Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Photoredox Generation of the Trifluoromethyl Radical from Borate Complexes via Single Electron Reduction

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Content

General Methods: All reactions were performed under an argon atmosphere. 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 irradiation, a strip of light emitting diodes (2835-120LED 1M-Blue, 12V) was used.

Reagents. The following starting compounds were prepared according to literature procedures: potassium trifluoromethyltrifluoroborate (CF_3BF_3K),[1] potassium pentafluoroethyltrifluoroborate ($C_2F_5BF_3K$),[2] potassium heptafluoropropyltrifluoroborate (n-$C_3F_7BF_3K$),[3] borate complexes **1a-c**,[4] 1,2-dihydronaphthalene,[5] 1-phenylcyclopentene,[6] 1-phenylcyclohexene,[7] 1-phenylcycloheptene,[8] 1-methylene-1,2,3,4-tetrahydronaphthalene,[9] 1-vinylnaphthalene,[10] 4-vinyl-1,1'-biphenyl,[11] methyl 4-vinylbenzoate,[12] 4-vinylbenzyl acetate,[13] O-(*tert*-butyl)dimethylsilyl(4-vinylphenyl)methanol,[14] 1-(azidomethyl)-4-vinylbenzene,[15] *tert*-butyl 4-vinylbenzylcarbamate,[16] 1-(phthalimidomethyl)-4-vinylbenzene,[17] photocatalyst $Cu(dap)_2PF_6$.[18]

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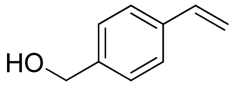
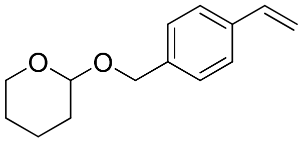
_p_-Vinylbenzyl alcohol.[14]



A solution of methyl _p_-vynylbenzoate (5.64 g, 34.8 mmol) in THF (12 mL) was added to a stirred suspension of $LiAlH_4$ (1.41 g, 37.1 mmol) in THF (25 mL) within 10 minutes by cooling the mixture with ice-water bath (the reaction is strongly exothermic, and the solvent may even boil despite external cooling). When the addition is complete, the cooling bath was removed, and mixture was stirred at room temperature for 30 minutes. Then, the flask was again cooled with an ice-water bath, and the mixture was quenched by careful dropwise addition of 40% aqueous KOH (15 mL) (CAUTION! Gas evolution). The mixture was extracted with hexane (2×50 mL), the combined organic layers were concentrated, and the residue was purified by column chromatography (silica gel, from CH_2Cl_2 to MTBE/CH_2Cl_2, 4/1) to afford 4.26 g (91% yield) of the product as a colorless oil. R_f 0.22 (CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.43 (d, _J_ = 8.1 Hz, 2H), 7.33 (d, _J_ = 8.1 Hz, 2H), 6.74 (dd, _J_ = 17.6 Hz, 10.8 Hz, 1H), 5.78 (d, _J_ = 17.6 Hz, 1H), 5.27 (d, _J_ = 11.0 Hz, 1H), 4.68 (br s, 2H), 1.96 (br s, 1H).

2-[(4-vinylbenzyl)oxy]tetrahydro-2H-pyran.



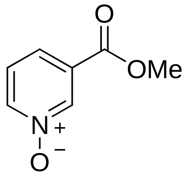
A mixture of _p_-vinylbenzyl alcohol (468 mg, 3.49 mmol), dihydropyran (0.50 mL, 0.48 g, 5.48 mmol, 1.6 eq.) and NH_2SO_3H (65 mg, 0.67 mmol, 0.19 equiv) was stirred for 24 hours at room temperature. The mixture was diluted with hexane (10 mL), filtered, the precipitate was washed with additional hexane (10 mL). The filtrates were combined and subjected to column chromatography (silica gel, from CH_2Cl_2/hexane 1/2 to CH_2Cl_2). The product was obtained as a pale yellow oil (717 mg, 94 % yield). R_f 0.53 (CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.42 (d, _J_ = 7.5 Hz, 2H), 7.36 (d, _J_ = 7.9 Hz, 2H), 6.74 (dd, _J_ = 17.6 Hz, 10.8 Hz, 1H), 5.77 (d, _J_ = 17.6 Hz, 1H), 5.26 (d, _J_ = 11.0 Hz, 1H), 4.80 (d, _J_ = 12.1 Hz, 1H), 4.73 (br s, 1H), 4.53 (d, _J_ = 12.1 Hz, 1H), 4.01–3.88 (m, 1H), 3.63–3.51 (m, 1H), 2.00–1.48 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 138.0, 136.9, 136.6, 128.1, 126.2, 113.7, 97.7, 68.5, 62.1, 30.6, 25.5, 19.4.

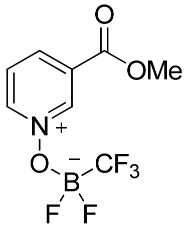
HRMS (ESI): Calcd for $C_{14}H_{18}NaO_2$ (M+Na): 241.1199. Found: 241.1203.

Methyl nicotinate *N*-oxide.[19]



m-Chloroperbenzoic acid (20.3 g of 75% by weight, 88 mmol, 1.1 equiv) was added portionwise to a stirred solution of methyl nicotinate (10.96 g, 80 mmol) in CH_2Cl_2 (80 mL) with external cooling with water bath at room temperature, and the resulting mixture was kept at room temperature for 60 hours. Then, K_2CO_3 (21.5 g, 156 mmol, 1.95 equiv) was added portionwise with stirring, and the mixture was stirred until in turns into thick paste which is hard to stir with a magnetic stirrer (about 15 min). The paste was diluted with CH_2Cl_2 (200 mL), filtered, and the precipitate was washed with CH_2Cl_2 (5×50 mL). The filtrates were combined, and the solvent was removed on a rotary evaporator. The obtained crystalline residue was recrystallized from toluene (40 mL) to afford 11.48 g (94 % yield) of the product as off-white crystals. Mp 102–104 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.73 (s, 1H), 8.31 (d, *J* = 6.6 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.35 (dd, *J* = 7.9 Hz, 6.6 Hz, 1H), 3.93 (s, 3H).

[3-(Methoxycarbonyl)pyridinium-1-yloxy](trifluoromethyl)difluoroborate (1d).



Boron trifluoride etherate (4.45 g, 31.36 mmol, 1.03 equiv) was added to a stirred suspension of CF_3BF_3K (5.55 g, 31.55 mmol, 1.04 equiv) and methyl nicotinate *N*-oxide (4.64 g, 30.33 mmol) in CH_2Cl_2 (31 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours. Fine white precipitate was filtered off and washed with CH_2Cl_2 (3×30 mL). The combined filtrates were evaporated, the residue was dissolved in hot CH_2Cl_2 (35 mL), and the solution was kept in a freezer (–20 °C). The mother liquor was removed from the deposited crystals, and the crystals were dried under vacuum to afford the product (7.09 g, 86 %).

Colorless crystals. Mp 99–100 °C with decomp (CH_2Cl_2).

^1H NMR (300 MHz, acetone-d6) δ: 9.22 (s, 1H), 9.12 (d, *J* = 6.2 Hz, 1H), 9.04 (d, *J* = 8.1 Hz, 1H), 8.38 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.09 (s, 3H).

^{13}C NMR (75 MHz, acetone-d6) δ: 162.4 , 146.6, 144.0, 143.0, 132.2, 129.5, 54.1.

^{19}F NMR (282 MHz, acetone-d6) δ: –76.5 (q, *J* = 32.5 Hz, 3F), –162.0 (q, *J* = 44.5, 2F).

^{11}B (96 MHz, acetone-d6): 0.4 (tq, *J* = 43.4, 34.7 Hz).

HRMS (ESI): Calcd for $C_8H_7BF_5NNaO_3$ (M+Na): 294.0333. Found: 294.0329.

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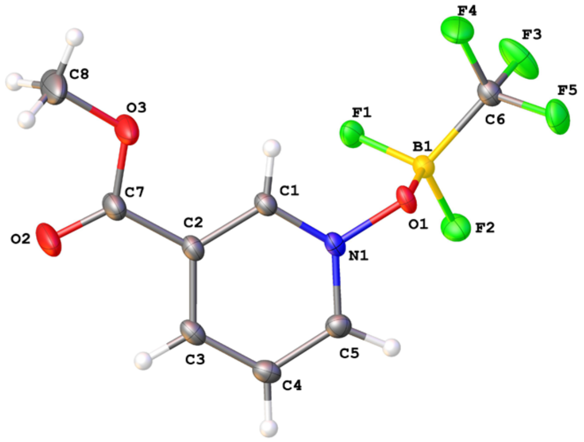
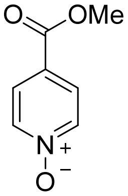


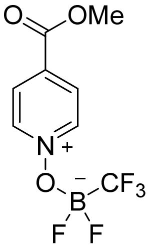
Figure S1. X-ray structure of complex **1d**.

Methyl isonicotinate *N*-oxide.[20]



m-Chloroperbenzoic acid (9.15 g of 75% by weight, 39.8 mmol, 1.1 equiv) was added portionwise to a stirred solution of methyl isonicotinate (4.93 g, 36.0 mmol) in CH_2Cl_2 (36 mL) with external cooling with water bath at room temperature, and the resulting mixture was heated at reflux for 6 hours. Then, K_2CO_3 (8.39 g, 60.8 mmol, 1.69 equiv) was added portionwise with stirring and the reaction mixture was stirred until in turns into thick paste which is hard to stir with magnetic stirrer (about 15 min). The paste was diluted with CH_2Cl_2 (108 mL), filtered, and the precipitate was washed with CH_2Cl_2 (3×100 mL). The filtrates were combined, and the solvent was removed on a rotary evaporator. The obtained crystalline residue was recrystallized from toluene (20 mL) to afford 5.00 g (91 % yield) of the product as off-white crystals. Mp 121–123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.22 (d, J = 7.2 Hz, 2H), 7.87 (d, *J* = 7.2 Hz, 2H), 3.95 (s; 3H).

[4-(Methoxycarbonyl)pyridinium-1-yloxy](trifluoromethyl)difluoroborate (1e).



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Borontrifluoride etherate (935 mg, 6.59 mmol, 1.10 equiv) was added to a stirred suspension of CF_3BF_3K (1.13 g, 6.42 mmol, 1.07 equiv) and methyl isonicotinate *N*-oxide (918 mg, 6.00 mmol) in CH_2Cl_2 (6.0 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 16 hours. The mixture was diluted with CH_2Cl_2 (15 mL), fine white precipitate was filtered off and washed with CH_2Cl_2 (3×20 mL). The combined filtrates were evaporated, the crystalline residue was dissolved in hot CH_2Cl_2 (24 mL), and the solution was kept in a freezer (–20 °C). The mother liquor was removed from the deposited crystals, and the crystals were dried under vacuum to afford the product (1.285 g, 79 % yield). Colorless crystals. Mp 95–99 °C (dec.).

^{1}H NMR (300 MHz, acetone-d6) δ: 9.04 (d, *J* = 6.8 Hz, 2H), 8.58 (d, *J* = 6.8 Hz, 2H), 4.06 (s; 3H).

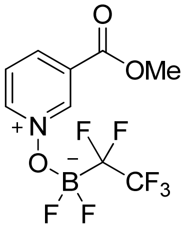
^{13}C NMR (75 MHz, acetone-d6) δ: 163.2 , 144.6, 142.6, 128.7, 54.2.

^{19}F NMR (282 MHz, acetone-d6) δ: –76.6 (q, *J* = 33.2 Hz, 3F), –161.9 (q, *J* = 43.8, 2F).

^{11}B NMR (96 MHz, acetone-d6) δ: 0.4 (tq; *J* = 43.8, 33.2 Hz).

HRMS (ESI): Calcd for $C_8H_7BF_5NNaO_3$ (M + Na): 294.0333. Found: 294.0339.

[3-(Methoxycarbonyl)pyridinium-1-yloxy](pentafluoroethyl)difluoroborate (1f).



Boron trifluoride etherate (715 mg, 5.04 mmol, 1.01 equiv) was added to a stirred suspension of $C_2F_5BF_3K$ (1.16 g, 5.14 mmol, 1.03 equiv) and methyl nicotinate *N*-oxide (765 mg, 5.00 mmol) in CH_2Cl_2 (5 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours and diluted with CH_2Cl_2 (15 mL). Fine white precipitate was filtered off and washed with CH_2Cl_2 (15 mL). The combined filtrates were evaporated, and the residue was subjected to column chromatography (silica gel, CH_2Cl_2) to afford the product (1.31 g, 82 %).

Colorless crystals. Mp 100–102 °C ($CHCl_3$). R_f 0.27 (CH_2Cl_2).

^{1}H NMR (300 MHz, acetone-d6) δ: 9.21 (s, 1H), 9.12 (d, *J* = 6.2 Hz, 1H), 9.04 (d, *J* = 8.1 Hz, 1H), 8.40 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.09 (s, 3H).

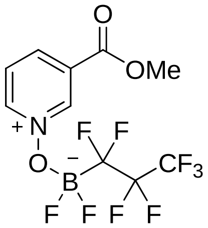
^{13}C NMR (75 MHz, acetone-d6) δ: 162.5, 146.7, 144.1, 143.1, 132.2, 129.6, 121.9 (qt, *J* = 283.6, 31.5 Hz), 54.1.

^{19}F NMR (282 MHz, acetone-d6) δ: –85.0 (t, *J* = 5.3 Hz, 3F), –137.3 (m, 2F), –159.5 (q, *J* = 45.9, 2F).

^{11}B (96 MHz, acetone-d6): 1.2 (tt, *J* = 47.1, 21.7 Hz).

HRMS (ESI): Calcd for $C_9H_7BF_7NNaO_3$ (M+Na): 344.0301. Found: 344.0293.

[3-(Methoxycarbonyl)pyridinium-1-yloxy](*n*-heptafluoropropyl)difluoroborate (1g).



Boron trifluoride etherate (752 mg, 5.30 mmol, 1.03 equiv) was added to a stirred suspension of *n*-$C_3F_7BF_3K$ (1.453 g, 5.26 mmol, 1.03 equiv) and methyl nicotinate *N*-oxide (783 mg, 5.12 mmol) in CH_2Cl_2 (5 mL) with cooling in an ice bath, and the reaction mixture was stirred at room temperature for 15 hours and diluted with CH_2Cl_2 (15 mL). Fine white precipitate was filtered off and washed with CH_2Cl_2 (15 mL). The combined filtrates were evaporated, and the residue was subjected to column chromatography (silica gel, CH_2Cl_2) to afford the product (1.755 g, 92 % yield).

Colorless crystals. Mp 89–90 °C. R_f 0.28 (CH_2Cl_2).

^{1}H NMR (300 MHz, acetone-d6) δ: 9.21 (s, 1H), 9.11 (d, *J* = 6.2 Hz, 1H), 9.04 (d, *J* = 8.1 Hz, 1H), 8.38 (dd, *J* = 8.1, 6.2 Hz, 1H), 4.09 (s, 3H).

^{13}C NMR (75 MHz, acetone-d6) δ: 162.5 , 146.7, 144.1, 143.1, 132.2, 129.6, 119.6 (qt, *J* = 287.2, 35.1 Hz), 111.5 (m), 54.1.

^{19}F NMR (282 MHz, acetone-d6) δ: –82.5 (t, *J* = 9.5 Hz, 3F), –129.2 (t, *J* = 5.3 Hz, 2F), –135.0 (br.s, 2F), –158.6 (q, *J* = 42.4, 2F).

^{11}B (96 MHz, acetone-d6): 1.2 (tt, *J* = 46.7, 21.0 Hz).

HRMS (ESI): Calcd for $C_{10}H_7BF_9NNaO_3$ (M+Na): 394.0269. Found: 394.0266.

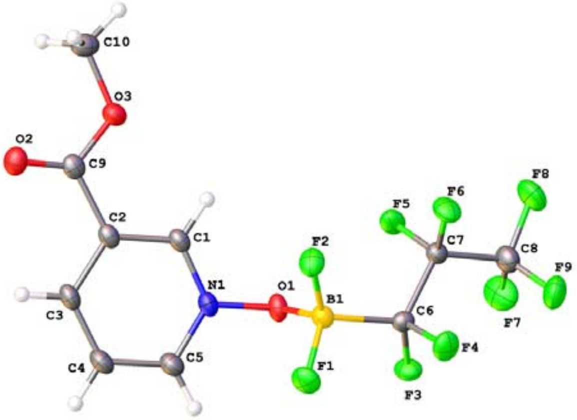


Figure S2. X-ray structure of complex **1f**.

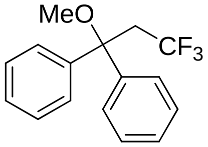
Methoxytrifluoromethylation of alkenes (General procedure).

Degassed methanol (3.0 mL) was added to a mixture of $KHCO_3$ (160 mg, 1.6 mmol, 2.67 equiv), $Cu(dap)_2PF_6$ (6.0 mg, 0.006 mmol, 0.01 equiv) and alkene (0.60 mmol) in the Schlenk tube. [Dichloromethane was added in reactions of 1,2-diphenylethylene (2 mL of CH_2Cl_2) and 1-(phthalimidomethyl)-4-vinylbenzene (1 mL of CH_2Cl_2) to improve their solubility in the reaction mixture.] Complex **1d** (203 mg, 0.75 mmol, 1.25 equiv) was added, and the vessel was irradiated for 1 hour with a strip of blue LED with stirring; during irradiation the mixture was cooled with tap water. The mixture was diluted [for **3a-g,j,l,m,o,p,t,u**, with MTBE (3 mL); for **3i,k,n,q,r,s**, with hexane (3 mL)], and water (6 mL) was added with stirring, minor frothing may occur at this step. Organic layer was separated and aqueous layer was extracted with the corresponding solvent (3×3 mL). The combined organic layers were dried over Na_2SO_4, concentrated, and the residue was subjected to column chromatography on silica gel.

Photo S1. Reaction setup.

Photo S2. Reaction setup with LED irradiation.

(3,3,3-Trifluoro-1-methoxy-1-phenylpropyl)benzene (3a).[21]



Yield 160 mg (95%). Colorless crystals. Mp 61–62 °C. R$_f$ 0.14 (CH_2Cl_2/hexane, 1/10).

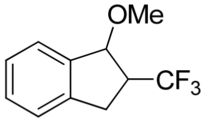
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.28–7.08 (m, 10H), 3.13 (q, *J* = 10.0; 2H), 3.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 144.0, 128.3, 127.4, 126.7, 125.8 (q, *J* = 278.2 Hz), 79.9 (q, *J* = 1.7 Hz), 51.1, 38.9 (q, *J* = 26.2 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –60.6 (t, *J* = 10.1 Hz).

HRMS (ESI): Calcd for $C_{16}H_{15}F_3NaO$ (M+Na): 303.0967. Found: 303.0964.

1-Methoxy-2-(trifluoromethyl)indane (3b).



Yield 109 mg (84%). Mixture of two isomers (ratio 1.5:1). Colorless oil. R$_f$ 0.35 and 0.41 (CH_2Cl_2/hexane, 1/1) (both spots were collected together).

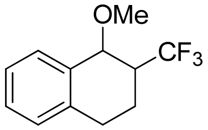
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52–7.23 (m, 4H), 5.08 (d, *J* = 3.7 Hz, major) and 4.84 (d, *J* = 5.5 Hz, minor) (1H), 3.56 (s, major) and 3.45 (s, minor) (3H), 3.43–3.29 (m, 1H), 3.25–3.00 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 141.6, 140.8, 140.5, 140.3, 129.4, 129.3, 127.7 (q, *J* = 277.5 Hz, major), 127.4, 126.9, 126.5 (q, *J* = 277.5 Hz, minor), 125.44, 125.37, 125.32, 124.9, 84.8 (q, *J* = 2.8 Hz, major), 82.5 (q, *J* = 2.0 Hz, minor), 57.2 (major), 57.0 (minor), 49.0 (q, *J* = 26.5 Hz, major), 47.9 (q, *J* = 27.3 Hz, minor), 31.06 (q, *J* = 2.8 Hz, major), 30.96 (q, *J* = 2.6 Hz, minor).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –60.4 (d, *J* = 10.6 Hz, minor), –71.1 (d, *J* = 8.5 Hz, major).

HRMS (ESI): Calcd for $C_{11}H_{11}F_3NaO$ (M+Na): 239.0654. Found: 239.0654.

1-Methoxy-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene (3c).



Yield 109 mg (79%). Mixture of two isomers (ratio 1:1). Colorless oil. R$_f$ 0.33 and 0.42 (CH_2Cl_2/hexane, 1/1) (both spots collected together).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45–7.15 (m, 2x4H), 4.62 (d, *J* = 5.1 Hz, 1H), 4.47 (s, 1H), 3.42 (s, 3H), 3.38 (s, 3H), 3.10 (dd, *J* = 17.4, 6.4 Hz, 1H), 2.96–2.74 (m, 4H), 2.58-2.19 (m, 3H), 2.10–1.96 (m, 1H), 1.93–1.76(m, 1H).

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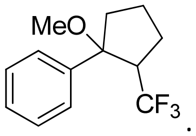
[21] Yasu, Y.; Koike, T.; Akita, M. *Angew. Chem. Int. Ed.* **2012**, *51*, 9567–9571.

^{13}C NMR (75 MHz, $CDCl_3$), δ: 137.8, 136.3, 134.4, 134.0, 130.0, 129.6, 129.1, 128.9, 128.5, 128.2, 127.5 (q, *J* = 279.7 Hz), 127.3 (q, *J* = 279.2 Hz), 126.4, 125.6, 75.9 (q, *J* = 2.4 Hz), 75.1 (q, *J* = 2.9 Hz), 56.9, 55.9, 44.3 (q, *J* = 26.5 Hz), 43.3 (q, *J* = 24.9 Hz),27.6, 26.8, 20.9 (q, *J* = 2.8 Hz), 16.8 (q, *J* = 2.4 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –69.6 (d, *J* = 8.5 Hz), –70.7 (d, *J* = 8.5 Hz).

HRMS (ESI): Calcd for $C_{12}H_{13}F_3NaO$ (M+Na): 253.0811. Found: 253.0819.

[1-Methoxy-2-(trifluoromethyl)cyclopentyl]benzene (3d).



Yield 91 mg (62%). Mixture of two isomers (ratio 11:1). Colorless oil. R_f 0.24 (CH_2Cl_2/hexane, 1/4).

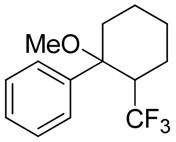
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55–7.30 (m, 5H both isomers), 3.21 (s, minor) and 2.98 (s, major) (3H), 2.96–2.82 (m, major) and 2.77–2.65 (m, minor) (1H), 2.42–2.19 (m, 3H both isomers), 2.12–1.81 (m, 3H both isomers).

^{13}C NMR (75 MHz, $CDCl_3$), δ: major isomer: 138.3, 128.06 (br), 128.02, 127.96, 126.7 (q, *J* = 278.6 Hz), 88.6 (q, *J* = 1.5 Hz), 54.9 (q, *J* = 24.3 Hz), 49.4, 30.4 (q, *J* = 1.5 Hz), 25.0 (q, *J* = 2.6 Hz), 21.0. minor isomer (observed peaks only): 128.5, 127.4, 126.5 (br), 55.3 (q, *J* = 25.4 Hz), 51.4, 34.8 (br), 25.1 (q, *J* = 2.2 Hz), 22.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.6 (d, *J* = 10.6 Hz, minor), –66.9 (d, *J* = 10.6 Hz, major).

HRMS (ESI): Calcd for $C_{13}H_{15}F_3NaO$ (M+Na): 267.0967. Found: 267.0967.

[1-Methoxy-2-(trifluoromethyl)cyclohexyl]benzene (3e).



Yield 101 mg (65%). Mixture of two isomers (ratio 3.8:1). Colorless oil. R_f 0.29 (CH_2Cl_2/hexane, 1/4).

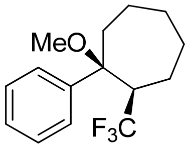
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47–7.26 (m, 5H, both isomers), 3.31 (s, minor) and 2.92 (s, major) (3H), 2.76–2.58 (m) and 2.40–1.38 (m) (9H, both isomers).

^{13}C NMR (75 MHz, $CDCl_3$), δ: major isomer: 142.6, 128.23, 127.7, 127.14 (br), 126.79 (q, *J* = 280.9 Hz), 76.9 (q, *J* = 1.1 Hz), 50.4 (q, *J* = 22.7 Hz), 48.5, 25.7 (q, *J* = 1.7 Hz), 22.2 (q, *J* = 2.8 Hz), 20.7, 20.6 (br), minor isomer: 142.8, 128.21, 127.08, 126.85 (q, *J* = 282.5 Hz), 126.6 (br), 78.4, 52.9 (q, *J* = 23.2 Hz), 50.3, 33.4 (br), 25.1, 22.4 (q, *J* = 2.8 Hz), 21.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –60.9 (d, *J* = 12.7 Hz, major), –64.4 (d, *J* = 8.5 Hz, minor).

HRMS (ESI): Calcd for $C_{14}H_{17}F_3NaO$ (M+Na): 281.1124. Found: 281.1114.

(1*R,2*S**)-1-Methoxy-1-phenyl-2-(trifluoromethyl)cycloheptane (3f).**



Yield 155 mg (95%). Colorless oil. Mp 70–71 °C. R_f 0.24 (CH_2Cl_2/hexane, 1/4). Stereochemistry was determined by 2D ^1H-^1H NOESY and ^1H-^{19}F HOESY experiments.

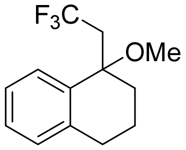
^1H NMR (300 MHz, $CDCl_3$) δ: 7.44–7.22 (m, 5H), 3.34 (s, 3H), 2.60–2.44 (m, 1H), 2.25–1.83 (m, 6H), 1.82–1.51 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 144.9 (br), 128.0, 127.4 (q, *J* = 282.5 Hz), 126.9, 126.5 (br), 81.1 (br), 56.0 (q, *J* = 22.1 Hz), 51.2, 37.5 (br), 27.8, 26.6, 22.6 (q, *J* = 3.0 Hz), 21.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –63.8 (d, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{15}H_{19}F_3NaO$ (M+Na): 295.1280. Found: 295.1269

1-Methoxy-1-(2,2,2-trifluoroethyl)-1,2,3,4-tetrahydronaphthalene (3g).



Yield 133 mg (91%). Colorless oil. R_f 0.61 (CH_2Cl_2/hexane, 1/4).

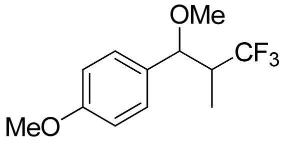
^1H NMR (300 MHz, $CDCl_3$) δ: 7.54–7.45 (m, 1H), 7.33–7.21 (m, 2H), 7.20-7.12 (m, 1H), 3.11 (s; 3H), 2.95-2.75 (m, 2H), 2.75–2.57 (m, 2H),2.33–2.14 (m, 2H), 2.12–1.82 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 138.5, 137.9, 129.3, 127.8, 126.7, 126.4, 125.8 (q, *J* = 278.8 Hz), 75.9 (q, *J* = 1.8 Hz), 50.4, 45.2 (q, *J* = 26.4 Hz), 29.6, 29.3 (br), 20.6.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –60.2 (t; *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{13}H_{15}F_3NaO$ (M+Na): 267.0967. Found: 267.0970.

1-Methoxy-4-(3,3,3-trifluoro-1-methoxy-2-methylpropyl)benzene (3h).



Yield 125 mg (84%). Mixture of two isomers (ratio 1:1). Colorless oil. R_f 0.67 (CH_2Cl_2).

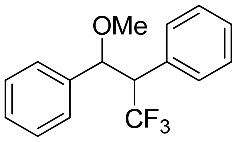
^1H NMR (300 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 8.2 Hz, 2x2H), 6.92 (d, *J* = 8.2 Hz, 2x2H), 4.47 (d, *J* = 3.7 Hz, 1H), 4.21 (d, *J* = 7.8 Hz, 1H), 3.83 (s, 2x3H), 3.27 (s, 3H), 3.18 (s, 3H), 2.63 (octet, *J* = 7.9 Hz, 1H), 2.47-2.26 (m, 1H), 1.12 (d, *J* = 7.3 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 159.8, 159.4, 131.4, 130.5, 129.0, 127.9, 114.0, 113.9 127.6 (q, *J* = 280.5 Hz), 82.3 (q, *J* = 1.9 Hz), 80.2 (q, *J* = 2.7 Hz), 57.2, 56.6, 55.31, 55.29, 45.5 (q, *J* = 24.9 Hz), 44.2 (q, *J* = 24.7 Hz), 10.3 (q, *J* = 3.1 Hz), 7.2 (q, *J* = 2.7 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –69.6 (d, *J* = 8.5 Hz), –70.6 (d, *J* = 8.5 Hz).

HRMS (ESI): Calcd for $C_{12}H_{15}F_3NaO_2$ (M+Na): 271.0916. Found: 271.0906.

{2,2,2-Trifluoro-1-[methoxy(phenyl)methyl]ethyl}benzene (3i).[20]

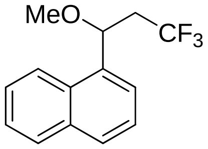


Yield 109 mg (65%). Mixture of two isomers (4:1). Colorless oil. R_f 0.14 and 0.25 (CH_2Cl_2/hexane, 1/4) (both spots collected together).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.35–7.05 (m, 10H), 4.90 (d, *J* = 5.0 Hz, minor) and 4.71 (d, *J* = 9.4 Hz, major) (1H), 3.76 (quintet, *J* = 9.1 Hz, major) and 3.64–3.49 (m, minor) (1H), 3.32 (s, major) and 3.28 (s, minor) (3H).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –63.9 (d, *J* = 8.5 Hz, major), –66.2 (d, *J* = 8.5 Hz, minor).

1-(3,3,3-Trifluoro-1-methoxypropyl)naphthalene (3j).



Yield 116 mg (76%). Colorless oil. R_f 0.61 (CH_2Cl_2/hexane, 1/1).

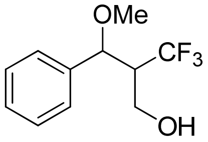
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.20 (d, *J* = 8.1 Hz, 1H), 7.99–7.86 (m, 2H), 7.70–7.52 (m, 4H), 5.29 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.39 (s, 3H), 2.94–2.73 (m, 1H), 2.72–2.52 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 135.5, 134.2, 130.6, 129.3, 129.0, 126.7, 126.2 (q, *J* = 277.5 Hz), 126.0, 125.6, 124.4, 122.7, 75.9 (q, *J* = 3.1 Hz), 57.1, 41.8 (q, *J* = 27.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –65.0 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{14}H_{13}F_3NaO$ (M+Na): 277.0811. Found: 277.0800.

3,3,3-Trifluoro-2-[methoxy(phenyl)methyl]propan-1-ol (3k).



Yield 83 mg (59%). Mixture of two isomers (ratio 1.5:1). Colorless oil. R_f 0.42 (EtOAc/hexane, 1/3).

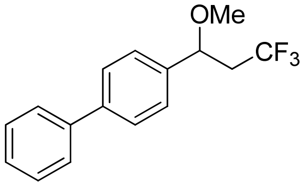
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.51–7.30 (m, 5H), 4.70 (d, *J* = 4.8 Hz, minor) and 4.64 (d, *J* = 7.5 Hz, 1H, major) (1H), 4.09–3.78 (m) and 3.56–3.43 (m) (2H), 3.31 (s, minor) and 3.26 (s, major) (3H), 2.95 (t, *J* = 6.1 Hz, minor) and 2.82–2.64 (m, major) (1H), 2.61–2.44 (m, minor) and 2.22 (t, *J* = 5.6 Hz, major) (1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 138.8, 137.7, 128.9, 128.74, 128.71, 128.5, 127.7, 126.8, 126.5 (q, *J* = 281.4, major), 126.4 (q, *J* = 280.9, minor), 81.4 (q, *J* = 2.4 Hz, minor), 80.7 (q, *J* = 2.0 Hz, major), 58.3 (q, *J* = 3.3 Hz, major), 58.1 (q, *J* = 2.9 Hz, minor), 57.5 (minor), 57.1 (major), 51.9 (q, *J* = 23.2 Hz, minor), 51.5 (q, *J* = 23.2 Hz, major).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –65.0 (d, *J* = 8.5 Hz, major), –67.2 (d, *J* = 8.5 Hz, minor).

HRMS (ESI): Calcd for $C_{11}H_{13}F_3NaO_2$ (M+Na): 257.0760. Found: 257.0752.

1-(1,1'-Biphenyl-4-yl)-3,3,3-trifluoropropyl methyl ether (3l).



Yield 158 mg (94%). Colorless crystals. Mp 40–41 °C. R_f 0.18 (CH_2Cl_2/hexane, 1/4).

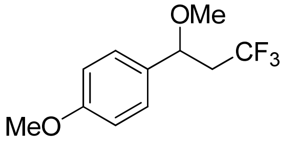
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75–7.60 (m, 4H), 7.56–7.37 (m, 5H), 4.57 (dd, *J* = 8.2, 4.0 Hz, 1H), 3.32 (s, 3H), 2.85–2.65 (m, 1H), 2.56–2.36 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 140.73, 140.72, 139.2, 129.0, 127.65, 127.63, 127.23, 127.08, 125.9 (q; *J* = 277.3 Hz), 77.7 (q; *J* = 3.3 Hz), 57.1, 42.4 (q; *J* = 27.5 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.4 (t; *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{16}H_{15}F_3NaO$ (M+Na): 303.0967. Found: 303.0965.

1-Methoxy-4-(3,3,3-trifluoro-1-methoxypropyl)benzene (3m).[22]

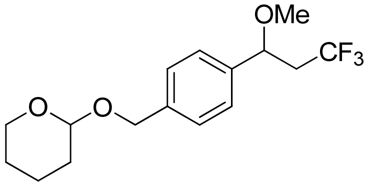


Yield 121 mg (86%). Colorless oil. R_f 0.50 (CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.44 (dd, *J* = 8.4, 4.4 Hz, 1H), 3.84 (s, 3H), 3.22 (s, 3H), 2.78-2.57 (m, 1H), 2.48-2.28 (m, 1H).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

2-{[4-(3,3,3-Trifluoro-1-methoxypropyl)benzyl]oxy}tetrahydro-2*H*-pyran (3n).



Yield 181 mg (95%). Colorless oil. R_f 0.33 (CH_2Cl_2). Only one set of signals is observed in NMR spectra, since two stereocenters are located far away from each other.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.74 (t, *J* = 3.0 Hz, 1H), 4.51 (d, *J* = 12.1 Hz, 1H), 4.47 (dd, *J* = 8.6, 4.0 Hz, 1H), 4.02–3.86 (m, 1H), 3.64-3.50 (m, 1H), 3.23 (s, 3H), 2.77–2.53 (m, 1H), 2.47-.2.26 (m, 1H), 2.01–1.46 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 139.3, 138.8, 128.2, 126.6, 125.8 (q, *J* = 277.4 Hz), 98.0, 77.6 (q, *J* = 3.9 Hz), 68.6, 62.2, 56.7, 42.3 (q, *J* = 27.5 Hz), 30.6, 25.5, 19.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{16}H_{21}F_3NaO_3$ (M+Na): 341.1335. Found: 341.1326.

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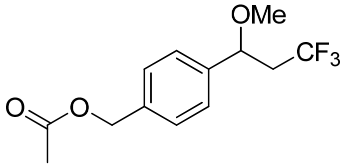
[22] Yang, B.; Xu, X.-H.; Qing, F.-L. *Org. Lett.* **2015**, *17*, 1906–1909.

4-(3,3,3-Trifluoro-1-methoxypropyl)benzyl acetate (3o).



Yield 144 mg (87%). Colorless oil. R_f 0.17 (CH_2Cl_2).

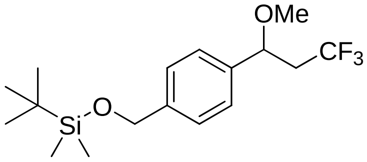
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.12 (s, 2H), 4.47 (dd, *J* = 8.5, 4.1 Hz, 1H), 3.23 (s, 3H), 2.75–2.55 (m, 1H), 2.45-2.25 (m, 1H), 2.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 170.9, 140.2, 136.3, 128.7, 126.8, 125.7 (q, *J* = 277.3 Hz), 77.6 (q, *J* = 3.3 Hz), 65.9, 56.8, 42.3 (q, *J* = 27.5 Hz), 21.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{13}H_{15}F_3NaO_3$ (M+Na): 299.0866. Found: 299.0865.

***tert*-Butyl(dimethyl){[4-(3,3,3-trifluoro-1-methoxypropyl)benzyl]oxy}silane (3p).**



Yield 177 mg (85%). Colorless oil. R_f 0.24 (CH_2Cl_2/hexane, 1/3).

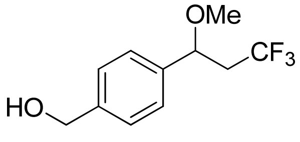
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.36 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.77 (s, 2H), 4.47 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.23 (s, 3H), 2.77–2.55 (m, 1H), 2.47–2.27 (m, 1H), 0.97 (s, 9H), 0.13 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 141.9, 138.7, 126.6, 125.8 (q, *J* = 277.2 Hz), 77.7 (q, *J* = 3.3 Hz), 64.8, 56.7, 42.4 (q, *J* = 27.6 Hz), 26.1, 18.6, –5.2.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{17}H_{27}F_3NaO_2Si$ (M+Na): 371.1625. Found: 371.1609.

[4-(3,3,3-Trifluoro-1-methoxypropyl)phenyl]methanol (3q).



Yield 122 mg (87%). Colorless oil. R_f 0.18 (EtOAc/hexane = 1/3).

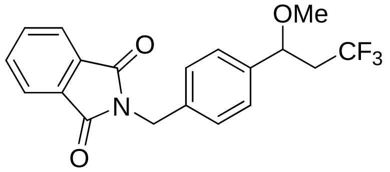
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 7.5 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 4.70 (d, *J* = 4.7 Hz, 2H), 4.47 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.22 (s, 3H), 2.77-2.57 (m, 1H), 2.47–2.27 (m, 1H), 2.18 (t, *J* = 4.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 141.3, 139.4, 127.5, 126.9, 125.7 (q, *J* = 277.2 Hz), 77.7 (q, *J* = 2.9 Hz), 65.0, 56.7, 42.2 (q, *J* = 27.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{11}H_{13}F_3NaO_2$ (M+Na): 257.0760. Found: 257.0760.

2-[4-(3,3,3-Trifluoro-1-methoxypropyl)benzyl]-1*H*-isoindole-1,3(2*H*)-dione (3r).



Yield 198 mg (91%). Colorless crystals. Mp 85–87 °C. R_f 0.45 (CH_2Cl_2).

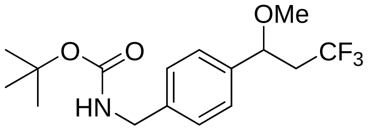
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.89–7.79 (m, 2H), 7.76–7.65 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 4.85 (s, 2H), 4.43 (dd, *J* = 8.5, 3.8 Hz, 1H), 3.19 (s, 3H), 2.71–2.48 (m, 1H), 2.41–2.20 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 168.0, 139.8, 136.7, 134.1, 132.2, 129.1, 126.9, 125.7 (q, *J* = 277.0 Hz), 123.4, 77.5 (q, *J* = 3.3 Hz), 56.7, 42.2 (q, *J* = 27.6 Hz), 41.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{19}H_{16}F_3NNaO_3$ (M+Na): 386.0974. Found: 386.0966.

***tert*-Butyl 4-(3,3,3-trifluoro-1-methoxypropyl)benzylcarbamate (3s).**



Yield 168 mg (84%). Colorless oil. R_f 0.39 (EtOAc/hexane = 1/3).

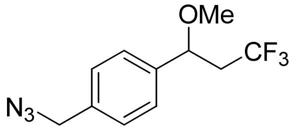
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.33–7.24 (m, 4H), 5.06 (br s, 1H), 4.44 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.32 (br s, 2H), 3.20 (s, 3H), 2.73–2.51 (m, 1H), 2.44–2.22 (m, 1H), 1.46 (br. s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 156.1, 139.5, 139.1, 127.9, 126.8, 125.7 (q, *J* = 277.3 Hz), 79.6 (br), 77.6 (q, *J* = 3.3 Hz), 56.6, 44.3 (br), 42.2 (q, *J* = 27.5 Hz), 28.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{16}H_{22}F_3NNaO_3$ (M+Na): 356.1444. Found: 356.1436.

1-[4-(Azidomethyl)phenyl]-3,3,3-trifluoropropyl methyl ether (3t).



Yield 129 mg (83%). Colorless oil. R_f 0.52 (CH_2Cl_2).

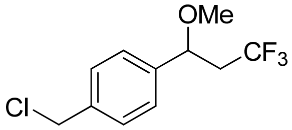
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37 (s, 4H), 4.50 (dd, *J* = 8.4, 4.2 Hz, 1H), 4.38 (s, 2H), 3.25 (s, 3H), 2.78–2.57 (m, 1H), 2.48–2.28 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 140.3, 135.8, 128.7, 127.1, 125.7 (q, *J* = 277.4 Hz), 77.6 (q, *J* = 3.3 Hz), 56.8, 54.5, 42.3 (q, *J* = 27.6 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{11}H_{12}F_3N_3NaO$ (M+Na): 282.0825. Found: 282.0814.

1-[4-(Chloromethyl)phenyl]-3,3,3-trifluoropropyl methyl ether (3u).



Yield 102 mg (67%). Colorless oil. R$_f$ 0.70 (CH_2Cl_2).

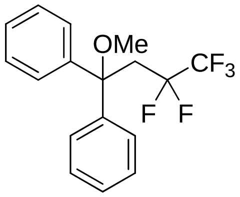
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.62 (s, 2H), 4.50 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.25 (s, 3H), 2.78–2.55 (m, 1H), 2.48–2.27 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 140.5, 137.8, 129.1, 127.0, 125.7 (q, *J* = 277.5 Hz), 77.6 (q, *J* = 2.8 Hz), 56.8, 45.8, 42.3 (q, *J* = 27.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –64.5 (t, *J* = 10.6 Hz).

HRMS (ESI): Calcd for $C_{11}H_{12}ClF_3NaO$ (M+Na): 275.0421. Found: 275.0424.

(3,3,4,4,4-Pentafluoro-1-methoxy-1-phenylbutyl)benzene (4a).



According to the General procedure using complex **1f**; for the work-up, hexane was used. Yield 186 mg (94%). Colorless crystals, Mp 80–81 °C. R$_f$ 0.33 (CH_2Cl_2/hexane = 1/10).

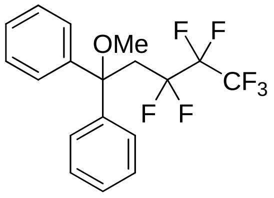
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61–7.25 (m, 10H), 3.30 (t, *J* = 17.6 Hz, 2H), 3.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 144.2, 128.3, 127.4, 126.7, 119.3 (qt, *J* = 286.4, 35.9 Hz), 115.3 (tq, *J* = 257.4, 36.8 Hz), 80.4, 51.1, 34.4 (t, *J* = 19.1 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –87.5 (s, 3F), –117.6 (t, *J* = 18.0 Hz, 2F).

HRMS (ESI): Calcd for $C_{17}H_{15}F_5NaO_3$ (M+Na): 353.0935. Found: 353.0931.

(3,3,4,4,5,5,5-Heptafluoro-1-methoxy-1-phenylpentyl)benzene (4b).



According to the General procedure using complex **1g**; for the work-up, hexane was used. Yield 217 mg (95%). Colorless crystals. Mp 72–73 °C. R$_f$ 0.25 (CH_2Cl_2/hexane = 1/10).

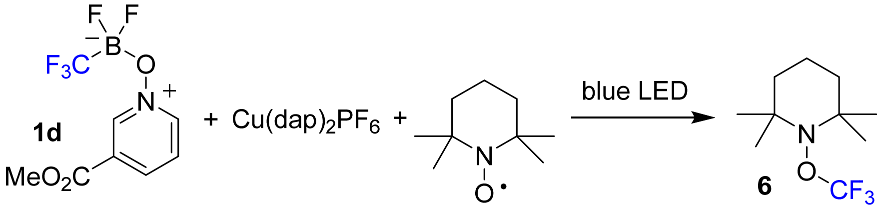
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.55–7.29 (m, 10H), 3.33 (t, *J* = 18.2 Hz, 2H), 3.25 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$), δ: 144.3, 128.3, 127.4, 126.7, 118.1 (qt, *J* = 287.5, 34.0 Hz), 117.5 (tt, *J* = 258.7, 30.1 Hz), 109.0 (ts, *J* = 264.3, 37.6 Hz), 80.5, 51.1, 34.1 (t, *J* = 19.1 Hz).

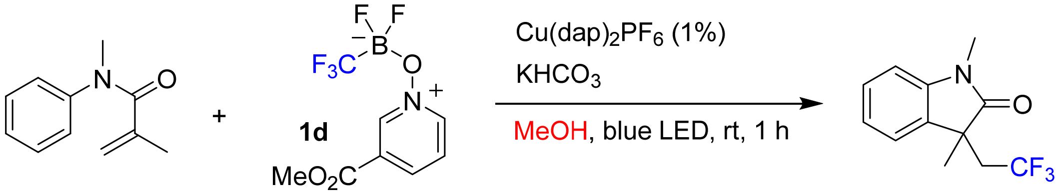
^{19}F NMR (282 MHz, $CDCl_3$) δ: –80.9 (t, *J* = 9.5 Hz, 3F), –114.4 (m, 2F), –128.6 (m, 2F).

HRMS (ESI): Calcd for $C_{18}H_{15}F_7NaO_3$ (M+Na): 403.0903. Found: 403.0892.

Trapping experiments.



Complex **1d** (42.5 mg, 0.157 mmol, 1.31 equiv) was added to a stirred mixture of Cu(dap)$_2$PF$_6$ (121 mg, 0.122 mmol, 1.01 equiv), $KHCO_3$ (40 mg, 0.40 mmol, 3.3 equiv), and TEMPO (18.8 mg, 0.120 mmol) in MeOH (1.2 mL), and the reaction mixture was irradiated with blue LED with stirring and cooling with tap water for 1 hour. Then, $PhCF_3$ was added (22.5 mg, 0.154 mmol) as an internal standard, the precipitate was allowed to settle down and a part of solution (ca. 0.6 mL) was taken, and analyzed by ^{19}F NMR. Compound **6** (79% yield), ^{19}F NMR (282 MHz, MeOH) δ: –57.1 (s).[23]



1,3-Dimethyl-3-(2,2,2-trifluoroethyl)-1,3-dihydro-2*H*-indol-2-one.[24]

According to the General procedure (see page S8) using *N*-methacryloyl-*N*-methylaniline instead of arylalkene).

Yield 33 mg (23 %). Colorless oil. Chromatography (CH_2Cl_2 to EtOAc/CH_2Cl_2, 1/10). R_f = 0.45 (EtOAc/CH_2Cl_2, 1/19).

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37–7.24 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 2H), 3.24 (s, 3H), 2.92–2.57 (m, 2H), 1.41 (s, 3H).

^{19}F NMR (282 MHz, $CDCl_3$) δ: –62.7 (t, *J* = 10.6 Hz; 3F).

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[23] Yu, Q.; Ma, S. *Chem. Eur. J.* **2013**, *19*, 13304–13308.

[24] Kawamura, S.; Sodeoka, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 8740–8743.

Cyclic voltammetry.

Voltammetric studies were carried out using with the scan rate 0.1 V·s^{-1} in a temperature-controlled (25 °C) cell (V = 5 mL) under a nitrogen atmosphere. A glassy-carbon (GC) disk (*d* = 2 mm) was used as the working electrode. A saturated calomel electrode (SCE) separated from the solution being studied by a salt bridge filled with the supporting electrolyte (0.05 M Et_4NClO_4 in methanol) was used as the reference electrode. A platinum plate (S = 3 cm^2) was used as the counter electrode. The GC electrode was polished before each measurement. All experiments were performed with the concentration of a studied compound of 1 mM in methanol.

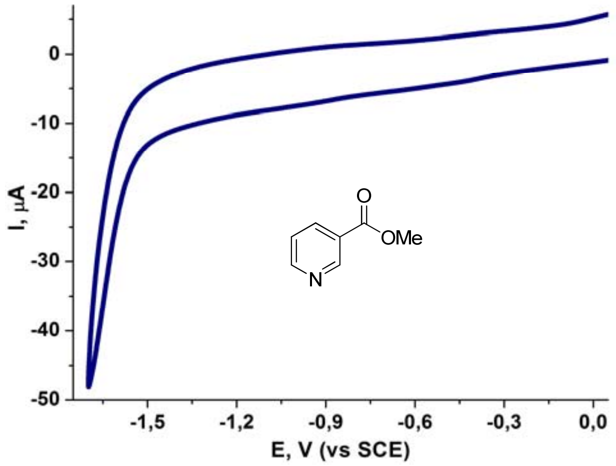

Figure S3. Methyl nicotinate (initial cathodic scan). E$_{red}$ < –1.7 V (supporting electrolyte discharge) (lit. ~ – 2.4 V[25]).

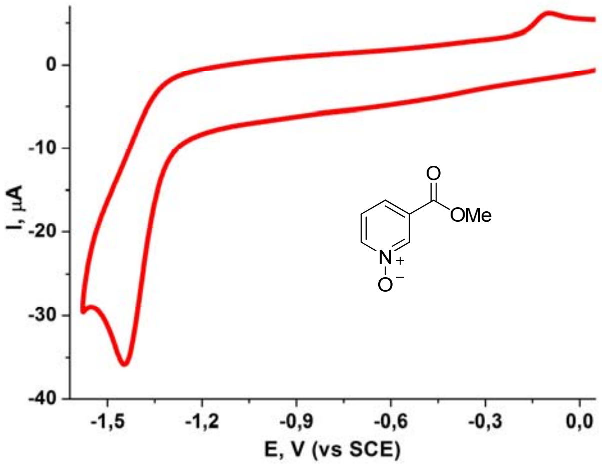

Figure S4. 3-(Methoxycarbonyl)pyridine 1-oxide (initial cathodic scan). E$_{red}$ = –1.45 V.

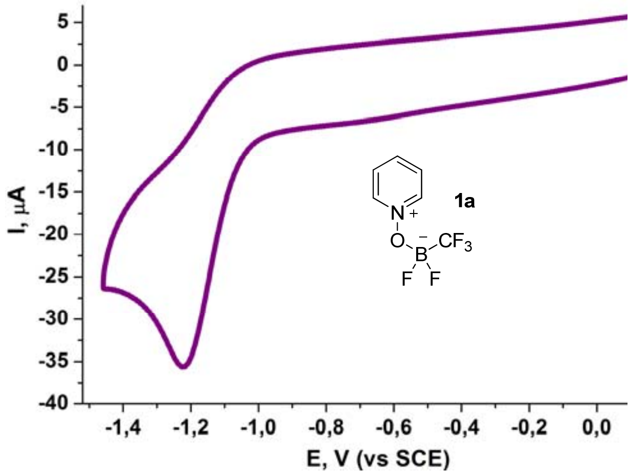

Figure S5. Compound**1a** (initial cathodic scan). E$_{red}$ = –1.22 V.

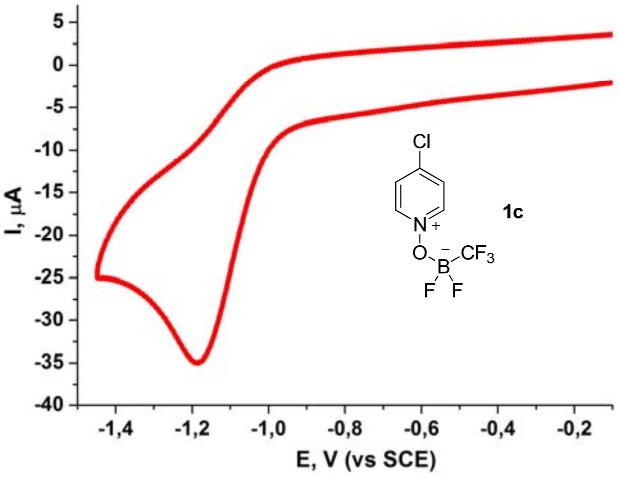

Figure S6. Compound **1c** (initial cathodic scan). E$_{red}$ = –1.18 V.

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[25] Sevov, C. S.; Brooner, R. E. M.; Chenard, E.; Assary, R. S.; Moore, J. S.; Rodriguez-Lopez, J.; Sanford, M. S. *J. Am. Chem. Soc.* **2015**, *137*, 14465–14472.

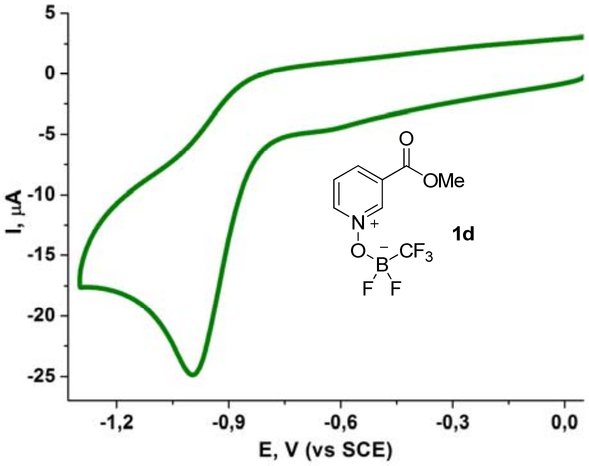

Figure S7. Compound **1d** (initial cathodic scan). E$_{red}$ = –1.01 V.

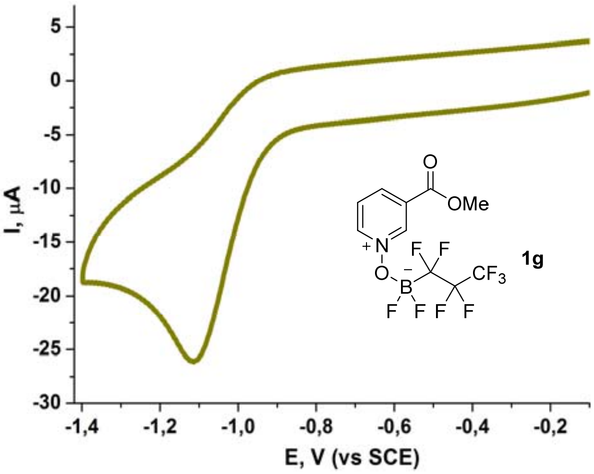

Figure S8. Compound **1g** (initial cathodic scan). E$_{red}$ = –1.11 V.

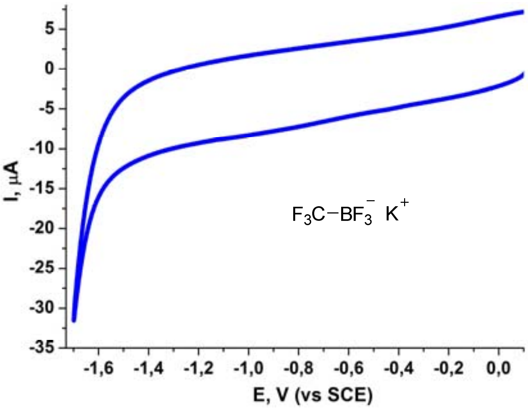

Figure S9. Potassium trifluoro(trifluoromethyl)-borate (initial cathodic scan). E$_{red}$ < –1.70 V (supporting electrolyte discharge).

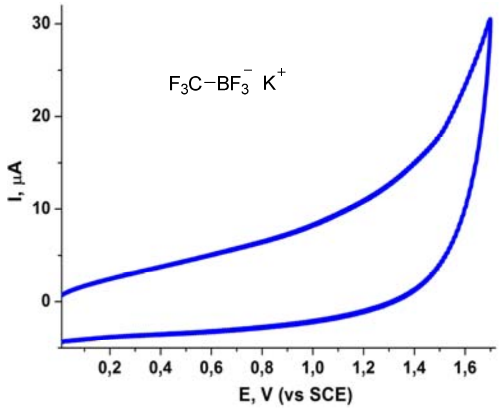

Figure S10. Potassium trifluoro(trifluoromethyl)borate (initial cathodic scan). E$_{ox}$ > +1.70 V (supporting electrolyte discharge).

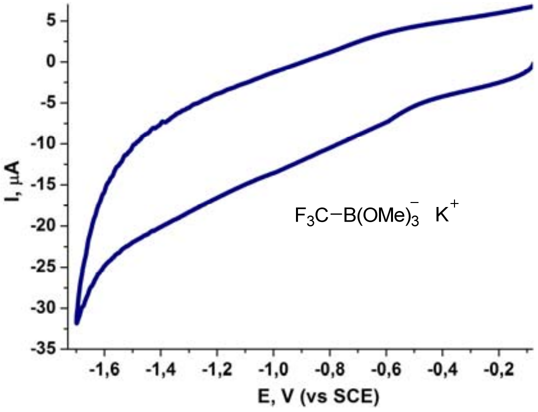

Figure S11. Potassium trimethoxy(trifluoromethyl)-borate (initial cathodic scan). E$_{red}$ < –1.70 V (supporting electrolyte discharge).

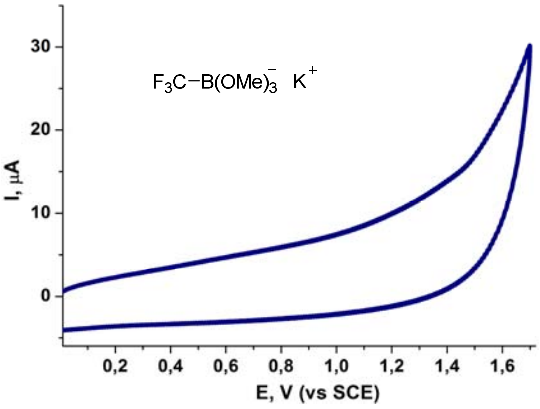

Figure S12. Potassium trimethoxy(trifluoromethyl)-borate (initial anodic scan). E$_{ox}$ > +1.70 V (supporting electrolyte discharge).

For $Cu(dap)_2^+$, the potential of Cu(II)/Cu(I) is determined by the mean value of oxidation and reoxidation peaks. For $Cu(dap)_2PF_6$, the initial oxidation potential is significantly shifted owing to solubility issues. Therefore, data for $Cu(dap)_2Cl$ were taken for the description of electrochemical properties of the cation $Cu(dap)_2^+$. The determined potential of Cu(II)/Cu(I) couple of 0.65 V (in methanol) is very close to the literature value of 0.62 V in acetonitrile.[26] This also suggests that electrochemical properties of $Cu(dap)_2^+$ should not depend on solvent.

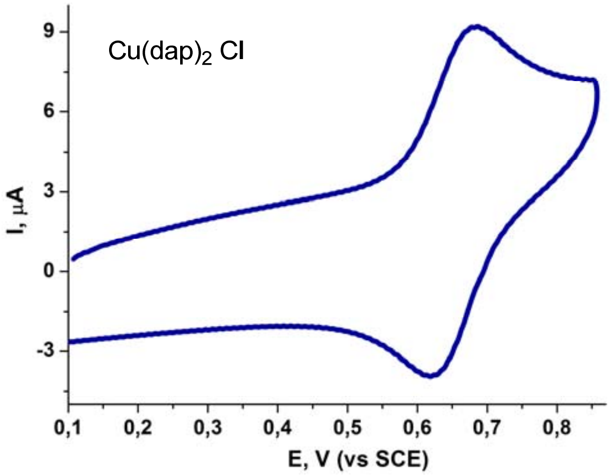

Figure S13. $Cu(dap)_2Cl$ (initial anodic scan). E_{ox} = +0.68 V, E_{reox} = +0.62 V.

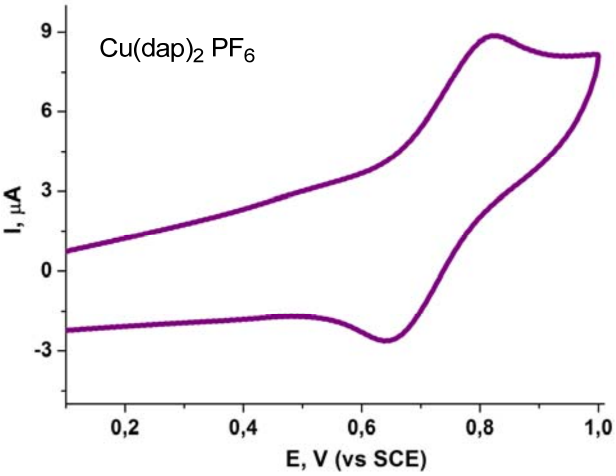

Figure S14. $Cu(dap)_2PF_6$ (initial anodic scan). E_{ox} = +0.82 V, E_{reox} = +0.64 V.

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[26] Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 546–548.

Quantum yield determination

Calibration of the light source.

The photon flux of the light source for quantum yield determination was determined by standard ferrioxalate actinometry[27] with 0.15 M solution in 0.05 M aqueous sulfuric acid as actinometer. A buffered solution of 1,10-phenanthroline was prepared by dissolution of phenanthroline hydrate (200 mg, 1.0 mmol), sodium acetate (246 mg, 3.0 mmol) and acetic acid (0.23 mL, 4.0 mmol) in water (adjusted to 6 mL). Solutions were stored in the dark, and all manipulations with ferrioxalate solution were performed in dull red light. To determine the photon flux, ferrioxalate solution (2.5 mL) was irradiated with stirring in a standard 1-cm quartz cuvette for 600 seconds with blue 10W LED (λ_{max} = 460 nm, spectra is given in Figure S15). Light from LED was passed through 8-mm round aperture in a screen placed right before the cuvette. After irradiation, the content of the cuvette was transferred to a 100-mL measuring flask and the cuvette was rinsed with distilled water (ca 50 mL). Then, phenanthroline buffered solution was added (0.50 mL) and total volume was adjusted to 100 mL with water. The resulting solution was allowed to stand for 20 minutes in the dark, and its absorbance at 510 nm was measured. Control measurement after 15 hours in the dark showed no change in absorbance indicating that under the applied conditions: (a) developing with phenanthroline was complete within 20 minutes, and (b) no $Fe(phen)_3^{2+}$ is formed as a result of side dark reactions of unreacted ferrioxalate. Additionally, the determined content of $Fe(phen)_3^{2+}$ indicated that phenanthroline was indeed used in excess and is not exhausted in the complexation reaction. Control dark sample was prepared in the same way excluding exposure to the light source.

Data processing

Correction for non-monochromaticy of the light source and for incomplete absorption

The quantum yield of the light-induced ferrioxalate decomposition was reported to vary insignificantly over the wavelength region that was used,[27c] and it was taken as a constant value of 1.1. Figure S15 illustrates the derivation of the correction for incomplete absorption. The fraction of photons from the light source absorbed by the sample (f) can be derived from the areas under black (S_{black}) and green (S_{green}) lines: $f = 1–(S_{green}/S_{black})$, f = 0.835.

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[27] (a) Parker, C. A. *Proc. Royal Soc. A* **1953**, *220*, 104–116. (b) Hatchard, C. G.; Parker, C. A. *Proc. Royal Soc. A* **1956**, *235*, 518–536. (c) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* **2004**, *76*, 2105–2146.

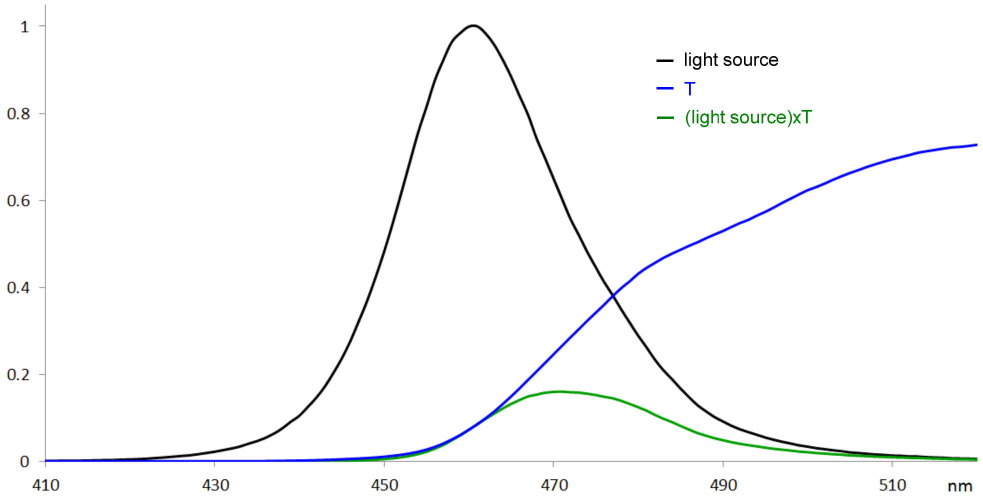


Figure S15. Correction for incomplete absorption. Black line shows the spectrum of the light source normalized to its maximum. Blue line is the transmittance (T) of the sample. Green line shows the spectrum of the light from the light source passed through the sample.

Photon flux determination

With the known molar absorptivity for $Fe(phen)_3^{2+}$ $\varepsilon(510)=11100$ ($M^{-1}\cdot cm^{-1}$),[27c] the amount of Fe^{2+} formed under irradiation was determined as

$$n(Fe^{2+}) = (\Delta A*V)/(L*\varepsilon)$$

where ΔA is the difference between absorbances of irradiated and dark samples, V is the measuring flask volume (0.100 L), and L is the light path length (1.00 cm), and photon flux was determined as

$$flux = n(Fe^{2+})/(\Phi*t*f)$$

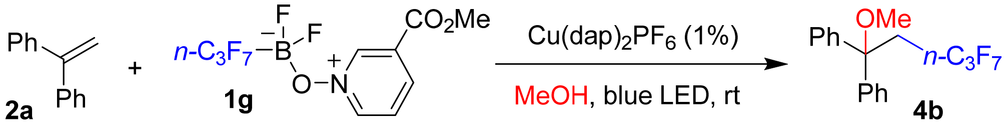
where Φ is quantum yield of ferrioxalate decomposition (1.1), t is the irradiation time (10 min = 600 sec) and f = 0.835 is the correction for incomplete absorption. The results of three independent experiments are summarized in Table S1.

Table S1. Photon flux determination.

run	A(510)	delta A	$[Fe^{2+}]$, mol/L	Fe^{2+} amount (μmole)	flux, μeinstein/min
dark	0.100224	0		0	0
#1	0.493101	0.392877	3.53943E-05	3.539430756	0.38548
#2	0.5114	0.411176	3.70429E-05	3.704288978	0.403435
#3	0.514276	0.414052	3.7302E-05	3.730197242	0.406256
mean				3.657972325	0.39839
deviation				0.10347409	0.011269

Quantum yield for the perfluoroalkylation reaction.

The following process was studied:



Then reaction was performed in a sealed screw-capped quartz cuvette under argon using triacetoneamine as a proton scavenger and in the presence of menthol as internal standard for GC yield determination. The complete light absorption (> 99%) over the whole light source spectrum was checked prior to irradiation.

Borate complex **1g** (230 mg, 0.620 mmol), menthol (80.1 mg, 0.512 mmol), triacetoneamine (110.4 mg, 0.638 mmol), 1,1-diphenylethylene (81.6 mg, 0.453 mmol), Cu(dap)$_2$PF$_6$ (4.8 mg, 0.0048 mmol) and MeOH (3.0 ml) were mixed under argon with stirring in the dark and the resulting mixture was transferred under argon with a syringe into 1-cm quartz cuvette containing a stirring bar. The cuvette was sealed with a silicon cap and irradiated with light source of known photon flux with stirring. To determine the amount of the product formed, aliquots (approximately 50 μL) of the reaction mixture were taken with a microsyringe every 30 minutes and quenched by pouring into a mixture of saturated aqueous sodium bicarbonate (0.150 ml) and hexane (1.2 mL). After vigorous shaking, hexane layer was analyzed by GC, and the product yield was determined by comparison with menthol. The dependence of the product yield from time (in minutes) is shown in Figure S16.

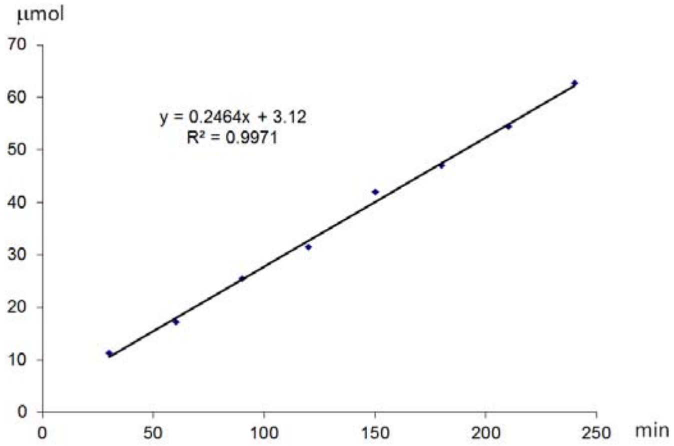
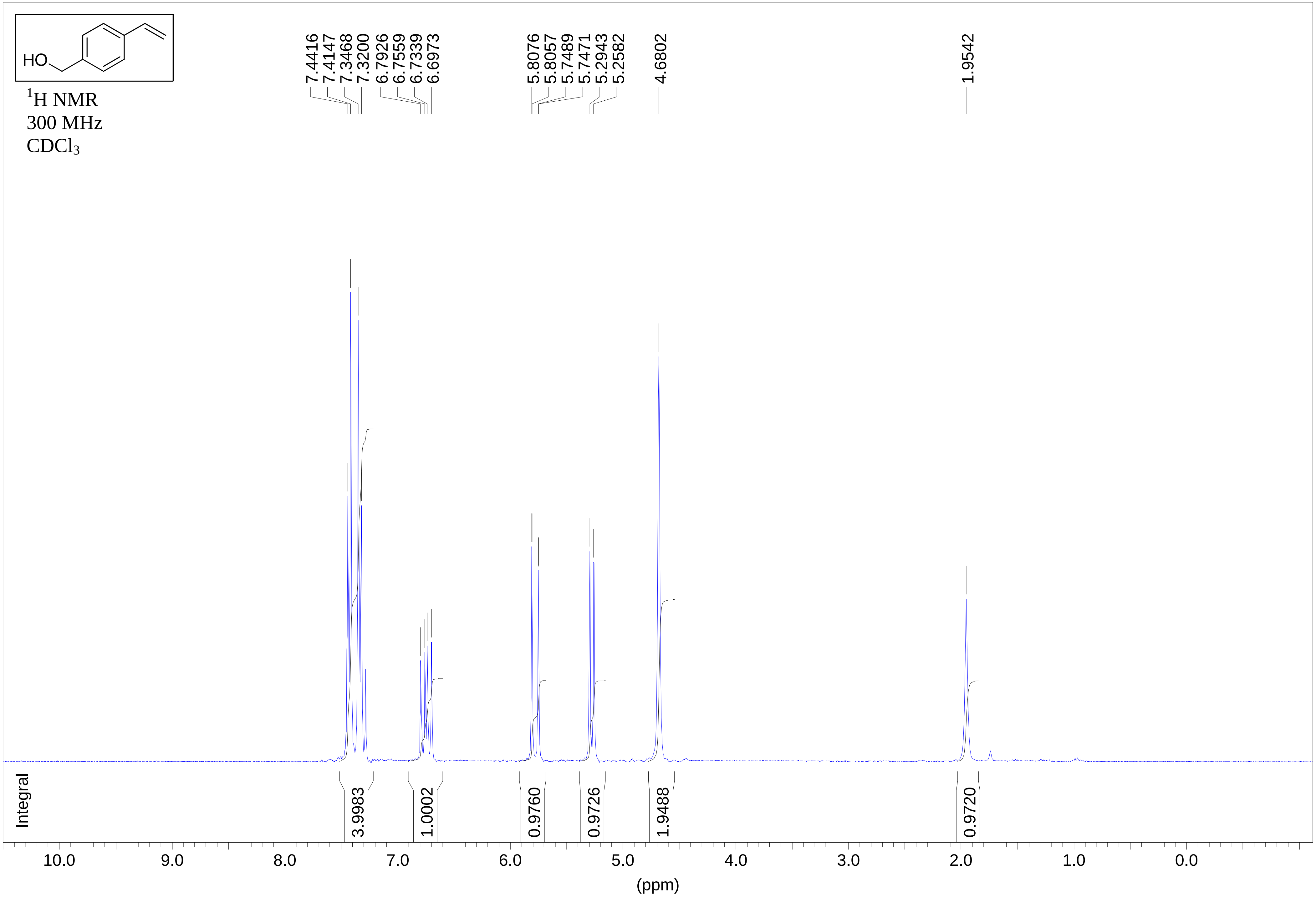


Figure S16. The slope parameter is equal to the reaction rate of 0.246 μmol·min^{-1}.

Quantum yield is derived as follows:

$$\Phi = \frac{\text{moles of product formed}}{\text{einsteins of light absorbed}} = \frac{0.246\ \mu\text{mol}\cdot\text{min}^{-1}}{0.398\ \mu\text{einstein}\cdot\text{min}^{-1}} = 0.62$$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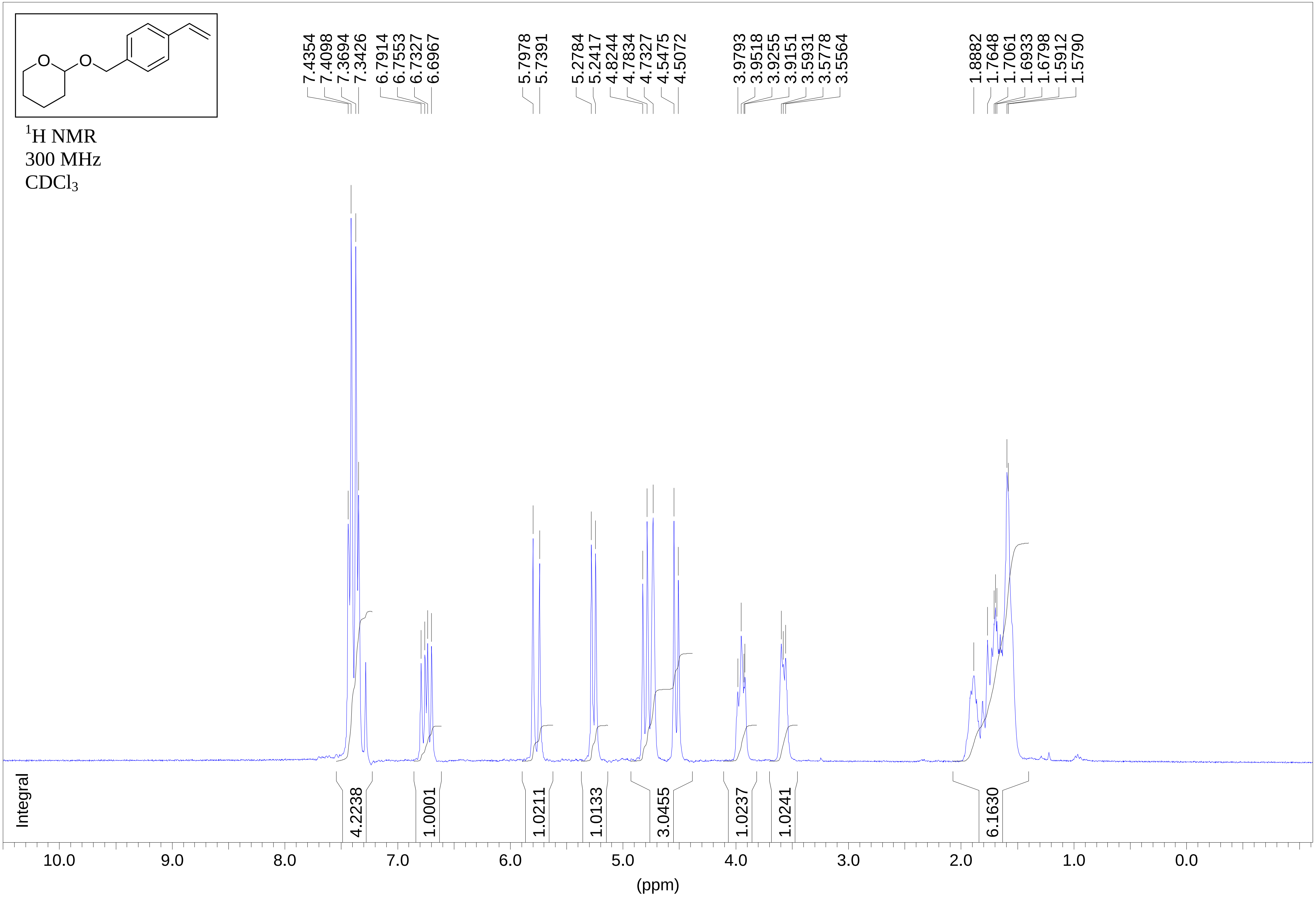
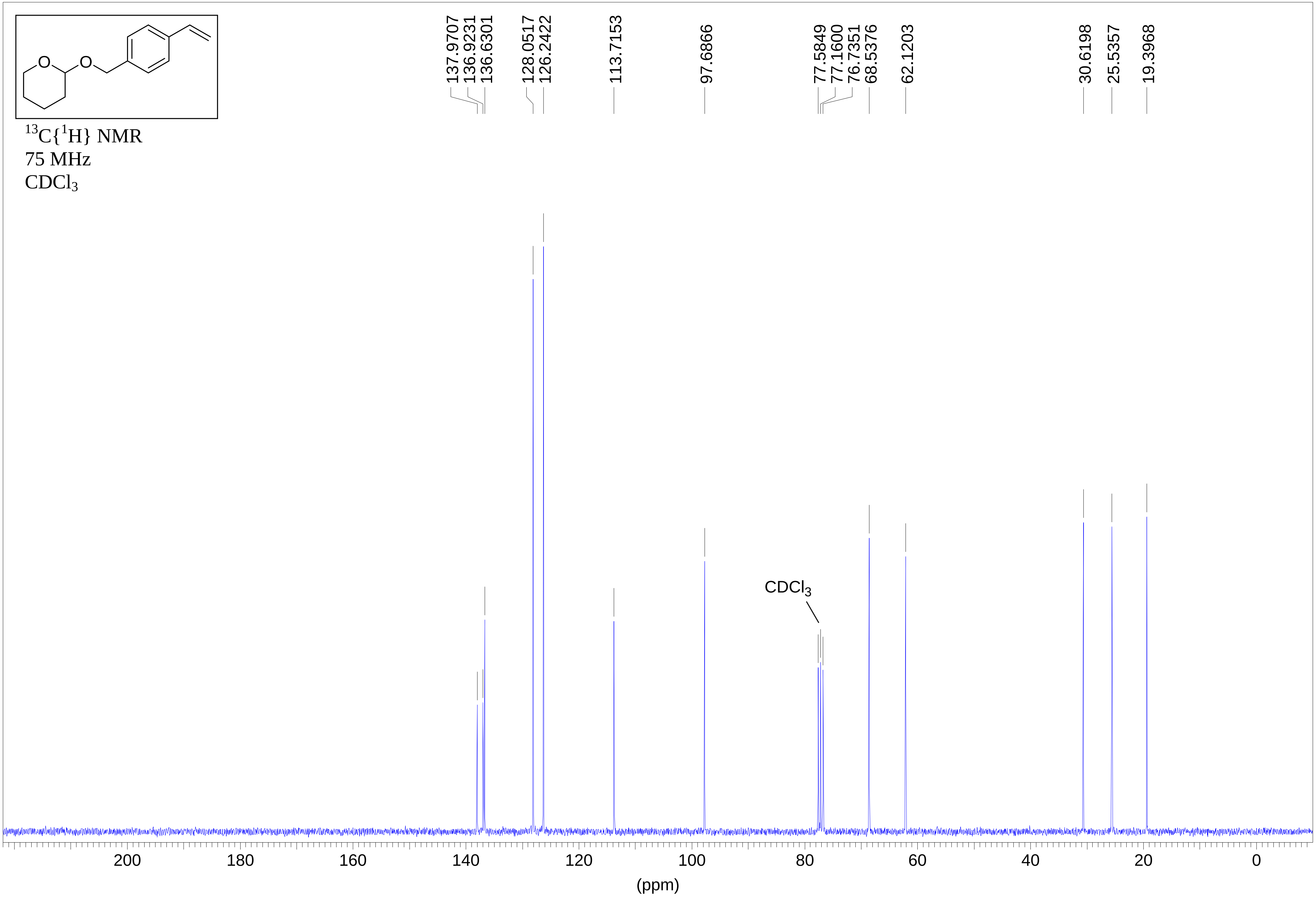
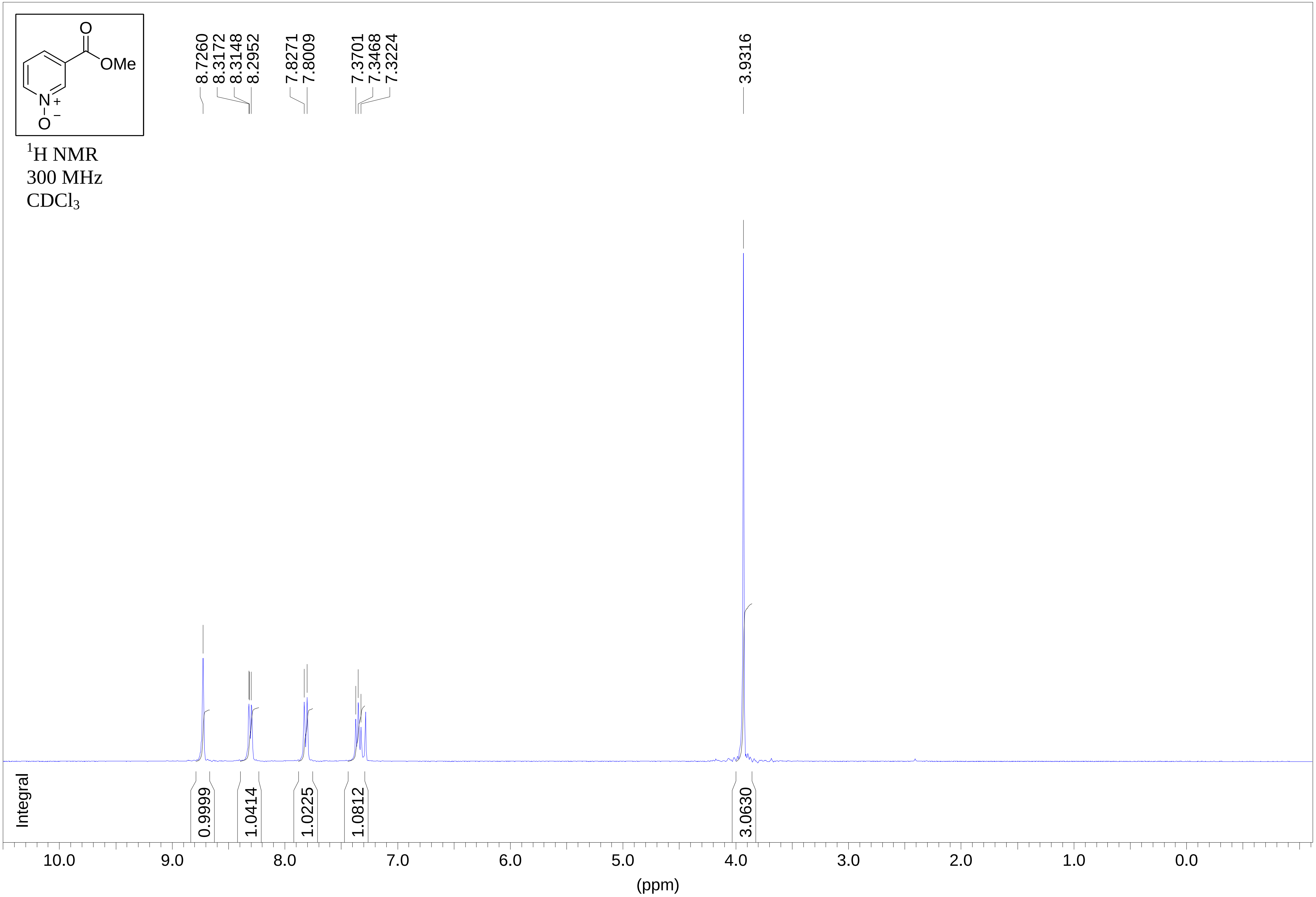
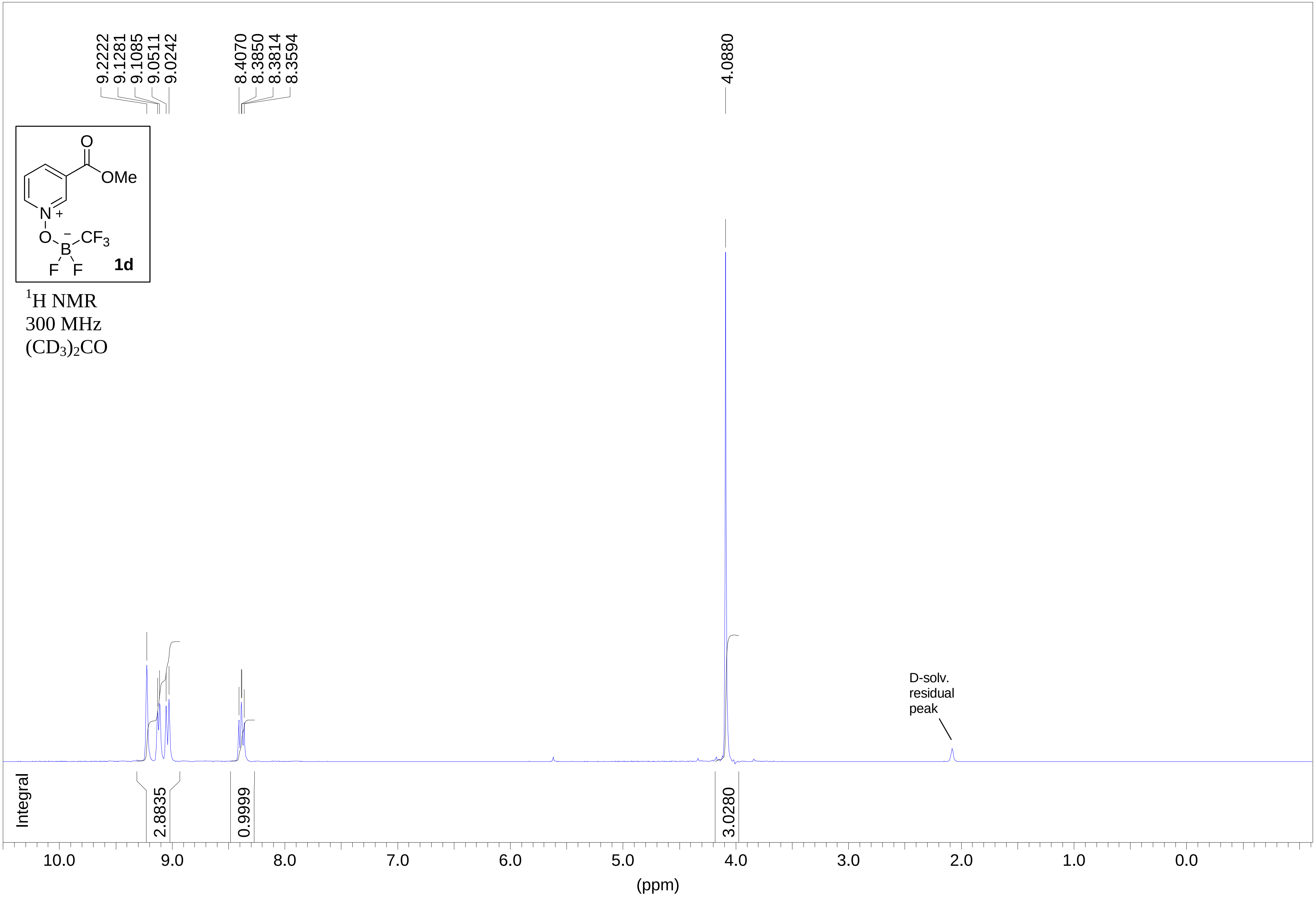
CDCl₃
7.4416
7.4147
7.3468
7.3200
6.7926
6.7559
6.7339
6.6973
5.8076
5.8057
5.7489
5.7471
5.2943
5.2582
4.6802
1.9542
Integral
3.9983
1.0002
0.9760
0.9726
1.9488
0.9720
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

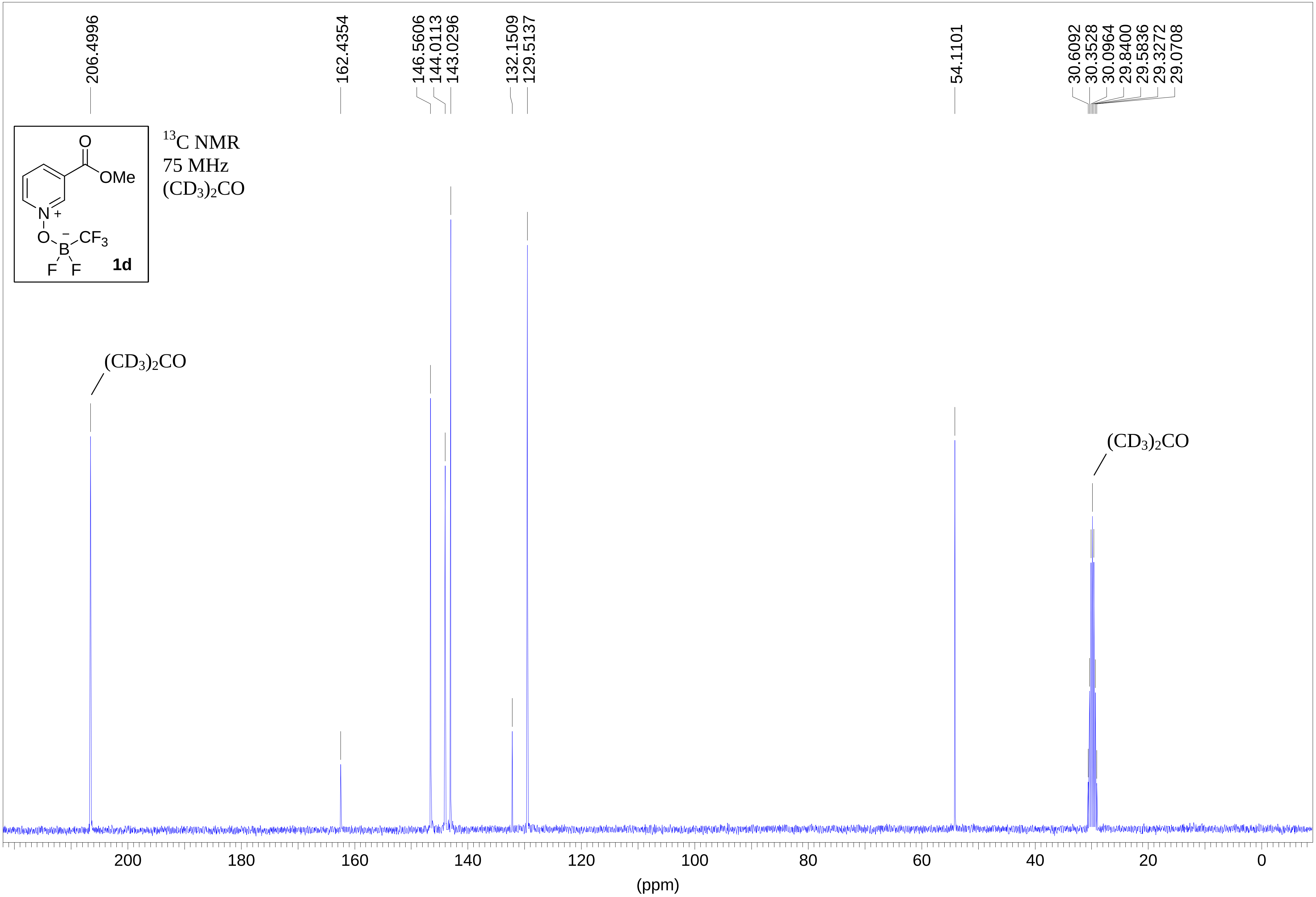


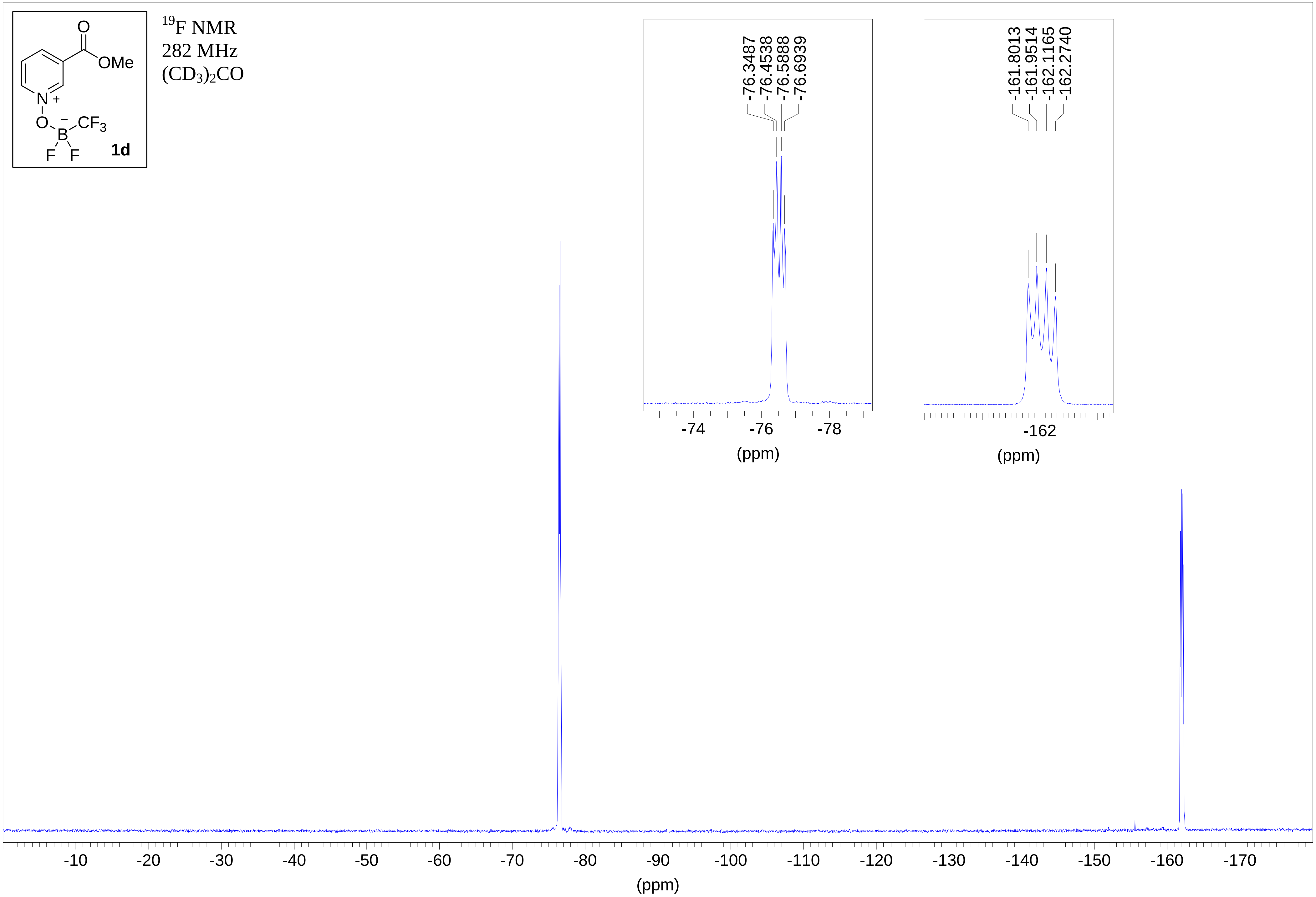
^{1}H NMR
300 MHz
$CDCl_3$
7.4354
7.4098
7.3694
7.3426
6.7914
6.7553
6.7327
6.6967
5.7978
5.7391
5.2784
5.2417
4.8244
4.7834
4.7327
4.5475
4.5072
3.9793
3.9518
3.9255
3.9151
3.5931
3.5778
3.5564
1.8882
1.7648
1.7061
1.6933
1.6798
1.5912
1.5790
Integral
4.2238
1.0001
1.0211
1.0133
3.0455
1.0237
1.0241
6.1630
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


13C{1H} NMR
75 MHz
CDCl3
137.9707
136.9231
136.6301
128.0517
126.2422
113.7153
97.6866
77.5849
77.1600
76.7351
68.5376
62.1203
30.6198
25.5357
19.3968
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)
O
O

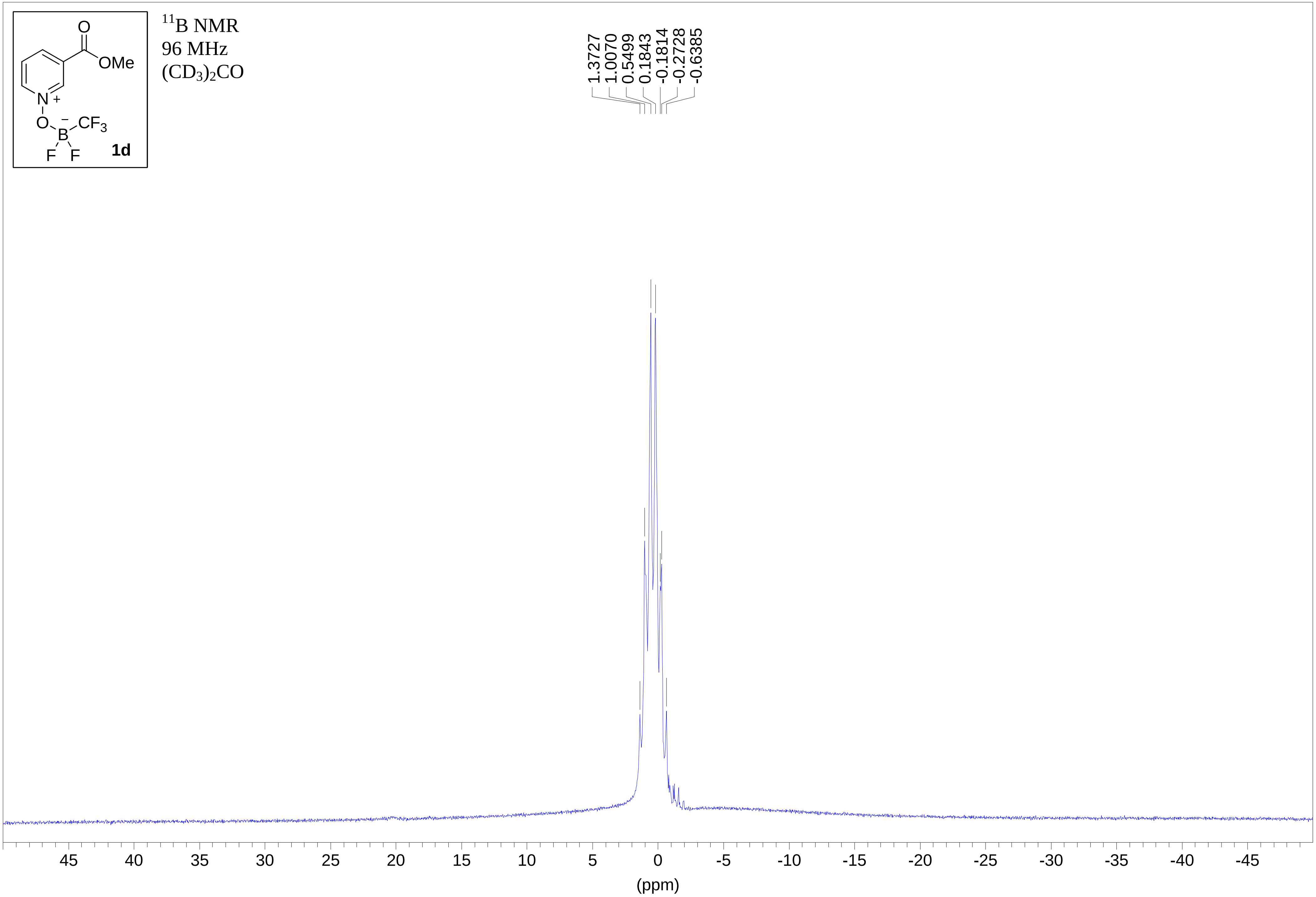

O
OMe
N+
O−
^{1}H NMR
300 MHz
$CDCl_3$
8.7260
8.3172
8.3148
8.2952
7.8271
7.8009
7.3701
7.3468
7.3224
3.9316
Integral
0.9999
1.0414
1.0225
1.0812
3.0630
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


9.2222
9.1281
9.1085
9.0511
9.0242
8.4070
8.3850
8.3814
8.3594
4.0880
O
OMe
N+
O
−
B
CF3
F
F
1d
1H NMR
300 MHz
(CD3)2CO
D-solv.
residual
peak
Integral
2.8835
0.9999
3.0280
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


206.4996
162.4354
146.5606
144.0113
143.0296
132.1509
129.5137
54.1101
30.6092
30.3528
30.0964
29.8400
29.5836
29.3272
29.0708
O
OMe
N+
O
−
B
CF3
F
F
1d
13C NMR
75 MHz
(CD3)2CO
(CD3)2CO
(CD3)2CO
200
180
160
140
120
100
80
60
40
20
0
(ppm)

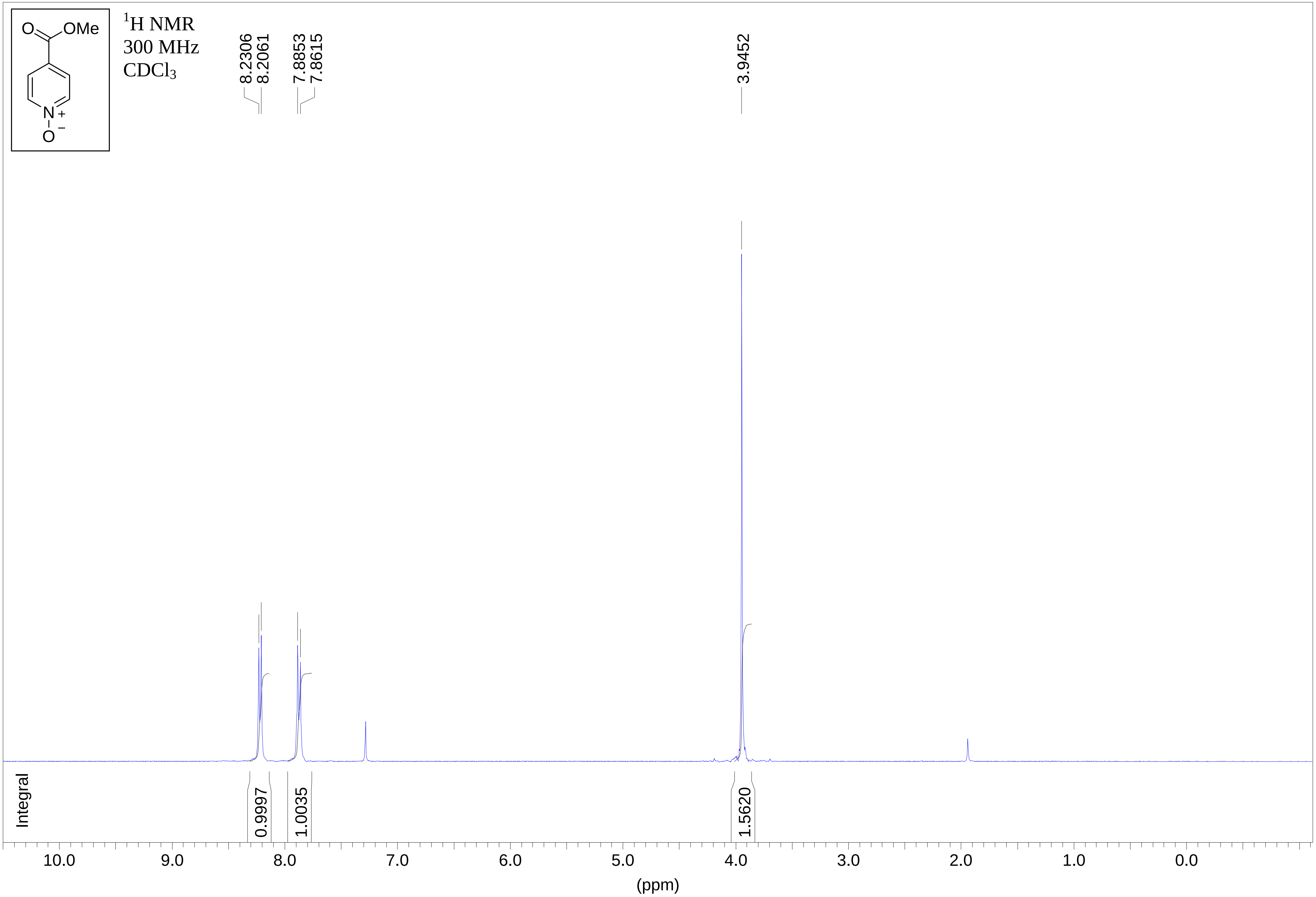


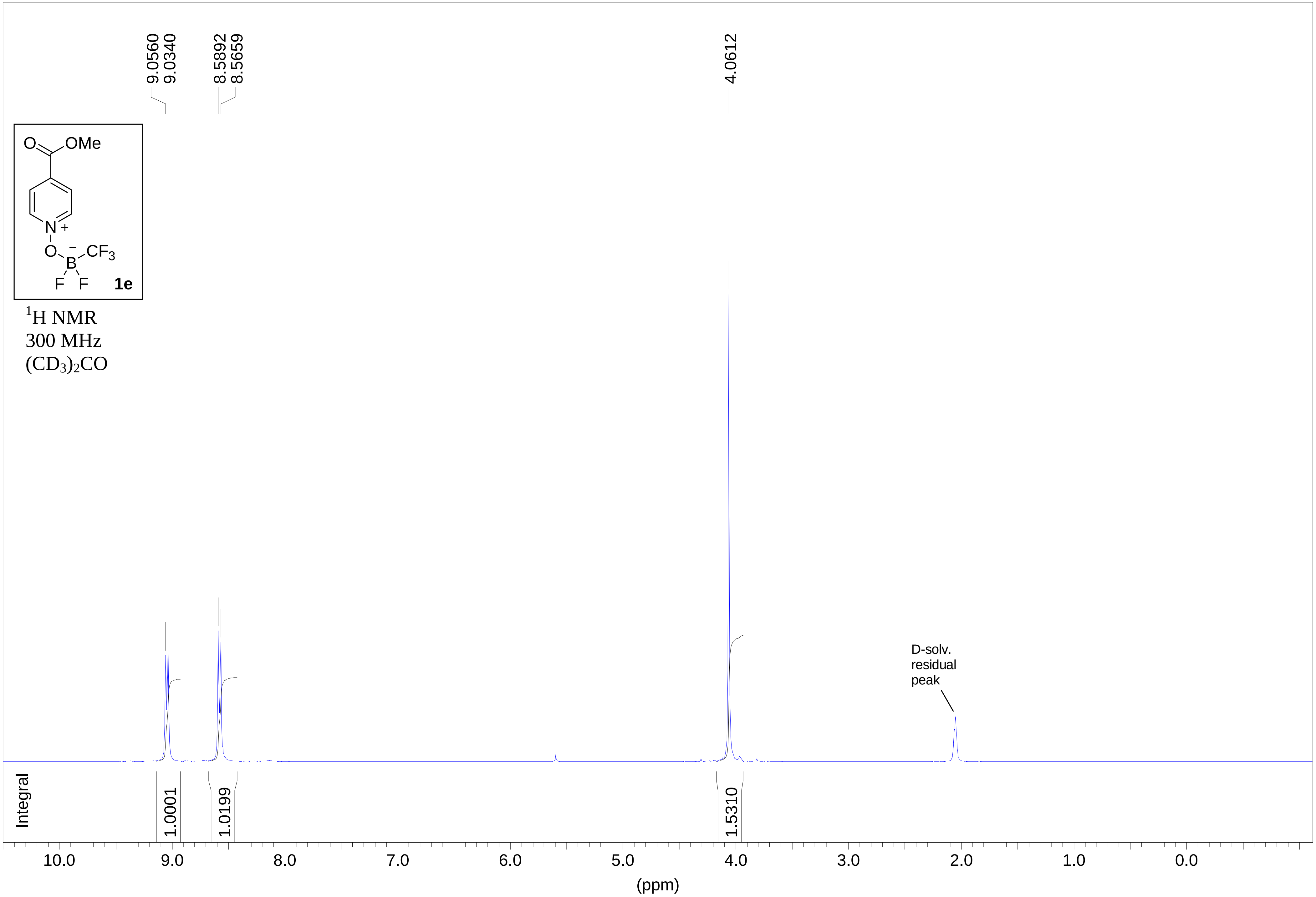
^{19}F NMR
282 MHz
$(CD_3)_2CO$
O
OMe
N+
O
−
B
CF_3
F
F
1d
-76.3487
-76.4538
-76.5888
-76.6939
-74
-76
-78
(ppm)
-161.8013
-161.9514
-162.1165
-162.2740
-162
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
(ppm)

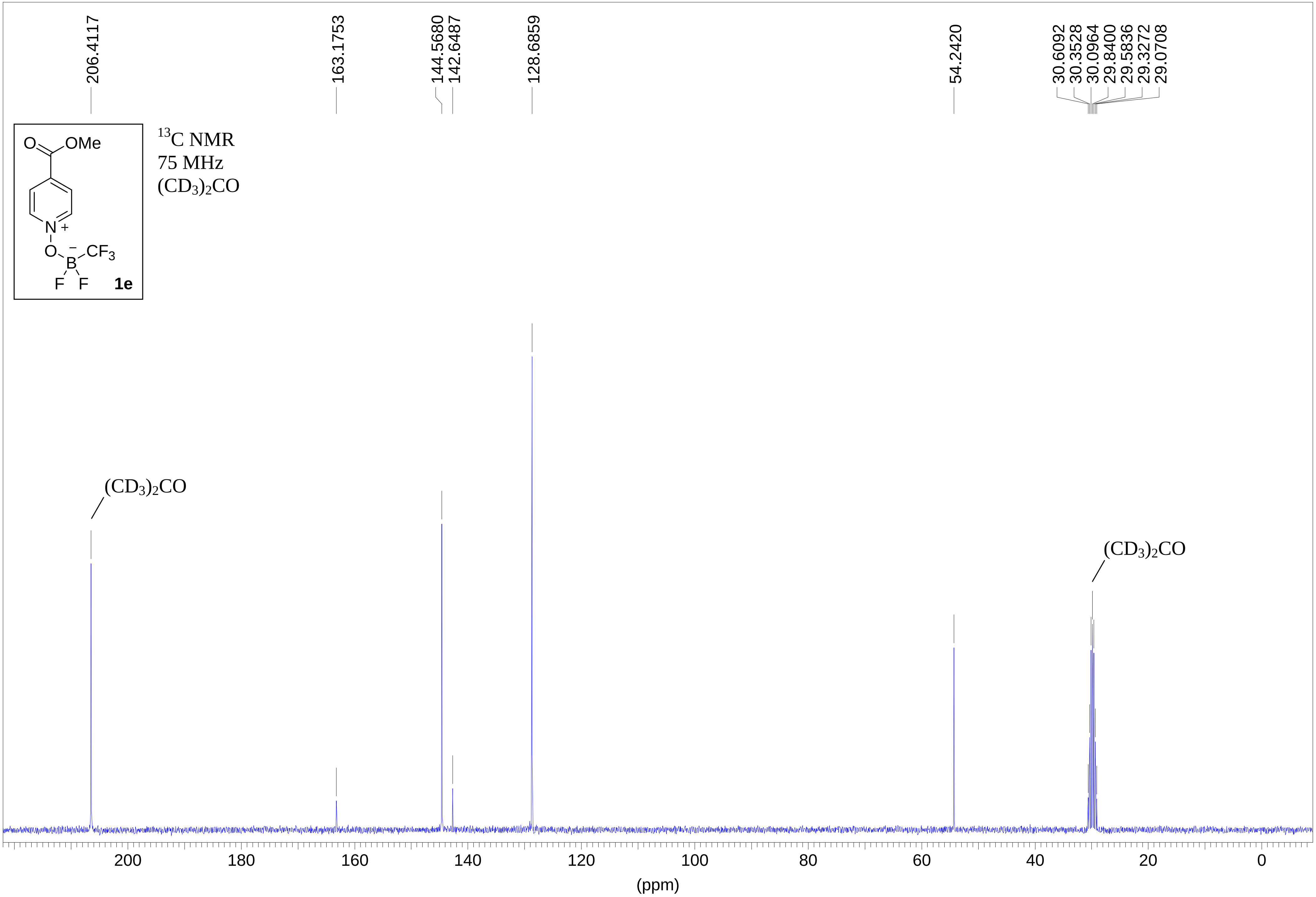


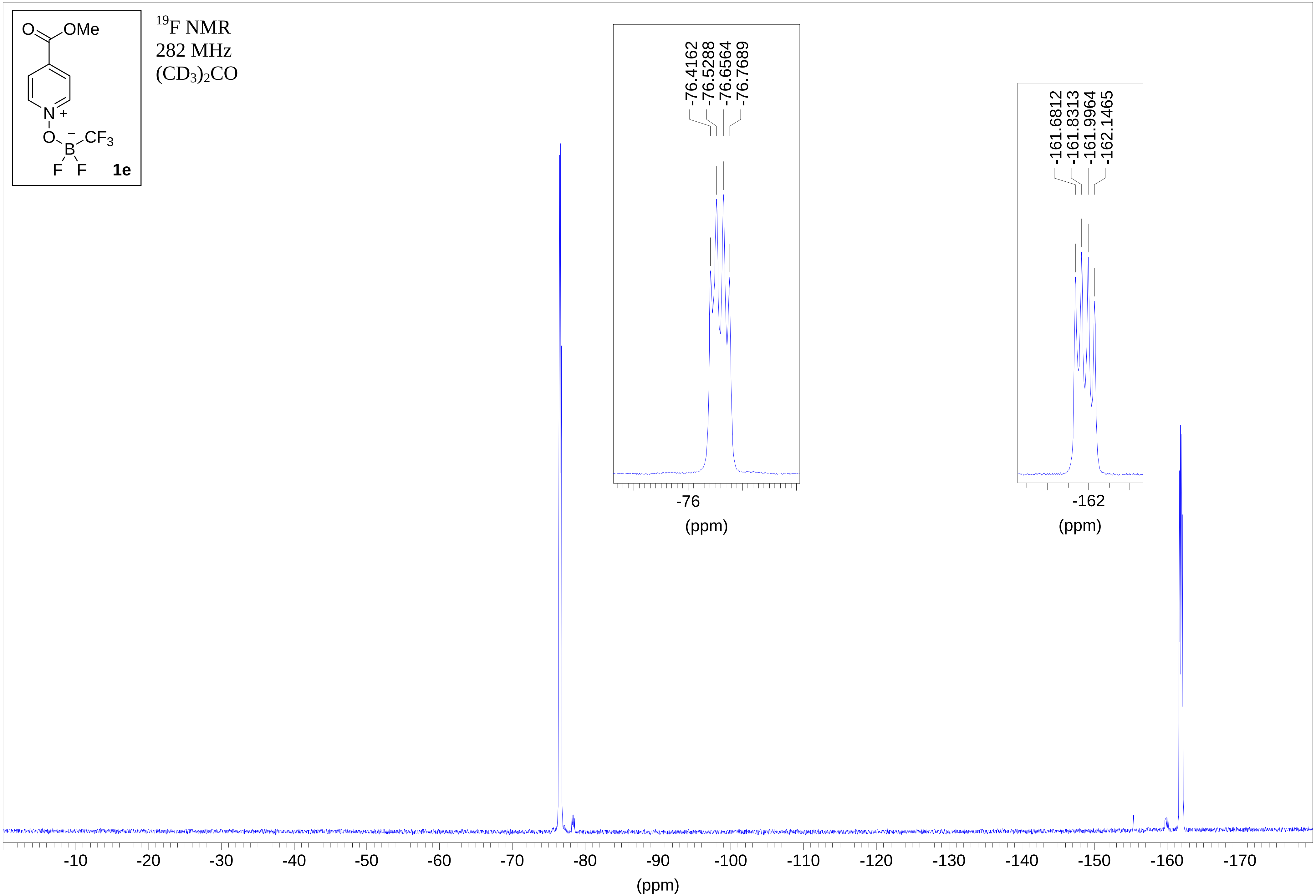
1d

^{11}B NMR
96 MHz
$(CD_3)_2CO$
1.3727
1.0070
0.5499
0.1843
-0.1814
-0.2728
-0.6385
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
(ppm)


O
OMe
N+
O−
1H NMR
300 MHz
CDCl3
8.2306
8.2061
7.8853
7.8615
3.9452
Integral
0.9997
1.0035
1.5620
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

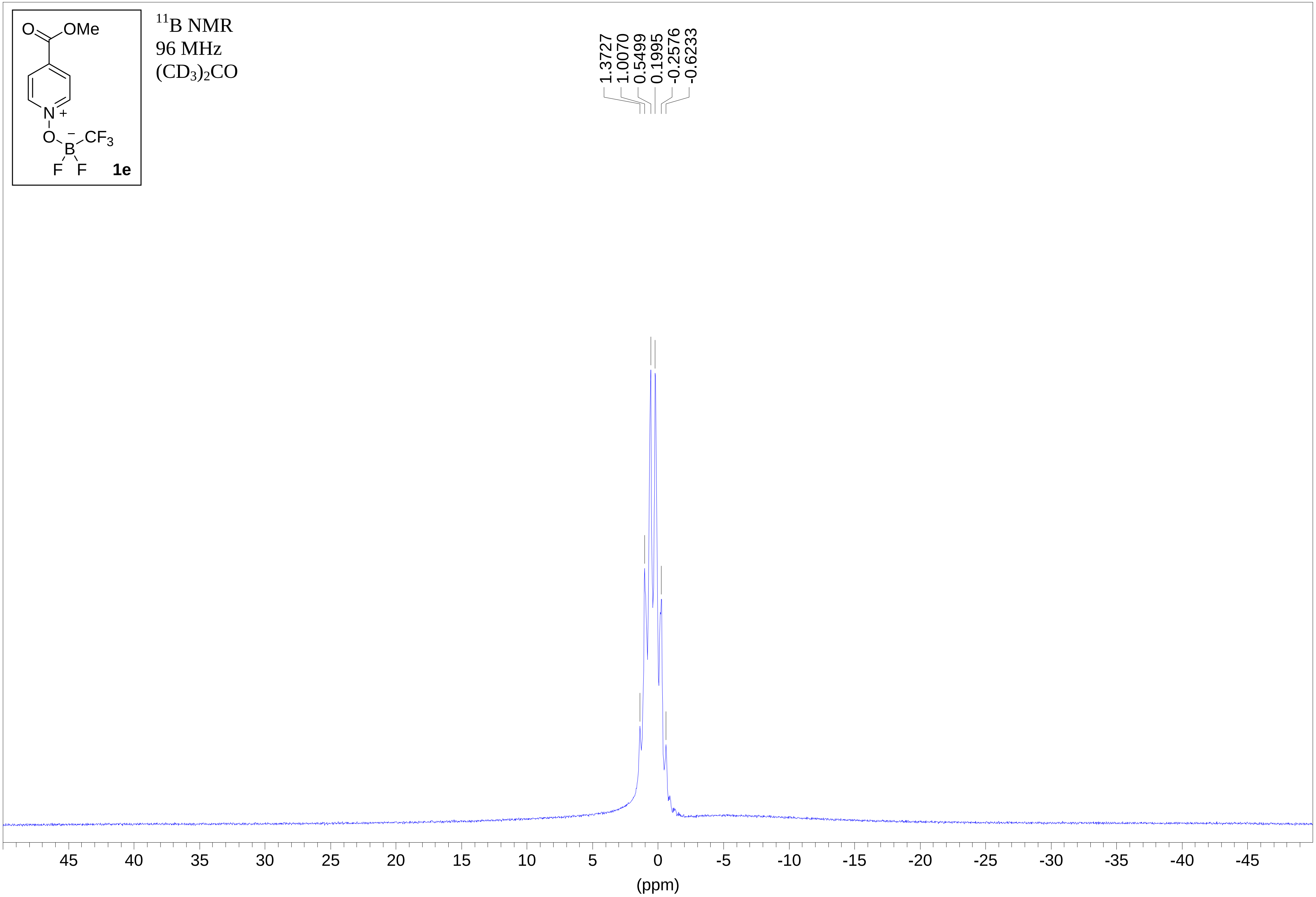

9.0560
9.0340
8.5892
8.5659
4.0612
O
OMe
N+
O
−
B
CF3
F
F
1e
1H NMR
300 MHz
(CD3)2CO
D-solv. residual peak
Integral
1.0001
1.0199
1.5310
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

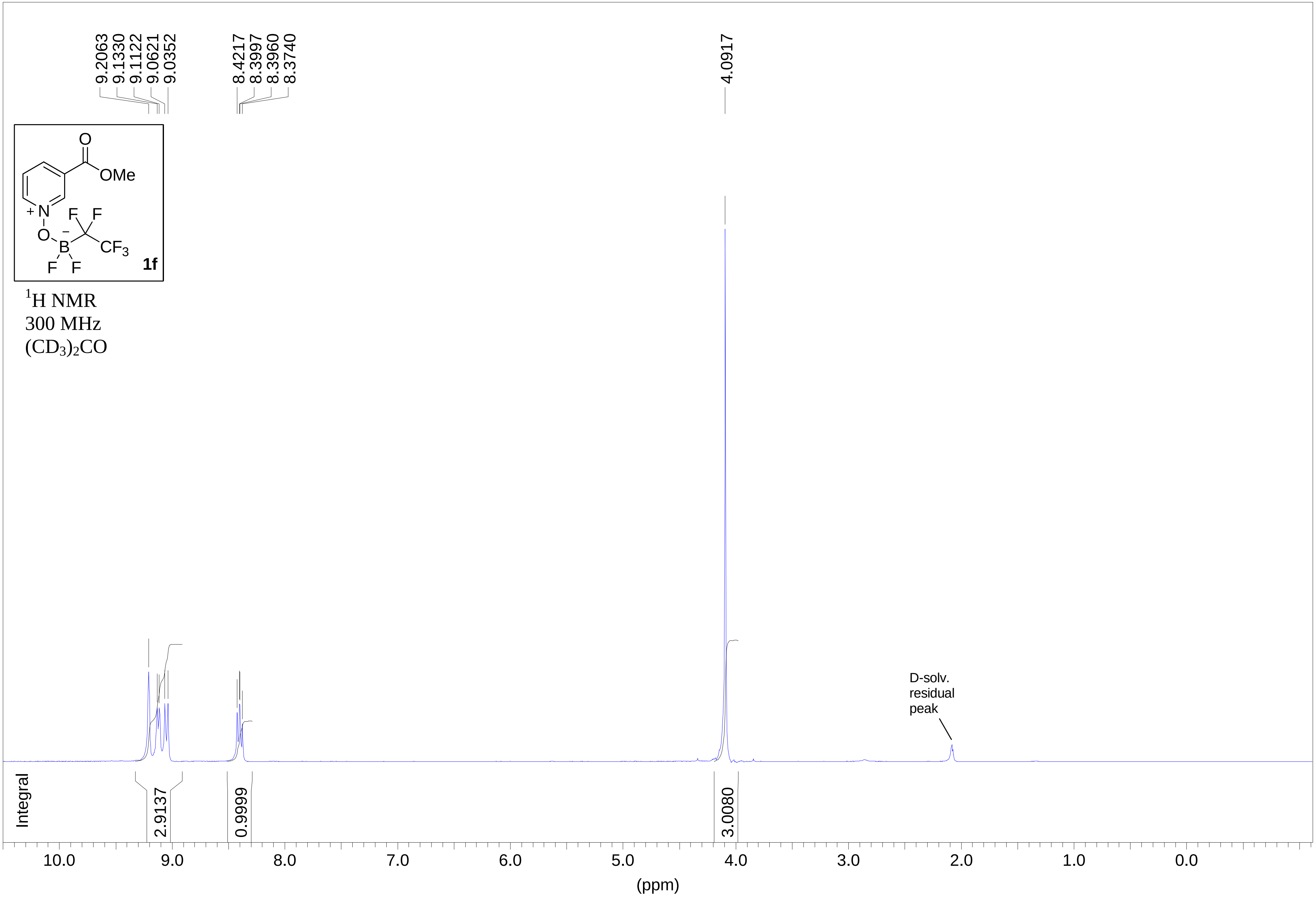

206.4117
163.1753
144.5680
142.6487
128.6859
54.2420
30.6092
30.3528
30.0964
29.8400
29.5836
29.3272
29.0708
O
OMe
N+
O
−
B
CF3
F
F
1e
13C NMR
75 MHz
(CD3)2CO
(CD3)2CO
(CD3)2CO
200
180
160
140
120
100
80
60
40
20
0
(ppm)



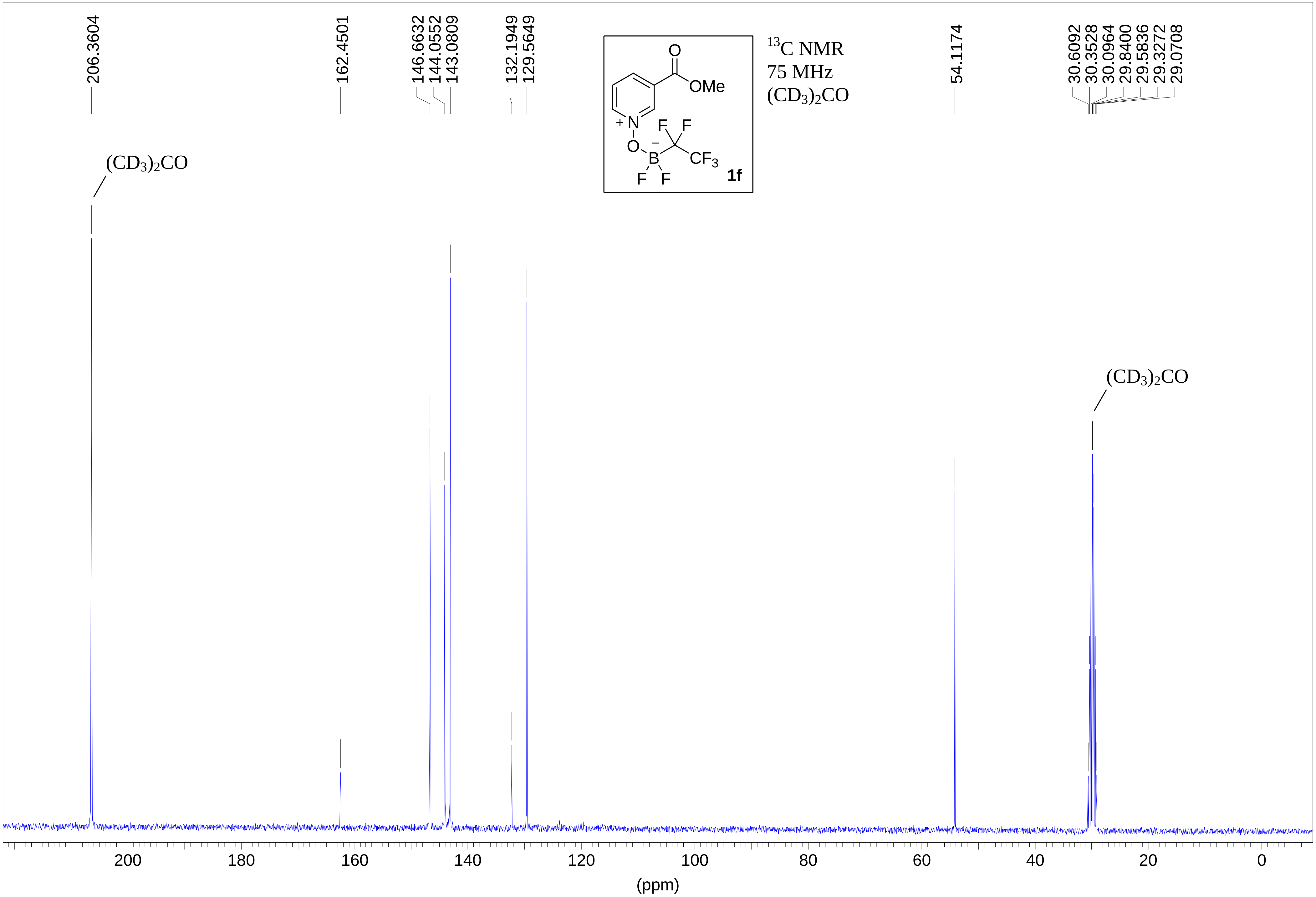
1e

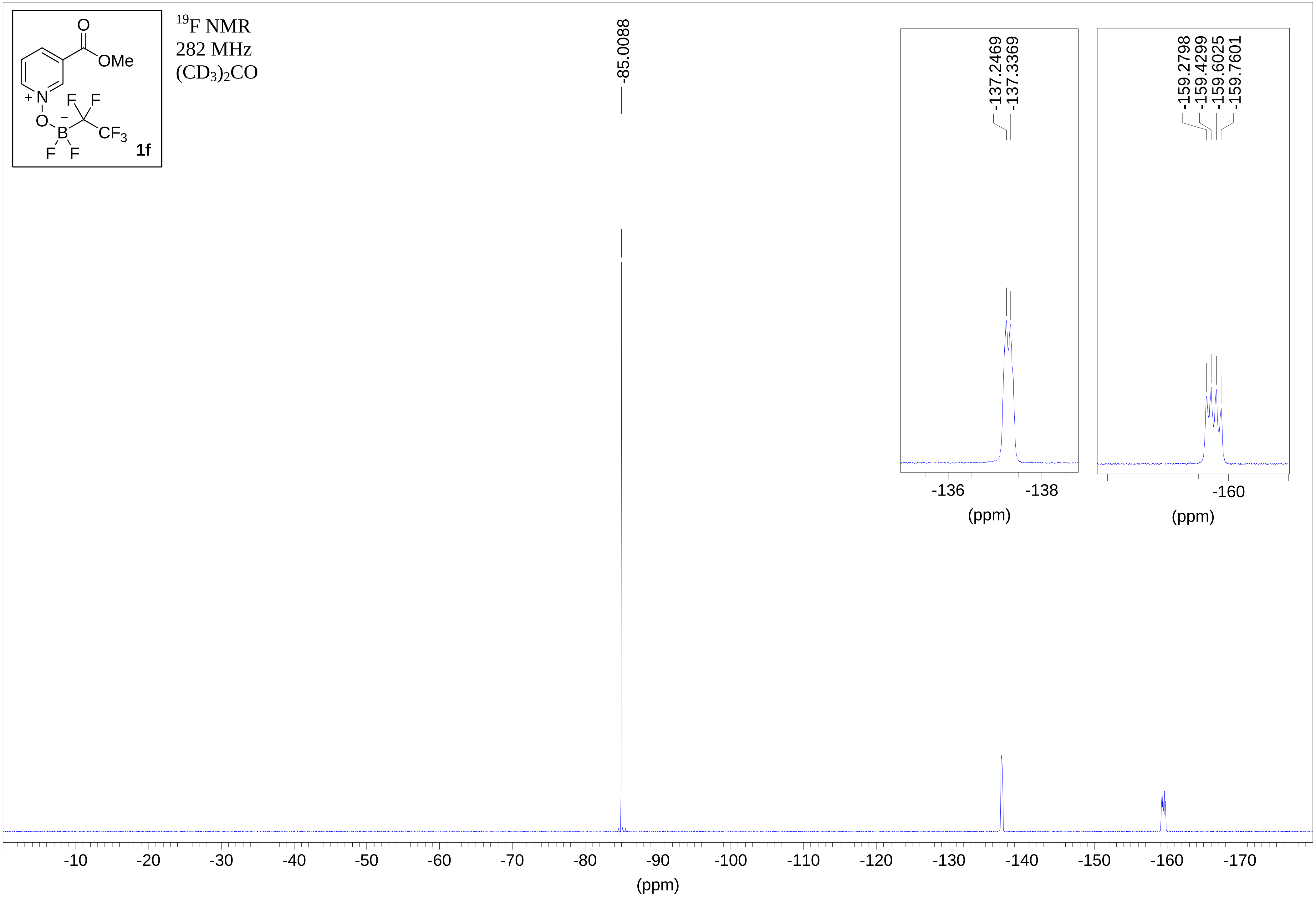
O
OMe
N+
O
–
B
CF3
F
F
19F NMR
282 MHz
(CD3)2CO
-76.4162
-76.5288
-76.6564
-76.7689
-76
(ppm)
-161.6812
-161.8313
-161.9964
-162.1465
-162
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
(ppm)


O
OMe
N+
O
−
CF3
B
F
F
1e
11B NMR
96 MHz
(CD3)2CO
1.3727
1.0070
0.5499
0.1995
-0.2576
-0.6233
45
40
35
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
(ppm)

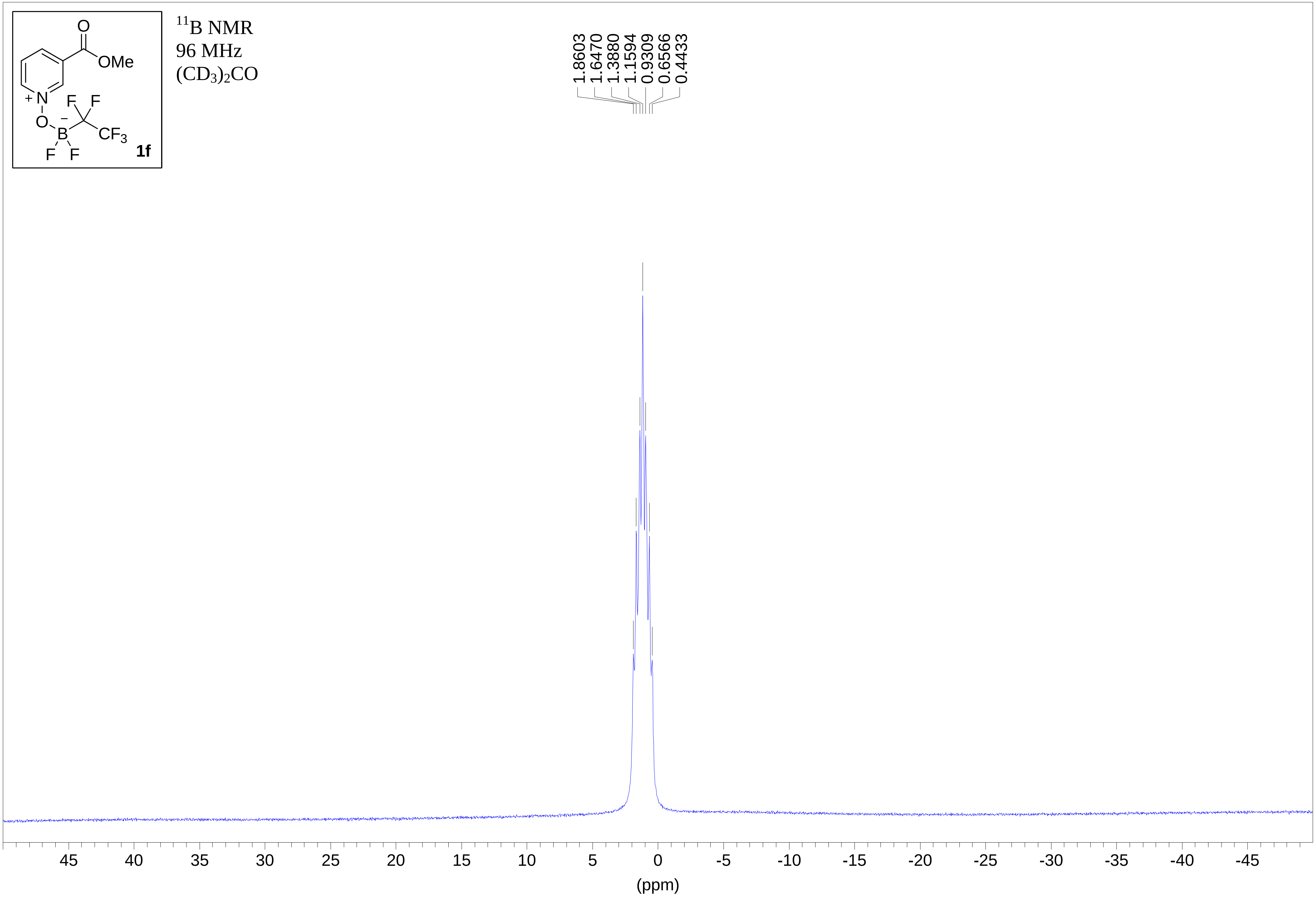


^{1}H NMR
300 MHz
$(CD_3)_2CO$


206.3604
162.4501
146.6632
144.0552
143.0809
132.1949
129.5649
54.1174
30.6092
30.3528
30.0964
29.8400
29.5836
29.3272
29.0708
^{13}C NMR
75 MHz
$(CD_3)_2CO$
$(CD_3)_2CO$
$(CD_3)_2CO$
O
OMe
+N
O
O
B
F
F
F
F
CF_3
1f
200
180
160
140
120
100
80
60
40
20
0
(ppm)

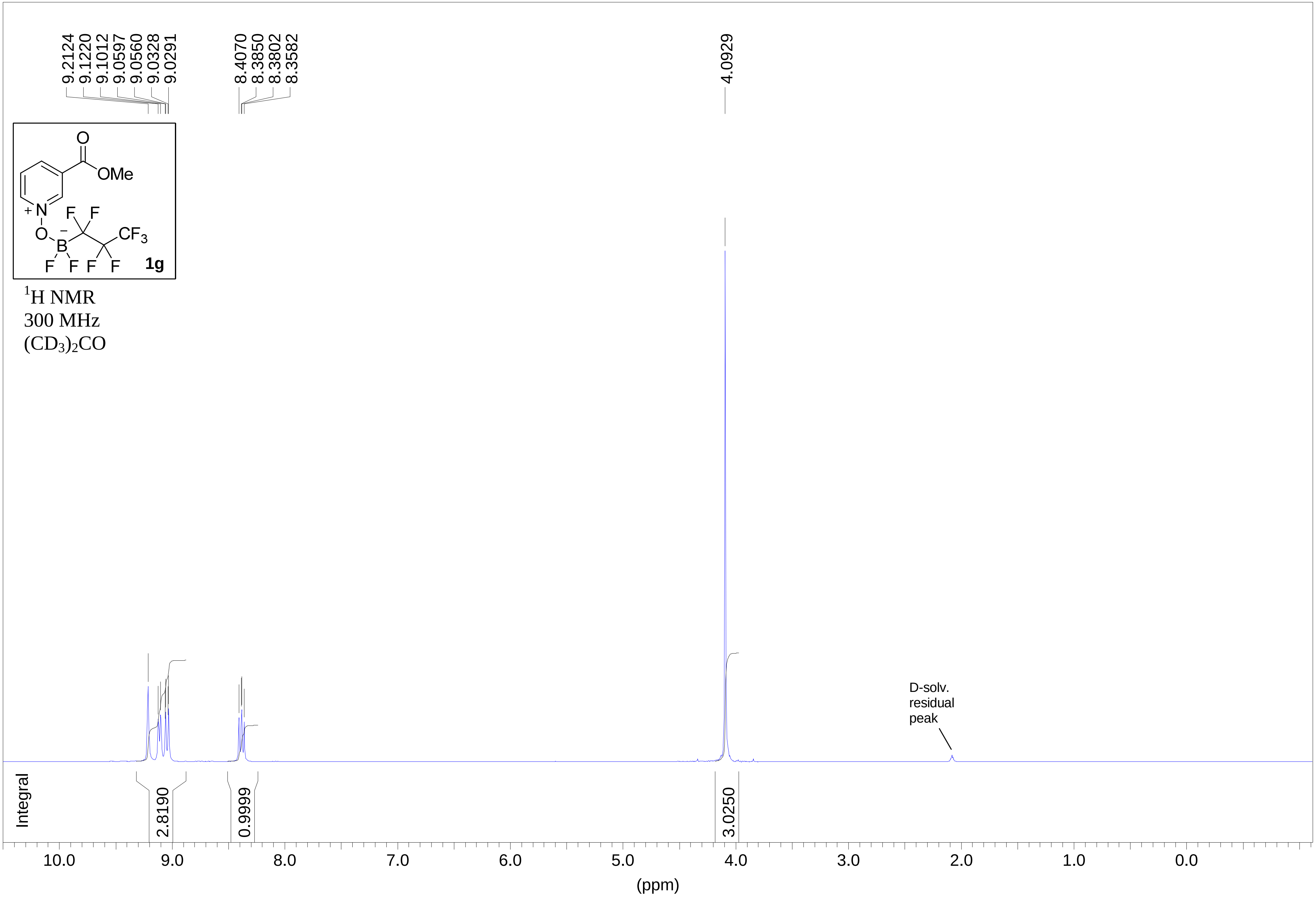


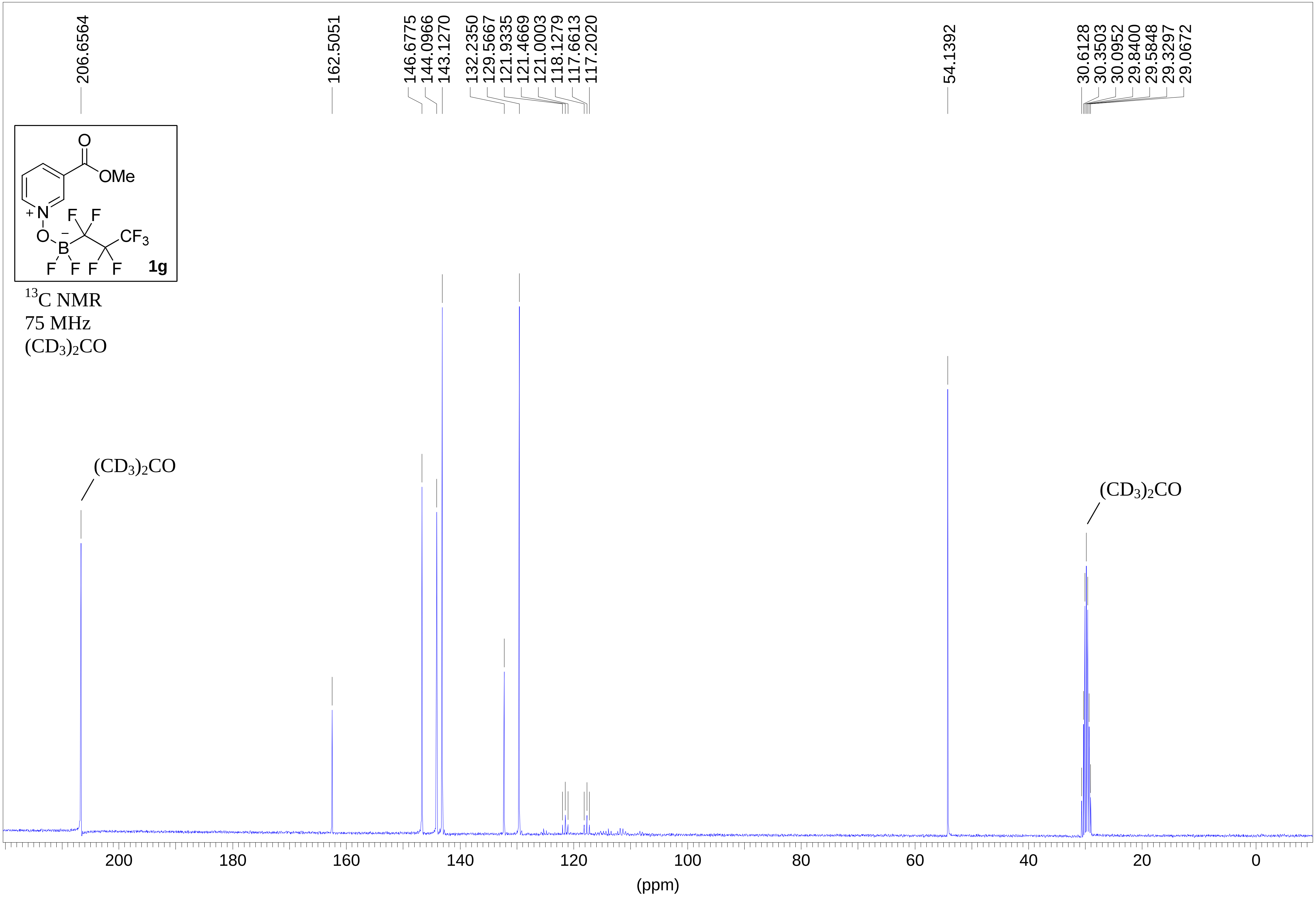
O
OMe
+N
O
–
B
F F
F F
CF3
1f
^{19}F NMR
282 MHz
$(CD_3)_2CO$
-85.0088
-137.2469
-137.3369
-159.2798
-159.4299
-159.6025
-159.7601
-136
-138
(ppm)
-160
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
(ppm)



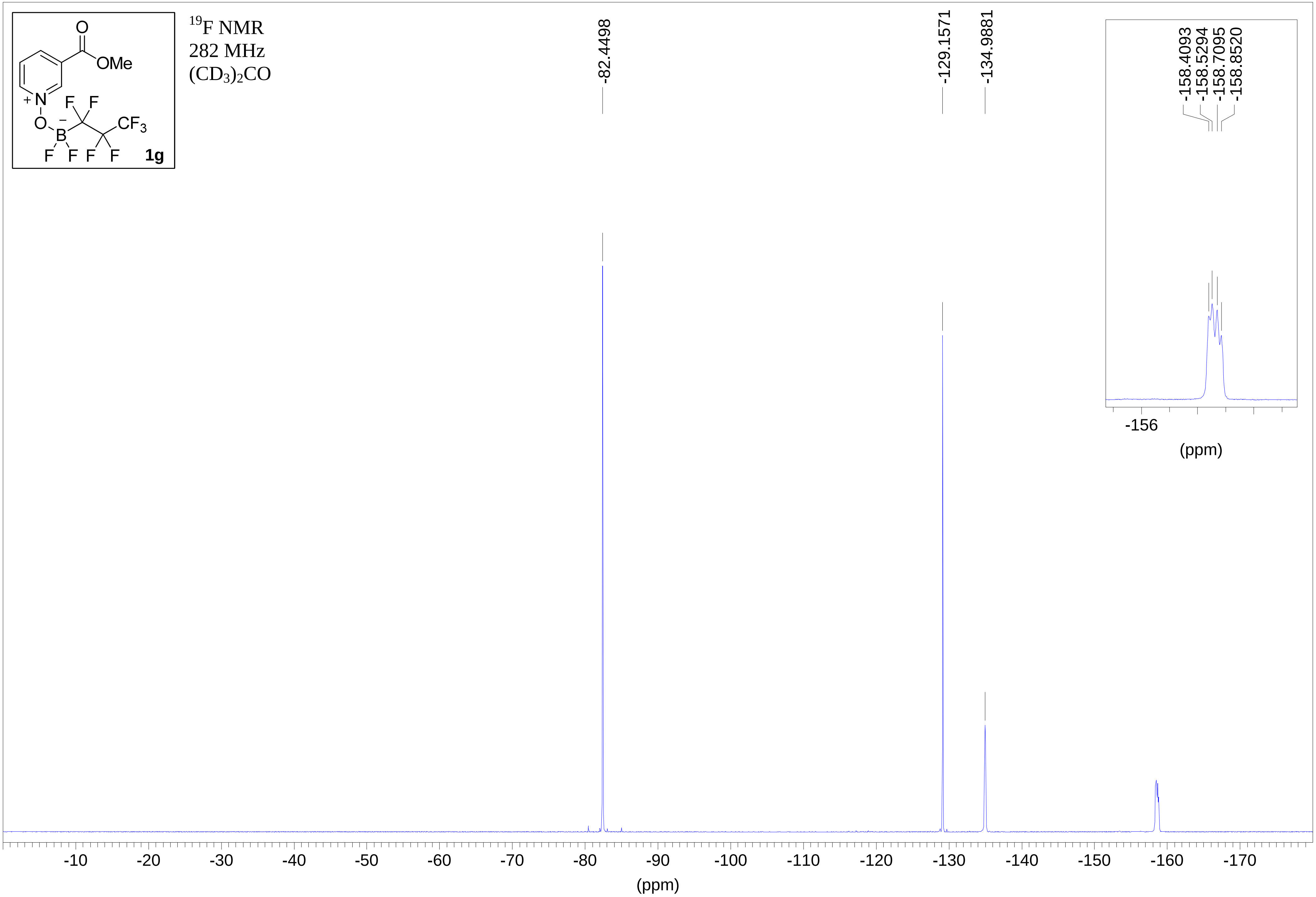
1f

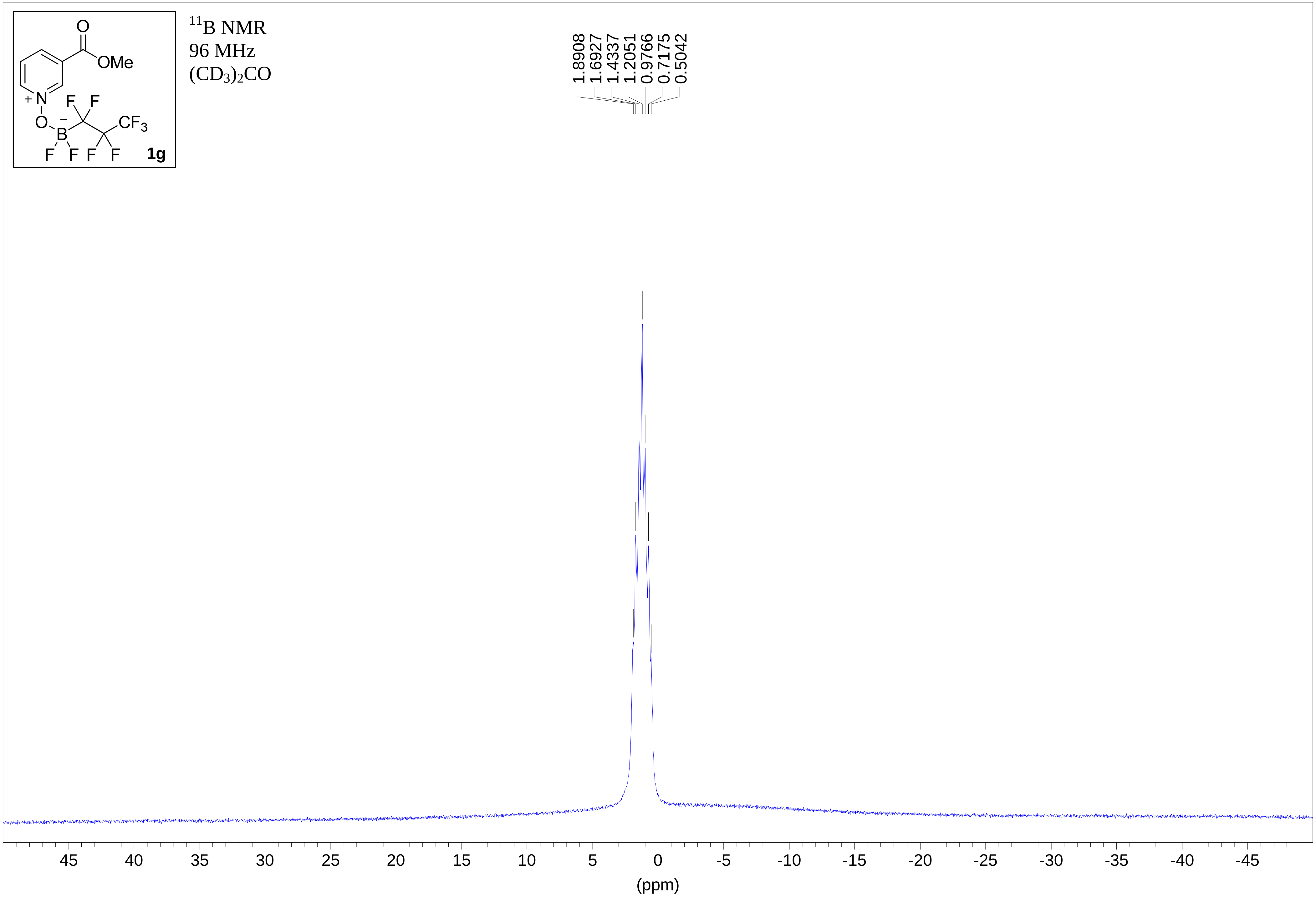
^{11}B NMR
96 MHz
$(CD_3)_2CO$


9.2124
9.1220
9.1012
9.0597
9.0560
9.0328
9.0291
8.4070
8.3850
8.3802
8.3582
4.0929
O
OMe
+N
O
B
F F
F
F F
F F
CF3
1g
¹H NMR
300 MHz
(CD3)2CO
D-solv.
residual
peak
Integral
2.8190
0.9999
3.0250
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



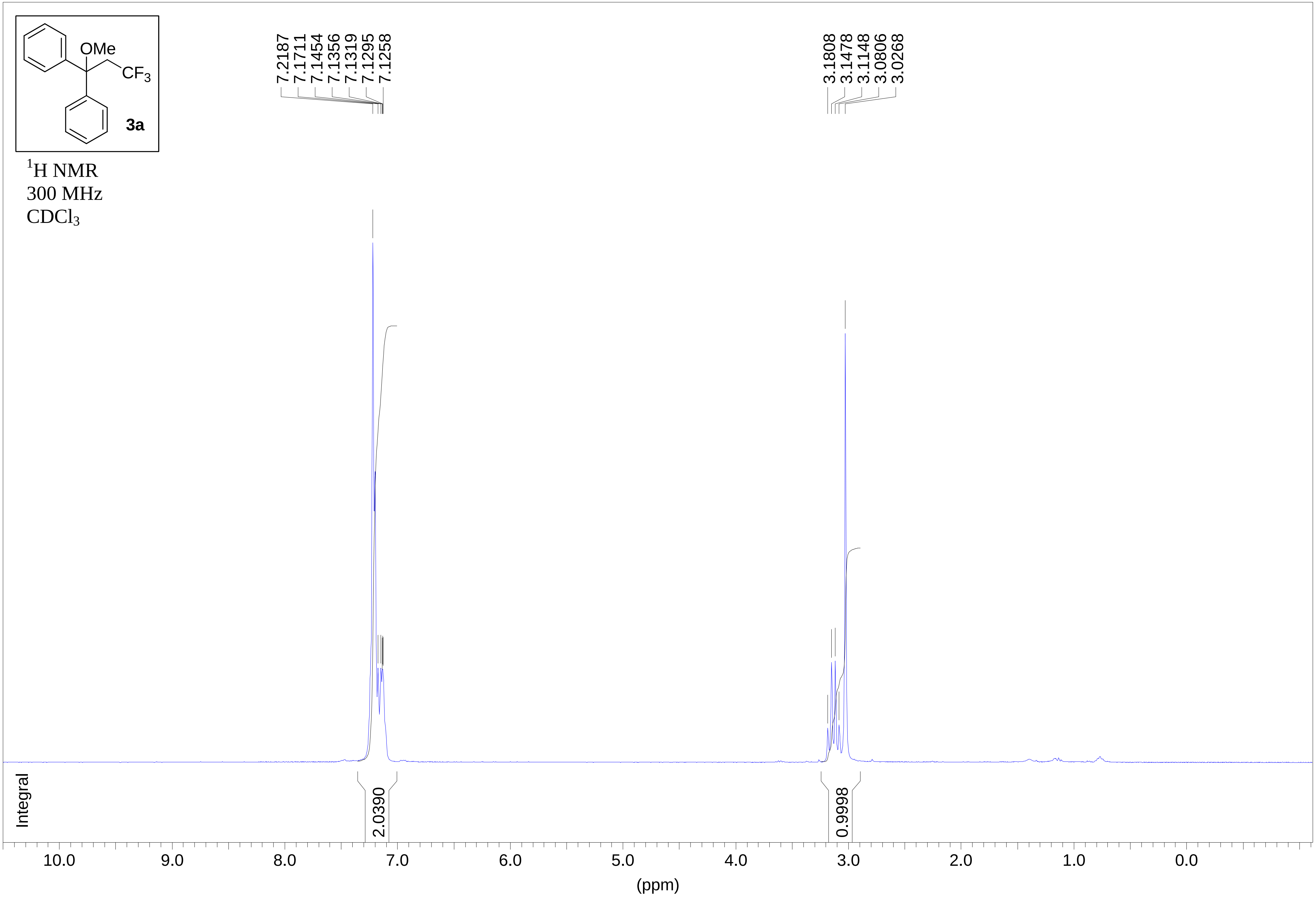
^{13}C NMR
75 MHz
$(CD_3)_2CO$

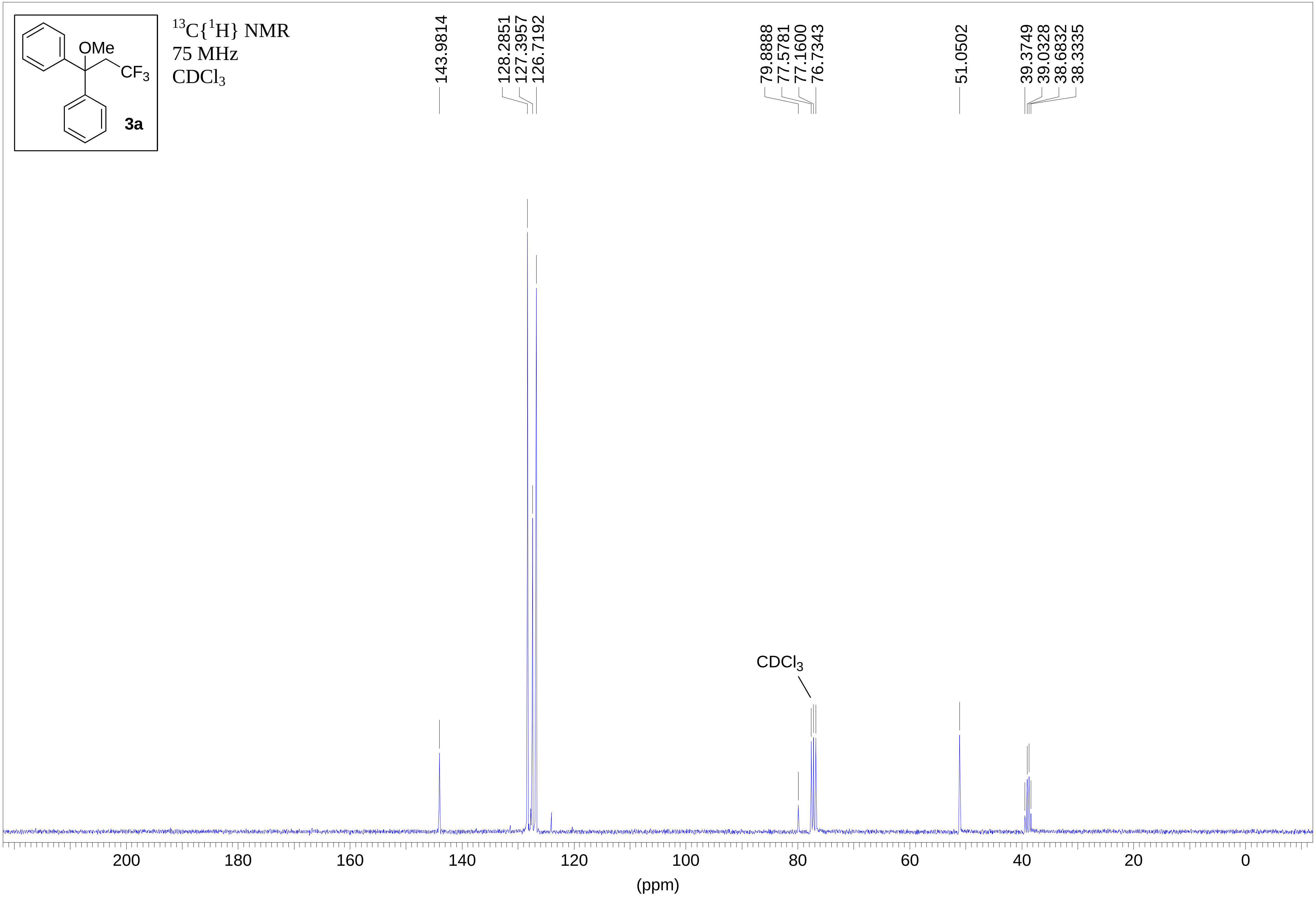

^{19}F NMR
282 MHz
$(CD_3)_2CO$
OMe
O
N
O
B
F
CF$_3$
1g
-82.4498
-129.1571
-134.9881
-158.4093
-158.5294
-158.7095
-158.8520
-156
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
(ppm)



1g

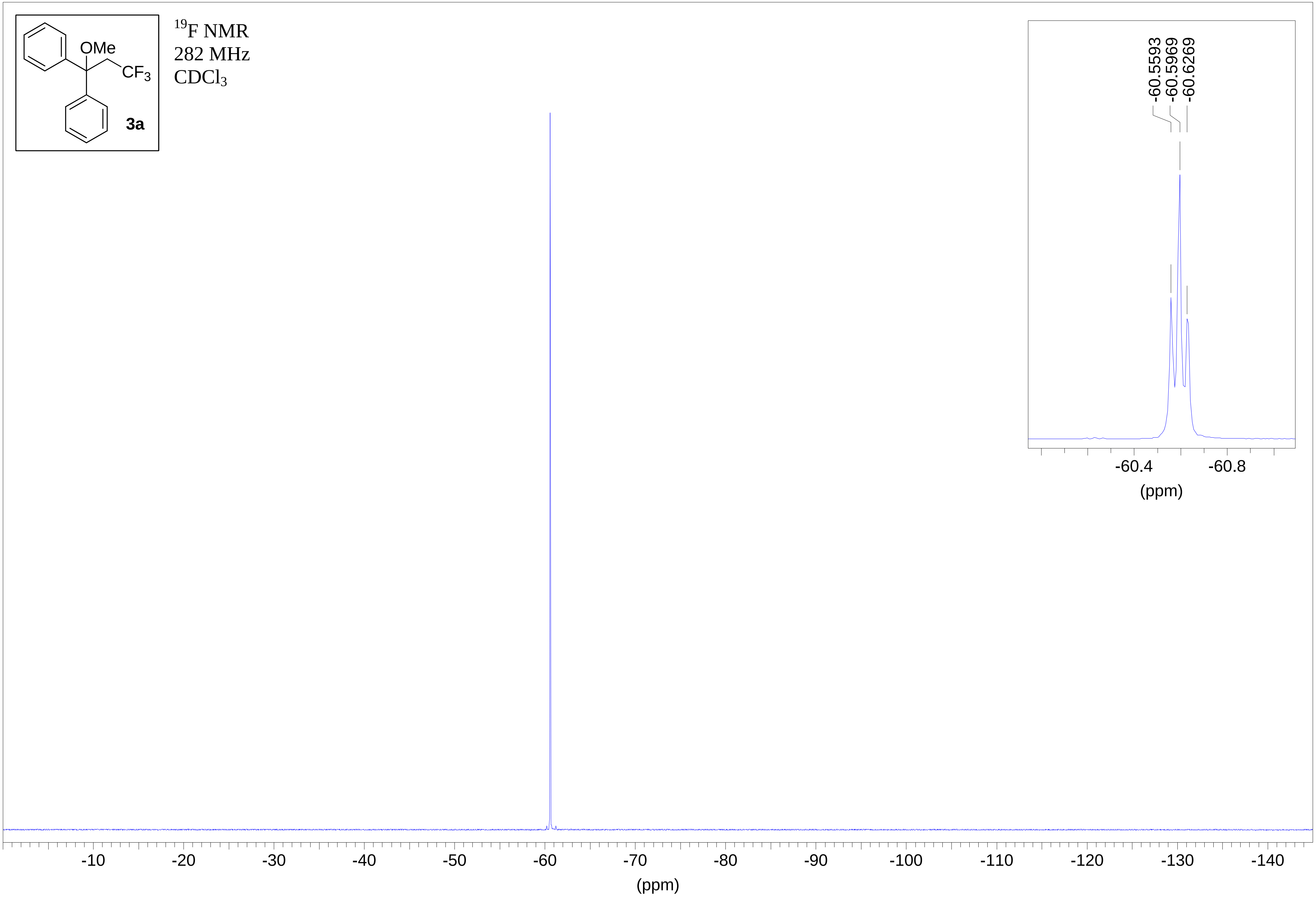
^{11}B NMR
96 MHz
$(CD_3)_2CO$

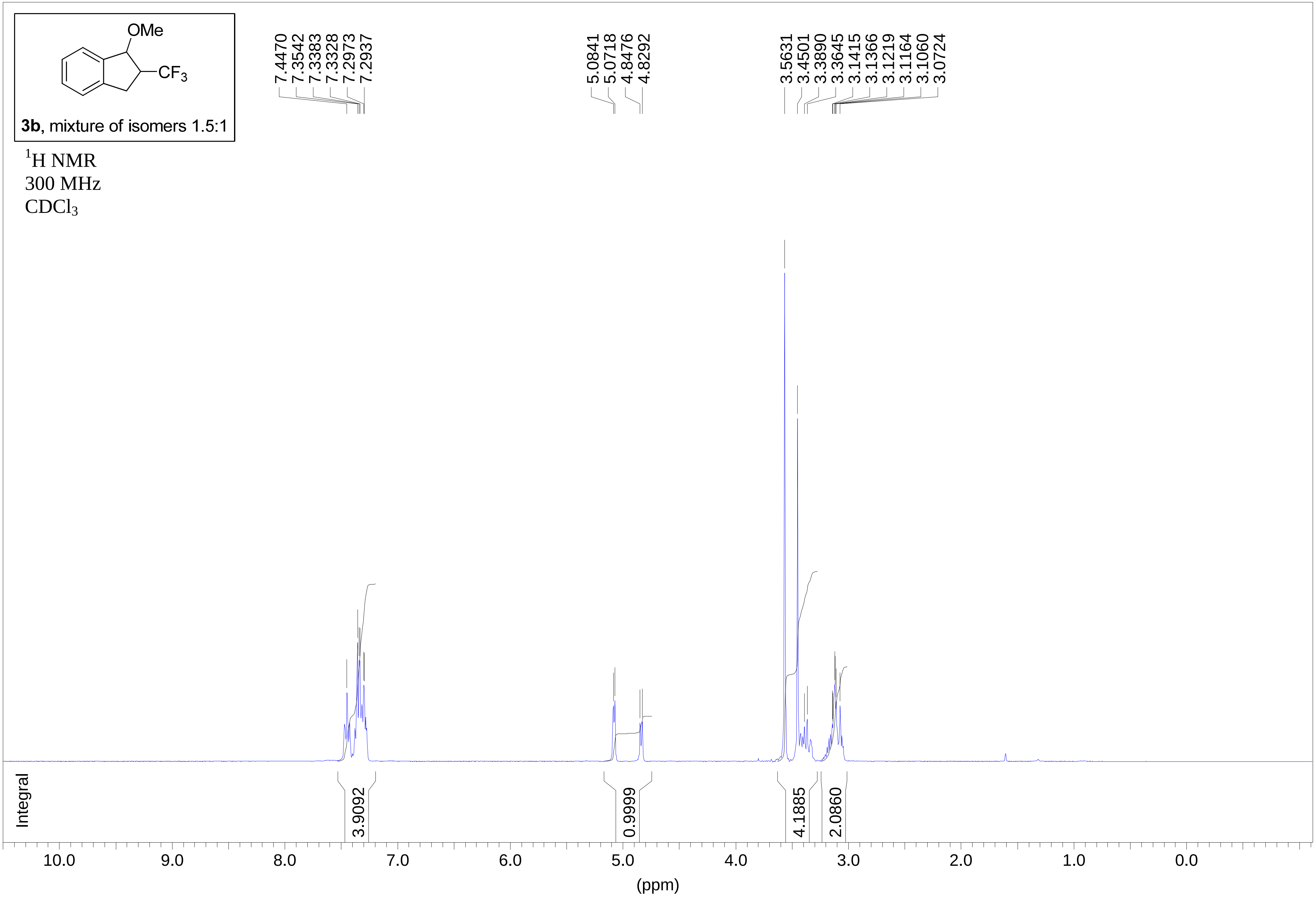

OMe
CF_3
3a
^1H NMR
300 MHz
$CDCl_3$
7.2187
7.1711
7.1454
7.1356
7.1319
7.1295
7.1258
3.1808
3.1478
3.1148
3.0806
3.0268
Integral
2.0390
0.9998
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



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

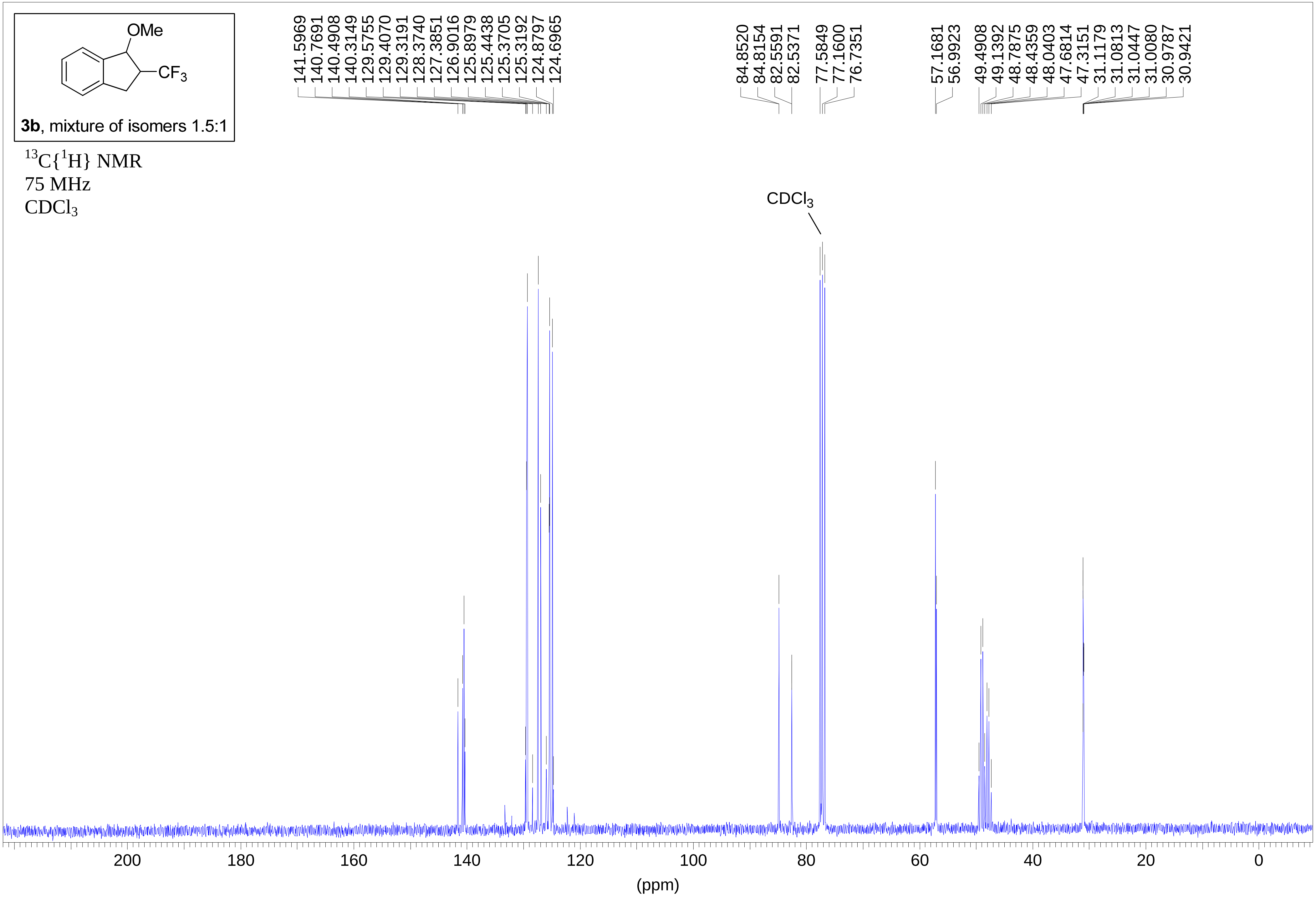
3a


OMe
CF3
3a
19F NMR
282 MHz
CDCl3
-60.5593
-60.5969
-60.6269
-60.4
-60.8
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)



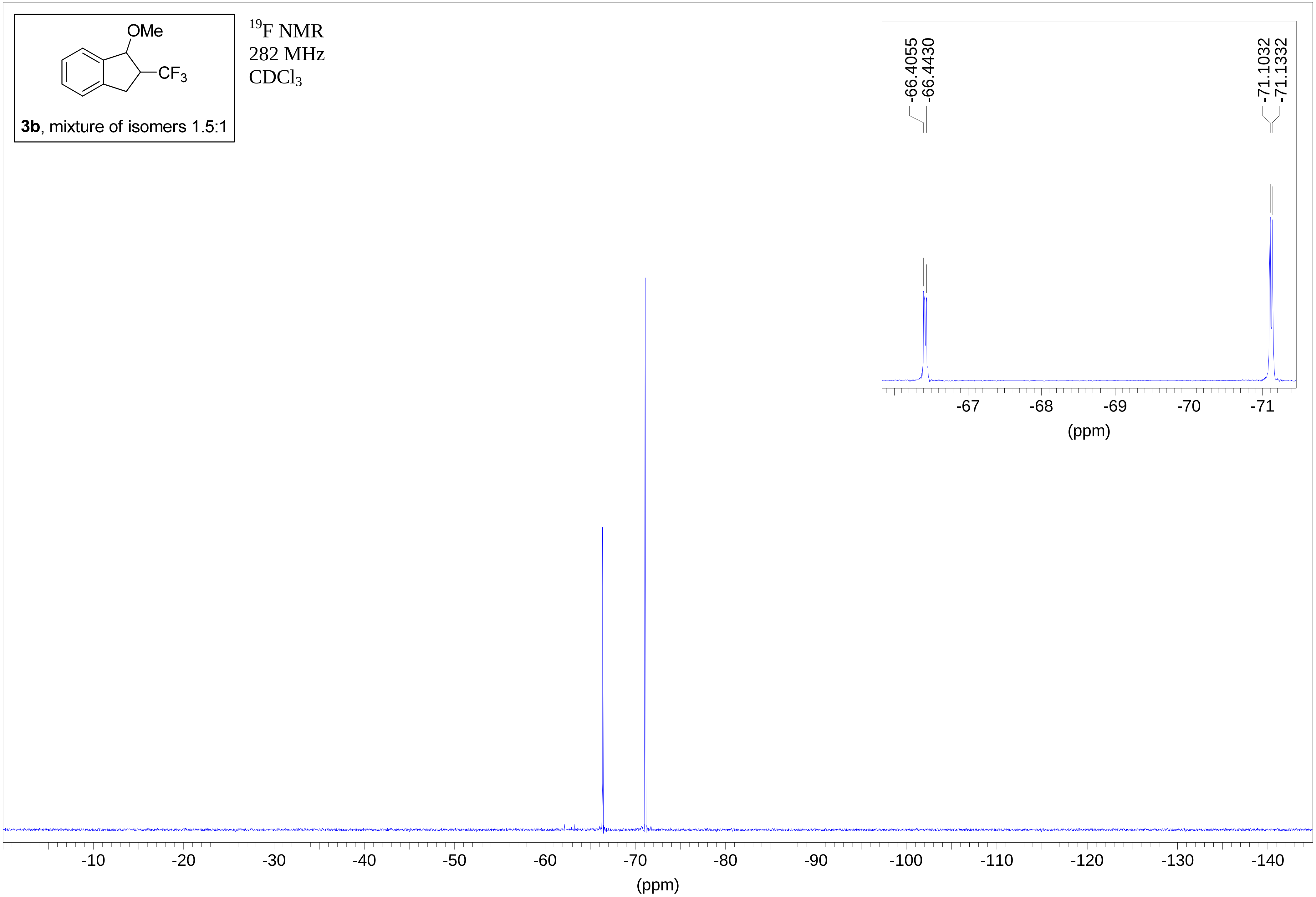
3b, mixture of isomers 1.5:1

^{1}H NMR
300 MHz
CDCl$_3$

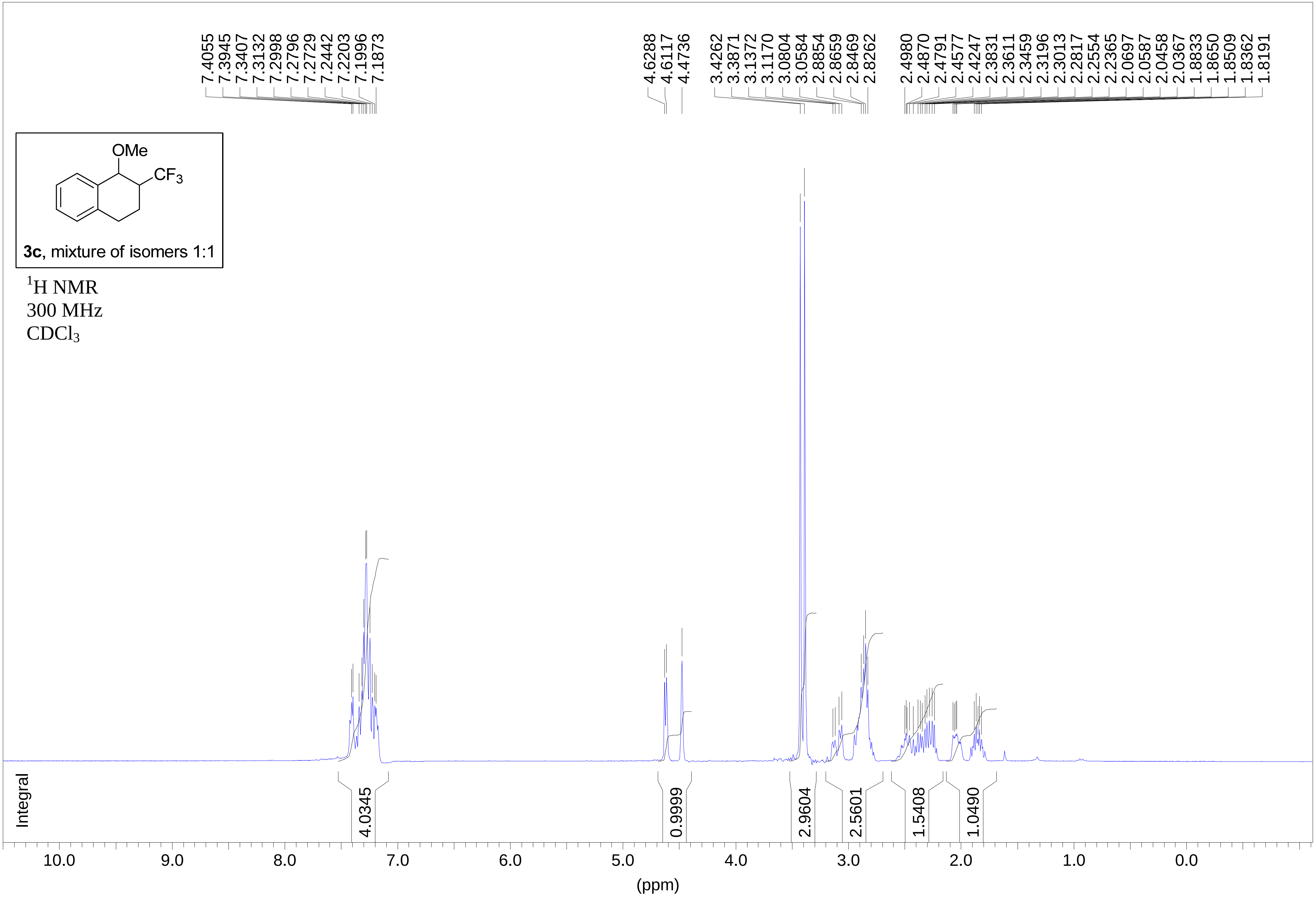


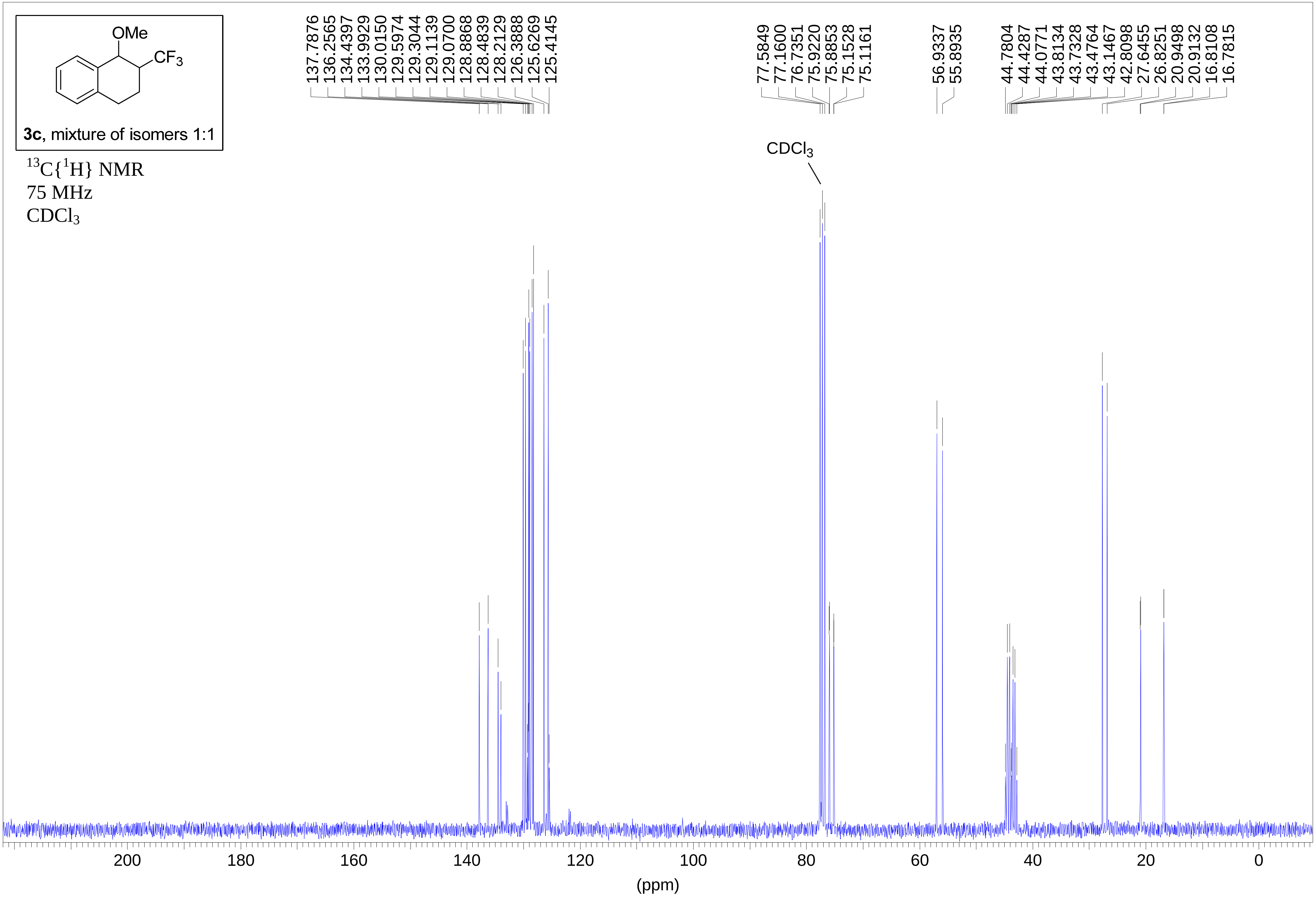
3b, mixture of isomers 1.5:1

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



3b, mixture of isomers 1.5:1

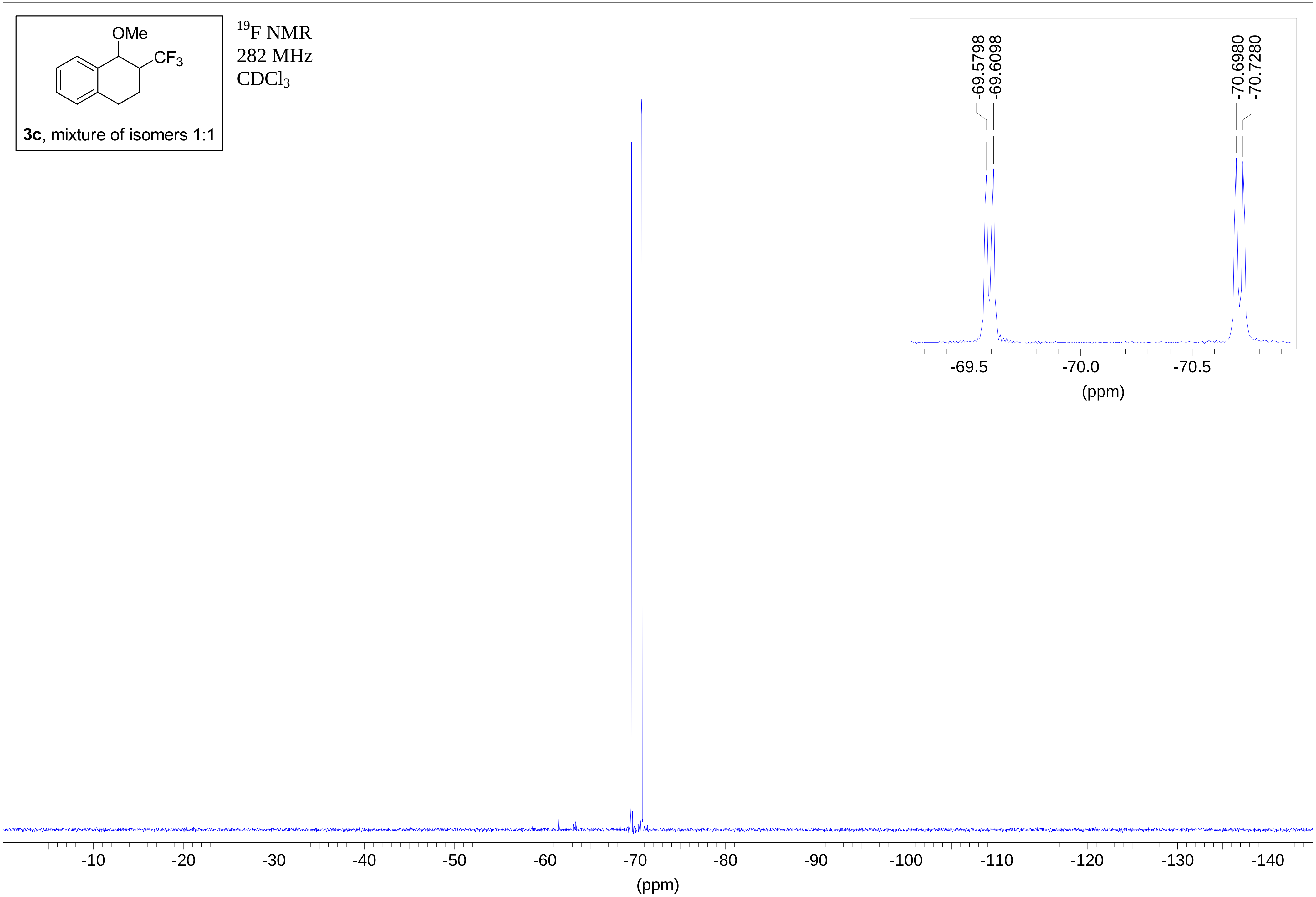

7.4055
7.3945
7.3407
7.3132
7.2998
7.2796
7.2729
7.2442
7.2203
7.1996
7.1873
4.6288
4.6117
4.4736
3.4262
3.3871
3.1372
3.1170
3.0804
3.0584
2.8854
2.8659
2.8469
2.8262
2.4980
2.4870
2.4791
2.4577
2.4247
2.3831
2.3611
2.3459
2.3196
2.3013
2.2817
2.2554
2.2365
2.0697
2.0587
2.0458
2.0367
1.8833
1.8650
1.8509
1.8362
1.8191
OMe
CF3
3c, mixture of isomers 1:1
1H NMR
300 MHz
CDCl3
Integral
4.0345
0.9999
2.9604
2.5601
1.5408
1.0490
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

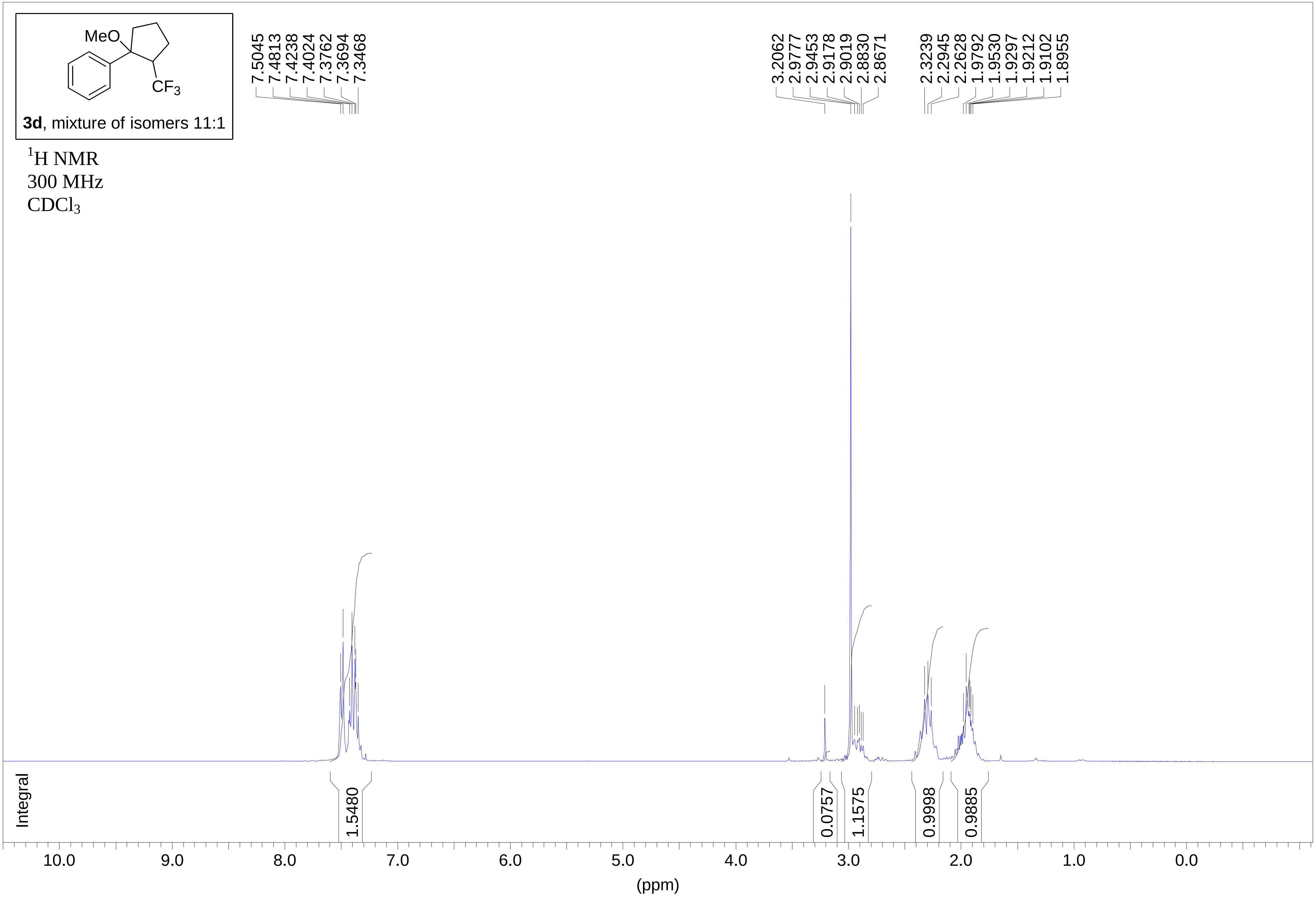


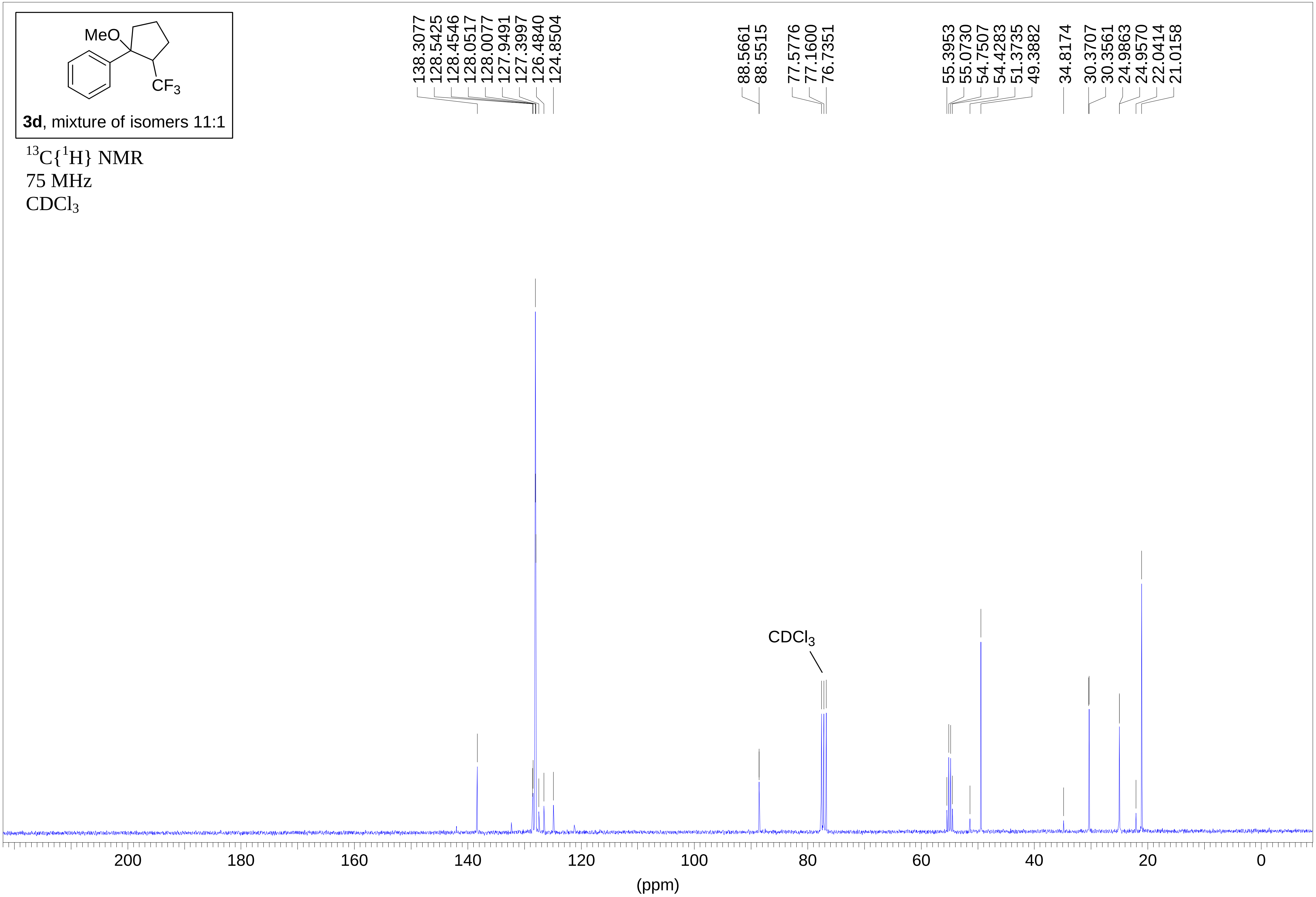
3c, mixture of isomers 1:1

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

3c, mixture of isomers 1:1

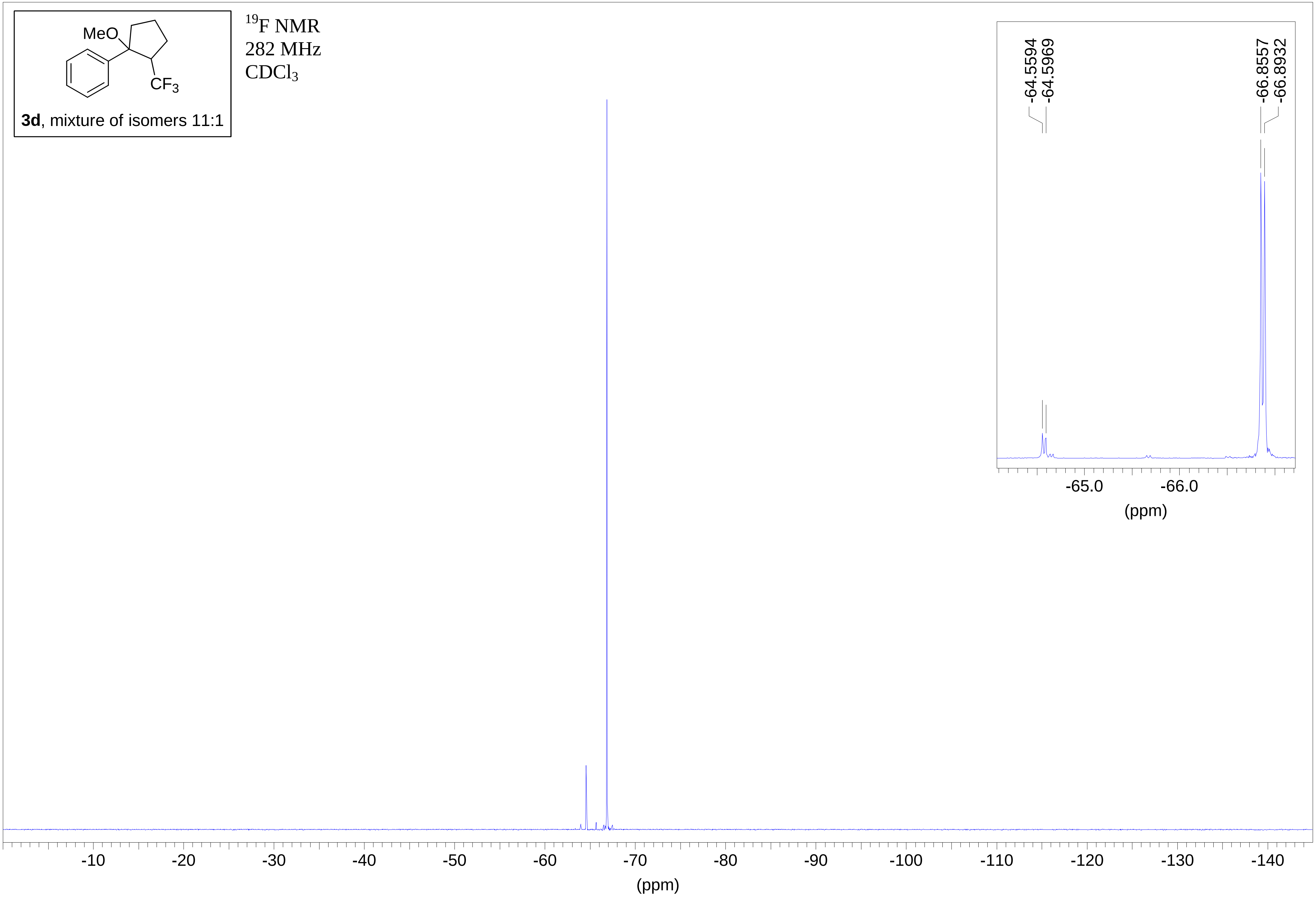



MeO
CF3
3d, mixture of isomers 11:1
^{1}H NMR
300 MHz
$CDCl_3$
7.5045
7.4813
7.4238
7.4024
7.3762
7.3694
7.3468
3.2062
2.9777
2.9453
2.9178
2.9019
2.8830
2.8671
2.3239
2.2945
2.2628
1.9792
1.9530
1.9297
1.9212
1.9102
1.8955
Integral
1.5480
0.0757
1.1575
0.9998
0.9885
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



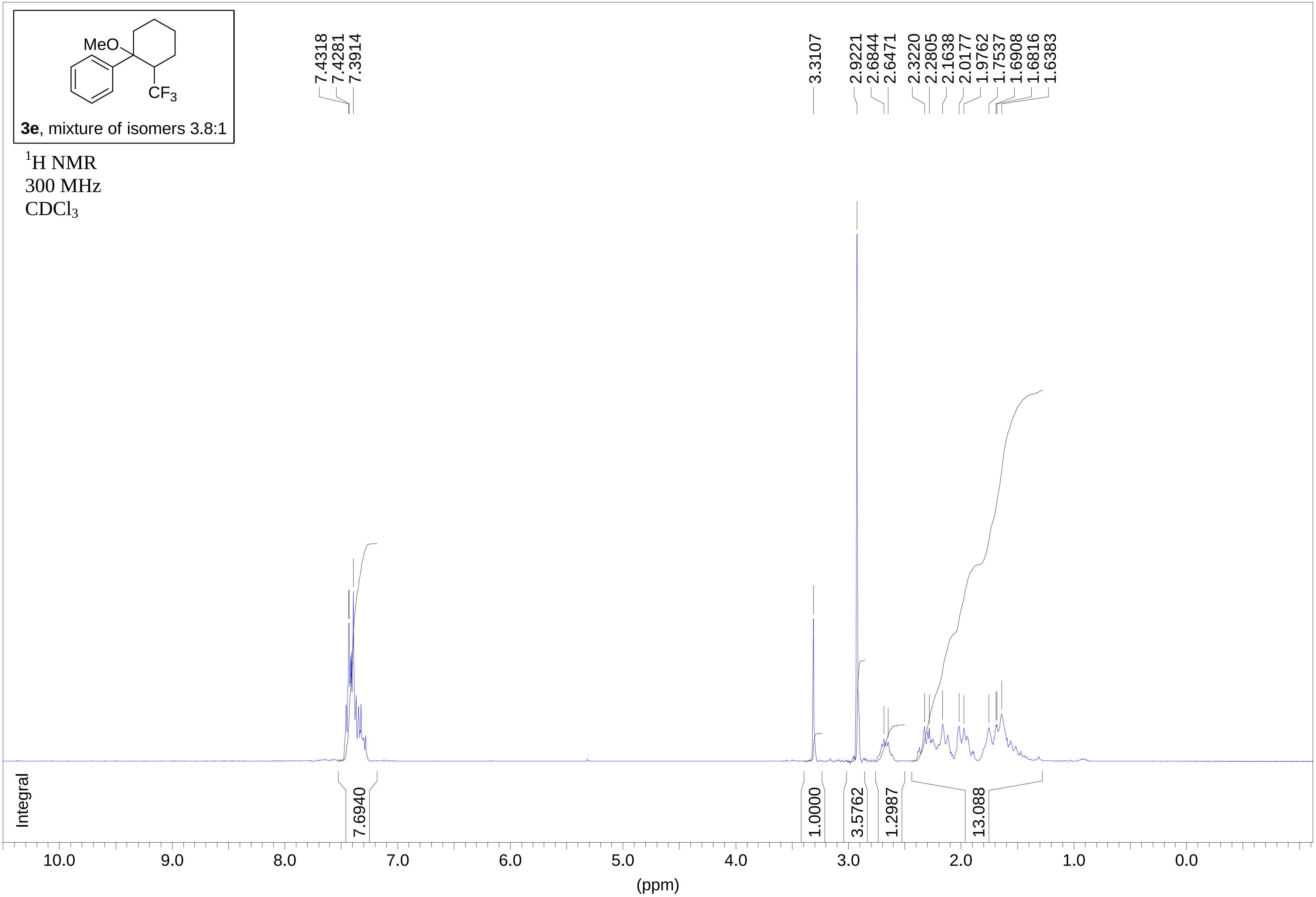
3d, mixture of isomers 11:1

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



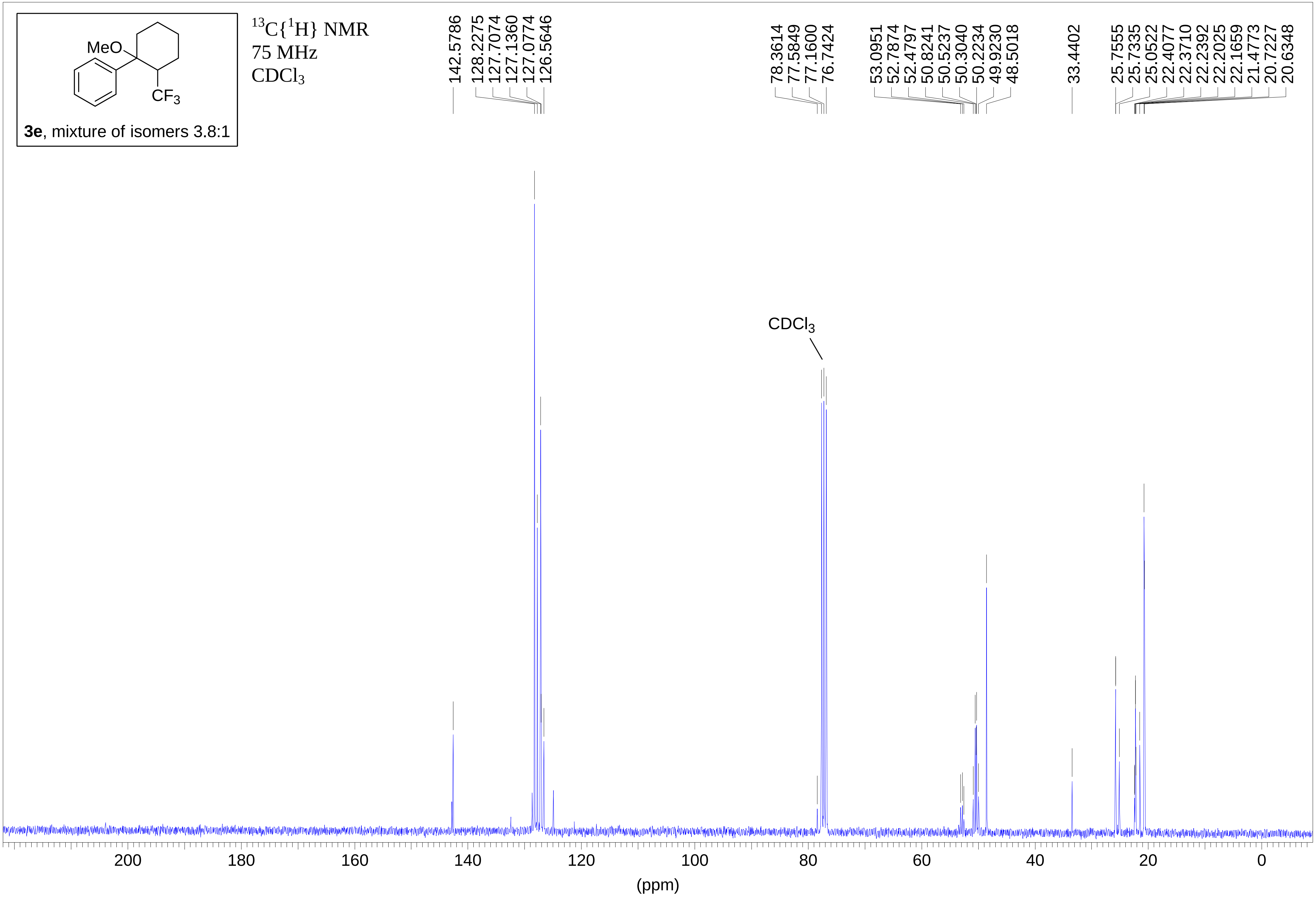
3d, mixture of isomers 11:1

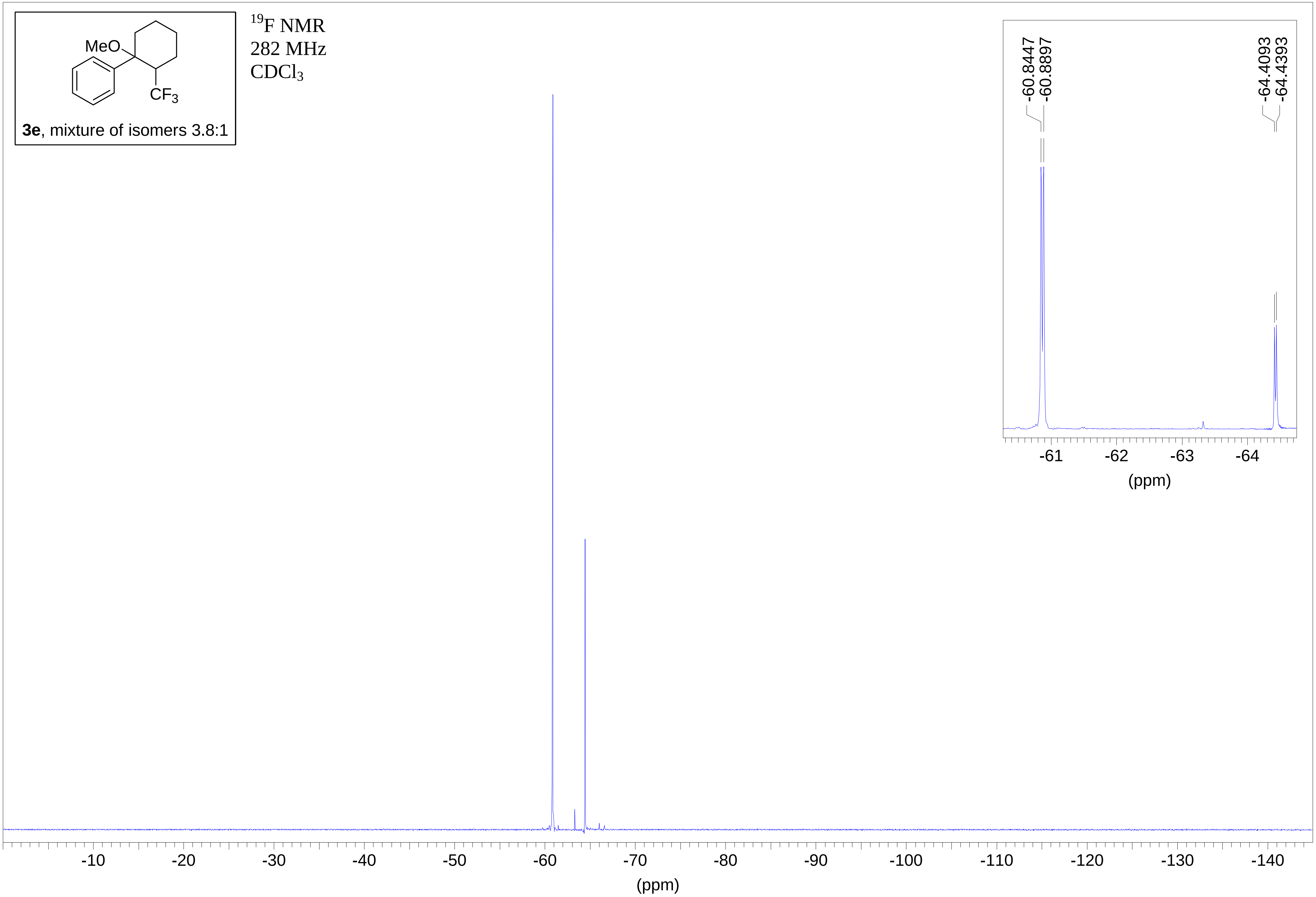
^{19}F NMR
282 MHz
$CDCl_3$



3e, mixture of isomers 3.8:1

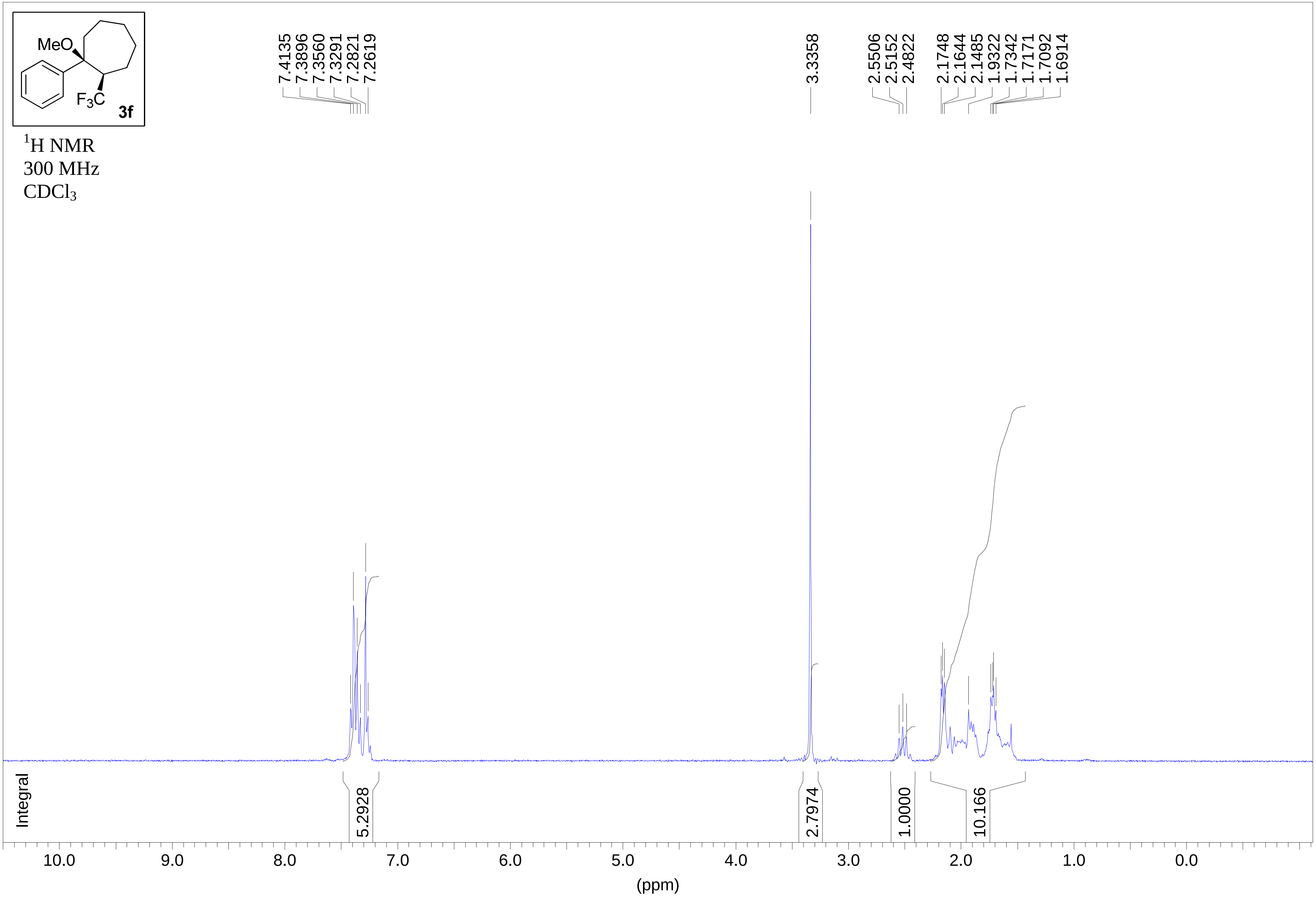
^{1}H NMR
300 MHz
$CDCl_3$


MeO
CF3
3e, mixture of isomers 3.8:1
13C{1H} NMR
75 MHz
CDCl3
142.5786
128.2275
127.7074
127.1360
127.0774
126.5646
78.3614
77.5849
77.1600
76.7424
53.0951
52.7874
52.4797
50.8241
50.5237
50.3040
50.2234
49.9230
48.5018
33.4402
25.7555
25.7335
25.0522
22.4077
22.3710
22.2392
22.2025
22.1659
21.4773
20.7227
20.6348
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



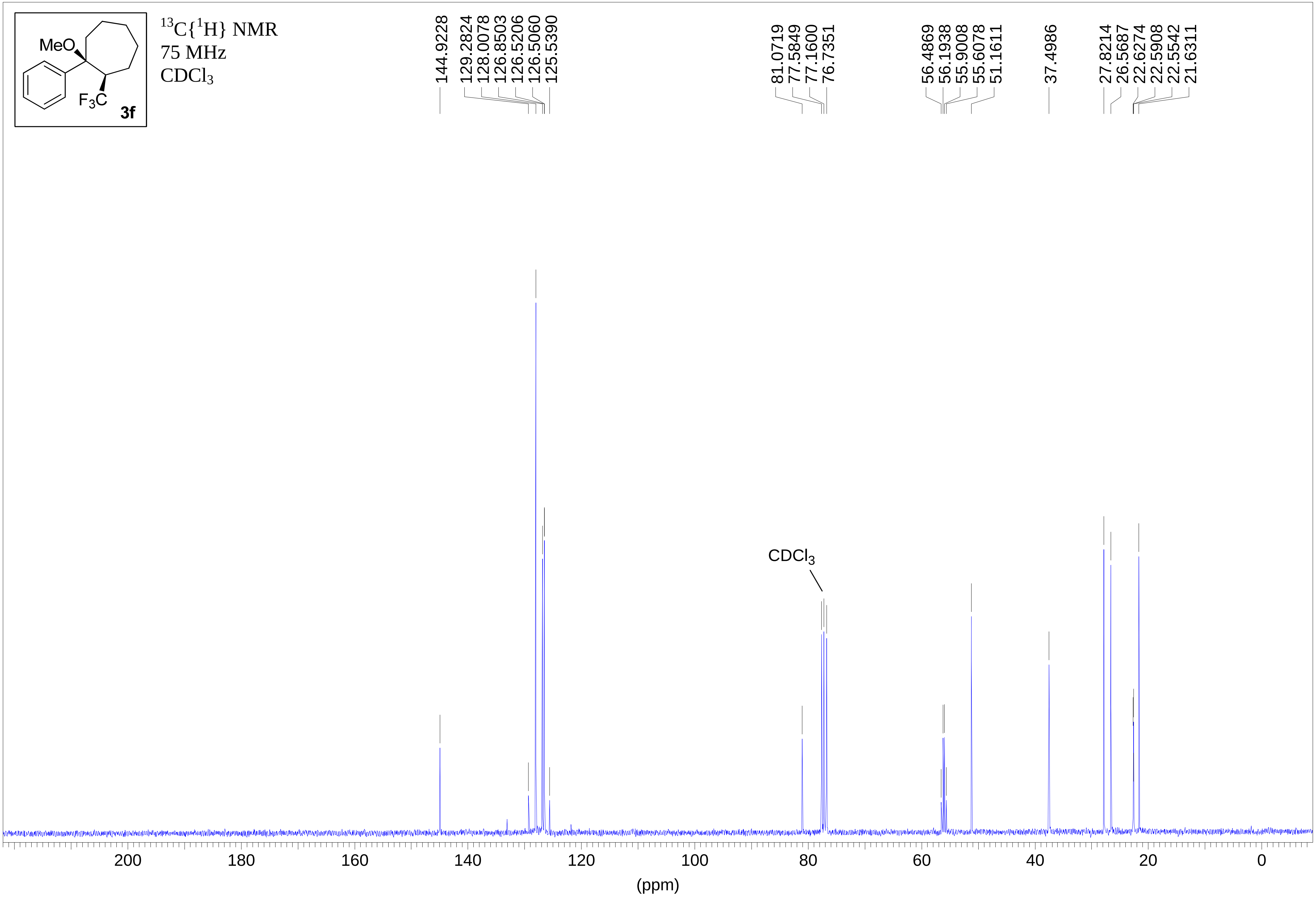
3e, mixture of isomers 3.8:1

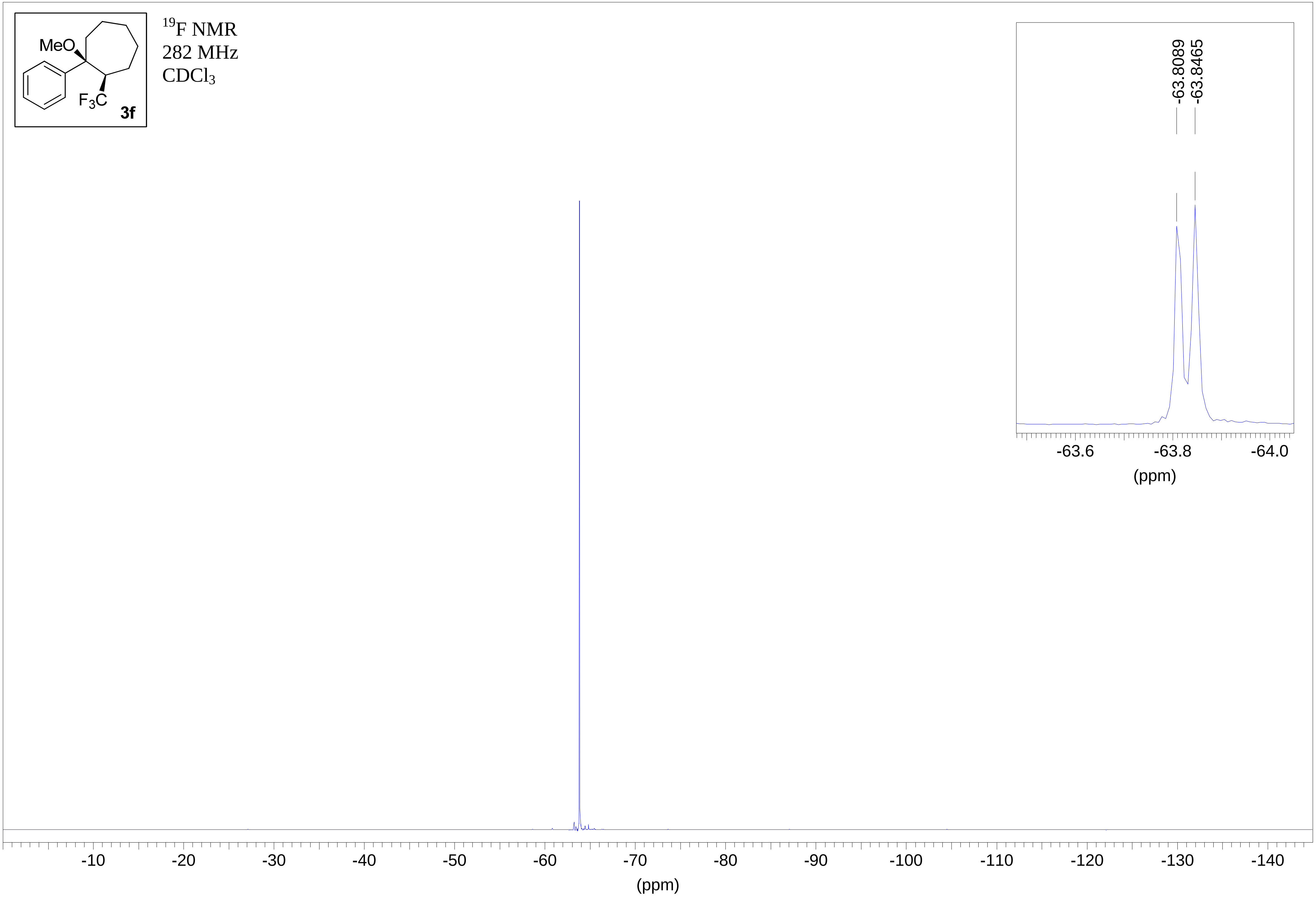
^{19}F NMR
282 MHz
CDCl$_3$



3f

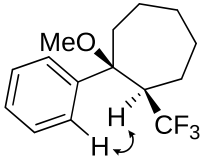
^1H NMR
300 MHz
$CDCl_3$


MeO
F3C
3f
13C{1H} NMR
75 MHz
CDCl3
144.9228
129.2824
128.0078
126.8503
126.5206
126.5060
125.5390
81.0719
77.5849
77.1600
76.7351
56.4869
56.1938
55.9008
55.6078
51.1611
37.4986
27.8214
26.5687
22.6274
22.5908
22.5542
21.6311
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



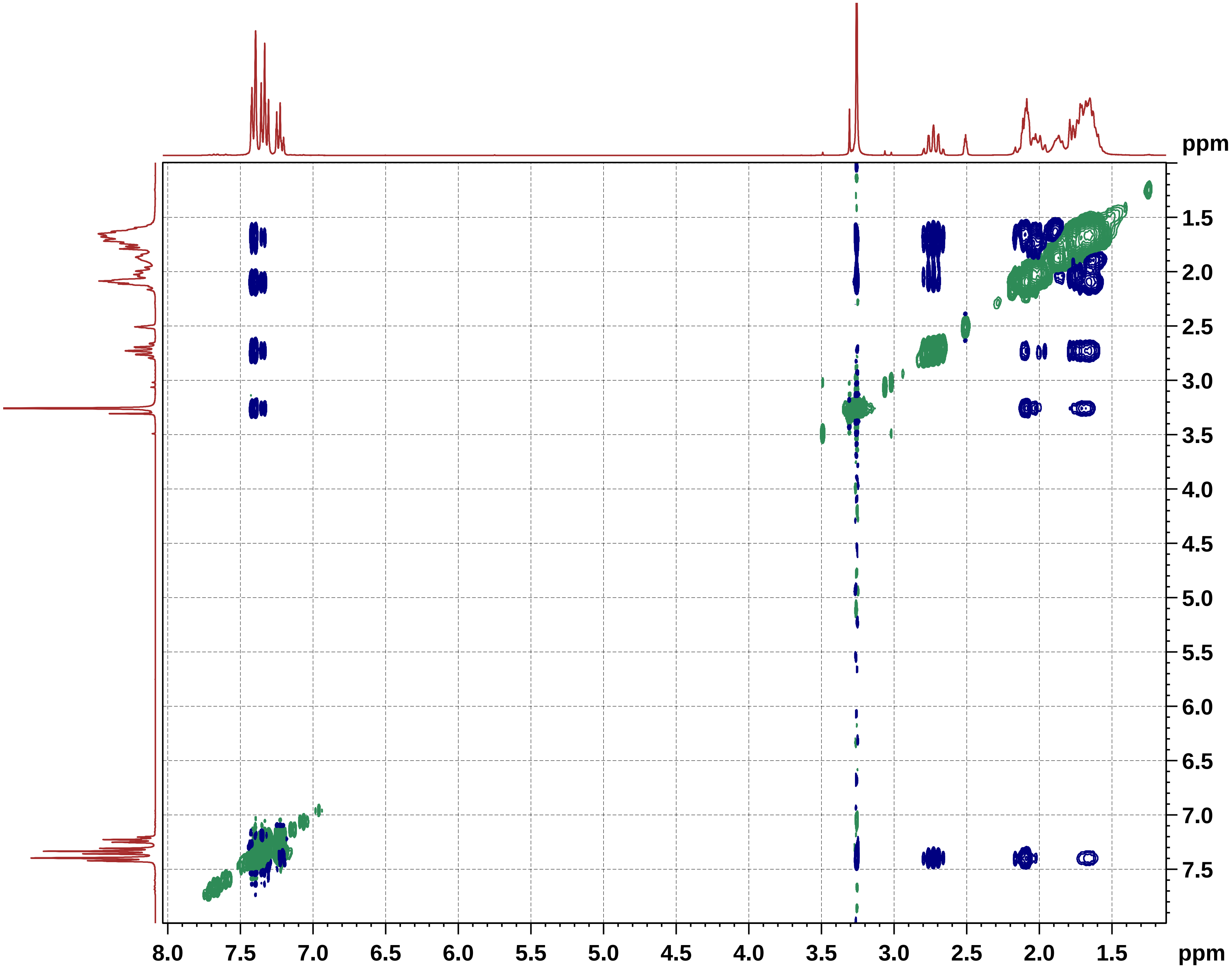
3f

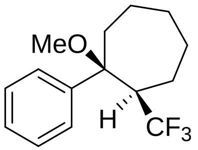
MeO
F_3C
^{19}F NMR
282 MHz
$CDCl_3$
-63.8089
-63.8465
-63.6
-63.8
-64.0
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)



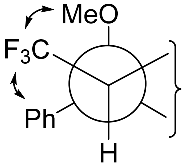
3f

^{1}H-^{1}H NOESY

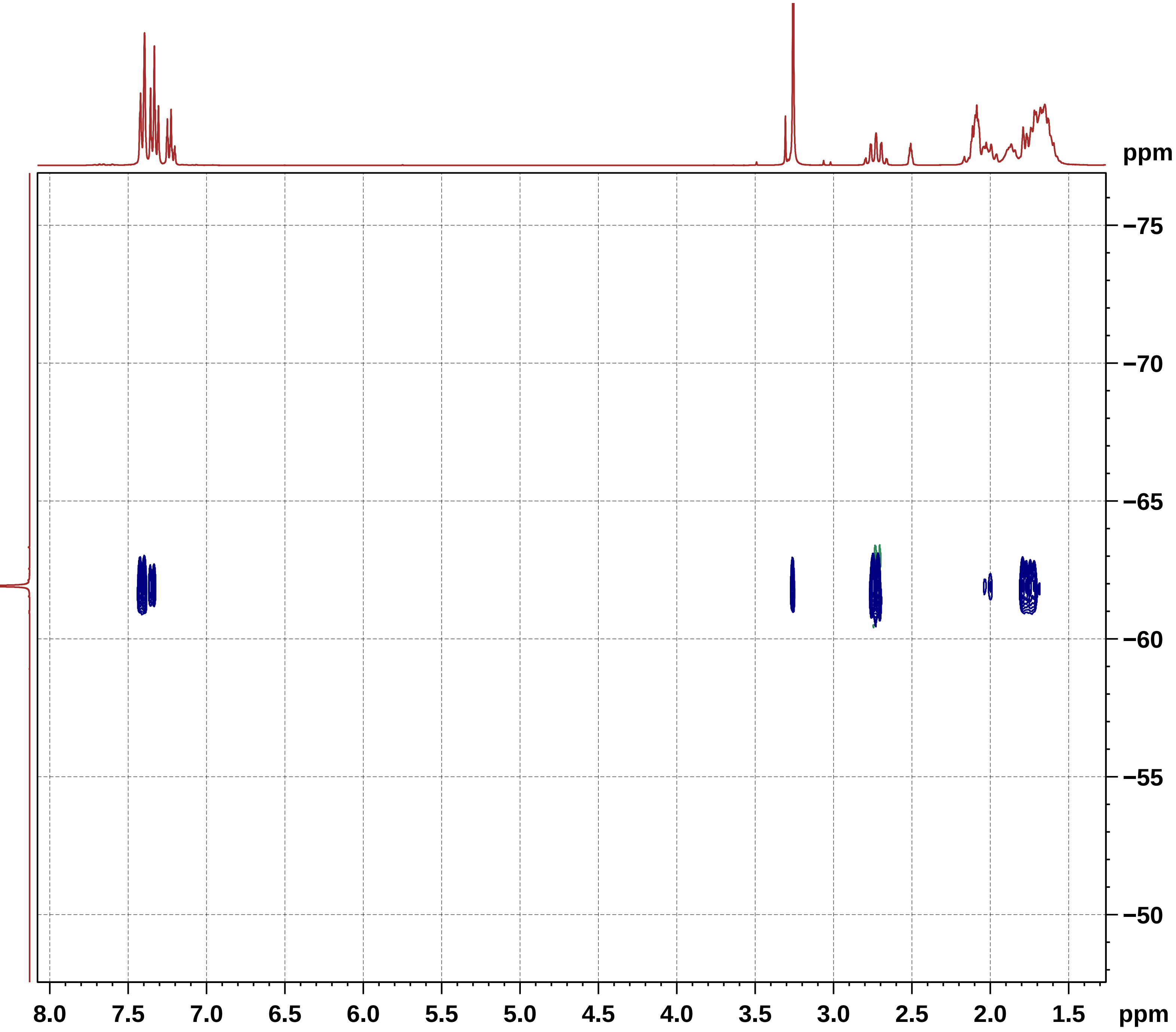


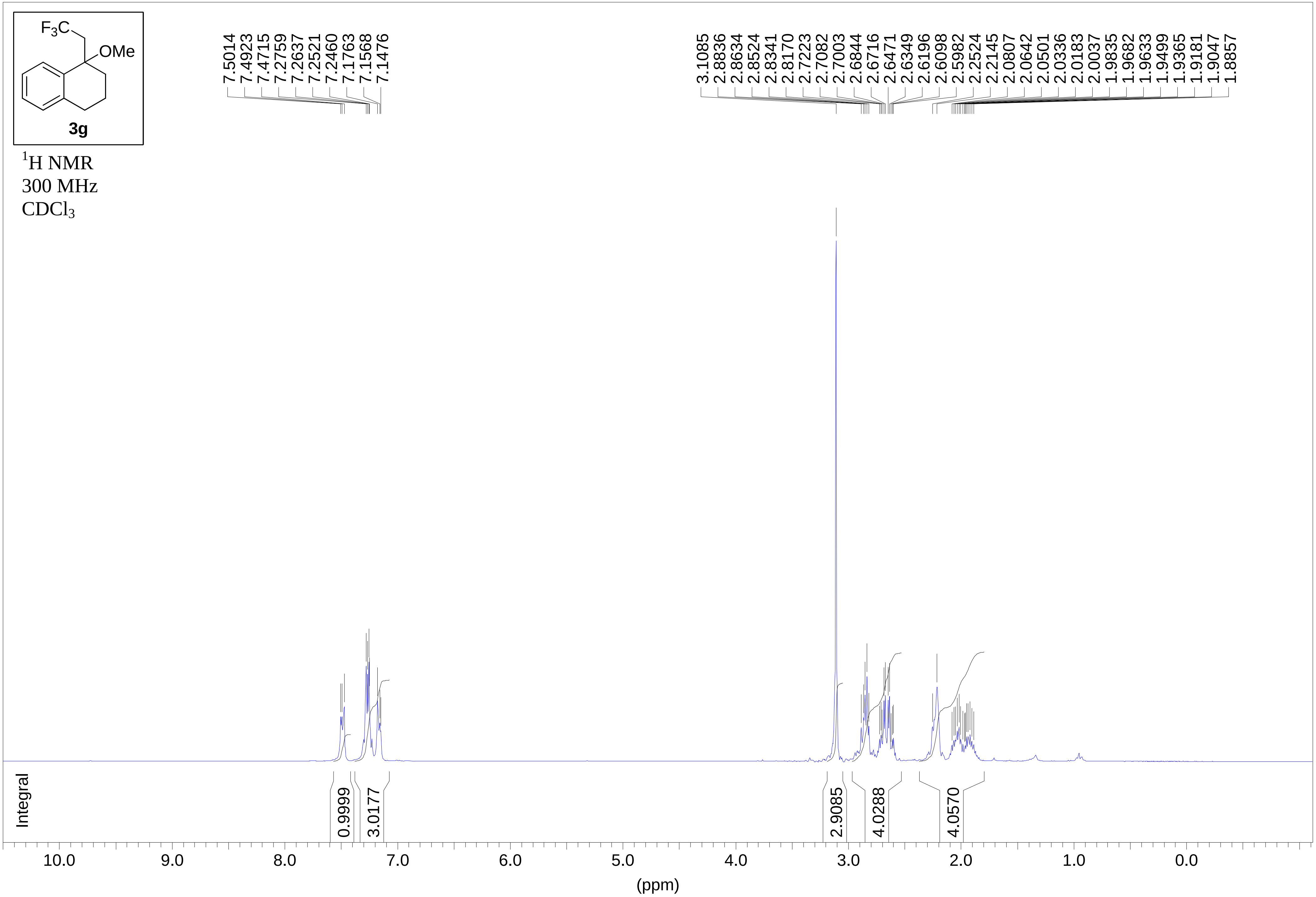


3f

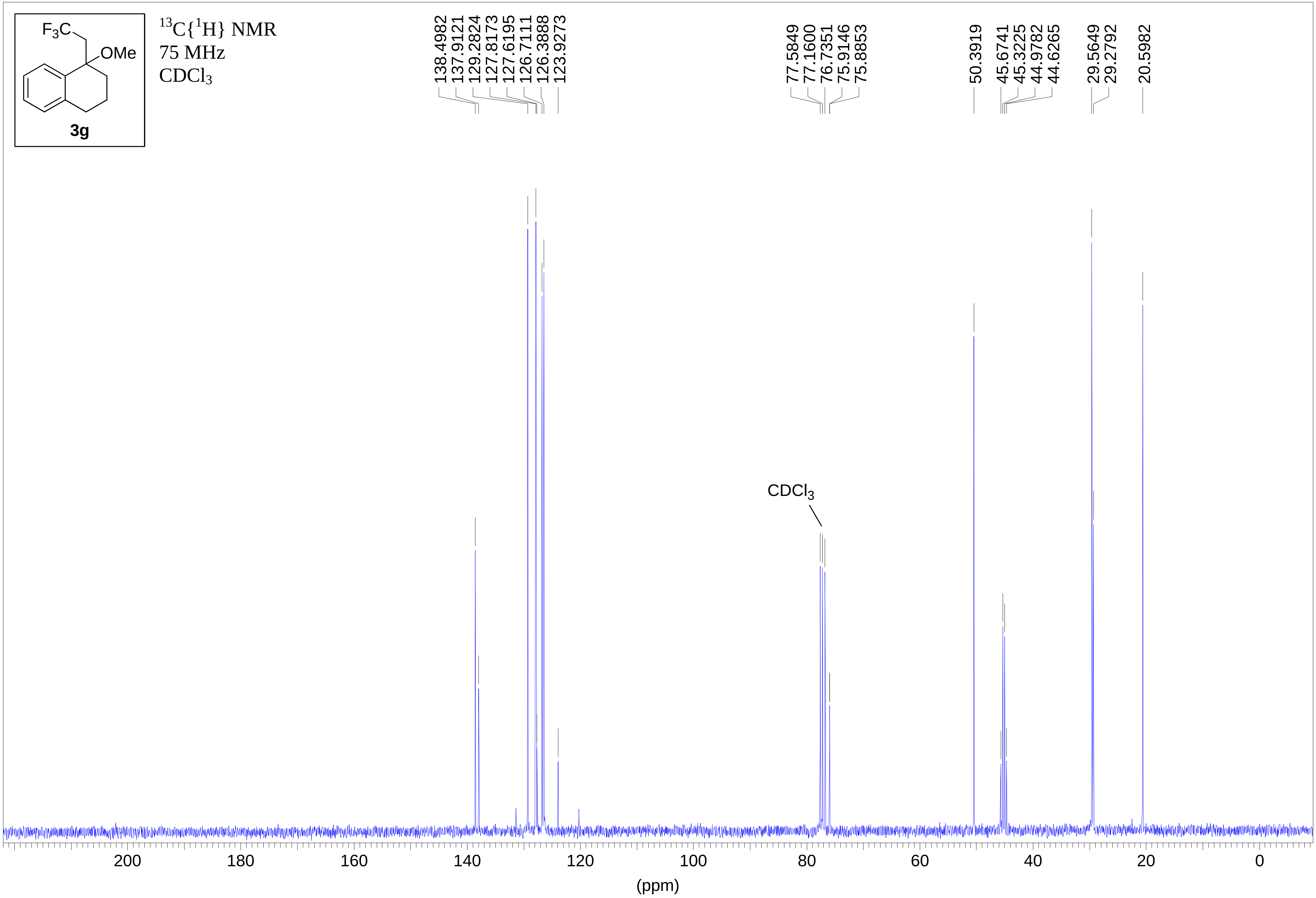


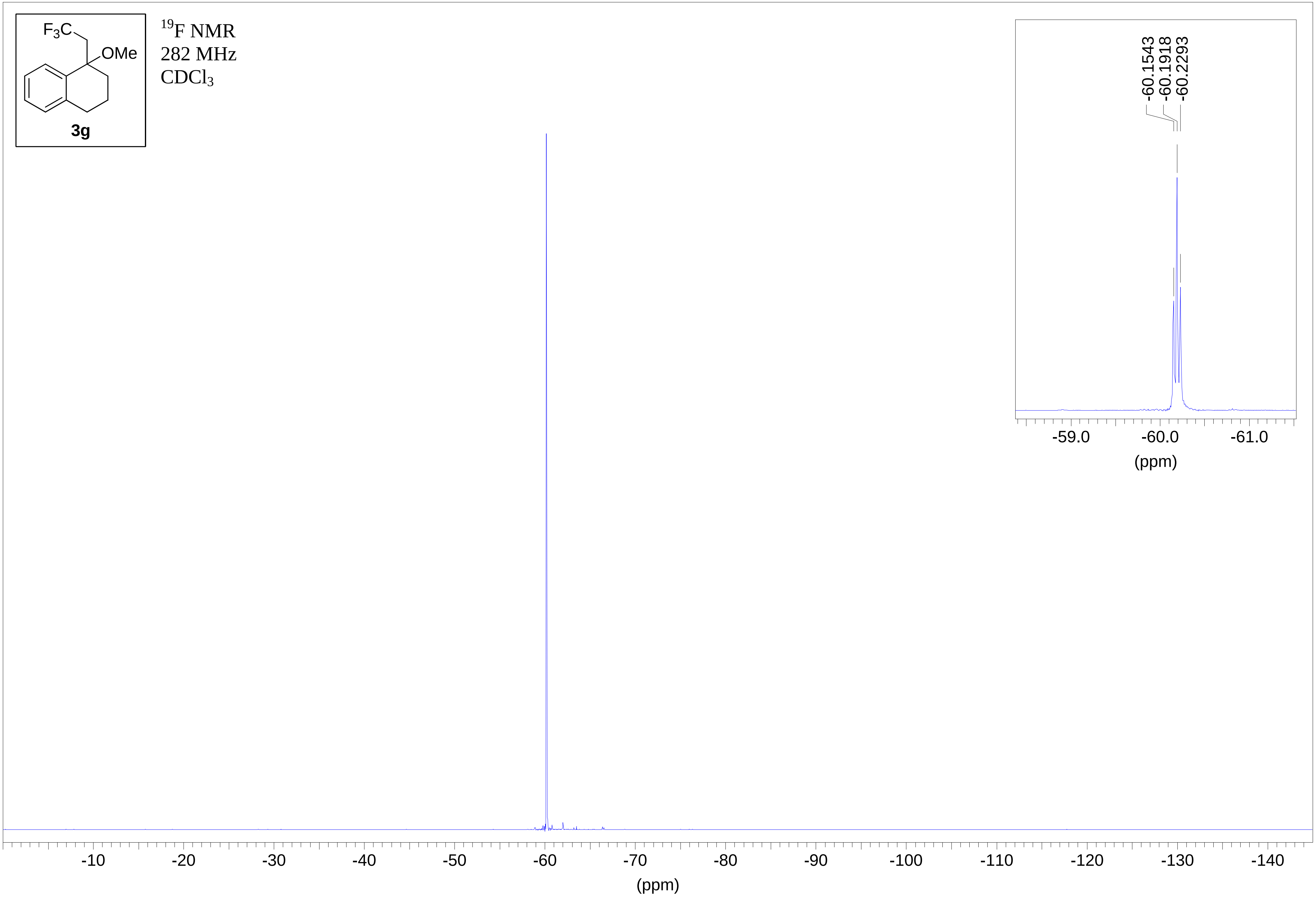
^{1}H-^{19}F HOESY





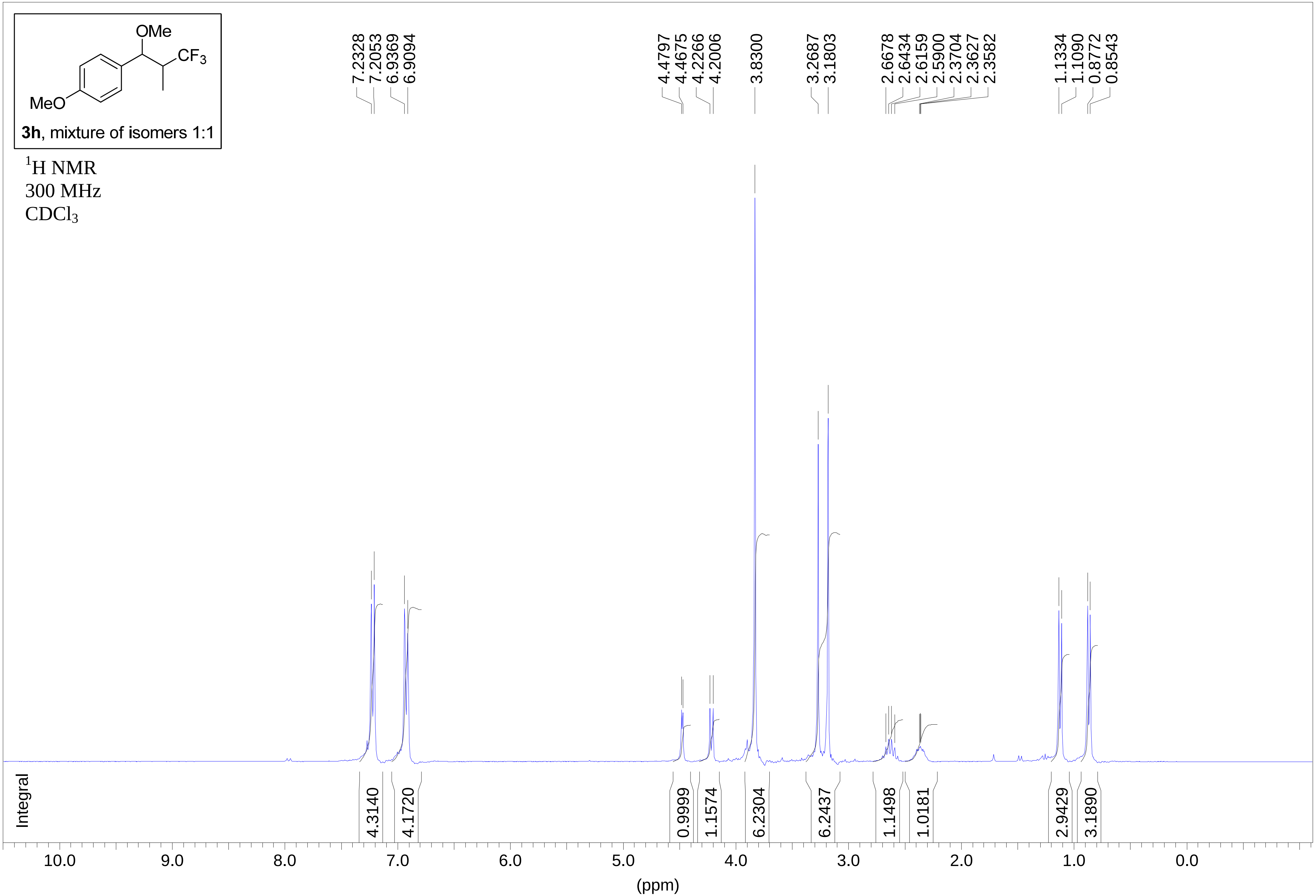
F_3C
OMe
3g
^{1}H NMR
300 MHz
$CDCl_3$
7.5014
7.4923
7.4715
7.2759
7.2637
7.2521
7.2460
7.1763
7.1568
7.1476
3.1085
2.8836
2.8634
2.8524
2.8341
2.8170
2.7223
2.7082
2.7003
2.6844
2.6716
2.6471
2.6349
2.6196
2.6098
2.5982
2.2524
2.2145
2.0807
2.0642
2.0501
2.0336
2.0183
2.0037
1.9835
1.9682
1.9633
1.9499
1.9365
1.9181
1.9047
1.8857
Integral
0.9999
3.0177
2.9085
4.0288
4.0570
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

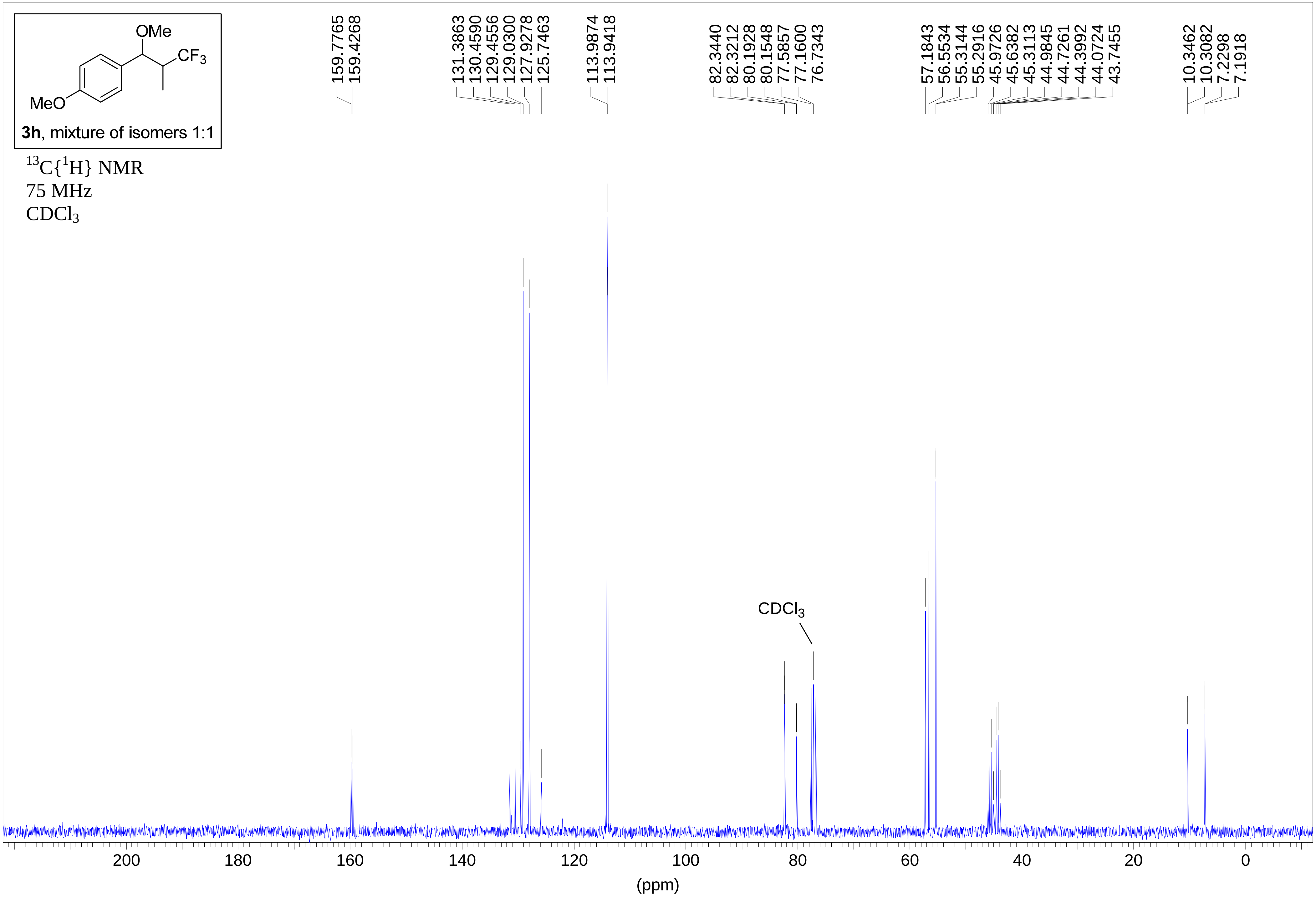

F3C
OMe
3g
13C{1H} NMR
75 MHz
CDCl3
138.4982
137.9121
129.2824
127.8173
127.6195
126.7111
126.3888
123.9273
77.5849
77.1600
76.7351
75.9146
75.8853
50.3919
45.6741
45.3225
44.9782
44.6265
29.5649
29.2792
20.5982
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

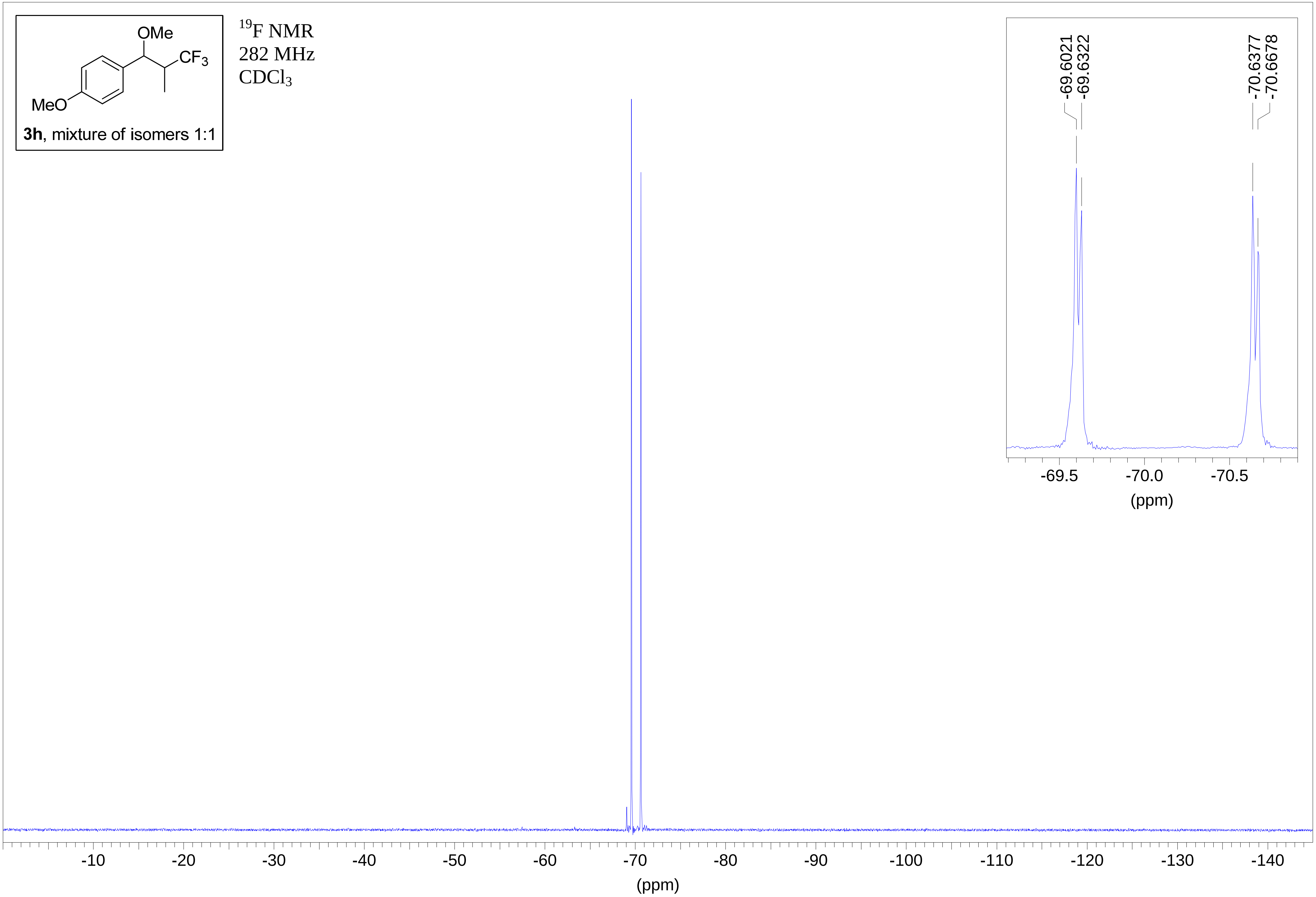


3g

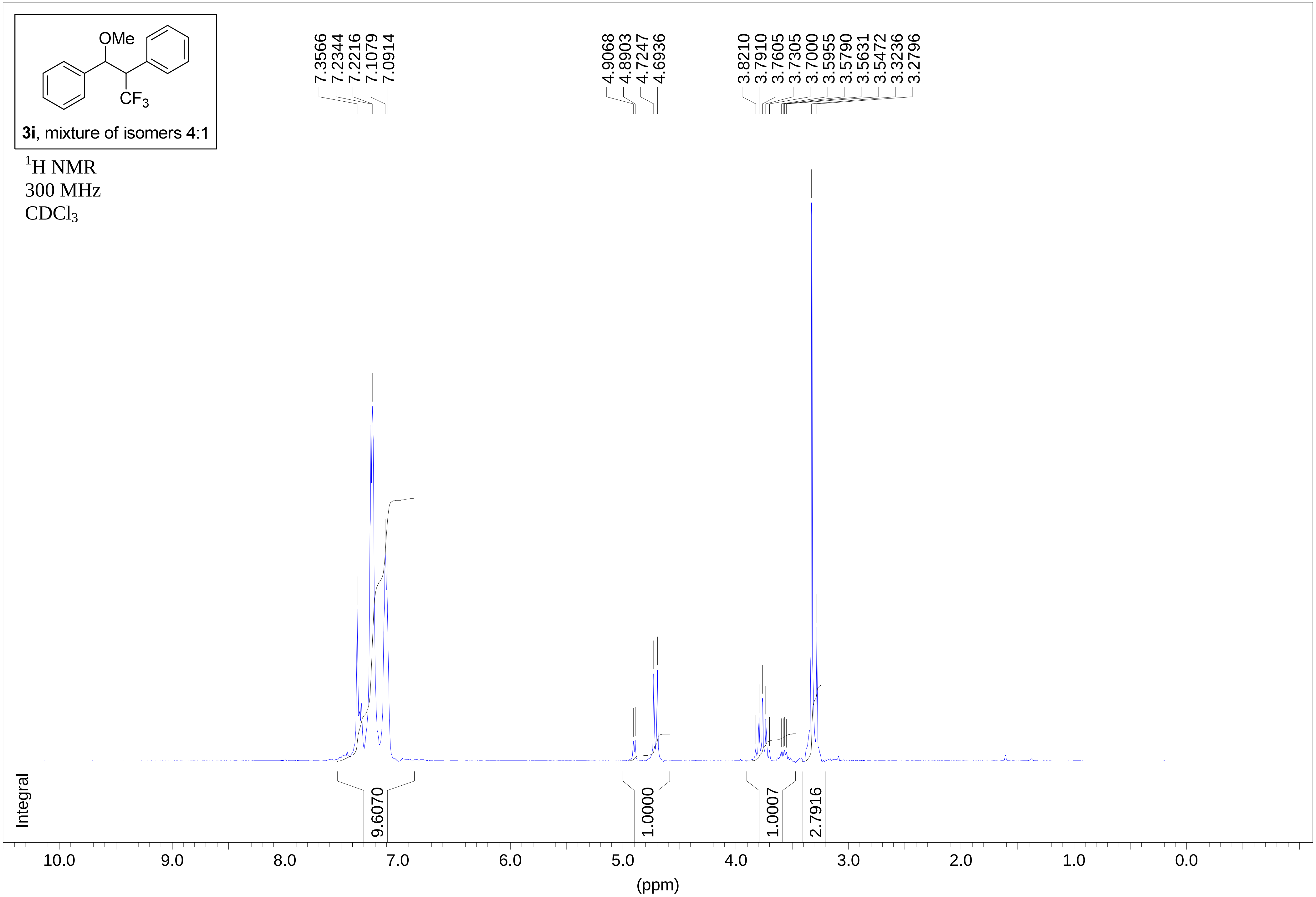
^{19}F NMR
282 MHz
$CDCl_3$


OMe
CF3
MeO
3h, mixture of isomers 1:1
1H NMR
300 MHz
CDCl3
7.2328
7.2053
6.9369
6.9094
4.4797
4.4675
4.2266
4.2006
3.8300
3.2687
3.1803
2.6678
2.6434
2.6159
2.5900
2.3704
2.3627
2.3582
1.1334
1.1090
0.8772
0.8543
Integral
4.3140
4.1720
0.9999
1.1574
6.2304
6.2437
1.1498
1.0181
2.9429
3.1890
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OMe
CF3
MeO
3h, mixture of isomers 1:1
13C{1H} NMR
75 MHz
CDCl3
159.7765
159.4268
131.3863
130.4590
129.4556
129.0300
127.9278
125.7463
113.9874
113.9418
82.3440
82.3212
80.1928
80.1548
77.5857
77.1600
76.7343
57.1843
56.5534
55.3144
55.2916
45.9726
45.6382
45.3113
44.9845
44.7261
44.3992
44.0724
43.7455
10.3462
10.3082
7.2298
7.1918
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

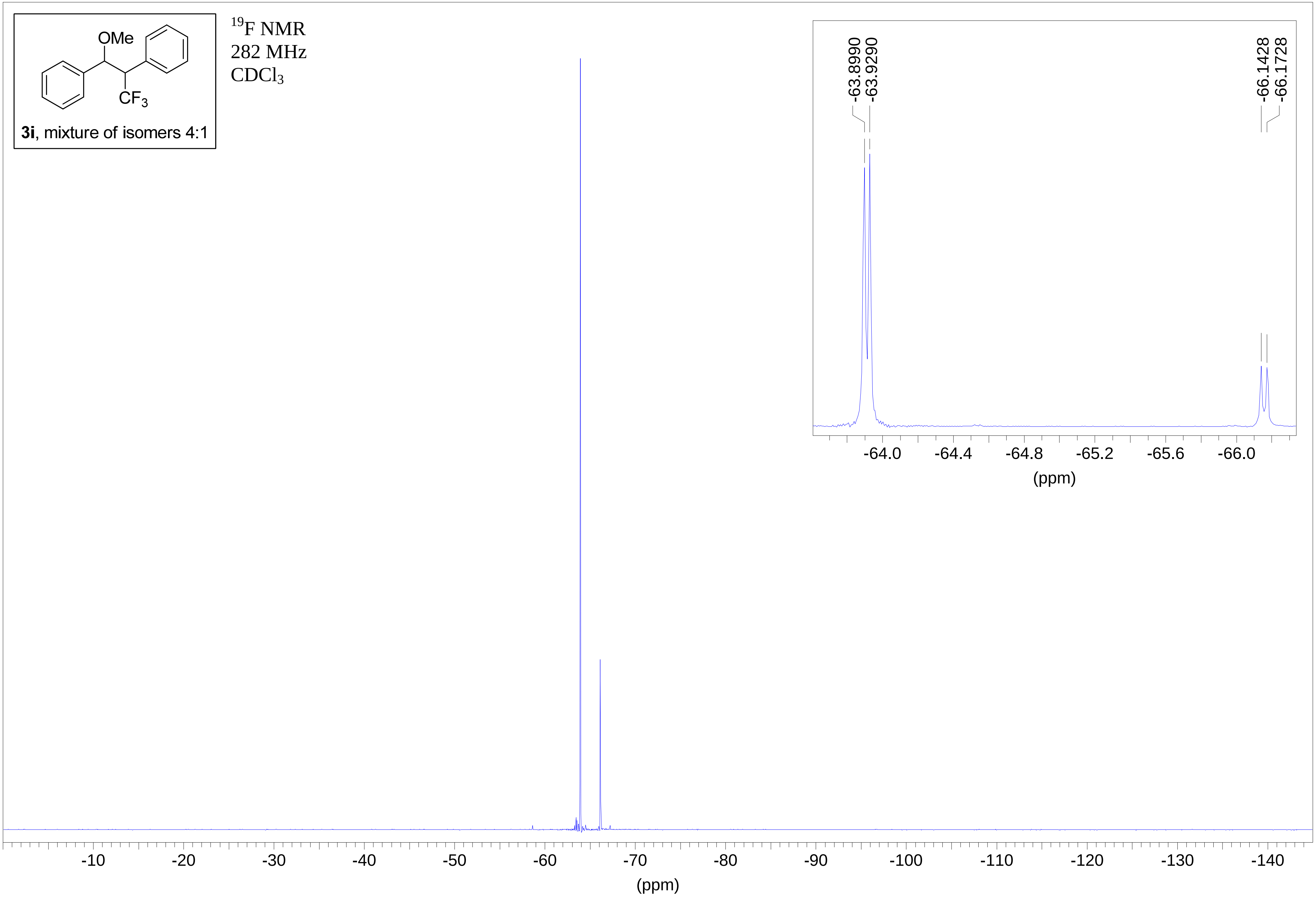


3h, mixture of isomers 1:1



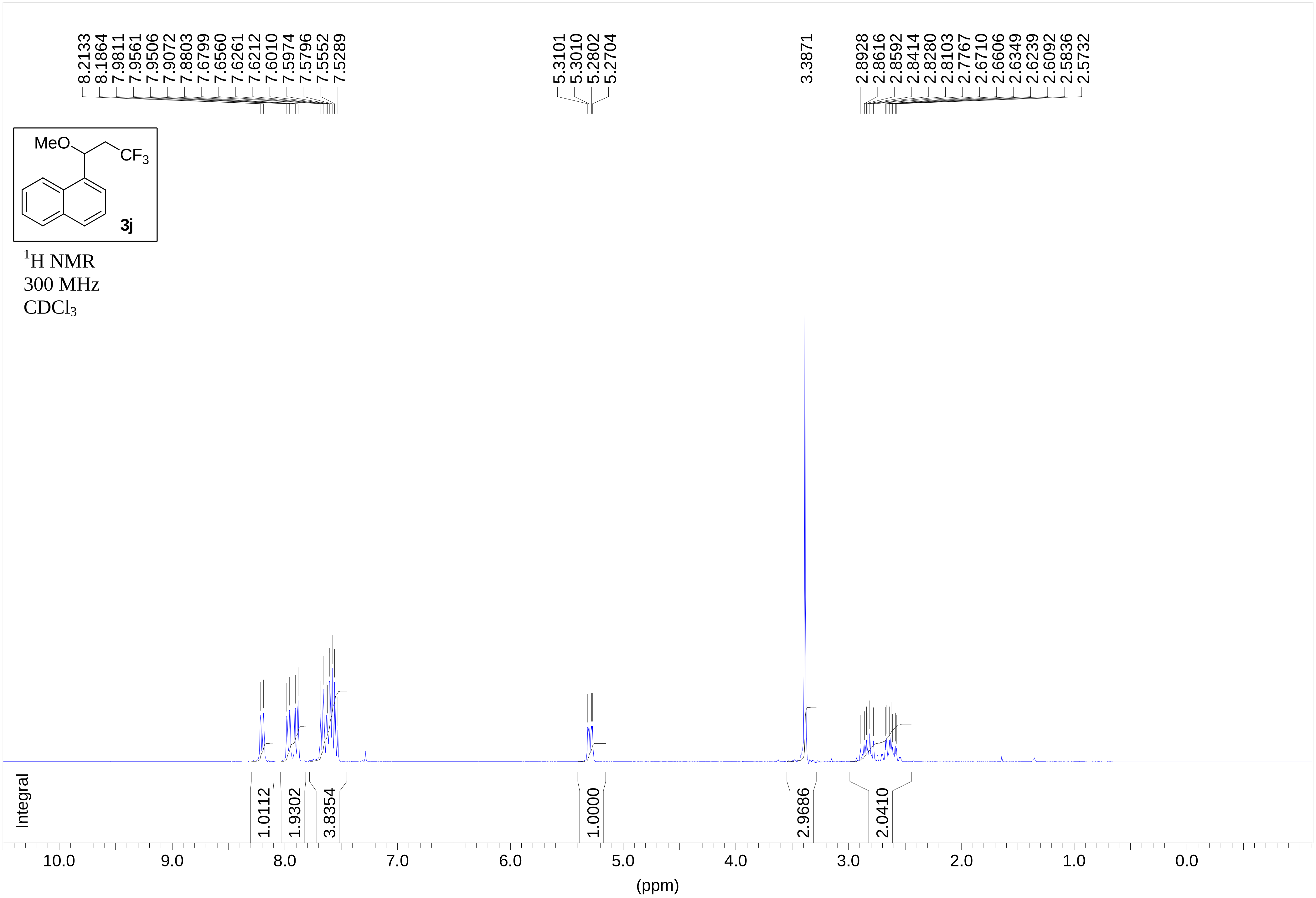
3i, mixture of isomers 4:1

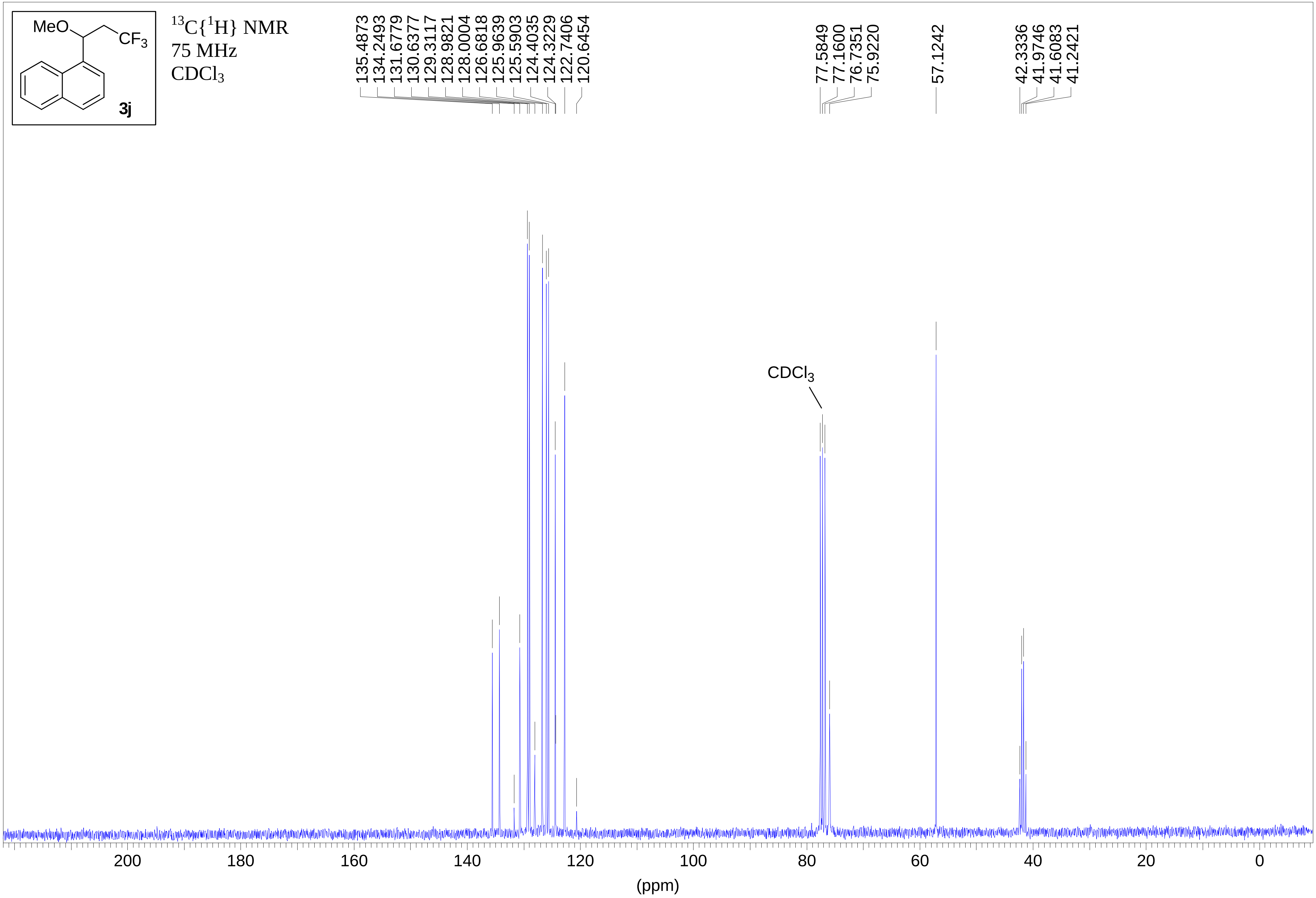
^{1}H NMR
300 MHz
$CDCl_3$



3i, mixture of isomers 4:1

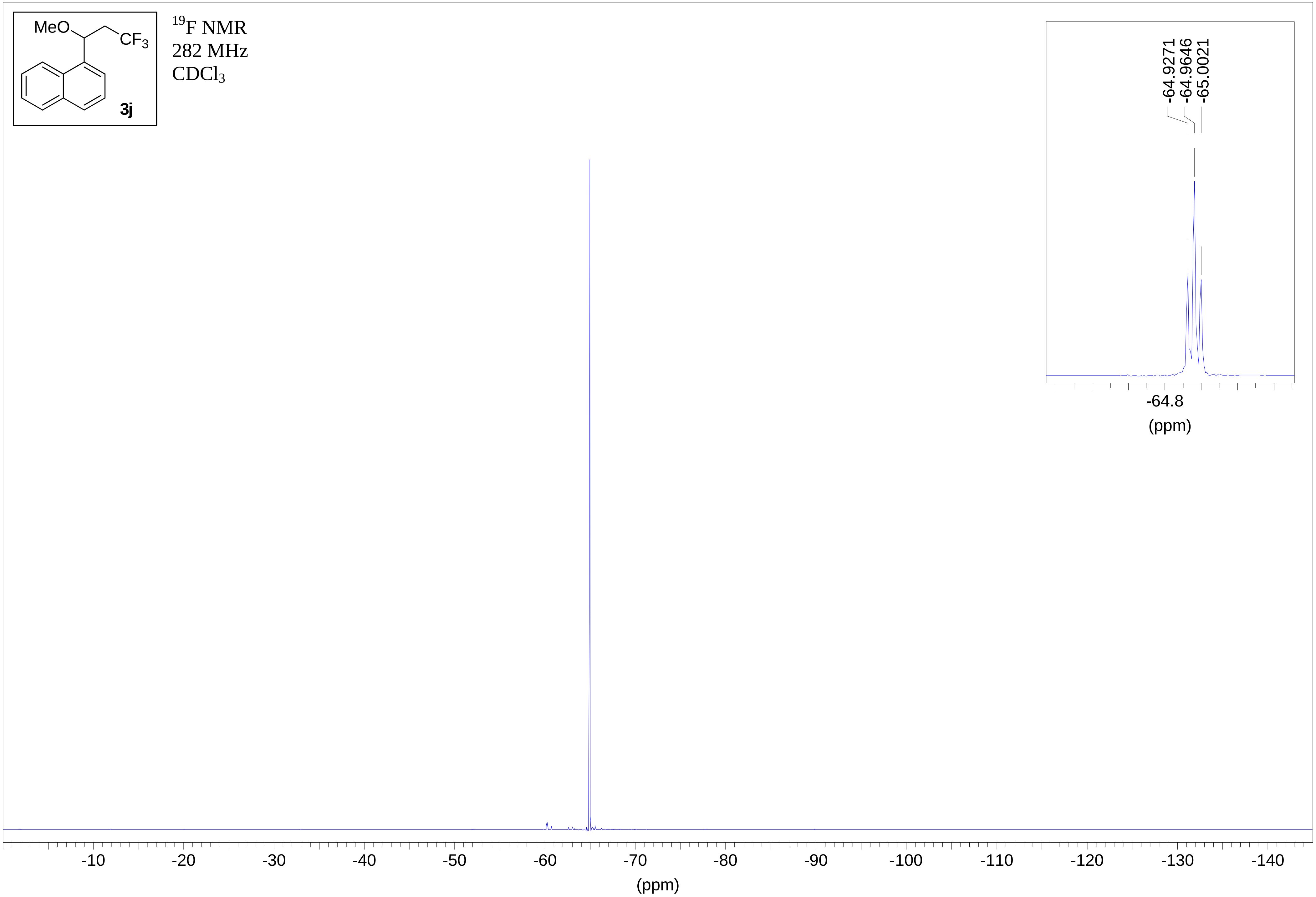
^{19}F NMR
282 MHz
$CDCl_3$

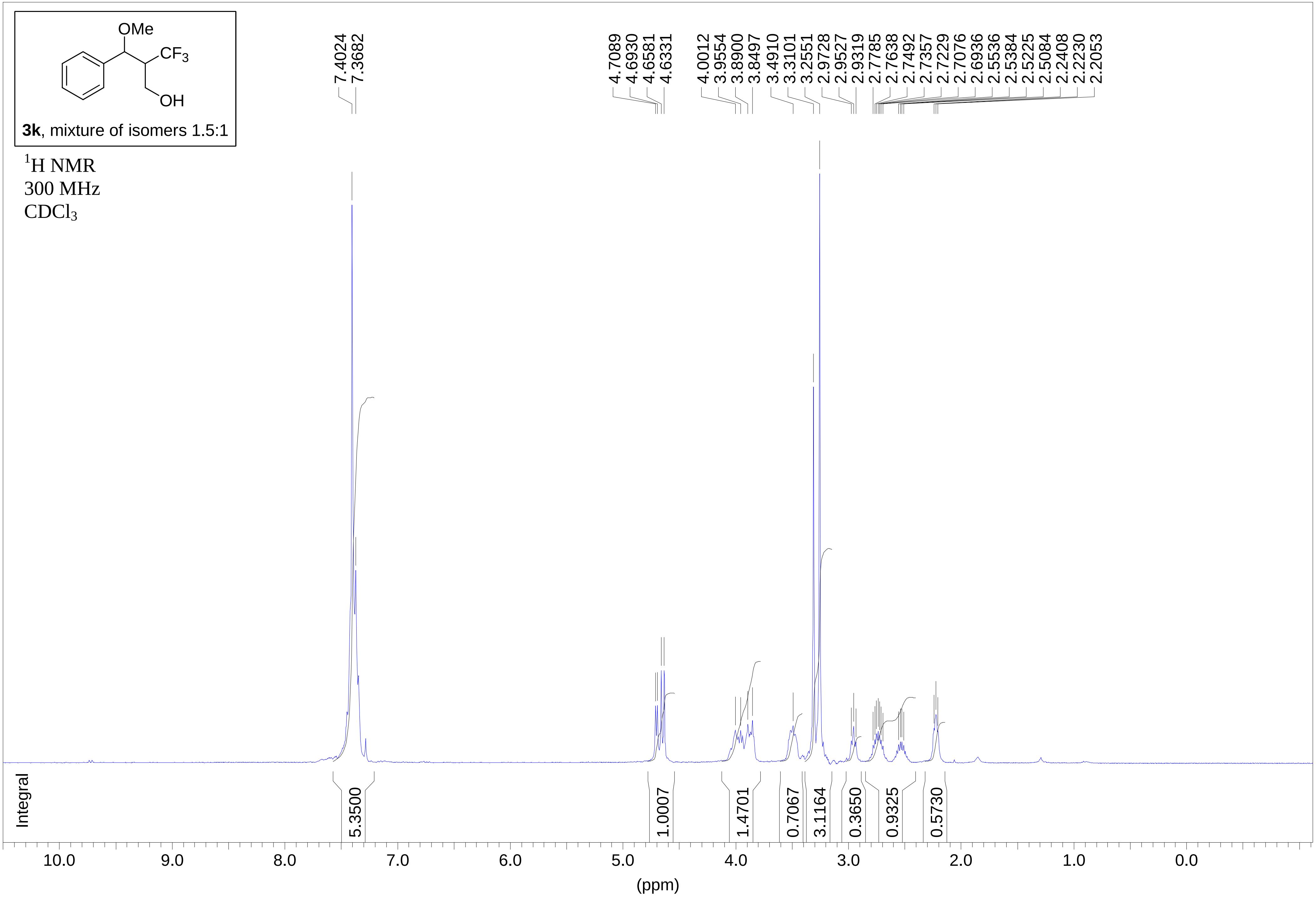

8.2133
8.1864
7.9811
7.9561
7.9506
7.9072
7.8803
7.6799
7.6560
7.6261
7.6212
7.6010
7.5974
7.5796
7.5552
7.5289
5.3101
5.3010
5.2802
5.2704
3.3871
2.8928
2.8616
2.8592
2.8414
2.8280
2.8103
2.7767
2.6710
2.6606
2.6349
2.6239
2.6092
2.5836
2.5732
MeO
CF3
3j
1H NMR
300 MHz
CDCl3
Integral
1.0112
1.9302
3.8354
1.0000
2.9686
2.0410
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

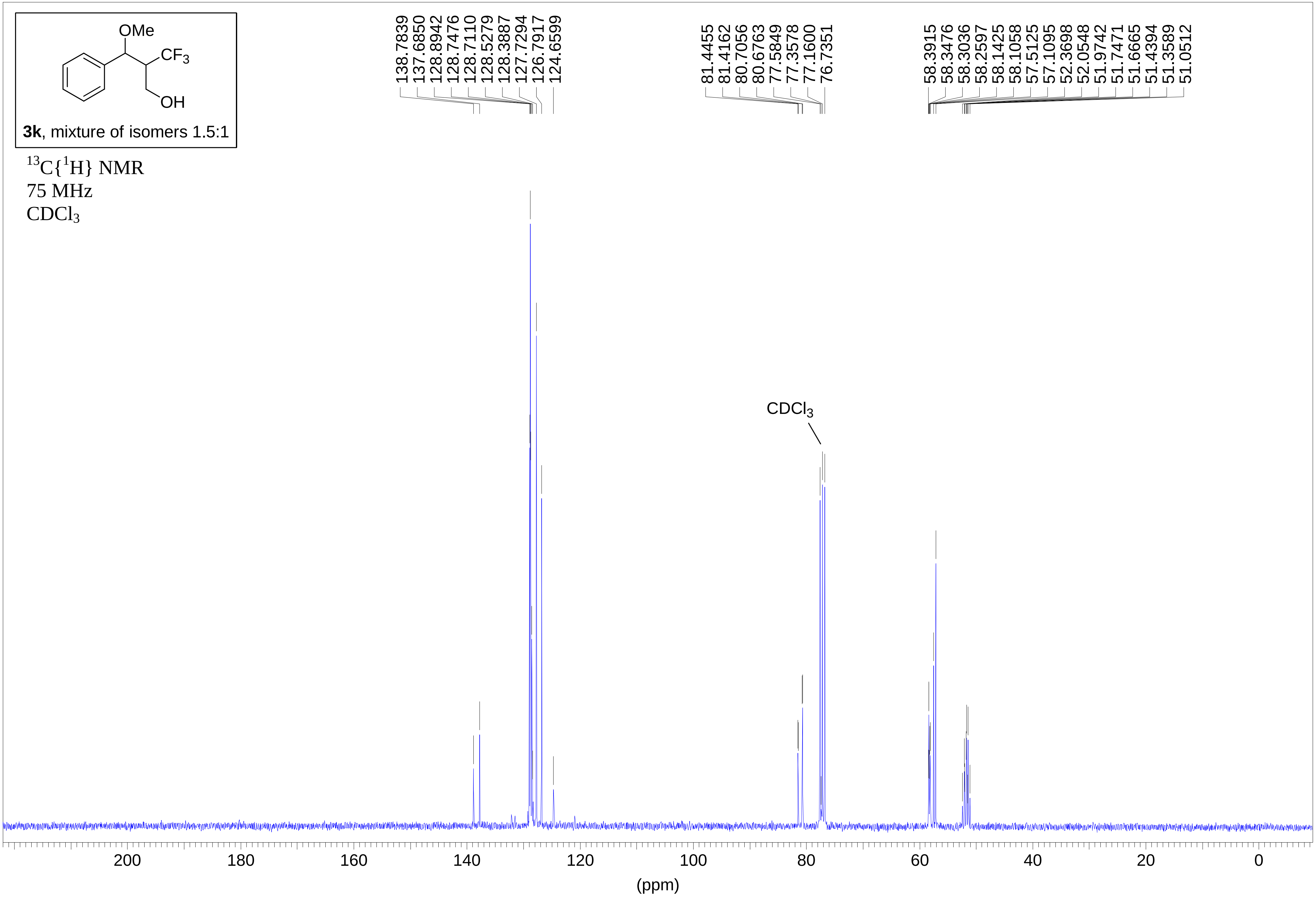


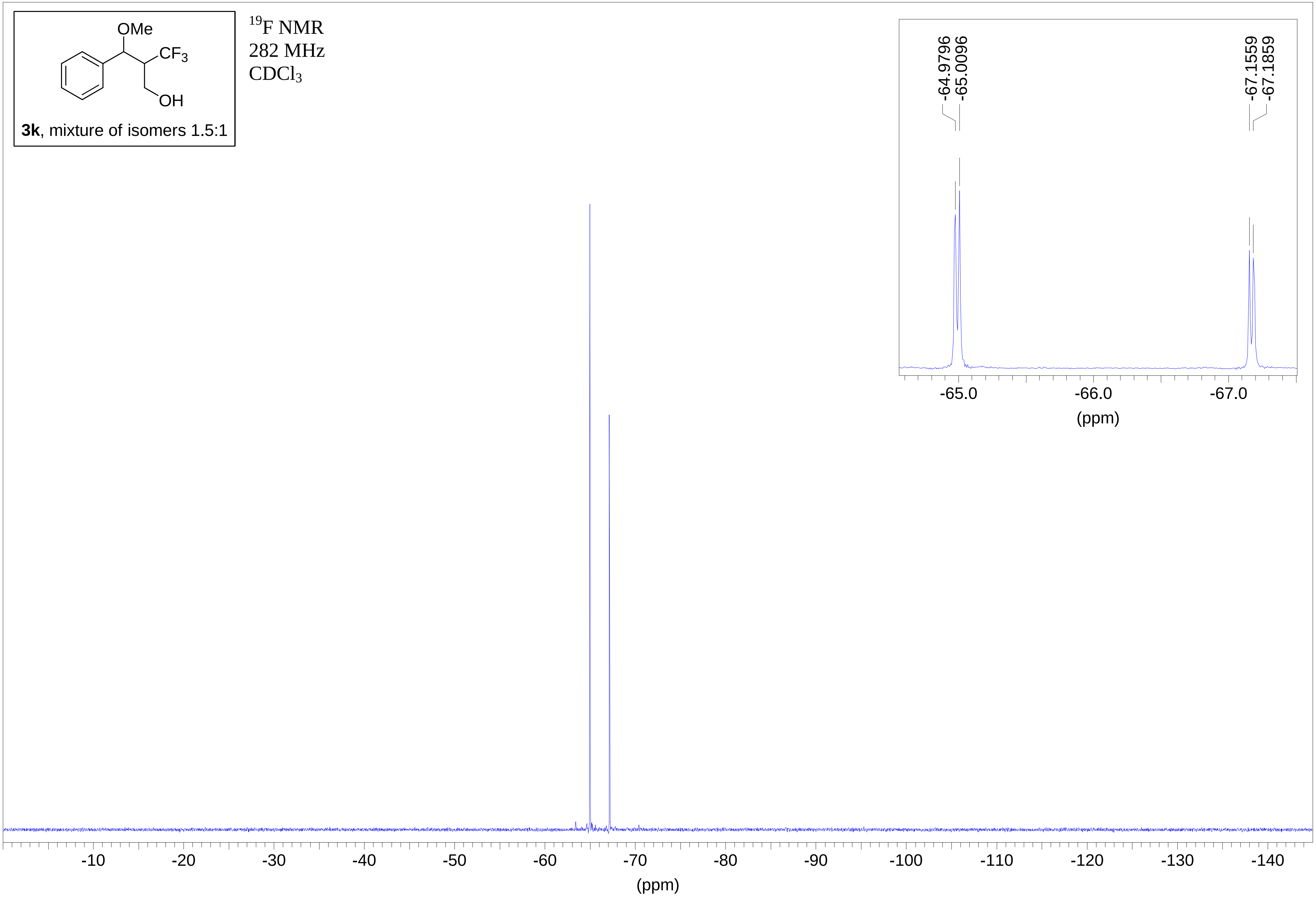
3j

MeO
CF3
^{13}C{^{1}H} NMR
75 MHz
$CDCl_3$
135.4873
134.2493
131.6779
130.6377
129.3117
128.9821
128.0004
126.6818
125.9639
125.5903
124.4035
124.3229
122.7406
120.6454
77.5849
77.1600
76.7351
75.9220
57.1242
42.3336
41.9746
41.6083
41.2421
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)


MeO
CF3
3j
19F NMR
282 MHz
CDCl3
-64.9271
-64.9646
-65.0021
-64.8
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)

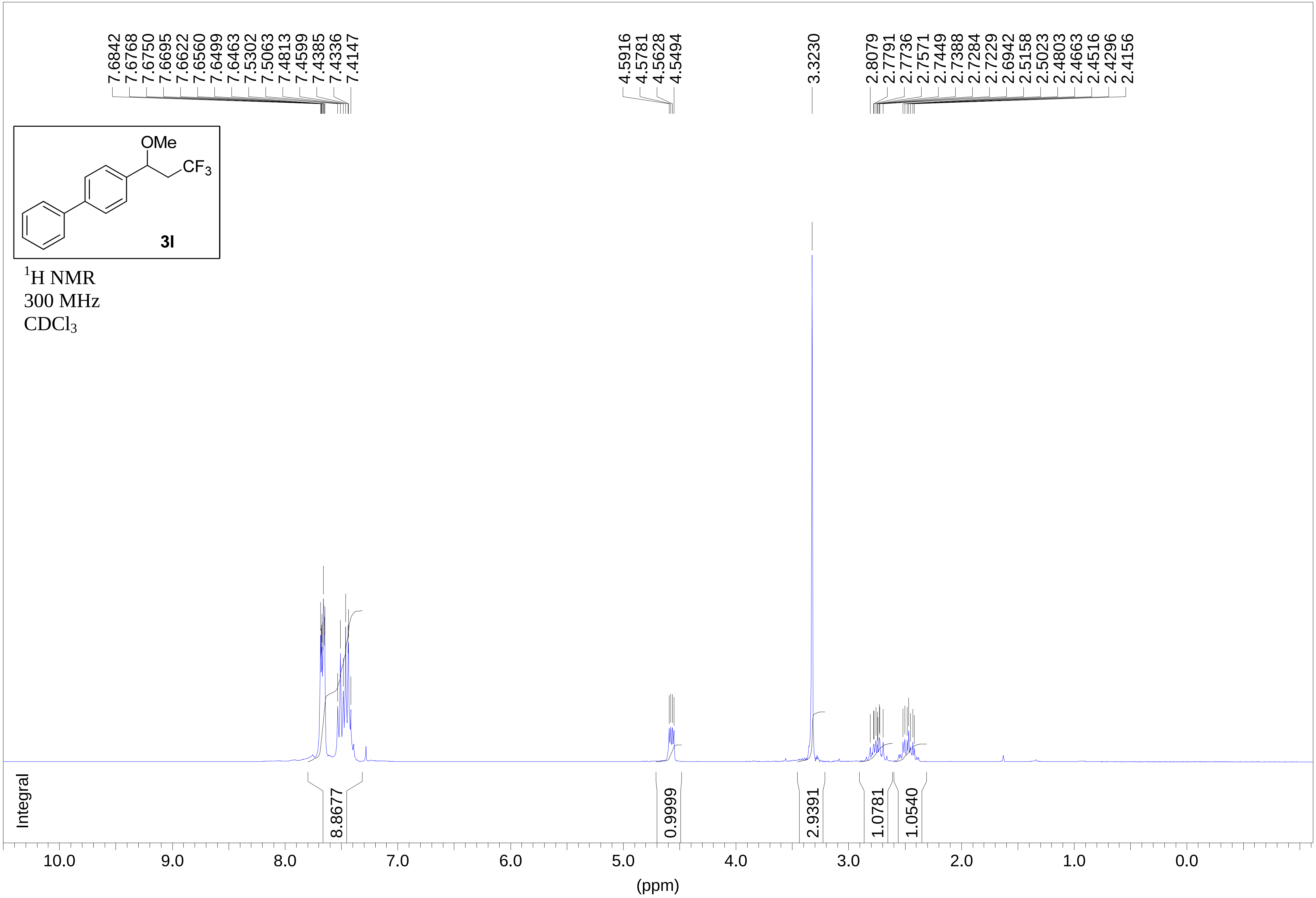

OMe
CF3
OH
3k, mixture of isomers 1.5:1
1H NMR
300 MHz
CDCl3
7.4024
7.3682
4.7089
4.6930
4.6581
4.6331
4.0012
3.9554
3.8900
3.8497
3.4910
3.3101
3.2551
2.9728
2.9527
2.9319
2.7785
2.7638
2.7492
2.7357
2.7229
2.7076
2.6936
2.5536
2.5384
2.5225
2.5084
2.2408
2.2230
2.2053
Integral
5.3500
1.0007
1.4701
0.7067
3.1164
0.3650
0.9325
0.5730
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

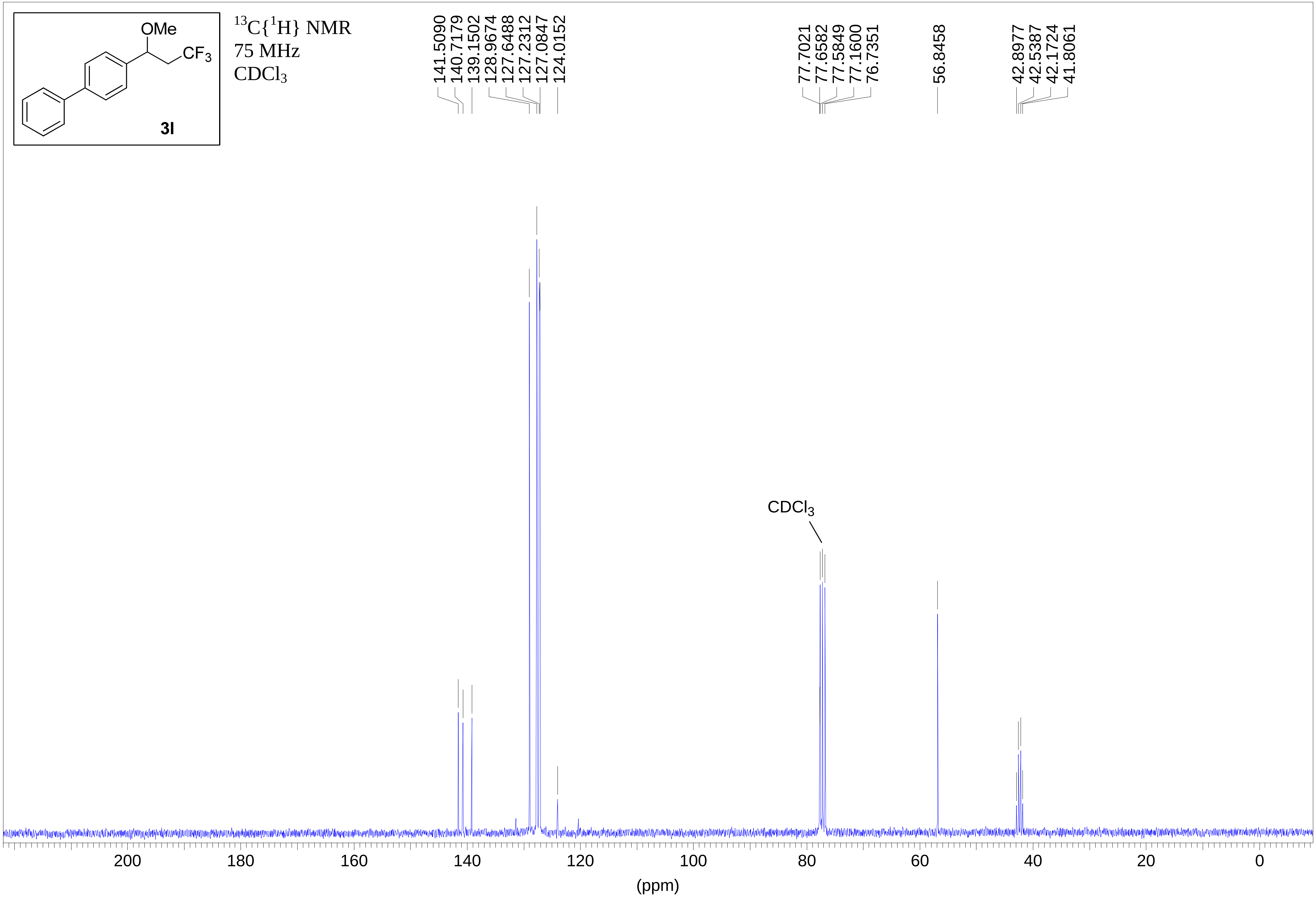

OMe
CF3
OH
3k, mixture of isomers 1.5:1
13C{1H} NMR
75 MHz
CDCl3
138.7839
137.6850
128.8942
128.7476
128.7110
128.5279
128.3887
127.7294
126.7917
124.6599
81.4455
81.4162
80.7056
80.6763
77.5849
77.3578
77.1600
76.7351
58.3915
58.3476
58.3036
58.2597
58.1425
58.1058
57.5125
57.1095
52.3698
52.0548
51.9742
51.7471
51.6665
51.4394
51.3589
51.0512
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

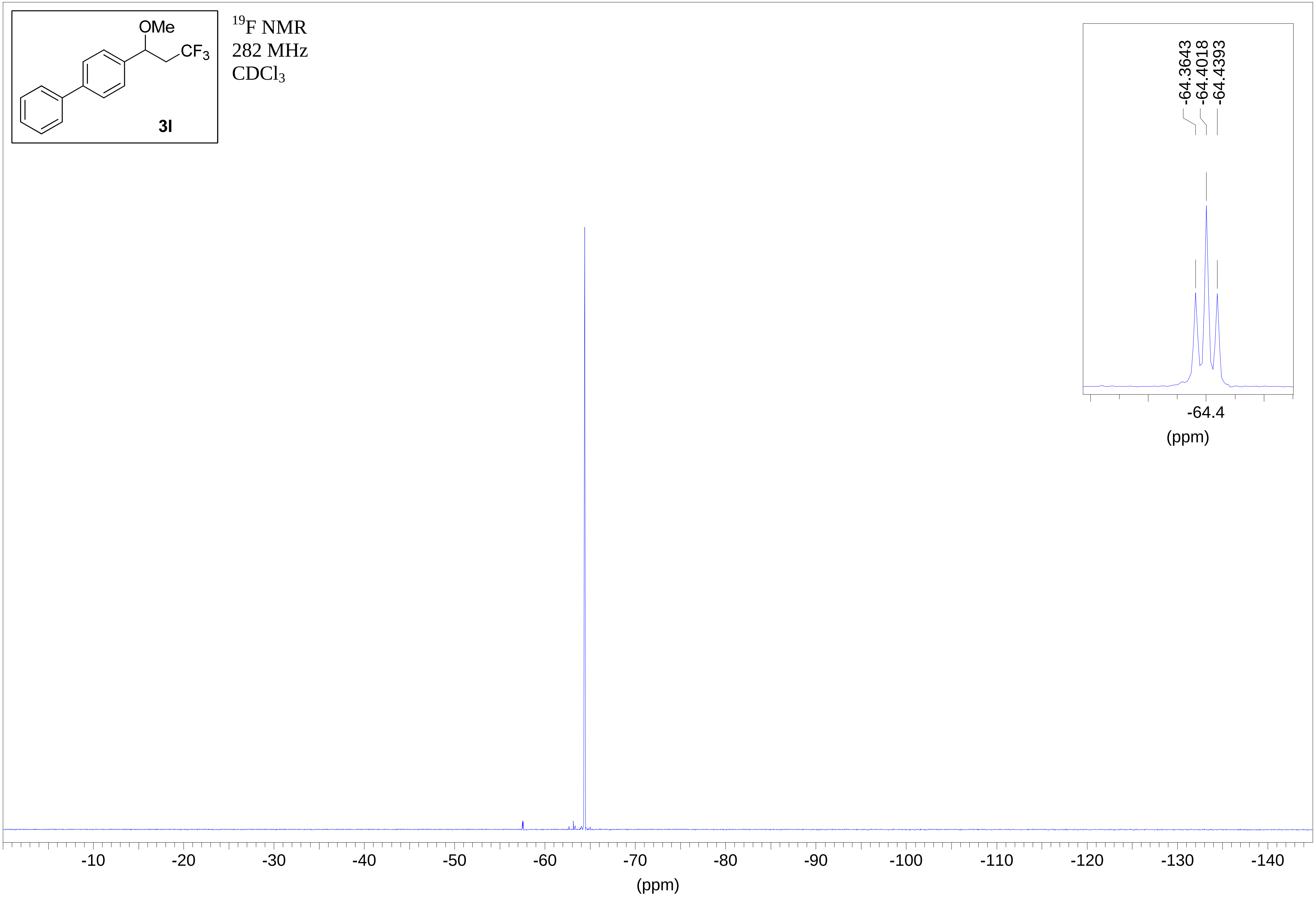


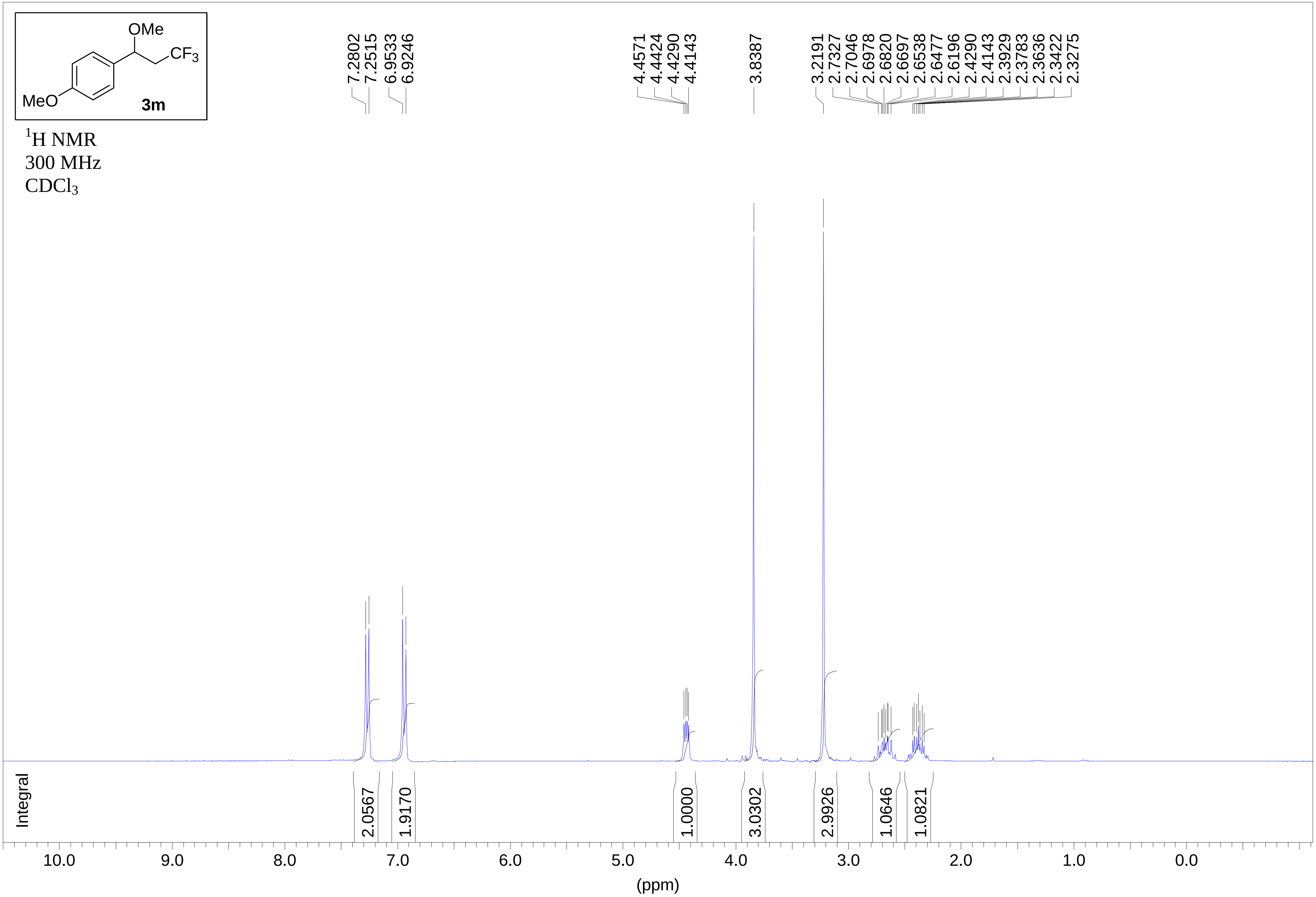
3k, mixture of isomers 1.5:1

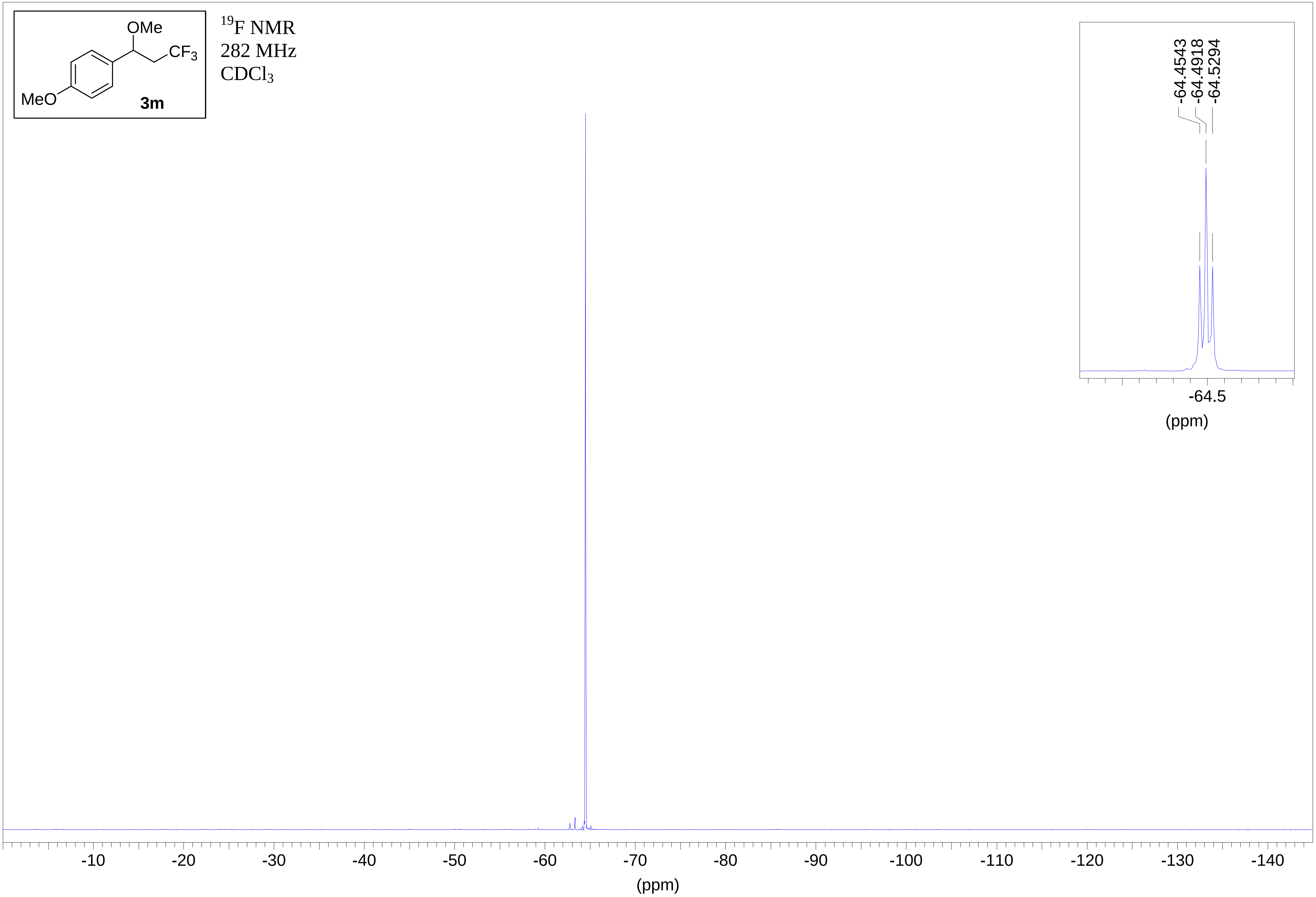
^{19}F NMR
282 MHz
$CDCl_3$

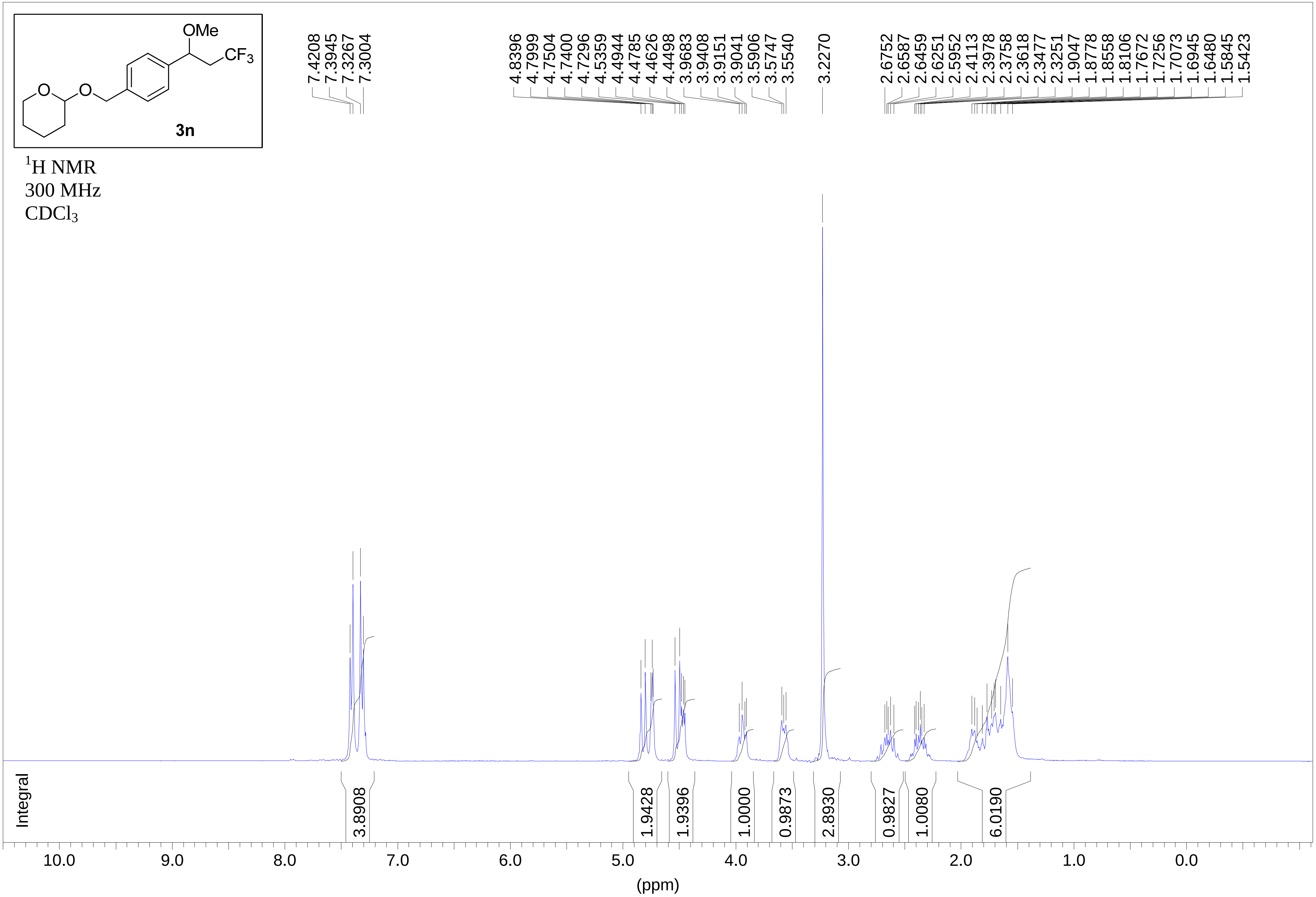

7.6842
7.6768
7.6750
7.6695
7.6622
7.6560
7.6499
7.6463
7.5302
7.5063
7.4813
7.4599
7.4385
7.4336
7.4147
4.5916
4.5781
4.5628
4.5494
3.3230
2.8079
2.7791
2.7736
2.7571
2.7449
2.7388
2.7284
2.7229
2.6942
2.5158
2.5023
2.4803
2.4663
2.4516
2.4296
2.4156
OMe
CF3
3l
1H NMR
300 MHz
CDCl3
Integral
8.8677
0.9999
2.9391
1.0781
1.0540
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

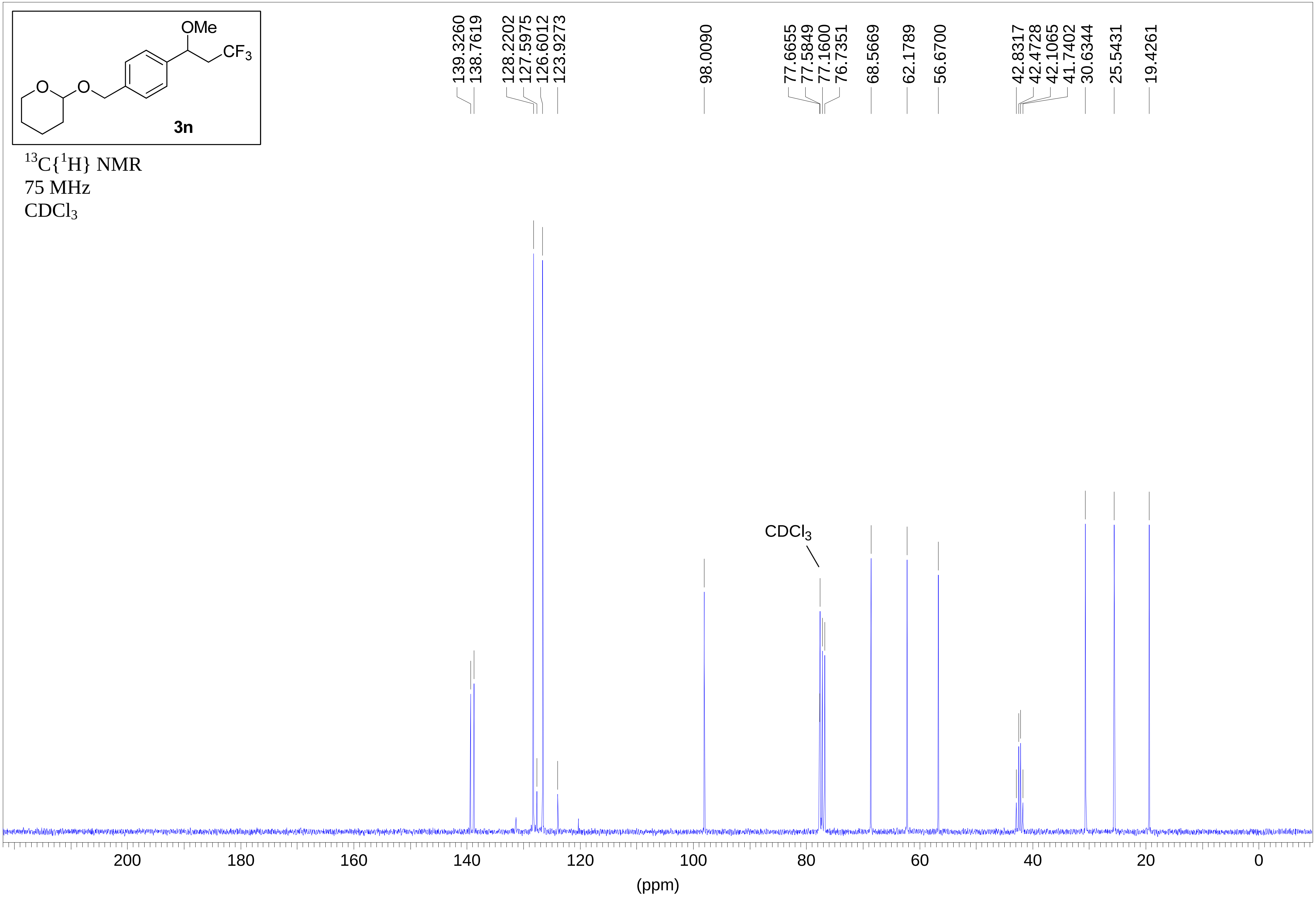

OMe
CF3
3l
13C{1H} NMR
75 MHz
CDCl3
141.5090
140.7179
139.1502
128.9674
127.6488
127.2312
127.0847
124.0152
77.7021
77.6582
77.5849
77.1600
76.7351
56.8458
42.8977
42.5387
42.1724
41.8061
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

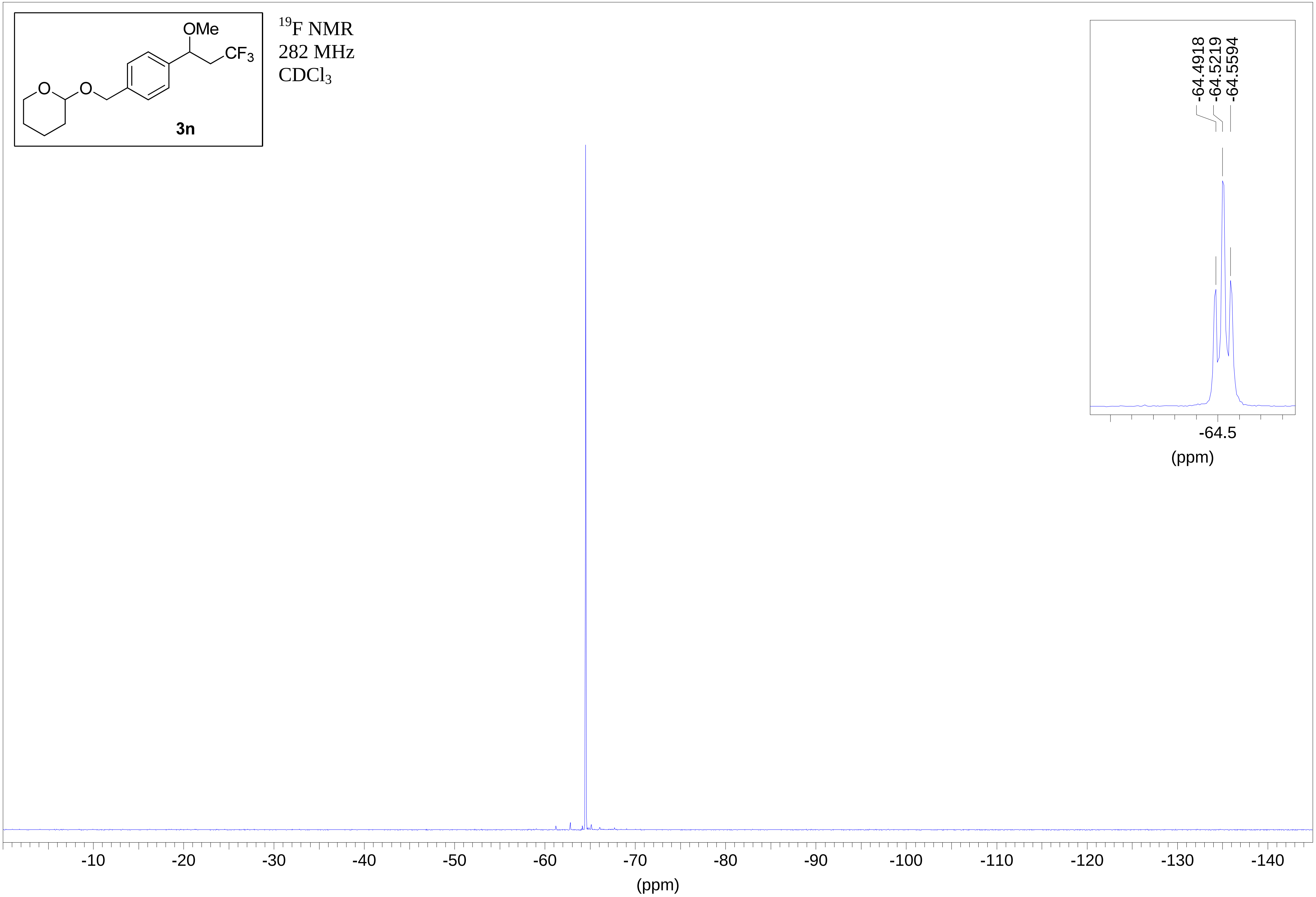

OMe
CF$_3$
3l
^{19}F NMR
282 MHz
CDCl$_3$
-64.3643
-64.4018
-64.4393
-64.4
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)


OMe
CF3
MeO
3m
1H NMR
300 MHz
CDCl3
7.2802
7.2515
6.9533
6.9246
4.4571
4.4424
4.4290
4.4143
3.8387
3.2191
2.7327
2.7046
2.6978
2.6820
2.6697
2.6538
2.6477
2.6196
2.4290
2.4143
2.3929
2.3783
2.3636
2.3422
2.3275
Integral
2.0567
1.9170
1.0000
3.0302
2.9926
1.0646
1.0821
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OMe
CF$_3$
MeO
3m
^{19}F NMR
282 MHz
CDCl$_3$
-64.4543
-64.4918
-64.5294
-64.5
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)

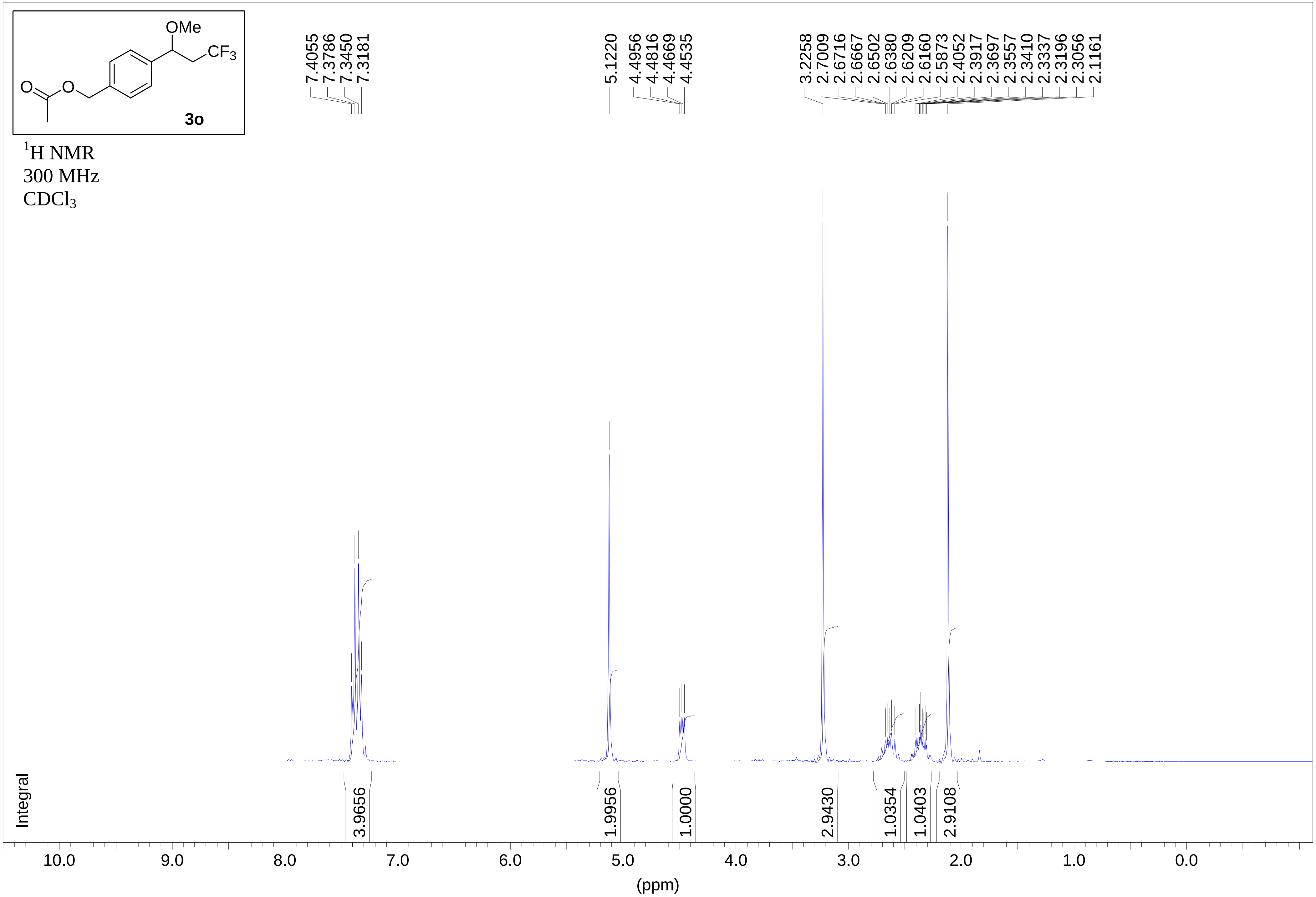

OMe
CF$_3$
O
O
3n
^{1}H NMR
300 MHz
CDCl$_3$
7.4208
7.3945
7.3267
7.3004
4.8396
4.7999
4.7504
4.7400
4.7296
4.5359
4.4944
4.4785
4.4626
4.4498
3.9683
3.9408
3.9151
3.9041
3.5906
3.5747
3.5540
3.2270
2.6752
2.6587
2.6459
2.6251
2.5952
2.4113
2.3978
2.3758
2.3618
2.3477
2.3251
1.9047
1.8778
1.8558
1.8106
1.7672
1.7256
1.7073
1.6945
1.6480
1.5845
1.5423
Integral
3.8908
1.9428
1.9396
1.0000
0.9873
2.8930
0.9827
1.0080
6.0190
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OMe
CF3
O
O
3n
13C{1H} NMR
75 MHz
CDCl3
139.3260
138.7619
128.2202
127.5975
126.6012
123.9273
98.0090
77.6655
77.5849
77.1600
76.7351
68.5669
62.1789
56.6700
42.8317
42.4728
42.1065
41.7402
30.6344
25.5431
19.4261
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)



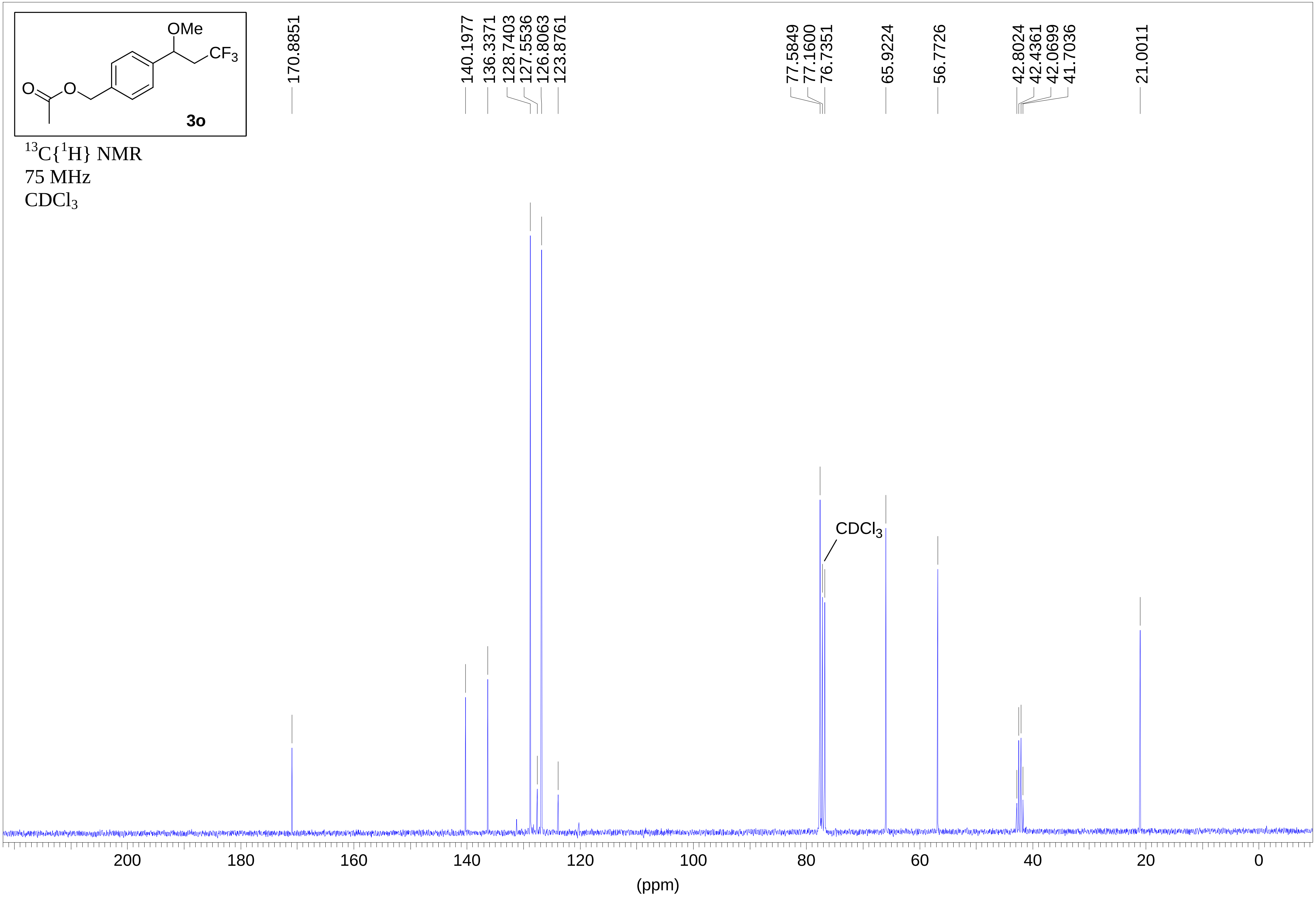
3n

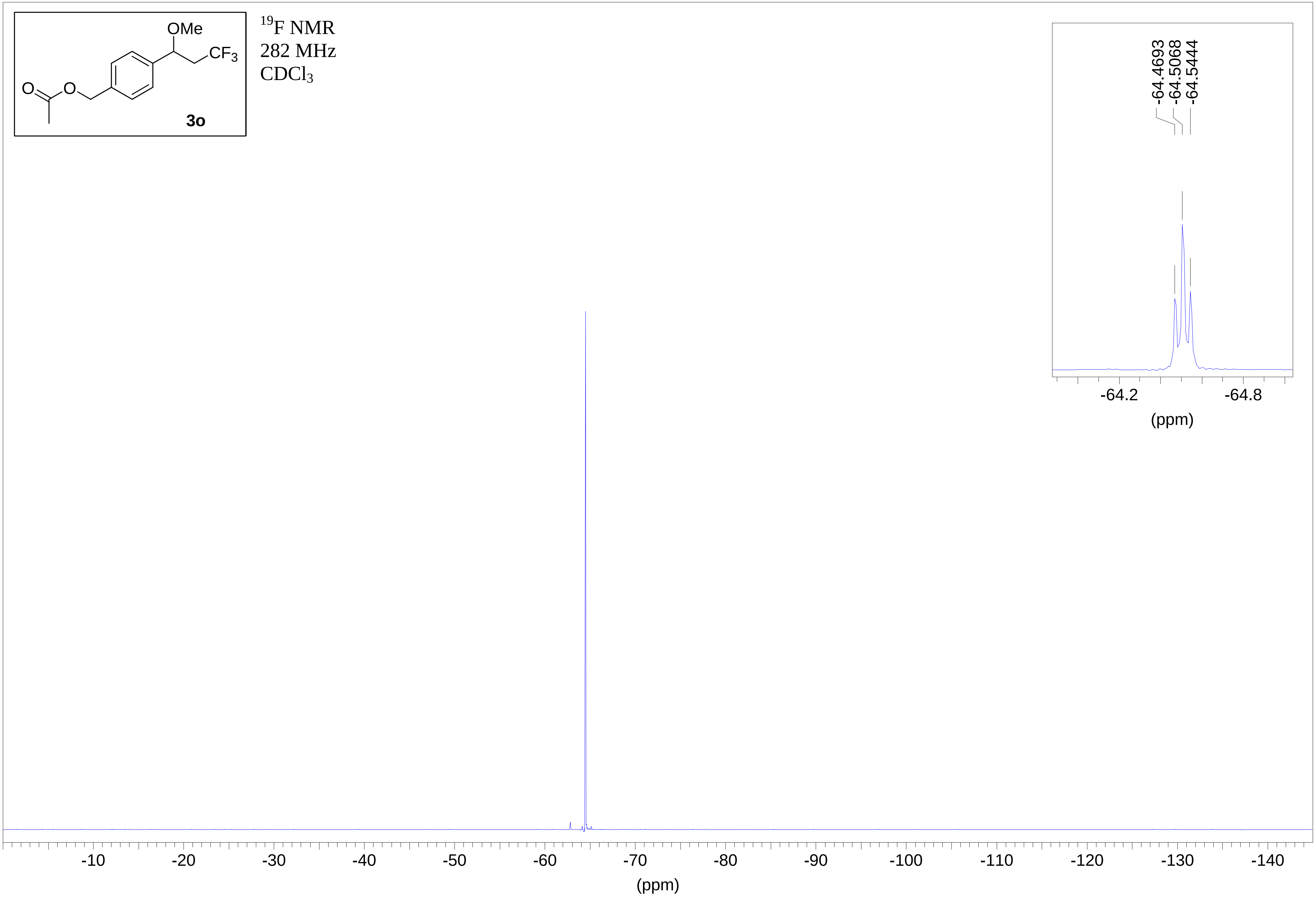
^{19}F NMR
282 MHz
CDCl$_3$



3o

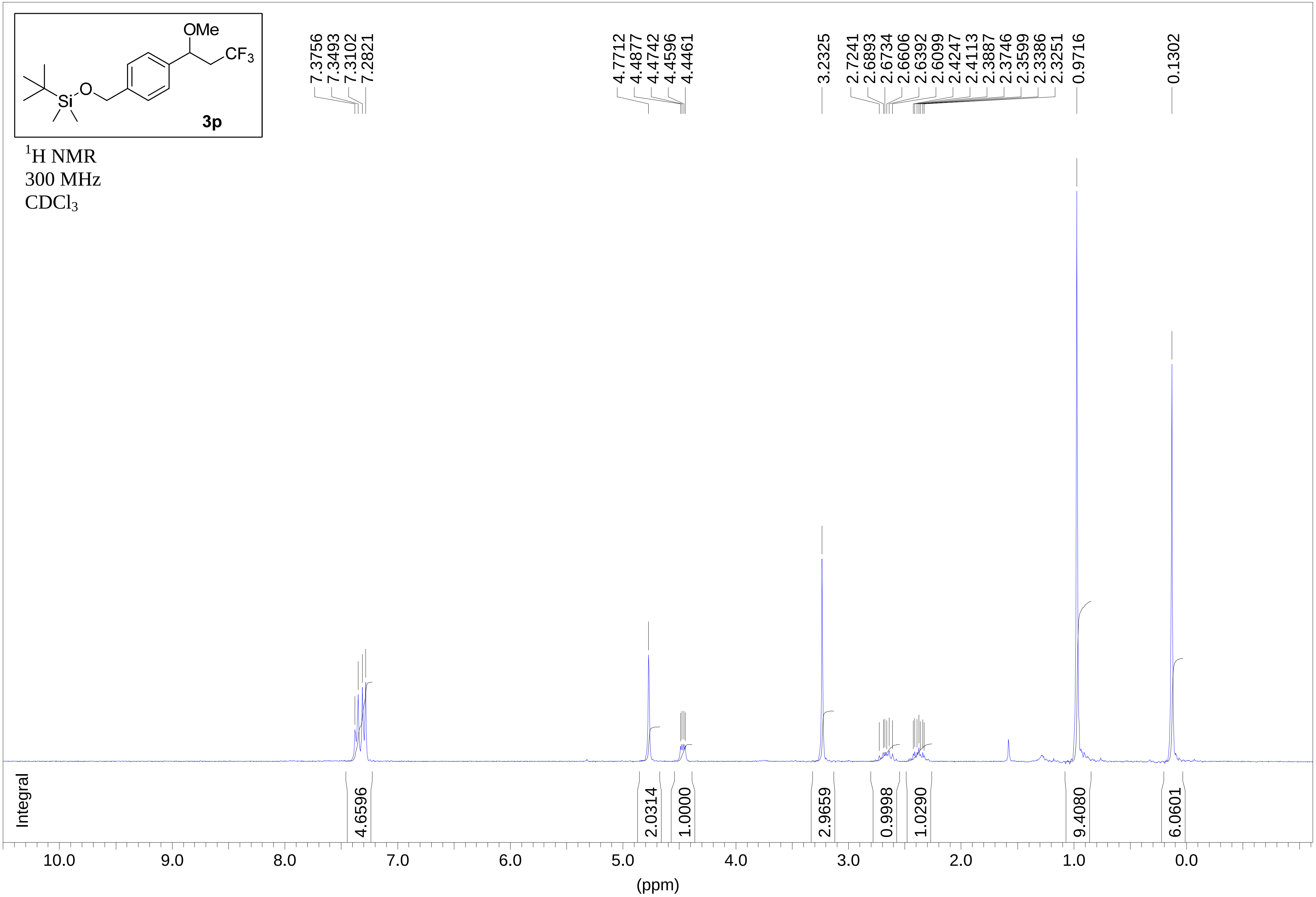
^{1}H NMR
300 MHz
CDCl$_3$

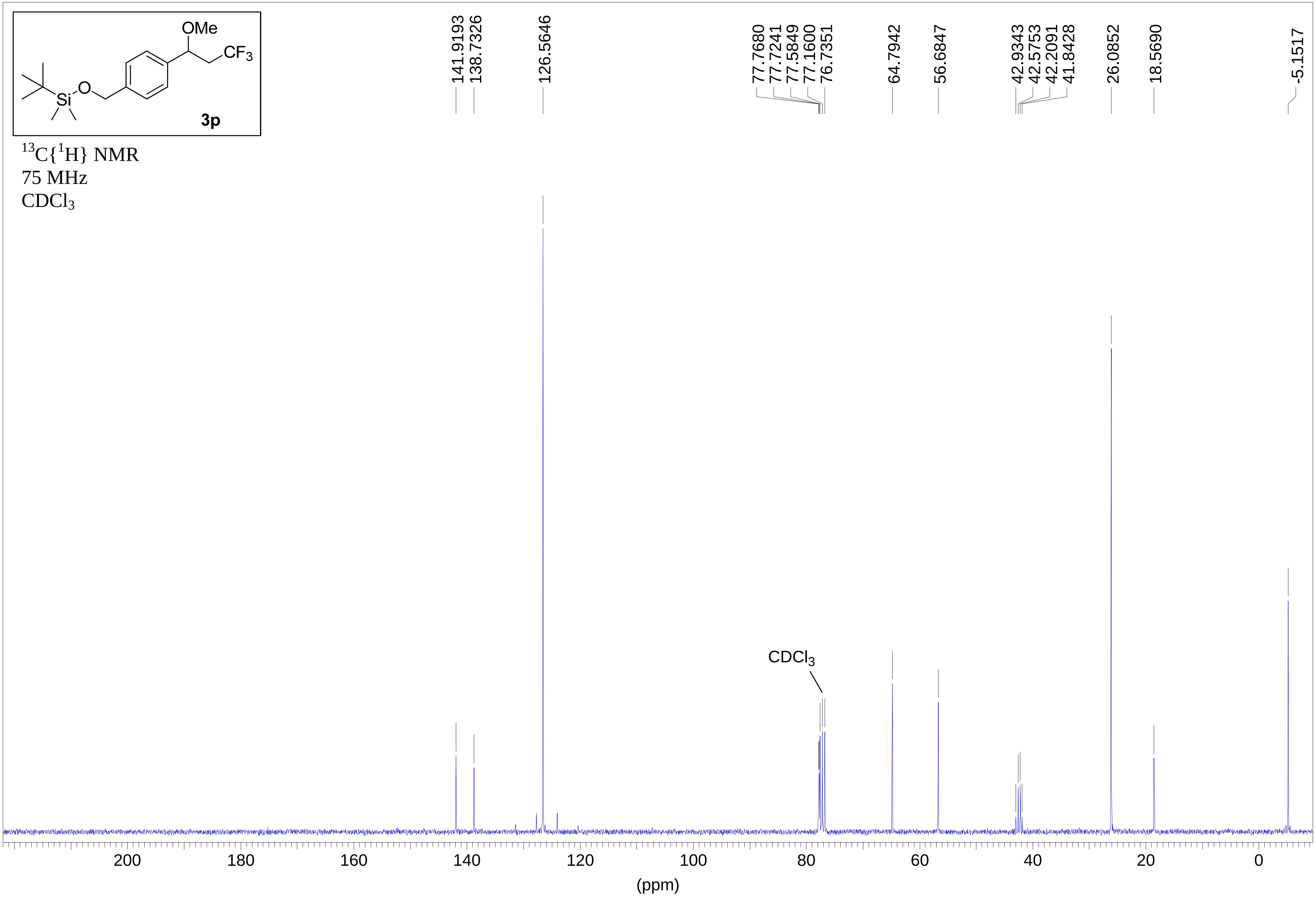

OMe
CF3
O
O
3o
13C{1H} NMR
75 MHz
CDCl3
170.8851
140.1977
136.3371
128.7403
127.5536
126.8063
123.8761
77.5849
77.1600
76.7351
65.9224
56.7726
42.8024
42.4361
42.0699
41.7036
21.0011
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

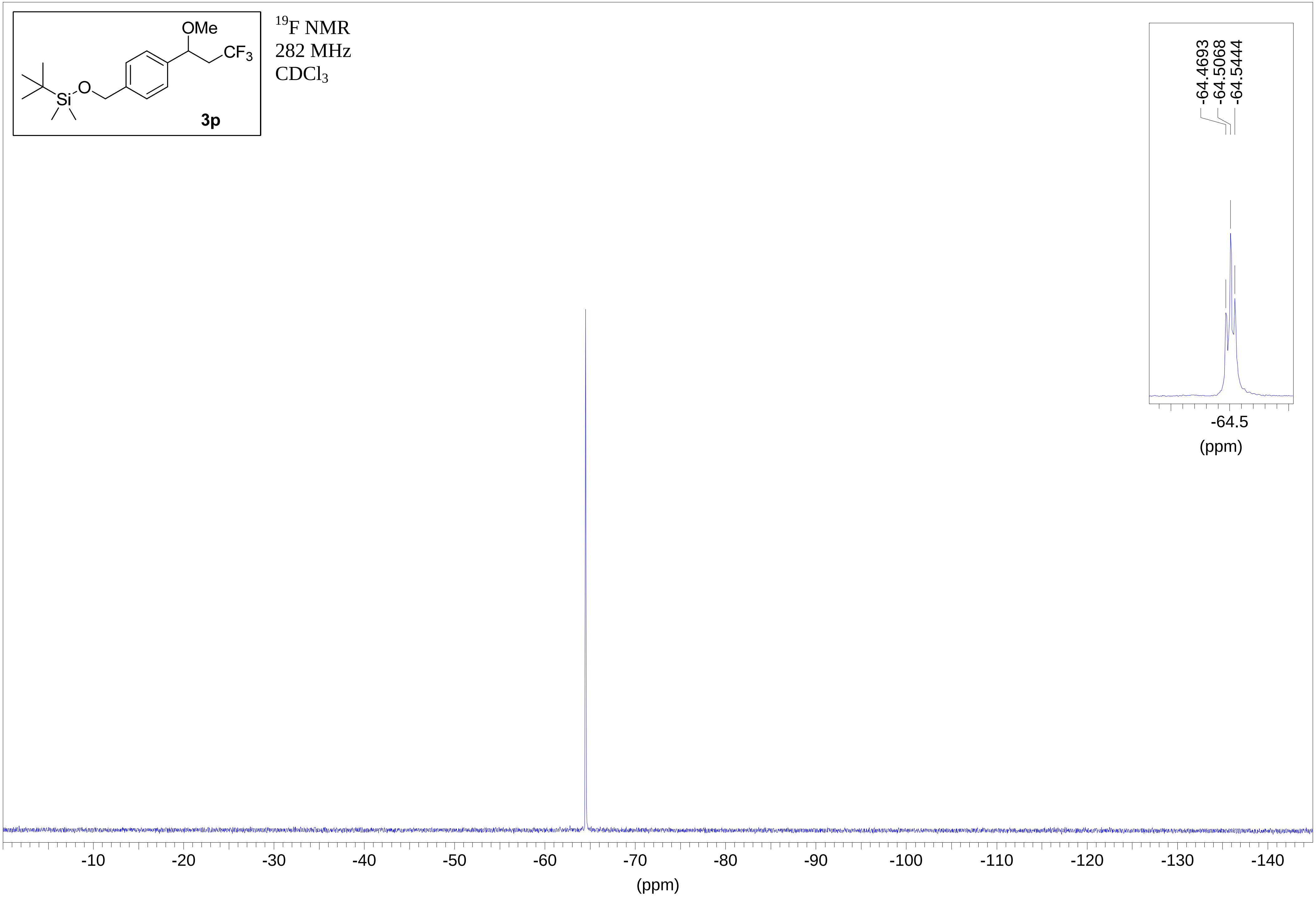


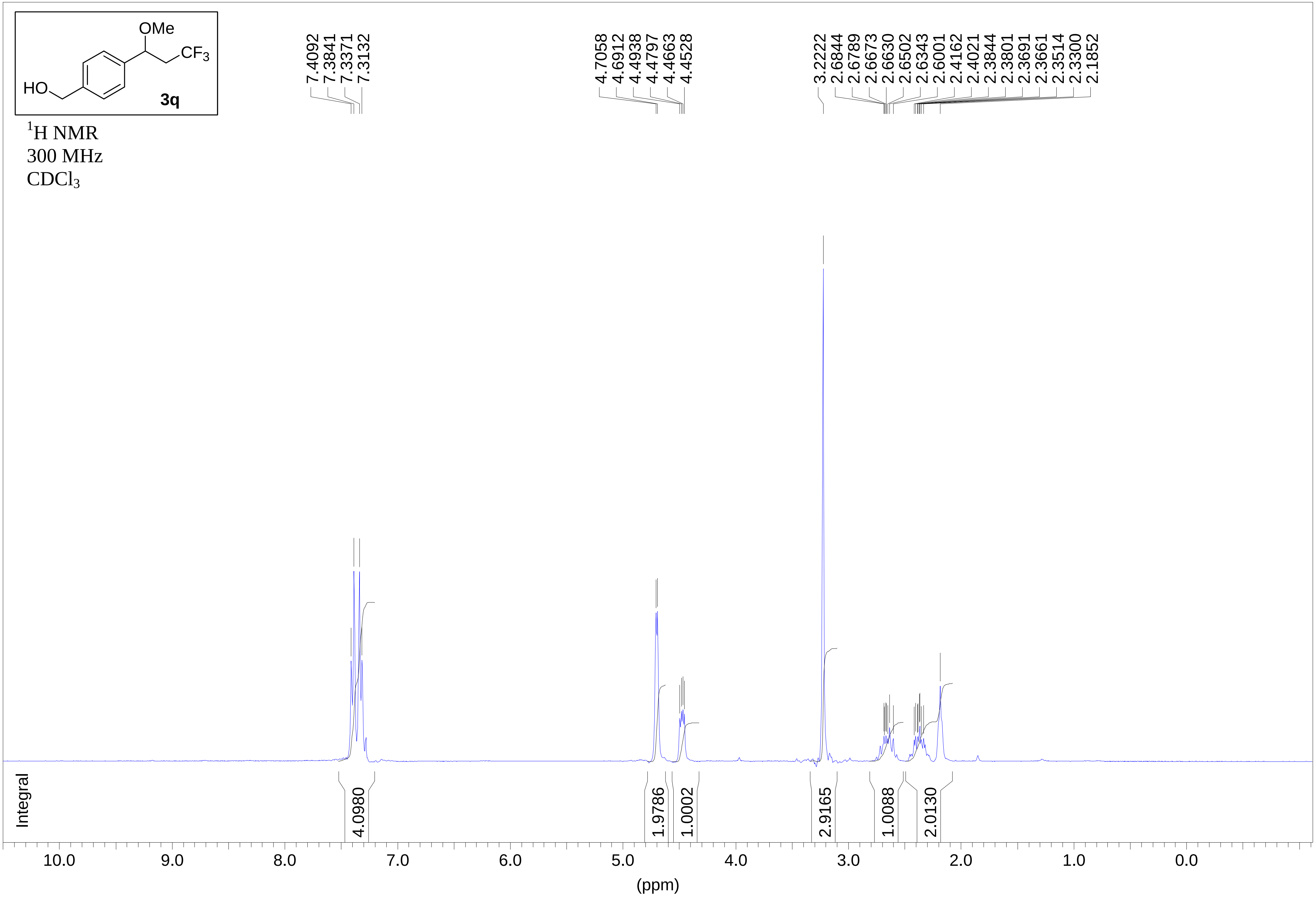
3o

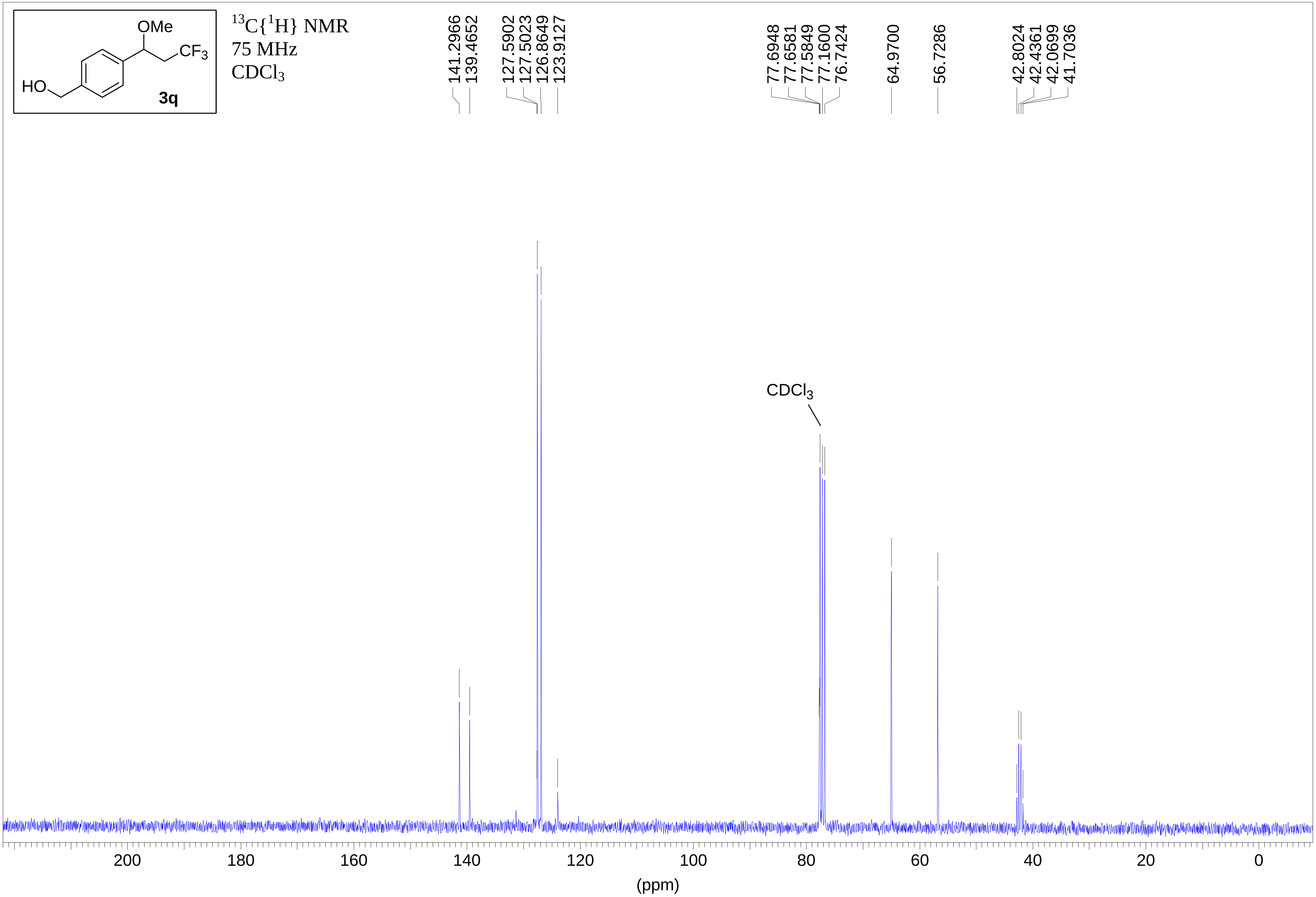
^{19}F NMR
282 MHz
$CDCl_3$

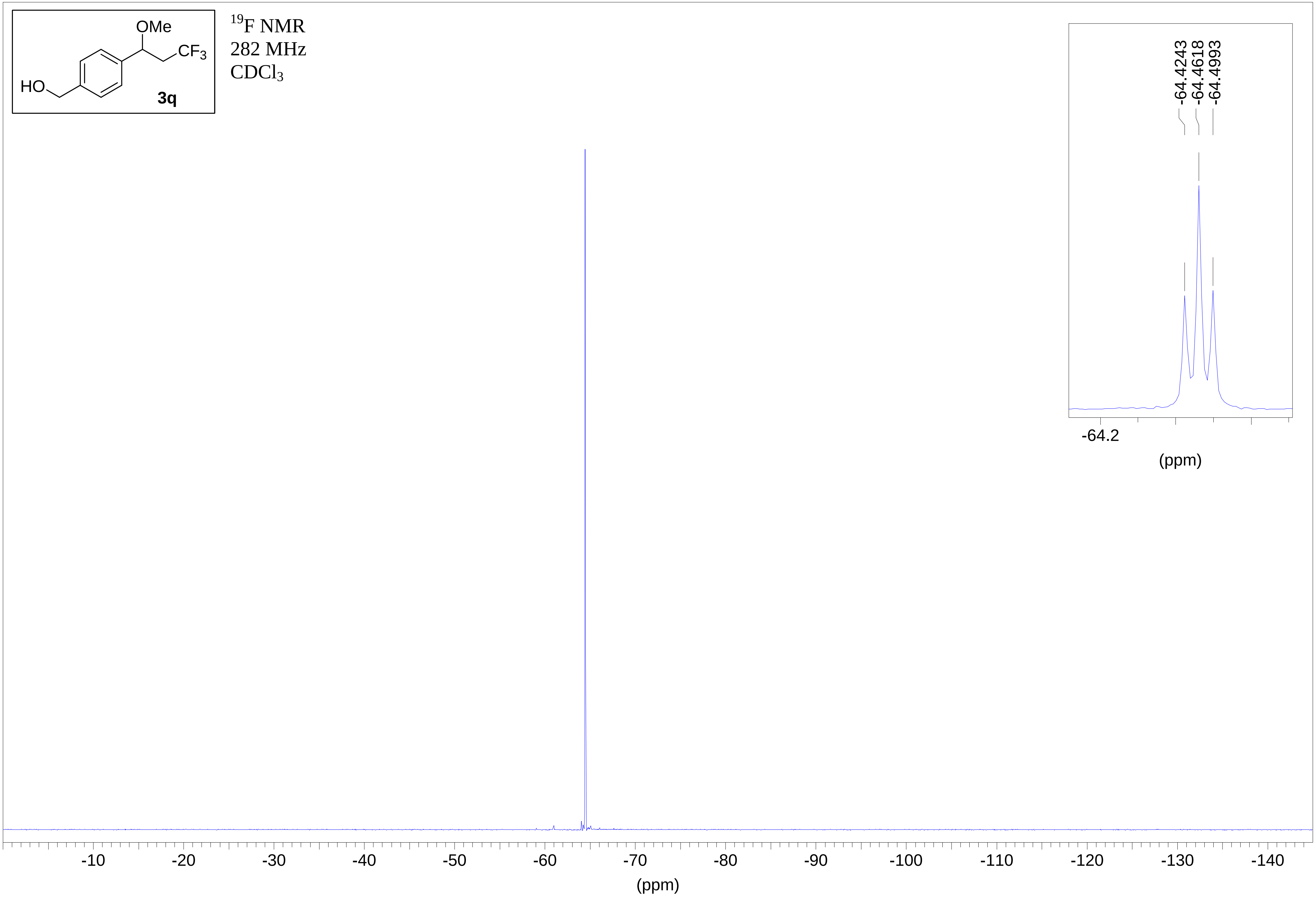

OMe
CF$_3$
Si
O
3p
^{1}H NMR
300 MHz
CDCl$_3$
7.3756
7.3493
7.3102
7.2821
4.7712
4.4877
4.4742
4.4596
4.4461
3.2325
2.7241
2.6893
2.6734
2.6606
2.6392
2.6099
2.4247
2.4113
2.3887
2.3746
2.3599
2.3386
2.3251
0.9716
0.1302
Integral
4.6596
2.0314
1.0000
2.9659
0.9998
1.0290
9.4080
6.0601
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

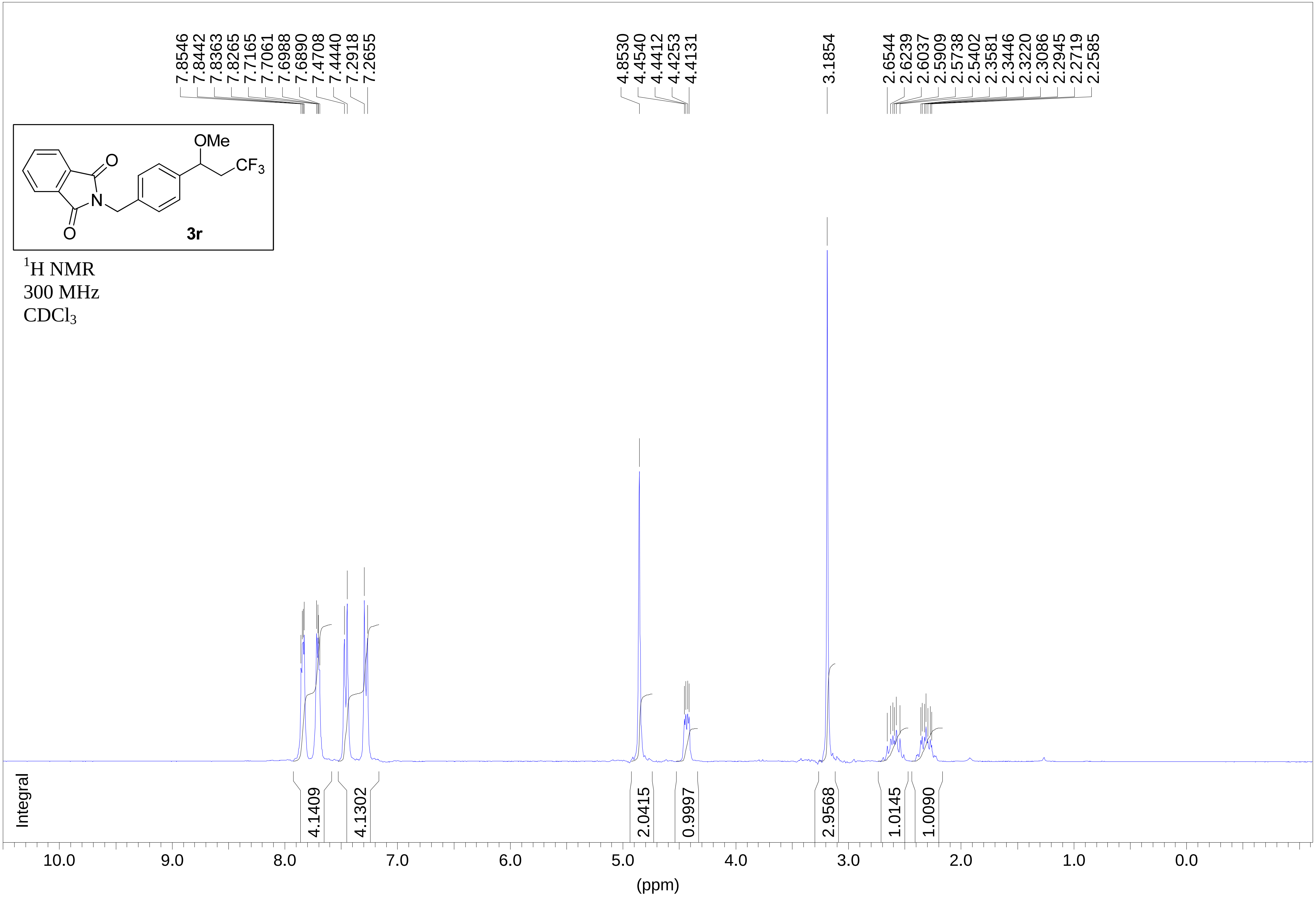

OMe
CF3
Si
O
3p
13C{1H} NMR
75 MHz
CDCl3
141.9193
138.7326
126.5646
77.7680
77.7241
77.5849
77.1600
76.7351
64.7942
56.6847
42.9343
42.5753
42.2091
41.8428
26.0852
18.5690
-5.1517
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

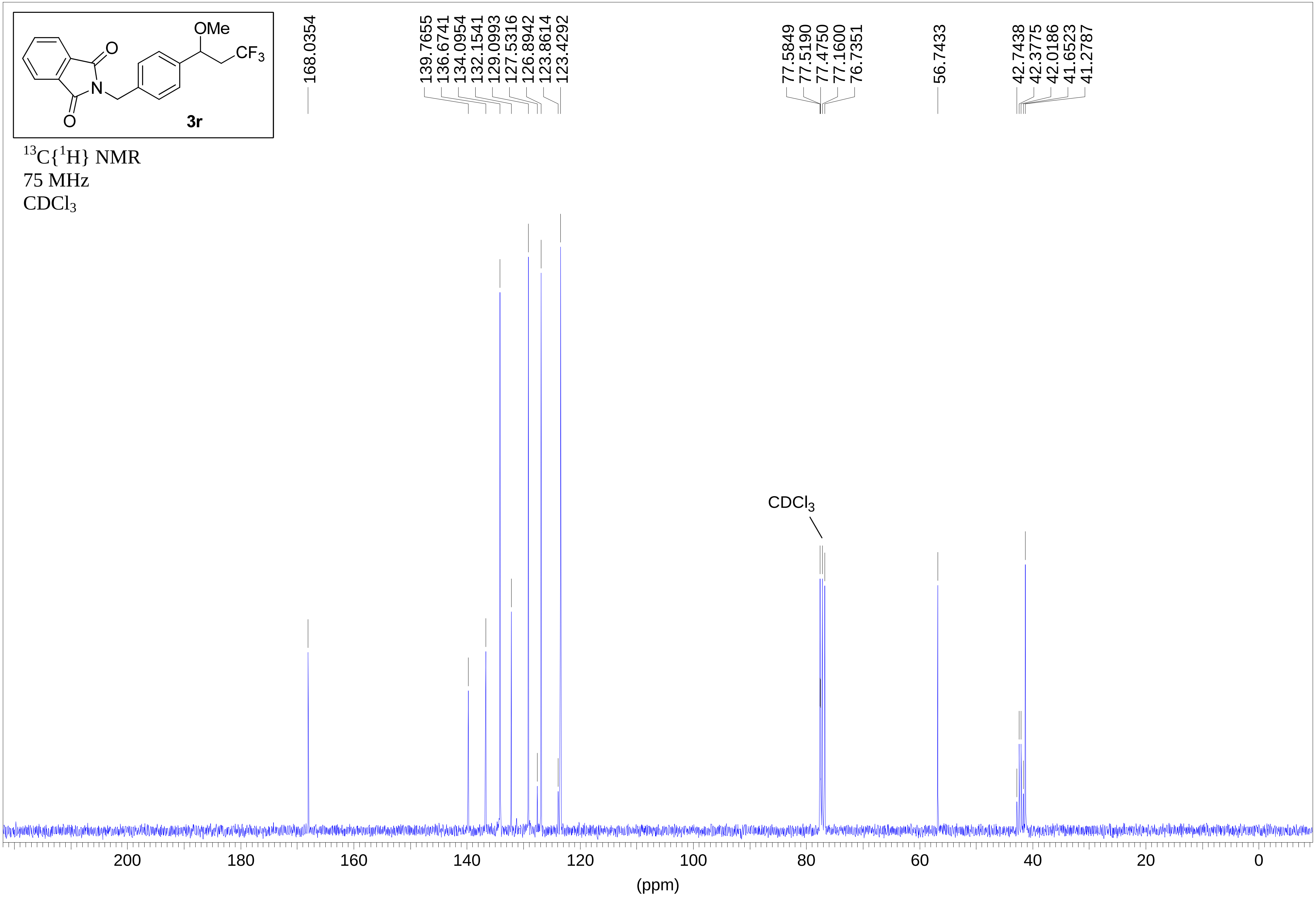

OMe
CF$_3$
Si
O
3p
^{19}F NMR
282 MHz
CDCl$_3$
-64.4693
-64.5068
-64.5444
-64.5
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)


OMe
CF3
HO
3q
1H NMR
300 MHz
CDCl3
7.4092
7.3841
7.3371
7.3132
4.7058
4.6912
4.4938
4.4797
4.4663
4.4528
3.2222
2.6844
2.6789
2.6673
2.6630
2.6502
2.6343
2.6001
2.4162
2.4021
2.3844
2.3801
2.3691
2.3661
2.3514
2.3300
2.1852
Integral
4.0980
1.9786
1.0002
2.9165
1.0088
2.0130
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


HO
OMe
CF3
3q
13C{1H} NMR
75 MHz
CDCl3
141.2966
139.4652
127.5902
127.5023
126.8649
123.9127
77.6948
77.6581
77.5849
77.1600
76.7424
64.9700
56.7286
42.8024
42.4361
42.0699
41.7036
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

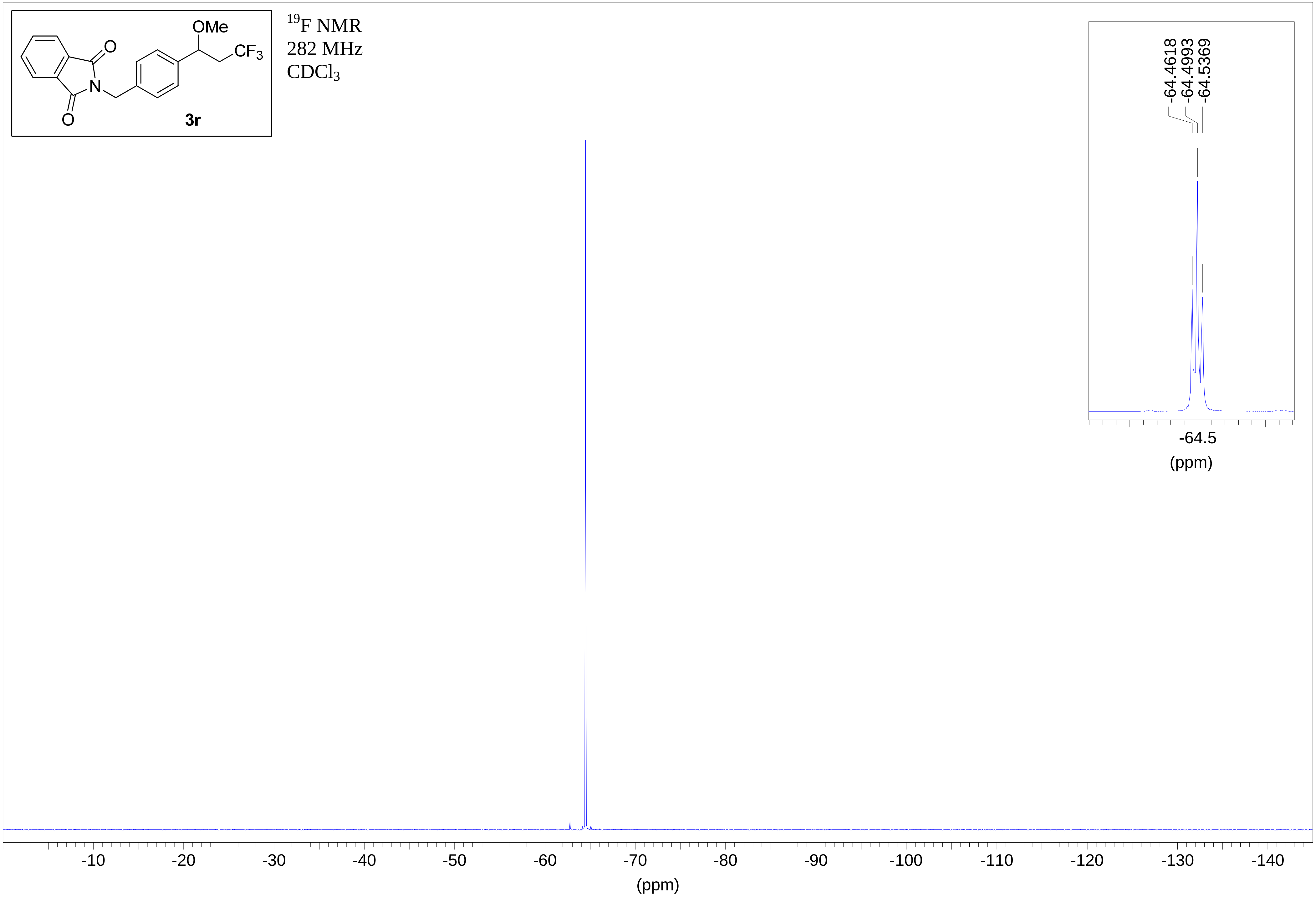

OMe
CF3
HO
3q
19F NMR
282 MHz
CDCl3
-64.4243
-64.4618
-64.4993
-64.2
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)


7.8546
7.8442
7.8363
7.8265
7.7165
7.7061
7.6988
7.6890
7.4708
7.4440
7.2918
7.2655
4.8530
4.4540
4.4412
4.4253
4.4131
3.1854
2.6544
2.6239
2.6037
2.5909
2.5738
2.5402
2.3581
2.3446
2.3220
2.3086
2.2945
2.2719
2.2585
OMe
CF_3
O
N
O
3r
^{1}H NMR
300 MHz
$CDCl_3$
Integral
4.1409
4.1302
2.0415
0.9997
2.9568
1.0145
1.0090
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)



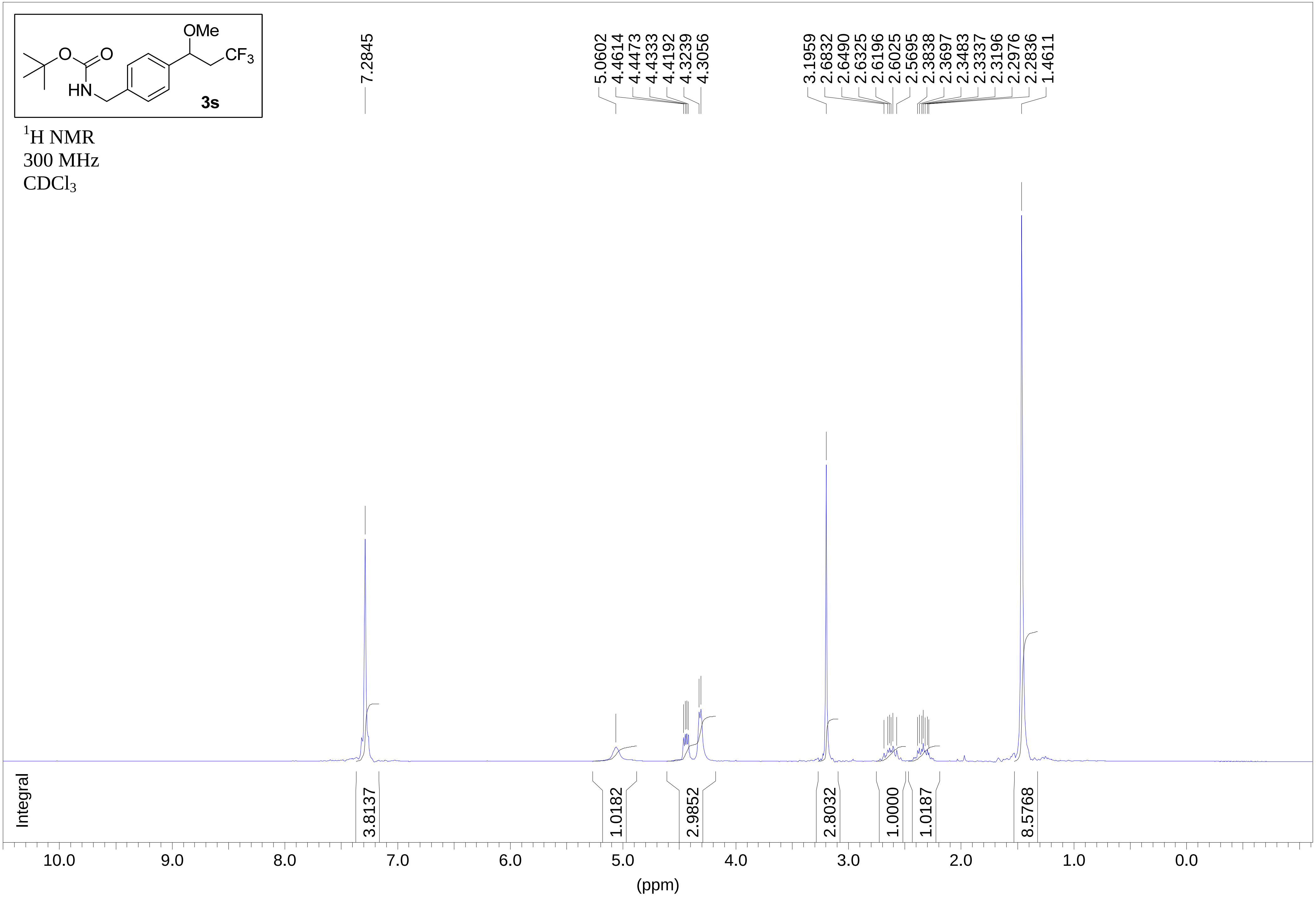
3r

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



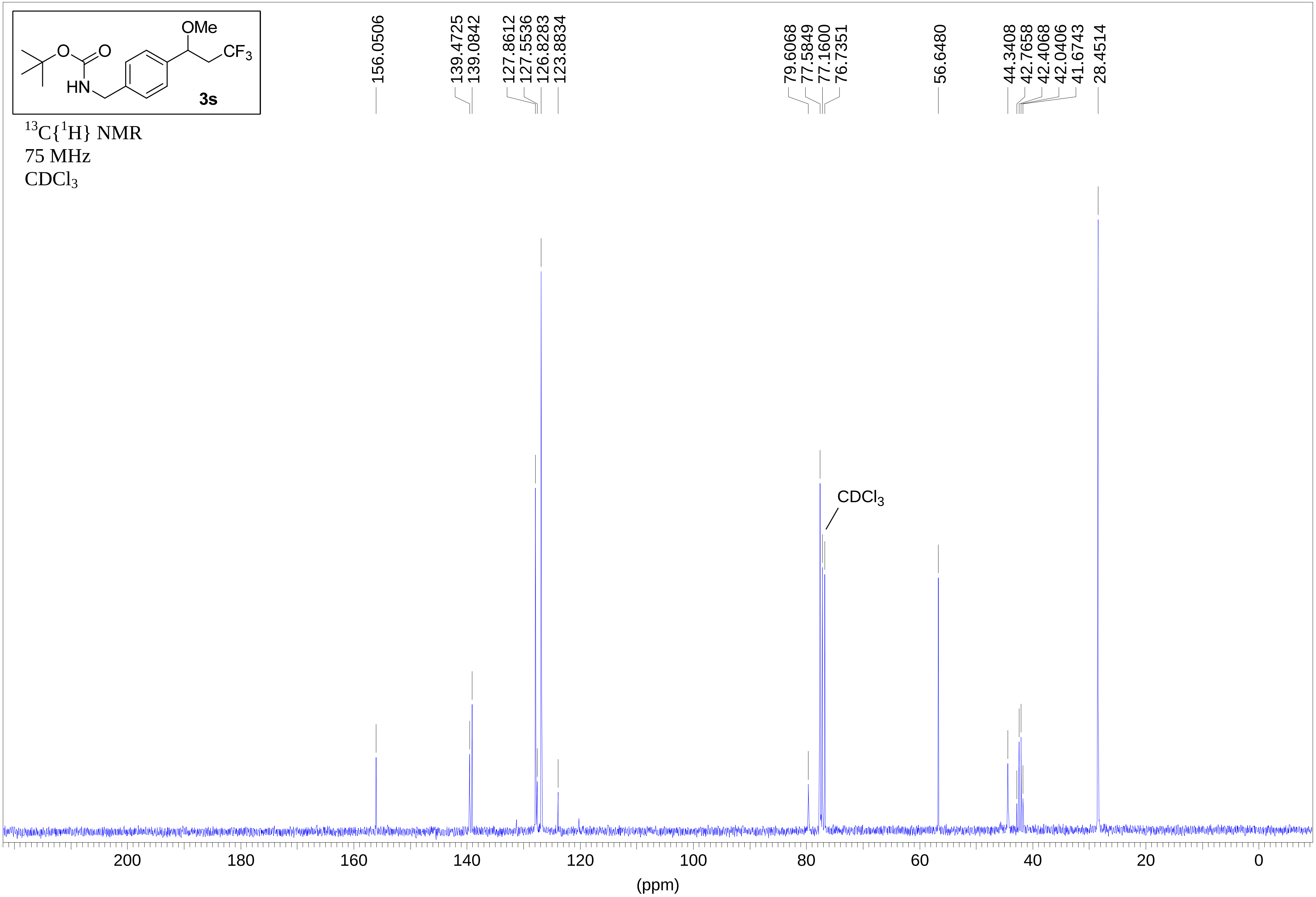
3r

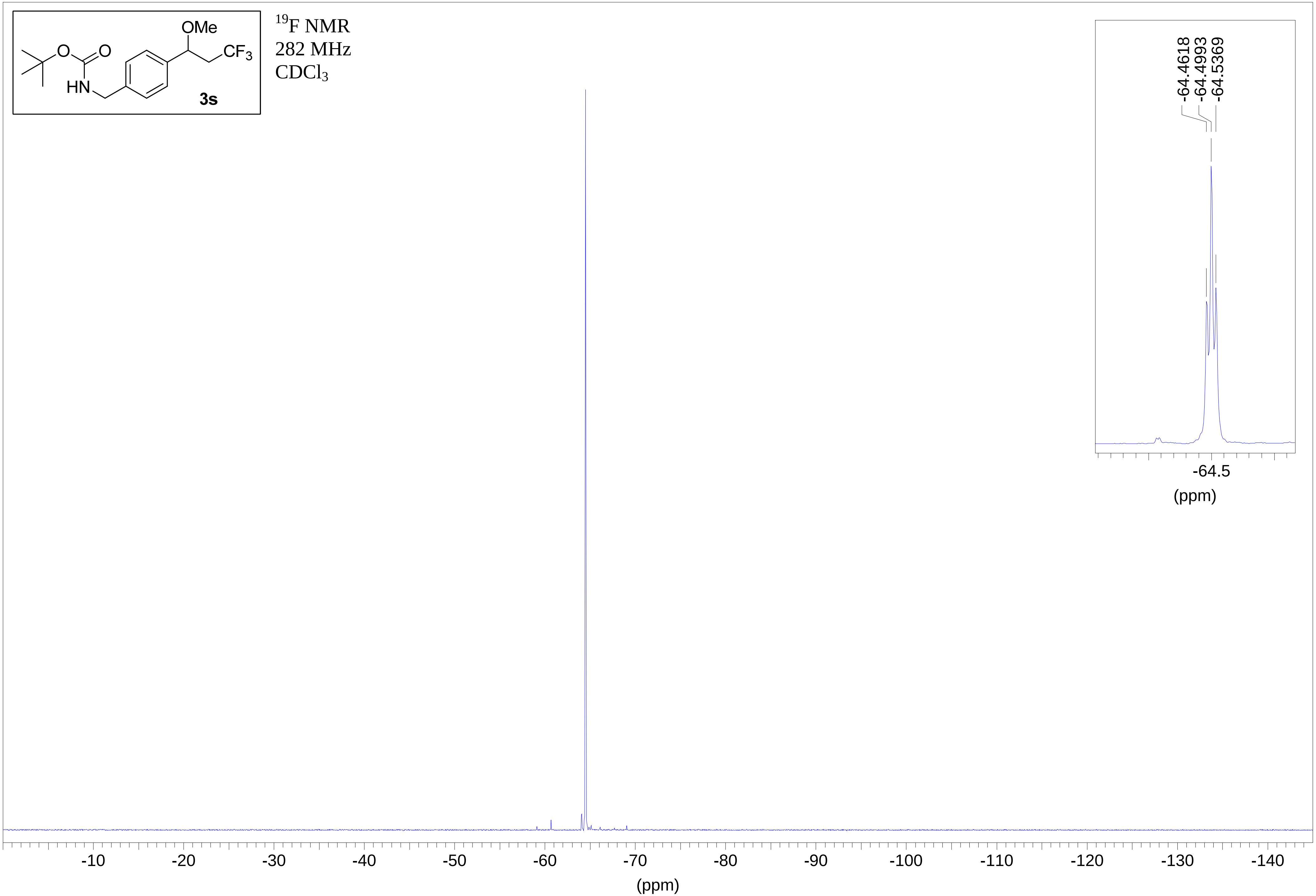
OMe
CF$_3$
O
N
O
^{19}F NMR
282 MHz
CDCl$_3$
-64.4618
-64.4993
-64.5369
-64.5
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)



3s

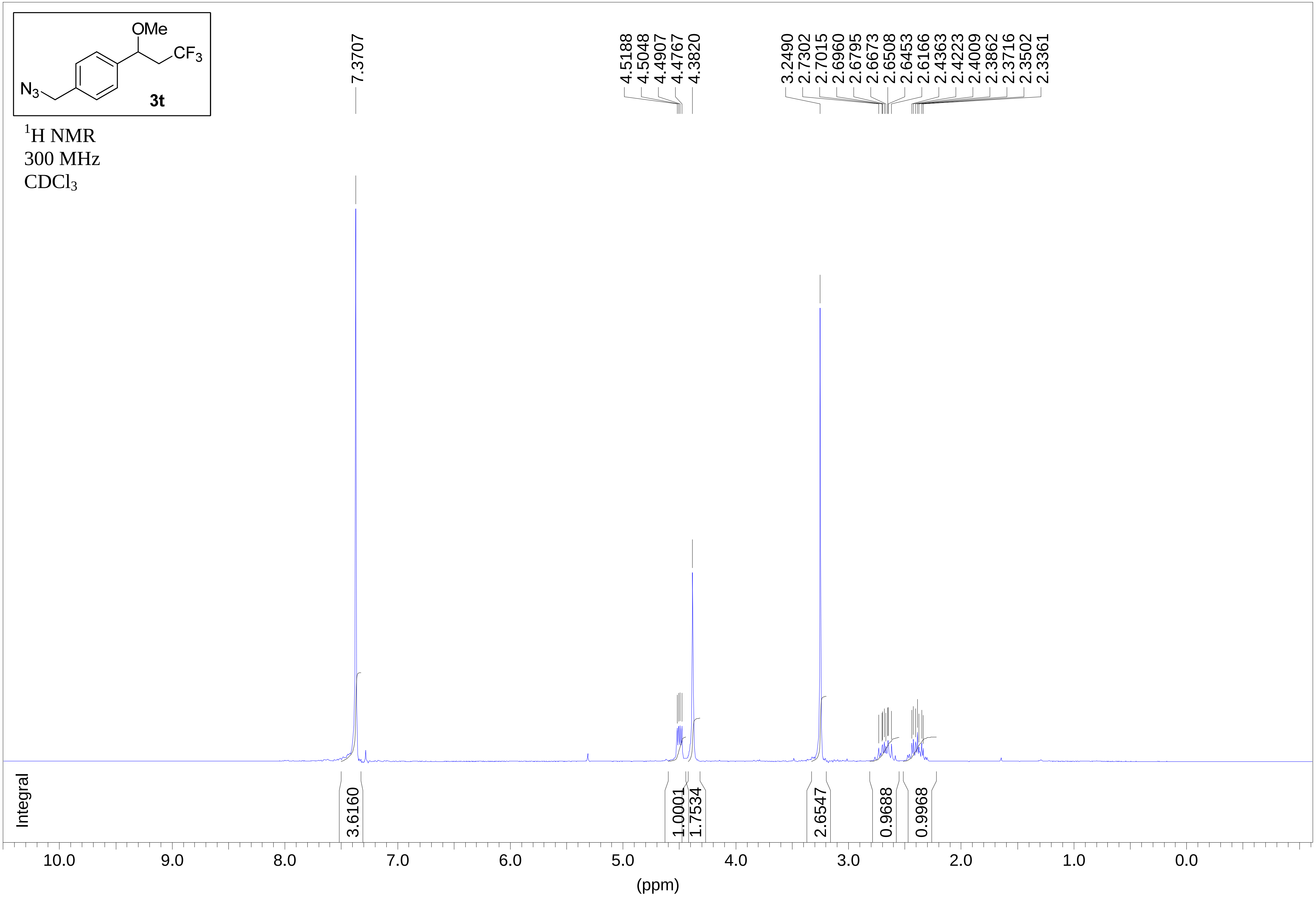
^{1}H NMR
300 MHz
$CDCl_3$

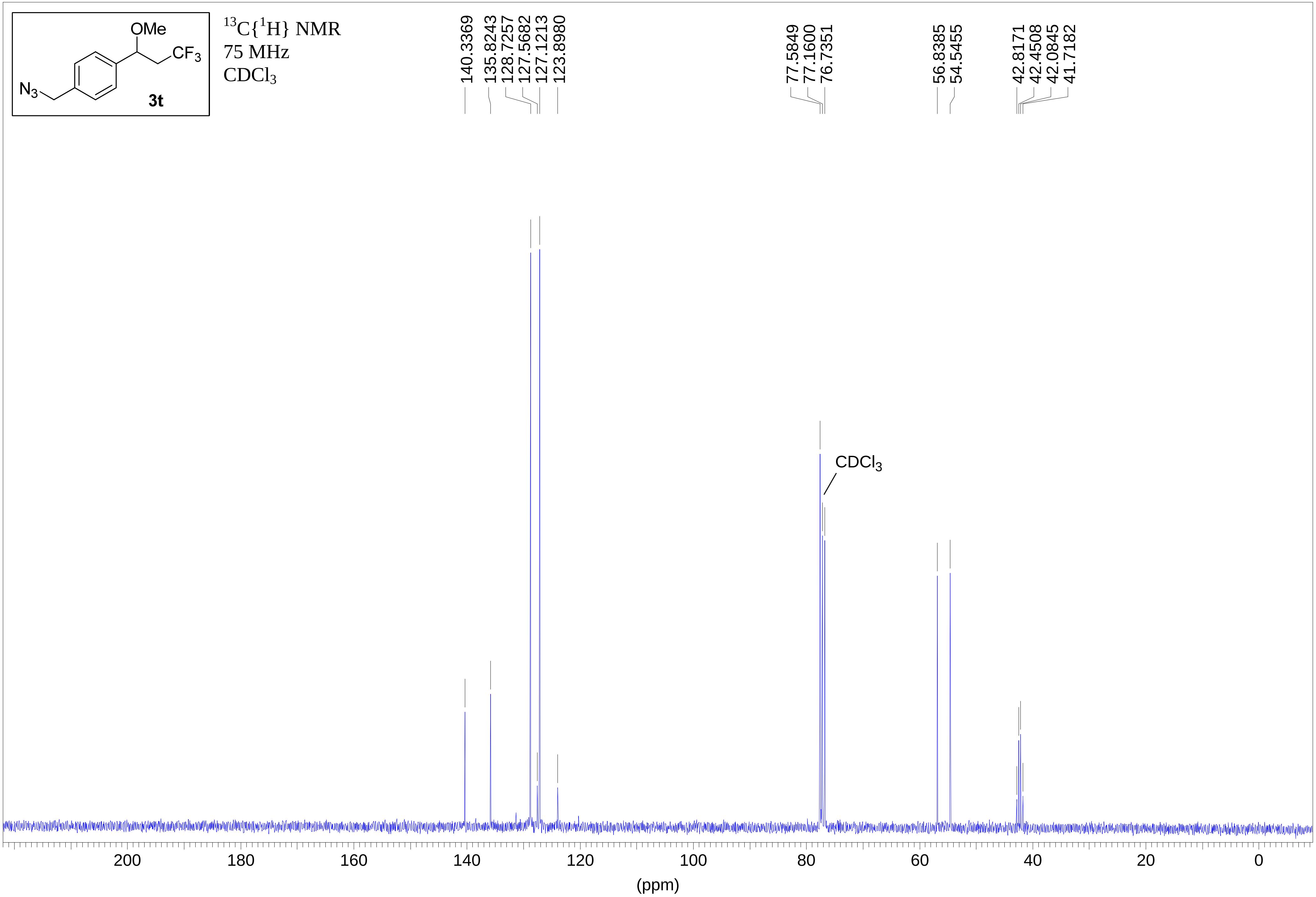

OMe
O
O
HN
CF3
3s
13C{1H} NMR
75 MHz
CDCl3
156.0506
139.4725
139.0842
127.8612
127.5536
126.8283
123.8834
79.6068
77.5849
77.1600
76.7351
56.6480
44.3408
42.7658
42.4068
42.0406
41.6743
28.4514
CDCl3
200
180
160
140
120
100
80
60
40
20
0
(ppm)

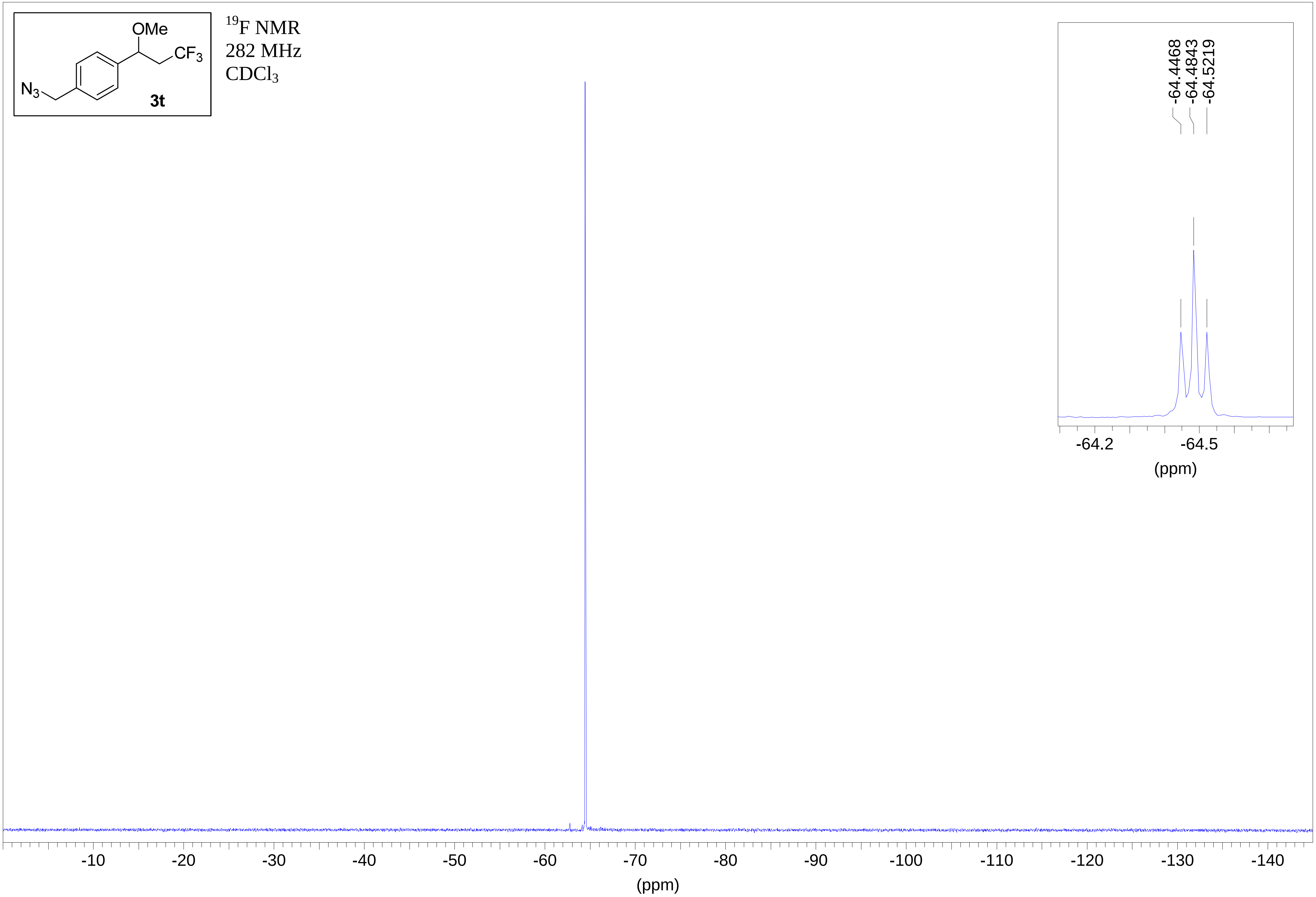


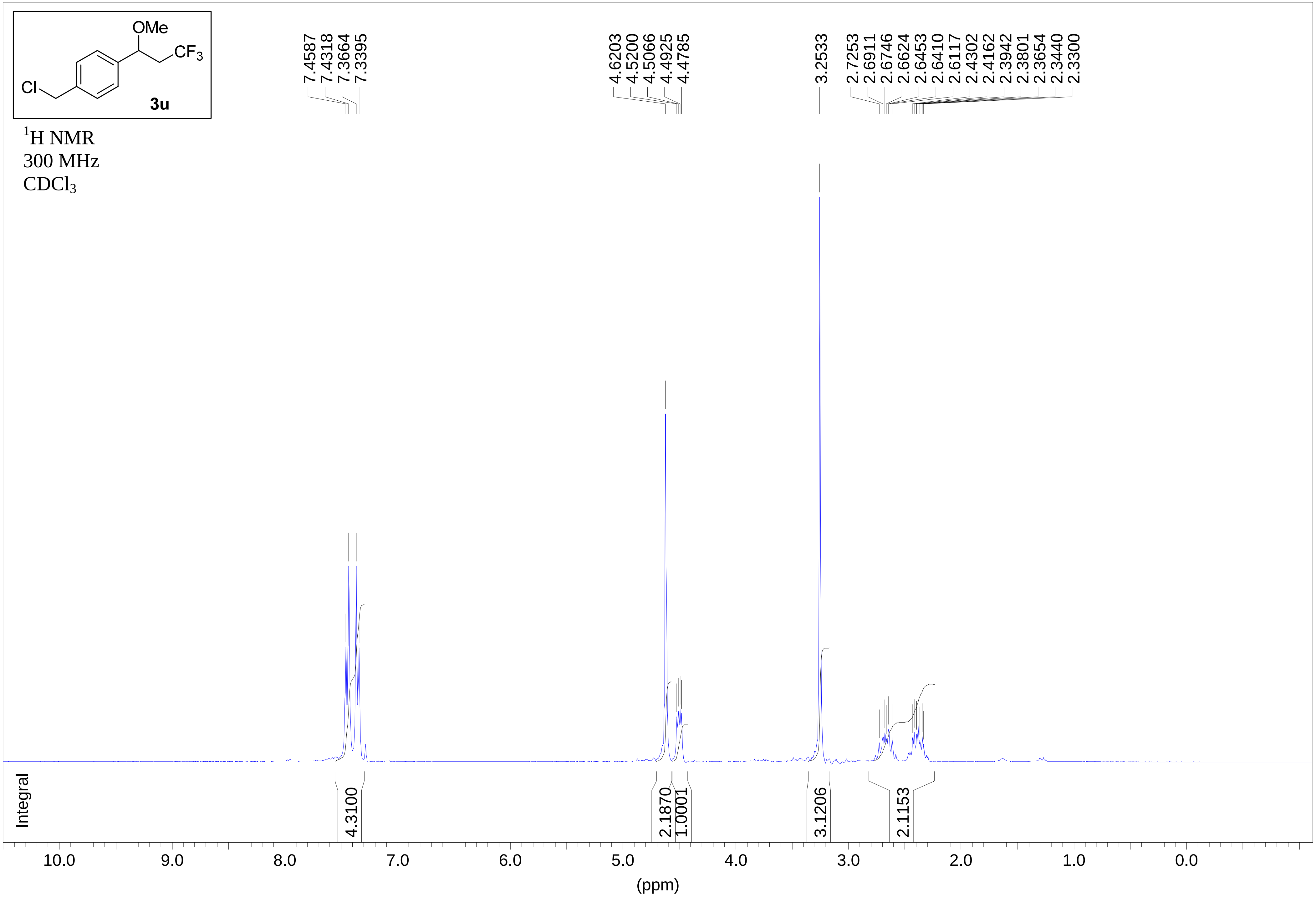
3s

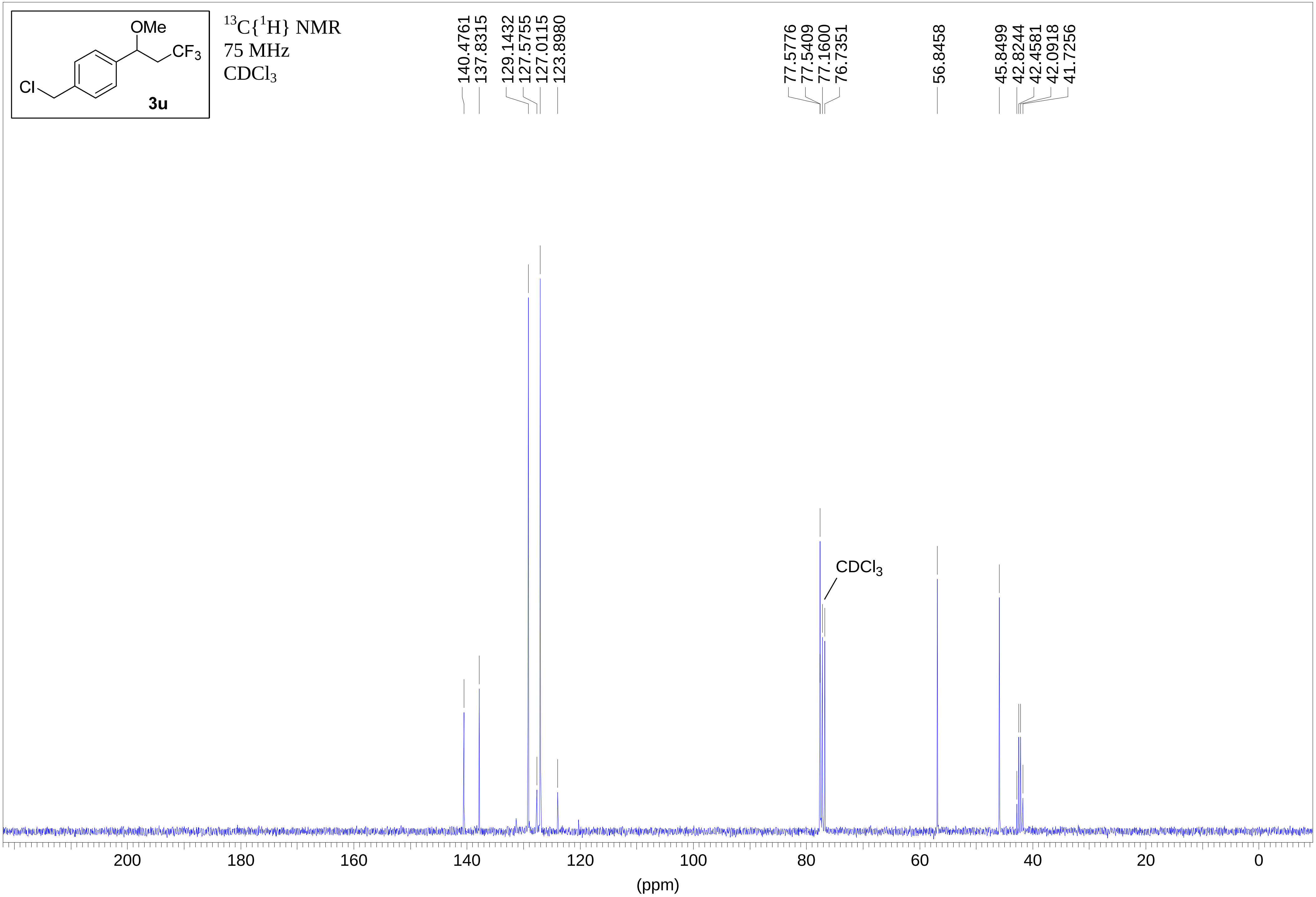
^{19}F NMR
282 MHz
$CDCl_3$


OMe
CF$_3$
N$_3$
3t
^{1}H NMR
300 MHz
CDCl$_3$
7.3707
4.5188
4.5048
4.4907
4.4767
4.3820
3.2490
2.7302
2.7015
2.6960
2.6795
2.6673
2.6508
2.6453
2.6166
2.4363
2.4223
2.4009
2.3862
2.3716
2.3502
2.3361
Integral
3.6160
1.0001
1.7534
2.6547
0.9688
0.9968
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


OMe
CF$_3$
N$_3$
3t
^{13}C{^{1}H} NMR
75 MHz
CDCl$_3$
140.3369
135.8243
128.7257
127.5682
127.1213
123.8980
77.5849
77.1600
76.7351
56.8385
54.5455
42.8171
42.4508
42.0845
41.7182
CDCl$_3$
200
180
160
140
120
100
80
60
40
20
0
(ppm)

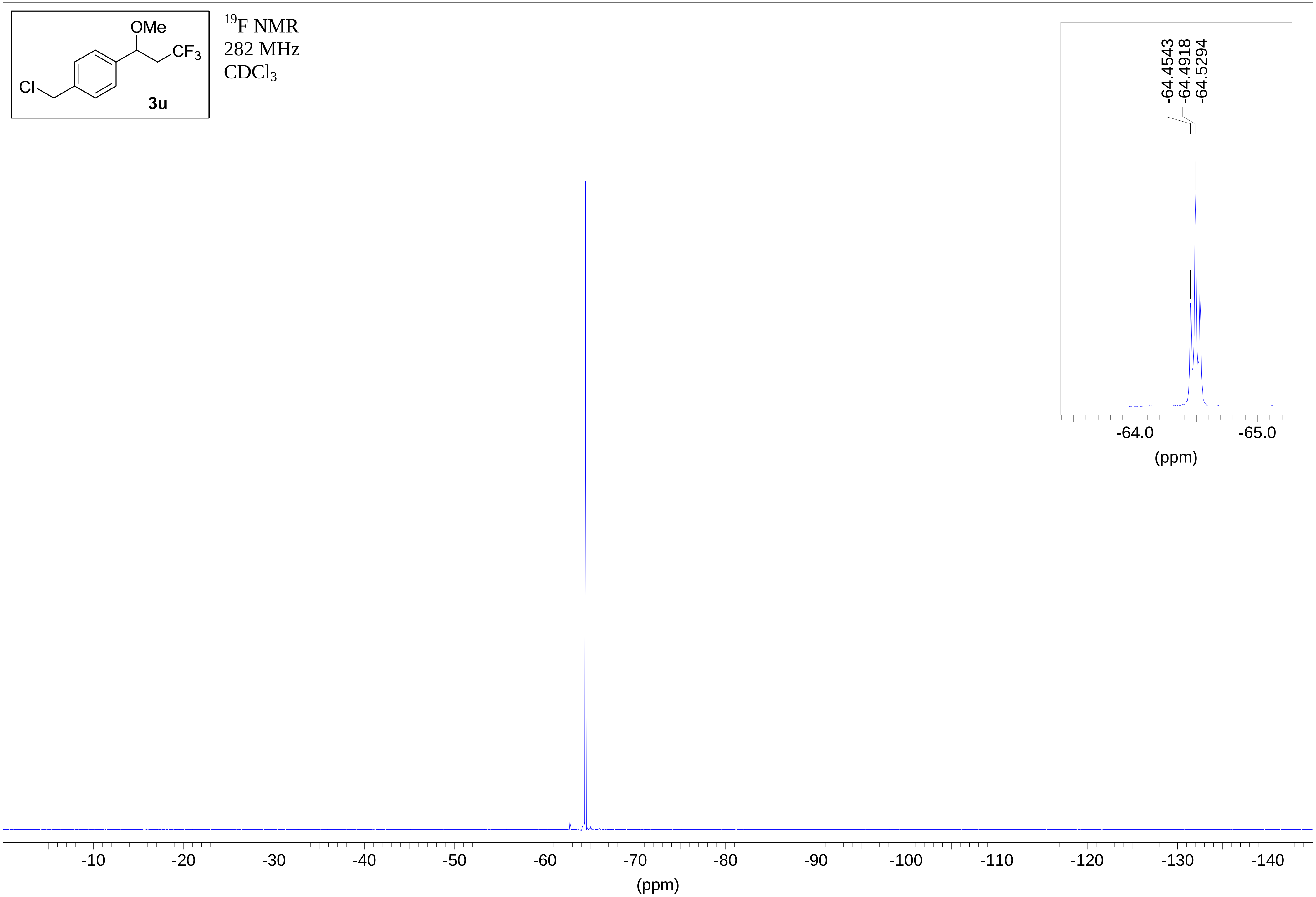

OMe
CF$_3$
N$_3$
3t
^{19}F NMR
282 MHz
CDCl$_3$
-64.4468
-64.4843
-64.5219
-64.2
-64.5
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)


OMe
CF3
Cl
3u
^{1}H NMR
300 MHz
CDCl$_3$
7.4587
7.4318
7.3664
7.3395
4.6203
4.5200
4.5066
4.4925
4.4785
3.2533
2.7253
2.6911
2.6746
2.6624
2.6453
2.6410
2.6117
2.4302
2.4162
2.3942
2.3801
2.3654
2.3440
2.3300
Integral
4.3100
2.1870
1.0001
3.1206
2.1153
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

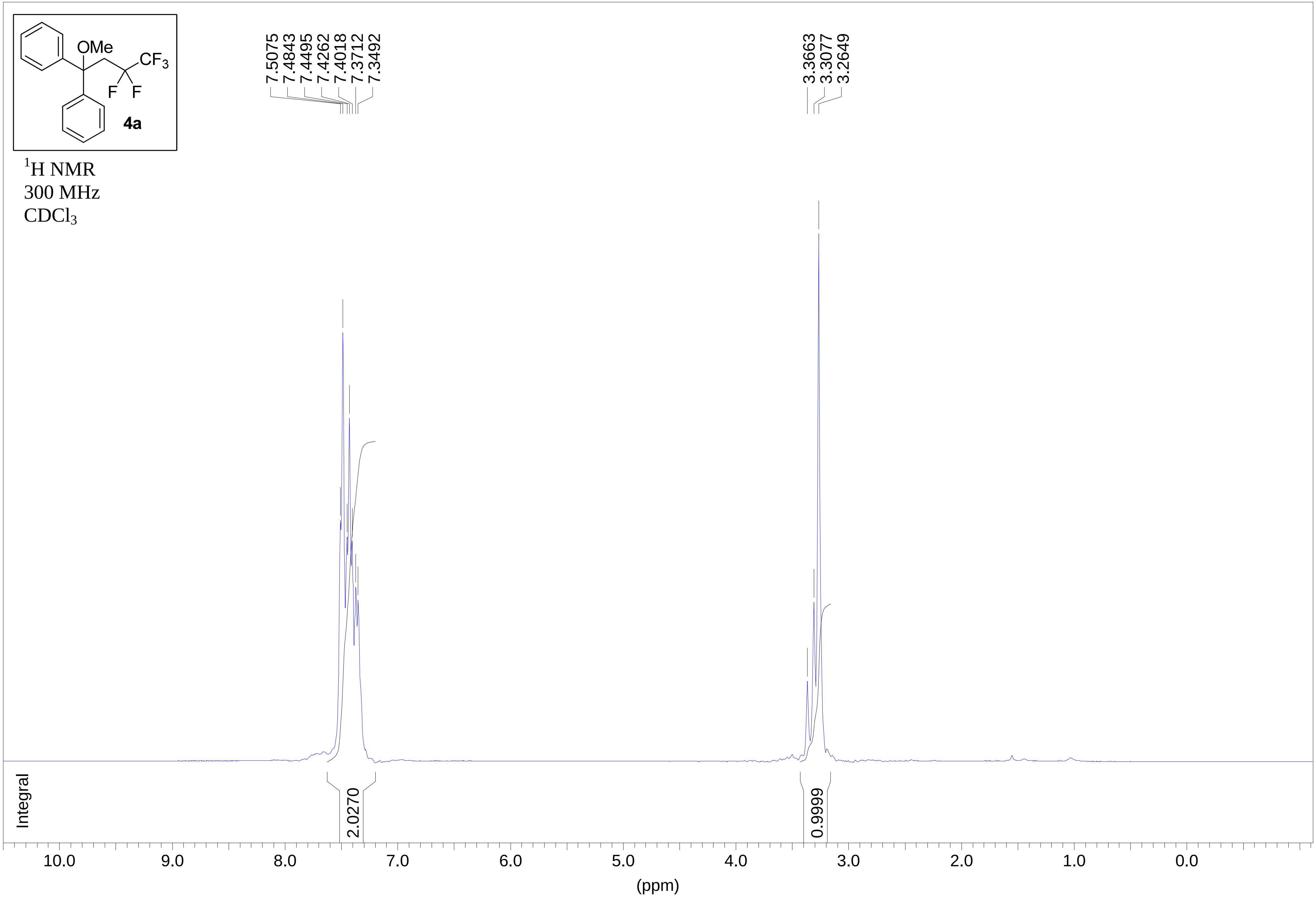


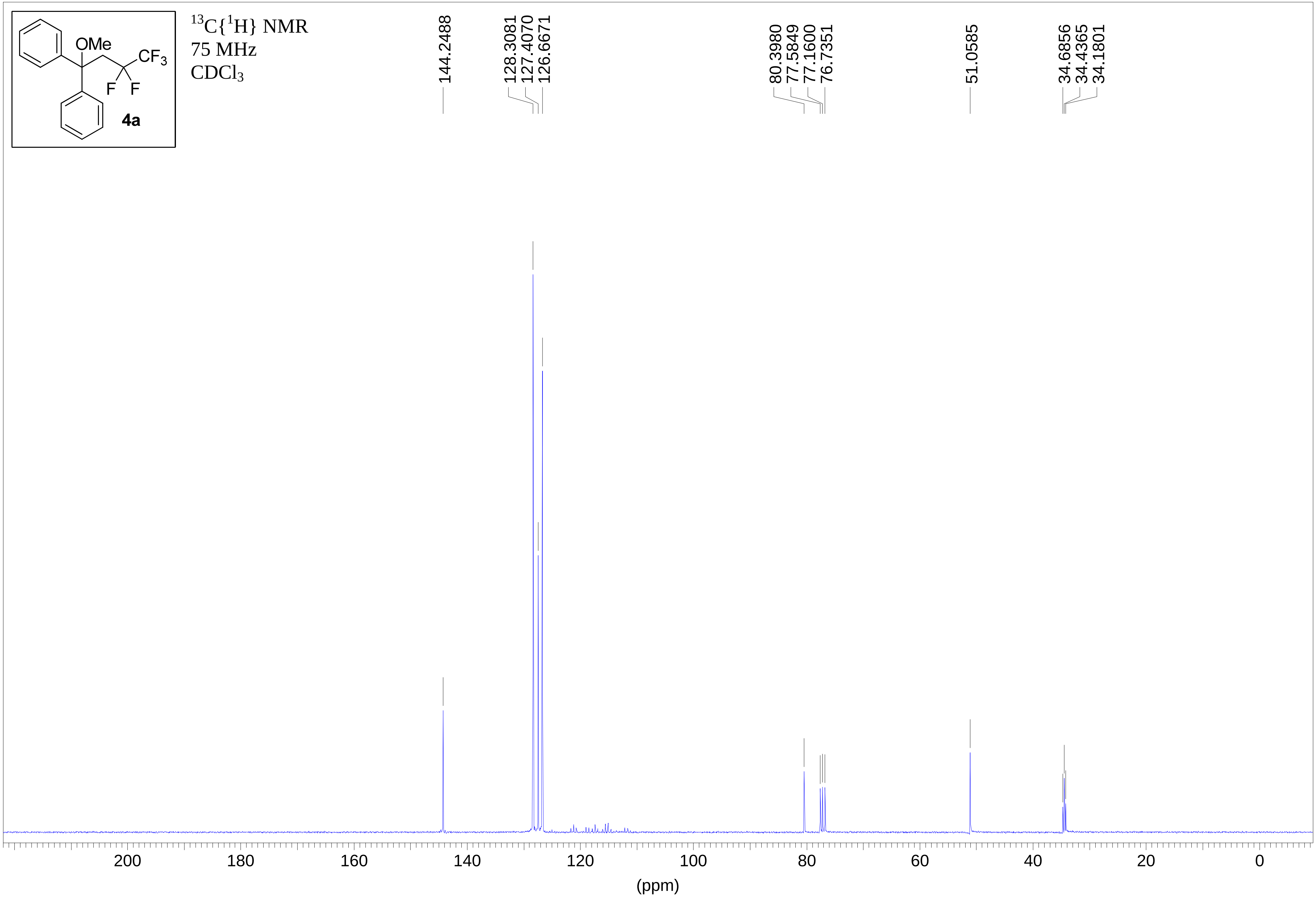
3u

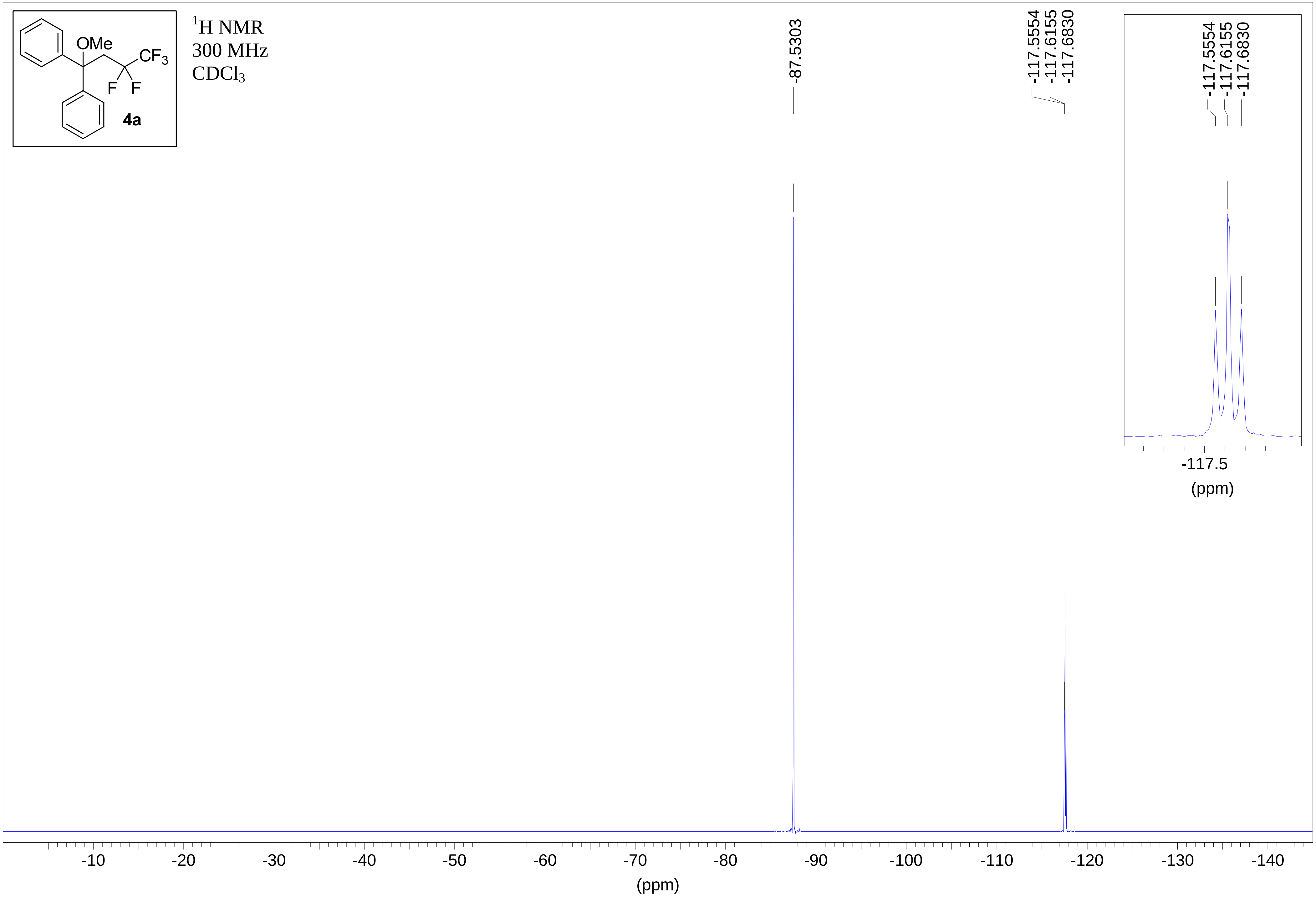
$^{13}C\{^{1}H\}$ NMR
75 MHz
$CDCl_3$

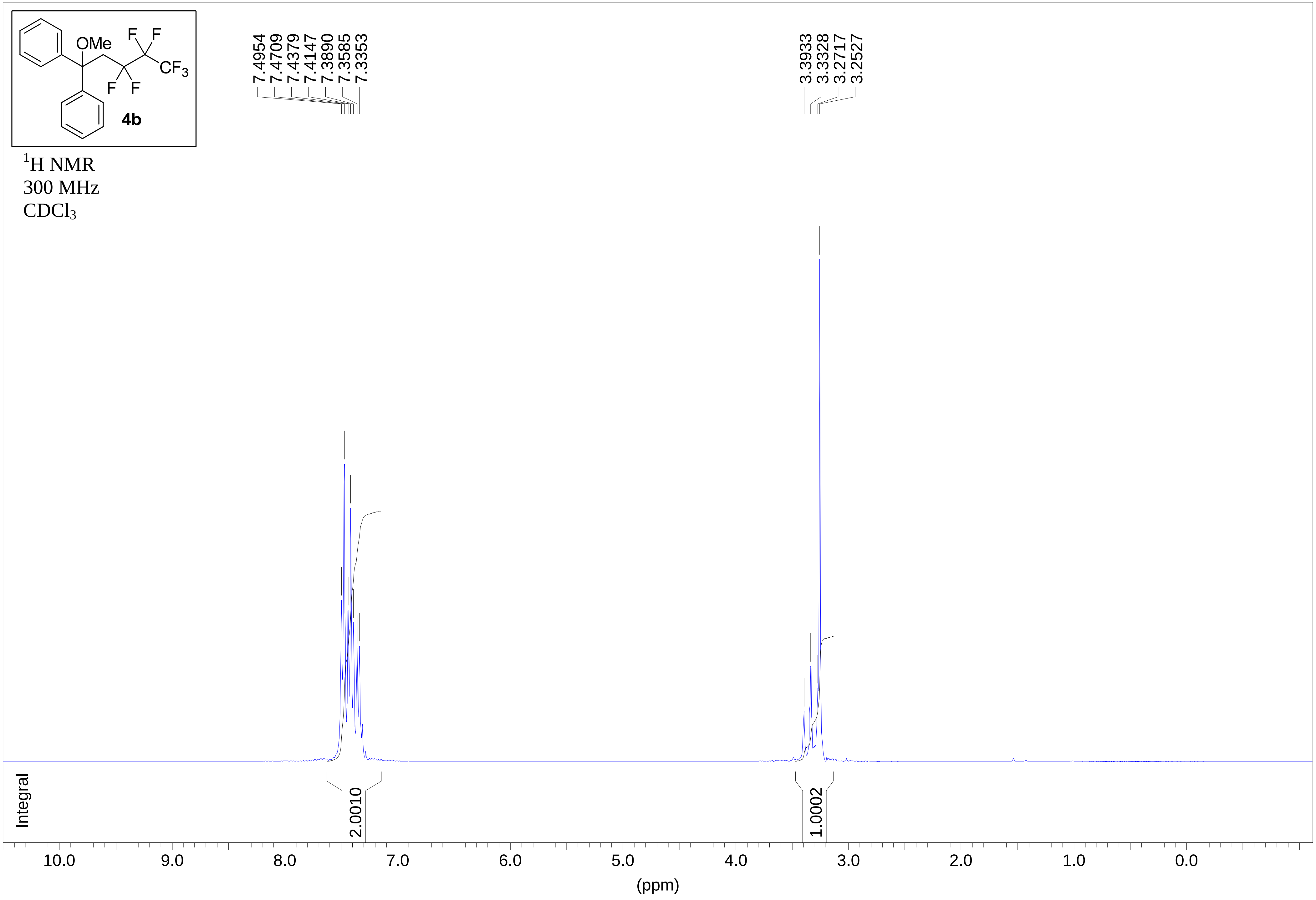


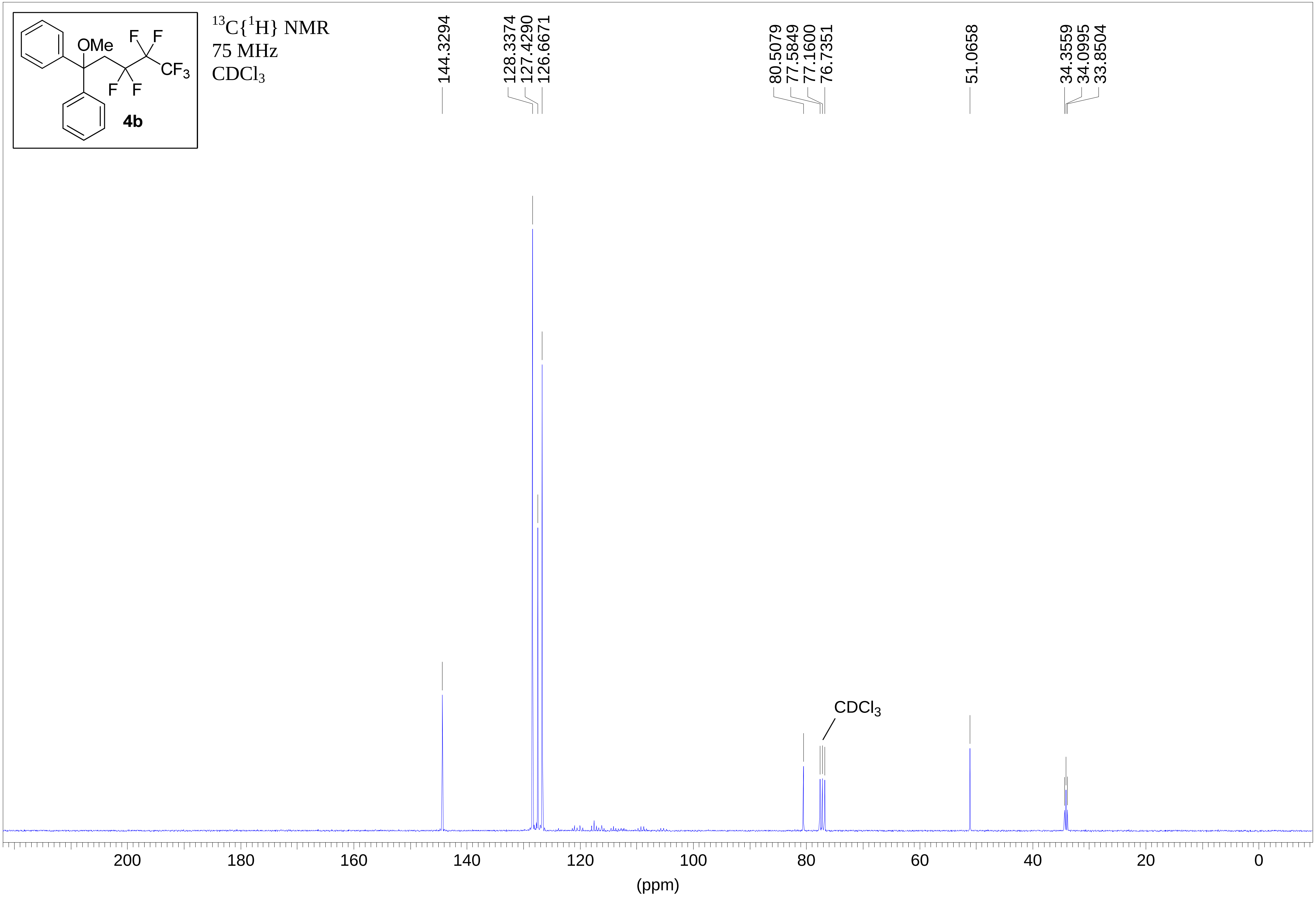
^{19}F NMR
282 MHz
$CDCl_3$


OMe
CF3
F F
4a
^{1}H NMR
300 MHz
CDCl3
7.5075
7.4843
7.4495
7.4262
7.4018
7.3712
7.3492
3.3663
3.3077
3.2649
Integral
2.0270
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)


OMe
CF3
F F
4a
13C{1H} NMR
75 MHz
CDCl3
144.2488
128.3081
127.4070
126.6671
80.3980
77.5849
77.1600
76.7351
51.0585
34.6856
34.4365
34.1801
200
180
160
140
120
100
80
60
40
20
0
(ppm)

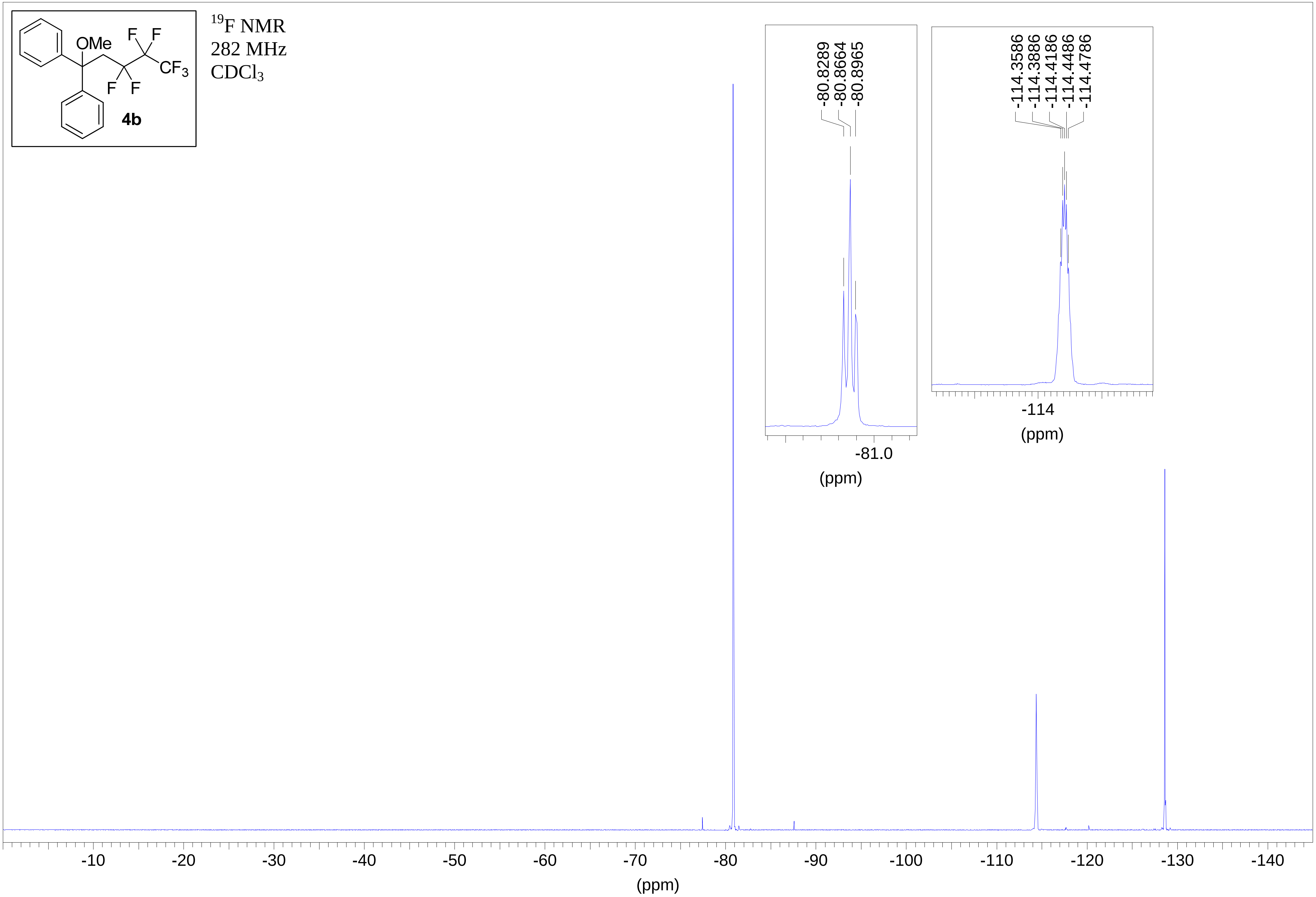

OMe
CF3
F
F
4a
1H NMR
300 MHz
CDCl3
-87.5303
-117.5554
-117.6155
-117.6830
-117.5554
-117.6155
-117.6830
-117.5
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)

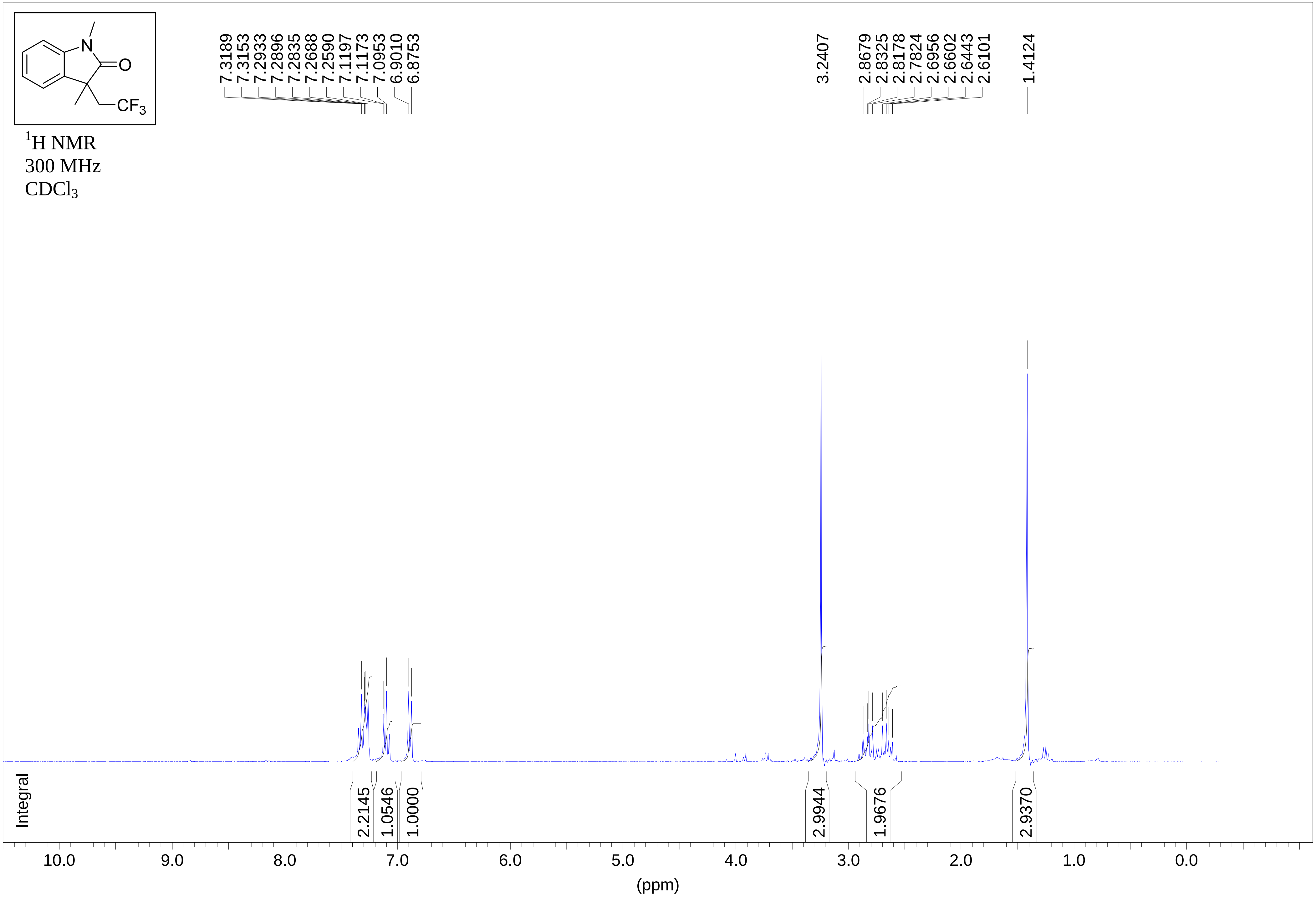

OMe
F
F
CF$_3$
F
F
4b
^{1}H NMR
300 MHz
CDCl$_3$
7.4954
7.4709
7.4379
7.4147
7.3890
7.3585
7.3353
3.3933
3.3328
3.2717
3.2527
Integral
2.0010
1.0002
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)

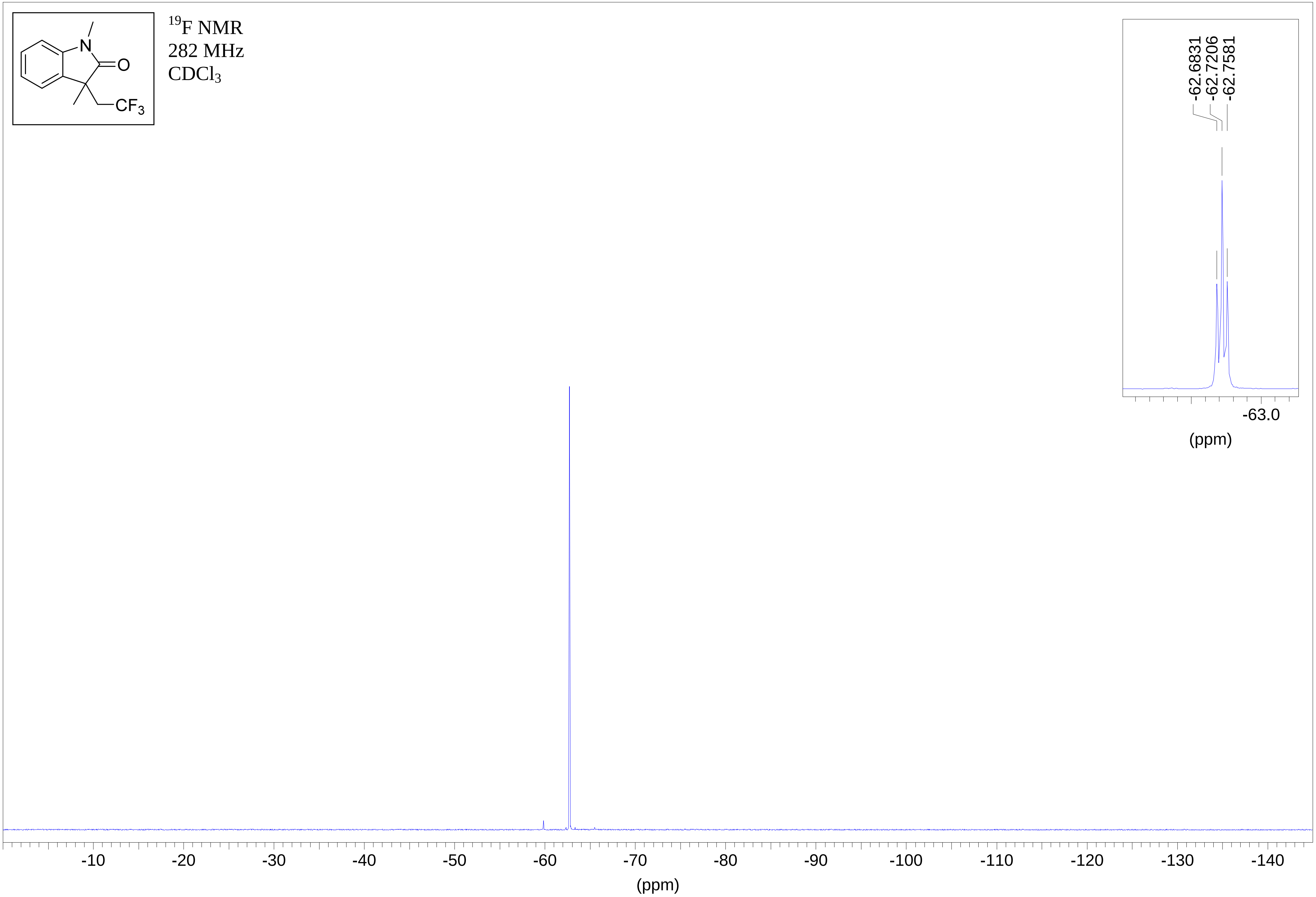


4b

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


OMe
F
F
CF3
F
F
4b
19F NMR
282 MHz
CDCl3
-80.8289
-80.8664
-80.8965
-81.0
(ppm)
-114.3586
-114.3886
-114.4186
-114.4486
-114.4786
-114
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)


N
O
CF3
^{1}H NMR
300 MHz
$CDCl_3$
7.3189
7.3153
7.2933
7.2896
7.2835
7.2688
7.2590
7.1197
7.1173
7.0953
6.9010
6.8753
3.2407
2.8679
2.8325
2.8178
2.7824
2.6956
2.6602
2.6443
2.6101
1.4124
Integral
2.2145
1.0546
1.0000
2.9944
1.9676
2.9370
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
(ppm)


N
O
CF3
19F NMR
282 MHz
CDCl3
-62.6831
-62.7206
-62.7581
-63.0
(ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
(ppm)