Supporting Information

Geminal Silicon/Zinc Reagent as equivalent of difluoromethylene bis-carbanion

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Content

Content of NMR spectra

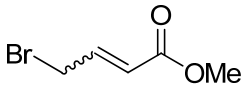
General Methods. All reactions were performed in Schlenk flasks under an argon atmosphere. DMF was distilled under vacuum from P_2O_5 and stored over MS 4A. Tetrahydrofuran was either vacuum transferred from sodium/benzophenone (for small scale experiments) or distilled from $LiAlH_4$ prior to use. Diglyme was distilled from sodium. Column chromatography was carried out employing silica gel (230-400 mesh). Precoated silica gel plates F-254 were used for thin-layer analytical chromatography visualizing with UV and/or acidic aq. $KMnO_4$ solution.

(Bromodifluoromethyl)trimethylsilane (**1**),[1] $CoBr_2$·dppe,[2] [1-(bromomethyl)vinyl]benzene (**4c**),[3] (6-bromocyclohex-1-en-1-yl)benzene (**4d**)[4] were prepared according to literature procedures.

Commercial reagents.

Allyl chloride (**4a**) methallyl chloride (**4b**), 3-bromocyclohexene (**4e**), cesium fluoride.
Commercial aldehydes were distilled under vacuum prior to use.

Methyl 4-bromobut-2-enoate (4f).[5]



A suspension of methylcrotonate (8.5 g, 85 mmol) and *N*-bromosuccinimide (15.9 g, 89 mmol) in carbon tetrachloride (40 mL) brought to reflux followed by addition of benzoylperoxide (10 mg). Then, the mixture was refluxed for 9 hours irradiating with CFL bulb (13 W). During this time two portions of benzoylperoxide (10 mg each portion) were added after three-hour intervals. The mixture was cooled to room temperature, quenched with water, and extracted with hexane twice. The combined organic phase was dried with Na_2SO_4, concentrated on a rotary evaporator, and the residue was distilled under vacuum. The fraction boiling at 95–98 °C/20 Torr was collected as a colorless liquid. Yield 10.2 g (67%).

Mixture of isomers, *E*/*Z* 13 : 1.

^{1}H NMR (300 MHz, $CDCl_3$), δ: *E*-isomer, 3.70 (m, 3H), 3.97 (d, 2H, *J* = 7.3), 5.99 (d, 2H, *J* = 15.6), 6.96 (dt, 1H, *J* = 15.6, 7.3); selected signals of *Z*-isomer, 4.49 (d, 2H, *J* = 8.0), 5.88 (d, 1H, *J* = 10.8), 6.37 (dt, 1H, *J* = 10.8, 8.0).

^{13}C NMR (75 MHz, $CDCl_3$), δ: *E*-isomer, 29.1, 51.8, 124.2, 142.0, 165.8; selected signals of *Z*-isomer, 25.9, 51.5, 121.5, 143.1.

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[1] Kosobokov, M. D.; Dilman, A. D.; Levin, V. V.; Struchkova, M. I. *J. Org. Chem.* **2012**, *77*, 5850–5855.

[2] Konarev, D. V.; Kuzmin, A. V.; Simonov, S. V.; Khasanov, S. S.; Yudanova, E. I.; Lyubovskaya, R. N. *Dalton Trans.* **2011**, *40*, 4453–4458.

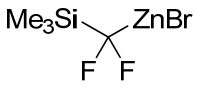
[3] Maligres, P. E.; Waters, M. M.; Lee, J.; Reamer, R. A.; Askin, D.; Ashwood, M. S.; Cameron, M. *J. Org. Chem.* **2002**, *67*, 1093–1101.

[4] Zemtsov, A. A.; Kondratyev, N. S.; Levin, V. V.; Struchkova, M. I.; Dilman, A. D. *J. Org. Chem.* **2014**, *79*, 818–822.

[5] Pullin, R. D. C.; Rathi, A. H.; Melikhova, E. Y.; Winter, C.; Thompson, A. L.; Donohoe, T. J. *Org. Lett.* **2013**, *15*, 5492–5495.

Prepartion of isopropylzinc iodide (*i*-PrZnI). 2-Iodopropane (20 mmol, 2 mL) was added to a stirred suspension of zinc dust (120 mmol, 7.85 g) in THF (7 mL), and the mixture was vigorously stirred. The exothermic reaction begins, and the temperature was allowed to rise until the solvent starts boiling. At this point, THF (33 mL) was added gradually at such a rate to maintain the temperature slightly below refluxing point. When all THF was added, the reaction flask was immersed into room temperature water bath, and the remaining 2-iodopropane (80 mmol, 8 mL) was added within two minutes. The resulting mixture was stirred 18 hours. The stirring was discontinued, and the unreacted zinc was allowed to settle down (ca. 20 h). The concentration of organozinc reagent was determined by iodometric titration.

Preparation of difluoro(trimethylsilyl)methylzinc bromide (2).



Diglyme (15 mL) was added to a solution of *i*-PrZnI (15 mL of 2M solution in THF, 30 mmol), and the reaction flask was immersed in ice/water bath. Then, Me_3SiCF_2Br (5.08 g, 25 mmol) and $CoBr_2$·dppe (0.25 mmol, 153 mg) were successively added. The mixture was stirred for 20 min to form dark grey homogeneous solution, which was kept for 20 hours at 5 °C. The concentration of the reagent **2** was determined by ^{19}F NMR spectroscopy using $PhCF_3$ as internal standard to be 0.67M. Yield 90%.

Analysis of **2** can be conveniently performed by measuring ^{19}F NMR spectra of reaction mixtures without deuterated co-solvent:

^{19}F NMR (282 MHz, THF/diglyme), δ: –130.4 (s, major), –130.7 (s, minor); major : minor = 93 : 7.

Preparation of crystals. An aliquot of a solution of **2** was concentrated [first, the vacuum of about 10-20 Torr was applied at room temperature; then, oil pump vacuum was used with heating in water bath at 30 °C]. The residue was dissolved in methyl *tert*-butyl ether (*ca.* double volume of the residue), and the solution was allowed to stand overnight in the freezer (ca. –30 °C) to afford clear colorless crystals of Me_3SiCF_2ZnBr·diglyme. Mp 72–74 °C.

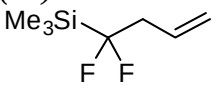
^1H NMR (300 MHz, CD_3CN), δ: 0.02 (s, 9H); diglyme: 3.29 (s, 3H), 3.45–3.5 (m, 4H), 3.53–3.60 (m, 4H).

^{13}C NMR (75 MHz, CD_3CN), δ: –4.6 (t, J = 3.5), 58.9, 70.8, 72.2, 159.5 (t, J = 272.9).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –132.3 (s, 2F).

Synthesis of silanes 5a,b. Reagent **2** (22.5 mmol) was prepared from 25 mmol of Me_3SiCF_2Br. From the obtained solution, volatile components (THF, *i*-PrI) were evaporated under vacuum [first, the vacuum of about 10-20 Torr was applied at room temperature; then, oil pump vacuum was used with heating in water bath at 30 °C]. The residue was cooled with ice/water bath, allylating substrate (**4a** or **4b**, 27.5 mmol) and CuCN (1.25 mmol, 112 mg) were added, and the mixture was allowed to warm slowly (during 5 h) to room temperature and stirred for additional 12 h. The product and a part of diglyme were distilled from the reaction mixture at 12 Torr collecting in a receiver flask cooled to –30 °C. The collected distillate was washed with water (5 mL), aqueous HCl (1M, 3×5 mL), water (3 mL) and brine (3 mL). The liquid was dried over $MgSO_4$, filtered, and distilled at atmospheric pressure.

*(1,1-Difluorobut-3-enyl)(trimethyl)silane (**5a**).*



Yield 3.24 g (88%). Bp 120–122 °C. Colorless liquid.

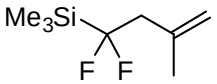
^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.20 (s, 9H), 2.63 (td, 2H, *J* = 21.1, 6.7), 5.12–5.29 (m, 2H), 5.76–5.96 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: –4.2 (t, *J* = 2.0), 41.4 (t, *J* = 21.0), 119.9, 129.1 (t, *J* = 259.7), 129.9 (t, *J* = 8.3).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –112.7 (t, *J* = 21.1).

Calcd for $C_7H_{14}F_2Si$ (164.27): C, 51.18; H, 8.59. Found: C, 51.18; H, 8.58.

*(1,1-Difluoro-3-methylbut-3-enyl)(trimethyl)silane (**5b**).*



Yield 2.72 g (68%). Colorless liquid. Bp 136–148 °C.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.18 (s, 9H), 1.84 (s, 3H), 2.56 (t, 2H, *J* = 22.0), 4.86 (s, 1H), 4.96 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 4.2 (t, *J* = 1.7), 23.8 (t, *J* = 1.7), 44.6 (t, *J* = 20.3), 116.4, 129.8 (t, *J* = 260.2), 138.8 (t, *J* = 5.3).

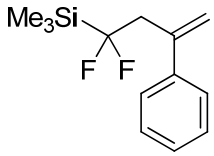
^{19}F NMR (282 MHz, $CDCl_3$), δ: –110.4 (t, *J* = 22.0).

Calcd for $C_8H_{16}F_2Si$ (178.29): C, 53.89; H, 9.05. Found: C, 53.74; H, 9.11.

Synthesis of silanes 5c,d.

Reagent **2** (5 mmol) was prepared from 5.5 mmol of Me_3SiCF_2Br. The obtained solution was cooled with ice/water bath, allylating reagent (**4c** or **4d**, 5 mmol) and CuCN (0.25 mol, 22 mg) were added, and the mixture was allowed to warm slowly (during 5 h) to room temperature and stirred for additional 12 h. The mixture diluted with water (7 mL) and the product was extracted with hexane (3×5 mL). The combined organic phases were washed with HCl (1M, 3×5 mL), water (3 mL) and brine (3 mL), dried with $MgSO_4$, and concentrated on a rotary evaporator. The residue was chromatographed on silica gel.

*(1,1-Difluoro-3-phenylbut-3-enyl)(trimethyl)silane (**5c**).*



Yield 0.84 g (70%). Colorless oil.

Chromatography: hexane/CH_2Cl_2 = 20/1(R_f 0.11).

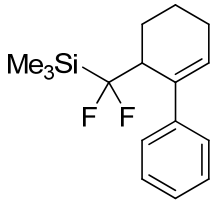
^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.22 (s, 9H), 3.11 (t, 2H, *J* = 21.1), 5.36 (s, 1H), 5.58 (s, 1H), 7.28–7.53 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: –4.2 (t, *J* = 2.2), 41.4 (t, *J* = 20.7), 118.5, 126.4, 127.6, 128.3, 129.1 (t, *J* = 260.8), 140.7 (t, *J* = 5.3), 141.7.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –110.7 (t, *J* = 21.1).

Calcd for $C_{13}H_{18}F_2Si$ (240.36): C, 64.96; H, 7.55. Found: C, 64.77; H, 7.51.

*[Difluoro(2-phenylcyclohex-2-en-1-yl)methyl](trimethyl)silane (**5d**).*



Yield 1.12 g (80%). Colorless oil. The compound is prone to oxidation upon storage on air.

Chromatography: hexane/CH_2Cl_2 = 20/1 → 10/1. R_f = 0.81 (hexane/CH_2Cl_2, 10/1).

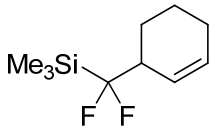
^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.20 (s, 9H), 1.60–1.93 (m, 3H); 1.97–2.13 (m, 1H), 2.20–2.35 (m, 2H), 3.21–3.44 (m, 1H), 6.11 (t, 1H, *J* = 3.9), 7.19–7.38 (m, 5H).

^{13}C NMR (50 MHz, $CDCl_3$), δ: –3.5 (t, *J* = 2.5), 18.2 (d, *J* = 3.5), 24.3 (dd, *J* = 8.5, 1.4), 25.5, 42.1 (dd, *J* = 17.0, 19.0), 126.3, 128.0, 131.6, 135.0 (t, *J* = 4.6), 136.9, 144.7.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –112.5 (dd, 1F, *J* = 322.8; 28.5), –99.7 (dd, 1F, J = 322.8, 8.9).

Calcd for $C_{16}H_{22}F_2Si$ (280.43): C, 68.53; H, 7.91. Found: C, 68.55; H, 8.13.

*[Cyclohex-2-en-1-yl(difluoro)methyl](trimethyl)silane (**5e**).*



Reagent **2** (19.8 mmol) was prepared from 22 mmol of Me_3SiCF_2Br. From the obtained solution, volatile components (THF, *i*-PrI) were evaporated under vacuum [first, the vacuum of about 10-20 Torr was applied at room temperature; then, oil pump vacuum was used with heating in water bath at 30 °C]. The residue was cooled with ice/water bath, 3-bromocyclohexene (20 mmol, 2.30 mL) and CuCN (1 mmol, 90 mg) were added, and the mixture was allowed to warm slowly (during 5 h) to room temperature and stirred for additional 12 h. The mixture diluted with water (5 mL) and the product was extracted with pentane (3×5 mL). The combined organic phases were washed with HCl (1M, 3×5 mL), water (3 mL) and brine (3 mL), dried with $MgSO_4$. Pentane was evaporated at atmospheric pressure and the product was distilled under vacuum [86–90 °C (bath temperature)/8 Torr] to afford 3.19 g (79%) of **5e** as a colorless liquid.

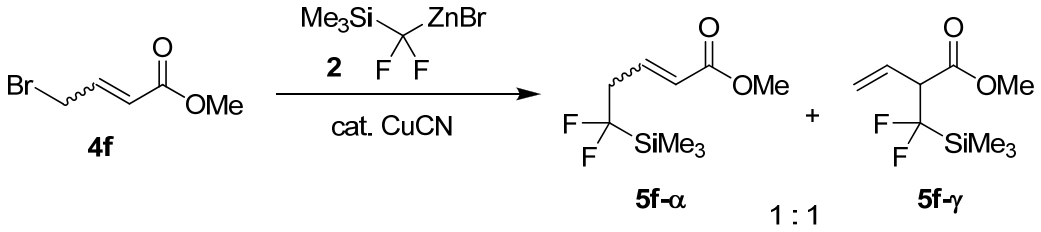
^{1}H NMR (200 MHz, $CDCl_3$), δ: 0.21 (s, 9H), 1.40–1.67 (m, 2H); 1.72–1.94 (m, 2H), 1.95–2.11 (m, 2H), 2.51–2.86 (m, 1H), 5.64–5.77 (m, 1H), 5.81–5.96 (m,1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: –3.2 (t, *J* = 2.5), 21.6, 23.1 (t, *J* = 5.8), 25.1, 43.8 (t, *J* = 19.7), 123.9 (dd, *J* = 7.2, 9.4), 130.4, 130.7 (t, *J* = 262.3).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –117.3 (dd, 1F, *J* = 317.1, 21.3), –114.5 (dd, 1F, *J* = 317.1, 16.6).

Calcd for $C_{10}H_{18}F_2Si$ (204.33): C, 58.78; H, 8.88. Found: C, 58.81; H, 8.86.

Reaction of bromide 4f with reagent 2.



Reagent **2** (3 mmol) was prepared from 3.3 mmol of Me_3SiCF_2Br. The obtained solution was cooled with ice/water bath, bromide **4f** (537 mg, 3 mmol) and CuCN (0.15 mol, 13 mg) were added, and the mixture was kept for 17 h in ice/water bath. The mixture diluted with water (3 mL) and the product was extracted with pentane (3×5 mL). The combined organic phases were washed with HCl (1M, 3×5 mL), water (3 mL) and brine (3 mL), dried with $MgSO_4$. The solvent was evaporated by heating under atmospheric pressure, and the residue was chromatographed on a short pad of silica gel eluting with hexane/EtOAc = 25/1. Yield 493.5 mg (74%).

Mixture of **5f-α**/**5f-γ**, 1 : 1 (for **5f-α**, *E*/*Z* = 13 : 1). Colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$), δ: *E*-**5f-α** and **5f-γ**, 0.15 (s, 9H), 0.17 (s, 9H), 2.70 (tdd, 2H, *J* = 20.5, 7.5, 1.5), 3.52 (ddd, 1H, 19.1, 15.0, 9.5), 3.71 (s, 3H), 3.72 (s, 3H), 5.21–5.38 (m, 2H), 5.86–6.04 (m, 2H), 6.93 (dt, 1H, *J* = 15.4, 7.5). Selected signals of minor isomer (*Z*-**5f-α**): 3.26 (tdd, *J* = 22.0, 7.0, 1.8), 6.30–6.43 (m).

^{13}C NMR (75 MHz, $CDCl_3$), –4.5 (t, *J* = 2.3), –3.7 (t, *J* = 2.3), 39.3 (t, *J* = 21.6), 51.6, 52.2, 57.4 (t, *J* = 21.3), 121.5, 125.6, 127.0 (t, *J* = 267.8), 128.3 (t, *J* = 260.8), 129.4 (dd, *J* = 8.1, 5.8), 139.8 (t, *J* = 8.3), 166.2, 169.2 (dd, *J* = 7.5, 5.8).

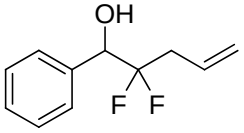
^{19}F NMR (282 MHz, $CDCl_3$), δ: –115.6 (dd, 1F, *J* = 324.3, 19.1), –113.4 (dd, 1F, *J* = 324.3, 15.0), –112.9 (t, 2F, *J* = 20.5); minor isomer (*Z*-**5f-α**), –114.8 (t, 2F, *J* = 22.0).

Calcd for $C_9H_{16}F_2O_2Si$ (222.30): C, 48.63; H, 7.25. Found: C, 48.73; H, 7.40.

Reaction of aldehydes with silanes 5a-e leading to alcohols 6a-l (general procedure A).

Cesium fluoride (11 mg, 0.075 mmol) was added to a solution of aldehyde (0.5 mmol) and silane **5** (0.65 mmol) in DMF (1 mL) at room temperature, and the mixture was stirred for 18 h. Then, $Bu_4NF{\cdot}3H_2O$ (205 mg, 0.65 mmol) was added, and the mixture was stirred for 1 h at room temperature. For the work-up, water (7 mL) was added, and the mixture was extracted with methyl *tert*-butyl ether (3×3 mL). The combined organic phases were filtered through Na_2SO_4, concentrated under vacuum, and the residue was purified by column chromatography on silica gel.

*2,2-Difluoro-1-phenylpent-4-en-1-ol (**6a**).*



Yield 88 mg (89%). Colorless oil. Bp 85–91 °C (bath temp.)/0.40 Torr.

Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.40 (hexanes/EtOAc, 5/1).

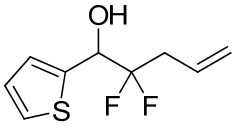
^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.40–2.60 (m, 2H), 2.63–2.86 (m, 1H), 4.88 (td, 1H, *J* = 10.3, 4.0), 5.15–5.30 (m, 2H), 5.84 (ddt, 1H, *J* = 17.2, 10.3, 7.1), 7.36–7.51 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 37.2 (t, *J* = 24.3), 75.1 (t, *J* = 28.2), 120.6; 122.5 (t, *J* = 246.6), 127.6, 128.4, 128.7, 128.8, 136.6 (t, *J* = 2.2).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –110.1 (dm, 1F, *J* = 248.0), –109.1 (dm, 1F, *J* = 248.0).

Calcd for $C_{11}H_{12}F_2O$ (198.21): C, 66.66; H, 6.10. Found: C, 66.67; H, 6.19.

*2,2-difluoro-1-thien-2-ylpent-4-en-1-ol (**6b**).*



Yield 77 mg (75%). Pale-yellow oil. Bp 76–80 °C (bath temp.)/0.55 Torr.

Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.30 (hexanes/EtOAc, 5/1).

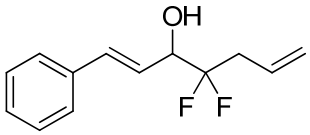
^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.52–2.91 (m, 3H), 5.14 (td, 1H, *J* = 10.7, 4.6), 5.19–5.33 (m, 2H), 5.78–5.94 (m, 1H), 7.01–7.09 (m, 1H), 7.13–7.20 (m, 1H), 7.33–7.41 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 37.4 (t, *J* = 24.3), 71.6 (t, *J* = 29.9), 120.9, 122.1 (t, *J* = 247.2), 125.3, 126.4, 126.9, 128.6 (t, *J* = 5.0), 139.0 (t, *J* = 2.2).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –110.7 (dtd, 1F, *J* = 248.0, 19.1, 12.7), –109.5 (dddd, 1F, *J* = 248.0, 19.1, 15.9, 10.0).

Calcd for $C_9H_{10}F_2OS$ (204.24): C, 52.93; H, 4.94. Found: C, 52.69; H, 4.78.

*(1E)-4,4-Difluoro-1-phenylhepta-1,6-dien-3-ol (**6c**).*



Yield 103 mg (92%). Colorless oil.

Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.34 (hexanes/EtOAc, 5/1).

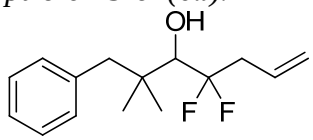
^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.35 (d, 1H, *J* = 4.6), 2.60–2.94 (m, 2H), 4.42–4.58 (m, 1H), 5.21–5.38 (m, 2H), 5.81–5.99 (m, 1H), 6.28 (dd, 1H, *J* = 16.1, 6.4), 6.80 (d, 1H, *J* = 16.1), 7.27–7.49 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 37.5 (t, *J* = 24.3), 73.8 (t, *J* = 28.8), 120.8, 122.6 (t, *J* = 246.6), 125.6 (t, *J* = 3.3), 126.9, 128.4, 128.8, 128.9 (t, *J* = 5.5), 134.6, 136.1.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –111.3 (ddt, 1F, *J* = 248.0, 21.2, 11.7), –109.3 (dddd, 1F, *J* = 248.0, 22.3, 13.8, 9.6).

Calcd for $C_{13}H_{14}F_2O$ (224.25): C, 69.63; H, 6.29.Found: C, 69.73; H, 6.31.

*4,4-Difluoro-2,2-dimethyl-1-phenylhept-6-en-3-ol (**6d**).*



Yield 91 mg (72%). Colorless oil. Bp 110–120 °C (bath temp.)/0.39 Torr.

Chromatography hexanes/EtOAc, 10/1. R_f 0.21 (hexanes/EtOAc, 10/1).

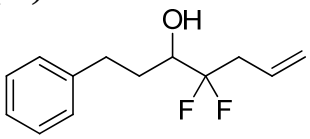
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.05 (s, 3H), 1.09 (s, 3H), 1.99 (d, 1H, *J* = 8.8), 2.64 (d, 1H, *J* = 13.2), 2.71–2.94 (m, 2H), 2.88 (d, 1H, *J* = 13.2), 3.49 (ddd, 1H, *J* = 21.3, 8.8, 4.0), 5.21–5.31 (m, 2H), 5.79–5.94 (m, 1H), 7.19–7.35 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.6, 23.9, 38.6, 40.3 (t, *J* = 25.4), 46.3, 76.4 (dd, *J* = 27.7, 25.4), 120.4, 125.2 (t, *J* = 249.4), 126.3, 128.0, 129.6 (dd, *J* = 7.2, 3.9), 131.0, 138.3.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –108.6 (dtd, 1F, *J* = 252.2, 19.1, 10.6), –101.6 (dt, 1F, *J* = 252.2, 21.3).

Calcd for $C_{15}H_{20}F_2O$ (254.32): C, 70.84; H, 7.93. Found: C, 70.87; H, 7.99.

*4,4-Difluoro-1-phenylhept-6-en-3-ol (**6e**).*



Yield 31 mg (27%). Colorless crystals. Mp 26–28 °C. Bp 89–103 °C (bath temp.)/0.45 Torr.

Chromatography hexanes/EtOAc, 10/1. R_f 0.21 (hexanes/EtOAc, 10/1).

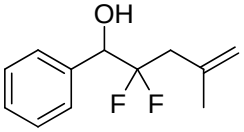
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.77–2.08 (m, 3H), 2.56–2.85 (m, 3H), 2.94 (ddd, 1H, *J* = 14.3, 9.5, 5.2), 3.67–3.83 (m, 1H), 5.18–5.29 (m, 2H), 5.84 (ddt, 1H, *J* = 17.4, 10.1, 7.3), 7.20–7.36 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 31.7 (t, *J* = 2.8), 31.8, 37.5 (t, *J* = 24.9), 72.1 (t, *J* = 28.8), 120.6, 123.2 (t, *J* = 245.5), 126.2, 128.59, 128.63, 129.0 (t, *J* = 5.5), 141.3.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –112.7 (dtd, 1F, *J* = 250.1, 20.1, 12.7), –109.6 (dddd, 1F, *J* = 250.1, 23.3, 14.8, 8.5).

Calcd for $C_{13}H_{16}F_2O$ (226.26): C, 69.01; H, 7.13.Found: C, 68.94 ; H, 7.29.

2,2-Difluoro-4-methyl-1-phenylpent-4-en-1-ol ***(6f)***.



Yield 99 mg (93%). Colorless crystals. Mp 41–43 °C. Bp 94–108 °C (bath temp.)/ 0.44 Torr. Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.32 (hexanes/EtOAc, 5/1).

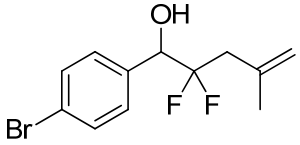
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.85 (s, 3H), 2.45 (ddd, 1H, *J* = 24.2, 13.8, 11.0), 2.62 (d, 1H, *J* = 3.6), 2.73 (dt, 1H, *J* = 24.7, 13.7), 4.86–4.88 (m, 2H), 5.01 (br, 1H), 7.36–7.50 (m, 5H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.6, 40.2 (t, *J* = 23.8), 75.1 (t, *J* = 28.2), 116.8, 122.7 (t, *J* = 247.7), 127.6, 128.3, 128.7, 136.6, 137.7 (t, *J* = 2.8).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –109.1 (ddt, 1F, *J* = 249.1, 23.3, 11.7), –107.7 (dddd, 1F, *J* = 249.1, 23.3, 13.8, 9.6).

Calcd for $C_{12}H_{14}F_2O$ (212.24): C, 67.91; H, 6.65. Found: C, 67.94; H, 6.77.

1-(4-Bromophenyl)-2,2-difluoro-4-methylpent-4-en-1-ol ***(6g)***.



Yield 128 mg (88%). Colorless crystals. Mp 37–39 °C. Bp 118–121 °C (bath temp.)/ 0.45 Torr. Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.38 (hexanes/EtOAc, 5/1).

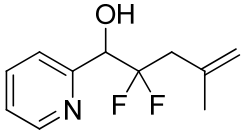
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.83 (s, 3H, CH_3), 2.42 (ddd, 1H, *J* = 25.3, 14.7, 11.9), 2.64 (d, 1H, *J* = 4.0), 2.70 (dt, 1H, *J* = 25.3, 14.7), 4.76–4.86 (m, 1H), 4.86 (br, 1H), 5.00 (br, 1H), 7.33 (d, 2H, *J* = 8.7), 7.52 (d, 2H, *J* = 8.7).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.6, 40.2 (t, *J* = 23.8), 74.5 (t, *J* = 28.6), 117.1, 122.6 (t, *J* = 248.3), 122.9, 129.4, 131.6, 135.5 (d, *J* = 3.3), 137.5 (t, *J* = 2.8).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –109.1 (ddt, 1F, *J* = 250.1, 25.3, 11.9), –107.2 (dddd, 1F, *J* = 250.1, 25.3, 14.7, 11.9).

Calcd for $C_{12}H_{13}BrF_2O$ (291.13): C, 49.51; H, 4.50. Found: C, 49.36; H, 4.62.

2,2-Difluoro-4-methyl-1-pyridin-2-ylpent-4-en-1-ol ***(6h)***.



Yield 48 mg (45%). Colorless crystals. Mp 55–56 °C. Bp 80–85 °C (bath temp.)/ 0.18 Torr. Chromatography hexanes/EtOAc, 5/1 → 3/1. R_f 0.22 (hexanes/EtOAc, 5/1).

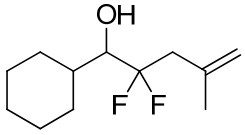
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.86 (s, 3H), 2.52 (ddd, 1H, *J* = 25.0, 15.0, 8.1), 2.84 (dt, 1H, *J* = 23.5, 15.0), 4.86 (dt, 1H, *J* = 15.0, 5.3), 4.90–4.93 (br, 1H), 5.00 (br, 1H), 5.38 (d, 1H, *J* = 5.3), 7.31 (dd, 1H, *J* = 7.6, 4.7), 7.40–7.46 (m, 1H), 7.73 (td, 1H, *J* = 7.6, 1.5), 8.59 (d, 1H, *J* = 4.7).

^{13}C NMR (50 MHz, $CDCl_3$), δ: 23.7, 40.5 (t, *J* = 23.4), 72.8 (t, *J* = 29.8), 116.8, 123.0 (t, *J* = 249.1), 123.1 (t, *J* = 2.8), 123.6, 136.8, 137.6 (d, *J* = 4.3), 147.9, 154.0 (d, *J* = 4.3).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –110.9 (dddd, 1F, *J* = 250.1, 23.5, 15.0, 8.1), –105.6 (dddd, 1F, *J* = 250.1, 25.0, 15.0, 5.3).

Calcd for $C_{11}H_{13}F_2NO$ (213.22): C, 61.96; H, 6.15, N, 6.57. Found: C, 61.92; H, 6.26, N, 6.61.

1-Cyclohexyl-2,2-difluoro-4-methylpent-4-en-1-ol ***(6i).***



Yield 90 mg (82%). Colorless crystals. Mp 39–41 °C. Bp 81–85 °C (bath temp.)/ 0.37 Torr.

Chromatography hexanes/EtOAc, 20/1 → 10/1. R_f 0.21 (hexanes/EtOAc, 10/1).

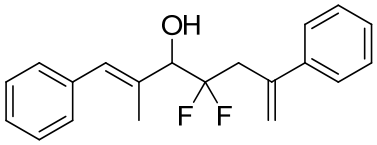
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.06–1.37 (m, 5H), 1.63–1.98 (m, 7H), 1.85 (s, 3H, CH_3), 2.52–2.83 (m, 2H), 3.50 (dtd, 1H, *J* = 16.5, 7.3, 4.6), 4.90 (br, 1H), 5.00 (br, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.7 (t, *J* = 2.2), 26.1, 26.3, 26.4, 27.3, 30.3 (t, *J* = 2.2), 38.4, 41.5 (t, *J* = 24.3), 76.3 (dd, *J* = 27.6, 26.5), 116.7, 124.2 (t, *J* = 247.7), 138.2 (dd, *J* = 4.4, 2.2).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –107.8 (dddd, 1F, *J* = 251.2, 23.3, 16.5, 10.6), –104.9 (dddd, 1F, *J* = 251.2, 23.3, 15.9, 7.3).

Calcd for $C_{12}H_{20}F_2O$ (218.28): C, 66.03; H, 9.24. Found: C, 66.16; H, 9.44.

(1E)-4,4-Difluoro-2-methyl-1,6-diphenylhepta-1,6-dien-3-ol ***(6j).***



Yield 121 mg (77%). Colorless oil.

Chromatography hexanes/EtOAc, 10/1 → 5/1. R_f 0.39 (hexanes/EtOAc, 5/1).

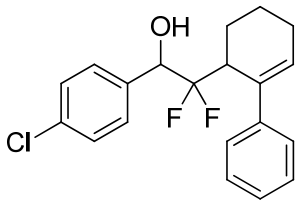
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.97 (s, 3H), 2.22 (br d, 1H, *J* = 4.4), 3.07–3.40 (m, 2H), 4.29–4.43 (m, 1H), 5.38 (s, 1H), 5.59 (s, 1H), 6.64 (s, 1H), 7.24–7.51 (m, 10H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 14.9 (t, *J* = 2.8), 38.6 (t, *J* = 24.3), 77.8 (dd, *J* = 28.8, 26.5), 120.0, 122.9 (t, *J* = 249.4), 126.4, 127.1, 127.8, 128.3, 128.5, 129.2, 130.5, 133.7, 136.9, 140.4 (dd, *J* = 4.4, 2.2), 141.4.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –107.4 (ddt, 1F, *J* = 249.1, 21.8, 9.2), –105.4 (ddd, 1F, *J* = 249.1, 12.1, 8.5).

Calcd for $C_{20}H_{20}F_2O$ (314.37): C, 76.41; H, 6.41. Found: C, 76.37; H, 6.44.

1-(4-Chlorophenyl)-2,2-difluoro-2-(2-phenylcyclohex-2-en-1-yl)ethanol ***(6k).***



The product is formed as mixture of isomers (1/1). Yield 167 mg (96%).

Chromatography hexanes/EtOAc, 10/1 → 5/1.

Upper isomer

84 mg. Colorless crystals. Mp 118–120 °C (hexanes). R_f 0.12 (hexanes/EtOAc, 10/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.63–1.95 (m, 3H), 1.98 (d, 1H, *J* = 5.6), 2.21–2.34 (m, 3H), 3.56–3.70 (m, 1H), 4.25 (ddd, 1H, *J* = 20.7, 5.6, 3.9), 6.12 (t, 1H, *J* = 3.9), 7.19 (d, 2H, *J* = 8.2), 7.23–7.32 (m, 3H), 7.30–7.42 (m, 4H).

^{13}C NMR (50 MHz, $CDCl_3$), δ: 18.2 (d, *J* = 2.8), 22.9 (d, *J* = 7.1), 25.5, 38.1 (dd, *J* = 24.1, 21.3), 72.9 (dd, *J* = 32.7, 25.6), 123.0 (dd, *J* = 255.5, 249.9), 126.6, 127.2, 128.3, 128.7, 129.4, 133.5, 134.2, 134.4, 135.3, 143.8.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –115.1 (ddd, 1F, *J* = 252.2, 21.2, 3.9), –106.7 (dd, 1F, *J* = 252.2, 20.7).

Calcd for $C_{20}H_{19}ClF_2O$ (348.81): C, 68.87; H, 5.49. Found: C, 69.00; H, 5.34.

Lower isomer

83 mg. Colorless crystals. Mp 55–58 °C (pentane). R_f 0.11 (hexanes/EtOAc, 10/1).

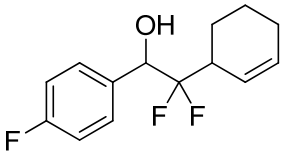
^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.67–1.95 (m, 3H), 2.19–2.38 (m, 4H), 3.36–3.51 (m, 1H), 4.74 (ddd, 1H, *J* = 16.5, 7.8, 5.1), 6.06 (t, 1H, *J* = 3.7), 7.17–7.33 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 18.2 (d, *J* = 3.3), 23.9 (dd, *J* = 5.5, 2.2), 25.4, 39.2 (dd, *J* = 22.7, 20.5), 73.8 (dd, *J* = 30.6, 26.0), 123.4 (t, *J* = 253.2), 126.64, 126.70, 128.3, 128.5, 129.6 (d, *J* = 2.2), 132.4, 134.62, 134.65 (t, *J* = 3.3), 135.2 (d, *J* = 2.2), 144.1.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –108.9 (ddd, 1F, *J* = 255.4, 21.2, 7.8), –105.4 (dt, 1F, *J* = 255.4, 16.5).

HRMS (ESI) Calcd for $C_{20}H_{23}ClF_2NO$ (M + NH_4): 366.1431. Found: 366.1439.

2-Cyclohex-2-en-1-yl-2,2-difluoro-1-(4-fluorophenyl)ethanol ***(6l)****.*



Mixture of isomers 1 : 1.

Yield 113 mg (88%). Colorless crystals. Mp 40–46 °C. Bp 140–145 °C (bath temp.)/ 0.08 Torr.

Chromatography hexanes/EtOAc, 20/1 → 10/1. R_f 0.23 (hexanes/EtOAc, 10/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 1.41–1.74 (m) and 1.76–2.08 (m) (7H), 2.50–2.61 (m, 1H), 2.63–2.88 (m, 1H), 4.87–5.02 (m, 1H), 5.61–5.69 (m) and 5.73–5.82 (m) (1H), 5.86–6.00 (m, 1H), 7.03–7.13 (m, 2H), 7.39–7.49 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 21.0, 21.2, 22.2 (t, *J* = 4.4), 22.7 (t, *J* = 4.4), 24.73, 24.78, 39.4 (t, *J* = 22.7), 73.2 (t, *J* = 28.8), 73.5 (t, *J* = 28.2), 115.36 (d, *J* = 21.6), 115.41 (d, *J* = 21.6), 122.54 (t, *J* = 5.5), 122.58 (t, *J* = 5.5), 123.2 (t, *J* = 249.4), 123.3 (t, *J* = 249.4), 129.71 (t, *J* = 6.6), 129.75 (t, *J* = 6.6), 131.2, 131.5, 132.6 (m, *J* = 3.3), 163.1 (d, *J* = 247.3).

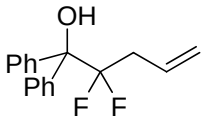
^{19}F NMR (282 MHz, $CDCl_3$), δ: –116.9 (d, 1F, *J* = 10.6), –116.8 (d, 1F, *J* = 12.7), –116.7 (dt, 1F, *J* = 250.1, 14.8), –115.7 (ddd, 1F, *J* = 250.1, 17.0, 10.6), –114.0 (tt, 1F, *J* = 8.5, 6.4), –113.9 (tt, 1F, *J* = 8.5, 6.4).

Calcd for $C_{14}H_{15}F_3O$ (256.26): C, 65.62; H, 5.90. Found: C, 65.76; H, 6.09.

Synthesis of products 6m and 7.

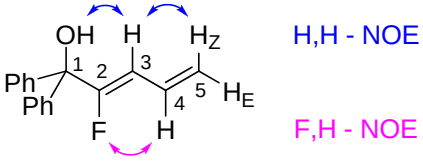
Reaction of benzophenone with **5a** was performed according to *general procedure A*.

*2,2-Difluoro-1,1-diphenylpent-4-en-1-ol (**6m**).*



Yield 41 mg (30%). Colorless oil. Bp 123–124 °C (bath temp.)/ 0.04 Torr.
Chromatography CH_2Cl_2. R_f 0.81 (CH_2Cl_2).
^{1}H NMR (300 MHz, $CDCl_3$), δ: 2.73 (td, 2H, *J* = 19.2, 7.3), 2.91 (s, 1H), 5.12–5.30 (m, 2H), 5.92 (ddt, 1H, *J* = 16.9, 10.5, 7.3), 7.31–7.44 (m, 6H), 7.61–7.70 (m, 4H).
^{13}C NMR (75 MHz, $CDCl_3$), δ: 37.6 (t, *J* = 24.3), 80.3 (t, *J* = 25.4), 120.1, 124.8 (t, *J* = 253.2), 127.7 (t, *J* = 2.5), 127.9, 128.2, 129.1 (t, *J* = 4.4), 141.8.
^{19}F NMR (282 MHz, $CDCl_3$), δ: –107.0 (t, 2F, *J* = 19.2).
Calcd for $C_{17}H_{16}F_2O$ (274.31): C, 74.44; H, 5.88. Found: C, 74.48; H, 5.82.

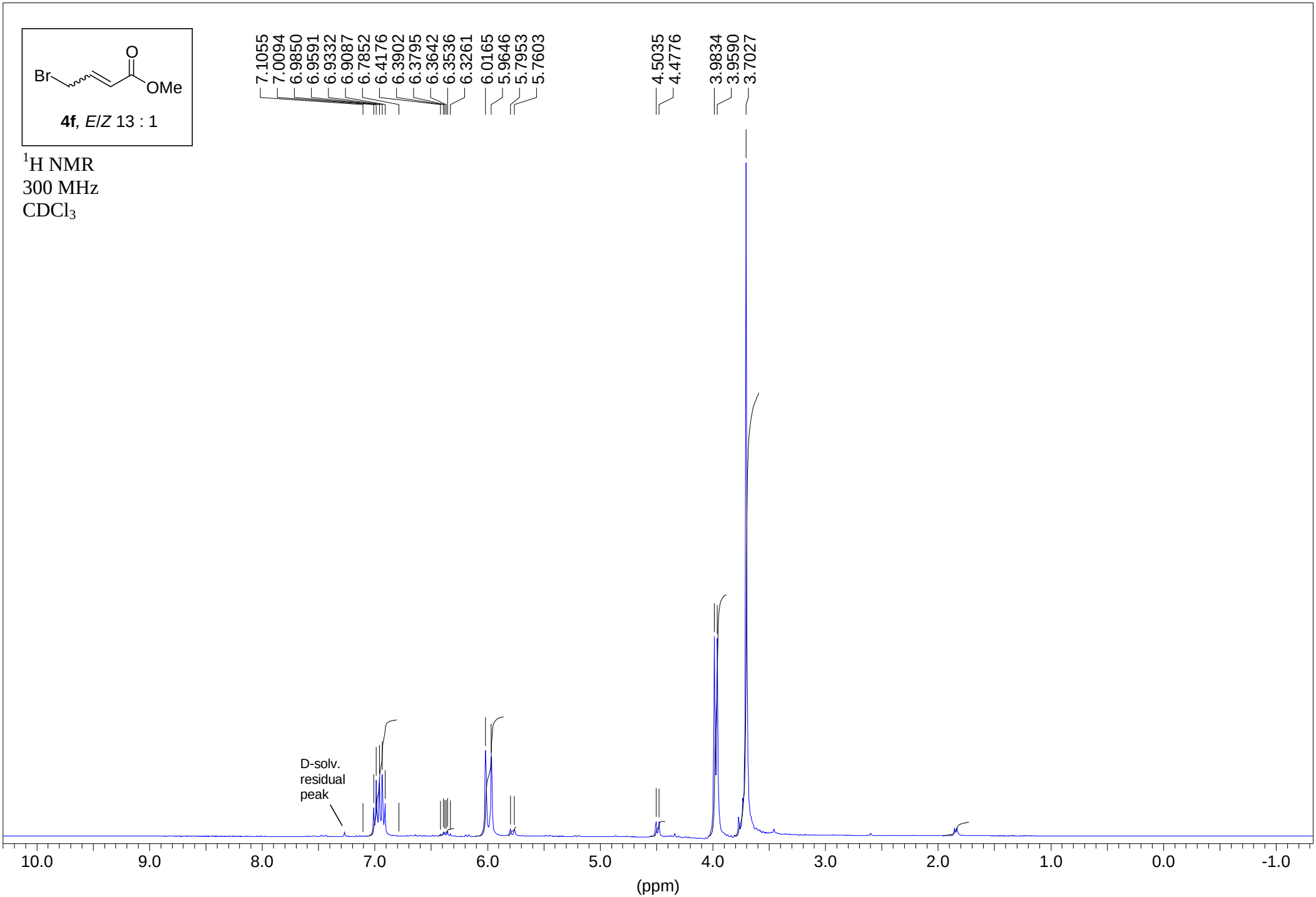
*(2Z)-2-Fluoro-1,1-diphenylpenta-2,4-dien-1-ol (**7**).*



Yield 32 mg (25%). Colorless crystals. Mp 45–49 °C (pentane).
Chromatography hexanes/EtOAc, 10/1. R_f 0.27 (hexanes/EtOAc, 10/1).

Signal assignment and double bond geometry is based on 2D NMR spectra:
^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, ^{1}H-^{1}H NOESY, ^{1}H-^{19}F HOESY.

^{1}H NMR (300 MHz, DMSO-d_6), δ: 5.13 (d, 1H, *J* = 10.7, H_E), 5.26 (d, 1H, *J* = 17.3, H_Z), 5.69 (dd, 1H, *J* = 35.4, 10.7, H(3)), 6.57 (dt, 1H, *J* = 17.3, 10.7, H(4)), 6.62 (br, 1H, OH), 7.25–7.39 (m, 10H, 2Ph).
^{13}C NMR (50 MHz, DMSO-d_6), δ: 78.0 (d, *J* = 27.0), 108.6 (d, *J* = 9.9), 118.4 (d, *J* = 2.8), 127.2, 127.4, 127.8, 129.0 (d, *J* = 52.5), 143.7, 161.7 (d, *J* = 271.1).
^{19}F NMR (282 MHz, DMSO-d_6), δ: –110.1 (d, 1F, *J* = 35.4).
Calcd for $C_{17}H_{15}FO$ (254.30): C, 80.29; H, 5.95. Found: C, 80.32; H, 5.99.


Br
O
OMe
4f, E/Z 13 : 1
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300 MHz
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7.0094
6.9850
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6.9087
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6.3536
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5.7603
4.5035
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3.9590
3.7027
D-solv.
residual
peak
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5.0
4.0
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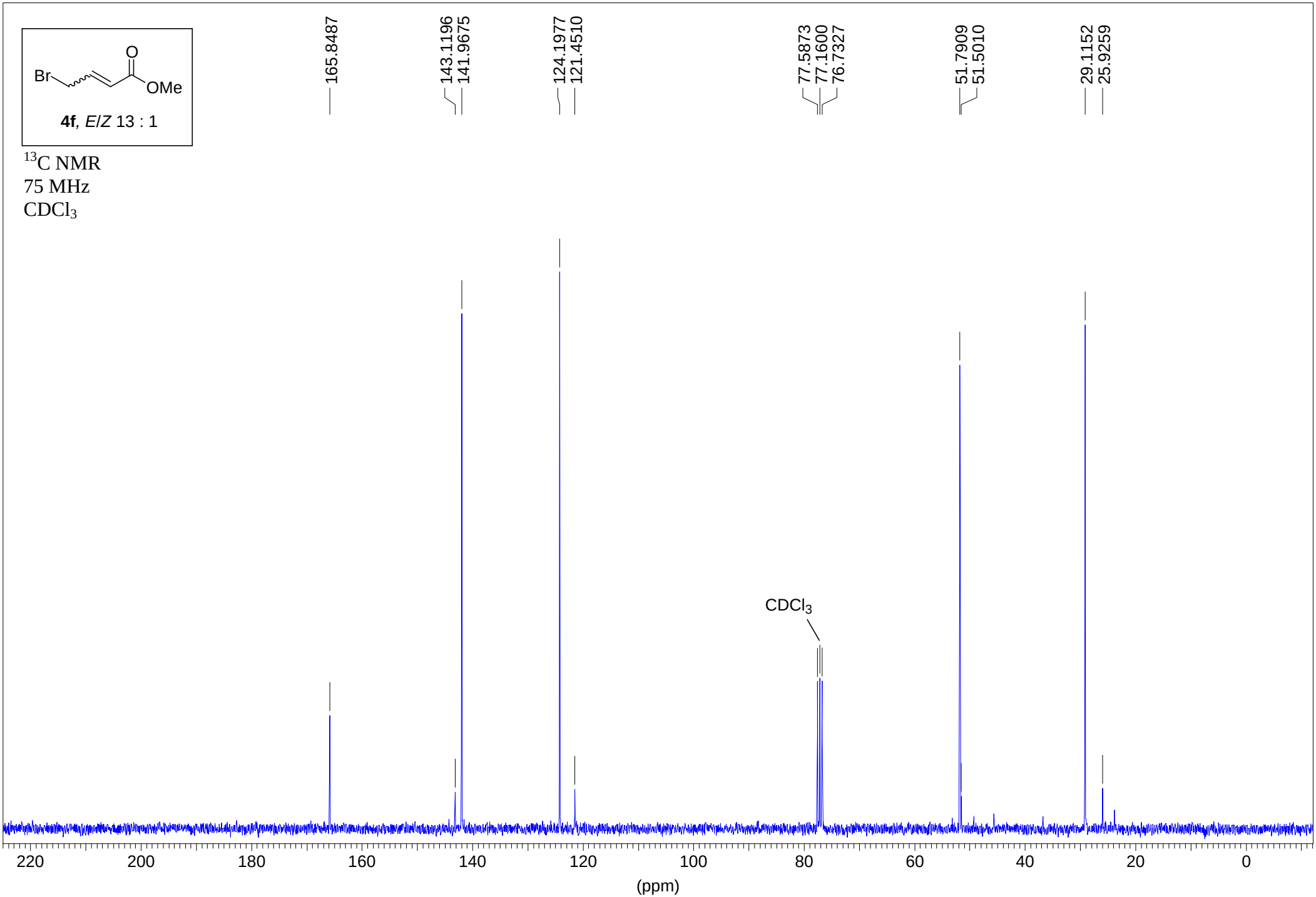
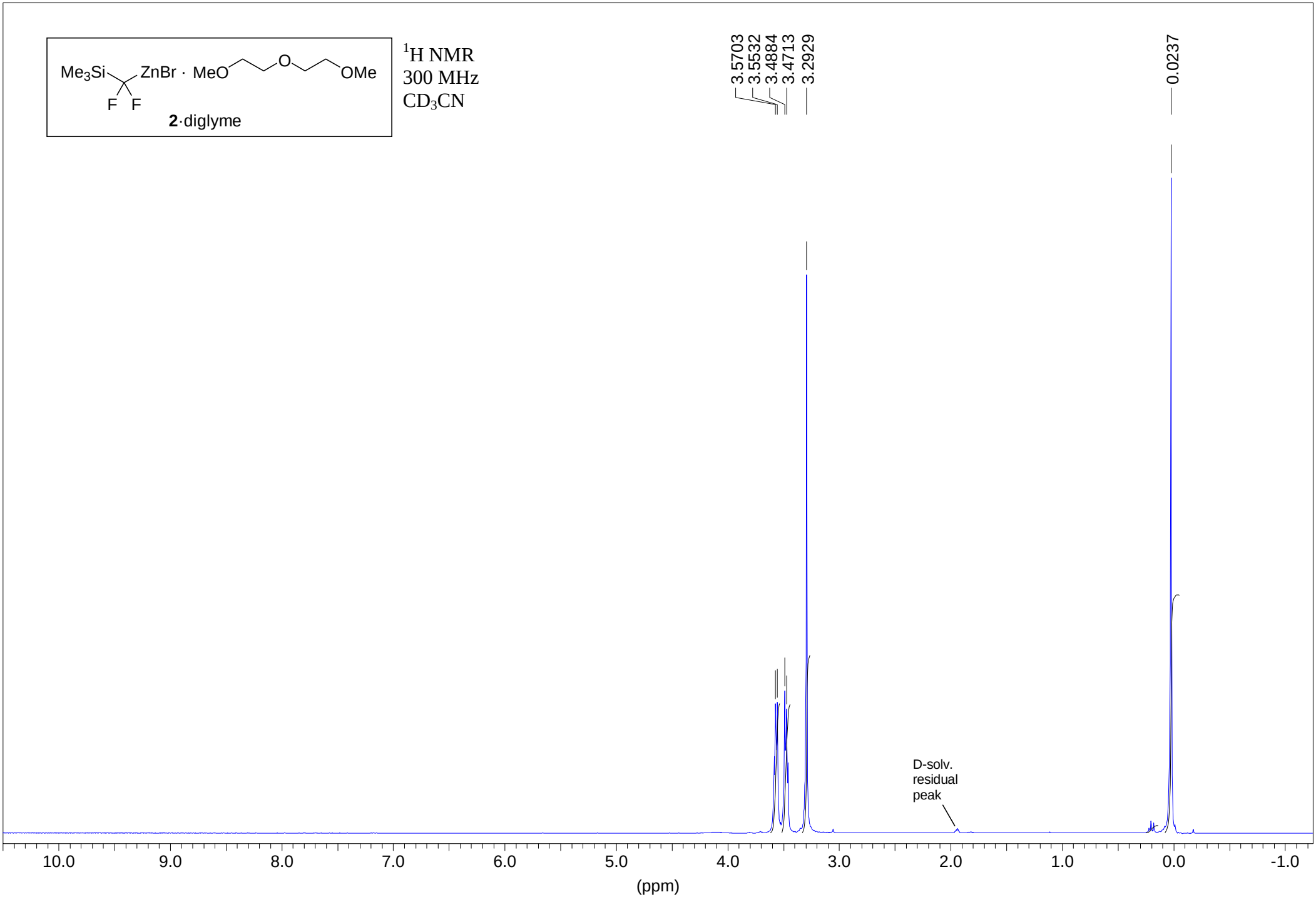
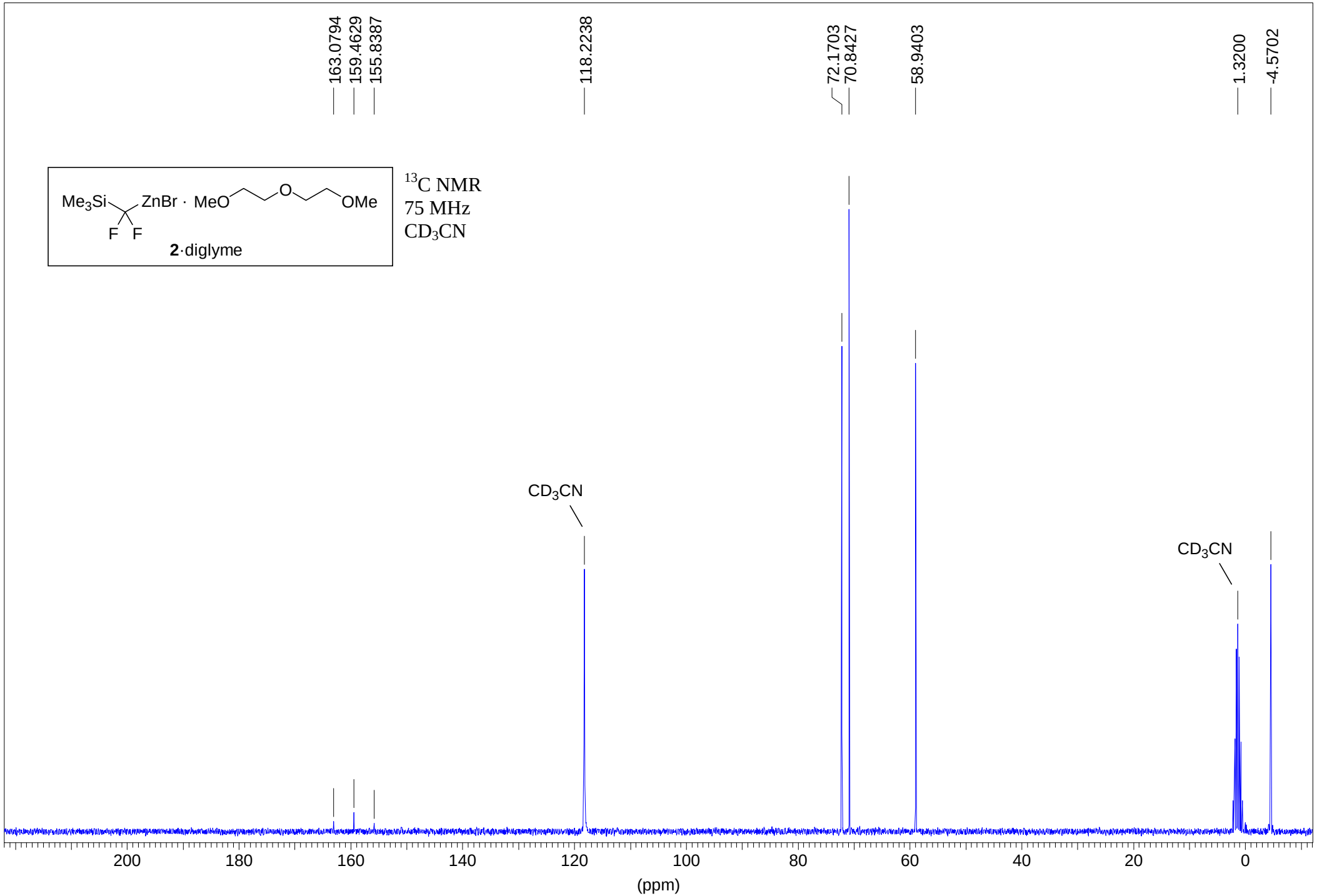
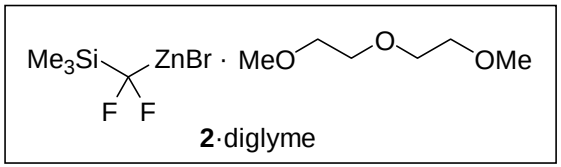
-1.0
(ppm)


Br
O
OMe
4f, E/Z 13 : 1
13C NMR
75 MHz
CDCl3
165.8487
143.1196
141.9675
124.1977
121.4510
77.5873
77.1600
76.7327
51.7909
51.5010
29.1152
25.9259
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

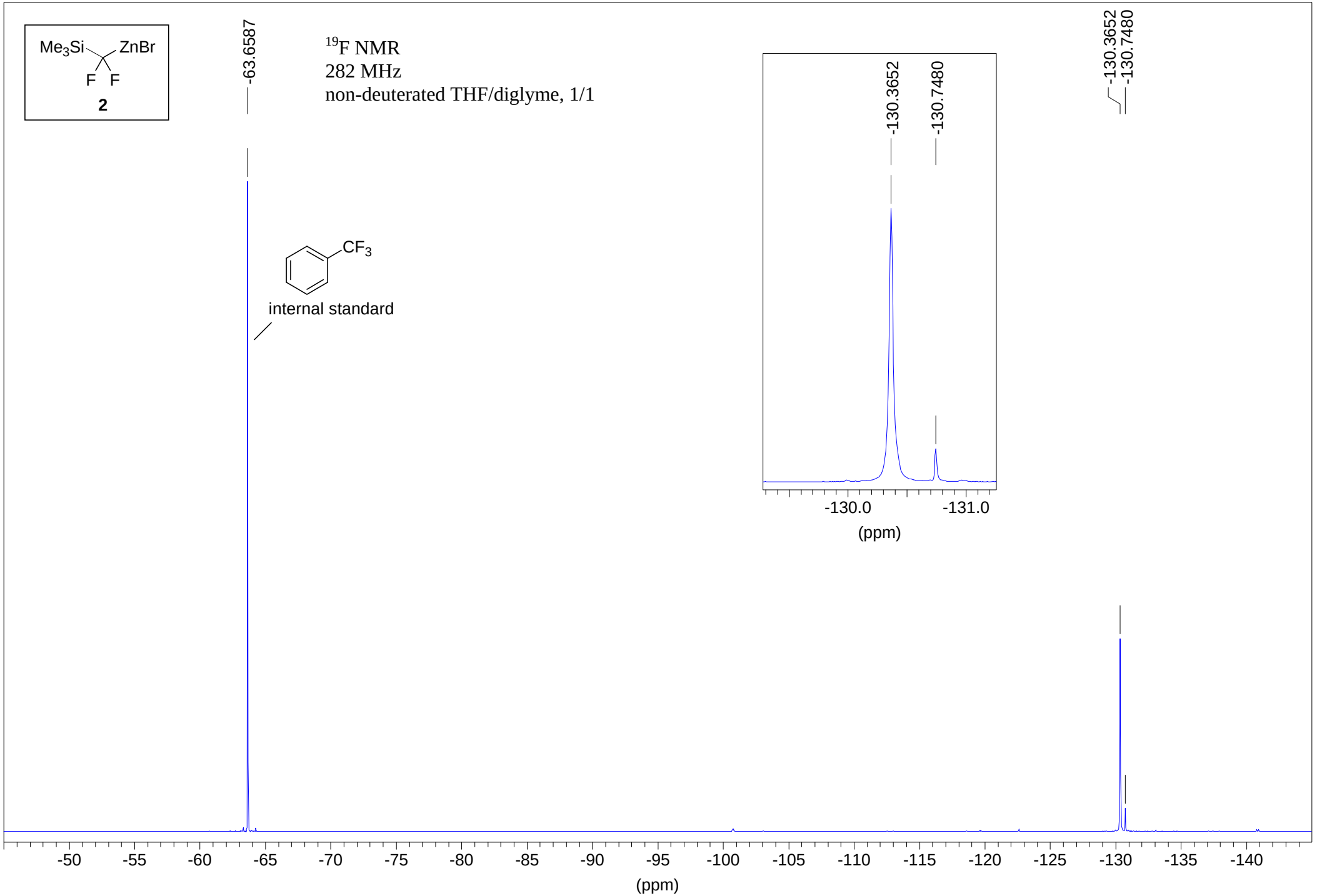

Me3Si
ZnBr · MeO
O
OMe
F F
2·diglyme
1H NMR
300 MHz
CD3CN
3.5703
3.5532
3.4884
3.4713
3.2929
0.0237
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

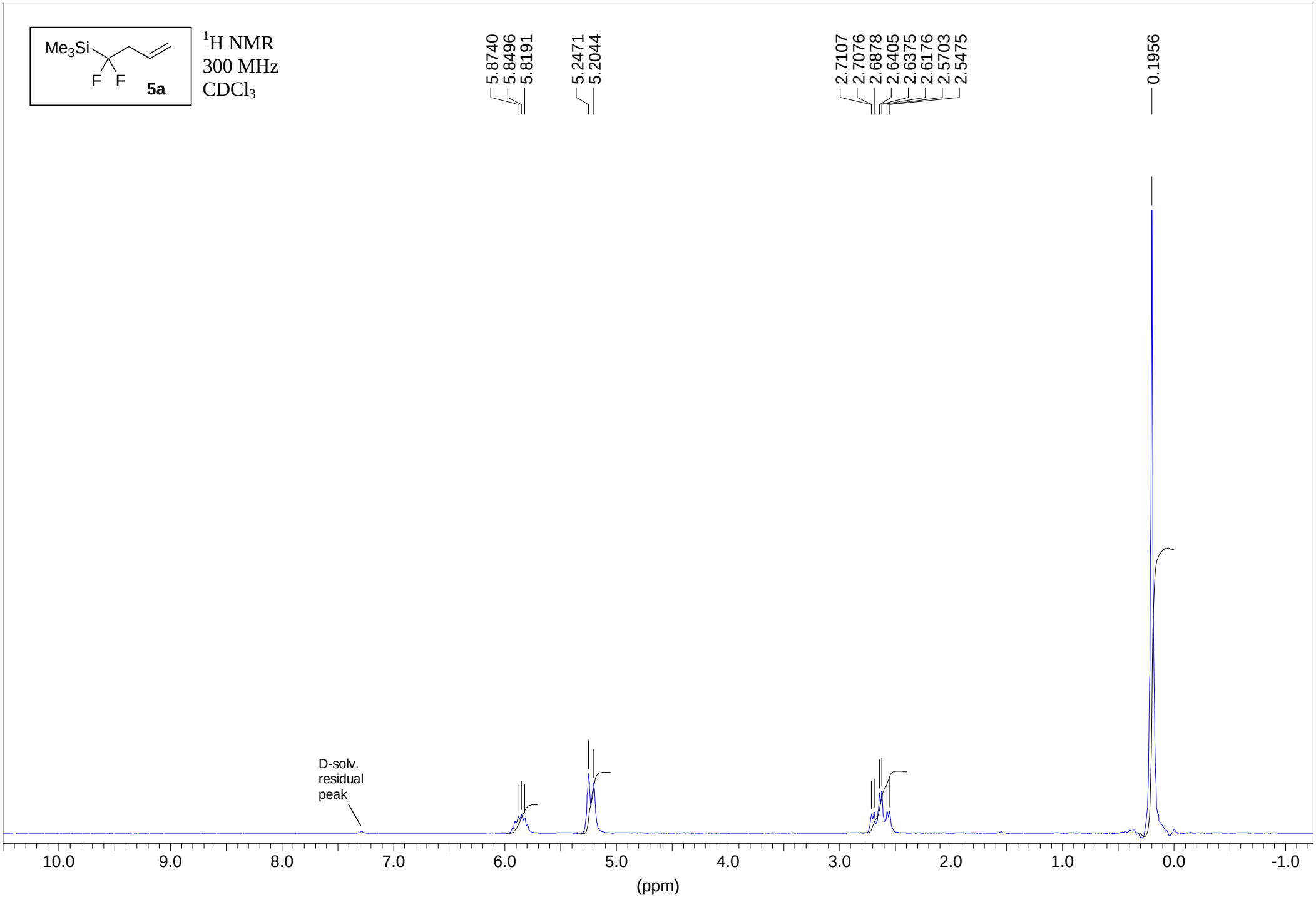

163.0794
159.4629
155.8387
118.2238
72.1703
70.8427
58.9403
1.3200
-4.5702
Me3Si
ZnBr · MeO
O
OMe
F F
2·diglyme
13C NMR
75 MHz
CD3CN
CD3CN
CD3CN
200
180
160
140
120
100
80
60
40
20
0
(ppm)

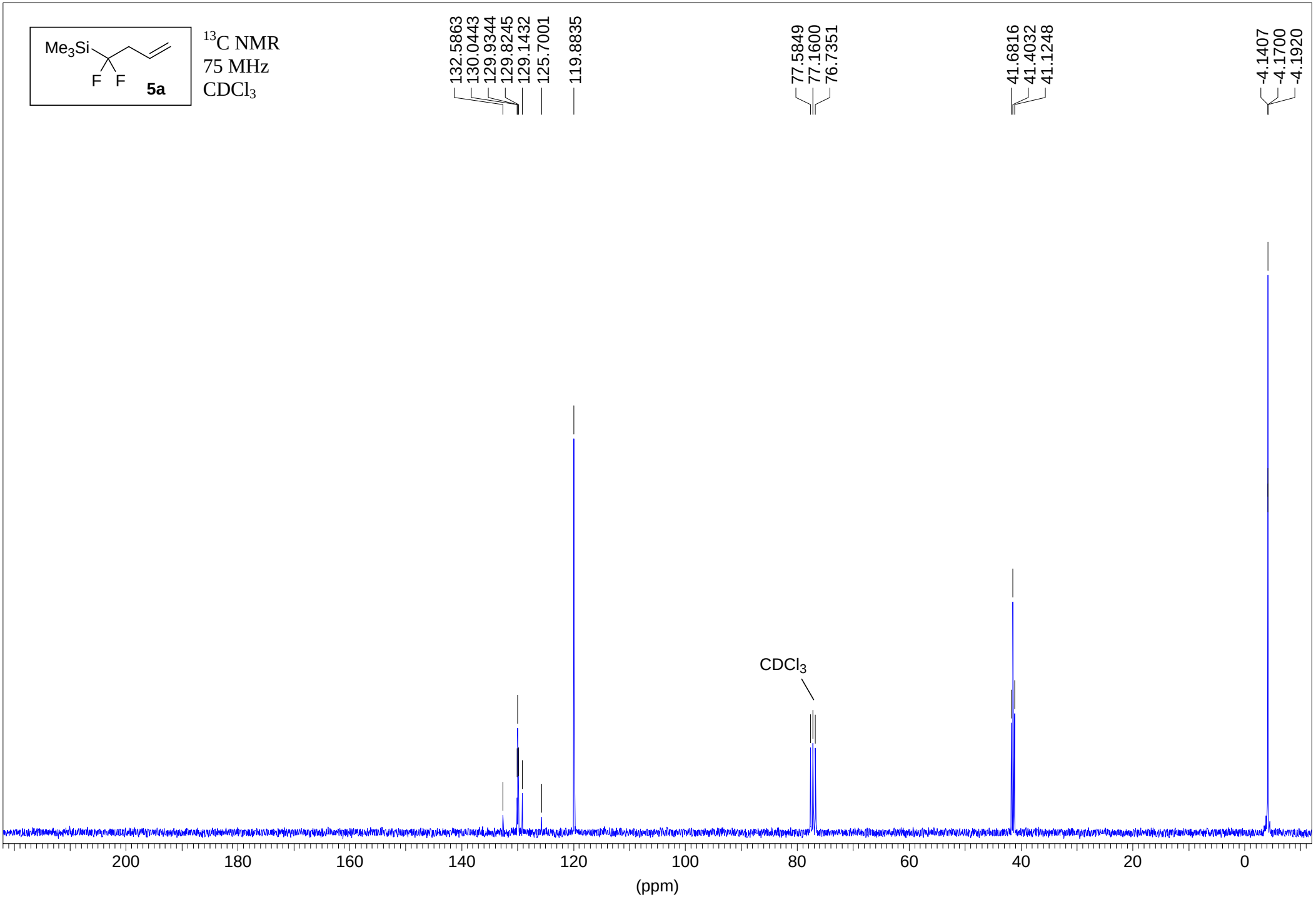


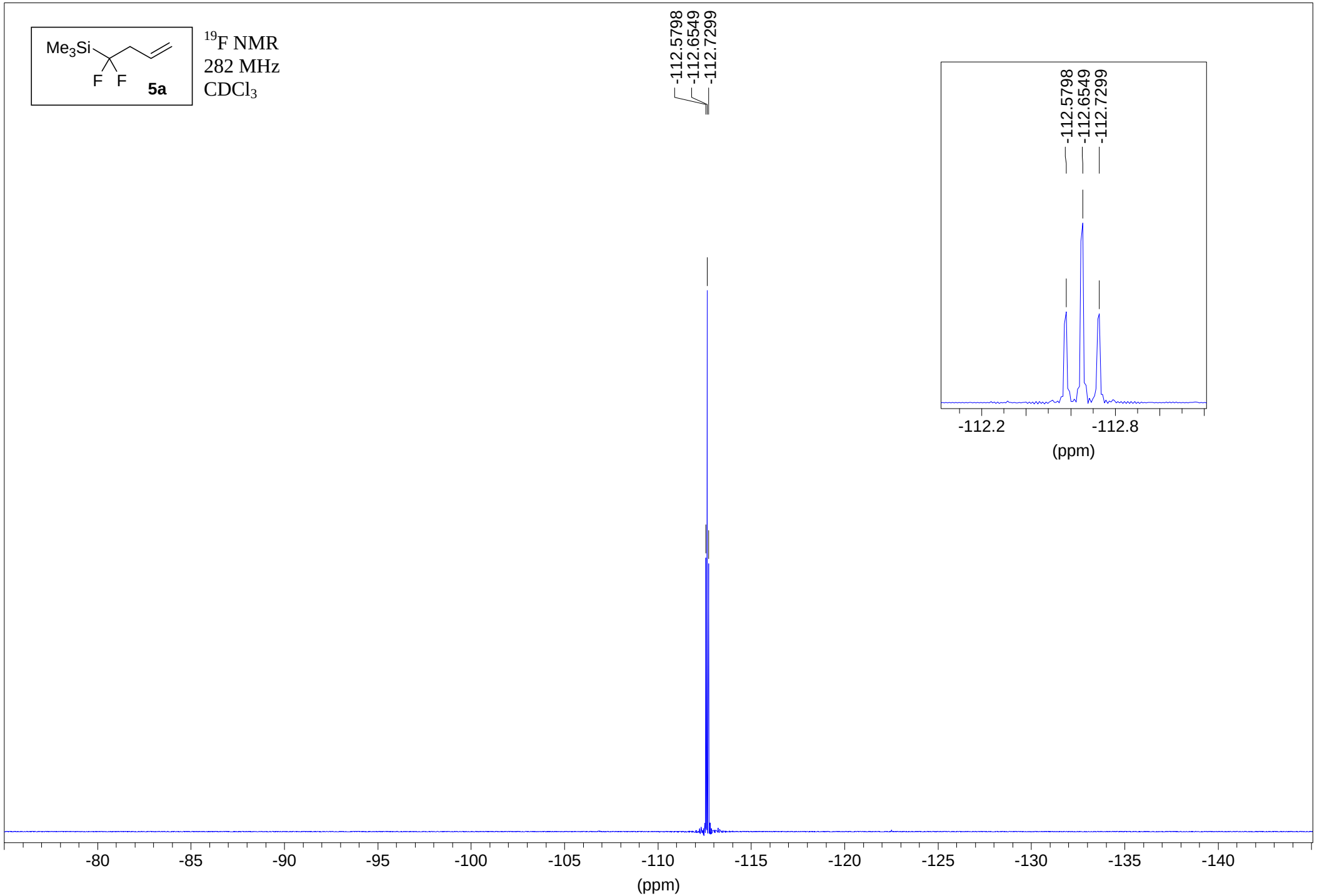
2·diglyme

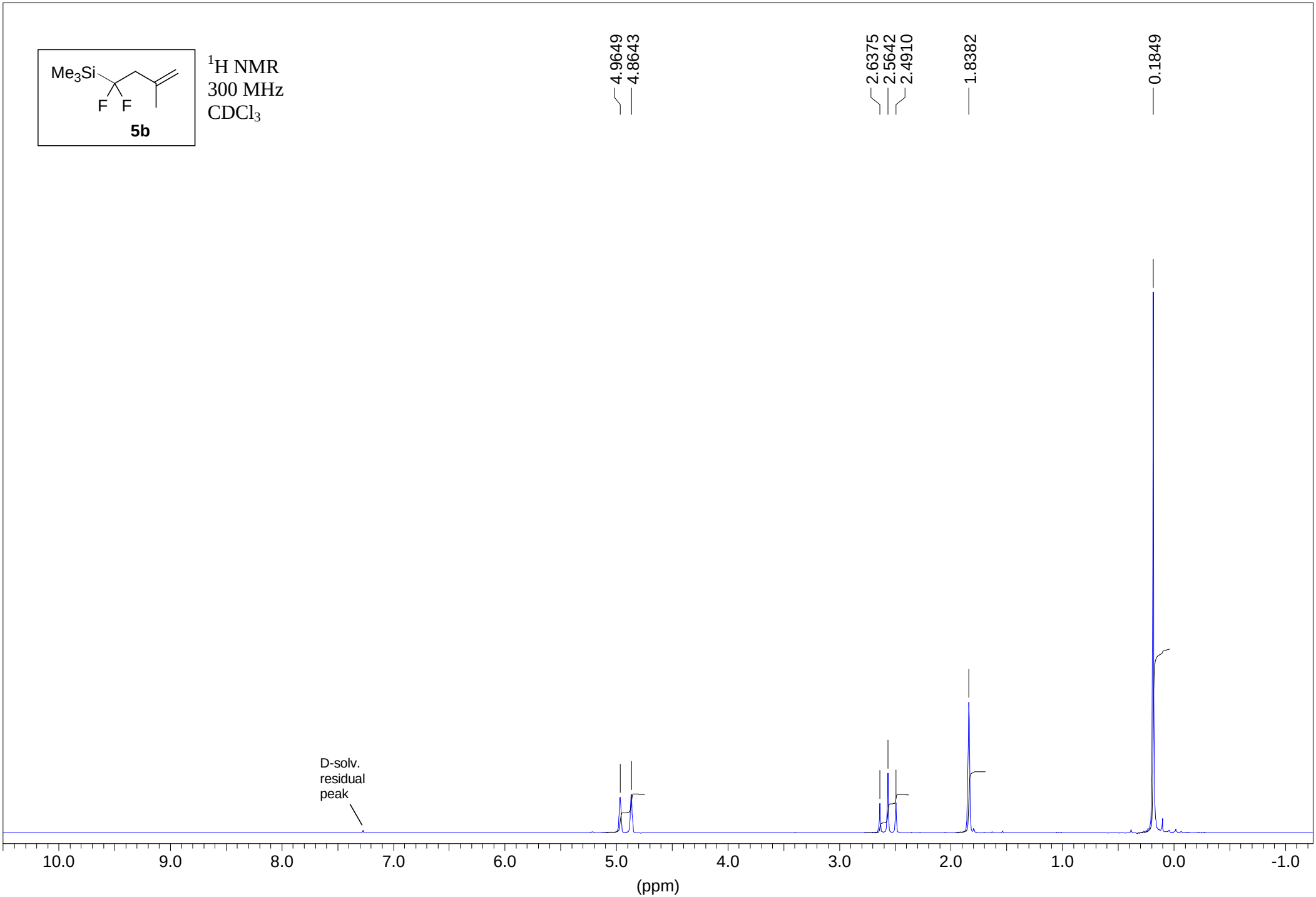
^{19}F NMR
282 MHz
CD_3CN

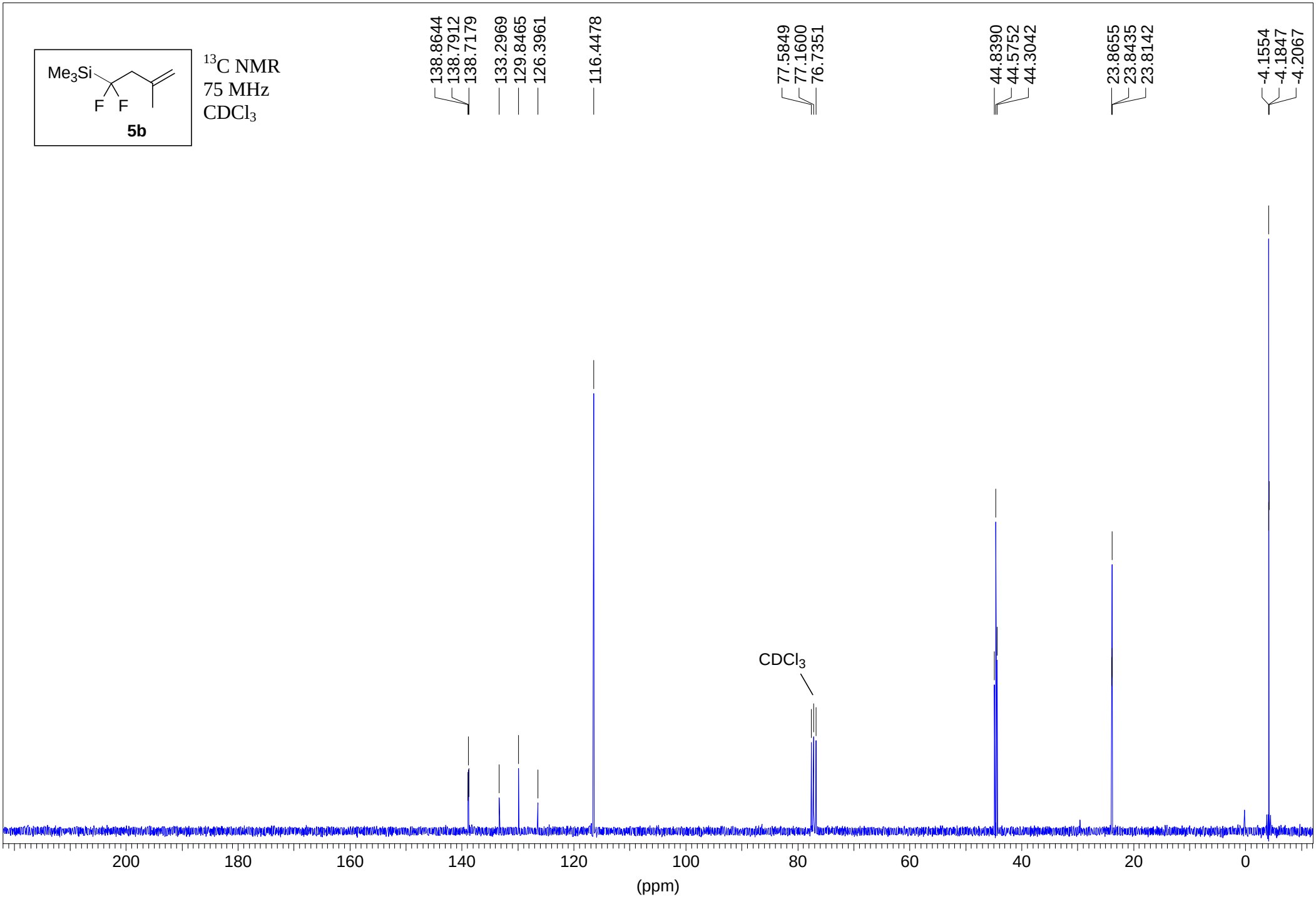

Me3Si
ZnBr
F F
2
-63.6587
19F NMR
282 MHz
non-deuterated THF/diglyme, 1/1
CF3
internal standard
-130.3652
-130.7480
-130.0
-131.0
(ppm)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140
(ppm)

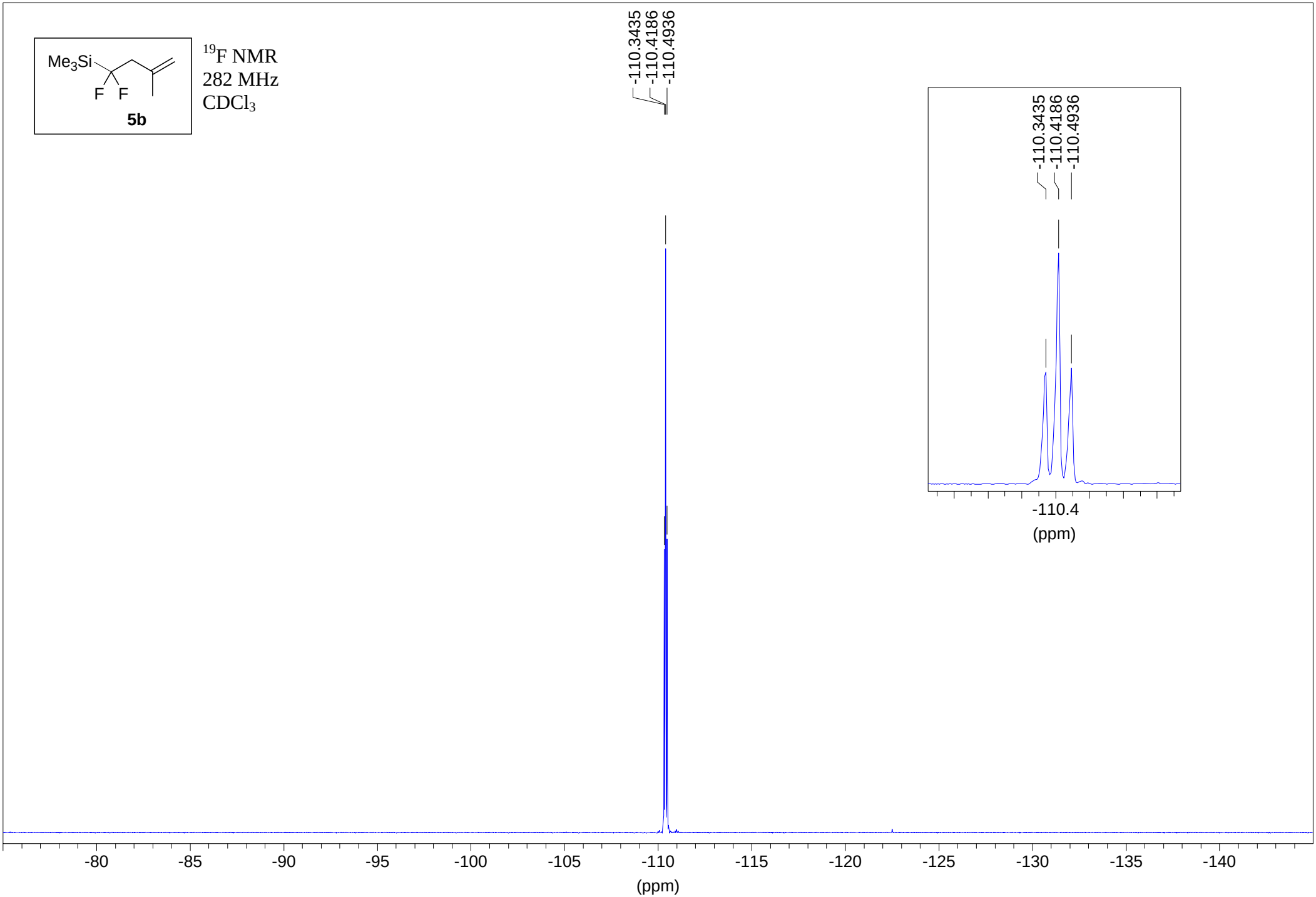

Me3Si
F F
5a
1H NMR
300 MHz
CDCl3
5.8740
5.8496
5.8191
5.2471
5.2044
2.7107
2.7076
2.6878
2.6405
2.6375
2.6176
2.5703
2.5475
0.1956
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

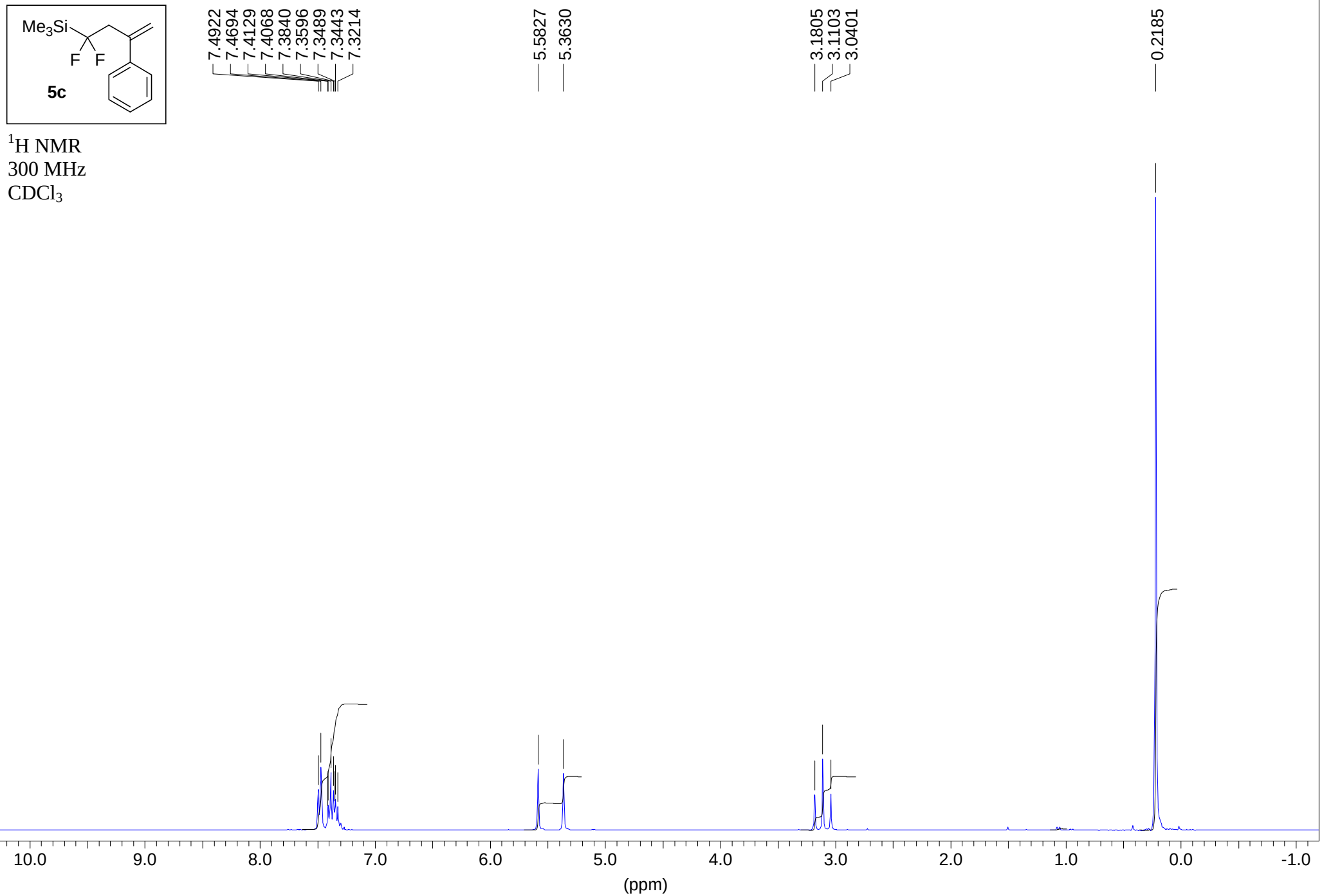

Me3Si
F F
5a
13C NMR
75 MHz
CDCl3
132.5863
130.0443
129.9344
129.8245
129.1432
125.7001
119.8835
77.5849
77.1600
76.7351
41.6816
41.4032
41.1248
-4.1407
-4.1700
-4.1920
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

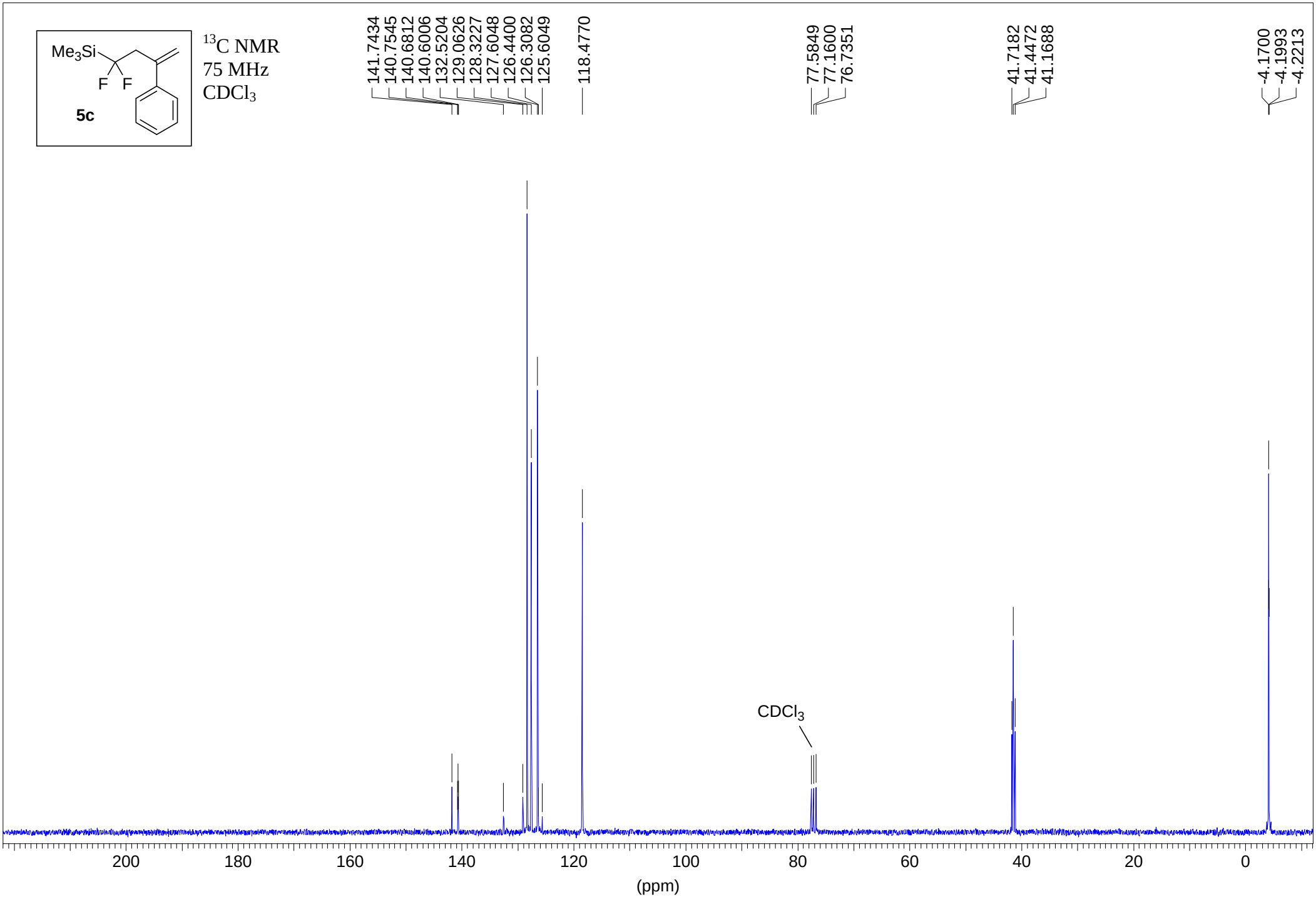

Me3Si
F F
5a
19F NMR
282 MHz
CDCl3
-112.5798
-112.6549
-112.7299
-112.2
-112.8
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)

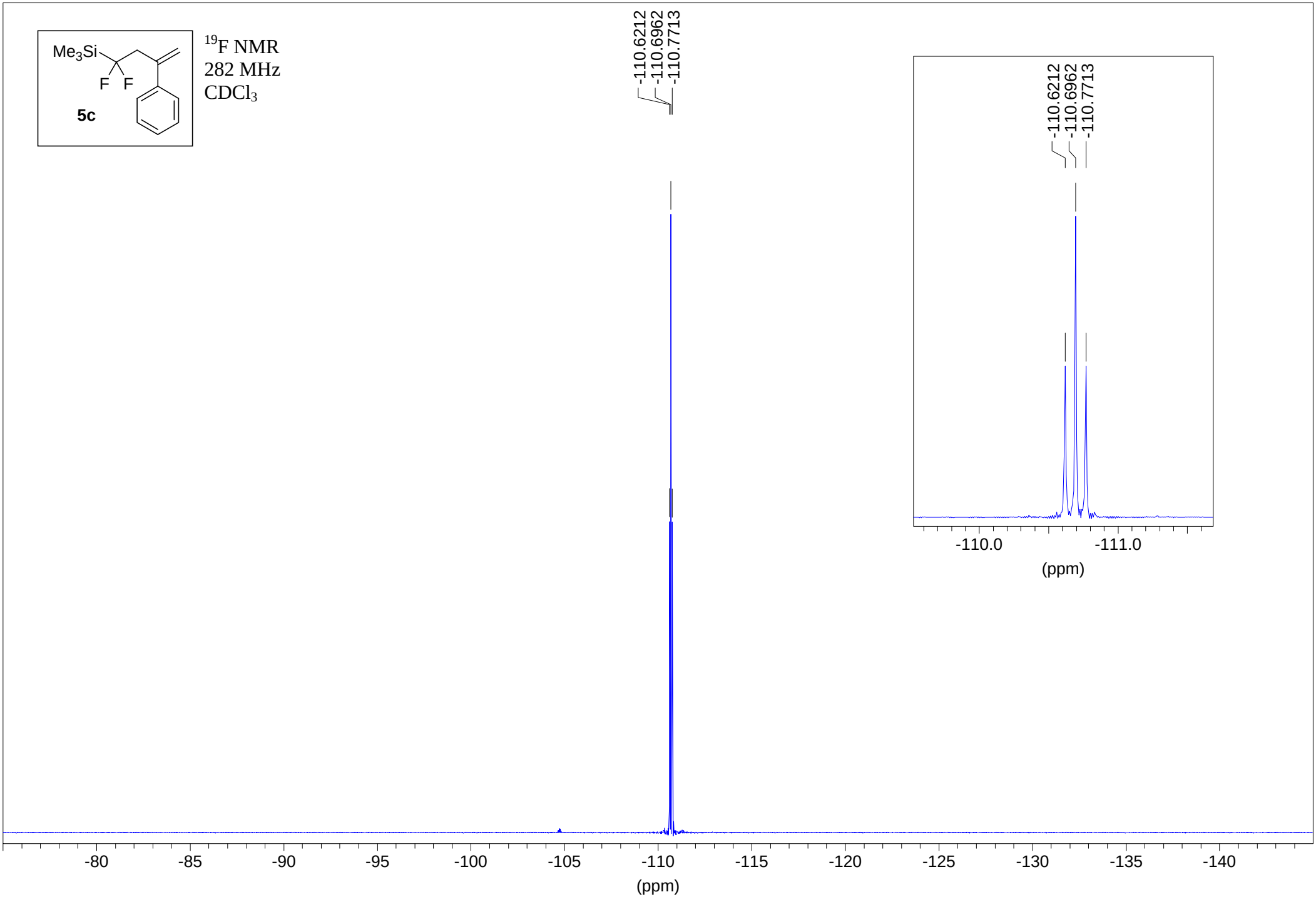

Me3Si
F F
5b
1H NMR
300 MHz
CDCl3
4.9649
4.8643
2.6375
2.5642
2.4910
1.8382
0.1849
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

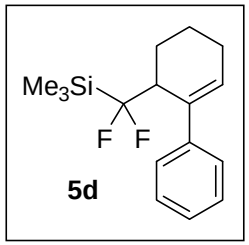

Me3Si
F F
5b
13C NMR
75 MHz
CDCl3
138.8644
138.7912
138.7179
133.2969
129.8465
126.3961
116.4478
77.5849
77.1600
76.7351
44.8390
44.5752
44.3042
23.8655
23.8435
23.8142
-4.1554
-4.1847
-4.2067
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)


Me3Si
F F
5b
19F NMR
282 MHz
CDCl3
-110.3435
-110.4186
-110.4936
-110.4
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)

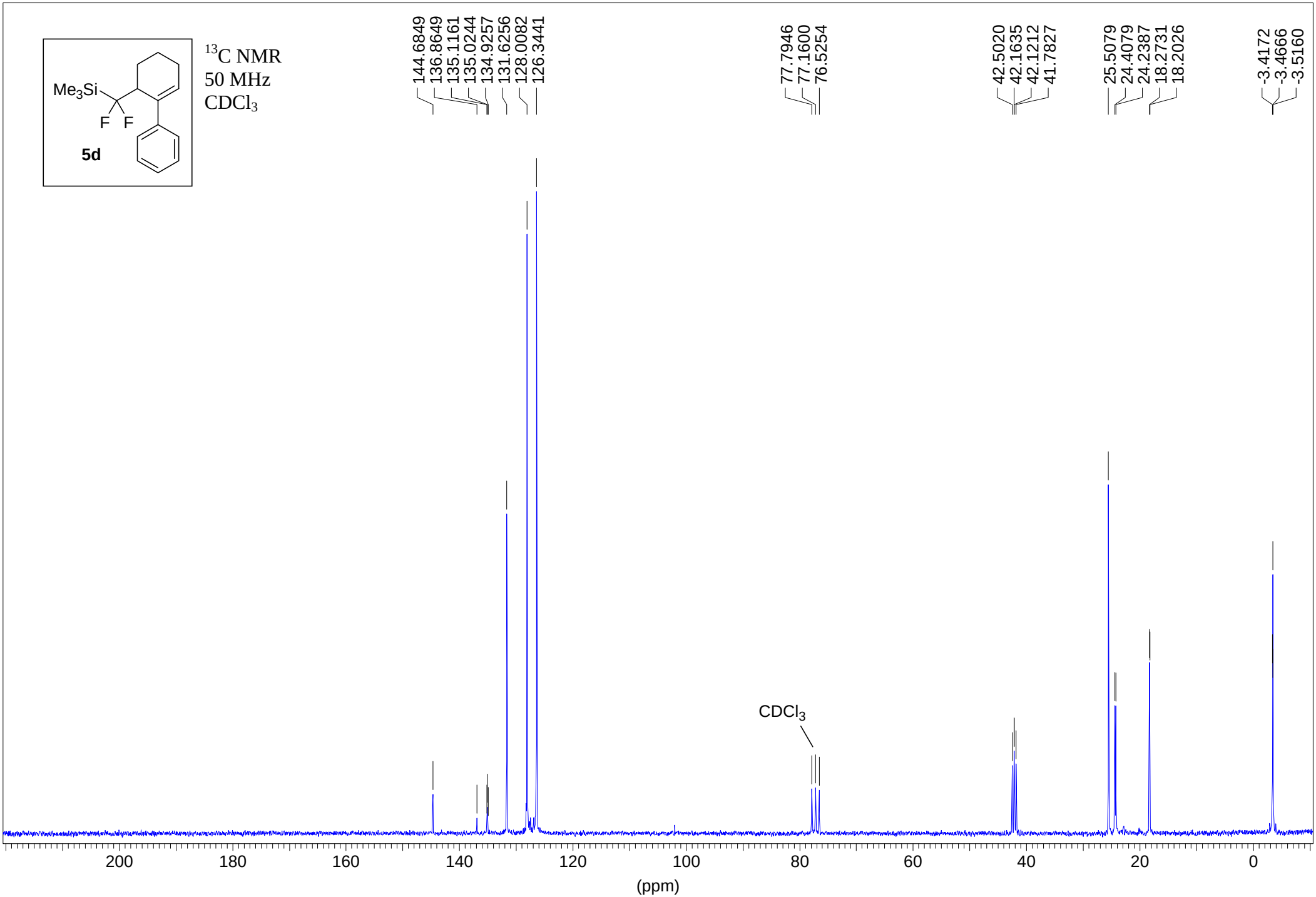

Me3Si
F F
5c
7.4922
7.4694
7.4129
7.4068
7.3840
7.3596
7.3489
7.3443
7.3214
5.5827
5.3630
3.1805
3.1103
3.0401
0.2185
1H NMR
300 MHz
CDCl3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

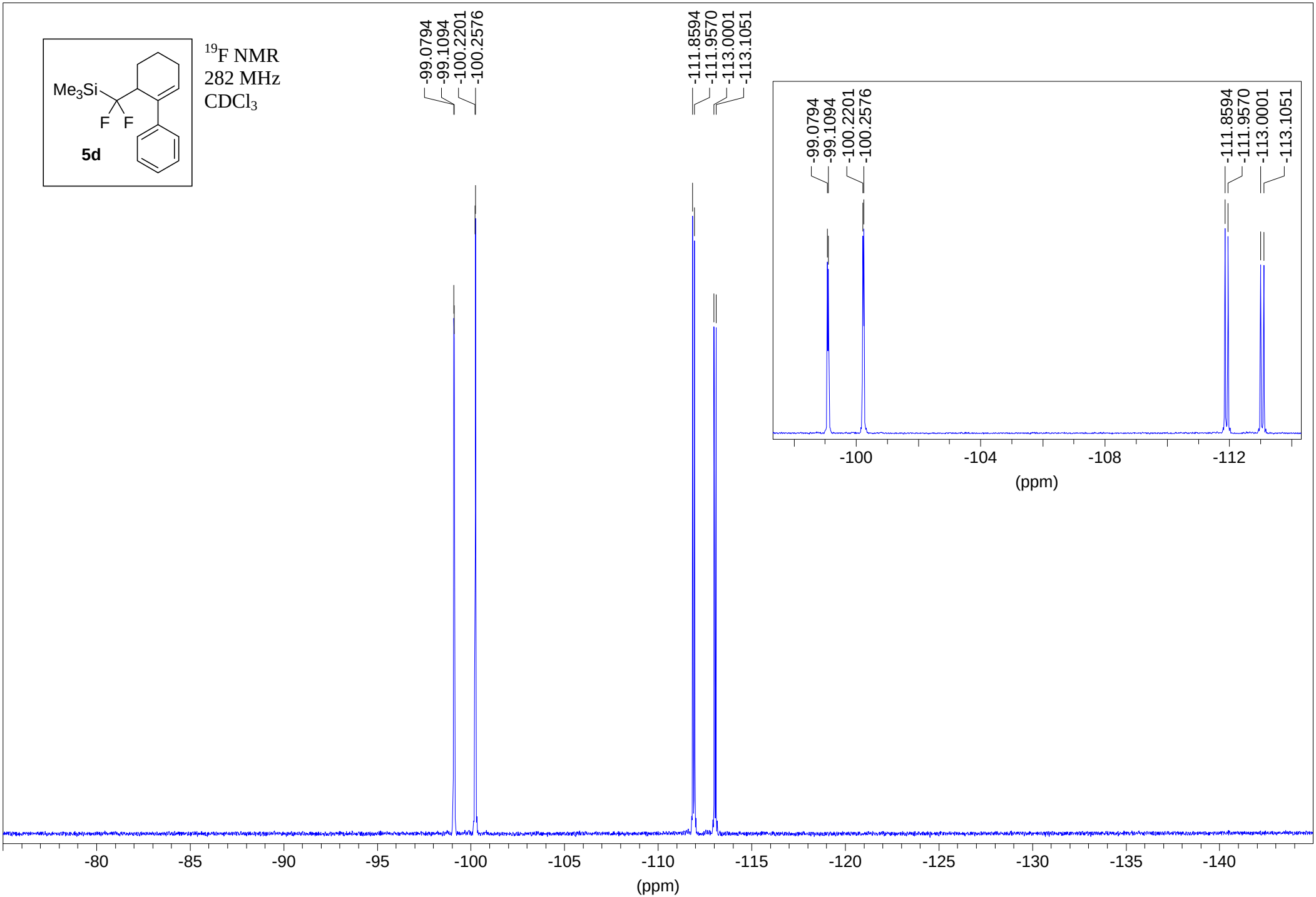

Me3Si
F F
5c
13C NMR
75 MHz
CDCl3
141.7434
140.7545
140.6812
140.6006
132.5204
129.0626
128.3227
127.6048
126.4400
126.3082
125.6049
118.4770
77.5849
77.1600
76.7351
41.7182
41.4472
41.1688
-4.1700
-4.1993
-4.2213
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

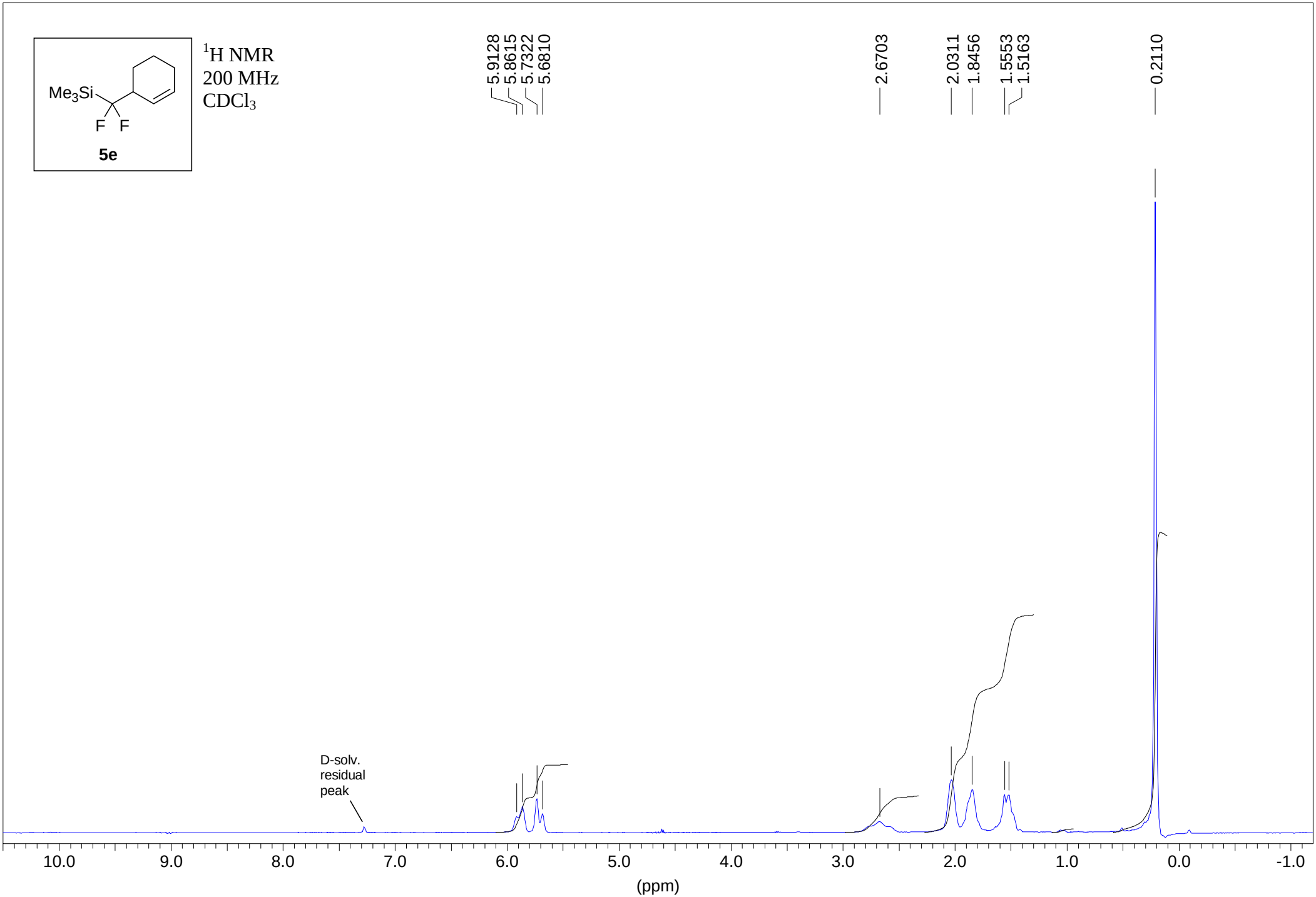

Me3Si
F F
5c
19F NMR
282 MHz
CDCl3
-110.6212
-110.6962
-110.7713
-110.6212
-110.6962
-110.7713
-110.0
-111.0
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)

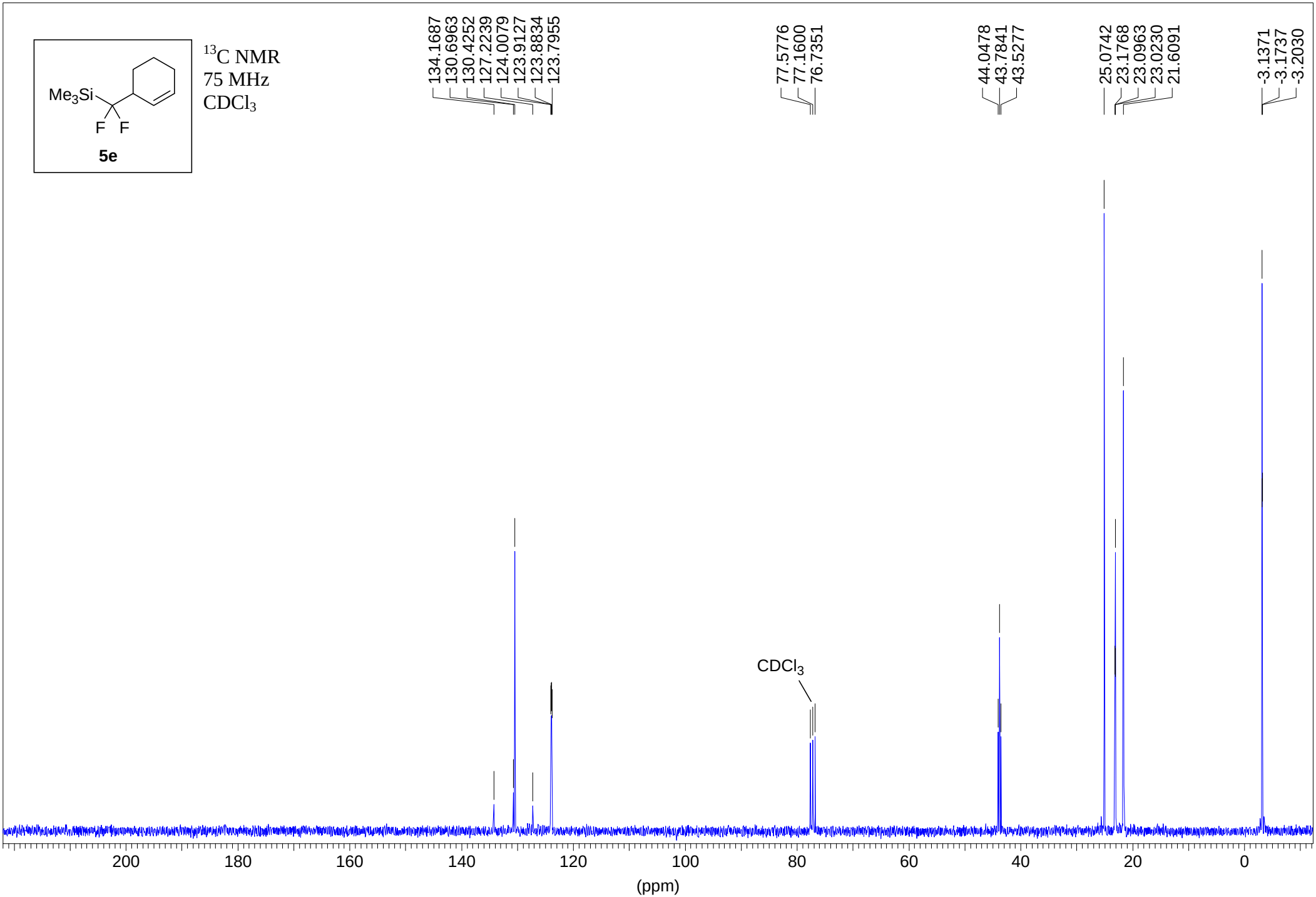


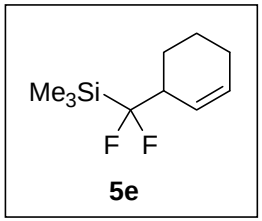
^{1}H NMR
300 MHz
$CDCl_3$


Me3Si
F F
5d
13C NMR
50 MHz
CDCl3
144.6849
136.8649
135.1161
135.0244
134.9257
131.6256
128.0082
126.3441
77.7946
77.1600
76.5254
42.5020
42.1635
42.1212
41.7827
25.5079
24.4079
24.2387
18.2731
18.2026
-3.4172
-3.4666
-3.5160
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)


Me3Si
F F
5d
19F NMR
282 MHz
CDCl3
-99.0794
-99.1094
-100.2201
-100.2576
-111.8594
-111.9570
-113.0001
-113.1051
-100
-104
-108
-112
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)

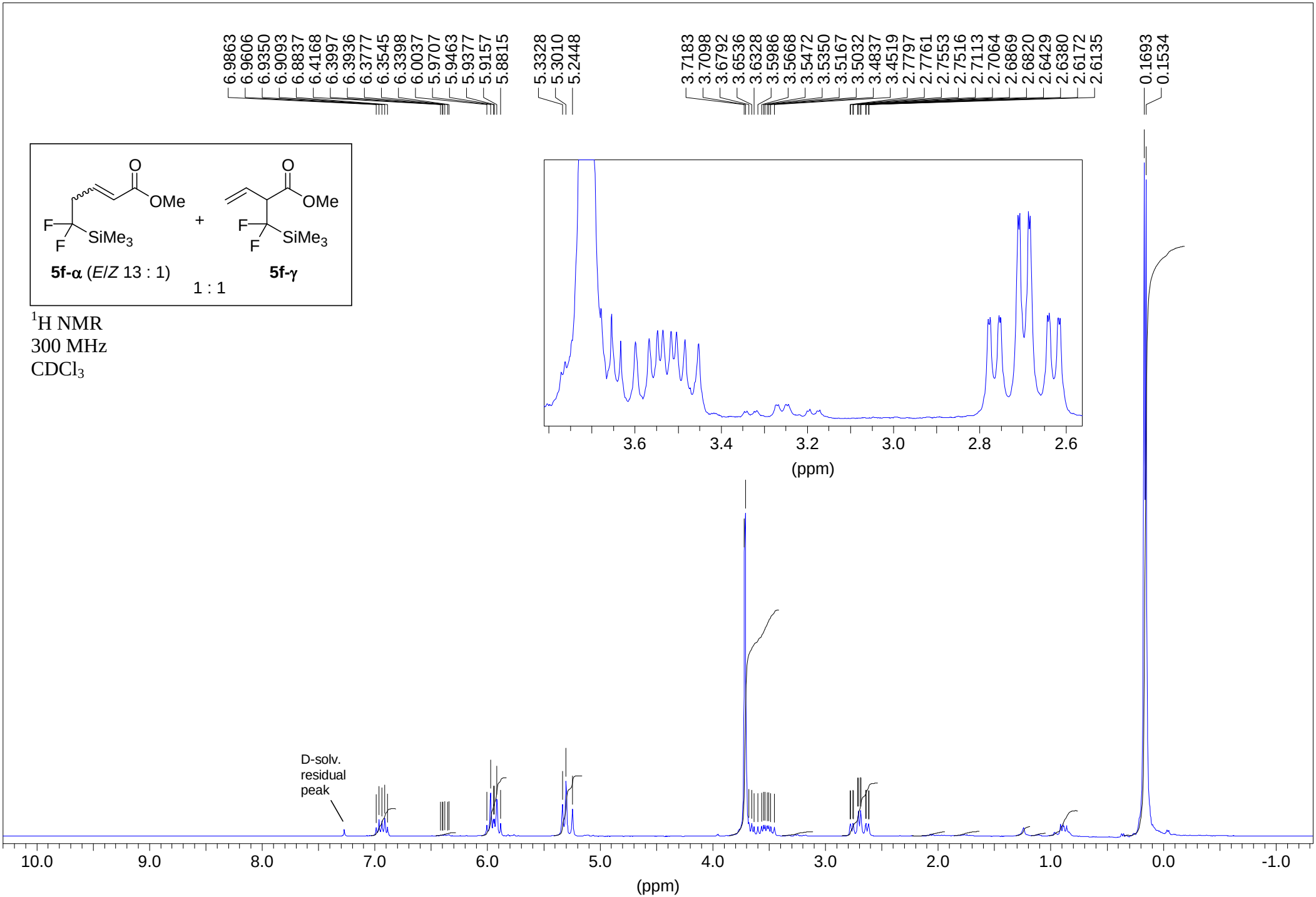

Me3Si
F F
5e
1H NMR
200 MHz
CDCl3
5.9128
5.8615
5.7322
5.6810
2.6703
2.0311
1.8456
1.5553
1.5163
0.2110
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

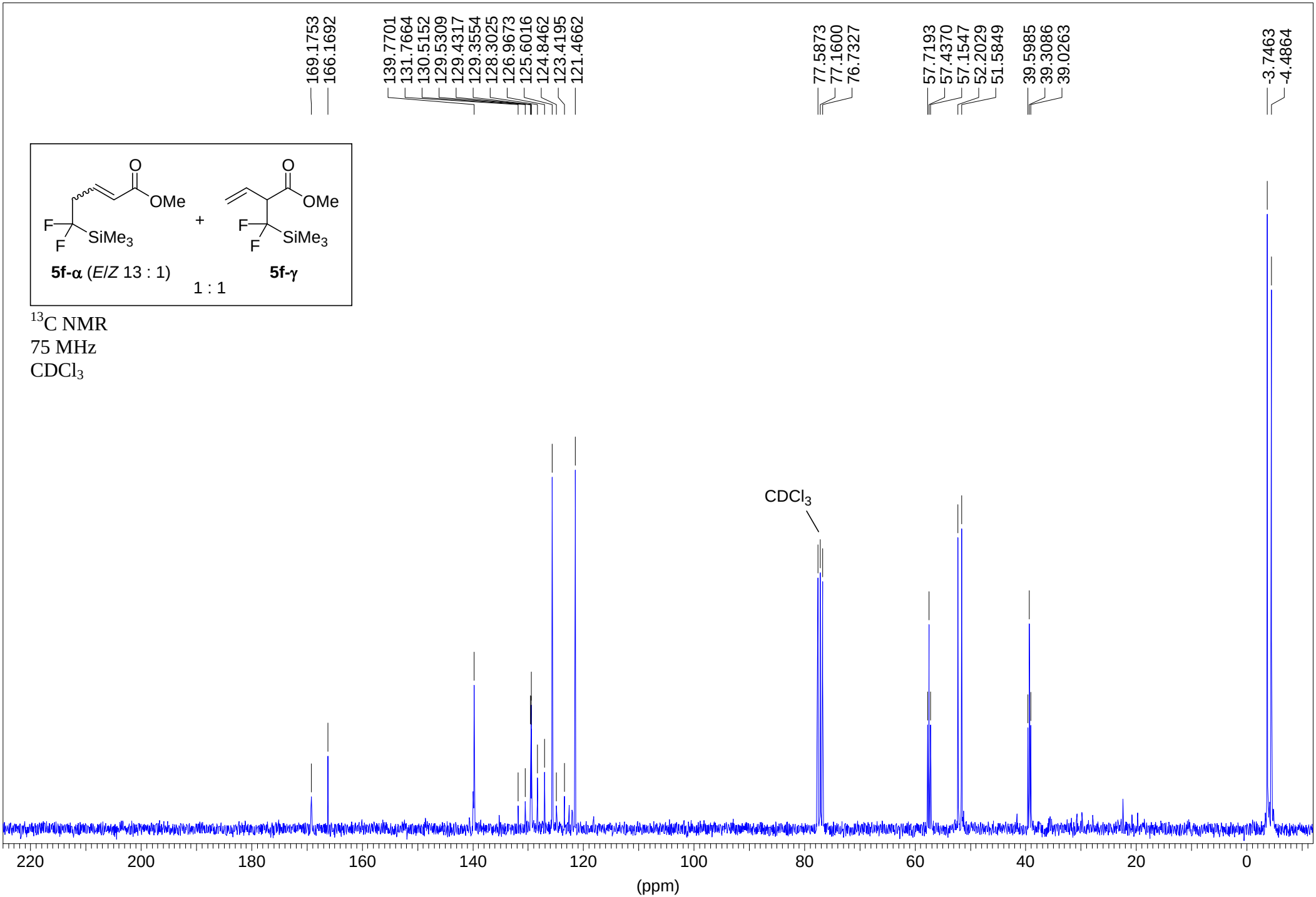

Me3Si
F F
5e
13C NMR
75 MHz
CDCl3
134.1687
130.6963
130.4252
127.2239
124.0079
123.9127
123.8834
123.7955
77.5776
77.1600
76.7351
44.0478
43.7841
43.5277
25.0742
23.1768
23.0963
23.0230
21.6091
-3.1371
-3.1737
-3.2030
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

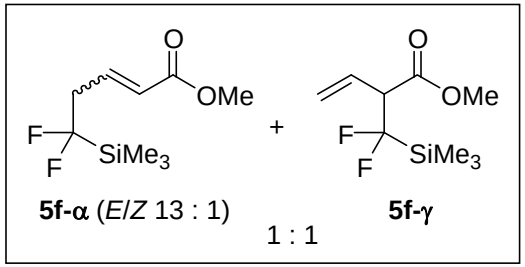


5e

^{19}F NMR
282 MHz
$CDCl_3$


6.9863
6.9606
6.9350
6.9093
6.8837
6.4168
6.3997
6.3936
6.3777
6.3545
6.3398
6.0037
5.9707
5.9463
5.9377
5.9157
5.8815
5.3328
5.3010
5.2448
3.7183
3.7098
3.6792
3.6536
3.6328
3.5986
3.5668
3.5472
3.5350
3.5167
3.5032
3.4837
3.4519
2.7797
2.7761
2.7553
2.7516
2.7113
2.7064
2.6869
2.6820
2.6429
2.6380
2.6172
2.6135
0.1693
0.1534
O
OMe
F
F
SiMe3
+
5f-α (E/Z 13 : 1)
5f-γ
1 : 1
1H NMR
300 MHz
CDCl3
3.6
3.4
3.2
3.0
2.8
2.6
(ppm)
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

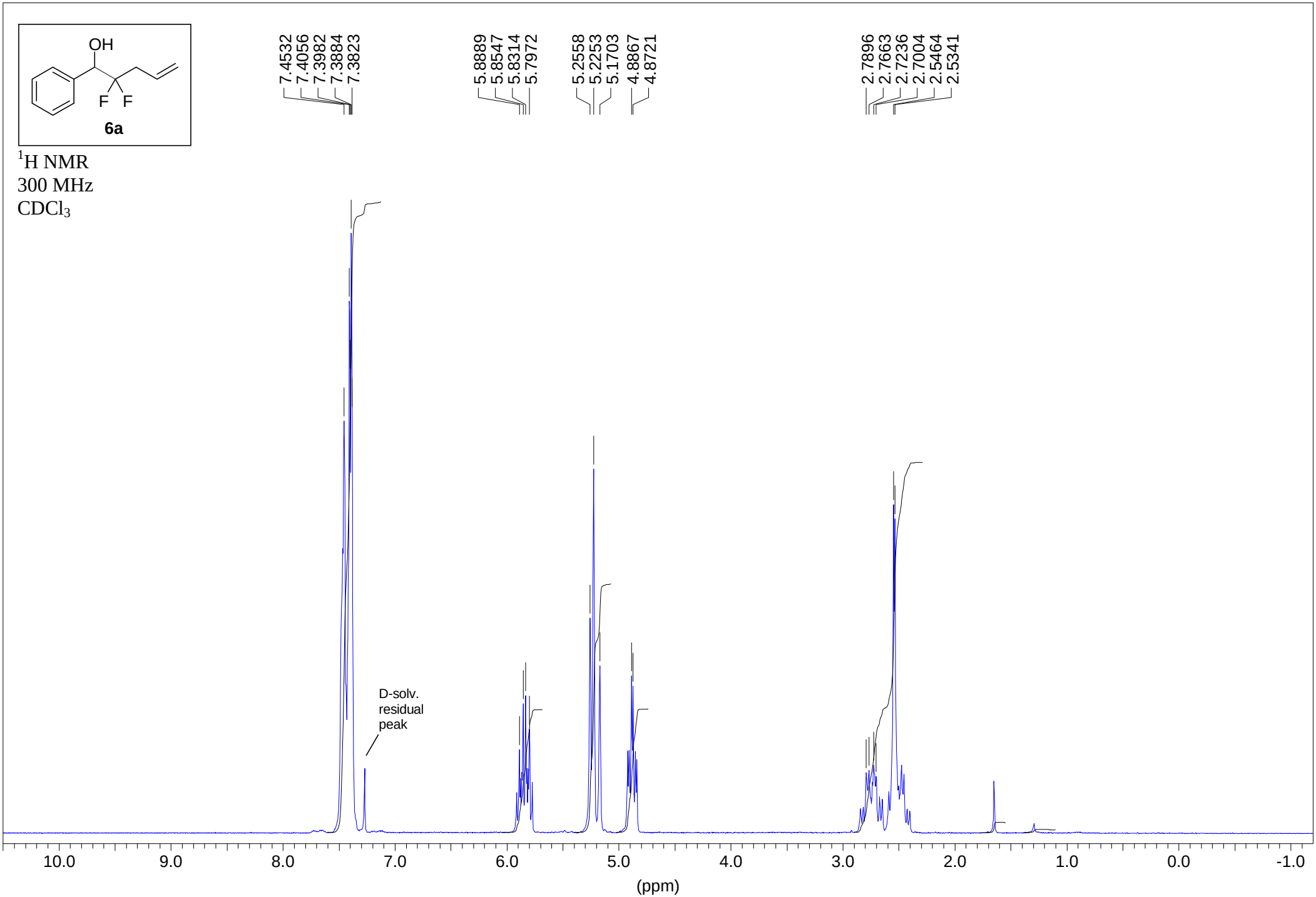

169.1753
166.1692
139.7701
131.7664
130.5152
129.5309
129.4317
129.3554
128.3025
126.9673
125.6016
124.8462
123.4195
121.4662
77.5873
77.1600
76.7327
57.7193
57.4370
57.1547
52.2029
51.5849
39.5985
39.3086
39.0263
-3.7463
-4.4864
O
OMe
F
F
SiMe3
+
O
OMe
F
F
SiMe3
5f-α (E/Z 13 : 1)
5f-γ
1 : 1
13C NMR
75 MHz
CDCl3
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

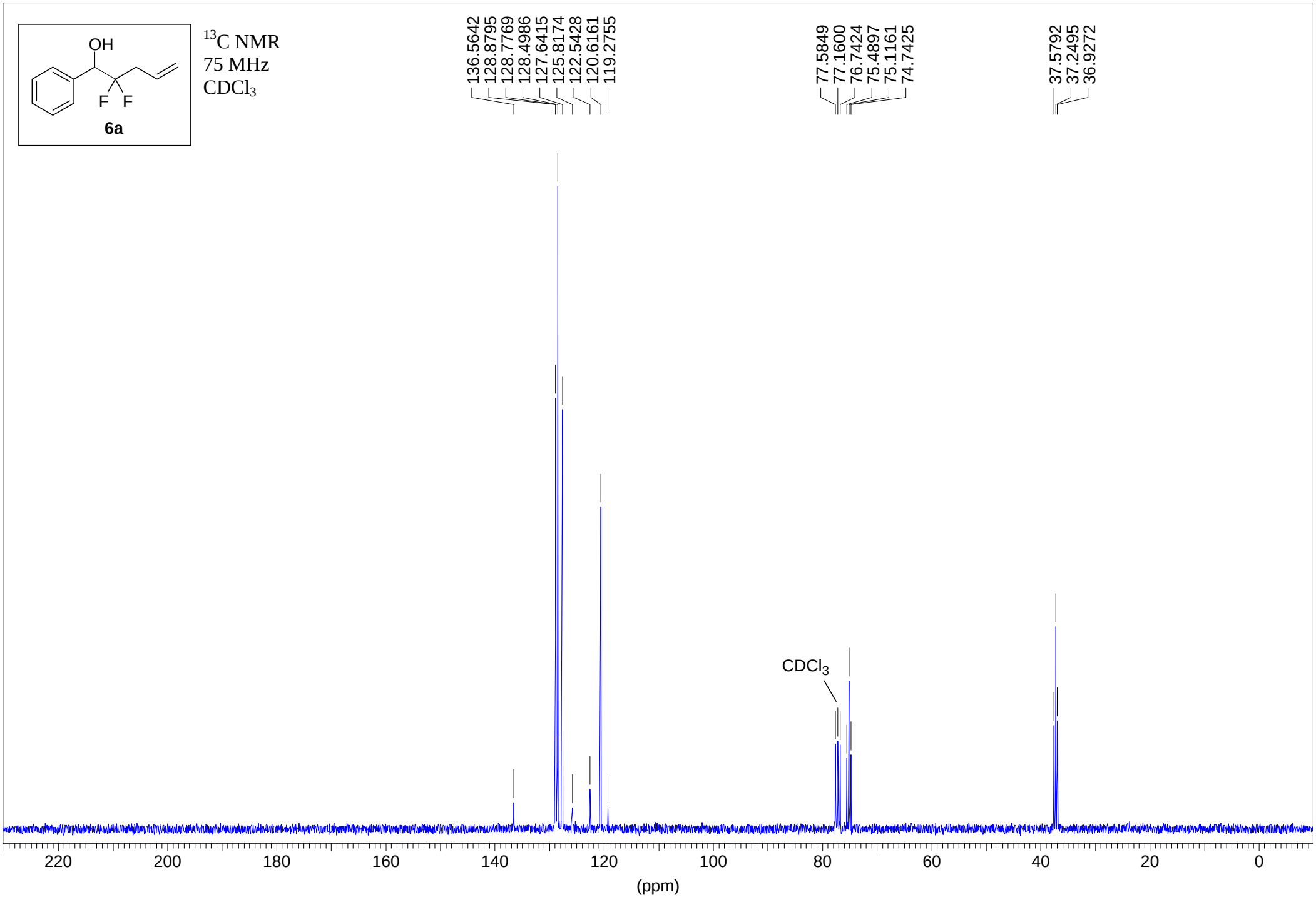


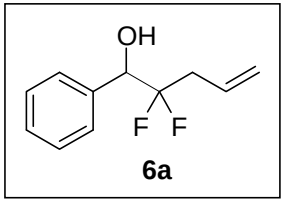
5f-α (*E*/*Z* 13 : 1) + **5f-γ**

1 : 1

^{19}F NMR
282 MHz
$CDCl_3$

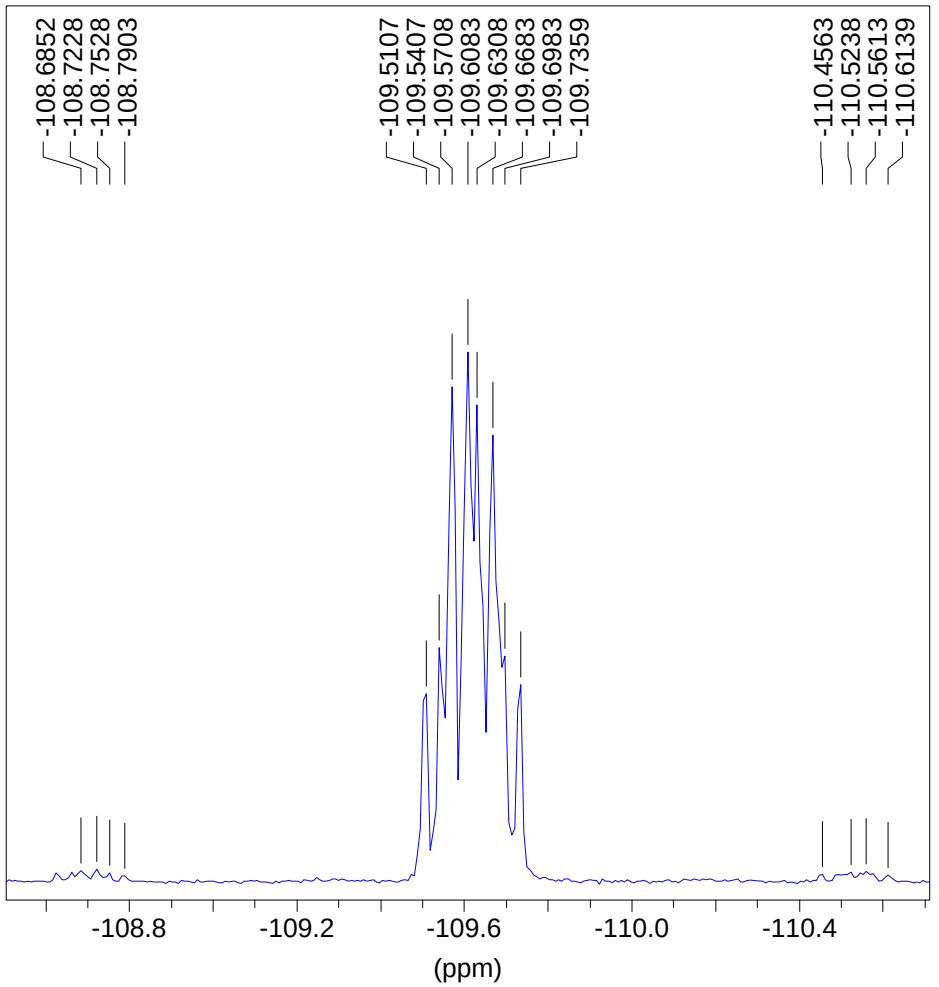

OH
F F
6a
7.4532
7.4056
7.3982
7.3884
7.3823
5.8889
5.8547
5.8314
5.7972
5.2558
5.2253
5.1703
4.8867
4.8721
2.7896
2.7663
2.7236
2.7004
2.5464
2.5341
1H NMR
300 MHz
CDCl3
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

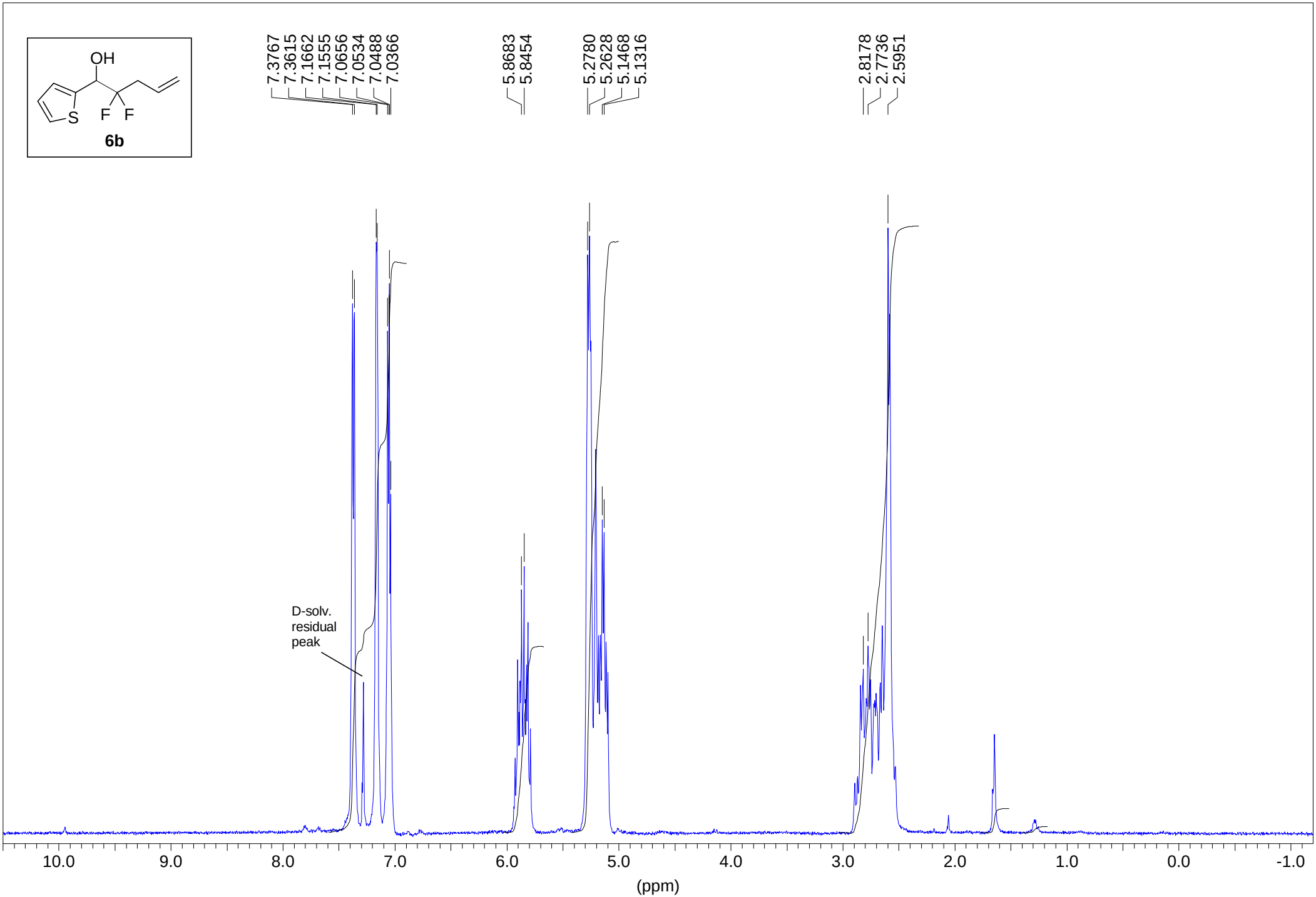

OH
F F
6a
13C NMR
75 MHz
CDCl3
136.5642
128.8795
128.7769
128.4986
127.6415
125.8174
122.5428
120.6161
119.2755
77.5849
77.1600
76.7424
75.4897
75.1161
74.7425
37.5792
37.2495
36.9272
CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)

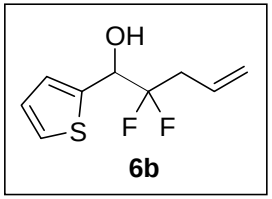


6a

^{19}F NMR
282 MHz
$CDCl_3$




OH
S
F
F
6b
7.3767
7.3615
7.1662
7.1555
7.0656
7.0534
7.0488
7.0366
5.8683
5.8454
5.2780
5.2628
5.1468
5.1316
2.8178
2.7736
2.5951
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)



6b

^{13}C NMR
75 MHz
$CDCl_3$

139.0476
128.7037
128.6378
128.5645
126.9382
126.4181
125.3339
122.0519
120.8798
118.7847

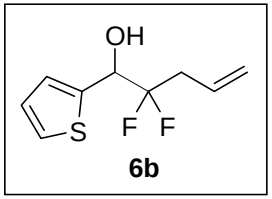
77.5849
77.1600
76.7424
71.9880
71.5925
71.1969

37.6744
37.3521
37.0298

$CDCl_3$

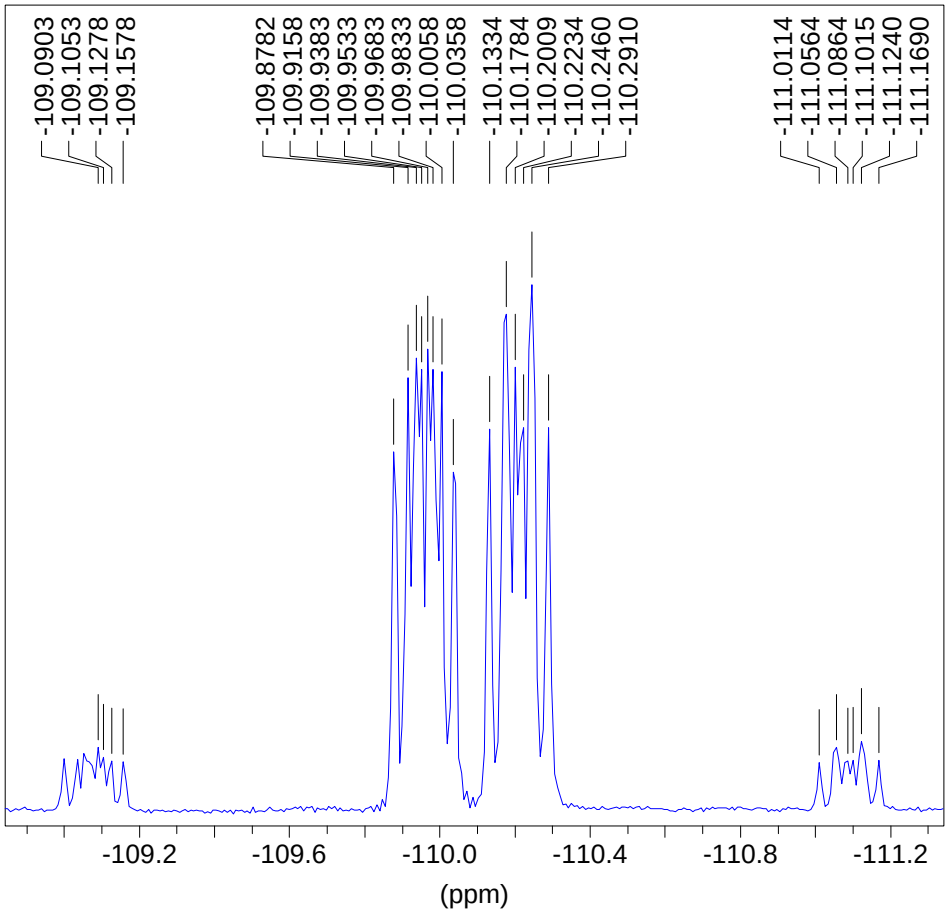
220 200 180 160 140 120 100 80 60 40 20 0

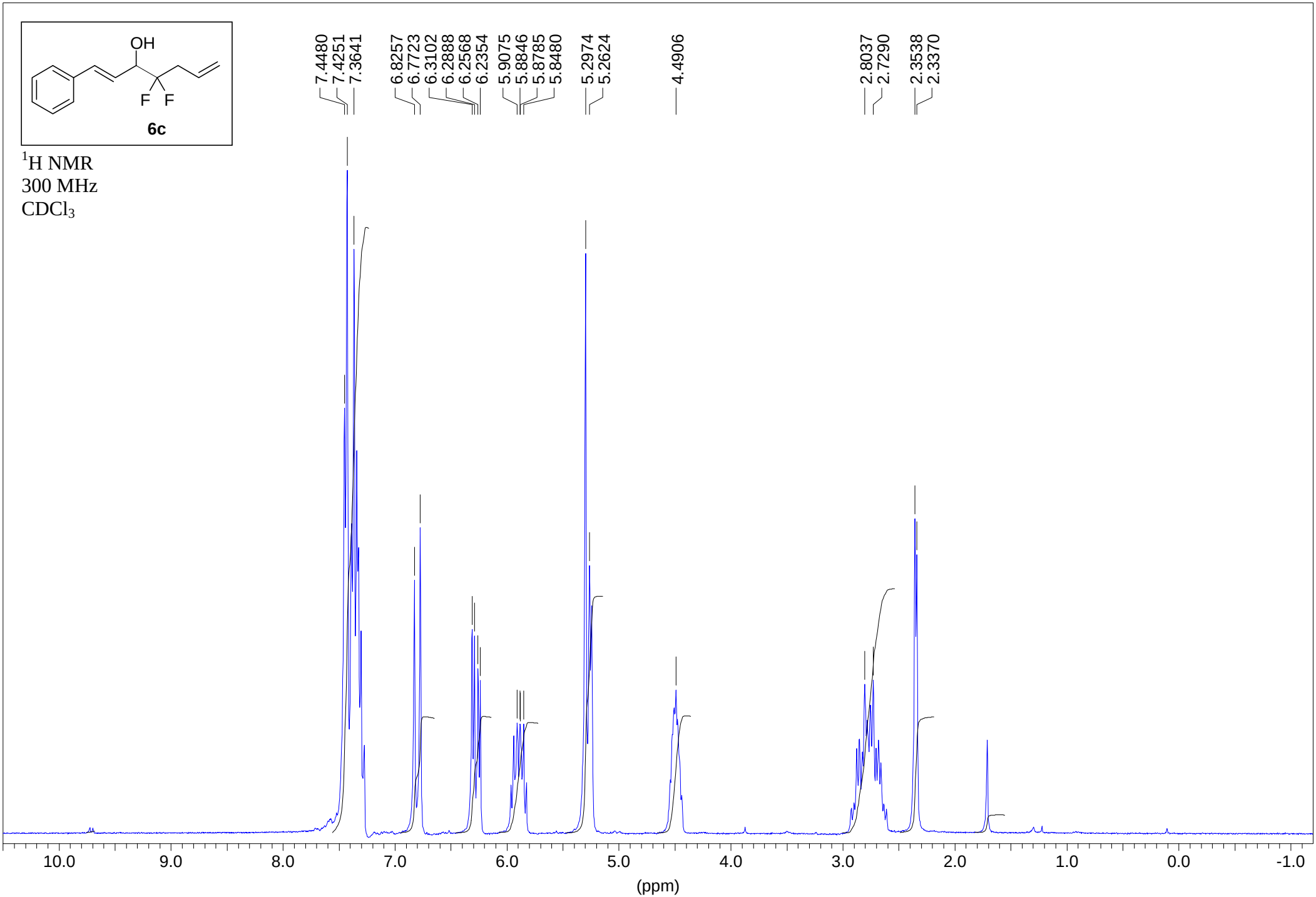
(ppm)

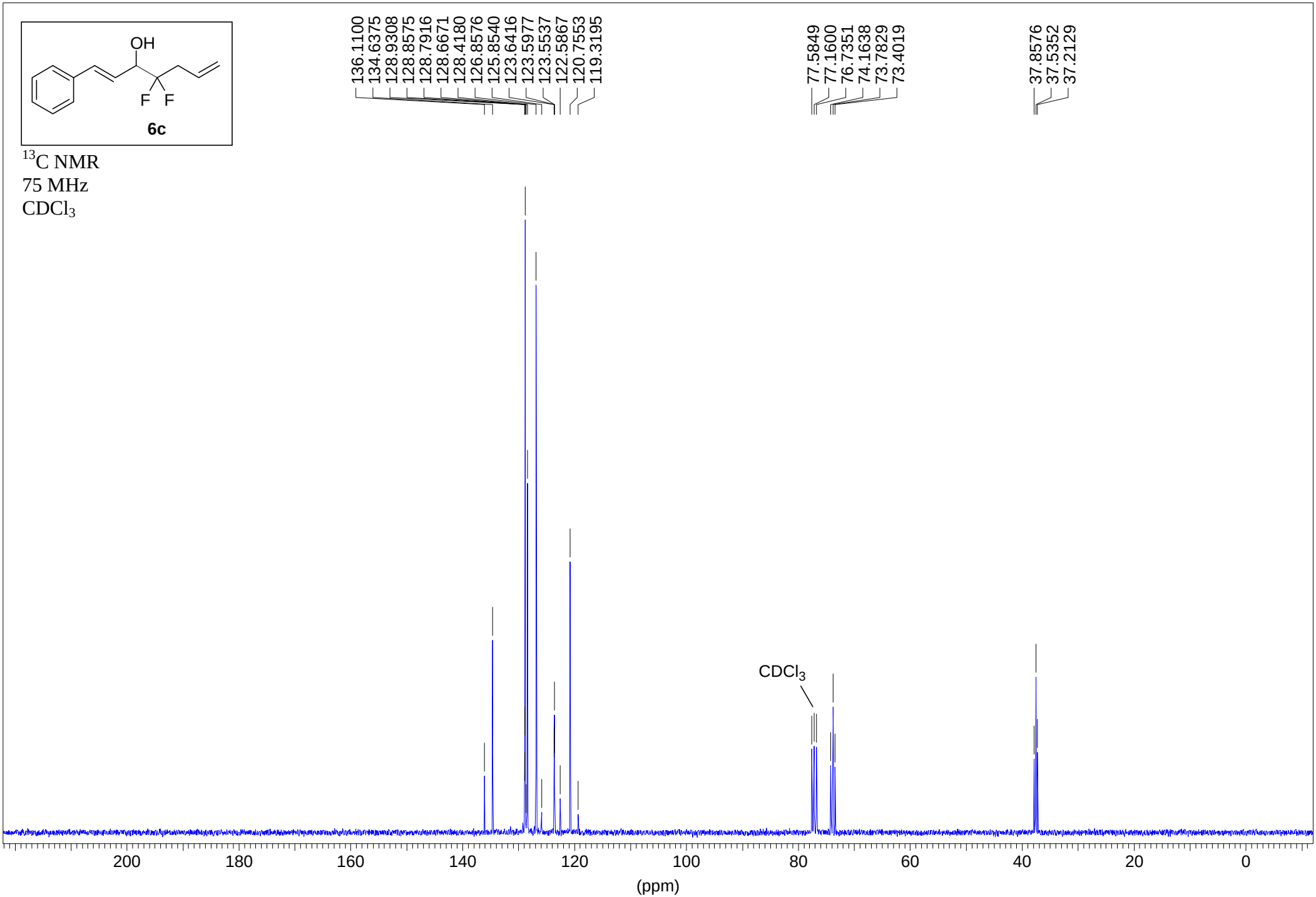


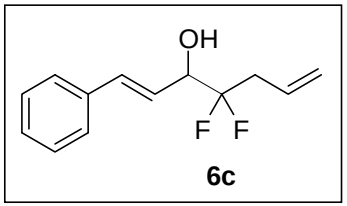
6b

^{19}F NMR
282 MHz
$CDCl_3$



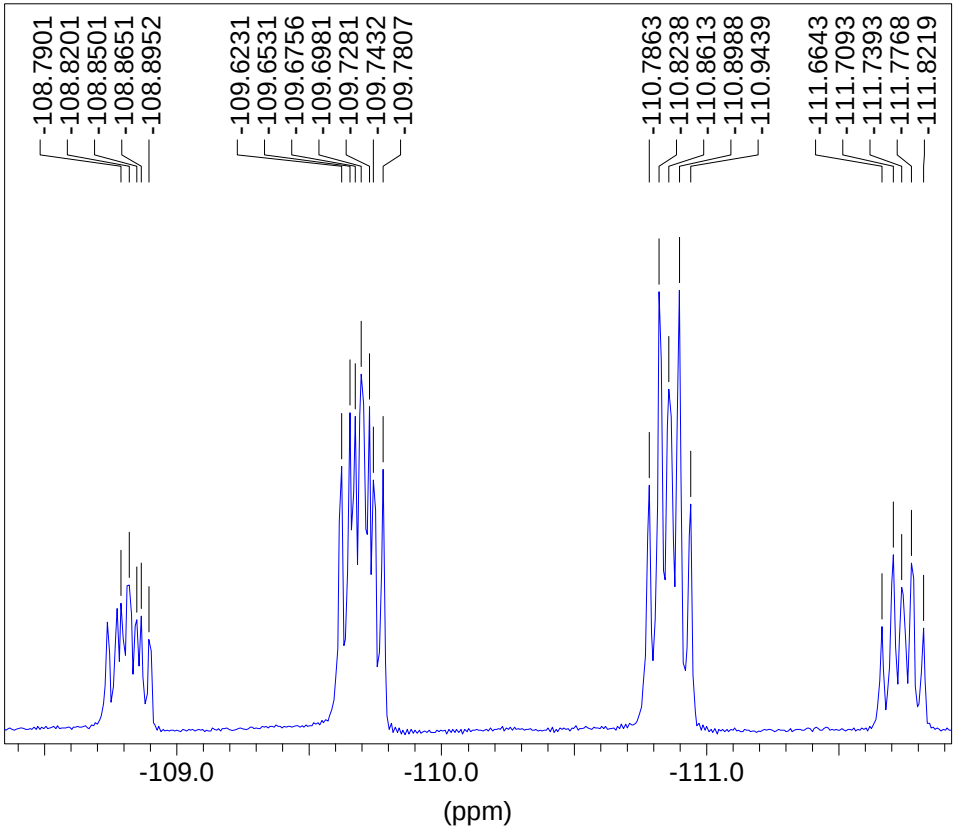

OH
F F
6c
7.4480
7.4251
7.3641
6.8257
6.7723
6.3102
6.2888
6.2568
6.2354
5.9075
5.8846
5.8785
5.8480
5.2974
5.2624
4.4906
2.8037
2.7290
2.3538
2.3370
1H NMR
300 MHz
CDCl3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

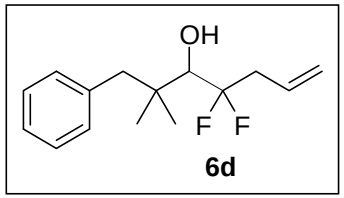

OH
F F
6c
136.1100
134.6375
128.9308
128.8575
128.7916
128.6671
128.4180
126.8576
125.8540
123.6416
123.5977
123.5537
122.5867
120.7553
119.3195
77.5849
77.1600
76.7351
74.1638
73.7829
73.4019
37.8576
37.5352
37.2129
13C NMR
75 MHz
CDCl3
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



6c

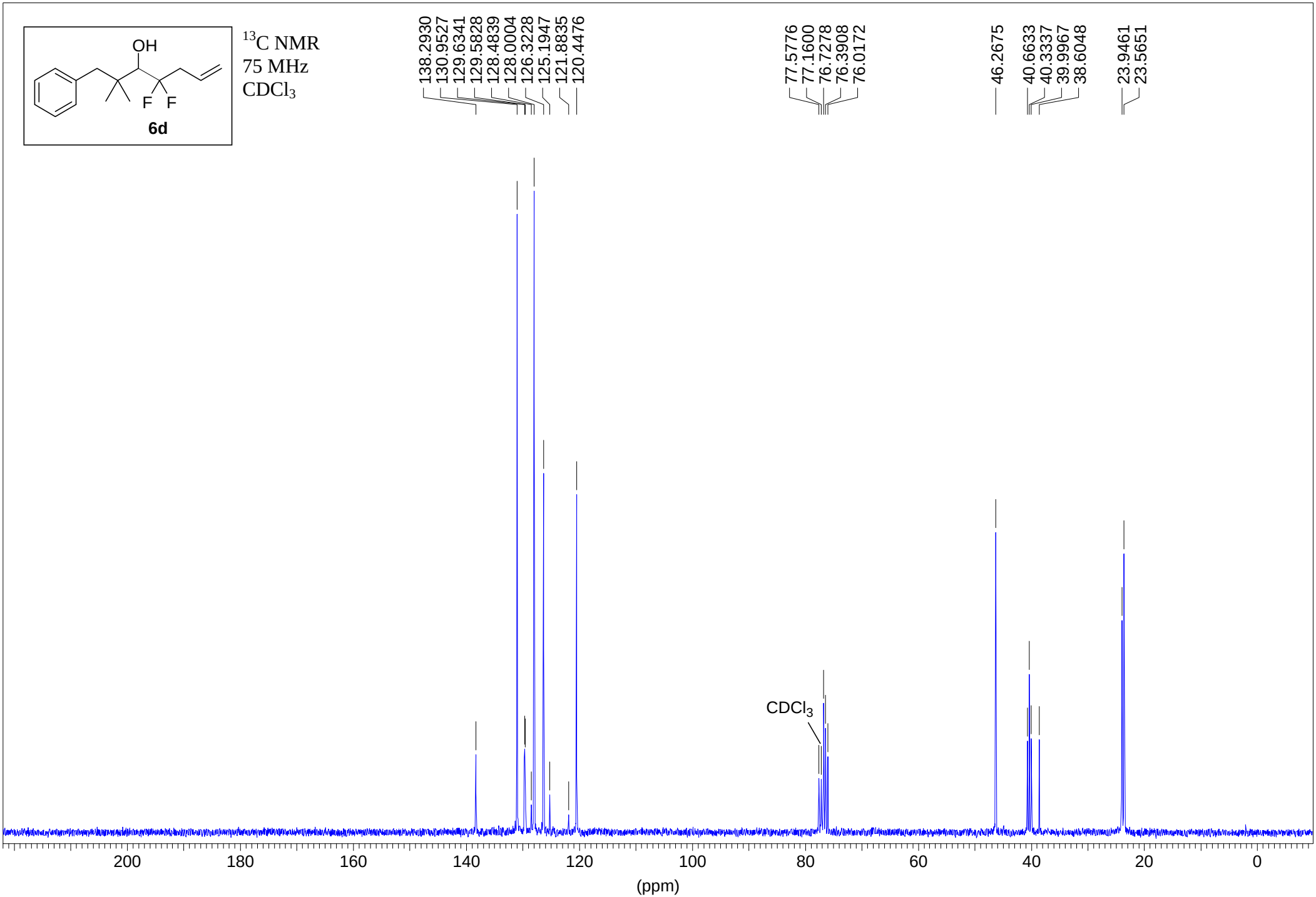
^{19}F NMR
282 MHz
$CDCl_3$

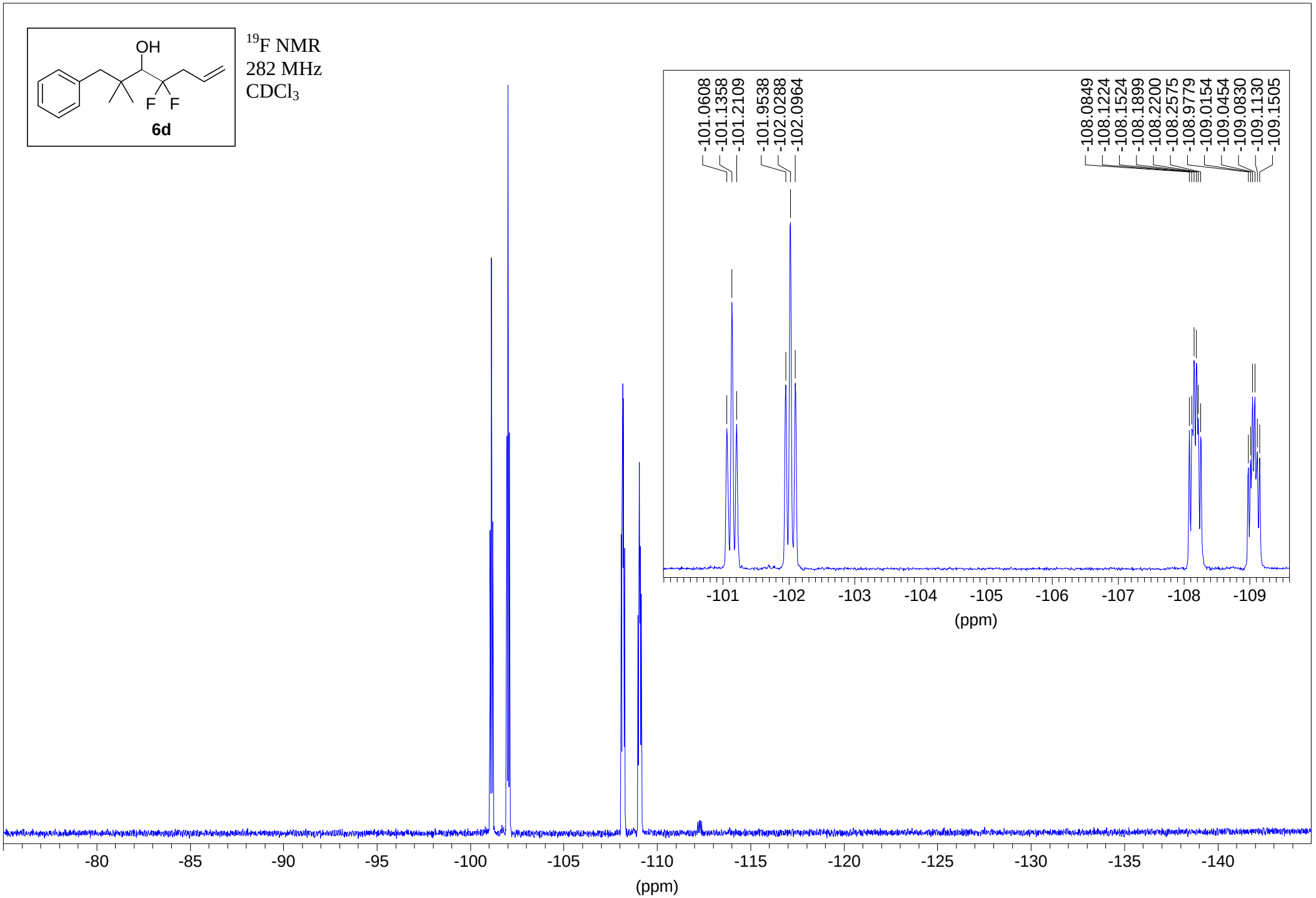


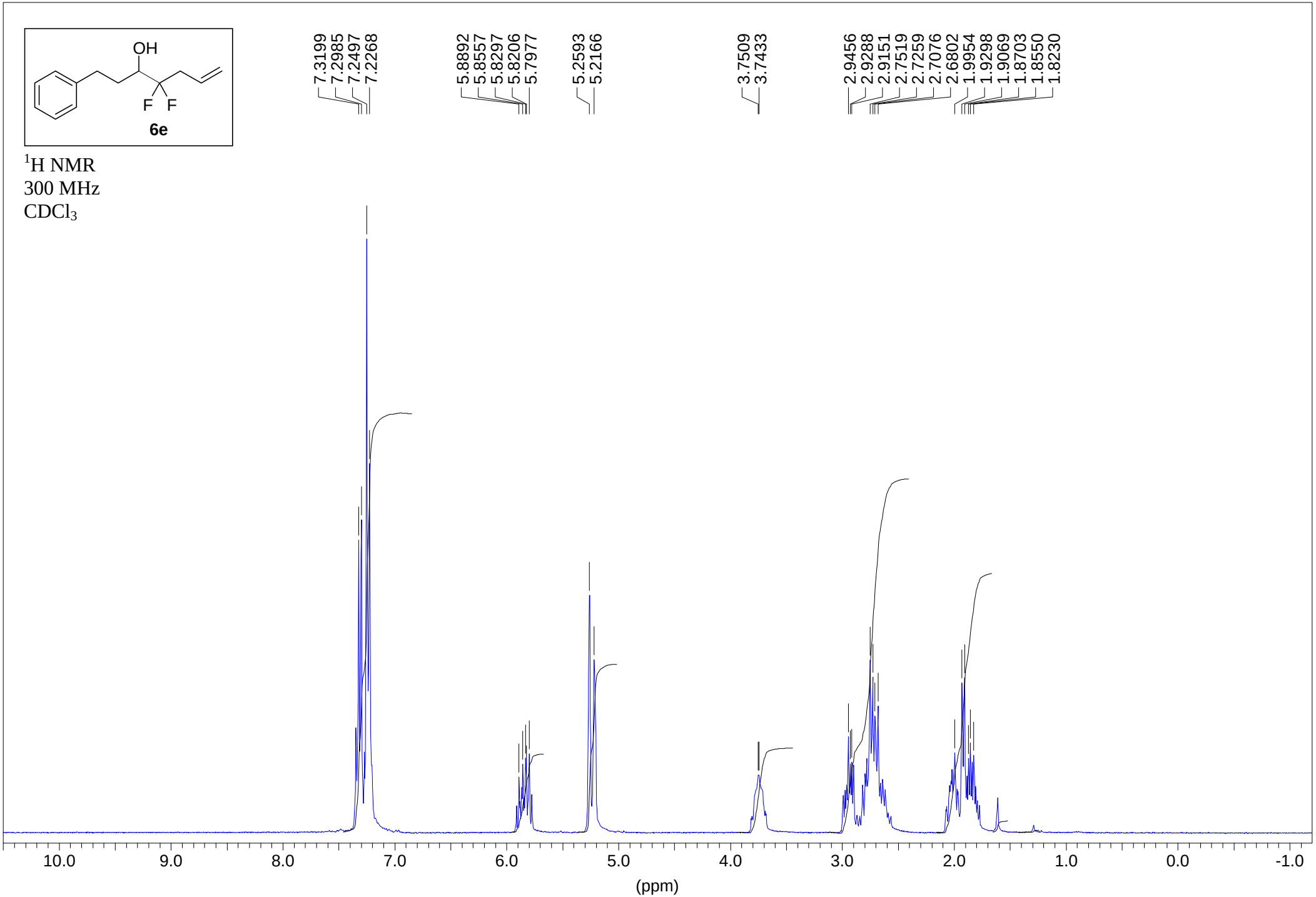


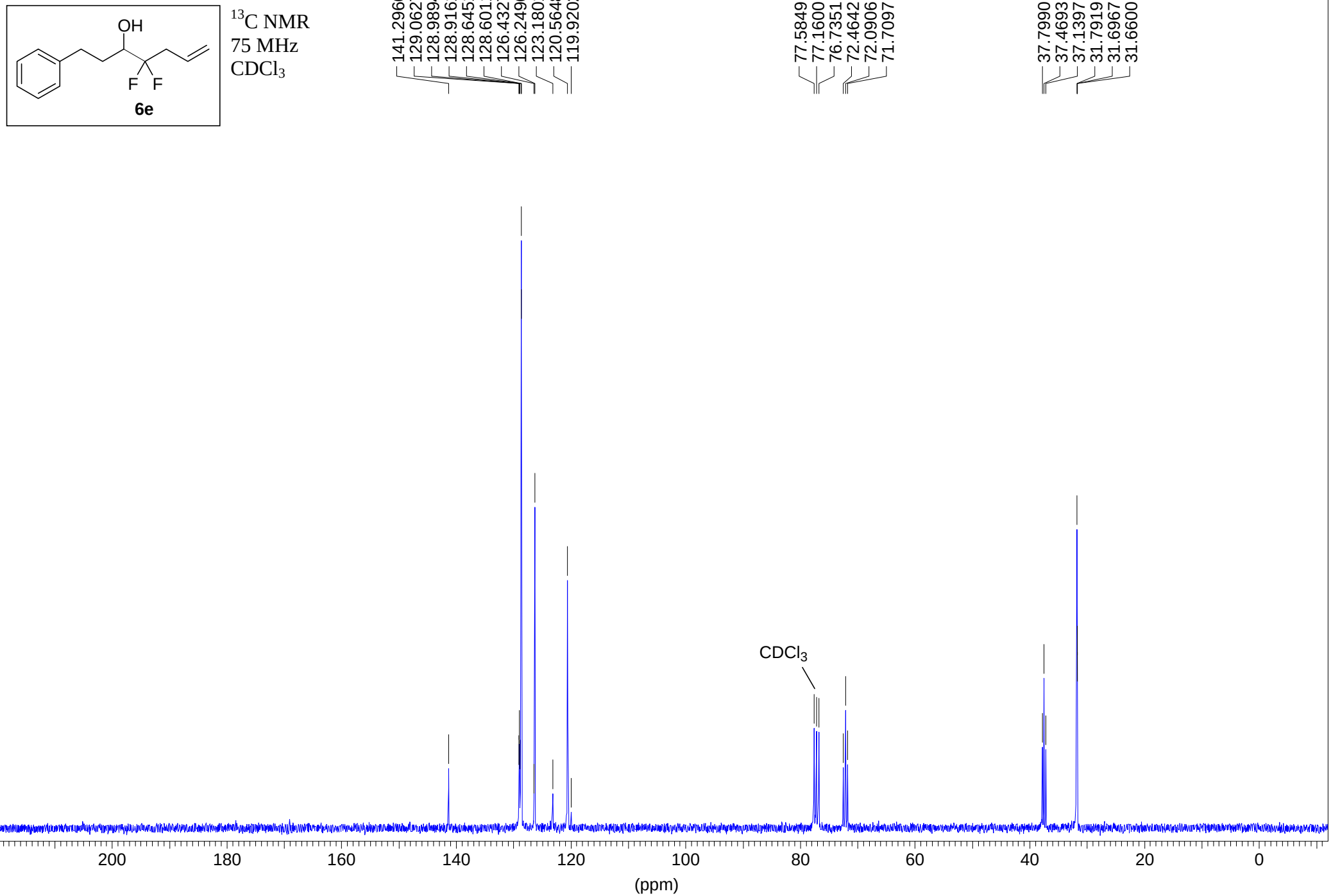
6d

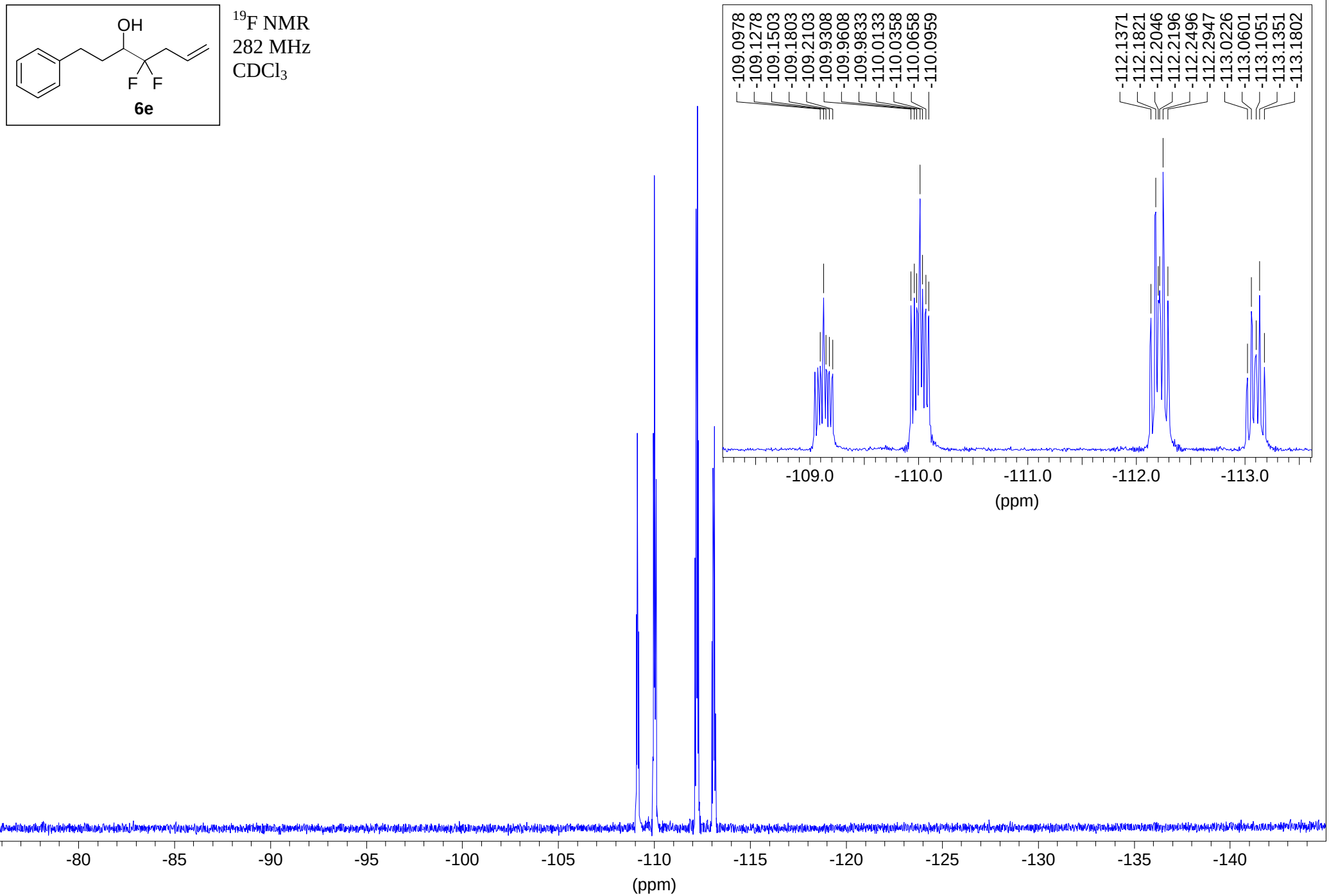
^{1}H NMR
300 MHz
$CDCl_3$

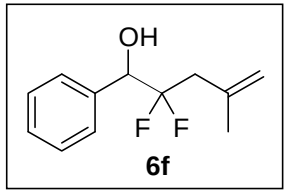

OH
F F
6d
^{13}C NMR
75 MHz
$CDCl_3$
138.2930
130.9527
129.6341
129.5828
128.4839
128.0004
126.3228
125.1947
121.8835
120.4476
77.5776
77.1600
76.7278
76.3908
76.0172
46.2675
40.6633
40.3337
39.9967
38.6048
23.9461
23.5651
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)


OH
F F
6d
19F NMR
282 MHz
CDCl3
-101.0608
-101.1358
-101.2109
-101.9538
-102.0288
-102.0964
-108.0849
-108.1224
-108.1524
-108.1899
-108.2200
-108.2575
-108.9779
-109.0154
-109.0454
-109.0830
-109.1130
-109.1505
-101
-102
-103
-104
-105
-106
-107
-108
-109
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)


OH
F F
6e
7.3199
7.2985
7.2497
7.2268
5.8892
5.8557
5.8297
5.8206
5.7977
5.2593
5.2166
3.7509
3.7433
2.9456
2.9288
2.9151
2.7519
2.7259
2.7076
2.6802
1.9954
1.9298
1.9069
1.8703
1.8550
1.8230
1H NMR
300 MHz
CDCl3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)


OH
F F
6e
^{13}C NMR
75 MHz
CDCl$_3$
141.2966
129.0627
128.9894
128.9161
128.6451
128.6011
126.4327
126.2496
123.1801
120.5648
119.9202
77.5849
77.1600
76.7351
72.4642
72.0906
71.7097
37.7990
37.4693
37.1397
31.7919
31.6967
31.6600
CDCl$_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)


OH
F F
6e
19F NMR
282 MHz
CDCl3
-109.0978
-109.1278
-109.1503
-109.1803
-109.2103
-109.9308
-109.9608
-109.9833
-110.0133
-110.0358
-110.0658
-110.0959
-112.1371
-112.1821
-112.2046
-112.2196
-112.2496
-112.2947
-113.0226
-113.0601
-113.1051
-113.1351
-113.1802
-109.0
-110.0
-111.0
-112.0
-113.0
(ppm)
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
(ppm)



6f

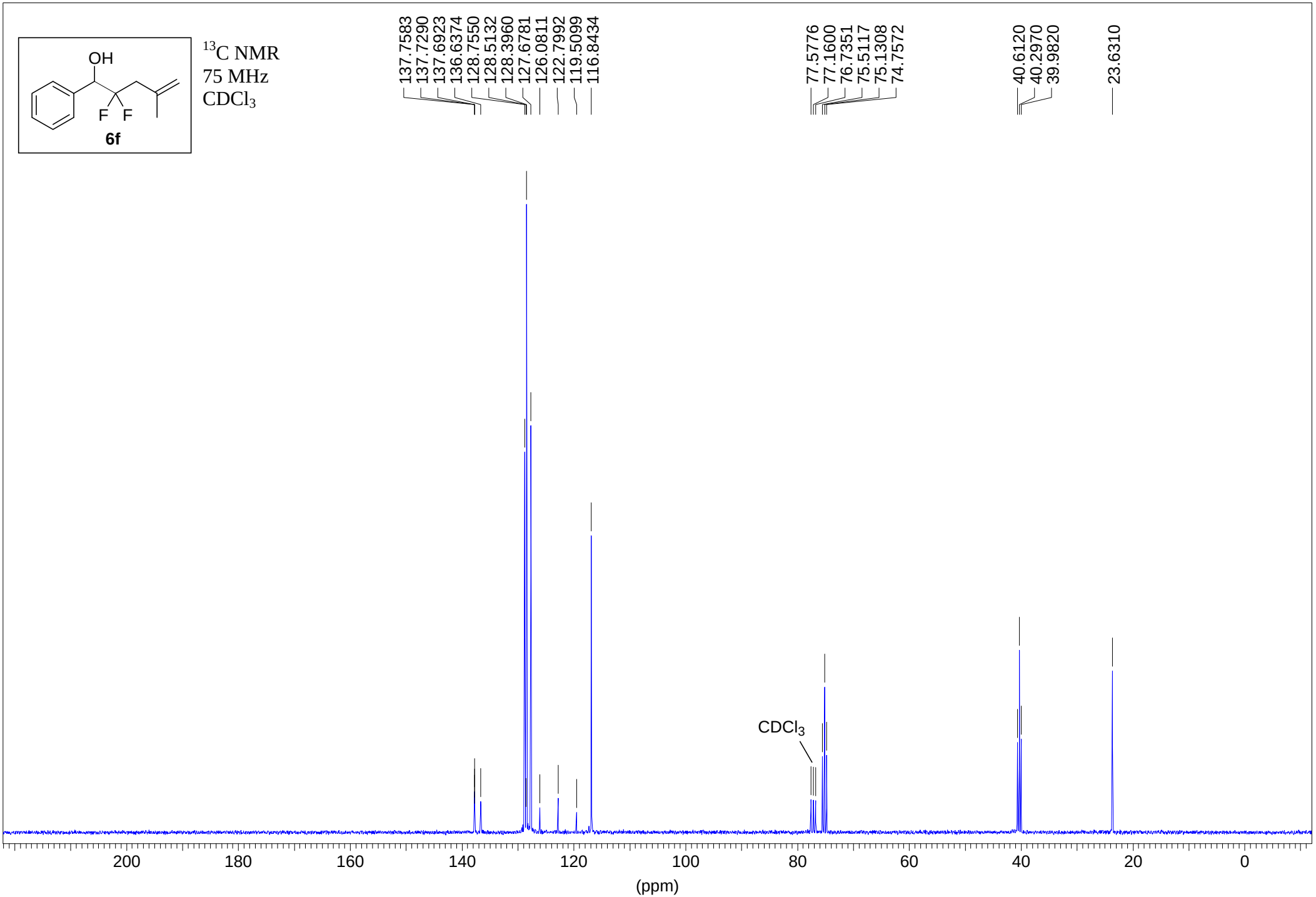
^{1}H NMR
300 MHz
$CDCl_3$

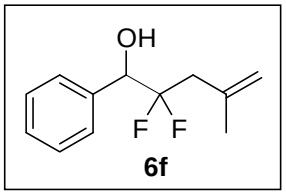
7.4526
7.4053
7.3992
7.3886
7.3809
5.0062
4.8704
2.7641
2.6833
2.6360
2.6268
2.5292
2.4911
2.4804
2.4484
2.4118
2.4011
2.3630
1.8459

D-solv.
residual
peak

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

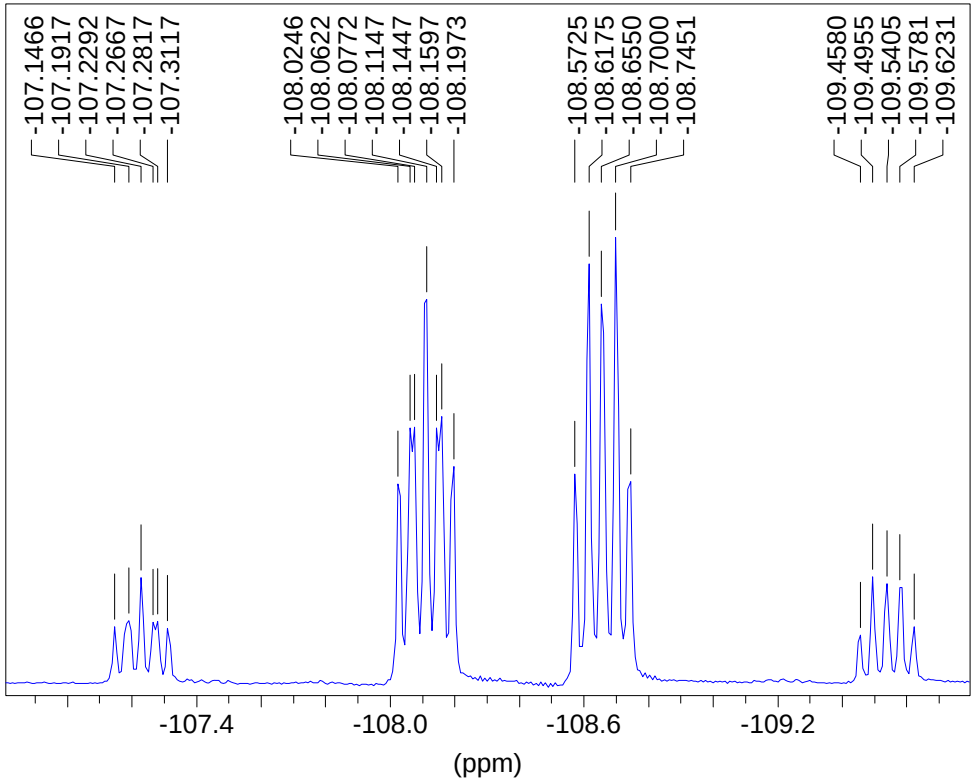
(ppm)

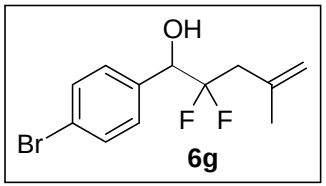

OH
F F
6f
13C NMR
75 MHz
CDCl3
137.7583
137.7290
137.6923
136.6374
128.7550
128.5132
128.3960
127.6781
126.0811
122.7992
119.5099
116.8434
77.5776
77.1600
76.7351
75.5117
75.1308
74.7572
40.6120
40.2970
39.9820
23.6310
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



6f

^{19}F NMR
282 MHz
$CDCl_3$





7.5319
7.5045
7.3398
7.3123

5.0016
4.8628
4.8247

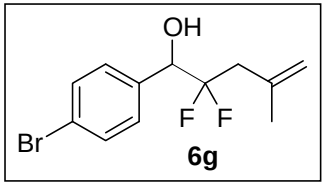
2.7443
2.6619
2.6451
2.6299
2.6162
2.5002
2.4652
2.4179
1.8307

^{1}H NMR
300 MHz
$CDCl_3$

D-solv. residual peak

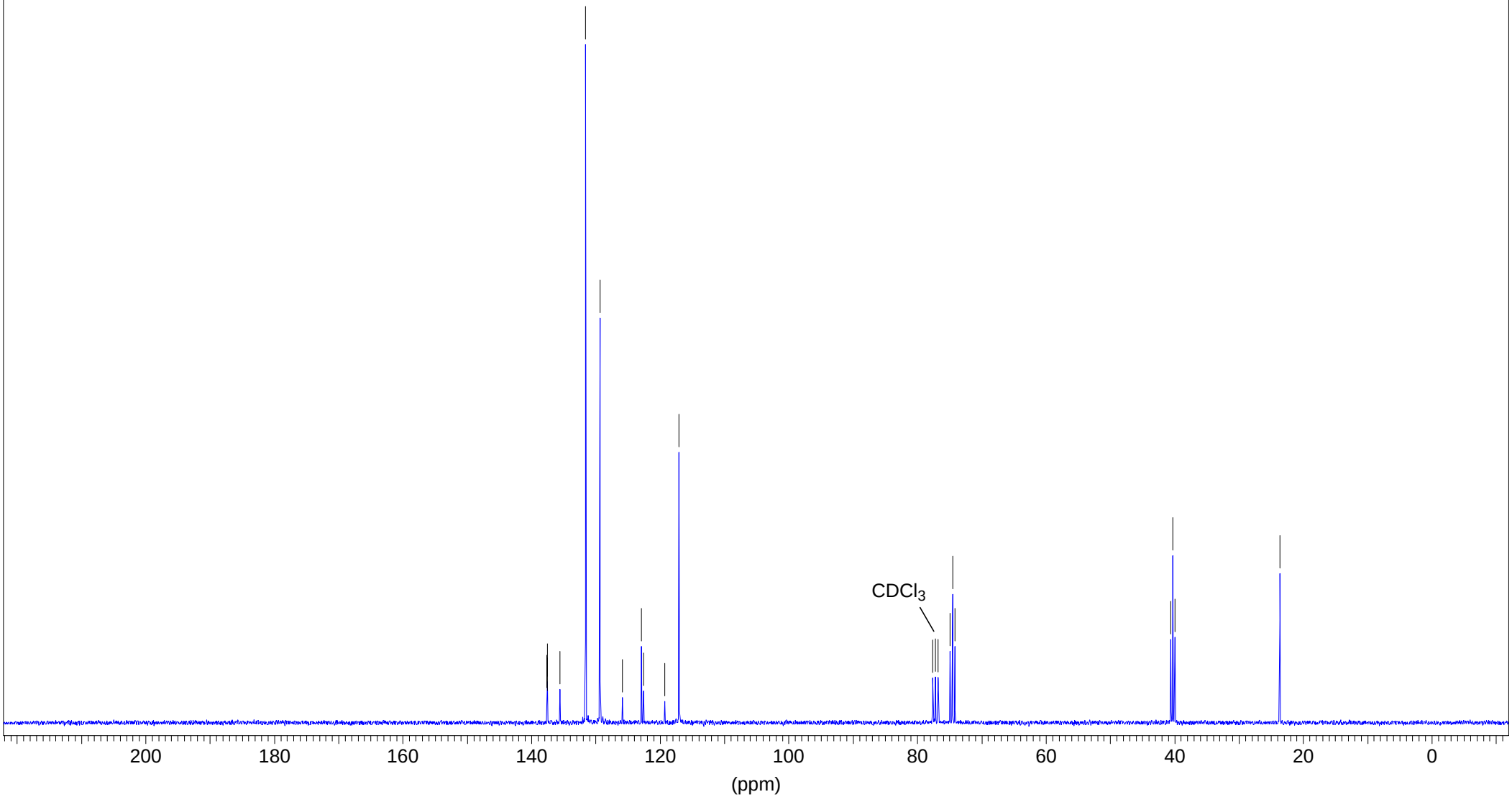
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0

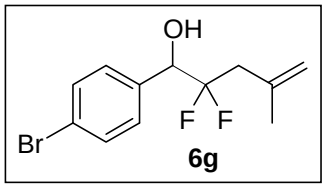
(ppm)



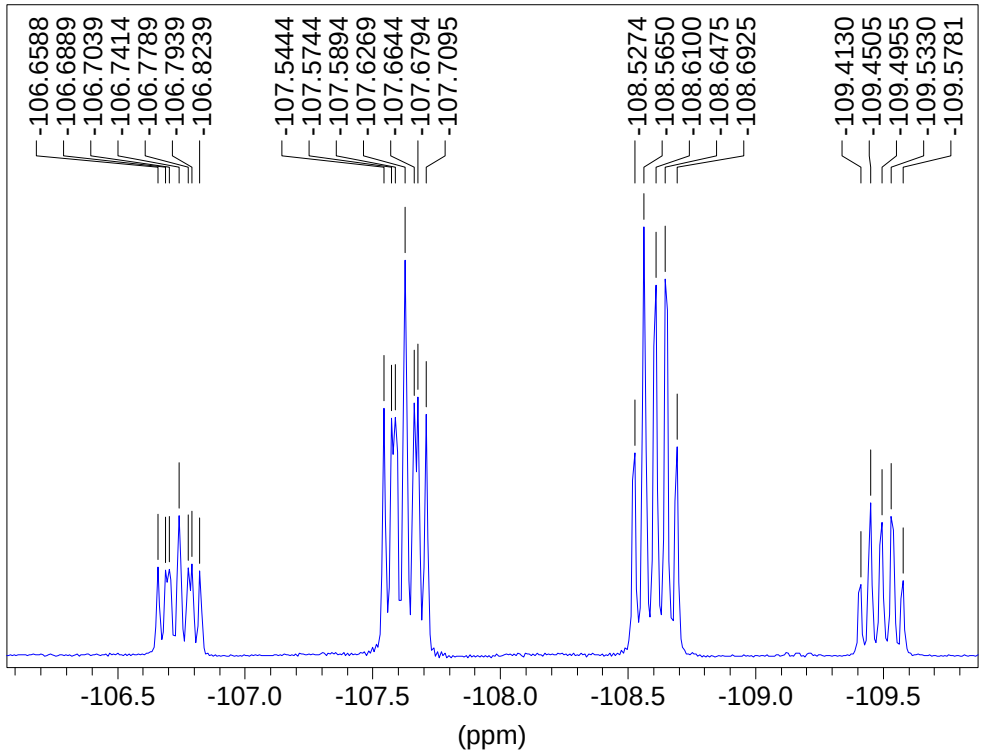
^{13}C NMR
75 MHz
$CDCl_3$

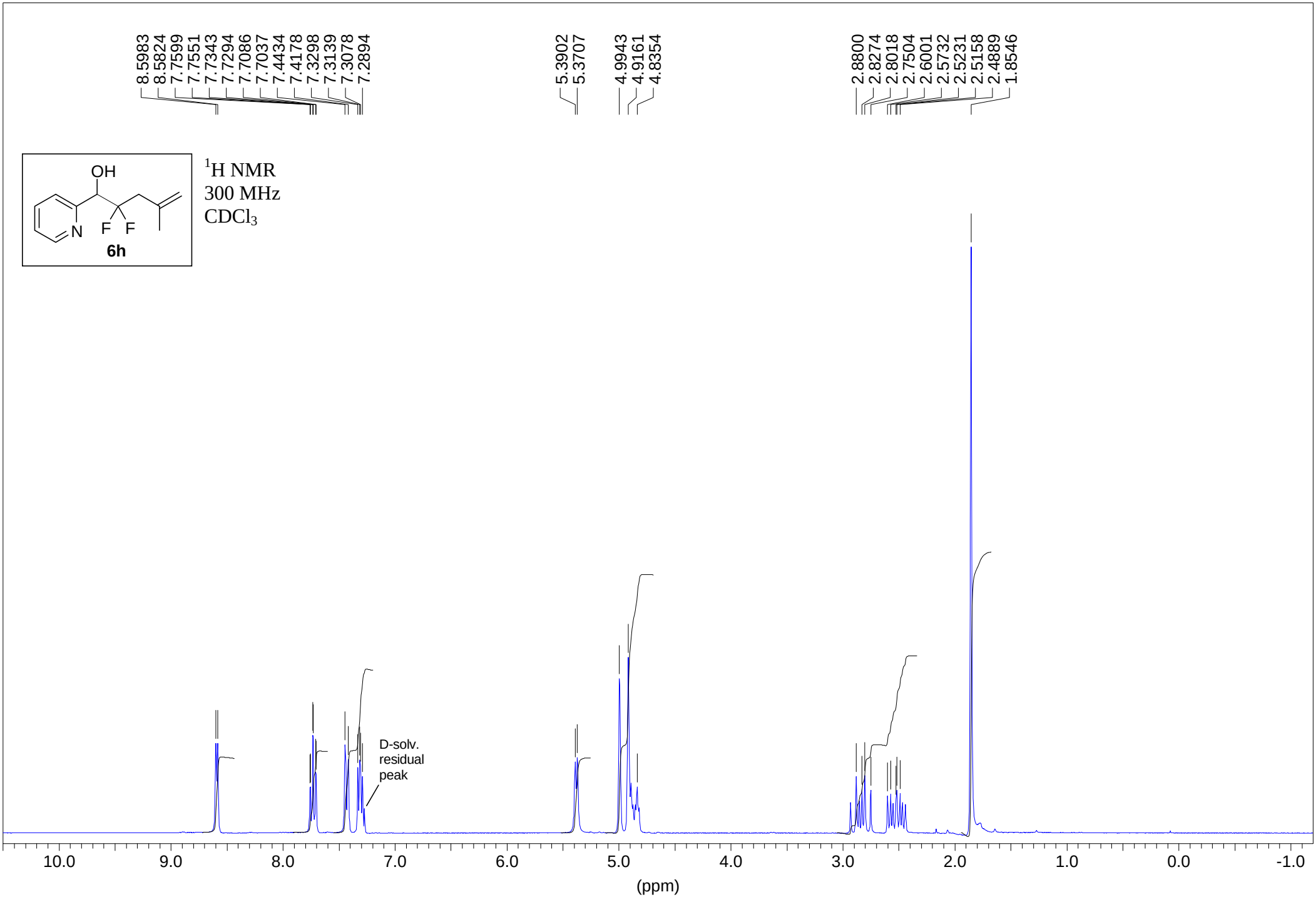
137.5751
137.5385
137.5019
135.5459
131.5680
129.3557
125.8247
122.9164
122.5501
119.2535
117.0705
77.5849
77.1600
76.7424
74.8964
74.5154
74.1345
40.5608
40.2458
39.9308
23.6310

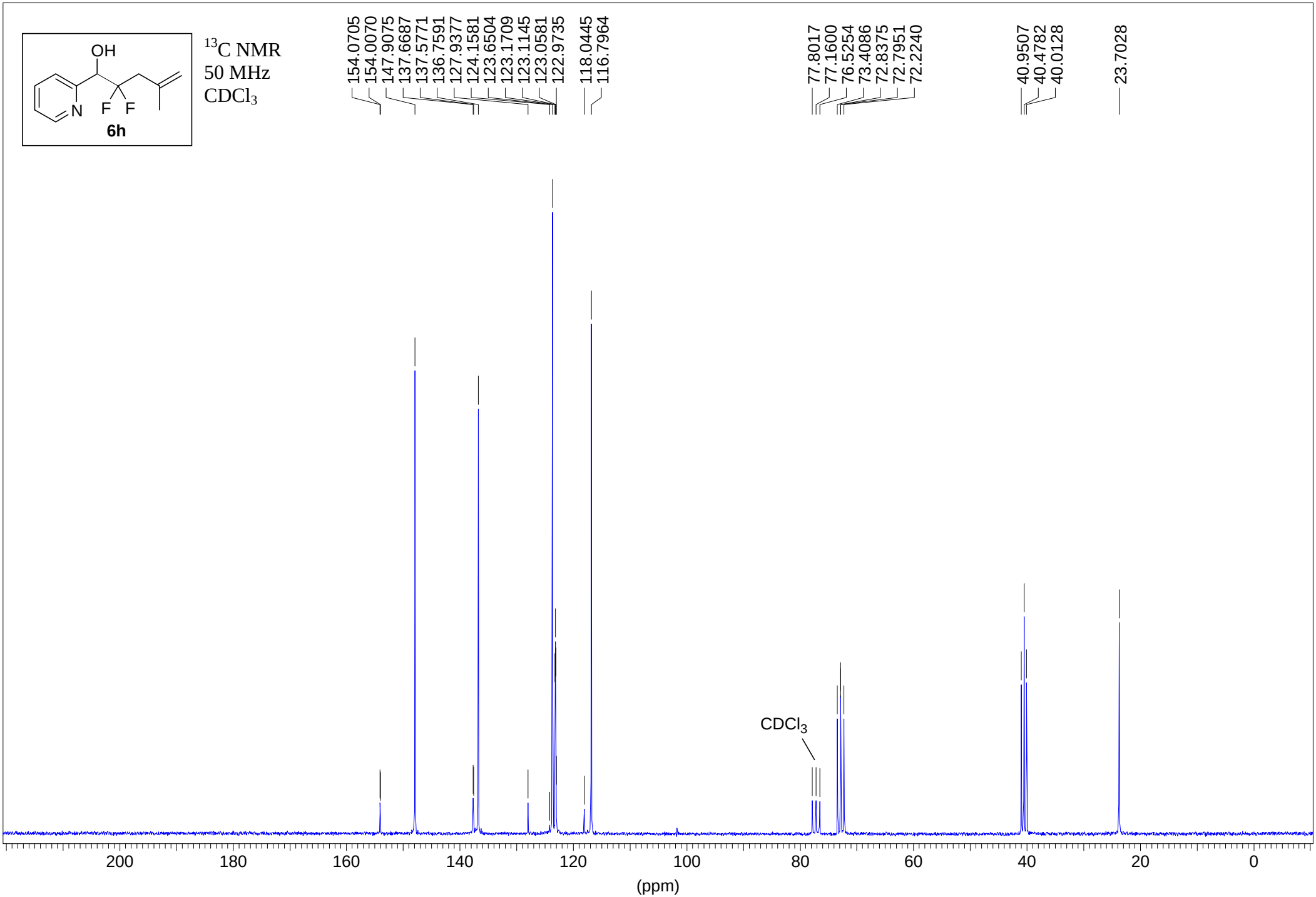


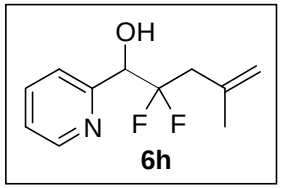


^{19}F NMR
282 MHz
$CDCl_3$



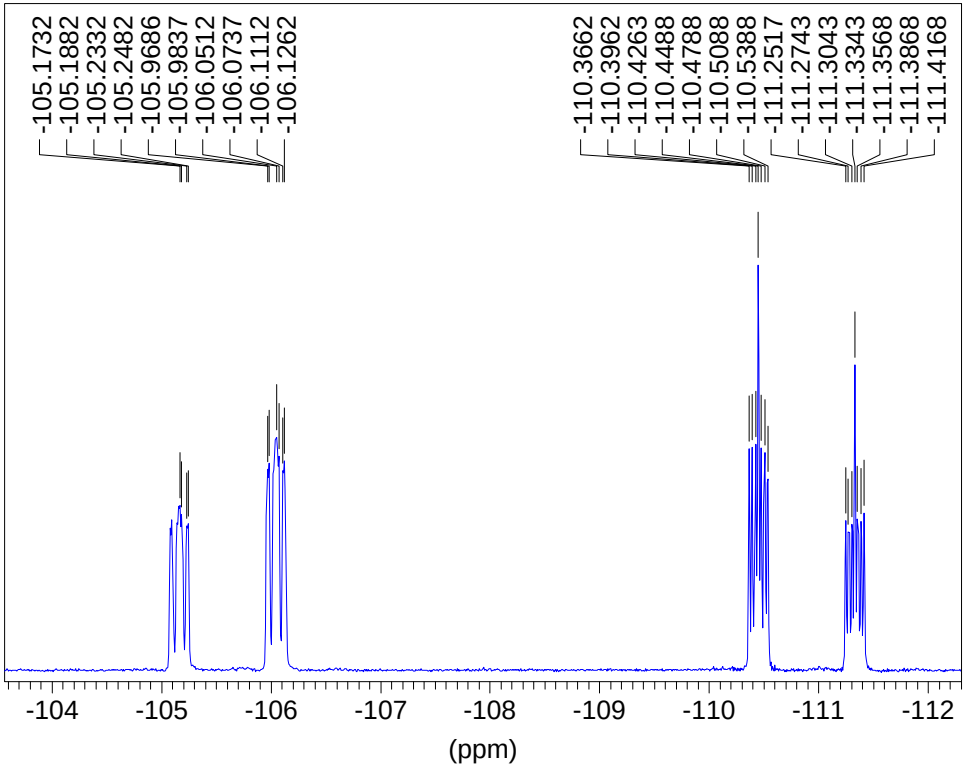

8.5983
8.5824
7.7599
7.7551
7.7343
7.7294
7.7086
7.7037
7.4434
7.4178
7.3298
7.3139
7.3078
7.2894
5.3902
5.3707
4.9943
4.9161
4.8354
2.8800
2.8274
2.8018
2.7504
2.6001
2.5732
2.5231
2.5158
2.4889
1.8546
OH
N
F F
6h
1H NMR
300 MHz
CDCl3
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

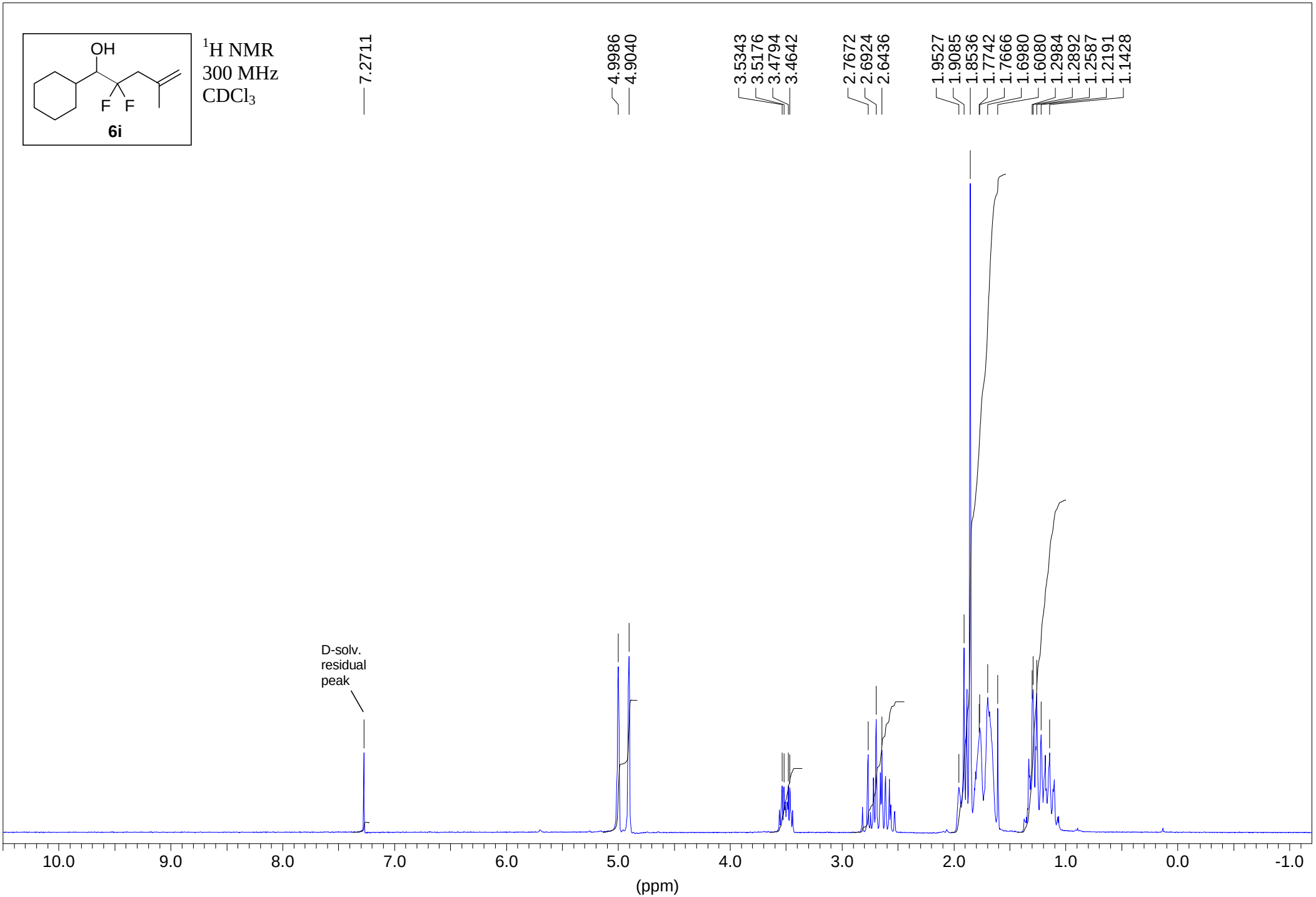

OH
N
F F
6h
13C NMR
50 MHz
CDCl3
154.0705
154.0070
147.9075
137.6687
137.5771
136.7591
127.9377
124.1581
123.6504
123.1709
123.1145
123.0581
122.9735
118.0445
116.7964
77.8017
77.1600
76.5254
73.4086
72.8375
72.7951
72.2240
40.9507
40.4782
40.0128
23.7028
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

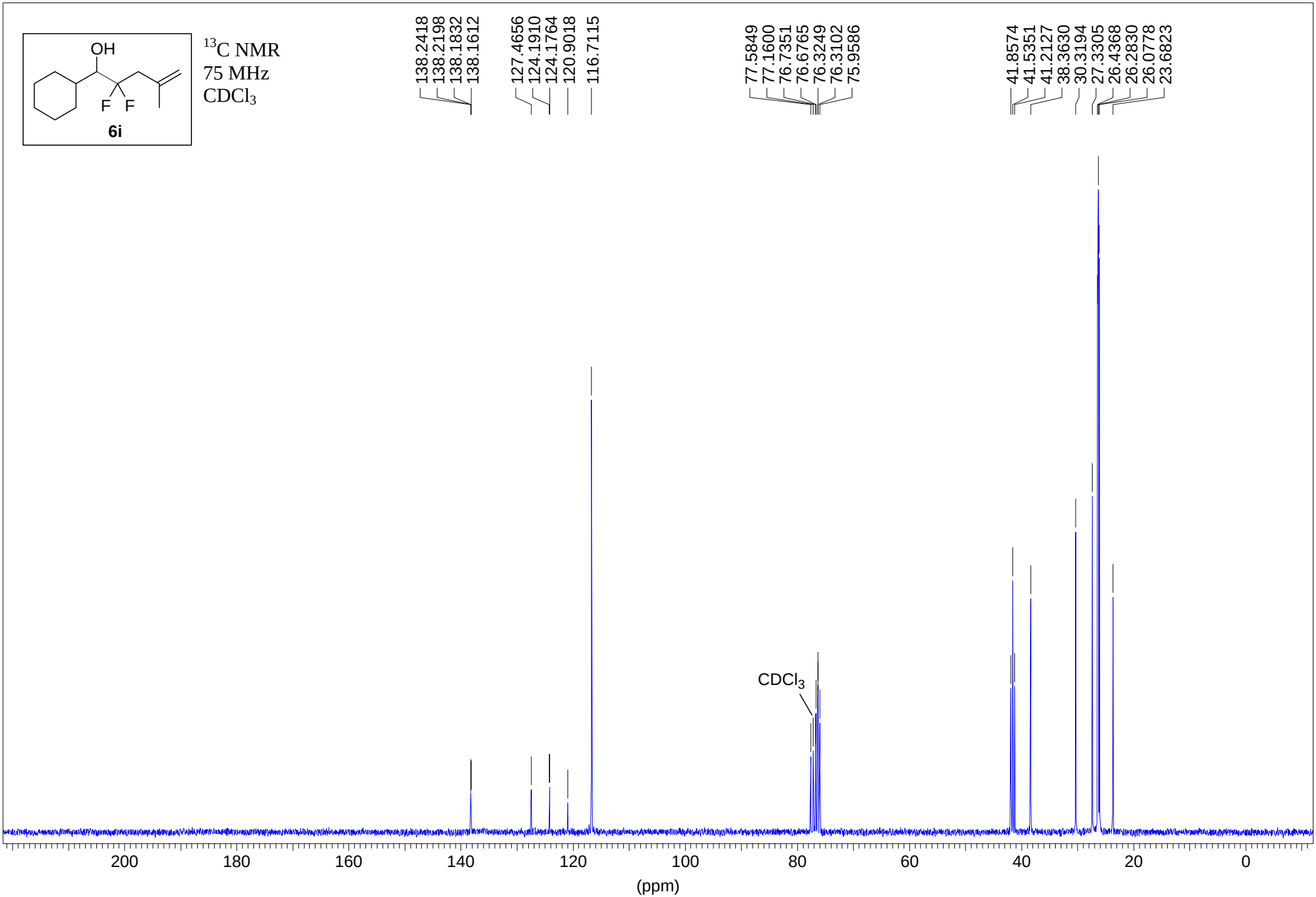


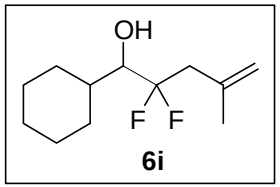
6h

^{19}F NMR
282 MHz
$CDCl_3$



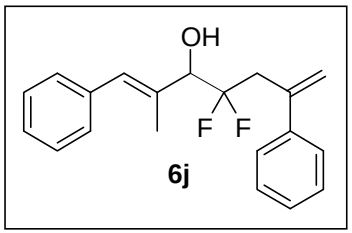

OH
F F
6i
1H NMR
300 MHz
CDCl3
7.2711
4.9986
4.9040
3.5343
3.5176
3.4794
3.4642
2.7672
2.6924
2.6436
1.9527
1.9085
1.8536
1.7742
1.7666
1.6980
1.6080
1.2984
1.2892
1.2587
1.2191
1.1428
D-solv.
residual
peak
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)


OH
F F
6i
13C NMR
75 MHz
CDCl3
138.2418
138.2198
138.1832
138.1612
127.4656
124.1910
124.1764
120.9018
116.7115
77.5849
77.1600
76.7351
76.6765
76.3249
76.3102
75.9586
41.8574
41.5351
41.2127
38.3630
30.3194
27.3305
26.4368
26.2830
26.0778
23.6823
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



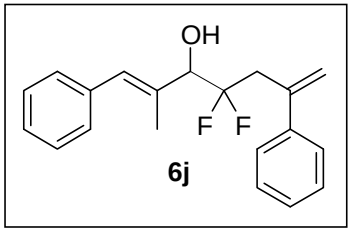
6i

^{19}F NMR
282 MHz
$CDCl_3$



6j

^{1}H NMR
300 MHz
$CDCl_3$



6j

^{13}C NMR
75 MHz
$CDCl_3$

141.4138
140.3589
140.3223
136.9378
133.7291
130.4765
129.2238
128.4546
128.3008
128.0224
127.7514
127.0774
126.3741
126.2056
122.9017
119.6052
118.9532

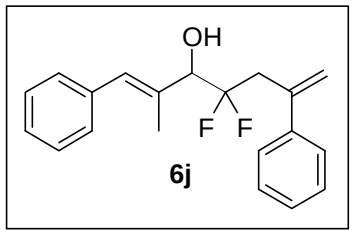
78.1343
77.7827
77.7607
77.5776
77.4164
77.1600
76.7351

38.9125
38.5902
38.2678

14.8915
14.8622
14.8182

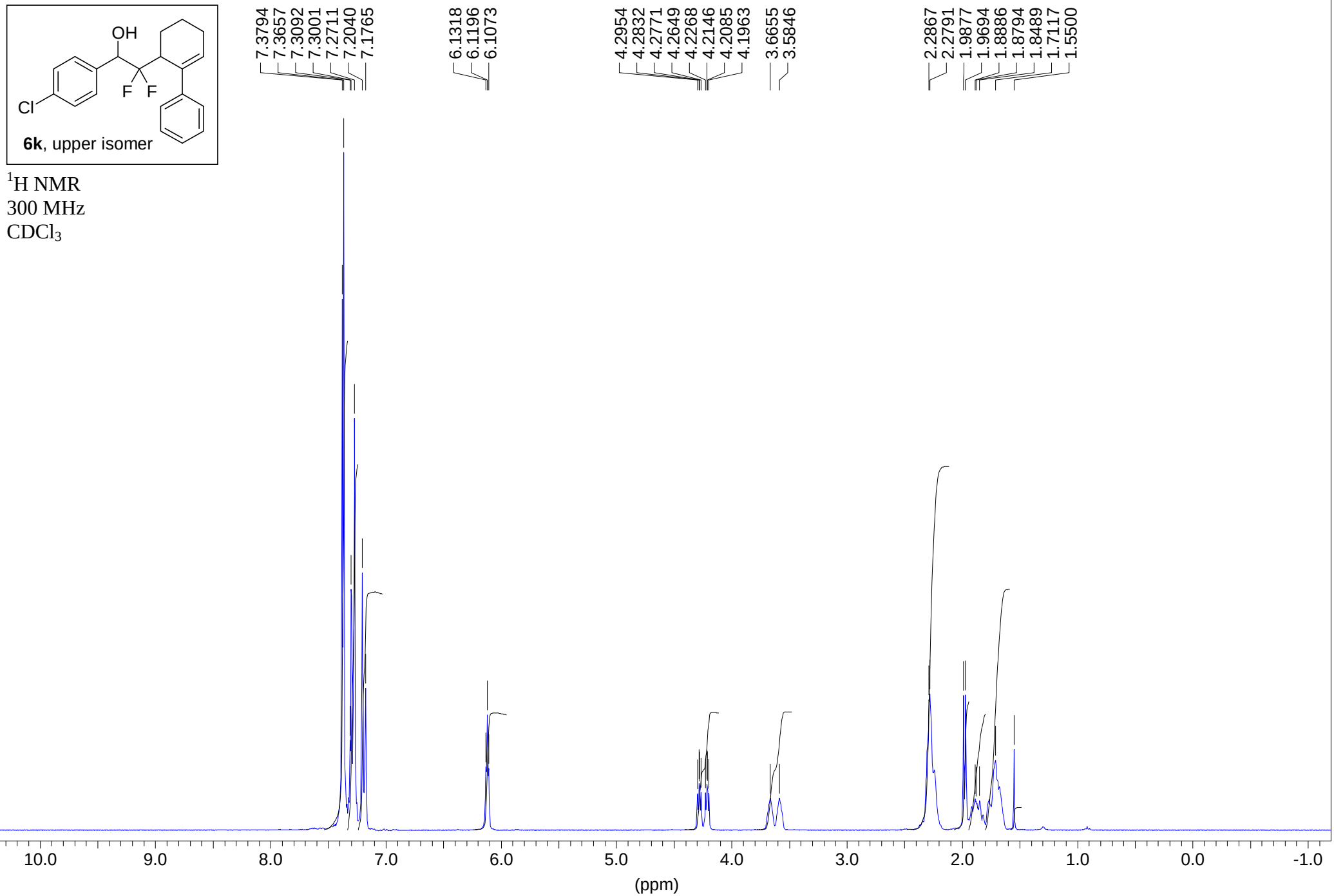
D-solv.
residual
peak

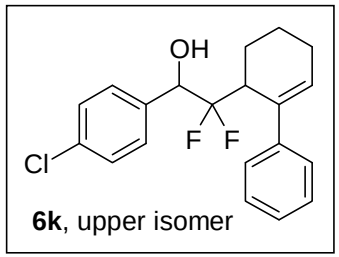
200 180 160 140 120 100 80 60 40 20 0
(ppm)



6j

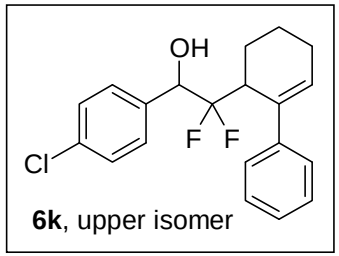
^{19}F NMR
282 MHz
$CDCl_3$


OH
F F
Cl
6k, upper isomer
1H NMR
300 MHz
CDCl3
7.3794
7.3657
7.3092
7.3001
7.2711
7.2040
7.1765
6.1318
6.1196
6.1073
4.2954
4.2832
4.2771
4.2649
4.2268
4.2146
4.2085
4.1963
3.6655
3.5846
2.2867
2.2791
1.9877
1.9694
1.8886
1.8794
1.8489
1.7117
1.5500
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)



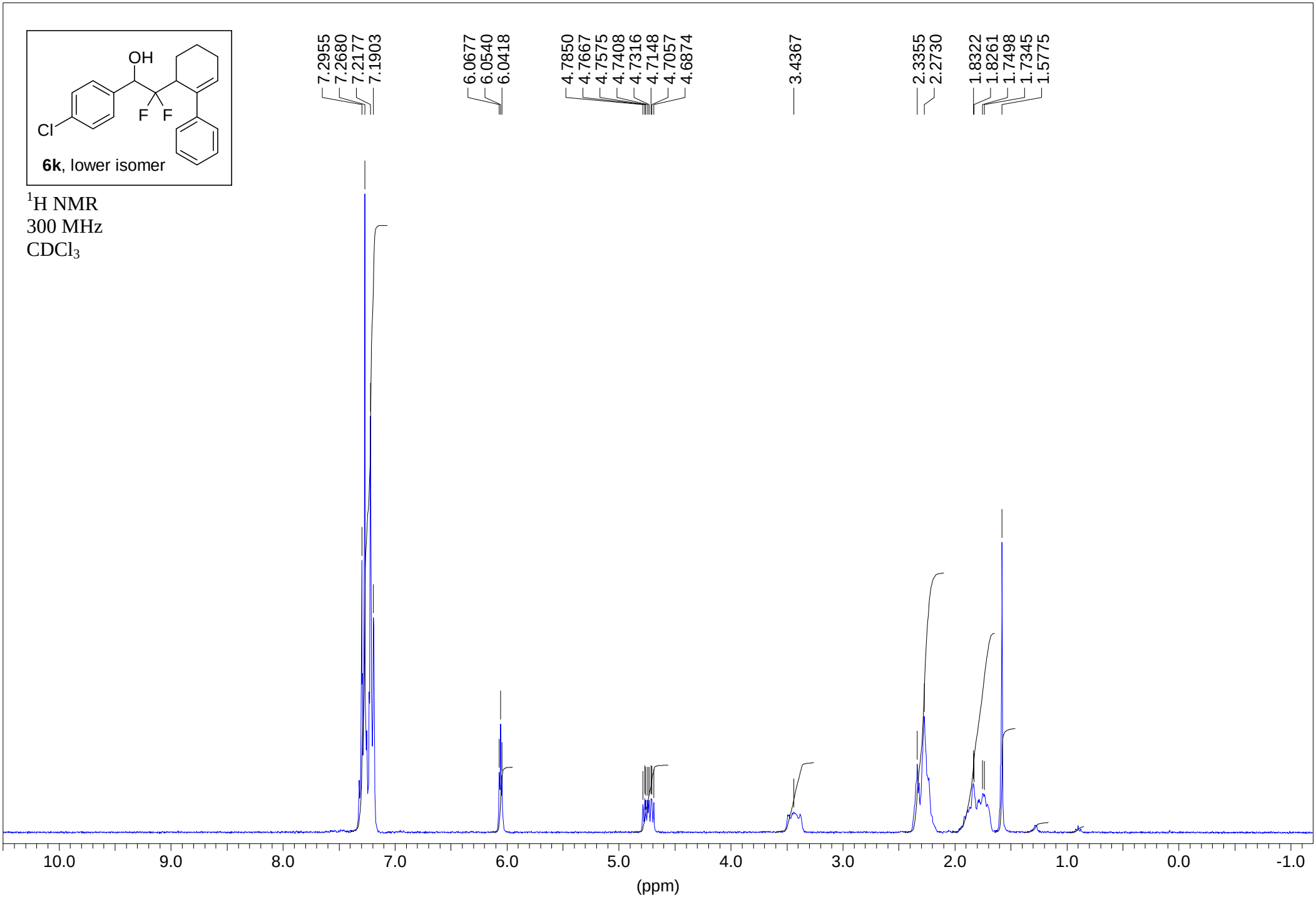
6k, upper isomer

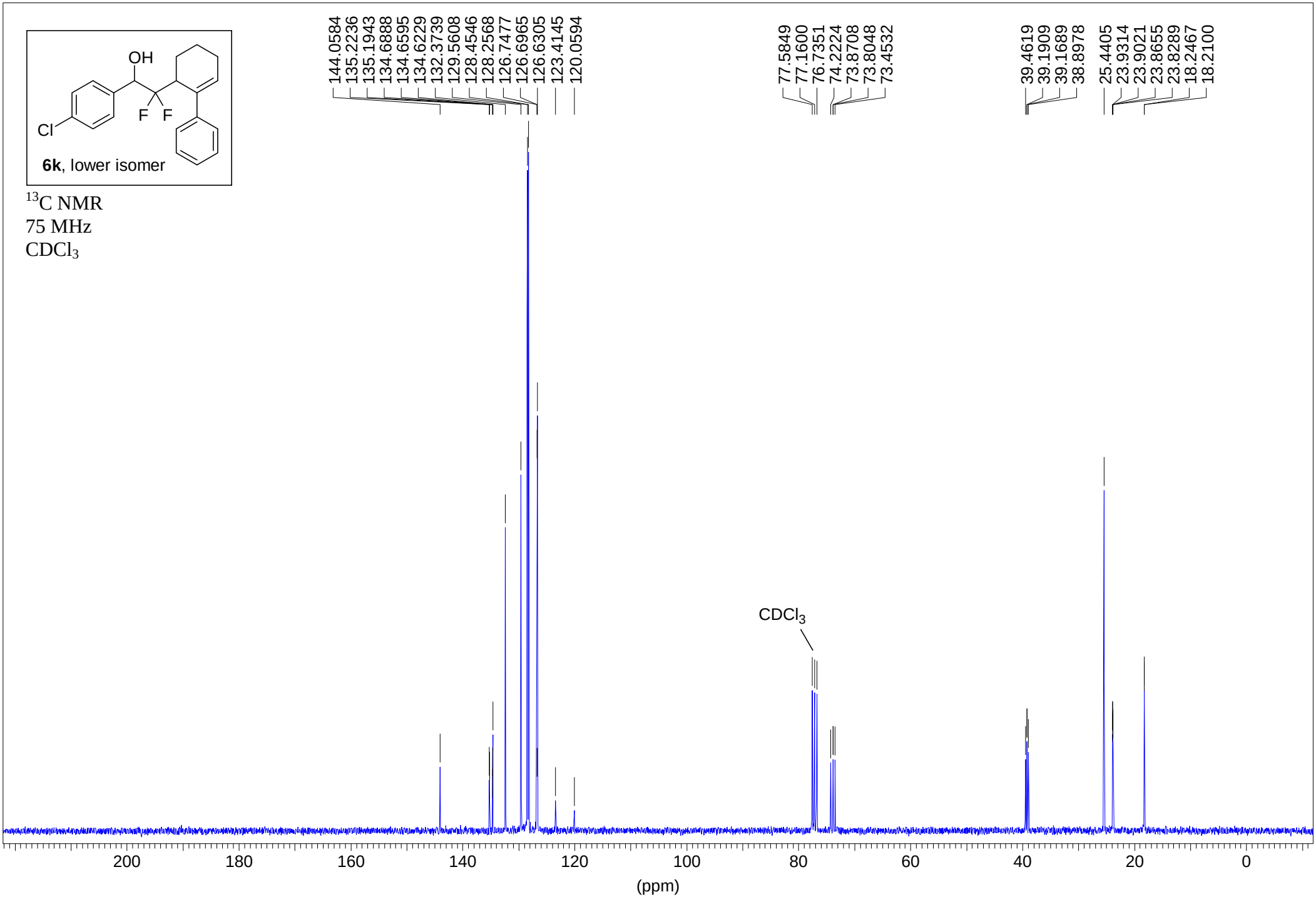
^{13}C NMR
50 MHz
$CDCl_3$

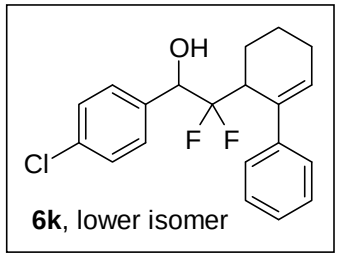


6k, upper isomer

^{19}F NMR
282 MHz
$CDCl_3$

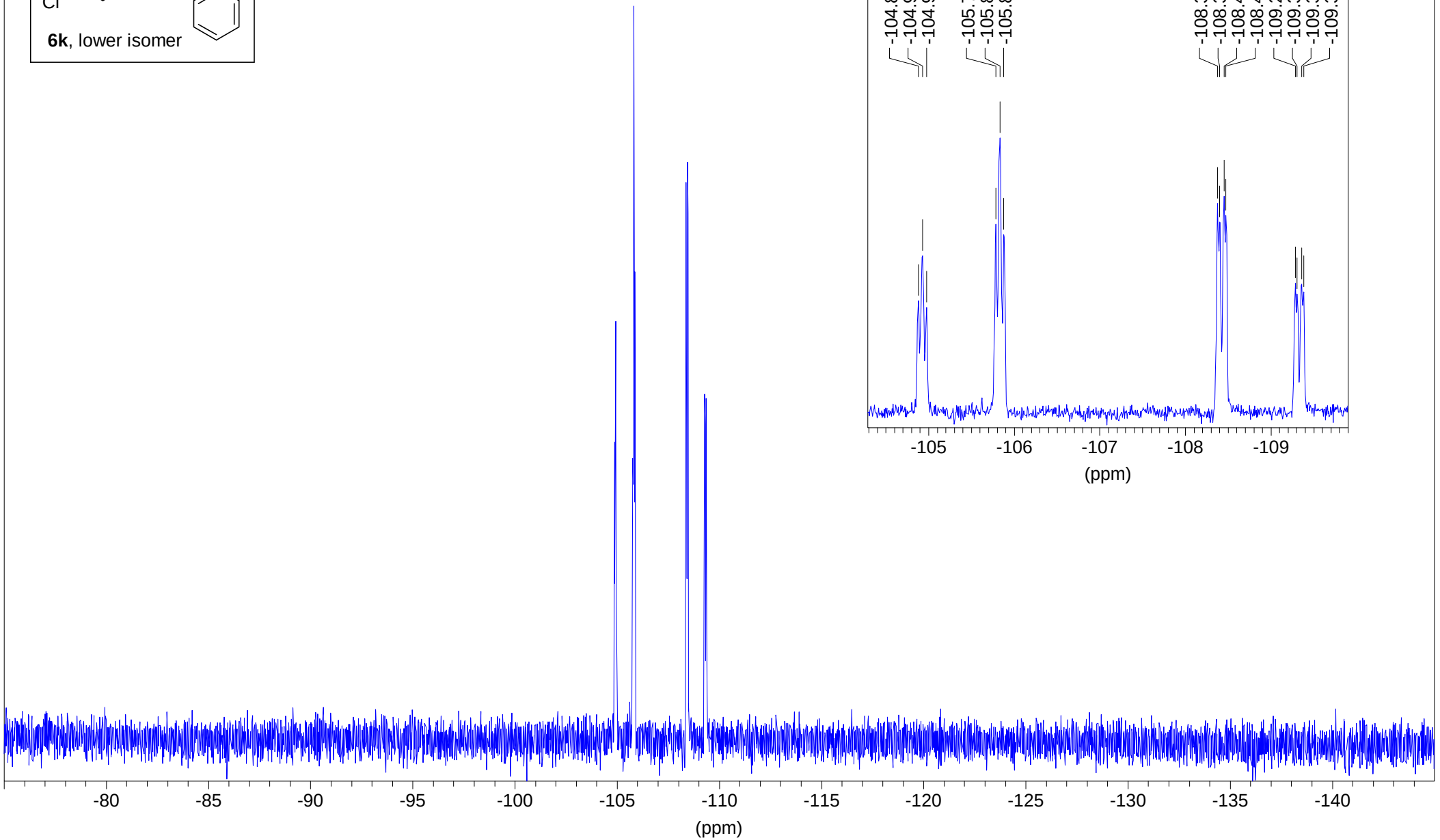

OH
F F
Cl
6k, lower isomer
1H NMR
300 MHz
CDCl3
7.2955
7.2680
7.2177
7.1903
6.0677
6.0540
6.0418
4.7850
4.7667
4.7575
4.7408
4.7316
4.7148
4.7057
4.6874
3.4367
2.3355
2.2730
1.8322
1.8261
1.7498
1.7345
1.5775
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
(ppm)

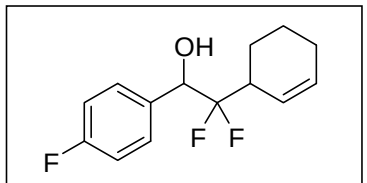

OH
F F
Cl
6k, lower isomer
13C NMR
75 MHz
CDCl3
144.0584
135.2236
135.1943
134.6888
134.6595
134.6229
132.3739
129.5608
128.4546
128.2568
126.7477
126.6965
126.6305
123.4145
120.0594
77.5849
77.1600
76.7351
74.2224
73.8708
73.8048
73.4532
39.4619
39.1909
39.1689
38.8978
25.4405
23.9314
23.9021
23.8655
23.8289
18.2467
18.2100
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



6k, lower isomer

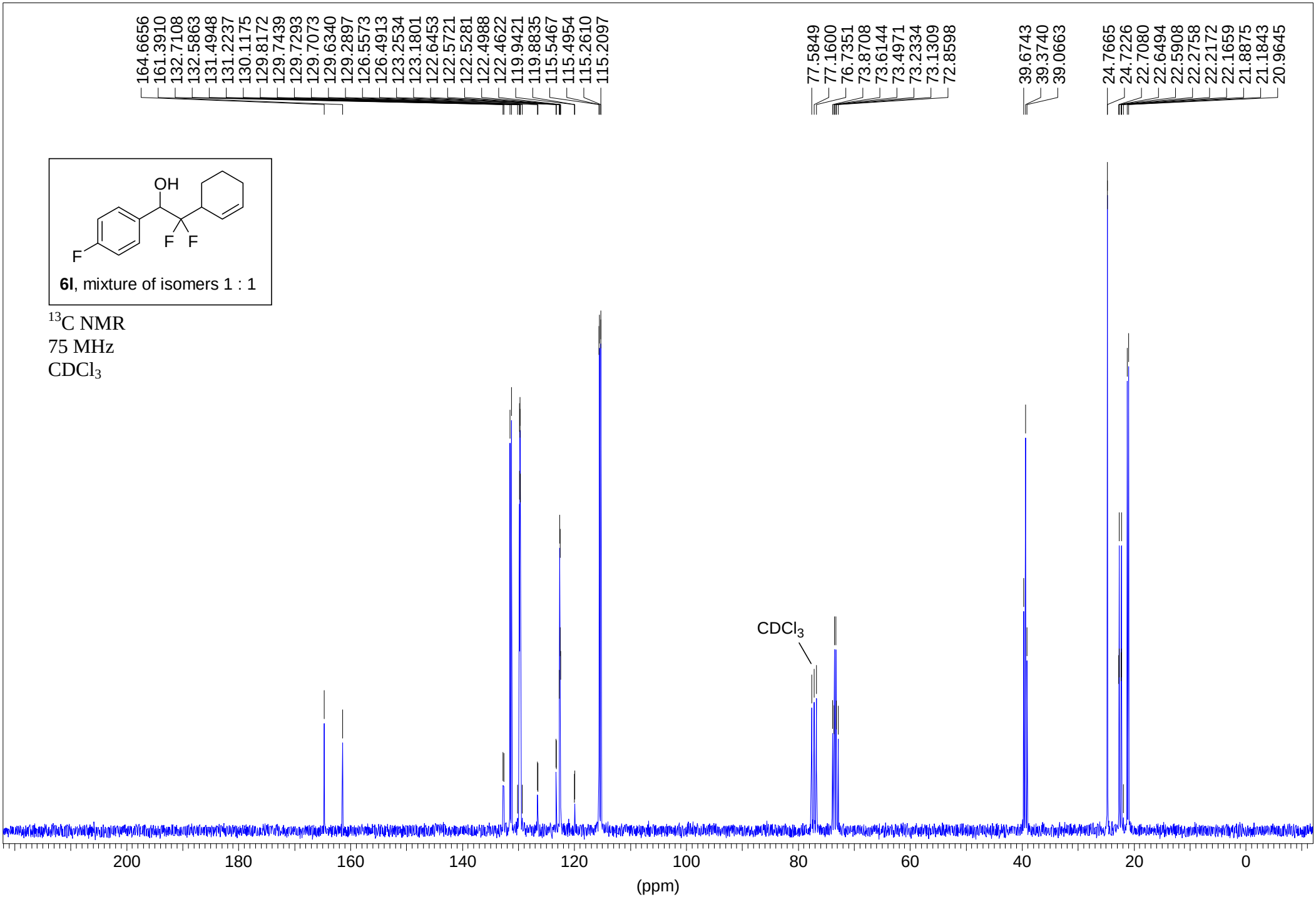
^{19}F NMR
282 MHz
$CDCl_3$

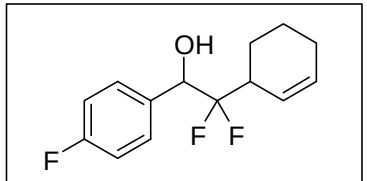




6l, mixture of isomers 1 : 1

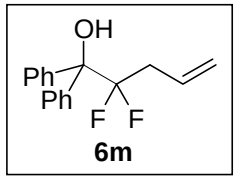
^{1}H NMR
300 MHz
$CDCl_3$


164.6656
161.3910
132.7108
132.5863
131.4948
131.2237
130.1175
129.8172
129.7439
129.7293
129.7073
129.6340
129.2897
126.5573
126.4913
123.2534
123.1801
122.6453
122.5721
122.5281
122.4988
122.4622
119.9421
119.8835
115.5467
115.4954
115.2610
115.2097
77.5849
77.1600
76.7351
73.8708
73.6144
73.4971
73.2334
73.1309
72.8598
39.6743
39.3740
39.0663
24.7665
24.7226
22.7080
22.6494
22.5908
22.2758
22.2172
22.1659
21.8875
21.1843
20.9645
OH
F
F F
6l, mixture of isomers 1 : 1
13C NMR
75 MHz
CDCl3
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



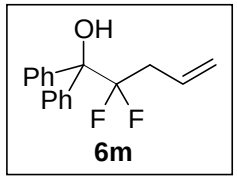
6l, mixture of isomers 1 : 1

^{19}F NMR
282 MHz
$CDCl_3$



6m

^{1}H NMR
300 MHz
$CDCl_3$



6m

^{13}C NMR
75 MHz
$CDCl_3$

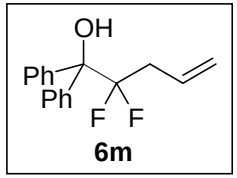
141.7801
129.1872
129.1286
129.0626
128.1616
128.0224
127.9272
127.7587
127.7220
127.6927
124.8137
121.4439
120.1326

80.5958
80.2514
79.9071
77.5849
77.1600
76.7424

37.9455
37.6232
37.3008

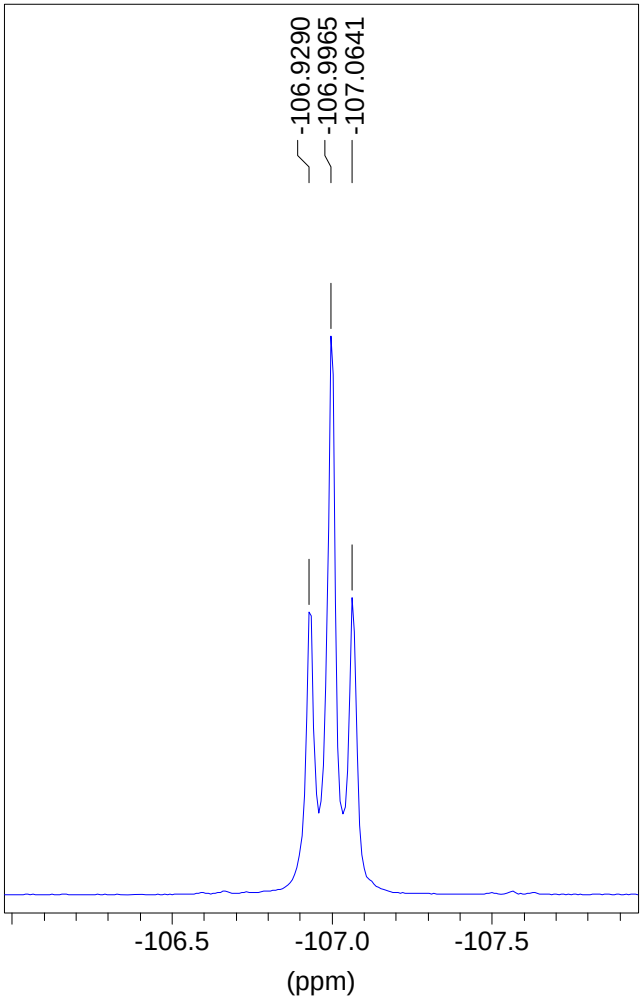
$CDCl_3$

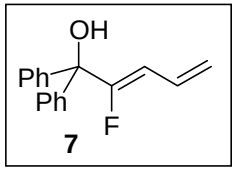
200 180 160 140 120 100 80 60 40 20 0
(ppm)



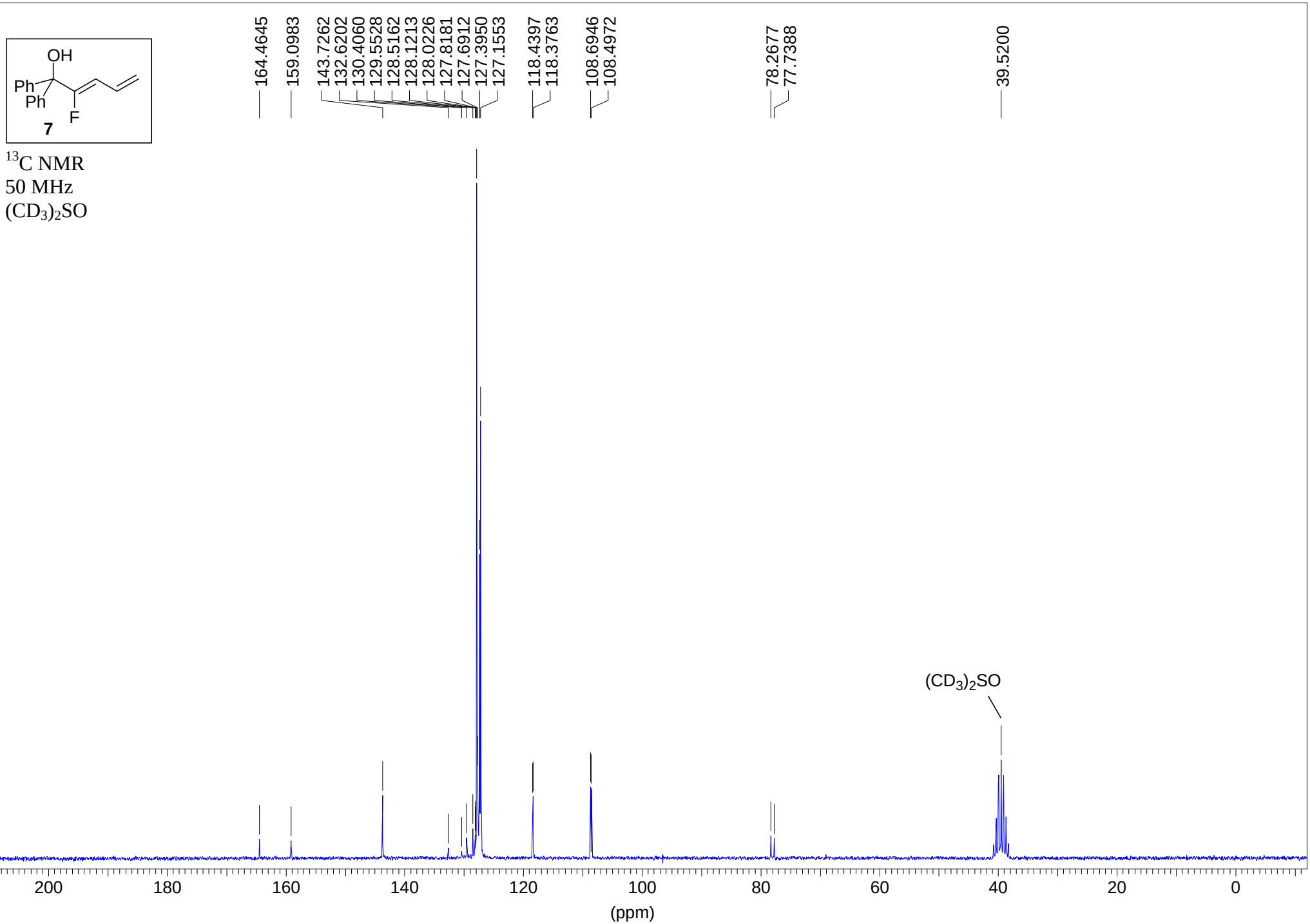
6m

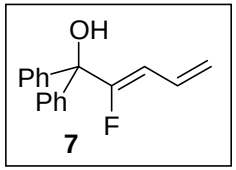
^{19}F NMR
282 MHz
$CDCl_3$



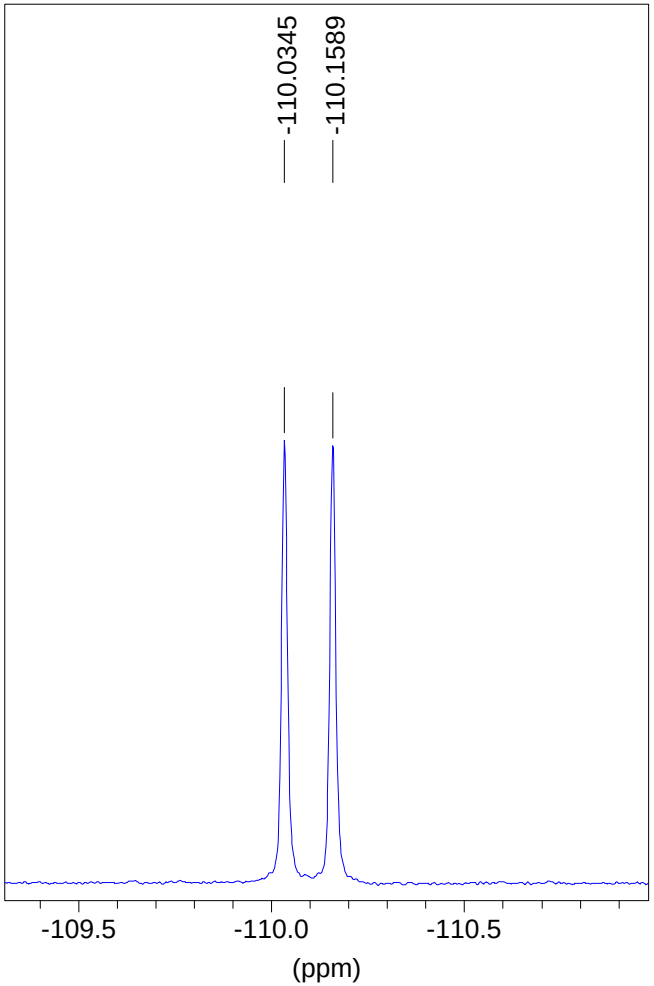


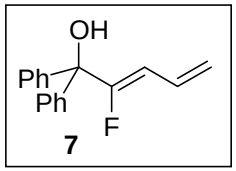
^{1}H NMR
300 MHz
$(CD_3)_2SO$


OH
Ph
Ph
F
7
164.4645
159.0983
143.7262
132.6202
130.4060
129.5528
128.5162
128.1213
128.0226
127.8181
127.6912
127.3950
127.1553
118.4397
118.3763
108.6946
108.4972
78.2677
77.7388
39.5200
13C NMR
50 MHz
(CD3)2SO
(CD3)2SO
200
180
160
140
120
100
80
60
40
20
0
(ppm)

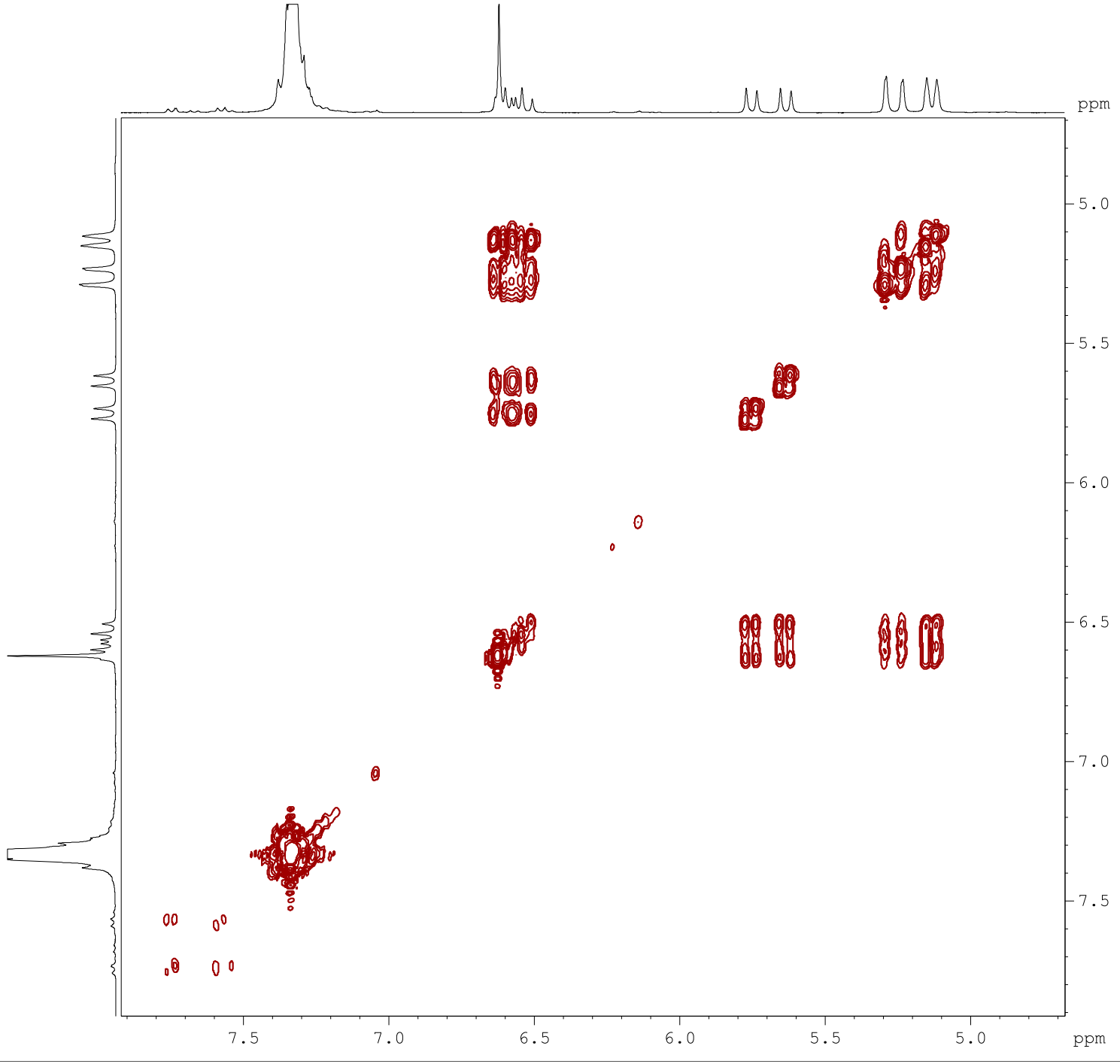


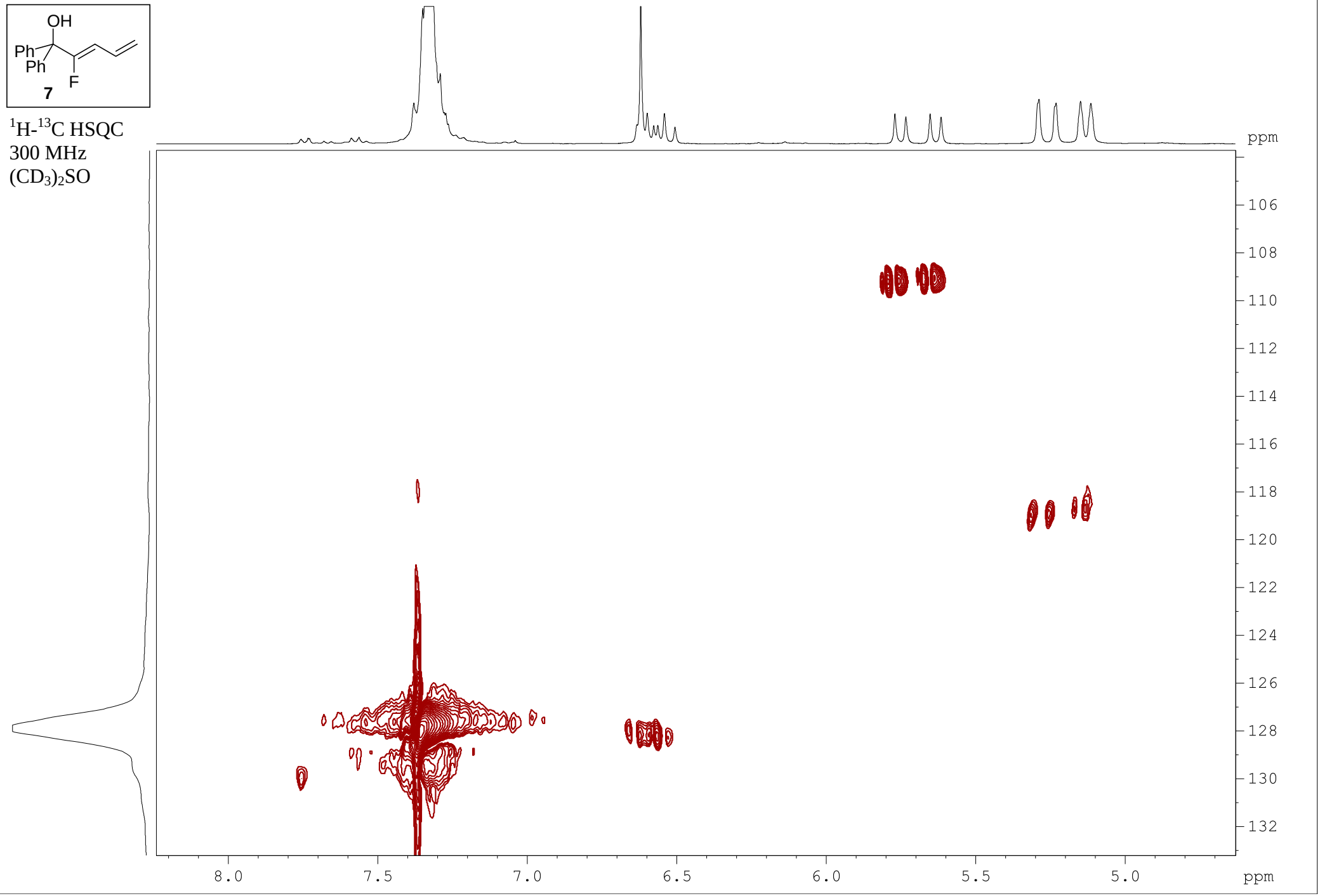
^{19}F NMR
282 MHz
$(CD_3)_2SO$

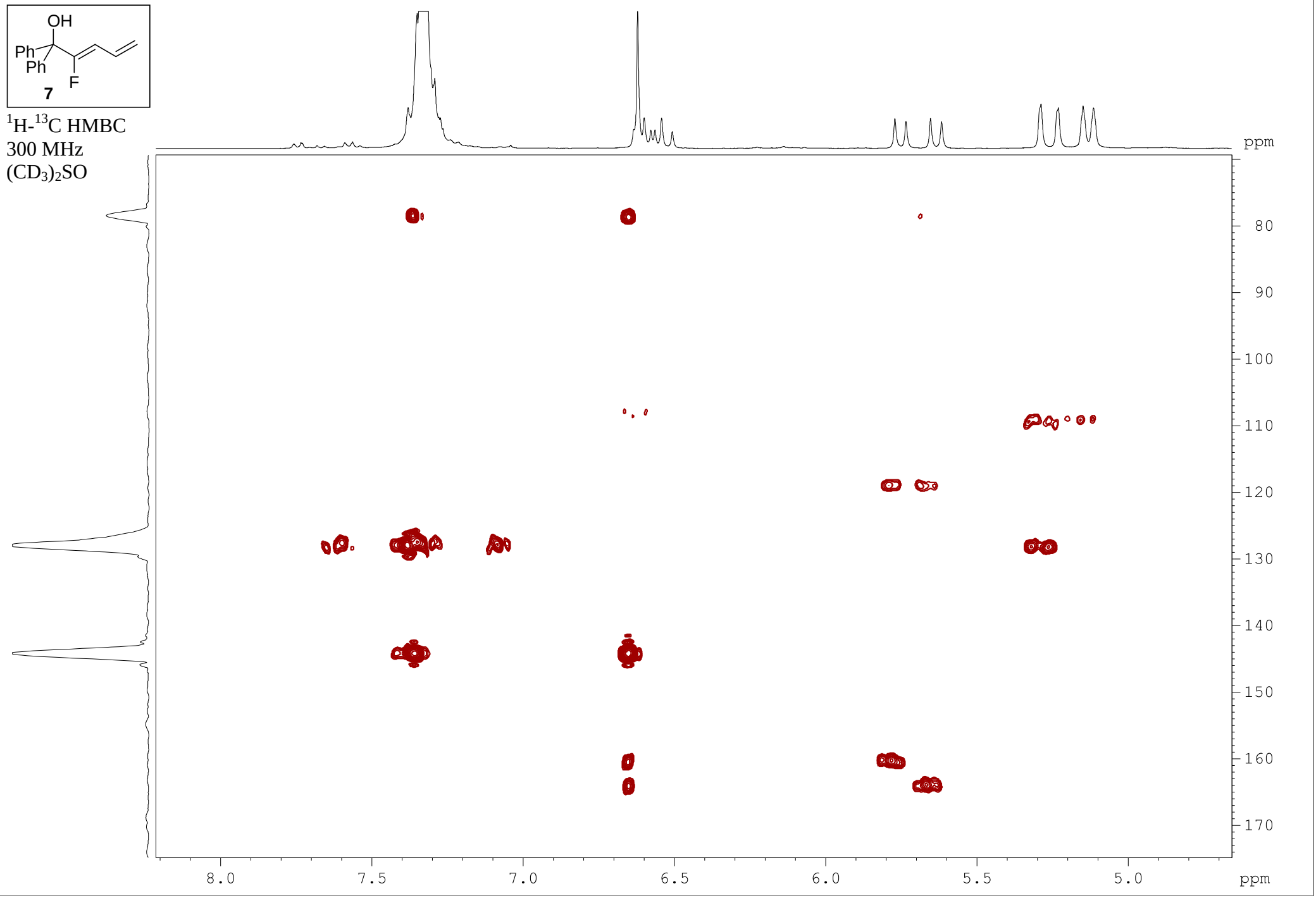


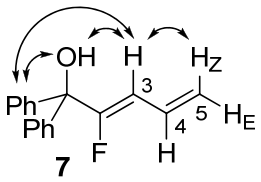


^{1}H-^{1}H COSY
300 MHz
$(CD_3)_2SO$



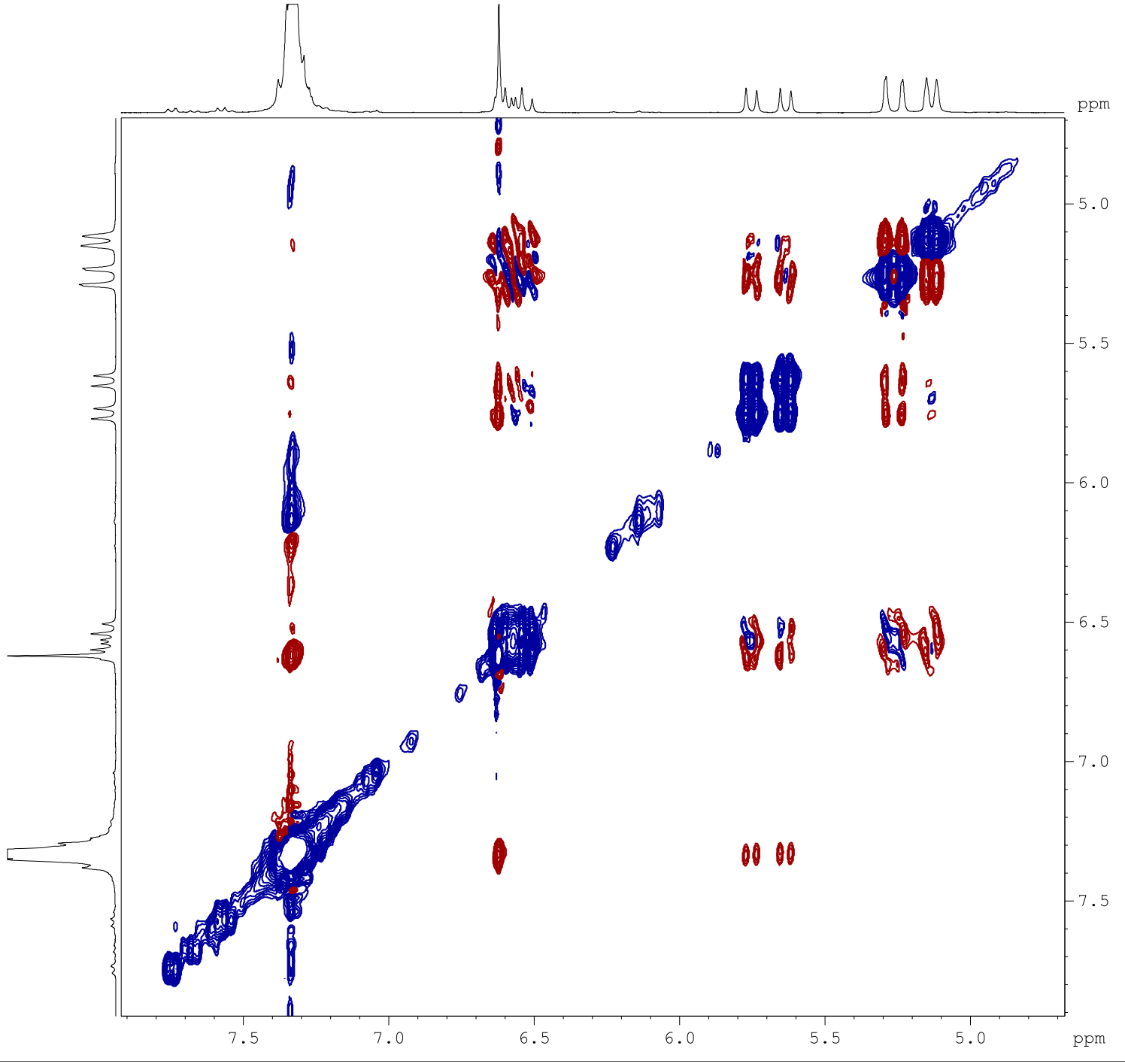

OH
Ph
Ph
F
7
^{1}H-^{13}C HSQC
300 MHz
$(CD_3)_2SO$
ppm
106
108
110
112
114
116
118
120
122
124
126
128
130
132
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm

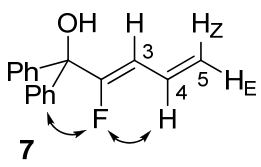

OH
Ph
Ph
F
7
^{1}H-^{13}C HMBC
300 MHz
$(CD_3)_2SO$
ppm
80
90
100
110
120
130
140
150
160
170
8.0
7.5
7.0
6.5
6.0
5.5
5.0
ppm



7

^{1}H-^{1}H NOESY
300 MHz
$(CD_3)_2SO$





7

^{1}H-^{19}F HOESY
300 MHz
$(CD_3)_2SO$