Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Light-mediated copper-catalyzed phosphorus/halogen exchange in 1,1-difluoroalkylphosphonium salts

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Content

Experimental

General Methods. All reactions were performed under an argon atmosphere. 1,2-Dichloroethane was distilled from CaH_2. MeCN was distilled twice: from P_2O_5 and CaH_2 successively and stored over MS 3Å. 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. High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI) and time-of-flight (TOF) mass analyzer. The measurements were done in a positive ion mode (interface capillary voltage – 4500 V) or in a negative ion mode (3200 V); mass range from m/z 50 to m/z 3000. For the irradiation, 400 nm LED, the strip of diodes smd 3528, 50 cm (3528-120LED-1M, 12 V, IP 33) was used. Reactions were performed in a glass tube (outer diameter 16 mm, inner diameter 13.4 mm). The reaction tube was placed in a glass jacket, which was wrapped by a strip of LEDs. The distance between the reaction vessel and diodes was about 1 cm. Absorption spectra were recorded at SF-2000 UV/Vis spectrophotometer (OKB Spectr) in 1 cm quartz cuvettes at room temperature. Phosphobetaine **1** was obtained according to a literature procedure.[1]

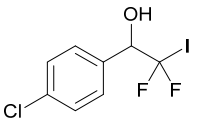
Synthesis of iododifluoromethylated alcohols 5

(General procedure 1).

A reaction tube equipped with a magnetic stirring bar was charged with betaine **1** (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), aldehyde (1 mmol) and Me_3SiCl (190 μL, 1.5 mmol, 1.5 equiv) were added successively. The suspension was stirred at 45–50 °C until complete dissolution of betaine **1** (2–5 h). Methyl iodide (155 μL, 2.5 mmol, 2.5 eq) was added, and the mixture was stirred for additional 5 min. Then, CuI (19 mg, 0.1 mmol, 0.1 eq) was added and the reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. For the desilylative work-up, ethanol (750 μL) and trifluoroacetic acid (250 μL) were added and the mixture was stirred at room temperature for 5 h. The mixture was diluted with water (5 mL) and extracted with EtOAc/hexane (1/2, 3×10 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 eluting with hexane/EtOAc.

[1] J. Zheng, J. Cai, J.-H. Lin, Y. Guo and J.-C. Xiao, *Chem. Commun.*, 2013, **49**, 7513–7515.

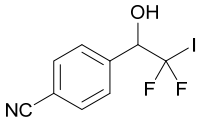
1-(4-Chlorophenyl)-2,2-difluoro-2-iodoethan-1-ol (5a).[2]



Yield 254 mg (80%). Light yellow crystals. Mp 43-45 °C. Chromatography: hexane/EtOAc, 5/1 R_f 0.32 (hexane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.51-7.33 (m, 4H), 4.68 (ddd, *J* = 10.6, 7.5, 4.4 Hz, 1H), 2.84 (d, *J* = 4.4 Hz, 1H).

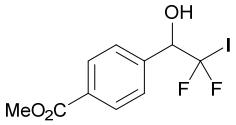
4-(2,2-Difluoro-1-hydroxy-2-iodoethyl)benzonitrile (5b).[3]



Yield 263 mg (85%). White crystals. Mp 106-107 °C. Chromatography: hexane/EtOAc, 3/1 R_f 0.26 (hexane/EtOAc 3/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.85-7.54 (m, 4H), 4.75 (ddd, *J* = 10.5, 7.2, 4.1, 1H), 3.04 (d, *J* = 4.1 Hz, 1H).

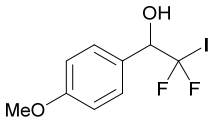
Methyl 4-(2,2-difluoro-1-hydroxy-2-iodoethyl)benzoate (5c).[2]



Yield 308 mg (90%). White crystals. Mp 82-83 °C. Chromatography: hexane/EtOAc, 4/1 R_f 0.25 (hexane/EtOAc 4/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.01 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 4.74 (ddd, *J* = 10.0, 7.8, 4.8 Hz, 1H), 4.17 (d, *J* = 4.8 Hz, 1H), 3.91 (s, 3H).

2,2-Difluoro-2-iodo-1-(4-methoxyphenyl)ethan-1-ol (5d).[2]



Yield 235.5 mg (75%). White crystals. Mp 63-65 °C. Chromatography: hexane/EtOAc, 5/1. R_f 0.18 (hexane/EtOAc 7/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.42 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 4.65 (ddd, *J* = 12.9, 8.7, 4.7 Hz, 1H), 3.85 (s, 3H), 2.81 (br, 1H).

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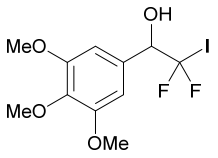
[2] M. D. Kosobokov, V. V. Levin, M. I. Struchkova and A. D. Dilman, *Org. Lett.*, 2014, **16**, 3784–3787.
[3] V. V. Levin, V. O. Smirnov, M. I. Struchkova and A. D. Dilman, *J. Org. Chem.*, 2015, **80**, 9349–9353.

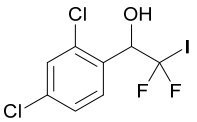
2,2-Difluoro-2-iodo-1-(3,4,5-trimethoxyphenyl)ethan-1-ol (5e).[4]



Yield 303 mg (81%). White crystals. Mp 174-175 °C. Chromatography: hexane/EtOAc, 1/1 R_f 0.36 (hexane/EtOAc 1/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.72 (s, 2H), 4.70–4.59 (m, 1H), 3.90 (s, 6H), 3.89 (s, 3H), 2.89 (br, 1H).

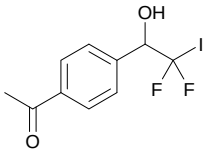
1-(2,4-Dichlorophenyl)-2,2-difluoro-2-iodoethan-1-ol (5f).[4]



Yield 300 mg (85%). Light yellow oil. Chromatography: hexane/EtOAc, 7/1. R_f 0.34 (hexane/EtOAc 7/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.69 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.36 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.36 (dd, *J* = 11.2, 6.9 Hz, 1H), 2.90 (br, 1H).

1-[4-(2,2-Difluoro-1-hydroxy-2-iodoethyl)phenyl]ethanone (5g).



Yield 267 mg (82%). White crystals. Mp 109-111 °C. Chromatography: hexanes/EtOAc, 2/1. R_f 0.29 (hexanes/EtOAc, 2/1).

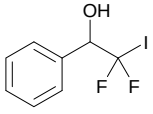
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.98 (d, *J* = 8.3 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 4.75 (ddd, *J* = 11.1, 7.3, 4.5 Hz, 1H), 3.16 (d, *J* = 4.5 Hz, 1H), 2.62 (s, 3H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 198.6, 140.2 (d, *J* = 3.3 Hz), 137.6, 128.41, 128.35, 107.3 (dd, *J* = 319.5, 317.6 Hz), 79.4 (t, *J* = 23.6 Hz), 26.8.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –48.8 (dd, *J* = 183.3, 7.3 Hz, 1F), –54.0 (dd, *J* = 183.3, 11,1 Hz, 1F).

HRMS (ESI): Calcd for $C_{10}H_{10}F_2IO_2$ (M+H) 326.9688; found 326.9691.

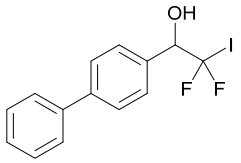
2,2-Difluoro-2-iodo-1-phenylethan-1-ol (5h).[2]



Yield 230 mg (81%). Light yellow oil. Chromatography: hexane/EtOAc, 5/1. R_f 0.40 (hexane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.65-7.33 (m, 5H), 4.70 (dd, *J* = 10.6, 7.8 Hz, 1H), 3.00 (br, 1H).

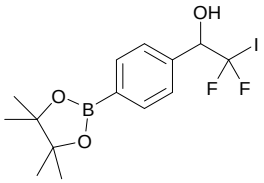
1-(1,1'-Biphenyl-4-yl)-2,2-difluoro-2-iodoethanol (5i).[4]



Yield 299 mg (83%). White crystals. Mp 106-107 °C. Chromatography: hexane/EtOAc, 6/1. R_f 0.33 (hexane/EtOAc 6/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.71-7.54 (m, 6H), 7.53-7.33 (m, 3H), 4.77 (dd, *J* = 10.7, 7.6 Hz, 1H), 2.82 (br, 1H).

2,2-Difluoro-2-iodo-1-[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethanol (5j).



Yield 287 mg (70%). White crystals. Mp 117-119 °C. Chromatography: hexanes/EtOAc, 5/1. R_f 0.22 (hexanes/EtOAc, 5/1).

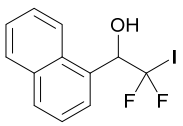
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.82 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 4.66 (dd, *J* = 10.4, 7.7 Hz, 1H), 3.15 (br, 1H), 1.35 (s, 12H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 137.7 (d, *J* = 2.8 Hz), 134.8, 127.4, 107.7 (dd, *J* = 319.6, 317.3 Hz), 84.2, 80.0 (t, *J* = 23.3 Hz), 25.0.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –48.5 (dd, *J* = 181.2, 7.7 Hz, 1F), –53.5 (dd, *J* = 181.2, 10.4 Hz, 1F).

HRMS (ESI): Calcd for $C_{14}H_{18}BF_2IO_3Na$ (M+Na) 433.0256; found 433.0253.

2,2-Difluoro-2-iodo-1-(1-naphthyl)ethanol (5k).[4]

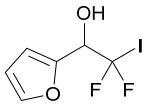


Yield 250 mg (75%). Yellow oil. Chromatography: hexane/EtOAc, 20/1. R_f 0.21 (hexane/EtOAc 20/1).

[4] L. I. Panferova, M. I. Struchkova and A. D. Dilman, *Synthesis*, 2017, **49**, 4124–4132.

^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.03 (d, *J* = 7.8 Hz, 1H), 7.99-7.84 (m, 3H), 7.68-7.42 (m, 3H), 5.58 (ddd, *J* = 10.7, 6.7, 4.1 Hz, 1H), 3.35 (d, *J* = 4.1 Hz, 1H).

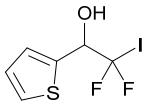
2,2-Difluoro-1-(2-furyl)-2-iodoethanol (5l).[3]



Yield 219 mg (80%). Light yellow oil. Chromatography: hexane/EtOAc, 8/1. R_f 0.23 (hexane/EtOAc 8/1)

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.49 (d, *J* = 1.9 Hz, 1H), 6.56 (d, *J* = 3.4 Hz, 1H), 6.44 (dd, *J* = 3.4, 1.9 Hz, 1H), 4.80 (t, *J* = 9.1 Hz, 1H), 3.37 (br, 1H).

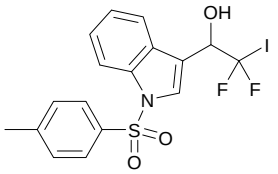
2,2-Difluoro-2-iodo-1-thien-2-ylethanol (5m).[4]



Yield 203 mg (70%). Light yellow oil. Chromatography: hexane/EtOAc, 6/1. R_f 0.20 (hexane/EtOAc 6/1)

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.42 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 4.93 (td, *J* = 8.7, 5.3 Hz, 1H), 3.25 (d, *J* = 5.3 Hz, 1H).

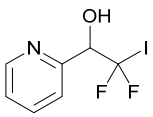
2,2-Difluoro-2-iodo-1-{1-[(4-methylphenyl)sulfonyl]-1*H*-indol-3-yl}ethanol (5n).[3]



Yield 357 mg (75%). Yellow oil. Chromatography: CH_2Cl_2. R_f 0.26 (CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.96 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.20-7.30 (m, 3H), 4.93 (ddd, *J* = 13.2, 8.8, 5.0 Hz, 1H), 3.19 (d, *J* = 4.0 Hz, 1H), 2.33 (s, 3H).

2,2-Difluoro-2-iodo-1-(pyridine-2-yl)ethanol (5o).



Yield 157 mg (55%). Yellow oil. Chromatography: hexanes/EtOAc, 2/1. R_f 0.23 (hexanes/EtOAc, 2/1).

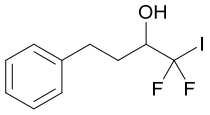
^{1}H NMR (300 MHz, $CDCl_3$), δ: 8.68-8.63 (m, 1H), 7.79 (td, *J* = 7.7, 1.6 Hz, 1H), 7.48-7.35 (m, 2H), 4.53 (dd, *J* = 9.0, 6.1 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 152.1 (d, *J* = 6.5 Hz), 148.2, 137.2, 124.6, 123.4 (dd, *J* = 3.9, 1.1 Hz), 107.9 (dd, *J* = 320.1, 317.5 Hz), 77.4 (dd, *J* = 25.2, 22.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –46.5 (dd, *J* = 184.5, 6.1 Hz, 1F), –54.0 (dd, *J* = 184.5, 9.0 Hz, 1F).

HRMS (ESI): Calcd for $C_7H_7F_2INO$ (M+H) 285.9535; found 285.9540.

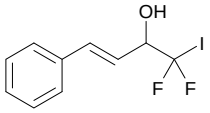
1,1-Difluoro-1-iodo-4-phenylbutan-2-ol (5p).[5]



Yield 200 mg (64%). Colorless oil. Chromatography: hexane/EtOAc, 5/1 R_f 0.43 (hexane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.41-7.30 (m, 2H), 7.30-7.18 (m, 3H), 3.53-3.24 (m, 1H), 2.98 (ddd, *J* = 14.0, 9.0, 5.1 Hz, 1H), 2.79 (dt, *J* = 14.0, 8.3 Hz, 1H), 2.38 (d, *J* = 6.0 Hz, 1H), 2.26-1.99 (m, 1H), 2.00-1.76 (m, 1H).

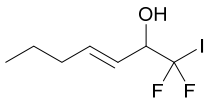
(3*E*)-1,1-Difluoro-1-iodo-4-phenylbut-3-en-2-ol (5q).[5]



Yield 232 mg (75%). Yellow oil. Chromatography: hexane/EtOAc, 7/1 R_f 0.30 (hexane/EtOAc 7/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.54-7.43 (m, 2H), 7.43-7.30 (m, 3H), 6.91 (d, *J* = 15.9 Hz, 1H), 6.18 (dd, *J* = 16.0, 5.9 Hz, 1H), 4.24-4.13 (m, 1H), 2.46 (br, 1H).

(*E*)-1,1-Difluoro-1-iodohept-3-en-2-ol (5r).



Yield 188 mg (68%). Yellow oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.38 (hexanes/EtOAc, 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 5.98 (dtd, *J* = 15.4, 6.8, 1.3 Hz, 1H), 5.45 (ddq, *J* = 15.4, 6.3, 1.3 Hz, 1H), 3.90 (br, 1H), 2.75 (br, 1H), 2.07 (q, *J* = 6.8 Hz, 2H), 1.44 (sext, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H).

[5] W. Miao, C. Ni, Y. Zhao and J. Hu, *Org. Lett.*, 2016, **18**, 2766–2769.

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$), δ: 138.8, 124.1 (dd, *J* = 3.9, 1.1 Hz), 108.8 (t, *J* = 318.4 Hz), 78.7 (dd, *J* = 24.3, 22.7 Hz), 34.5, 21.9, 13.7.

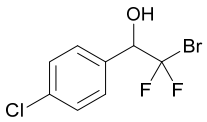
^{19}F NMR (282 MHz, $CDCl_3$), δ: –49.8 (dd, *J* = 178.2, 9.2 Hz, 1F), –53.7 (dd, *J* = 178.2, 7.5 Hz, 1F).

HRMS (ESI): Calcd for $C_7H_{11}F_2IONa$ (M+Na) 298.9715; found 298.9708.

Synthesis of bromodifluoromethylated alcohols 6a,b,d-f (General procedure 2).

A reaction tube equipped with a magnetic stirring bar was charged with betaine **1** (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Acetonitrile (2 mL), aldehyde (1 mmol) and Me_3SiCl (190 μL, 1.5 mmol, 1.5 equiv) were added successively. The suspension was stirred at 45–50 °C until complete dissolution of betaine **1** (2–5 h). Then, dimethylsulfate (117 μL, 1.2 mmol, 1.2 uqiv) was added. The mixture was stirred for 5 min, then cooled to room temperature, and the solvent was evaporated under vacuum (8 Torr). Then, acetonitrile (2 mL), CuBr (15 mg, 0.1 mmol, 0.1 equiv), tetrabutylammonium bromide (644 mg, 2 mmol, 2 equiv) were added [for the synthesis of compound **6f**, *N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (21 μL, 0.1 mmol, 0.1 equiv) was added]. The reaction vessel was irradiated with 400 nm LED overnight; during irradiation the mixture was cooled with room temperature water. The work-up is the same as in General procedure 1.

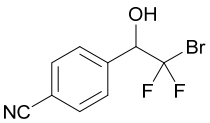
2-Bromo-1-(4-chlorophenyl)-2,2-difluoroethanol (6a).[2]



Yield 223 mg (82%). Colorless oil. Chromatography: hexane/EtOAc, 5/1 R_f 0.35 (hexane/EtOAc 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.52-7.30 (m, 4H), 5.01 (t, *J* = 7.5 Hz, 1H), 3.00 (s, 1H).

4-(2-Bromo-2,2-difluori-1-hydroxyethyl)benzonitrile (6b).



After column chromatography (hexanes/EtOAc, 3/1, R_f 0.35), the obtained material was purified by preparative HPLC (reversed-phase column C_{18}, 21.2×250 mm, 5 μm, flow rate 12 mL/min, 5% water in acetonitrile, retention time 4.31 min). Yield 173 mg (66%). White crystals. Mp 103-105 °C.

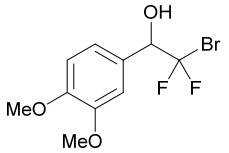
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.73 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 5.08 (ddd, *J* = 10.1, 6.4, 4.0 Hz, 1H), 3.34 (d, *J* = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 139.9 (d, *J* = 1.7 Hz), 132.1, 130.2, 128.9, 123.6 (t, *J* = 311.0 Hz), 118.5, 112.9, 77.5 (t, *J* = 25.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –56.6 (dd, *J* = 165.3, 6.4 Hz, 1F), –60.1 (dd, *J* = 165.3, 10.1 Hz, 1F).

HRMS (ESI): Calcd for $C_9H_6{}^{79}BrF_2NONa$ (M+Na) 283.9493; found 283.9501; Calcd for $C_9H_6{}^{81}BrF_2NONa$ (M+Na) 285.9473; found 285.9483.

2-Bromo-1-(3,4-dimethoxyphenyl)-2,2-difluoroethanol (6c).



A reaction tube equipped with a magnetic stirring bar was charged with betaine **1** (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), 3,4-dimethoxybenzaldehyde (166 mg, 1 mmol) and Me_3SiCl (190 μL, 1.5 mmol, 1.5 equiv) were added successively. The suspension was heated at 45–50 °C for 5 h until complete dissolution of betaine **1**. Then, allyl bromide (171 μL, 2 mmol, 2 equiv) was added. The mixture was cooled to room temperature, and the solvent was evaporated under vacuum (8 Torr). Then, dichloroethane (2 mL), CuBr (15 mg, 0.1 mmol, 0.1 equiv), tetrabutylammonium bromide (322 mg, 1 mmol, 1 equiv) were added, and the reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. Then, ethanol (750 μL) and trifluoroacetic acid (250 μL) were added, and the mixture was stirred at room temperature for 2 h. The mixture diluted with water (5 mL) and extracted with EtOAc/hexane (1/2, 3×10 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 eluting with hexane/EtOAc, 2/1. Yield 211 mg (71%). Colorless oil. R_f 0.27 (hexanes/EtOAc, 2/1).

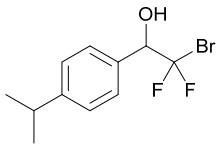
^{1}H NMR (300 MHz, $CDCl_3$), δ: 6.98 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.92 (dd, *J* = 10.2, 7.3 Hz, 1H), 3.84 (s, 6H), 3.25 (br, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 149.9, 148.9, 127.0 (d, *J* = 2.1 Hz), 124.4 (t, *J* = 311.0 Hz), 120.9, 119.8, 110.8, 78.3 (t, *J* = 25.0 Hz), 56.0, 55.9.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –56.6 (dd, *J* = 161.9, 7.3 Hz, 1F), –59.9 (dd, *J* = 161.9, 10.2 Hz, 1F).

HRMS (ESI): Calcd for $C_{10}H_{11}{}^{79}BrF_2O_3Na$ (M+Na) 318.9752; found 318.9758; Calcd for $C_{10}H_{11}{}^{81}BrF_2O_3Na$ (M+Na) 320.9732; found 320.9740.

2-Bromo-2,2-difluoro-1-(4-isopropylphenyl)ethanol (6d).



Yield 209 mg (75%). Colorless oil. Chromatography: hexanes/EtOAc, 8/1. R_f 0.25 (hexanes/EtOAc, 8/1).

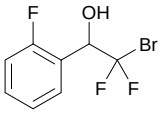
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.42 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.97 (ddd, *J* = 10.4, 7.2, 4.7 Hz, 1H), 3.02-2.90 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 6H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 150.5, 132.4 (d, *J* = 10.8 Hz), 131.8 (d, *J* = 1.7 Hz), 128.7 (d, *J* = 12.7 Hz), 128.0, 126.6, 124.3 (dd, *J* = 311.8, 310.2 Hz), 78.6 (t, *J* = 25.0 Hz), 34.0, 24.0.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –56.5 (dd, *J* = 161.5, 7.2 Hz, 1F), –59.8 (dd, *J* = 161.5, 10.4 Hz, 1F).

Calcd for $C_{11}H_{13}BrF_2O$ (279.12): C, 47.33; H, 4.69. Found: C, 47.35; H, 4.65.

2-Bromo-2,2-difluoro-1-(2-fluorophenyl)ethanol (6e).



Yield 196 mg (77%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.35 (hexanes/EtOAc, 5/1).

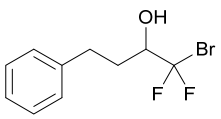
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.65 (t, *J* = 7.4 Hz, 1H), 7.48-7.34 (m, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.17-7.07 (m, 1H), 5.50-5.37 (m, 1H), 3.22 (br, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 160.6 (d, *J* = 248.8 Hz), 131.3 (d, *J* = 8.6 Hz), 129.2, 124.5 (d, *J* = 3.6 Hz), 123.6 (td, *J* = 311.8, 1.7 Hz), 121.8 (d, *J* = 13.0 Hz), 115.6 (d, *J* = 21.9 Hz), 72.4 (td, *J* = 26.2, 25.8, 3.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –57.8 (dt, *J* = 162.1, 7.8 Hz, 1F), –60.3 (dt, *J* = 162.1, 10.1 Hz, 1F), –117.7 (m, 1F).

Calcd for $C_8H_8BrF_3O$ (255) C, 37.68; H, 2.37. Found: C, 37.54; H, 2.31.

1-Bromo-1,1-difluoro-4-phenylbutan-2-ol (6f).



Yield 159 mg (60%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.44 (hexanes/EtOAc, 5/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.54-7.03 (m, 5H), 3.93-3.78 (m, 1H), 3.12-2.89 (m, 1H), 2.79 (dt, *J* = 13.9, 8.3 Hz, 1H), 2.52 (d, *J* = 6.0 Hz, 1H), 2.23-2.07 (m, 1H), 2.05-1.89 (m, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 140.6, 128.8, 128.6, 126.5, 125.7 (t, *J* = 310.5 Hz), 75.7 (t, *J* = 23.4 Hz).

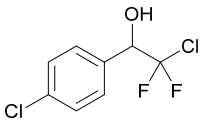
^{19}F NMR (282 MHz, $CDCl_3$), δ: –56.9 (dd, *J* = 162.3, 8.2 Hz, 1F), –59.8 (dd, *J* = 162.3, 8.2 Hz, 1F).

HRMS (ESI): Calcd for $C_{10}H_{11}{}^{79}BrF_2ONa$ (M+Na) 286.9854; found 286.9860; Calcd for $C_{10}H_{11}{}^{81}BrF_2ONa$ (M+Na) 288.9833; found 288.9843.

Synthesis of chlorodifluoromethylated alcohols 7 (General procedure 3).

A reaction tube equipped with magnetic stirring bar was charged with betaine **1** (428 mg, 1.2 mmol, 1.2 equiv), evacuated and backfilled with argon. Dichloroethane (2 mL), aldehyde (1 mmol) and Me_3SiCl (190 μL, 1.5 mmol, 1.5 equiv) were added successively. The suspension was heated at 45–50 °C until complete dissolution of betaine **1** (2–5 h). Then, benzyltriethylammonium chloride (113.5 mg, 0.5 mmol, 0.5 equiv) and CuCl (10 mg, 0.1 mmol, 0.1 equiv) were added [for **7g**, *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (21 μL, 0.1 mmol, 0.1 equiv) was added]. The reaction vessel was irradiated with 400 nm LED for 18 h; during irradiation the mixture was cooled with room temperature water. The work-up is the same as in General procedure 1.

2-Chloro-1-(4-chlorophenyl)-2,2-difluoroethanol (7a).[6]



Yield 191 mg (84%). Colorless oil. Chromatography: hexane/EtOAc, 10/1 R_f 0.27 (hexane/EtOAc 10/1).

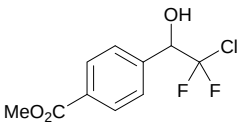
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.59-7.30 (m, 4H), 5.04 (t, *J* = 7.8 Hz, 1H), 3.43 (br, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 135.6, 132.8 (d, *J* = 2.2 Hz), 129.3 (t, *J* = 1.5 Hz), 128.9 (t, *J* = 296.9 Hz), 128.8, 76.7 (t, *J* = 27.8 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –63.1 (dd, *J* = 165.9, 7.8 Hz, 1F), –64.9 (dd, *J* = 165.9, 7.8 Hz, 1F).

[6] E. D. Bergmann, P. Moses, M. Neeman, S. Cohen, A. Kaluszyner and S. Reuter, *J. Am. Chem. Soc*,. 1957, **79**, 4174–4178.

Methyl 4-(2-chloro-2,2-difluoro-1-hydroxyethyl)benzoate (7b).



Yield 215 mg (86%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.16 (hexanes/EtOAc, 5/1).

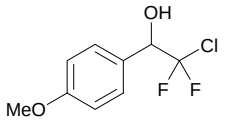
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.99 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 5.12 (td, *J* = 7.5, 3.1 Hz, 1H), 4.28 (br, 1H), 3.88 (s, 3H).

^{13}C{1H} NMR (75 MHz, $CDCl_3$), δ: 167.7 (d, *J* = 3.3 Hz), 140.3, 131.1, 129.9, 129.2 (t, *J* = 296.4 Hz), 128.4, 77.5 (t, *J* = 27.9 Hz), 52.9.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –63.3 (dd, *J* = 165.8, 7.5 Hz, 1F), –65.2 (dd, *J* = 165.8, 7.5 Hz, 1F).

HRMS (ESI): Calcd for $C_{10}H_9{}^{35}ClF_2O_3Na$ (M+Na) 273.0100; found 273.0104; calcd for $C_{10}H_9{}^{37}ClF_2O_3Na$ (M+Na) 275.0072; found 275.0078.

2-Chloro-1-(4-chlorophenyl)-2,2-difluoroethanol (7c).



Yield 164 mg (74%). Colorless oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.32 (hexanes/EtOAc, 5/1).

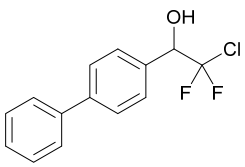
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.41 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.00 (td, *J* = 8.1, 4.1 Hz, 1H), 3.83 (s, 3H), 3.16 (d, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 160.5, 129.2 (t, *J*= 296.5), 129.2, 126.6, 114.0, 77.1 (t, *J* = 27.7 Hz), 55.4.

^{19}F NMR (282 MHz, $CDCl_3$), δ: –63.9 (dd, *J* = 164.6, 8.1 Hz, 1F), –65.7 (dd, *J* = 164.6, 8.1 Hz, 1F).

HRMS (ESI): Calcd for $C_9H_9{}^{35}ClF_2O_2Na$ (M+Na) 245.0151; found 245.0158; calcd for $C_9H_9{}^{37}ClF_2O_2Na$ (M+Na) 247.0122; found 247.0129.

1-(1,1'-Biphenyl-4-yl)-2-chloro-2,2-difluoroethanol (7d).



Yield 230 mg (86%). White crystals. Mp 107-109 °C. Chromatography: hexanes/EtOAc, 5/1. R_f 0.30 (hexanes/EtOAc, 5/1).

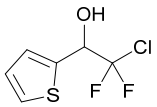
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.76-7.51 (m, 6H), 7.51-7.30 (m, 3H), 5.13 (ddd, *J* = 8.7, 7.2, 4.3 Hz, 1H), 2.76 (d, *J* = 4.3 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 142.6, 140.5, 133.3 (d, *J* = 1.1 Hz), 129.1 (t, *J* = 297.3 Hz), 129.0, 128.4, 127.8, 127.3, 77.3 (t, *J* = 27.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –63.5 (dd, *J* = 165.3, 7.2 Hz, 1F), –65.6 (dd, *J* = 165.3, 8.7 Hz, 1F).

HRMS (ESI): Calcd for $C_{14}H_{11}{}^{35}ClF_2ONa$ (M+Na) 291.0359; found 291.0360; Calcd for $C_{14}H_{11}{}^{37}ClF_2ONa$ (M+Na) 293.0330; found 293.0334.

2-Chloro-2,2-difluoro-1-thien-2-ylethanol (7e).



Yield 150 mg (76%). Light yellow oil. Chromatography: hexanes/EtOAc, 5/1. R_f 0.34 (hexanes/EtOAc).

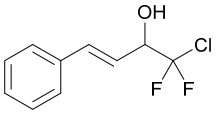
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.40 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 7.06 (dd, *J* = 5.0, 3.6 Hz, 1H), 5.33 (td, *J* = 7.6, 5.0 Hz, 1H), 2.83 (d, *J* = 5.0 Hz, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 136.6 (d, *J* = 1.6 Hz), 128.5 (t, *J* = 296.8 Hz), 127.9, 127.2, 127.0, 74.2 (t, *J* = 29.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –64.3 (dd, *J* = 165.3, 7.6 Hz, 1F), –65.8 (dd, *J* = 165.3, 7.6 Hz, 1F).

HRMS (ESI): Calcd for $C_6H_5{}^{35}ClF_2OSNa$ (M+Na) 220.9610; found 220.9621; calcd for $C_6H_5{}^{37}ClF_2OSNa$ (M+Na) 222.9580; found 222.9551.

(3*E*)-1-Chloro-1,1-difluoro-4-phenylbut-3-en-2-ol (7f).



Yield 137 mg (63%). Light yellow oil. Chromatography: hexanes/EtOAc, 7/1. R_f 0.32 (hexanes/EtOAc, 7/1).

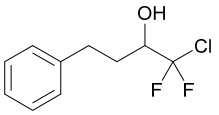
^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.61-7.29 (m, 5H), 6.87 (d, *J* = 16.0 Hz, 1H), 6.24 (dd, *J* = 16.0, 7.0 Hz, 1H), 4.68 (q, *J* = 7.0 Hz, 1H), 2.77 (br, 1H).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$), δ: 136.5, 135.6, 127.2 (t, *J* = 296.8 Hz), 128.8, 127.0, 121.5, 76.2 (t, *J* = 27.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$), δ: –64.2 (dd, *J* = 164.3, 7.0 Hz, 1F), –65.6 (dd, *J* = 164.3, 7.0 Hz, 1F).

HRMS (ESI): Calcd for $C_{10}H_9{}^{35}ClF_2ONa$ (M+Na) 241.0202; found 241.0203; Calcd for $C_{10}H_9{}^{37}ClF_2ONa$ (M+Na) 243.0173; found 243.0186.

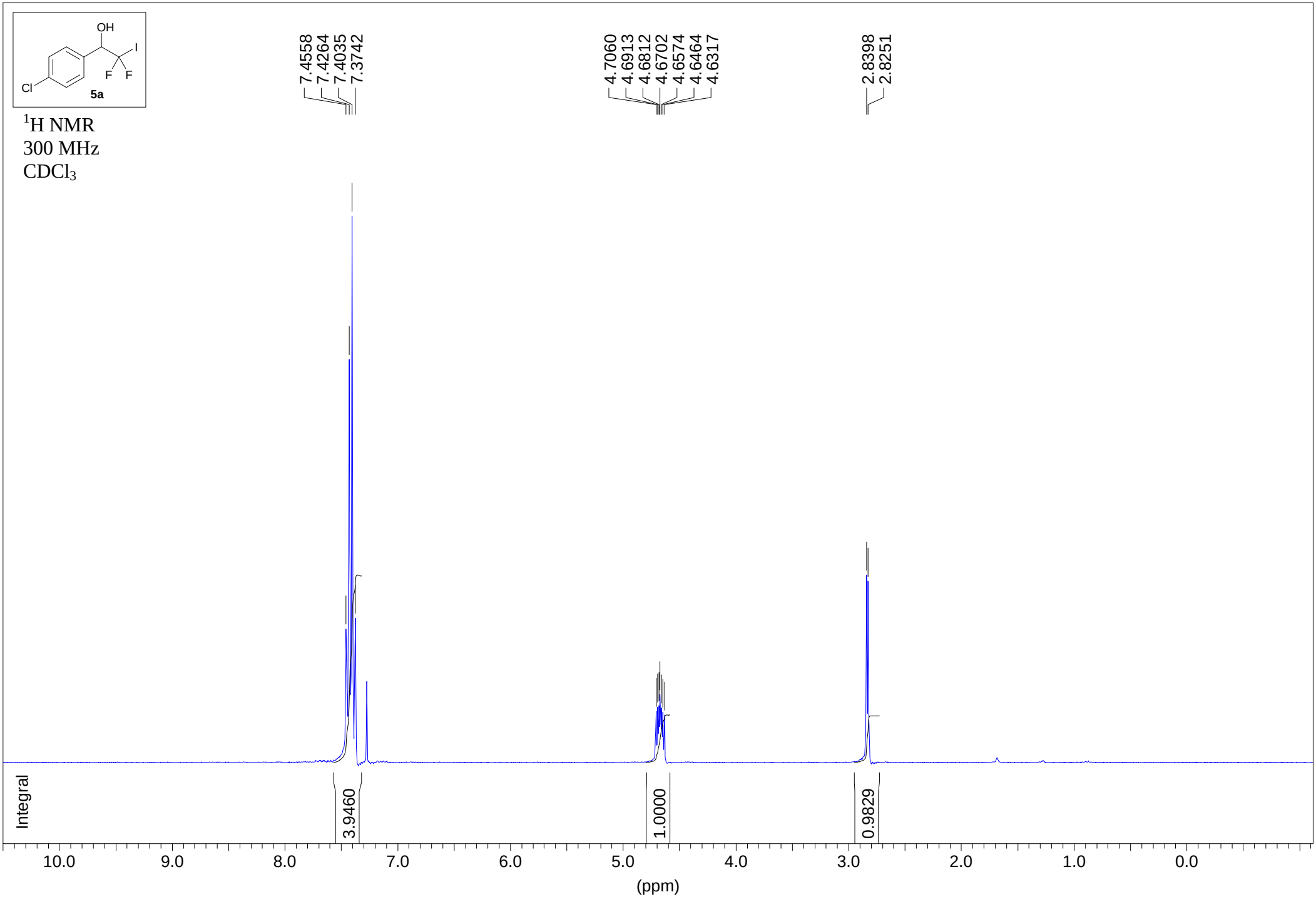
1-Chloro-1,1-difluoro-4-phenylbutan-2-ol (7g).[7]



Yield 132 mg (60%). Colorless oil. Chromatography: hexane/EtOAc, 10/1. R_f 0.32 (hexane/EtOAc 10/1).

^{1}H NMR (300 MHz, $CDCl_3$), δ: 7.47-7.33 (m, 2H), 7.32-7.24 (m, 3H), 4.07-3.80 (m, 1H), 3.00 (ddd, *J* = 14.0, 9.0, 5.1 Hz, 1H), 2.80 (dt, *J* = 13.9, 8.3 Hz, 1H), 2.52 (d, *J* = 6.0 Hz, 1H), 2.21-2.08 (m, 1H), 2.07-1.86 (m, 1H).

[7] T. Kitazume, M. Asai, T. Tsukamoto and T. Yamazaki, *J. Fluorine Chem.*, 1992, **56**, 271–284.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4.6812
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4.6574
4.6464
4.6317
2.8398
2.8251
1H NMR
300 MHz
CDCl3
Integral
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1.0000
0.9829
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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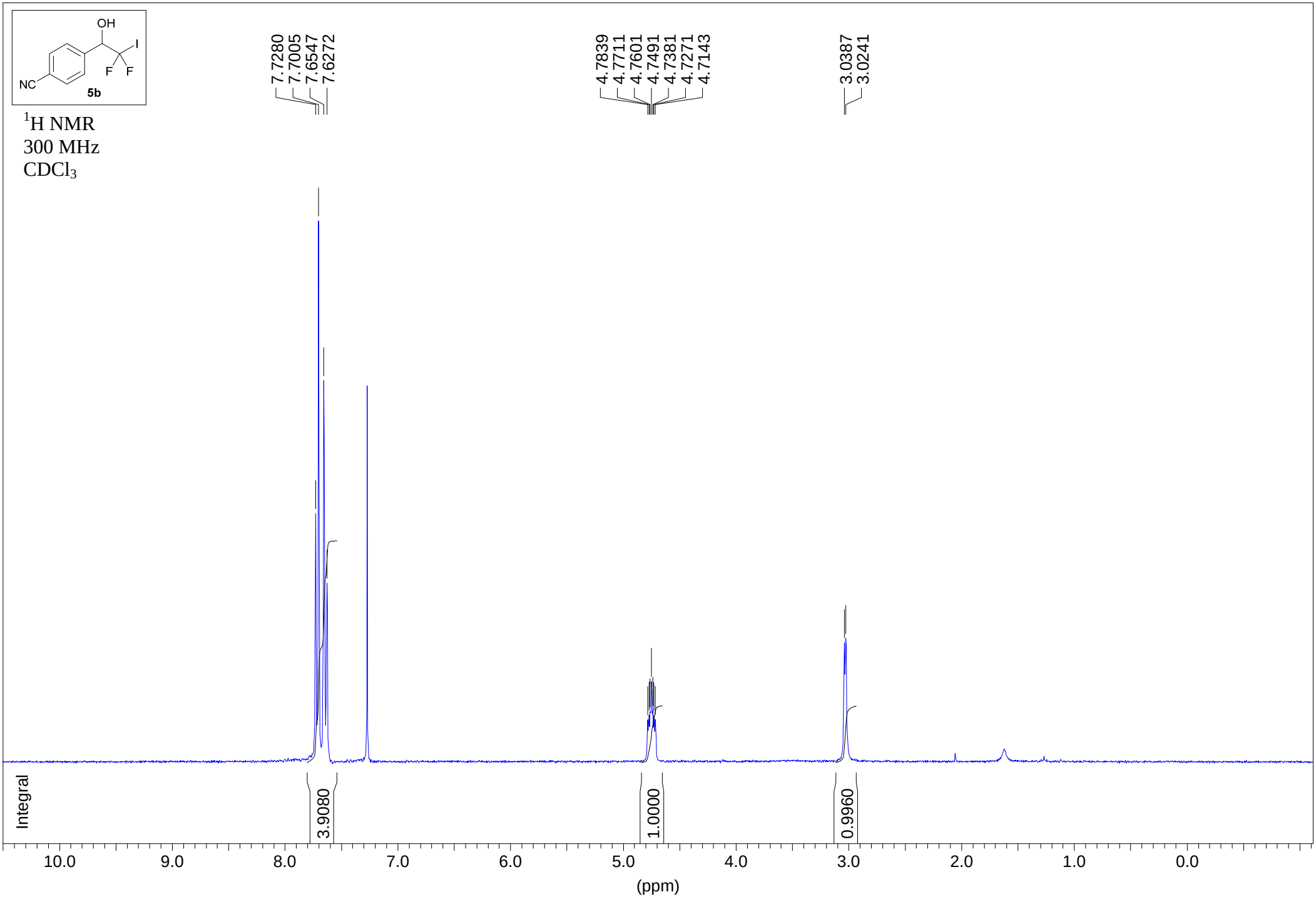
(ppm)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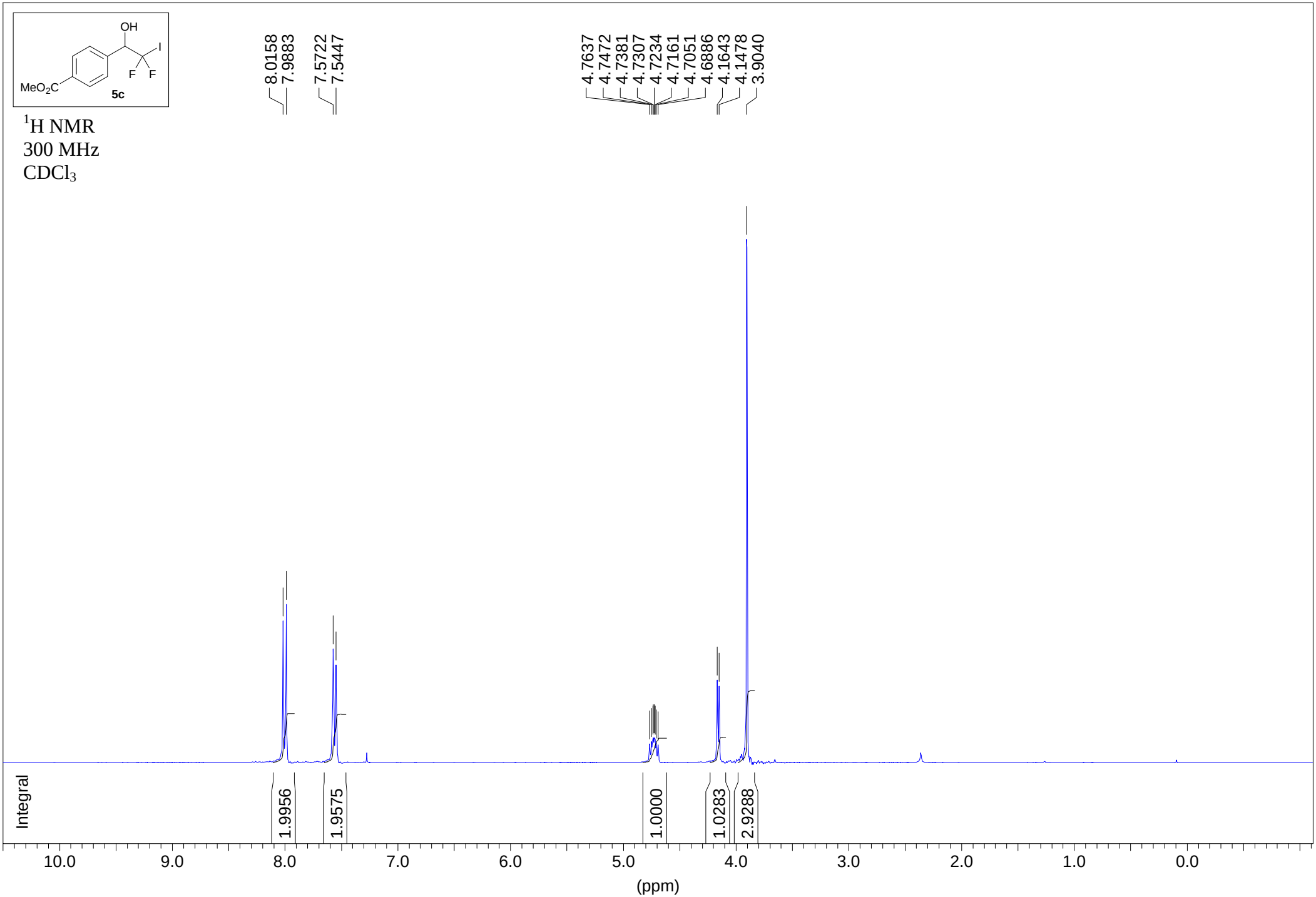
(ppm)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4.7234
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3.9040
1H NMR
300 MHz
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Integral
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3.0
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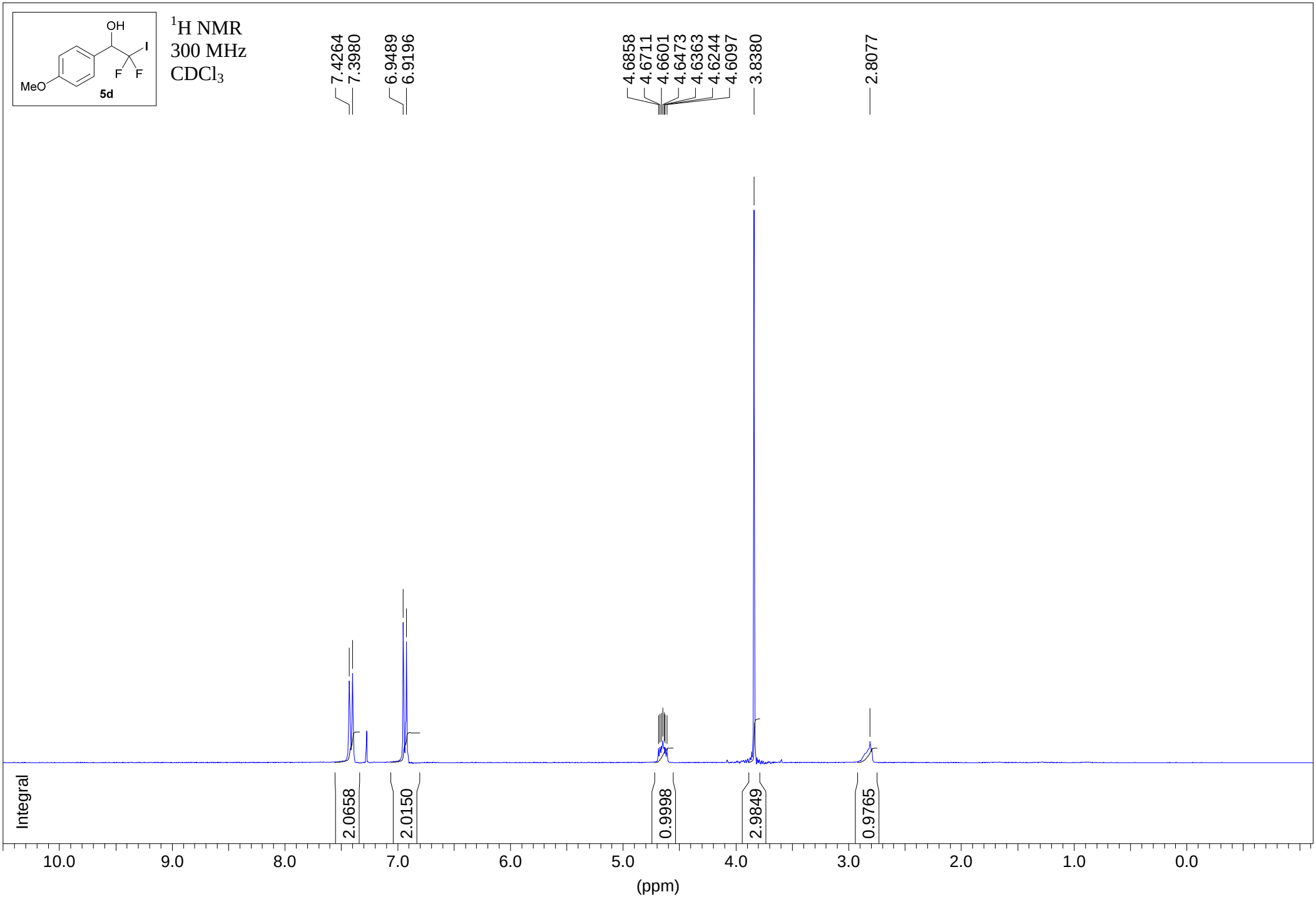
(ppm)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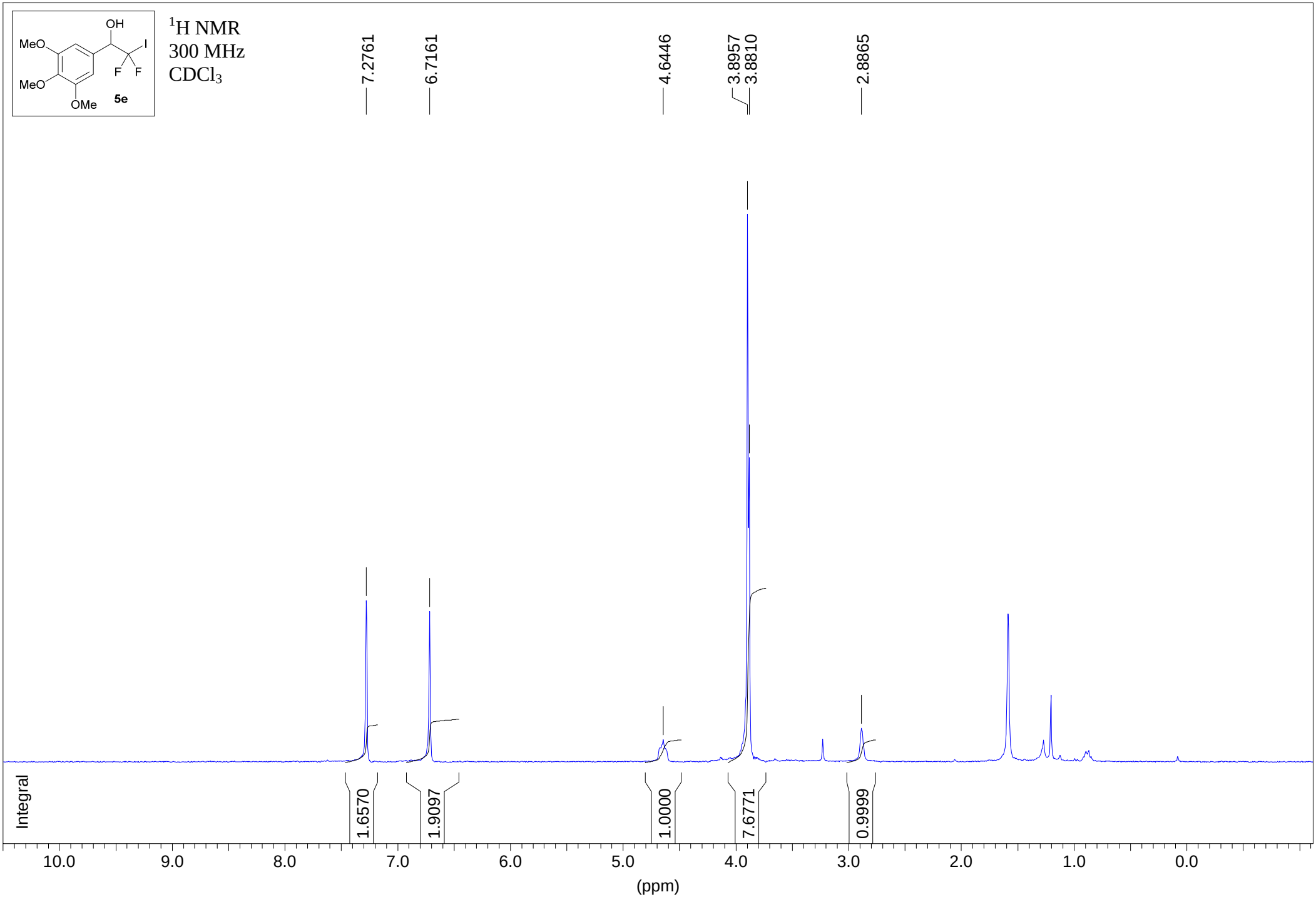
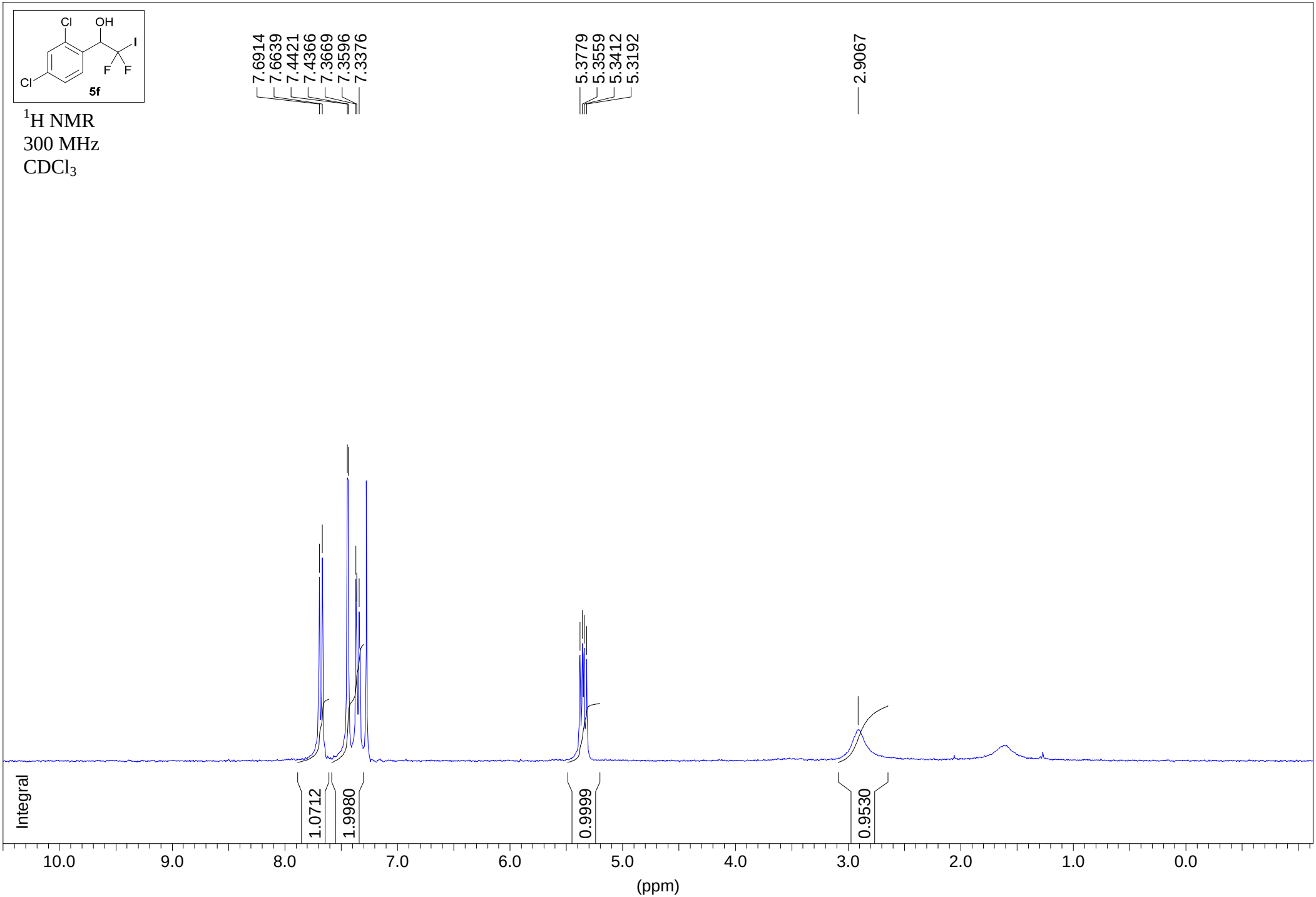
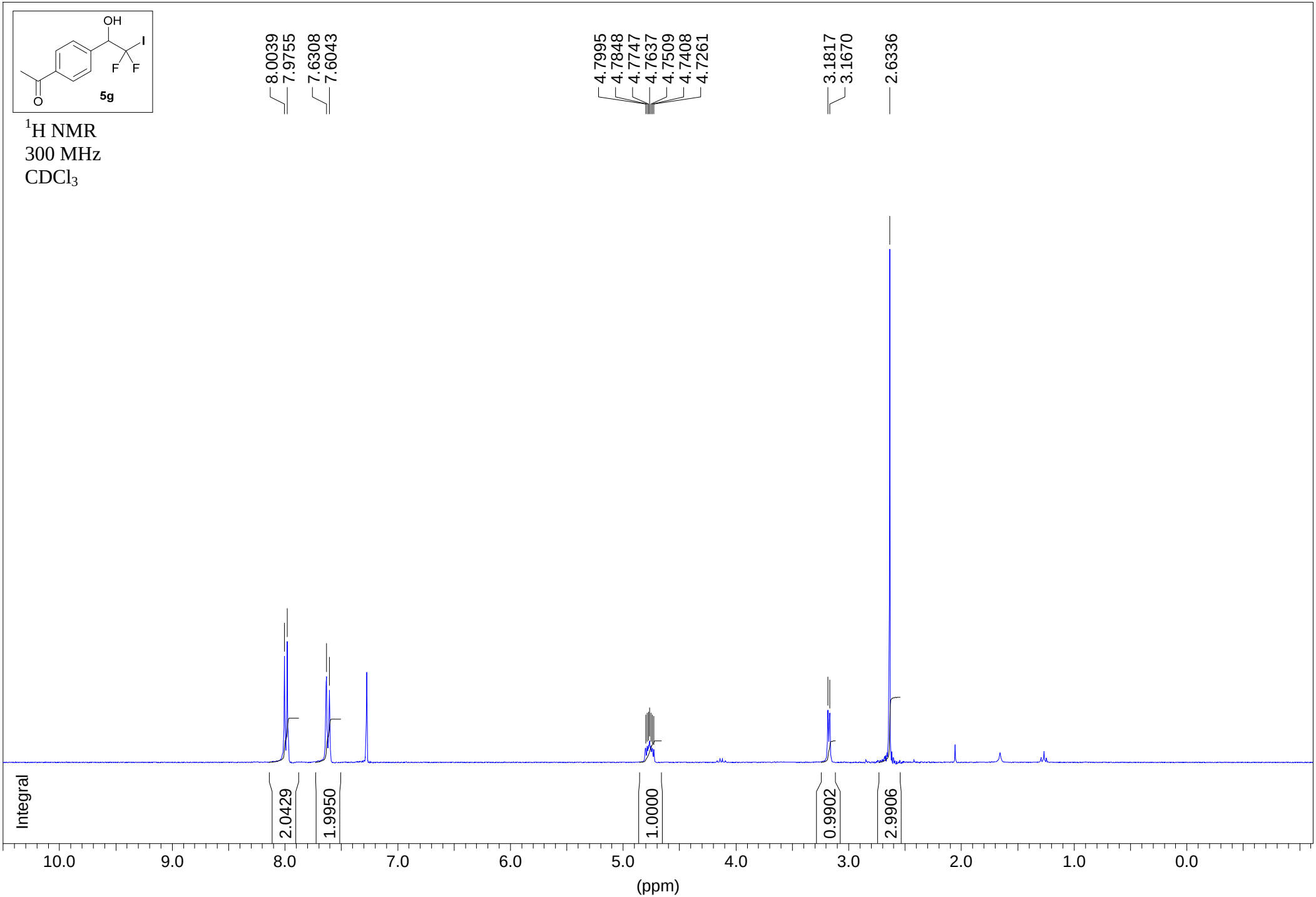
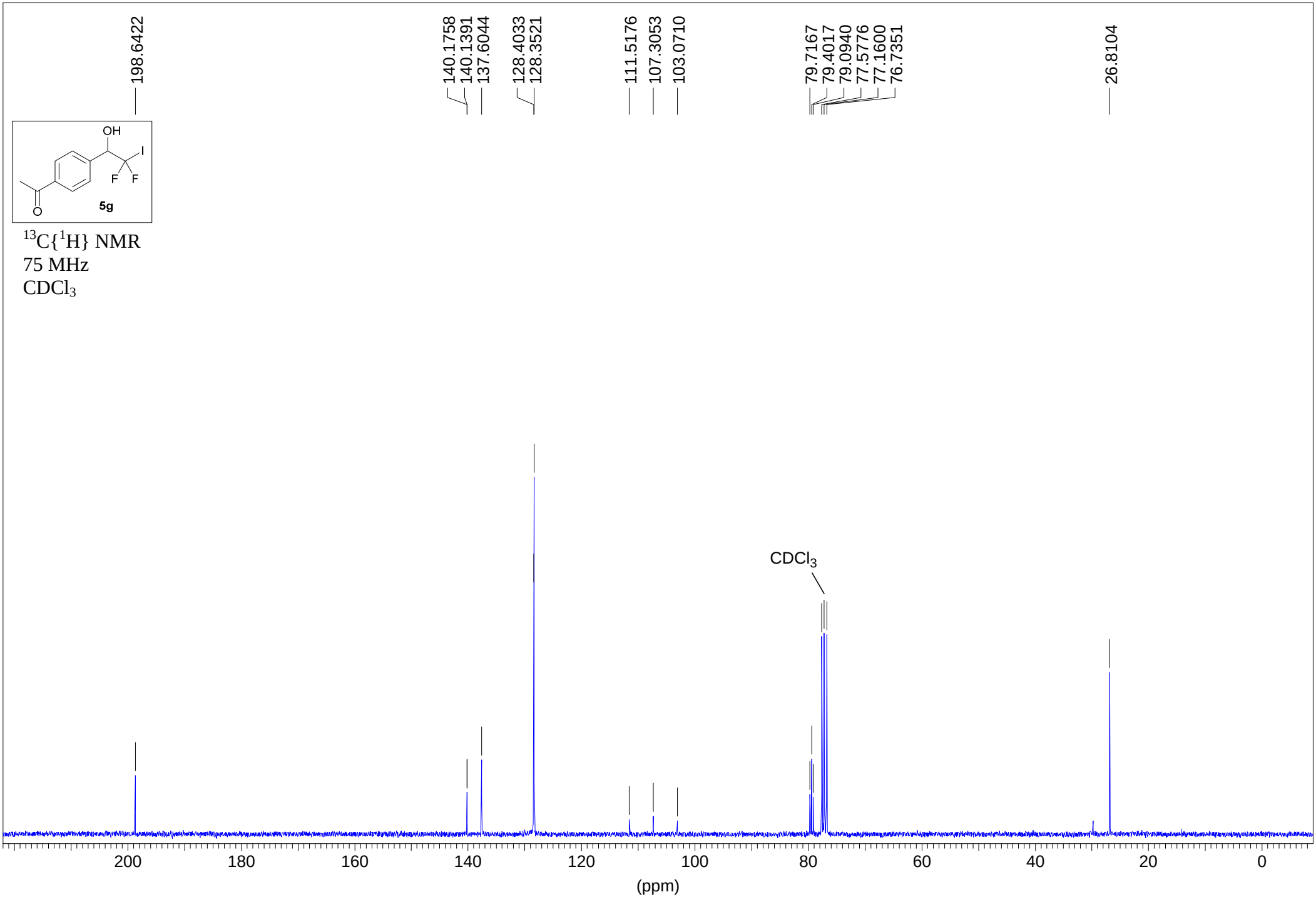
7.4264
7.3980
6.9489
6.9196
4.6858
4.6711
4.6601
4.6473
4.6363
4.6244
4.6097
3.8380
2.8077
Integral
2.0658
2.0150
0.9998
2.9849
0.9765
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

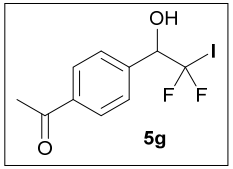

OH
MeO
I
F F
MeO
OMe
5e
1H NMR
300 MHz
CDCl3
7.2761
6.7161
4.6446
3.8957
3.8810
2.8865
Integral
1.6570
1.9097
1.0000
7.6771
0.9999
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


Cl
OH
I
F
F
Cl
5f
7.6914
7.6639
7.4421
7.4366
7.3669
7.3596
7.3376
5.3779
5.3559
5.3412
5.3192
2.9067
1H NMR
300 MHz
CDCl3
Integral
1.0712
1.9980
0.9999
0.9530
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

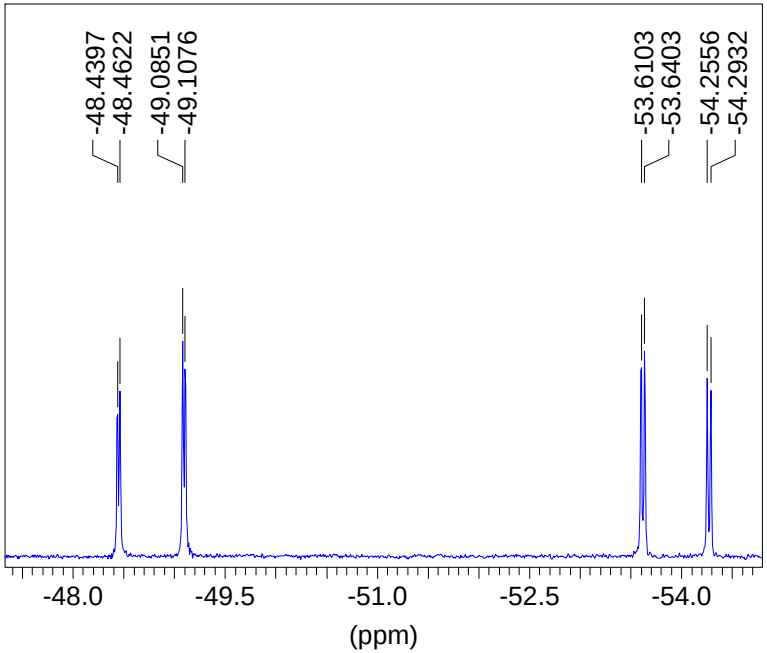

OH
I
F
F
O
5g
8.0039
7.9755
7.6308
7.6043
4.7995
4.7848
4.7747
4.7637
4.7509
4.7408
4.7261
3.1817
3.1670
2.6336
^{1}H NMR
300 MHz
$CDCl_3$
Integral
2.0429
1.9950
1.0000
0.9902
2.9906
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

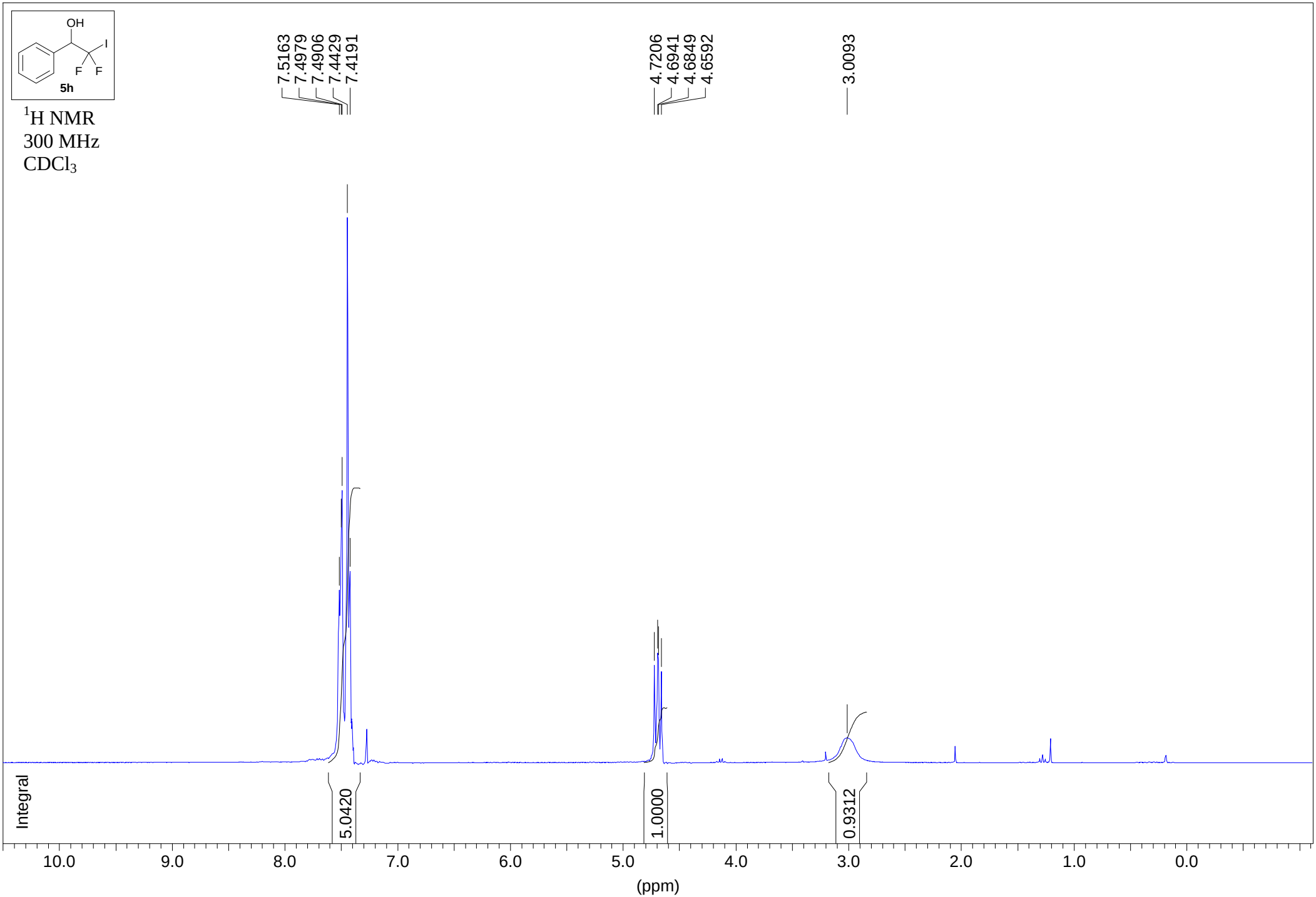


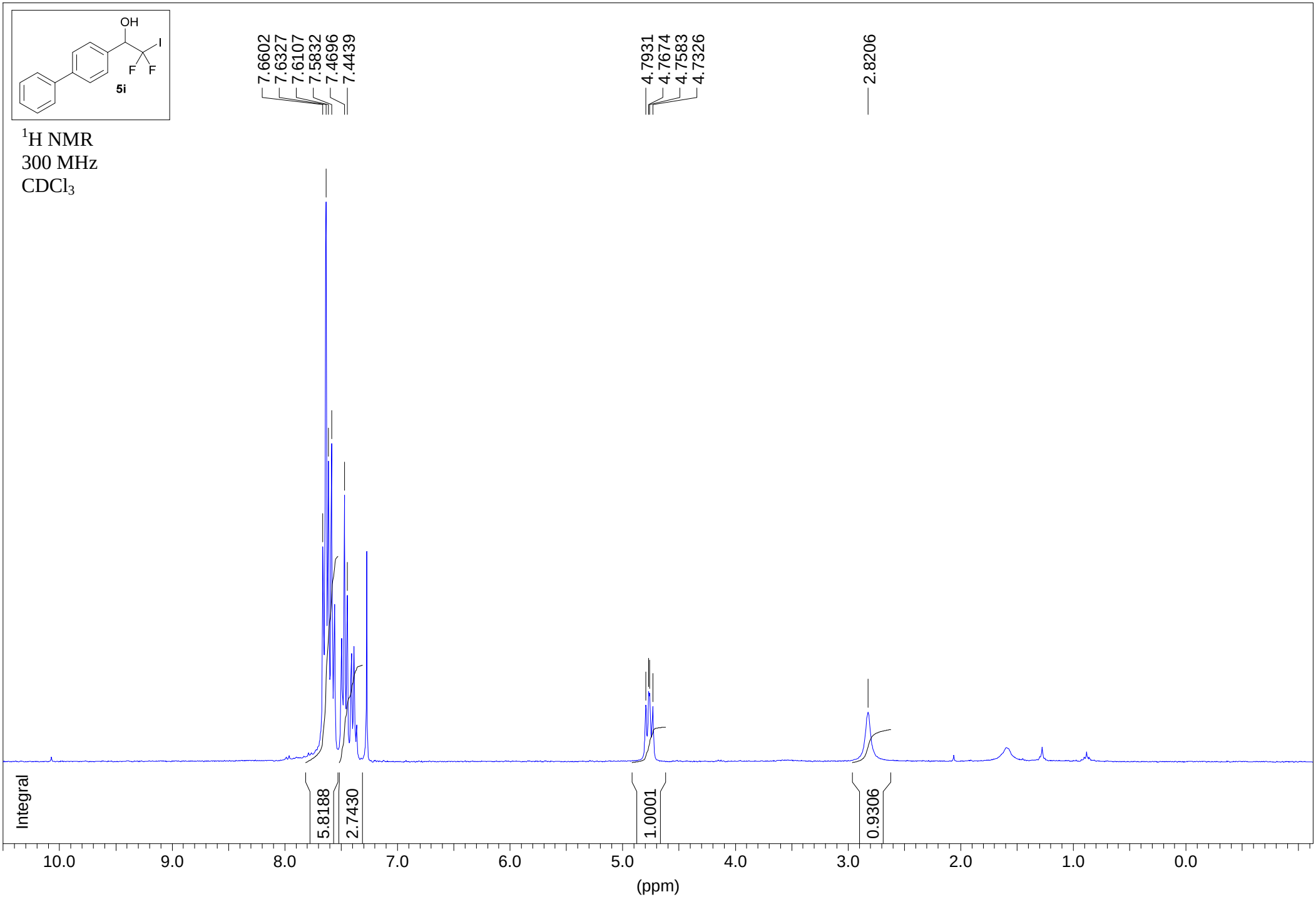
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

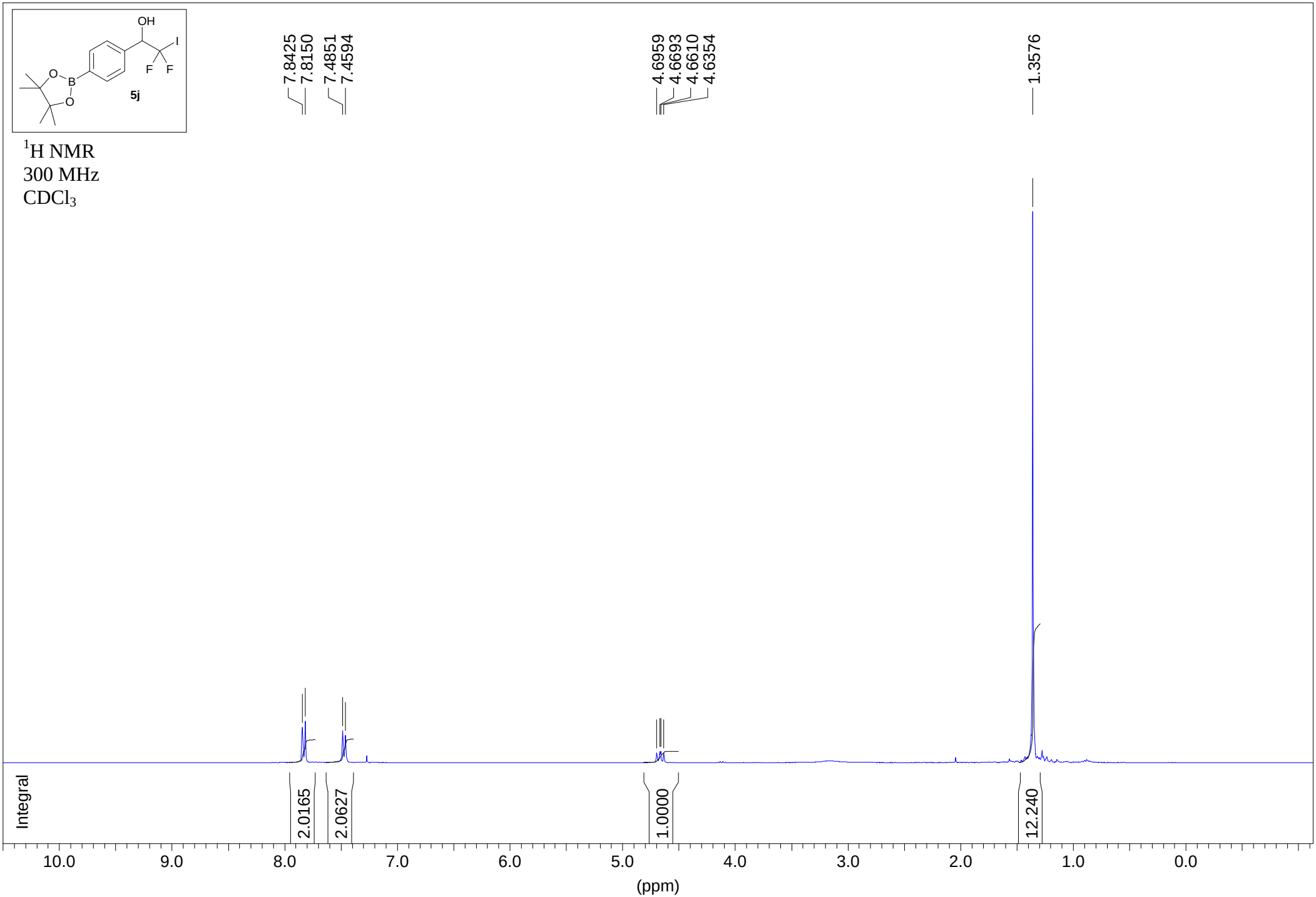


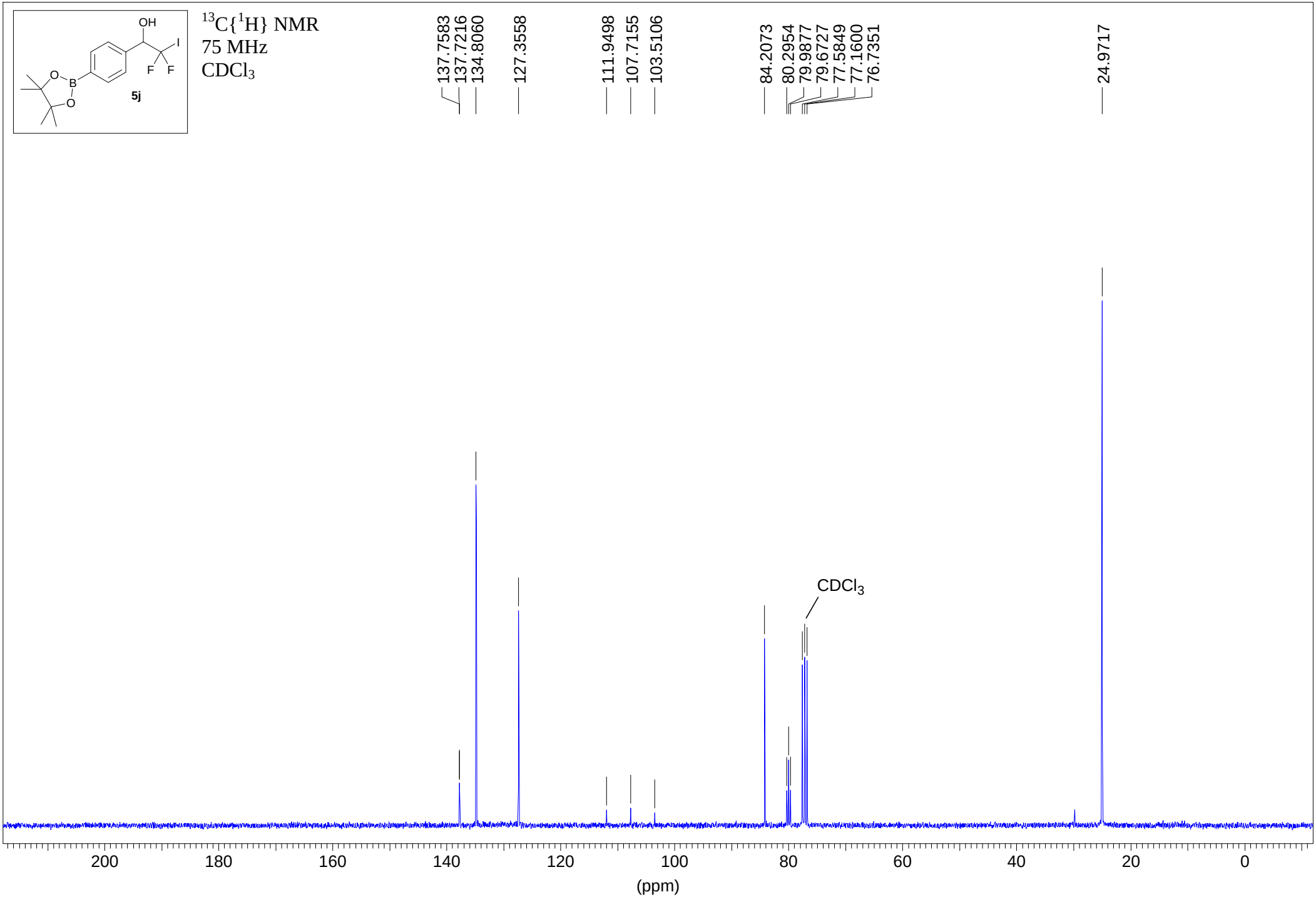
^{19}F NMR
282 MHz
$CDCl_3$

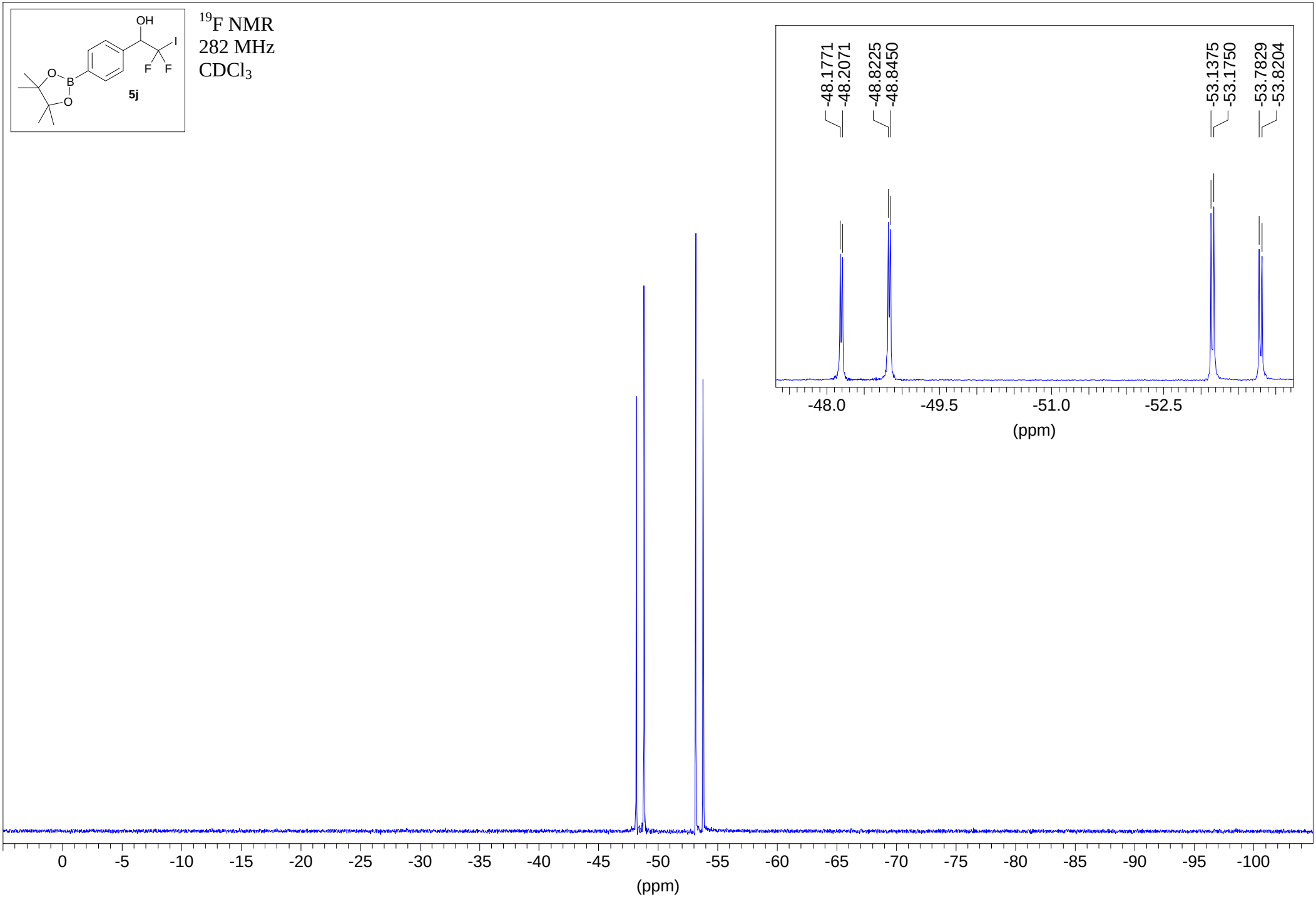


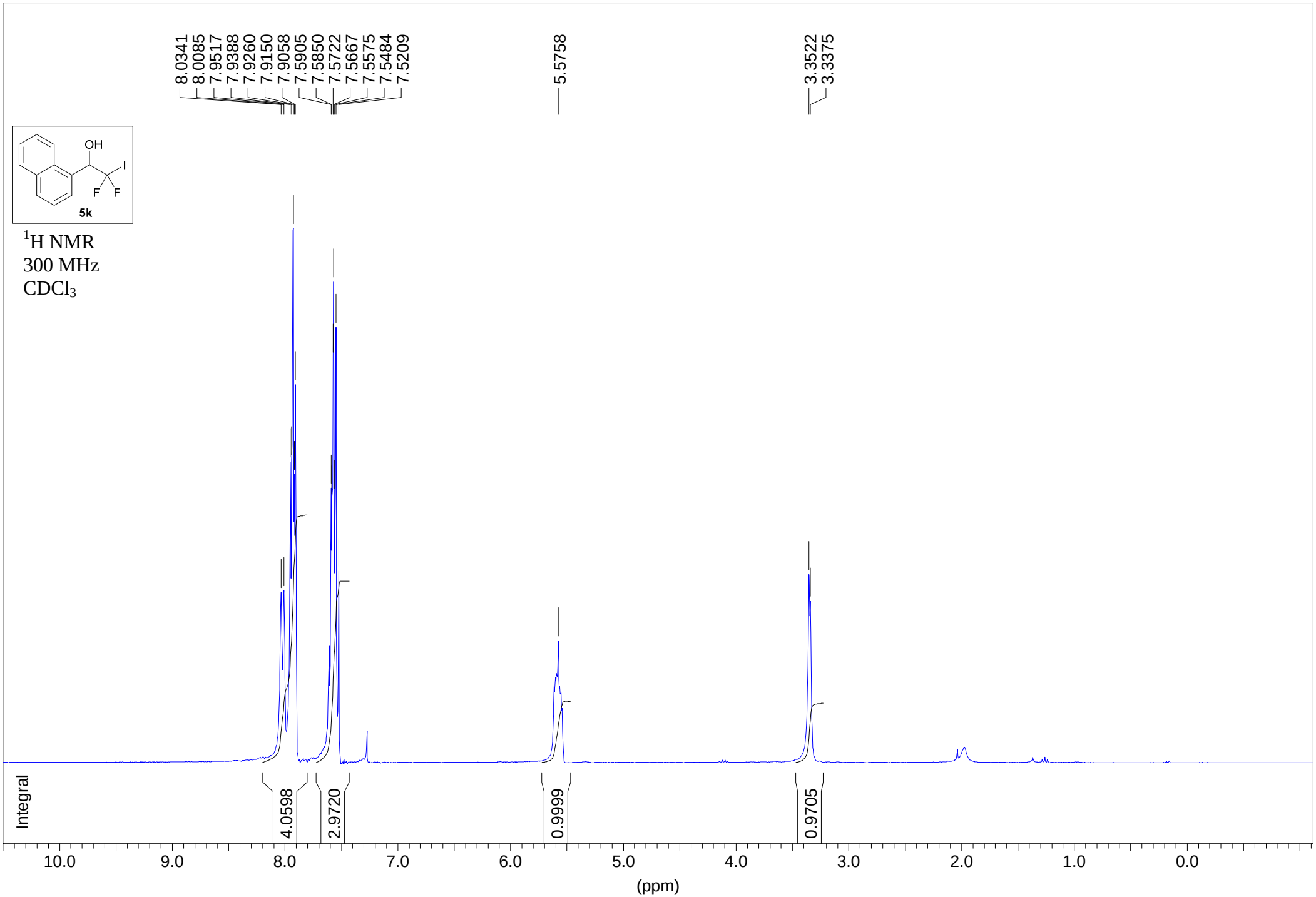

OH
I
F
F
5h
7.5163
7.4979
7.4906
7.4429
7.4191
4.7206
4.6941
4.6849
4.6592
3.0093
^{1}H NMR
300 MHz
$CDCl_3$
Integral
5.0420
1.0000
0.9312
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

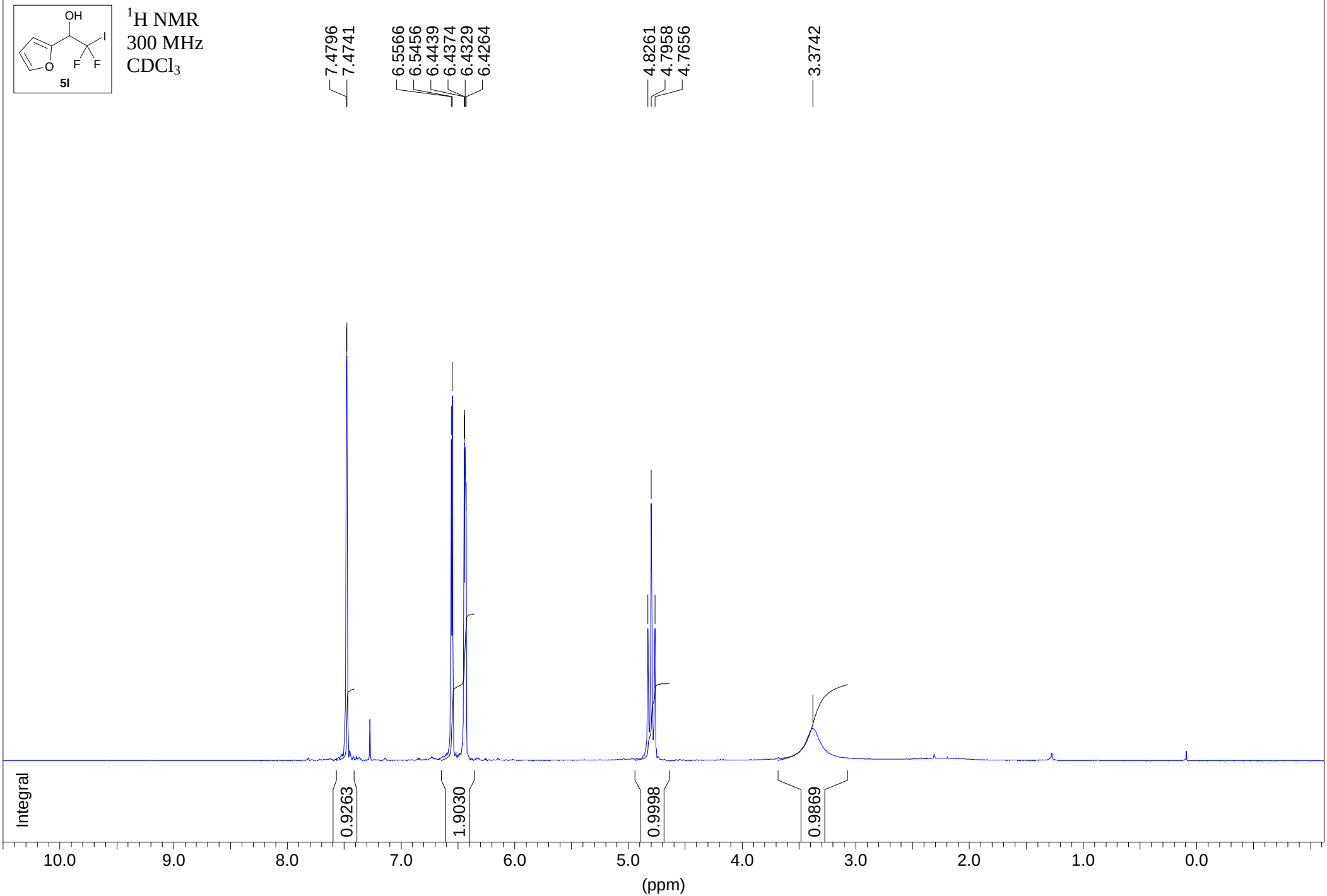

OH
I
F F
5i
7.6602
7.6327
7.6107
7.5832
7.4696
7.4439
4.7931
4.7674
4.7583
4.7326
2.8206
1H NMR
300 MHz
CDCl3
Integral
5.8188
2.7430
1.0001
0.9306
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

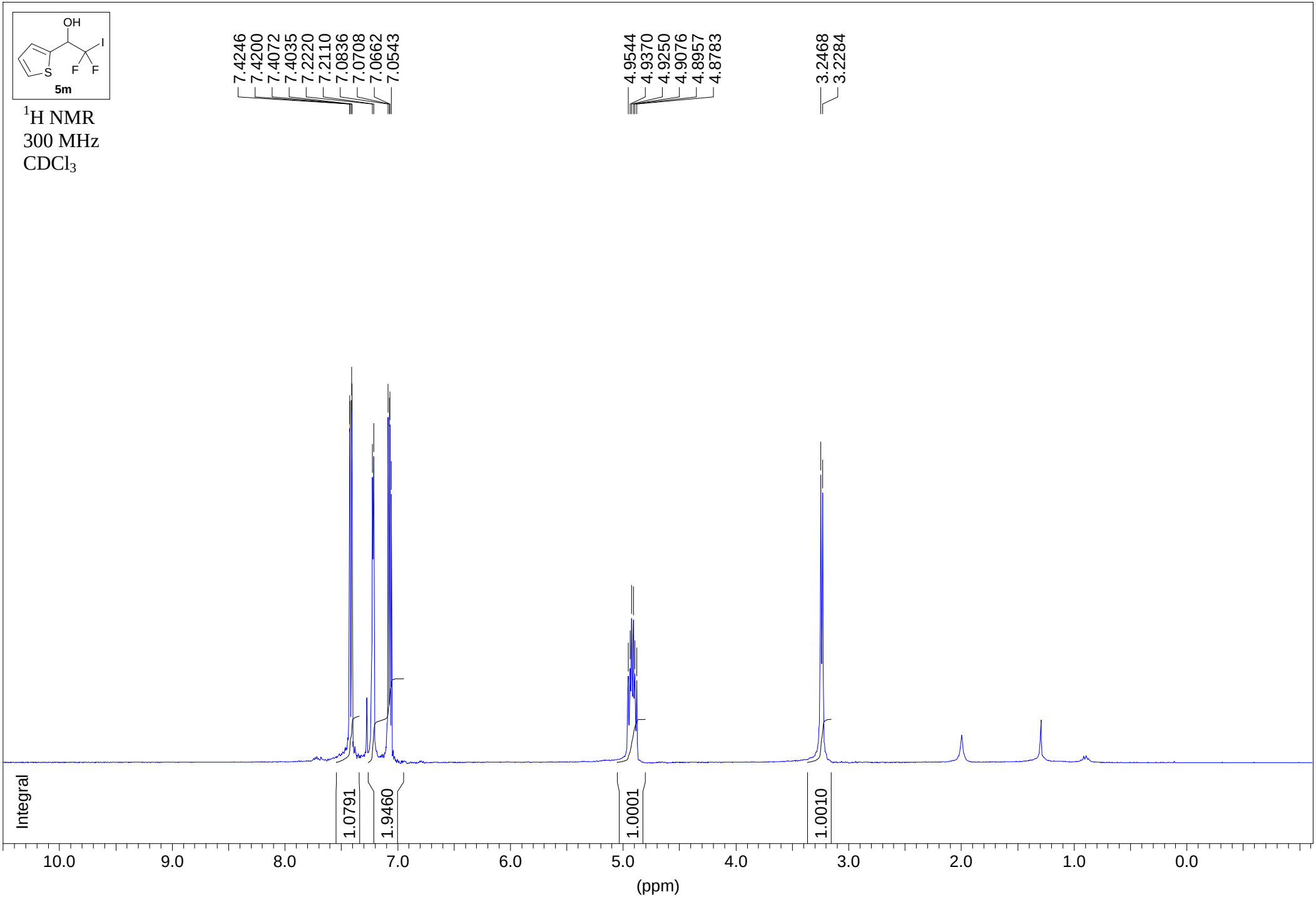

OH
I
F
F
O
B
O
5j
7.8425
7.8150
7.4851
7.4594
4.6959
4.6693
4.6610
4.6354
1.3576
^{1}H NMR
300 MHz
$CDCl_3$
Integral
2.0165
2.0627
1.0000
12.240
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

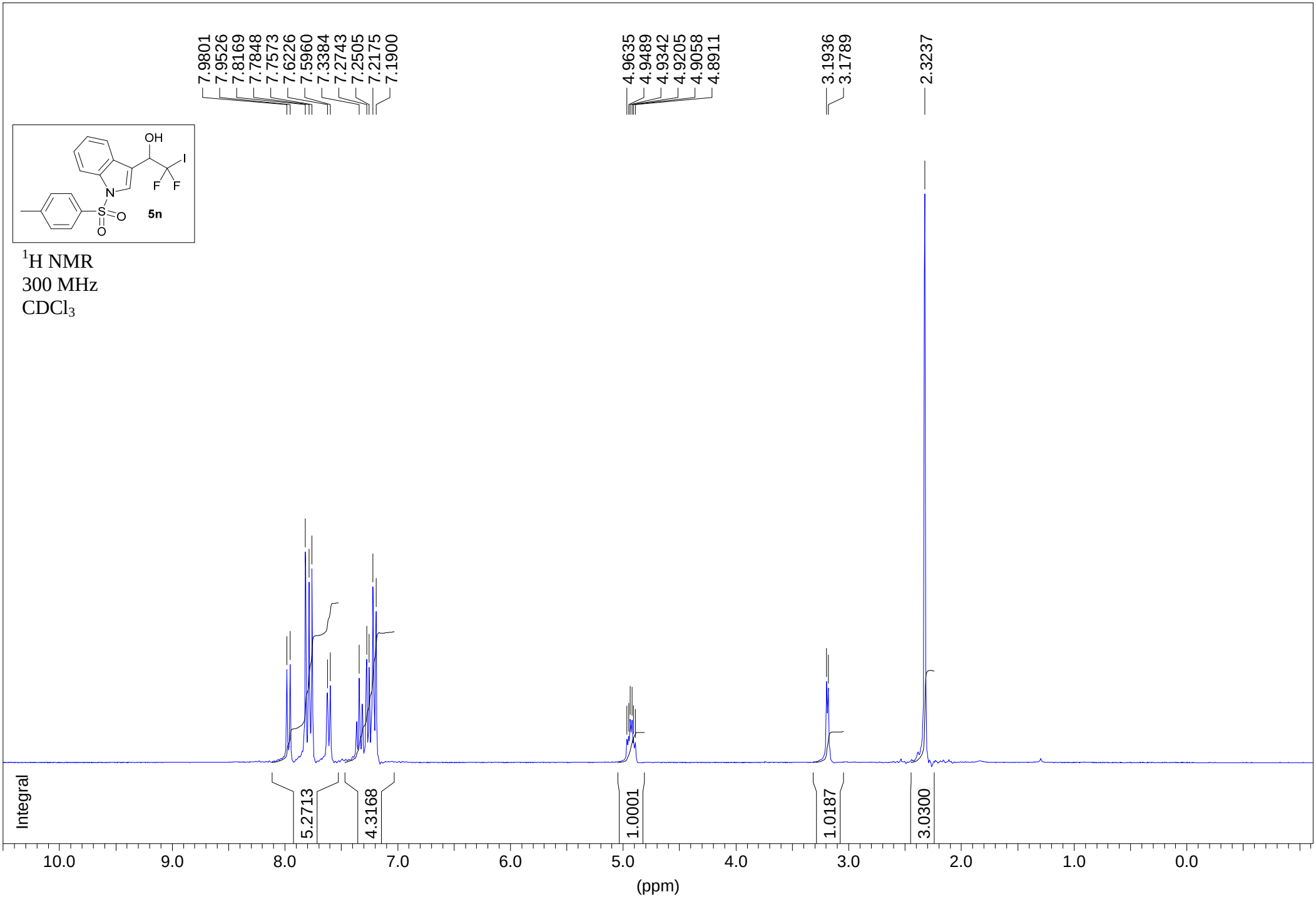

OH
I
F F
O
B
O
5j
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
137.7583
137.7216
134.8060
127.3558
111.9498
107.7155
103.5106
84.2073
80.2954
79.9877
79.6727
77.5849
77.1600
76.7351
24.9717
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

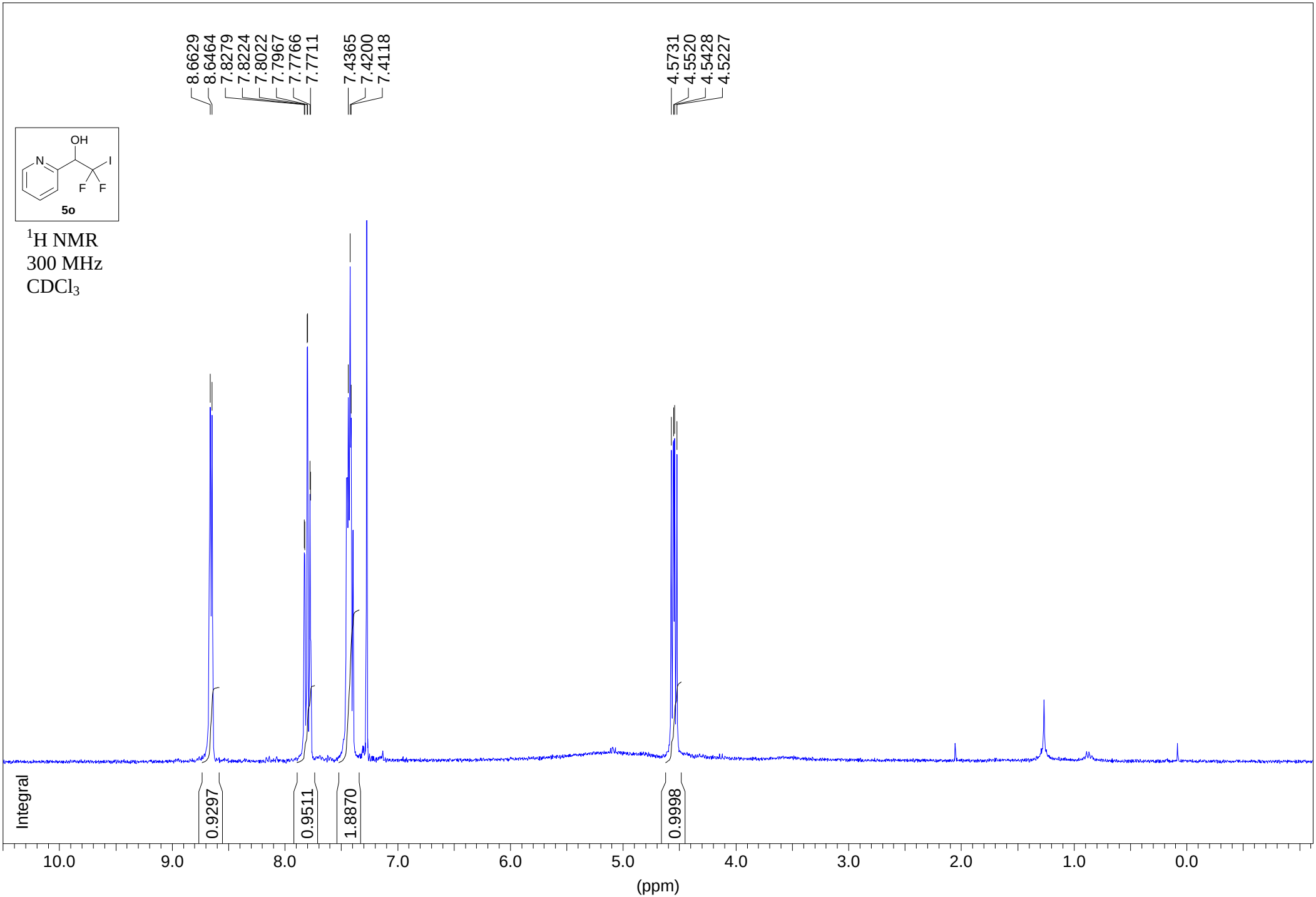

OH
I
F F
O
B
O
5j
^{19}F NMR
282 MHz
$CDCl_3$
-48.1771
-48.2071
-48.8225
-48.8450
-53.1375
-53.1750
-53.7829
-53.8204
-48.0
-49.5
-51.0
-52.5
(ppm)
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100
(ppm)

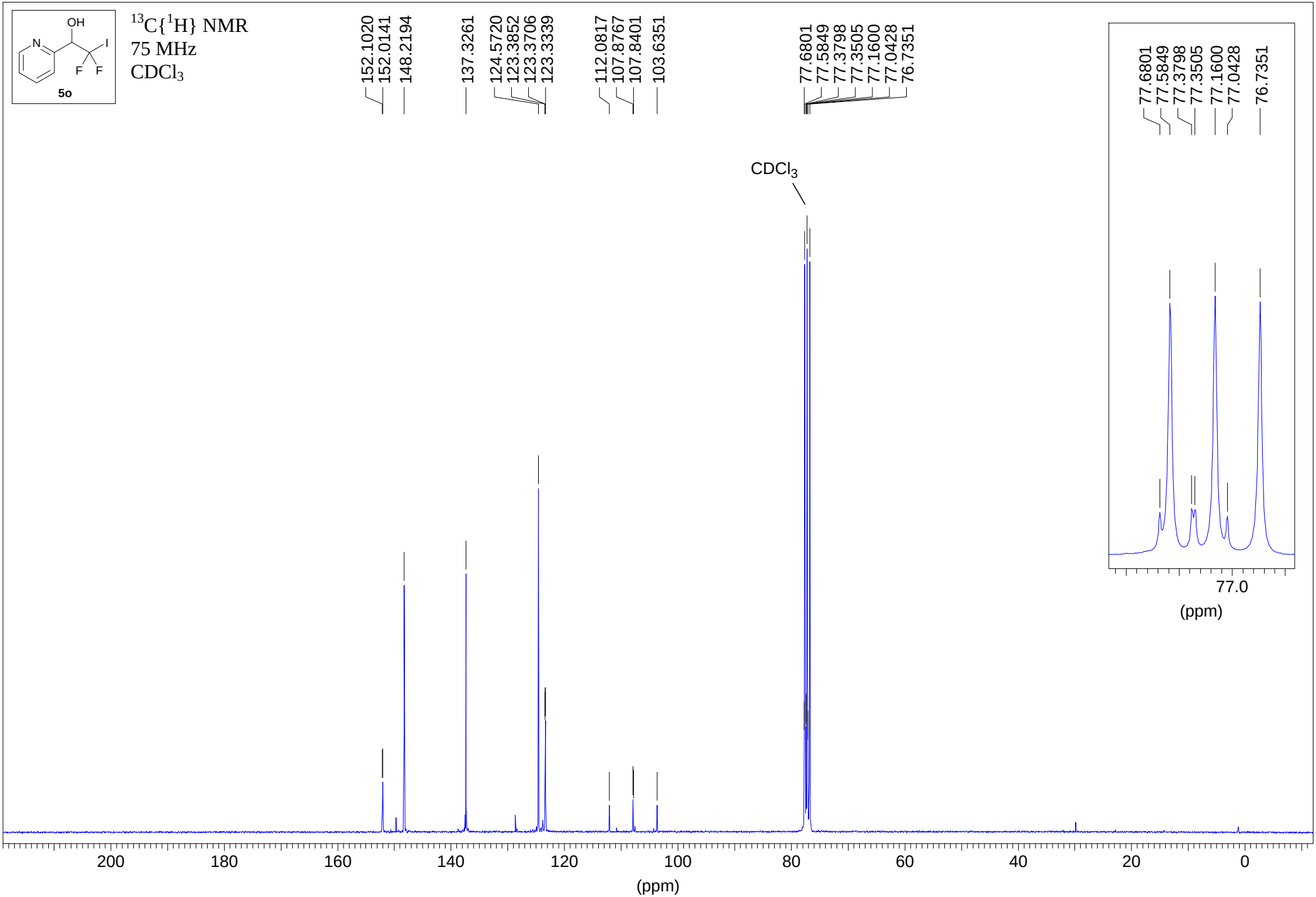

8.0341
8.0085
7.9517
7.9388
7.9260
7.9150
7.9058
7.5905
7.5850
7.5722
7.5667
7.5575
7.5484
7.5209
5.5758
3.3522
3.3375
OH
I
F
F
5k
1H NMR
300 MHz
CDCl3
Integral
4.0598
2.9720
0.9999
0.9705
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

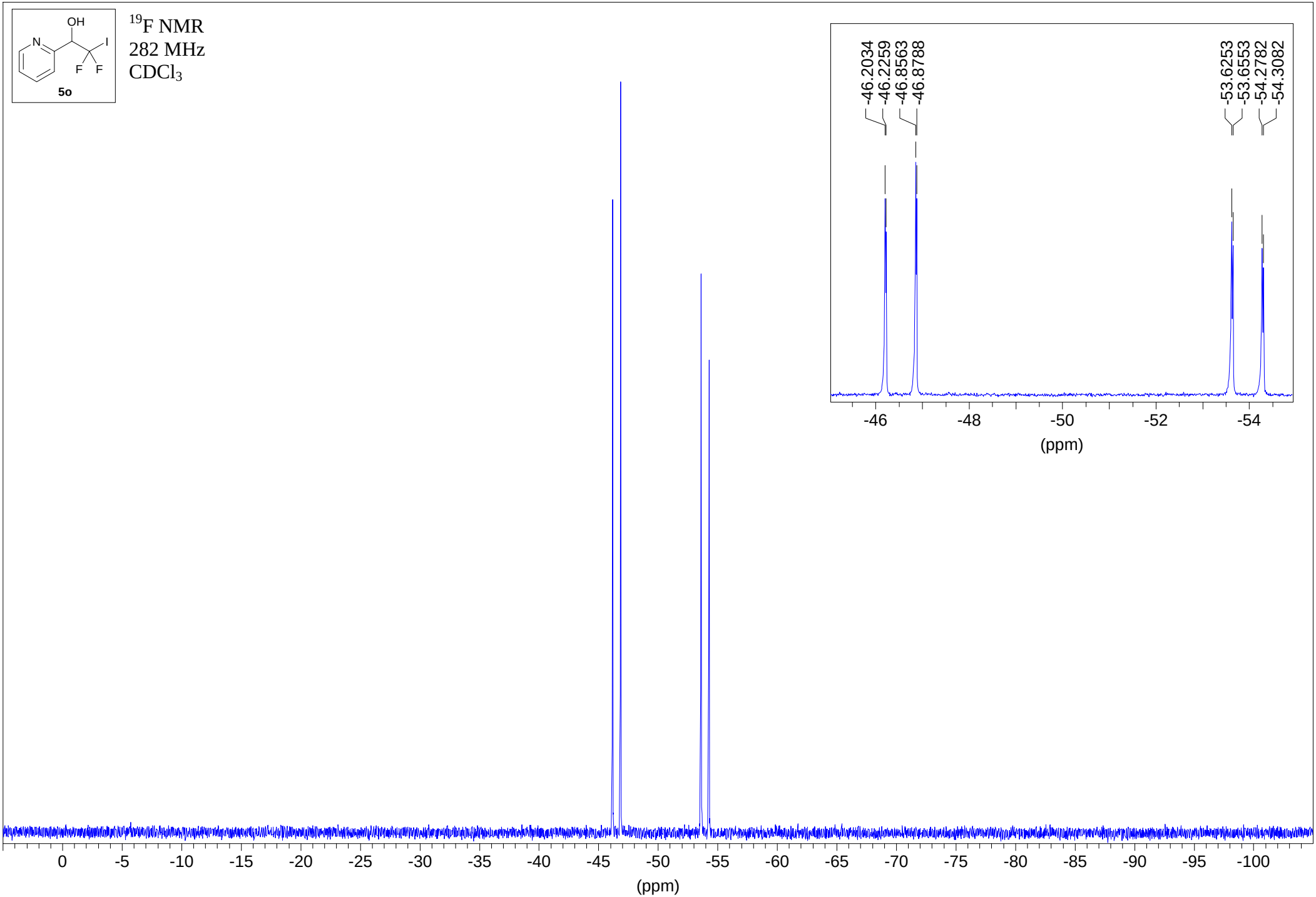

OH
I
O
F
F
5l
^{1}H NMR
300 MHz
$CDCl_3$
7.4796
7.4741
6.5566
6.5456
6.4439
6.4374
6.4329
6.4264
4.8261
4.7958
4.7656
3.3742
Integral
0.9263
1.9030
0.9998
0.9869
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

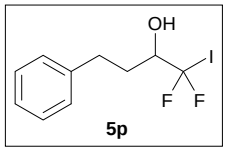

OH
I
S
F
F
5m
7.4246
7.4200
7.4072
7.4035
7.2220
7.2110
7.0836
7.0708
7.0662
7.0543
4.9544
4.9370
4.9250
4.9076
4.8957
4.8783
3.2468
3.2284
1H NMR
300 MHz
CDCl3
Integral
1.0791
1.9460
1.0001
1.0010
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


7.9801
7.9526
7.8169
7.7848
7.7573
7.6226
7.5960
7.3384
7.2743
7.2505
7.2175
7.1900
4.9635
4.9489
4.9342
4.9205
4.9058
4.8911
3.1936
3.1789
2.3237
OH
I
F
F
N
S
O
O
5n
1H NMR
300 MHz
CDCl3
Integral
5.2713
4.3168
1.0001
1.0187
3.0300
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


8.6629
8.6464
7.8279
7.8224
7.8022
7.7967
7.7766
7.7711
7.4365
7.4200
7.4118
4.5731
4.5520
4.5428
4.5227
OH
N
I
F
F
5o
1H NMR
300 MHz
CDCl3
Integral
0.9297
0.9511
1.8870
0.9998
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OH
N
I
F
F
5o
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
152.1020
152.0141
148.2194
137.3261
124.5720
123.3852
123.3706
123.3339
112.0817
107.8767
107.8401
103.6351
77.6801
77.5849
77.3798
77.3505
77.1600
77.0428
76.7351
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)
77.0
(ppm)


OH
N
I
F
F
5o
19F NMR
282 MHz
CDCl3
-46.2034
-46.2259
-46.8563
-46.8788
-53.6253
-53.6553
-54.2782
-54.3082
-46
-48
-50
-52
-54
(ppm)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)



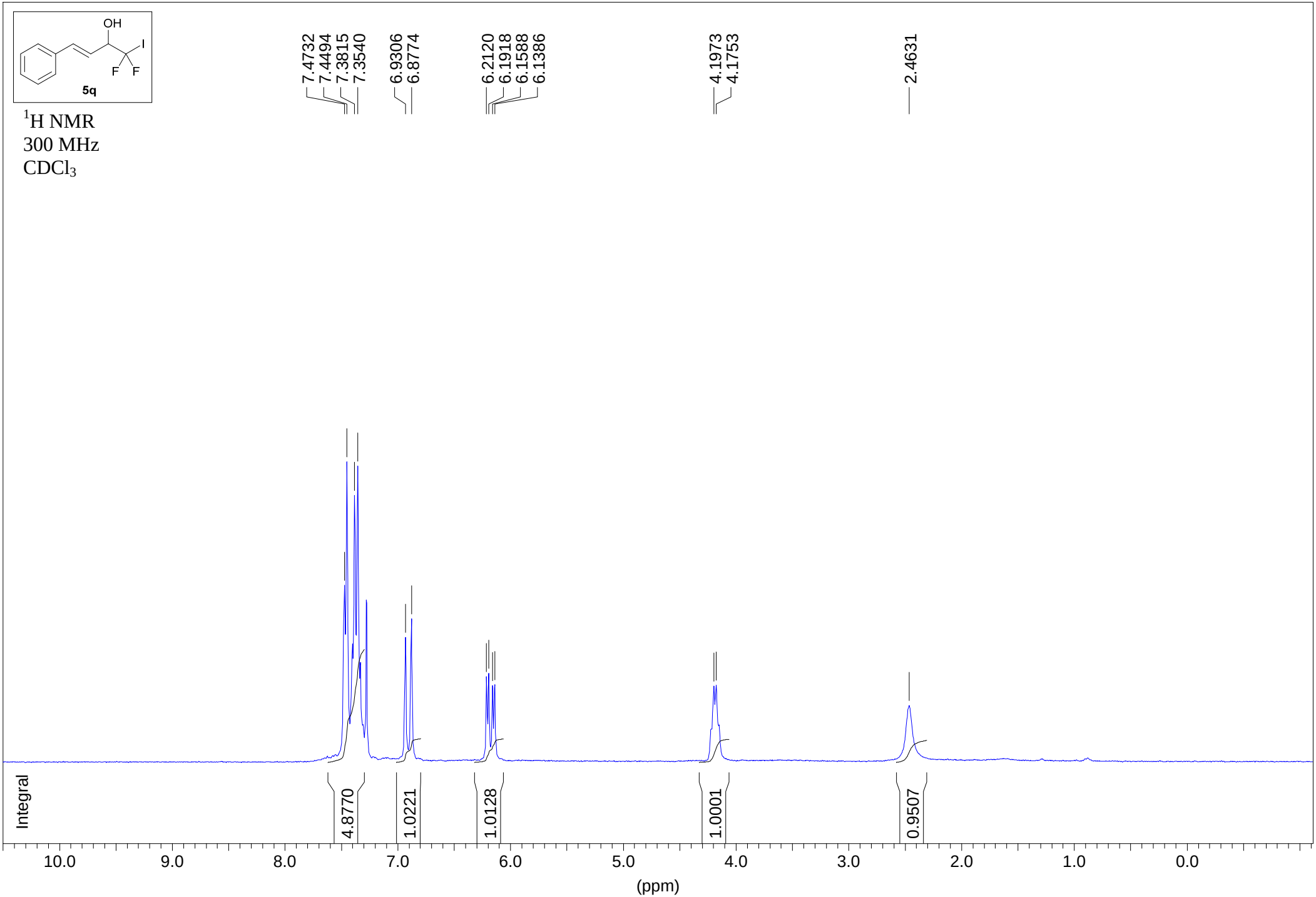
^{1}H NMR
300 MHz
$CDCl_3$

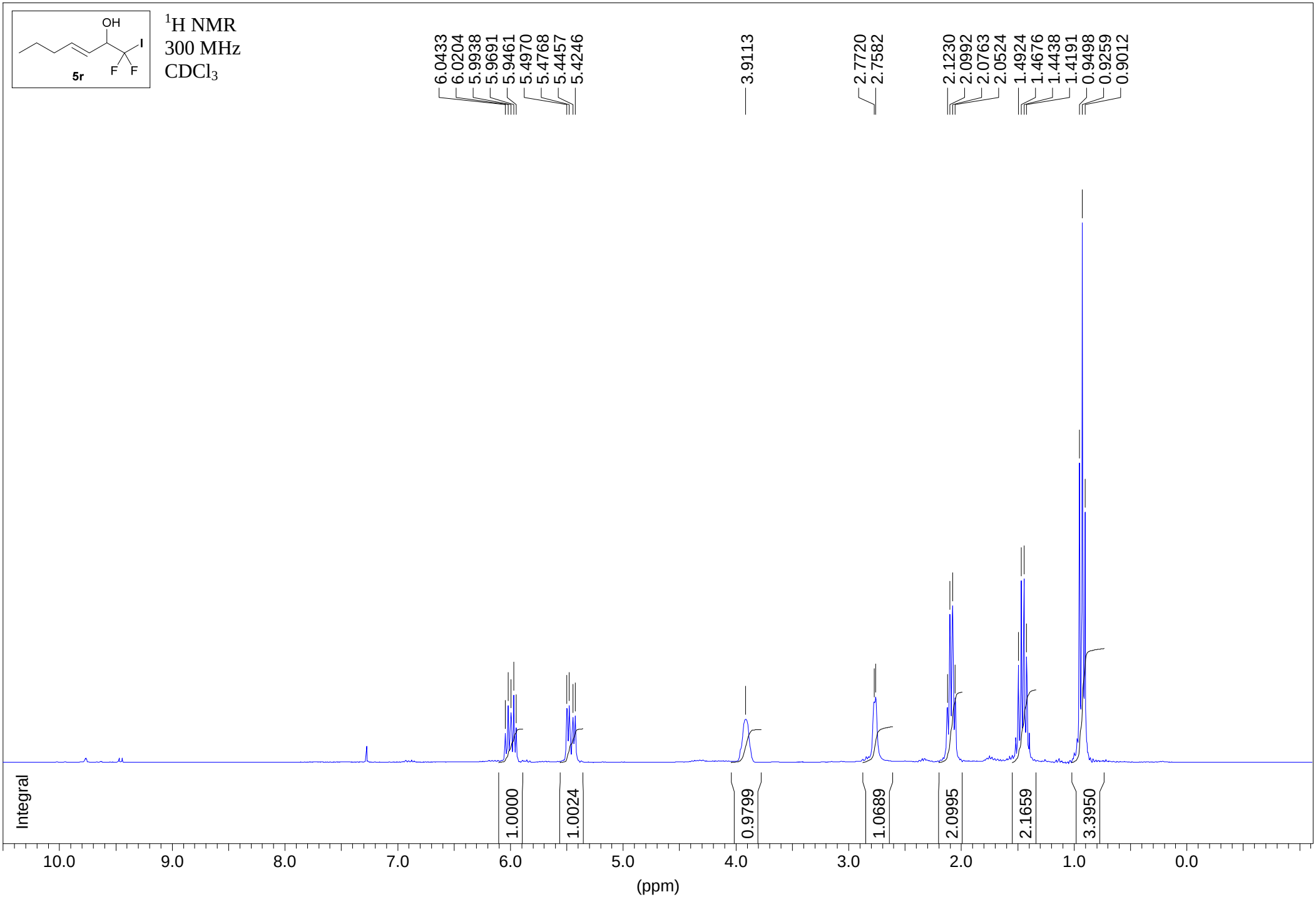
7.3375
7.3146
7.2725
7.2670
7.2541
7.2450
7.2294

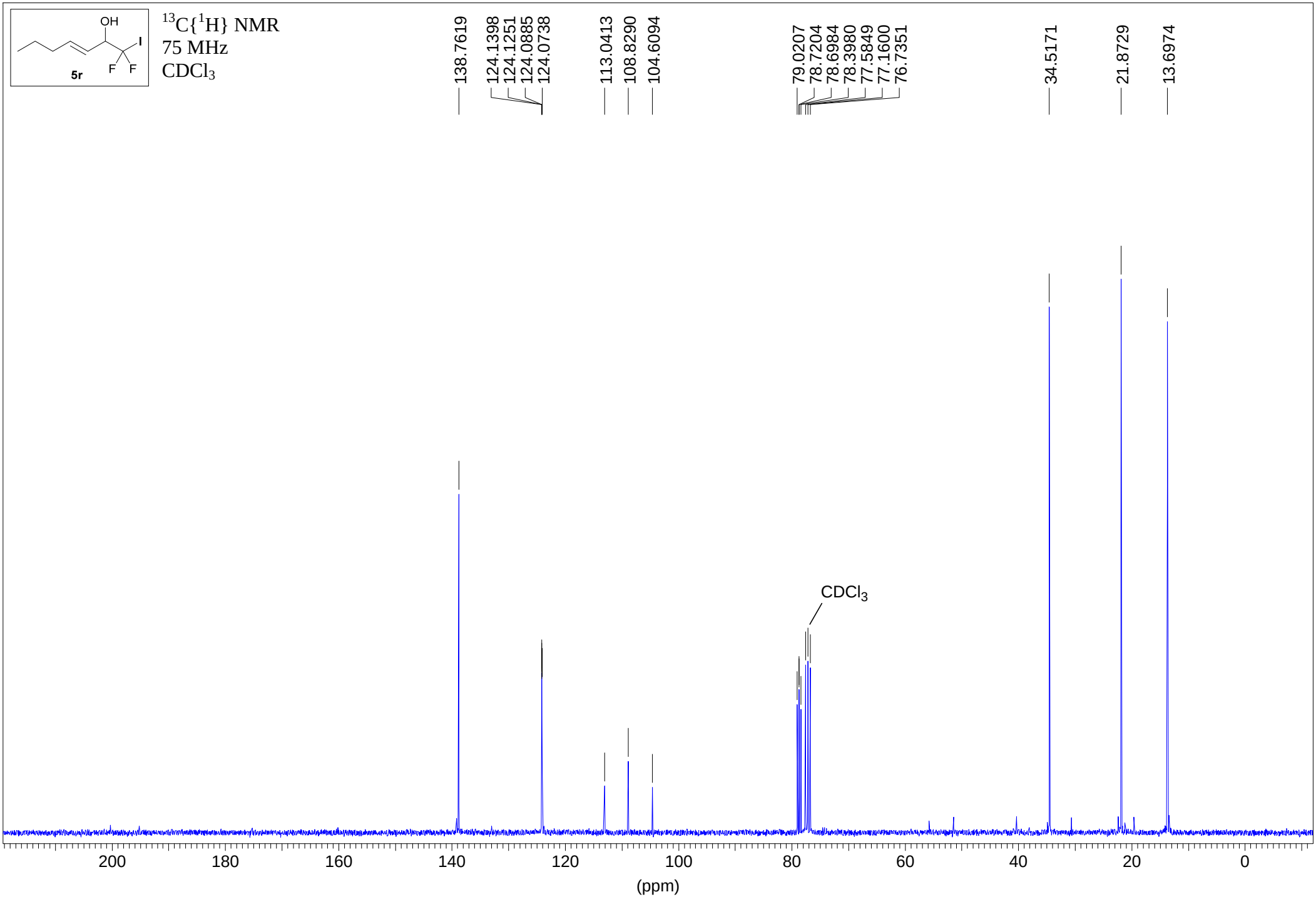
3.3934
3.3842
3.3732
3.3641
3.3604
3.3513
3.3403
3.3320
2.9672
2.9507
2.9369
2.9205
2.8334
2.8059
2.7775
2.7591
2.3824
2.3622
2.0717
2.0680
2.0643
1.9149
1.8975
1.8819
1.8654

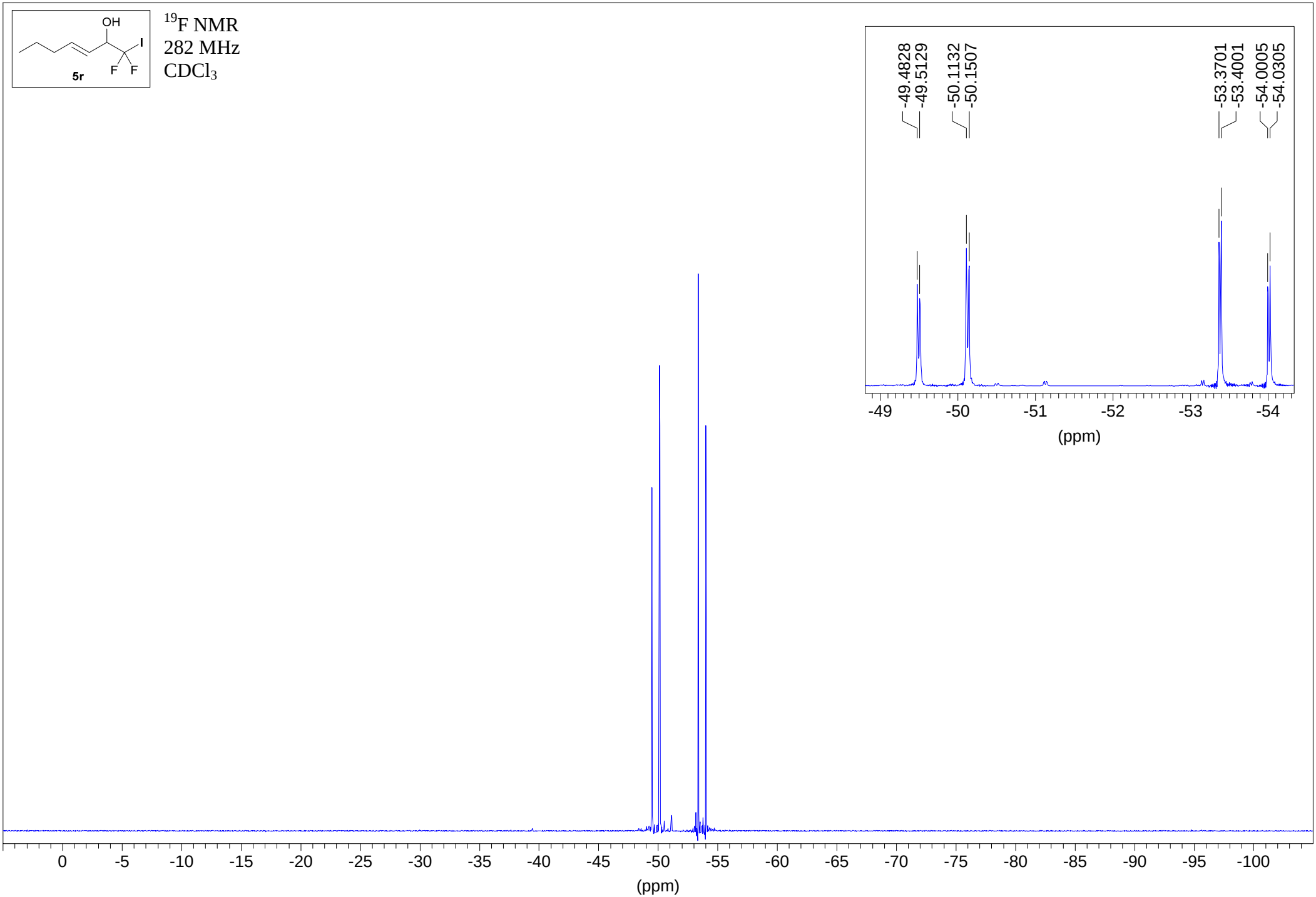
Integral
5.0430
1.0001
2.0855
0.9699
2.0336

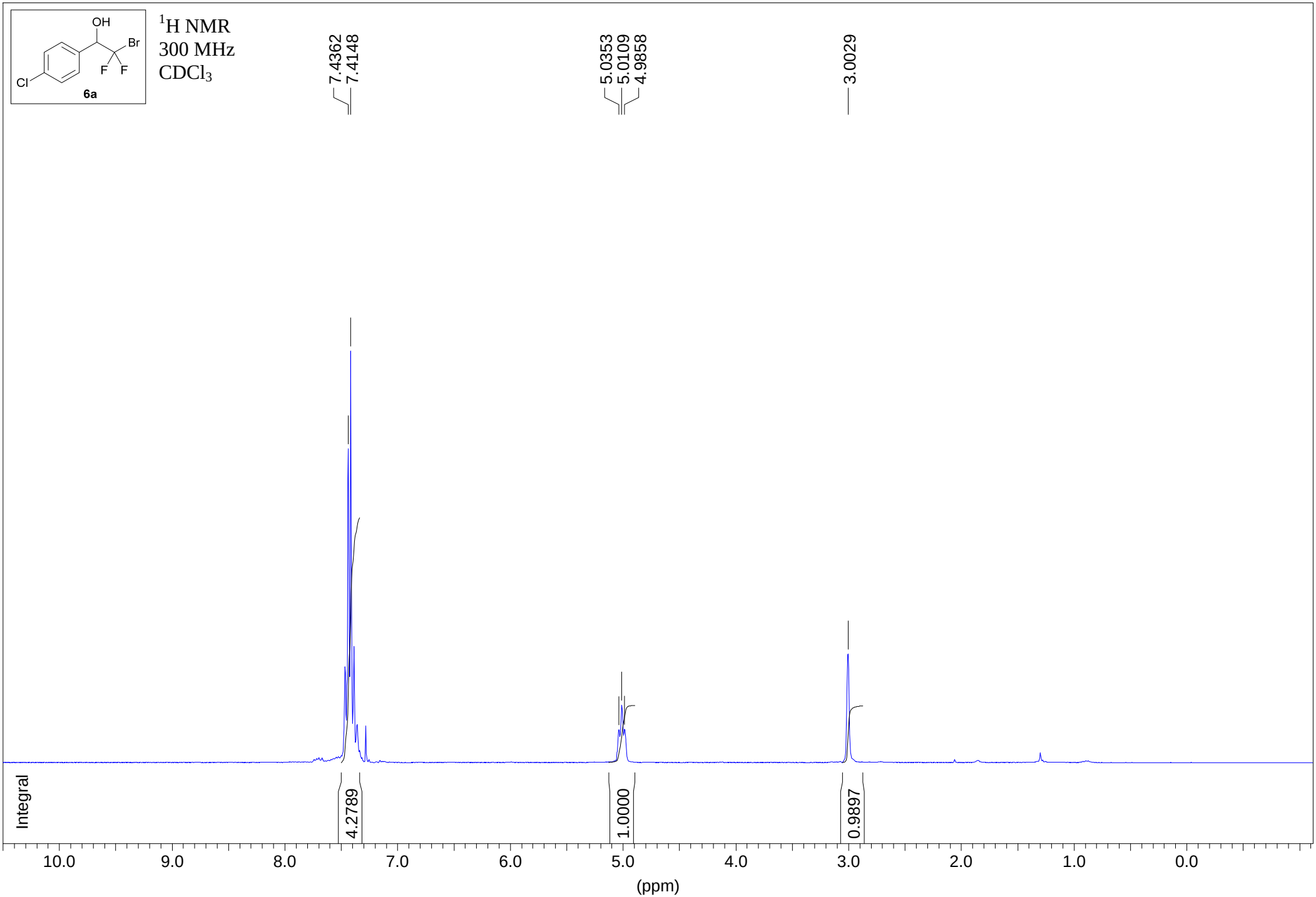
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
(ppm)

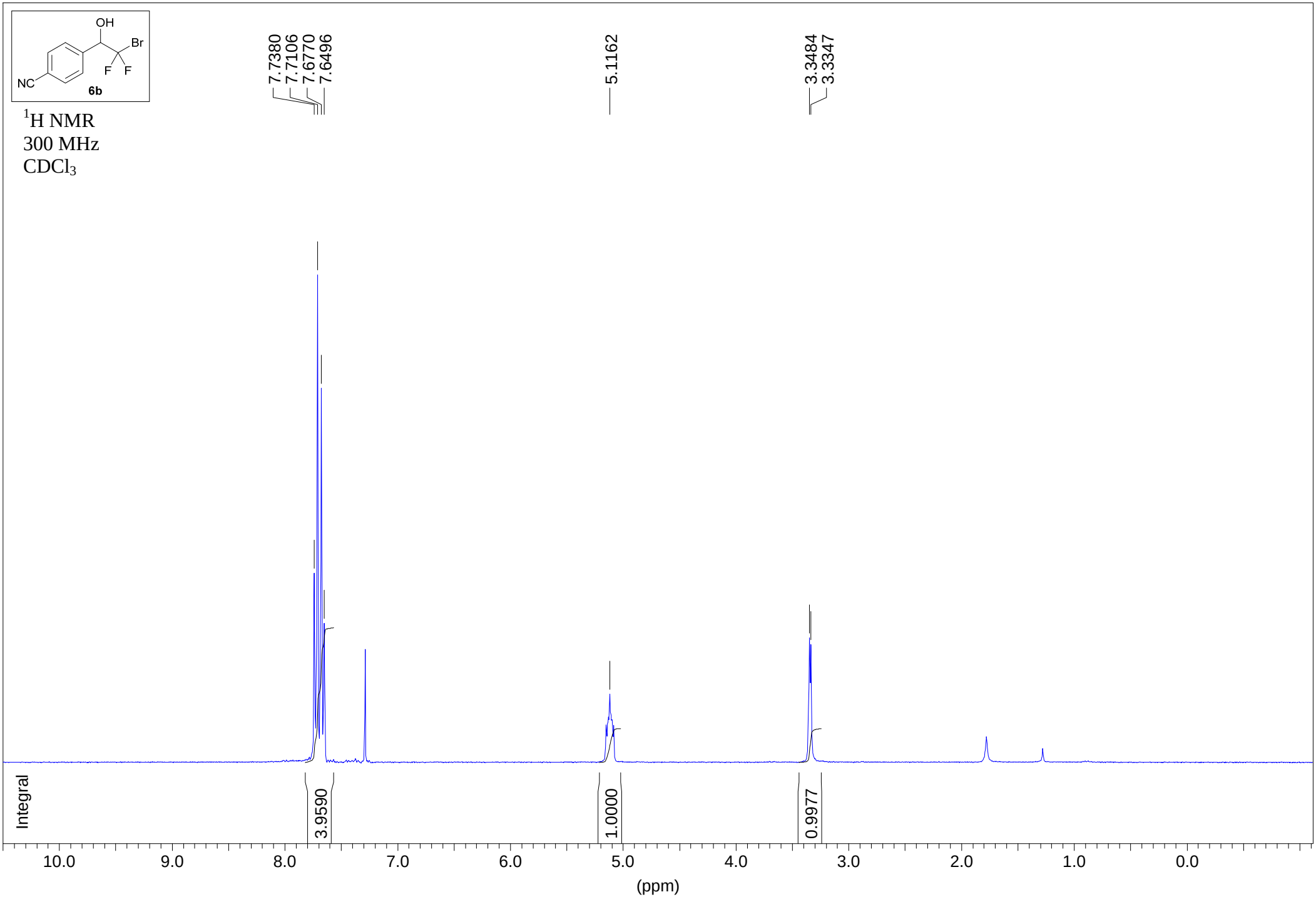

OH
I
F F
5q
7.4732
7.4494
7.3815
7.3540
6.9306
6.8774
6.2120
6.1918
6.1588
6.1386
4.1973
4.1753
2.4631
1H NMR
300 MHz
CDCl3
Integral
4.8770
1.0221
1.0128
1.0001
0.9507
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

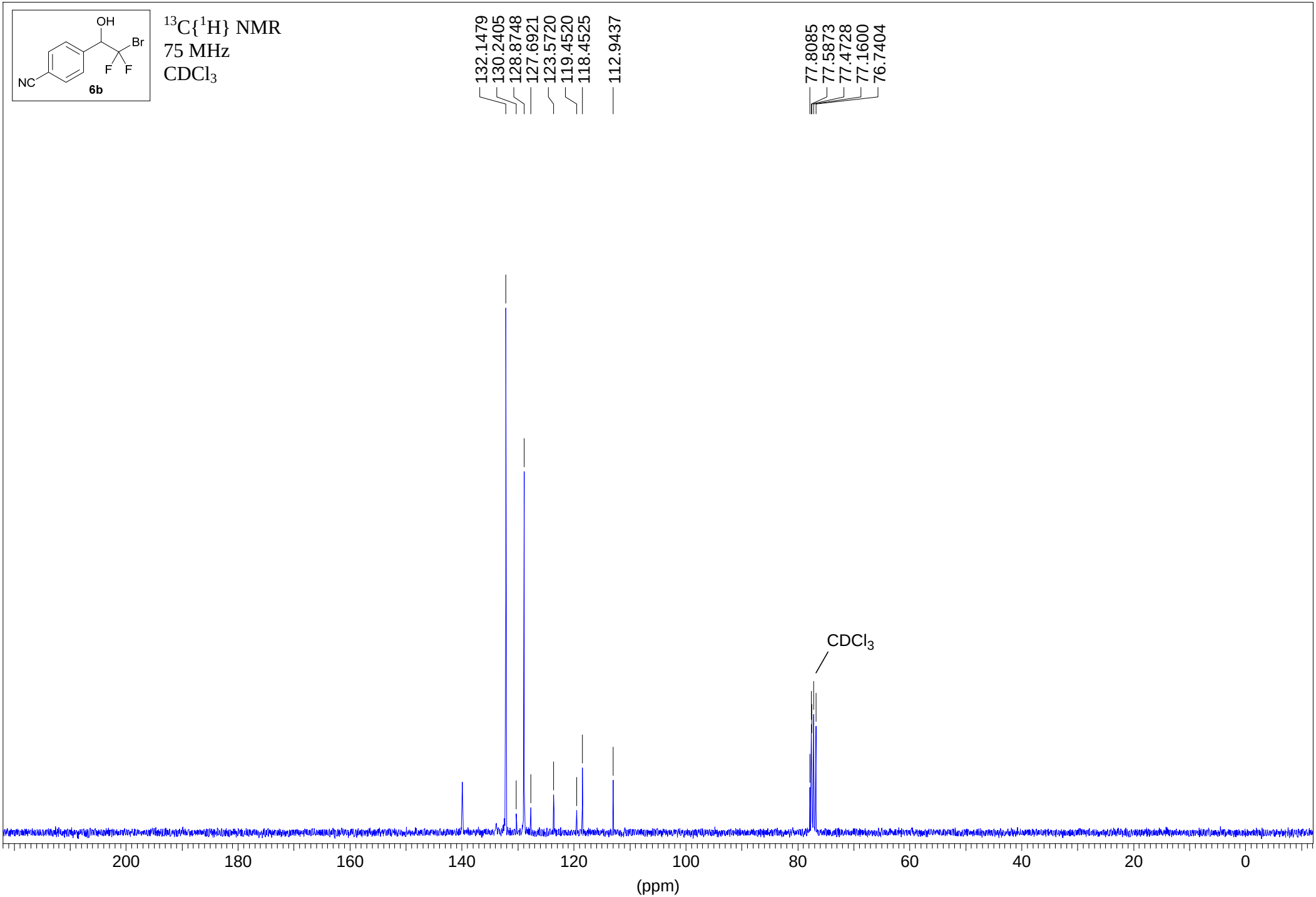

OH
I
F F
5r
^{1}H NMR
300 MHz
$CDCl_3$
6.0433
6.0204
5.9938
5.9691
5.9461
5.4970
5.4768
5.4457
5.4246
3.9113
2.7720
2.7582
2.1230
2.0992
2.0763
2.0524
1.4924
1.4676
1.4438
1.4191
0.9498
0.9259
0.9012
Integral
1.0000
1.0024
0.9799
1.0689
2.0995
2.1659
3.3950
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

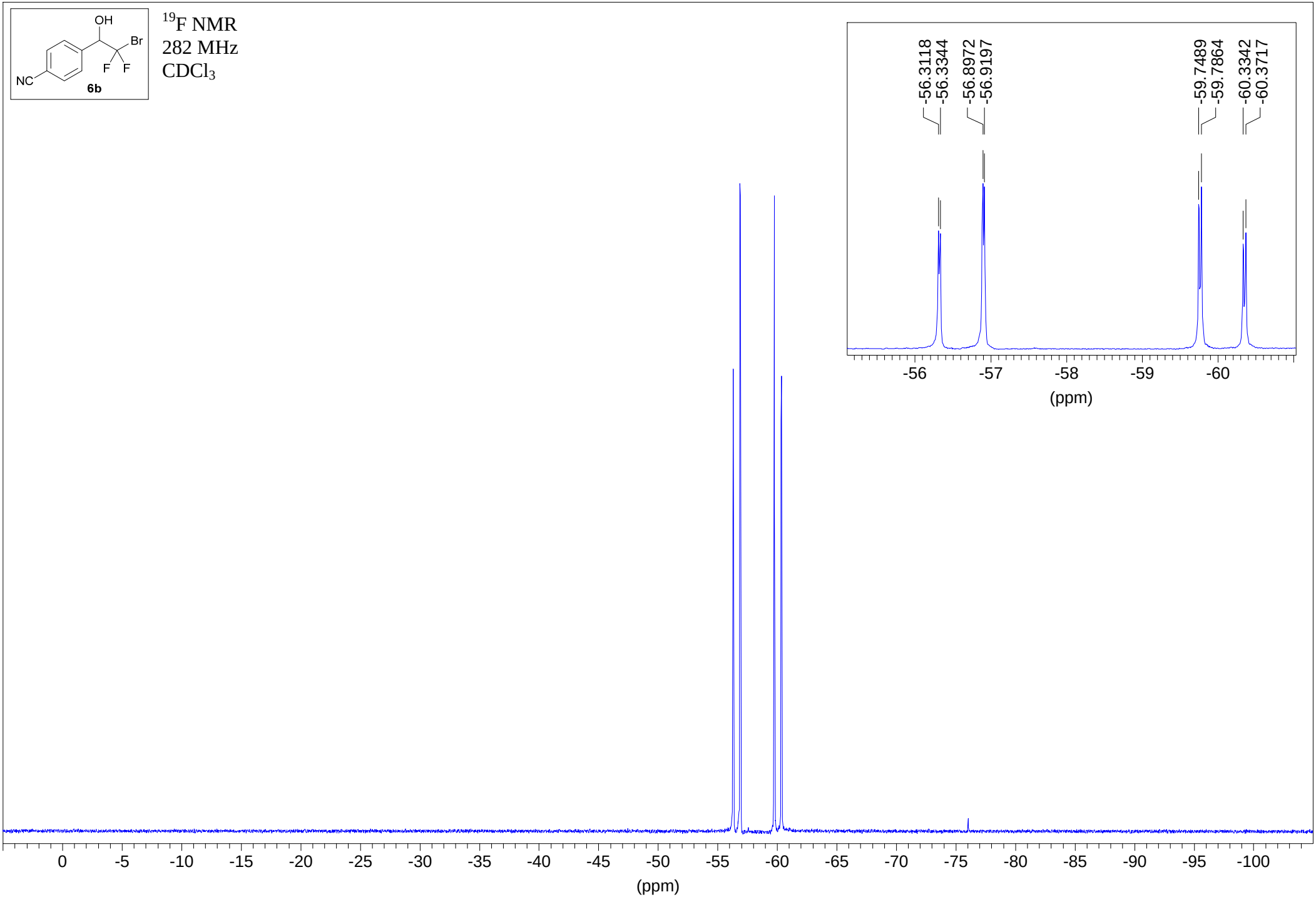

OH
I
F
F
5r
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
138.7619
124.1398
124.1251
124.0885
124.0738
113.0413
108.8290
104.6094
79.0207
78.7204
78.6984
78.3980
77.5849
77.1600
76.7351
34.5171
21.8729
13.6974
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

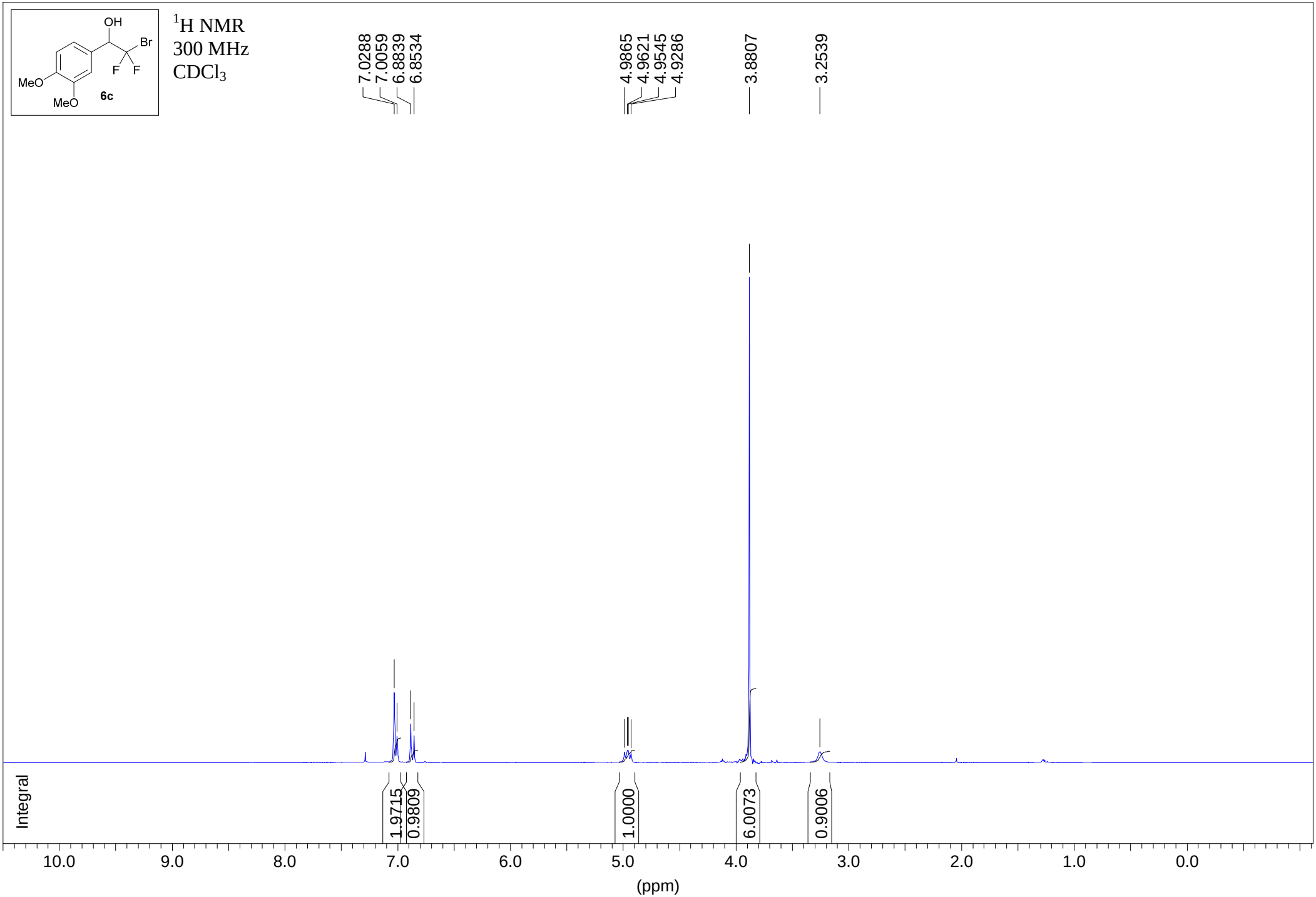

OH
I
F F
5r
19F NMR
282 MHz
CDCl3
-49.4828
-49.5129
-50.1132
-50.1507
-53.3701
-53.4001
-54.0005
-54.0305
-49
-50
-51
-52
-53
-54
(ppm)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)

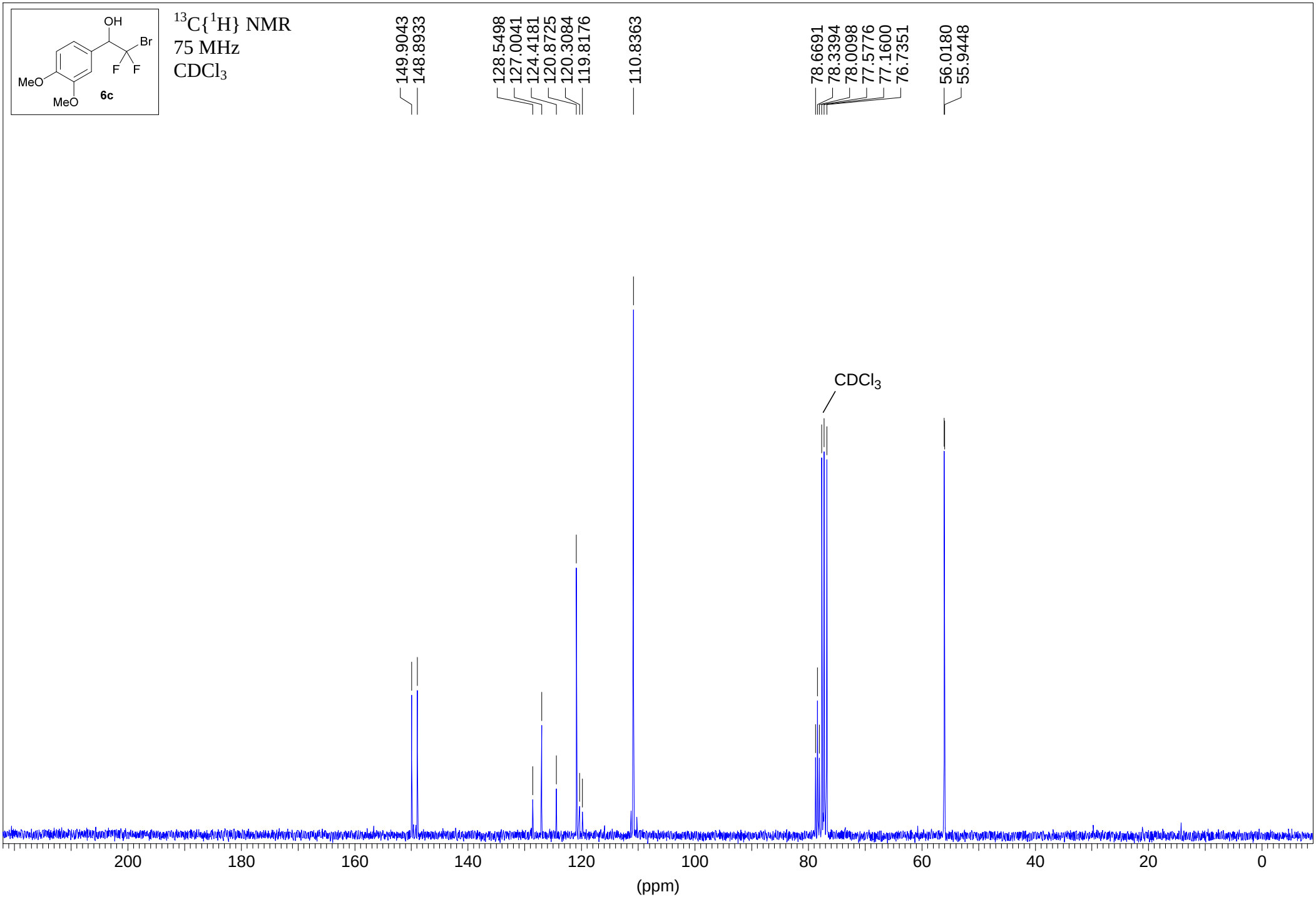

OH
Br
F
F
Cl
6a
^{1}H NMR
300 MHz
$CDCl_3$
7.4362
7.4148
5.0353
5.0109
4.9858
3.0029
Integral
4.2789
1.0000
0.9897
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

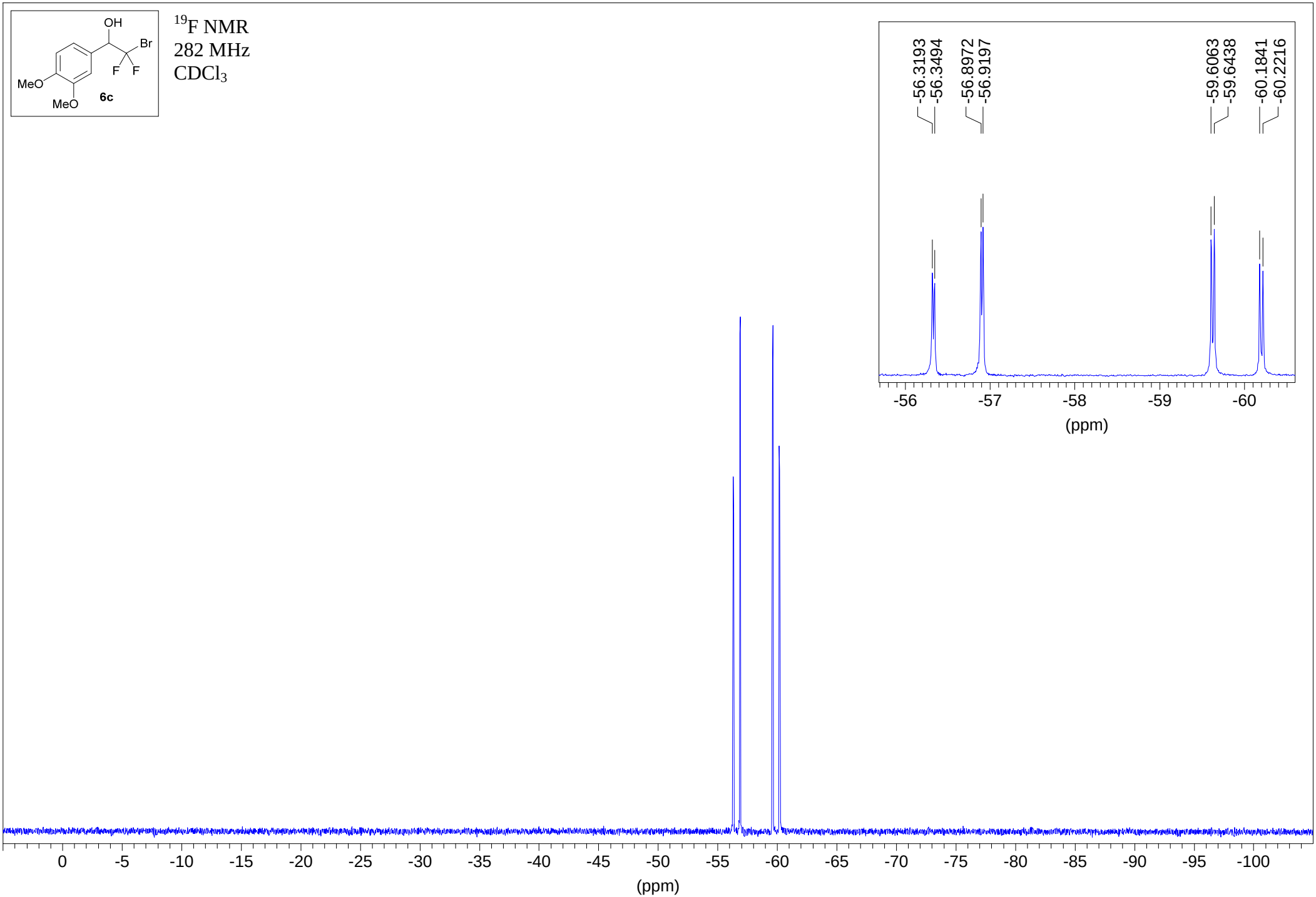

OH
Br
F
F
NC
6b
7.7380
7.7106
7.6770
7.6496
5.1162
3.3484
3.3347
^{1}H NMR
300 MHz
$CDCl_3$
Integral
3.9590
1.0000
0.9977
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

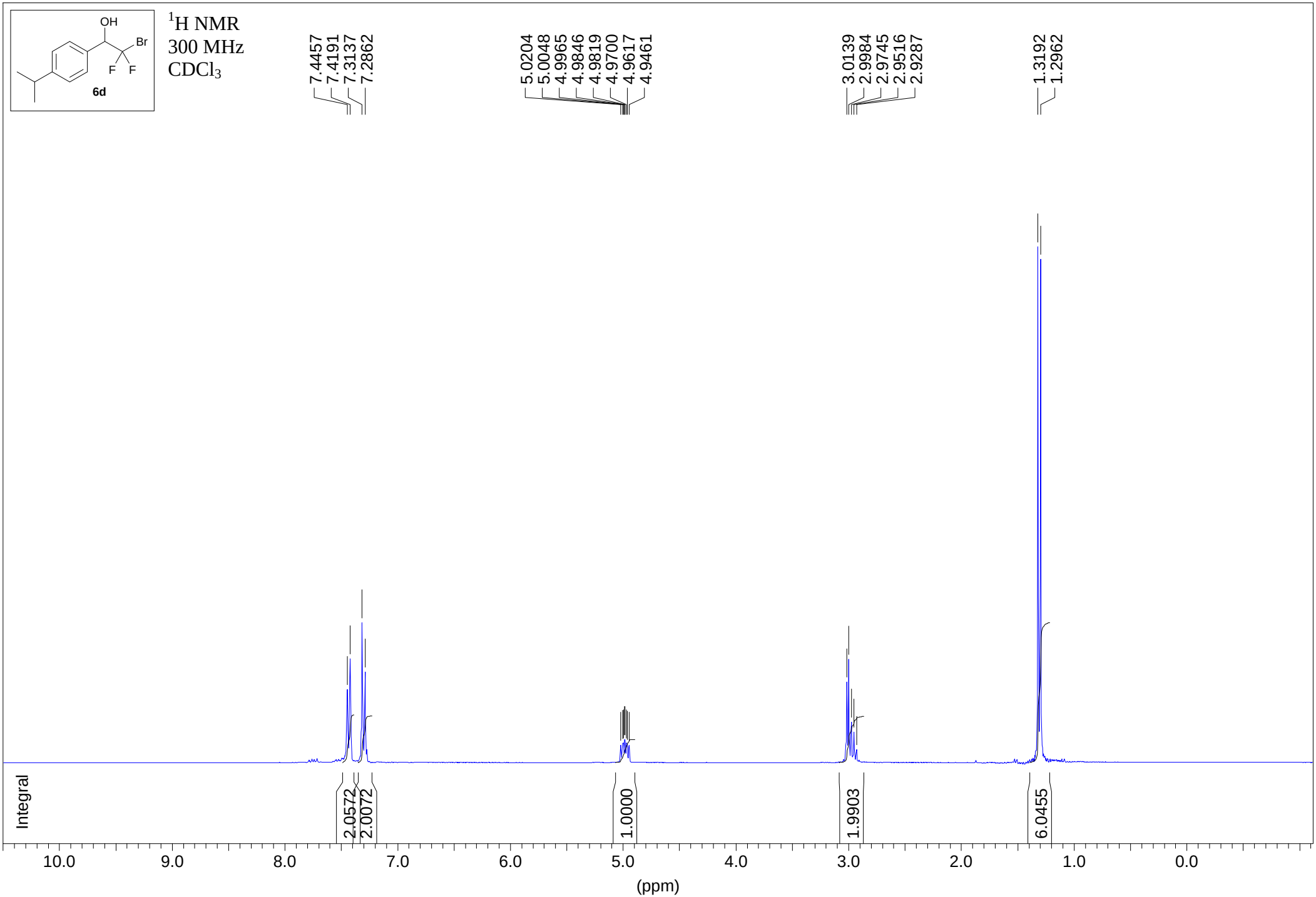

OH
Br
F
F
NC
6b
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
132.1479
130.2405
128.8748
127.6921
123.5720
119.4520
118.4525
112.9437
77.8085
77.5873
77.4728
77.1600
76.7404
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

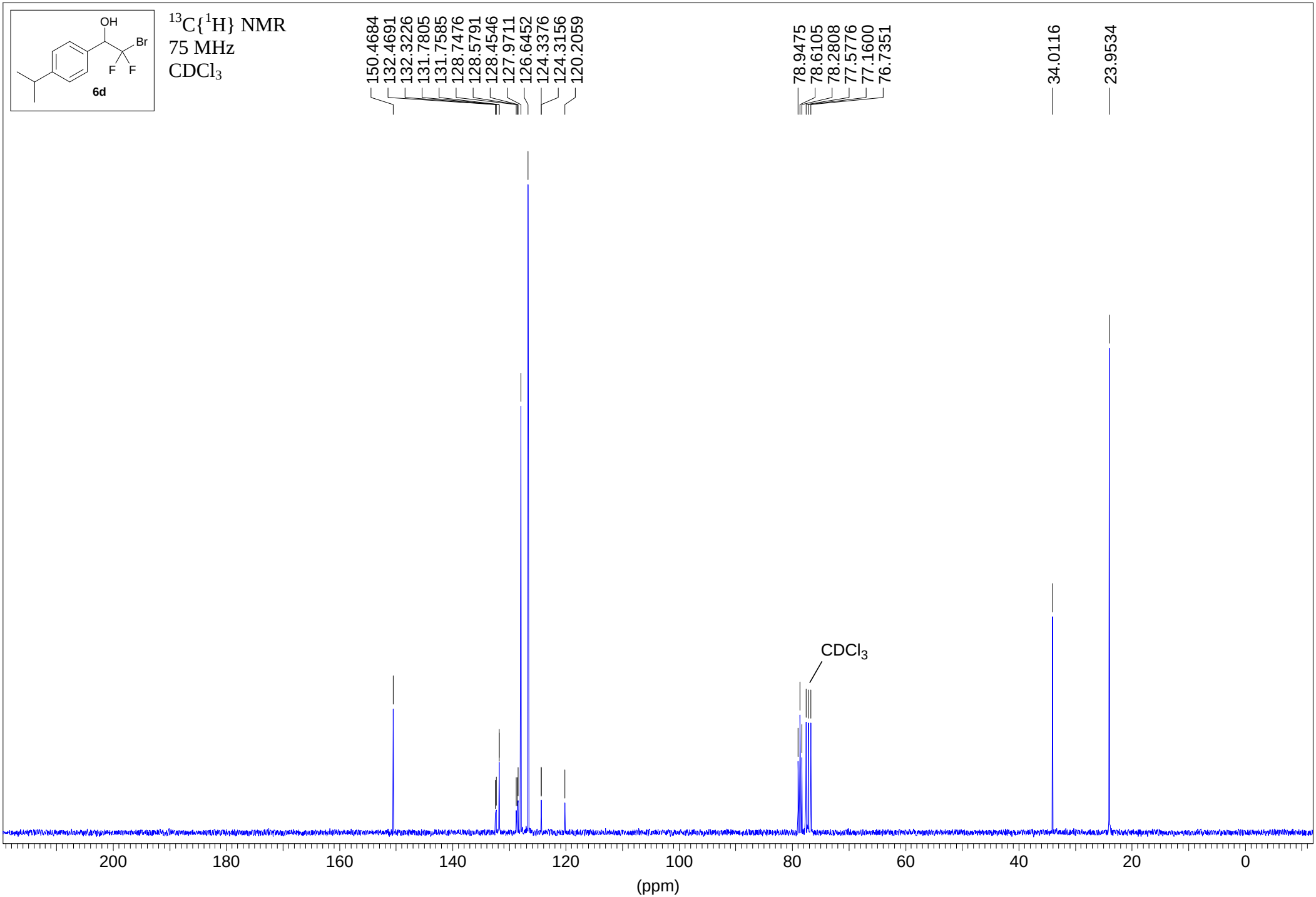

OH
Br
F
F
NC
6b
19F NMR
282 MHz
CDCl3
-56.3118
-56.3344
-56.8972
-56.9197
-59.7489
-59.7864
-60.3342
-60.3717
-56
-57
-58
-59
-60
(ppm)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)

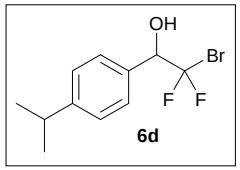

OH
Br
F
F
MeO
MeO
6c
^{1}H NMR
300 MHz
$CDCl_3$
7.0288
7.0059
6.8839
6.8534
4.9865
4.9621
4.9545
4.9286
3.8807
3.2539
Integral
1.9715
0.9809
1.0000
6.0073
0.9006
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OH
Br
F
F
MeO
MeO
6c
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
149.9043
148.8933
128.5498
127.0041
124.4181
120.8725
120.3084
119.8176
110.8363
78.6691
78.3394
78.0098
77.5776
77.1600
76.7351
56.0180
55.9448
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

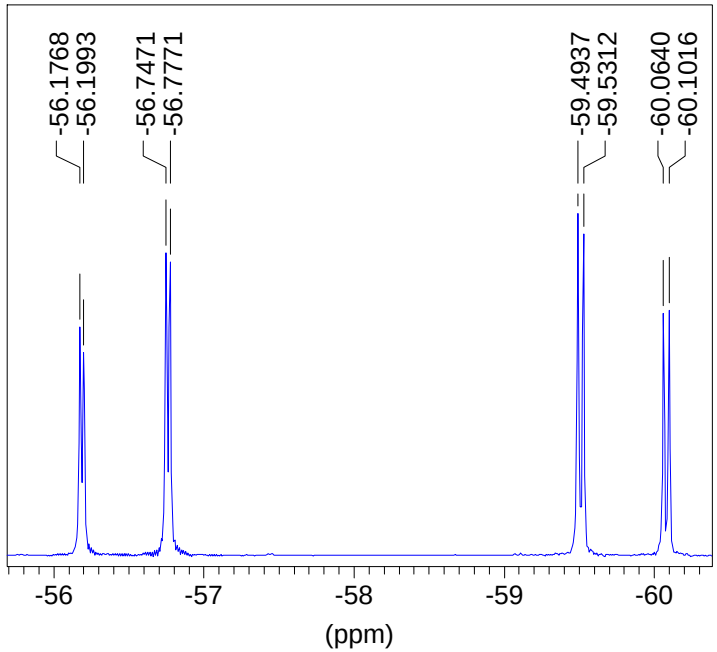

OH
Br
F F
MeO
MeO
6c
19F NMR
282 MHz
CDCl3
-56.3193
-56.3494
-56.8972
-56.9197
-59.6063
-59.6438
-60.1841
-60.2216
-56
-57
-58
-59
-60
(ppm)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)

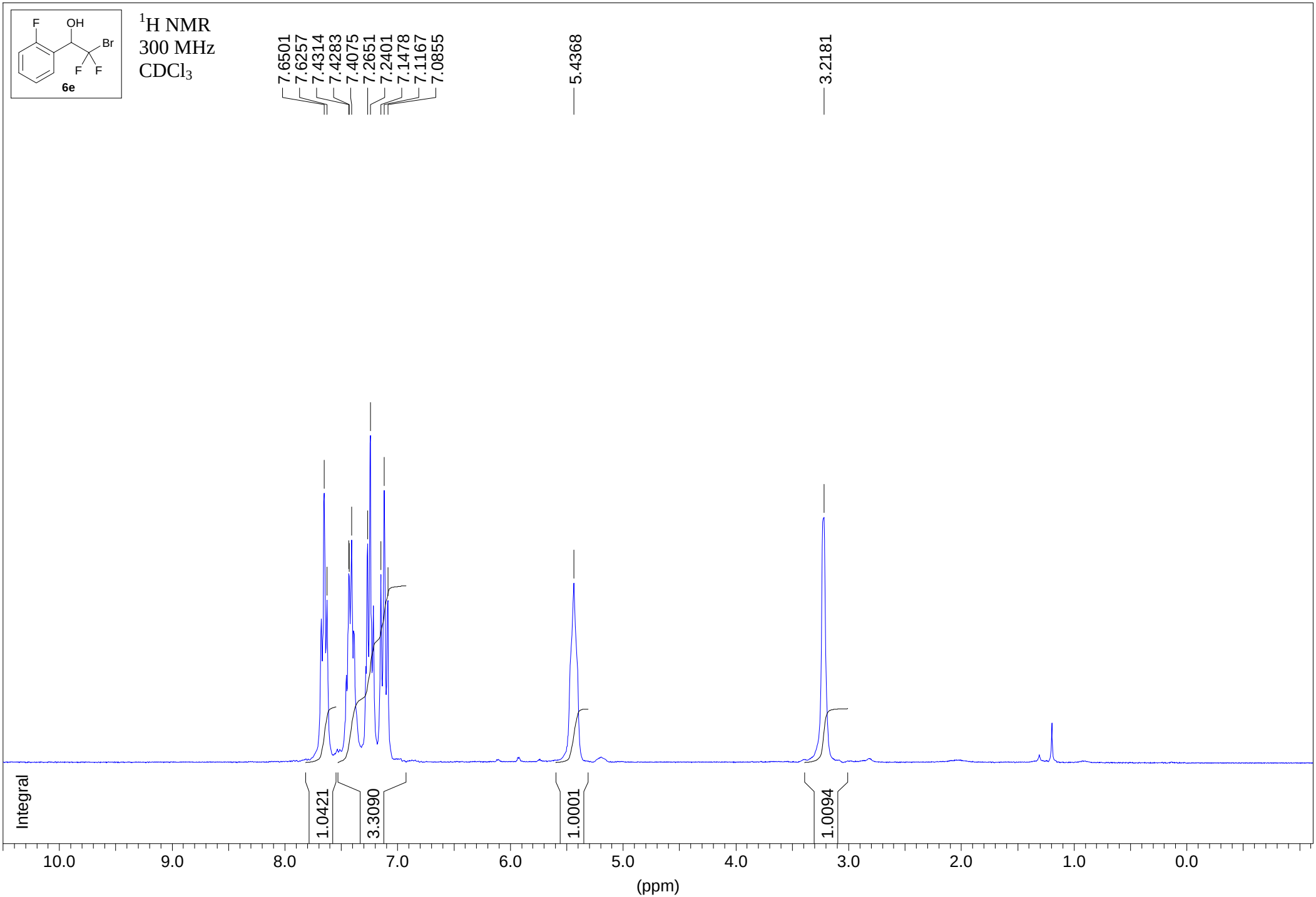

OH
Br
F F
6d
^{1}H NMR
300 MHz
$CDCl_3$
7.4457
7.4191
7.3137
7.2862
5.0204
5.0048
4.9965
4.9846
4.9819
4.9700
4.9617
4.9461
3.0139
2.9984
2.9745
2.9516
2.9287
1.3192
1.2962
Integral
2.0572
2.0072
1.0000
1.9903
6.0455
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

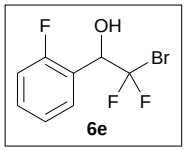

OH
Br
F
F
6d
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
150.4684
132.4691
132.3226
131.7805
131.7585
128.7476
128.5791
128.4546
127.9711
126.6452
124.3376
124.3156
120.2059
78.9475
78.6105
78.2808
77.5776
77.1600
76.7351
34.0116
23.9534
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



^{19}F NMR
282 MHz
$CDCl_3$

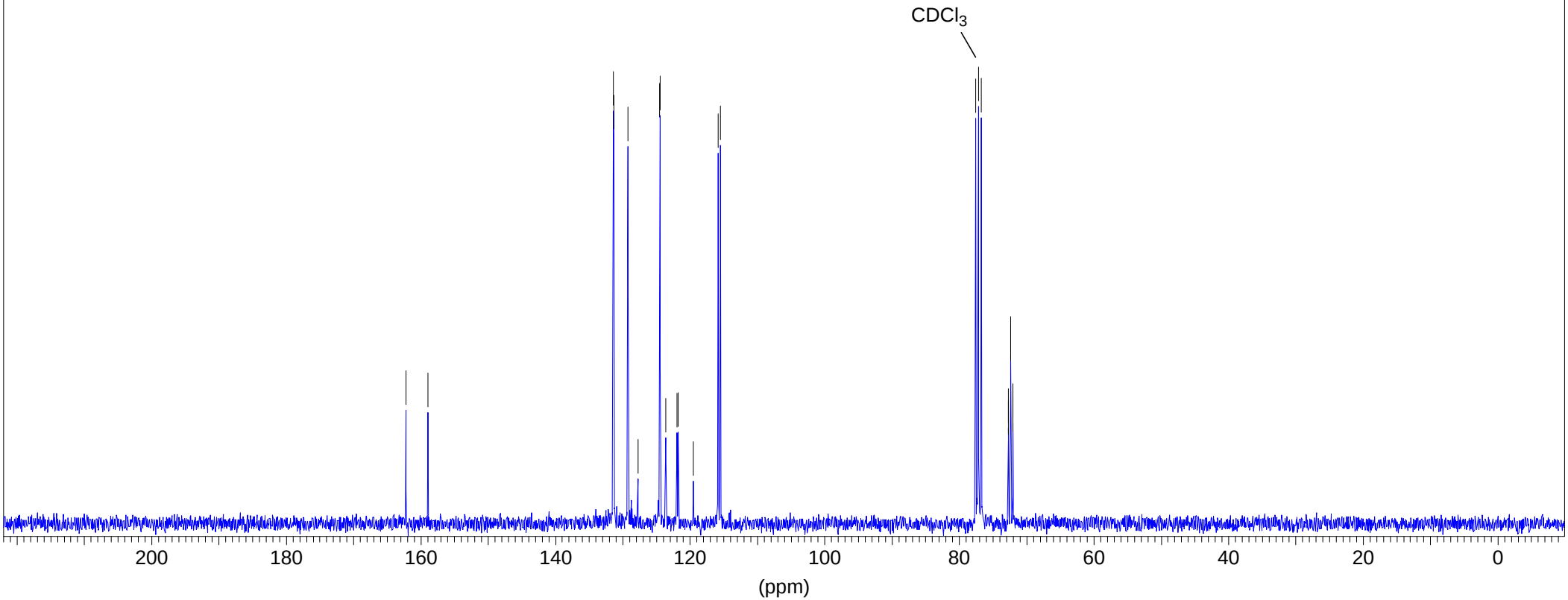


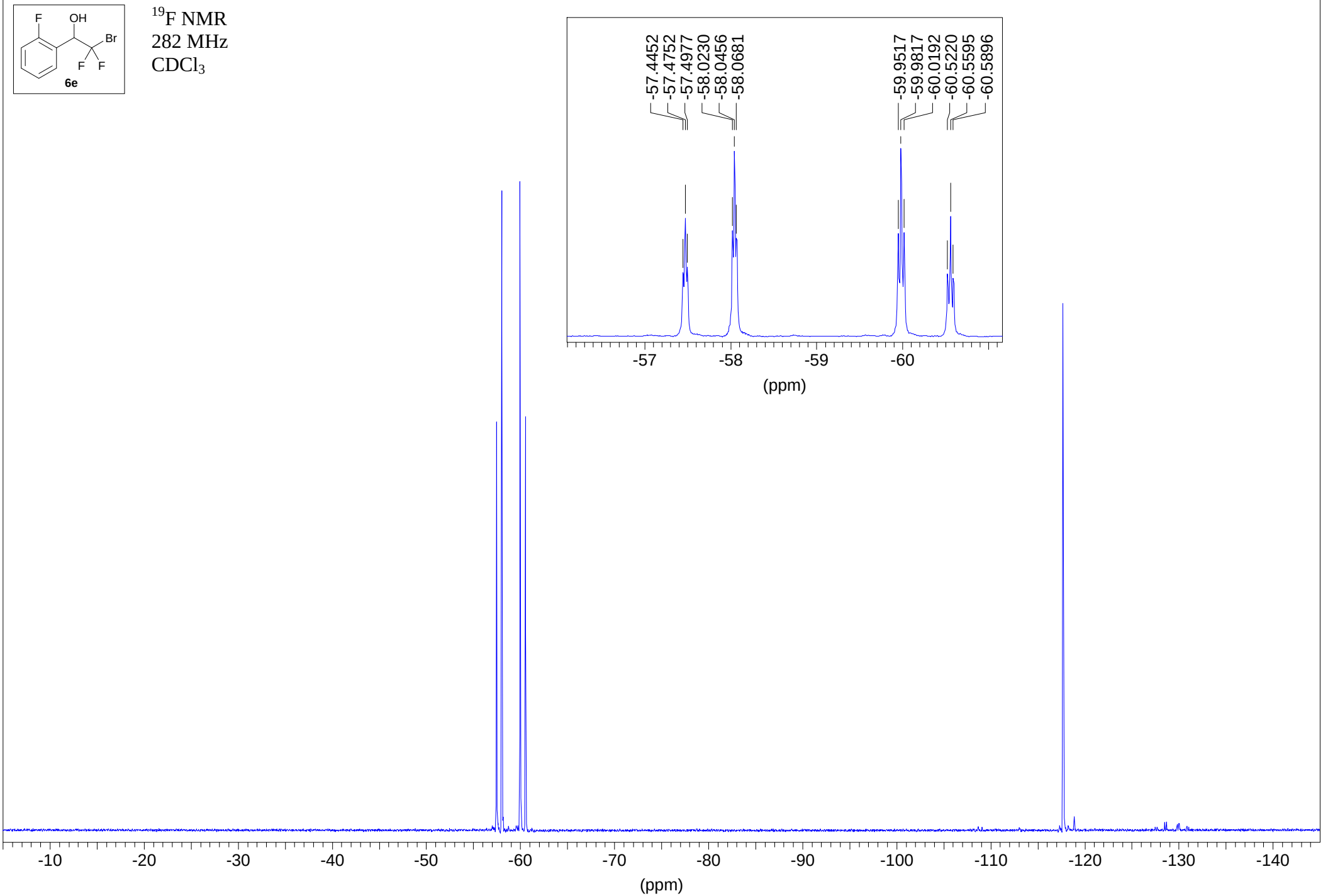

F
OH
Br
F
F
6e
^{1}H NMR
300 MHz
$CDCl_3$
7.6501
7.6257
7.4314
7.4283
7.4075
7.2651
7.2401
7.1478
7.1167
7.0855
5.4368
3.2181
Integral
1.0421
3.3090
1.0001
1.0094
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

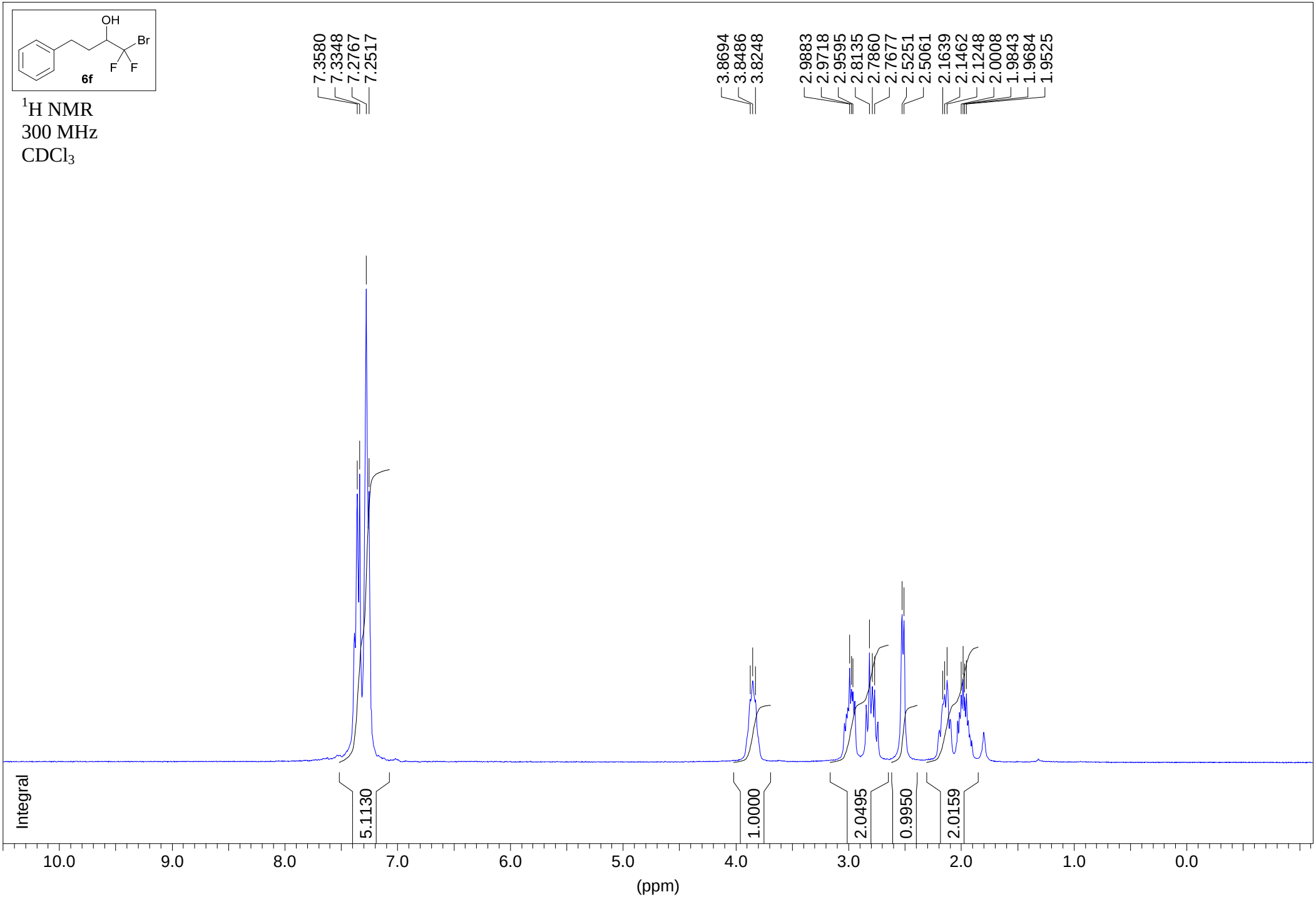


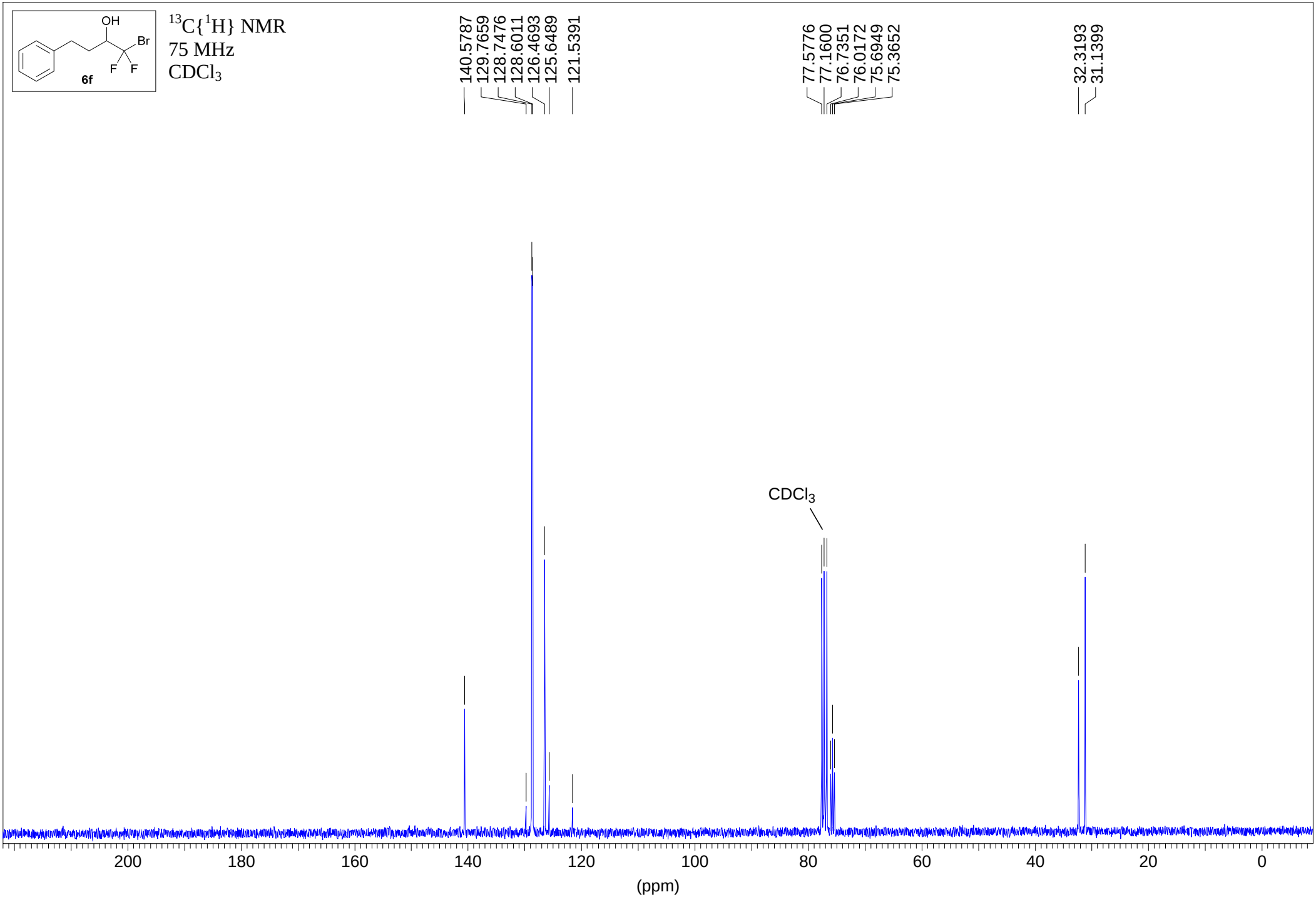
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

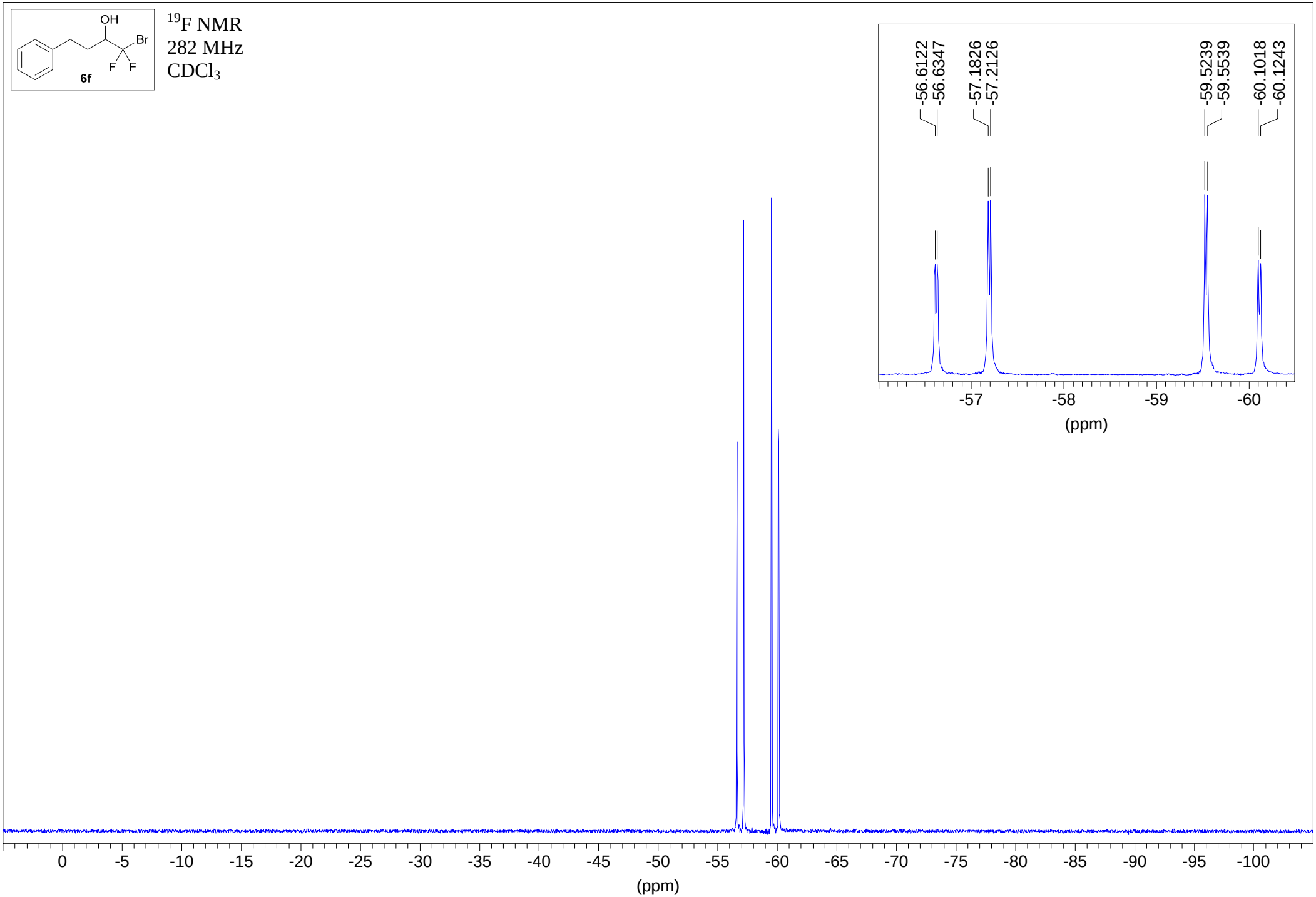
162.2188
158.9222
131.3996
131.2823
129.1945
127.7294
124.5134
124.4694
123.6196
121.9128
121.7443
119.4806
115.7738
115.4881
77.5849
77.1600
76.7351
72.7280
72.6840
72.3763
72.3324
72.0320
71.9881

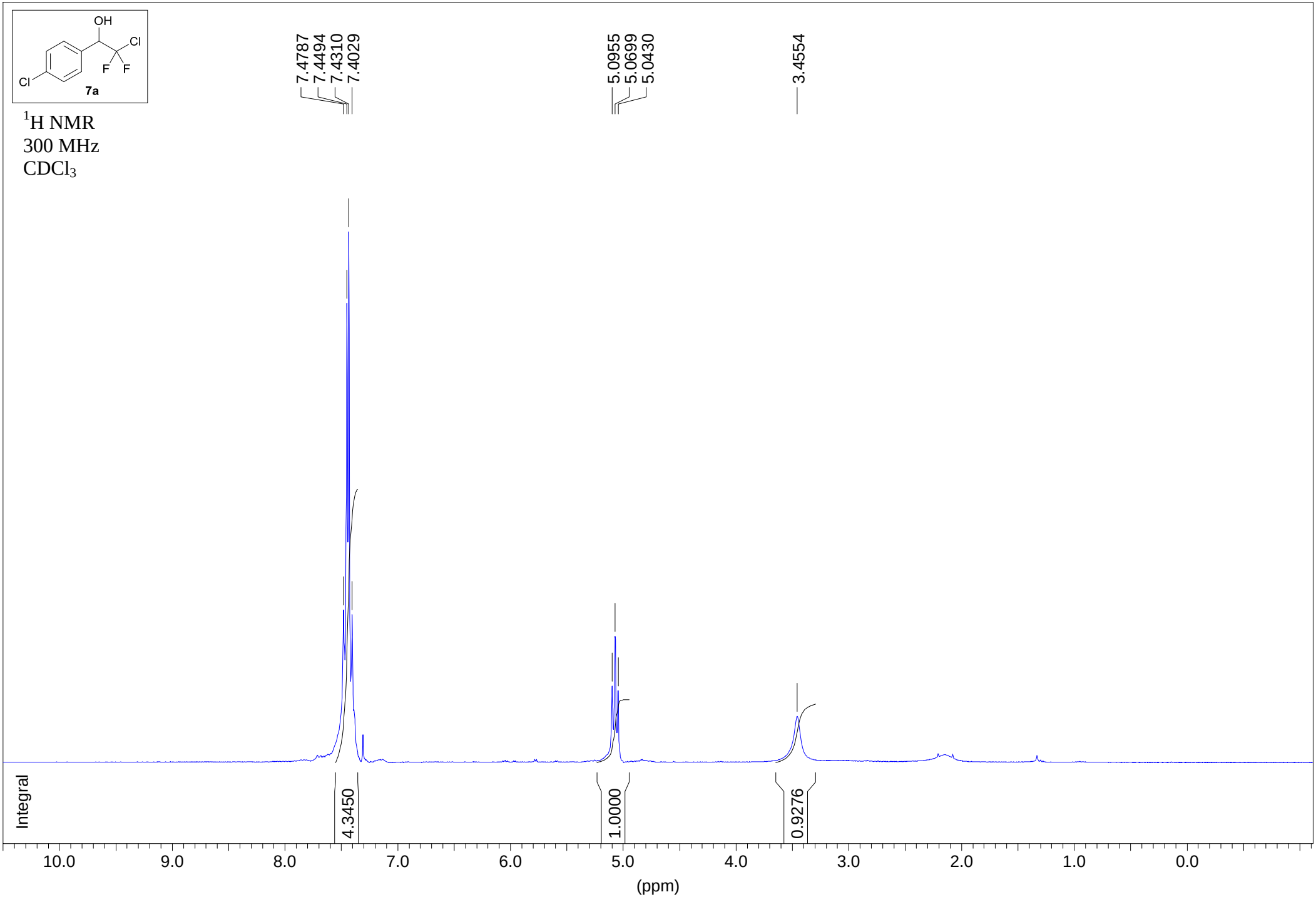


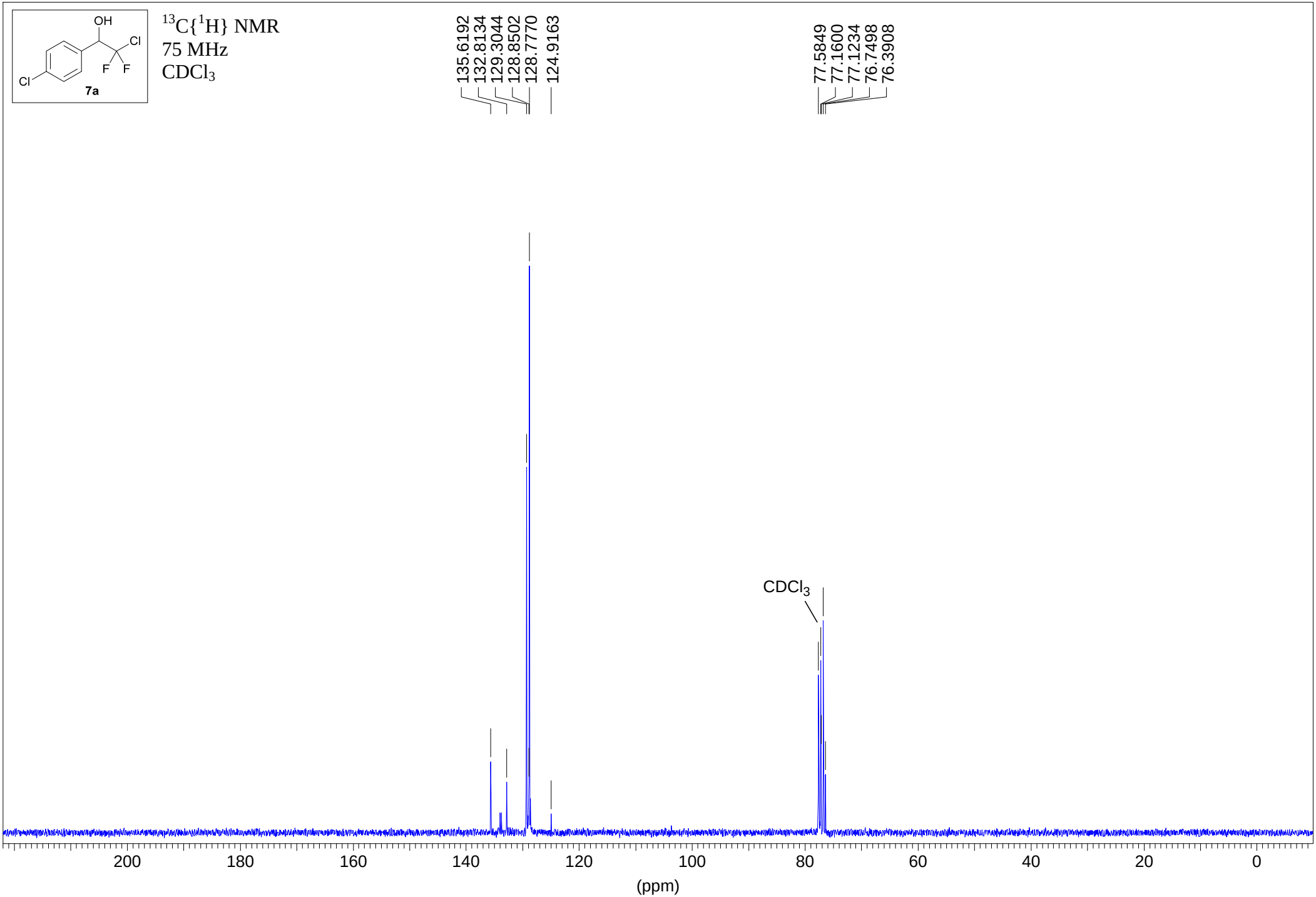

F
OH
Br
F
F
6e
19F NMR
282 MHz
CDCl3
-57.4452
-57.4752
-57.4977
-58.0230
-58.0456
-58.0681
-59.9517
-59.9817
-60.0192
-60.5220
-60.5595
-60.5896
-57
-58
-59
-60
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)

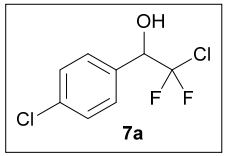

OH
Br
F
F
6f
7.3580
7.3348
7.2767
7.2517
3.8694
3.8486
3.8248
2.9883
2.9718
2.9595
2.8135
2.7860
2.7677
2.5251
2.5061
2.1639
2.1462
2.1248
2.0008
1.9843
1.9684
1.9525
1H NMR
300 MHz
CDCl3
Integral
5.1130
1.0000
2.0495
0.9950
2.0159
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OH
Br
F
F
6f
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
140.5787
129.7659
128.7476
128.6011
126.4693
125.6489
121.5391
77.5776
77.1600
76.7351
76.0172
75.6949
75.3652
32.3193
31.1399
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

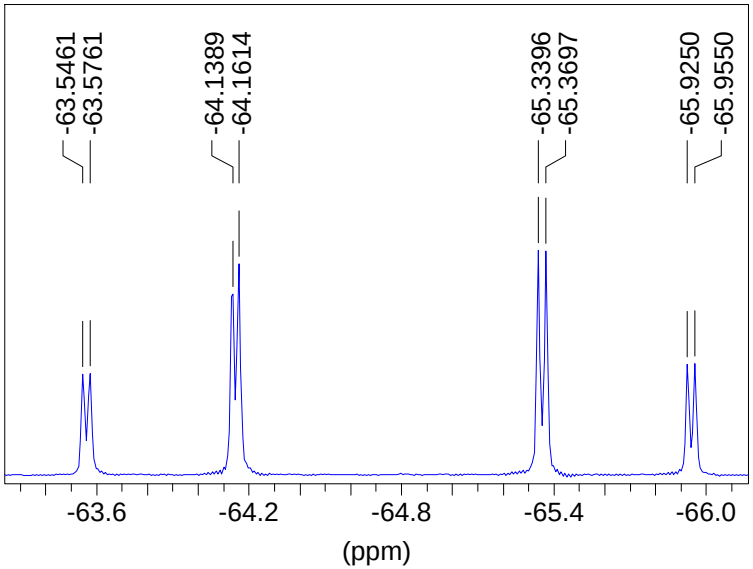

OH
Br
F
F
6f
^{19}F NMR
282 MHz
$CDCl_3$
-56.6122
-56.6347
-57.1826
-57.2126
-59.5239
-59.5539
-60.1018
-60.1243
-57
-58
-59
-60
(ppm)
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
(ppm)

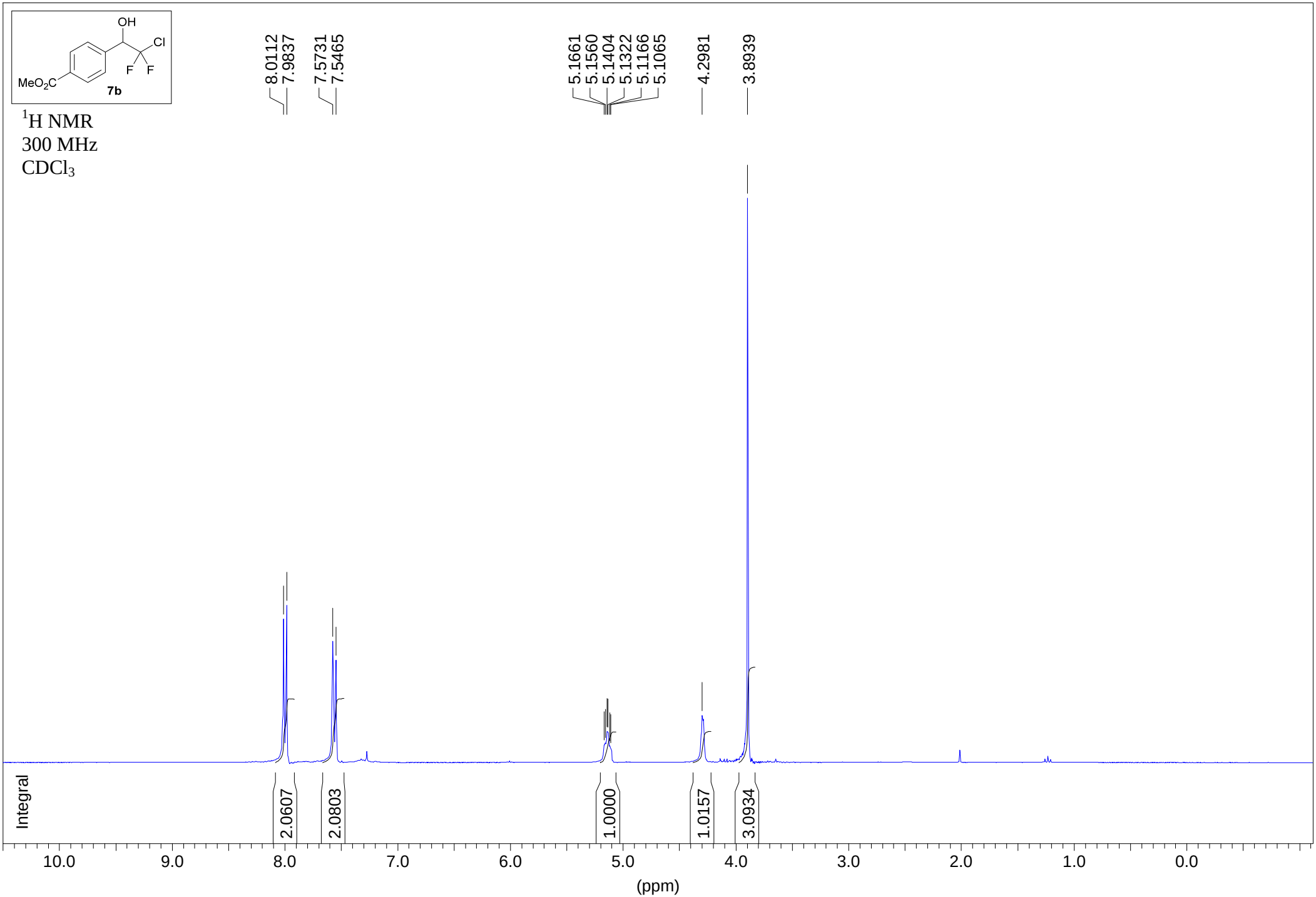

OH
Cl
F
F
Cl
7a
7.4787
7.4494
7.4310
7.4029
5.0955
5.0699
5.0430
3.4554
1H NMR
300 MHz
CDCl3
Integral
4.3450
1.0000
0.9276
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

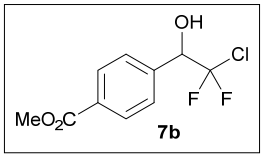

OH
Cl
F
F
Cl
7a
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
135.6192
132.8134
129.3044
128.8502
128.7770
124.9163
77.5849
77.1600
77.1234
76.7498
76.3908
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



^{19}F NMR
282 MHz
$CDCl_3$

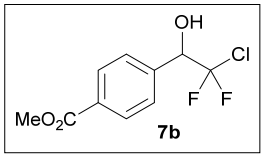



OH
Cl
F F
MeO2C
7b
1H NMR
300 MHz
CDCl3
8.0112
7.9837
7.5731
7.5465
5.1661
5.1560
5.1404
5.1322
5.1166
5.1065
4.2981
3.8939
Integral
2.0607
2.0803
1.0000
1.0157
3.0934
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

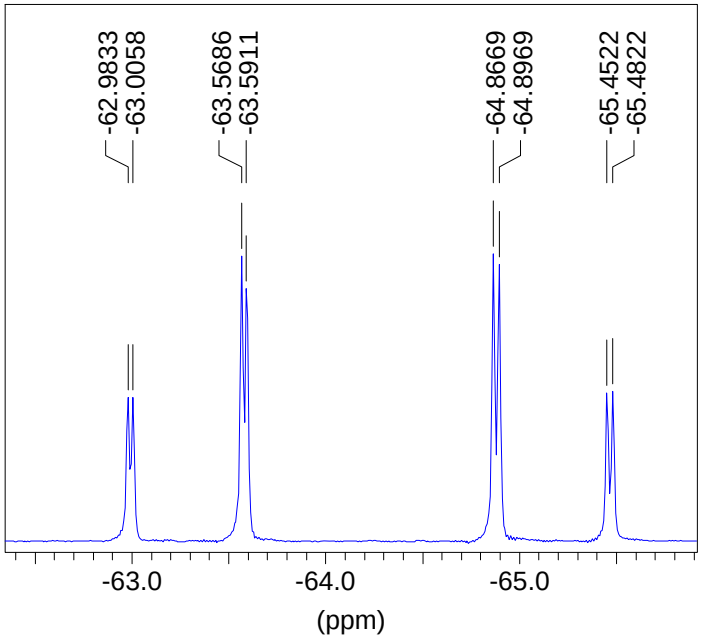


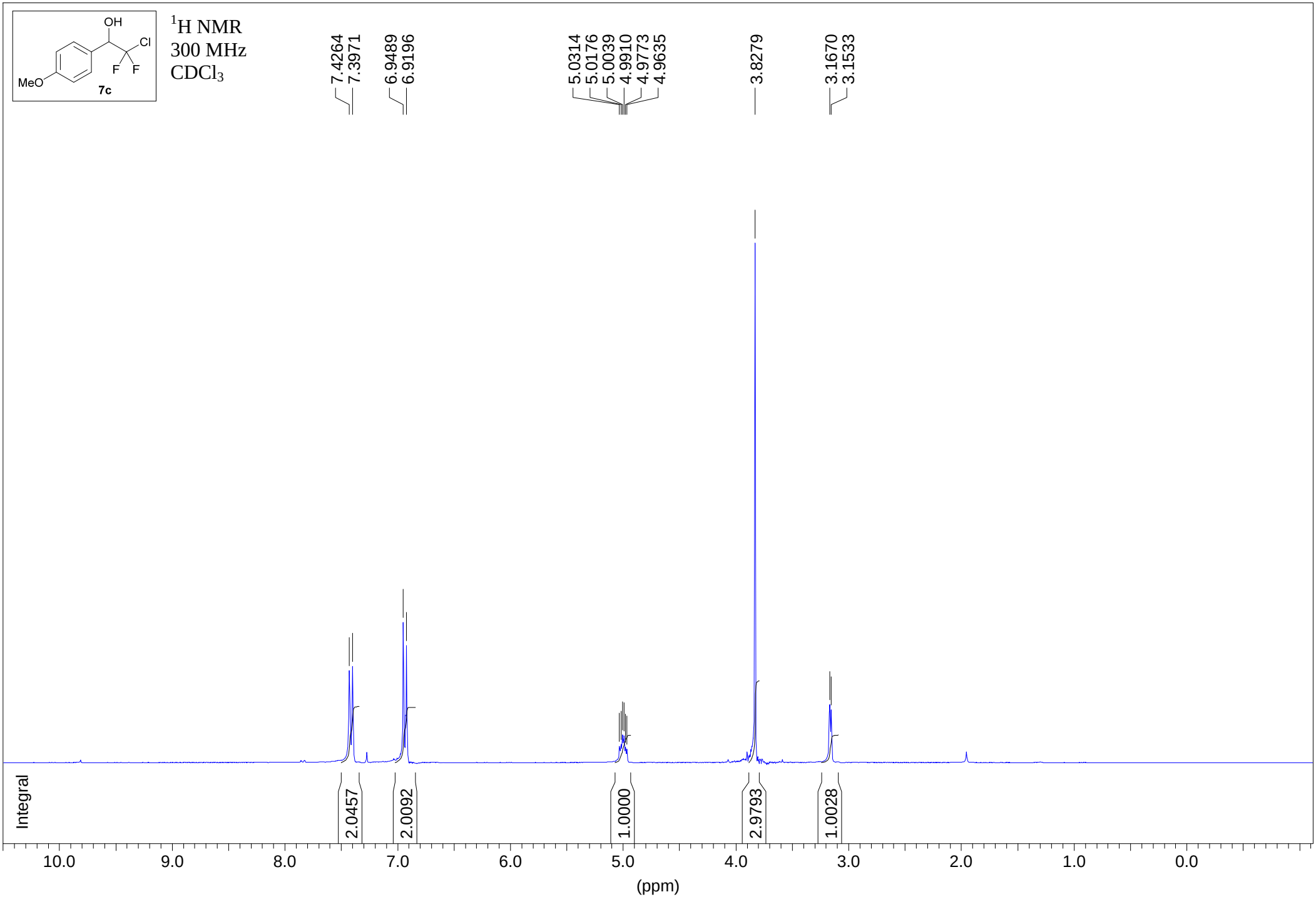
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

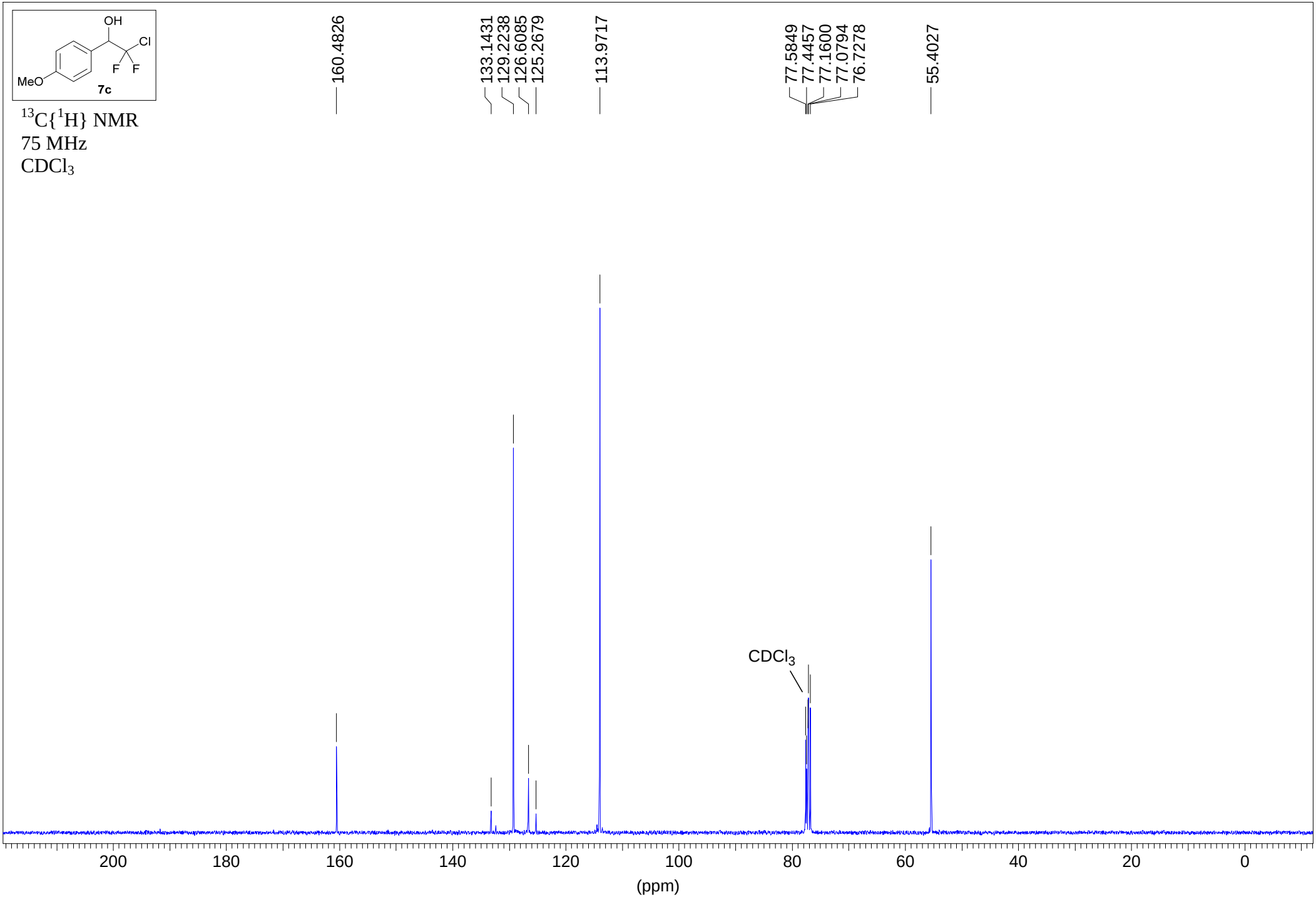
167.7571
167.7131
140.2564
133.1577
131.0919
129.9418
129.2238
128.4473
125.2826
77.9805
77.5263
77.1600
76.7937
52.8533
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

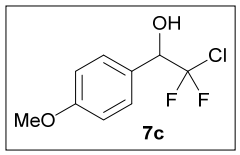


^{19}F NMR
282 MHz
$CDCl_3$

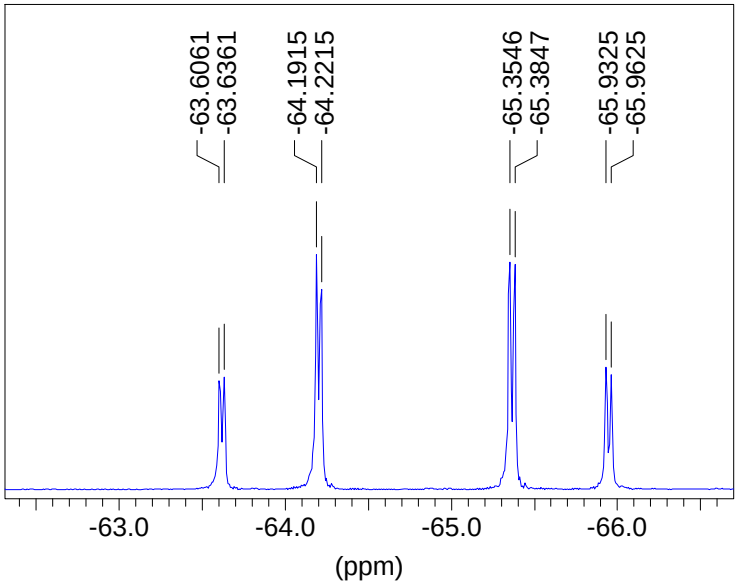


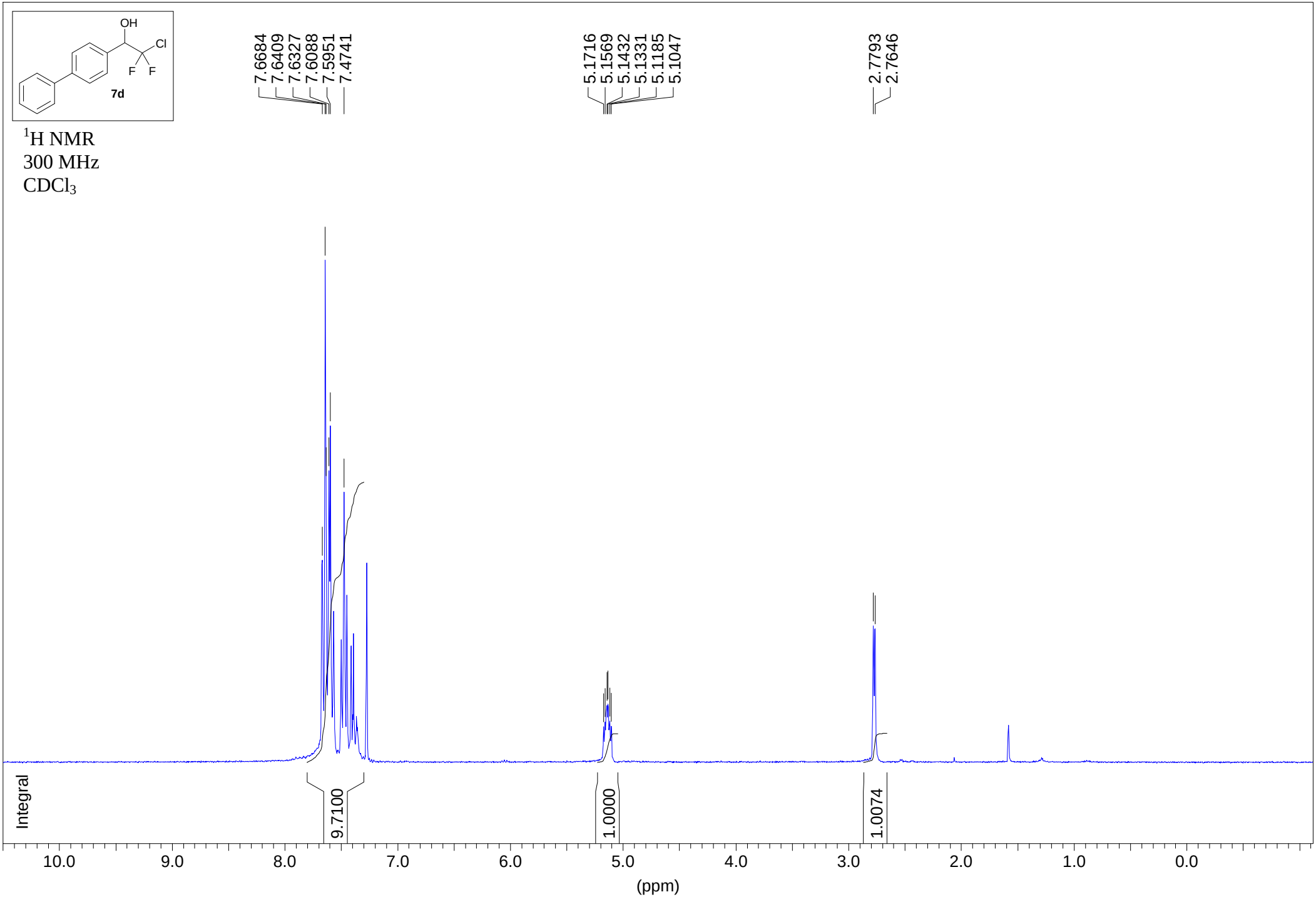

OH
Cl
F
F
MeO
7c
^{1}H NMR
300 MHz
$CDCl_3$
7.4264
7.3971
6.9489
6.9196
5.0314
5.0176
5.0039
4.9910
4.9773
4.9635
3.8279
3.1670
3.1533
Integral
2.0457
2.0092
1.0000
2.9793
1.0028
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

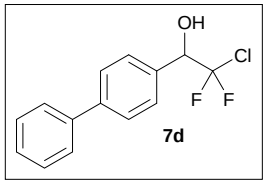

OH
Cl
F F
MeO
7c
160.4826
133.1431
129.2238
126.6085
125.2679
113.9717
77.5849
77.4457
77.1600
77.0794
76.7278
55.4027
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



^{19}F NMR
282 MHz
$CDCl_3$




OH
Cl
F F
7d
7.6684
7.6409
7.6327
7.6088
7.5951
7.4741
5.1716
5.1569
5.1432
5.1331
5.1185
5.1047
2.7793
2.7646
1H NMR
300 MHz
CDCl3
Integral
9.7100
1.0000
1.0074
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



7d

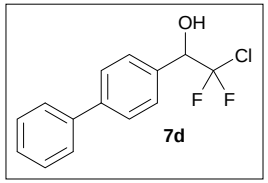
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

142.5712
140.4907
133.2676
133.0552
129.1139
128.9894
128.3594
127.8173
127.3045
125.1800

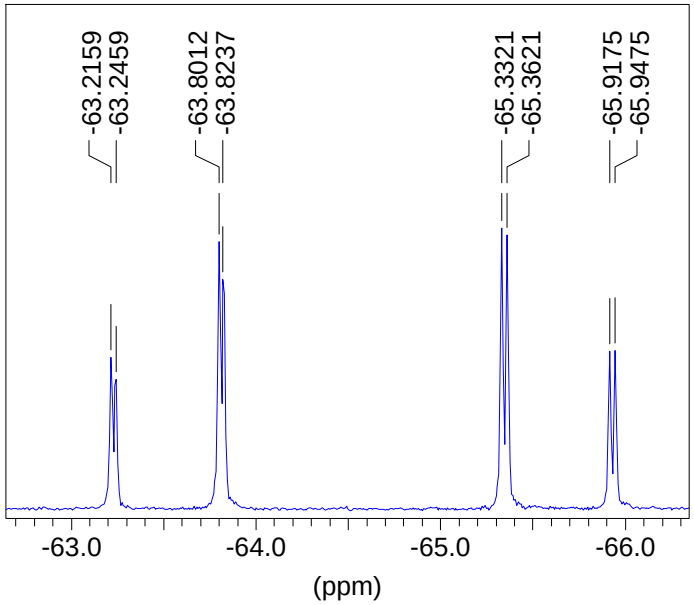
77.7021
77.5849
77.3431
77.1600
76.9769
76.7351

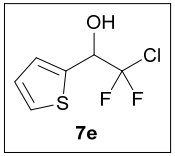
$CDCl_3$

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

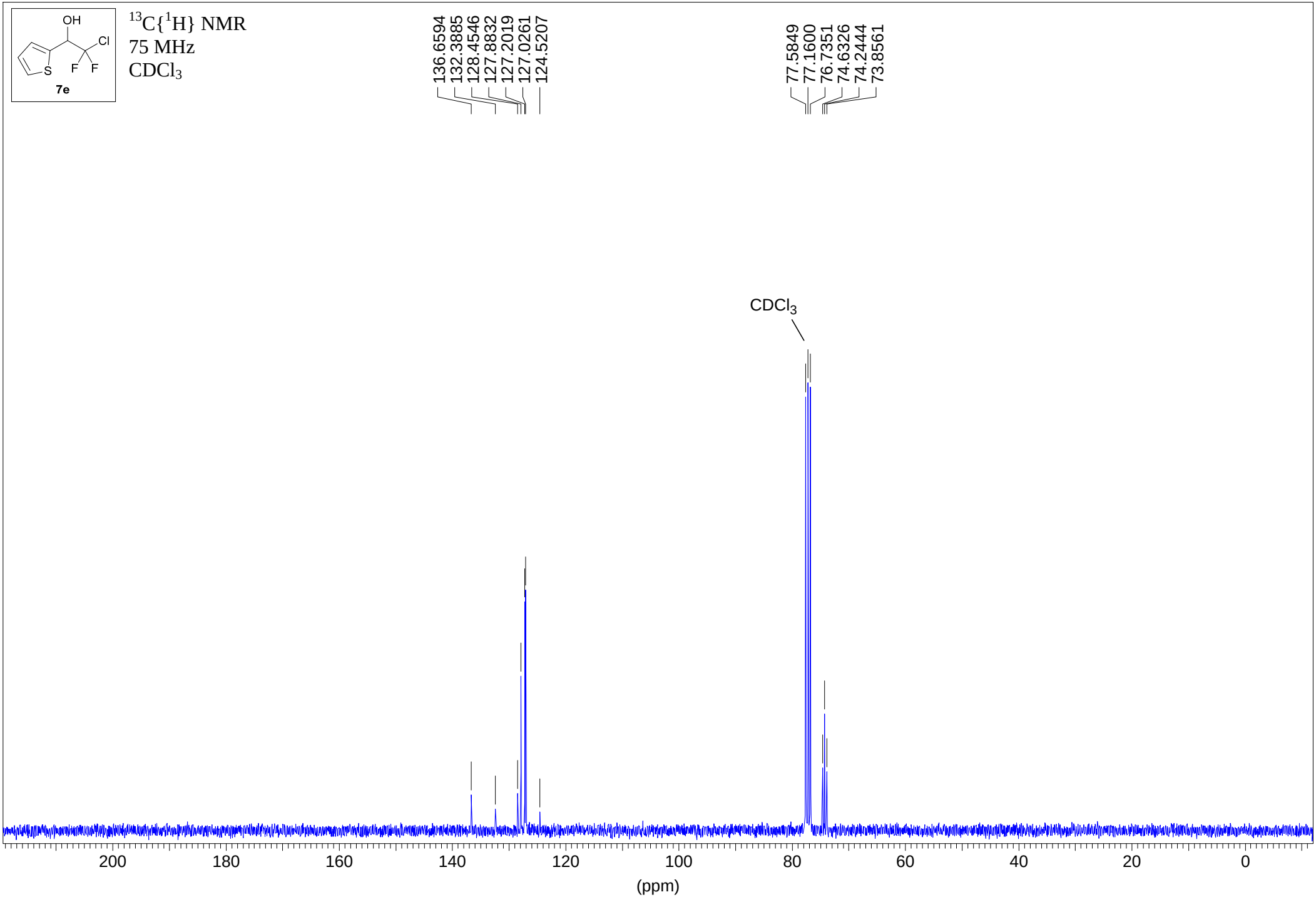


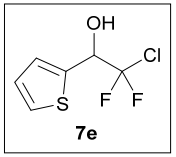
^{19}F NMR
282 MHz
$CDCl_3$



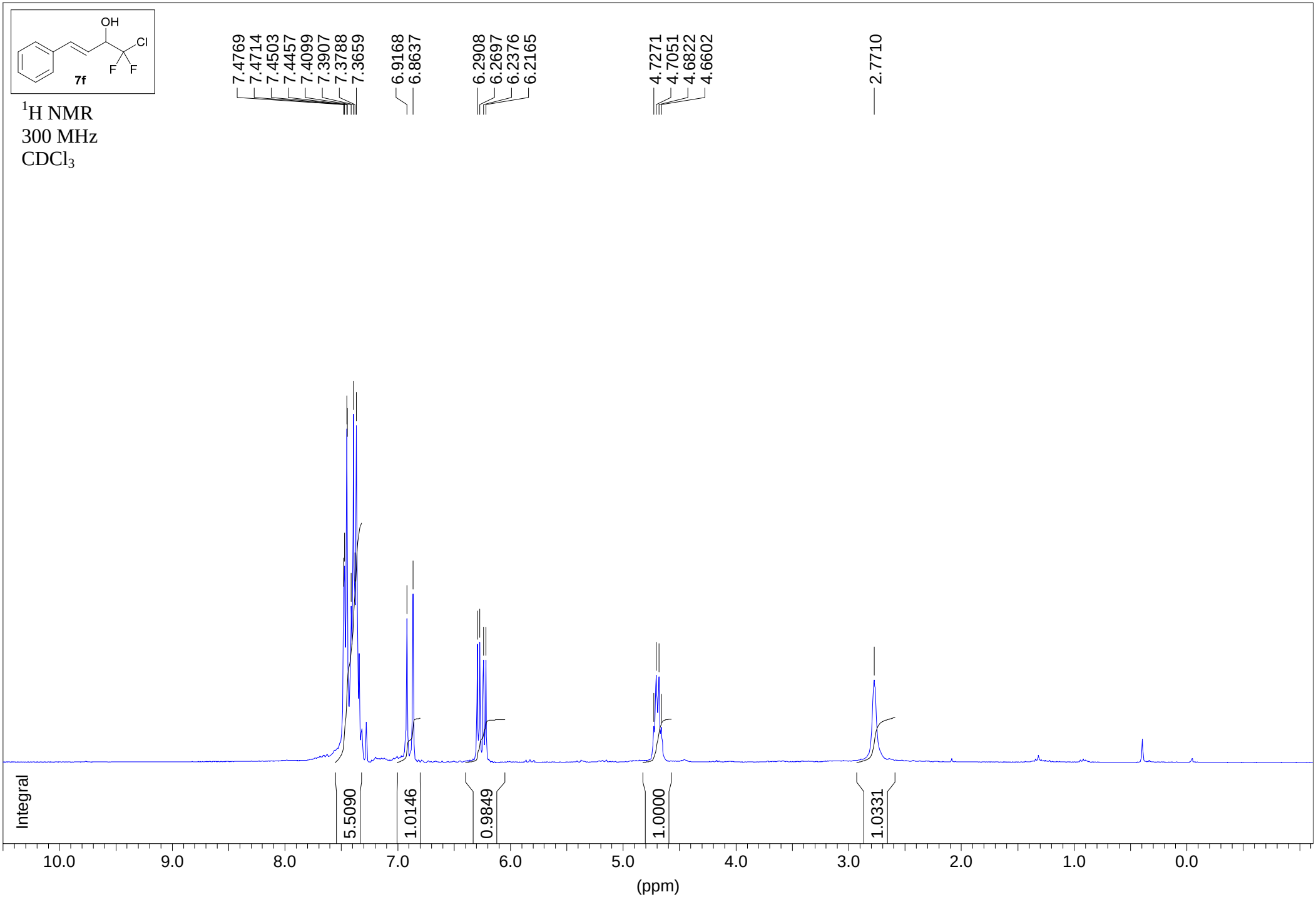


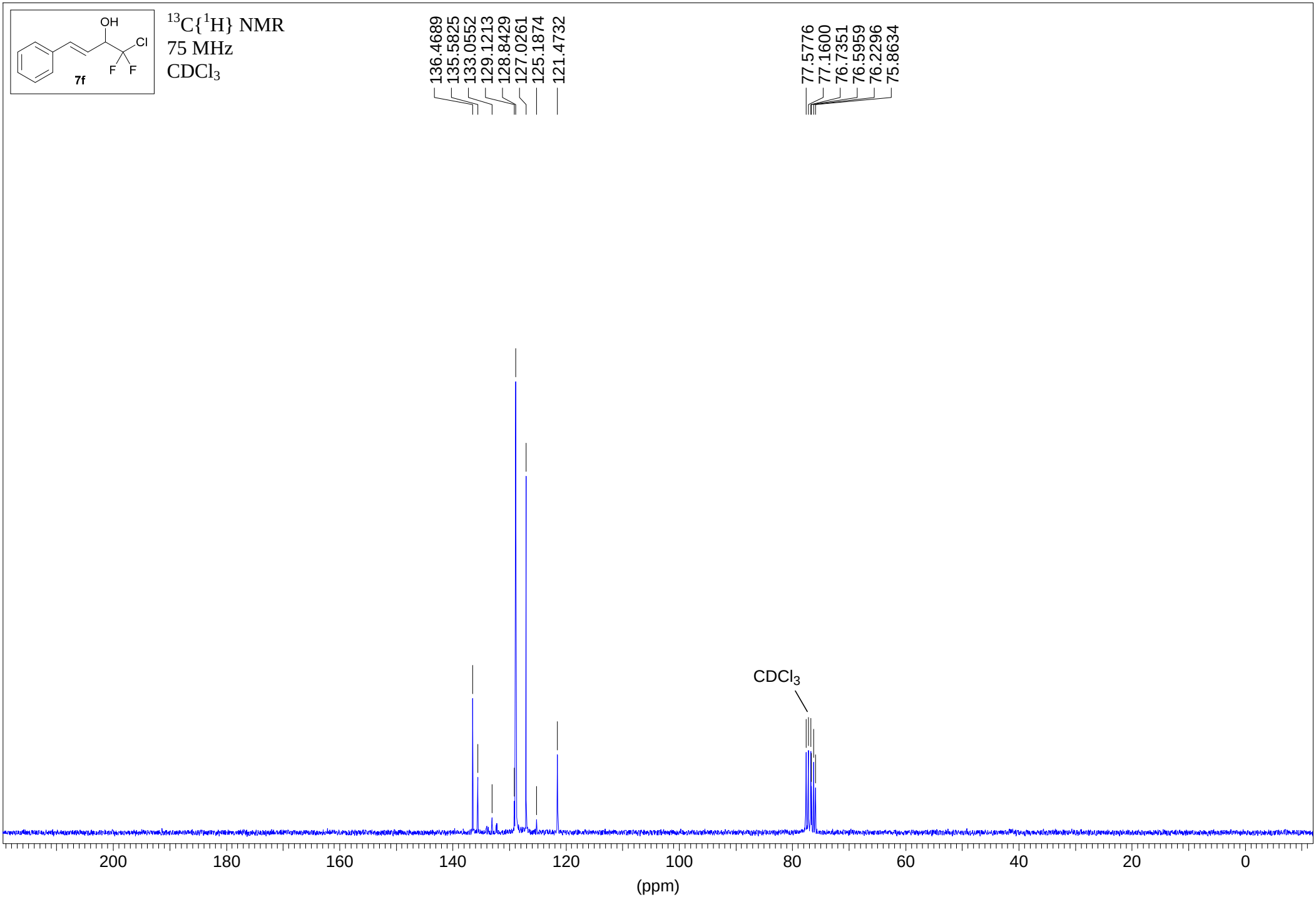
^{1}H NMR
300 MHz
$CDCl_3$

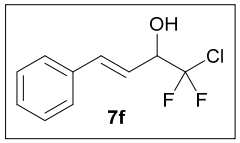

OH
Cl
S
F
F
7e
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
136.6594
132.3885
128.4546
127.8832
127.2019
127.0261
124.5207
77.5849
77.1600
76.7351
74.6326
74.2444
73.8561
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



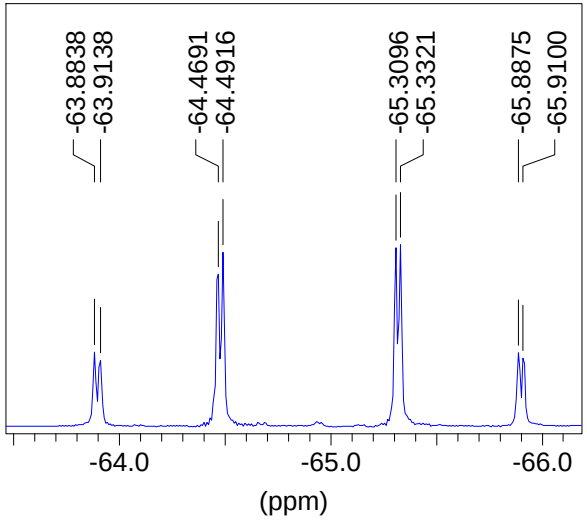
^{19}F NMR
282 MHz
$CDCl_3$

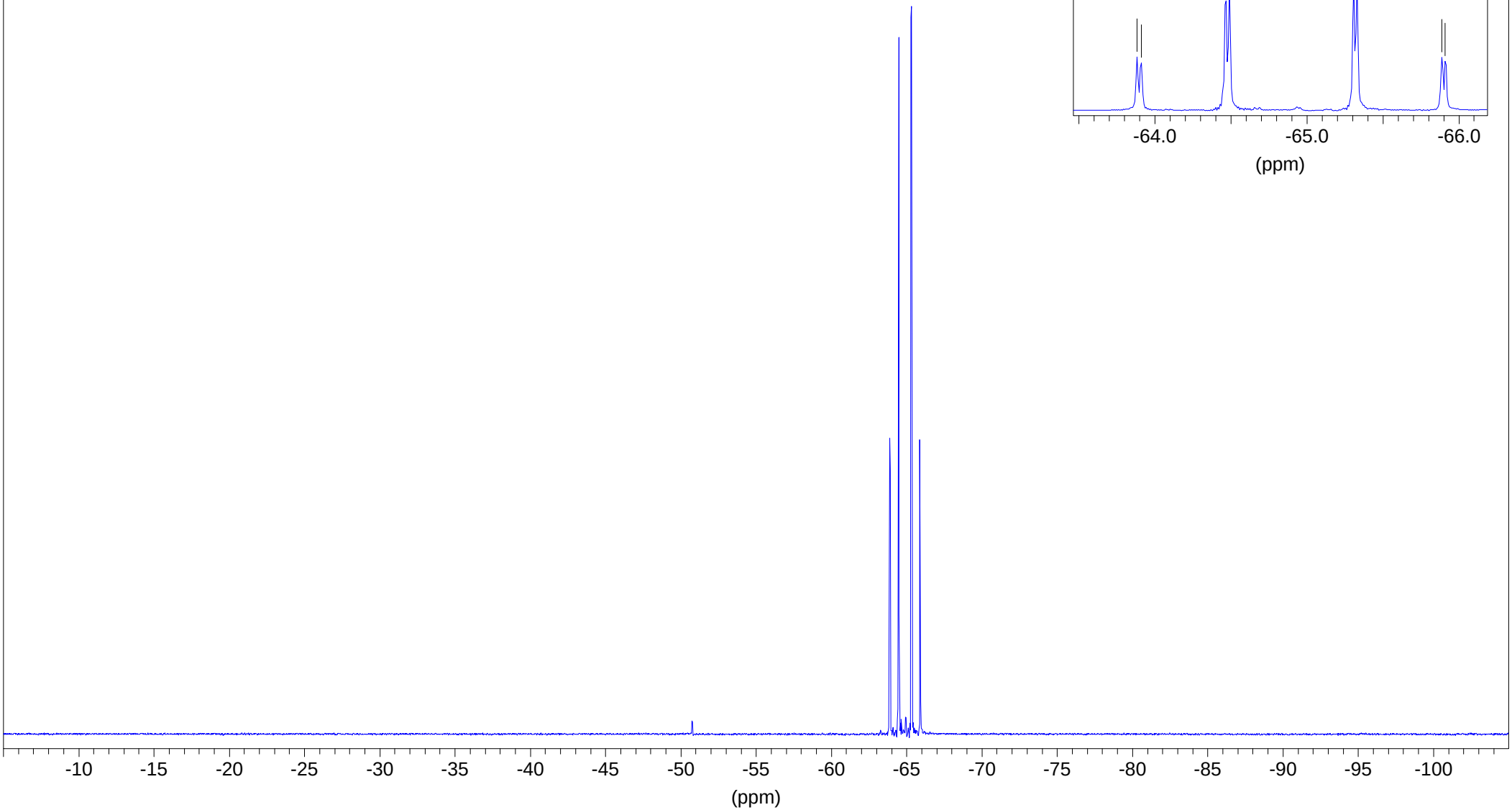

OH
Cl
F
F
7f
7.4769
7.4714
7.4503
7.4457
7.4099
7.3907
7.3788
7.3659
6.9168
6.8637
6.2908
6.2697
6.2376
6.2165
4.7271
4.7051
4.6822
4.6602
2.7710
1H NMR
300 MHz
CDCl3
Integral
5.5090
1.0146
0.9849
1.0000
1.0331
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

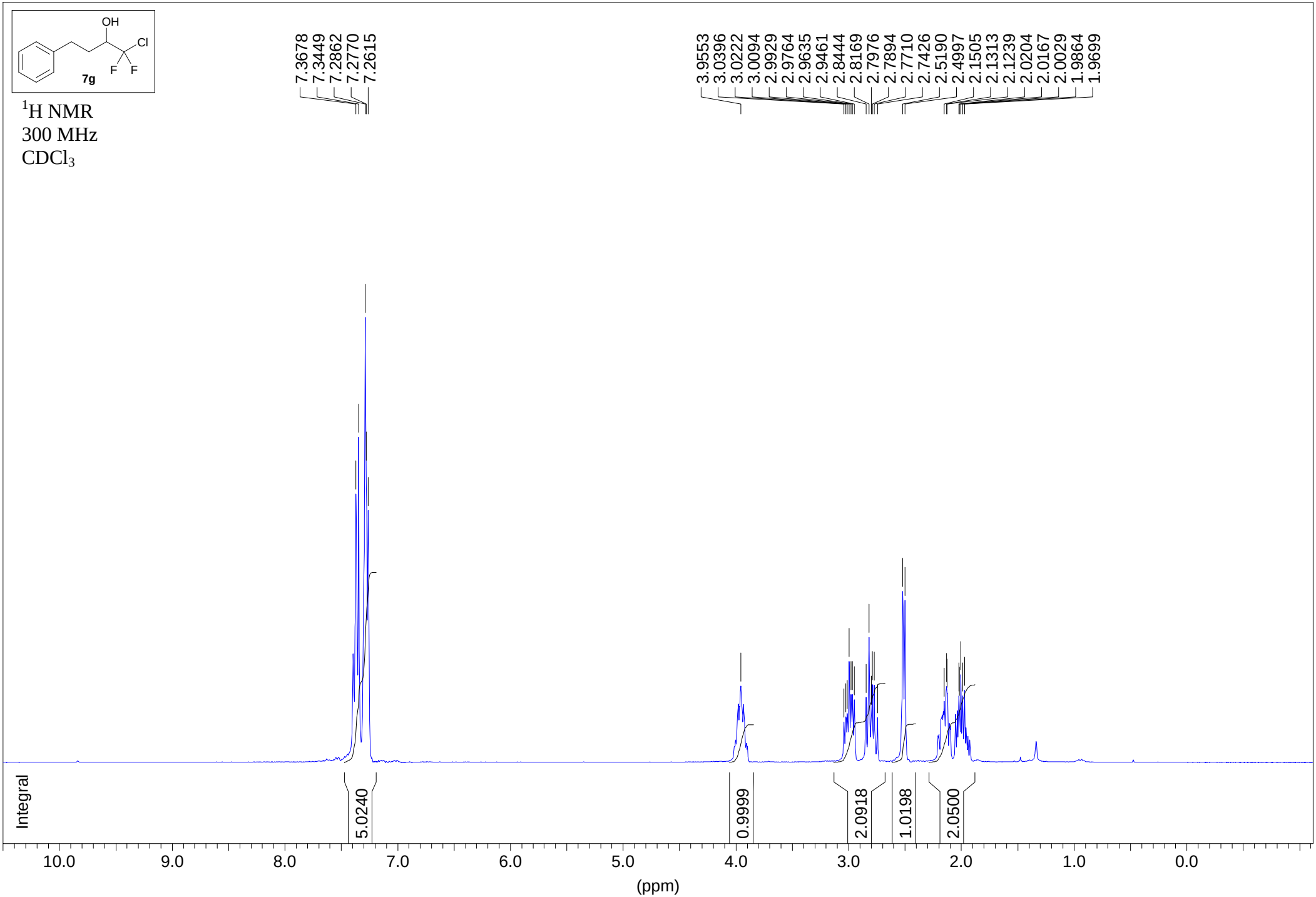

OH
Cl
F
F
7f
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$
136.4689
135.5825
133.0552
129.1213
128.8429
127.0261
125.1874
121.4732
77.5776
77.1600
76.7351
76.5959
76.2296
75.8634
$CDCl_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)



^{19}F NMR
282 MHz
$CDCl_3$






OH
Cl
F F
7g
7.3678
7.3449
7.2862
7.2770
7.2615
3.9553
3.0396
3.0222
3.0094
2.9929
2.9764
2.9635
2.9461
2.8444
2.8169
2.7976
2.7894
2.7710
2.7426
2.5190
2.4997
2.1505
2.1313
2.1239
2.0204
2.0167
2.0029
1.9864
1.9699
1H NMR
300 MHz
CDCl3
Integral
5.0240
0.9999
2.0918
1.0198
2.0500
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

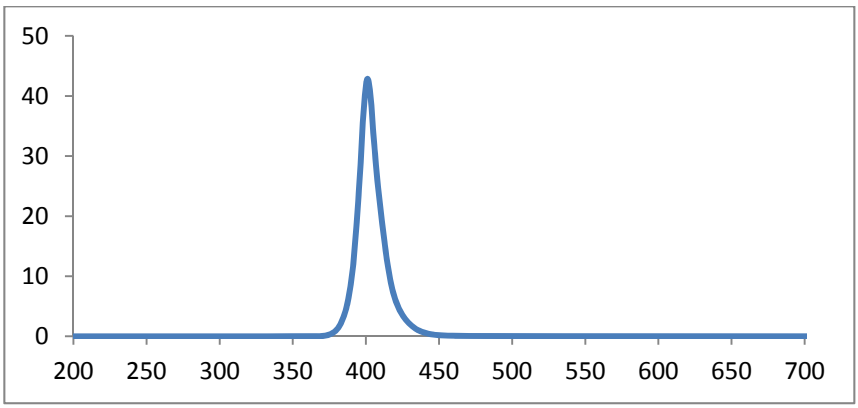


Figure S1. Spectrum of the light emitting diode.

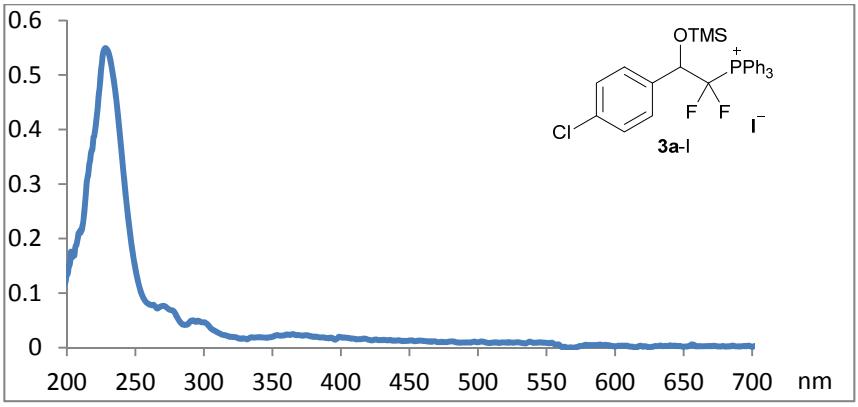


Figure S2. Spectrum of salt **3a**-I. 1×10^{-4} M in dichloroethane. The salt was obtained according to General procedure 1.

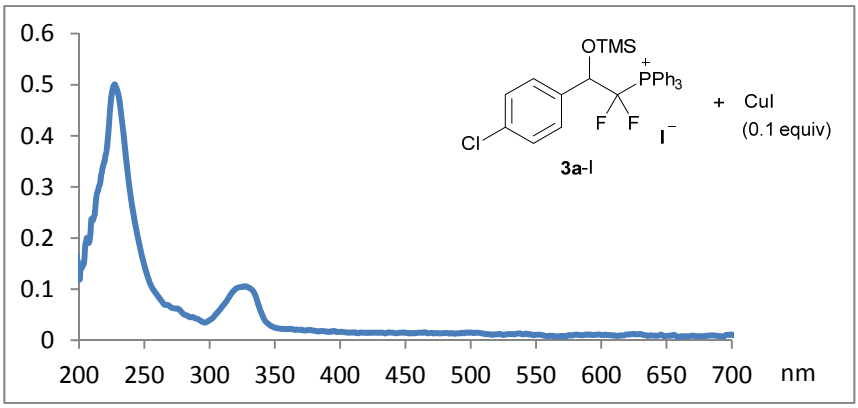


Figure S3. Spectrum of the reaction mixture of salt **3a**-I + CuI (0.1 equiv) after 1.5 h of irradiation; 1×10^{-5} M in dichloroethane. The mixture was obtained according to General procedure 1.