Synthesis of 1,5-Dioxocanes via the Two-Fold C-O Bond Forming Nucleophilic 4+4-Cyclodimerization of Cycloprop-2-en-1-ylmethanols

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Supporting Information

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1. General Information

NMR spectra were recorded on a Bruker Avance DPX-400 instrument, equipped with a quadruple-band gradient probe (H/C/P/F QNP) or a Bruker Avance DRX-500 with a dual carbon/proton cryoprobe (CPDUL). The abbreviation ‘app. t’ is used to describe apparent triplets (i.e., double doublets with unresolved central line, or unresolved higher order multiplets in a shape of a triplet) in ^{1}H NMR spectra. ^{13}C NMR spectra were registered with broadband decoupling. The (+) and (-) designations represent positive and negative intensities of signals in ^{13}C DEPT-135 experiments. IR spectra were recorded on a Shimadzu FT-IR 8400S instrument. HRMS was carried out on LCT Premier (Micromass Technologies) instrument; ESI TOF detection techniques were used. GC analyses were performed on a Shimadzu GC-2010 gas chromatograph with FID detector and equipped with an AOC-20i auto-injector and an AOC-20S auto-sampler tray (150 vials); 30 m 0.25 mm 0.25 mm capillary column, SHR5XLB, polydimethylsiloxane; 5% Ph was employed. Helium (99.96%), additionally purified by passing consecutively through a CRS oxygen/moisture/hydrocarbon trap (#202839) and VICI oxygen/moisture trap (P100-1), was used as a carrier gas. Hydrogen gas was used as FID fuel; zero-grade air and zero-grade nitrogen were used as an oxidant and make-up gas, respectively, for the FID. All these gases were purified by passing through CRS #202839 traps. The following GC parameters were used for all analyses: carrier gas flow rate 2.5 mL/min; oven temperature program: 50 ^{o}C (2 min) - 20 ^{o}C/min - 230 ^{o}C (6 min), injector temperature 275 ^{o}C. HPLC analyses were performed on a Dynamax SD-200 instrument equipped with Dynamax UV-C detector and Alltech Econosphere Si 5U column (L 150 mm ID 4.6 mm). Glassware employed in moisture-free syntheses was flame-dried in vacuum prior to use. A combination of glove box and standard Schlenk technique was used to handle moisture sensitive materials. Column chromatography was carried out on silica gel (Sorbent Technologies, 40-63 μm). Pre-coated silica gel plates (Sorbent Technologies Silica XG 200 μm) were used for TLC analyses. Anhydrous diethyl ether and THF were obtained by passing degassed commercially available HPLC-grade inhibitor-free solvents consecutively through two columns filled with activated alumina and stored over molecular sieves under nitrogen. Other anhydrous solvents were obtained according to standard procedures. Water was purified by dual stage deionization followed by dual stage reverse osmosis. Synthesis of starting materials: 1-aryl-2-(trimethylsilyl)cycloprop-2-ene carboxylates (**9a**-**o**) and 1-arylcycloprop-2-ene carboxylates (**10a**-**e**) was detailed in our recent report.[1] Powdered potassium hydroxide was obtained by grinding commercially available pelleted reagent employing conventional electric-powered blade coffee-grinder housed inside a nitrogen-filled glove box. All other reagents were purchased from commercial vendors and used as received.

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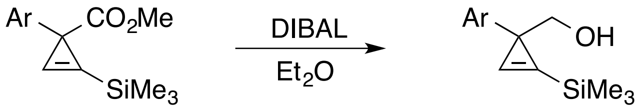
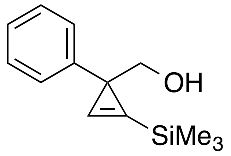
(1) Edwards, A.; Rubin, M. *Tetrahedron* **2015**, *71*, 3237.

2. Preparation of (1-aryl-2-(trimethylsilyl)cycloprop-2-en-yl)methanols (11a-o)

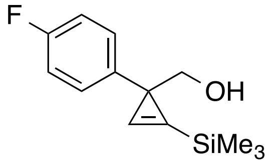
These silylated alcohols were prepared by reduction of known methyl esters **9a-o** with DIBAL according to the following scheme:



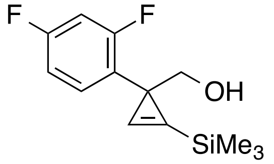
(1)



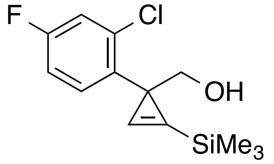
(1-Phenyl-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11a) (Typical Procedure): An oven dried round bottom flask was charged with methyl 1-phenyl-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9a**) (1.0 g, 4.06 mmol, 1.0 equiv) and diethyl ether (11 mL) under anhydrous nitrogen atmosphere. The mixture was stirred at -78 ºC and DIBAL (1.21 g, 1.52 µL, 8.52 mmol, 2.10 equiv) was then added dropwise via syringe. Upon complete addition, the reaction was stirred for one hour while maintaining -78ºC. The mixture was then allowed to warm to room temperature and the stirring was continued for one hour, and then quenched with saturated aqueous ammonium chloride, which was added dropwise until the solution turned into a gel. A 10% aqueous solution of HCl was then added very slowly until just the moment when the gel dissolved (pH of the aqueous layer must remain above ~4), and extracted with diethyl ether (3 x 10 mL). Combined organic layers were washed with saturated sodium bicarbonate, brine, dried with magnesium sulfate, filtered, and concentrated. The recovered oil was then purified by column chromatography eluting with 6:1 hexane:EtOAc mixture to provide the titled compound as colorless crystals, mp: 37.2 - 37.8 °C in 87% yield (771 mg, 3.53 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.31 – 7.26 (m, 2H), 7.22 – 7.12 (m, 3H), 4.17 (d, *J* = 11.0 Hz, 1H), 3.99 (d, *J* = 11.0 Hz, 1H), 1.36 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 146.9, 128.1 (2C, +), 126.1 (2C, +), 125.3 (+), 124.0, 123.5 (+), 68.9 (-), 30.1, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3389, 3057, 3022, 2957, 2897, 2870, 1693, 1599, 1495, 1445, 1408, 1250, 1065, 1013, 989, 866, 843, 756, 727, 698; HRMS (TOF ES): Found 217.1050, calculated for $C_{13}H_{17}OSi$ (M-H) 217.1049 (0.5 ppm).



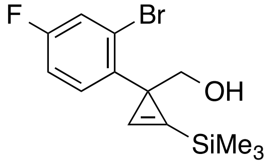
(1-(4-Fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11b): This compound was obtained via typical procedure using methyl 1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9b**) (397 mg, 1.5 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.10 equiv). The titled compound was obtained as a pale yellow solid, 40.8-41.4 °C in 75% yield (267 mg, 1.13 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1H), 7.13 (dd, *J* = 8.9, 5.3 Hz, 2H), 6.95 (t, *J* = 8.8 Hz, 2H), 4.13 (d, *J* = 11.5 Hz, 1H), 3.94 (d, *J* = 11.6 Hz, 1H), 1.35 (s, 1H), 0.16 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.0 (d, *J* = 243.2 Hz), 142.6 (d, *J* = 3.1 Hz), 127.6 (d, *J* = 7.7 Hz, 2C, +), 124.6, 123.6 (+), 114.8 (d, *J* = 21.3 Hz, 2C, +), 69.2 (-), 29.6, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3396, 3377, 3367, 2959, 2899, 2872, 2361, 1691, 1603, 1508, 1410, 1250, 1229, 1159, 1059, 1013, 989, 868, 843, 814, 760, 727, 717; HRMS (TOF ES): Found 243.1200, calculated for $C_{13}H_{17}FOSiLi$ (M+Li) 243.1193 (2.9 ppm).



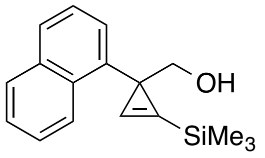
(1-(2,4-Difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11c): This compound was obtained via typical procedure using methyl 1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9c**) (424 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.10 equiv). The titled compound was obtained as colorless crystals, mp 57.7-58.8 ^{o}C in 80% yield (305 mg, 1.20 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02 (s, 1H), 7.07 (td, J = 8.4, 6.4 Hz, 1H), 6.81 – 6.69 (m, 2H), 3.96 (d, J = 11.0 Hz, 1H), 3.67 (d, J = 11.2 Hz, 1H), 1.24 (s, 1H), 0.19 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.8 (dd, J = 247.2, 11.8 Hz), 161.5 (dd, J = 246.7, 12.0 Hz), 131.1 (dd, J = 9.5, 7.0 Hz, +), 129.0 (dd, J = 16.3, 3.7 Hz), 129.0, 127.0 (+), 111.2 (dd, J = 20.8, 3.6 Hz, +), 103.9 (dd, J = 27.0, 25.1 Hz, +), 69.8 (d, J = 3.1 Hz, -), 27.5, -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3259, 3244, 2957, 2872, 1693, 1609, 1601, 1502, 1464, 1418, 1269, 1250, 1136, 1099, 1053, 1022, 966, 881, 843, 818, 760, 741, 731, 717, 700, 615; HRMS (TOF ES): Found 254.0943, calculated for $C_{13}H_{16}F_2OSi$ (M+) 254.0938 (2.0 ppm).



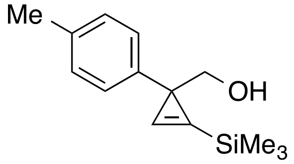
(1-(2-Chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)-methanol (11d): This compound was obtained via typical procedure using methyl 1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9d**) (448 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.1 equiv). The titled compound was obtained as colorless crystals, mp 61.7-63.2 ^{o}C in 53% yield (214 mg, 0.790 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (s, 1H), 7.20 (dd, J = 8.5, 6.2 Hz, 1H), 7.06 (dd, J = 8.6, 2.6 Hz, 1H), 6.90 (td, J = 8.3, 2.6 Hz, 1H), 3.90 (d, J = 11.2 Hz, 1H), 3.71 (d, J = 11.2 Hz, 1H), 1.09 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.3 (d, J = 248.0 Hz), 139.6 (d, J = 3.6 Hz), 135.0 (d, J = 10.3 Hz), 132.2 (d, J = 8.7 Hz, +), 129.4, 129.1 (+), 117.0 (d, J = 24.5 Hz, +), 114.3 (d, J = 20.7 Hz, +), 69.1 (-), 31.3, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3398, 3379, 3360, 3342, 2959, 2899, 2870, 1680, 1599, 1580, 1485, 1408, 1389, 1250, 1223, 1192, 1068, 1036, 1014, 995, 939, 876, 843, 820, 760, 741, 717; HRMS (TOF ES): Found 270.0643, calculated for $C_{13}H_{16}ClFOSi$ (M+) 270.0643 (0.0 ppm).



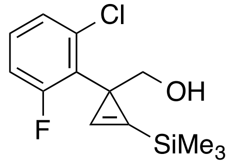
(1-(2-Bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)-methanol (11e): This compound was obtained via typical procedure using methyl 1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9e**) (515 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.10 equiv). The titled compounds was obtained as a pale yellow solid, mp 51.6-52.8 ^{o}C in 62% yield (292 mg, 0.926 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.15 (s, 1H), 7.26 – 7.19 (m, 2H), 6.95 (td, J = 8.3, 2.6 Hz, 1H), 3.85 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.2 Hz, 1H), 1.13 (s, 1H), 0.26 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.1 (d, J = 249.1 Hz), 141.2 (d, J = 3.6 Hz), 132.5 (d, J = 8.4 Hz, +), 129.7 (+), 129.3, 124.4 (d, J = 9.5 Hz), 120.1 (d, J = 24.1 Hz, +), 114.8 (d, J = 20.7 Hz, +), 68.9 (-), 33.2, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3394, 3381, 3366, 2959, 2899, 2868, 1682, 1595, 1580, 1479, 1410, 1383, 1250, 1221, 1196, 1065, 1032, 1014, 993, 889, 860, 843, 820, 760, 739, 717; HRMS (TOF ES): Found 321.0299, calculated for $C_{13}H_{16}BrFOSiLi$ (M+Li) 321.0298 (0.3 ppm).



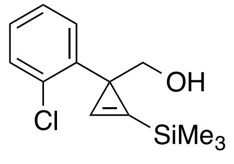
(1-(Naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11f): This compound was obtained via typical procedure using methyl 1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9f**) (445 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled compound was obtained as a light brown oil in 53% yield (213 mg, 0.794 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.38 – 8.35 (m, 2H), 7.88 – 7.85 (m, 1H), 7.76 – 7.71 (m, 1H), 7.59 – 7.41 (m, 3H), 7.40 (s, 1H), 3.96 (d, J = 11.6 Hz, 1H), 3.89 (d, J = 11.1 Hz, 1H), 1.39 (s, 1H), 0.28 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 142.5, 134.2, 131.9, 131.0 (+), 129.9, 128.9 (+), 127.3 (+), 126.6 (+), 125.9 (+), 125.8 (+), 125.7 (+), 125.0 (+), 69.9 (-), 31.3, -0.8 (3C, +); FTIR (KBr, cm^{-1}): 3441, 3423, 3406, 3389, 3344, 3059, 3045, 2955, 2899, 2864, 2361, 1732, 1680, 1593, 1508, 1393, 1250, 1020, 887, 843, 800, 779; HRMS (TOF ES): Found 291.1183, calculated for C$_{17}$H$_{20}$OSiNa (M+Na) 291.1181 (0.7 ppm).



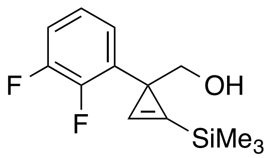
(1-(*p*-Tolyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11g): This compound was obtained via typical procedure using methyl 1-(*p*-tolyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9g**) (391 mg, 1.50 mmol, 1.0 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled compound was obtained as a pale yellow solid, mp 53.2-54.0 °C in 83% yield (288 mg, 1.24 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.70 (s, 1H), 7.13 – 7.04 (m, 4H), 4.13 (dd, J = 11.0, 5.1 Hz, 1H), 3.97 (dd, J = 11.4, 5.1 Hz, 1H), 2.31 (s, 3H), 1.15 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 143.8, 134.8, 128.9 (2C, +), 126.1 (2C, +), 124.2, 124.0 (+), 68.9 (-), 29.9, 21.0 (+), -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3398, 3385, 3022, 2993, 2957, 2920, 2899, 2868, 2361, 1690, 1512, 1466, 1408, 1250, 1061, 1018, 993, 868, 843, 760, 725; HRMS (TOF ES): Found 232.1283, calculated for C$_{14}$H$_{20}$OSi (M+) 232.1283 (0.0 ppm).



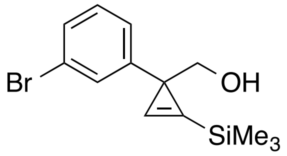
(1-(2-Chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11h): This compound was obtained via typical procedure using methyl 1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9h**) (448 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled compound was obtained as colorless crystals, mp 64.1 – 65.0 °C in 64% yield (259 mg, 0.96 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.13 (s, 1H), 7.20 (dd, J = 8.5, 6.2 Hz, 1H), 7.06 (dd, J = 8.6, 2.6 Hz, 1H), 6.90 (td, J = 8.3, 2.6 Hz, 1H), 3.90 (d, J = 11.2 Hz, 1H), 3.71 (d, J = 11.2 Hz, 1H), 1.08 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.3 (d, J = 248.0 Hz), 139.6 (d, J = 3.6 Hz), 135.0 (d, J = 10.3 Hz), 132.2 (d, J = 8.8 Hz, +), 129.4, 129.2 (+), 117.0 (d, J = 24.4 Hz, +), 114.3 (d, J = 20.8 Hz, +), 69.1 (-), 31.3, -1.0 (2C, +); FTIR (KBr, cm^{-1}): 3369, 3360, 2959, 1682, 1601, 1580, 1485, 1250, 1225, 1068, 1034, 1014, 993, 937, 876, 843, 820, 760, 741, 717; HRMS (TOF ES): Found 271.0724, calculated for C$_{13}$H$_{17}$ClFOSi (M+H) 271.0721 (1.1 ppm).



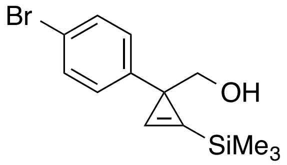
(1-(2-Chlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11i): This compound was obtained via typical procedure using methyl 1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9i**) (421 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled product was obtained as a pale yellow solid, mp 61.8 – 63.3 °C in 63% yield (240 mg, 0.947 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.16 (s, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.22 (m, 1H), 7.20 – 7.11 (m, 2H), 3.94 (d, J = 11.2 Hz, 1H), 3.74 (d, J = 11.1 Hz, 1H), 1.09 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 143.5, 134.4, 131.3 (+), 129.9 (+), 129.38 (+), 129.36, 128.0 (+), 127.1 (+), 69.1 (-), 32.0, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3389, 2957, 2899, 2870, 1682, 1468, 1431, 1250, 1074, 1038, 1014, 993, 885, 841, 744, 735, 719; HRMS (TOF ES): Found 259.0898, calculated for C$_{13}$H$_{17}$ClOSiLi (M+Li) 259.0897 (0.4 ppm).



(1-(2,3-Difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11j): This compound was obtained via typical procedure using methyl 1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9j**) (424 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled product was obtained as colorless crystals, mp 64.3-64.8 °C in 77% yield (292 mg, 1.15 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.01 (s, 1H), 7.02 – 6.92 (m, 2H), 6.89 – 6.83 (m, 1H), 4.00 (dd, J = 11.2, 5.8 Hz, 1H), 3.72 (dd, J = 11.2, 5.4 Hz, 1H), 1.19 (t, J = 6.0 Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 150.8 (dd, J = 247.8, 13.7 Hz), 149.9 (dd, J = 246.0, 12.5 Hz), 135.7 (d, J = 12.4 Hz), 128.5, 126.6 (+), 125.0 (t, J = 3.6 Hz, +), 124.0 (dd, J = 7.1, 4.4 Hz, +), 115.1 (d, J = 17.3 Hz, +), 69.7 (d, J = 3.1 Hz, -), 27.9 (d, J = 2.7 Hz), -1.3 (3C, +); FTIR (KBr, cm^{-1}): 3240, 3124, 2959, 2876, 1697, 1620, 1585, 1474, 1456, 1435, 1250, 1211, 1063, 1032, 903, 864, 841, 814, 787, 760, 733; HRMS (TOF ES): Found 253.0859, calculated for C$_{13}$H$_{15}$F$_2$OSi (M-H) 253.0860 (0.4 ppm).

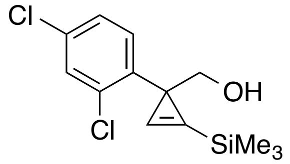


(1-(3-Bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11k): This compound was obtained via typical procedure using methyl 1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9k**) (488 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled product was obtained as colorless crystals, mp 58.5-59.7 °C in 90% yield (400 mg, 1.35 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.30 (d, J = 1.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.13 (d, J = 5.0 Hz, 2H), 4.12 (d, J = 10.8 Hz, 1H), 3.93 (d, J = 11.1 Hz, 1H), 1.26 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 149.8, 129.6 (+), 129.3 (+), 128.2 (+), 124.8 (+), 123.7, 122.7 (+), 122.6, 68.9 (-), 29.8, -0.9 (3C, +); FTIR (KBr, cm^{-1}): 3296, 3283, 3119, 2959, 2935, 2897, 2878, 1693, 1591, 1562, 1472, 1462, 1416, 1410, 1250, 1076, 1055, 1015, 995, 872, 843, 787, 758, 725, 702; HRMS (TOF ES): Found 295.0146, calculated for C$_{13}$H$_{16}$BrOSi (M-H) 295.0154 (2.7 ppm).

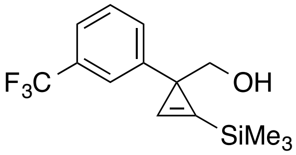


(1-(4-Bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11l): This compound was obtained via typical procedure using methyl 1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9l**) (488 mg, 1.50 mmol, 1.0 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 μL, 3.15 mmol, 2.10 equiv). The titled product was obtained as colorless crystals, mp 58.5 – 58.9 °C in 95% yield (423 mg, 1.14 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.65 (s, 1H), 7.37 (d, J = 8.6 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 4.12 (d, J = 11.1 Hz, 1H), 3.92 (d, J = 11.1 Hz, 1H), 1.26 (s, 1H), 0.16 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 146.2, 131.0 (2C, +), 127.9 (2C, +), 123.9, 122.8 (+), 119.0, 69.0 (-), 29.7, -0.9 (3C,

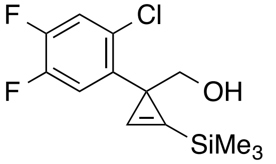
+); FTIR (KBr, cm^{-1}): 3371, 3356, 2957, 2897, 2872, 1693, 1487, 1406, 1394, 1250, 1076, 1055, 1007, 989, 868, 843, 762, 737, 717; HRMS (TOF ES): Found 295.0151, calculated for $C_{13}H_{16}BrOSi$ (M-H) 295.0154 (1.0 ppm).



(1-(2,4-Dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)-methanol (11m): This compound was obtained via typical procedure using methyl 1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9m**) (473 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.10 equiv). The titled product was obtained as a pale yellow solid, mp 60.3-61.4 °C in 74% yield (319 mg, 1.11 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.11 (s, 1H), 7.35 – 7.30 (m, 1H), 7.16 – 7.15 (m, 2H), 3.91 (d, *J* = 11.2 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 1.13 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 142.2, 135.1, 132.8, 132.2 (+), 129.6 (+), 129.3, 128.8 (+), 127.4 (+), 69.0 (-), 31.4, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3363, 2957, 2899, 2870, 1682, 1585, 1553, 1470, 1410, 1375, 1250, 1101, 1074, 1036, 1014, 993, 932, 887, 843, 822, 800, 760, 741, 719, 702; HRMS (TOF ES): Found 285.0274, calculated for $C_{13}H_{15}Cl_2OSi$ (M-H) 285.0269 (1.8 ppm).

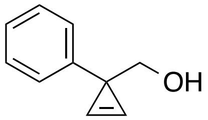


(1-(3-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11n): This compound was obtained via typical procedure using methyl 1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9n**) (472 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µl, 3.15 mmol, 2.10 equiv). The titled product was obtained as colorless crystals, mp 53.8-54.3 °C in 81% yield (349 mg, 1.22 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.67 (s, 1H), 7.59 – 7.33 (m, 4H), 4.17 (d, *J* = 11.2 Hz, 1H), 3.99 (d, *J* = 11.2 Hz, 1H), 1.25 (s, 1H), 0.18 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 148.3, 130.4 (q, *J* = 31.8 Hz), 129.5 (d, *J* = 1.4 Hz, +), 128.5 (+), 124.5 (q, *J* = 272.3 Hz) 123.6, 122.9 (q, *J* = 3.8 Hz, +), 122.7 (+), 121.9 (q, *J* = 3.8 Hz, +), 69.1 (-), 29.9, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3360, 2961, 2901, 2874, 1697, 1612, 1591, 1435, 1331, 1252, 1163, 1124, 1097, 1078, 1063, 1014, 868, 843, 800, 702; HRMS (TOF ES): Found 285.0924, calculated for $C_{14}H_{16}F_3OSi$ (M-H) 285.0923 (0.4 ppm).

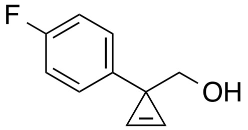


(1-(2-Chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (11o): This compound was obtained via typical procedure using methyl 1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-enecarboxylate (**9o**) (475 mg, 1.50 mmol, 1.00 equiv), diethyl ether (3.9 mL), and DIBAL (448 mg, 562 µL, 3.15 mmol, 2.10 equiv). The titled product was obtained as a pale yellow solid mp 98.4-99.8 °C in 57% yield (245 mg, 0.85 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.08 (s, 1H), 7.15 (dd, *J* = 10.0, 7.3 Hz, 1H), 7.03 (dd, *J* = 10.7, 8.4 Hz, 1H), 3.90 (d, *J* = 11.2 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 1.10 (s, 1H), 0.24 (s, 9H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 149.2 (dd, *J* = 249.2, 12.4 Hz), 148.9 (dd, *J* = 250.3, 13.7 Hz), 140.7, 129.3, 128.8 (dd, *J* = 7.9, 3.3 Hz), 128.5 (+), 119.4 (d, *J* = 17.6 Hz, +), 118.7 (d, *J* = 20.0 Hz, +), 69.0 (-), 31.5, -1.0 (3C, +); FTIR (KBr, cm^{-1}): 3240, 2962, 2880, 1688, 1599, 1497, 1462, 1387, 1302, 1275, 1252, 1171, 1080, 1020, 878, 841, 798, 760, 739, 719, 700, 679, 633; HRMS (TOF ES): Found 289.0627, calculated for $C_{13}H_{16}ClF_2OSi$ (M+H) 289.0627 (0.0 ppm).

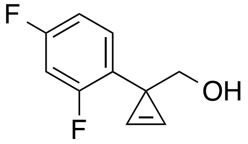
3. Preparation of (1-arylcycloprop-2-en-yl)methanols (3a-d)



(1-Phenylcycloprop-2-en-1-yl)methanol (3a) (Typical Procedure): An oven dried round bottom flask was charged with methyl 1-phenylcycloprop-2-enecarboxylate (**10a**) (460 mg, 2.64 mmol, 1.00 equiv) and anhydrous diethyl ether (6.9 mL). The formed solution was stirred under nitrogen atmosphere at -78ºC and DIBAL (789 mg, 989 µL, 5.54 mmol, 2.10 equiv) was added dropwise via syringe. Upon complete addition, the mixture was stirred for one hour at -78ºC, then allowed to warm to room temperature and the stirring was continued for one hour. The reaction was quenched by addition of saturated aqueous solution of ammonium chloride, which was added dropwise until the solution turned into a gel. A 10% HCl aqueous solution was then added very slowly until just the moment when the gel dissolved. The aqueous phase was extracted with ether (3 x 10 mL). Combined organic layers were washed consecutively with saturated sodium bicarbonate and brine; then dried with magnesium sulfate, filtered, and concentrated. The recovered product was purified by column chromatography eluting with mixture 6:1 hexane:EtOAc to afford the titled compound as a pale yellow solid, mp 55.4-57.1 °C in 82% yield (316 mg, 2.16 mmol). Spectral properties of this compound were identical to those described in our previous report.[2]



(1-(4-Fluorophenyl)cycloprop-2-en-1-yl)methanol (3b): This compound was obtained via typical procedure using methyl 1-(4-fluorophenyl)-cycloprop-2-enecarboxylate (**10b**) (182 mg, 0.947 mmol, 1.0 equiv), diethyl ether (2.46 ml, 23.7 mmol, 25.0 equiv), and DIBAL (283 mg, 355 µl, 1.99 mmol, 2.10 equiv). The titled compound was obtained as a pale yellow oil in 79% yield (123 mg, 0.748 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.35 (s, 2H), 7.22 – 7.15 (m, 2H), 7.02 – 6.94 (m, 2H), 4.04 (s, 2H), 1.45 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.4 (d, J = 244.2 Hz), 141.5 (d, J = 3.1 Hz), 128.0 (d, J = 7.8 Hz, 2C, +), 115.0 (d, J = 21.0 Hz, 2C, +), 113.5 (2C, +), 68.3 (-), 28.8; FTIR (KBr, cm^{-1}): 3423, 3404, 3387, 3364, 3346, 2926, 2876, 1641, 1601, 1502, 1474, 1406, 1225, 1159, 1099, 1067, 1011, 997, 968, 839, 818, 669, 611; HRMS (TOF ES): Found 171.0798, calculated for C$_{10}$H$_9$FLiO (M+Li) 171.0797 (0.6 ppm).



(1-(2,4-Difluorophenyl)cycloprop-2-en-1-yl)methanol (3c): This compound was obtained via typical procedure using methyl 1-(2,4-difluorophenyl)cycloprop-2-enecarboxylate (**9c**) (139 mg, 0.660 mmol, 1.00 equiv), diethyl ether (1.7 mL), and DIBAL (197 mg, 247 µL, 1.39 mmol, 2.10 equiv). The titled product was obtained as a pale yellow solid, mp 59.5-61.2 °C in 79% yield (94.5 mg, 0.519 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.57 (s, 2H), 7.17 – 7.09 (m, 1H), 6.83 – 6.70 (m, 2H), 3.84 (s, 2H), 1.32 (s, 1H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.8 (d, J = 247.4 Hz), 161.7 (d, J = 247.5 Hz), 131.0 (dd, J = 9.6, 6.8 Hz, +), 128.2 (dd, J = 16.2, 3.8 Hz), 116.2 (d, J = 1.7 Hz, 2C, +), 111.3 (dd, J = 21.0, 3.7 Hz, +), 104.1 (dd, J = 26.6, 25.0 Hz, +), 68.7 (d, J = 2.5 Hz, -), 26.4; FTIR (KBr, cm^{-1}): 3259, 3246, 3142, 3105, 2935, 2878, 1637, 1609, 1595, 1501, 1462, 1425, 1294, 1267, 1138, 1103, 1051, 1024, 1001, 984, 964, 851, 812, 729, 669, 623, 611; HRMS (TOF ES): Found 181.0468, calculated for C$_{10}$H$_7$OF$_2$ (M-H) 181.0465 (1.7 ppm).

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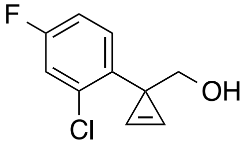
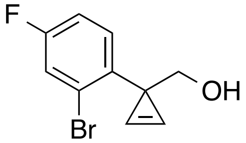
[2] Rubina, M.; Rubin, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2004**, *126*, 3688.



(1-(2-Chloro-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (3d): This compound was obtained via typical procedure using methyl 1-(2-chloro-4-fluorophenyl)cycloprop-2-enecarboxylate (**9d**) (113 mg, 0.496 mmol, 1.0 equiv), diethyl ether (1.3 mL), and DIBAL (148 mg, 186 μL, 1.04 mmol, 2.10 equiv). The titled product was obtained as a pale yellow oil in 91% yield (89.4 mg, 0.450 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 2H), 7.23 (dd, *J* = 8.5, 6.2 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.91 (td, *J* = 8.3, 2.6 Hz, 1H), 3.80 (s, 2H), 1.36 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.4 (d, *J* = 248.4 Hz), 138.8 (d, *J* = 3.6 Hz), 134.9 (d, *J* = 10.4 Hz), 131.8 (d, *J* = 8.7 Hz, +), 117.0 (d, *J* = 24.5 Hz, +), 116.9 (2C, +), 114.4 (d, *J* = 20.7 Hz, +), 68.0 (-), 29.7; FTIR (KBr, cm^{-1}): 3358, 3111, 2926, 2870, 2361, 1637, 1597, 1578, 1483, 1389, 1258, 1223, 1217, 1198, 1180, 1070, 1043, 1011, 968, 928, 891, 858, 818, 687, 669, 611; HRMS (TOF ES): Found 205.0417, calculated for $C_{10}H_8ClFLiO$ (M+Li) 205.0408 (4.4 ppm).

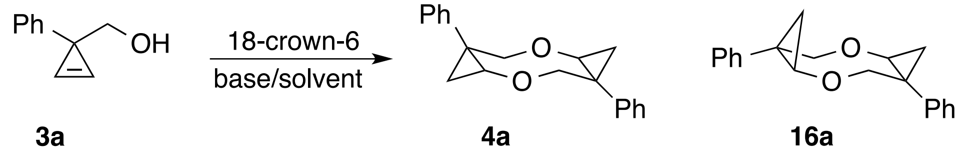


(1-(2-Bromo-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (3e): This compound was obtained via typical procedure using methyl 1-(2-bromo-4-fluorophenyl)cycloprop-2-enecarboxylate (**9e**) (128 mg, 0.472 mmol, 1.0 equiv), diethyl ether (1.3 mL), and DIBAL (141 mg, 177 μl, 0.992 mmol, 2.10 equiv). The titled product was obtained as a clear oil in 74% yield (85.0 mg, 0.350 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 2H), 7.27 – 7.21 (m, 2H), 6.96 (td, *J* = 8.3, 2.6 Hz, 1H), 3.81 (s, 2H), 1.40 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.3 (d, *J* = 249.4 Hz), 140.4 (d, *J* = 3.5 Hz), 132.1 (d, *J* = 8.3 Hz, +), 124.1 (d, *J* = 9.6 Hz), 120.1 (d, *J* = 24.4 Hz, +), 117.0 (2C, +), 115.0 (d, *J* = 20.8 Hz, +), 67.7 (-), 31.5; FTIR (KBr, cm^{-1}): 3321, 2934, 2862, 1637, 1597, 1572, 1477, 1383, 1290, 1256, 1209, 1192, 1178, 1067, 1034, 1011, 968, 922, 858, 818, 729, 708, 663, 608; HRMS (TOF ES): Found 264.9641, calculated for $C_{10}H_8BrFNaO$ (M+Na) 264.9640 (0.4 ppm).

4. Optimization of reaction conditions for cyclization of 3a

General procedure for optimization: Oven-dried Wheaton vial (3 mL) was charged with powdered base (in amount indicated in Table 1), (1-phenylcycloprop-2-en-1-yl)methanol (**3a**) (6.3 mg, 43 μmol), 18-crown-6 ether (2.5 mg, 9.4 μmol, 22 mol%) and anhydrous solvent (volume and type of solvent is specified in Table 1). The mixture was stirred at 55 °C for 3 hrs. Diastereoselectivities were determined by GC analysis of aliquots withdrawn directly from the reaction mixtures. Internal standard (CH_2Br_2, 3.0 μL, 7.43 mg, 42.8 μmol) was then added, and another aliquot (30-40 μL) was withdrawn, placed into NMR tube and diluted with $CDCl_3$ (~500 μL). Yields of **4a** were estimated from ^{1}H NMR data by integration of signal at 3.67 ppm versus internal standard (4.95 ppm).

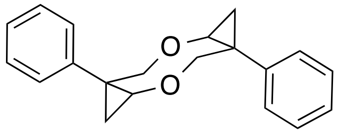
Table 1. Optimization of 4+4-cyclization of alcohol 3a



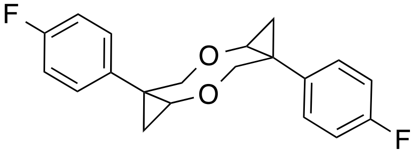
#	**Base (mass, mg)**	**Solvent (volume, mL)**	**Yield, %**^{a}	**dr (4a:16a)**^{b}
1	**KOH (12)**	**THF (1)**	**74**	**99:1**
2	*t*-BuOK (24)	THF (1)	70	99:1
3	KOH (12)	THF (3)	0	-
4	*t*-BuOK (24)	THF (3)	0	-
5	KOH (12)	DMSO (1)	32	83:17
6	*t*-BuOK (24)	DMSO (1)	75	85:15
7	KOH (12)	DMSO (3)	57	81:19
8	*t*-BuOK (24)	DMSO (3)	78	82:18
9	*t*-BuOK (24)	DMSO (0.5)	57	84:16
10	KOH (12)	Et_2O (1)	60	99:1
11	*t*-BuOK (24)	Et_2O (1)	58	98:2
12	KOH (12)	DMF (1)	36	89:11
13	*t*-BuOK (24)	DMF (1)	57	95:5
14	KOH (12)	DMA (1)	36	91:9
15	*t*-BuOK (24)	DMA (1)	68	90:10
16	KOH (12)	PhMe (1)	28	99:1
17	*t*-BuOK (24)	PhMe (1)	43	98:2
18	KOH (12)	CH_2Cl_2 (1)	0	-
19	*t*-BuOK (24)	CH_2Cl_2 (1)	0	-
20	KOH (12)	CCl_4 (1)	0	-
21	*t*-BuOK (24)	CCl_4 (1)	0	-
22	KOH (12)	1,4-dioxane (1)	0	-
23	*t*-BuOK (24)	1,4-dioxane (1)	0	-

a NMR yieds; *b* Determined by GC analyses of crude reaction mixtures

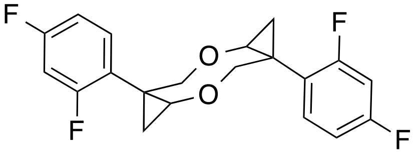
5. 4+4-Cyclodimerization of alcohols 3a-e



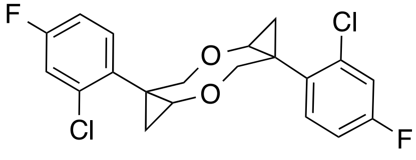
(1*R*,4*R***,6*S***,9*S***)-4,9-Diphenyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4a) (Typical Procedure):** An oven dried Wheaton vial (5 mL) equipped with a spin vane and a Mininert valve was charged with (1-phenylcycloprop-2-en-1-yl)methanol (**3a**) (29.2 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), powdered potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL) and the mixture was stirred overnight at 65 ºC. The reaction mixture then was stirred with dry magnesium sulfate, filtered, and concentrated. Preparative column chromatography of the residue eluting with 9:1 hexane:EtOAc mixture afforded the titled product as colorless crystals, mp 186.6-187.4 °C in 66% yield (19.3 mg, 0.066 mmol.); GC (R_t, min): 11.47 (main), 11.34 (minor); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 8H), 7.25 – 7.19 (m, 2H), 4.71 (d, J = 12.1 Hz, 2H), 3.73 (dd, J = 6.6, 3.6 Hz, 2H), 3.67 (d, J = 12.1 Hz, 2H), 1.31 – 1.22 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 142.7 (2C), 128.5 (4C, +), 127.4 (4C, +), 126.4 (2C, +), 76.9 (2C, -), 66.3 (2C, +), 33.3 (2C), 21.7 (2C, -); FTIR (KBr, cm^{-1}): 3084, 3055, 3022, 2986, 2959, 2934, 2876, 1601, 1495, 1454, 1360, 1310, 1269, 1258, 1165, 1070, 1049, 1024, 976, 916, 835, 820, 741, 692; HRMS (TOF ES): Found 292.1465, calculated for $C_{20}H_{20}O_2$ (M^+) 292.1463 (0.7 ppm).



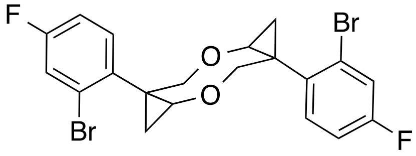
(1*R*,4*R***,6*S***,9*S***)-4,9-Bis(4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4b):** This compound was obtained via typical procedure using (1-(4-fluorophenyl)cycloprop-2-en-1-yl)methanol (**3b**) (32.8 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained as colorless crystals, MP: 209.1-210.4 °C in 63% yield (20.7 mg, 0.063 mmol.); GC (R_t, min): 11.30; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.23 (m, 4H), 7.03 – 6.95 (m, 4H), 4.62 (d, J = 12.0 Hz, 2H), 3.66 (dd, J = 8.01, 3.91 Hz, 2H), 3.63 (d, J = 12.0 Hz, 2H), 1.30 – 1.18 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6 (d, J = 244.8 Hz, 2C), 138.3 (d, J = 3.1 Hz, 2C), 129.3 (d, J = 7.8 Hz, 4C, +), 115.3 (d, J = 21.3 Hz, 4C, +), 77.2 (2C, -), 66.0 (2C, +), 33.0 (2C), 21.4 (2C, -); FTIR (KBr, cm^{-1}): 2947, 2912, 2889, 2862, 2357, 2339, 2330, 1595, 1512, 1504, 1487, 1454, 1232, 1217, 1161, 1074, 1036, 926, 841, 812, 729; HRMS (TOF ES): Found 327.1200, calculated for $C_{20}H_{17}F_2O_2$ (M-H) 327.1197 (0.9 ppm).



(1*R*,4*R***,6*S***,9*S***)-4,9-Bis(2,4-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4c):** This compound was obtained via typical procedure using (1-(2,4-difluorophenyl)cycloprop-2-en-1-yl)methanol (**3c**) (36.4 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained as colorless crystals, mp 205.0 – 208.2 °C in a mixture (~94:6) with minor diastereomer **16c**. Yield 59% (21.5 mg, 0.059 mmol.); GC (R_t, min): 10.71 (main), 10.77 (minor); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.26 (m, 2H), 6.86 – 6.72 (m, 4H), 4.52 (d, J = 12.0 Hz, 2H), 3.82 (d, J = 12.1 Hz, 2H), 3.78 (dd, J = 6.8, 3.5 Hz, 2H), 1.29 (dd, J = 6.4, 3.5 Hz, 2H), 1.08 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 162.3 (dd, *J* = 250.6, 12.4 Hz, 2C), 162.1 (dd, *J* = 247.7, 11.7 Hz, 2C), 133.0 (dd, *J* = 9.7, 5.8 Hz, 2C, +), 125.2 (dd, *J* = 13.5, 3.8 Hz, 2C), 111.4 (dd, *J* = 20.9, 3.6 Hz, 2C, +), 104.3 (t, *J* = 25.6 Hz, 2C, +), 77.3 (2C, -), 63.8 (d, *J* = 1.5 Hz, 2C, +), 29.5 (2C), 20.8 (2C, -); FTIR (KBr, cm^{-1}): 3063, 2986, 2953, 2874, 2359, 2339, 1614, 1595, 1504, 1462, 1423, 1362, 1312, 1263, 1231, 1163, 1140, 1097, 1078, 1045, 1034, 966, 851, 812, 741, 731, 615; HRMS (TOF ES): Found 363.0100, calculated for $C_{20}H_{15}F_4O_2$ (M-H) 363.1008 (2.2 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-chloro-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4d):** This compound was obtained via typical procedure using (1-(2-chloro-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (**3d**) (39.7 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained as colorless crystals, mp 234.7-236.4 °C in 75% yield (29.8 mg, 0.075 mmol.); GC (R$_t$, min): 13.08; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 (dd, *J* = 8.6, 6.1 Hz, 2H), 7.10 (dd, *J* = 8.5, 2.6 Hz, 2H), 6.95 (td, *J* = 8.3, 2.7 Hz, 2H), 4.67 (d, *J* = 12.0 Hz, 2H), 3.78 (dd, *J* = 6.9, 3.4 Hz, 2H), 3.71 (d, *J* = 12.1 Hz, 2H), 1.38 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.09 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.7 (d, *J* = 249.3 Hz, 2C), 136.4 (d, *J* = 10.4 Hz, 2C), 134.7 (d, *J* = 3.6 Hz, 2C), 133.7 (d, *J* = 8.7 Hz, 2C, +), 117.4 (d, *J* = 24.7 Hz, 2C, +), 114.1 (d, *J* = 21.0 Hz, 2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.2 (2C), 22.0 (2C, -); FTIR (KBr, cm^{-1}): 3074, 2976, 2957, 2934, 2874, 2359, 2341, 2330, 1601, 1574, 1487, 1458, 1392, 1354, 1304, 1258, 1202, 1161, 1080, 1057, 1028, 982, 897, 856, 843, 822, 733; HRMS (TOF ES): 403.0657, calculated for $C_{20}H_{16}Cl_2F_2O_2Li$ (M+Li) 403.0655 (0.5 ppm).

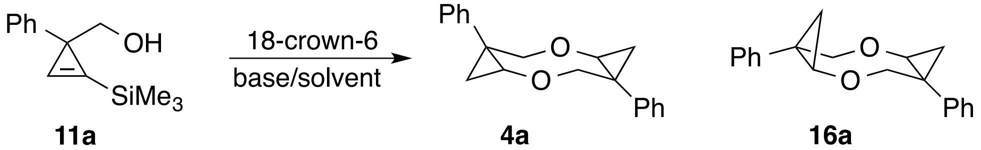


(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-bromo-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.04,6]decane (4e):** This compound was obtained via typical procedure using (1-(2-bromo-4-fluorophenyl)cycloprop-2-en-1-yl)methanol (**3e**) (48.6 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 221 – 223 (with decomposition) in 63% yield (30.5 mg, 0.063 mmol.); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 (dd, *J* = 8.6, 6.0 Hz, 2H), 7.30 (dd, *J* = 8.2, 2.6 Hz, 2H), 7.00 (td, *J* = 8.3, 2.7 Hz, 2H), 4.71 (d, *J* = 12.0 Hz, 2H), 3.77 (dd, *J* = 6.9, 3.4 Hz, 2H), 3.67 (d, *J* = 12.1 Hz, 2H), 1.41 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.11 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.6 (d, *J* = 250.3 Hz, 2C), 136.0 (d, *J* = 3.5 Hz, 2C), 133.9 (d, *J* = 8.6 Hz, 2C, +), 125.9 (d, *J* = 9.6 Hz, 2C), 120.6 (d, *J* = 24.3 Hz, 2C, +), 114.6 (d, *J* = 20.9 Hz, 2C, +), 76.8 (2C, -), 65.3 (2C, +), 35.0 (2C), 22.7 (2C, -); FTIR (KBr, cm^{-1}): 3094, 3067, 2972, 2957, 2928, 2889, 2868, 2361, 2345, 1597, 1582, 1487, 1458, 1356, 1306, 1259, 1204, 1163, 1078, 1053, 1024, 978, 881, 841, 816, 804, 731; HRMS (TOF ES): Found 482.9407, calculated for $C_{20}H_{15}Br_2F_2O_2$ (M-H) 482.9407 (0.0 ppm).

6. Optimization of reaction conditions for cyclization of 11a

General procedure for optimization: Oven-dried Wheaton vial (3 mL) was charged with powdered base (in amount indicated in Table 2), (1-phenyl-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11a**) (9.3 mg, 43 μmol), 18-crown-6 ether (2.5 mg, 9.4 μmol, 22 mol%) and anhydrous solvent (1 mL, type of solvent is specified in Table 2). The mixture was stirred at 65 °C for 24-72 hrs. Diastereoselectivities were determined by GC analysis of aliquots withdrawn directly from the reaction mixtures. Internal standard (CH_2Br_2, 3.0 μL, 7.43 mg, 42.8 μmol) was then added, and another aliquot (30-40 μL) was withdrawn, placed into NMR tube and diluted with $CDCl_3$ (~500 μL). Yields of **4a** were estimated from ^1H NMR data by integration of signal at 3.67 ppm versus internal standard (4.95 ppm).

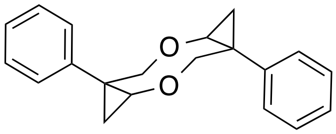
Table 2. Optimization of 4+4-cyclization of alcohol 11a



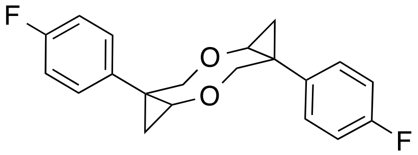
#	Base (mass, mg)	Solvent	Temp, °C (time, h)	Yield, %	dr (4a:16a)
1	KOH (4.5)	THF	65 (24)	72	98:2
2	KOH (9.5)	THF	65 (24)	68	98:2
3	**KOH (12)**	**THF**	**65 (24)**	**77**	**98:2**
4	KOH (24)	THF	65 (24)	73	98:2
5	KOH (12)	THF	75 (24)	49	97:3
6	KOH (12)	THF	55 (24)	56	98:2
7	KOH (12)	THF	45 (24)	21	98:2
8	KOH (12)	THF	35 (24)	0	-
9	*t*-BuOK (24)	THF	65 (24)	70	99:1
10	KOH (12)	DMSO	65 (24)	45	86:14
11	*t*-BuOK (24)	DMSO	65 (24)	67	87:13
12	KOH (12)	Et_2O	65 (24)	59	99:1
13	*t*-BuOK (24)	Et_2O	65 (24)	61	99:1
14	KOH (12)	DMF	65 (24)	29[a]	94:6
15	*t*-BuOK (24)	DMF	65 (24)	29[a]	91:9
16	KOH (12)	DMF	65 (72)	34[a]	93:7
17	*t*-BuOK (24)	DMF	65 (72)	21[a]	92:8
18	KOH (12)	DMA	65 (72)	54	93:7
19	*t*-BuOK (24)	DMA	65 (72)	48	92:8
20	KOH (12)	PhMe	65 (72)	71	98:2
21	*t*-BuOK (24)	PhMe	65 (72)	75	98:2

[a] Incomplete conversion: GC analysis showed presence of unreacted starting material **11a**.

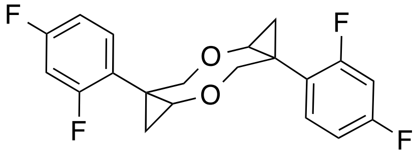
7. 4+4-Cyclodimerization of alcohols 11a-o



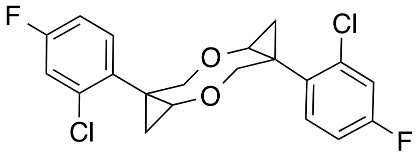
(1*R,4*R**,6*S**,9*S**)-4,9-Diphenyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]-decane (4a) (Typical procedure):** An oven dried Wheaton vial (5 mL) equipped with a spin vane and a Mininert valve was charged with (1-phenyl-2-(trimethylsilyl)cycloprop-2-en-1-yl)-methanol (**11a**) (43.7 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), powdered potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL) were placed in and stirred overnight at 65 ºC. The reaction mixture then was stirred with dry magnesium sulfate, filtered, and concentrated. Preparative column chromatography of the residue eluting with 9:1 hexane:EtOAc mixture afforded the titled product as colorless crystals in 64% yield (18.8 mg, 0.064 mmol.). Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **3a** (See page S11).



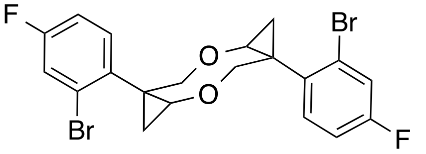
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4b):** This compound was obtained via typical procedure employing (1-(4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11b**) (47.3 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv), and THF (2.2 mL). The titled product was obtained in 59% yield (19.3 mg, 0.059 mmol). Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **3b** (See page S11).



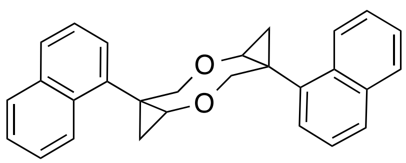
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2,4-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4c):** This compound was obtained via typical procedure employing (1-(2,4-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11c**) (50.9 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained in 62% yield (22.5 mg, 0.062 mmol). Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **3c** (See page S11).



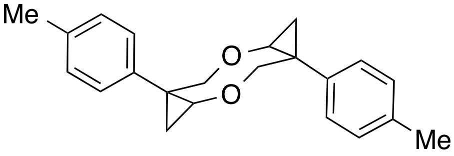
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-chloro-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4d):** This compound was obtained via typical procedure using (1-(2-chloro-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11d**) (54.2 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained in 79% yield (31.4 mg, 0.079 mmol). Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **3d** (See page S12).



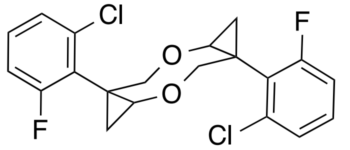
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-bromo-4-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4e):** This compound was obtained via typical procedure employing (1-(2-bromo-4-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11e**) (63.1 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.2 mL). The titled product was obtained in 63% yield (30.4 mg, 0.063 mmol). Physical and spectral properties of this compound were identical to those described above for the same material obtained in 4+4-cyclodimerization of alcohol **3b** (See page S12).



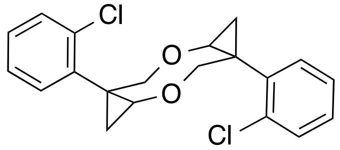
(1*R,4*R**,6*S**,9*S**)-4,9-Di(naphthalen-1-yl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4f):** This compound was obtained via typical procedure employing (1-(naphthalen-1-yl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11f**) (52.9 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 253-256 °C (with decomposition) in 55% yield (21.4 mg, 0.055 mmol); ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 5.8 Hz, 2H), 7.58 – 7.43 (m, 6H), 4.83 (d, *J* = 11.6 Hz, 2H), 4.04 (d, *J* = 11.7 Hz, 2H), 3.95 (dd, *J* = 6.8, 3.2 Hz, 2H), 1.61 (dd, *J* = 6.1, 3.2 Hz, 2H), 1.18 (t, *J* = 6.5 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 137.4 (2C), 134.4 (2C), 132.0 (2C), 129.2 (2C, +), 128.6 (2C, +), 128.0 (2C, +), 126.0 (2C, +), 125.7 (2C, +), 125.5 (2C, +), 124.0 (2C, +), 77.6 (2C, -), 64.5 (2C, +), 33.1 (2C), 22.0 (2C, -); FTIR (KBr, cm^{-1}): 3994, 3069, 3047, 2947, 2945, 2922, 2866, 1593, 1504, 1454, 1435, 1400, 1265, 1252, 1153, 1128, 1082, 1061, 1040, 1001, 968, 864, 837, 800, 775, 733, 706, 621; HRMS (TOF ES): Found 391.1695, calculated for $C_{28}H_{23}O_2$ (M-H) 391.1698 (0.8 ppm).



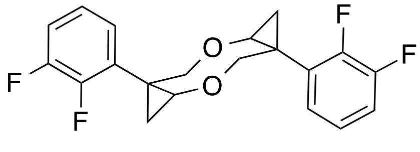
(1*R,4*R**,6*S**,9*S**)-4,9-Di-*p*-tolyl-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4g):** This compound was obtained via typical procedure employing (1-(*p*-tolyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11g**) (46.5 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.5 equiv) and THF (2.20 mL). The titled compound was obtained as colorless crystals, mp 170.2-172.8 °C in 78% yield (25.0 mg, 0.078 mmol); GC (R$_t$, min): 12.77; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18 (d, *J* = 8.2 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 4.66 (d, *J* = 12.0 Hz, 2H), 3.68 (dd, *J* = 6.6, 3.6 Hz, 2H), 3.64 (d, *J* = 12.0 Hz, 2H), 2.32 (s, 6H), 1.29 – 1.16 (m, 4H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 139.8 (2C), 136.0 (2C), 129.2 (4C, +), 127.3 (4C, +), 77.0 (2C, -), 66.2 (2C, +), 33.0 (2C), 21.6 (2C, -), 21.1 (2C, +); FTIR (KBr, cm^{-1}): 3088, 3049, 3013, 2982, 2943, 2922, 2872, 2361, 2332, 1518, 1458, 1447, 1360, 1265, 1161, 1113, 1076, 1034, 1020, 978, 835, 787, 739; HRMS (TOF ES): Found 327.1936, calculated for $C_{22}H_{24}O_2Li$ (M+Li) 327.1936 (0.0 ppm).



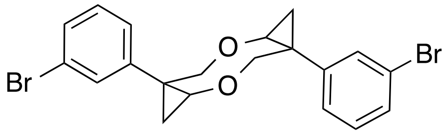
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-chloro-6-fluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4h):** This compound was obtained via typical procedure employing (1-(2-chloro-6-fluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11h**) (54.2 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 237-240 °C in 69% yield (27.3 mg, 0.069 mmol); GC (R$_t$, min): 13.11; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 – 7.36 (m, 2H), 7.13 – 7.08 (m, 2H), 6.98 – 6.92 (m, 2H), 4.67 (d, *J* = 12.0 Hz, 2H), 3.78 (dd, *J* = 6.8, 3.4 Hz, 2H), 3.71 (d, *J* = 12.6 Hz, 2H), 1.39 (dd, *J* = 6.7, 3.4 Hz, 2H), 1.09 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 161.7 (d, *J* = 249.3 Hz, 2C), 136.4 (d, *J* = 10.3 Hz, 2C), 134.7 (d, *J* = 3.4 Hz, 2C), 133.7 (d, *J* = 8.7 Hz, 2C, +), 117.4 (d, *J* = 24.6 Hz, 2C, +), 114.1 (d, *J* = 21.2 Hz, 2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.2 (2C), 22.0 (2C, -); FTIR (KBr, cm^{-1}): 3074, 2976, 2957, 2935, 2874, 2359, 2332, 1601, 1574, 1487, 1458, 1391, 1354, 1304, 1258, 1202, 1161, 1078, 1057, 1028, 982, 897, 856, 843, 820, 733, 685; HRMS (TOF ES): Found 395.0414, calculated for $C_{20}H_{15}Cl_2F_2O_2$ (M-H) 395.0417 (0.8 ppm).



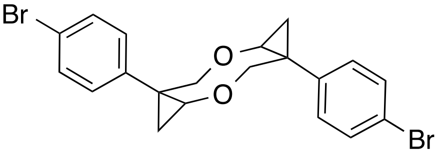
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2-chlorophenyl)-2,7-dioxatricyclo-[7.1.0.0^{4,6}]decane (4i):** This compound was obtained via typical procedure employing (1-(2-chlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11i**) (50.6 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 233-236 °C in 62% yield (22.4 mg, 0.062 mmol); GC (R$_t$, min): 14.02; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.35 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.25 – 7.15 (m, 4H), 4.73 (d, *J* = 12.0 Hz, 2H), 3.82 (dd, *J* = 6.8, 3.4 Hz, 2H), 3.77 (d, *J* = 12.0 Hz, 2H), 1.40 (dd, *J* = 6.7, 3.5 Hz, 2H), 1.11 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 138.7 (2C), 135.7 (2C), 132.8 (2C, +), 130.1 (2C, +), 128.5 (2C, +), 126.9 (2C, +), 76.8 (2C, -), 64.9 (2C, +), 33.9 (2C), 22.0 (2C, -); FTIR (KBr, cm^{-1}): 3070, 3055, 2976, 2949, 2932, 2885, 2870, 2359, 1474, 1458, 1433, 1356, 1306, 1288, 1267, 1252, 1188, 1171, 1128, 1080, 1030, 976, 914, 839, 754, 727, 685; HRMS (TOF ES): Found 359.0602, calculated for $C_{20}H_{17}Cl_2O_2$ (M-H) 359.0606 (1.1 ppm).



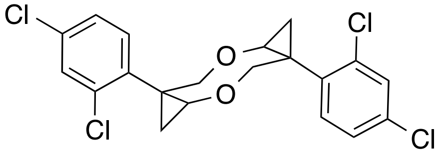
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2,3-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4j):** This compound was obtained via typical procedure employing (1-(2,3-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11j**) (50.9 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 211.0-214.8 in 57% yield (20.9 mg, 0.057 mmol.); GC (R$_t$, min): 11.22 (main), 11.14 (minor); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.14 – 6.96 (m, 6H), 4.56 (d, *J* = 12.1 Hz, 2H), 3.88 (d, *J* = 12.1 Hz, 2H), 3.84 (dd, *J* = 6.8, 3.5 Hz, 2H), 1.34 (dd, *J* = 6.5, 3.5 Hz, 2H), 1.13 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$): δ 150.9 (dd, *J* = 248.2, 13.2 Hz, 2C), 150.5 (dd, *J* = 249.1, 12.5 Hz, 2C), 131.6 (d, *J* = 10.0 Hz, 2C), 126.8 (2C, +), 124.1 (dd, *J* = 7.1, 4.7 Hz, 2C, +), 116.1 (d, *J* = 17.2 Hz, 2C, +), 77.1 (2C, -), 63.6 (2C, +), 29.9 (d, *J* = 2.5 Hz, 2C), 20.9 (d, *J* = 2.2 Hz, 2C, -); FTIR (KBr, cm^{-1}): 3088, 3045, 2976, 2928, 2868, 2363, 1626, 1589, 1474, 1456, 1356, 1312, 1261, 1221, 1190, 1159, 1086, 1065, 1041, 987, 941, 928, 895, 837, 798, 783, 725, 690; HRMS (TOF ES): Found 365.1161, calculated for $C_{20}H_{17}F_4O_2$ (M+H) 365.1165 (1.1 ppm).



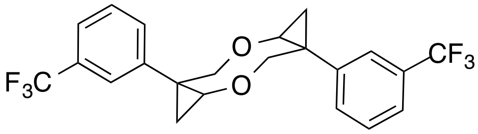
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(3-bromophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4k):** This compound was obtained via typical procedure employing (1-(3-bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11k**) (59.5 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 226-230 °C in 83% yield (37.5 mg, 0.083 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 1.8 Hz, 2H), 7.34 (dt, *J* = 7.6, 1.4 Hz, 2H), 7.23 – 7.14 (m, 4H), 4.66 (d, *J* = 12.1 Hz, 2H), 3.68 (dd, *J* = 6.4, 4.0 Hz, 2H), 3.60 (d, *J* = 12.2 Hz, 2H), 1.33 – 1.23 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 145.0 (2C), 130.5 (2C, +), 130.1 (2C, +), 129.6 (2C, +), 126.1 (2C, +), 122.7 (2C), 76.6 (2C, -), 66.2 (2C, +), 33.2 (2C), 21.9 (2C, -); FTIR (KBr, cm^{-1}): 3078, 3063, 2959, 2956, 2359, 2341, 2332, 1724, 1591, 1560, 1477, 1458, 1433, 1410, 1354, 1254, 1163, 1067, 1032, 835, 797, 771, 744, 735, 696, 669, 621; HRMS (TOF ES): Found 454.9825, calculated for $C_{20}H_{18}Br_2O_2Li$ (M+Li) 454.9834 (2.0 ppm).



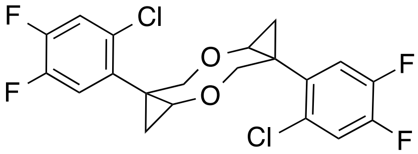
(1*R,4*R**,6*S**,9*S**)-4,9-Bis(4-bromophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4l):** This compound was obtained via typical procedure using (1-(4-bromophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11l**) (59.5 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv), and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 231.3-234.0 °C in 67% yield (30.2 mg, 0.067 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.6 Hz, 4H), 7.14 (d, *J* = 8.6 Hz, 4H), 4.64 (d, *J* = 12.1 Hz, 2H), 3.65 (dd, *J* = 6.5, 3.8 Hz, 2H), 3.59 (d, *J* = 12.2 Hz, 2H), 1.30 – 1.19 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 141.6 (2C), 131.6 (4C, +), 129.2 (4C, +), 120.3 (2C), 76.7 (2C, -), 66.2 (2C, +), 32.9 (2C), 21.8 (2C, -); FTIR (KBr, cm^{-1}): 3086, 3059, 2978, 2922, 2864, 1489, 1456, 1394, 1350, 1259, 1163, 1074, 1063, 1043, 1030, 1009, 978, 843, 818, 754, 714; HRMS (TOF ES): Found 454.9839, calculated for $C_{20}H_{18}Br_2O_2Li$ (M+Li) 454.9834 (1.1 ppm).



(1*R,4*R**,6*S**,9*S**)-4,9-Bis(2,4-dichlorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4m):** This compound was obtained via typical procedure employing (1-(2,4-dichlorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11m**) (57.5 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv) and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 250-252 ^{o}C (with decomposition) in 65% yield (28.1 mg, 0.065 mmol); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 - 7.32 (m, 2H), 7.24 – 7.19 (m, 2H), 4.67 (d, J = 12.1 Hz, 2H), 3.77 (dd, J = 6.9, 3.5 Hz, 2H), 3.70 (d, J = 12.1 Hz, 2H), 1.39 (dd, J = 6.8, 3.5 Hz, 2H), 1.09 (t, J = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 137.28 (2C), 136.44 (2C), 133.75 (2C), 133.53 (2C, +), 129.90 (2C, +), 127.21 (2C, +), 76.62 (2C, -), 64.78 (2C, +), 33.35 (2C), 22.02 (2C, -); FTIR (KBr, cm^{-1}): 3078, 3059, 2972, 2950, 2928, 2872, 1585, 1555, 1474, 1458, 1375, 1356, 1302, 1286, 1263, 1188, 1165, 1103, 1080, 1026, 976, 903, 841, 798, 777, 727, 702; HRMS (TOF ES): Found 426.9818, calculated for $C_{20}H_{15}Cl_4O_2$ (M-H) 426.9826 (1.8 ppm).

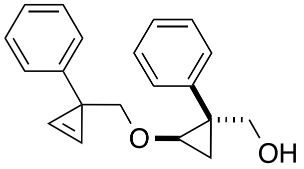


(1*R*,4*R***,6*S***,9*S***)-4,9-Bis(3-(trifluoromethyl)phenyl)-2,7-dioxatricyclo[7.1.0.04,6]decane (4n):** This compound was obtained via typical procedure employing (1-(3-(trifluoromethyl)phenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (57.3 mg, 0.20 mmol, 1.0 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv) and THF (2.20 mL). The titled product was obtained as colorless crystals, mp 137.1-140.4 ^{o}C in 70% yield (30.1 mg, 0.070 mmol); GC (R_t, min): 10.83; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.39 (m, 8H), 4.71 (d, J = 12.2 Hz, 2H), 3.72 (dd, J = 6.6, 3.8 Hz, 2H), 3.66 (d, J = 12.2 Hz, 2H), 1.41 – 1.28 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 155.8 (q, J = 31.2 Hz, 2C), 143.6 (2C), 131.0 (2C, +), 129.0 (2C, +), 124.3 (q, J = 272.4 Hz, 2C), 124.1 (q, J = 3.9 Hz, 2C, +), 123.3 (q, J = 3.8 Hz, 2C, +), 76.6 (2C, -), 66.3 (2C, +), 33.3 (2C), 21.9 (2C, -); FTIR (KBr, cm^{-1}): 3084, 3045, 2980, 2959, 2924, 2872, 2359, 1612, 1593, 1489, 1462, 1445, 1358, 1335, 1296, 1263, 1163, 1119, 1074, 1049, 1038, 978, 841, 798, 735, 700, 662; HRMS (TOF ES): Found 428.1211, calculated for $C_{22}H_{18}F_6O_2$ (M^+) 428.1211 (0.0 ppm).



(1*R*,4*R***,6*S***,9*S***)-4,9-Bis(2-chloro-4,5-difluorophenyl)-2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (4o):** This compound was obtained via typical procedure using (1-(2-chloro-4,5-difluorophenyl)-2-(trimethylsilyl)cycloprop-2-en-1-yl)methanol (**11o**) (57.8 mg, 0.20 mmol, 1.00 equiv), 18-crown-6 ether (12.0 mg, 0.045 mmol, 0.225 equiv), potassium hydroxide (61.7 mg, 1.10 mmol, 5.50 equiv) and THF (2.20 mL). The titled product was obtained as a pale yellow solid, mp 239-242 ^{o}C (with decomposition) in 32% yield (13.9 mg, 0.032 mmol); GC (R_t, min): 12.57 (main), 12.64 (minor); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 – 7.17 (m, 4H), 4.67 (d, J = 12.2 Hz, 2H), 3.76 (dd, J = 6.9, 3.5 Hz, 2H), 3.65 (d, J = 12.2 Hz, 2H), 1.43 (dd, J = 6.9, 3.5 Hz, 2H), 1.13 (t, J = 6.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 149.4 (dd, J = 251.9, 13.6 Hz, 2C), 148.8 (dd, J = 249.4, 12.6 Hz, 2C) 135.5 – 135.4 (m, 2C), 130.4 (dd, J = 7.9, 3.4 Hz, 2C), 121.1 (d, J = 17.9 Hz, 2C, +), 119.1 (d, J = 20.2 Hz, 2C, +), 76.6 (2C, -) 64.8 (2C, +), 33.5 (2C), 22.2 (2C, -); FTIR (KBr, cm^{-1}): 3065, 3051, 2972, 2959, 2926, 2870, 1736, 1599, 1495, 1460, 1410, 1315, 1267, 1244, 1180, 1148, 1121, 1078, 1059, 1040, 993, 922, 879, 839, 800, 739, 650, 625; HRMS (TOF ES): Found 439.0471, calculated for $C_{20}H_{14}Cl_2F_4O_2Li$ (M+Li) 439.0467 (0.9 ppm).

8. Isolation of linear dimer intermediate 14



((1*R,2*R**)-1-Phenyl-2-((1-phenylcycloprop-2-en-1-yl)methoxy)-cyclopropyl)methanol (14):** An oven dried Wheaton vial (5 mL) equipped with spin vane and Mininert valve was charged with (1-phenylcycloprop-2-en-1-yl)methanol (50.0 mg, 0.342 mmol, 1.00 equiv.), 18-crown-6 ether (20.0 mg, 0.076 mmol, 0.225 equiv.), powdered potassium hydroxide (48.0 mg, 0.855 mmol, 2.50 equiv) and THF (4.0 mL). The mixture was stirred for approximately one hour at 45ºC closely monitored by TLC. Retention factors of starting alcohol **3a**, intermediate **14**, and cyclic product **4a** are 0.19, 0.31, and 0.59, respectively (eluent - hexane:EtOAc 3:1). When maximum concentration of the spot with R_f 0.31 (hexane:EtOAc 3:1) was observed, anhydrous magnesium sulfate was immediately added to the reaction mixture, which was then filtered, and concentrated. The intermediate **14** was isolated by preparative column chromatography eluting with a mixture of hexane and ethyl acetate (3:1) to afford a pale yellow oil in 9% yield (9.0 mg, 0.031 mmol); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 – 7.10 (m, 12H), 4.02 (d, *J* = 10.3 Hz, 1H), 3.97 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 11.6 Hz, 1H), 3.76 (d, *J* = 11.6 Hz, 1H), 3.51 (dd, *J* = 6.5, 3.6 Hz, 1H), 1.73 (s, 1H), 1.09 (dd, *J* = 6.1, 3.6 Hz, 1H), 1.01 (t, *J* = 6.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 129.0, 128.8 (2C, +), 128.6 (2C, +), 128.5, 128.1 (2C, +), 126.7 (+), 126.3 (2C, +), 125.8 (+), 112.9 (2C, +), 78.4 (+), 66.2 (-), 63.4 (-), 33.6, 17.2 (-), 11.4; FTIR (KBr, cm^{-1}): 3445, 3099, 3082, 3057, 3024, 2930, 2868, 1645, 1601, 1495, 1447, 1393, 1360, 1161, 1072, 1026, 918, 752, 698, 636, 569, 542; HRMS (TOF ES): Found 291.1384, calculated for $C_{20}H_{19}O_2$ (M-H) 291.1391 (3.0 ppm).

9. X-ray crystallography of tricyclic product 4g

Table 3. Crystal data and structure refinement for 4g.

Identification code	q32c	
Empirical formula	$C_{22}H_{24}O_2$	
Formula weight	320.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 19.9651(7) Å	α= 90°.
	b = 6.1398(2) Å	β= 116.9270(10)°.
	c = 15.2881(6) Å	γ = 90°.
Volume	1670.87(10) $Å^3$	
Z	4	
Density (calculated)	1.274 g/cm^3	
Absorption coefficient	0.623 mm^{-1}	
F(000)	688	
Crystal size	0.30 x 0.08 x 0.04 mm^3	
Theta range for data collection	4.97 to 69.35°.	
Index ranges	-22<=h<=23, -7<=k<=6, -18<=l<=16	
Reflections collected	7532	
Independent reflections	1507 [R(int) = 0.0163]	
Completeness to theta = 66.00°	98.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.873	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1507 / 0 / 157	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0941	
R indices (all data)	R1 = 0.0349, wR2 = 0.0944	
Largest diff. peak and hole	0.274 and -0.186 e.$Å^{-3}$	

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for 4g. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O	4600(1)	-2172(1)	5110(1)	16(1)
C(1)	4414(1)	-1542(2)	4114(1)	16(1)
C(2)	4079(1)	713(2)	3894(1)	15(1)
C(3)	4630(1)	2599(2)	4321(1)	16(1)
C(4)	4316(1)	2121(2)	3255(1)	19(1)
C(5)	3307(1)	1001(2)	3818(1)	15(1)
C(6)	2910(1)	2956(2)	3487(1)	18(1)
C(7)	2204(1)	3230(2)	3443(1)	19(1)
C(8)	1861(1)	1569(2)	3715(1)	19(1)
C(9)	2253(1)	-382(2)	4038(1)	19(1)
C(10)	2963(1)	-662(2)	4093(1)	17(1)
C(11)	1095(1)	1880(2)	3665(1)	25(1)

Table 5. Bond lengths [Å] and angles [°] for q32c.

O-C(3)#1	1.4053(13)	C(3)#1-O-C(1)	112.89(8)
O-C(1)	1.4477(13)	O-C(1)-C(2)	110.89(9)
C(1)-C(2)	1.5076(15)	O-C(1)-H(1A)	108.4(8)
C(1)-H(1A)	0.991(13)	C(2)-C(1)-H(1A)	110.9(7)
C(1)-H(1B)	0.977(14)	O-C(1)-H(1B)	109.4(7)
C(2)-C(5)	1.5020(14)	C(2)-C(1)-H(1B)	110.7(8)
C(2)-C(3)	1.5258(15)	H(1A)-C(1)-H(1B)	106.4(11)
C(2)-C(4)	1.5325(15)	C(5)-C(2)-C(1)	117.50(9)
C(3)-O#1	1.4053(13)	C(5)-C(2)-C(3)	117.38(9)
C(3)-C(4)	1.4866(15)	C(1)-C(2)-C(3)	116.12(9)
C(3)-H(3)	0.965(15)	C(5)-C(2)-C(4)	119.12(9)
C(4)-H(4A)	0.974(15)	C(1)-C(2)-C(4)	115.20(9)
C(4)-H(4B)	0.946(15)	C(3)-C(2)-C(4)	58.17(7)
C(5)-C(10)	1.3978(16)	O#1-C(3)-C(4)	116.16(10)
C(5)-C(6)	1.4004(16)	O#1-C(3)-C(2)	119.86(9)
C(6)-C(7)	1.3907(16)	C(4)-C(3)-C(2)	61.14(7)
C(6)-H(6)	0.964(15)	O#1-C(3)-H(3)	114.8(8)
C(7)-C(8)	1.3922(18)	C(4)-C(3)-H(3)	119.1(8)
C(7)-H(7)	0.942(16)	C(2)-C(3)-H(3)	115.5(8)
C(8)-C(9)	1.3930(17)	C(3)-C(4)-C(2)	60.69(7)
C(8)-C(11)	1.5088(15)	C(3)-C(4)-H(4A)	118.6(8)
C(9)-C(10)	1.3928(16)	C(2)-C(4)-H(4A)	118.5(9)
C(9)-H(9)	0.965(15)	C(3)-C(4)-H(4B)	114.7(8)
C(10)-H(10)	0.975(15)	C(2)-C(4)-H(4B)	114.5(8)
C(11)-H(11A)	0.96(2)	H(4A)-C(4)-H(4B)	117.6(12)
C(11)-H(11C)	0.97(2)	C(10)-C(5)-C(2)	121.10(10)
C(11)-H(11B)	0.96(2)	C(10)-C(5)-C(6)	117.41(10)
C(6)-C(5)-C(2)	121.48(10)	C(7)-C(6)-H(6)	118.7(8)
C(7)-C(6)-C(5)	121.10(11)	C(5)-C(6)-H(6)	120.2(8)
C(6)-C(7)-C(8)	121.44(11)	C(9)-C(10)-C(5)	121.11(10)
C(6)-C(7)-H(7)	119.2(9)	C(9)-C(10)-H(10)	119.9(8)
C(8)-C(7)-H(7)	119.4(9)	C(5)-C(10)-H(10)	119.0(8)
C(7)-C(8)-C(9)	117.56(10)	C(8)-C(11)-H(11A)	112.4(12)
C(7)-C(8)-C(11)	121.10(11)	C(8)-C(11)-H(11B)	110.8(12)
C(9)-C(8)-C(11)	121.33(11)	H(11A)-C(11)-H(11B)	106.6(17)
C(10)-C(9)-C(8)	121.37(11)	C(8)-C(11)-H(11C)	111.0(12)
C(10)-C(9)-H(9)	119.1(8)	H(11A)-C(11)-H(11C)	104.5(17)
C(8)-C(9)-H(9)	119.5(8)	H(11B)-C(11)-H(11C)	111.3(17)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1

Table 6. Anisotropic displacement parameters (Å^{2}x 10^3) for 4g. The anisotropic displacement factor exponent takes the form: -2p^2[h^2 a*2U^{11} + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O	12(1)	17(1)	18(1)	3(1)	5(1)	1(1)
C(1)	14(1)	15(1)	17(1)	-1(1)	6(1)	0(1)
C(2)	13(1)	16(1)	15(1)	0(1)	5(1)	0(1)
C(3)	12(1)	14(1)	20(1)	2(1)	5(1)	1(1)
C(4)	15(1)	21(1)	20(1)	4(1)	8(1)	1(1)
C(5)	13(1)	18(1)	13(1)	-2(1)	4(1)	0(1)
C(6)	17(1)	17(1)	18(1)	1(1)	6(1)	0(1)
C(7)	17(1)	20(1)	18(1)	0(1)	4(1)	5(1)
C(8)	14(1)	26(1)	13(1)	-4(1)	4(1)	1(1)
C(9)	16(1)	23(1)	16(1)	0(1)	7(1)	-2(1)
C(10)	16(1)	17(1)	16(1)	0(1)	5(1)	1(1)
C(11)	16(1)	35(1)	22(1)	-2(1)	8(1)	3(1)

Table 7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 4g.

	x	y	z	U(eq)
H(1A)	4058(7)	-2630(20)	3662(10)	14(3)
H(1B)	4864(7)	-1610(20)	4016(9)	16(3)
H(3)	4444(7)	3840(20)	4531(10)	17(3)
H(4A)	3951(8)	3130(20)	2791(10)	22(3)
H(4B)	4656(8)	1440(20)	3067(10)	19(3)
H(6)	3122(8)	4140(20)	3278(10)	21(3)
H(7)	1951(8)	4570(30)	3220(10)	23(3)
H(9)	2028(8)	-1570(20)	4227(10)	21(3)
H(10)	3228(8)	-2040(20)	4327(10)	21(3)
H(11A)	956(11)	690(40)	3960(15)	61(6)
H(11B)	714(12)	1970(30)	2994(15)	58(6)
H(11C)	1086(12)	3150(40)	4037(16)	64(6)

Table 8. Torsion angles [°] for 4g.

C(3)#1-O-C(1)-C(2)	-119.27(9)
O-C(1)-C(2)-C(5)	-69.90(11)
O-C(1)-C(2)-C(3)	76.48(11)
O-C(1)-C(2)-C(4)	141.74(9)
C(5)-C(2)-C(3)-O#1	145.81(10)
C(1)-C(2)-C(3)-O#1	-0.62(14)
C(4)-C(2)-C(3)-O#1	-105.32(11)
C(5)-C(2)-C(3)-C(4)	-108.87(11)
C(1)-C(2)-C(3)-C(4)	104.70(11)
O#1-C(3)-C(4)-C(2)	111.26(11)
C(5)-C(2)-C(4)-C(3)	105.89(11)
C(1)-C(2)-C(4)-C(3)	-106.29(10)
C(1)-C(2)-C(5)-C(10)	10.09(15)
C(3)-C(2)-C(5)-C(10)	-135.87(11)
C(4)-C(2)-C(5)-C(10)	157.18(10)
C(1)-C(2)-C(5)-C(6)	-171.26(10)
C(3)-C(2)-C(5)-C(6)	42.79(14)
C(4)-C(2)-C(5)-C(6)	-24.17(15)
C(10)-C(5)-C(6)-C(7)	0.39(16)
C(2)-C(5)-C(6)-C(7)	-178.31(10)
C(5)-C(6)-C(7)-C(8)	-0.61(17)
C(6)-C(7)-C(8)-C(9)	0.20(17)
C(6)-C(7)-C(8)-C(11)	179.94(10)
C(7)-C(8)-C(9)-C(10)	0.41(16)
C(11)-C(8)-C(9)-C(10)	-179.32(10)
C(8)-C(9)-C(10)-C(5)	-0.63(17)
C(6)-C(5)-C(10)-C(9)	0.22(16)
C(2)-C(5)-C(10)-C(9)	178.92(9)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z+1

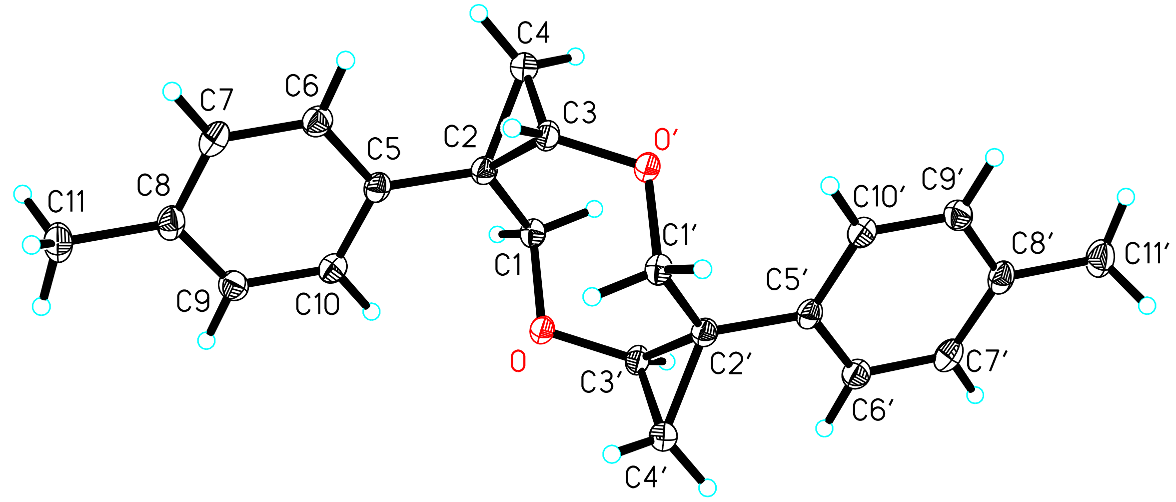


Figure 1. ORTEP drawing of 2,7-dioxatricyclo[7.1.0.0^{4,6}]decane (**4g**) showing 50% probability amplitude displacement ellipsoids and atom numbering scheme

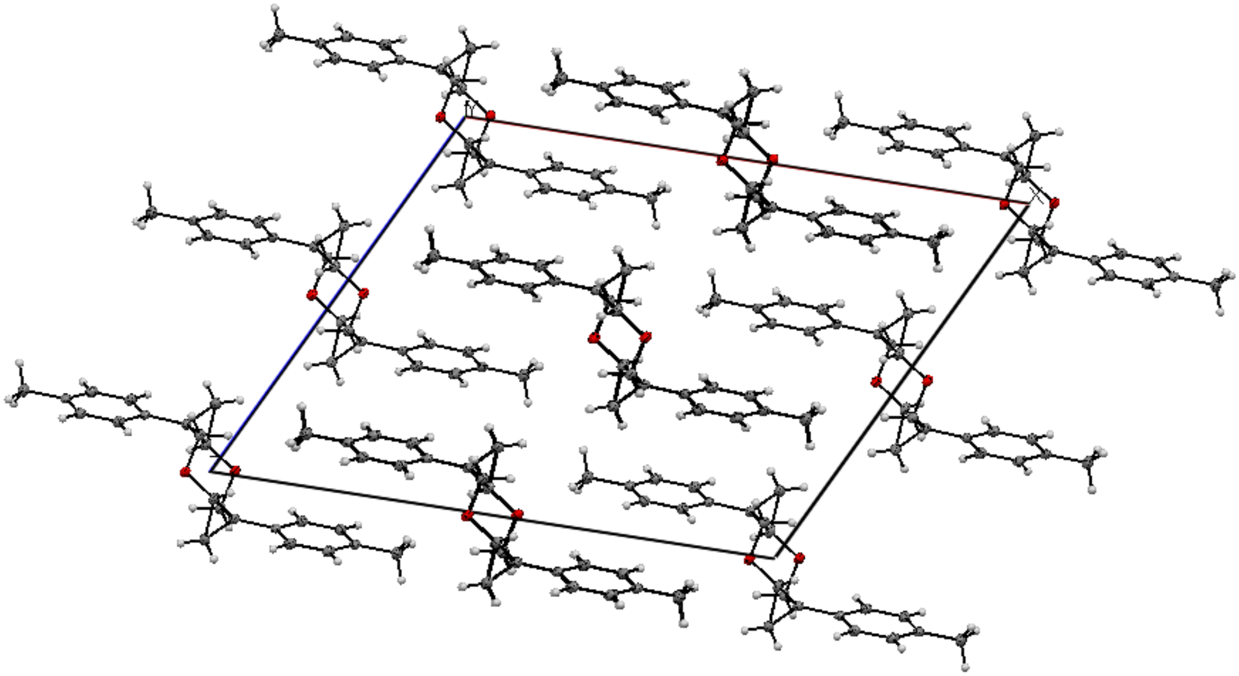
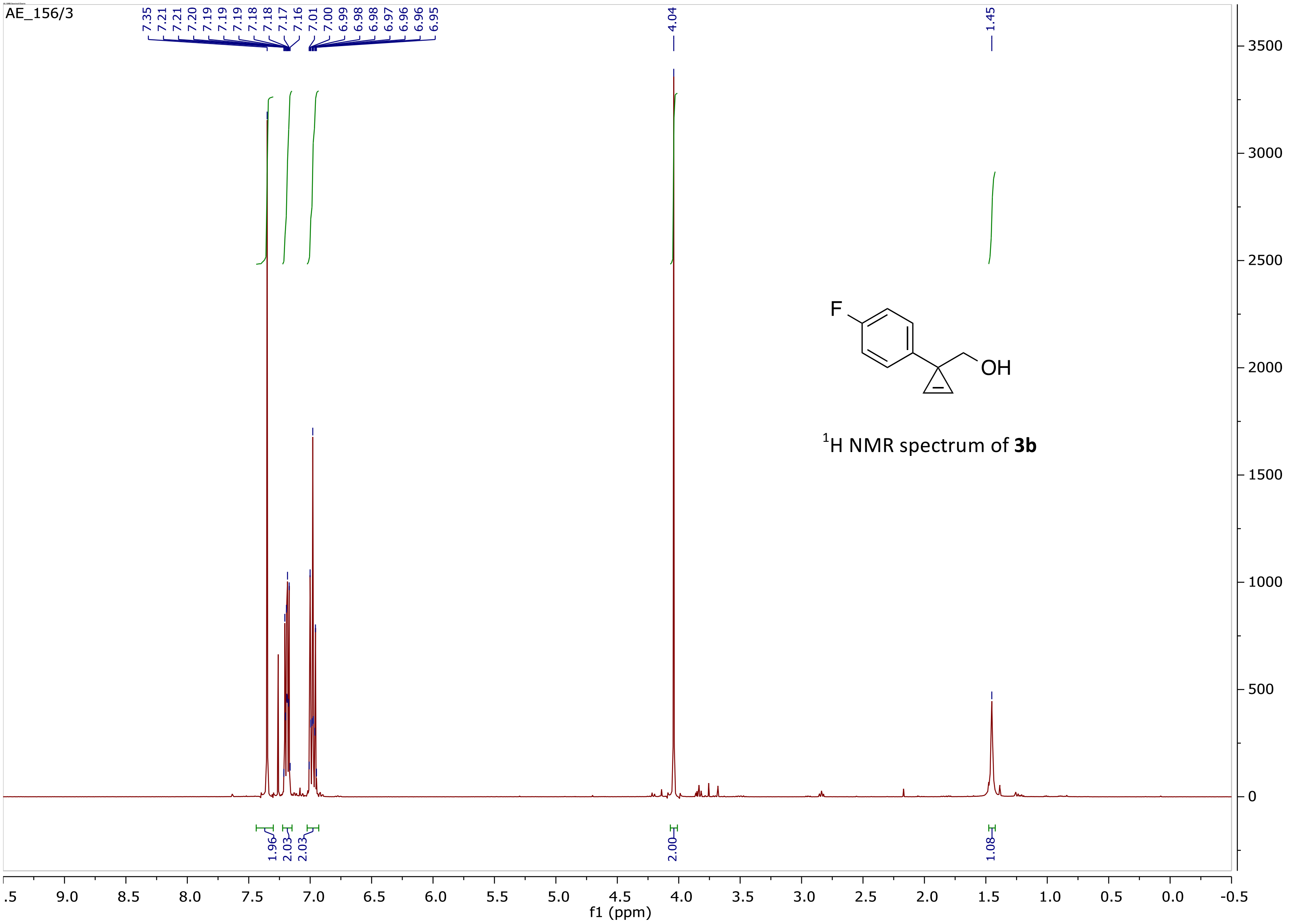
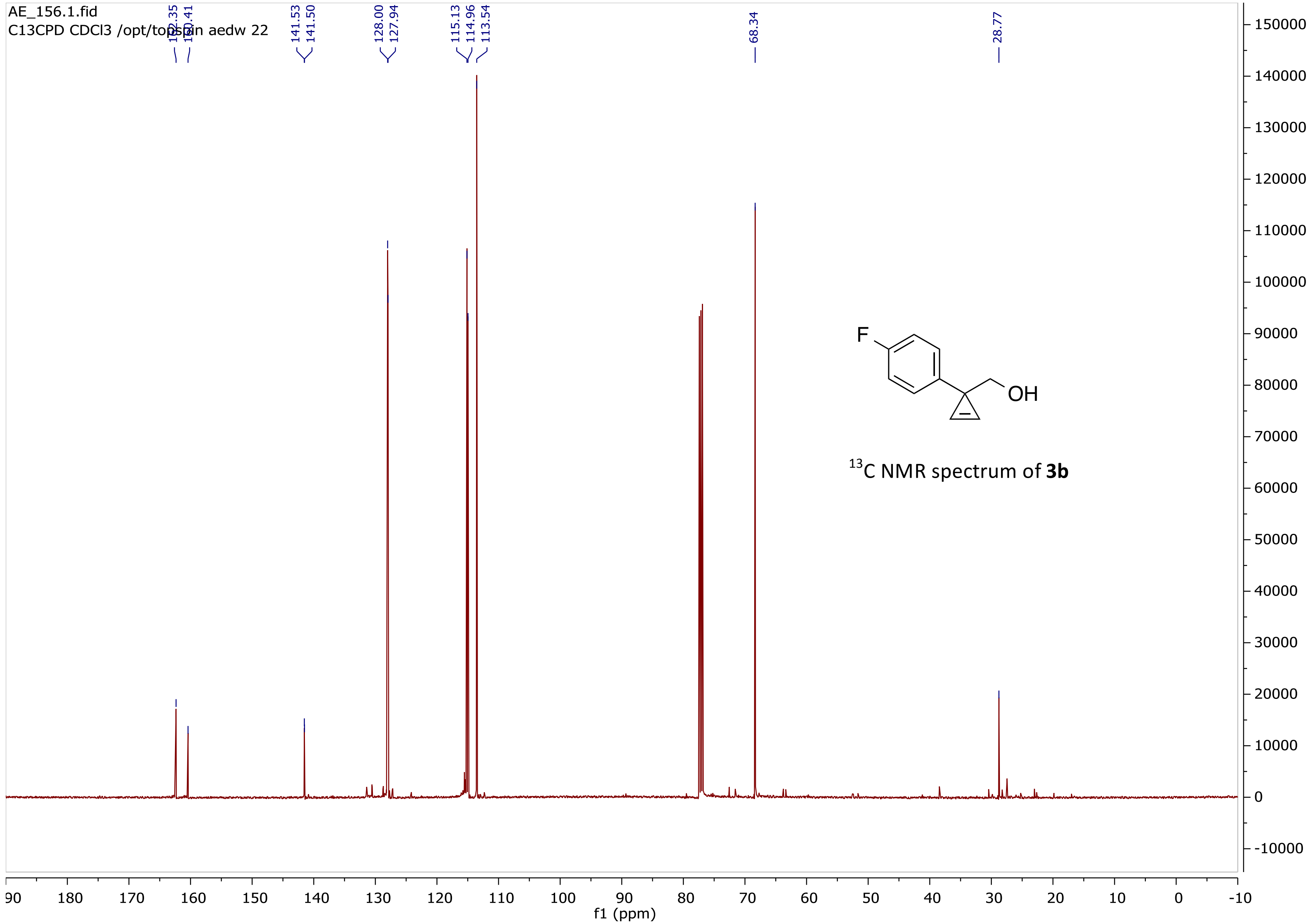


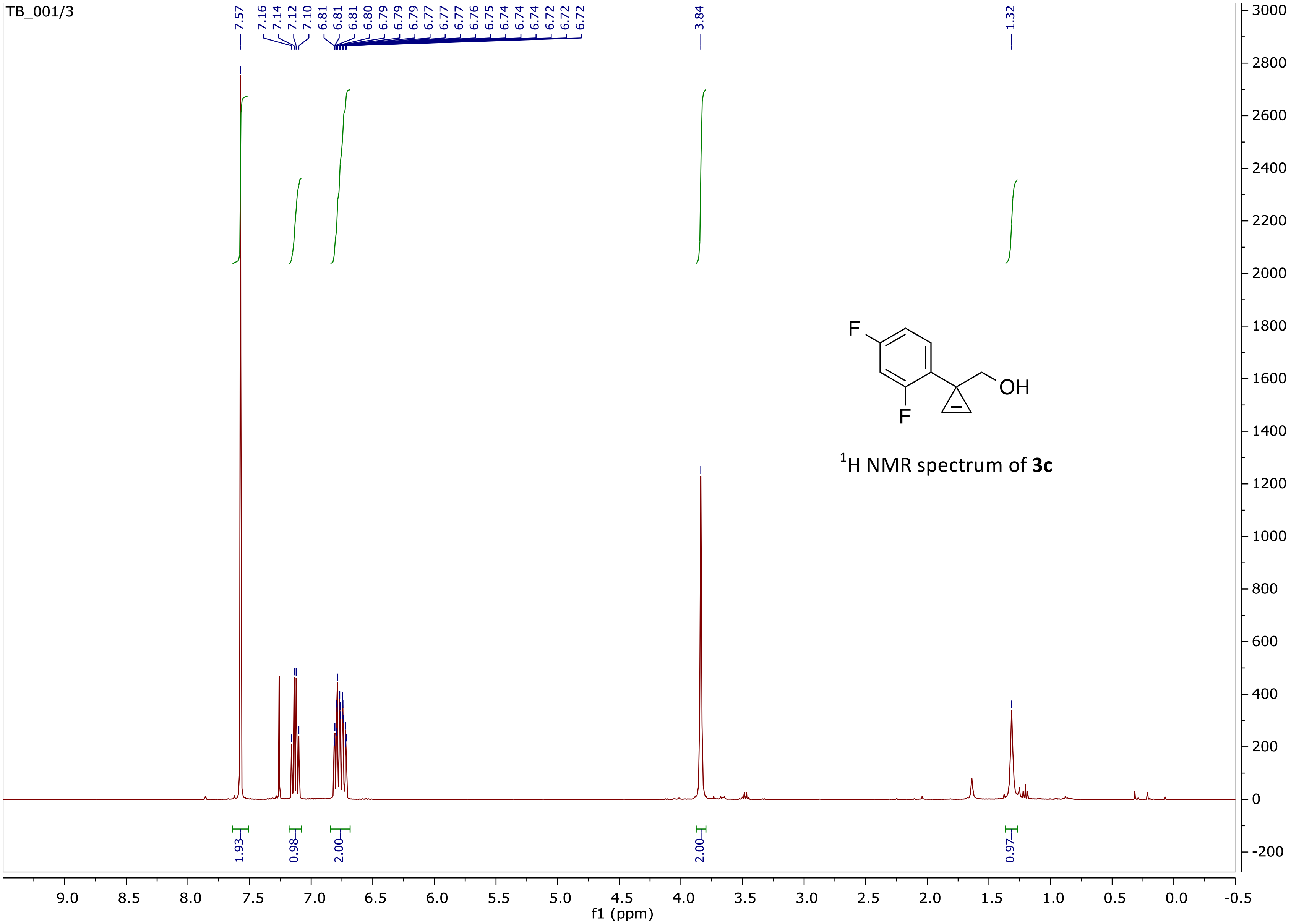
Figure 2. Packing of **4g** molecules in the crystalline lattice cell



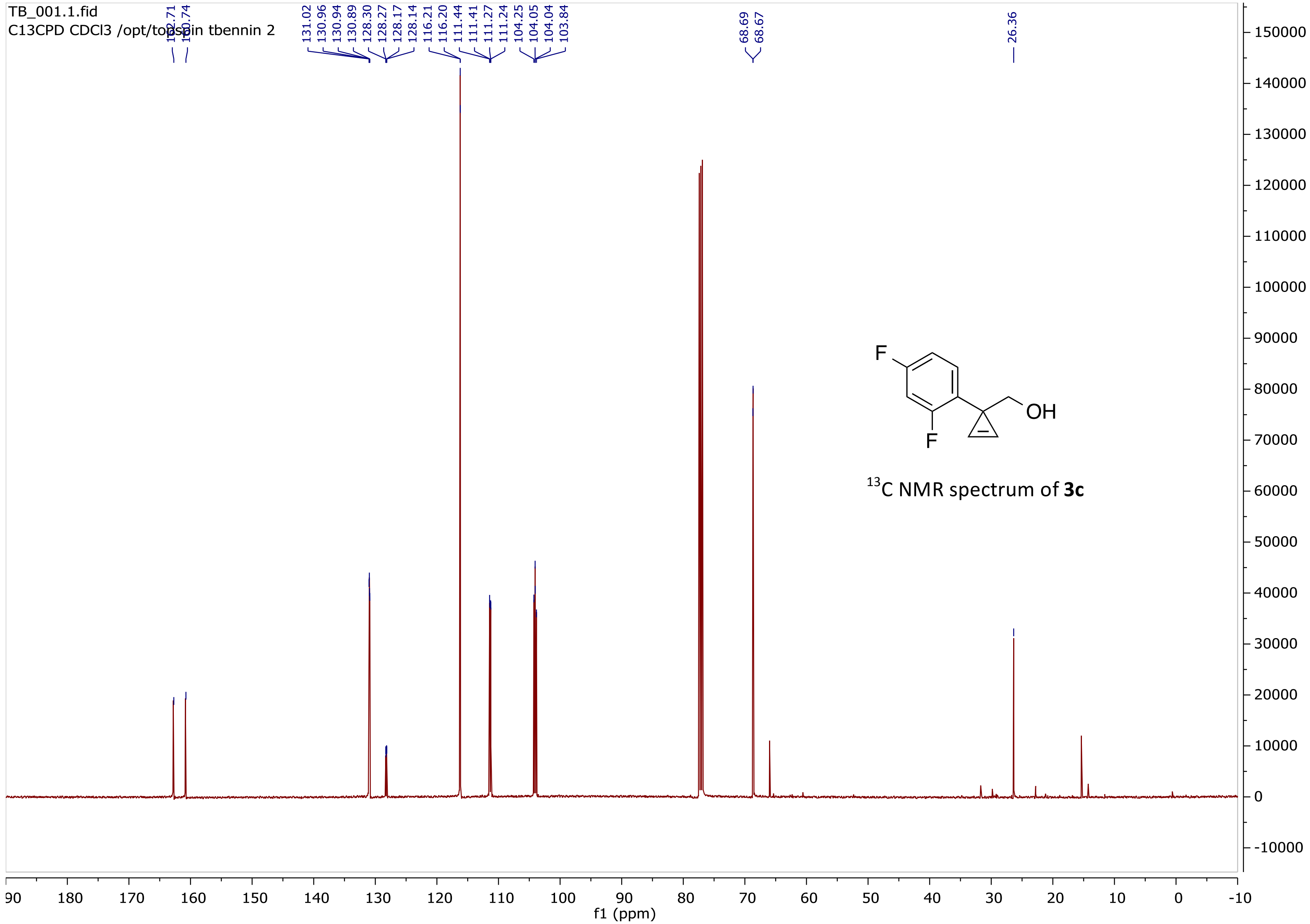
^{1}H NMR spectrum of **3b**



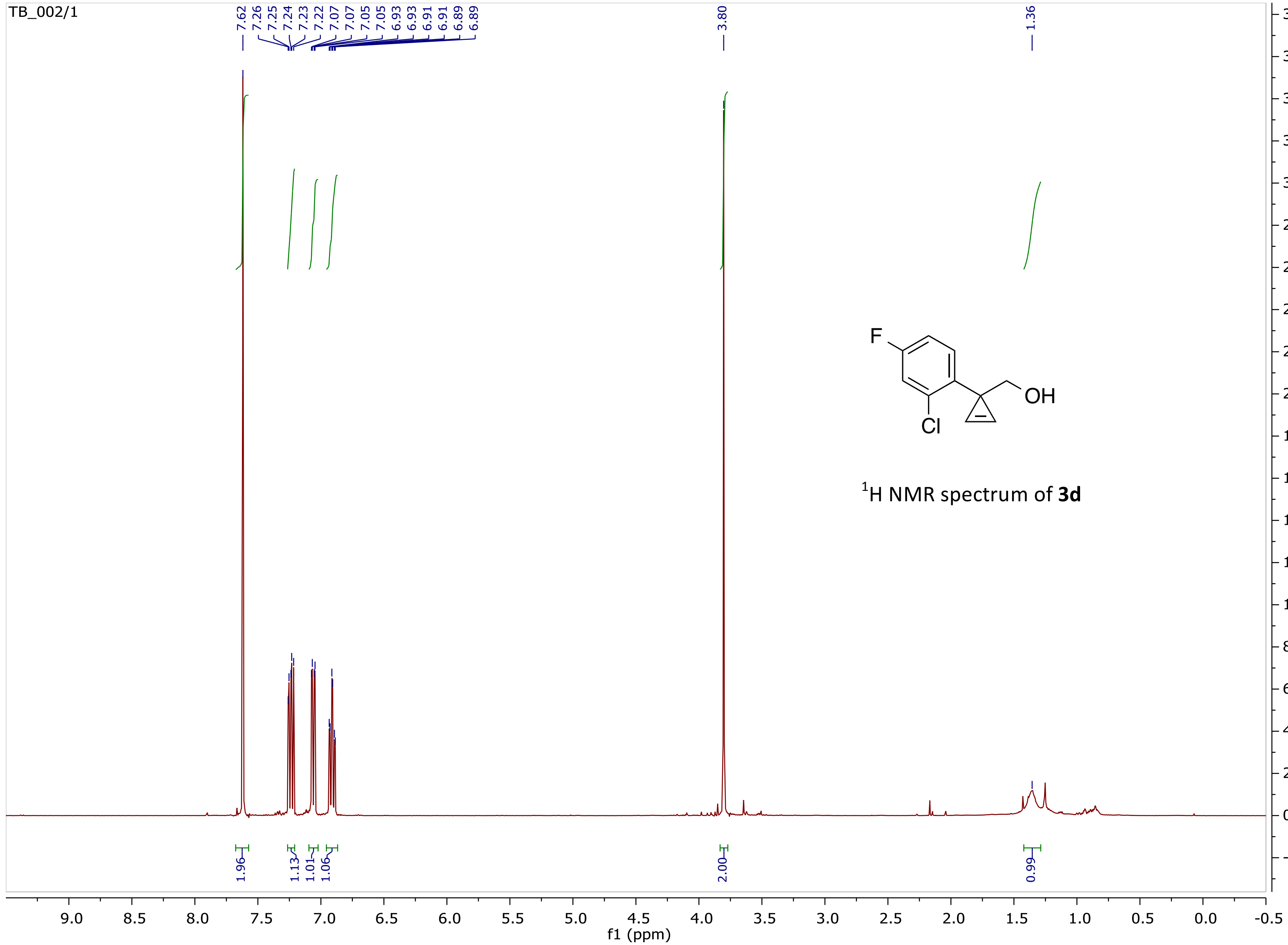
^{13}C NMR spectrum of **3b**



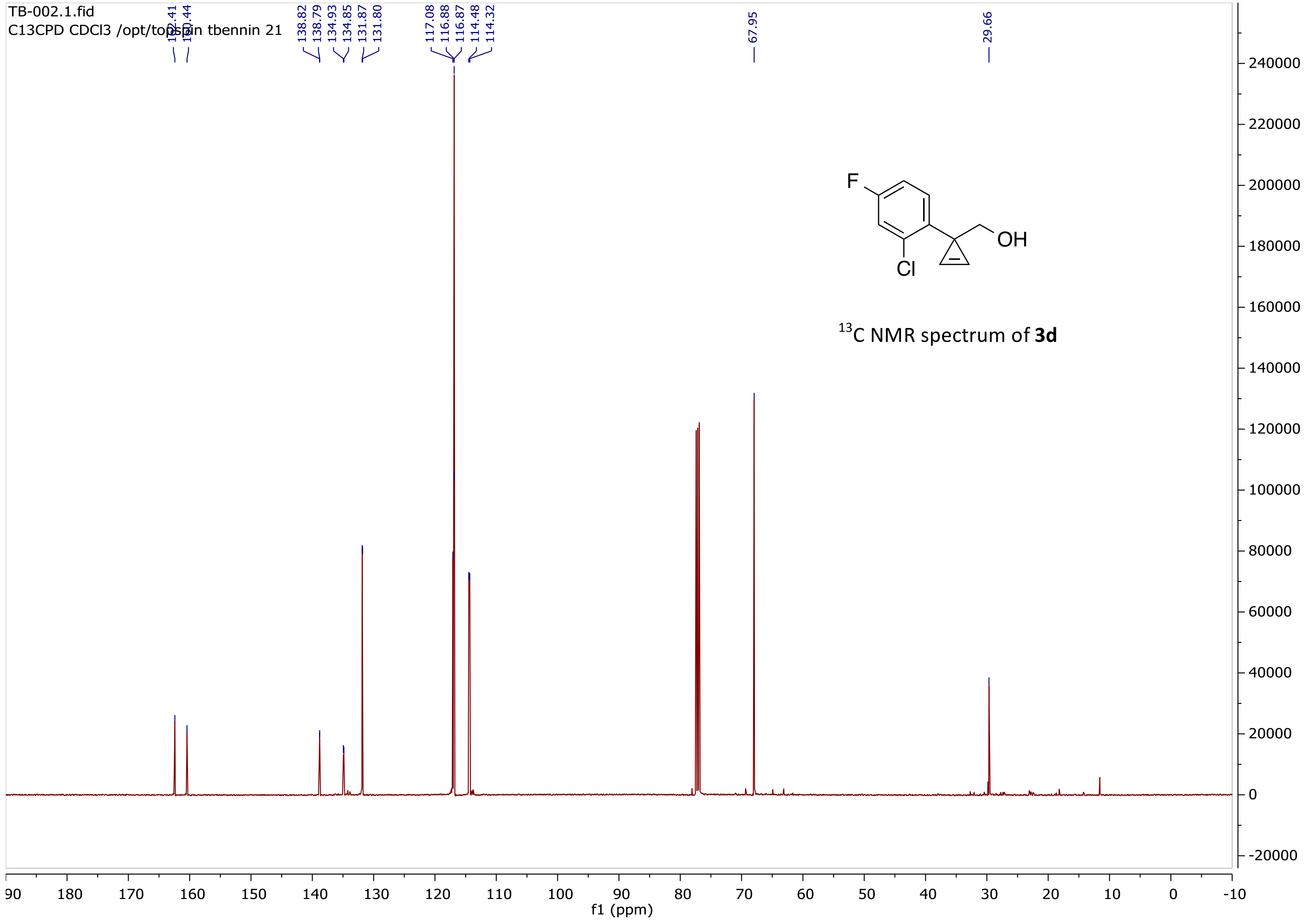
^{1}H NMR spectrum of **3c**



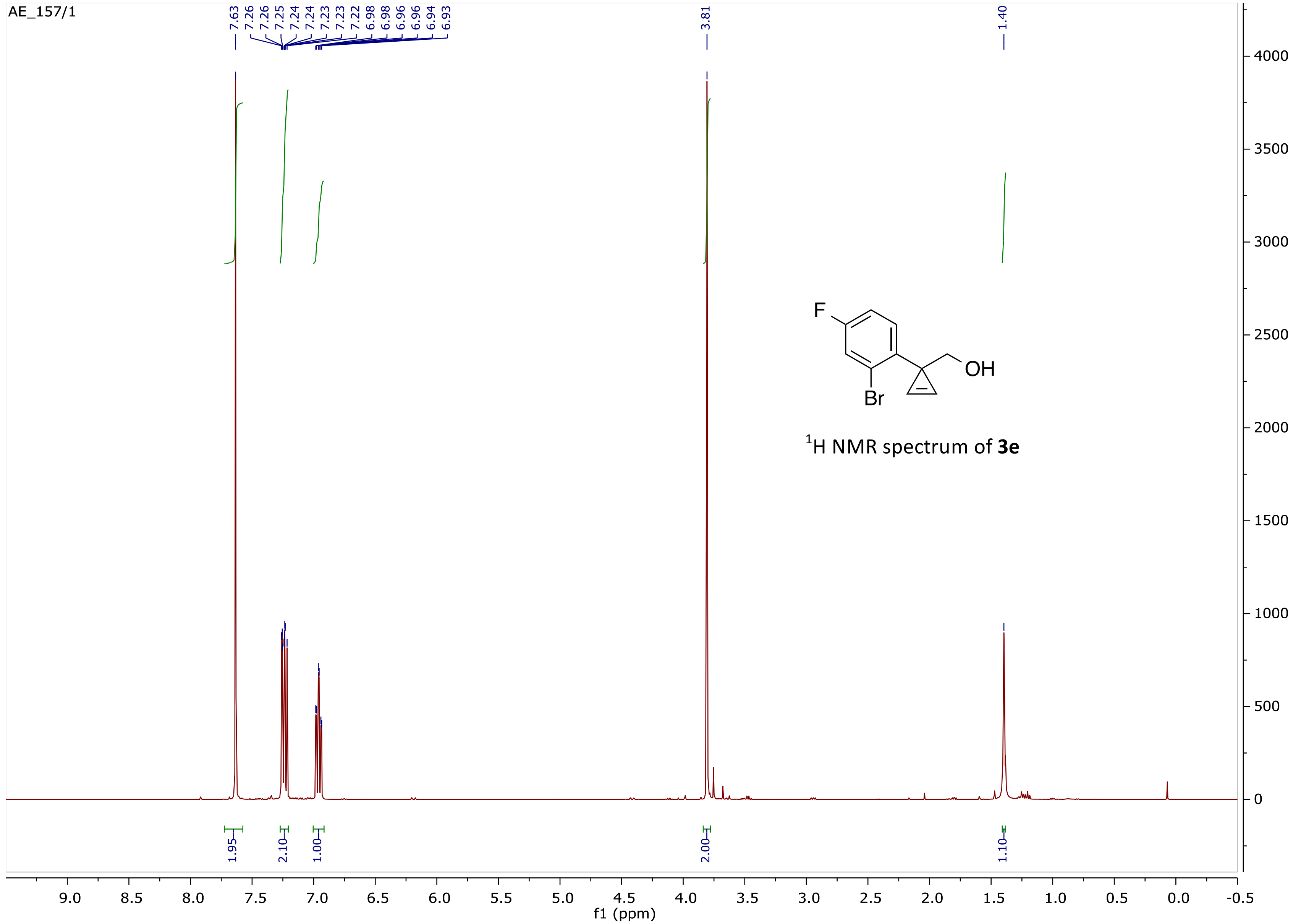
^{13}C NMR spectrum of **3c**



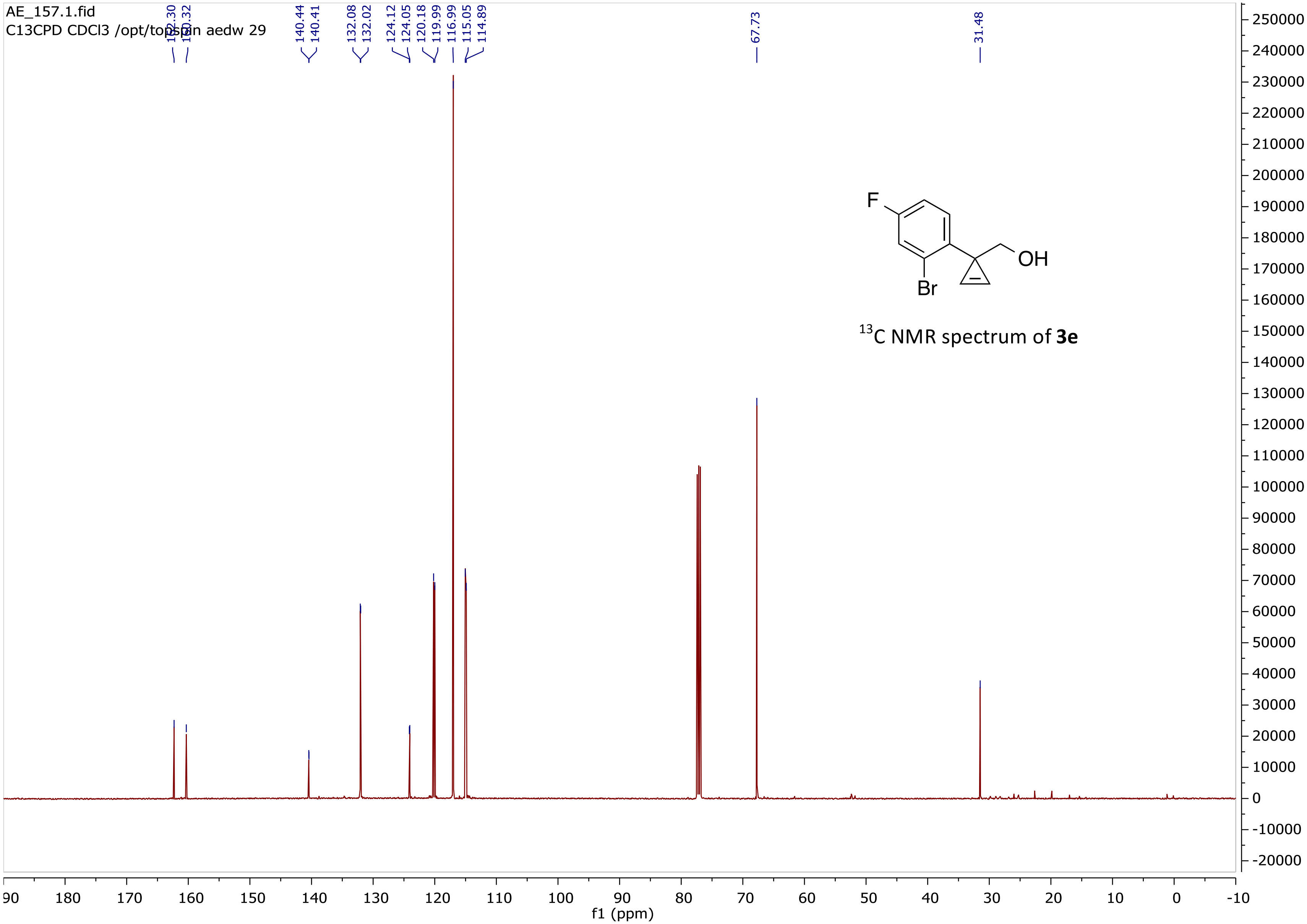
^{1}H NMR spectrum of **3d**



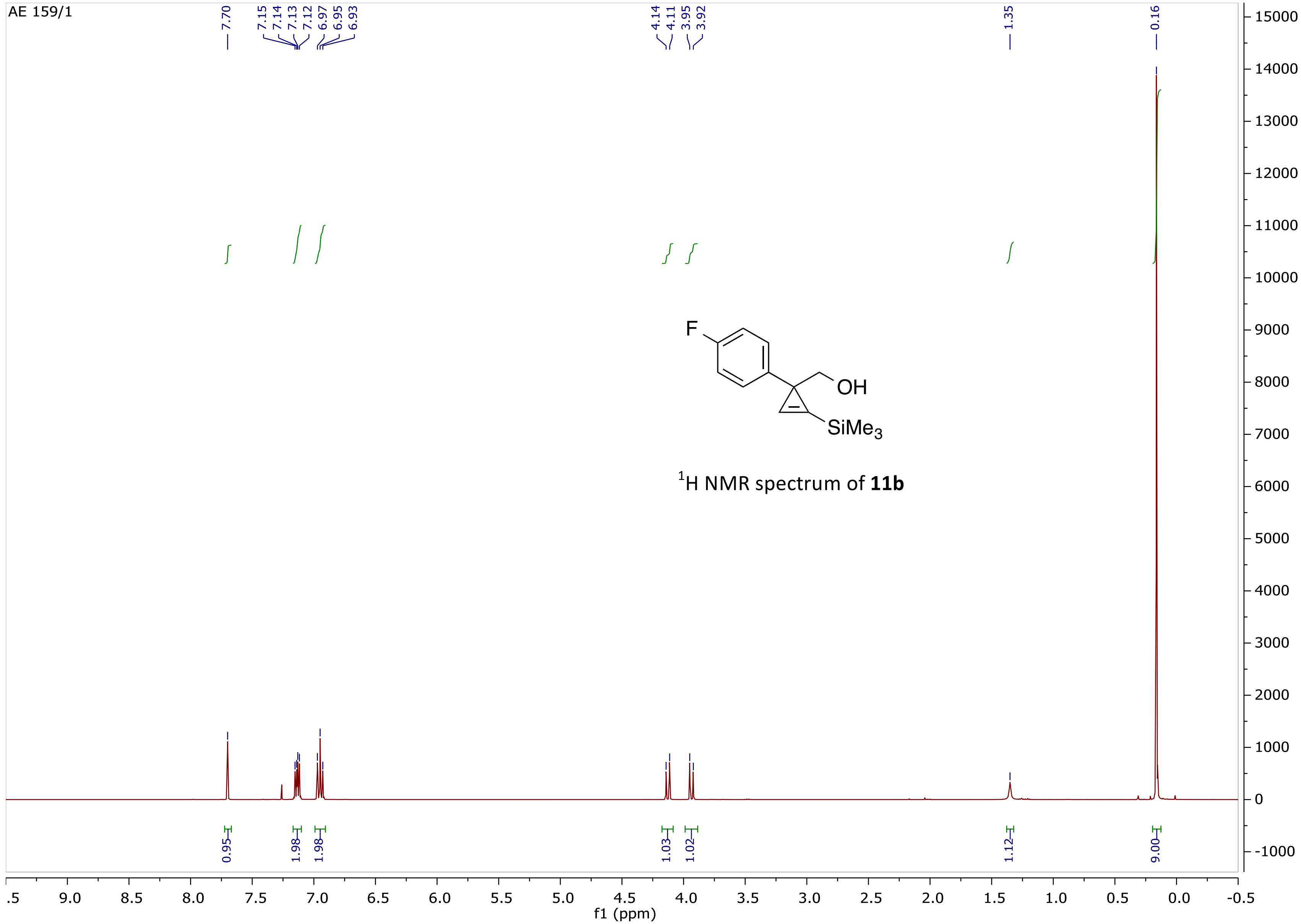
^{13}C NMR spectrum of **3d**



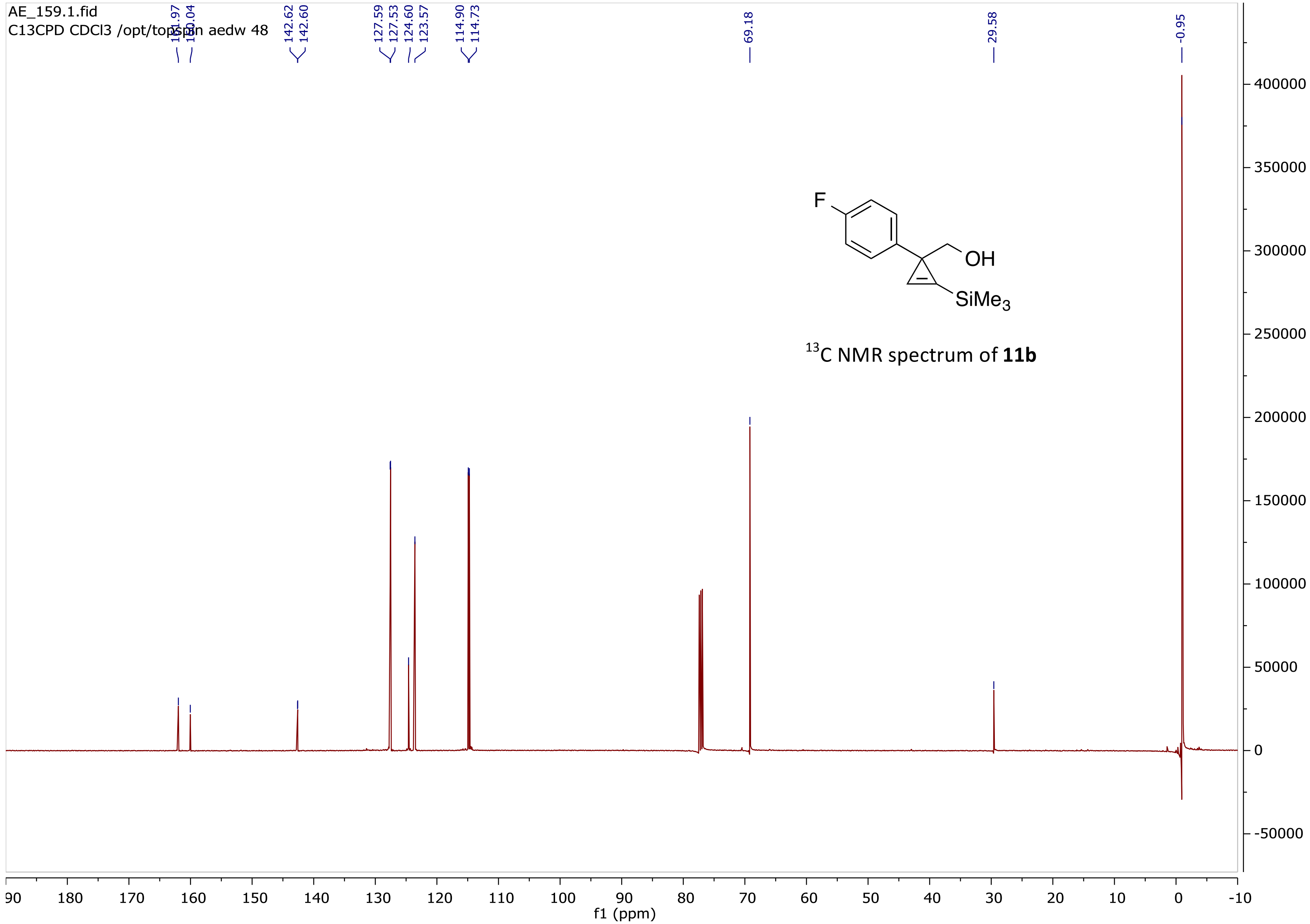
^{1}H NMR spectrum of **3e**



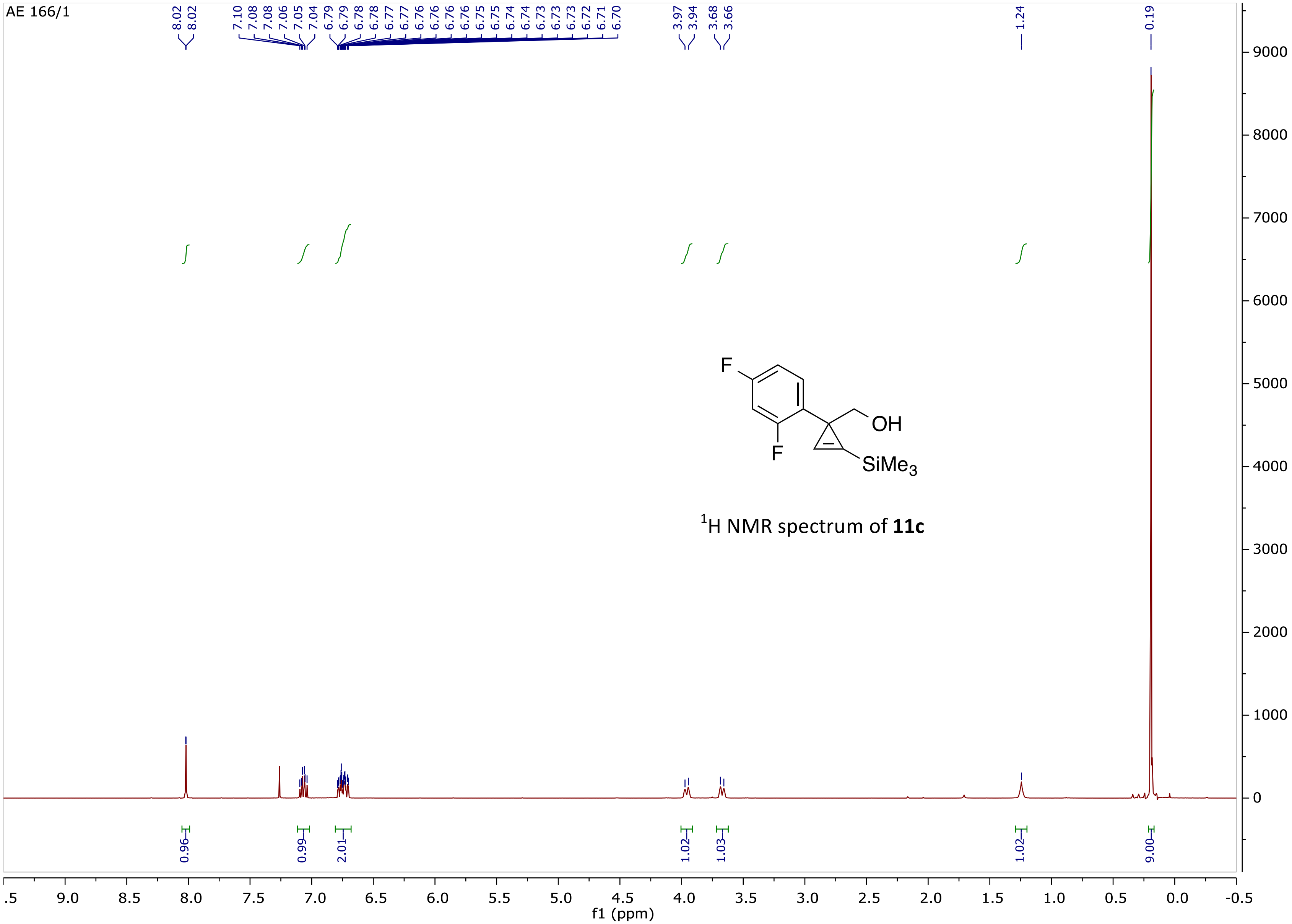
^{13}C NMR spectrum of **3e**



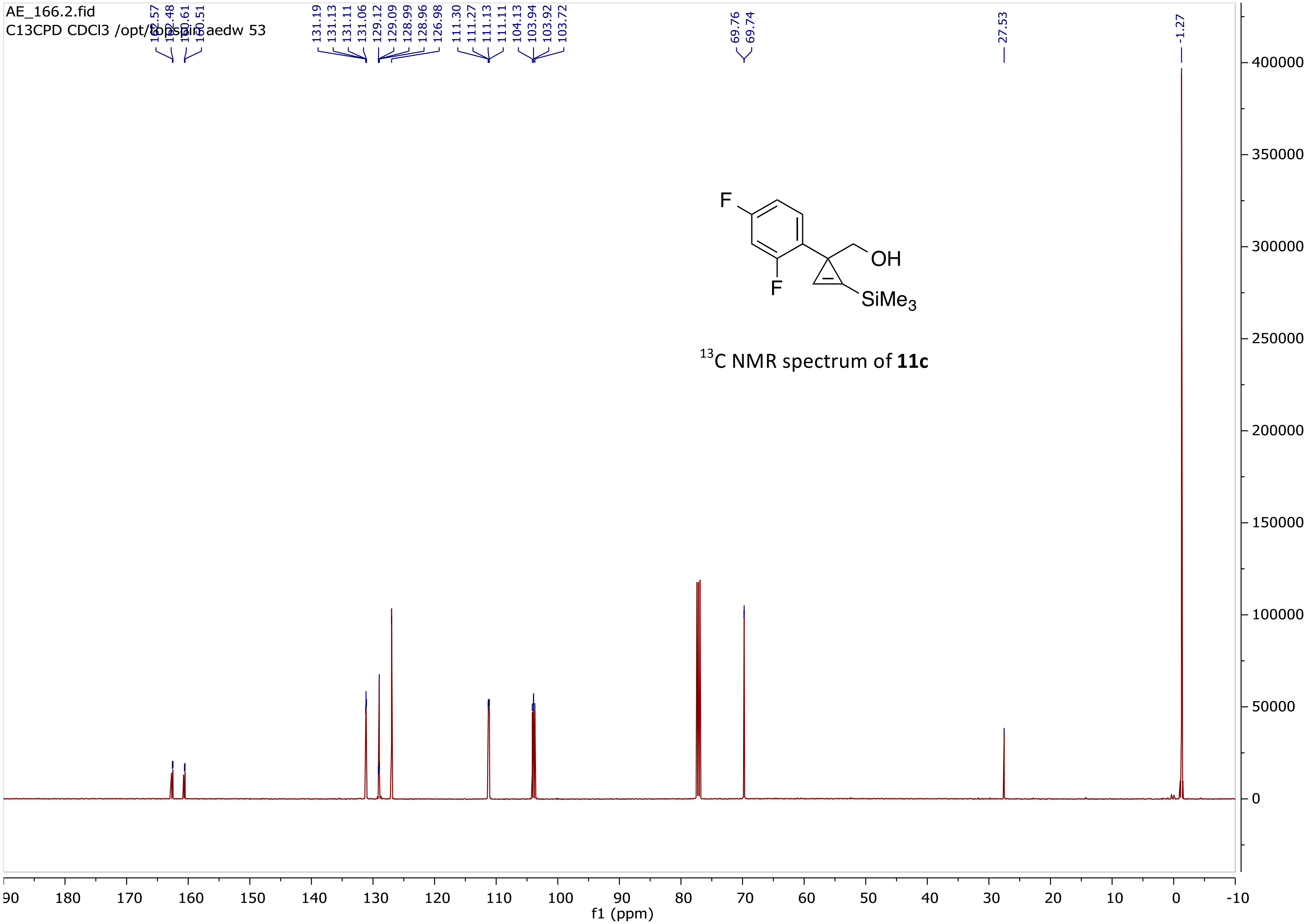
^{1}H NMR spectrum of **11b**



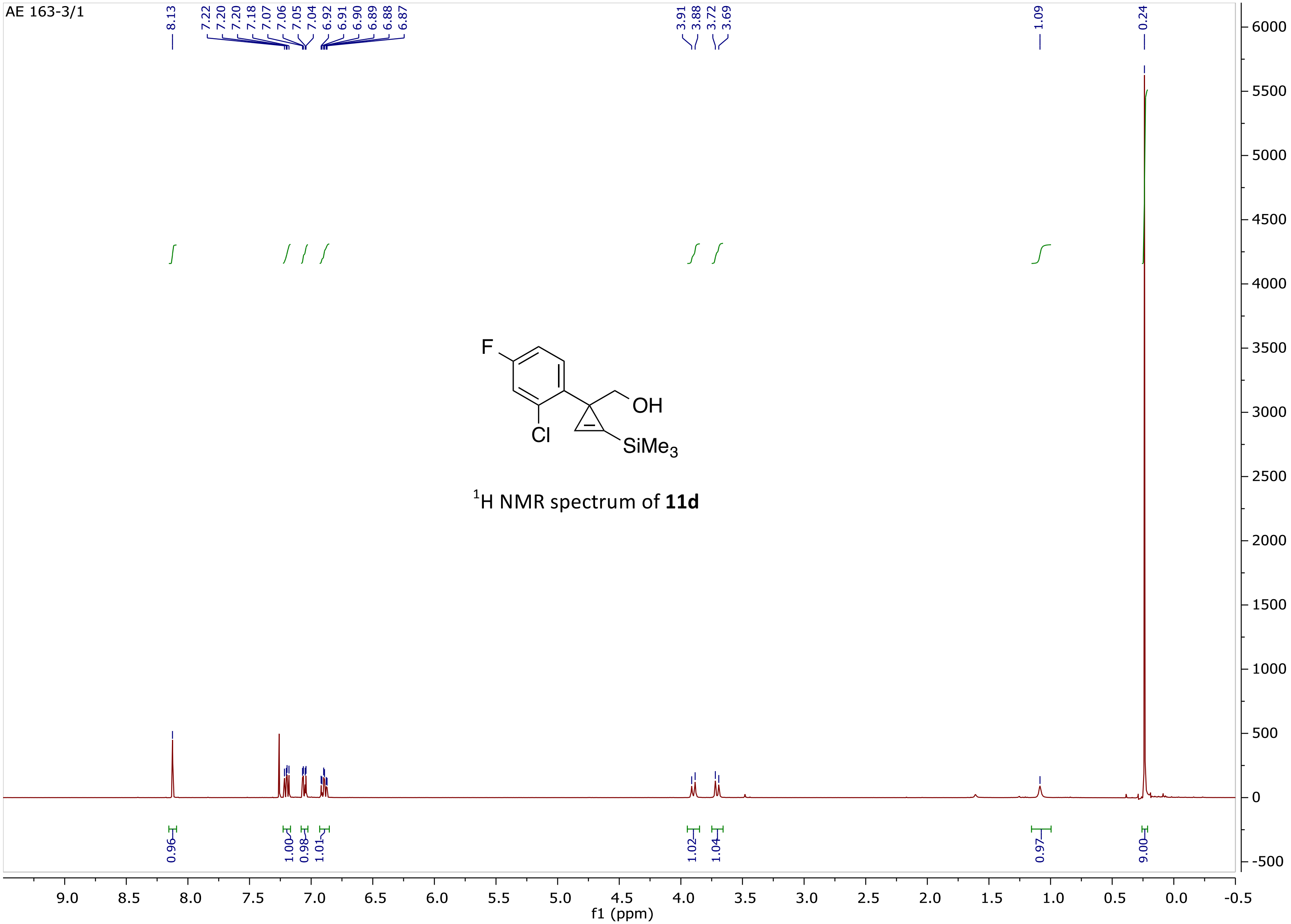
^{13}C NMR spectrum of **11b**



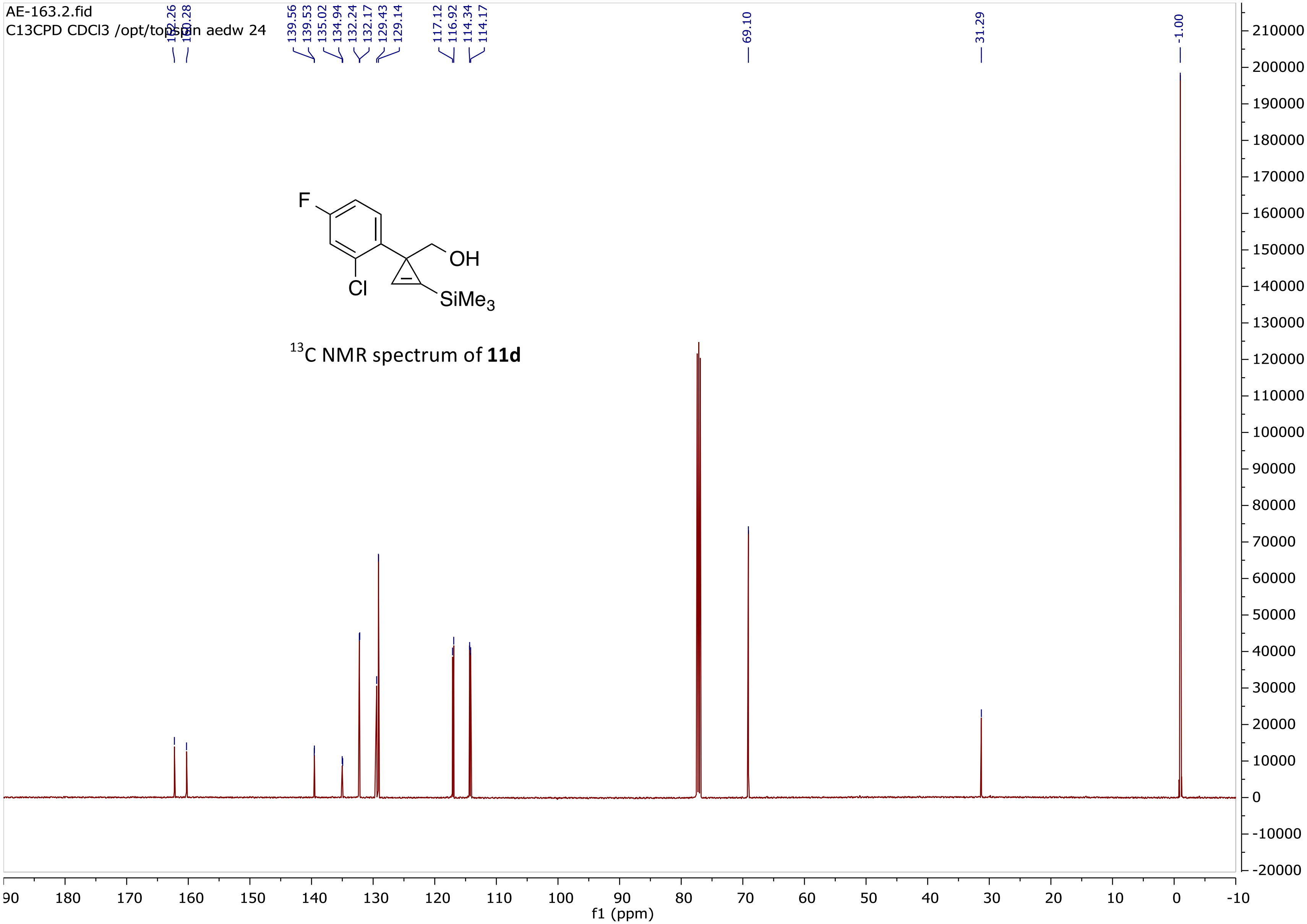
^{1}H NMR spectrum of **11c**



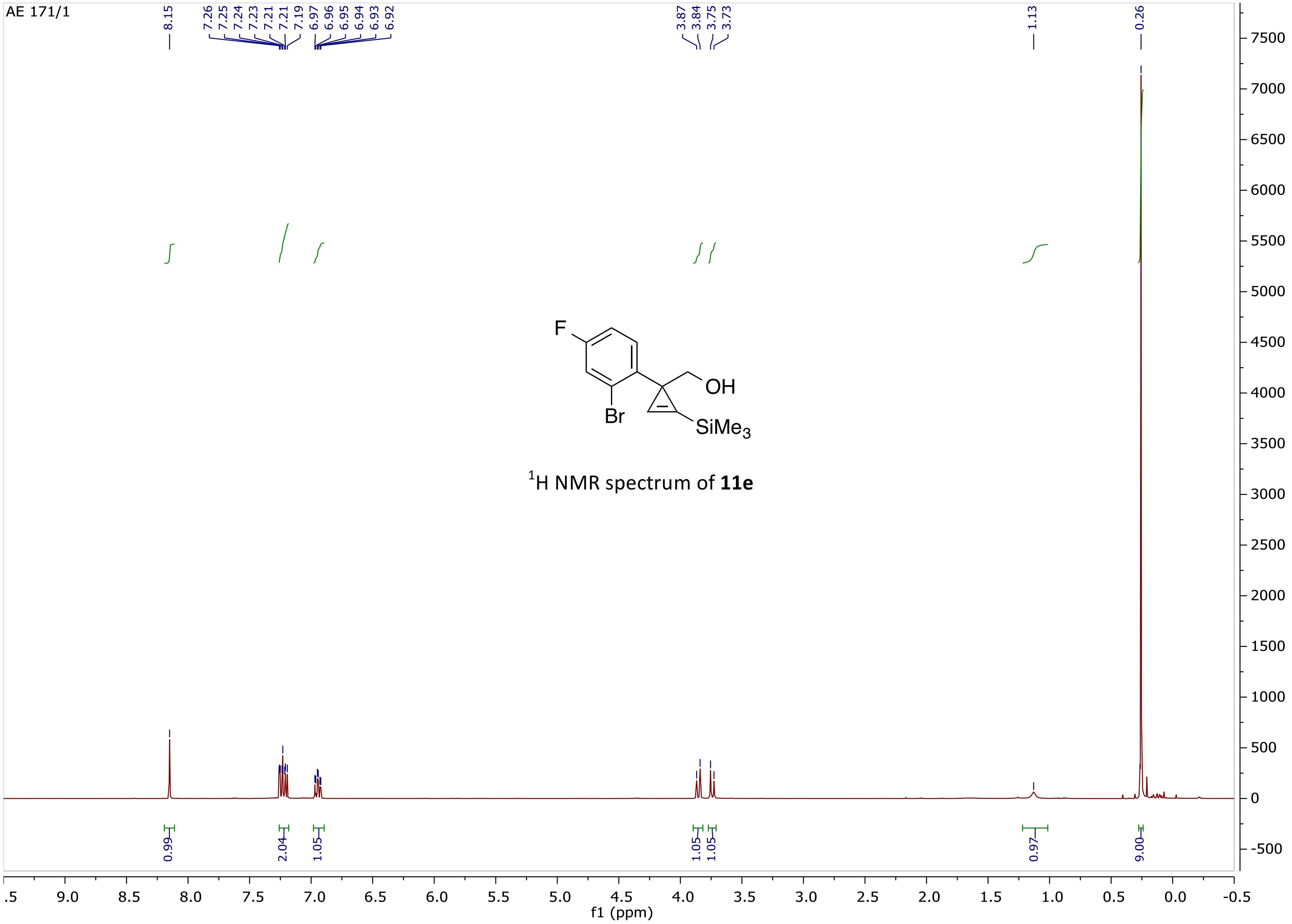
^{13}C NMR spectrum of **11c**



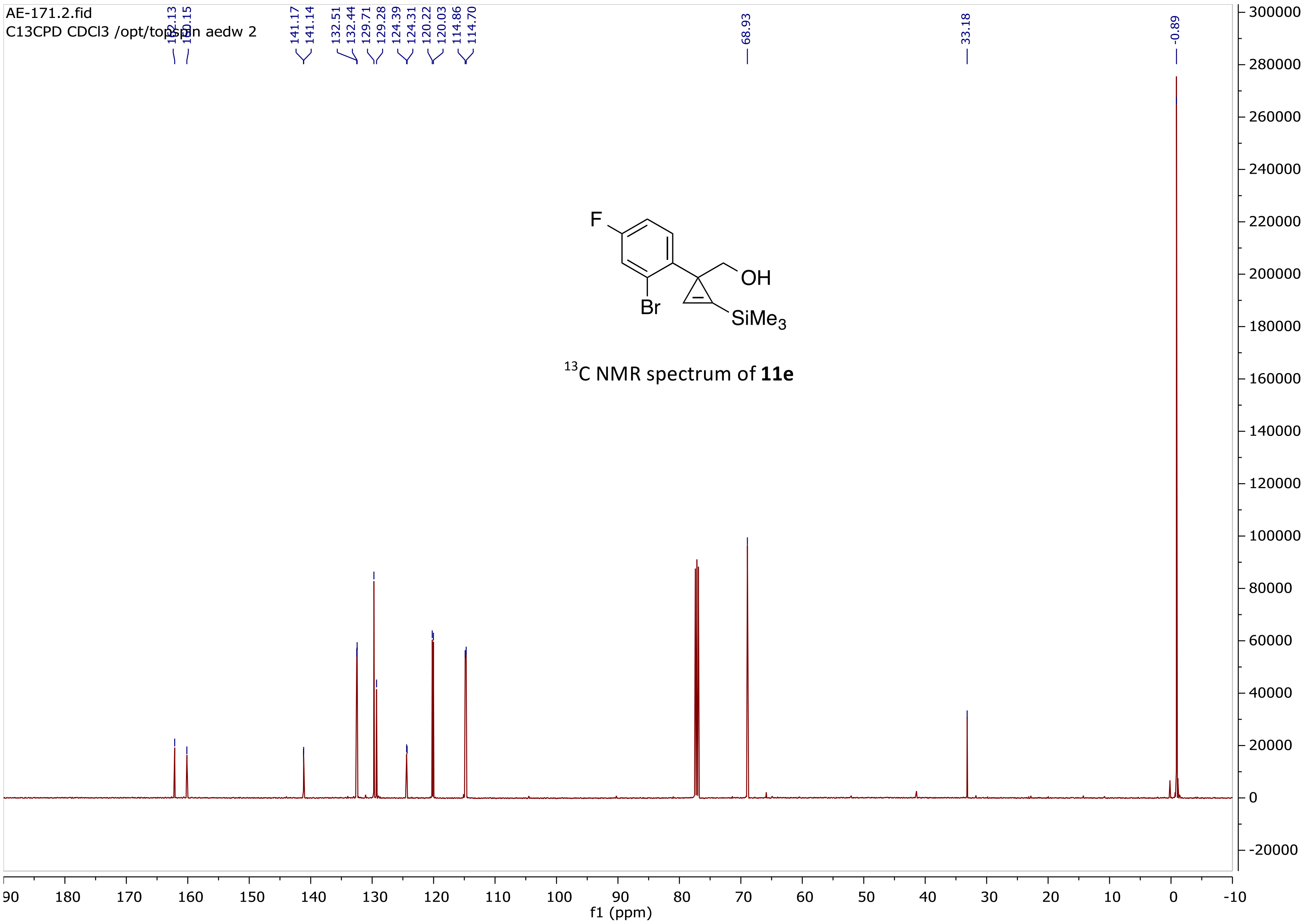
^{1}H NMR spectrum of **11d**



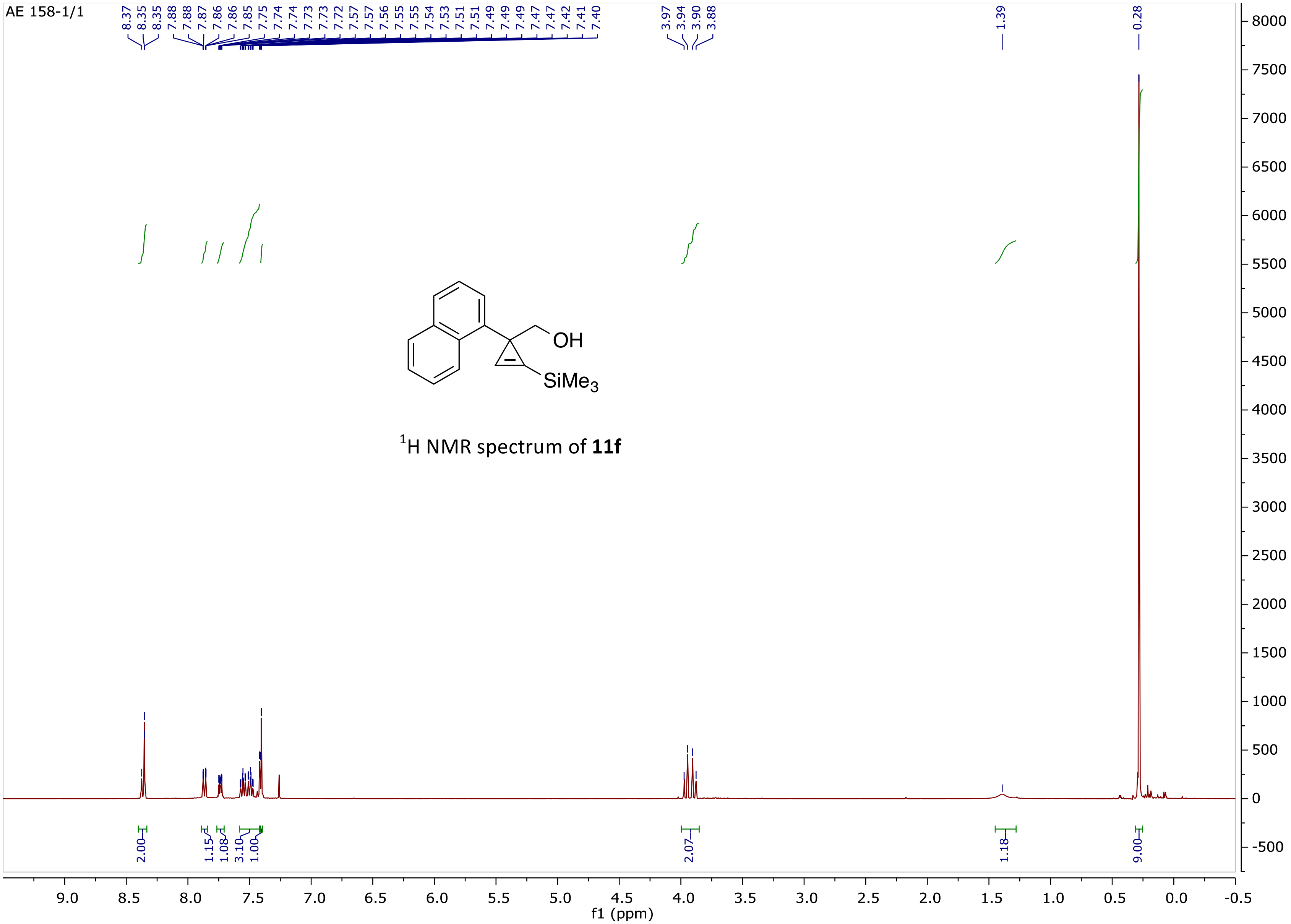
^{13}C NMR spectrum of **11d**



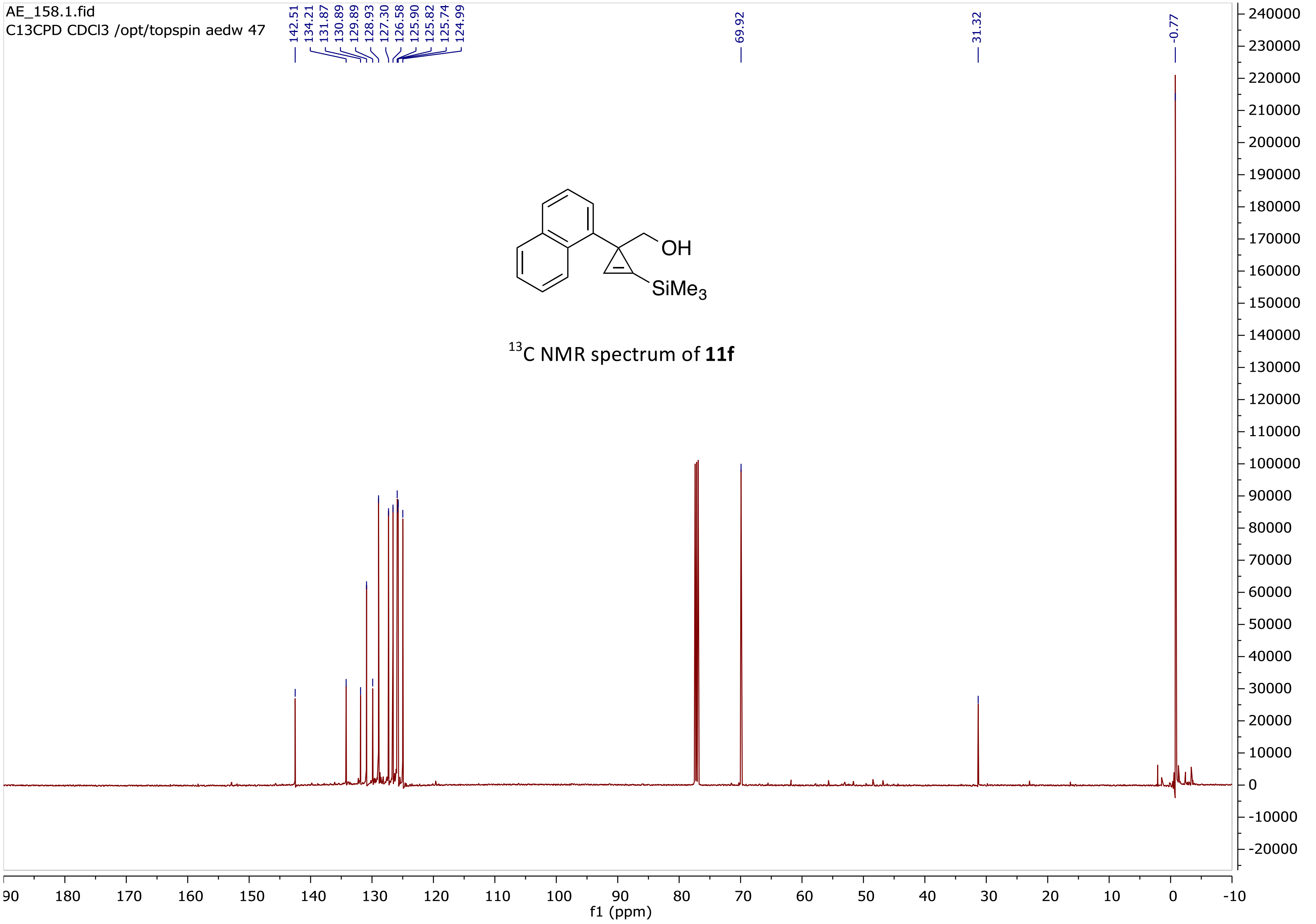
^{1}H NMR spectrum of **11e**



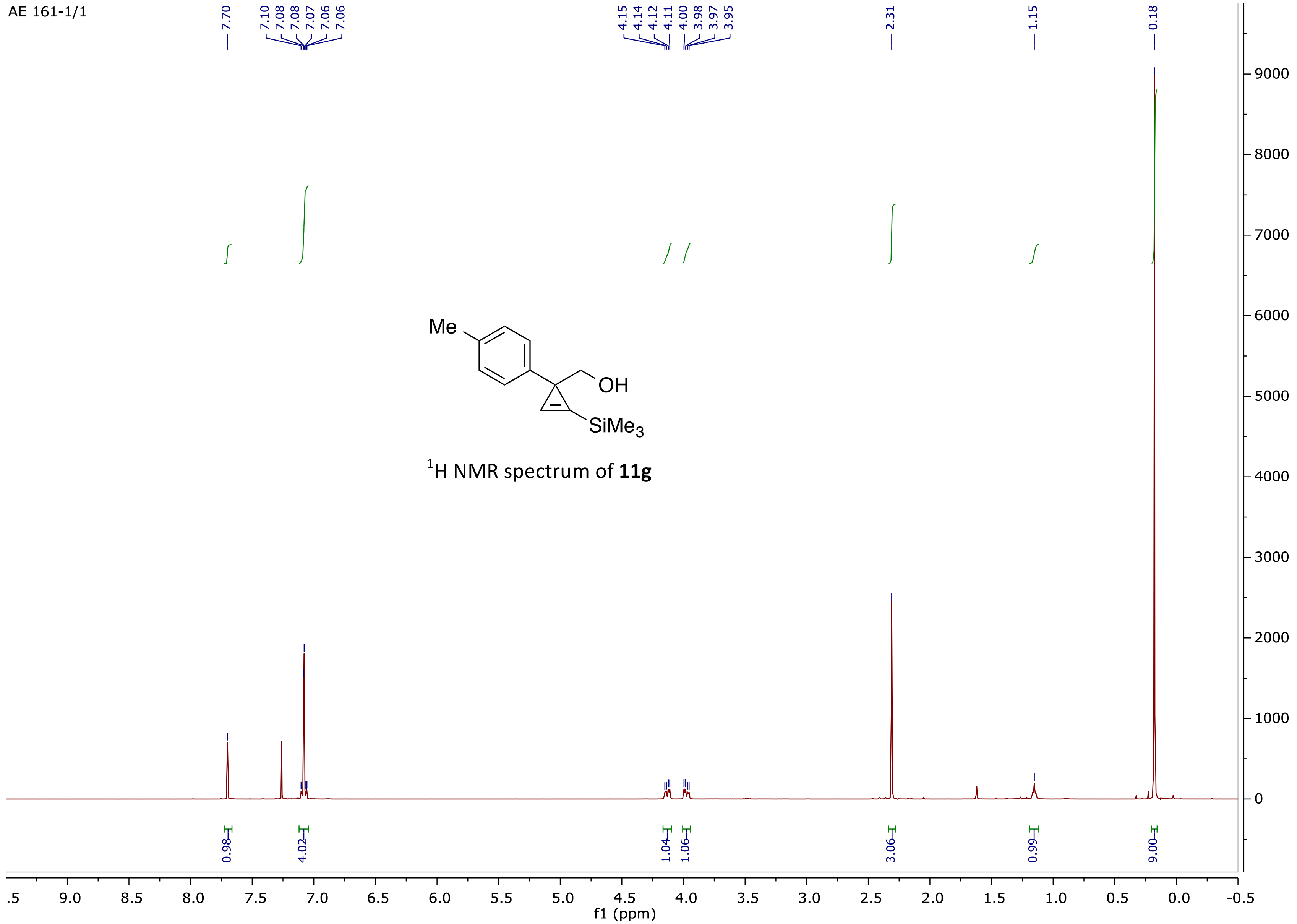
^{13}C NMR spectrum of **11e**



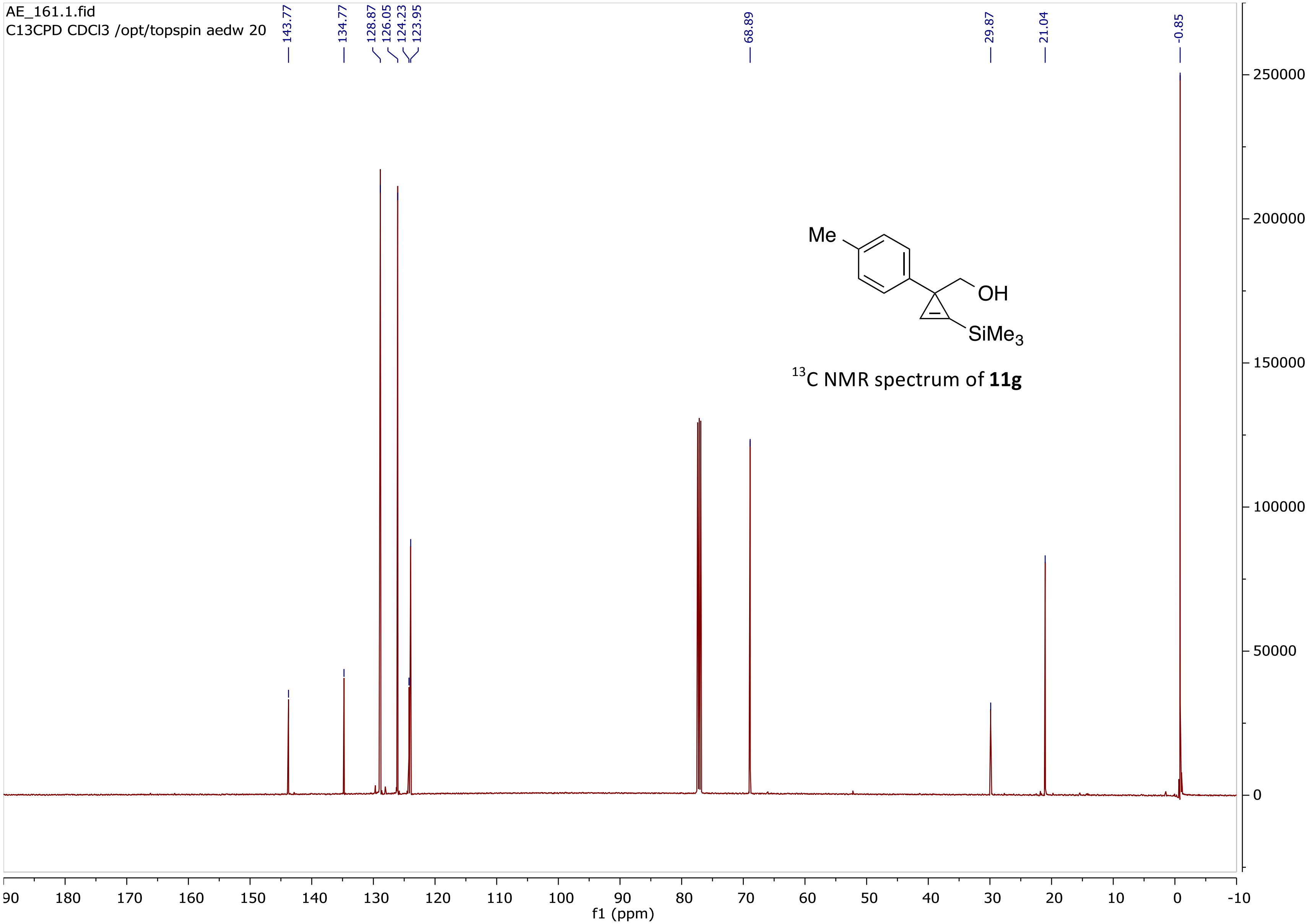
^{1}H NMR spectrum of **11f**



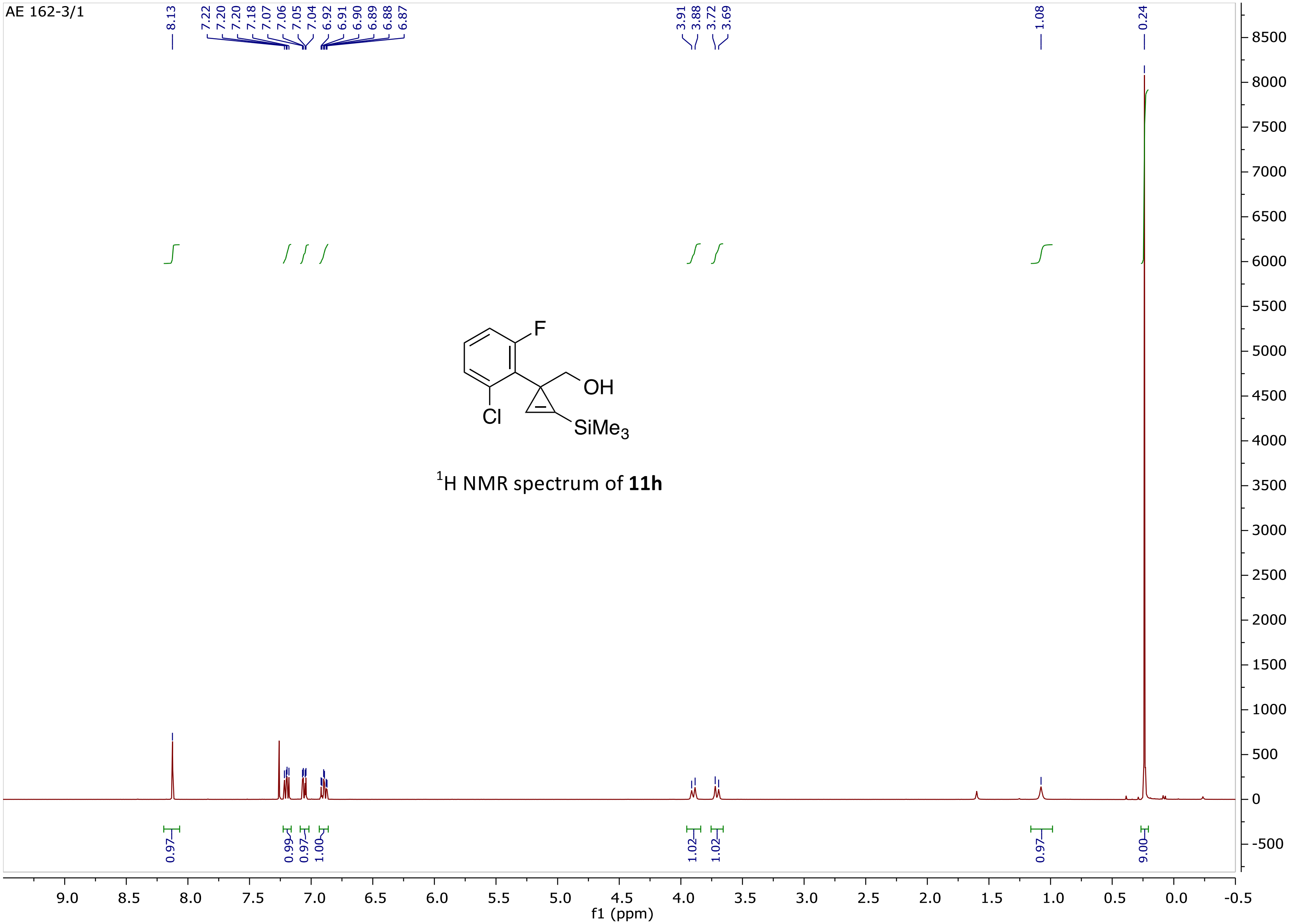
^{13}C NMR spectrum of **11f**



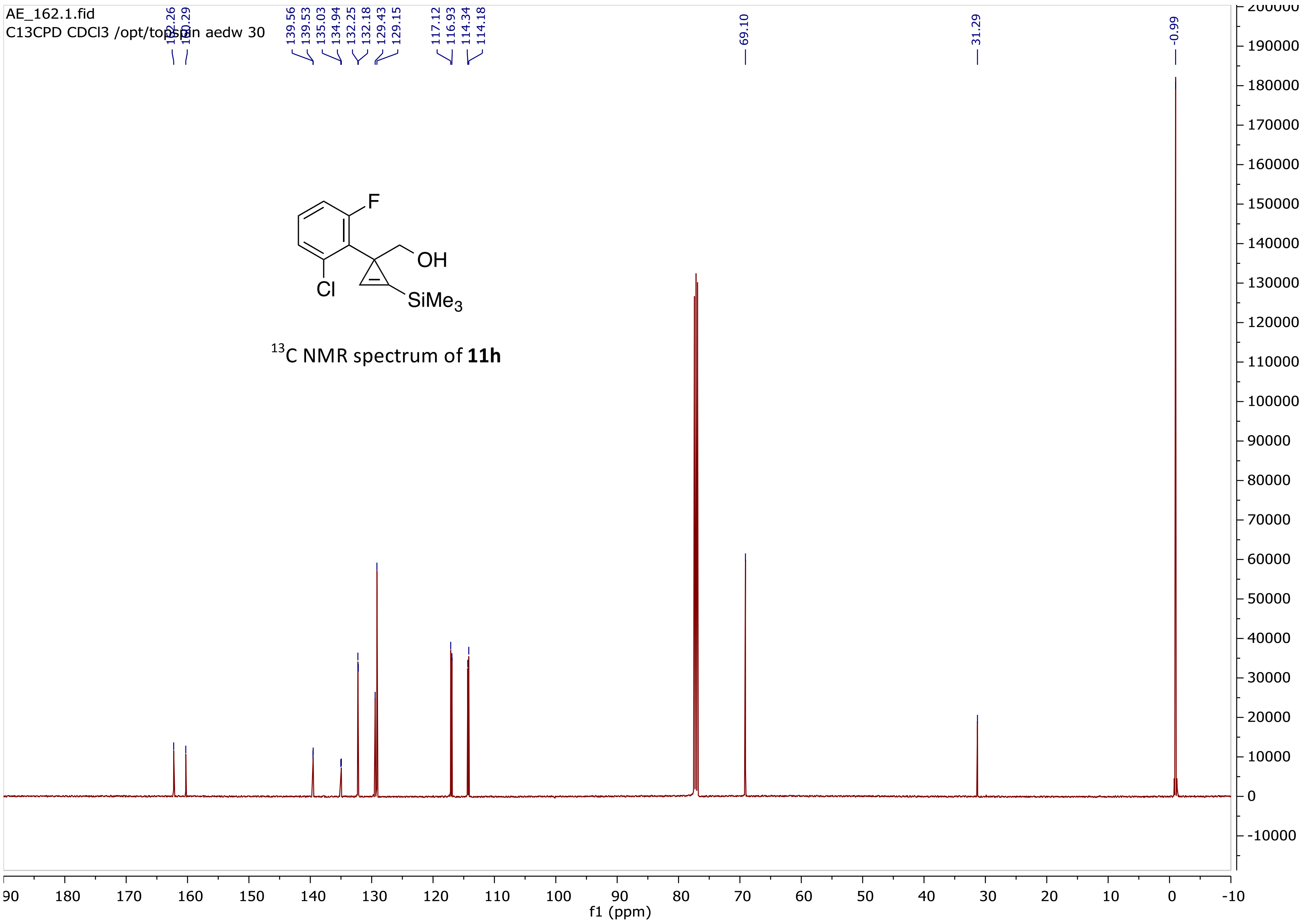
^{1}H NMR spectrum of **11g**



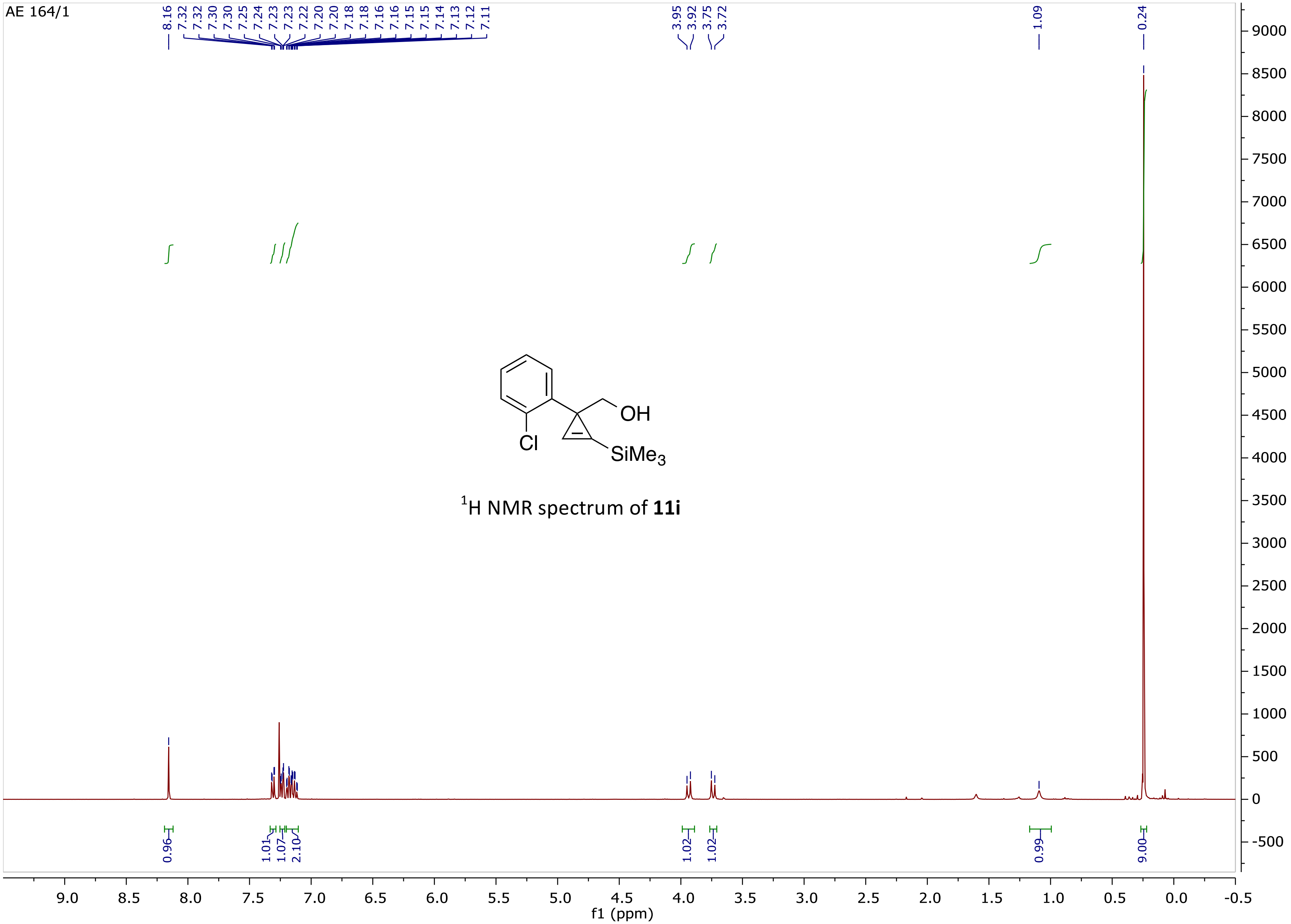
^{13}C NMR spectrum of **11g**



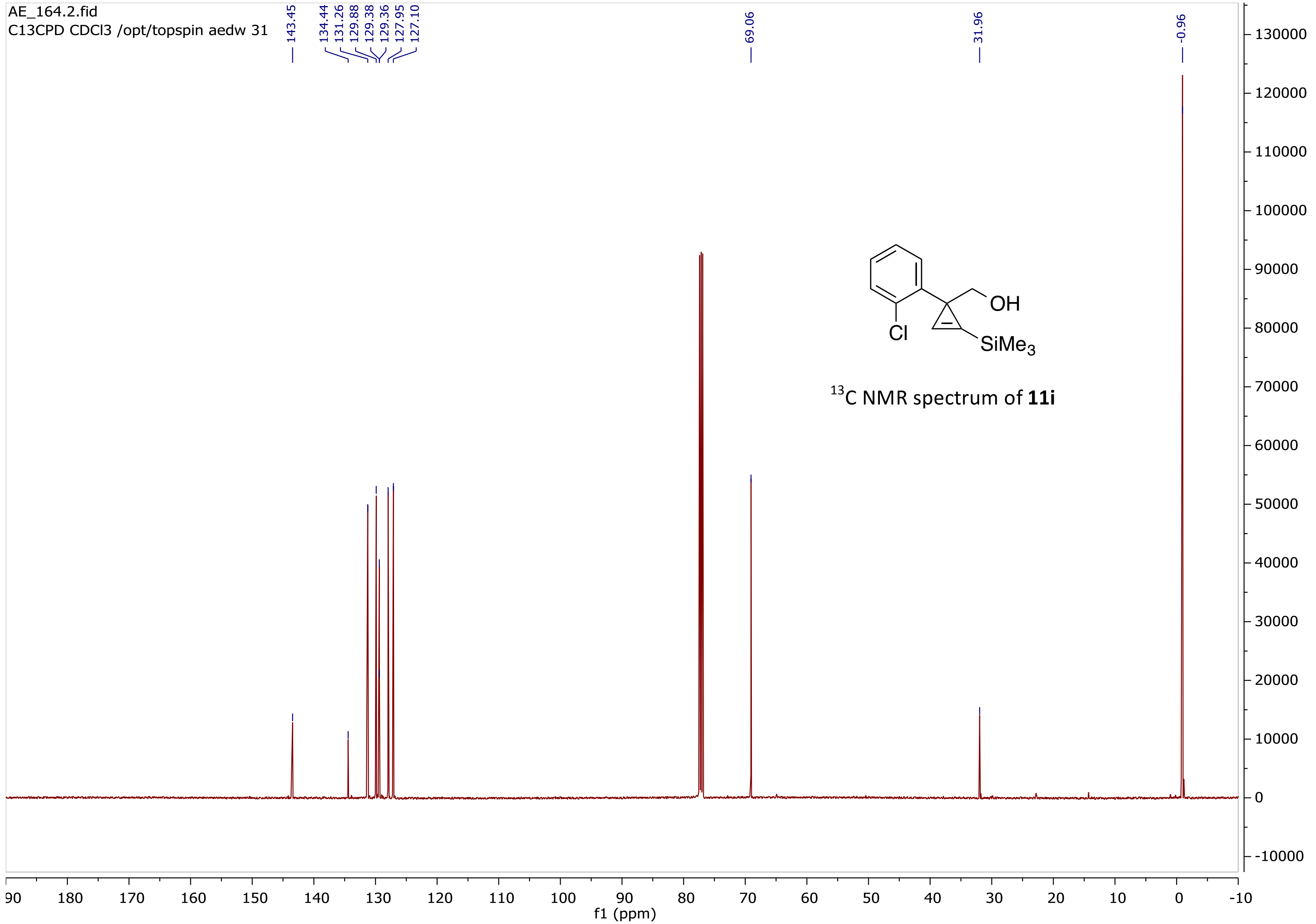
^{1}H NMR spectrum of **11h**



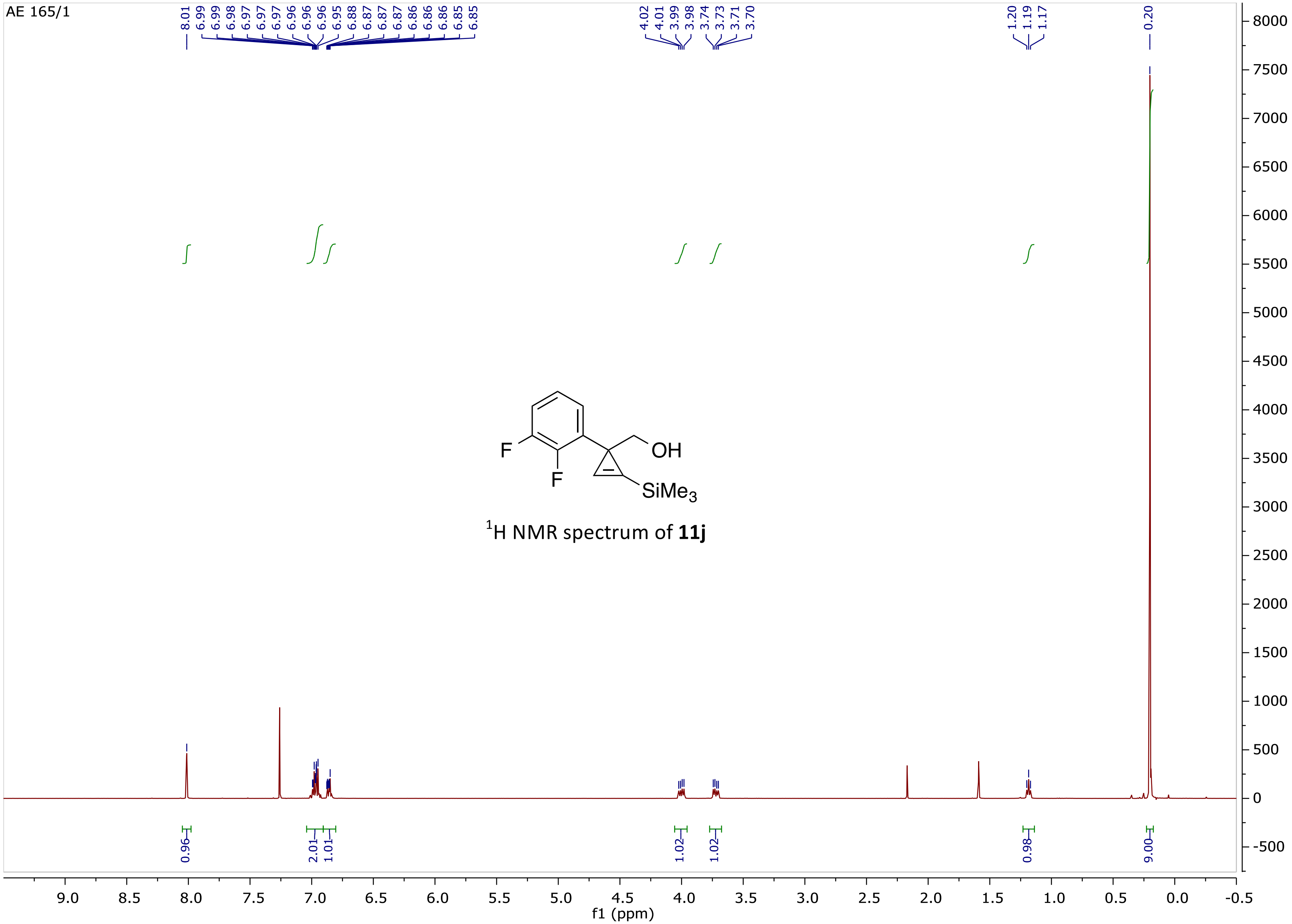
^{13}C NMR spectrum of **11h**



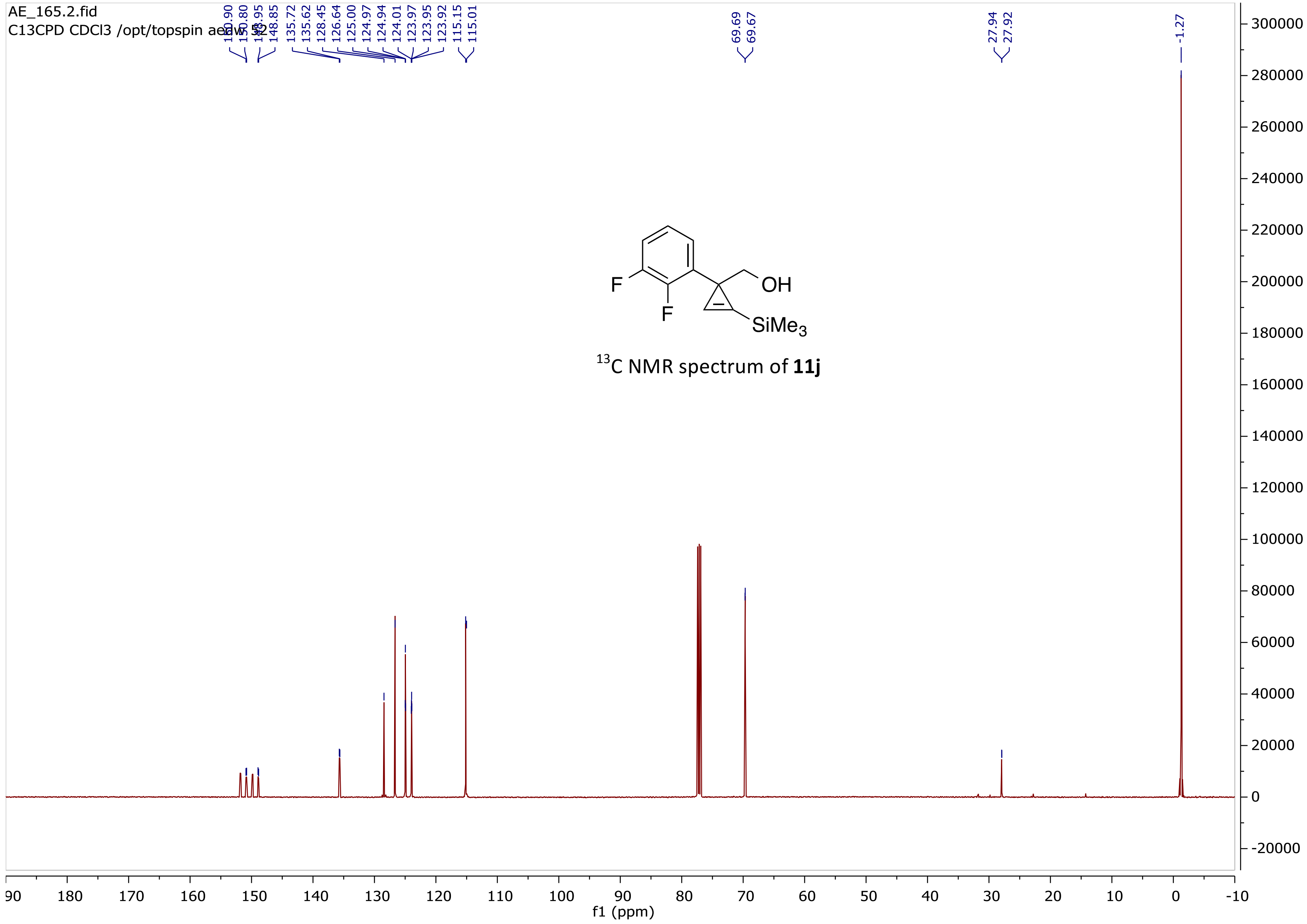
^{1}H NMR spectrum of **11i**

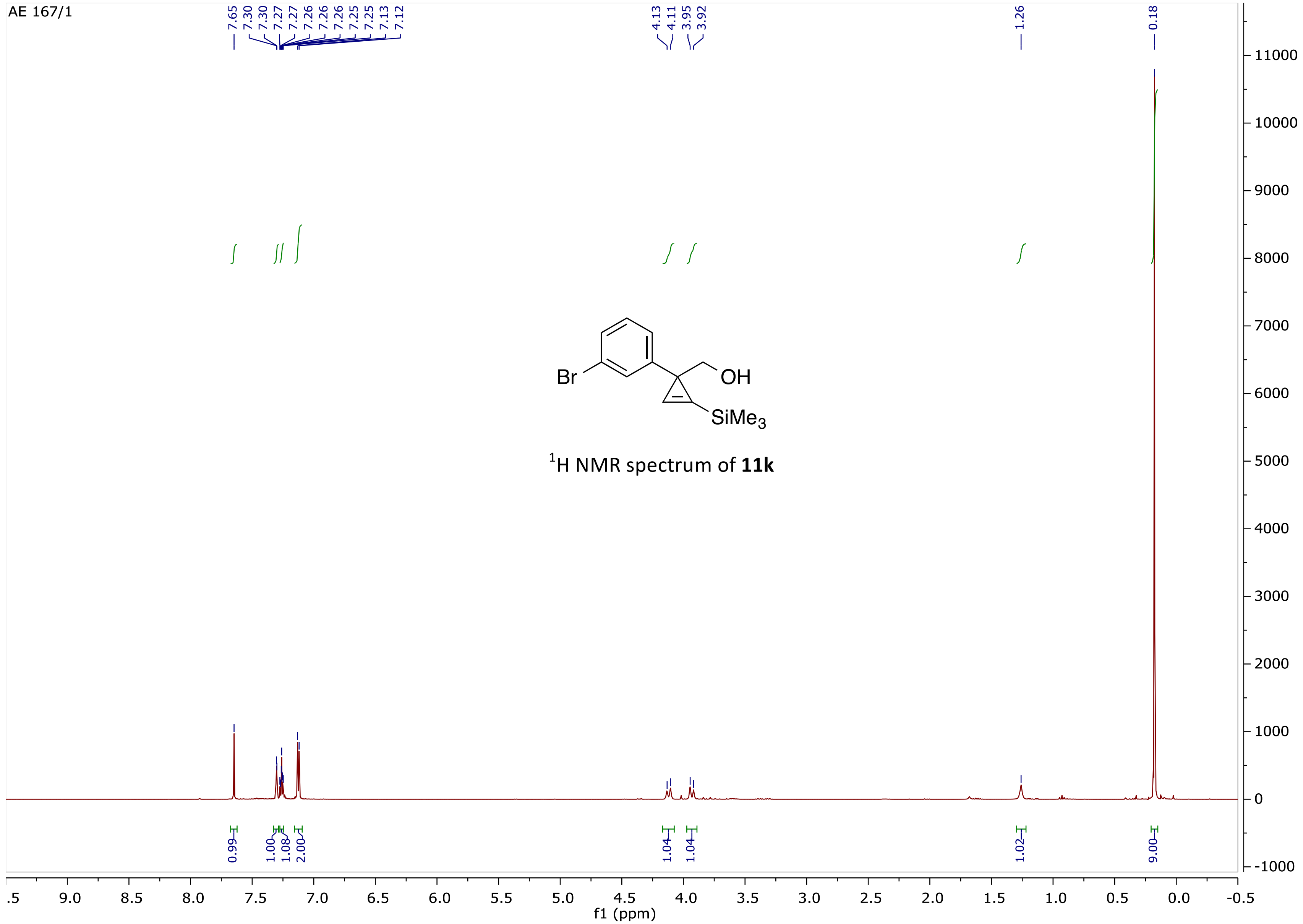


^{13}C NMR spectrum of **11i**

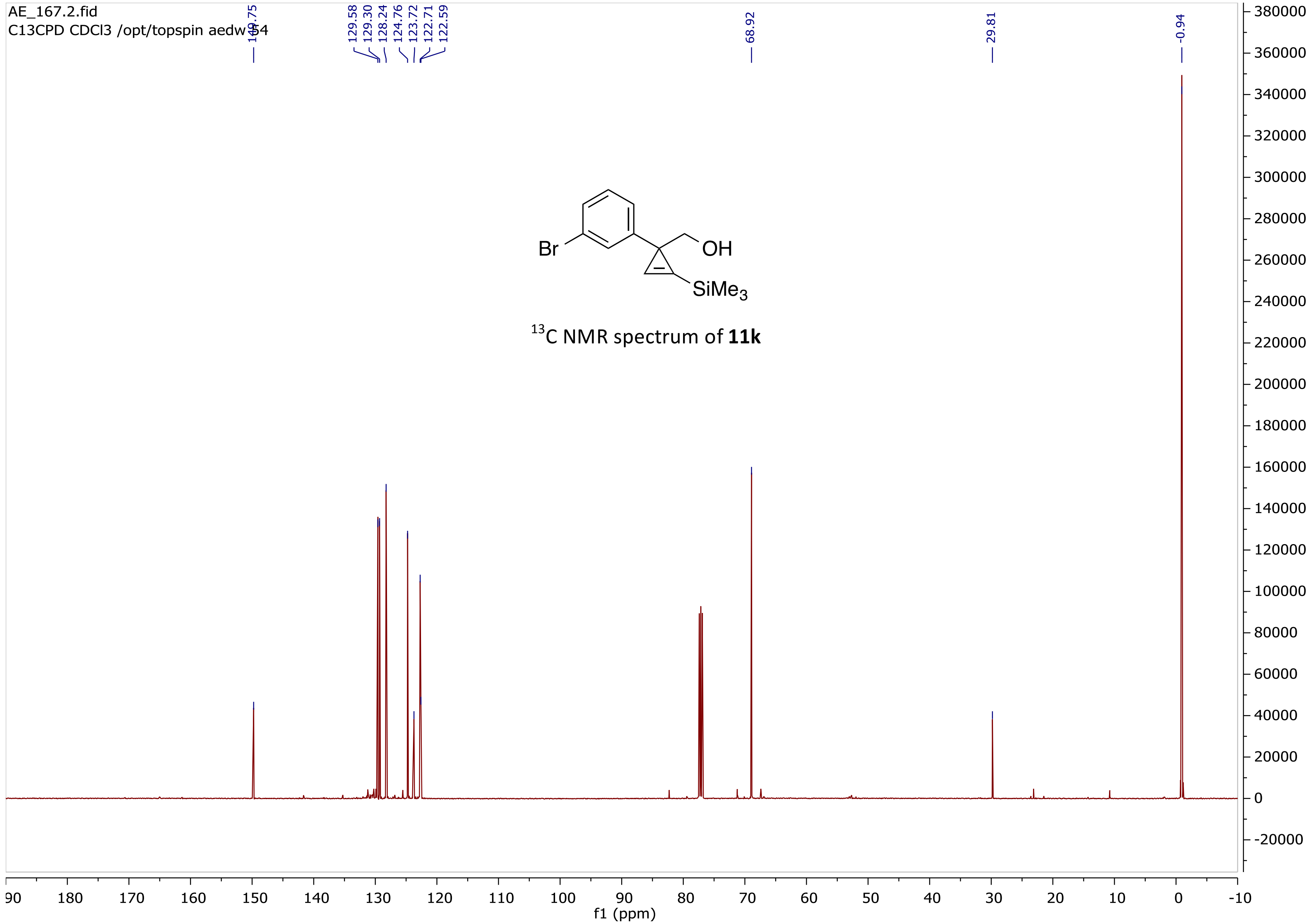


^{1}H NMR spectrum of **11j**

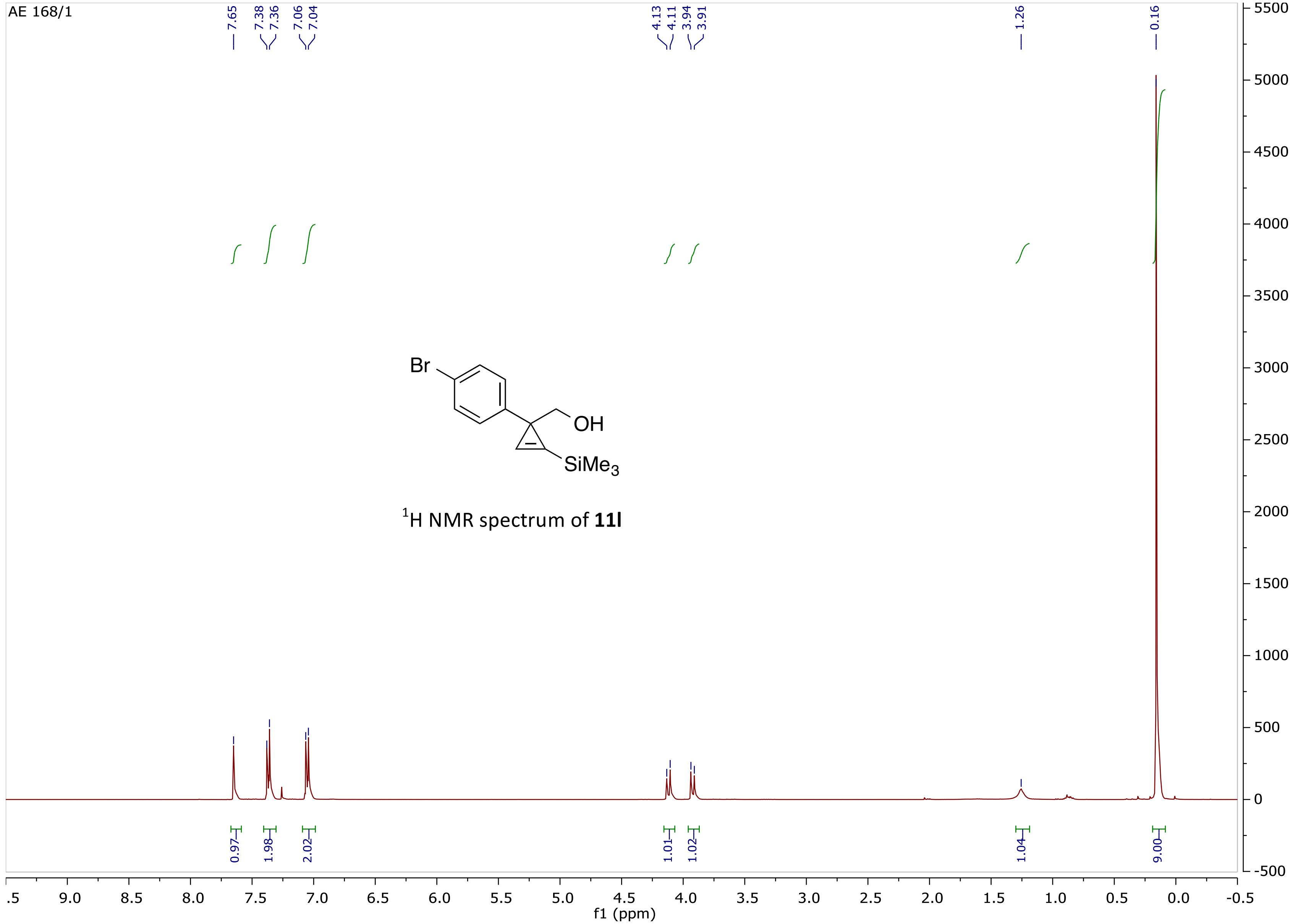

^{13}C NMR spectrum of **11j**



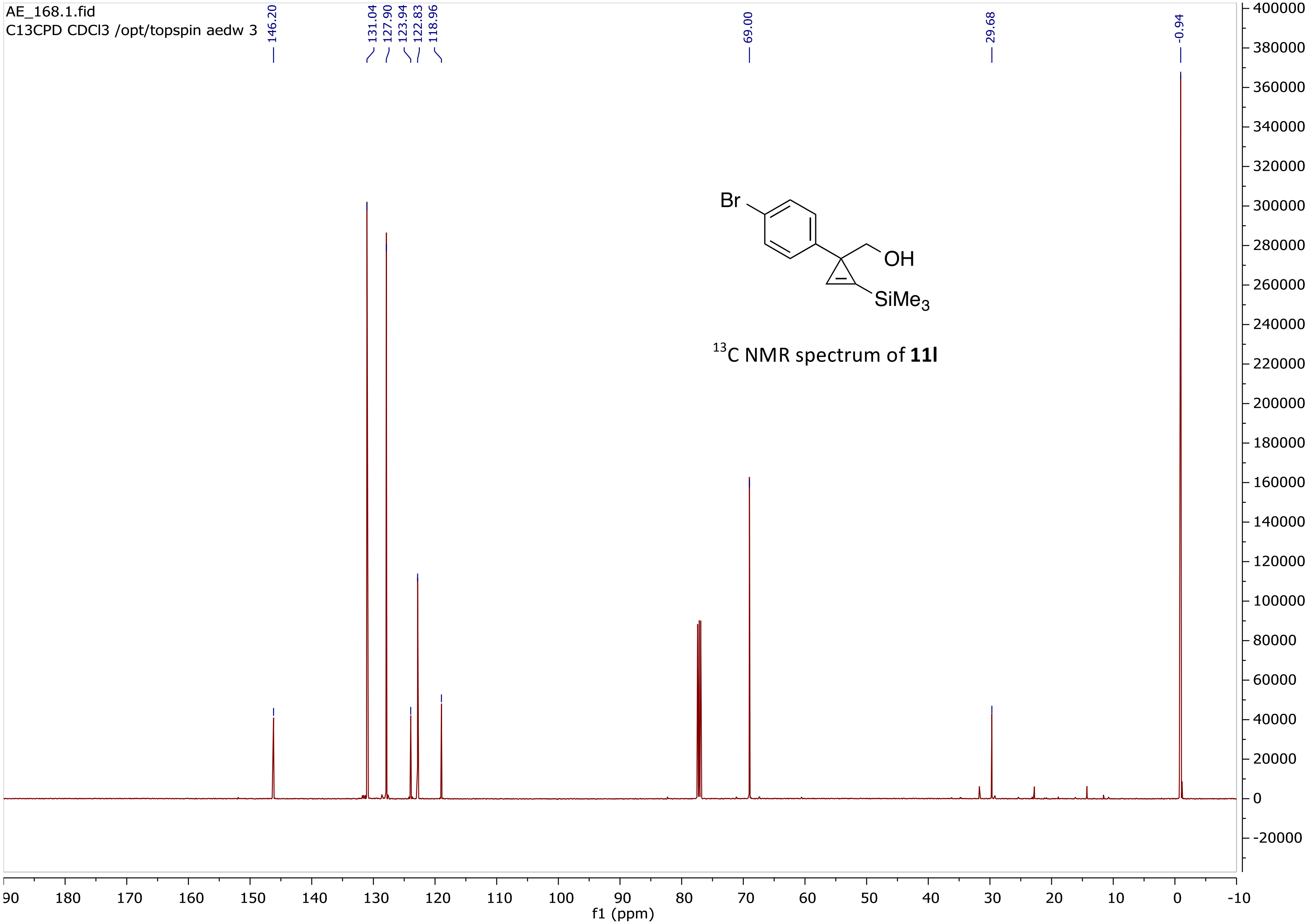
^{1}H NMR spectrum of **11k**



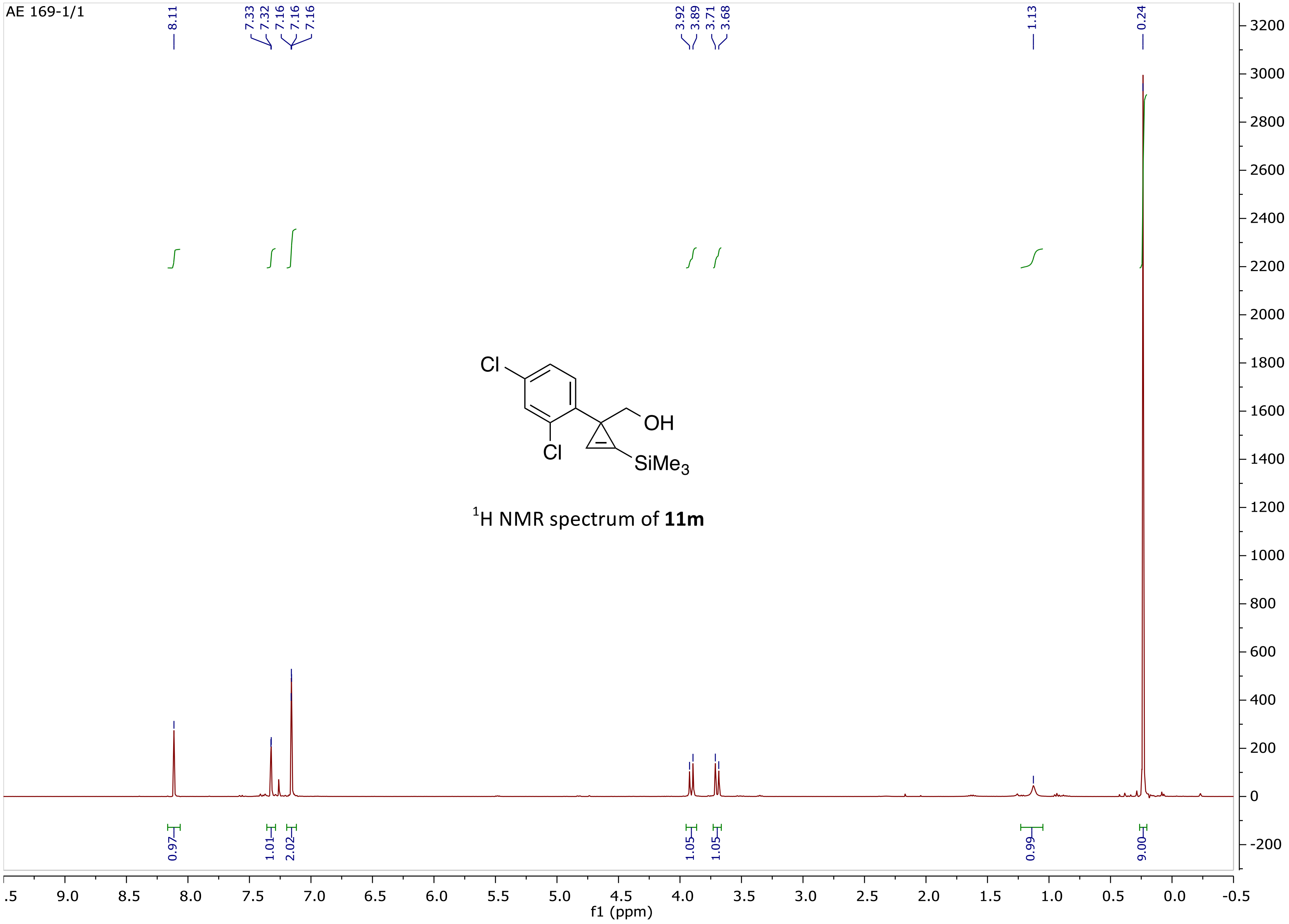
^{13}C NMR spectrum of **11k**



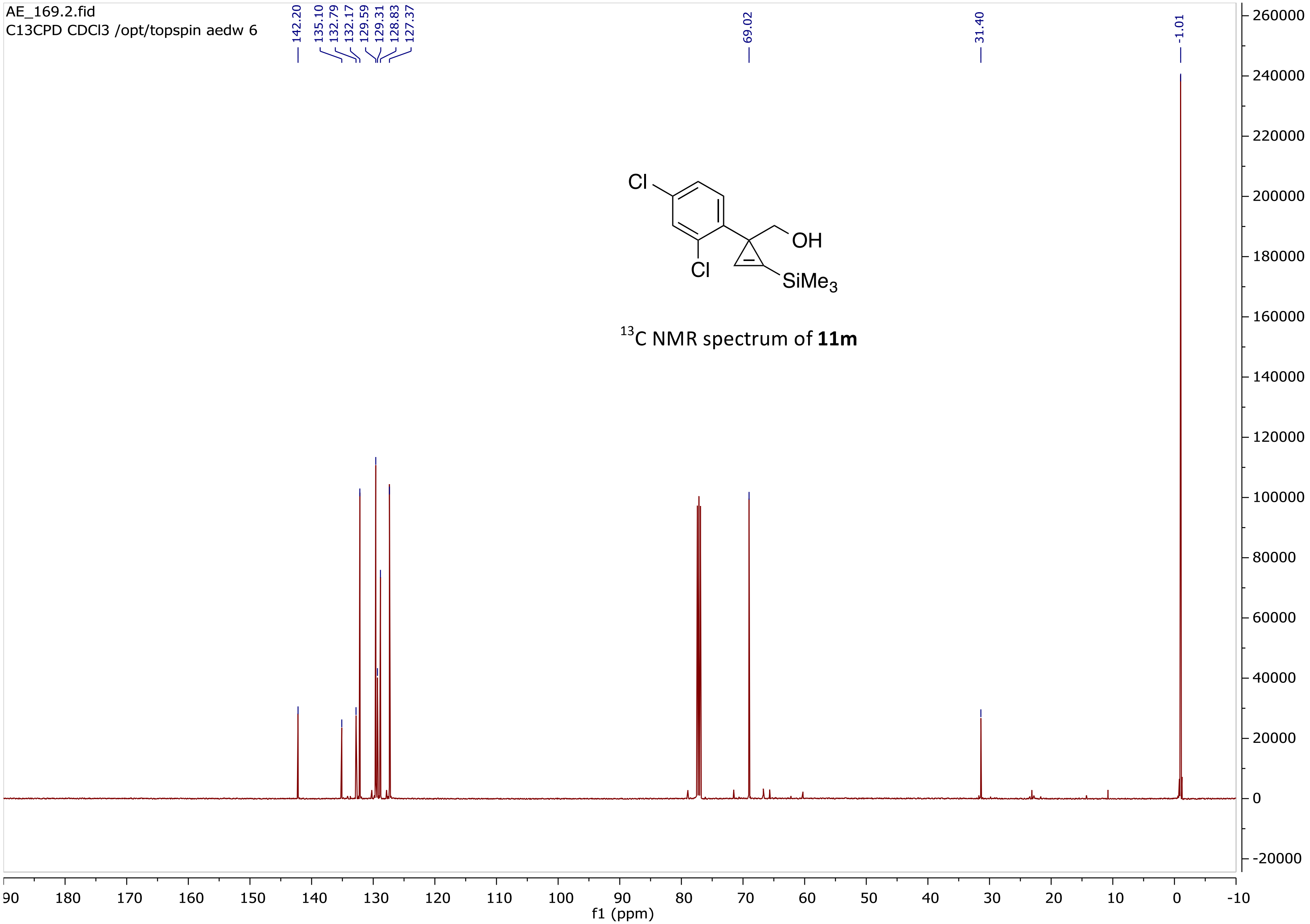
^{1}H NMR spectrum of **11l**



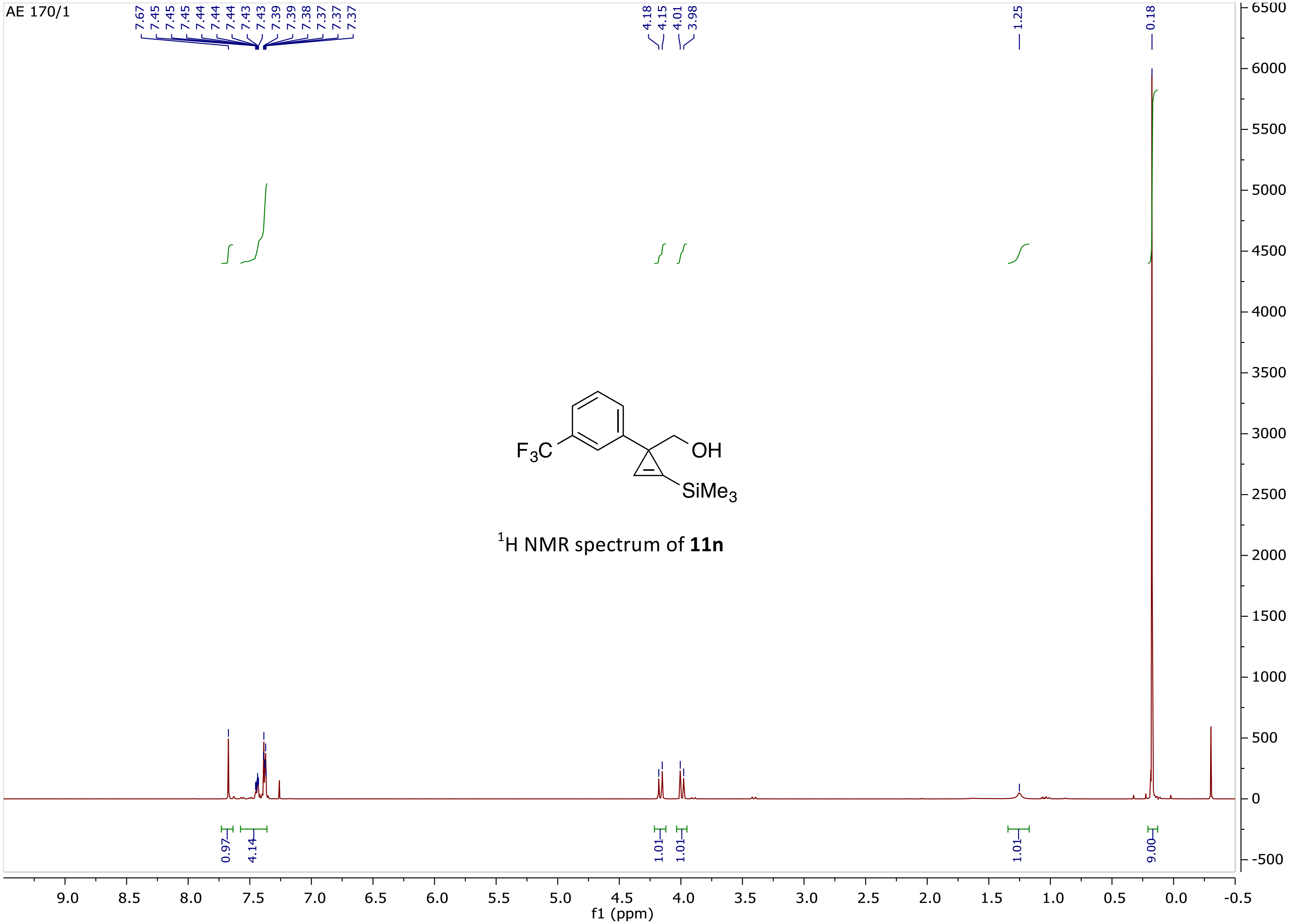
^{13}C NMR spectrum of **11l**



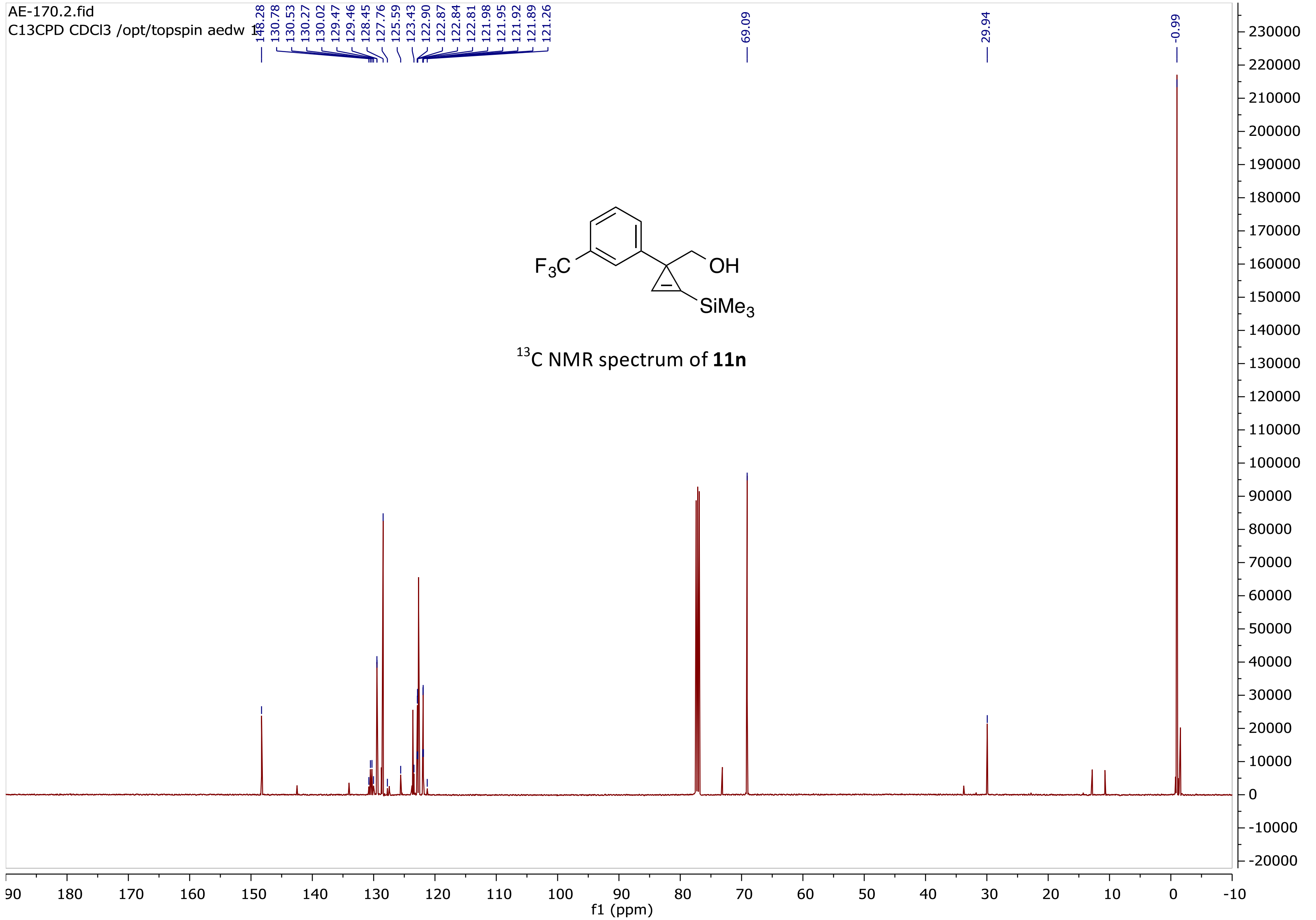
^{1}H NMR spectrum of **11m**



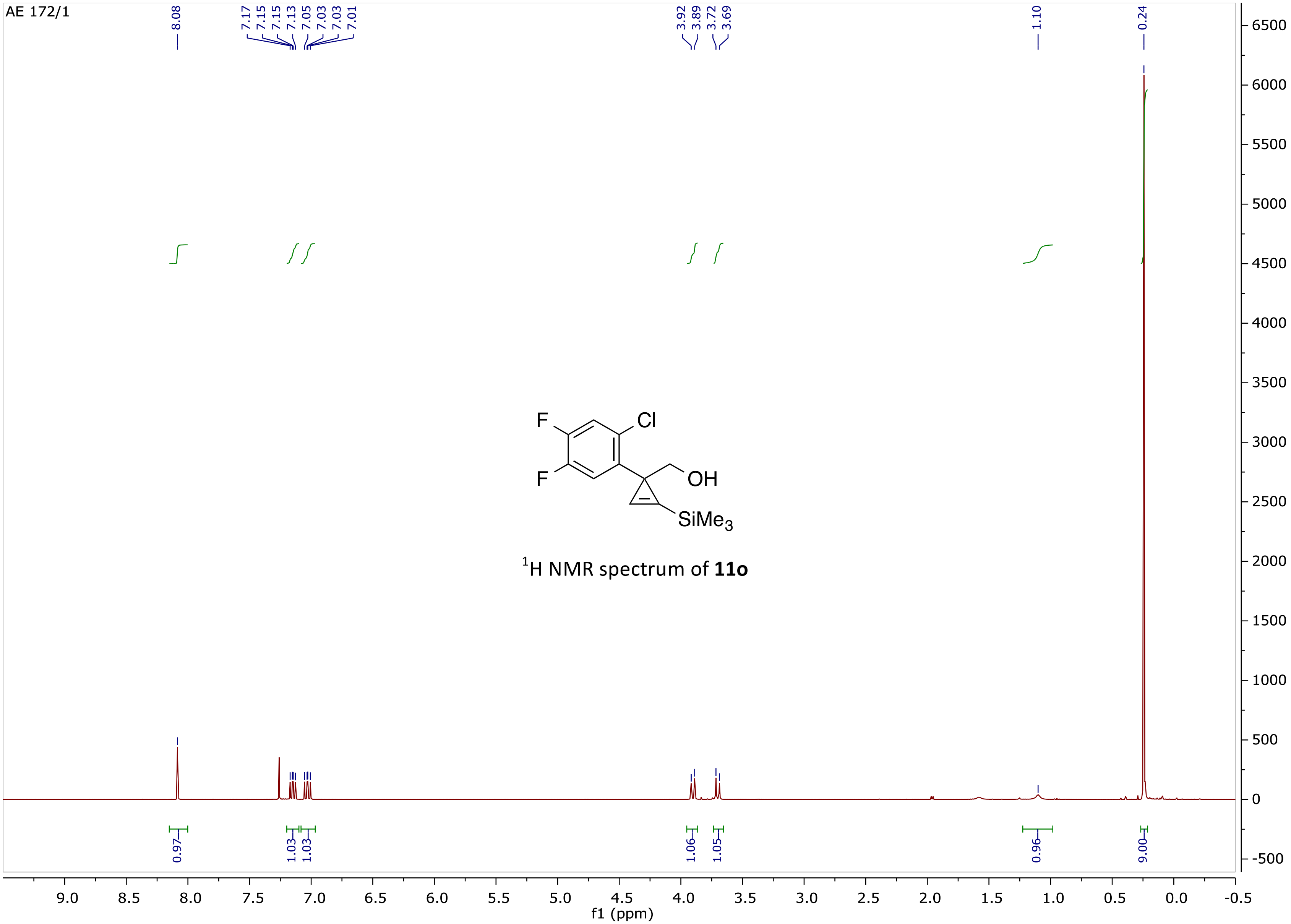
^{13}C NMR spectrum of **11m**



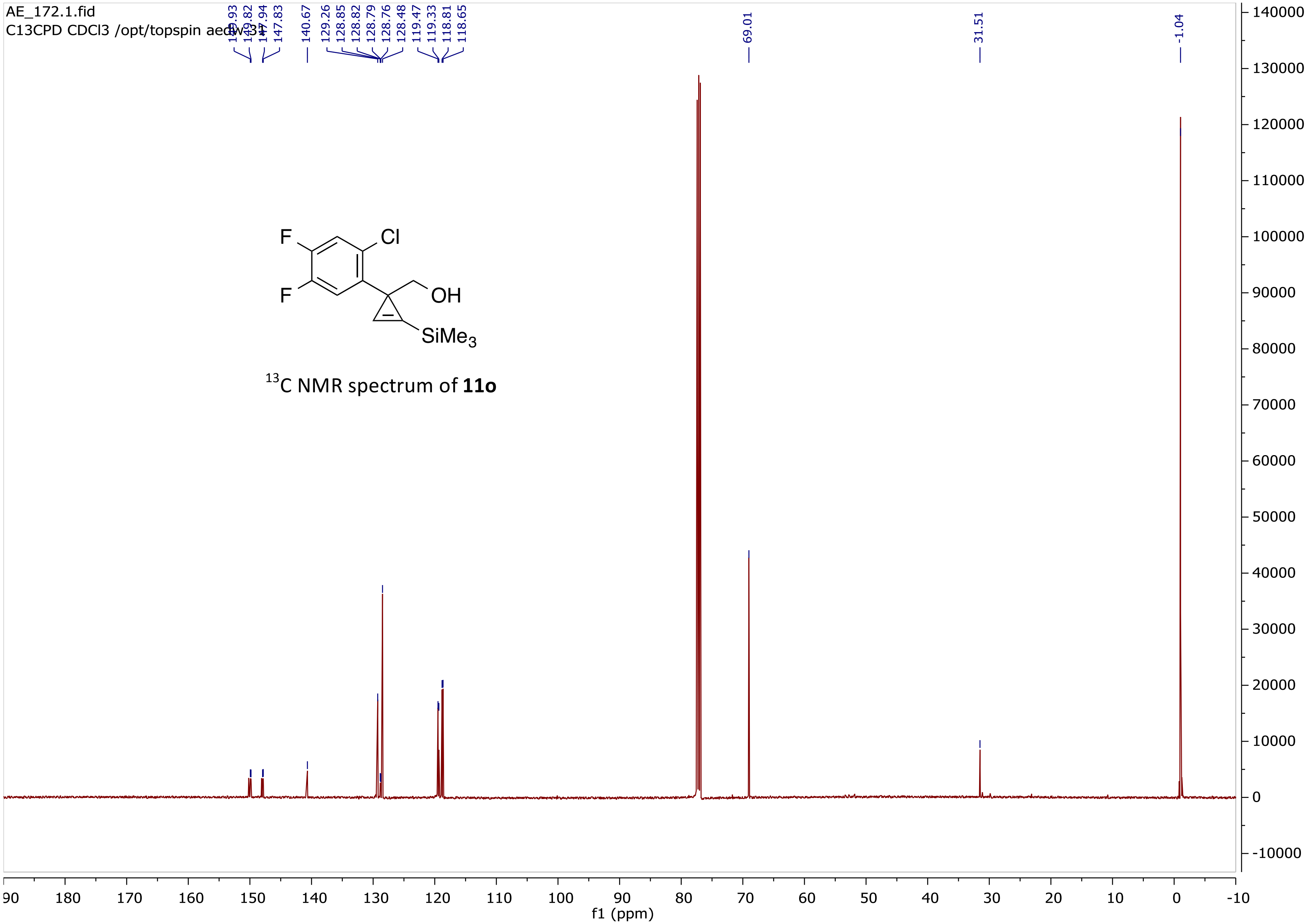
^{1}H NMR spectrum of **11n**



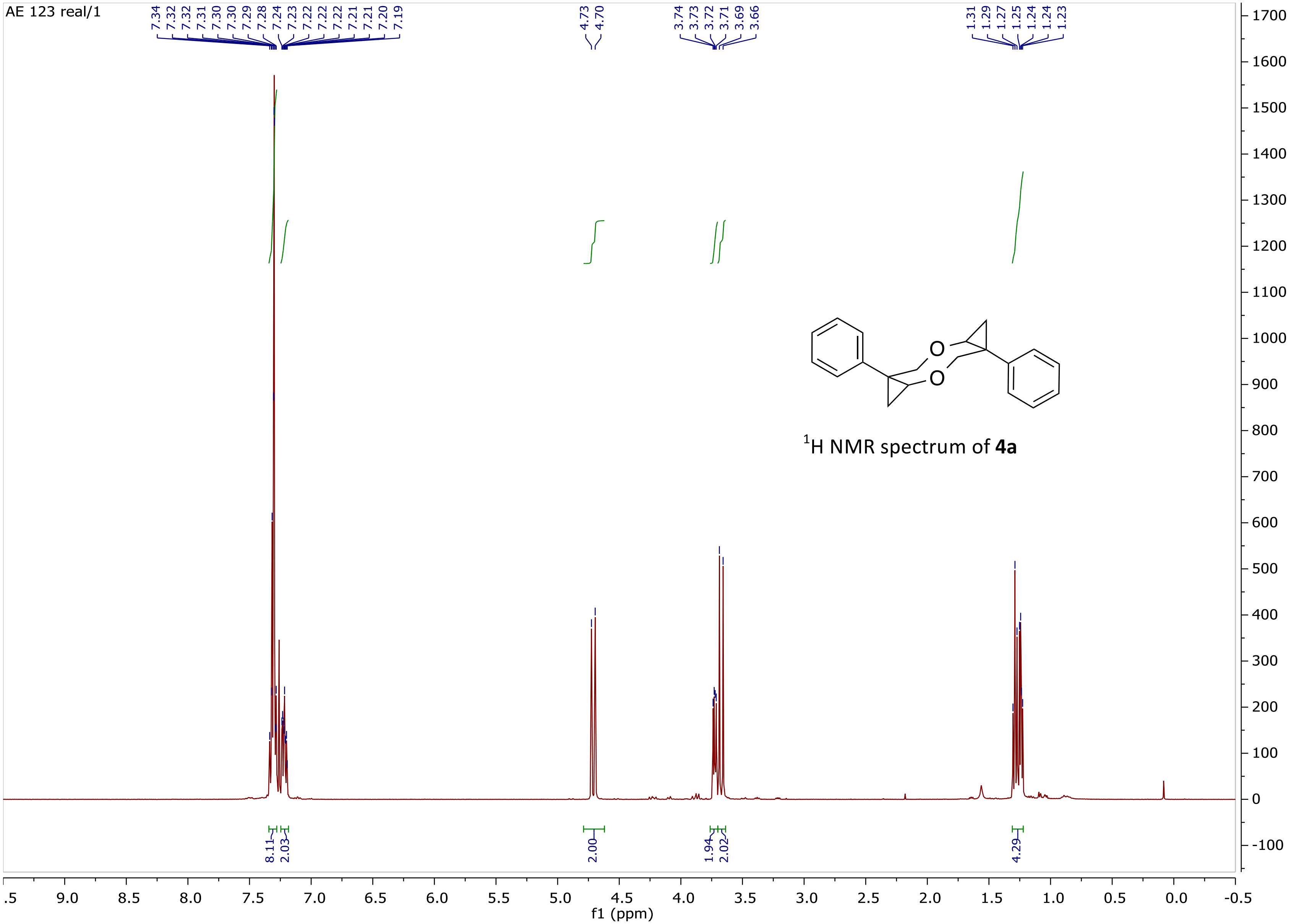
^{13}C NMR spectrum of **11n**



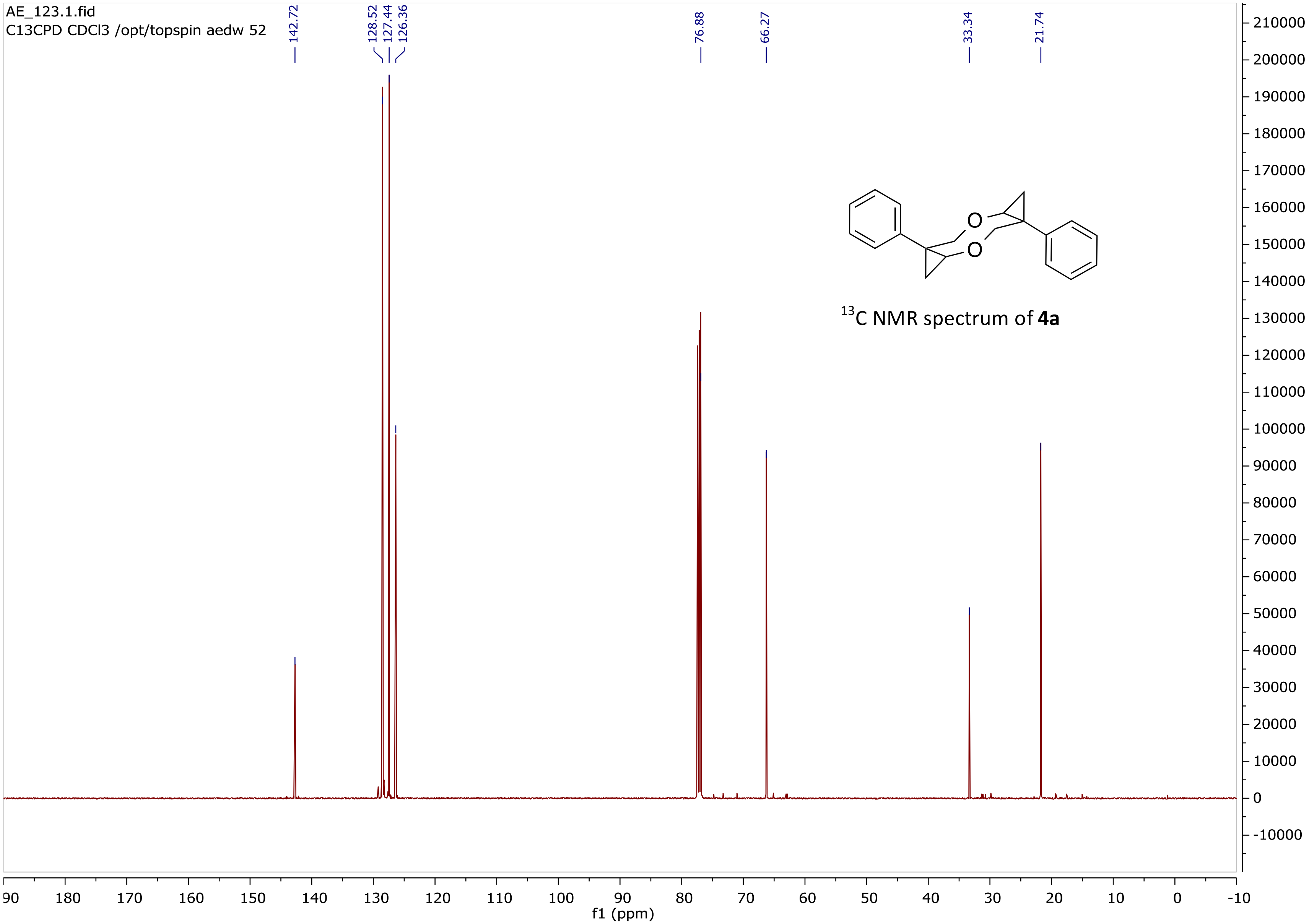
^{1}H NMR spectrum of **11o**



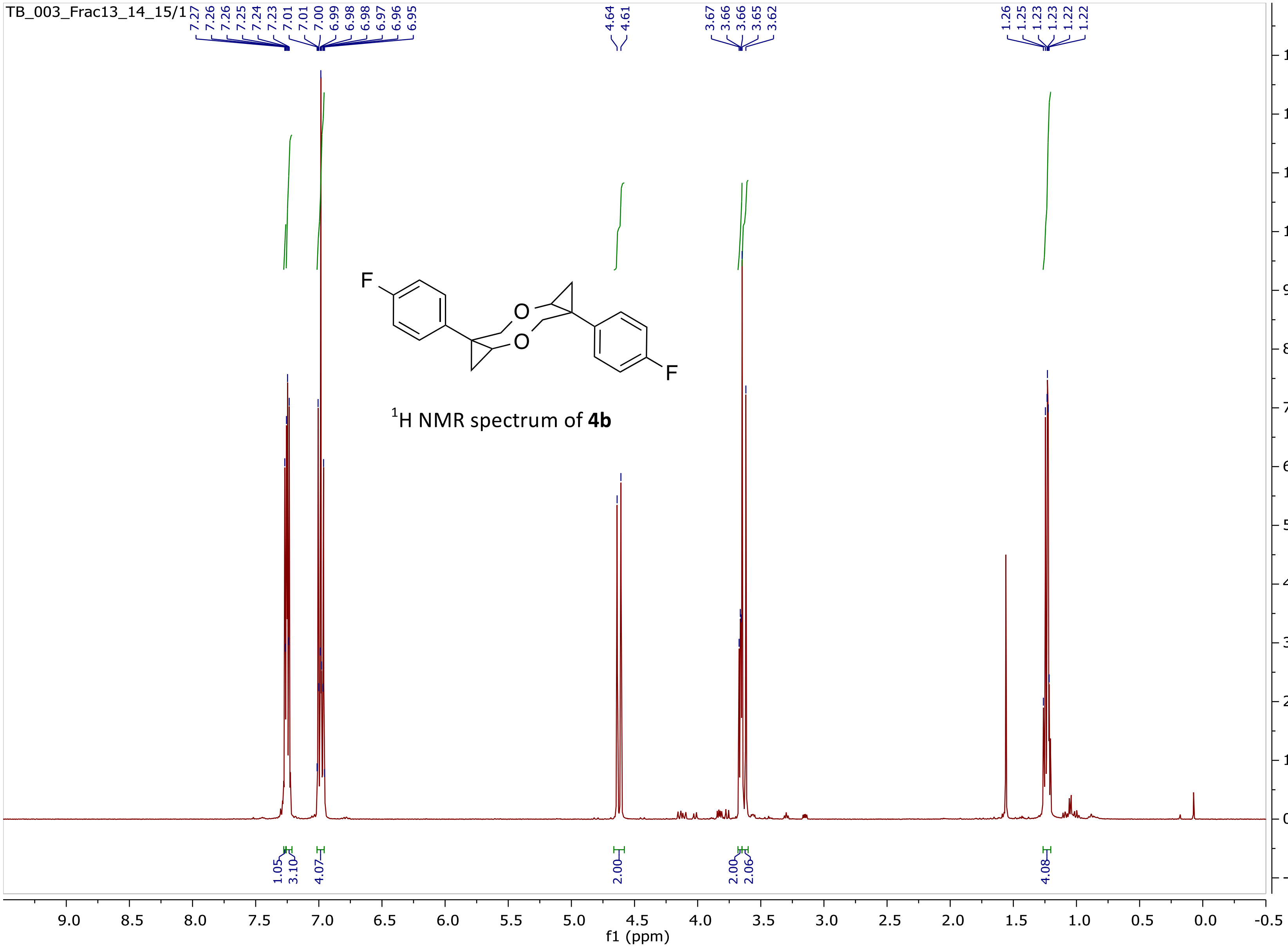
^{13}C NMR spectrum of **11o**



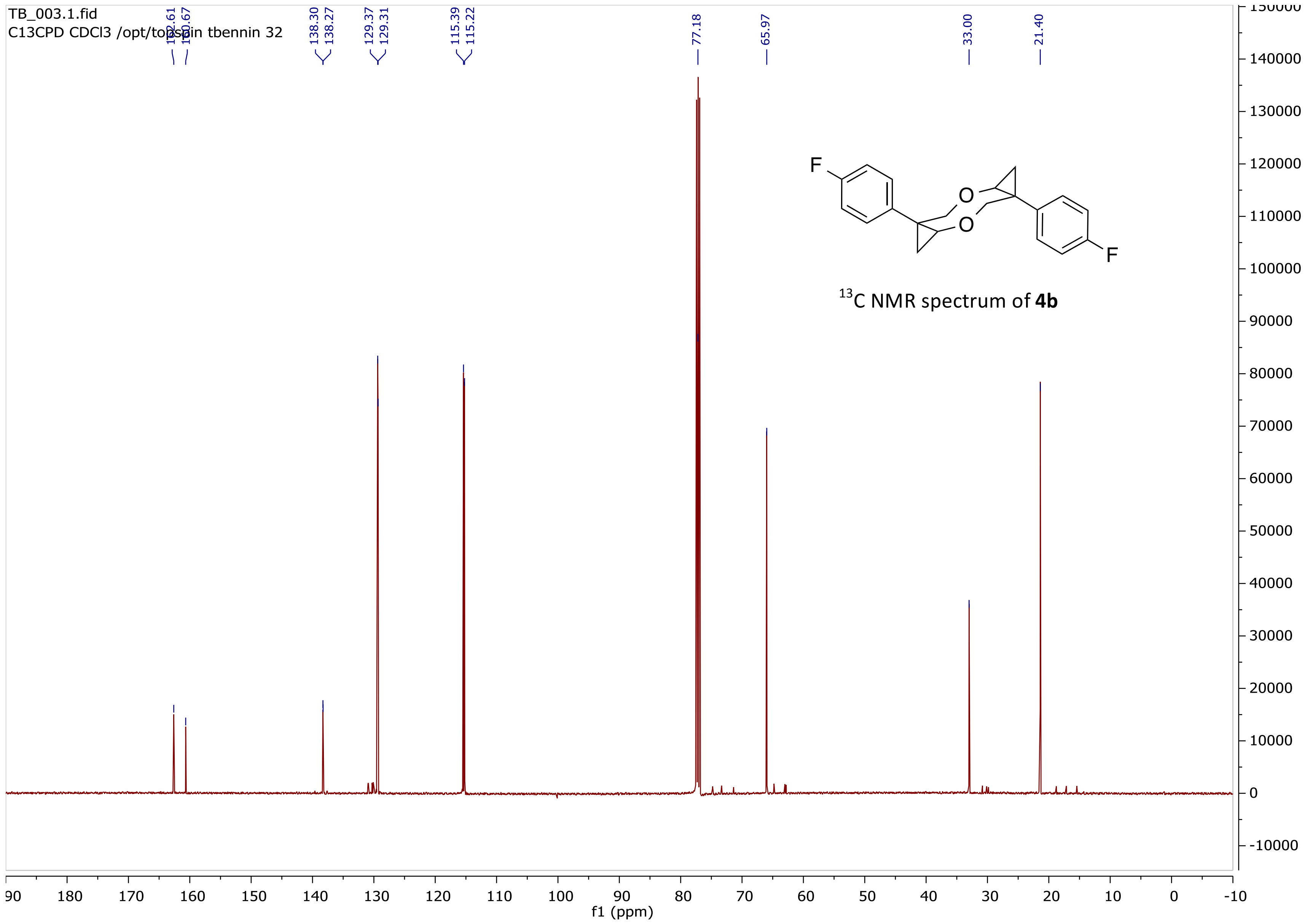
^{1}H NMR spectrum of **4a**



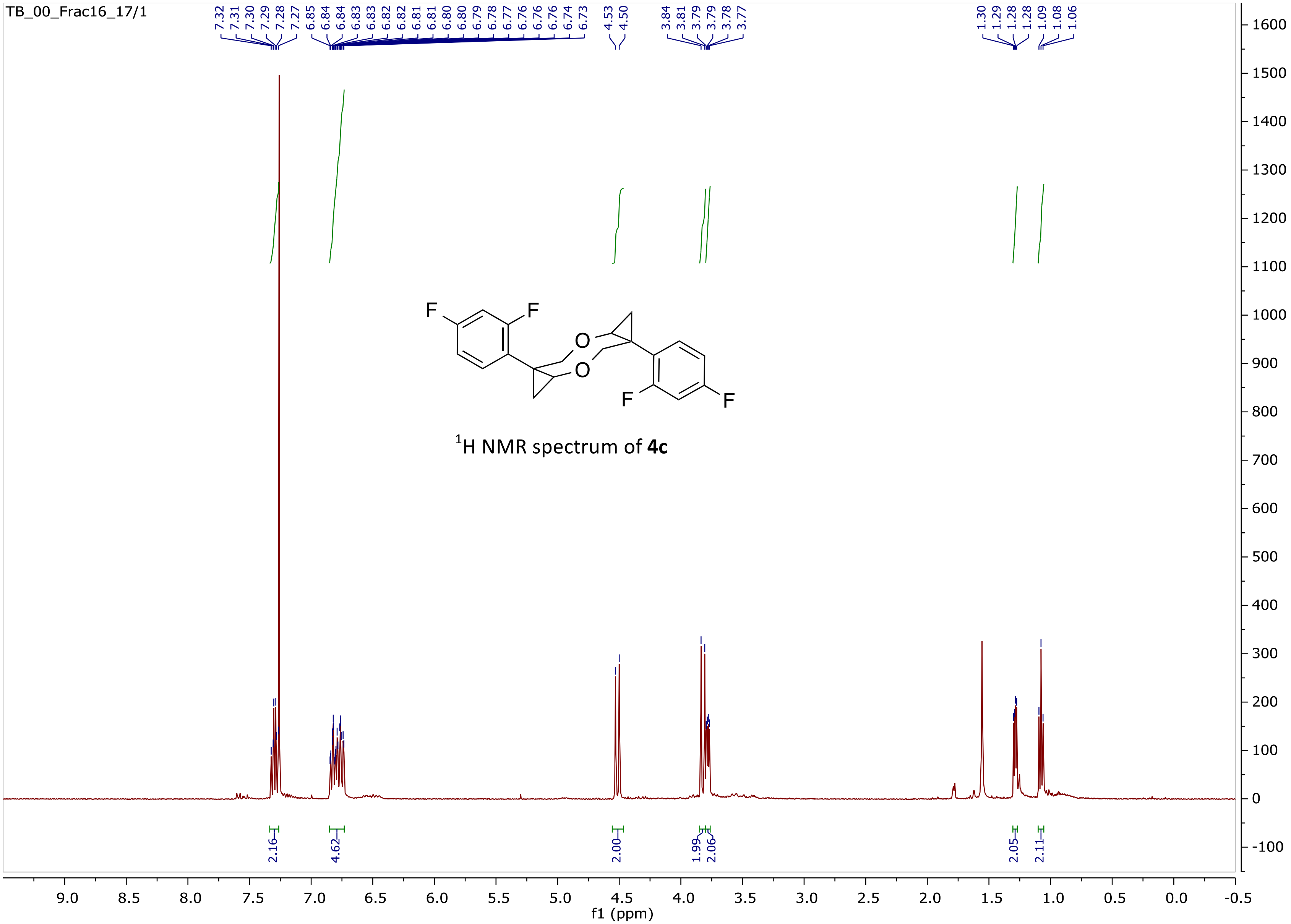
^{13}C NMR spectrum of **4a**



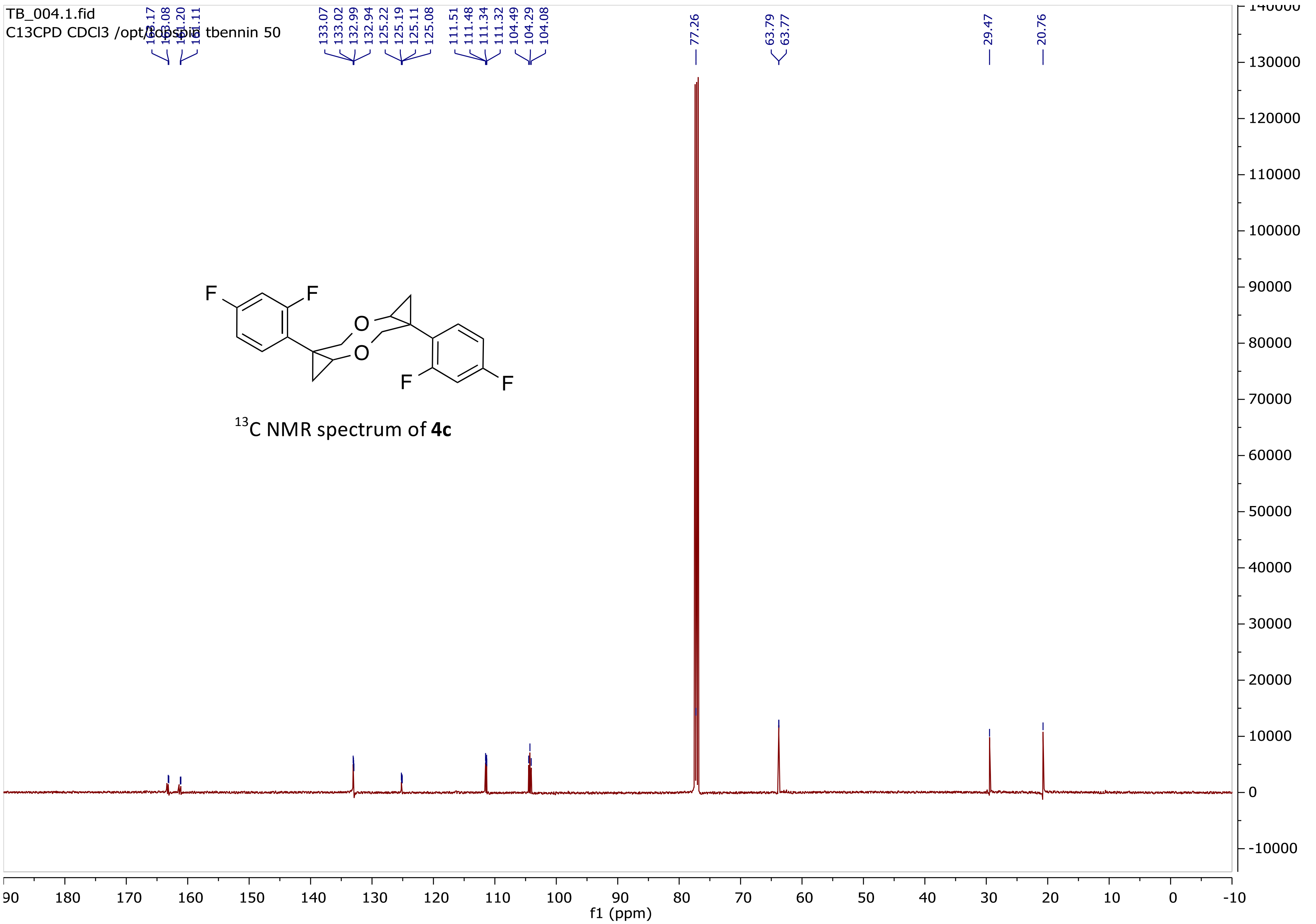
^{1}H NMR spectrum of **4b**



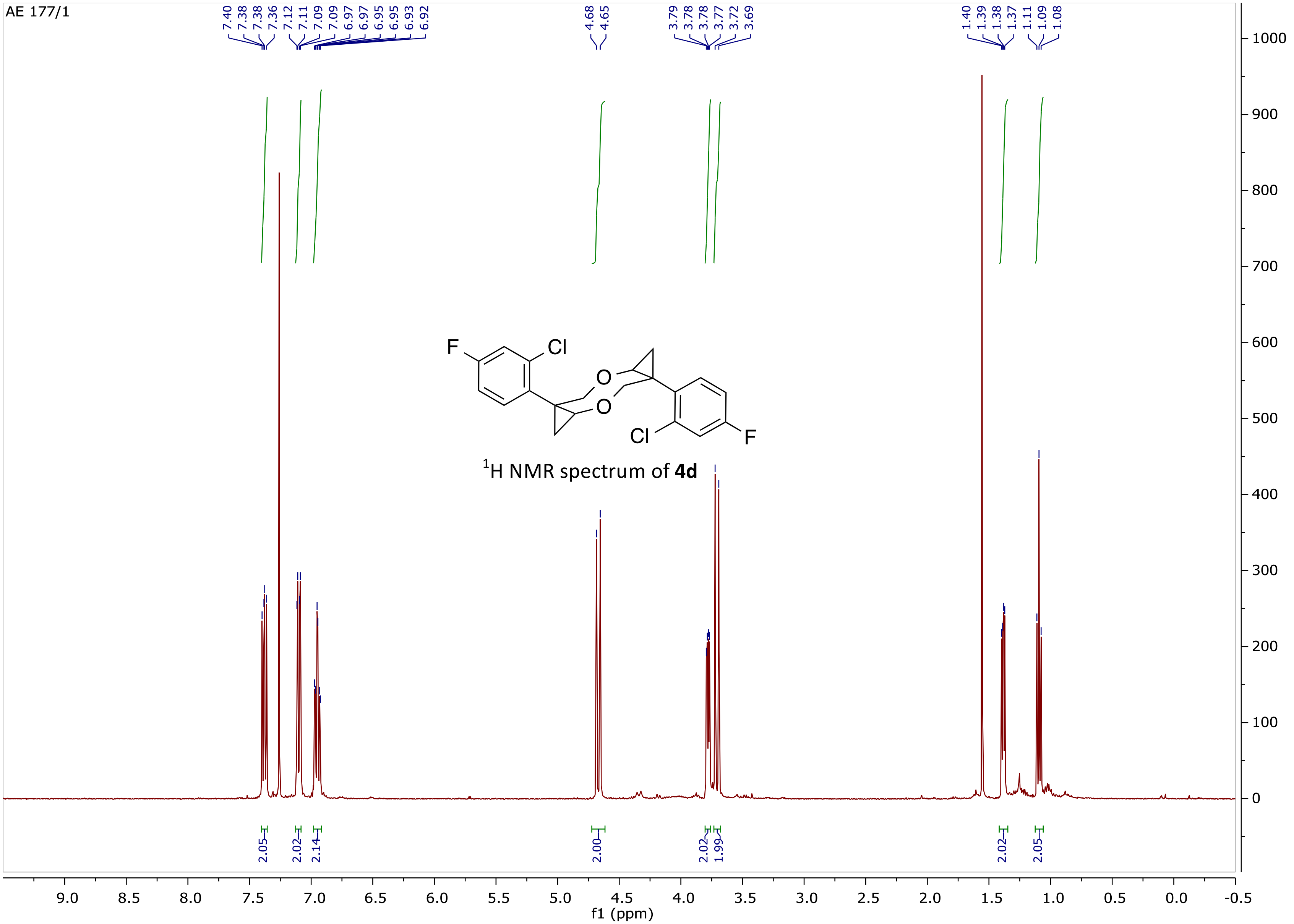
^{13}C NMR spectrum of **4b**



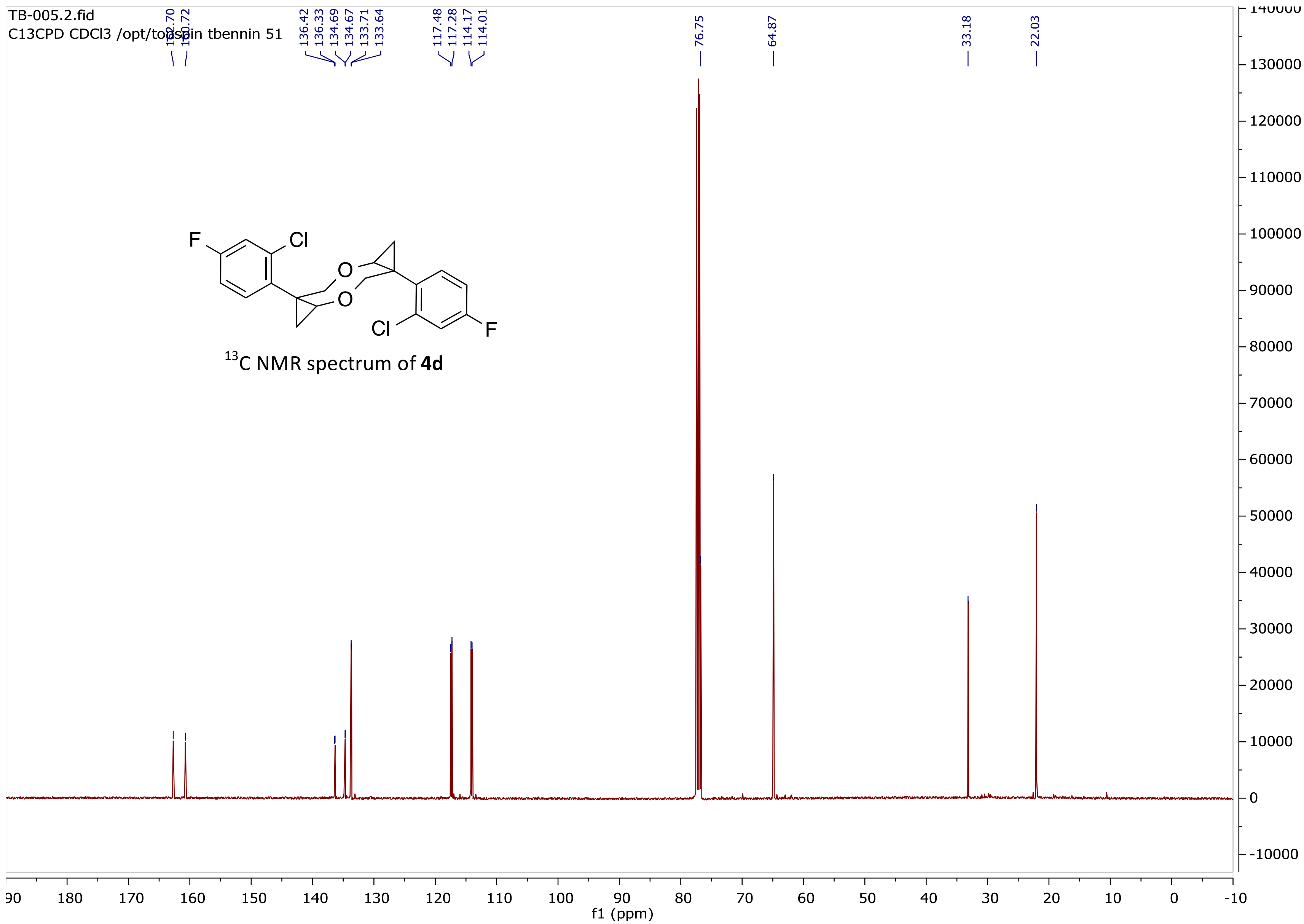
^{1}H NMR spectrum of **4c**



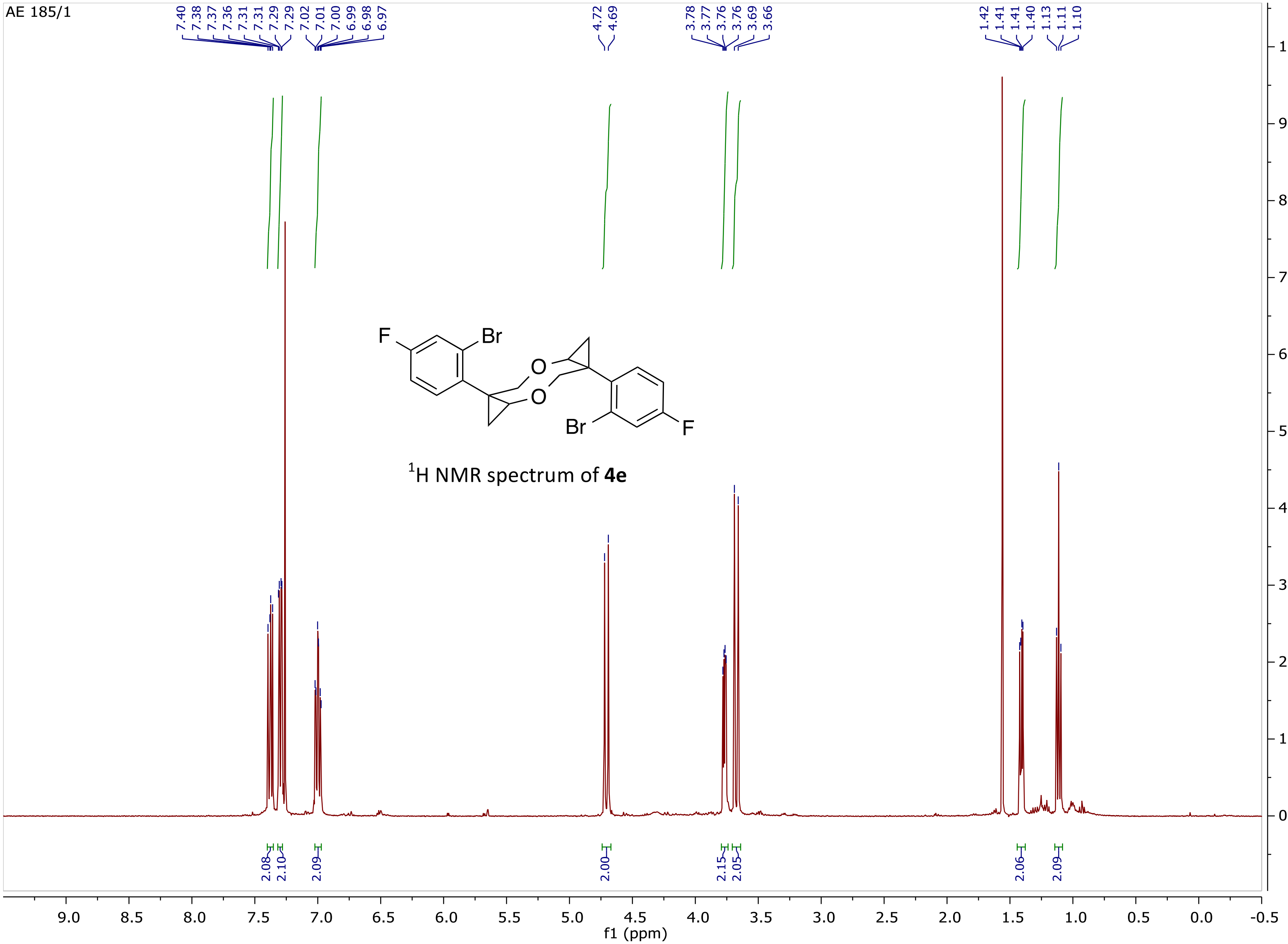
^{13}C NMR spectrum of **4c**



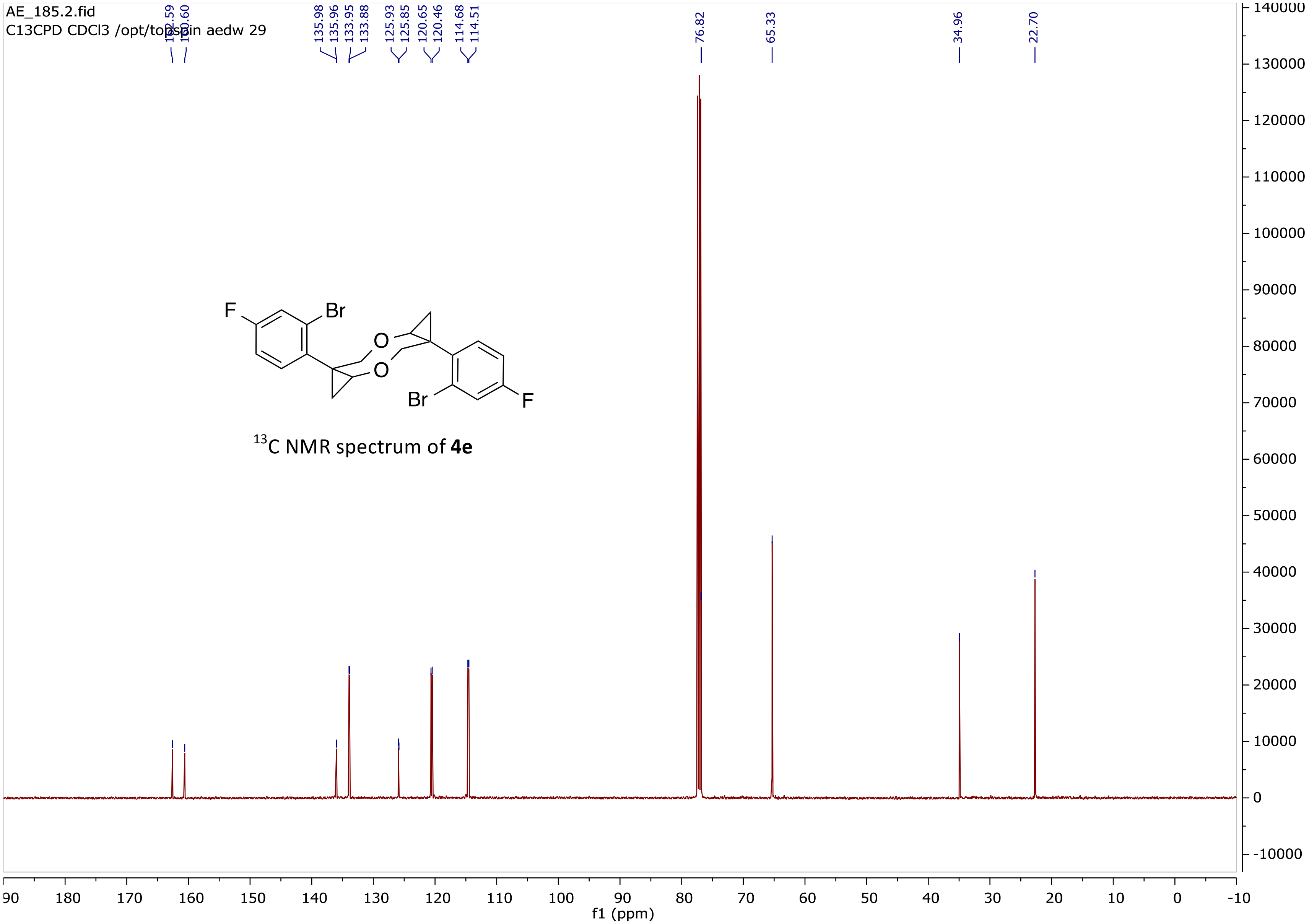
^{1}H NMR spectrum of **4d**



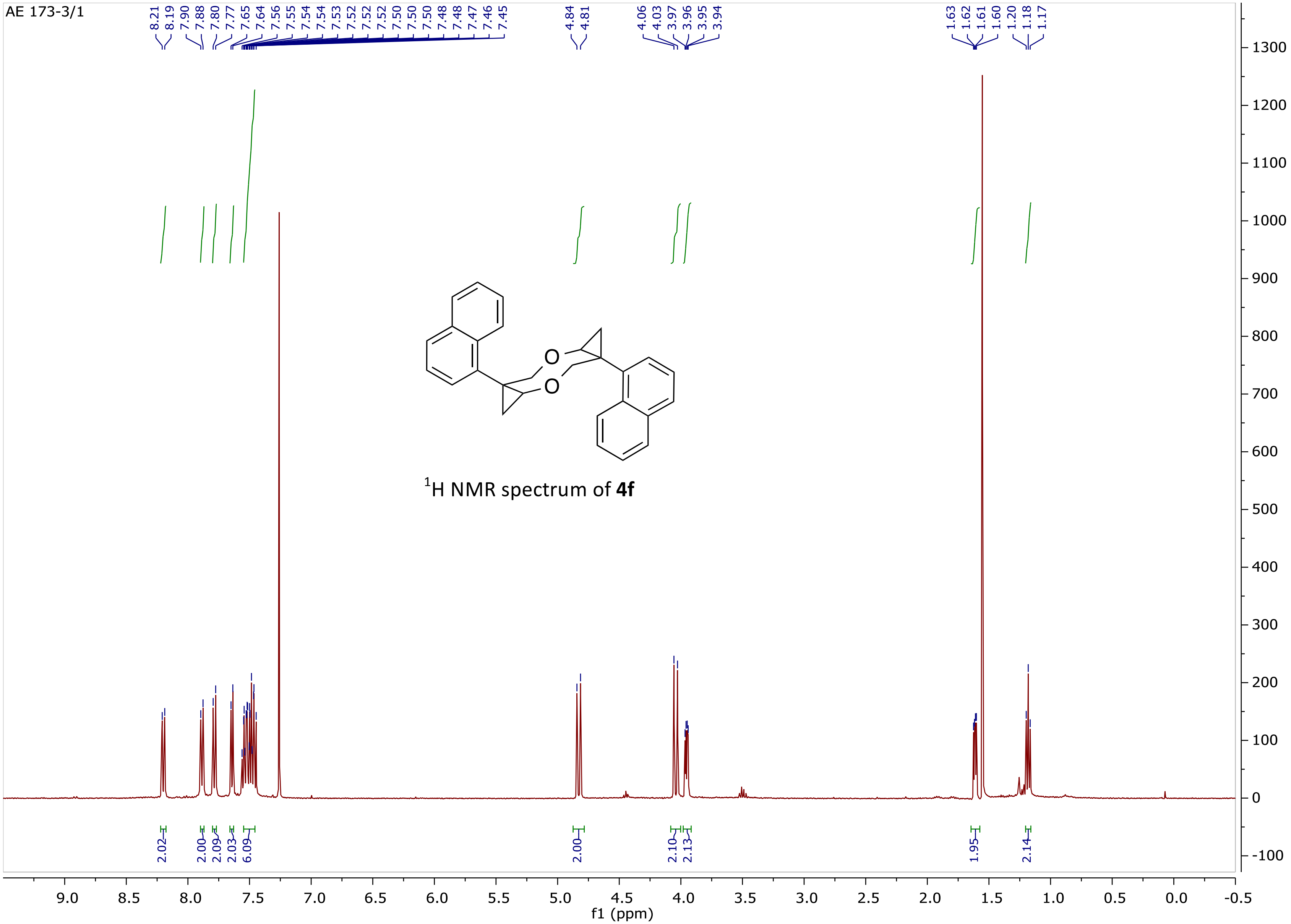
^{13}C NMR spectrum of **4d**



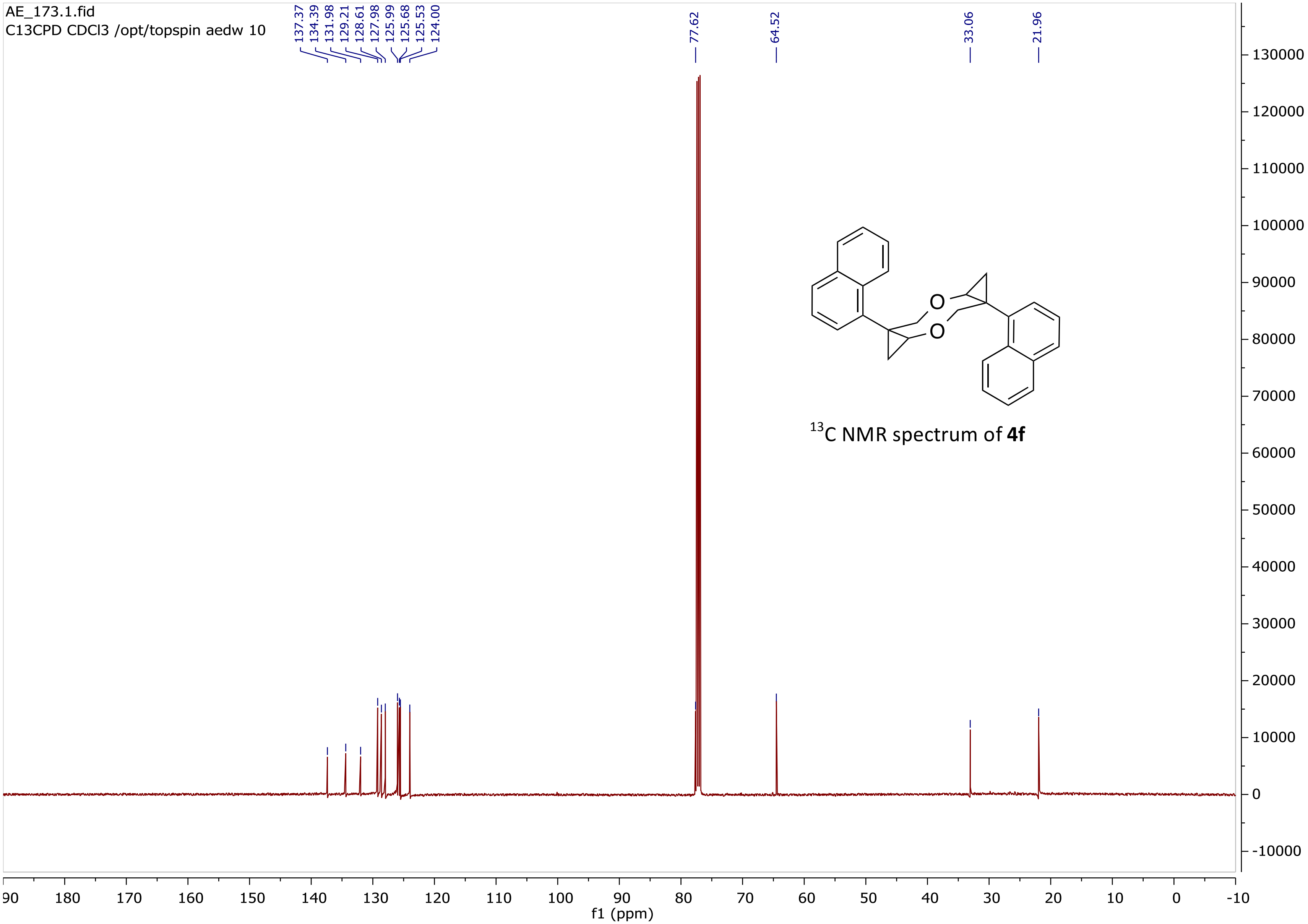
^{1}H NMR spectrum of **4e**



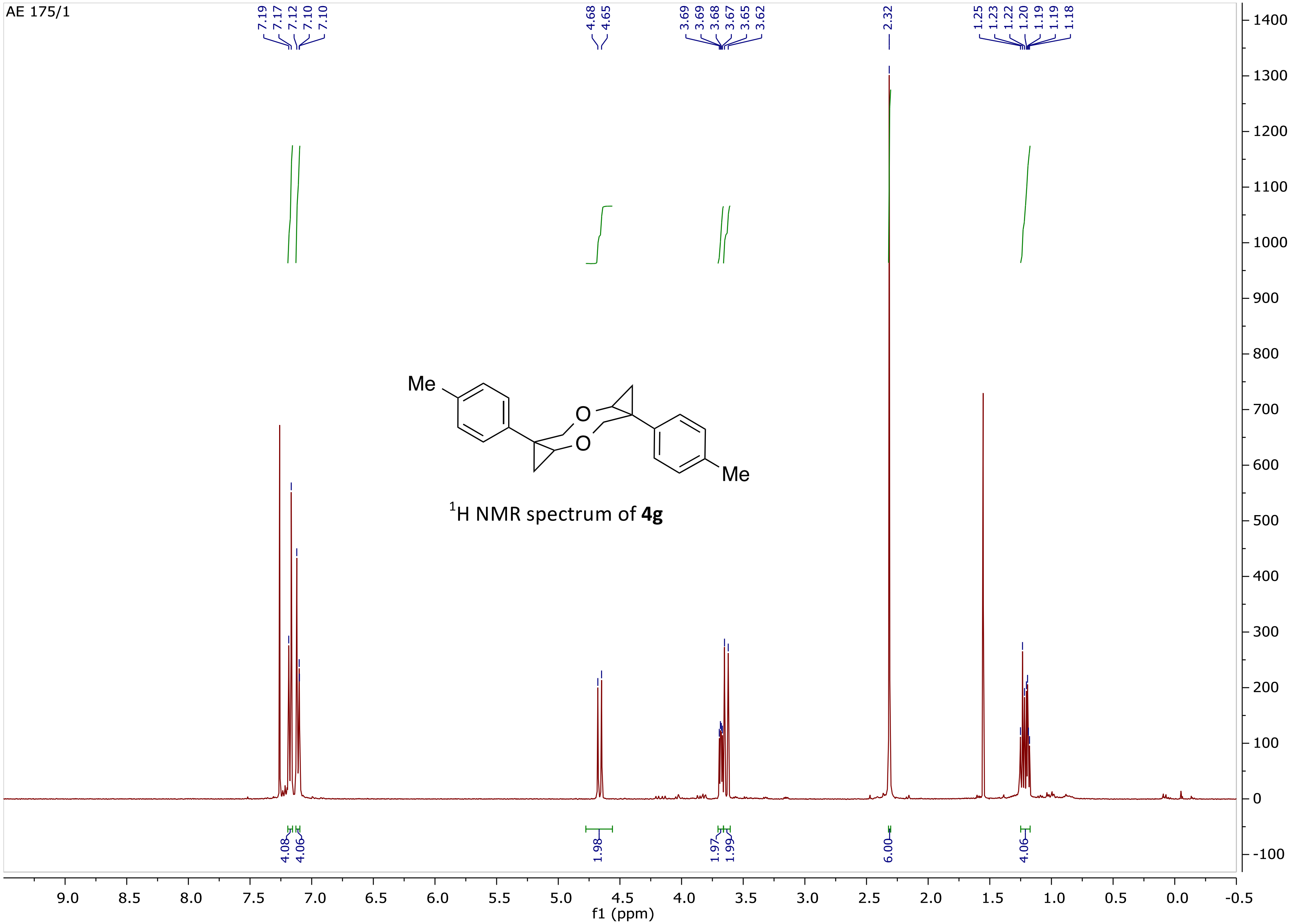
^{13}C NMR spectrum of **4e**



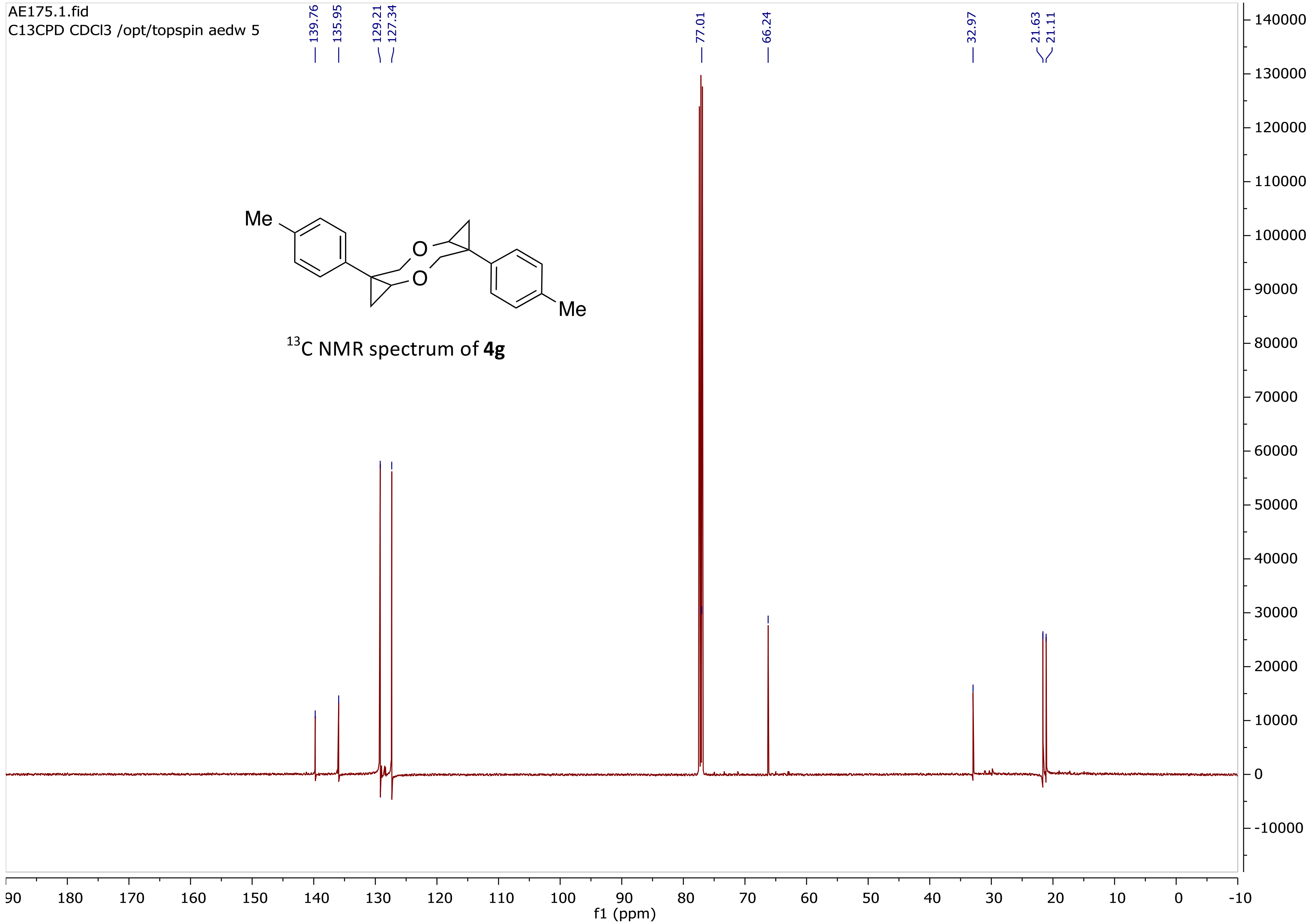
^{1}H NMR spectrum of **4f**



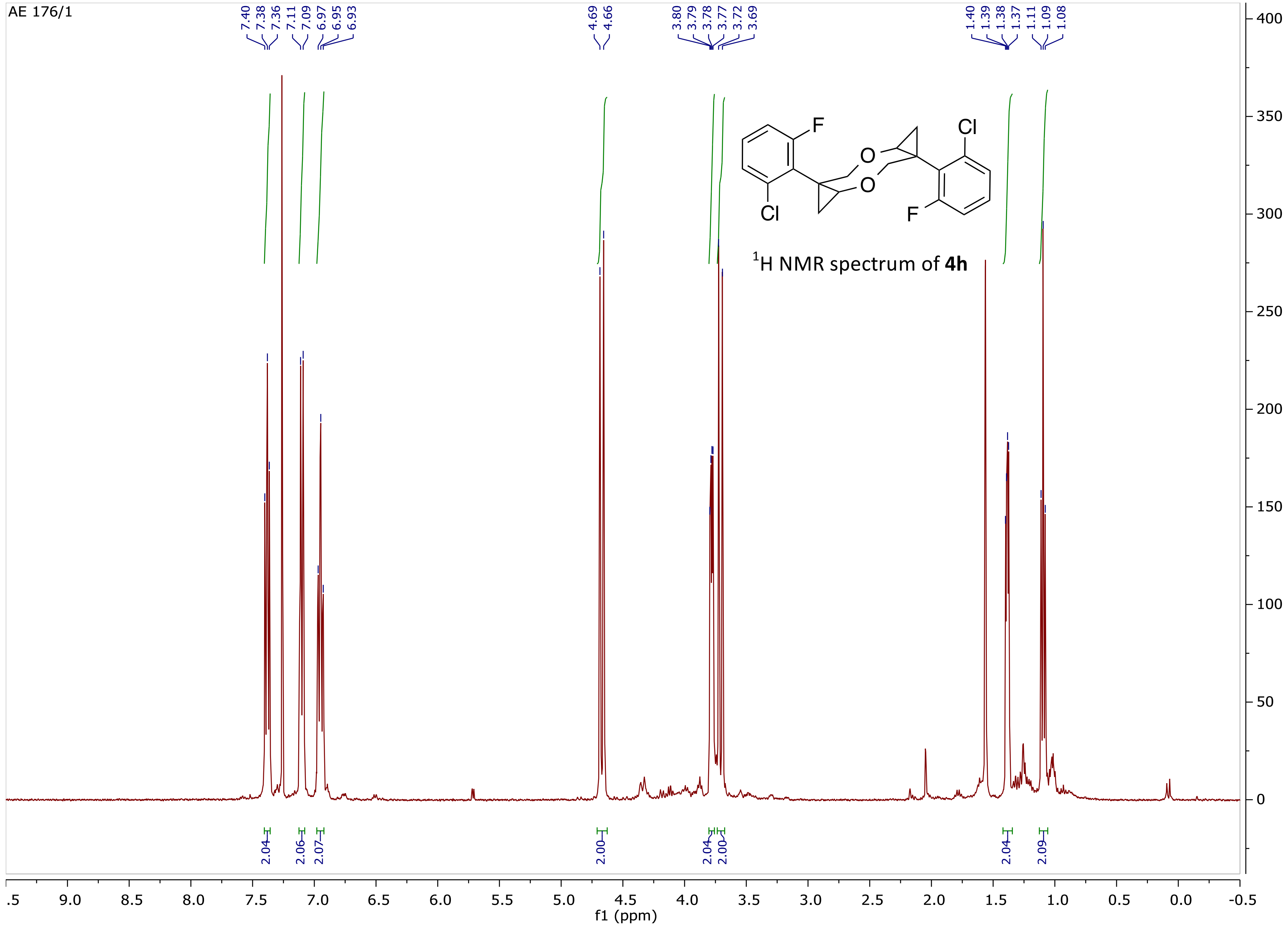
^{13}C NMR spectrum of **4f**



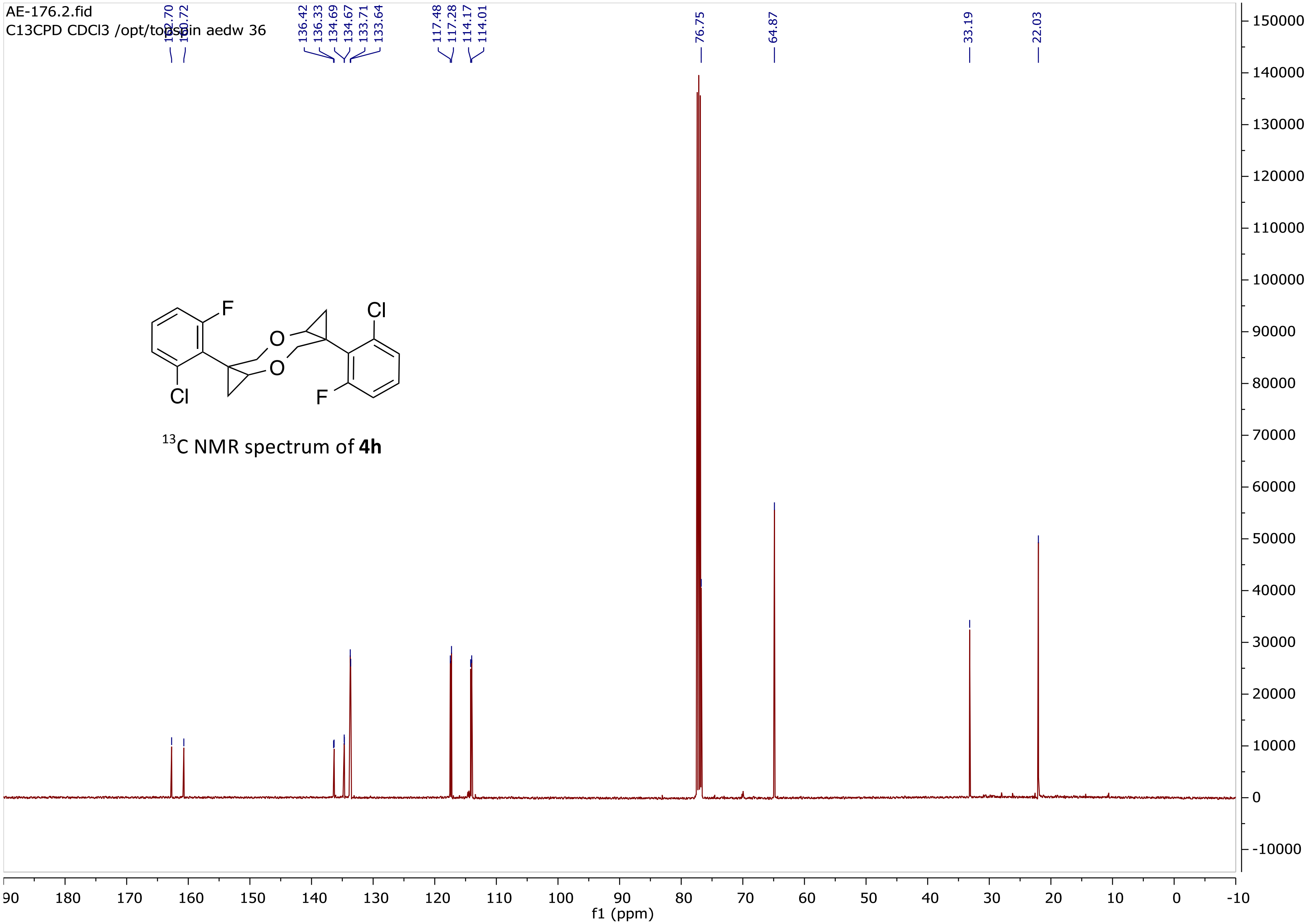
^{1}H NMR spectrum of **4g**



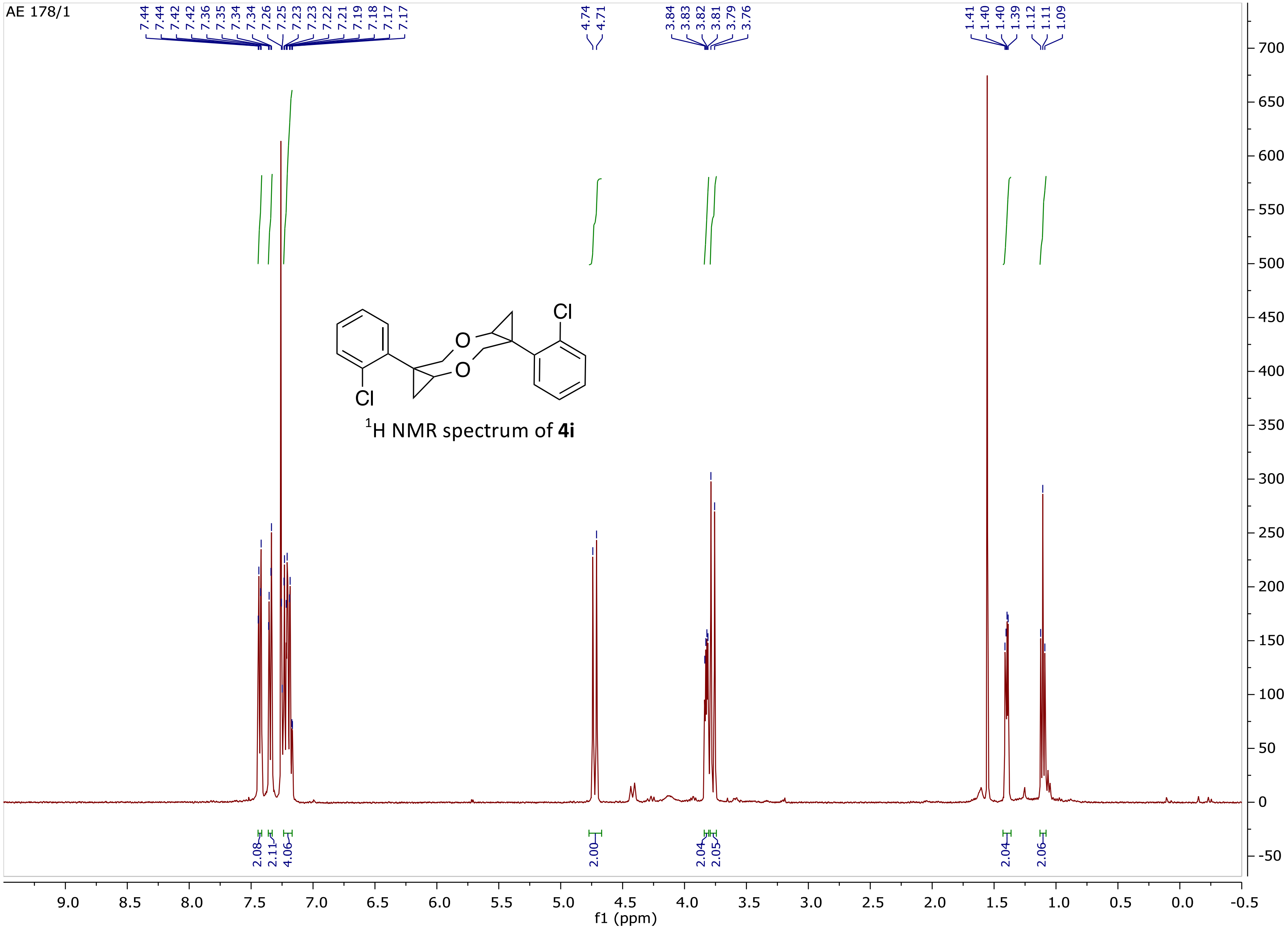
^{13}C NMR spectrum of **4g**



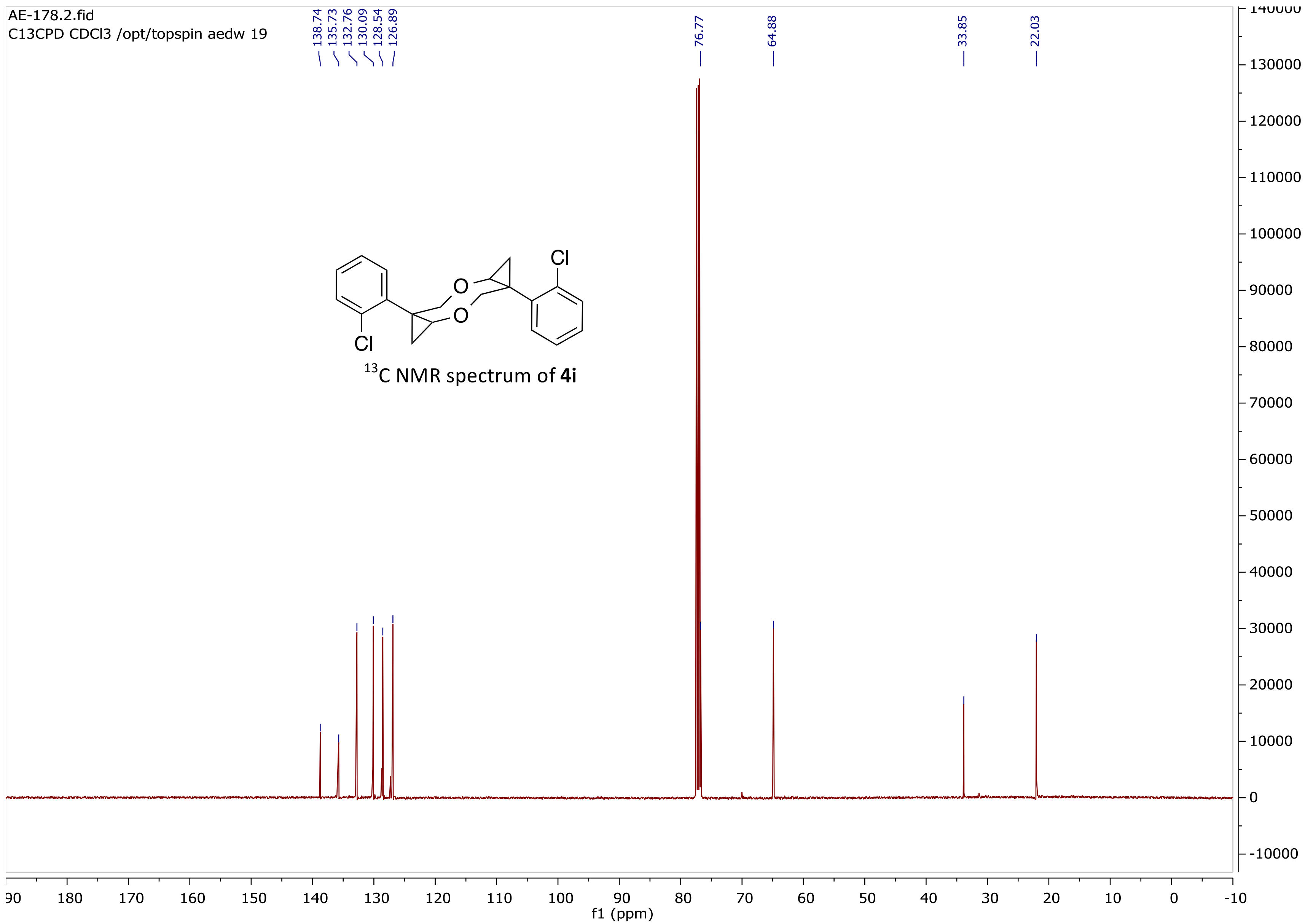
^{1}H NMR spectrum of **4h**



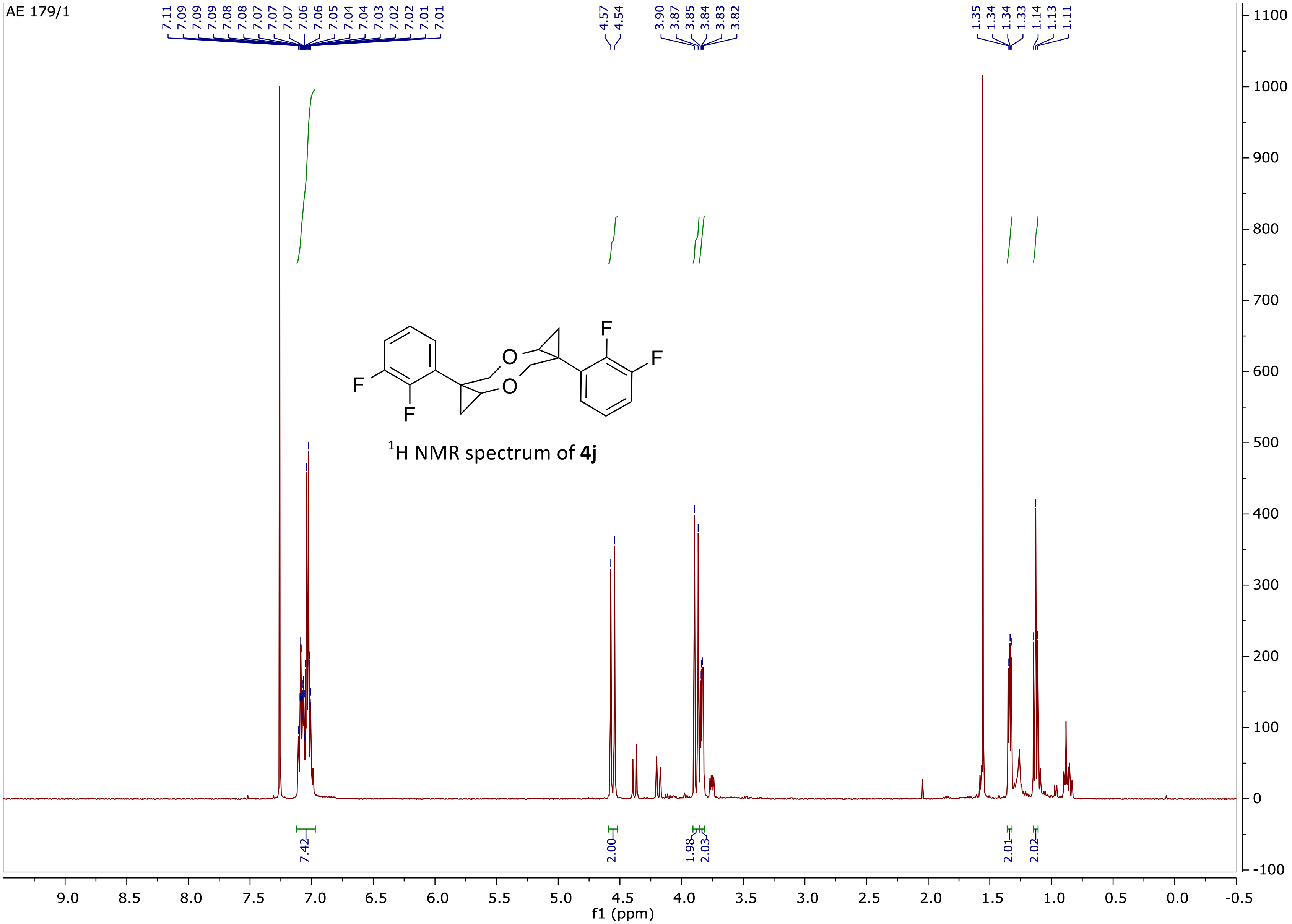
^{13}C NMR spectrum of **4h**



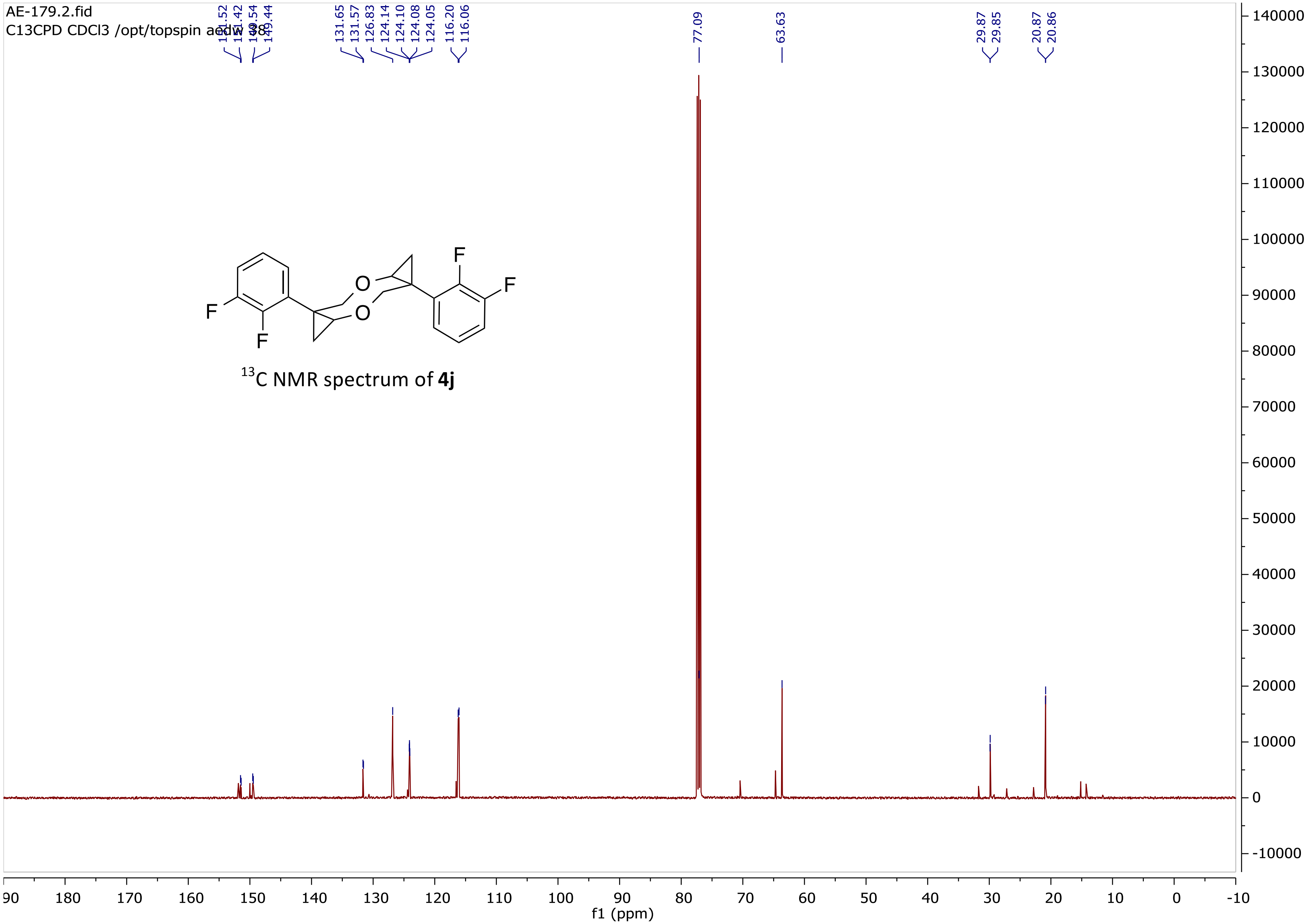
^{1}H NMR spectrum of **4i**



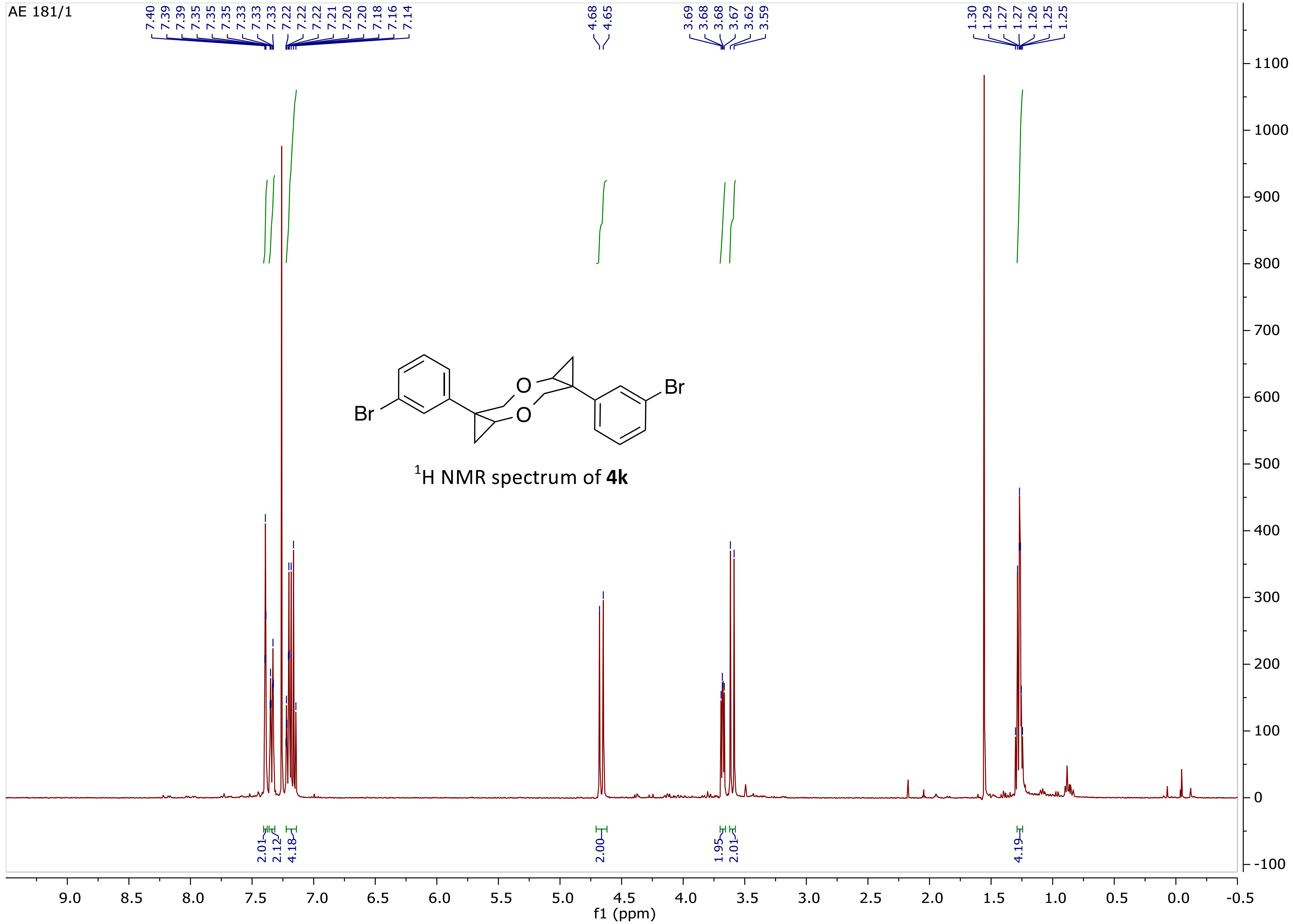
^{13}C NMR spectrum of **4i**



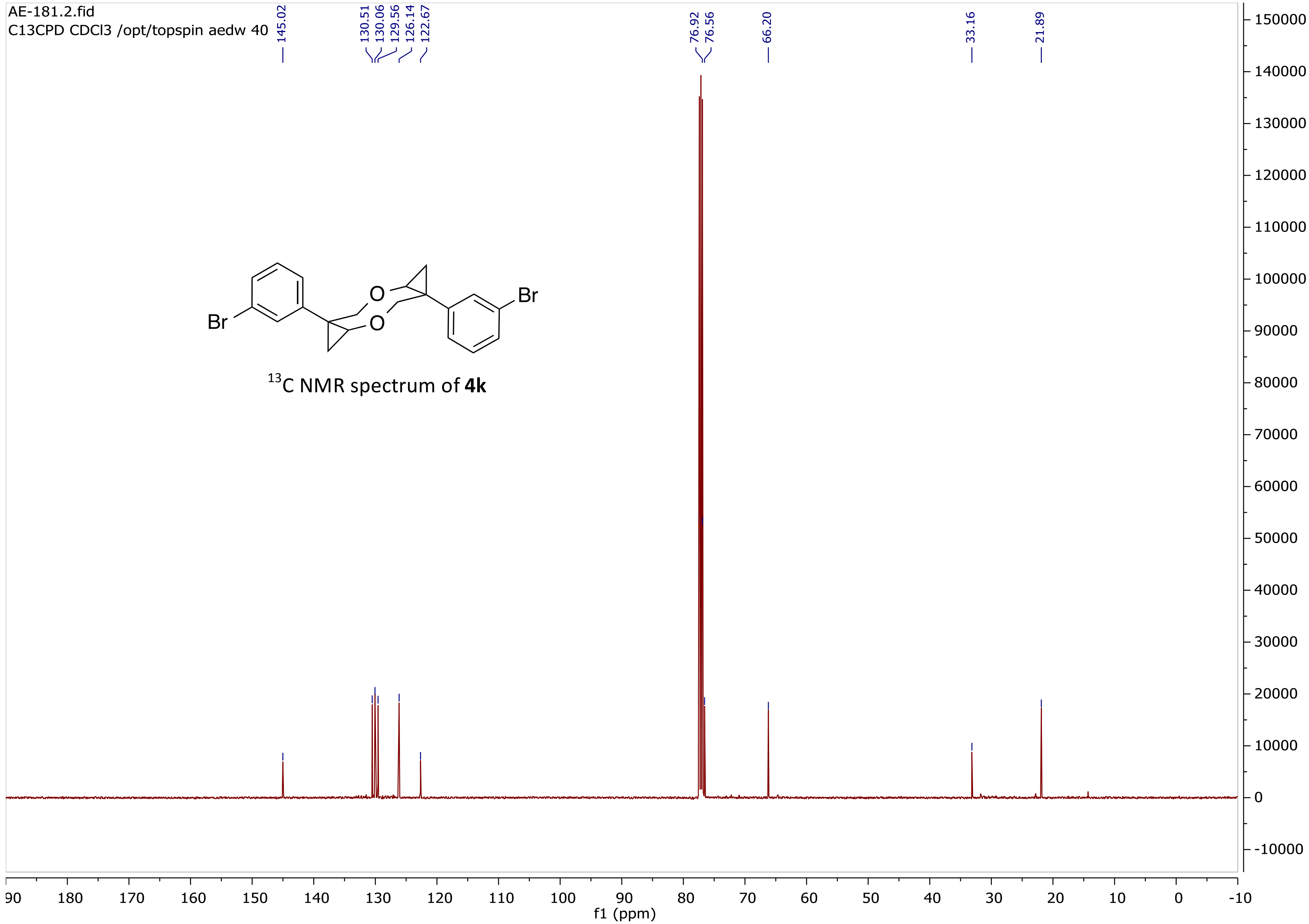
^{1}H NMR spectrum of **4j**



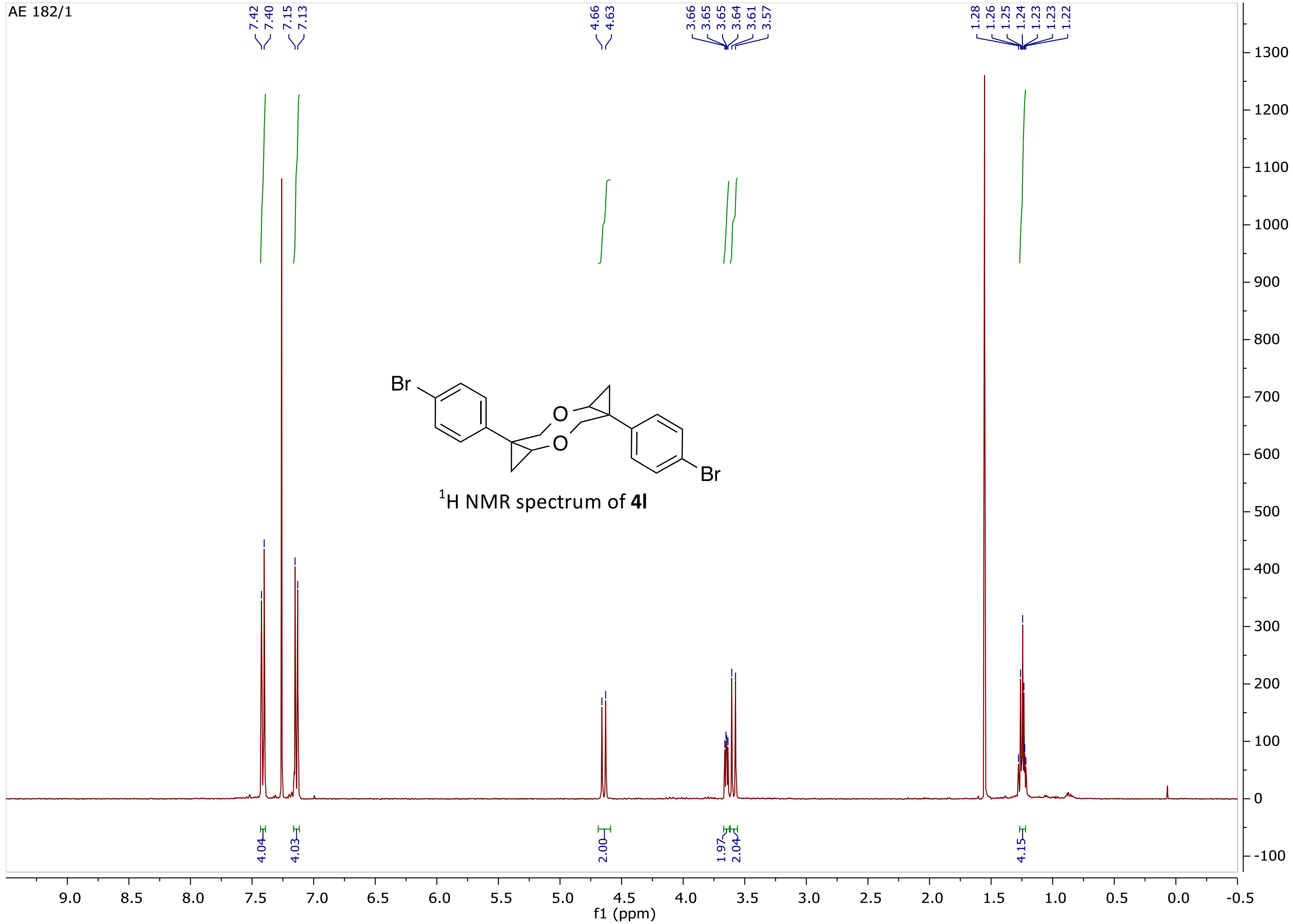
^{13}C NMR spectrum of **4j**



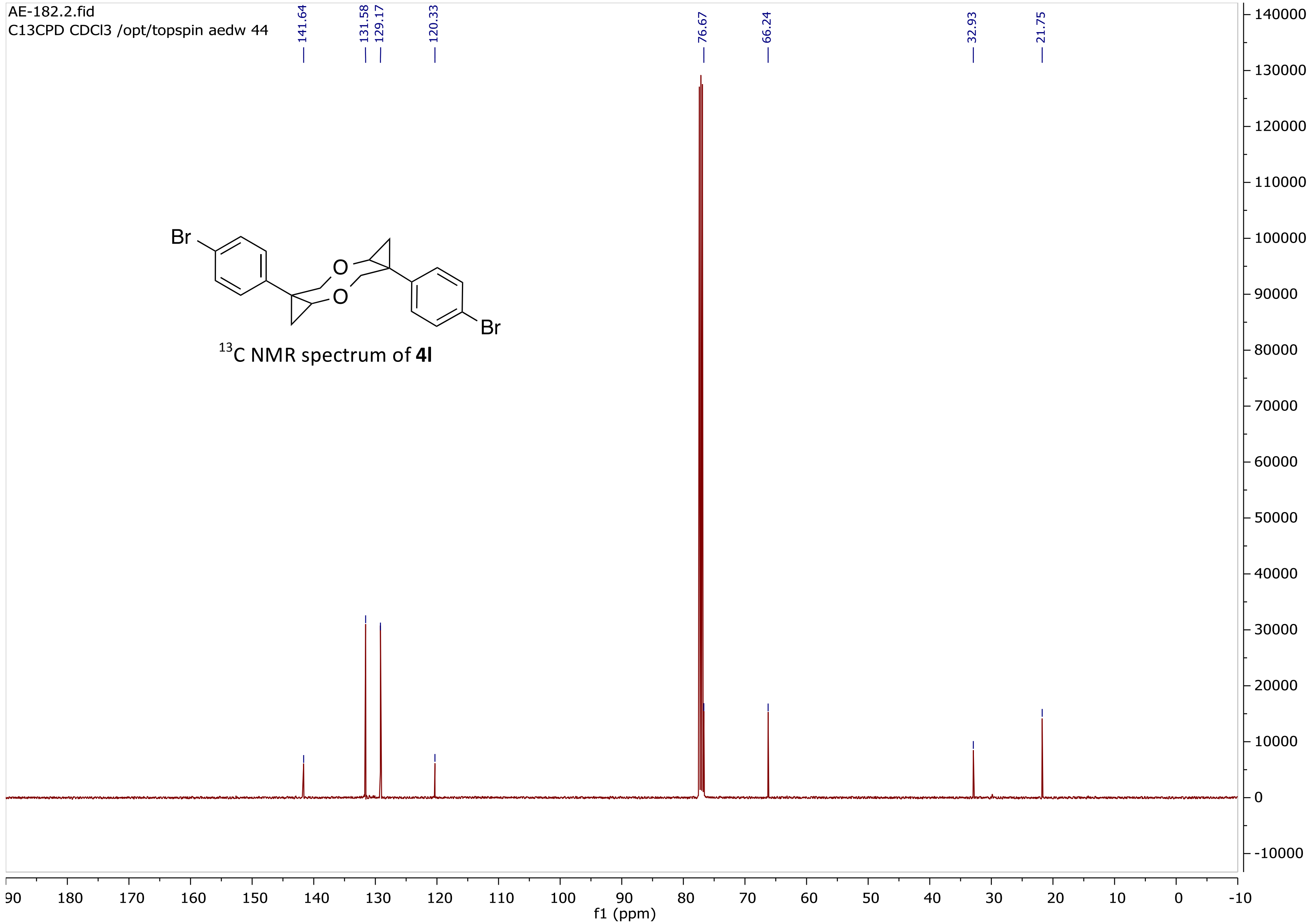
^{1}H NMR spectrum of **4k**



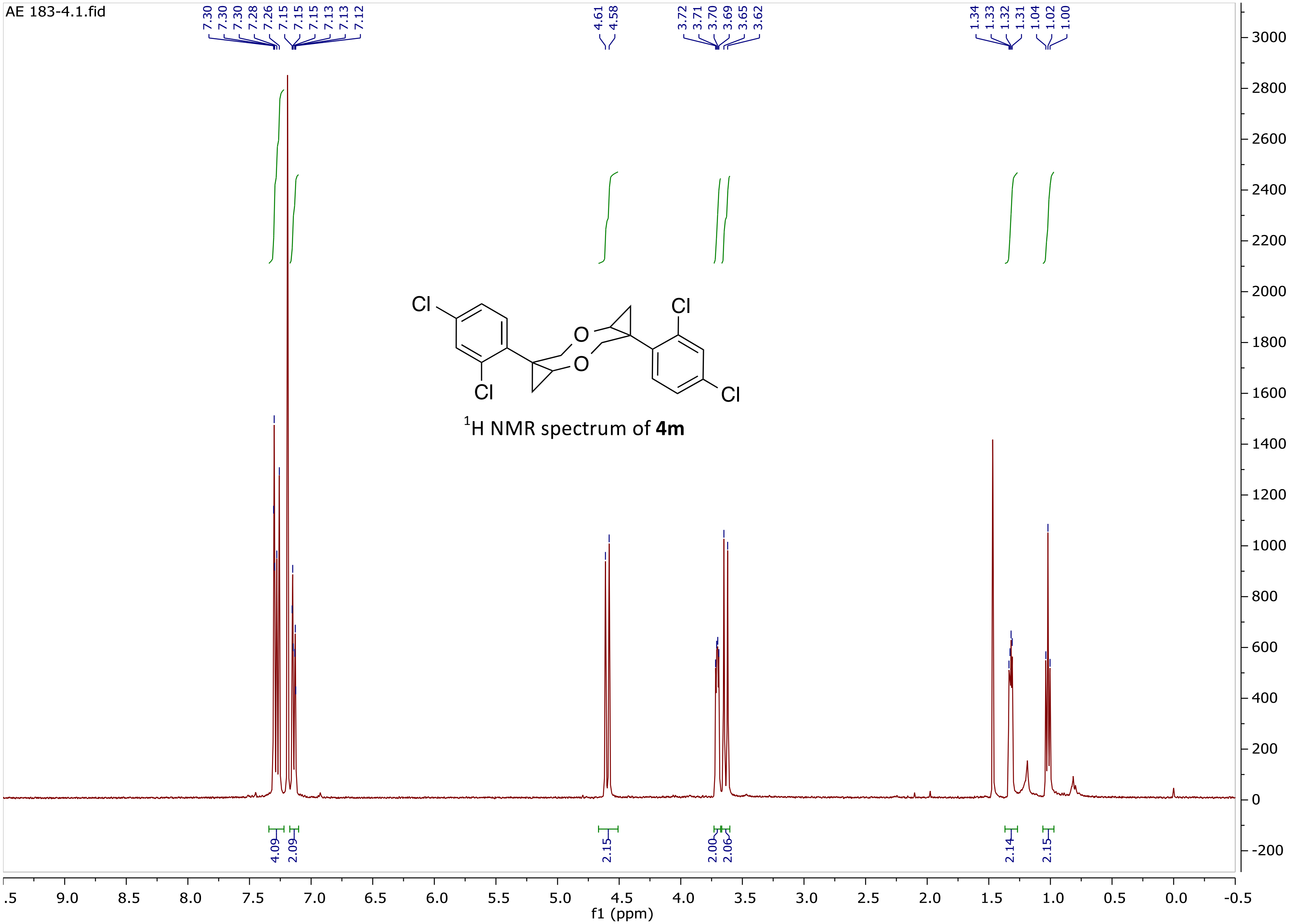
^{13}C NMR spectrum of **4k**



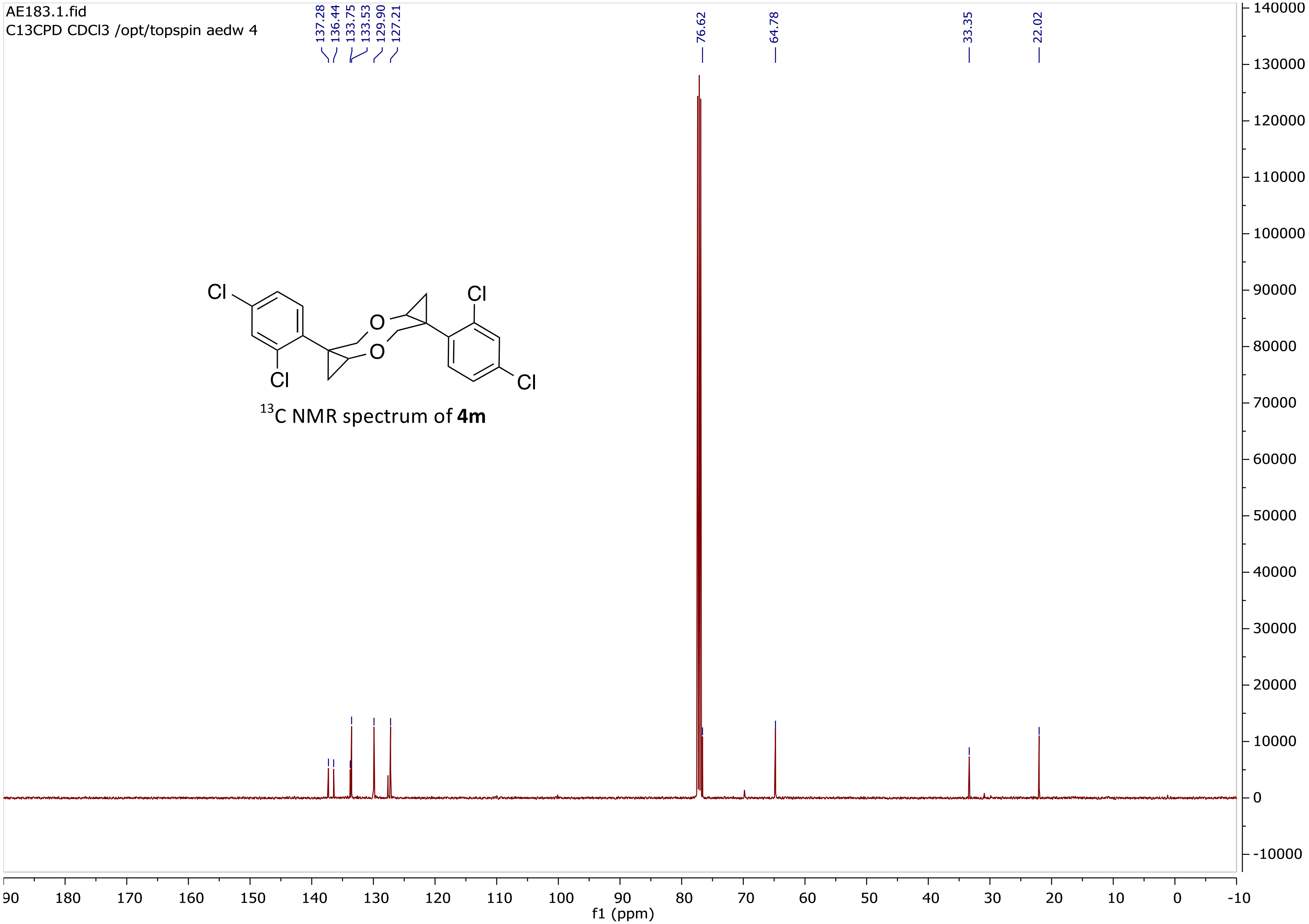
^{1}H NMR spectrum of **4l**



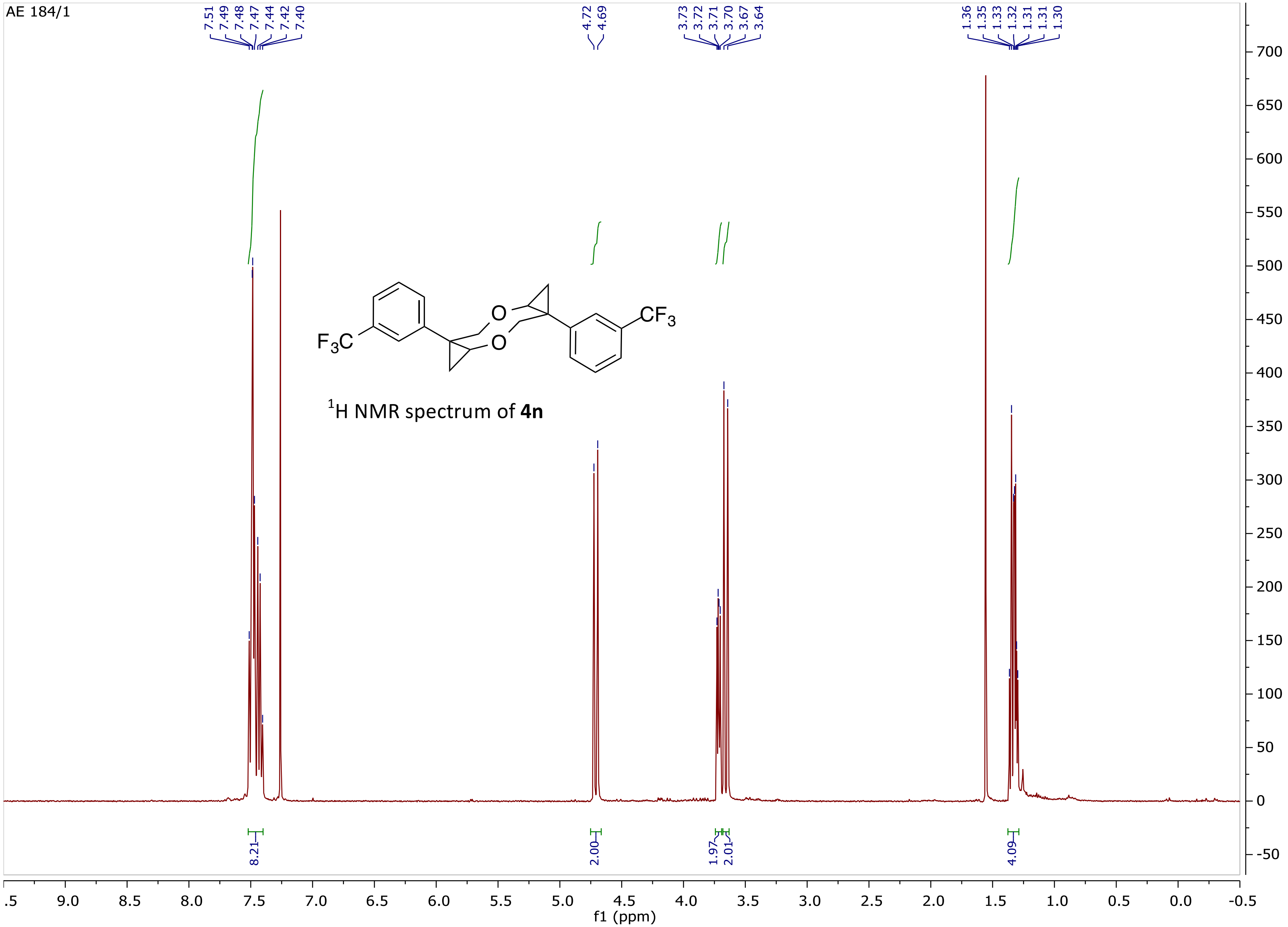
^{13}C NMR spectrum of **4l**



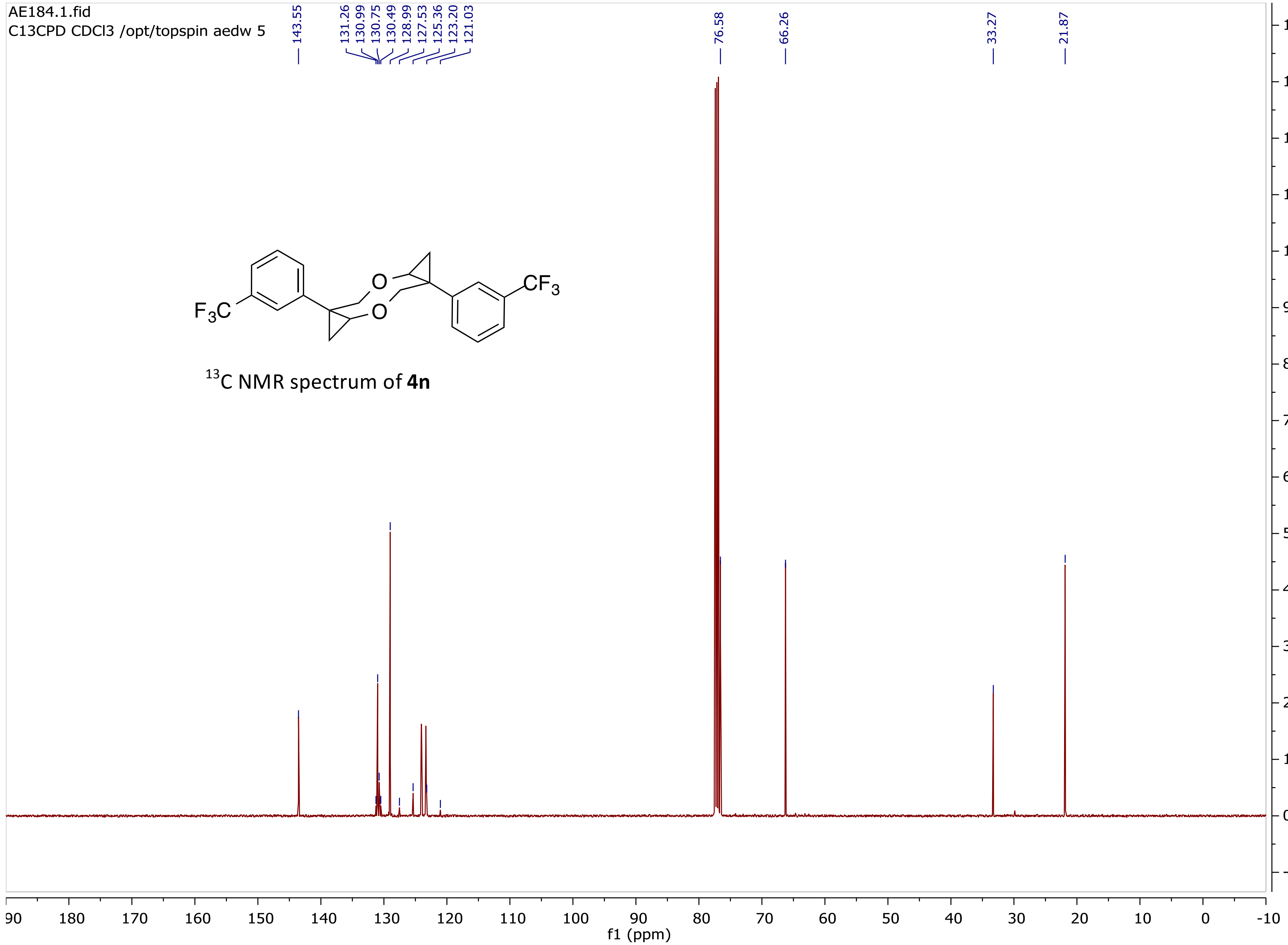
^{1}H NMR spectrum of **4m**



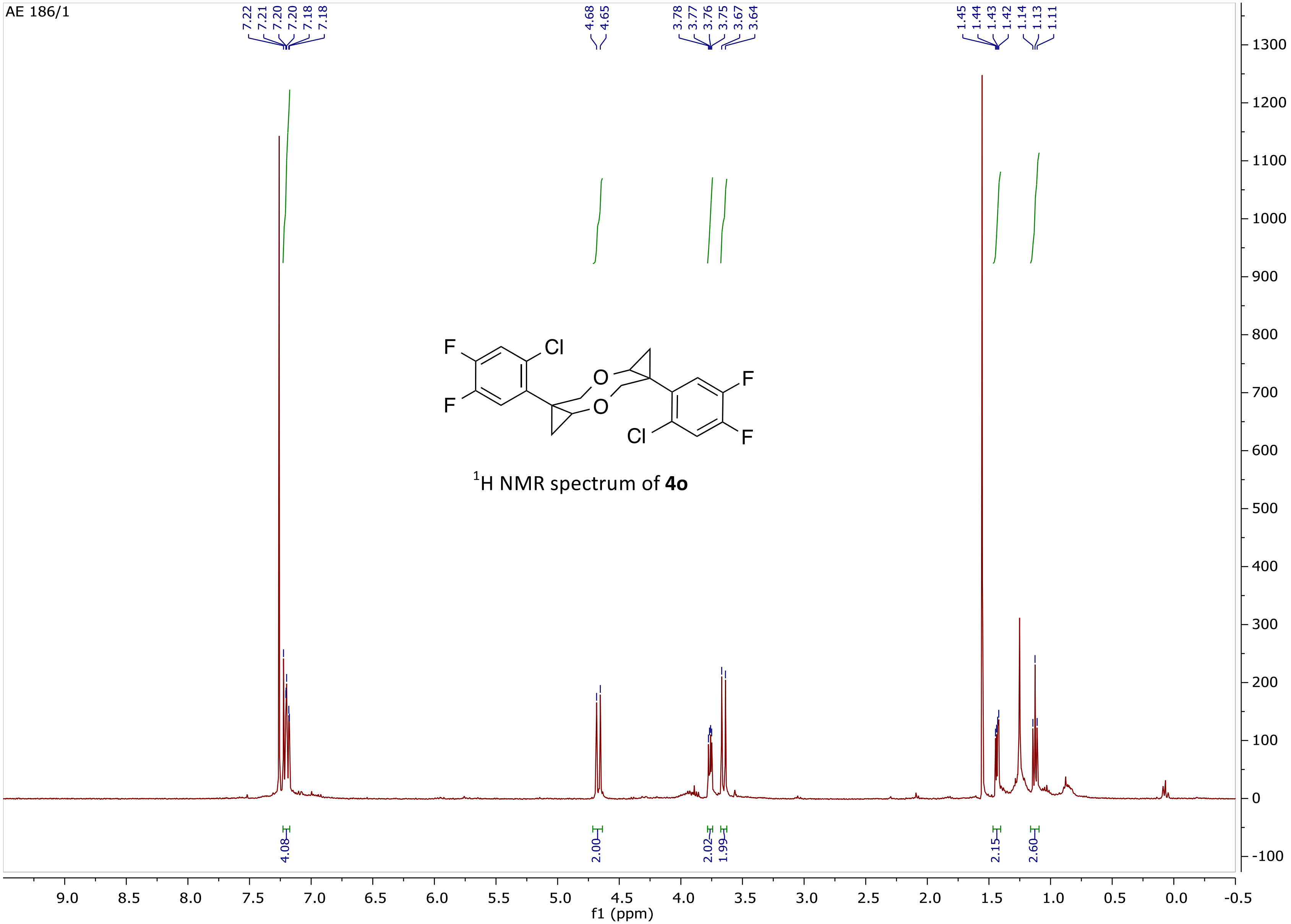
^{13}C NMR spectrum of **4m**



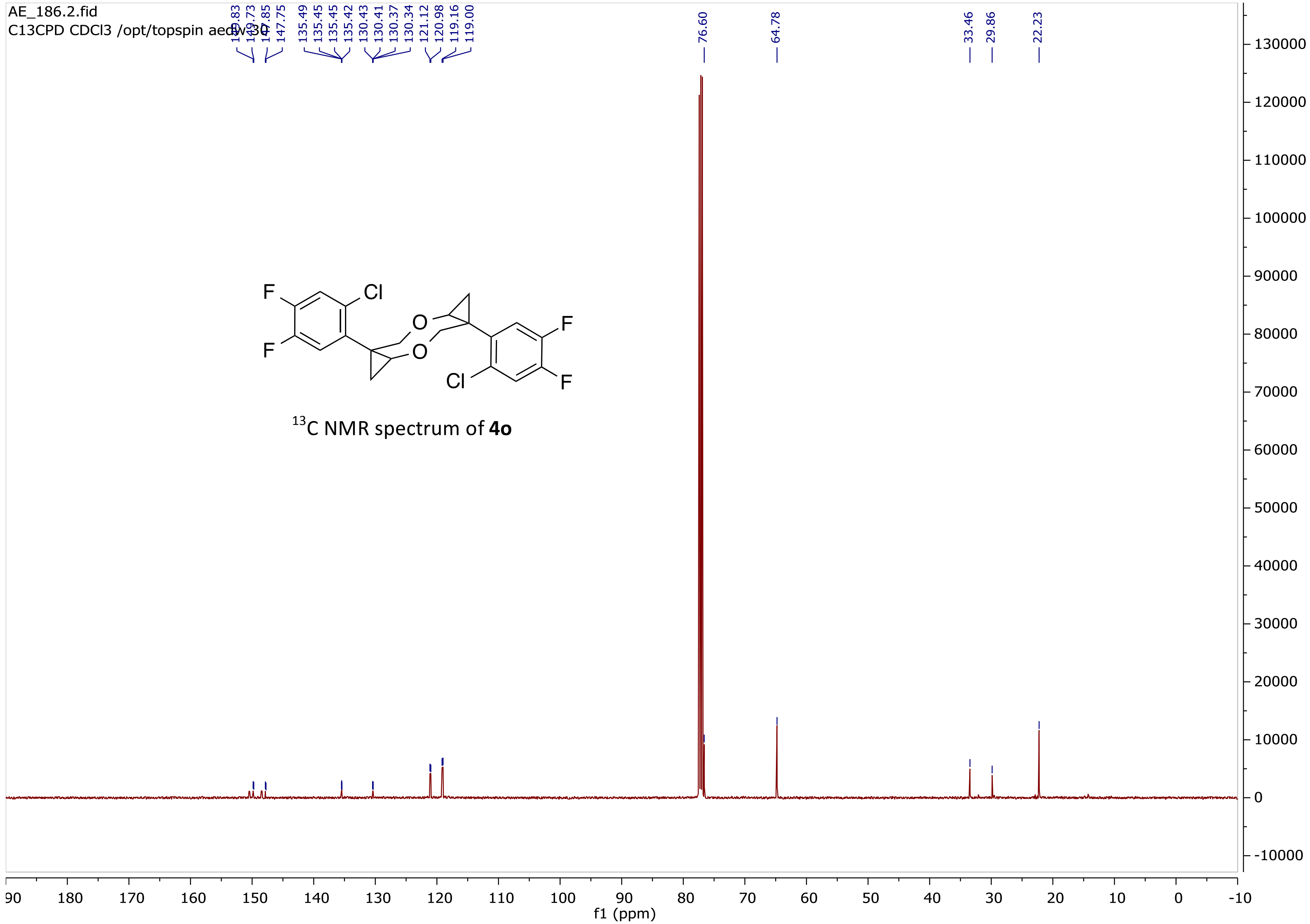
^{1}H NMR spectrum of **4n**



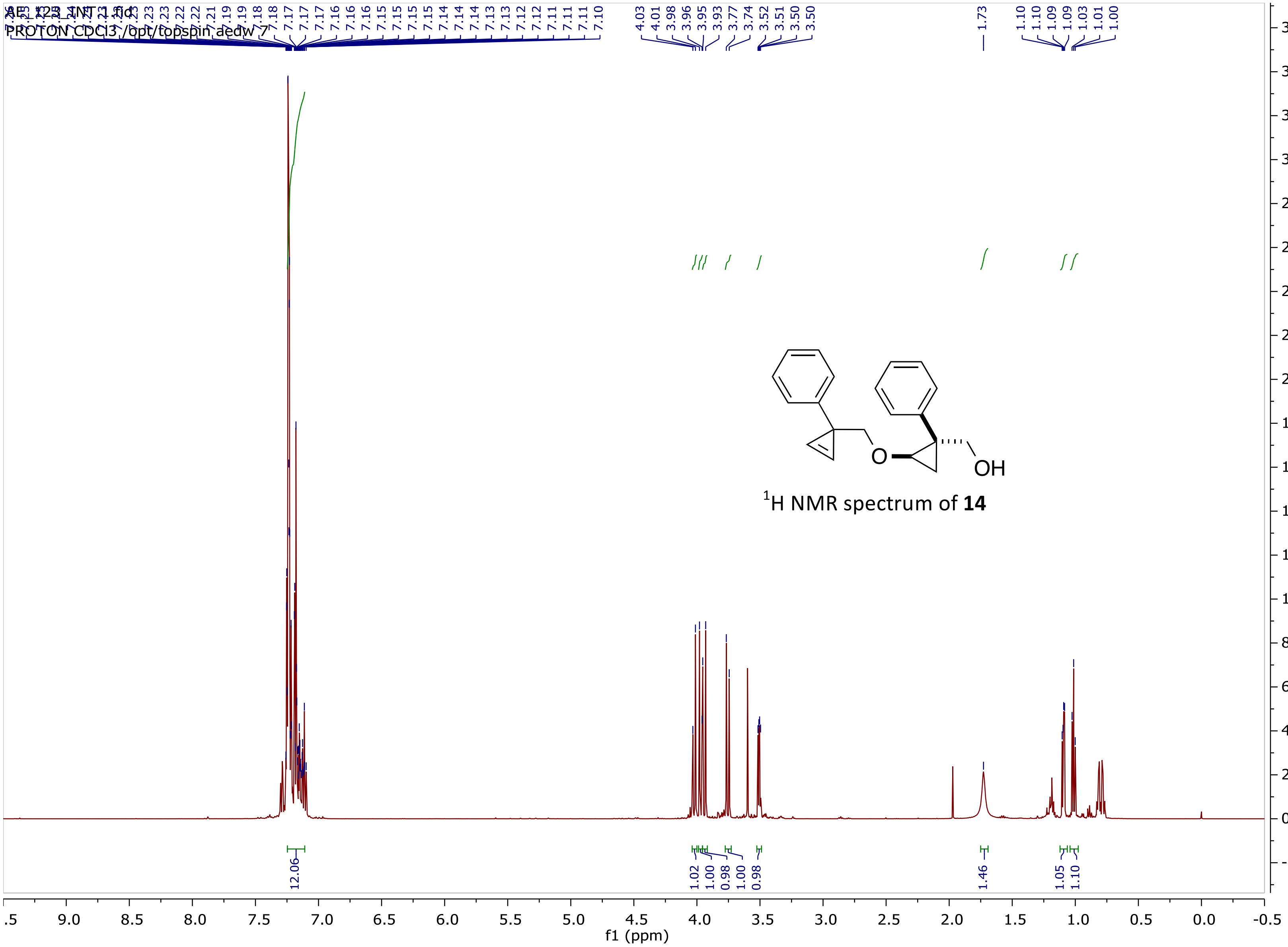
^{13}C NMR spectrum of **4n**



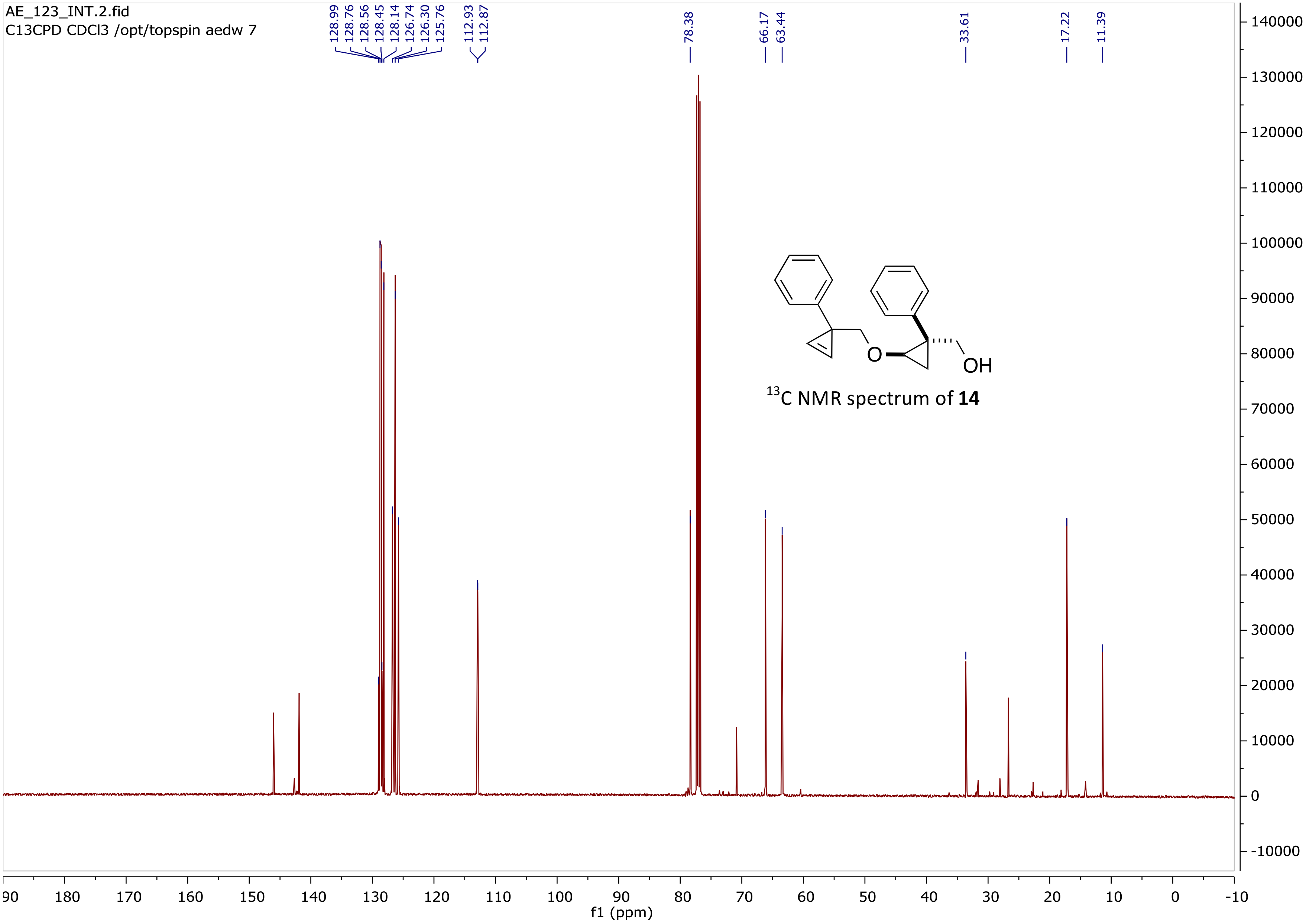
^{1}H NMR spectrum of **4o**



^{13}C NMR spectrum of **4o**



^{1}H NMR spectrum of **14**



^{13}C NMR spectrum of **14**