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Electronic Supplementary Information

Anti-Aminofluorination of Alkenes with Amidines Mediated by Hypervalent Iodine(III) Reagents

Hui Chen Atsushi Kaga and Shunsuke Chiba*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore.

E-mail: shunsuke@ntu.edu.sg

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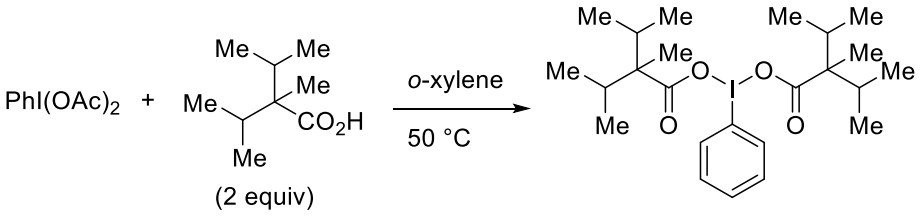
1. General

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{1}H, δ = 7.26) as the internal standard unless otherwise stated]. ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ = 77.00) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dddd = doublet of doublet of doublet of doublet, dt = doublet of triplet, tt = triplet of triplet, m = multiplet, br = broad. IR spectra were recorded on a Shimadzu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. $PhI(OAc)_2$, Et_3N•3HF, and benzonitrile were purchased from Sigma-Aldrich Co., Inc. 3,5-difluorobenzonitrile was purchased from Apollo Scientific Ltd.

Caution: Hydrofluoric acid (HF) is an extremely dangerous chemical, which should be handled with great caution. It is very toxic by inhalation, skin and eye contact as well as ingestion. Appropriate personal protection equipment such as goggles, gloves, and laboratory coats should be worn when handling HF. Although Et_3N•3HF is much less corrosive than HF, any contact and ingestion should be avoided.

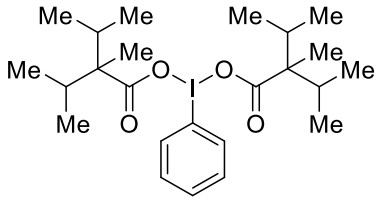
2. Synthesis of iodobenzene di(2-isopropyl-2,3-dimethylbutanoate) PhI[OCOC(*i*-Pr)$_2$Me]$_2$



To a 50 mL round-bottomed flask was added $PhI(OAc)_2$ (1.023 g, 3.18 mmol) and 2-isopropyl-2,3-dimethylbutanoic acid[1] (1.005 g, 6.35 mmol) in 20 mL *o*-xylene. The flask was heated at 50 ºC under reduced pressure (30 mbar) to remove the solvent and generated acetic acid. The residue was added 20 mL *o*-xylene and evaporated again to

provide the iodobenzene di(2-isopropyl-2,3-dimethylbutanoate) (1.644 g, 3.17 mmol) in quantitative yield as a yellow oil.

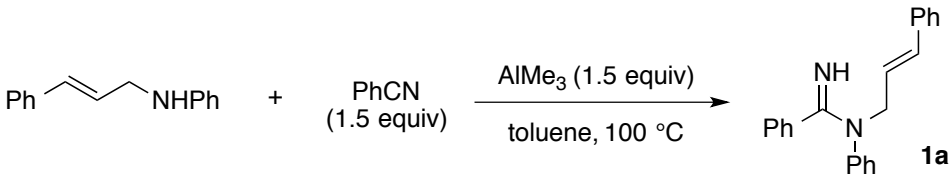
Iodobenzene di(2-isopropyl-2,3-dimethylbutanoate):



IR (NaCl) 3061, 2970, 2878, 1694, 1643, 1584, 1472, 1443, 1393, 1373, 1246, 1161, 1125, 1051, 781, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (12H, d, J = 6.8 Hz), 0.80 (12H, d, J = 6.8 Hz), 0.92 (6H, s), 1.87 (4H, sept, J = 6.8 Hz), 7.45 (2H, t, J = 7.6 Hz), 7.55 (1H, t, J = 7.6 Hz), 8.06 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 17.5, 18.4, 32.7, 53.4, 121.9, 130.4, 131.2, 135.0, 181.1; ESIHRMS: Found: m/z 519.1980. Calcd for $C_{24}H_{40}O_4I$: $(M+H)^+$ 519.1971.

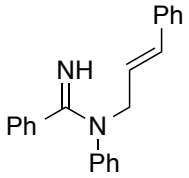
3. Synthesis of *N*-alkenylamidines 1[2]

A typical procedure for synthesis of *N*-alkenylamidine 1a:



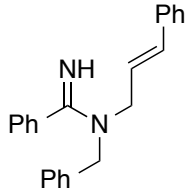
To a mixture of *N*-cinnamylaniline[3] (2.774 g, 13.25 mmol) in toluene (15 mL) was added trimethylaluminum (2M solution in toluene, 10.0 mL, 20.0 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred for 1 h. A solution of benzonitrile (2.0 mL, 19.50 mmol) in toluene (4.0 mL) was added and the mixture was heated to 100 °C for 20 h. After being cooled to room temperature, the reaction was carefully quenched with 20% NaOH solution (30 mL), and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The resulting residue was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 80:20 then triethylamine:ethyl acetate = 3:97) to afford **1a** (2.604 g, 8.34 mmol) in 63% yield as a pale yellow solid.

***N*-Cinnamyl-*N*-phenylbenzimidamide (1a):**[4]



mp: 87-88 °C; IR (NaCl) 3310, 3032, 2924, 1674, 1566, 1497, 1435, 1396, 1234, 1180, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 (2H, d, *J* = 4.4 Hz), 6.44-6.54 (2H, m), 6.95-7.00 (3H, m), 7.09-7.21 (6H, m), 7.25-7.36 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 124.9, 125.5, 126.4, 126.9, 127.3, 127.6, 128.0, 128.4, 128.6, 128.8, 131.9, 136.9, 138.6, 145.3, 167.8; ESIHRMS: Found: m/z 313.1699. Calcd for $C_{22}H_{21}N_2$: $(M+H)^+$ 313.1705.

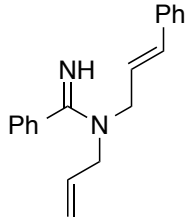
***N*-Benzyl-*N*-cinnamylbenzimidamide (1b):**[4]



50% yield as a pale yellow solid from (*E*)-*N*-benzyl-3-phenylprop-2-en-1-amine[5] and benzonitrile.

mp: 73-74 °C; IR (NaCl) 3310, 3024, 2932, 1667, 1566, 1450, 1358, 1180, 1134, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.02 (2H, d, *J* = 5.6 Hz), 4.61 (2H, s), 5.34 (1H, s br), 6.18 (1H, dt, *J* = 6.0, 16.0 Hz), 6.38 (1H, d, *J* = 16.0 Hz), 7.21-7.42 (15H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.1, 50.1, 125.0, 126.2, 126.4, 126.9, 127.3, 127.4, 128.37, 128.39, 128.43, 128.8, 132.3, 136.5, 137.9, 138.4, 169.4; ESIHRMS: Found: m/z 327.1864. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

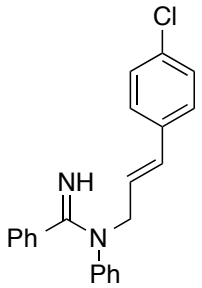
***N*-Allyl-*N*-cinnamylbenzimidamide (1c):**[4]



62% yield as a pale yellow oil from (*E*)-*N*-allyl-3-phenylprop-2-en-1-amine[6] and benzonitrile. This compound was purified by flash column chromatography (silica gel; CH_2Cl_2:MeOH = 98:2 then triethylamine:ethyl acetate = 3:97).

IR (NaCl) 3318, 3063, 3024, 2916, 1574, 1443, 1420, 1358, 1188, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.93 (2H, d, *J* = 4.4 Hz), 4.07 (2H, d, *J* = 6.0 Hz), 5.17-5.21 (2H, m), 5.79-5.88 (1H, m), 6.21 (1H, dt, *J* = 6.0, 16.0 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 7.22 (1H, t, *J* = 7.2 Hz), 7.31 (2H, t, *J* = 7.6 Hz), 7.36-7.38 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.2, 49.7, 116.8, 125.4, 126.3, 126.5, 127.5, 128.4, 128.5, 128.9, 132.2, 133.8, 136.7, 138.5, 169.1; ESIHRMS: Found: m/z 277.1701. Calcd for $C_{19}H_{21}N_2$: $(M+H)^+$ 277.1705.

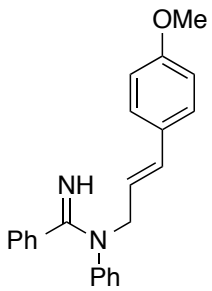
(*E*)-*N*-(3-(4-Chlorophenyl)allyl)-*N*-phenylbenzimidamide (1d):[4]



59% yield as a pale yellow solid from (*E*)-*N*-(3-(4-chlorophenyl)allyl)aniline[7] and benzonitrile.

mp: 129-130 °C; IR (NaCl) 3310, 3024, 2909, 1659, 1566, 1489, 1396, 1288, 1150, 1088, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 (2H, ddd, *J* = 1.2, 3.2, 14.8 Hz), 6.33 (1H, s br), 6.45-6.46 (2H, m), 6.96-7.99 (3H, m), 7.12 (2H, t, *J* = 7.6 Hz), 7.18-7.31 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 125.1, 126.2, 126.9, 127.57, 127.64, 128.1, 128.5, 128.7, 128.9, 130.7, 132.9, 135.4, 138.4, 145.2, 167.8; ESIHRMS: Found: m/z 347.1315. Calcd for $C_{22}H_{20}N_2Cl$: $(M+H)^+$ 347.1315.

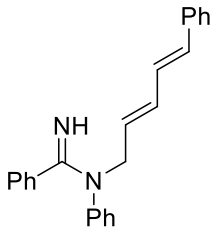
(*E*)-*N*-(3-(4-Methoxyphenyl)allyl)-*N*-phenylbenzimidamide (1e):[4]



83% yield as a pale yellow oil from (*E*)-*N*-(3-(4-methoxyphenyl)allyl)aniline[7] and benzonitrile.

IR (NaCl) 3310, 3032, 2932, 2839, 1566, 1504, 1396, 1350, 1250, 1034, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.76 (3H, s), 4.70 (2H, d, *J* = 6.0 Hz), 6.33 (1H, dt, *J* = 6.0, 16.0 Hz), 6.45 (1H, d, *J* = 16.0 Hz), 6.81 (2H, d, *J* = 8.8 Hz), 6.95-7.00 (3H, m), 7.11 (2H, t, *J* = 7.6 Hz), 7.14-7.20 (3H, m), 7.27-7.31 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7, 55.2, 113.8, 123.2, 124.9, 126.9, 127.5, 127.6, 128.0, 128.6, 128.7, 129.7, 131.4, 138.6, 145.3, 159.0, 167.7; ESIHRMS: Found: m/z 343.1811. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

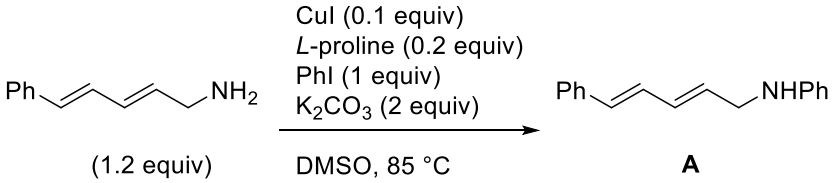
_N_-Phenyl-_N_-((2_E_,4_E_)-5-phenylpenta-2,4-dien-1-yl)benzimidamide (1f):



64% yield as a yellow oil from *N*-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-yl)aniline **A** (preparation method was shown below) and benzonitrile.

IR (NaCl) 3314, 3059, 3024, 1587, 1568, 1494, 1447, 1393, 1359, 1179, 989 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.66 (2H, d, *J* = 6.0 Hz), 6.06 (1H, td, *J* = 6.0, 15.2 Hz), 6.35 (1H, dd, *J* = 10.4, 15.2 Hz), 6.47 (1H, d, *J* = 15.6 Hz), 6.77 (1H, dd, *J* = 10.4, 15.6 Hz), 6.97-7.00 (3H, m), 7.11-7.21 (6H, m), 7.26-7.36 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.4, 125.0, 126.2, 126.8, 127.3, 127.6, 128.0, 128.47, 128.50, 128.7, 128.8, 129.7, 131.9, 132.3, 137.2, 138.5, 145.3, 167.7; ESIHRMS: Found: m/z 339.1868. Calcd for $C_{24}H_{23}N_2$: $(M+H)^+$ 339.1861.

Preparation of _N_-((2_E_,4_E_)-5-phenylpenta-2,4-dien-1-yl)aniline A:

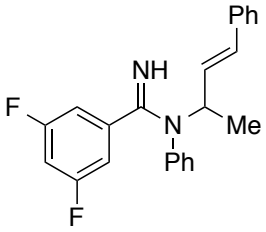


To a 50 mL two-neck round-bottomed flask under a nitrogen atmosphere was added iodobenzene (0.95 mL, 8.53 mmol), (2*E*,4*E*)-5-phenylpenta-2,4-dien-1-

amine[8] (1.629 g, 10.23 mmol), CuI (0.163 g, 0.85 mmol), *L*-proline (0.196 g, 1.71 mmol), and K_2CO_3 (2.358 g, 17.06 mmol) in DMSO (10 mL). The mixture was then heated to 85 °C. After 20 h, the mixture was cooled down to room temperature and quenched with pH 9 buffer (20 mL). The mixture was then extracted three times with diethyl ether, and the combined organic layers were washed with pH 9 buffer, water, brine, dried over $MgSO_4$, and concentrated. The crude material was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 95:5) to provide the aniline **A** (1.582 g, 6.72 mmol) in 79% yield as a yellow solid.

mp: 70-71 °C; IR (NaCl) 3420, 3021, 2926, 1601, 1504, 1447, 1429, 1317, 1254, 989 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.79 (1H, s br), 3.86 (2H, d, *J* = 5.6 Hz), 5.92 (1H, td, *J* = 5.6, 15.2 Hz), 6.42 (1H, dd, *J* = 10.4, 15.2 Hz), 6.51 (1H, d, *J* = 15.6 Hz), 6.64 (2H, d, *J* = 7.6 Hz), 6.72 (1H, t, *J* = 8.0 Hz), 6.78 (1H, dd, *J* = 10.4, 15.6 Hz), 7.17-7.23 (3H, m), 7.30 (2H, t, *J* = 8.0 Hz), 7.37 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.9, 113.0, 117.6, 126.3, 127.5, 128.3, 128.6, 129.2, 131.2, 131.9, 132.1, 137.2, 148.0; ESIHRMS: Found: m/z 236.1434. Calcd for $C_{17}H_{18}N$: $(M+H)^+$ 236.1439.

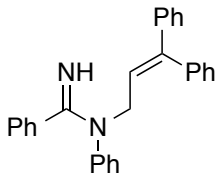
(*E*)-3,5-Difluoro-*N*-phenyl-*N*-(4-phenylbut-3-en-2-yl)benzimidamide (1g):[4]



62% yield as a yellow oil from (*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline and 3,5-difluorobenzonitrile.

IR (NaCl) 3318, 3063, 3032, 2978, 1589, 1489, 1404, 1304, 1234, 1140, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (3H, d, *J* = 6.8 Hz), 5.59 (1H, s br), 6.34 (1H, dd, *J* = 6.4, 16.0 Hz), 6.51 (1H, d, *J* = 16.0 Hz), 6.59 (1H, tt, *J* = 2.4, 8.8 Hz), 6.79 (2H, d, *J* = 6.0 Hz), 7.00 (2H, d, *J* = 7.6 Hz), 7.08-7.25 (4H, m), 7.28-7.36 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.8, 54.0, 103.9 (t, *J* = 25.2 Hz), 110.8 (dd, *J* = 7.4, 18.9 Hz), 126.4, 126.8, 127.5, 128.5, 128.6, 130.4, 130.5, 130.7, 136.9, 140.7, 142.2 (t, *J* = 8.8 Hz), 162.3 (dd, *J* = 12.4, 248.2 Hz), 165.7; ESIHRMS: Found: m/z 363.1670. Calcd for $C_{23}H_{21}N_2F_2$: $(M+H)^+$ 363.1673.

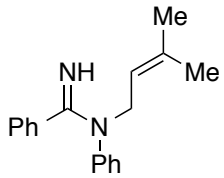
***N*-(3,3-Diphenylallyl)-*N*-phenylbenzimidamide (1h):**[4]



67% yield as a sticky pale yellow oil from *N*-(3,3-diphenylallyl)aniline[4] and benzonitrile.

IR (NaCl) 3310, 3055, 3032, 2940, 1589, 1566, 1497, 1443, 1396, 1180, 1142, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.81 (2H, d, *J* = 6.4 Hz), 6.42 (1H, t, *J* = 6.4 Hz), 6.85-6.91 (4H, m), 6.97 (1H, t, *J* = 7.6 Hz), 7.08 (2H, t, *J* = 7.6 Hz), 7.14-7.29 (13H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.5, 124.8, 125.0, 127.1, 127.2, 127.3, 127.4, 127.7, 127.98, 128.00, 128.04, 128.6, 128.7, 129.6, 138.5, 139.1, 141.8, 143.8, 144.7, 167.9; ESIHRMS: Found: m/z 389.2020. Calcd for $C_{28}H_{25}N_2$: $(M+H)^+$ z 389.2018.

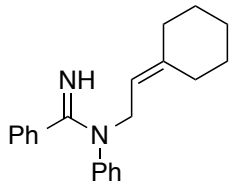
***N*-(3-Methylbut-2-en-1-yl)-*N*-phenylbenzimidamide (1i):**[4]



57% yield as a yellow oil from *N*-(3-methylbut-2-en-1-yl)aniline[9] and benzonitrile.

IR (NaCl) 3010, 3055, 2924, 1674, 1566, 1498, 1396, 1234, 1180, 1142, 1026, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (3H, s), 1.69 (3H, d, *J* = 1.2 Hz), 4.53 (2H, d, *J* = 6.4 Hz), 5.45 (1H, tq, *J* = 1.2, 6.4 Hz), 6.39 (1H, s br), 6.95-6.99 (3H, m), 7.09-7.18 (5H, m), 7.26-7.30 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 25.6, 49.6, 120.5, 124.8, 127.1, 127.7, 127.9, 128.5, 128.6, 134.6, 138.7, 145.3, 167.8; ESIHRMS: Found: m/z 265.1706. Calcd for $C_{18}H_{21}N_2$: $(M+H)^+$ 265.1705.

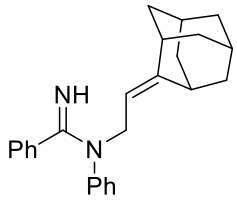
***N*-(2-Cyclohexylideneethyl)-*N*-phenylbenzimidamide (1j):**[4]



64% yield as a yellow solid from *N*-(2-cyclohexylideneethyl)aniline[4] and benzonitrile.

mp: 38-39 °C; IR (NaCl) 3318, 2924, 2855, 1566, 1497, 1443, 1404, 1335, 1219, 1180 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23-1.46 (6H, m), 1.97-2.06 (4H, m), 4.53 (2H, d, *J* = 6.8 Hz), 5.41 (1H, t, *J* = 6.8 Hz), 6.96-6.99 (3H, m), 7.10-7.20 (5H, m), 7.27-7.31 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 27.3, 28.3, 28.7, 36.9, 48.4, 116.7, 124.9, 127.5, 127.7, 127.9, 128.4, 128.6, 138.8, 142.9, 145.1, 167.9; ESIHRMS: Found: m/z 305.2015. Calcd for $C_{21}H_{25}N_2$: $(M+H)^+$ 305.2018.

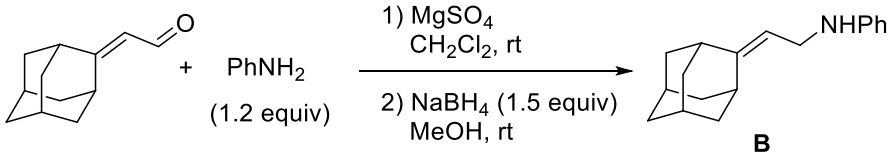
_N_-(2-(Adamantan-2-ylidene)ethyl)-_N_-phenylbenzimidamide (1k):



75% yield as a white solid from *N*-(2-(adamantan-2-ylidene)ethyl)aniline **B** (preparation method was shown below) and benzonitrile.

mp: 95-96 °C; IR (NaCl) 3300, 3061, 2907, 2847, 1672, 1587, 1564, 1493, 1385, 1308, 1182, 1140, 959 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.31-1.34 (2H, m), 1.67-1.83 (10H, m), 2.35 (1H, m), 2.65 (1H, m), 4.51 (2H, d, *J* = 6.8 Hz), 5.40 (1H, t, *J* = 6.8 Hz), 6.94-6.99 (3H, m), 7.10 (2H, t, *J* = 7.6 Hz), 7.15-7.17 (3H, m), 7.27-7.30 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.2, 32.1, 36.9, 38.5, 39.4, 40.3, 47.8, 111.6, 124.8, 127.6, 127.7, 127.8, 128.3, 128.5, 138.8, 144.9, 150.9, 167.9; ESIHRMS: Found: m/z 357.2327. Calcd for $C_{25}H_{29}N_2$: $(M+H)^+$ 357.2331.

Preparation of _N_-(2-adamantan-2-ylidene)ethyl)aniline B:

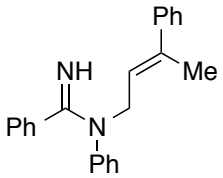


To a 50 mL two-neck round-bottomed flask under a nitrogen atmosphere was added 2-(adamantan-2-ylidene)acetaldehyde[10] (2.505 g, 14.21 mmol), aniline (1.56 mL, 17.05 mmol) and anhydrous $MgSO_4$ (1.50 g, 12.46 mmol) in CH_2Cl_2 (15 mL). The reaction mixture was stirred at room temperature for 12 h. The mixture was then filtered and washed with CH_2Cl_2. The filtrate was then concentrated to give the crude imine, which was dissolved in 15 mL

methanol. $NaBH_4$ (0.806 g, 21.32 mmol) was then added in four portions at room temperature. The reaction mixture was stirred for 0.5h after addition of the $NaBH_4$. The solvent was removed in vacuo and water (20 mL) was added. The mixture was then extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over $MgSO_4$. Removal of the solvents in vacuo gave the crude product, which was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 90:10) to give amine **B** (2.715 g, 10.72 mmol) in 75% yield as a yellow oil.

IR (NaCl) 3412, 3049, 2913, 2847, 1601, 1504, 1449, 1427, 1317, 1252, 1098 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.73-1.97 (12H, m), 2.38 (1H, m), 2.89 (1H, m), 3.53 (1H, s br), 3.68 (2H, d, *J* = 6.8 Hz), 5.25 (1H, t, *J* = 6.8 Hz), 6.62 (2H, d, *J* = 8.4 Hz), 6.69 (1H, t, *J* = 7.6 Hz), 7.17 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.4, 32.4, 37.1, 39.0, 39.7, 40.3, 40.7, 112.9, 113.2, 117.2, 129.1, 148.5, 151.8; ESIHRMS: Found: m/z 254.1910. Calcd for $C_{18}H_{24}N$: $(M+H)^+$ 254.1909.

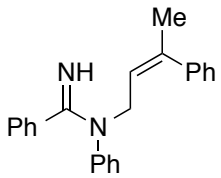
(*E*)-*N*-Phenyl-*N*-(3-phenylbut-2-en-1-yl)benzimidamide (1l):[4]



1o (E/Z = 20:1) was obtained in 63% yield as a pale yellow oil from (*E*)-*N*-(3-phenylbut-2-en-1-yl)aniline (E/Z = 20:1)[7] and benzonitrile.

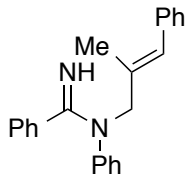
IR (NaCl) 3310, 3032, 2924, 1589, 1566, 1498, 1443, 1396, 1180, 1150, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.92 (3H, s), 4.75 (2H, d, *J* = 6.4 Hz), 6.06 (1H, t, *J* = 6.4 Hz), 6.43 (1H, s br), 6.96-7.01 (3H, m), 7.10-7.22 (6H, m), 7.26-7.35 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8, 50.0, 124.0, 125.0, 125.7, 126.8, 127.2, 127.6, 127.96, 128.03, 128.6, 128.7, 137.1, 138.6, 143.2, 145.2, 167.9; ESIHRMS: Found: m/z 327.1860. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

(*Z*)-*N*-Phenyl-*N*-(3-phenylbut-2-en-1-yl)benzimidamide (1m):[4]



67% yield as a yellow oil from (*Z*)-*N*-(3-phenylbut-2-en-1-yl)aniline[4] and benzonitrile. IR (NaCl) 3010, 3032, 2970, 1589, 1566, 1497, 1435, 1396, 1180, 1142, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.01 (3H, s), 4.47 (2H, d, *J* = 6.4 Hz), 5.82 (1H, t, *J* = 6.4 Hz), 6.01 (1H, s br), 6.80-7.82 (2H, m), 6.92-7.98 (3H, m), 7.07 (2H, t, *J* = 7.6 Hz), 7.13-7.27 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 50.3, 122.9, 124.8, 126.7, 127.1, 127.6, 127.8, 127.9, 128.0, 128.5, 128.7, 138.5, 139.5, 141.1, 144.9, 167.7; ESIHRMS: Found: m/z 327.1858. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

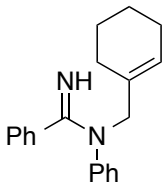
(*E*)-*N*-(2-Methyl-3-phenylallyl)-*N*-phenylbenzimidamide (1n):[4]



59% yield as a pale yellow oil from (*E*)-*N*-(2-methyl-3-phenylallyl)aniline[4] and benzonitrile.

IR (NaCl) 3318, 3048, 3032, 2916, 1558, 1497, 1435, 1396, 1227, 1180, 1026, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (3H, s), 4.89 (2H, s), 6.50 (1H, s), 6.96-7.03 (3H, m), 7.12 (2H, d, *J* = 7.6 Hz), 7.17-7.23 (6H, m), 7.29-7.35 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 58.3, 124.8, 126.0, 126.2, 126.4, 127.7, 128.0, 128.1, 128.6, 128.8, 128.9, 134.9, 138.0, 138.8, 145.6, 168.1; ESIHRMS: Found: m/z 327.1864. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

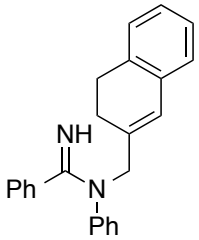
***N*-(Cyclohex-1-en-1-ylmethyl)-*N*-phenylbenzimidamide (1o):**[4]



53% yield as a pale yellow oil from *N*-(cyclohex-1-en-1-ylmethyl)aniline[11] and benzonitrile.

IR (NaCl) 3318, 2924, 2855, 1589, 1566, 1497, 1435, 1396, 1180, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.53-1.67 (4H, m), 1.99-2.03 (4H, m), 4.45 (2H, s), 5.65-5.66 (1H, m), 6.94-6.97 (3H, m), 7.08-7.22 (5H, m), 7.29-7.31 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 22.5, 25.0, 26.7, 56.8, 122.8, 124.5, 126.3, 127.7, 128.0, 128.4, 128.6, 134.0, 138.8, 145.8, 167.9; ESIHRMS: Found: m/z 291.1860. Calcd for $C_{20}H_{23}N_2$: $(M+H)^+$ 291.1861.

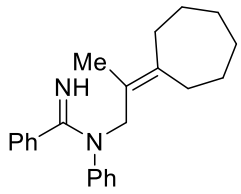
_N_-((3,4-Dihydronaphthalen-2-yl)methyl)-_N_-phenylbenzimidamide (1p):[4]



59% yield as a pale yellow oil from *N*-((3,4-dihydronaphthalen-2-yl)methyl)aniline[12] and benzonitrile.

IR (NaCl) 3318, 3032, 2932, 2886, 1566, 1497, 1450, 1396, 1304, 1180, 1142 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (2H, dd, *J* = 8.0, 8.4 Hz), 2.81 (2H, dd, *J* = 8.0, 8.4 Hz), 4.76 (2H, s), 6.43 (1H, s), 6.93-7.01 (4H, m), 7.07-7.13 (5H, m), 7.18-7.23 (3H, m), 7.32-7.34 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 27.8, 55.7, 123.7, 124.7, 125.8, 126.29, 126.30, 126.5, 127.1, 127.6, 128.1, 128.5, 128.8, 134.2, 134.8, 138.0, 138.7, 145.4, 168.1; ESIHRMS: Found: m/z 339.1863. Calcd for $C_{24}H_{23}N_2$: $(M+H)^+$ 339.1861.

_N_-(2-Cycloheptylidenepropyl)-_N_-phenylbenzimidamide (1q):

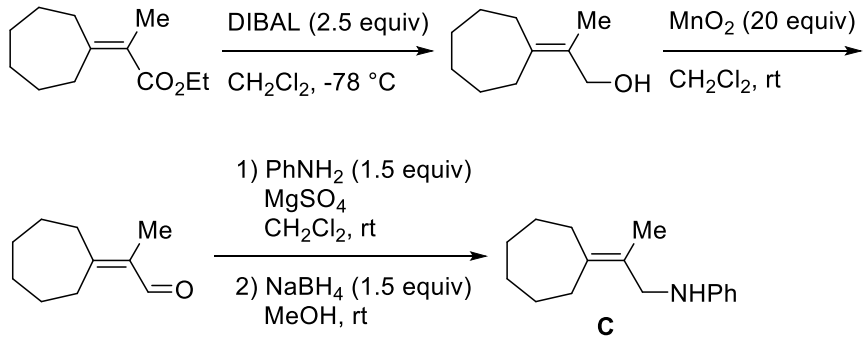


71% yield as a pale yellow oil from *N*-(2-cycloheptylidenepropyl)aniline **C** (preparation method was shown below) and benzonitrile.

Yellow oil; IR (NaCl) 3318, 3059, 2918, 2851, 1587, 1574, 1495, 1445, 1396, 1175, 1136, 939 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.51 (8H, m), 1.77 (3H, s), 2.12-2.20 (4H, m), 4.62 (2H, s), 6.94-6.99 (3H, m), 7.09 (2H, t, *J* = 7.6 Hz), 7.16-7.18 (3H,

m), 7.28-7.30 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.0, 27.2, 27.5, 28.4, 29.0, 31.0, 32.0, 52.0, 124.8, 125.1, 127.5, 127.7, 127.9, 128.3, 128.5, 138.0, 139.1, 145.0; ESIHRMS: Found: m/z 333.2340. Calcd for $C_{23}H_{29}N_2$: $(M+H)^+$ 333.2331.

Preparation of *N*-(2-Cycloheptylidenepropyl)aniline C:



To a 50 mL two-neck round-bottomed flask was added ethyl 2-cycloheptylidenepropanoate[13] (1.059 g, 5.40 mmol) in CH_2Cl_2 (10 mL). DIBAL (1M solution in toluene, 13.5 mL, 13.5 mmol) was added in a dropwise manner at -78 °C. The reaction mixture was stirred at the same temperature for 2 h and raised to 0 °C. The reaction was carefully quenched by 2M HCl and extracted with ethyl acetate. The combined organic layers were washed with saturated $NaHCO_3$ and water, dried over $MgSO_4$, and concentrated. Removal of the solvents in vacuo gave the crude product, which was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 4:1) to give 2-cycloheptylidenepropan-1-ol (0.378 g, 2.45 mmol, not pure, contains some regioisomer 2-(cyclohept-1-en-1-yl)propan-1-ol, used directly for the next step) in 45% yield as a colorless oil.

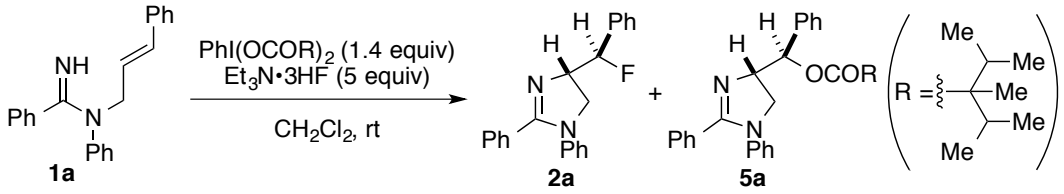
To a 50 mL two-neck round-bottomed flask was added 2-cycloheptylidenepropan-1-ol (0.378 g, 2.45 mmol) and MnO_2 (4.260 g, 49.0 mmol) in CH_2Cl_2 (10 mL). After stirring for 1h at room temperature, the solid was filtered through celite and washed with CH_2Cl_2. The filtrate was concentrated to afford the crude 2-cycloheptylidenepropanal, which was used for the next reductive amination step without further purification.

Aniline **C** was prepared in a similar way to aniline **B** from 2-cycloheptylidenepropanal and aniline (1.5 equiv was used).

Yield: 44% (two steps from 2-(cyclohept-1-en-1-yl)propan-1-ol); pale yellow oil; IR (NaCl) 3418, 2920, 2851, 1601, 1504, 1443, 1425, 1315, 1250, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51-1.60 (8H, m), 1.75 (3H, s), 2.25-2.34 (4H, m), 3.47 (1H, s br), 3.66 (2H, s), 6.60 (2H, d, J = 8.0 Hz), 6.68 (1H, t, J = 7.2 Hz), 7.17 (2H, t, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 27.2, 28.3, 28.7, 29.1, 31.2, 32.2, 47.0, 112.6, 117.0, 125.4, 129.2, 138.5, 148.9; ESIHRMS: Found: m/z 252.1735. Calcd for $C_{16}H_{23}NNa$: $(M+Na)^+$ 252.1728.

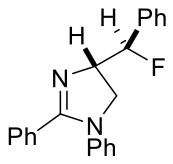
4. Aminofluorination of alkenylamidines for the synthesis of 2-imidazolines 2

Typical Procedure: synthesis of 2a



To a stirred solution of PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (215.7 mg, 0.416 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of *N*-cinnamyl-*N*-phenylbenzimidamide (**1a**) (92.8 mg, 0.297 mmol) in 2 mL CH_2Cl_2 and Et_3N•3HF (242 μL, 1.485 mmol). The reaction mixture was then stirred for 20 h at room temperature under a N_2 atmosphere. The mixture was quenched with 2M NaOH solution. The organic compounds were then extracted twice with CH_2Cl_2. The combined organic extracts were washed with 2M NaOH and brine, and finally dried over $MgSO_4$. The solvent was removed in vacuo to afford a crude residue, which was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 80:20 then hexane:ethyl acetate = 50:50) to provide **2a** (72.0 mg, 0.218 mmol) in 79% yield as well as aminooxygenation product **5a** (11.8 mg, 0.025 mmol) in 8% yield.

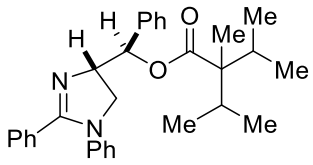
(*S)-4-((*R**)-Fluoro(phenyl)methyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2a):**



Pale yellow solid; mp: 105-107 °C; IR (NaCl) 3061, 3030, 2953, 1614, 1593, 1574, 1495, 1447, 1387, 1292, 1244, 1146, 962 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.01-4.03 (2H, m), 4.64 (1H, dddd, J = 3.6, 4.4, 9.6, 23.6 Hz), 5.82 (1H, dd, J = 3.6, 47.2 Hz), 6.75-6.77 (2H, m), 6.99 (1H, tt, J = 1.2, 7.6 Hz), 7.14 (2H, tt, J = 2.0, 7.6 Hz),

7.25-7.42 (8H, m), 7.50-7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.4 (d, J = 5.8 Hz), 69.0 (d, J = 22.3 Hz), 93.9 (d, J = 177.4 Hz), 123.0, 123.8, 125.4 (d, J = 8.2 Hz), 128.1, 128.2, 128.4, 128.7, 128.9, 130.1, 130.7, 137.6 (d, J = 20.0 Hz), 142.6, 163.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.5 (1F, dd, J = 23.7, 47.0 Hz); ESIHRMS: Found: m/z 331.1611. Calcd for $C_{22}H_{20}N_2F$: $(M+H)^+$ 331.1611.

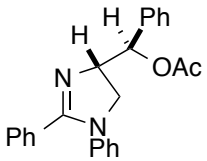
(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (5a):**



8% yield from **1a**, $PhI[OCOC(i\text{-}Pr)_2Me]_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

Yellow oil; IR (NaCl) 3063, 2970, 1738, 1715, 1614, 1593, 1504, 1454, 1393, 1300, 1229, 1146, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 (3H, d, J = 6.8 Hz), 0.81 (3H, d, J = 6.8 Hz), 0.84 (3H, d, J = 6.8 Hz), 0.85 (3H, d, J = 6.8 Hz), 1.01 (3H, s), 1.95-2.04 (2H, m), 4.04-4.13 (2H, m), 4.64 (1H, ddd, J = 4.0, 8.0, 10.8 Hz), 6.11 (1H, d, J = 4.0 Hz), 6.70-6.72 (2H, m), 6.99 (1H, t, J = 7.2 Hz), 7.15 (2H, t, J = 7.6 Hz), 7.21-7.29 (3H, m), 7.31-7.46 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.3, 17.6, 18.2, 18.4, 32.7, 32.8, 52.8, 54.8, 68.7, 77.2, 122.9, 123.7, 126.9, 127.9, 128.0, 128.3, 128.7, 128.8, 130.0, 130.7, 138.5, 142.7, 162.9, 175.4; ESIHRMS: Found: m/z 469.2857. Calcd for $C_{31}H_{37}N_2O_2$: $(M+H)^+$ 469.2855.

(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (3a):**[8]

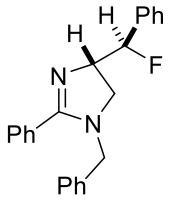


18% yield from **1a**, $PhI(OAc)_2$ (1.3 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

Yellow oil; IR (NaCl) 3040, 2940, 2886, 1736, 1643, 1597, 1497, 1412, 1304, 1234, 1026, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (3H, s), 3.86 (1H, dd, J = 6.0,

10.0 Hz), 4.16 (1H, dd, *J* = 10.0, 10.8 Hz), 4.71 (1H, ddd, *J* = 4.0, 6.0, 10.8 Hz), 6.09 (1H, d, *J* = 4.0 Hz), 6.59-6.61 (2H, m), 6.98 (1H, t, *J* = 7.6 Hz), 7.09-7.13 (2H, m), 7.24-7.45 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 54.4, 67.3, 76.6, 122.8, 123.8, 126.6, 127.9, 128.1, 128.2, 128.6, 128.7, 130.1, 130.2, 137.1, 142.1, 163.3, 169.8; ESIHRMS: Found: m/z 371.1763. Calcd for $C_{24}H_{23}N_2O_2$: $(M+H)^+$ 371.1760.

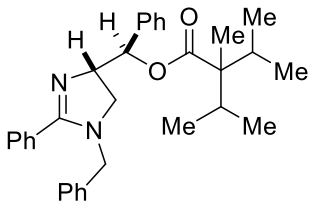
(*S)-1-Benzyl-4-((*R**)-fluoro(phenyl)methyl)-2-phenyl-4,5-dihydro-1*H*-imidazole (2b):**



70% yield from **1b**, $PhI[OCOC(i\text{-}Pr)_2Me]_2$ (1.4 equiv) and $Et_3N{\bullet}3HF$ (5 equiv); reaction time: 24 h.

White solid; mp: 72-73 °C; IR (NaCl) 3065, 3030, 2928, 1614, 1593, 1574, 1495, 1454, 1410, 1360, 1300, 1246, 1136, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (1H, dd, *J* = 10.0, 11.2 Hz), 3.43 (1H, dd, *J* = 8.4, 10.0 Hz), 4.21 (1H, d, *J* = 16.0 Hz), 4.38 (1H, d, *J* = 16.0 Hz), 4.64 (1H, dddd, *J* = 3.6, 8.4, 11.2, 23.6 Hz), 5.76 (1H, dd, *J* = 3.6, 47.6 Hz), 7.21 (2H, d, *J* = 7.2 Hz), 7.25-7.43 (11H, m), 7.60-7.62 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.1 (d, *J* = 5.7 Hz), 52.4, 69.3 (d, *J* = 22.3 Hz), 94.1 (d, *J* = 176.7 Hz), 125.4 (d, *J* = 8.0 Hz), 126.8, 127.3, 128.0, 128.2, 128.3, 128.5, 128.6, 130.1, 130.6, 137.5, 137.7 (d, *J* = 20.1 Hz), 167.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -195.2 (1F, dd, *J* = 23.7, 47.4 Hz); ESIHRMS: Found: m/z 345.1760. Calcd for $C_{23}H_{22}N_2F$: $(M+H)^+$ 345.1767.

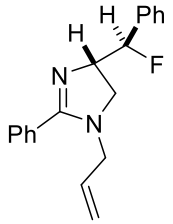
(*R)-((*S**)-1-Benzyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (5b):**



9% yield from **1b**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 24 h.

Yellow oil; IR (NaCl) 3063, 2968, 2878, 1728, 1614, 1574, 1495, 1454, 1393, 1308, 1227 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.80 (3H, d, *J* = 6.8 Hz), 0.83 (3H, d, *J* = 6.8 Hz), 0.84 (6H, d, *J* = 6.8 Hz), 1.04 (3H, s), 1.97-2.05 (2H, m), 3.43-3.51 (2H, m), 4.11 (1H, d, *J* = 16.0 Hz), 4.43 (1H, d, *J* = 16.0 Hz), 4.54 (1H, ddd, *J* = 4.8, 9.6, 9.6 Hz), 6.01 (1H, d, *J* = 4.8 Hz), 7.21 (2H, d, *J* = 6.8 Hz), 7.24-7.43 (11H, m), 7.55-7.57 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.4, 17.46, 17.54, 18.3, 18.4, 32.72, 32.74, 52.2, 52.8, 53.1, 69.3, 77.4, 127.0, 127.1, 127.4, 127.8, 128.2, 128.3, 128.4, 128.7, 130.1, 130.8, 137.7, 138.7, 167.4, 175.3; ESIHRMS: Found: m/z 483.3001. Calcd for $C_{32}H_{39}N_2O_2$: $(M+H)^+$ 483.3012.

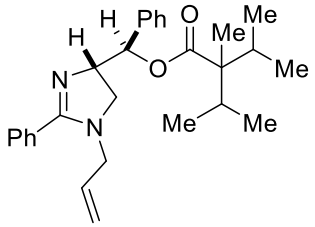
(*S)-1-Allyl-4-((*R**)-fluoro(phenyl)methyl)-2-phenyl-4,5-dihydro-1*H*-imidazole (2c):**



64% yield from **1c**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 24 h.

Colorless oil; IR (NaCl) 3063, 2928, 1620, 1593, 1574, 1497, 1454, 1416, 1288, 1246, 991, 924 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.43 (1H, dd, *J* = 10.0, 10.8 Hz), 3.49 (1H, dd, *J* = 8.4, 10.0 Hz), 3.59-3.76 (2H, m), 4.52 (1H, dddd, *J* = 3.6, 8.4, 10.8, 23.6 Hz), 5.17 (1H, dd, *J* = 1.2, 10.0 Hz), 5.21 (1H, dd, *J* = 1.6, 17.2 Hz), 5.73 (1H, tdd, *J* = 5.2, 10.0, 17.2 Hz), 5.77 (1H, dd, *J* = 3.6, 47.6 Hz), 7.29-7.44 (8H, m), 7.55-7.57 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 50.1 (d, *J* = 5.8 Hz), 51.2, 69.4 (d, *J* = 22.3 Hz), 94.2 (d, *J* = 176.5 Hz), 116.7, 125.4 (d, *J* = 8.0 Hz), 128.0, 128.1, 128.3, 128.4, 130.0, 130.8, 133.8, 137.9 (d, *J* = 20.2 Hz), 167.8; ^{19}F NMR (376 MHz, CDCl$_3$) δ -195.4 (1F, dd, *J* = 23.7, 47.4 Hz); ESIHRMS: Found: m/z 295.1604. Calcd for $C_{19}H_{20}N_2F$: $(M+H)^+$ 295.1611.

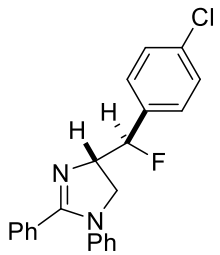
(*R)-((*S**)-1-Allyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (5c):**



8% yield from **1c**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 24 h.

Pale yellow oil; IR (NaCl) 2968, 2940, 1722, 1612, 1595, 1572, 1497, 1449, 1410, 1227, 1153, 1107, 926 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.81 (3H, d, *J* = 7.2 Hz), 0.84 (3H, d, *J* = 7.2 Hz), 0.86 (6H, d, *J* = 7.2 Hz), 1.05 (3H, s), 1.97-2.06 (2H, m), 3.48-3.58 (3H, m), 3.78 (1H, dddd, *J* = 1.2, 1.6, 5.2, 16.4 Hz), 4.52 (1H, ddd, *J* = 4.4, 8.8, 10.4 Hz), 5.16-5.24 (2H, m), 5.73 (1H, tdd, *J* = 5.2, 10.4, 17.2 Hz), 6.01 (1H, d, *J* = 4.4 Hz), 7.24-7.28 (1H, m), 7.31-7.41 (7H, m), 7.50-7.53 (2H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.4, 17.47, 17.53, 18.3, 18.4, 32.7, 32.8, 51.8, 52.1, 52.8, 69.2, 77.5, 116.8, 127.1, 127.8, 128.2 (overlapped), 128.3, 130.0, 130.8, 134.0, 138.9, 167.4, 175.4; ESIHRMS: Found: m/z 433.2851. Calcd for $C_{28}H_{37}N_2O_2$: $(M+H)^+$ 433.2855.

(*S)-4-((*R**)-(4-Chlorophenyl)fluoromethyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2d):**

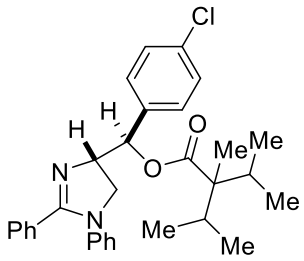


71% yield from **1d**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

White solid; mp: 152-153 °C; IR (NaCl) 3021, 2934, 2880, 1614, 1591, 1568, 1485, 1385, 1314, 1287, 1240, 1148, 1084, 1045, 1015 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.99 (1H, dd, *J* = 7.6, 9.6 Hz), 4.06 (1H, dd, *J* = 9.6, 10.4 Hz), 4.59 (1H, dddd, *J* = 4.4, 7.6, 10.4, 21.6 Hz), 5.71 (1H, dd, *J* = 4.4, 47.2 Hz), 6.75 (2H, d, *J* = 7.6 Hz), 7.00 (1H, t, *J* = 7.6 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.27 (2H, t, *J* = 7.6 Hz), 7.34-7.38 (5H, m),

7.48-7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8 (d, *J* = 5.6 Hz), 68.8 (d, *J* = 22.8 Hz), 93.6 (d, *J* = 177.4 Hz), 122.9, 123.8, 127.0 (d, *J* = 7.9 Hz), 128.1, 128.6, 128.75, 128.84, 130.2, 130.6, 134.2, 136.2 (d, *J* = 20.5 Hz), 142.6, 163.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -193.3 (1F, dd, *J* = 20.7, 47.0 Hz); ESIHRMS: Found: m/z 365.1221. Calcd for $C_{22}H_{19}N_2FCl$: $(M+H)^+$ 365.1221.

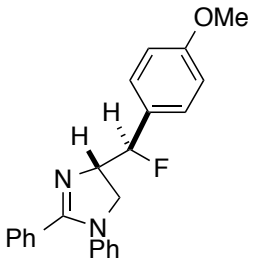
(*R)-(4-Chlorophenyl)((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)methyl 2-isopropyl-2,3-dimethylbutanoate (5d):**



8% yield from **1d**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

Pale yellow oil; IR (NaCl) 2968, 2880, 1726, 1593, 1574, 1495, 1393, 1287, 1225, 1146, 1051 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (3H, d, *J* = 7.2 Hz), 0.81 (3H, d, *J* = 6.8 Hz), 0.84 (3H, d, *J* = 6.8 Hz), 0.85 (3H, d, *J* = 6.8 Hz), 1.01 (3H, s), 1.96-2.04 (2H, m), 4.00 (1H, dd, *J* = 8.0, 9.6 Hz), 4.11 (1H, dd, *J* = 9.6, 10.4 Hz), 4.61 (1H, ddd, *J* = 4.8, 8.0, 10.4 Hz), 6.00 (1H, d, *J* = 4.8 Hz), 6.69 (2H, d, *J* = 7.6 Hz), 7.00 (1H, t, *J* = 7.6 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.23-7.29 (3H, m), 7.31-7.37 (4H, m), 7.42-7.44 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.4, 17.6, 18.3, 18.4, 32.7, 32.8, 52.9, 55.2, 68.4, 76.7, 122.9, 123.8, 128.0, 128.5 (overlapped), 128.7, 128.8, 130.1, 130.7, 133.8, 137.0, 142.6, 163.1, 175.4; ESIHRMS: Found: m/z 503.2461. Calcd for $C_{31}H_{36}N_2O_2Cl$: $(M+H)^+$ 503.2465.

(*S)-4-((*R**)-Fluoro(4-methoxyphenyl)methyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2e):**

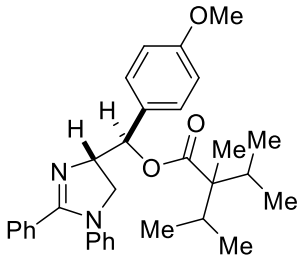


62% yield dr = 7.1:1 (the major diastereomer could be recrystallized from hexane/CH_2Cl_2) from **1e**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

The major diastereomer:

White solid; mp: 157-158 °C; IR (NaCl) 3063, 2943, 2886, 1614, 1591, 1514, 1495, 1385, 1287, 1250, 1177, 1144, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.78 (3H, s), 4.00-4.08 (2H, m), 4.62 (1H, dddd, *J* = 4.0, 8.4, 10.0, 21.6 Hz), 5.71 (1H, dd, *J* = 4.0, 47.2 Hz), 6.75 (2H, d, *J* = 8.0 Hz), 6.91 (2H, d, *J* = 8.4 Hz), 6.97 (1H, t, *J* = 7.6 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 7.26 (2H, t, *J* = 7.6 Hz), 7.32-7.34 (3H, m), 7.50 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8 (d, *J* = 5.6 Hz), 55.2, 68.9 (d, *J* = 23.3 Hz), 94.0 (d, *J* = 175.7 Hz), 113.9, 122.8, 123.6, 127.0 (d, *J* = 7.3 Hz), 128.0, 128.6, 128.8, 129.7 (d, *J* = 20.2 Hz), 130.0, 130.8, 142.7, 159.5, 163.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.3 (1F, dd, *J* = 21.4, 47.0 Hz); ESIHRMS: Found: m/z 361.1714. Calcd for $C_{23}H_{22}N_2OF$: $(M+H)^+$ 361.1716.

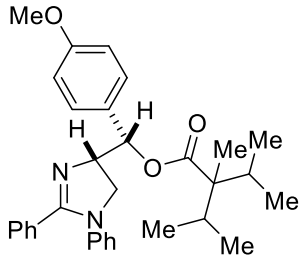
(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(4-methoxyphenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (5e):**



15.6% yield (major diastereomer, two diastereomers can be separated, overall yield 21%, dr = 2.8:1) from **1e**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

Sticky brown oil; IR (NaCl) 3063, 2968, 1715, 1614, 1593, 1514, 1495, 1393, 1304, 1250, 1177, 1146 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.80 (3H, d, *J* = 6.8 Hz), 0.83 (3H, d, *J* = 7.2 Hz), 0.87 (3H, d, *J* = 6.8 Hz), 0.89 (3H, d, *J* = 6.8 Hz), 1.04 (3H, s), 1.96-2.08 (2H, m), 3.73 (3H, s), 3.76 (1H, dd, *J* = 6.0, 10.0 Hz), 4.16 (1H, dd, *J* = 10.0, 10.4 Hz), 4.67 (1H, ddd, *J* = 4.8, 6.0, 10.4 Hz), 5.95 (1H, d, *J* = 4.8 Hz), 6.43-6.45 (2H, m), 6.76-6.79 (2H, m), 6.92 (1H, t, *J* = 7.6 Hz), 7.03-7.07 (2H, m), 7.22-7.26 (2H, m), 7.31-7.43 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.36, 17.42, 18.3, 18.4, 32.6, 32.7, 52.7, 55.0, 55.2, 67.1, 76.0, 113.2, 122.6, 123.4, 128.0, 128.4, 128.8, 128.9, 129.1, 130.0, 130.9, 142.4, 159.3, 162.8, 175.4; ESIHRMS: Found: m/z 499.2966. Calcd for $C_{32}H_{39}N_2O_3$: $(M+H)^+$ 499.2961.

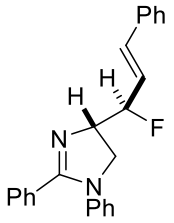
(*S)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(4-methoxyphenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (2e'):**



5.6% yield (minor diastereomer, two diastereomers can be separated, overall yield 21%, dr = 2.8:1) from **1e**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

Sticky brown oil; IR (NaCl) 3063, 2968, 1722, 1614, 1593, 1495, 1393, 1302, 1250, 1229, 1146, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (3H, d, *J* = 6.8 Hz), 0.80 (3H, d, *J* = 6.8 Hz), 0.83 (3H, d, *J* = 6.4 Hz), 0.85 (3H, d, *J* = 6.4 Hz), 1.00 (3H, s), 1.94-2.03 (2H, m), 3.78 (3H, s), 4.04-4.14 (2H, m), 4.62 (1H, ddd, *J* = 4.4, 8.0, 10.4 Hz), 6.03 (1H, d, *J* = 4.4 Hz), 6.70 (2H, d, *J* = 7.6 Hz), 6.85 (2H, d, *J* = 8.8 Hz), 6.98 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.25 (2H, t, *J* = 7.6 Hz), 7.32-7.34 (3H, m), 7.44-7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.4, 17.6, 18.3, 18.4, 32.7, 32.8, 52.8, 55.1, 55.2, 68.7, 77.2, 113.7, 122.8, 123.6, 128.0, 128.3, 128.7, 128.8, 130.0, 130.7, 130.9, 142.8, 159.2, 162.9, 175.5; ESIHRMS: Found: m/z 499.2969. Calcd for $C_{32}H_{39}N_2O_3$: $(M+H)^+$ 499.2961.

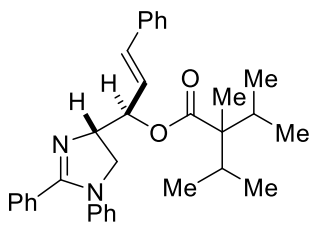
(*S)-4-((*R**,*E*)-1-Fluoro-3-phenylallyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2f):**



62% yield, dr = 2.0:1 (as an inseparable mixture) from **1f**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Yellow solid; mp: 109-110 °C; IR (NaCl) 3026, 2940, 1593, 1574, 1495, 1447, 1387, 1302, 1285, 1250, 1144, 974 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.00 (1H×0.33, dd, *J* = 6.4, 10.0 Hz), 4.06 (1H×0.67, dd, *J* = 7.6, 9.6 Hz), 4.13-4.19 (1H×0.33+1H×0.67, m), 4.48 (1H×0.67, dddd, *J* = 4.4, 7.6, 10.8, 20.4 Hz), 4.66 (1H×0.33, dddd, *J* = 4.8, 6.0, 10.8, 13.2 Hz), 5.30 (1H×0.33, ddd, *J* = 4.8, 5.6, 46.8 Hz), 5.34 (1H×0.67, ddd, *J* = 4.4, 4.8, 48.4 Hz), 6.28-6.40 (1H×0.33+1H×0.67, m), 6.71 (2H×0.33, d, *J* = 8.0 Hz), 6.76-6.81 (1H×0.33+3H×0.67, m), 6.94-7.00 (1H×0.33+1H×0.67, m), 7.09 (2H×0.33, t, *J* = 7.6 Hz), 7.15 (2H×0.67, t, *J* = 7.6 Hz), 7.21-7.43 (8H×0.33+6H×0.67, m), 7.42 (2H×0.67, d, *J* = 7.2 Hz), 7.47 (2H×0.33, d, *J* = 7.6 Hz), 7.52 (2H×0.67, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 54.1 (d, *J* = 5.1 Hz), 54.4 (d, *J* = 2.4 Hz), 66.8 (d, *J* = 24.6 Hz), 67.7 (d, *J* = 22.2 Hz), 93.5 (d, *J* = 172.0 Hz), 93.6 (d, *J* = 174.6 Hz), 122.9, 123.2 (d, *J* = 18.9 Hz), 123.7, 124.6 (d, *J* = 17.8 Hz), 126.7, 128.1, 128.5, 128.6, 128.68, 128.72, 128.75, 128.8, 130.1, 130.7, 132.9 (d, *J* = 11.3 Hz), 134.4 (d, *J* = 11.9 Hz), 135.9, 136.0, 142.2, 142.6, 163.6, 163.7; ^{19}F NMR (376 MHz, CDCl$_3$) δ -190.5 (1F×0.67, ddd, *J* = 18.4, 18.4, 47.8 Hz), -184.4 (1F×0.33, ddd, *J* = 12.4, 13.2, 46.2 Hz); ESIHRMS: Found: m/z 357.1765. Calcd for $C_{24}H_{22}N_2F$: $(M+H)^+$ 357.1767.

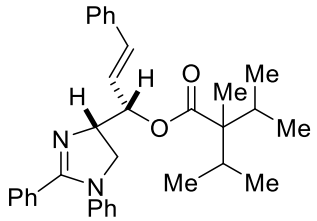
(*R,*E*)-1-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-3-phenylallyl 2-isopropyl-2,3-dimethylbutanoate (5f):**



8% yield (major diastereomer, two diastereomers can be separated, overall yield 14%, dr = 1.3:1) from **1f**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Sticky yellow oil; IR (NaCl) 3061, 2970, 2878, 1732, 1715, 1599, 1504, 1454, 1385, 1300, 1231, 1146, 1051, 966, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.80 (3H, d, *J* = 6.8 Hz), 0.83 (3H, d, *J* = 6.8 Hz), 0.85 (3H, d, *J* = 6.8 Hz), 0.89 (3H, d, *J* = 6.8 Hz), 0.99 (3H, s), 1.93-2.04 (2H, m), 4.07 (1H, dd, *J* = 8.0, 9.2 Hz), 4.19 (1H, dd, *J* = 9.2, 11.2 Hz), 4.57 (1H, ddd, *J* = 3.6, 8.0, 11.2 Hz), 5.80 (1H, dd, *J* = 3.6, 7.2 Hz), 6.22 (1H, dd, *J* = 7.2, 16.0 Hz), 6.74-6.79 (3H, m), 6.99 (1H, t, *J* = 7.6 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.24-7.38 (8H, m), 7.47-7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.3, 17.7, 18.3, 18.5, 32.4, 32.8, 52.8, 55.0, 67.3, 75.9, 122.7, 123.6, 125.3, 126.6, 128.0, 128.1, 128.5, 128.7, 128.8, 130.0, 130.9, 134.0, 136.3, 142.7, 162.9, 175.4; ESIHRMS: Found: m/z 495.3018. Calcd for $C_{33}H_{39}N_2O_2$: $(M+H)^+$ 495.3012.

(*S,*E*)-1-((S*)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-3-phenylallyl 2-isopropyl-2,3-dimethylbutanoate (5f'):**

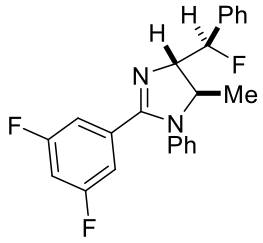


6% yield (minor diastereomer, two diastereomers can be separated, overall yield 14%, dr = 1.3:1) from **1f**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Sticky yellow oil; IR (NaCl) 3026, 2968, 2878, 1721, 1593, 1572, 1497, 1389, 1298, 1229, 1146, 1123, 968 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81-0.84 (9H, m), 0.94 (3H, d, *J* = 6.8 Hz), 1.01 (3H, s), 1.94-2.04 (2H, m), 3.89 (1H, dd, *J* = 6.0, 9.6 Hz), 4.24 (1H, dd, *J* = 9.6, 10.8 Hz), 4.58 (1H, ddd, *J* = 4.0, 6.0, 10.8 Hz), 5.69 (1H, dd, *J* = 4.0, 7.6 Hz), 6.32 (1H, dd, *J* = 7.6, 16.0 Hz), 6.69 (2H, d, *J* = 7.6 Hz), 6.79 (1H, d, *J* = 16.0 Hz), 6.96 (1H, t, *J* = 7.2 Hz), 7.10 (2H, t, *J* = 7.6 Hz), 7.20-7.29 (5H, m), 7.33-7.37 (3H, m), 7.46-7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.3, 17.6, 18.3, 18.4, 32.4, 32.8, 52.8, 55.0, 66.6, 75.6, 122.5, 123.4, 124.0, 126.7, 127.8, 128.1,

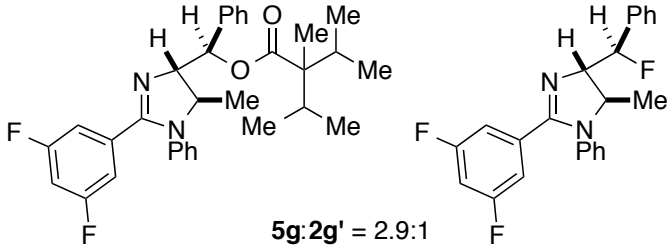
128.4, 128.6, 128.7, 130.1, 131.0, 134.7, 136.4, 142.3, 163.2, 175.5; ESIHRMS: Found: m/z 495.3008. Calcd for $C_{33}H_{39}N_2O_2$: $(M+H)^+$ 495.3012.

(4*S,5*R**)-2-(3,5-Difluorophenyl)-4-((*R**)-fluoro(phenyl)methyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazole (2g):**



60.3% yield of the major diastereomer (the minor diastereomer was mixed with **5g**, and overall yield of **2g** was 69%, with dr = 7.2:1 determined by crude ^{1}H NMR) from **1g**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h. Yellow oil; IR (NaCl) 3086, 3067, 2968, 2924, 1614, 1587, 1495, 1435, 1385, 1329, 1233, 1121, 1063, 1030, 989, 868 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (3H, d, *J* = 6.4 Hz), 3.99 (1H, dq, *J* = 6.4, 6.4 Hz), 4.16 (1H, ddd, *J* = 3.6, 6.4, 23.6 Hz), 5.82 (1H, dd, *J* = 3.6, 47.2 Hz), 6.75 (1H, tt, *J* = 2.4, 8.8 Hz), 6.89 (2H, d, *J* = 8.4 Hz), 7.04-7.06 (2H, m), 7.14 (1H, t, *J* = 7.2 Hz), 7.24 (2H, t, *J* = 7.6 Hz), 7.30-7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 61.8 (d, *J* = 5.0 Hz), 77.7 (d, *J* = 21.9 Hz), 93.6 (d, *J* = 177.2 Hz), 105.4 (t, *J* = 25.2 Hz), 112.1 (dd, *J* = 7.7, 19.3 Hz), 125.3 (d, *J* = 8.1 Hz), 125.8, 126.0, 128.2, 128.4, 129.3, 134.2 (t, *J* = 9.9 Hz), 136.9 (d, *J* = 20.1 Hz), 142.3, 162.1 (t, *J* = 3.1 Hz), 162.4 (dd, *J* = 12.4, 247.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -196.1 (1F, dd, *J* = 23.7, 46.6 Hz), -109.2 (2F, m); ESIHRMS: Found: m/z 381.1573. Calcd for $C_{23}H_{20}N_2F_3$: $(M+H)^+$ 381.1579.

(*R)-((4*S**,5*R**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl 2-isopropyl-2,3-dimethylbutanoate (5g) & (4*S**,5*S**)-2-(3,5-difluorophenyl)-4-((*R**)-fluoro(phenyl)methyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazole (2g'):**

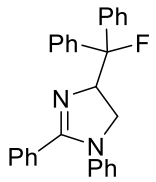


5g:**2g'** = 2.9:1

Inseparable mixture of **5g** (major diastereomer of aminooxygenation product: the minor diastereomer was mixed with unidentified impurity, which was not characterized) and **2g'** (minor diastereomer of aminofluorination product, partially mixed with other unidentified impurity), **5g**:**2g'** = 2.9:1, contains 14.1% yield of **5g** and 4.9% of **2g'**, made from **1g**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Brown oil; IR (NaCl) 3088, 2970, 2880, 1728, 1587, 1495, 1454, 1435, 1393, 1329, 1227, 1123, 989, 910, 868 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (3H, d, *J* = 6.8 Hz), 0.84 (3H, d, *J* = 6.8 Hz), 0.88 (3H, d, *J* = 6.4 Hz), 0.90 (3H, d, *J* = 6.4 Hz), 1.07 (3H, s), 1.16 (3H, d, *J* = 6.4 Hz), 1.41 (3H × 0.35, dd, *J* = 2.0, 6.8 Hz), 1.98-2.09 (2H, m), 4.05 (1H, dq, *J* = 6.4, 7.2 Hz), 4.19 (1H, dd, *J* = 4.4, 7.2 Hz), 4.48 (1H × 0.35, dq, *J* = 6.8, 9.2 Hz), 4.66 (1H × 0.35, ddd, *J* = 9.2, 9.2, 19.2 Hz), 5.69 (1H × 0.35, dd, *J* = 9.2, 46.4 Hz), 6.03 (1H, d, *J* = 4.4 Hz), 6.71-6.75 (3H + 1H × 0.35, m), 6.86 (2H × 0.35, d, *J* = 7.6 Hz), 6.91-6.98 (2H + 2H × 0.35, m), 7.09-7.13 (1H + 1H × 0.35, m), 7.17-7.44 (7H + 5H × 0.35, m), 7.52 (2H × 0.35, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3 (d, *J* = 3.3 Hz), 14.4, 17.3, 17.6, 18.2, 18.4, 21.9, 32.7, 32.9, 52.8, 63.0, 63.7, 71.3 (d, *J* = 27.6 Hz), 77.1, 77.2, 92.8 (d, *J* = 170.2 Hz), 105.3 (t, *J* = 25.2 Hz), 105.4 (t, *J* = 25.2 Hz), 112.0 (dd, *J* = 7.6, 19.3 Hz), 124.8, 125.3, 125.5, 125.8, 126.7 (d, *J* = 6.8 Hz), 127.1, 128.0, 128.2, 128.3, 128.6 (d, *J* = 1.8 Hz), 129.1, 129.2, 134.3 (t, *J* = 9.9 Hz), 137.5, 138.4 (d, *J* = 18.9 Hz), 140.8, 141.9, 161.2 (t, *J* = 3.2 Hz), 162.2 (dd, *J* = 12.4, 247.1 Hz), 162.3 (dd, *J* = 12.4, 247.4 Hz), 175.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -176.5 (1F × 0.35, dd, *J* = 7.9, 46.2 Hz), -109.3 (2F, dd, *J* = 7.5, 7.9 Hz), -109.2 (2F × 0.35, dd, *J* = 7.5, 7.9 Hz); ESIHRMS: Found: m/z 519.2817. Calcd for $C_{32}H_{37}N_2O_2F_2$: $(M+H)^+$ 519.2823; Found: m/z 381.1579. Calcd for $C_{23}H_{20}N_2F_3$: $(M+H)^+$ 381.1579.

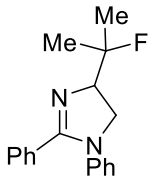
4-(Fluorodiphenylmethyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2h):



83% yield from **1h**, $PhI(OPiv)_2$ (1.3 equiv) and $Et_3N•3HF$ (2 equiv); reaction time: 6 h.

White solid; mp: 164-166 °C; IR (NaCl) 3055, 3028, 2951, 1591, 1566, 1495, 1477, 1447, 1393, 1306, 1271, 1130, 1030, 970 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.92 (1H, dd, *J* = 6.4, 10.4 Hz), 4.28 (1H, dd, *J* = 10.4, 10.8 Hz), 5.31 (1H, ddd, *J* = 6.4, 10.8, 16.8 Hz), 6.46 (2H, d, *J* = 7.6 Hz), 6.90 (1H, t, *J* = 7.6 Hz), 7.02 (2H, t, *J* = 7.6 Hz), 7.17-7.29 (7H, m), 7.35 (2H, t, *J* = 7.6 Hz), 7.40-7.42 (2H, m), 7.49 (2H, d, *J* = 7.6 Hz), 7.66 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.0 (d, *J* = 4.9 Hz), 69.9 (d, *J* = 24.7 Hz), 99.1 (d, *J* = 178.4 Hz), 123.0, 123.6, 126.5 (d, *J* = 9.0 Hz), 126.6 (d, *J* = 8.4 Hz), 127.46, 127.52, 127.9 (d, *J* = 1.8 Hz), 128.0, 128.2, 128.4, 128.9, 129.9, 130.8, 140.5 (d, *J* = 23.9 Hz), 142.4 (d, *J* = 21.5 Hz), 142.6, 163.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -155.5 (1F, m); ESIHRMS: Found: m/z 407.1922. Calcd for $C_{28}H_{24}N_2F$: $(M+H)^+$ 407.1924.

4-(2-Fluoropropan-2-yl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2i):

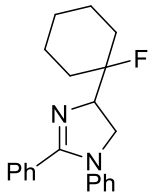


73% yield from **1i**, $PhI(OPiv)_2$ (1.3 equiv) and $Et_3N•3HF$ (2 equiv); reaction time: 20 h.

Brown solid; mp: 98-99 °C; IR (NaCl) 3061, 2980, 2936, 1593, 1572, 1495, 1385, 1300, 1263, 1142, 928 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, d, *J* = 21.6 Hz), 1.53 (3H, d, *J* = 21.6 Hz), 3.98 (1H, dd, *J* = 7.2, 9.6 Hz), 4.18 (1H, dd, *J* = 9.6, 10.4 Hz), 4.26 (1H, ddd, *J* = 7.2, 10.4, 11.6 Hz), 6.78 (2H, d, *J* = 8.0 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 7.15 (2H, dd, *J* = 7.6, 8.0 Hz), 7.27 (2H, dd, *J* = 7.2, 7.6 Hz), 7.35 (1H, t, *J* = 7.6 Hz), 7.50 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9 (d, *J* = 23.9 Hz), 25.3 (d, *J* = 23.2 Hz), 54.5 (d, *J* = 4.6 Hz), 71.2 (d, *J* = 24.3 Hz), 96.2 (d, *J* =

168.5 Hz), 122.8, 123.6, 128.1, 128.7 (overlapped), 130.0, 130.9, 142.6, 163.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -149.2 (1F, sepd, *J* = 12.4, 21.4 Hz); ESIHRMS: Found: m/z 283.1608. Calcd for $C_{18}H_{20}N_2F$: $(M+H)^+$ 283.1611.

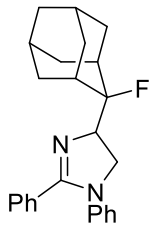
4-(1-Fluorocyclohexyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2j):



87% yield from **1j**, $PhI(OPiv)_2$ (1.3 equiv) and Et_3N•3HF (2 equiv); reaction time: 14 h. When this reaction was carried out using 4.00 mmol **1j** (1.218 g), the corresponding product **2j** (3.37 mmol, 1.088 g) was obtained in 84% after 24h.

White solid; mp: 141-142 °C; IR (NaCl) 3061, 2934, 2857, 1614, 1593, 1574, 1495, 1385, 1350, 1302, 1271, 1144, 1024, 991 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22-1.31 (1H, m), 1.44-1.89 (8H, m), 2.04-2.07 (1H, m), 4.00 (1H, dd, *J* = 7.6, 9.6 Hz), 4.14 (1H, dd, *J* = 9.6, 10.8 Hz), 4.26 (1H, ddd, *J* = 7.6, 10.8, 14.4 Hz), 6.78 (2H, d, *J* = 7.6 Hz), 6.98 (1H, t, *J* = 7.2 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.27 (2H, t, *J* = 7.6 Hz), 7.35 (1H, t, *J* = 7.6 Hz), 7.49-7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (d, *J* = 1.6 Hz), 21.5 (d, *J* = 1.8 Hz), 25.3, 30.1 (d, *J* = 22.1 Hz), 33.2 (d, *J* = 21.6 Hz), 54.0 (d, *J* = 4.8 Hz), 71.0 (d, *J* = 24.1 Hz), 96.6 (d, *J* = 173.4 Hz), 122.7, 123.5, 128.1, 128.7, 128.8, 130.0, 131.2, 142.8, 162.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -169.4 (1F, m); ESIHRMS: Found: m/z 323.1926. Calcd for $C_{21}H_{24}N_2F$: $(M+H)^+$ 323.1924.

4-(2-Fluoroadamantan-2-yl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2k):

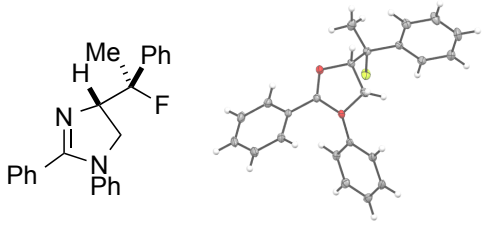


95% yield from **1k**, $PhI(OPiv)_2$ (1.3 equiv) and Et_3N•3HF (2 equiv); reaction time: 21 h.

White solid; mp: 130-131 °C; IR (NaCl) 3011, 2913, 2862, 1614, 1593, 1574, 1495, 1454, 1385, 1315, 1269, 1138, 970 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.60-1.76

(4H, m), 1.84-1.91 (6H, m), 2.10-2.19 (3H, m), 2.81 (1H, m), 3.93 (1H, dd, *J* = 8.4, 8.8 Hz), 4.15 (1H, ddd, *J* = 2.0, 8.8, 10.8 Hz), 4.82 (1H, ddd, *J* = 8.4, 10.8, 29.6 Hz), 6.79-6.81 (2H, m), 6.95 (1H, t, *J* = 7.2 Hz), 7.11-7.15 (2H, m), 7.22-7.34 (3H, m), 7.51-7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 27.1, 32.4 (d, *J* = 19.6 Hz), 32.97 (d, *J* = 3.1 Hz), 33.00 (d, *J* = 3.2 Hz), 34.0 (d, *J* = 19.2 Hz), 34.7 (d, *J* = 8.4 Hz), 35.0 (d, *J* = 7.6 Hz), 37.8, 53.6 (d, *J* = 5.8 Hz), 65.8 (d, *J* = 23.1 Hz), 99.7 (d, *J* = 182.8 Hz), 122.9, 123.3, 128.0, 128.6, 128.9, 129.7, 131.3, 143.2, 162.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -168.5 (1F, d, *J* = 29.7 Hz); ESIHRMS: Found: m/z 375.2241. Calcd for $C_{25}H_{28}N_2F$: $(M+H)^+$ 375.2237.

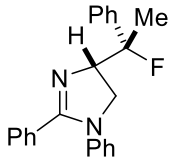
(*S)-4-((*R**)-1-Fluoro-1-phenylethyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2l):**



71% yield, dr = >20:1 (the major diastereomer could be recrystallized from hexane/CH_2Cl_2) from **1l** (E/Z = 20:1), $PhI(OPiv)_2$ (1.3 equiv) and Et_3N•3HF (2 equiv); reaction time: 20 h.

Colorless crystal (CCDC-1409623); mp: 143-144 °C; IR (NaCl) 3063, 3028, 2949, 1591, 1572, 1495, 1447, 1381, 1302, 1263, 1140, 1072, 901 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (3H, d, *J* = 22.8 Hz), 3.77 (1H, dd, *J* = 7.6, 10.0 Hz), 3.94 (1H, dd, *J* = 10.0, 10.8 Hz), 4.62 (1H, ddd, *J* = 7.6, 10.8, 23.6 Hz), 6.71 (2H, d, *J* = 7.6 Hz), 6.94 (1H, t, *J* = 7.6 Hz), 7.10 (2H, t, *J* = 7.6 Hz), 7.25-7.43 (8H, m), 7.54 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4 (d, *J* = 25.0 Hz), 54.4 (d, *J* = 4.8 Hz), 71.6 (d, *J* = 22.8 Hz), 97.8 (d, *J* = 178.2 Hz), 122.9, 123.5, 124.4 (d, *J* = 9.9 Hz), 127.4, 128.1, 128.3 (d, *J* = 1.2 Hz), 128.6, 128.8, 130.0, 131.0, 142.8, 143.1 (d, *J* = 21.4 Hz), 163.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -165.5 (1F, qd, *J* = 22.6, 22.9 Hz); ESIHRMS: Found: m/z 345.1774. Calcd for $C_{23}H_{22}N_2F$: $(M+H)^+$ 345.1767.

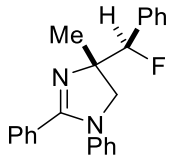
(*S)-4-((*S**)-1-Fluoro-1-phenylethyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2m):**



68% yield from **1m**, $PhI(OPiv)_2$ (1.3 equiv) and Et_3N•3HF (2 equiv); reaction time: 20 h.

White solid; mp: 137-138 °C; IR (NaCl) 3061, 2980, 2936, 1591, 1568, 1495, 1447, 1393, 1302, 1263, 1175, 1028, 891 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (3H, d, *J* = 24.0 Hz), 3.78 (1H, dd, *J* = 5.6, 10.0 Hz), 4.13 (1H, dd, *J* = 10.0, 10.4 Hz), 4.65 (1H, ddd, *J* = 5.6, 7.6, 10.4 Hz), 6.25-6.27 (2H, m), 6.87 (1H, t, *J* = 7.6 Hz), 6.95-6.98 (2H, m), 7.18-7.32 (6H, m), 7.36-7.44 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4 (d, *J* = 22.2 Hz), 54.6 (d, *J* = 3.2 Hz), 71.8 (d, *J* = 28.7 Hz), 97.4 (d, *J* = 173.2 Hz), 123.0, 123.7, 125.4 (d, *J* = 10.0 Hz), 127.4, 127.5 (d, *J* = 1.6 Hz), 128.0, 128.3, 128.6, 129.9, 130.7, 140.1 (d, *J* = 21.6 Hz), 142.1, 163.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -152.0 (1F, dq, *J* = 7.5, 24.1 Hz); ESIHRMS: Found: m/z 345.1764. Calcd for $C_{23}H_{22}N_2F$: $(M+H)^+$ 345.1767.

(*S)-4-((*R**)-Fluoro(phenyl)methyl)-4-methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2n):**

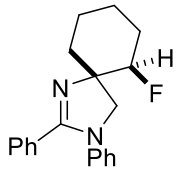


63% yield from **1n**, $PhI(OPiv)_2$ (1.3 equiv) and Et_3N•3HF (2 equiv); reaction time: 24 h.

White solid; mp: 81-82 °C; IR (NaCl) 2938, 2882, 1612, 1593, 1574, 1495, 1450, 1385, 1366, 1315, 1283, 1128, 1015 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.37 (3H, d, *J* = 0.8 Hz), 3.73 (1H, dd, *J* = 2.0, 9.6 Hz), 4.22 (1H, dd, *J* = 0.8, 9.6 Hz), 5.53 (1H, d, *J* = 45.2 Hz), 6.70 (2H, d, *J* = 7.6 Hz), 6.98 (1H, t, *J* = 7.6 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.28 (2H, t, *J* = 7.6 Hz), 7.32-7.44 (6H, m), 7.50-7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.9 (d, *J* = 2.9 Hz), 60.5 (d, *J* = 4.7 Hz), 70.9 (d, *J* = 21.8 Hz), 97.0 (d, *J* = 178.8 Hz), 122.8, 123.6, 126.8 (d, *J* = 8.0 Hz), 127.9, 128.1, 128.3, 128.7,

128.9, 130.1, 130.8, 136.6 (d, J = 21.0 Hz), 142.7, 161.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -186.0 (1F, d, J = 45.1 Hz); ESIHRMS: Found: m/z 345.1771. Calcd for $C_{23}H_{22}N_2F$: $(M+H)^+$ 345.1767.

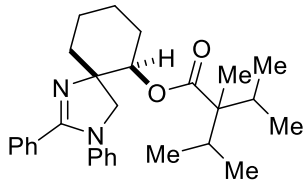
(5*S,6*R**)-6-Fluoro-2,3-diphenyl-1,3-diazaspiro[4.5]dec-1-ene (2o):**



56% yield from **1o**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Sticky yellow oil; IR (NaCl) 3061, 2938, 2862, 1612, 1593, 1572, 1495, 1447, 1393, 1306, 1146, 1028 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.62 (3H, m), 1.70-1.87 (4H, m), 2.08-2.16 (1H, m), 3.75 (1H, dd, J = 2.0, 9.6 Hz), 4.11 (1H, d, J = 9.6 Hz), 4.66 (1H, ddd, J = 4.0, 9.6, 48.4 Hz), 6.78 (2H, d, J = 7.6 Hz), 6.97 (1H, t, J = 7.6 Hz), 7.14 (2H, t, J = 7.6 Hz), 7.25-7.28 (2H, m), 7.34 (1H, tt, J = 1.2, 7.6 Hz), 7.49-7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.4 (d, J = 8.7 Hz), 28.6 (d, J = 18.8 Hz), 36.1, 58.6, 71.3 (d, J = 17.8 Hz), 94.4 (d, J = 177.8 Hz), 122.5, 123.3, 128.1, 128.6, 128.9, 129.9, 131.0, 143.0, 161.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -186.4 (1F, m); ESIHRMS: Found: m/z 309.1773. Calcd for $C_{20}H_{22}N_2F$: $(M+H)^+$ 309.1767.

(5*S,6*R**)-2,3-Diphenyl-1,3-diazaspiro[4.5]dec-1-en-6-yl 2-isopropyl-2,3-dimethylbutanoate (5o):**

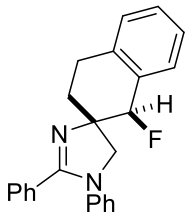


3% yield from **1o**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Colorless oil; IR (NaCl) 2965, 2938, 2862, 1715, 1593, 1573, 1495, 1454, 1389, 1310, 1233, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 (3H, d, J = 6.4 Hz), 0.74 (3H, d, J = 6.4 Hz), 0.80 (3H, d, J = 6.8 Hz), 0.84 (3H, d, J = 6.8 Hz), 0.92 (3H, s), 1.26-1.94 (9H, m), 2.18-2.22 (1H, m), 3.78 (1H, d, J = 9.2 Hz), 4.18 (1H, d, J = 9.2 Hz), 5.01 (1H, dd, J = 4.4, 10.8 Hz), 6.79 (2H, d, J = 7.2 Hz), 6.98 (1H, t, J = 7.6 Hz), 7.16 (2H,

t, J = 7.6 Hz), 7.26 (2H, t, J = 7.6 Hz), 7.35 (1H, t, J = 7.6 Hz), 7.46-7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 17.0, 17.7, 18.2, 18.4, 21.7, 23.4, 28.5, 32.2, 32.7, 36.6, 37.8, 52.6, 58.9, 70.9, 122.4, 123.2, 128.0, 128.6, 128.87, 128.90, 131.1, 143.0, 160.4, 175.3; ESIHRMS: Found: m/z 447.3008. Calcd for $C_{29}H_{39}N_2O_2$: $(M+H)^+$ 447.3012.

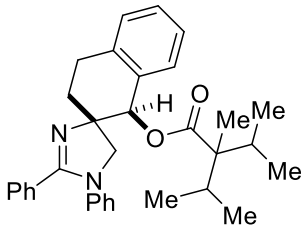
(1'*R*,2'*S*)-1'-Fluoro-1,2-diphenyl-1,3',4',5-tetrahydro-1'*H*-spiro[imidazole-4,2'-naphthalene] (2p):



90% yield from **1p**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et_3N•3HF (5 equiv); reaction time: 20 h.

White solid; mp: 131-132 °C; IR (NaCl) 3017, 2934, 1611, 1591, 1570, 1495, 1456, 1395, 1308, 1271 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (1H, ddd, J = 5.6, 6.0, 13.6 Hz), 2.25 (1H, ddd, J = 6.4, 7.6, 13.6 Hz), 2.93 (1H, ddd, J = 6.0, 6.4, 16.4 Hz), 3.13 (1H, ddd, J = 5.6, 7.6, 16.4 Hz), 3.87 (1H, d, J = 9.6 Hz), 4.17 (1H, d, J = 9.6 Hz), 5.57 (1H, d, J = 51.6 Hz), 6.77 (2H, d, J = 8.0 Hz), 6.95 (1H, t, J = 7.6 Hz), 7.13 (2H, t, J = 8.0 Hz), 7.16-7.28 (5H, m), 7.35 (1H, t, J = 7.6 Hz), 7.47 (1H, d, J = 7.6 Hz), 7.52 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 31.5 (d, J = 2.2 Hz), 58.8 (d, J = 5.0 Hz), 69.7 (d, J = 18.1 Hz), 92.9 (d, J = 176.2 Hz), 122.4, 123.3, 126.3, 128.2, 128.50, 128.53, 128.6, 128.9, 129.0, 130.1, 131.0, 133.2 (d, J = 18.0 Hz), 136.4 (d, J = 4.0 Hz), 142.7, 162.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -179.4 (1F, d, J = 51.5 Hz); ESIHRMS: Found: m/z 357.1772. Calcd for $C_{24}H_{22}N_2F$: $(M+H)^+$ 357.1767.

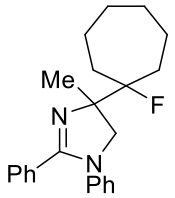
(1'*R,2'*S**)-1,2-Diphenyl-1,3',4',5-tetrahydro-1'*H*-spiro[imidazole-4,2'-naphthalen]-1'-yl 2-isopropyl-2,3-dimethylbutanoate (5p):**



7% yield from **1p**, PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (1.4 equiv) and Et$_3$N•3HF (5 equiv); reaction time: 20 h.

Yellow oil; IR (NaCl) 3063, 2968, 2936, 1715, 1593, 1574, 1495, 1454, 1393, 1323, 1225, 1146, 930 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.76-0.80 (9H, m), 0.86 (3H, d, *J* = 6.8 Hz), 1.00 (3H, s), 1.89-2.06 (2H, m), 2.11-2.25 (2H, m), 2.92 (1H, ddd, *J* = 4.8, 5.2, 16.8 Hz), 3.27 (1H, ddd, *J* = 6.8, 8.0, 16.8 Hz), 3.68 (1H, d, *J* = 9.6 Hz), 4.20 (1H, d, *J* = 9.6 Hz), 6.18 (1H, s), 6.74 (2H, d, *J* = 8.0 Hz), 6.97 (1H, t, *J* = 7.2 Hz), 7.09-7.24 (7H, m), 7.33 (1H, t, *J* = 7.2 Hz), 7.43-7.45 (3H, m); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.5, 17.3, 17.4, 18.1, 18.5, 25.6, 31.7, 32.5, 32.8, 52.7, 61.6, 69.3, 74.9, 122.0, 123.2, 125.7, 128.1 (overlapped), 128.6, 128.7, 129.1, 130.0, 130.8, 130.9, 134.2, 136.7, 142.5, 161.3, 176.0; ESIHRMS: Found: m/z 447.3008. Calcd for $C_{29}H_{39}N_2O_2$: $(M+H)^+$ 447.3012.

4-(1-Fluorocycloheptyl)-4-methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2q):



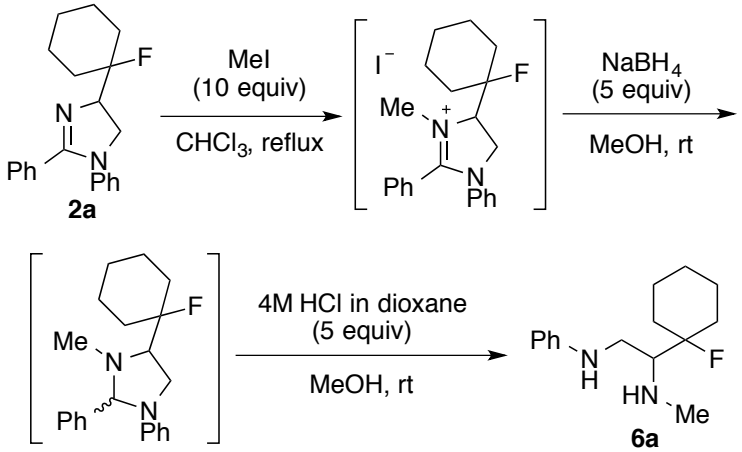
95% yield from **1q**, PhI(OPiv)$_2$ (1.3 equiv) and Et$_3$N•3HF (2 equiv); reaction time: 21 h.

Pale yellow oil; IR (NaCl) 3061, 2932, 2860, 1593, 1574, 1504, 1447, 1393, 1371, 1312, 1179, 1146, 910 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.44 (3H, s), 1.50-1.72 (8H, m), 1.87-2.22 (4H, m), 3.77 (1H, dd, *J* = 1.2, 9.6 Hz), 4.14 (1H, d, *J* = 9.6 Hz), 6.75 (2H, d, *J* = 7.6 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 7.26 (2H, t, *J* = 7.6 Hz), 7.33 (1H, t, *J* = 7.6 Hz), 7.50 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 22.8 (d, *J* = 3.7 Hz), 23.0 (d, *J* = 5.6 Hz), 24.5 (d, *J* = 3.0 Hz), 29.7, 30.1,

33.8 (d, J = 23.8 Hz), 34.7 (d, J = 23.3 Hz), 61.7 (d, J = 5.5 Hz), 74.4 (d, J = 23.5 Hz), 102.3 (d, J = 174.9 Hz), 122.6, 123.3, 128.1, 128.6, 128.8, 129.8, 131.2, 142.8, 160.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -151.2 (1F, tt, J = 19.6, 27.0 Hz); ESIHRMS: Found: m/z 351.2243. Calcd for $C_{23}H_{28}N_2F$: $(M+H)^+$ 351.2237.

5. Reductive ring-opening of 2-imidazolines 2

Typical procedure: synthesis of 6j



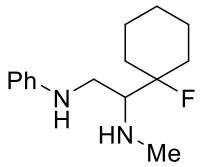
A solution of 4-(1-fluorocyclohexyl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole **2j** (83.9 mg, 0.260 mmol) in $CHCl_3$ (5.0 mL) was added MeI (163 μL, 2.602 mmol). The reaction mixture was heated under reflux for 16h. The volatile materials were removed in vacuo. The crude amidinium iodide was used directly for the next step.

To a stirred solution of the crude amidinium iodide in methanol (5 mL) was added $NaBH_4$ (49.2 mg, 1.301 mmol) in three batches at 0 °C (ice-water bath). After the addition of $NaBH_4$, the reaction mixture was warmed to room temperature. After 30 minutes, the solvent was removed in vacuo and water (15 mL) was added. The mixture was then extracted with Et_2O and the combined organic layers were washed with brine, and then dried over $MgSO_4$. Removal of the solvents in vacuo gave the crude aminal product.

The crude aminal was dissolved in 5 mL MeOH and 4M HCl in dioxane (0.33 mL) was added. The reaction was stirred at room temperature for 20h. The solvent was removed in vacuo and saturated $NaHCO_3$ was added. The mixture was extracted with Et_2O and the combined organic layers were washed with brine, and then dried over $MgSO_4$. Removal of the solvents in vacuo gave the crude product, which was purified

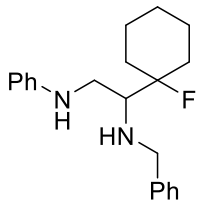
by flash column chromatography (silica gel; hexane : ethyl acetate = 85 : 15) afforded **6j** (48.3 mg, 0.193 mmol) in 74% yield as a pale yellow oil.

1-(1-Fluorocyclohexyl)-*N*^{1}-methyl-*N*^{2}-phenylethane-1,2-diamine (6j):



Yellow oil; IR (NaCl) 3416, 3360, 3049, 2934, 2862, 1603, 1504, 1483, 1449, 1319, 1258, 1179, 1138, 932 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16-1.26 (1H, m), 1.45-1.69 (8H, m), 1.91-1.96 (2H, m), 2.48 (3H, s), 2.67 (1H, ddd, *J* = 4.4, 6.0, 15.2 Hz), 3.03 (1H, dd, *J* = 6.0, 12.0 Hz), 3.33 (1H, dd, *J* = 4.4, 12.0 Hz), 4.30 (1H, s br), 6.63 (2H, dd, *J* = 0.8, 8.4 Hz), 6.70 (1H, t, *J* = 7.2 Hz), 7.18 (2H, dd, *J* = 7.6, 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5 (d, *J* = 2.1 Hz), 21.6 (d, *J* = 2.4 Hz), 25.3, 32.0 (d, *J* = 22.6 Hz), 32.6 (d, *J* = 22.3 Hz), 35.7, 42.1 (d, *J* = 5.1 Hz), 65.1 (d, *J* = 21.4 Hz), 98.9 (d, *J* = 171.1 Hz), 112.9, 117.3, 129.2, 148.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -162.9 (1F, m); ESIHRMS: Found: m/z 251.1924. Calcd for $C_{15}H_{24}N_2F$: $(M+H)^+$ 251.1924.

***N*^{1}-Benzyl-1-(1-fluorocyclohexyl)-*N*^{2}-phenylethane-1,2-diamine (7j):**

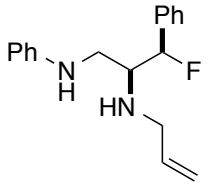


71% yield from **2j** and BnBr (4 equiv).

White solid; mp: 44-45 °C; IR (NaCl) 3418, 3368, 3024, 2936, 2862, 1603, 1504, 1452, 1319, 1256, 1125, 932 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19-1.26 (1H, m), 1.44-1.69 (8H, m), 1.93-1.96 (2H, m), 2.84 (1H, ddd, *J* = 4.4, 6.4, 15.6 Hz), 3.02 (1H, dd, *J* = 6.4, 12.0 Hz), 3.35 (1H, dd, *J* = 4.4, 12.0 Hz), 3.84 (1H, d, *J* = 13.6 Hz), 3.87 (1H, d, *J* = 13.6 Hz), 4.30 (1H, s br), 6.58 (2H, dd, *J* = 0.8, 8.4 Hz), 6.70 (1H, t, *J* = 7.6 Hz), 7.17 (2H, dd, *J* = 7.6, 8.4 Hz), 7.24-7.33 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.59 (d, *J* = 2.1 Hz), 21.60 (d, *J* = 2.0 Hz), 25.3, 32.1 (d, *J* = 22.4 Hz), 32.6 (d, *J* = 22.3 Hz), 42.5 (d, *J* = 4.7 Hz), 52.8, 62.3 (d, *J* = 21.4 Hz), 99.1 (d, *J* = 171.2

Hz), 112.9, 117.3, 127.1, 128.2, 128.5, 129.2, 140.5, 148.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.1 (1F, m); ESIHRMS: Found: m/z 327.2236. Calcd for $C_{21}H_{28}N_2F$: $(M+H)^+$ 327.2237.

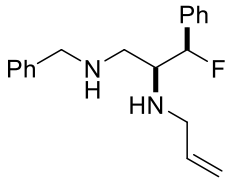
(2*S,3*R**)-*N*^{2}-Allyl-3-fluoro-*N*^{1},3-diphenylpropane-1,2-diamine (8a):**



66% yield from **2a** and allyl bromide (10 equiv).

Pale yellow oil; IR (NaCl) 3364, 3028, 2922, 2841, 1603, 1504, 1454, 1431, 1317, 1261, 1125, 993, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.10-3.30 (5H, m), 4.19 (1H, s br), 5.07 (1H, dd, *J* = 1.2, 10.4 Hz), 5.13 (1H, dd, *J* = 1.2, 17.2 Hz), 5.64 (1H, dd, *J* = 4.4, 46.8 Hz), 5.80 (1H, tdd, *J* = 6.0, 10.4, 17.2 Hz), 6.54 (2H, d, *J* = 8.0 Hz), 6.68 (1H, t, *J* = 7.2 Hz), 7.13 (2H, t, *J* = 7.6 Hz), 7.32-7.42 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0 (d, *J* = 4.7 Hz), 49.5, 60.1 (d, *J* = 23.1 Hz), 93.3 (d, *J* = 174.7 Hz), 113.1, 116.3, 117.5, 125.6 (d, *J* = 7.6 Hz), 128.5, 128.6, 129.1, 136.5, 137.4 (d, *J* = 20.1 Hz), 148.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.6 (1F, dd, *J* = 19.2, 46.6 Hz); ESIHRMS: Found: m/z 285.1774. Calcd for $C_{18}H_{22}N_2F$: $(M+H)^+$ 285.1767.

(2*S,3*R**)-*N*^{2}-Allyl-*N*^{1}-benzyl-3-fluoro-3-phenylpropane-1,2-diamine (8b):**

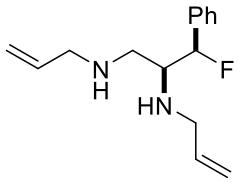


77% yield from **2b** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3312, 3063, 3028, 2918, 2826, 1495, 1454, 1360, 1123, 995, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (2H, s br), 2.64 (1H, dd, *J* = 7.6, 12.4 Hz), 2.71 (1H, dd, *J* = 4.0, 12.4 Hz), 3.03 (1H, dddd, *J* = 4.0, 4.4, 7.6, 19.6 Hz), 3.14-3.26 (2H, m), 3.70 (1H, d, *J* = 13.2 Hz), 3.75 (1H, d, *J* = 13.2 Hz), 5.05 (1H, dd, *J* = 1.6, 10.4 Hz), 5.11 (1H, dd, *J* = 1.6, 17.2 Hz), 5.58 (1H, dd, *J* = 4.4, 46.8 Hz), 5.80 (1H, tdd, *J* = 6.0, 10.4, 17.2 Hz), 7.21-7.38 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.5 (d, *J* = 5.0 Hz), 50.1, 53.8, 60.7 (d, *J* = 22.9 Hz), 94.0 (d, *J* = 174.2 Hz), 116.0,

125.7 (d, J = 7.8 Hz), 126.9, 128.0, 128.2, 128.3, 128.4, 136.9, 137.9 (d, J = 20.1 Hz), 140.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.4 (1F, dd, J = 19.6, 47.0 Hz); ESIHRMS: Found: m/z 299.1929. Calcd for $C_{19}H_{24}N_2F$: $(M+H)^+$ 299.1924.

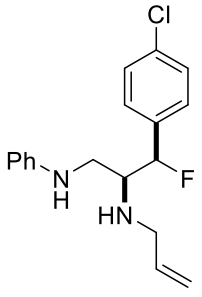
(2*S,3*R**)-*N*^{1},*N*^{2}-Diallyl-3-fluoro-3-phenylpropane-1,2-diamine (8c):**



80% yield from **2c** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3312, 3075, 2922, 2822, 1643, 1454, 1402, 1306, 1273, 1115, 991, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (2H, s br), 2.60 (1H, dd, J = 7.6, 12.0 Hz), 2.67 (1H, dd, J = 3.6, 12.0 Hz), 3.02 (1H, dddd, J = 3.6, 4.8, 7.6, 20.0 Hz), 3.14-3.32 (4H, m), 5.04-5.16 (4H, m), 5.59 (1H, dd, J = 4.8, 46.8 Hz), 5.77-5.90 (2H, m), 7.30-7.39 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.6 (d, J = 4.9 Hz), 50.1, 52.4, 60.8 (d, J = 22.6 Hz), 93.9 (d, J = 174.0 Hz), 115.8, 116.0, 125.6 (d, J = 8.0 Hz), 128.2, 128.4, 136.8, 136.9, 137.9 (d, J = 20.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -191.1 (1F, dd, J = 20.3, 47.0 Hz); ESIHRMS: Found: m/z 249.1766. Calcd for $C_{15}H_{22}N_2F$: $(M+H)^+$ 249.1767.

(2*S,3*R**)-*N*^{2}-Allyl-3-(4-chlorophenyl)-3-fluoro-*N*^{1}-phenylpropane-1,2-diamine (8d):**

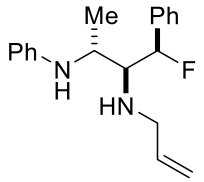


74% yield from **2d** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3362, 3075, 2920, 2841, 1603, 1504, 1495, 1431, 1317, 1261, 1092, 993, 922 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (1H, s br), 3.07-3.33 (5H, m), 4.17 (1H, s br), 5.08 (1H, dd, J = 1.2, 10.4 Hz), 5.14 (1H, dd, J = 1.2, 17.2 Hz), 5.60 (1H, dd, J = 4.4, 46.8 Hz), 5.79 (1H, tdd, J = 6.0, 10.4, 17.2 Hz), 6.54-6.56 (2H, m),

6.70 (1H, t, J = 8.0 Hz), 7.15 (2H, t, J = 8.0 Hz), 7.27 (2H, d, J = 8.4 Hz), 7.38 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.0 (d, J = 4.6 Hz), 49.6, 60.0 (d, J = 23.2 Hz), 92.7 (d, J = 175.1 Hz), 113.1, 116.4, 117.6, 127.0 (d, J = 7.7 Hz), 128.8, 129.2, 134.4 (d, J = 1.3 Hz), 136.0 (d, J = 20.5 Hz), 136.4, 148.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.2 (1F, dd, J = 19.9, 47.4 Hz); ESIHRMS: Found: m/z 319.1384. Calcd for $C_{18}H_{21}N_2ClF$: $(M+H)^+$ 319.1377.

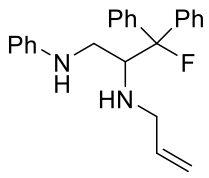
(1*R,2*S**,3*R**)-*N*^{2}-Allyl-1-fluoro-*N*^{3},1-diphenylbutane-2,3-diamine (8g):**



71% yield from **2g** and allyl bromide (10 equiv). Compound **8g** contains a trace amount of unknown inseparable impurity, which was detected by ^{19}F NMR. This impurity was probably derived from the 3,5-difluorophenyl moiety during the hydrolysis process of **2g**.

Colorless oil; IR (NaCl) 3364, 3051, 2972, 2926, 1601, 1504, 1454, 1315, 1256, 1155, 1123, 993, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (1H, s br), 1.25 (3H, d, J = 6.0 Hz), 2.79-2.91 (3H, m), 3.80-4.09 (2H, m), 4.88-4.96 (2H, m), 5.30 (1H, dd, J = 8.4, 46.4 Hz), 5.59 (1H, tdd, J = 6.0, 10.4, 17.2 Hz), 6.65-6.70 (3H, m), 7.17 (2H, t, J = 7.6 Hz), 7.35-7.37 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.3, 48.5, 52.1, 64.7 (d, J = 24.6 Hz), 94.1 (d, J = 175.6 Hz), 113.7, 116.2, 117.2, 126.9 (d, J = 6.1 Hz), 128.5, 128.9 (d, J = 1.6 Hz), 129.3, 136.6, 137.9 (d, J = 20.0 Hz), 147.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -173.9 (1F, dd, J = 10.5, 46.2 Hz); ESIHRMS: Found: m/z 299.1930. Calcd for $C_{19}H_{24}N_2F$: $(M+H)^+$ 299.1924.

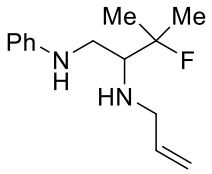
N^2-Allyl-3-fluoro-N^1,3,3-triphenylpropane-1,2-diamine (8h):



59% yield from **2h** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3360, 3306, 3063, 3009, 2928, 2857, 1643, 1601, 1504, 1450, 1427, 1314, 1283, 1152, 1049, 908 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.51 (1H, s br), 2.92-3.05 (3H, m), 3.26-3.29 (1H, m), 3.70-3.79 (1H, m), 4.16 (1H, s br), 4.96-4.99 (2H, m), 5.65-5.75 (1H, m), 6.49 (2H, d, *J* = 7.2 Hz), 6.68 (1H, t, *J* = 7.2 Hz), 7.11-7.15 (2H, m), 7.25-7.37 (6H, m), 7.47 (2H, d, *J* = 8.0 Hz), 7.52 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.3 (d, *J* = 3.9 Hz), 50.3, 61.7 (d, *J* = 20.8 Hz), 101.5 (d, *J* = 180.7 Hz), 113.3, 115.8, 117.4, 124.7 (d, *J* = 10.1 Hz), 125.0 (d, *J* = 10.1 Hz), 127.67, 127.73, 128.4 (d, *J* = 1.0 Hz), 128.5 (d, *J* = 0.9 Hz), 129.1, 137.1, 141.83 (d, *J* = 24.3 Hz), 141.84 (d, *J* = 22.4 Hz), 148.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -166.2 (1F, d, *J* = 27.8 Hz); ESIHRMS: Found: m/z 383.1897. Calcd for $C_{24}H_{25}N_2FNa$: $(M+Na)^+$ 383.1899.

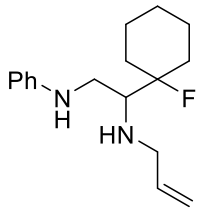
N^2-Allyl-3-fluoro-3-methyl-N^1-phenylbutane-1,2-diamine (8i):



72% yield from **2i** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3416, 3362, 3076, 2980, 2934, 2851, 1603, 1504, 1483, 1429, 1373, 1319, 1256, 1144, 1130, 993, 920 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (3H, d, *J* = 22.4 Hz), 1.43 (3H, d, *J* = 22.4 Hz), 2.88 (1H, ddd, *J* = 4.4, 6.4, 12.8 Hz), 2.99 (1H, dd, *J* = 6.4, 12.0 Hz), 3.30 (1H, dd, *J* = 4.4, 12.0 Hz), 3.33 (2H, d, *J* = 6.0 Hz), 4.27 (1H, s br), 5.08 (1H, ddd, *J* = 1.6, 2.8, 16.4 Hz), 5.18 (1H, ddd, *J* = 1.6, 3.2, 10.0 Hz), 5.88 (1H, tdd, *J* = 6.0, 10.0, 16.4 Hz), 6.62 (2H, d, *J* = 7.6 Hz), 6.71 (1H, t, *J* = 7.2 Hz), 7.16-7.20 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8 (d, *J* = 24.4 Hz), 24.9 (d, *J* = 24.2 Hz), 43.1 (d, *J* = 5.9 Hz), 51.2, 62.8 (d, *J* = 21.5 Hz), 98.5 (d, *J* = 166.1 Hz), 113.0, 115.9, 117.4, 129.2, 137.0, 148.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -140.6 (1F, sepd, *J* = 13.2, 21.4 Hz); ESIHRMS: Found: m/z 237.1764. Calcd for $C_{14}H_{22}N_2F$: $(M+H)^+$ 237.1767.

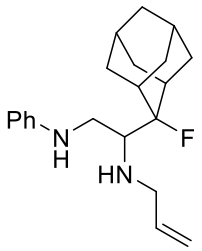
N^1-Allyl-1-(1-fluorocyclohexyl)-N^2-phenylethane-1,2-diamine (8j):



73% yield from **2j** and allyl bromide (10 equiv).

Pale yellow oil; IR (NaCl) 3418, 3358, 2934, 2862, 1603, 1504, 1481, 1449, 1321, 1258, 1152, 993, 924 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20-1.25 (1H, m), 1.38-1.68 (8H, m), 1.90-1.97 (2H, m), 2.80 (1H, ddd, *J* = 5.2, 6.4, 15.6 Hz), 3.01 (1H, dd, *J* = 6.4, 12.0 Hz), 3.30-3.32 (3H, m), 4.30 (1H, s br), 5.07 (1H, d, *J* = 10.0 Hz), 5.17 (1H, d, *J* = 17.2 Hz), 5.87 (1H, tdd, *J* = 6.0, 10.0, 17.2 Hz), 6.62 (2H, d, *J* = 8.4 Hz), 6.70 (1H, t, *J* = 7.2 Hz), 7.17 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6 (overlapped), 25.3, 32.0 (d, *J* = 22.3 Hz), 32.6 (d, *J* = 22.4 Hz), 42.5 (d, *J* = 4.8 Hz), 51.3, 62.2 (d, *J* = 21.4 Hz), 98.9 (d, *J* = 171.1 Hz), 113.0, 115.8, 117.3, 129.2, 137.1, 148.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -163.3 (1F, m); ESIHRMS: Found: m/z 277.2077. Calcd for $C_{17}H_{26}N_2F$: $(M+H)^+$ 277.2080.

N^1-Allyl-1-(2-fluoroadamantan-2-yl)-N^2-phenylethane-1,2-diamine (8k):

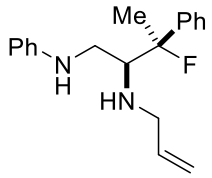


69% yield from **2k** and allyl bromide (15 equiv).

Colorless oil; IR (NaCl) 3424, 3362, 3049, 2914, 2860, 1603, 1504, 1474, 1456, 1321, 1258, 1152, 991, 972, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.58-1.84 (11H, m), 2.13-2.15 (3H, m), 2.49 (1H, m), 3.02 (1H, dd, *J* = 6.8, 12.0 Hz), 3.28 (1H, ddd, *J* = 4.0, 6.8, 30.8 Hz), 3.35 (2H, d, *J* = 6.0 Hz), 3.41 (1H, dd, *J* = 4.0, 12.0 Hz), 4.41 (1H, s br), 5.07 (1H, dd, *J* = 1.2, 10.4 Hz), 5.19 (1H, dd, *J* = 1.6, 17.2 Hz), 5.88 (1H, tdd, *J* = 6.0, 10.4, 17.2 Hz), 6.64 (2H, d, *J* = 8.0 Hz), 6.69 (1H, t, *J* = 7.2 Hz), 7.17 (2H, t, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.6, 26.9, 32.7 (d, *J* = 20.5 Hz), 32.8 (d, *J* = 4.0 Hz), 33.1 (d, *J* = 3.6 Hz), 33.6 (d, *J* = 19.2 Hz), 34.6 (d, *J* = 7.8 Hz), 35.1 (d, *J* =

8.1 Hz), 37.5, 41.1, 51.1, 55.5 (d, J = 20.2 Hz), 103.0 (d, J = 178.3 Hz), 113.0, 115.8, 117.2, 129.2, 137.5, 148.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -162.0 (1F, d, J = 30.5 Hz); ESIHRMS: Found: m/z 329.2393. Calcd for $C_{21}H_{30}N_2F$: $(M+H)^+$ 329.2393.

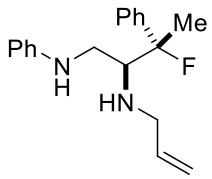
(2*S,3*R**)-*N*^{2}-Allyl-3-fluoro-*N*^{1},3-diphenylbutane-1,2-diamine (8l):**



69% yield from **2l** and allyl bromide (10 equiv).

Pale yellow oil; IR (NaCl) 3416, 3364, 3055, 2982, 2934, 1603, 1504, 1447, 1375, 1319, 1260, 1180, 1070, 920 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (1H, s br), 1.77 (3H, d, J = 23.6 Hz), 2.88 (1H, dd, J = 7.6, 12.4 Hz), 3.04 (1H, ddd, J = 4.4, 7.6, 22.8 Hz), 3.16 (1H, dd, J = 4.4, 12.4 Hz), 3.26-3.36 (2H, m), 4.03 (1H, s br), 5.05 (1H, ddd, J = 1.2, 3.2, 10.0 Hz), 5.14 (1H, ddd, J = 1.6, 3.2, 17.2 Hz), 5.83 (1H, tdd, J = 6.0, 10.0, 17.2 Hz), 6.46 (2H, d, J = 7.6 Hz), 6.66 (1H, t, J = 7.6 Hz), 7.09-7.14 (2H, m), 7.28-7.40 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7 (d, J = 24.8 Hz), 43.1 (d, J = 4.3 Hz), 51.3, 63.0 (d, J = 22.2 Hz), 100.6 (d, J = 175.3 Hz), 113.1, 115.8, 117.3, 124.2 (d, J = 10.0 Hz), 127.6, 128.4 (d, J = 1.2 Hz), 129.3, 137.2, 142.9 (d, J = 21.4 Hz), 148.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -157.4 (1F, dq, J = 22.9, 23.3 Hz); ESIHRMS: Found: m/z 321.1730. Calcd for $C_{19}H_{23}N_2FNa$: $(M+Na)^+$ 321.1743.

(2*S,3*S**)-*N*^{2}-Allyl-3-fluoro-*N*^{1},3-diphenylbutane-1,2-diamine (8m):**

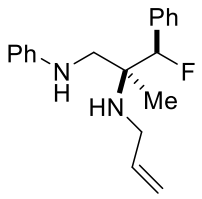


72% yield from **2m** and allyl bromide (10 equiv).

Yellow oil; IR (NaCl) 3385, 3360, 3055, 2982, 2934, 2853, 1603, 1504, 1447, 1377, 1317, 1260, 1180, 1153, 1123, 1069, 993, 922 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (1H, s br), 1.78 (3H, d, J = 24.0 Hz), 2.89 (1H, dd, J = 7.2, 12.4 Hz), 3.09-3.15 (3H, m), 3.22 (1H, dd, J = 4.0, 12.4 Hz), 4.11 (1H, s br), 5.01-5.09 (2H, m), 5.77 (1H, tdd, J = 6.0, 11.2, 16.4 Hz), 6.51 (2H, d, J = 8.4 Hz), 6.68 (1H, t, J = 7.6 Hz), 7.14

(2H, t, J = 7.6 Hz), 7.30-7.42 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6 (d, J = 23.9 Hz), 43.0 (d, J = 4.2 Hz), 51.0, 63.4 (d, J = 23.9 Hz), 99.9 (d, J = 173.2 Hz), 113.0, 115.9, 117.4, 124.8 (d, J = 9.4 Hz), 127.8, 128.3, 129.2, 137.0, 142.7 (d, J = 21.9 Hz), 148.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -150.6 (1F, dq, J = 16.5, 23.3 Hz); ESIHRMS: Found: m/z 299.1926. Calcd for $C_{19}H_{24}N_2F$: $(M+H)^+$ 299.1924.

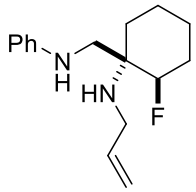
(2*S,3*R**)-*N*^{2}-Allyl-3-fluoro-2-methyl-*N*^{1},3-diphenylpropane-1,2-diamine (8n):**



52% yield from **2n** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3383, 3009, 2924, 2847, 1603, 1506, 1452, 1429, 1379, 1317, 1179, 1007, 922 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, d, J = 1.6 Hz), 1.36 (1H, s br), 3.08 (1H, d, J = 12.0 Hz), 3.24-3.27 (3H, m), 4.34 (1H, s br), 5.06 (1H, dd, J = 1.6, 10.4 Hz), 5.18 (1H, dd, J = 1.6, 17.2 Hz), 5.55 (1H, d, J = 45.2 Hz), 5.88 (1H, tdd, J = 5.6, 10.4, 17.2 Hz), 6.63 (2H, d, J = 7.6 Hz), 6.69 (1H, t, J = 7.2 Hz), 7.18 (2H, t, J = 7.6 Hz), 7.33-7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4 (d, J = 3.1 Hz), 44.1, 46.9 (d, J = 3.4 Hz), 58.3 (d, J = 22.2 Hz), 96.1 (d, J = 177.9 Hz), 112.9, 115.4, 117.2, 126.9 (d, J = 7.8 Hz), 128.1, 128.5, 129.2, 136.2 (d, J = 20.9 Hz), 136.9, 148.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -187.8 (1F, dd, J = 19.2, 45.1 Hz); ESIHRMS: Found: m/z 299.1931. Calcd for $C_{19}H_{24}N_2F$: $(M+H)^+$ 299.1924.

***N*-(((1*S**,2*R**)-1-(Allylamino)-2-fluorocyclohexyl)methyl)aniline (8o):**

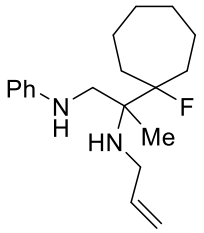


61% yield from **2o** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3372, 3076, 2938, 2862, 1603, 1504, 1485, 1427, 1321, 1254, 1180, 1084, 991, 918 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (1H, s br), 1.43-1.68 (6H, m), 1.79-1.87 (2H, m), 3.09-3.22 (4H, m), 4.22 (1H, s br), 4.60 (1H, ddd, J = 4.0, 4.4, 47.6 Hz), 5.05-5.08 (1H, m), 5.18-5.22 (1H, m), 5.89 (1H, tdd, J = 6.0, 10.4, 17.2

Hz), 6.64 (2H, d, J = 8.0 Hz), 6.68 (1H, t, J = 7.6 Hz), 7.16 (2H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.0 (d, J = 5.0 Hz), 27.1 (d, J = 20.3 Hz), 29.2, 43.5, 44.6 (d, J = 4.2 Hz), 56.8 (d, J = 19.0 Hz), 92.8 (d, J = 175.4 Hz), 112.9, 115.5, 117.0, 129.2, 137.1, 148.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -190.1 (1F, m); ESIHRMS: Found: m/z 263.1926. Calcd for $C_{16}H_{24}N_2F$: $(M+H)^+$ 263.1924.

N^2-Allyl-2-(1-fluorocycloheptyl)-N^1-phenylpropane-1,2-diamine (8q):



68% yield from **2q** and allyl bromide (10 equiv).

Colorless oil; IR (NaCl) 3437, 3364, 3049, 2928, 2857, 1603, 1504, 1485, 1379, 1321, 1273, 1179, 1015, 916 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (3H, s), 1.44-1.92 (10H, m), 1.98-2.08 (3H, m), 3.13 (2H, s), 3.19-3.21 (2H, m), 4.42 (1H, s br), 5.02 (1H, dd, J = 1.6, 10.4 Hz), 5.18 (1H, dd, J = 2.0, 17.2 Hz), 5.88 (1H, tdd, J = 5.6, 10.4, 17.2 Hz), 6.60 (2H, d, J = 7.6 Hz), 6.67 (1H, t, J = 7.2 Hz), 7.15-7.19 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0 (d, J = 5.8 Hz), 22.9 (d, J = 4.2 Hz), 23.0 (d, J = 6.9 Hz), 29.6, 30.1, 33.9 (d, J = 24.3 Hz), 34.7 (d, J = 24.1 Hz), 45.0 (d, J = 2.9 Hz), 46.1 (d, J = 2.7 Hz), 61.2 (d, J = 19.4 Hz), 106.0 (d, J = 173.7 Hz), 112.6, 114.7, 116.8, 129.2, 137.9, 148.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -148.0--147.7 (1F, m); ESIHRMS: Found: m/z 305.2388. Calcd for $C_{19}H_{30}N_2F$: $(M+H)^+$ 305.2393.

6. References

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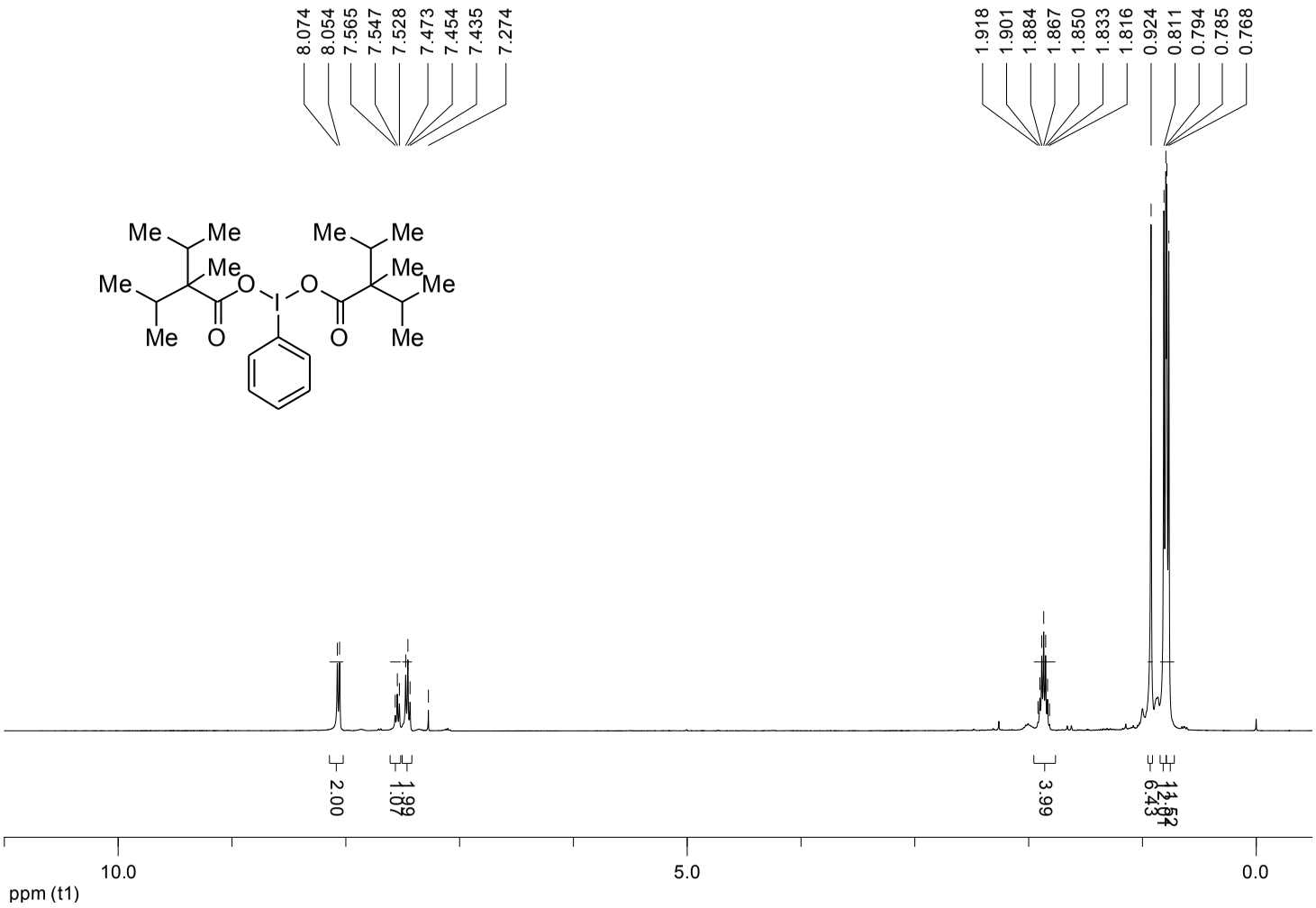
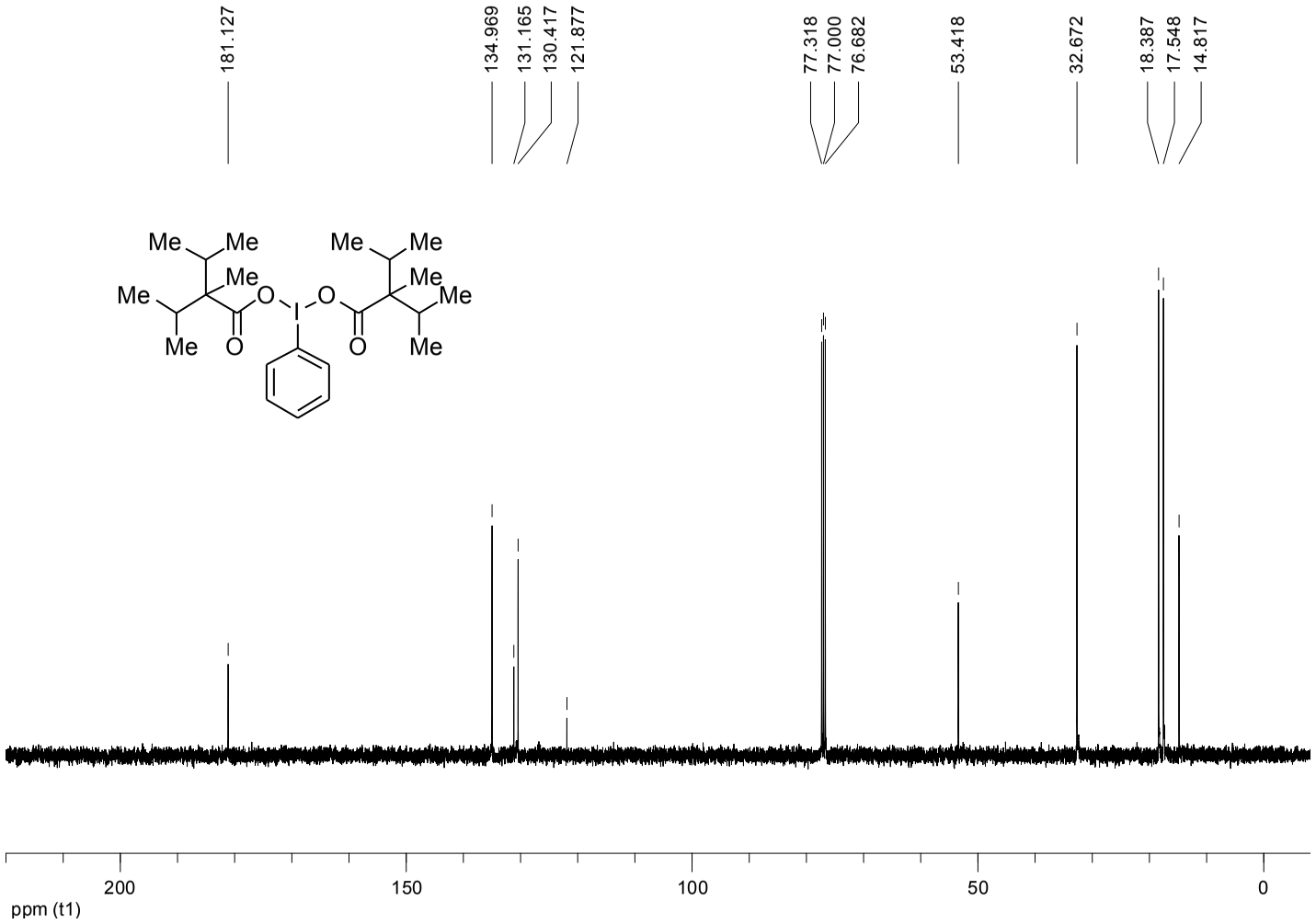
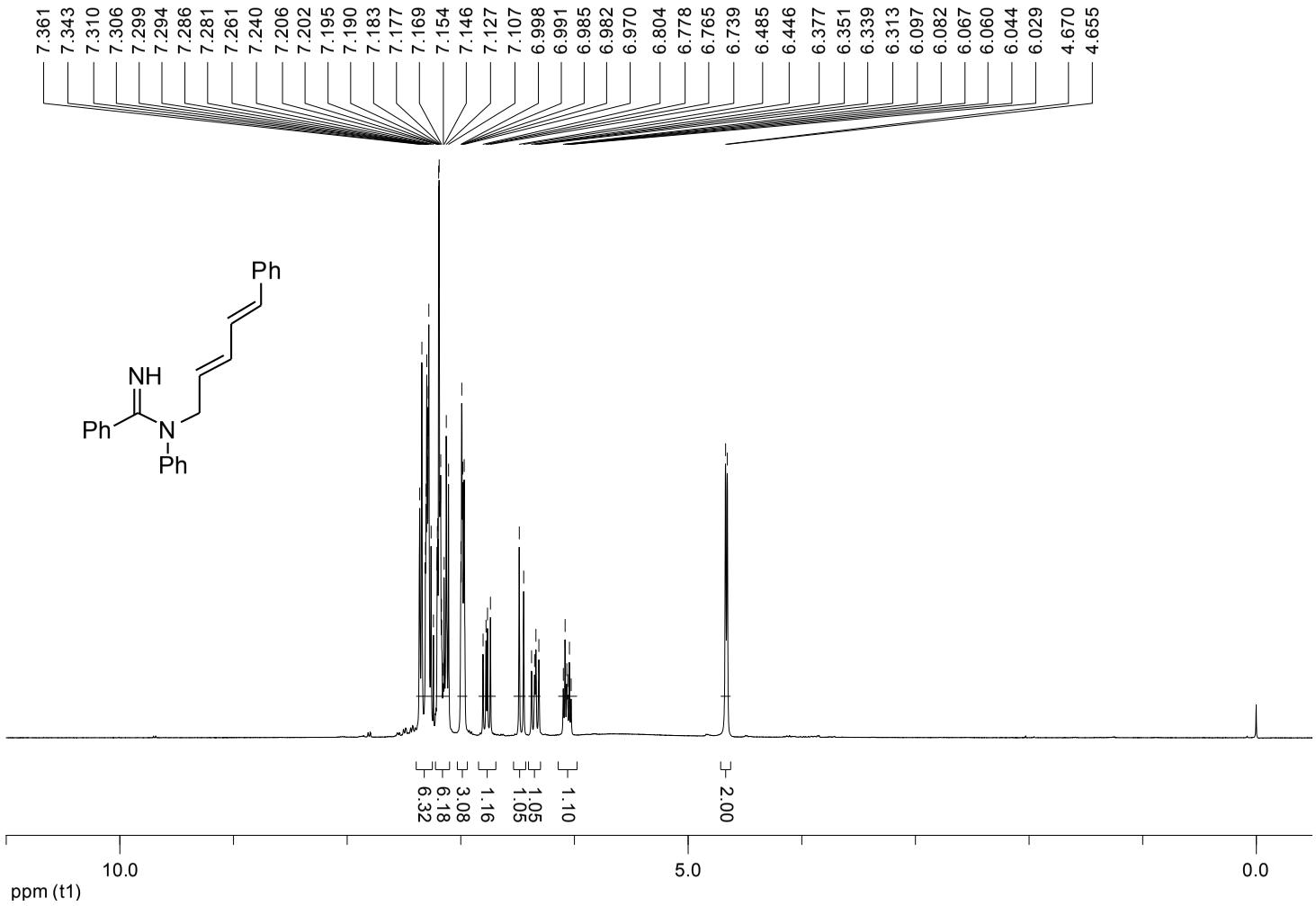
^{1}H NMR spectrum of PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (400 MHz, $CDCl_3$)



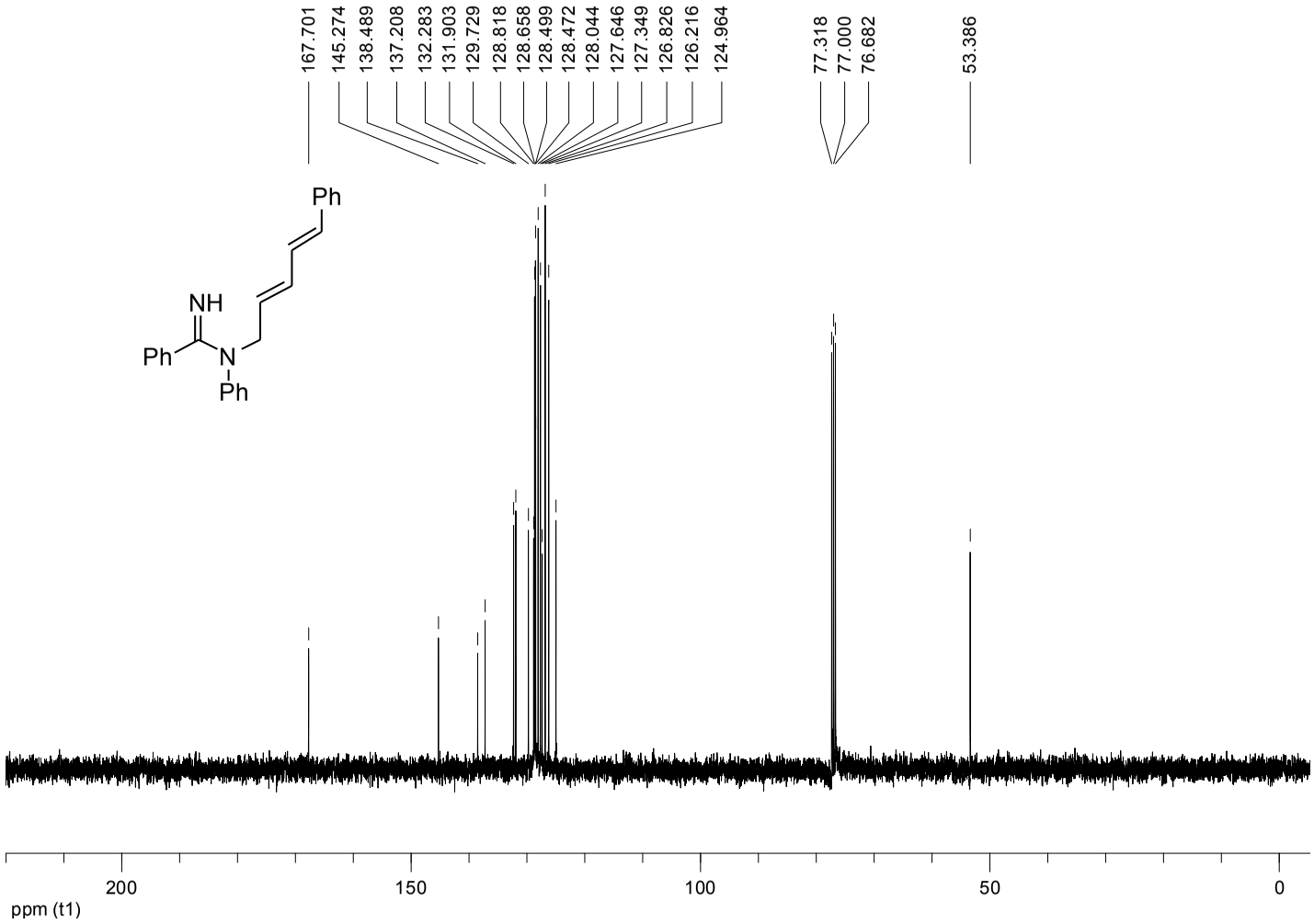
^{13}C NMR spectrum of PhI[OCOC(*i*-Pr)$_2$Me]$_2$ (100 MHz, $CDCl_3$)



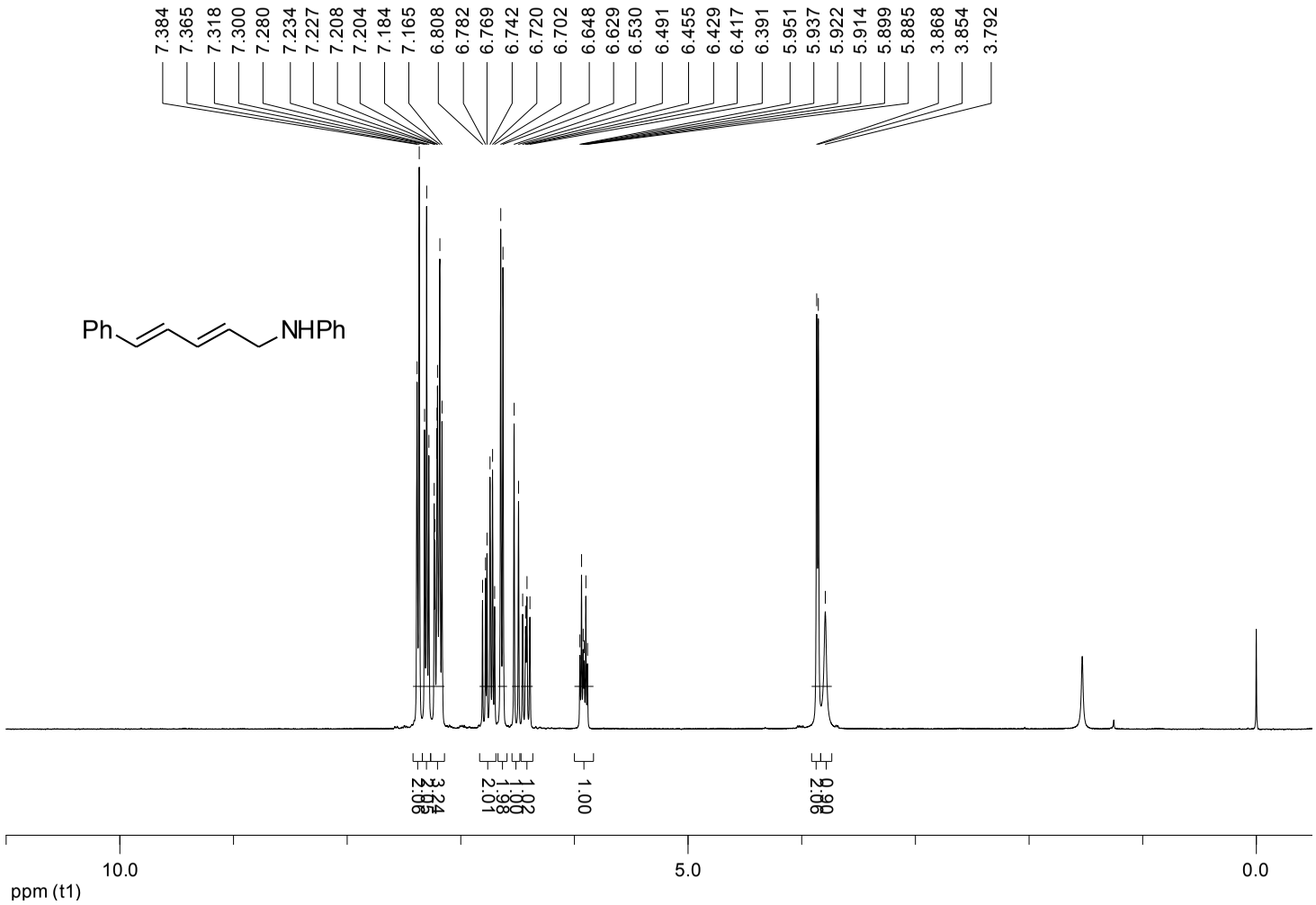
^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)



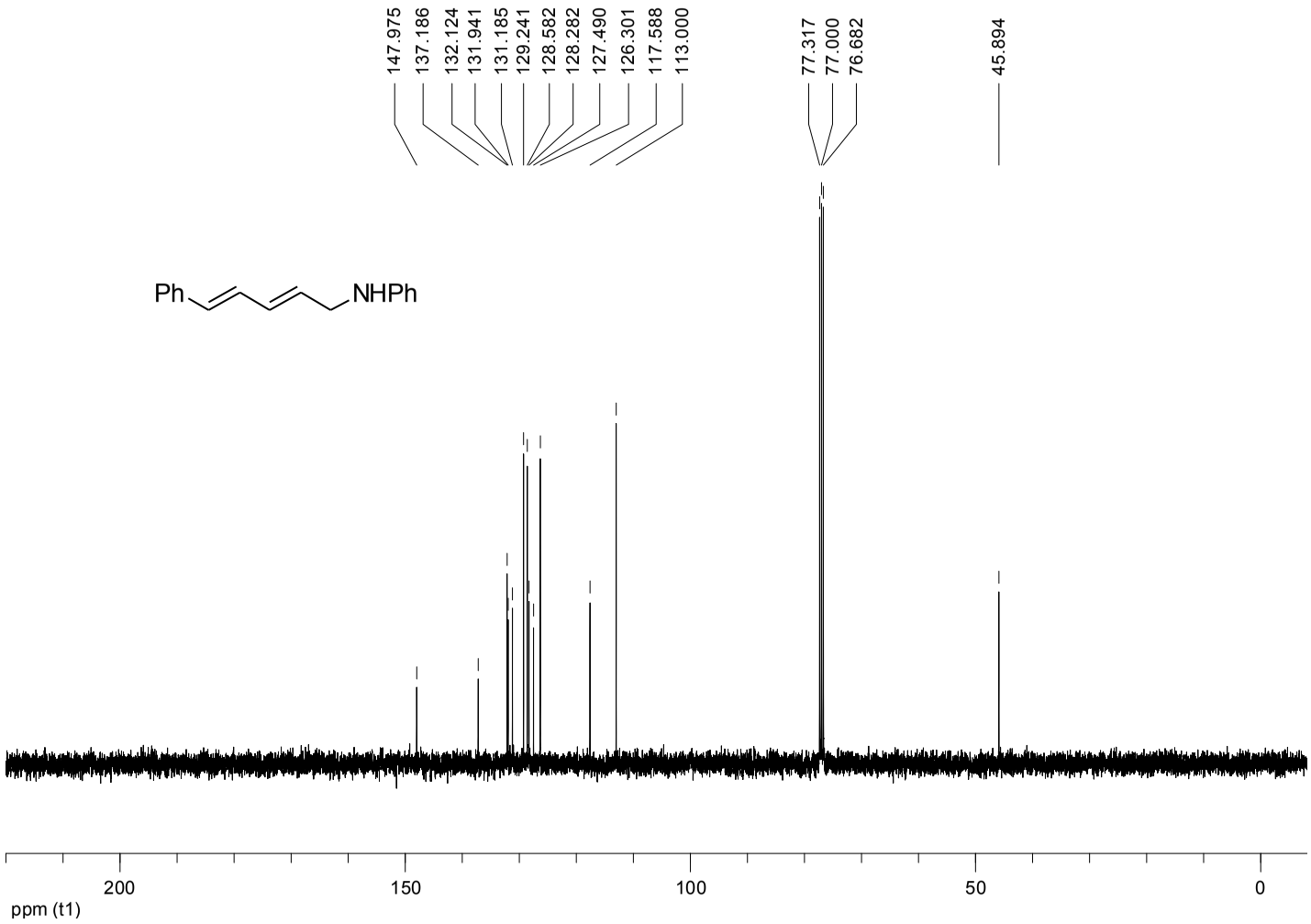
^{13}C NMR spectrum of **1f** (100 MHz, $CDCl_3$)



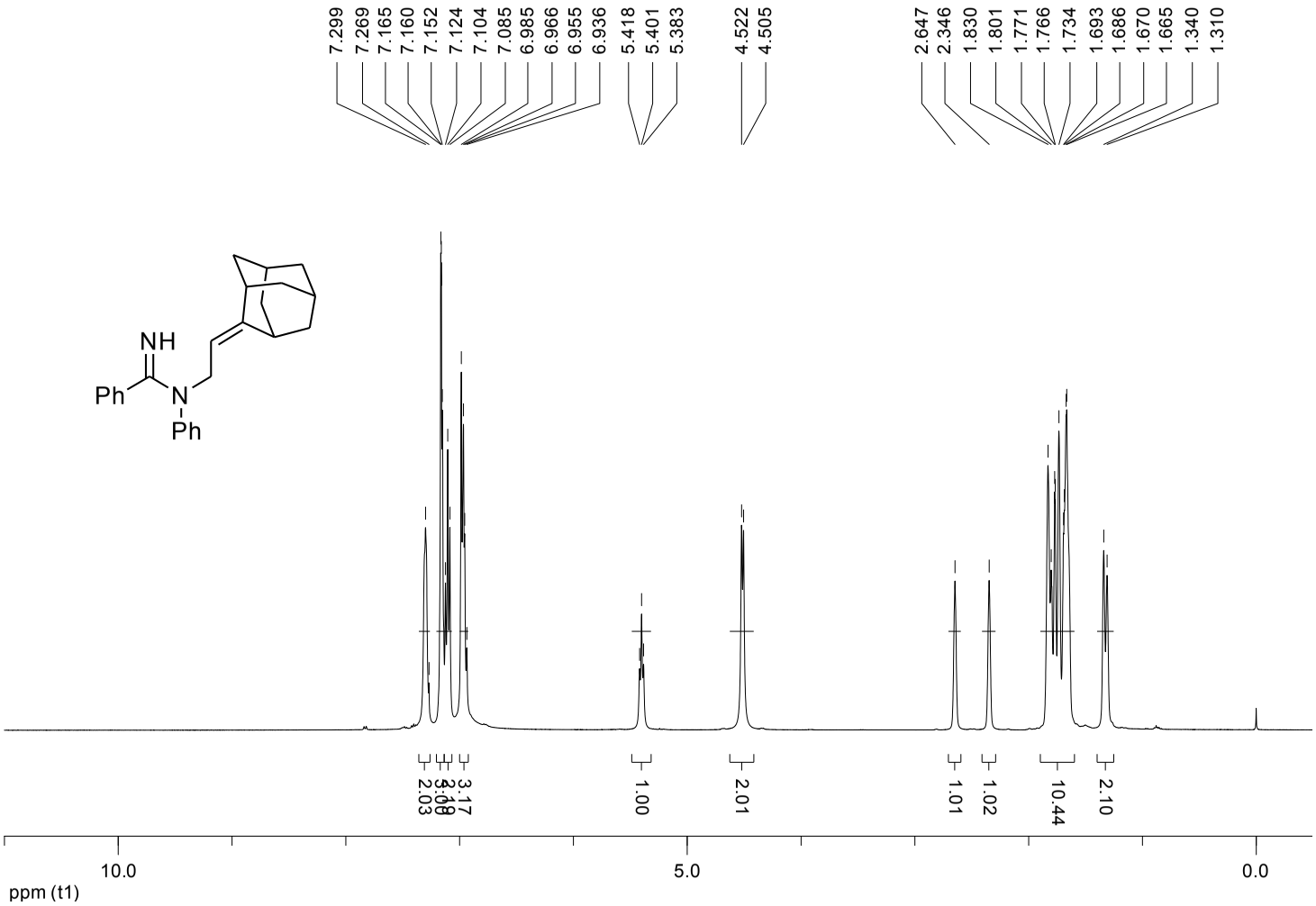
^{1}H NMR spectrum of **A** (400 MHz, $CDCl_3$)



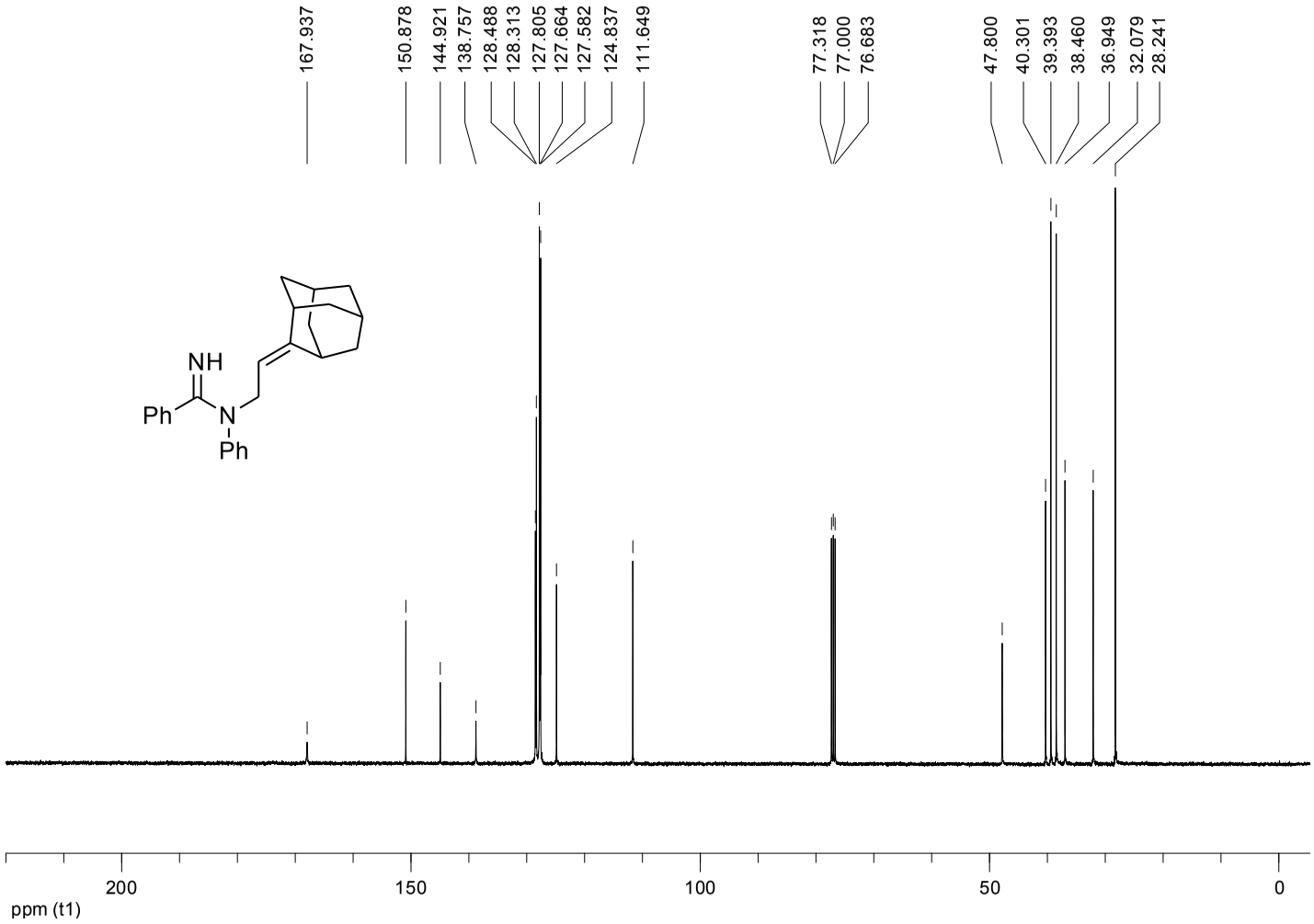
^{13}C NMR spectrum of **A** (100 MHz, $CDCl_3$)



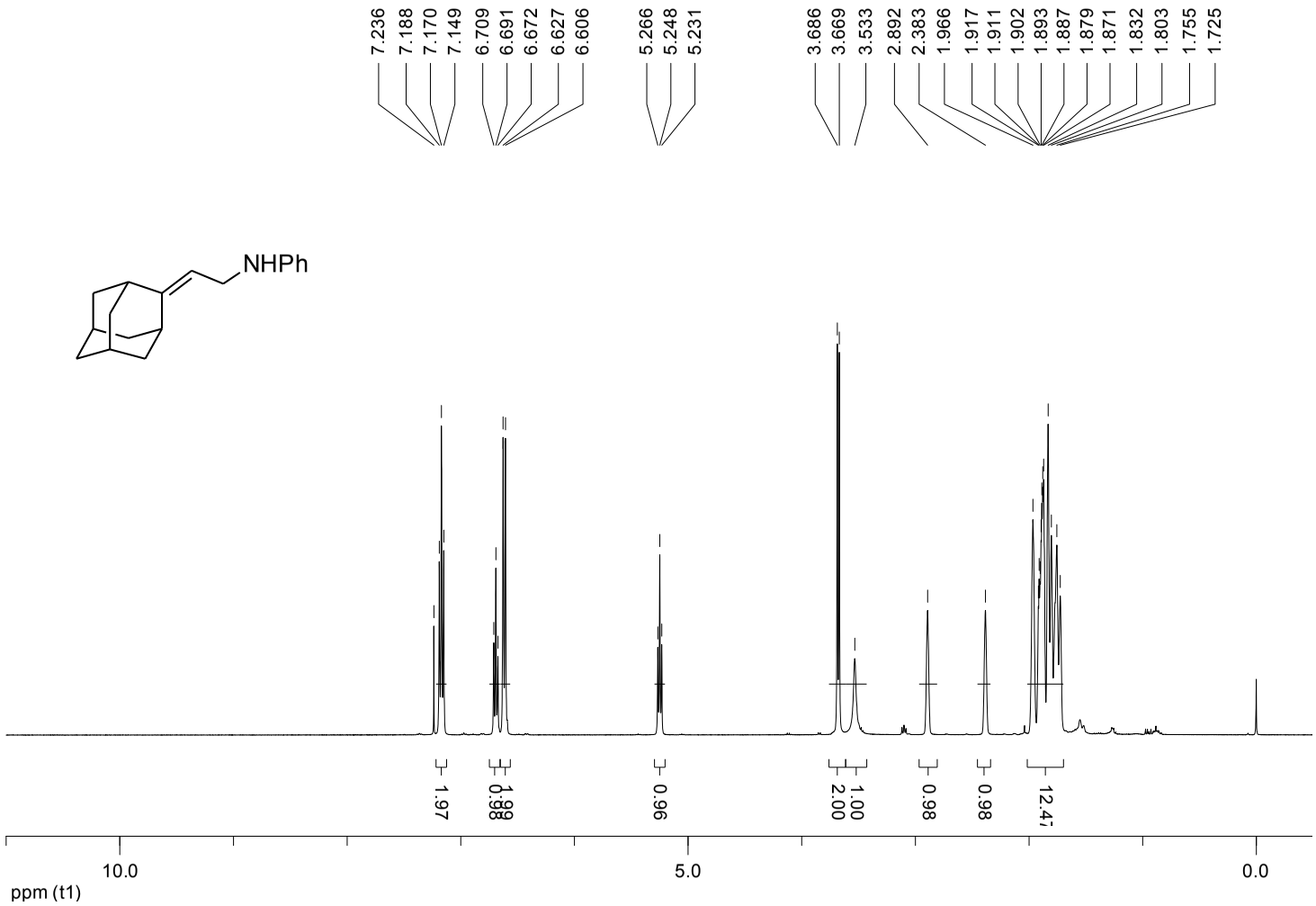
^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)



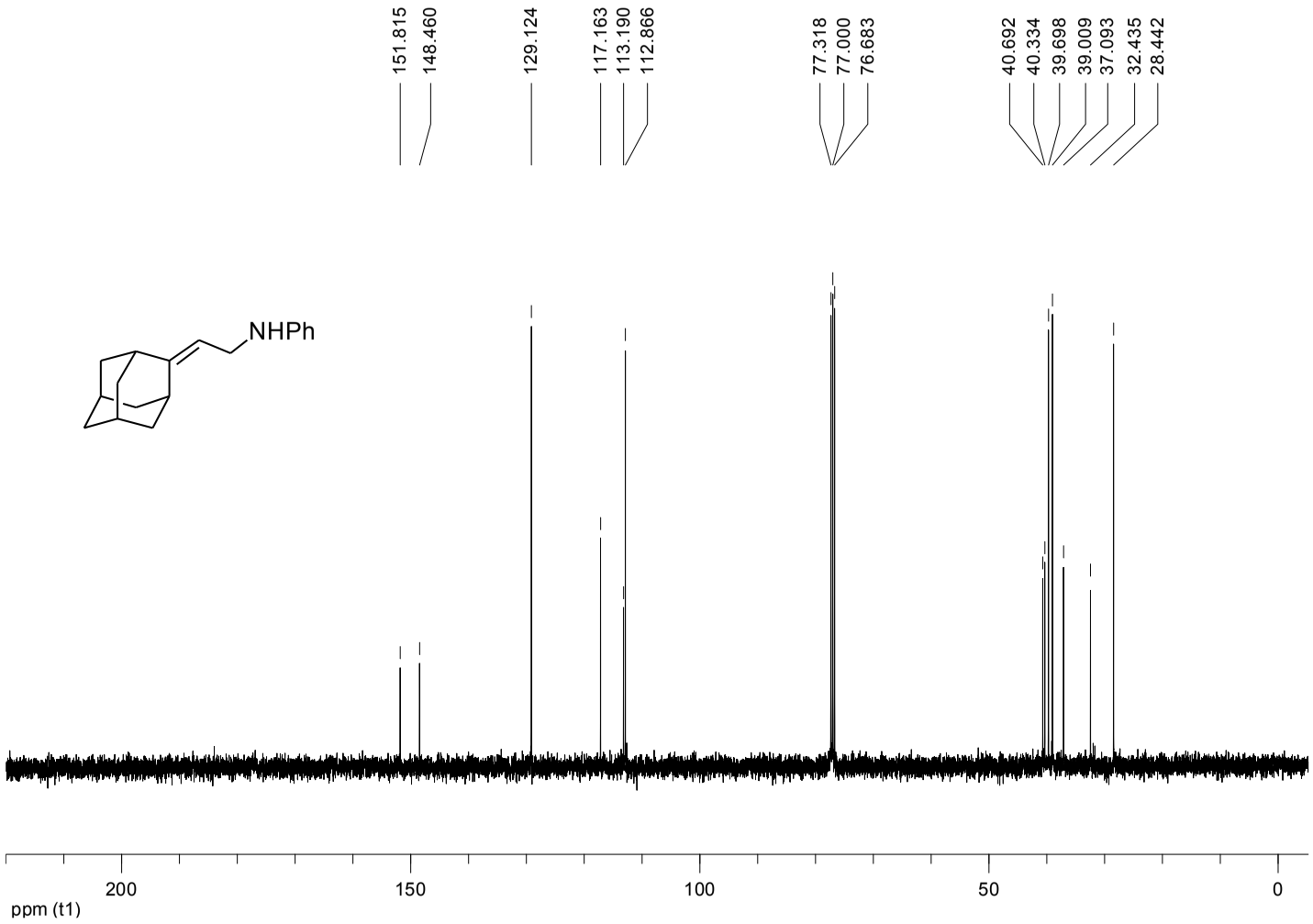
^{13}C NMR spectrum of **1k** (100 MHz, $CDCl_3$)



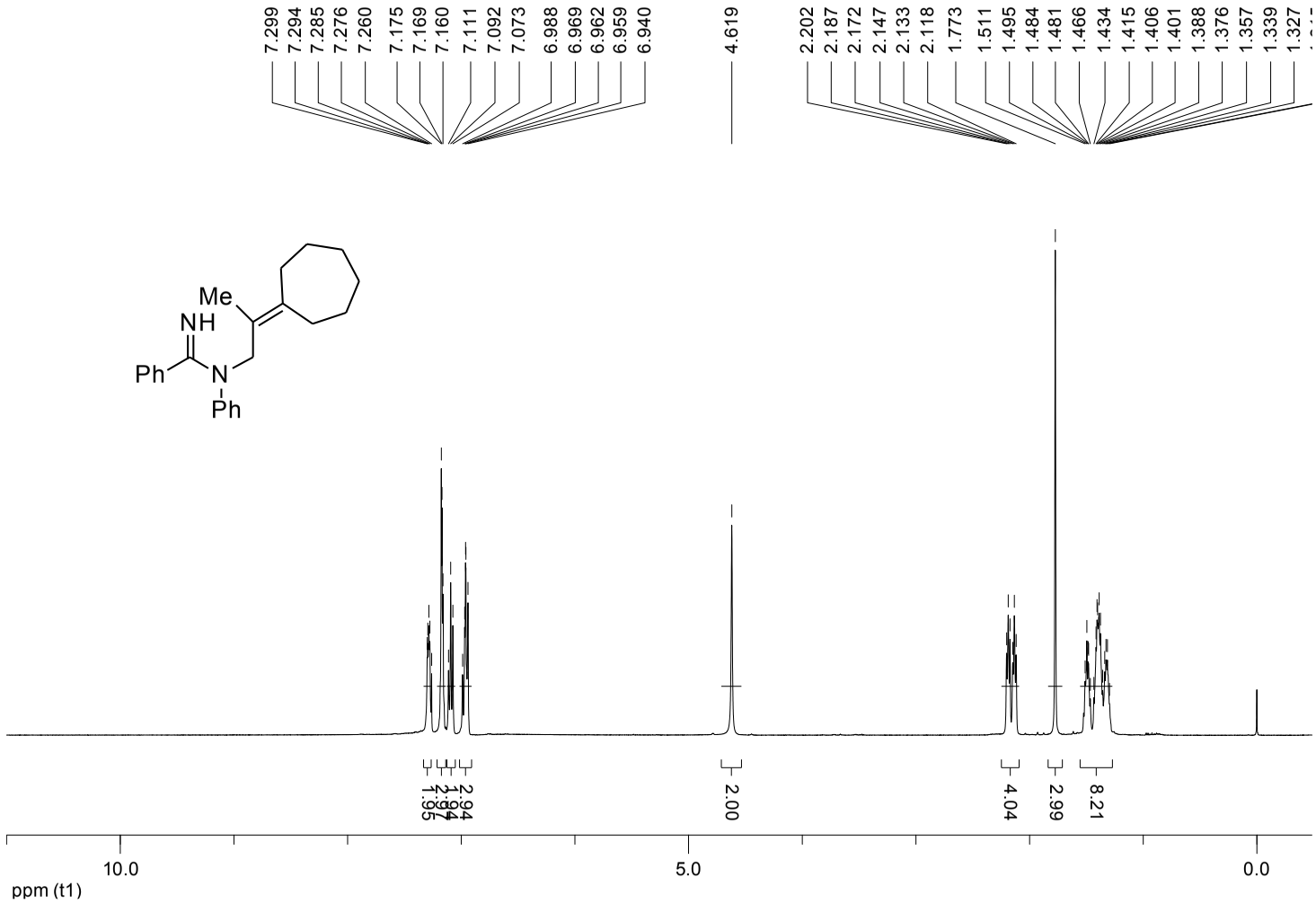
^{1}H NMR spectrum of **B** (400 MHz, $CDCl_3$)



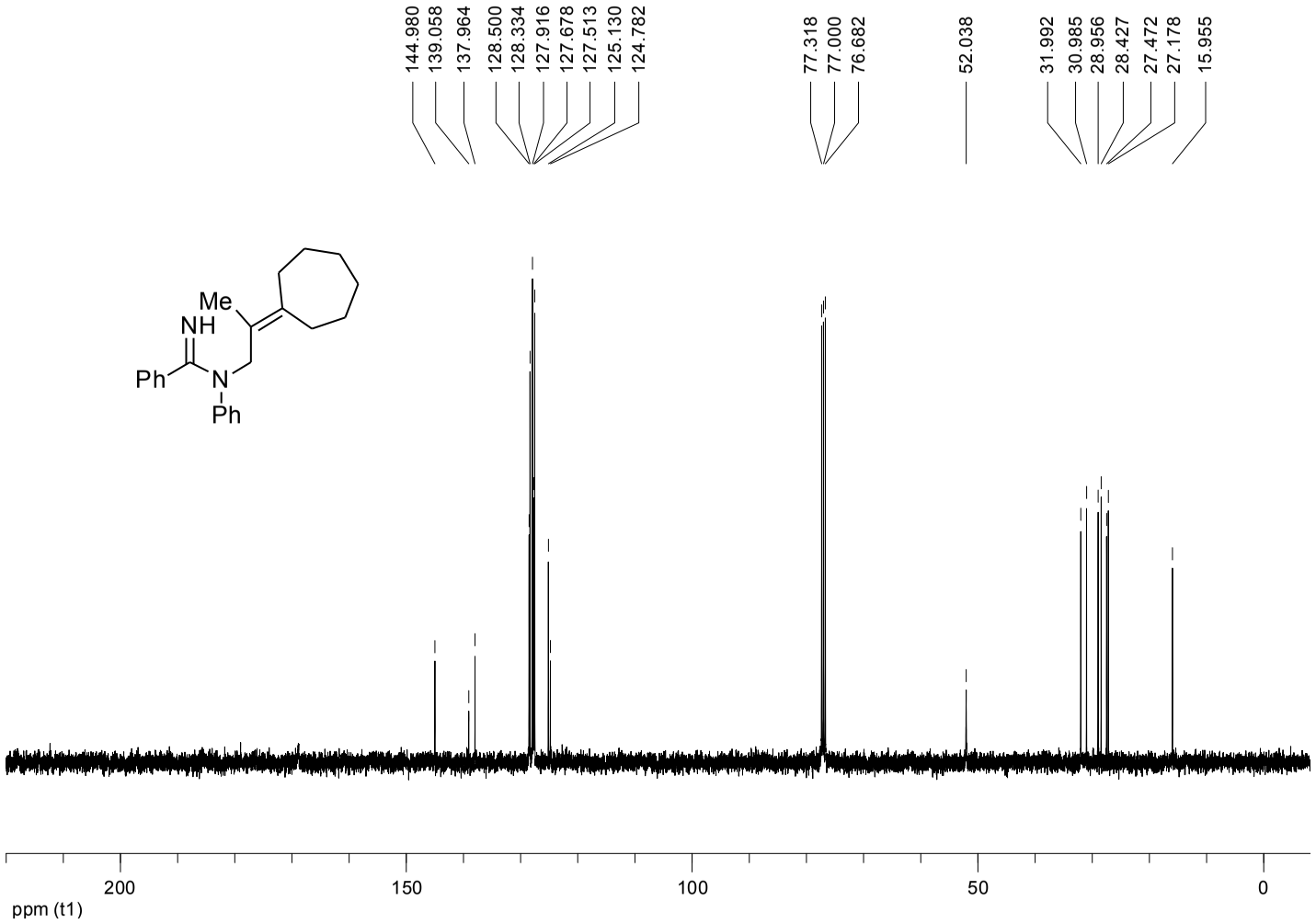
^{13}C NMR spectrum of **B** (100 MHz, $CDCl_3$)



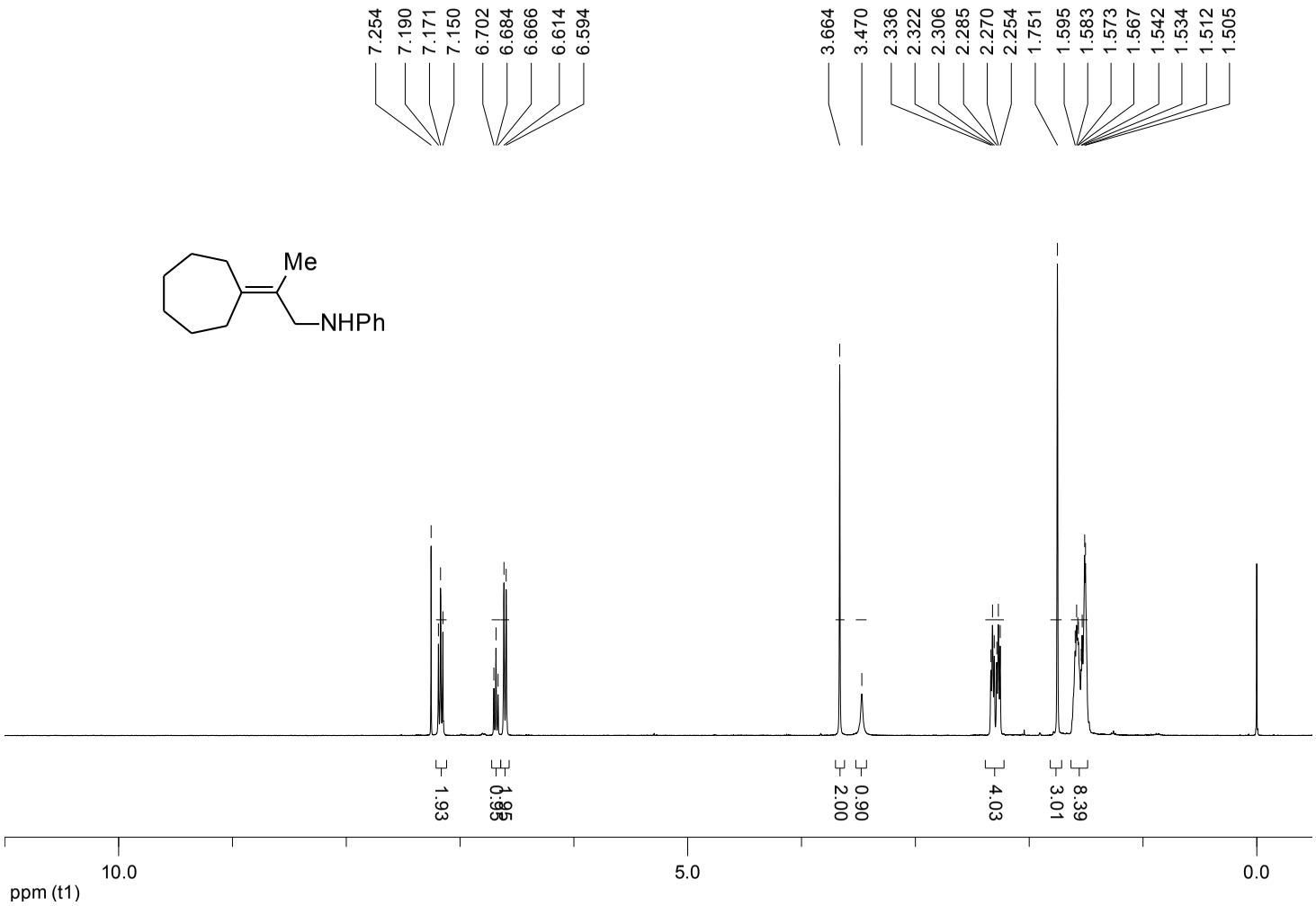
^{1}H NMR spectrum of **1q** (400 MHz, $CDCl_3$)



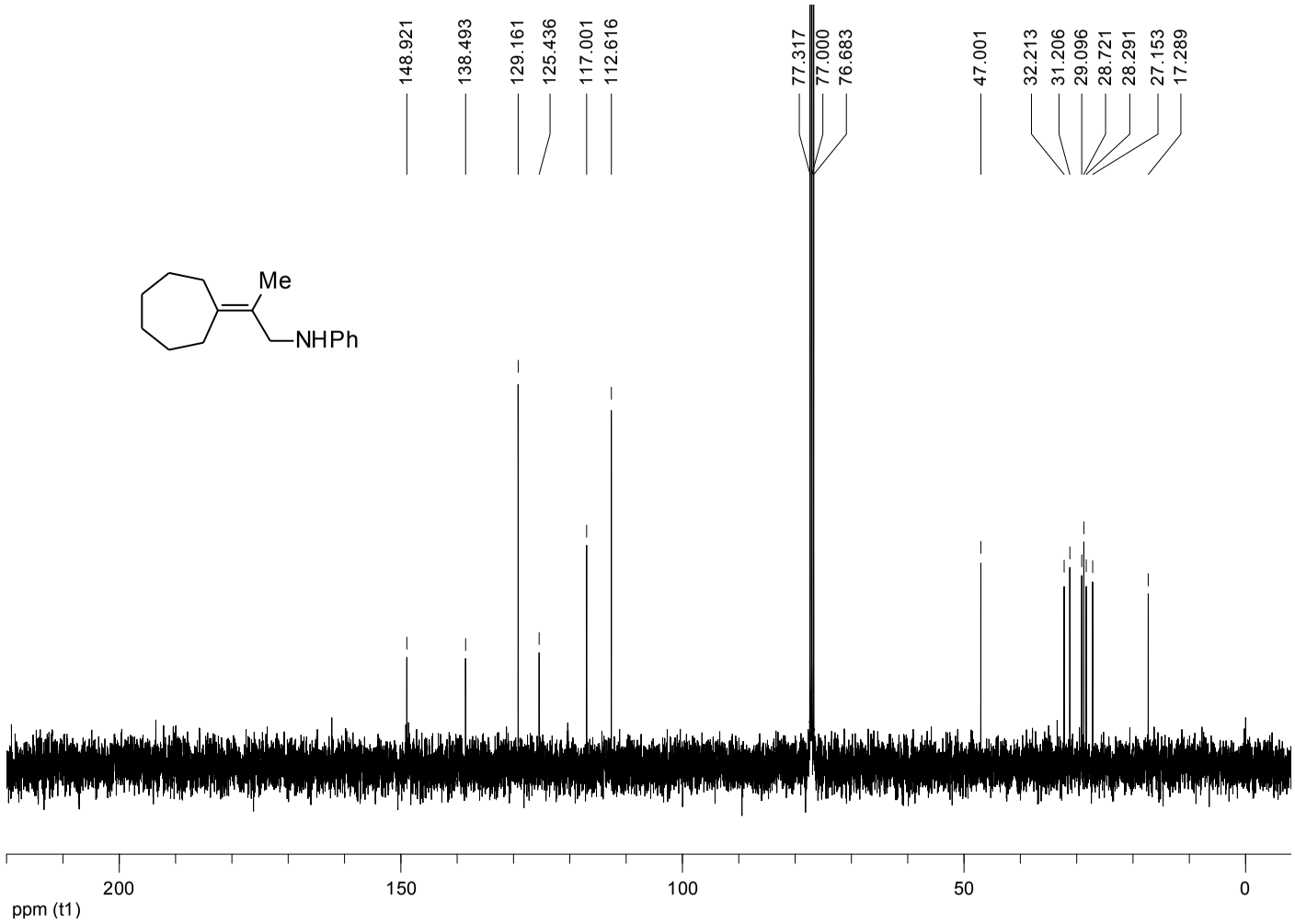
^{13}C NMR spectrum of **1q** (100 MHz, $CDCl_3$)



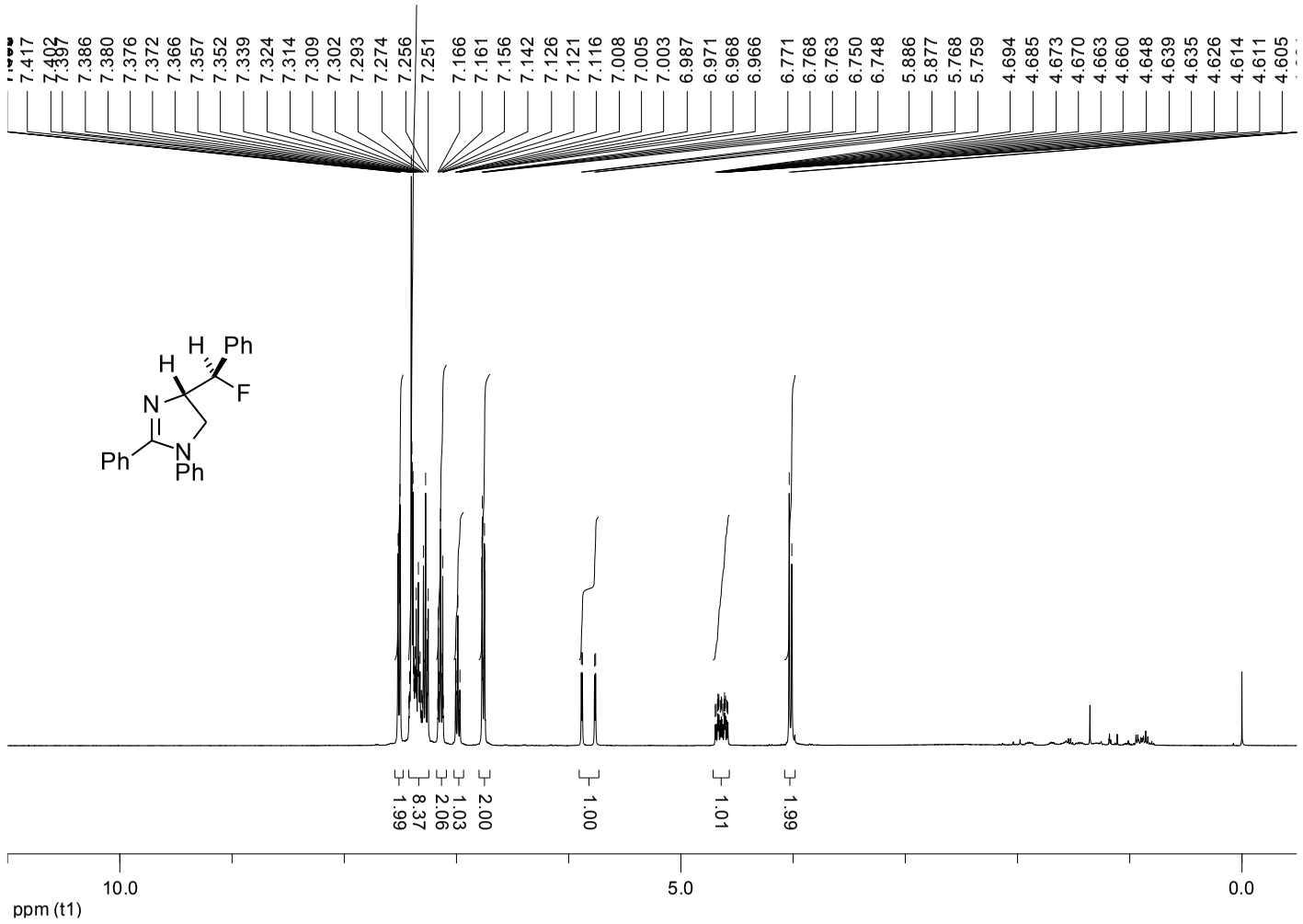
^{1}H NMR spectrum of **C** (400 MHz, $CDCl_3$)



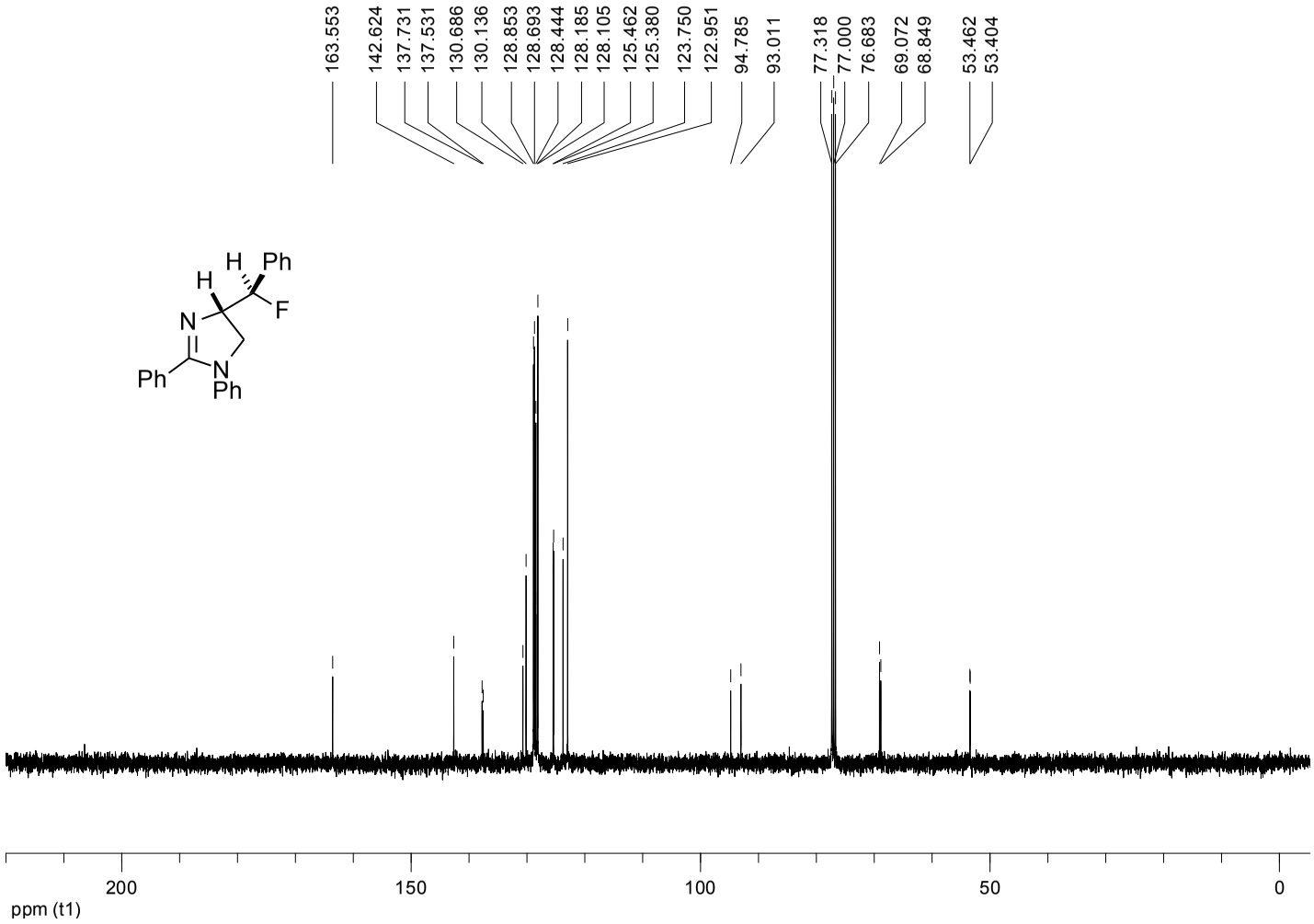
^{13}C NMR spectrum of **C** (100 MHz, $CDCl_3$)



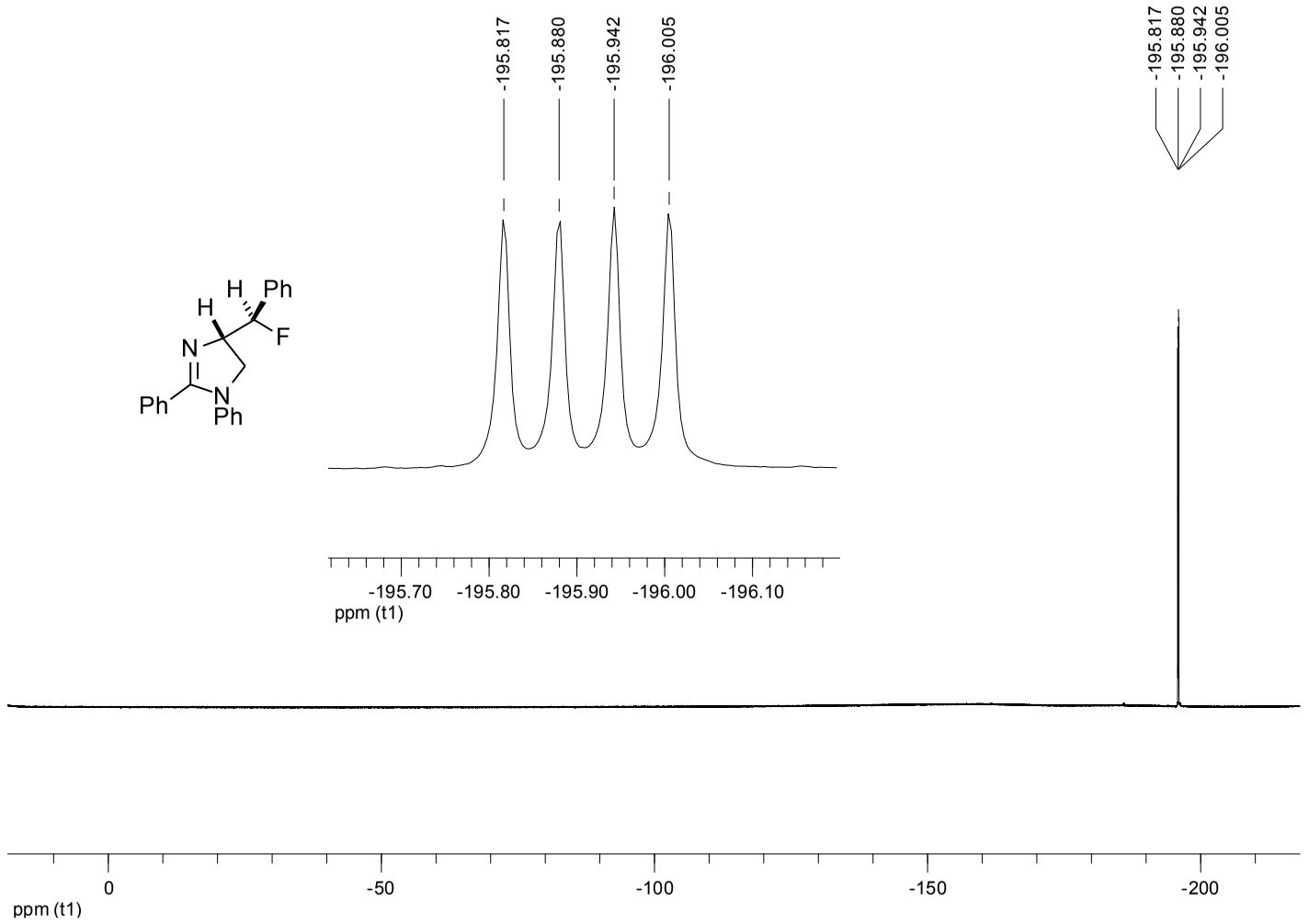
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



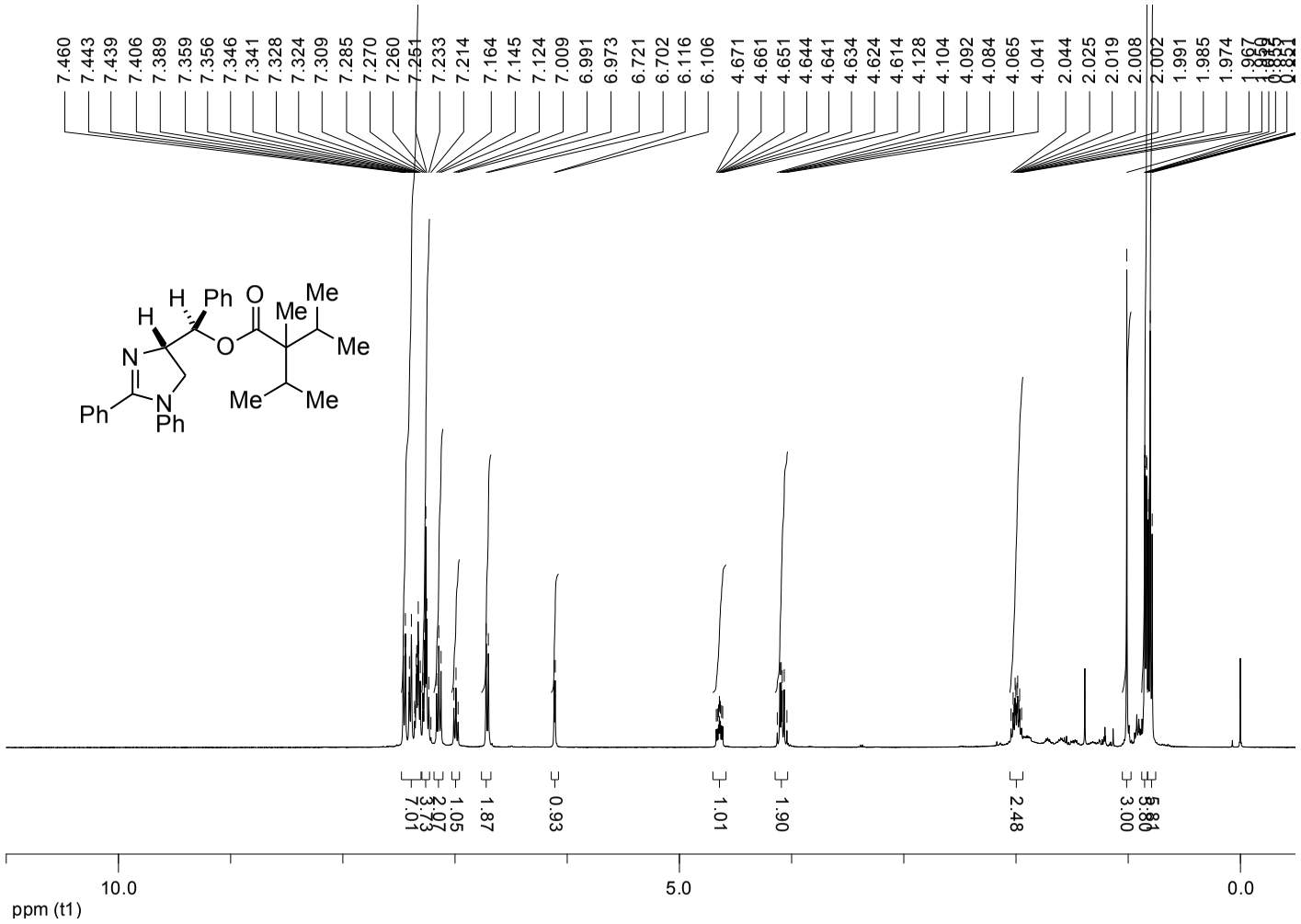
^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)



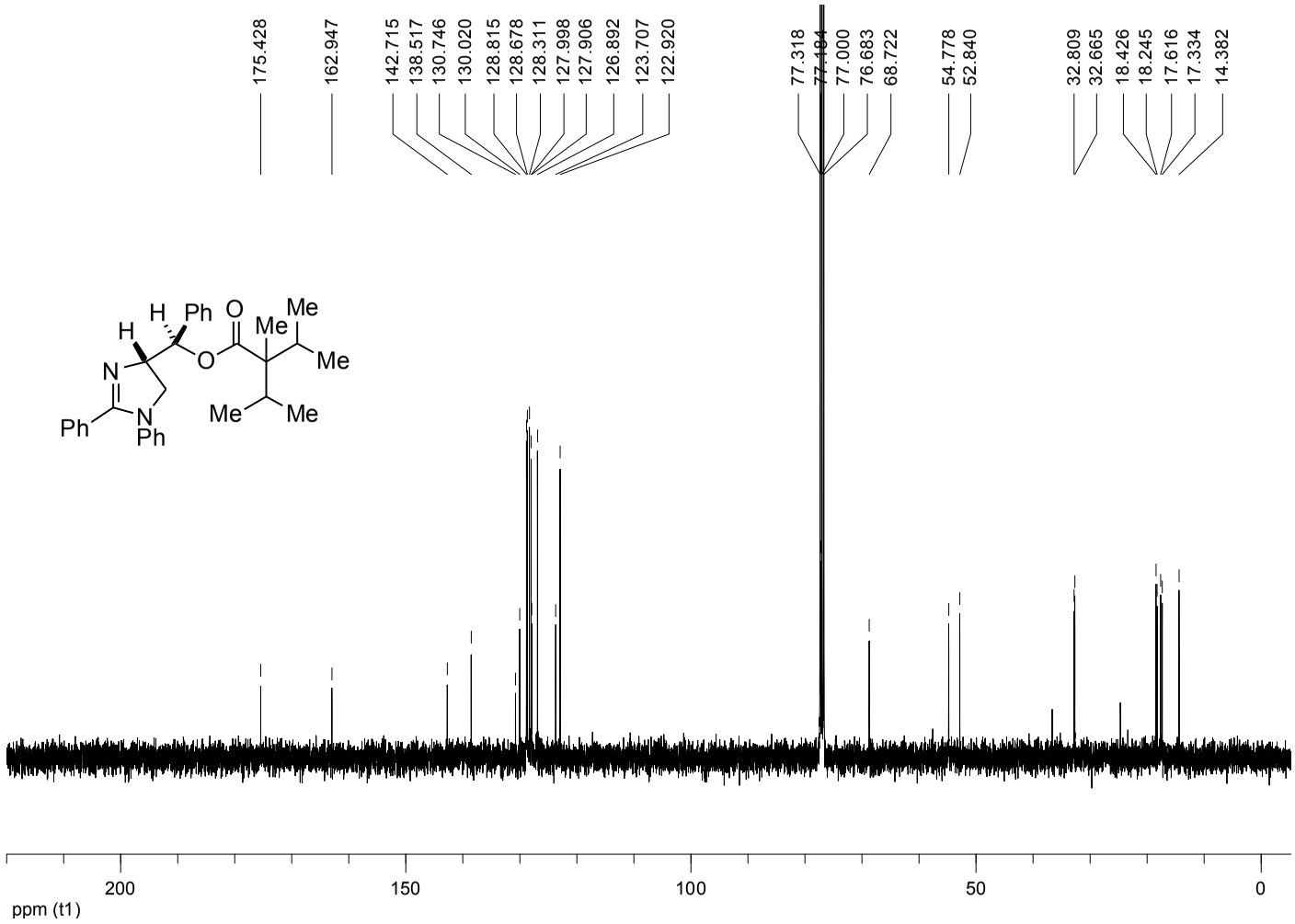
^{19}F NMR spectrum of **2a** (376 MHz, $CDCl_3$)



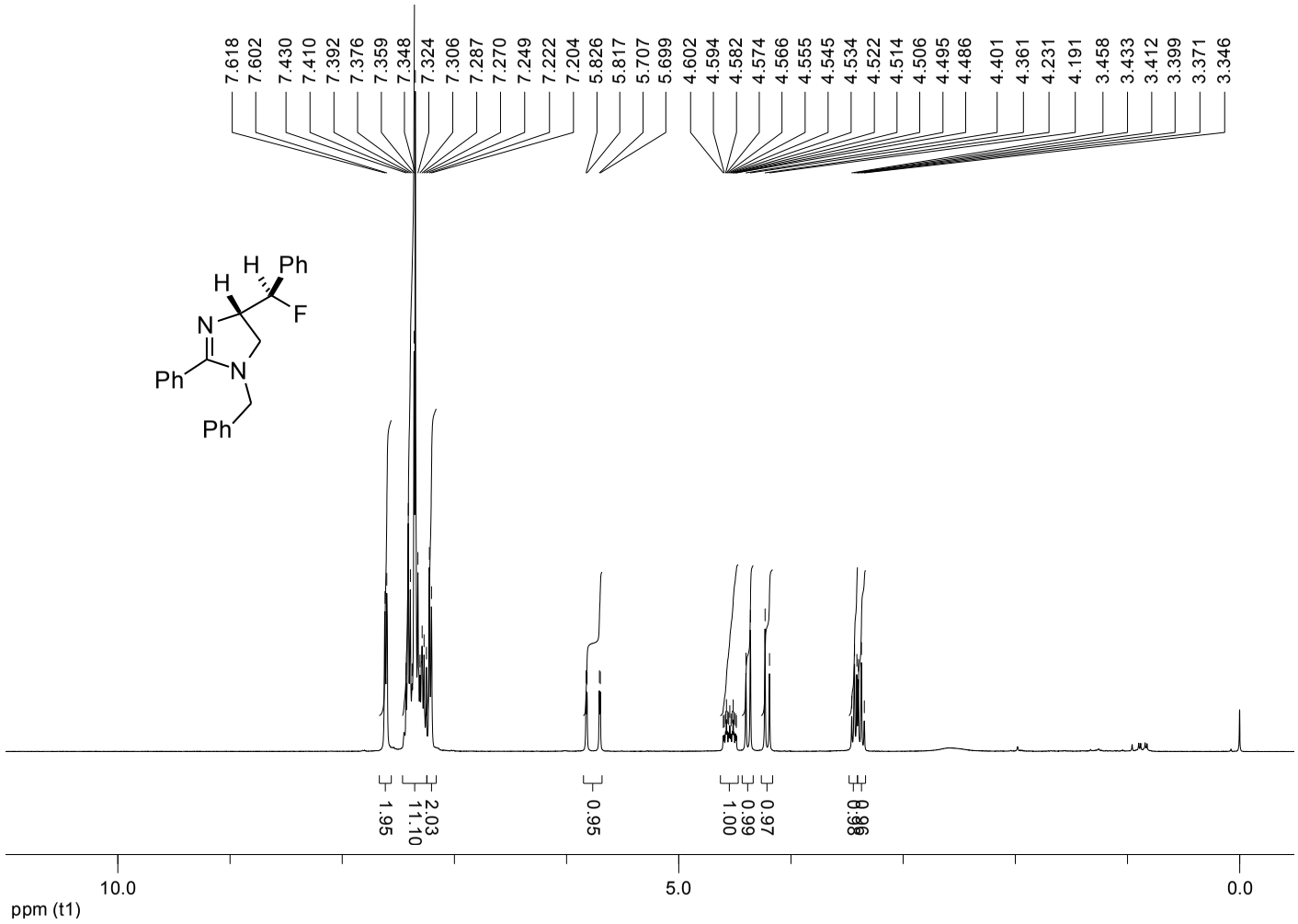
^{1}H NMR spectrum of **5a** (400 MHz, $CDCl_3$)



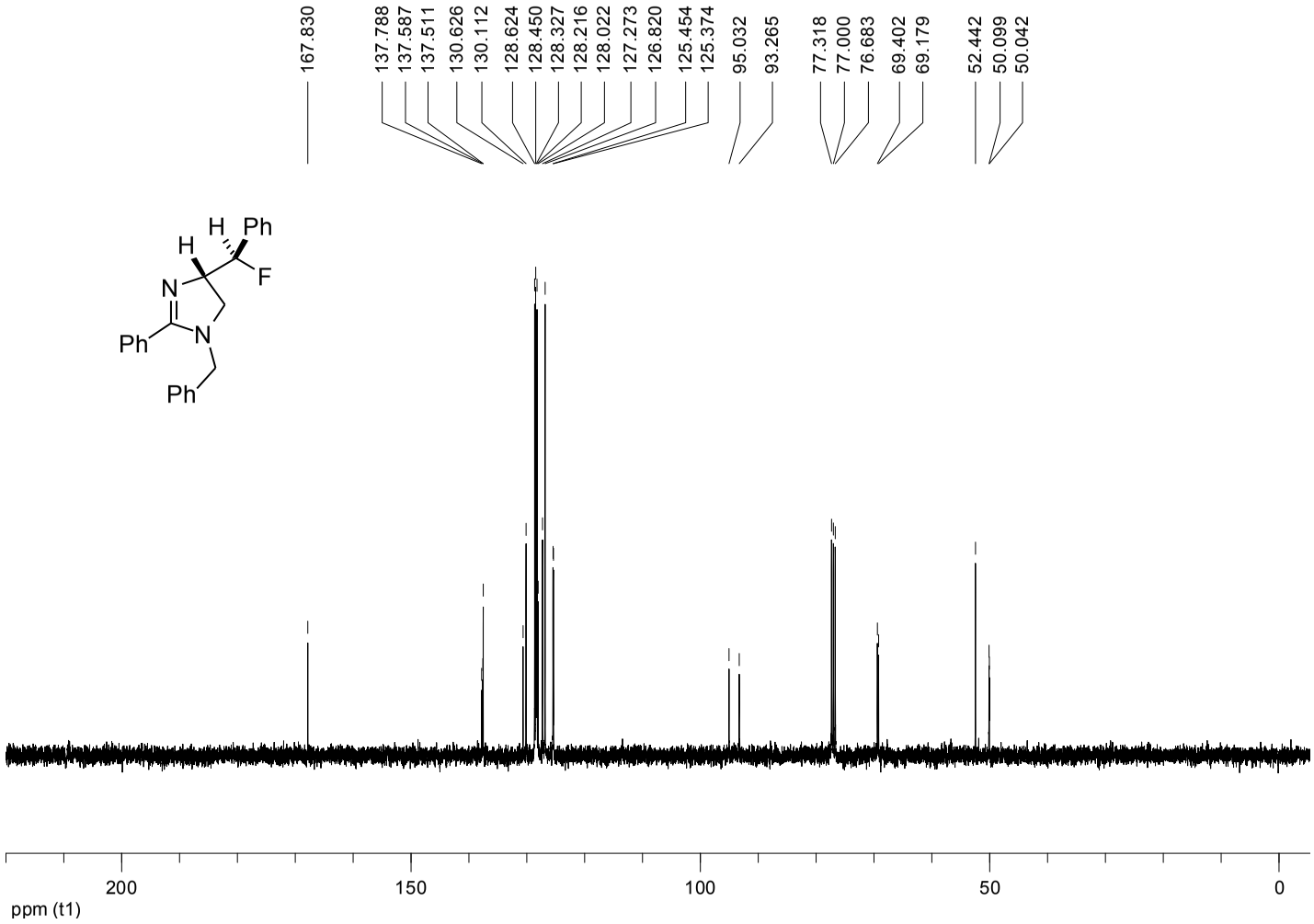
^{13}C NMR spectrum of **5a** (100 MHz, $CDCl_3$)



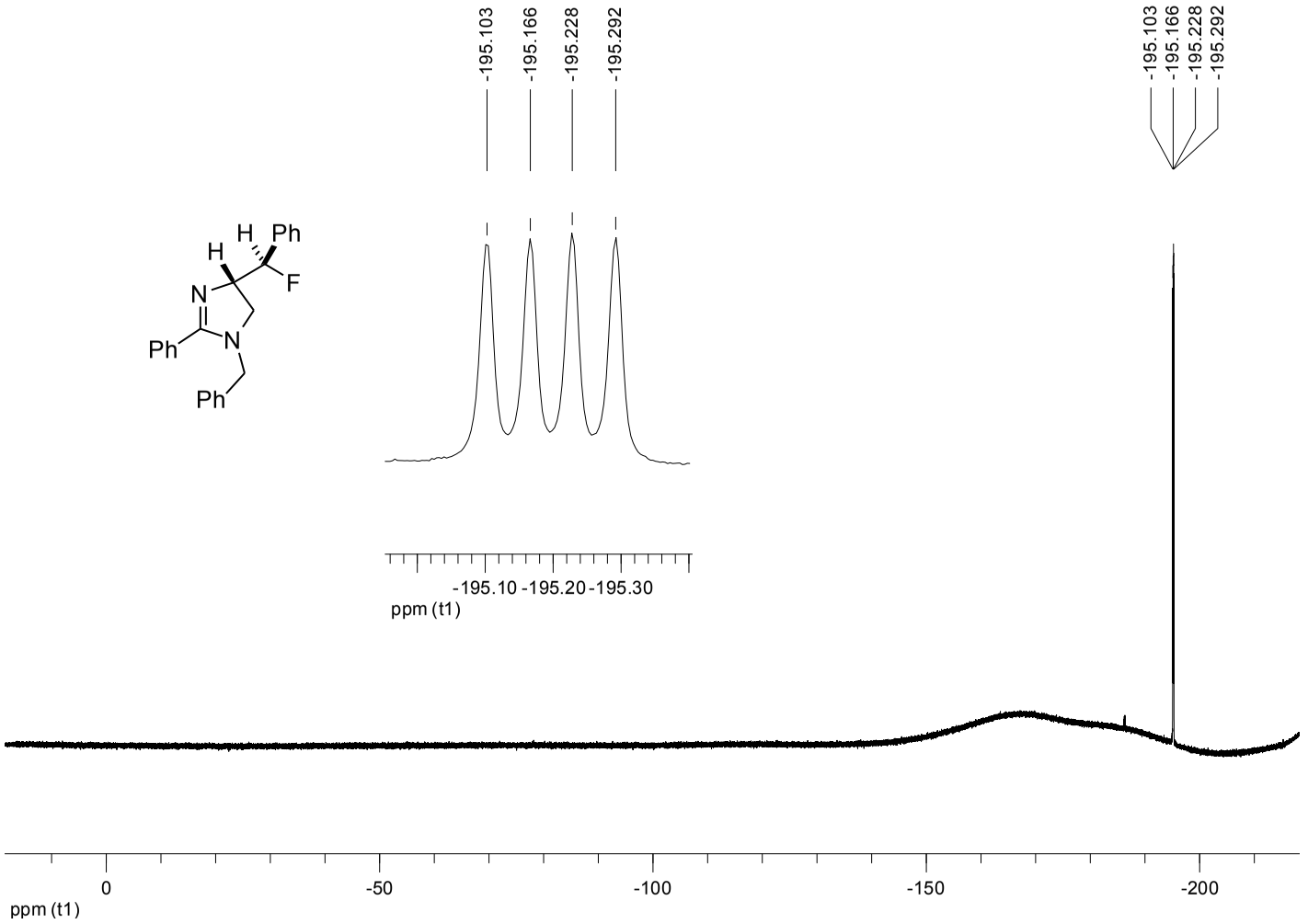
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



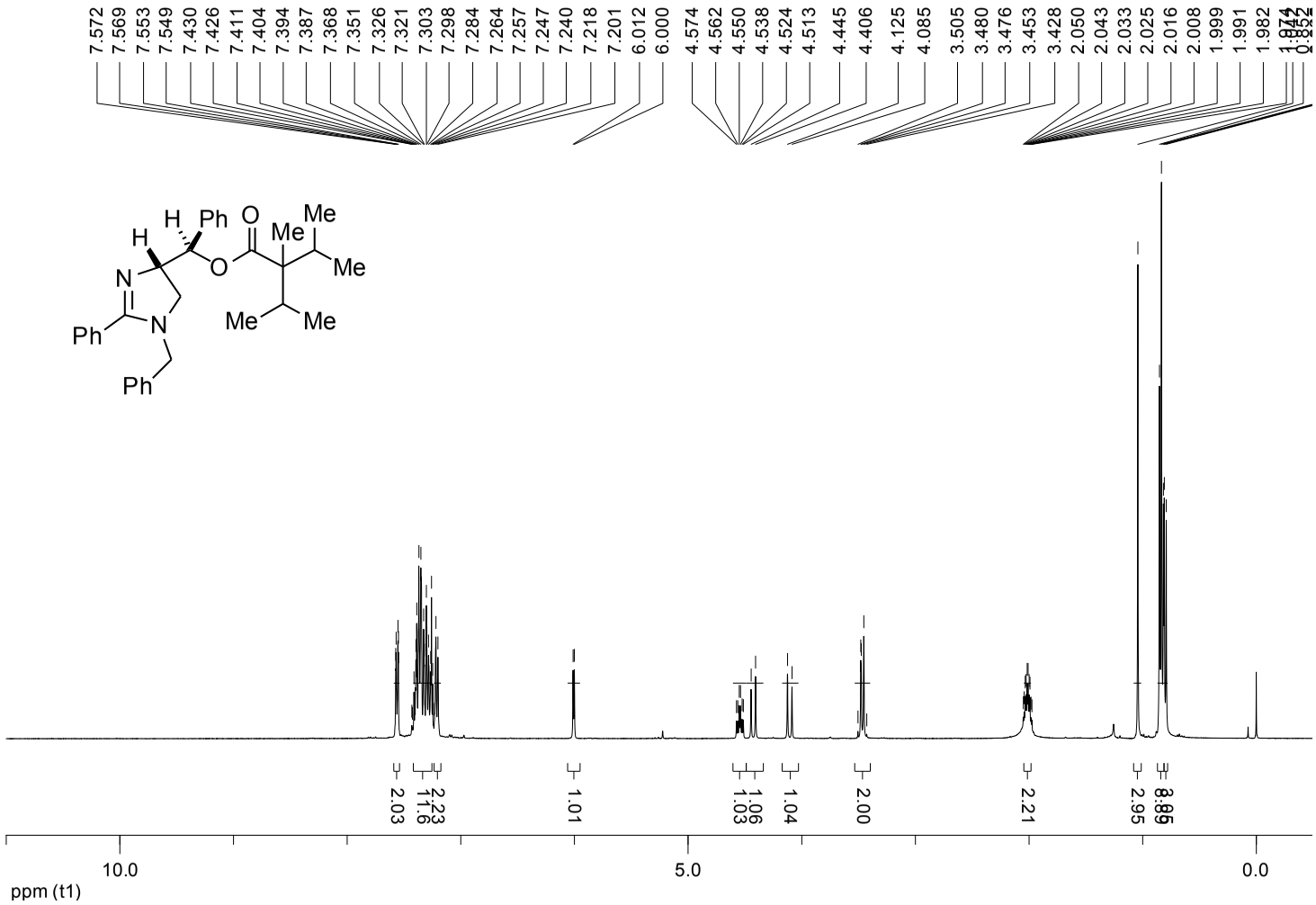
^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)



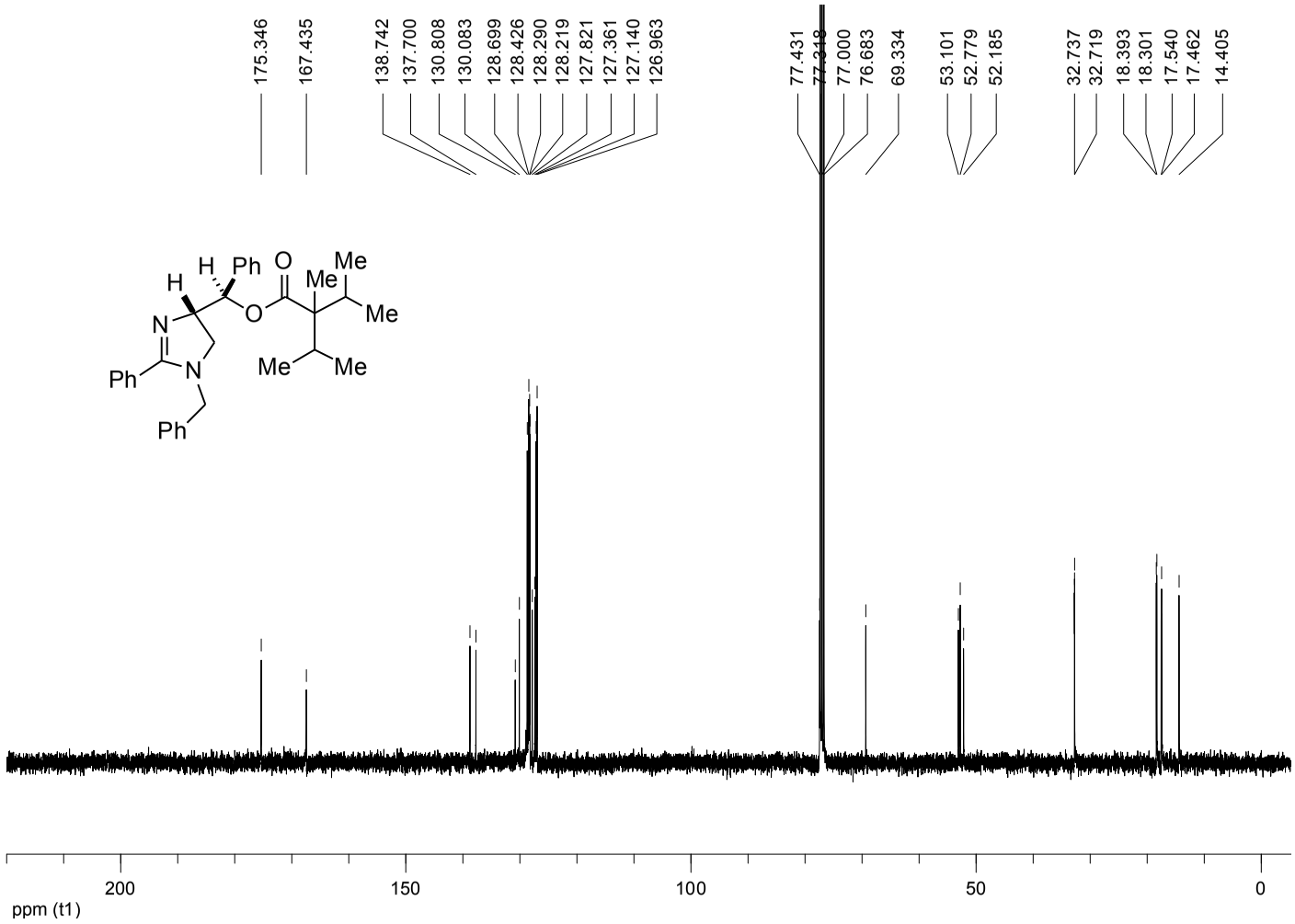
^{19}F NMR spectrum of **2b** (376 MHz, $CDCl_3$)



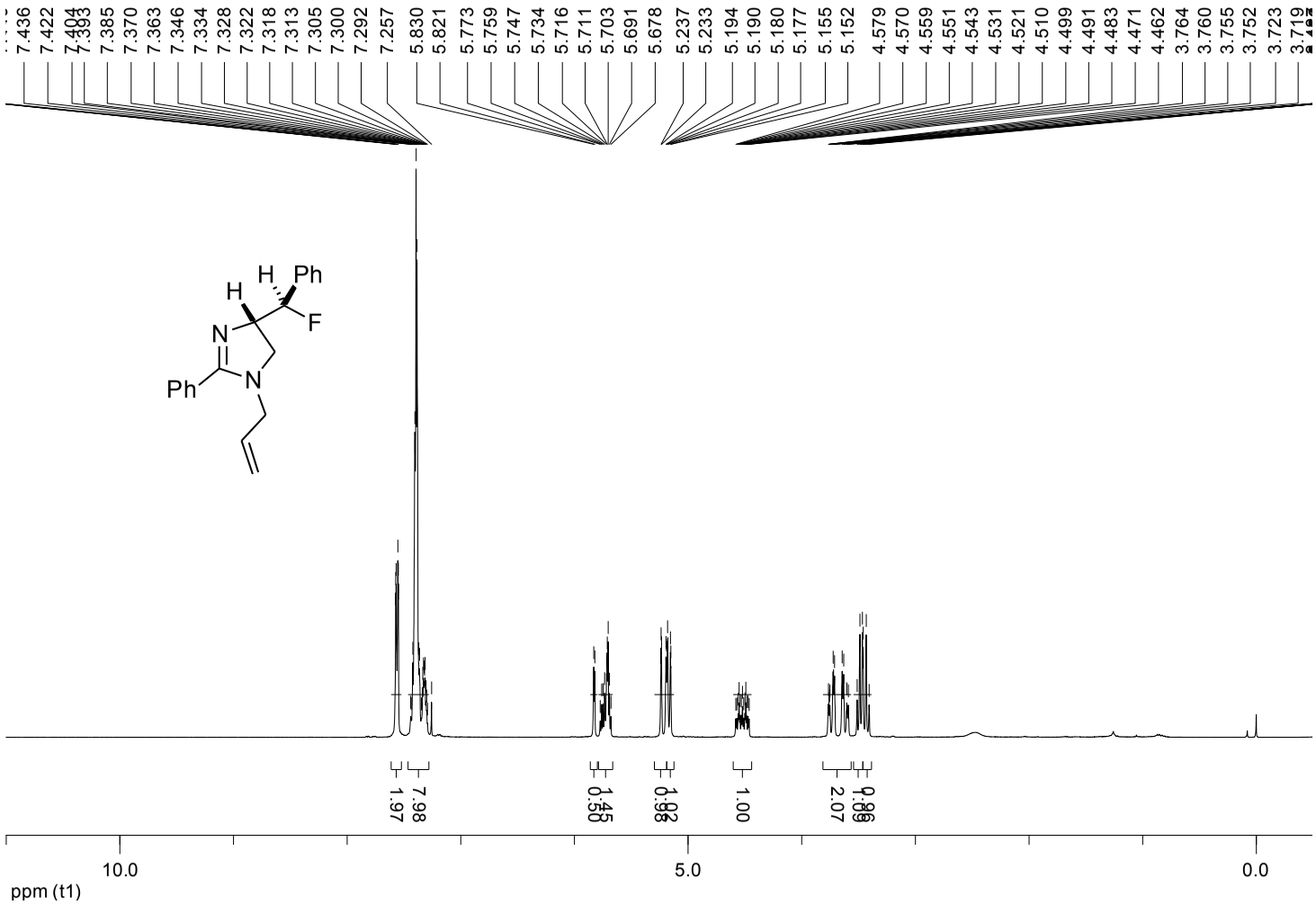
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



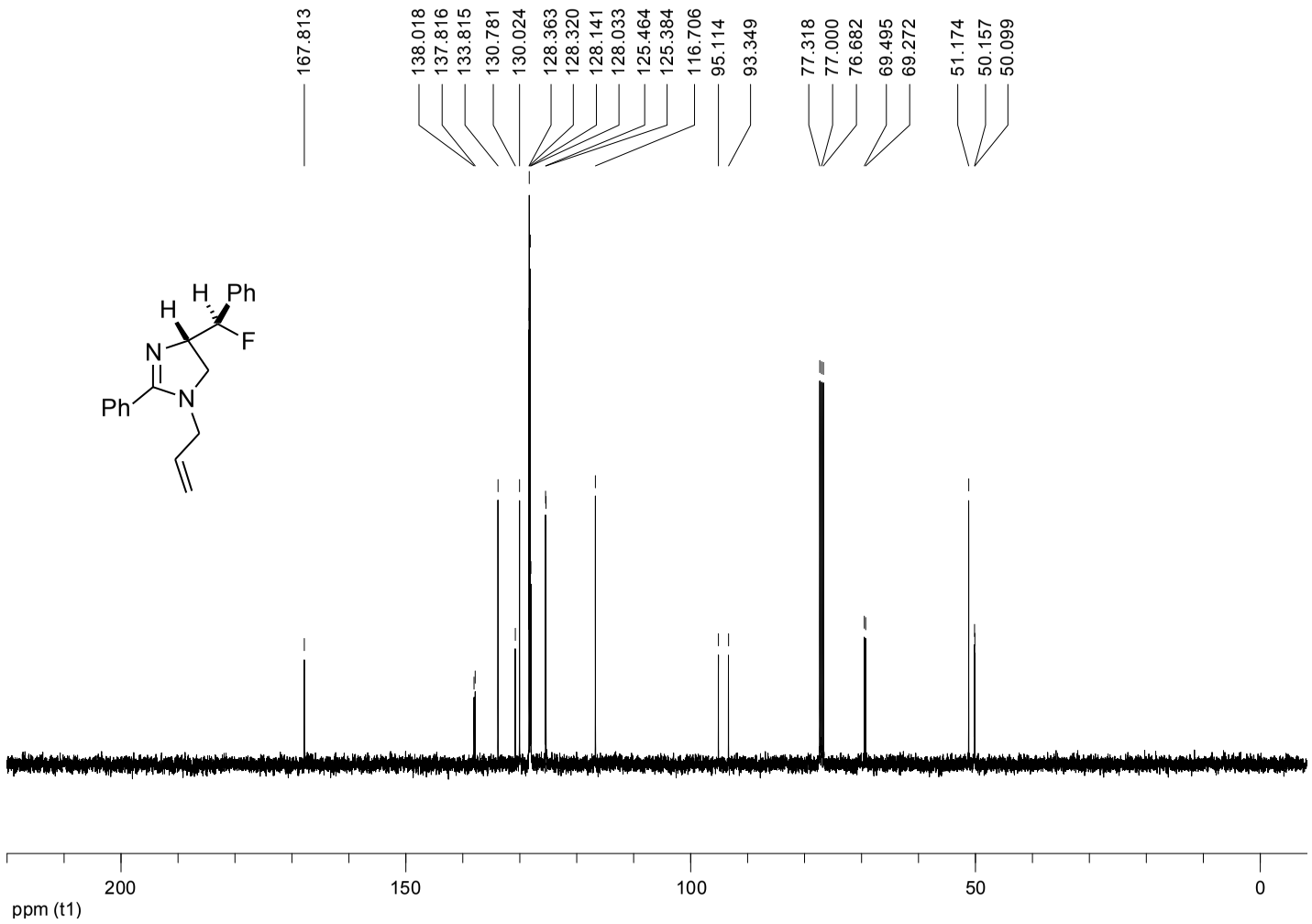
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



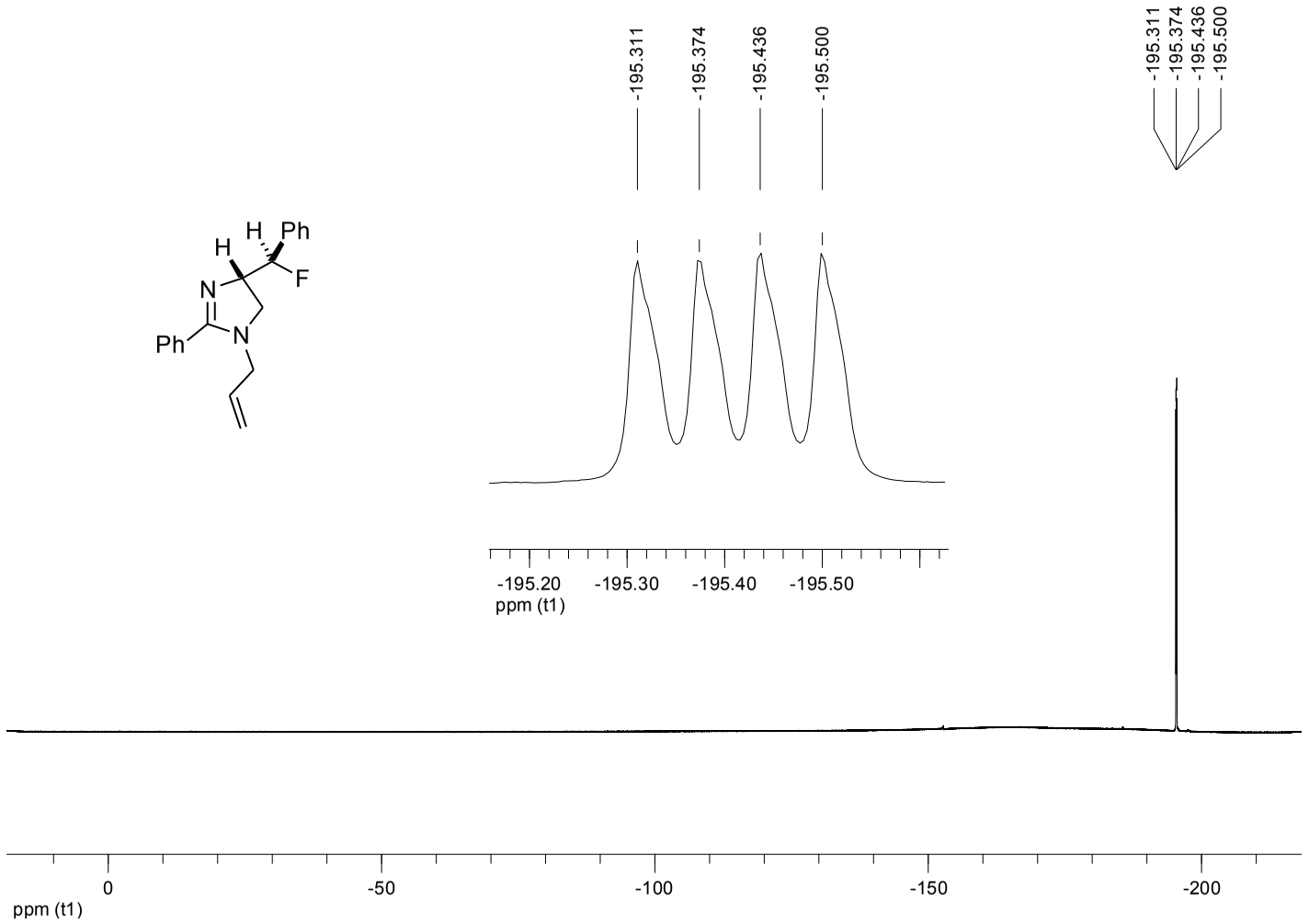
^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)



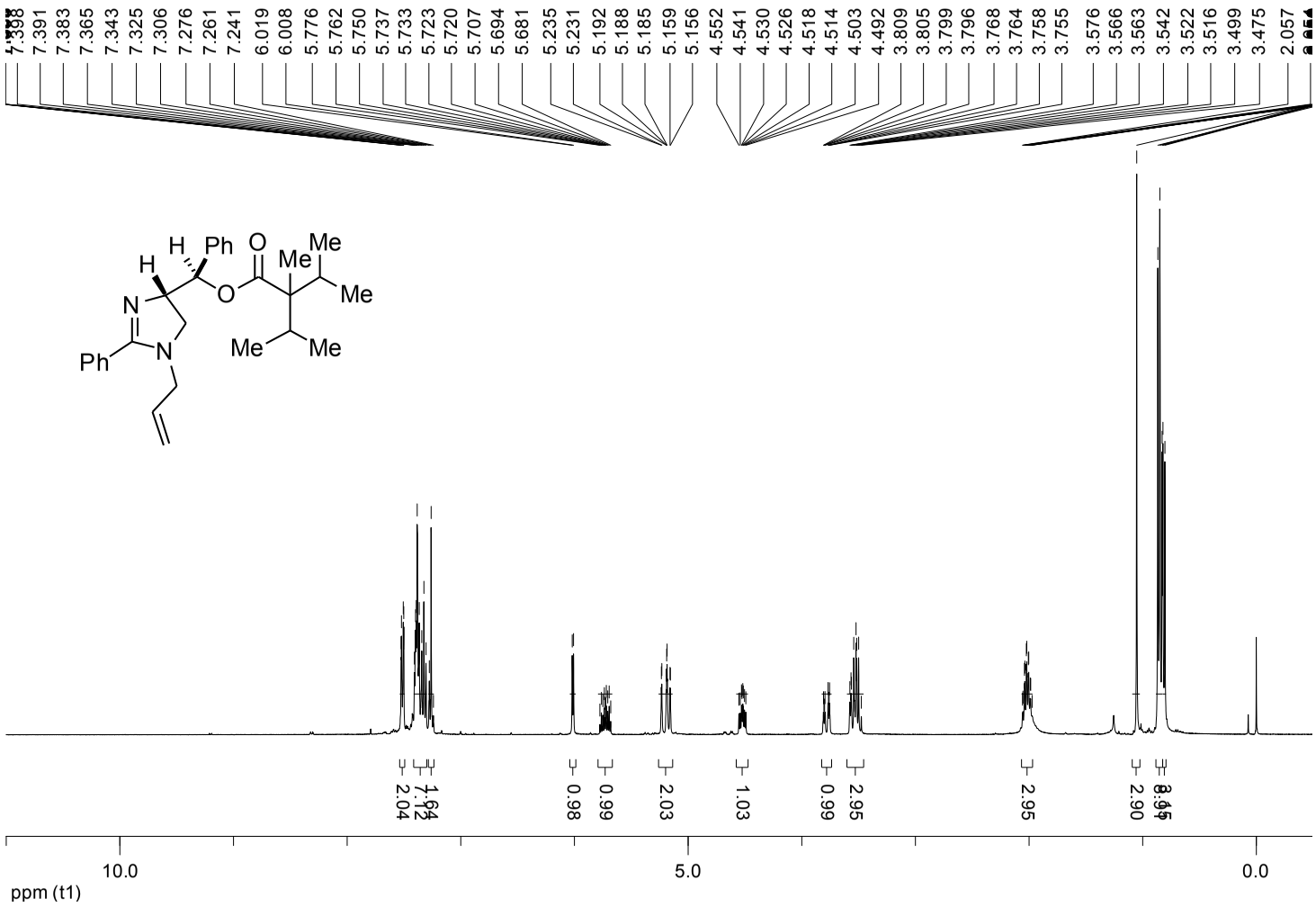
^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)



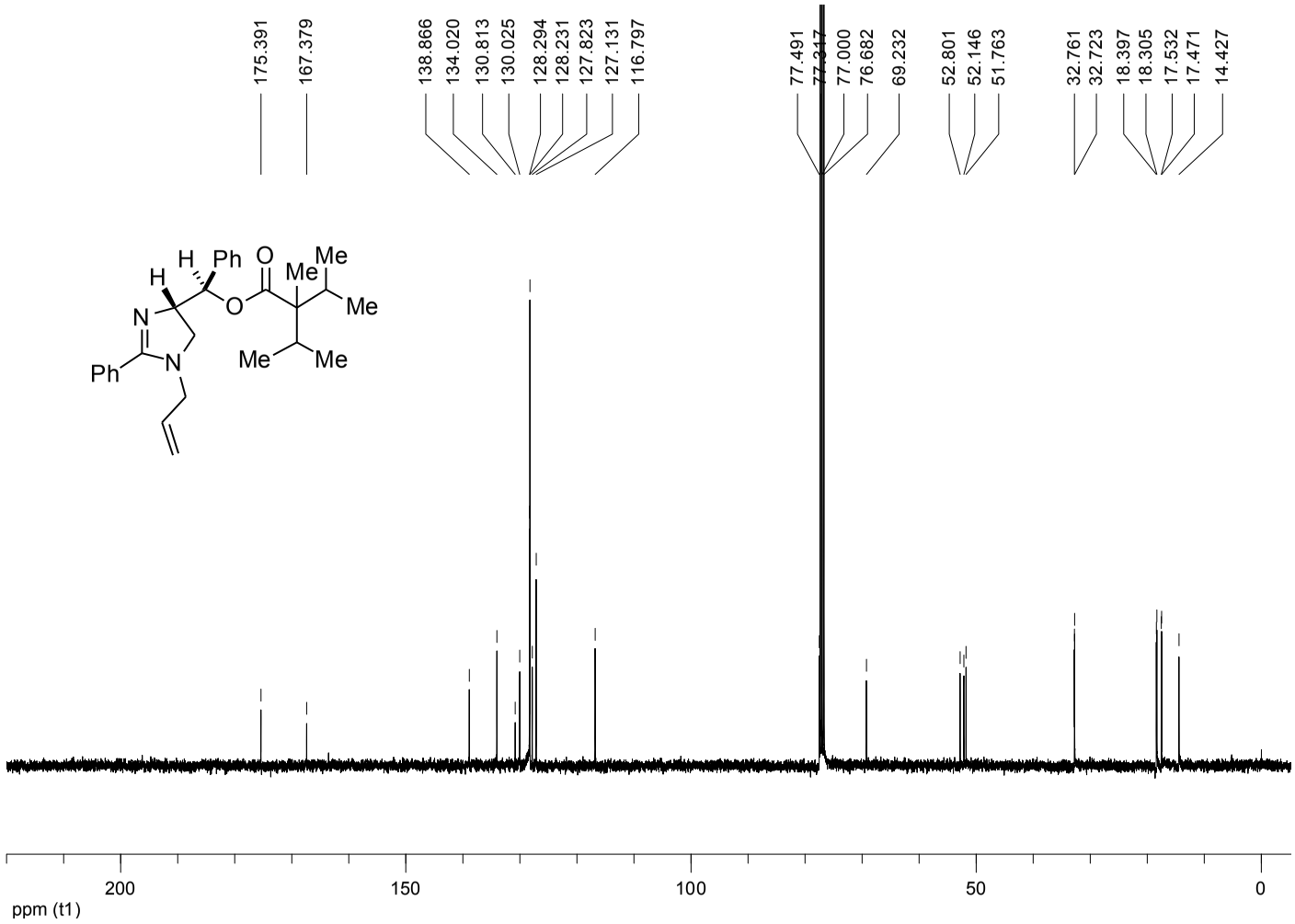
^{19}F NMR spectrum of **2c** (376 MHz, $CDCl_3$)



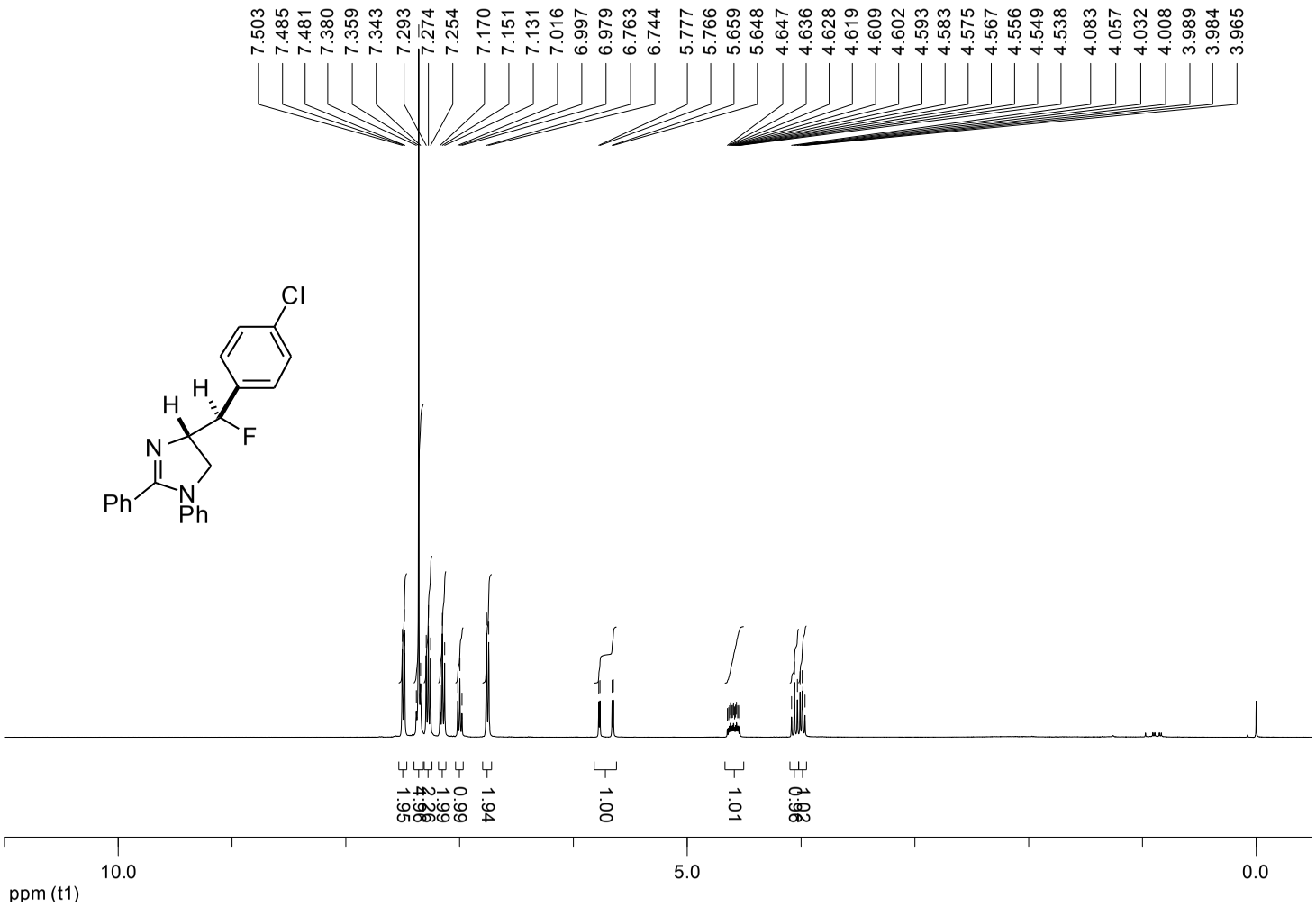
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



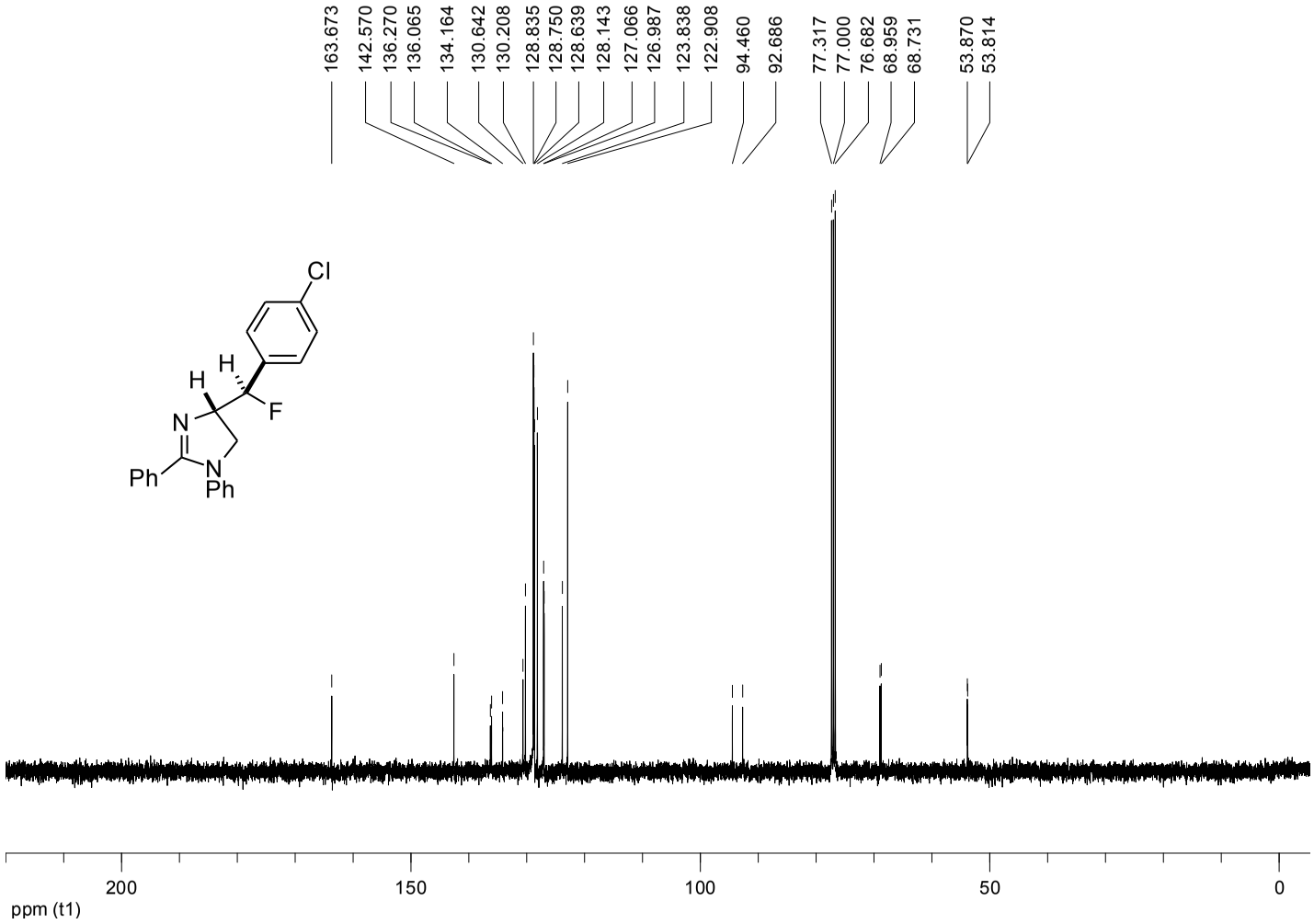
^{13}C NMR spectrum of **5c** (100 MHz, $CDCl_3$)



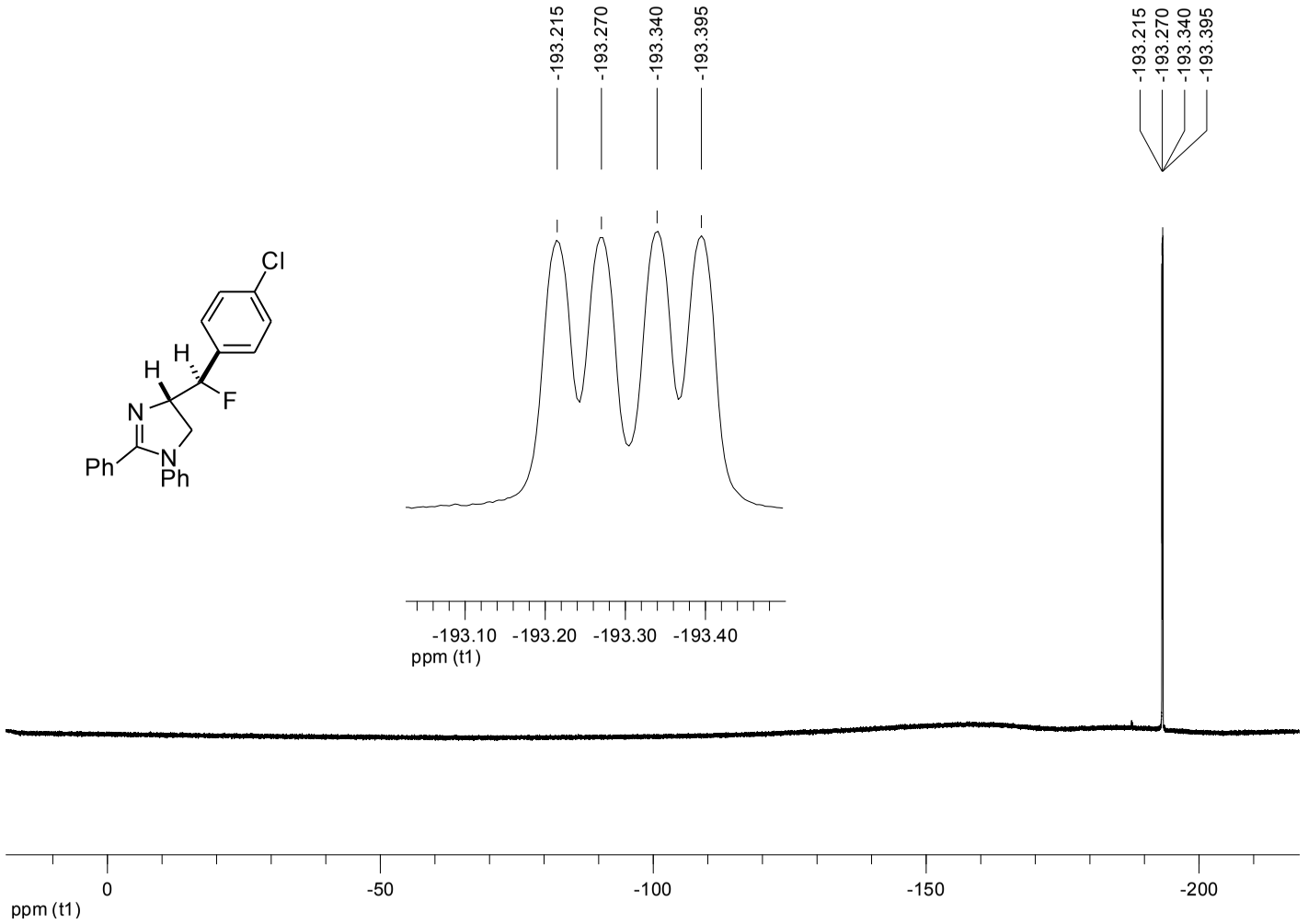
^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)



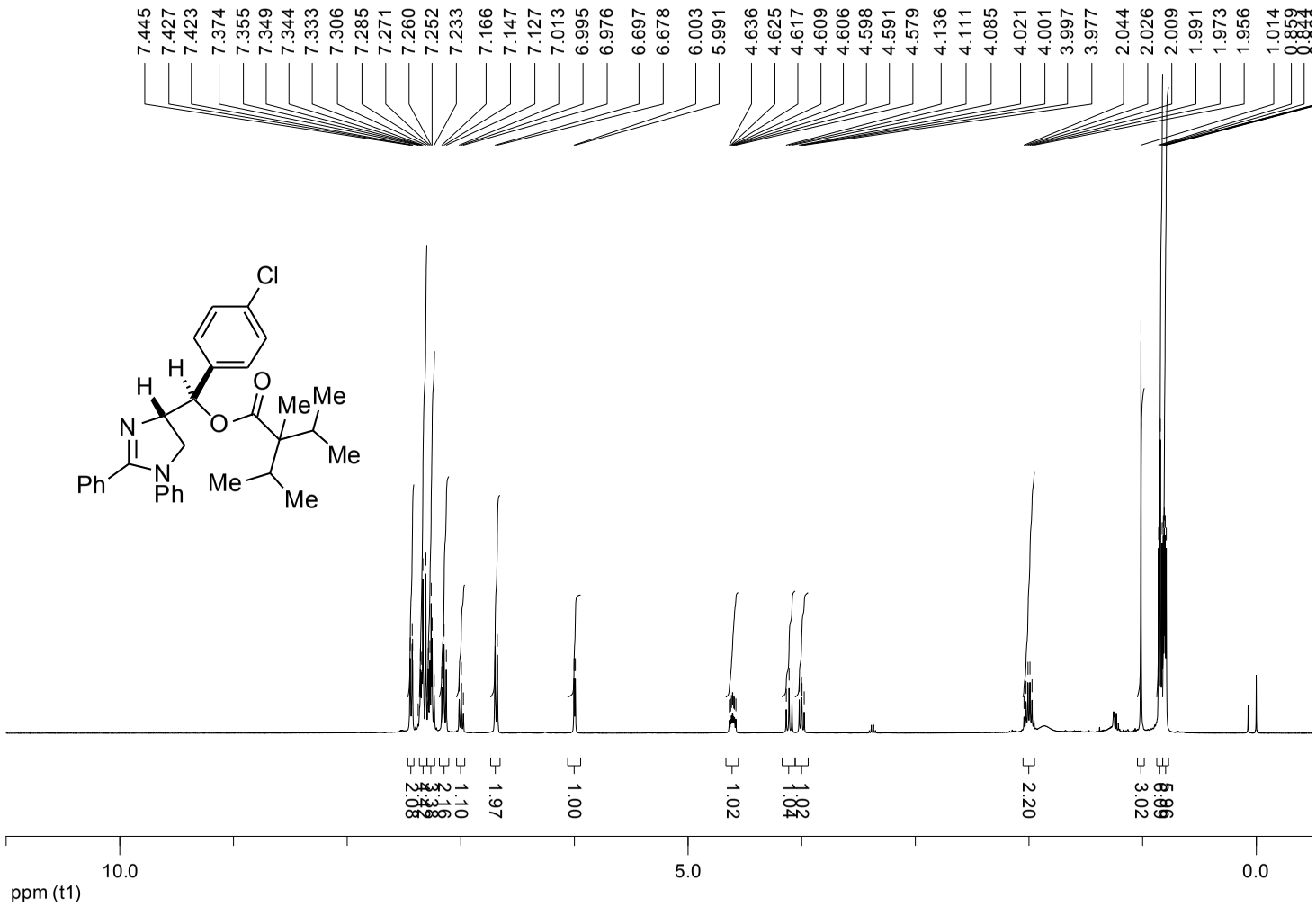
^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of **2d** (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



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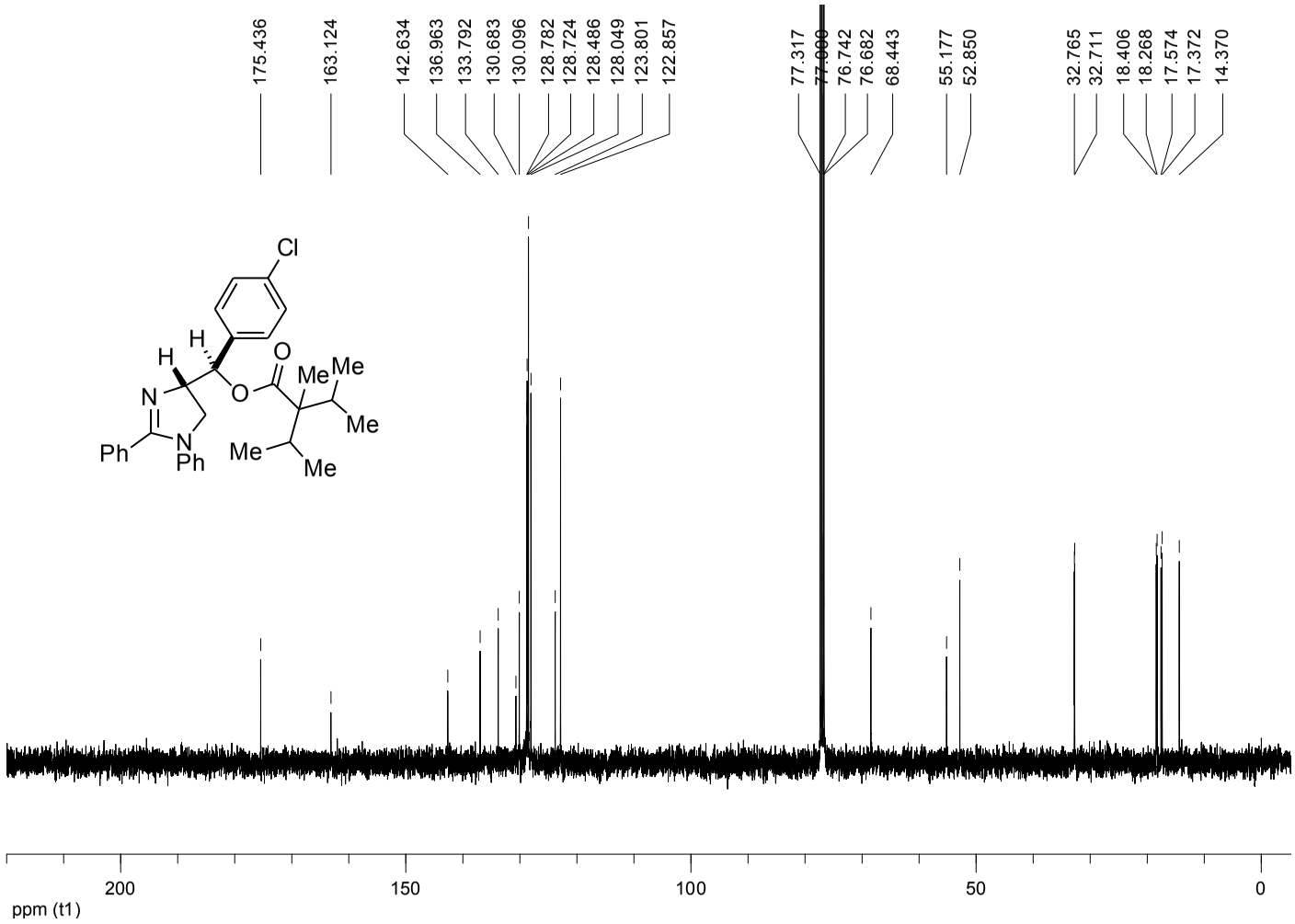
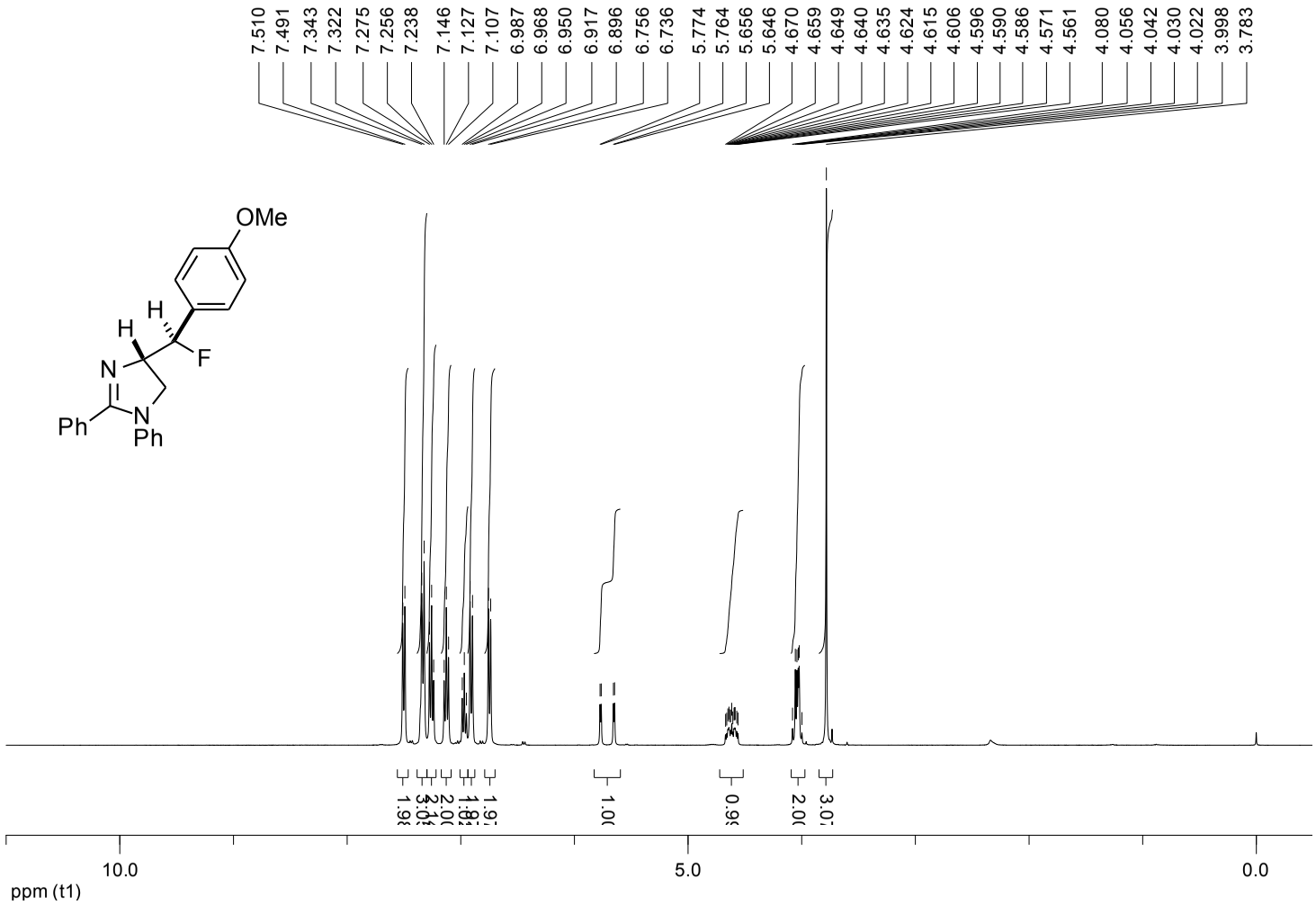


^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)



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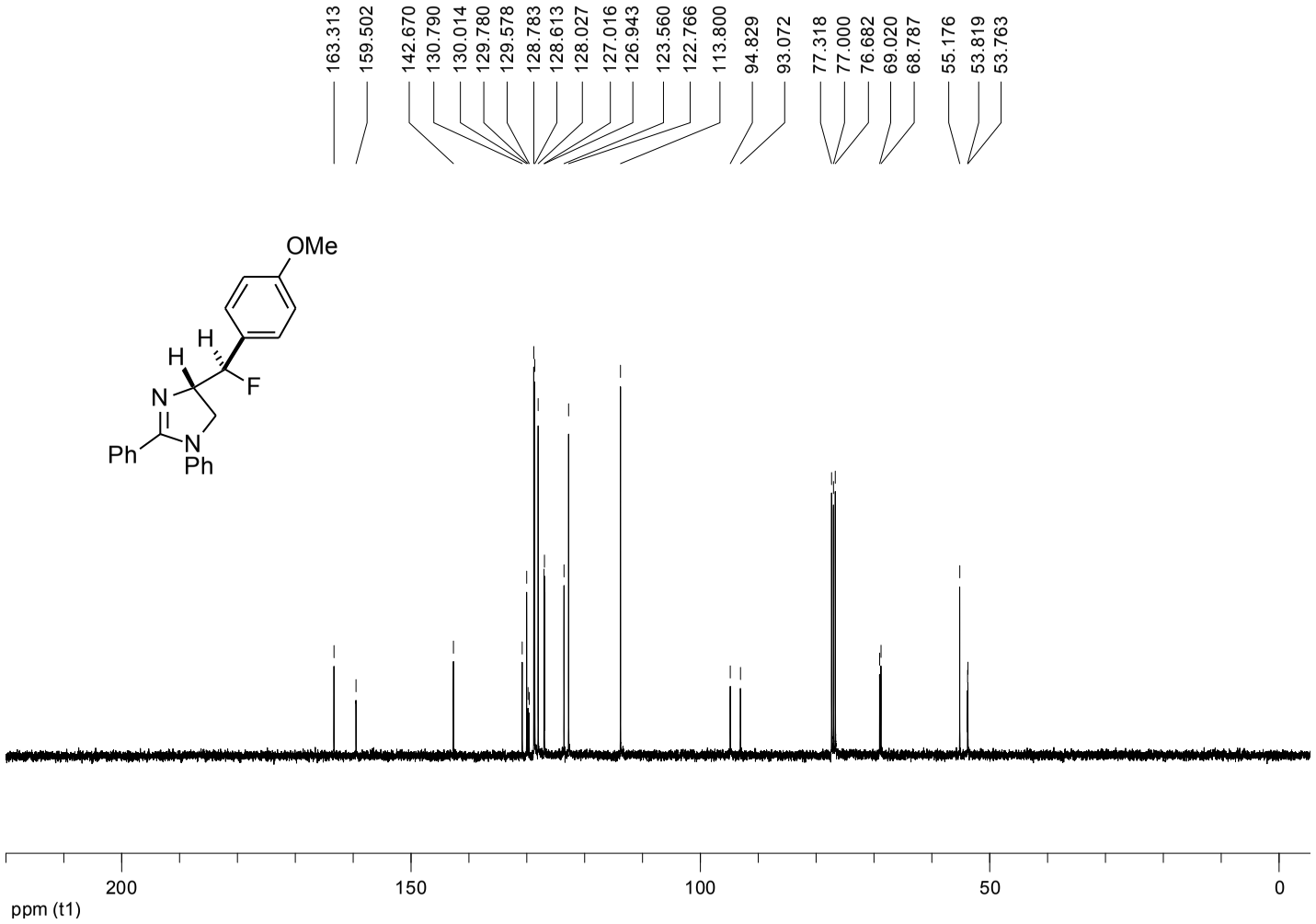
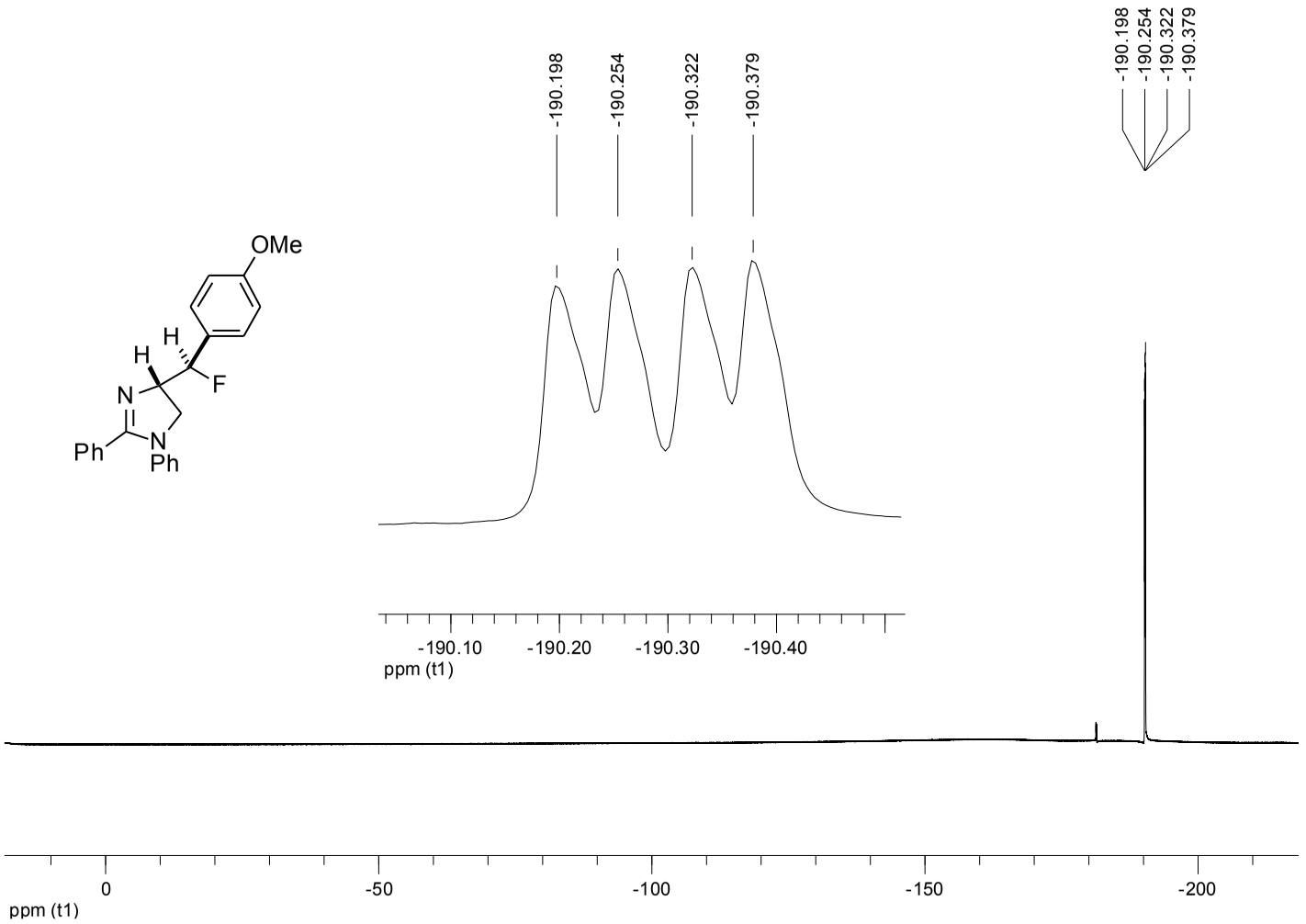
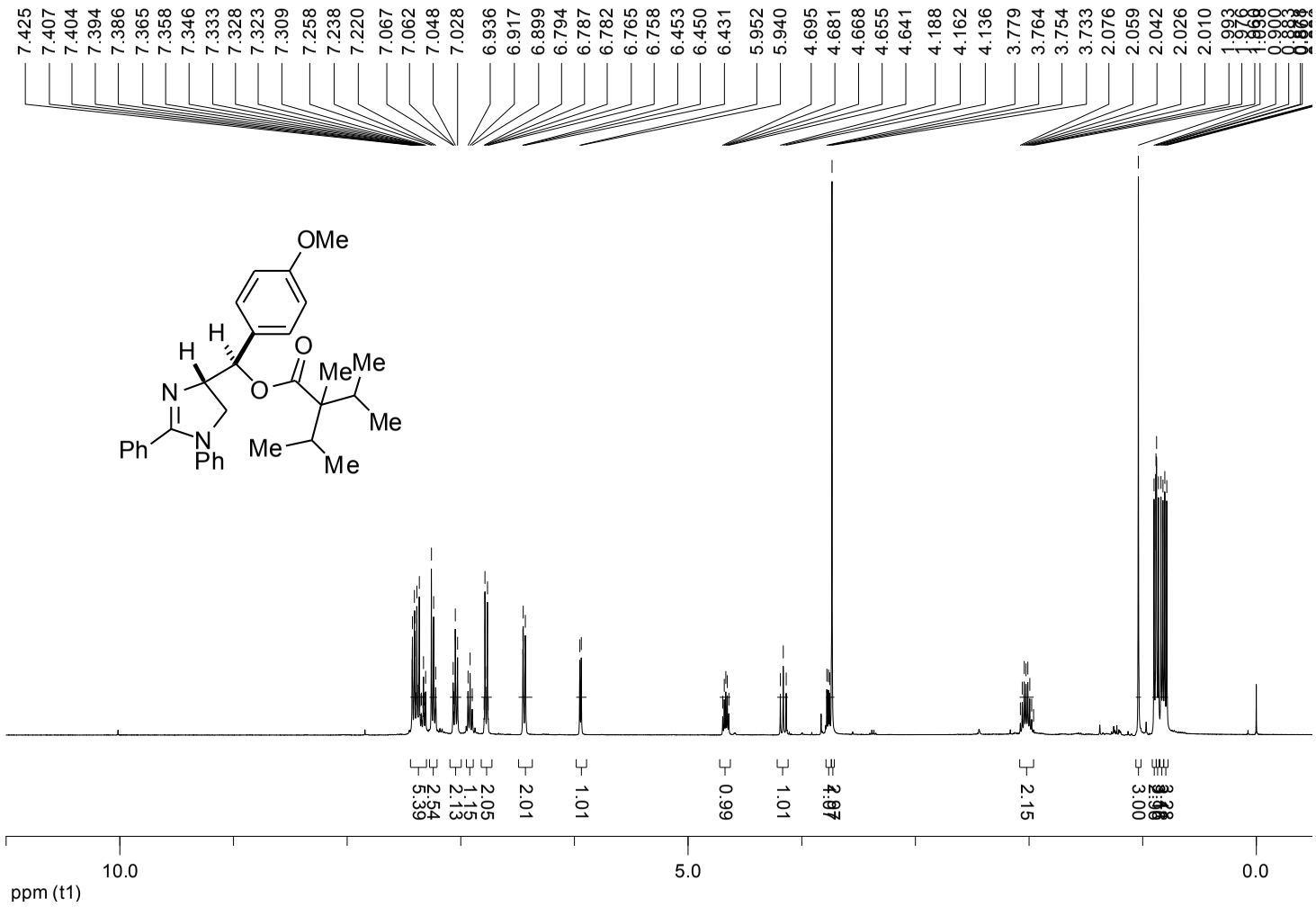


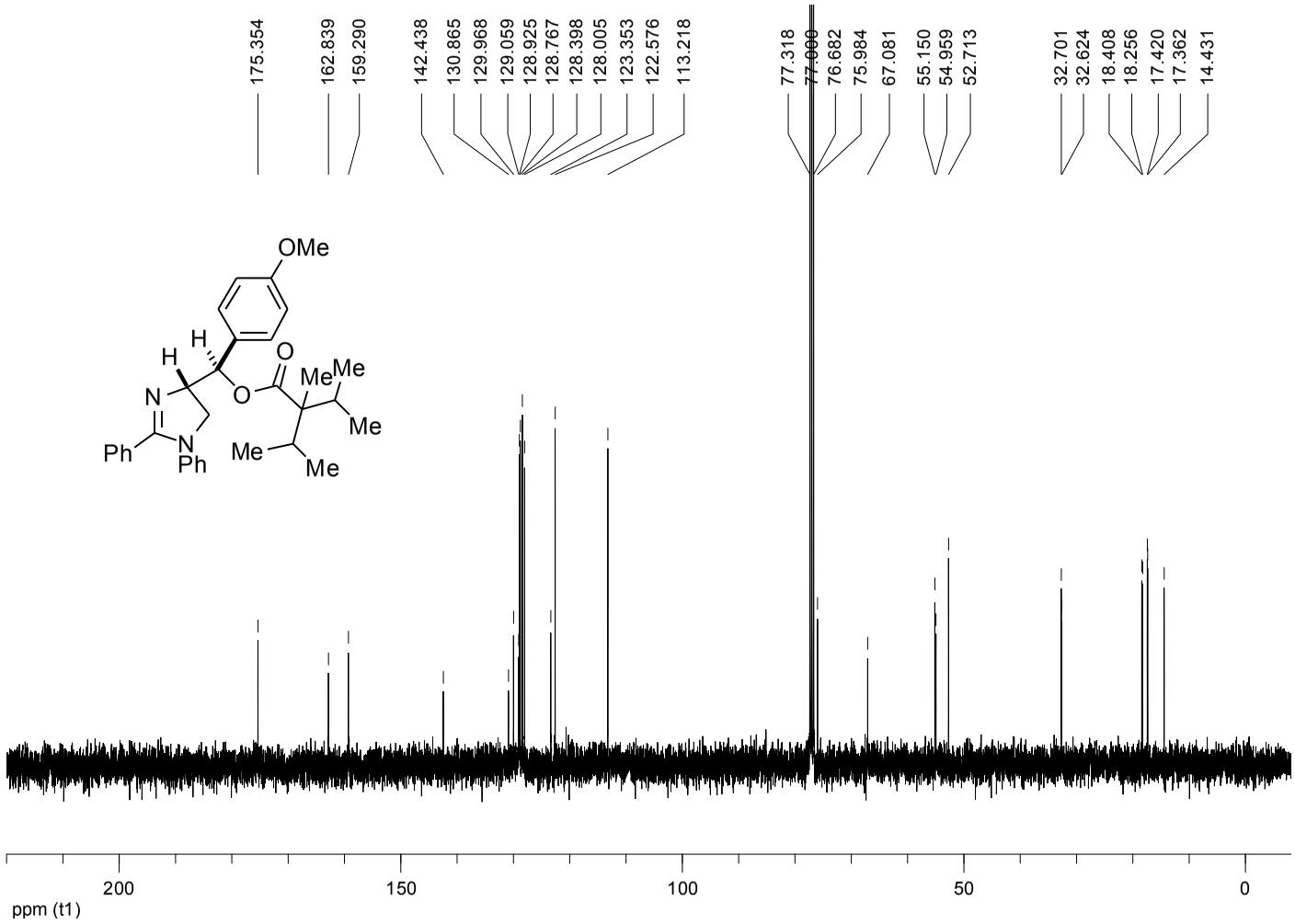
^{19}F NMR spectrum of **2e** (376 MHz, $CDCl_3$)



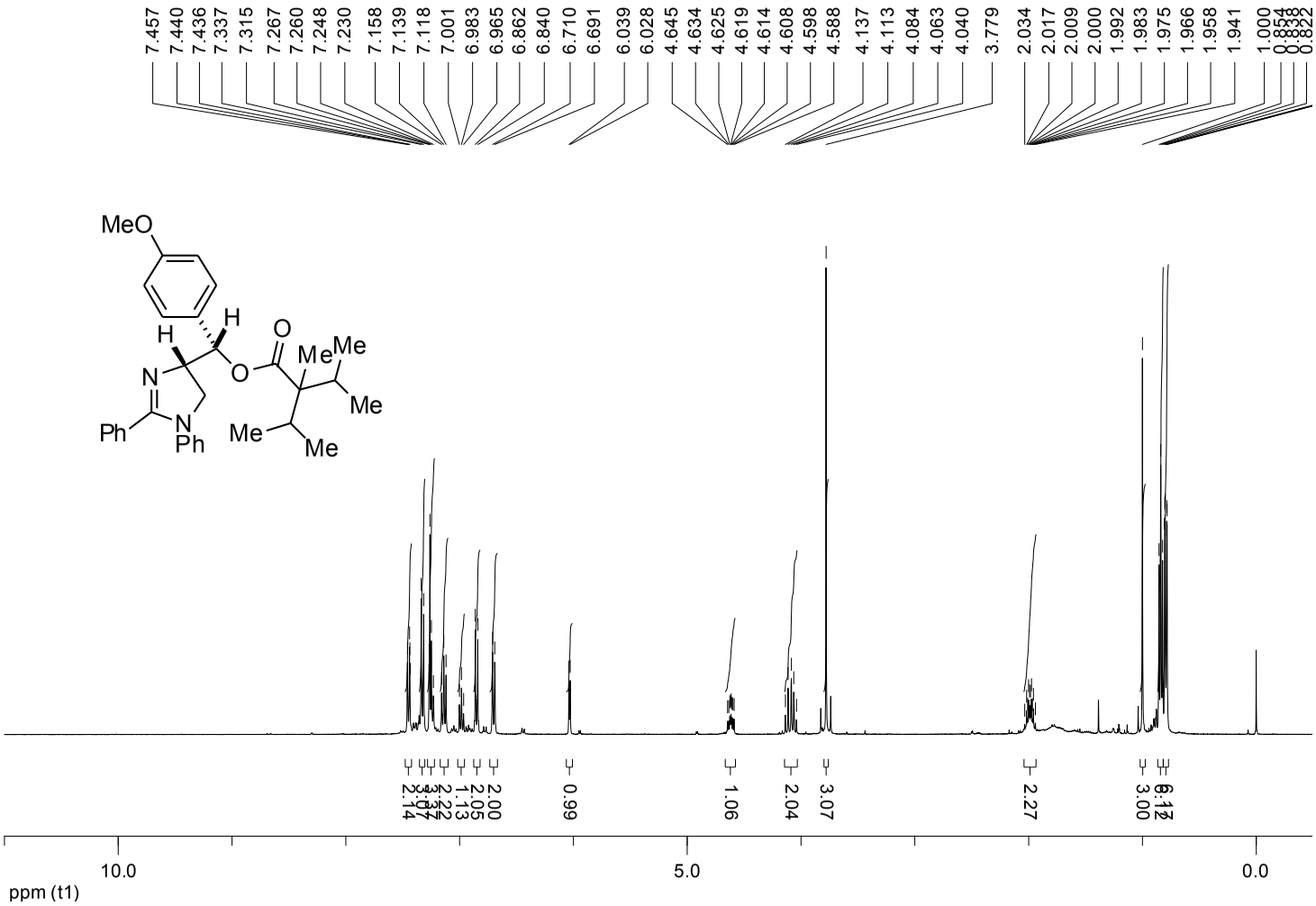
^{1}H NMR spectrum of **5e** (the major stereoisomer) (400 MHz, $CDCl_3$)



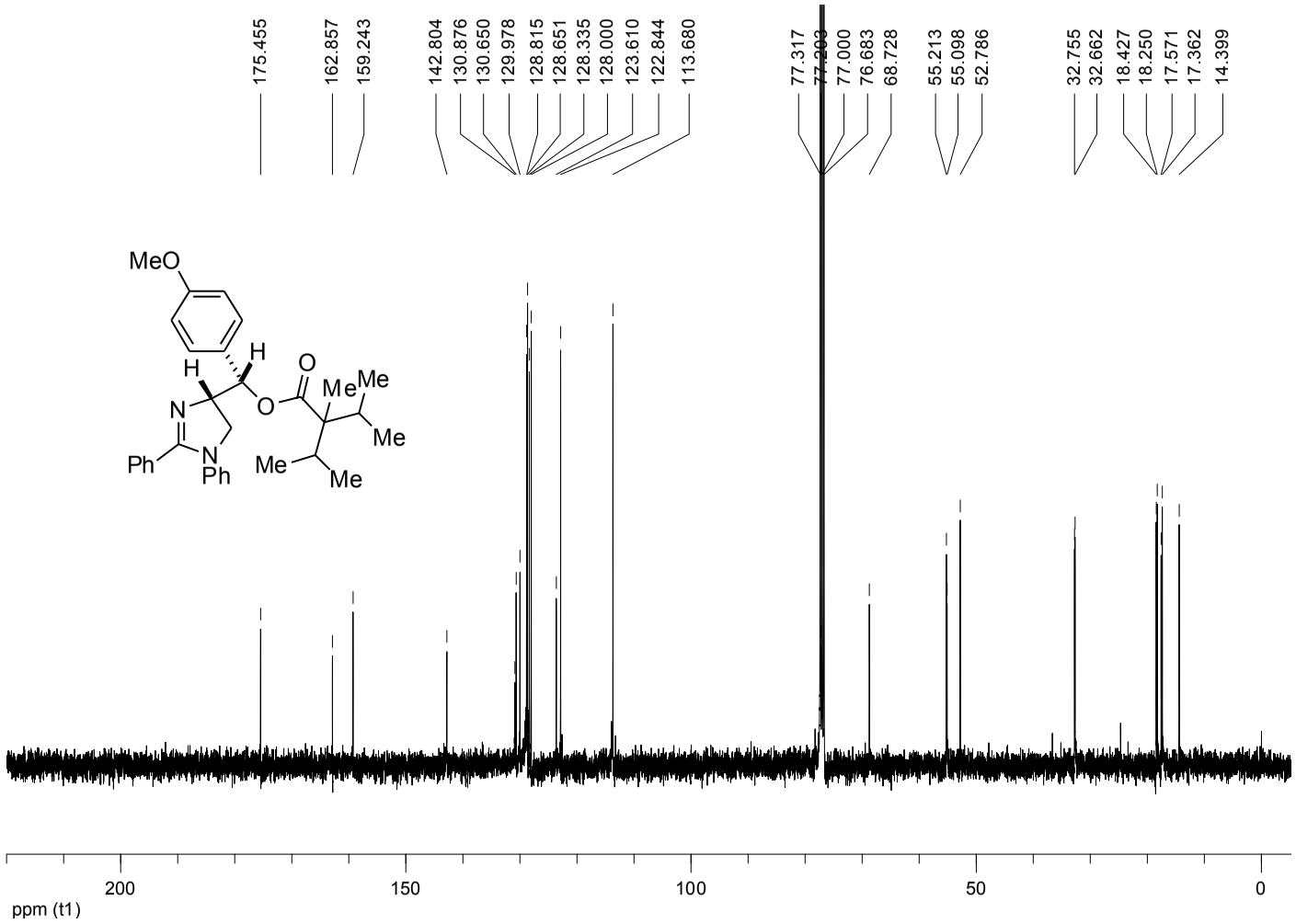
^{13}C NMR spectrum of **5e** (the major stereoisomer) (100 MHz, $CDCl_3$)



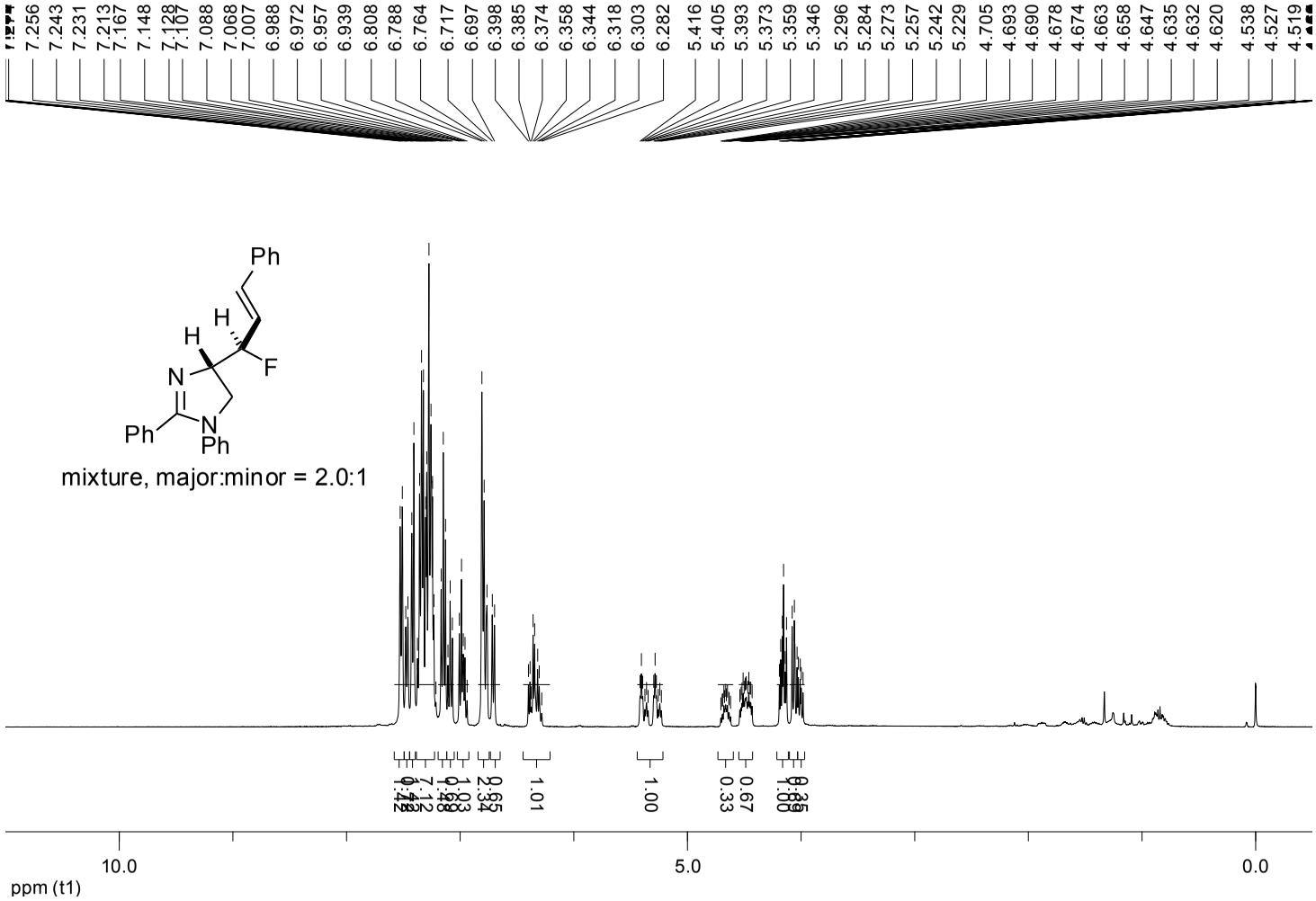
^{1}H NMR spectrum of **5e'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



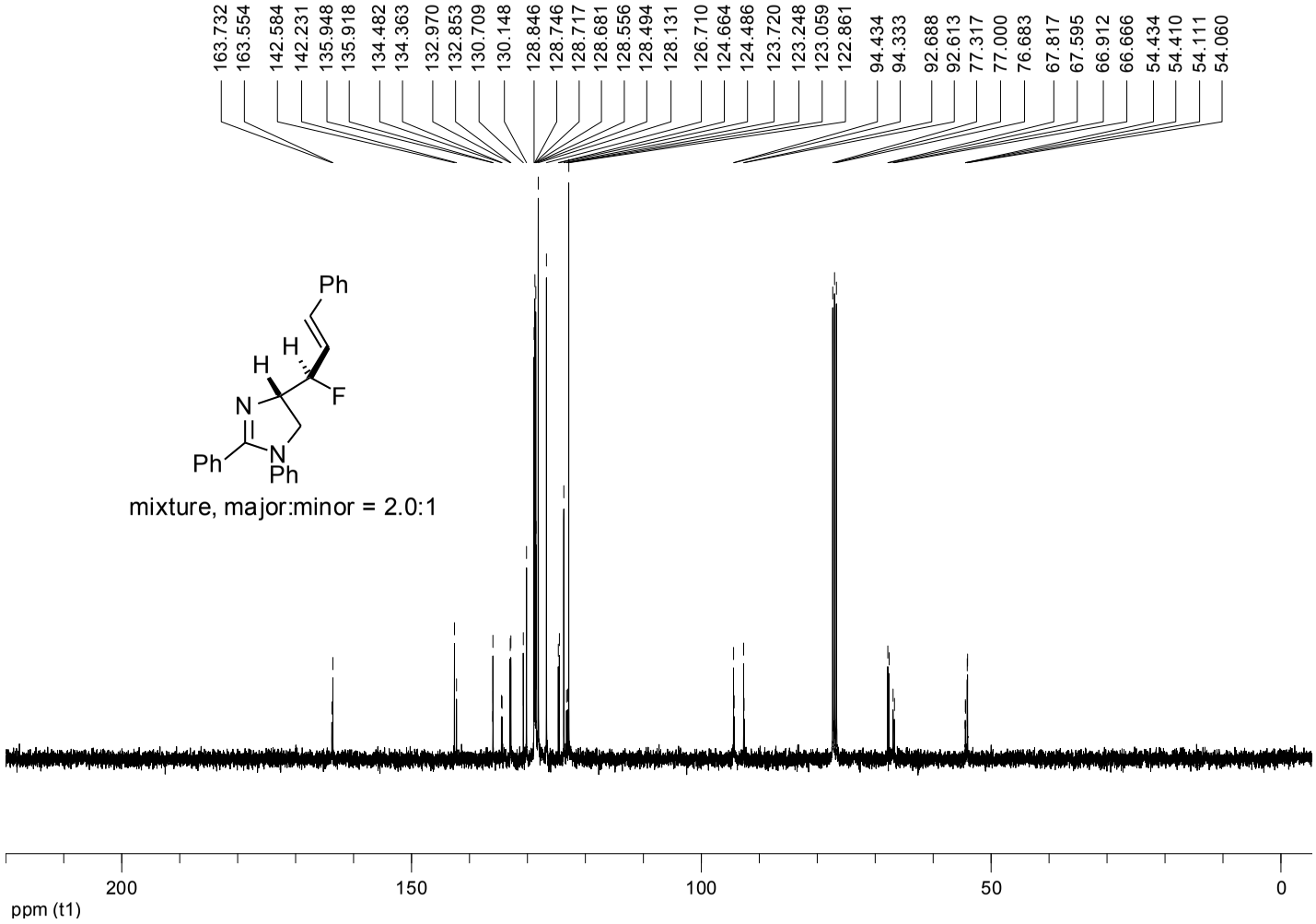
^{13}C NMR spectrum of **5e'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



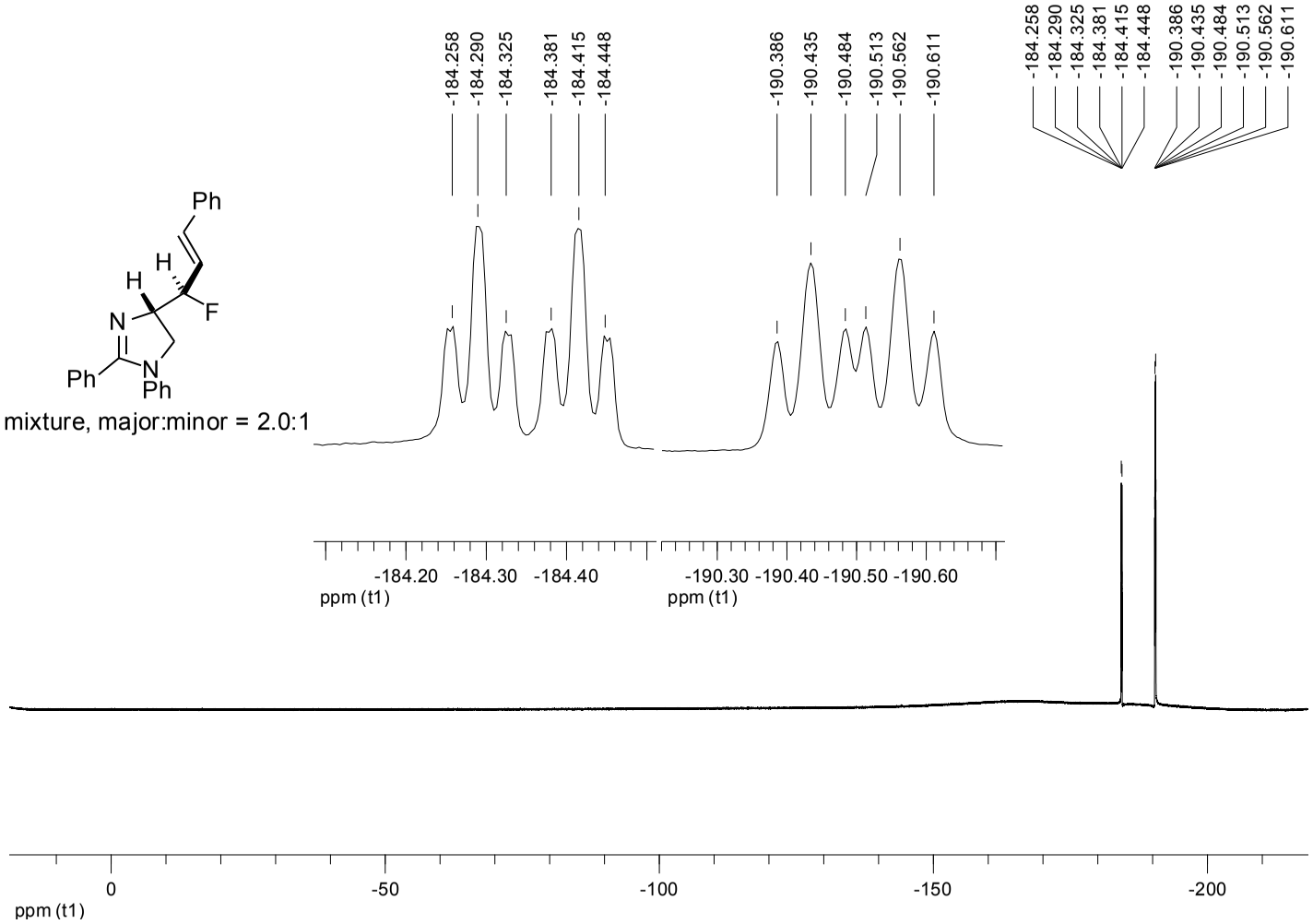
^{1}H NMR spectrum of **2f** (mixture, major:minor = 2.0:1) (400 MHz, $CDCl_3$)



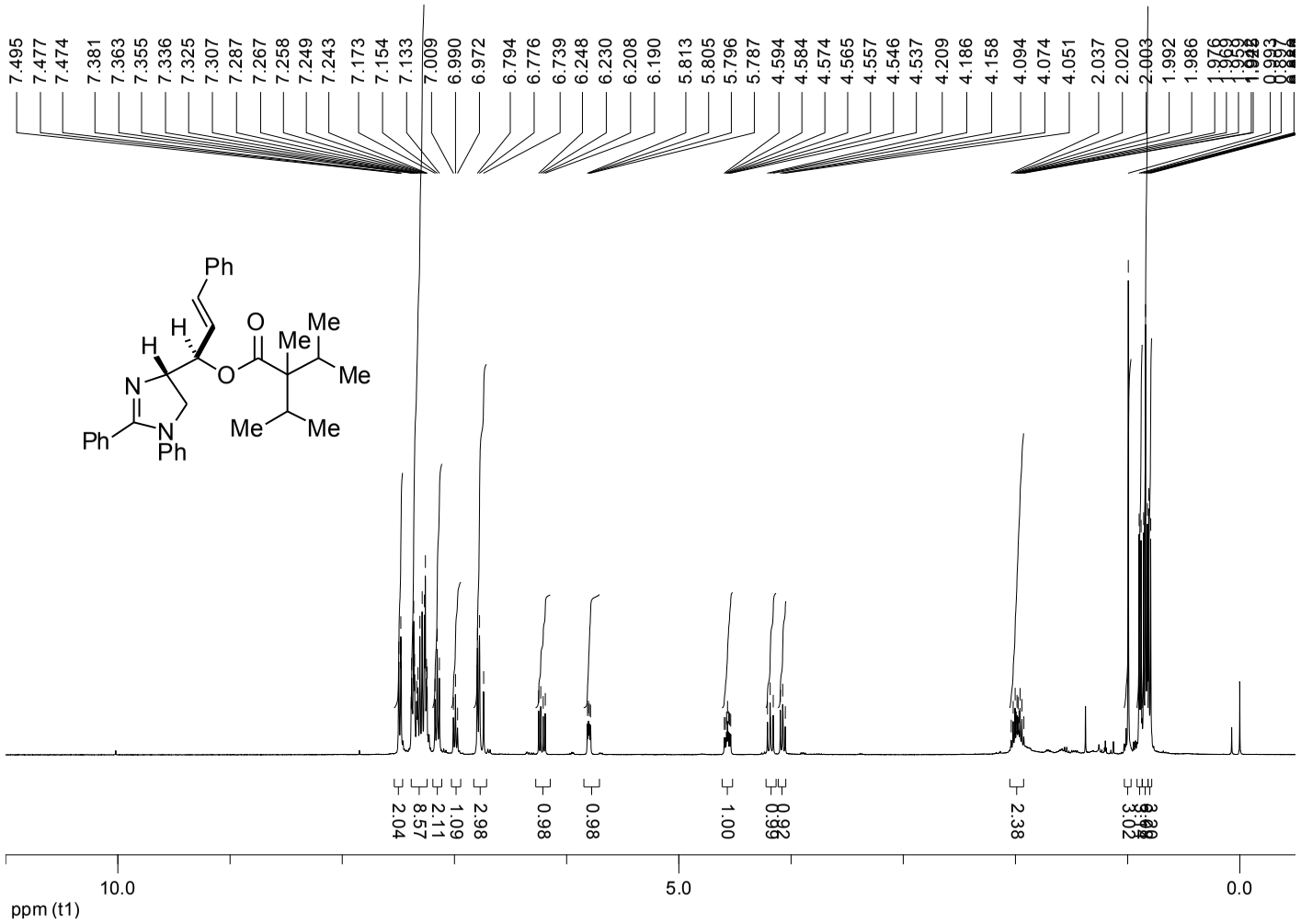
^{13}C NMR spectrum of **2f** (mixture, major:minor = 2.0:1) (100 MHz, $CDCl_3$)



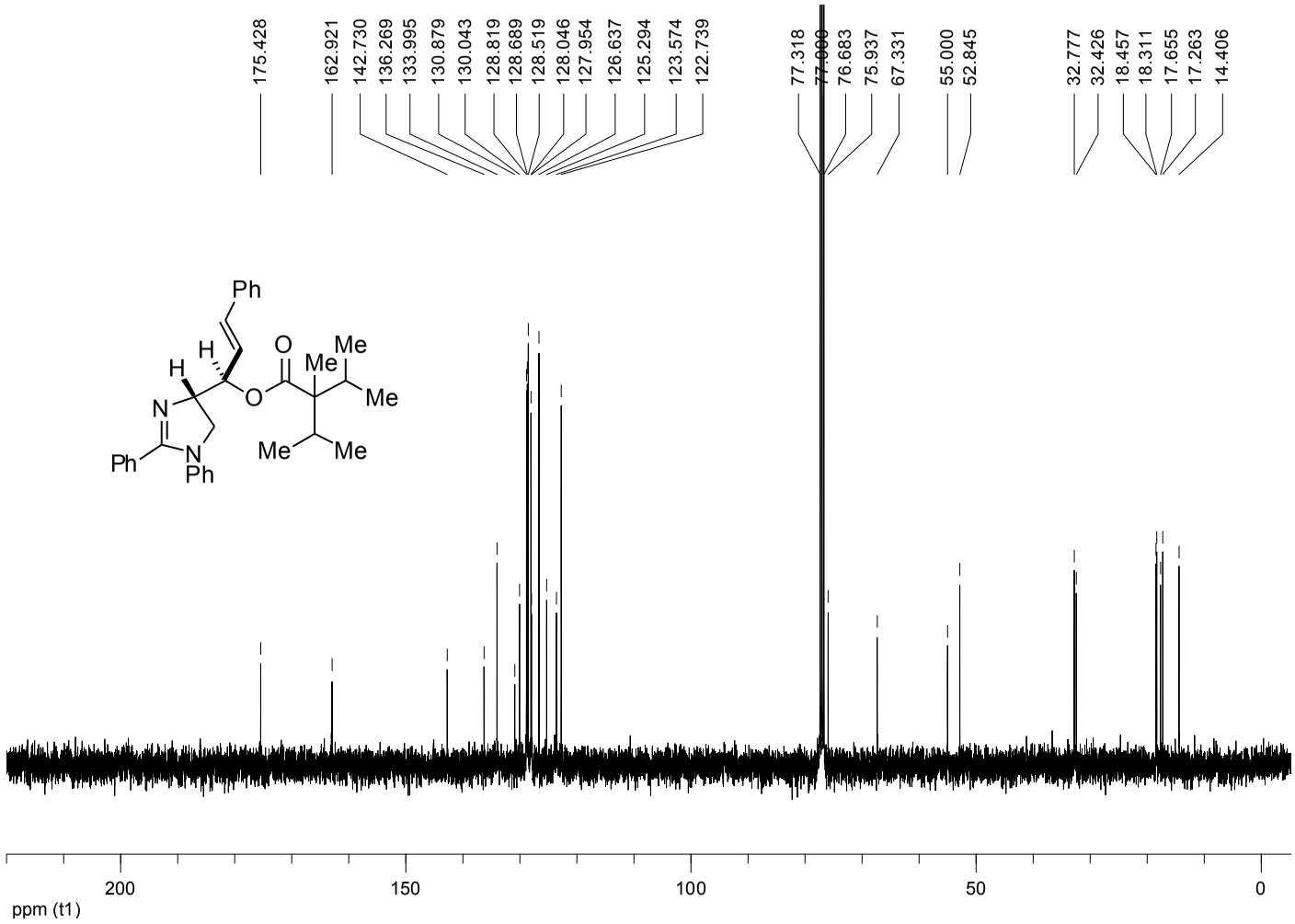
^{19}F NMR spectrum of **2f** (mixture, major:minor = 2.0:1) (376 MHz, $CDCl_3$)



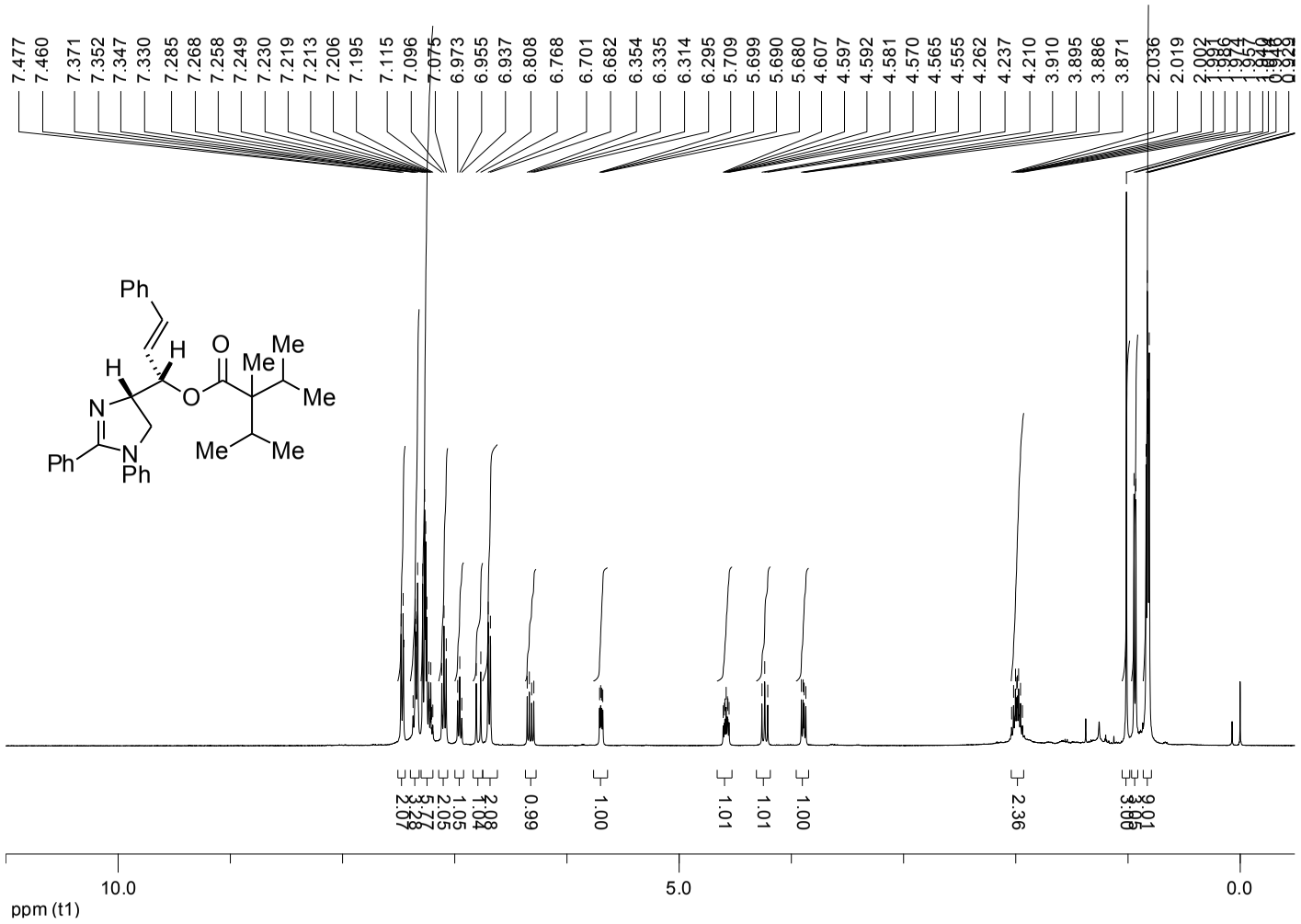
^{1}H NMR spectrum of **5f** (the major stereoisomer) (400 MHz, $CDCl_3$)



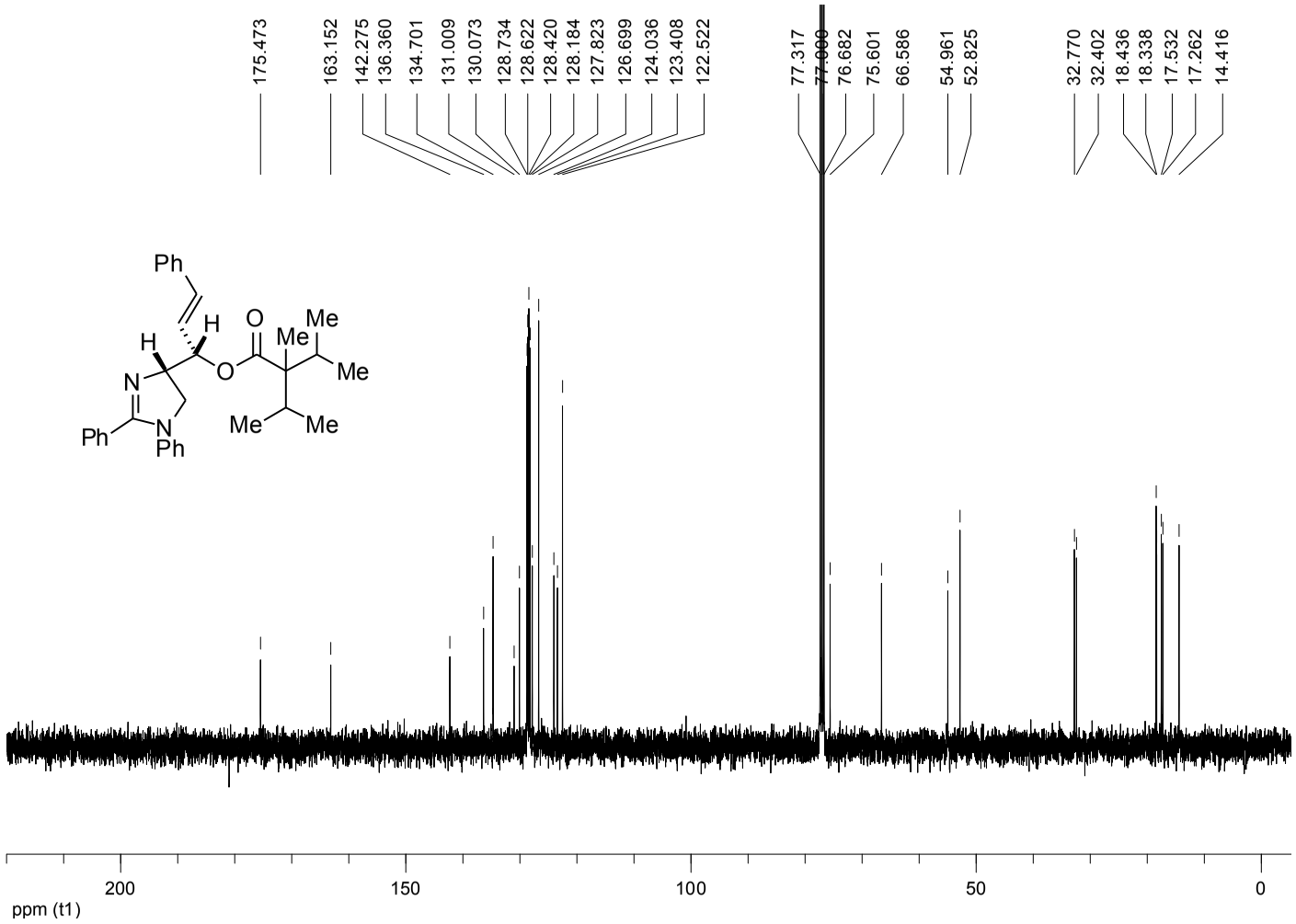
^{13}C NMR spectrum of **5f** (the major stereoisomer) (100 MHz, $CDCl_3$)



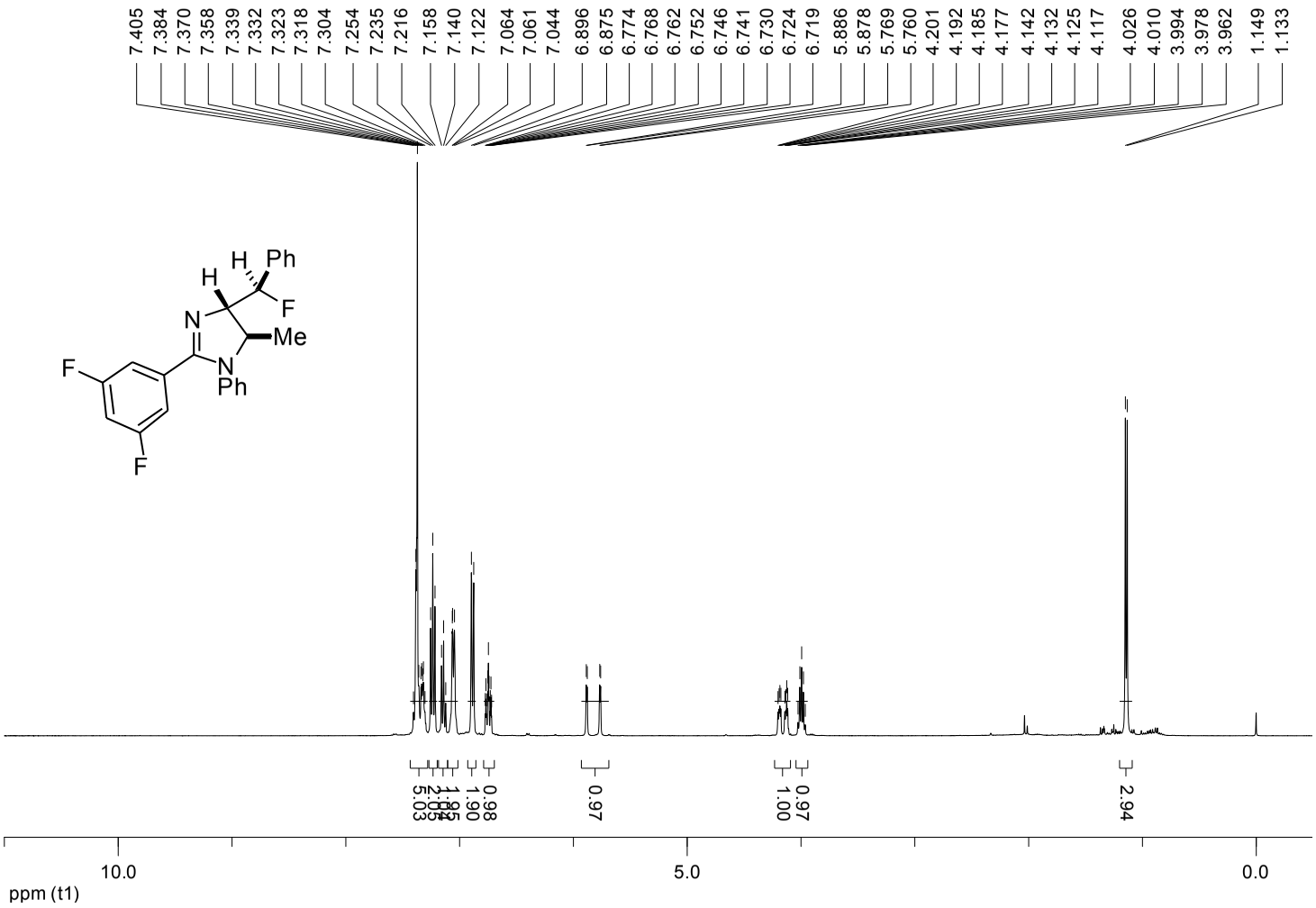
^{1}H NMR spectrum of **5f'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



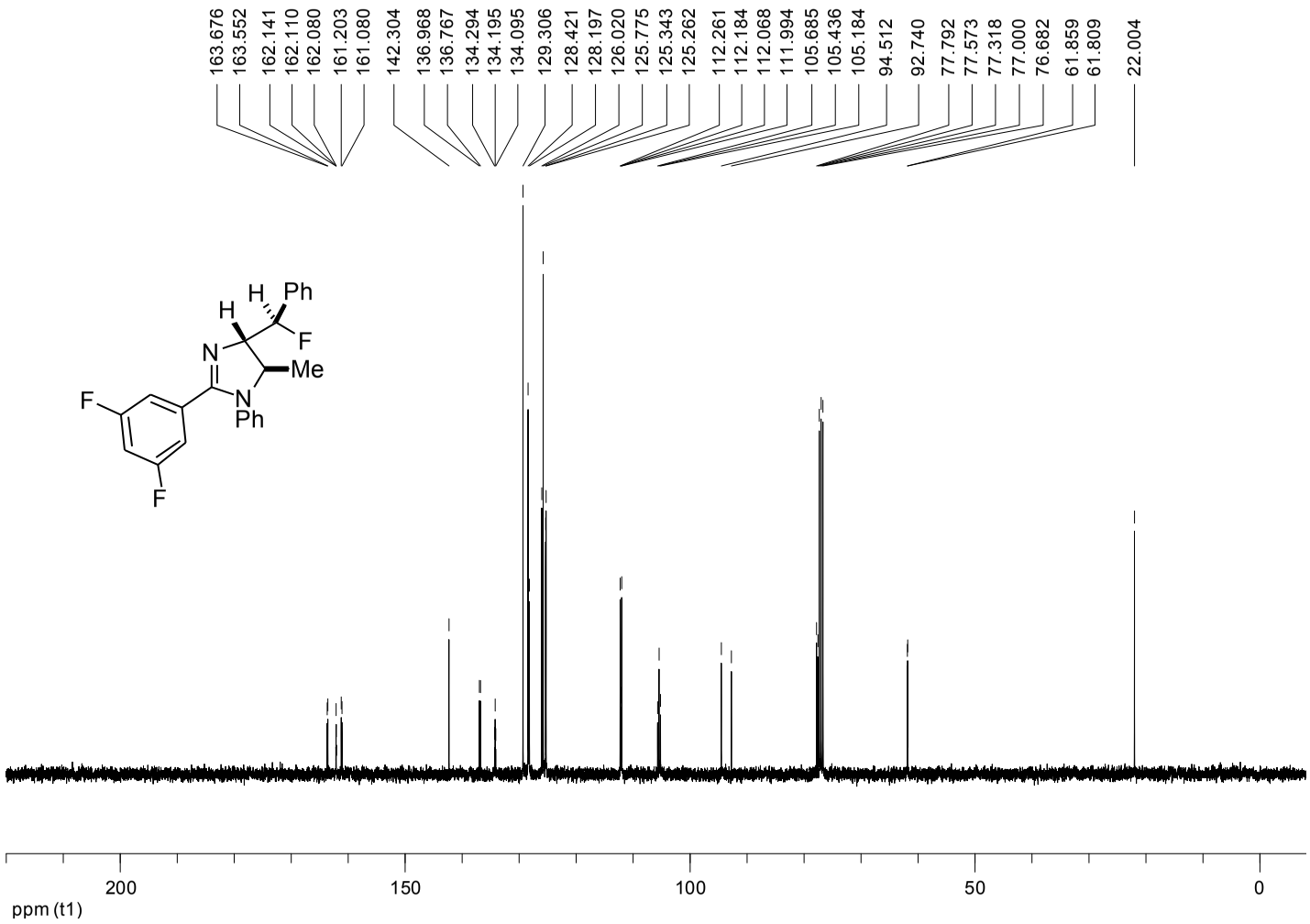
^{13}C NMR spectrum of **5f'** (the minor stereoisomer) (100 MHz, $CDCl_3$)



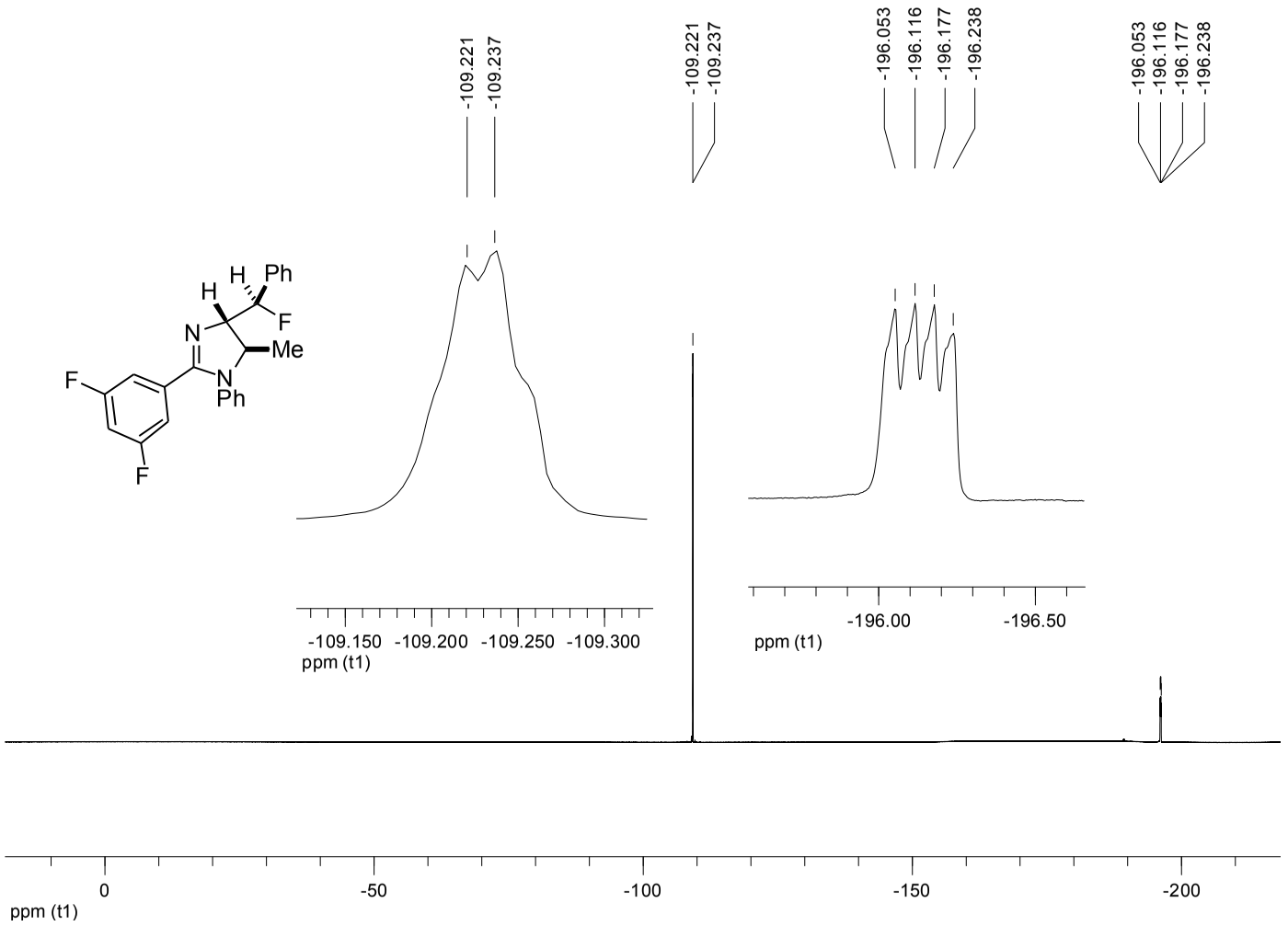
^{1}H NMR spectrum of **2g** (the major stereoisomer) (400 MHz, $CDCl_3$)



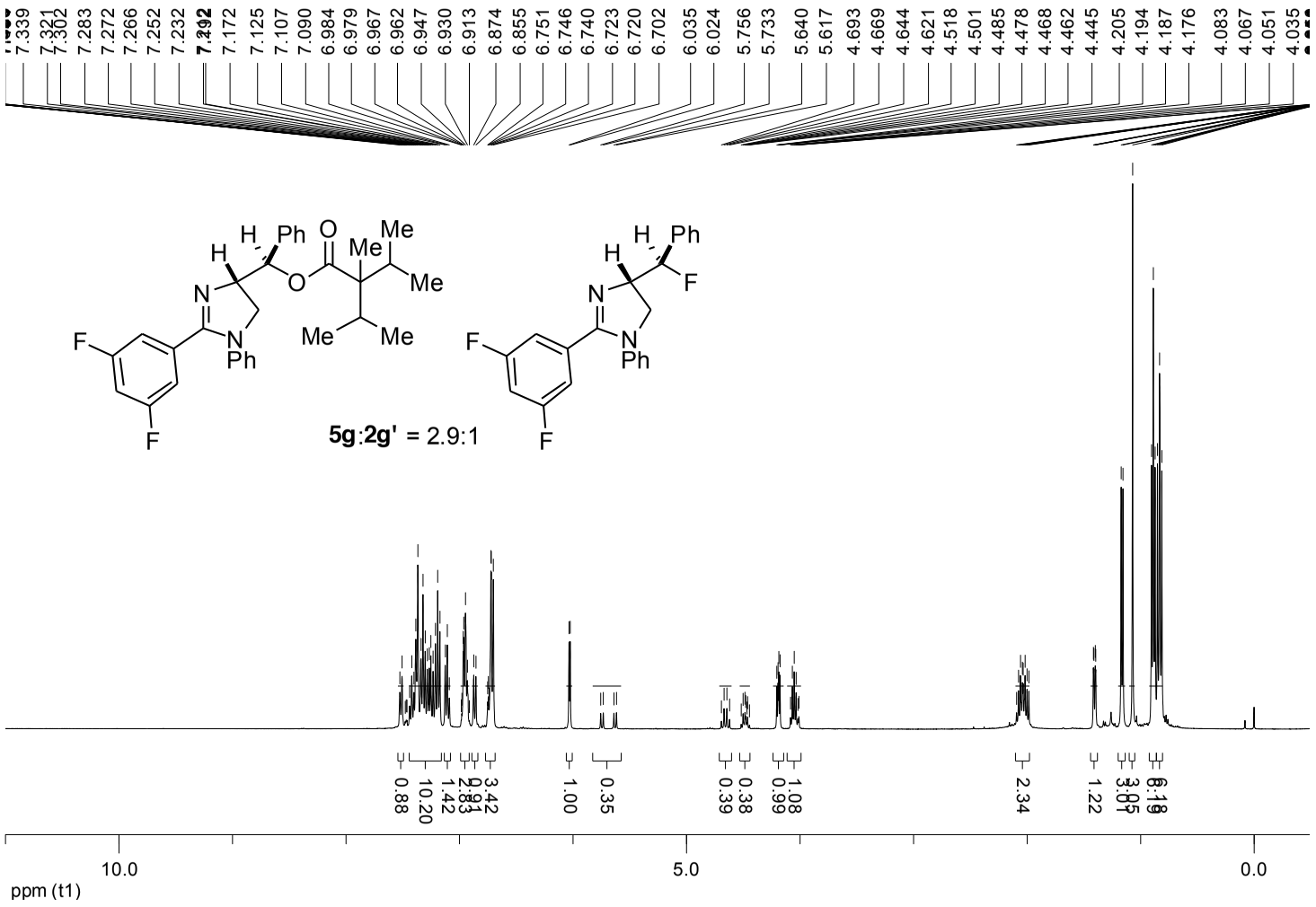
^{13}C NMR spectrum of **2g** (the major stereoisomer) (100 MHz, $CDCl_3$)



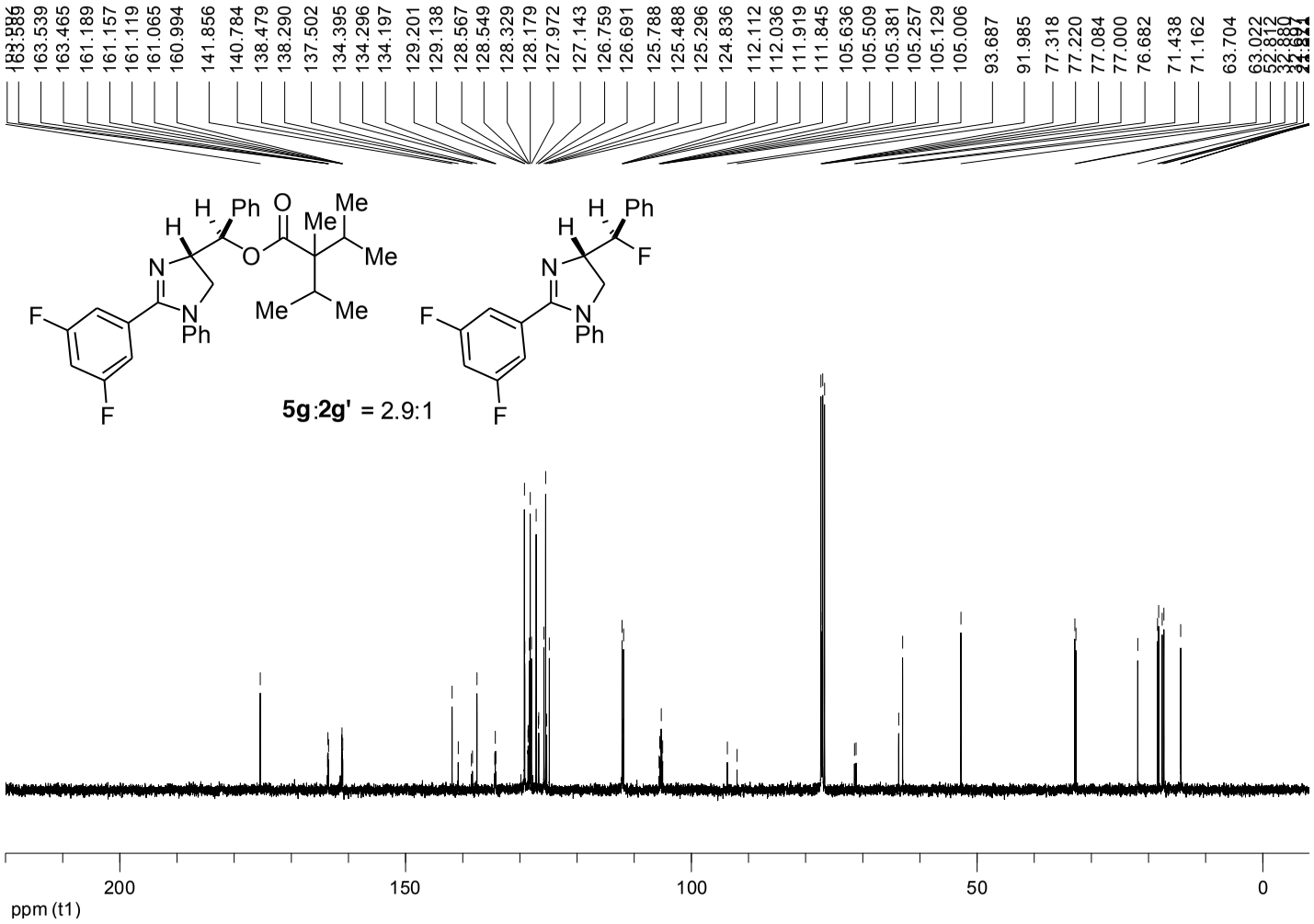
^{19}F NMR spectrum of **2g** (the major stereoisomer) (376 MHz, $CDCl_3$)



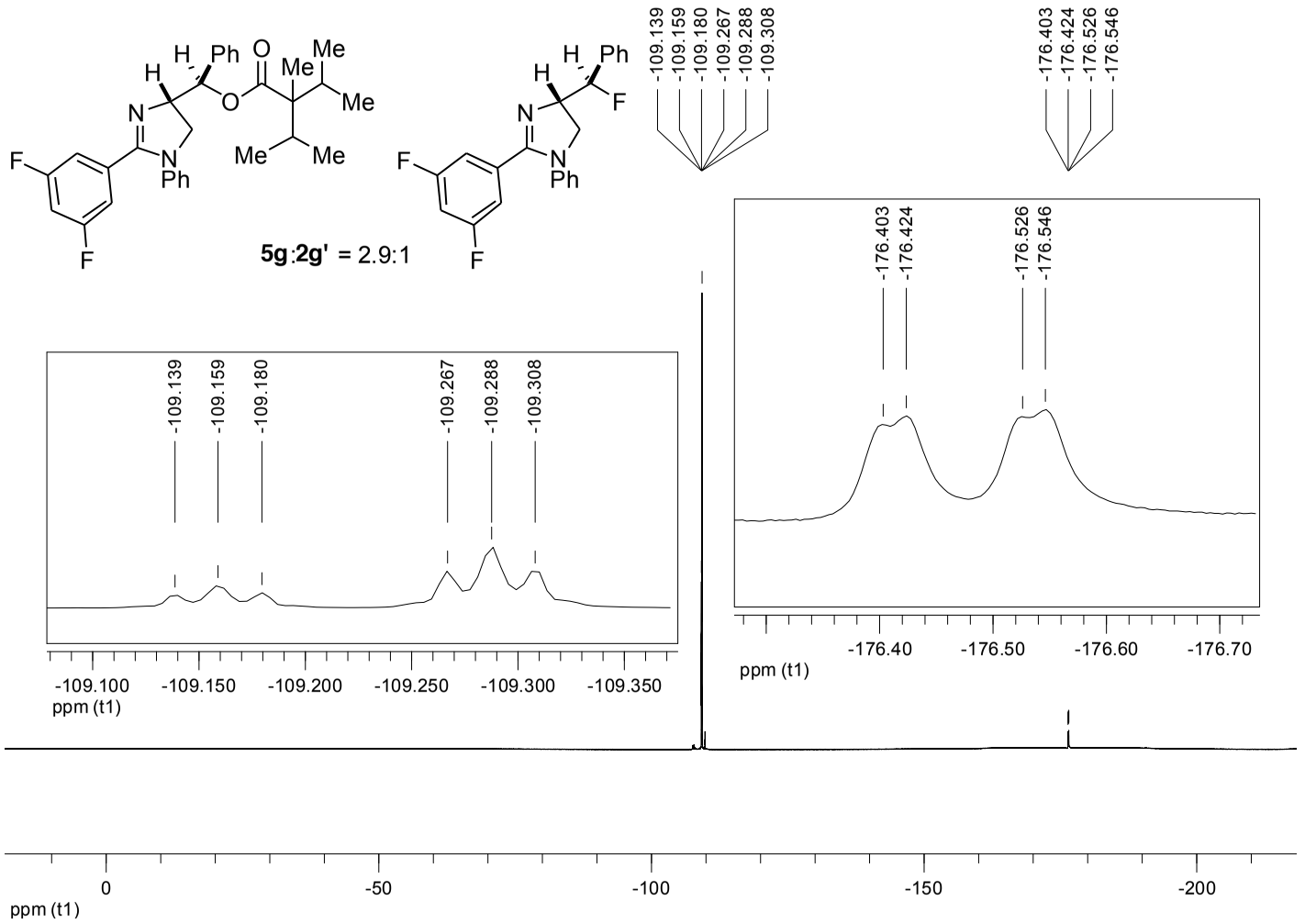
^{1}H NMR spectrum of mixture of **5g** and **2g'** (**5g**:**2g'** = 2.9:1) (400 MHz, $CDCl_3$)



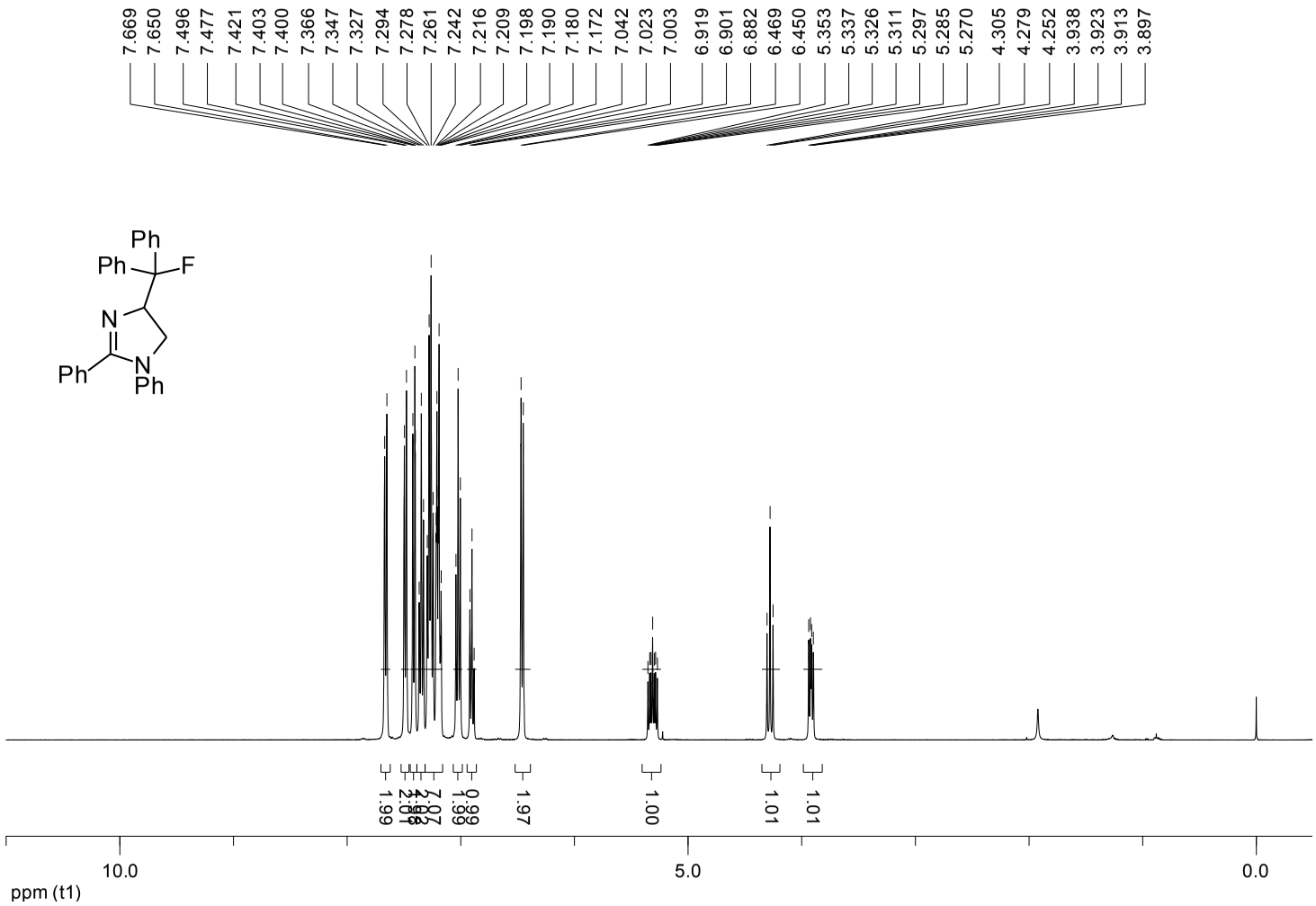
^{13}C NMR spectrum of **5g** and **2g'** (**5g**:**2g'** = 2.9:1) (100 MHz, $CDCl_3$)



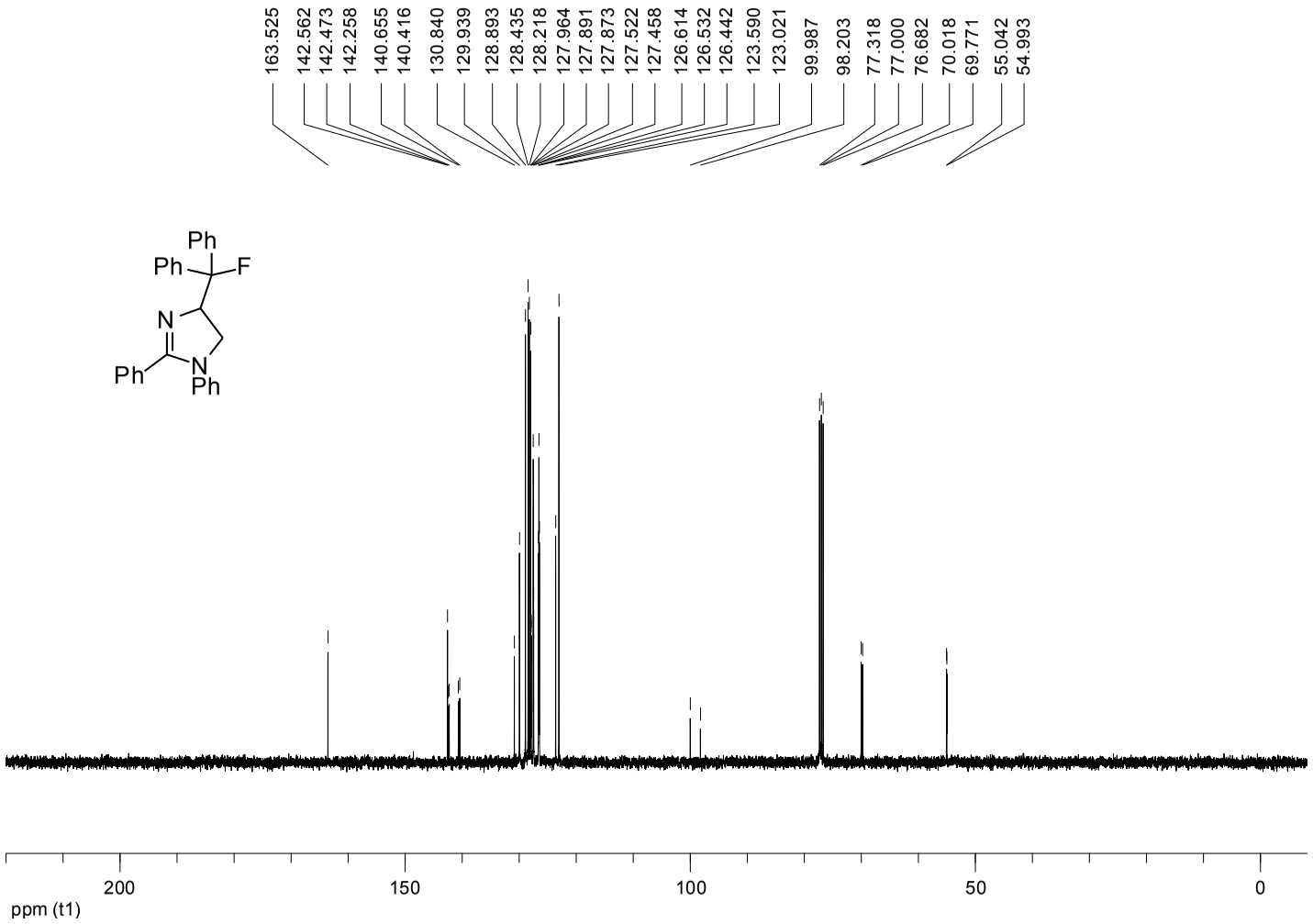
^{19}F NMR spectrum of **5g** and **2g'** (**5g**:**2g'** = 2.9:1) (376 MHz, $CDCl_3$)



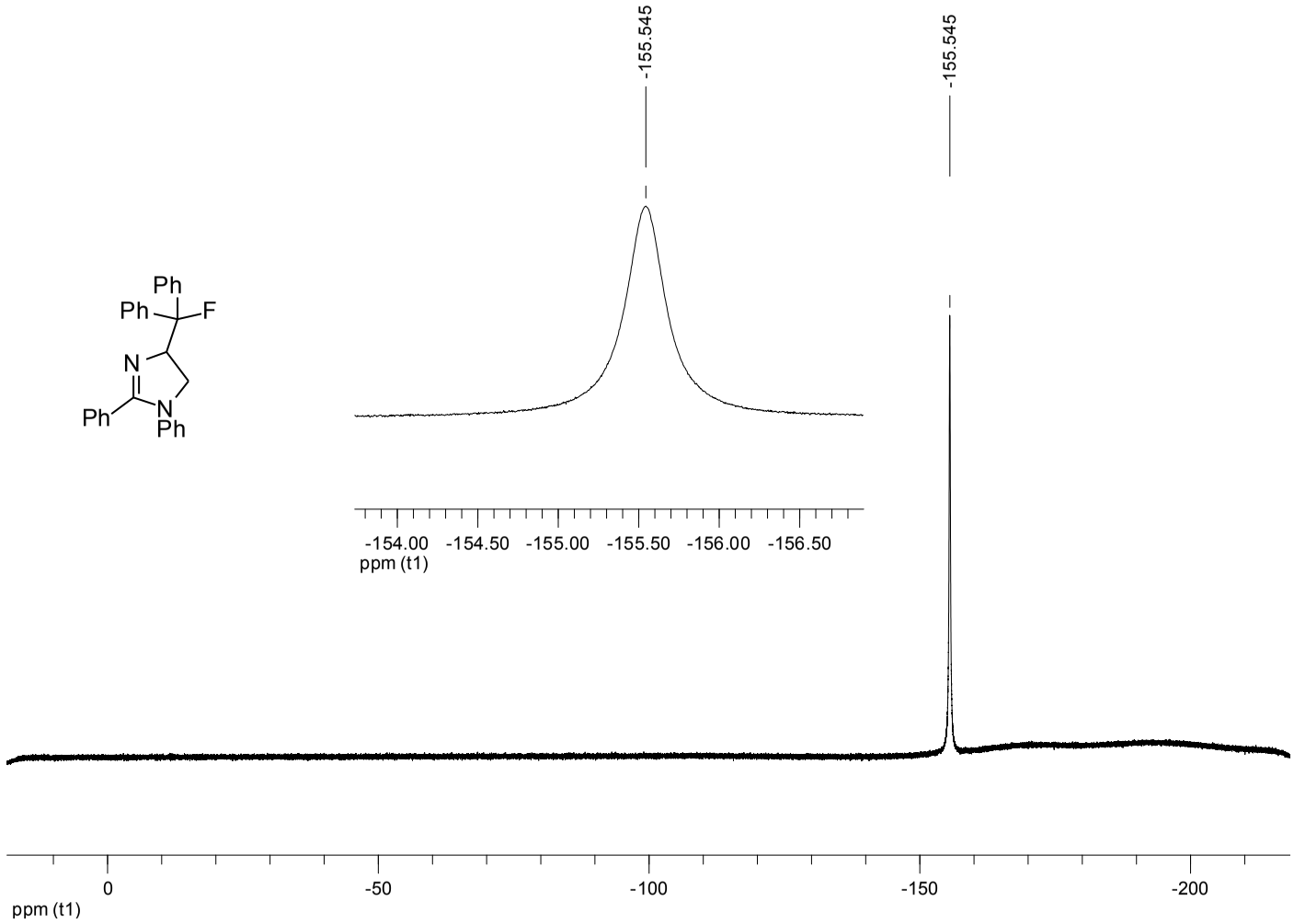
^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)



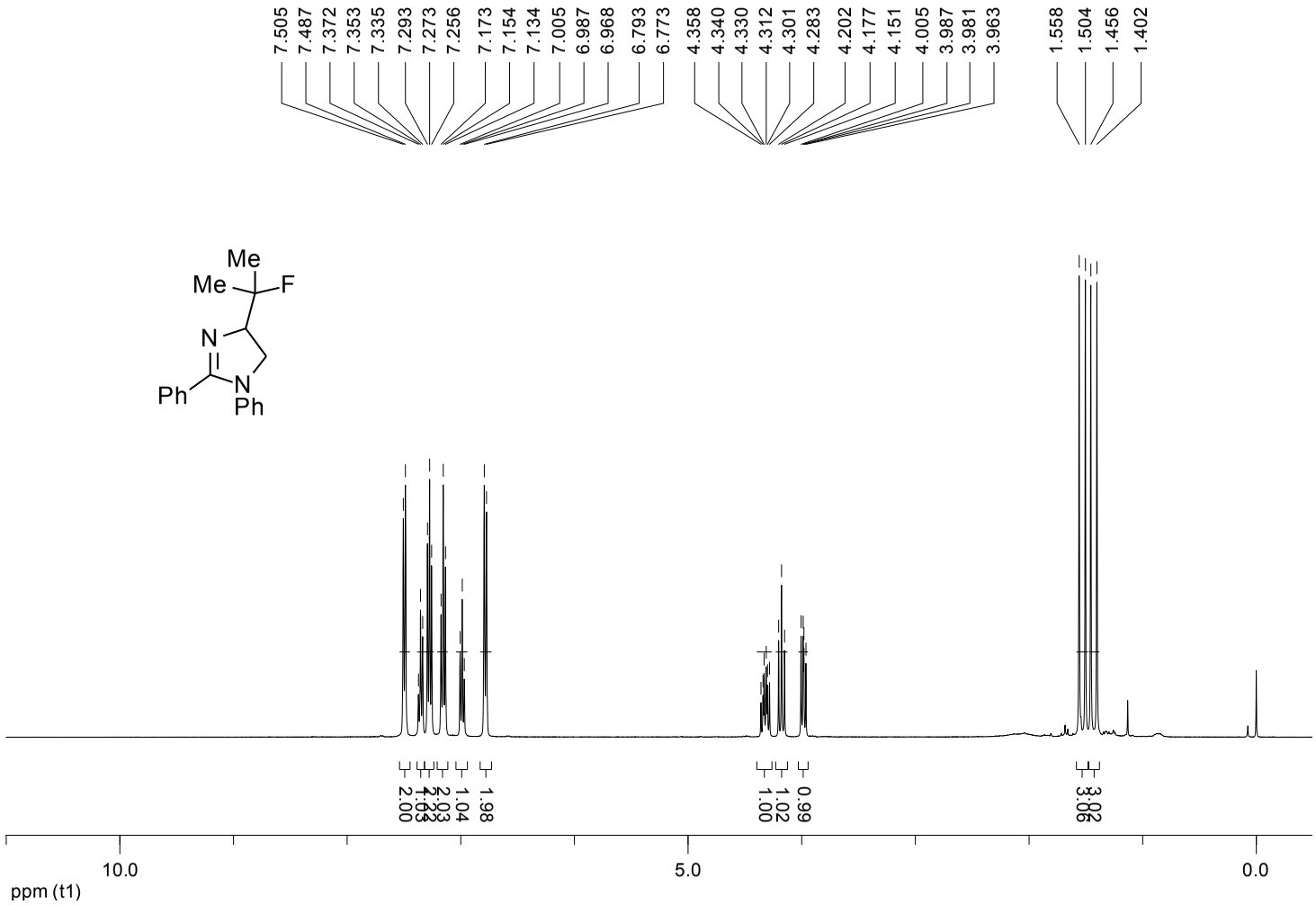
^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)



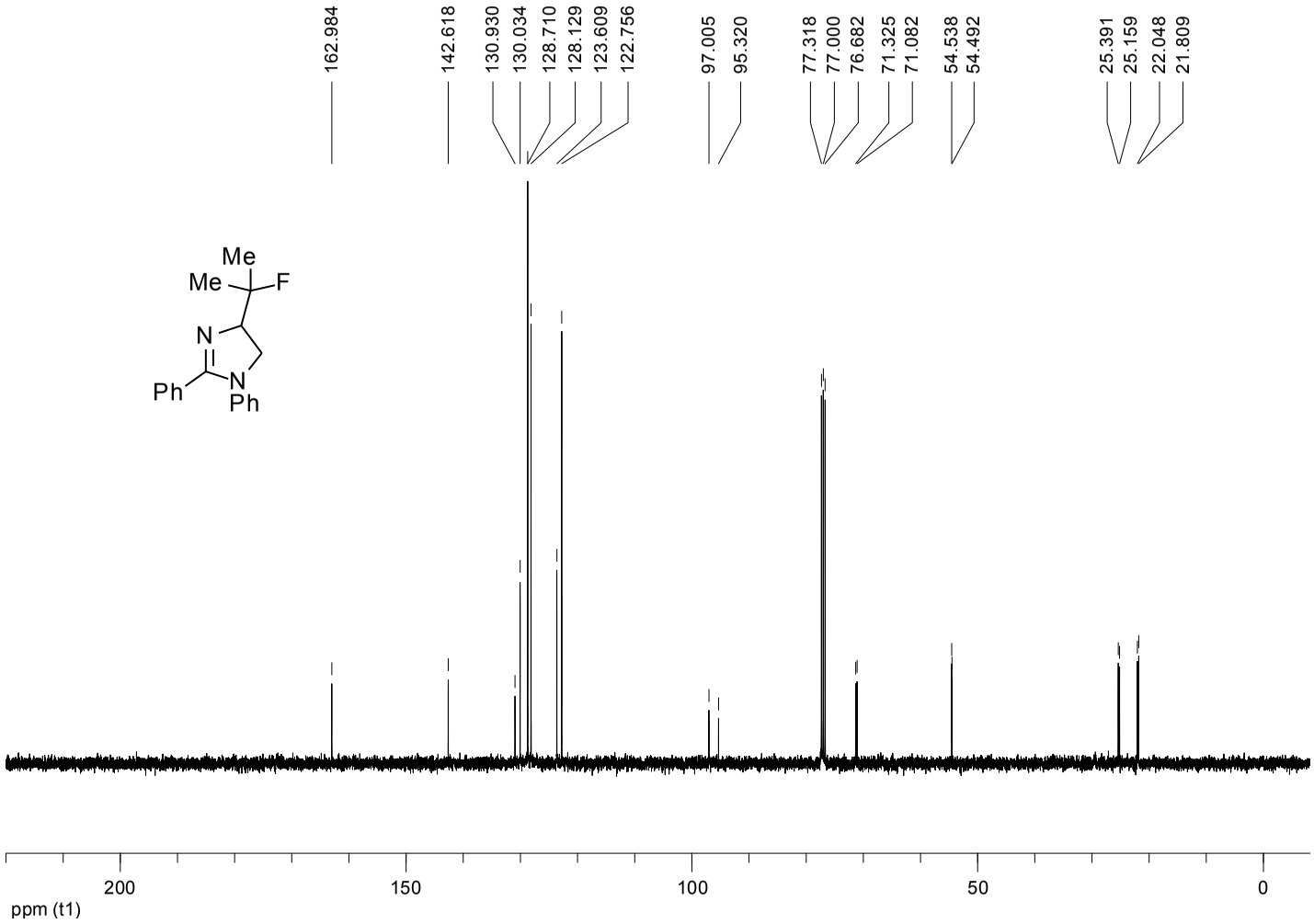
^{19}F NMR spectrum of **2h** (376 MHz, $CDCl_3$)



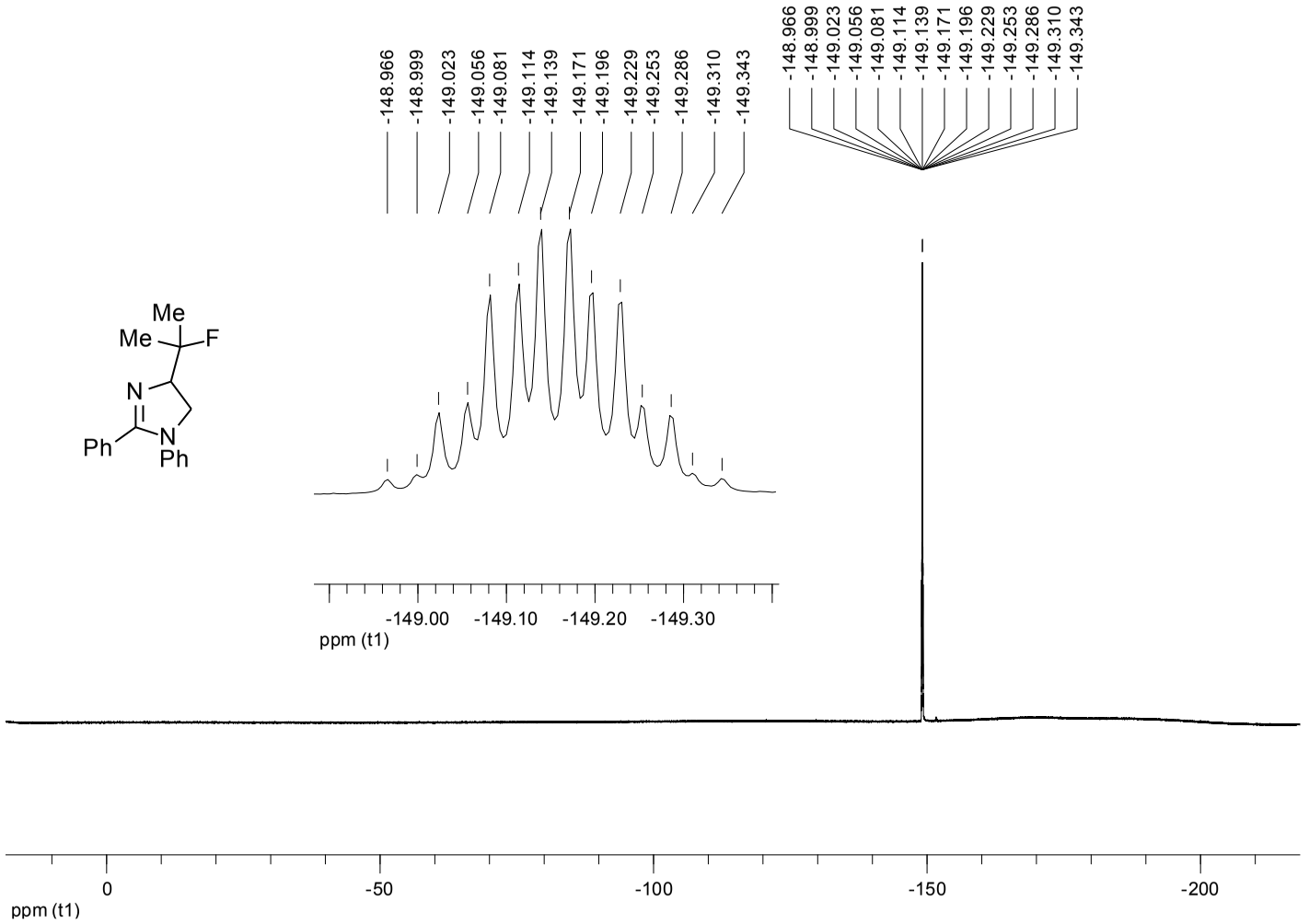
^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)



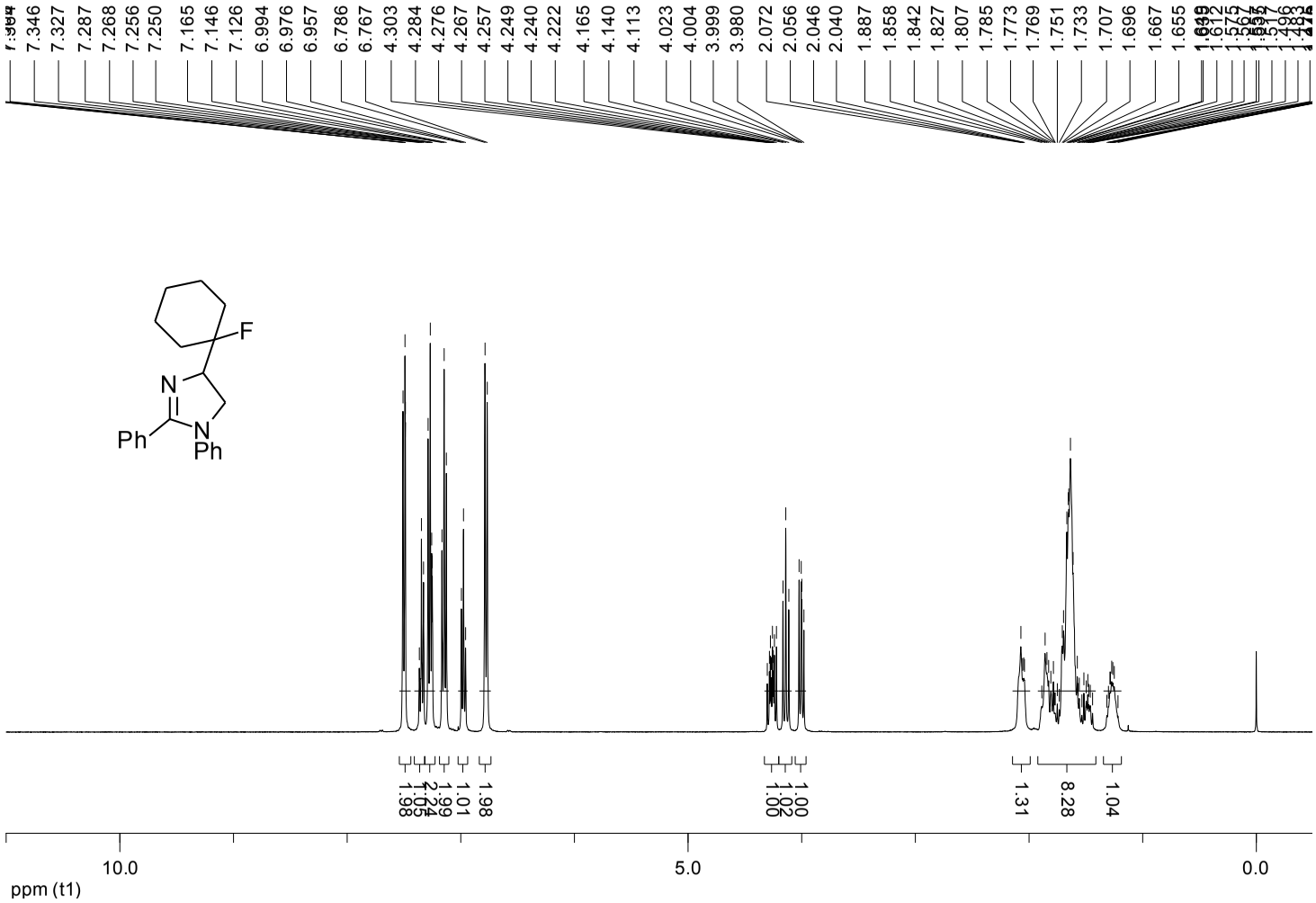
^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)



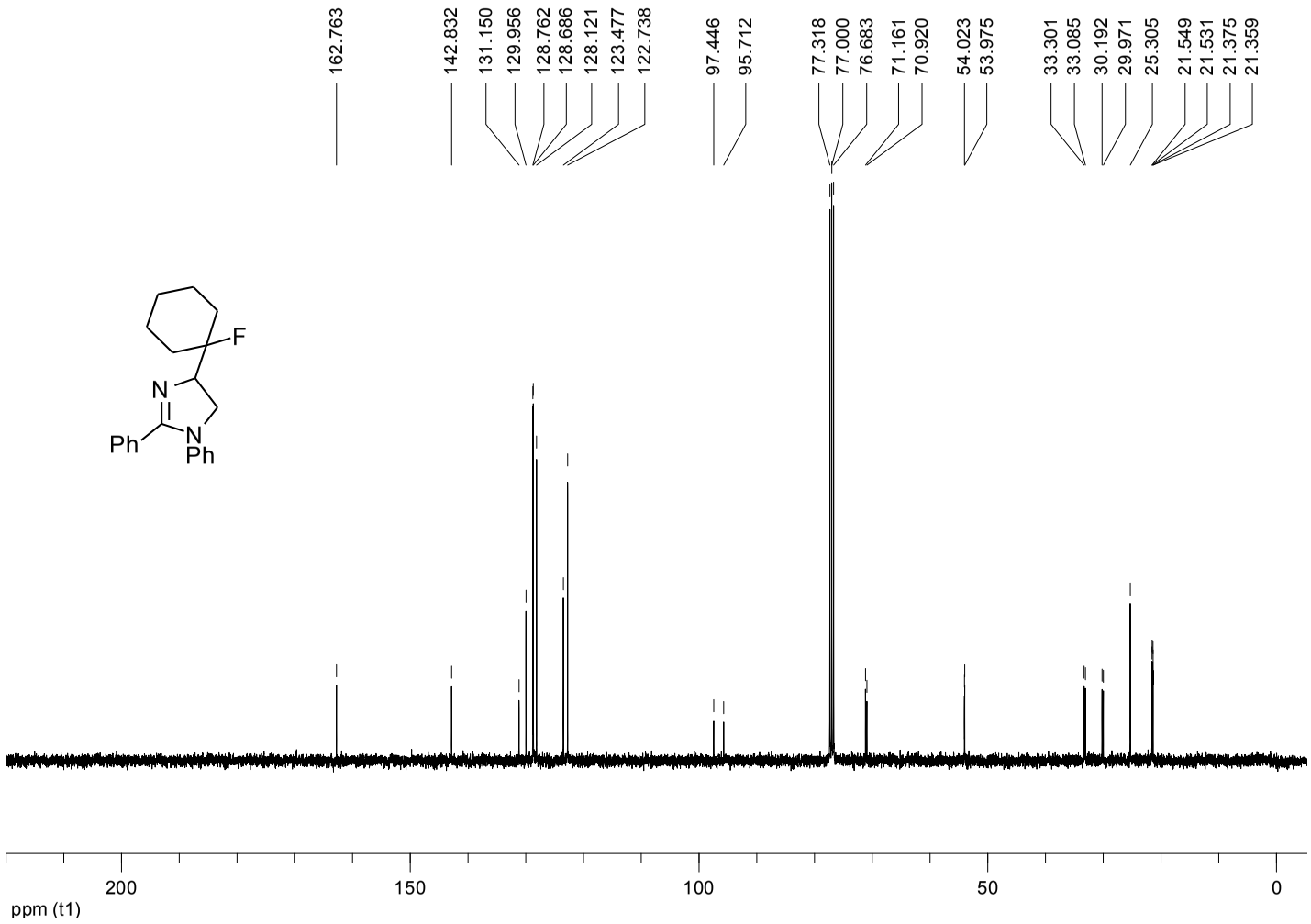
^{19}F NMR spectrum of **2i** (376 MHz, $CDCl_3$)



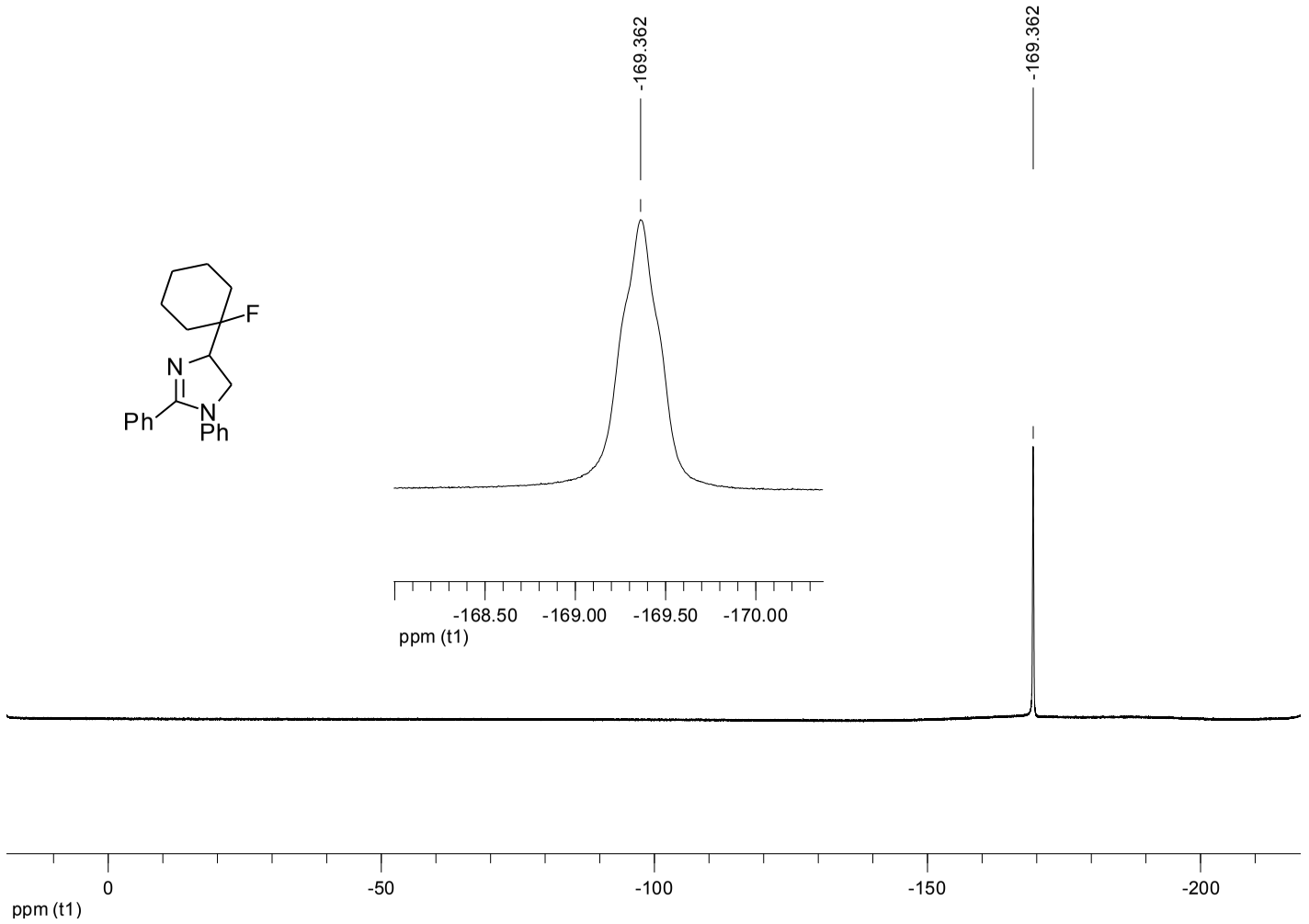
^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)



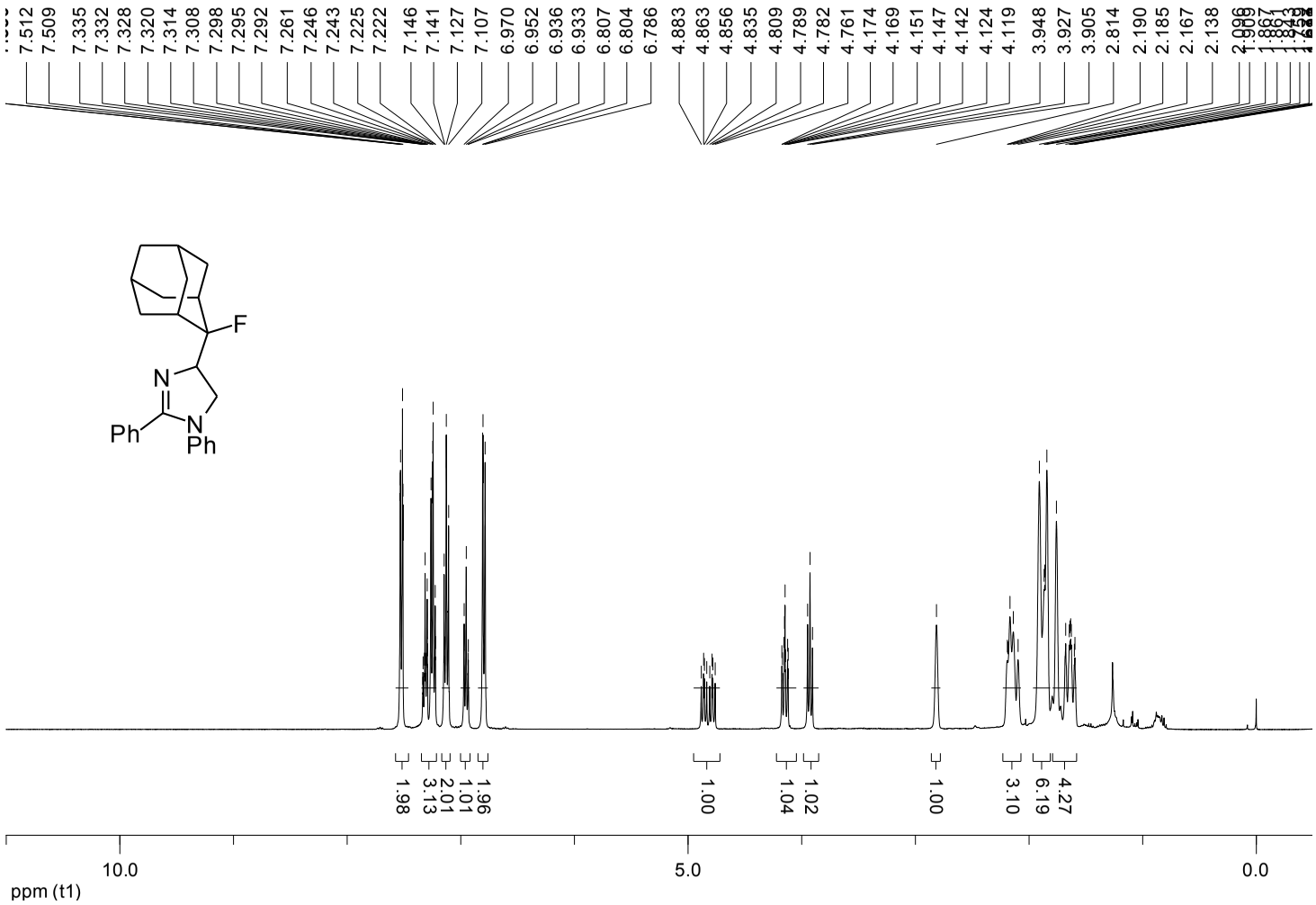
^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$)



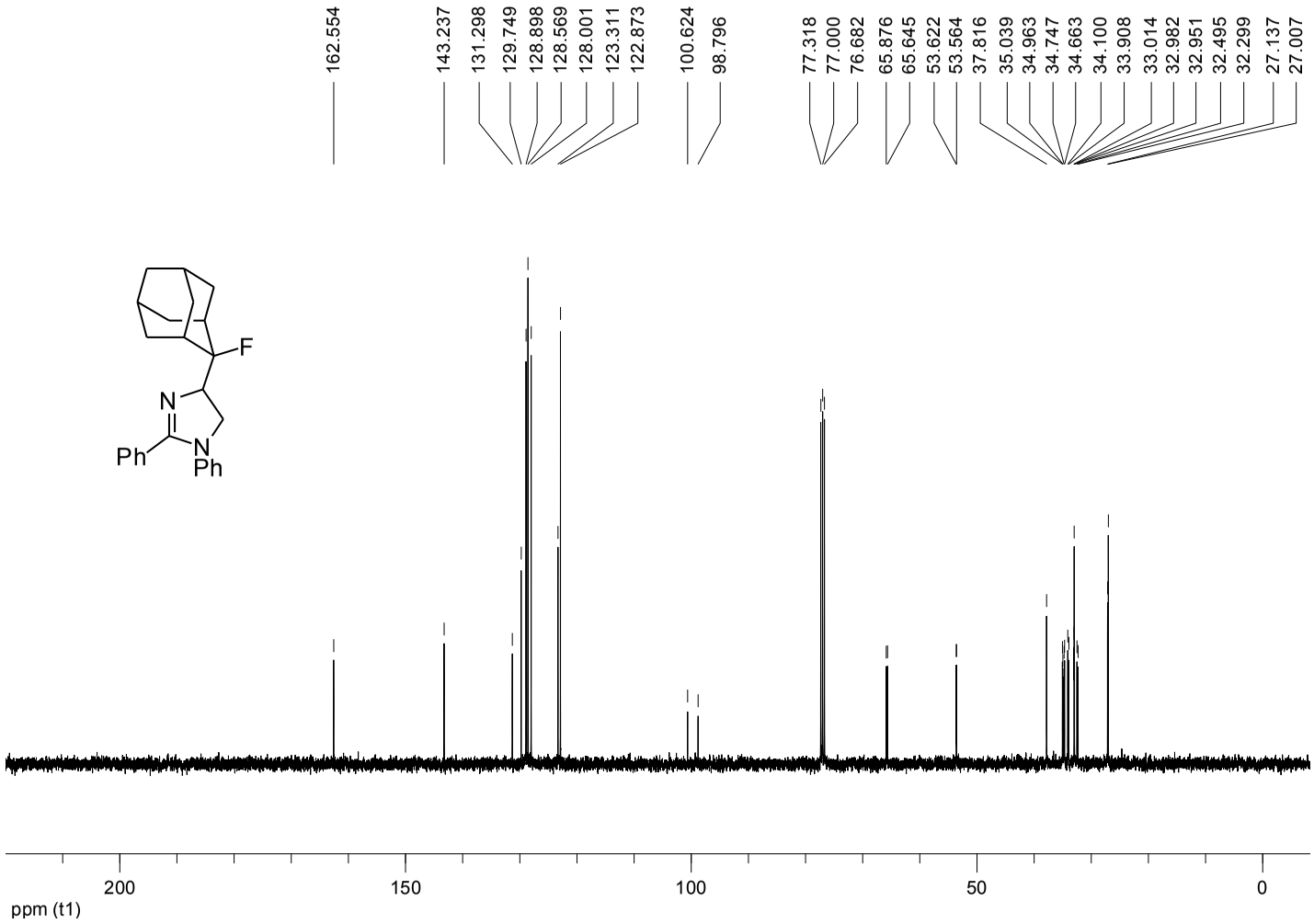
^{19}F NMR spectrum of **2j** (376 MHz, $CDCl_3$)



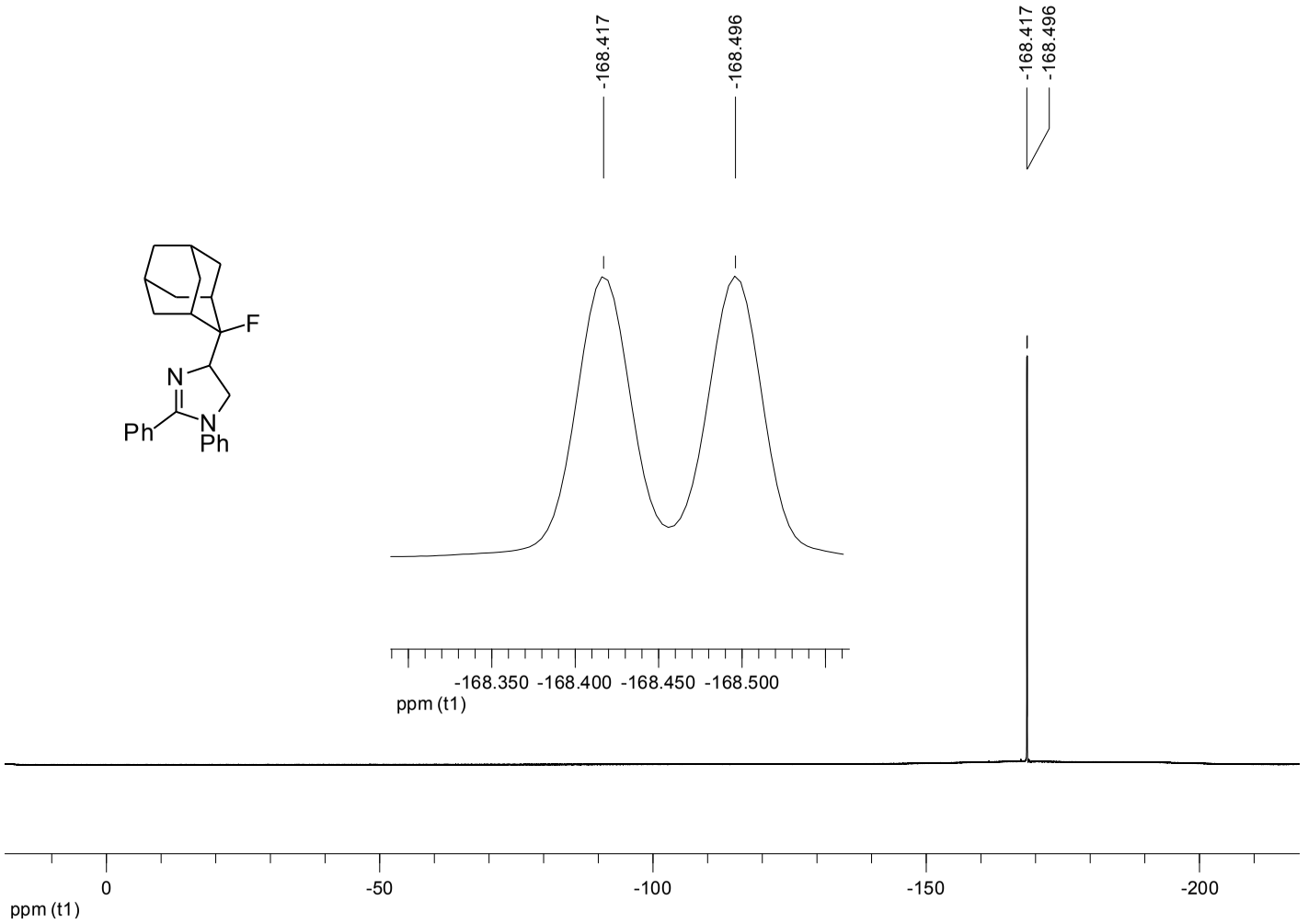
^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)



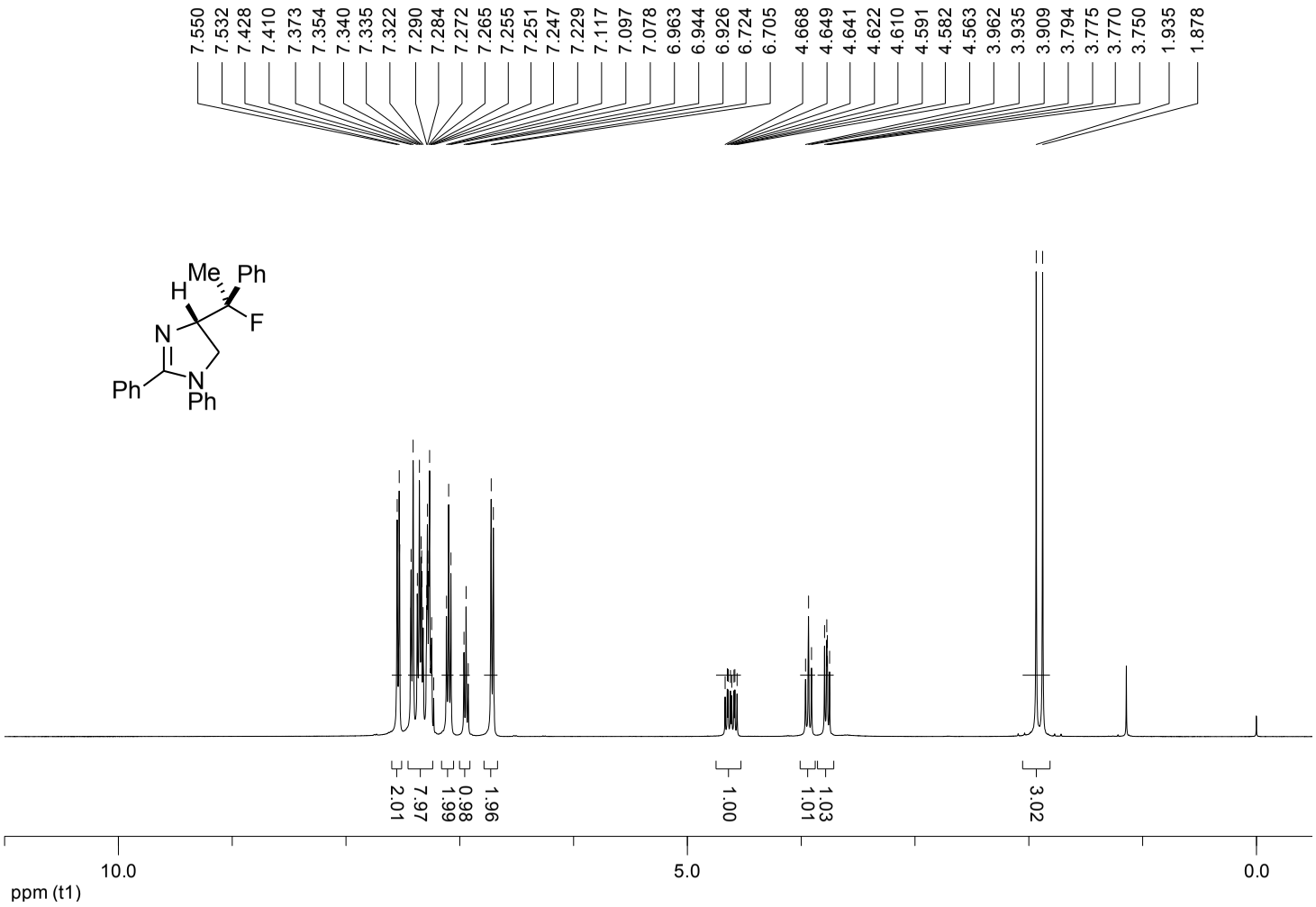
^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)



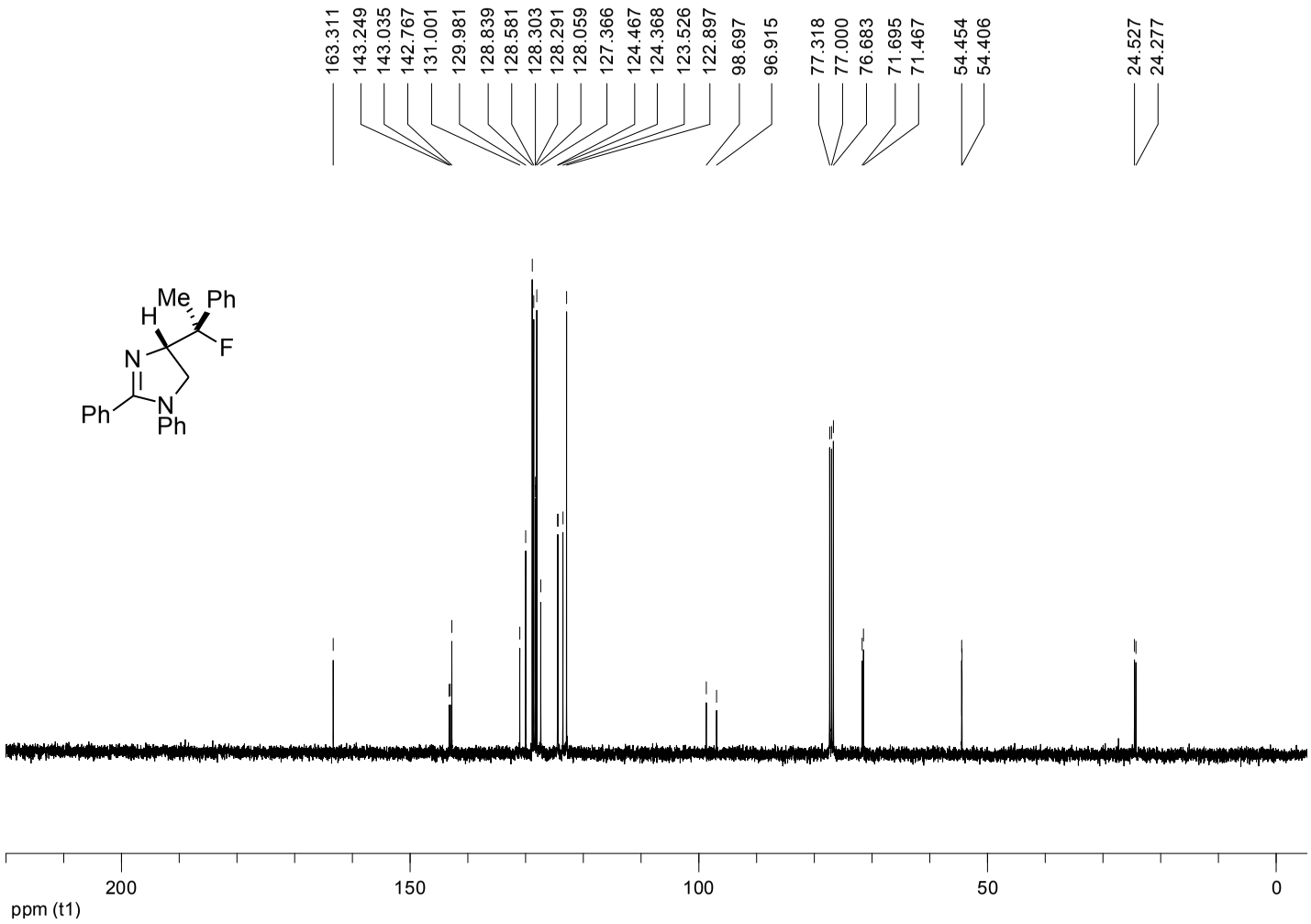
^{19}F NMR spectrum of **2k** (376 MHz, $CDCl_3$)



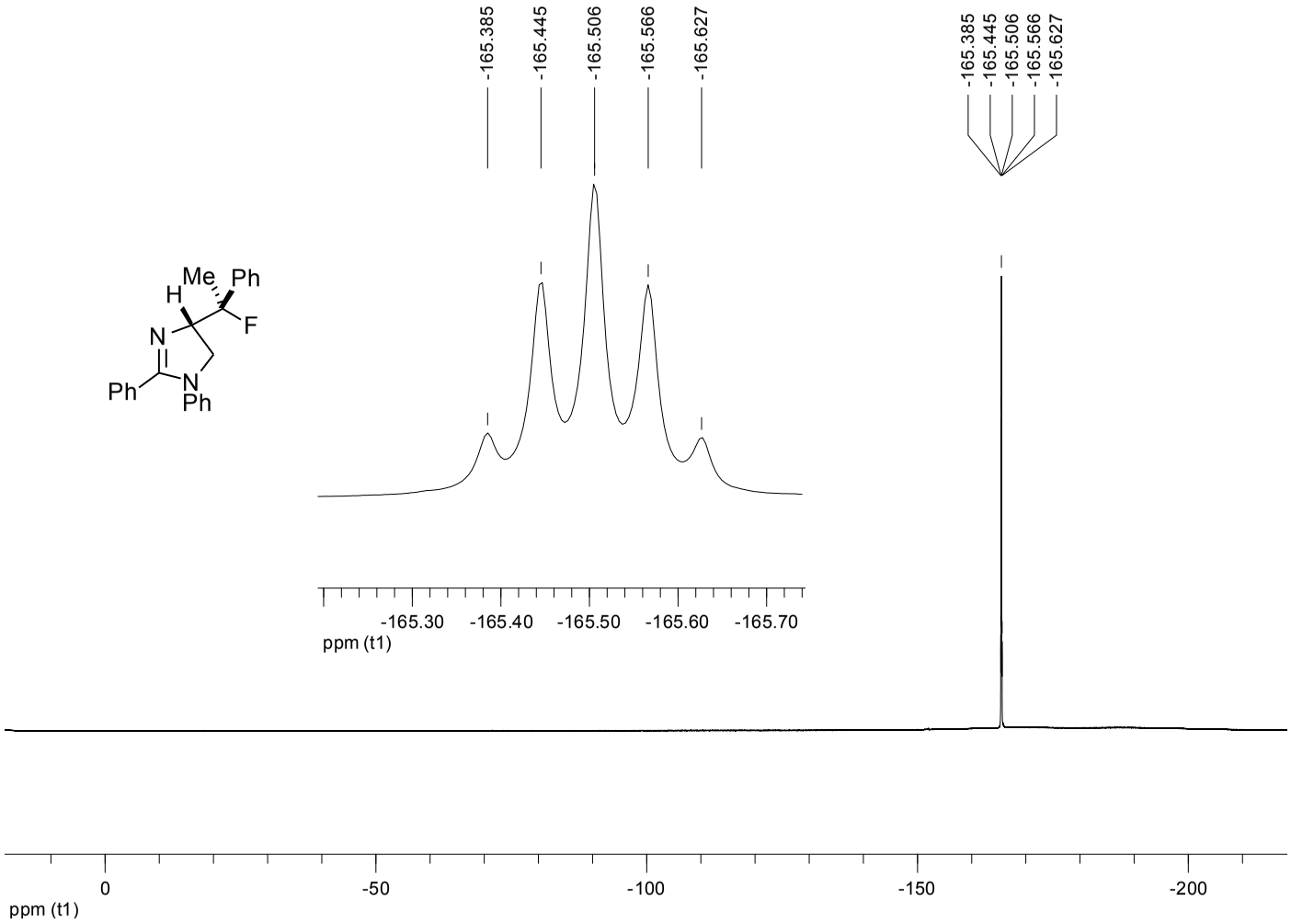
^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$)



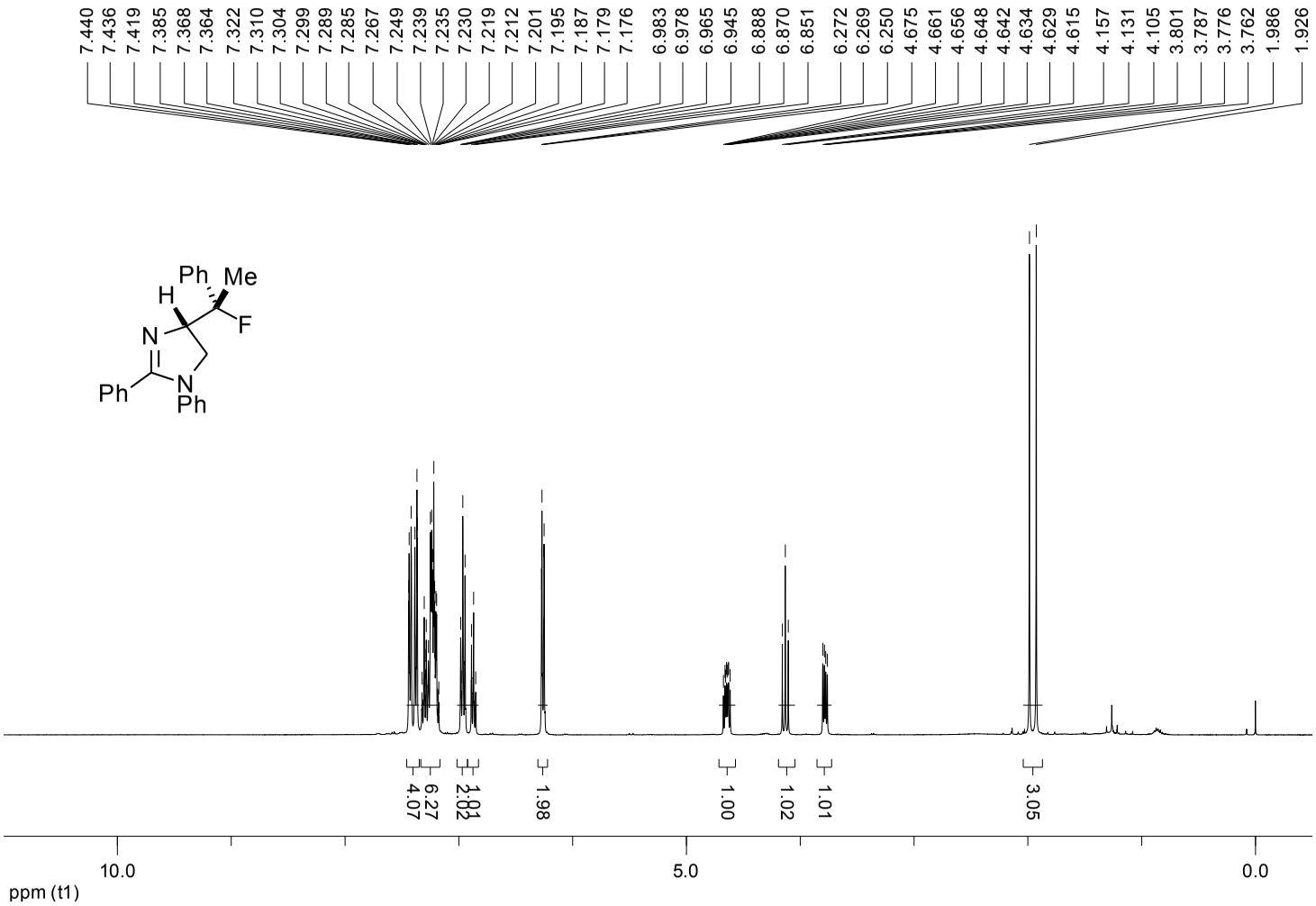
^{13}C NMR spectrum of **2l** (100 MHz, $CDCl_3$)



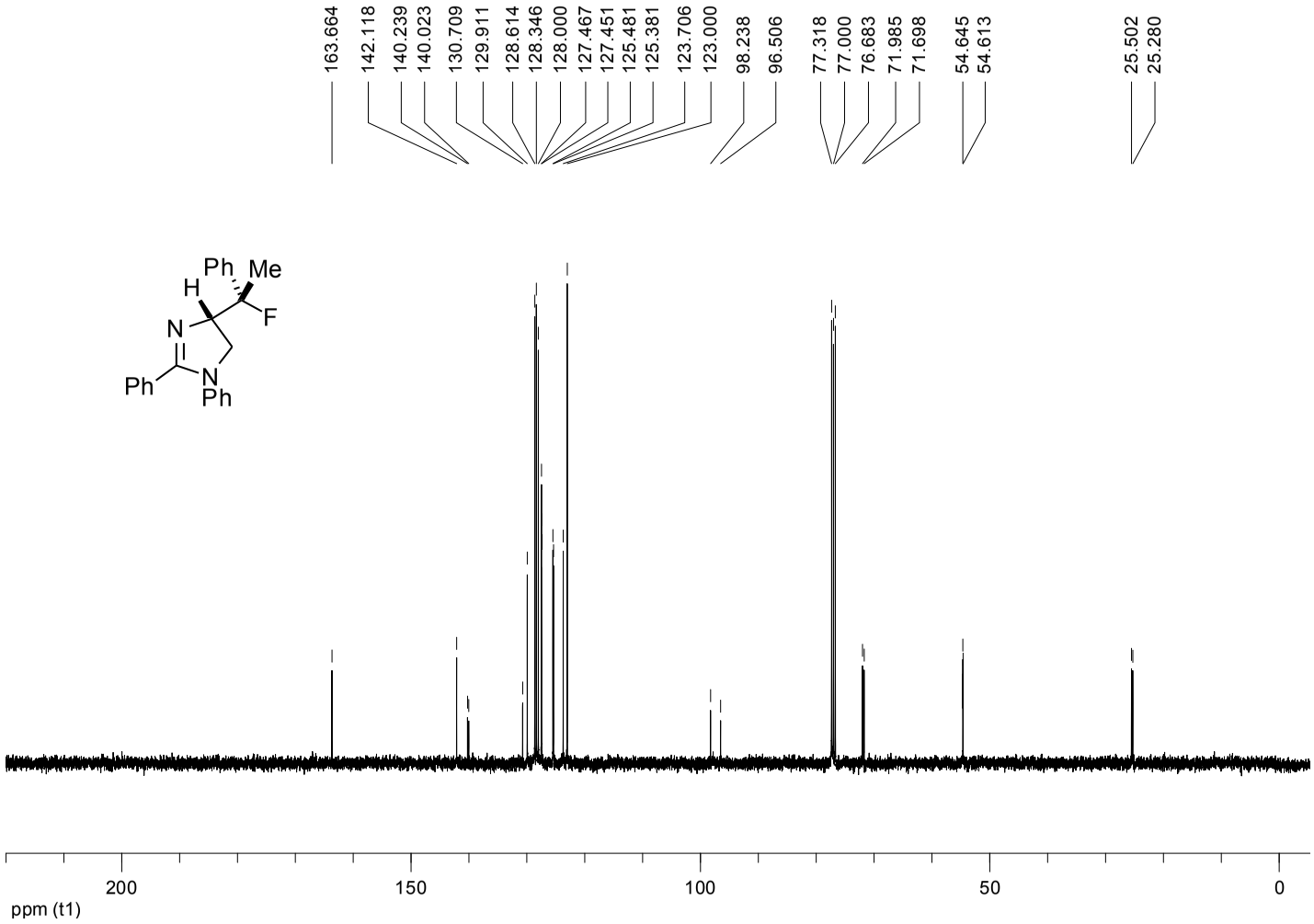
^{19}F NMR spectrum of **2l** (376 MHz, $CDCl_3$)



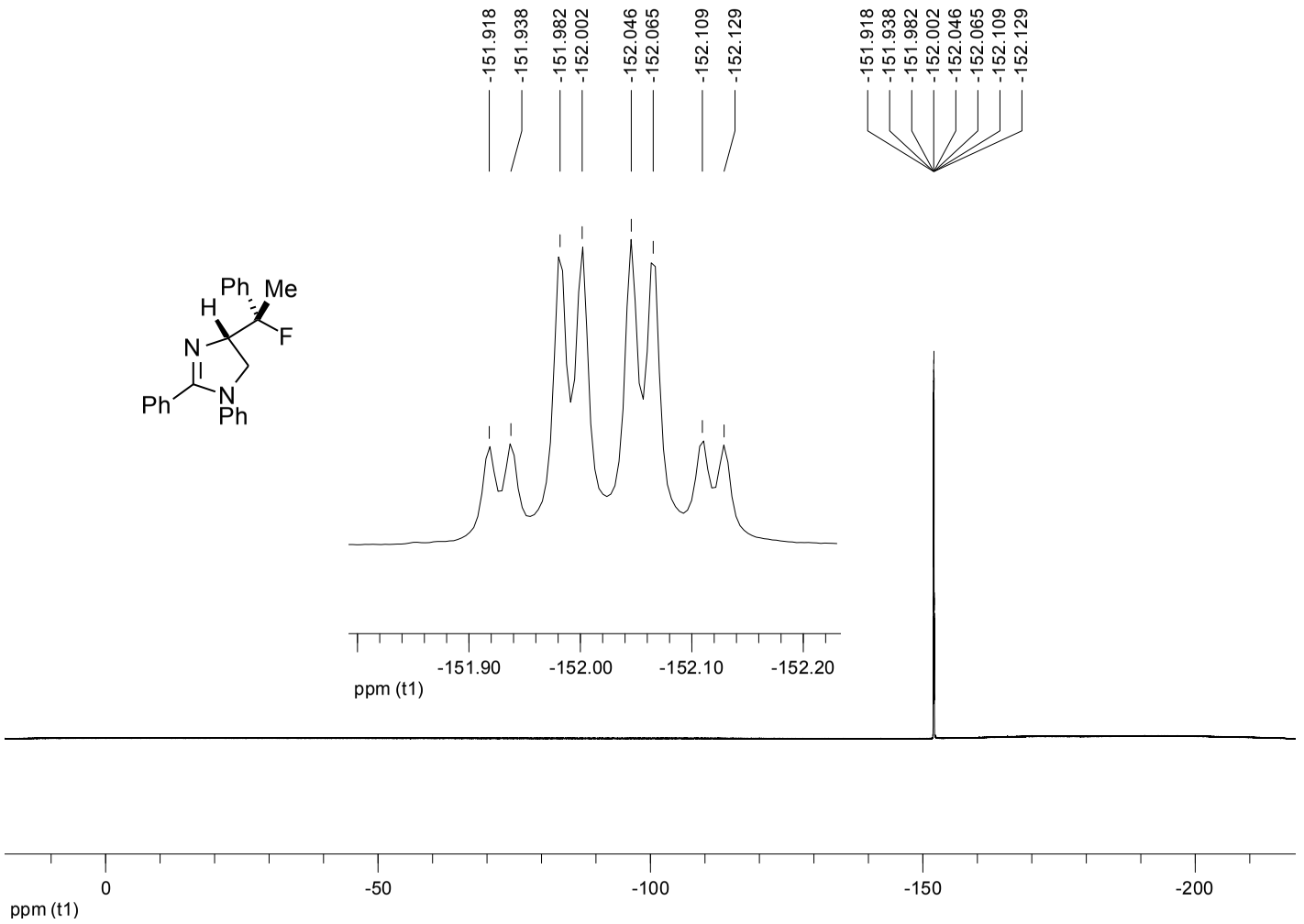
^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$)



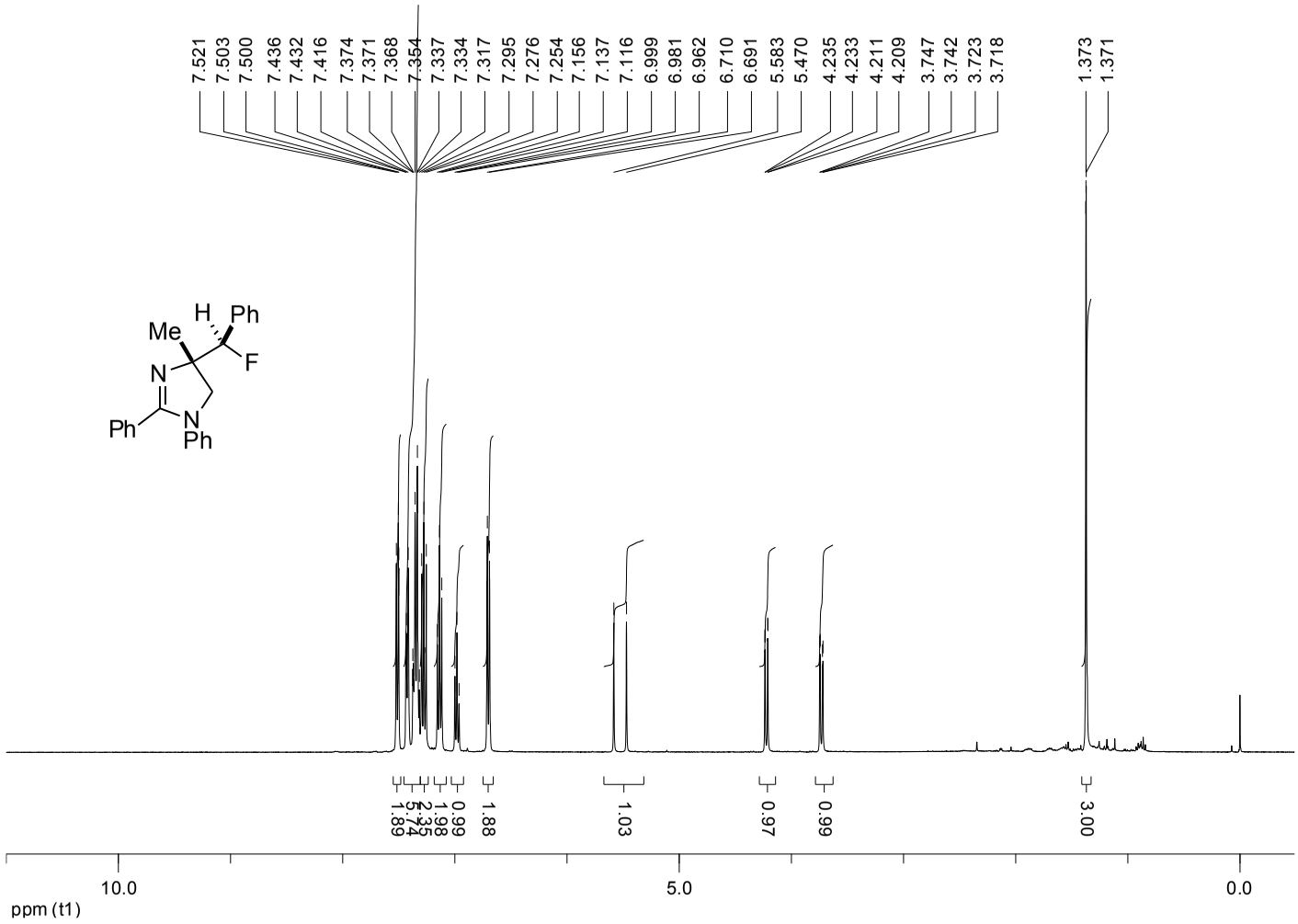
^{13}C NMR spectrum of **2m** (100 MHz, $CDCl_3$)



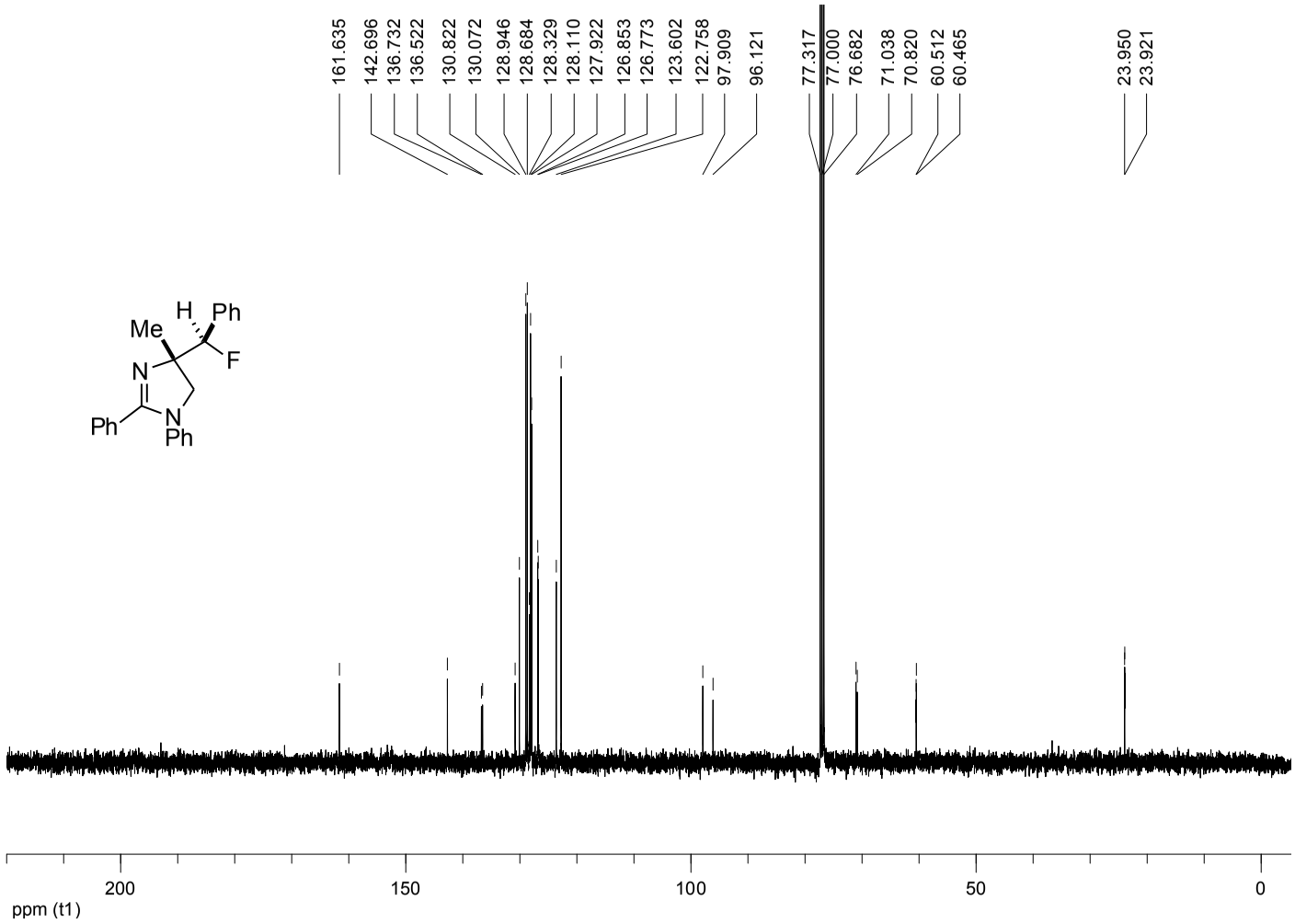
^{19}F NMR spectrum of **2m** (376 MHz, $CDCl_3$)



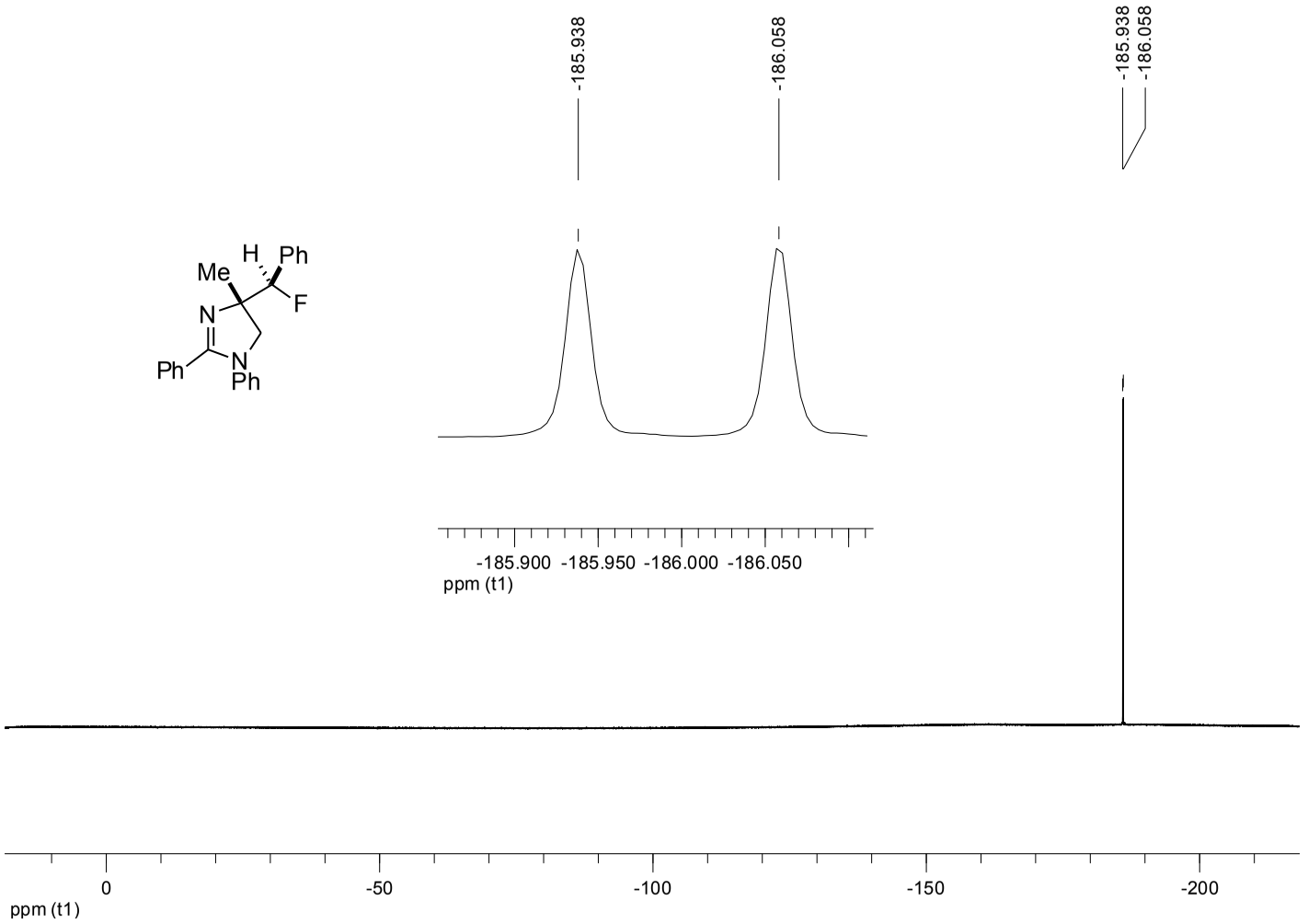
^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)



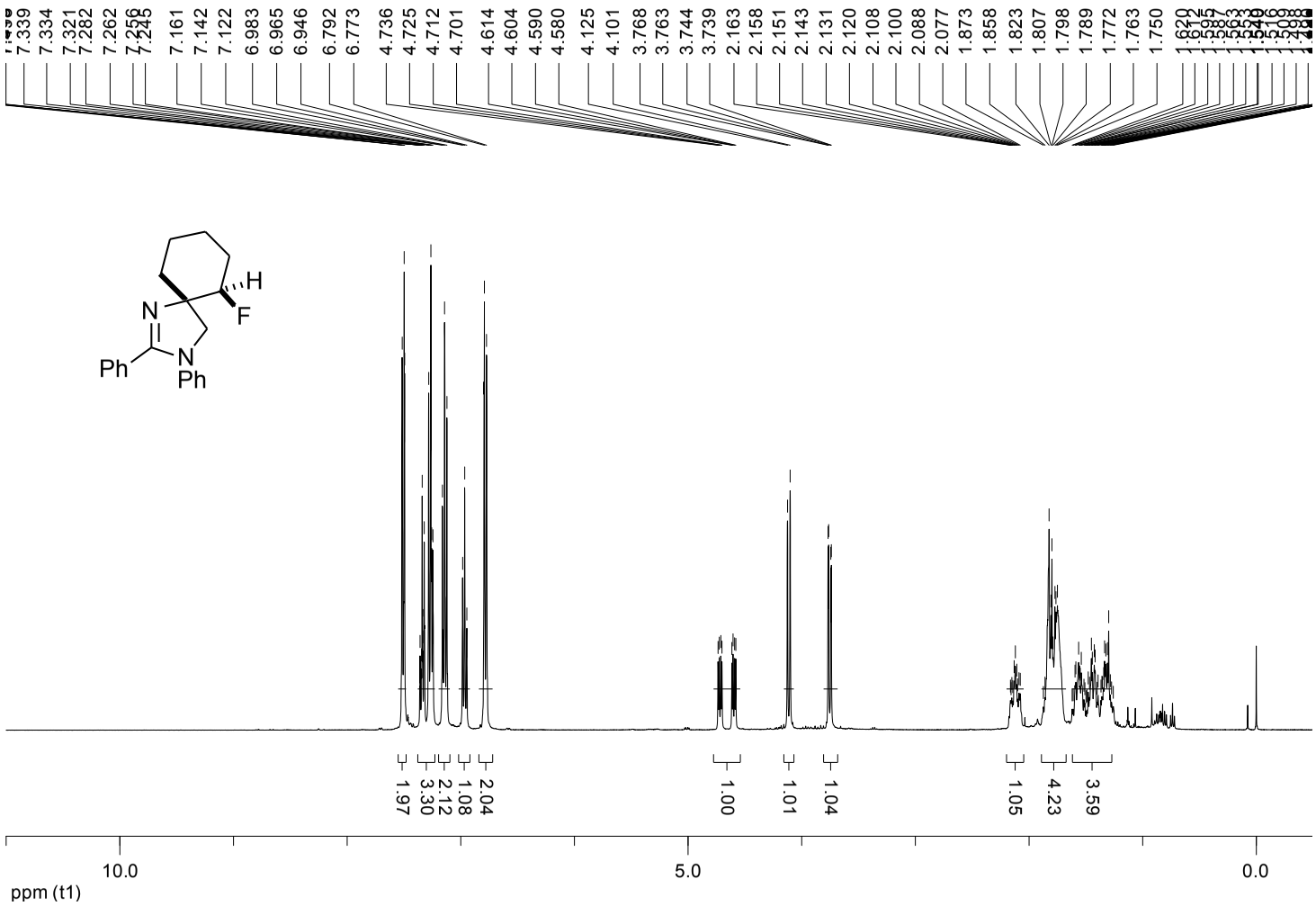
^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)



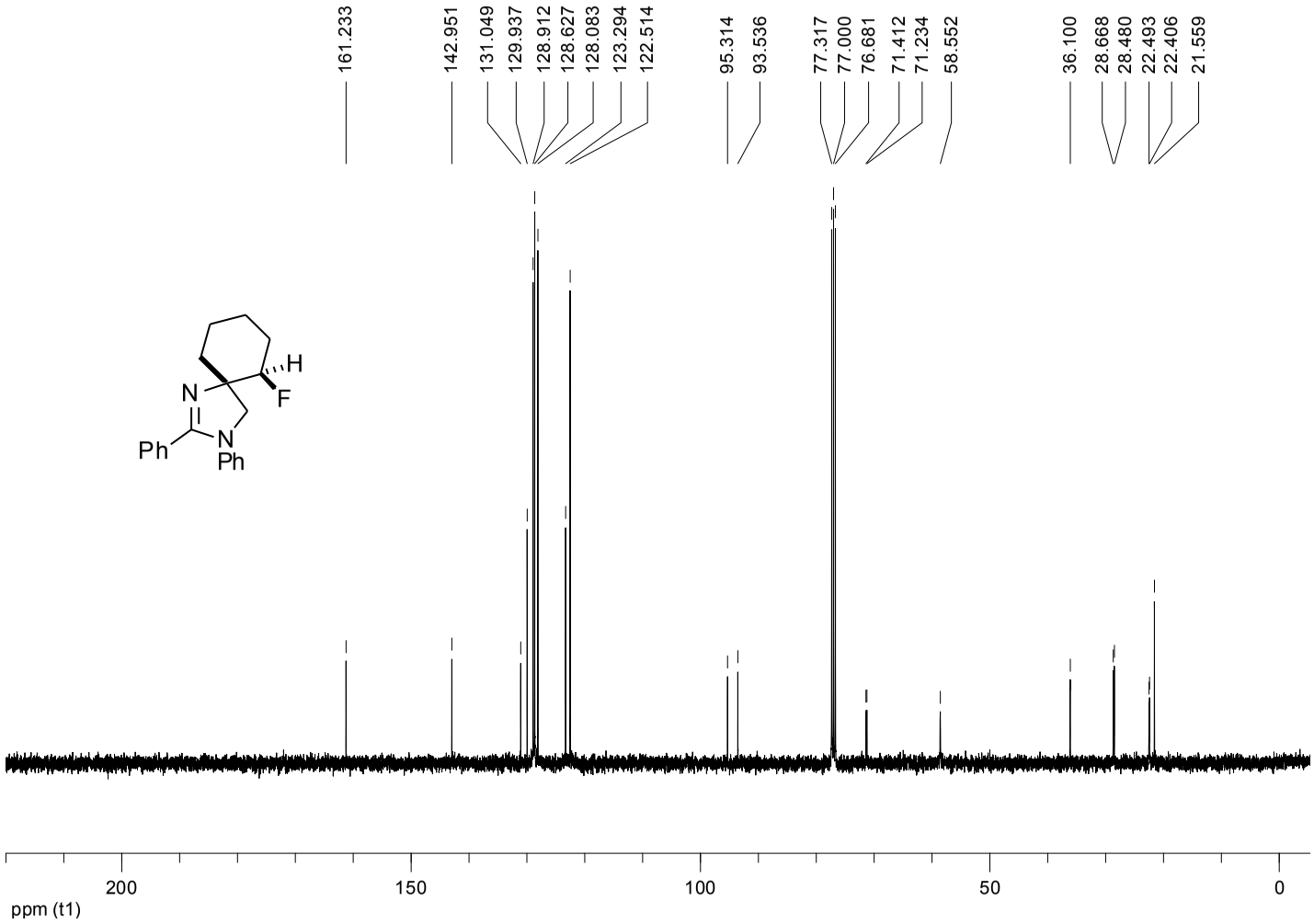
^{19}F NMR spectrum of **2n** (376 MHz, $CDCl_3$)



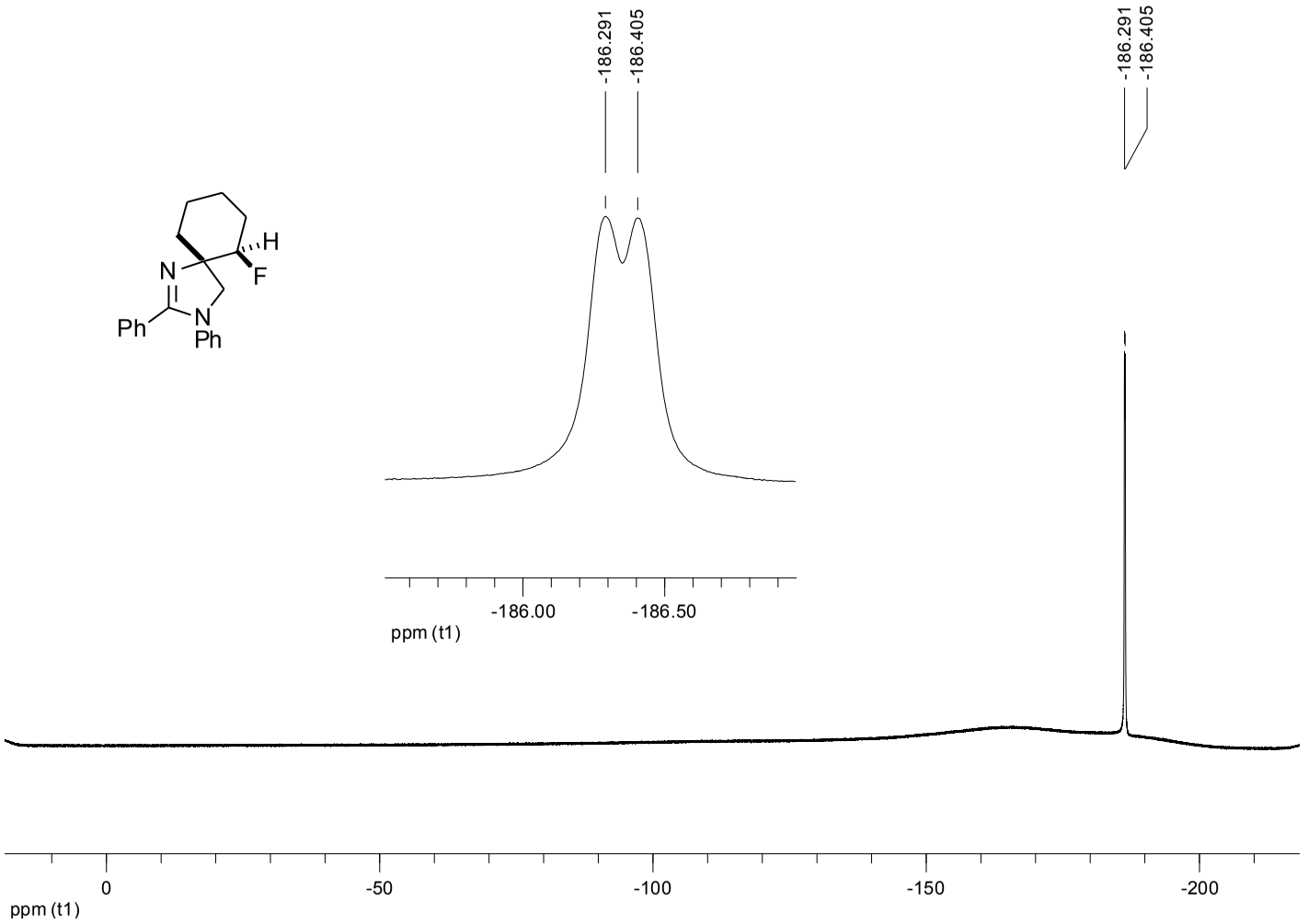
^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)



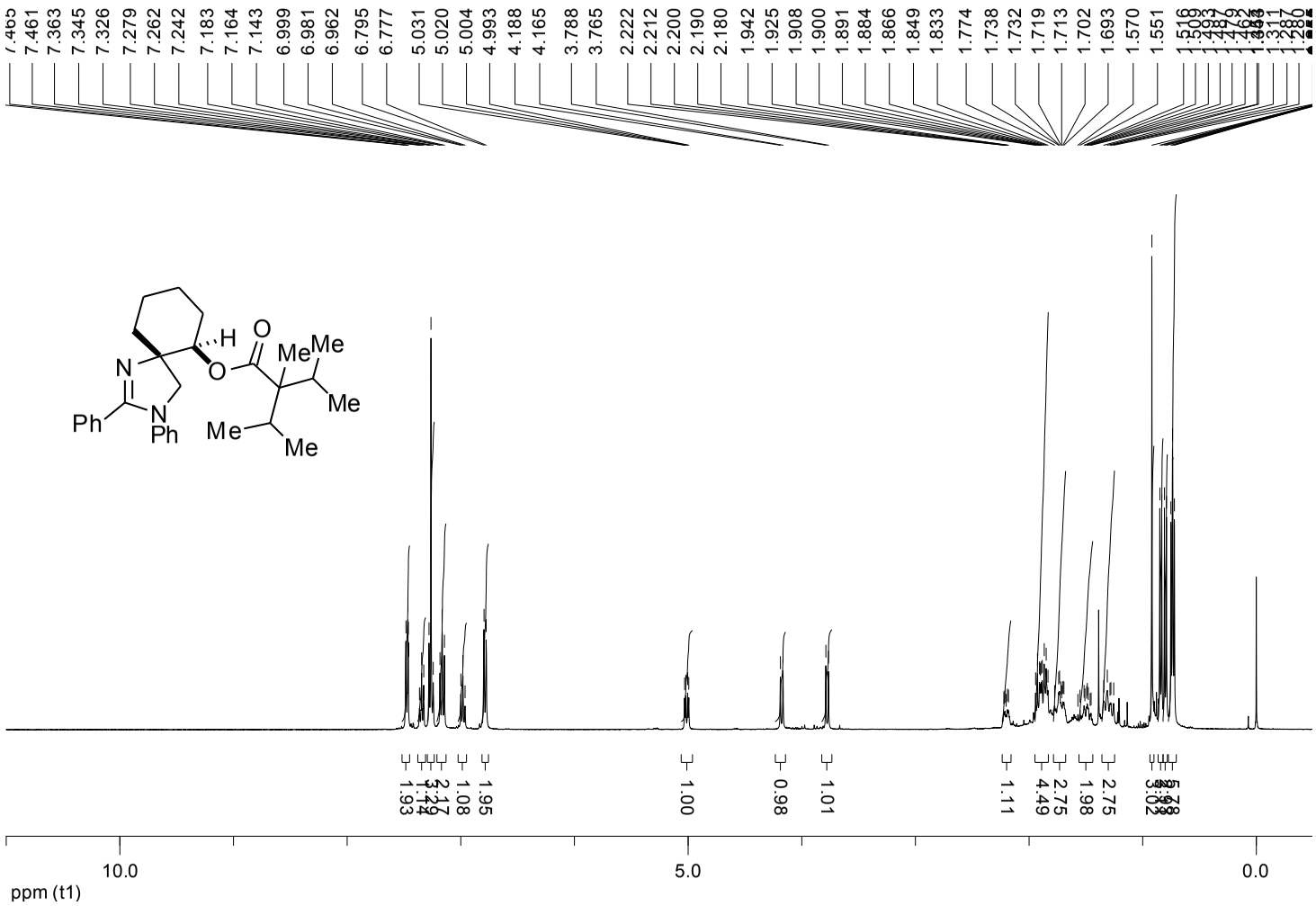
^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)



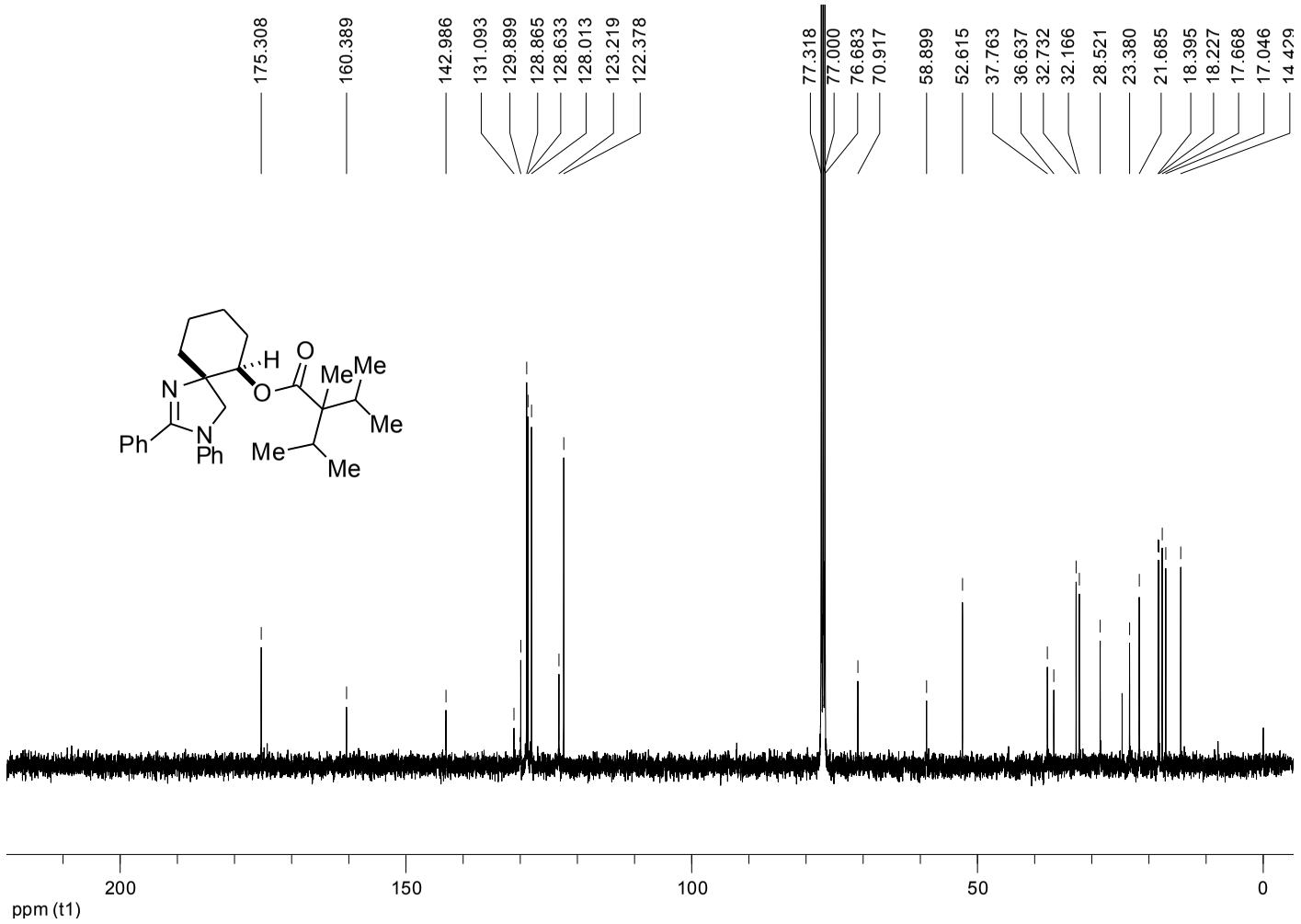
^{19}F NMR spectrum of **2o** (376 MHz, $CDCl_3$)



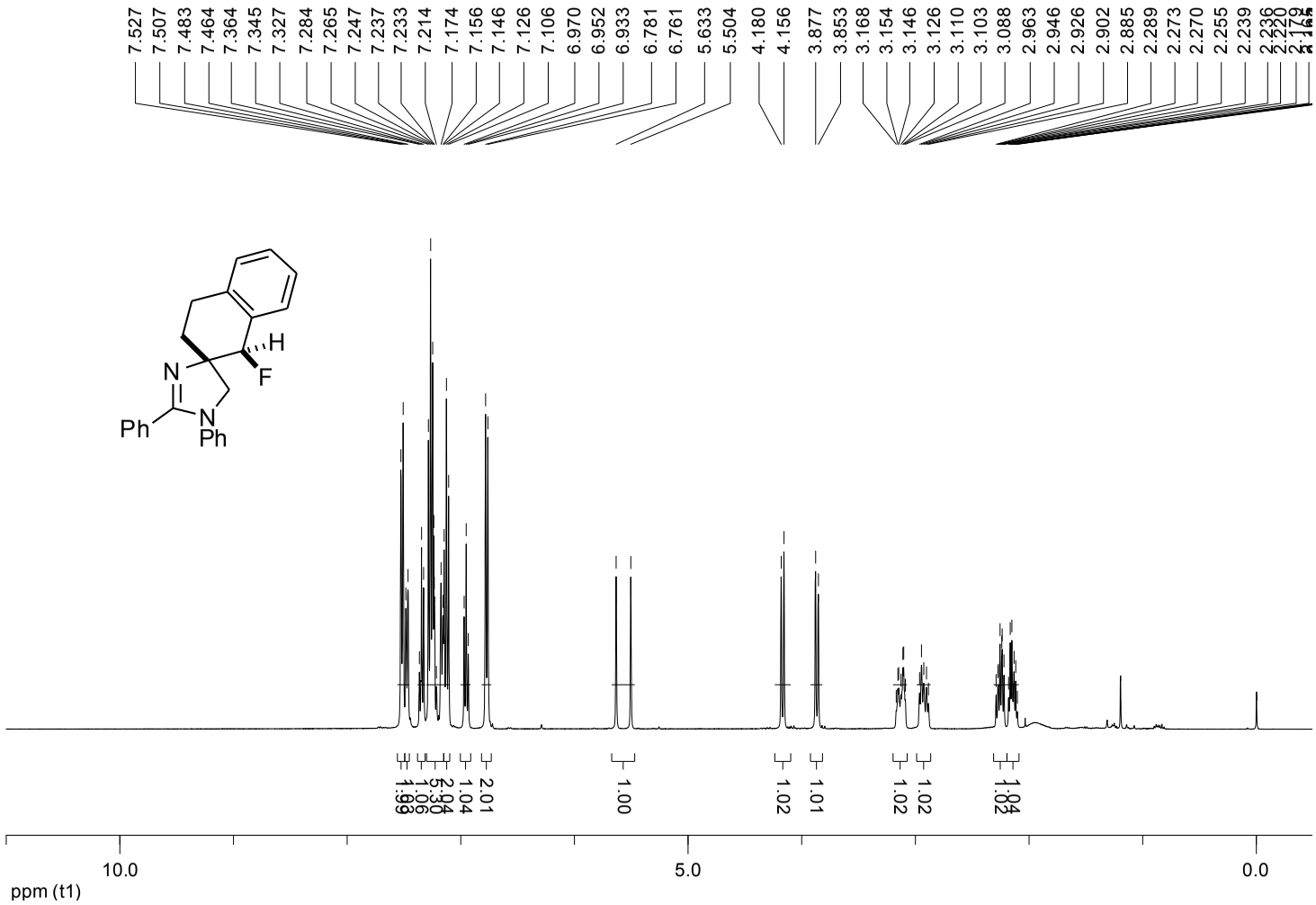
^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$)



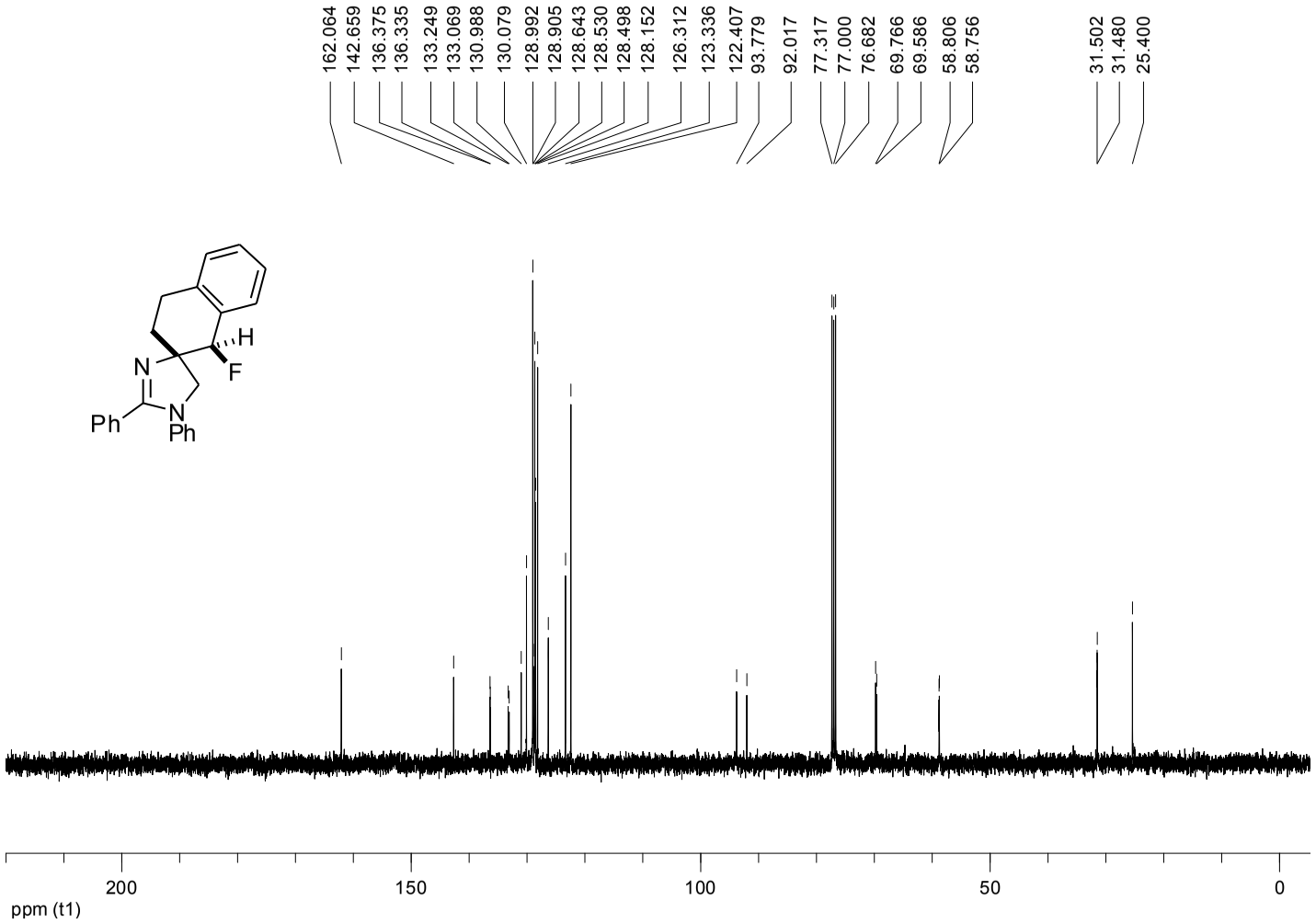
^{13}C NMR spectrum of **5o** (100 MHz, $CDCl_3$)



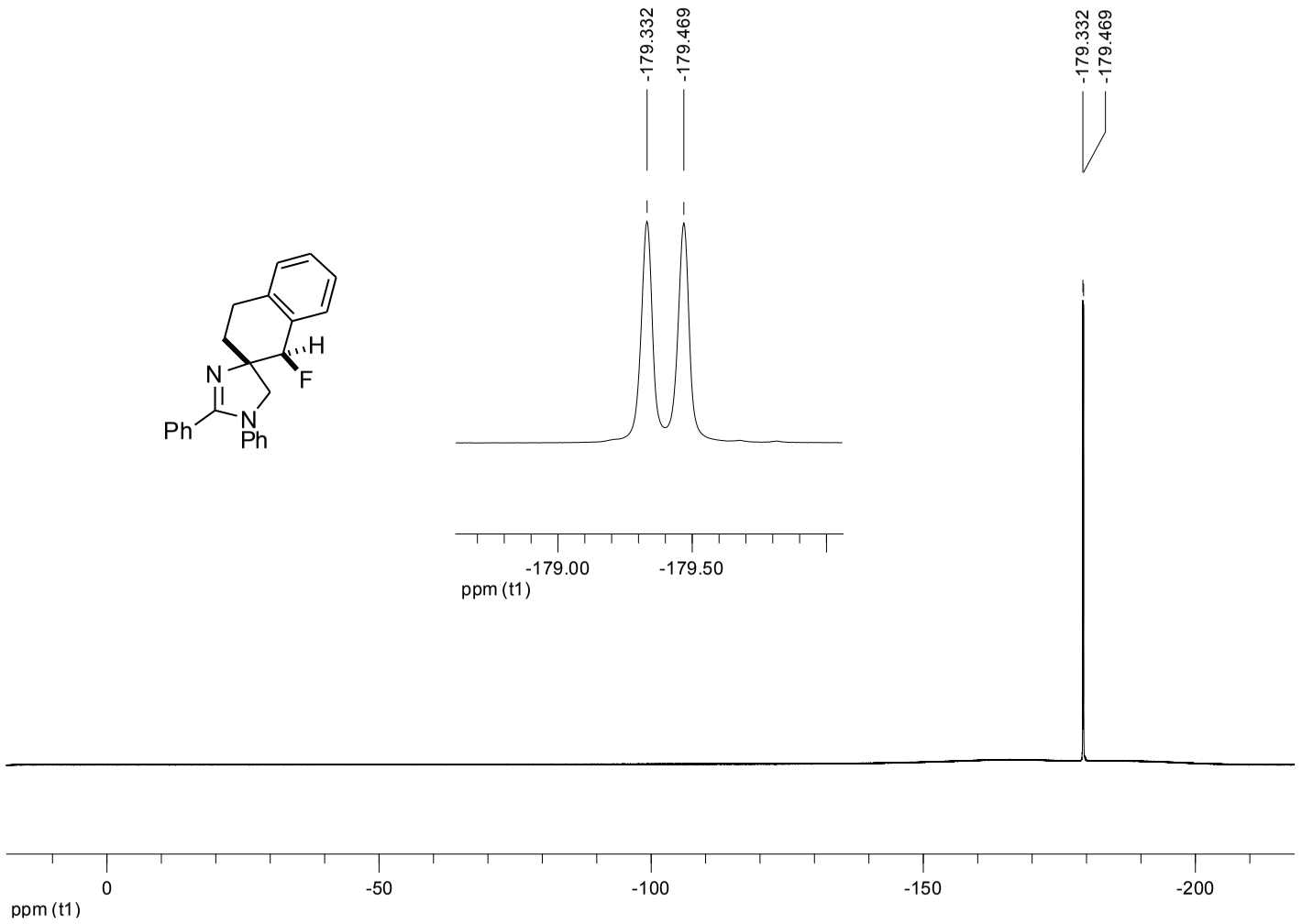
^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)



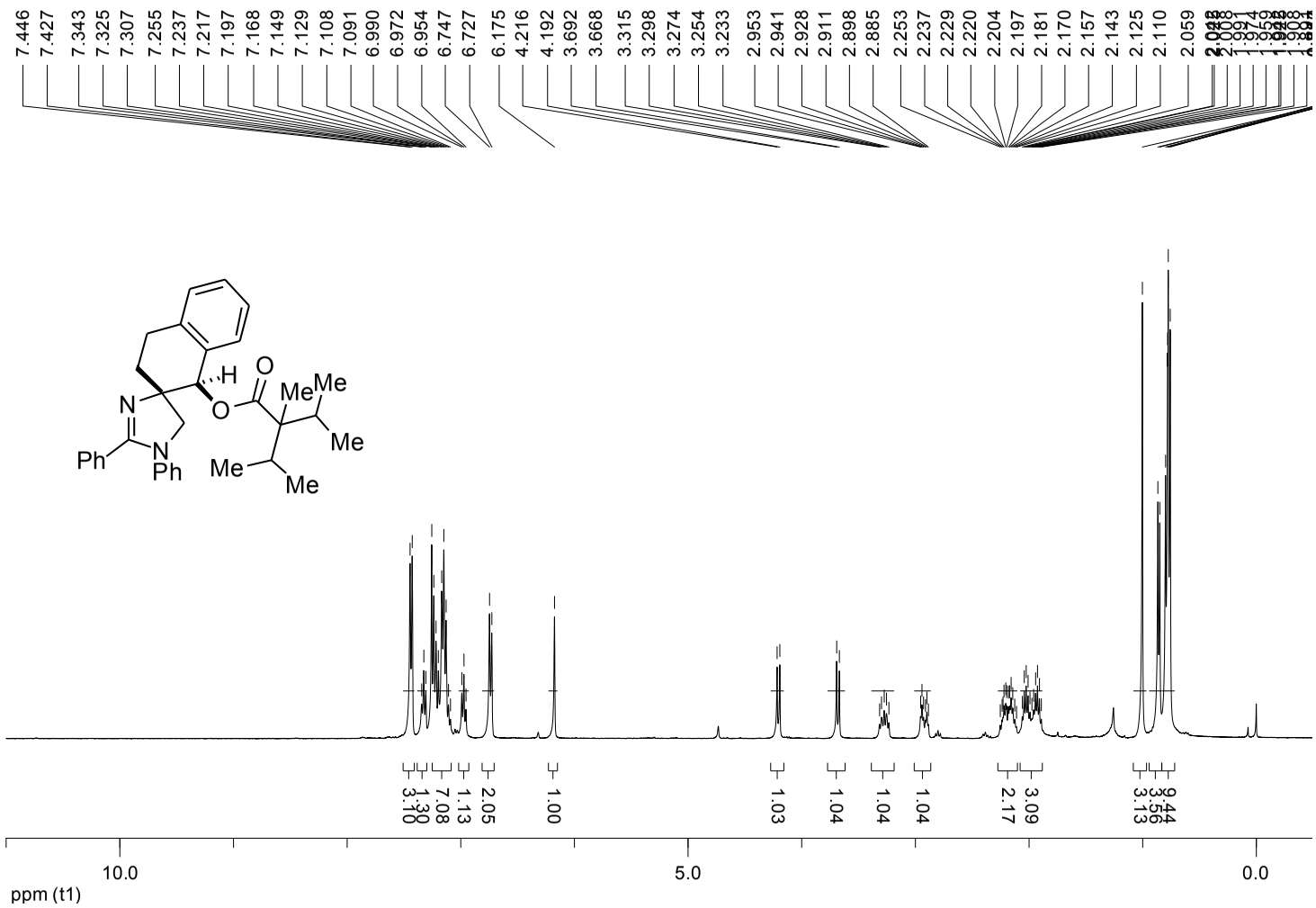
^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)



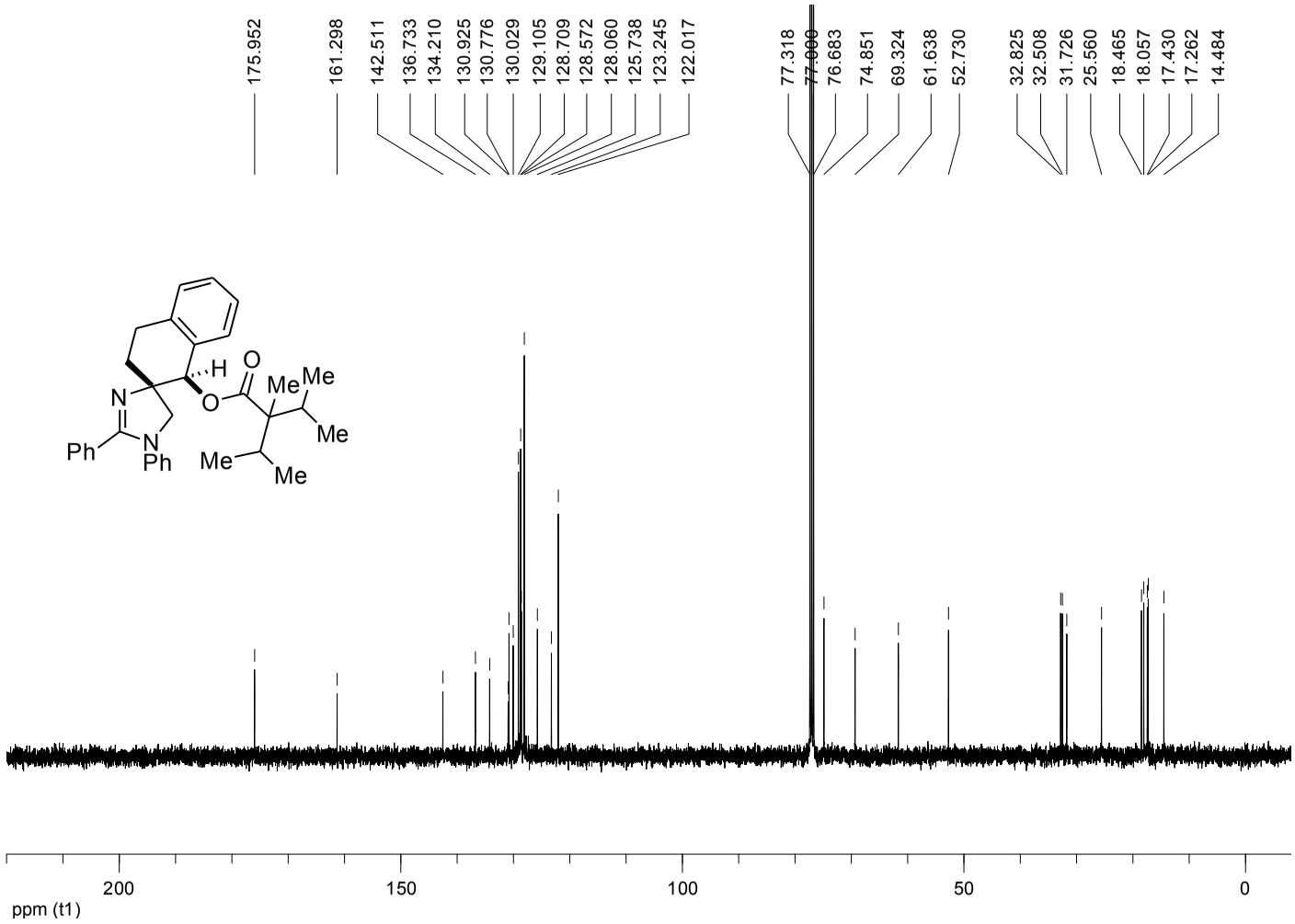
^{19}F NMR spectrum of **2p** (376 MHz, $CDCl_3$)



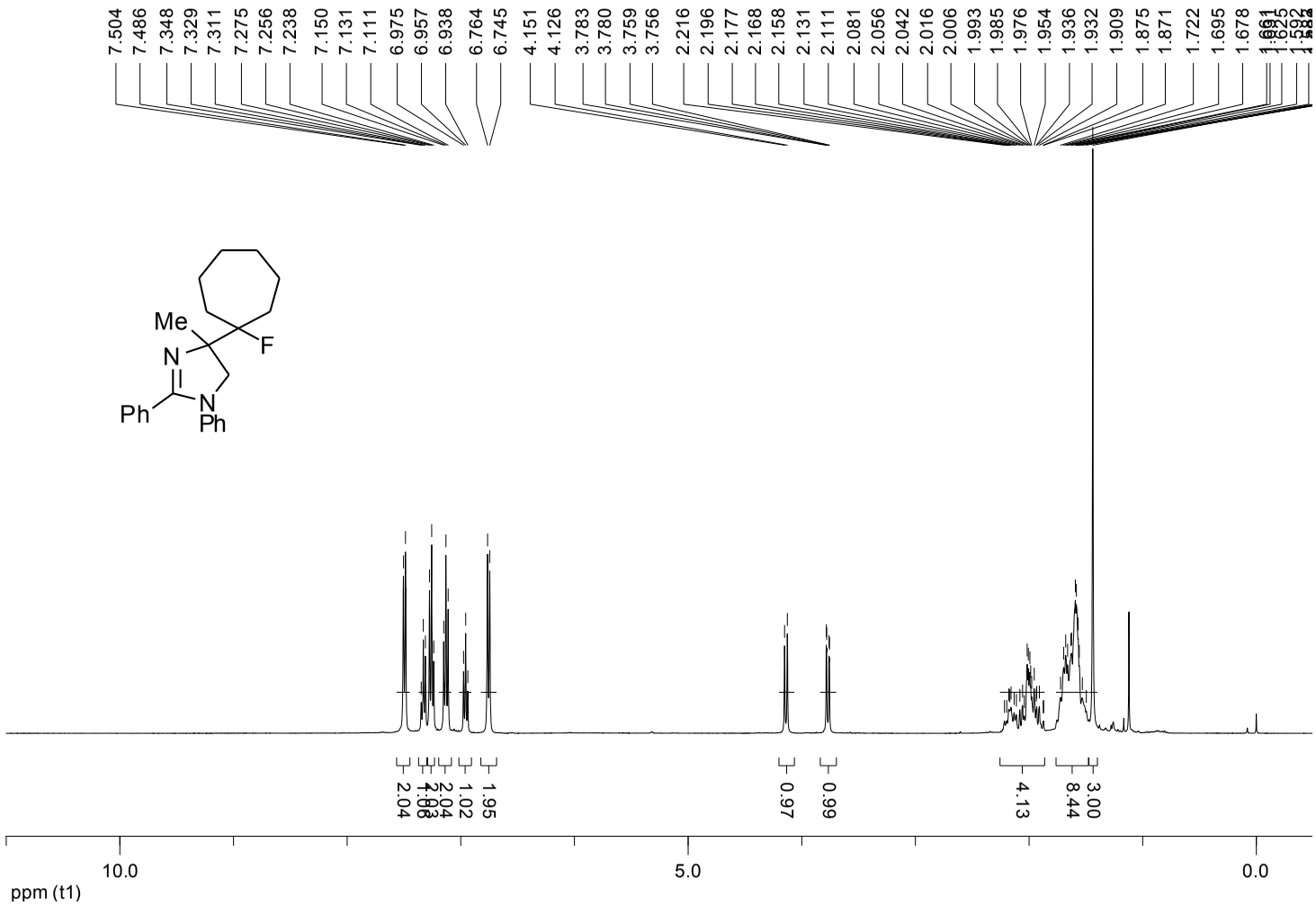
^{1}H NMR spectrum of **5p** (400 MHz, $CDCl_3$)



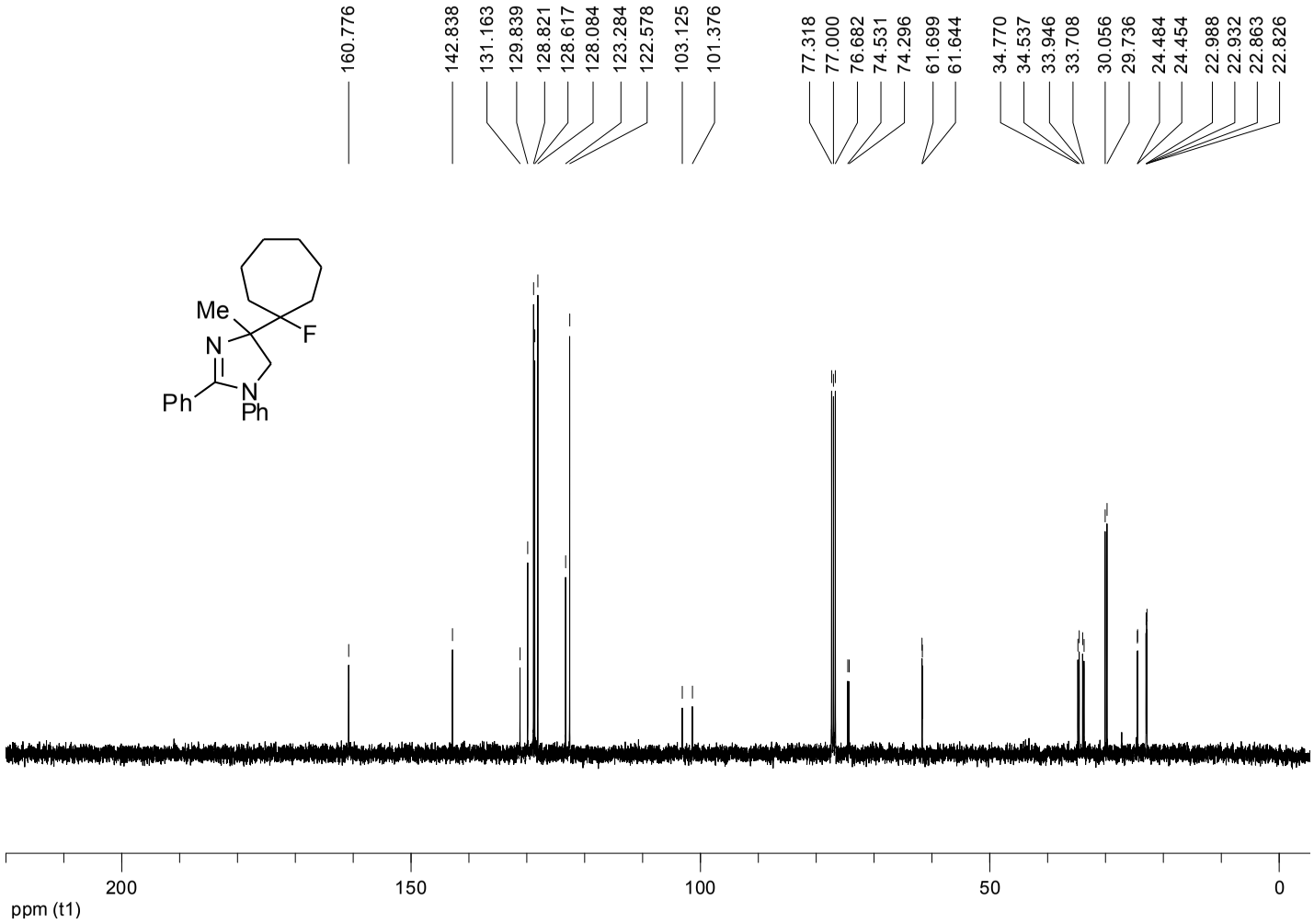
^{13}C NMR spectrum of **5p** (100 MHz, $CDCl_3$)



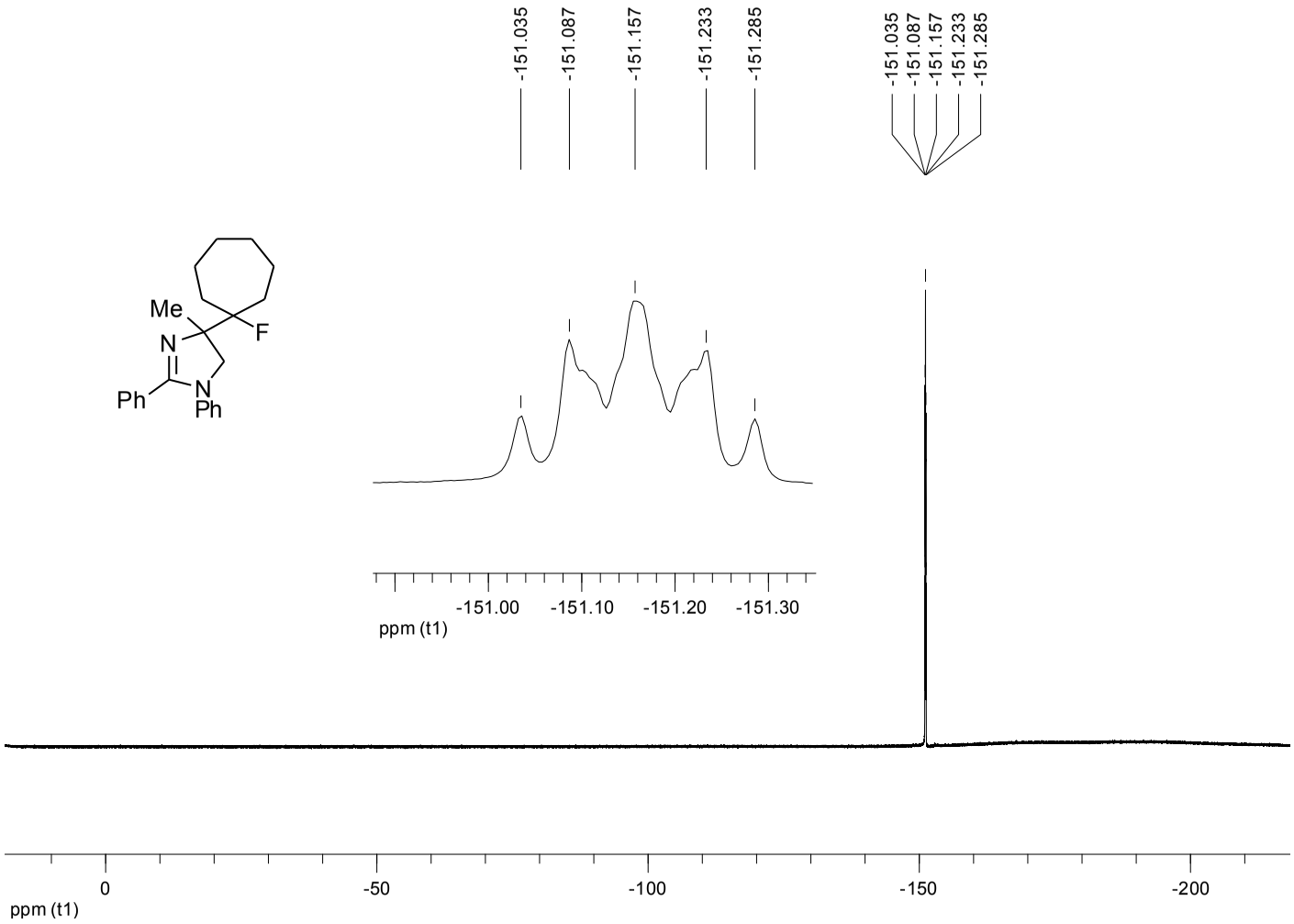
^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)



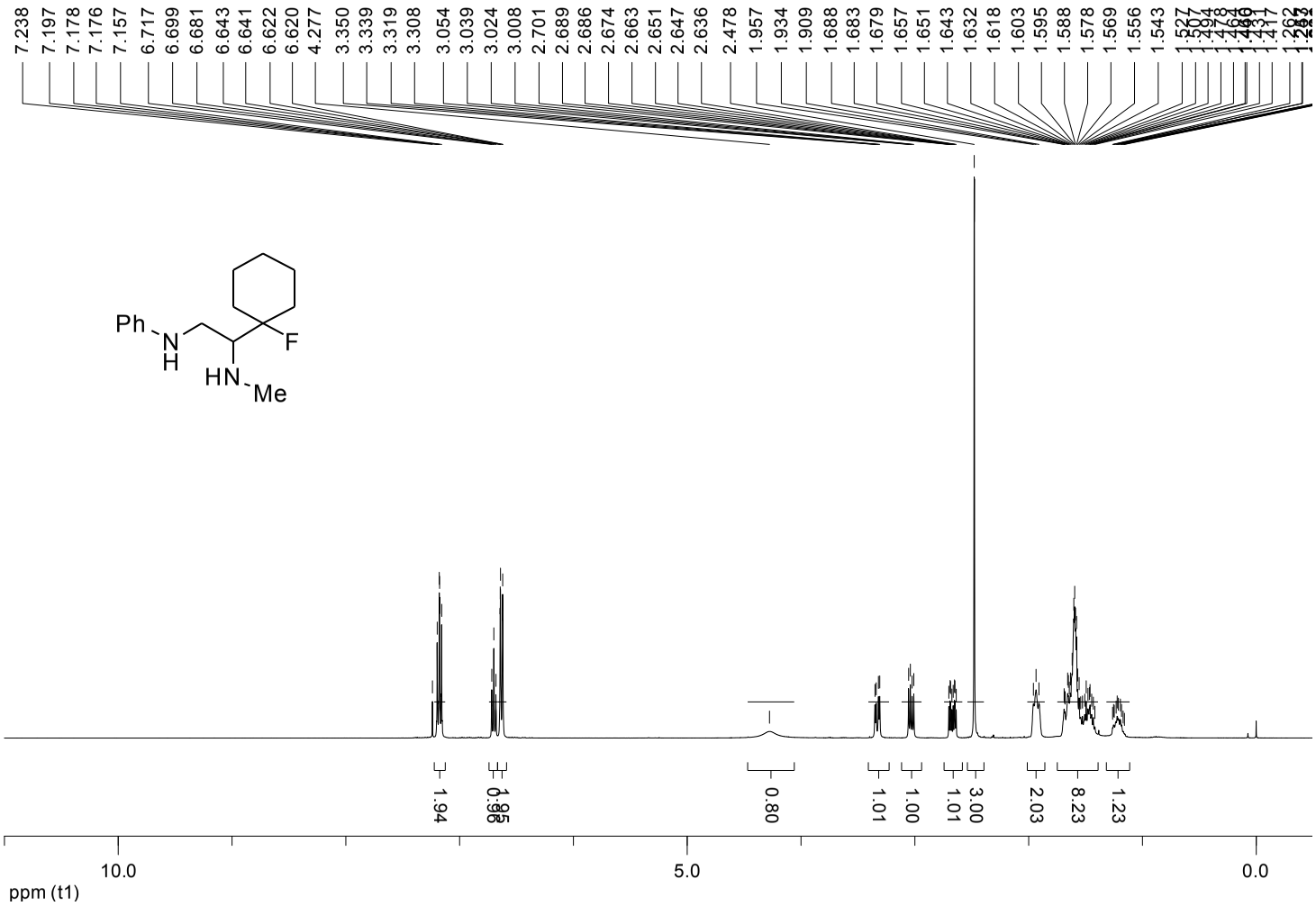
^{13}C NMR spectrum of **2q** (100 MHz, $CDCl_3$)



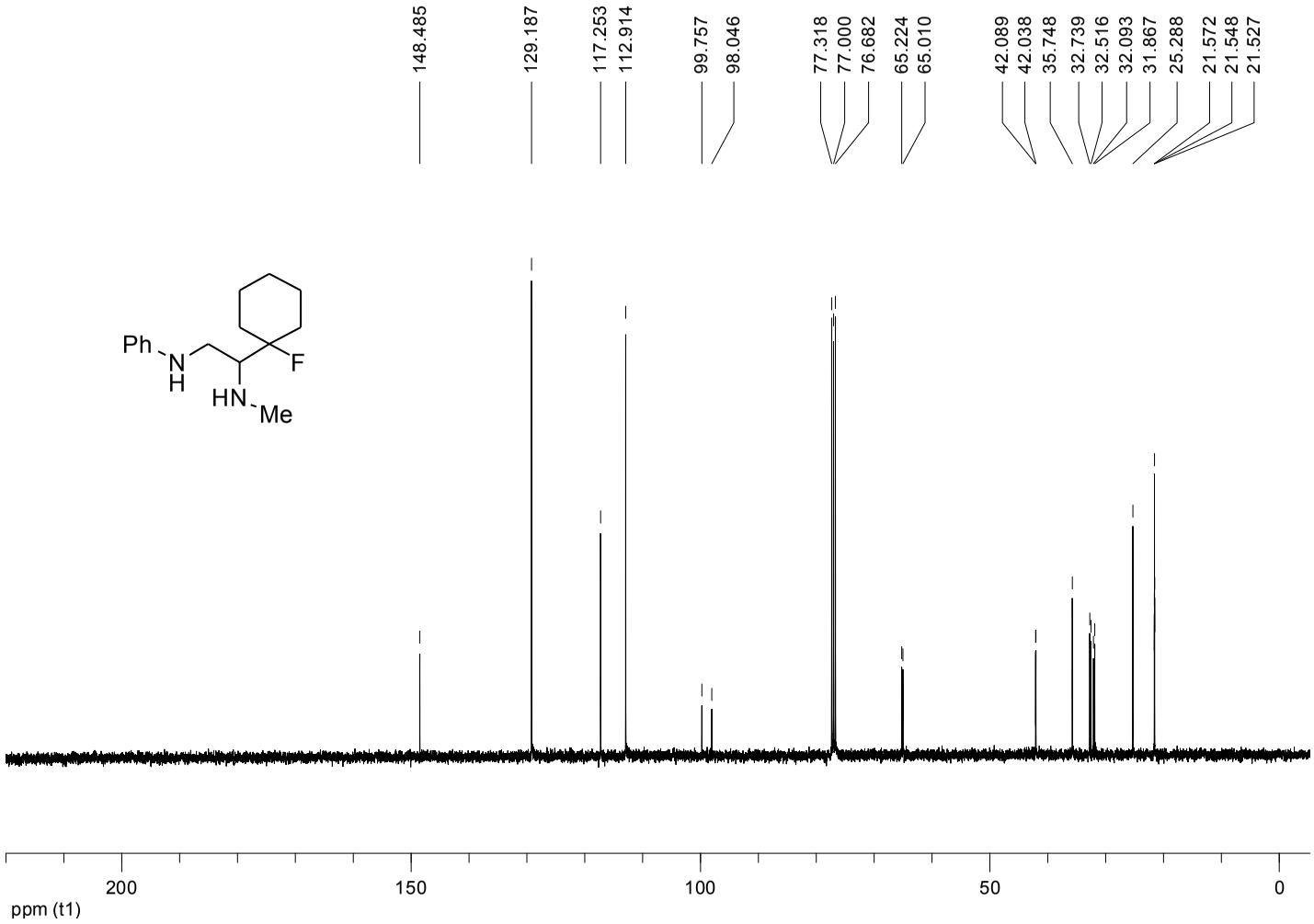
^{19}F NMR spectrum of **2q** (376 MHz, $CDCl_3$)



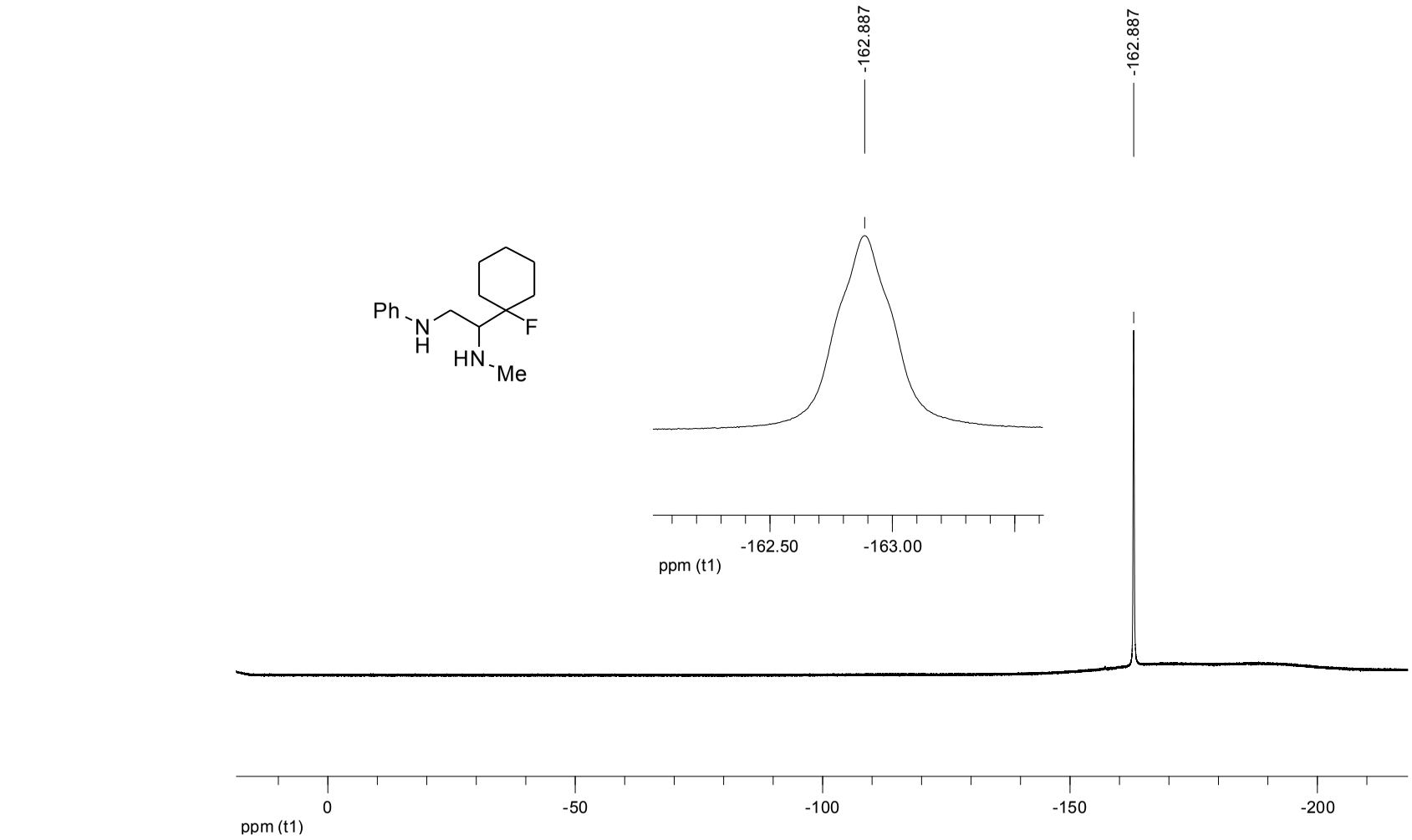
^{1}H NMR spectrum of **6j** (400 MHz, $CDCl_3$)



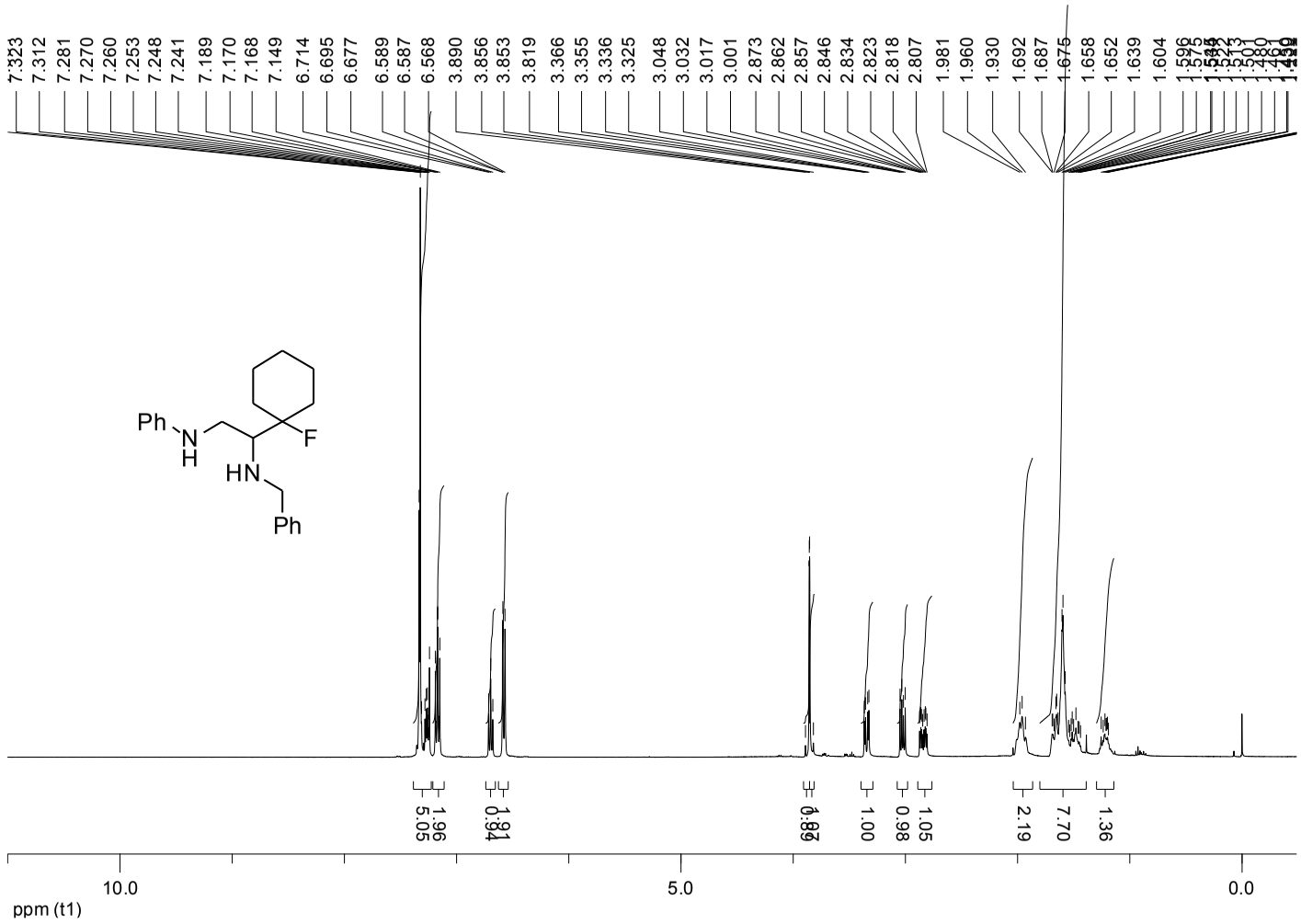
^{13}C NMR spectrum of **6j** (100 MHz, $CDCl_3$)



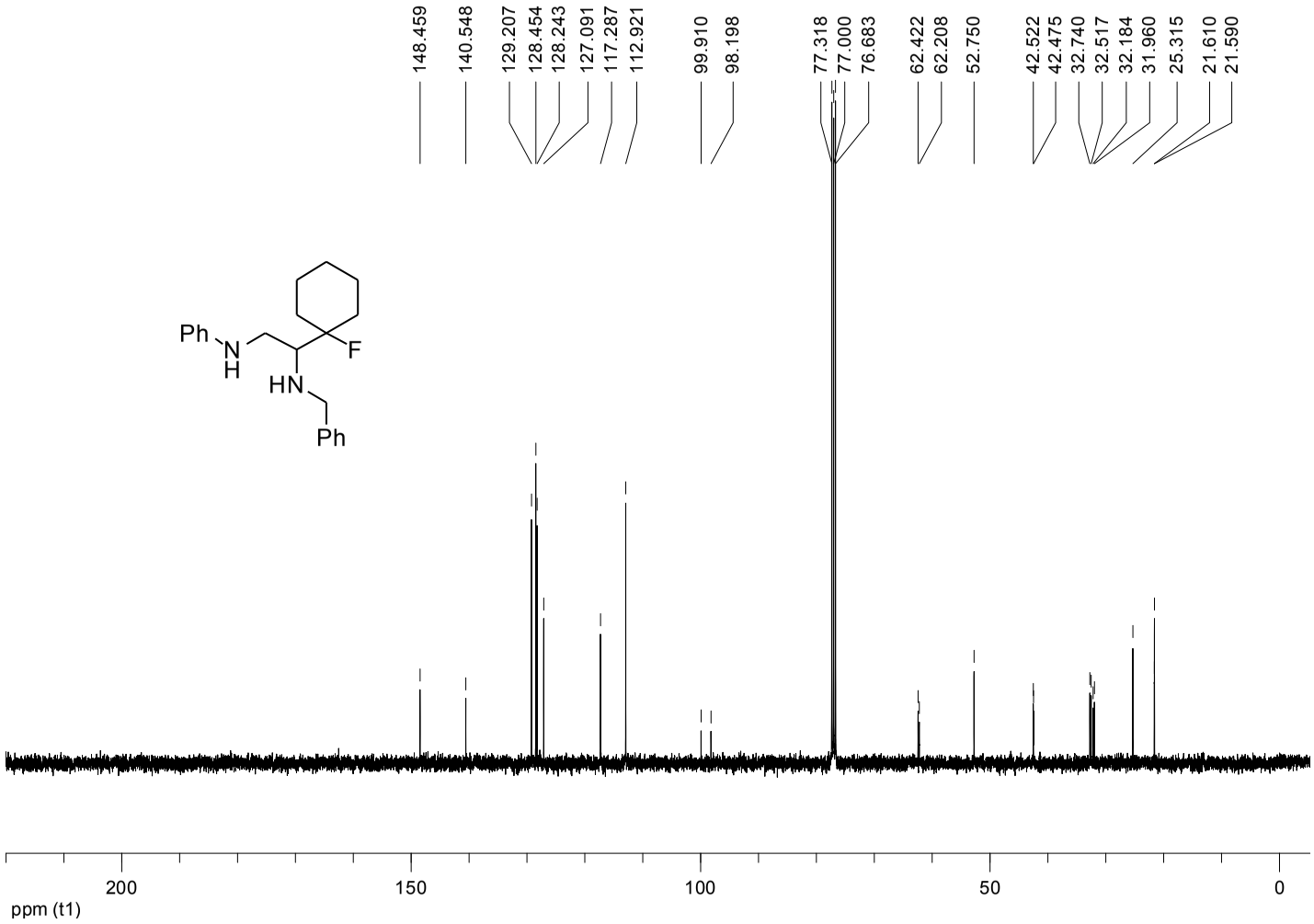
^{19}F NMR spectrum of **6j** (376 MHz, $CDCl_3$)



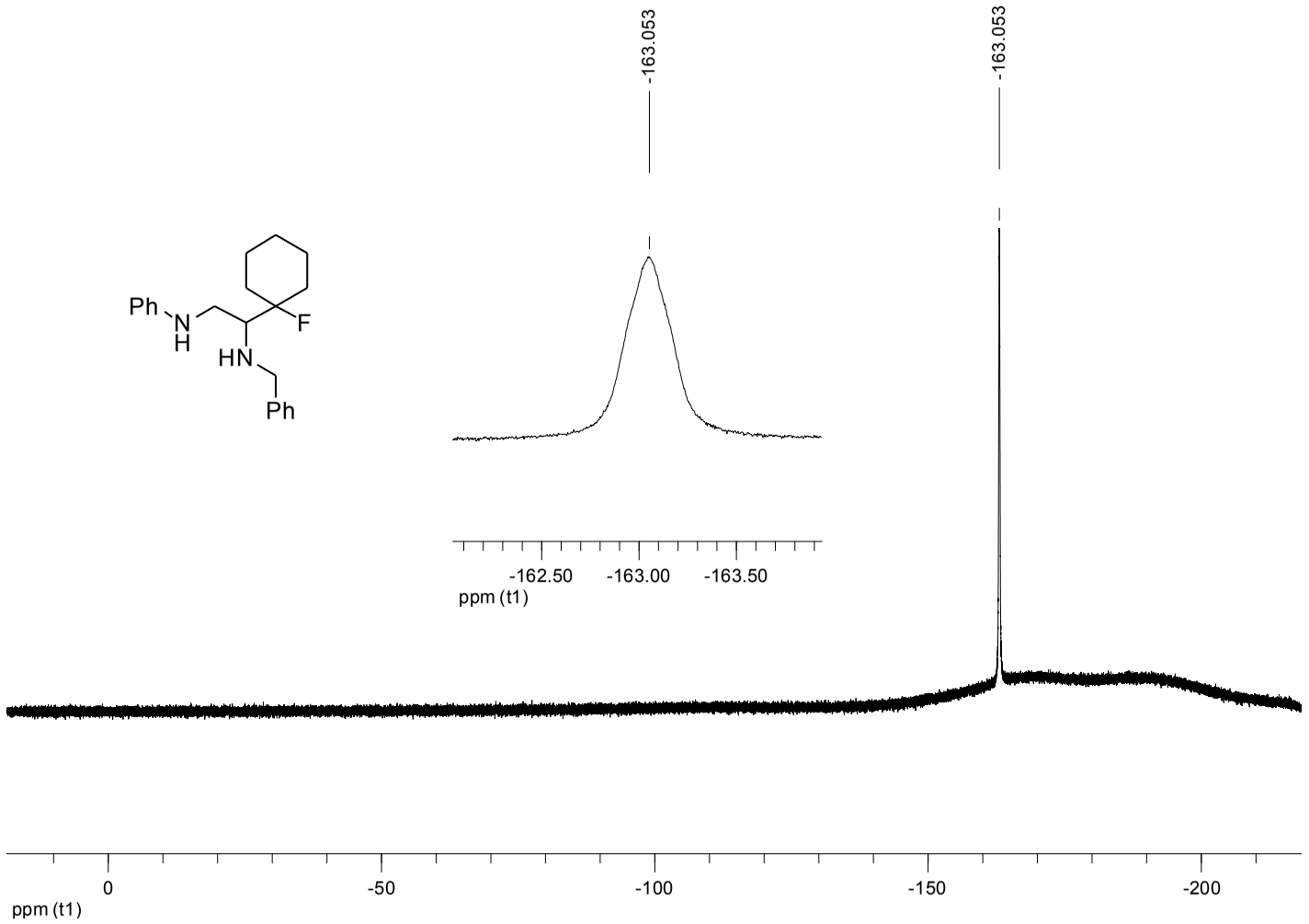
^{1}H NMR spectrum of **7j** (400 MHz, $CDCl_3$)



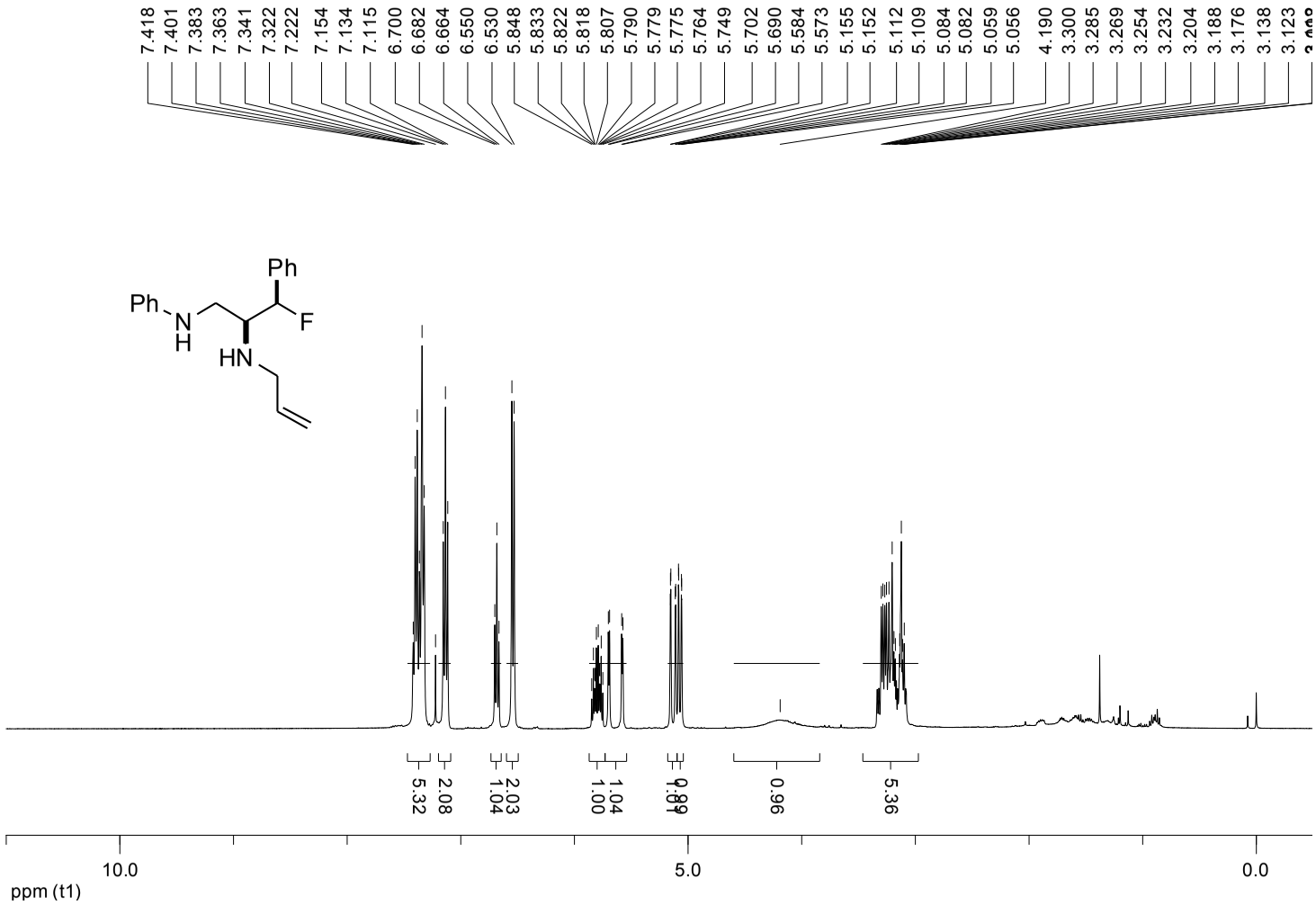
^{13}C NMR spectrum of **7j** (100 MHz, $CDCl_3$)



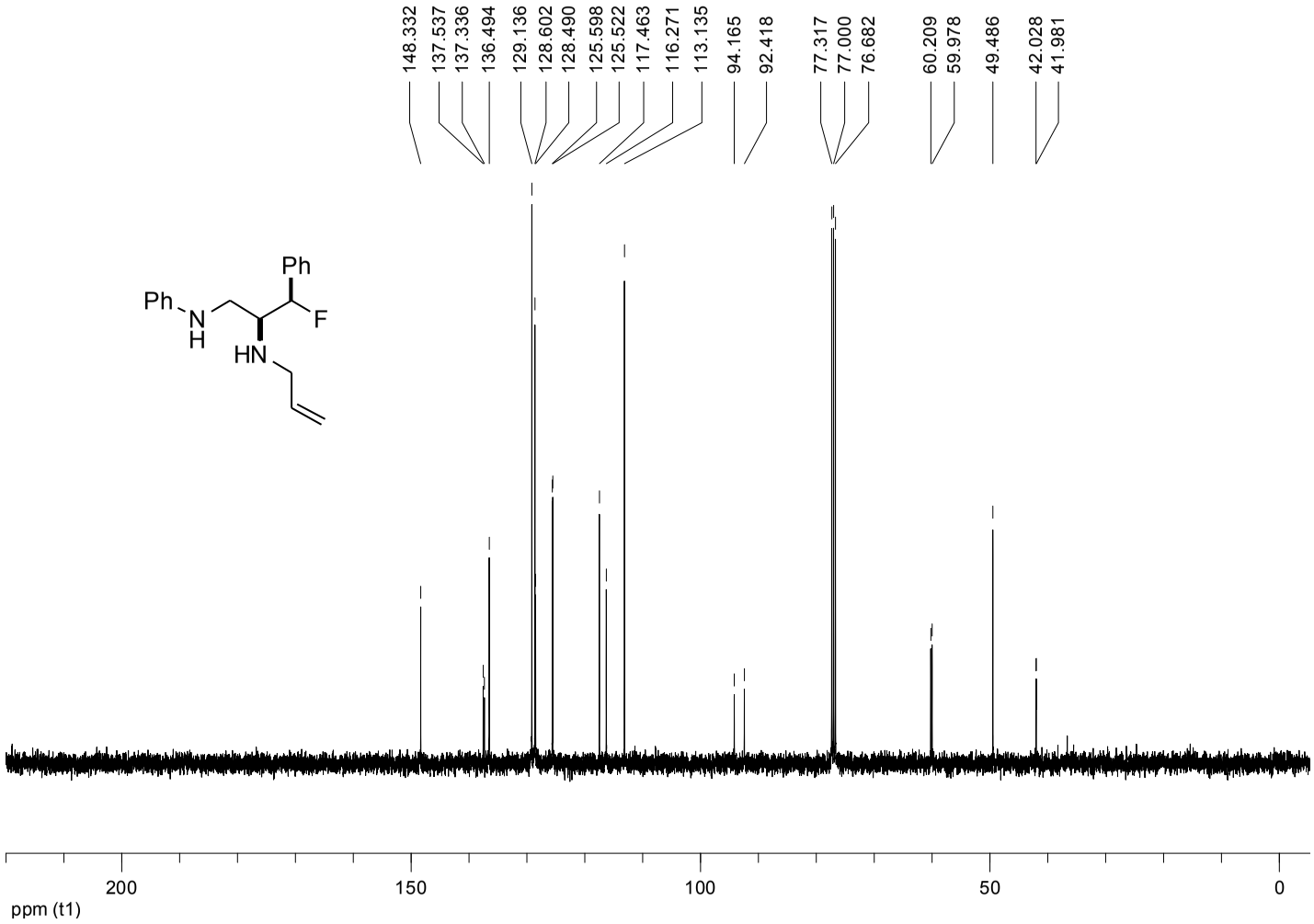
^{19}F NMR spectrum of **7j** (376 MHz, $CDCl_3$)



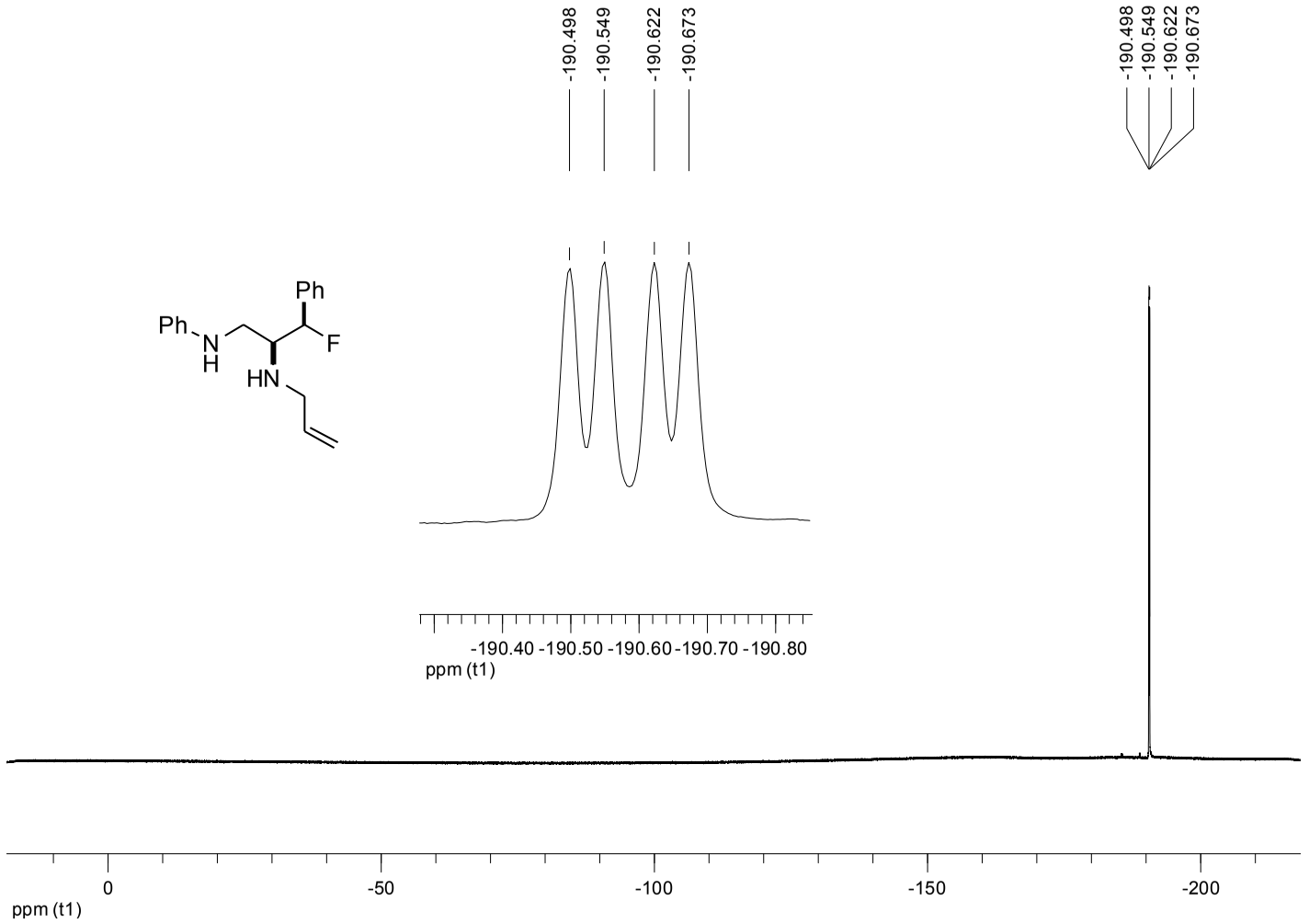
^{1}H NMR spectrum of **8a** (400 MHz, $CDCl_3$)



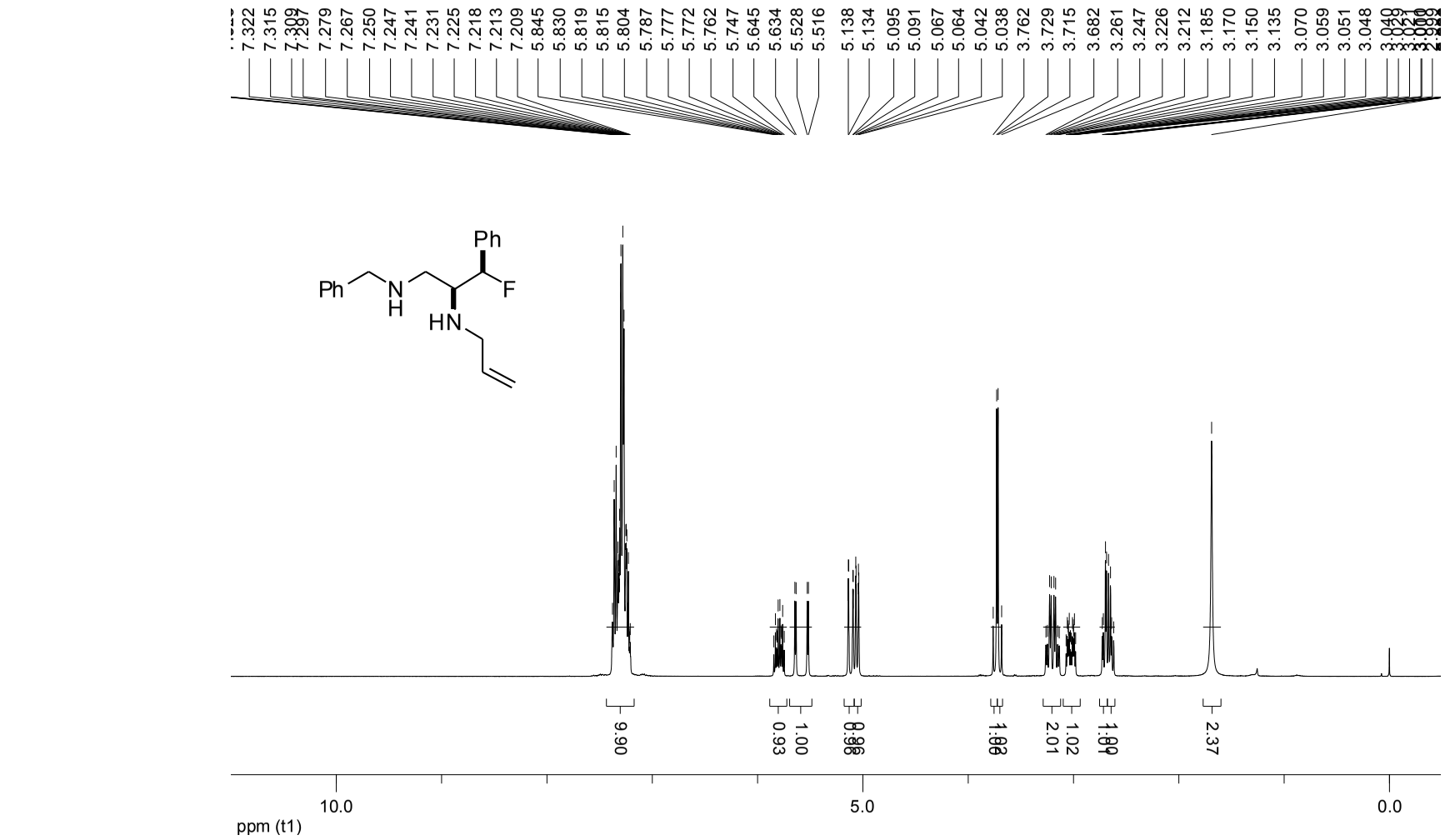
^{13}C NMR spectrum of **8a** (100 MHz, $CDCl_3$)



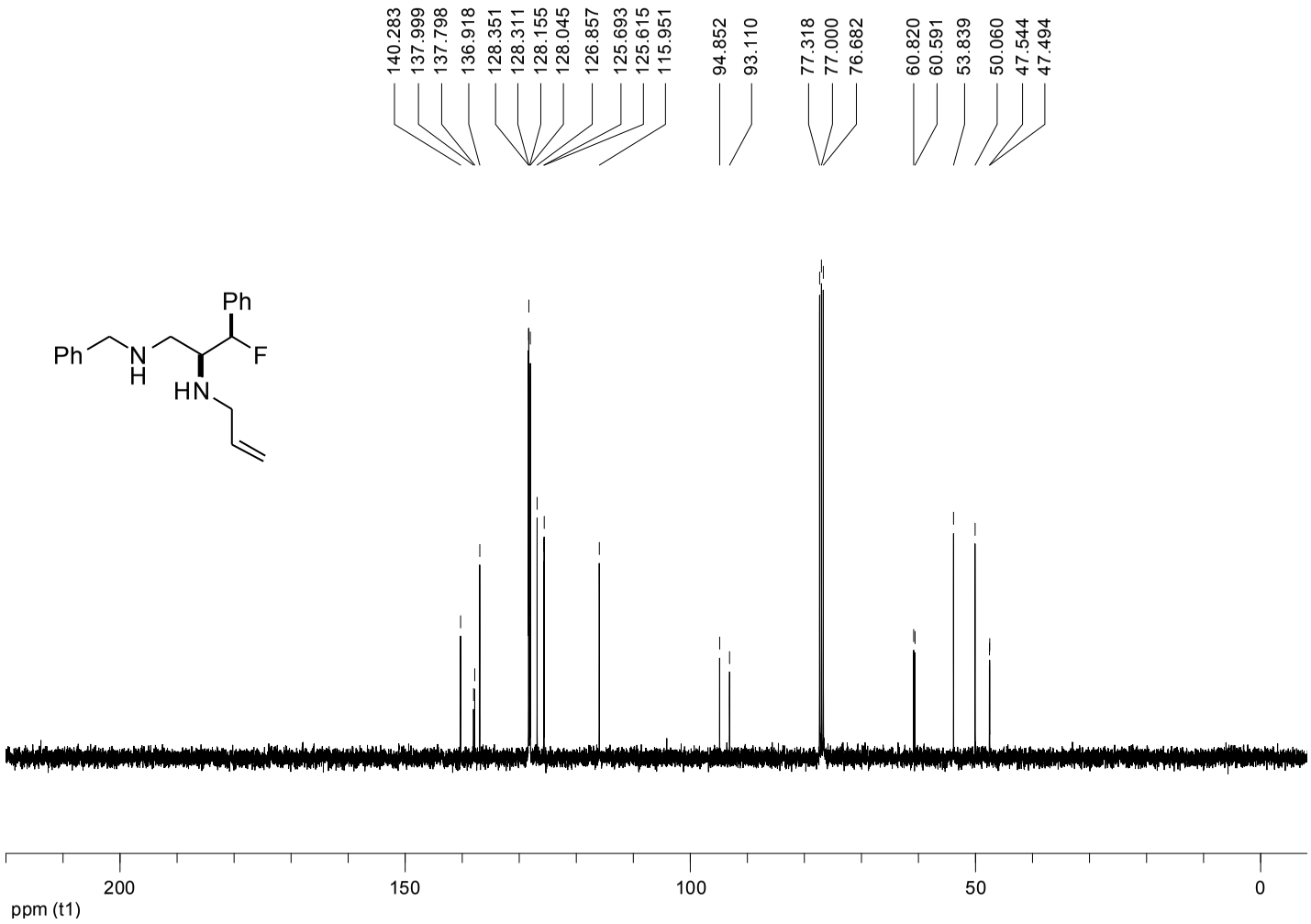
^{19}F NMR spectrum of **8a** (376 MHz, $CDCl_3$)



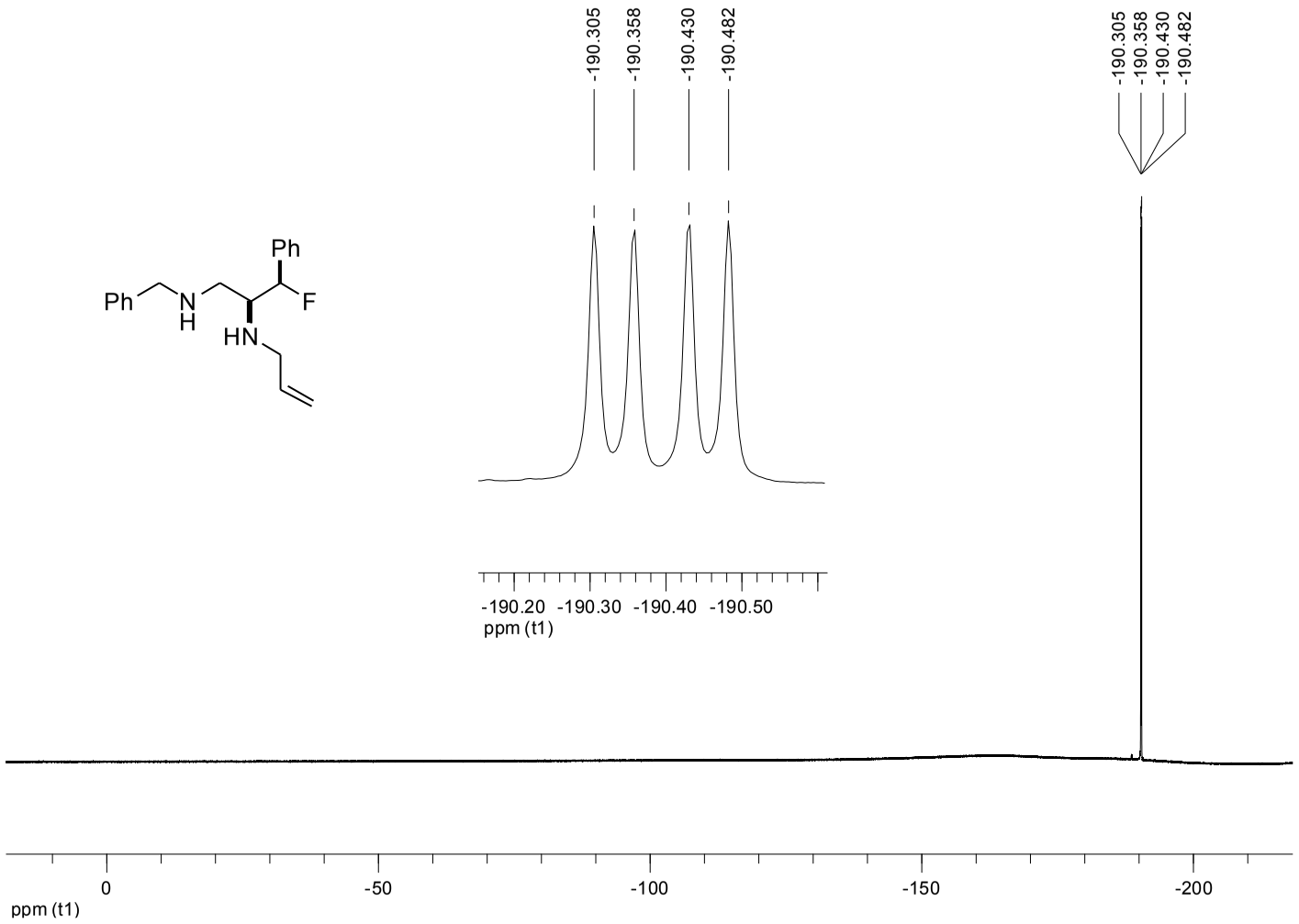
^{1}H NMR spectrum of **8b** (400 MHz, $CDCl_3$)



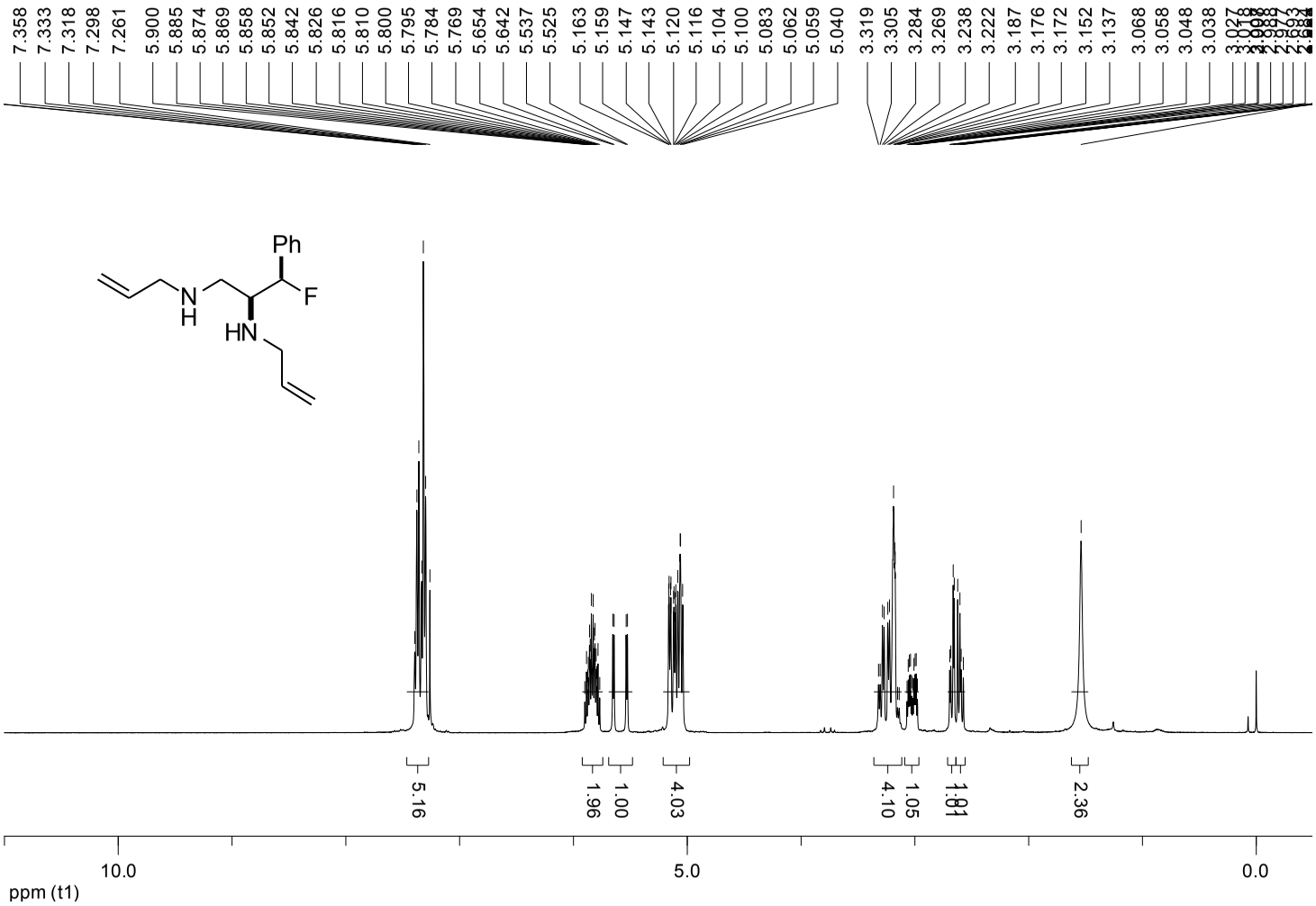
^{13}C NMR spectrum of **8b** (100 MHz, $CDCl_3$)



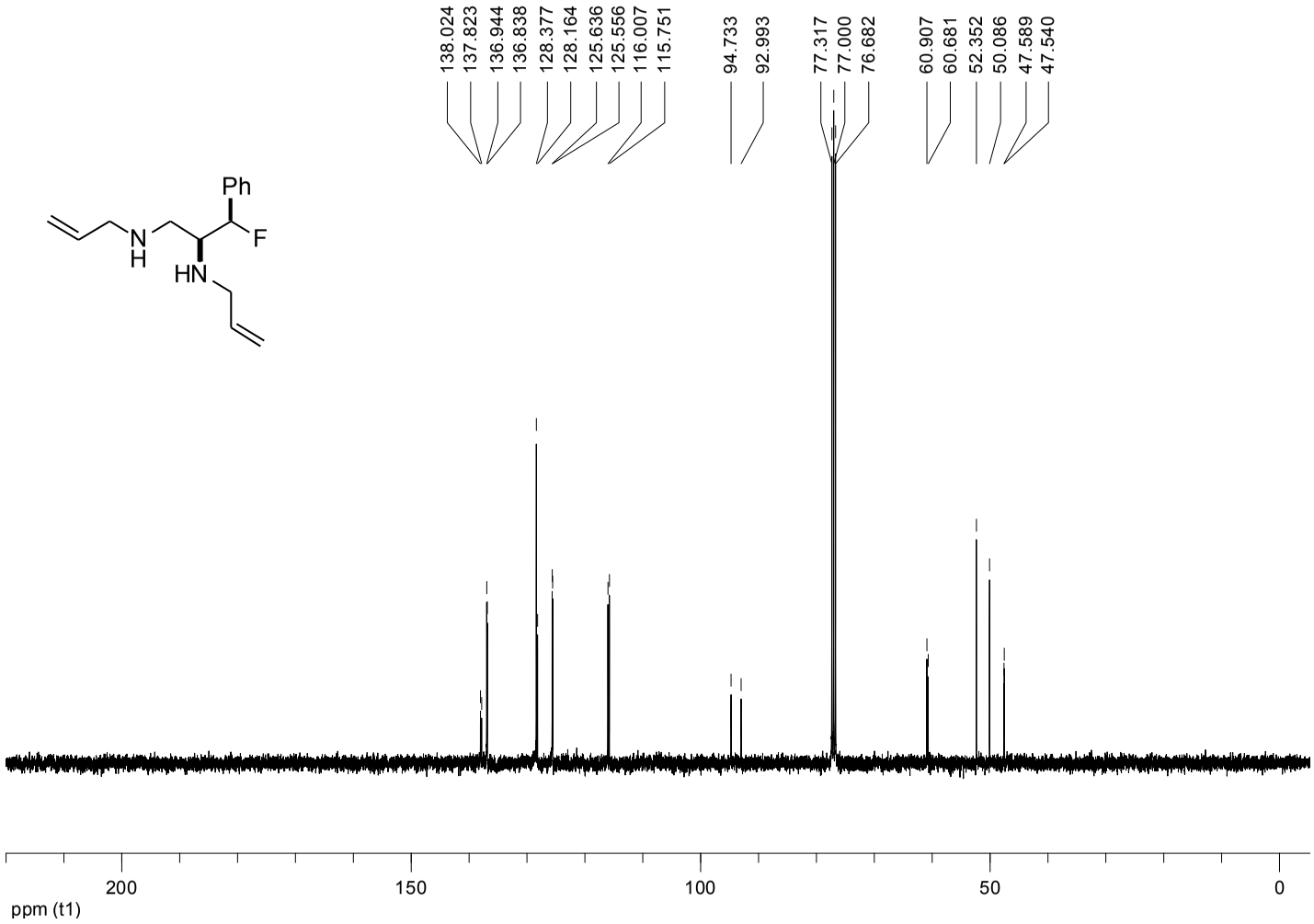
^{19}F NMR spectrum of **8b** (376 MHz, $CDCl_3$)



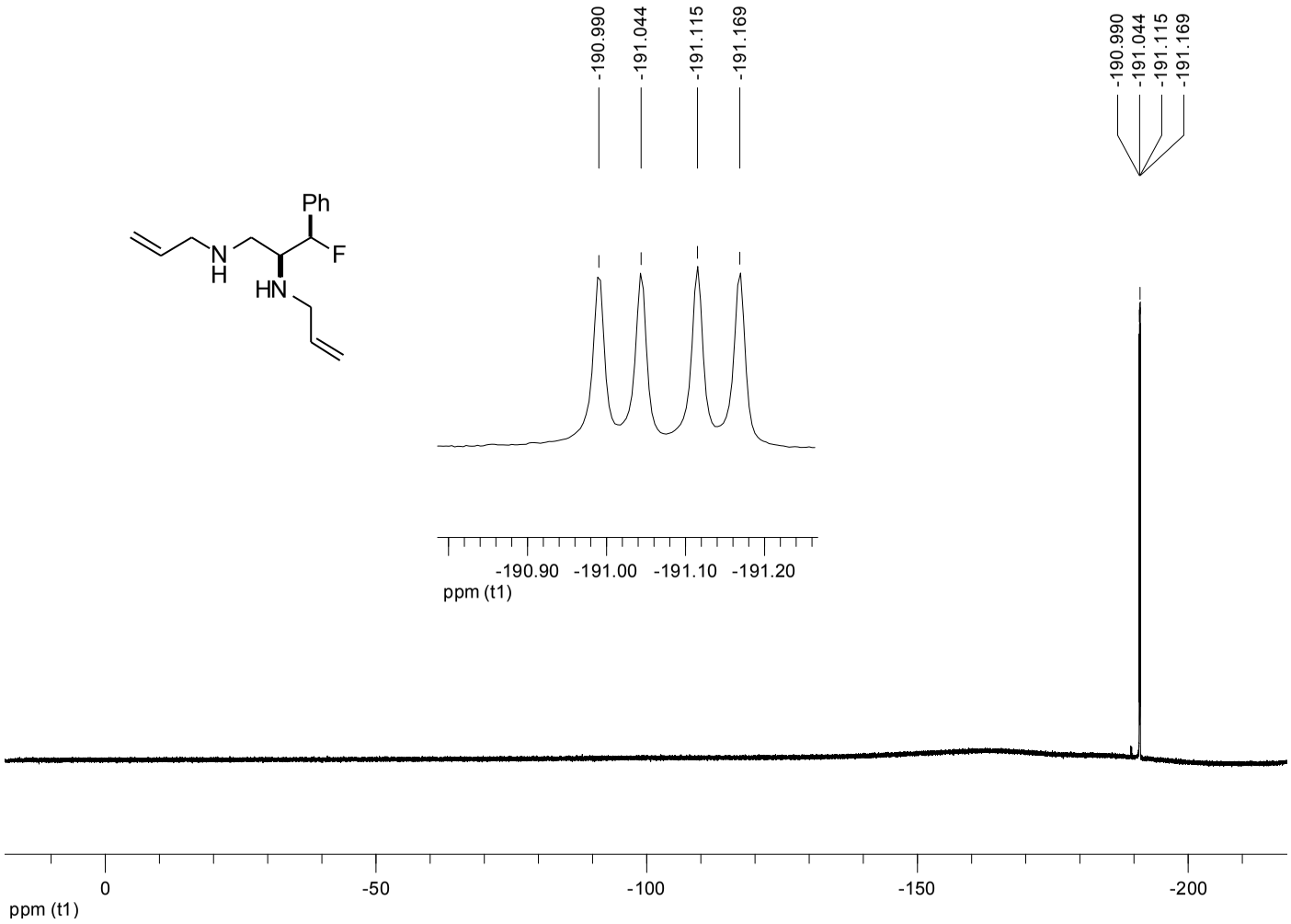
^{1}H NMR spectrum of **8c** (400 MHz, $CDCl_3$)



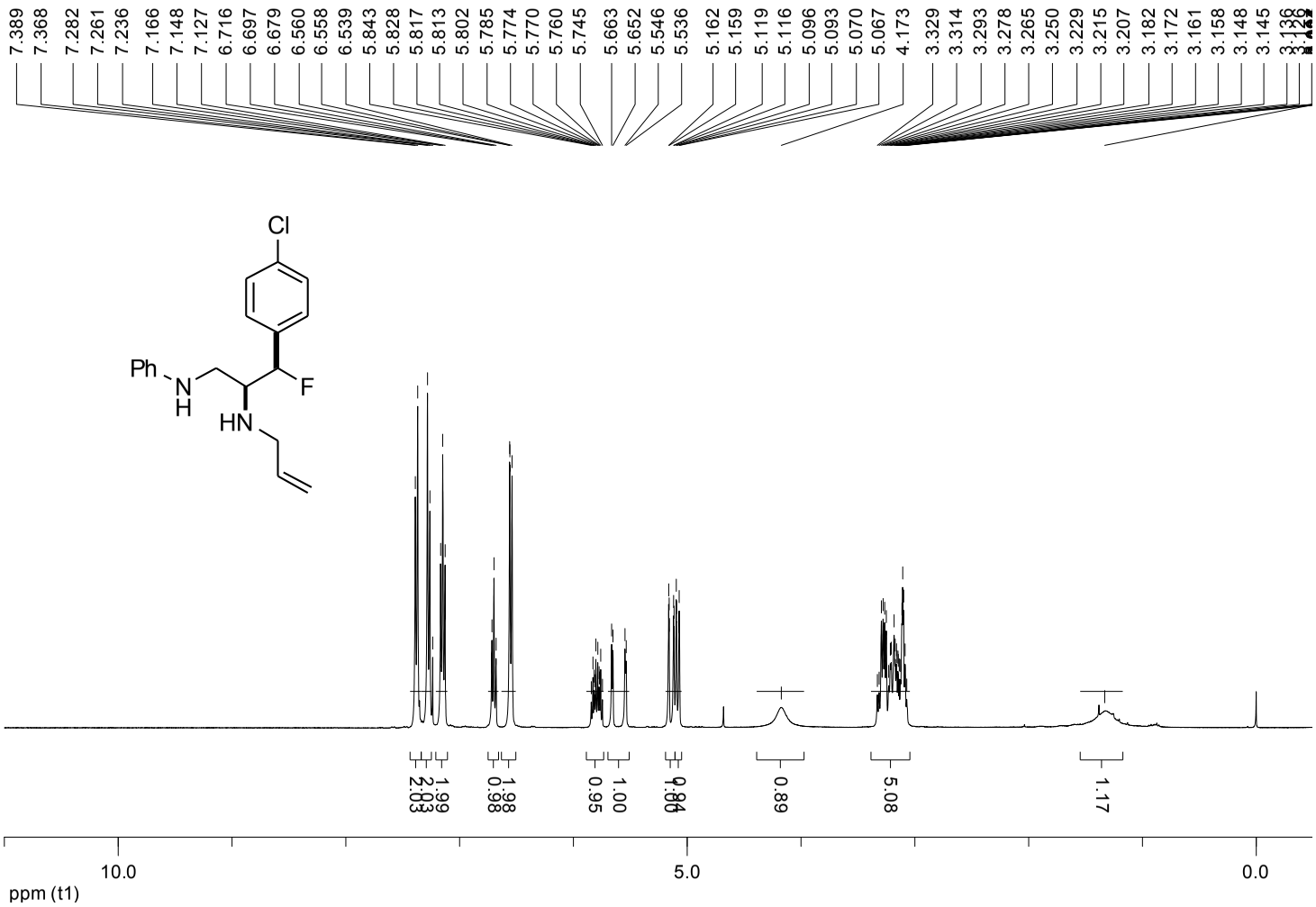
^{13}C NMR spectrum of **8c** (100 MHz, $CDCl_3$)



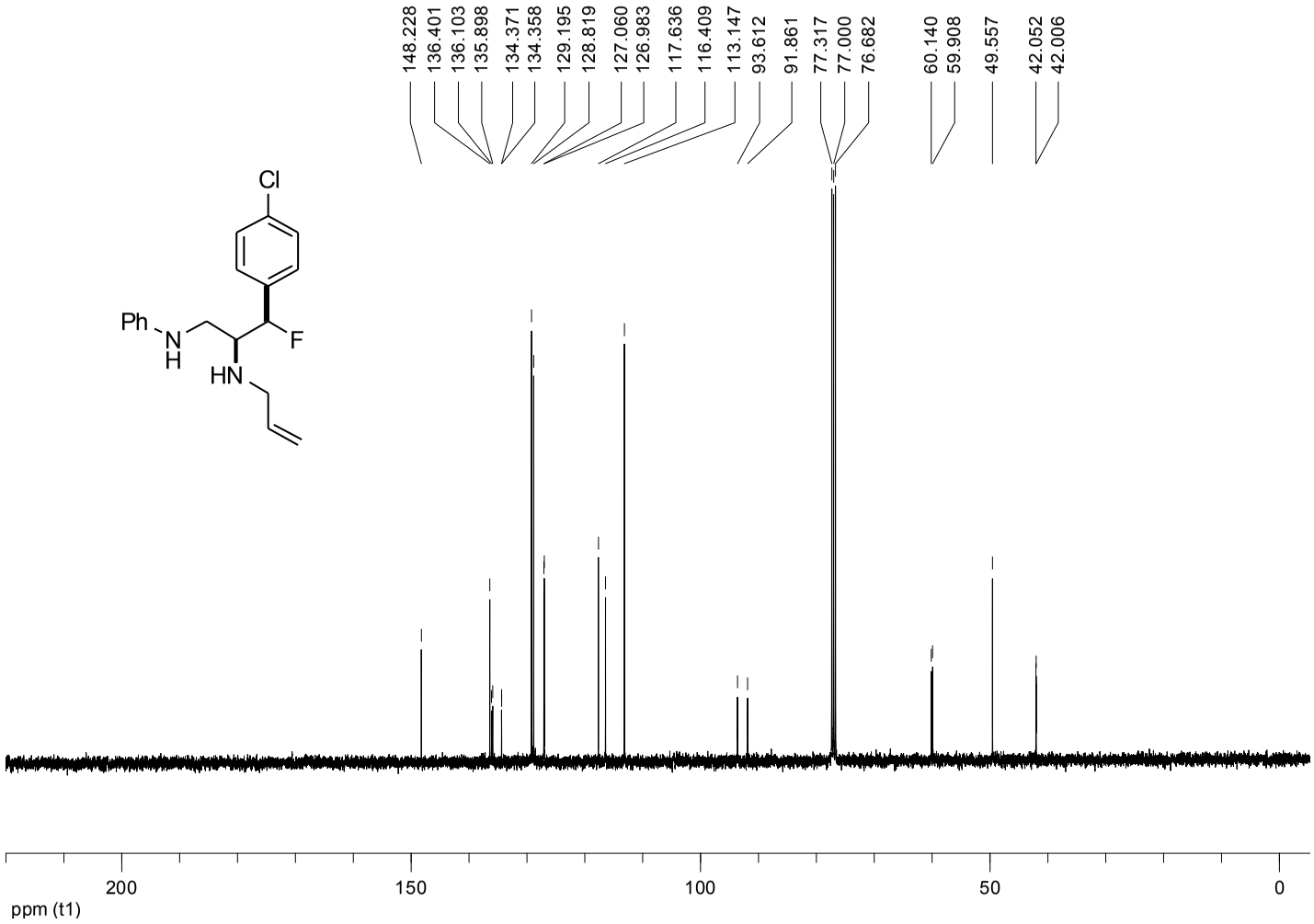
^{19}F NMR spectrum of **8c** (376 MHz, $CDCl_3$)



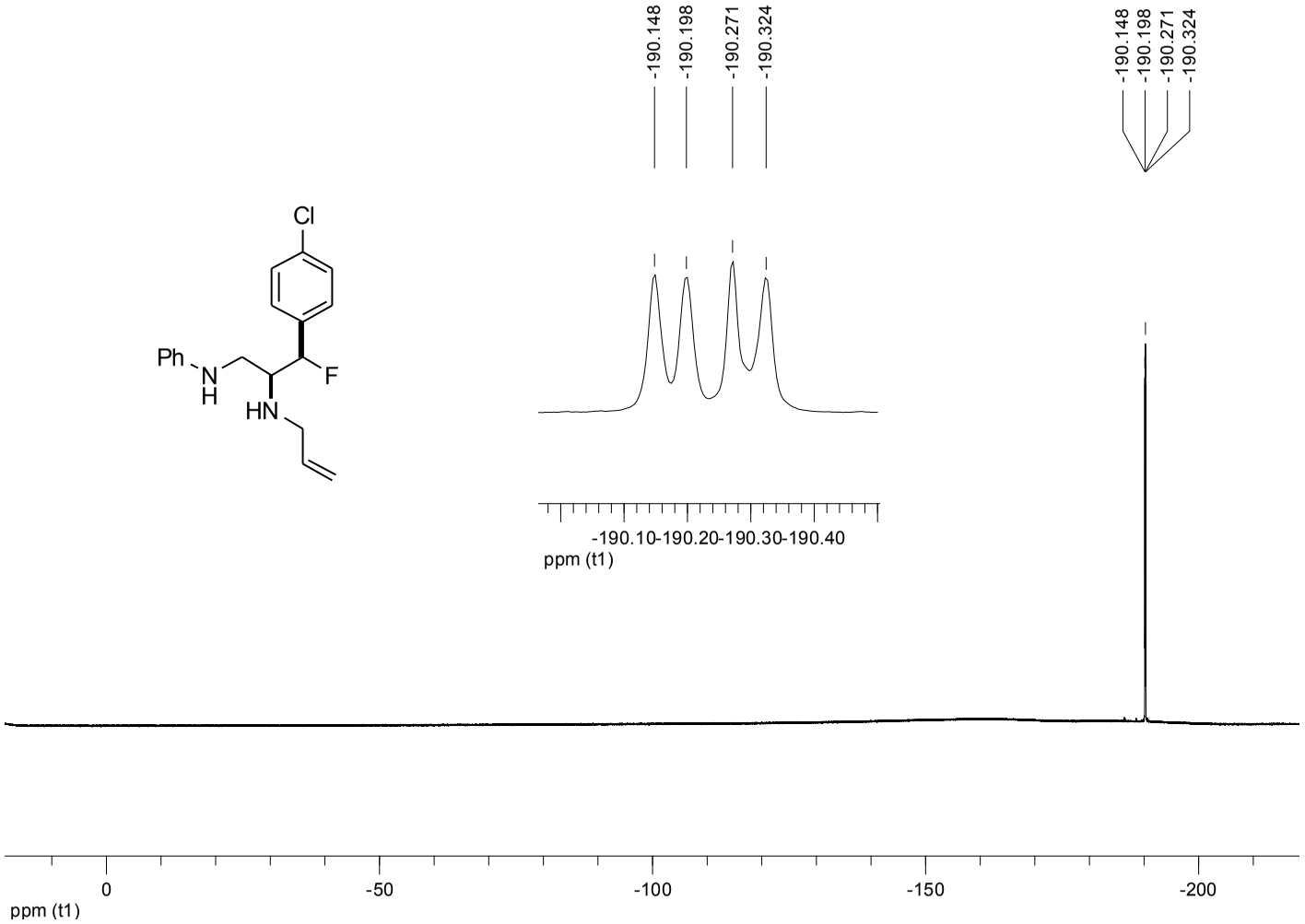
^{1}H NMR spectrum of **8d** (400 MHz, $CDCl_3$)



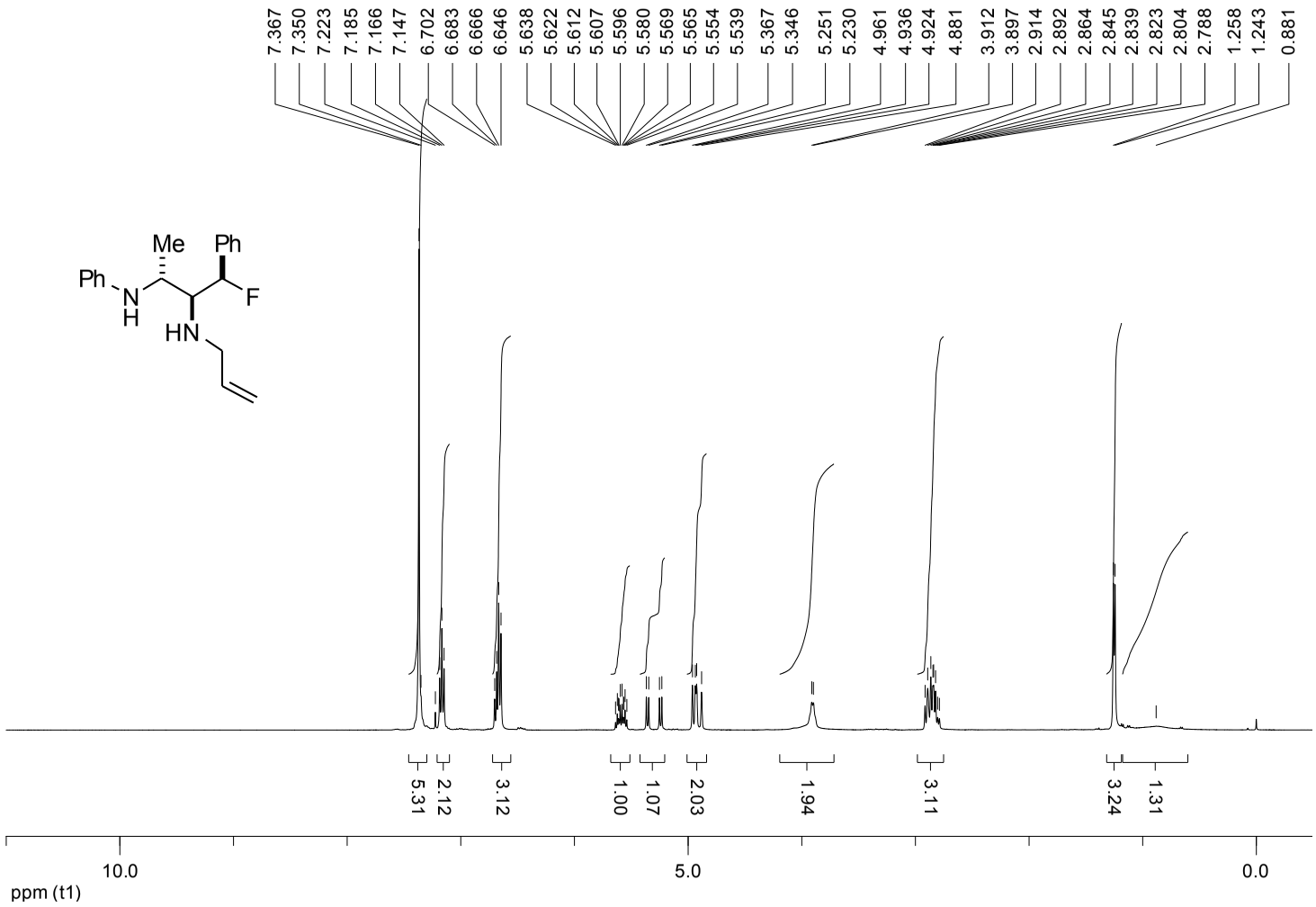
^{13}C NMR spectrum of **8d** (100 MHz, $CDCl_3$)



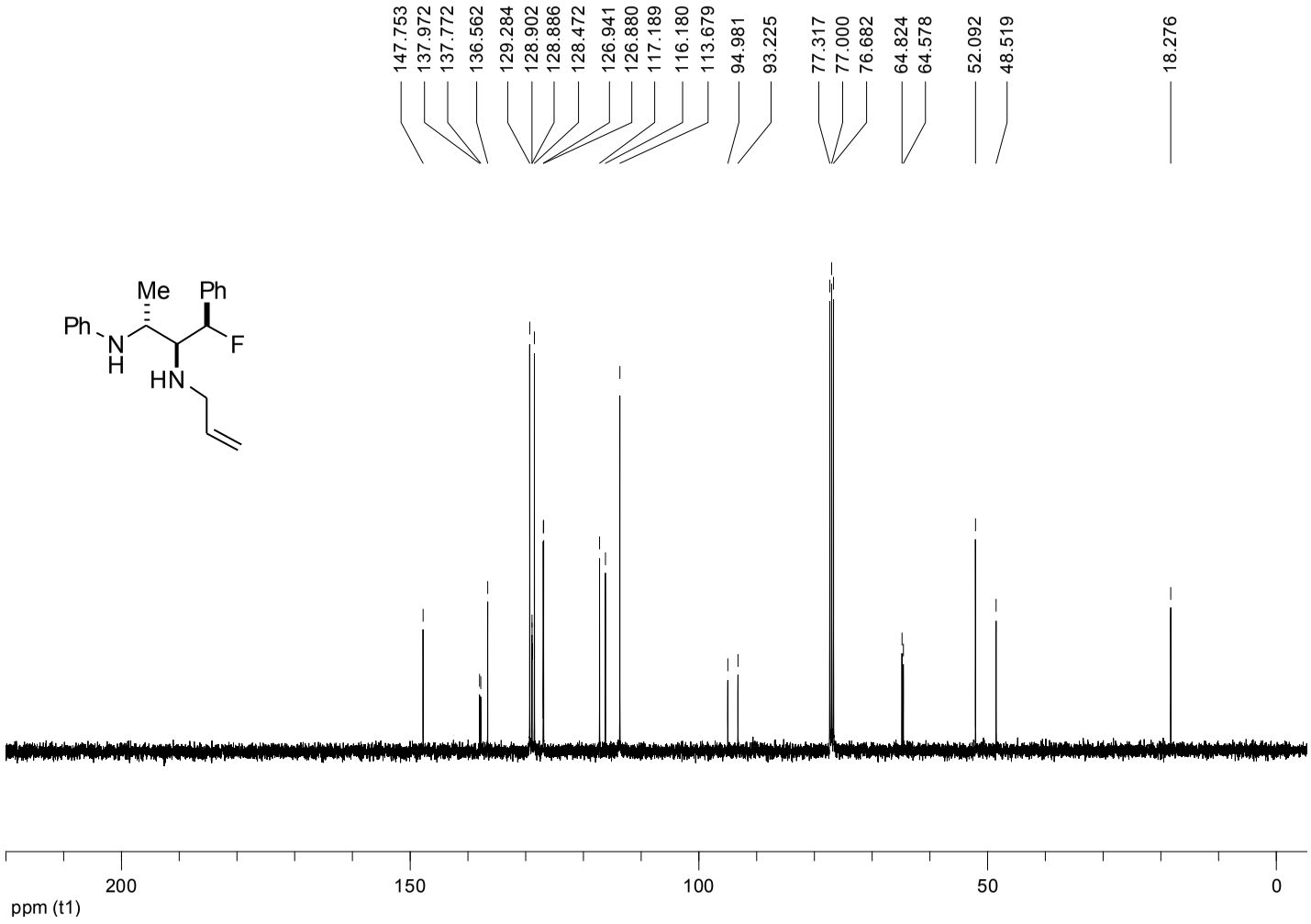
^{19}F NMR spectrum of **8d** (376 MHz, $CDCl_3$)



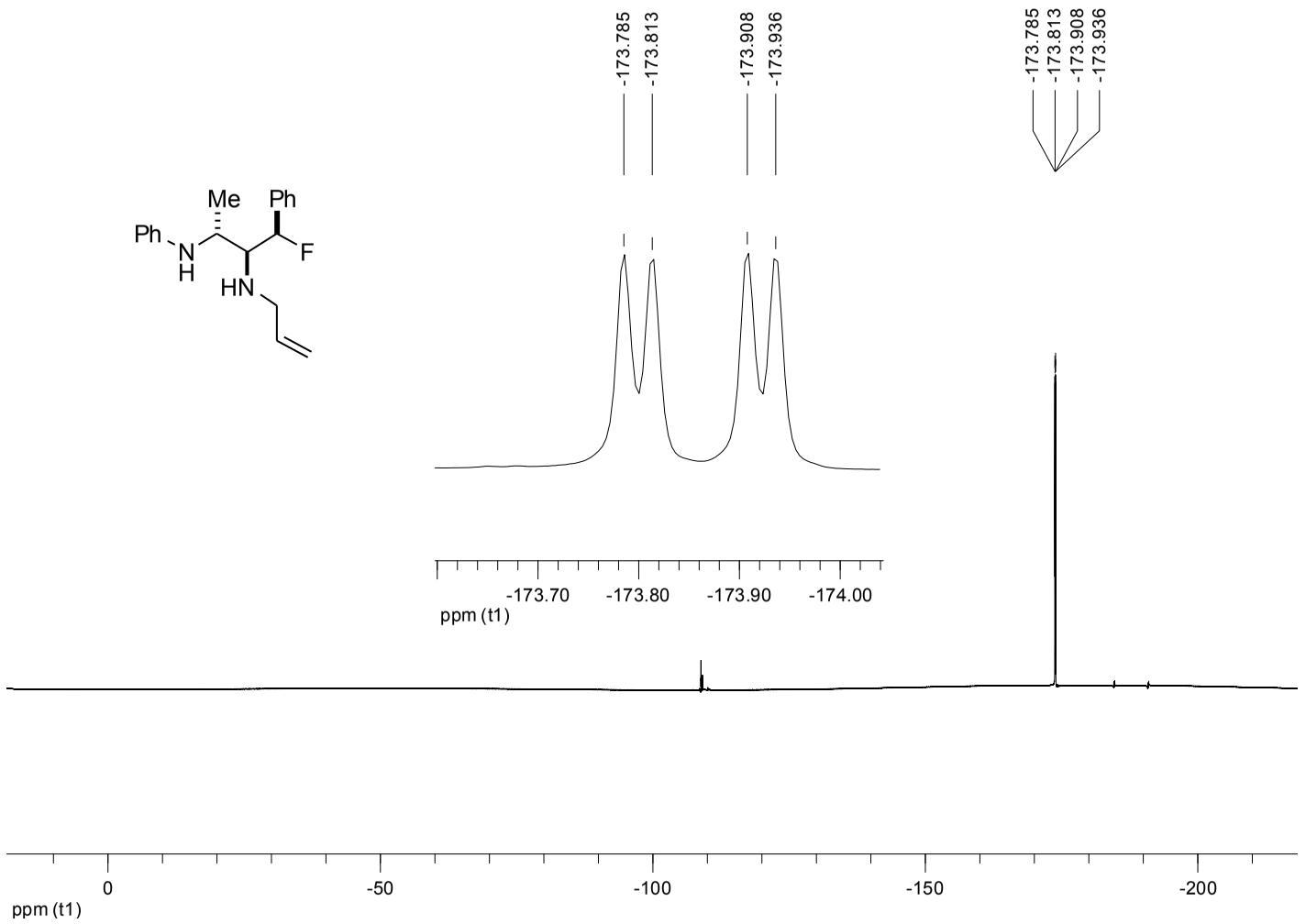
^{1}H NMR spectrum of **8g** (400 MHz, $CDCl_3$)



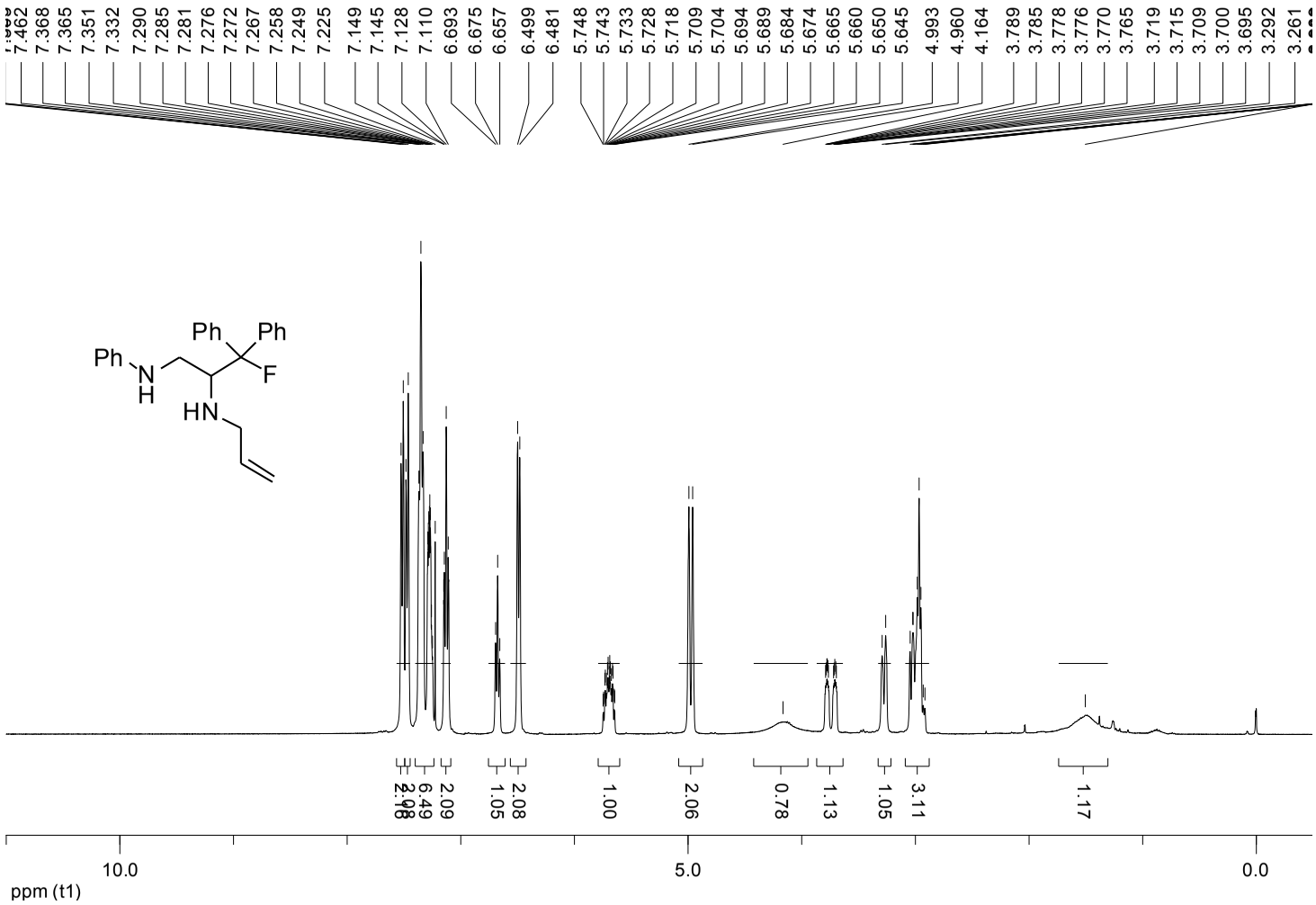
^{13}C NMR spectrum of **8g** (100 MHz, $CDCl_3$)



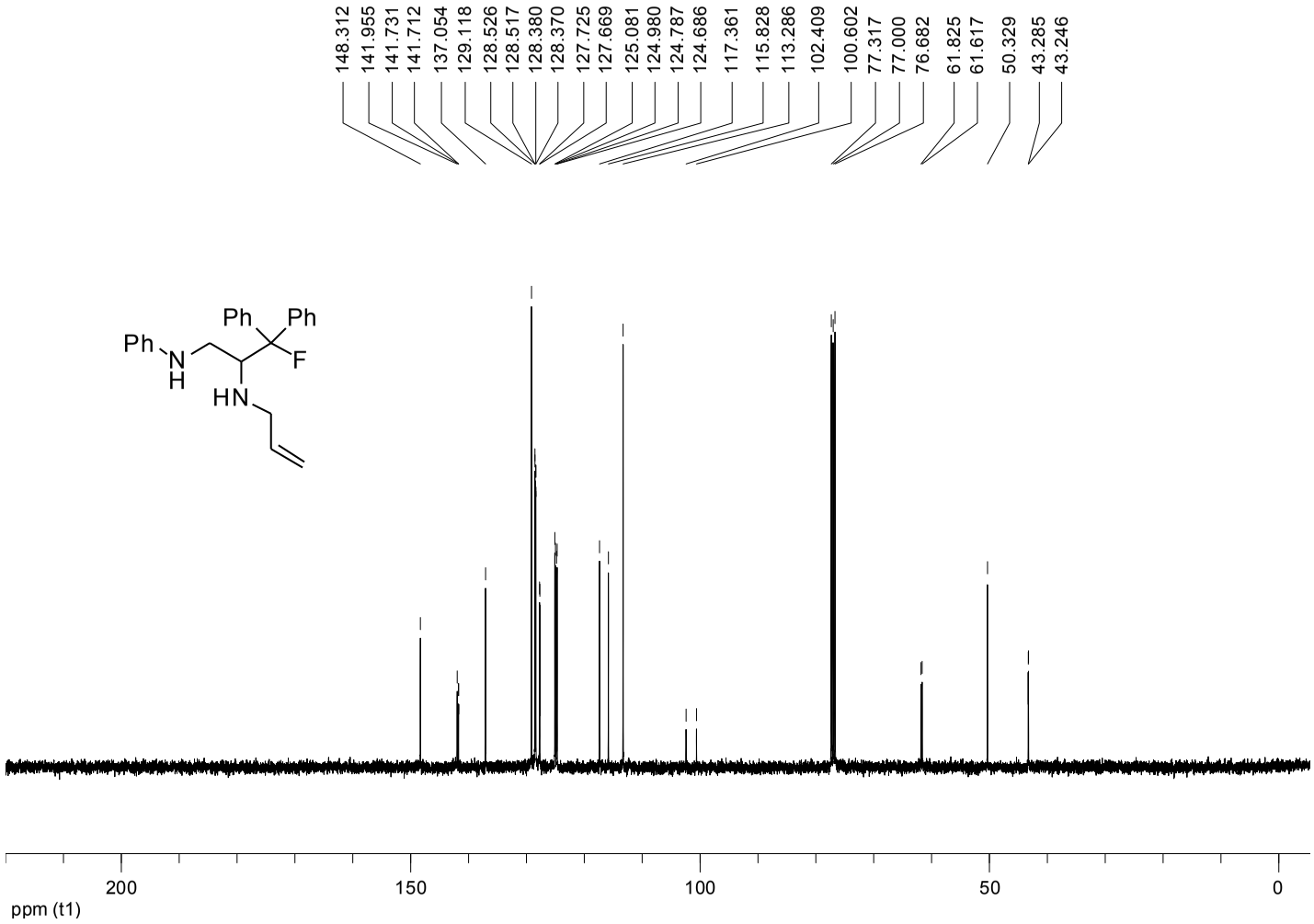
^{19}F NMR spectrum of **8g** (376 MHz, $CDCl_3$)



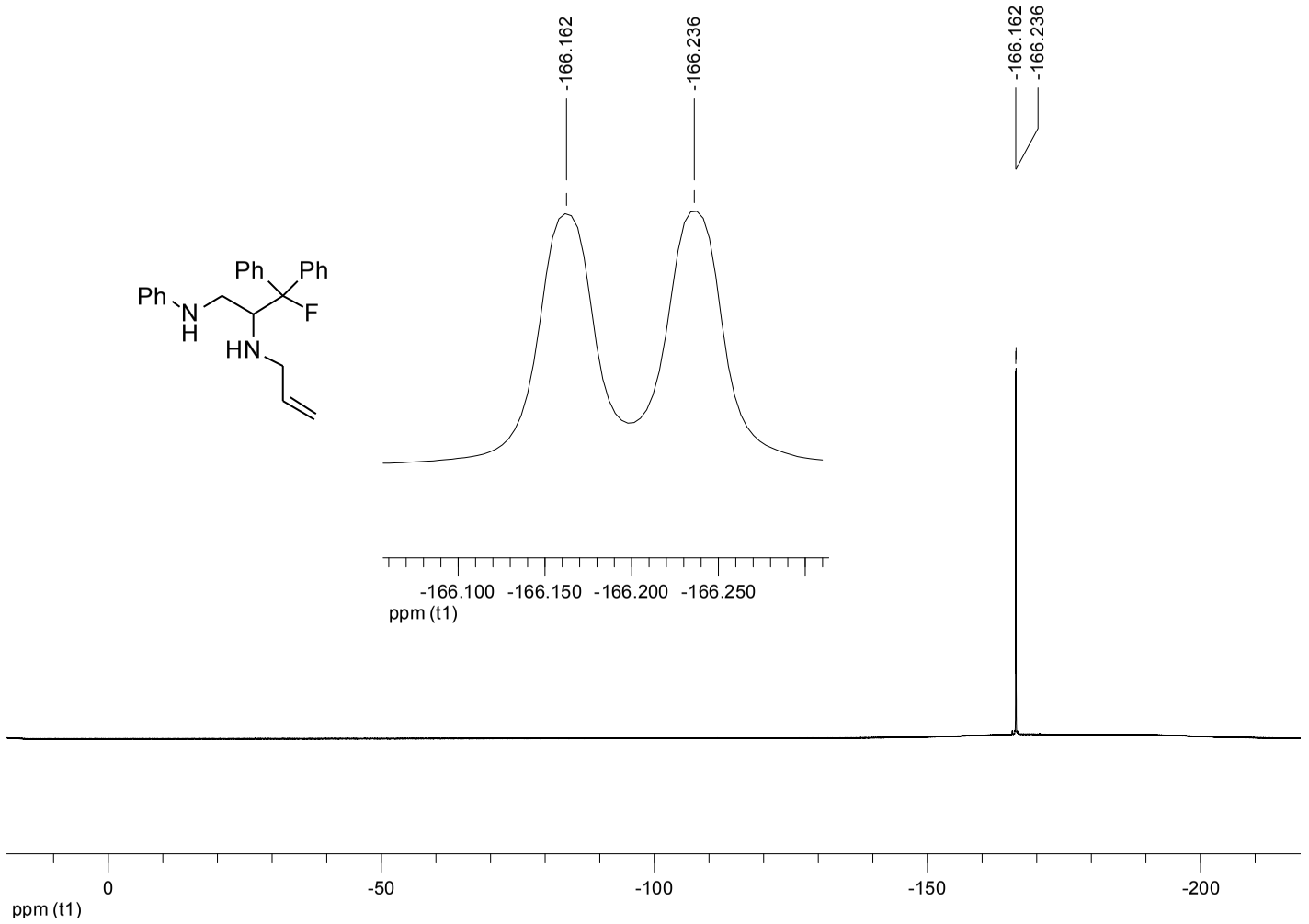
^{1}H NMR spectrum of **8h** (400 MHz, $CDCl_3$)



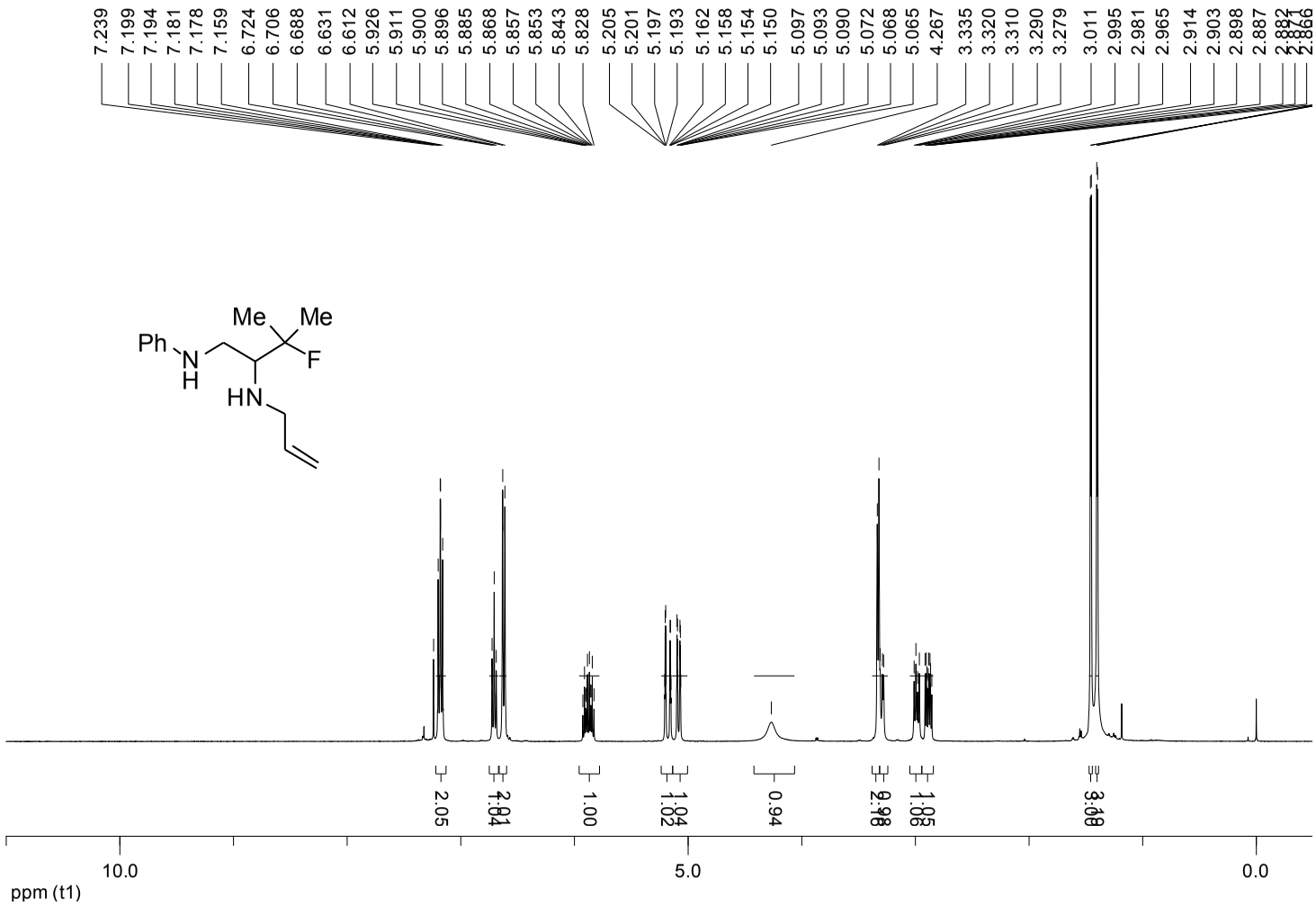
^{13}C NMR spectrum of **8h** (100 MHz, $CDCl_3$)



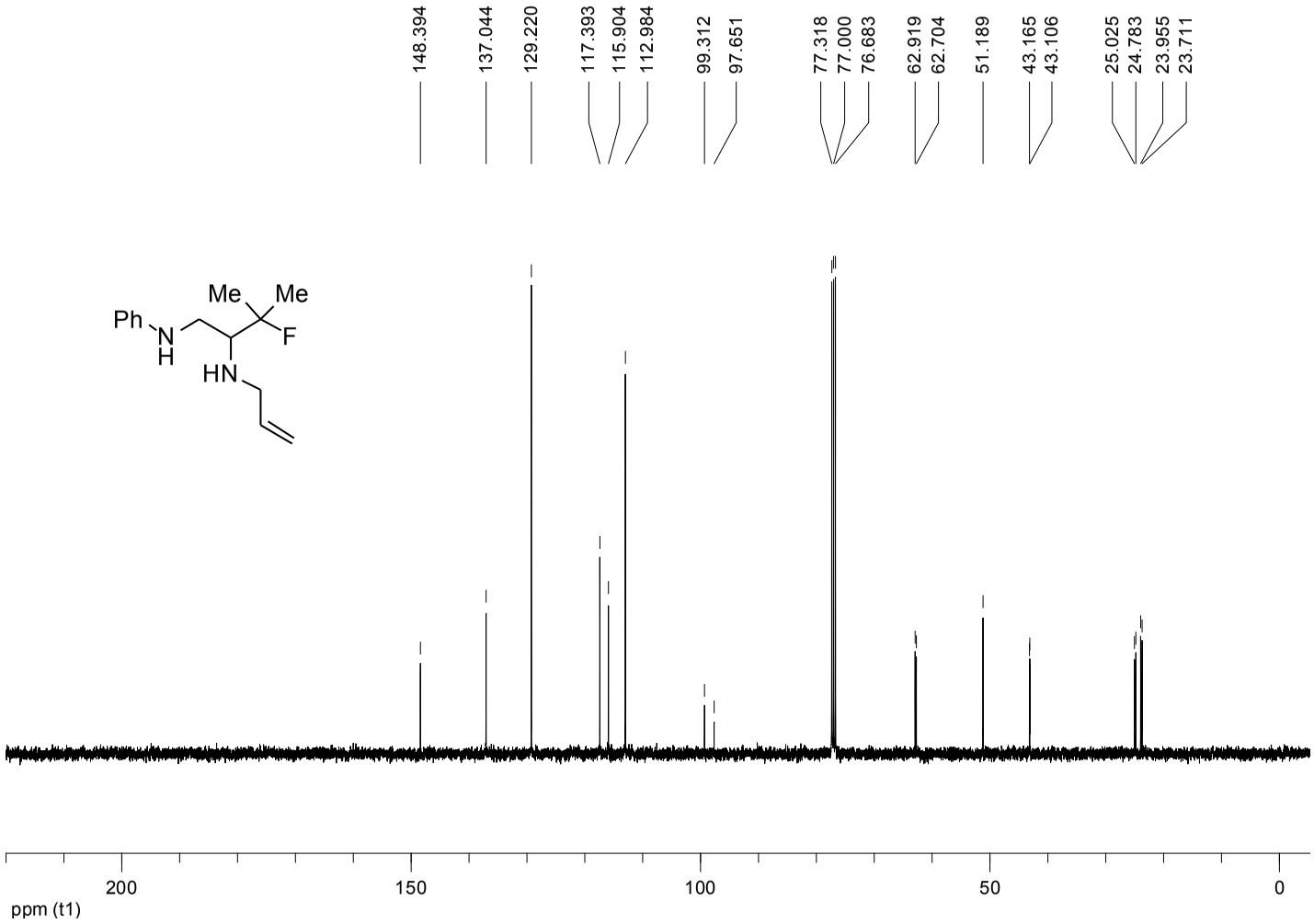
^{19}F NMR spectrum of **8h** (376 MHz, $CDCl_3$)



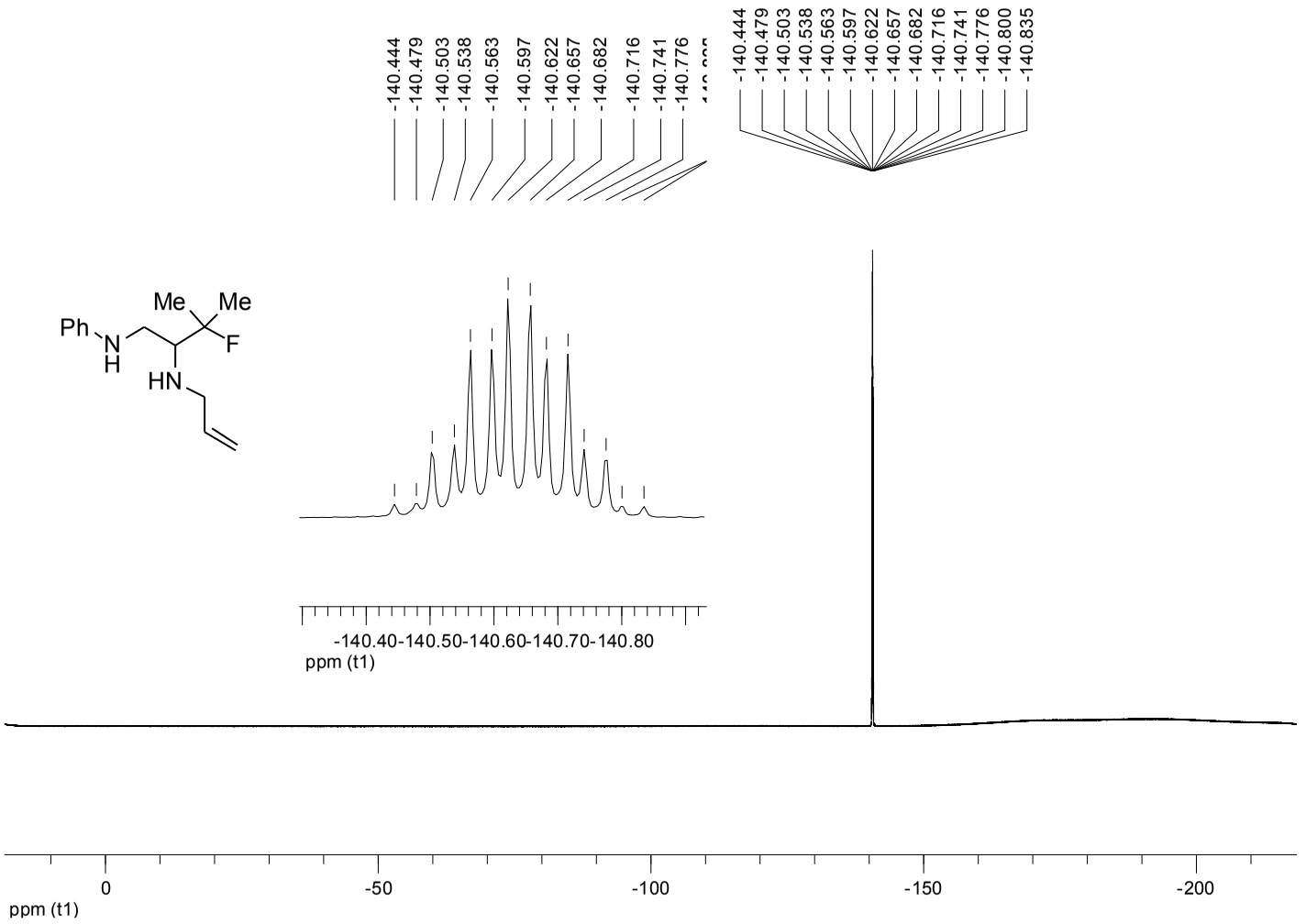
^{1}H NMR spectrum of **8i** (400 MHz, $CDCl_3$)



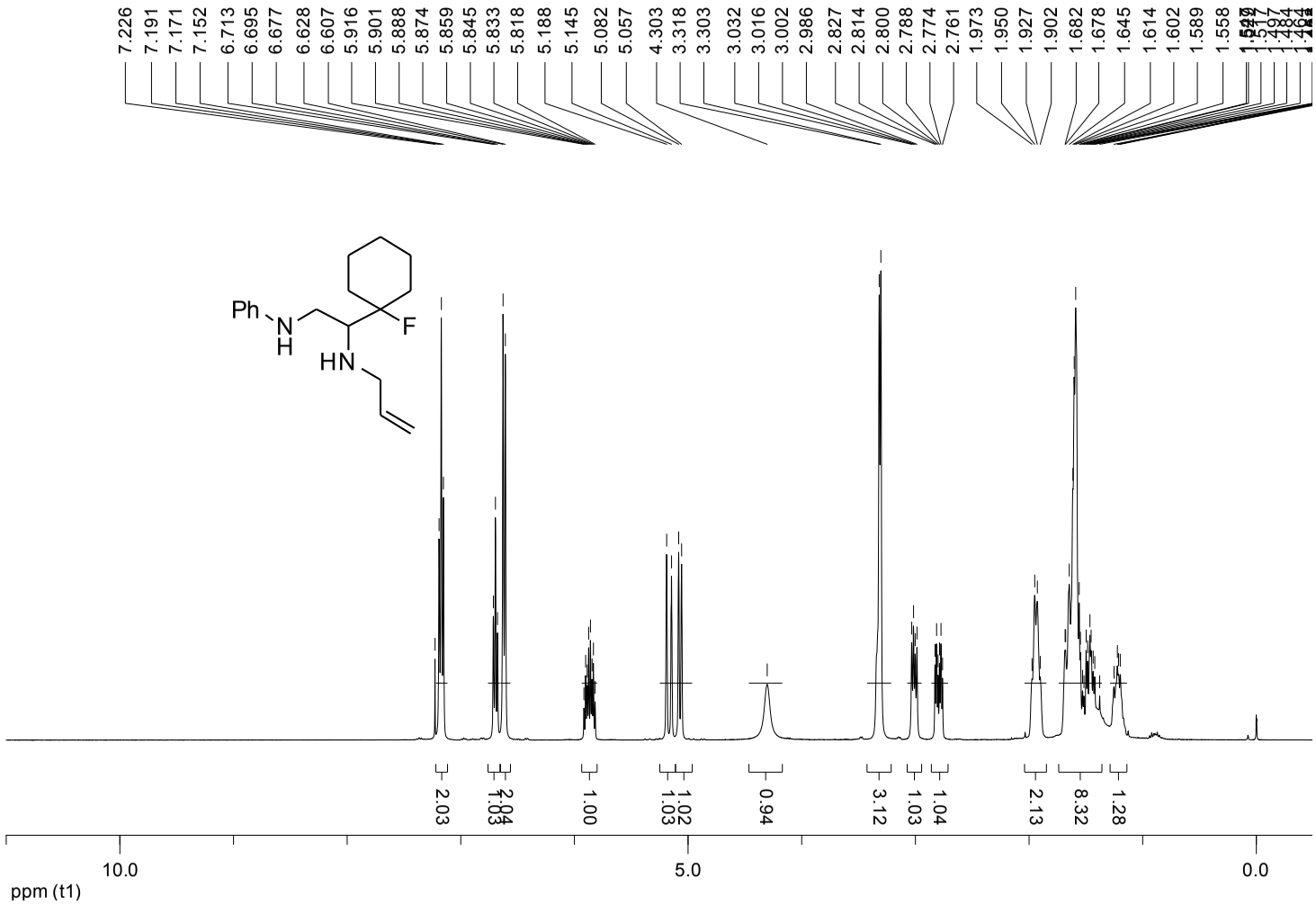
^{13}C NMR spectrum of **8i** (100 MHz, $CDCl_3$)



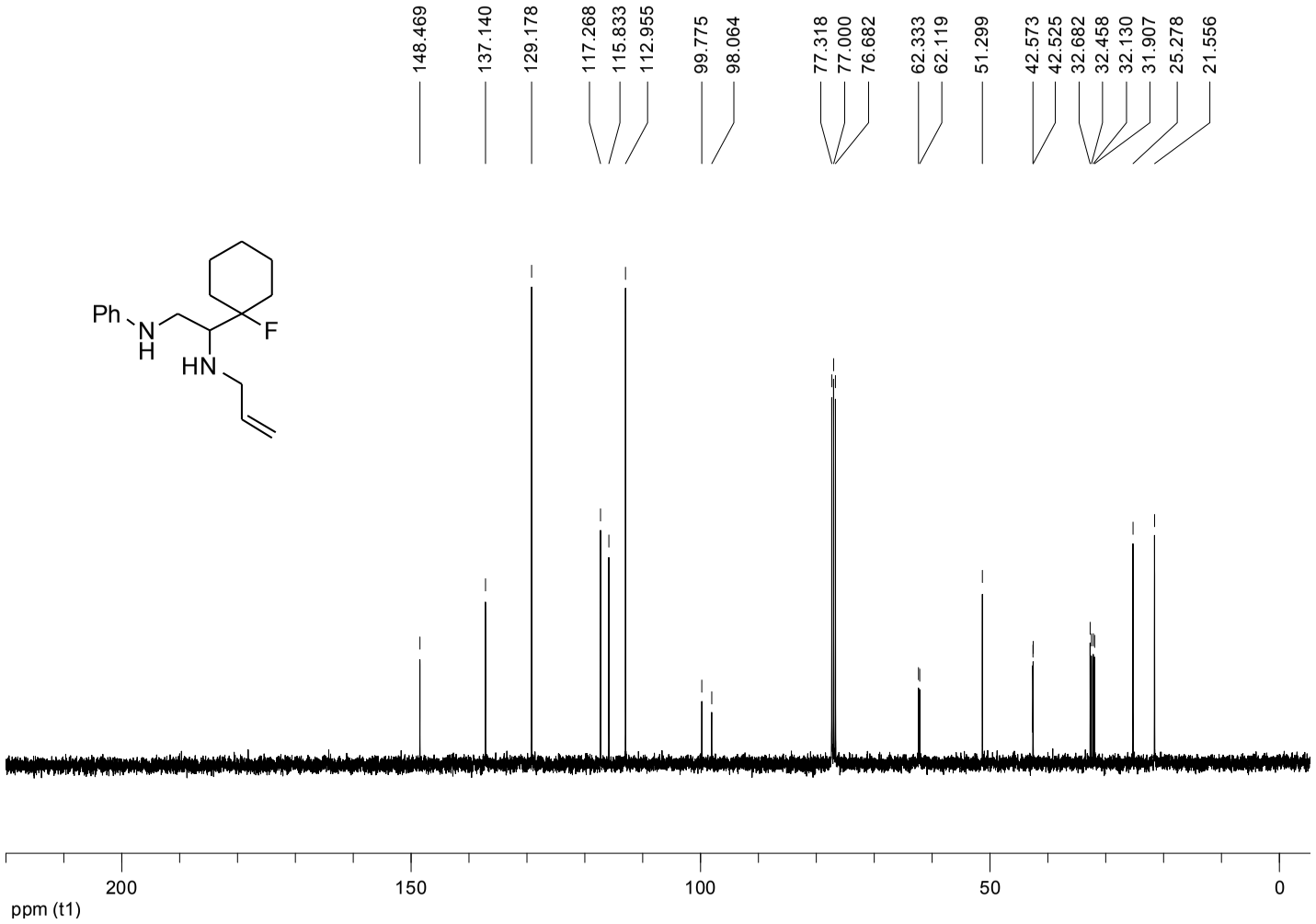
^{19}F NMR spectrum of **8i** (376 MHz, $CDCl_3$)



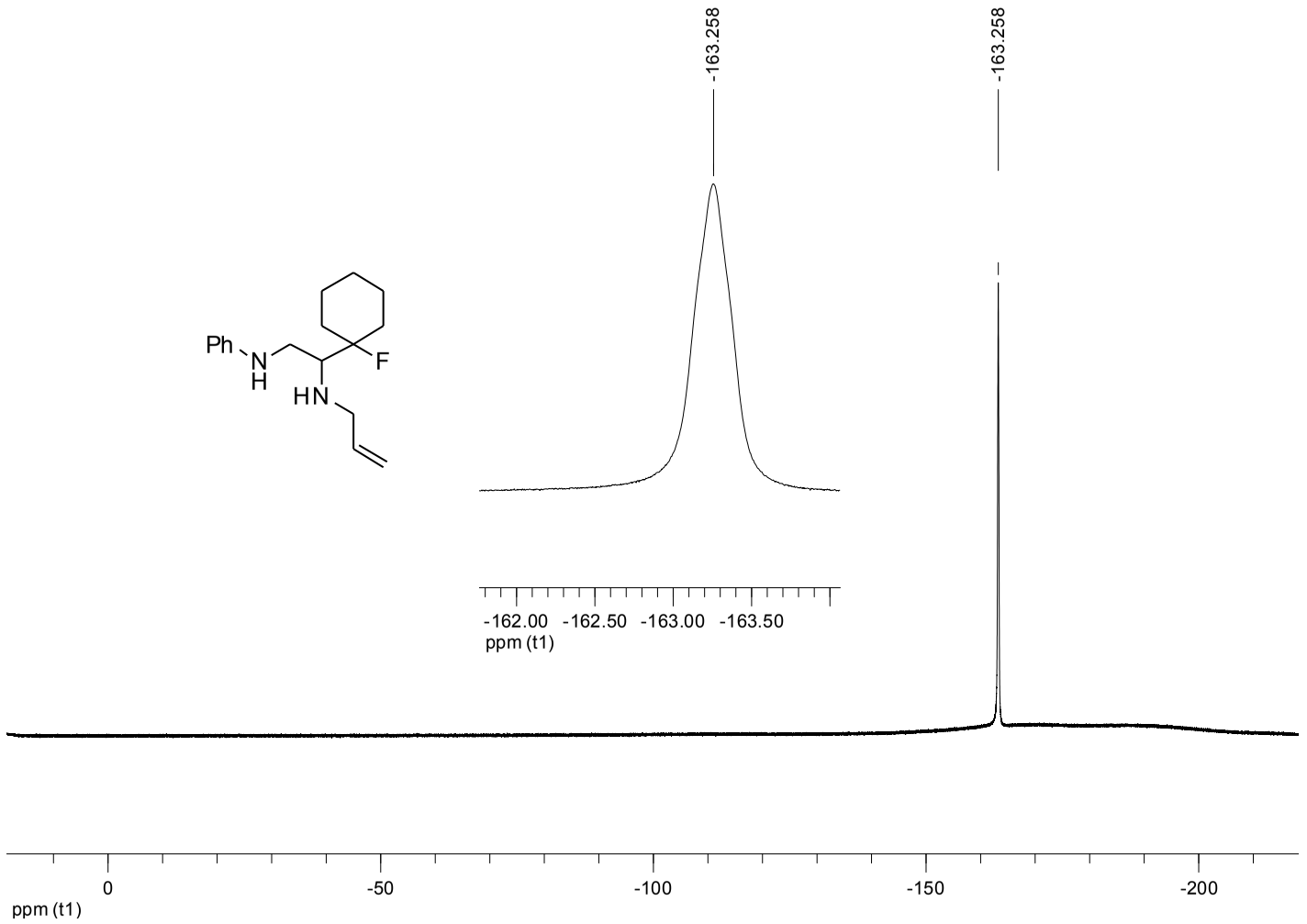
^{1}H NMR spectrum of **8j** (400 MHz, $CDCl_3$)



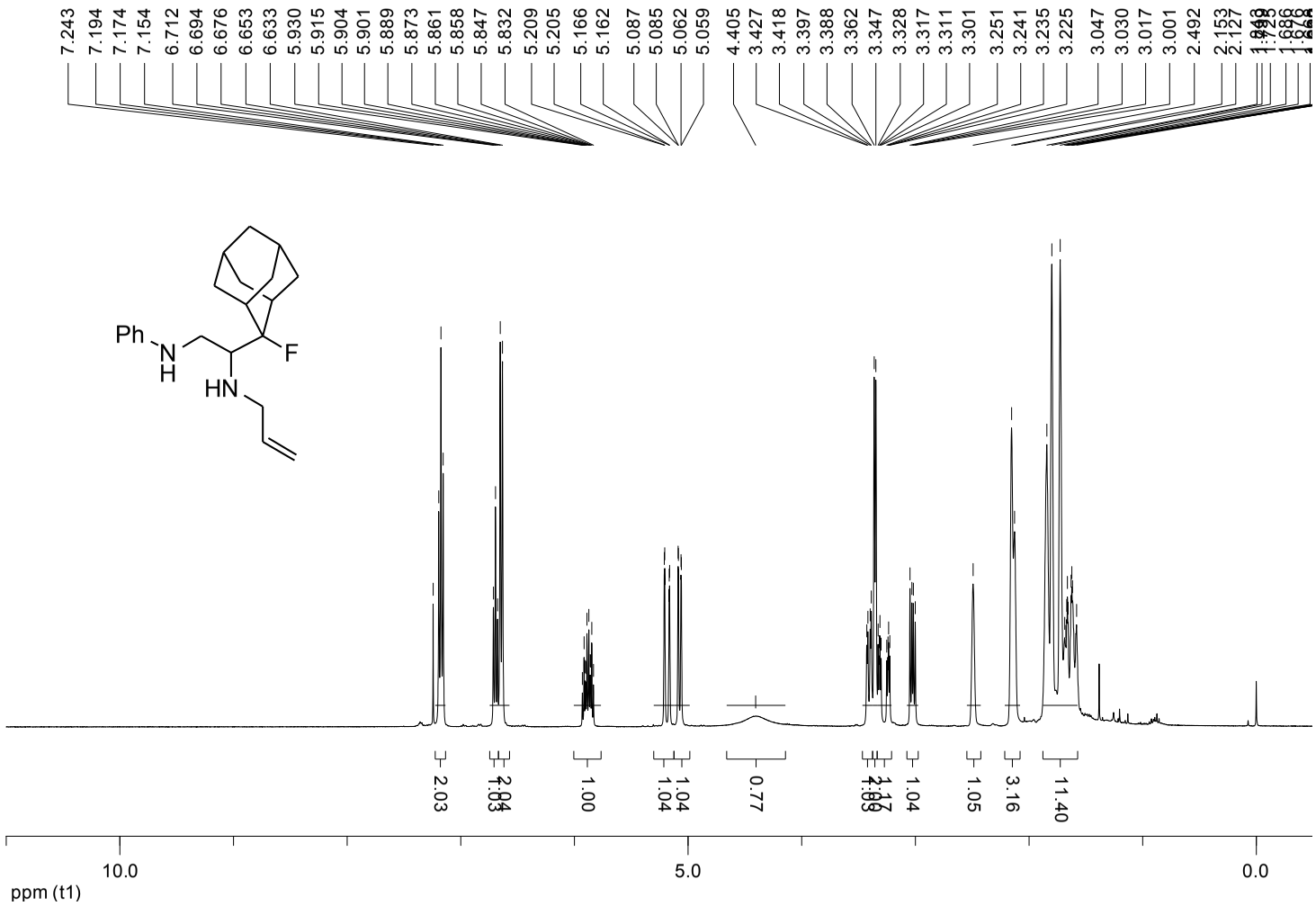
^{13}C NMR spectrum of **8j** (100 MHz, $CDCl_3$)



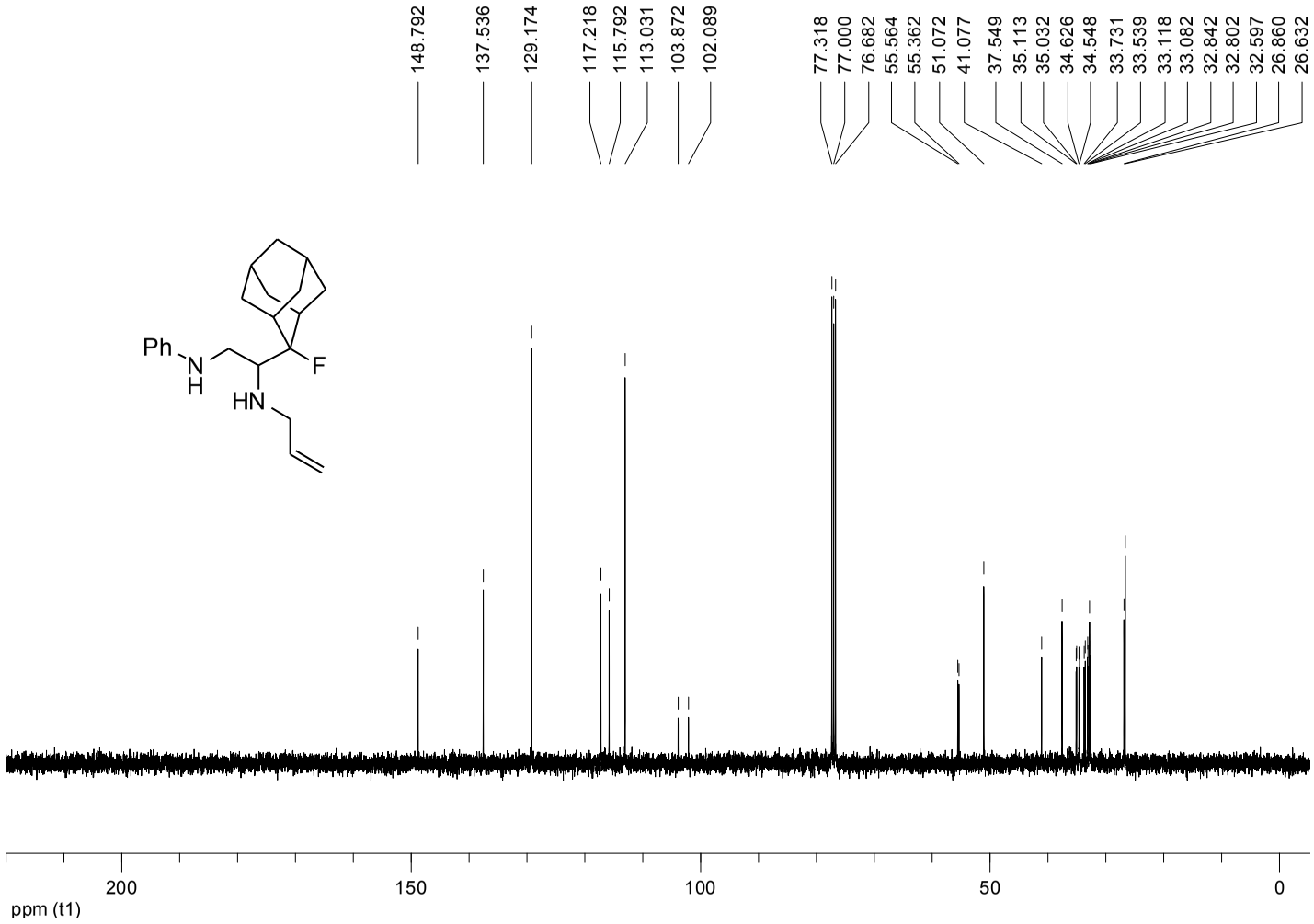
^{19}F NMR spectrum of **8j** (376 MHz, $CDCl_3$)



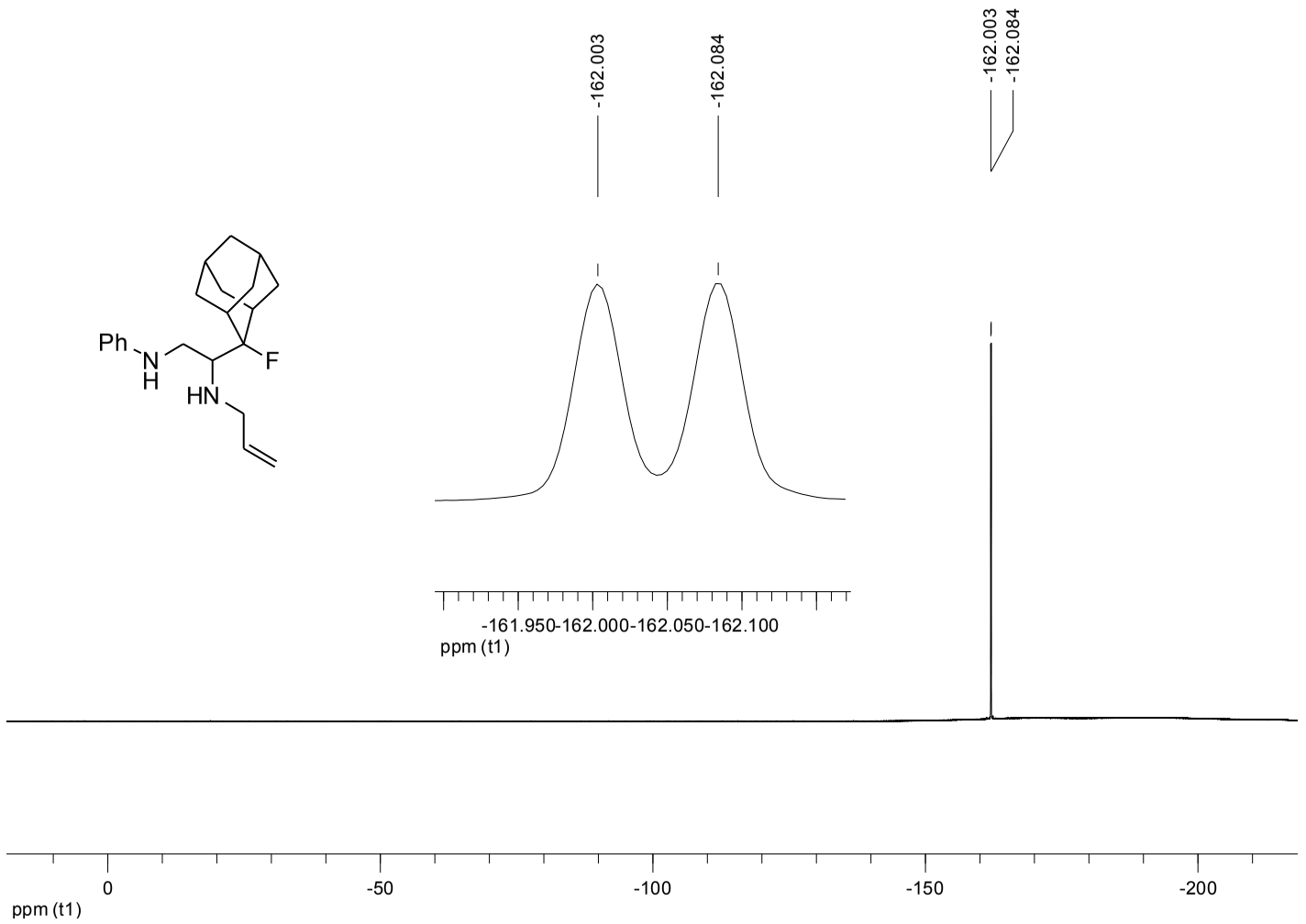
^{1}H NMR spectrum of **8k** (400 MHz, $CDCl_3$)



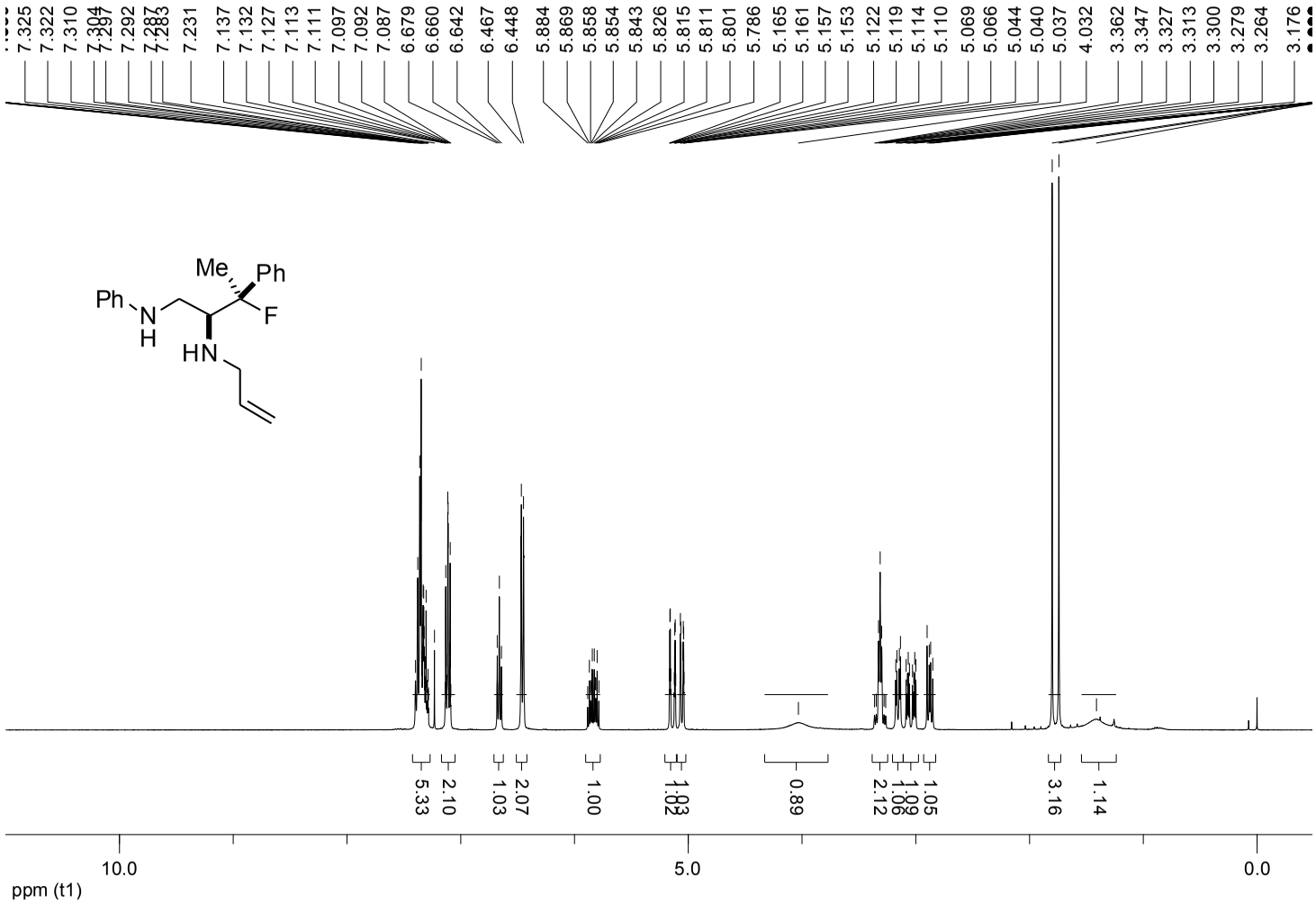
^{13}C NMR spectrum of **8k** (100 MHz, $CDCl_3$)



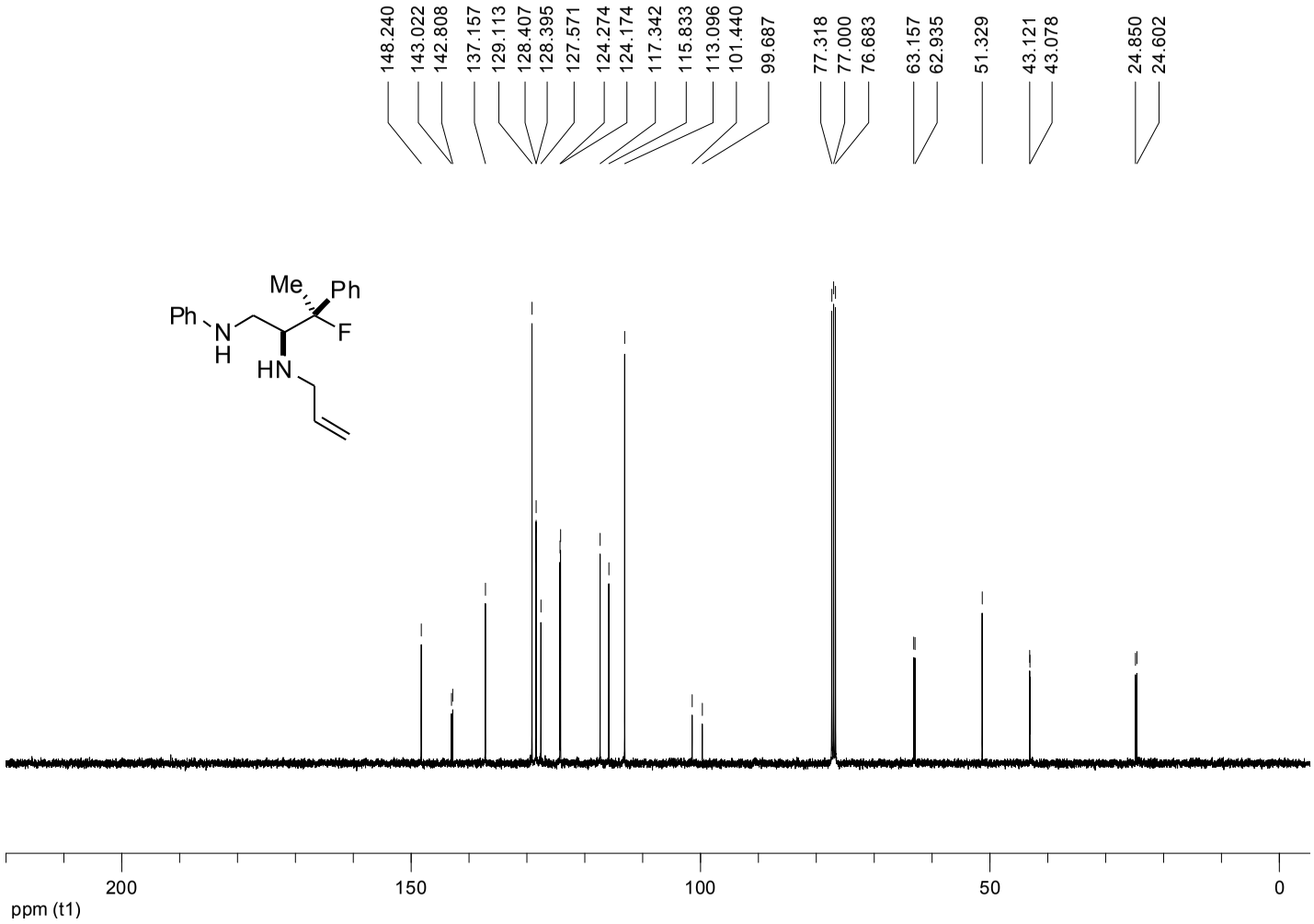
^{19}F NMR spectrum of **8k** (376 MHz, $CDCl_3$)



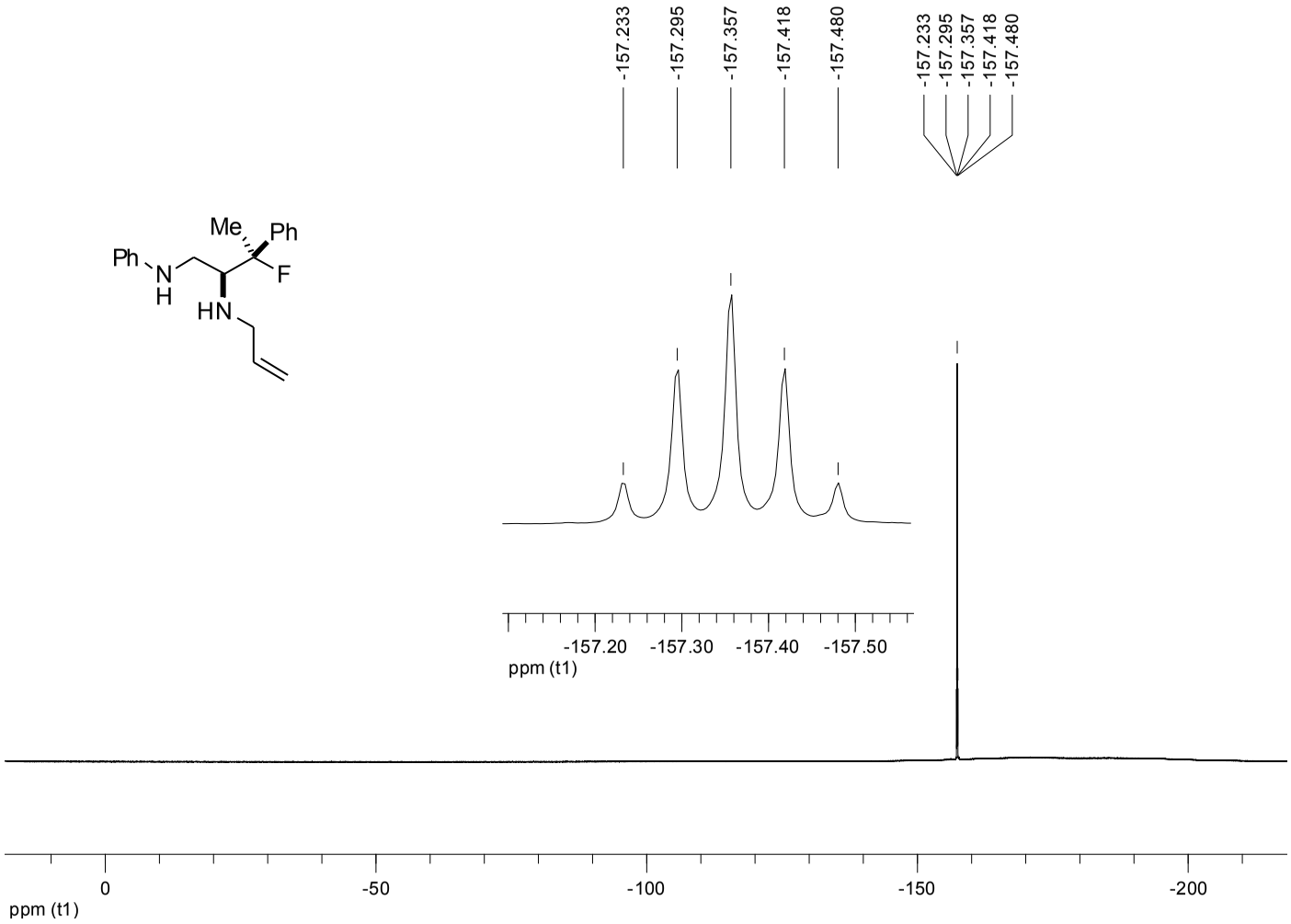
^{1}H NMR spectrum of **8l** (400 MHz, $CDCl_3$)



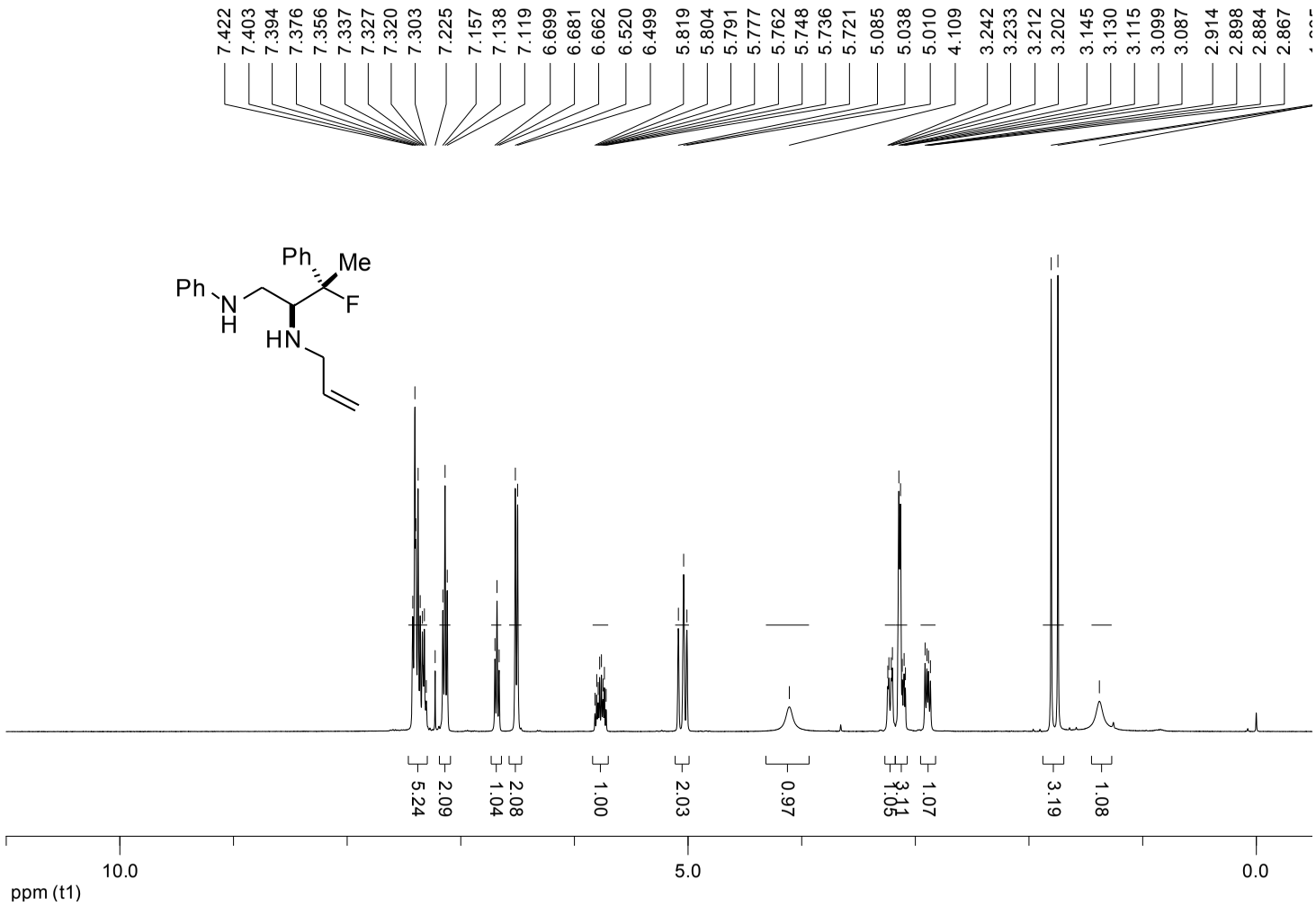
^{13}C NMR spectrum of **8l** (100 MHz, $CDCl_3$)



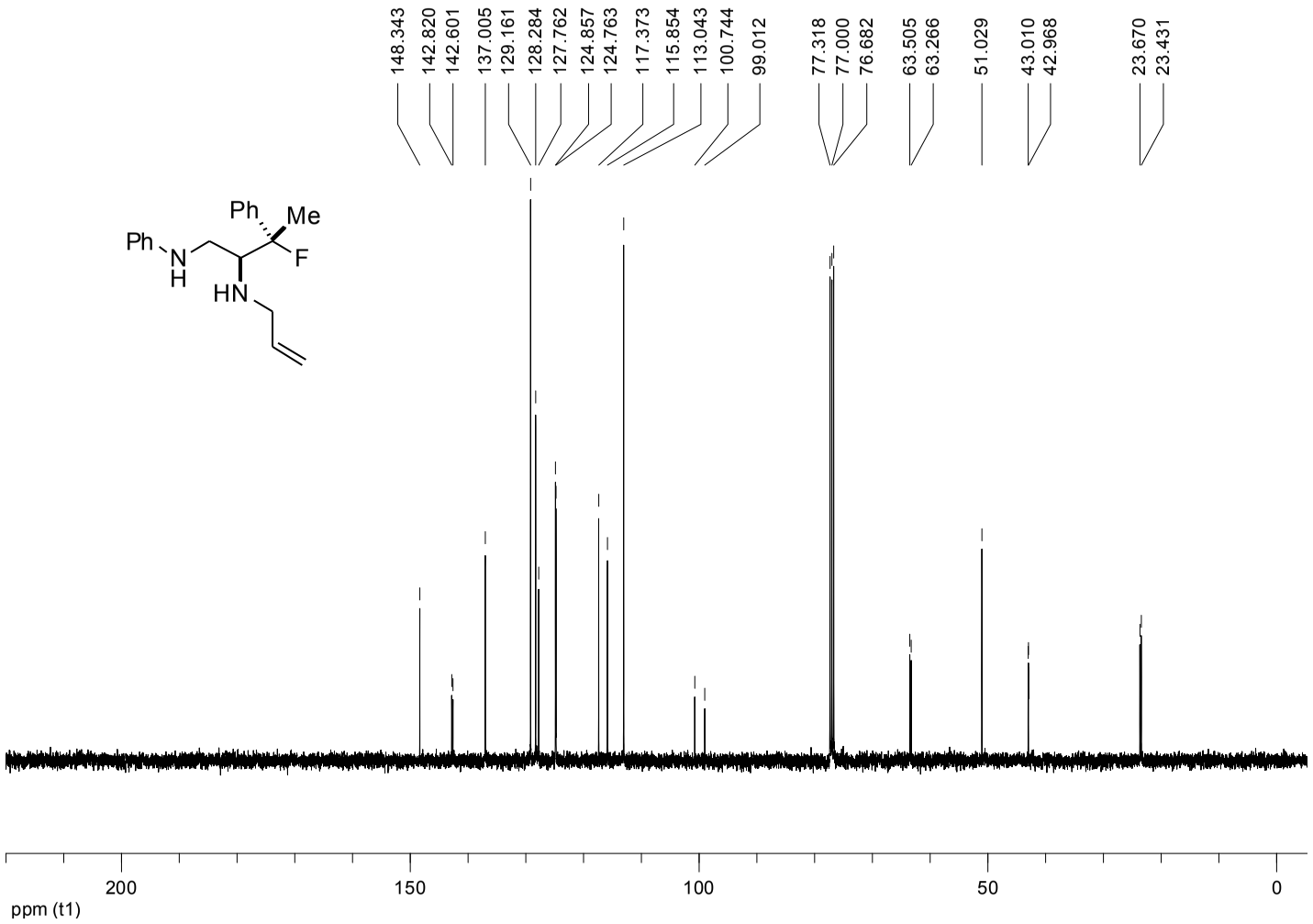
^{19}F NMR spectrum of **8l** (376 MHz, $CDCl_3$)



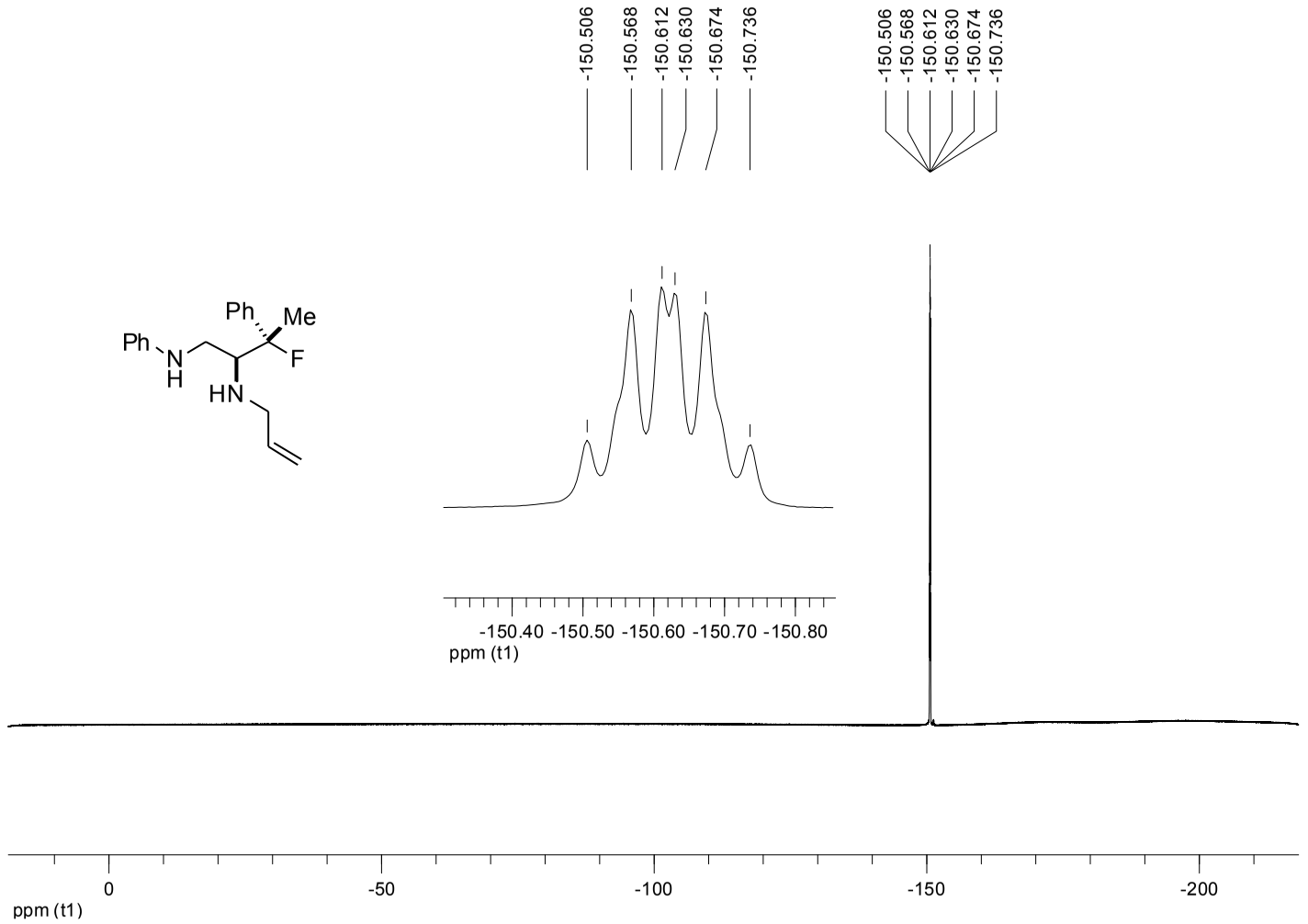
^{1}H NMR spectrum of **8m** (400 MHz, $CDCl_3$)



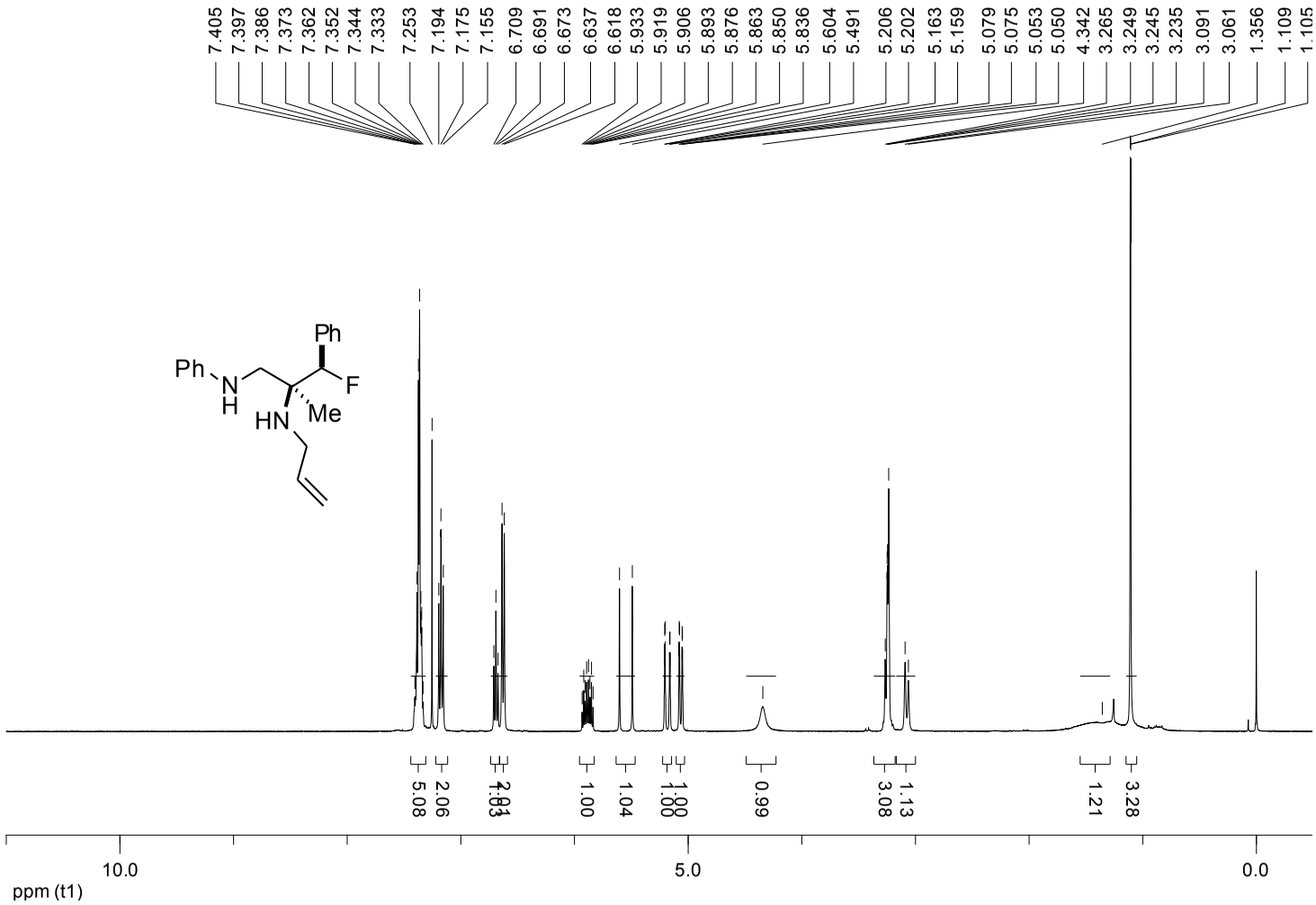
^{13}C NMR spectrum of **8m** (100 MHz, $CDCl_3$)



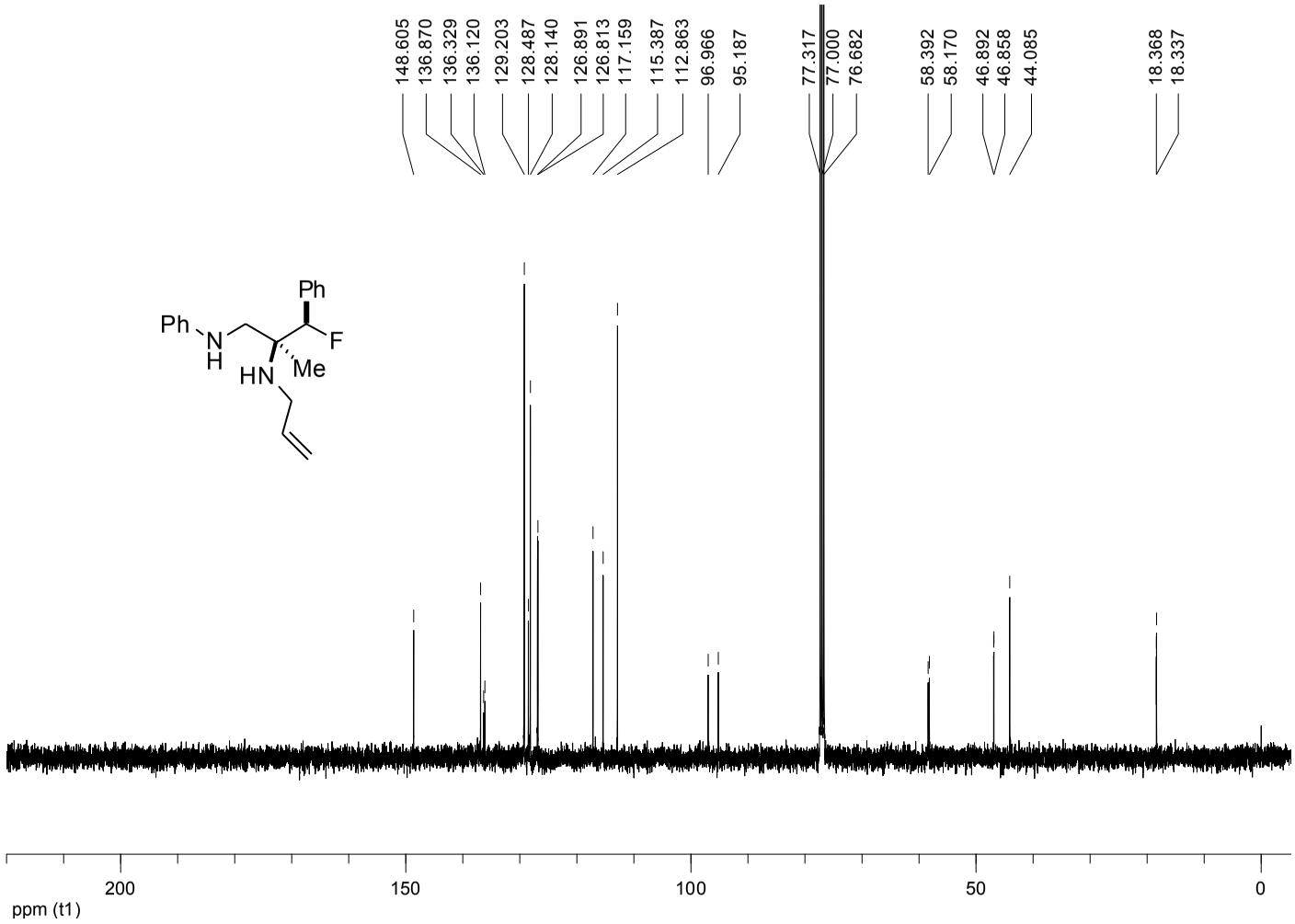
^{19}F NMR spectrum of **8m** (376 MHz, $CDCl_3$)



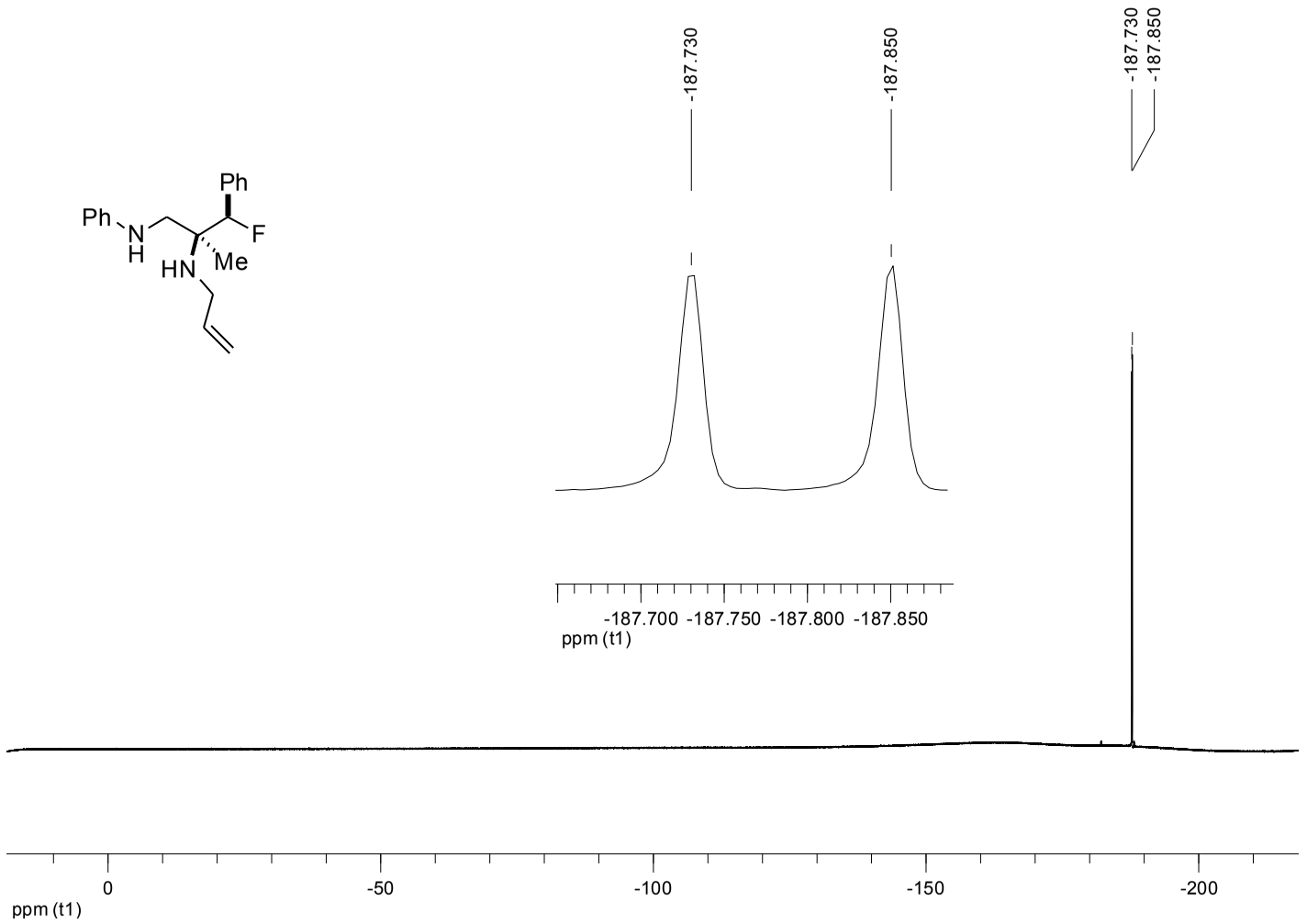
^{1}H NMR spectrum of **8n** (400 MHz, $CDCl_3$)



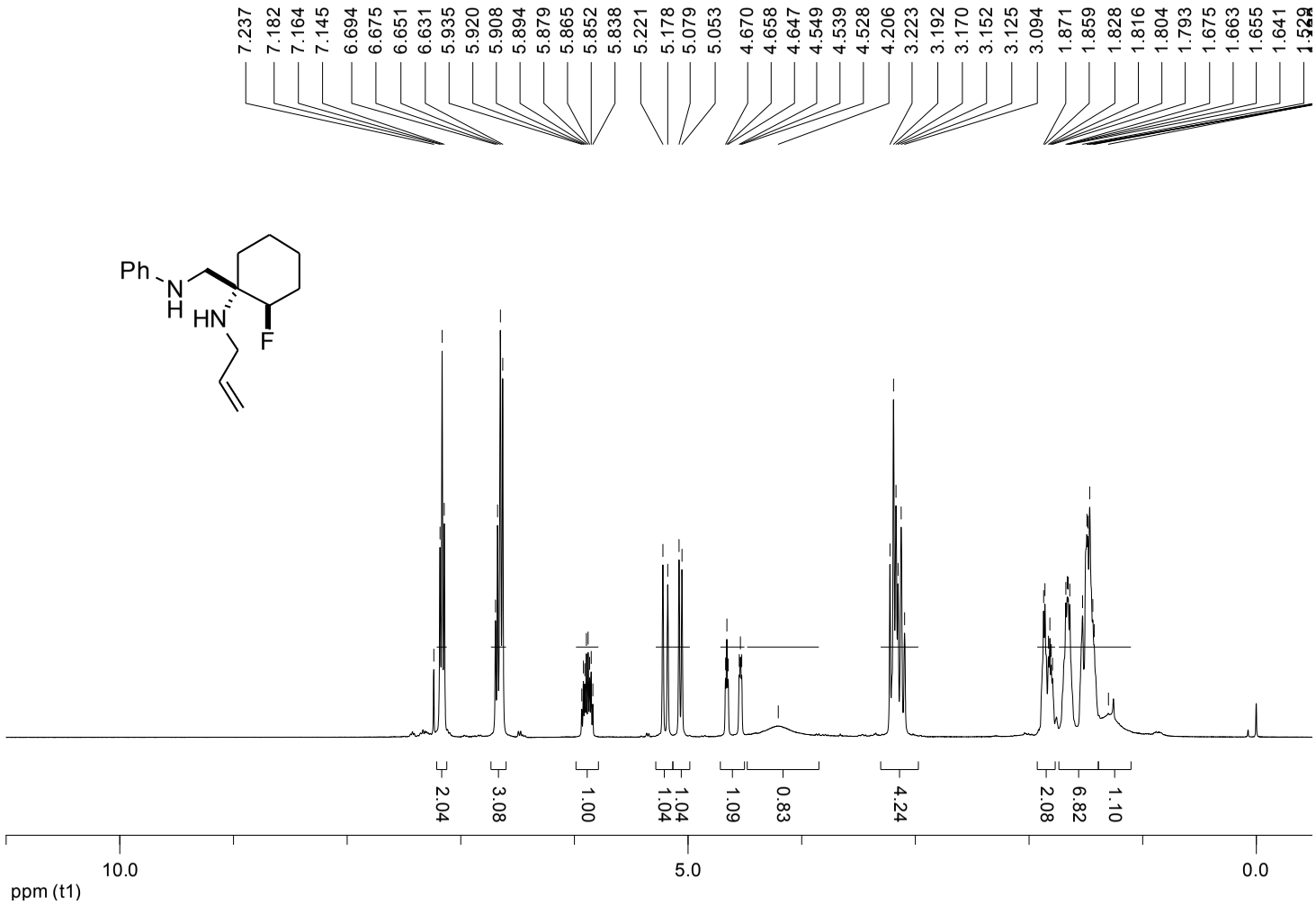
^{13}C NMR spectrum of **8n** (100 MHz, $CDCl_3$)



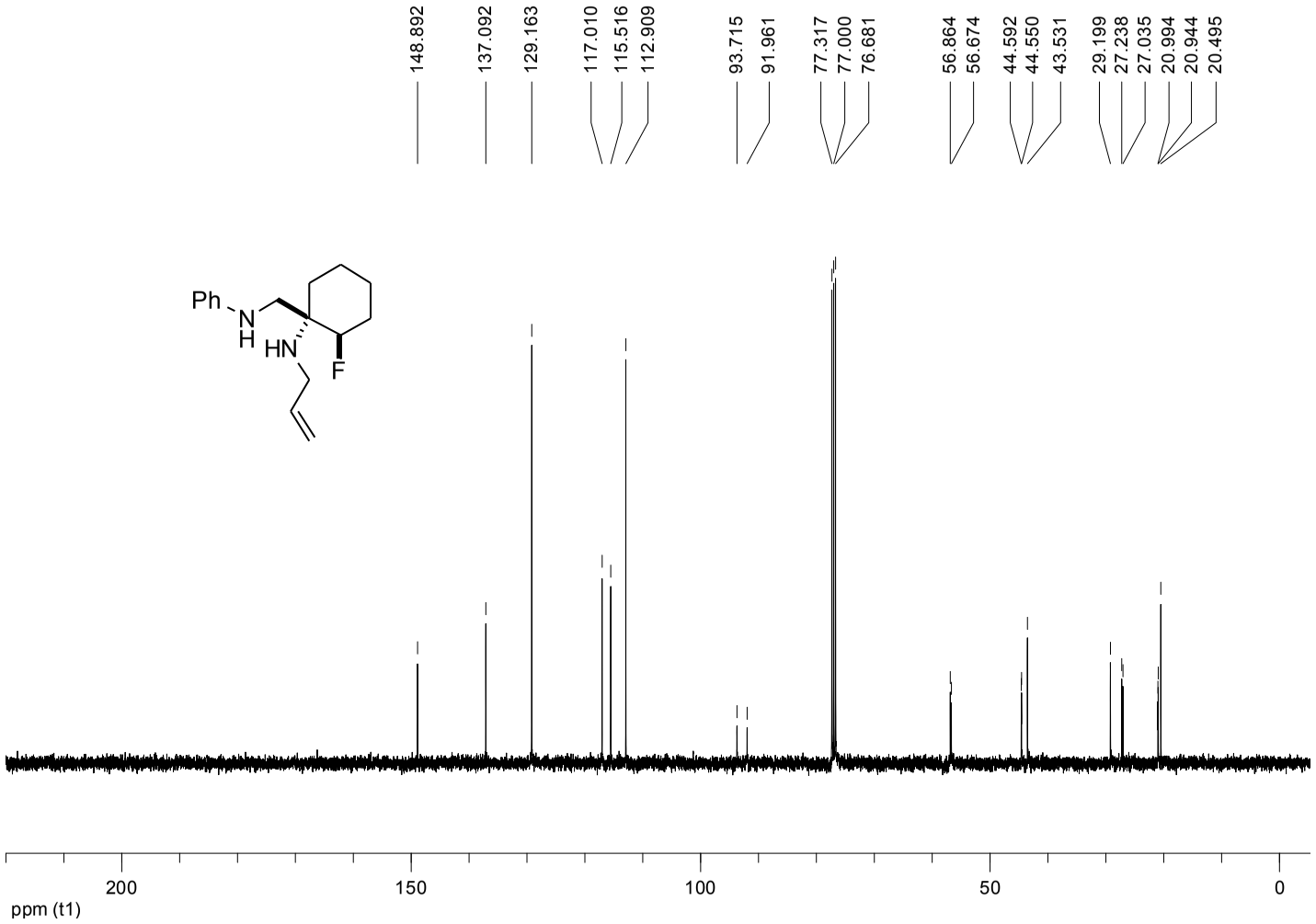
^{19}F NMR spectrum of **8n** (376 MHz, $CDCl_3$)



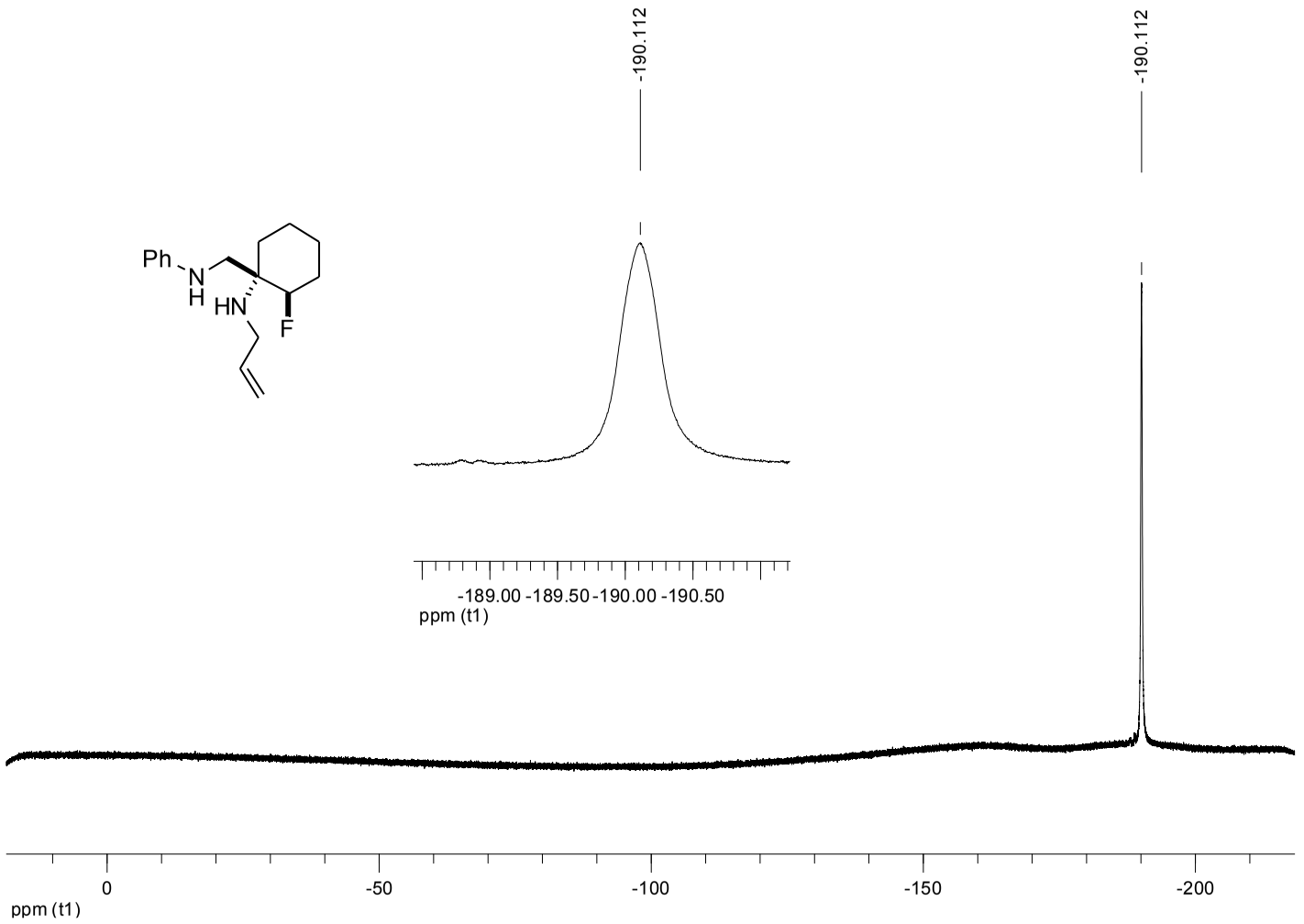
^{1}H NMR spectrum of **8o** (400 MHz, $CDCl_3$)



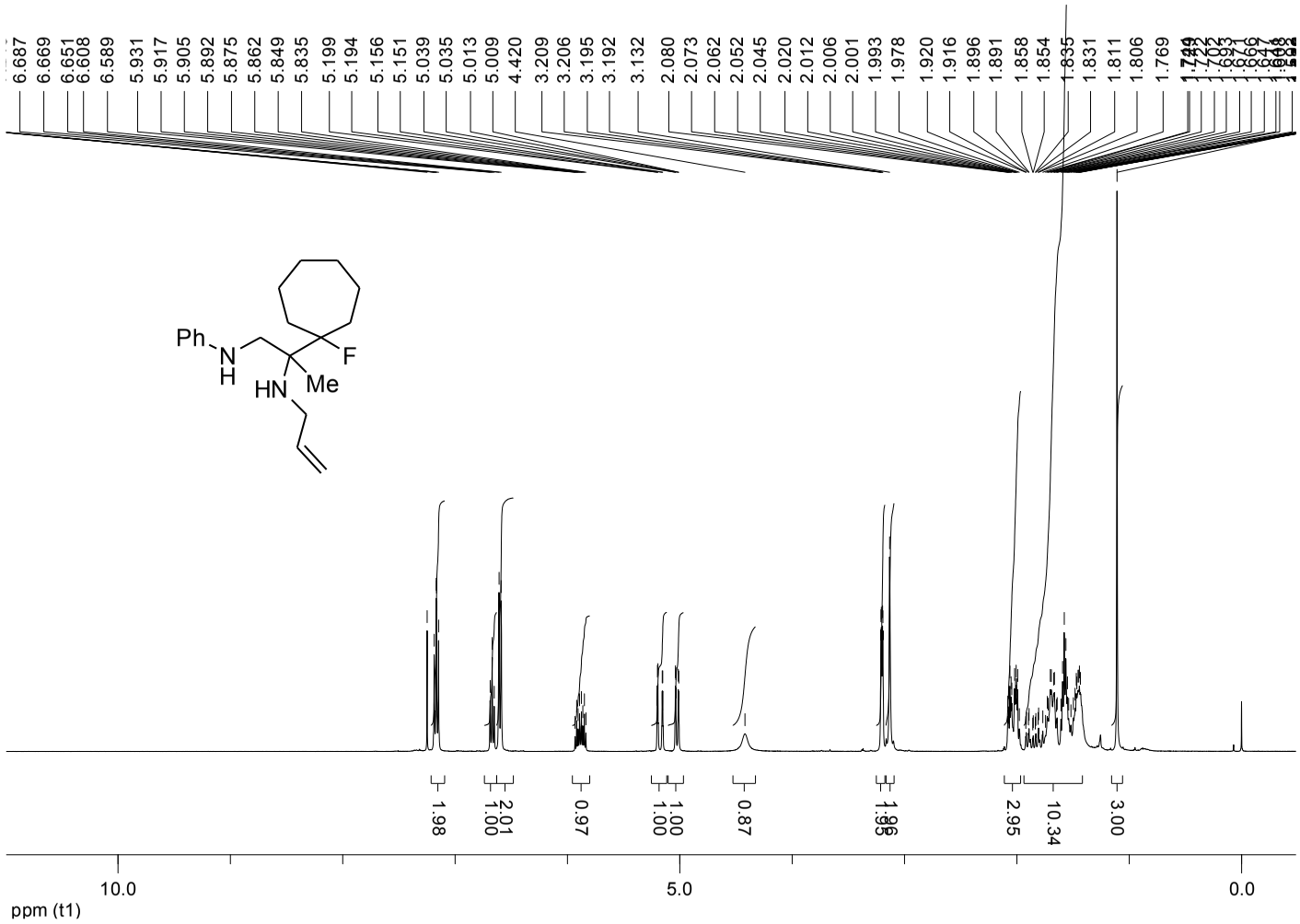
^{13}C NMR spectrum of **8o** (100 MHz, $CDCl_3$)



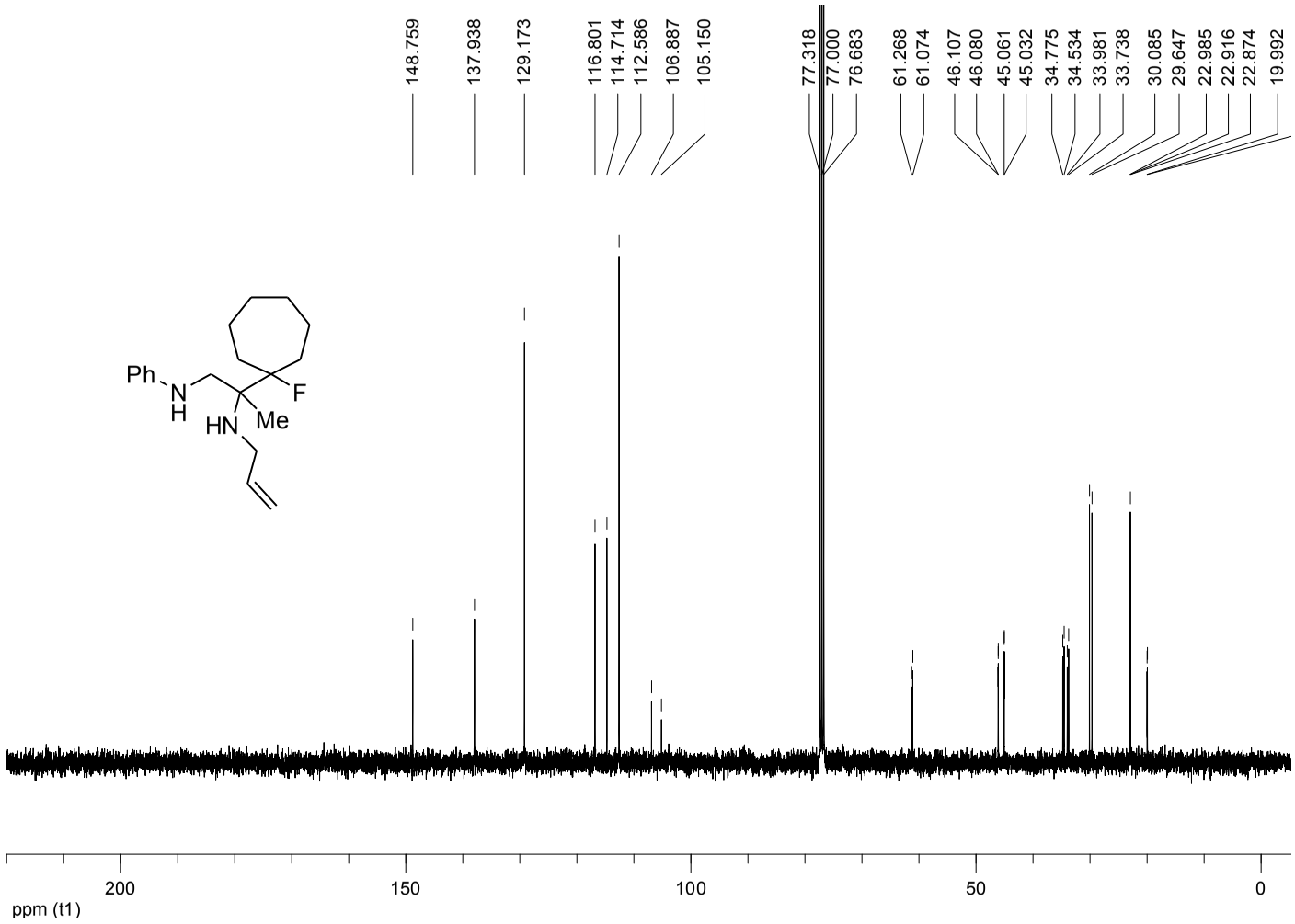
^{19}F NMR spectrum of **8o** (376 MHz, $CDCl_3$)



^{1}H NMR spectrum of **8q** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **8q** (100 MHz, $CDCl_3$)



^{19}F NMR spectrum of **8q** (376 MHz, $CDCl_3$)