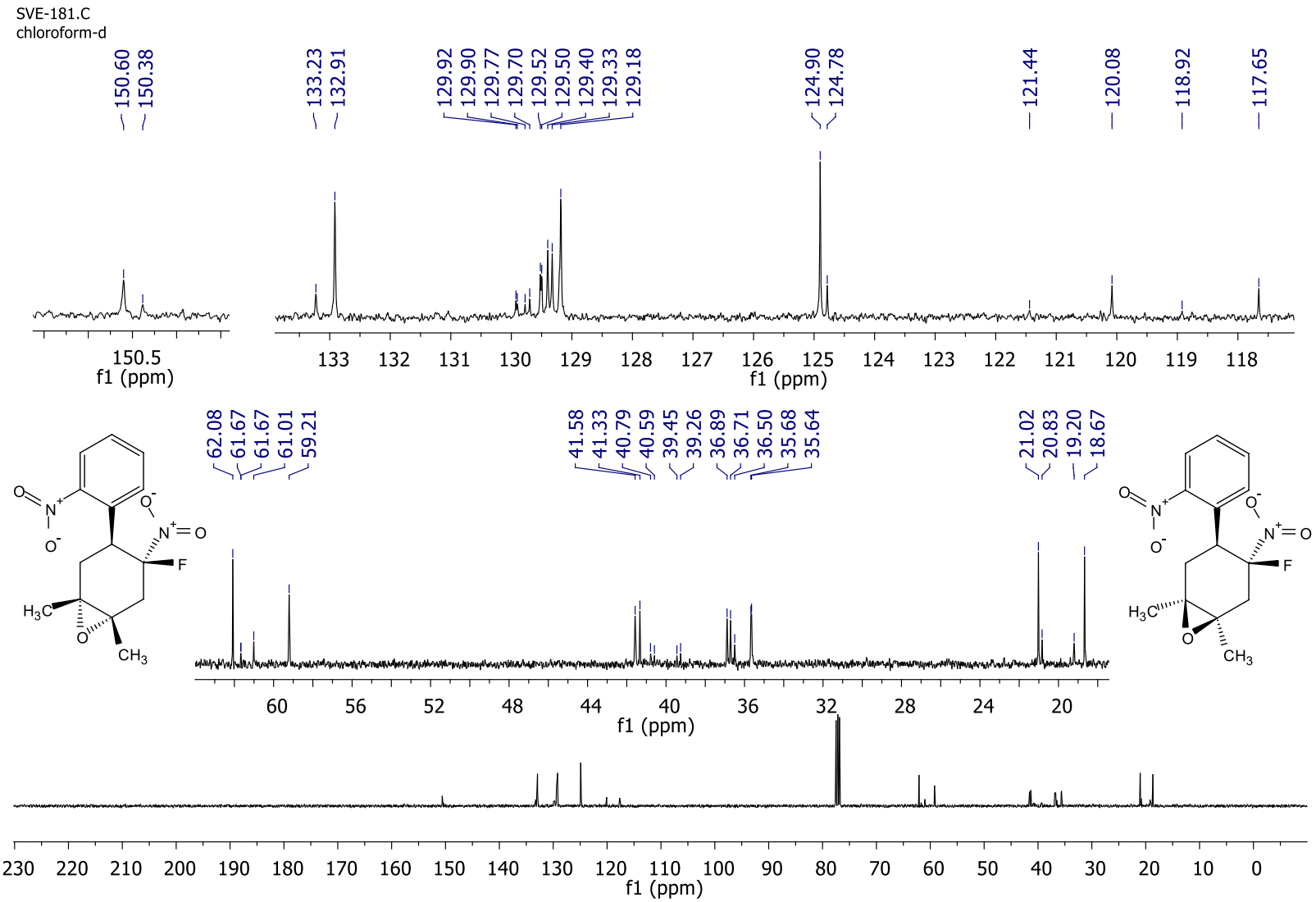
^{13}C NMR spectrum of 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzonitrile (**2g**)



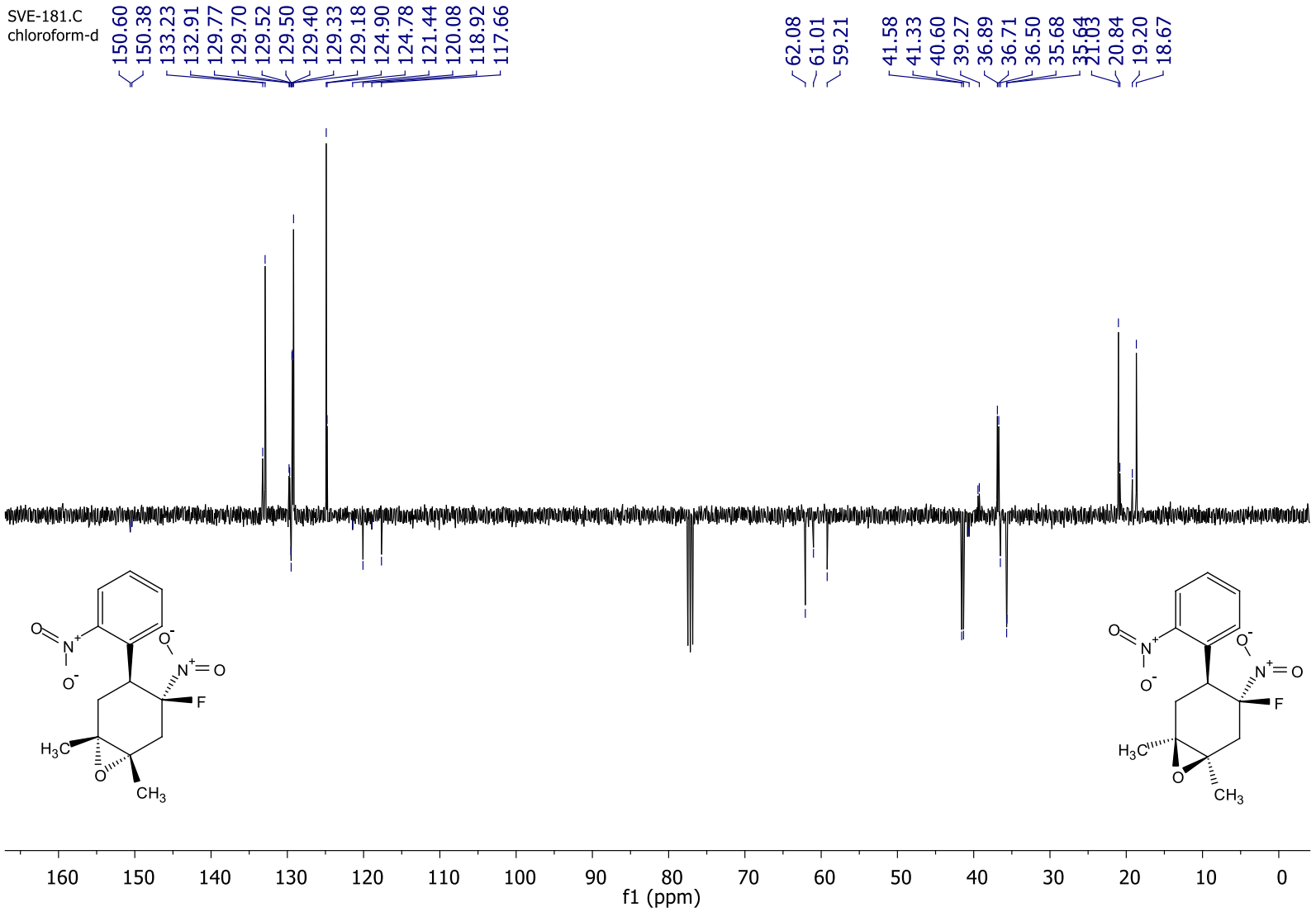
^{19}F NMR spectrum of 4-((1R*,3S*,4S*,6S*)-4-fluoro-1,6-dimethyl-4-nitro-7-oxabicyclo[4.1.0]heptan-3-yl)benzonitrile (**2g**)



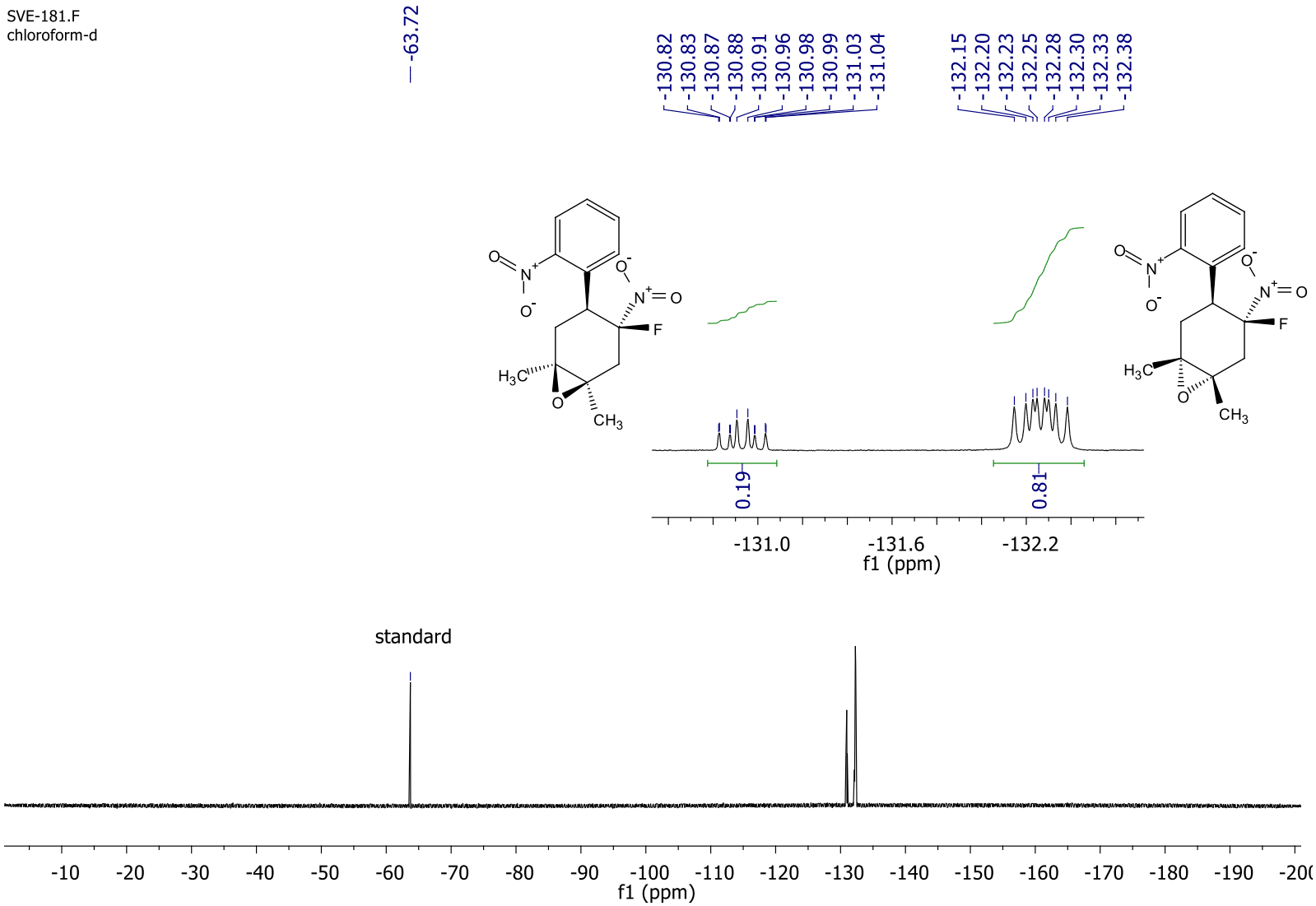
^{1}H NMR spectrum of mixture of 81% of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-major) and 19% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-minor)



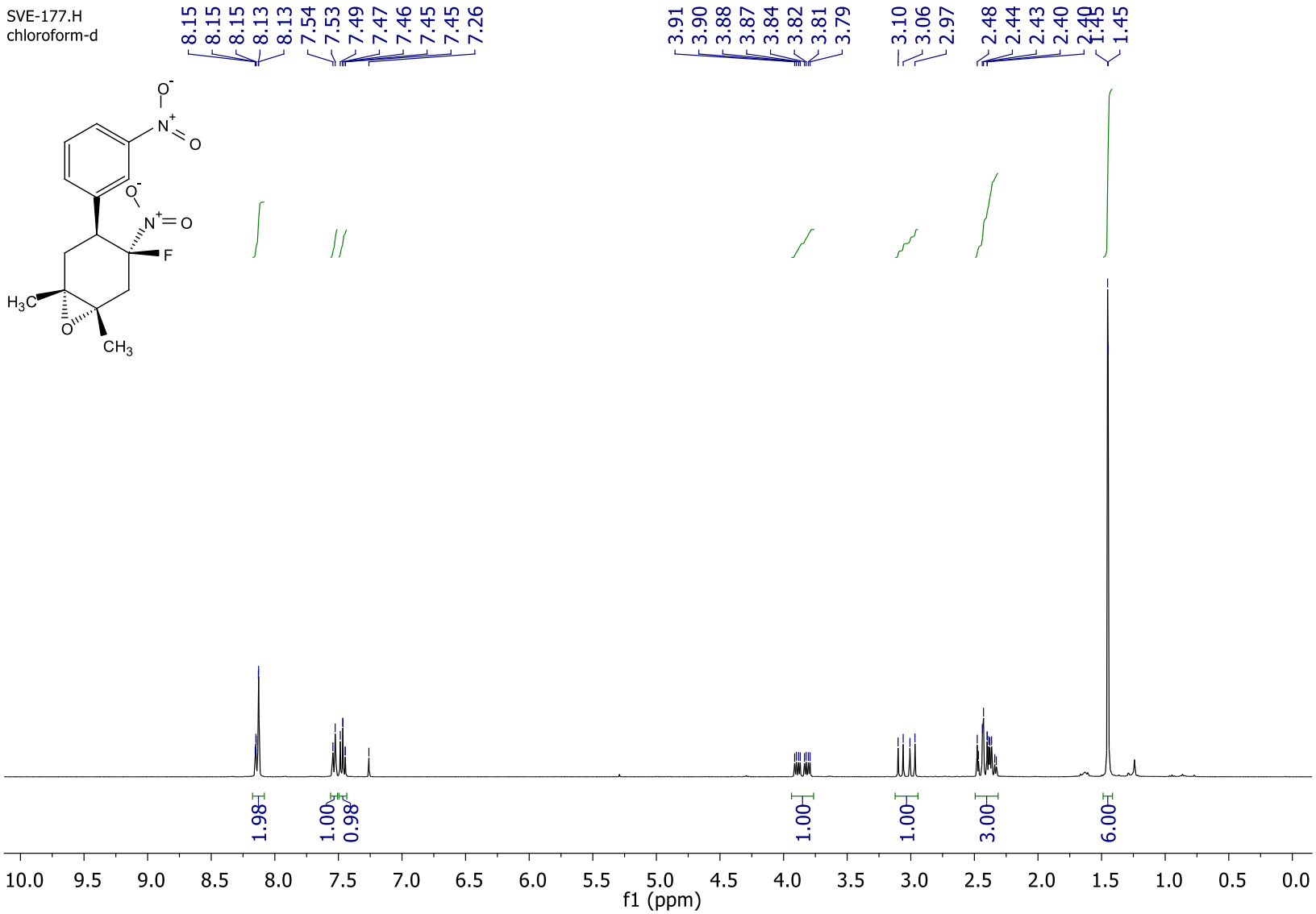
^{13}C NMR spectrum of mixture of 81% of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-major) and 19% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-minor)



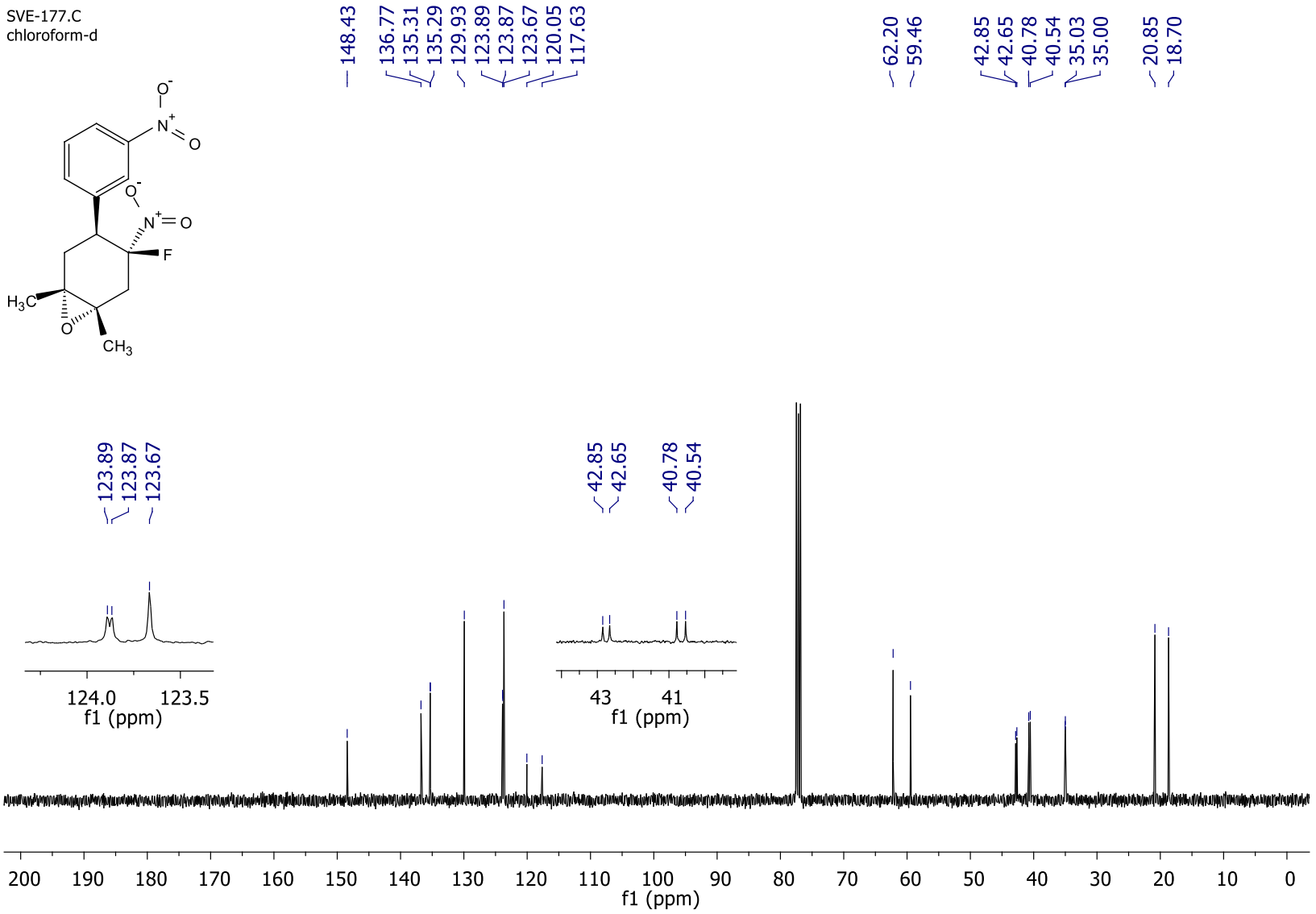
^{13}C APT NMR spectrum of mixture of 81% of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-major) and 19% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-minor)



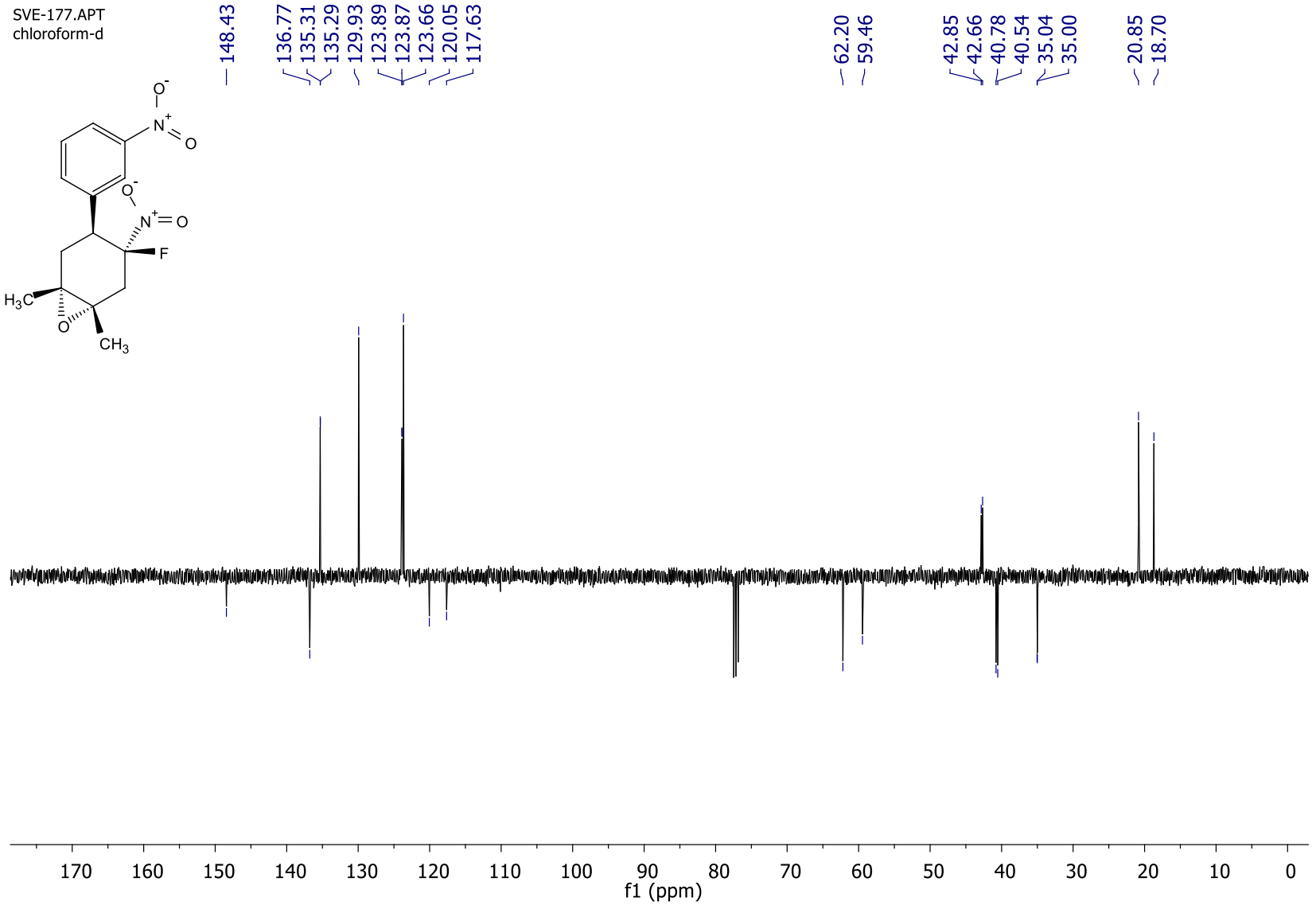
^{19}F NMR spectrum of mixture of 81% of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-major) and 19% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(2-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2h**-minor)



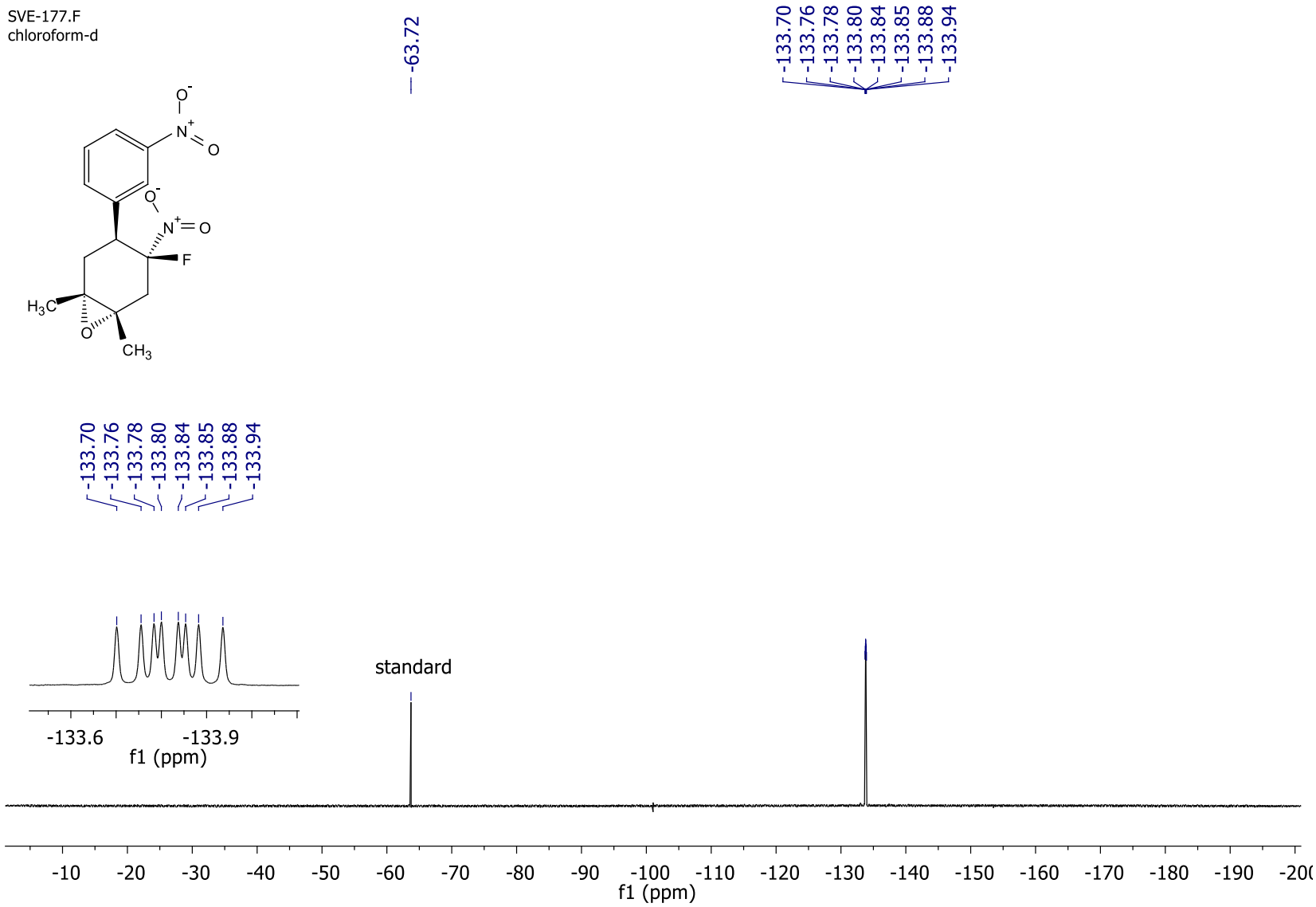
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(3-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2i**)



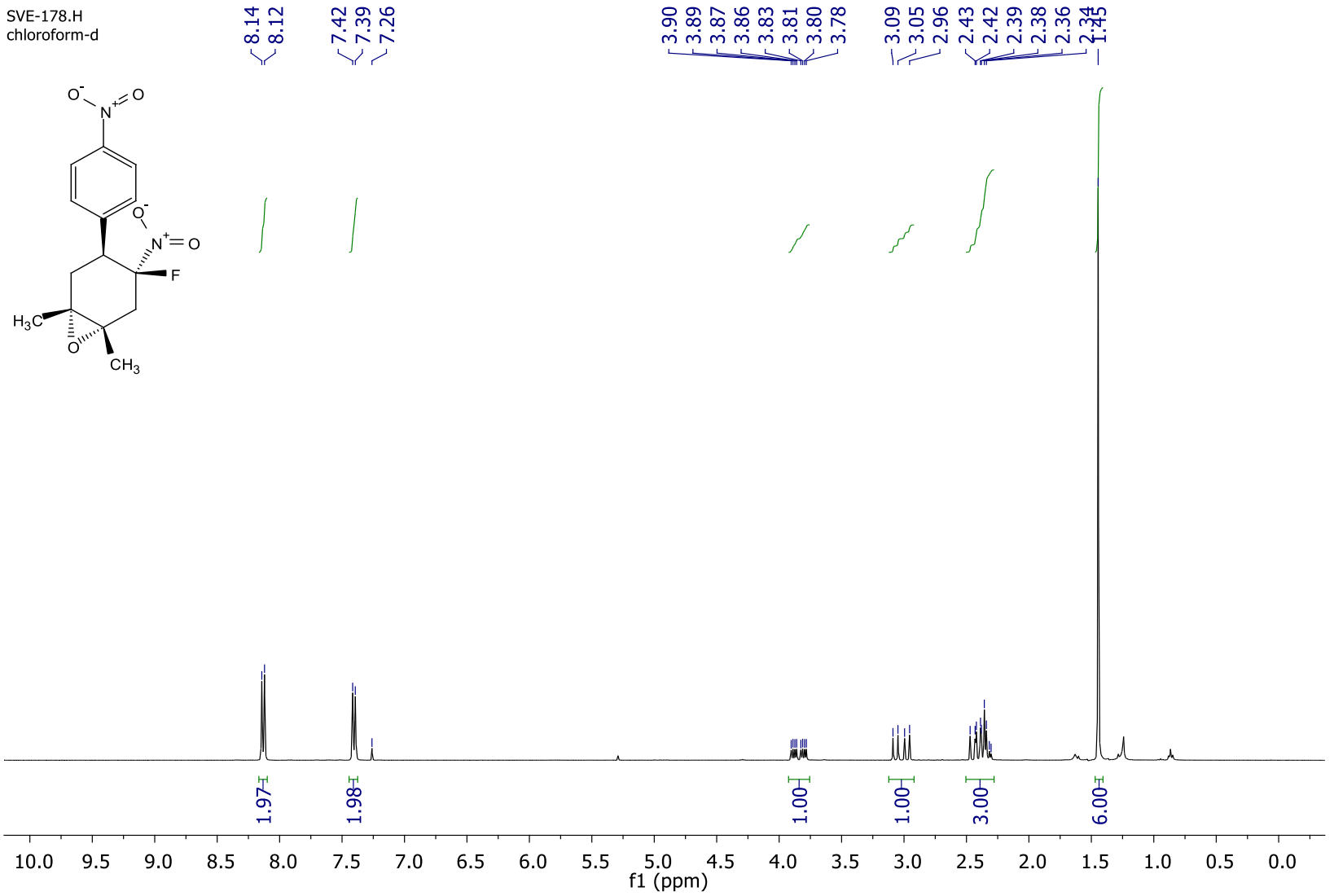
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(3-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2i**)



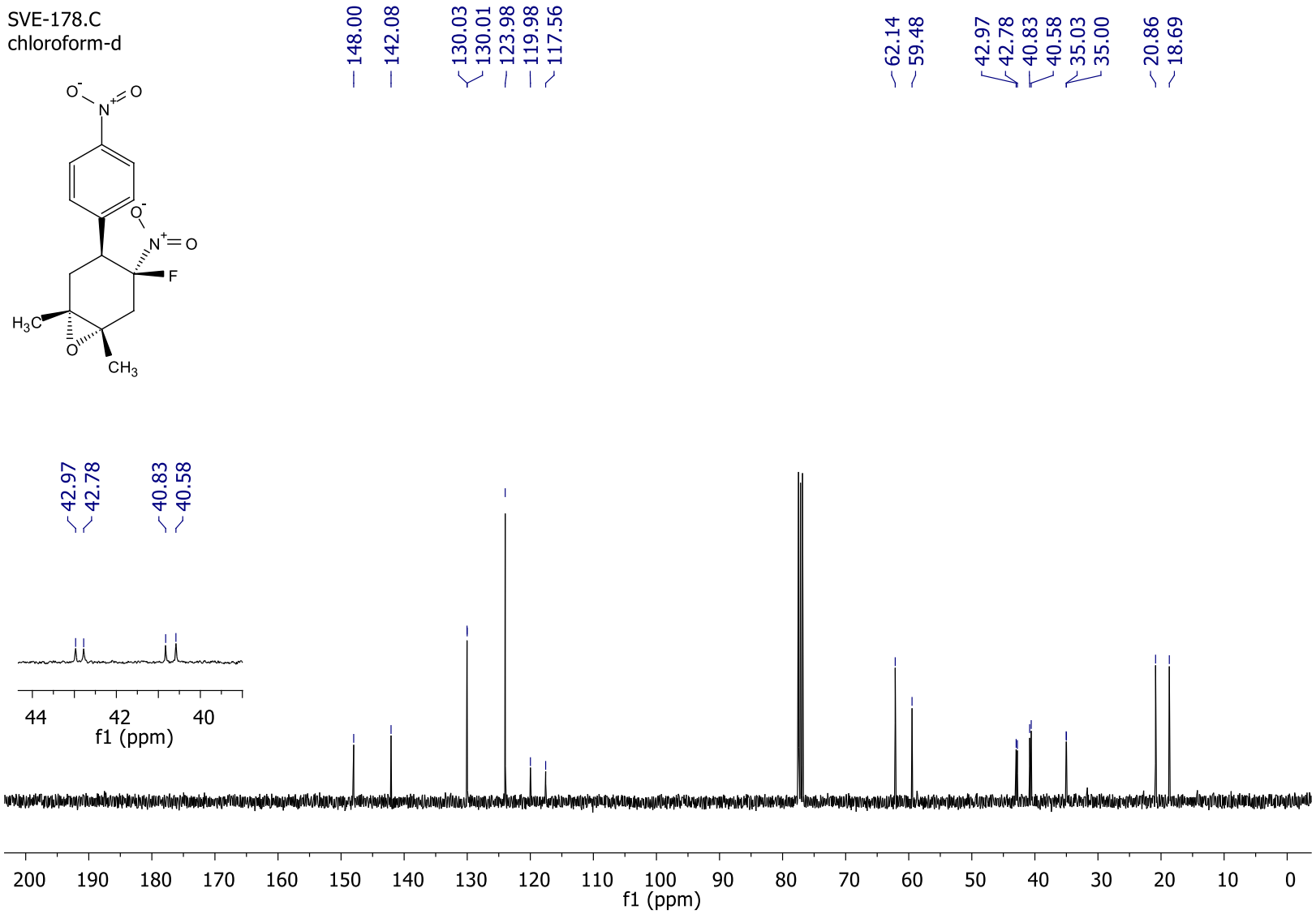
^{13}C APT NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(3-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2i**)



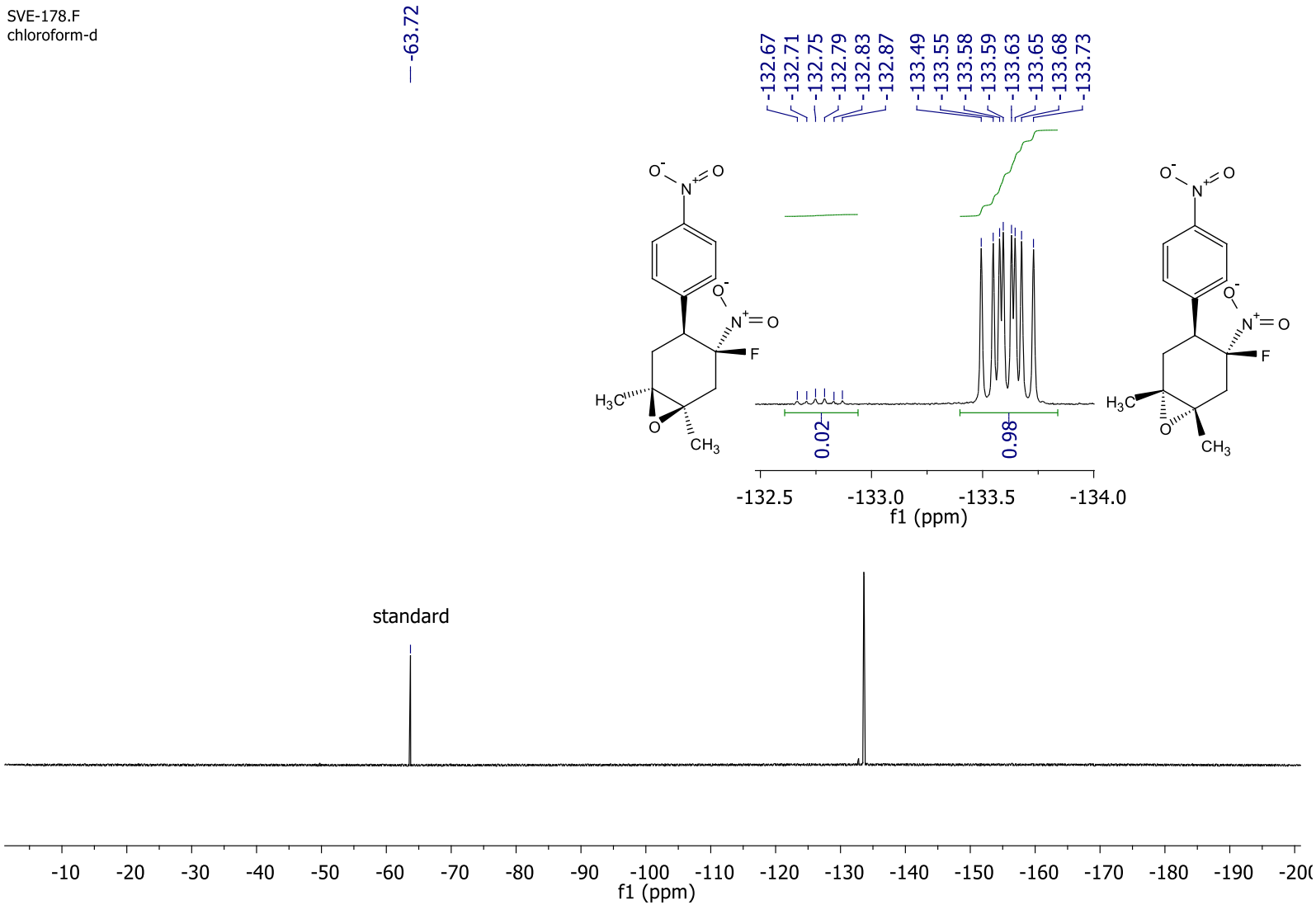
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(3-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2i**)



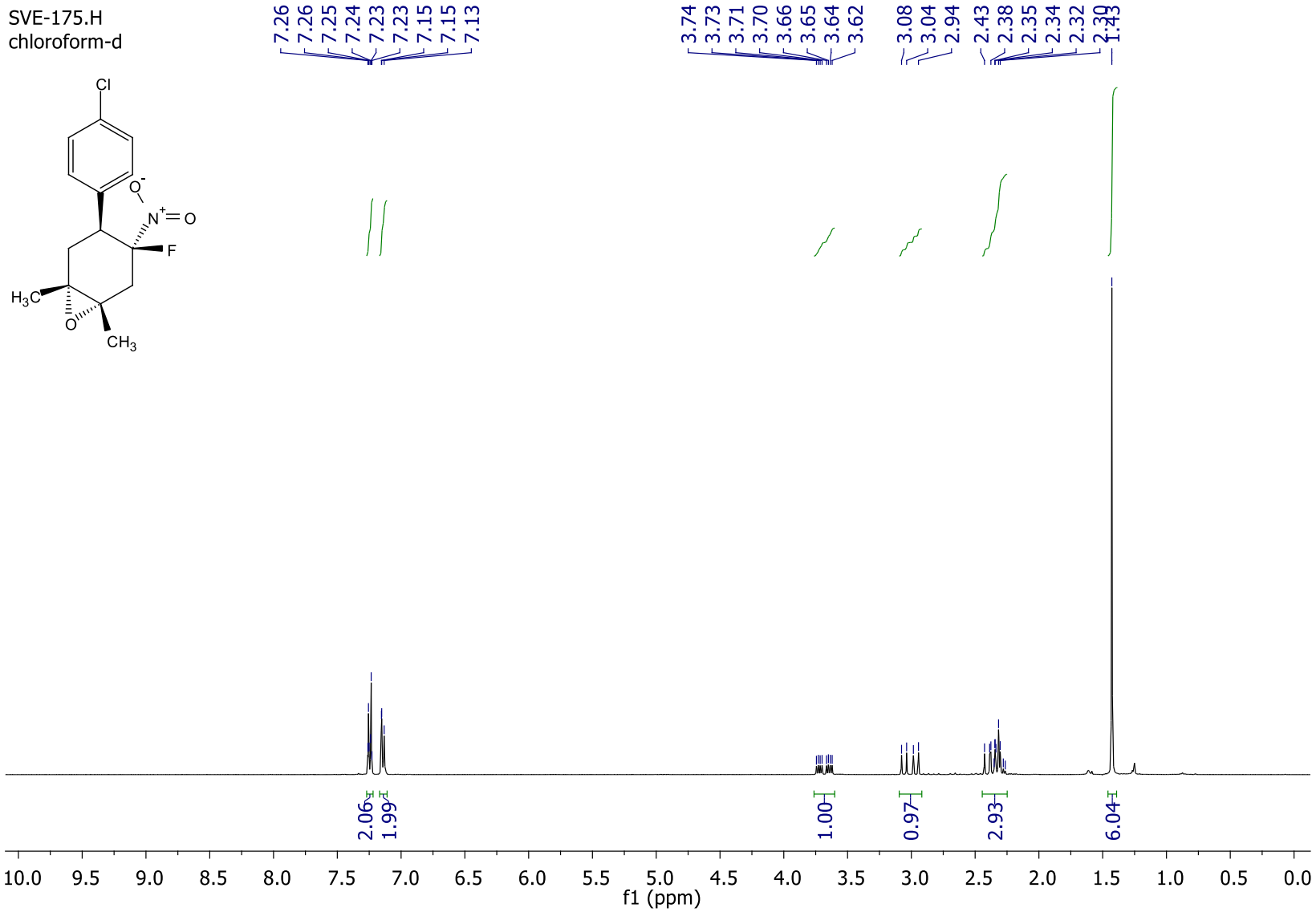
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2j**)



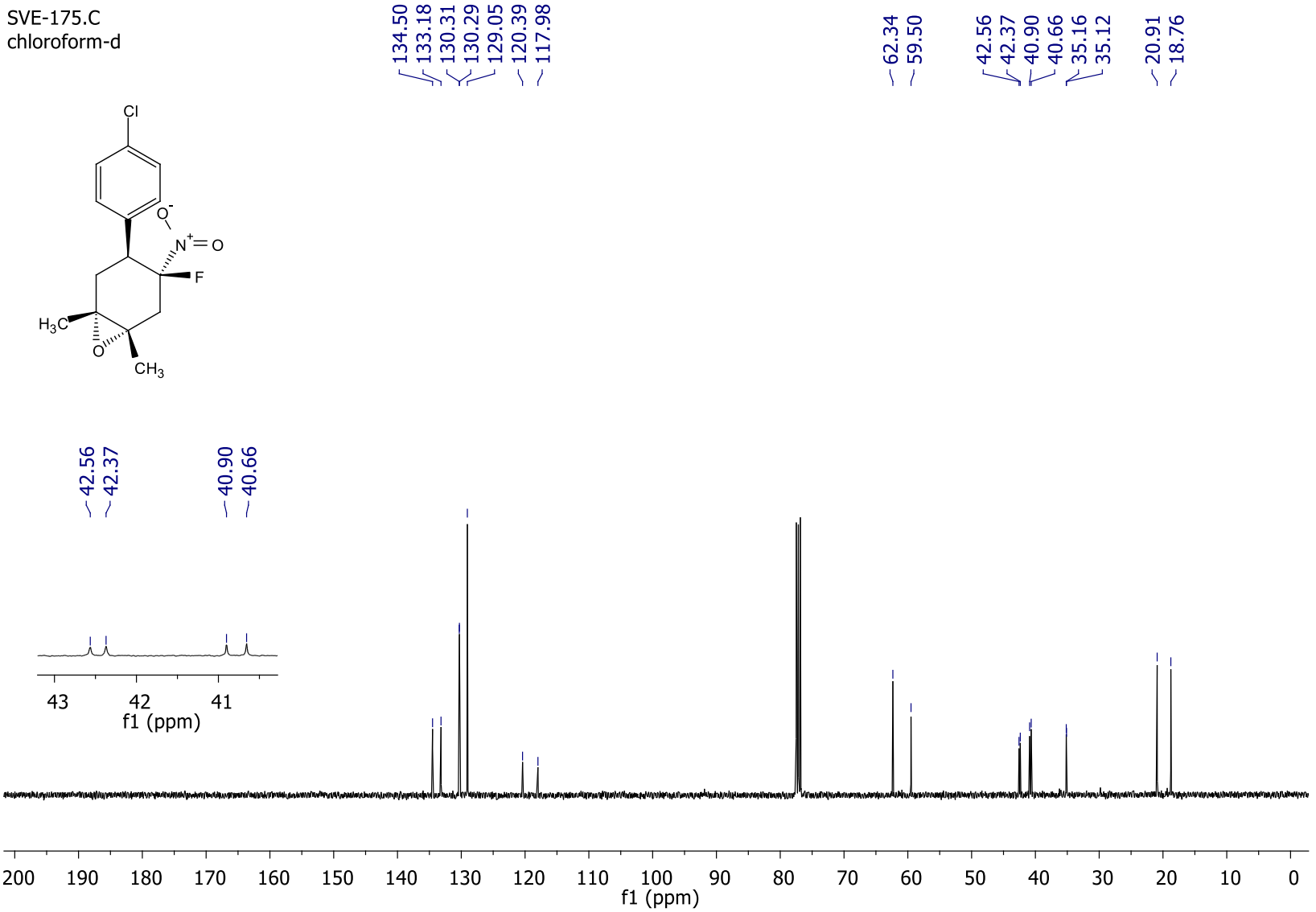
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2j**)



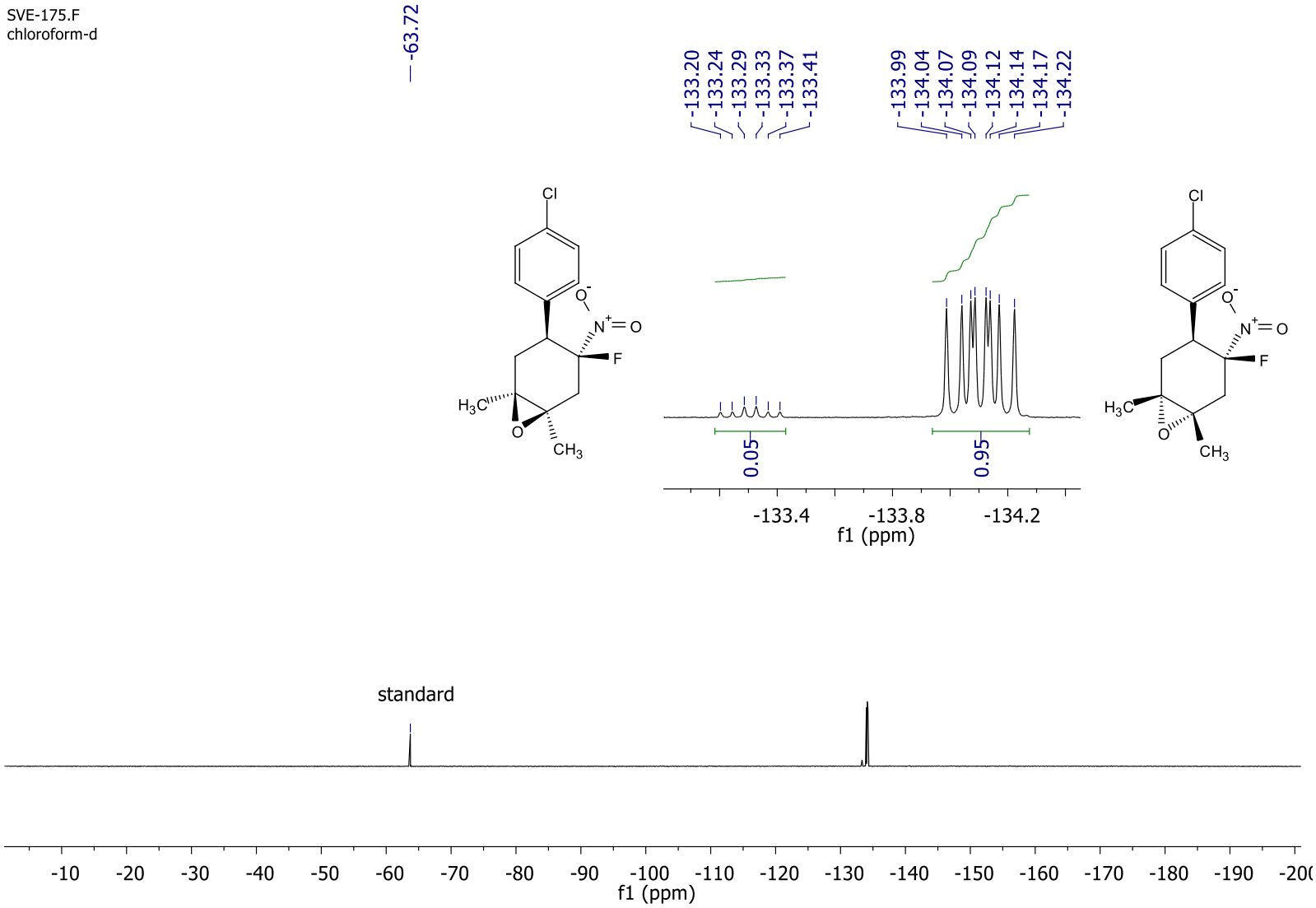
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2j**-major) with 2% of (1R*,3S*,4S*,6S*)-3-fluoro-1,6-dimethyl-3-nitro-4-(4-nitrophenyl)-7-oxabicyclo[4.1.0]heptane (**2j**-minor)



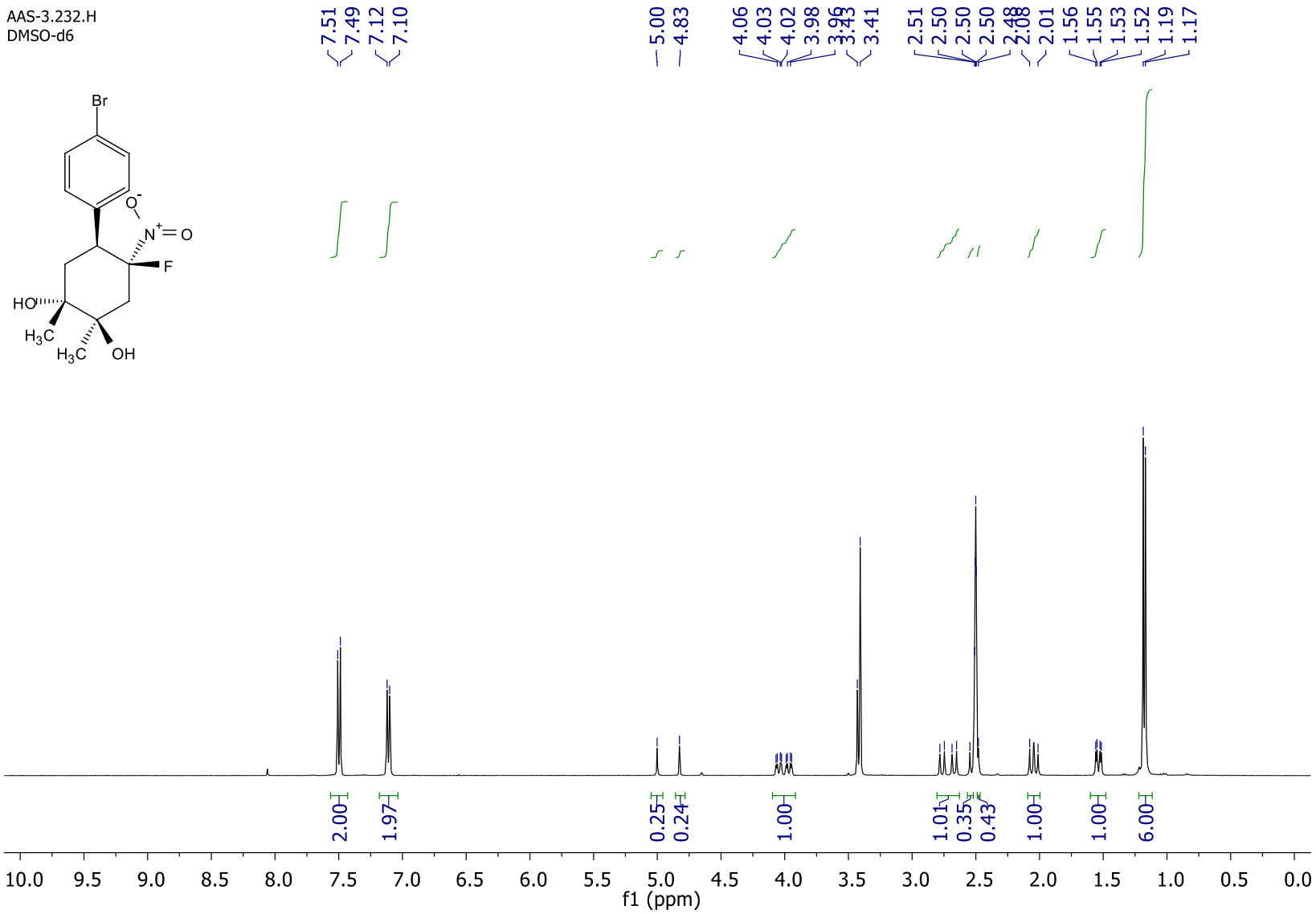
^{1}H NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-chlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2k**)



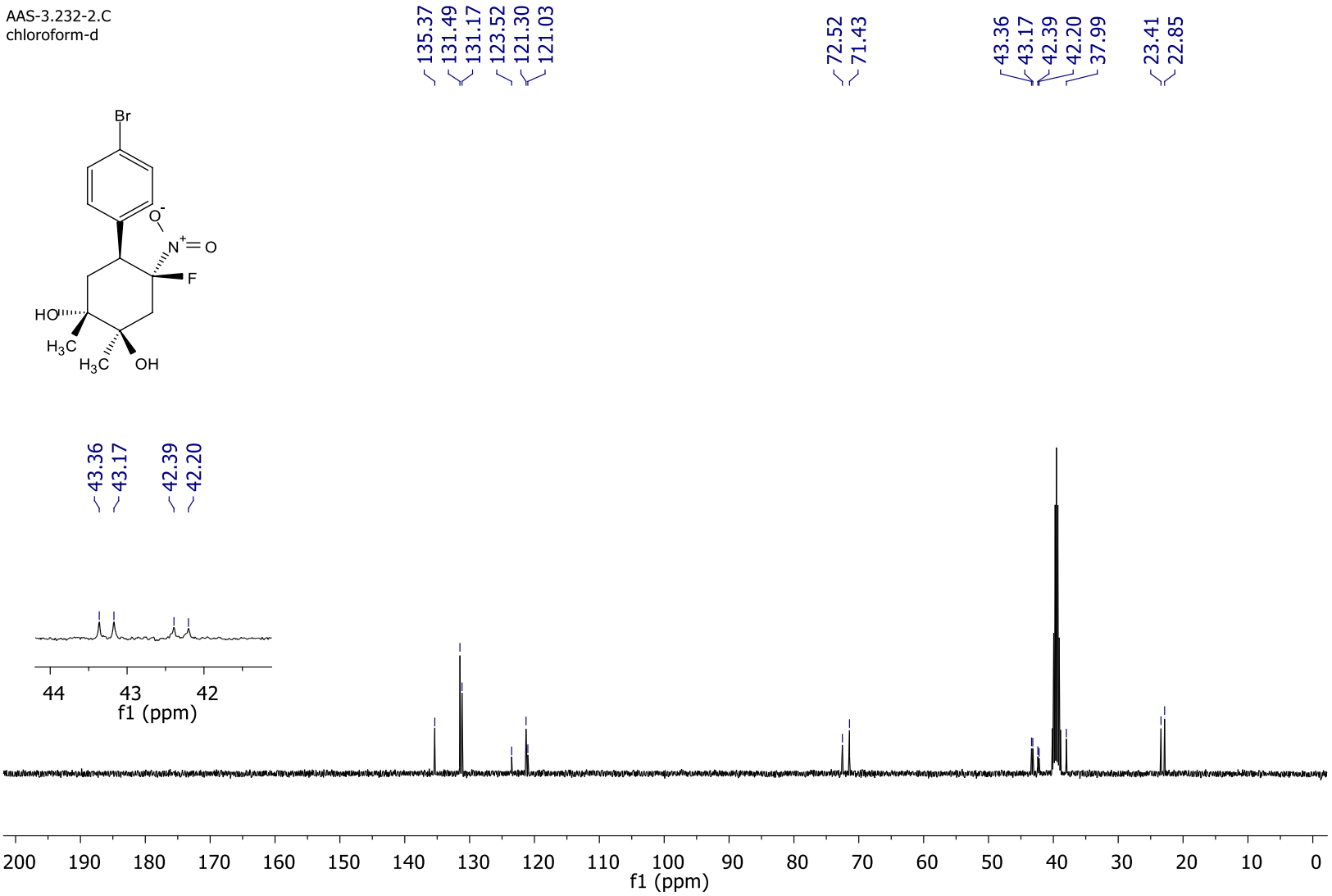
^{13}C NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-chlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2k**)



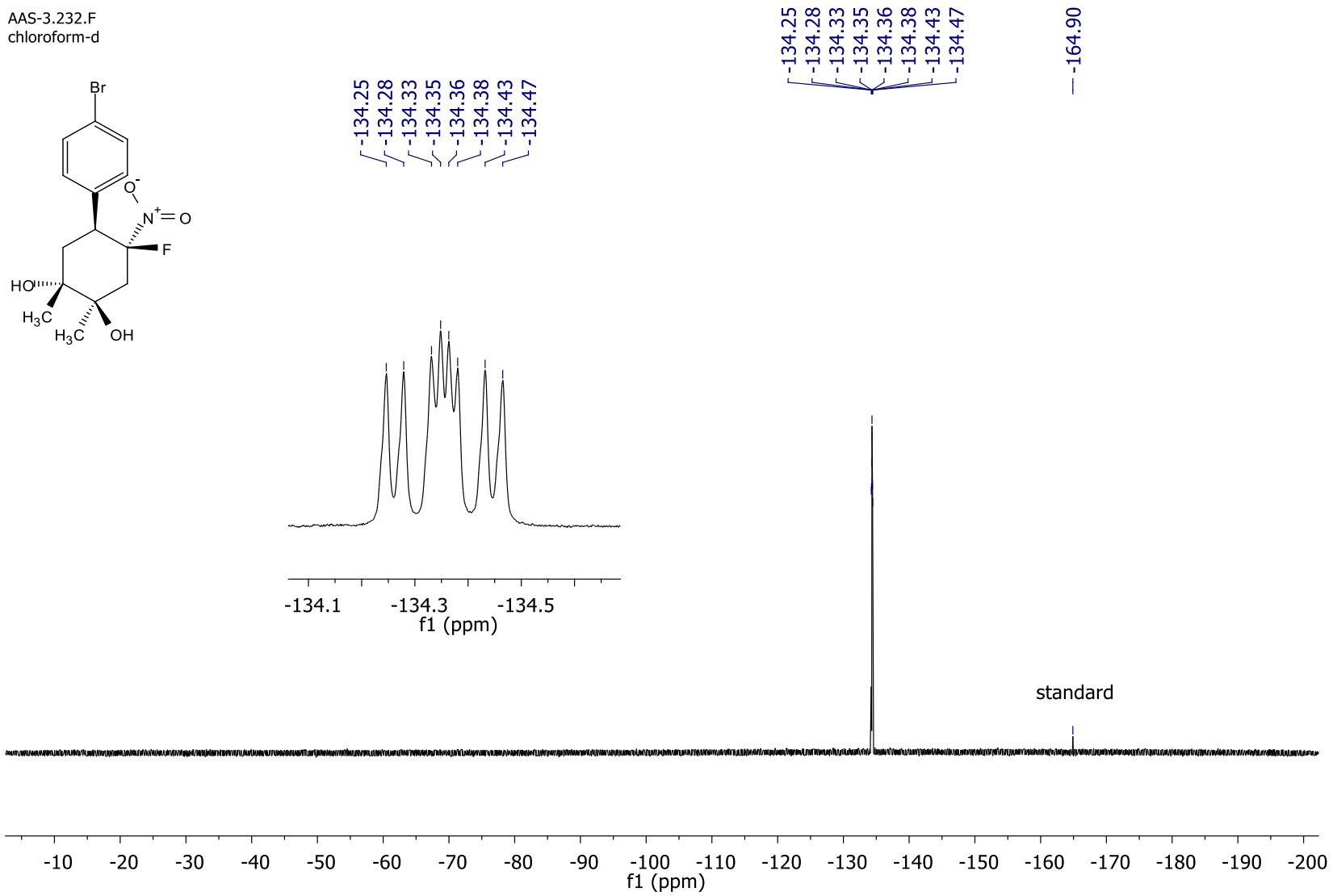
^{19}F NMR spectrum of (1S*,3S*,4S*,6R*)-4-(4-chlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2k**-major) with 5% of (1R*,3S*,4S*,6S*)-4-(4-chlorophenyl)-3-fluoro-1,6-dimethyl-3-nitro-7-oxabicyclo[4.1.0]heptane (**2k**-minor)



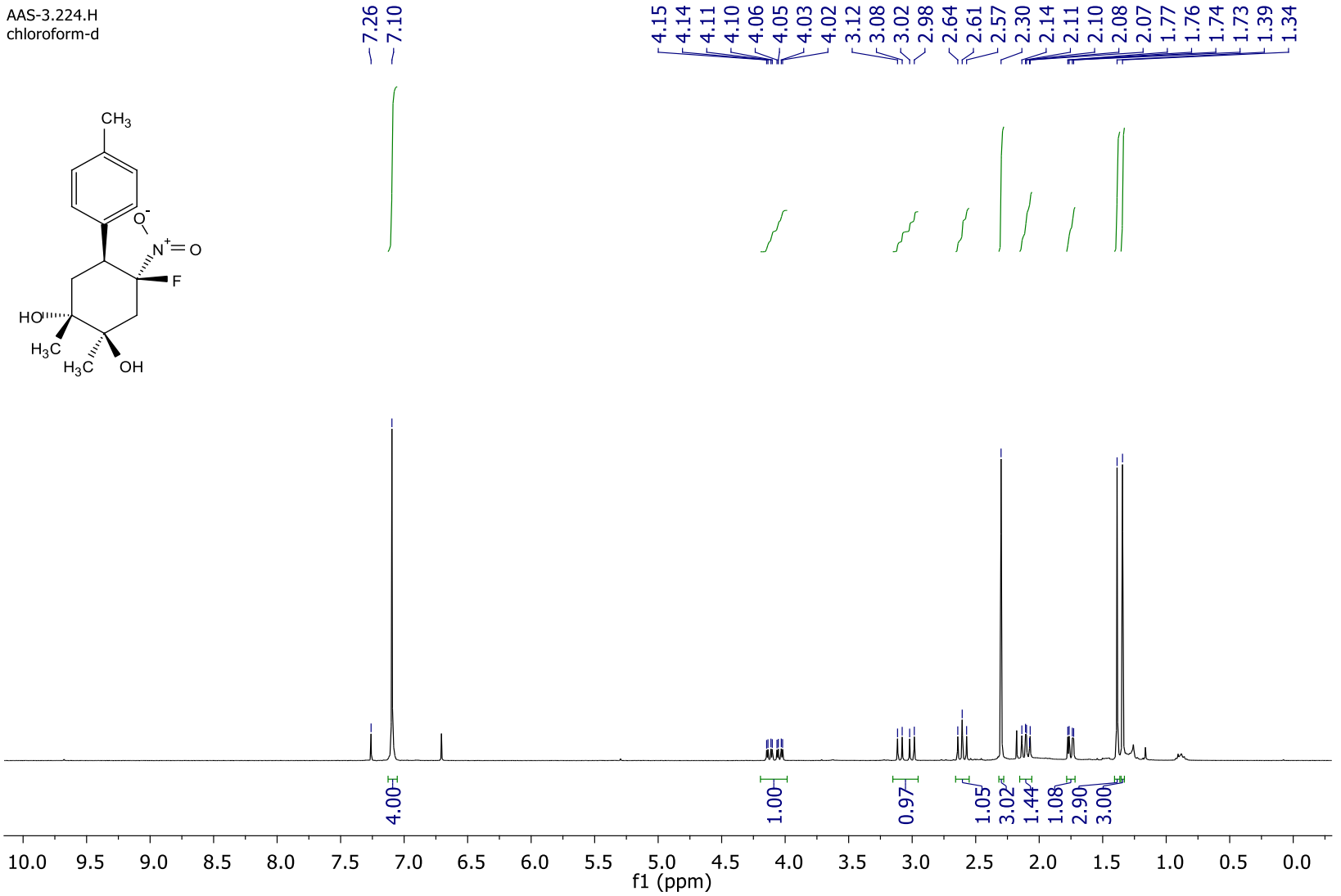
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-5-(4-bromophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3a**)



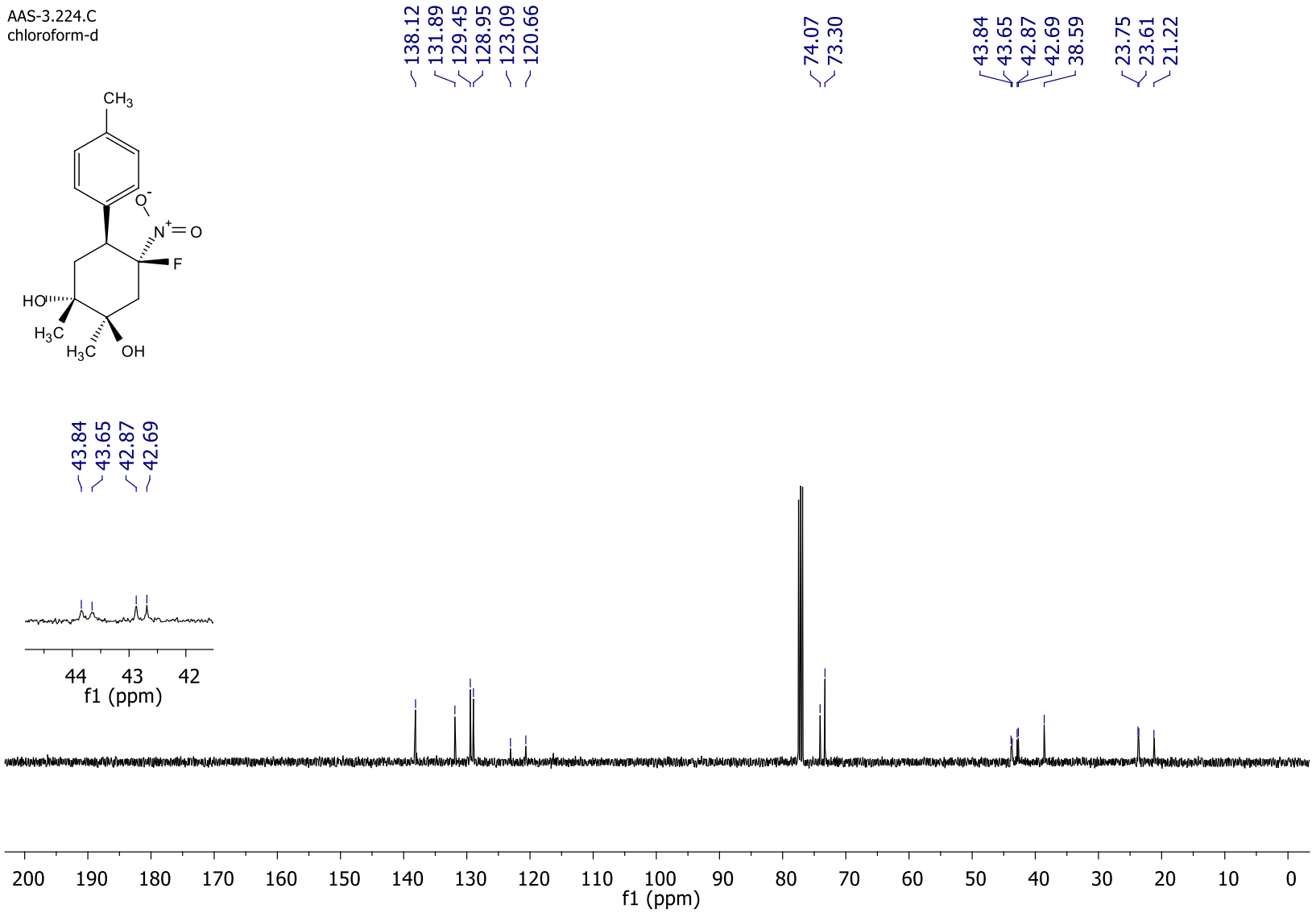
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-5-(4-bromophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3a**)



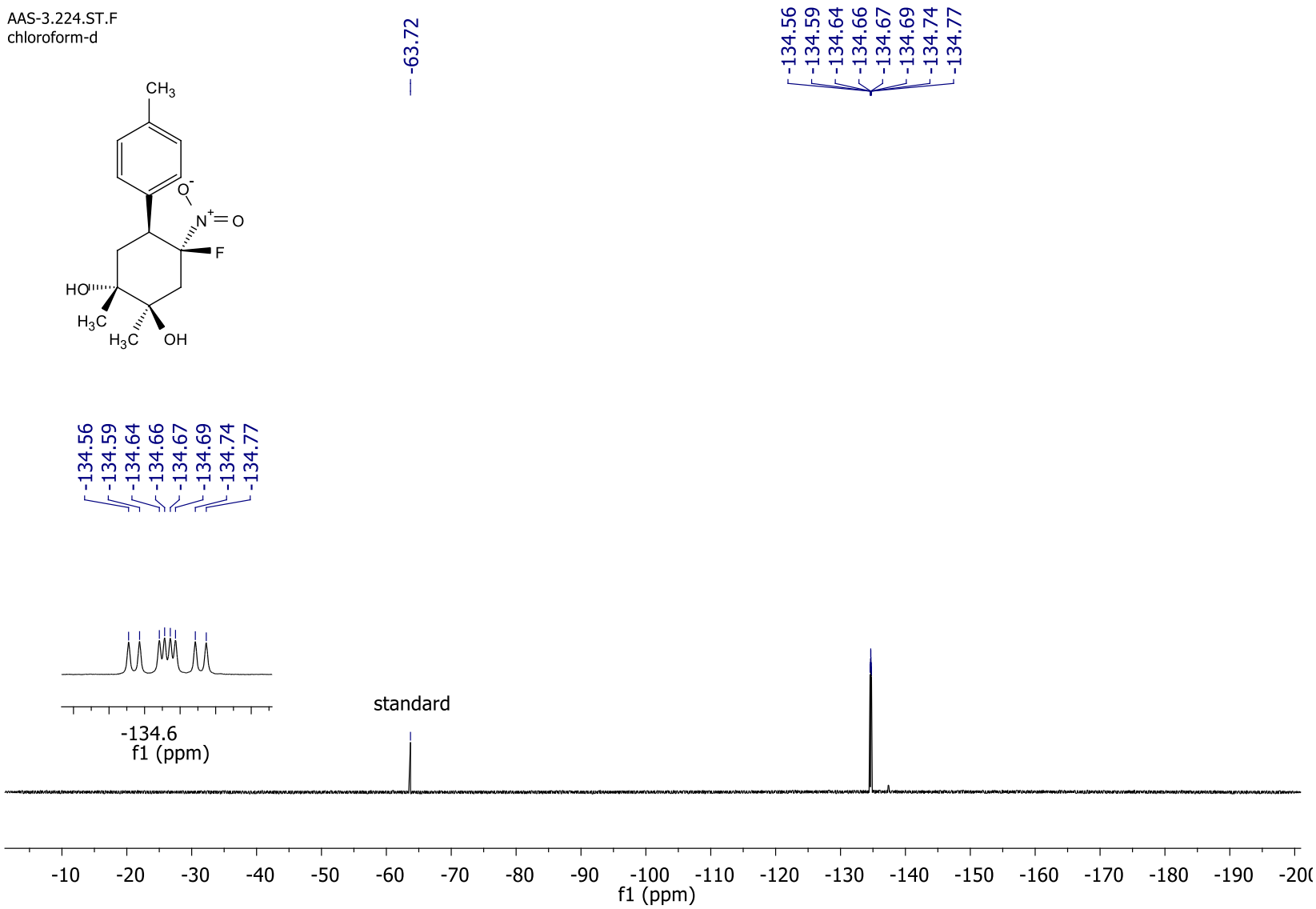
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-5-(4-bromophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3a**)



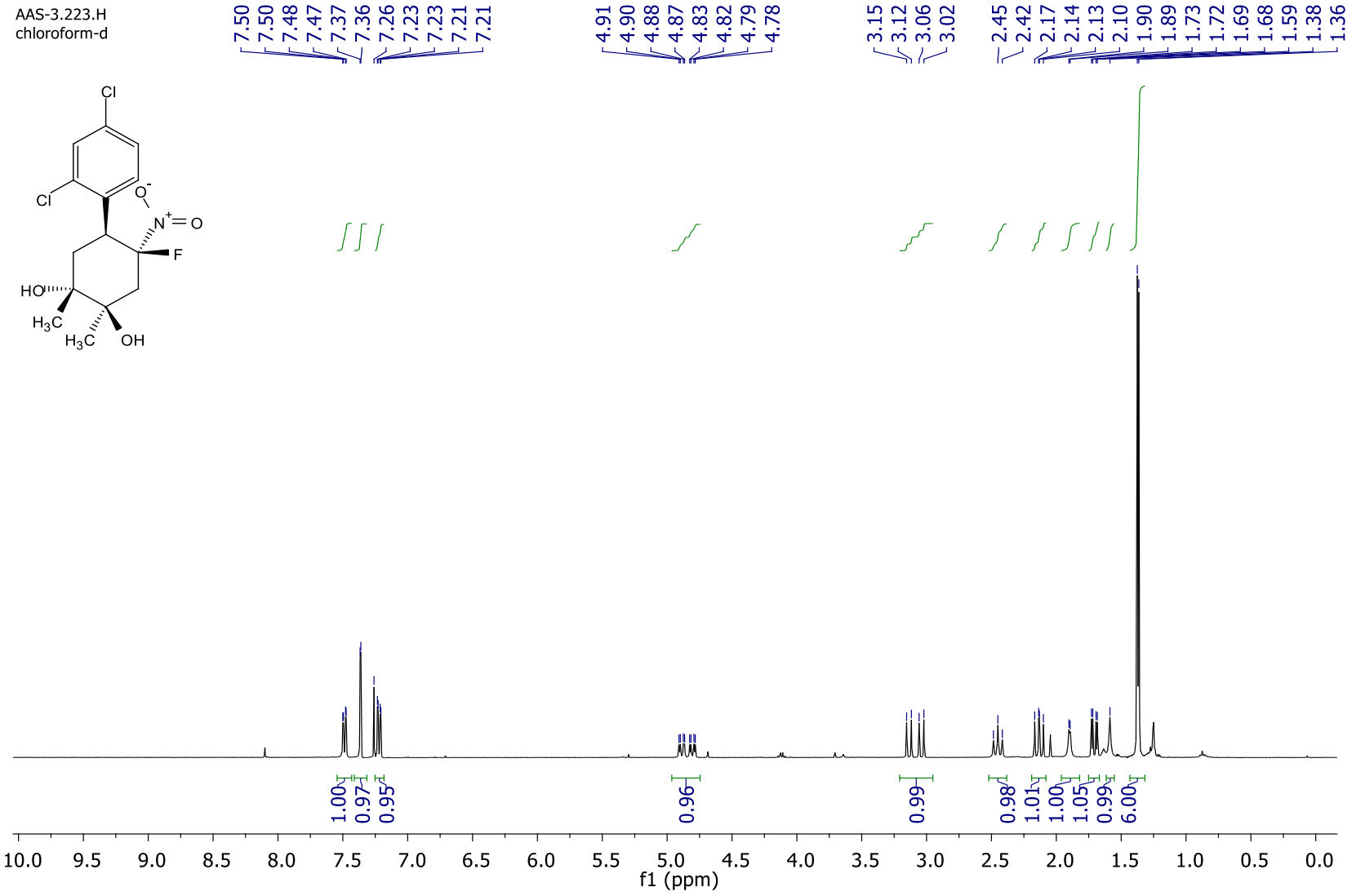
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(p-tolyl)cyclohexane-1,2-diol (**3c**)



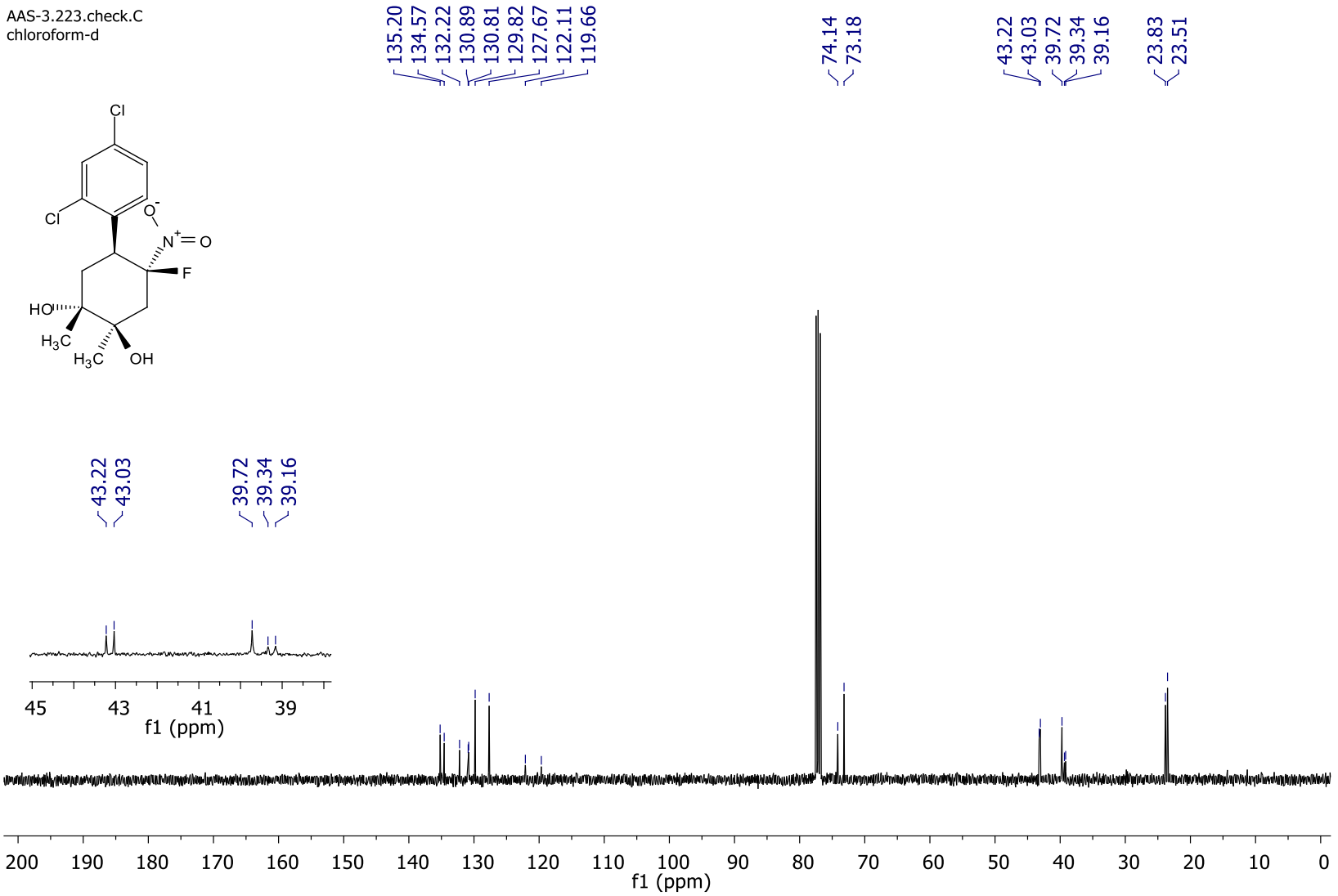
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(p-tolyl)cyclohexane-1,2-diol (**3c**)



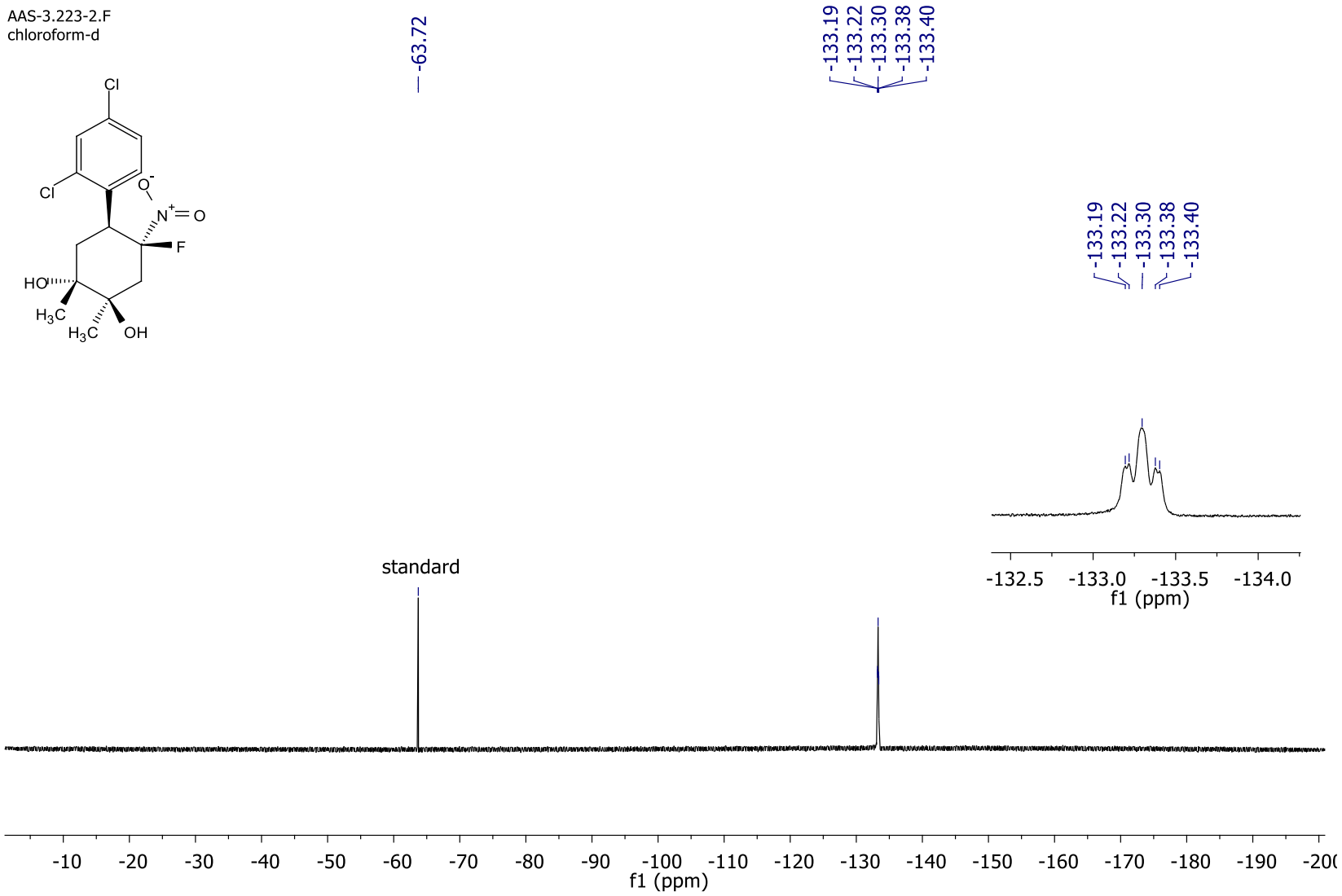
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(p-tolyl)cyclohexane-1,2-diol (**3c**)



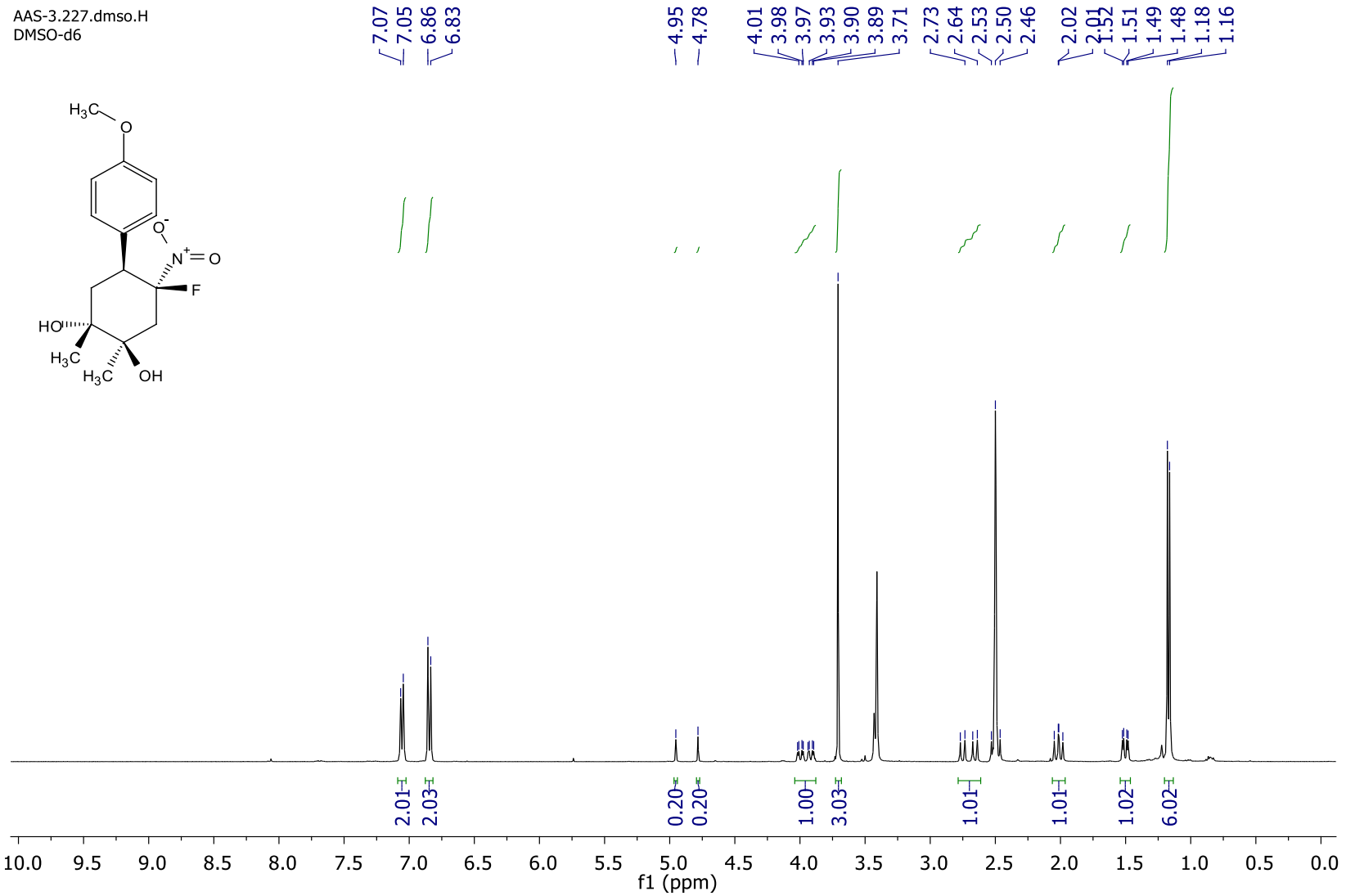
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-5-(2,4-dichlorophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3b**)



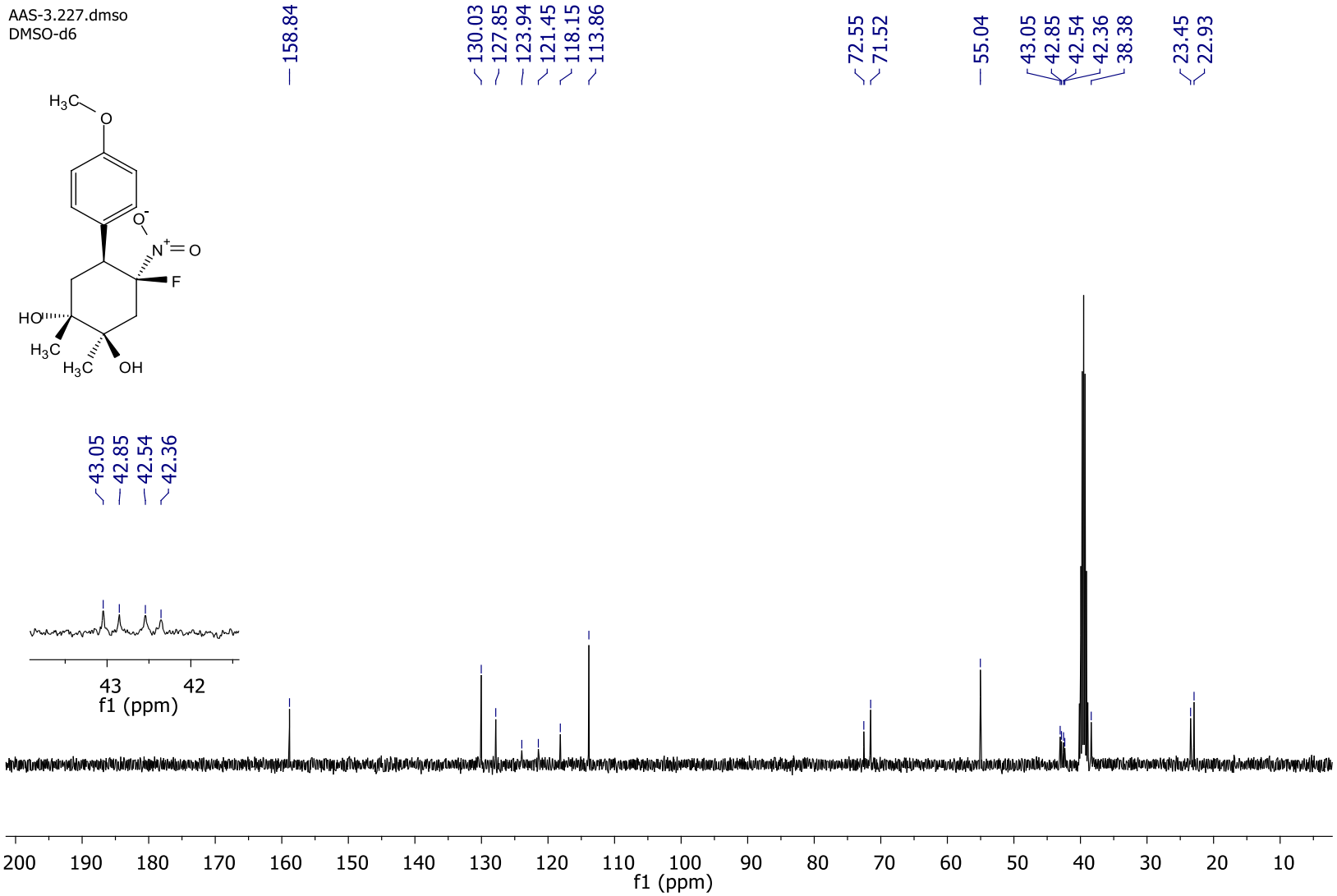
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-5-(2,4-dichlorophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3b**)



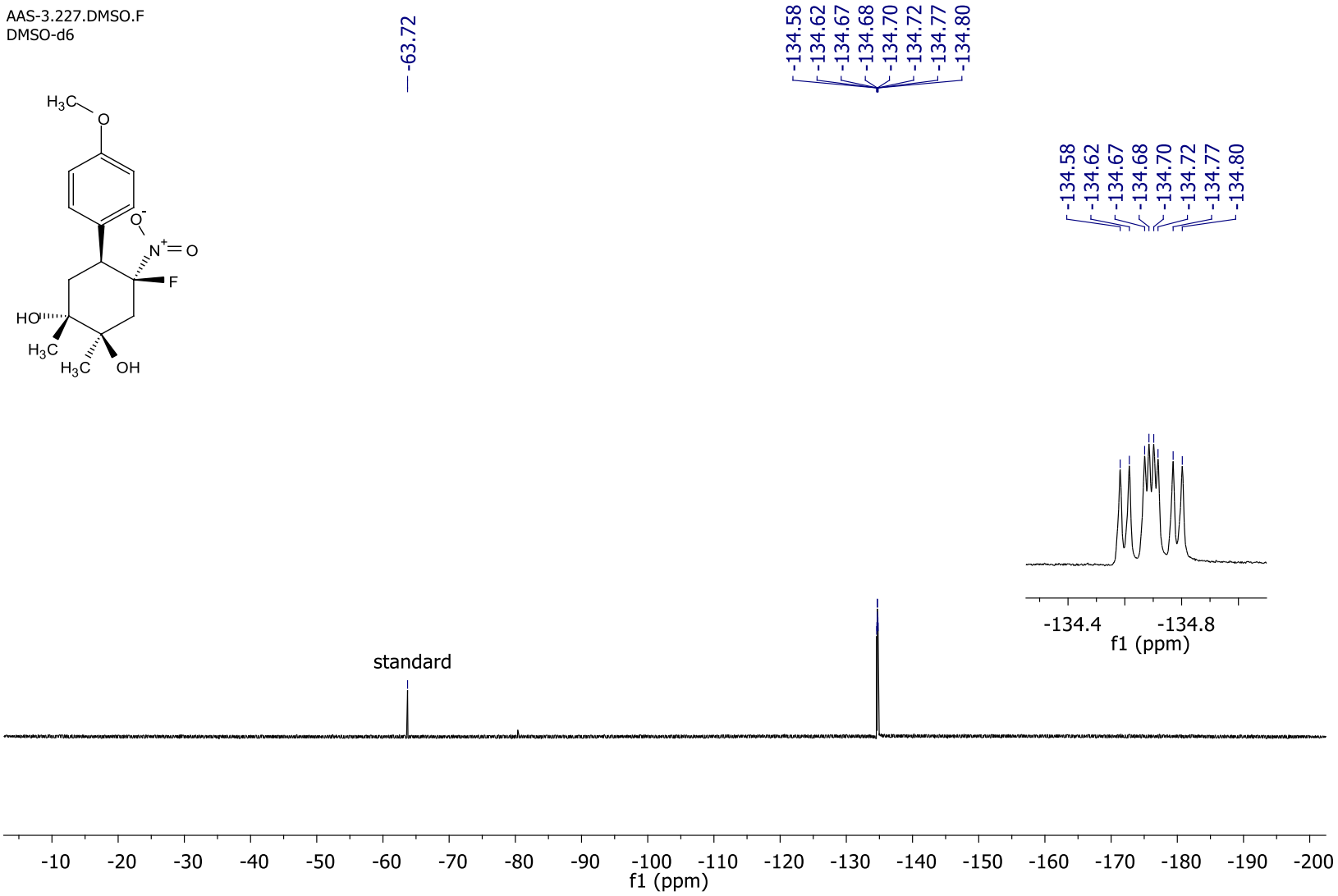
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-5-(2,4-dichlorophenyl)-4-fluoro-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3b**)



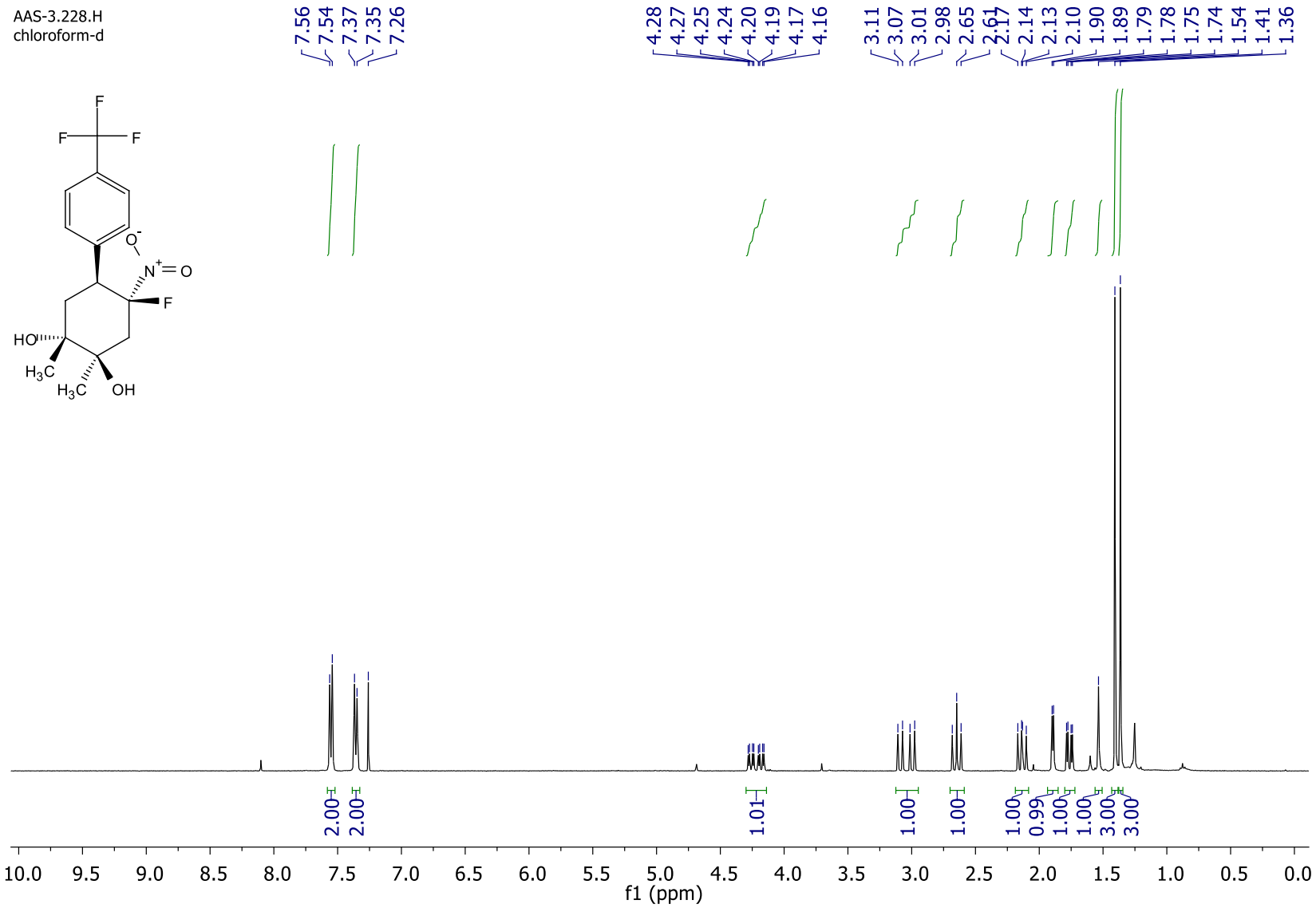
^{1}H NMR spectrum of(1R*,2R*,4S*,5S*)-4-fluoro-5-(4-methoxyphenyl)-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3d**)



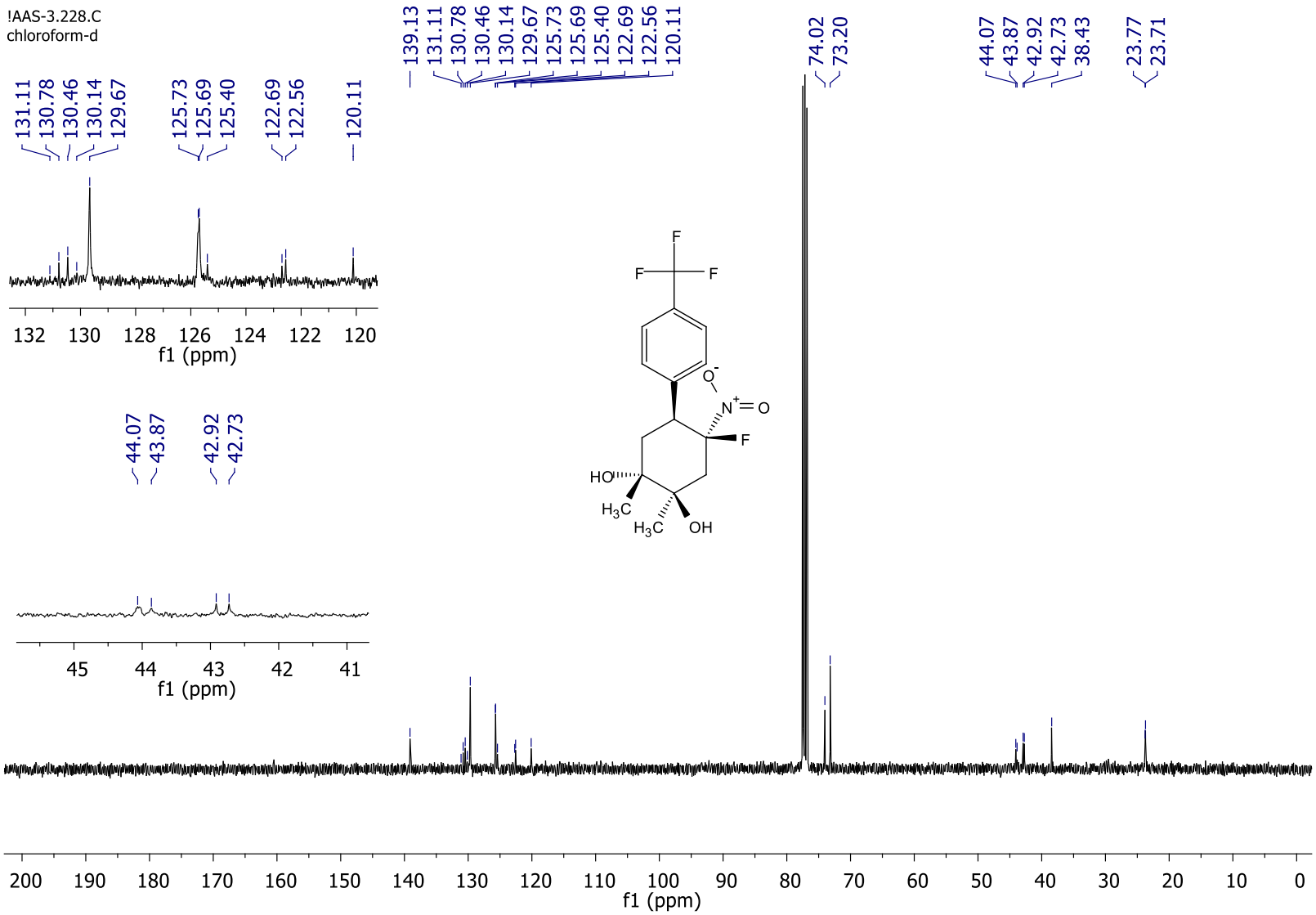
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-5-(4-methoxyphenyl)-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3d**)



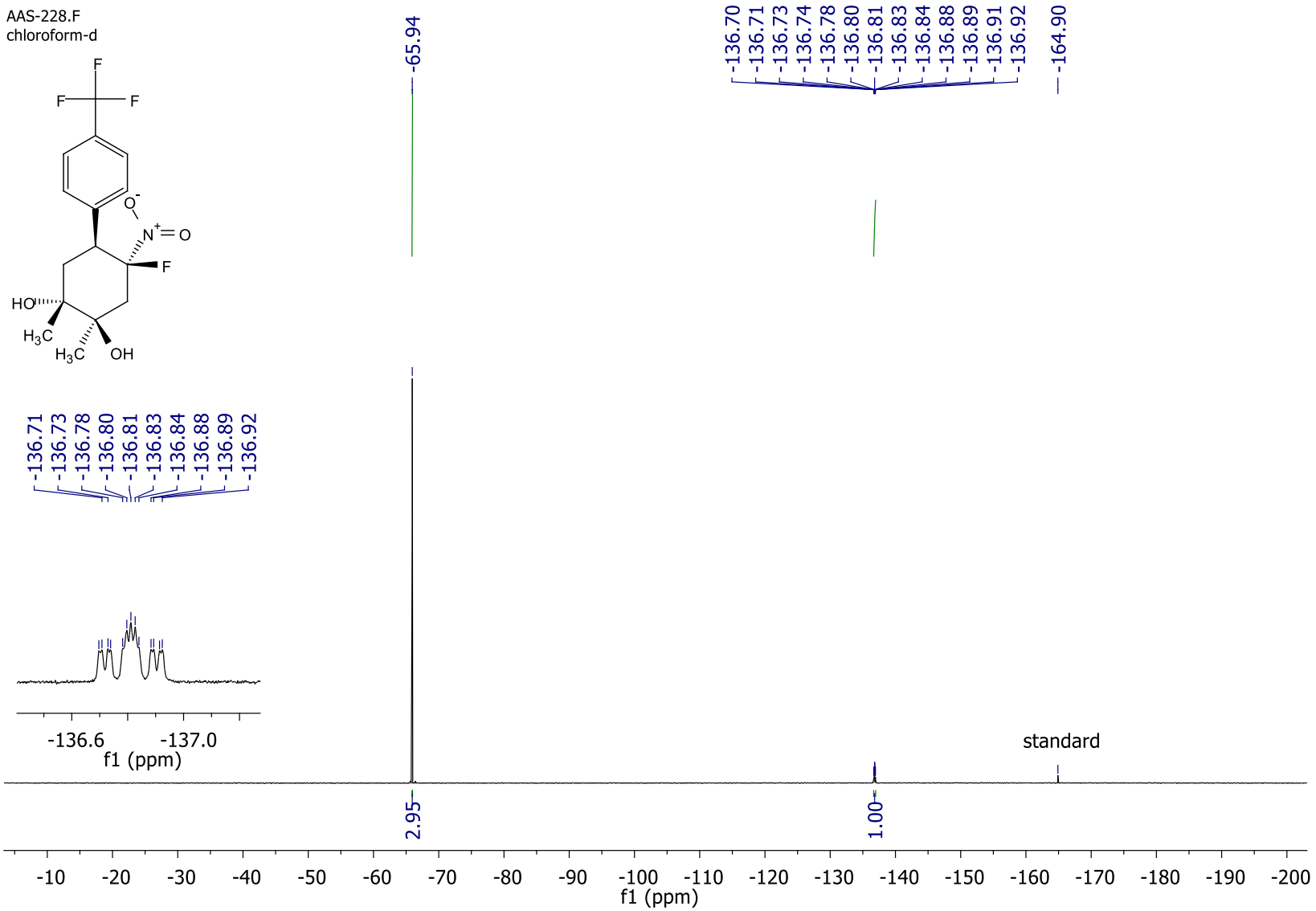
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-5-(4-methoxyphenyl)-1,2-dimethyl-4-nitrocyclohexane-1,2-diol (**3d**)



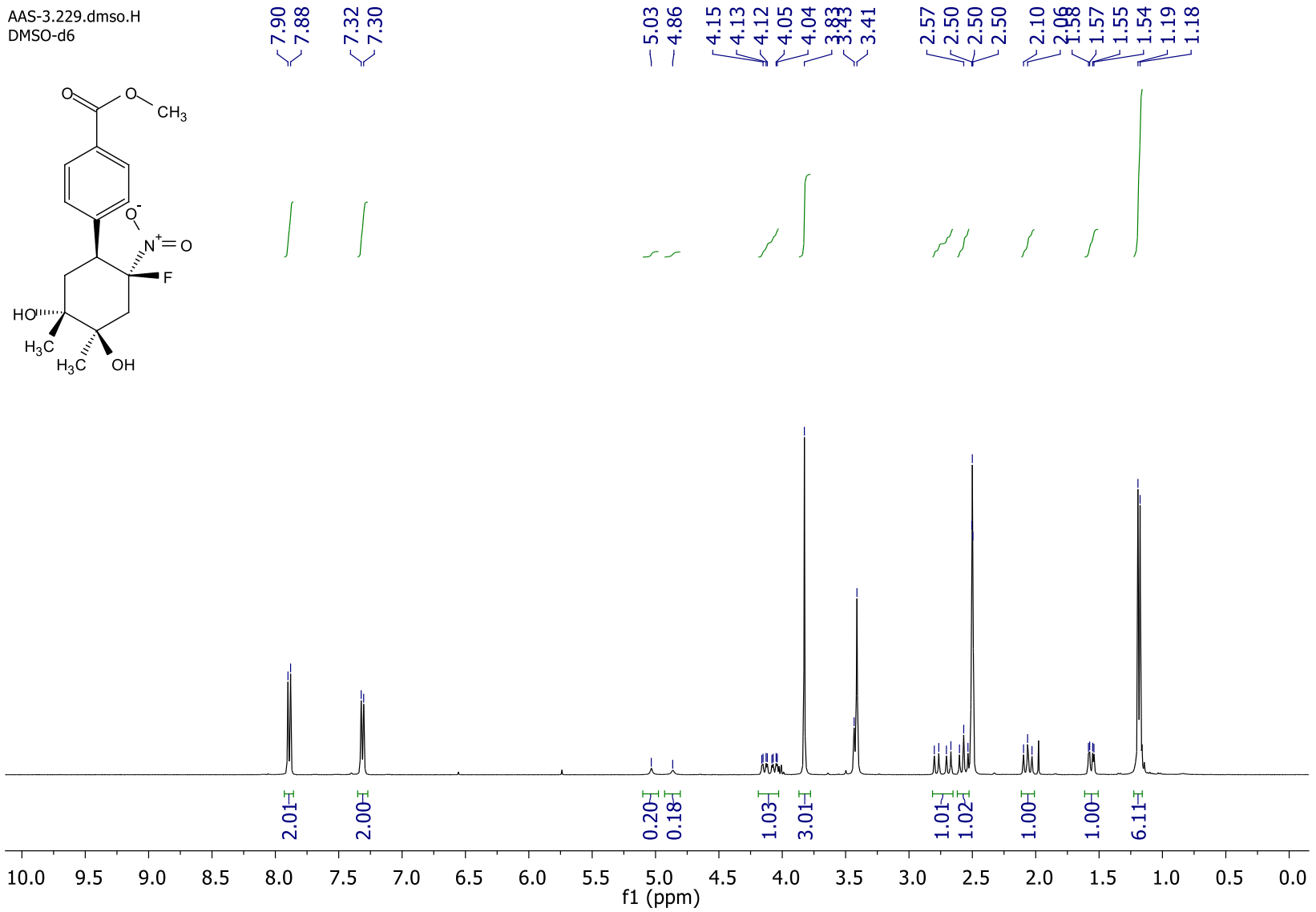
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(4-(trifluoromethyl)phenyl)cyclohexane-1,2-diol (**3e**)



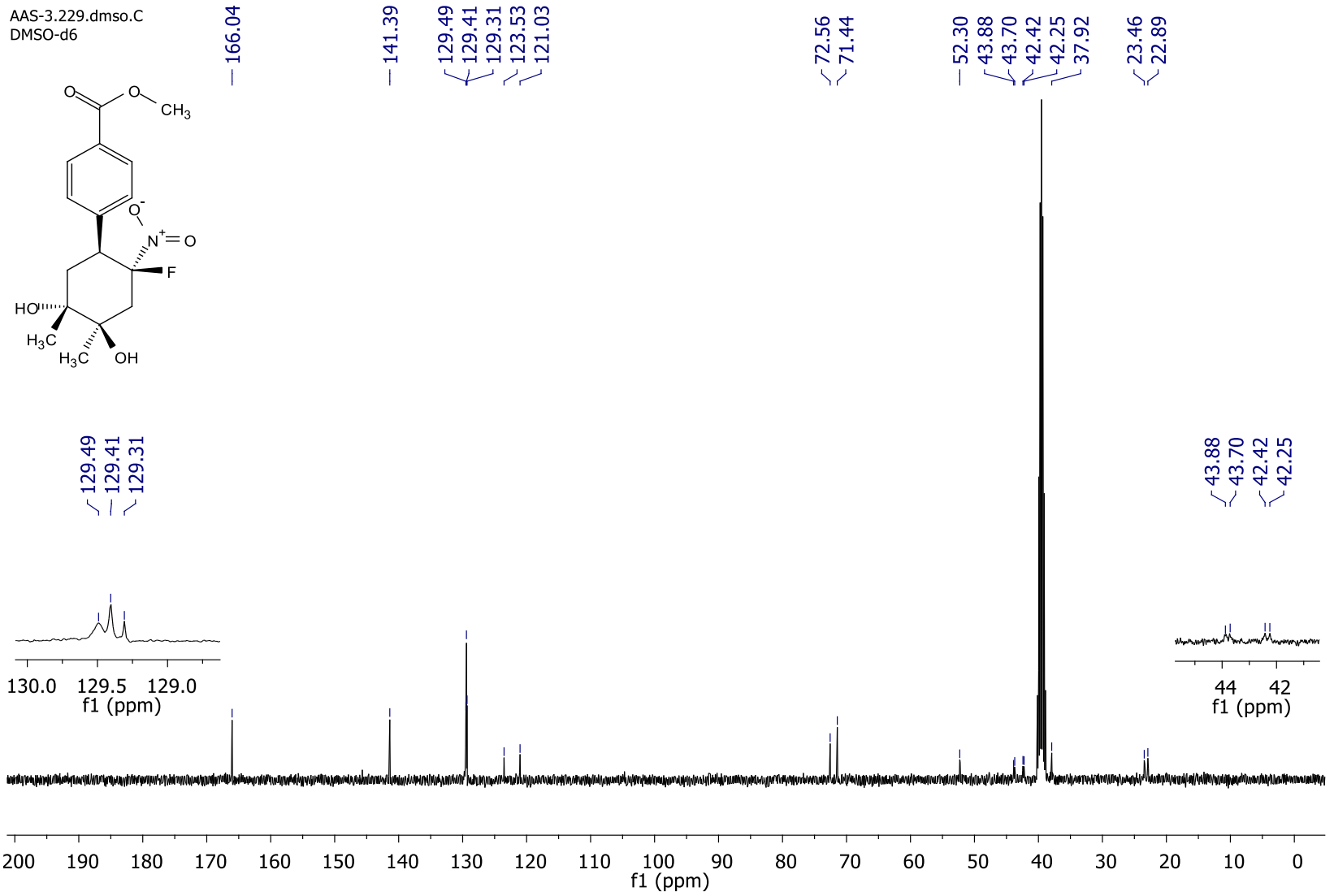
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(4-(trifluoromethyl)phenyl)cyclohexane-1,2-diol (**3e**)



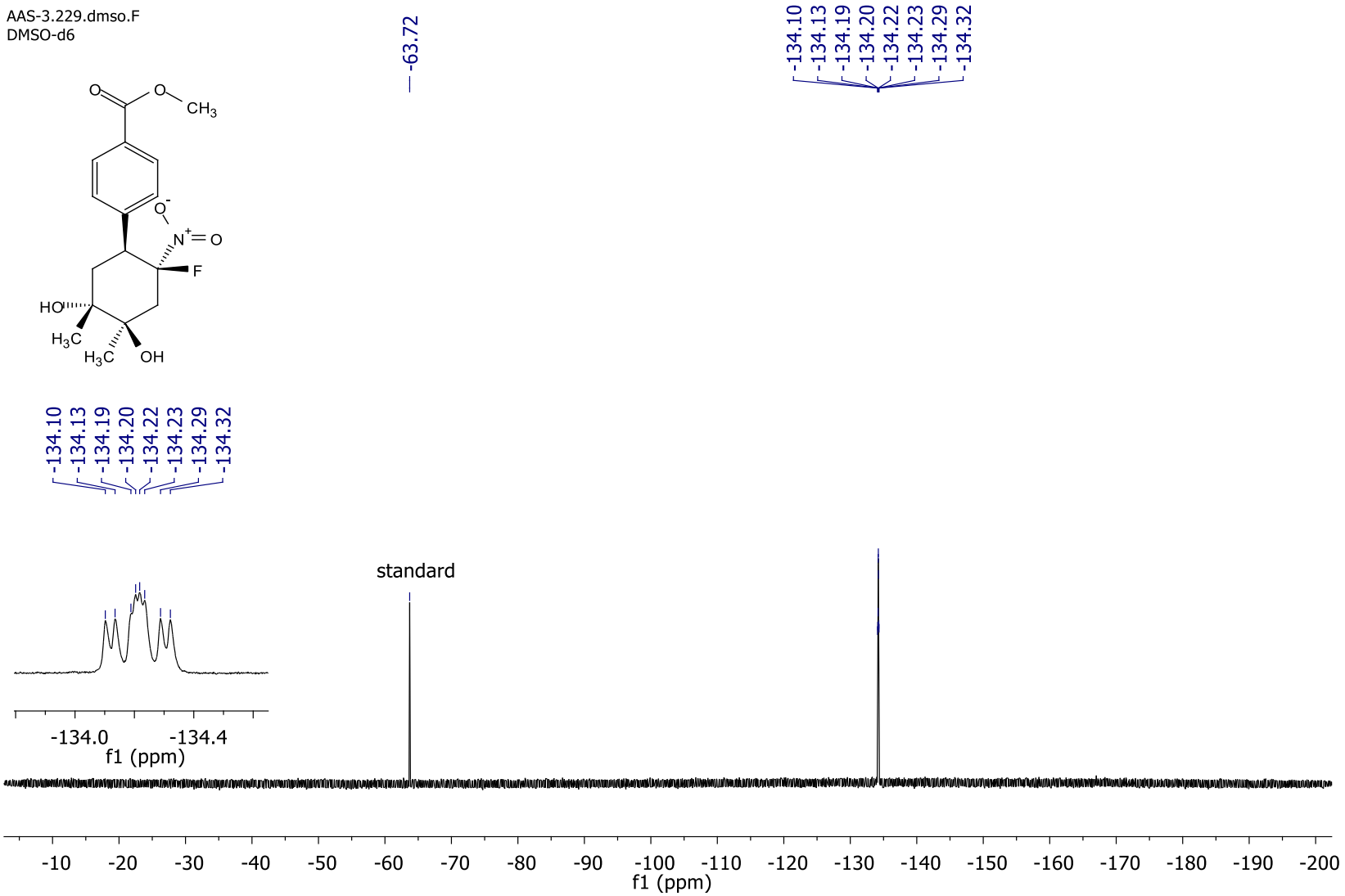
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(4-(trifluoromethyl)phenyl)cyclohexane-1,2-diol (**3e**)



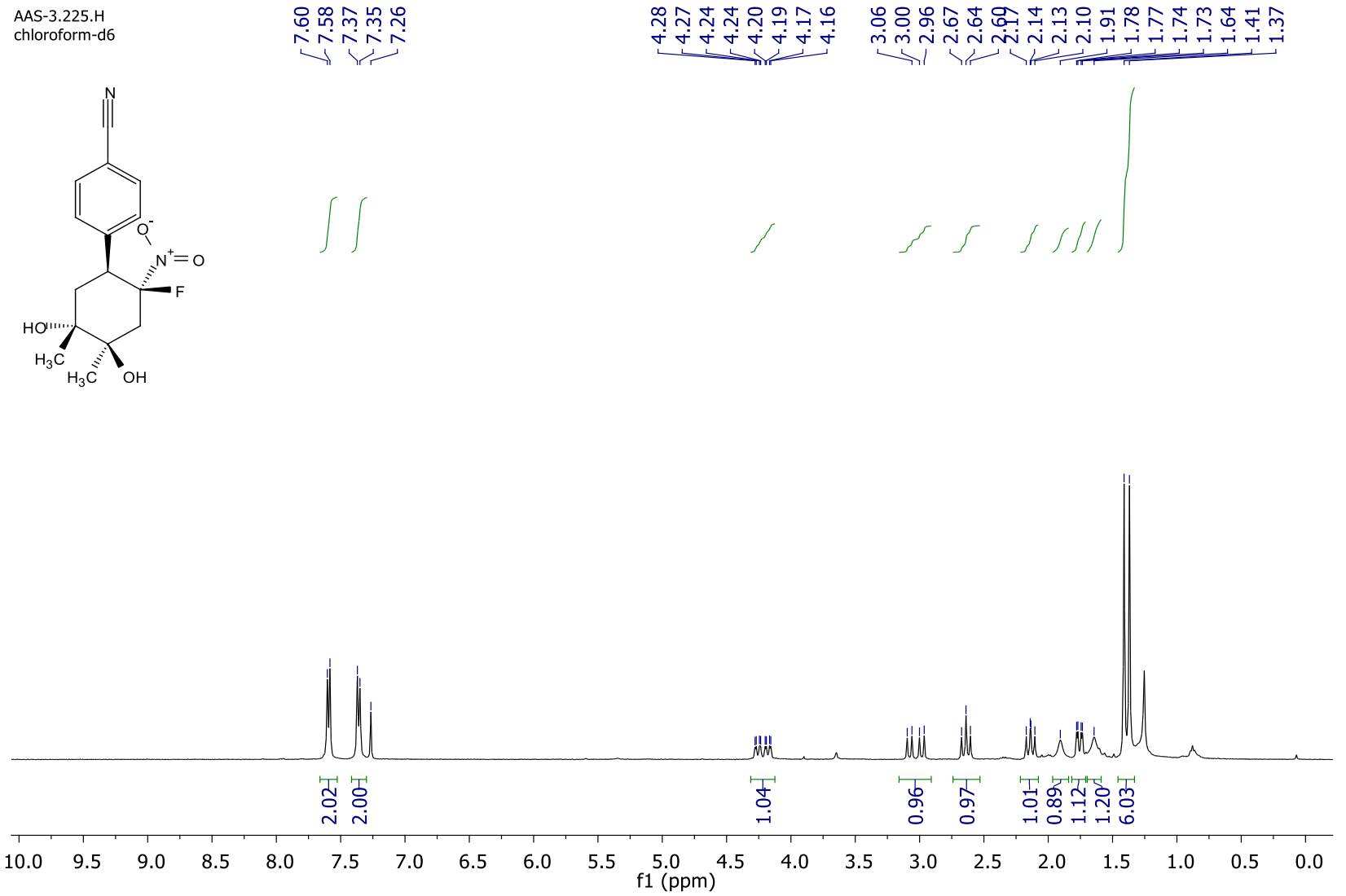
^{1}H NMR spectrum of methyl 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)-benzoate (**3f**)



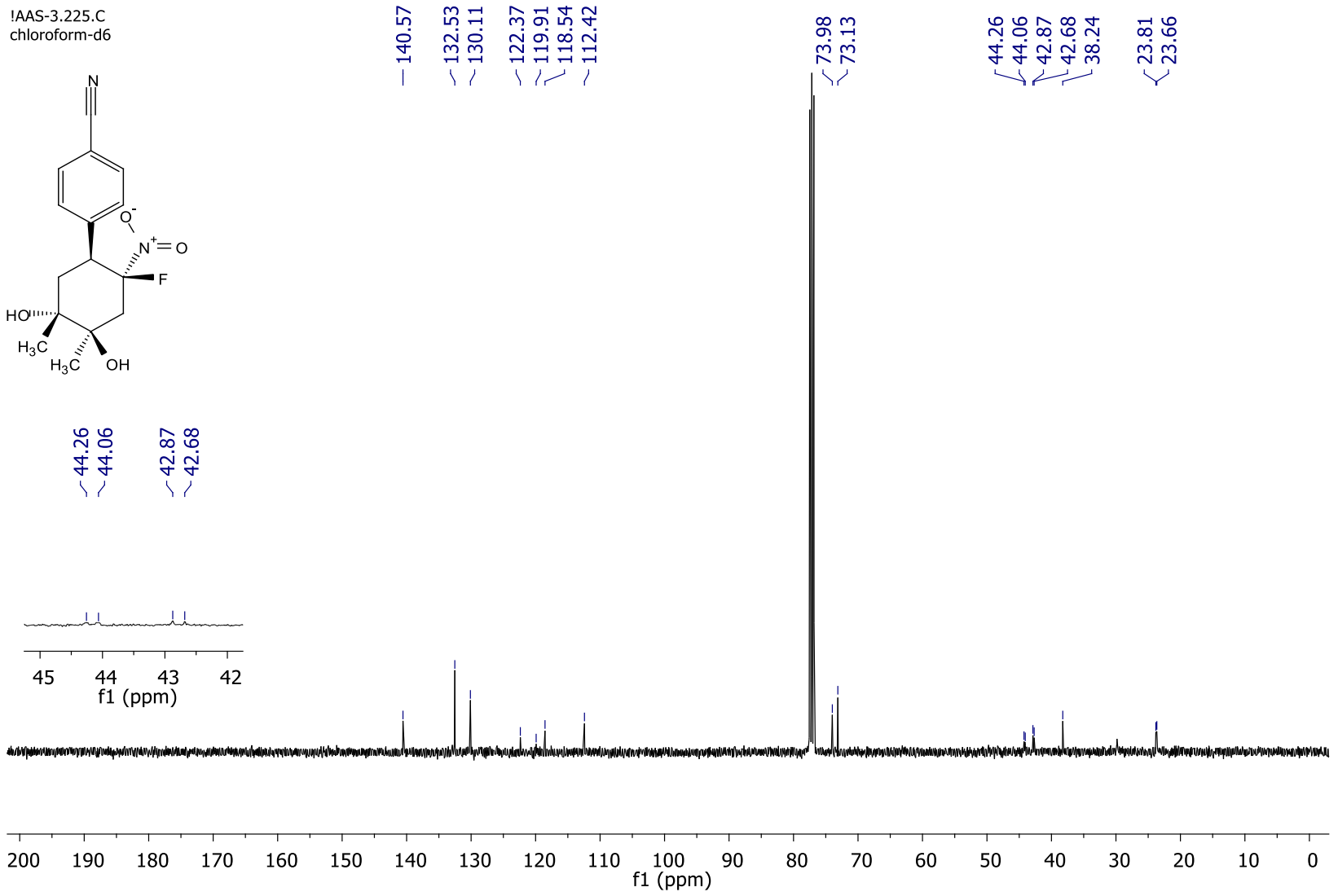
^{13}C NMR spectrum of methyl 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)-benzoate (**3f**)



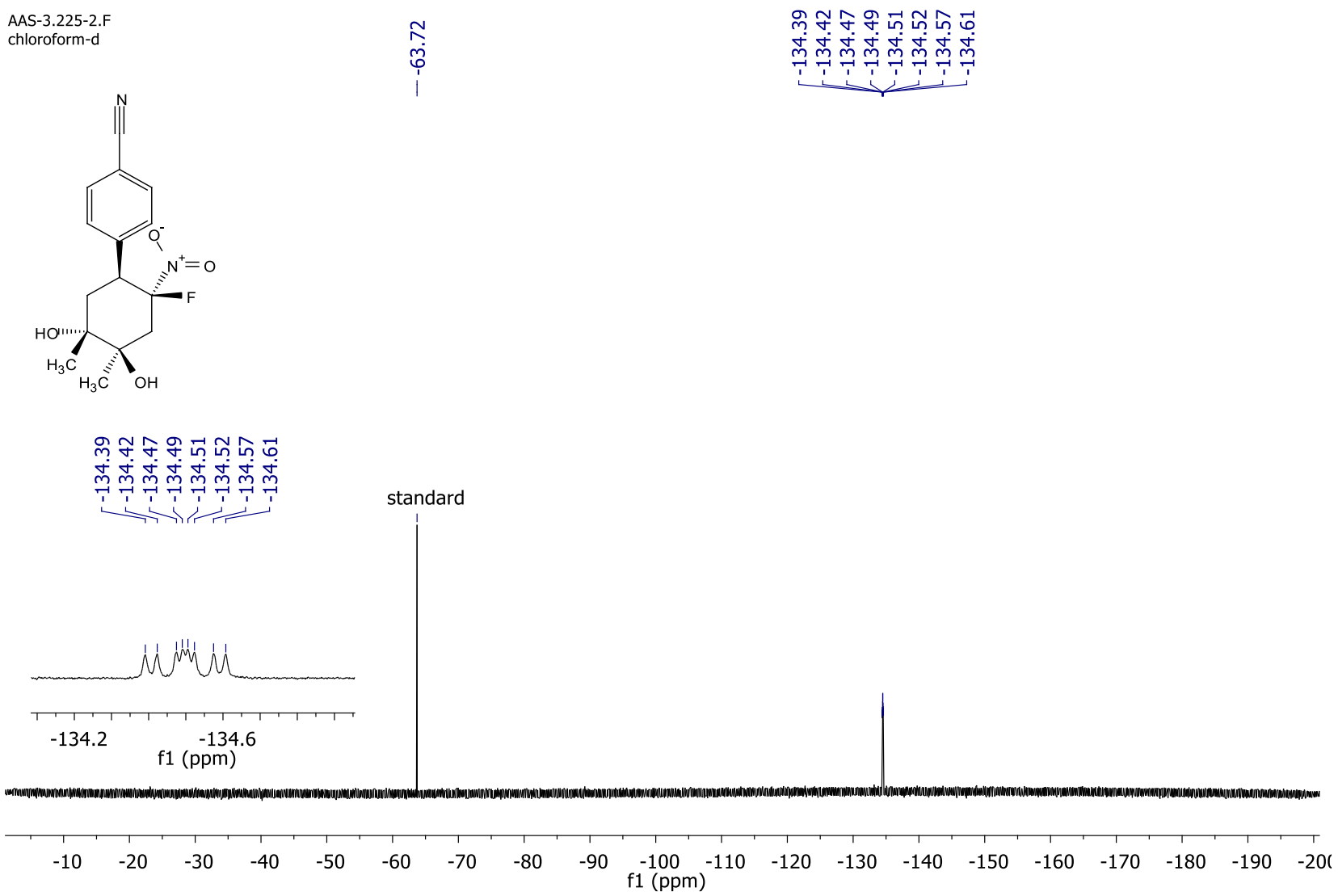
^{19}F NMR spectrum of methyl 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)-benzoate (**3f**)



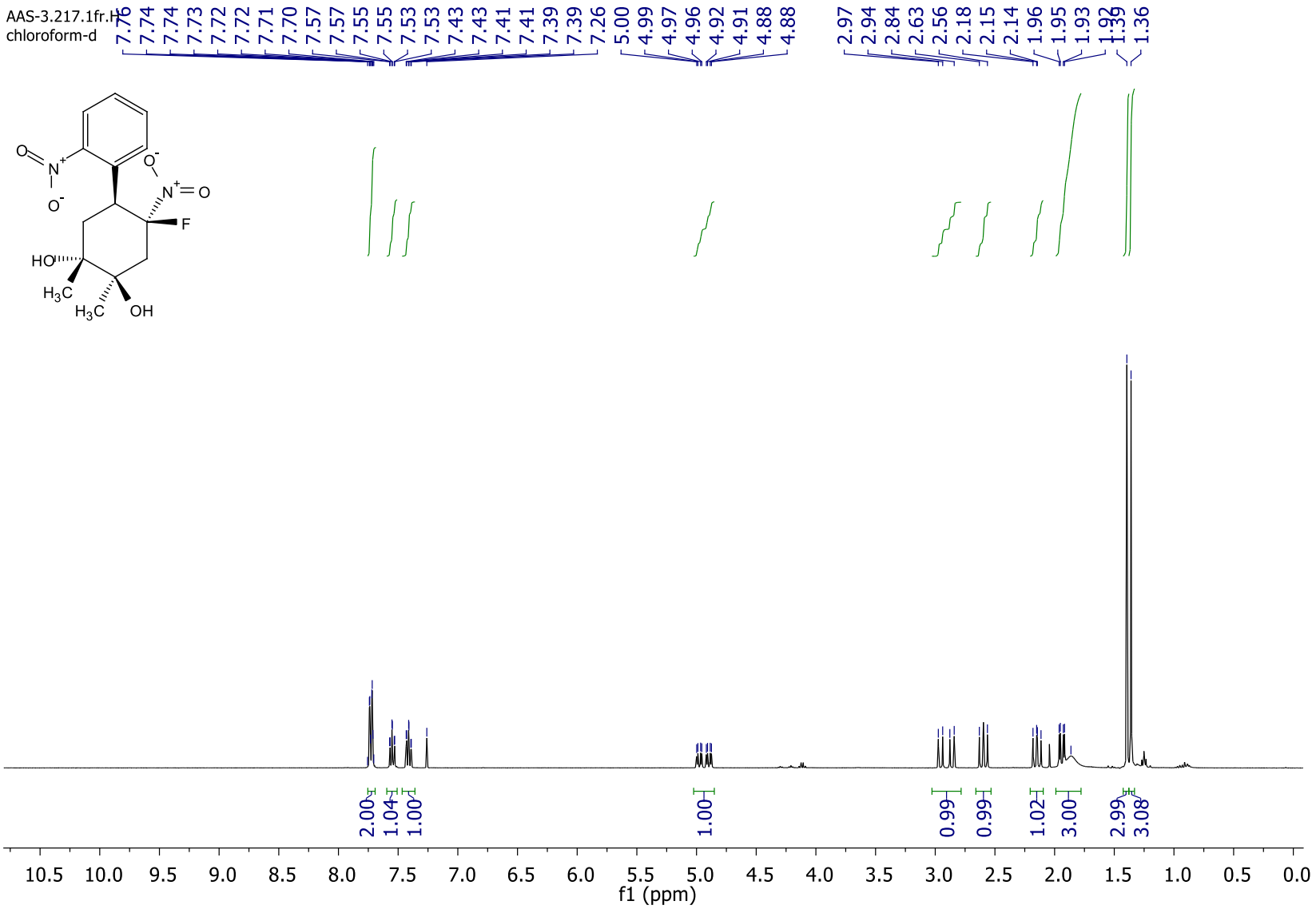
^{1}H NMR spectrum of 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)benzonitrile (**3g**)



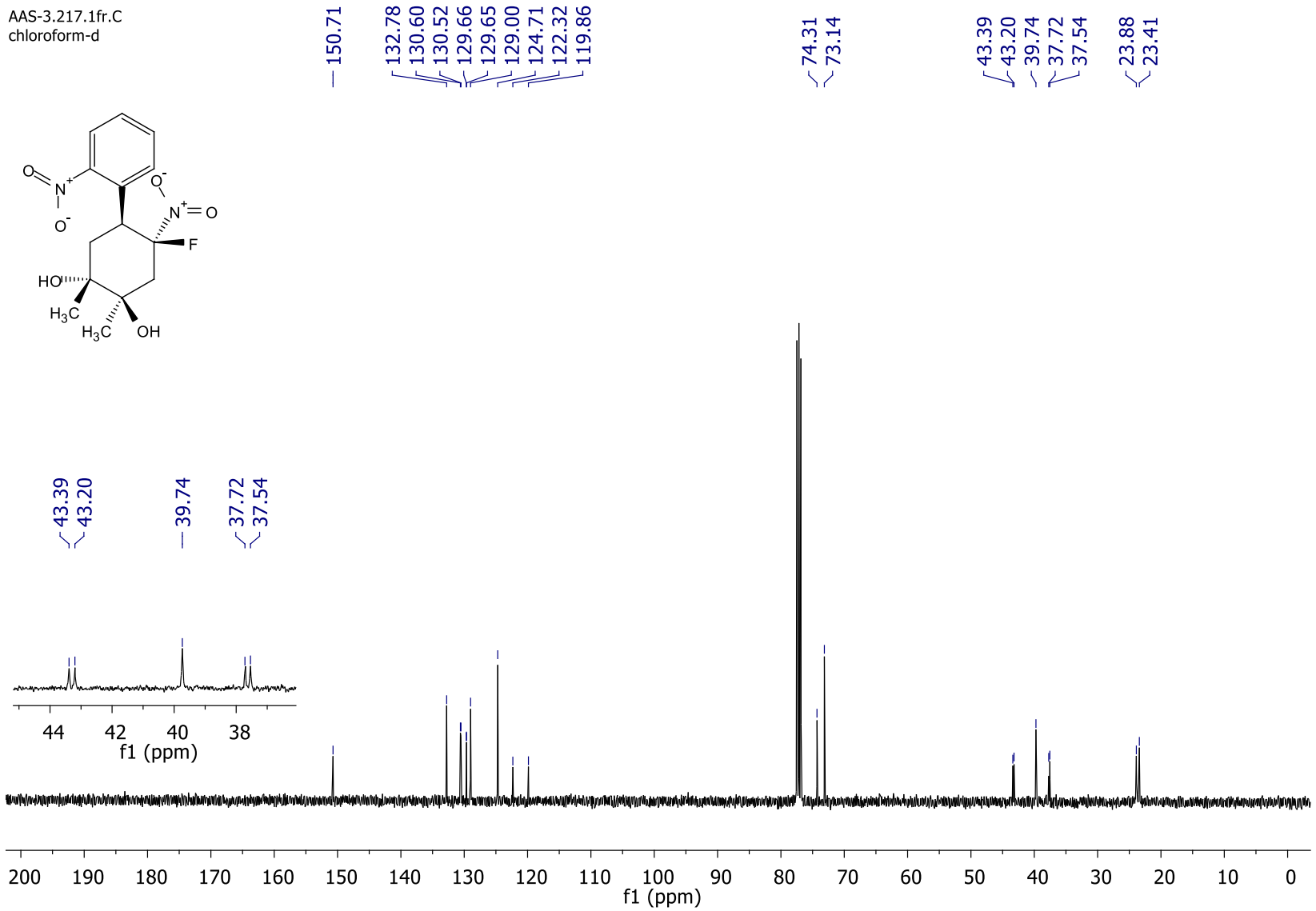
^{13}C NMR spectrum of 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)benzonitrile (**3g**)



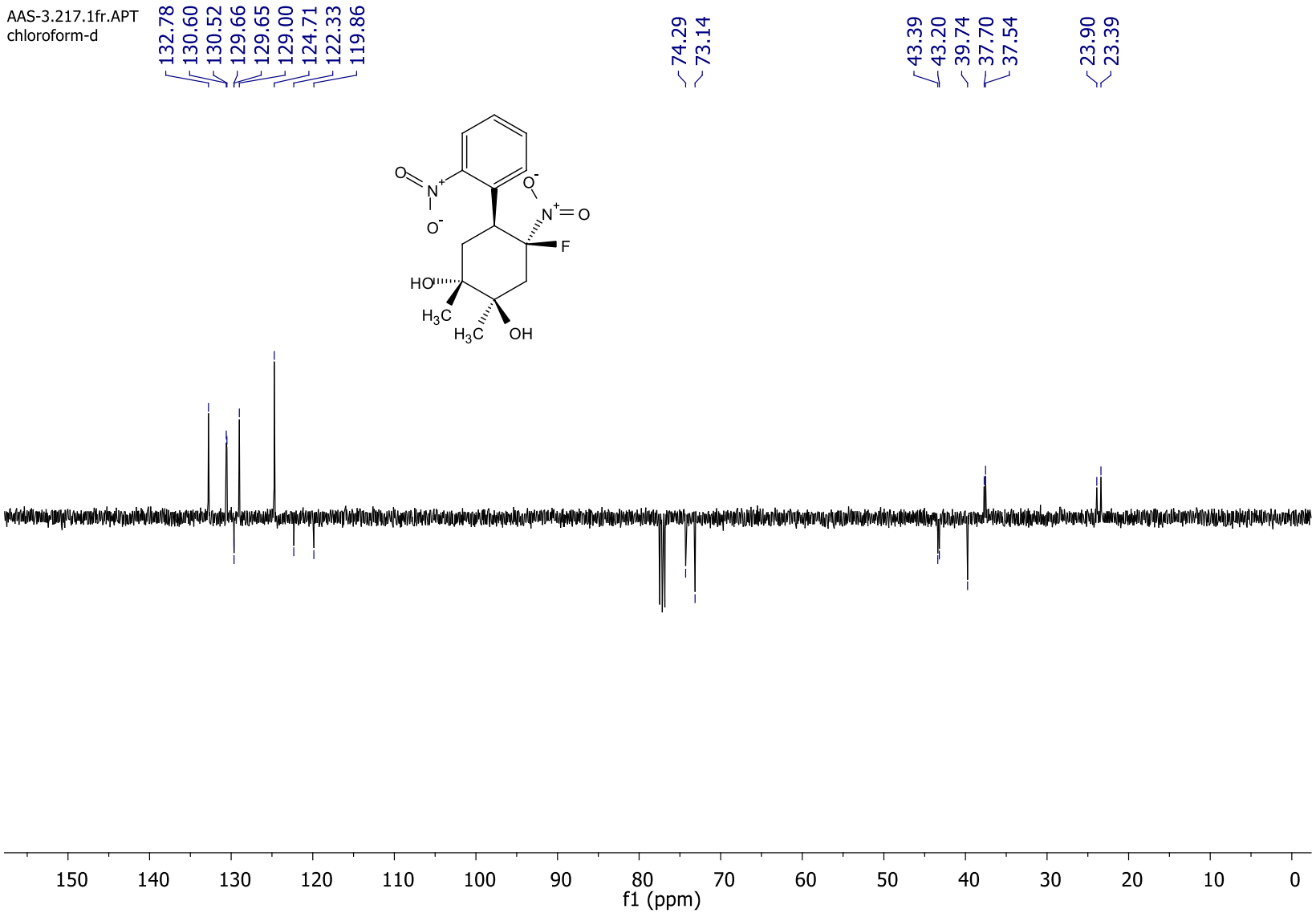
^{19}F NMR spectrum of 4-((1S*,2S*,4R*,5R*)-2-fluoro-4,5-dihydroxy-4,5-dimethyl-2-nitrocyclohexyl)benzonitrile (**3g**)



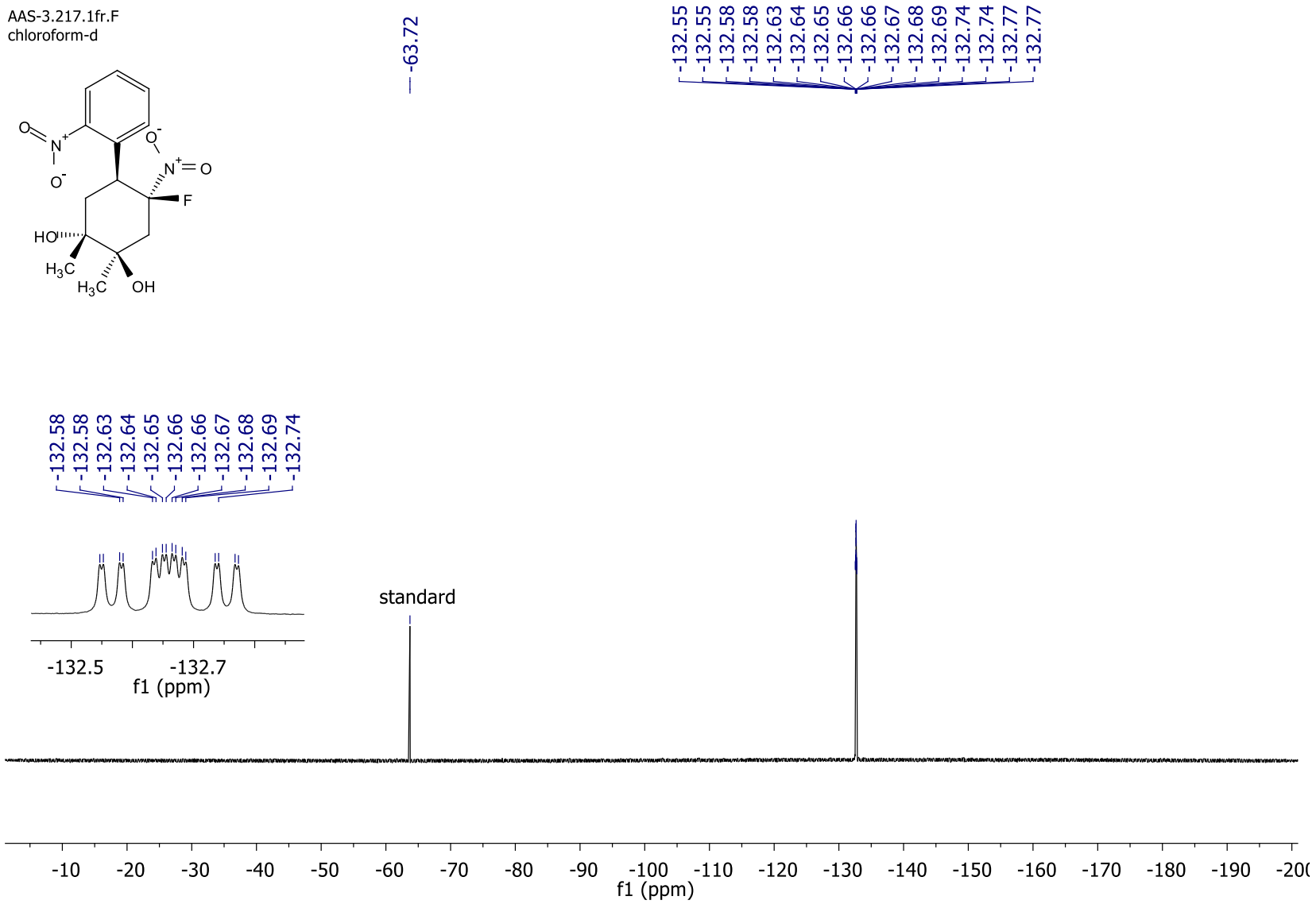
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(2-nitrophenyl)cyclohexane-1,2-diol (**3h**)



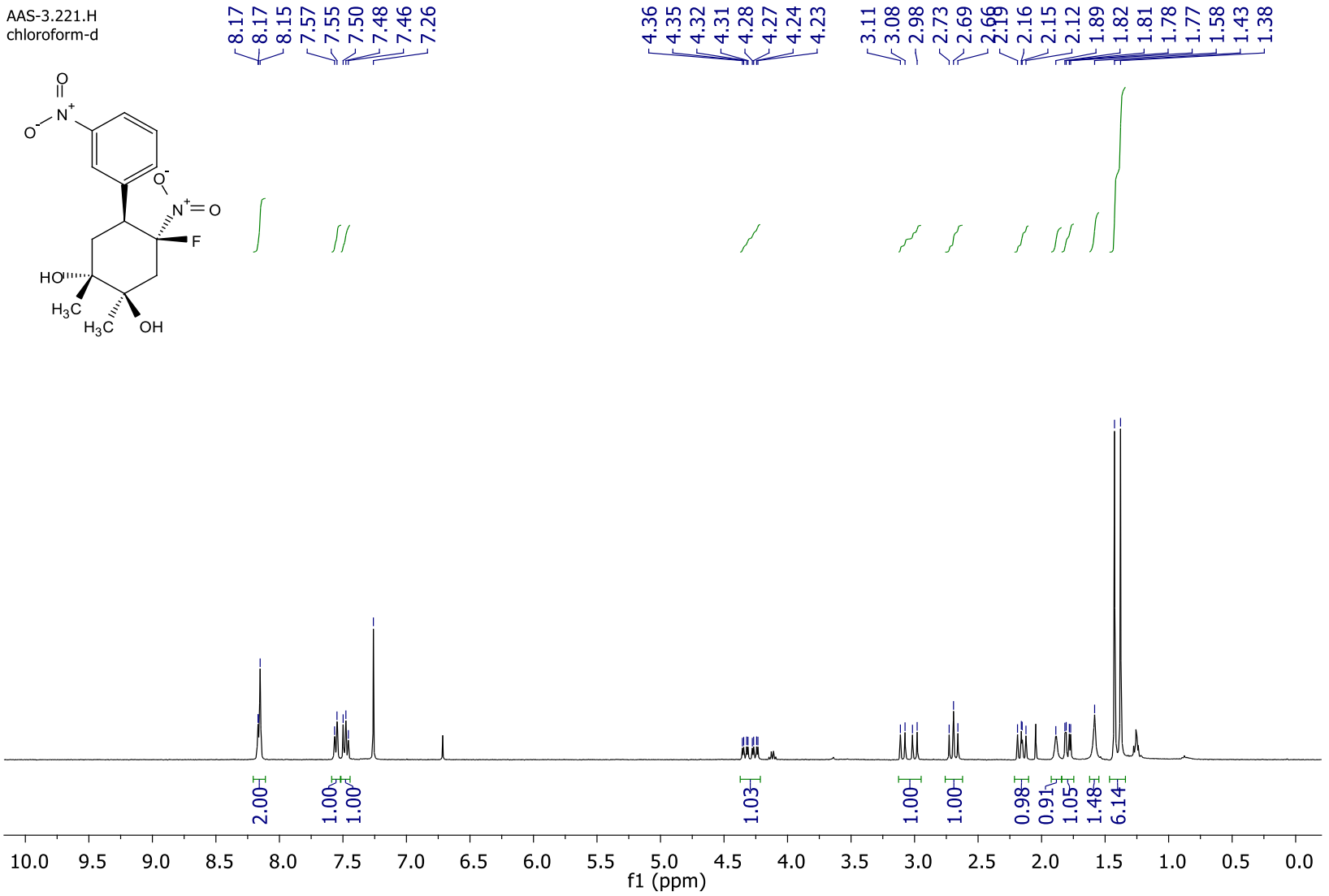
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(2-nitrophenyl)cyclohexane-1,2-diol (**3h**)



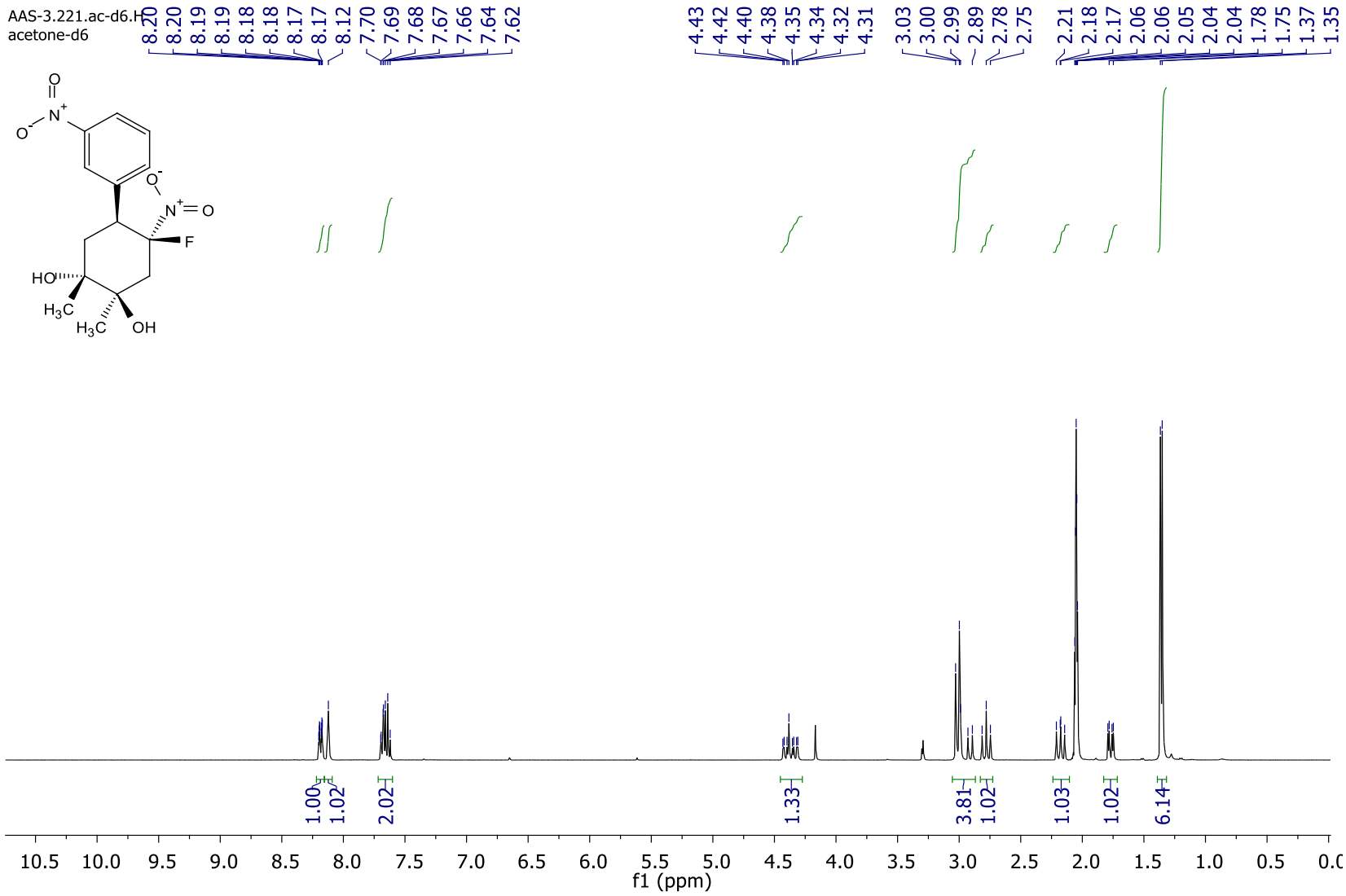
^{13}C APT NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(2-nitrophenyl)cyclohexane-1,2-diol (**3h**)



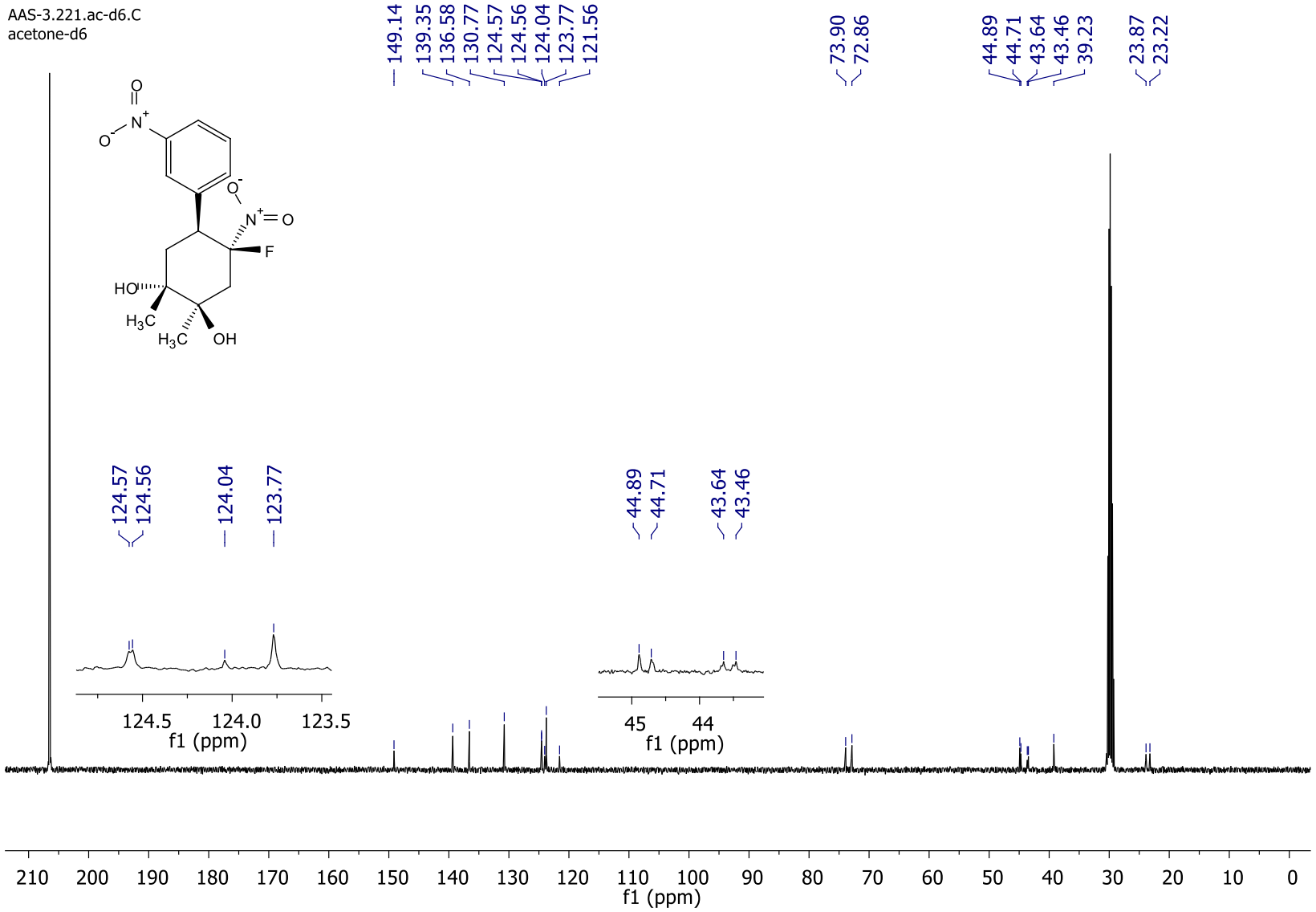
^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(2-nitrophenyl)cyclohexane-1,2-diol (**3h**)



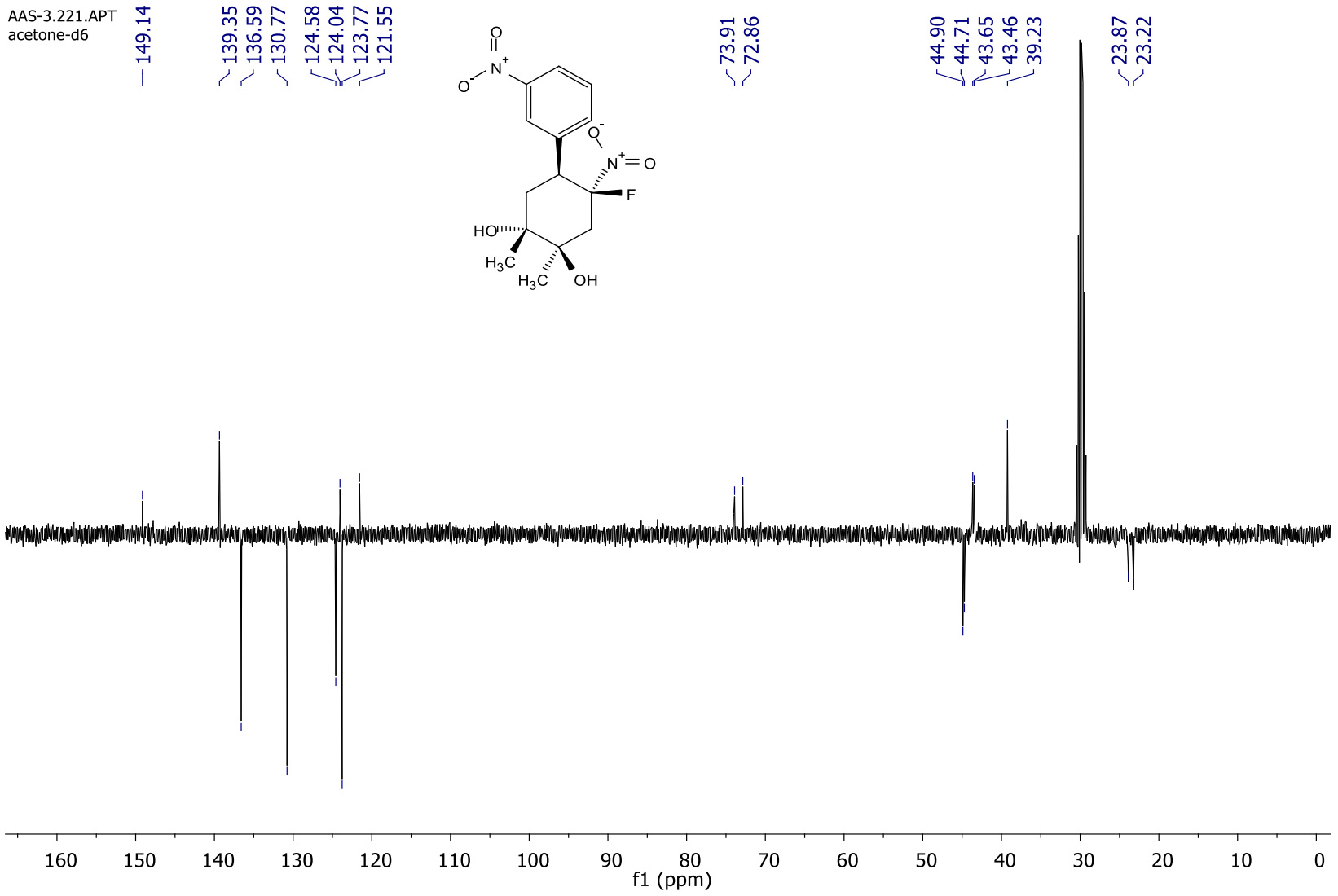
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $CDCl_3$ (**3i**)



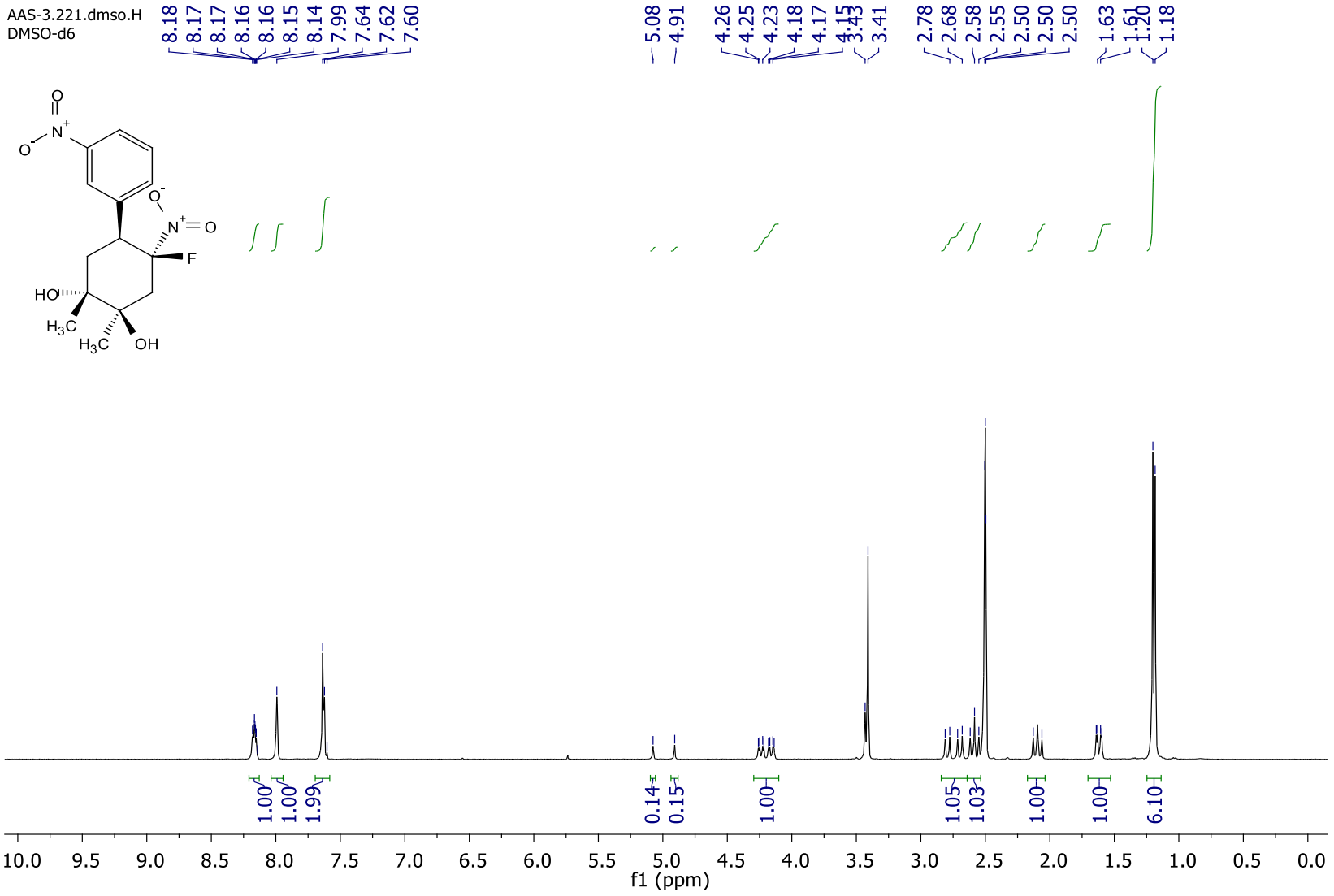
^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2CO$ (**3i**)



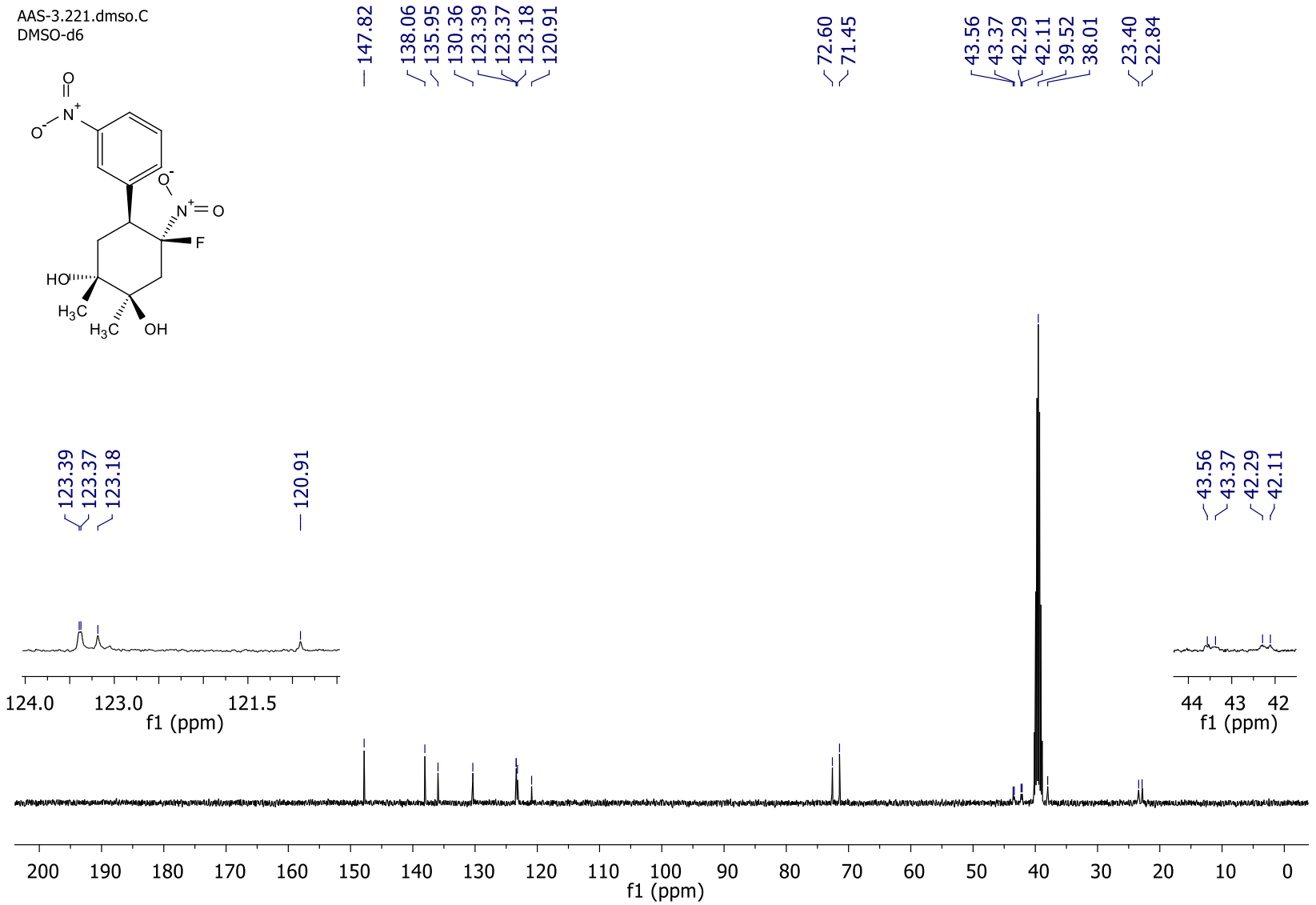
^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2CO$ (**3i**)



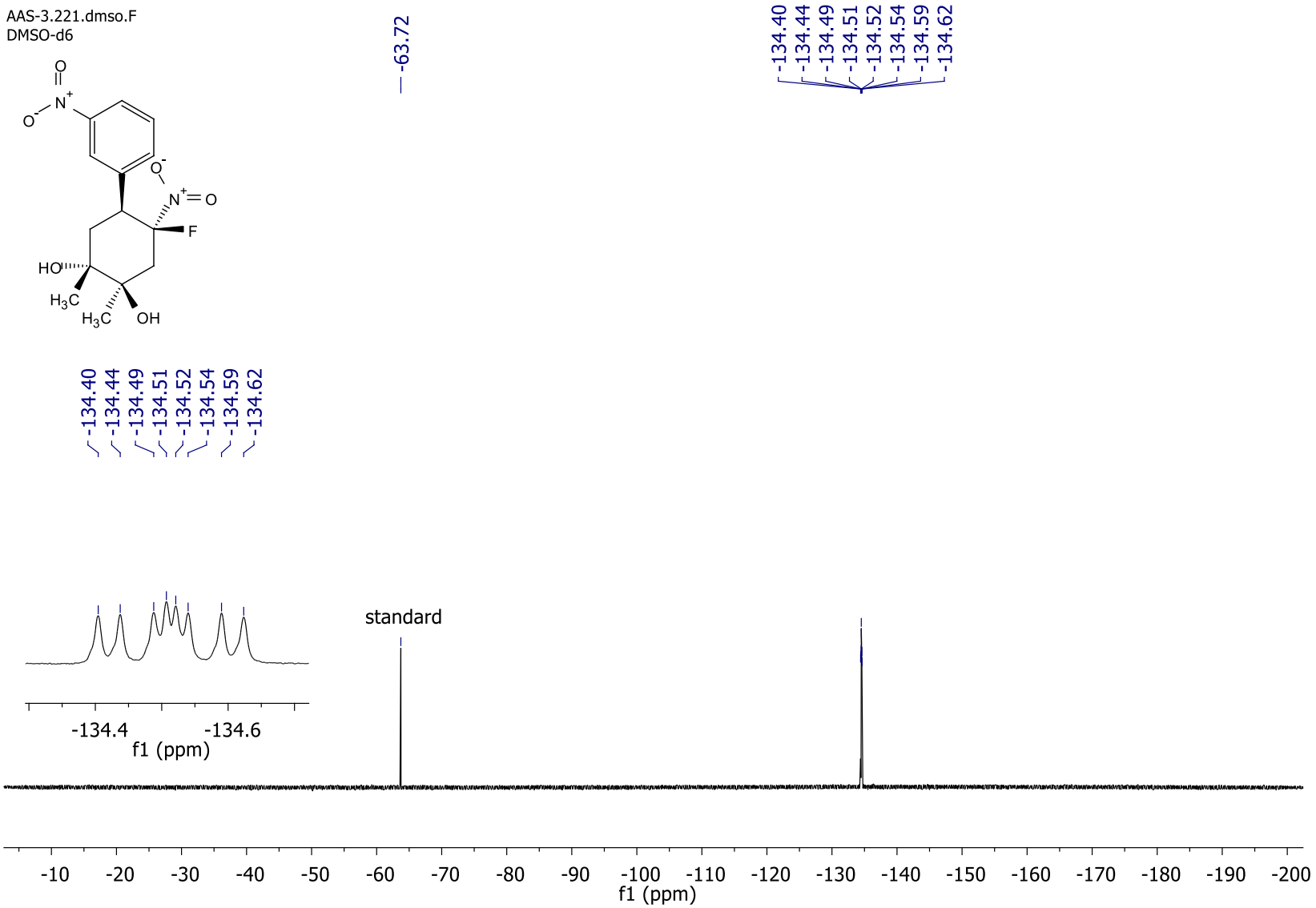
^{13}C APTNMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2CO$ (**3i**)



^{1}H NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2SO$ (**3i**)



^{13}C NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2SO$ (**3i**)



^{19}F NMR spectrum of (1R*,2R*,4S*,5S*)-4-fluoro-1,2-dimethyl-4-nitro-5-(3-nitrophenyl)cyclohexane-1,2-diol in $(CD_3)_2SO$ (**3i**)