Supporting Information For

Palladium-Catalyzed Salt-Free Double Decarboxylative Aryl Allylation

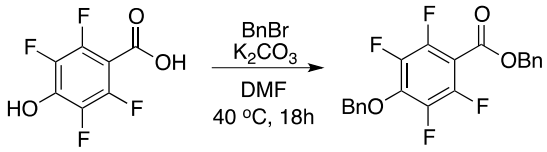
Ryan A. Daley, Joseph J. Topczewski

Department of Chemistry
University of Minnesota – Twin Cities
Minneapolis, Minnesota 55455

Table of Contents

General: All reactions sensitive to air or moisture were carried out in oven-dried glassware using standard Schlenk line techniques or in a nitrogen filled glovebox. All reactions were mixed by magnetic stirring (100-600 rpm). All reactions conducted at elevated temperatures used aluminum block heating with an external thermocouple. Dry THF was obtained from a commercial solvent purification system using activated alumina columns and stored under a positive pressure of argon. 2,3,6-trifluorobenzoic acid was dried at 40 ^{o}C under reduced pressure overnight. Other reagents and solvents were purchased from commercial suppliers and used as received. Reactions were monitored by gas chromatography or thin layer chromatography (TLC) using pre-coated plastic plates impregnated with a fluorescent indicator (254 nm). Visualization was carried out with UV light (254 nm) or PMA stains. Column chromatography was performed using a Teledyne Isco CombiFlash Rf purification system utilizing normal phase pre-column load cartridges and gold high performance columns.

Instrumentation: All proton (^{1}H) NMR spectra were recorded at 400 MHz or 500 MHz on a Bruker spectrometer. All carbon (^{13}C) NMR spectra were recorded at 101 or 126 MHz on a Bruker spectrometer. All fluorine (^{19}F) NMR spectra were recorded at 376 MHz on a Bruker spectrometer. Chemical shifts are expressed in ppm and are referenced to residual solvent as an internal standard (^{1}H: $CHCl_3$, 7.27 ppm; ^{13}C: $CDCl_3$, 77.2 ppm). Infrared (IR) spectra were performed as a film on NaCl plates on a Nexus 670 FT-IR and are reported in cm^{-1}. Mass spectrums were taken on Bruker BioTOF II or an Agilent 7890B GC/Agilent 7200 Accurate Mass GQ-TOF. Gas chromatography (GC) was performed on a Shimadzu GC-2010 Plus using a SH-Rxi-5ms 15 m column and a flame ionization detector. The GC temperature ramp was as follows: Hold at 100 ^{o}C (1 min), 50 ^{o}C/min gradient (100-200 ^{o}C), hold at 200 ^{o}C (3 min), 50 ^{o}C/min gradient (200-250 ^{o}C), hold at 250 ^{o}C (2 min) Yields reported based on GC analysis were determined by linear regression of a 5-point calibration curve with biphenyl as the internal standard.



S1s

A vial was charged with 2,3,5,6-tetrafluoro-4-hydroxybenzoic acid (839 mg, 3.99 mmol), DMF (10 mL), K_2CO_3 (1.60 g, 11.6 mmol), and BnBr (1.2 mL, 1.0 mmol). The vial was sealed and heated to 40 ºC. After 18 h, the reaction was cooled to rt and quenched by the addition of water (50 mL). The resulting solution was extracted with EtOAc (20mL X 3). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The mixture was then purified by filtration through a plug of silica (40% EtOAc/Hexanes,150 mL) and concentrated in vacuo. Residual DMF and BnBr were removed under reduced pressure by heating to 40 ºC overnight. This afforded **S1s** as a white solid (1.29 g, 3.30 mmol, 83%).

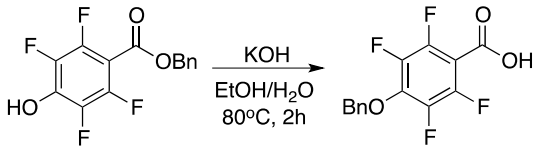
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.35 (m, 10 H), 5.40 (s, 2H), 5.36 (s, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.7, 145.9 (dddd, J_{C-F} = 256.8, 13.4, 7.0, 4.1 Hz), 141.1 (ddt, J_{C-F} = 248.5, 15.1, 4.2 Hz), 139.9 (tt, J_{C-F} = 11.3, 3.8 Hz), 135.2, 135.0, 129.1, 128.8, 128.7, 128.6, 128.32, 128.3, 106.1 (t, J_{C-F} = 15.2 Hz), 76.3 (t, J_{C-F} = 4.0 Hz), 68.0.

^{19}F NMR (376 MHz, $CDCl_3$): -139.6 – -139.7 (m), -155.2 – -155.3 (m).

IR (KBr, thin film, cm^{-1}): 3444, 3035, 2964, 1732, 1648, 1223, 996.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$calculated for $C_{21}H_{14}F_4O_3Na^+$ 413.0771, observed 413.0777.



S1s **1s**

A vial was charged with phenol **S1s** (550 mg, 1.41 mmol), and KOH (347 mg, 6.17 mmol, in 8 mL ethanol and 2 mL water). The vial was sealed and heated to 80ºC. After 2 h, the reaction was cooled to rt and diluted with water (50 mL). The solution was acidified with HCl (1M, 50 mL). The resulting solution was extracted with EtOAc (20mL X 3). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was dissolved in EtOAc (2 mL) and then added dropwise into stirring hexanes (15 mL) to induce crystallization. The flask was cooled, and the supernatant was decanted. The resulting solid was washed with hexanes (2 X 2 mL). The procedure was repeated to give acid **1s** as a white solid (423 mg, 1.41 mmol, 81%).

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.50 – 7.35 (m, 5H), 5.32 (s, 2H), 3.33 (s, 1H).

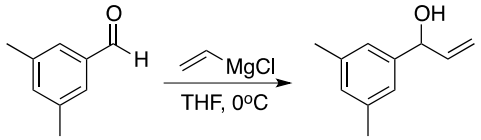
^{13}C NMR (126 MHz, DMSO-*d*$_6$): δ 160.7, 144.7 (dddd, J_{C-F} = 249.8, 11.8, 8.5, 3.7 Hz), 141.1 (apparent ddt, J_{C-F} = 246.3, 15.4, 4.1 Hz), 138.6 (t, J_{C-F} = 12.6 Hz), 136.0, 129.3, 129.01, 128.95, 109.3 (t, J_{C-F} = 17.6), 76.7 (t, J_{C-F} = 3.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -143.9 – -143.2 (m), -155.5 – -157.0 (m).

IR (KBr, thin film, cm^{-1}): 3421, 1705, 1647, 1488, 1423, 1252, 990.

HRMS (ESI-TOF) *m/z*: $[(M-HCO_2)^-]$ Calculated for $C_{13}H_7F_4O^-$ 255.0433, found 255.0438.

General Procedure for the synthesis of secondary alcohols



S2k

To a solution of 3,5-dimethylbenzaldehyde (1.60 mL, 10.7 mmol) in anhydrous THF (40 mL), under argon, cooled in an ice bath, vinyl magnesium (8.0 mL, 1.6 M in THF, 12.8 mmol) was added. After 20 min, the reaction was quenched by the addition of water (40 mL). The resulting solution was extracted with EtOAc (20mL X 3). The combined organic layers were washed with brine (40 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Alcohol **S2k** (1.59 g, 9.81 mmol, 92%) was isolated as an orange oil and used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 2H), 6.96 (s, 1H), 6.08 (ddd, *J* = 17.2, 10.6, 6.0 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.4 Hz, 1H), 5.17 (d, *J* = 5.6 Hz, 1H), 2.35 (s, 6H).

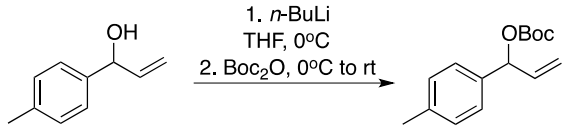
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 140.4, 138.1, 129.4, 124.2, 114.8, 75.4, 21.4.

IR (KBr, thin film, cm^{-1}): 3366, 3012, 2918, 1608, 1458, 849.

HRMS (EI-TOF) *m/z*: $[M]^+$calculated for $C_{11}H_{14}O^+$ 162.1039, observed 162.1019.

A variation of the general procedure was used to synthesize alcohols **S2a**-**S2b**, **S2c**-**S2n**. Cinnamyl alcohol **S2b'** was purchased. Branched alcohols **S2a'**, **S2b'**, **S2i**, and **S2m** were isomerized to linear alcohols following a known procedure.[1] Alcohol **S2n** was synthesized following reported procedures.[1] The compounds obtained from this method provided an identical ^{1}H NMR spectrums **S2a**,[2] **S2b**,[2] **S2c**,[2] **S2d**,[3] **S2e**,[4] **S2f**,[2] **S2g**,[3] **S2h**,[5] **S2i**,[6] **S2j**,[2] **S2l**,[4] **S2m**,[7] **S2n**.[8]

General procedure A for synthesis of Boc carbonates



S2a **2a**

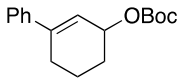
The boc-protection was adapted from the literature. [9] To a solution of alcohol **S2a** (3.65 g, 24.6 mmol) in anhydrous THF (50 mL), cooled in an ice bath, *n*-BuLi (11 mL, 2.5 M in hexanes, 28 mmol) was added dropwise. After 10 min, Boc_2O (6.3 mL, 29 mmol) was added dropwise and the reaction was warmed to rt. After 16 h, the reaction was quenched by the addition of H_2O (100 mL) and extracted with EtOAc (3 X 50 mL). The combined organic layers were washed with brine (50 mL) and dried ($MgSO_4$). Final purification by column chromatography (0-15% EtOAc/hexanes) afforded compound **2a** as a yellow oil (4.72 g, 19.0 mmol, 77%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 6.10 – 5.99 (m, 2H), 5.36 – 5.23 (m, 2H), 2.36 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 138.0, 136.4, 135.8, 129.2, 127.0, 116.9, 82.2, 79.2, 27.8, 21.2.

IR (KBr, thin film, cm^{-1}): 2981, 2931, 1742, 1275, 1253, 1162, 1103.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$Calculated for $C_{15}H_{20}O_3Na^+$ 271.1305, observed 271.1306.



2n

A variation of the general procedure was used with slight modifications. Final purification by column chromatography (0-15% ethyl acetate/hexanes) afforded carbonate **2n** as a white solid (320mg, 71%).

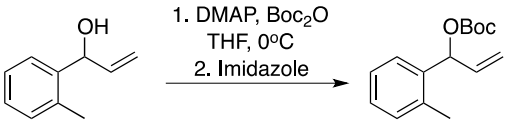
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.37 (m, 2H), 7.38 – 7.26 (m, 3H), 6.19 – 6.14 (m, 1H), 5.33 – 5.27 (m, 1H), 2.59 – 2.35 (m, 2H), 2.03-1.76 (m, 4H), 1.54 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 142.6, 141.2, 128.3, 127.7, 125.6, 122.0, 81.9, 71.6, 28.0, 27.9, 27.5, 19.3.

IR (KBr, thin film, cm^{-1}): 2978, 2937, 1734, 1515, 1277, 1157.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calculated for $C_{17}H_{22}O_3Na^+$ 297.1461, observed 297.1466.

General Procedure B for synthesis of Boc carbonates



S2e **2e**

The procedure for Boc formation was adapted from known procedures.[10, 11] To a solution of alcohol **S2e** (1.04 g, 6.36 mmol) in anhydrous THF (9 mL), cooled in an ice bath, DMAP (10.7 mg, 87.5 μmol) and Boc_2O (2.2 mL, 9.6 mmol) were sequentially added. The reaction was allowed to warm to rt. After 2 h, the reaction was quenched by addition of imidazole (439 mg, 8.39 mmol). After 30 min, the mixture was diluted with water (20 mL) and extracted with EtOAc (3 X 20 mL). The combined organic layers were washed with brine (20 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Final purification by column chromatography (0-15% EtOAc/hexanes) afforded compound **2e** as a clear oil (1.17 g, 4.63 mmol, 73%).

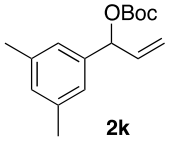
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (td, J = 7.5, 1.8 Hz, 1H), 7.36 – 7.28 (m, 1H), 7.17 (td, J = 7.6, 1.2 Hz, 1H), 7.11-7.05 (m, 1H), 6.35 (d, J = 6.0 Hz, 1H), 6.07 (ddd, J = 17.1, 10.4, 6.0, Hz, 1H), 5.35 (d, J = 17.1 Hz, 1H), 5.29 (d, J = 10.4 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.9 (d, J_{C-F} = 249.5 Hz), 152.5, 134.9, 129.8 (d, J_{C-F} = 8.8 Hz), 128.1 (d, J_{C-F} = 3.7 Hz), 126.3 (d, J_{C-F} = 13.9 Hz), 124.3 (d, J_{C-F} = 3.4 Hz) 117.5, 115.6 (d, J_{C-F} = 21.4 Hz), 82.6, 73.0 (d, J_{C-F} = 2.5 Hz), 27.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -118.0.

IR (KBr, thin film, cm^{-1}): 2982, 2936, 1746, 1492, 1275, 1254, 1163, 786.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{14}H_{17}FO_3Na^+$ 275.1054, observed 275.1054.



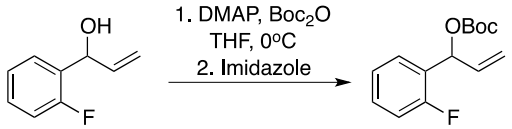
2k

General procedure B was followed. The reaction was not quenched with imidazole. Final purification by column chromatography (0-15% ethyl acetate/hexanes) afforded carbonate **2k** as a clear oil (81%, 1.29 g).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (s, 2H), 6.97 (s, 1H), 6.09-5.97 (m, 2H), 5.38-5.32 (d, J = 17.0 Hz, 1H), 5.26 (d, J = 10.3 Hz, 1H), 2.34 (s, 6H), 1.51 (s, 9H).

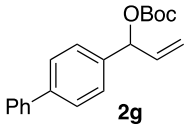
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 138.6, 138.1, 136.4, 129.9, 124.8, 116.8, 82.2, 79.4, 27.8, 21.3.
IR (KBr, thin film, cm^{-1}): 2981, 2921, 1742, 1273, 1254, 850.
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{16}H_{22}O_3Na^+$ 285.1461, observed 285.1467.

General Procedure C for synthesis of Boc carbonates



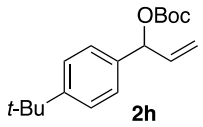
S2l **2l**

The procedure for Boc formation was adapted from known procedures.[10, 11] A flask was charged with DMAP (8.3 mg, 83 μmol), THF (12 mL), and Boc_2O (2.7 mL, 12 mmol) and placed in an ice bath. A separate vial was charged with alcohol **S2l** (890 mg, 5.98 mmol) and THF (6 mL). The alcohol solution was then added dropwise to the round bottom and the vial was rinsed with THF (2 X 3 mL). The reaction was warmed to rt. After 2 h, the reaction was quenched by addition of imidazole (817 mg, 12.0 mmol). After 20 min, the reaction was concentrated under reduced pressure. Final purification by column chromatography (0-15% EtOAc/hexanes) afforded carbonate **2l** as a clear oil (60%, 880 mg).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 – 7.38 (m, 1H), 7.27 – 7.14 (m, 3H), 6.25 (d, *J* = 6.0, 1H) 6.04 (ddd, *J* = 17.7, 10.1, 5.9 Hz, 1H), 5.30 – 5.22 (m, 2H), 2.40 (s, 3H), 1.49 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 137.0, 135.54, 135.46, 130.5, 128.0, 126.6, 126.3, 117.2, 82.2, 76.2, 27.8, 19.2.
IR (KBr, thin film, cm^{-1}): 3068, 3981, 2934, 1743, 1491, 1461, 1369, 1279, 1163, 1101.
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calculated for $C_{16}H_{22}O_3Na^+$ 285.1461, observed 285.1467.



2g

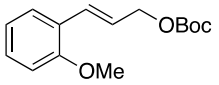
General procedure C was followed. Final purification by column chromatography (0-15% ethyl acetate/hexanes) afforded carbonate **2g** as a clear oil (60%, 880 mg).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.58 (m, 4H), 7.49 – 7.44 (m, 4H), 7.37 (tt, J = 7.2, 1.6 Hz, 1H), 6.15 – 6.04 (m, 2H), 5.39 (ddd, *J* = 16.8, 5.2, 1.6 Hz, 1H), 5.31 (dd, *J* = 9.2, 1.2 Hz, 1H), 1.51 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 141.2, 140.7, 137.8, 136.2, 128.8, 127.5, 127.4, 127.4, 127.1, 117.3, 82.4, 79.0, 27.8.
IR (KBr, thin film, cm^{-1}): 3057, 3031, 2981, 2934, 1737, 1487, 1276, 1167, 764.
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ Calculated for $C_{20}H_{22}O_3$ 333.1461, found 333.1450.



2h

General procedure C was followed. Final purification by column chromatography (0-15% ethyl acetate/hexanes) afforded carbonate **2n** as a clear oil (70%, 811 mg).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.11 – 6.03 (m, 2H), 5.36 (d, *J* = 16.4 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 1.51 (s, 9H), 1.35 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.8, 151.2, 136.3, 135.7, 126.8, 125.5, 116.9, 82.2, 79.1, 34.6, 31.3, 27.8.
IR (KBr, thin film, cm^{-1}): 2965, 1742, 1275, 1254, 1163.
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{18}H_{26}O_3Na^+$ 313.1774, observed 313.1759.

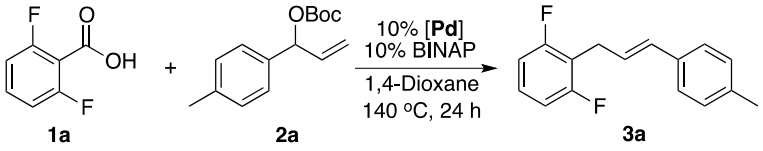


2m

A variation of the general procedure was used with slight modifications. Final purification by column chromatography (0-30% ethyl acetate/hexanes) afforded carbonate **2m** as a clear oil (40%, 516 mg).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.26 (td, *J* = 7.9, 1.7 Hz, 1H), 7.02 (d, *J* = 16.1 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 6.35 (dt, *J* = 16.0, 6.6 Hz, 1H), 4.76 (dd, *J* = 6.6, 1.3 Hz, 2H), 3.86 (s, 3H), 1.53 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 156.9, 153.4, 129.6, 129.2, 127.2, 125.2, 123.5, 120.6, 110.9, 82.1, 68.1, 55.4, 27.8.
IR (KBr, thin film, cm^{-1}): 2980, 2838, 1739, 1599, 1490, 1276, 1161.
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{20}O_4Na^+$ 287.1254, observed 287.1253.

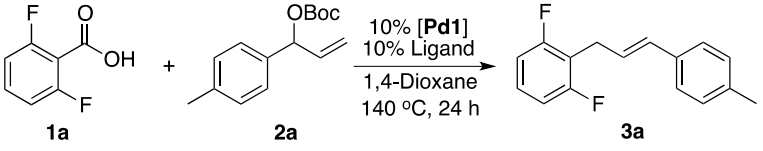
General procedure B or C was followed for the remaining carbonates. Characterization data has been reported for these compounds: **2a'**,[12] **2b**,[13] **2b'**,[12] **2c**,[13] **2d**,[13] **2f**,[14] **2i**,[12] **2j**.[14] The material obtained from these methods provided an identical ^{1}H NMR.

General Procedure for Optimization of Decarboxylative Allylation



1a **2a** **3a**

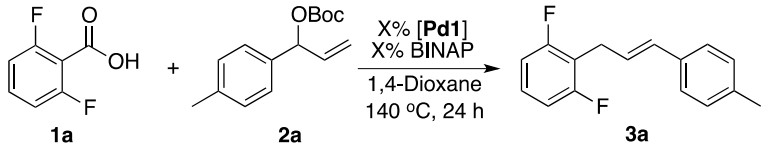
Precatalyst Screen: In a glovebox, a stock solution of 2,6-diflourobenzoic acid (**1a**, 141 mg, 0.892 mmol), carbonate **2a** (336 mg, 1.35 mmol) and biphenyl (internal standard, 33.3 mg, 216 µmol) was prepared in 1,4-dioxane (4.5 mL). Separate 4-mL vials were each charged with a different palladium pre-catalyst (2.9-3.3 µmol for dimeric pre-catalysts, 5.6-6.6 µmol for monomeric pre-catalyst), and BINAP (6.1-6.4 µmol). To each vial, an aliquot of the stock solution was added (0.32 mL). The vials were sealed with a teflon lined cap, removed from the glove box, the cap was secured with electrical tape, and heated to 140 °C.After 24 h, the reactions were cooled to rt, diluted with DCM, filtered through silica gel, and analyzed by GC-FID to determine the percent yield. The yields were calibrated using biphenyl as a standard. The reactions were run in triplicate and the average values are reported.



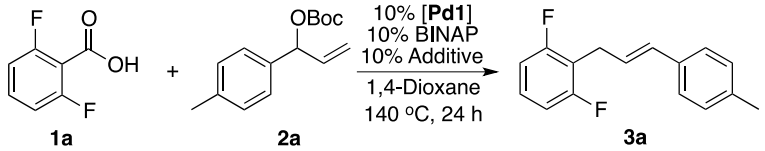
1a **2a** **3a**

Bidentate Ligand Screen: In a glovebox, a stock solution of 2,6-diflourobenzoic acid (**1a**, 170 mg, 1.08 mmol), carbonate **2a** (405 mg, 1.63 mmol), and biphenyl (internal standard, 43.0 mg, 279 µmol) was prepared in 1,4-dioxane (3.4 mL). A second stock solution of (1,5-cyclooctadiene)bis(trimethylsilylmethyl)palladium(II) (**Pd1**, 42.0 mg, 108 µmol) was prepared in 1,4-dioxane (3.4 mL). Separate 4-mL vials were each charged with a different bidentate ligand (6.1-6.6 µmol). To each vial, an aliquot of the palladium stock solution (0.12 mL) was added, followed by the addition of substrate stock solution (0.2 mL). The vials were sealed with a teflon lined cap, removed from the glove box, the cap was secured with electrical tape, and heated to 140 °C. After 24h, the reactions were cooled to rt, diluted with DCM, filtered through silica gel, and analyzed by GC-FID to determine the percent yield. The yields were calibrated using biphenyl as a standard. The reactions were run in triplicate and the average values are reported.

Monodentate Ligand Screen, **BINAP:Pd Ratio Screen**: These screens was performed using the same procedure as the bidentate ligand screen



Catalyst Loading Screen: In a glovebox, a stock solution of 2,6-diflourobenzoic acid (**1a**, 110 mg, 698 µmol), carbonate **2a** (261 mg, 1.05 mmol), and biphenyl (internal standard, 29.3 mg, 190 µmol) was prepared in 1,4-dioxane (1.32 mL). A second stock solution of (1,5-cyclooctadiene)bis(trimethylsilylmethyl)palladium(II) (**Pd1**, 6.2 mg, 16 µmol) and BINAP (9.9 mg, 16 µmol) was prepared in 1,4-dioxane (1.0 mL) and allowed to stir for 5 min at rt. Separate vials were charged with substrate stock solution (0.12 mL) and additional 1,4-dioxane (0-0.2 mL) to insure the final concentrations of the reactions were equivalent. An aliquot of the palladium stock solution (0-0.2 mL) was added to each vial. The vials were sealed with a teflon lined cap, removed from the glove box, the cap was secured with electrical tape, and heated to 140 °C. After 24 h, the reactions were cooled to rt, diluted with DCM, filtered through silica gel, and analyzed by GC to determine the percent yield. The yields were calibrated using biphenyl as a standard. The reactions were run in triplicate and the average values are reported.



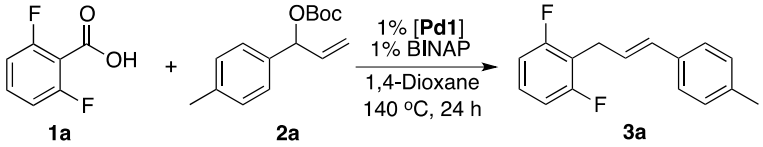
Radical Inhibition Test: In a glovebox, a stock solution of 2,6-diflourobenzoic acid (**1a**, 70.3 mg, 443 µmol), carbonate **2a** (167 mg, 672 µmol), and biphenyl (internal standard, 17.5 mg, 113 µmol) was prepared in 1,4-dioxane (1.4 mL). A second stock solution of (1,5-cyclooctadiene)bis(trimethylsilylmethyl)palladium(II) (**Pd1**, 19.9 mg, 51 µmol) and BINAP (31.8 mg, 51 µmol) was prepared in 1,4-dioxane (0.96 mL) and allowed to stir for 5 min at rt. Palladium stock solution (0.84 mL) was then added to the substrate stock solution.

Separate 4-mL vials were charged with different additives (TEMPO or BHT, 6.4-7.0 µmol). An aliquot of the combined stock solution (0.32 mL) was added to each vial. The vials were sealed with a teflon lined cap, removed from the glove box, the cap was secured with

electrical tape, and heated to 140 °C. After 24 h, the reactions were cooled to rt, diluted with DCM, filtered through silica gel, and analyzed by GC to determine the percent yield. The yields were calibrated using biphenyl as a standard. The reactions were run in duplicate and the average values are reported below. The addition of BHT or TEMPO did not noticeably alter the yield. We propose that these data support a two electron mechanism.

Entry	Additive	% 3a
1	None	73%
2	TEMPO	76%
3	BHT	70%

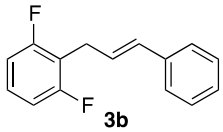
General Procedure for Decarboxylative Allylation



Preparation of Palladium Catalyst Solution: In a glovebox, a 4 mL vial was charged with (1,5-Cyclooctadiene)bis(trimethylsilylmethyl)palladium(II) (**Pd1**, 2.1 mg, 5.4 μmol), BINAP (3.3 mg, 5.3 μmol), and anhydrous 1,4-dioxane (1.0 mL). This solution was stirred at rt for 5 min. Based on the molarity of the solution (5.4 μM in Pd), 0.97 mL was used for every 0.5 mmol benzoic acid. This provides 1 mol % Pd and 1 mol % BINAP.

Procedure for decarboxylation reaction: In a glovebox, a 20 mL vial was charged with Boc-cinnamyl carbonate **2a** (161 mg, 0.65 mmol), 2,6-diflourobenzoic acid **1a** (67.1 mg, 0.424 mmol), 1,4-dioxane (1.3 mL), and an aliquot of the palladium complex solution (0.84 mL, described above). The vial was sealed with a teflon lined cap, removed from the glovebox, the cap was secured with electrical tape, and heated on a hotplate pre-heated to 140 °C. A thermometer submerged in mesitylene on the same plate read 135-136 °C. After 24 h, the reaction was cooled to rt and concentrated under reduced pressure. Hexanes was added (2 mL) and the reaction mixture was concentrated under reduced pressure to remove residual 1,4-dioxane. The crude oil was purified directly by column chromatography (0-1% dichloromethane in hexanes) to afford compound **3a** as a clear oil (83%, 86.9 mg). In a duplicate reaction, the product was isolated in (90%, 94.3 mg). The average yield of 87% is reported. Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.

The general procedure was used starting from carbonate **2a'**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3a** as a clear oil (87%, 91.6 mg), (77%, 80.4 mg) and (77%, 80.1 mg) in triplicate trials. The average of 80% is reported. Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.

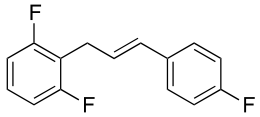


3b

The general procedure was used starting from carbonate **2b**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3b** as a clear oil (83%, 81.8 mg) and (82%, 81.3 mg) in duplicate trials. The average of 83% is reported.

Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.

The general procedure was used starting from carbonate **2b'**. Final purification by column chromatography (3% dichloromethane/hexanes) afforded compound **3b** as a clear oil (83%, 81.6 mg), (75%, 73.3 mg), (77%, 76.3 mg), and (81%, 81.3 mg) in quadruplicate trials. The average of 79% is reported. Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.



3c

The general procedure was used starting from carbonate **2c**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3c** as a clear oil in (76%, 80.5 mg) and (85%, 89.8 mg) in duplicate trials. The average of 81% is reported.

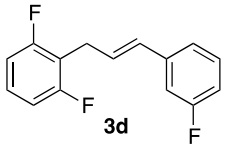
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.28 (m, 2H), 7.24 – 7.16 (m, 1H), 7.0 (t, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 8.0 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.6, 6.8 Hz, 1H), 3.59 (d, *J* = 6.7 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.1 (d, J_{C-F} = 245.7 Hz), 161.4 (dd, J_{C-F} = 248.2, 8.8 Hz), 133.4 (d, J_{C-F} = 2.5 Hz), 130.1, 127.9 (t, J_{C-F} = 10.1 Hz), 127.6 (d, J_{C-F} = 7.6 Hz), 126.1, 115.4, 115.3, 111.2 (dd, J_{C-F} = 20.2, 6.3 Hz), 25.7 (t, J_{C-F} = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.2, -115.8.

IR (KBr, thin film, cm^{-1}): 3036, 2926, 1625, 1592, 1469, 1233, 782.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{15}H_{11}F_3^+$ 248.0808, observed 248.0813.



3d

The general procedure was used starting from carbonate **2d**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3d** as a clear oil (81%, 86.1 mg) and (75%, 80.1 mg) in duplicate trials. The average of 78% is reported.

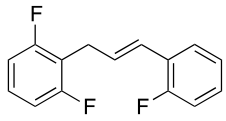
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.17 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 10.2 Hz, 1H), 6.94 – 6.88 (m, 3H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.34 (dt, *J* = 15.8, 6.5 Hz, 1H), 3.60 (d, *J* = 6.5 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 163.1 (d, J_{C-F} = 245.7 Hz), 161.4 (dd, J_{C-F} = 247.0, 7.6 Hz), 139.6 (d, J_{C-F} = 8.8 Hz), 130.2 (d, J_{C-F} = 2.5 Hz), 129.9 (d, J_{C-F} = 8.8 Hz), 127.9 (t, J_{C-F} = 10.1 Hz), 127.8, 122.0 (d, J_{C-F} = 2.5 Hz), 115.5 (t, J_{C-F} = 20.2 Hz), 114.0 (d, J_{C-F} = 21.4 Hz), 112.6 (d, J_{C-F} = 22.7 Hz), 111.2 (dd, J_{C-F} = 20.2, 6.3 Hz), 25.6 (t, J_{C-F} = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.8, -115.7.

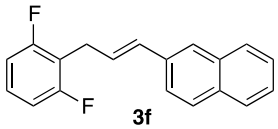
IR (KBr, thin film, cm^{-1}): 3035, 2929, 1625, 1584, 1470, 1267, 781.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{15}H_{11}F_3^+$ 248.0807, found 248.0812.



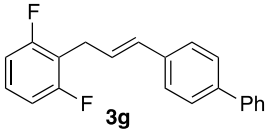
3e

The general procedure was used starting from carbonate **2e**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3e** as a clear oil in (97%, 106 mg), (97%, 106 mg), and (75%, 79.9 mg) in triplicate trials. The average of 90% is reported.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (td, *J* = 7.7, 1.8 Hz, 1H), 7.25 – 7.15 (m, 2H), 7.10 – 6.99 (m, 2H), 6.96 – 6.86 (m, 2H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.41 (dt, *J* = 16.0, 6.7 Hz, 1H), 3.64 (dd, *J* = 6.8 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 160.0 (d, J_{C-F} = 248.7 Hz), 161.4 (dd, J_{C-F} = 247.3, 8.7 Hz), 129.0 (d, J_{C-F} = 4.8 Hz), 128.4 (d, J_{C-F} = 8.3 Hz), 127.9 (t, J_{C-F} = 10.2 Hz), 127.3 (d, J_{C-F} = 3.8 Hz), 125.0 (d, J_{C-F} = 12.3 Hz), 124.0 (d, J_{C-F} = 3.6 Hz), 123.7 (d, J_{C-F} = 3.6 Hz), 115.6 (d, J_{C-F} = 22.2 Hz), 115.4 (t, J_{C-F} = 20.2 Hz), 111.2 (dd, J_{C-F} = 20.2, 6.3 Hz), 26.1 (t, J_{C-F} = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ 115.6, 118.4.
IR (KBr, thin film, cm^{-1}): 3043, 2925, 1625, 1592, 1470, 1236.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{15}H_{11}F_3^+$ 248.0807, observed 248.0801.



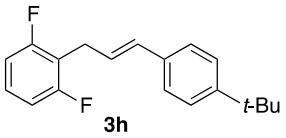
3f

The general procedure was used starting from carbonate **2f**. Final purification by column chromatography (0-2.5% dichloromethane/hexanes) afforded compound **3f** as a white solid (77%, 102 mg) and (79%, 96 mg) in duplicate trials. The average of 78% is reported.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 – 7.76 (m, 3H), 7.72 (s, 1H), 7.61 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.53 – 7.41 (m, 2H), 7.32 – 7.15 (m, 1H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.67 (d, *J* = 15.8 Hz, 1H), 6.49 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.70 (d, *J* = 6.7 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 161.6 (dd, J_{C-F} = 248.5, 8.1 Hz), 134.7, 133.7, 132.9, 131.4, 128.1, 127.9, 127.7, 126.8, 126.2, 125.93, 125.88, 125.7, 123.6, 115.7 (t, J_{C-F} = 20.2), 111.2 (dd, J_{C-F} = 18.2, 7.1 Hz), 25.9, (t, J_{C-F} = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7.
IR (KBr, thin film, cm^{-1}): 3047, 1625, 1588, 1468, 1269, 1000.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{19}H_{14}F_2^+$ 280.1058, observed 280.1054.



3g

The general procedure was used starting from carbonate **2g**. Final purification by column chromatography (0-2.5% dichloromethane/hexanes) afforded compound **3g** as a white solid (82%, 109 mg) and (80%, 105 mg) in duplicate trials. The average of 81% is reported.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 – 7.58 (m, 2H), 7.57-7.52 (m, 2H), 7.48 – 7.40 (m, 4H), 7.38 – 7.32 (m, 1H), 7.25 – 7.16 (m, 1H), 6.96 – 6.86 (m, 2H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.36 (dt, *J* = 15.8, 6.6 Hz, 1H), 3.62 (dd, *J* = 6.5, 1.5 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (dd, J_{C-F} = 239.4, 8.8 Hz), 140.8, 140.0, 136.3, 130.8, 128.8, 127.8 (t, J_{C-F} = 10.1 Hz), 127.21, 127.17, 126.9, 126.6, 126.5, 115.7 (t, J_{C-F} = 20.2 Hz), 111.2 (dd, J_{C-F} = 6.3, 20.2 Hz), 25.8.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7.
IR (KBr, thin film, cm^{-1}): 3434, 1651, 1626, 1590, 1269, 1267, 1199, 1016.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{21}H_{16}F_2^+$ 306.1215, found 306.1204.



3h

The general procedure was used starting from carbonate **2h**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3h** as a clear oil in (81%, 99.0 mg) and (82%, 106 mg) in duplicate trials. The average of 82% is reported.

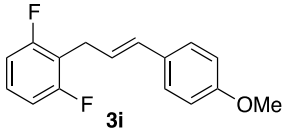
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 4H), 7.24 – 7.14 (m, 1H), 6.91 (m, 2H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.28 (dt, *J* = 15.7, 6.7 Hz, 1H), 3.62-3.57 (d, *J* = 6.8 Hz, 2H), 1.33 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (dd, J_{C-F} = 247.0, 7.6 Hz), 150.3, 134.5, 131.0, 127.7 (t, J_{C-F} = 11.3 Hz), 125.9, 125.5, 125.4, 115.9 (t, J_{C-F} = 20.2 Hz), 111.1 (dd, J_{C-F} = 20.2, 6.3 Hz), 34.5, 31.3, 25.8 (t, J_{C-F} = 2.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7.

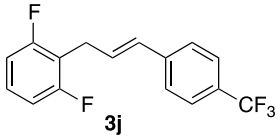
IR (KBr, thin film, cm^{-1}): 3030, 2964, 1625, 1591, 1470, 1266, 966.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{19}H_{20}F_2^+$ 286.1528, found 286.1520.



3i

The general procedure was used starting from carbonate **2i**. The reaction was heated at 140 °C for 18 h. Final purification by column chromatography (0-5% EtOAc/ 1% dichloromethane/ pentane) afforded compound **3i** as a clear oil in (80%, 89.1 mg) and (81%, 90.0 mg) in duplicate trials. The average of 81% is reported. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR.[16]



3j

The general procedure was starting from carbonate **2j**. The reaction was heated at 140 °C for 5 days. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3j** as a clear oil in (79%, 101 mg) and (73%, 93.8 mg) in duplicate trials. The average of 76% is reported.

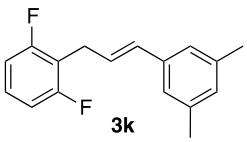
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.29 – 7.17 (m, 1H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.54 – 6.39 (m, 2H), 3.65 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.4 (dd, J_{C-F} = 248.5, 8.1 Hz), 140.7, 130.0, 129.1, 129.0 (q, J_{C-F} = 32.8 Hz), 128.1 (t, J_{C-F} = 10.1 Hz), 126.3, 125.4 (q, J_{C-F} = 3.8 Hz), 124.2 (q, J_{C-F} = 272.2 Hz), 115.1 (t, J_{C-F} = 20.2 Hz), 111.2 (dd, J_{C-F} = 20.2, 6.3 Hz), 25.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.5, -115.7.

IR (KBr, thin film, cm^{-1}): 3018, 2913, 1629, 1613, 1469, 1268.

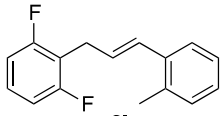
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{16}H_{11}F_5^+$ 298.0775, found 298.0791.



3k

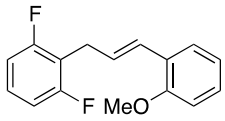
The general procedure was used starting from carbonate **2k**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3k** as a clear oil (78%, 86.5 mg) and (74%, 80.9 mg) in duplicate trials. The average of 76% is reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 – 7.13 (m, 1H), 6.99 (s, 2H), 6.95 – 6.84 (m, 3H), 6.42 (d, J = 15.8 Hz, 1H), 6.30 (dt, J = 15.7, 6.5 Hz, 1H), 3.59 (d, J = 6.4 Hz, 2H), 2.31 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (dd, J_{C-F} = 248.2, 8.8 Hz), 137.9, 137.2, 131.4, 129.0, 127.8 (t, J_{C-F} = 10.1 Hz), 125.9, 124.1, 115.9 (t, J_{C-F} = 20.2 Hz), 111.2 (dd, J_{C-F} = 20.2, 6.3 Hz), 25.8 (t, J_{C-F} = 3.8 Hz), 21.3.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.7.
IR (KBr, thin film, cm^{-1}): 3026, 2918, 1624, 1591, 1468, 1017.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{16}F_2^+$ 258.1215, observed 258.1212.



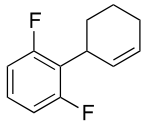
3l

The general procedure was used starting from carbonate **2l**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3l** as a clear oil (86%, 89.2 mg) and (85%, 88.3 mg) in duplicate trials. The average of 86% is reported.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.38 (m, 1H), 7.26-7.12 (m, 4H), 6.95 – 6.87 (m, 2H), 6.71 (d, J = 15.6 Hz, 1H), 6.19 (dt, J = 15.6, 6.7 Hz, 1H), 3.64 (d, J = 4.8 Hz, 2H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (dd, J_{C-F} = 248.2, 8.8 Hz), 136.4, 135.2, 130.1, 129.2, 127.8 (t, J_{C-F} = 10.1 Hz), 127.6, 127.2, 126.0, 125.6, 115.9 (t, J_{C-F} = 20.2 Hz), 111.1 (dd, J_{C-F} = 20.2, 5.0 Hz), 26.1, 19.7.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.8.
IR (KBr, thin film, cm^{-1}): 3023, 2926, 2860, 1625, 1482, 1469, 1265.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{16}H_{14}F_2^+$ 244.1058, found 244.1058.



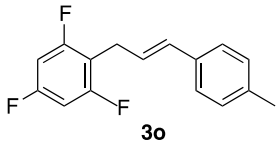
3m

The general procedure was used starting from carbonate **2m**. The reaction was heated at 140 °C for 18 h. Final purification by column chromatography (0-10% EtOAc/1% dichloromethane/hexanes) afforded compound **3m** as a white solid (93%, 104 mg), and (95%, 106 mg) in duplicate trials. The average of 94% is reported.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 7.7, 1.7 Hz, 1H), 7.24 – 7.13 (m, 2H), 6.94 – 6.80 (m, 5H), 6.32 (dt, J = 15.9, 6.8 Hz, 1H), 3.86 (s, 3H), 3.62 (d, J = 6.9, Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.5 (dd, J_{C-F} = 247.0, 8.9 Hz), 156.5, 128.2, 127.6 (t, J_{C-F} = 10.2 Hz), 126.9, 126.7, 126.3, 126.1, 120.6, 116.0 (t, J_{C-F} = 20.2 Hz), 111.1 (dd, J_{C-F} = 20.2, 6.3 Hz), 110.9, 55.5, 26.3 (t, J_{C-F} = 2.9 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.6.
IR (KBr, thin film, cm^{-1}): 3045, 2937, 2837, 1625, 1593, 1489, 1244, 1109.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{16}H_{14}F_2O^+$ 260.1007, found 260.1002.



3n

The general procedure was used starting from carbonate **2n**. By crude ^{1}H and ^{19}F NMR complete conversion of **2n** was observed but no product **3n** was observed.



3o

The general procedure was used starting from carbonate **2a**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3o** as a white solid (62%, 72.1 mg) and (56%, 63.6 mg) in duplicate trials. The average of 59% is reported.

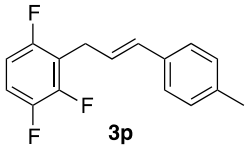
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 8.1 Hz, 2H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.5, 6.7 Hz, 1H), 3.55 (d, *J* = 6.7 Hz, 2H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.4 (ddd, J_{C-F} = 248.1, 14.9, 11.7 Hz), 161.2 (dt, J_{C-F} = 247.4, 15.6 Hz), 137.1, 134.3, 131.2, 129.2, 126.1, 124.1, 112.0 (td, J_{C-F} = 20.7, 4.6 Hz), 100.0 (ddd, J_{C-F} = 25.2, 22.7, 8.8 Hz), 25.4 (t, *J* = 2.6 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.2 (t, J_{F-F} = 5.5 Hz), -112.8 (d, J_{F-F} = 5.5 Hz).

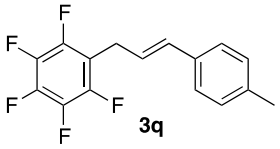
IR (KBr, thin film, cm^{-1}): 3109, 3028, 2913, 1643, 1606, 1434, 1434, 971, 836.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{16}H_{13}F_3^+$ 262.0964, found 262.0953.



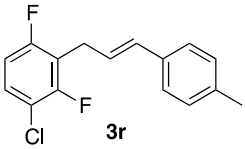
3p

The general procedure was used starting from carbonate **2a**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3p** as a white solid (57%, 64.5 mg) and (57%, 64.3 mg) in duplicate trials. The average of 57% is reported. Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.



3q

The general procedure was used starting from carbonate **2a**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3q** as a yellow solid (31%, 39.9 mg) and (21%, 26.6 mg) in duplicate trials. The average of 26% is reported. Characterization data for this compound has been reported.[15] The material obtained from this method provided an identical ^{1}H NMR.

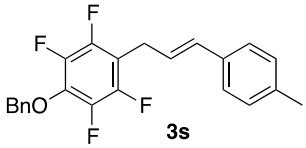


3r

The general procedure was followed starting from carbonate **2a**. The reaction was heated at 160°C for 48 h. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3r** as a yellow oil (28%, 33.1 mg) and (28%, 33.9 mg) in duplicate trials. The average of 28% is reported.

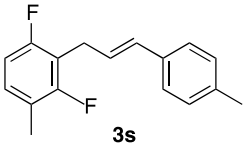
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (apparent d, *J* = 8.1 Hz, 3H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.88 (td, *J* = 8.7, 1.8 Hz, 1H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.7, 6.8 Hz, 1H), 3.61 (d, *J* = 6.8 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 159.7 (dd, J_{C-F} = 247.2, 7.3 Hz), 156.6 (dd, J_{C-F} = 249.0, 8.9 Hz), 137.2, 134.2, 131.7, 129.2, 128.1 (d, J_{C-F} = 9.6 Hz), 126.1, 124.3, 117.6 (dd, J_{C-F} = 21.5, 19.9 Hz), 116.5 (dd, J_{C-F} = 18.9, 4.1 Hz), 111.7 (dd, J_{C-F} = 24.0, 4.1 Hz), 26.3, 21.2.
^{19}F NMR (376 MHz, $CDCl_3$): δ -115.6 (d, J_{F-F} = 7.0 Hz), -116.5 (d, J_{F-F} = 7.2 Hz).
IR (KBr, thin film, cm^{-1}): 3024, 2952, 1512, 1495, 1248, 1082, 799.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{16}H_{13}ClF_2^+$ 278.0668, found 278.0671.



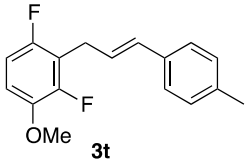
3s

The general procedure was followed starting from carbonate **2a**.The reaction was heated at 160°C for 48 h. Final purification by column chromatography 20% benzene/hexanes afforded compound **3s** as a yellow solid (80%, 66.5 mg) and (84%, 69.4 mg) in duplicate trials. The average of 82% is reported.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.45 (m, 2H), 7.44 – 7.36 (m, 3H), 7.25 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.19 (dt, *J* = 15.7, 6.7 Hz, 1H), 5.25 (s, 2H), 3.57 (d, *J* = 6.5 Hz, 2H), 2.35 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.1 (apparent d, J_{C-F} = 244.4 Hz), 141.4 (dd, J_{C-F} = 248.6, 14.5 Hz), 137.3, 135.7, 135.3 – 135.2 (m), 134.0, 131.9, 129.3, 128.8, 128.6, 128.4, 126.1, 123.9, 112.4 (t, J_{C-F} = 18.9 Hz), 76.4, 25.7, 21.2.
^{19}F NMR (376 MHz, $CDCl_3$): δ -145.5 – -145.7 (m), -152.57 – -162.61 (m).
IR (KBr, thin film, cm^{-1}): 3031, 2923, 1683, 1493, 1455, 1127, 994.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{23}H_{18}F_4O^+$ 386.1288, found 386.1288.



3s

A variation of the general procedure was followed starting from carbonate **2a**. Final purification by column chromatography (0-1% dichloromethane/hexanes) afforded compound **3s** as a white solid (84%, 93.0 mg) and (86%, 96.6 mg) in duplicate trials. The average of 85% is reported.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 7.9 Hz, 2H), 7.02 (td, *J* = 8.5, 6.4 Hz, 1H), 6.79 (td, *J* = 8.7, 1.5 Hz, 1H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.26 (dt, *J* = 15.8, 6.7 Hz, 1H), 3.57 (dd, *J* = 6.7, 1.5 Hz, 2H), 2.33 (s, 3H), 2.27 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.6 (dd, J_{C-F} = 244.2, 8.3 Hz), 159.5 (dd, J_{C-F} = 245.8, 8.5 Hz), 136.9, 134.5, 131.0, 129.3, 128.8 (dd, J_{C-F} = 10.1, 7.6), 126.1, 125.5, 120.3 (dd, J_{C-F} = 18.2, 3.7 Hz), 115.2 (t, J_{C-F} = 20.7 Hz), 110.4 (dd, J_{C-F} = 22.1, 3.9 Hz), 26.0 (t, J_{C-F} = 3.1 Hz), 21.2, 14.3 (d, J_{C-F} = 3.7 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -118.8 (d, J_{F-F}= 6.7 Hz), -119.8 (d, J_{F-F} = 6.7 Hz).
IR (KBr, thin film, cm^{-1}): 3027, 3922, 1628, 1598, 1248, 966.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{16}F_2^+$ 258.1215, found 258.1204.



3t

The general procedure was followed starting from carbonate **2a**. The reaction was heated at 160°C for 48 h. Final purification by column chromatography (0-10% EtOAc/hexanes with 1% DCM) afforded compound **3t** as an orange oil (63%, 74.2 mg) and (61%, 71.8 mg) in duplicate trials. The average of 62% is reported.

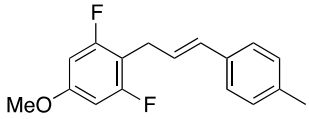
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.86 – 6.77 (m, 2H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.27 (dt, *J* = 15.7, 6.7 Hz, 1H), 3.89 (s, 3H), 3.60 (d, *J* = 6.8, 2H), 2.34 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.0 (dd, J_{C-F} = 240.2, 7.2 Hz), 150.7 (dd, J_{C-F} = 246.9, 8.6 Hz), 144.3 (dd, J_{C-F} = 11.5, 3.1 Hz), 136.9, 134.5, 131.2, 129.2, 126.1, 125.1, 116.9 (dd, J_{C-F} = 21.8, 17.7 Hz), 111.1 (dd, J_{C-F} = 9.6, 2.9 Hz), 110.0 (dd, J_{C-F} = 23.6, 4.1 Hz), 56.8, 26.1 (t, J_{C-F} = 2.9 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -126.0 (d, J_{F-F} = 3.0 Hz), -136.3 (d, J_{F-F} = 2.1 Hz).

IR (KBr, thin film, cm^{-1}): 3026, 3921, 1618, 1510, 1474, 1248, 804.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{16}F_2O^+$ 274.1164, found 274.1158.



3u

The general procedure was used starting from carbonate **2a**. The reaction was heated at 160 °C for 48 h. Final purification by column chromatography (0-10% EtOAc/1% dichloromethane/hexanes) afforded compound **3u** as an orange oil (82%. 96.2 mg) and (84%, 99.3 mg) in duplicate trials. The average of 83% is reported.

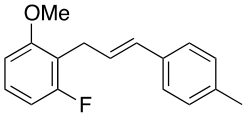
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.53 – 6.46 (m, 2H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.26 (dt, *J* = 15.7, 6.6 Hz, 1H), 3.81 (s, 2H), 3.52 (d, *J* = 6.7 Hz, 3H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.8 (dd, J_{C-F} = 245.2, 12.2 Hz), 159.3 (t, J_{C-F} = 14.1 Hz), 136.9, 134.6, 130.6, 129.2, 126.0, 125.8, 107.8 (t, J_{C-F} = 21.1 Hz), 97.9 (dd, J_{C-F} = 21.4, 7.6 Hz), 55.7, 25.3 (t, J_{C-F} = 2.6 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -114.9.

IR (KBr, thin film, cm^{-1}): 3024, 3920, 1637, 1589, 1503, 1143, 1041.

HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{16}F_2O^+$ 274.1164, found 274.1156.



3w

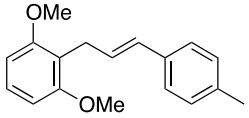
The general procedure was followed starting from carbonate **2a**. The reaction was heated at 160°C for 5 days. Final purification by column chromatography 5% DCM/5% EtOAc/Hexanes afforded compound **3w** as a yellow oil (64%, 71.3 mg) and (59%, 65.4 mg) in duplicate trials. The average of 62% is reported.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.0 Hz, 2H), 7.19 (td, *J* = 8.3, 6.7 Hz, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 6.77 – 6.67 (m, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.30 (dt, *J* = 15.8, 6.5 Hz, 1H), 3.89 (s, 3H), 3.59 (d, *J* = 6.5, Hz, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 161.6 (d, J_{C-F} = 243.5 Hz), 158.7 (d, J_{C-F} = 8.7 Hz), 136.6, 135.0, 130.2, 129.1, 127.4 (d, J_{C-F} = 10.6 Hz), 126.6, 126.0, 116.0 (d, J_{C-F} = 18.7 Hz), 107.9 (d, J_{C-F} = 23.2 Hz), 106.2 (d, J_{C-F} = 2.8 Hz), 56.0, 26.1 (d, J_{C-F} = 3.9 Hz), 21.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -117.3.

IR (KBr, thin film, cm^{-1}): 2920, 1614, 1471, 1273, 1241, 1089.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{17}FO^+$ 256.1258, found 256.1258.

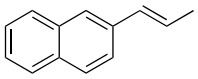


3x

The general procedure was followed from carbonate **2a**. The reaction was heated at 180 °C for 48 h. Final purification by column chromatography (5% EtOAc/5% dichloromethane/hexanes) afforded compound **3X** as an orange solid (60%, 70.3 mg) and (68%, 78.4 mg) in duplicate trials. The average of 64% is reported.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.59 (d, *J* = 8.2 Hz, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.30 (dt, *J* = 16.0, 6.0 Hz, 1H), 3.86 (s, 6H), 3.57 (d, *J* = 6.2 Hz, 2H), 2.32 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.3, 136.2, 135.4, 129.3, 129.0, 127.9, 127.1, 125.9, 116.7, 103.9, 55.9, 26.5, 21.1.
IR (KBr, thin film, cm^{-1}): 2934, 2835, 1595, 1475, 1474, 1257, 1112.
HRMS (EI-TOF) *m/z*: $[M]^+$ Calculated for $C_{17}H_{16}F_2O^+$ 274.1164, found 274.1156.

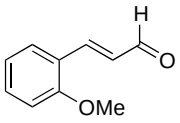
Identification of Byproducts of Decarboxylative Cross-Coupling

In the process of optimization and product isolation, a variety of byproducts were identified.



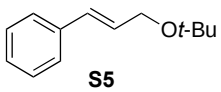
S3

Compound **S3** was isolated as a byproduct in the purification of **3f**. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR. [17]



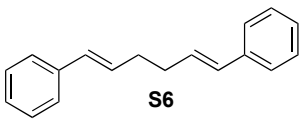
S4

Compound **S4** (5.6 mg) was isolated as a byproduct in the purification of **3m**. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR. [18]

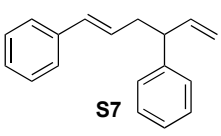


S5

Compound **S5** (26.1) was isolated as a byproduct in the purification of **3b**. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR. [19]

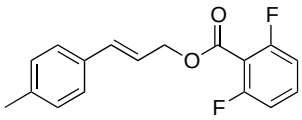


S6

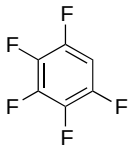


S7

Compounds **S6** and **S7** were isolated as a 1:1.4 ratio mixture (14.4 mg) in the purification of **3b**. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR **S6**,[20] **S7**.[21]



Compound **S8** was observed via crude GC during screening. The identity of **S8** was confirmed by comparison to an authentic standard synthesized by following a literature procedure.[15] Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{1}H NMR.[15]



S9

Compound **S9** was observed via crude ^{19}F NMR during the synthesis of **3q**. Characterization data for this compound has been reported. The material obtained from this method provided an identical ^{19}F NMR. [22]

REFERENCES

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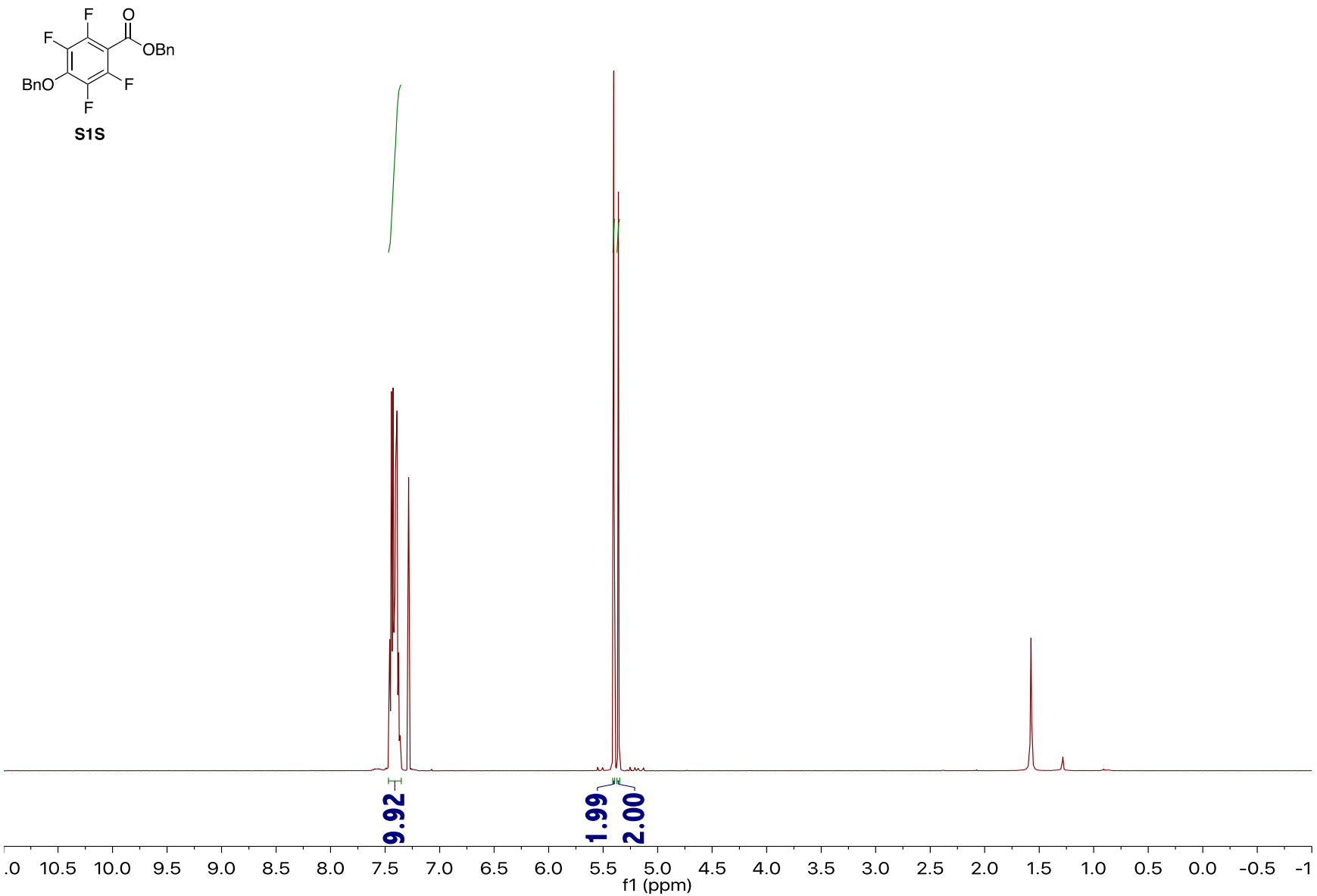
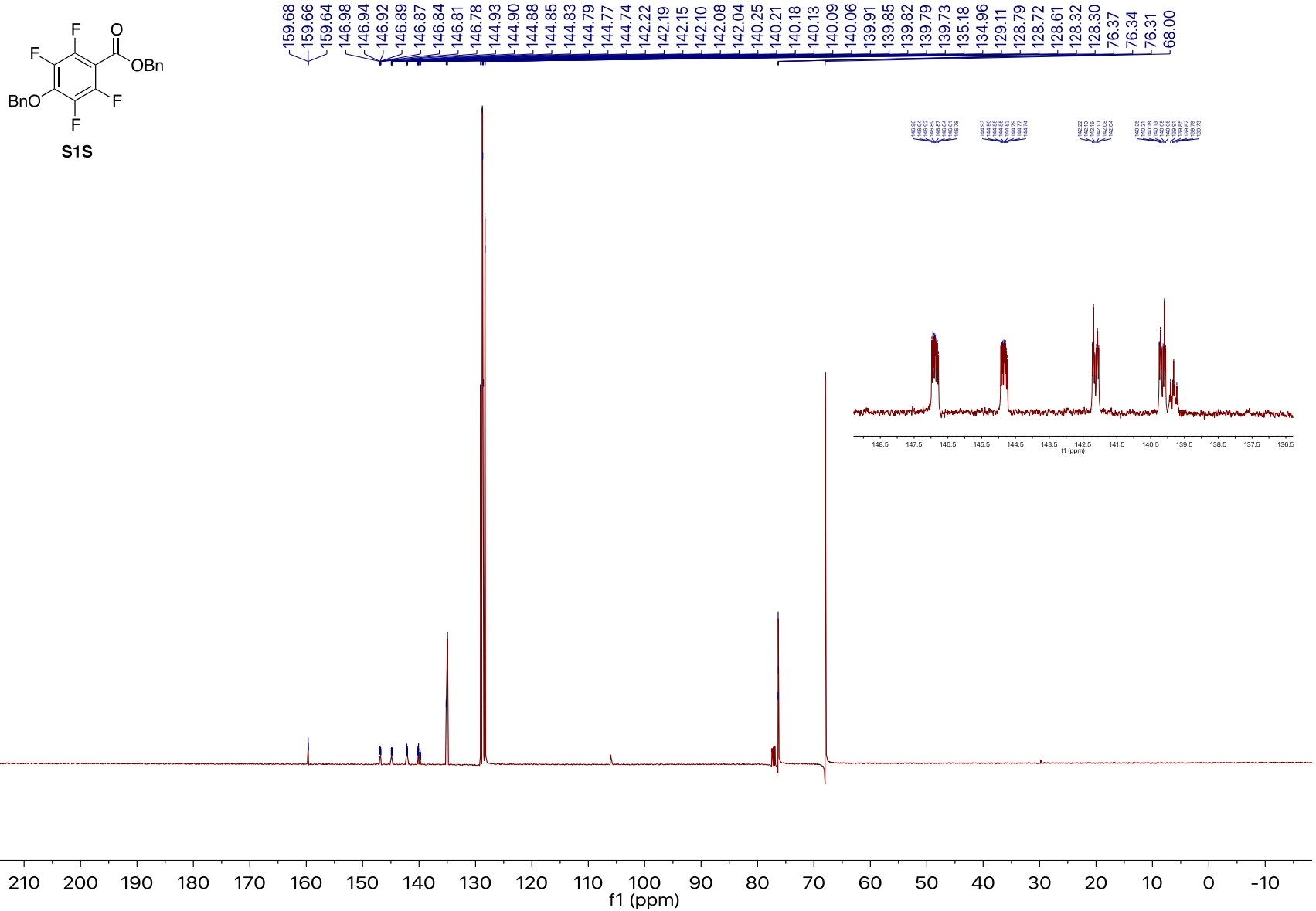
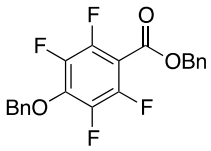


S1S

Compound S1S: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

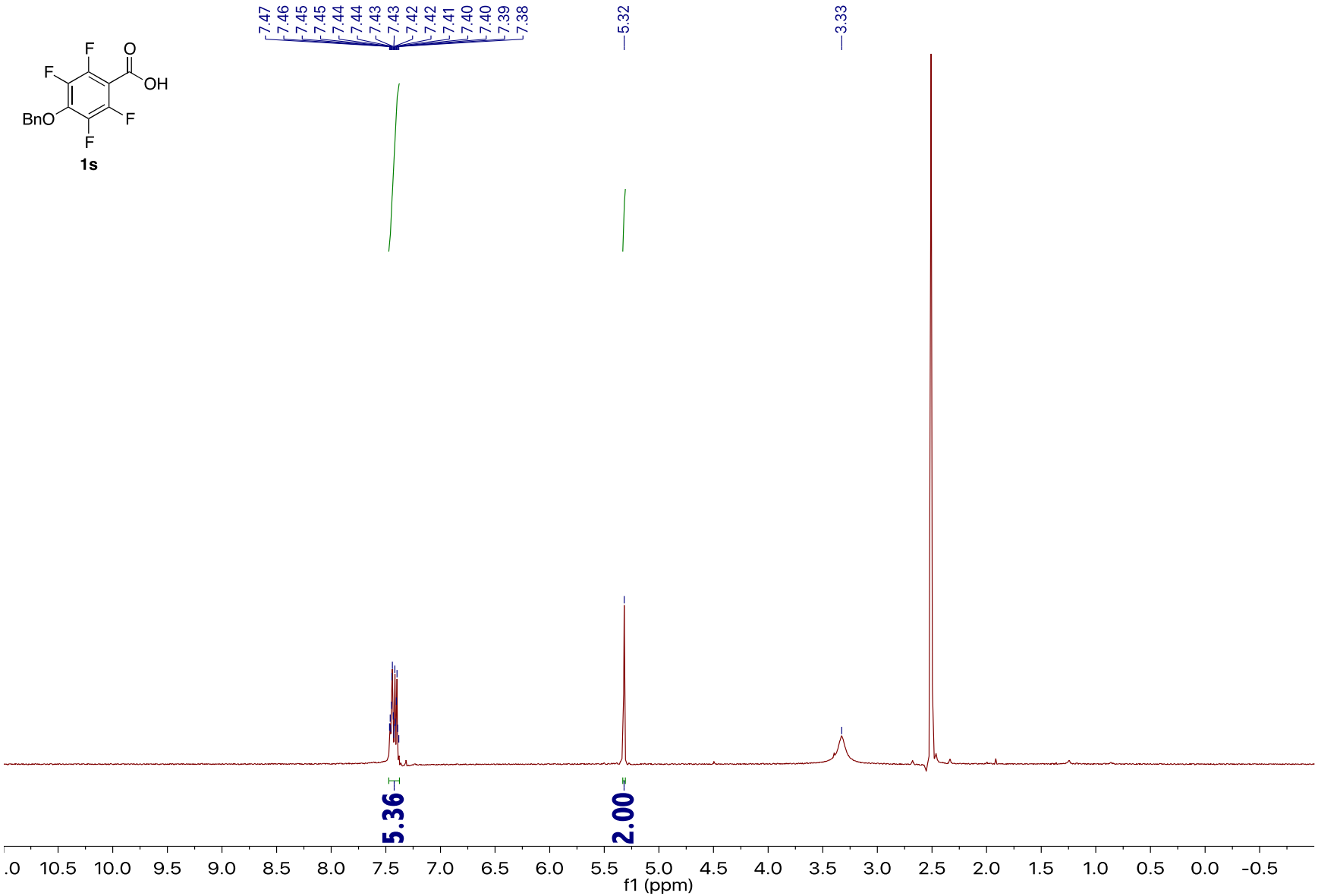


Compound S1S: 126 MHz ^{1}H NMR spectrum in $CDCl_3$



S1S

Compound S1S: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



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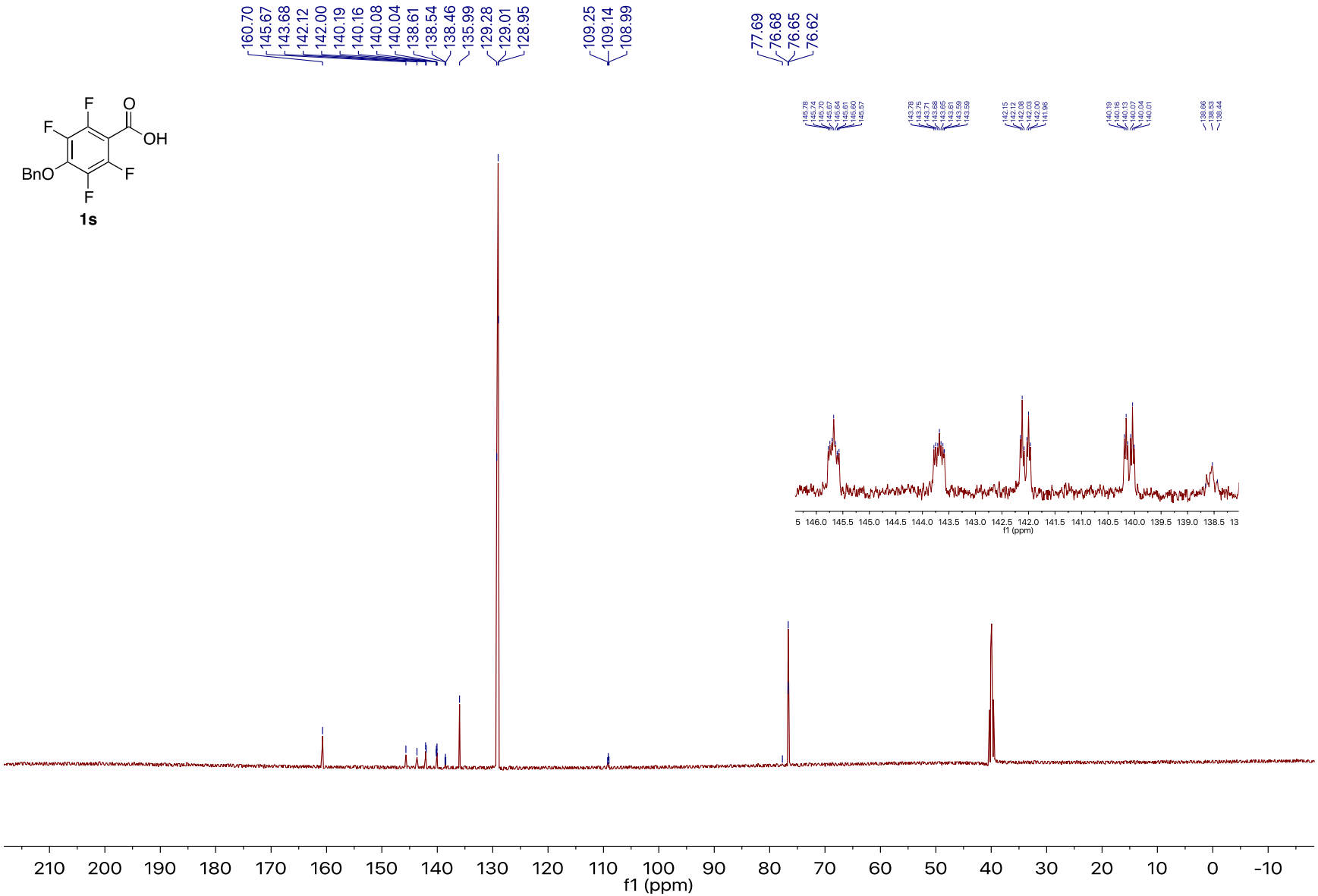

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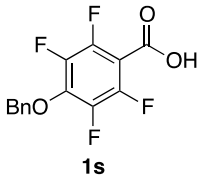
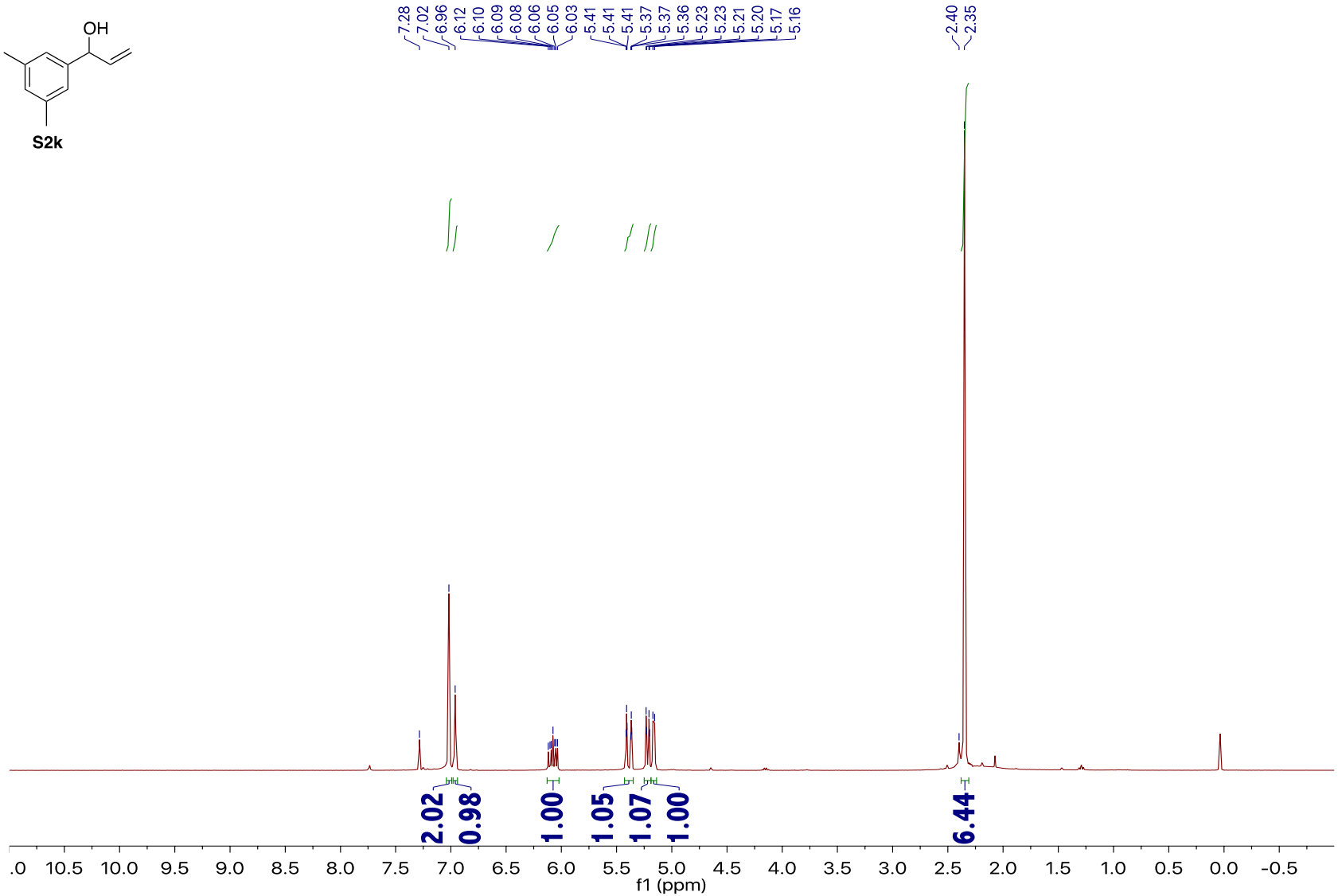
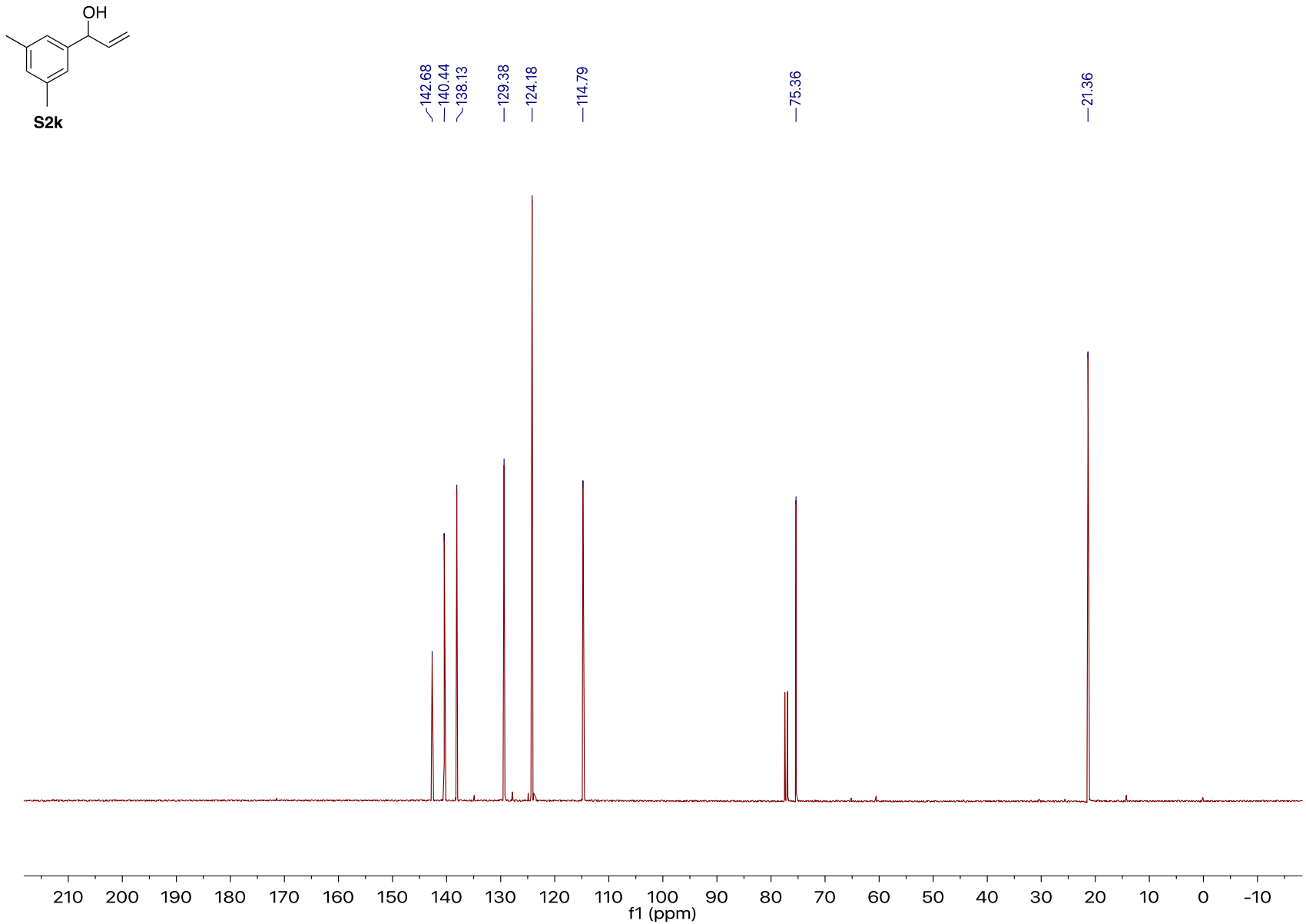


1s

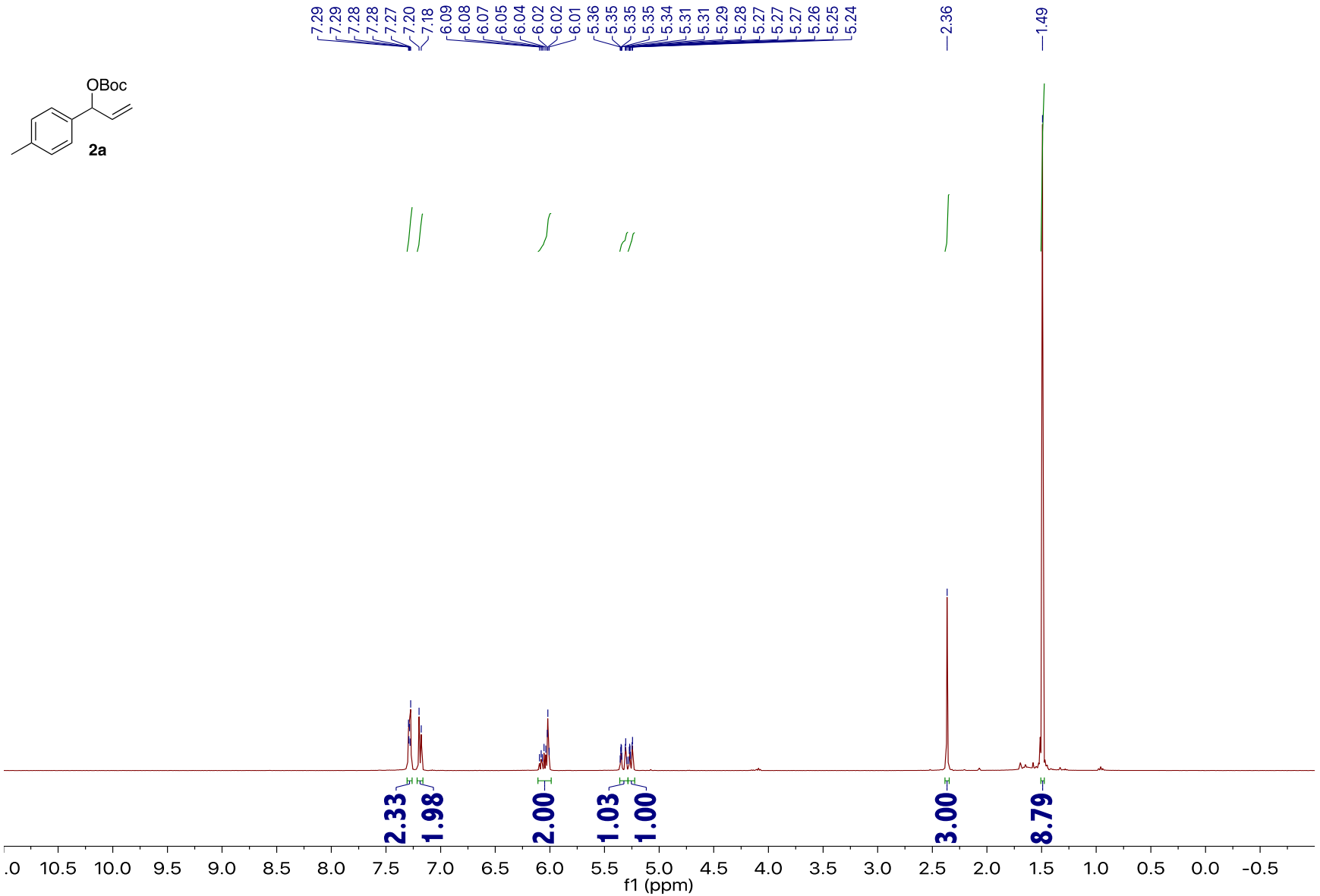
Compound 1s: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



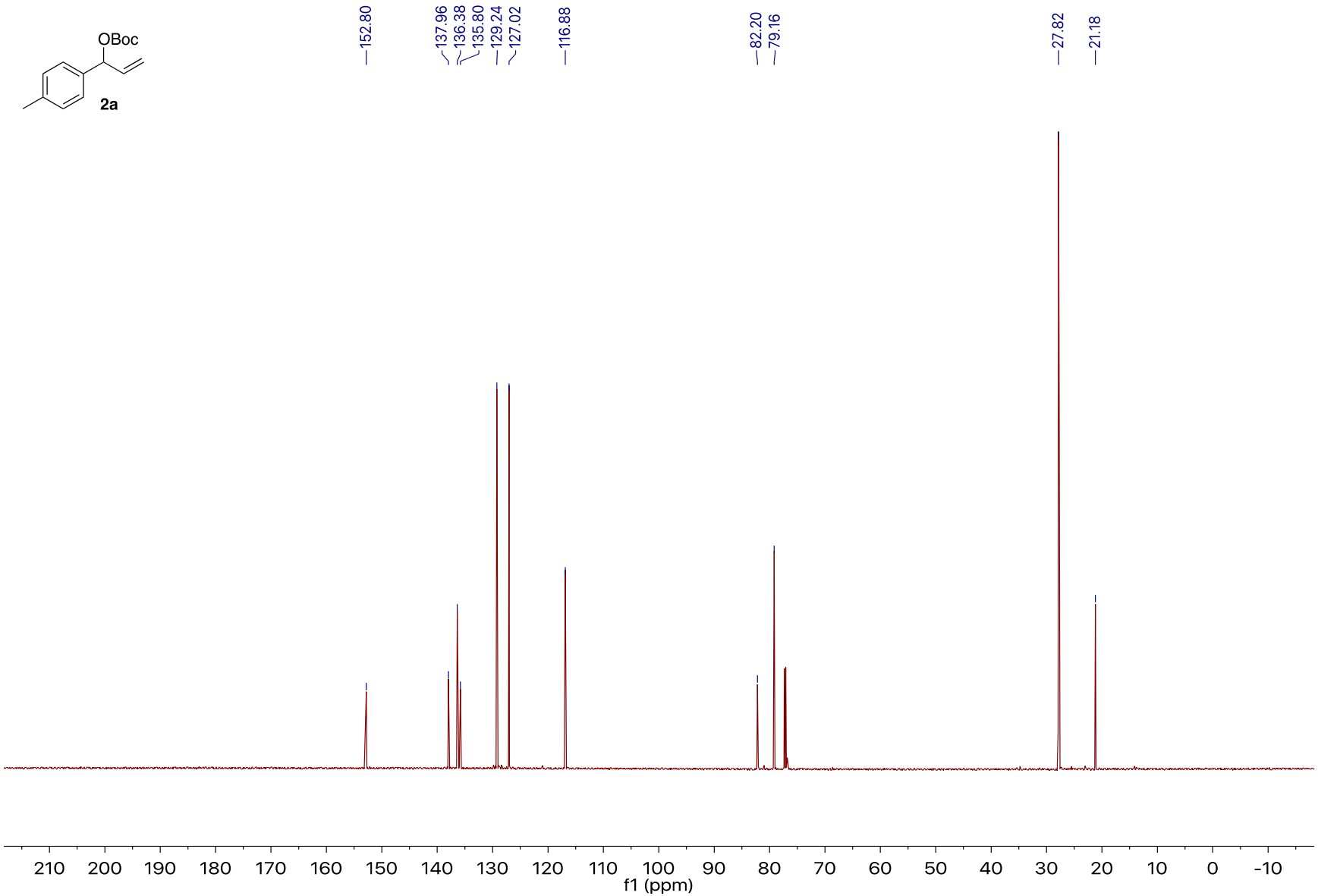
Compound S2k: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



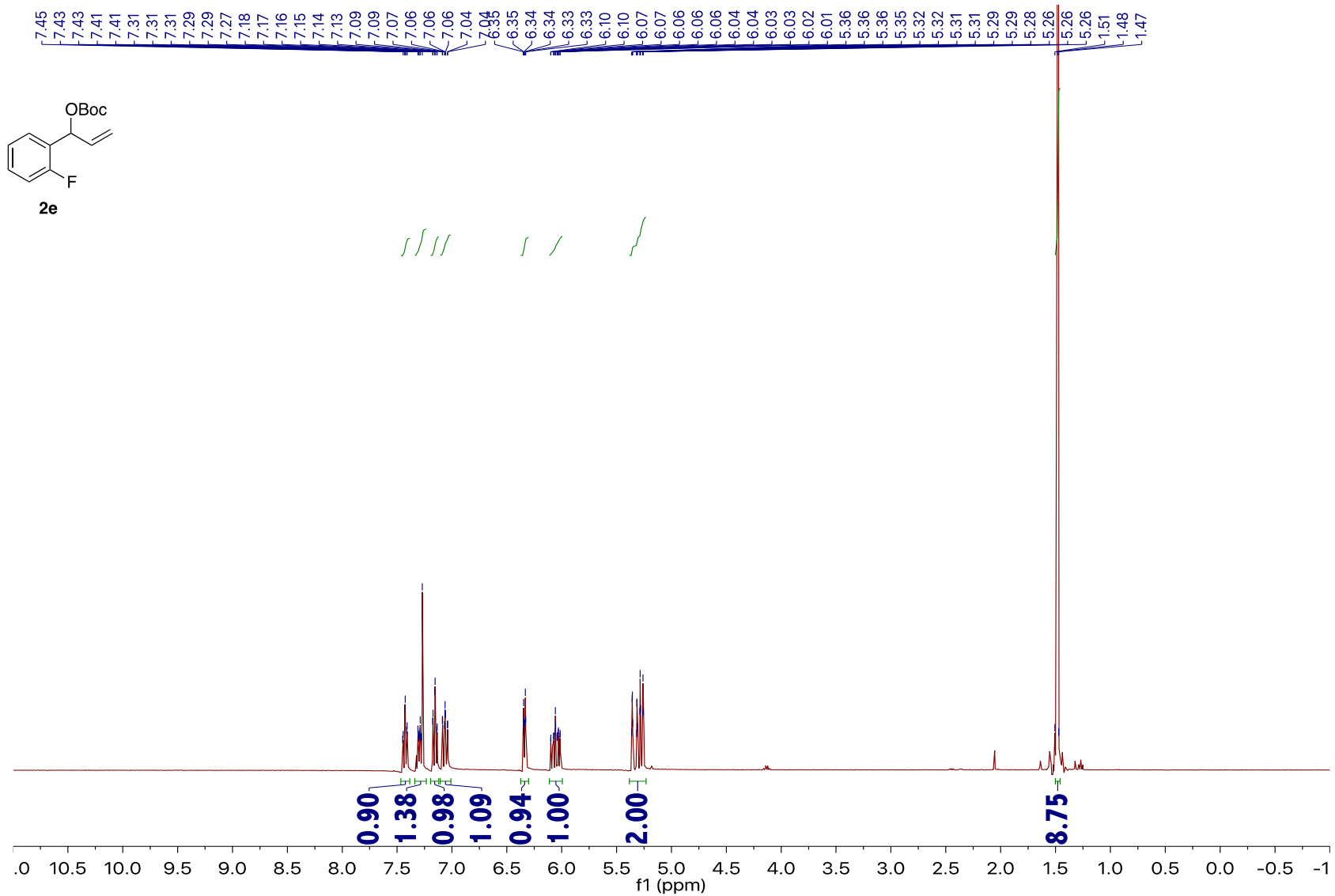
Compound S2k: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



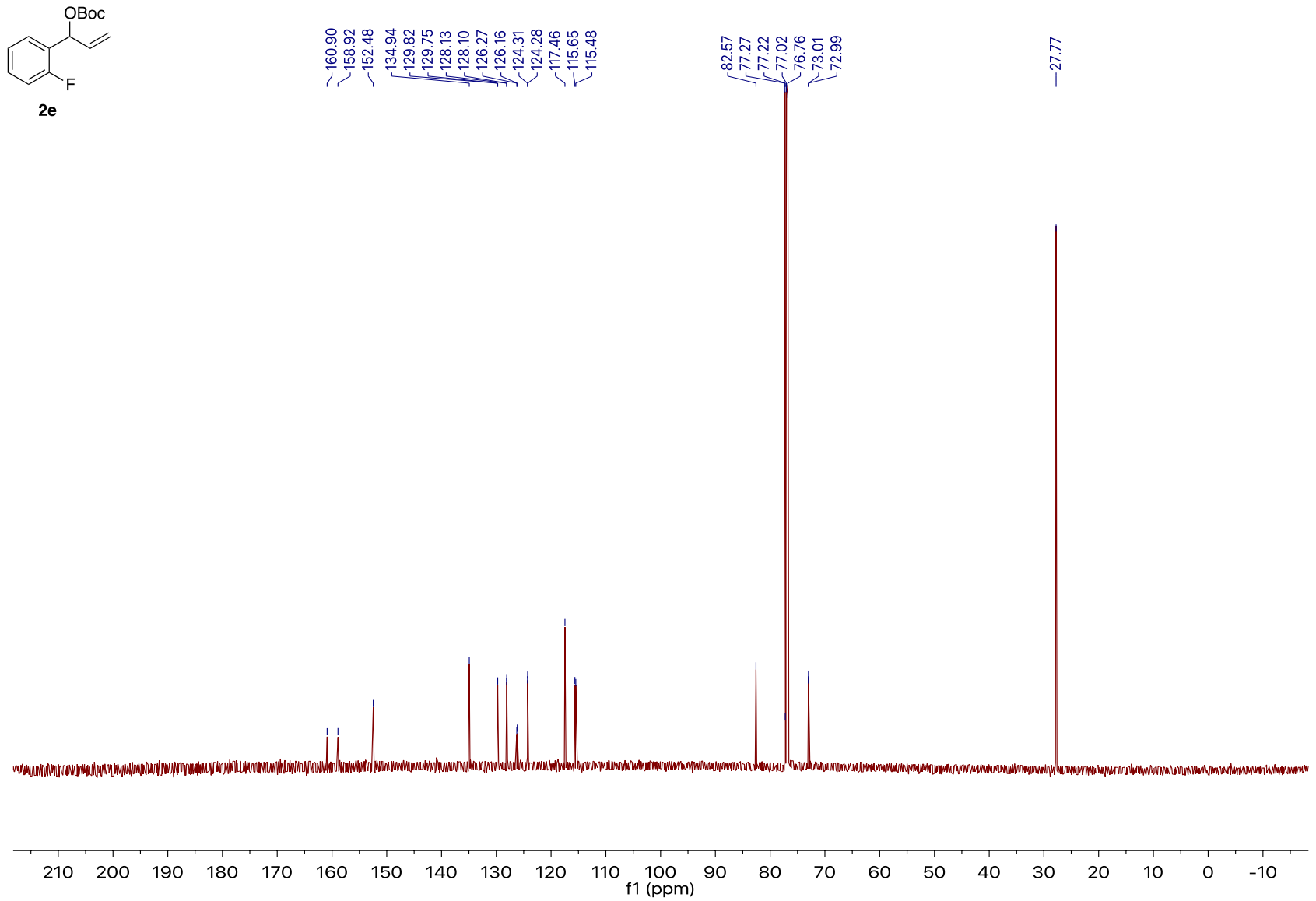
Compound 2a: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



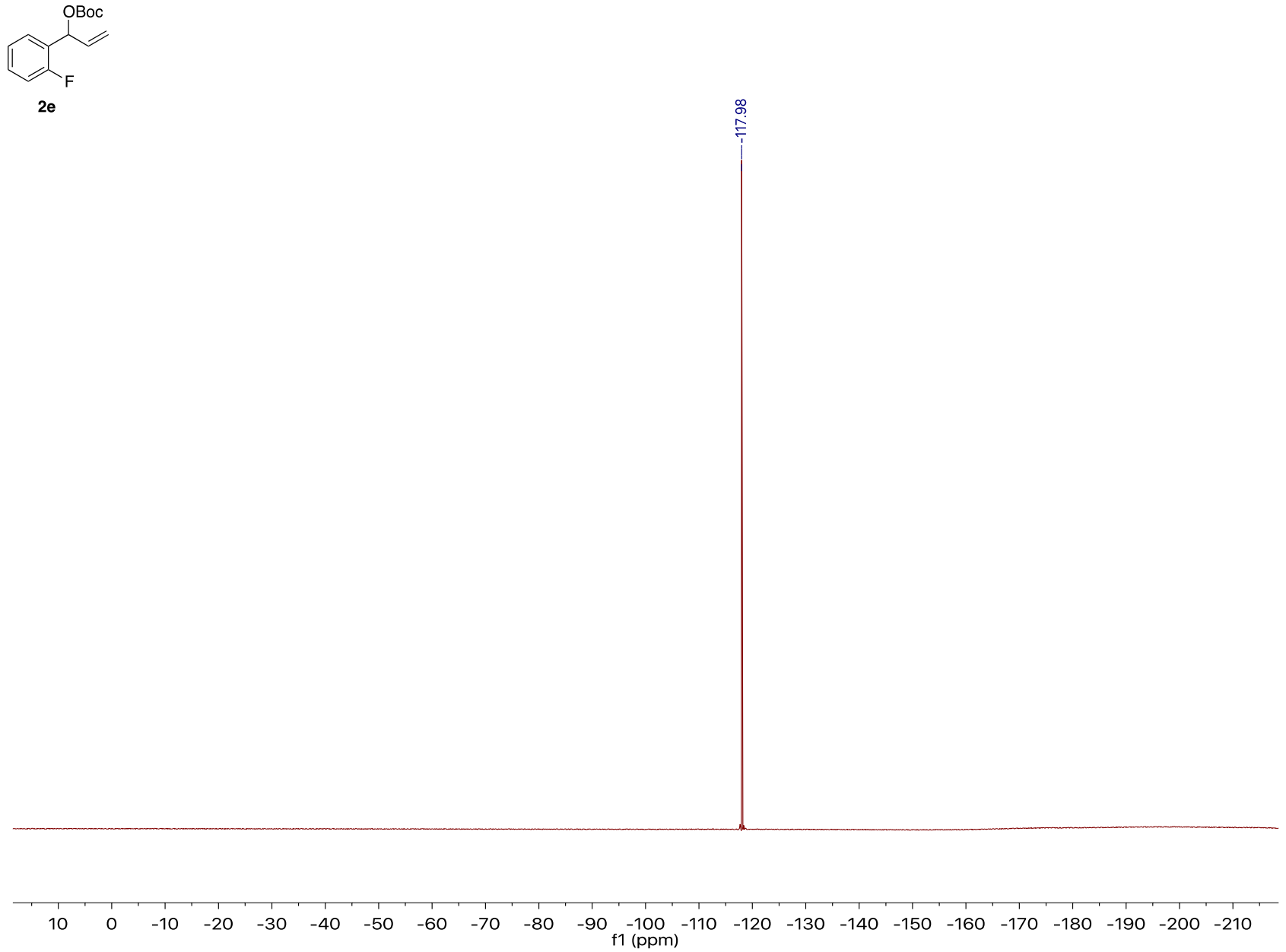
Compound 2a: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



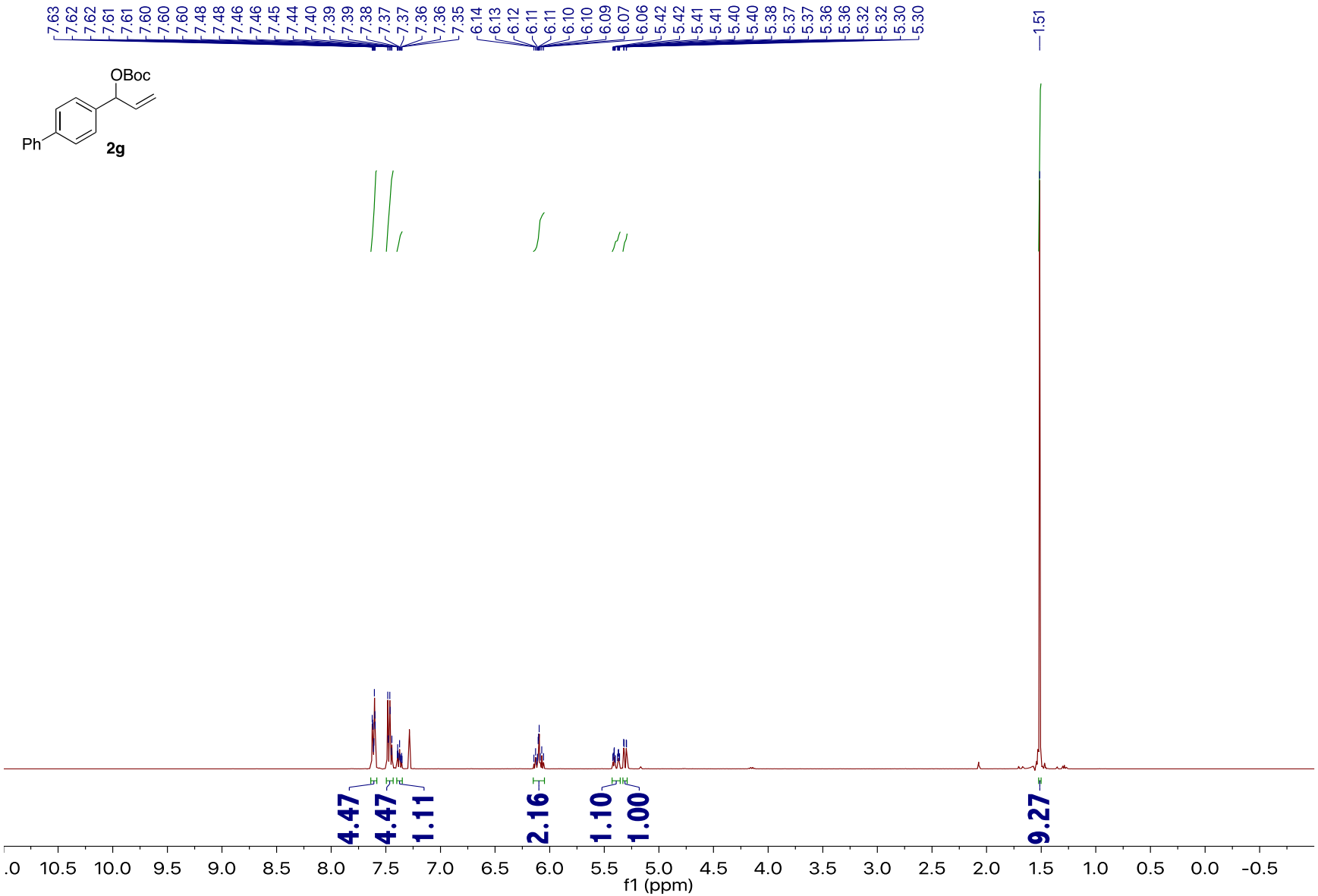
Compound 2e: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



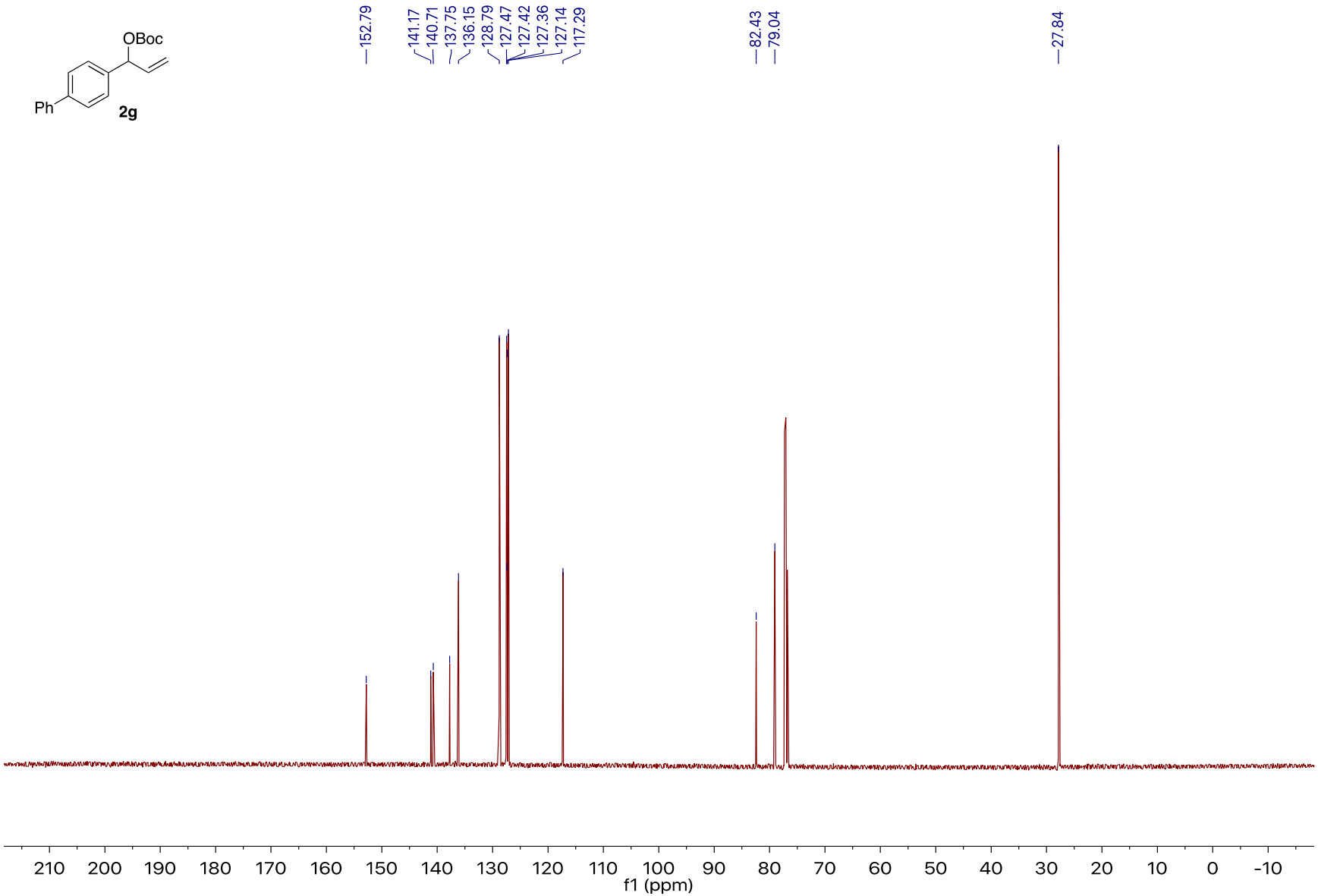
Compound 2e: 126 MHz ^{1}H NMR spectrum in $CDCl_3$



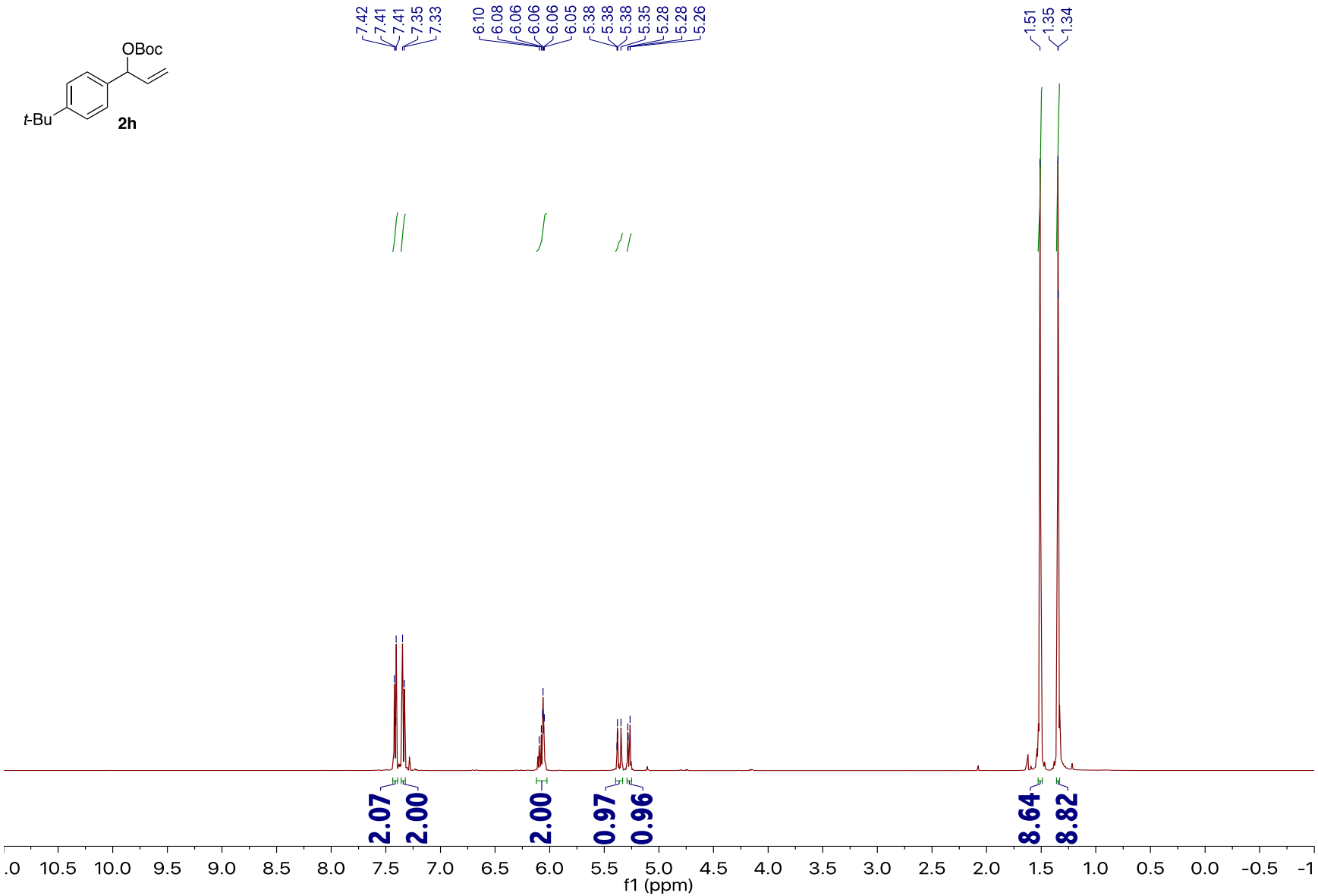
Compound 2e: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



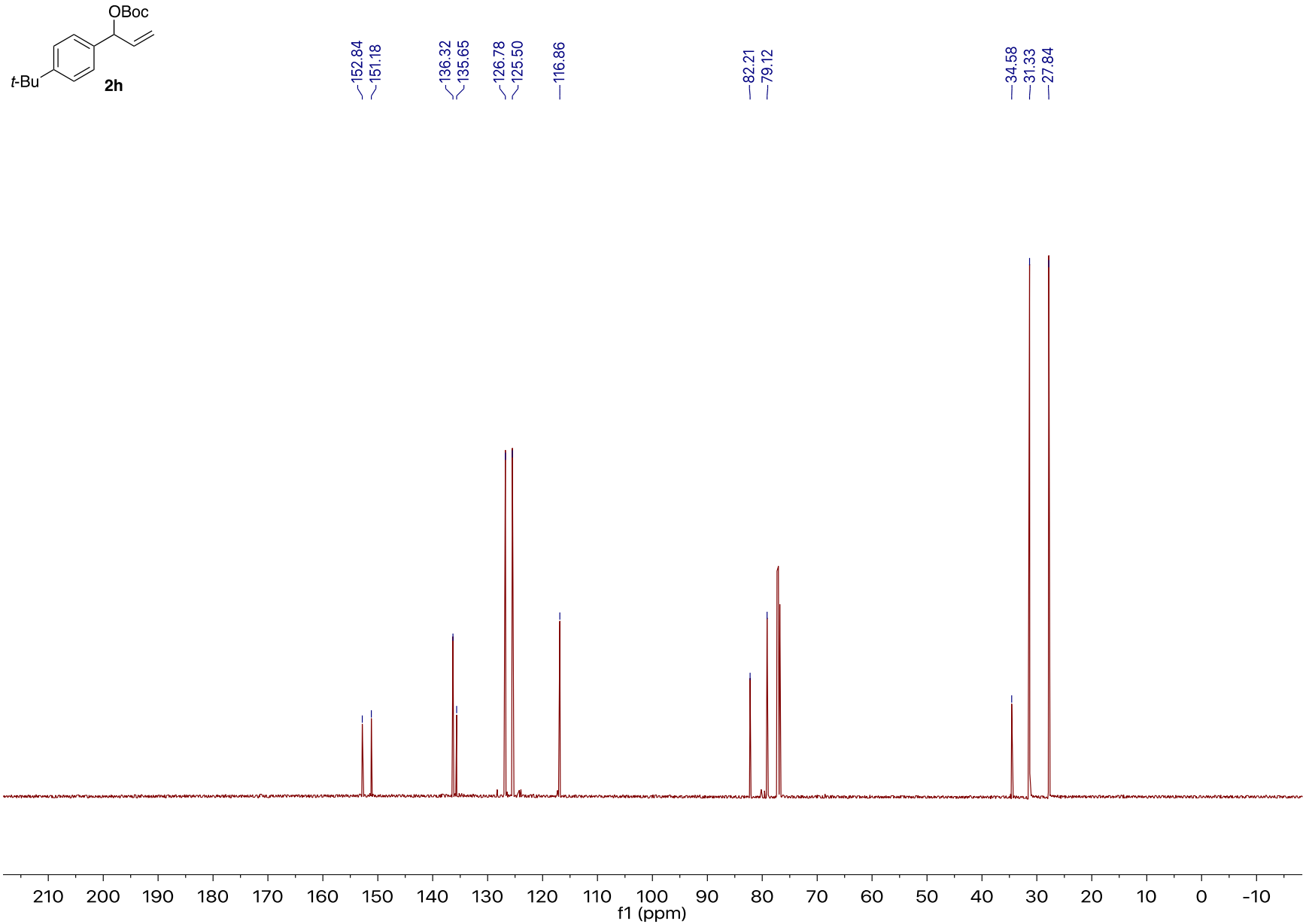
Compound 2g: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



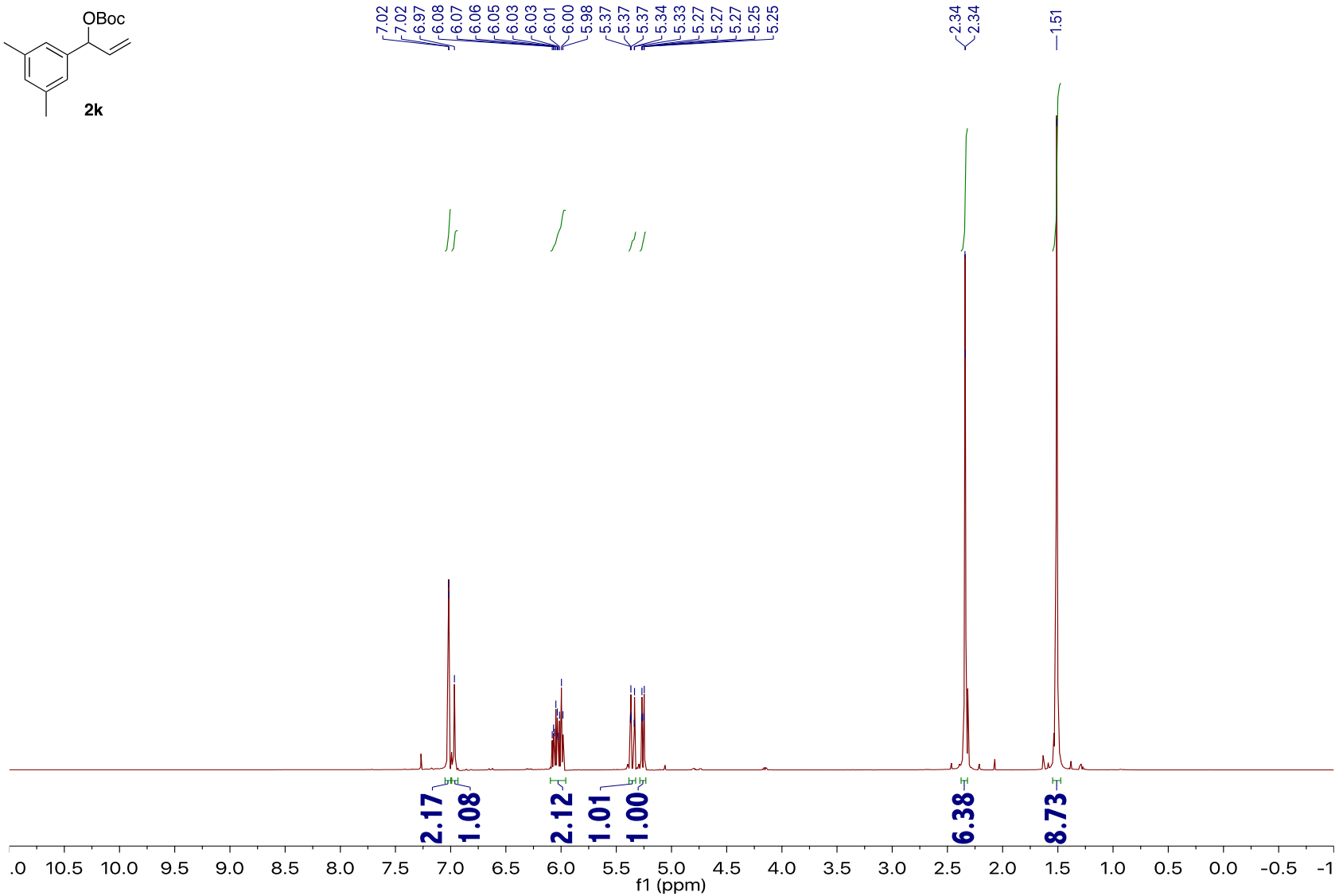
Compound 2g: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



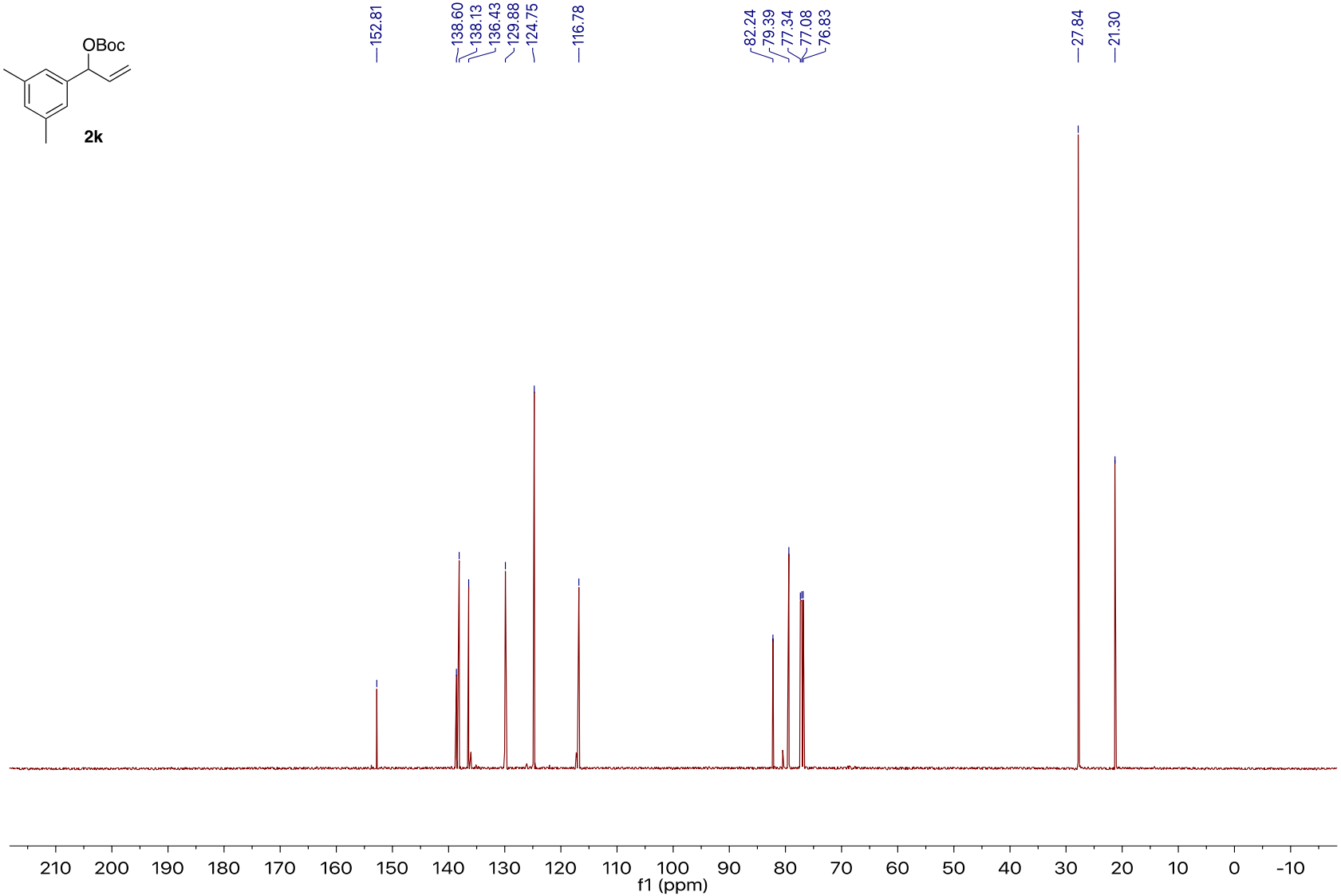
Compound 2h: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



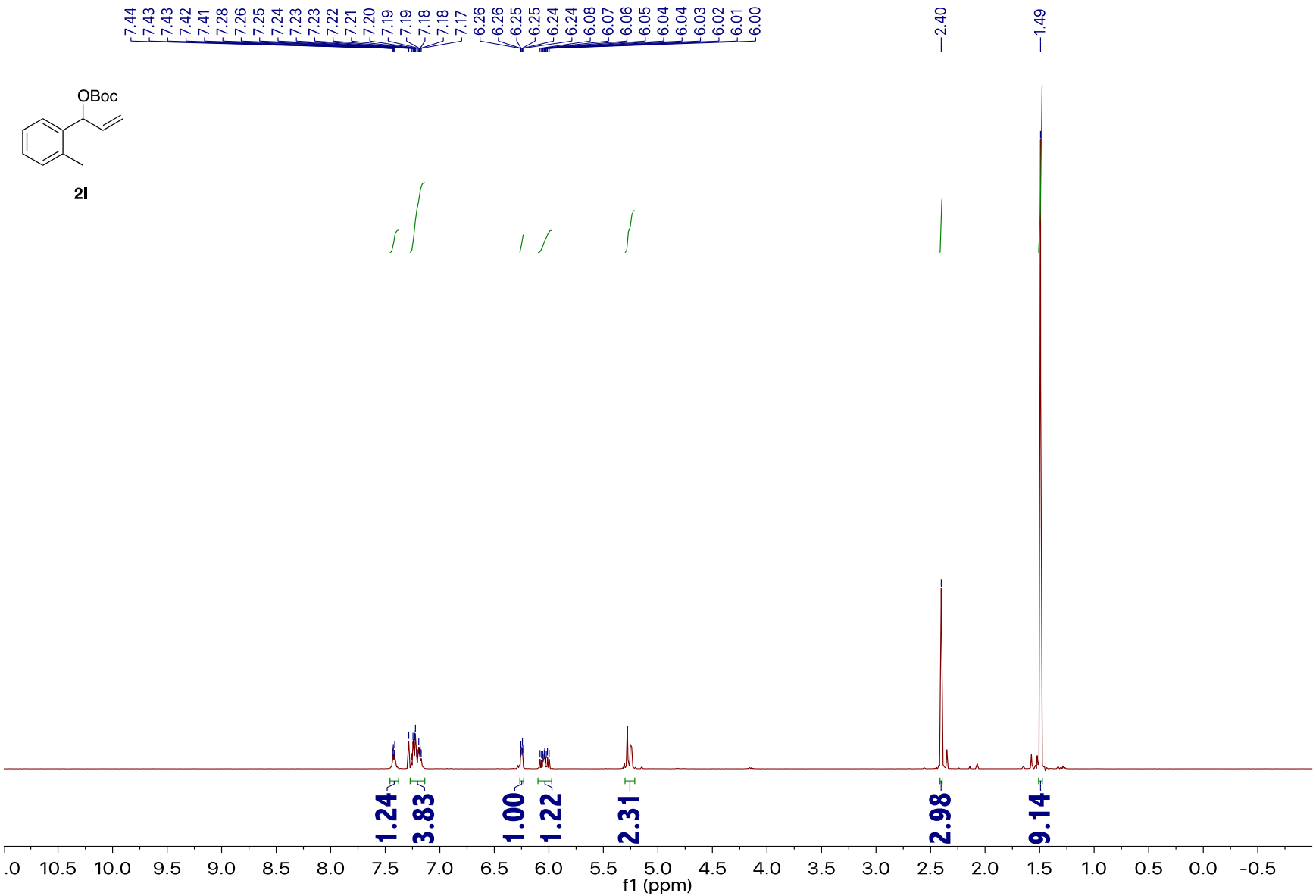
Compound 2h: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



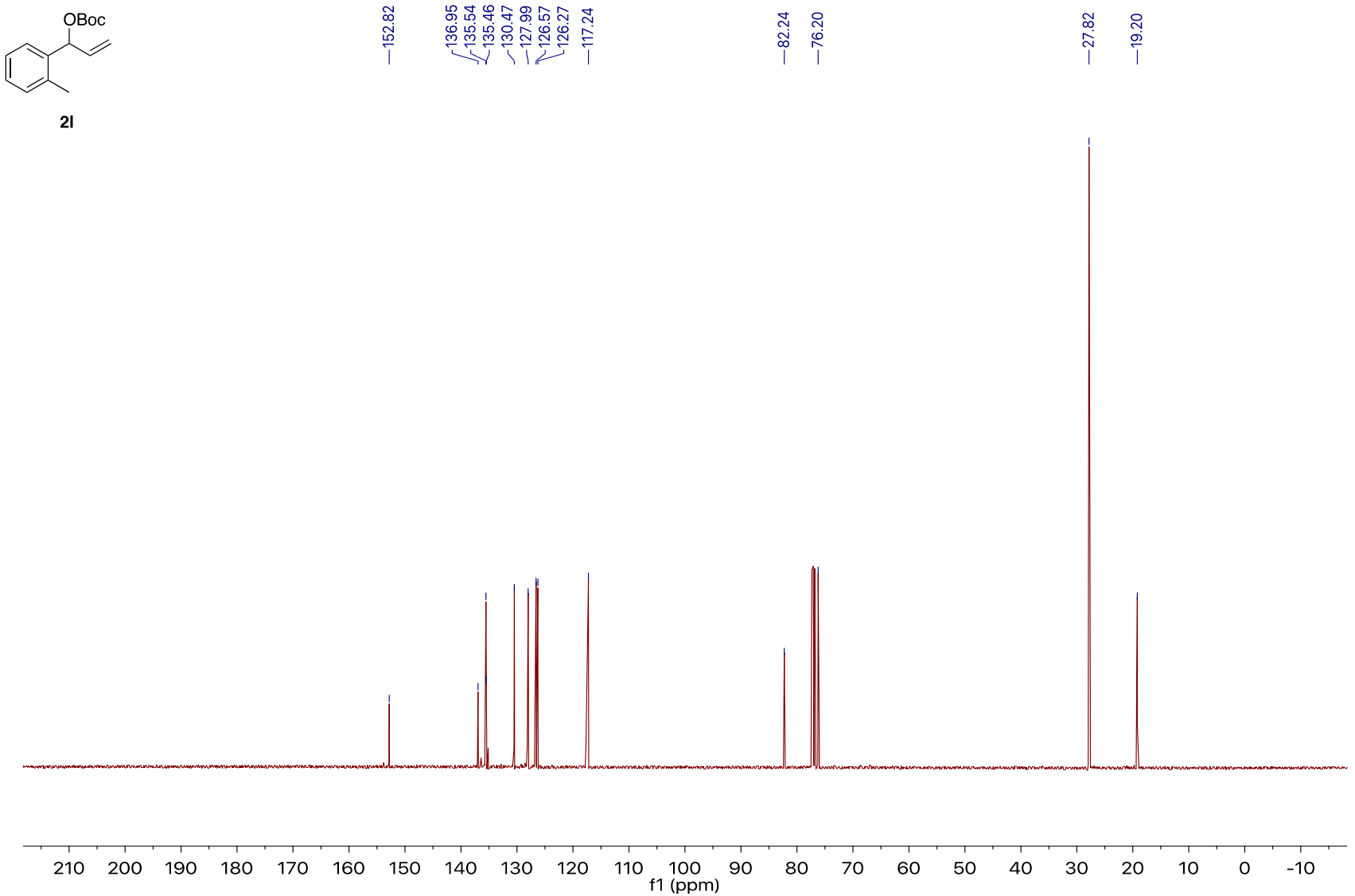
Compound 2k: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



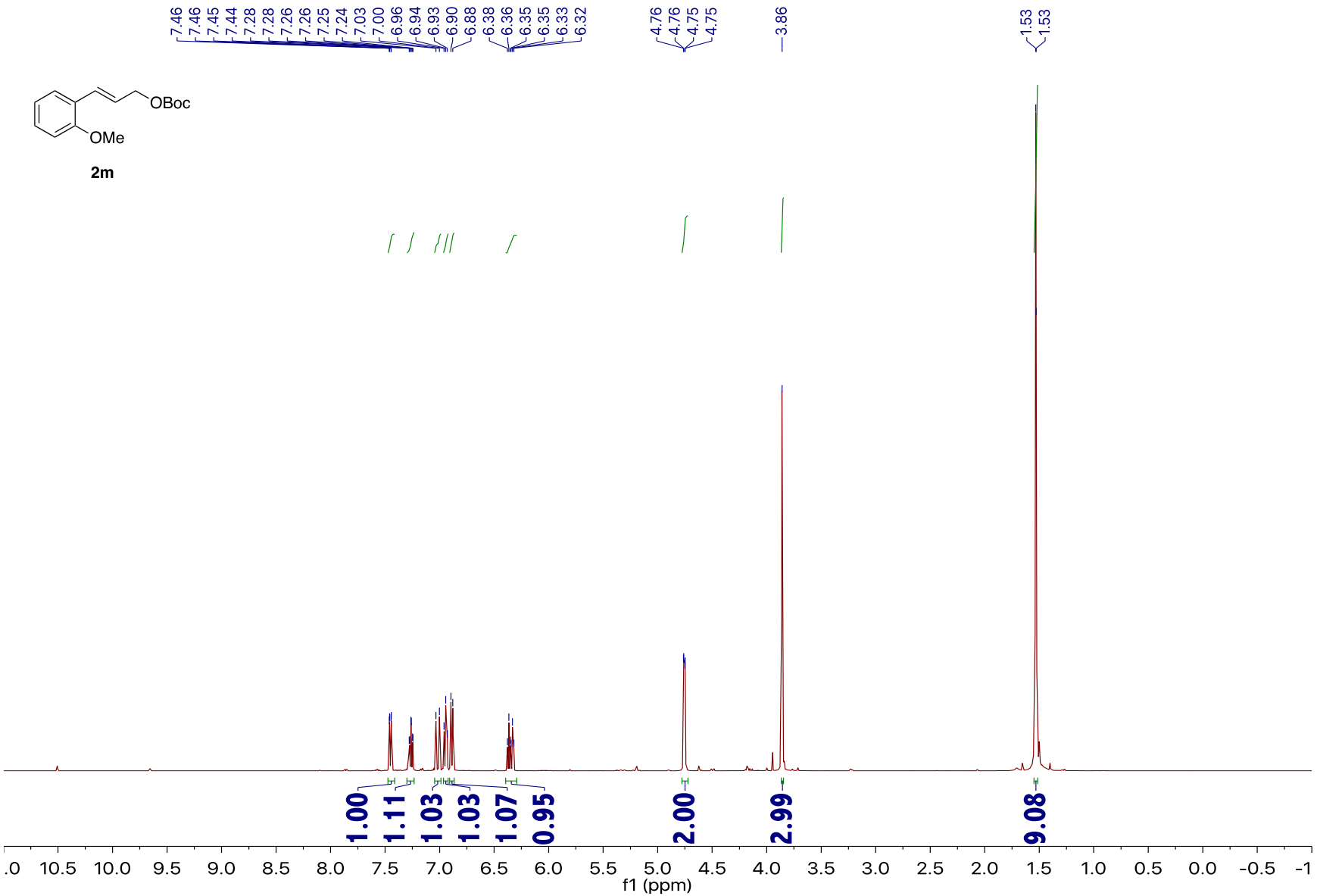
Compound 2k: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



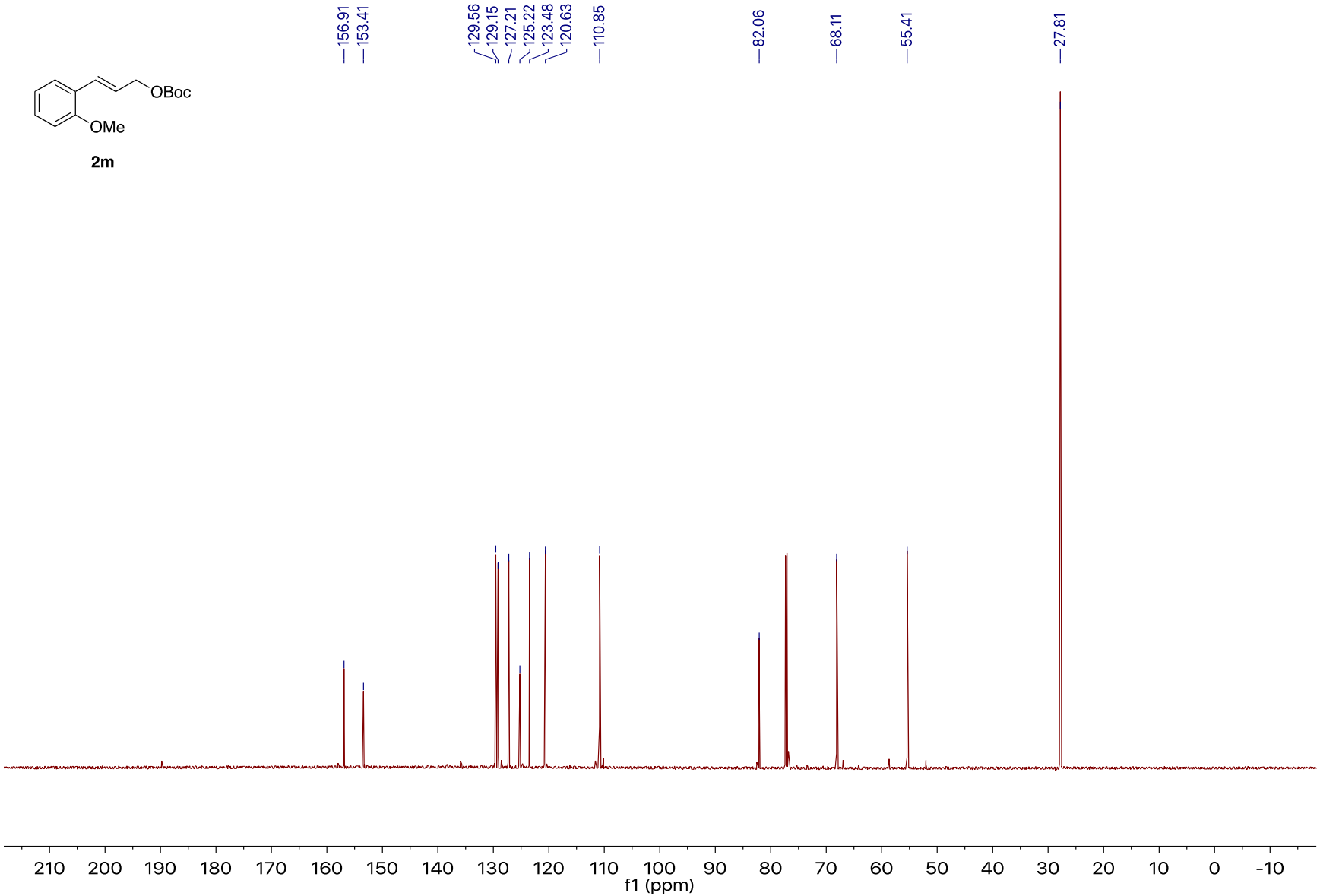
Compound 2i: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



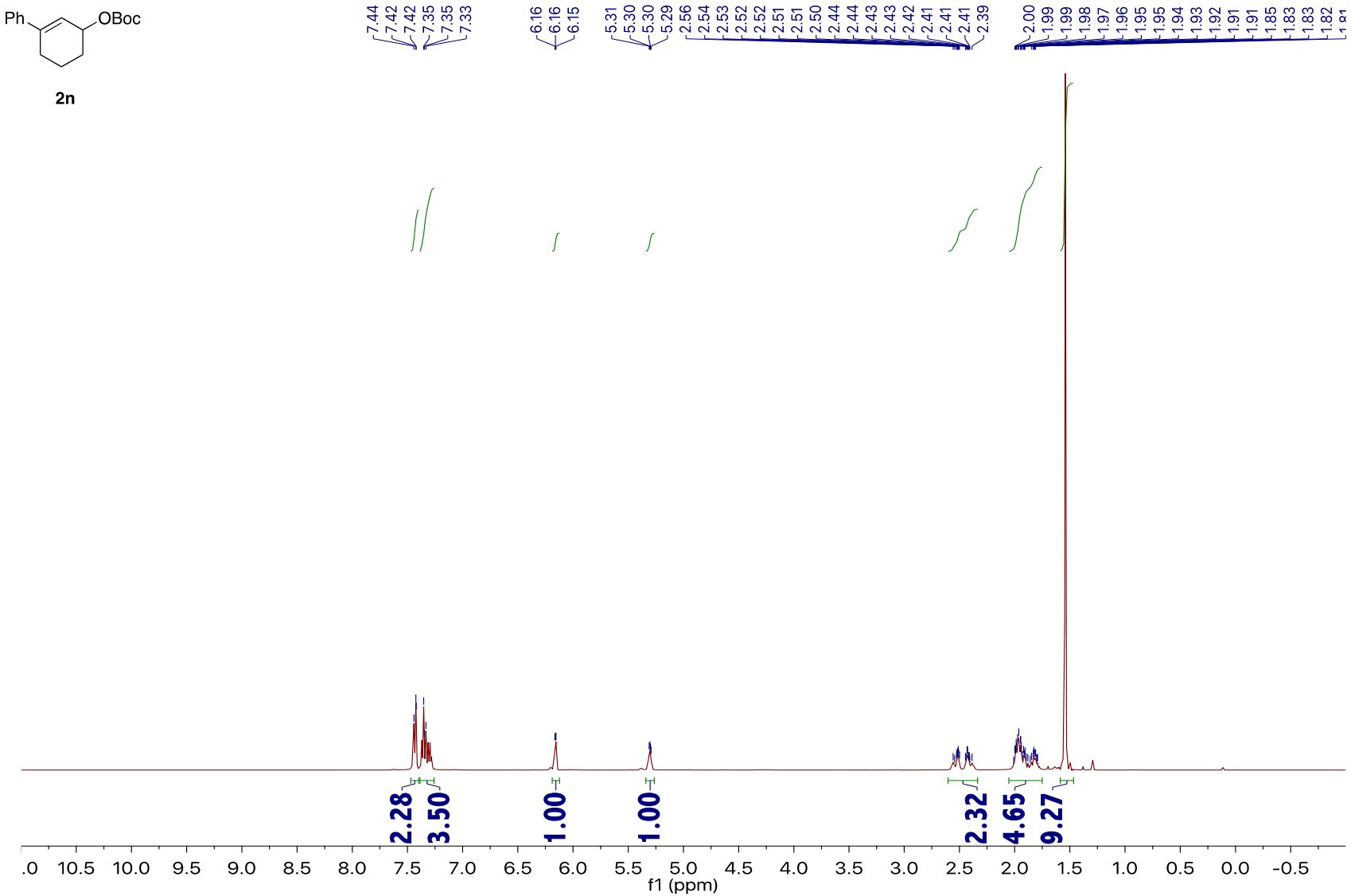
Compound 2i: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



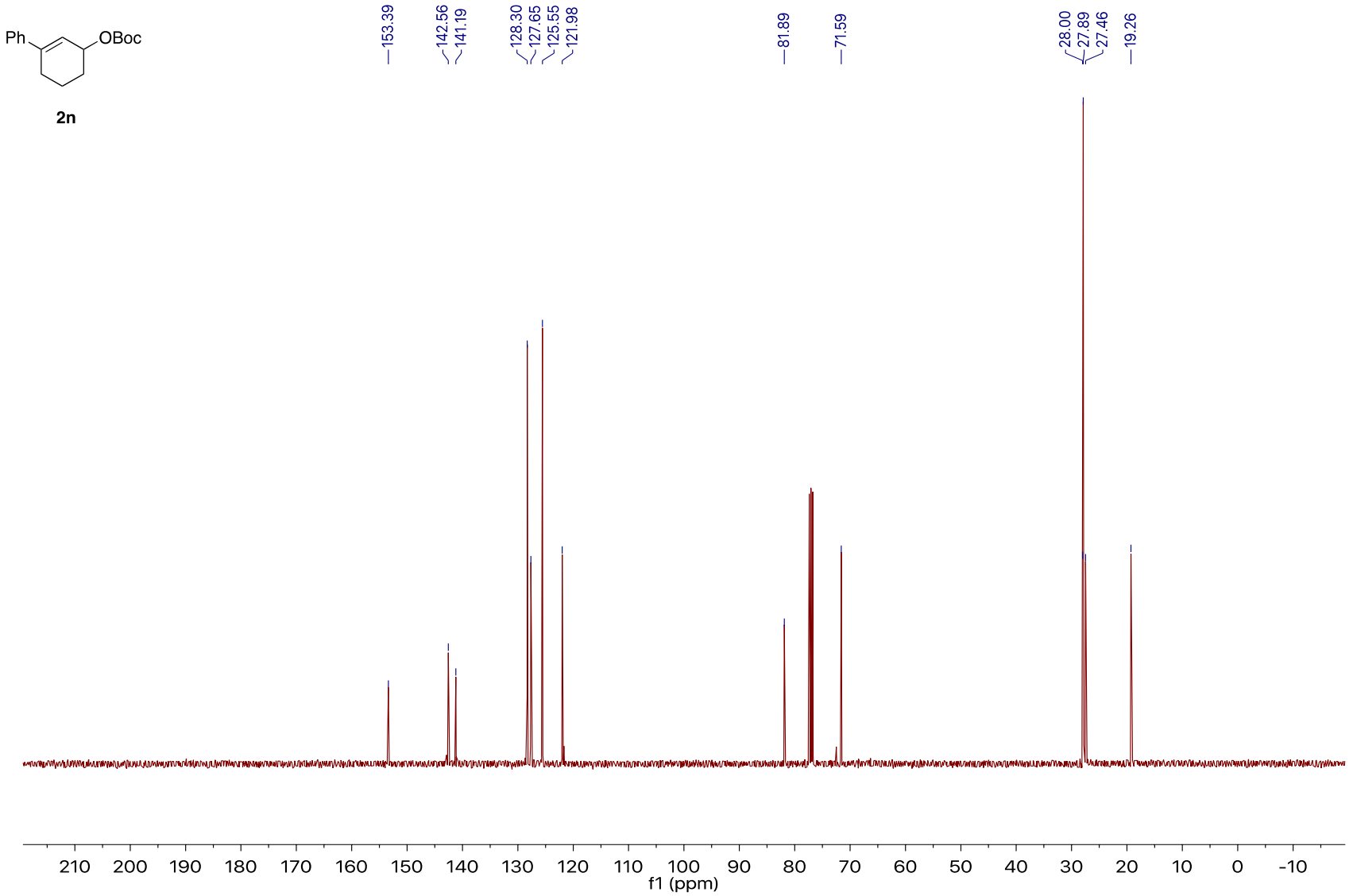
Compound 2m: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



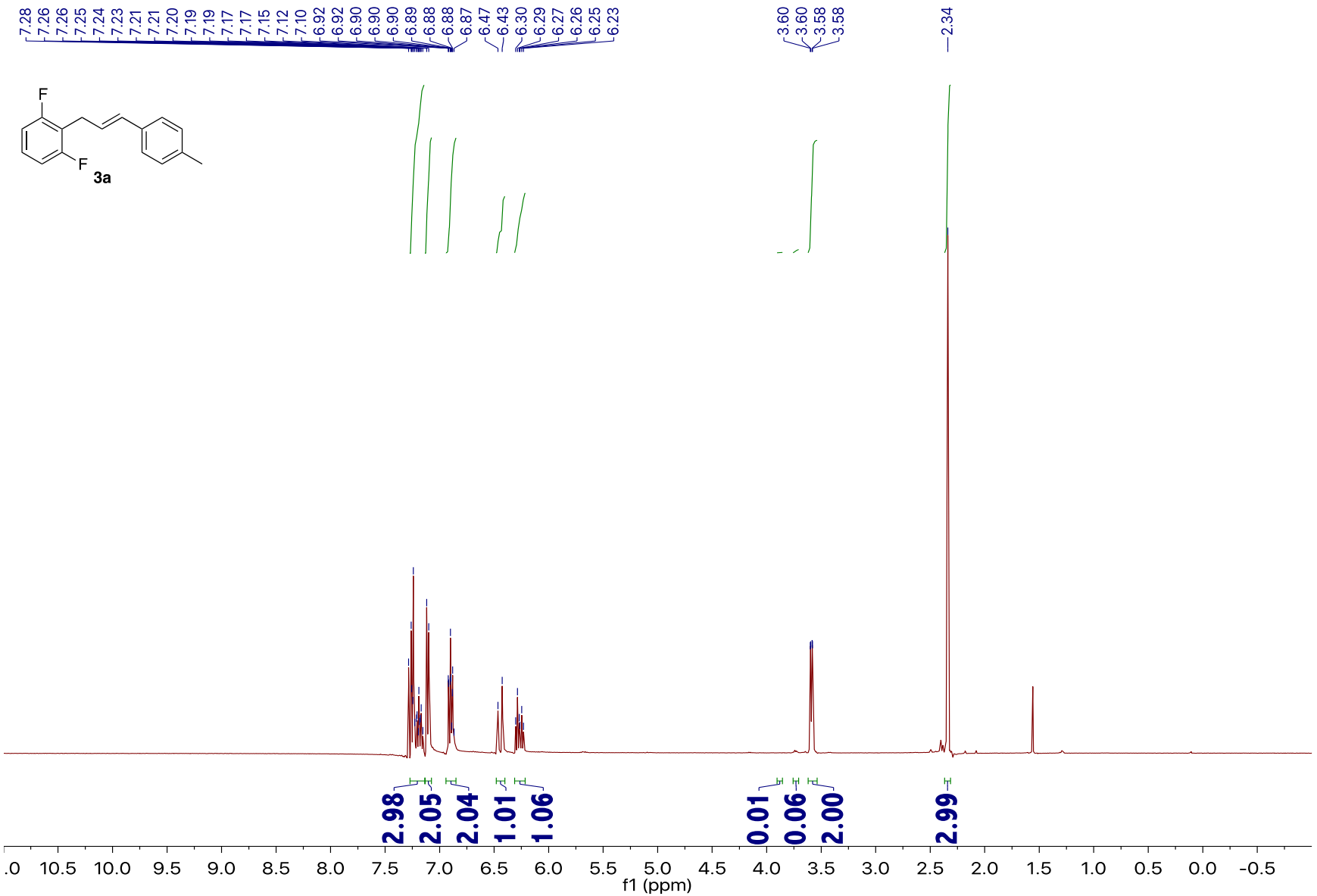
Compound 2m: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



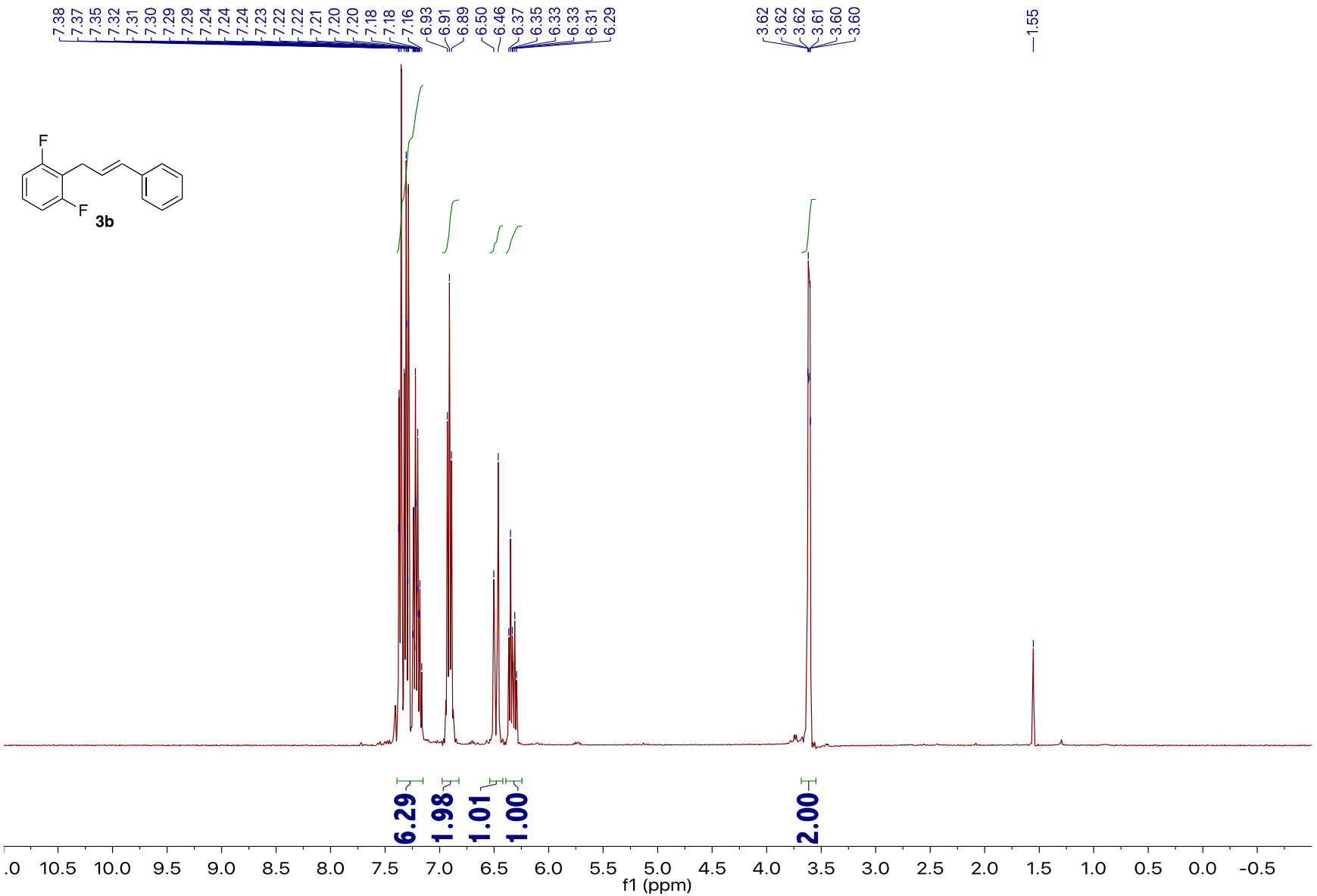
Compound 2n: 126 MHz ^{1}H NMR spectrum in $CDCl_3$



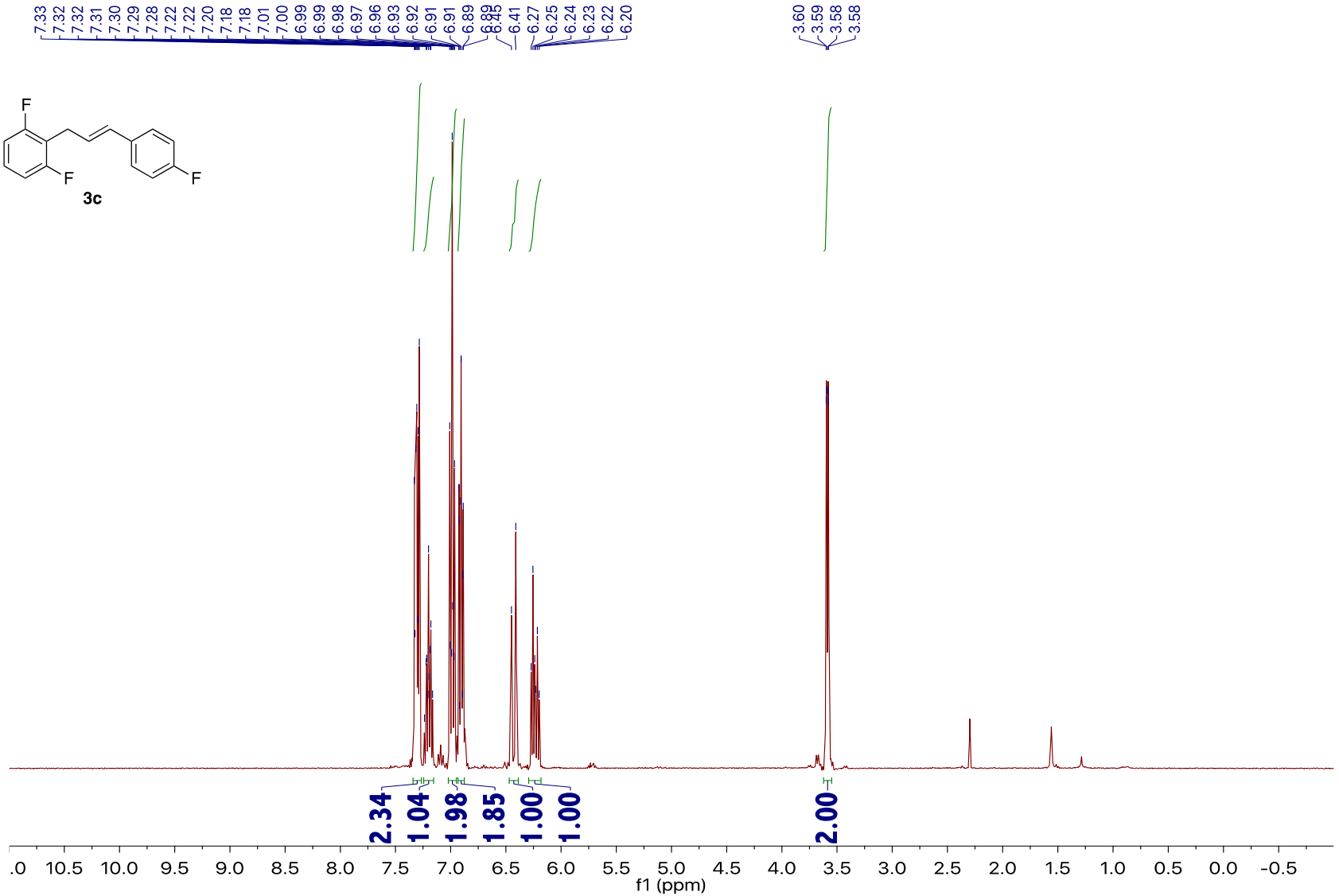
Compound 2n: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



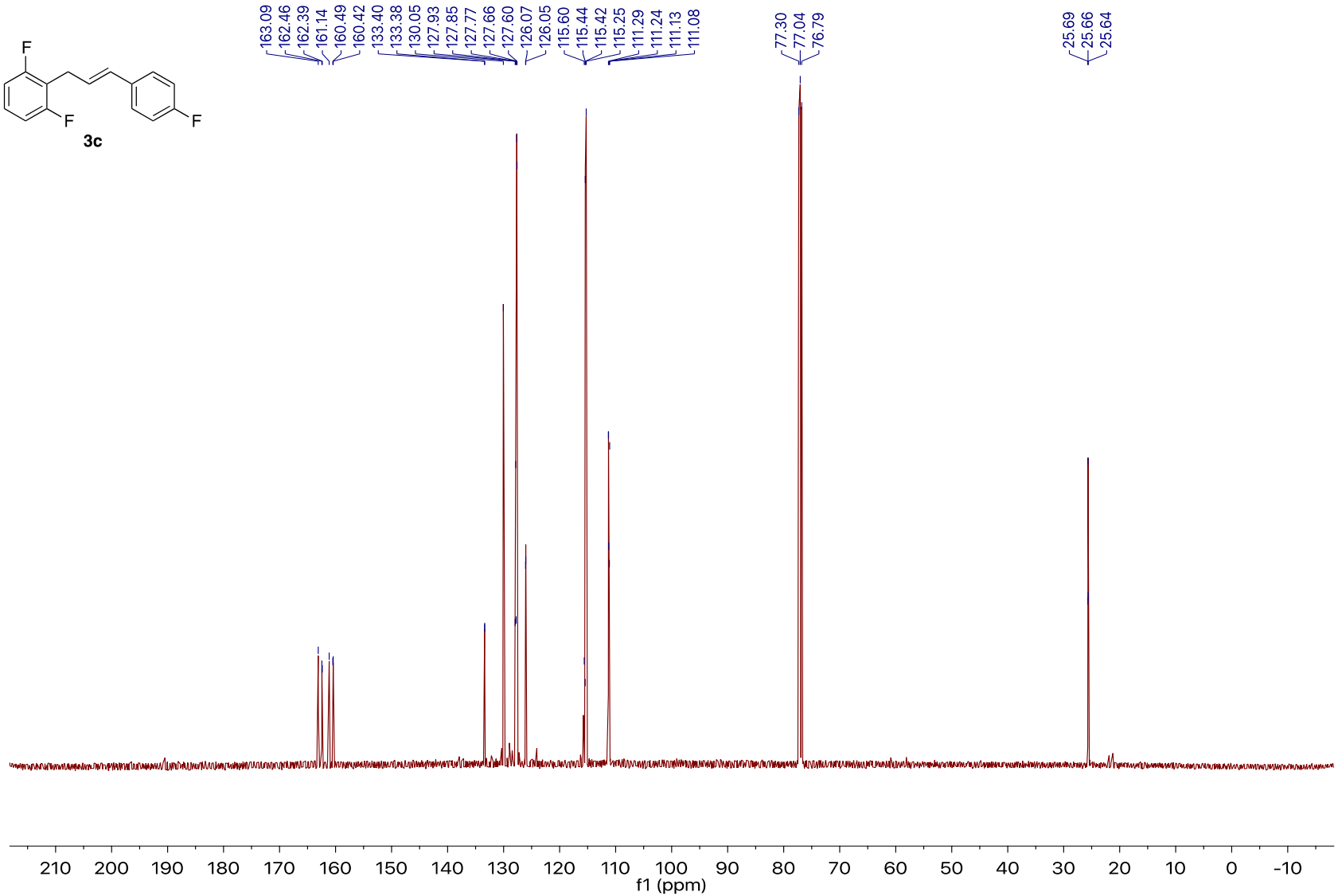
Compound 3a: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



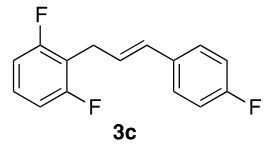
Compound 3b: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



Compound 3c: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

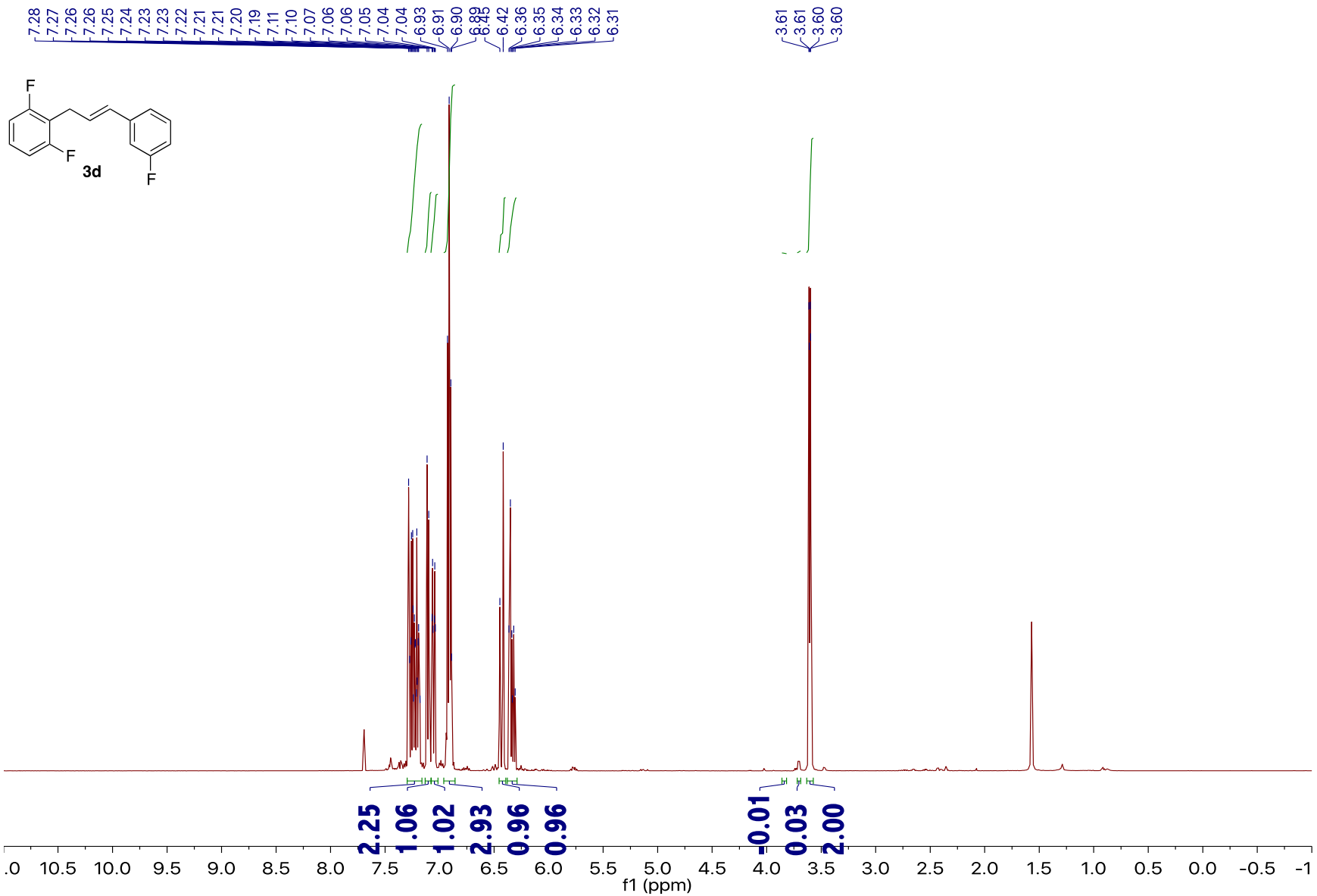


Compound 3c: 126 MHz ^{13}C NMR spectrum in $CDCl_3$

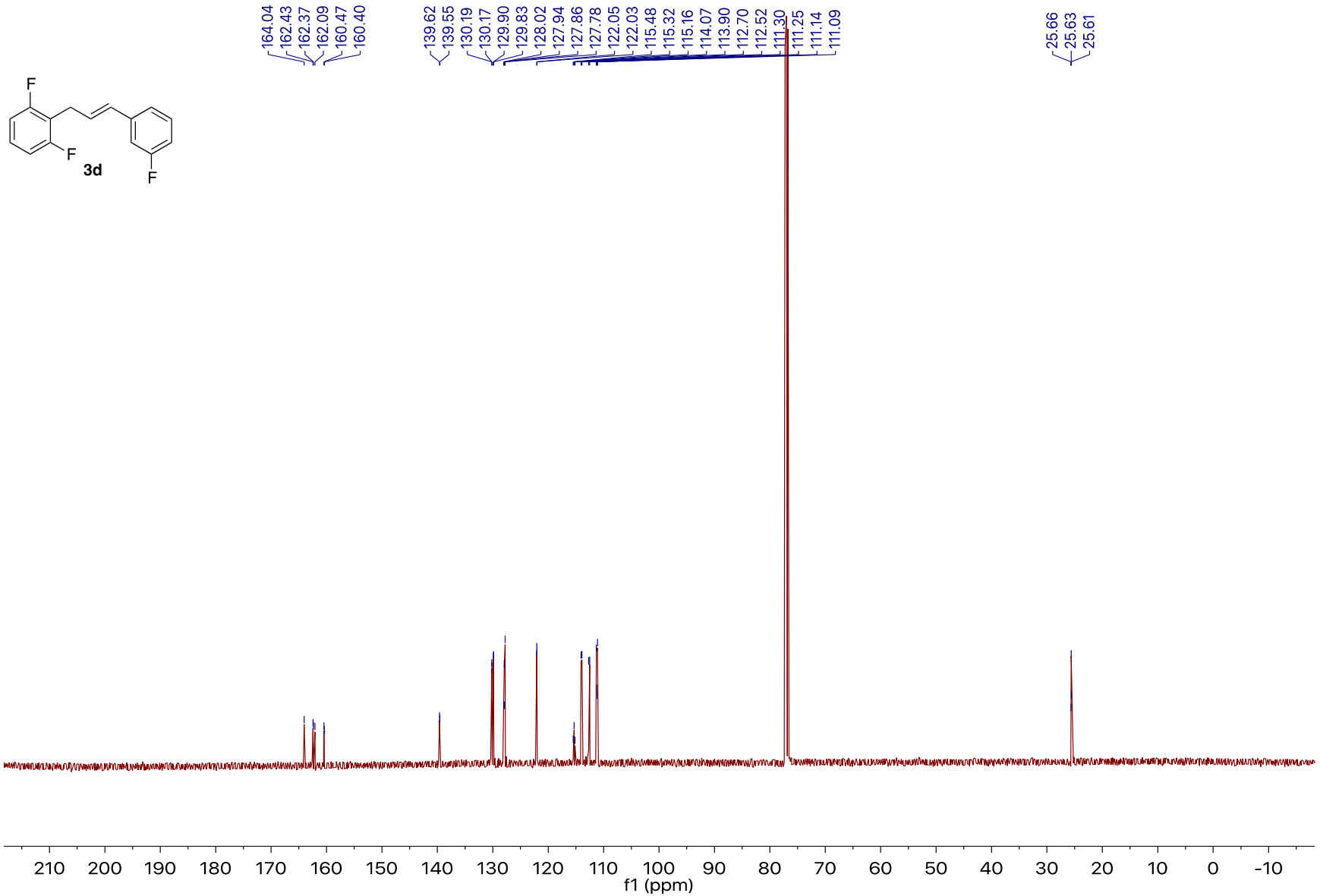


3c

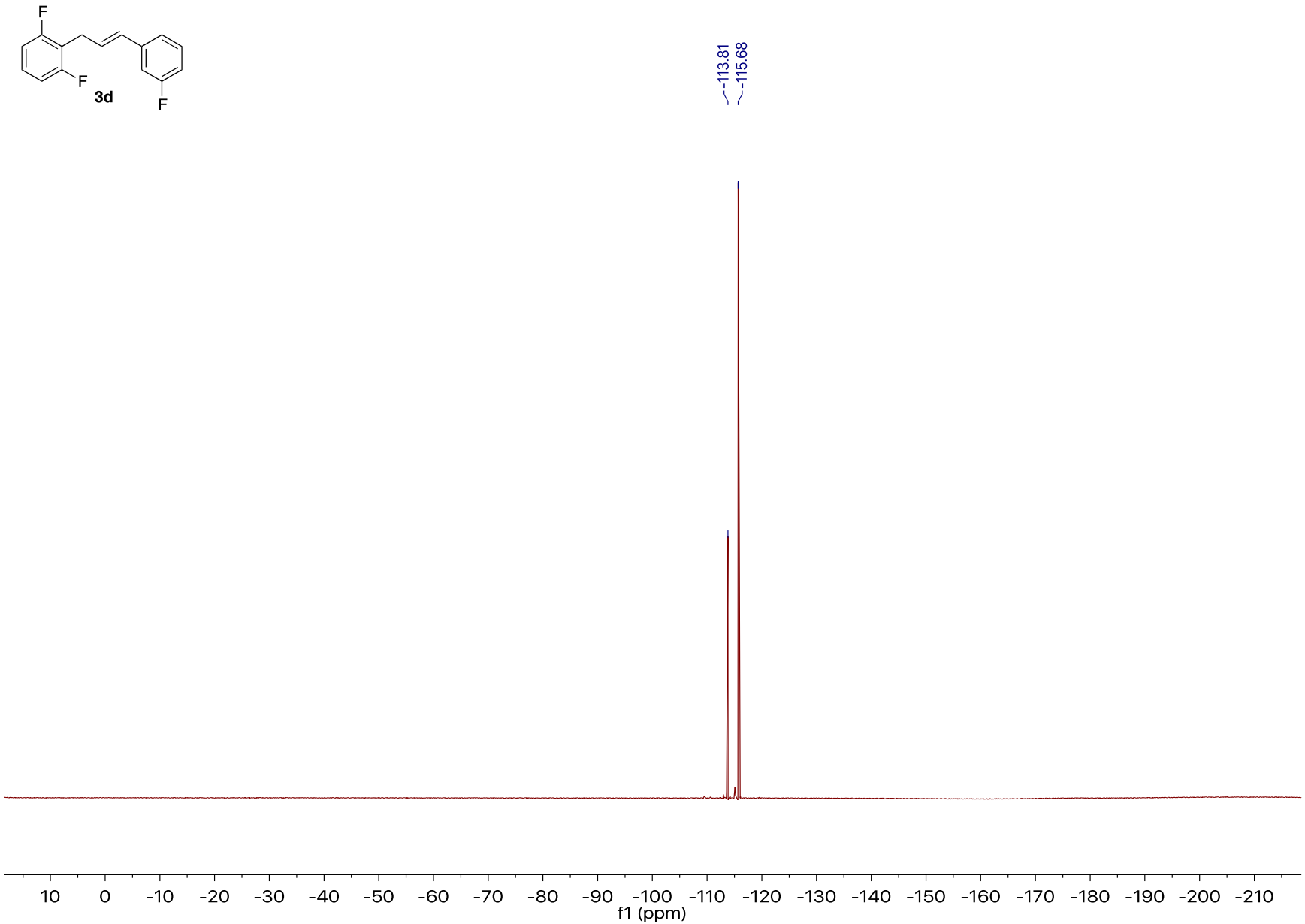
Compound 3c: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



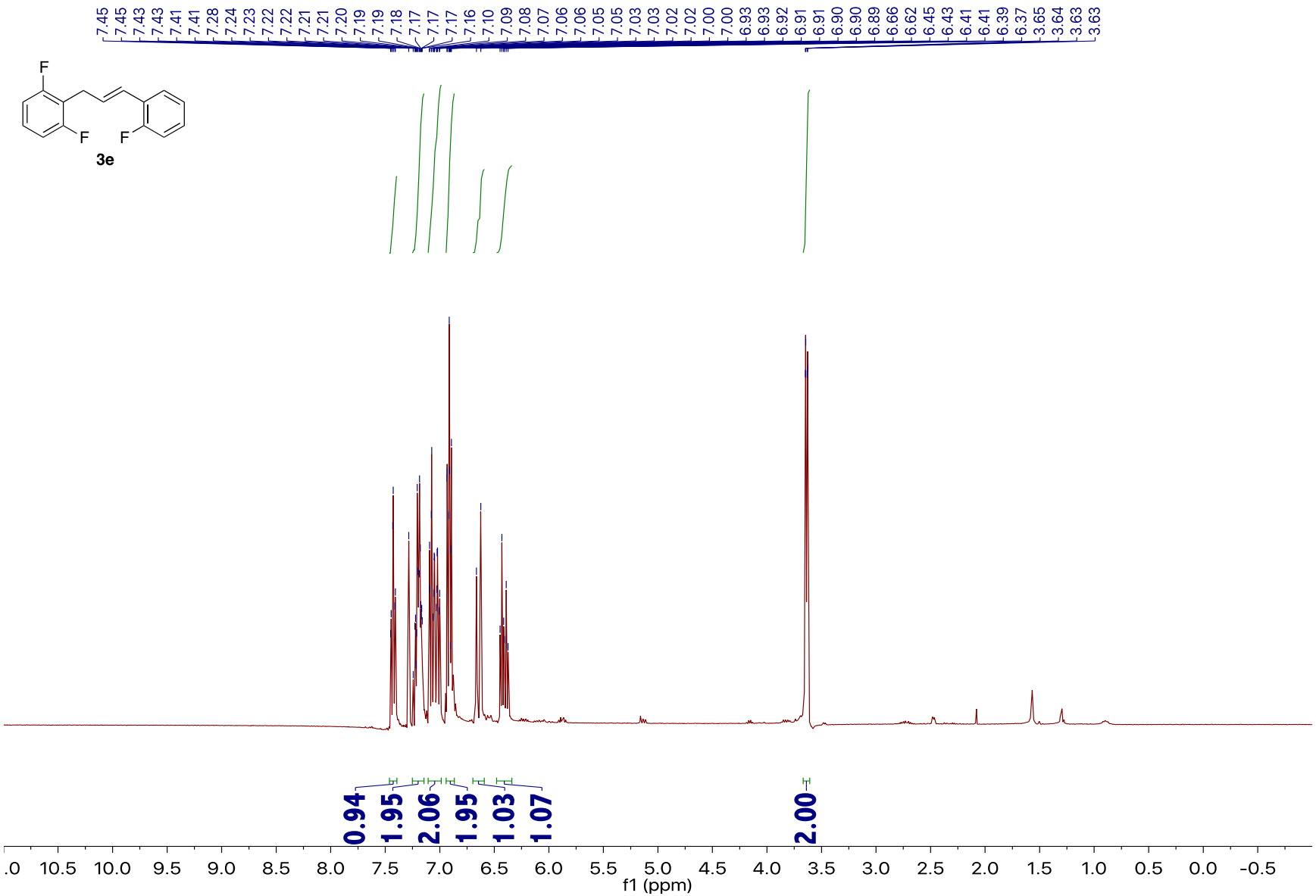
Compound 3d: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



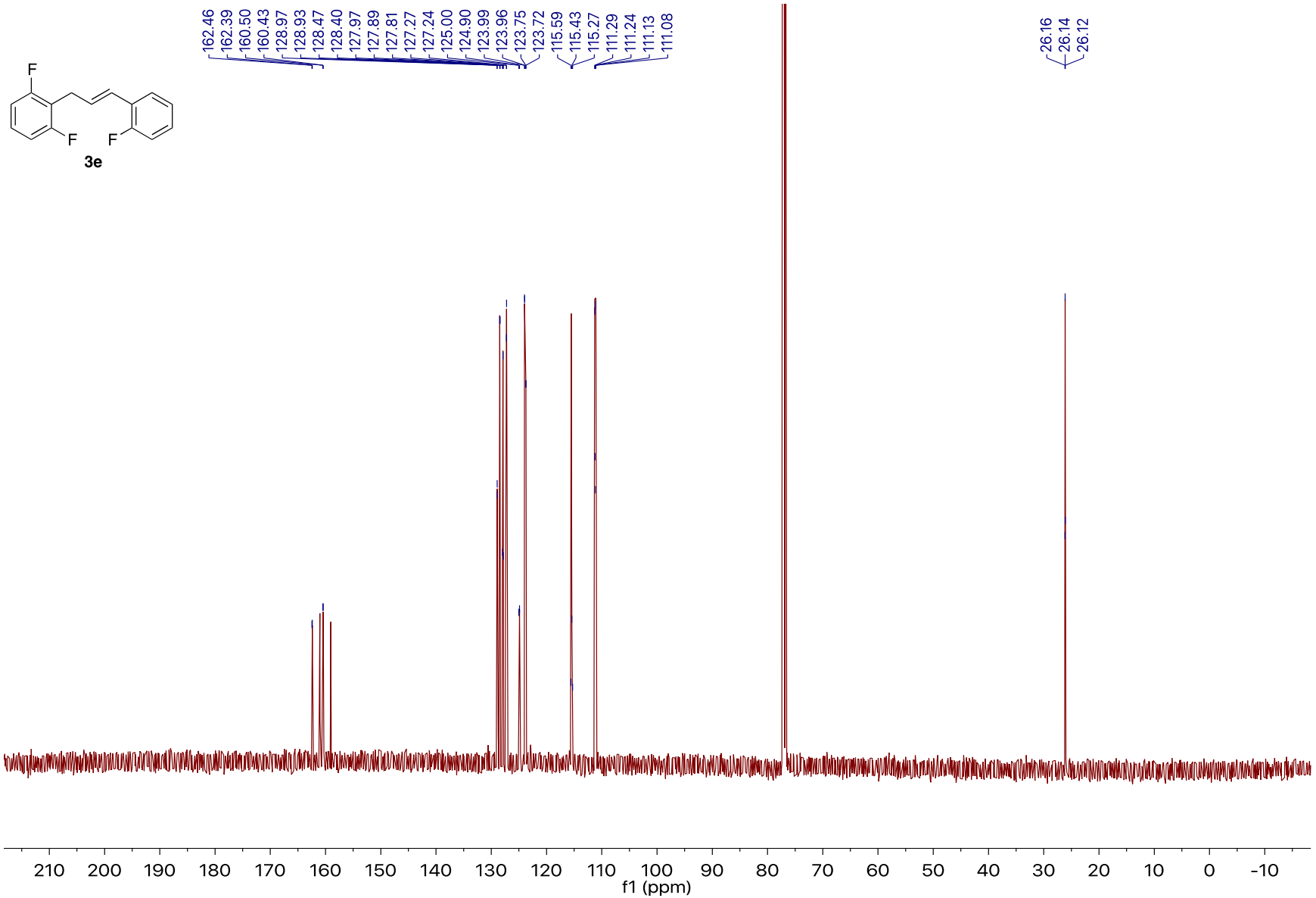
Compound 3d: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



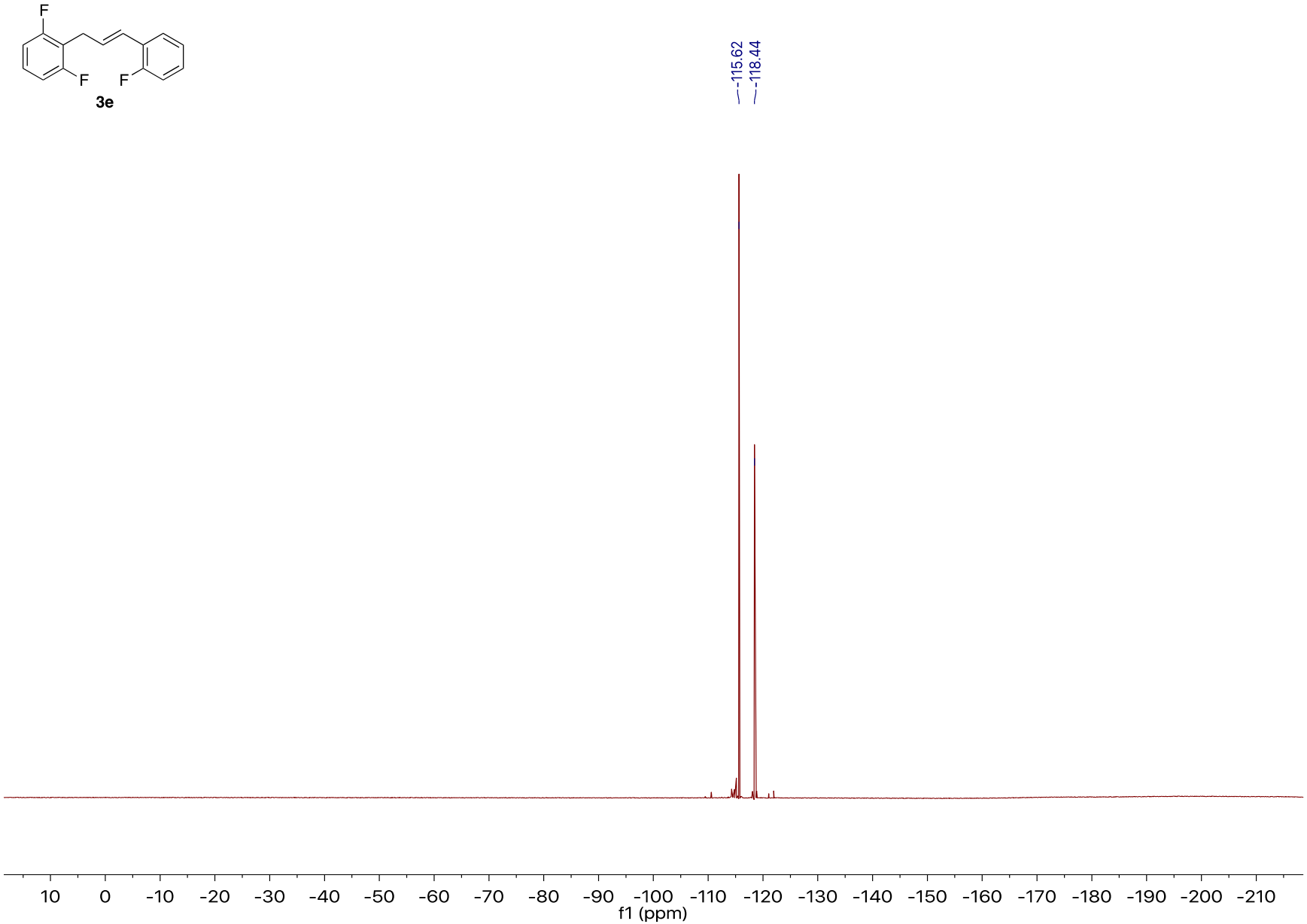
Compound 3d: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



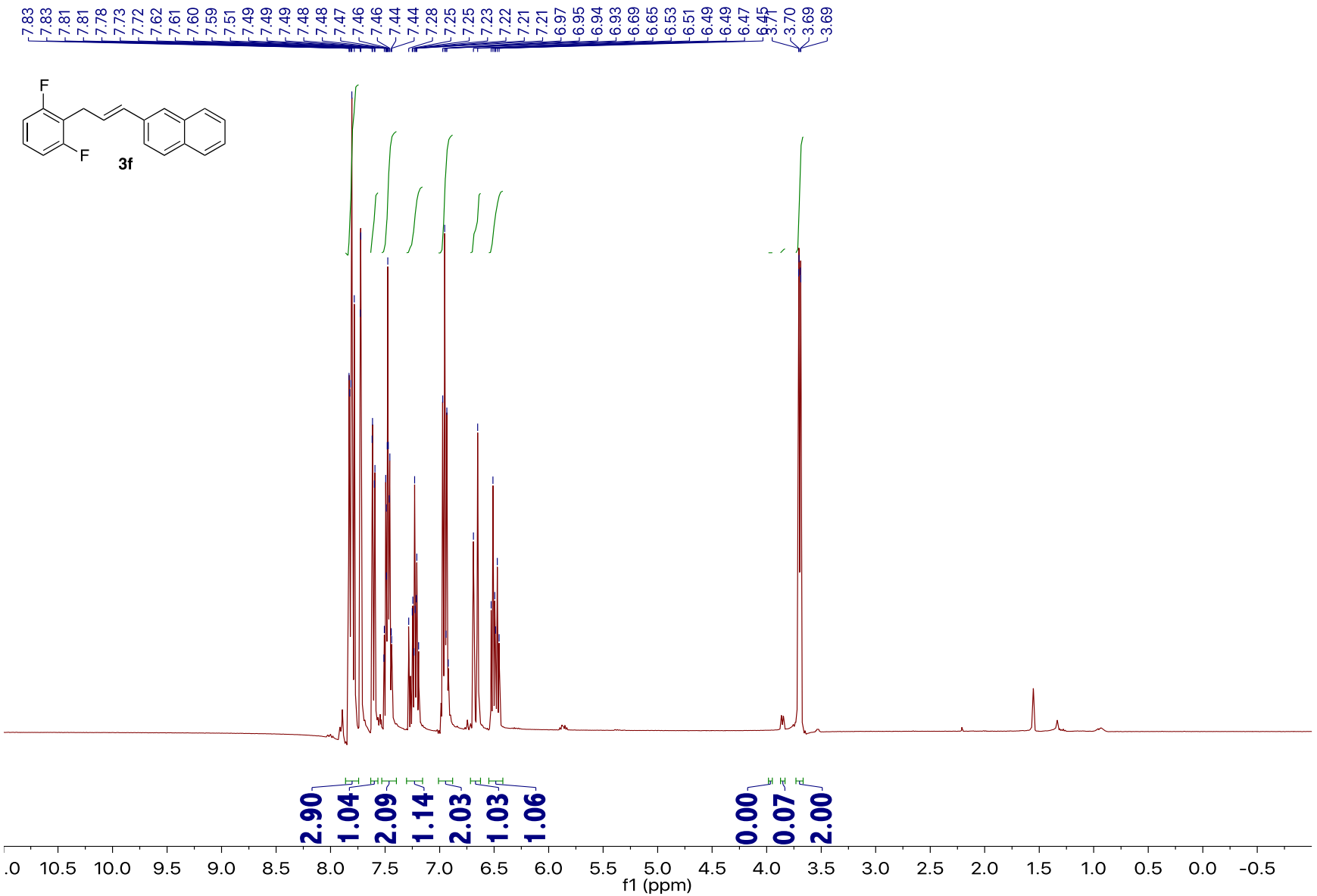
Compound 3e: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



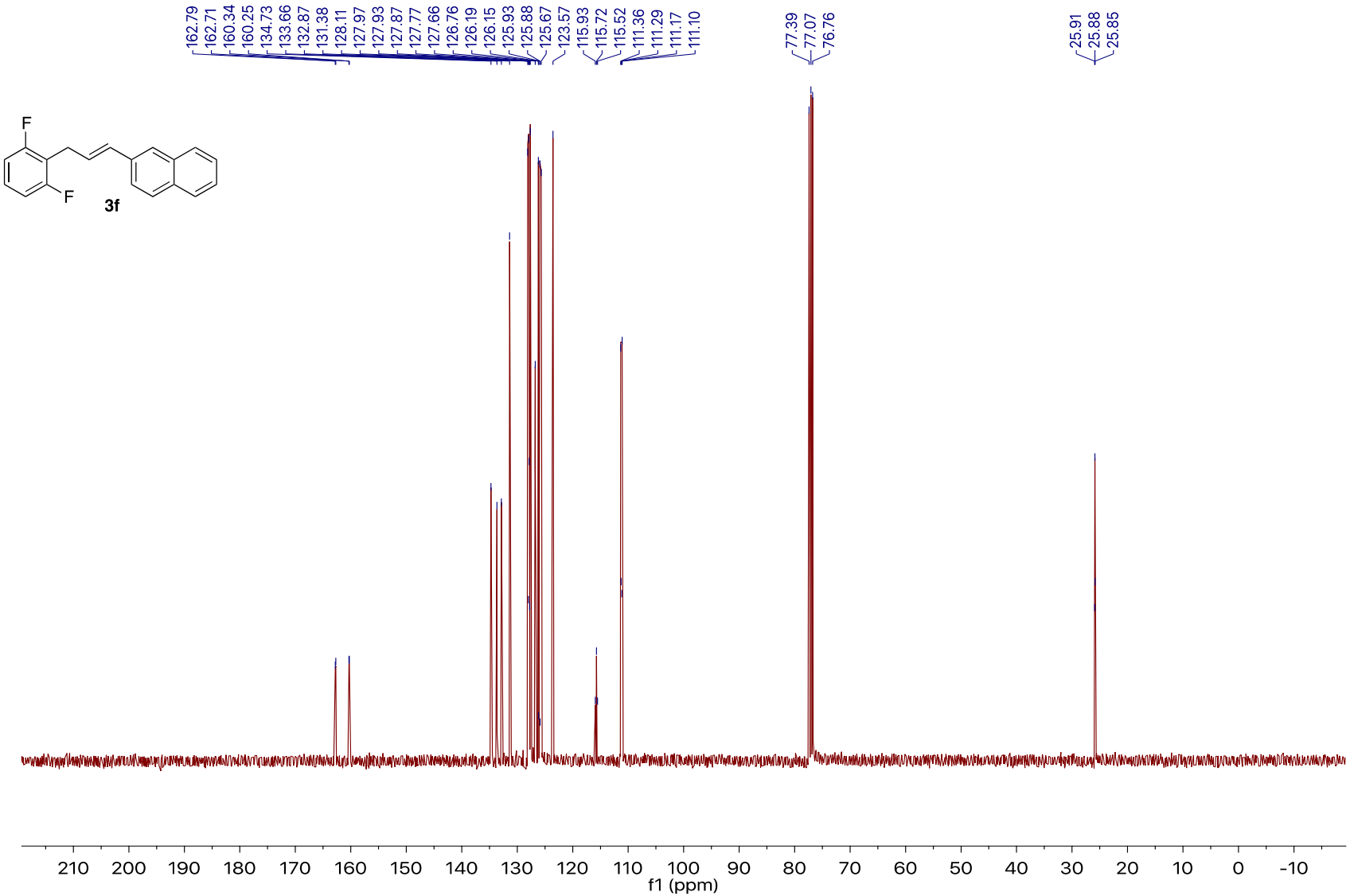
Compound 3e: 126 MHz ^{1}H NMR spectrum in $CDCl_3$



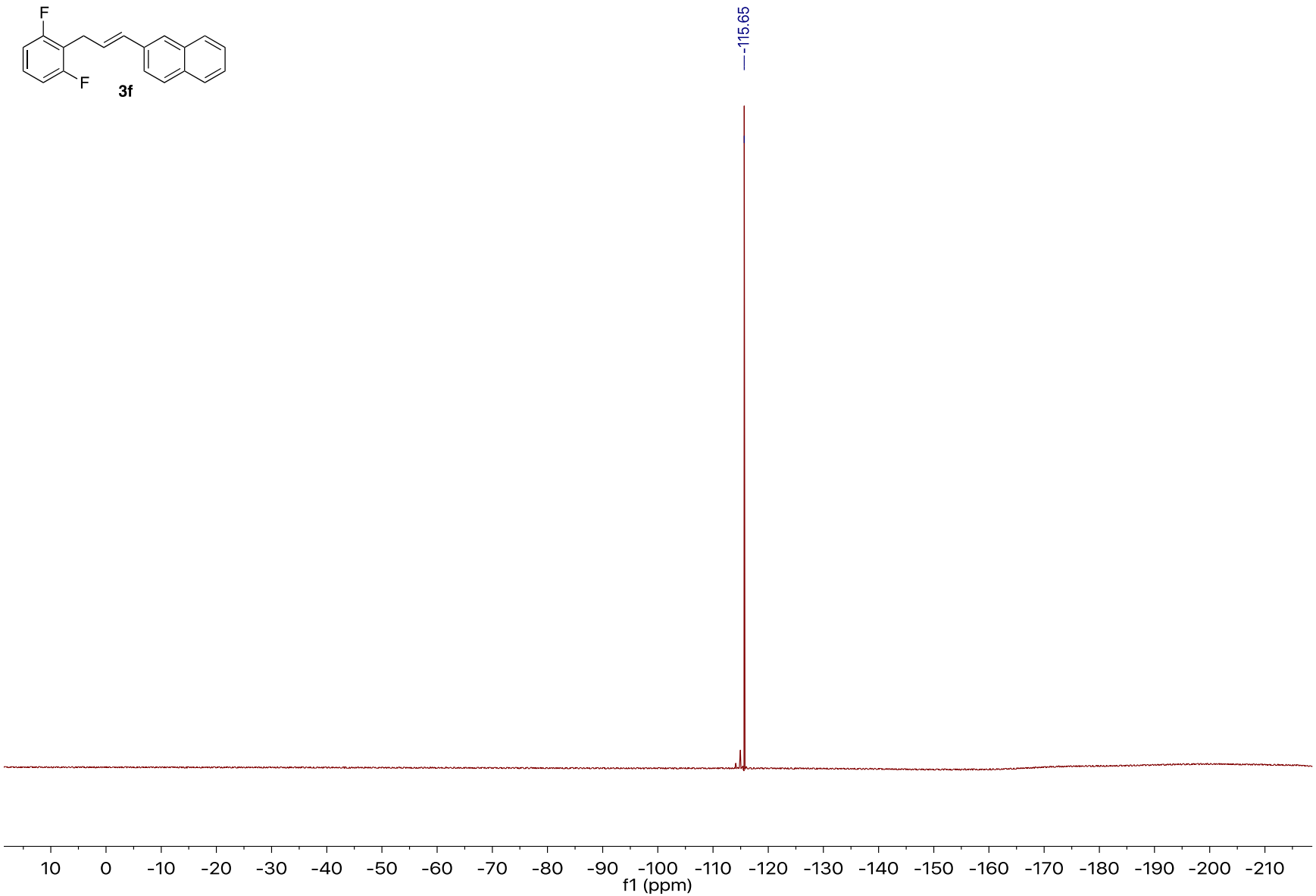
Compound 3e: 376 MHz ^{19}F NMR spectrum in CDCl



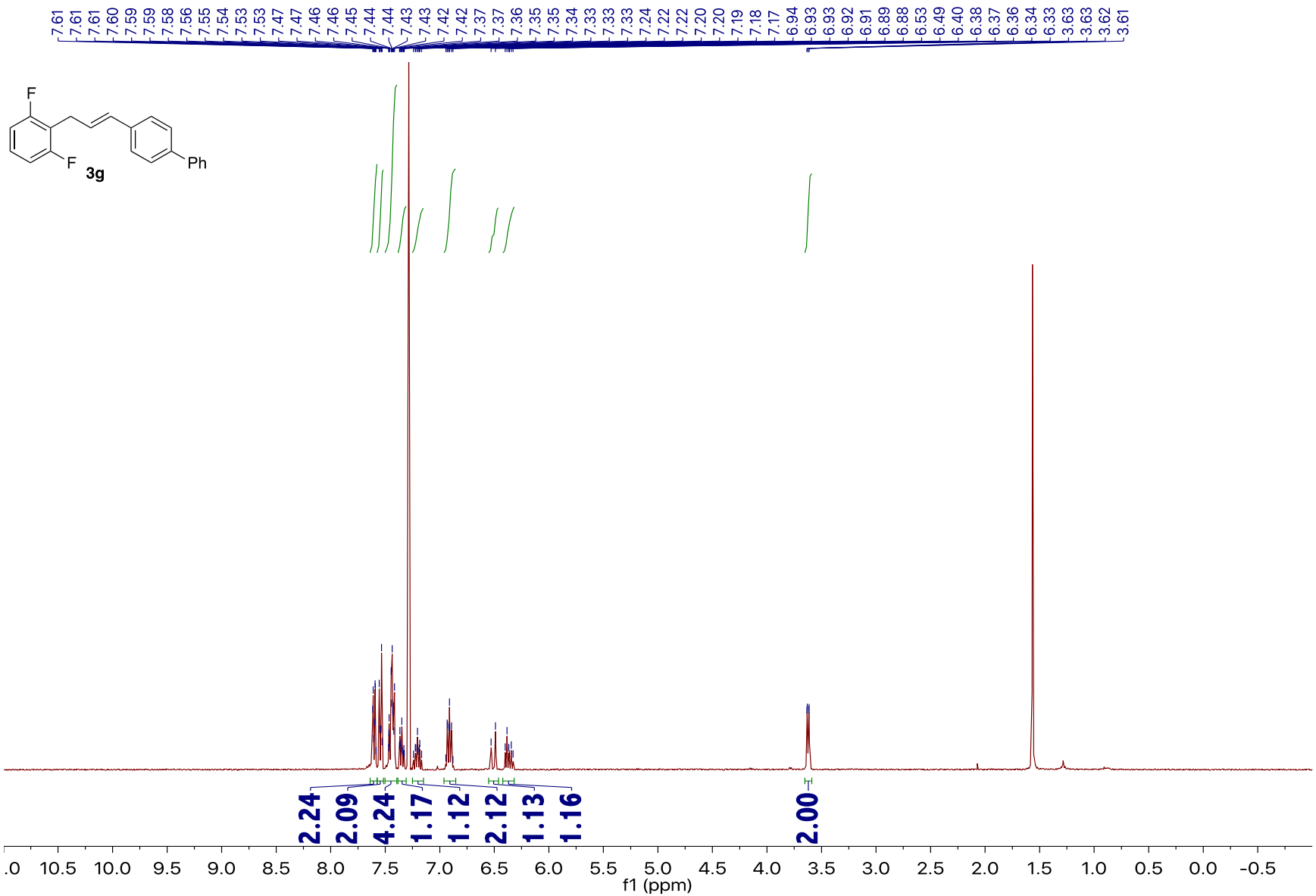
Compound 3f: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



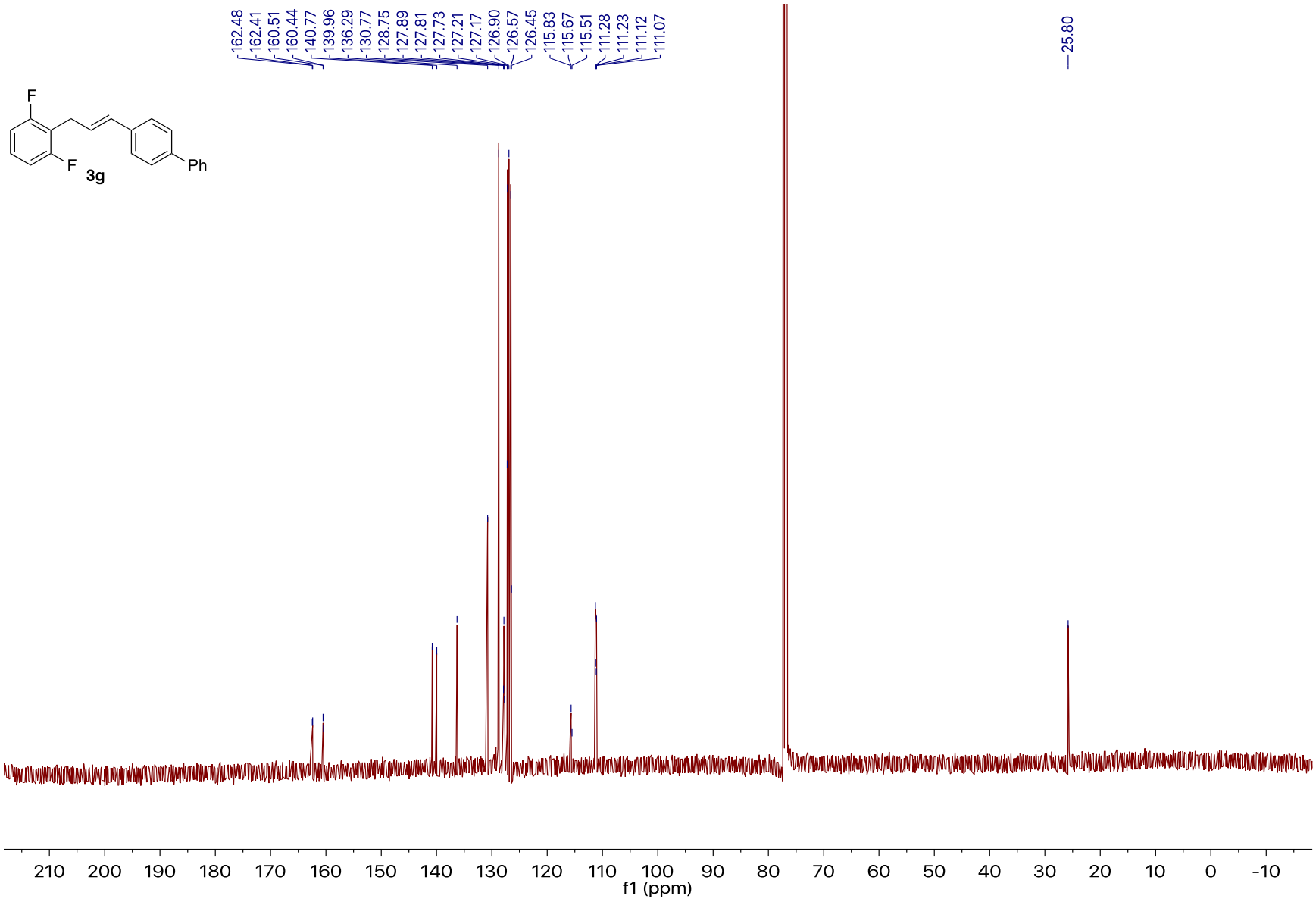
Compound 3f: 101 MHz ^{13}C NMR spectrum in $CDCl_3$



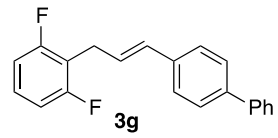
Compound 3f: 376 MHz ^{19}F NMR spectrum in $CDCl_3$

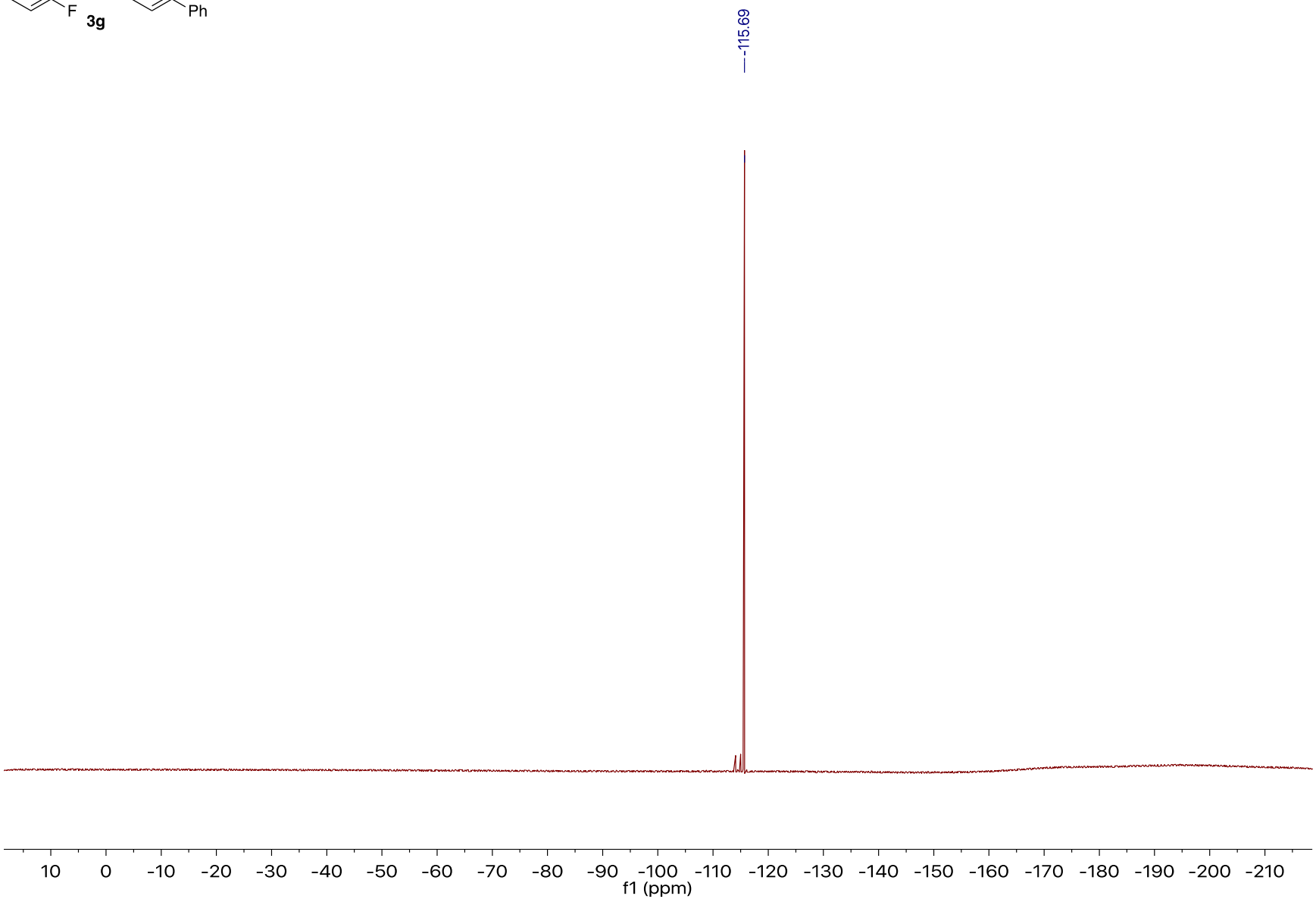


Compound 3g: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

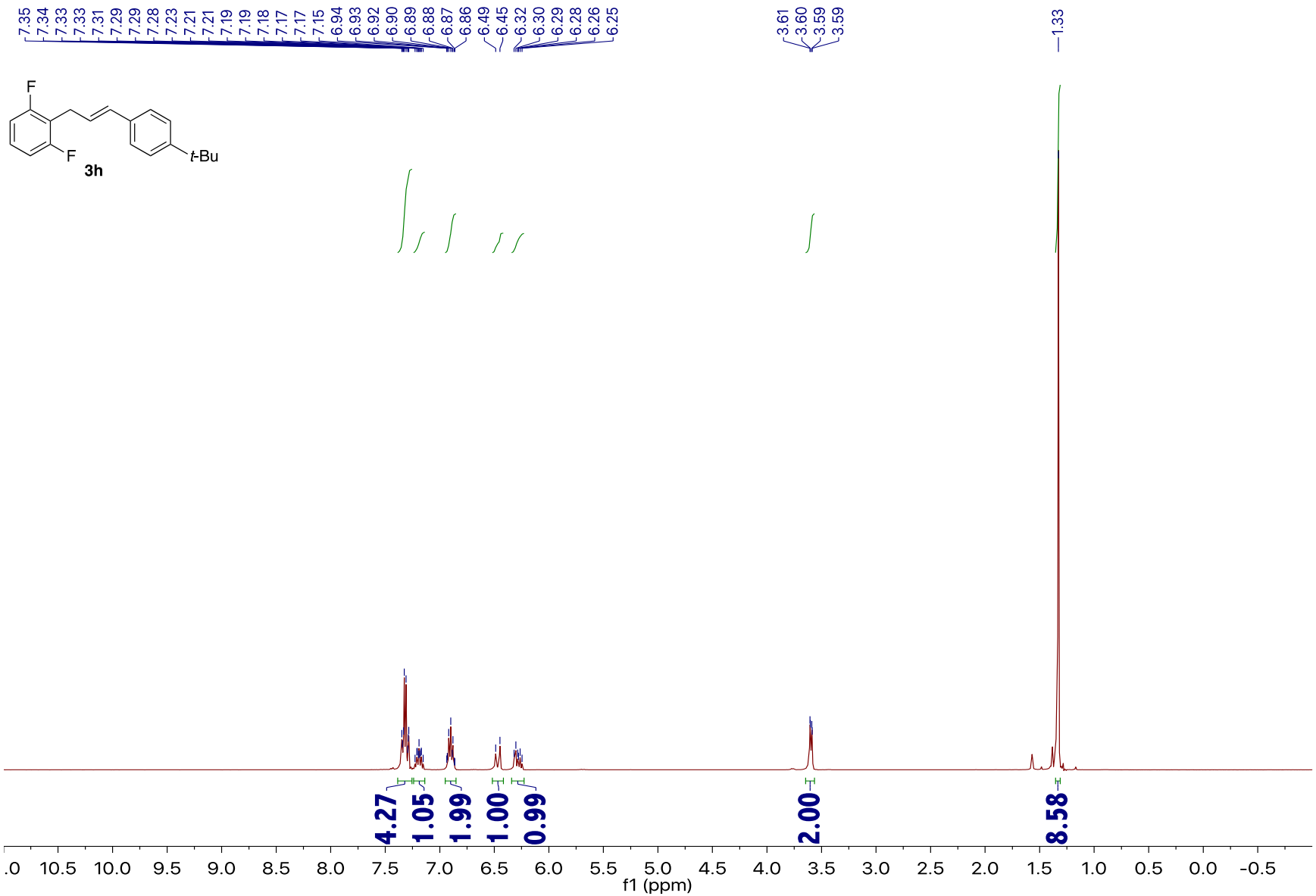


Compound 3g: 126 MHz ^{13}C NMR spectrum in $CDCl_3$

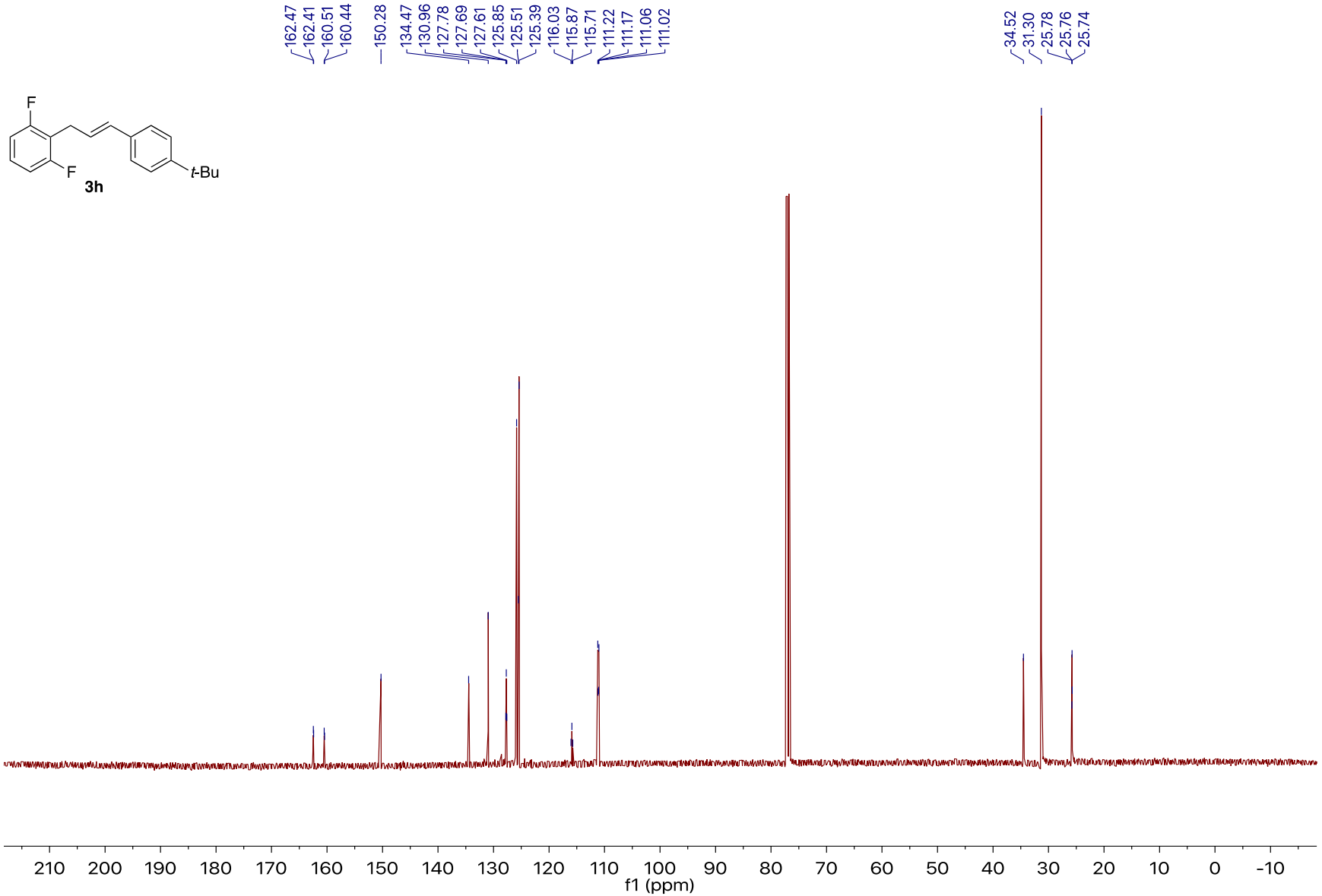




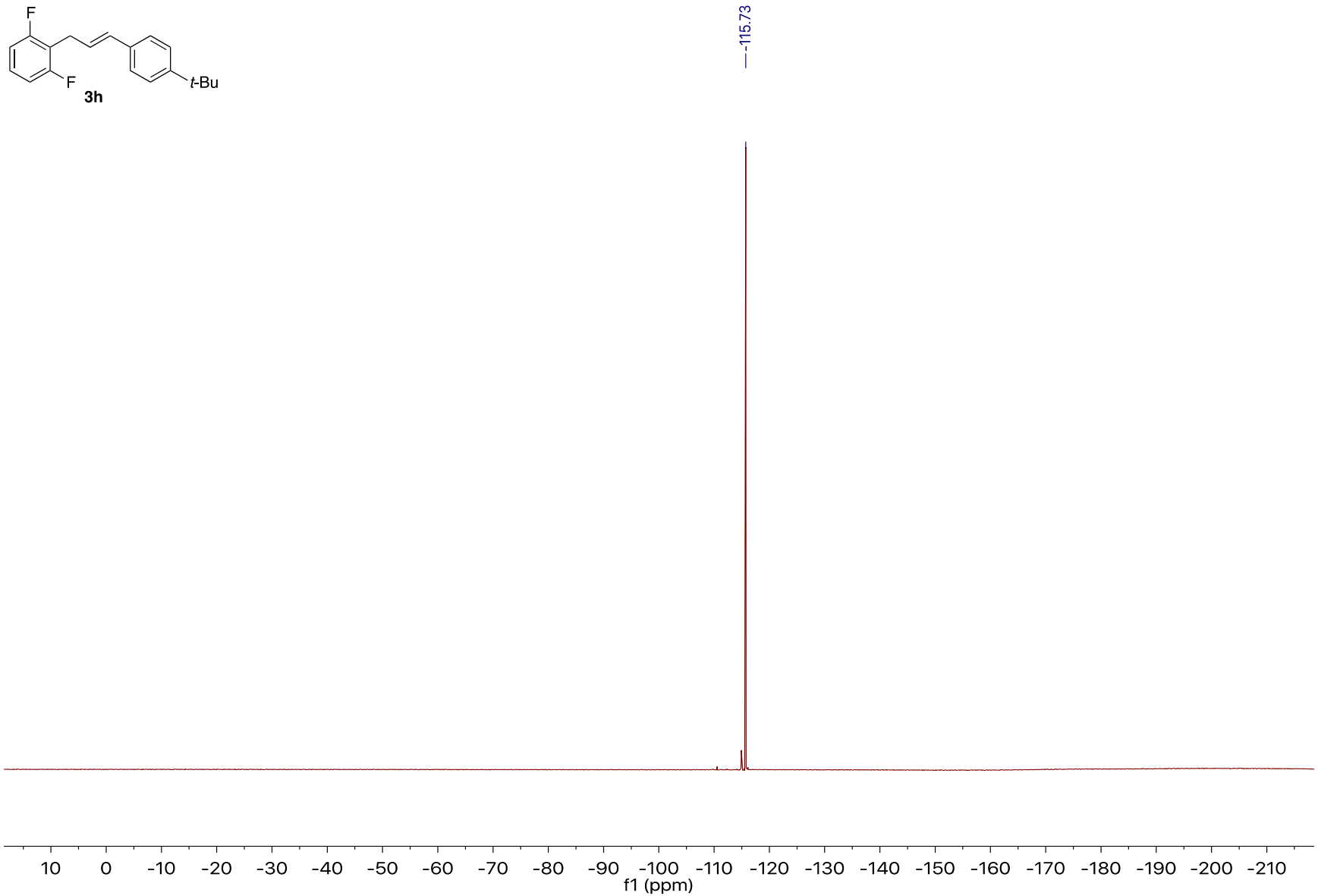
Compound 3g: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



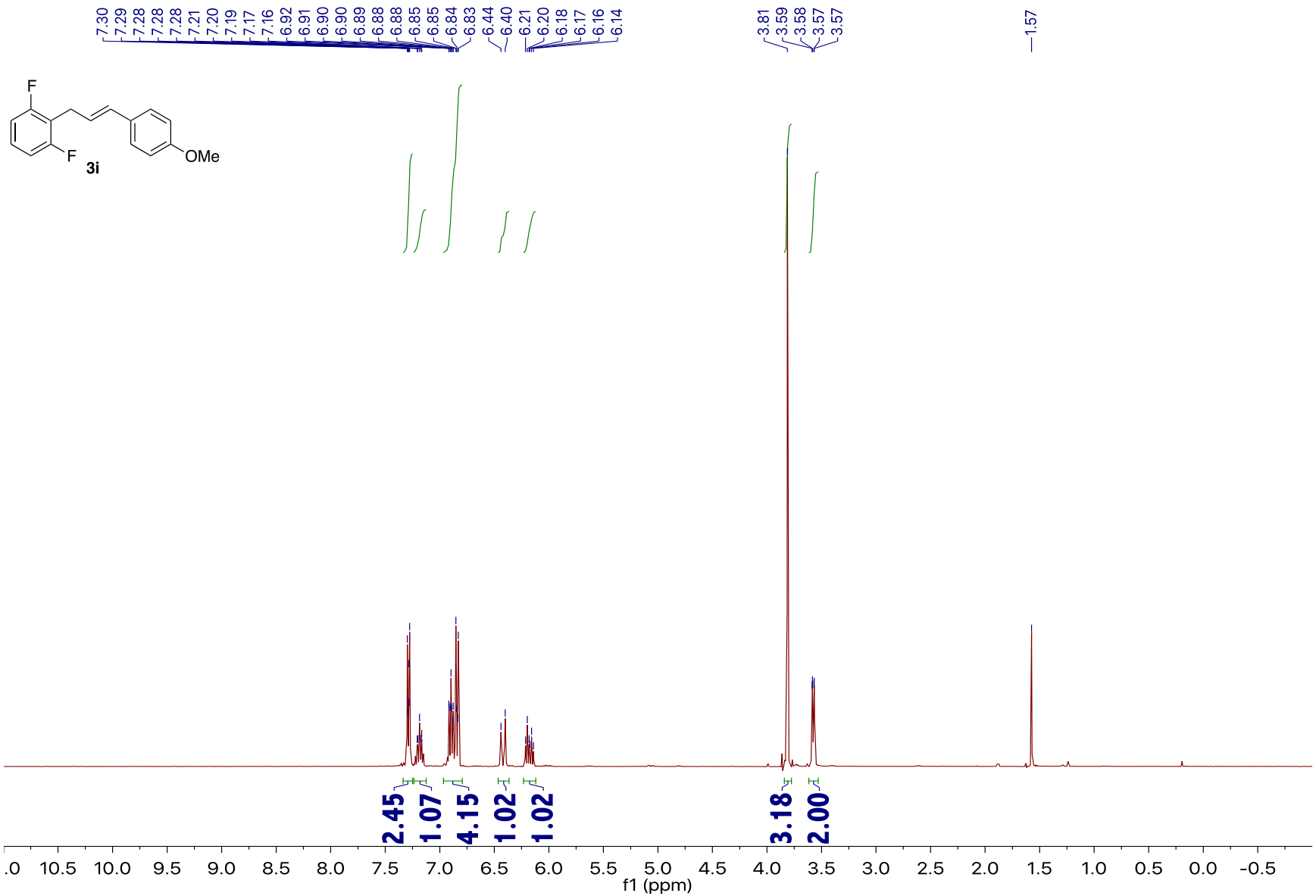
Compound 3h: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



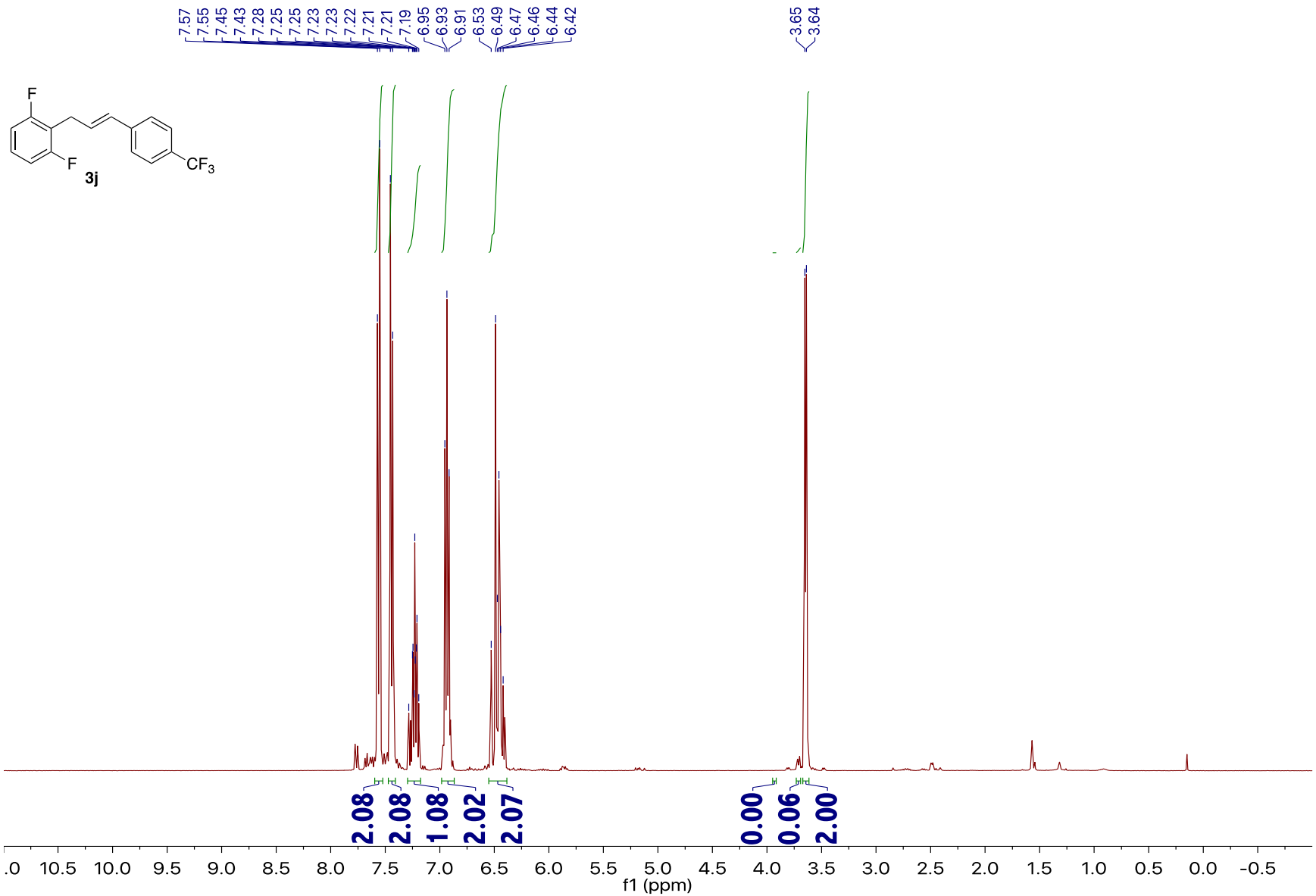
Compound 3h: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



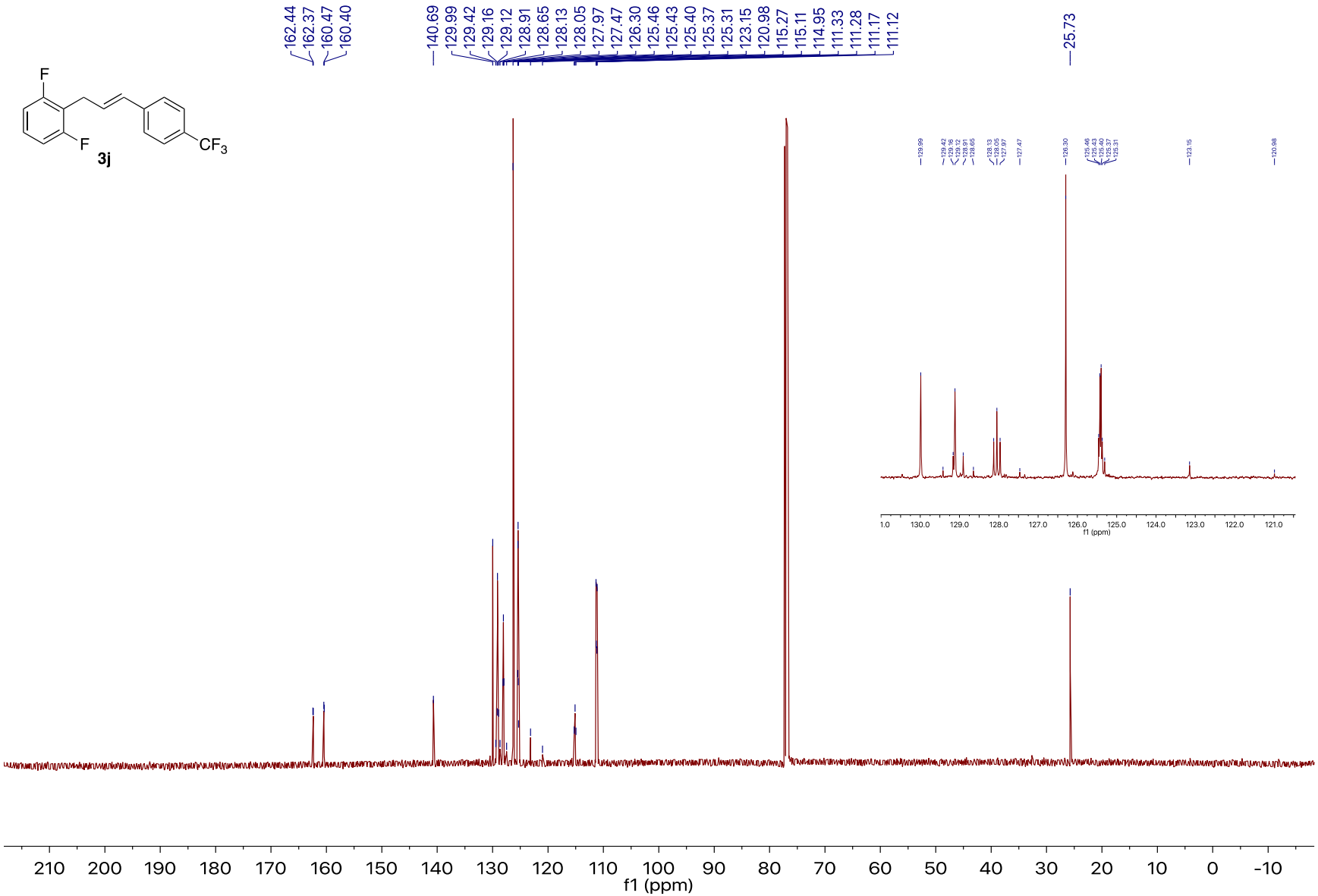
Compound 3g: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



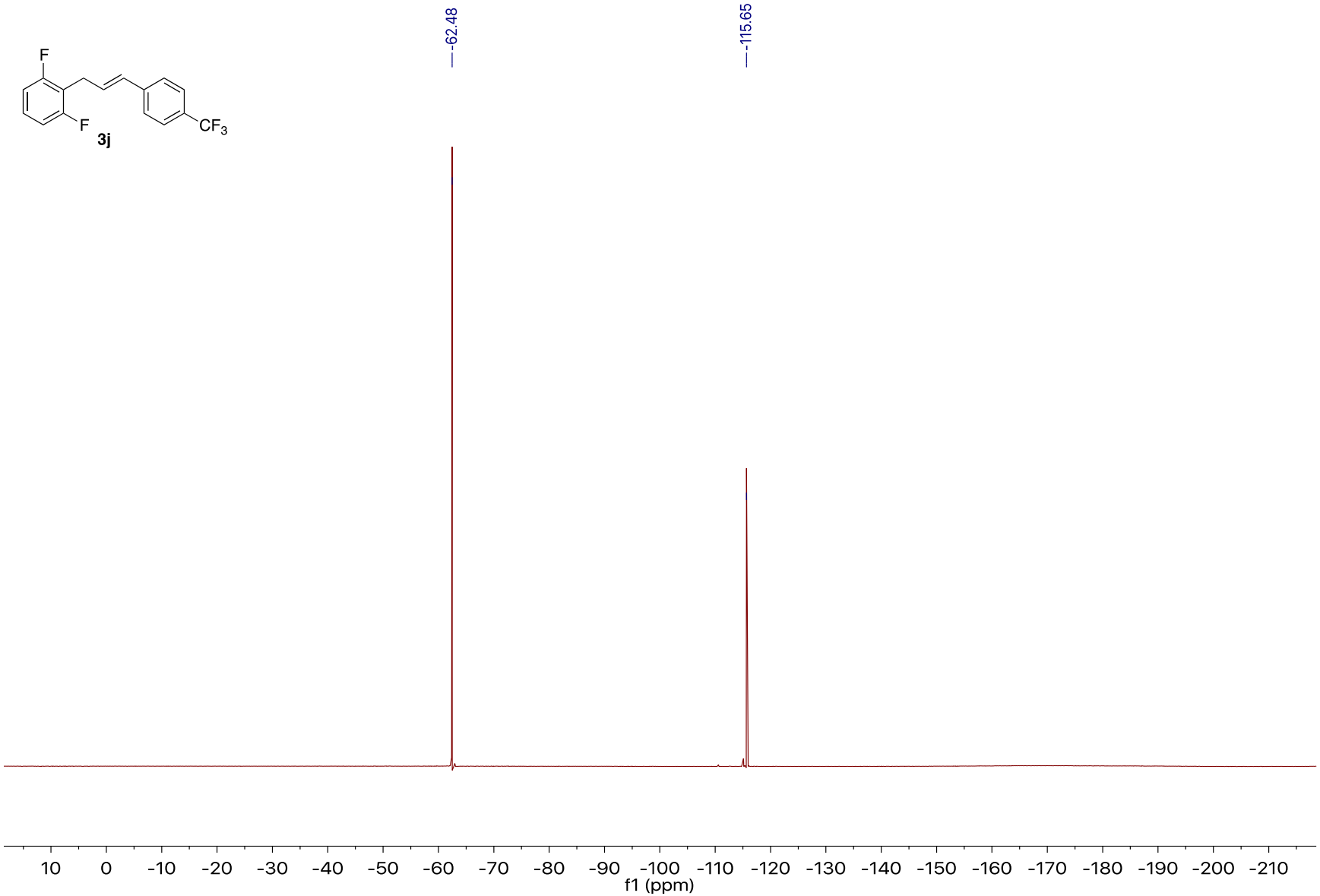
Compound 3i: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



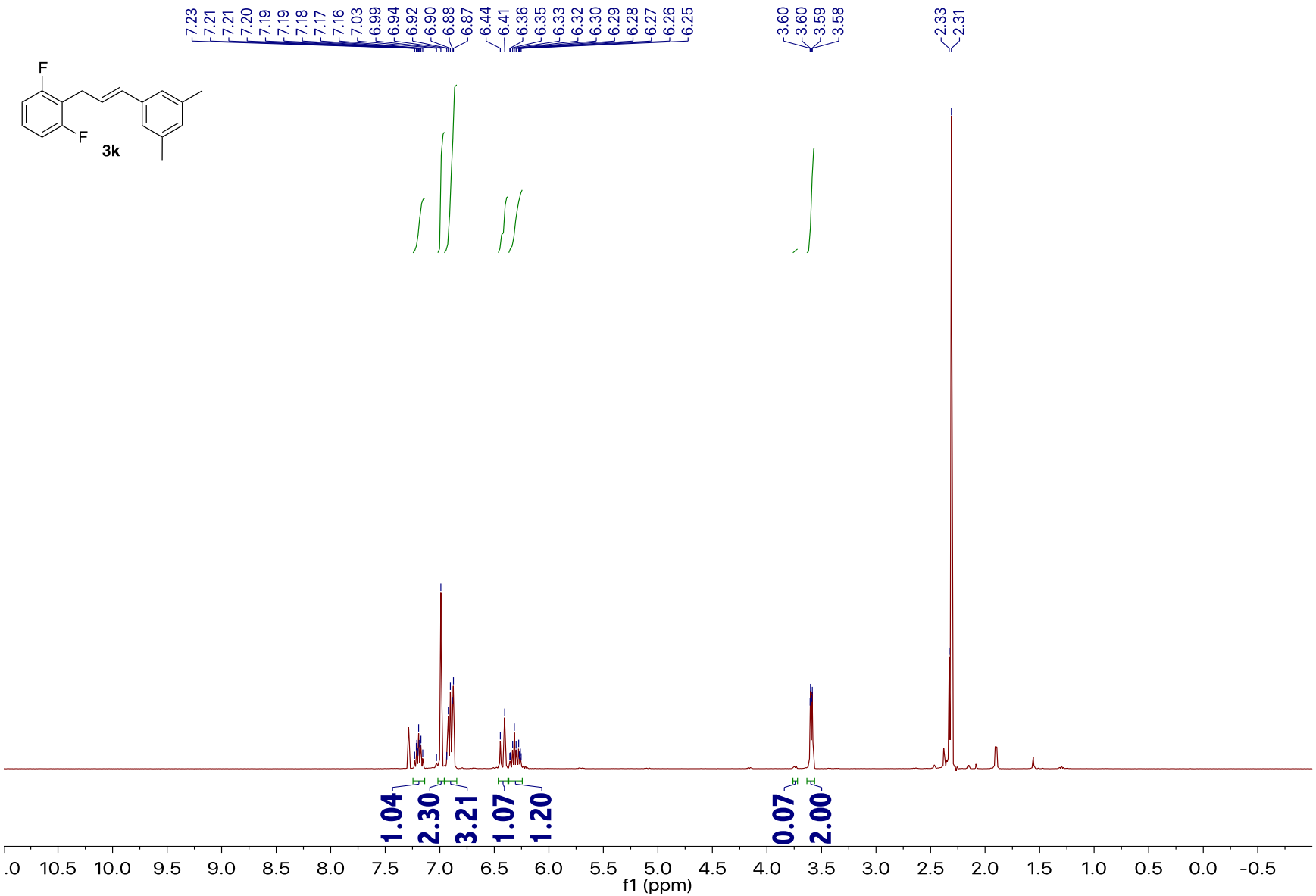
Compound 3j: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



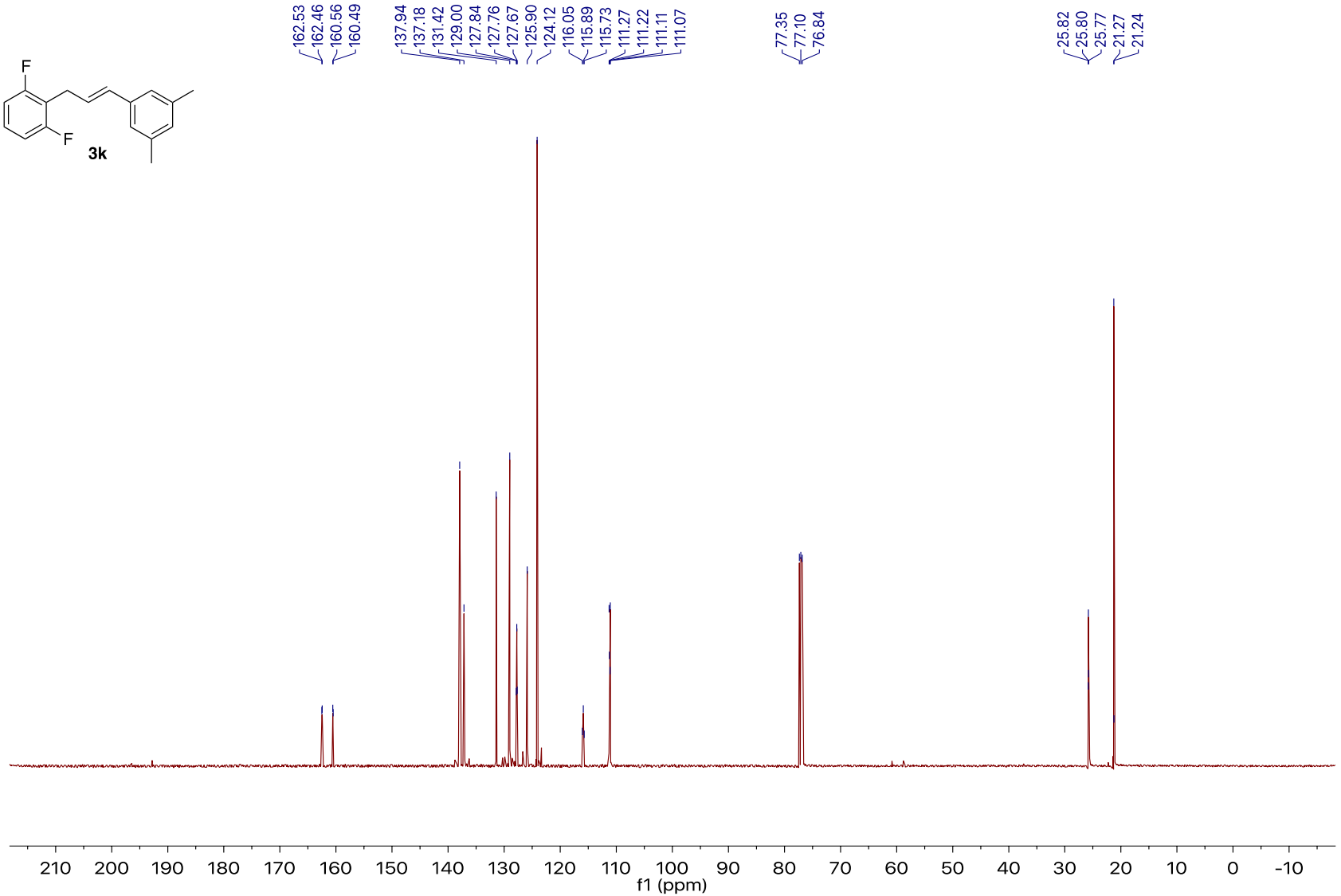
Compound 3j: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



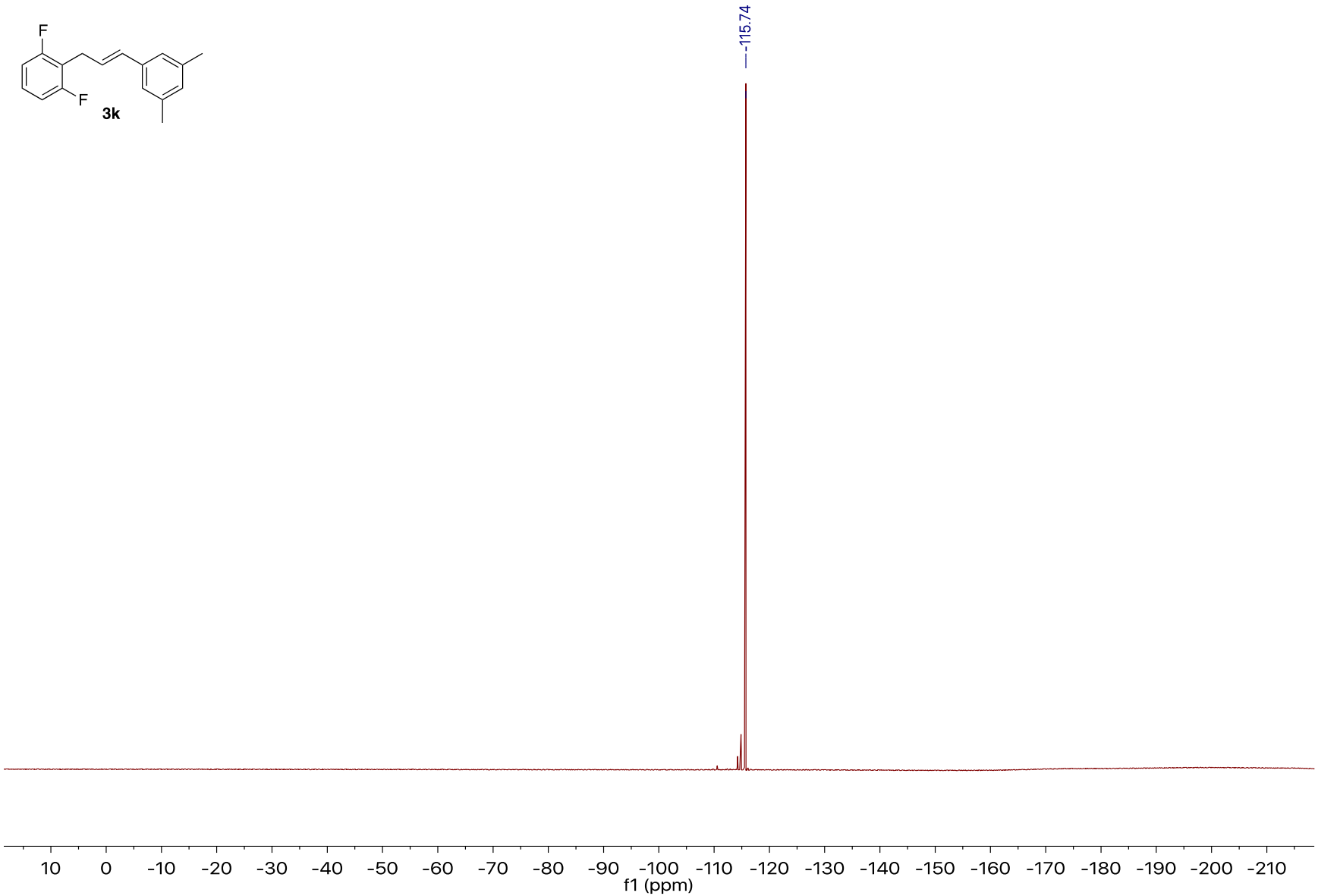
Compound 3j: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



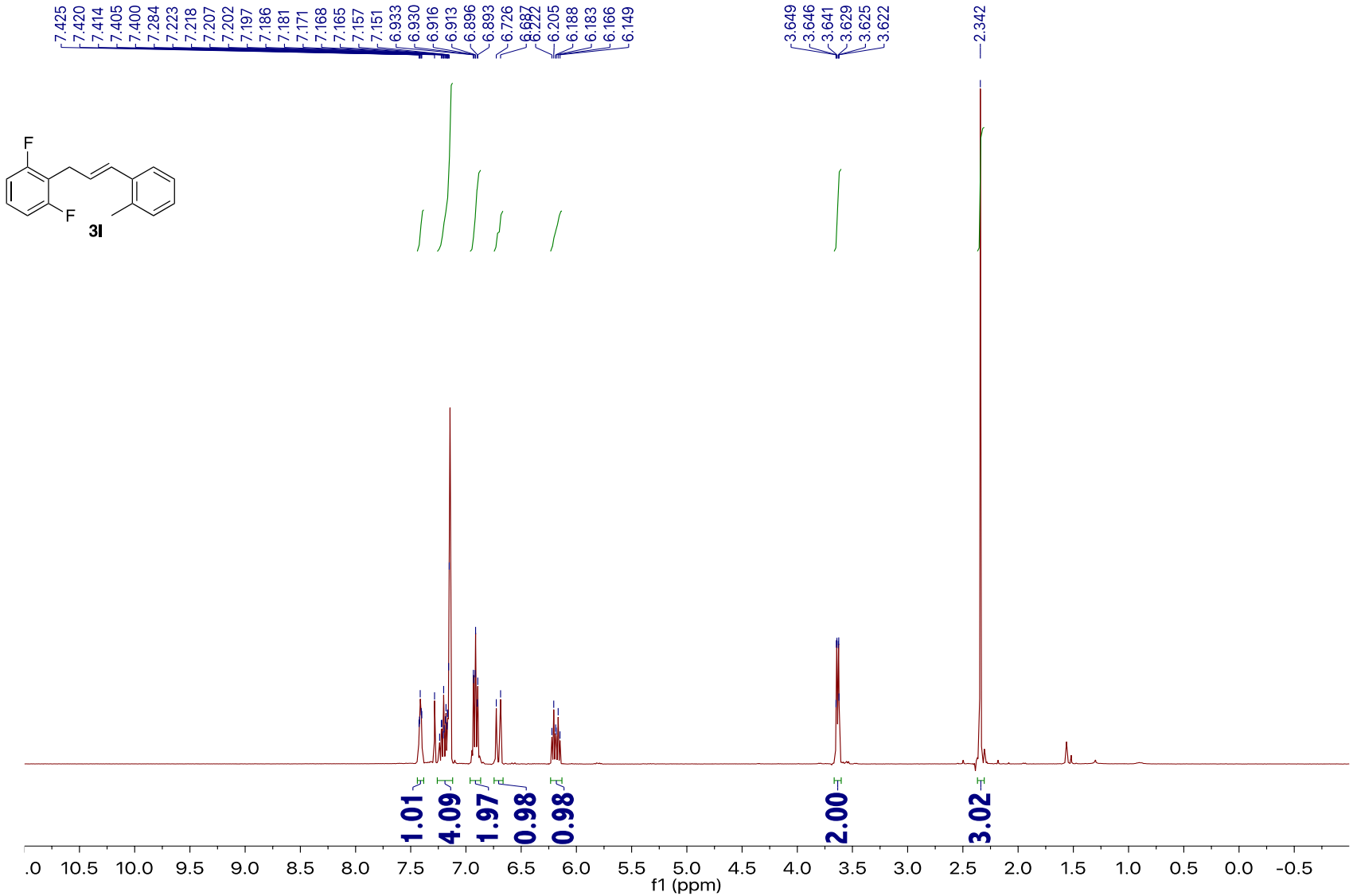
Compound 3k: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



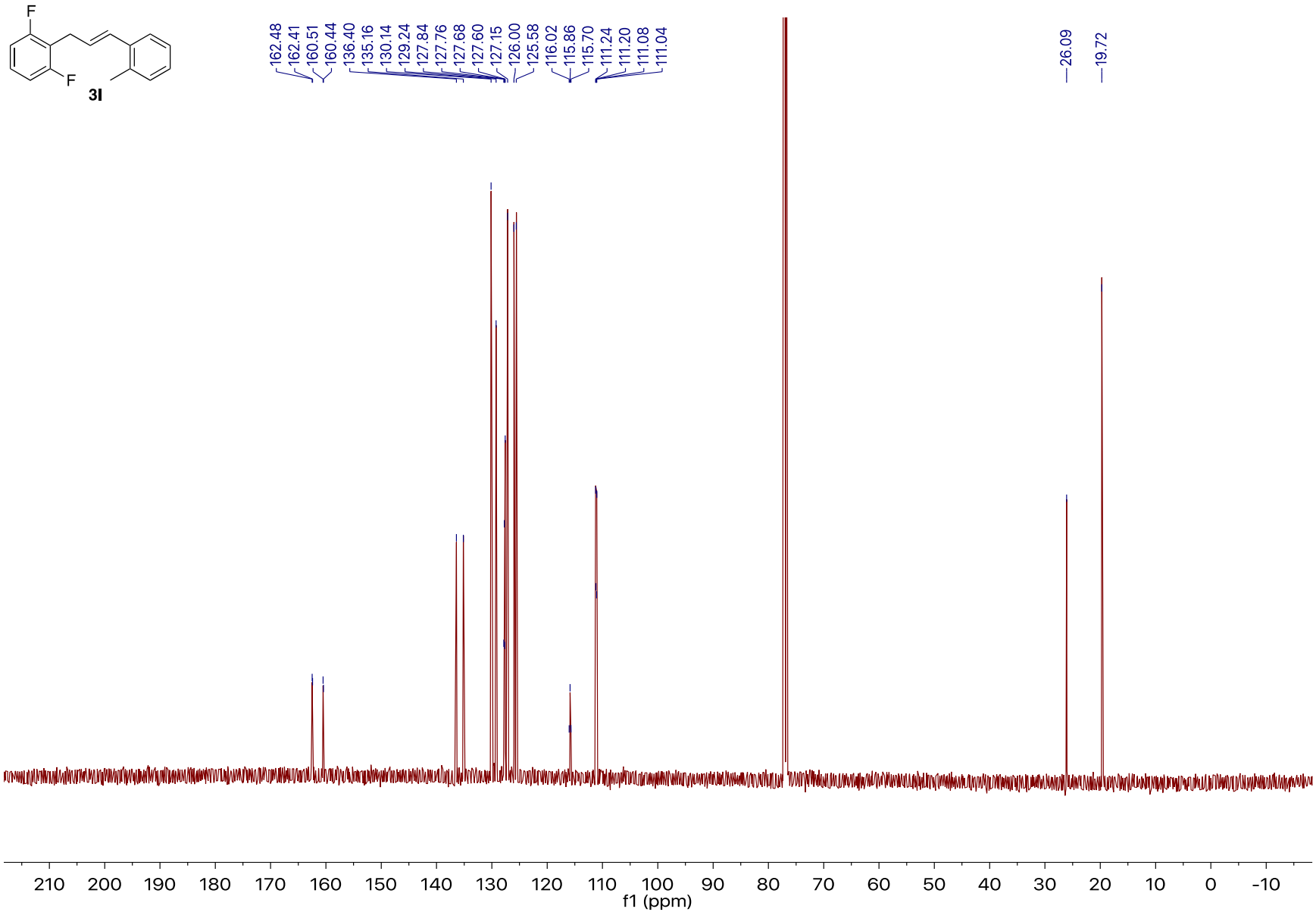
Compound 3k: 500 MHz ^{13}C NMR spectrum in $CDCl_3$



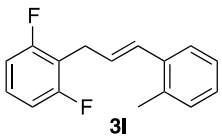
Compound 3k: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



Compound 3l: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

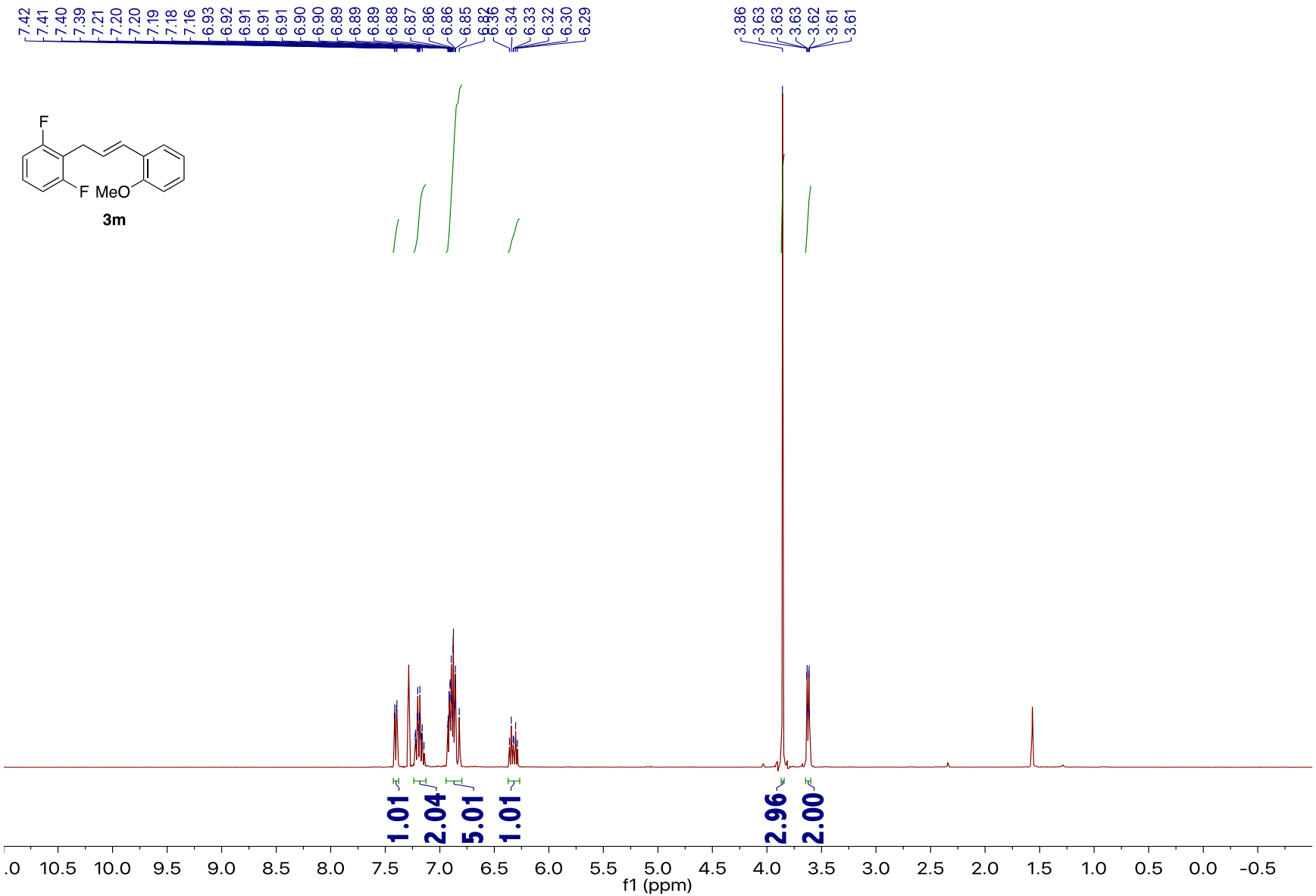


Compound 3l: 126 MHz ^{13}C NMR spectrum in $CDCl_3$

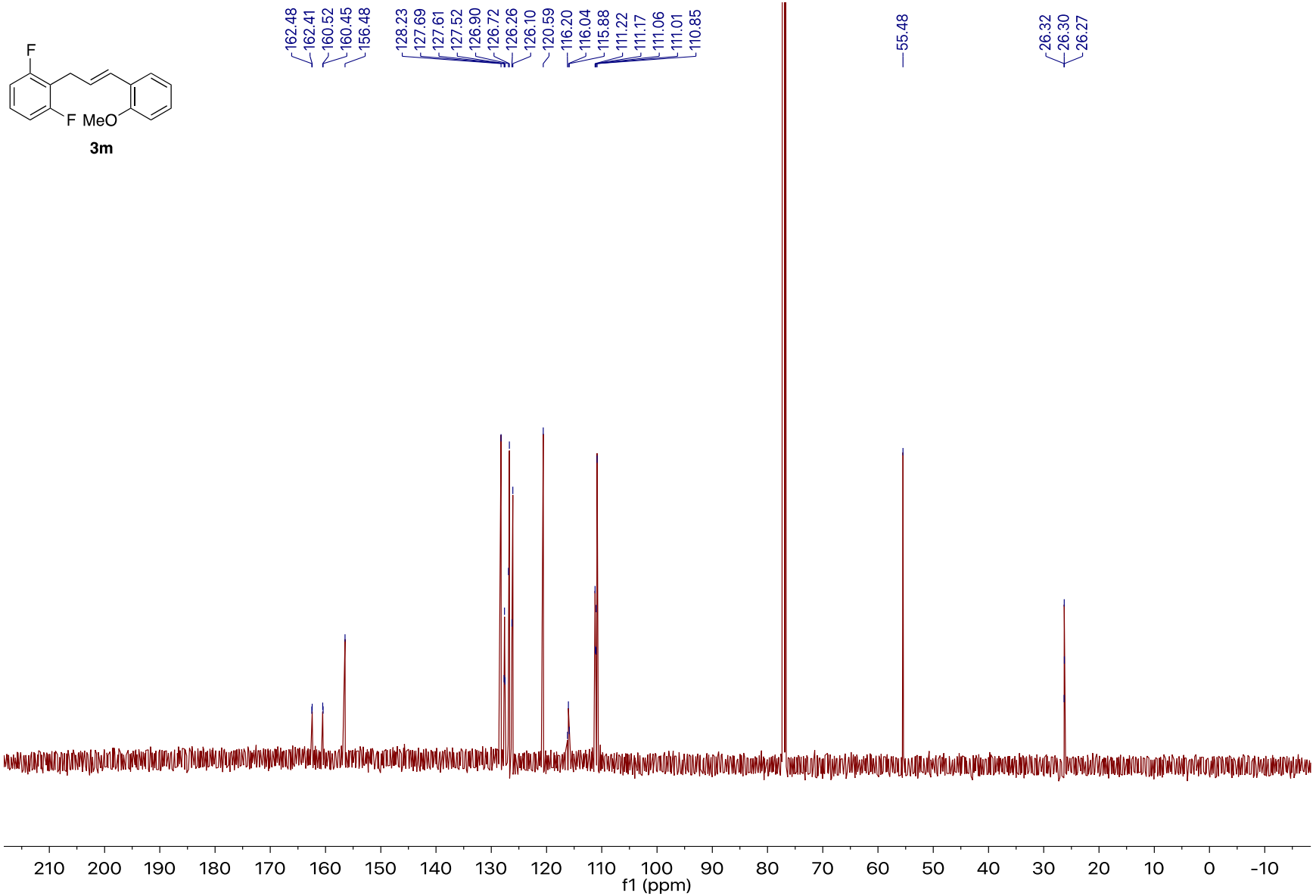


3l

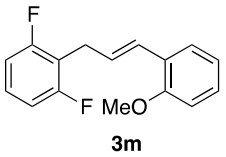
Compound 3l: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



Compound 3m: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

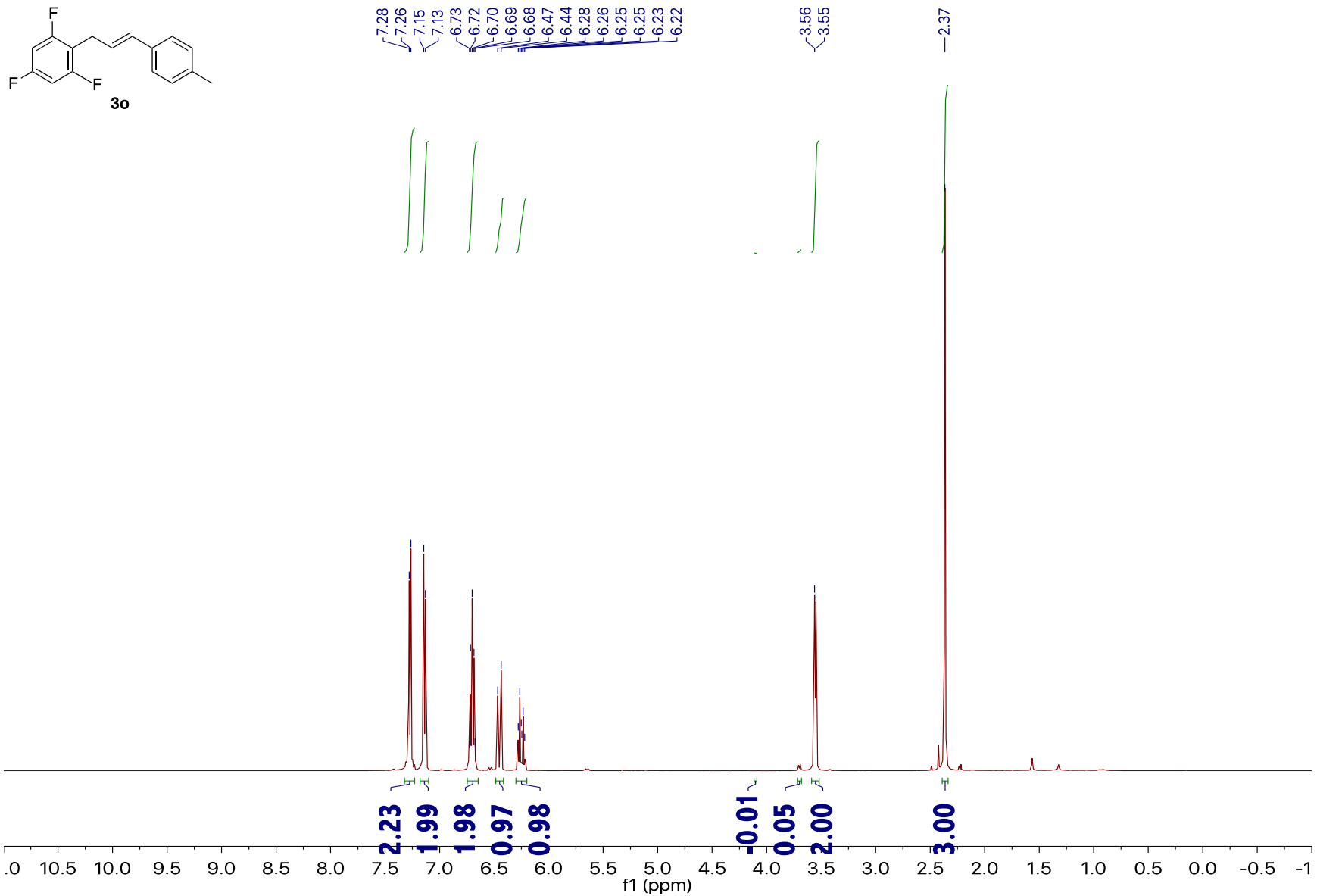


Compound 3m: 126 MHz ^{13}C NMR spectrum in $CDCl_3$

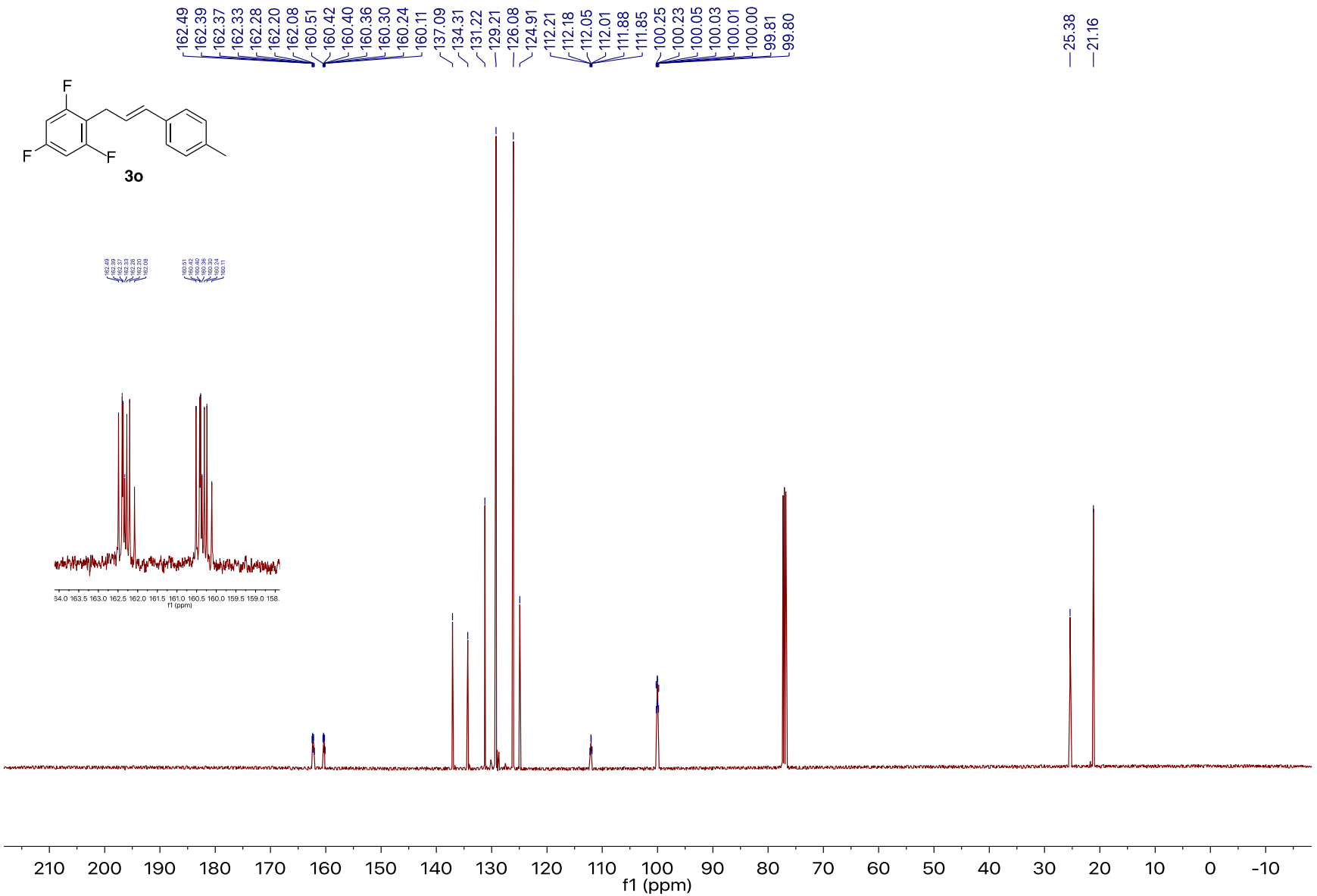


3m

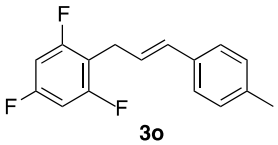
Compound 3m: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



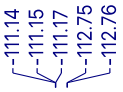
Compound 3o: 400 MHz ^{1}H NMR spectrum in $CDCl_3$

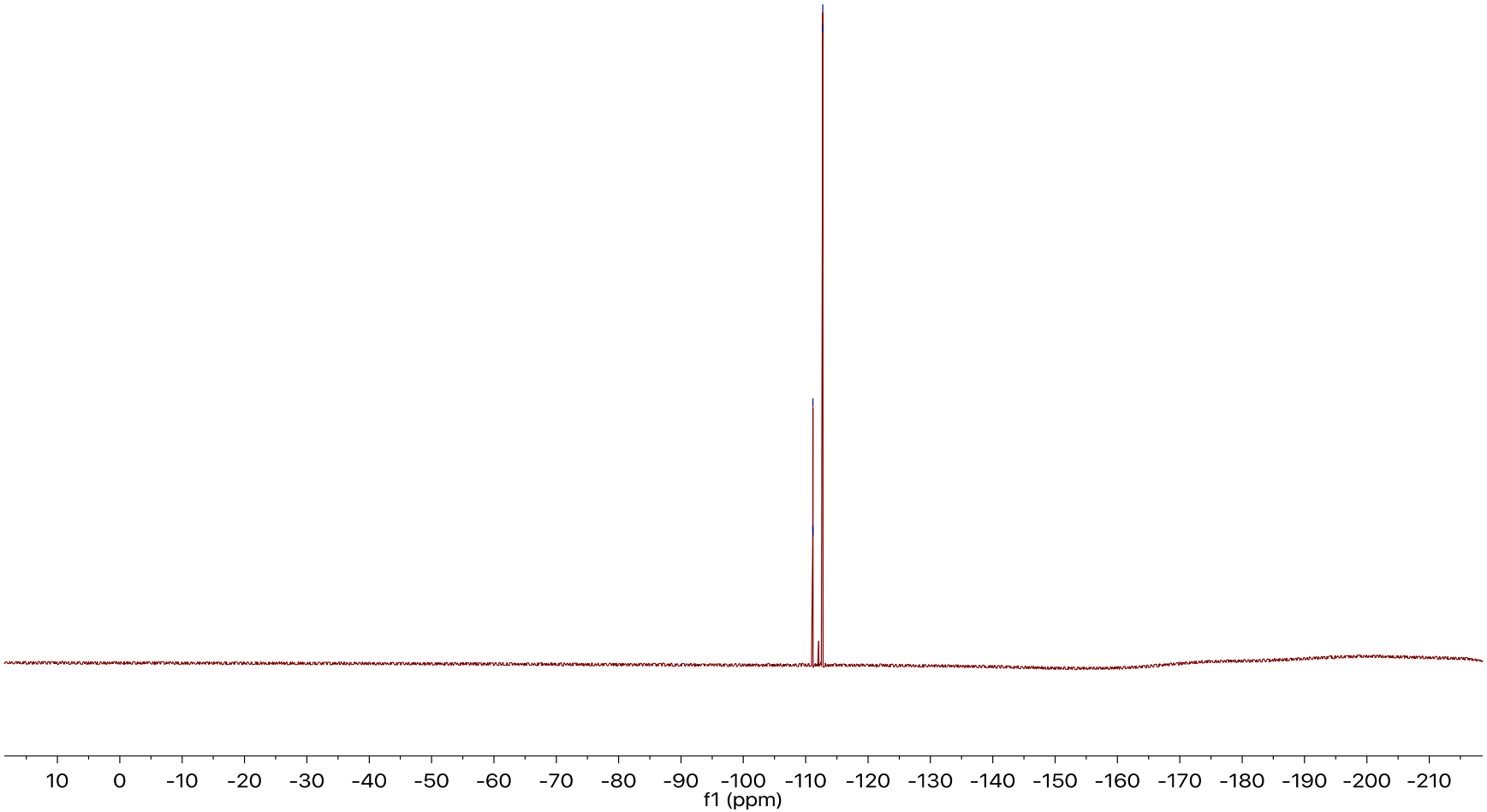


Compound 3o: 500 MHz ^{13}C NMR spectrum in $CDCl_3$

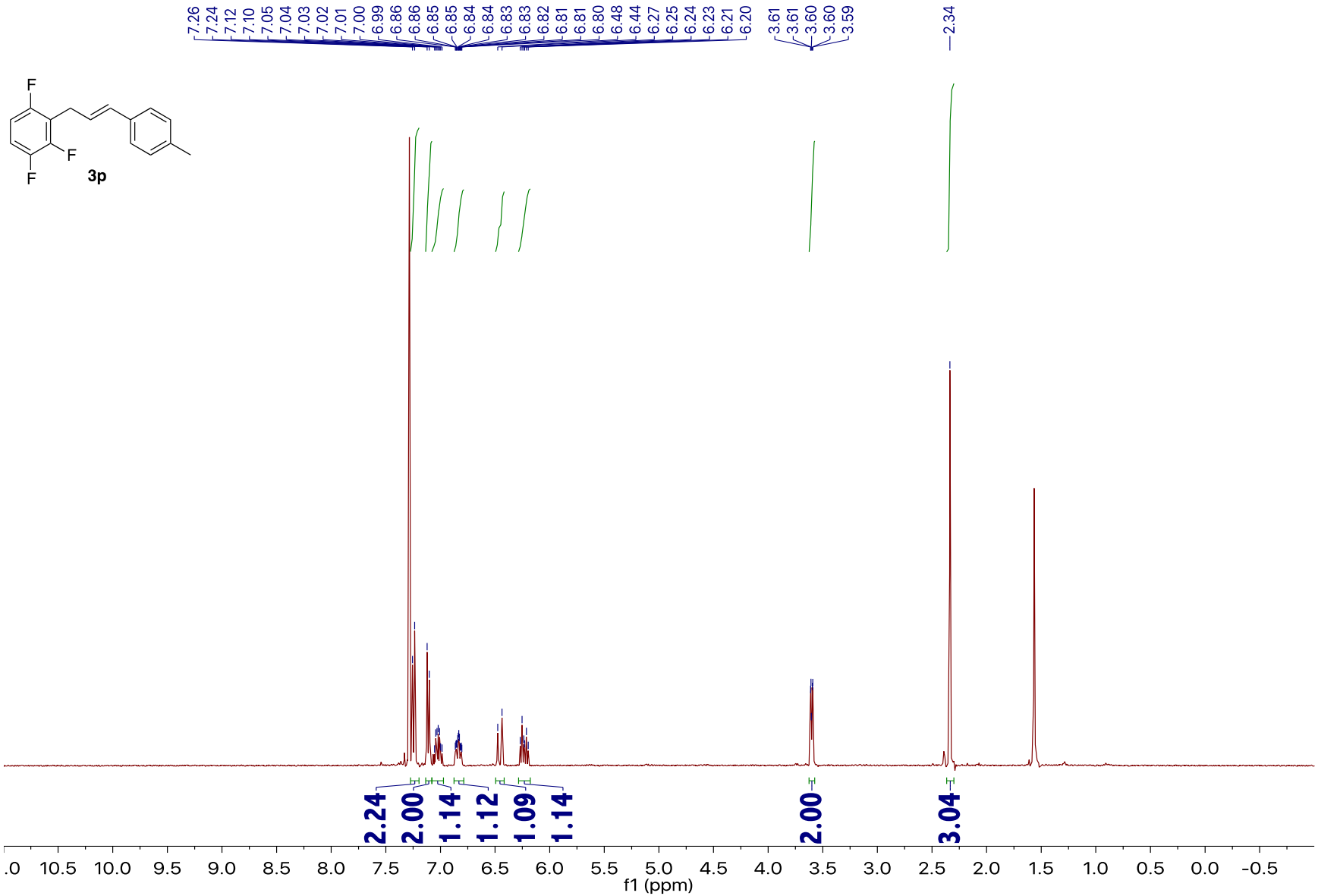


3o

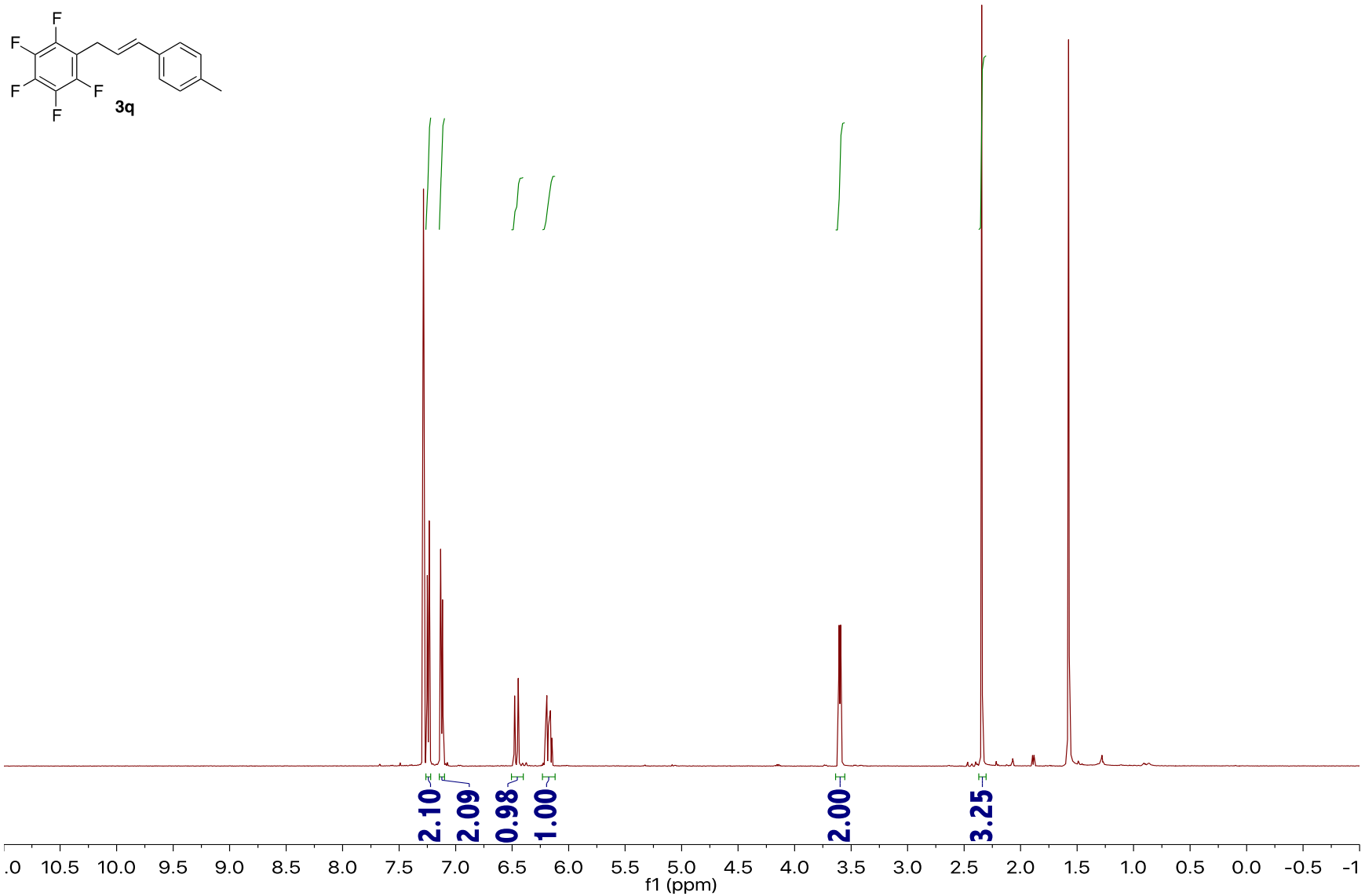




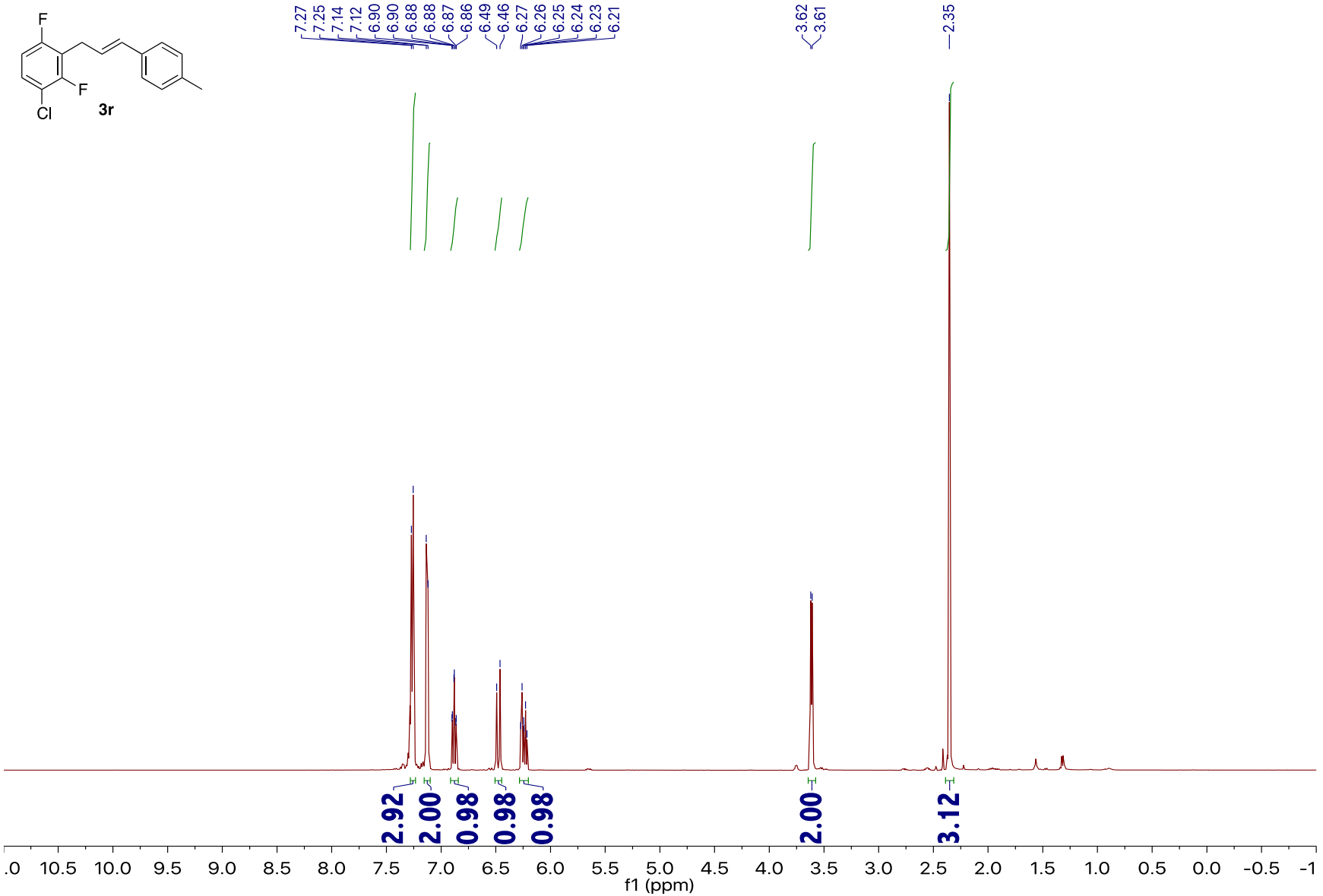
Compound 3o: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



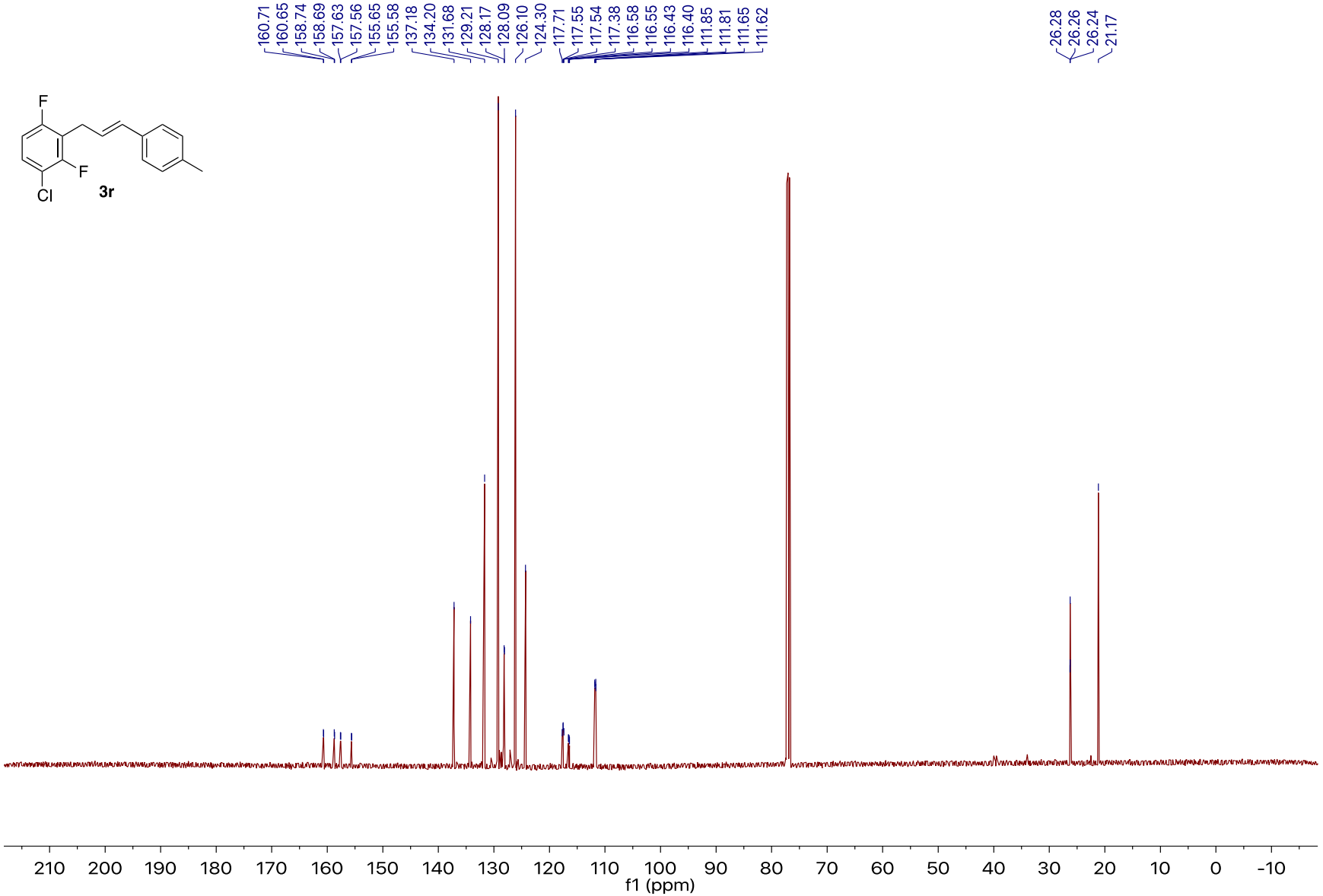
Compound 3p: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



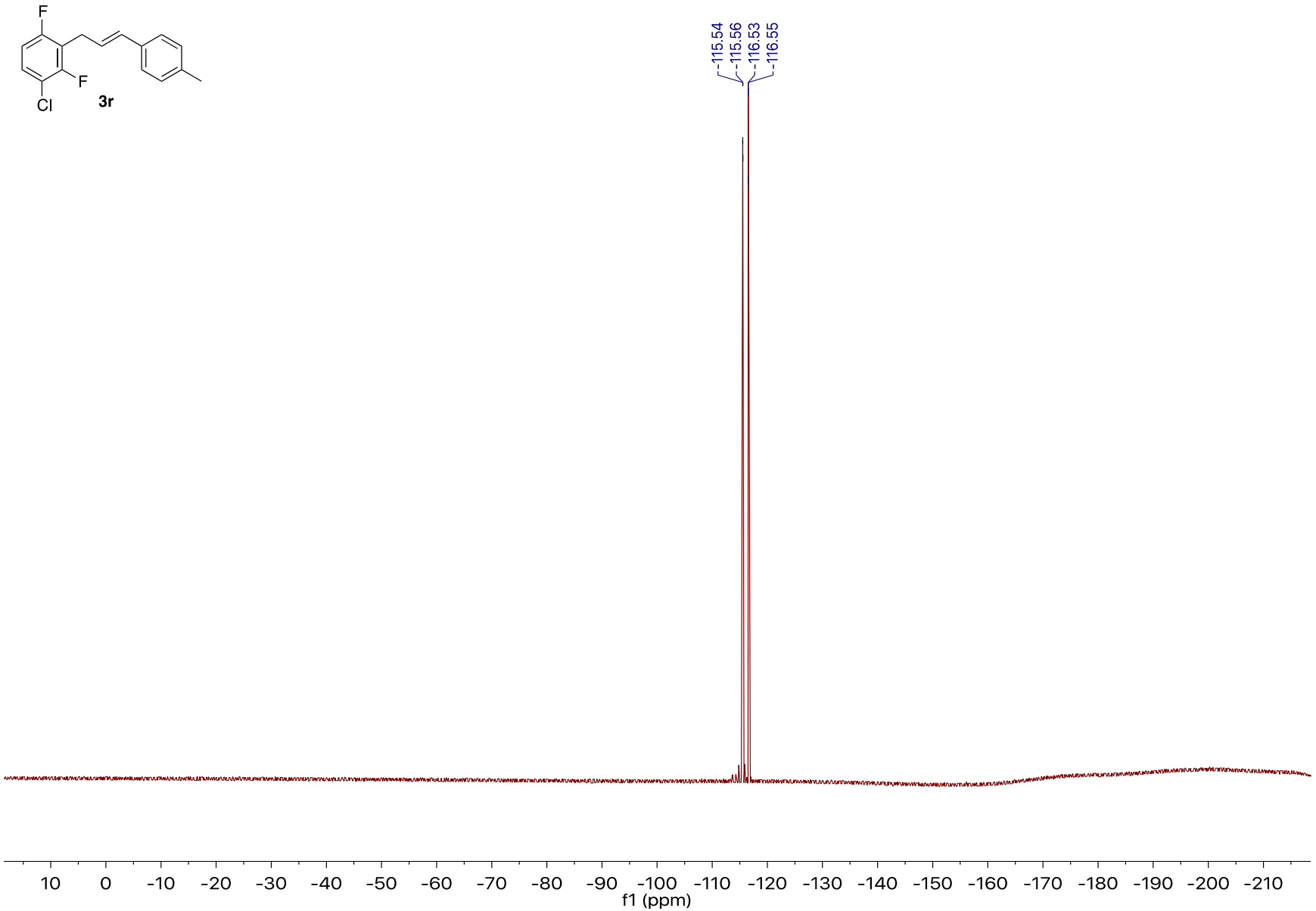
Compound 3q: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



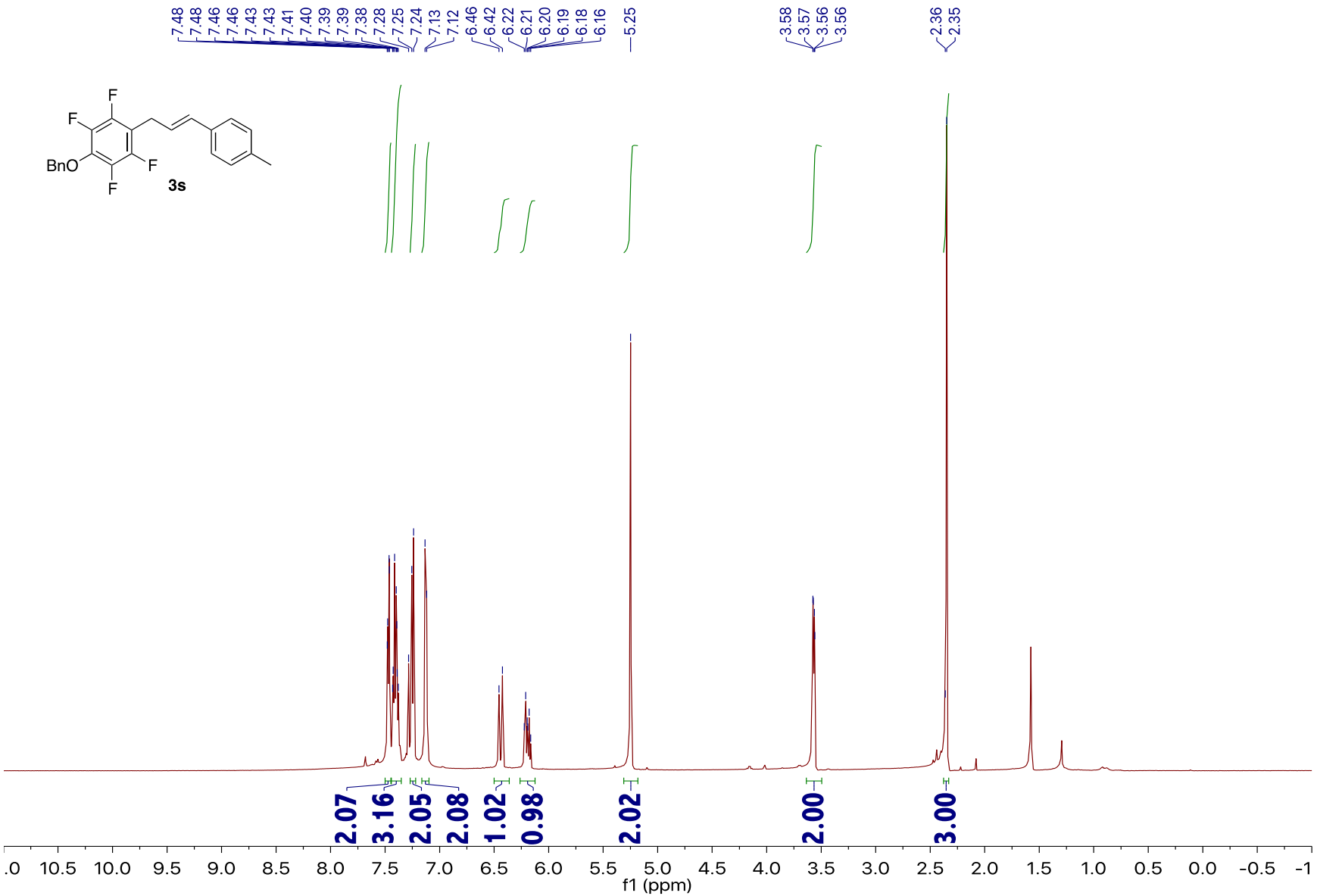
Compound 3r: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



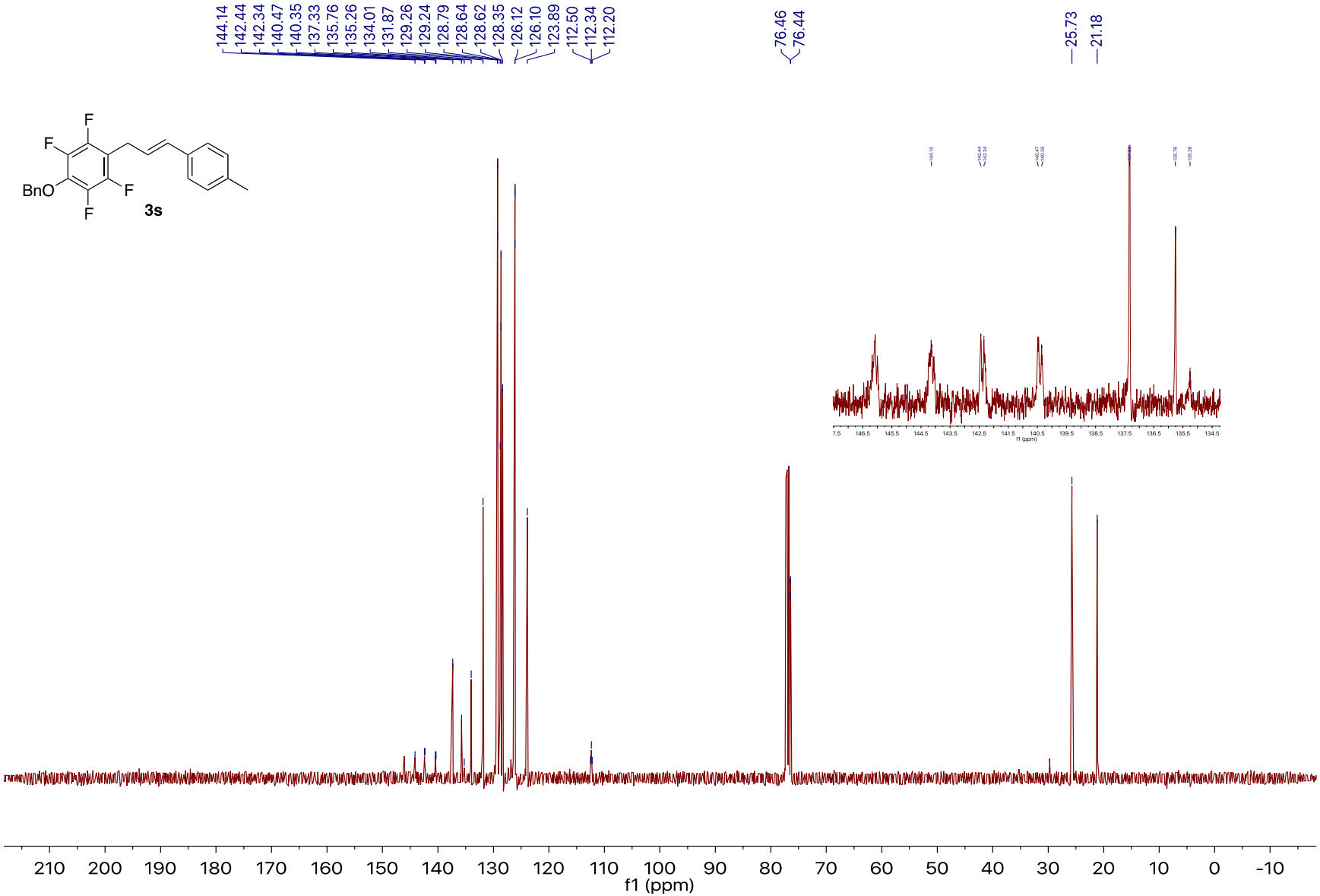
Compound 3r: 500 MHz ^{13}C NMR spectrum in $CDCl_3$



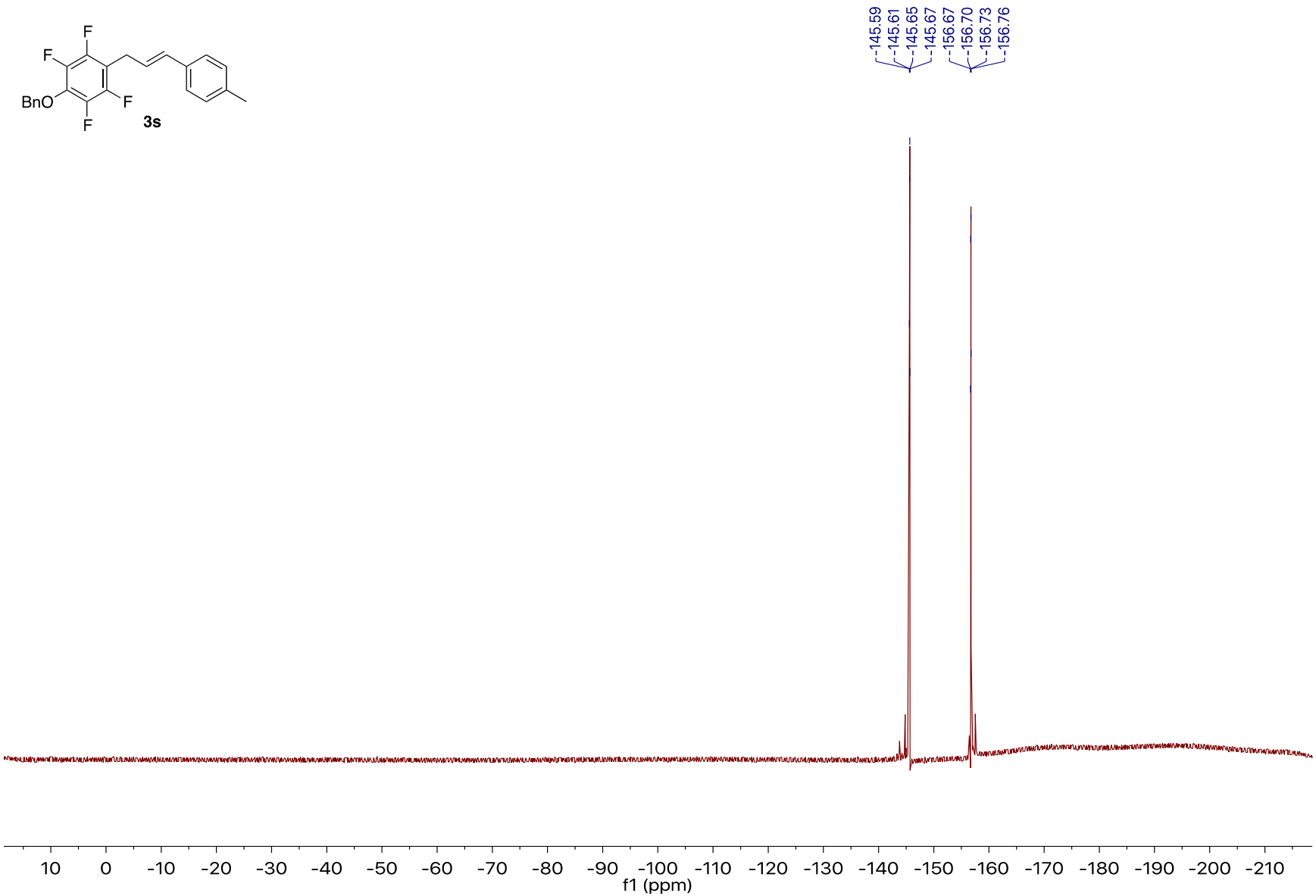
Compound 3r: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



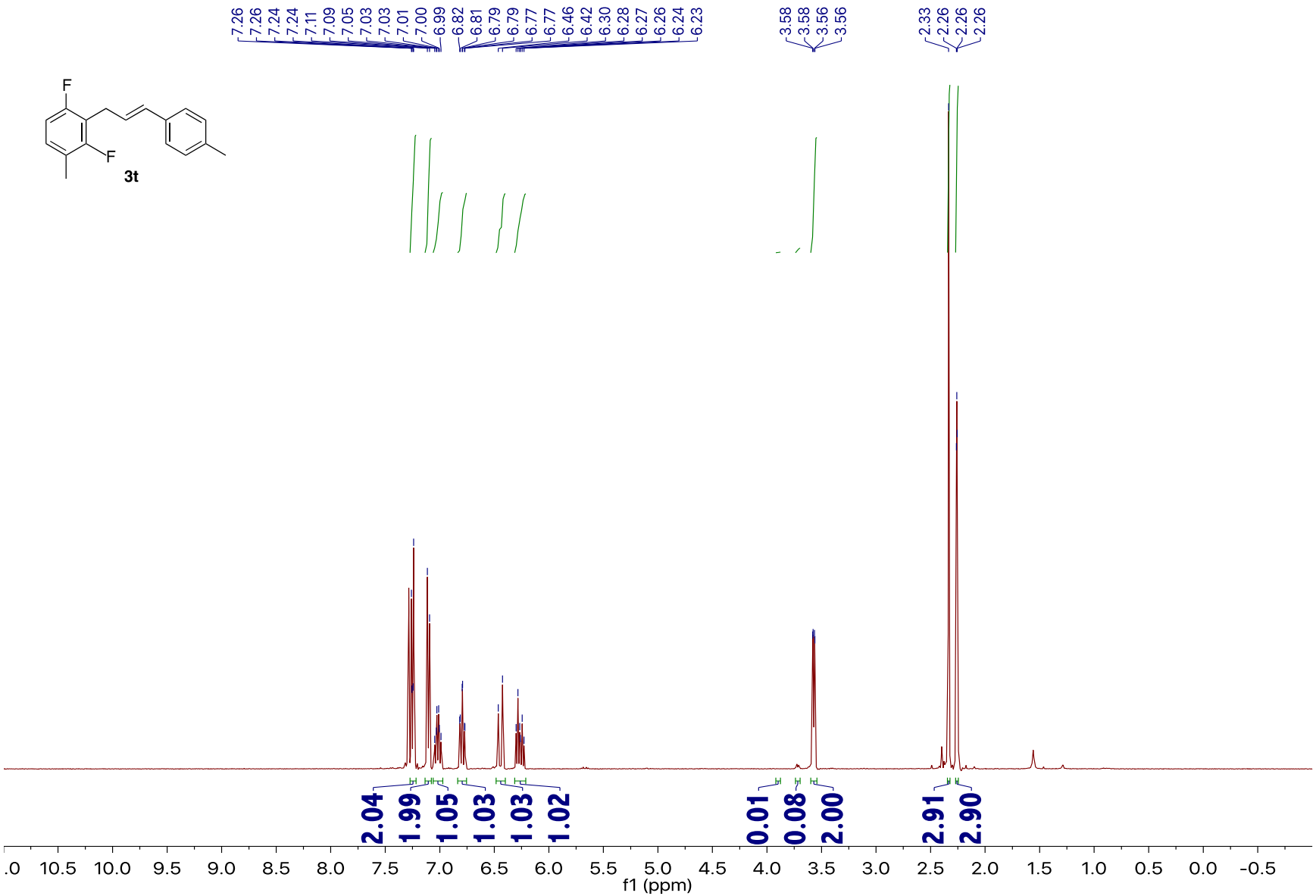
Compound 3s: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



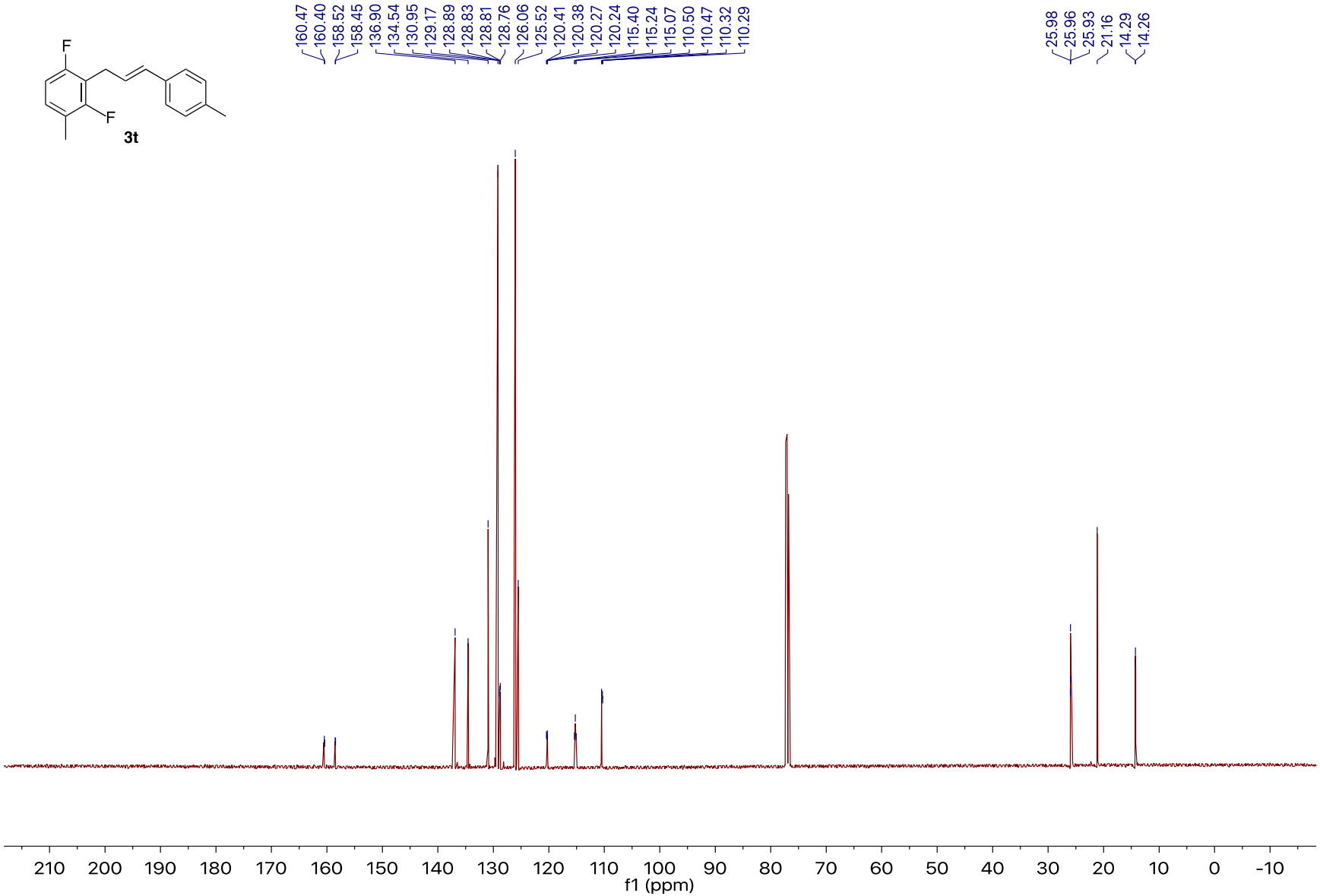
Compound 3s: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



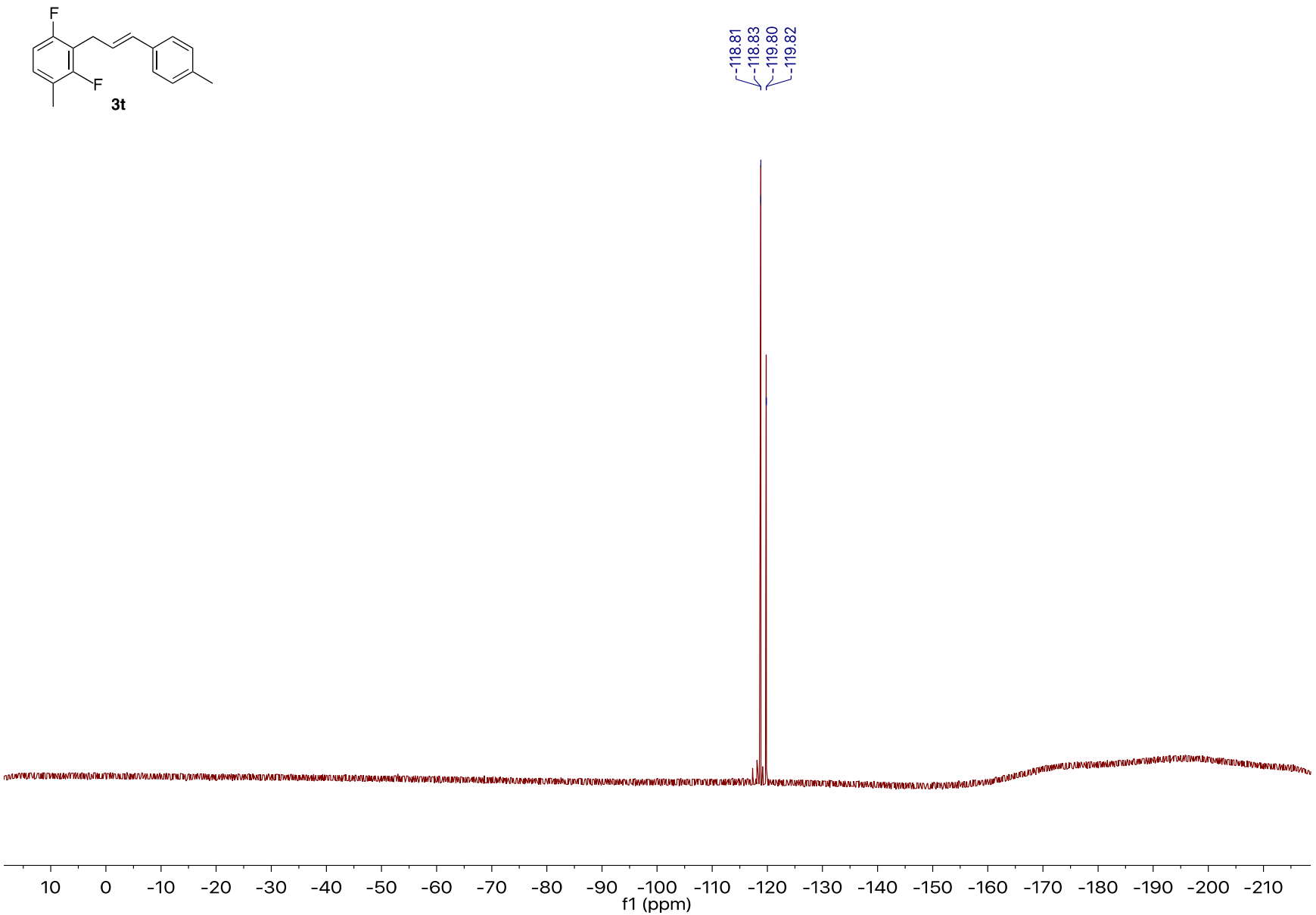
Compound 3s: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



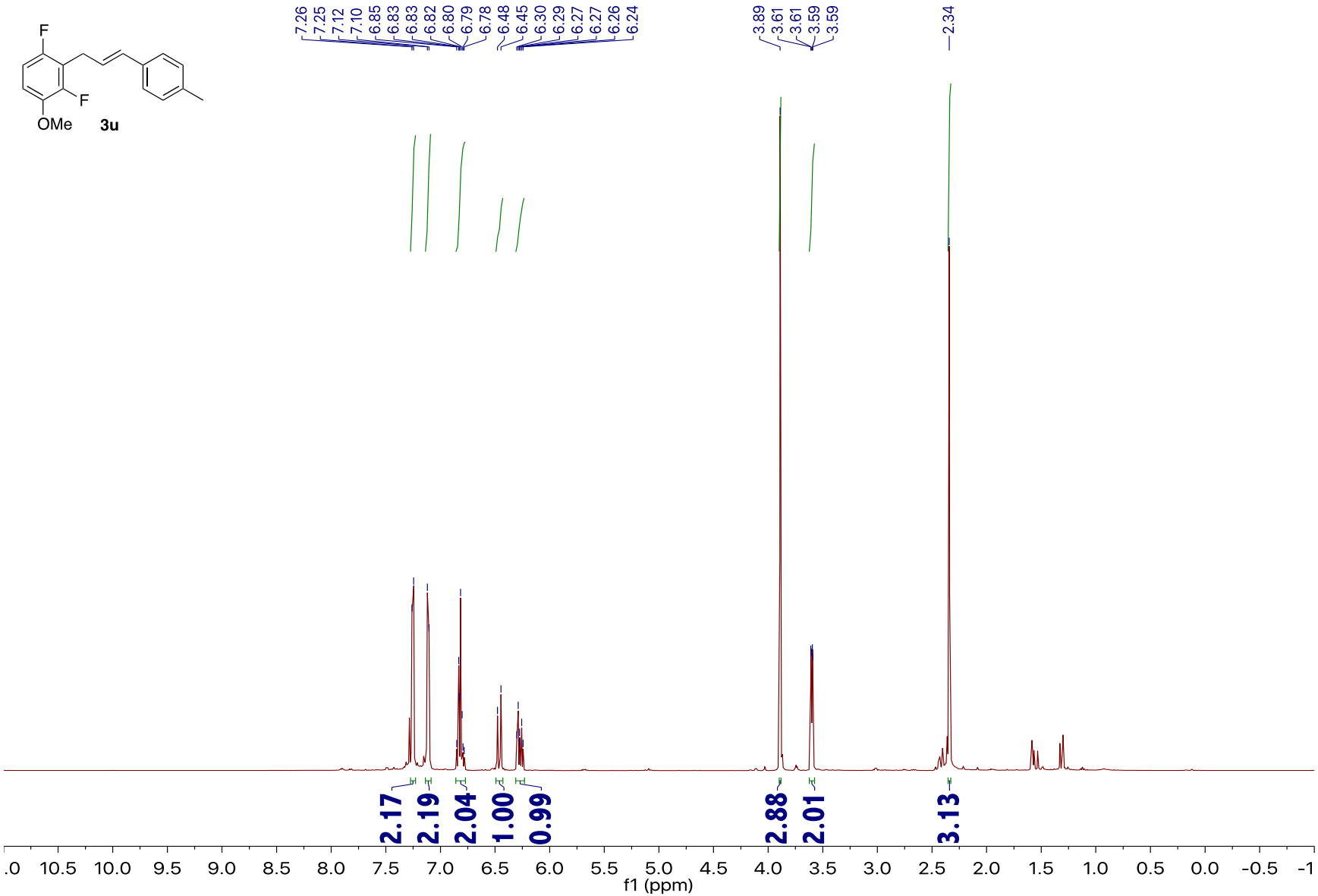
Compound 3t: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



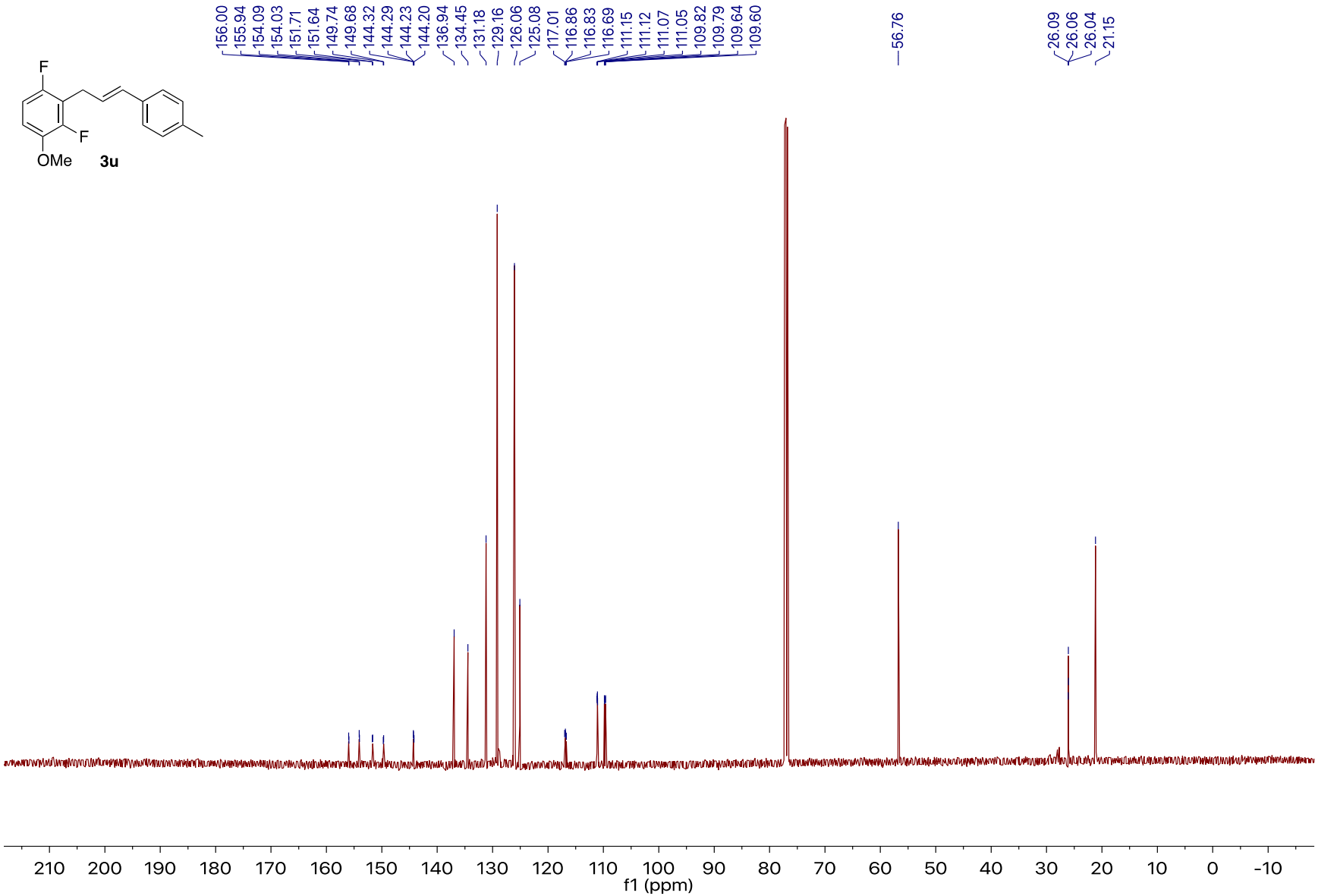
Compound 3t: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



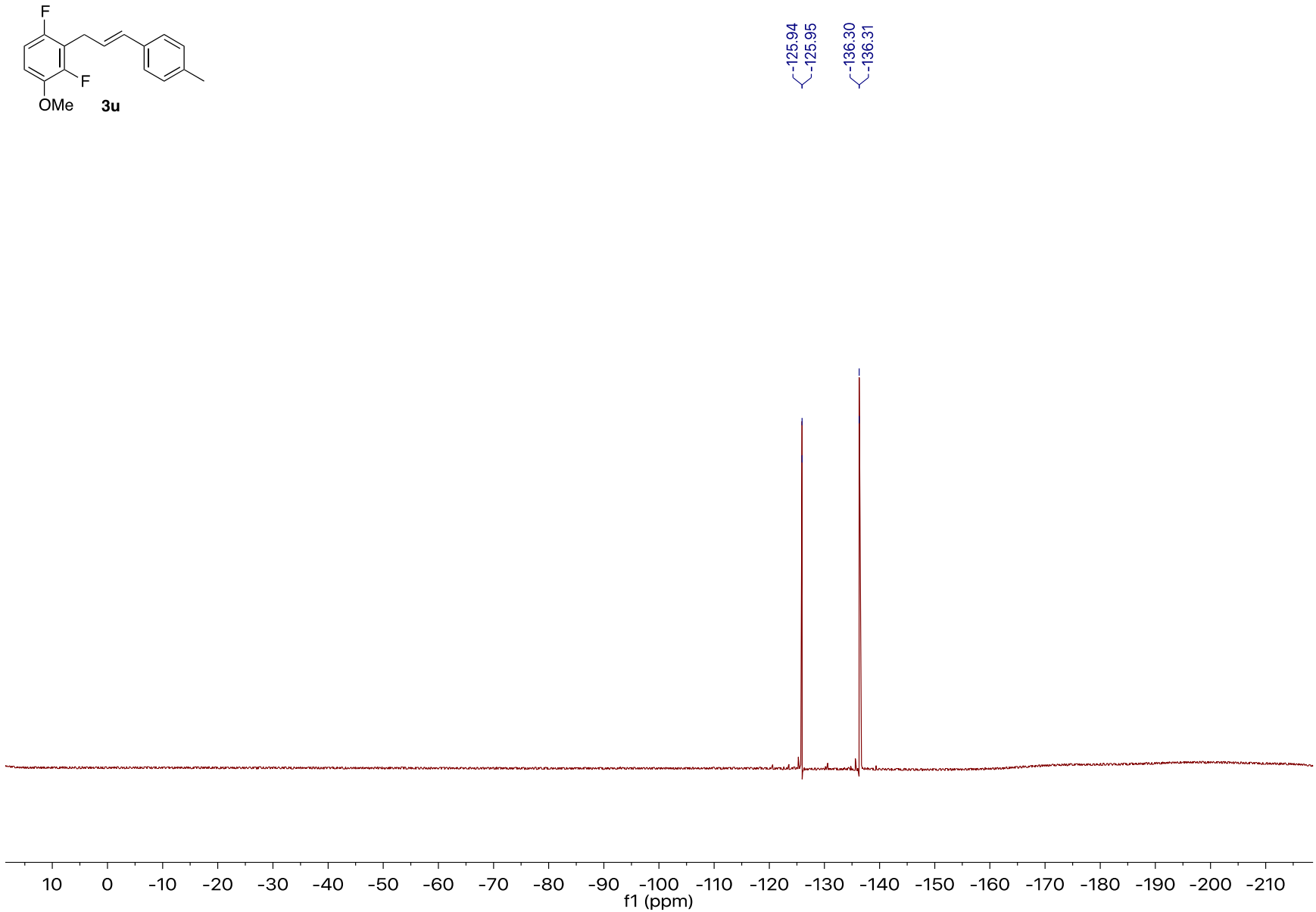
Compound 3t: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



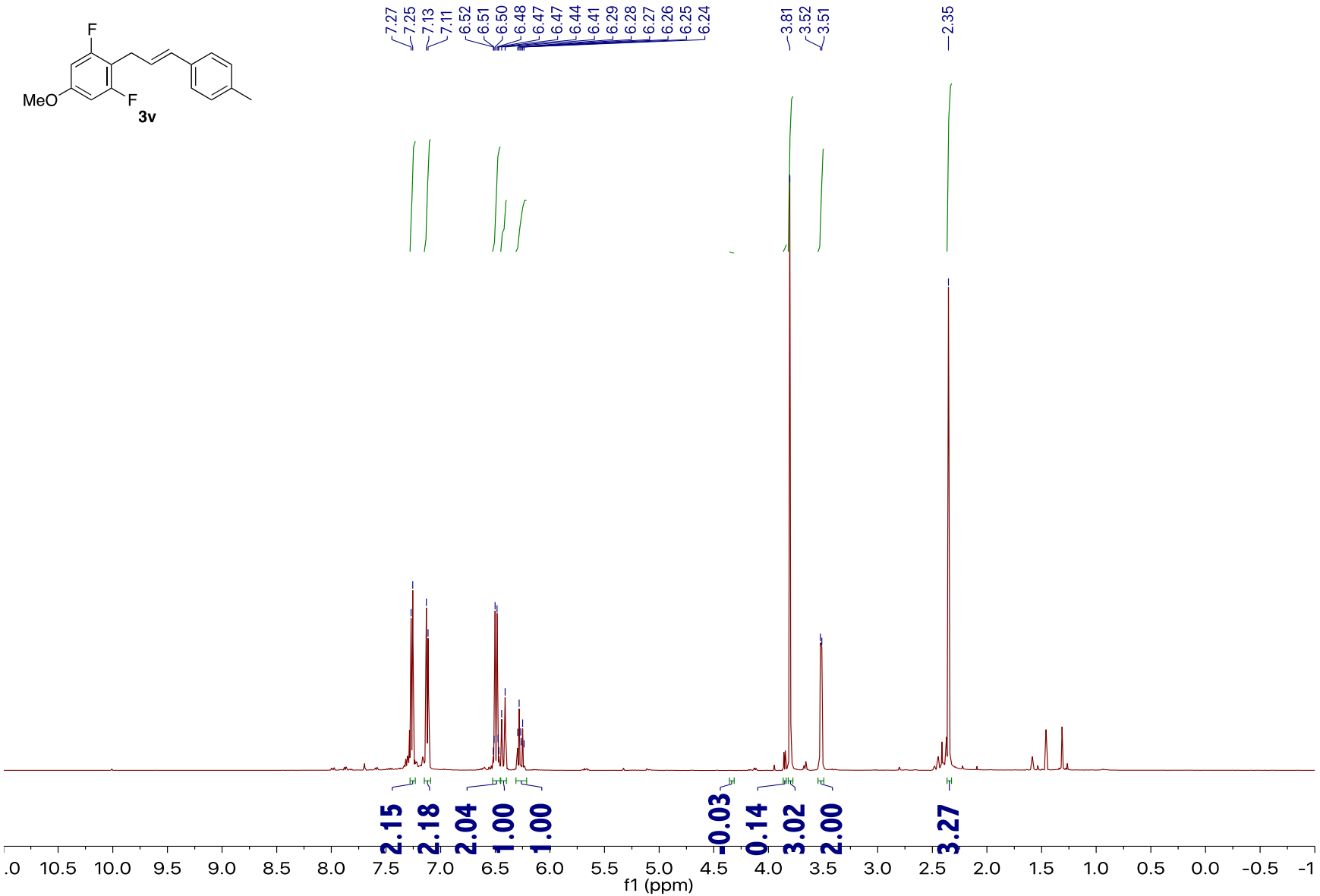
Compound 3u: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



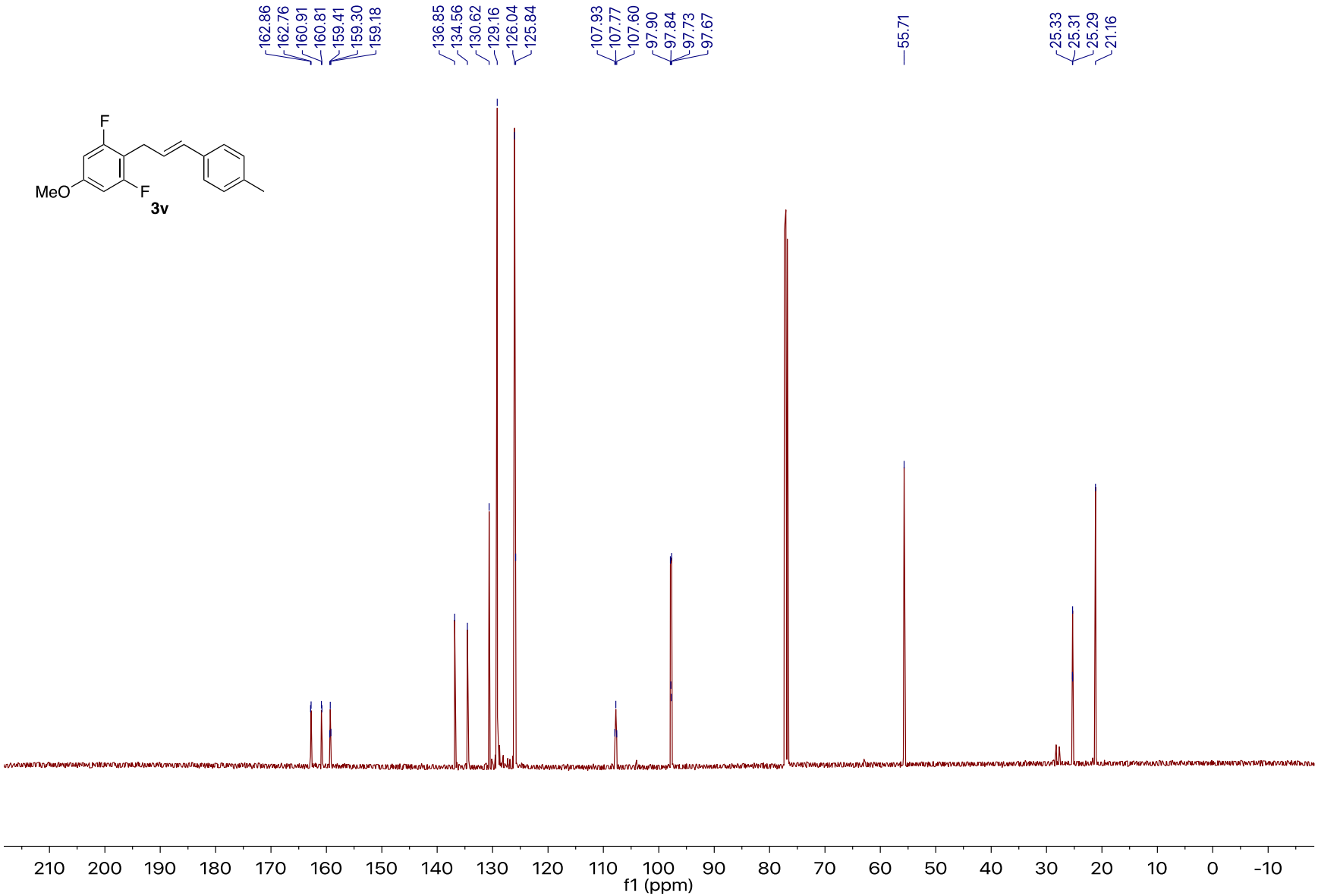
Compound 3u: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



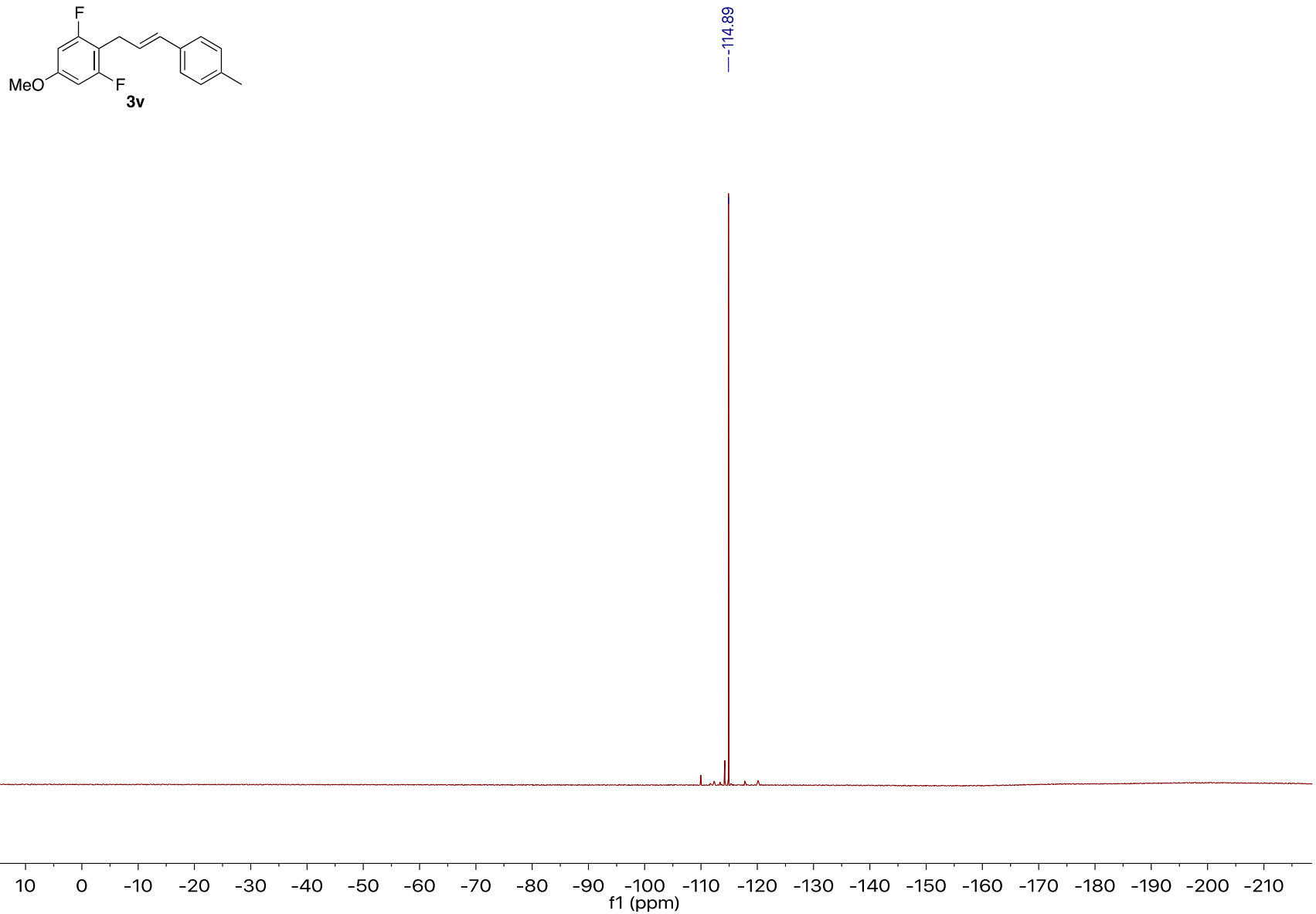
Compound 3u: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



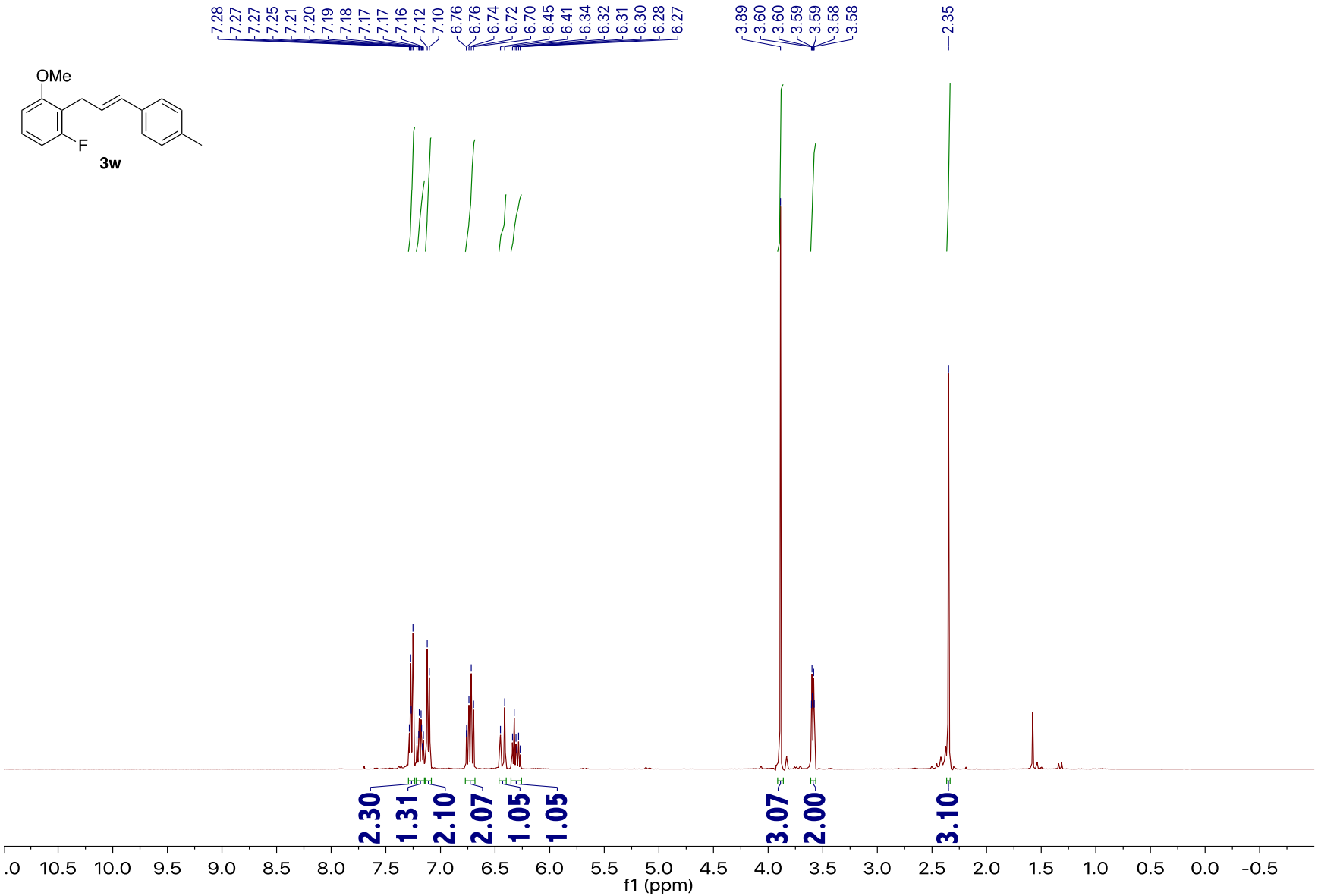
Compound 3v: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



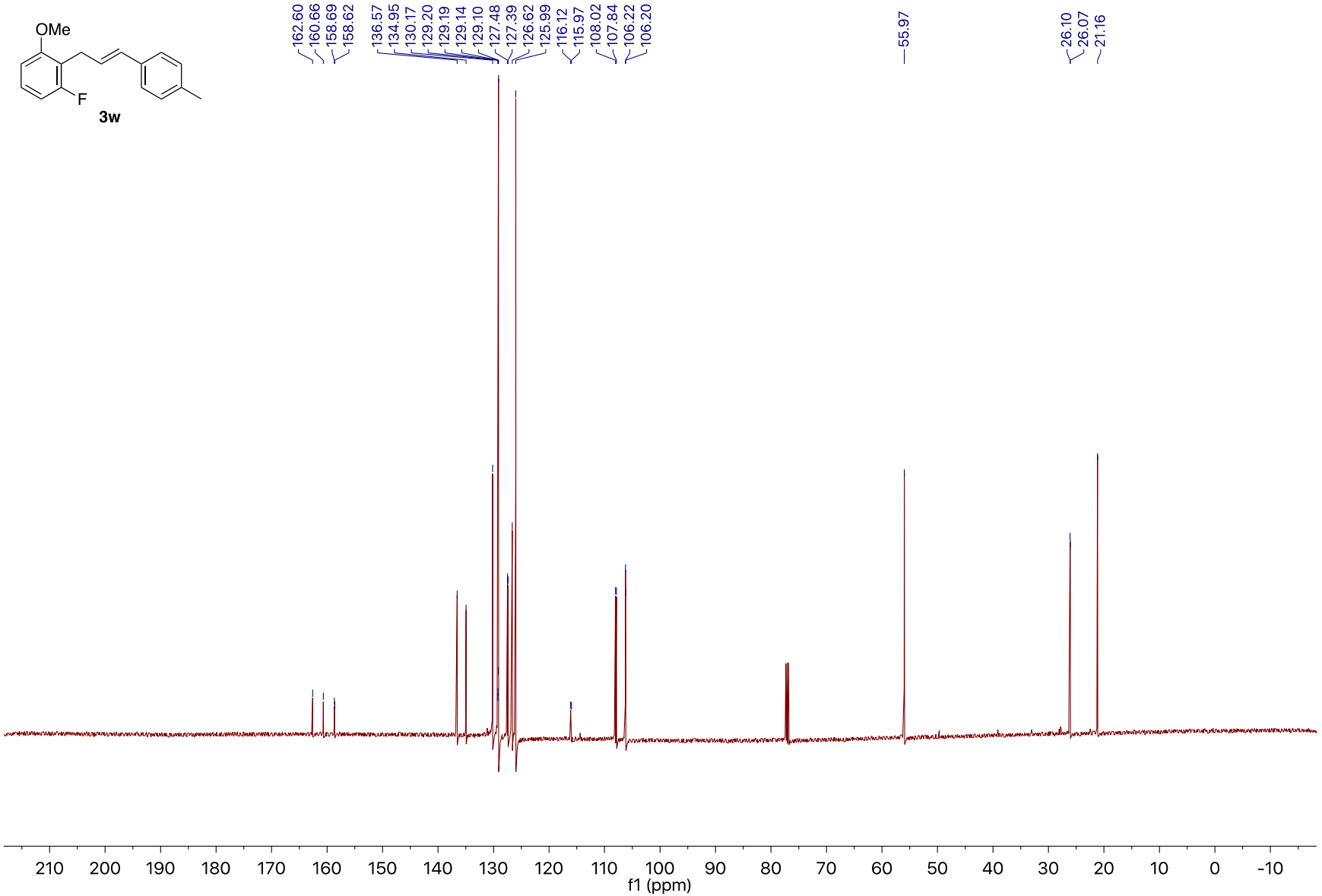
Compound 3v: 500 MHz ^{13}C NMR spectrum in $CDCl_3$



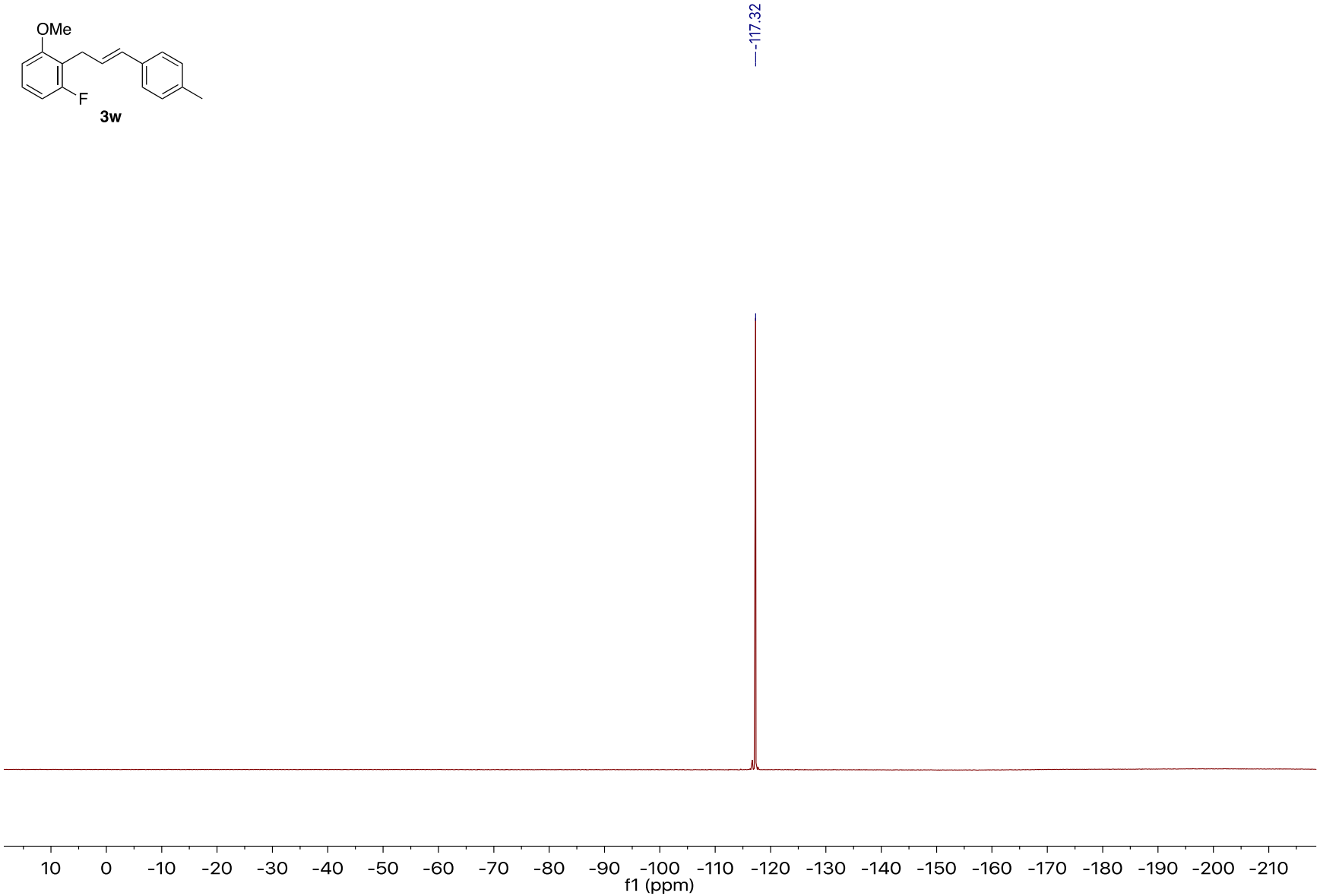
Compound 3v: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



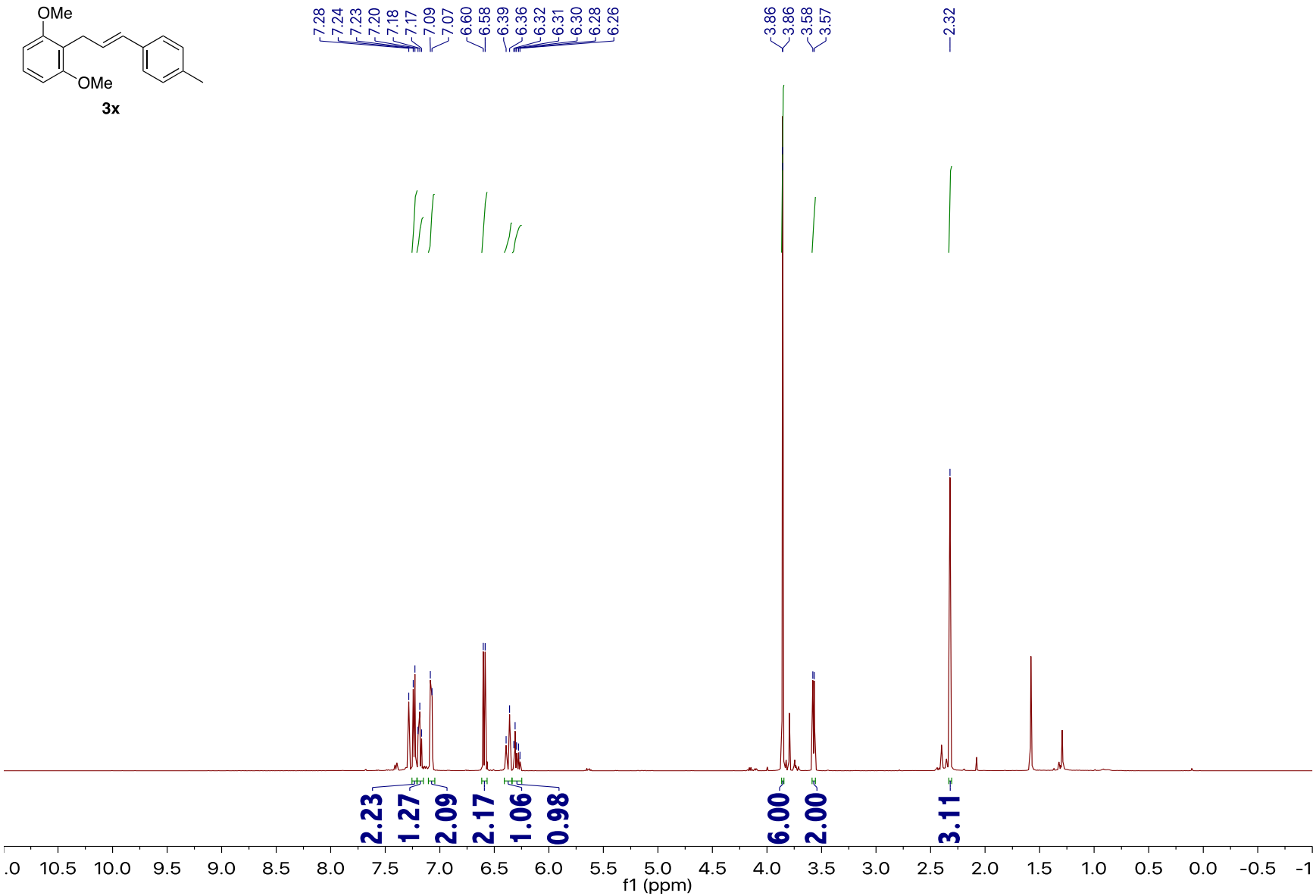
Compound 3w: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



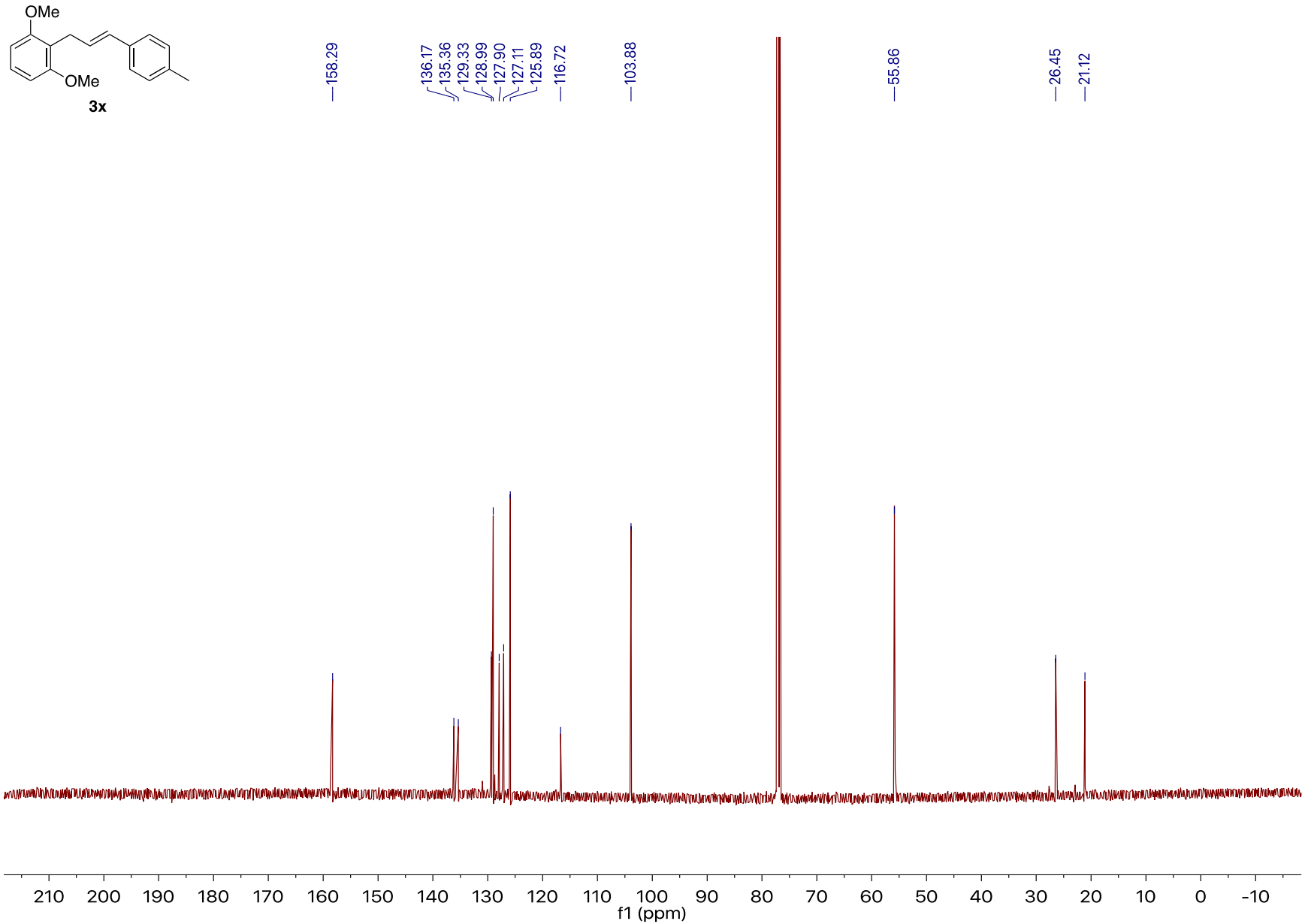
Compound 3w: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



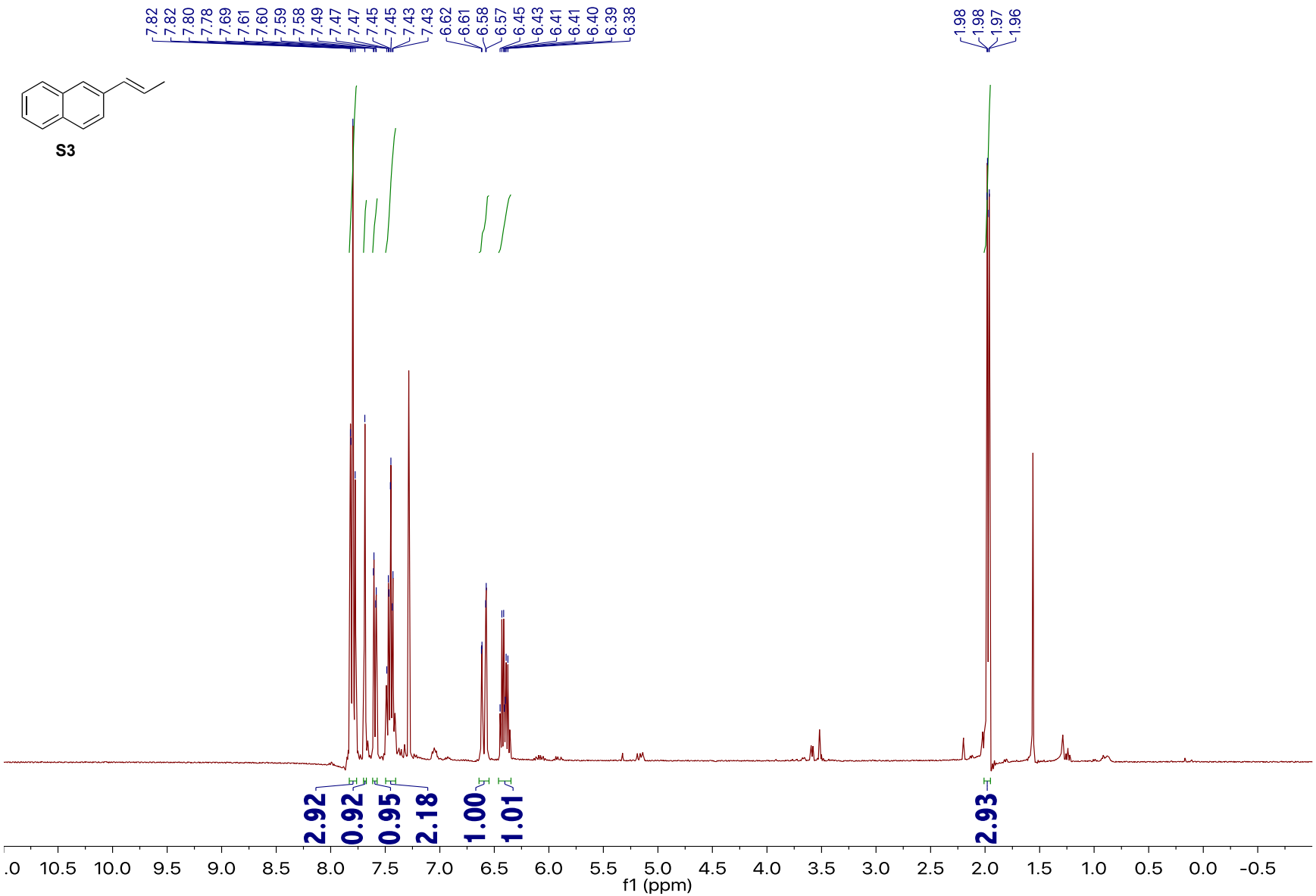
Compound 3w: 376 MHz ^{19}F NMR spectrum in $CDCl_3$



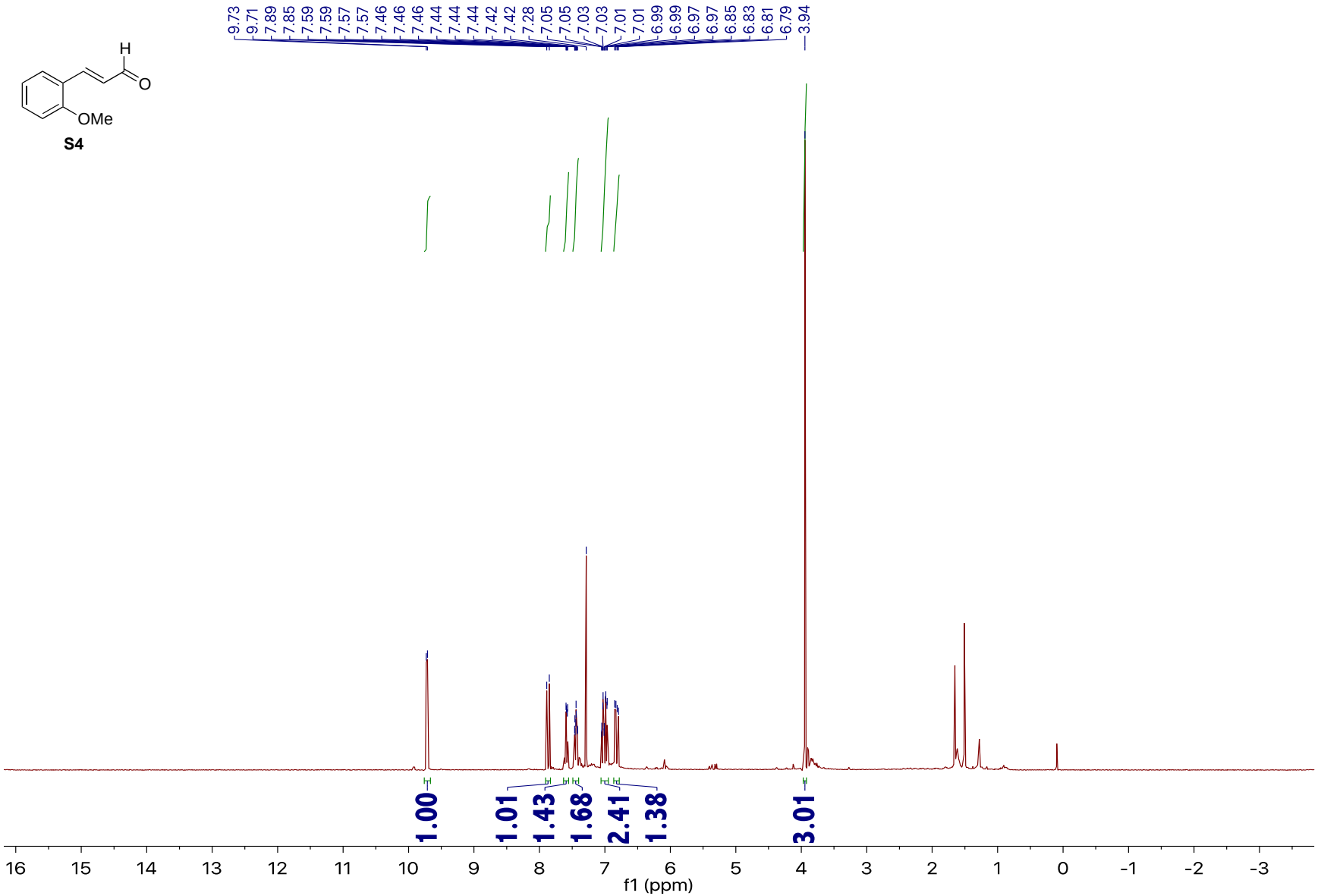
Compound 3X: 500 MHz ^{1}H NMR spectrum in $CDCl_3$



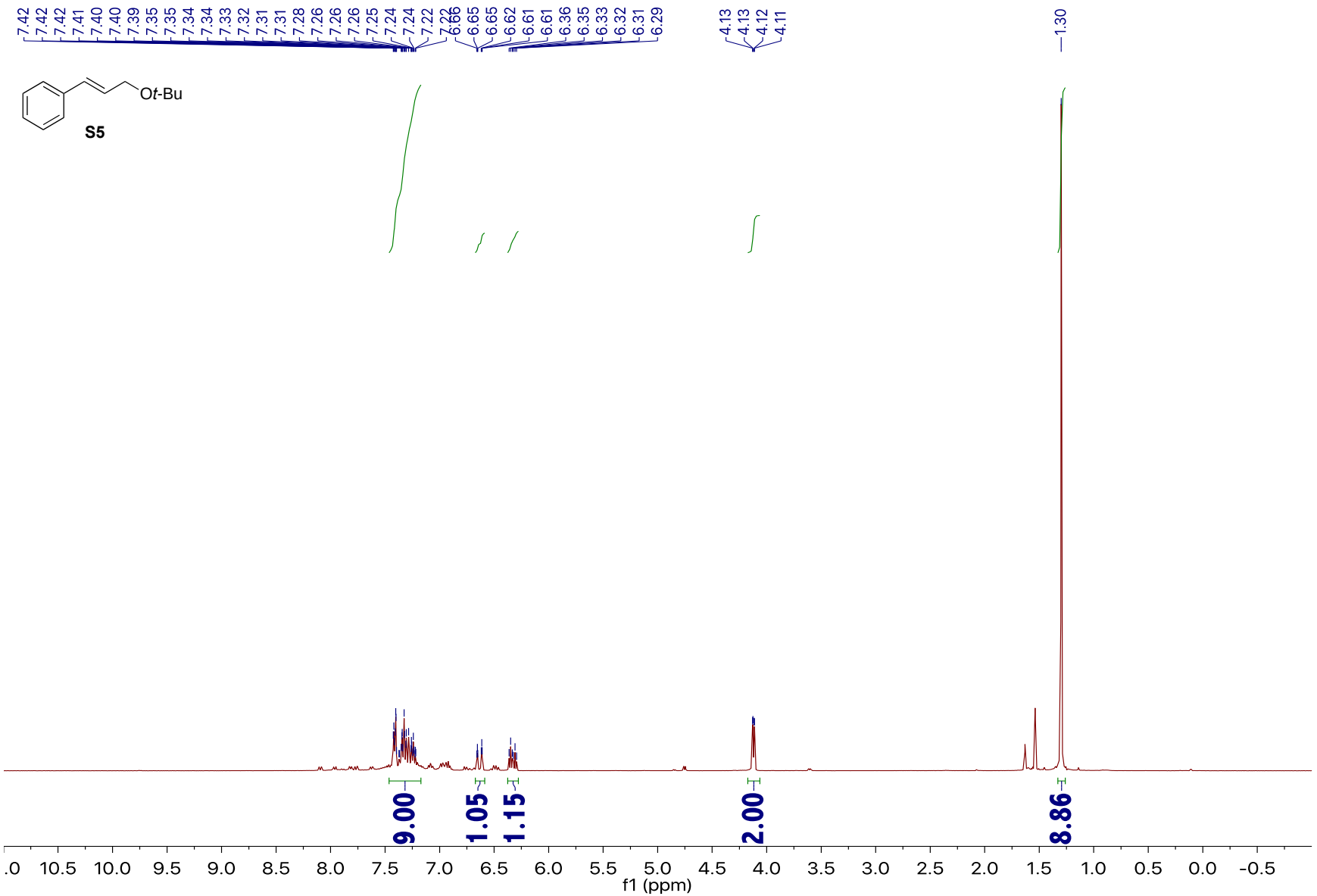
Compound 3X: 126 MHz ^{13}C NMR spectrum in $CDCl_3$



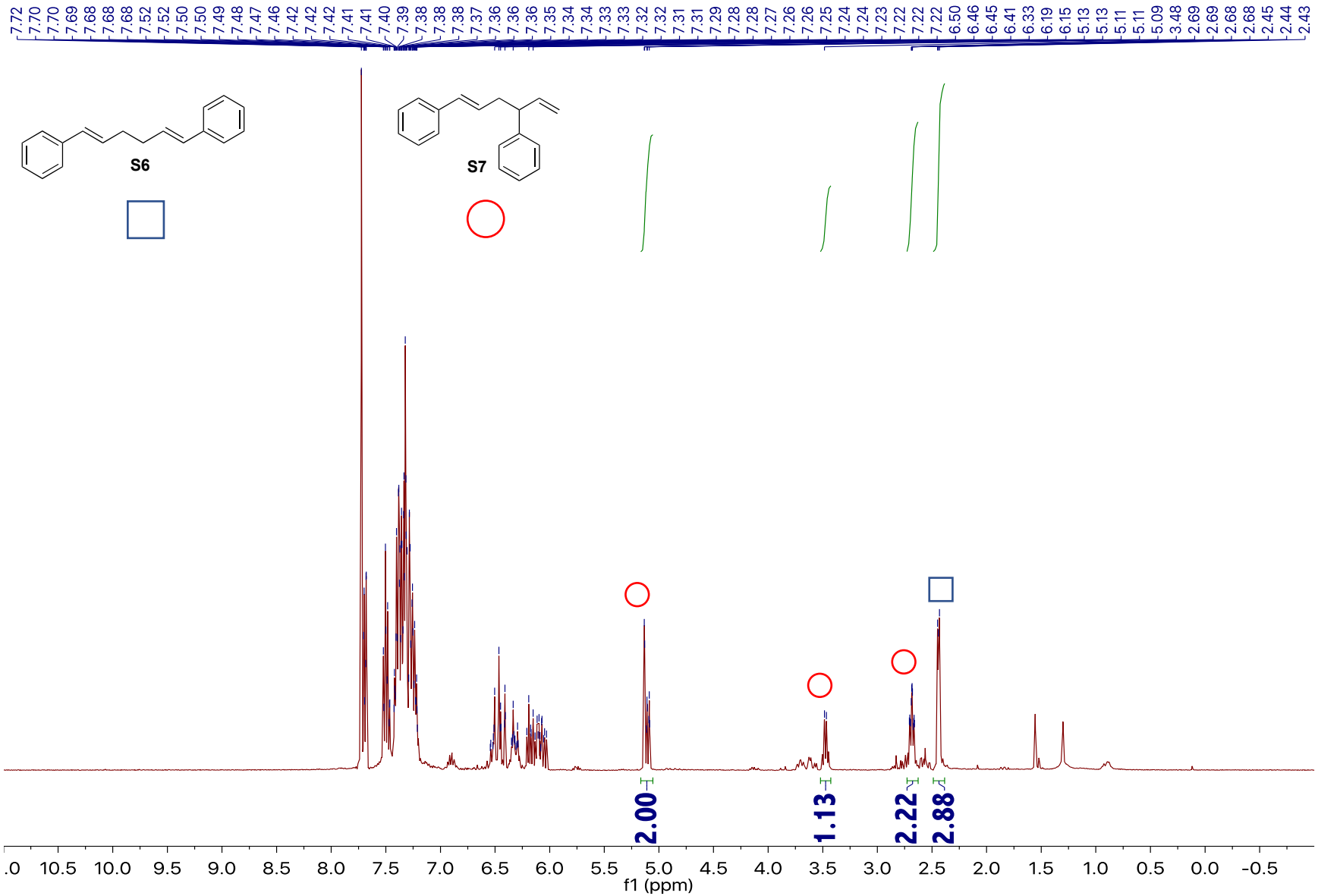
Compound S3: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



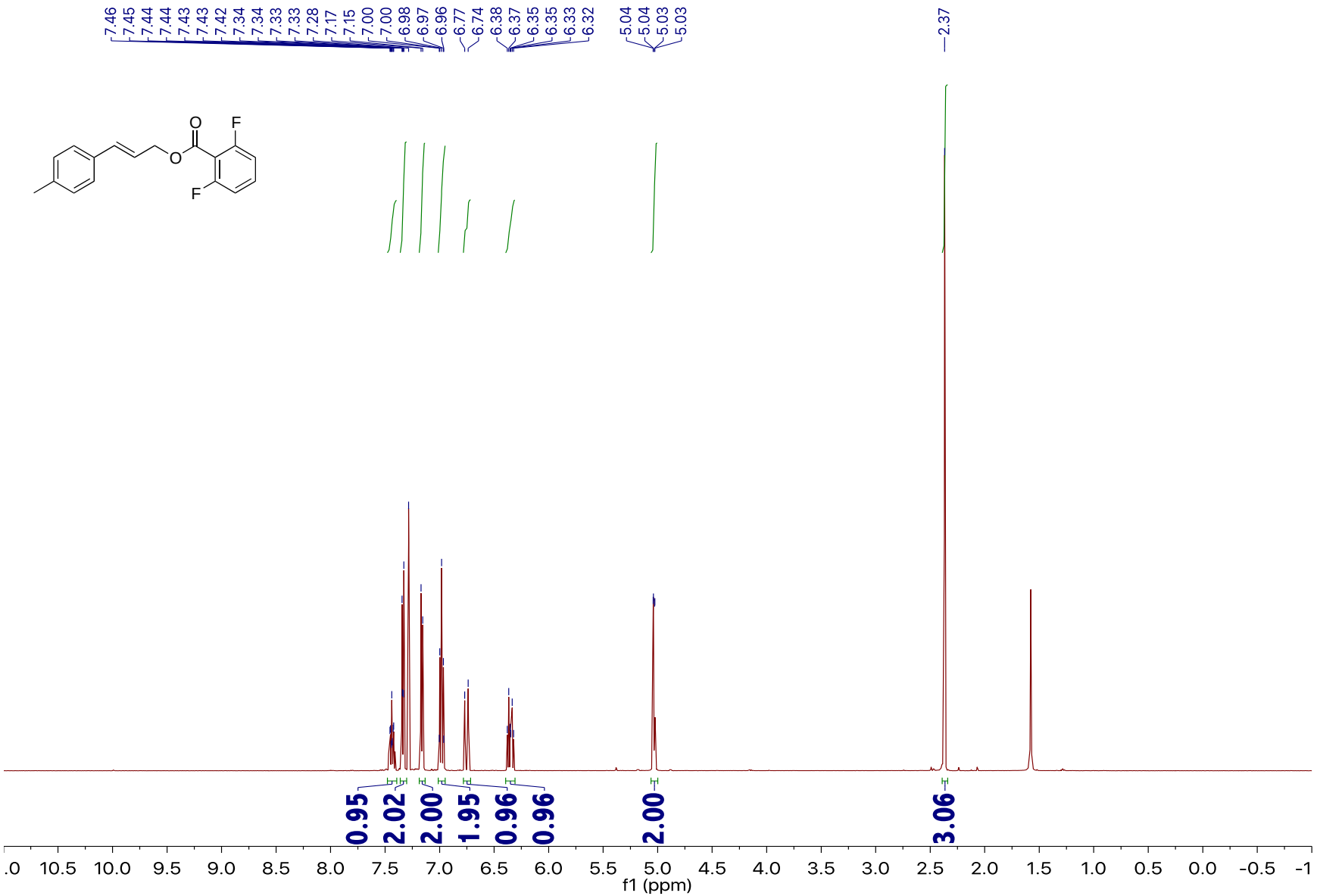
Compound S4: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



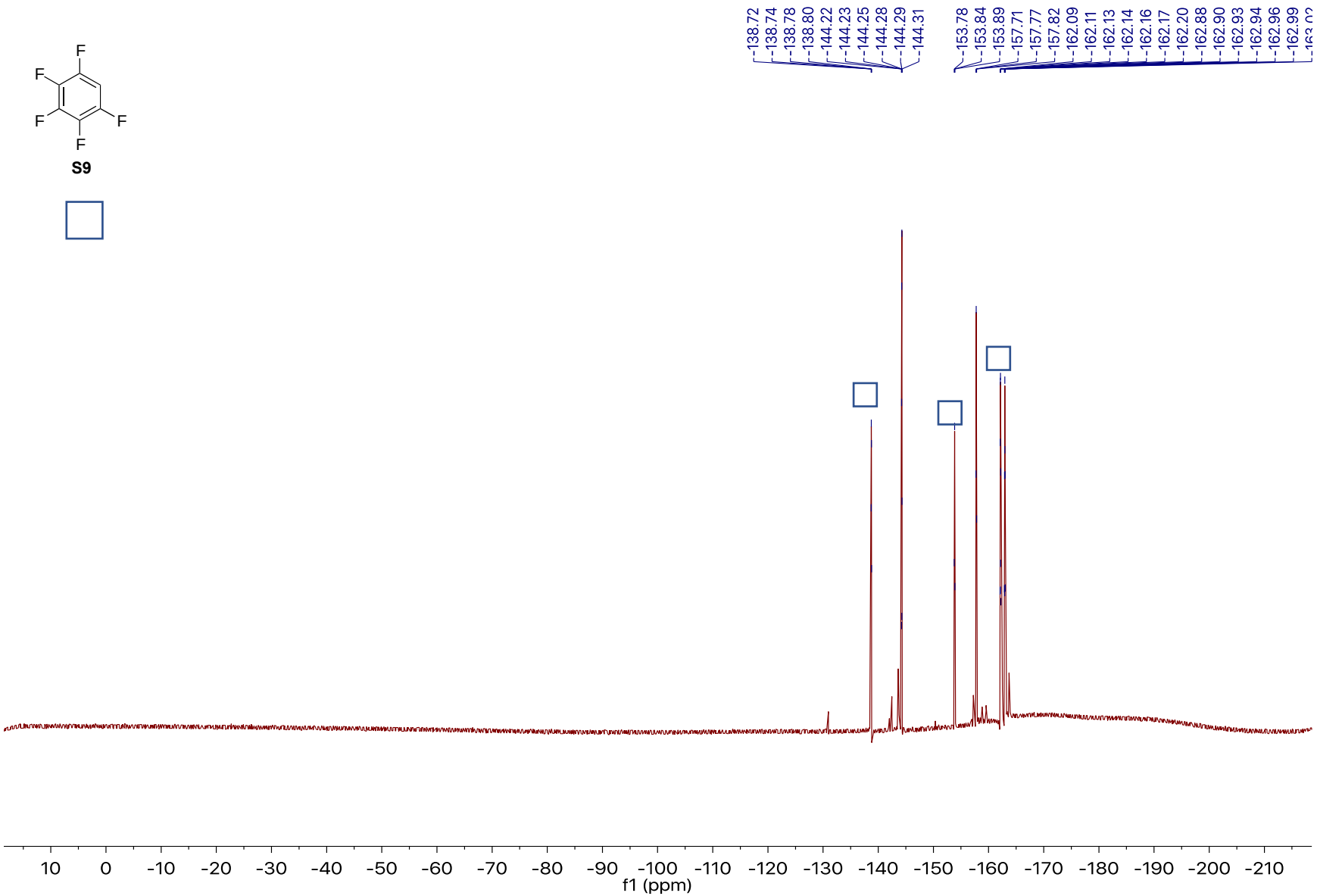
Compound S5: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



Compounds S6 and S7: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



Compound S8: 400 MHz ^{1}H NMR spectrum in $CDCl_3$



Compound S9: 376 MHz ^{19}F NMR spectrum in $CDCl_3$