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The first example of fluoro-Meinwald rearrangement

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Experimental data

All reagents were purchased from commercial sources and used without any further purification. All solvents were dried before use by the standard procedures [D. B. G. Williams, M. Lawton, *J. Org. Chem.* 2010, **75**, 8351–8354]. Melting points (M.p.) were measured with a Büchi B-545 melting point apparatus. NMR (^{1}H, ^{13}C and ^{19}F) spectra were registered in deuterated chloroform ($CDCl_3$) with Bruker AV-400 and Agilent 400-MR spectrometers. Chemical shifts for ^{1}H NMR spectroscopic data were referenced to internal tetramethylsilane (δ = 0.0 ppm) and the residual solvent resonance (δ = 7.26 ppm). Chemical shifts for ^{13}C NMR spectroscopic data were referenced to the residual solvent resonance (δ = 77.16 ppm). Chemical shifts for ^{19}F NMR spectroscopic data were referenced to $PhCF_3$ (δ = −63.72 ppm) added as a standard. Data are reported as follows: chemical shift, integration multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, qui = quintet, sext = sextet, sept = septet, br = board, m = multiplet, dd = *doublet of doublets*, ddd = *doublet of doublet of doublets*, ddt = *doublet of doublet of triplets*) and coupling constants (Hz). The starting 6-aryl-5-fluoro-5-nitrolbicyclo[2.2.1]hept-2-enes **2** and 6-(2,4-dichlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.2]oct-2-ene **7** were prepared as mixture of *exo*- and *endo*-isomers according to the described procedure and are the known compounds [S. A. Ponomarev, R. V. Larkovich, A. S. Aldoshin, A. A. Tabolin, S. L. Ioffe, J. Groß, T. Opatz and V. G. Nenajdenko, *Beilstein J. Org. Chem.* 2021, **17**, 283].

General procedure for base-induced HNO_2-elimination from (4+2)-cycloadducts

In a typical experiment, a solution of a selected cycloadduct **2** or **7** (0.2 mmol, 1 mol. equiv.) in THF (1 mL) was loaded into a vial covered with aluminum foil. Then, potassium *tert*-butoxide (2-4 mol. equiv.) was added in several portions over 20 min to the vigorously stirred reaction mixture in the

dark. The reaction mixture was stirred overnight at room temperature (TLC monitoring). After completion of the reaction, the mixture was passed through a layer of neutral alumina charged into a column covered with an aluminum foil using DCM as eluent. The solution of pure product **2** was collected into a flask covered with aluminum foil and then concentrated under vacuum.

2-(4-Chlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (2a). 73 mg (89%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 – 2.25 (m, 1H), 2.39 (d, *J* = 6.1 Hz, 1H), 3.42 – 3.47 (m, 1H), 3.79 – 3.85 (m, 1H), 6.91 – 6.96 (m, 1H), 7.00 – 7.04 (m, 1H), 7.27 – 7.32 (m, 2H), 7.32 – 7.37 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.7 (d, $^{3}J_{CF}$ = 5.0 Hz), 50.9 (d, $^{2}J_{CF}$ = 20.5 Hz), 69.6 (d, $^{3}J_{CF}$ = 5.9 Hz), 122.4 (d, $^{2}J_{CF}$ = 1.5 Hz), 126.7 (d, $^{4}J_{CF}$ = 6.3 Hz), 128.7, 131.8 (d, $^{3}J_{CF}$ = 5.4 Hz), 131.9 (d, $^{6}J_{CF}$ = 3.8 Hz), 141.5 (d, $^{4}J_{CF}$ = 4.2 Hz), 143.3 (d, $^{3}J_{CF}$ = 6.0 Hz), 175.0 (d, $^{1}J_{CF}$ = 303.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -119.22 – -119.15 (m) ppm.

2-(4-Bromophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (2b). 45 mg (91%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.17 – 2.24 (m, 1H), 2.35 – 2.42 (m, 1H), 3.44 (s, 1H), 3.82 (s, 1H), 6.90 – 6.96 (m, 1H), 6.98 – 7.05 (m, 1H), 7.24 – 7.32 (m, 2H), 7.41 – 7.50 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.6 (d, $^{3}J_{CF}$ = 4.8 Hz), 50.9 (d, $^{2}J_{CF}$ = 20.5 Hz), 69.5 (d, $^{3}J_{CF}$ = 5.8 Hz), 120.0 (d, $^{6}J_{CF}$ = 3.5 Hz), 122.5 (d, $^{2}J_{CF}$ = 1.8 Hz), 127.1 (д, $^{4}J_{CF}$ = 6.1 Гц), 131.7, 132.3 (d, $^{3}J_{CF}$ = 5.2 Hz), 141.5 (d, $^{4}J_{CF}$ = 4.2 Hz), 143.3 (d, $^{3}J_{CF}$ = 5.9 Hz), 175.1 (d, $^{1}J_{CF}$ = 304.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -118.74 – -118.69 (m) ppm.

2-Fluoro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (2c). 155 mg (81%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.21 (ddd, *J* = 7.8, 3.4, 1.9 Hz, 1H), 2.40 (d, *J* = 6.1 Hz, 1H), 3.49 – 3.40 (m, 1H), 3.92 – 3.83 (m, 1H), 6.94 (dd, *J* = 4.7, 3.0 Hz, 1H), 7.04 (dt, *J* = 4.6, 2.1 Hz, 1H), 7.19 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 2H), 7.46 – 7.41 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 49.7 (d, $^{3}J_{CF}$ = 5.1 Hz), 50.8 (d, $^{2}J_{CF}$ = 20.7 Hz), 69.5 (d, $^{3}J_{CF}$ = 5.9 Hz), 123.2 (d, $^{2}J_{CF}$ = 1.5 Hz), 125.5 (d, $^{4}J_{CF}$ = 6.0 Hz), 126.4 (d, $^{6}J_{CF}$ = 2.2 Hz), 128.6, 133.4 (d, $^{3}J_{CF}$ = 5.0 Hz), 141.5 (d, $^{4}J_{CF}$ = 4.1 Hz), 143.5 (d, $^{3}J_{CF}$ = 6.0 Hz), 174.6 (d, $^{1}J_{CF}$ = 302.9 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -120.52 – -120.46 (m) ppm.

2-(4-*tert*-Butylphenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (2d). 101 mg (78%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 9H), 2.16 – 2.22 (m, 1H), 2.37 (dt, *J* = 6.0, 1.4 Hz, 1H), 3.40 – 3.45 (m, 1H), 3.83 – 3.89 (m, 1H), 6.89 – 6.94 (m, 1H), 7.01 (dt, *J* = 4.6, 2.1 Hz, 1H), 7.38 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.6, 49.7 (d, $^{3}J_{CF}$ = 5.2 Hz), 50.8 (d, $^{2}J_{CF}$ = 20.7 Hz), 69.5 (d, $^{3}J_{CF}$ = 5.9 Hz), 123.0 (d, $^{2}J_{CF}$ = 1.8 Hz), 125.2 (д, $^{4}J_{CF}$ = 5.8 Hz), 125.5, 130.6 (d, $^{3}J_{CF}$ = 5.1 Hz), 141.4 (d, $^{4}J_{CF}$ = 4.1 Hz), 143.4 (d, $^{3}J_{CF}$ = 6.0 Hz), 149.3 (d, $^{6}J_{CF}$ = 2.2 Hz), 174.0 (д, $^{1}J_{CF}$ = 301.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -121.73 – -121.64 (m) ppm.

2-(2,4-Dichlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (2e). 80 mg (95%); pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.19 – 2.25 (m, 1H), 2.50 (dt, *J* = 6.1, 1.6 Hz, 1H), 3.38 – 3.44 (m, 1H), 3.80 – 3.86 (m, 1H), 6.92 – 6.98 (m, 1H), 7.06 – 7.10 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.18 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.37 (d, *J* = 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 50.3 (d, $^{2}J_{CF}$ = 20.3 Hz), 52.6 (d, $^{3}J_{CF}$ = 4.1 Hz), 71.1 (d, $^{3}J_{CF}$ = 5.2 Hz), 121.7 (d, $^{2}J_{CF}$ = 3.2 Hz), 127.0, 129.8, 130.4 (d, $^{4}J_{CF}$ = 3.2 Hz), 131.3 (d, $^{3}J_{CF}$ = 3.7 Hz), 133.0, 133.1 (d, $^{4}J_{CF}$ = 1.8 Hz), 141.0 (d, $^{4}J_{CF}$ = 3.8 Hz), 144.8 (d, $^{3}J_{CF}$ = 5.8 Hz), 176.1 (d, $^{1}J_{CF}$ = 303.4 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -118.73 – -118.66 (m) ppm.

2-Fluoro-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**2f**). 34 mg (77%); yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 – 2.31 (m, 1H), 2.41 – 2.46 (m, 1H), 3.48 – 3.53 (m, 1H), 3.88 – 3.94 (m, 1H), 6.92 – 6.97 (m, 1H), 7.03 – 7.08 (m, 1H), 7.48 – 7.55 (m, 2H), 8.15 – 8.21 (m, 2H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.34 (s) ppm. The analysis of the sample was consistent with the previously reported data [A. V. Shastin, V. G. Nenajdenko, V. M. Muzalevskiy, E. S. Balenkova, R. Fröhlich, G. Haufe, *Tetrahedron*, 2008, **64**, 9725.].

2-(2,4-Dichlorophenyl)-3-fluorobicyclo[2.2.2]octa-2,5-diene (**8**). 37 mg (76%); yellowish oil. Anal. calcd. for $C_{14}H_{11}Cl_2F$ (%): C, 62.48; H, 4.12; found C, 63.89; H, 4.46; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 – 1.52 (m, 2H), 1.66 – 1.75 (m, 1H), 1.77 – 1.86 (m, 1H), 3.56 – 3.66 (m, 1H), 3.71 – 3.79 (m, 1H), 6.36 – 6.43 (m, 1H), 6.45 – 6.52 (m, 1H), 7.10 (dd, *J* = 8.3, 0.6 Hz, 1H), 7.18 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.40 (d, *J* = 2.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 25.1 (d, $^{3}J_{CF}$ = 1.7 Hz), 25.9 (d, $^{4}J_{CF}$ = 1.0 Hz), 38.7 (d, $^{2}J_{CF}$ = 21.4 Hz), 41.6 (d, $^{3}J_{CF}$ = 2.2 Hz), 115.6 (d, $^{2}J_{CF}$ = 3.7 Hz), 126.9, 129.7, 131.8 (d, $^{4}J_{CF}$ = 2.3 Hz), 132.8 (d, $^{3}J_{CF}$ = 1.5 Hz), 132.9, 133.3, 134.0, 136.0 (d, $^{3}J_{CF}$ = 2.8 Hz), 162.7 (d, $^{1}J_{CF}$ = 285.7 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -114.80 – -114.66 (m) ppm.

Procedure for UV-irradiation of norbornadienes 2

In a typical experiment, a solution of norbornadiene **2** (0.2 mmol, 1 mol. equiv.) in dichloromethane (5 mL) was loaded into a quartz vial placed in an ice bath. The mixture was stirred for 6-7 hours under UV irradiation (254 nm, 6 W) until completion. The progress of the reaction was monitored by TLC and ^{19}F NMR. After completion of the reaction, the mixture was concentrated under vacuum and then separated by column chromatography on silica using a hexane/dichloromethane (4:1) mixture as eluent. Thus, the target acyl fluoride **3** and ketone **4** as a side product were isolated as pure compounds.

(1*S,5*R**,6*R**)-6-(4-Chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride** (**3a**). 26 mg (45%); colorless oil. IR (neat): 1829 (-C=O) cm^{-1}.^{1}H NMR (400 MHz, $CDCl_3$, ^{1}H-^{13}C HMBC, ^{1}H-

^{13}C HSQC): δ = 2.26 (q, *J* = 6.4 Hz, 1H, H^4), 2.71 – 2.82 (m, 2H, $H^{3,5}$), 2.89 – 2.98 (m, 1H, H^5), 5.78 – 5.84 (m, 1H, $H^{1,2}$), 5.91 – 5.97 (m, 1H, $H^{1,2}$), 7.33 (s, 4H, $H^{9,10,12,13}$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, ^{1}H-^{13}C HMBC, ^{1}H-^{13}C HSQC): δ = 30.9 (d, $^3J_{CF}$ = 1.5 Hz, C^4), 34.5 (C^5), 38.4 (d, $^2J_{CF}$ = 59.6 Hz, C^6), 39.0 (d, $^3J_{CF}$ = 1.4 Hz, C^3), 128.8 ($C^{1,2}$), 129.2 ($C^{9,10,12,13}$), 130.3 ($C^{9,10,12,13}$), 133.7 ($C^{1,2}$), 134.2 (C^{11}), 135.4 (d, $^3J_{CF}$ = 2.4 Hz, C^7), 158.1 (d, $^1J_{CF}$ = 359.8 Hz, C^8) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = 46.48 (d, J_{HF} = 5.9 Hz) ppm.

(1*S,3*R**,4*R**)-3-(4-Chlorophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one** (**4a**). 11 mg (19%); colorless oil. HRMS (ESI): calcd. for $C_{13}H_{12}{}^{35}ClO_2$ $[M+H]^+$ = 235.0520; found 235.0517. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 9.4 Hz, 1H), 2.27 (d, *J* = 9.4 Hz, 1H), 3.27 (dd, *J* = 3.5, 1.4 Hz, 1H), 3.29 – 3.33 (m, 1H), 3.43 (d, *J* = 2.9 Hz, 1H), 6.17 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.40 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.26 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.3, 49.5, 51.8, 57.0, 128.5, 129.5, 129.6, 132.8, 138.2, 141.3, 211.8 ppm.

(1*S,5*R**,6*R**)-6-(4-Bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride** (**3b**). 24 mg (43%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.26 (q, *J* = 6.4 Гц, 1H), 2.70 – 2.82 (m, 2H), 2.88 – 2.98 (m, 1H), 5.78 – 5.85 (m, 1H), 5.90 – 5.97 (m, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.45 – 7.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.9 (d, $^3J_{CF}$ = 1.9 Hz), 34.5, 38.4 (d, $^2J_{CF}$ = 59.5 Hz), 39.0 (d, $^3J_{CF}$ = 1.4 Hz), 122.3, 128.7, 130.6, 132.1, 133.8, 135.9 (d, $^3J_{CF}$ = 2.7 Hz), 158.0 (d, $^1J_{CF}$ = 359.8 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = 46.57 (d, J_{HF} = 5.9 Hz) ppm.

(1*S,3*R**,4*R**)-3-(4-Bromophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one** (**4b**). 10 mg (18%); colorless oil. HRMS (ESI): calcd. for $C_{13}H_{12}{}^{79}BrO_2$ $[M+H]^+$ = 279.0015; found 279.0011. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.13 (d, *J* = 9.3 Hz, 1H), 2.27 (d, *J* = 9.3 Hz, 1H), 3.25 – 3.29 (m, 1H), 3.29 – 3.35 (m, 1H), 3.41 (d, *J* = 3.0 Hz, 1H), 6.13 – 6.19 (m, 1H), 6.39 (dd, *J* = 5.4, 2.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 46.3, 49.5, 51.8, 57.0, 120.9, 129.7, 129.9, 131.5, 138.7, 141.3, 211.7 ppm.

(1*S,5*R**,6*R**)-6-Phenylbicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride** (**3c**). 25 mg (30%); colorless oil. HRMS (ESI): calcd. for $C_{13}H_{11}FNaO$ $[M+Na]^+$ 225.0686; found 225.0685. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (q, *J* = 6.3 Hz, 1H), 2.71 – 2.84 (m, 2H), 2.88 – 3.01 (m, 1H), 5.78 – 5.84 (m, 1H), 5.93 – 5.99 (m, 1H), 7.27 – 7.43 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8 (d, $^3J_{CF}$ = 1.8 Hz), 34.5, 38.8 (d, $^3J_{CF}$ = 1.4 Hz), 39.1 (d, $^2J_{CF}$ = 59.0 Hz), 128.2, 128.8, 129.0, 129.1, 133.4, 136.9 (d, $^3J_{CF}$ = 2.5 Hz), 158.5 (d, $^1J_{CF}$ = 359.9 Hz) ppm. ^{9}F NMR (376 MHz, $CDCl_3$) δ 46.33 (d, J_{HF} = 6.1 Hz) ppm.

Procedure for hydrolysis of acyl fluorides 3

An aqueous solution of 1 M NaOH (10 mL) was added to acyl fluoride **3** (0.12-0.17 mmol). The mixture was stirred at room temperature for 15 h (TLC monitoring). After completion of the reaction, the mixture was poured into an aqueous solution of 5% HCl (25 mL) and then extracted with dichloromethane. The combined organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The pure product **5** was isolated by column chromatography on silica gel using a hexane/ethyl acetate (2:1) mixture as eluent.

(1*S,5*R**,6*R**)-6-(4-Chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid** (**5a**). 36 mg (90%); colorless solid. M.p. 137-139 °C. HRMS (ESI): calcd. for $C_{13}H_{12}{}^{35}ClO_2$ $[M+H]^+$ = 235.0520; found 235.0513. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (t, *J* = 6.7 Hz, 1H), 2.53 – 2.61 (m, 1H), 2.62 – 2.73 (dd, *J* = 18.3, 7.0 Hz, 1H), 2.89 (dd, *J* = 18.4, 1.9 Hz, 1H), 5.62 – 5.68 (m, 1H), 5.89 (dd, *J* = 5.4, 2.1 Hz, 1H), 7.26 – 7.30 (m, 2H), 7.32 – 7.38 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 34.4, 37.9, 40.0, 128.8, 130.1, 130.4, 132.2, 133.5, 137.7, 175.0 ppm.

(1*S,5*R**,6*R**)-6-(4-Bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid** (**5b**). 30 mg (93%); colorless solid. M.p. 143-145°C. HRMS (ESI): calcd. for $C_{13}H_{12}BrO_2$ $[M+H]^+$ = 279.0015; found 279.0018. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.15 (t, *J* = 6.7 Hz, 1H), 2.55 – 2.60 (m, 1H), 2.62 – 2.73 (m, 1H), 2.84 – 2.95 (m, 1H), 5.63 – 5.69 (m, 1H), 5.90 (dd, *J* = 5.4, 2.1 Hz, 1H), 7.27 – 7.32 (m, 2H), 7.40 – 7.47 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.9, 34.4, 37.8, 40.0, 121.6, 130.1, 130.7, 131.8, 132.3, 138.3, 173.6 ppm.

Procedure for preparation of amides 6

Pyrrolidine (0.08-0.1 mmol, 2 mol. equiv.) was added to a solution of acyl fluoride **3** (0.04-0.05 mmol, 1 mol. equiv.) in dichloromethane (1-1.2 mL). The mixture was stirred at room temperature for 5 min (TLC monitoring). After completion of the reaction, the mixture was extracted with an aqueous solution of 5% HCl (15 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under vacuum. The pure product **6** was isolated by column chromatography on silica gel using a hexane/ethyl acetate (2:1) mixture as eluent.

((1*S,5*R**,6*R**)-6-(4-Chlorophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone** (**6a**). 13 mg (89%); colorless oil. HRMS (ESI): calcd. for $C_{17}H_{19}ClNO$ $[M+H]^+$ = 288.1150; found 288.1152. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.67 – 1.85 (m, 4H), 1.92 – 2.05 (m, 1H), 2.60 – 2.74 (m, 2H), 3.01 (d, *J* = 17.1 Hz, 1H), 3.10 – 3.21 (m, 1H), 3.21 – 3.31 (m, 1H), 3.31 – 3.41 (m, 1H), 3.42 – 3.53 (m, 1H), 5.66 – 5.73 (m, 1H), 5.81 – 5.88 (m, 1H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz,

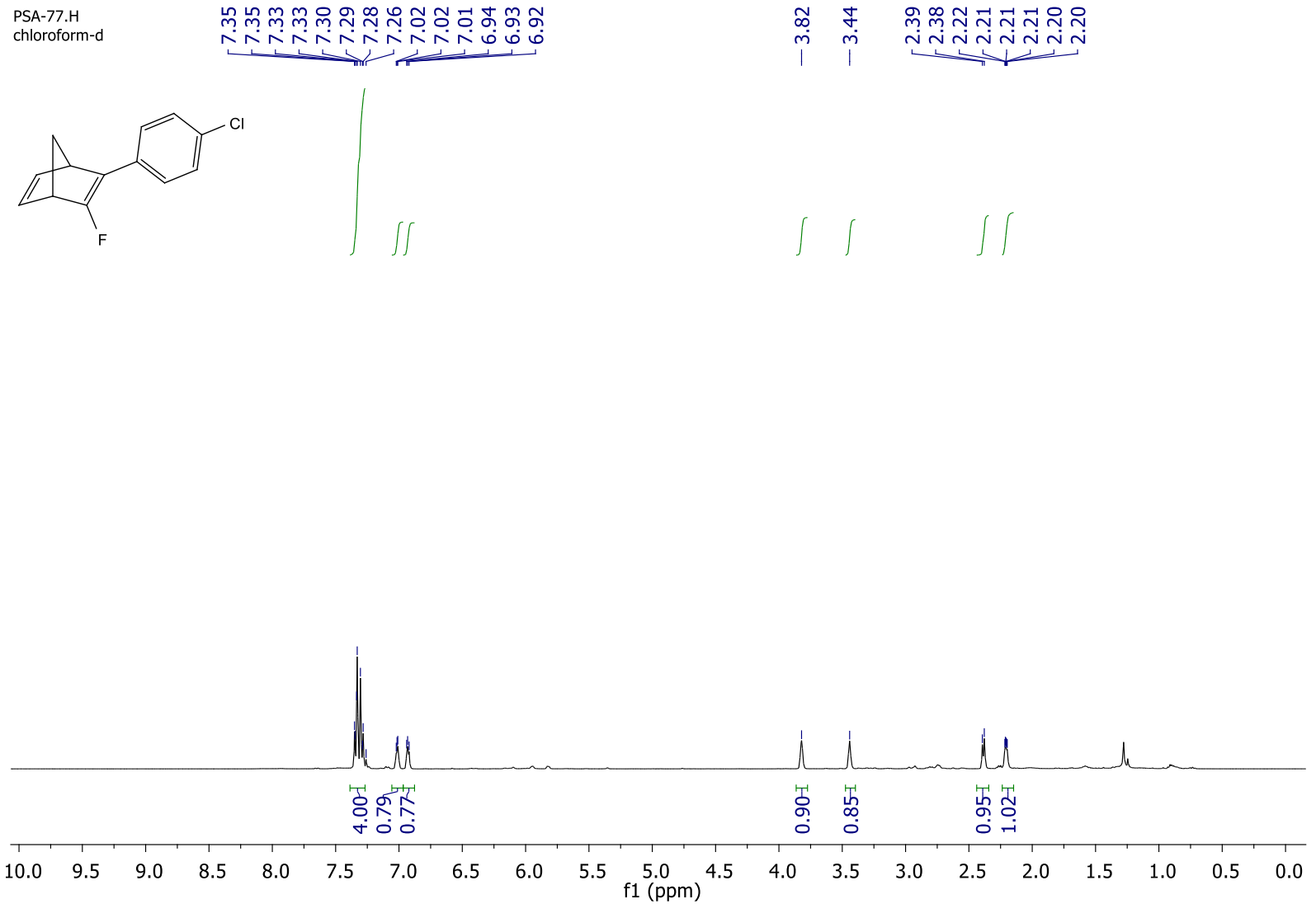
2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.2, 26.2, 31.1, 34.6, 35.6, 39.3, 45.7, 46.8, 126.9, 128.2, 128.8, 132.0, 133.7, 139.3, 166.9 ppm.

((1*S,5*R**,6*R**)-6-(4-Bromophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone** (**6b**). 13 mg (95%); colorless oil. HRMS (ESI): calcd. for $C_{17}H_{19}BrNO$ $[M+H]^+$ = 332.0645; found 332.0650. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.69 – 1.85 (m, 4H), 1.93 – 2.06 (m, 1H), 2.58 – 2.76 (m, 2H), 2.93 – 3.09 (m, 1H), 3.11 – 3.21 (m, 1H), 3.22 – 3.31 (m, 1H), 3.31 – 3.42 (m, 1H), 3.43 – 3.54 (m, 1H), 5.67 – 5.74 (m, 1H), 5.81 – 5.88 (m, 1H), 6.97 – 7.04 (m, 2H), 7.35 – 7.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.3, 26.2, 29.8, 34.7, 35.7, 39.3, 45.7, 46.8, 120.1, 127.3, 128.1, 131.7, 133.8, 139.9, 166.8 ppm.

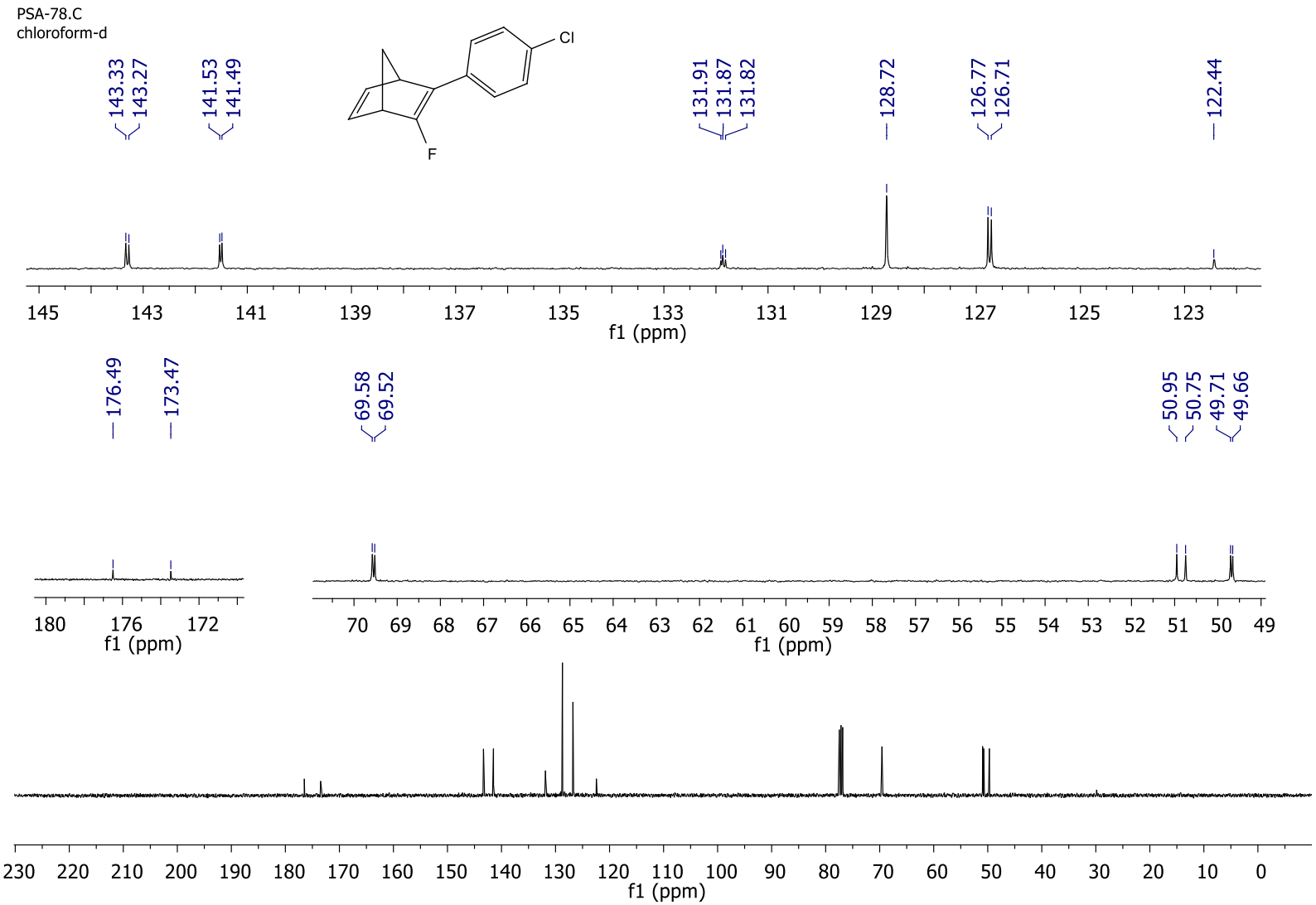
Table S1 Optimization of the reaction conditions for synthesis of norbornadienes **2**[a]

#	Substrate	T °C	Base	Conv.[b] %	Yield[b] %
1	**1a**	65[c]	DBU (4 eq)	40	34
2	**1a**	rt	Bu^{t}OK (1 eq)	28	25
3	**1a**	rt	Bu^{t}OK (2 eq)	64	60
4	**1a**	rt	Bu^{t}OK (3 eq)	79	72
5	**1a**	rt	Bu^{t}OK (4 eq)	100	100 (89)[d]
6	**1f**	rt	DBU (4 eq)	100	0
7	**1f**	rt	Bu^{t}OK (1.1 eq)	80	80
8	**1f**	rt	Bu^{t}OK (2 eq)	100	77[d]
9	**1f**	rt	Bu^{t}OK (4 eq)	100	trace

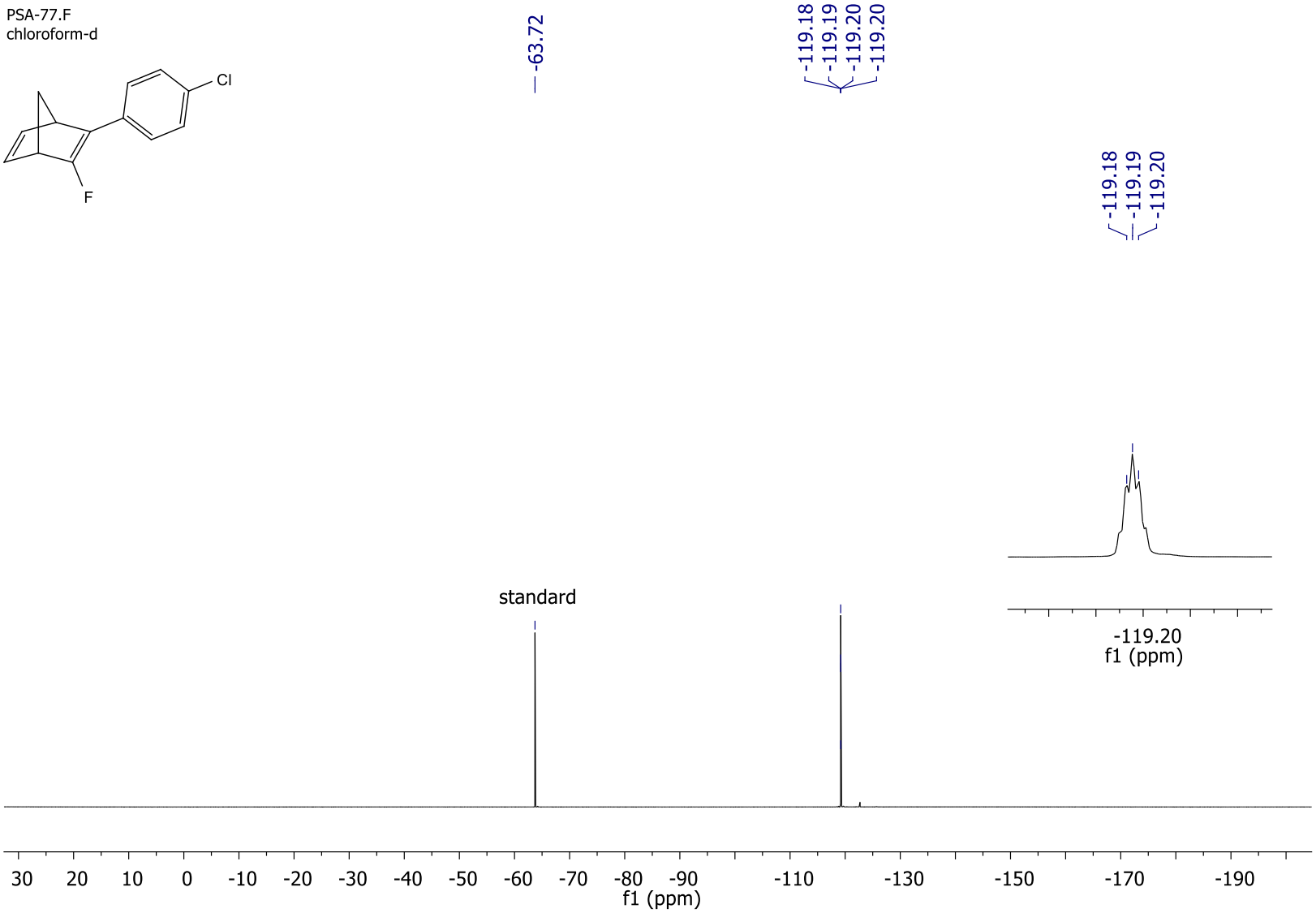
(a) – reaction conditions: 0.2 mmol of **1** in THF (1 ml); overnight
(b) – calculated via ^{19}F NMR spectra using $CF_3C_6H_5$ as an internal standard
(c) – reaction time 15h
(d) – isolated by flash column chromatography on neutral Al_2O_3



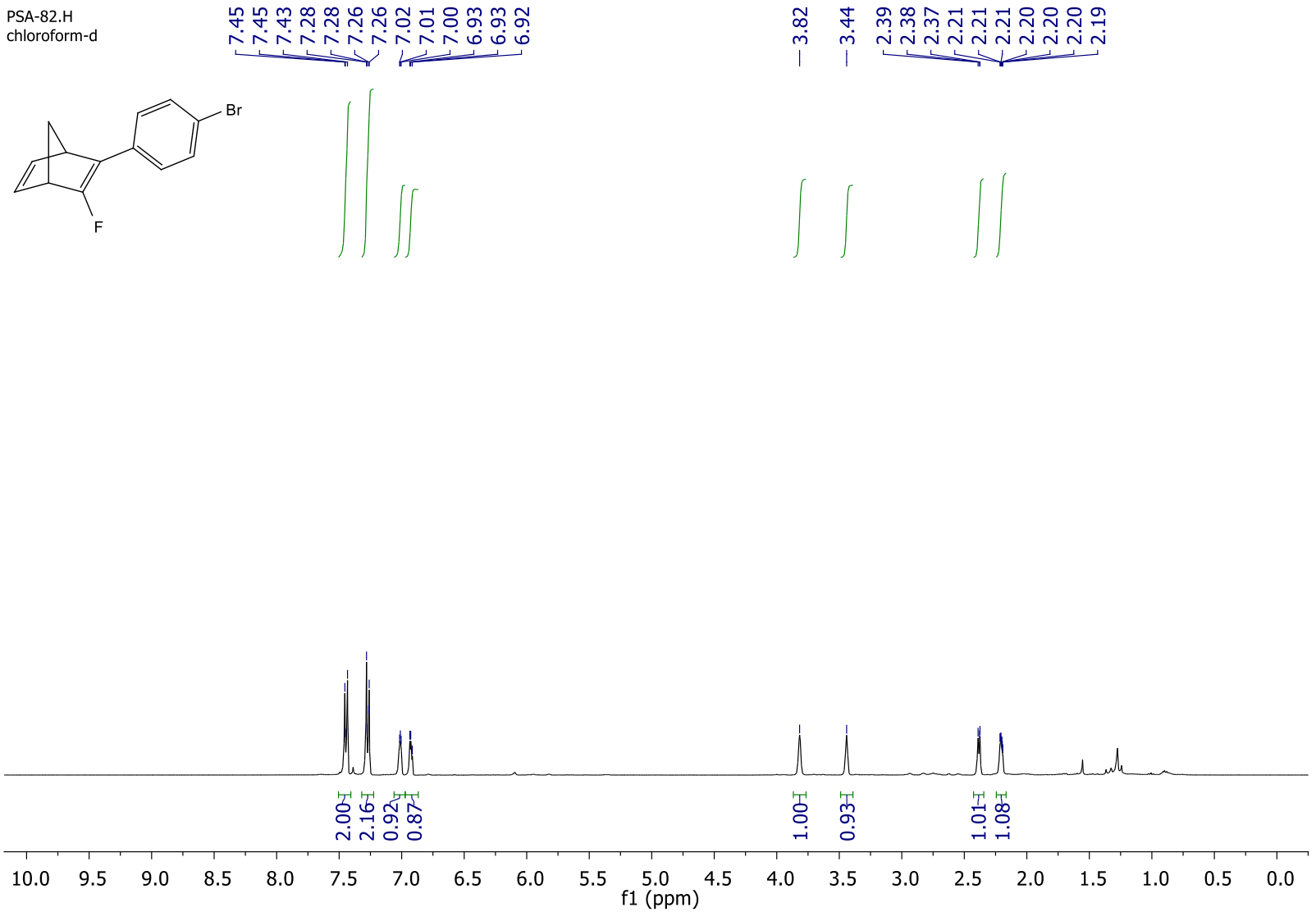
^{1}H NMR spectrum of 2-(4-chlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2a**)



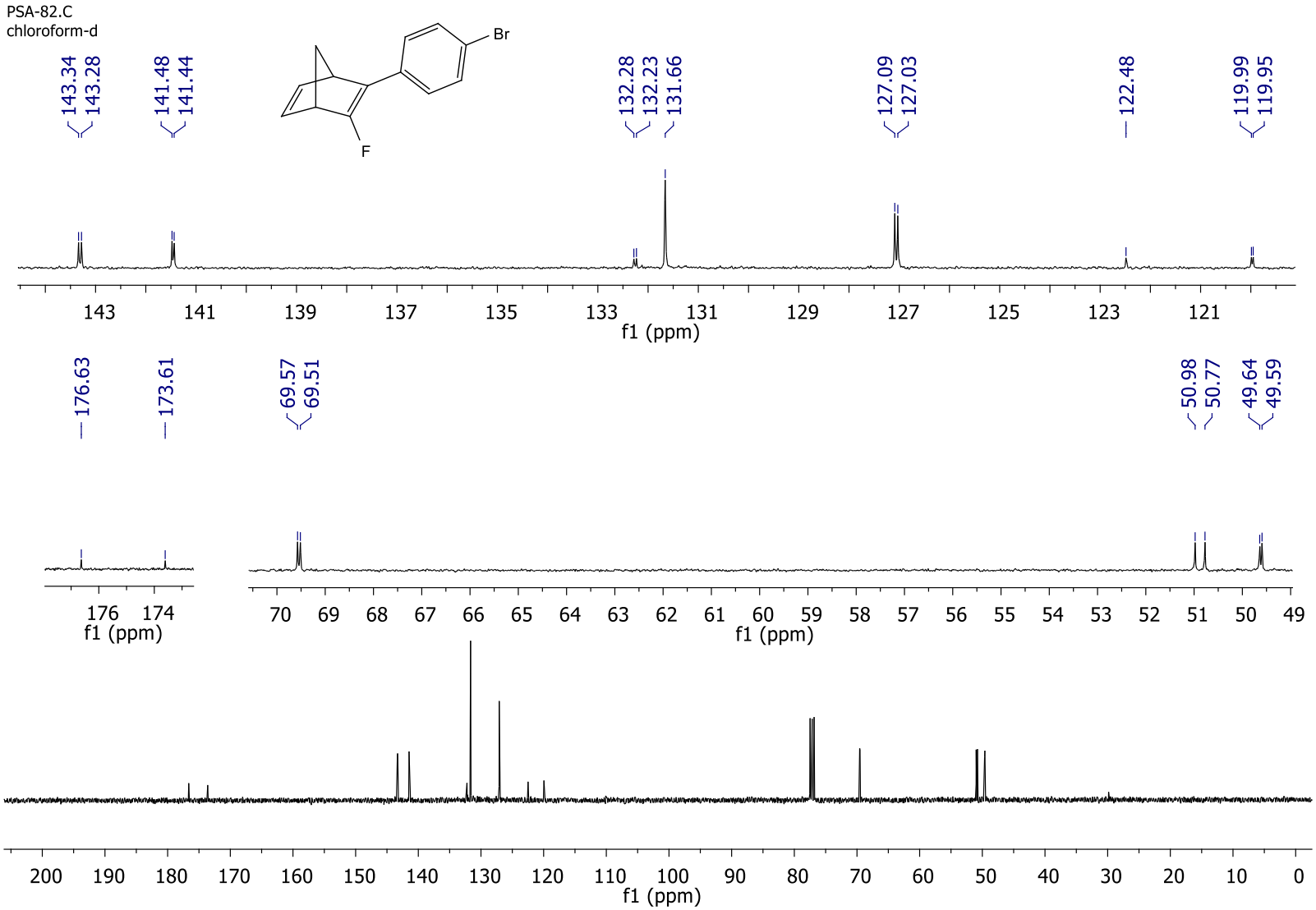
^{13}C NMR spectrum of 2-(4-chlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2a**)



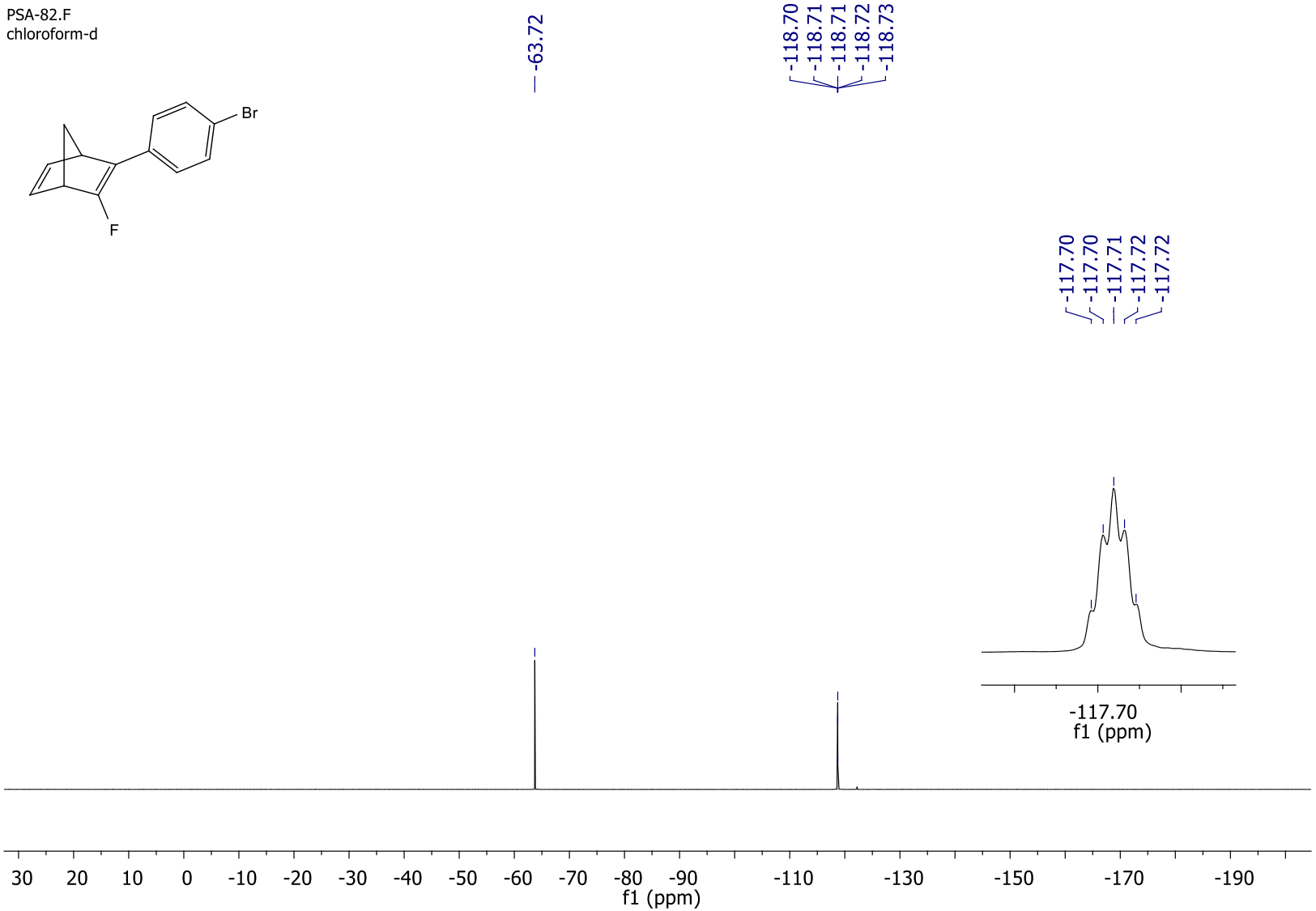
^{19}F NMR spectrum of 2-(4-chlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2a**)



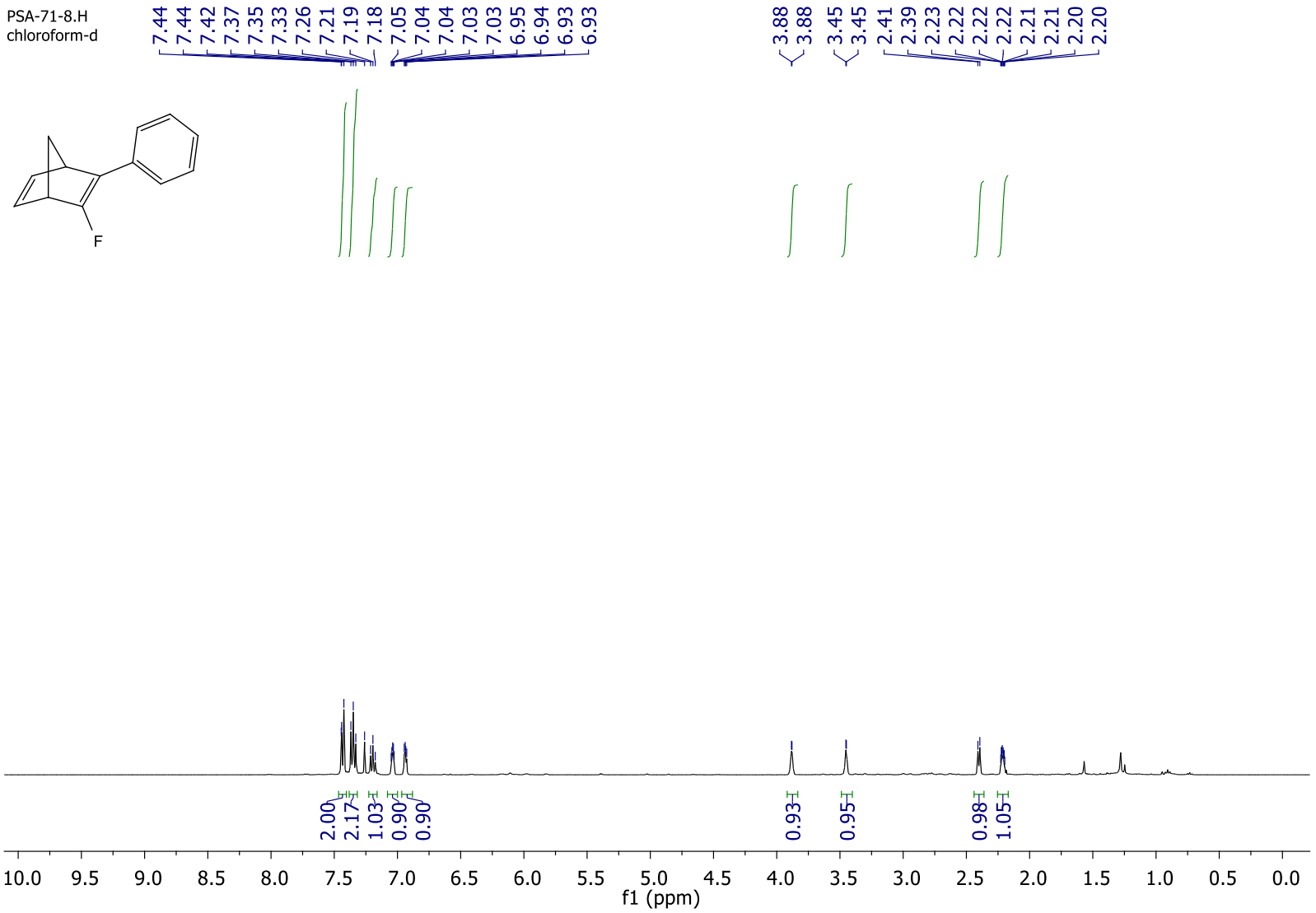
^{1}H NMR spectrum of 2-(4-bromophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2b**)



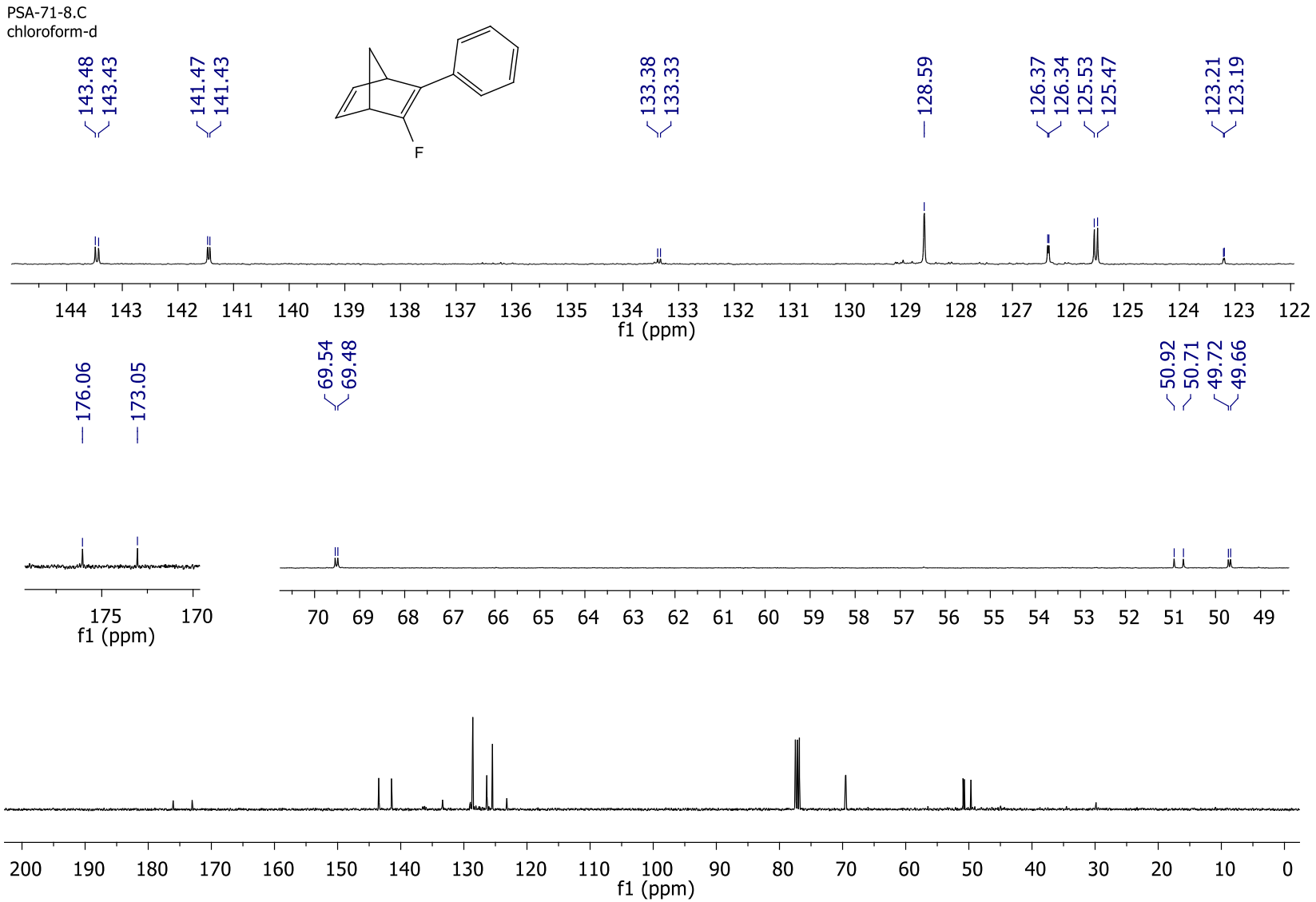
^{13}C NMR spectrum of 2-(4-bromophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2b**)



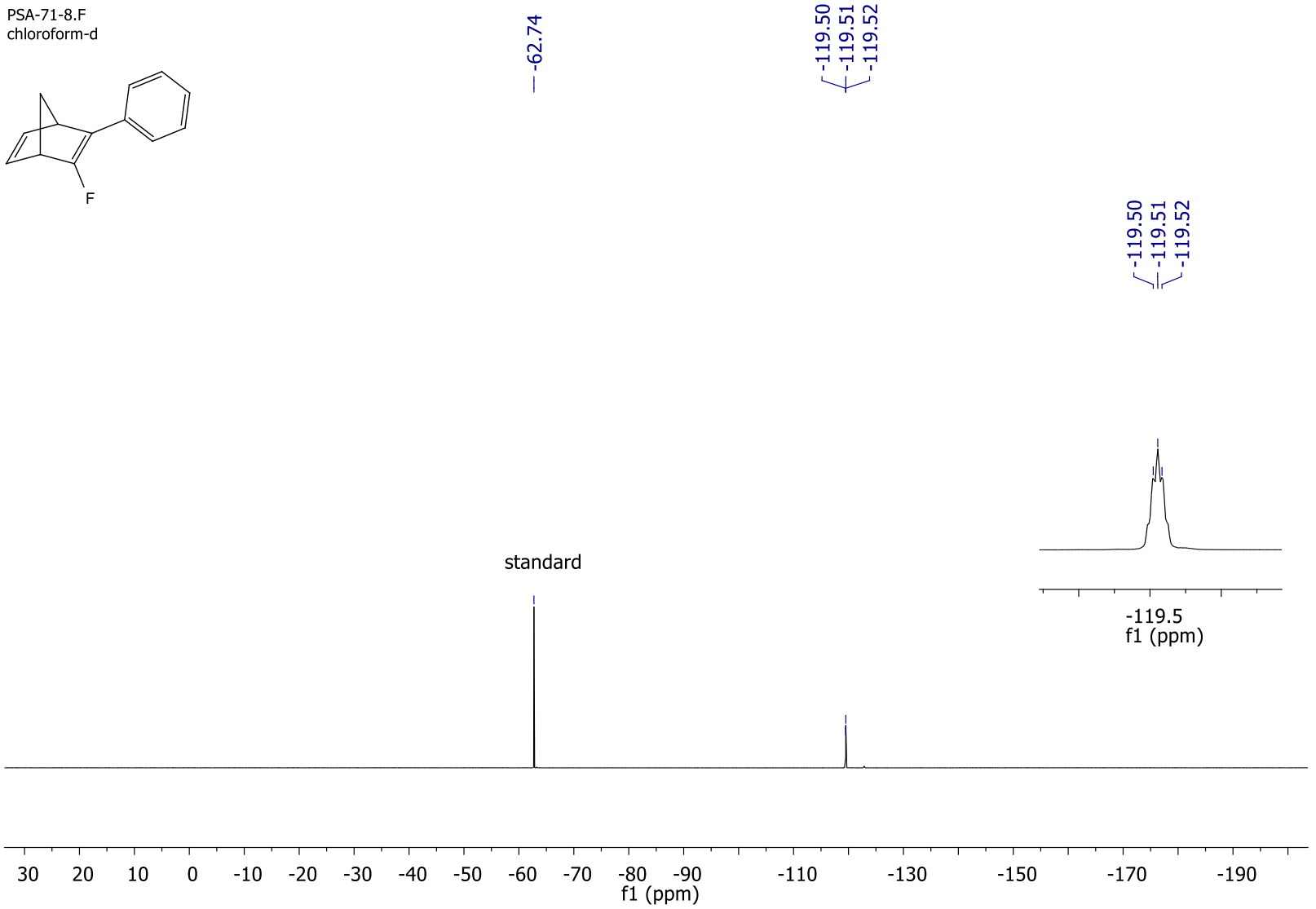
^{19}F NMR spectrum of 2-(4-bromophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2b**)



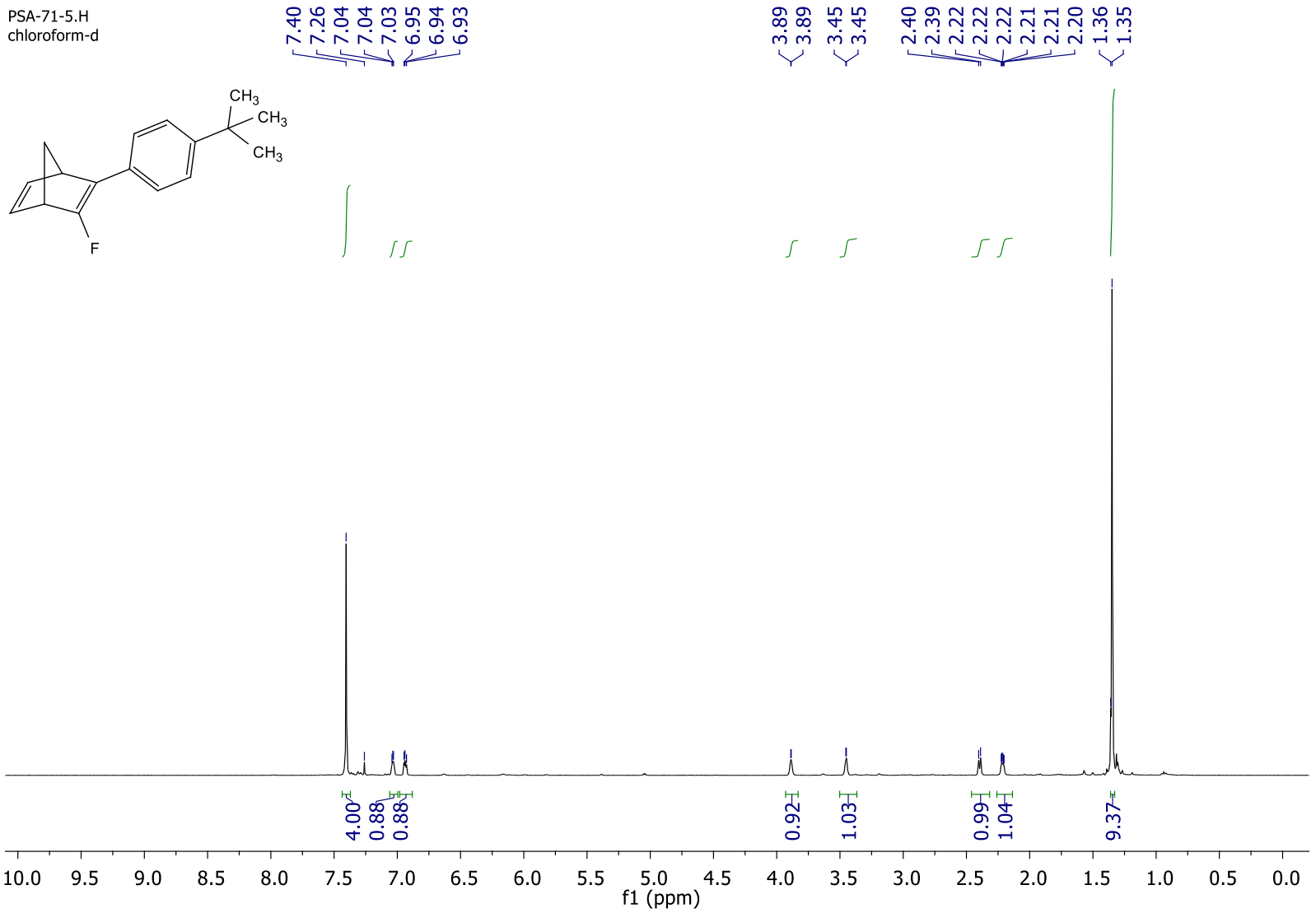
^{1}H NMR spectrum of 2-fluoro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (**2c**)



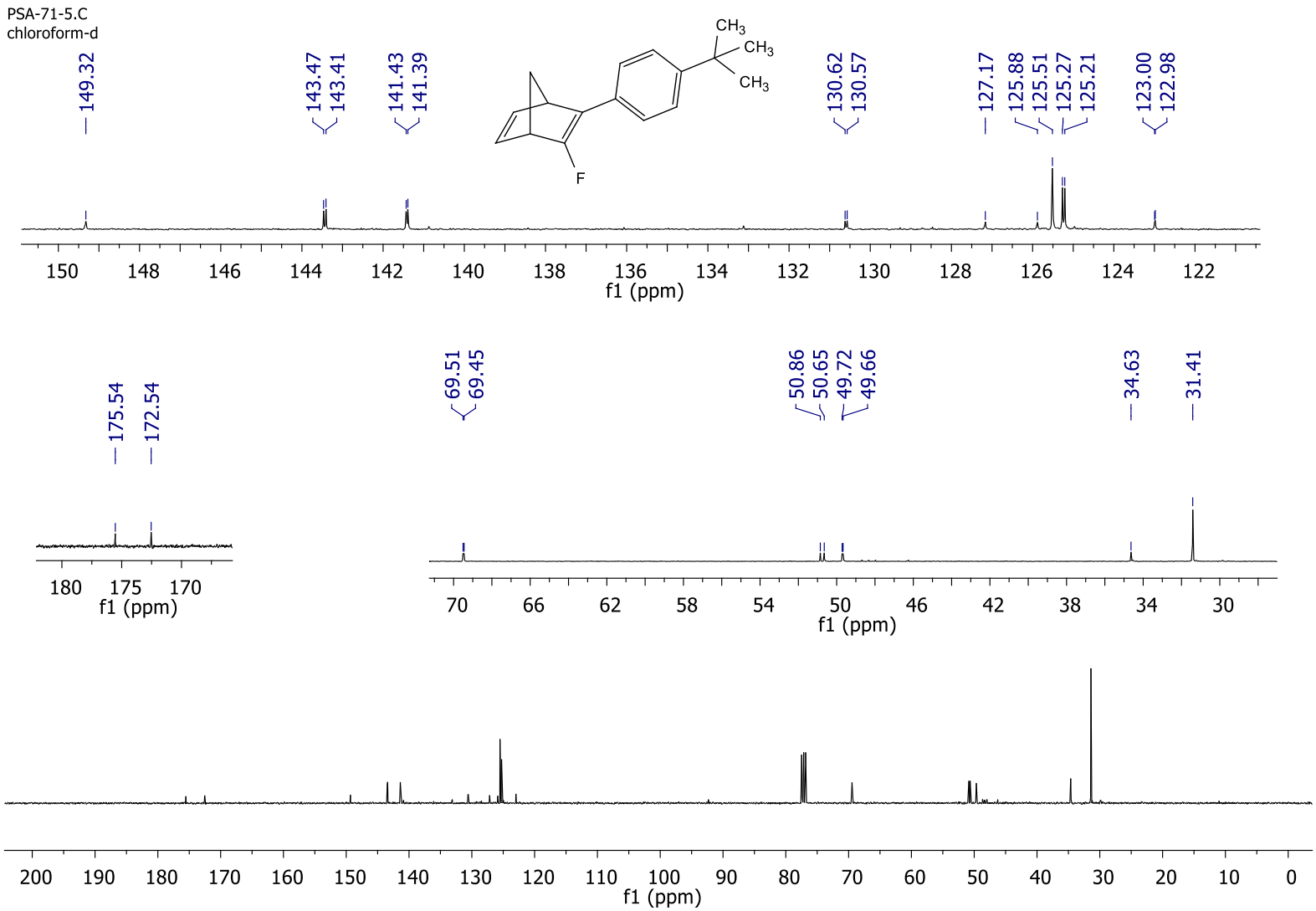
^{13}C NMR spectrum of 2-fluoro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (**2c**)



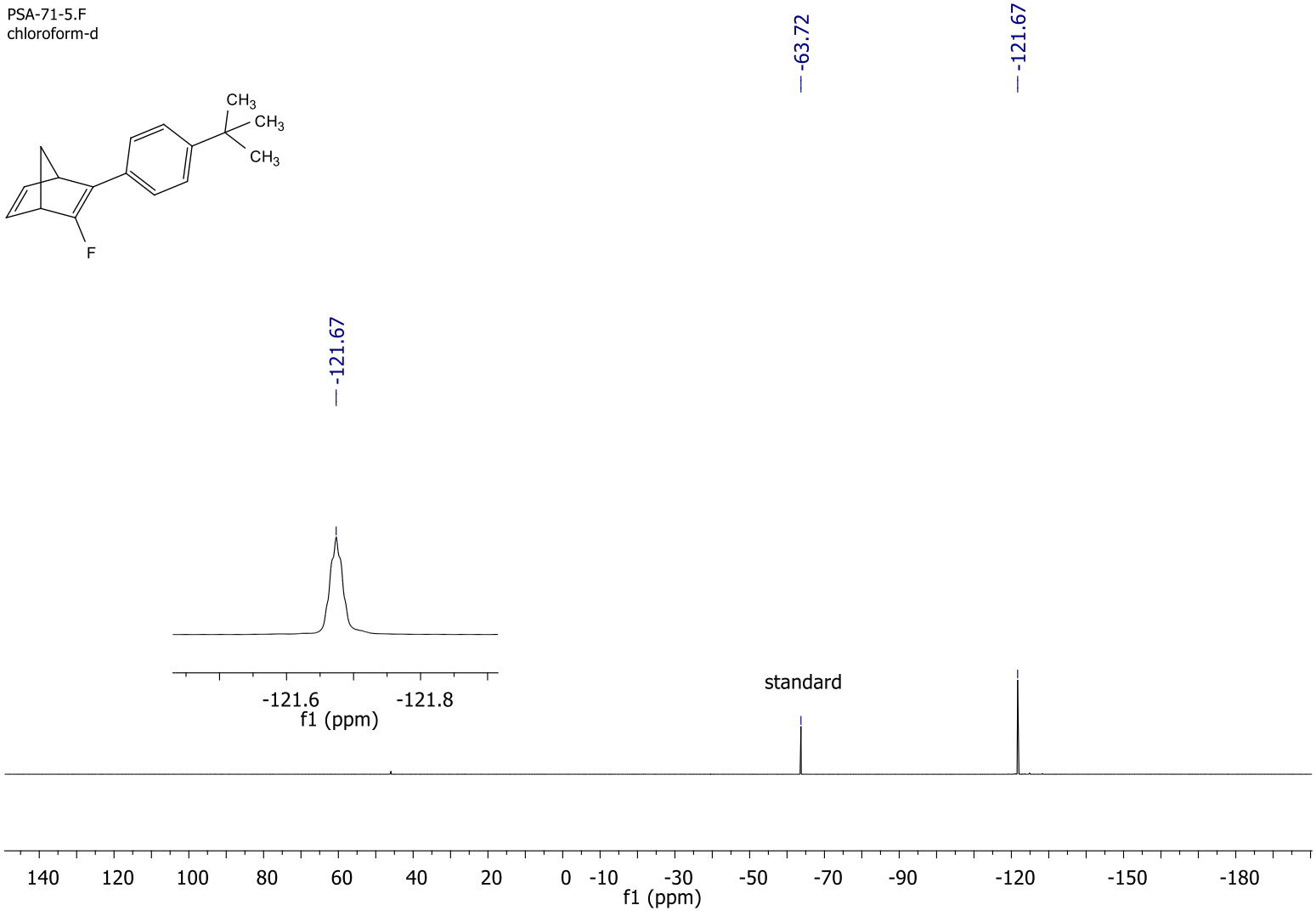
^{19}F NMR spectrum of 2-fluoro-3-phenylbicyclo[2.2.1]hepta-2,5-diene (**2c**)



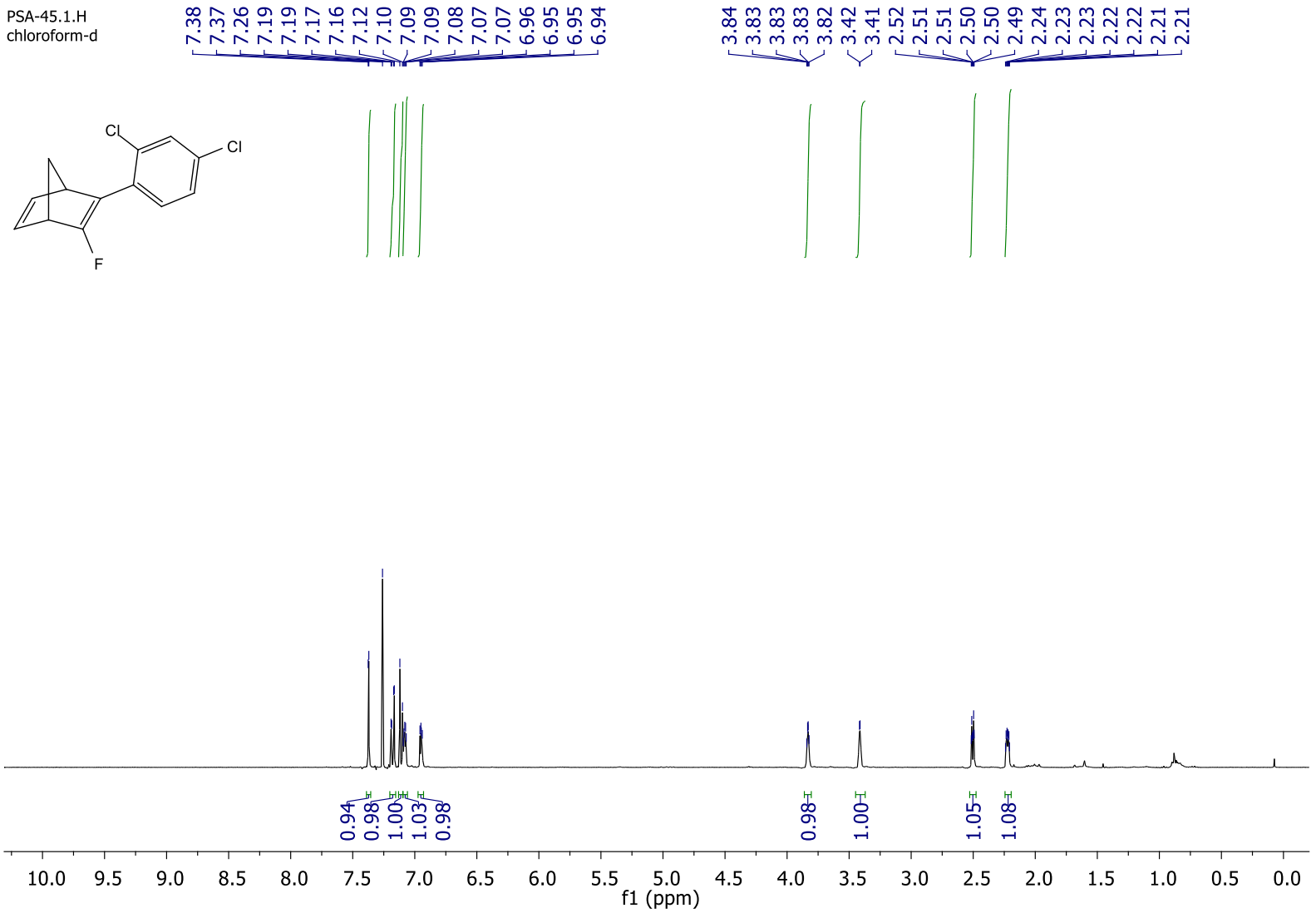
^{1}H NMR spectrum of 2-(4-*tert*-butylphenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2d**)



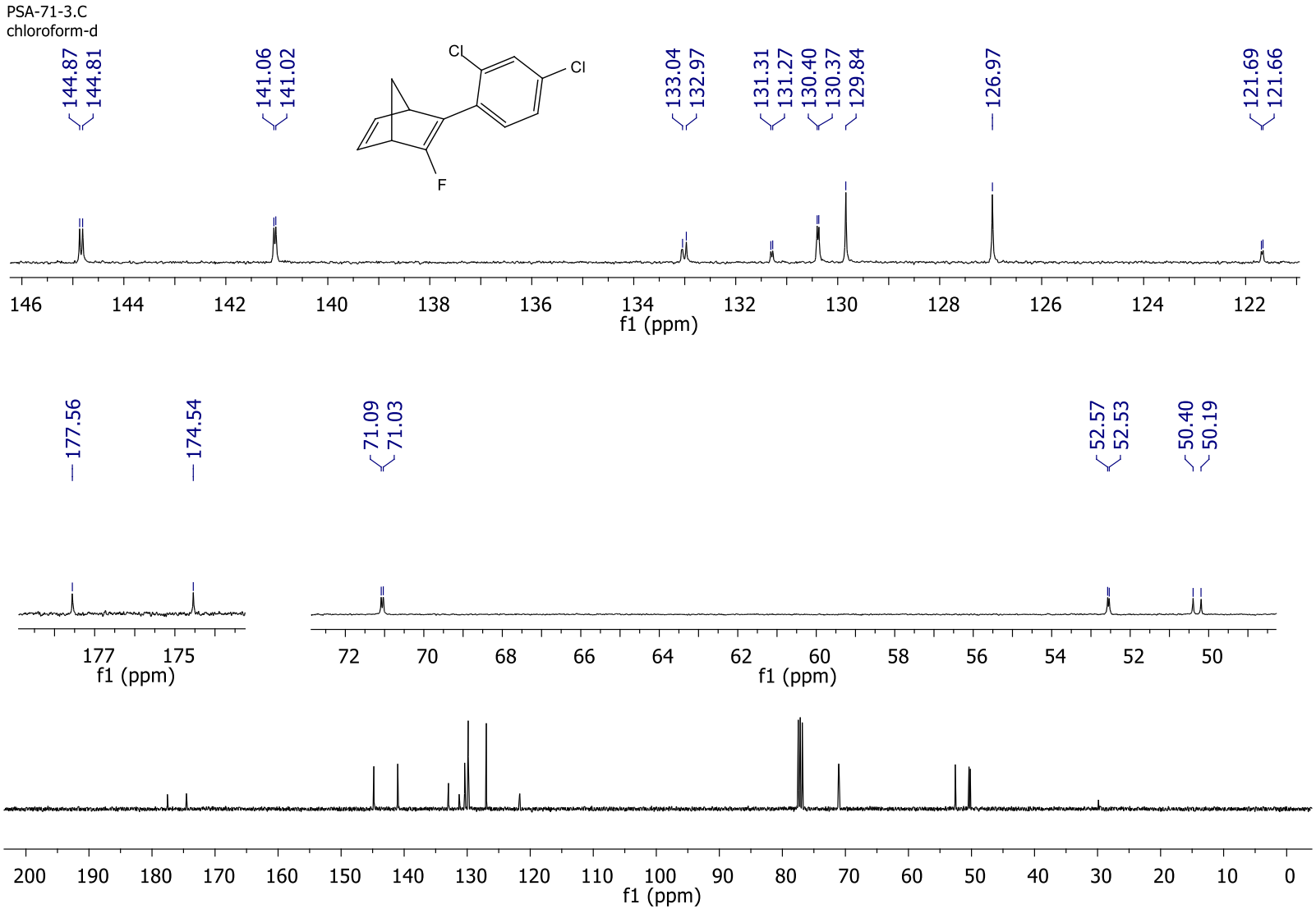
^{13}C NMR spectrum of 2-(4-*tert*-butylphenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2d**)



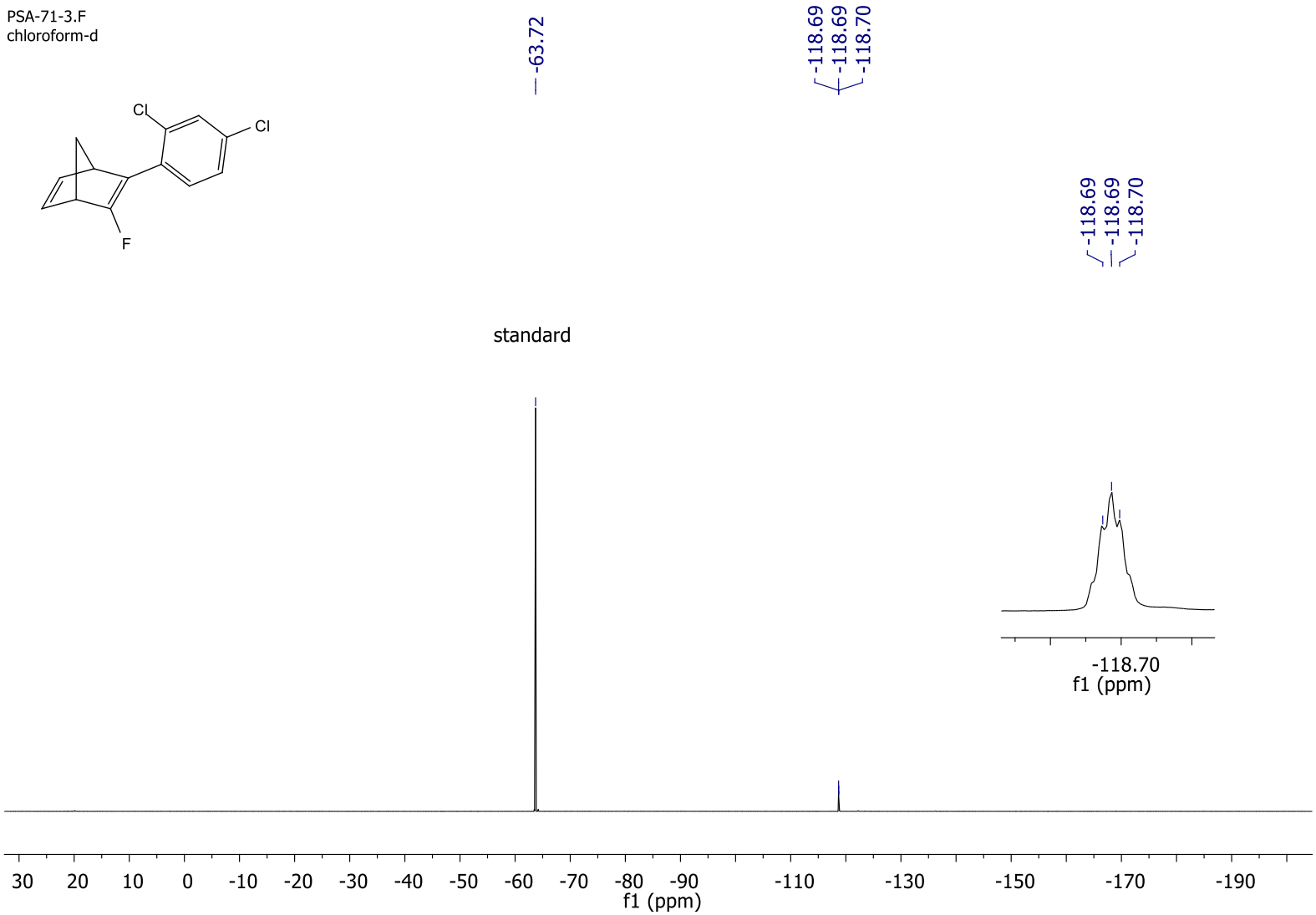
^{19}F NMR spectrum of 2-(4-*tert*-butylphenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2d**)



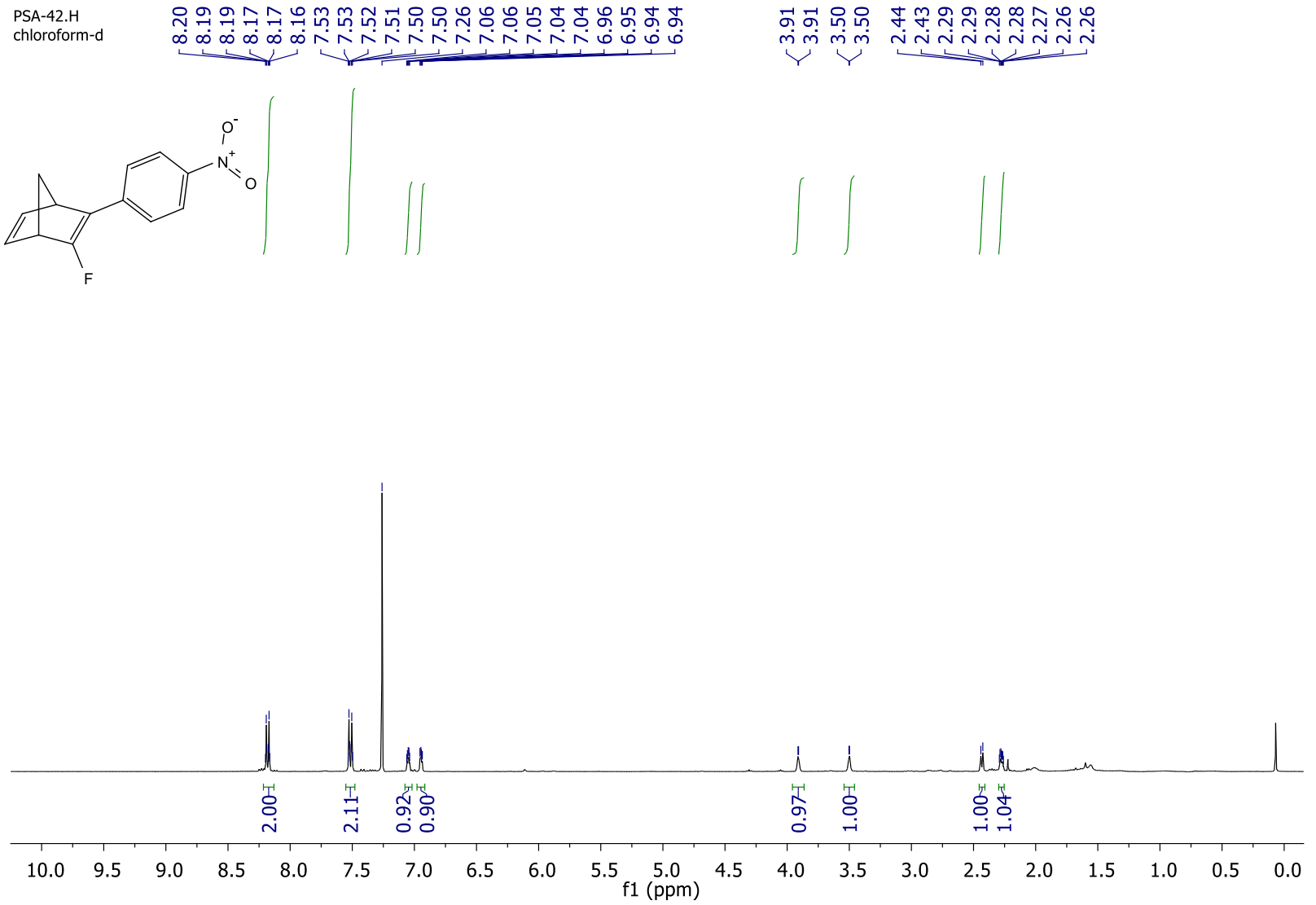
^{1}H NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2e**)



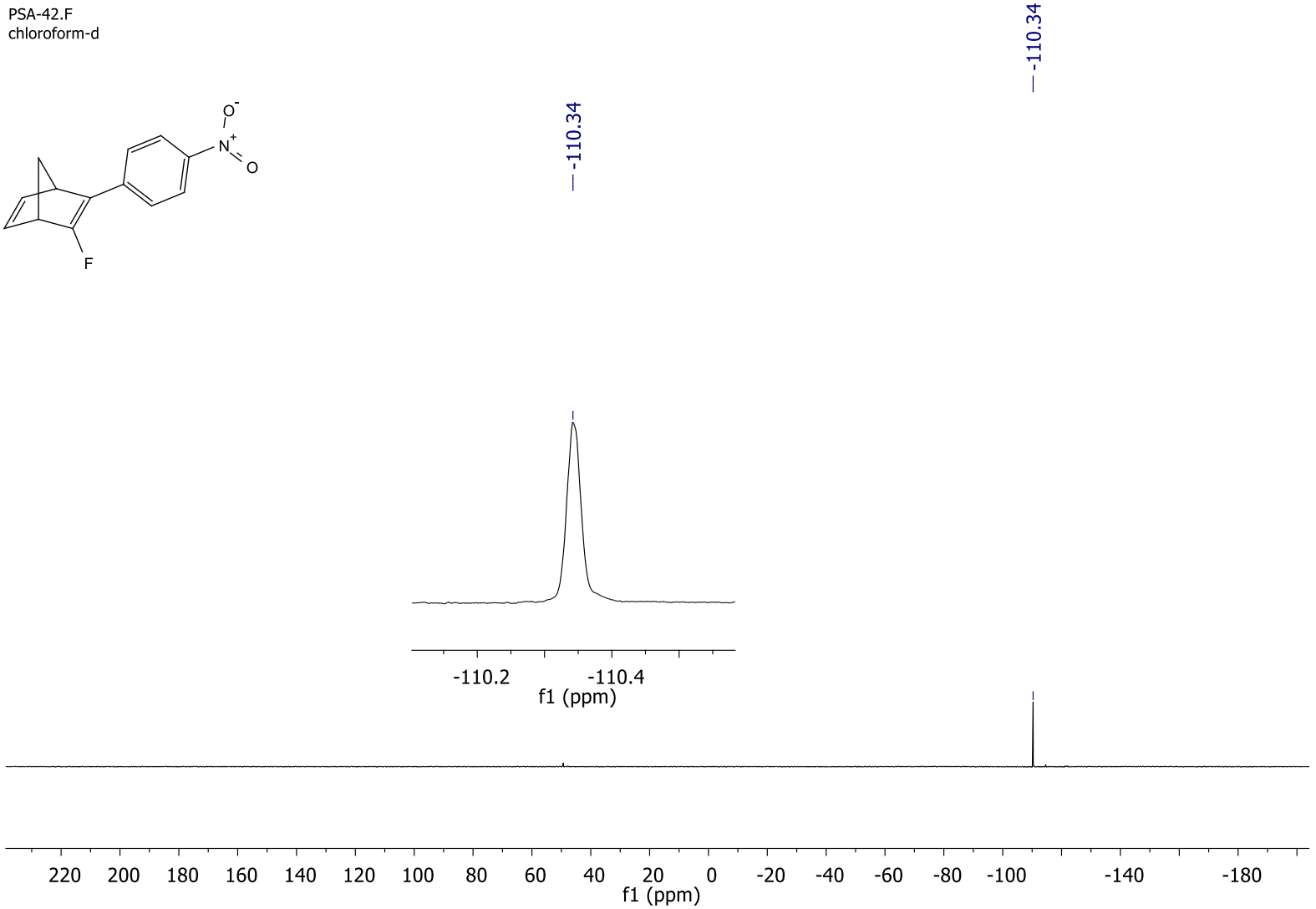
^{13}C NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2e**)



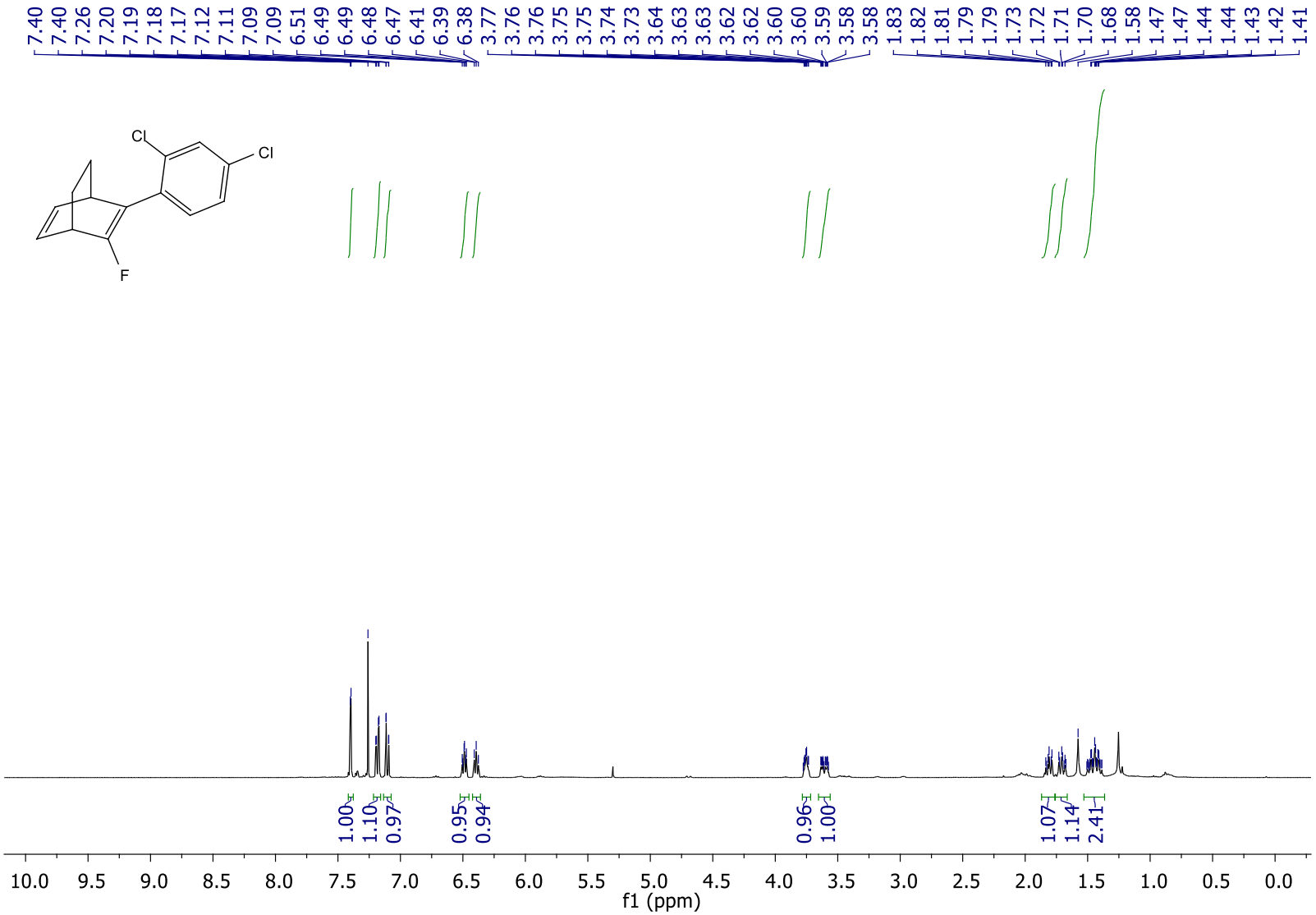
^{19}F NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.1]hepta-2,5-diene (**2e**)



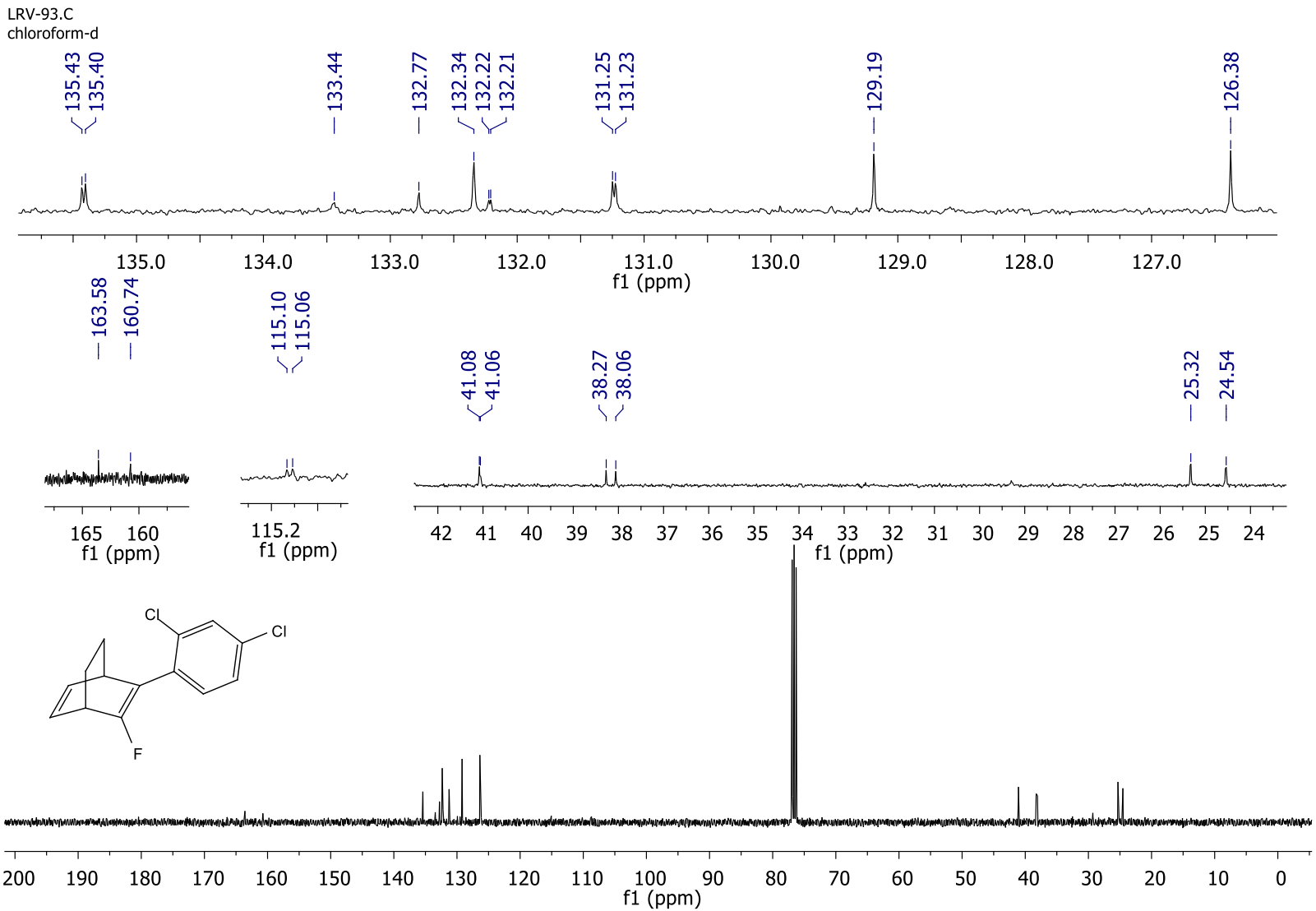
^{1}H NMR spectrum of 2-fluoro-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**2f**)



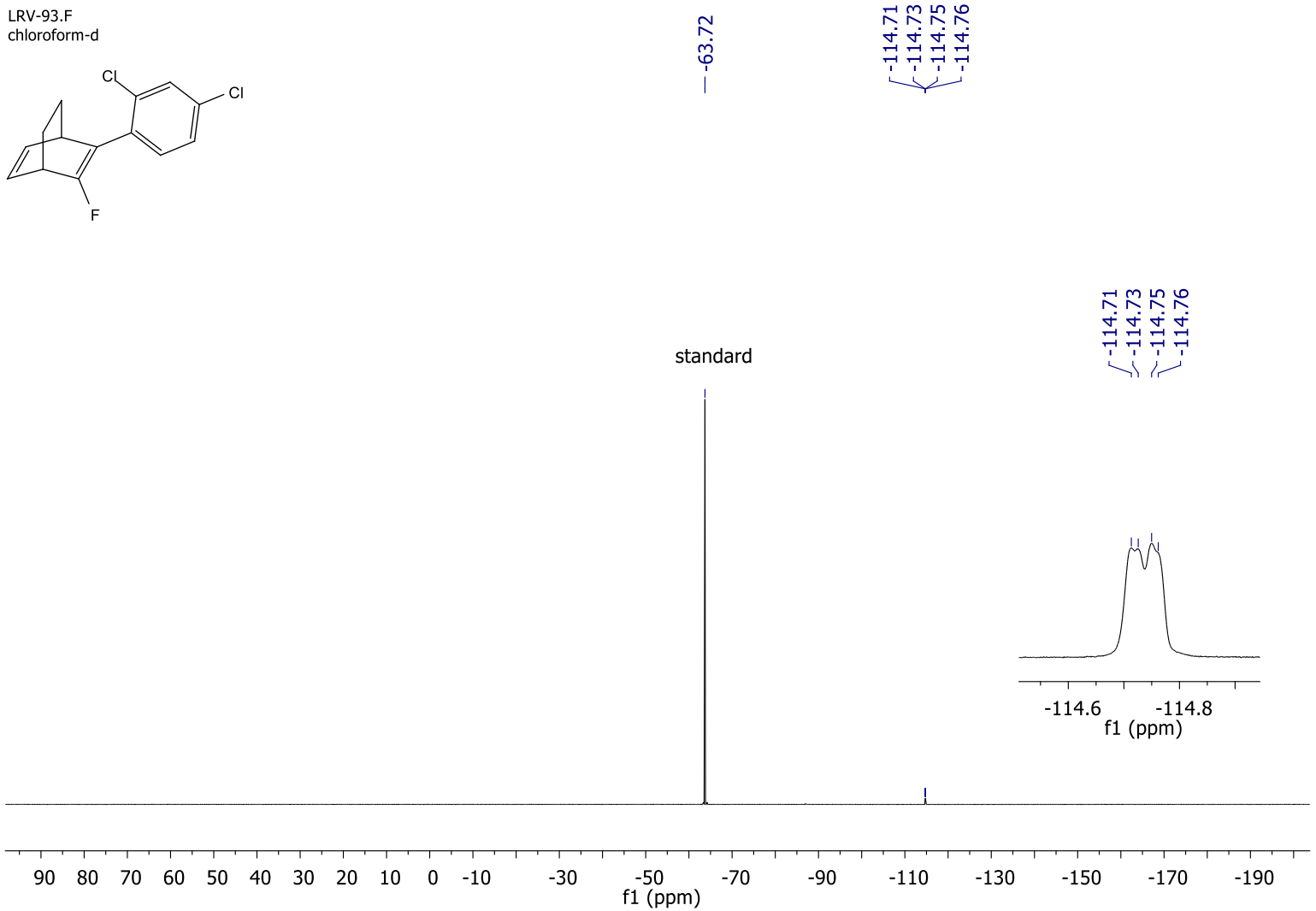
^{19}F NMR spectrum of 2-fluoro-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**2f**)



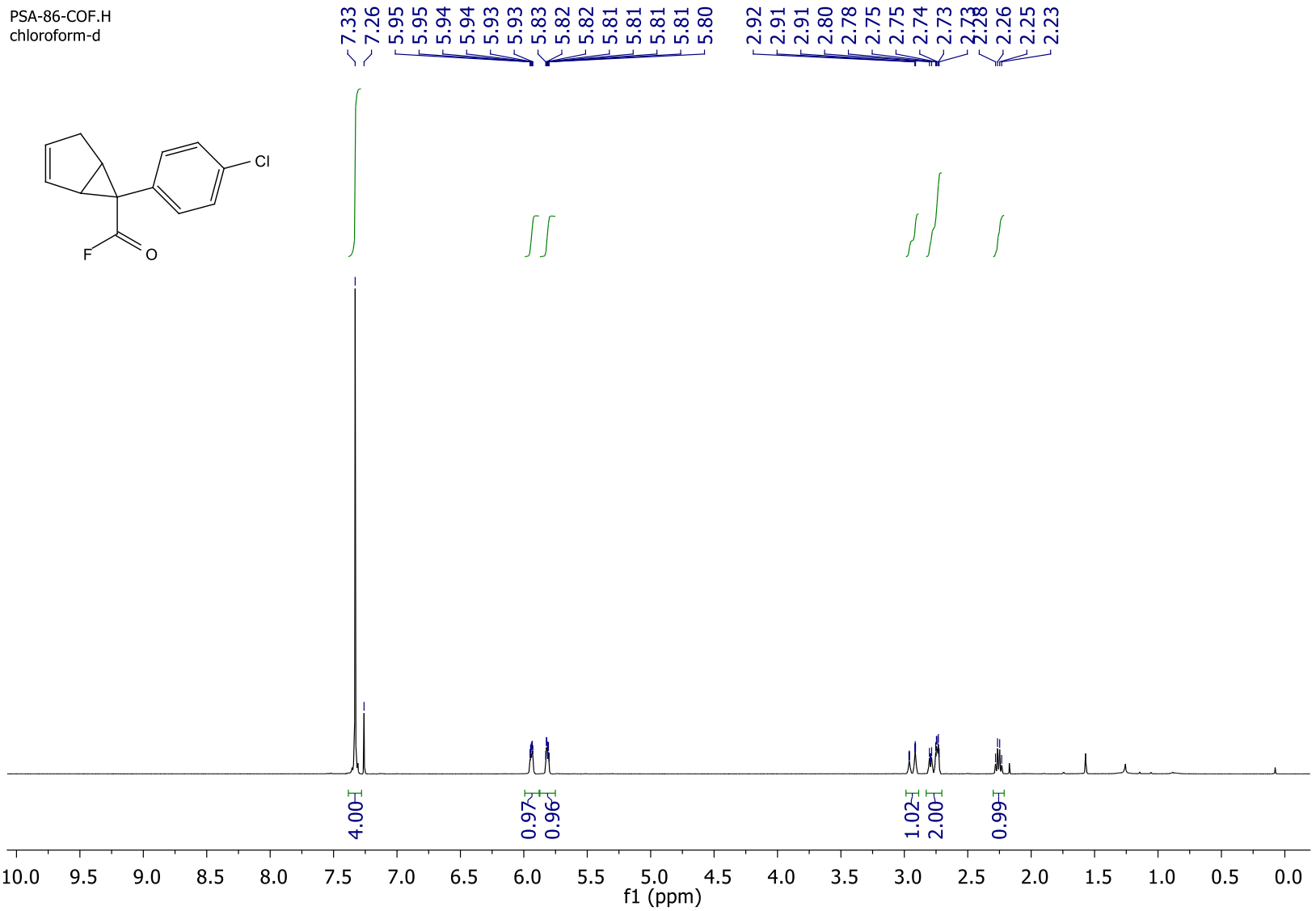
^{1}H NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.2]octa-2,5-diene (**8**)



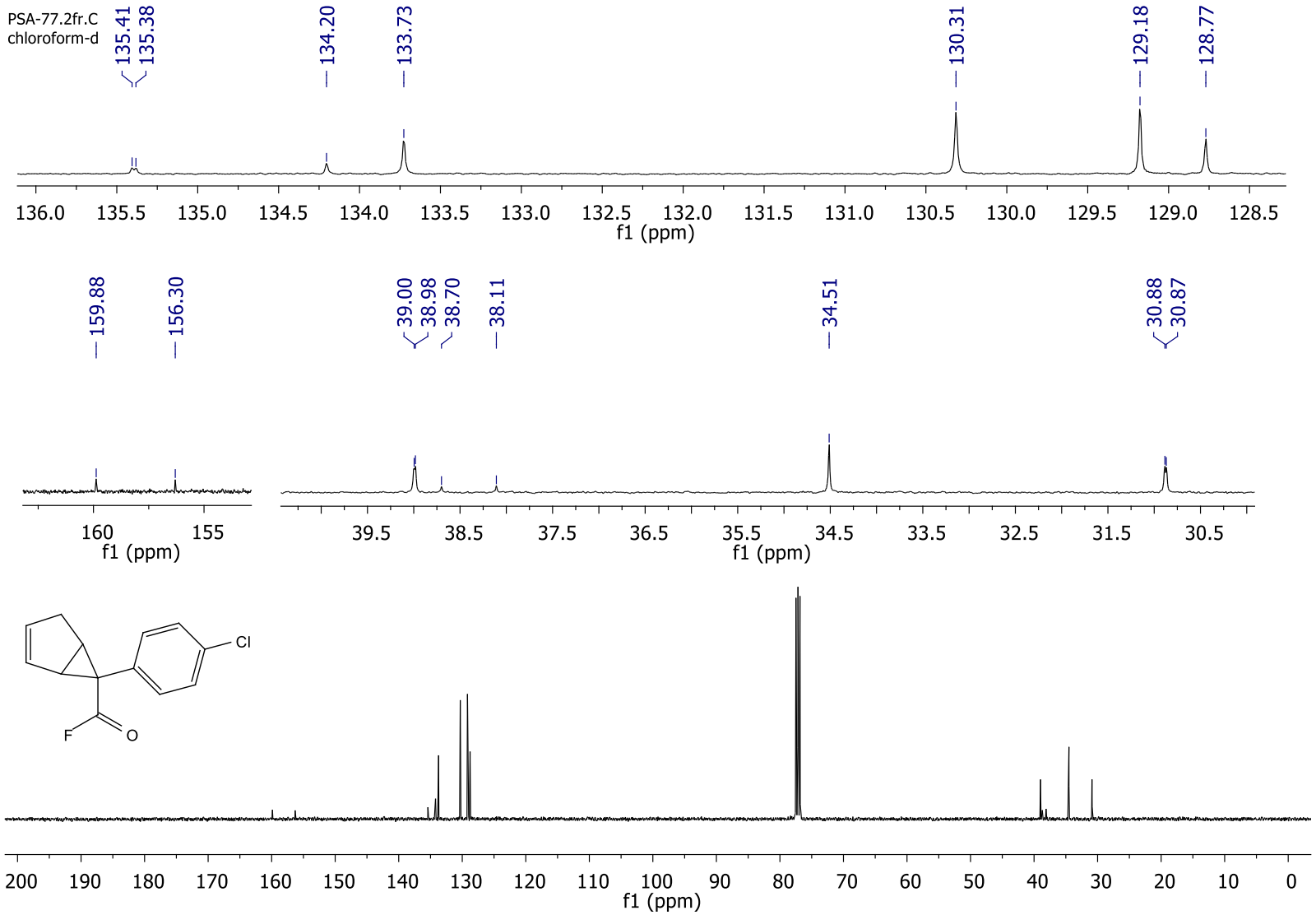
^{13}C NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.2]octa-2,5-diene (**8**)



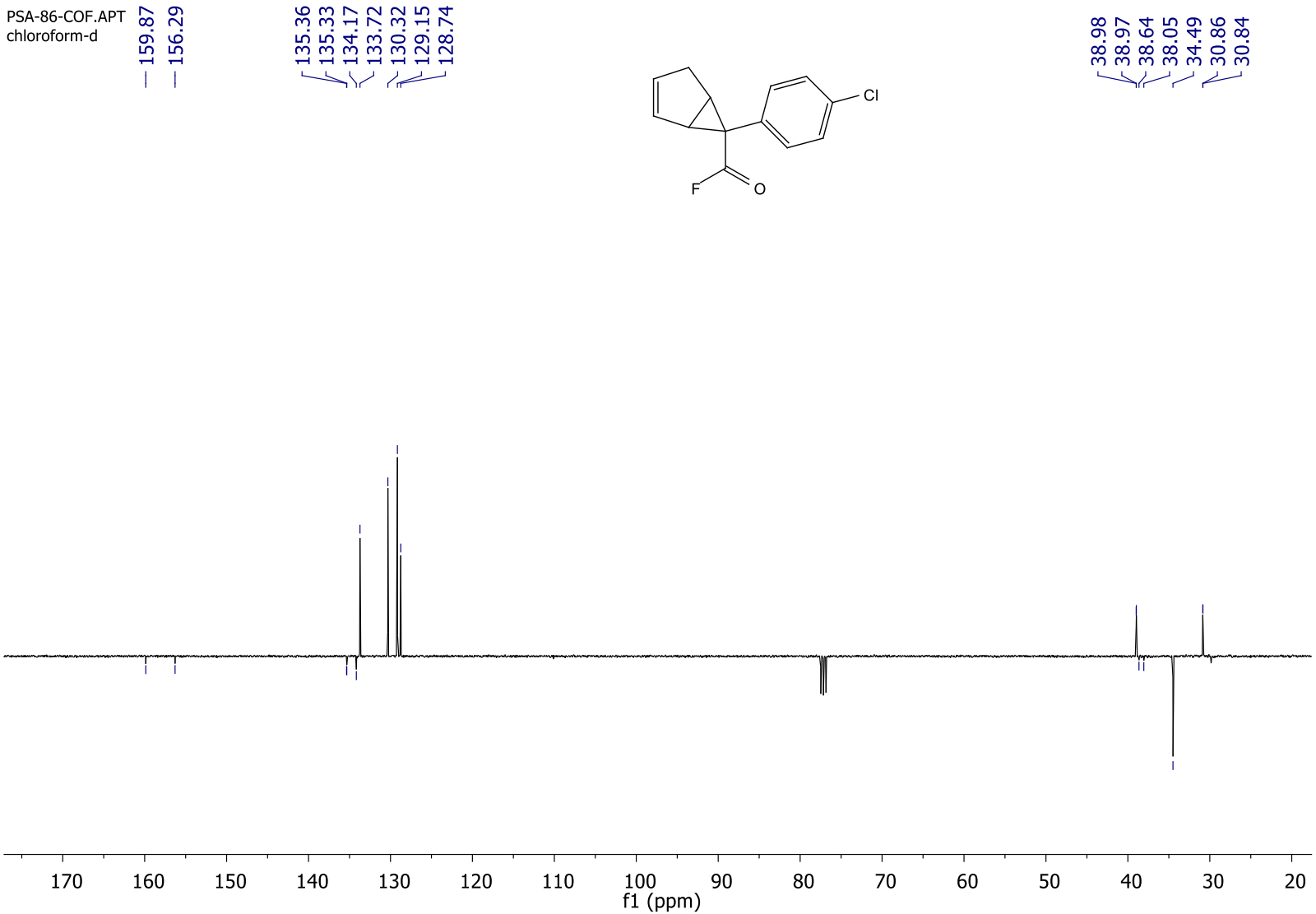
^{19}F NMR spectrum of 2-(2,4-dichlorophenyl)-3-fluorobicyclo[2.2.2]octa-2,5-diene (**8**)



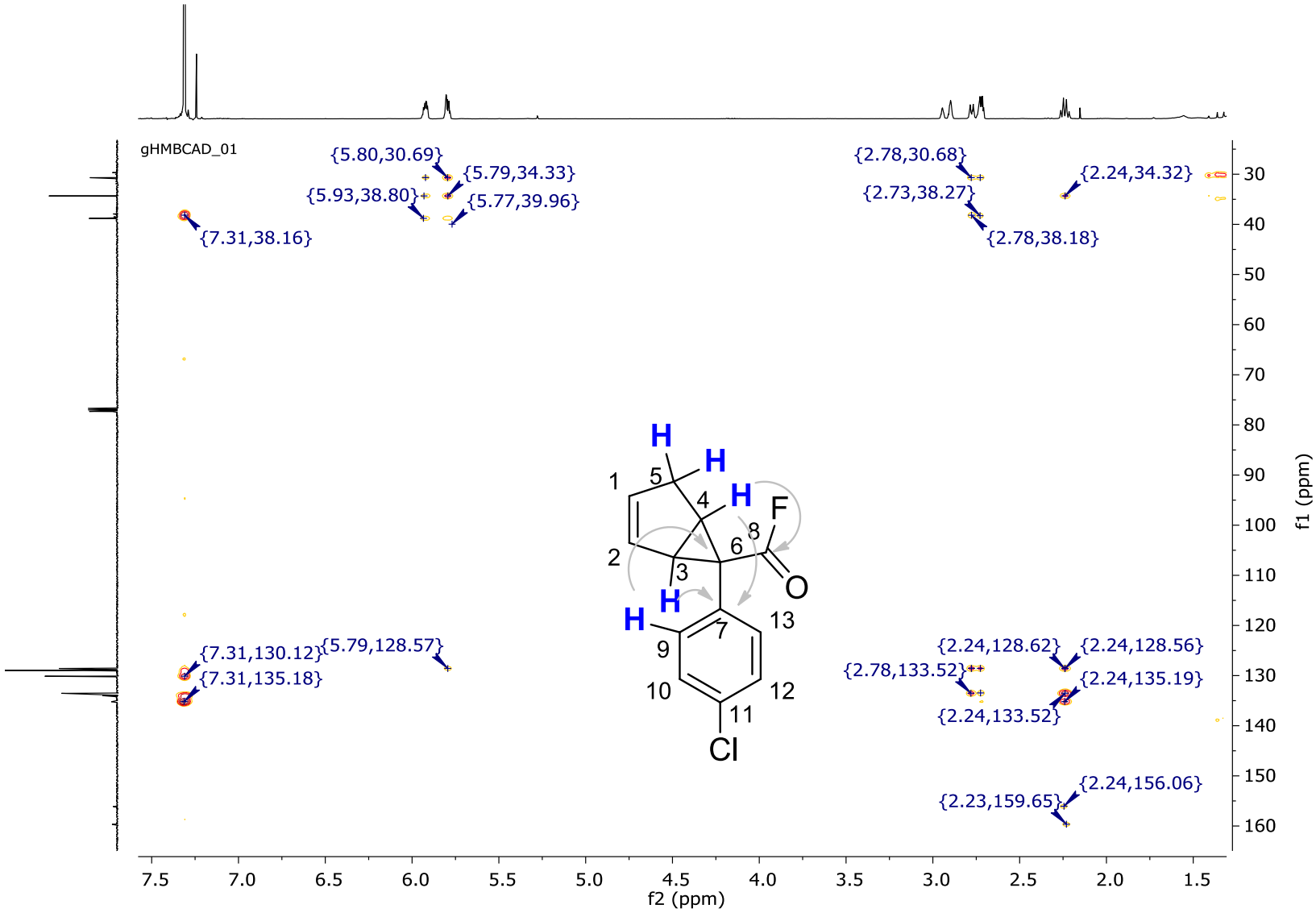
^{1}H NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



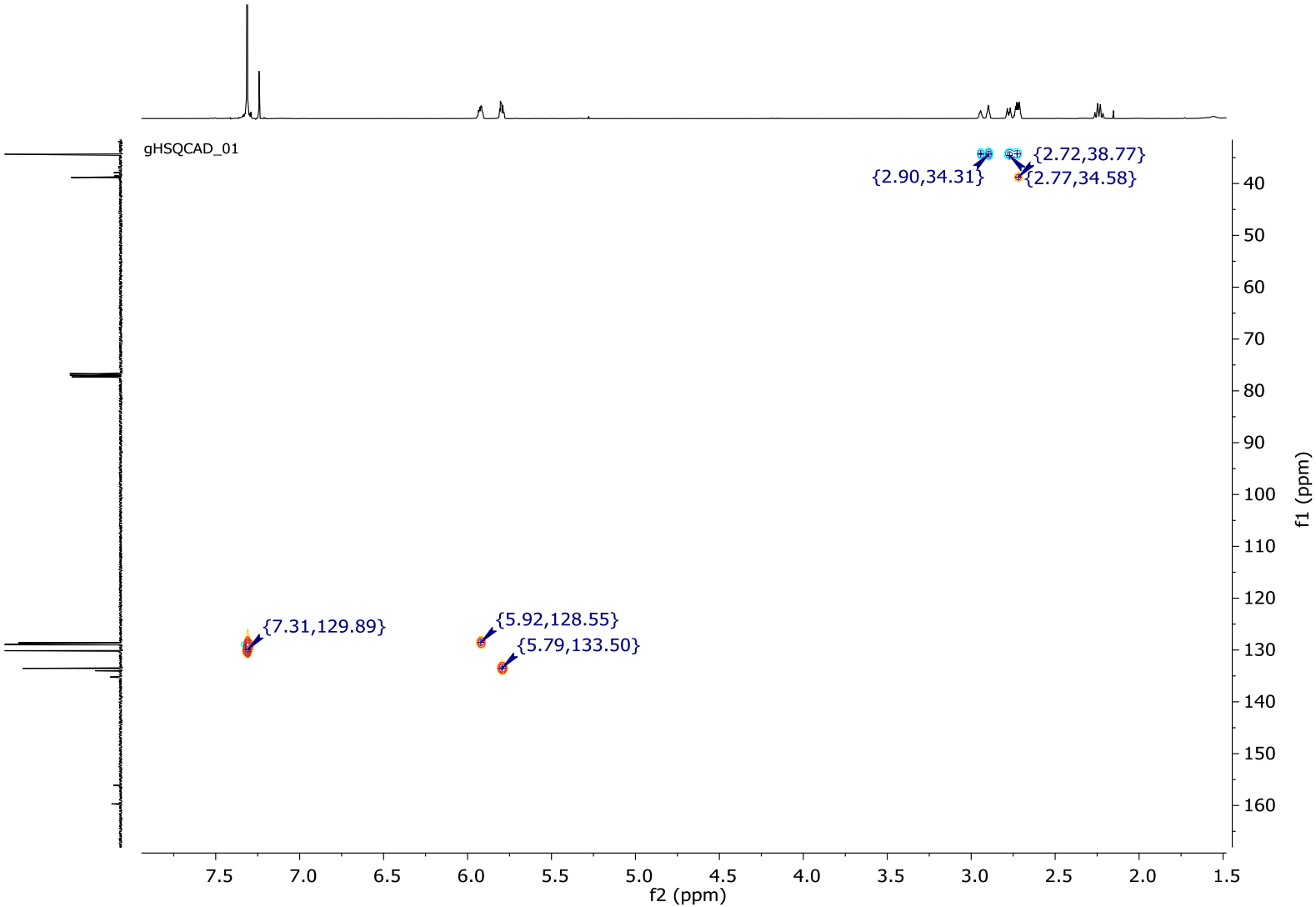
^{13}C NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



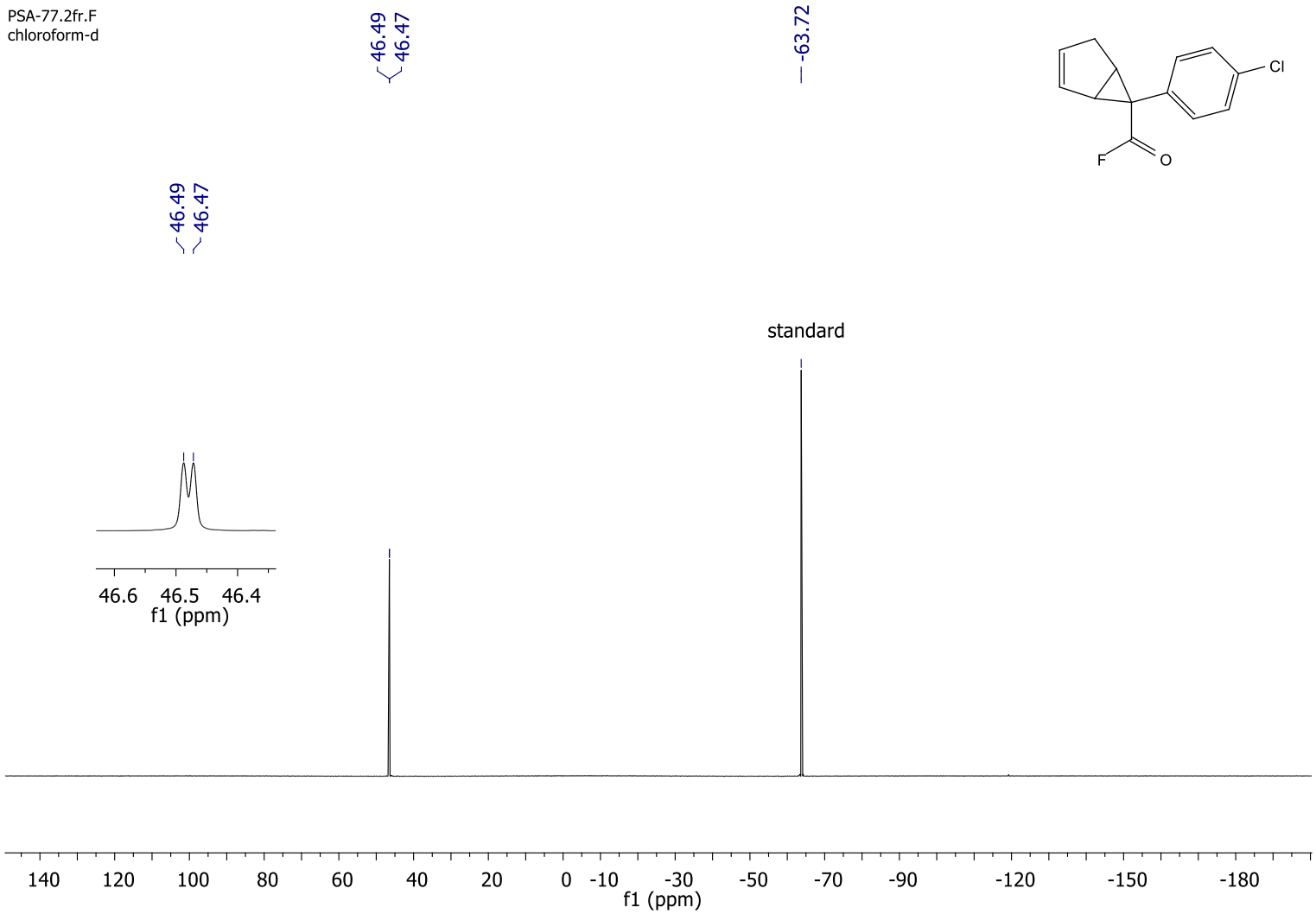
^{13}C APT NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



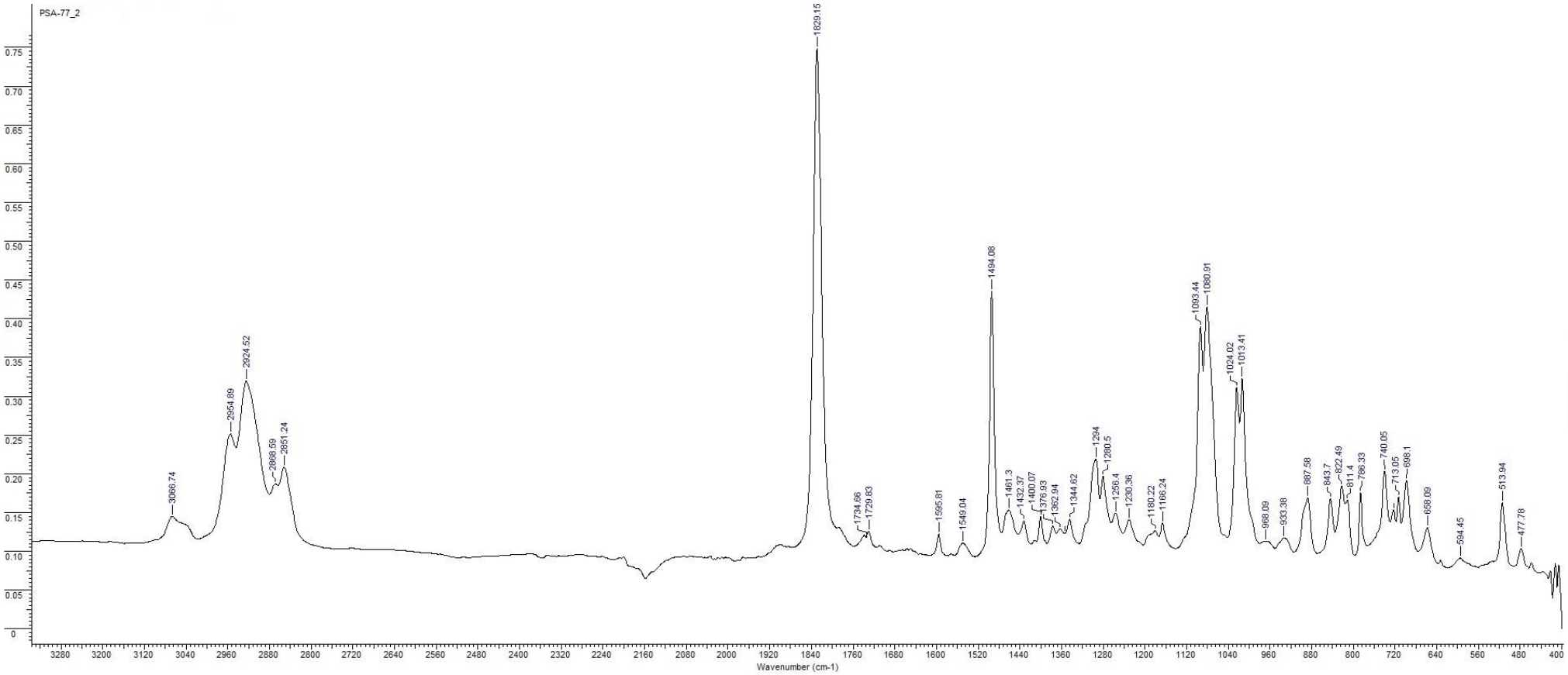
^{1}H-^{13}C HMBC spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



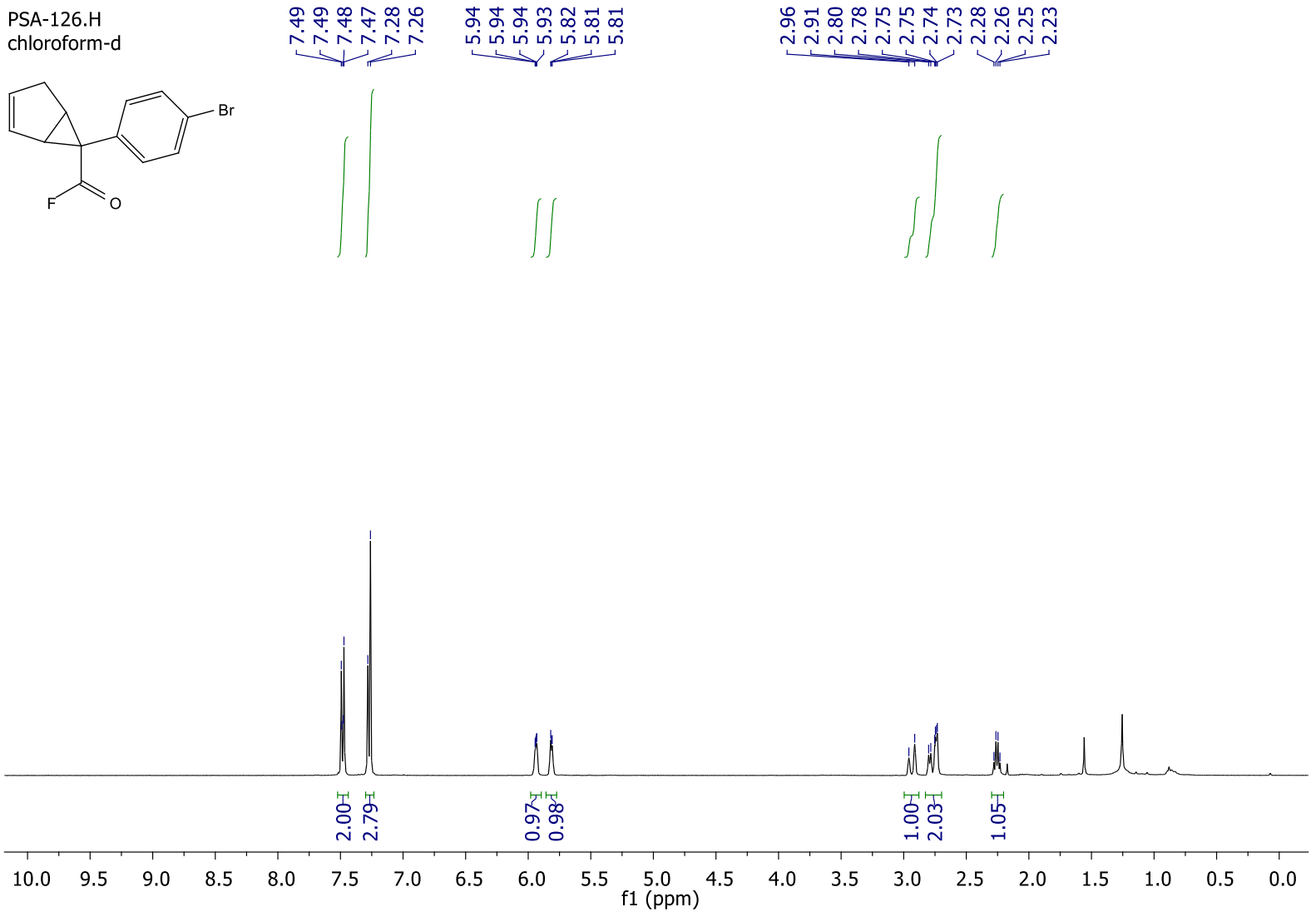
^{1}H-^{13}C HSQC spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



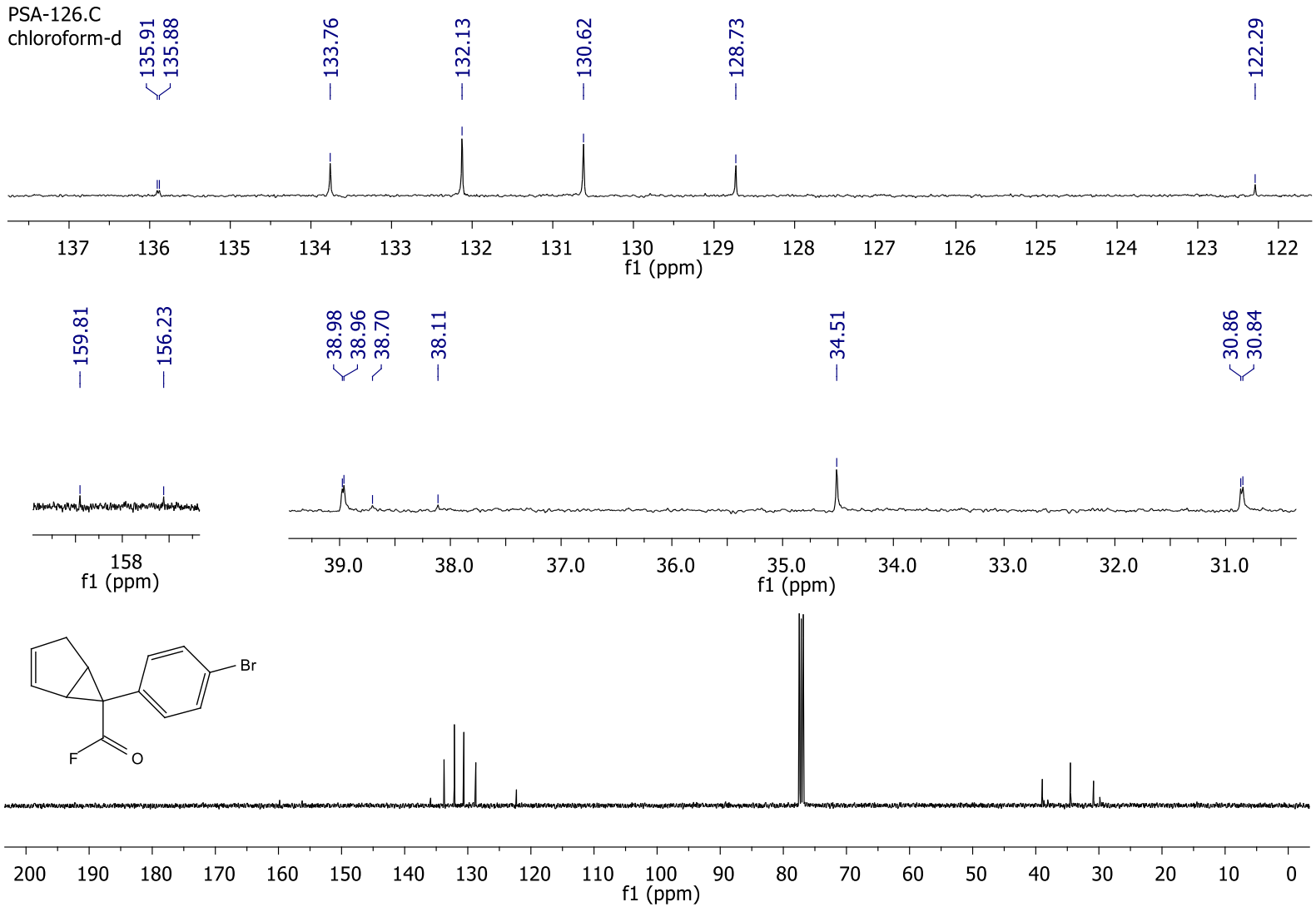
^{19}F NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



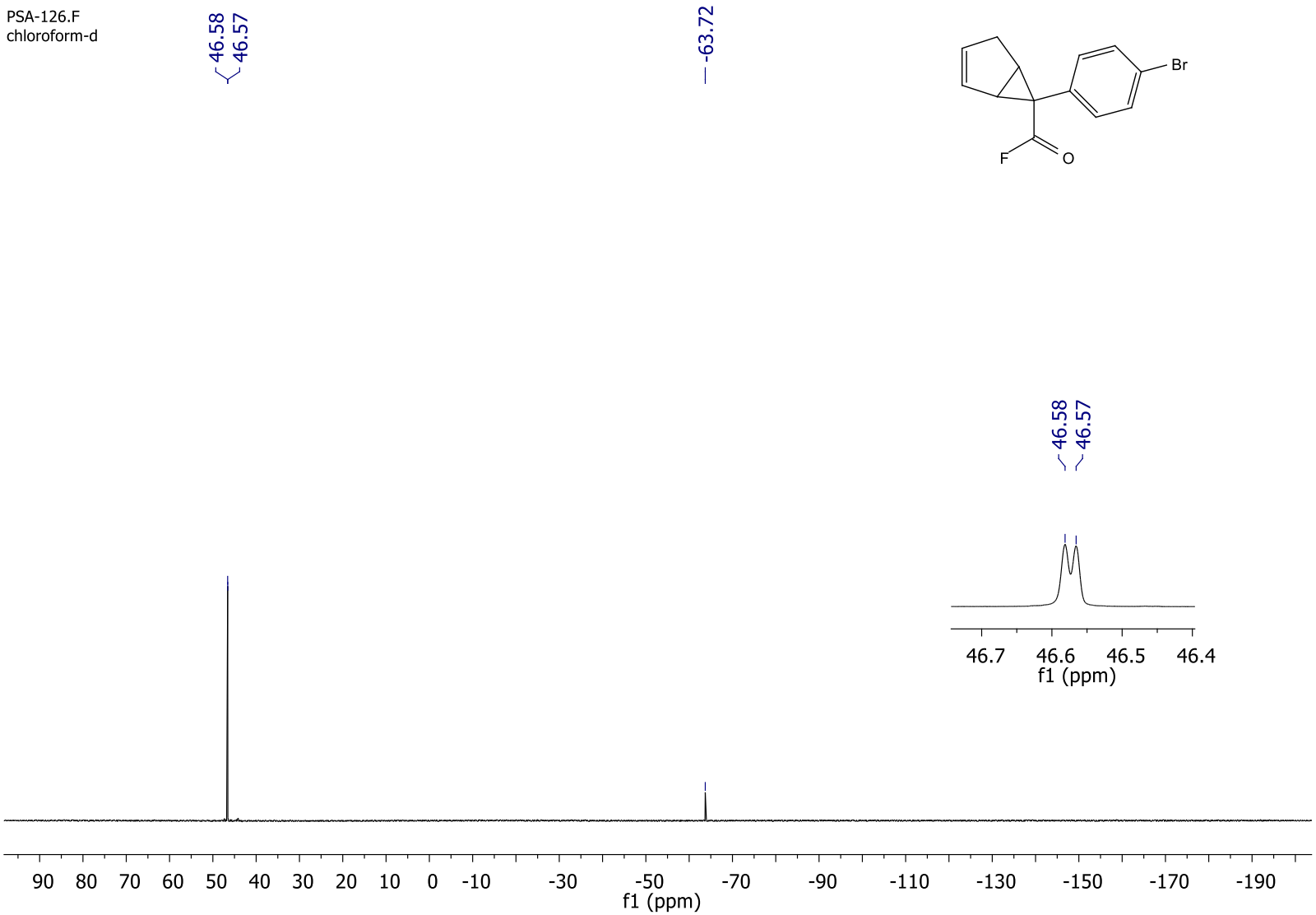
FTIR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3a**)



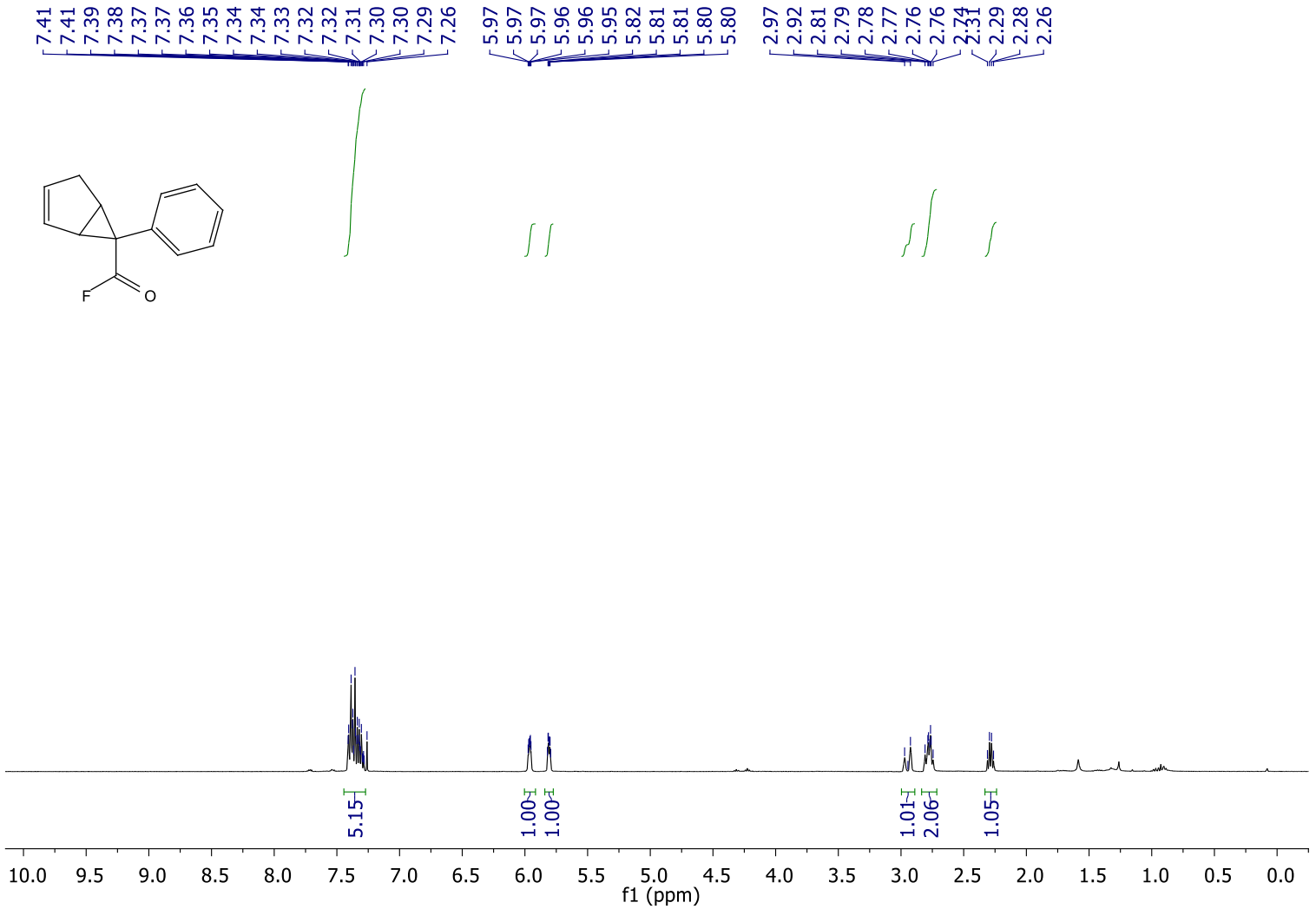
^{1}H NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3b**)



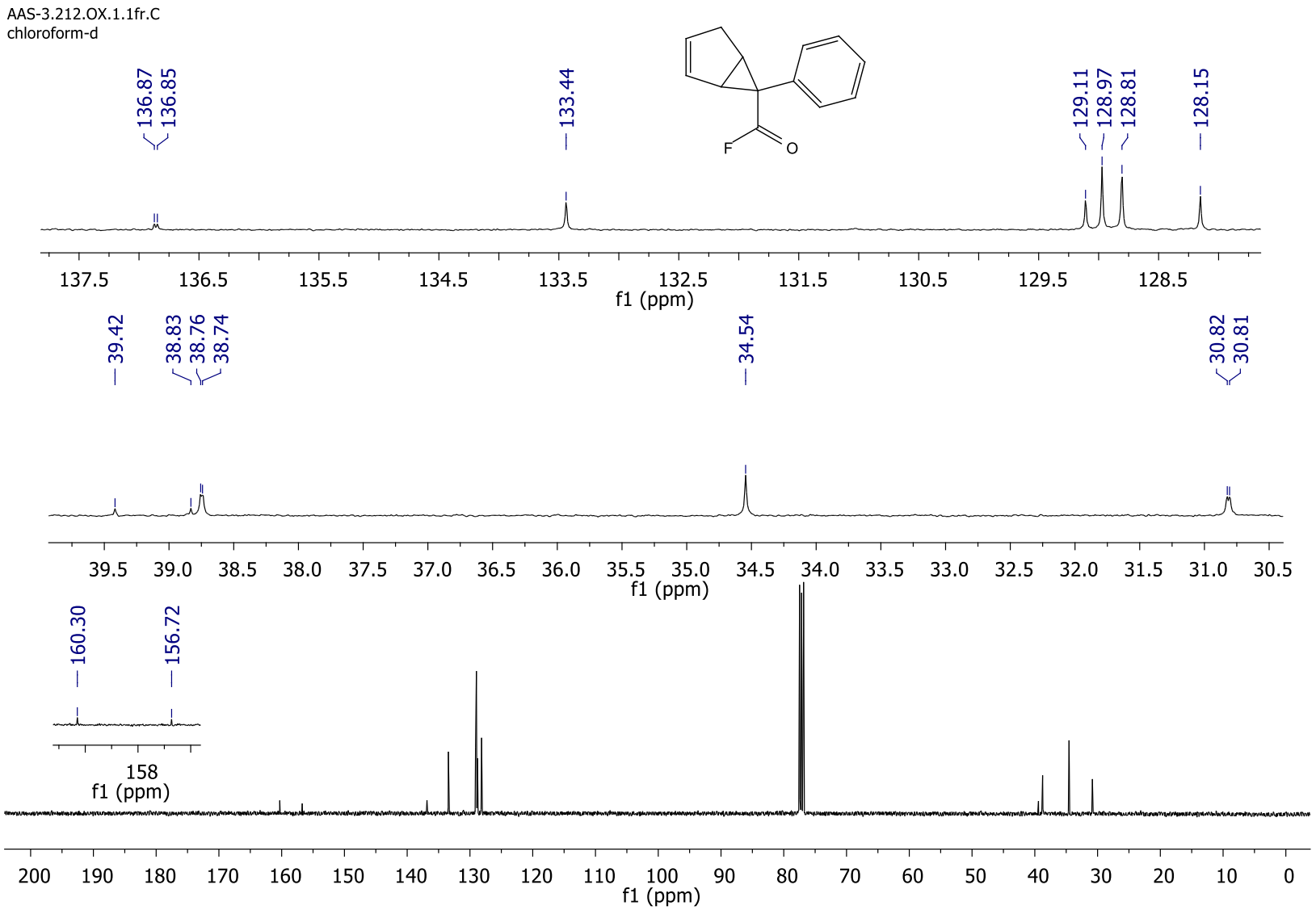
^{13}C NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3b**)



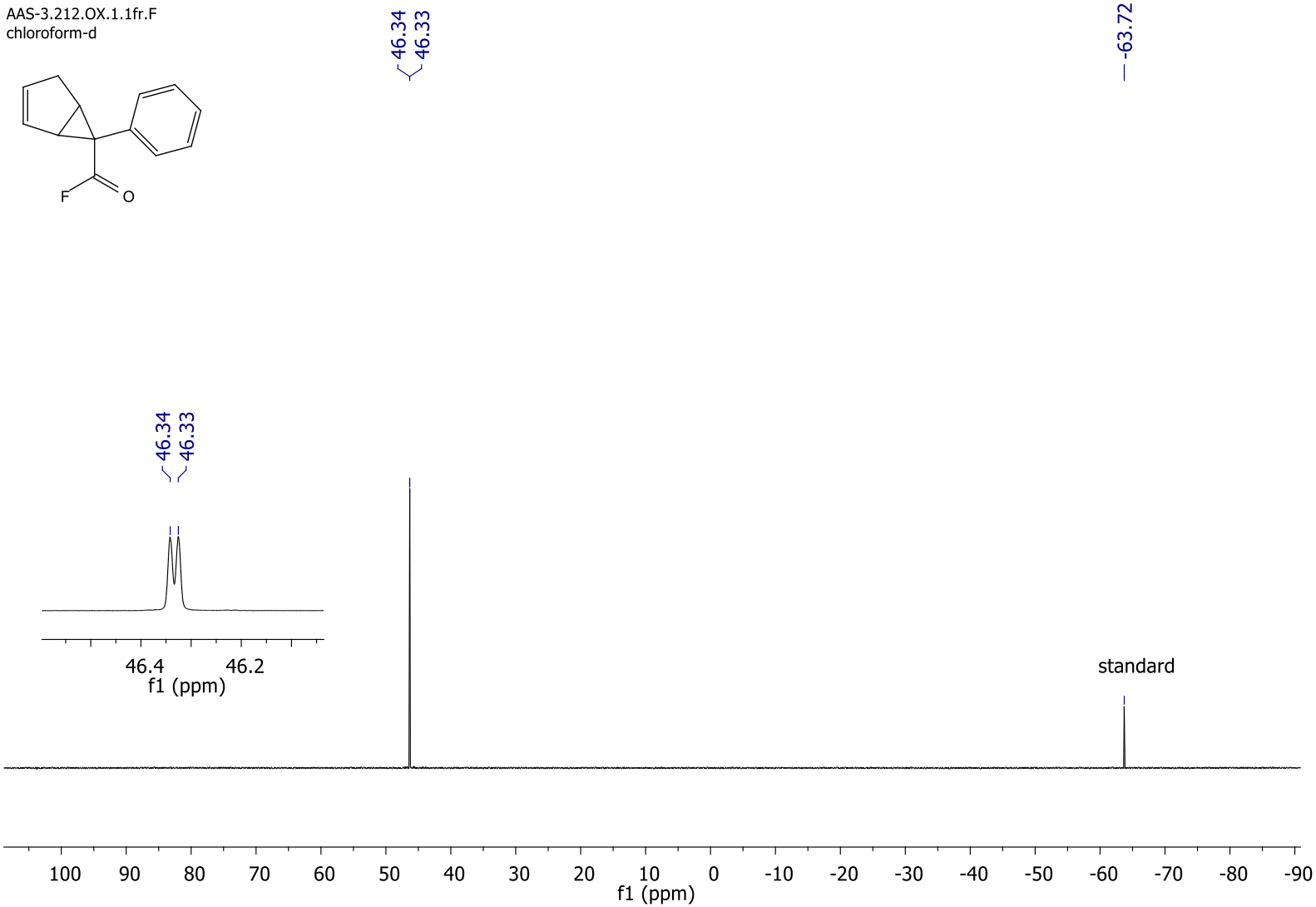
^{19}F NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3b**)



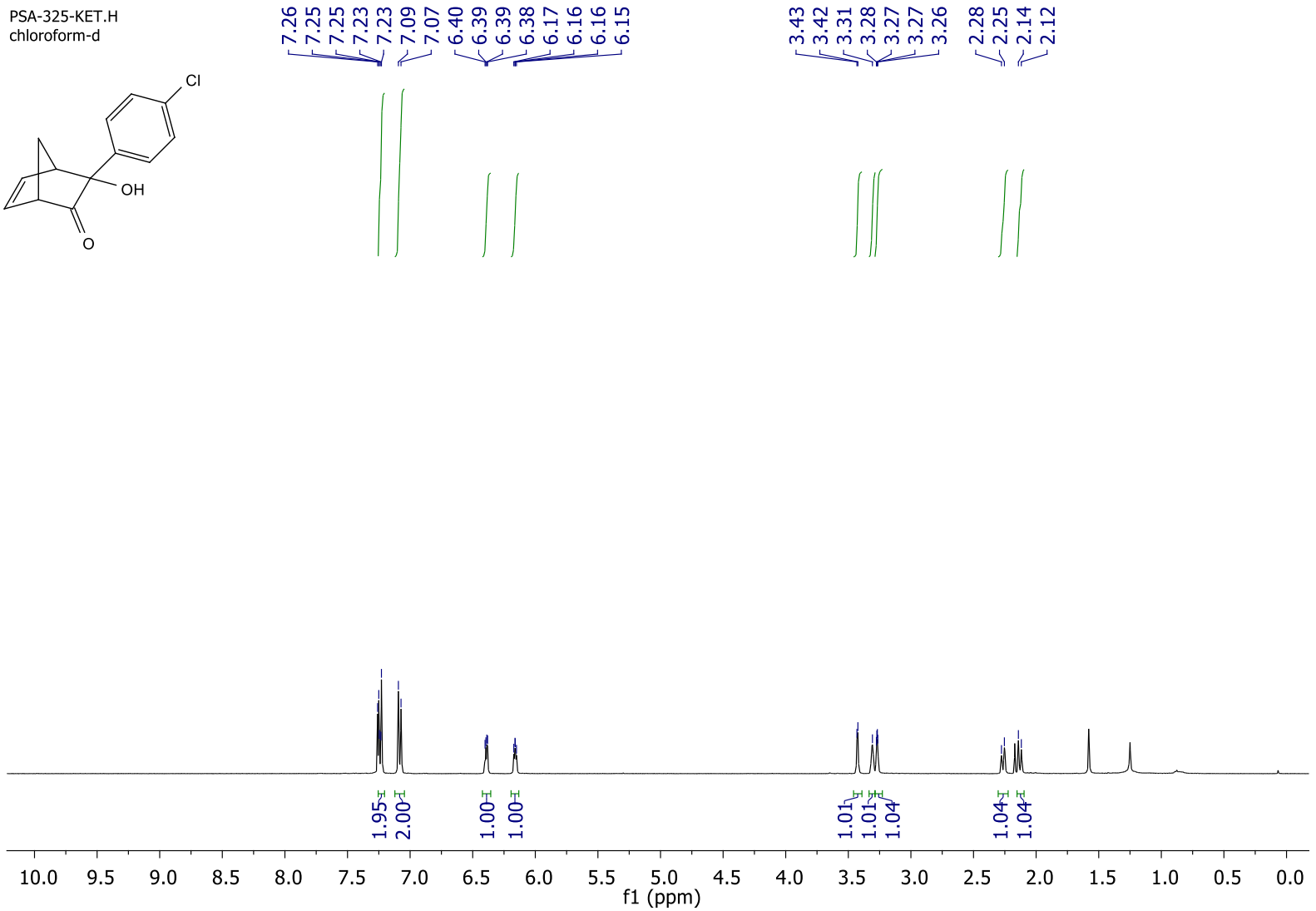
^{1}H NMR spectrum of (1*S**,5*R**,6*R**)-6-phenylbicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3c**)



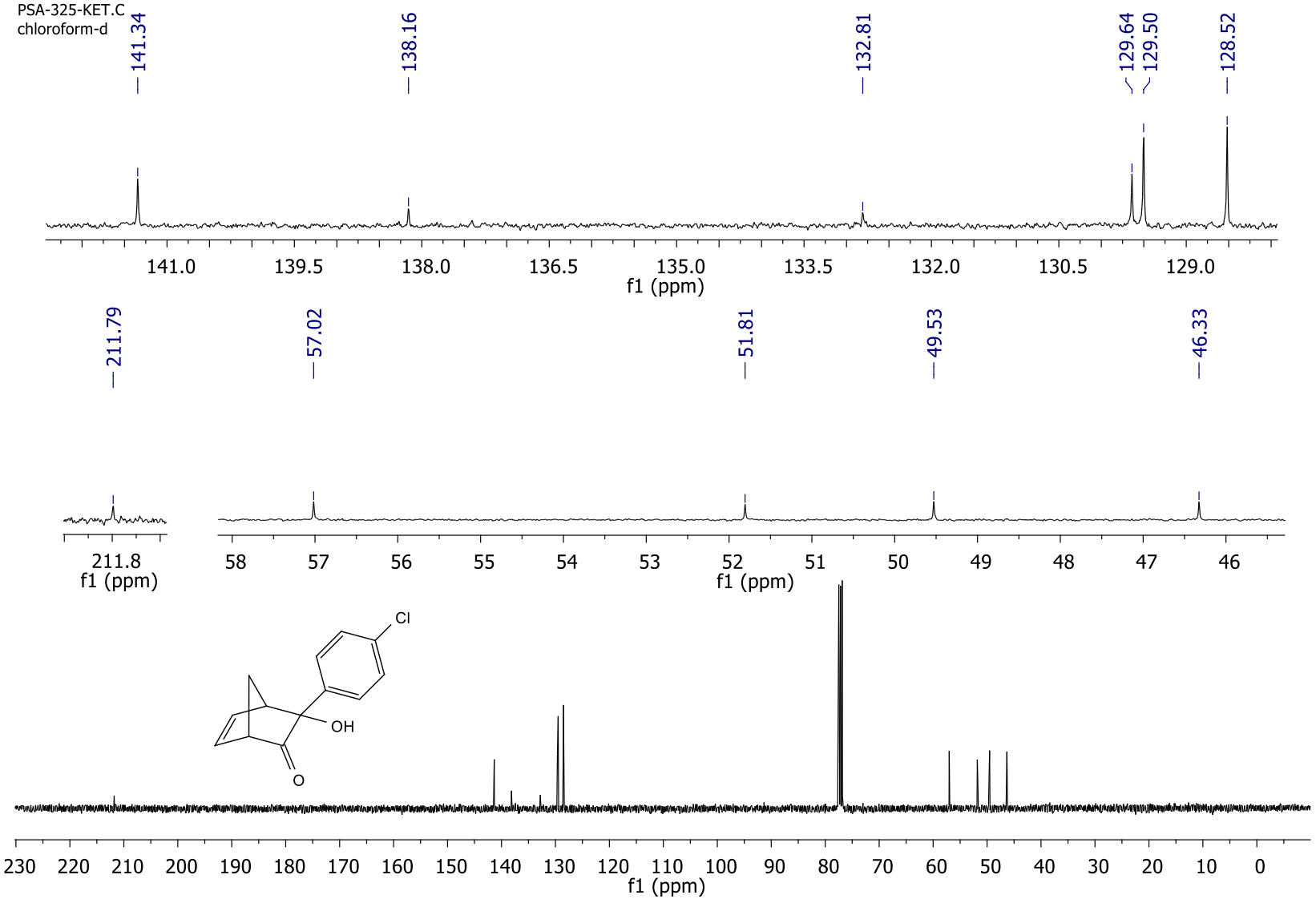
^{13}C NMR spectrum of (1*S**,5*R**,6*R**)-6-phenylbicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3c**)



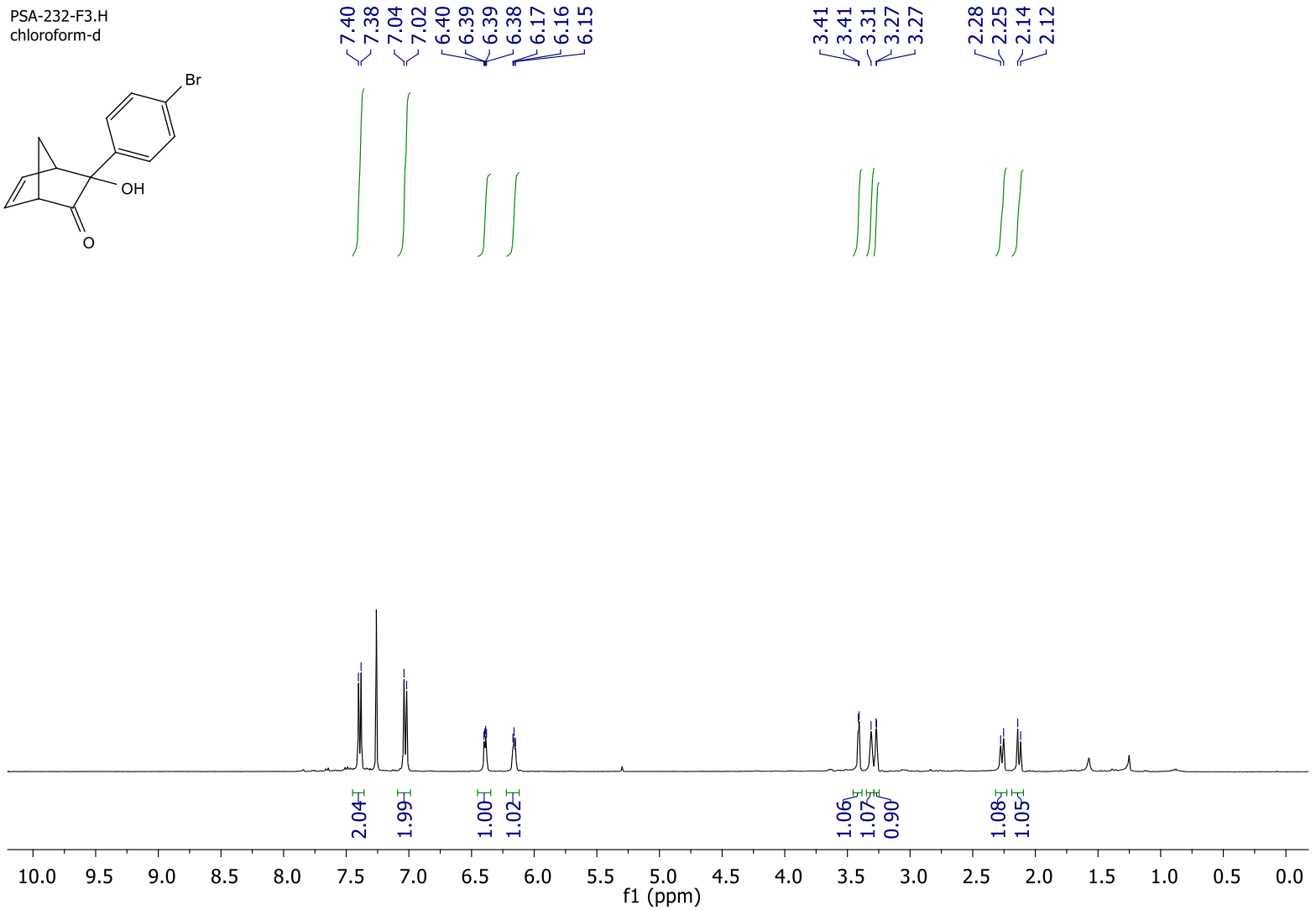
^{19}F NMR spectrum of (1*S**,5*R**,6*R**)-6-phenylbicyclo[3.1.0]hex-2-ene-6-carbonyl fluoride (**3c**)



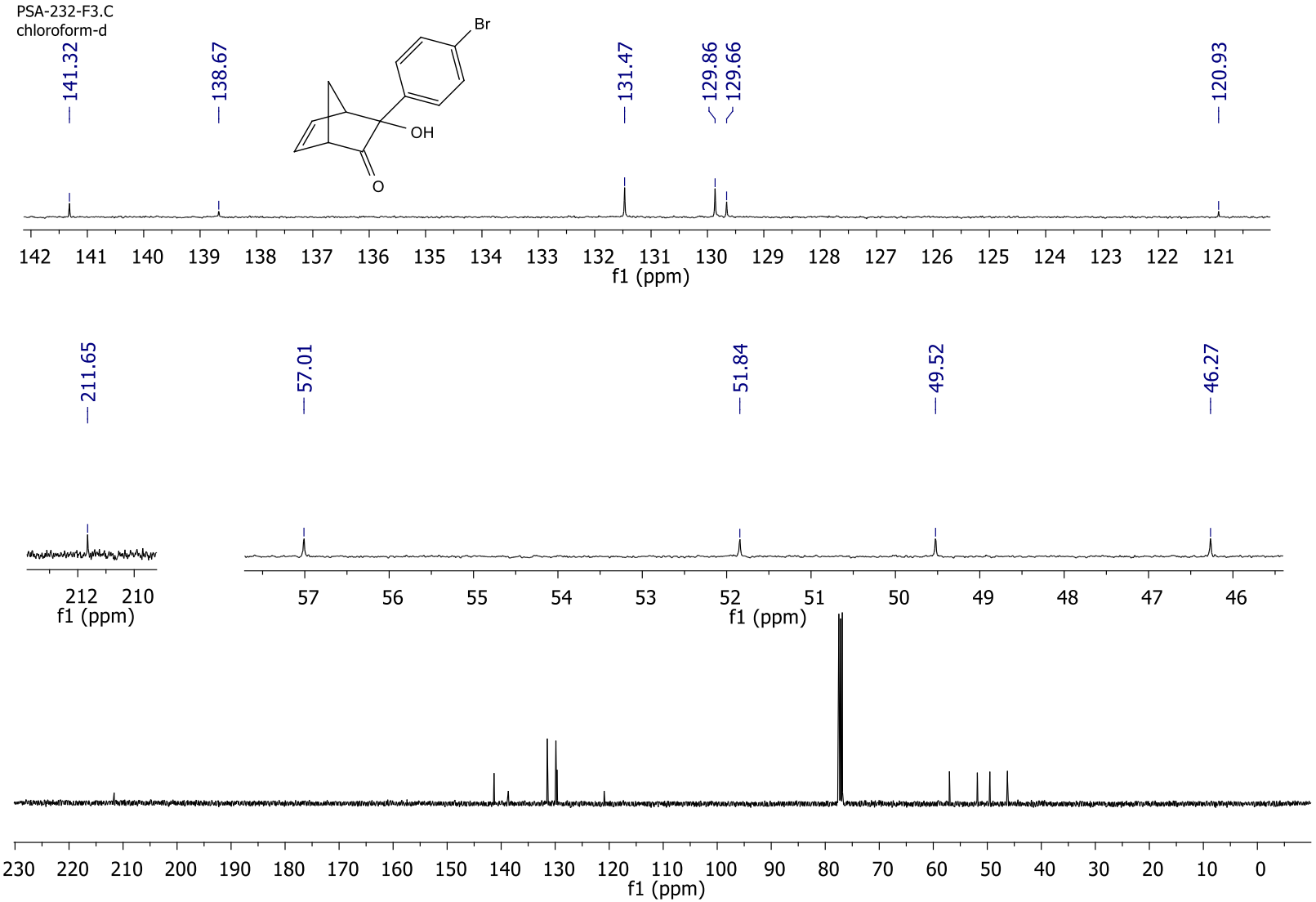
^{1}H NMR spectrum of (1*S**,3*R**,4*R**)-3-(4-chlorophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one (**4a**)



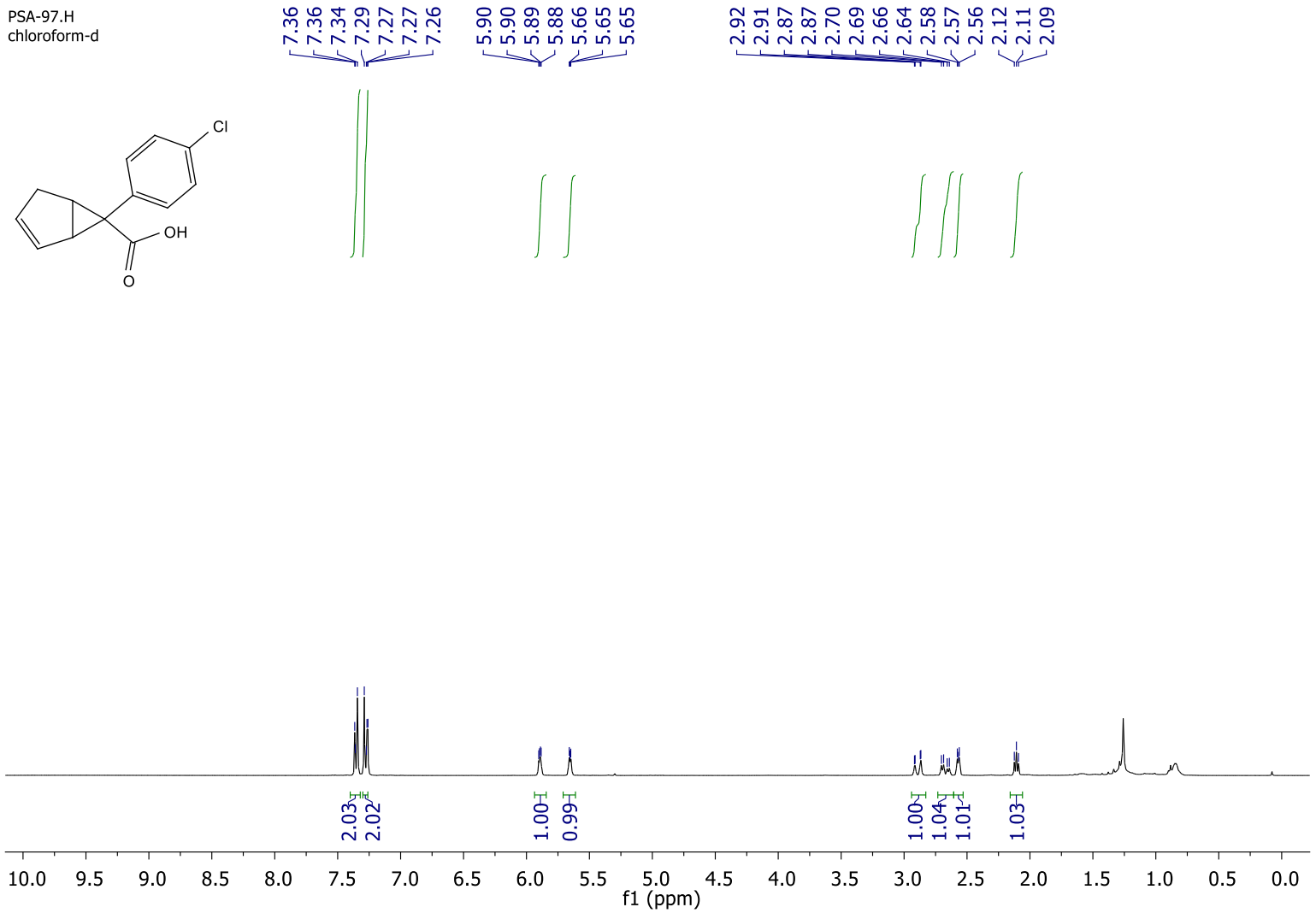
^{13}C NMR spectrum of (1*S**,3*R**,4*R**)-3-(4-chlorophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one (**4a**)



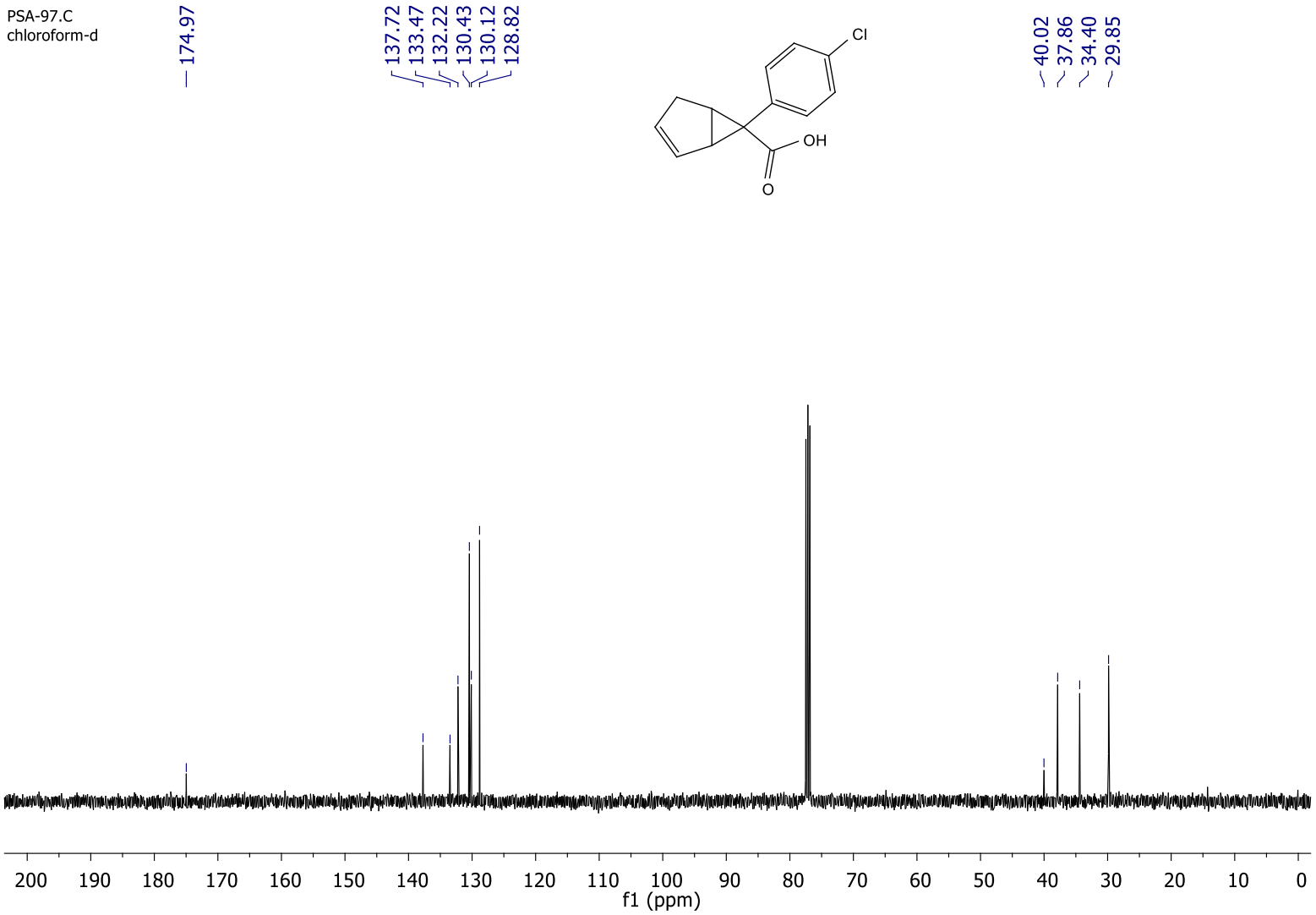
^{1}H NMR spectrum of (1*S**,3*R**,4*R**)-3-(4-bromophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one (**4b**)



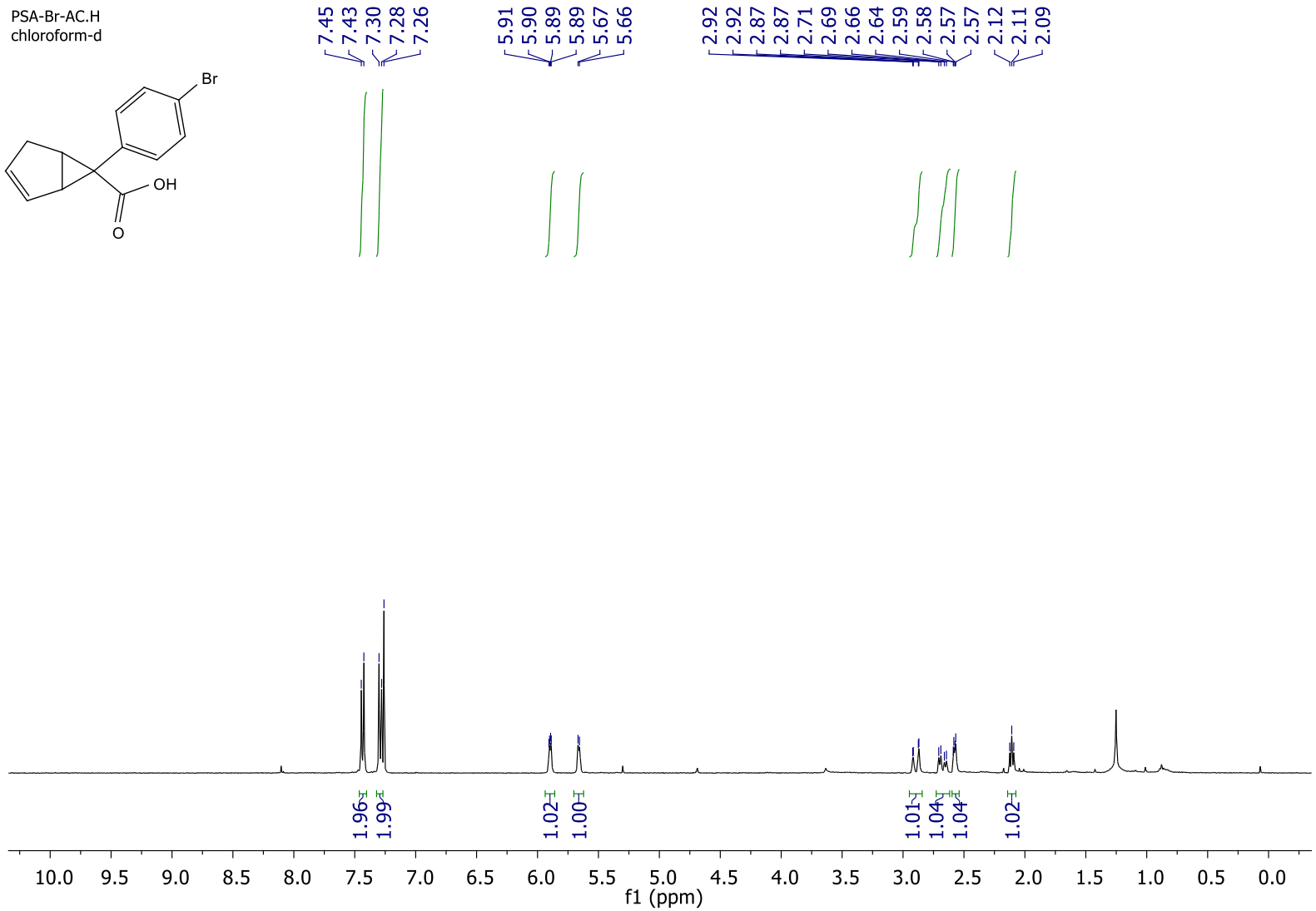
^{13}C NMR spectrum of (1*S**,3*R**,4*R**)-3-(4-bromophenyl)-3-hydroxybicyclo[2.2.1]hept-5-en-2-one (**4b**)



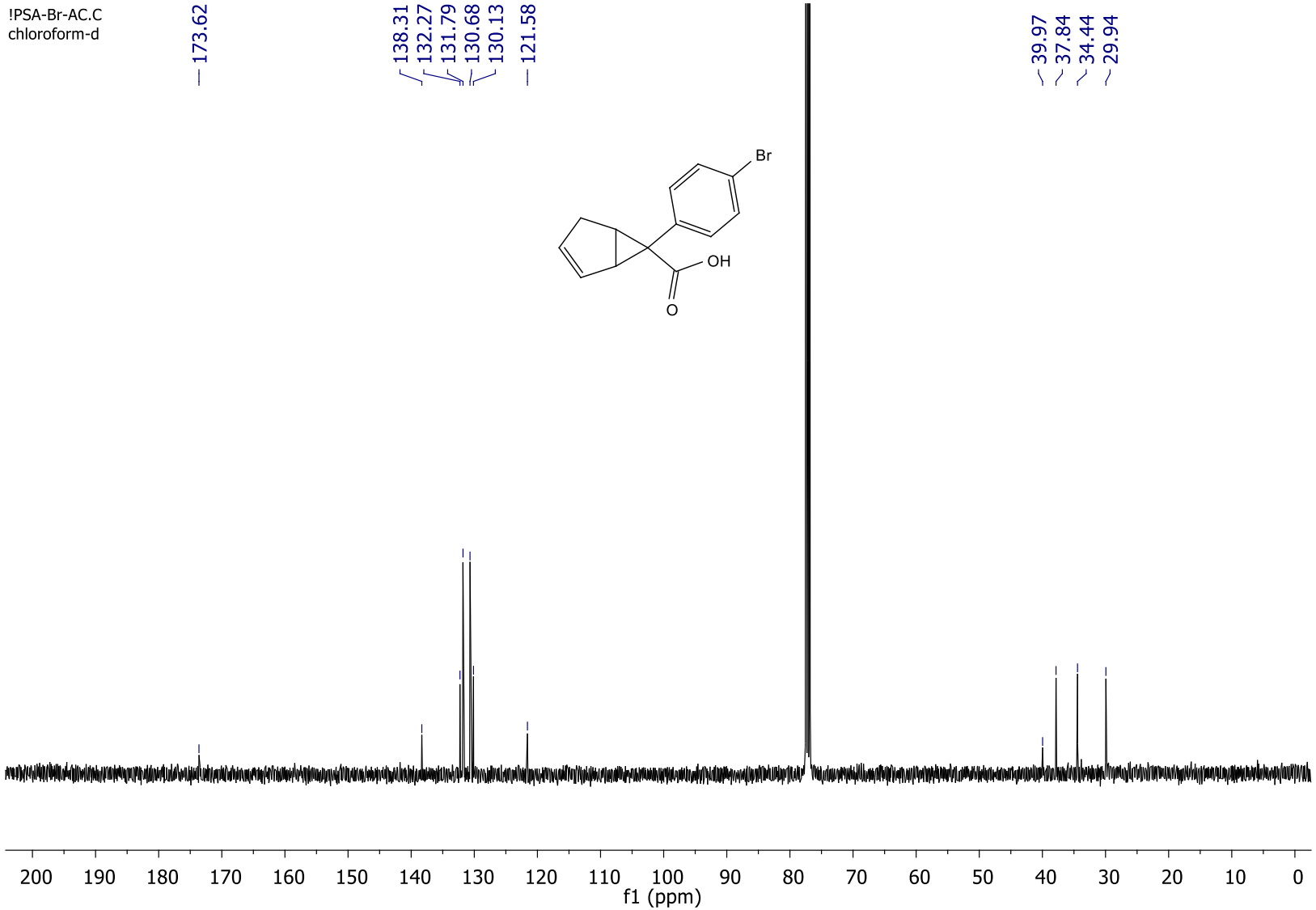
^{1}H NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid (**5a**)



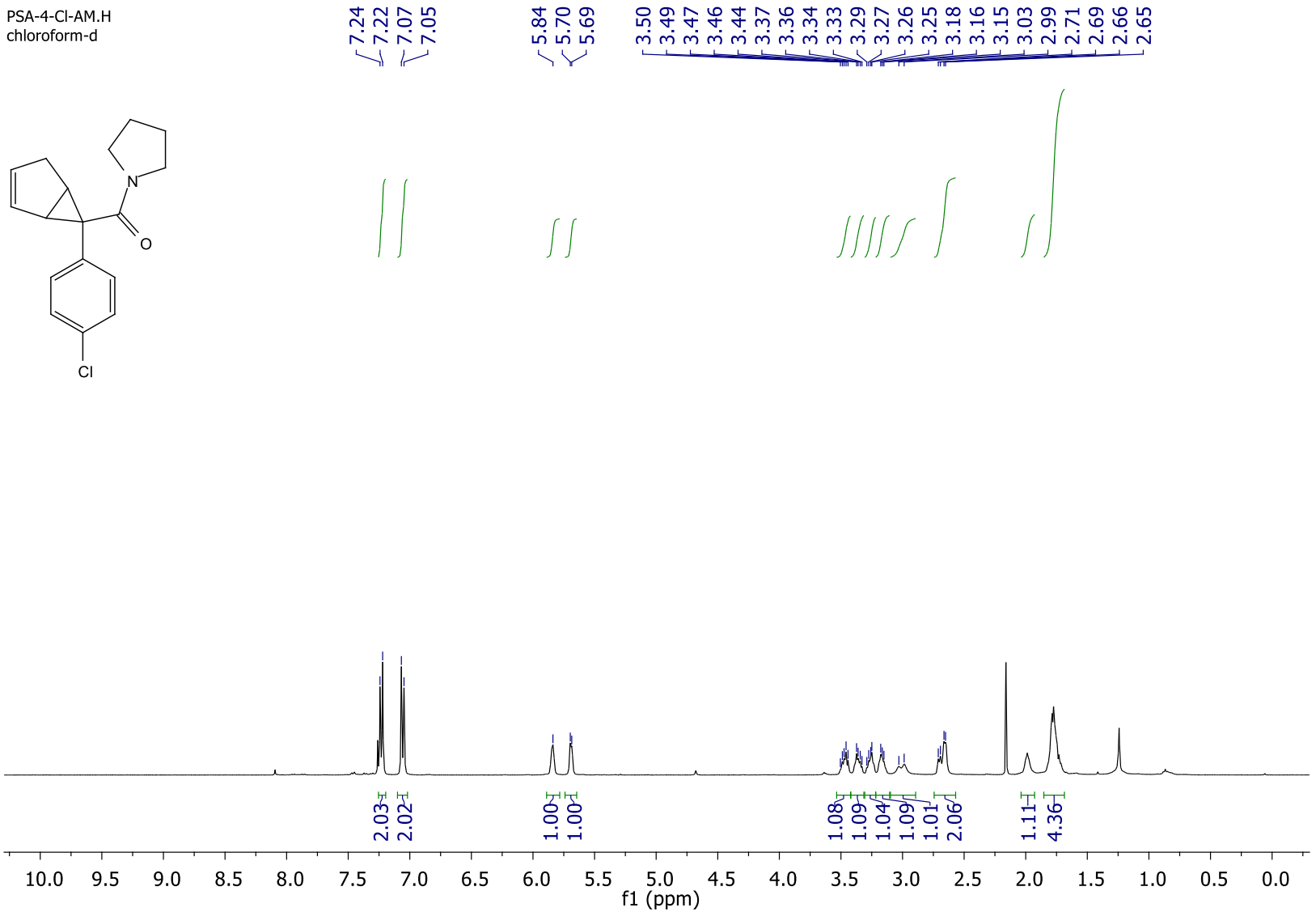
^{13}C NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid (**5a**)



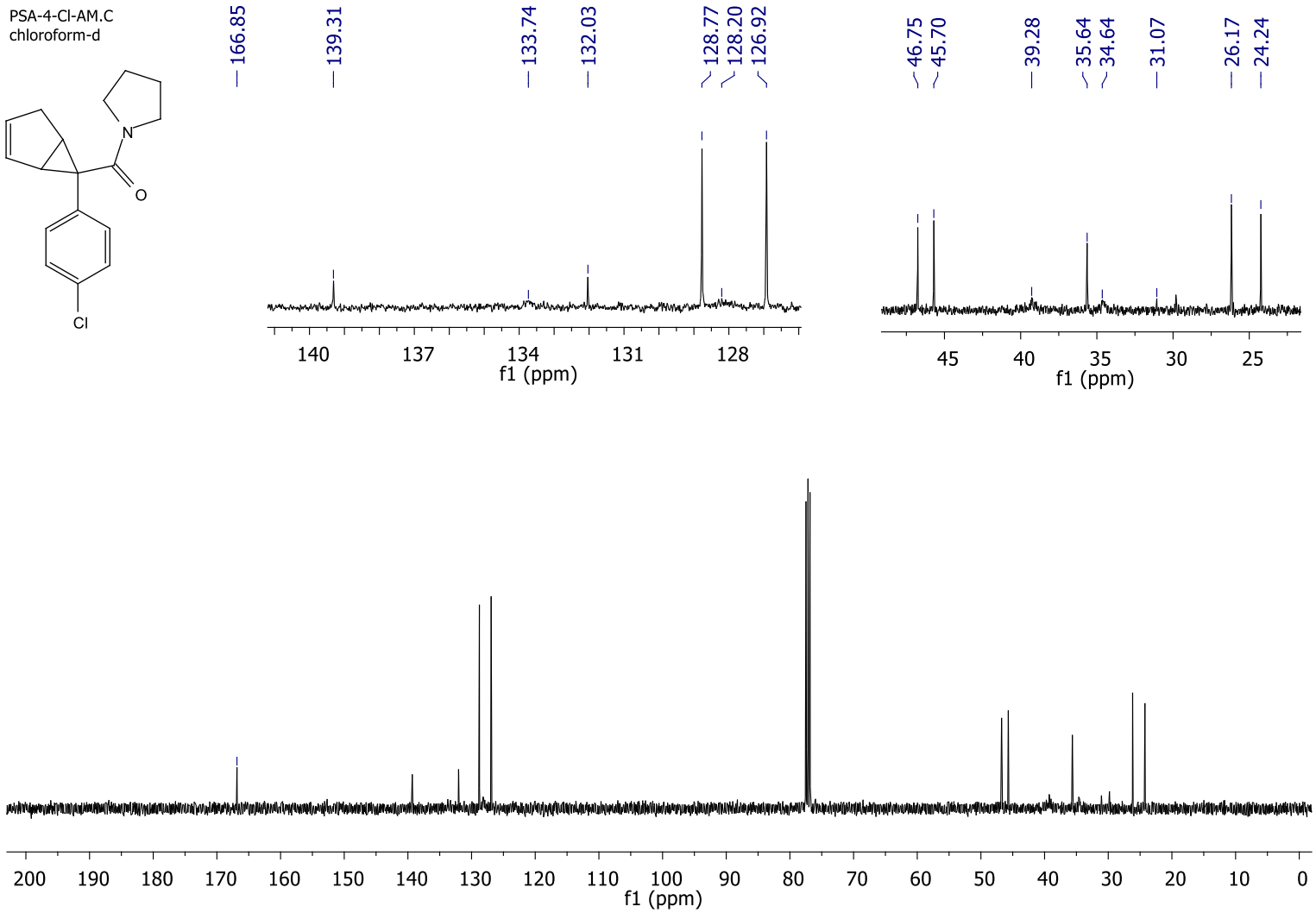
^{1}H NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid (**5b**)



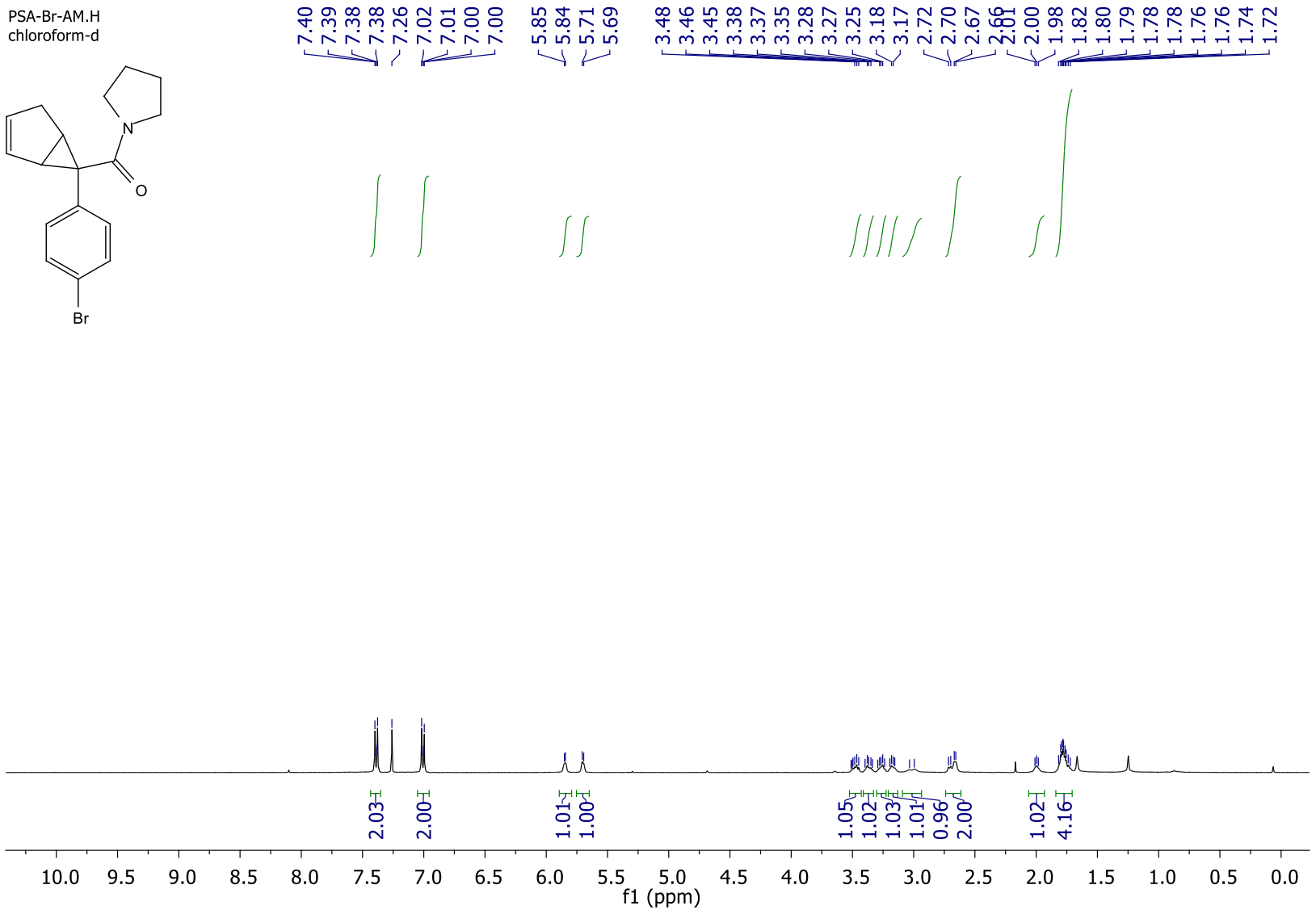
^{13}C NMR spectrum of (1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylic acid (**5b**)



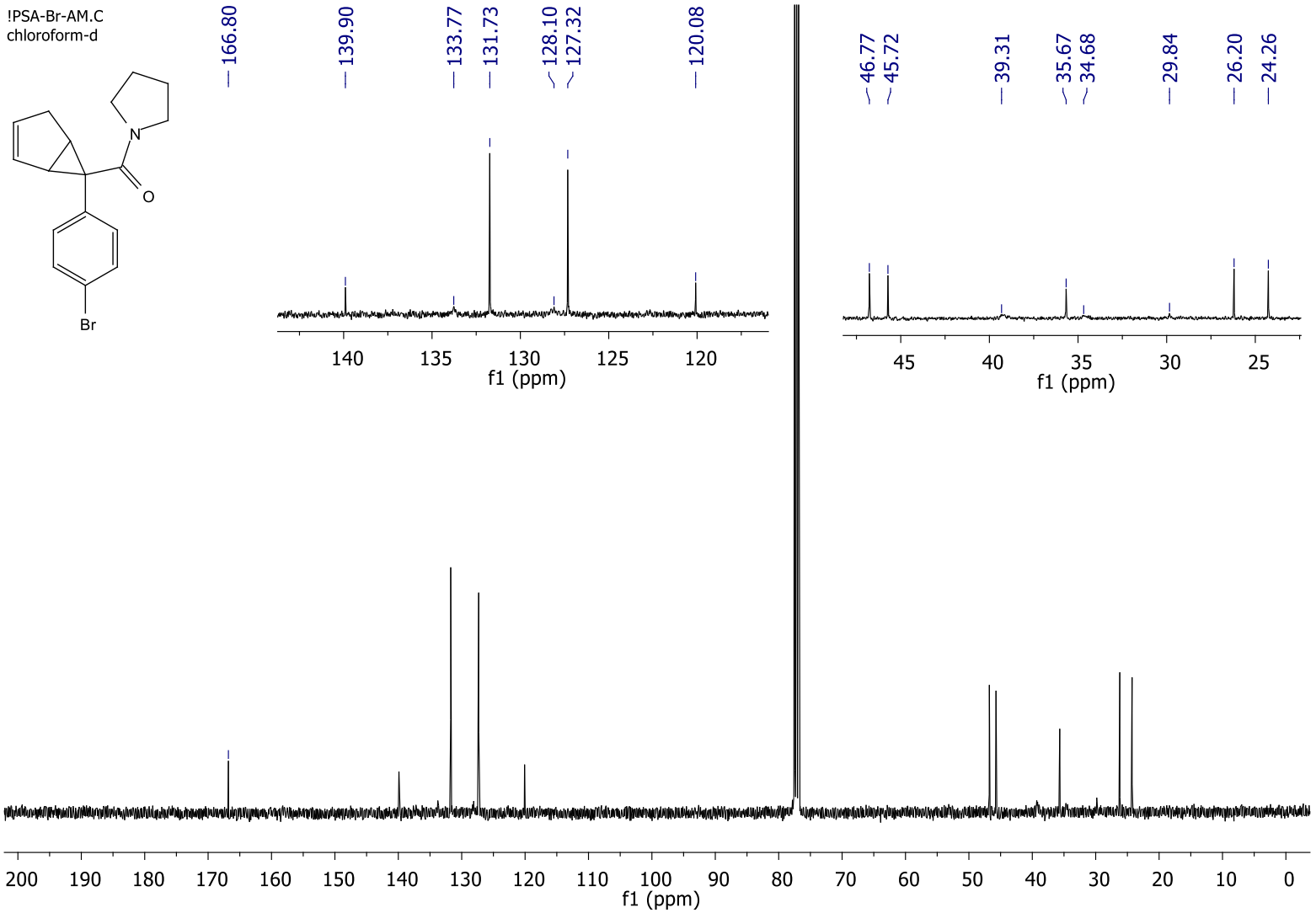
^{1}H NMR spectrum of ((1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone (**6a**)



^{13}C NMR spectrum of ((1*S**,5*R**,6*R**)-6-(4-chlorophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone (**6a**)



^{1}H NMR spectrum of ((1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone (**6b**)



^{13}C NMR spectrum of ((1*S**,5*R**,6*R**)-6-(4-bromophenyl)bicyclo[3.1.0]hex-2-en-6-yl)(pyrrolidin-1-yl)methanone (**6b**)