Supporting Information

Diastereoselective Aminooxygenation and Diamination of Alkenes with Amidines by Hypervalent Iodine(III) Reagents

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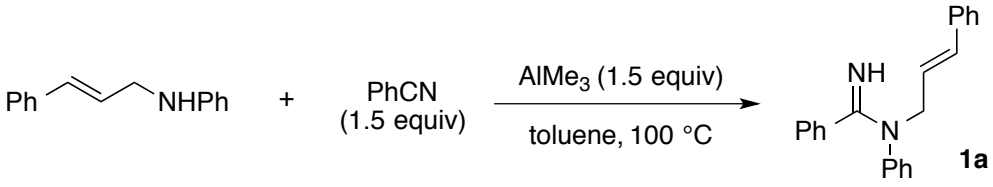
1. General

^{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, tt = triplet of triplet, ddd = doublet of doublet of doublet, dt = doublet 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. $PhI(OAc)_2$, $PhI(OCOCF_3)_2$, benzonitrile and 2-naphthonitrile were purchased from Sigma-Aldrich Co., Inc. 4-(trifluoromethyl)benzonitrile and 3,5-difluorobenzonitrile were purchased from Apollo Scientific Ltd. $PhI(OBz)_2$ was prepared according to a known procedure.[1] $PhI(NTs_2)_2$ and $PhI(NMs_2)_2$ were synthesized according to the Muñiz's procedure.[2]

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

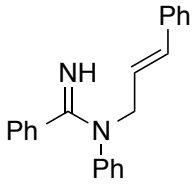
A typical procedure for synthesis of *N*-alkenylamidine 1a:



To a mixture of *N*-cinnamylaniline[4] (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

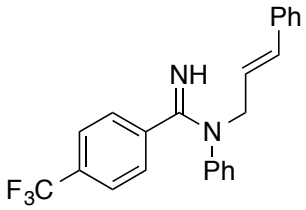
triethylamine:ethyl acetate = 3:97) afforded **1a** (2.604 g, 8.34 mmol) in 63% yield as a pale yellow solid.

***N*-Cinnamyl-*N*-phenylbenzimidamide (1a):**



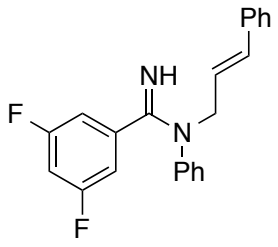
mp: 87-88 °C; IR (NaCl) 3310, 3032, 2924, 1674, 1566, 1497, 1435, 1396, 1234, 1180, 949 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 (2H, d, J = 4.4 Hz), 6.44-6.54 (2H, m), 6.95-7.00 (3H, m), 7.09-7.21 (6H, m), 7.25-7.36 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.6, 124.9, 125.5, 126.4, 126.9, 127.3, 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*-Cinnamyl-*N*-phenyl-4-(trifluoromethyl)benzimidamide (1b):**



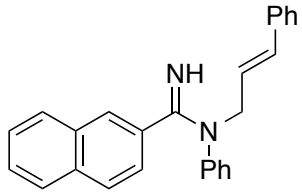
79% yield as a yellow oil from *N*-cinnamylaniline and 4-(trifluoromethyl)benzonitrile. IR (NaCl) 3318, 3032, 2932, 1589, 1497, 1412, 1327, 1173, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (2H, d, J = 5.2 Hz), 6.42-6.54 (2H, m), 6.98-7.03 (3H, m), 7.13-7.36 (7H, m), 7.41-7.46 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.7, 123.7 (q, J = 270.4 Hz), 124.9, 125.1 (q, J = 3.7 Hz), 125.6, 126.4, 127.1, 127.5, 128.0, 128.4, 129.0, 130.7 (q, J = 32.4 Hz), 132.4, 136.8, 142.0, 144.6, 166.2; ESIHRMS: Found: m/z 381.1578. Calcd for $C_{23}H_{20}N_2F_3$: $(M+H)^+$ 381.1579.

***N*-Cinnamyl-3,5-difluoro-*N*-phenylbenzimidamide (1c):**



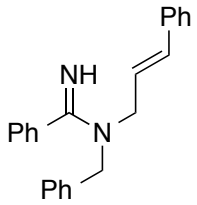
86% yield as a yellow oil from *N*-cinnamylaniline and 3,5-difluorobenzonitrile.
IR (NaCl) 3318, 3032, 2924, 1574, 1497, 1435, 1396, 1157, 1119, 988, 864 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.68 (2H, d, *J* = 5.2 Hz), 6.40-6.52 (2H, m), 6.64 (1H, tt, *J* = 2.4, 8.8 Hz), 6.84 (2H, d, *J* = 5.6 Hz), 6.98-7.06 (3H, m), 7.15-7.36 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8, 104.3 (t, *J* = 25.1 Hz), 111.0 (dd, *J* = 7.3, 18.9 Hz), 124.7, 125.7, 126.4, 127.0, 127.5, 128.4, 129.0, 132.5, 136.7, 141.7 (t, *J* = 8.6 Hz), 144.5, 162.4 (dd, *J* = 12.4, 248.3 Hz), 165.1; ESIHRMS: Found: m/z 349.1519. Calcd for $C_{22}H_{19}N_2F_2$: $(M+H)^+$ 349.1516.

_N_-Cinnamyl-_N_-phenyl-2-naphthimidamide (1d):



65% yield as a pale yellow solid from *N*-cinnamylaniline and 3,5-difluorobenzonitrile.
mp: 130-131 °C; IR (NaCl) 3302, 3032, 2932, 1566, 1497, 1404, 1358, 1165, 972 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.78 (2H, d, *J* = 4.4 Hz), 6.48-6.57 (2H, m), 6.94 (1H, tt, *J* = 2.0, 6.8 Hz), 7.05-7.11 (4H, m), 7.19-7.38 (6H, m), 7.42-7.46 (2H, m), 7.62 (1H, d, *J* = 8.8 Hz), 7.71-7.77 (2H, m), 7.88 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.8, 125.02, 125.04, 125.5, 126.38, 126.42, 126.7, 127.0, 127.4, 127.5, 127.6, 127.7, 128.3, 128.4, 128.8, 132.1, 132.7, 133.2, 136.1, 137.0, 145.2, 167.8; ESIHRMS: Found: m/z 363.1857. Calcd for $C_{26}H_{23}N_2$: $(M+H)^+$ 363.1861.

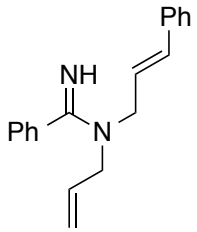
_N_-Benzyl-_N_-cinnamylbenzimidamide (1e):



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}; ^{1}H 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.

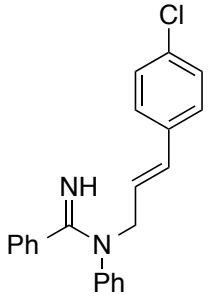
_N_-Allyl-_N_-cinnamylbenzimidamide (1f):



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 (1g):

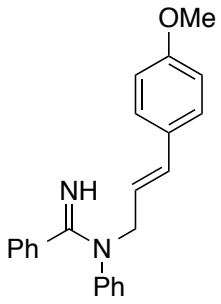


59% yield as a pale yellow solid from (*E*)-*N*-(3-(4-chlorophenyl)allyl)aniline[7] and benzonitrile.

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.

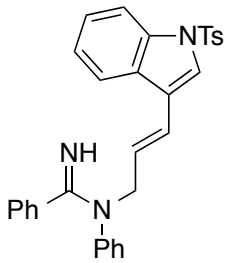
(*E*)-*N*-(3-(4-Methoxyphenyl)allyl)-*N*-phenylbenzimidamide (1h):



83% yield as a pale yellow oil from (*E*)-*N*-(3-(4-chlorophenyl)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.

(*E*)-*N*-Phenyl-*N*-(3-(1-tosyl-1*H*-indol-3-yl)allyl)benzimidamide (1i):

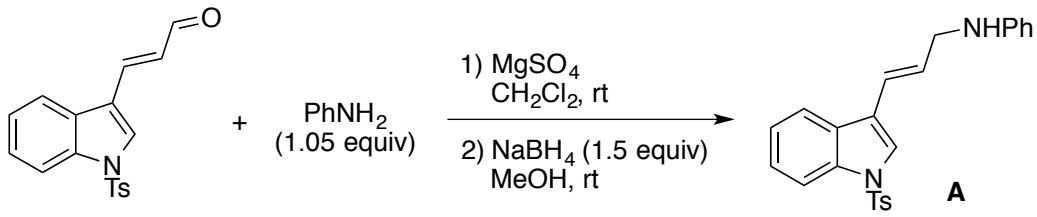


62% yield as a sticky yellow oil from (*E*)-*N*-(3-(1-tosyl-1*H*-indol-3-yl)allyl)aniline **A** (preparation method was shown below) and benzonitrile.

IR (NaCl) 3318, 3055, 2940, 1566, 1497, 1443, 1366, 1173, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 4.76 (2H, d, *J* = 5.2 Hz), 6.52 (1H, dt, *J* = 5.2, 16.0 Hz), 6.58 (1H, d, *J* = 16.0 Hz), 6.98-7.02 (3H, m), 7.14 (2H, t, *J* = 8.0 Hz), 7.19-7.32 (9H, m), 7.55 (1H, s), 7.65 (1H, d, *J* = 8.0 Hz), 7.74 (2H, d, *J* = 8.4 Hz), 7.97 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 54.0, 113.6, 120.2, 120.3, 122.3, 123.3,

123.6, 124.8, 125.1, 126.8, 126.9, 127.0, 127.7, 128.1, 128.7, 128.9, 129.1, 129.8, 135.1, 135.4, 138.5, 144.9, 145.3, 167.8; ESIHRMS: Found: m/z 506.1904. Calcd for $C_{31}H_{28}N_3O_2S$: $(M+H)^+$ 506.1902.

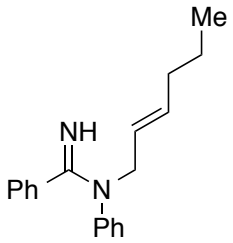
Preparation of (*E*)-*N*-(3-(1-tosyl-1*H*-indol-3-yl)allyl)aniline A.



To a 50 mL two-neck round-bottomed flask under a nitrogen atmosphere was added (*E*)-3-(1-tosyl-1*H*-indol-3-yl)acrylaldehyde[8] (1.319 g, 4.05 mmol), aniline (0.39 mL, 4.25 mmol) and anhydrous $MgSO_4$ (1.02 g, 8.47 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred at room temperature for 12 h. The mixture was then filterd and washed with CH_2Cl_2. The filtrate was then concentrated to give the crude imine, which was dissolved in 10 mL methanol. $NaBH_4$ (0.230 g, 6.08 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:CH_2Cl_2 = 75:15:15) to give amine **A** (1.260 g, 3.13 mmol) in 77% yield as yellow solid.

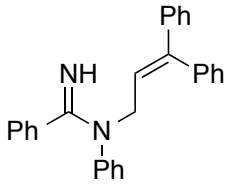
mp: 119-120 °C; IR (NaCl) 3402, 3024, 2916, 1597, 1504, 1443, 1366, 1173, 1126 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (3H, s), 3.86 (1H, s br), 3.95 (2H, dd, *J* = 1.2, 5.6 Hz), 6.58 (1H, dt, *J* = 5.6, 16.0 Hz), 6.65-6.69 (3H, m), 6.73 (1H, t, *J* = 7.2 Hz), 7.17-7.21 (4H, m), 7.24 (1H, t, *J* = 7.2 Hz), 7.32 (1H, t, *J* = 7.2 Hz), 7.55 (1H, s), 7.68 (1H, d, *J* = 7.6 Hz), 7.74 (2H, d, *J* = 8.4 Hz), 7.98 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 46.5, 113.0, 113.7, 117.7, 120.1, 120.3, 122.0, 123.4, 123.7, 124.9, 126.8, 128.4, 129.0, 129.3, 129.9, 135.1, 135.5, 145.0, 148.0; ESIHRMS: Found: m/z 403.1493. Calcd for $C_{24}H_{23}N_2O_2S$: $(M+H)^+$ 403.1480.

(*E*)-*N*-(Hex-2-en-1-yl)-*N*-phenylbenzimidamide (1j):



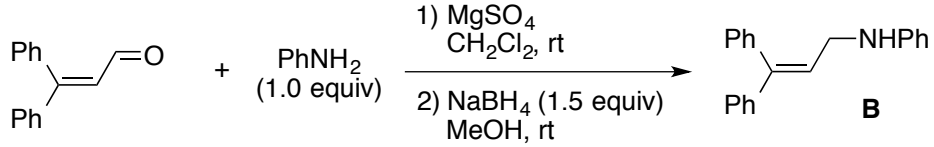
67% yield as a pale yellow oil from (*E*)-*N*-(hex-2-en-1-yl)aniline[9] and benzonitrile.
IR (NaCl) 3310, 3032, 2924, 1589, 1566, 1497, 1396, 1350, 1180, 1126, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2 Hz), 1.33 (2H, tq, *J* = 7.2, 7.2 Hz), 1.98 (2H, dt, *J* = 7.2, 7.2 Hz), 4.50 (2H, d, *J* = 5.6 Hz), 5.55 (1H, dt, *J* = 7.2, 15.2 Hz), 5.68 (1H, dt, *J* = 5.6, 15.2 Hz), 6.95-6.98 (3H, m), 7.09-7.18 (5H, m), 7.26-7.30 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 22.2, 34.2, 53.3, 124.7, 125.3, 126.9, 127.6, 127.9, 128.4, 128.6, 133.3, 138.7, 145.2, 167.6; ESIHRMS: Found: m/z 279.1860. Calcd for $C_{19}H_{23}N_2$: $(M+H)^+$ 279.1861.

***N*-(3,3-Diphenylallyl)-*N*-phenylbenzimidamide (1k):**



67% yield as a sticky pale yellow oil from *N*-(3,3-diphenylallyl)aniline **B** (preparation method was shown below) 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.

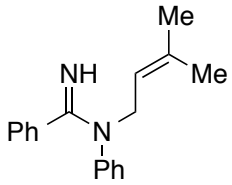
Preparation of *N*-(3,3-diphenylallyl)aniline B.



Aniline **B** was prepared in a similar way to aniline **A** from 3,3-diphenylacrylaldehyde[10] and aniline (1 equiv was used).

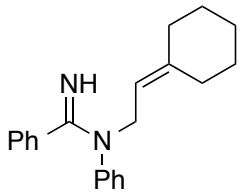
Yield: 71%; Yellow oil; IR (NaCl) 3410, 3055, 3024, 2909, 1605, 1504, 1443, 1319, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.78 (1H, s br), 3.82 (2H, d, *J* = 6.8 Hz), 6.18 (1H, t, *J* = 6.8 Hz), 6.56-6.58 (2H, m), 6.89 (1H, t, *J* = 7.6 Hz), 7.13-7.41 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.3, 113.0, 117.5, 126.3, 127.4, 127.5, 128.0, 128.1, 128.3, 129.2, 129.7, 139.2, 141.9, 144.2, 147.9; ESIHRMS: Found: m/z 286.1596. Calcd for $C_{21}H_{20}N$: $(M+H)^+$ 286.1596.

_N_-(3-Methylbut-2-en-1-yl)-_N_-phenylbenzimidamide (1l):



57% yield as a yellow oil from *N*-(3-methylbut-2-en-1-yl)aniline[11] 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.

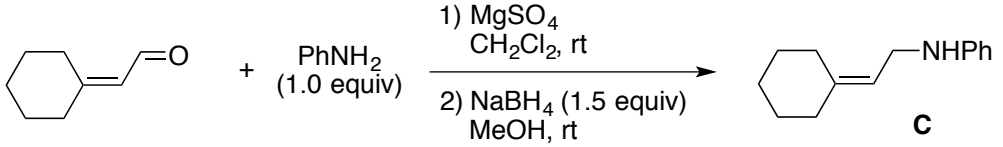
_N_-(2-Cyclohexylideneethyl)-_N_-phenylbenzimidamide (1m):



64% yield as a yellow solid from *N*-(2-cyclohexylideneethyl)aniline **C** (preparation method was shown below) 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.

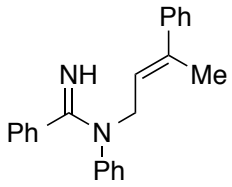
Preparation of *N*-(2-cyclohexylideneethyl)aniline C.



Aniline **C** was prepared in a similar way to aniline **A** from 2-cyclohexylideneacetaldehyde[12] and aniline (1 equiv was used).

Yield: 60%; Yellow oil; IR (NaCl) 3410, 3048, 2924, 2847, 1605, 1504, 1443, 1319, 1250 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.50-1.56 (6H, m), 2.11-2.22 (4H, m), 3.54 (1H, s br), 3.69 (2H, d, *J* = 6.8 Hz), 5.28 (1H, t, *J* = 6.8 Hz), 6.60-6.62 (2H, m), 6.99 (1H, t, *J* = 7.6 Hz), 7.15-7.19 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.7, 27.8, 28.5, 29.0, 37.0, 41.1, 112.9, 117.2, 118.2, 129.1, 143.7, 148.4; ESIHRMS: Found: m/z 202.1598. Calcd for $C_{14}H_{20}N$: $(M+H)^+$ 202.1596.

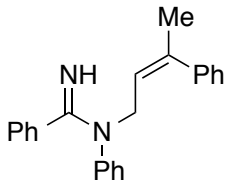
(*E*)-*N*-Phenyl-*N*-(3-phenylbut-2-en-1-yl)benzimidamide (1n):



1n (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.

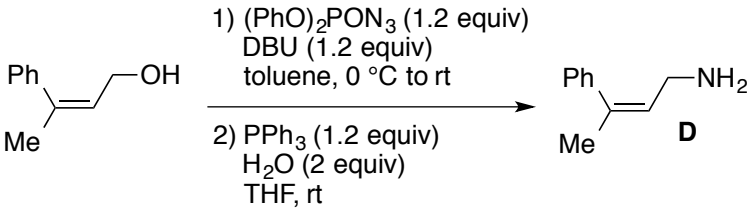
(*Z*)-*N*-Phenyl-*N*-(3-phenylbut-2-en-1-yl)benzimidamide (1o):

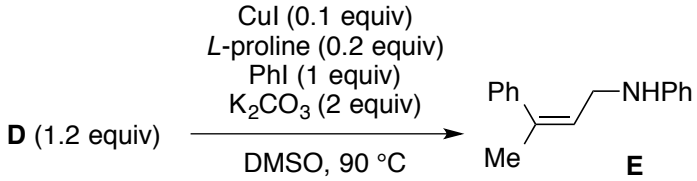


67% yield as a yellow oil from (*Z*)-*N*-(3-phenylbut-2-en-1-yl)aniline **E** (preparation method was shown below) and benzonitrile.

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.

Preparation of (*Z*)-*N*-(3-phenylbut-2-en-1-yl)aniline E.





A mixture of (*Z*)-3-phenylbut-2-en-1-ol[13] (1.240 g, 8.47 mmol) and diphenyl phosphorazidate (2.763 g, 10.04 mmol) was dissolved in dry toluene (15 mL). The mixture was cooled to 0 °C under N_2, and DBU (1.5 mL, 10.04 mmol) was added. The reaction was warmed to room temperature and stirred for 2 h. The reaction was then quenched with water and extracted with ethyl acetate. 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 = 95:5) to give (*Z*)-(4-azidobut-2-en-2-yl)benzene (1.336g, 7.71 mmol, this compound will partially epimerize to the corresponding (*E*) diastereomer at

room temperature, used immediately for the next Staudinger reaction) in 92% yield as a colorless oil.

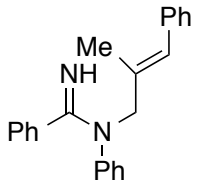
To a mixture of (*Z*)-(4-azidobut-2-en-2-yl)benzene (0.941 g, 5.43 mmol) and triphenylphosphine (1.709 g, 6.52 mmol) in THF (10 mL) was added H_2O (0.2 mL, 11.11 mmol) at 0 °C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was evaporated and the resulting residue was purified by flash column chromatography (silica gel; CH_2Cl_2:ethyl acetate = 35:65 then triethylamine:ethyl acetate = 5:95) afforded amine **D** (0.758 g, 5.15 mmol) in 95% yield as a colorless oil.

IR (NaCl) 3356, 3294, 3055, 3024, 2970, 1574, 1489, 1443, 1381, 1304 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (3H, d, *J* = 1.2 Hz), 3.22 (2H, dd, *J* = 0.8, 6.8 Hz), 5.57 (1H, tq, *J* = 1.2, 6.8 Hz), 7.15-7.17 (2H, m), 7.23-7.27 (1H, m), 7.33 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 40.6, 126.8, 127.8, 128.1, 128.7, 137.4, 141.4; ESIHRMS: Found: m/z 148.1125. Calcd for $C_{10}H_{14}N$: $(M+H)^+$ 148.1126.

To a 50 mL two-neck round-bottomed flask under a nitrogen atmosphere was added iodobenzene (0.48 mL, 4.29 mmol), amine **D** (0.758 g, 5.15 mmol), CuI (0.082 g, 0.43 mmol), *L*-proline (0.099 g, 0.86 mmol), and K_2CO_3 (1.186 g, 8.58 mmol) in DMSO (8 mL). The mixture was then heated to 90 °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 = 90:10) afforded the aniline **E** (0.838 g, 3.75 mmol) in 87% yield as a yellow solid.

mp: 63-64 °C; IR (NaCl) 3402, 3055, 3017, 2845, 1605, 1504, 1435, 1312, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08 (3H, d, *J* = 1.2 Hz), 3.66 (2H, d, *J* = 6.8 Hz), 5.63 (1H, tq, *J* = 1.2, 6.8 Hz), 6.52 (2H, d, *J* = 8.0 Hz), 6.67 (1H, t, *J* = 7.6 Hz), 7.11-7.15 (2H, m), 7.20-7.23 (3H, m), 7.35 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 42.8, 112.9, 117.3, 124.3, 127.1, 127.7, 128.2, 129.1, 139.8, 141.0, 148.0; ESIHRMS: Found: m/z 224.1438. Calcd for $C_{16}H_{18}N$: $(M+H)^+$ 224.1439.

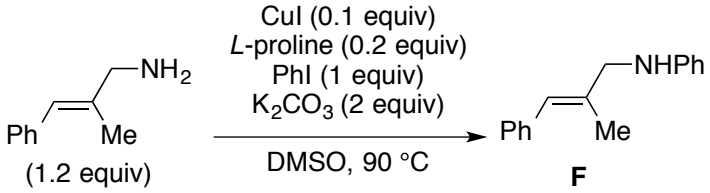
(*E*)-*N*-(2-Methyl-3-phenylallyl)-*N*-phenylbenzimidamide (1p):



59% yield as a pale yellow oil from (*E*)-*N*-(2-methyl-3-phenylallyl)aniline **F** (preparation method was shown below) 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.

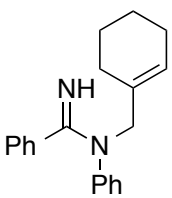
Preparation of (*E*)-*N*-(2-methyl-3-phenylallyl)aniline F.



Aniline **F** was prepared in a similar way to aniline **E** from (*E*)-2-methyl-3-phenylprop-2-en-1-amine[14] and iodobenzene.

Yield: 68%; yellow oil; IR (NaCl) 3418, 3048, 3024, 2909, 1605, 1504, 1443, 1312, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.92 (3H, s), 3.83 (2H, s), 3.94 (1H, s br), 6.53 (1H, s), 6.65 (2H, d, *J* = 7.6 Hz), 6.68-6.72 (1H, m), 7.16-7.26 (5H, m), 7.31 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3, 52.3, 112.9, 117.4, 125.6, 126.3, 128.1, 128.8, 129.2, 135.8, 137.8, 148.3; ESIHRMS: Found: m/z 224.1442. Calcd for $C_{16}H_{18}N$: $(M+H)^+$ 224.1439.

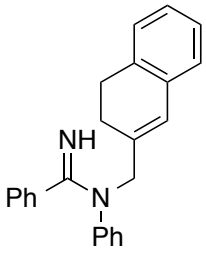
***N*-(Cyclohex-1-en-1-ylmethyl)-*N*-phenylbenzimidamide (1q):**



53% yield as a pale yellow oil from *N*-(cyclohex-1-en-1-ylmethyl)aniline[15] 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.

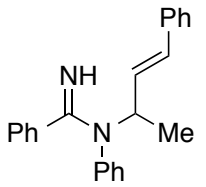
_N_-((3,4-Dihydronaphthalen-2-yl)methyl)-_N_-phenylbenzimidamide (1r):



59% yield as a pale yellow oil from *N*-((3,4-dihydronaphthalen-2-yl)methyl)aniline[16] 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.

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

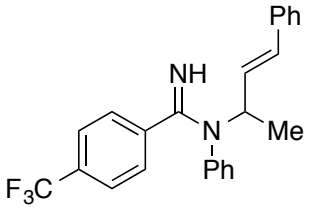


23% yield as a yellow oil from (*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline[17] and benzonitrile.

IR (NaCl) 3310, 3055, 3032, 2978, 1566, 1497, 1450, 1396, 1180, 972, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.38 (3H, d, J = 7.2 Hz), 5.65 (1H, dq, J = 6.4, 7.2 Hz),

6.17 (1H, s br), 6.36 (1H, dd, J = 6.4, 16.0 Hz), 6.50 (1H, d, J = 16.0 Hz), 7.01-7.08 (3H, m), 7.12-7.17 (5H, m), 7.20-7.37 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 53.9, 126.3, 126.4, 127.3, 127.5, 127.8, 128.2, 128.39, 128.44, 130.39, 130.43, 130.8, 137.0, 138.7, 140.9, 168.2; ESIHRMS: Found: m/z 327.1857. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

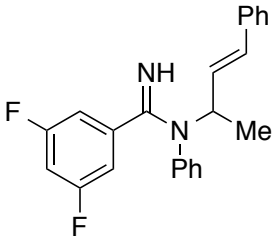
(*E*)-*N*-Phenyl-*N*-(4-phenylbut-3-en-2-yl)-4-(trifluoromethyl)benzimidamide (1t):



44% yield as a yellow solid from (*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline and 4-(trifluoromethyl)benzonitrile.

mp: 71-73 °C; IR (NaCl) 3318, 3032, 2970, 2932, 1566, 1497, 1412, 1327, 1165, 1126, 1065, 972 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (3H, d, J = 6.8 Hz), 5.63 (1H, s br), 6.35 (1H, dd, J = 6.4, 16.0 Hz), 6.52 (1H, d, J = 16.0 Hz), 7.01 (2H, d, J = 7.2 Hz), 7.08 (1H, t, J = 7.2 Hz), 7.15 (2H, t, J = 7.2 Hz), 7.23 (1H, t, J = 7.2 Hz), 7.31 (2H, t, J = 7.6 Hz), 7.35-7.38 (4H, m), 7.42 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 54.0, 123.7 (q, J = 270.6 Hz), 125.0 (q, J = 3.7 Hz), 126.4, 126.8, 127.5, 127.9, 128.5 (overlapped), 130.3 (q, J = 32.4 Hz), 130.6, 130.69, 130.72, 137.0, 140.8, 142.7, 166.9; ESIHRMS: Found: m/z 395.1732. Calcd for $C_{24}H_{22}N_2F_3$: $(M+H)^+$ 395.1735.

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

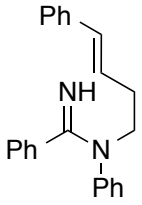


62% yield as a yellow oil from (*E*)-*N*-(4-phenylbut-3-en-2-yl)aniline and 3,5-difluorobenzonitrile.

IR (NaCl) 3318, 3063, 3032, 2978, 1589, 1489, 1404, 1304, 1234, 1140, 972 cm^{-1}; ^{1}H 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.

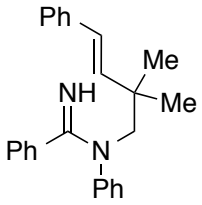
(*E*)-*N*-Phenyl-*N*-(4-phenylbut-3-en-1-yl)benzimidamide (1v):



47% yield as a yellow oil from (*E*)-*N*-(4-phenylbut-3-en-1-yl)aniline[18] and benzonitrile.

IR (NaCl) 3010, 3024, 2932, 1566, 1497, 1443, 1404, 1342, 1180, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (2H, dt, J = 7.2, 7.2 Hz), 4.09 (2H, t, J = 7.2 Hz), 6.24 (1H, dt, J = 7.2, 16.0 Hz), 6.43 (1H, d, J = 16.0 Hz), 6.96-6.99 (3H, m), 7.10-7.31 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.9, 51.2, 125.0, 125.9, 126.9, 127.2, 127.5, 127.6, 127.9, 128.3, 128.7 (overlapped), 131.6, 137.5, 138.6, 145.1, 167.8; ESIHRMS: Found: m/z 327.1860. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

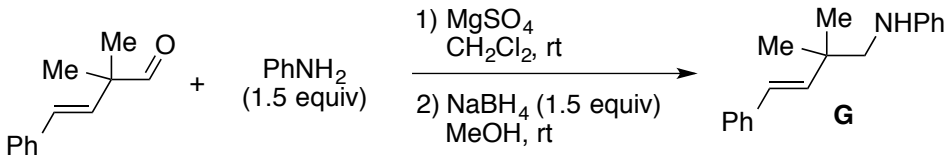
(*E*)-*N*-(2,2-Dimethyl-4-phenylbut-3-en-1-yl)-*N*-phenylbenzimidamide (1w):



60% yield as a pale yellow oil from (*E*)-*N*-(2,2-dimethyl-4-phenylbut-3-en-1-yl)aniline **G** (preparation method was shown below) and benzonitrile.

IR (NaCl) 3318, 3055, 3032, 2963, 2924, 1574, 1497, 1450, 1404, 1335, 1180, 1134, 972, 910 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (6H, s), 4.16 (2H, s), 6.20 (1H, d, J = 16.0 Hz), 6.26 (1H, d, J = 16.0 Hz), 6.87 (1H, t, J = 7.2 Hz), 6.95-7.26 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.1, 40.2, 60.0, 124.8, 125.8, 126.1, 126.6, 127.5, 127.8, 127.9, 128.2, 128.3, 128.4, 138.0, 139.4, 139.6, 146.2, 169.0; ESIHRMS: Found: m/z 355.2173. Calcd for $C_{25}H_{27}N_2$: $(M+H)^+$ 355.2174.

Preparation of (*E*)-*N*-(2,2-dimethyl-4-phenylbut-3-en-1-yl)aniline G.

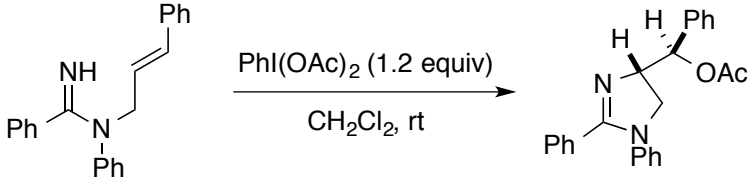


Aniline **G** was prepared in a similar way to aniline **A** from (*E*)-2,2-dimethyl-4-phenylbut-3-enal[19] and aniline (1.5 equiv).

Yield 84%; yellow solid; mp: 49-50 °C; IR (NaCl) 3410, 3024, 2963, 2870, 1605, 1504, 1427, 1319, 1258, 1219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (6H, s), 3.06 (2H, s), 3.60 (1H, s br), 6.20 (1H, d, *J* = 16.4 Hz), 6.42 (1H, d, *J* = 16.4 Hz), 6.59-6.61 (2H, m), 6.67 (1H, t, *J* = 7.6 Hz), 7.12-7.38 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 37.7, 54.6, 112.7, 117.1, 126.2, 127.2, 128.1, 128.6, 129.2, 137.3, 137.7, 148.7; ESIHRMS: Found: m/z 252.1749. Calcd for $C_{18}H_{22}N$: $(M+H)^+$ 252.1752.

3. Aminooxygenation of alkenylamidines for the synthesis of dihydroimiazoles 2, 3, 4a and tetrahydropyrimidine 2w

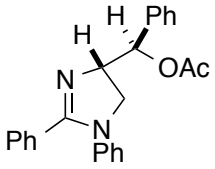
Typical Procedure:



1a **2a**

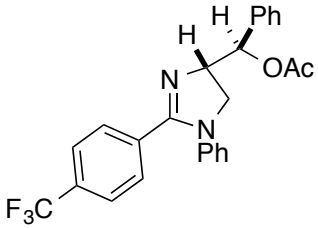
To a stirred solution of $PhI(OAc)_2$ (116.4 mg, 0.361 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of *N*-Cinnamyl-*N*-phenylbenzimidamide (**1a**) (94.1 mg, 0.301 mmol) in 2 mL CH_2Cl_2. The reaction mixture was then stirred for 20 h at room temperature under a N_2 atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with CH_2Cl_2. The combined organic extracts were washed with water 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 = 50:50 then triethylamine:ethyl acetate = 2:98) to provide **2a** (87.7 mg, 0.237 mmol) in 79% yield.

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



Yellow oil; IR (NaCl) 3040, 2940, 2886, 1736, 1643, 1597, 1497, 1412, 1304, 1234, 1026, 918 cm^{-1}; ^1H 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.

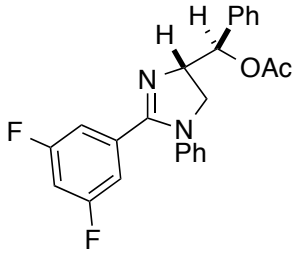
(*R)-Phenyl((*S**)-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-yl)methyl acetate (2b):**



75% yield from **1b** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

Yellow oil; IR (NaCl) 3032, 2947, 1744, 1597, 1497, 1412, 1373, 1327, 1234, 1126, 1018, 849 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (3H, s), 3.87 (1H, dd, *J* = 6.0, 10.0 Hz), 4.16 (1H, dd, *J* = 10.0, 10.8 Hz), 4.70 (1H, ddd, *J* = 4.0, 6.0, 10.8 Hz), 6.07 (1H, d, *J* = 4.0 Hz), 6.58-6.60 (2H, m), 7.00 (1H, t, *J* = 7.6 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.26-7.39 (5H, m), 7.52 (2H, d, *J* = 8.4 Hz), 7.57 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 54.9, 68.3, 76.8, 123.0, 123.7 (q, *J* = 270.6 Hz), 124.2, 125.1 (q, *J* = 3.7 Hz), 126.7, 128.0, 128.3, 128.9, 129.1, 131.8 (q, *J* = 32.4 Hz), 134.2, 137.1, 142.1, 162.0, 169.9; ESIHRMS: Found: m/z 439.1630. Calcd for $C_{25}H_{22}N_2O_2F_3$: $(M+H)^+$ 439.1633.

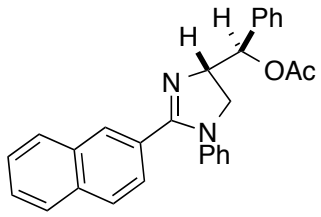
(*R)-((*S**)-2-(3,5-Difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2c):**



75% yield from **1c** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 23 h.

Yellow oil; IR (NaCl) 3071, 3040, 2940, 1744, 1589, 1489, 1435, 1396, 1234, 1119, 988, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.84 (1H, dd, *J* = 6.4, 10.0 Hz), 4.14 (1H, dd, *J* = 10.0, 10.8 Hz), 4.70 (1H, ddd, *J* = 4.0, 6.4, 10.8 Hz), 6.04 (1H, d, *J* = 4.0 Hz), 6.59-6.61 (2H, m), 6.78 (1H, tt, *J* = 2.4, 8.8 Hz), 6.94-7.00 (2H, m), 7.03 (1H, t, *J* = 7.6 Hz), 7.14-7.18 (2H, m), 7.26-7.39 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 55.1, 68.0, 76.7, 105.6 (t, *J* = 25.1 Hz), 111.9 (dd, *J* = 7.6, 19.1 Hz), 123.1, 124.6, 126.8, 128.1, 128.3, 129.0, 133.7 (t, *J* = 9.9 Hz), 136.9, 141.9, 161.4 (t, *J* = 3.0 Hz), 162.4 (dd, *J* = 12.4, 247.8 Hz), 169.9; ESIHRMS: Found: m/z 407.1570. Calcd for $C_{24}H_{21}N_2O_2F_2$: $(M+H)^+$ 407.1571.

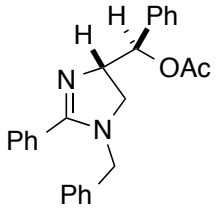
(*R)-((*S**)-2-(Naphthalen-2-yl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2d):**



56% yield from **1d** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 18 h.

Yellow oil; IR (NaCl) 3040, 2940, 2886, 1736, 1589, 1497, 1389, 1304, 1234, 1142, 1026, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.91 (1H, dd, *J* = 6.0, 10.0 Hz), 4.19 (1H, dd, *J* = 10.0, 10.8 Hz), 4.71 (1H, ddd, *J* = 4.0, 6.0, 10.8 Hz), 6.13 (1H, d, *J* = 4.0 Hz), 6.64 (2H, d, *J* = 7.6 Hz), 6.95 (1H, t, *J* = 7.6 Hz), 7.08 (2H, t, *J* = 7.6 Hz), 7.27 (1H, t, *J* = 7.2 Hz), 7.33 (2H, t, *J* = 7.6 Hz), 7.40-7.50 (5H, m), 7.69 (1H, d, *J* = 8.4 Hz), 7.78 (2H, d, *J* = 8.0 Hz), 8.06 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 54.8, 68.3, 76.9, 122.7, 123.6, 125.6, 126.3, 126.7, 127.0, 127.6, 127.7, 127.9, 128.2, 128.3, 128.6, 128.7, 129.0, 132.7, 134.0, 137.4, 142.7, 163.1, 170.0; ESIHRMS: Found: m/z 421.1920. Calcd for $C_{28}H_{25}N_2O_2$: $(M+H)^+$ 421.1916.

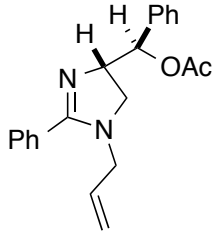
(*R)-((*S**)-1-Benzyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2e):**



88% yield from **1e** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

Pale yellow oil; IR (NaCl) 3201, 3032, 2932, 2886, 1736, 1612, 1574, 1497, 1450, 1366, 1304, 1242 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.30 (1H, dd, *J* = 7.2, 10.0 Hz), 3.42 (1H, dd, *J* = 10.0, 10.8 Hz), 4.11 (1H, d, *J* = 16.0 Hz), 4.24 (1H, d, *J* = 16.0 Hz), 4.61 (1H, ddd, *J* = 4.4, 7.2, 10.8 Hz), 5.98 (1H, d, *J* = 4.4 Hz), 7.09 (2H, d, *J* = 7.2 Hz), 7.24-7.42 (11H, m), 7.48-7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 51.6, 52.4, 68.5, 77.2, 126.7, 127.1, 127.2, 127.9, 128.1, 128.2, 128.5, 128.6, 130.0, 130.9, 137.4, 137.6, 167.6, 170.0; ESIHRMS: Found: m/z 385.1914. Calcd for $C_{25}H_{25}N_2O_2$: $(M+H)^+$ 385.1916.

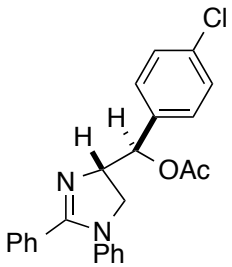
(*R)-((*S**)-1-Allyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2f):**



73% yield from **1f** and $PhI(OAc)_2$ (1.4 equiv); reaction time: 32 h.

Pale yellow oil; IR (NaCl) 3063, 3032, 2932, 1744, 1574, 1497, 1450, 1412, 1373, 1234, 1026, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.35 (1H, dd, *J* = 7.2, 10.0 Hz), 3.48 (1H, dd, *J* = 10.0, 10.8 Hz), 3.49-3.66 (2H, m), 4.58 (1H, ddd, *J* = 4.4, 7.2, 10.8 Hz), 5.10-5.15 (2H, m), 5.63 (1H, ddt, *J* = 5.2, 10.0, 14.8 Hz), 6.00 (1H, d, *J* = 4.4 Hz), 7.26-7.30 (1H, m), 7.32-7.40 (7H, m), 7.45-7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 51.0, 51.5, 68.5, 77.2, 116.5, 127.0, 127.8, 128.0, 128.2, 128.3, 129.9, 130.9, 133.8, 137.6, 167.5, 170.0; ESIHRMS: Found: m/z 335.1761. Calcd for $C_{21}H_{23}N_2O_3$: $(M+H)^+$ 335.1760.

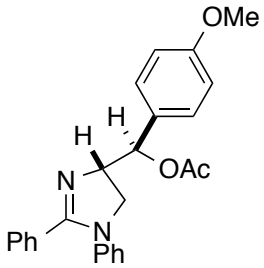
(*R)-(4-Chlorophenyl)((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)methyl acetate (2g):**



94% yield from **1g** and $PhI(OAc)_2$ (1.3 equiv); reaction time: 36 h.

Yellow oil; IR (NaCl) 3032, 2940, 1744, 1597, 1574, 1497, 1373, 1234, 1088, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.10 (3H, s), 3.79 (1H, dd, *J* = 6.0, 10.0 Hz), 4.19 (1H, dd, *J* = 10.0, 10.8 Hz), 4.86 (1H, ddd, *J* = 4.4, 6.0, 10.8 Hz), 5.97 (1H, d, *J* = 4.4 Hz), 6.59-6.61 (2H, m), 6.99 (1H, t, *J* = 7.6 Hz), 7.11-7.14 (2H, m), 7.24-7.44 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 54.7, 67.2, 76.3, 122.7, 123.8, 128.1, 128.2, 128.3, 128.6, 128.7, 130.1, 130.2, 133.8, 135.7, 142.1, 163.4, 169.8; ESIHRMS: Found: m/z 405.1369. Calcd for $C_{24}H_{22}N_2O_2Cl$: $(M+H)^+$ 405.1370.

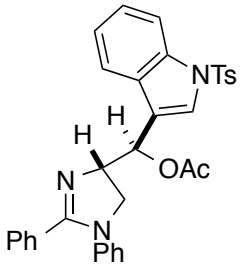
(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(4-methoxyphenyl)methyl acetate (2h):**



94% yield from **1h** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 20 h.

Pale yellow oil; IR (NaCl) 3017, 2940, 1744, 1597, 1497, 1381, 1296, 1242, 1180, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (3H, s), 3.77 (3H, s), 3.82 (1H, dd, *J* = 6.4, 10.0 Hz), 4.17 (1H, dd, *J* = 10.0, 10.4 Hz), 4.64 (1H, ddd, *J* = 4.0, 6.4, 10.4 Hz), 5.98 (1H, d, *J* = 4.0 Hz), 6.59-6.61 (2H, m), 6.85 (2H, d, *J* = 8.8 Hz), 6.96 (1H, t, *J* = 7.2 Hz), 7.11 (2H, t, *J* = 7.6 Hz), 7.26-7.36 (5H, m), 7.43-7.45 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 54.8, 55.1, 67.5, 76.6, 113.6, 122.7, 123.6, 128.06, 128.12, 128.5, 128.7, 129.2, 130.1, 130.4, 142.3, 159.3, 163.2, 170.0; ESIHRMS: Found: m/z 401.1868. Calcd for $C_{25}H_{25}N_2O_3$: $(M+H)^+$ 401.1865.

(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(1-tosyl-1*H*-indol-3-yl)methyl acetate (2i):**



79% yield, dr = 6.1:1 from **1i** and $PhI(OAc)_2$ (1.2 equiv), the mixture could be partially separated by column chromatography to give the pure **2i** (the major diastereomer) in 23% yield and the mixture of **2i** (major:minor = 4.0:1) in 56%; reaction time: 7 h.

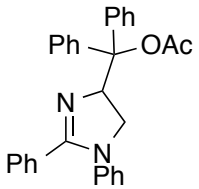
The major diastereomer :

Sticky yellow oil; IR (NaCl) 3024, 2940, 1744, 1597, 1574, 1497, 1450, 1373, 1227, 1173, 1126, 980 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (3H, s), 2.32 (3H, s), 3.88 (1H, dd, *J* = 6.4, 10.0 Hz), 4.10 (1H, dd, *J* = 10.0, 10.8 Hz), 4.79 (1H, ddd, *J* = 4.0, 6.4, 10.8 Hz), 6.44 (1H, d, *J* = 4.0 Hz), 6.66 (2H, d, *J* = 7.6 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 7.11-7.18 (4H, m), 7.21-7.33 (4H, m), 7.36 (1H, t, *J* = 7.6 Hz), 7.42-7.45 (2H, m), 7.57 (1H, s), 7.69-7.73 (3H, m), 7.93 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.5, 54.6, 66.7, 70.8, 113.6, 119.1, 120.3, 122.7, 123.4, 123.8, 123.9, 125.0, 126.8, 128.2, 128.7, 128.75, 128.80, 129.9, 130.2, 130.6, 135.0, 135.1, 142.5, 145.0, 163.4, 169.8; ESIHRMS: Found: m/z 564.1956. Calcd for $C_{33}H_{30}N_3O_4S$: $(M+H)^+$ 564.1957.

The mixture of two diastereomers (major:minor = 4.0:1):

Sticky yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 2.08 (3H × 0.25, s), 2.09 (3H, s), 2.31 (3H × 0.25, s), 2.32 (3H, s), 3.75 (1H × 0.25, dd, *J* = 6.4, 10.4 Hz), 3.87 (1H, dd, *J* = 6.4, 10.0 Hz), 4.04-4.13 (1H + 1H × 0.25, m), 4.75-4.86 (1H + 1H × 0.25, m), 6.23 (1H × 0.25, d, *J* = 6.4 Hz), 6.43 (1H, d, *J* = 4.0 Hz), 6.52 (2H × 0.25, d, *J* = 7.6 Hz), 6.66 (2H, d, *J* = 7.6 Hz), 6.94 (1H × 0.25, t, *J* = 7.6 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 7.06 (2H × 0.25, t, *J* = 7.6 Hz), 7.11-7.40 (9H + 9H × 0.25, m), 7.43-7.45 (2H, m), 7.57 (1H, s), 7.67-7.78 (3H + 4H × 0.25, m), 7.89-7.94 (1H + 1H × 0.25, m).

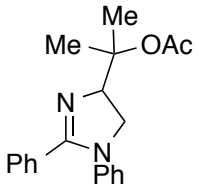
(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)diphenylmethyl acetate (2k):



94% yield from **1k** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 16 h.

white solid; mp: 69-70 °C; IR (NaCl) 3063, 3024, 2940, 1744, 1589, 1574, 1497, 1396, 1304, 1242, 1219, 1018, 980 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 3.88 (1H, dd, *J* = 5.2, 10.0 Hz), 4.39 (1H, dd, *J* = 10.0, 10.8 Hz), 6.10 (2H, d, *J* = 7.6 Hz), 6.18 (1H, dd, *J* = 5.2, 10.8 Hz), 6.87 (1H, t, *J* = 7.6 Hz), 6.94-6.98 (2H, m), 7.14-7.18 (5H, m), 7.24-7.33 (8H, m), 7.71 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.3, 54.8, 66.3, 87.8, 123.0, 123.5, 126.9, 127.3, 127.5, 127.6, 127.9, 128.0, 128.2, 128.3, 128.8, 129.8, 130.6, 140.3, 142.2, 162.4, 169.1; ESIHRMS: Found: m/z 447.2068. Calcd for $C_{30}H_{27}N_2O_2$: $(M+H)^+$ 447.2073.

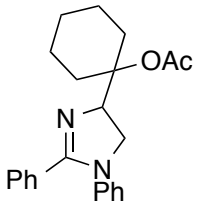
2-(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)propan-2-yl acetate (2l):



81% yield from **1l** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 20 h.

Brown oil; IR (NaCl) 2979, 2940, 1728, 1597, 1497, 1373, 1258, 1142, 1026, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.52 (3H, s), 1.68 (3H, s), 1.95 (3H, s), 3.89 (1H, dd, *J* = 6.8, 10.0 Hz), 4.22 (1H, dd, *J* = 10.0, 10.8 Hz), 4.54 (1H, dd, *J* = 6.8, 10.8 Hz), 6.77-6.79 (2H, m), 6.99 (1H, t, *J* = 7.2 Hz), 7.16 (2H, t, *J* = 7.6 Hz), 7.28 (2H, t, *J* = 7.6 Hz), 7.34-7.38 (1H, m), 7.49-7.51 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 22.3, 23.4, 54.7, 71.0, 83.4, 122.8, 123.7, 128.2, 128.72, 128.74, 130.2, 130.6, 142.5, 163.0, 170.3; ESIHRMS: Found: m/z 323.1761. Calcd for $C_{20}H_{23}N_2O_2$: $(M+H)^+$ 323.1760.

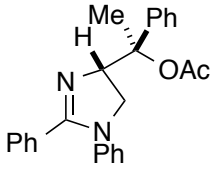
1-(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)cyclohexyl acetate (2m):



79% yield from **1m** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

Yellow oil; IR (NaCl) 3063, 2932, 2862, 1728, 1597, 1497, 1450, 1381, 1265, 1234, 1134, 1026, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25-1.31 (1H, m), 1.38-1.68 (6H, m), 1.82-1.95 (2H, m), 2.04 (3H, s), 2.60-2.63 (1H, m), 3.88 (1H, dd, *J* = 7.6, 9.6 Hz), 4.08 (1H, dd, *J* = 9.6, 10.8 Hz), 5.15 (1H, dd, *J* = 7.6, 10.8 Hz), 6.75 (2H, d, *J* = 8.4 Hz), 6.96 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.27 (2H, t, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.6, 22.1, 25.3, 29.4, 30.5, 54.0, 68.5, 85.5, 122.6, 123.3, 128.1, 128.62, 128.63, 129.8, 131.2, 142.8, 162.1, 170.3; ESIHRMS: Found: m/z 363.2071. Calcd for $C_{23}H_{27}N_2O_2$: $(M+H)^+$ 363.2073.

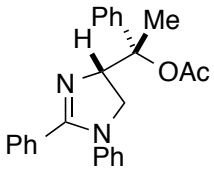
(*R)-1-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-1-phenylethyl acetate (2n):**



96% yield, dr = >20:1 (as an inseparable mixture) from **1n** (E/Z = 20:1) and $PhI(OAc)_2$ (1.2 equiv); reaction time: 20 h.

Pale yellow solid; mp: 123-124 °C; IR (NaCl) 3017, 2940, 1736, 1574, 1497, 1450, 1373, 1304, 1242, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (3H, s), 2.06 (3H, s), 3.82 (1H, dd, *J* = 6.4, 10.0 Hz), 4.10 (1H, dd, *J* = 10.0, 10.8 Hz), 4.65 (1H, dd, *J* = 7.6, 10.8 Hz), 6.60 (2H, d, *J* = 7.6 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 7.10 (2H, t, *J* = 7.6 Hz), 7.21-7.38 (8H, m), 7.47-7.49 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 22.1, 54.8, 72.9, 84.7, 122.9, 123.6, 125.5, 127.1, 128.0, 128.1, 128.6, 128.8, 130.0, 130.8, 141.7, 142.7, 163.1, 169.5; ESIHRMS: Found: m/z 385.1916. Calcd for $C_{25}H_{25}N_2O_2$: $(M+H)^+$ 385.1916.

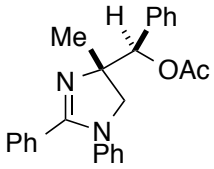
(*S)-1-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-1-phenylethyl acetate (2o):**



77% yield from **1o** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 17 h.

Pale yellow oil; IR (NaCl) 3032, 2940, 2886, 1736, 1597, 1497, 1450, 1389, 1304, 1242, 1173, 1042, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 2.13 (3H, s), 3.71 (1H, dd, *J* = 6.0, 10.8 Hz), 4.05 (1H, dd, *J* = 10.8, 10.8 Hz), 4.73 (1H, dd, *J* = 6.0, 10.8 Hz), 6.30 (2H, d, *J* = 7.6 Hz), 6.90 (1H, t, *J* = 7.6 Hz), 7.01 (2H, t, *J* = 7.6 Hz), 7.15-7.25 (5H, m), 7.29-7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.3, 54.5, 71.8, 84.7, 122.9, 123.7, 125.8, 127.2, 127.6, 128.0, 128.4, 128.7, 130.0, 130.6, 140.0, 142.1, 163.4, 169.5; ESIHRMS: Found: m/z 385.1913. Calcd for $C_{25}H_{25}N_2O_2$: $(M+H)^+$ 385.1916.

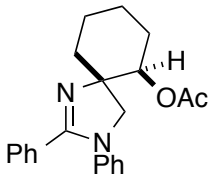
(*R)-((*S**)-4-Methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2p):**



63% yield from **1p** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 22 h.

Brown solid; mp: 121-122 °C; IR (NaCl) 3032, 2932, 1744, 1589, 1574, 1497, 1450, 1373, 1319, 1234, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.45 (3H, s), 2.07 (3H, s), 3.79 (1H, d, *J* = 9.6 Hz), 4.06 (1H, d, *J* = 9.6 Hz), 5.86 (1H, s), 6.54 (2H, d, *J* = 7.6 Hz), 6.94 (1H, t, *J* = 7.6 Hz), 7.09 (2H, t, *J* = 7.6 Hz), 7.23-7.35 (6H, m), 7.41 (2H, d, *J* = 6.4 Hz), 7.45 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 25.4, 61.1, 70.5, 80.0, 122.5, 123.4, 127.6, 127.8, 127.95, 128.04, 128.5, 128.7, 129.9, 130.8, 137.0, 142.5, 161.2, 169.8; ESIHRMS: Found: m/z 385.1916. Calcd for $C_{25}H_{25}N_2O_2$: $(M+H)^+$ 385.1916.

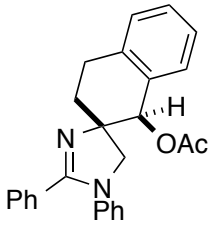
(5*S,6*R**)-2,3-Diphenyl-1,3-diazaspiro[4.5]dec-1-en-6-yl acetate (2q):**



73% yield from **1q** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 125-126 °C; IR (NaCl) 3024, 2940, 2862, 1736, 1597, 1497, 1450, 1381, 1312, 1242, 1142, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 1.24-1.53 (3H, m), 1.71-1.92 (4H, m), 1.94 (3H, s), 2.02-2.06 (1H, m), 3.88 (1H, d, *J* = 9.6 Hz), 4.01 (1H, d, *J* = 9.6 Hz), 5.00 (1H, dd, *J* = 4.4, 10.8 Hz), 6.75 (2H, d, *J* = 8.0 Hz), 6.97 (1H, t, *J* = 7.6 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), 7.47 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 21.8, 23.4, 27.9, 37.4, 59.0, 71.2, 76.5, 122.2, 123.1, 128.2, 128.6, 128.7, 130.0, 130.9, 142.9, 160.8, 170.0; ESIHRMS: Found: m/z 349.1915. Calcd for $C_{22}H_{25}N_2O_2$: $(M+H)^+$ 349.1916.

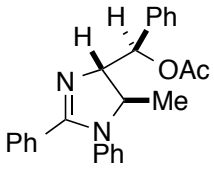
(1'*R,2'*S**)-1,2-Diphenyl-1,3',4',5-tetrahydro-1'*H*-spiro[imidazole-4,2'-naphthalen]-1'-yl acetate (2r):**



90% yield from **1r** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 20 h.

Brown solid; mp: 203-204 °C; IR (NaCl) 3024, 2940, 2870, 1728, 1589, 1497, 1450, 1396, 1327, 1227, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 2.07 (3H, s), 2.18 (1H, ddd, *J* = 5.6, 6.4, 13.2 Hz), 2.40 (1H, ddd, *J* = 6.4, 9.2, 15.2 Hz), 2.97 (1H, ddd, *J* = 6.4, 8.8, 15.6 Hz), 3.13 (1H, ddd, *J* = 5.6, 11.2, 17.2 Hz), 3.94 (1H, d, *J* = 10.0 Hz), 3.97 (1H, d, *J* = 10.0 Hz), 6.26 (1H, s), 6.71 (2H, d, *J* = 7.6 Hz), 6.94 (1H, t, *J* = 7.6 Hz), 7.10-7.30 (8H, m), 7.36 (1H, t, *J* = 7.2 Hz), 7.48 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 25.5, 32.6, 59.2, 69.8, 75.3, 121.8, 123.0, 126.2, 127.7, 128.2 (overlapped), 128.6 (overlapped), 128.8, 130.1, 131.0, 133.7, 136.2, 142.4, 161.3, 170.6; ESIHRMS: Found: m/z 397.1917. Calcd for $C_{26}H_{25}N_2O_2$: $(M+H)^+$ 397.1916.

(*R)-((4*S**,5*R**)-5-Methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2s):**



76% yield, dr = 14:1 from **1s** and $PhI(OAc)_2$ (1.2 equiv), the mixture could be partially separated by column chromatography to give the pure **2s** (the major diastereomer) in 61% yield and the mixture of **2s** (major:minor = 2.0:1) in 15%; reaction time: 22 h.

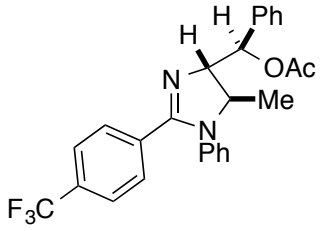
The major diastereomer :

Brown solid; mp: 130-131 °C; IR (NaCl) 3032, 2970, 2932, 1744, 1574, 1497, 1450, 1381, 1234, 1142, 1065, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (3H, d, *J* = 6.4 Hz), 2.10 (3H, s), 3.87 (1H, dq, *J* = 6.0, 6.4 Hz), 4.20 (1H, dd, *J* = 3.6, 6.0 Hz), 6.05 (1H, d, *J* = 3.6 Hz), 6.65-6.68 (2H, m), 7.03 (1H, tt, *J* = 1.6, 7.6 Hz), 7.11-7.15 (2H, m), 7.19-7.38 (8H, m), 7.45-7.47 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 22.4, 62.7, 76.8, 76.9, 124.87, 124.94, 126.9, 127.9, 128.0, 128.2, 128.82, 128.84, 128.9, 131.0, 137.0, 143.1, 163.6, 170.0; ESIHRMS: Found: m/z 385.1919. Calcd for $C_{25}H_{25}N_2O_2$: $(M+H)^+$ 385.1916.

The mixture of two diastereomers (major:minor = 2.0:1):

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (3H, d, *J* = 6.4 Hz), 1.28 (3H × 0.5, d, *J* = 6.8 Hz), 2.08 (3H × 0.5, s), 2.11 (3H, s), 3.87 (1H, dq, *J* = 6.0, 6.4 Hz), 4.20 (1H, dd, *J* = 4.0, 6.0 Hz), 4.45 (1H × 0.5, dq, *J* = 6.8, 8.8 Hz), 4.69 (1H × 0.5, dd, *J* = 8.8, 9.2 Hz), 5.98 (1H × 0.5, d, *J* = 9.2 Hz), 6.05 (1H, d, *J* = 4.0 Hz), 6.66 (2H, d, *J* = 7.6 Hz), 6.78 (2H × 0.5, d, *J* = 8.0 Hz), 7.02-7.06 (1H + 1H × 0.33, m), 7.11-7.38 (10H + 10H × 0.33, m), 7.45-7.47 (2H, m), 7.50-7.51 (2H × 0.33, m).

(*R)-((4*S**,5*R**)-5-Methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2t):**



73% yield, dr = 6.2:1 from **1t** and $PhI(OAc)_2$ (1.2 equiv), the mixture could be partially separated by column chromatography to give the pure **2t** (the major diastereomer) in 32% yield and the mixture of **2t** (major:minor = 3.0:1) in 41%; reaction time: 24 h.

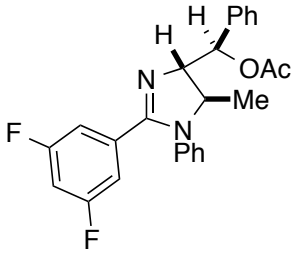
The major diastereomer :

Yellow solid; mp: 40-41 °C; IR (NaCl) 3024, 2970, 2932, 1744, 1597, 1497, 1412, 1381, 1327, 1234, 1134, 1065 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, d, *J* = 6.4 Hz), 2.12 (3H, s), 3.89 (1H, dq, *J* = 6.0, 6.4 Hz), 4.24 (1H, dd, *J* = 4.0, 6.0 Hz), 6.05 (1H, d, *J* = 4.0 Hz), 6.64 (2H, d, *J* = 8.0 Hz), 7.08 (1H, t, *J* = 7.2 Hz), 7.16 (2H, t, *J* = 7.6 Hz), 7.26-7.38 (5H, m), 7.47 (2H, d, *J* = 8.4 Hz), 7.57 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 22.3, 63.0, 76.8, 77.0, 123.7 (q, *J* = 270.7 Hz), 124.9 (q, *J* = 3.7 Hz), 125.2, 125.5, 126.9, 128.0, 128.2, 129.1, 129.2, 131.6 (q, *J* = 32.3 Hz), 134.5, 136.8, 142.5, 162.4, 169.9; ESIHRMS: Found: m/z 453.1791. Calcd for $C_{26}H_{24}N_2O_2F_3$: $(M+H)^+$ 453.1790.

The mixture of two diastereomers (major:minor = 3.0:1):

Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H + 3H × 0.33, d, *J* = 6.4 Hz), 2.08 (3H × 0.33, s), 2.12 (3H, s), 3.88 (1H, dq, *J* = 6.0, 6.4 Hz), 4.23 (1H, dd, *J* = 4.0, 6.0 Hz), 4.47 (1H × 0.33, dq, *J* = 6.4, 8.8 Hz), 4.71 (1H × 0.33, dd, *J* = 8.8, 8.8 Hz), 5.98 (1H × 0.33, d, *J* = 8.8 Hz), 6.05 (1H, d, *J* = 4.0 Hz), 6.64 (2H, d, *J* = 7.6 Hz), 6.78 (2H × 0.33, d, *J* = 8.0 Hz), 7.06-7.10 (1H + 1H × 0.33, m), 7.14-7.22 (2H + 2H × 0.33, m), 7.28-7.58 (9H + 9H × 0.33, m).

(*R)-((4*S**,5*R**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2u):**

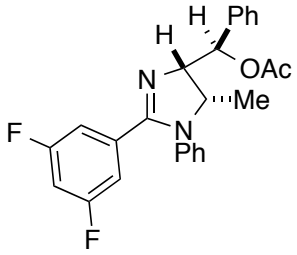


71% yield (major diastereomer, two diastereomers can be separated, overall yield 81%, dr = 7.1:1) from **1u** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

Yellow oil; IR (NaCl) 3071, 2970, 2924, 1744, 1589, 1489, 1443, 1389, 1327, 1234, 1119, 1026, 988, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, d, *J* = 6.4 Hz), 2.12 (3H, s), 3.85 (1H, dq, *J* = 6.0, 6.4 Hz), 4.23 (1H, dd, *J* = 4.0, 6.0 Hz), 6.03 (1H, d,

J = 4.0 Hz), 6.63-6.66 (2H, m), 6.73 (1H, tt, *J* = 2.4, 8.8 Hz), 6.95-7.01 (2H, m), 7.08-7.19 (3H, m), 7.26-7.38 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 22.2, 63.2, 76.6, 76.7, 105.4 (t, *J* = 25.1 Hz), 111.9 (dd, *J* = 7.6, 19.2 Hz), 125.3, 125.8, 126.9, 128.0, 128.2, 129.2, 134.1 (t, *J* = 9.8 Hz), 136.7, 142.2, 161.8 (t, *J* = 3.0 Hz), 162.3 (dd, *J* = 12.4, 247.5 Hz), 169.9; ESIHRMS: Found: m/z 421.1732. Calcd for $C_{25}H_{23}N_2O_2F_2$: $(M+H)^+$ 421.1728.

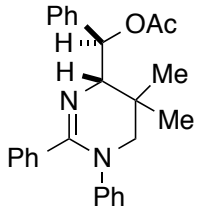
(*R)-((4*S**,5*S**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate (2u'):**



10% yield (minor diastereomer, two diastereomers can be separated, overall yield 81%, dr = 7.1:1) from **1u** and $PhI(OAc)_2$ (1.2 equiv); reaction time: 24 h.

Yellow oil; IR (NaCl) 3071, 3032, 2978, 1736, 1589, 1497, 1443, 1381, 1327, 1234, 1119, 988, 864 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, d, *J* = 6.4 Hz), 2.08 (3H, s), 4.44 (1H, dq, *J* = 6.4, 8.8 Hz), 4.69 (1H, dd, *J* = 8.8, 9.2 Hz), 5.95 (1H, d, *J* = 9.2 Hz), 6.72 (1H, tt, *J* = 2.4, 8.8 Hz), 6.80 (2H, d, *J* = 7.6 Hz), 6.84-6.89 (2H, m), 7.10 (1H, t, *J* = 7.6 Hz), 7.22 (2H, t, *J* = 7.6 Hz), 7.29-7.33 (1H, m), 7.37 (2H, t, *J* = 7.6 Hz), 7.48 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.3, 63.6, 70.9, 75.0, 105.3 (t, *J* = 25.1 Hz), 112.0 (dd, *J* = 7.6, 19.2 Hz), 125.0, 125.4, 127.7, 128.1, 128.2, 129.1, 134.3 (t, *J* = 9.9 Hz), 138.9, 140.7, 161.3 (t, *J* = 3.0 Hz), 162.3 (dd, *J* = 12.4, 247.1 Hz), 169.7; ESIHRMS: Found: m/z 421.1723. Calcd for $C_{25}H_{23}N_2O_2F_2$: $(M+H)^+$ 421.1728.

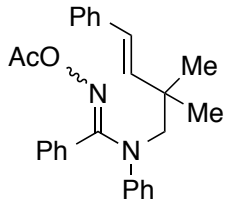
(*R)-((4*S**)-5,5-Dimethyl-1,2-diphenyl-1,4,5,6-tetrahydropyrimidin-4-yl)(phenyl)methyl acetate (2w):**



52% yield from **1w** and $PhI(OAc)_2$ (2.0 equiv); reaction time: 32 h.

Yellow oil; IR (NaCl) 3032, 2963, 2932, 1736, 1620, 1597, 1497, 1373, 1242, 1026, 972, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, s), 1.22 (3H, s), 2.08 (3H, s), 3.29 (1H, d, *J* = 12.0 Hz), 3.41 (1H, dd, *J* = 1.2, 12.0 Hz), 3.95 (1H, dd, *J* = 1.2, 6.8 Hz), 5.91 (1H, d, *J* = 6.8 Hz), 6.70-6.72 (2H, m), 6.93 (1H, tt, *J* = 1.2, 7.6 Hz), 7.02-7.10 (7H, m), 7.31 (1H, tt, *J* = 1.2, 7.6 Hz), 7.36-7.40 (2H, m), 7.54-7.56 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 22.0, 27.5, 32.6, 60.5, 66.3, 77.5, 124.3, 125.2, 127.5, 127.7, 127.9, 128.4, 128.58, 128.63, 128.8, 137.2, 139.7, 146.5, 154.9, 170.0; ESIHRMS: Found: m/z 413.2236. Calcd for $C_{27}H_{29}N_2O_2$: $(M+H)^+$ 413.2229.

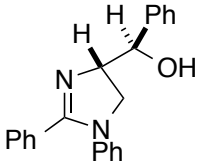
_N_'-Acetoxy-_N_-((_E_)-2,2-dimethyl-4-phenylbut-3-en-1-yl)-_N_-phenylbenzimidamide (5w):

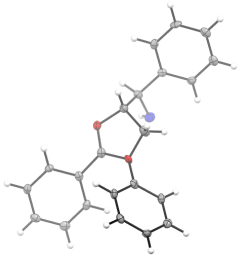


32% yield from **1w** as a single isomer and $PhI(OAc)_2$ (2.0 equiv); reaction time: 32 h.

Yellow oil; IR (NaCl) 3017, 2970, 2932, 1690, 1597, 1497, 1389, 1373, 1296, 1265, 1219 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (6H, s), 2.07 (3H, s), 3.82 (2H, s), 6.05 (1H, d, *J* = 16.0 Hz), 6.21 (1H, d, *J* = 16.0 Hz), 6.61-6.63 (2H, m), 6.81 (2H, s br), 7.05-7.25 (11H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.1, 25.9, 39.8, 61.3, 126.0, 126.1, 126.8, 126.9, 127.0, 127.3 (overlapped), 128.3, 128.5, 128.7, 137.4, 137.6, 138.l, 142.1, 156.9, 170.6; ESIHRMS: Found: m/z 413.2226. Calcd for $C_{27}H_{29}N_2O_2$: $(M+H)^+$ 413.2229.

(_R_*)-((_S_*)-1,2-Diphenyl-4,5-dihydro-1_H_-imidazol-4-yl)(phenyl)methanol (3a):

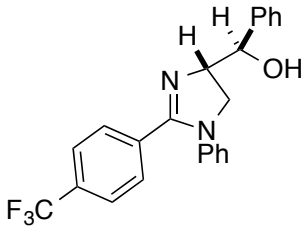




82% yield from **1a** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 7 h.

Colorless crystal (CCDC-1023045); mp: 211-212 °C; IR (NaCl) 3024, 2932, 2685, 1574, 1497, 1443, 1396, 1288, 1049 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.59 (1H, dd, *J* = 10.0, 10.8 Hz), 4.05 (1H, dd, *J* = 10.0, 10.0 Hz), 4.60 (1H, ddd, *J* = 3.2, 10.0, 10.8 Hz), 5.24 (1H, d, *J* = 3.2 Hz), 6.65-6.68 (2H, m), 6.93 (1H, t, *J* = 7.6 Hz), 7.06-7.10 (2H, m), 7.16-7.38 (8H, m), 7.44-7.46 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.9, 70.2, 72.5, 122.6, 123.5, 125.8, 127.0, 128.06, 128.12, 128.5, 128.8, 130.0, 130.6, 141.1, 142.4, 163.7; ESIHRMS: Found: m/z 329.1658. Calcd for $C_{22}H_{21}N_2O$: $(M+H)^+$ 329.1654.

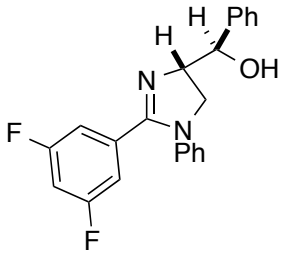
(*R)-Phenyl((S*)-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-yl)methanol (3b):**



80% yield from **1b** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 22 h.

White solid; mp: 175-176 °C; IR (NaCl) 3024, 2885, 2839, 1597, 1497, 1412, 1327, 1211 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.58 (1H, dd, *J* = 9.6, 10.4 Hz), 4.11 (1H, dd, *J* = 9.6, 9.6 Hz), 4.70 (1H, ddd, *J* = 2.8, 9.6, 10.4 Hz), 5.17 (1H, d, *J* = 2.8 Hz), 6.66-6.68 (2H, m), 6.98 (1H, t, *J* = 7.6 Hz), 7.11 (2H, t, *J* = 7.6 Hz), 7.20-7.32 (5H, m), 7.38 (2H, d, *J* = 8.4 Hz), 7.55 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.0, 70.4, 72.1, 122.8, 123.6 (q, *J* = 270.8 Hz), 124.1, 125.0 (q, *J* = 3.7 Hz), 125.6, 127.1, 128.2, 128.8, 129.2, 131.8 (q, *J* = 32.4 Hz), 133.8, 141.1, 142.0, 162.4; ESIHRMS: Found: m/z 397.1530. Calcd for $C_{23}H_{20}N_2OF_3$: $(M+H)^+$ 397.1528.

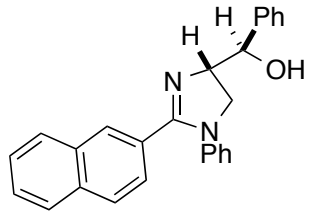
(*R)-((*S**)-2-(3,5-Difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3c):**



77% yield from **1c** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 23 h.

White solid; mp: 171-172 °C; IR (NaCl) 3156, 3017, 2886, 1582, 1489, 1435, 1396, 1319, 1119, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.54 (1H, dd, *J* = 9.6, 10.8 Hz), 4.10 (1H, dd, *J* = 9.6, 9.6 Hz), 4.56 (1H, ddd, *J* = 2.8, 9.6, 10.8 Hz), 5.11 (1H, d, *J* = 2.8 Hz), 6.58 (1H, tt, *J* = 2.4, 8.8 Hz), 6.68-6.70 (2H, m), 6.93-7.01 (3H, m), 7.11-7.15 (2H, m), 7.20-7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.1, 70.4, 72.0, 105.5 (t, *J* = 25.1 Hz), 111.9 (dd, *J* = 7.6, 19.1 Hz), 122.8, 124.3, 125.6, 127.0, 128.1, 128.9, 133.5 (t, *J* = 9.9 Hz), 141.1, 141.8, 161.6 (t, *J* = 2.9 Hz), 162.4 (dd, *J* = 12.4, 247.8 Hz); ESIHRMS: Found: m/z 365.1468. Calcd for $C_{22}H_{19}N_2OF_2$: $(M+H)^+$ 365.1465.

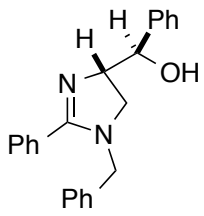
(*R)-((*S**)-2-(Naphthalen-2-yl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3d):**



65% yield from **1d** and $PhI(OCOCF_3)_2$ (1.5 equiv); reaction time: 24 h.

White solid; mp: 233-235 °C; IR (NaCl) 3024, 2878, 2832, 1589, 1489, 1404, 1281, 1096, 910 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 3.92 (1H, dd, *J* = 8.0, 9.6 Hz), 3.97 (1H, dd, *J* = 9.6, 10.4 Hz), 4.44 (1H, ddd, *J* = 4.8, 8.0, 10.4 Hz), 4.80 (1H, dd, *J* = 4.4, 4.8 Hz), 5.48 (1H, d, *J* = 4.4 Hz), 6.76 (2H, d, *J* = 7.6 Hz), 6.92 (1H, t, *J* = 7.6 Hz), 7.12 (2H, t, *J* = 8.0 Hz), 7.24 (1H, t, *J* = 7.2 Hz), 7.34 (2H, t, *J* = 7.6 Hz), 7.44-7.57 (5H, m), 7.86 (2H, t, *J* = 8.8 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 8.05 (1H, s); ^{13}C NMR (100 MHz, DMSO) δ 54.3, 70.6, 73.8, 122.1, 122.8, 125.6, 126.43, 126.45, 126.6, 127.0, 127.4, 127.5, 127.7, 128.1, 128.2, 128.5, 129.0, 132.1, 133.2, 143.3, 161.0; ESIHRMS: Found: m/z 379.1811. Calcd for $C_{26}H_{23}N_2O$: $(M+H)^+$ 379.1810.

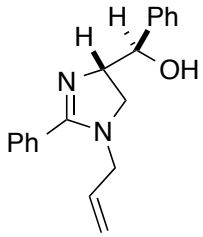
(*R)-((*S**)-1-Benzyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3e):**



92% yield from **1e** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 15 h.

White solid; mp: 112-113 °C; IR (NaCl) 3063, 3017, 2909, 2847, 1597, 1497, 1443, 1358, 1265, 1119, 1034, 910 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 3.08 (1H, dd, *J* = 9.6, 10.8 Hz), 3.34 (1H, dd, *J* = 9.2, 9.6 Hz), 4.08 (1H, d, *J* = 16.0 Hz), 4.34 (1H, d, *J* = 16.0 Hz), 4.48 (1H, ddd, *J* = 2.8, 9.2, 10.8 Hz), 5.16 (1H, d, *J* = 2.8 Hz), 7.14 (2H, d, *J* = 7.2 Hz), 7.18-7.35 (11H, m), 7.52-7.54 (2H, m); ^{13}C NMR (100 MHz, DMSO) δ 49.8, 52.4, 70.5, 72.8, 125.9, 126.7 (overlapped), 127.2, 128.0, 128.1, 128.4, 128.6, 130.0, 130.5, 137.6, 141.3, 168.1; ESIHRMS: Found: m/z 343.1805. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

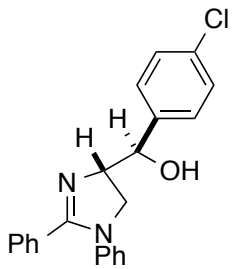
(*R)-((*S**)-1-Allyl-2-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3f):**



72% yield from **1f** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 142-143 °C; IR (NaCl) 3017, 2932, 2878, 1589, 1566, 1497, 1443, 1412, 1103, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.16 (1H, dd, *J* = 9.6, 10.8 Hz), 3.37 (1H, dd, *J* = 9.2, 9.6 Hz), 3.53 (1H, dd, *J* = 5.2, 16.8 Hz), 3.69 (1H, dd, *J* = 5.2, 16.8 Hz), 4.47 (1H, ddd, *J* = 2.8, 9.2, 10.8 Hz), 5.10-5.18 (3H, m), 5.63 (1H, ddt, *J* = 5.2, 10.0, 15.6 Hz), 7.23 (1H, t, *J* = 7.2 Hz), 7.28-7.37 (7H, m), 7.50-7.52 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.8, 51.1, 70.4, 72.8, 116.6, 125.9, 126.8, 128.0, 128.1, 128.3, 130.0, 130.6, 133.8, 141.3, 168.1; ESIHRMS: Found: m/z 293.1651. Calcd for $C_{19}H_{21}N_2O$: $(M+H)^+$ 293.1654.

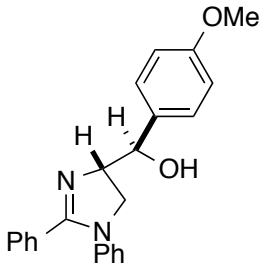
(*R)-(4-Chlorophenyl)((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)methanol (3g):**



76% yield from **1g** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 13 h.

White solid; mp: 229-230 °C; IR (NaCl) 3024, 2886, 2824, 1589, 1566, 1489, 1404, 1358, 1288, 1088, 1049, 988 cm^{-1}; ^1H NMR (400 MHz, DMSO) δ 3.84 (1H, dd, *J* = 7.6, 9.6 Hz), 3.95 (1H, dd, *J* = 9.6, 10.4 Hz), 4.34 (1H, ddd, *J* = 4.4, 7.6, 10.4 Hz), 4.71 (1H, dd, *J* = 4.0, 4.4 Hz), 5.58 (1H, d, *J* = 4.0 Hz), 6.71 (2H, d, *J* = 7.6 Hz), 6.94 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 8.0 Hz), 7.30-7.47 (9H, m); ^{13}C NMR (100 MHz, DMSO) δ 54.5, 70.3, 73.4, 122.1, 122.8, 127.6, 128.0, 128.35, 128.37, 128.5, 129.7, 131.2, 131.3, 142.3, 143.1, 161.1; ESIHRMS: Found: m/z 363.1261. Calcd for $C_{22}H_{20}N_2OCl$: $(M+H)^+$ 363.1264.

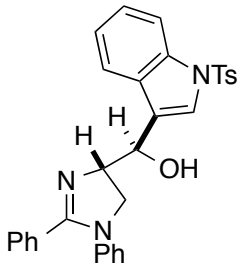
(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(4-methoxyphenyl)methanol (3h):**

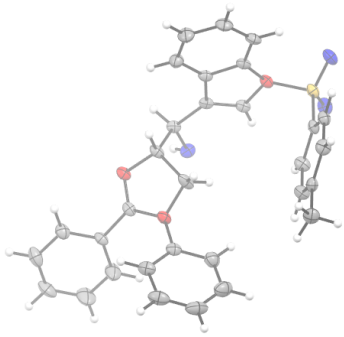


90% yield from **1h** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 14 h.

White solid; mp: 180-181 °C; IR (NaCl) 3024, 2955, 2839, 1589, 1497, 1458, 1396, 1296, 1242, 1173, 1034, 980 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.68 (1H, dd, *J* = 10.0, 10.4 Hz), 3.80 (3H, s), 4.01 (1H, dd, *J* = 9.6, 10.0 Hz), 4.60 (1H, ddd, *J* = 2.8, 9.6, 10.4 Hz), 5.22 (1H, d, *J* = 2.8 Hz), 6.69 (2H, d, *J* = 7.6 Hz), 6.88 (2H, d, *J* = 8.4 Hz), 6.95 (1H, t, *J* = 7.2 Hz), 7.10 (2H, t, *J* = 7.6 Hz), 7.26-7.37 (5H, m), 7.47-7.49 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.0, 55.2, 72.5, 113.6, 122.6, 123.4, 127.0, 128.1, 128.5, 128.8, 130.0, 130.7, 133.1, 142.5, 158.7, 163.6; ESIHRMS: Found: m/z 359.1758. Calcd for $C_{23}H_{23}N_2O_2$: $(M+H)^+$ 359.1760.

(*R)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(1-tosyl-1*H*-indol-3-yl)methanol (3i):**

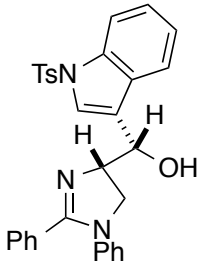




78% yield (major diastereomer, two diastereomers can be separated, overall yield 94%, dr = 4.9:1) from **1i** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

Colorless crystal (CCDC-1022937); mp: 208-210 °C; IR (NaCl) 3063, 2886, 2700, 1589, 1566, 1497, 1450, 1366, 1258, 1173, 1103, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.31 (3H, s), 3.45 (1H, dd, *J* = 10.0, 10.4 Hz), 4.01 (1H, dd, *J* = 10.0, 10.0 Hz), 4.68 (1H, ddd, *J* = 2.8, 10.0, 10.4 Hz), 5.41 (1H, d, *J* = 2.8 Hz), 6.70 (2H, d, *J* = 7.6 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 7.09-7.20 (8H, m), 7.30 (1H, t, *J* = 7.6 Hz), 7.43 (2H, d, *J* = 7.2 Hz), 7.50 (1H, d, *J* = 7.6 Hz), 7.59 (1H, s), 7.76 (2H, d, *J* = 8.4 Hz), 7.99 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.7, 67.6, 68.1, 113.8, 119.7, 122.7, 122.9, 123.2, 123.3, 123.7, 124.8, 126.8, 128.1, 128.6, 128.67, 128.70, 129.8, 130.2, 130.4, 135.3, 135.5, 142.2, 144.8, 164.1; ESIHRMS: Found: m/z 522.1857. Calcd for $C_{31}H_{28}N_3O_3S$: $(M+H)^+$ 522.1851.

(*S)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(1-tosyl-1*H*-indol-3-yl)methanol (3i'):**

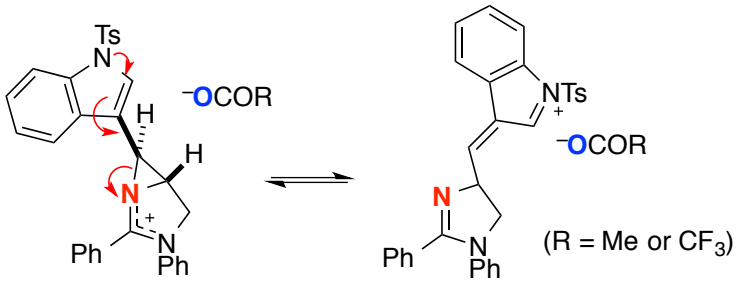


16% yield (major diastereomer, two diastereomers can be separated, overall yield 94%, dr = 4.9:1) from **1i** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

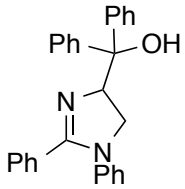
White solid; mp: 176-177 °C; IR (NaCl) 3364, 3063, 2932, 1597, 1566, 1497, 1450, 1373, 1296, 1173, 1126, 1088 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 3.70 (1H, s br), 3.78 (1H, dd, *J* = 8.0, 10.0 Hz), 3.92 (1H, dd, *J* = 10.0, 10.4 Hz), 4.77 (1H,

ddd, J = 8.0, 8.0, 10.4 Hz), 4.90 (1H, d, J = 8.0 Hz), 6.71 (2H, d, J = 7.6 Hz), 7.03 (1H, t, J = 7.6 Hz), 7.14-7.24 (5H, m), 7.28-7.32 (3H, m), 7.40 (1H, t, J = 7.6 Hz), 7.47 (2H, d, J = 7.2 Hz), 7.61 (1H, s), 7.75 (1H, d, J = 8.4 Hz), 7.84 (2H, d, J = 7.6 Hz), 7.96 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 56.0, 67.7, 71.5, 113.6, 121.1, 121.5, 123.0, 123.3, 124.0, 124.7, 124.9, 126.9, 128.3, 128.98, 129.02, 129.3, 129.9, 130.0, 130.8, 135.1, 135.5, 141.4, 145.0, 163.7; ESIHRMS: Found: m/z 522.1846. Calcd for $C_{31}H_{28}N_3O_3S$: $(M+H)^+$ 522.1851.

For the discussion on the generation of small amounts of the diastereoisomers in the reactions of indole-substituted amidine 1i: this might be attributed to partial ring opening of the putative aziridinium ion intermediate (see section 6.2 for more details) by electron-pushing from the indole moiety as shown below.



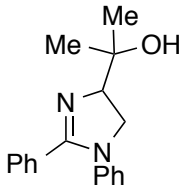
(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)diphenylmethanol (3k):



88% yield from **1k** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 16 h.

Brown solid; mp: 177-178 °C; IR (NaCl) 3017, 2955, 1589, 1566, 1497, 1450, 1396, 1281, 1165, 1034 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (1H, s br), 3.84-3.94 (2H, m), 5.44 (1H, dd, J = 10.0, 10.0 Hz), 6.62 (2H, d, J = 8.0 Hz), 6.93 (1H, t, J = 7.2 Hz), 7.07 (2H, t, J = 7.6 Hz), 7.17-7.33 (9H, m), 7.43 (2H, d, J = 7.2 Hz), 7.50 (2H, d, J = 7.6 Hz), 7.65 (2H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 70.5, 78.6, 122.9, 123.7, 126.1, 126.7, 126.9, 127.0, 128.0, 128.05, 128.08, 128.5, 128.9, 130.1, 130.7, 142.2, 144.6, 145.9, 164.4; ESIHRMS: Found: m/z 405.1961. Calcd for $C_{28}H_{25}N_2O$: $(M+H)^+$ 405.1967.

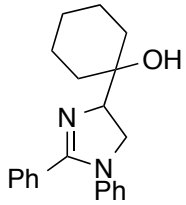
2-(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)propan-2-ol (3l):



90% yield from **1l** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 20 h.

Brown oil; IR (NaCl) 3325, 3063, 2978, 2731, 1667, 1612, 1535, 1497, 1389, 1304, 1196, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, s), 1.35 (3H, s), 2.55 (1H, s br), 3.90 (1H, dd, *J* = 8.8, 9.6 Hz), 4.05 (1H, dd, *J* = 9.6, 10.4 Hz), 4.18 (1H, dd, *J* = 8.8, 10.4 Hz), 6.77 (2H, d, *J* = 7.6 Hz), 6.98 (1H, t, *J* = 7.6 Hz), 7.14 (2H, t, *J* = 7.6 Hz), 7.27 (2H, t, *J* = 7.6 Hz), 7.35 (1H, t, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.7, 26.5, 54.9, 71.8, 73.2, 122.6, 123.5, 128.2, 128.7 (overlapped), 130.0, 131.0, 142.6, 162.9; ESIHRMS: Found: m/z 281.1654. Calcd for $C_{18}H_{21}N_2O$: $(M+H)^+$ 281.1654.

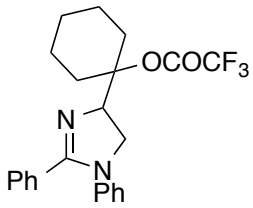
1-(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)cyclohexanol (3m):



12% yield from **1m** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 18 h.

Brown oil; IR (NaCl) 3387, 3063, 2932, 2855, 1597, 1574, 1497, 1389, 1304, 1265, 1142, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24-1.30 (1H, m), 1.37-1.43 (1H, m), 1.51-1.75 (7H, m), 1.88-1.91 (1H, m), 2.55 (1H, s br), 3.96-4.05 (2H, m), 4.20 (1H, dd, *J* = 10.0, 10.0 Hz), 6.78 (2H, d, *J* = 7.6 Hz), 6.99 (1H, t, *J* = 7.6 Hz), 7.15 (2H, t, *J* = 8.0 Hz), 7.28 (2H, t, *J* = 7.6 Hz), 7.36 (1H, t, *J* = 7.6 Hz), 7.48 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.55, 21.64, 26.0, 32.6, 35.0, 54.3, 72.2, 72.3, 122.8, 123.7, 128.2, 128.7, 128.8, 130.2, 130.7, 142.4, 163.2; ESIHRMS: Found: m/z 321.1965. Calcd for $C_{21}H_{25}N_2O$: $(M+H)^+$ 321.1967.

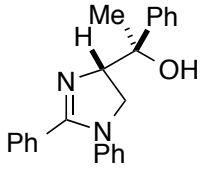
1-(1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)cyclohexyl 2,2,2-trifluoroacetate (3m'):

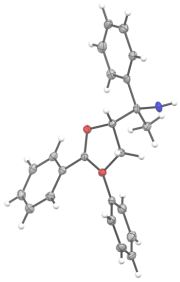


66% yield from **1m** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 18 h.

Yellow oil; IR (NaCl) 3062, 2940, 2862, 1775, 1667, 1589, 1497, 1450, 1381, 1165, 1126, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24-1.72 (7H, m), 1.90-2.00 (1H, m), 2.13-2.16 (1H, m), 2.58-2.62 (1H, m), 3.91 (1H, dd, *J* = 7.2, 10.0 Hz), 4.12 (1H, dd, *J* = 10.0, 11.2 Hz), 5.04 (1H, dd, *J* = 7.2, 10.8 Hz), 6.76-6.78 (2H, m), 7.01 (1H, t, *J* = 7.6 Hz), 7.14-7.18 (2H, m), 7.25-7.29 (2H, m), 7.36 (1H, tt, *J* = 1.2, 7.6 Hz), 7.46-7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 21.3, 24.9, 29.3, 30.6, 53.8, 68.1, 92.3, 114.5 (q, *J* = 285.6 Hz), 123.0, 124.0, 128.2, 128.7, 128.8, 130.1, 130.6, 142.3, 156.0 (q, *J* = 82.0 Hz), 163.1; ESIHRMS: Found: m/z 417.1789. Calcd for $C_{23}H_{24}N_2O_2F_3$: $(M+H)^+$ 417.1790.

(*R)-1-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-1-phenylethyl acetate (3n):**



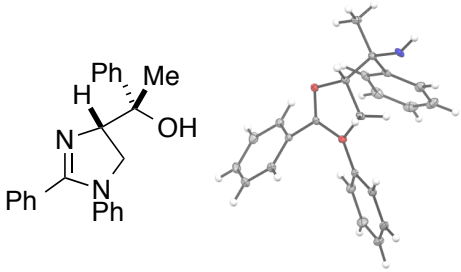


94% yield, dr = >20:1 (the major diastereomer could be recrystallized from hexane/CH_2Cl_2) from **1n** (E/Z = 20:1) and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 20 h.

Colorless crystal (CCDC-1022895); mp: 175-177 °C; IR (NaCl) 3186, 3017, 2909, 1589, 1566, 1489, 1450, 1396, 1288, 1142, 1072, 995, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.82 (3H, s), 2.78 (1H, s br), 3.65-3.74 (2H, m), 4.65 (1H, dd, *J* = 9.6, 10.4 Hz), 6.62 (2H, d, *J* = 7.6 Hz), 6.93 (1H, t, *J* = 7.6 Hz), 7.07 (2H, t, *J* = 7.6 Hz), 7.22-7.39 (6H, m), 7.47-7.50 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.1, 55.0, 73.0, 75.0, 122.7, 123.5, 125.2, 126.6, 128.1, 128.2, 128.5, 128.7, 130.1, 131.0, 142.3,

144.9, 164.1; ESIHRMS: Found: m/z 343.1812. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

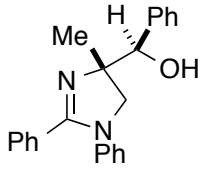
(*S)-1-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-1-phenylethanol (3o):**



79% yield from **1o** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 17 h.

Colorless crystal (CCDC-1022896); mp: 146-147 °C; IR (NaCl) 3356, 2978, 1597, 1497, 1450, 1396, 1304, 1142, 1026, 918 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.65 (3H, s), 3.09 (1H, s br), 3.81 (1H, dd, *J* = 7.2, 10.0 Hz), 4.00 (1H, dd, *J* = 10.0, 10.8 Hz), 4.53 (1H, dd, *J* = 7.2, 10.8 Hz), 6.53 (2H, d, *J* = 8.4 Hz), 6.93 (1H, t, *J* = 7.2 Hz), 7.06 (2H, t, *J* = 7.6 Hz), 7.20-7.35 (6H, m), 7.42-7.44 (2H, m), 7.53-7.56 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 55.0, 73.6, 75.5, 122.8, 123.6, 125.9, 127.0, 127.9, 128.1, 128.5, 128.7, 130.0, 130.8, 142.4, 144.5, 163.2; ESIHRMS: Found: m/z 343.1813. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

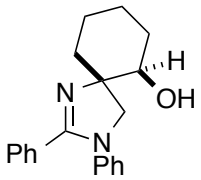
(R*)-((S*)-4-Methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3p):



79% yield from **1p** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 22 h.

White solid; mp: 178-179 °C; IR (NaCl) 3024, 2955, 2878, 1612, 1589, 1497, 1450, 1389, 1304, 1142, 1049 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.35 (3H, s), 3.31 (1H, d, *J* = 9.2 Hz), 4.35 (1H, d, *J* = 9.2 Hz), 4.87 (1H, s), 6.69 (2H, d, *J* = 7.6 Hz), 6.96 (1H, t, *J* = 7.6 Hz), 7.11 (2H, t, *J* = 7.6 Hz), 7.23-7.36 (6H, m), 7.41 (2H, d, *J* = 6.8 Hz), 7.46-7.48 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 58.9, 72.1, 77.9, 122.6, 123.6, 127.3, 127.6, 127.8, 128.1, 128.6, 128.8, 130.1, 130.8., 139.9, 142.5, 162.1; ESIHRMS: Found: m/z 343.1809. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

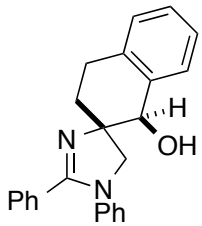
(5*S,6*R**)-2,3-Diphenyl-1,3-diazaspiro[4.5]dec-1-en-6-ol (3q):**



76% yield from **1q** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

Pale yellow solid; mp: 180-181 °C; IR (NaCl) 3348, 3017, 2932, 2855, 1589, 1497, 1450, 1389, 1319, 1150, 1072 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 1.10-1.26 (3H, m), 1.62-1.74 (5H, m), 3.54 (1H, d, *J* = 9.2 Hz), 3.62 (1H, s br), 3.71 (1H, dd, *J* = 3.6, 11.6 Hz), 4.28 (1H, d, *J* = 9.2 Hz), 6.75 (2H, d, *J* = 8.0 Hz), 6.94 (1H, t, *J* = 7.2 Hz), 7.12 (2H, t, *J* = 8.0 Hz), 7.26 (2H, t, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.2 Hz), 7.48 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 24.1, 30.3, 36.5, 56.3, 73.2, 73.3, 122.3, 123.1, 128.0, 128.5, 128.9, 130.0, 130.9, 142.8, 161.1; ESIHRMS: Found: m/z 307.1808. Calcd for $C_{20}H_{23}N_2O$: $(M+H)^+$ 307.1810.

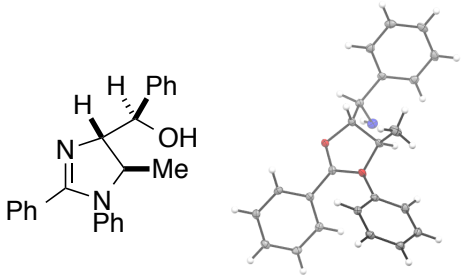
(1'*R,2'*S**)-)-1,2-Diphenyl-1,3',4',5-tetrahydro-1'*H*-spiro[imidazole-4,2'-naphthalen]-1'-ol (3r):**



96% yield from **1r** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 20 h.

Brown solid; mp: 185-186 °C; IR (NaCl) 3148, 2924, 2847, 1589, 1566, 1497, 1389, 1319, 1288, 1150, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 2.06 (1H, ddd, *J* = 3.6, 6.0, 13.2 Hz), 2.40 (1H, ddd, *J* = 8.0, 10.0, 17.6 Hz), 2.91-3.04 (2H, m), 3.20 (1H, s br), 3.65 (1H, d, *J* = 9.6 Hz), 4.11 (1H, d, *J* = 9.6 Hz), 4.98 (1H, s), 6.71 (2H, d, *J* = 7.6 Hz), 6.93 (1H, t, *J* = 7.2 Hz), 7.07-7.22 (5H, m), 7.27 (2H, t, *J* = 7.2 Hz), 7.35 (1H, t, *J* = 7.2 Hz), 7.50-7.59 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 32.2, 56.4, 71.4, 72.8, 122.3, 123.2, 126.0, 126.8, 127.3, 128.0, 128.2, 128.5, 128.9, 130.0, 130.9, 135.2, 137.5, 142.5, 161.9; ESIHRMS: Found: m/z 355.1809. Calcd for $C_{24}H_{23}N_2O$: $(M+H)^+$ 355.1810.

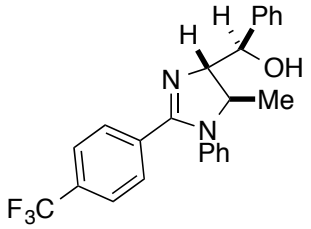
(*R)-((4*S**,5*R**)-5-Methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3s):**



72% yield, dr = >20:1 (the major diastereomer could be recrystallized from hexane/CH_2Cl_2) from **1s** (E/Z = 20:1) and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 22 h.

Colorless crystal (CCDC-1022940); mp: 222-223 °C; IR (NaCl) 3024, 2963, 1612, 1589, 1489, 1443, 1396, 1150, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.84 (3H, d, *J* = 6.4 Hz), 4.06 (1H, dq, *J* = 6.4, 8.0 Hz), 4.12 (1H, dd, *J* = 2.8, 8.0 Hz), 5.27 (1H, d, *J* = 2.8 Hz), 6.78 (2H, d, *J* = 7.2 Hz), 7.05 (1H, t, *J* = 7.2 Hz), 7.13-7.34 (8H, m), 7.39-7.44 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 60.1, 73.1, 78.6, 125.2, 125.9, 126.0, 127.1, 127.9, 128.1, 128.86, 128.91, 129.8, 130.8, 140.1, 141.8, 164.2; ESIHRMS: Found: m/z 343.1811. Calcd for $C_{23}H_{23}N_2O$: $(M+H)^+$ 343.1810.

(*R)-((4*S**,5*R**)-5-Methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3t):**

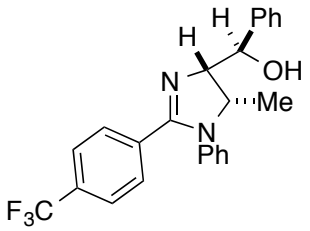


68% yield (major diastereomer, two diastereomers can be separated, overall yield 77%, dr = 7.1:1) from **1t** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 205-206 °C; IR (NaCl) 3145, 3024, 2893, 1597, 1497, 1450, 1420, 1319, 1126, 1065, 1026 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.76 (3H, d, *J* = 6.4 Hz), 4.06 (1H, dd, *J* = 2.8, 8.0 Hz), 4.17 (1H, dq, *J* = 6.4, 8.0 Hz), 5.04(1H, s br), 5.17 (1H, d, *J* = 2.8 Hz), 6.75 (2H, d, *J* = 7.6 Hz), 7.06 (1H, t, *J* = 7.6 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.19-7.30 (7H, m), 7.47 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 59.8, 72.3, 78.7, 123.6 (q, *J* = 270.8 Hz), 124.8 (q, *J* = 3.7 Hz), 125.5, 125.8

(overlapped), 127.0, 128.0, 129.0, 129.2, 131.5 (q, J = 32.4 Hz), 134.0, 140.5, 140.8, 162.4; ESIHRMS: Found: m/z 411.1685. Calcd for $C_{24}H_{22}N_2OF_3$: $(M+H)^+$ 411.1684.

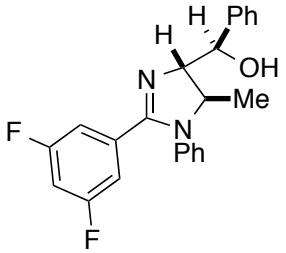
(*R)-((4*S**,5*S**)-5-Methyl-1-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3t'):**



9% yield (minor diastereomer, two diastereomers can be separated, overall yield 77%, dr = 7.1:1) from **1t** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 188-189 °C; IR (NaCl) 3163, 3024, 1597, 1558, 1497, 1450, 1412, 1327, 1265, 1126, 1065 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, d, J = 6.8 Hz), 4.04 (1H, dq, J = 6.8, 9.2 Hz), 4.63 (1H, dd, J = 7.6, 9.2 Hz), 5.15 (1H, d, J = 7.6 Hz), 6.80 (2H, d, J = 8.4 Hz), 7.06 (1H, t, J = 7.2 Hz), 7.18 (2H, t, J = 7.6 Hz), 7.30 (1H, t, J = 7.2 Hz), 7.39 (2H, t, J = 7.6 Hz), 7.46 (2H, d, J = 8.4 Hz), 7.52-7.55 (4H, m),; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 64.0, 72.8, 73.6, 123.8 (q, J = 270.7 Hz), 124.7, 124.8, 125.0 (q, J = 3.7 Hz), 126.7, 127.5, 128.3, 129.0, 129.2, 131.6 (q, J = 32.4 Hz), 134.8, 141.2, 142.5, 162.1; ESIHRMS: Found: m/z 411.1687. Calcd for $C_{24}H_{22}N_2OF_3$: $(M+H)^+$ 411.1684.

(*R)-((4*S**,5*R**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3u):**

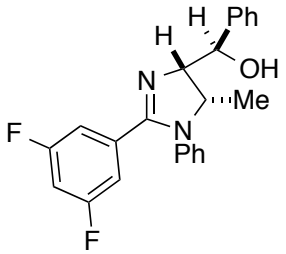


62.7% yield (major diastereomer, two diastereomers can be separated, overall yield 73%, dr = 5.9:1) from **1u** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 185-186 °C; IR (NaCl) 3017, 2970, 2893, 1589, 1489, 1435, 1396, 1319, 1119, 1034, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.79 (3H, d, J = 6.0 Hz), 4.06 (1H, dd, J = 2.8, 10.0 Hz), 4.12 (1H, dq, J = 6.0, 10.0 Hz), 5.15 (1H, d, J = 2.8

Hz), 6.58 (1H, tt, J = 2.4, 8.8 Hz), 6.77-6.79 (2H, m), 6.89-6.94 (2H, m), 7.07-7.11 (1H, m), 7.17-7.24 (3H, m), 7.28-7.34 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 60.0, 72.3, 78.7, 105.2 (t, J = 25.1 Hz), 112.0 (dd, J = 7.6, 19.1 Hz), 125.7, 125.8 (overlapped), 127.0, 128.0, 129.1, 133.7 (t, J = 9.7 Hz), 140.4, 140.7, 162.0, 162.2 (dd, J = 12.5, 247.3 Hz); ESIHRMS: Found: m/z 379.1618. Calcd for $C_{23}H_{21}N_2OF_2$: $(M+H)^+$ 379.1622.

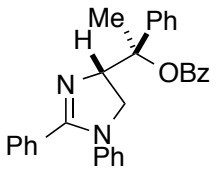
(*R)-((4*S**,5*S**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methanol (3u'):**



10.6% yield (minor diastereomer, two diastereomers can be separated, overall yield 73%, dr = 5.9:1) from **1u** and $PhI(OCOCF_3)_2$ (1.2 equiv); reaction time: 24 h.

White solid; mp: 173-174 °C; IR (NaCl) 3163, 3086, 3024, 2855, 1589, 1489, 1435, 1396, 1327, 1242, 1119, 988 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (3H, d, J = 6.4 Hz), 4.35 (1H, dq, J = 6.4, 9.2 Hz), 4.59 (1H, dd, J = 7.2, 9.2 Hz), 5.12 (1H, d, J = 7.2 Hz), 6.72 (1H, tt, J = 2.4, 8.8 Hz), 6.81 (2H, d, J = 7.2 Hz), 6.92-6.97 (2H, m), 7.08 (1H, t, J = 7.2 Hz), 7.20 (2H, t, J = 7.6 Hz), 7.29 (1H, t, J = 7.2 Hz), 7.38 (2H, t, J = 7.6 Hz), 7.51 (2H, t, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 64.2, 72.8, 73.5, 105.3 (t, J = 25.1 Hz), 111.9 (dd, J = 7.5, 19.1 Hz), 124.7, 125.0, 126.6, 127.5, 128.3, 129.1, 134.5 (t, J = 9.7 Hz), 141.1, 142.5, 161.3 (t, J = 3.0 Hz), 162.4 (dd, J = 12.5, 247.3 Hz); ESIHRMS: Found: m/z 379.1623. Calcd for $C_{23}H_{21}N_2OF_2$: $(M+H)^+$ 379.1622.

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

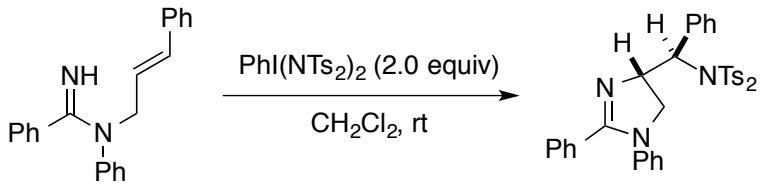


71% yield from **1a** (11% recovery) and $PhI(OCOPh)_2$ (1.2 equiv); reaction time: 38 h.

Sticky yellow oil; IR (NaCl) 3063, 3032, 2940, 1721, 1597, 1497, 1450, 1389, 1273, 1111 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.05 (1H, dd, *J* = 6.0, 10.0 Hz), 4.24 (1H, dd, *J* = 10.0, 10.8 Hz), 4.83 (1H, ddd, *J* = 3.6, 6.0, 10.8 Hz), 6.41 (1H, d, *J* = 3.6 Hz), 6.61-6.63 (2H, m), 6.99 (1H, t, *J* = 7.6 Hz), 7.09-7.13 (2H, m), 7.20-7.40 (10H, m), 7.46-7.54 (3H, m), 8.04 (1H, dd, *J* = 1.2, 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.3, 67.9, 77.2, 122.8, 123.8, 126.4, 128.0, 128.1, 128.3, 128.5, 128.7, 128.8, 129.8, 130.0, 130.2, 130.3, 133.0, 137.5, 142.2, 163.4, 165.4; ESIHRMS: Found: m/z 447.2068. Calcd for $C_{30}H_{27}N_2O_2$: $(M+H)^+$ 447.2073.

4. Diamination of alkenylamidines for the synthesis of dihydroimiazoles 6 and 7

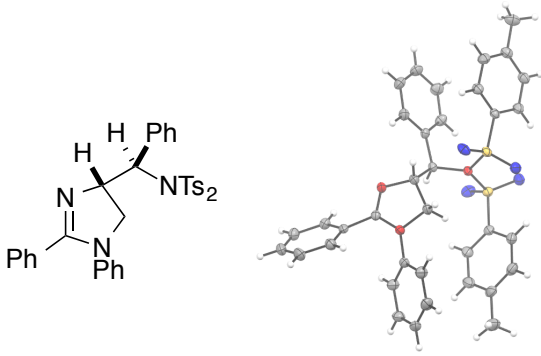
Typical Procedure:



1a **6a**

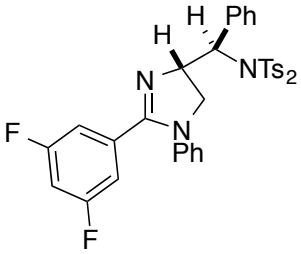
To a stirred solution of $PhI(NTs_2)_2$ (512.1 mg, 0.601 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of *N*-Cinnamyl-*N*-phenylbenzimidamide (**1a**) (93.8 mg, 0.300 mmol) in 2 mL CH_2Cl_2. The reaction mixture was then stirred for 48 h at room temperature under a N_2 atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with Et_2O. The combined organic extracts were washed with water 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 ethyl acetate then triethylamine:ethyl acetate = 2:98) to provide **6a** (150.5 mg, 0.237 mmol) in 79% yield with 9% yield recovery of **1a** (10.1 mg, 0.032 mmol).

***N*-((*R**)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-4-methyl-*N*-tosylbenzenesulfonamide (6a):**



Colorless crystal (CCDC-1022897); mp: 170-171 °C; IR (NaCl) 3063, 3032, 2955, 1589, 1497, 1450, 1381, 1296, 1165, 1088, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ **at –40 °C**) δ 2.26 (3H, s), 2.33 (3H, s), 3.16 (1H, dd, *J* = 6.0, 10.0 Hz), 4.25 (1H, dd, *J* = 10.0, 10.4 Hz), 5.48 (1H, d, *J* = 10.4 Hz), 5.71 (1H, ddd, *J* = 6.0, 10.4, 10.4 Hz), 6.50 (2H, d, *J* = 7.6 Hz), 6.83 (2H, d, *J* = 8.0 Hz), 6.99-7.07 (5H, m), 7.17 (2H, t, *J* = 7.6 Hz), 7.23-7.38 (8H, m), 7.85-7.89 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$ **at –40 °C**) δ 21.5, 21.7, 54.0, 63.7, 67.0, 121.3, 122.8, 127.8, 128.0, 128.1, 128.2, 128.3 (overlapped), 128.4, 128.7, 129.4, 129.7, 129.9, 130.0, 135.3, 135.4, 136.9, 140.3, 144.1, 145.1, 161.1; ESIHRMS: Found: m/z 636.1990. Calcd for $C_{36}H_{34}N_3O_4S_2$: $(M+H)^+$ 636.1991.

***N*-((*R**)-((*S**)-2-(3,5-Difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-4-methyl-*N*-tosylbenzenesulfonamide (6c):**

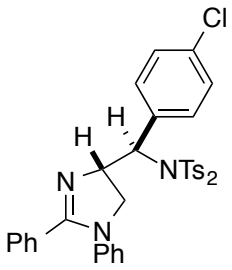


66% yield from **1c** and $PhI(NTs_2)_2$ (2.0 equiv) at 40 °C; reaction time: 13 h.

White solid; mp: 173-174 °C. IR (NaCl) 3024, 2970, 1582, 1489, 1435, 1373, 1165, 1119, 1080, 980, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ **at –40 °C**) δ 2.28 (3H, s), 2.35 (3H, s), 3.13 (1H, dd, *J* = 6.8, 10.4 Hz), 4.24 (1H, dd, *J* = 10.4, 10.4 Hz), 5.43 (1H, d, *J* = 10.4 Hz), 5.72 (1H, ddd, *J* = 6.8, 10.4, 10.4 Hz), 6.53 (2H, d, *J* = 7.6 Hz), 6.81-6.89 (5H, m), 6.96-7.02 (4H, m), 7.12 (1H, d, *J* = 7.6 Hz), 7.23 (2H, t, *J* = 7.6 Hz), 7.36-7.42 (3H, m), 7.83-7.87 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$ **at –40 °C**) δ

21.6, 21.7, 54.5, 64.1, 66.9, 105.7 (t, J = 25.6 Hz), 112.1 (dd, J = 6.9, 19.1 Hz), 121.6, 123.7, 128.1, 128.2 (overlapped), 128.48, 128.53, 128.7, 129.5, 129.6, 133.1 (t, J = 10.0 Hz), 135.0, 135.4, 136.9, 140.0, 144.3, 145.2, 159.2, 162.1 (dd, J = 12.4, 247.6 Hz); ESIHRMS: Found: m/z 672.1786. Calcd for $C_{36}H_{32}N_3O_4S_2F_2$: $(M+H)^+$ 672.1802.

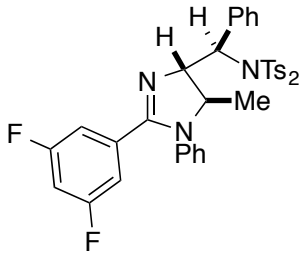
_N_-((_R_*)-(4-Chlorophenyl)((_S_*)-1,2-diphenyl-4,5-dihydro-1_H_-imidazol-4-yl)methyl)-4-methyl-_N_-tosylbenzenesulfonamide (6g):



74% yield from **1g** and $PhI(NTs_2)_2$ (2.0 equiv) at 40 °C; reaction time: 41 h.

White solid; mp: 182-183 °C. IR (NaCl) 3024, 2955, 1583, 1497, 1381, 1296, 1165, 1088, 995, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ **at –40 °C**) δ 2.28 (3H, s), 2.39 (3H, s), 3.16 (1H, dd, J = 5.6, 10.4 Hz), 4.25 (1H, dd, J = 10.4, 10.4 Hz), 5.43 (1H, d, J = 10.4 Hz), 5.59 (1H, ddd, J = 5.6, 10.4, 10.4 Hz), 6.52 (2H, d, J = 7.6 Hz), 6.84 (2H, d, J = 8.0 Hz), 7.05-7.14 (5H, m), 7.19 (2H, t, J = 7.6 Hz), 7.25-7.39 (7H, m), 7.76 (2H, d, J = 8.4 Hz), 7.83 (2H, d, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ **at –40 °C**) δ 21.6, 21.7, 54.0, 63.8, 66.2, 121.4, 123.0, 128.1, 128.15 (overlapped), 128.23, 128.4, 128.6, 128.8, 129.5, 129.8, 130.2, 131.2, 133.7, 133.9, 135.3, 136.7, 140.3, 144.5, 145.2, 161.3; ESIHRMS: Found: m/z 670.1598. Calcd for $C_{36}H_{33}N_3O_4S_2Cl$: $(M+H)^+$ 670.1601.

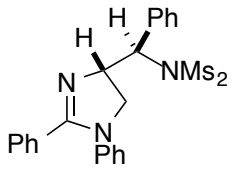
_N_-((_R_*)-((4_S_*,5_R_*)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1_H_-imidazol-4-yl)(phenyl)methyl)-4-methyl-_N_-tosylbenzenesulfonamide (6u):



79% yield, dr =11.1:1 (as an inseparable mixture) from **1u** and $PhI(NTs_2)_2$ (2.0 equiv) at 40 °C; reaction time: 41 h.

White solid; mp: 179-180 °C. IR (NaCl) 3071, 2970, 1574, 1489, 1443, 1373, 1304, 1165, 1119, 988, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ **at –40 °C**) δ 1.20 (3H×0.09, d, *J* = 6.0 Hz), 1.39 (3H, d, *J* = 6.0 Hz), 2.24 (3H, s), 2.31 (3H+3H×0.09, s), 2.39 (3H×0.09, s), 3.16 (1H, dq, *J* = 5.2, 6.0 Hz), 3.30-3.45 (1H×0.09, m), 5.28-5.41 (2H+1H×0.09, m), 5.95 (1H×0.09, d, *J* = 11.2 Hz), 6.60 (2H×0.09, d, *J* = 7.6 Hz), 6.70-7.76 (3H+1H×0.09, m), 6.87-6.99 (8H+2H×0.09, m), 7.04-7.07 (4H×0.09, m), 7.17-7.42 (6H+8H×0.09, m), 7.77-7.79 (2H+2H×0.09, m), 7.85 (2H, d, *J* = 6.4 Hz), 7.94 (2H×0.09, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ **at –40 °C**) (major diastereomer) δ 21.4, 21.5, 21.9, 64.1, 67.9, 72.3, 105.4 (t, *J* = 25.5 Hz), 112.0 (dd, *J* = 6.6, 19.6 Hz), 125.0, 125.5, 128.0, 128.1, 128.2, 128.3, 128.4, 129.0, 129.3, 130.2, 133.4 (t, *J* = 9.7 Hz), 135.1, 135.3, 137.0, 141.6, 144.1, 145.0, 160.4, 161.9 (dd, *J* = 12.5, 247.4 Hz); ESIHRMS: Found: m/z 686.1961. Calcd for $C_{37}H_{34}N_3O_4S_2F_2$: $(M+H)^+$ 686.1959.

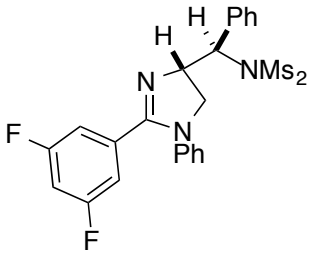
***N*-((*R**)-((*S**)-1,2-Diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (7a):**



85% yield from **1a** and $PhI(NMs_2)_2$ (2.0 equiv); reaction time: 23 h.

Yellow solid; mp: 169-171 °C; IR (NaCl) 3017, 2947, 1597, 1566, 1497, 1366, 1319, 1273, 1157, 1003, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.87 (6H, s br), 3.94 (1H, dd, *J* = 7.6, 9.6 Hz), 4.46 (1H, dd, *J* = 9.6, 9.6 Hz), 5.52 (1H, ddd, *J* = 7.6, 9.6, 10.4 Hz), 5.62 (1H, d, *J* = 10.4 Hz), 6.83-6.85 (2H, m), 7.00-7.04 (1H, m), 7.17-7.47 (10H, m), 7.78 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.9, 57.9, 65.1, 67.2, 122.7, 123.9, 128.1, 128.78, 128.81, 128.9, 129.0, 129.9, 130.2, 130.4, 135.3, 142.4, 162.7; ESIHRMS: Found: m/z 484.1360. Calcd for $C_{24}H_{26}N_3O_4S_2$: $(M+H)^+$ 484.1365.

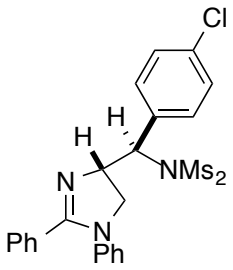
***N*-((*R**)-((*S**)-2-(3,5-Difluorophenyl)-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (7c):**



73% yield from **1c** and $PhI(NMs_2)_2$ (2.0 equiv); reaction time: 13 h.

Pale yellow oil; IR (NaCl) 3032, 2963, 1589, 1497, 1443, 1366, 1319, 1157, 1119, 988, 887 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.87 (6H, s br), 3.91 (1H, dd, *J* = 7.6, 9.6 Hz), 4.45 (1H, dd, *J* = 9.2, 9.6 Hz), 5.55 (1H, ddd, *J* = 7.6, 9.2, 10.8 Hz), 5.61 (1H, d, *J* = 10.8 Hz), 6.76 (1H, tt, *J* = 2.4, 8.8 Hz), 6.85-6.96 (4H, m), 7.10 (1H, t, *J* = 7.2 Hz), 7.22-7.27 (2H, m), 7.36-7.48 (3H, m), 7.76 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.9, 58.4, 65.4, 66.9, 105.7 (t, *J* = 25.1 Hz), 112.2 (dd, *J* = 7.7, 19.1 Hz), 123.1, 124.9, 128.88, 128.91, 129.3, 129.7, 133.6 (t, *J* = 9.9 Hz), 135.0, 141.9, 160.8 (t, *J* = 3.0 Hz), 162.4 (dd, *J* = 12.4, 247.9 Hz); ESIHRMS: Found: m/z 520.1179. Calcd for $C_{24}H_{24}N_3O_4S_2F_2$: $(M+H)^+$ 520.1176.

***N*-((*R**)-(4-Chlorophenyl)((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (7g):**

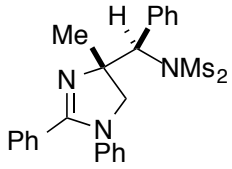


76% yield from **1g** and $PhI(NMs_2)_2$ (2.0 equiv); reaction time: 24 h.

White solid; mp: 89-90 °C; IR (NaCl) 3024, 2940, 1589, 1566, 1497, 1366, 1273, 1157, 1011, 964, 895 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.93 (6H, s br), 3.93 (1H, dd, *J* = 7.6, 9.6 Hz), 4.46 (1H, dd, *J* = 9.2, 9.6 Hz), 5.47 (1H, ddd, *J* = 7.6, 9.2, 10.4 Hz), 5.54 (1H, d, *J* = 10.4 Hz), 6.83 (2H, d, *J* = 7.6 Hz), 7.04 (1H, t, *J* = 7.6 Hz), 7.18-7.24 (4H, m), 7.30-7.38 (3H, m), 7.43 (2H, d, *J* = 8.4 Hz), 7.73 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.1, 57.8, 65.1, 66.5, 122.8, 124.1, 128.1, 128.99

(overlapped), 129.02, 130.2, 130.3, 131.3, 134.1, 134.8, 142.3, 162.9; ESIHRMS: Found: m/z 518.0967. Calcd for $C_{24}H_{25}N_3O_4S_2Cl$: $(M+H)^+$ 518.0975.

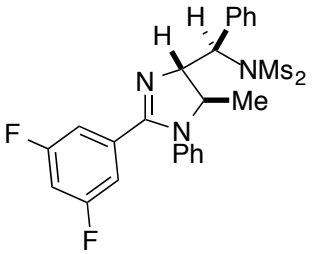
***N*-((*R**)-((*S**)-4-Methyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (7p):**



68% yield from **1p** and $PhI(NMs_2)_2$ (2.0 equiv); reaction time: 24 h.

Pale yellow oil; IR (NaCl) 3017, 2932, 1589, 1566, 1497, 1358, 1273, 1157, 1103, 1057, 972 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.44 (3H, s), 2.66 (3H, s), 3.20 (3H, s), 3.71 (1H, d, *J* = 9.6 Hz), 5.48 (1H, d, *J* = 9.6 Hz), 6.18 (1H, s), 6.88 (2H, d, *J* = 8.0 Hz), 7.00 (1H, t, *J* = 7.2 Hz), 7.17 (2H, t, *J* = 7.6 Hz), 7.29 (2H, t, *J* = 7.6 Hz), 7.35-7.42 (4H, m), 7.54 (2H, d, *J* = 7.6 Hz), 7.57 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.0, 43.7, 44.5, 61.2, 71.0, 71.3, 123.0, 123.7, 128.2, 128.5, 128.69, 128.71, 128.8, 130.1, 130.9, 131.1, 134.4, 142.2, 160.7; ESIHRMS: Found: m/z 498.1518. Calcd for $C_{25}H_{28}N_3O_4S_2$: $(M+H)^+$ 498.1521.

***N*-((*R**)-((4*S**,5*R**)-2-(3,5-Difluorophenyl)-5-methyl-1-phenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-*N*-(methylsulfonyl)methanesulfonamide (7u):**

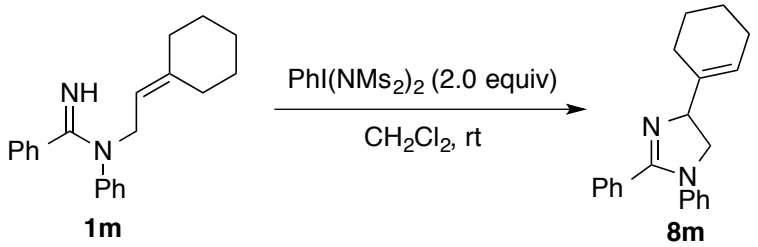


86% yield, dr = 7.7:1 (as an inseparable mixture) from **1u** and $PhI(NMs_2)_2$ (2.0 equiv); reaction time: 4 h.

Pale yellow oil; IR (NaCl) 2964, 2930, 1748, 1557, 1495, 1452, 1425, 1363, 1219, 1003 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (3H×0.13, d, *J* = 6.4 Hz), 1.62 (3H, d, *J* = 6.4 Hz), 2.75 (6H+6H×0.13, s br), 3.98 (1H, dq, *J* = 5.2, 6.4 Hz), 4.49 (1H×0.13, dq, *J* = 6.4, 7.6 Hz), 5.11 (1H, dd, *J* = 5.2, 10.8 Hz), 5.44 (1H, d, *J* = 10.8 Hz), 5.57 (1H×0.13, dd, *J* = 7.6, 11.6 Hz), 5.89 (1H×0.13, d, *J* = 11.6 Hz), 6.69-6.74 (1H+1H×0.13, m), 6.84 (2H×0.13, d, *J* = 7.2 Hz), 6.88-6.98 (4H+2H×0.13, m), 7.07

(1H×0.13, t, J = 7.6 Hz), 7.15 (1H, t, J = 7.6 Hz), 7.22 (2H×0.13, t, J = 7.6 Hz), 7.28 (2H, t, J = 7.6 Hz), 7.37-7.48 (3H+3H×0.13, m), 7.75-7.79 (2H+2H×0.13, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 43.6, 65.9, 66.7, 72.4, 105.6 (t, J = 25.2 Hz), 112.2 (dd, J = 7.5, 19.1 Hz), 124.8, 125.9, 128.77, 128.82, 129.5, 129.9, 133.8 (t, J = 9.7 Hz), 134.9, 142.2, 160.8 (t, J = 2.9 Hz), 162.3 (dd, J = 12.5, 247.6 Hz); ESIHRMS: Found: m/z 534.1329. Calcd for $C_{25}H_{26}N_3O_4S_2F_2$: $(M+H)^+$ 534.1333.

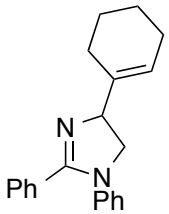
5. Synthesis of dihydroimiazole 8m



1m **8m**

To a stirred solution of $PhI(NMs_2)_2$ (329.1 mg, 0.600 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of *N*-(2-cyclohexylideneethyl)-*N*-phenylbenzimidamide (**1m**) (91.3 mg, 0.300 mmol) in 2 mL CH_2Cl_2. The reaction mixture was then stirred for 23 h at room temperature under a N_2 atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with ethyl acetate. The combined organic extracts were washed with water 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 = 65:35 then 100% ethyl acetate) to provide **8m** (63.2 mg, 0.209 mmol) in 70% yield.

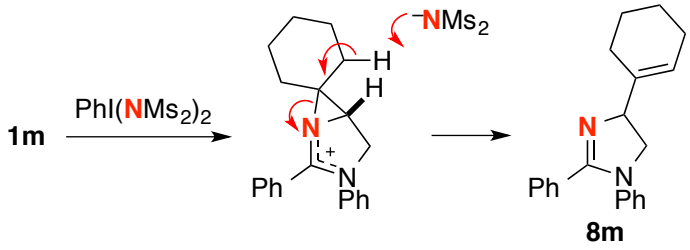
4-(Cyclohex-1-en-1-yl)-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (8m):



Yellow oil; IR (NaCl) 2932, 2862, 1597, 1497, 1381, 1296 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54-1.69 (4H, m), 2.01-2.06 (4H, m), 3.77 (1H, dd, J = 7.6, 9.2 Hz), 4.17 (1H, dd, J = 9.2, 10.8 Hz), 4.67 (1H, dd, J = 7.6, 10.8 Hz), 5.77 (1H, s br), 6.77 (2H, d, J = 7.6 Hz), 6.96 (1H, t, J = 7.6 Hz), 7.14 (2H, t, J = 7.6 Hz), 7.27 (2H, t, J = 7.6 Hz), 7.34 (1H, t, J = 7.6 Hz), 7.51-7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 22.6,

24.3, 25.1, 58.2, 69.8, 122.4, 123.1, 123.3, 128.0, 128.6, 128.8, 129.8, 131.2, 138.0, 143.1, 161.6; ESIHRMS: Found: m/z 303.1862. Calcd for $C_{21}H_{23}N_2$: $(M+H)^+$ 303.1861.

A proposed mechanism for the formation of 8m: Upon formation of the putative aziridinium ion intermediate (see section 6.2 for more details), the counter dimesylamido ion ($^-NMs_2$) might undergo deprotonation to form **8m**, rather than nucleophilic substitution at the tertiary C-N bond. This is presumably due to steric bulkiness of dimesylamido ion.

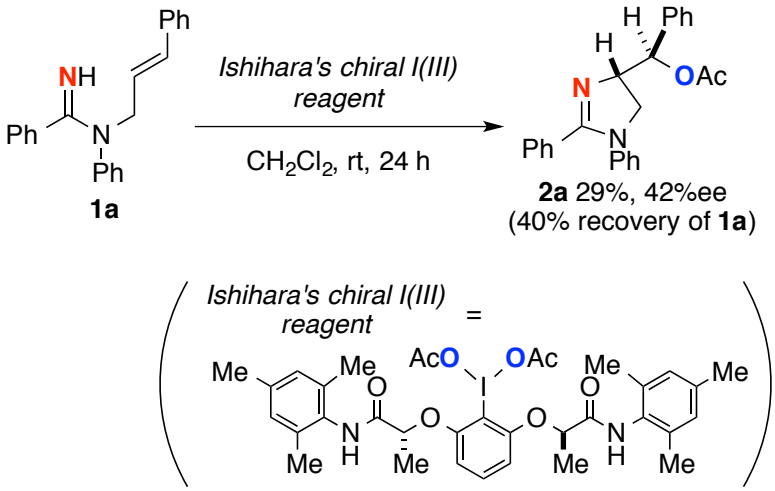


6. Preliminary studies on the reaction mechanism

6.1. The reaction of 1a with chiral hypervalent iodine (III) reagent

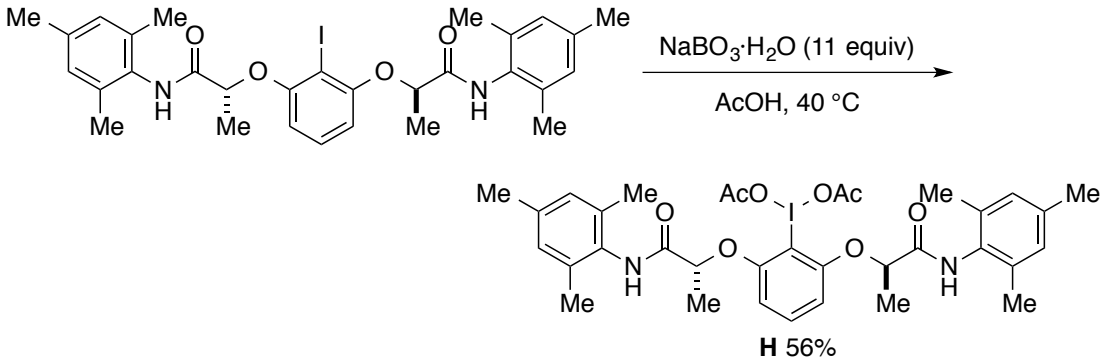
The reaction of **1a** with the chiral hypervalent iodine(III) reagent reported by Ishihara[21] gave **2a** only in 29% yield but with 42% ee (with 40% recovery of **1a**. The absolute stereochemistry was not determined) (Scheme S1). This result suggested that there is a certain interaction between amidine **1a** and hypervalent iodine(III) reagent in the C–N bond forming process.

Scheme S1.



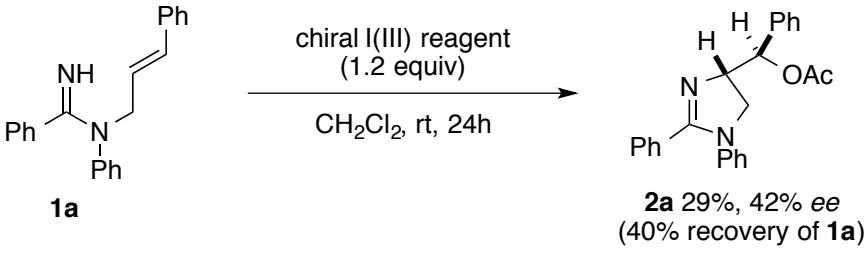
Synthesis of chiral hypervalent iodine (III) reagent and aminooxygenation of alkenylamidine 1a:

Synthesis of chiral hypervalent iodine (III) reagent:[20]



Sodium perborate tetrahydrate (766.2 mg, 4.98 mmol) was added portionwise during 30 min to a stirred solution of (2*R*,2'*R*)-2,2'-(2-Iodo-1,3-phenylene)bis(oxy)bis(*N*-mesitylpropanamide)[21] (278.2 mg, 0.453 mmol) in 4.5 mL glacial acetic acid held at 40 °C, and the mixture stirred at this temperature for 6h. The reaction was quenched with 10 mL water and the resulting solution was extracted with CH_2Cl_2 (10 mL × 2). The combined solvents were removed in vacuo to give the chiral hypervalent iodine (III) **H** (302.1 mg, 0.253 mmol, contains 42 % unreacted iodoarene) in 56% yield. The ^{1}H NMR data was consistent to the reported values.[21]

Aminooxygenation of 1a with chiral hypervalent iodine (III) reagent:



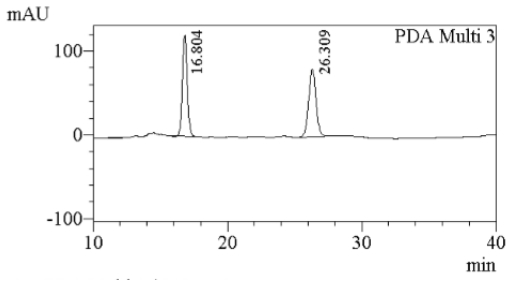
To a stirred solution of chiral hypervalent iodine (III) **H** (302.1 mg, 0.253 mmol, contains 42 % unreacted iodoarene) in CH_2Cl_2 (1.0 mL) was added a solution of *N*-Cinnamyl-*N*-phenylbenzimidamide (**1a**) (63.3 mg, 0.203 mmol) in 1 mL CH_2Cl_2. The reaction mixture was then stirred for 24 h at room temperature under a N_2 atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with CH_2Cl_2. The combined organic extracts were washed with water 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 = 75:25 then hexane:ethyl acetate = 50:50 then triethylamine:ethyl acetate = 2:98) to provide **2a** (21.7 mg, 0.059 mmol) in 29% yield and 42% *ee* (the absolute stereochemistry was not determined), as well as 40% recovery of **1a** (25.6 mg, 0.082 mmol) and 84% recovery of chiral iodoarene (233.4 mg, 0.380 mmol, based on the amount of hypervalent iodine (III) **H** and initially contained chiral iodoarene was used).

Determination of enantiomeric excess of 2a

General: Enantioselectivities were determined by Shimadzu, LC-20AD Prominence Liquid Chromatograph, column: Chiralcel, IA, 046 cm X 25 cm
LC Conditions: Mobile Phase: Hex : IPA; 95 : 5, 1.0 ml/min, injection volume: 5.0 μL
Detection: Diode array detector set at 230 nm

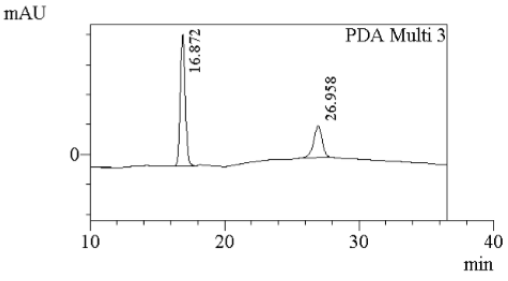
Racemic 2a:



PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.804	3019701	120094	49.592
2	26.309	3069395	80689	50.408
Total		6089096	200783	100.000

2a from using chiral hypervalent iodine (III) **H**:



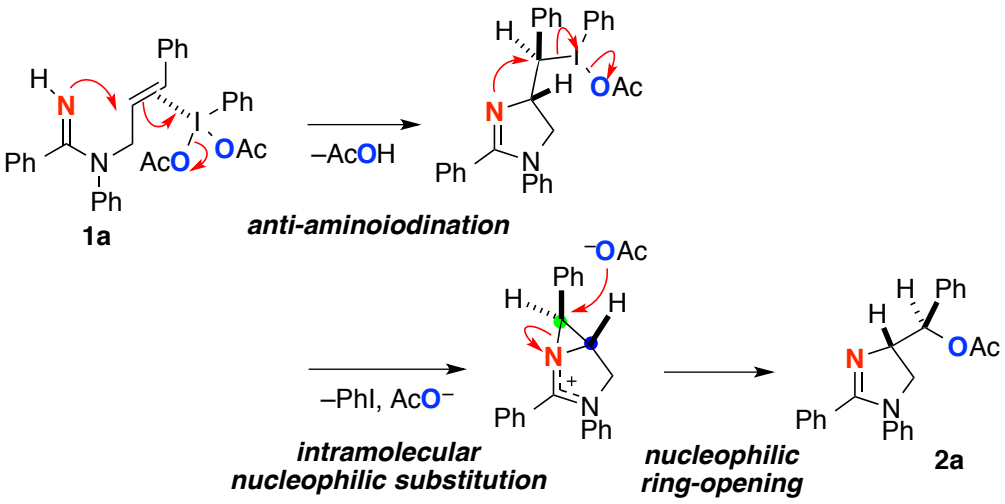
PDA Ch3 230nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	16.872	5658332	219332	71.251
2	26.958	2283035	52556	28.749
Total		7941367	271887	100.000

6.2. Mechanistic possibilities for the present *anti*-aminooxygenation and *anti*-diamination

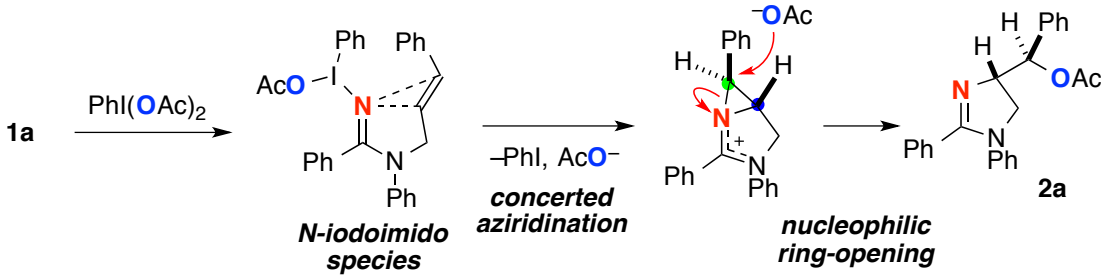
Based on the experimental results, two mechanistic scenarios could be envisaged for these *anti*-difunctionalization events with amidines and hypervalent I(III) reagents. As one of the possibilities, the present process with amidines might begin with *anti*-aminoiodination of the alkene through electrophilic activation of the alkene by $PhI(OAc)_2$, that is followed by intramolecular S_N2-type nucleophilic displacement to form aziridinium ion and further nucleophilic ring-opening with acetate ion to give **2a** (Scheme S2). Thus, the overall process includes inversion of three times, thus resulting in *anti*-aminooxygeantion of the alkene, which is perfectly consistent with the experimental outcomes.

Scheme S2. *Anti*-aminoiodination–S_N2-type substitution



Alternatively, the process might be triggered by an *N*-iodoimido species, which is formed by the reaction of the electron-rich amidine moiety and hypervalent I(III) reagents (Scheme S3). From the putative *N*-iodoimido species, aziridination of the alkene should take place in a concerted manner to give aziridinium intermediate, that is followed by ring-opening of the aziridine ring via (S_N2-like) nucleophilic attack of an acetate ion from the backside with respect to the cleaved C–N bond. Thus, the overall process could result in *anti*-aminooxygenation of the alkene, which is also consistent with the experimental outcomes.

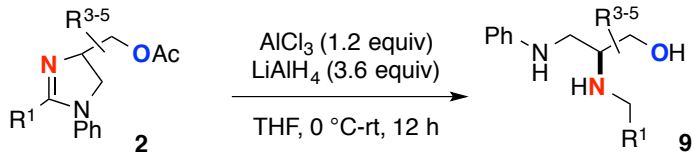
Scheme S3. Concerted aziridination–S_N2-type substitution

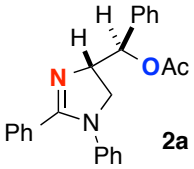
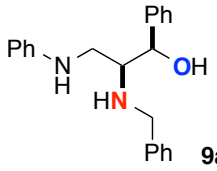
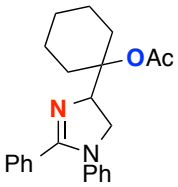
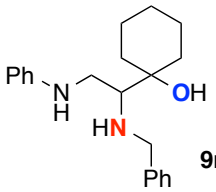
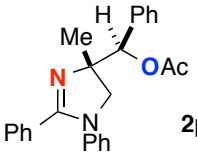
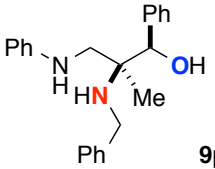
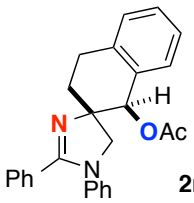
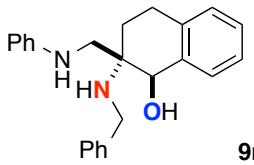
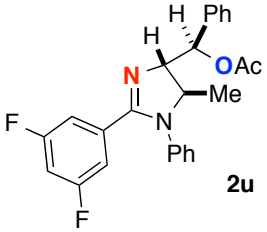
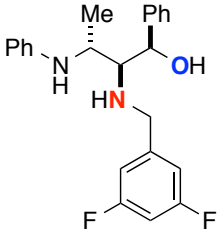


7. Reduction of dihydroimidazoles 2 by AlH_3

Having synthesized various dihydroimidazoles **2** through diastereoselective aminoacetoxylation of *N*-allylamidines **1**, we aimed to achieve chemical conversion of them into 2,3-diaminopropanols by reduction with AlH_3 prepared *in situ* from $LiAlH_4$ and $AlCl_3$ (Scheme S4). The AlH_3 reduction proceeded smoothly to give the corresponding 2,3-diaminopropanols **9** having benzyl protection at C2 nitrogen.

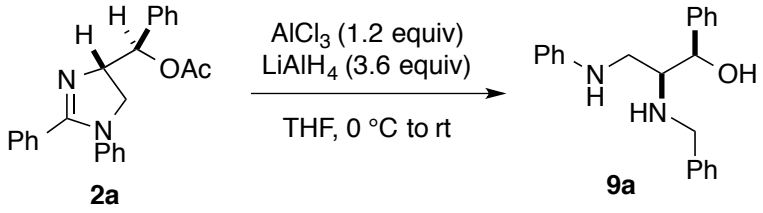
Scheme S4. Synthesis of 2,3-diaminopropanols by AlH_3 reduction[a]



entry	dihydroimidazoles **2**	2,3-diaminopropanols **9**/yield
1	 **2a**	 **9a** 80%
2	 **2m**	 **9m** 73%
3	 **2p**	 **9p** 77%
4	 **2r**	 **9r** 96%
5[b]	 **2u**	 **9u** 72%

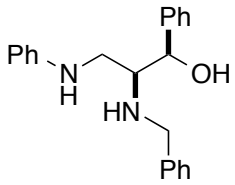
[a] The reactions were carried out using 0.2-0.3 mmol of **2** in THF (3 mL) at room temperature. Isolated yields were recorded above. [b] 1.6 equiv of $AlCl_3$ and 4.8 equiv of $LiAlH_4$ were used.

Typical procedure:



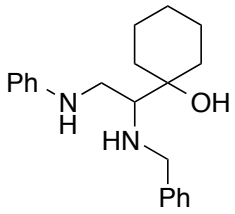
To a solution of $AlCl_3$ (39.6 mg, 0.297 mmol) in THF (2.0 mL) was added $LiAlH_4$ (33.8 mg, 0.891 mmol) at 0 ºC. After 30 min, a solution of (*R**)-((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl acetate **2a** (91.7 mg, 0.248 mmol) in THF (1.0 mL) was slowly added. The reaction mixture was then stirred for 12 h at room temperature, and quenched by slow addition of 10 mL 20% NaOH solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over $MgSO_4$. After evaporation of solvents, the crude product was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 80:20 then hexane:ethyl acetate = 50:50) afforded **9a** (65.9 mg, 0.198 mmol) in 80% yield as a yellow oil.

(1*R,2*S**)-2-(Benzylamino)-1-phenyl-3-(phenylamino)propan-1-ol (9a):**



IR (NaCl) 3387, 3055, 3024, 2855, 1605, 1504, 1458, 1319, 1258, 1196, 1111, 1065, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.96-3.10 (3H, m), 3.78 (1H, d, *J* = 13.2 Hz), 3.86 (1H, d, *J* = 13.2 Hz), 4.91 (1H, d, *J* = 4.0 Hz), 6.46 (2H, d, *J* = 8.0 Hz), 6.68 (1H, t, *J* = 7.6 Hz), 7.10 (2H, t, *J* = 7.6 Hz), 7.20-7.36 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.5, 51.3, 61.0, 72.6, 113.3, 117.7, 125.8, 127.2, 127.4, 128.0, 128.4, 128.5, 129.1, 139.8, 141.0, 148.2; ESIHRMS: Found: m/z 333.1969. Calcd for $C_{22}H_{25}N_2O$: $(M+H)^+$ 333.1967.

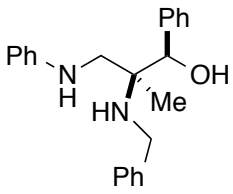
1-(1-(Benzylamino)-2-(phenylamino)ethyl)cyclohexanol (9m):



73% yield from **2m**; reaction time: 12 h.

Yellow oil; IR (NaCl) 3379, 3055, 3024, 2932, 2855, 1605, 1504, 1450, 1319, 1258, 1119, 964, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22-1.75 (10H, m), 2.63 (1H, dd, *J* = 4.0, 5.2 Hz), 3.16 (1H, d, *J* = 5.2, 12.4 Hz), 3.29 (1H, dd, *J* = 4.0, 12.4 Hz), 3.83 (1H, d, *J* = 12.8 Hz), 3.88 (1H, d, *J* = 12.8 Hz), 4.25 (1H, s br), 6.58 (2H, d, *J* = 7.6 Hz), 6.71 (1H, t, *J* = 7.2 Hz), 7.16 (2H, t, *J* = 7.6 Hz), 7.23-7.34 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.9, 25.8, 33.8, 36.3, 43.6, 54.2, 62.18, 62.19, 73.4, 113.1, 117.6, 127.2, 128.3, 128.5, 129.2, 140.4, 148.5; ESIHRMS: Found: m/z 325.2279. Calcd for $C_{21}H_{29}N_2O$: $(M+H)^+$ 325.2280.

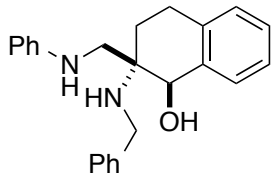
(1*R,2*S**)-2-(Benzylamino)-2-methyl-1-phenyl-3-(phenylamino)propan-1-ol (9p):**



77% yield from **2p**; reaction time: 12 h.

White solid; mp: 172-173 °C; IR (NaCl) 3395, 3310, 3024, 2870, 1604, 1512, 1435, 1327, 1165, 1042, 988 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (3H, s), 2.98 (1H, d, *J* = 12.8 Hz), 3.23 (1H, d, *J* = 12.8 Hz), 3.77 (1H, d, *J* = 12.4 Hz), 3.81 (1H, d, *J* = 12.8 Hz), 4.21 (1H, s br), 4.78 (1H, s), 6.60 (2H, d, *J* = 7.6 Hz), 6.70 (1H, t, *J* = 7.2 Hz), 7.15 (2H, t, *J* = 7.6 Hz), 7.25-7.41 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 46.0, 48.0, 59.0, 77.8, 113.3, 117.6, 127.1, 127.5, 127.7, 128.05, 128.08, 128.5, 129.2, 140.0, 140.4, 148.6; ESIHRMS: Found: m/z 347.2119. Calcd for $C_{23}H_{27}N_2O$: $(M+H)^+$ 347.2123.

(1*R,2*S**)-2-(Benzylamino)-2-((phenylamino)methyl)-1,2,3,4-tetrahydronaphthalen-1-ol (9r):**

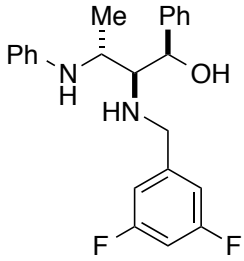


96% yield from **2r**; reaction time: 12 h.

White solid; mp: 110-111 °C; IR (NaCl) 3410, 3017, 2839, 1604, 1504, 1458, 1319, 1265, 1150, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94-2.08 (2H, m), 2.85-2.89

(2H, m), 3.12 (1H, d, J = 12.0 Hz), 3.40 (1H, d, J = 12.0 Hz), 3.70 (1H, d, J = 12.0 Hz), 3.75 (1H, d, J = 12.0 Hz), 4.59 (1H, s), 6.88 (2H, d, J = 8.0 Hz), 6.72 (1H, t, J = 7.6 Hz), 7.13-7.37 (11H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 25.0, 45.4, 46.0, 57.5, 72.0, 113.6, 117.7, 126.5, 127.1, 127.9, 128.1, 128.4, 128.8, 129.2, 130.5, 135.8, 136.2, 140.3, 148.7; ESIHRMS: Found: m/z 359.2124. Calcd for $C_{24}H_{27}N_2O$: $(M+H)^+$ 359.2123.

(1*R,2*S**,3*R**)-2-((3,5-Difluorobenzyl)amino)-1-phenyl-3-(phenylamino)butan-1-ol (9u):**



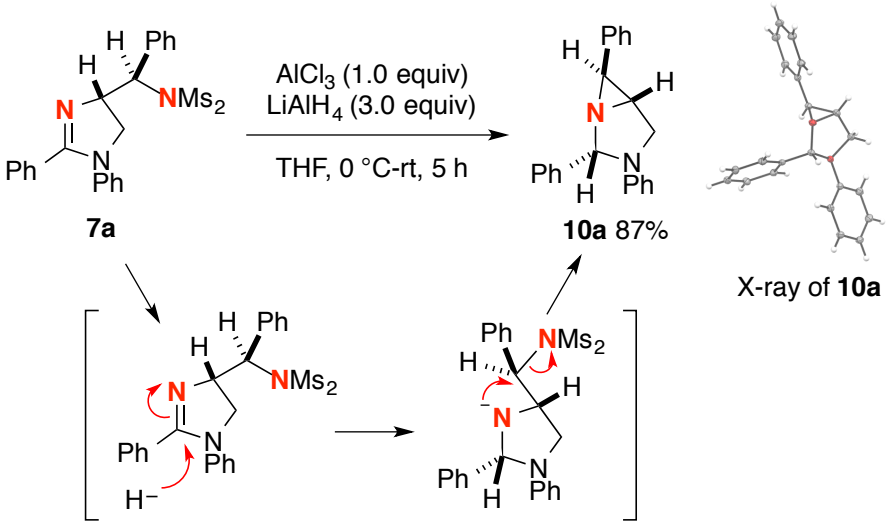
72% yield from **2u** (pure major diastereomer) with 1.6 equiv $AlCl_3$ and 4.8 equiv $LiAlH_4$; reaction time: 18 h.

Colorless oil; IR (NaCl) 3333, 3055, 3017, 2970, 1597, 1497, 1458, 1312, 1119, 988, 856 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (3H, d, J = 6.4 Hz), 2.69 (1H, dd, J = 1.2, 4.8 Hz), 3.59 (1H, dq, J = 1.2, 6.4 Hz), 3.79 (1H, d, J = 13.2 Hz), 3.90 (1H, d, J = 13.2 Hz), 4.94 (1H, d, J = 4.8 Hz), 6.63 (2H, d, J = 8.4 Hz), 6.71 (1H, tt, J = 2.4, 8.8 Hz), 6.80 (1H, t, J = 7.6 Hz), 6.83-6.88 (2H, m), 7.17 (2H, t, J = 7.6 Hz), 7.29-7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 49.4, 53.0, 64.8, 75.4, 102.5 (t, J = 25.2 Hz), 110.9 (dd, J = 6.6, 18.2 Hz), 115.7, 119.4, 125.8, 127.4, 128.5, 129.3, 142.7, 144.4 (t, J = 8.4 Hz), 146.3, 163.0 (dd, J = 12.5, 246.9 Hz); ESIHRMS: Found: m/z 383.1938. Calcd for $C_{23}H_{25}N_2OF_2$: $(M+H)^+$ 383.1935.

8. Reduction of diamination product 7a by AlH_3

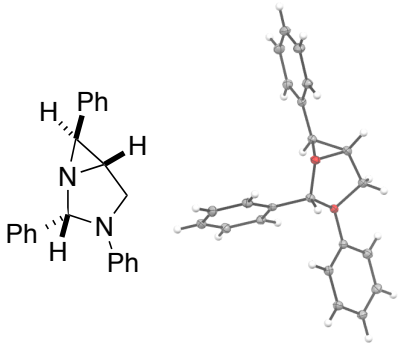
When diamination product **7a** was subjected to the AlH_3-reduction conditions, aziridine **10a** was isolated in 87% yield as a single diastereomer (Scheme S5). Presumably, hydride reduction of the C=N bond of **7a** first occurred in a face-selective manner from the opposite side of the C(4)-tether and the resulting nitrogen anion species underwent an intramolecular nucleophilic substitution reaction with inversion of the configuration to form aziridine **10a**.

Scheme S5. AlH_3-reduction of diamination product **7a**



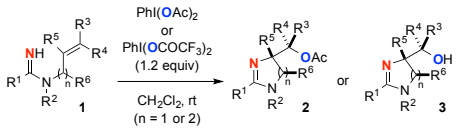
To a solution of $AlCl_3$ (41.3 mg, 0.310 mmol) in THF (2.0 mL) was added $LiAlH_4$ (35.2 mg, 0.929 mmol) at 0 ºC. After 30 min, a solution of *N*-((*R**)-((*S**)-1,2-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)(phenyl)methyl)-*N*-(methylsulfonyl)methane-sulfonamide **7a** (149.7 mg, 0.310 mmol) in THF (2.0 mL) was slowly added. The reaction mixture was then stirred for 5 h at room temperature, and quenched by slow addition of 10 mL 20% NaOH solution. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, and then dried over $MgSO_4$. After evaporation of solvents, the crude product was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 90:10 then hexane:ethyl acetate = 80:20) afforded **10a** (84.3 mg, 0.270 mmol) in 87% yield as a white solid.

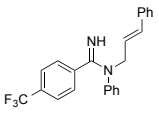
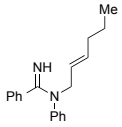
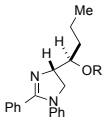
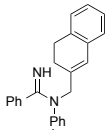
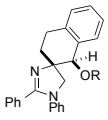
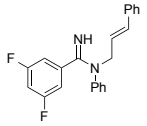
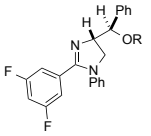
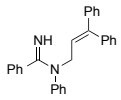
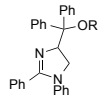
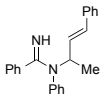
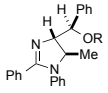
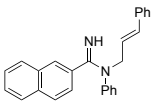
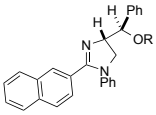
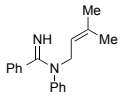
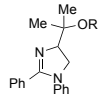
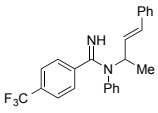
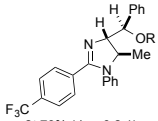
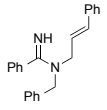
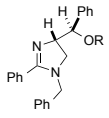
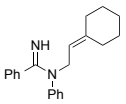
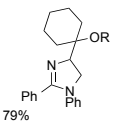
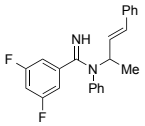
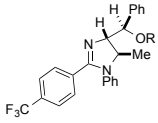
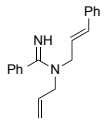
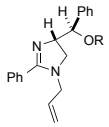
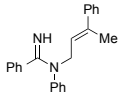
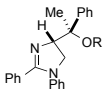
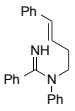
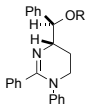
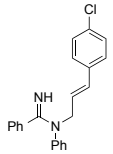
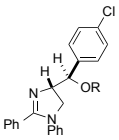
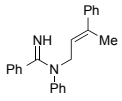
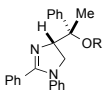
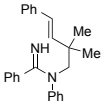
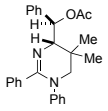
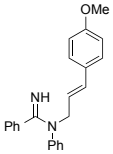
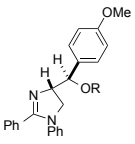
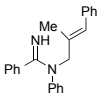
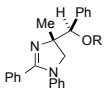
(2*R,5*S**,6*S**)-2,3,6-Triphenyl-1,3-diazabicyclo[3.1.0]hexane (10a):**



Colorless crystal (CCDC-1022898); mp: 140-141 °C; IR (NaCl) 3032, 2963, 2909, 2855, 2816, 1597, 1497, 1450, 1350, 1319, 1281, 1180, 1065 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (1H, dd, *J* = 3.2, 4.8 Hz), 3.03 (1H, d, *J* = 3.2 Hz), 3.61 (1H, dd, *J* = 4.8, 9.6 Hz), 4.37 (1H, d, *J* = 9.6 Hz), 5.50 (1H, s), 6.53 (2H, d, *J* = 8.0 Hz), 6.76 (1H, t, *J* = 7.2 Hz), 7.06 (2H, d, *J* = 7.6 Hz), 7.11-7.34 (8H, m), 7.47 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.9, 48.0, 52.6, 82.6, 115.5, 118.5, 126.4, 126.9, 127.3, 128.1, 128.2, 128.5, 128.8, 137.9, 138.7, 147.5; ESIHRMS: Found: m/z 313.1704. Calcd for $C_{22}H_{21}N_2$: $(M+H)^+$ 313.1705.

10. Table S1: Scheme 3 with starting materials and products



amidines 1	products 2 or 3	amidines 1	products 2 or 3	amidines 1	products 2 or 3
 **1b**	**2b** 75%; **3b** 80%	 **1j**	 **2j** 0%;[e] **3j** 0%[e]	 **1r**	 **2r** 90%; **3r** 96%
 **1c**	 **2c** 75%; **3c** 77%	 **1k**	 **2k** 94%; **3k** 88%	 **1s**	 **2s** 76% (dr = 14:1) **3s** 72% (dr = >20:1)
 **1d**	 **2d** 56%; **3d** 65%[b]	 **1l**	 **2l** 81%; **3l** 90%	 **1t**	 **2t** 73% (dr = 6.2:1) **3t** 77% (dr = 7.1:1)
 **1e**	 **2e** 88%; **3e** 92%	 **1m**	 **2m** 79% **3m** 12% with **3m'** 66% (R = $OCOCF_3$)[f]	 **1u**	 **2u** 81% (dr = 7.1:1) **3u** 73% (dr = 5.9:1)
 **1f**	 **2f** 73%;[c] **3f** 72%	 **1n** (*E*:*Z* = 21:1)	 **2n** 96% (dr = >20:1)[g] **3n** 94% (dr = >20:1)[g]	 **1v**	 **2v** 0%;[e] **3v** 0%[e]
 **1g**	 **2g** 94%;[d] **3g** 76%	 **1o**	 **2o** 77%; **3o** 79%	 **1w**	 **2w** 52%
 **1h**	 **2h** 94%; **3h** 90%	 **1p**	 **2p** 63%; **3p** 79%		**5w** 32% as a single isomer
1i	**2i** 79% (dr = 6.1:1) **3i** 94% (dr = 4.9:1)	**2q**	**2q** 73%; **3q** 76%		

[a] All the reactions were conducted using 0.3 mmol of *N*-allylamidines **1** in CH_2Cl_2 (3 mL) under a N_2 atmosphere. [b] 1.5 equiv of $PhI(OCOCF_3)_2$ was used. [c] 1.4 equiv of $PhI(OAc)_2$ was used. [d] 1.3 equiv of $PhI(OAc)_2$ was used. [e] Complex mixtures of unidentified compounds were formed. [f] **3m'**: R = $COCF_3$. [g] Alkene **1n** contains small amount of *Z*-isomer (*E*:*Z* = 21:1).

10. References

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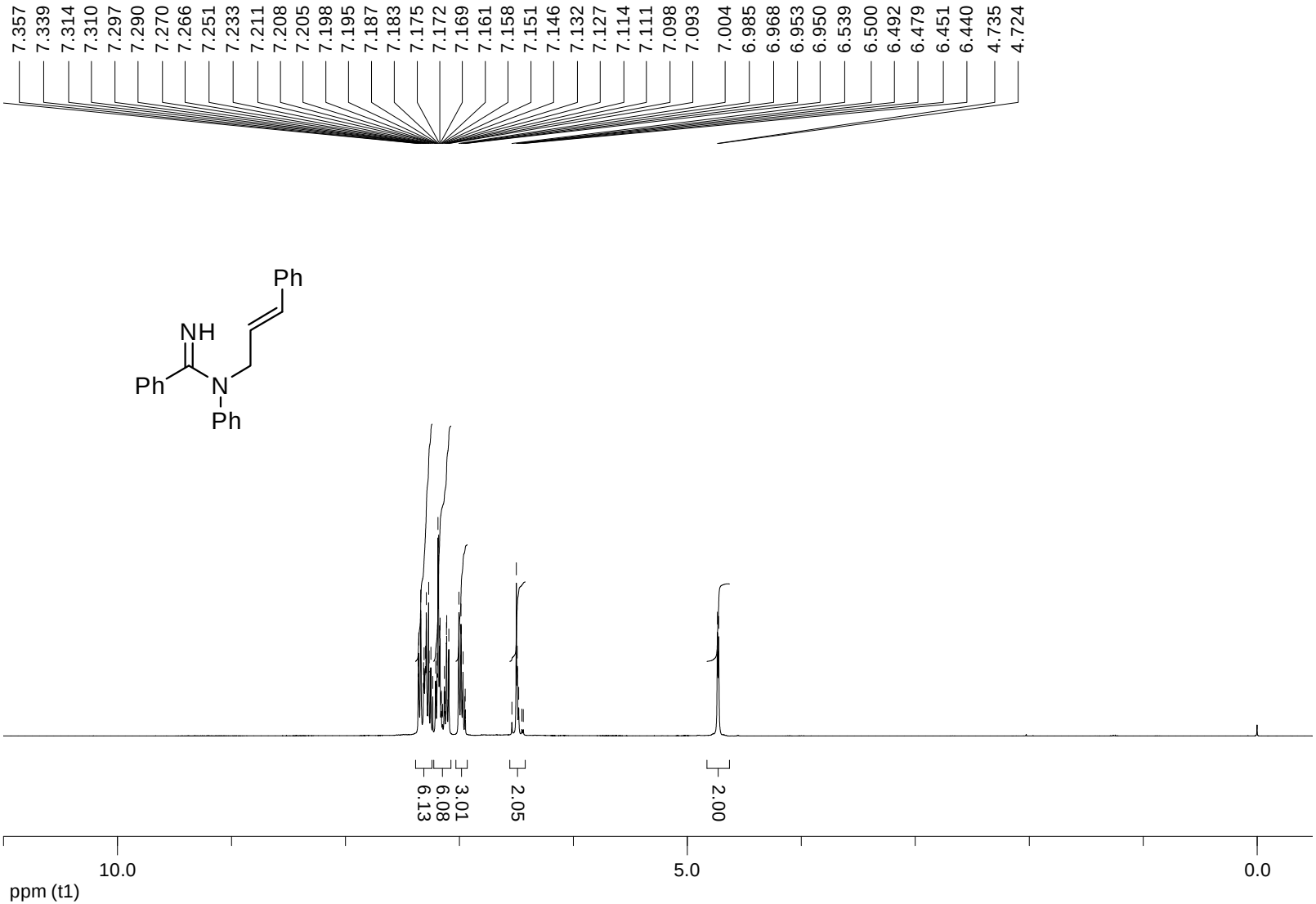
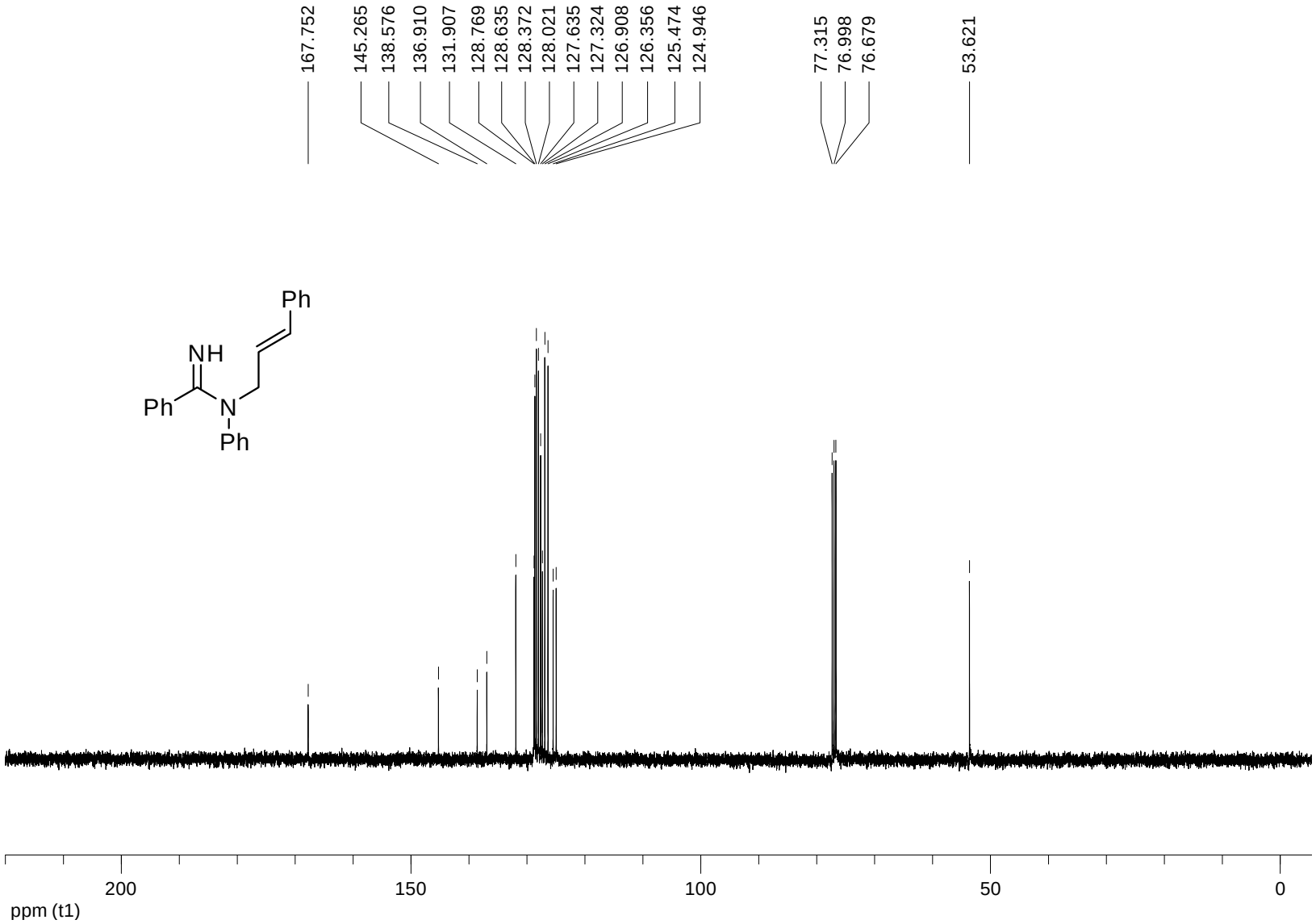
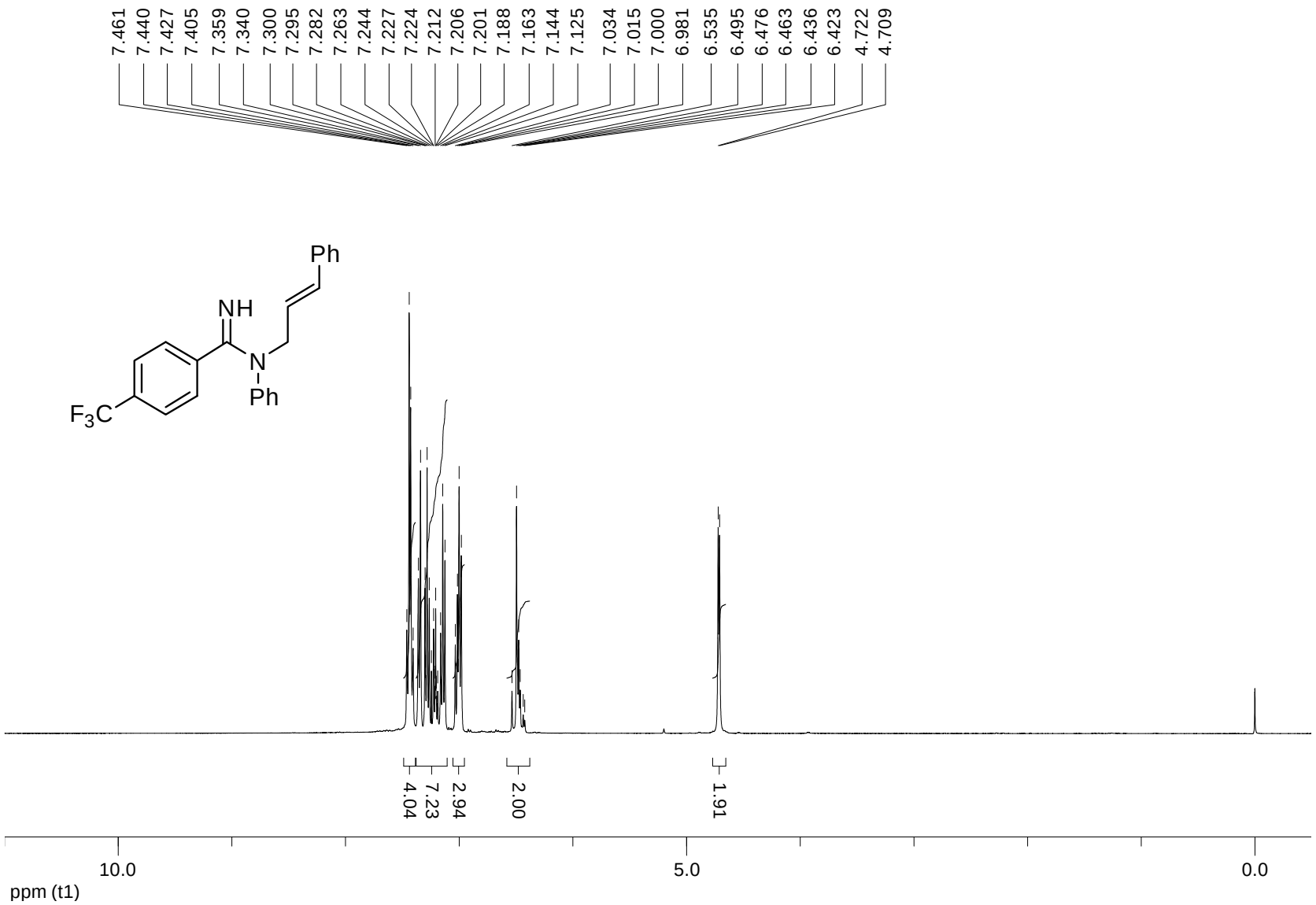
^{1}H NMR spectrum of **1a** (400 MHz, $CDCl_3$)



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



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



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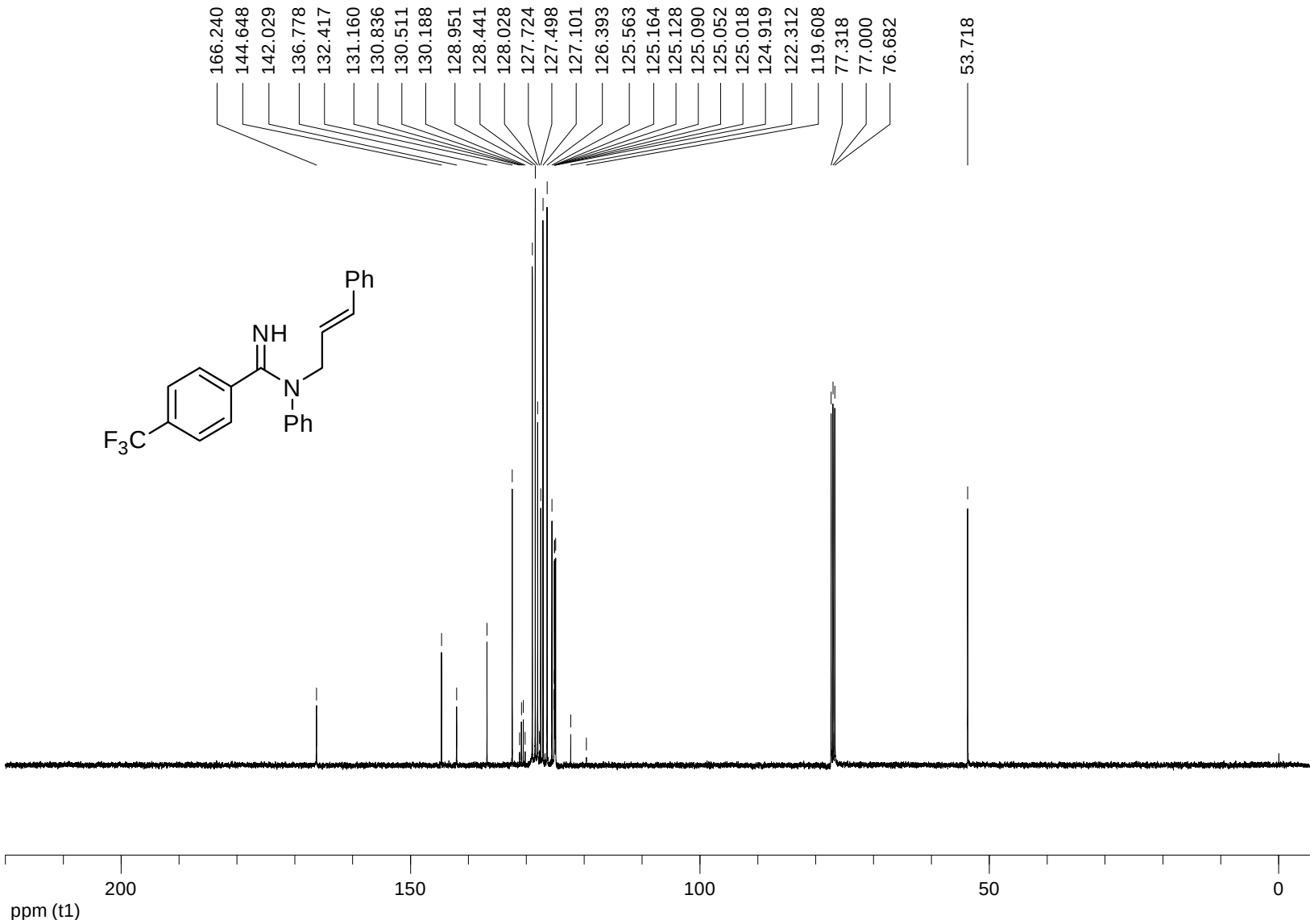
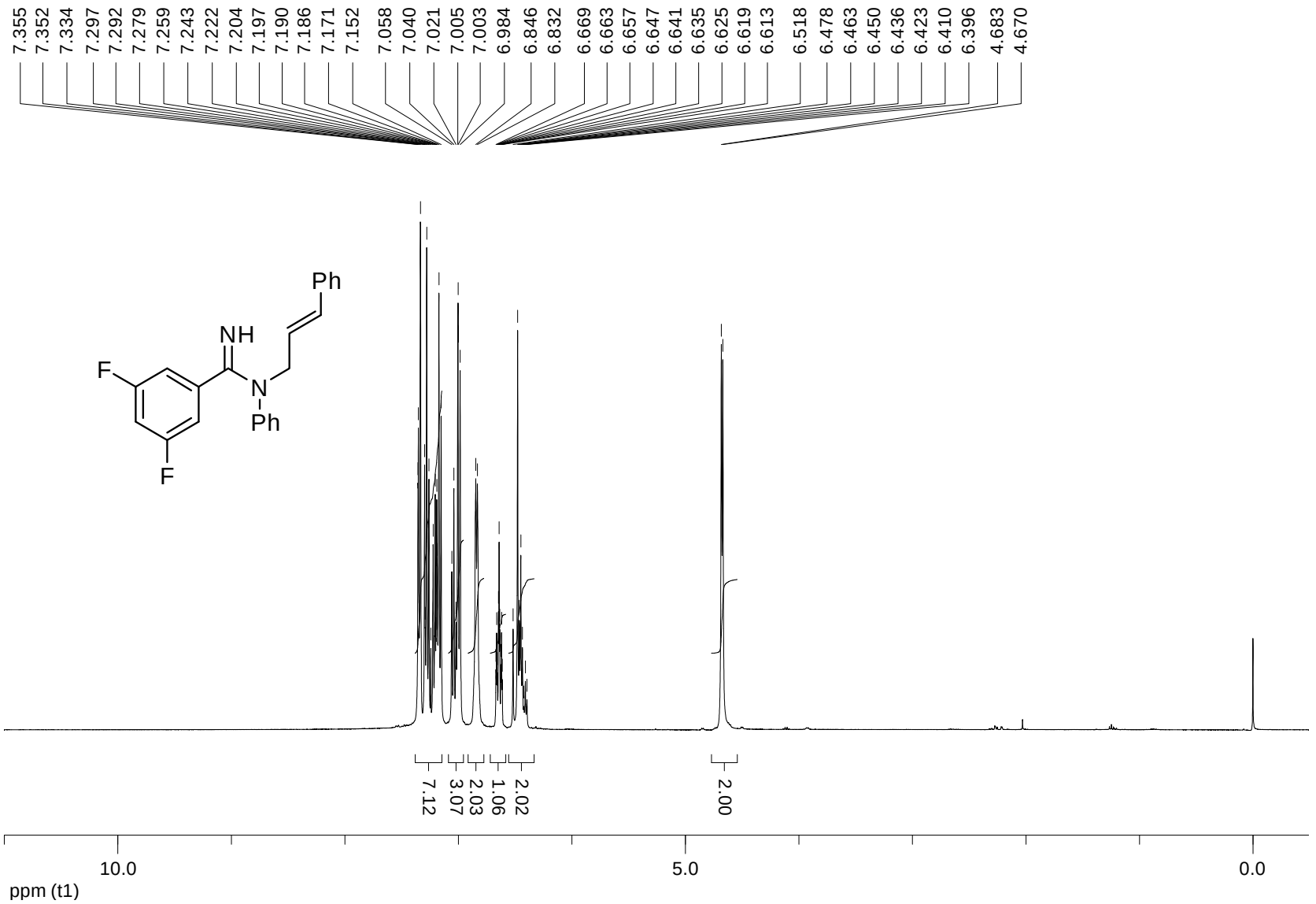


^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$)



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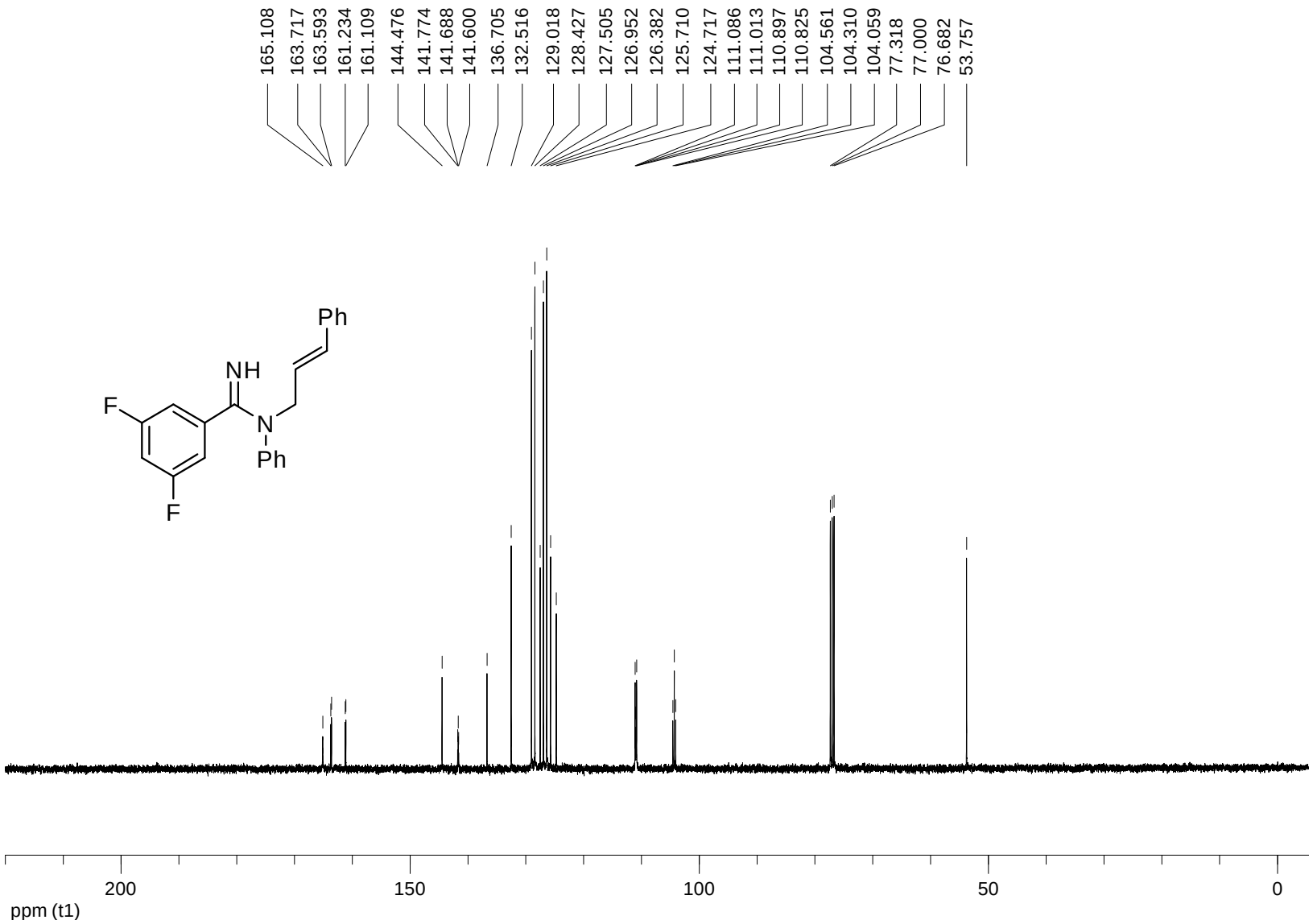

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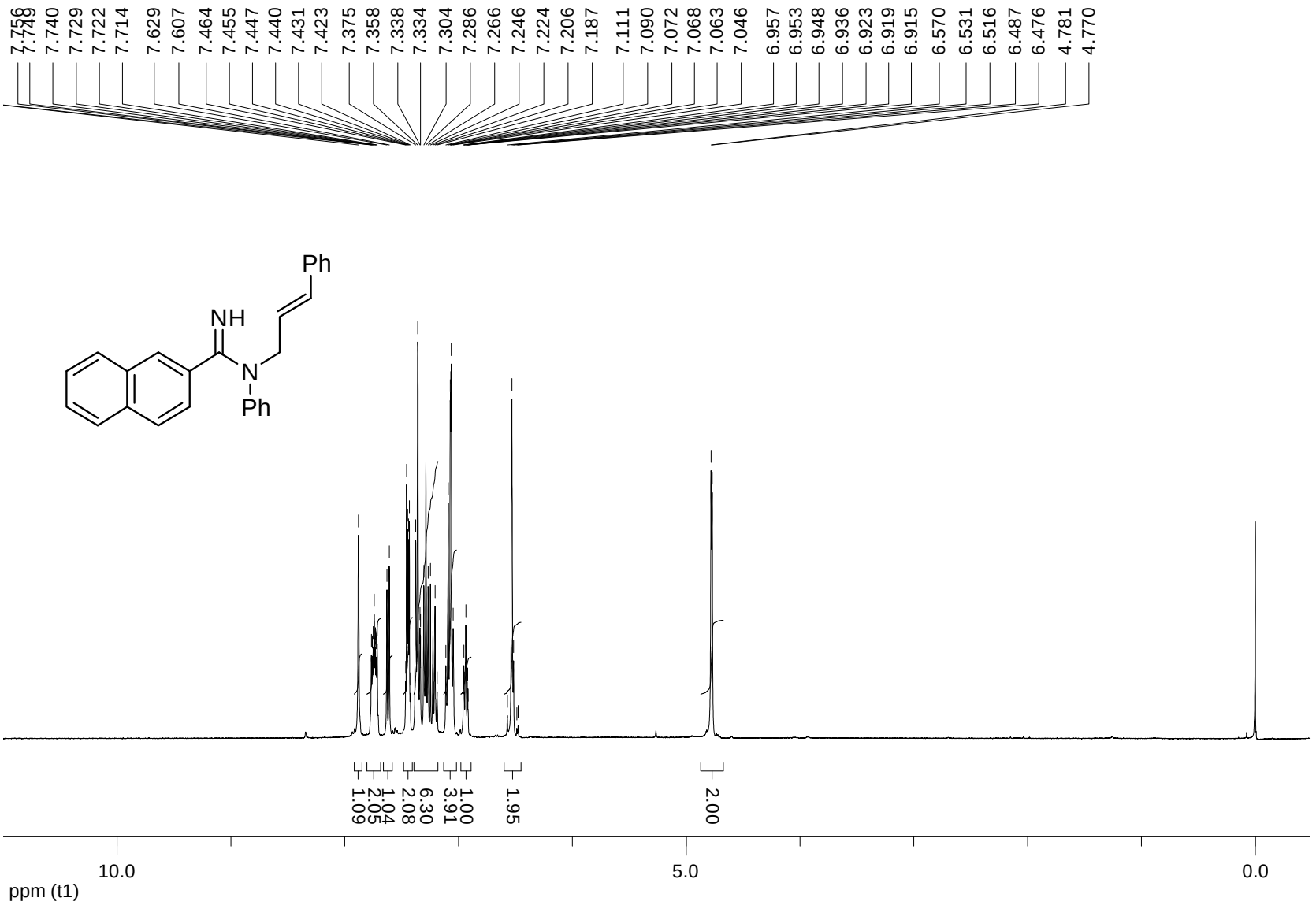

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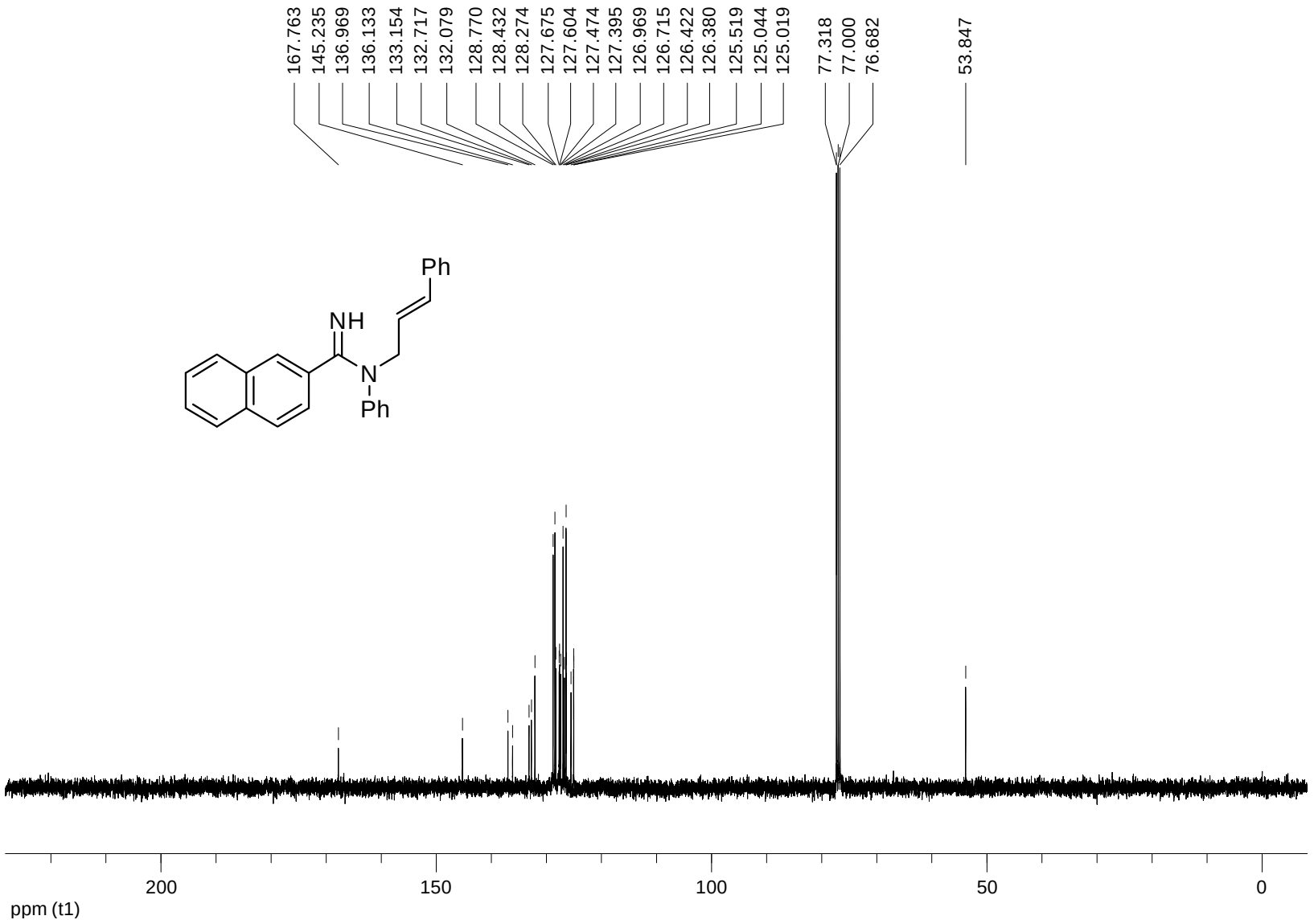

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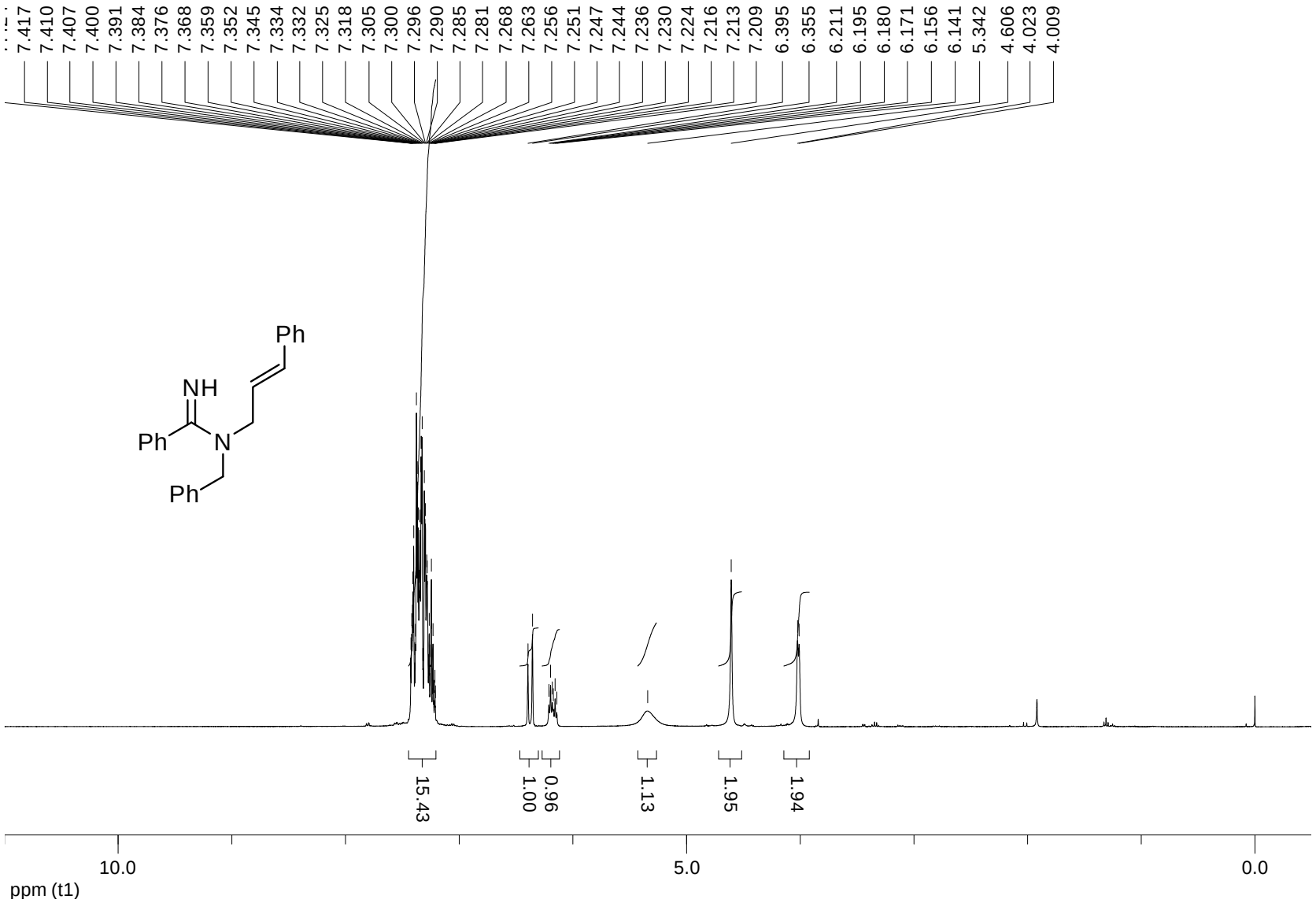

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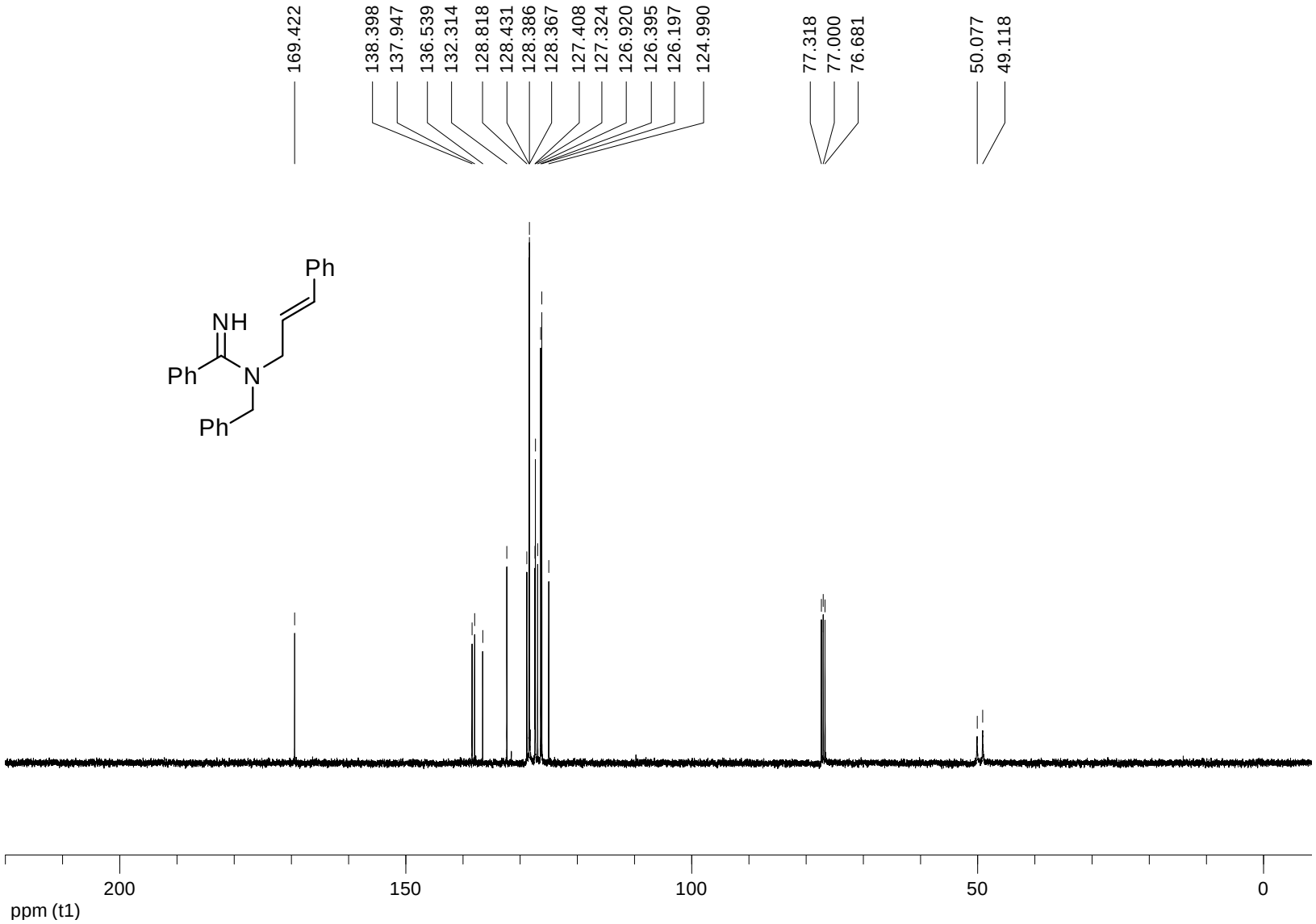
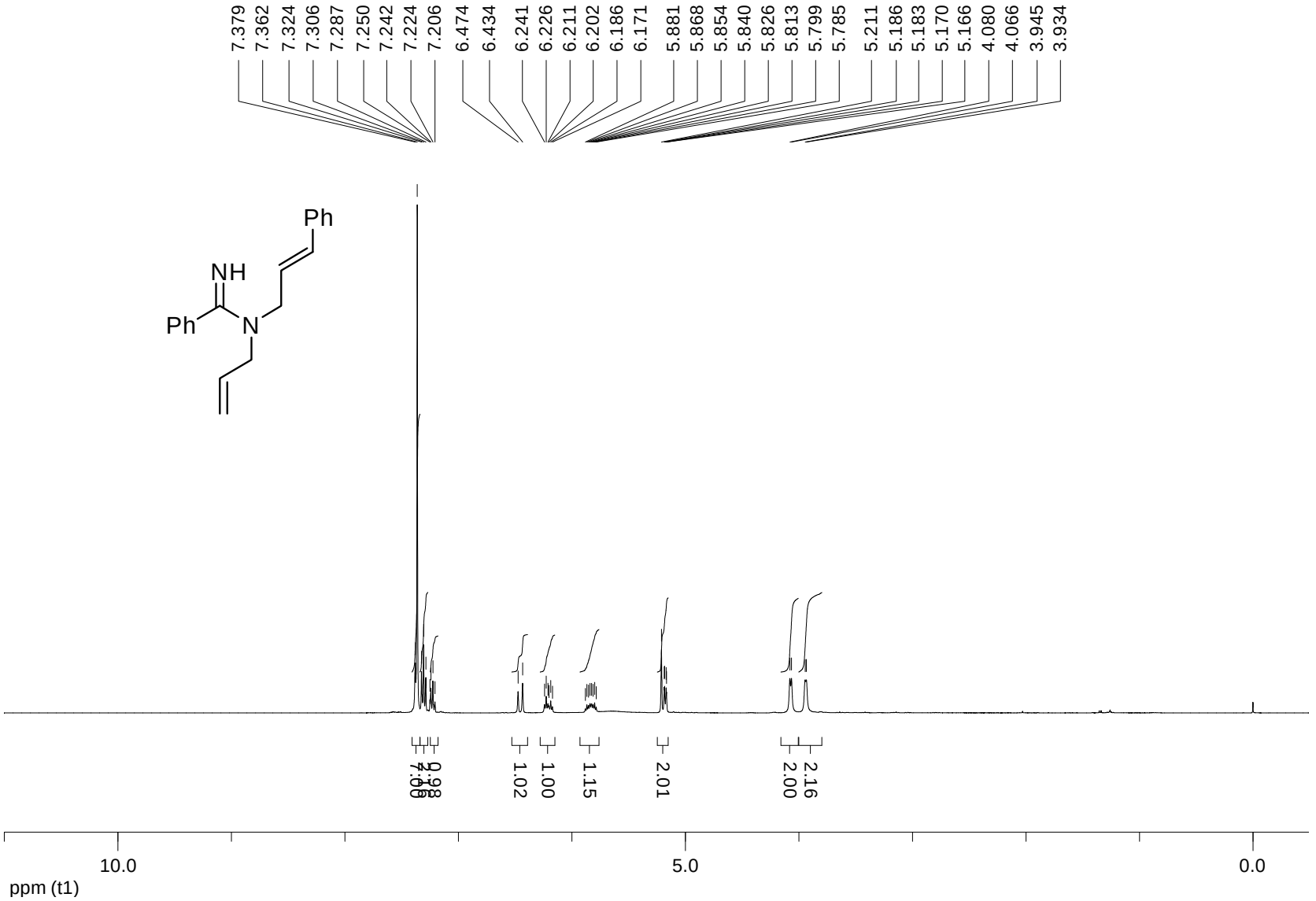
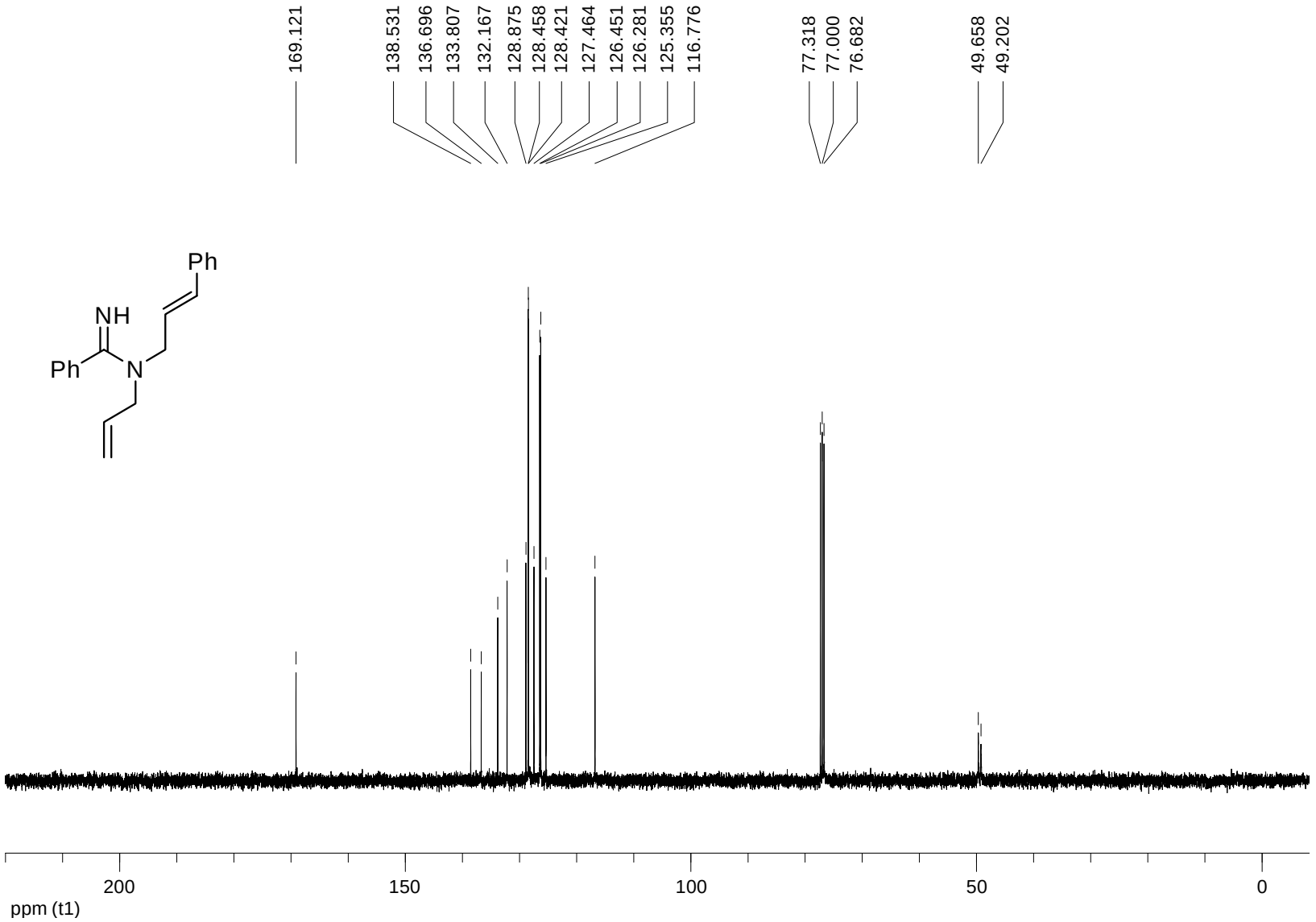


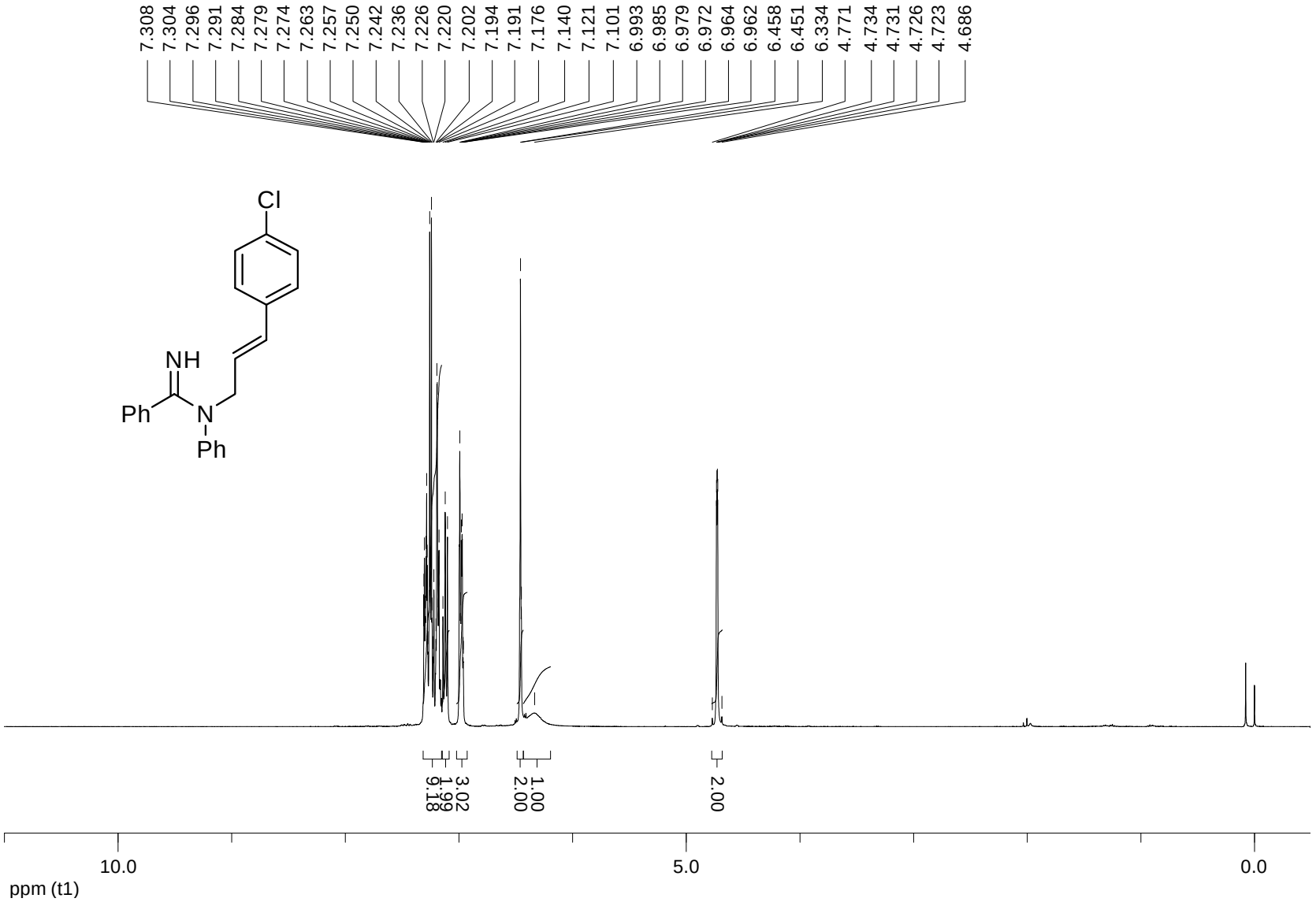
^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)



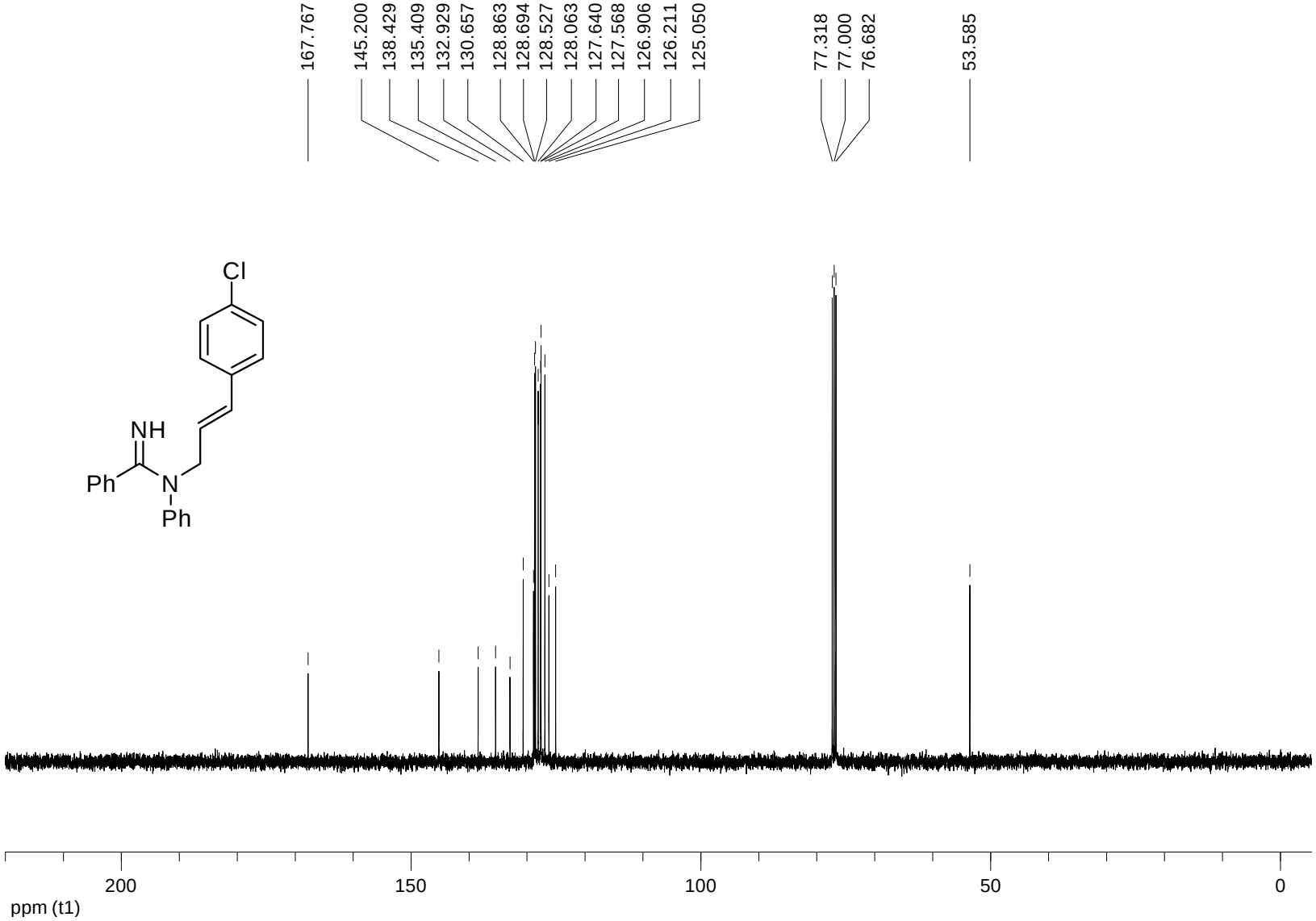
^{13}C NMR spectrum of **1f** (100 MHz, $CDCl_3$)



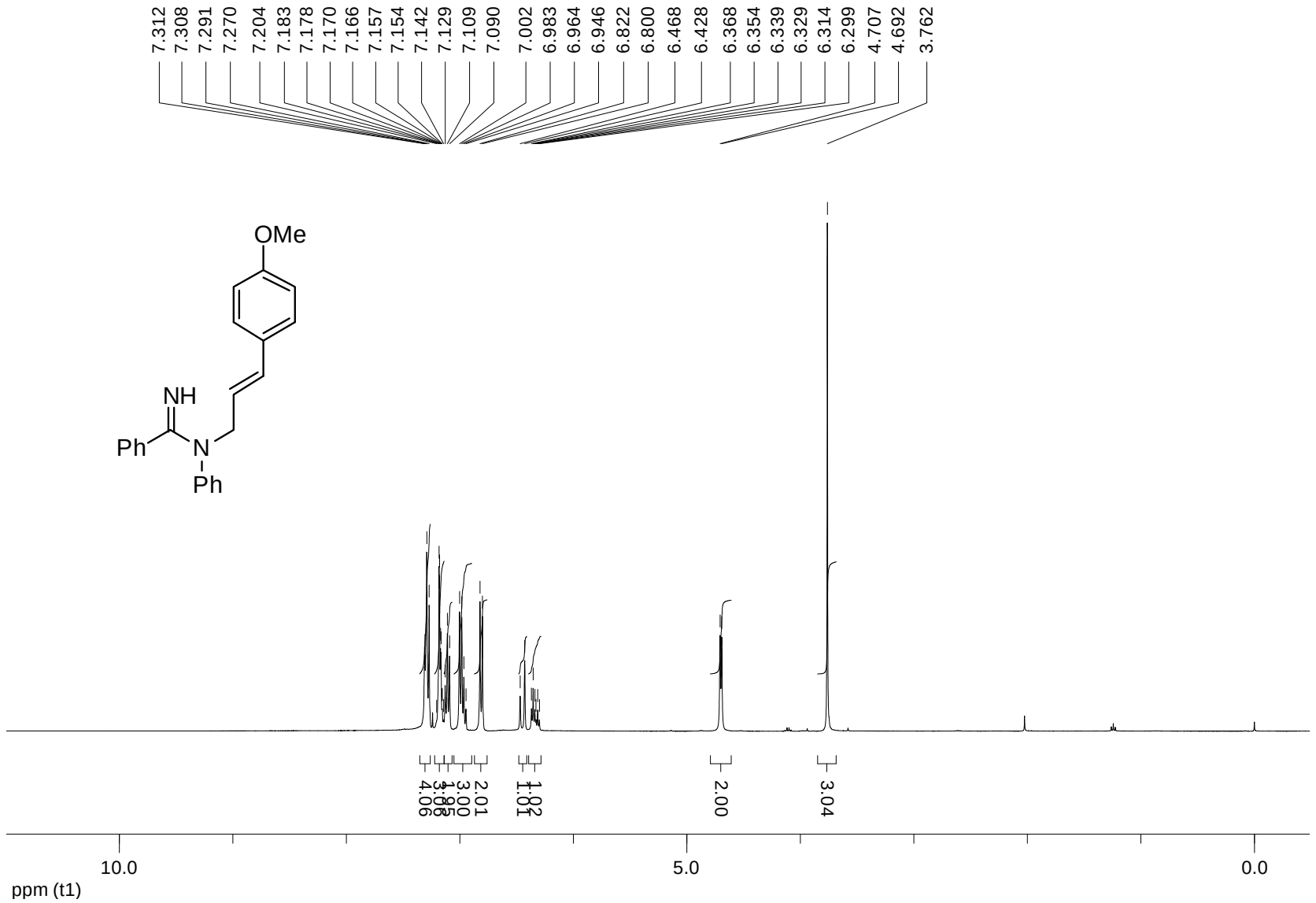
^{1}H NMR spectrum of **1g** (400 MHz, $CDCl_3$)



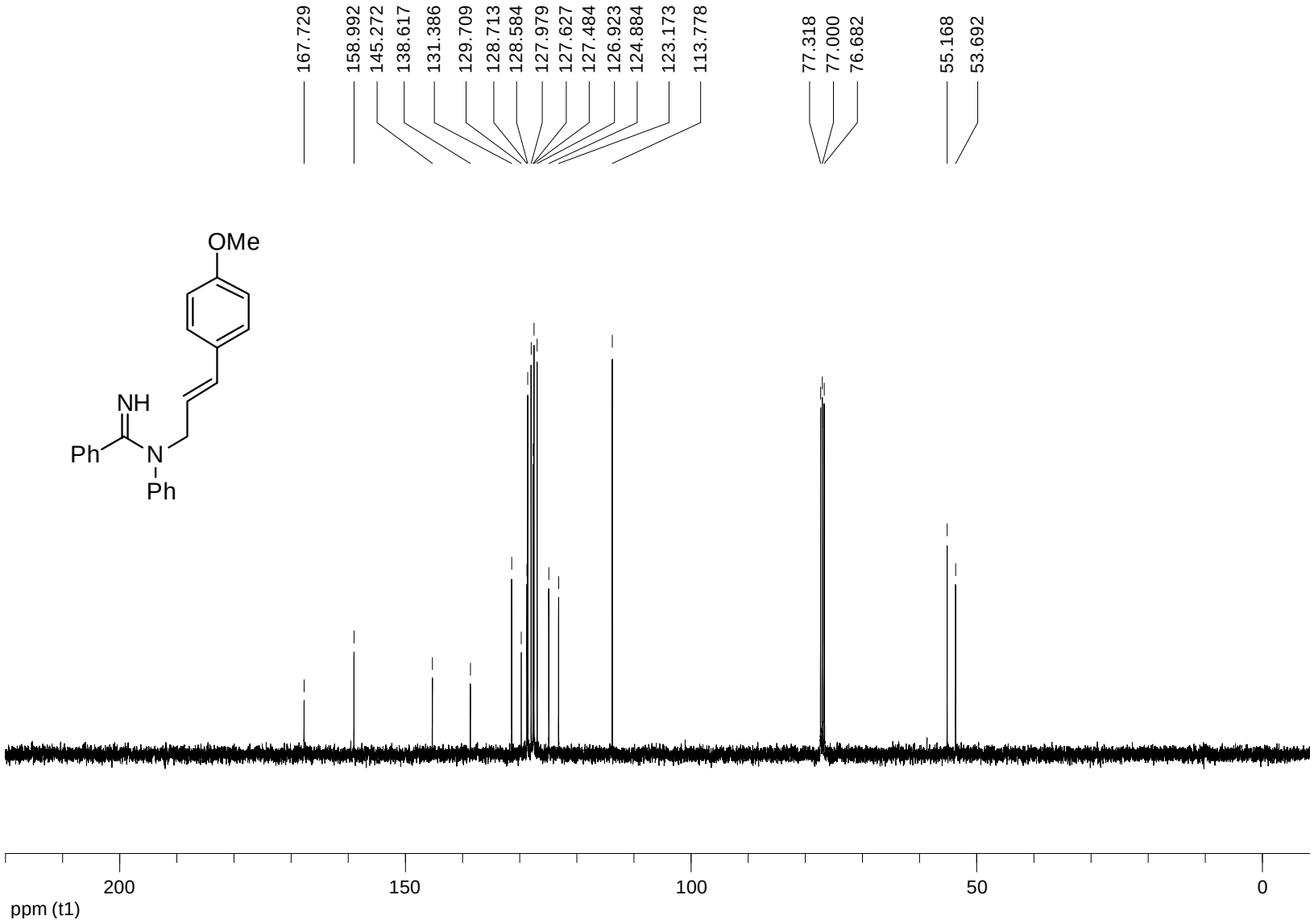
^{13}C NMR spectrum of **1g** (100 MHz, $CDCl_3$)



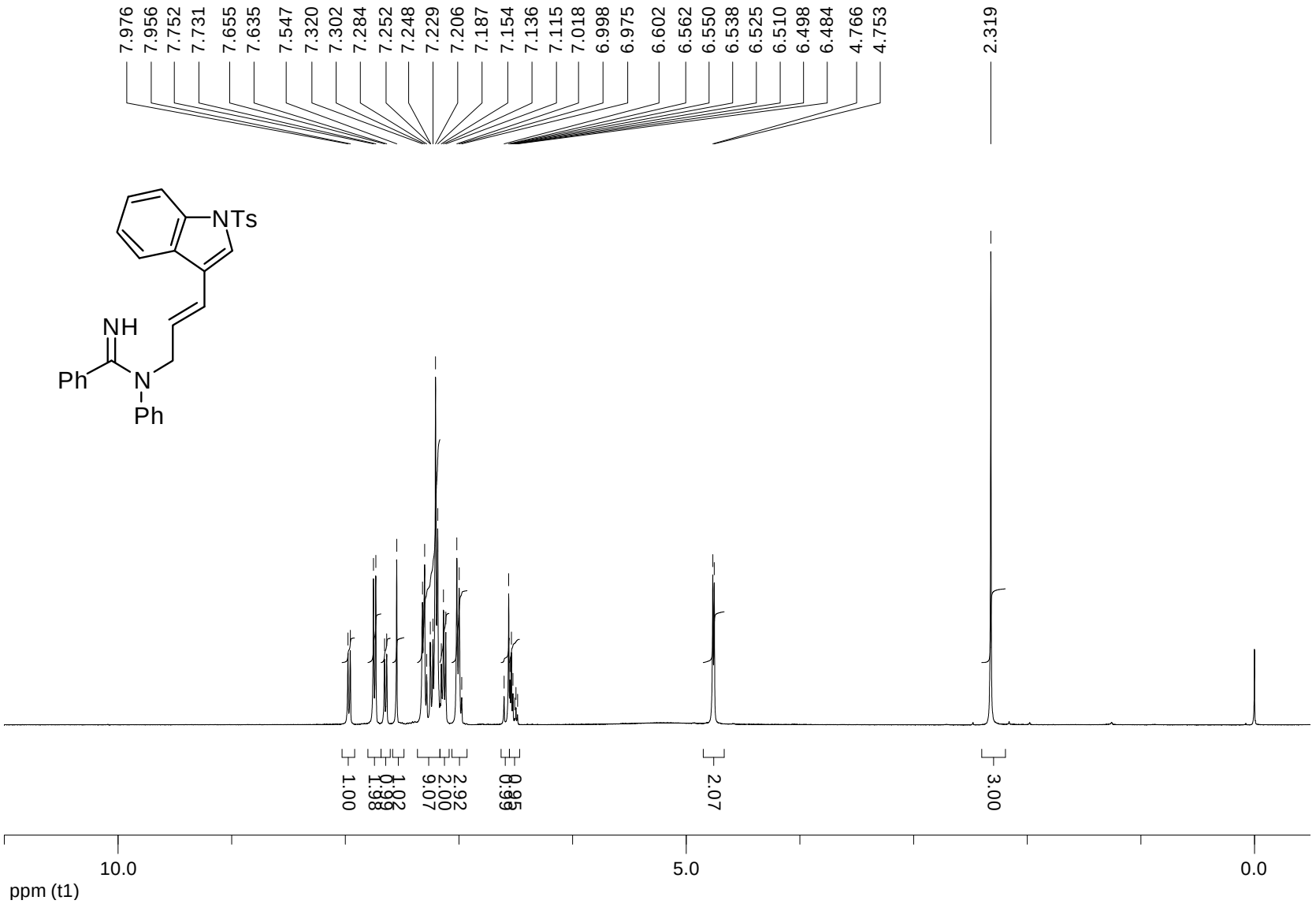
^{1}H NMR spectrum of **1h** (400 MHz, $CDCl_3$)



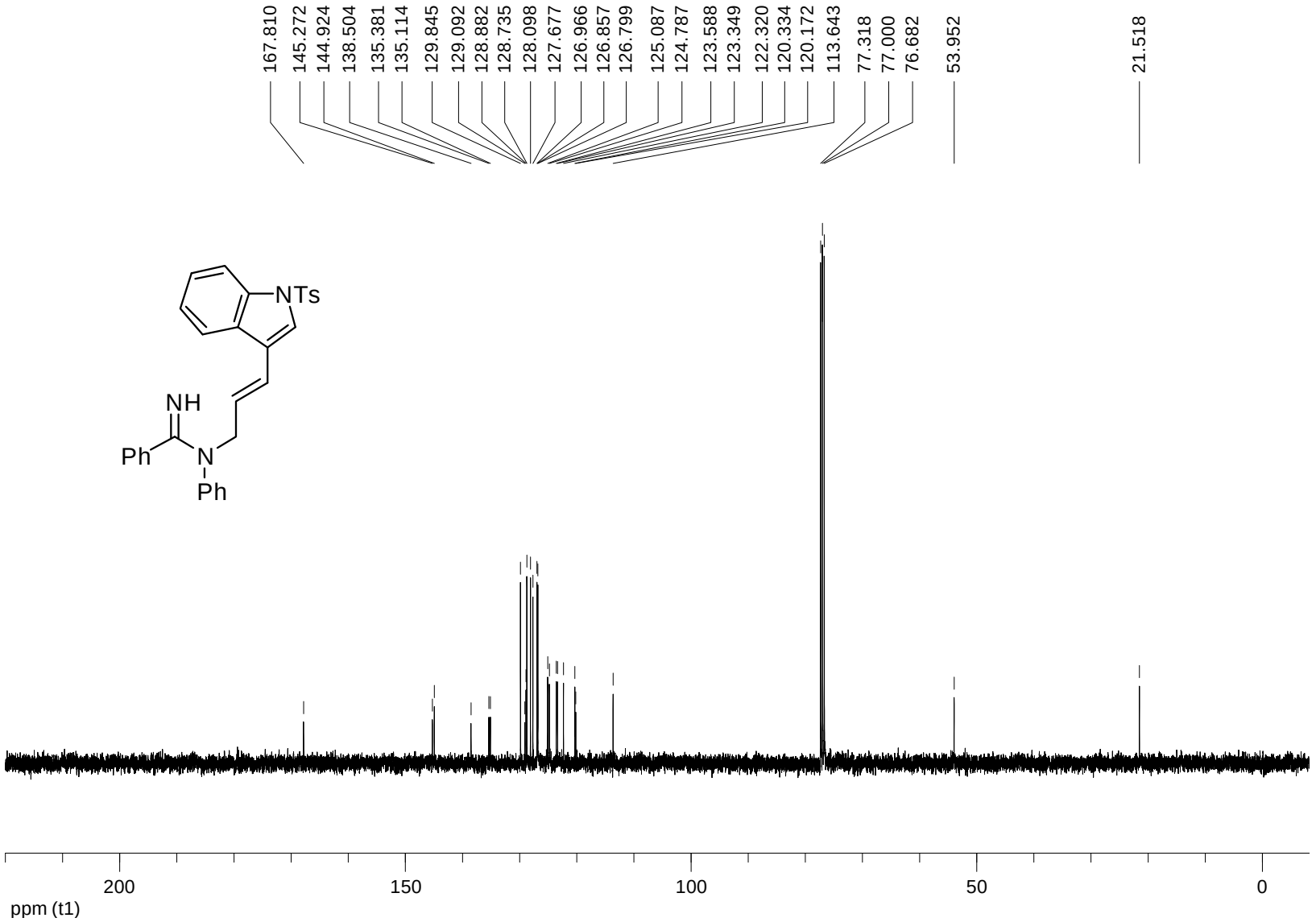
^{13}C NMR spectrum of **1h** (100 MHz, $CDCl_3$)



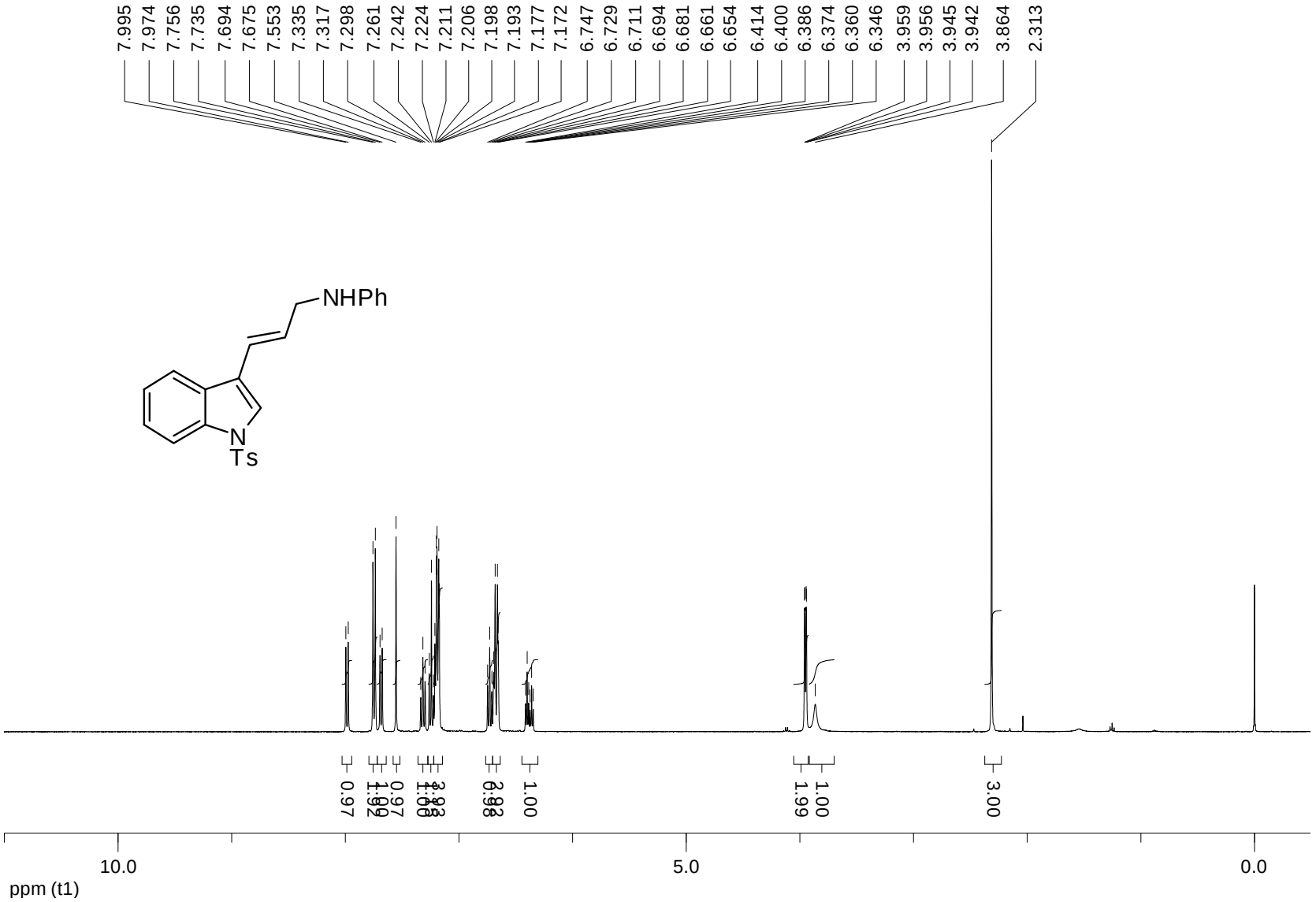
^{1}H NMR spectrum of **1i** (400 MHz, $CDCl_3$)



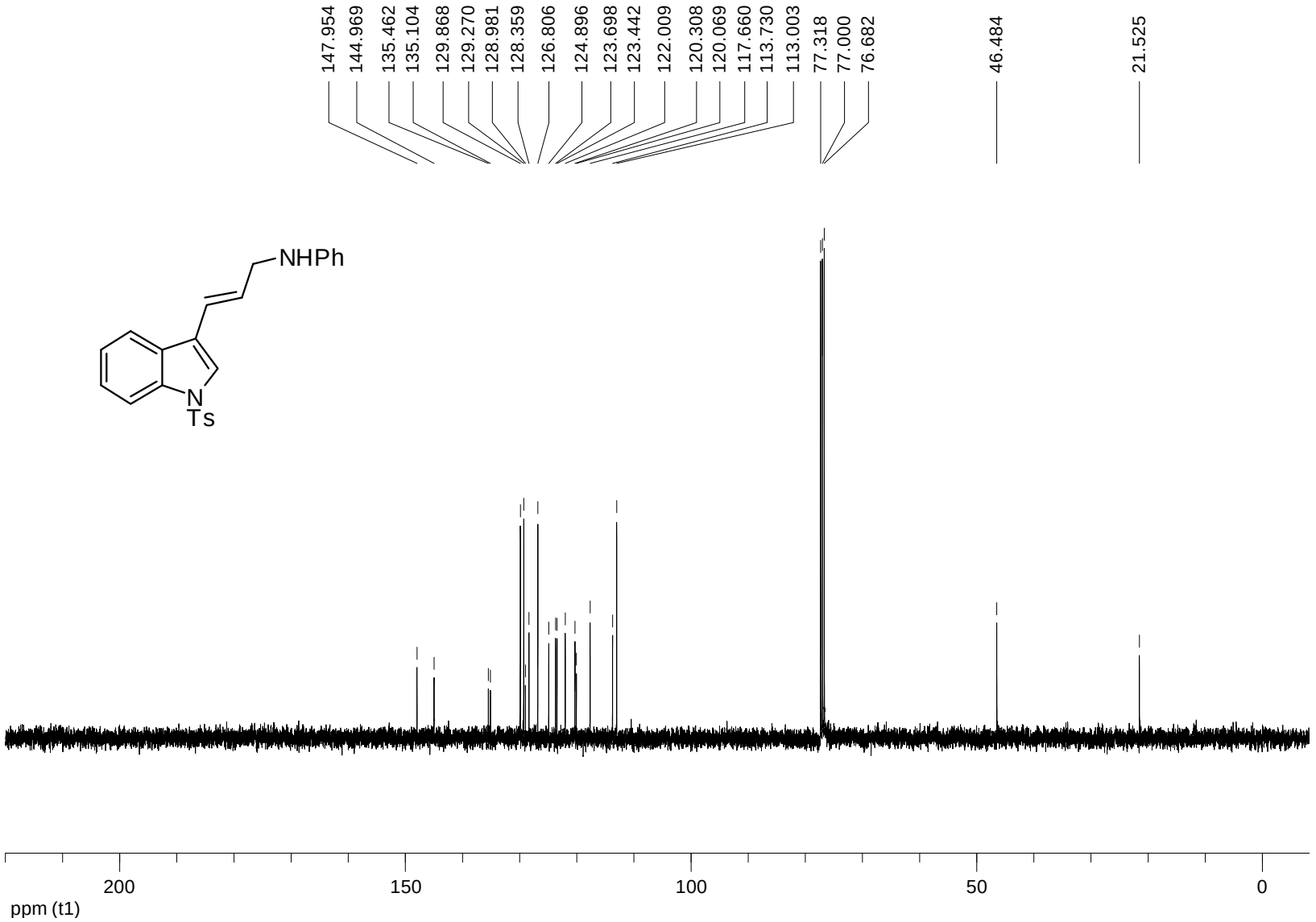
^{13}C NMR spectrum of **1i** (100 MHz, $CDCl_3$)



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



^{13}C NMR spectrum of **A** (400 MHz, $CDCl_3$)



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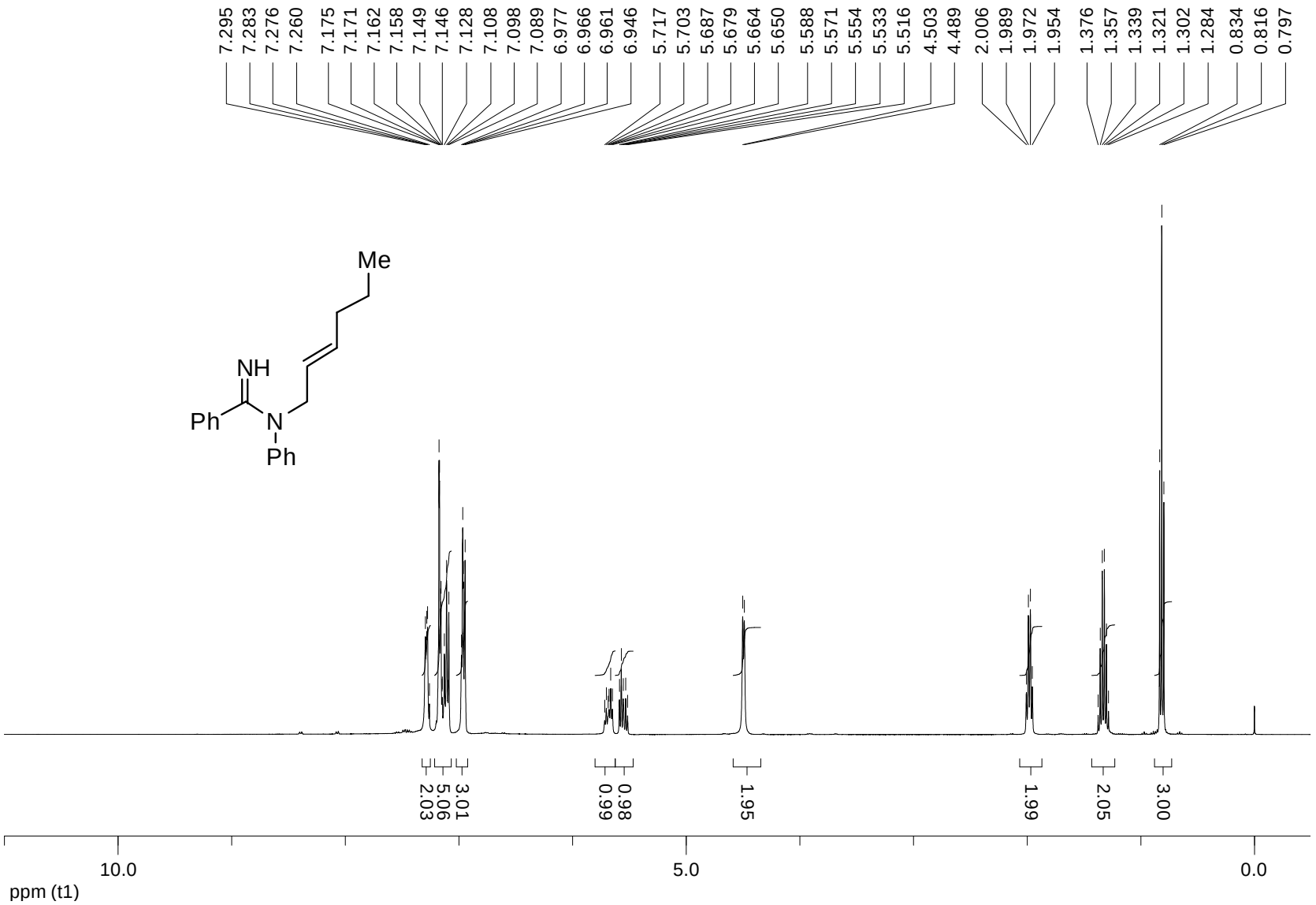

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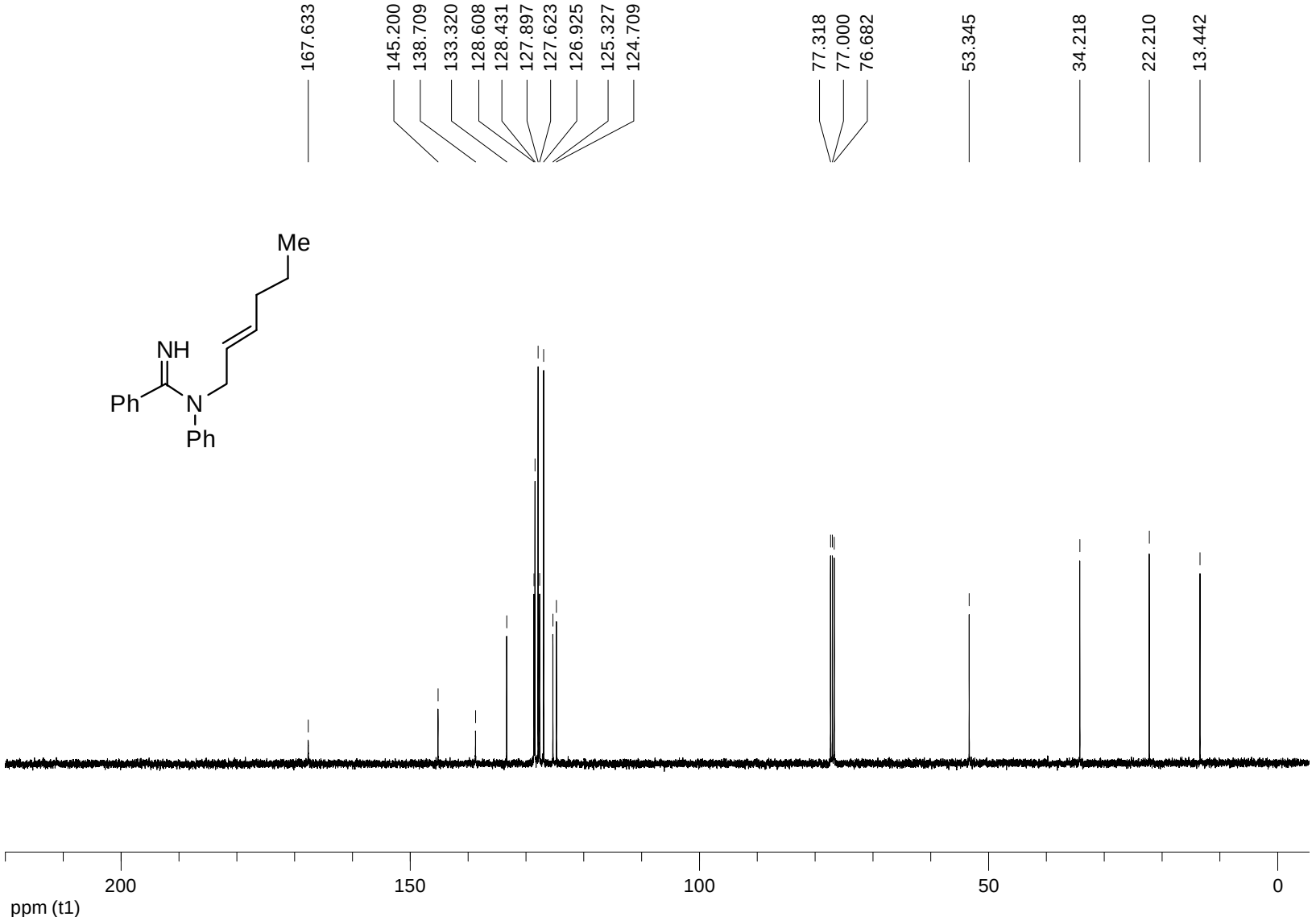
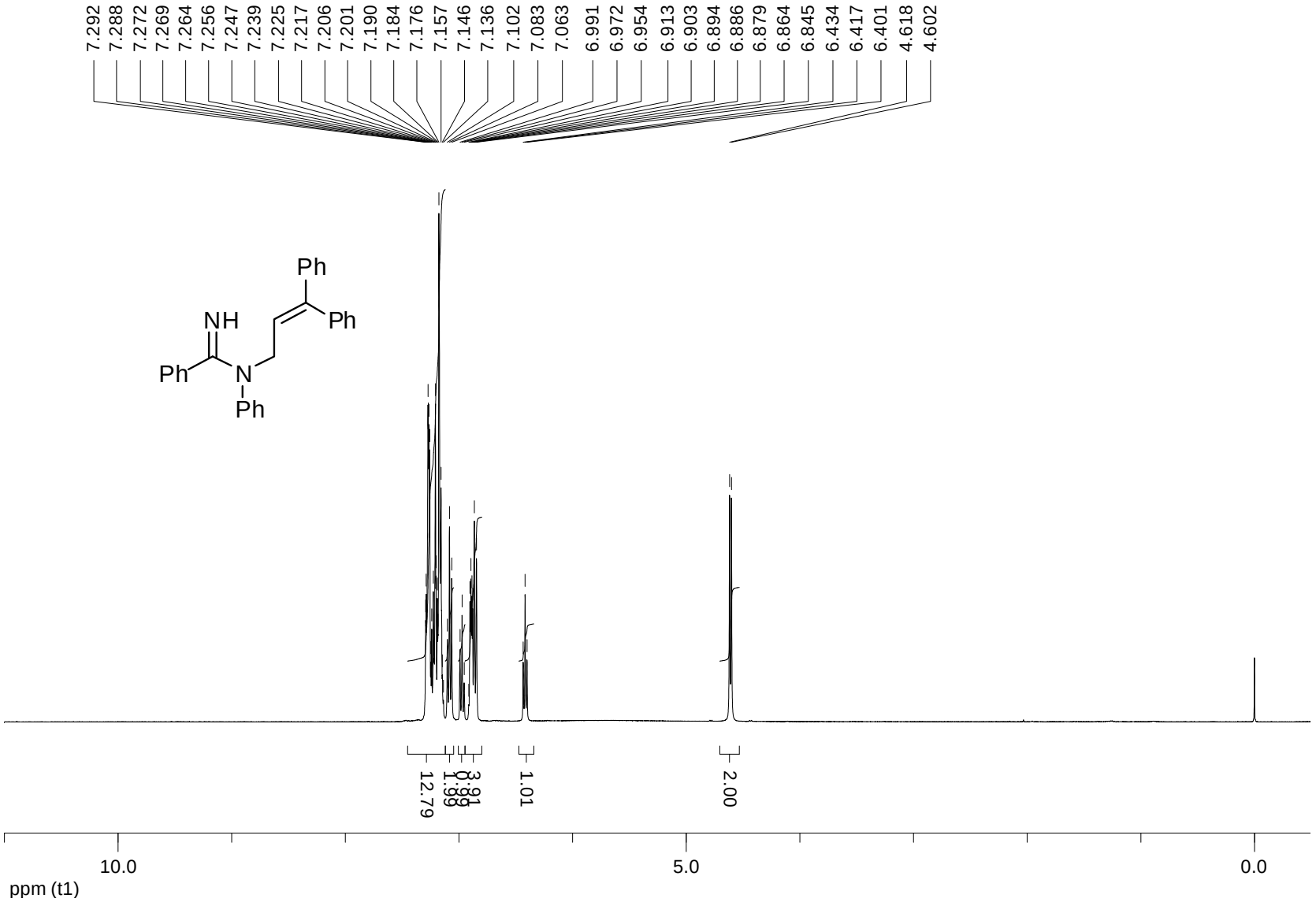
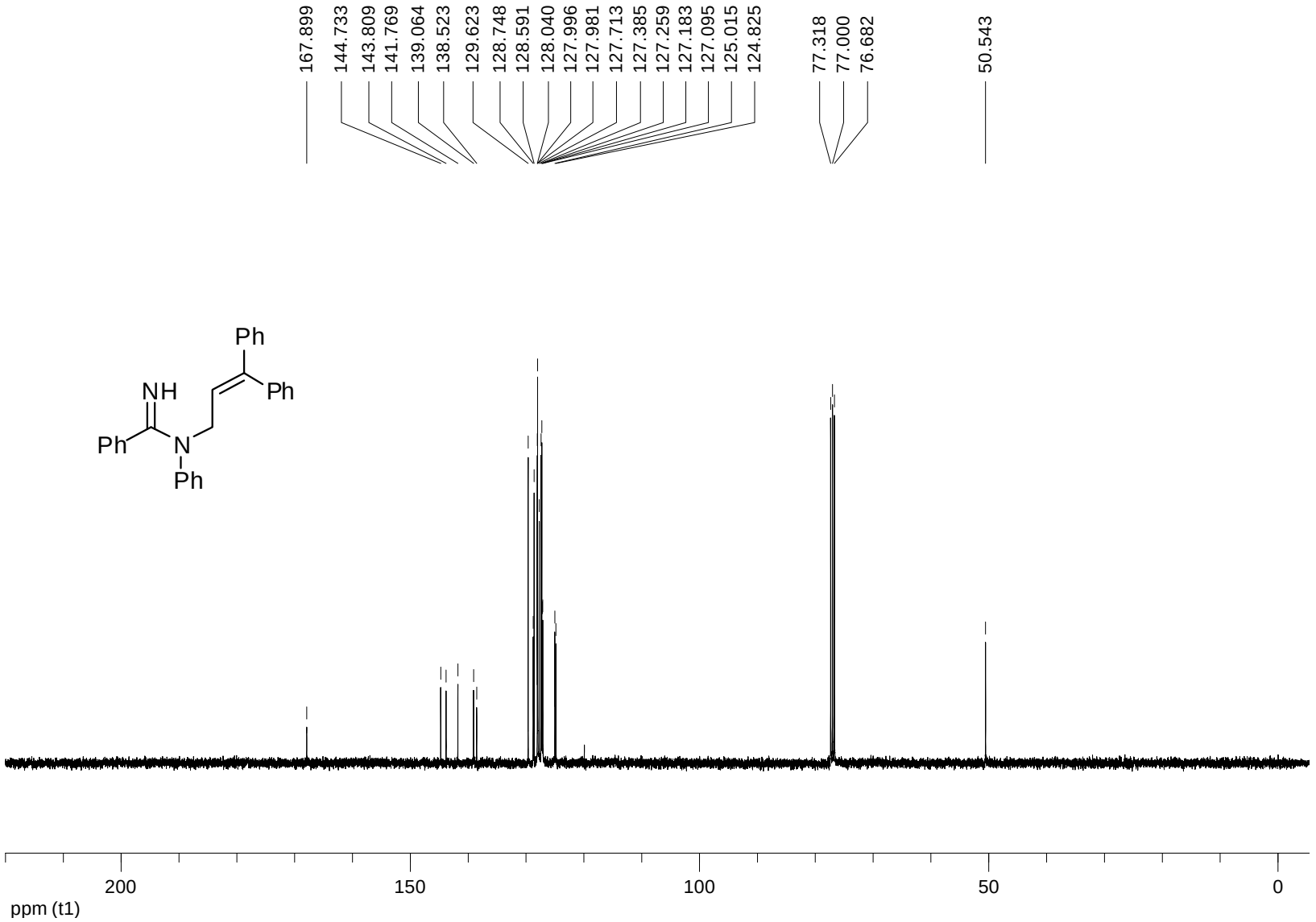


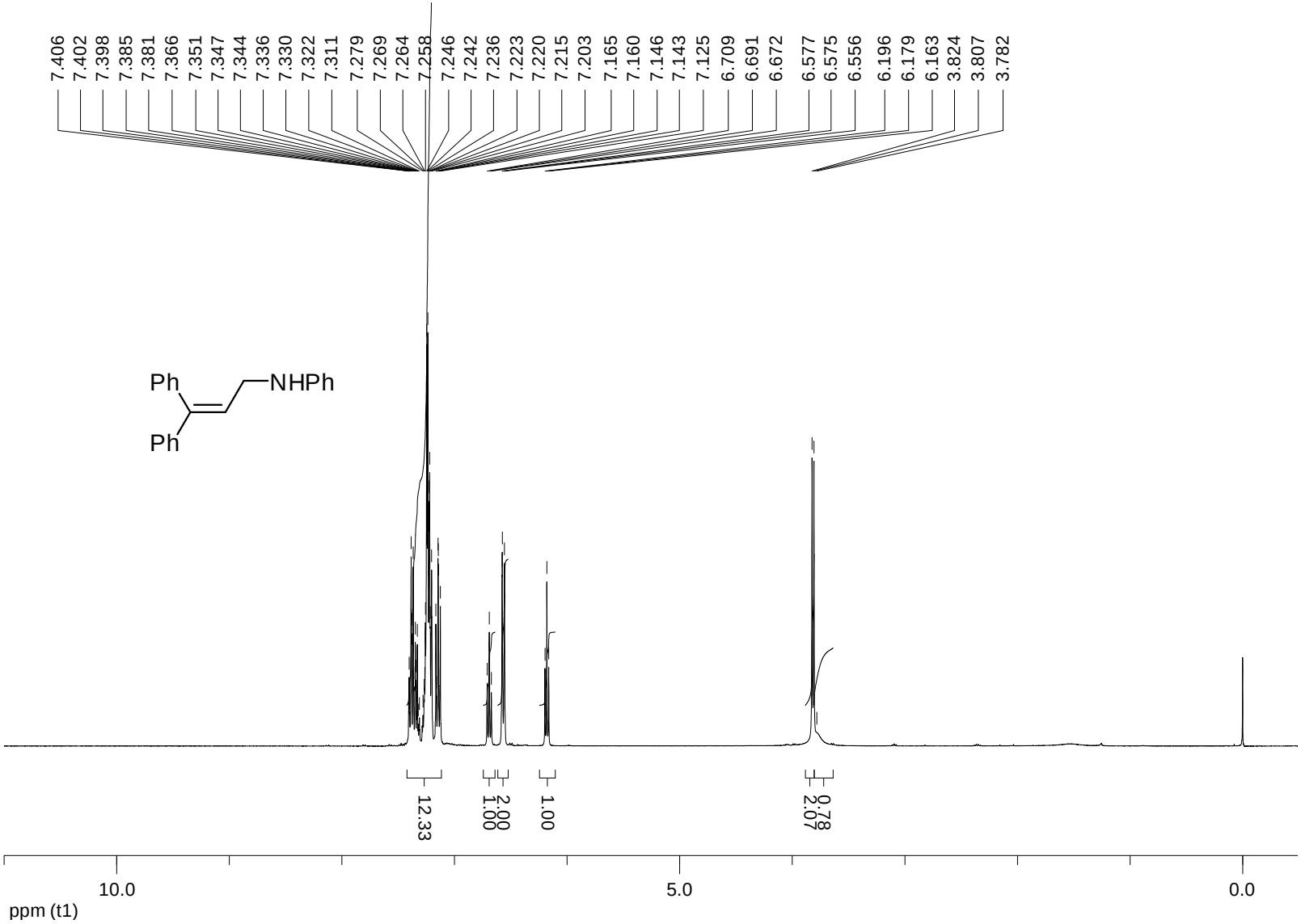
^{1}H NMR spectrum of **1k** (400 MHz, $CDCl_3$)



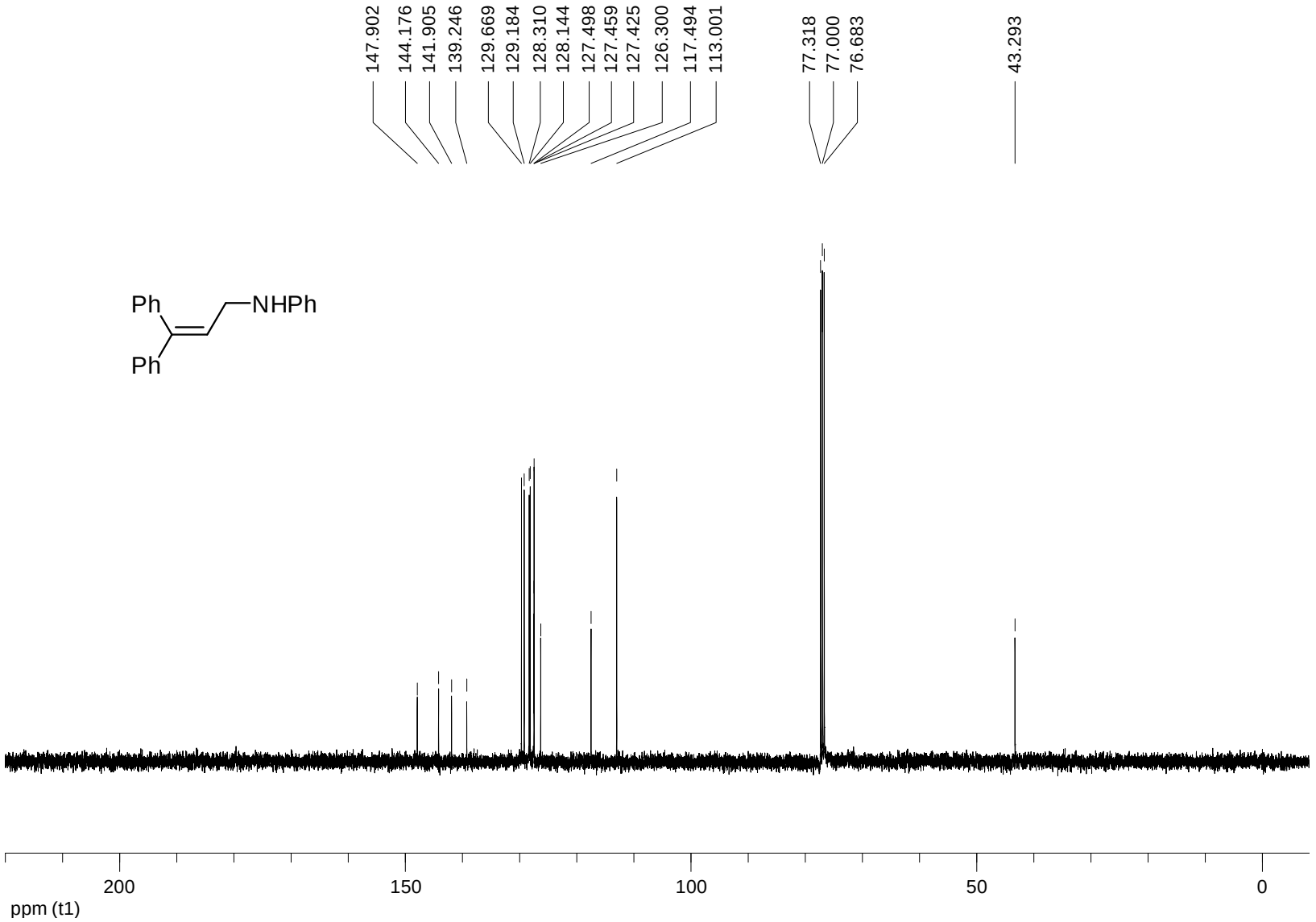
^{13}C NMR spectrum of **1k** (100 MHz, $CDCl_3$)



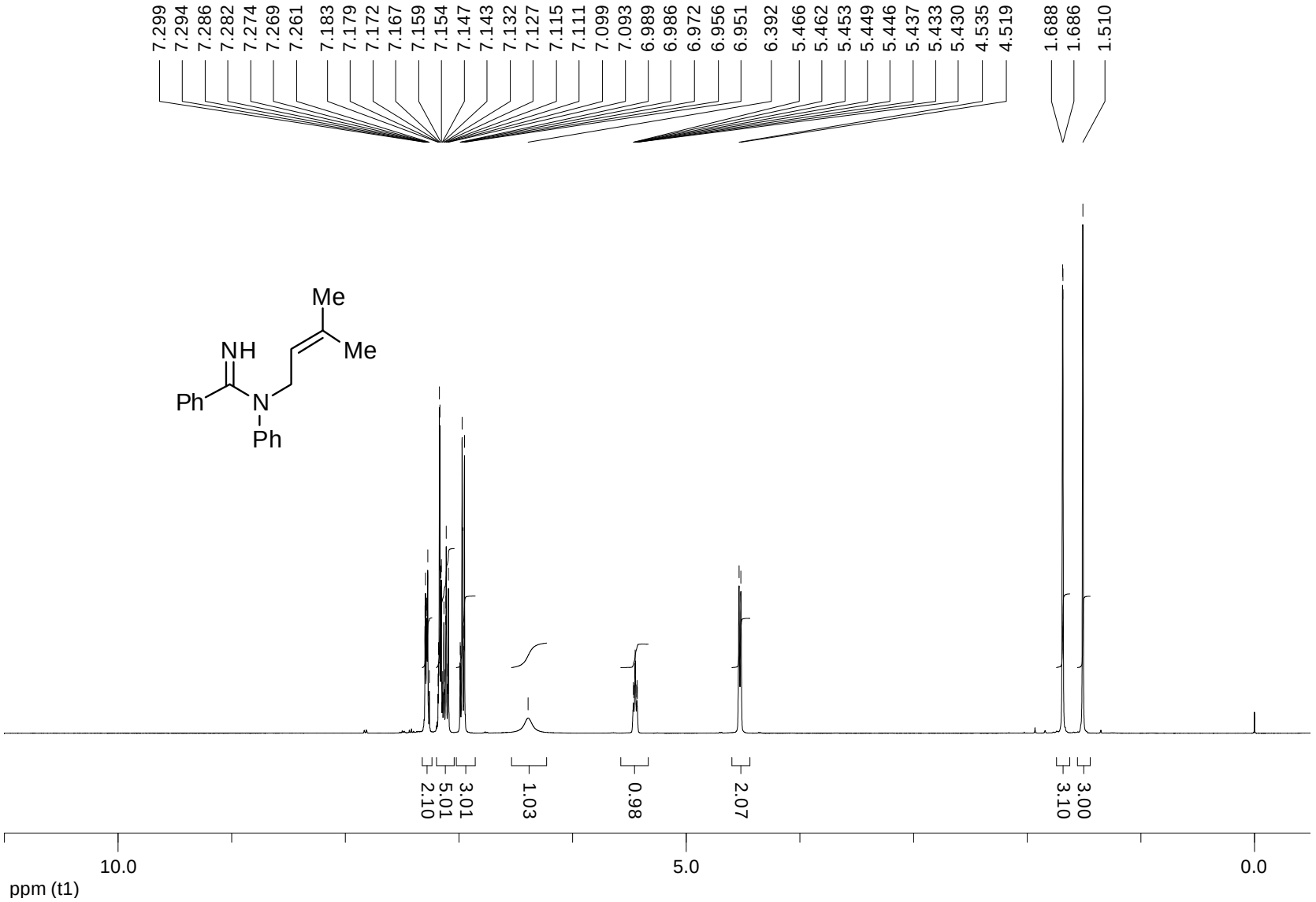
^{1}H NMR spectrum of **B** (400 MHz, $CDCl_3$)



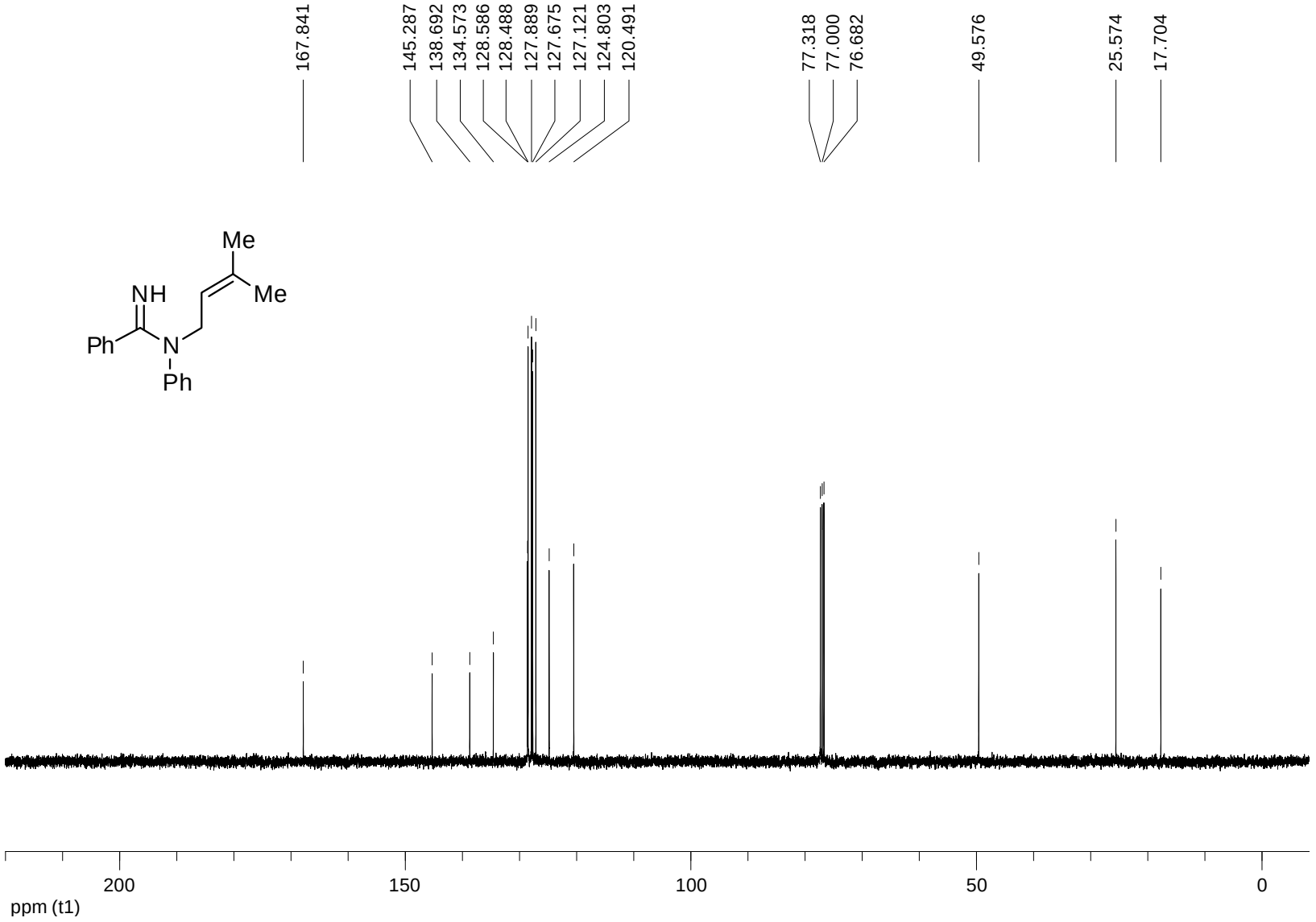
^{13}C NMR spectrum of **B** (100 MHz, $CDCl_3$)



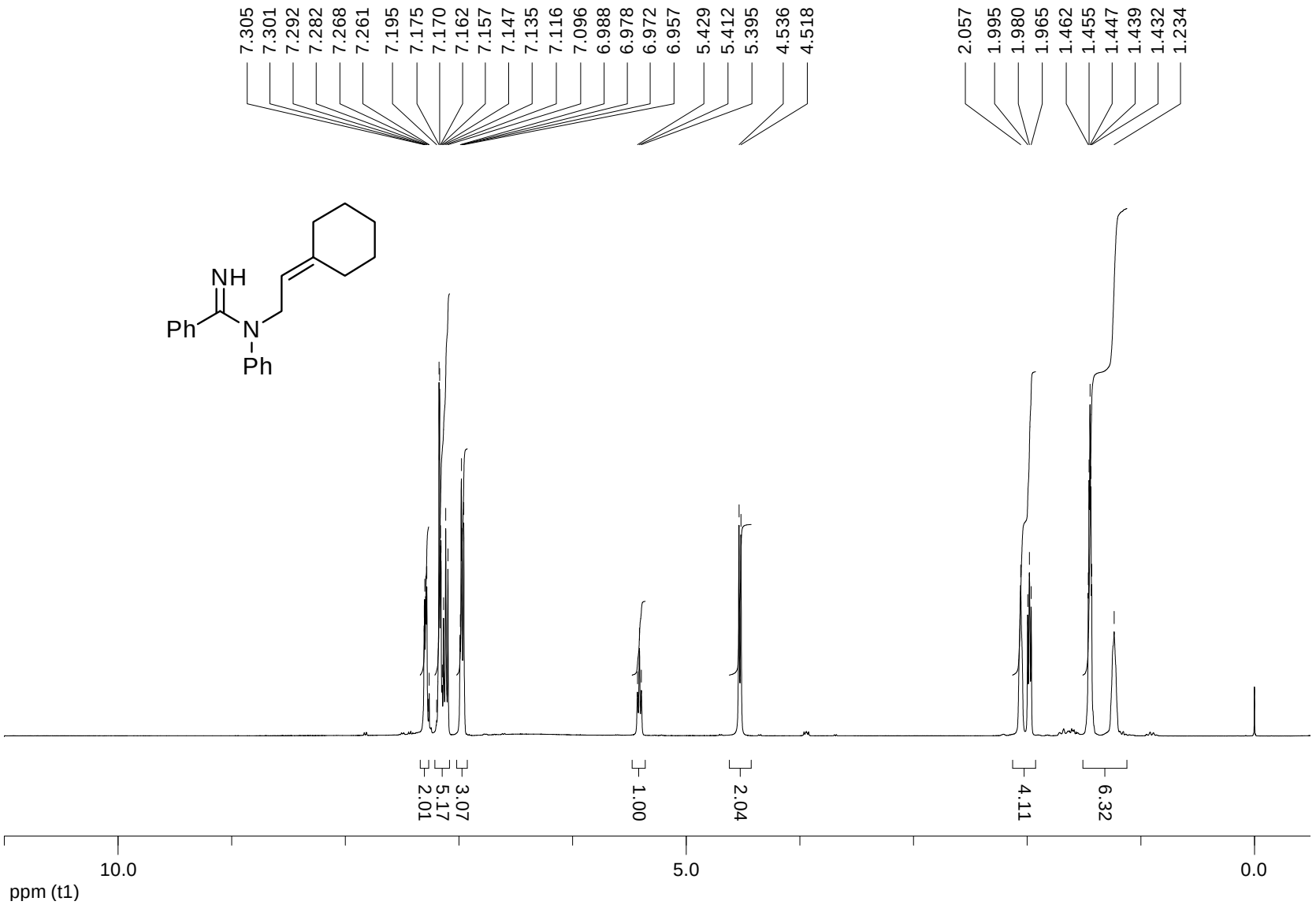
^{1}H NMR spectrum of **1l** (400 MHz, $CDCl_3$)



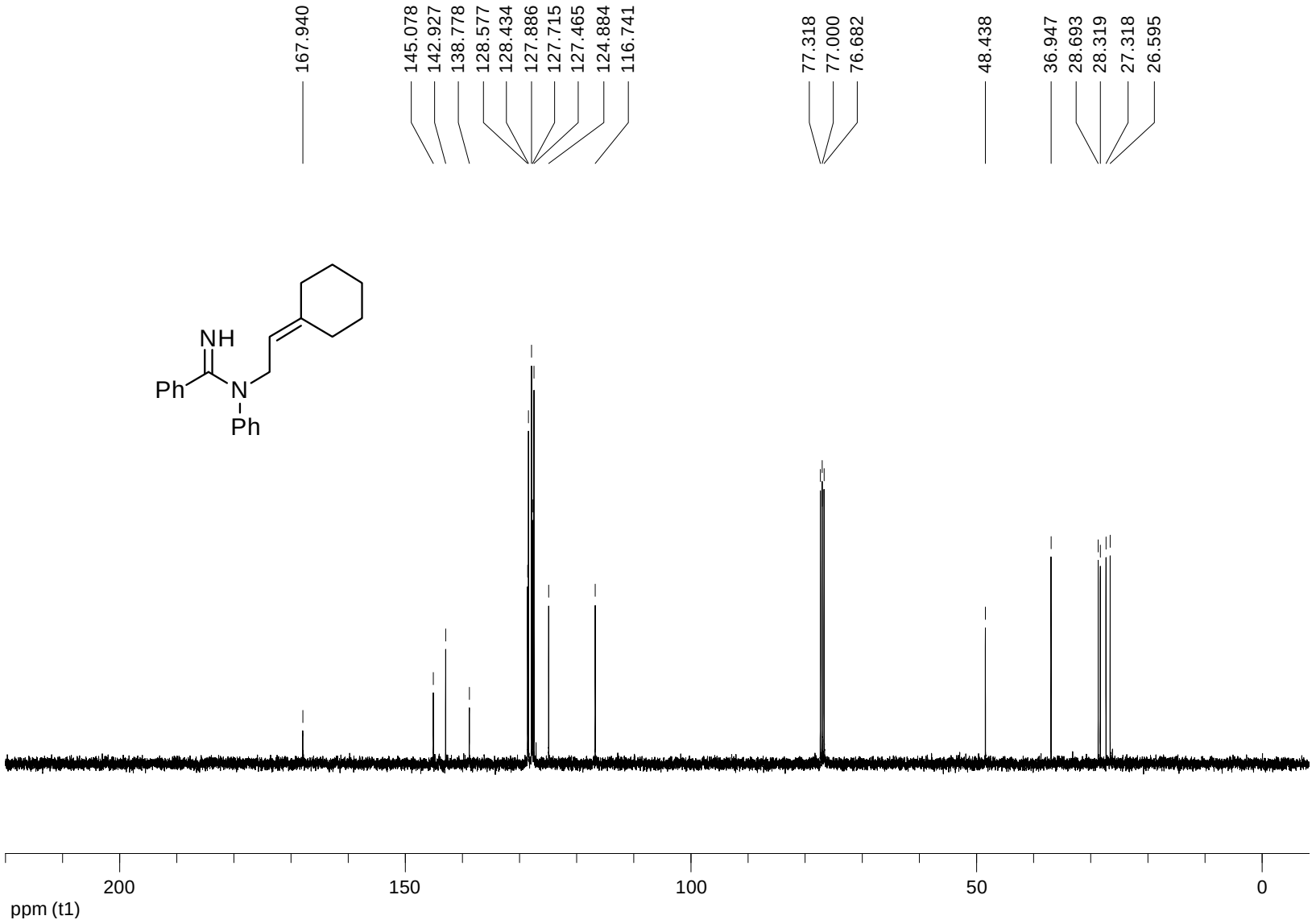
^{13}C NMR spectrum of **1l** (100 MHz, $CDCl_3$)



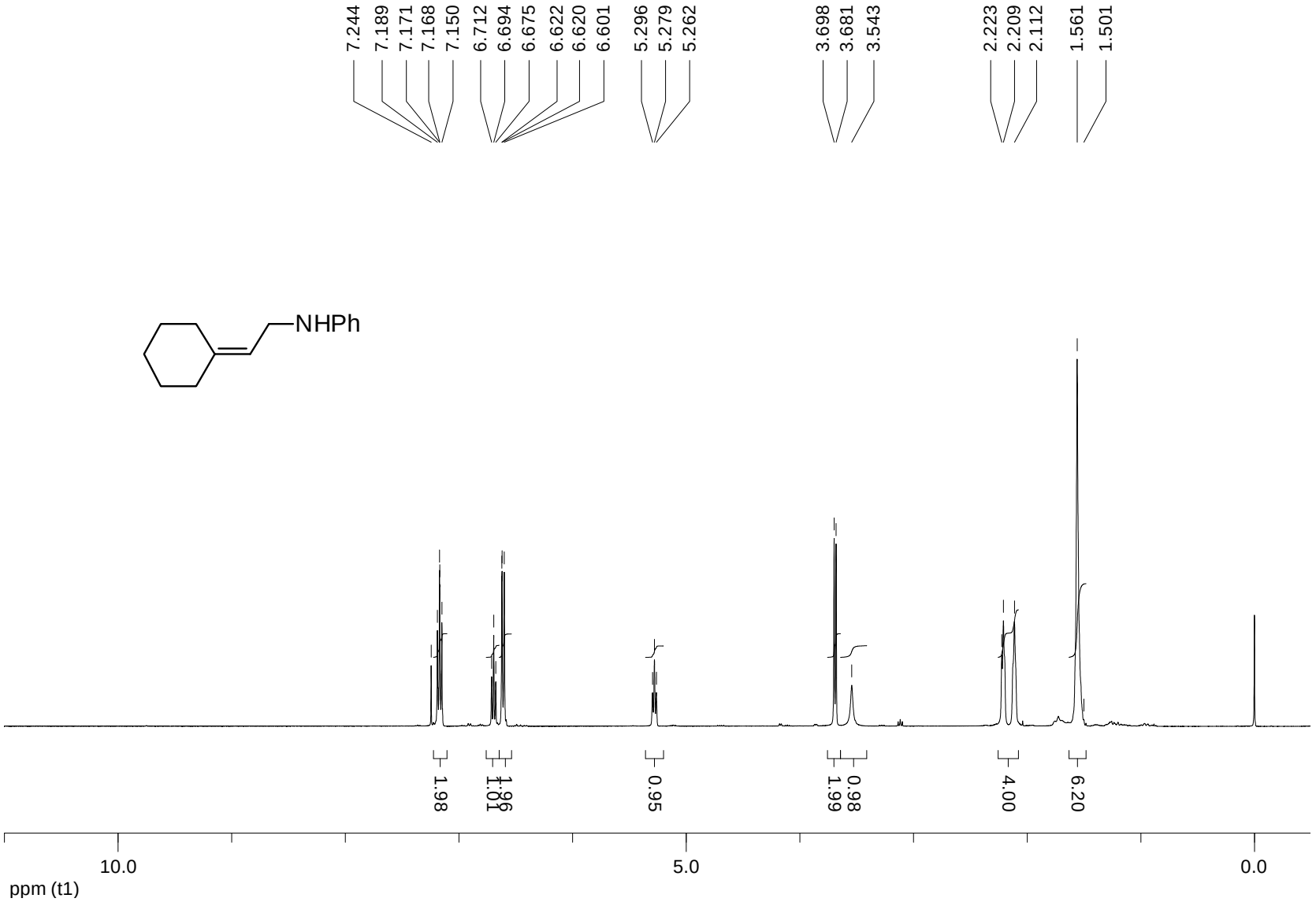
^{1}H NMR spectrum of **1m** (400 MHz, $CDCl_3$)



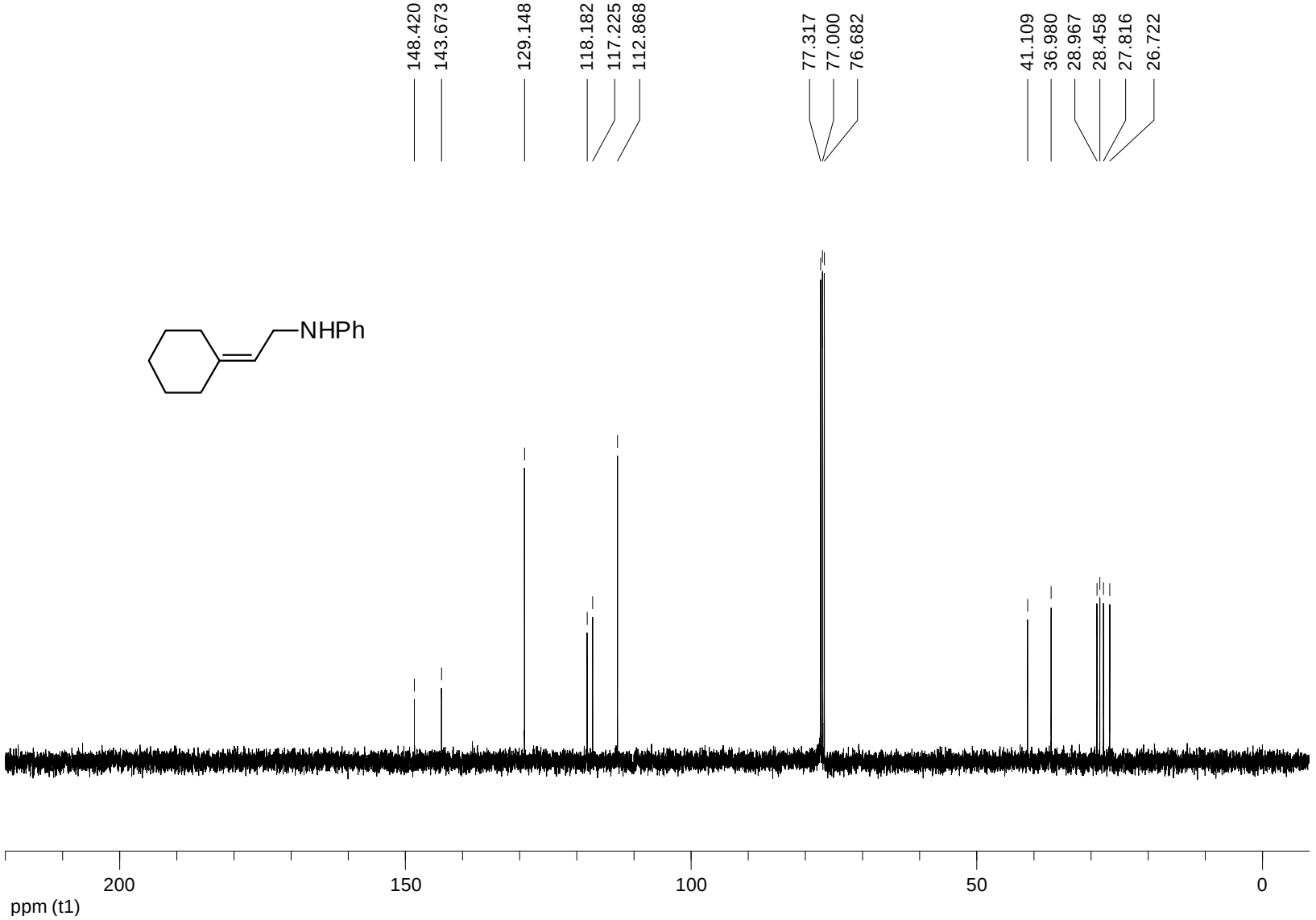
^{13}C NMR spectrum of **1m** (100 MHz, $CDCl_3$)



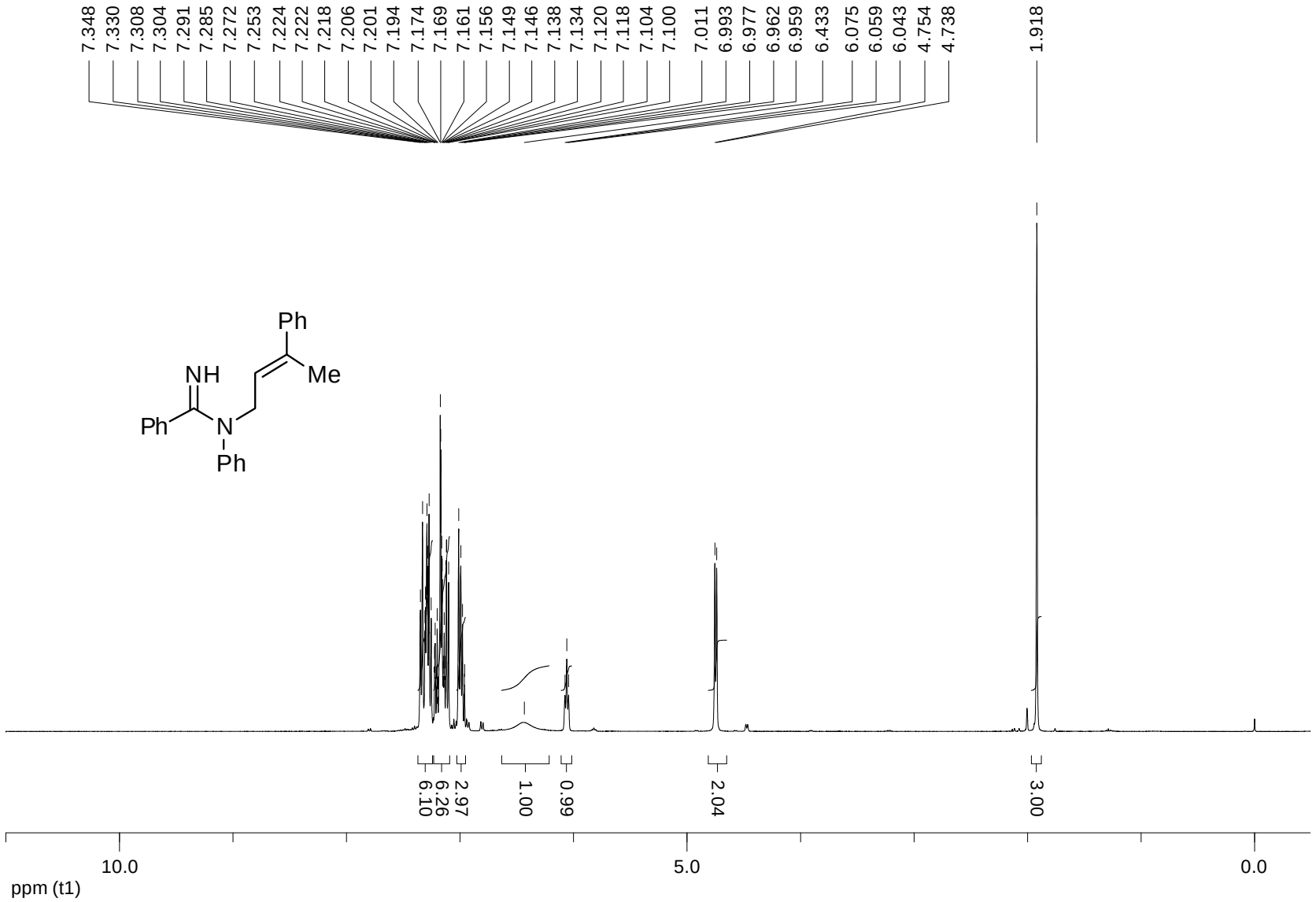
^{1}H NMR spectrum of **C** (400 MHz, $CDCl_3$)



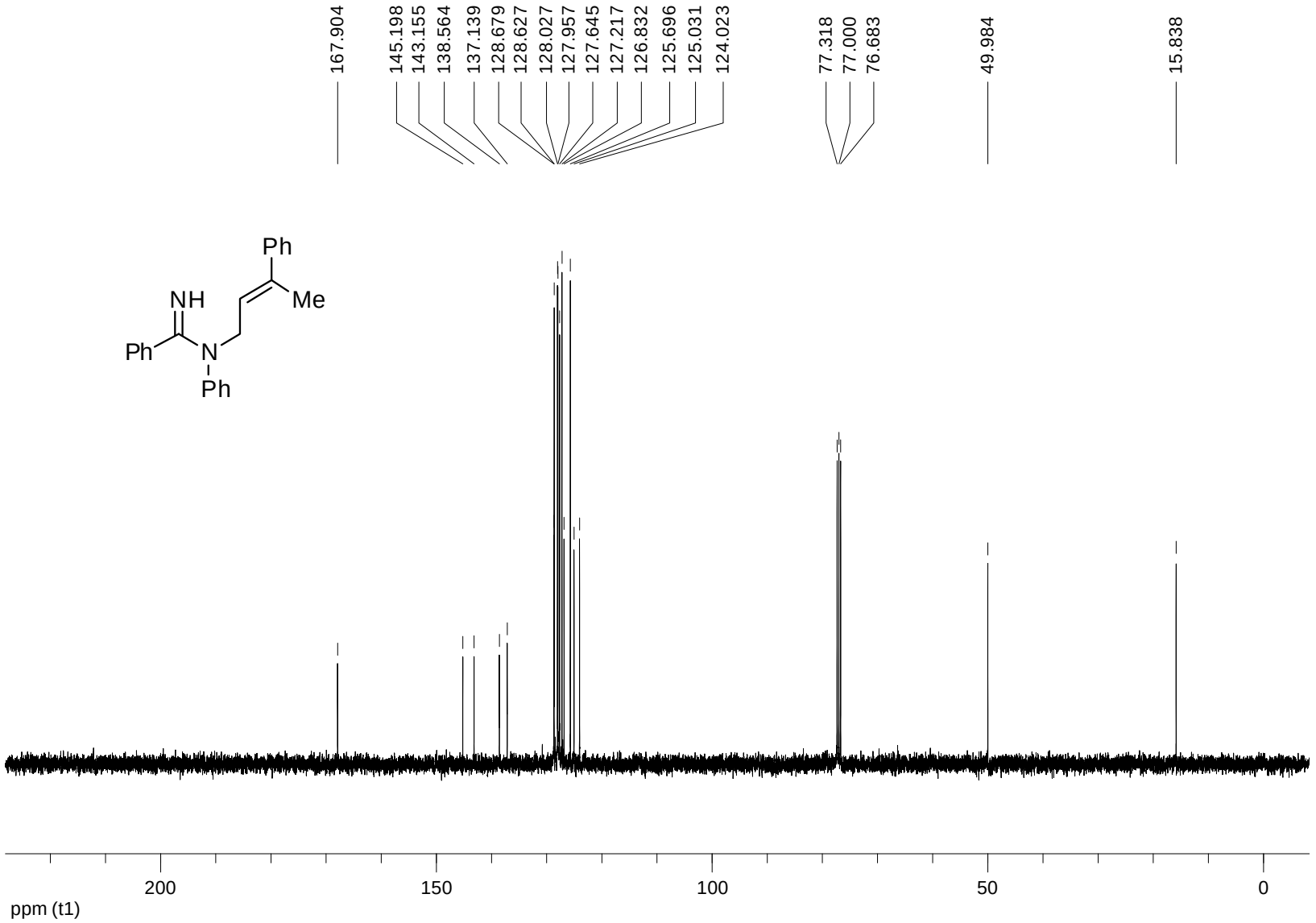
^{13}C NMR spectrum of **C** (100 MHz, $CDCl_3$)



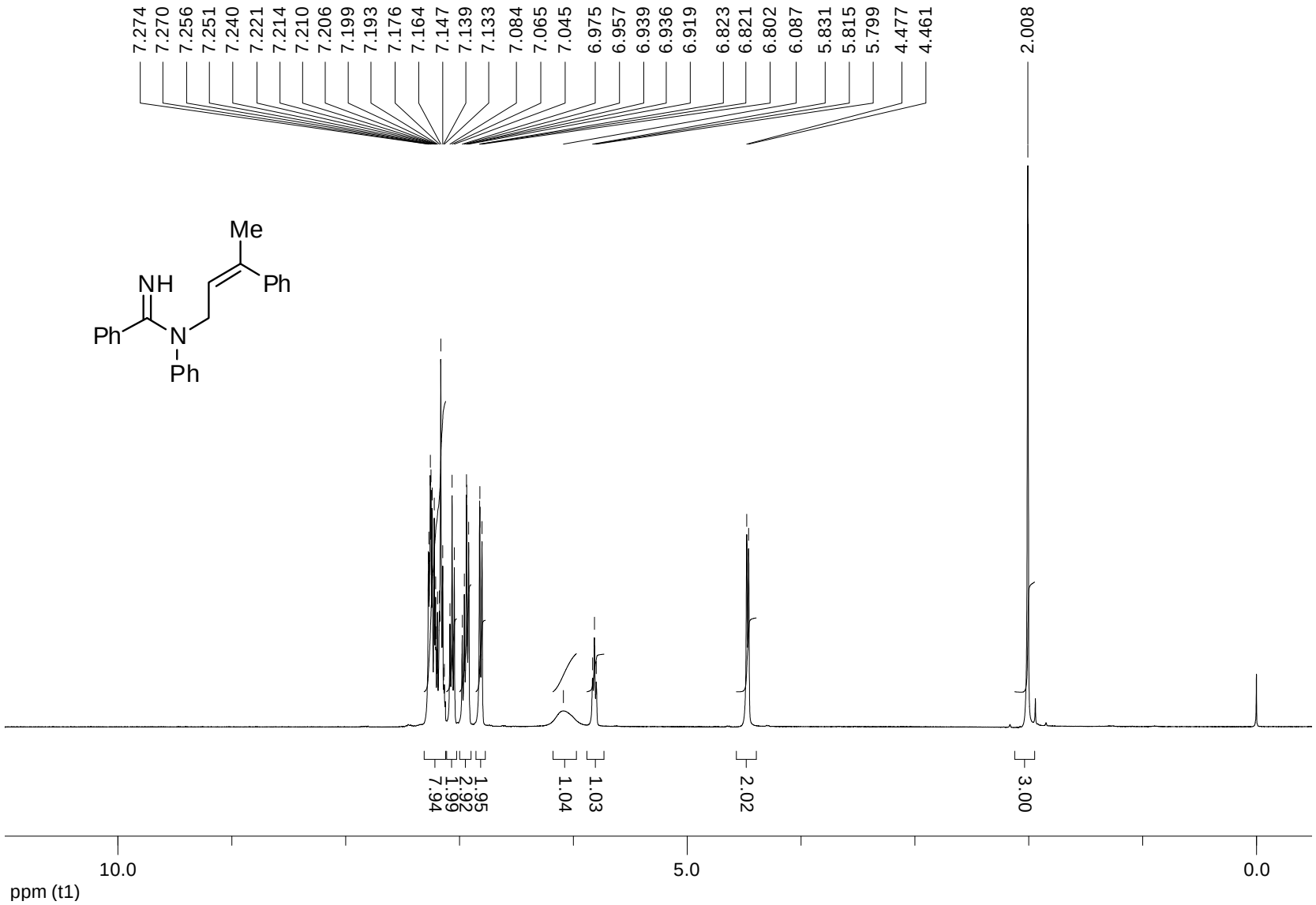
^{1}H NMR spectrum of **1n** (E/Z = 21:1) (400 MHz, $CDCl_3$)



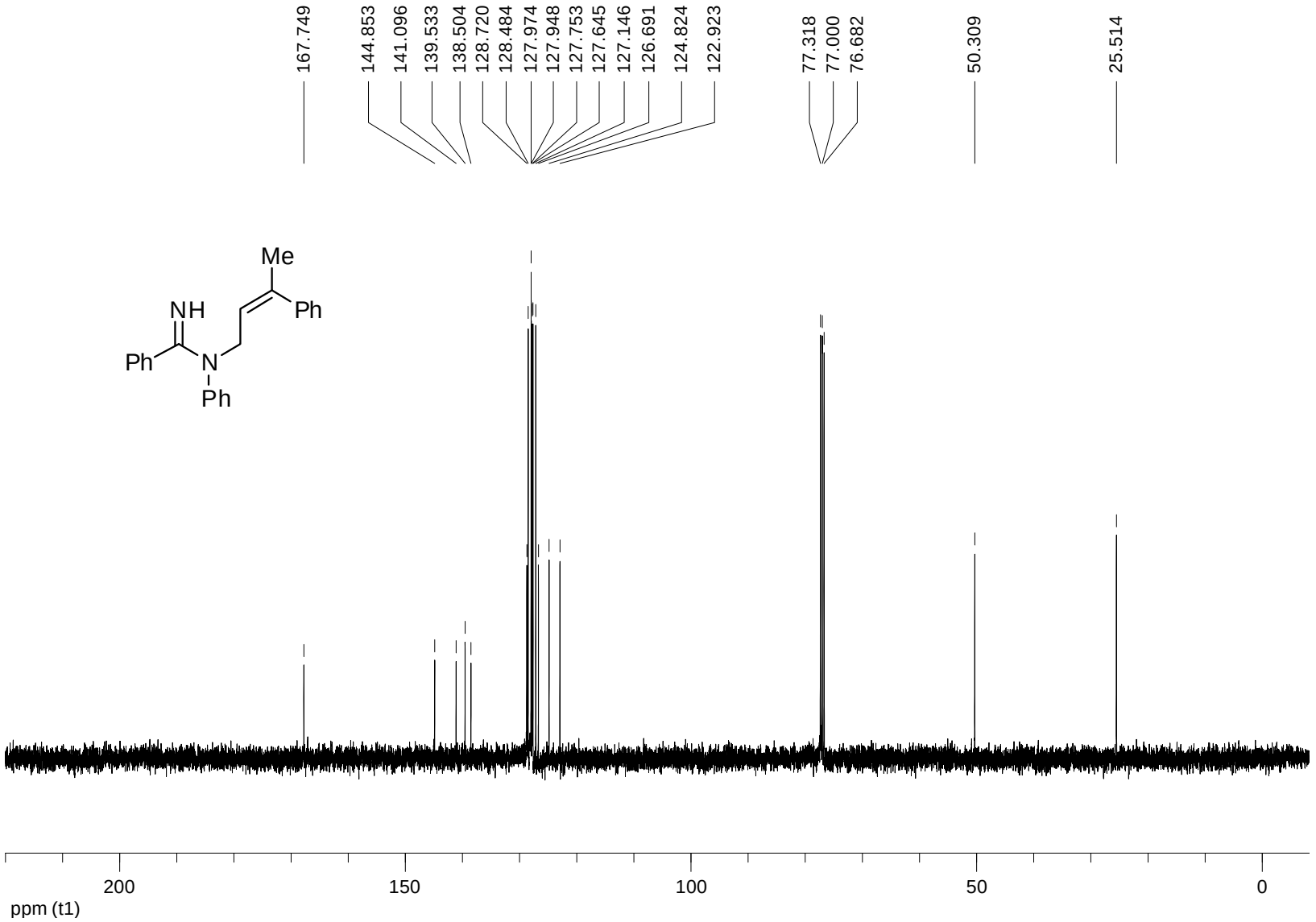
^{13}C NMR spectrum of **1n** (E/Z = 21:1) (100 MHz, $CDCl_3$)



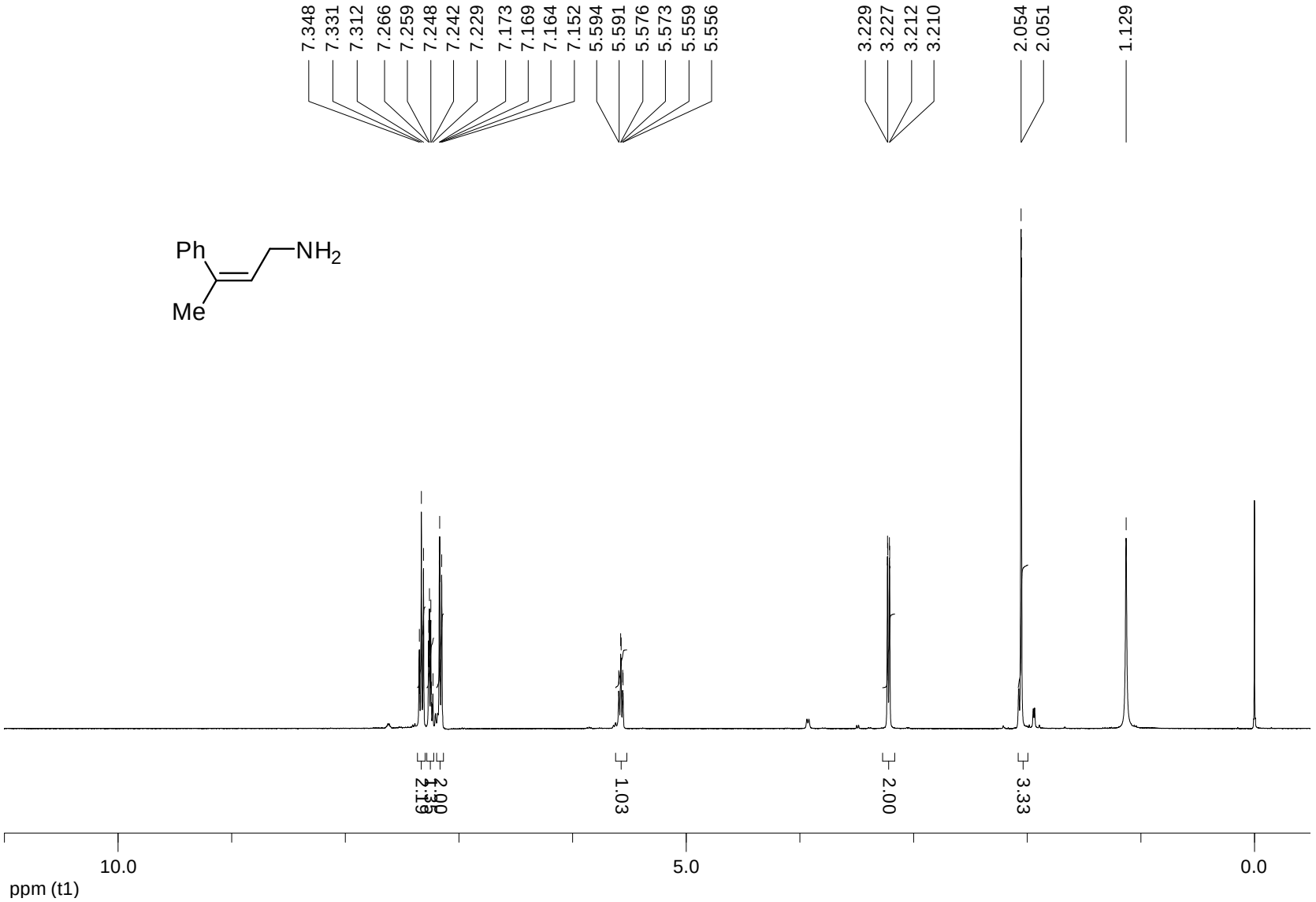
^{1}H NMR spectrum of **1o** (400 MHz, $CDCl_3$)



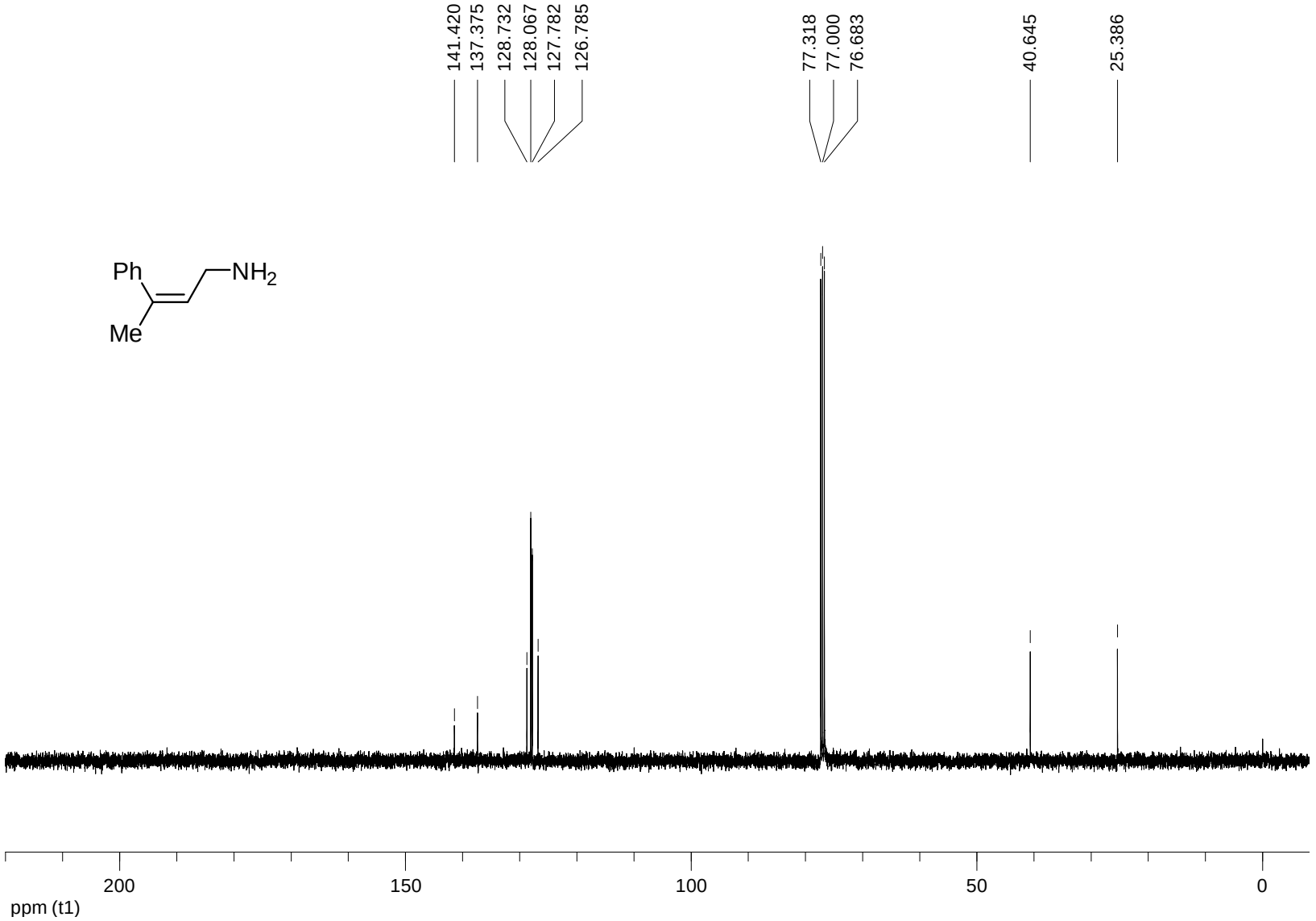
^{13}C NMR spectrum of **1o** (100 MHz, $CDCl_3$)



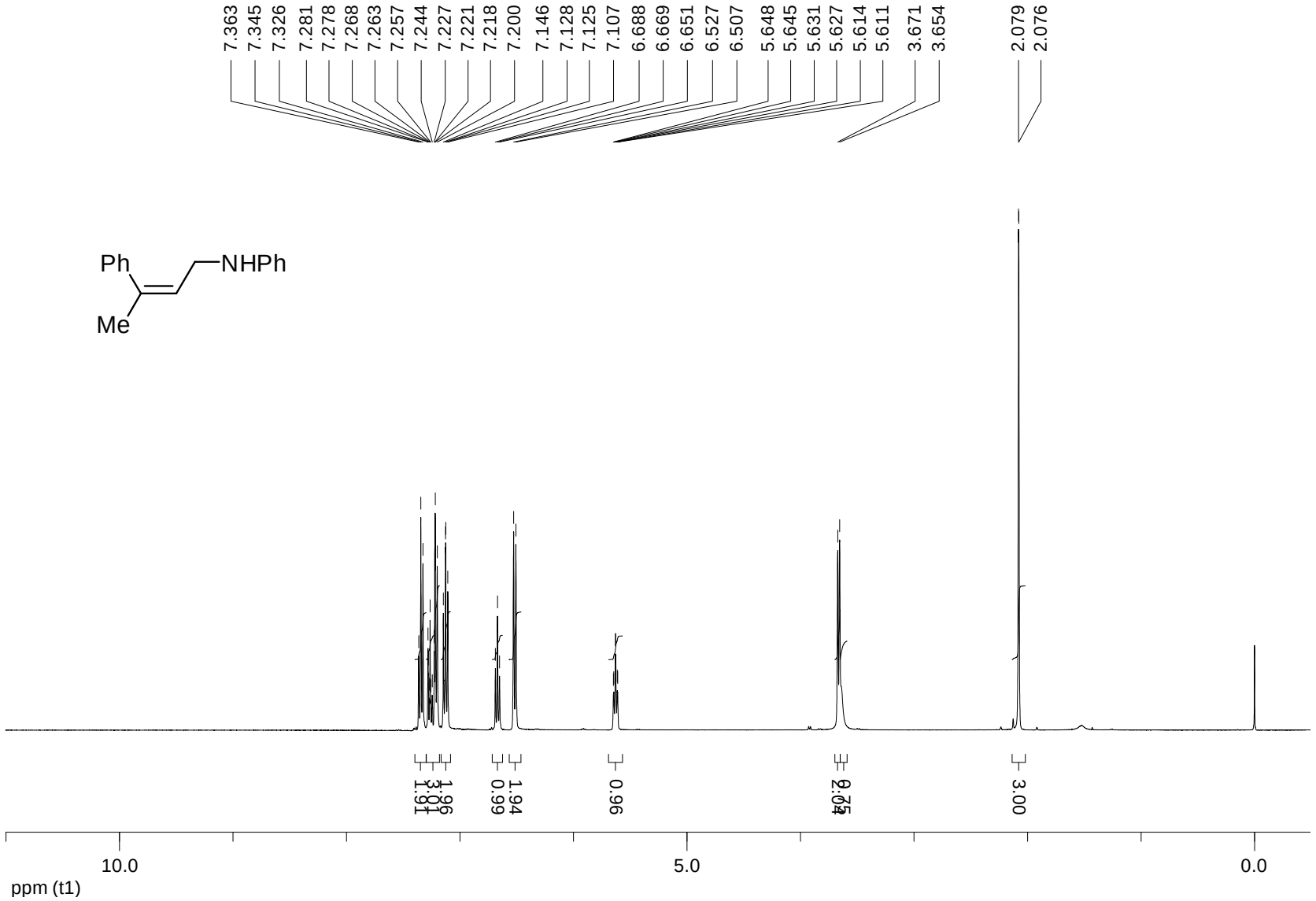
^{1}H NMR spectrum of **D** (400 MHz, $CDCl_3$)



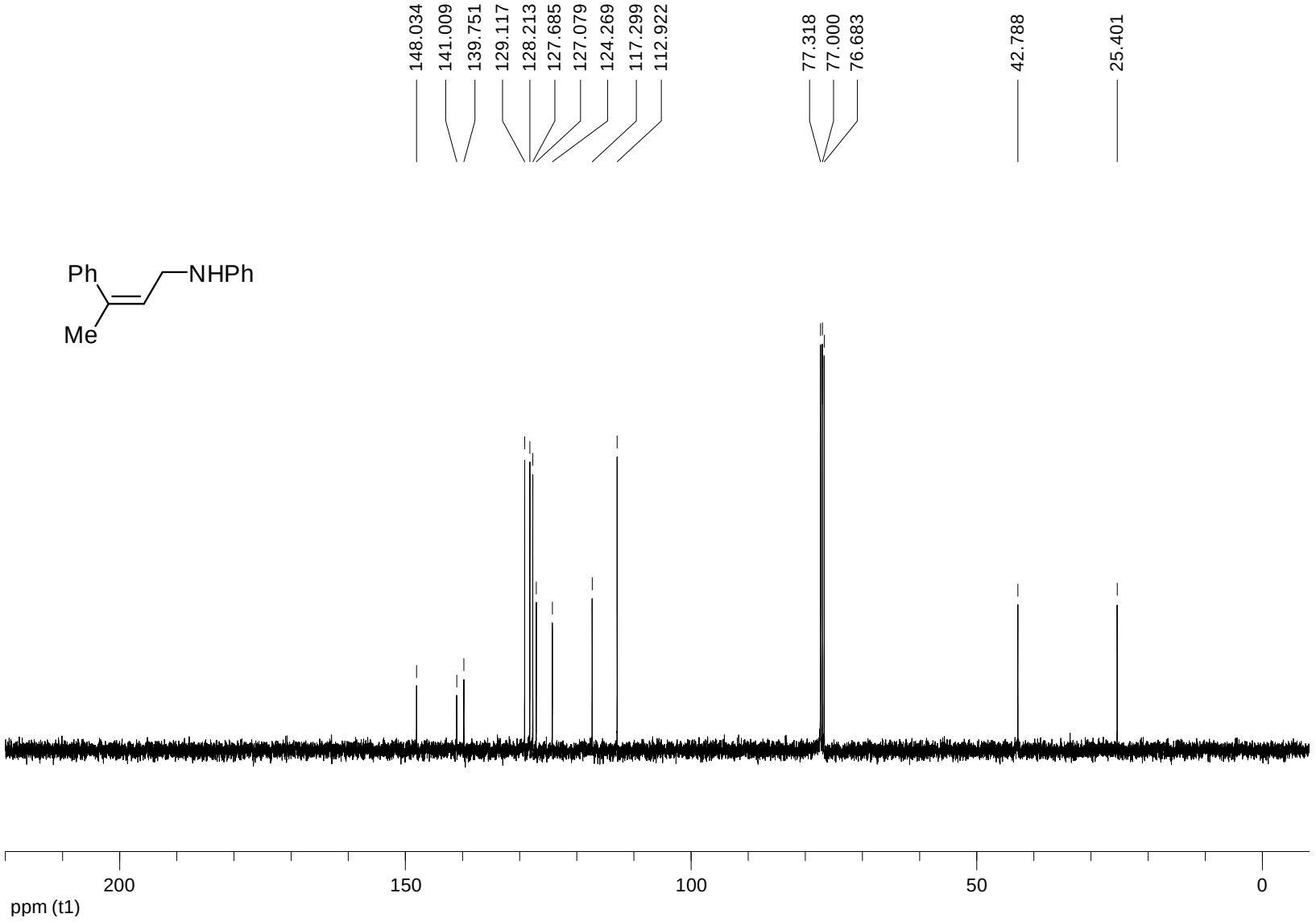
^{13}C NMR spectrum of **D** (100 MHz, $CDCl_3$)



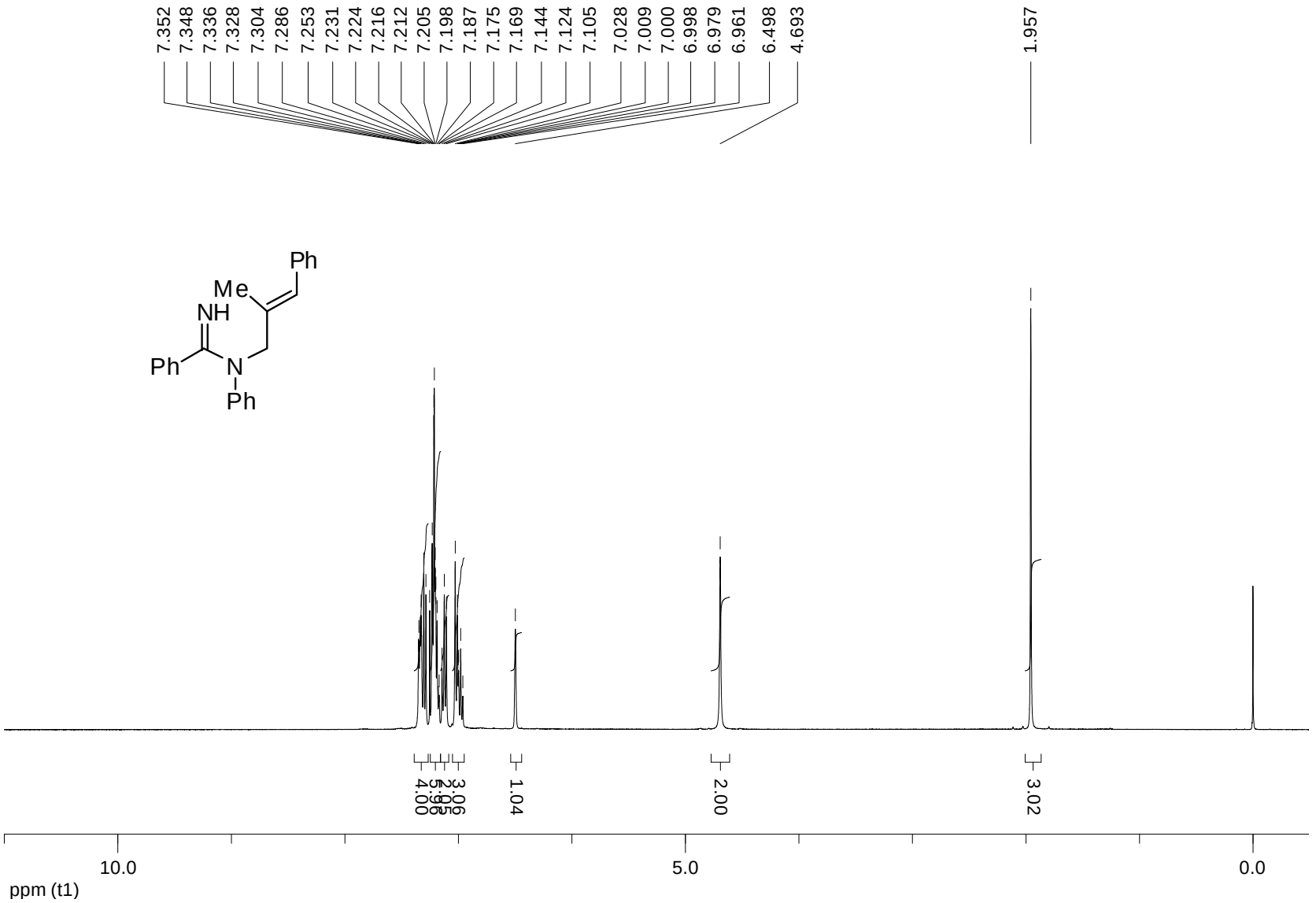
^{1}H NMR spectrum of **E** (400 MHz, $CDCl_3$)



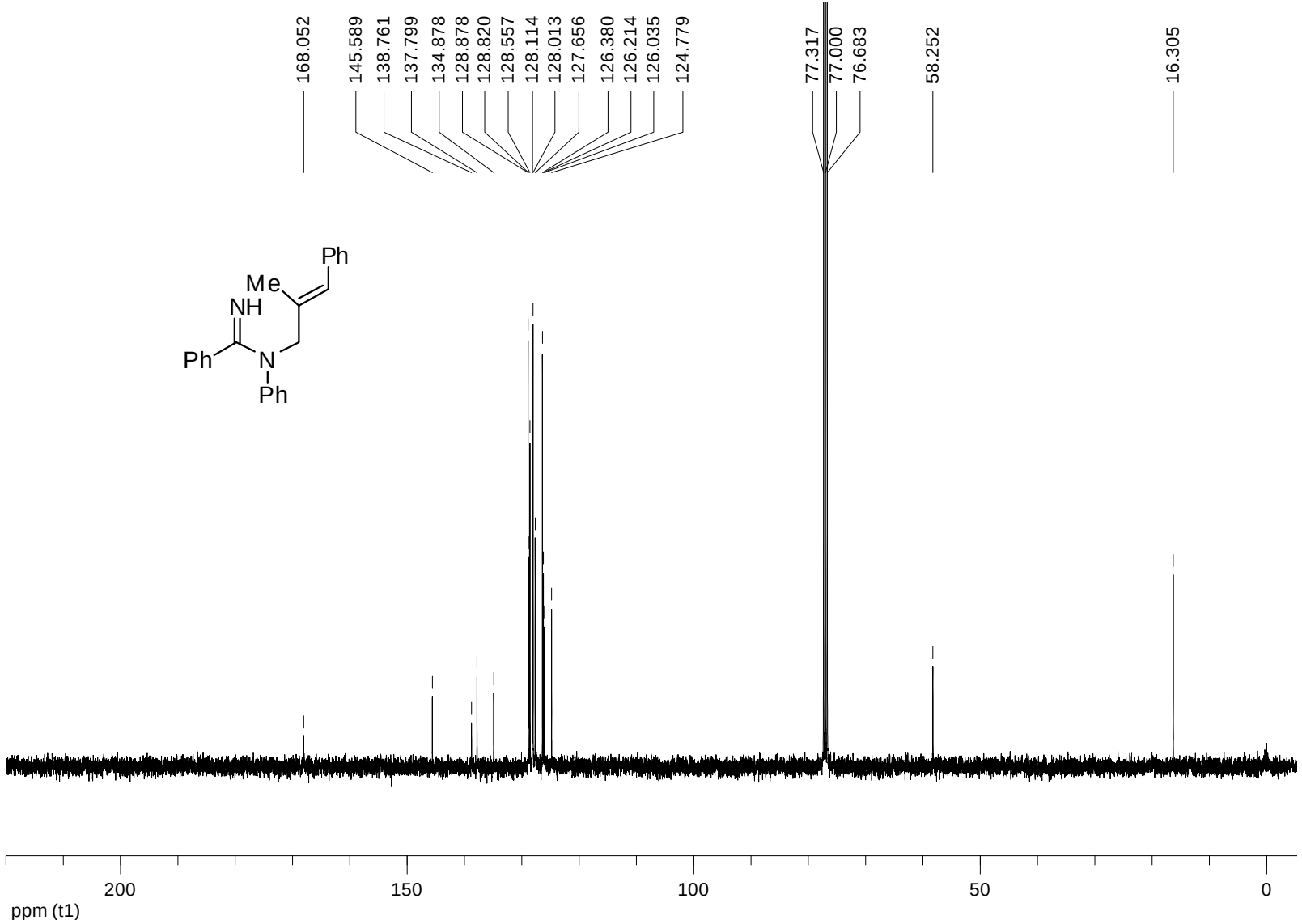
^{13}C NMR spectrum of **E** (100 MHz, $CDCl_3$)



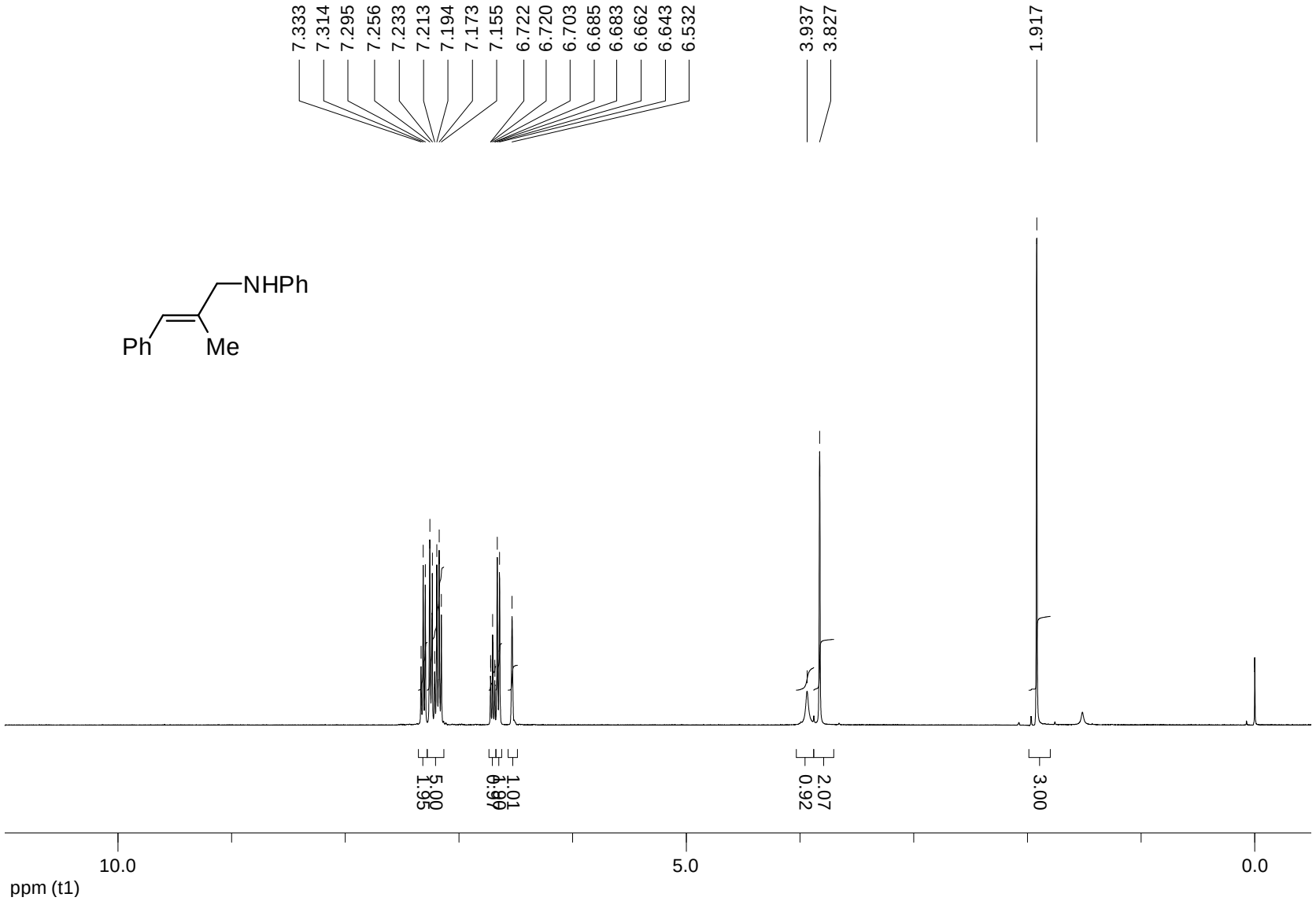
^{1}H NMR spectrum of **1p** (400 MHz, $CDCl_3$)



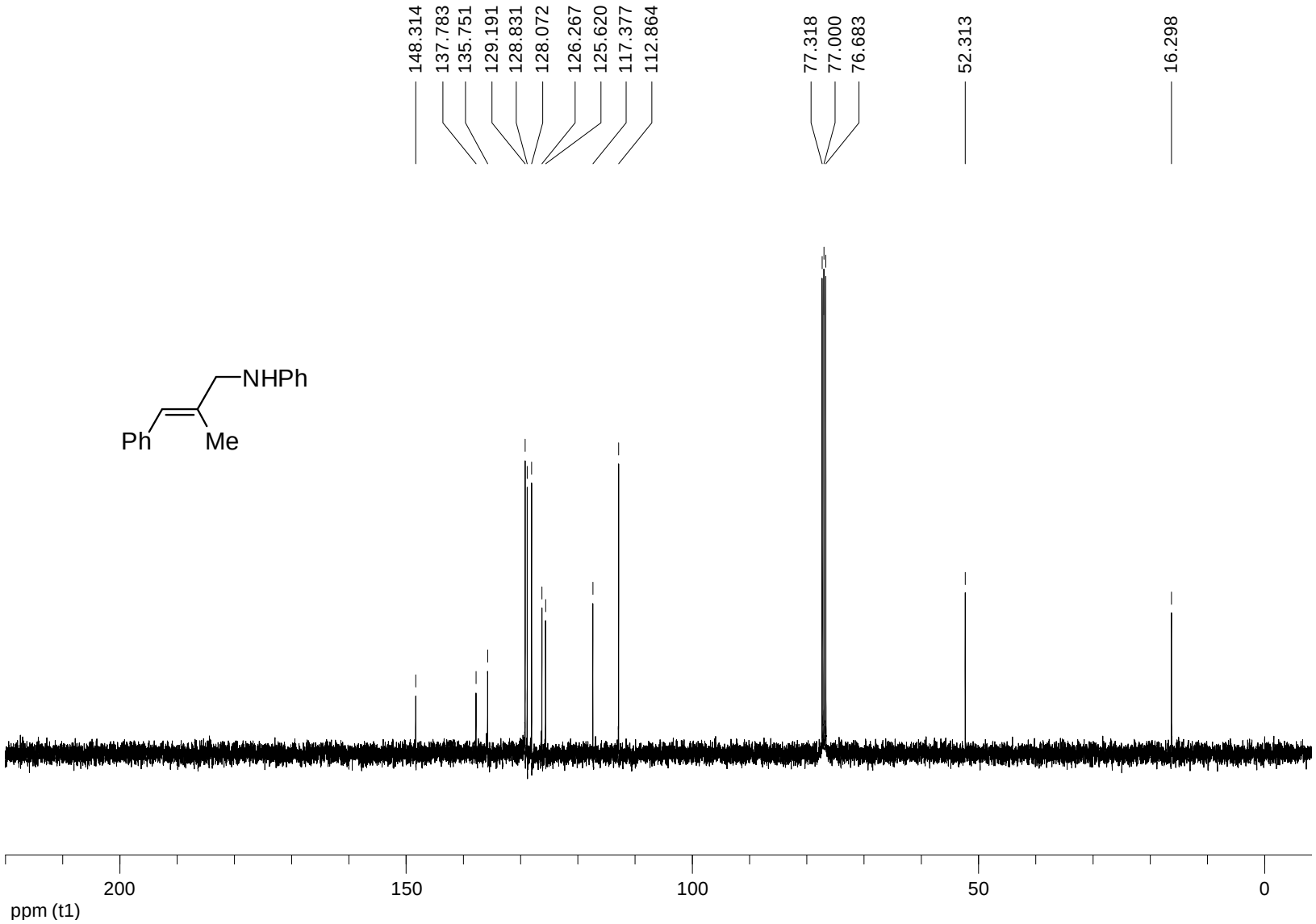
^{13}C NMR spectrum of **1p** (100 MHz, $CDCl_3$)



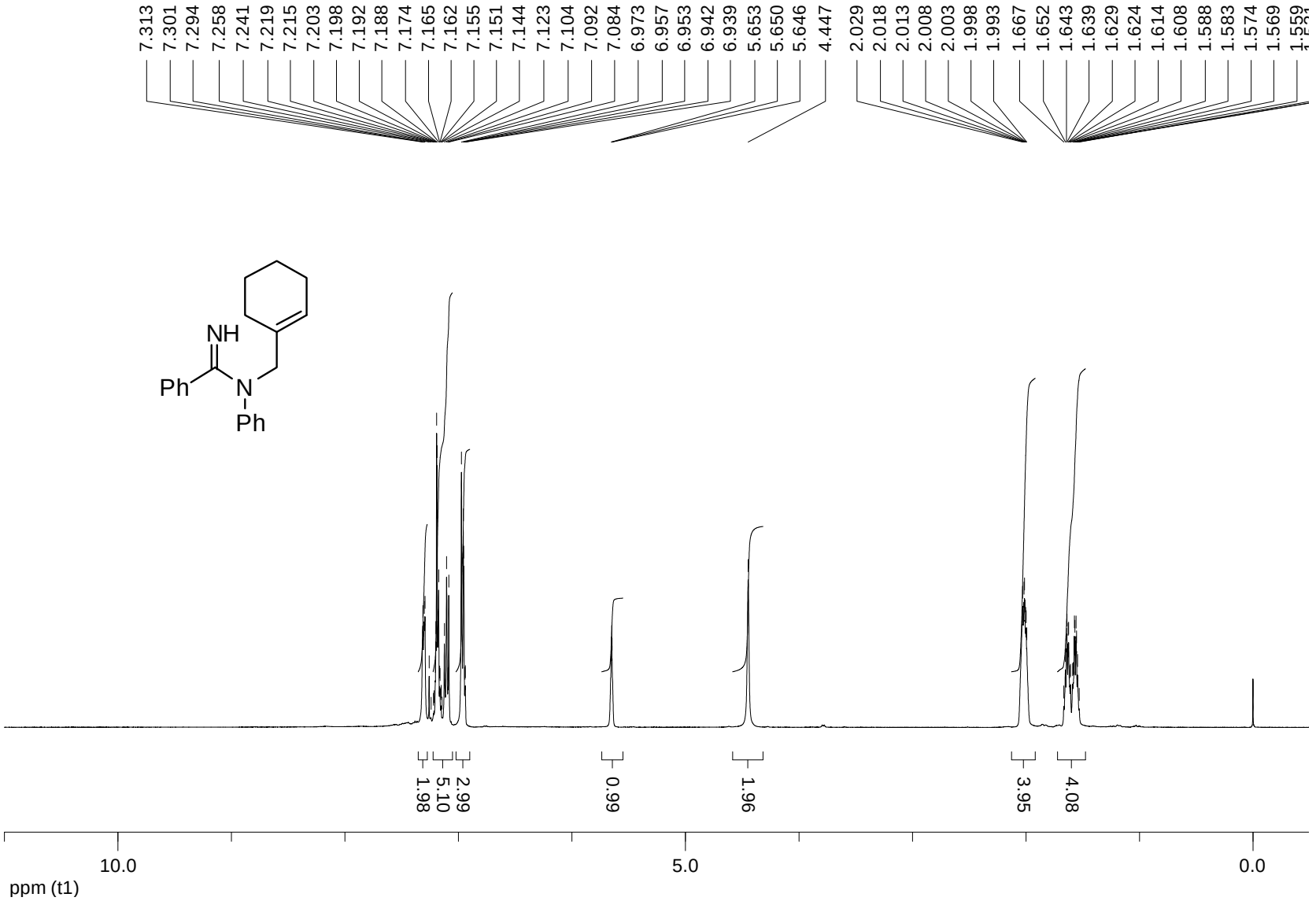
^{1}H NMR spectrum of **F** (400 MHz, $CDCl_3$)



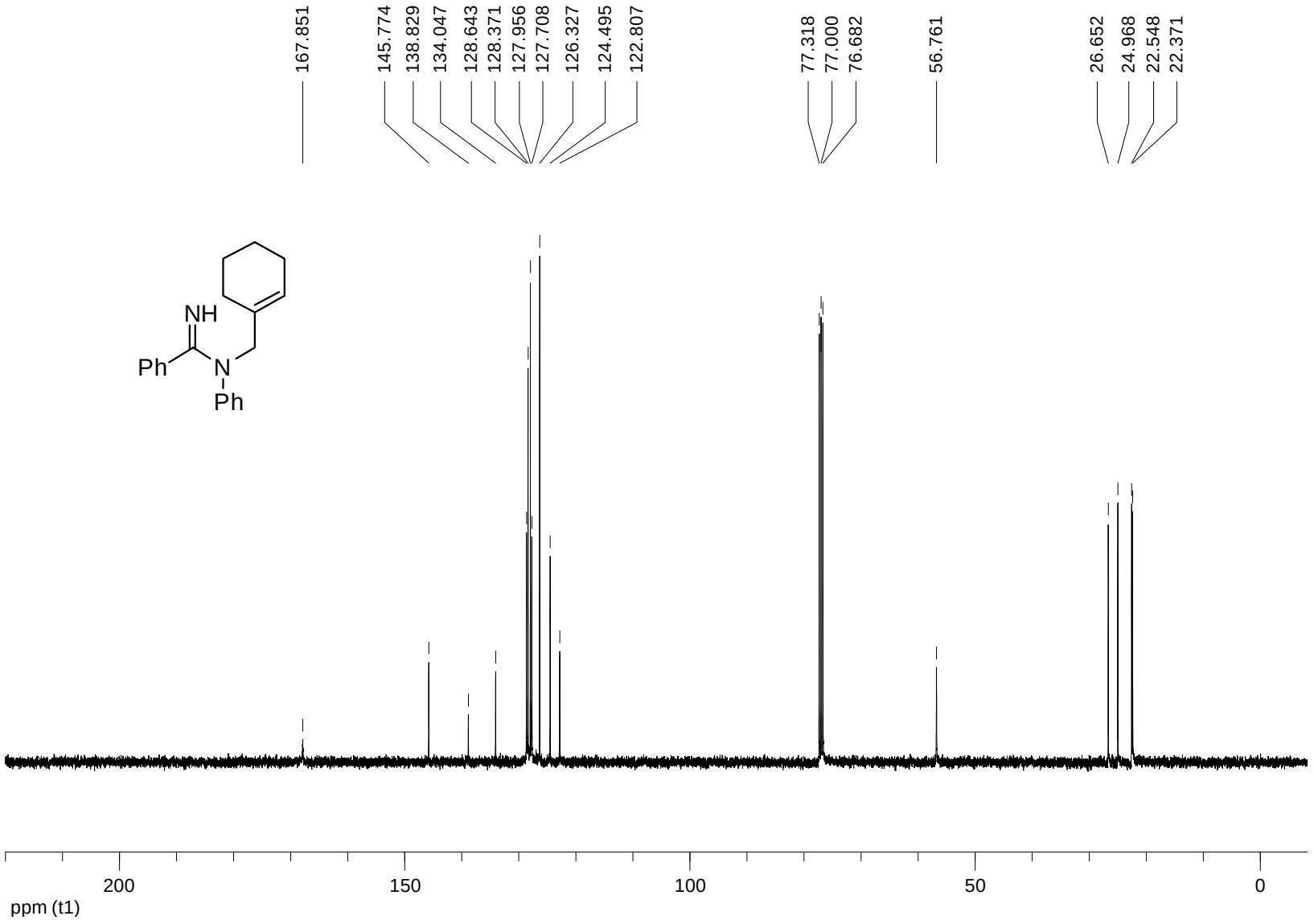
^{13}C NMR spectrum of **F** (100 MHz, $CDCl_3$)



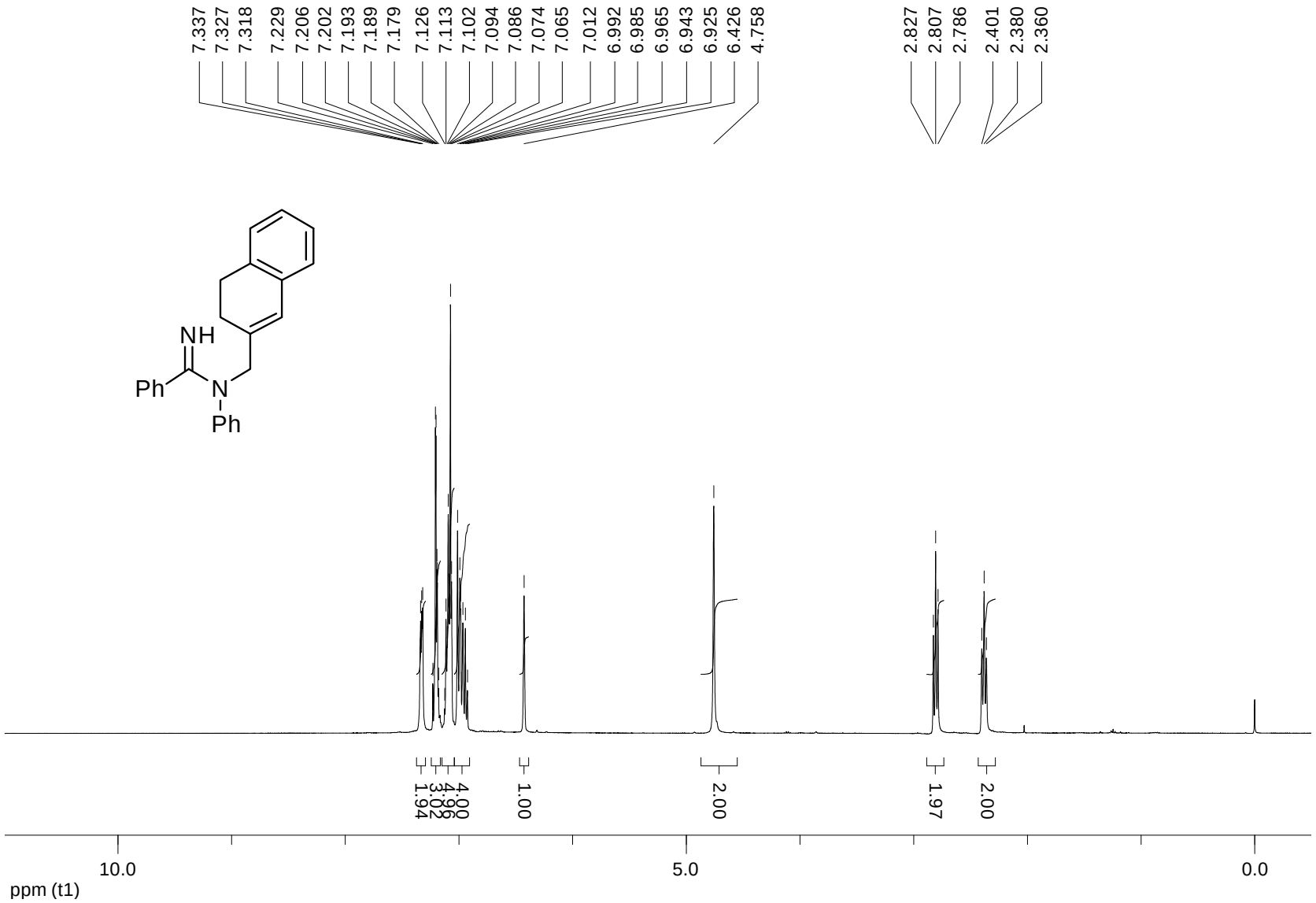
^{1}H NMR spectrum of **1q** (400 MHz, $CDCl_3$)



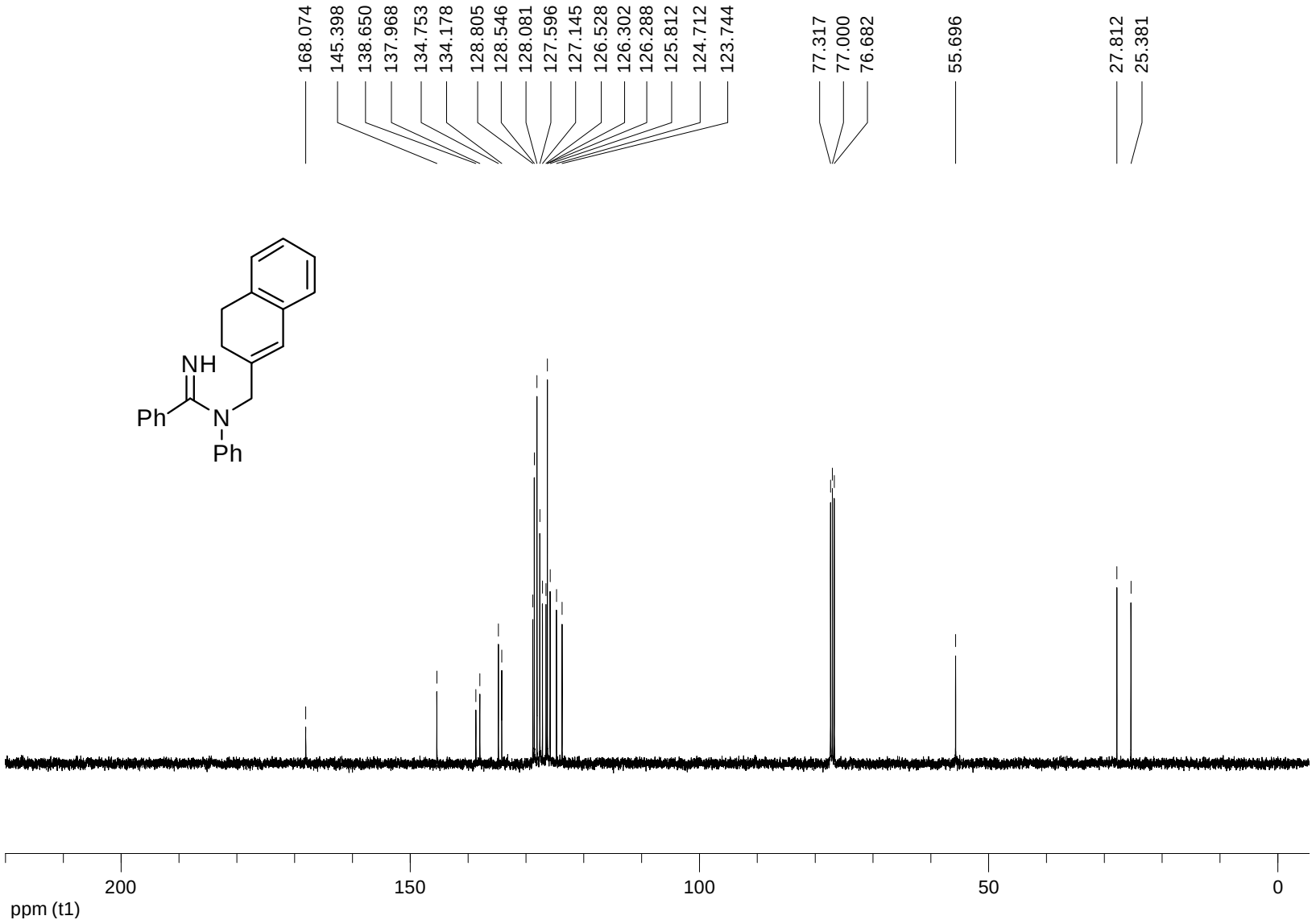
^{13}C NMR spectrum of **1q** (100 MHz, $CDCl_3$)



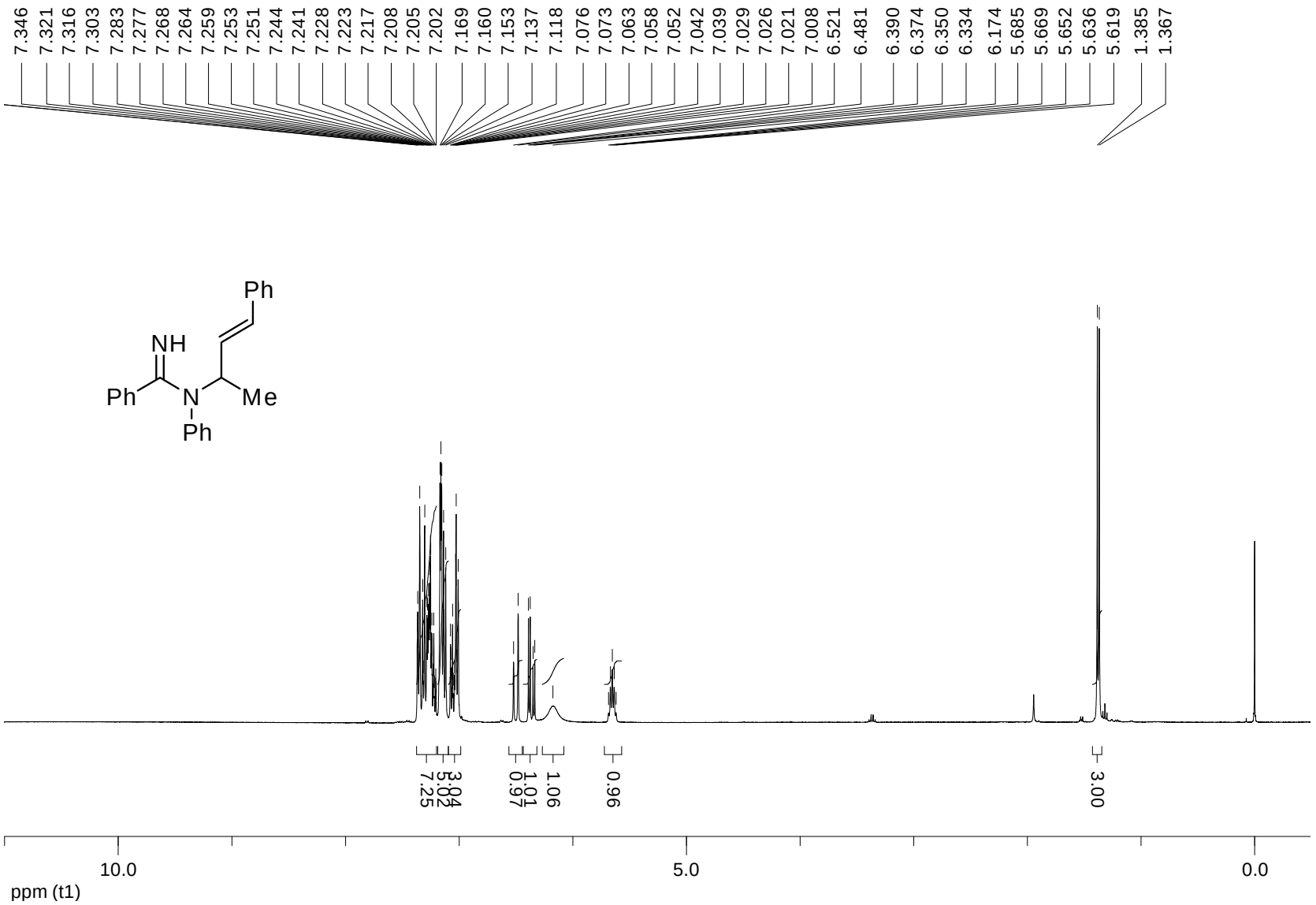
^{1}H NMR spectrum of **1r** (400 MHz, $CDCl_3$)



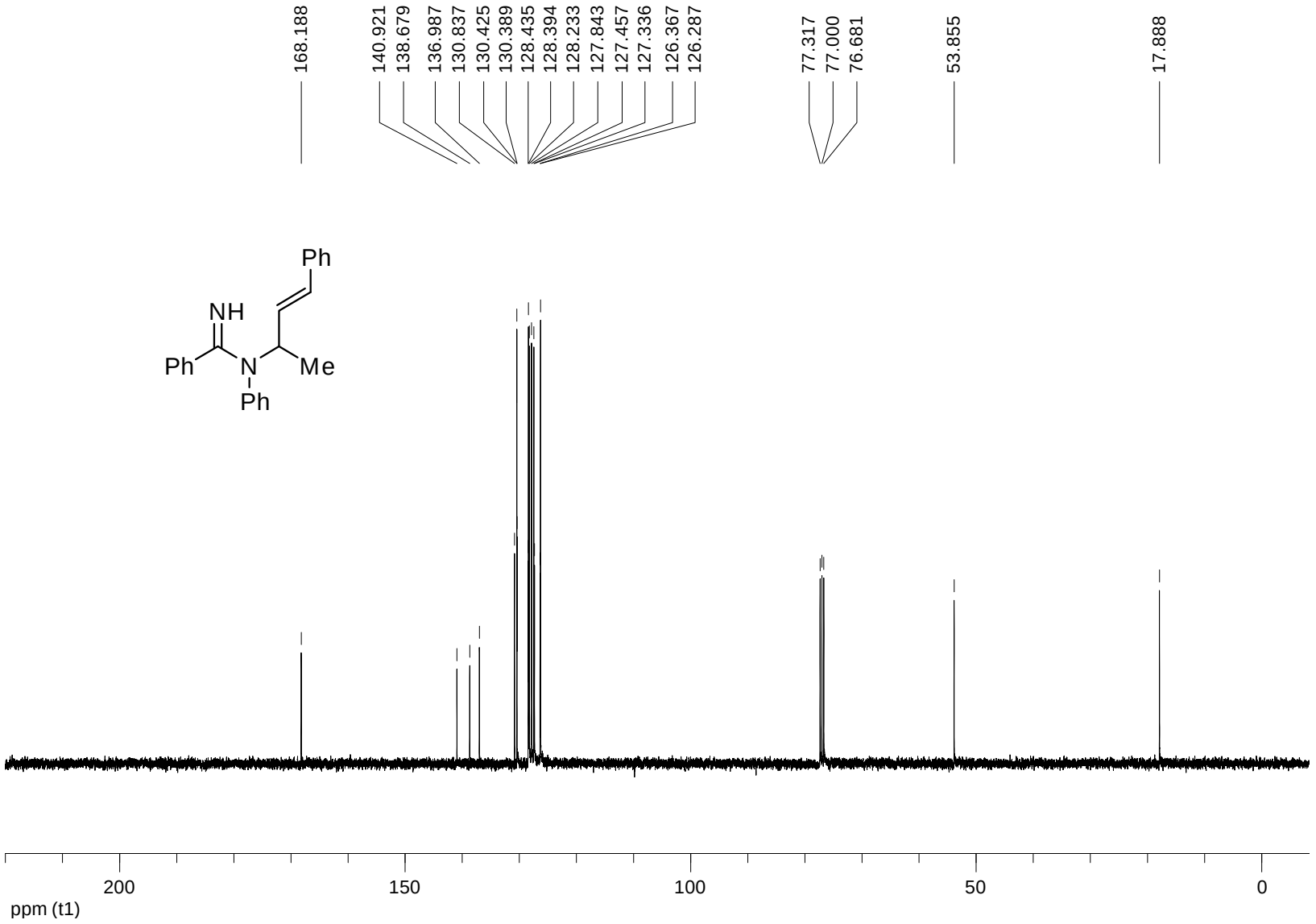
^{13}C NMR spectrum of **1r** (100 MHz, $CDCl_3$)



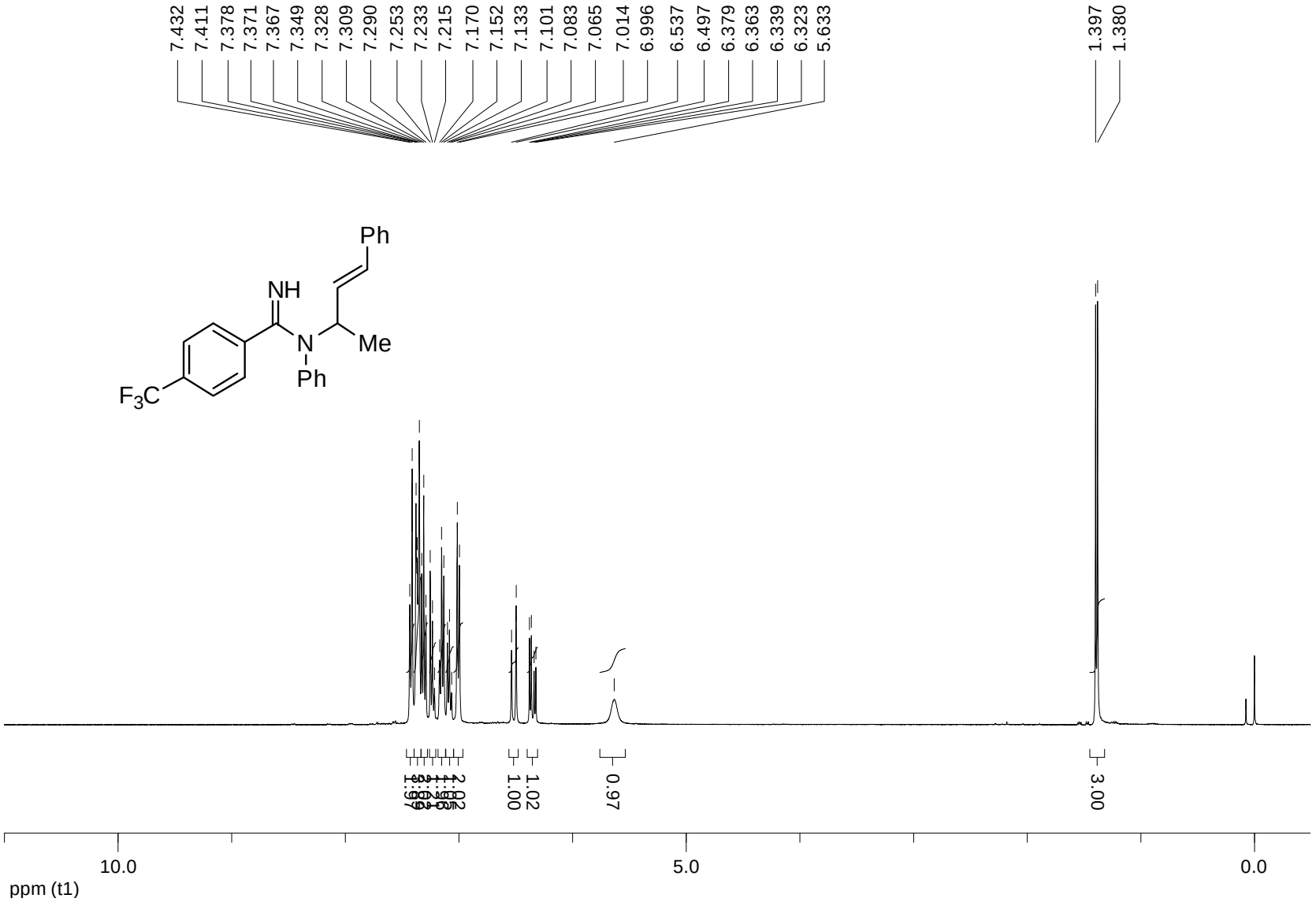
^{1}H NMR spectrum of **1s** (400 MHz, $CDCl_3$)



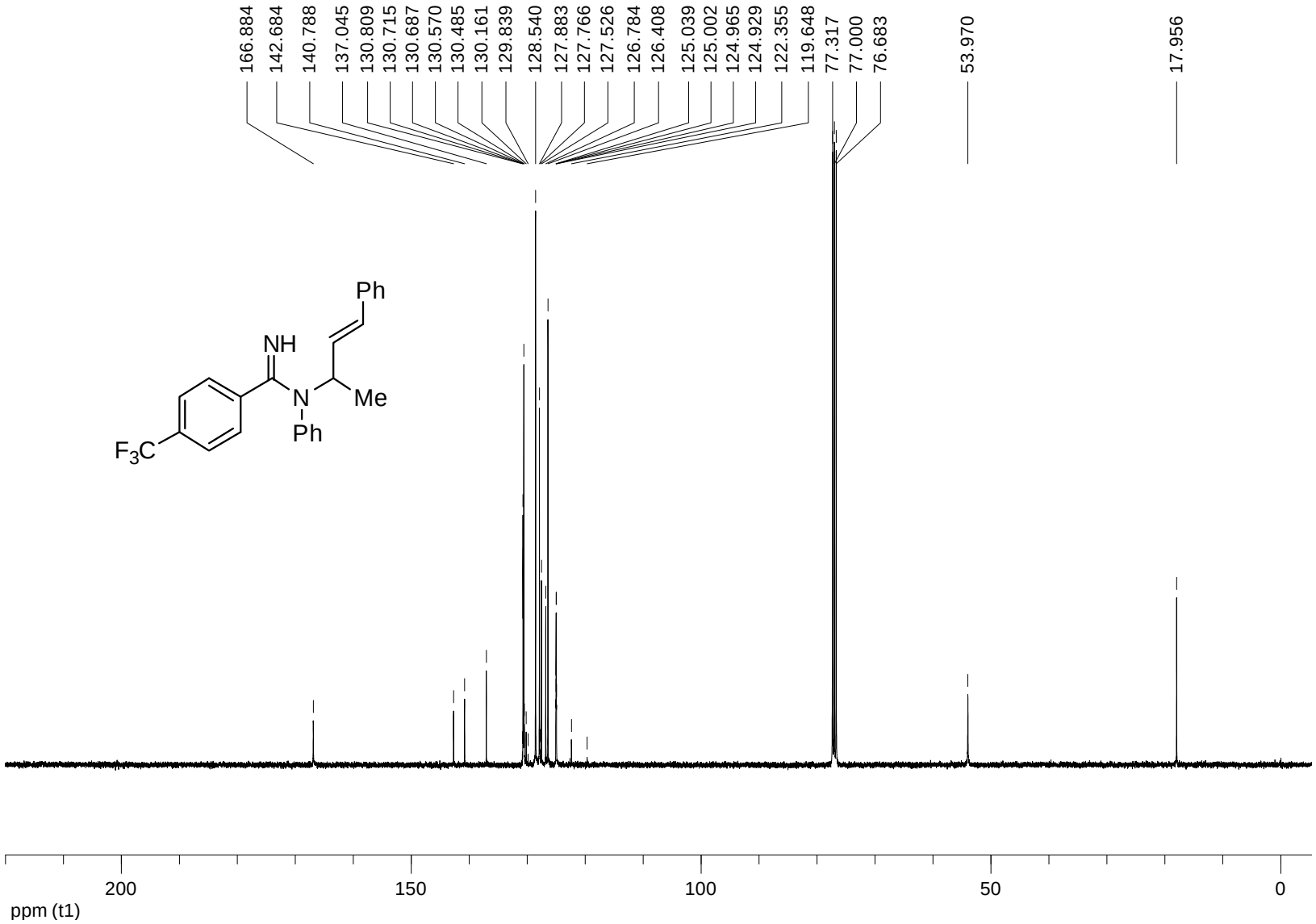
^{13}C NMR spectrum of **1s** (100 MHz, $CDCl_3$)



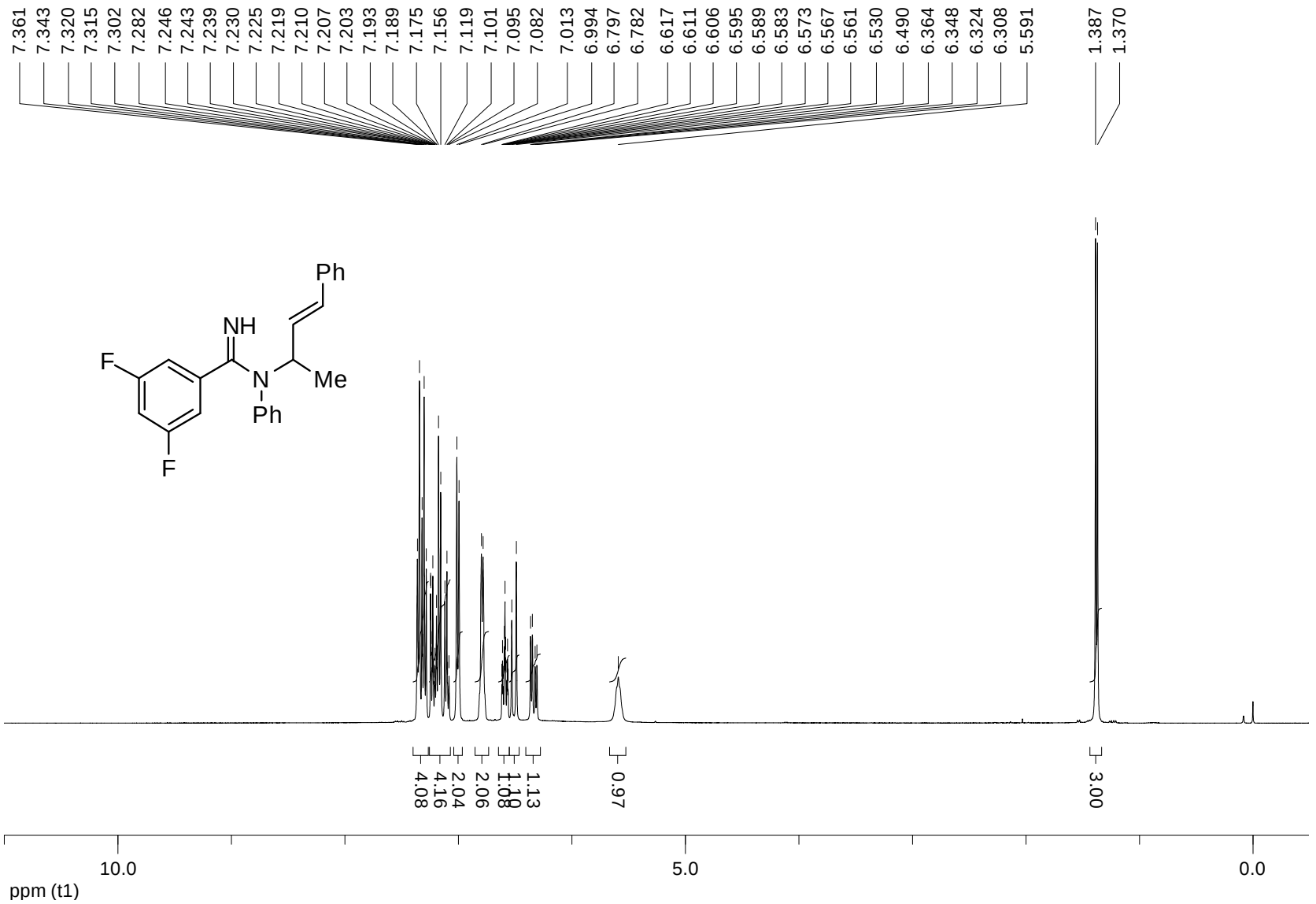
^{1}H NMR spectrum of **1t** (400 MHz, $CDCl_3$)



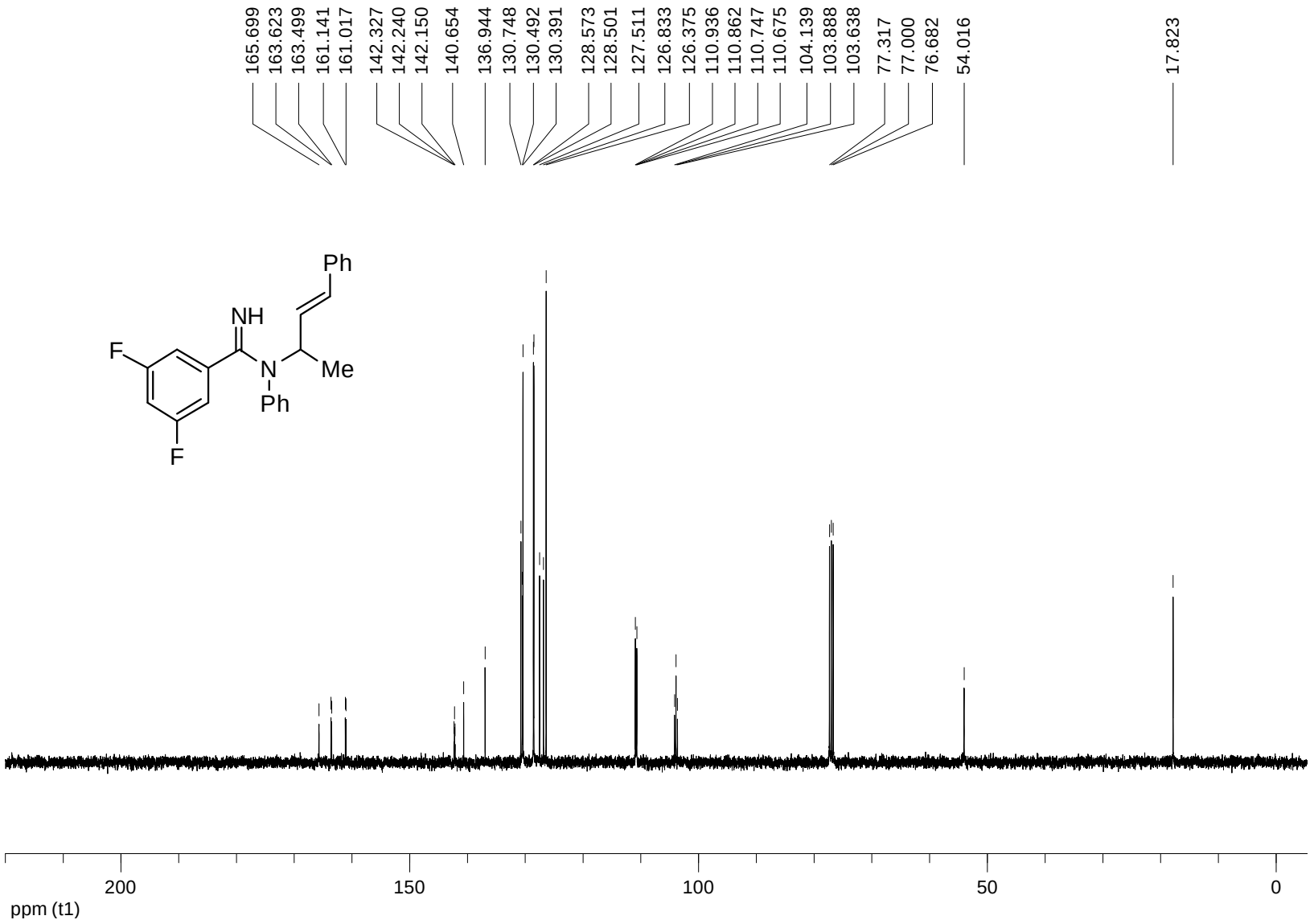
^{13}C NMR spectrum of **1t** (100 MHz, $CDCl_3$)



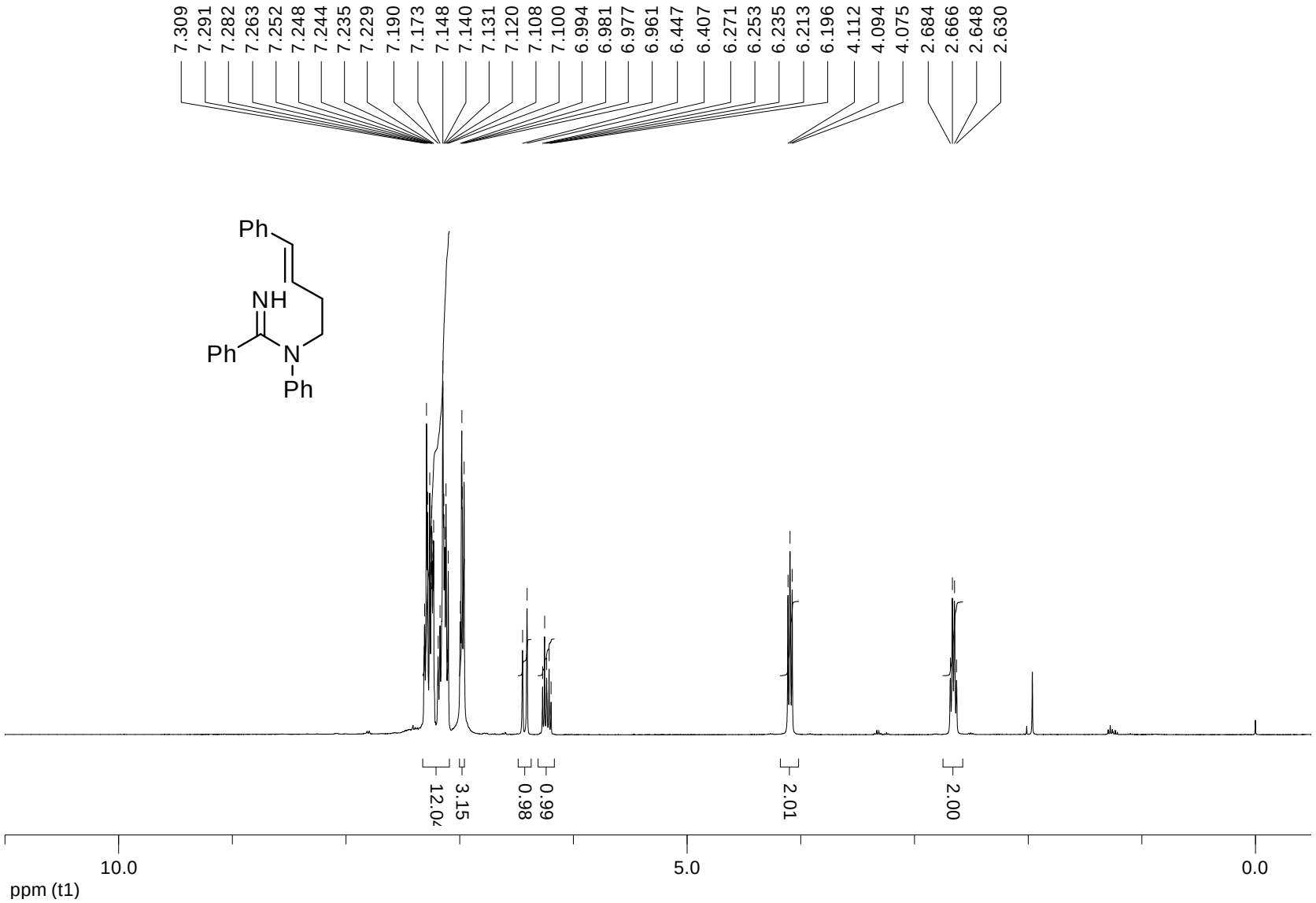
^{1}H NMR spectrum of **1u** (400 MHz, $CDCl_3$)



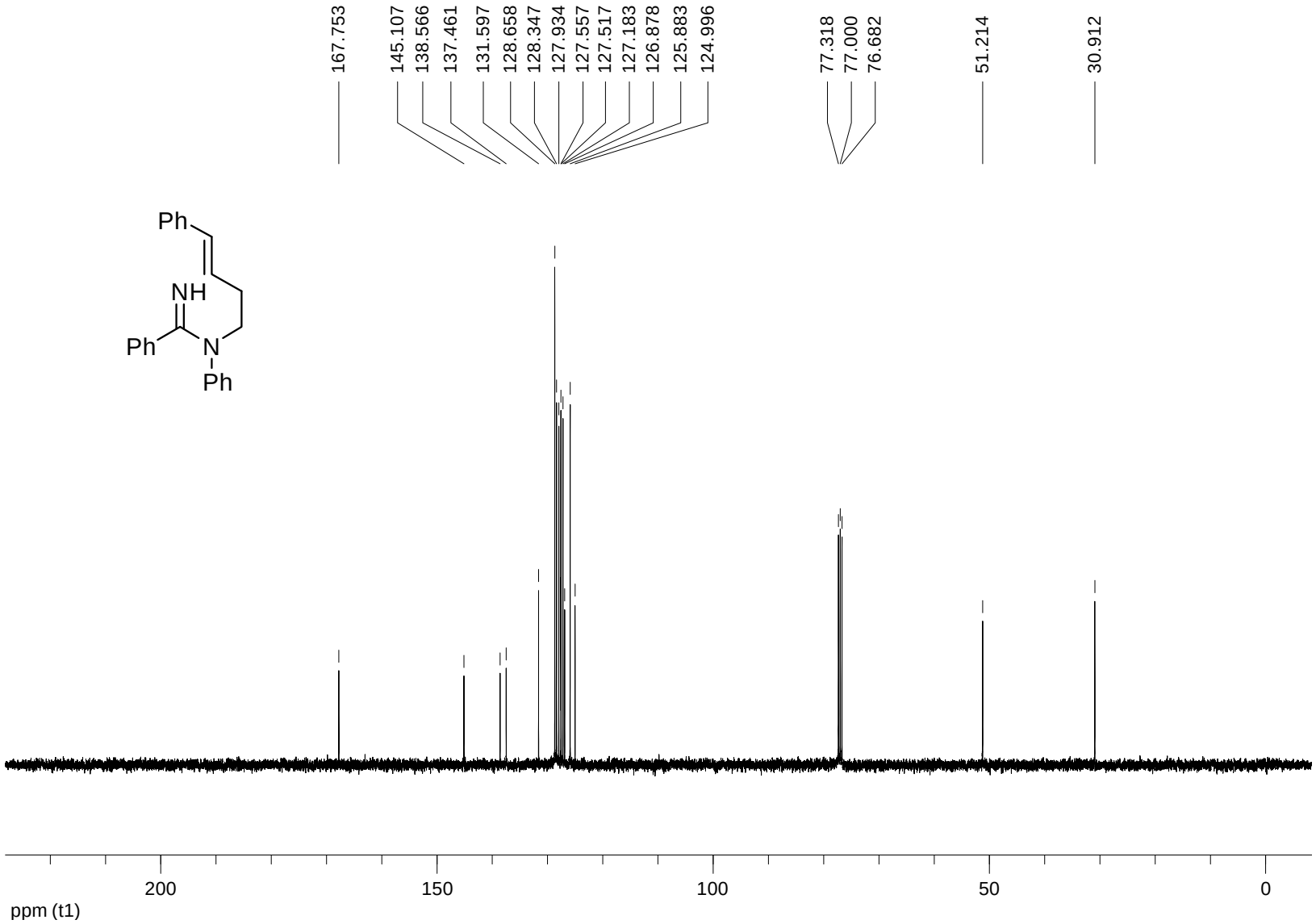
^{13}C NMR spectrum of **1u** (100 MHz, $CDCl_3$)



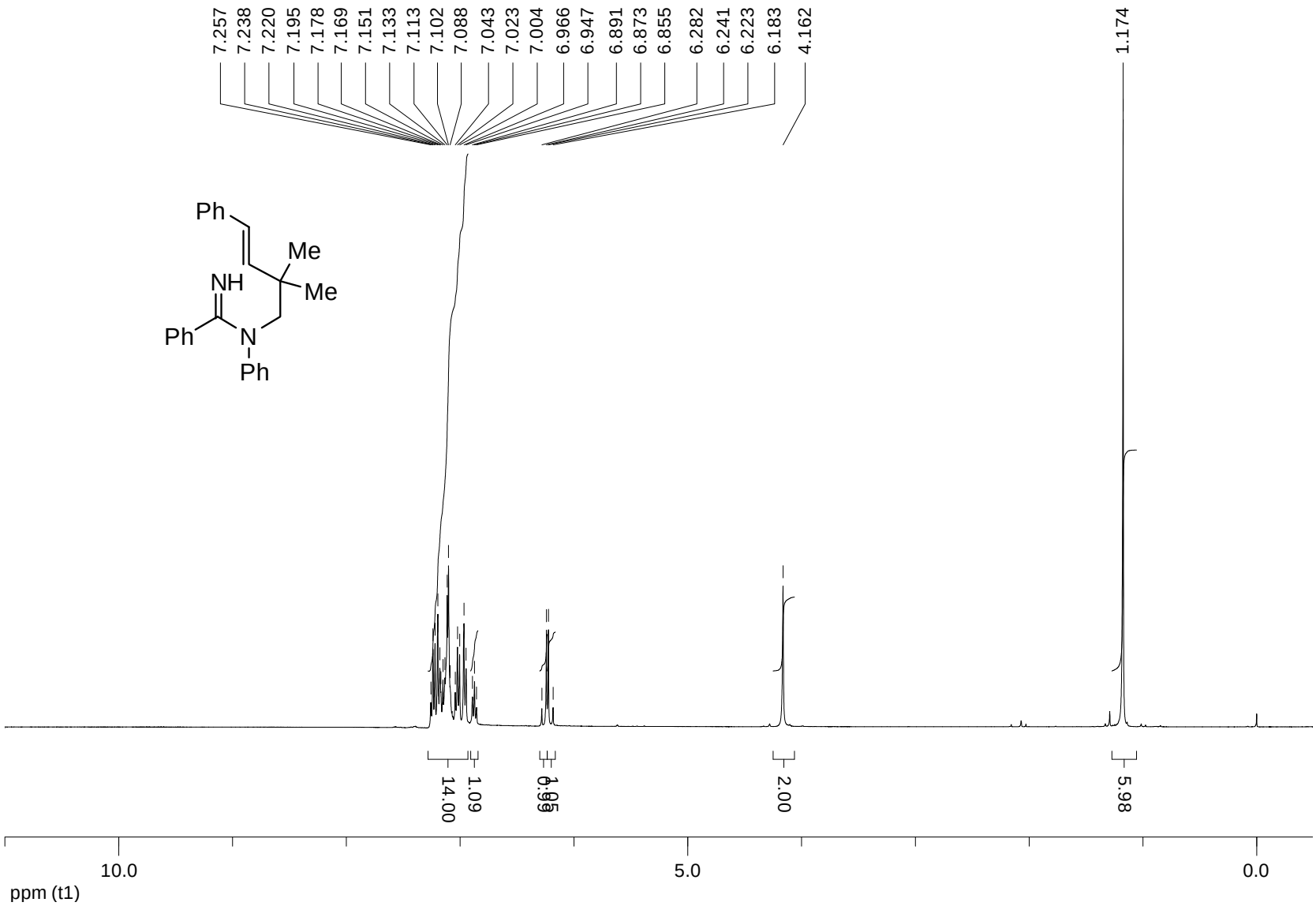
^{1}H NMR spectrum of **1v** (400 MHz, $CDCl_3$)



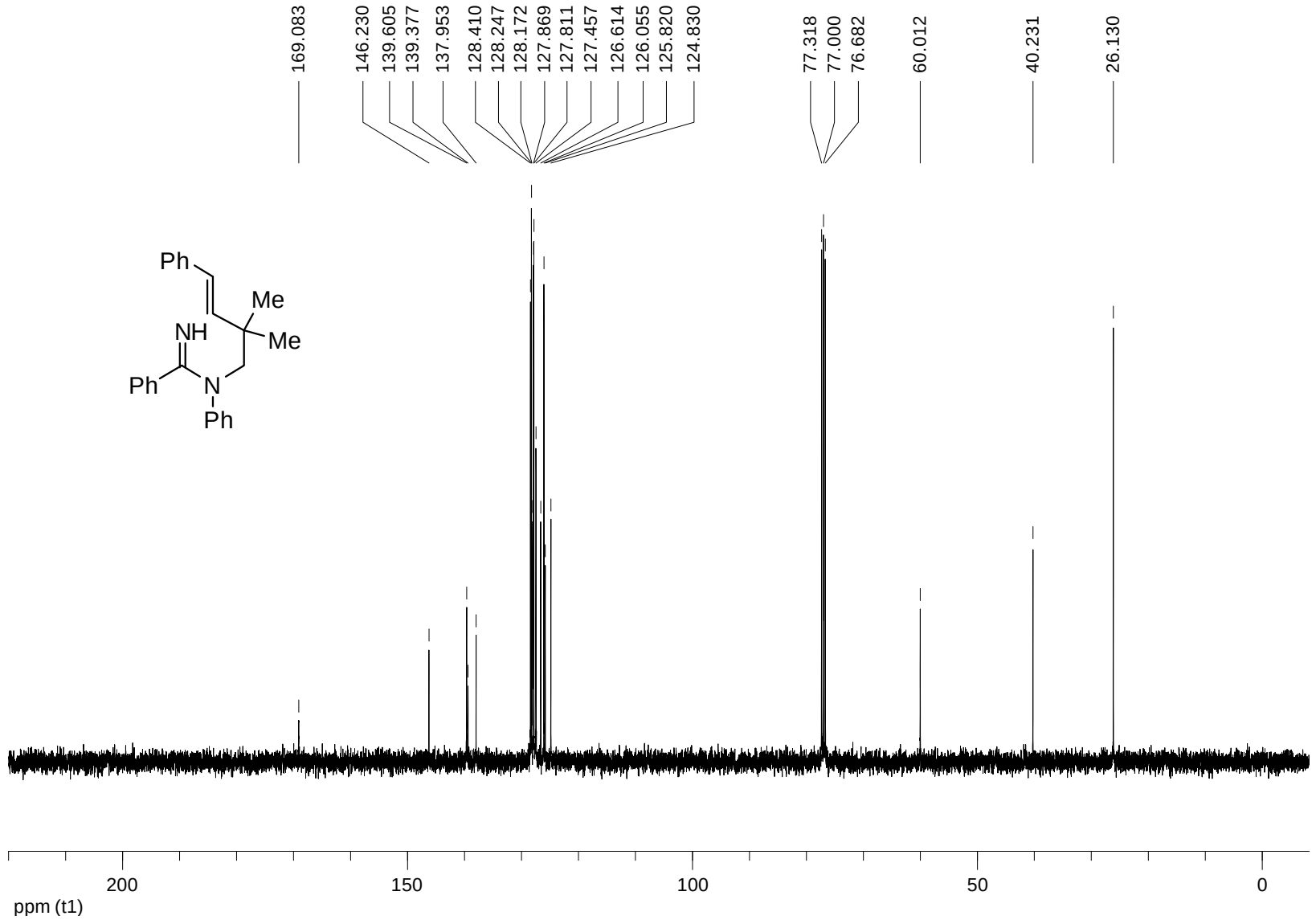
^{13}C NMR spectrum of **1v** (100 MHz, $CDCl_3$)



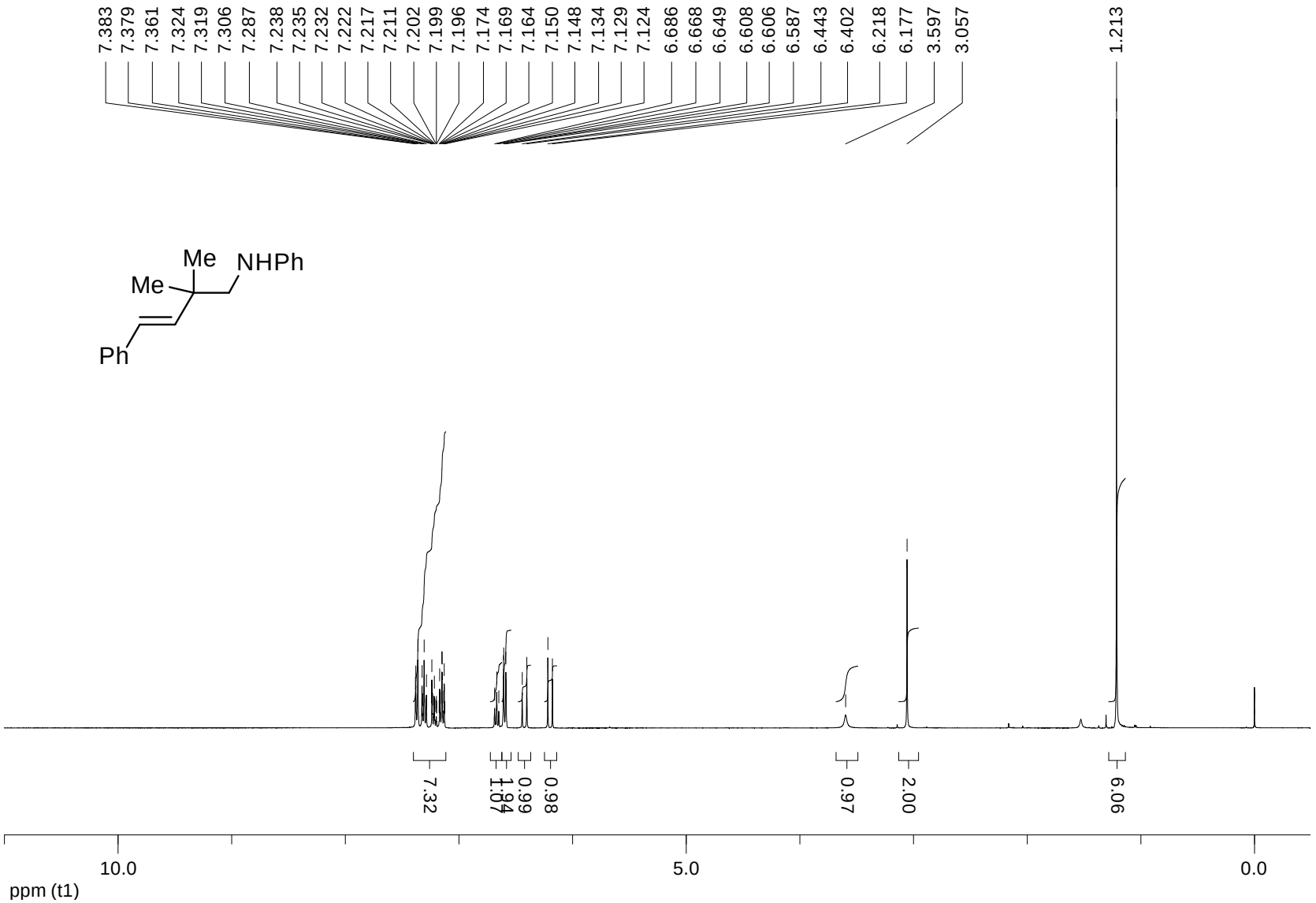
^{1}H NMR spectrum of **1w** (400 MHz, $CDCl_3$)



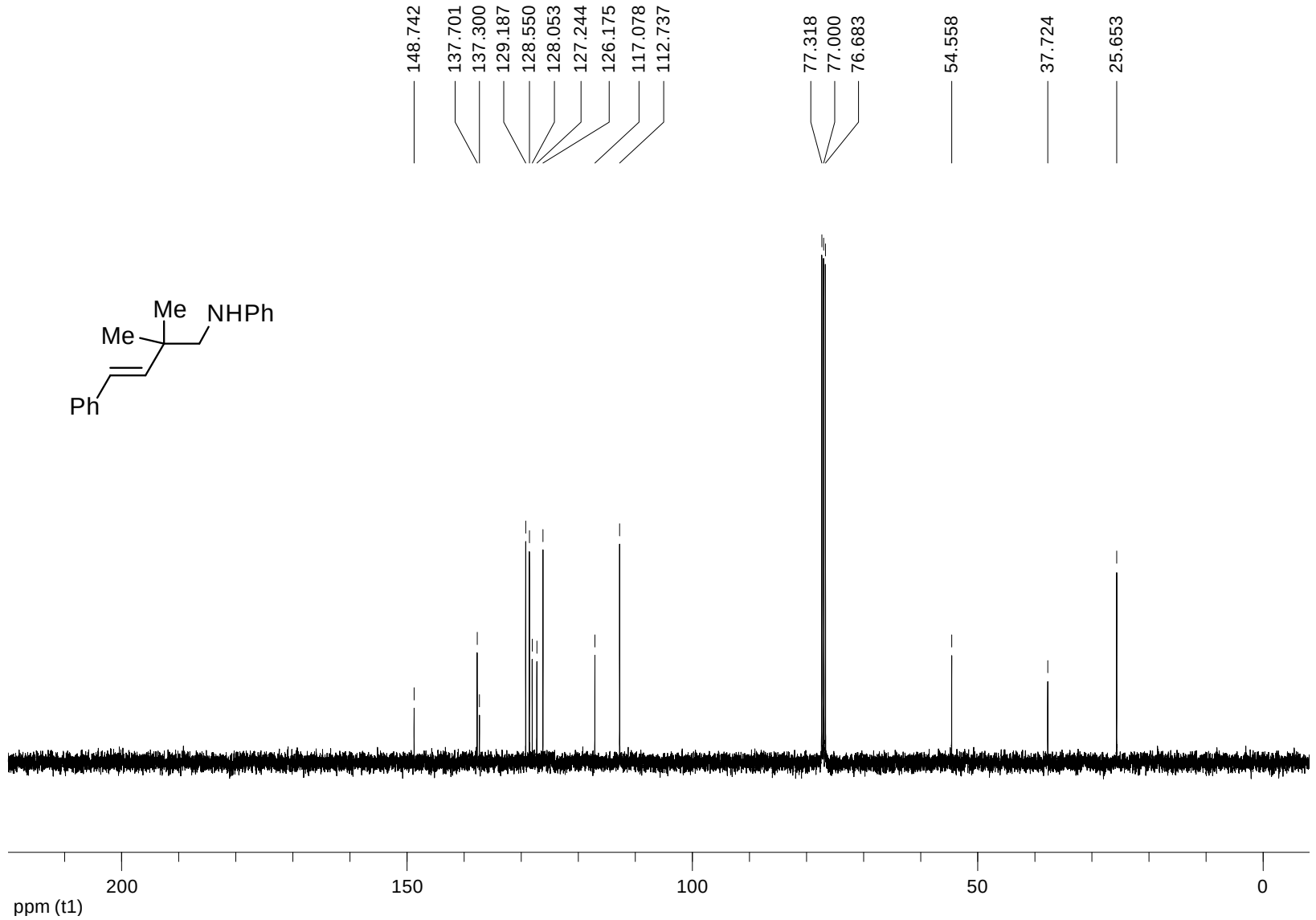
^{13}C NMR spectrum of **1w** (100 MHz, $CDCl_3$)



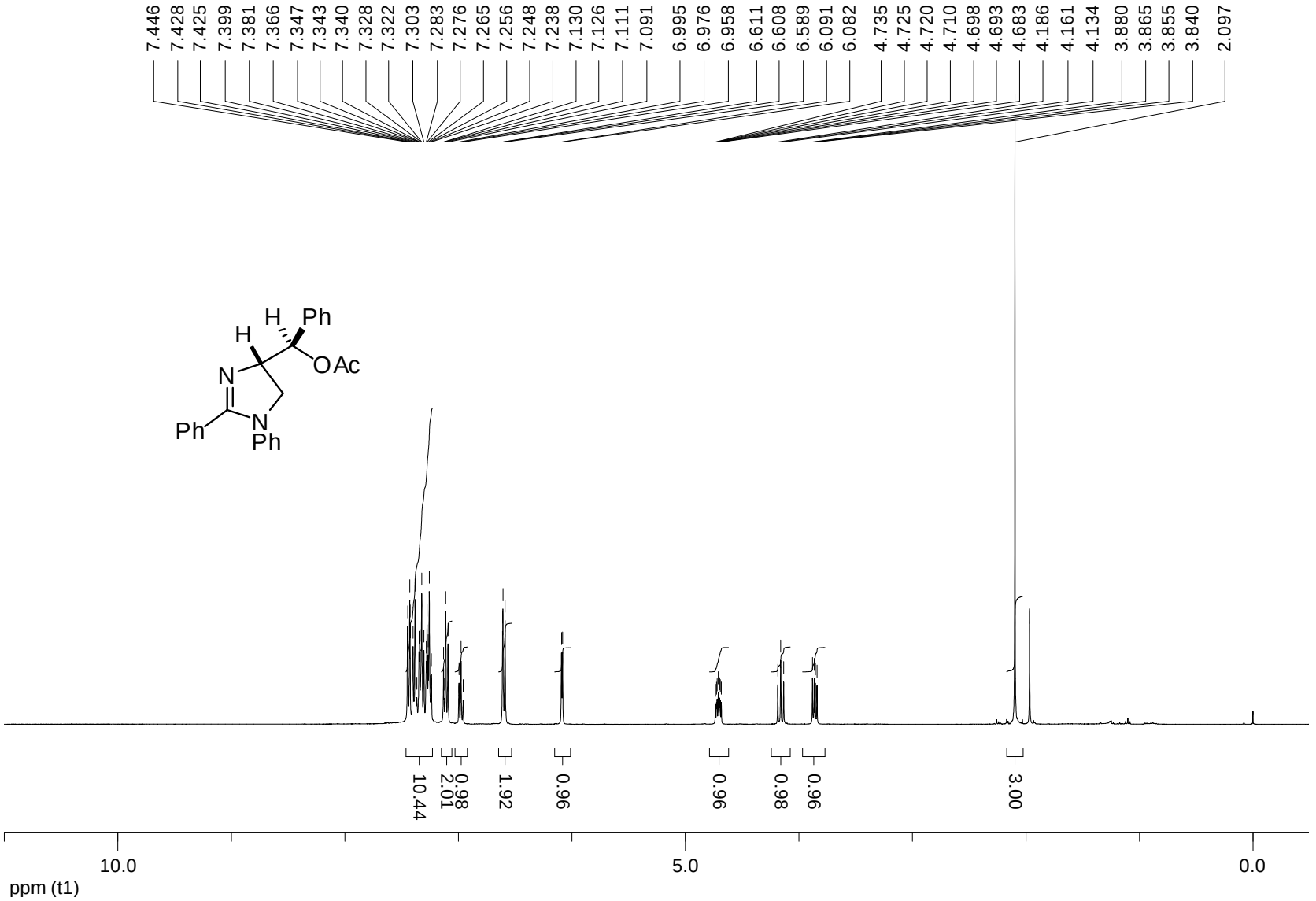
^{1}H NMR spectrum of **G** (400 MHz, $CDCl_3$)



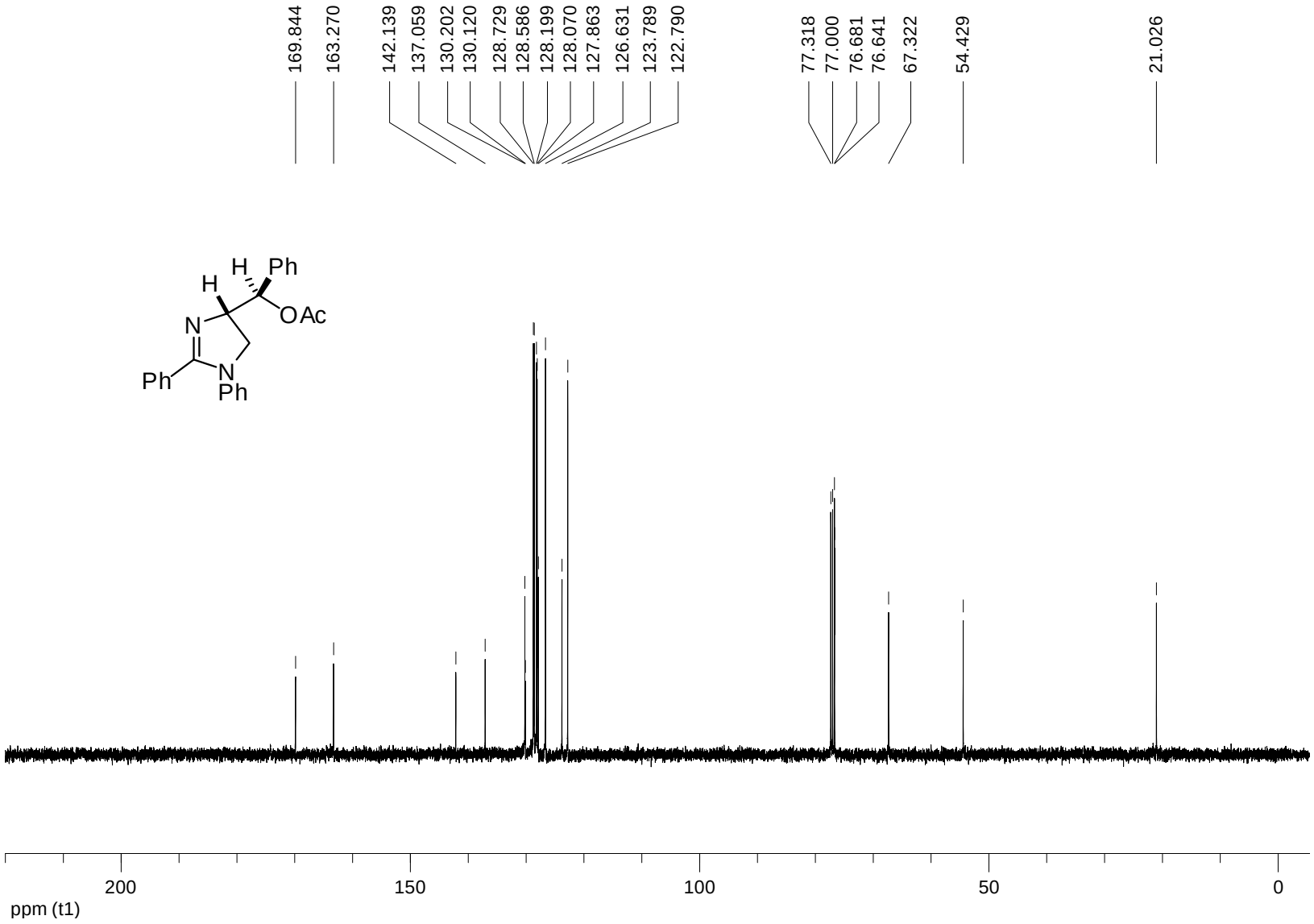
^{13}C NMR spectrum of **G** (100 MHz, $CDCl_3$)



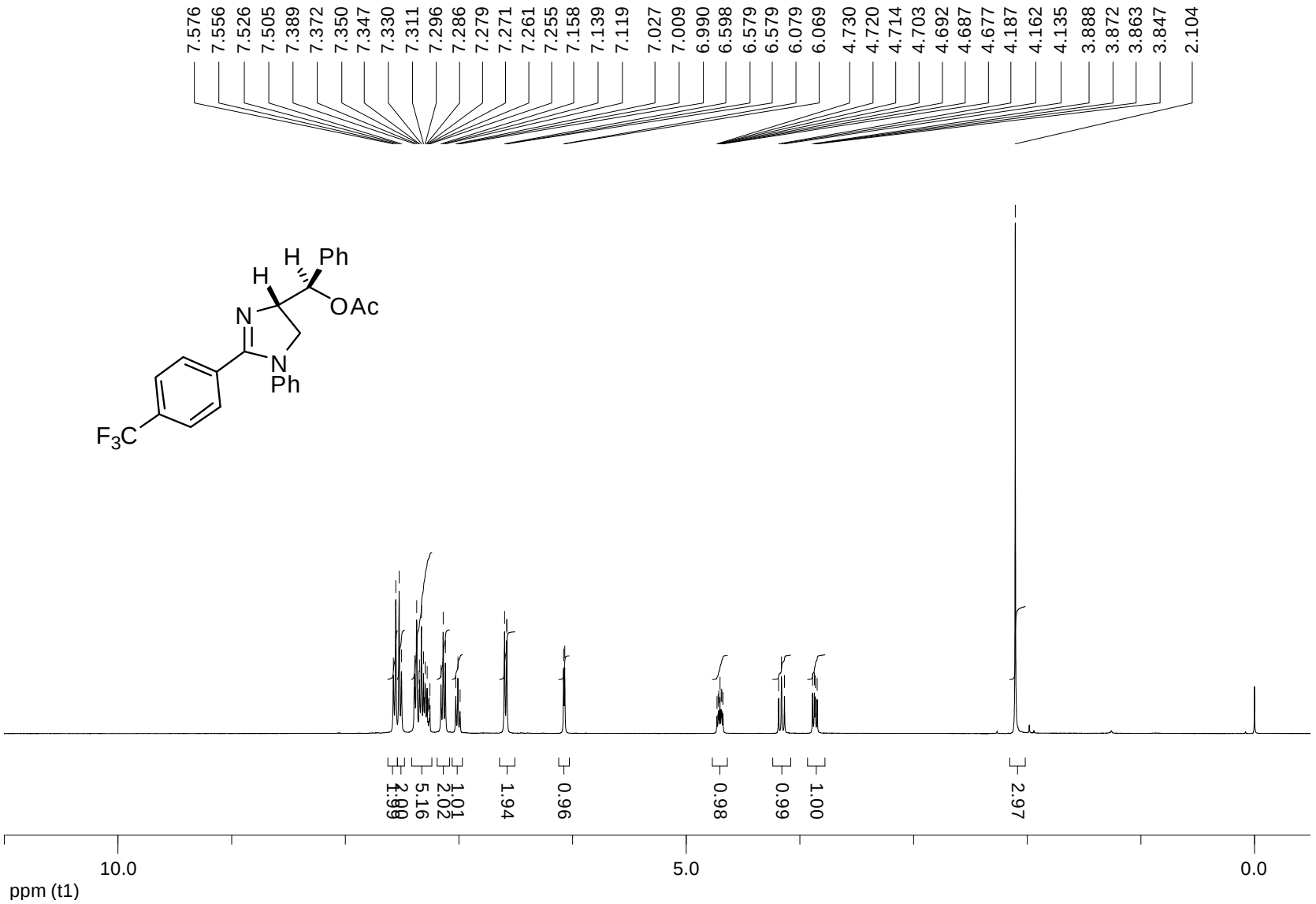
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



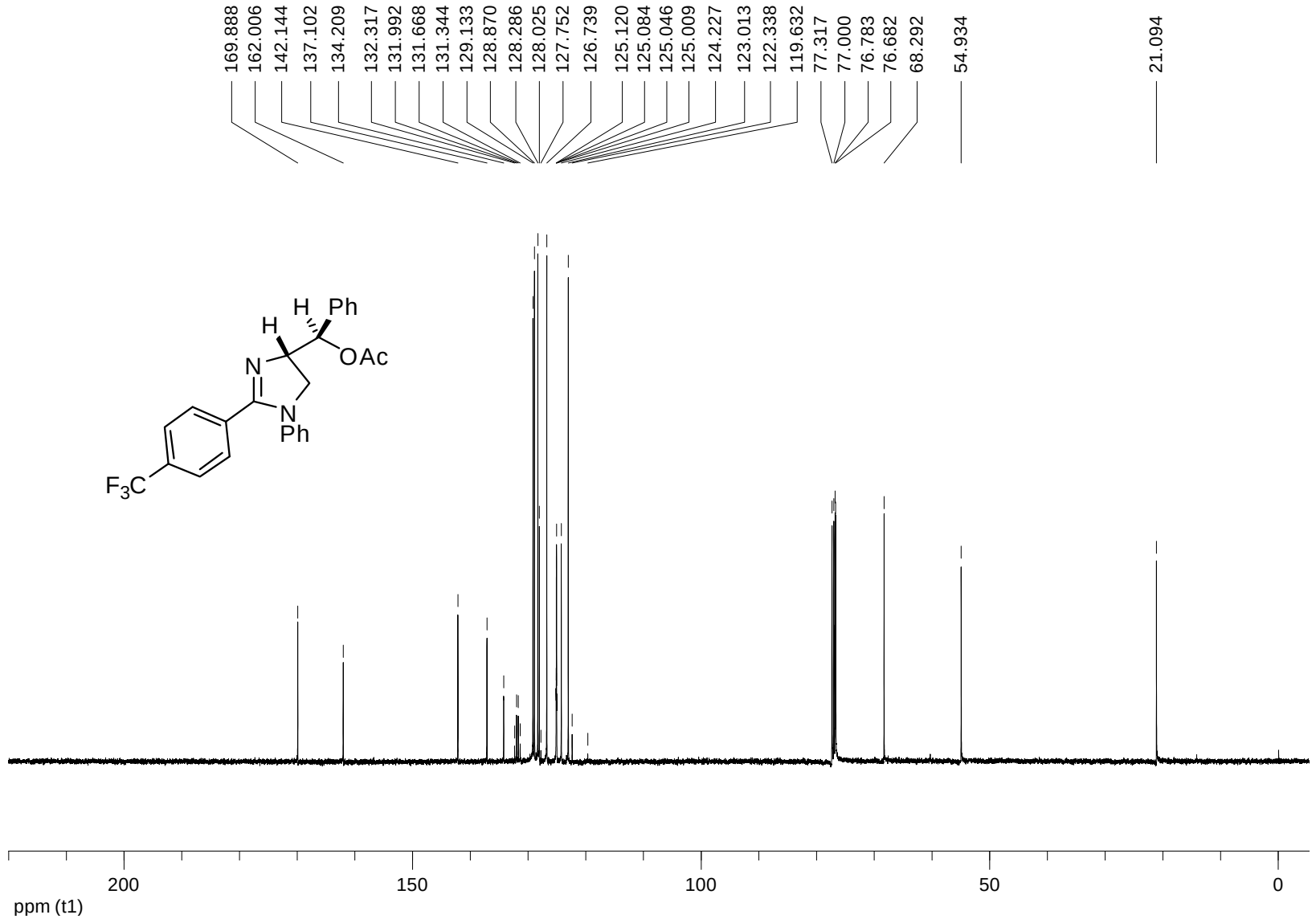
^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)



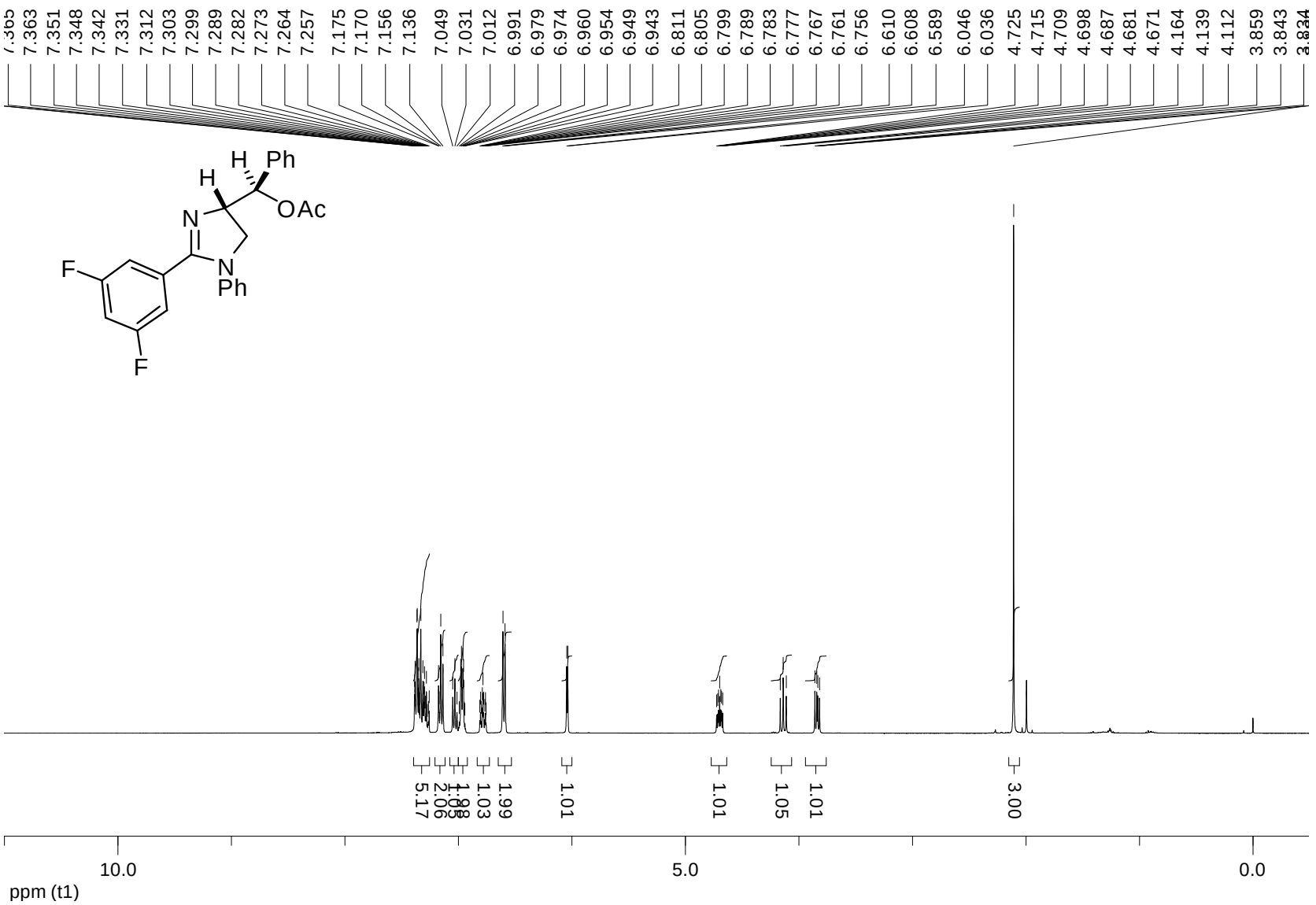
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



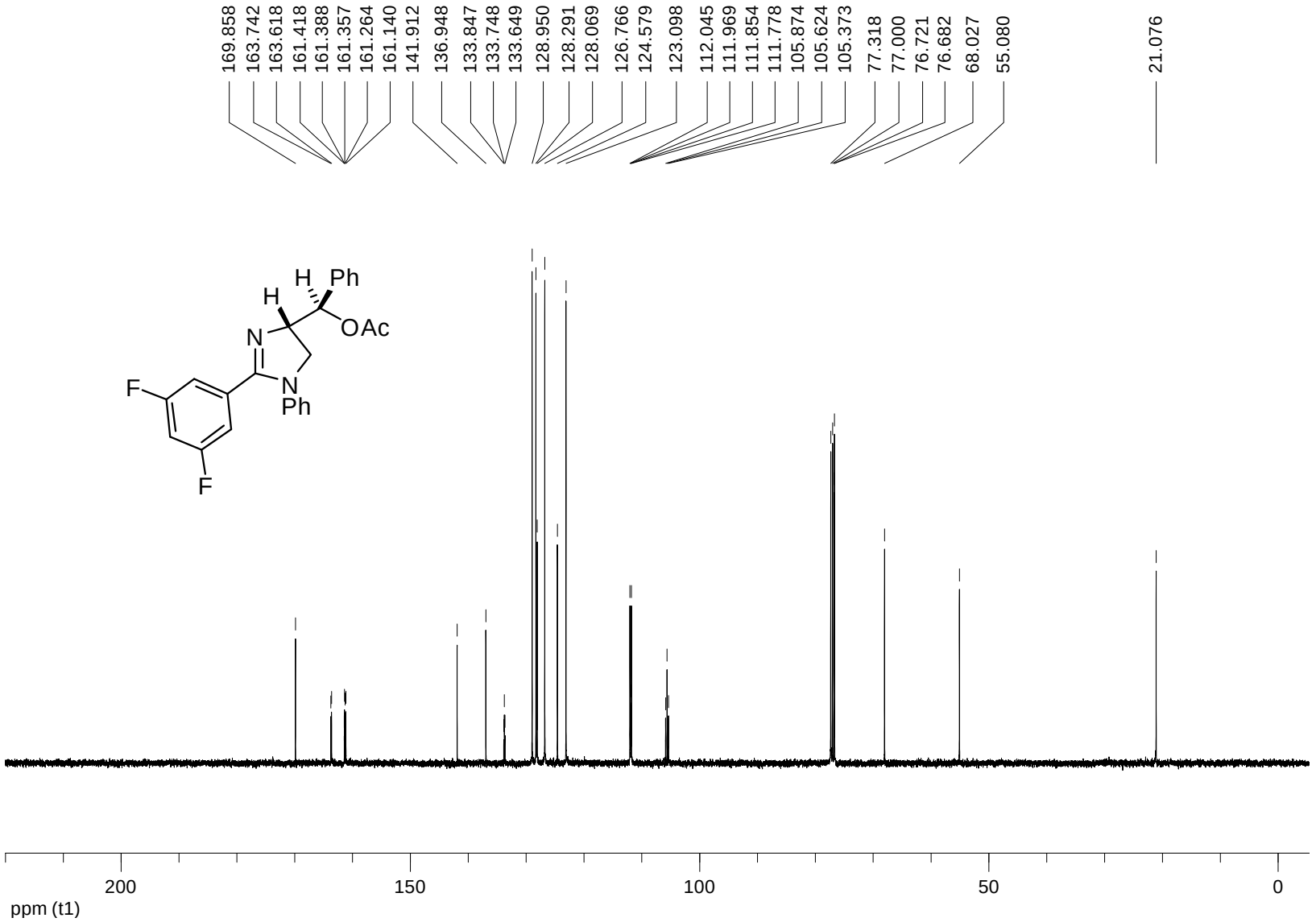
^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)



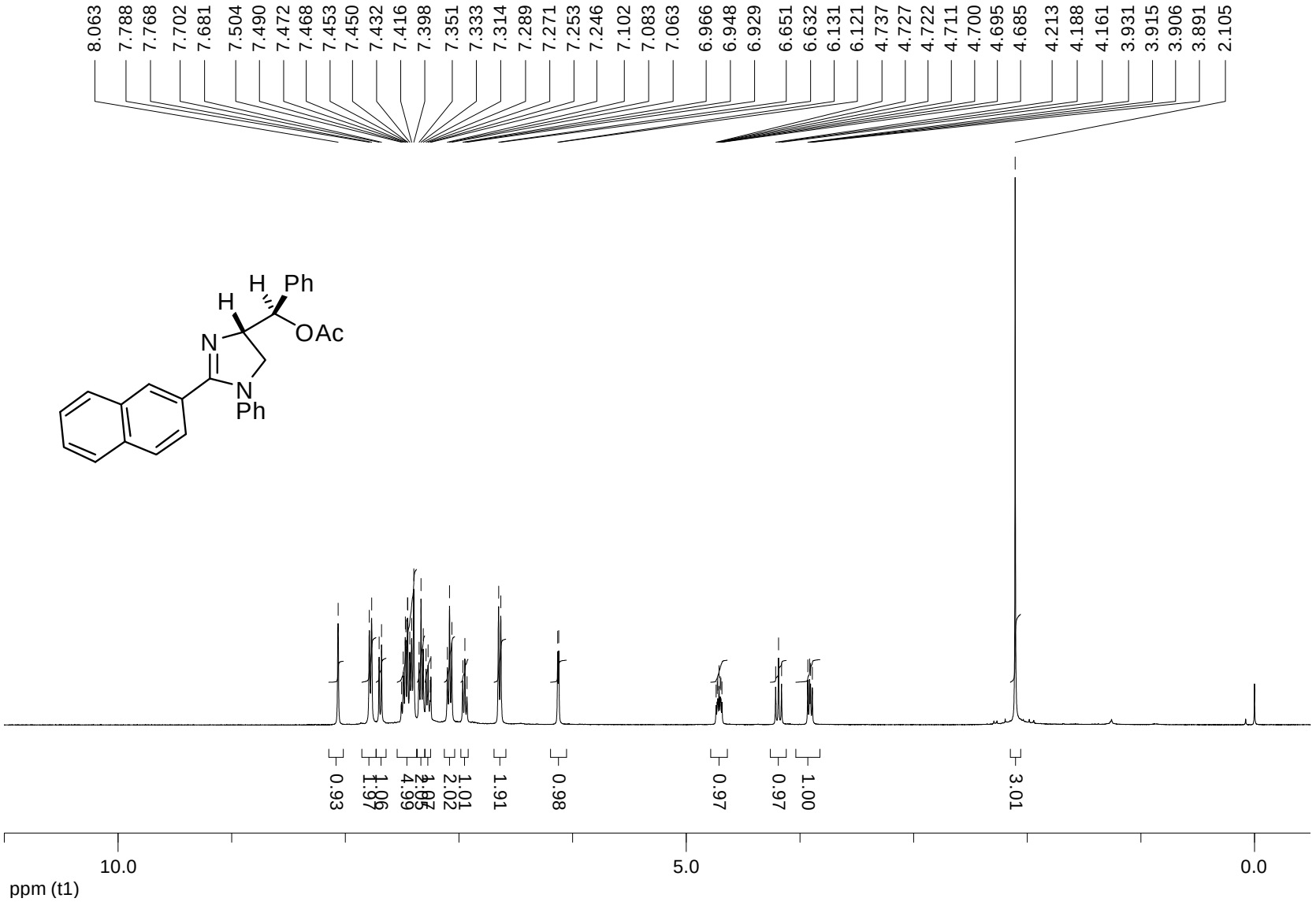
^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)



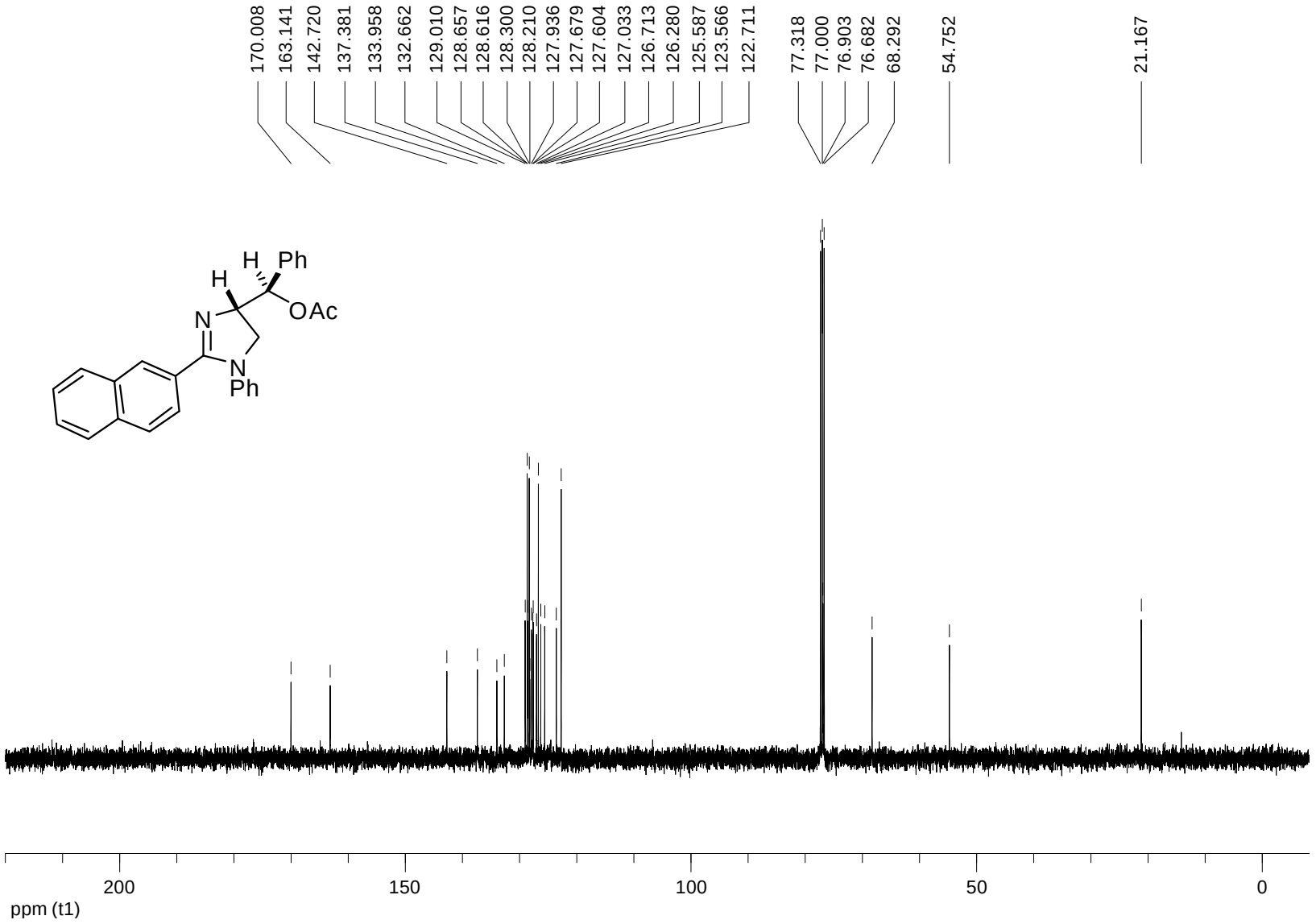
^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)



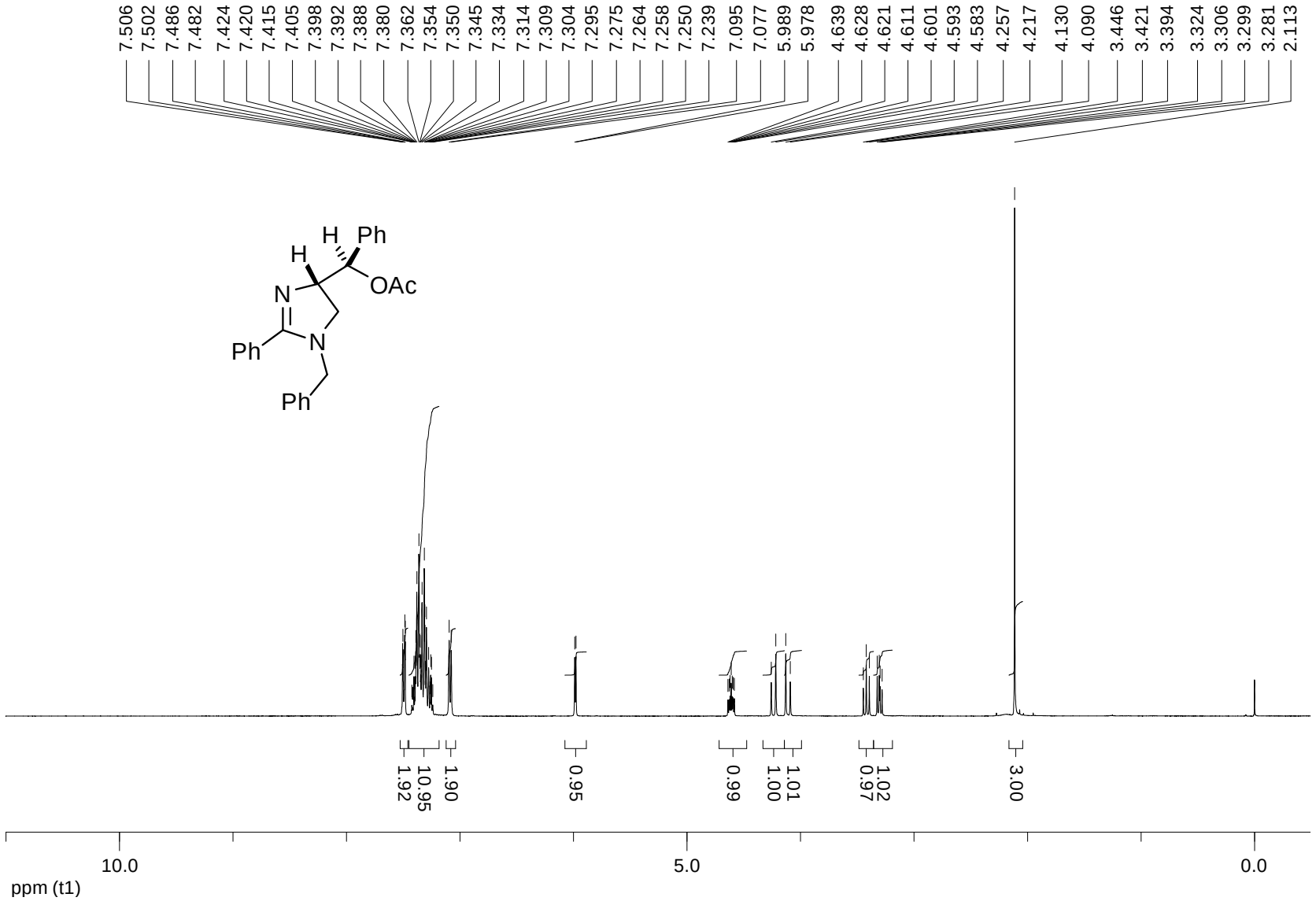
^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)



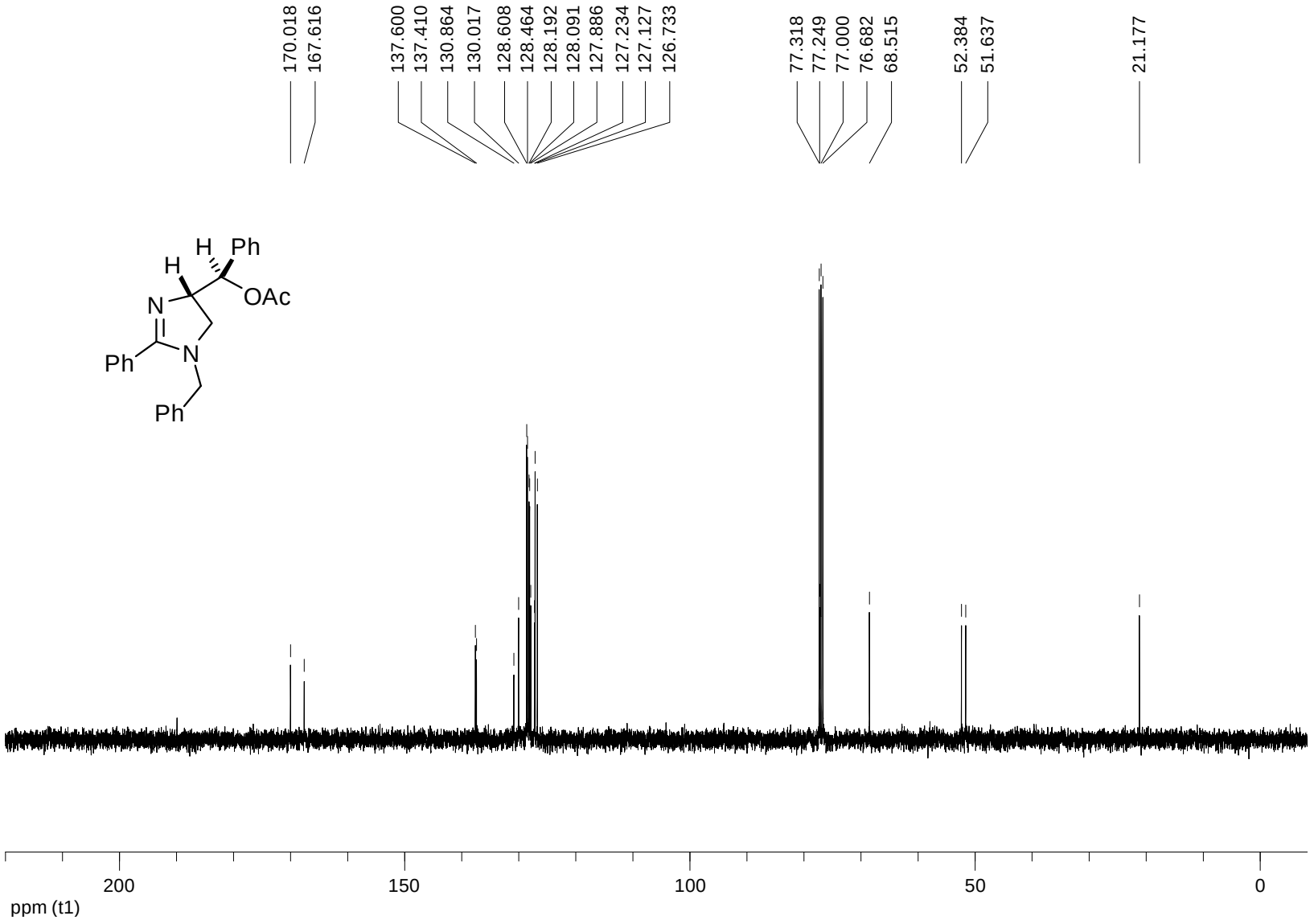
^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)



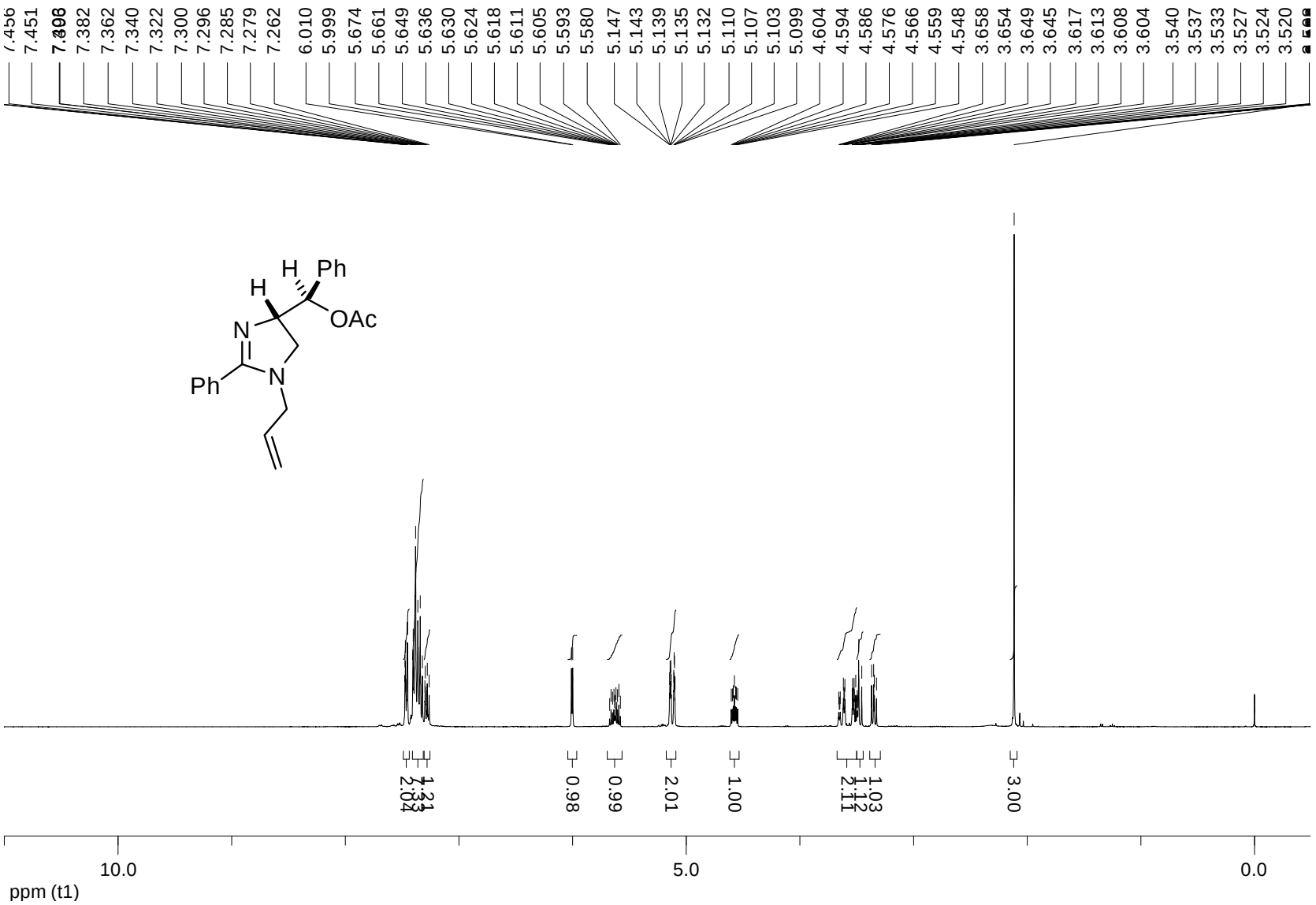
^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)



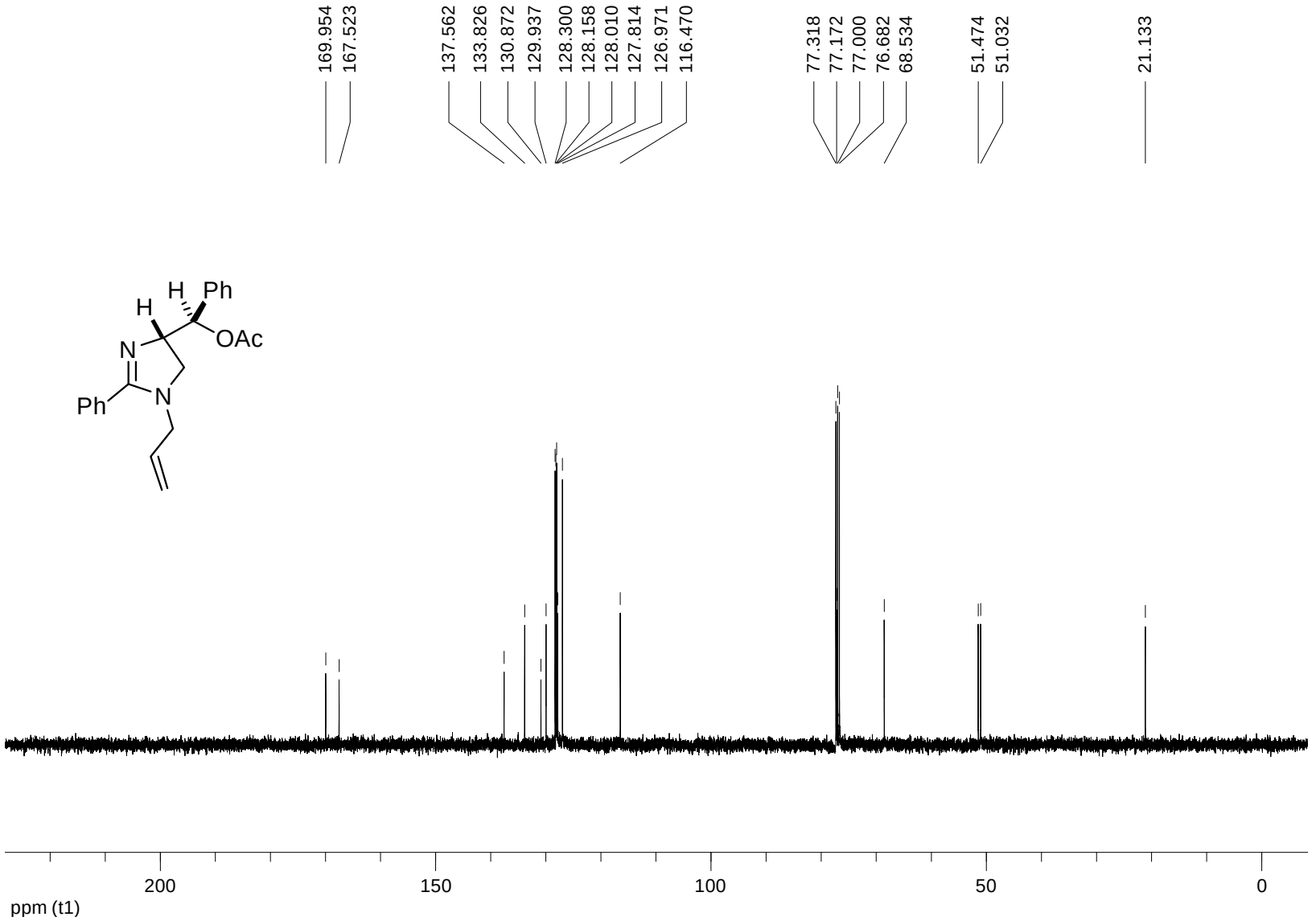
^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)



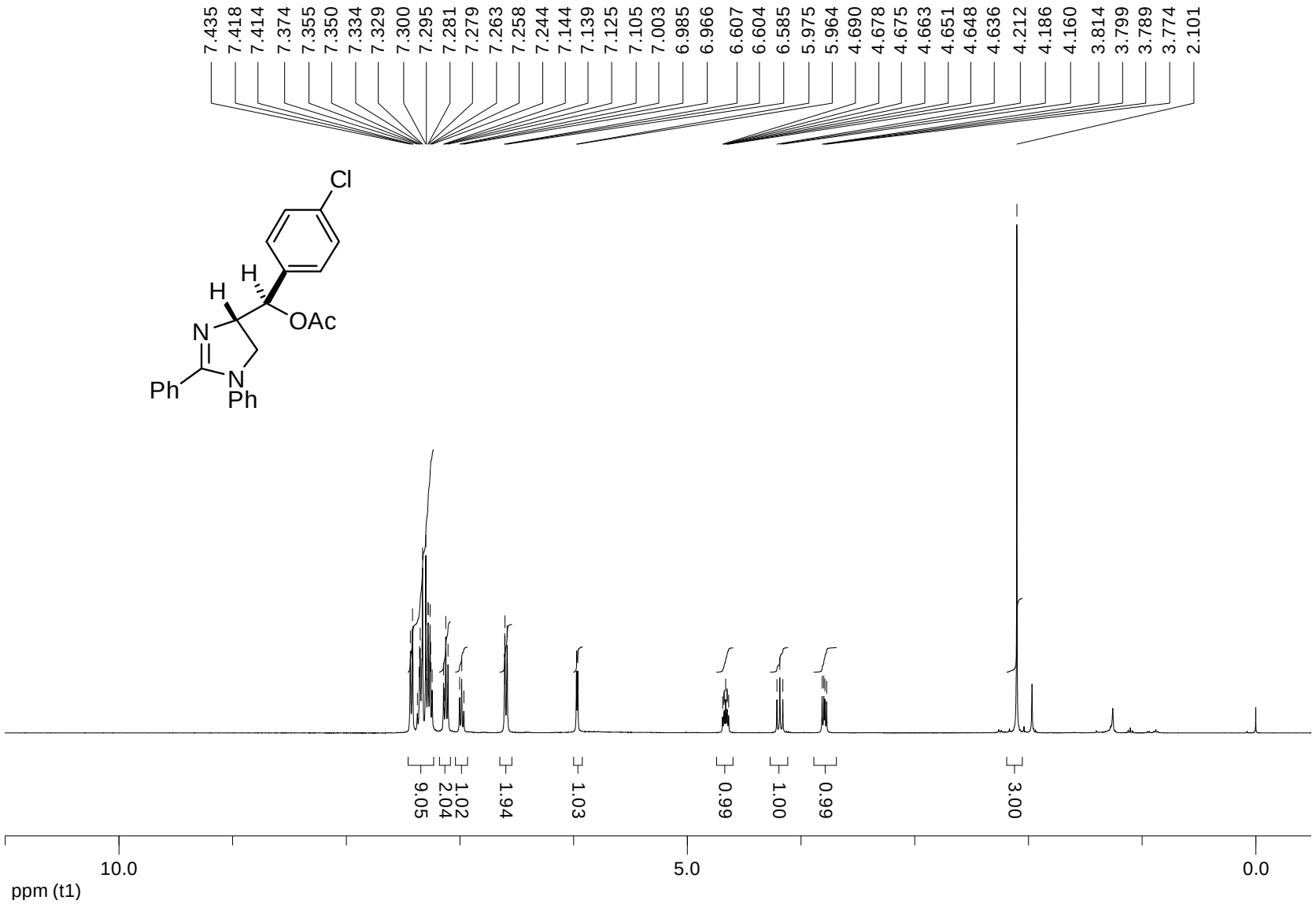
^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)



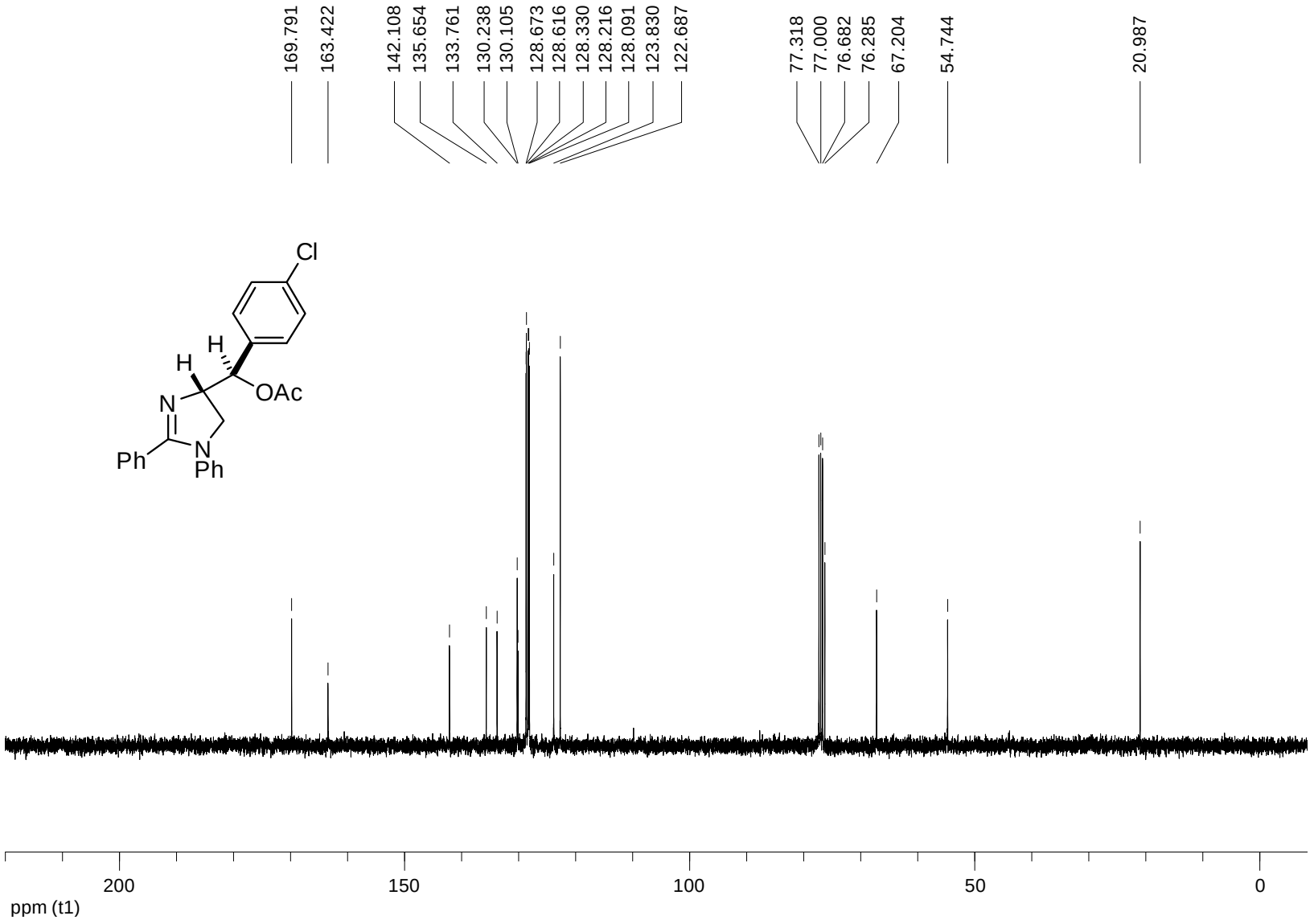
^{13}C NMR spectrum of **2f** (100 MHz, $CDCl_3$)



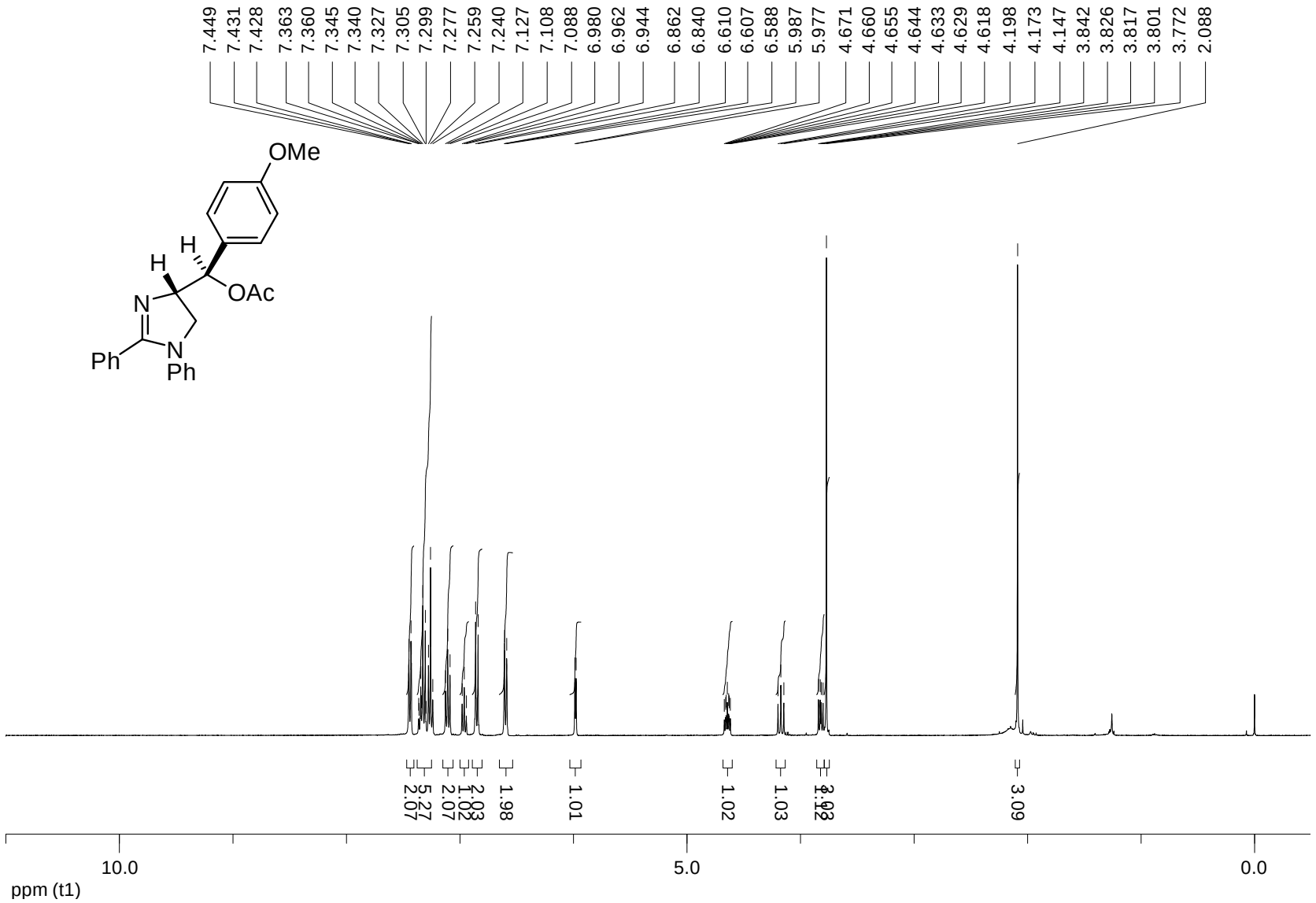
^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)



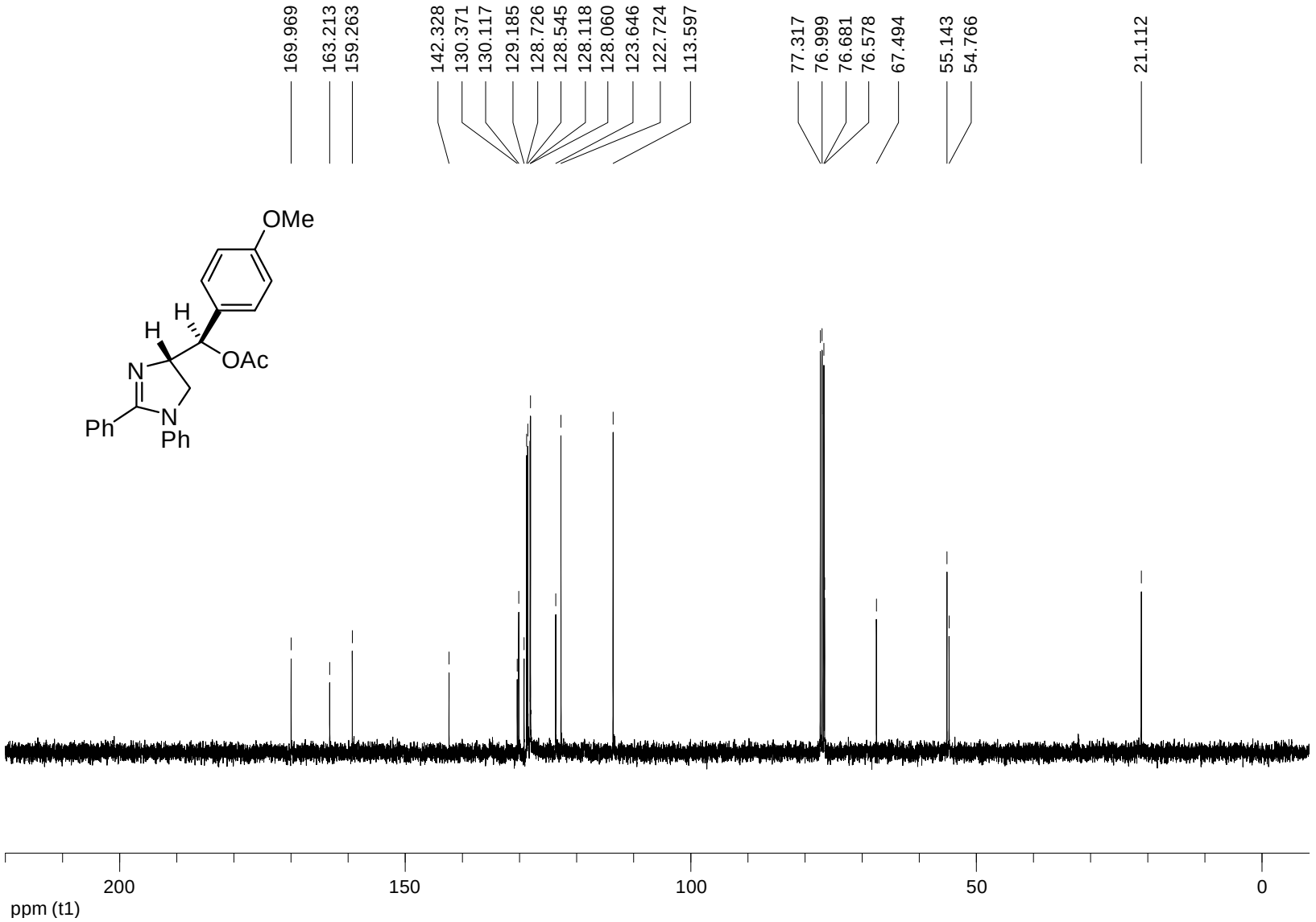
^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)



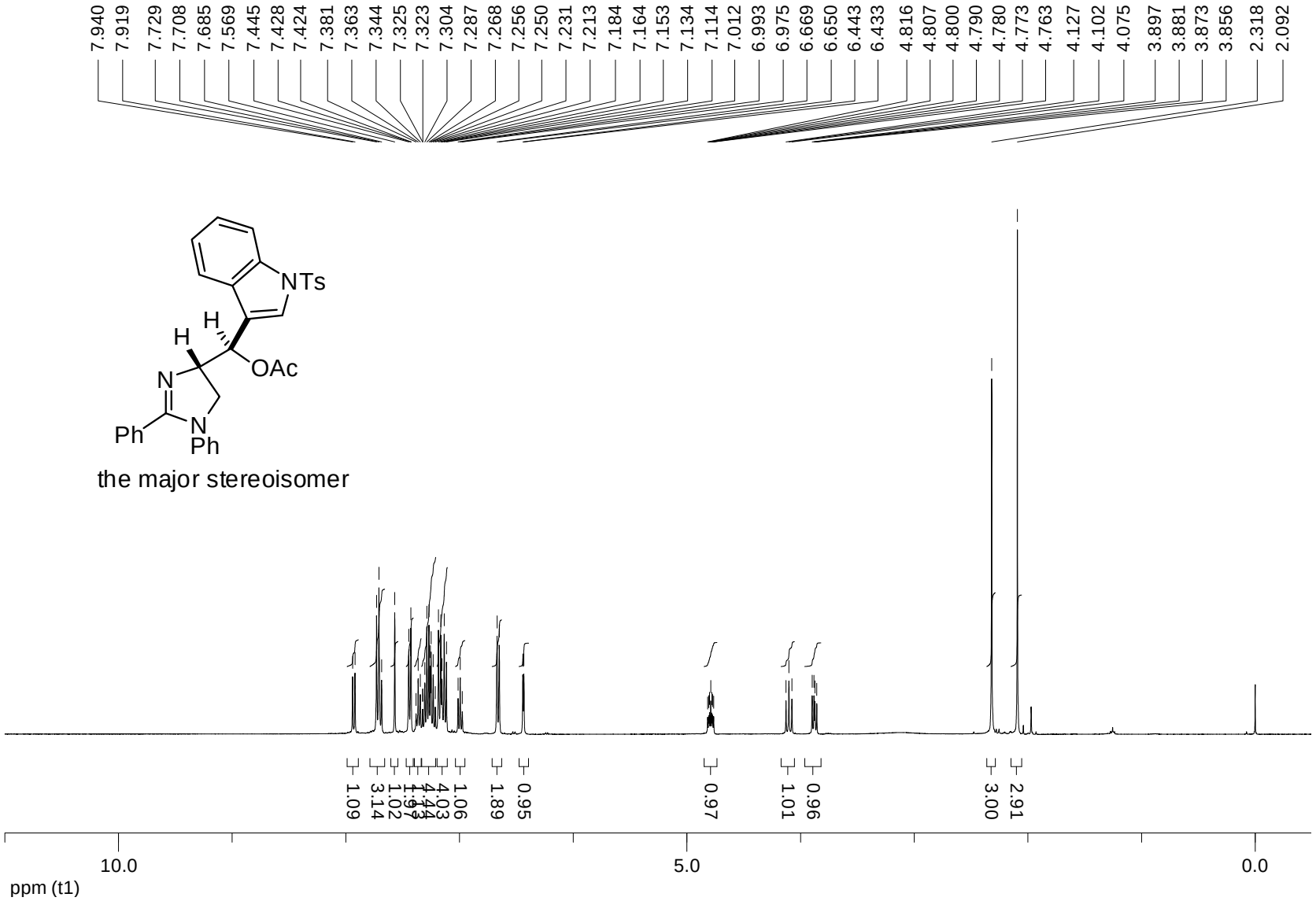
^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)



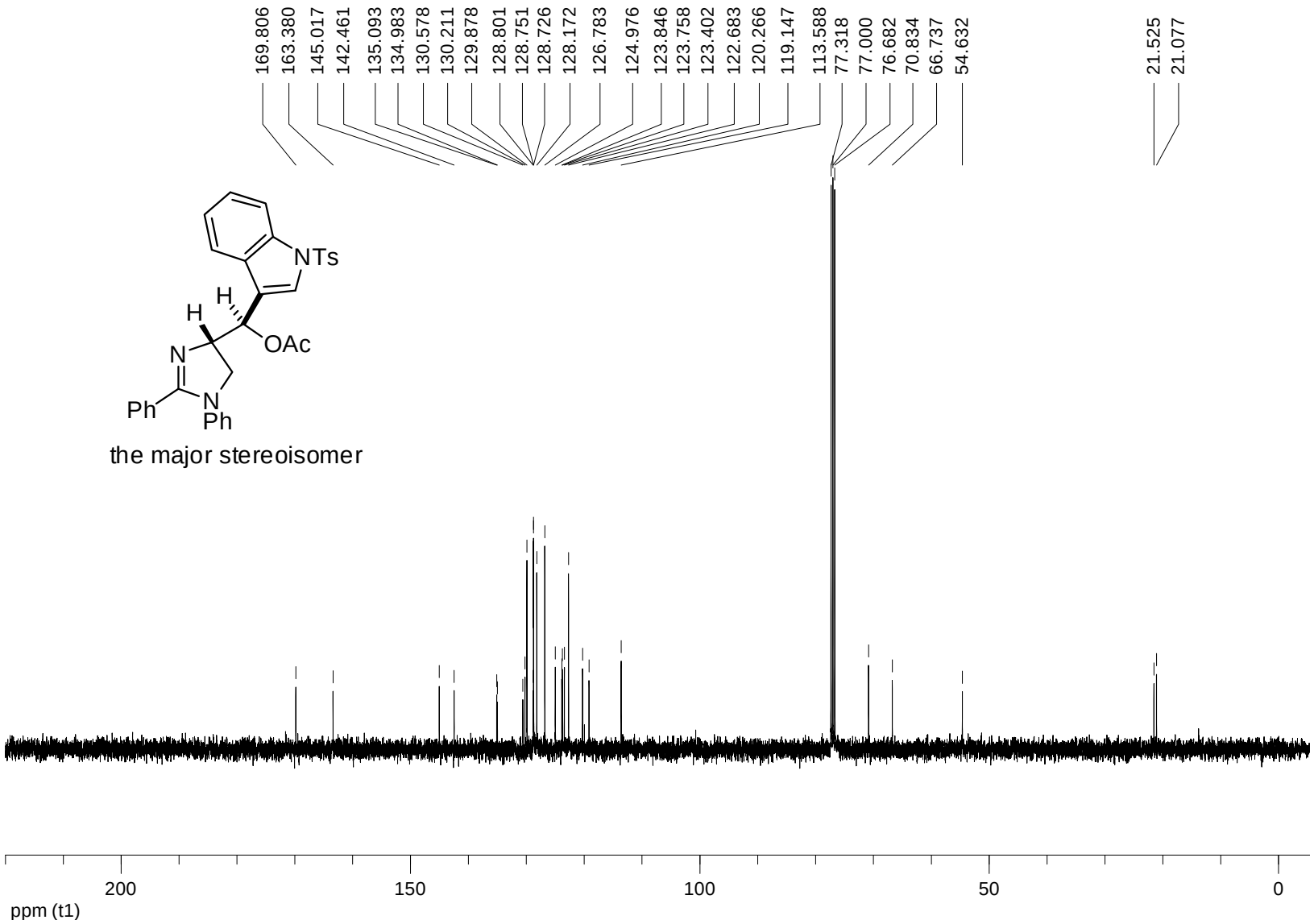
^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)



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

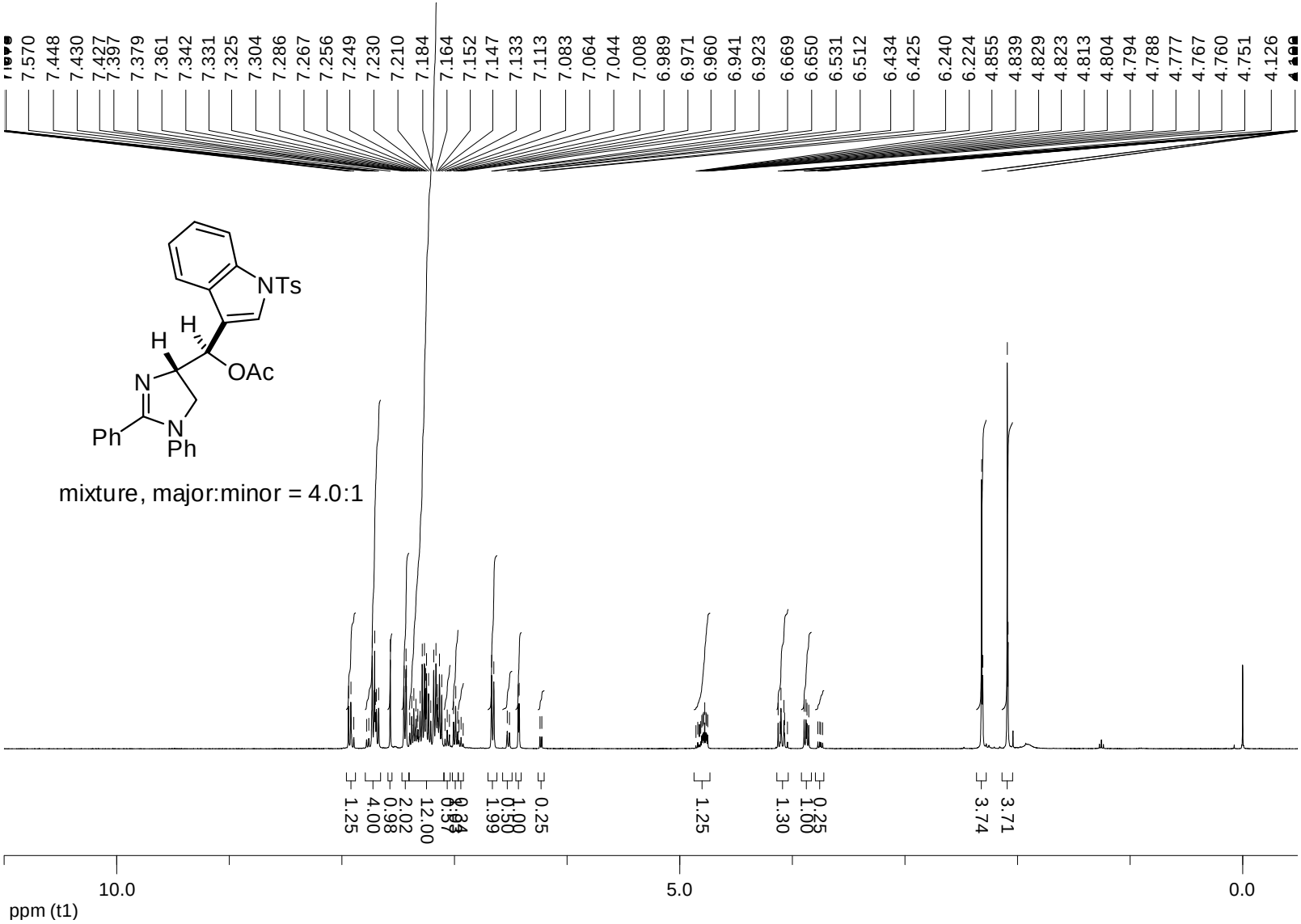


^{13}C NMR spectrum of **2i** (the major stereoisomer) (100 MHz, $CDCl_3$)

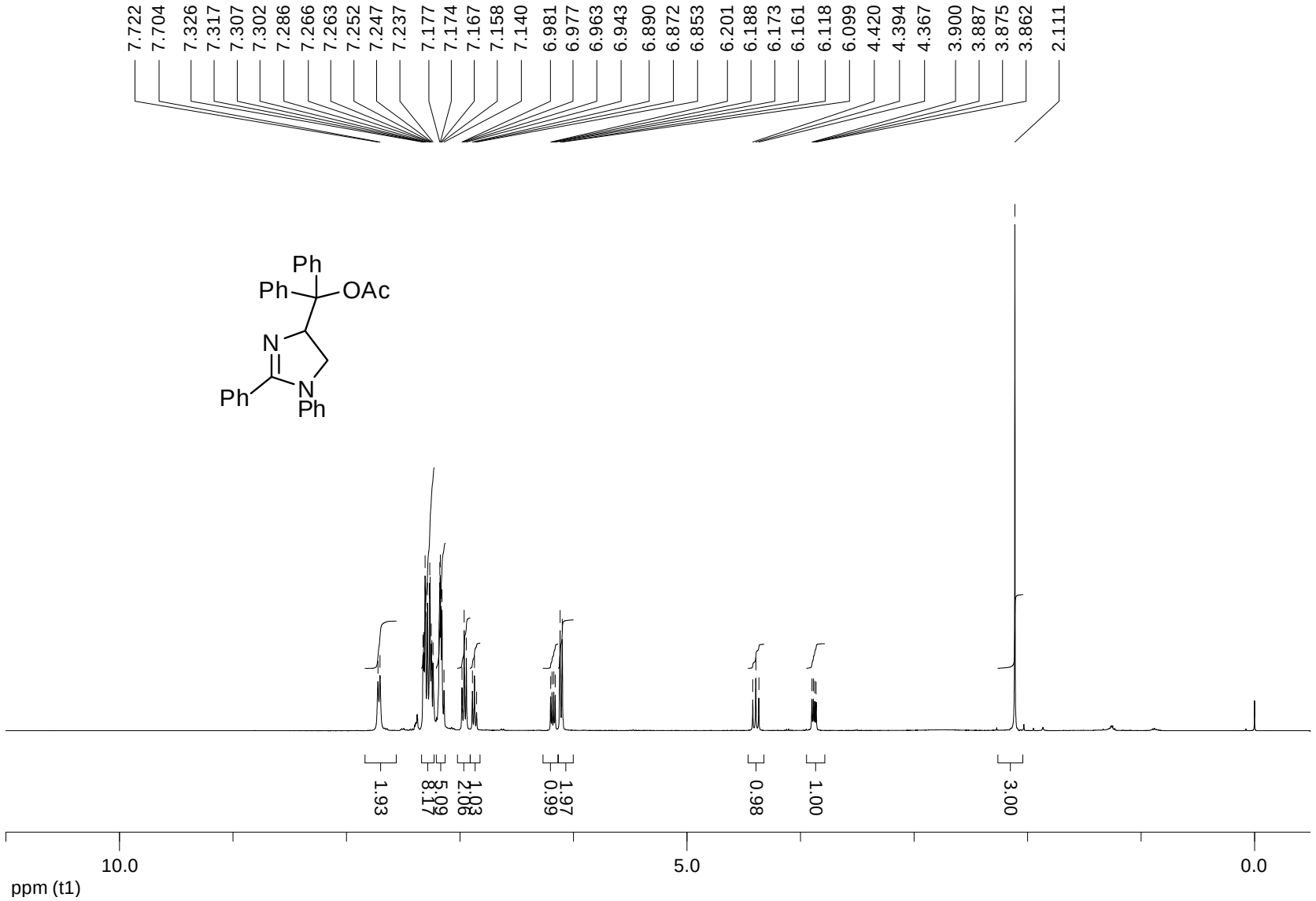


the major stereoisomer

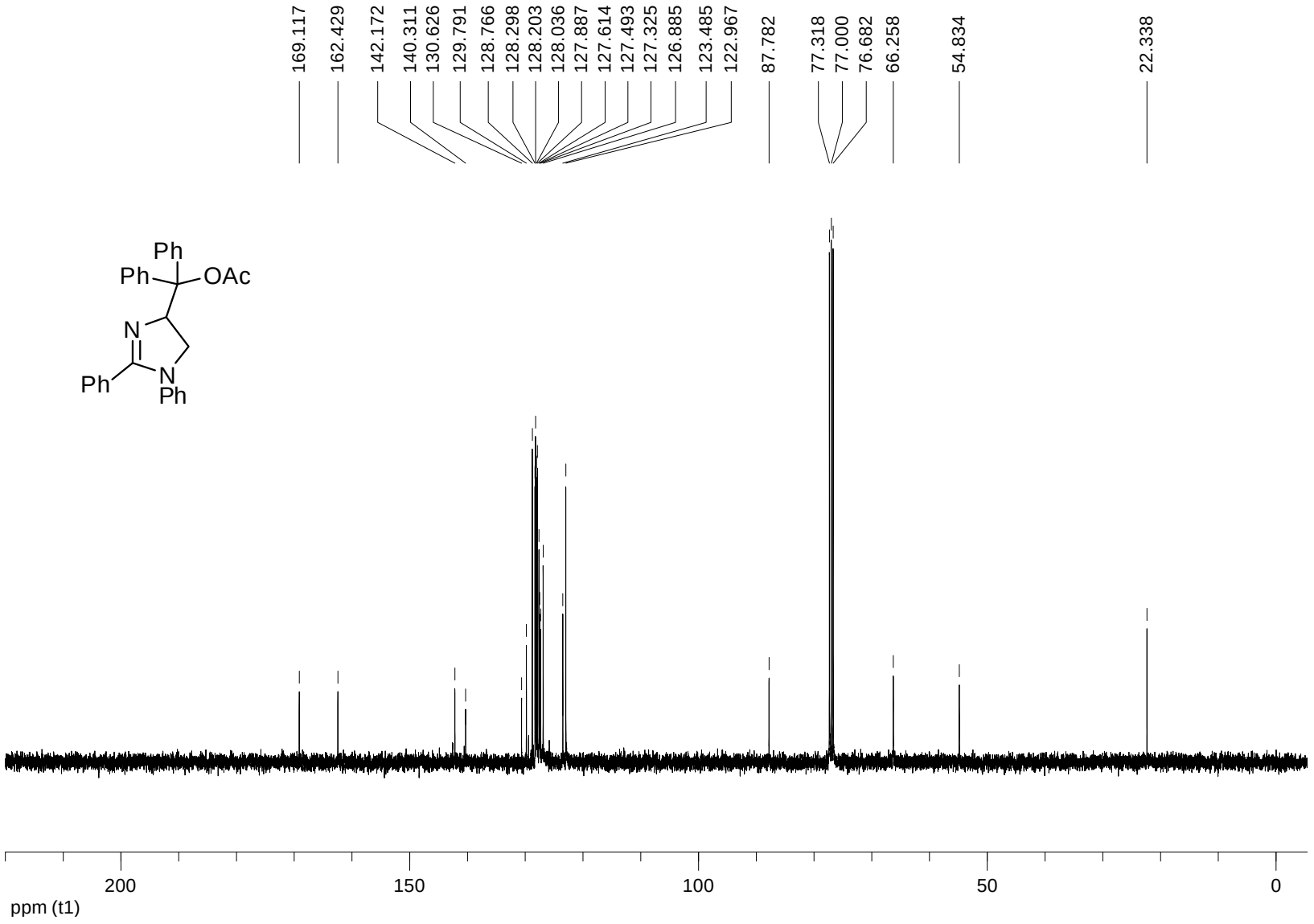
^{1}H NMR spectrum of **2i** (mixture, major:minor = 4.0:1) (400 MHz, $CDCl_3$)



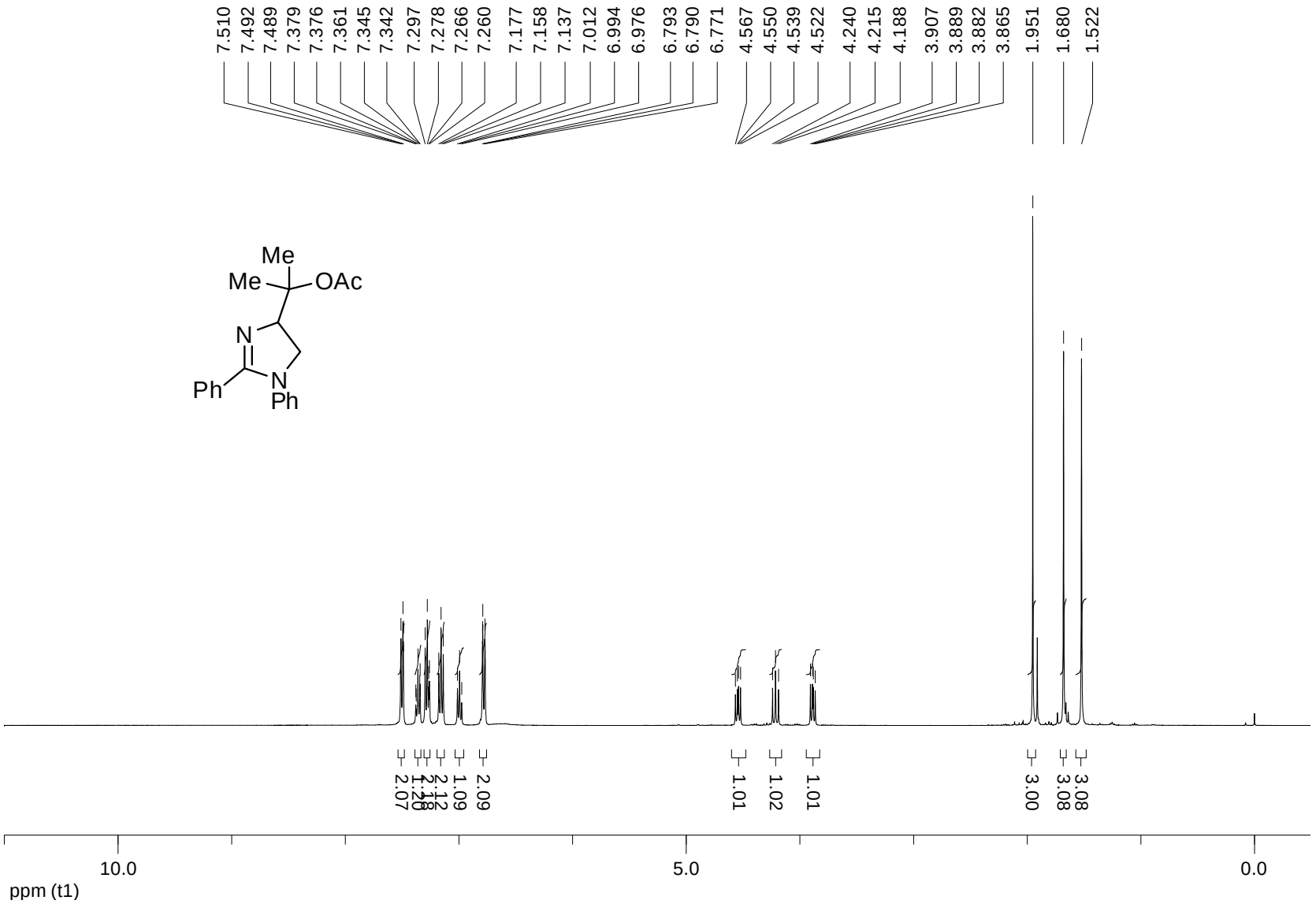
^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)



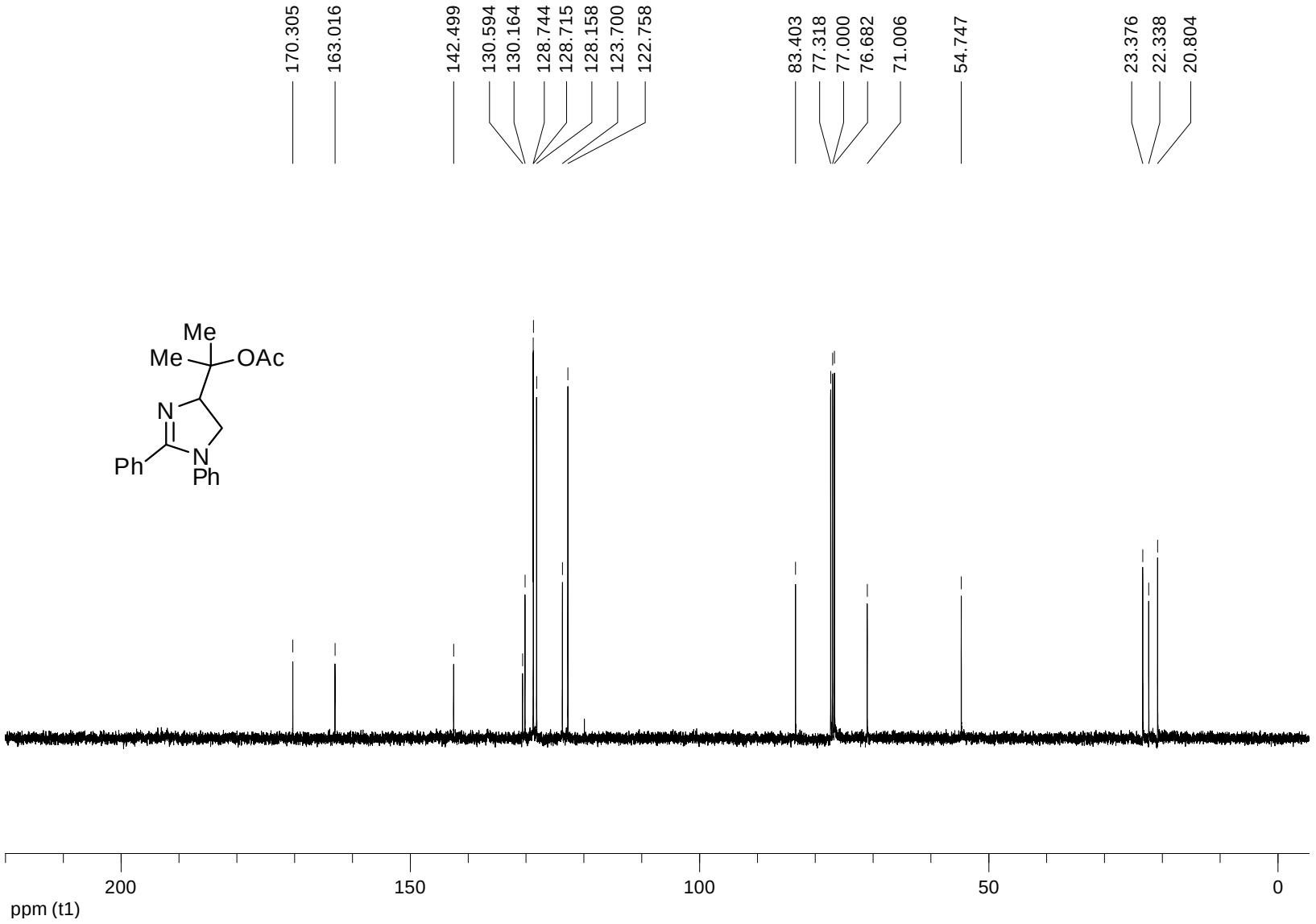
^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)



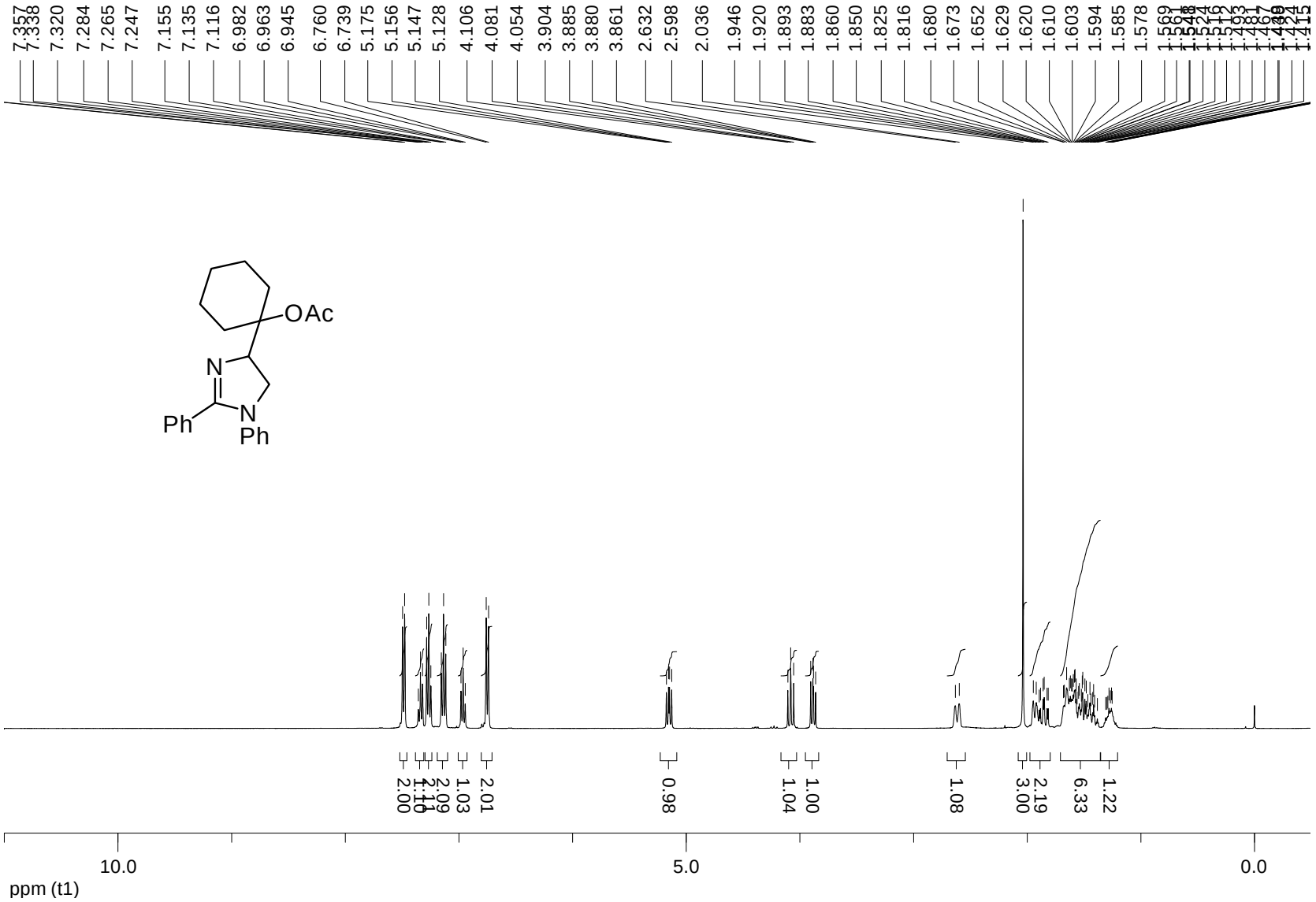
^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$)



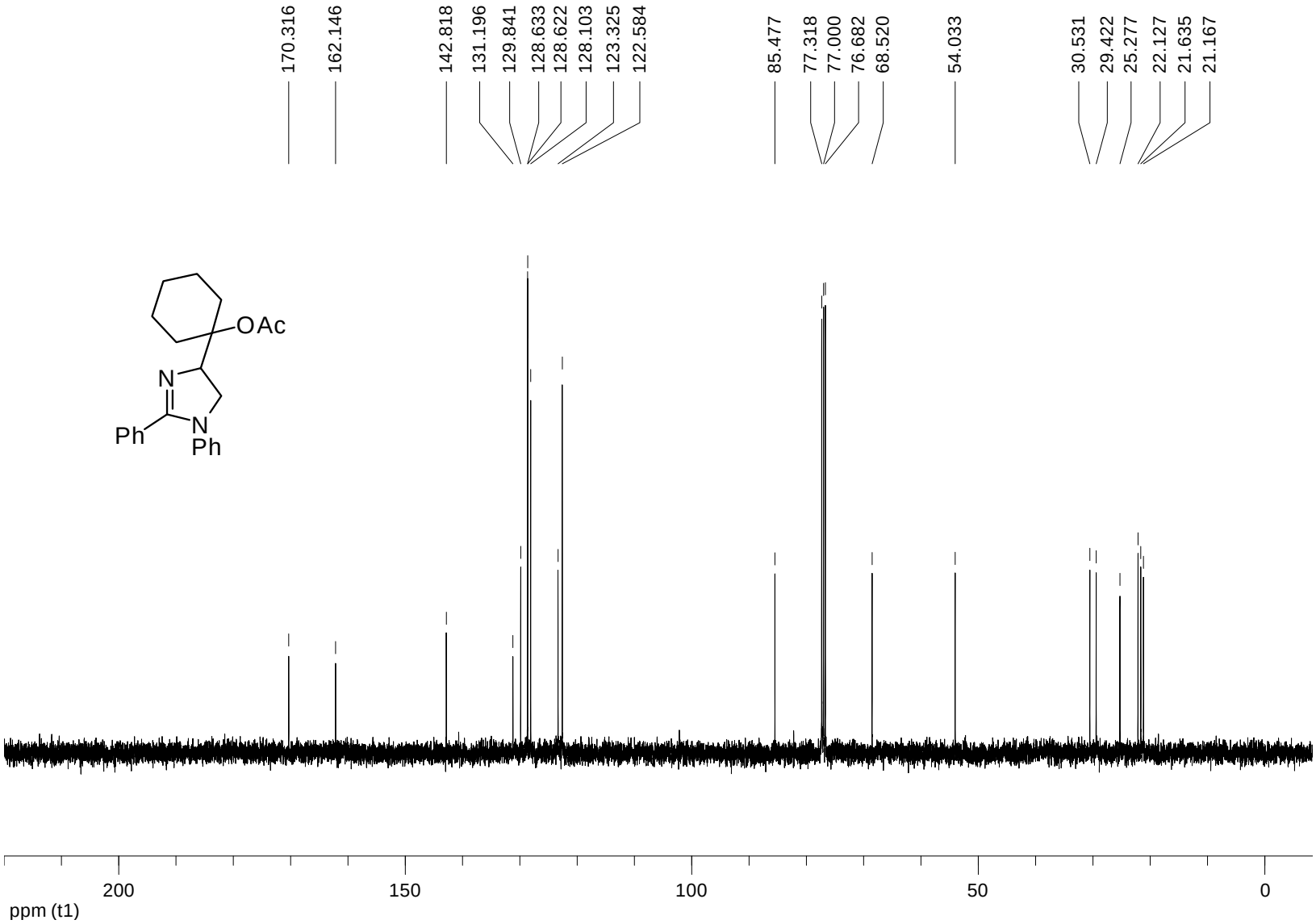
^{13}C NMR spectrum of **2l** (100 MHz, $CDCl_3$)



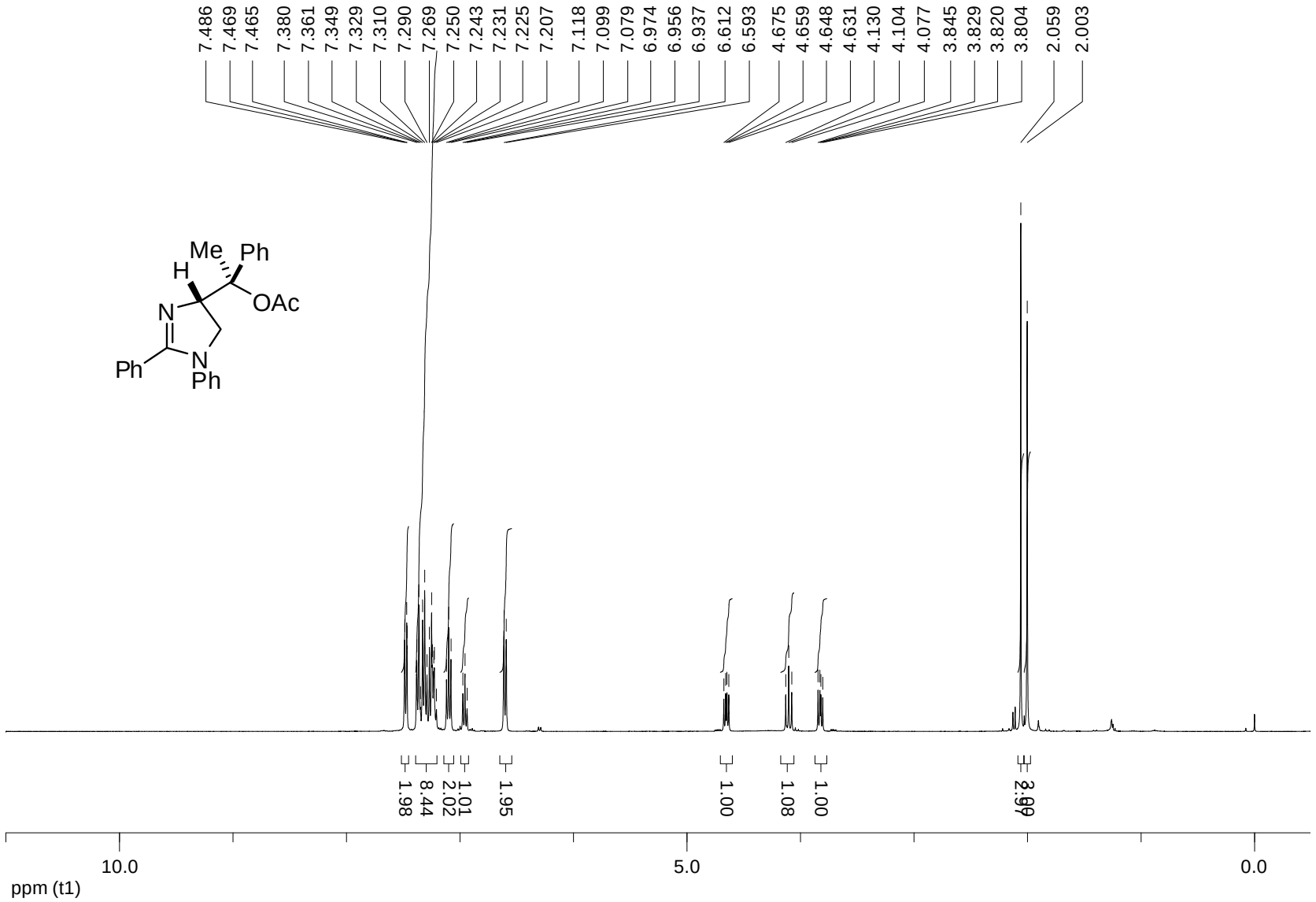
^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$)



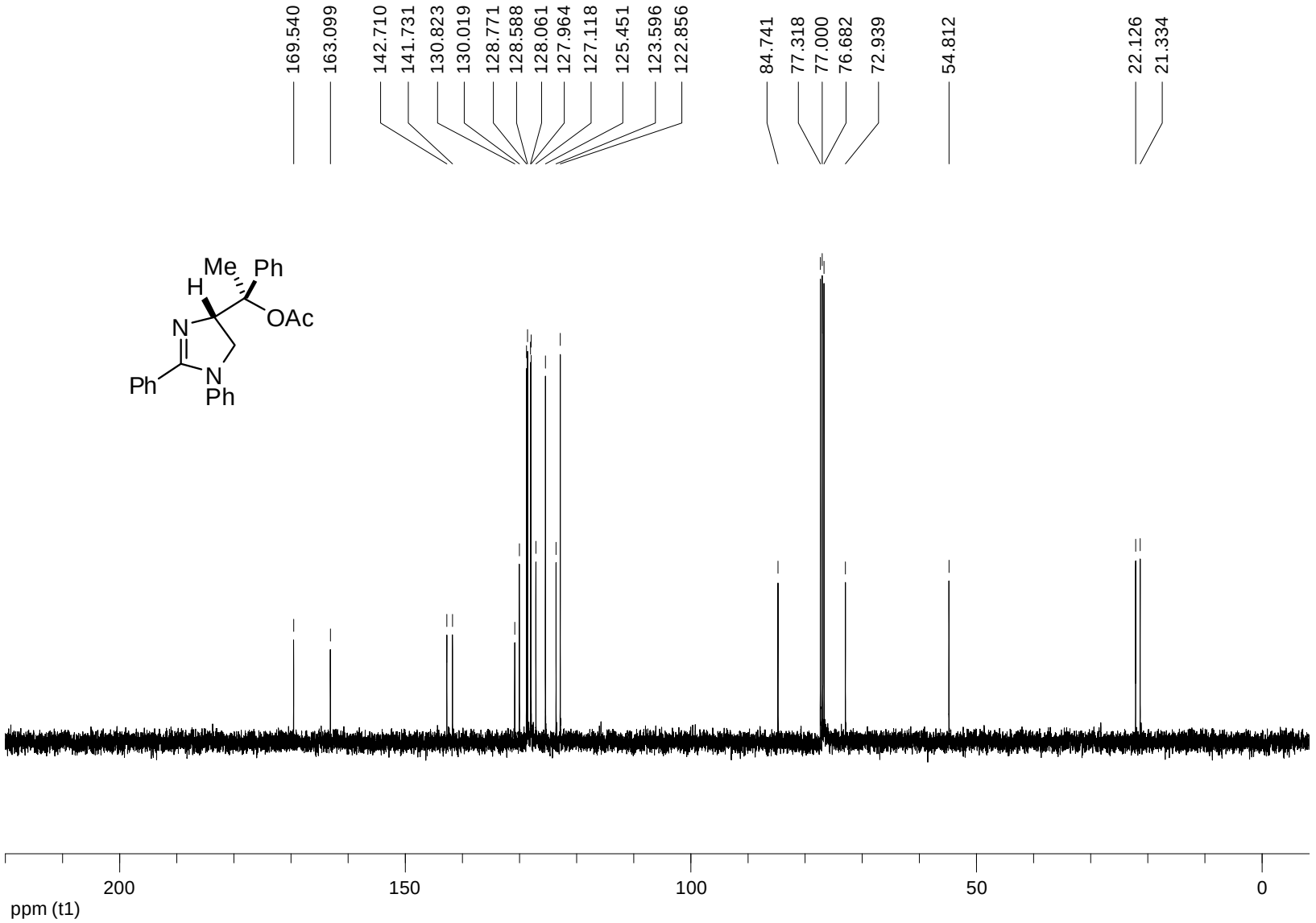
^{13}C NMR spectrum of **2m** (100 MHz, $CDCl_3$)



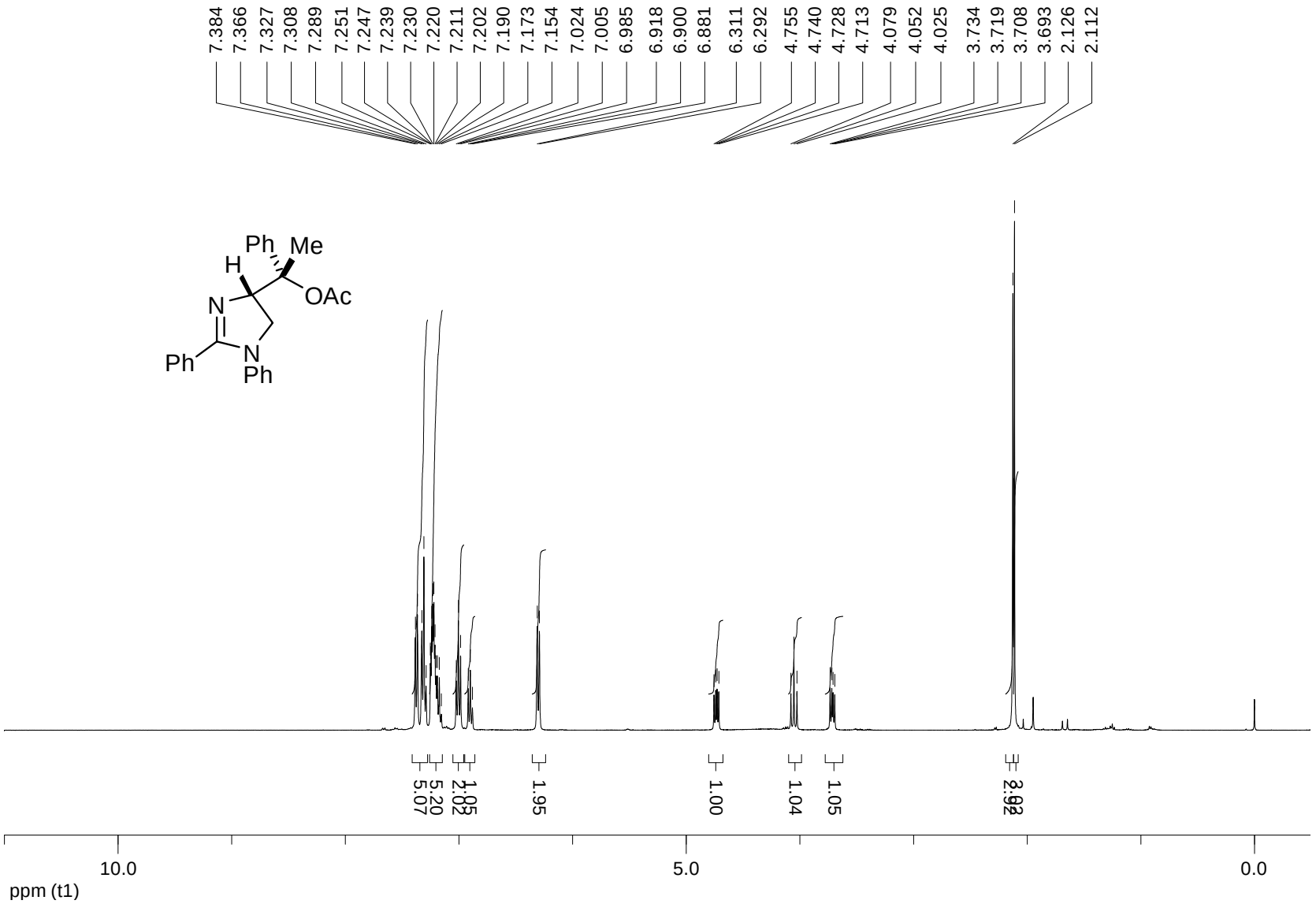
^{1}H NMR spectrum of **2n** (dr = >20:1) (400 MHz, $CDCl_3$)



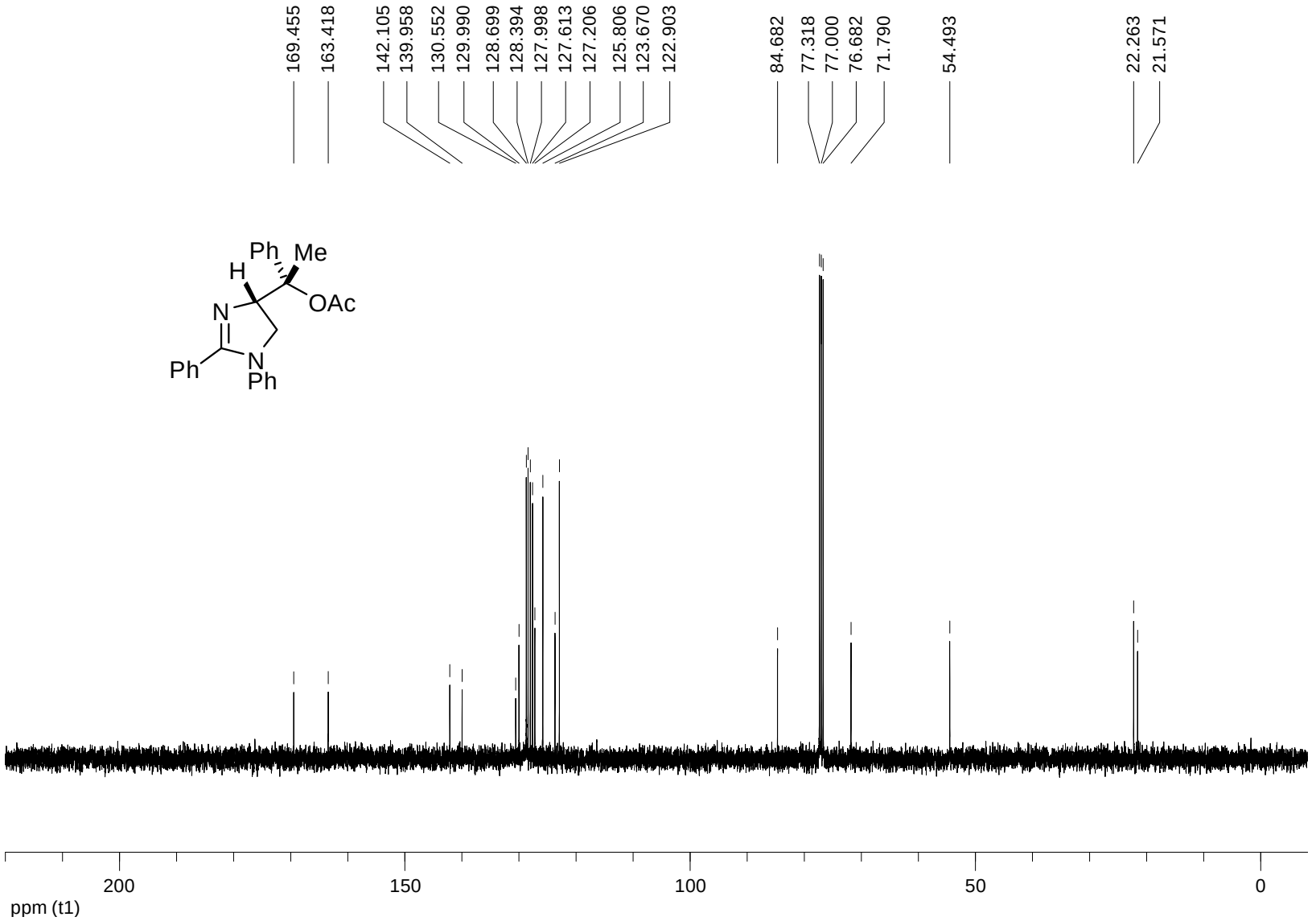
^{13}C NMR spectrum of **2n** (dr = >20:1) (100 MHz, $CDCl_3$)



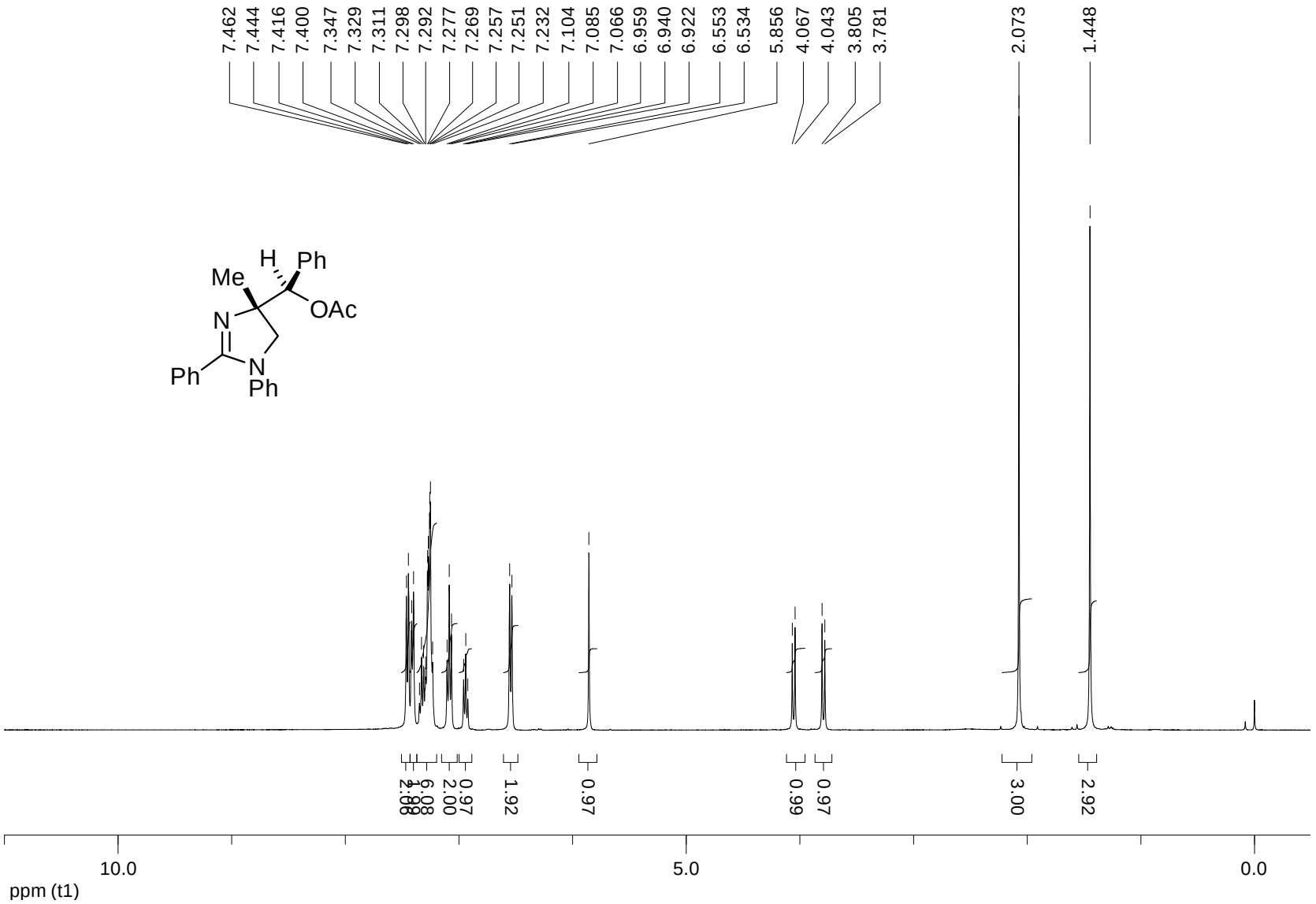
^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)



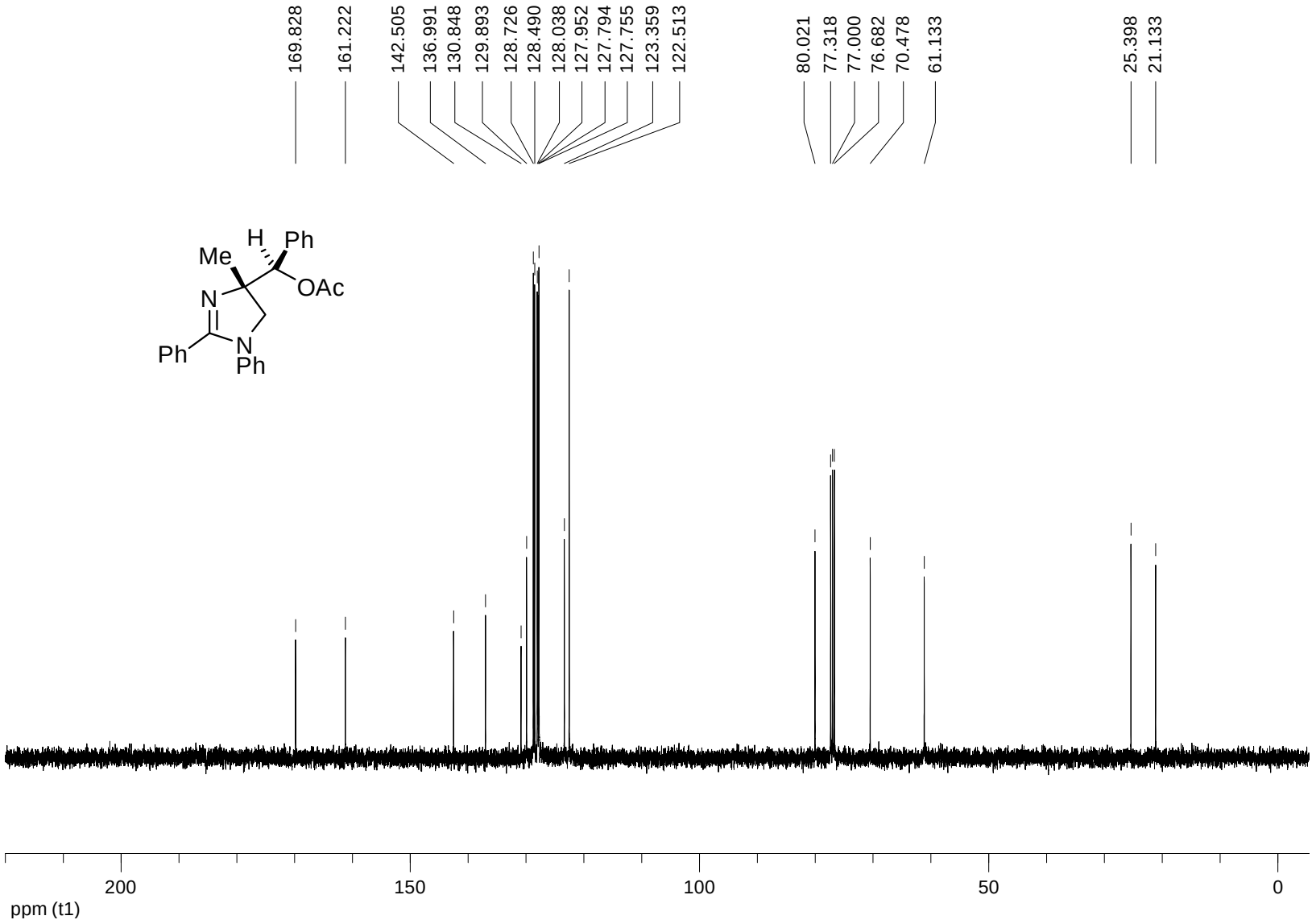
^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)



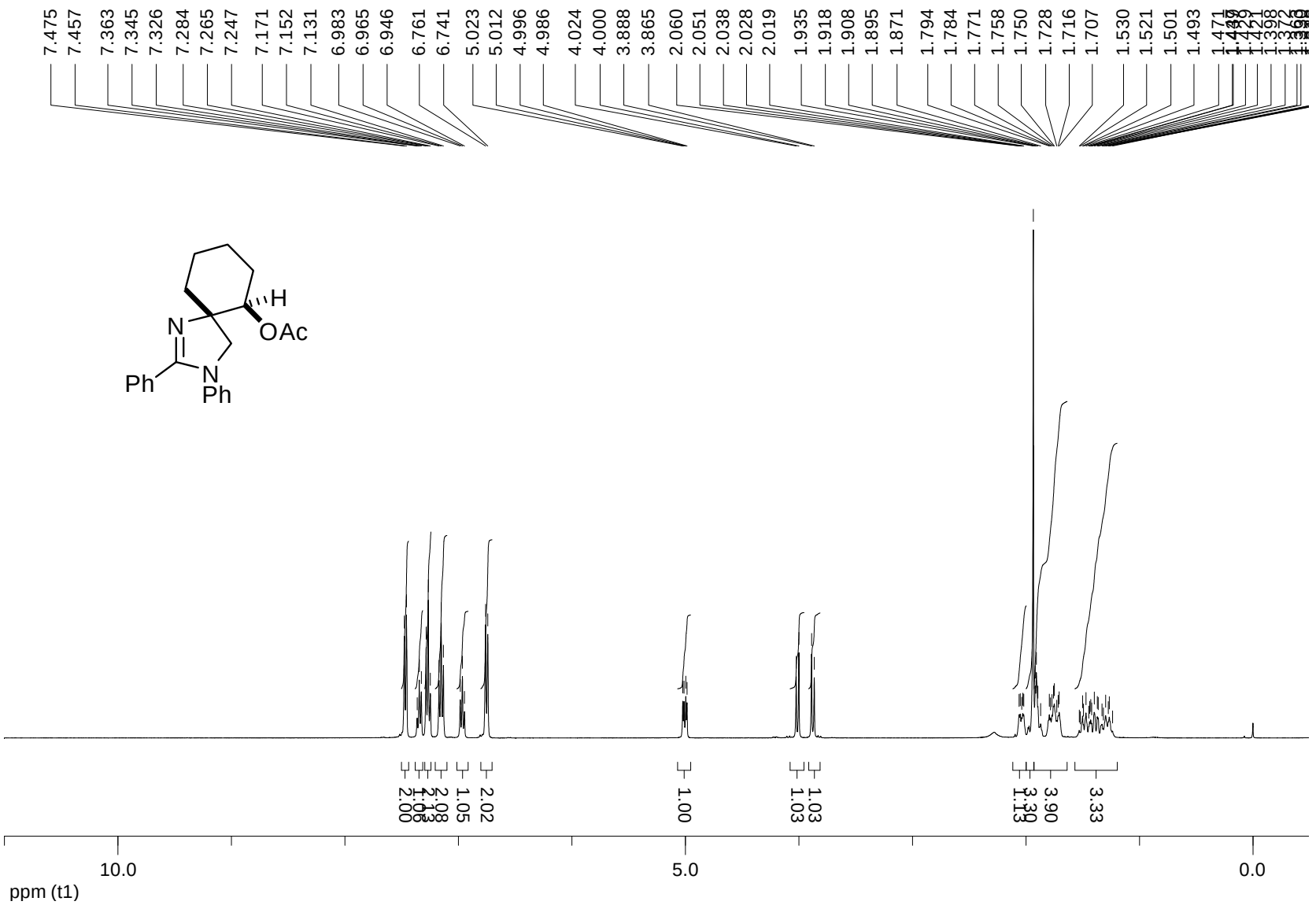
^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)



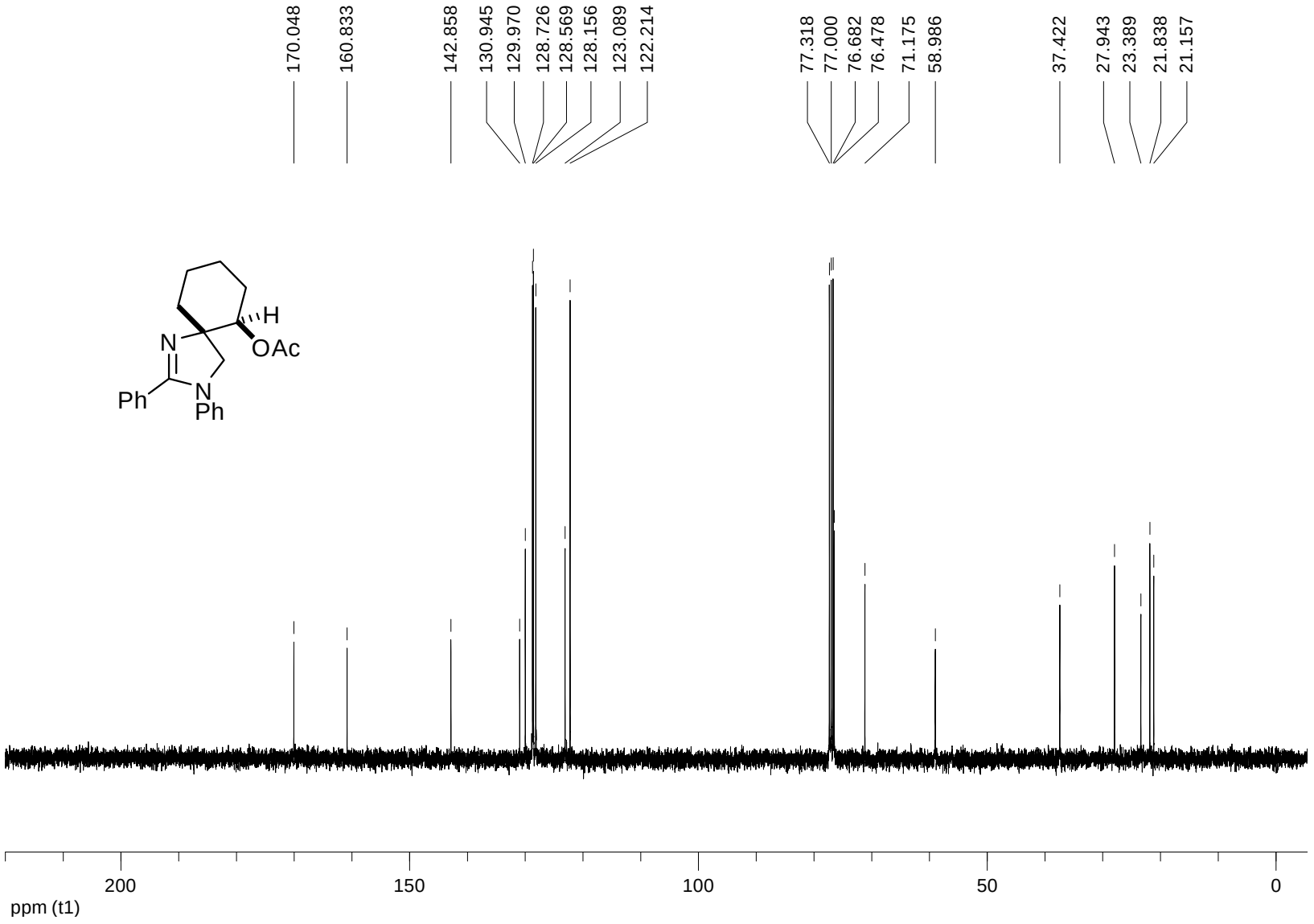
^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)



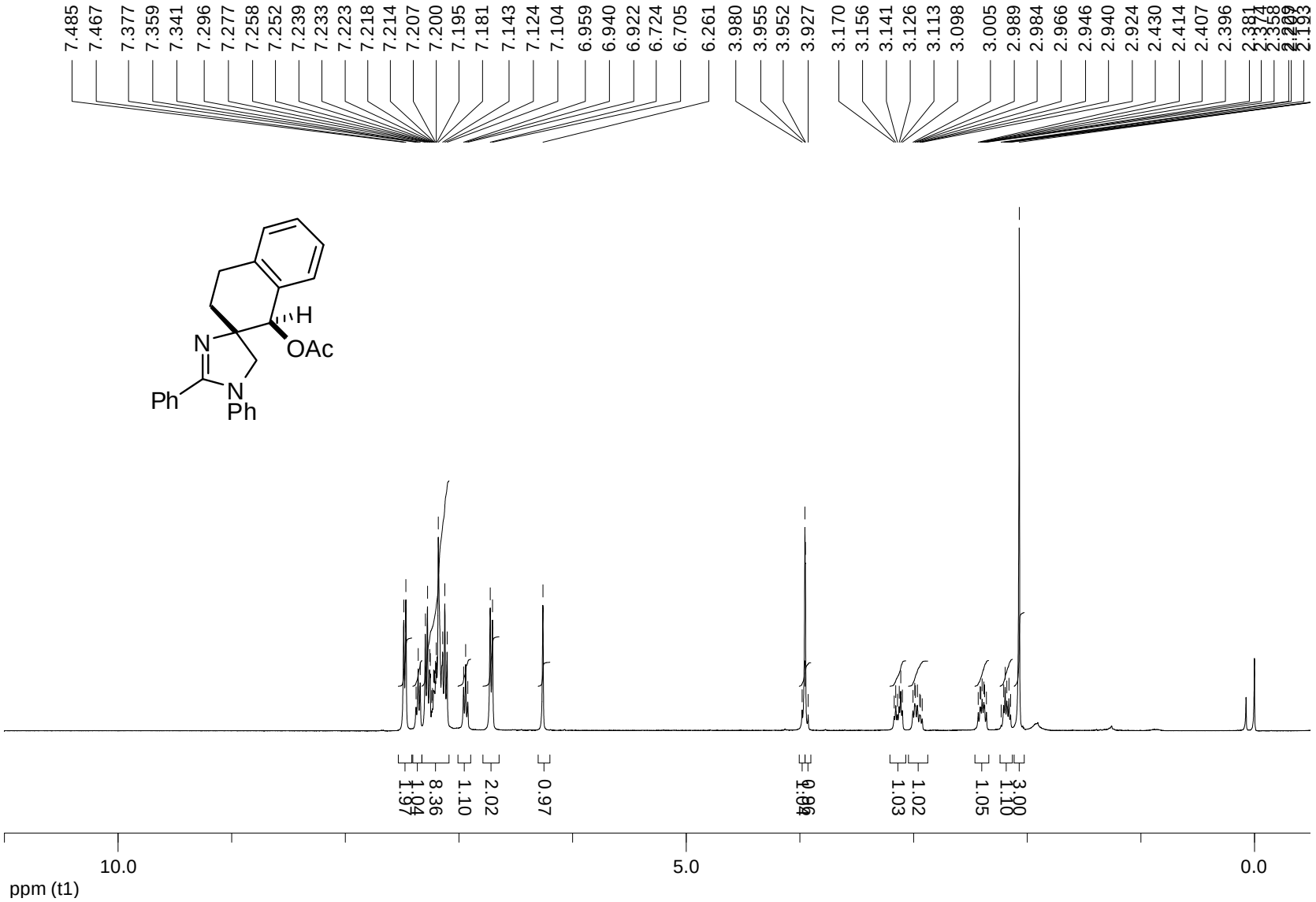
^{1}H NMR spectrum of **2q** (400 MHz, $CDCl_3$)



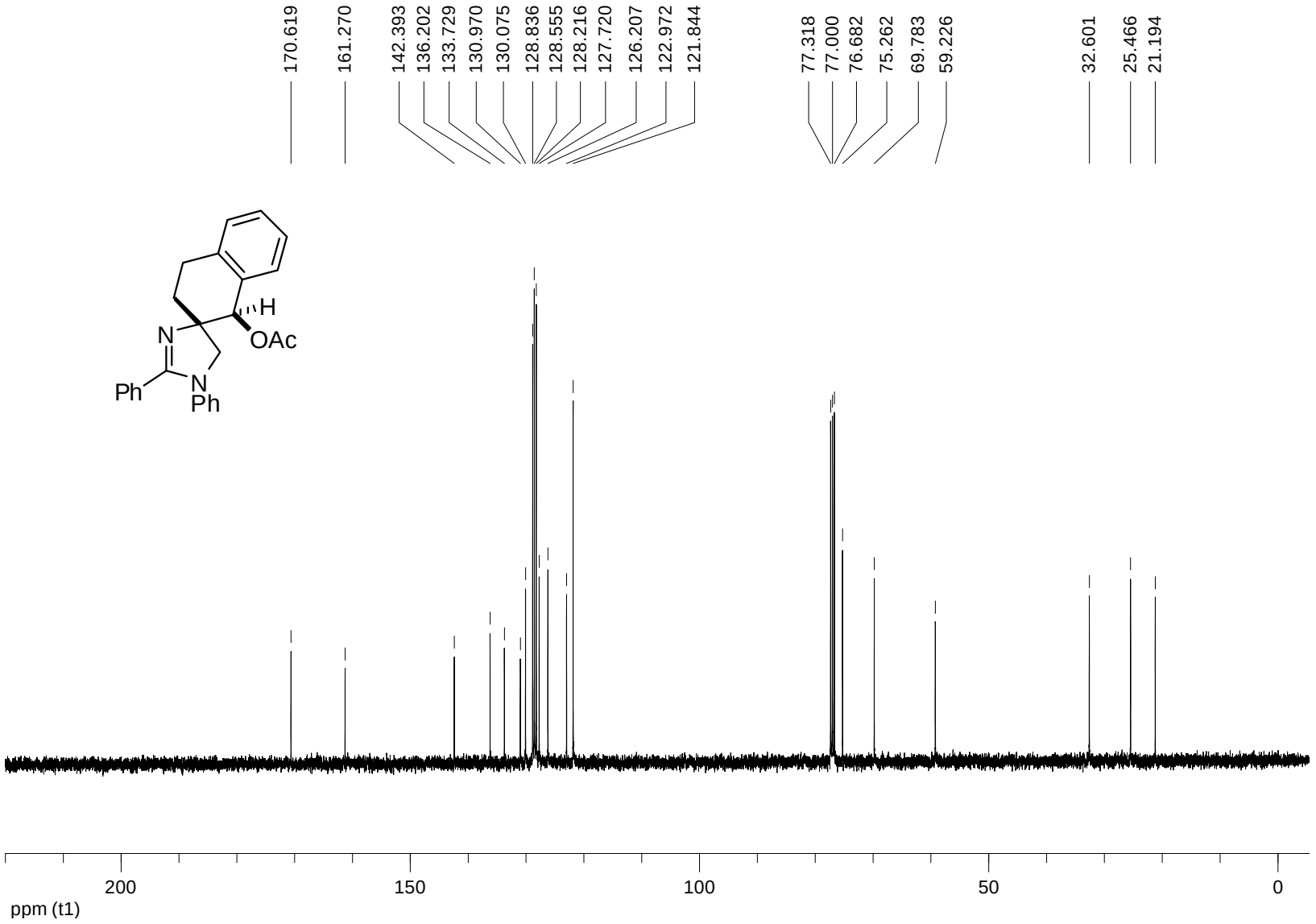
^{13}C NMR spectrum of **2q** (100 MHz, $CDCl_3$)



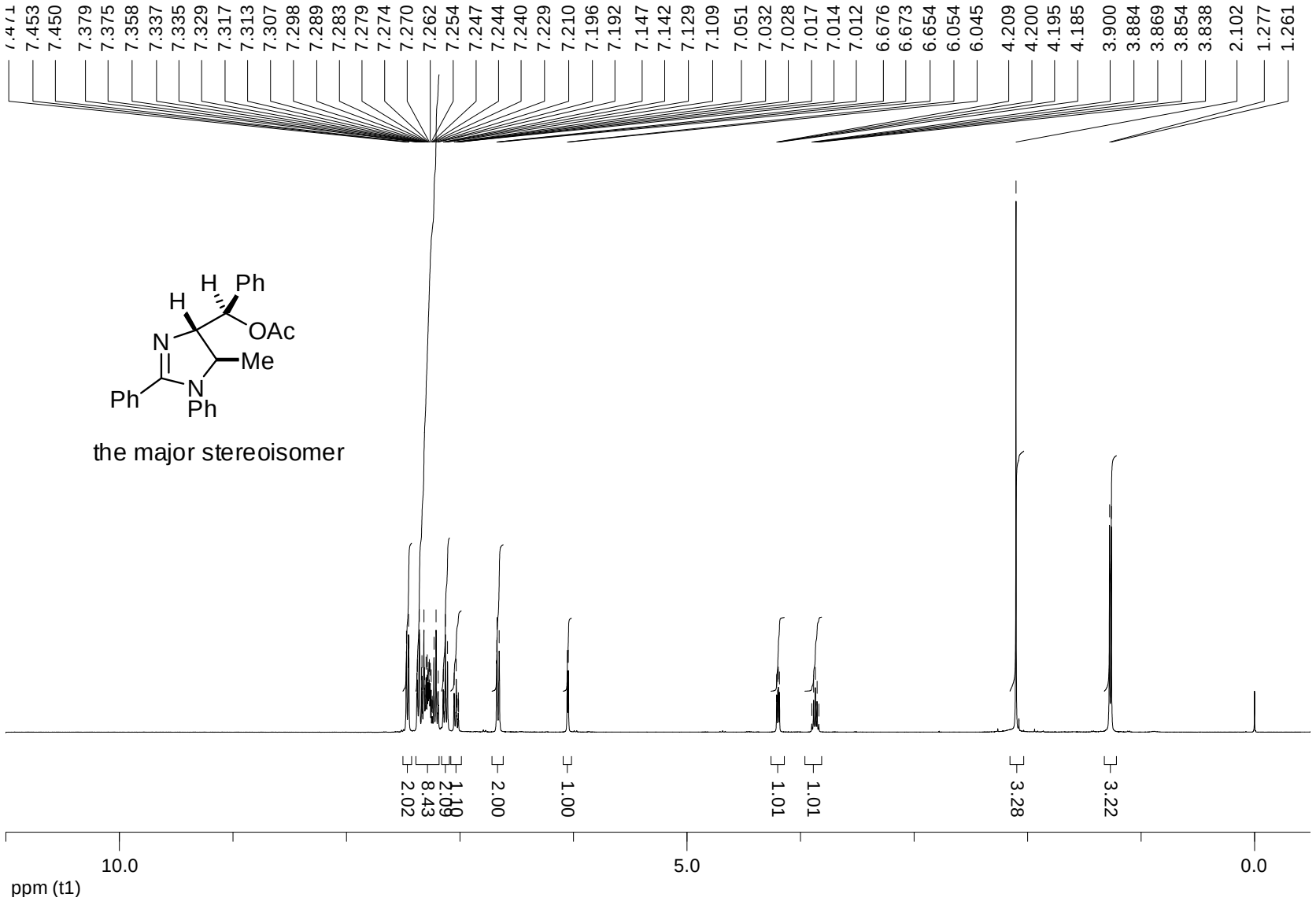
^{1}H NMR spectrum of **2r** (400 MHz, $CDCl_3$)



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

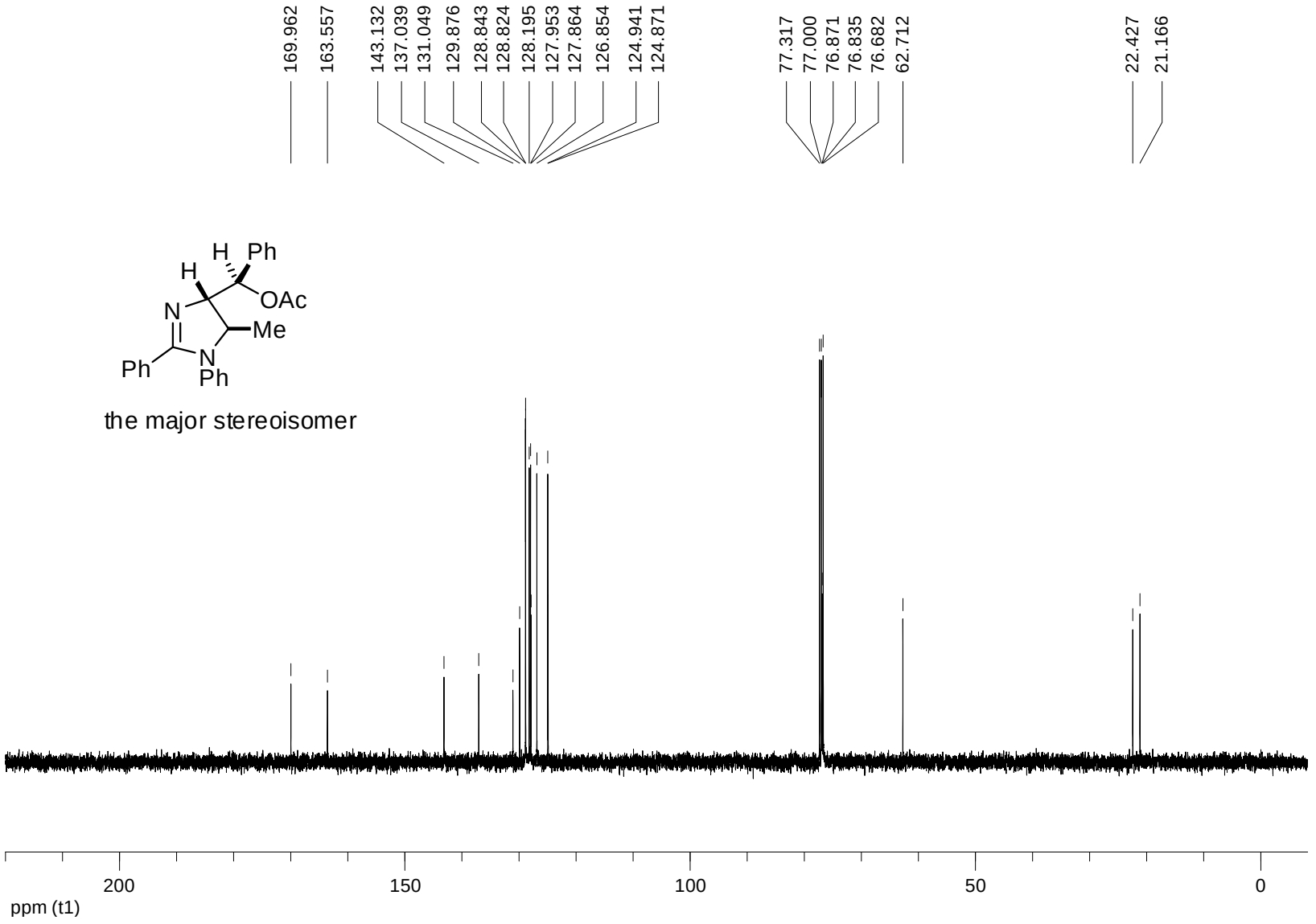


^{1}H NMR spectrum of **2s** (the major stereoisomer) (400 MHz, $CDCl_3$)

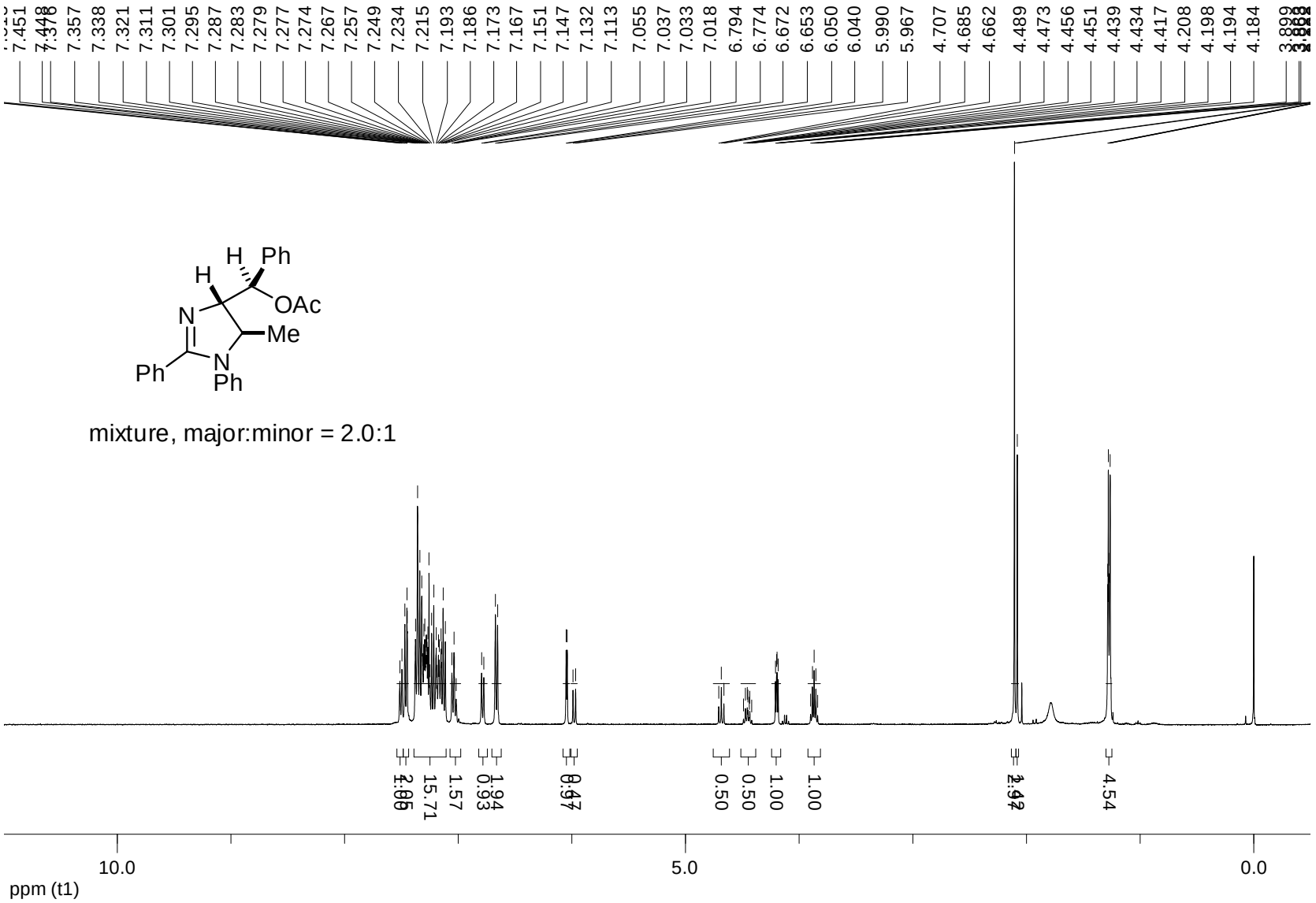


the major stereoisomer

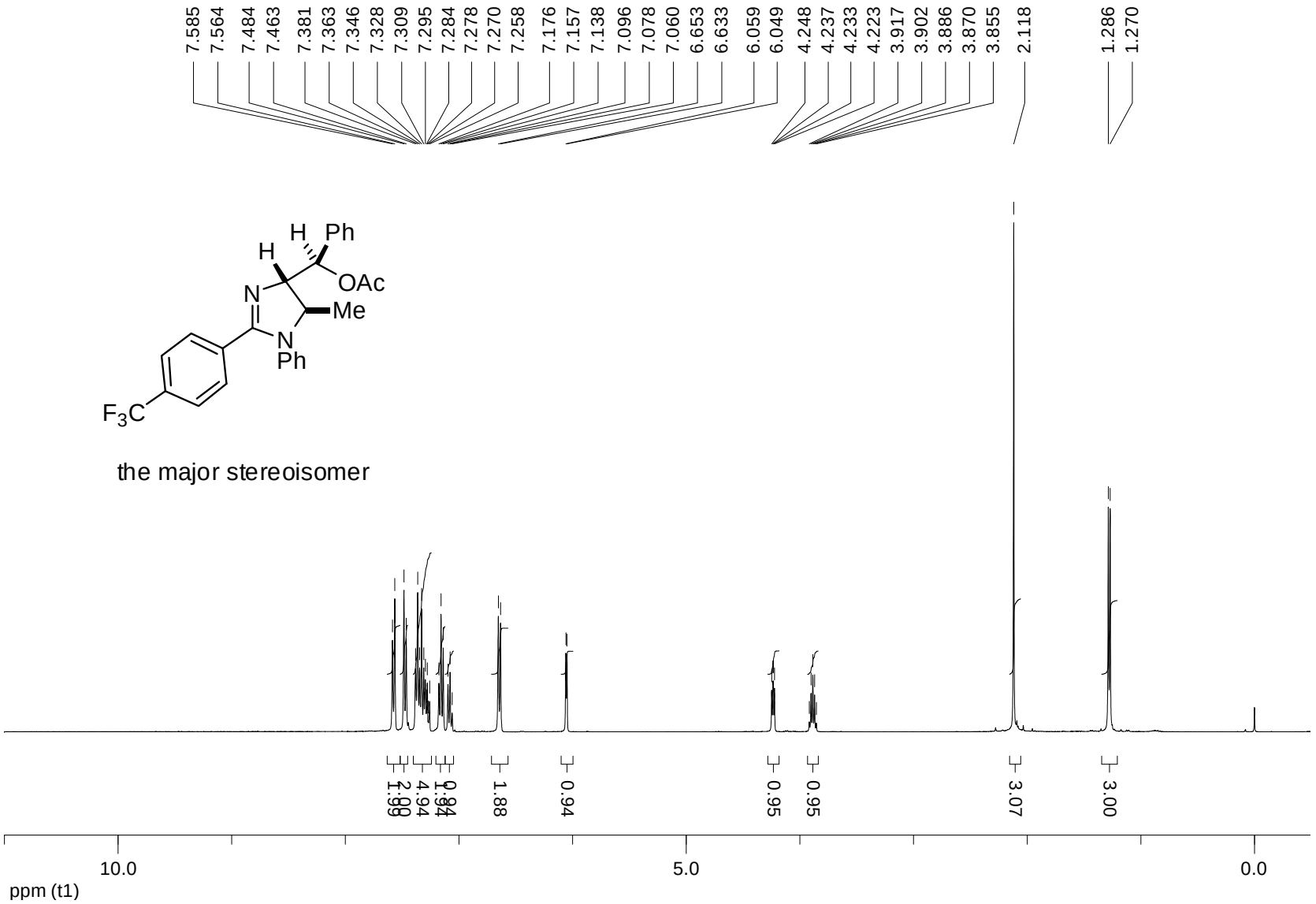
^{13}C NMR spectrum of **2s** (the major stereoisomer) (100 MHz, $CDCl_3$)



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

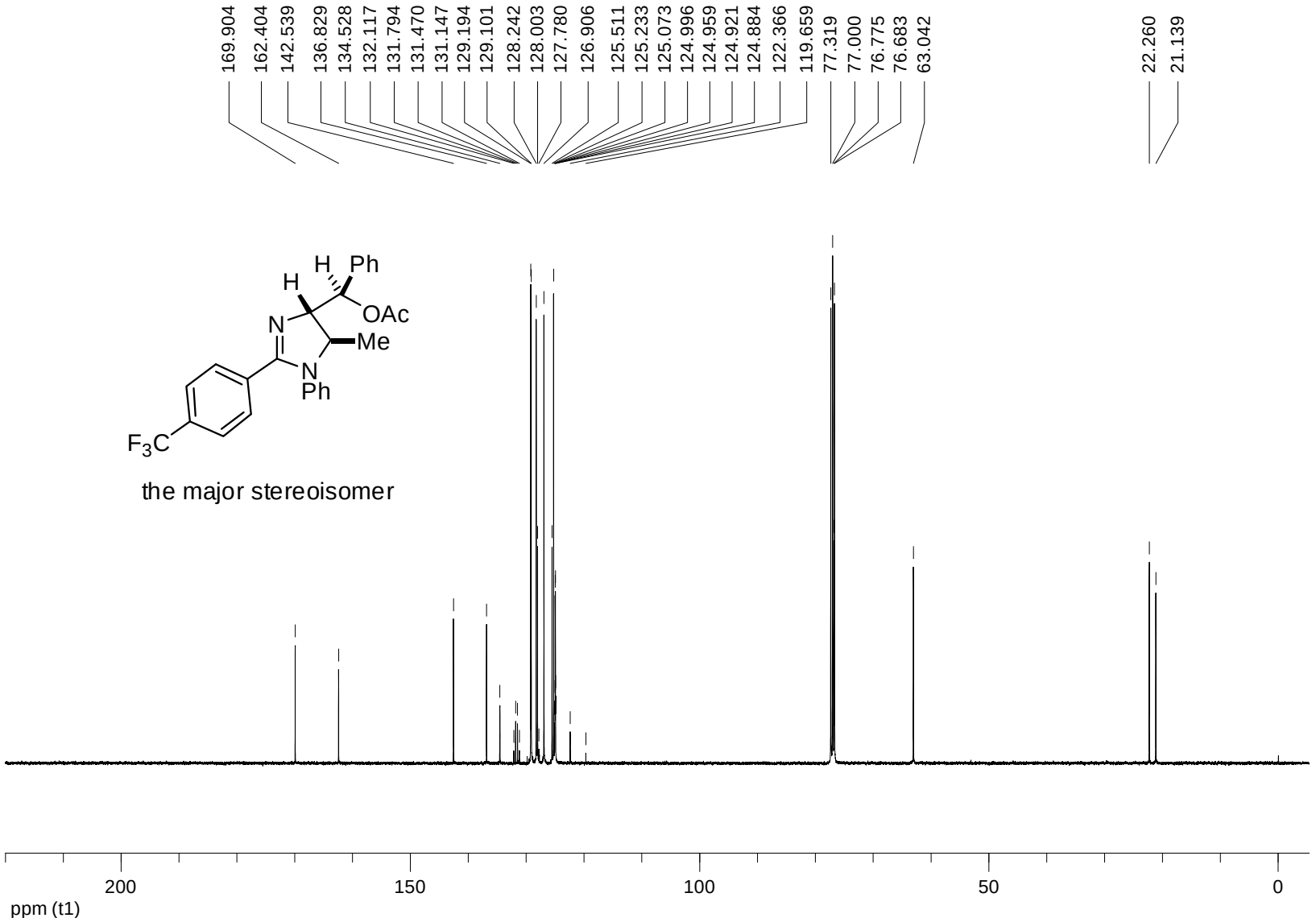


^{1}H NMR spectrum of **2t** (the major stereoisomer) (400 MHz, $CDCl_3$)

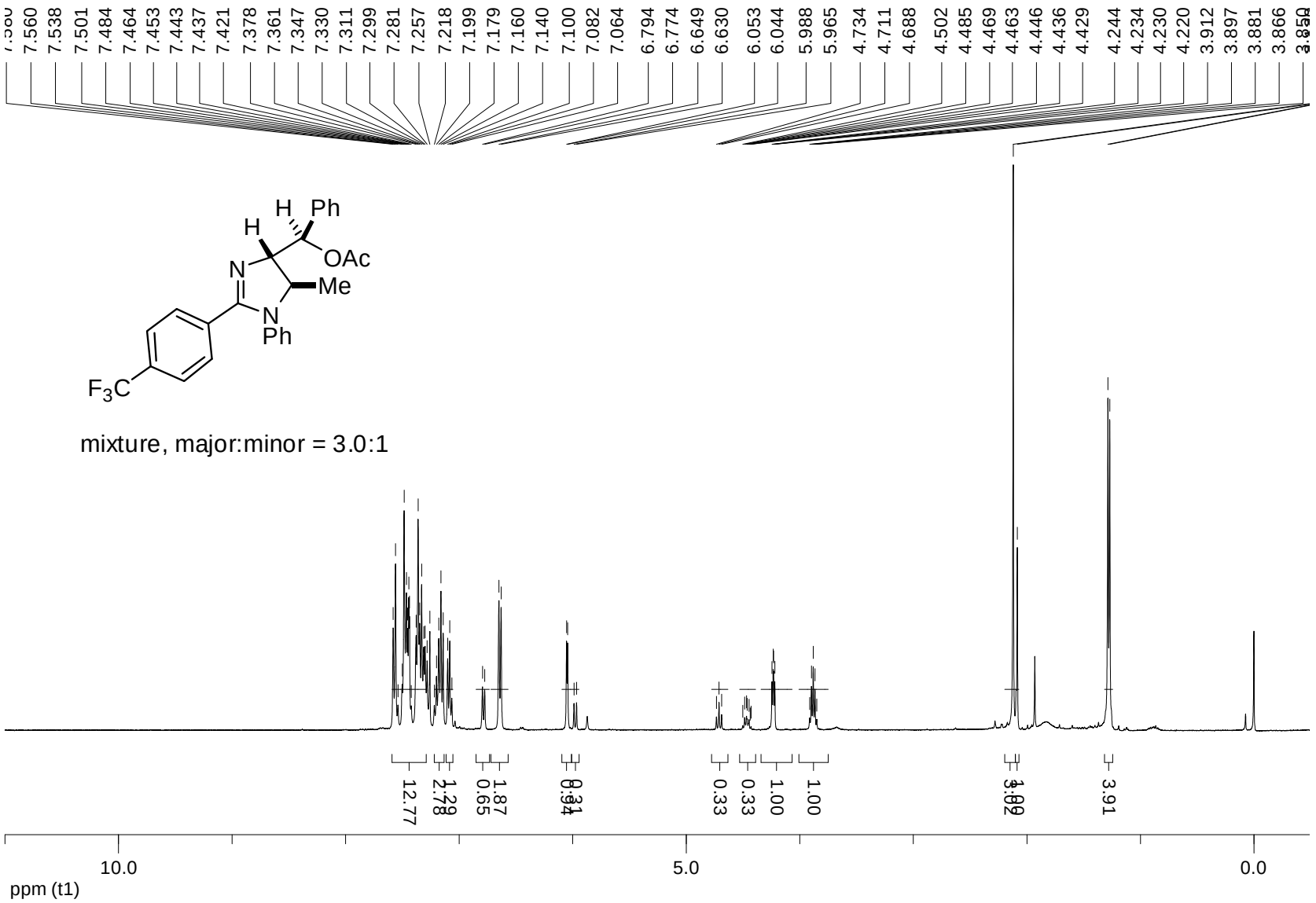


the major stereoisomer

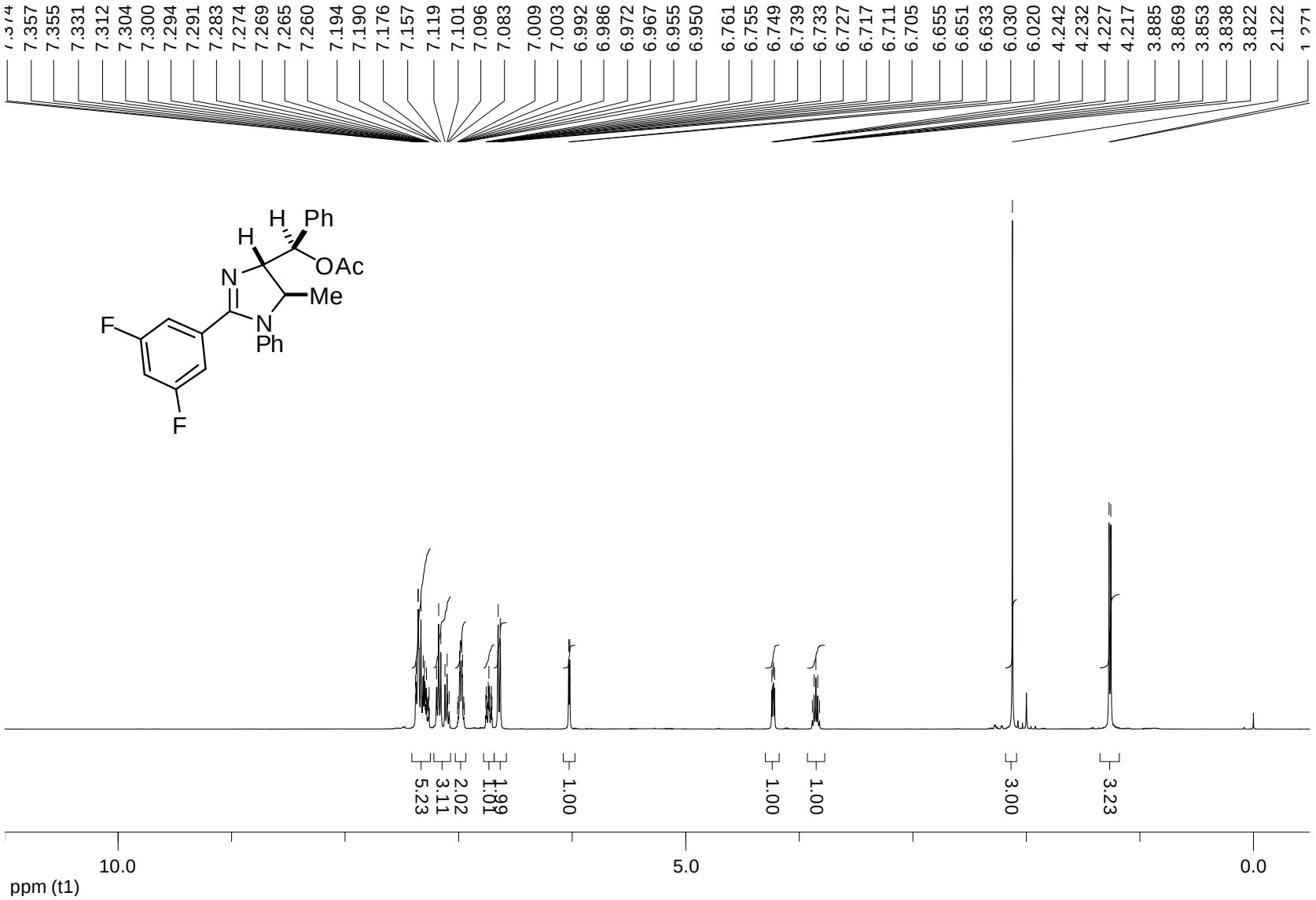
^{13}C NMR spectrum of **2t** (the major stereoisomer) (100 MHz, $CDCl_3$)



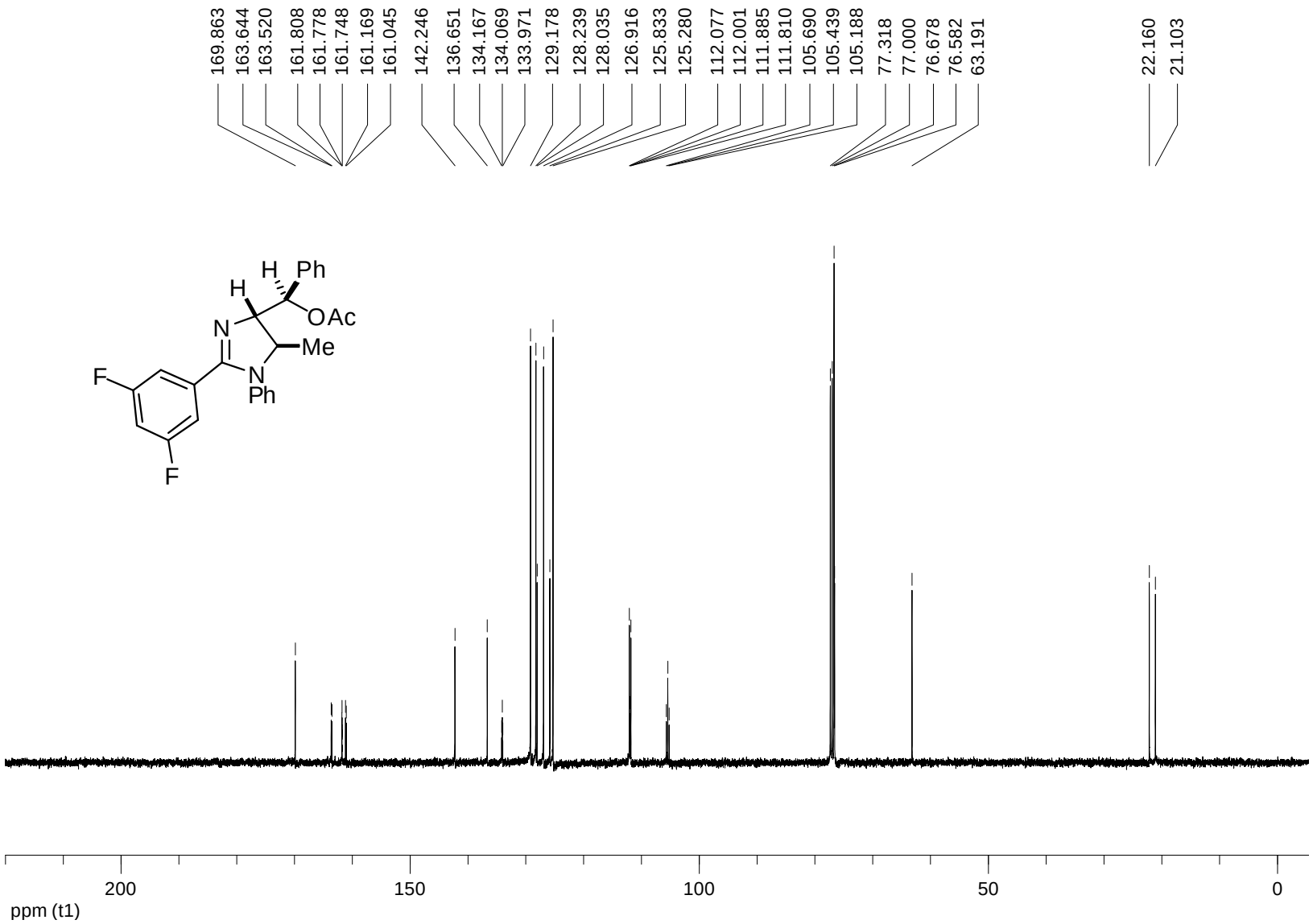
^{1}H NMR spectrum of **2t** (mixture, major:minor = 3.0:1) (400 MHz, $CDCl_3$)



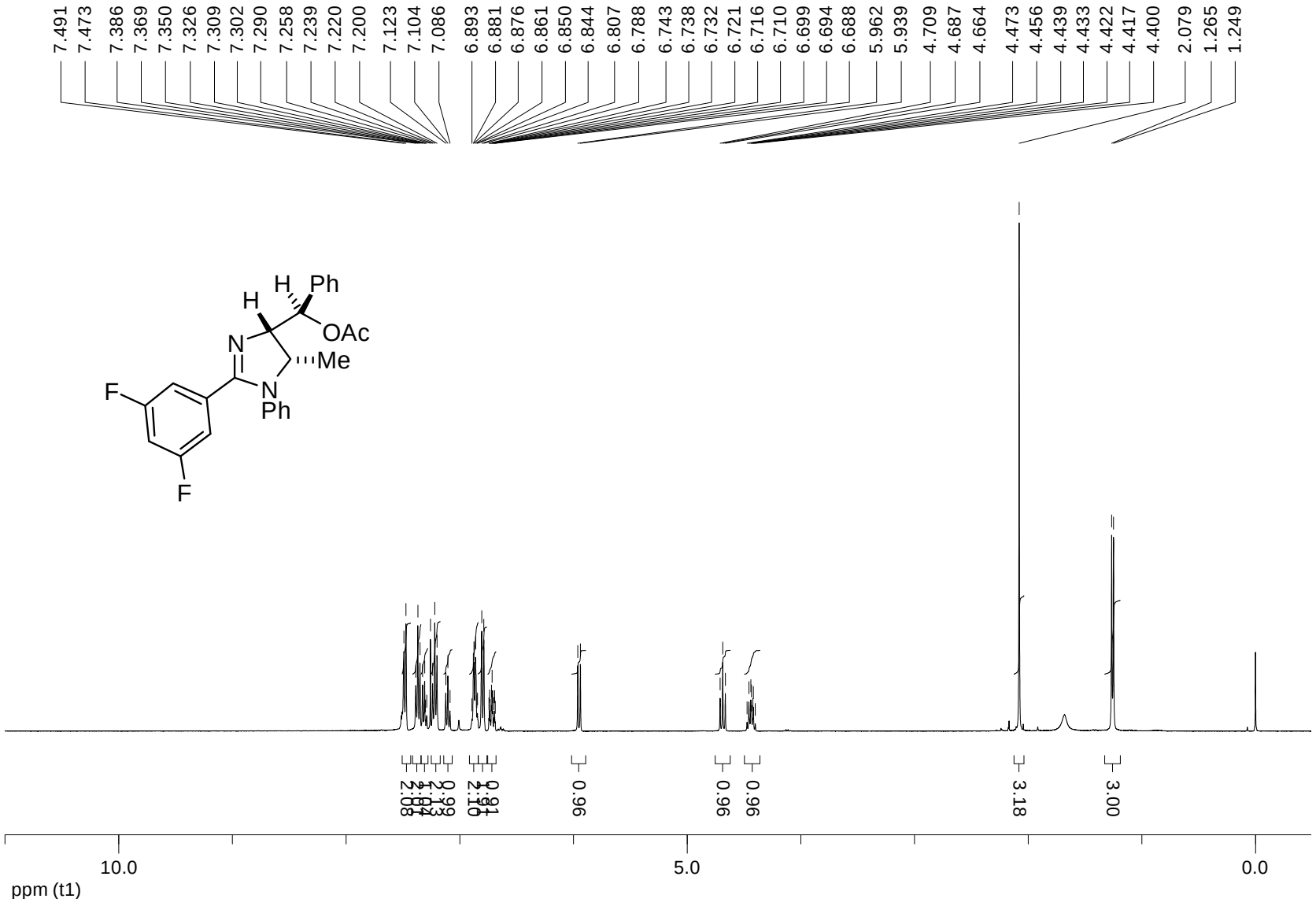
^{1}H NMR spectrum of **2u** (the major stereoisomer) (400 MHz, $CDCl_3$)



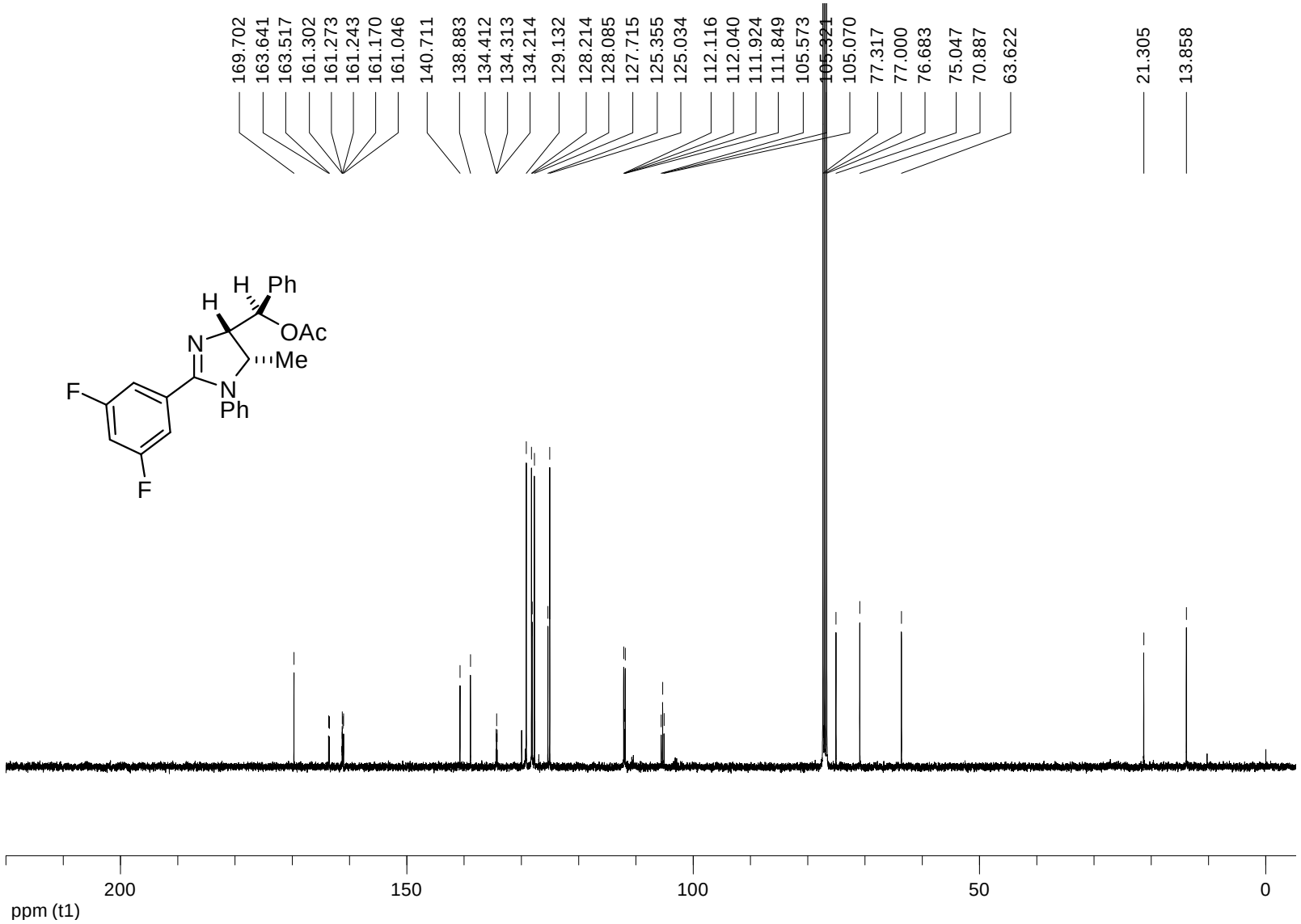
^{13}C NMR spectrum of **2u** (the major stereoisomer) (100 MHz, $CDCl_3$)



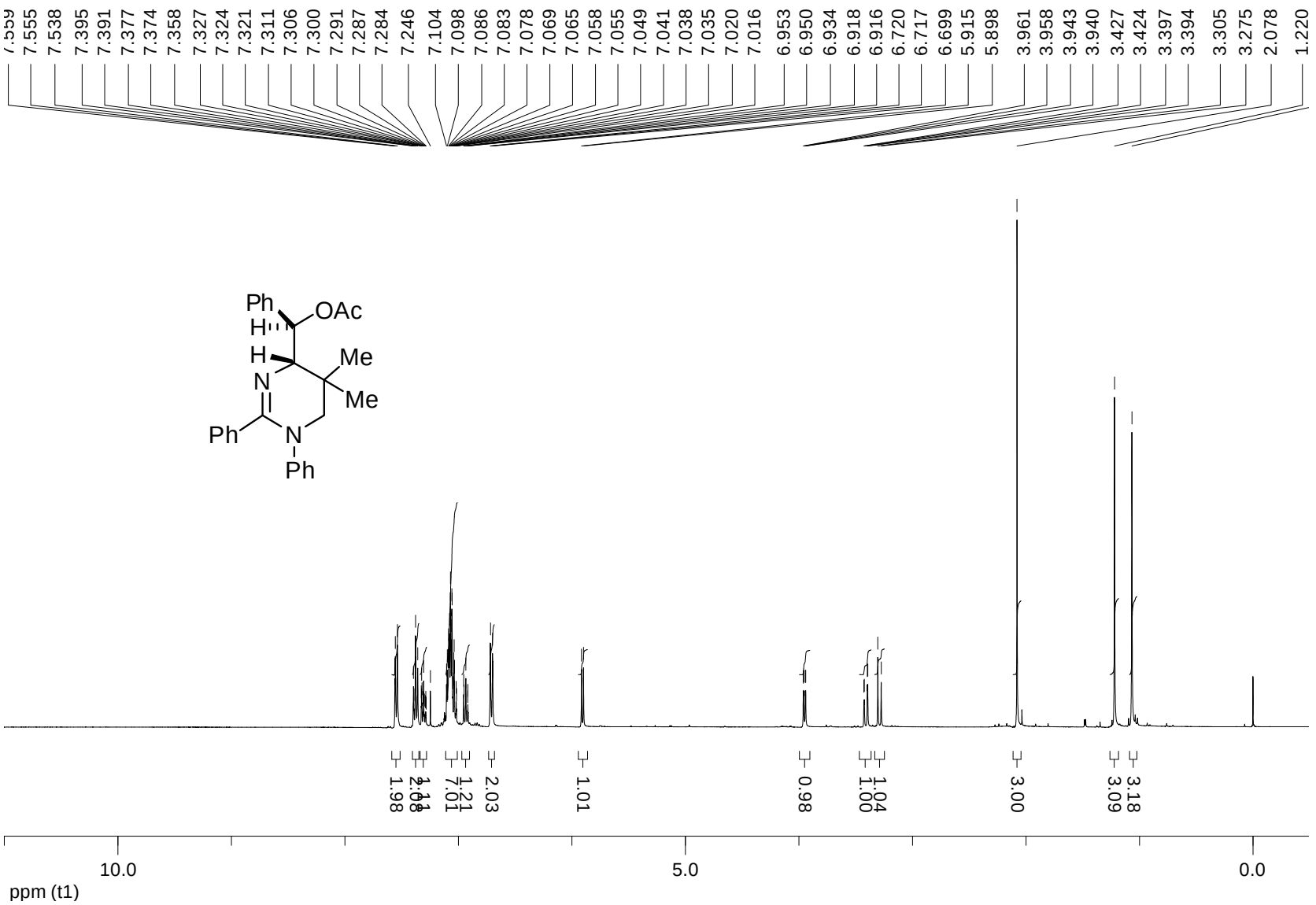
^{1}H NMR spectrum of **2u'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



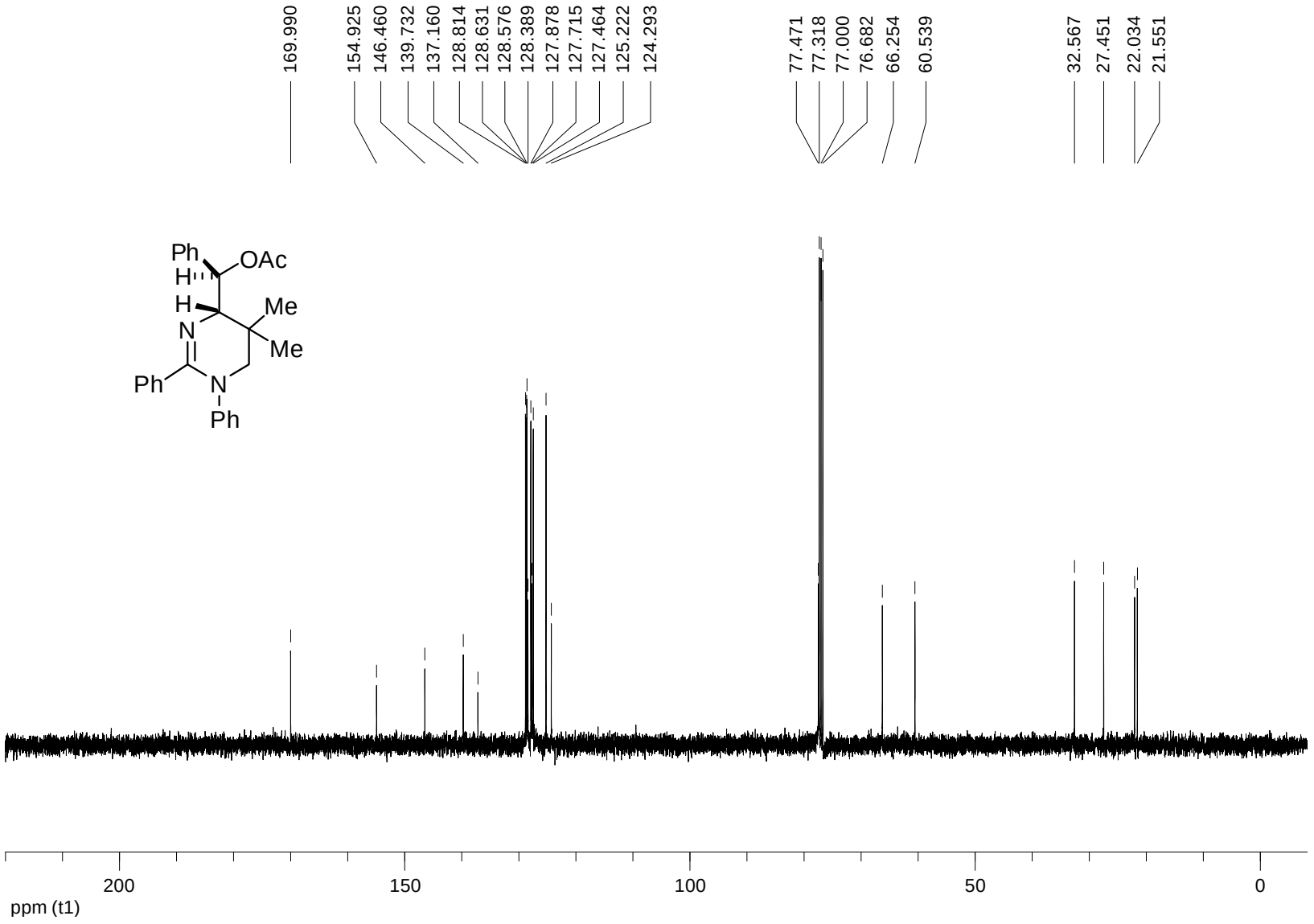
^{13}C NMR spectrum of **2u'** (the minor stereoisomer) (100 MHz, $CDCl_3$)



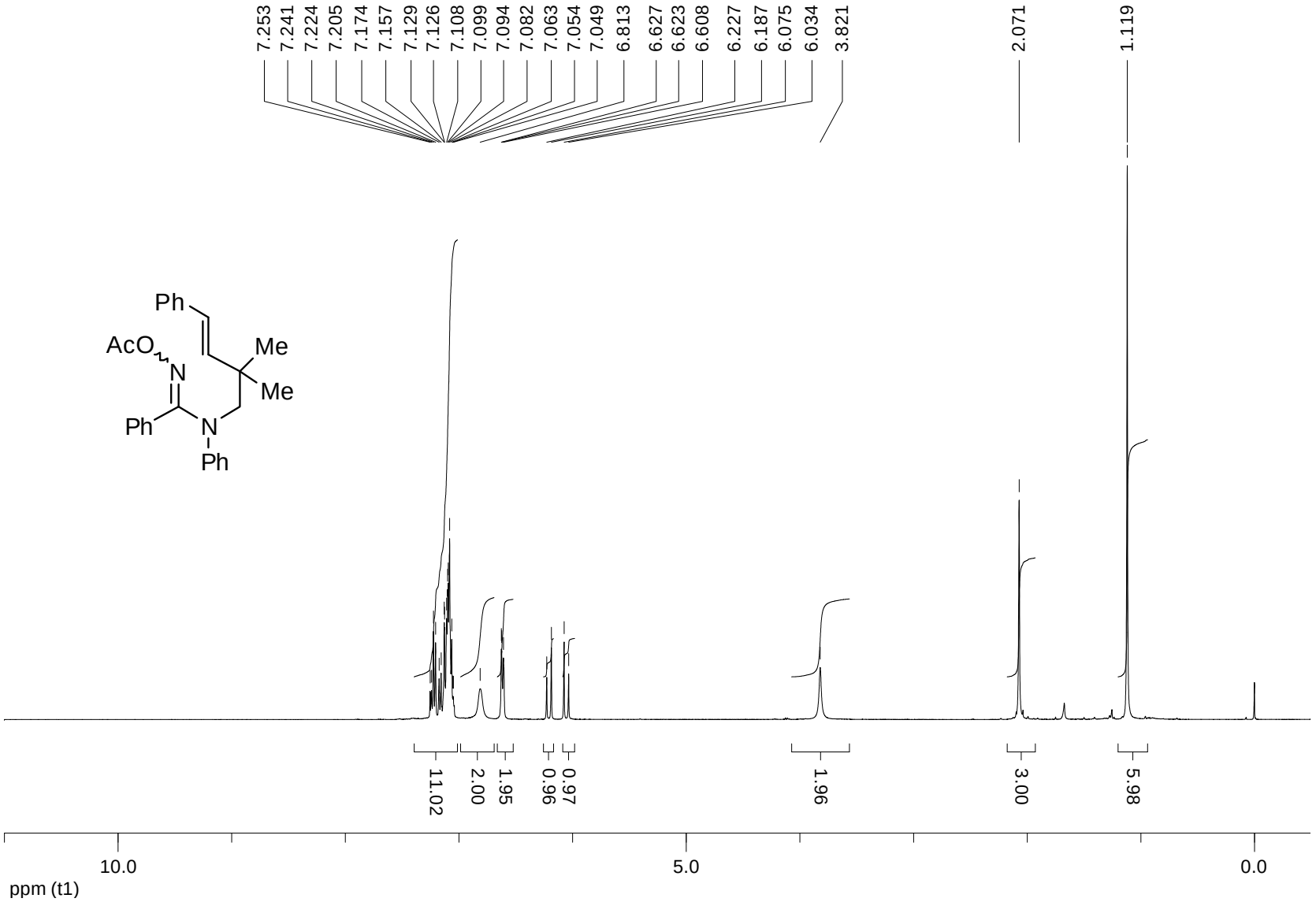
^{1}H NMR spectrum of **2w** (400 MHz, $CDCl_3$)



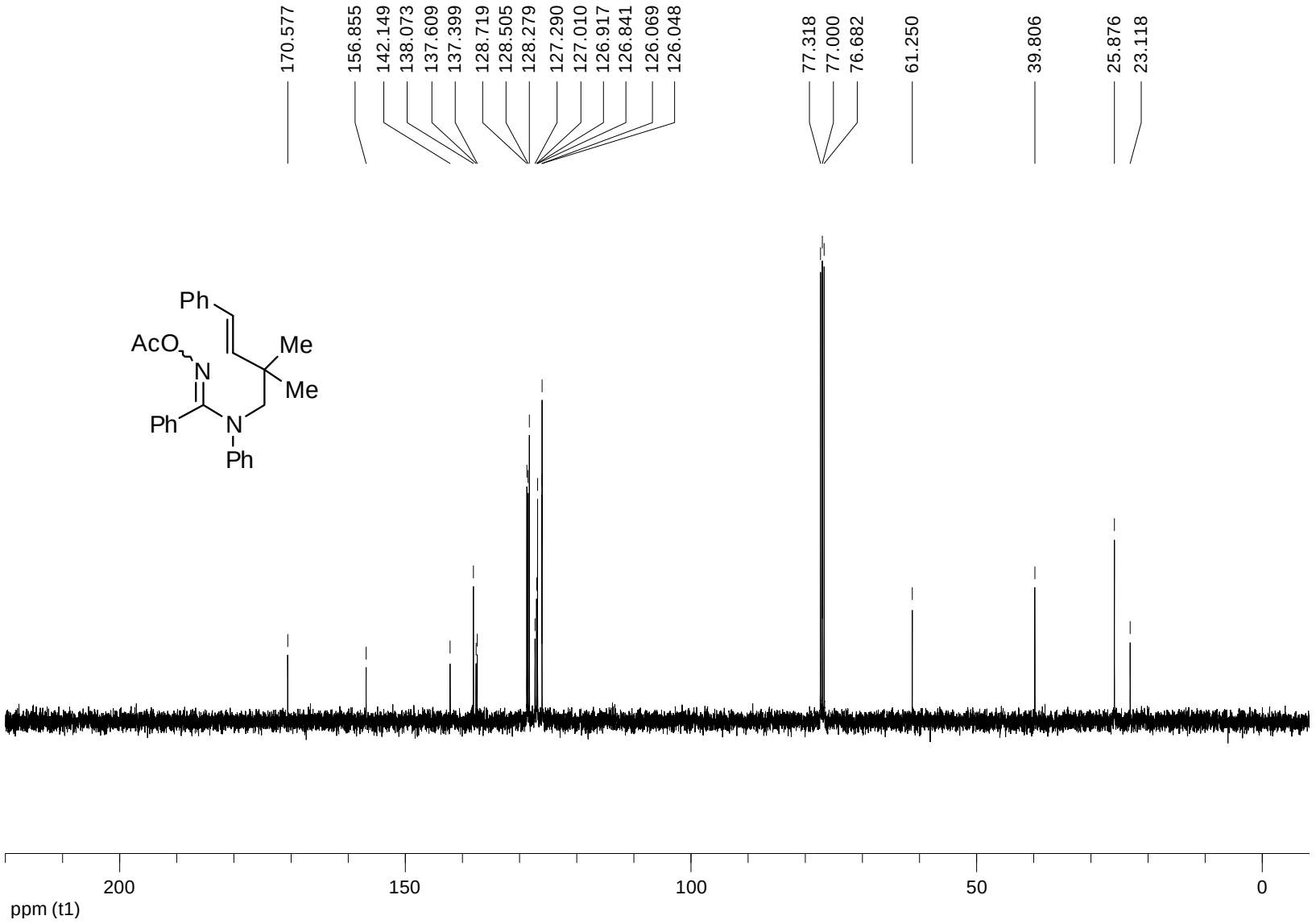
^{13}C NMR spectrum of **2w** (100 MHz, $CDCl_3$)



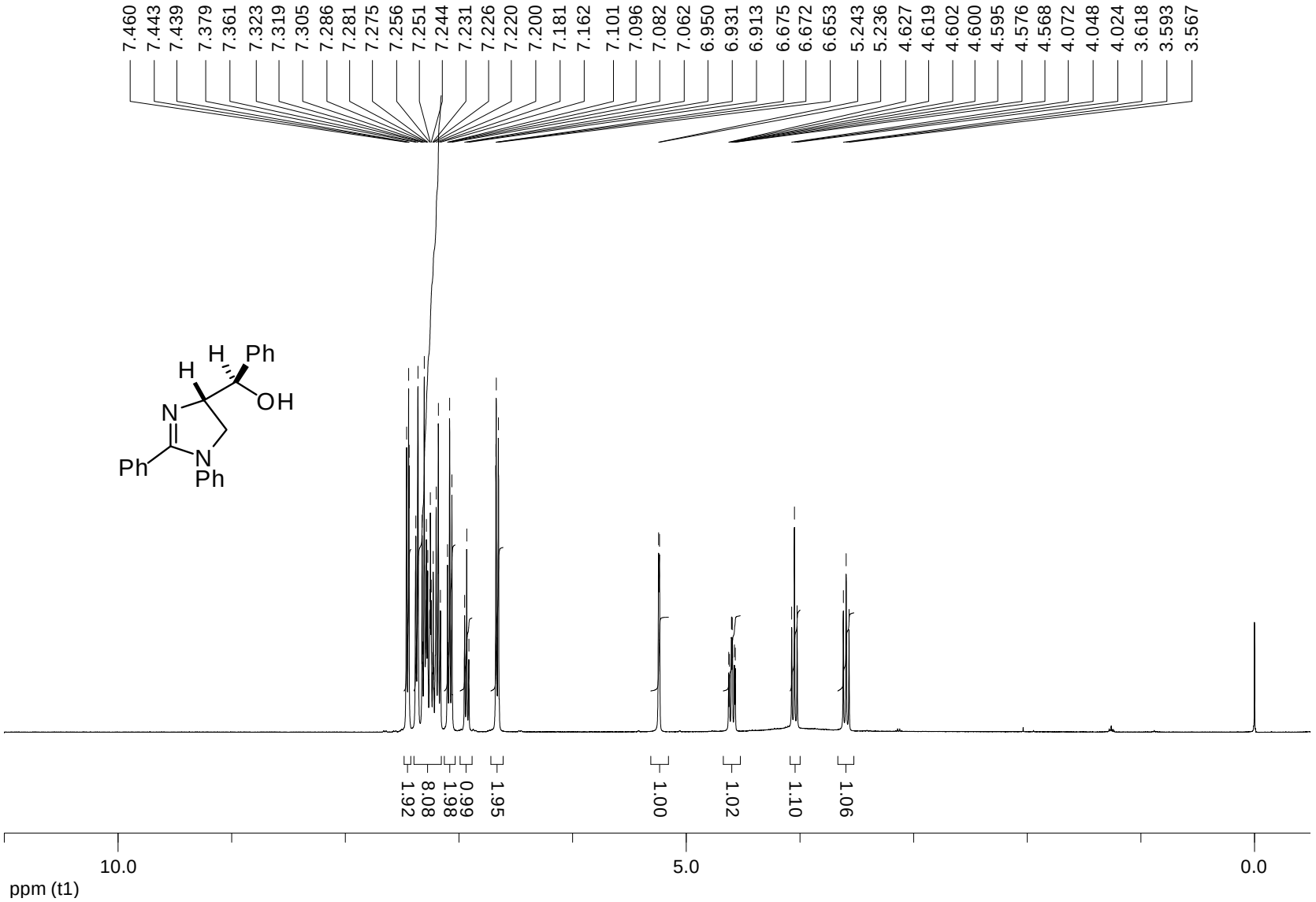
^{1}H NMR spectrum of **5w** (400 MHz, $CDCl_3$)



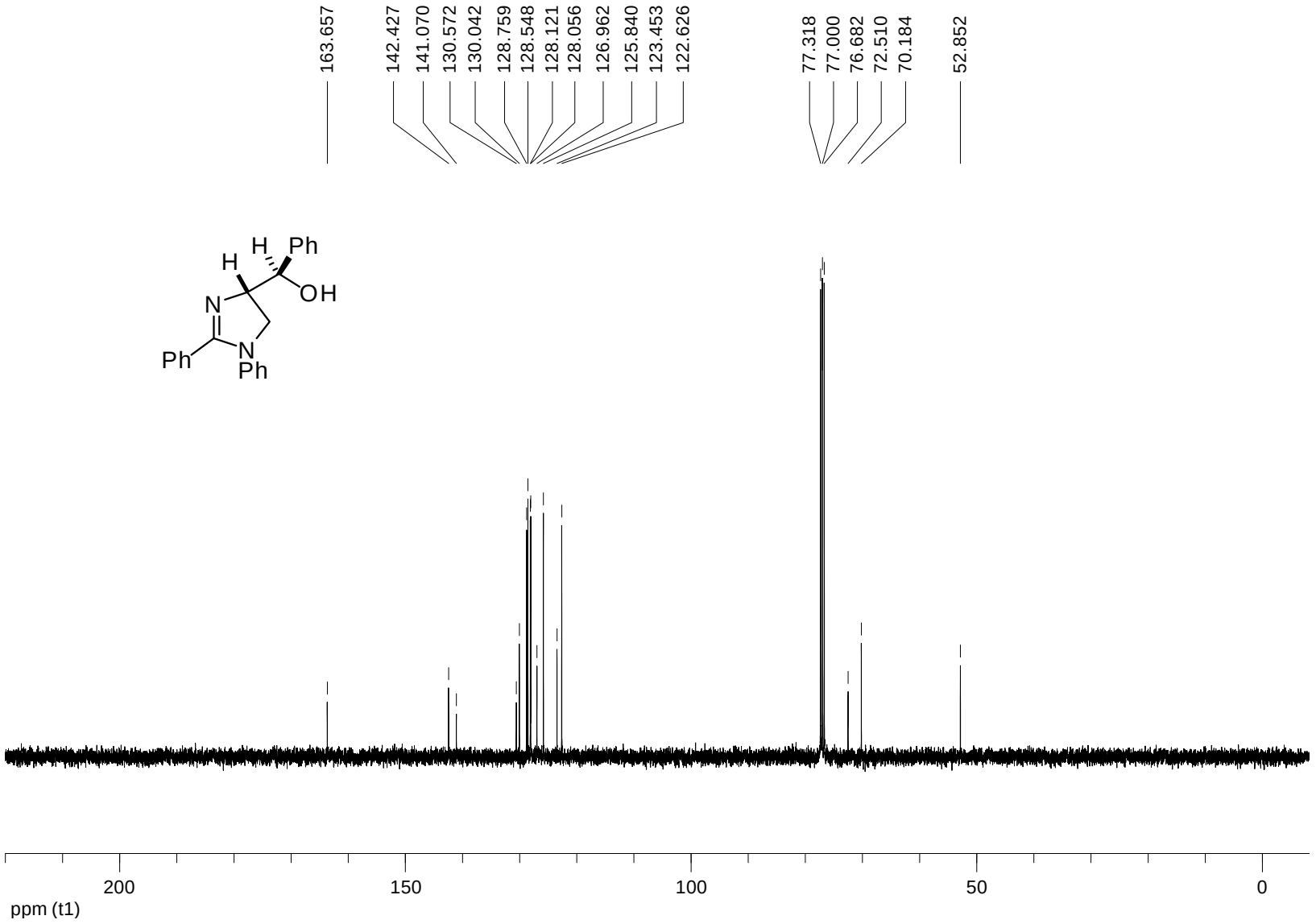
^{13}C NMR spectrum of **5w** (100 MHz, $CDCl_3$)



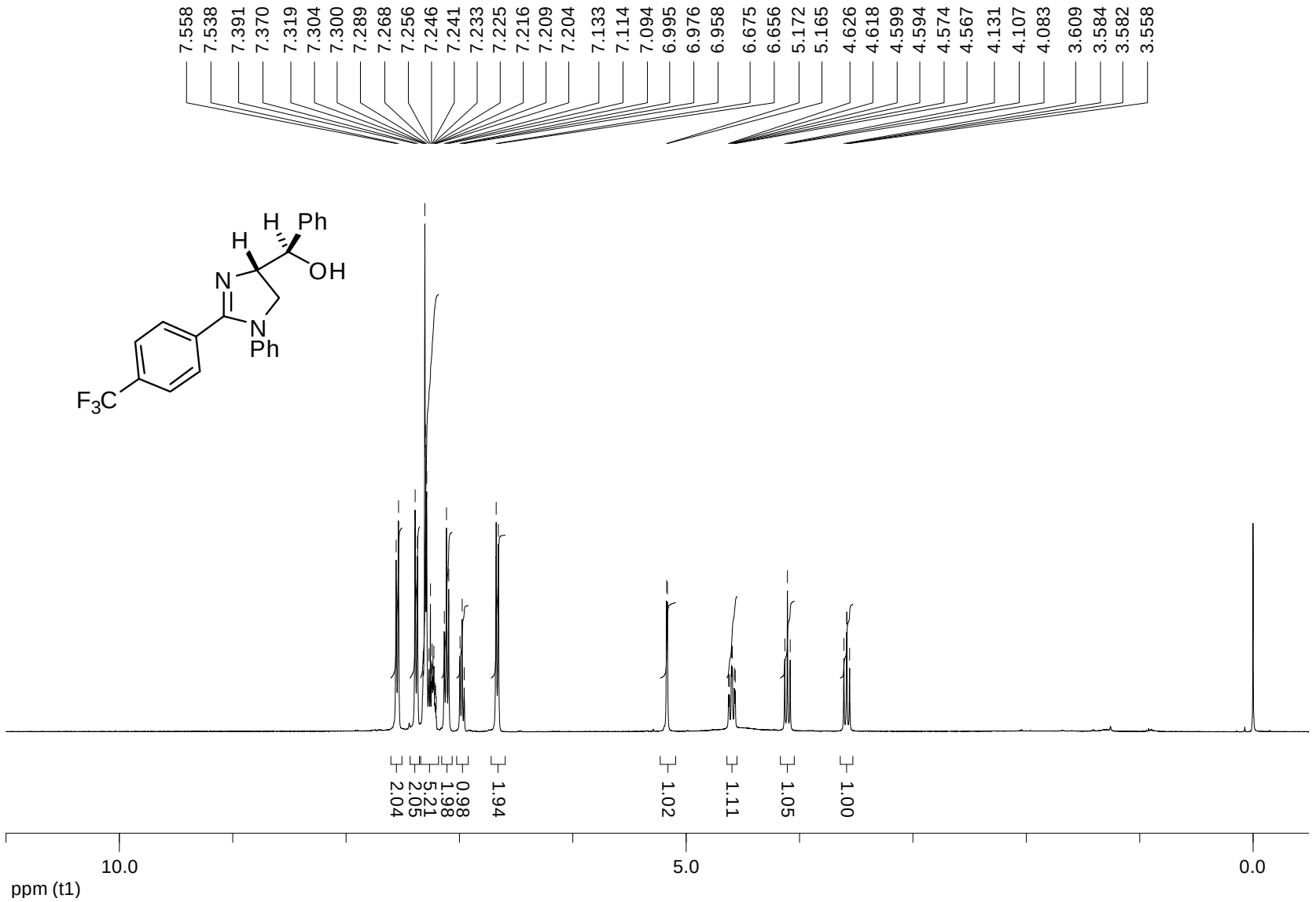
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



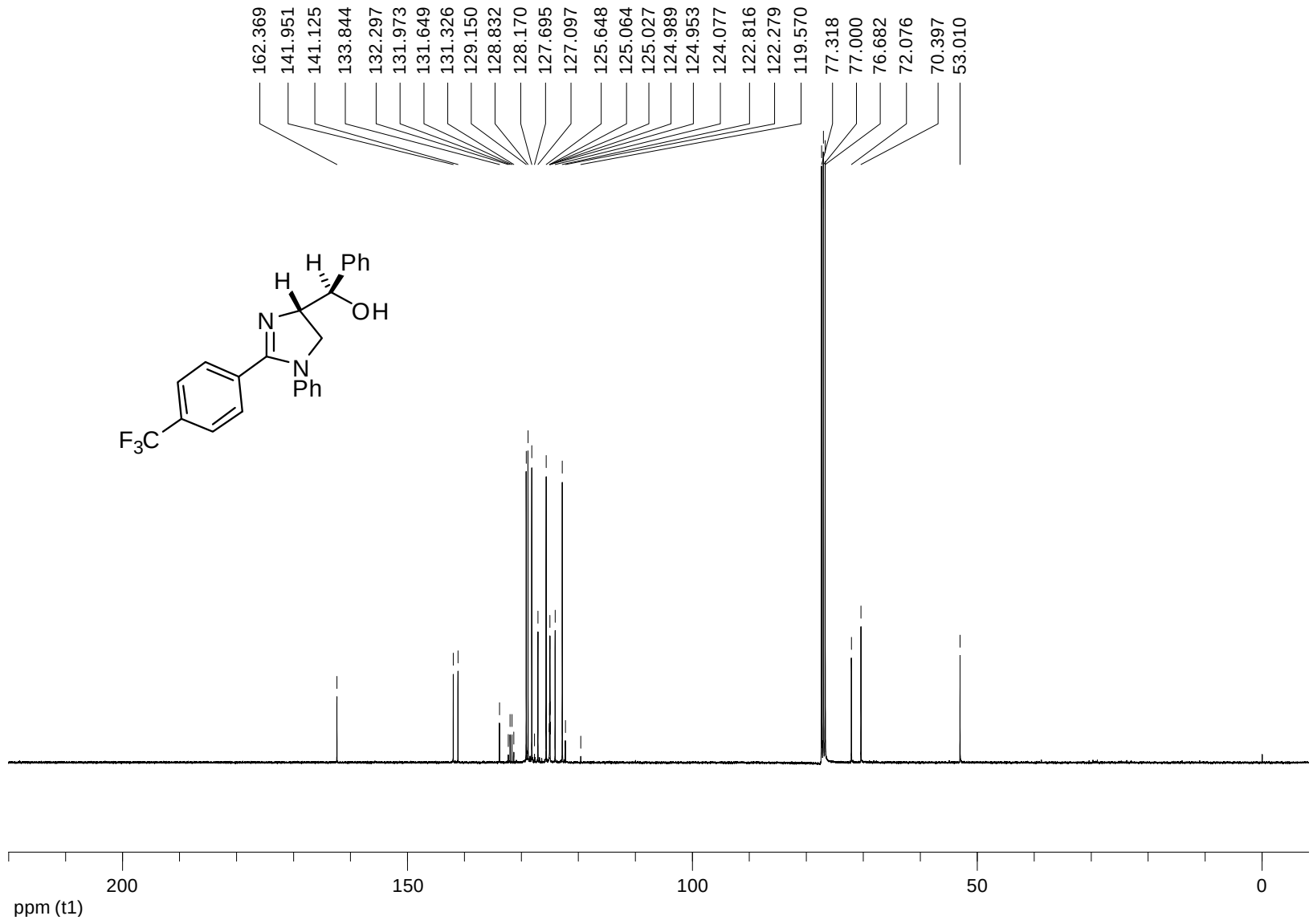
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



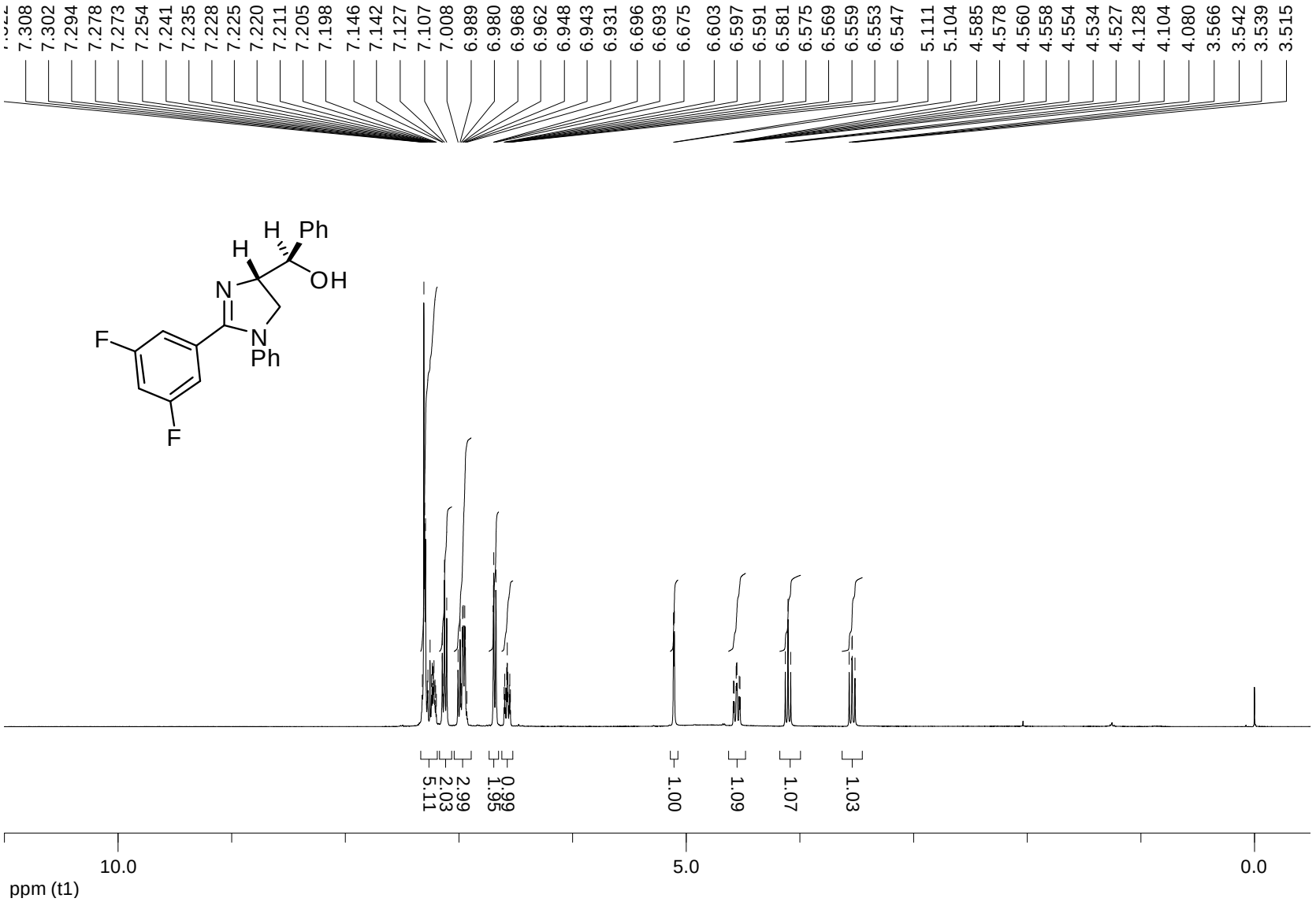
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



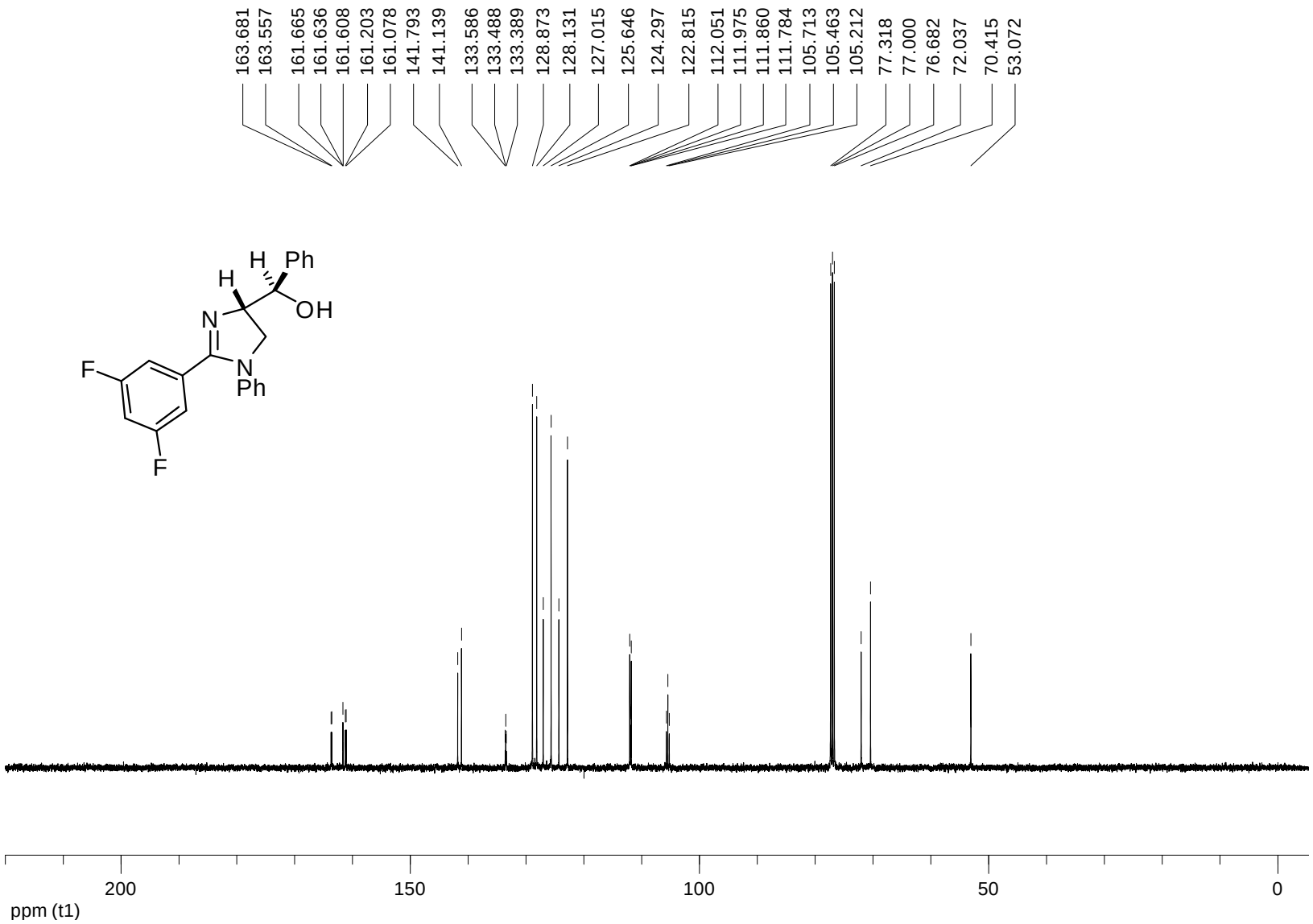
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



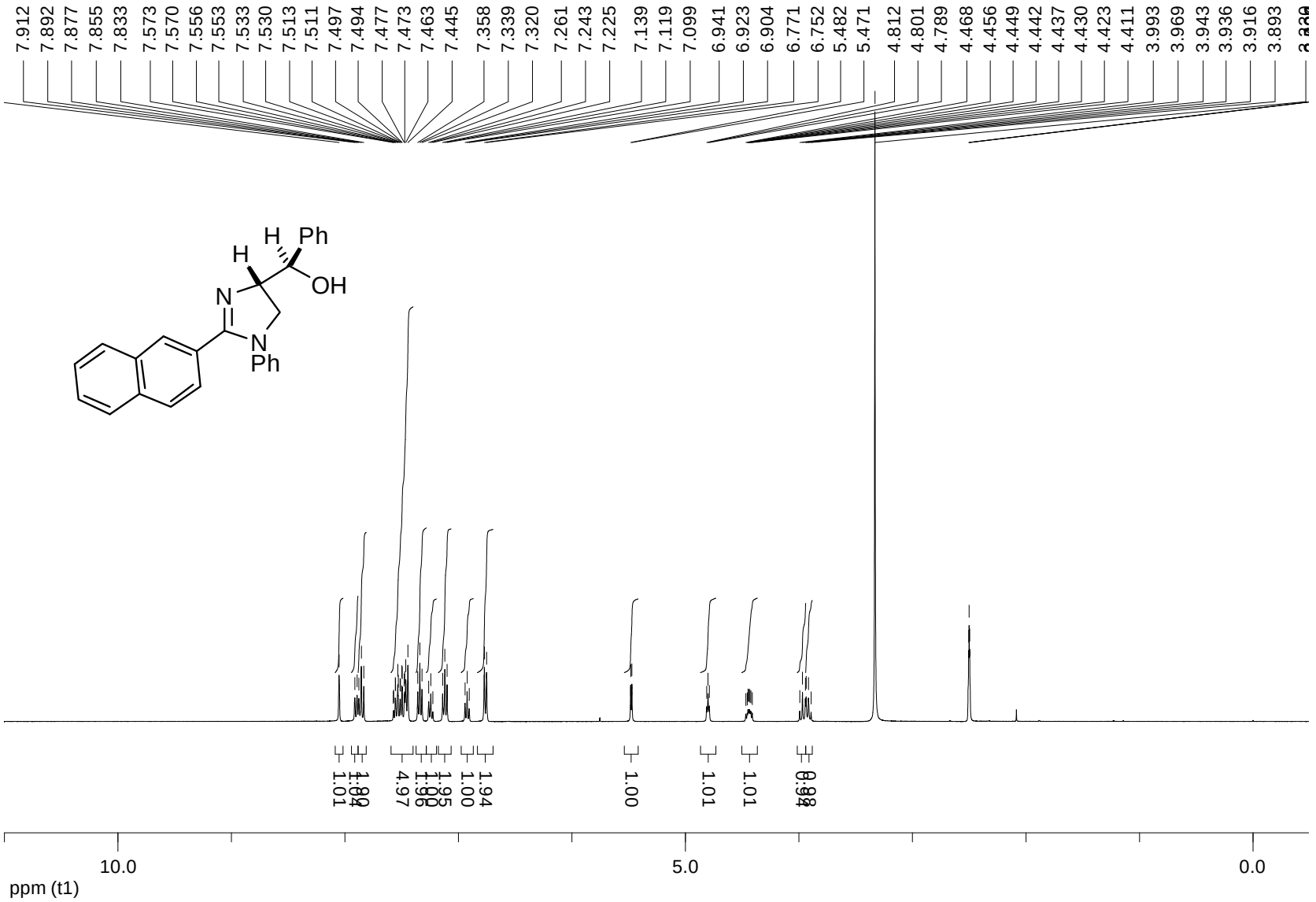
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



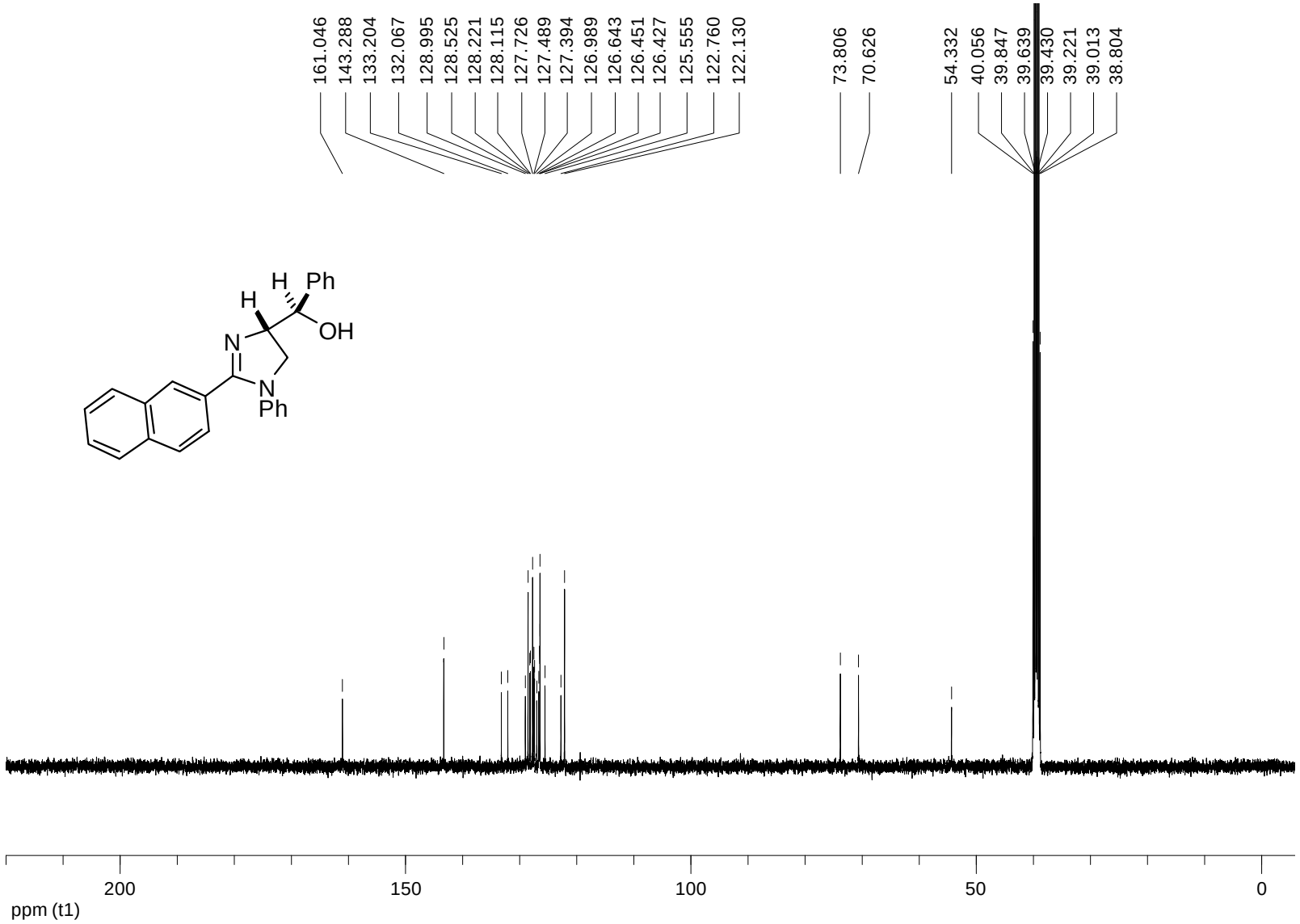
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



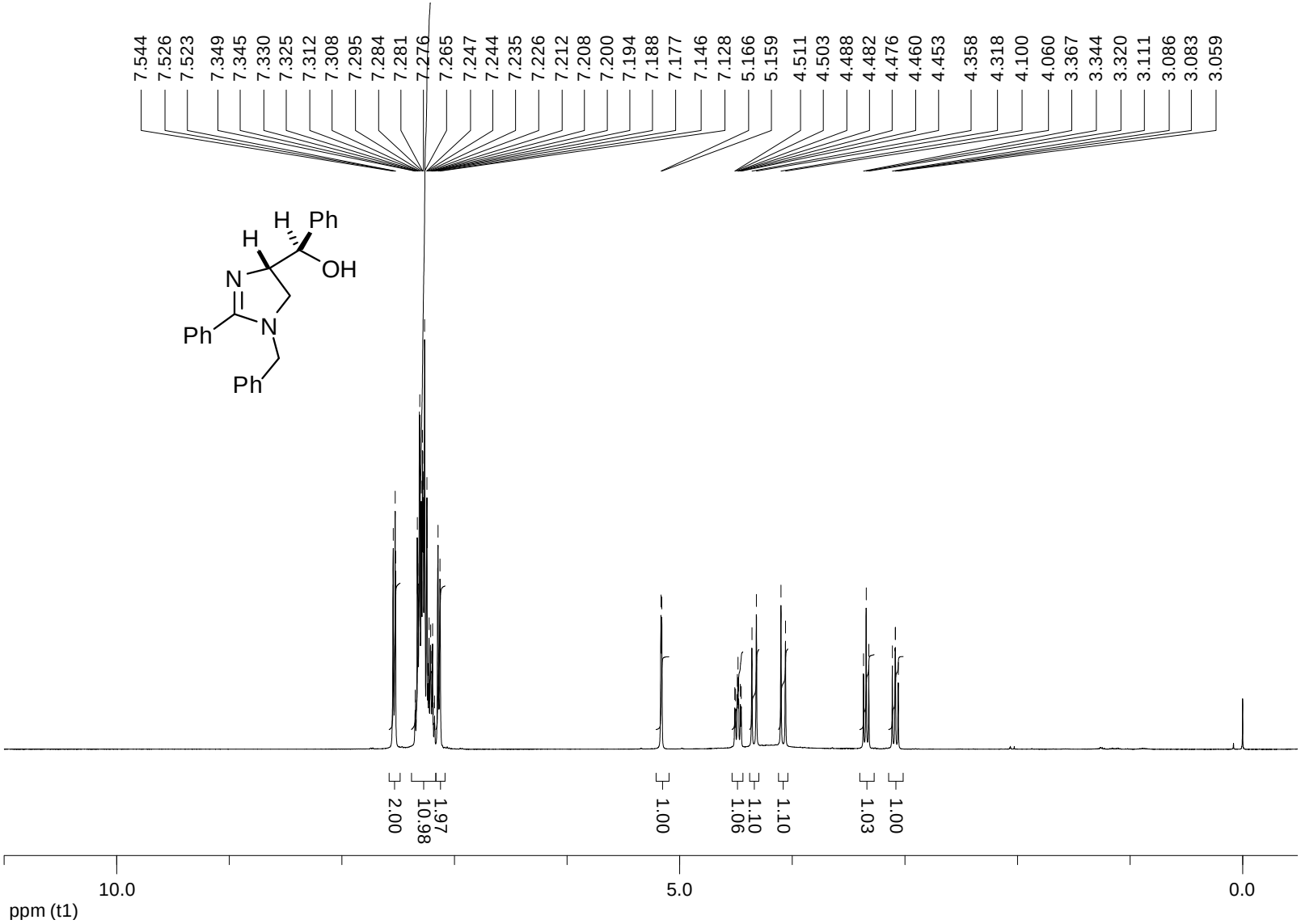
^{1}H NMR spectrum of **3d** (400 MHz, DMSO-d_6)



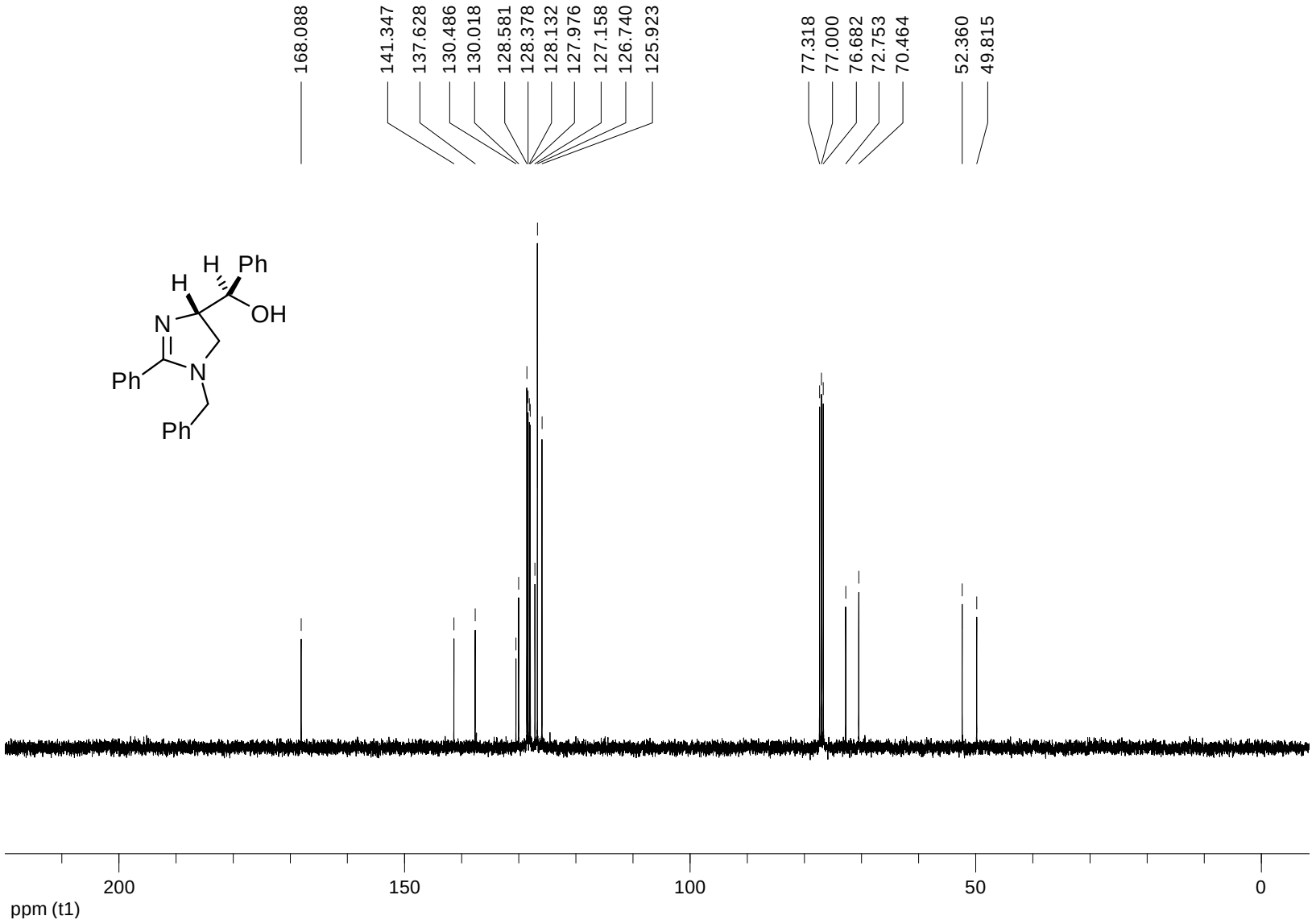
^{13}C NMR spectrum of **3d** (100 MHz, DMSO-d_6)



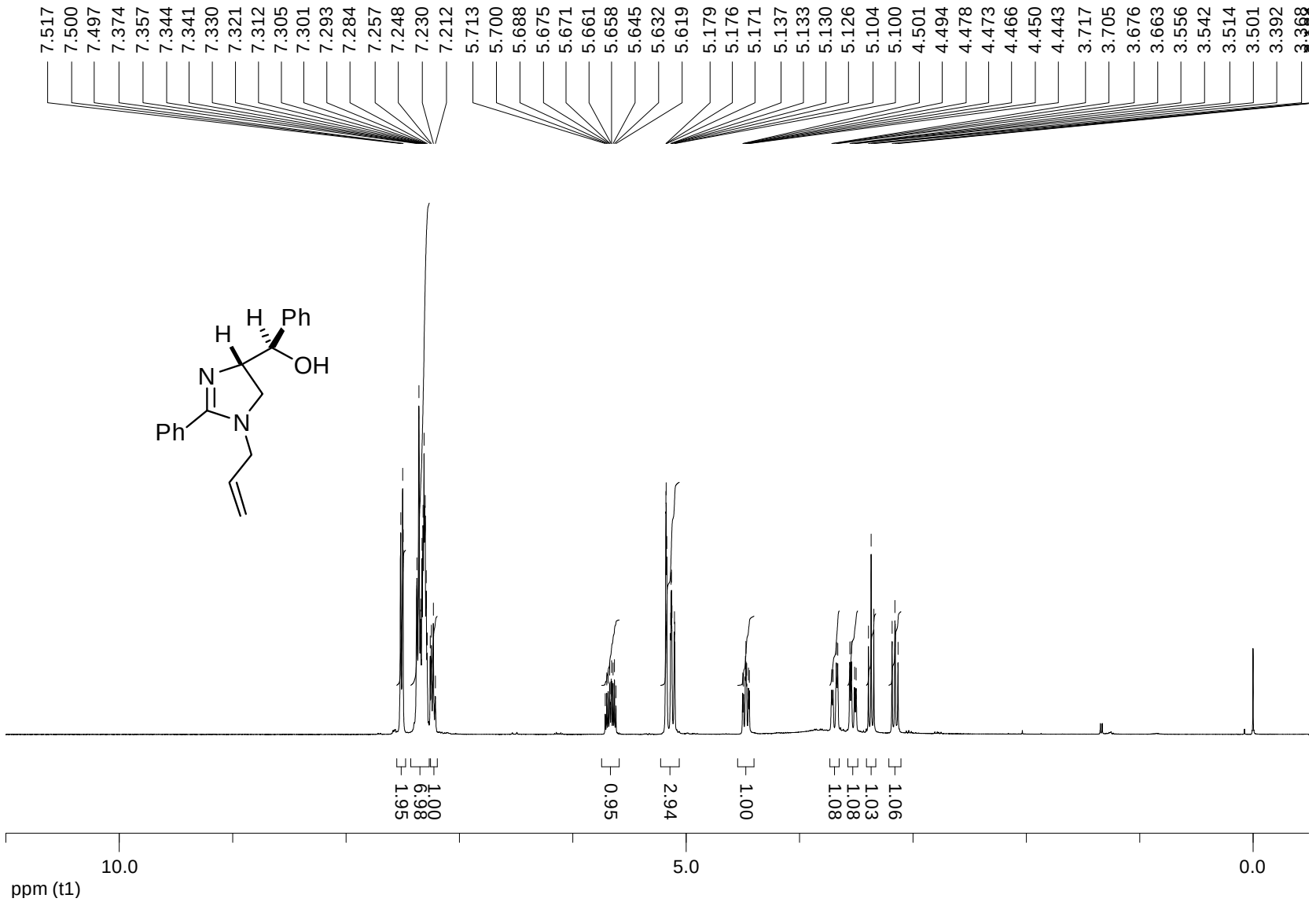
^{1}H NMR spectrum of **3e** (400 MHz, $CDCl_3$)



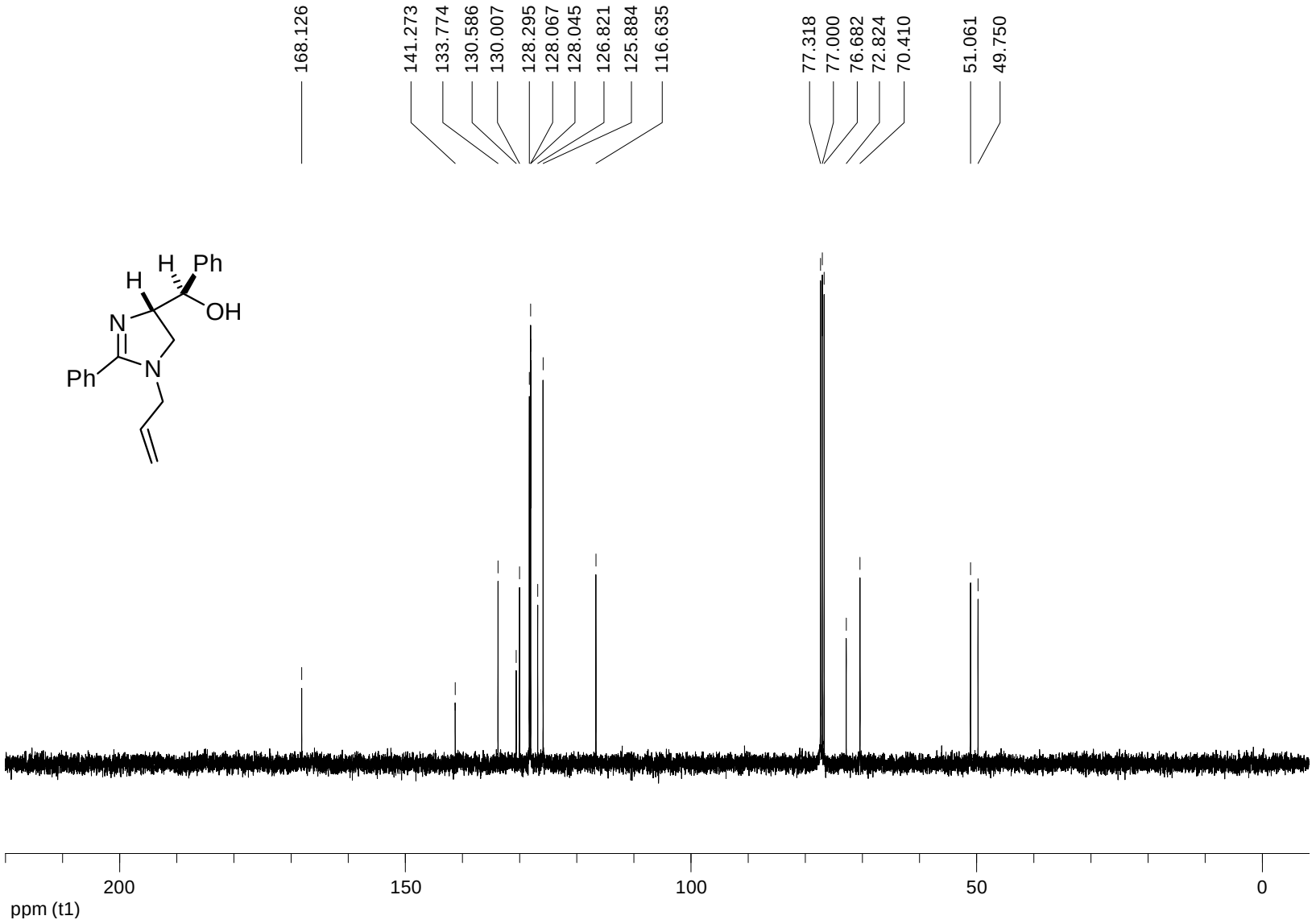
^{13}C NMR spectrum of **3e** (100 MHz, $CDCl_3$)



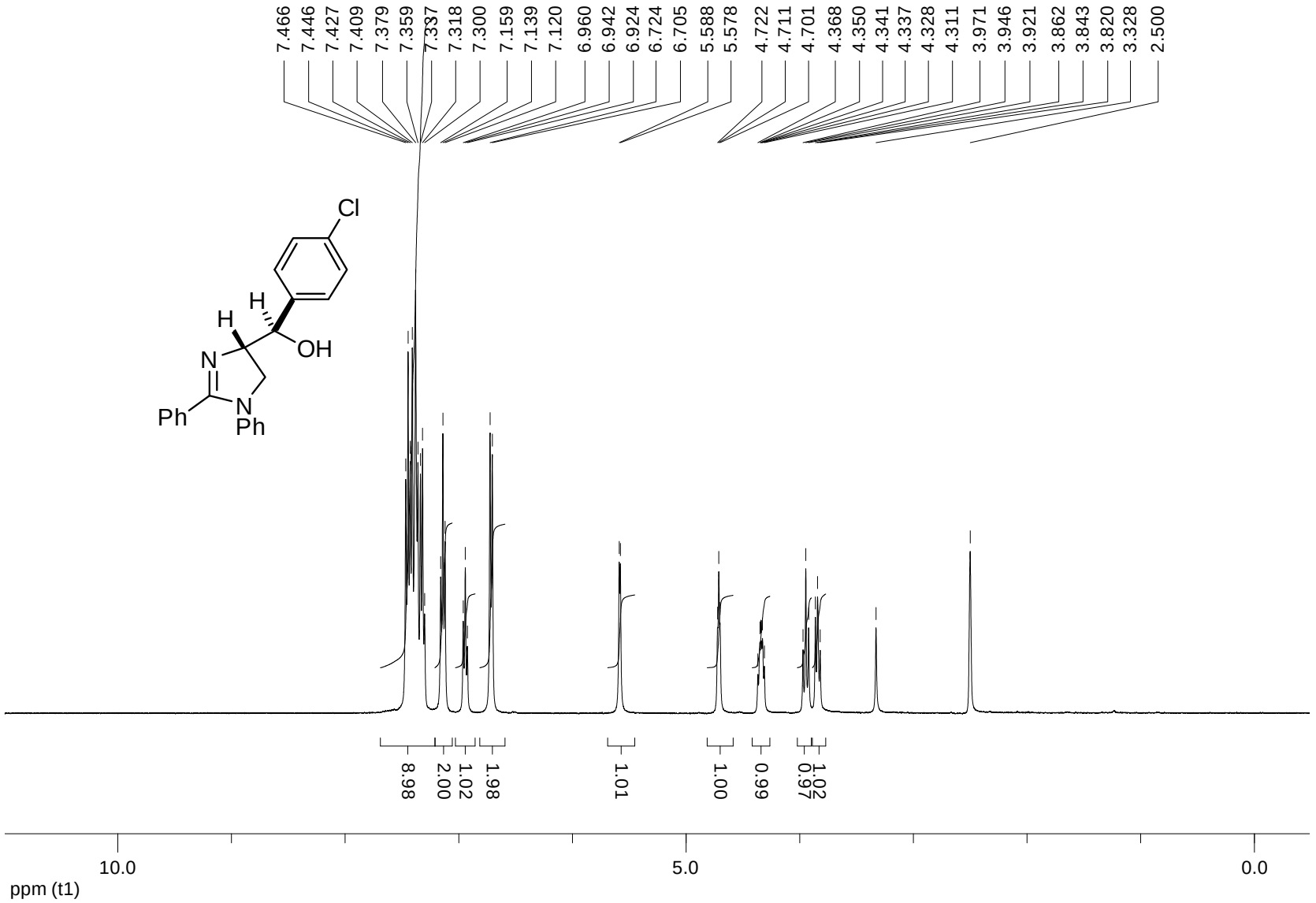
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



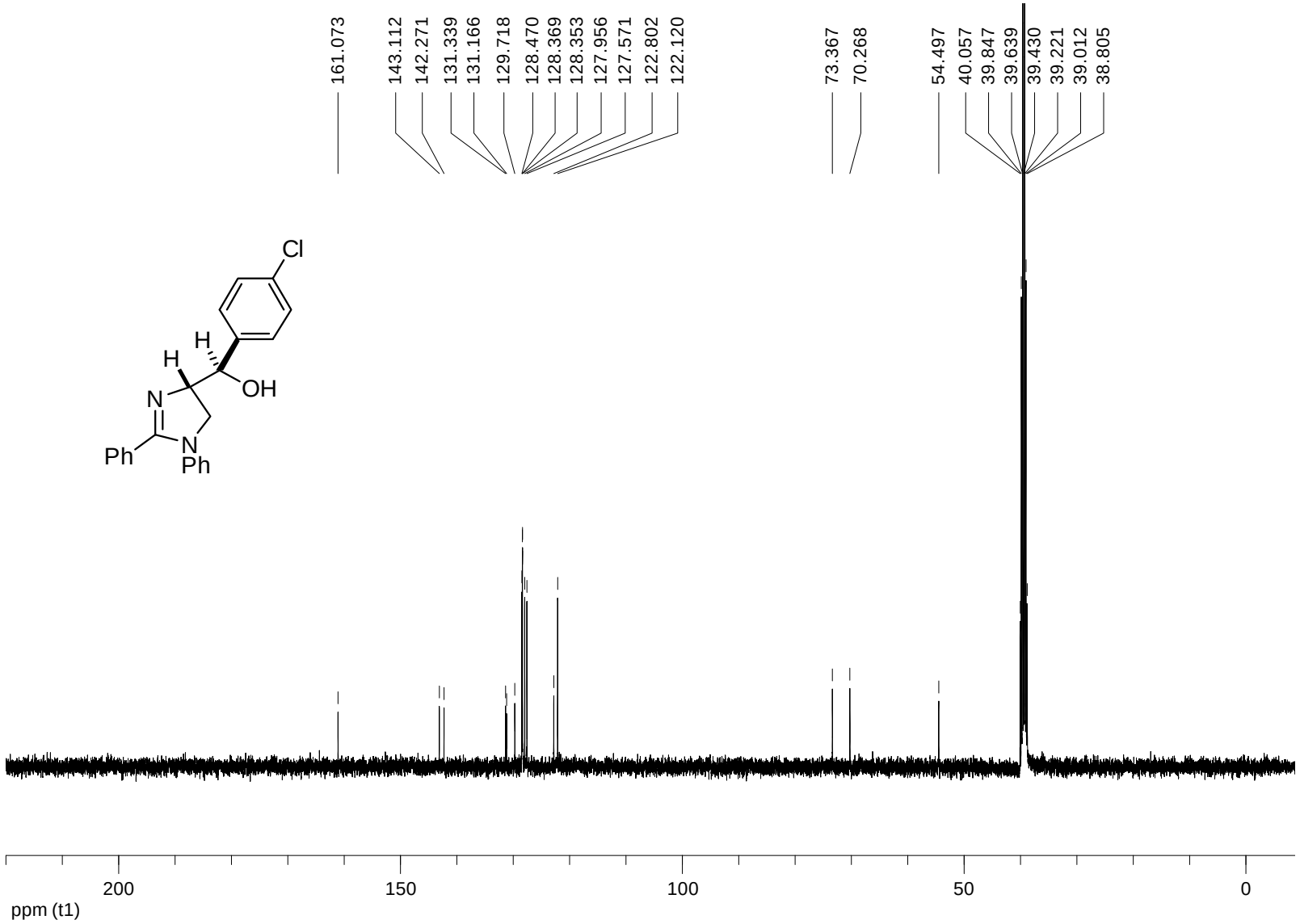
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



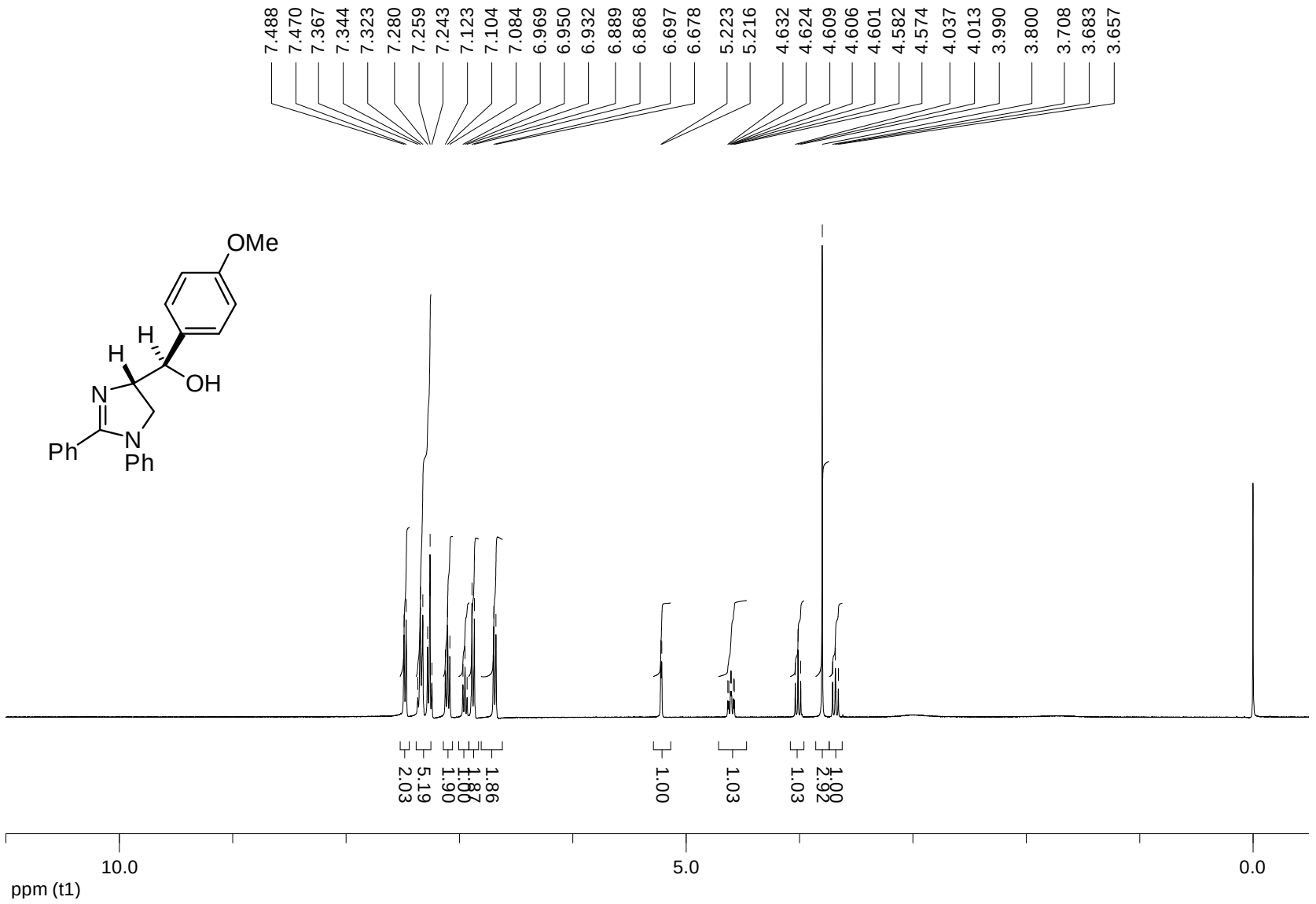
^{1}H NMR spectrum of **3g** (400 MHz, DMSO-d_6)



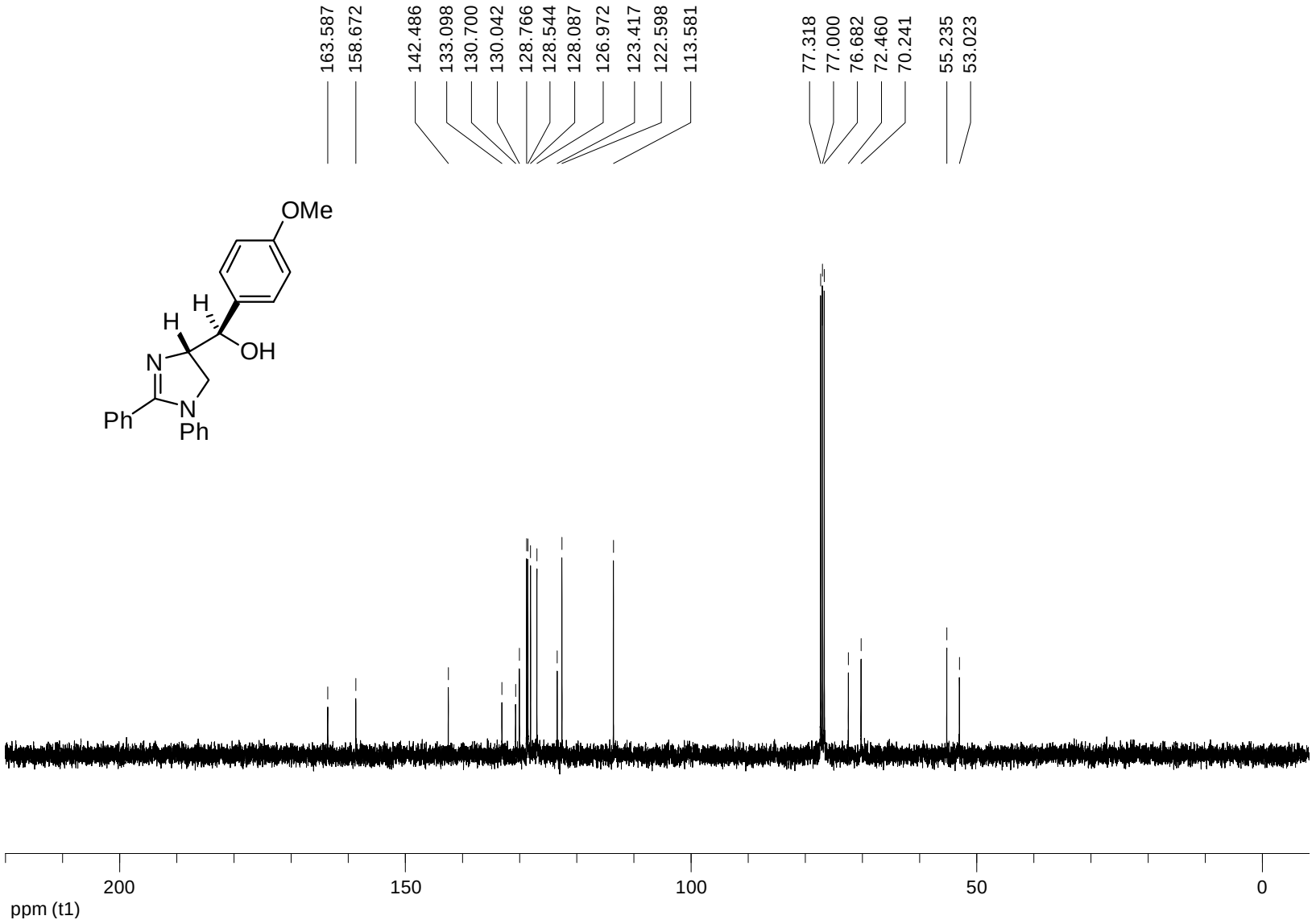
^{13}C NMR spectrum of **3g** (100 MHz, DMSO-d_6)



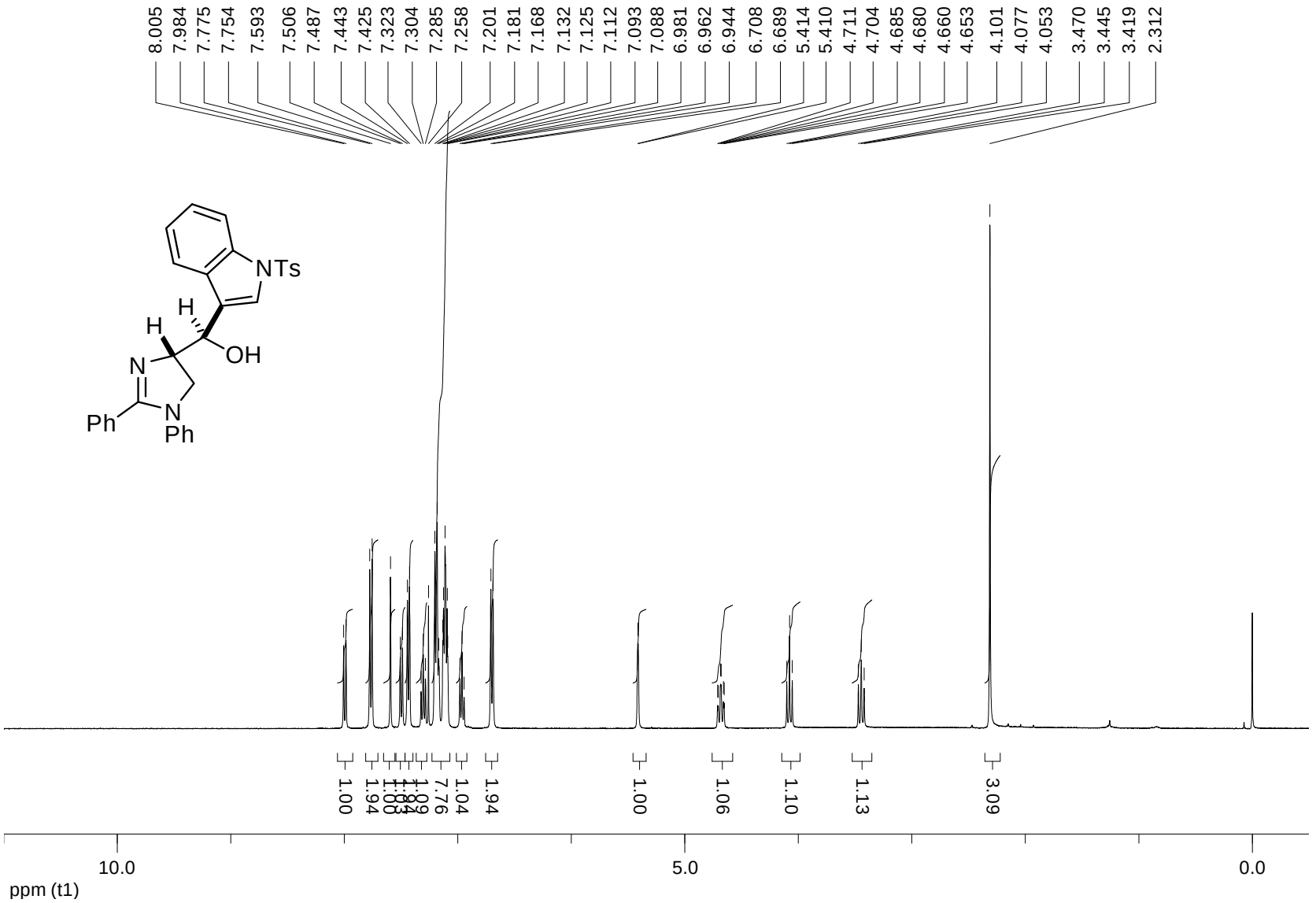
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



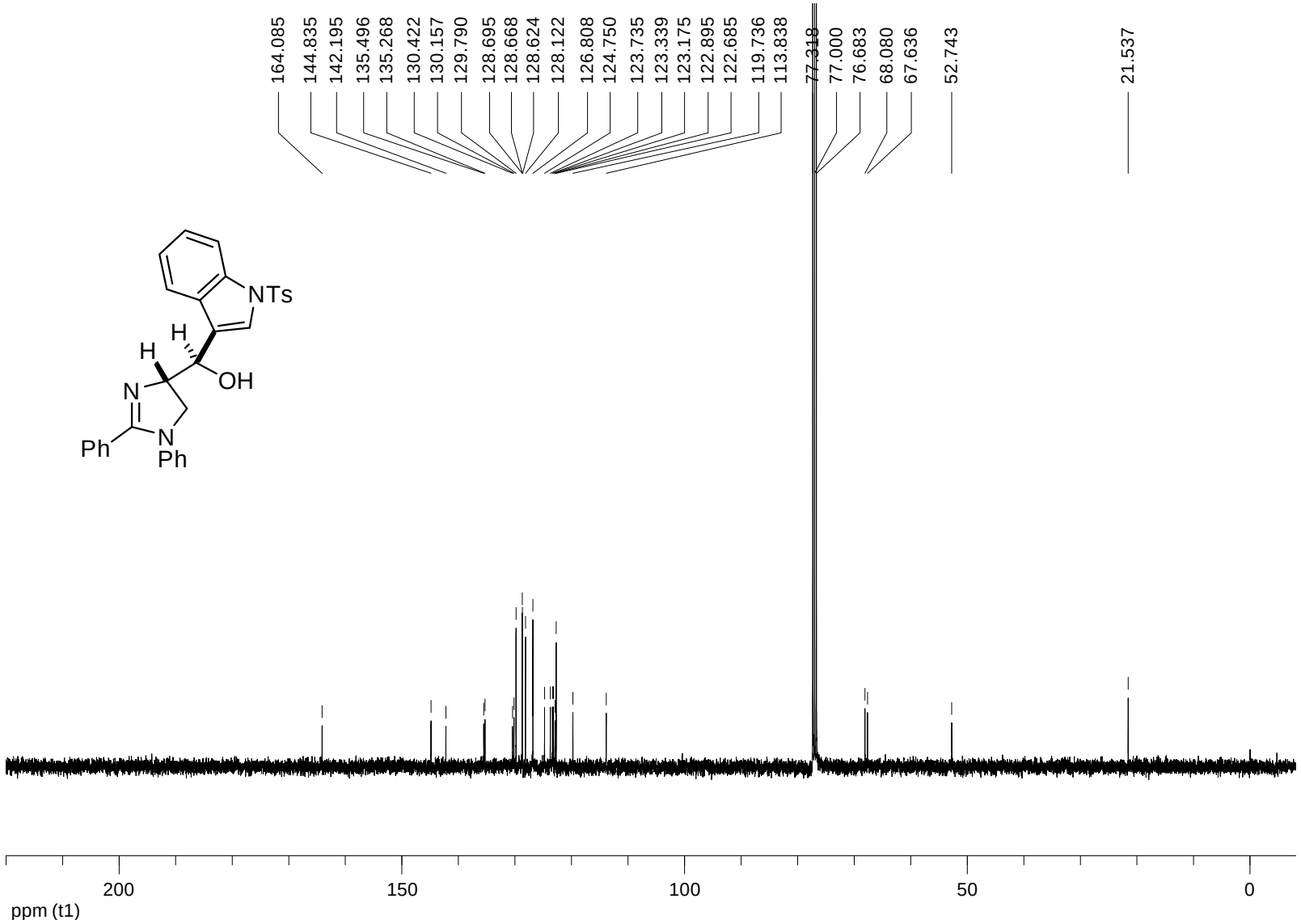
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



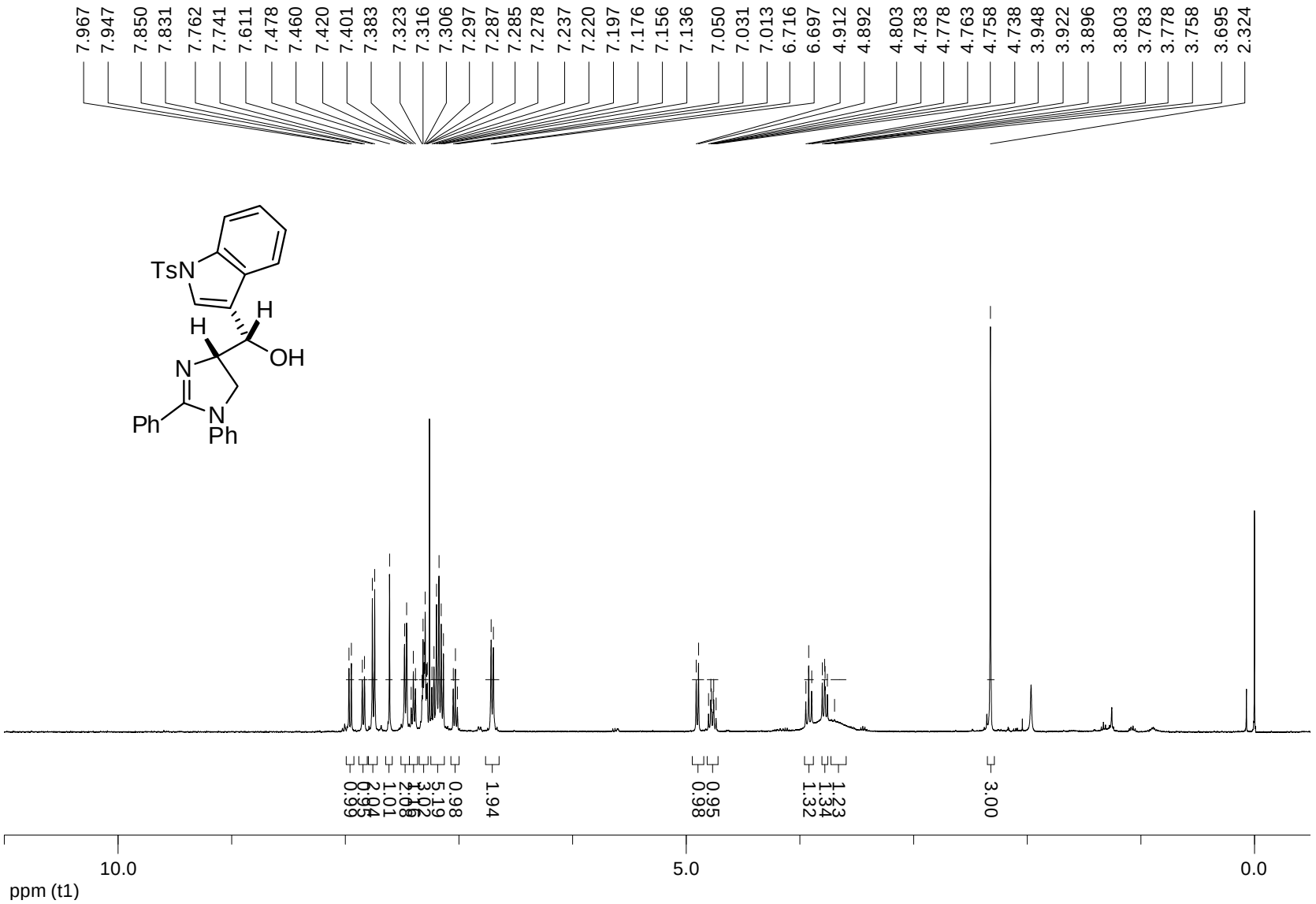
^{1}H NMR spectrum of **3i** (the major stereoisomer) (400 MHz, $CDCl_3$)



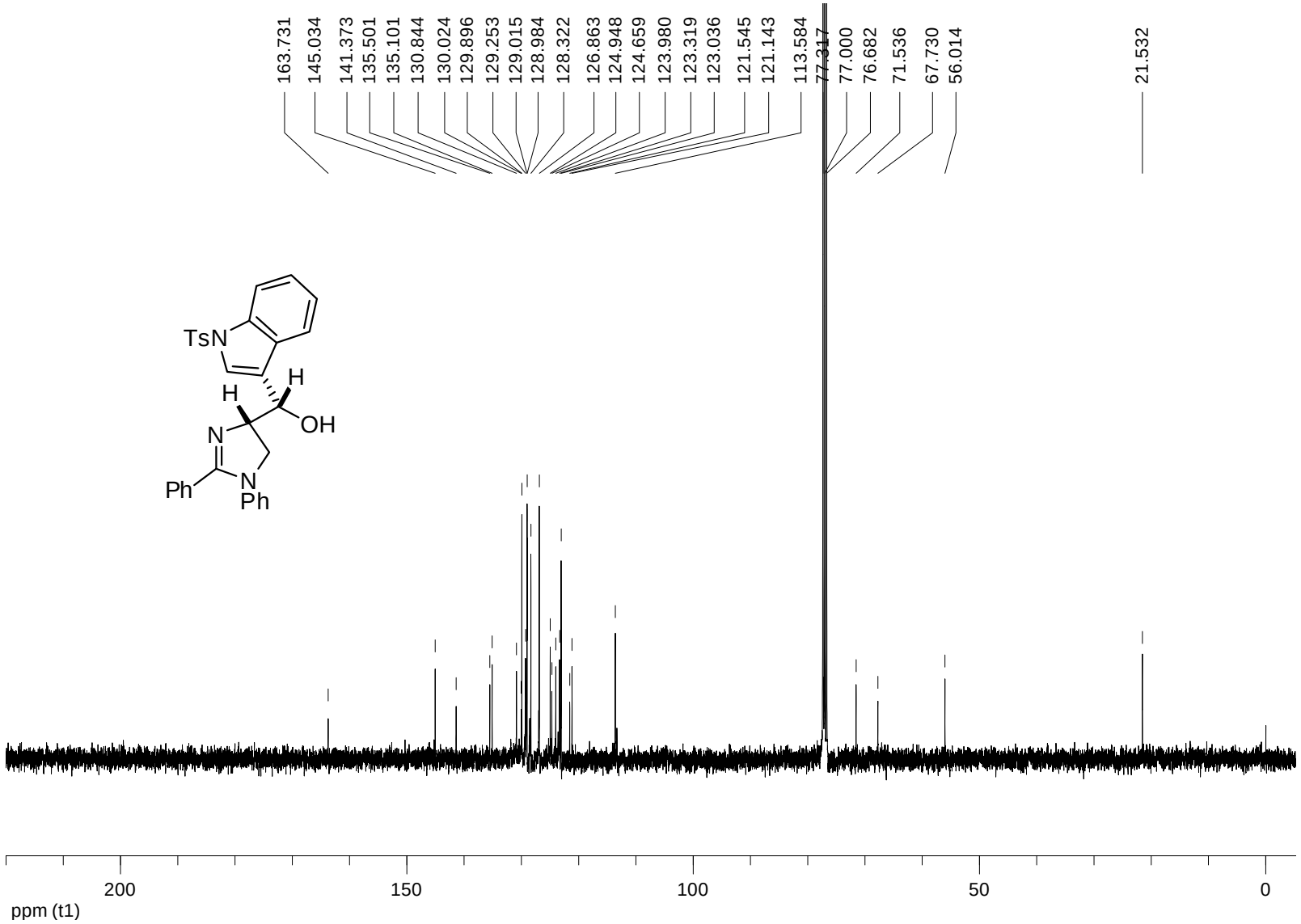
^{13}C NMR spectrum of **3i** (the major stereoisomer) (100 MHz, $CDCl_3$)



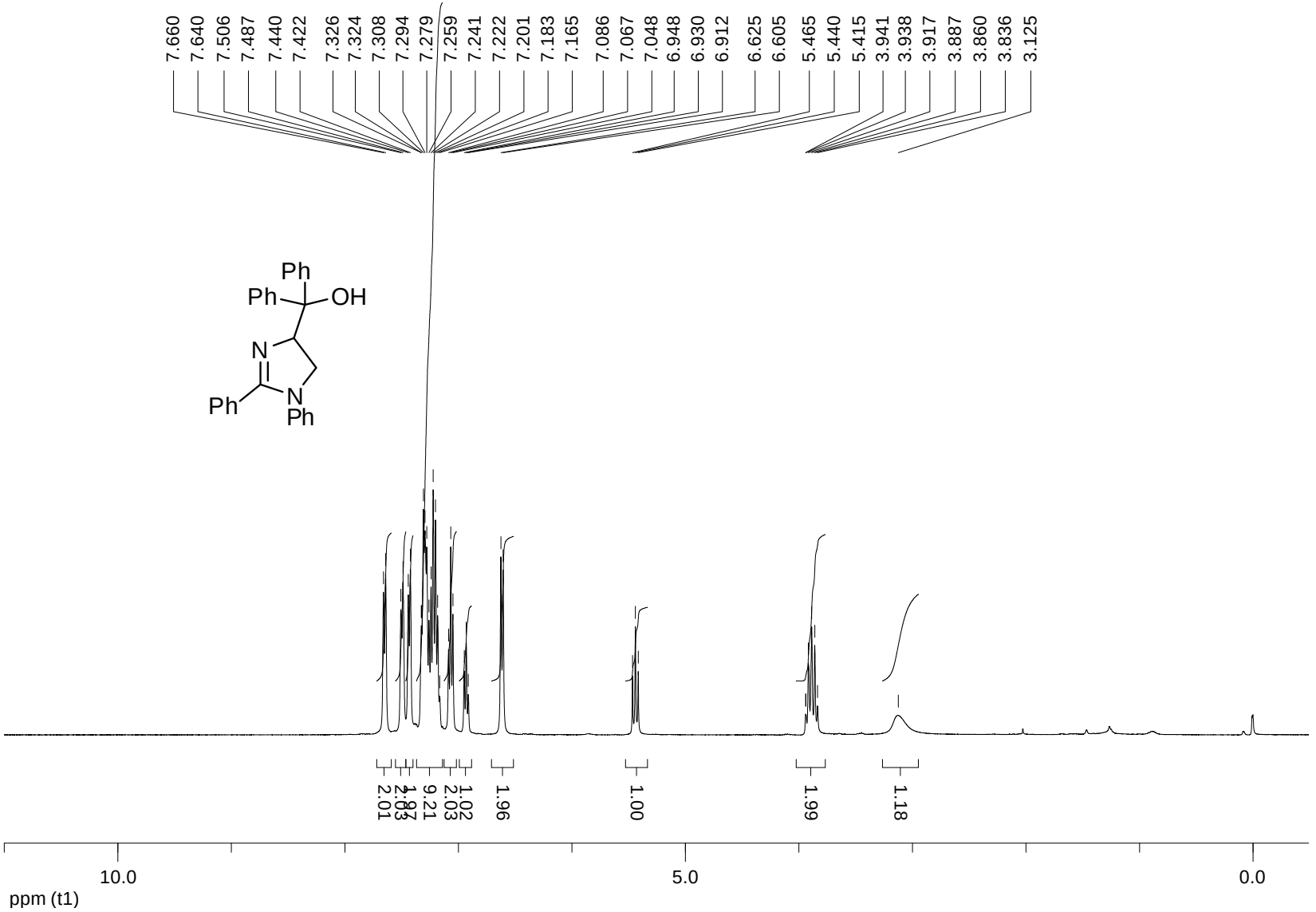
^{1}H NMR spectrum of **3i'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



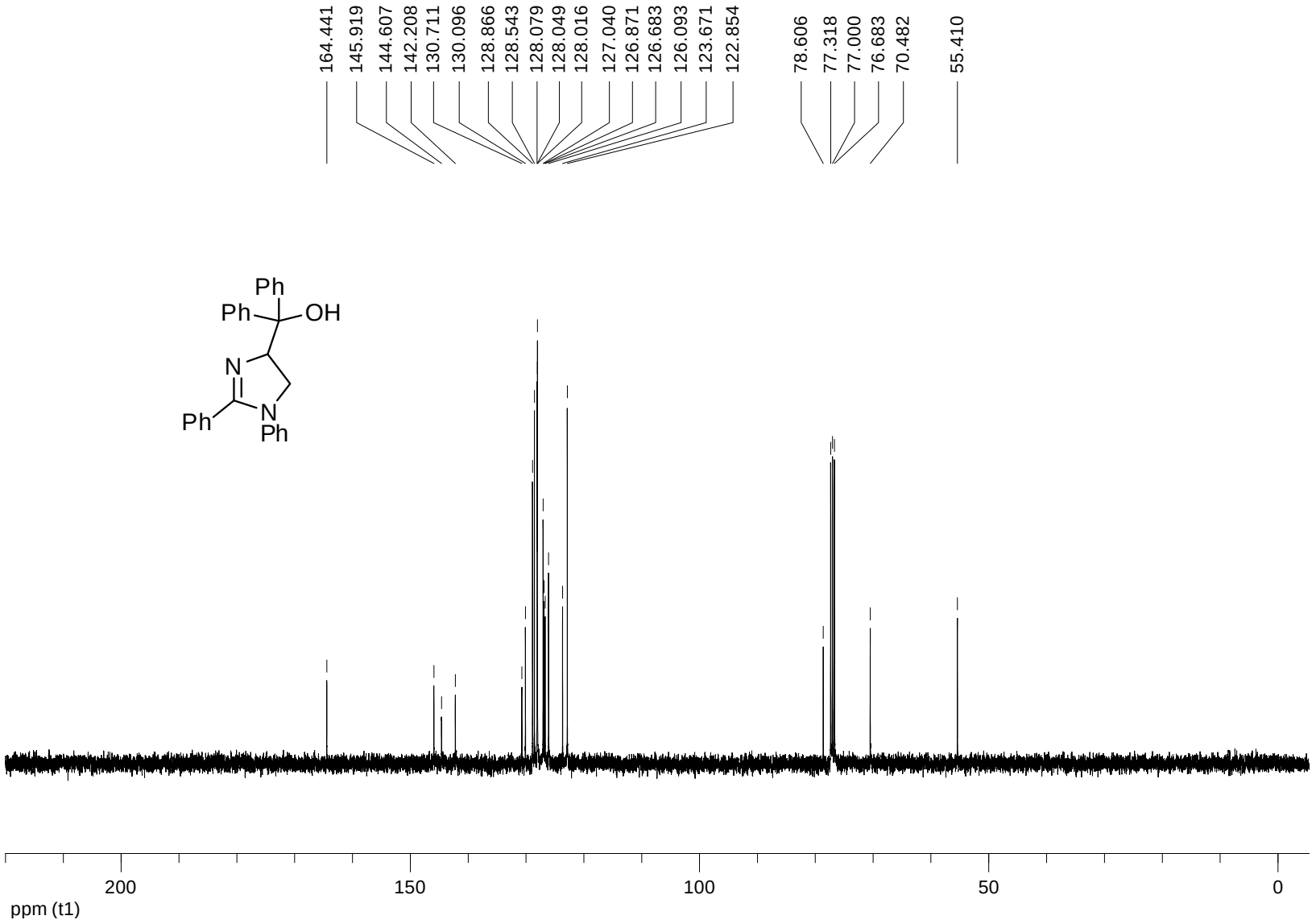
^{13}C NMR spectrum of **3i'** (the minor stereoisomer) (100 MHz, $CDCl_3$)



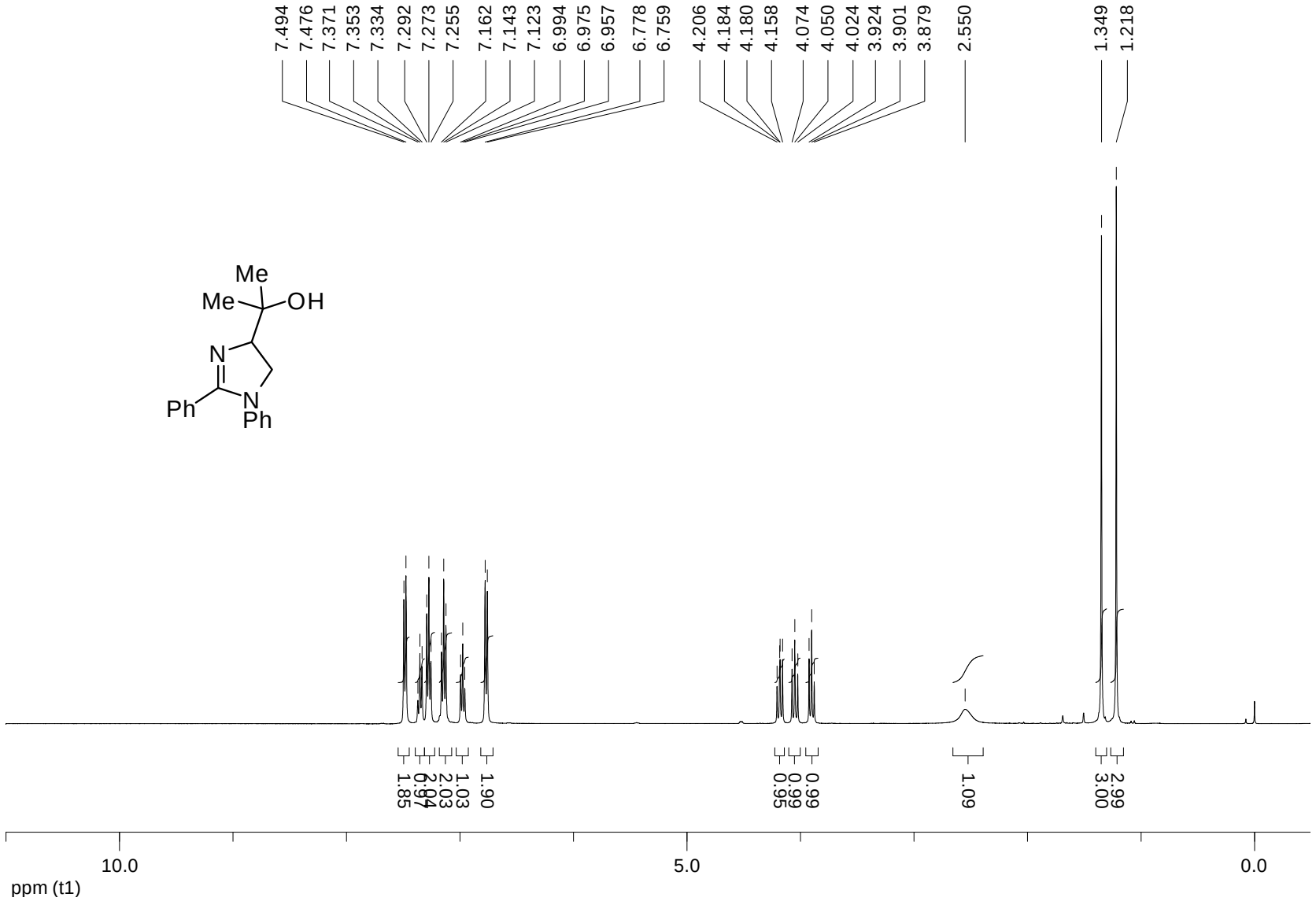
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



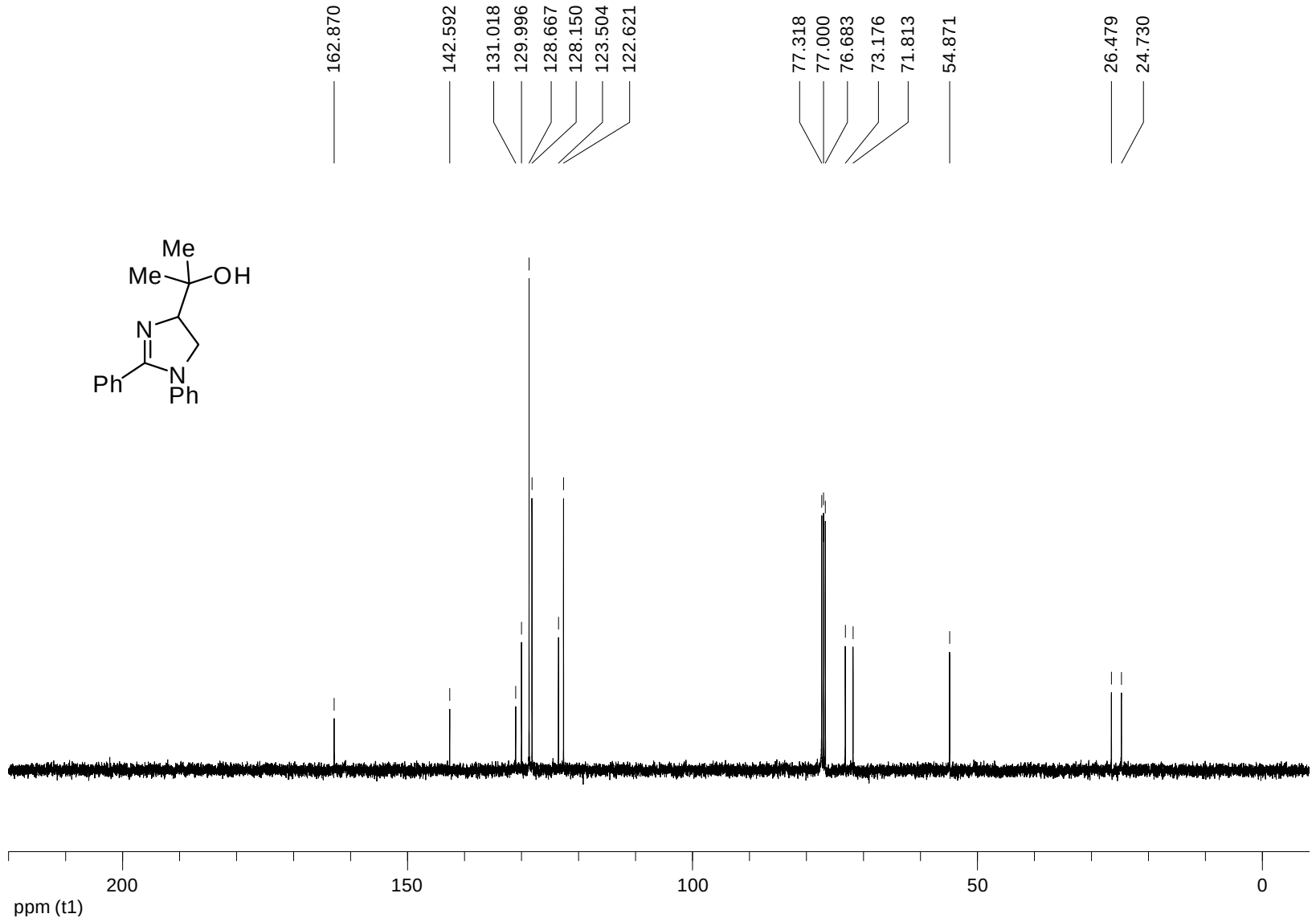
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



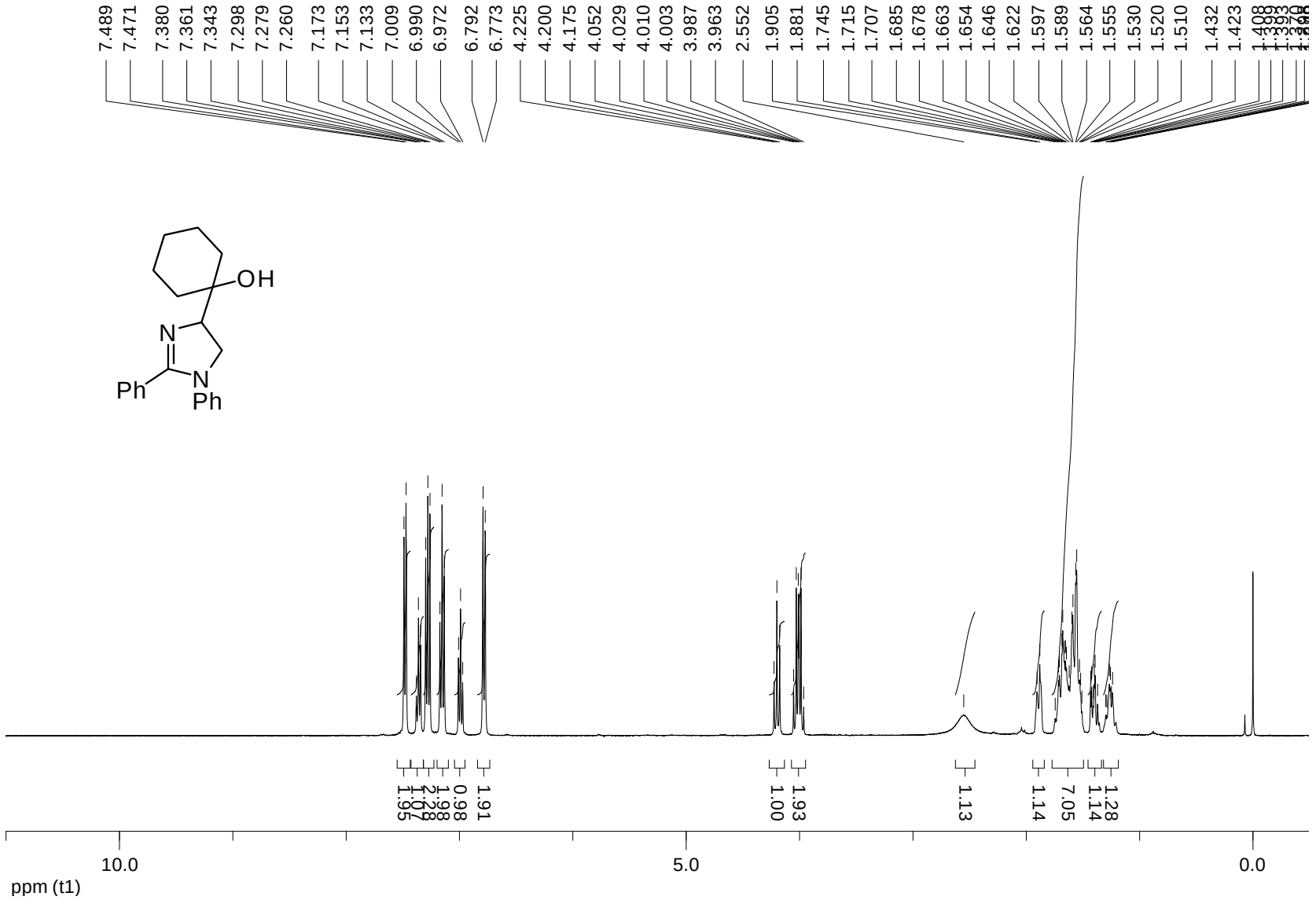
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



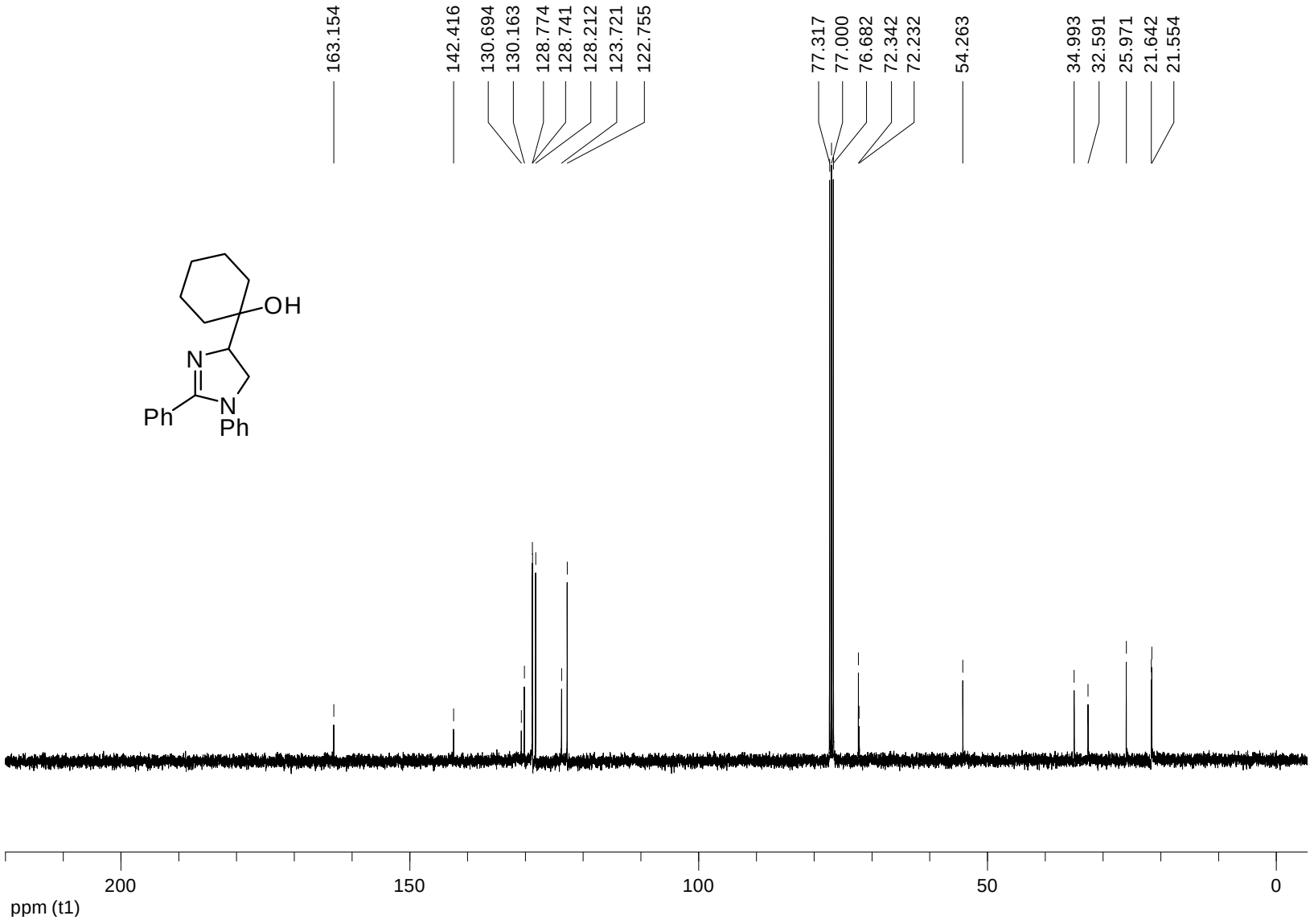
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



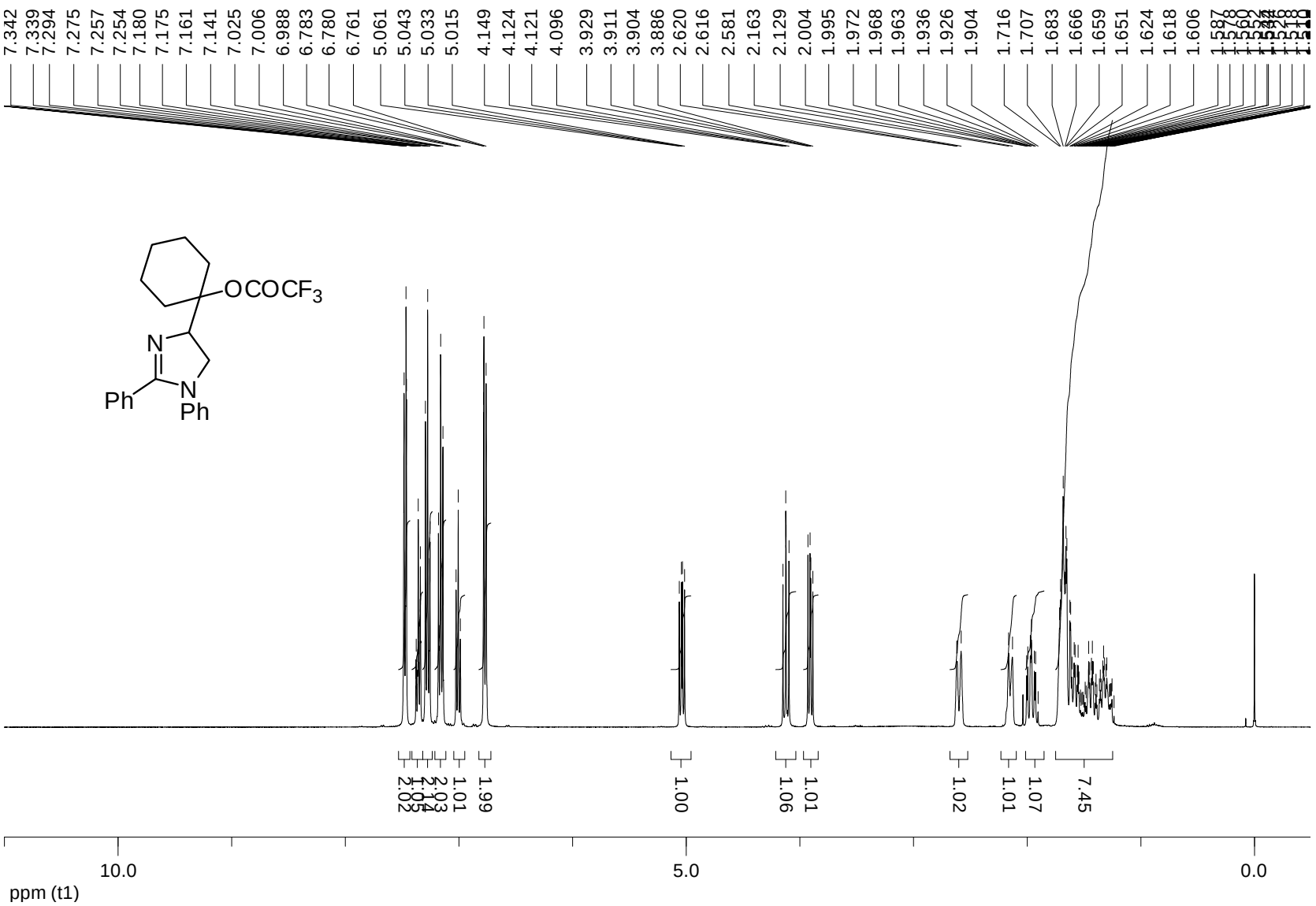
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



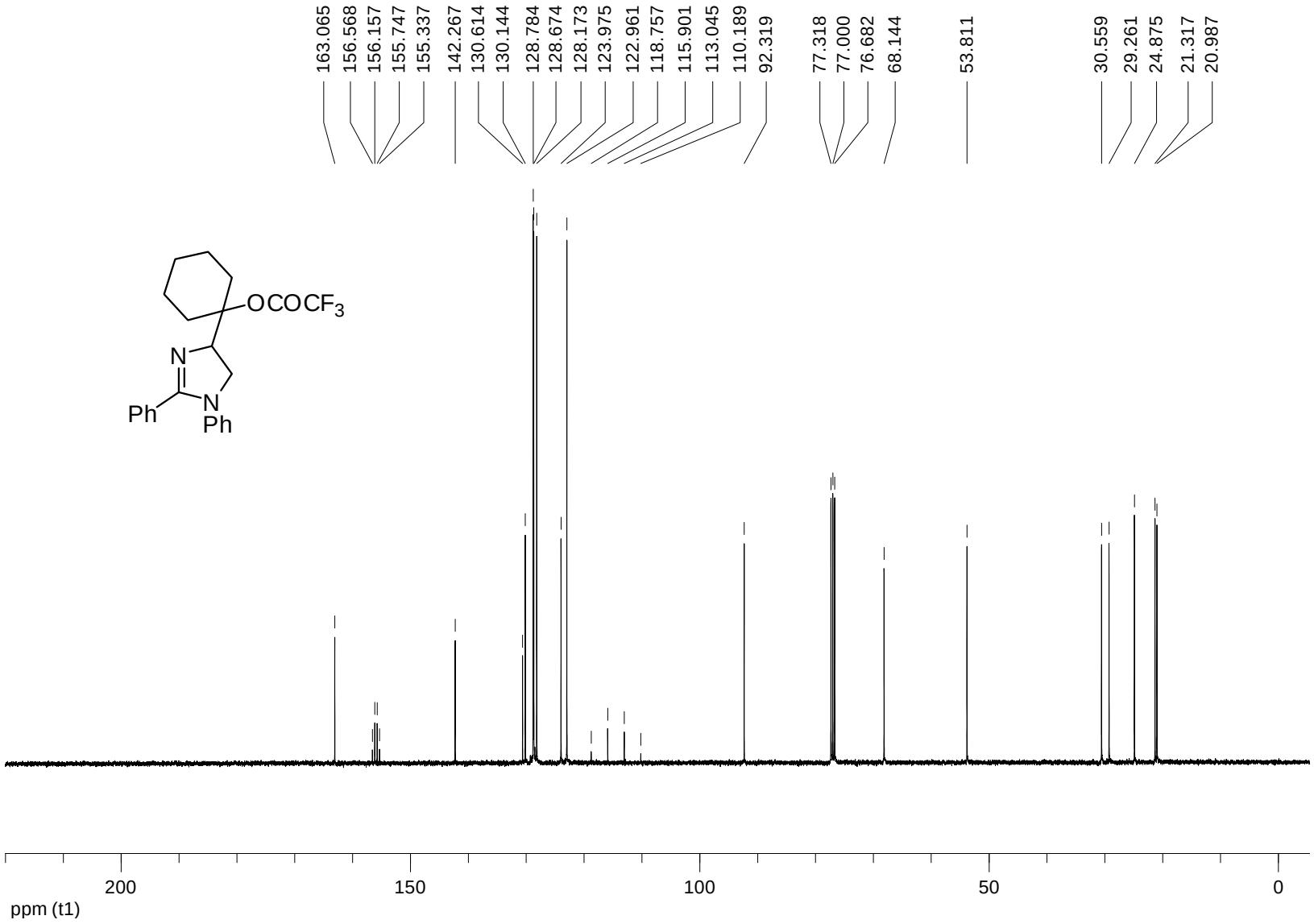
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



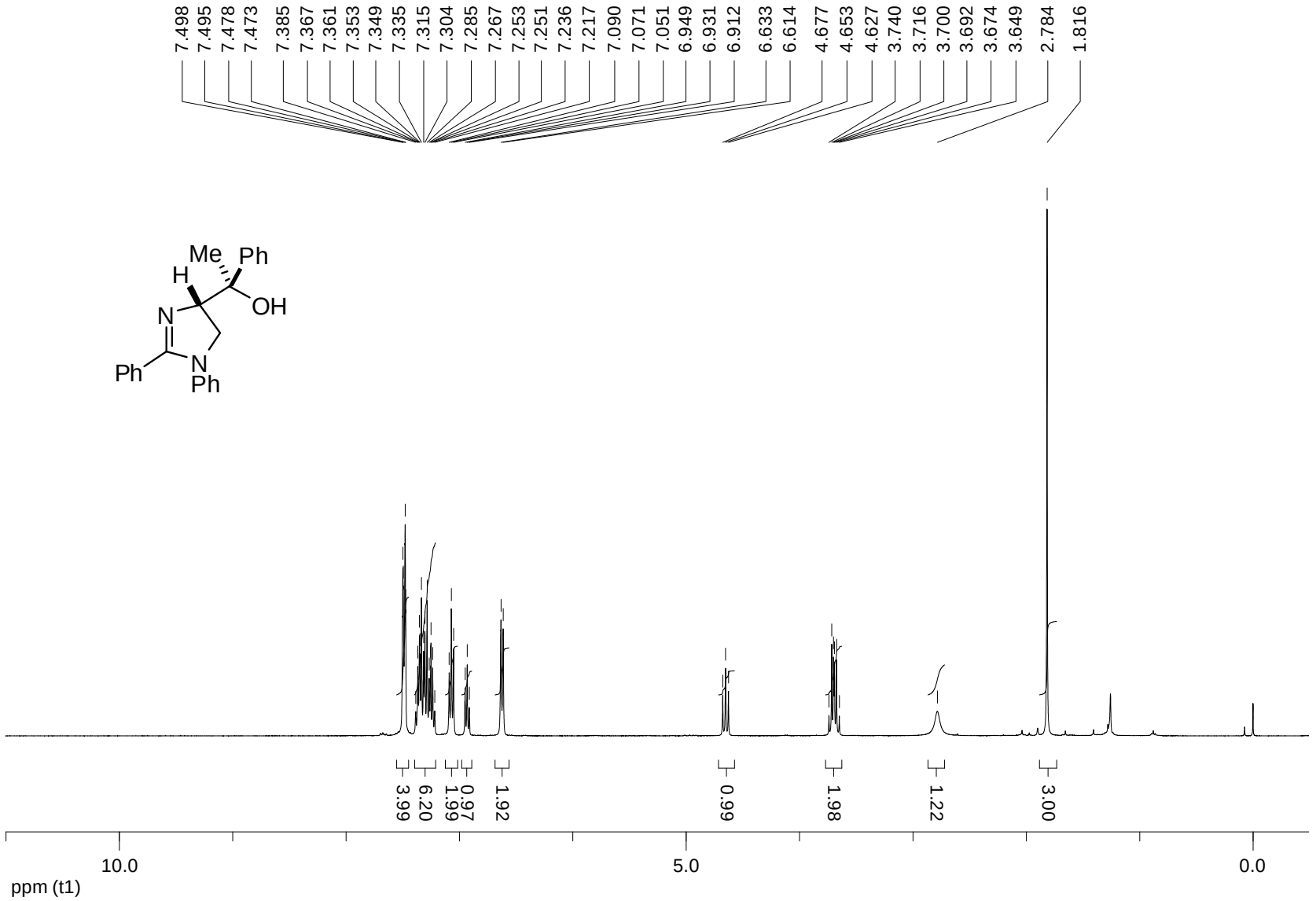
^{1}H NMR spectrum of **3m'** (400 MHz, $CDCl_3$)



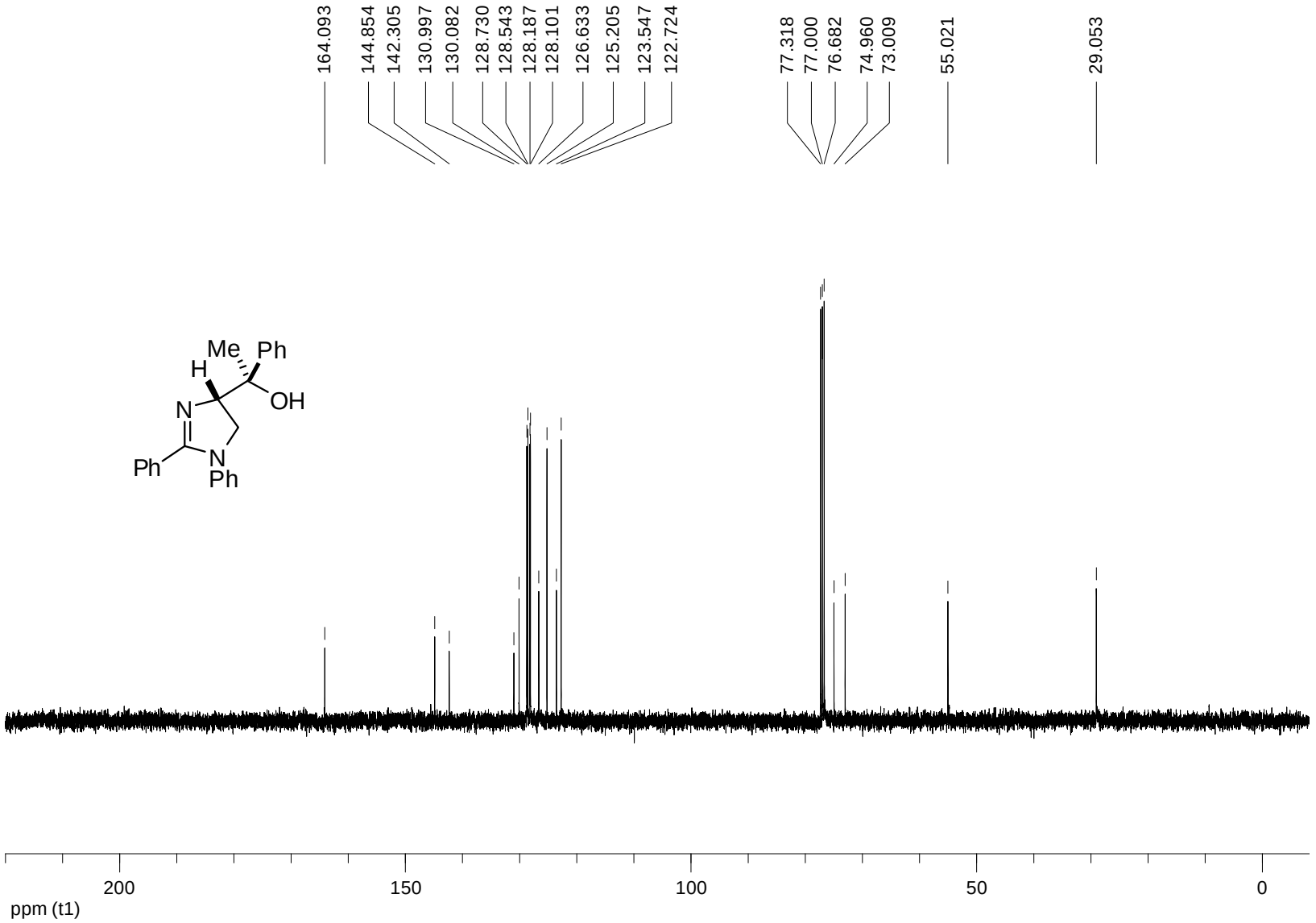
^{13}C NMR spectrum of **3m'** (100 MHz, $CDCl_3$)



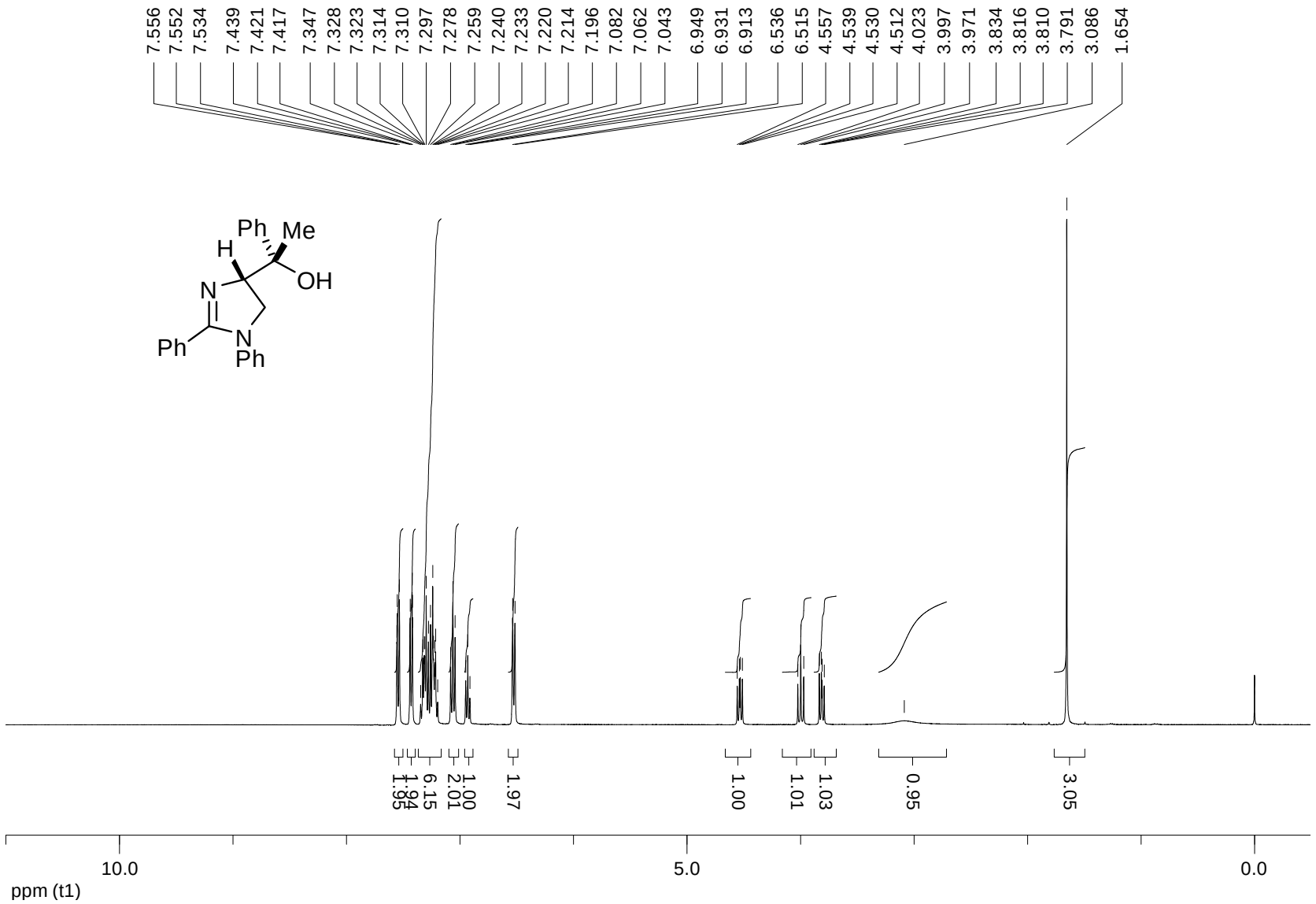
^{1}H NMR spectrum of **3n** (dr = >20:1) (400 MHz, $CDCl_3$)



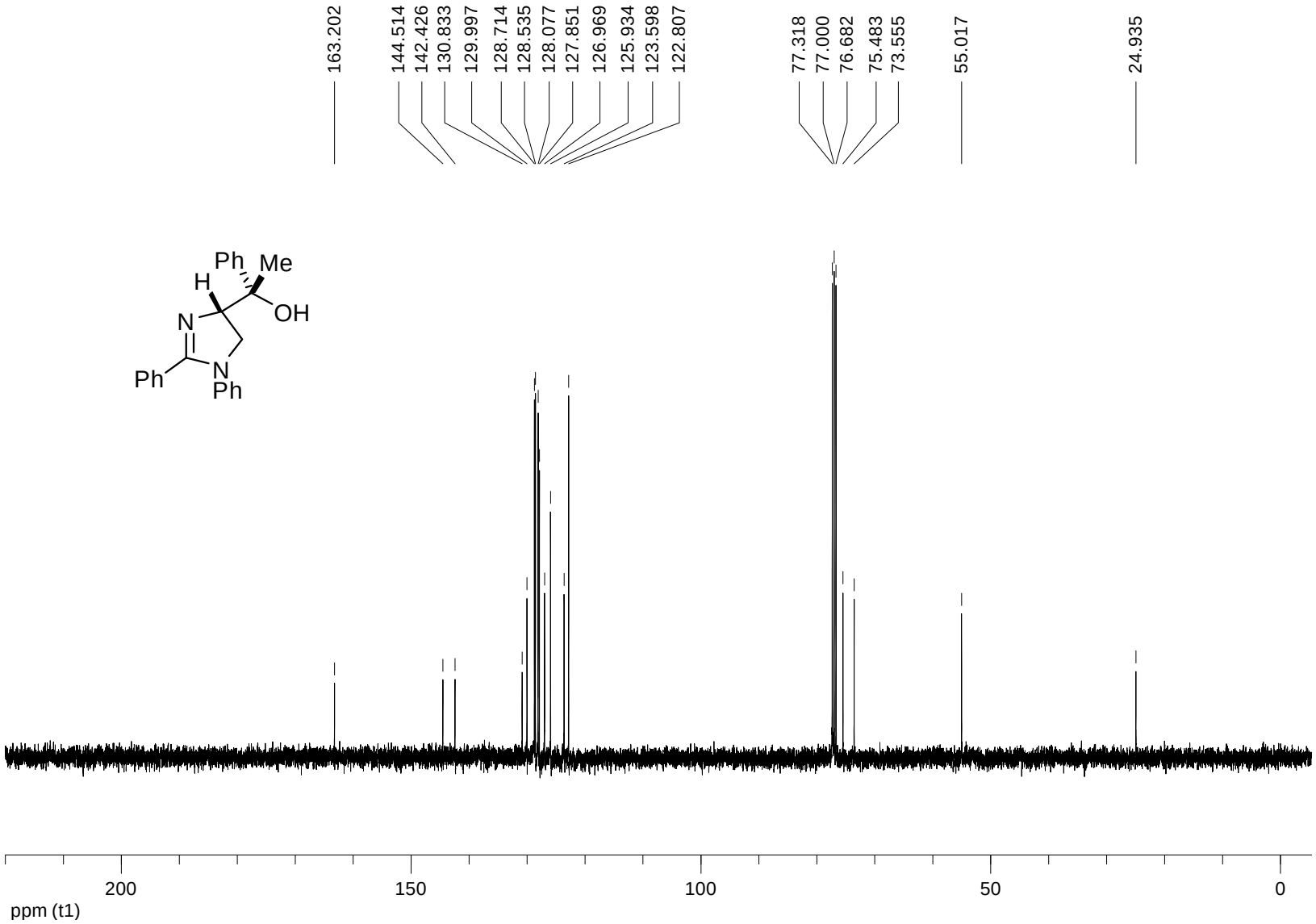
^{13}C NMR spectrum of **3n** (dr = >20:1) (100 MHz, $CDCl_3$)



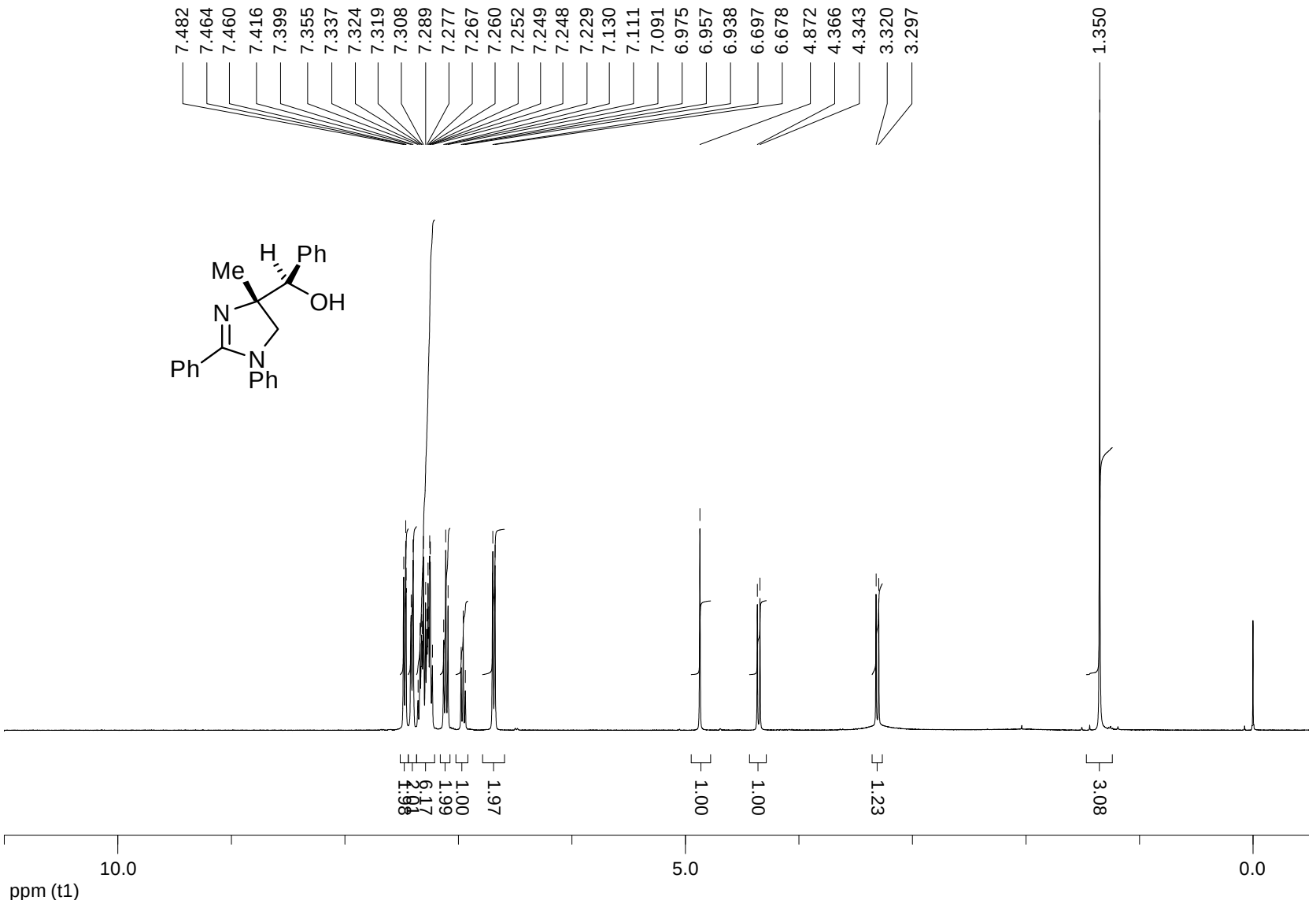
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



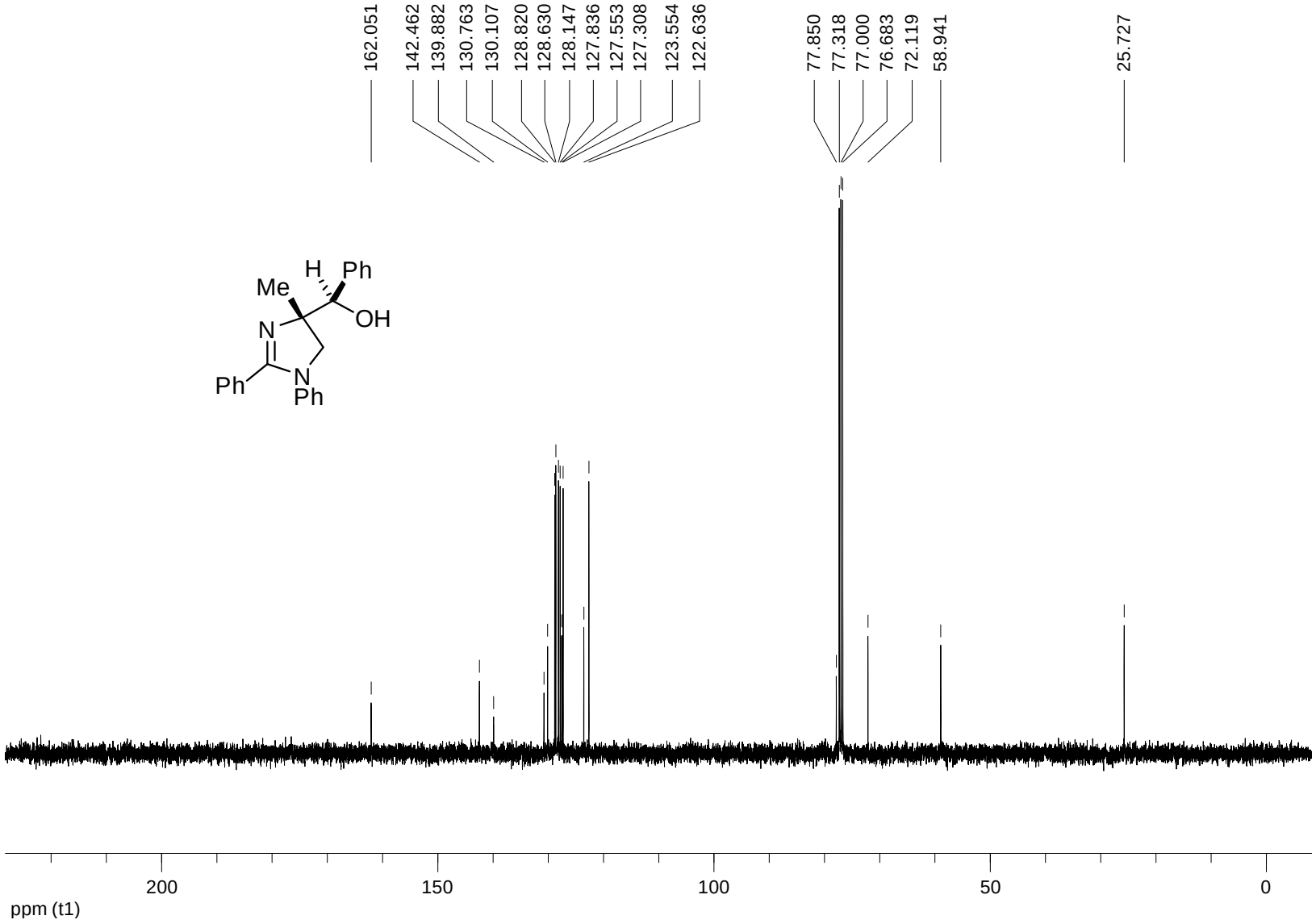
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



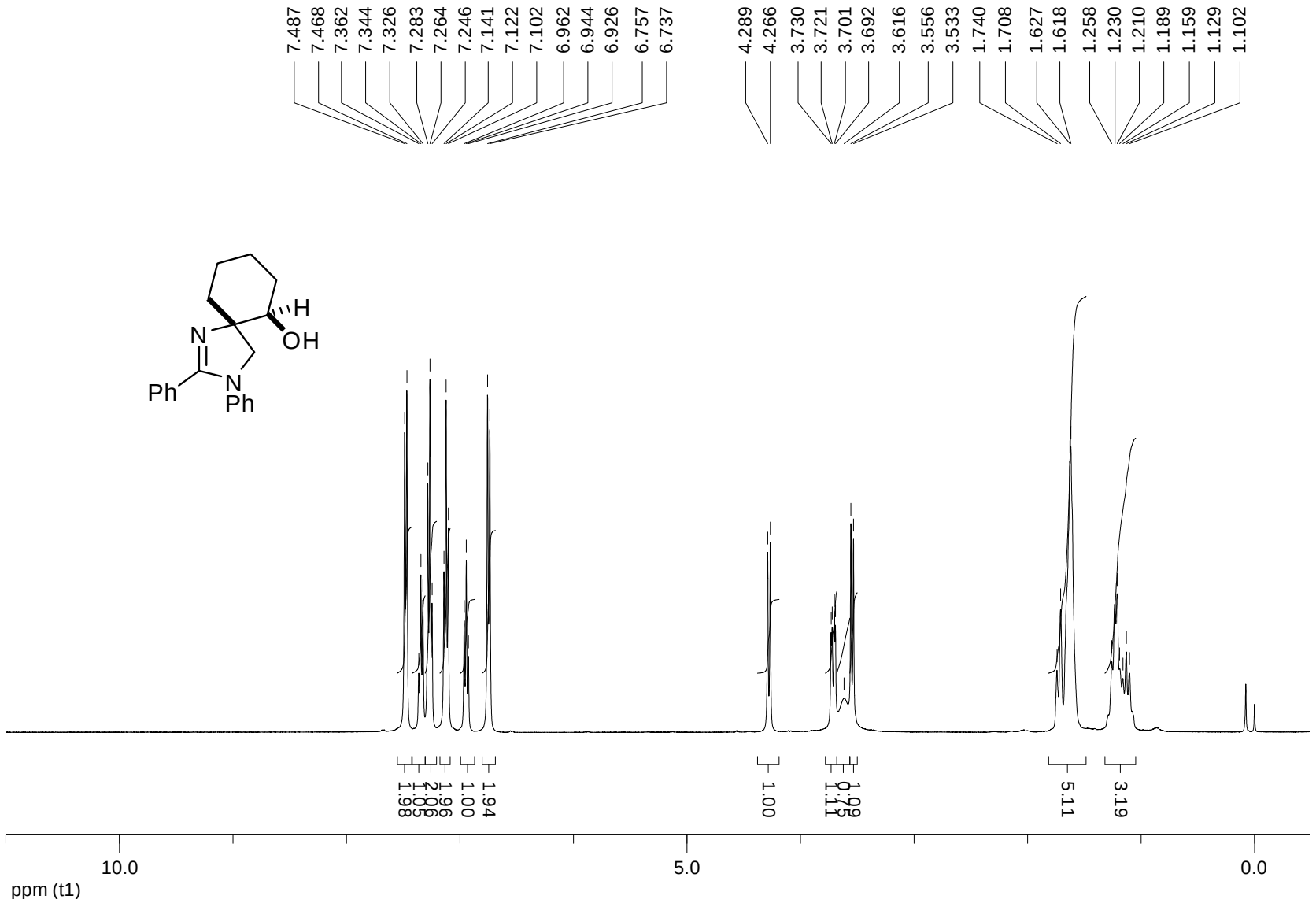
^{1}H NMR spectrum of **3p** (400 MHz, $CDCl_3$)



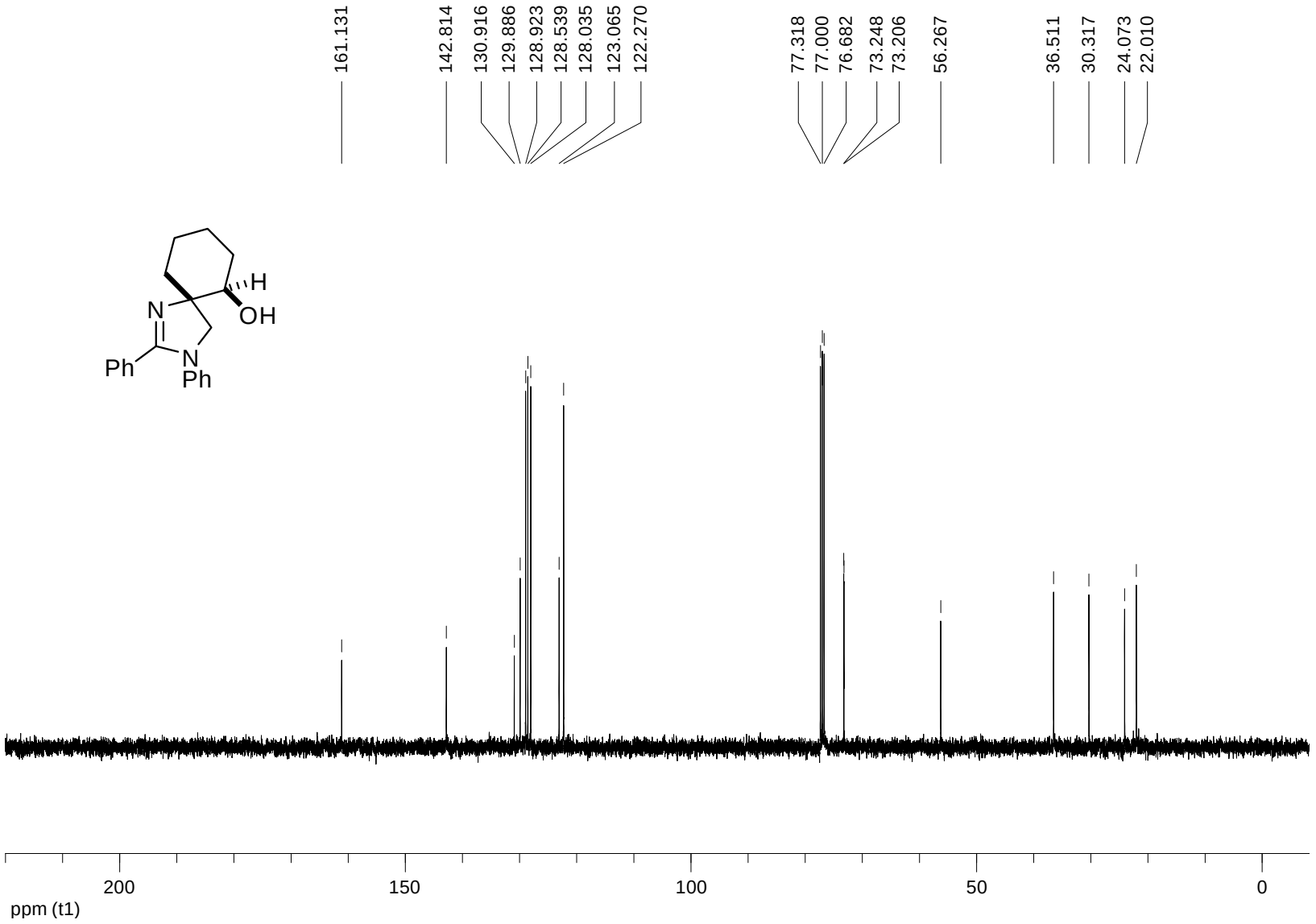
^{13}C NMR spectrum of **3p** (100 MHz, $CDCl_3$)



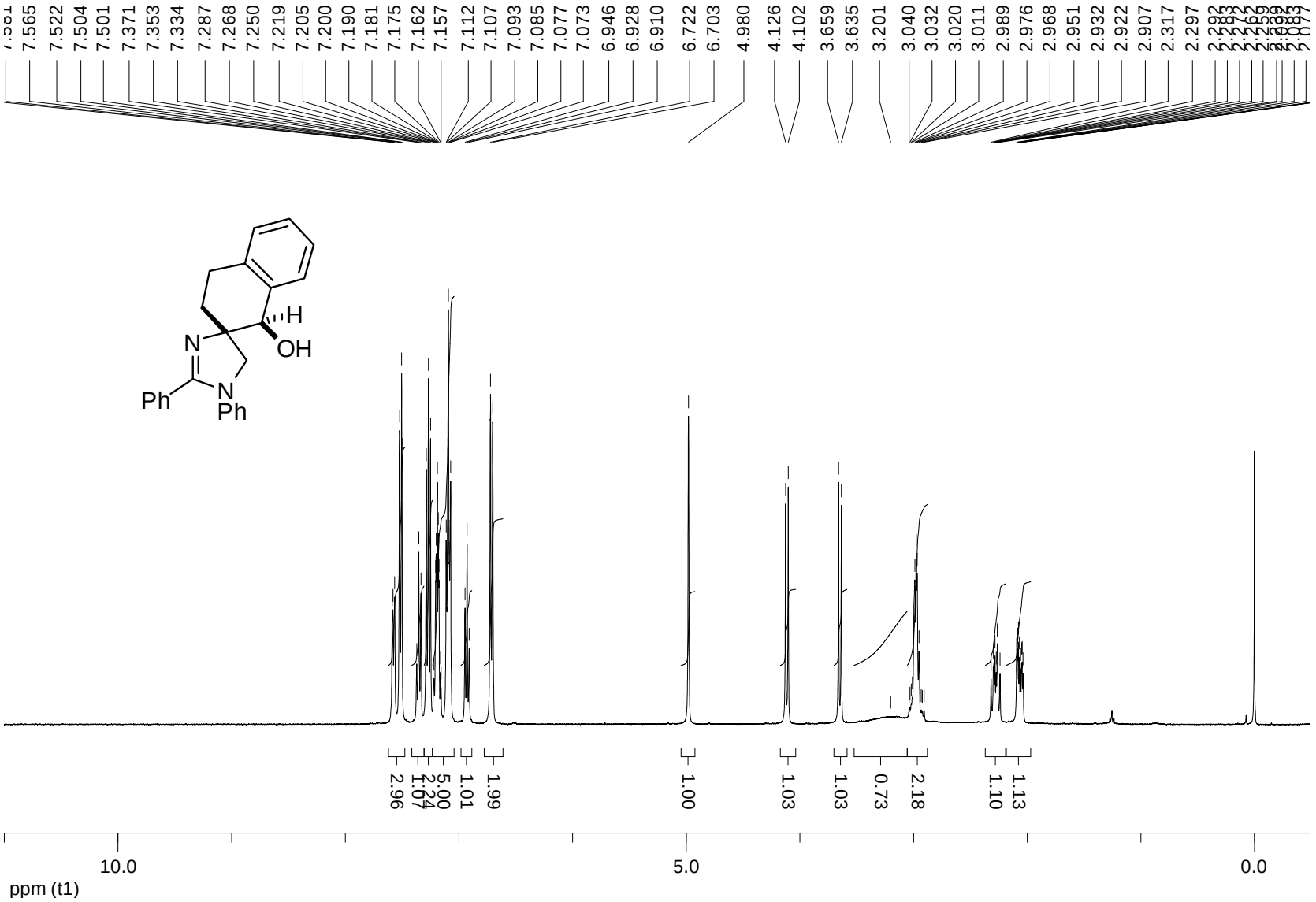
^{1}H NMR spectrum of **3q** (400 MHz, $CDCl_3$)



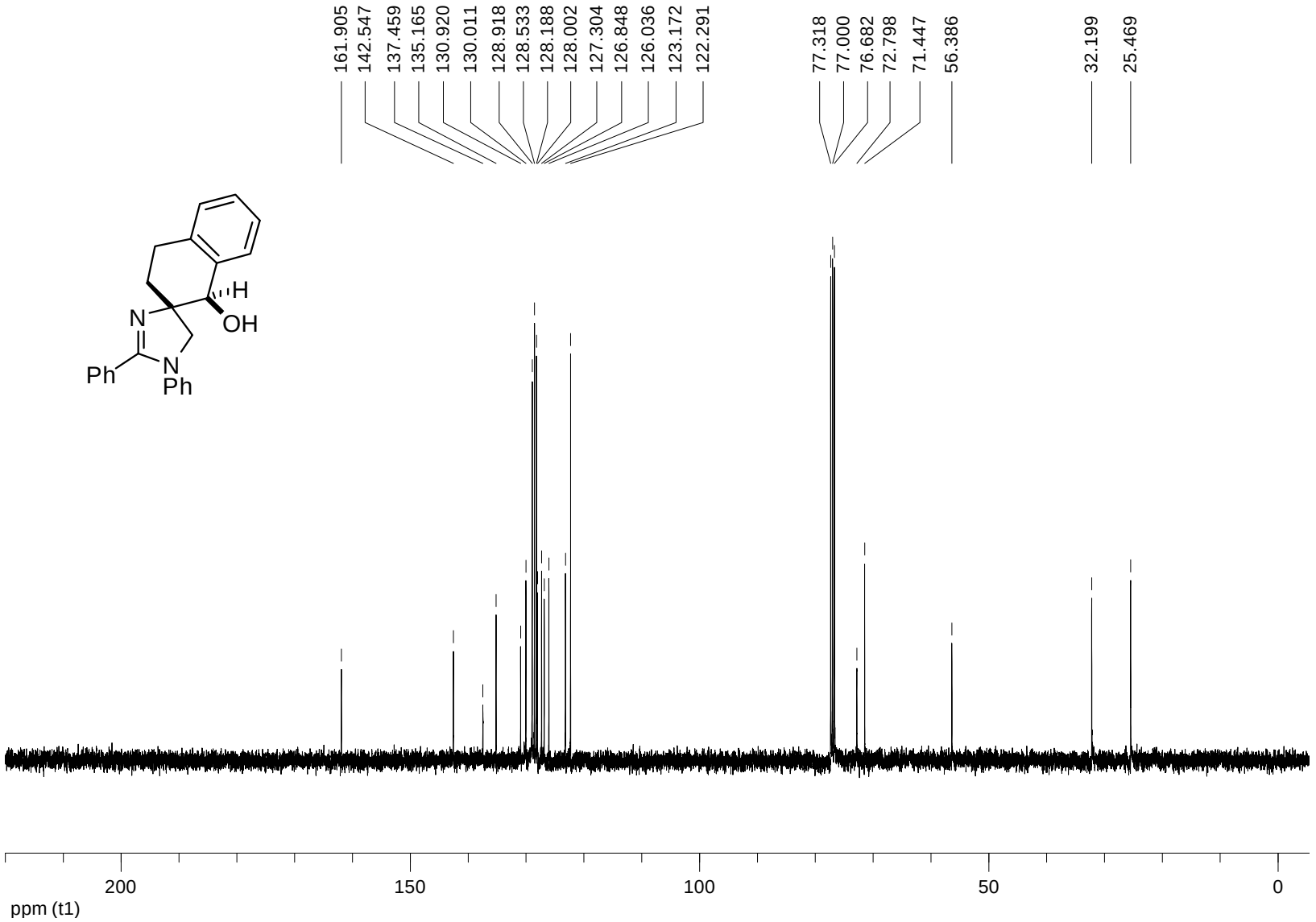
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)



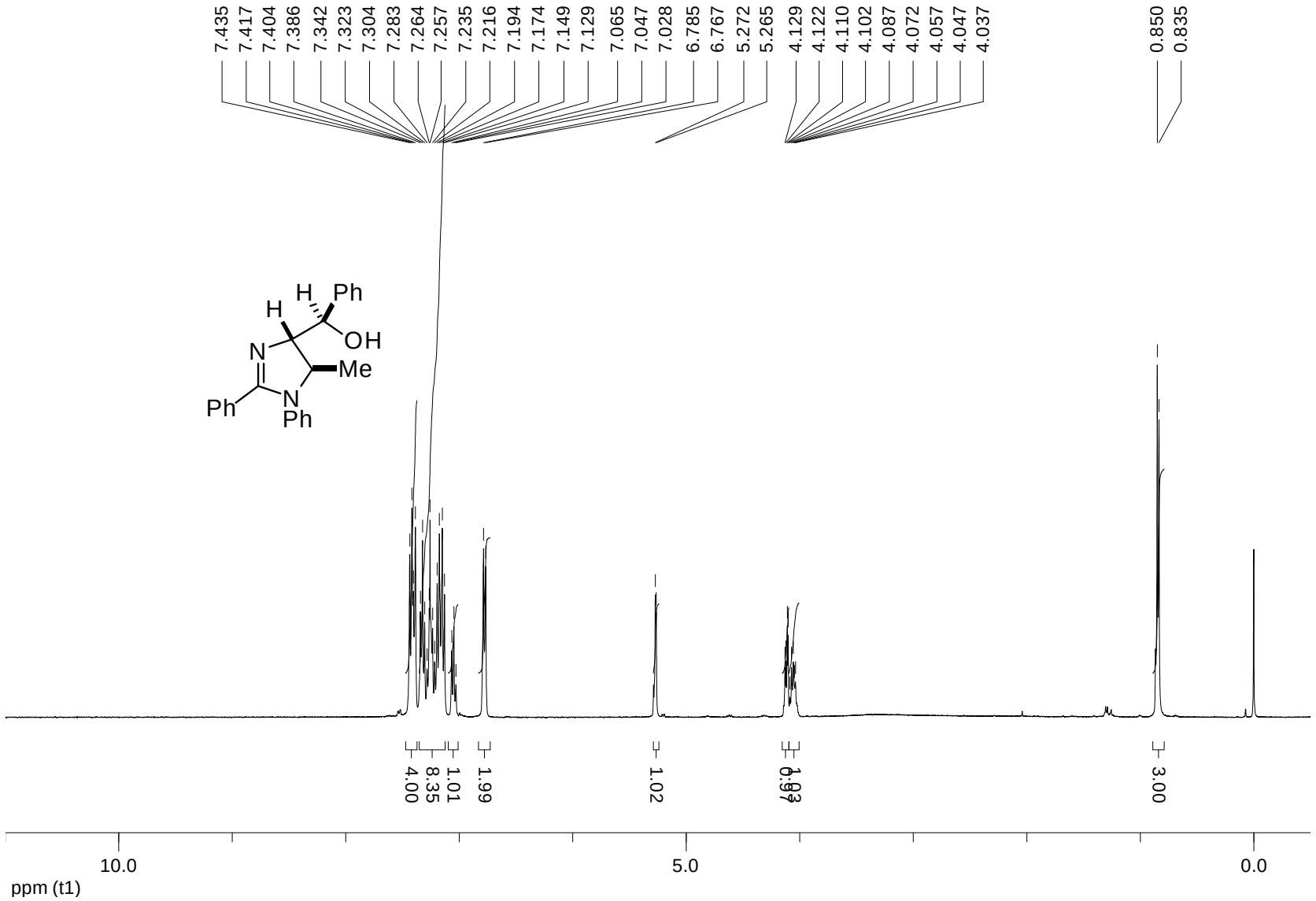
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



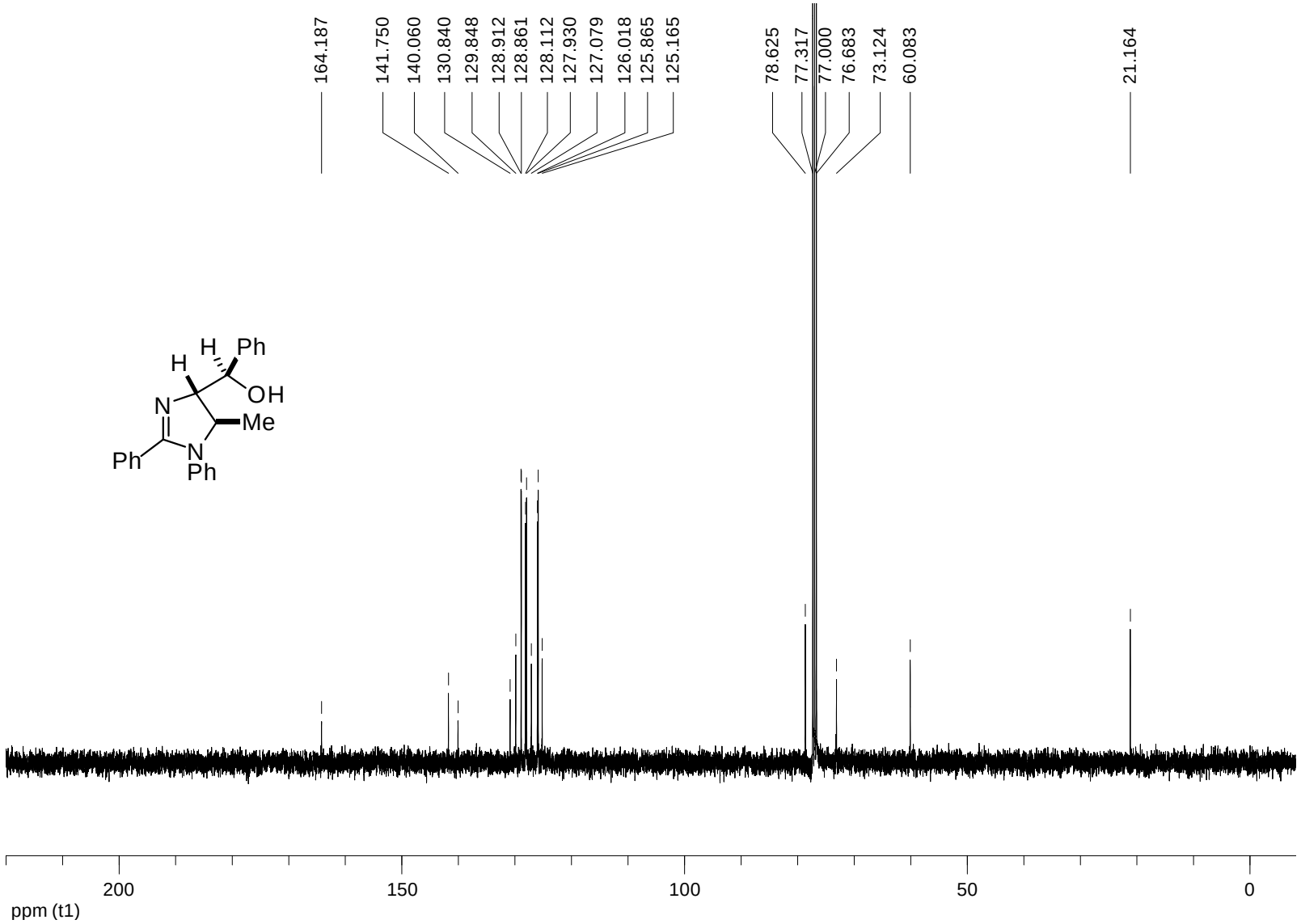
^{13}C NMR spectrum of **3r** (100 MHz, $CDCl_3$)



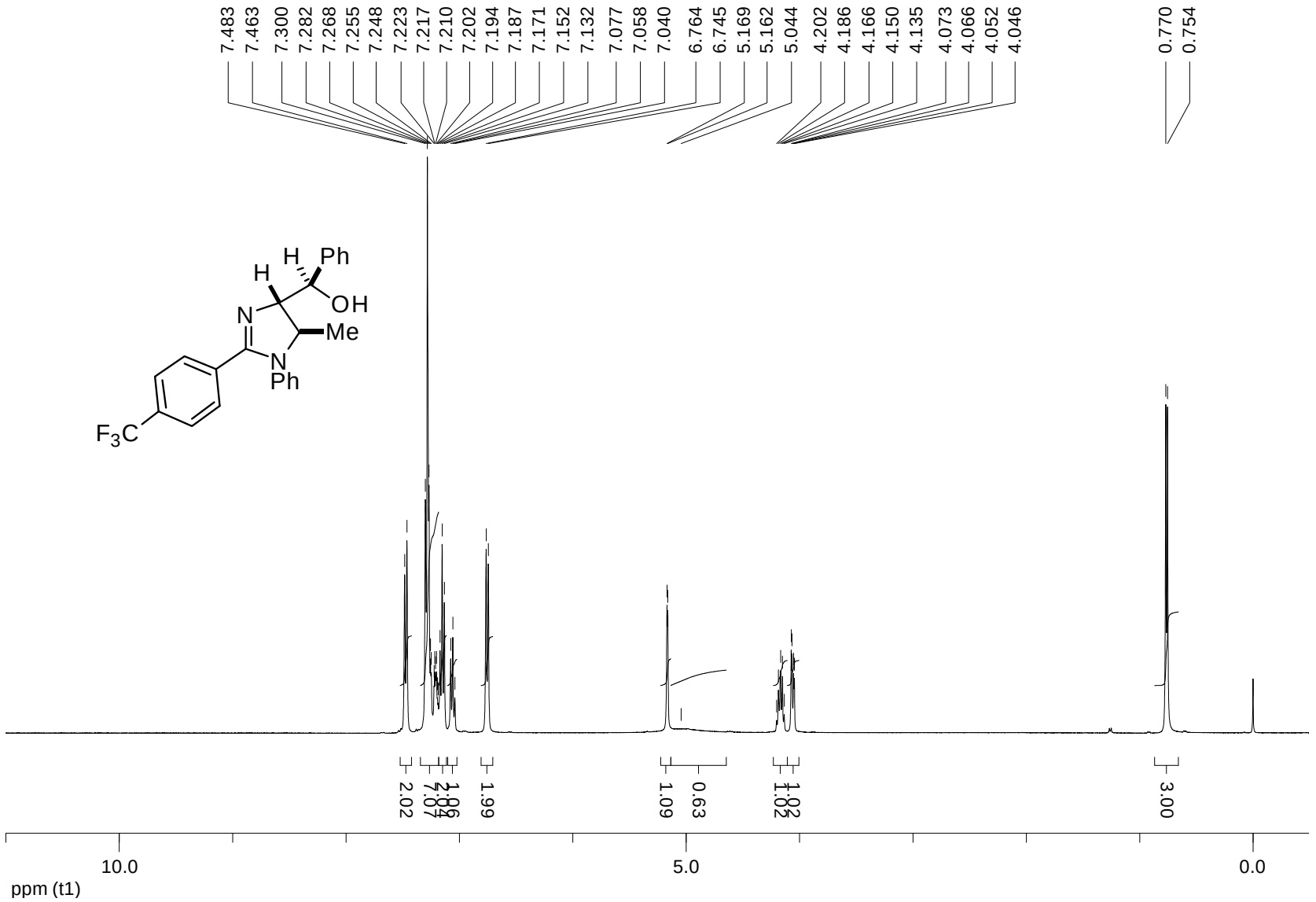
^{1}H NMR spectrum of **3s** (the major stereoisomer) (400 MHz, $CDCl_3$)



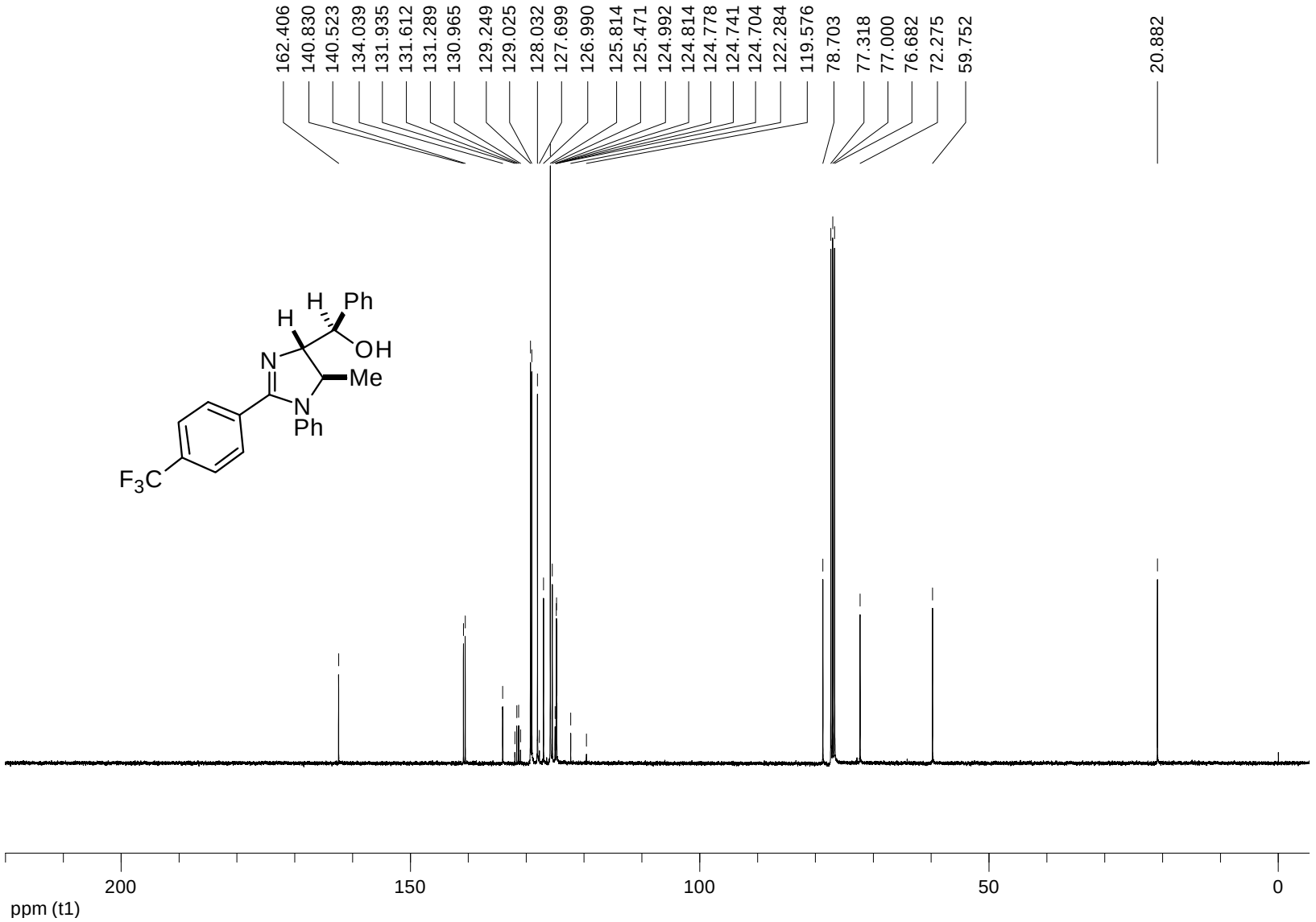
^{13}C NMR spectrum of **3s** (the major stereoisomer) (100 MHz, $CDCl_3$)



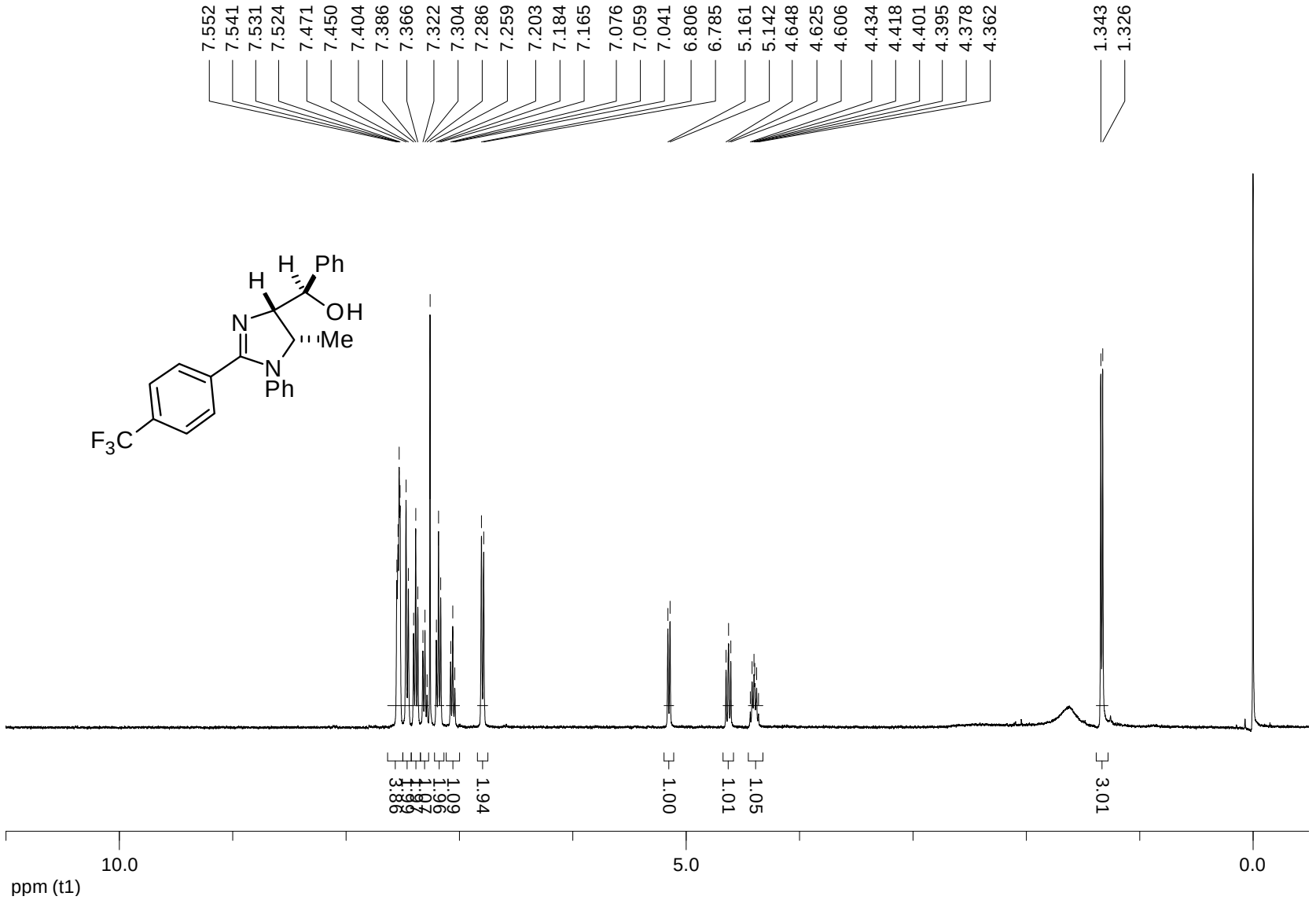
^{1}H NMR spectrum of **3t** (the major stereoisomer) (400 MHz, $CDCl_3$)



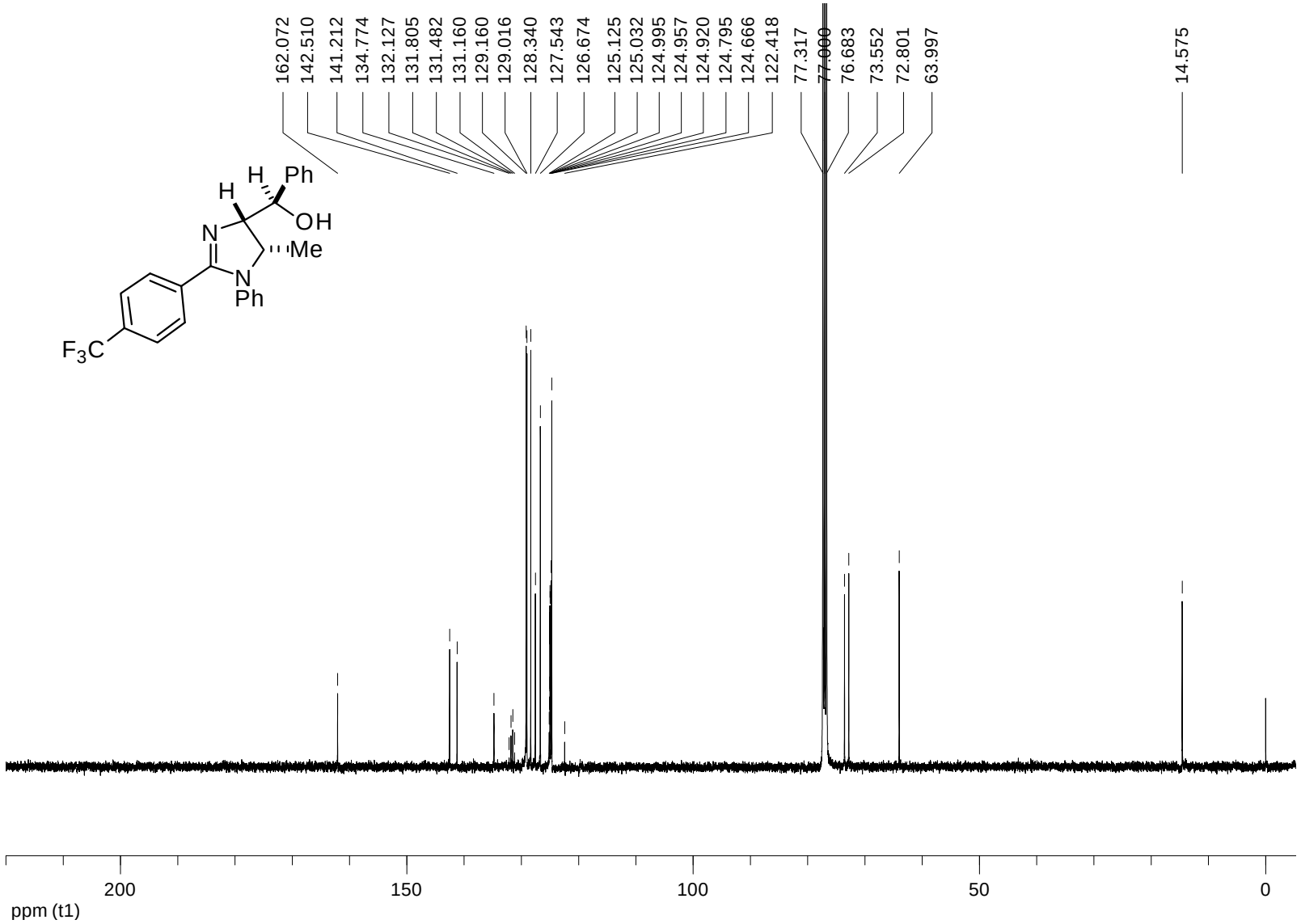
^{13}C NMR spectrum of **3t** (the major stereoisomer) (100 MHz, $CDCl_3$)



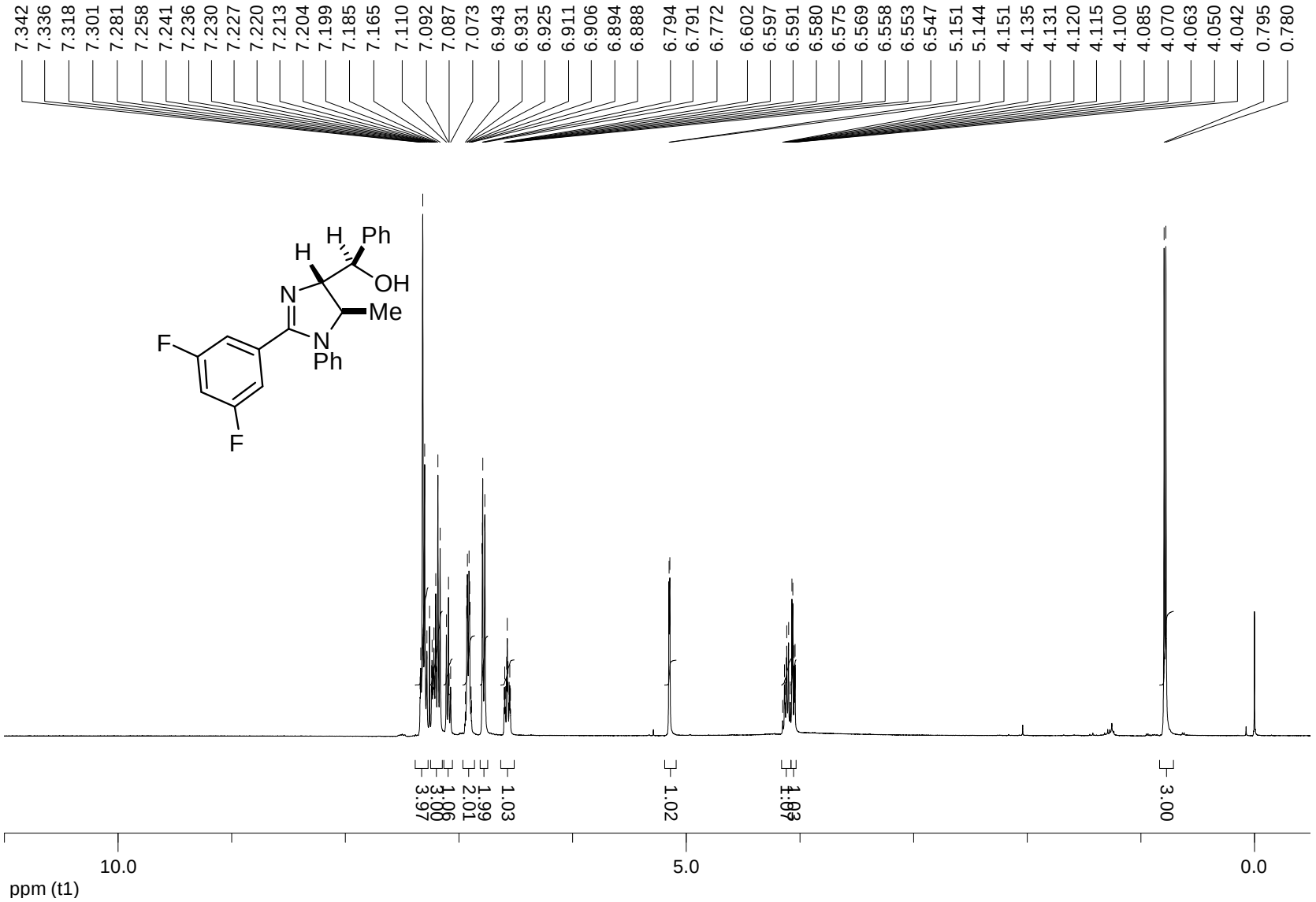
^{1}H NMR spectrum of **3t'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



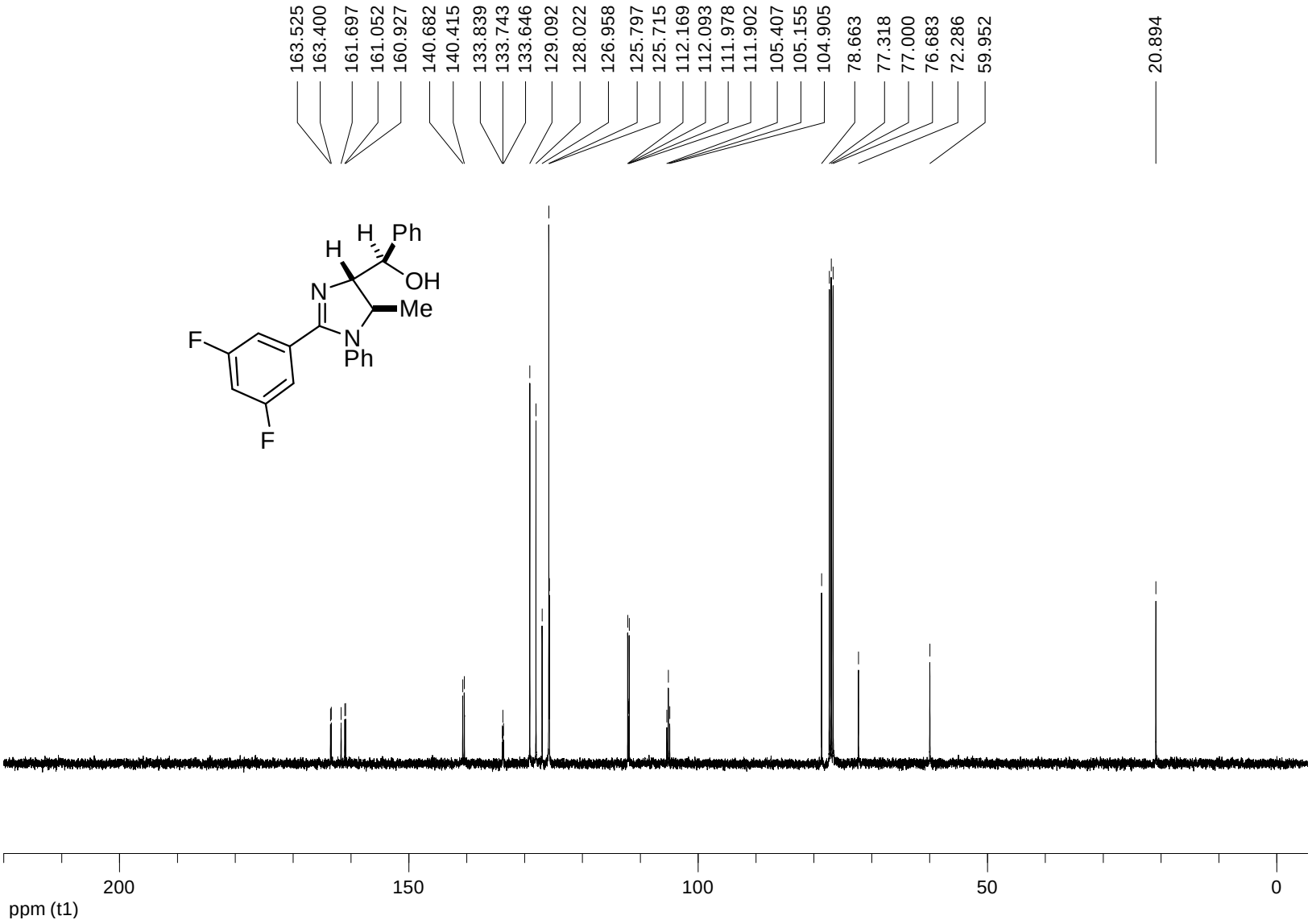
^{13}C NMR spectrum of **3t'** (the minor stereoisomer) (100 MHz, $CDCl_3$)



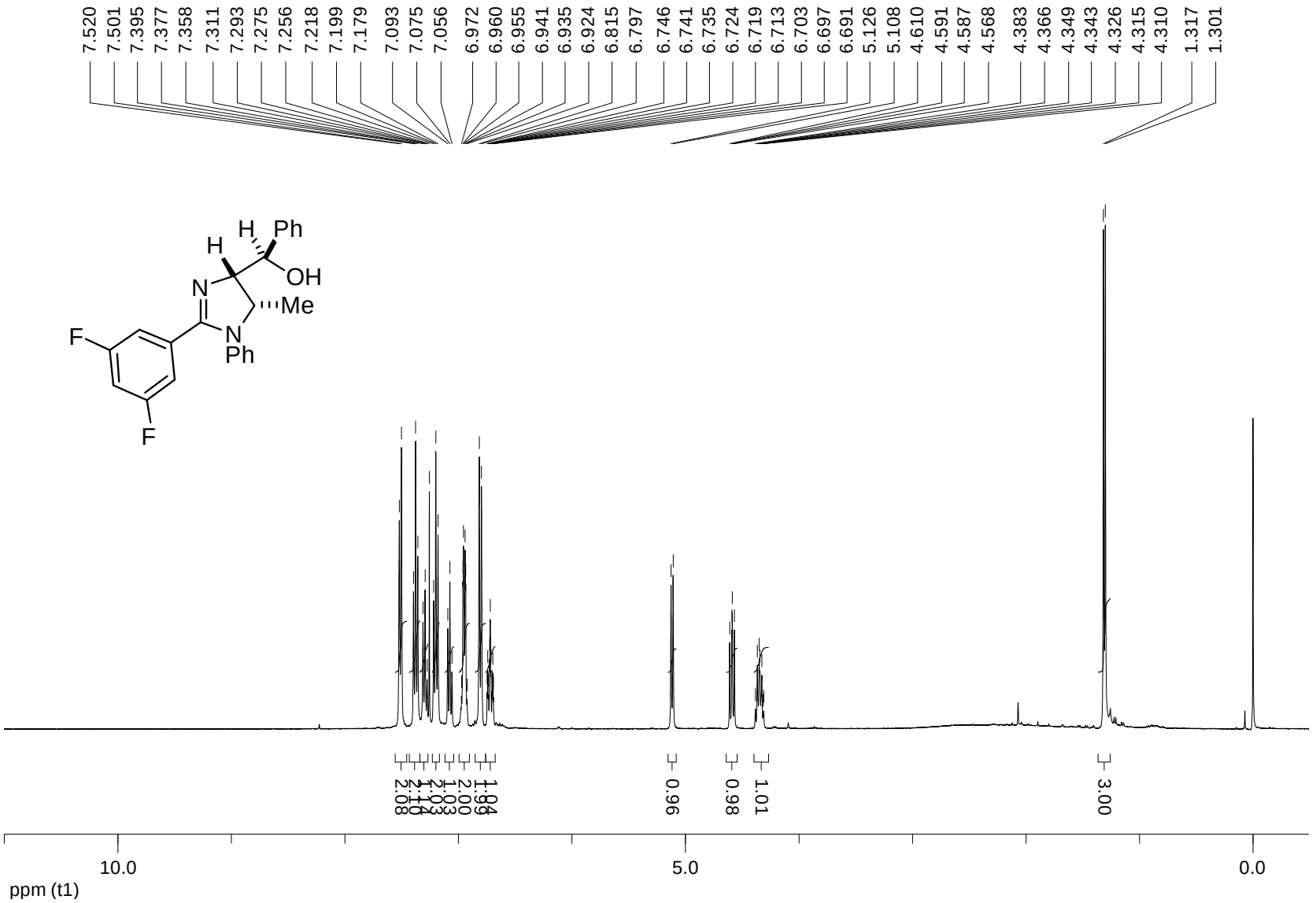
^{1}H NMR spectrum of **3u** (the major stereoisomer) (400 MHz, $CDCl_3$)



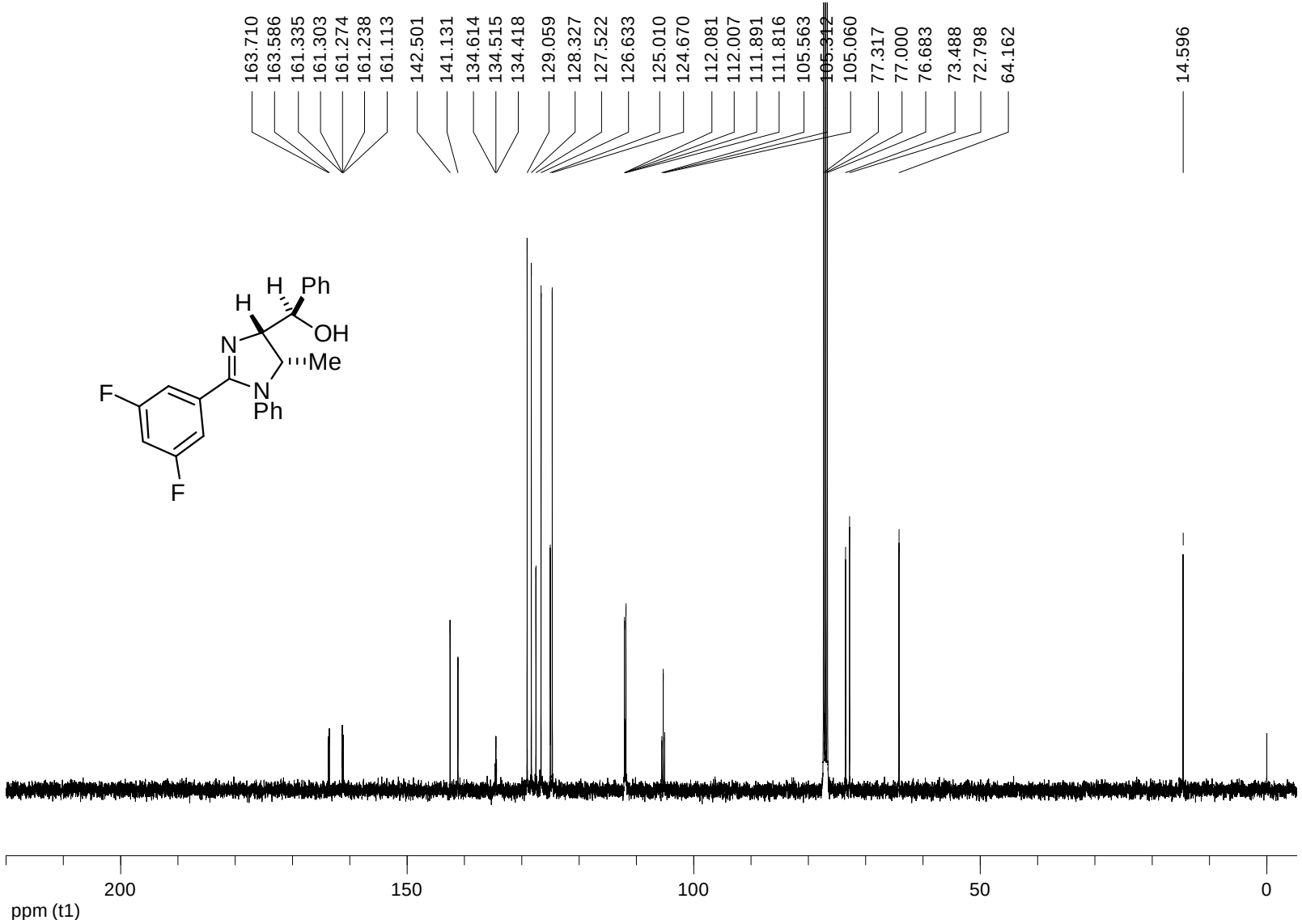
^{13}C NMR spectrum of **3u** (the major stereoisomer) (100 MHz, $CDCl_3$)



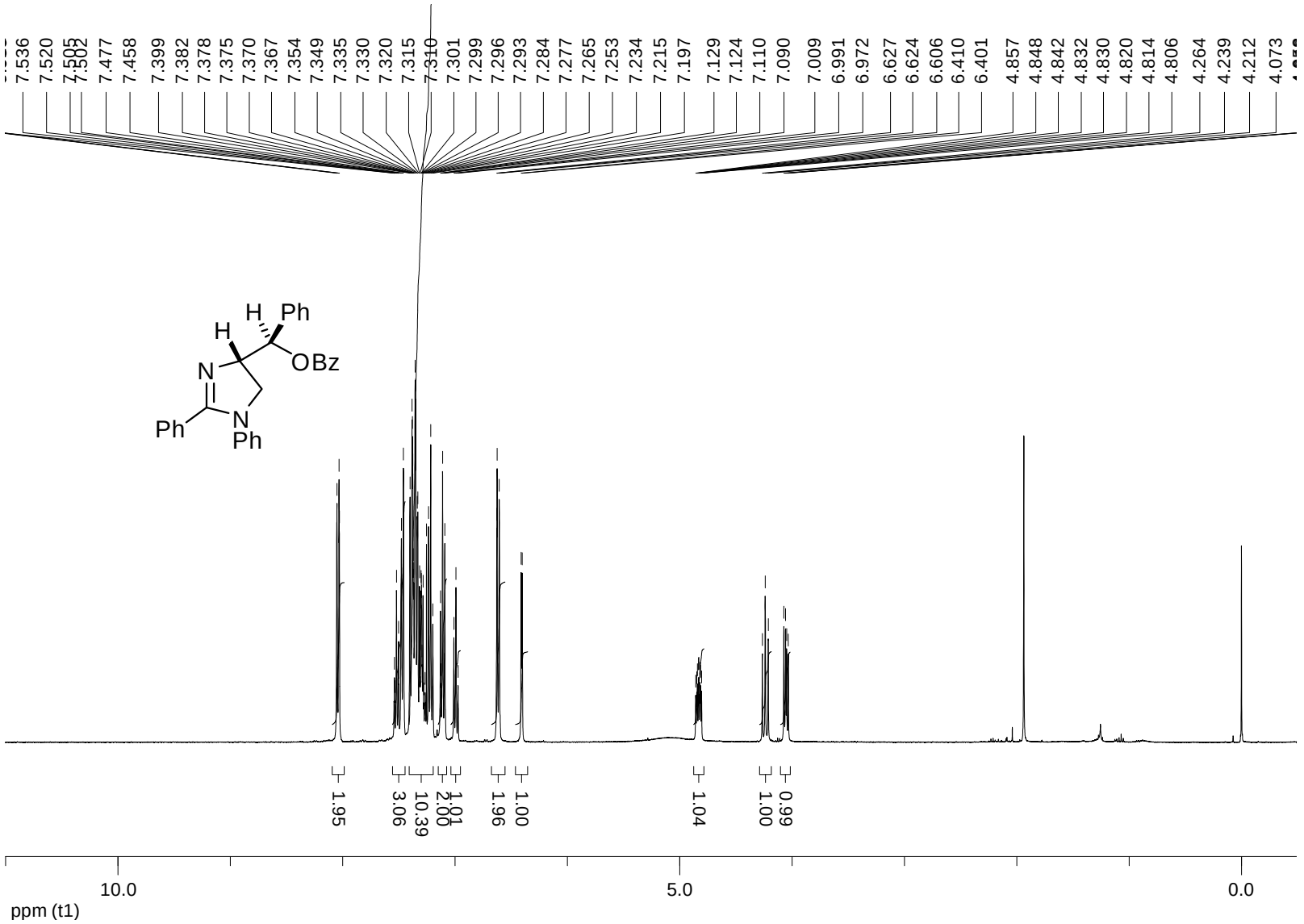
^{1}H NMR spectrum of **3u'** (the minor stereoisomer) (400 MHz, $CDCl_3$)



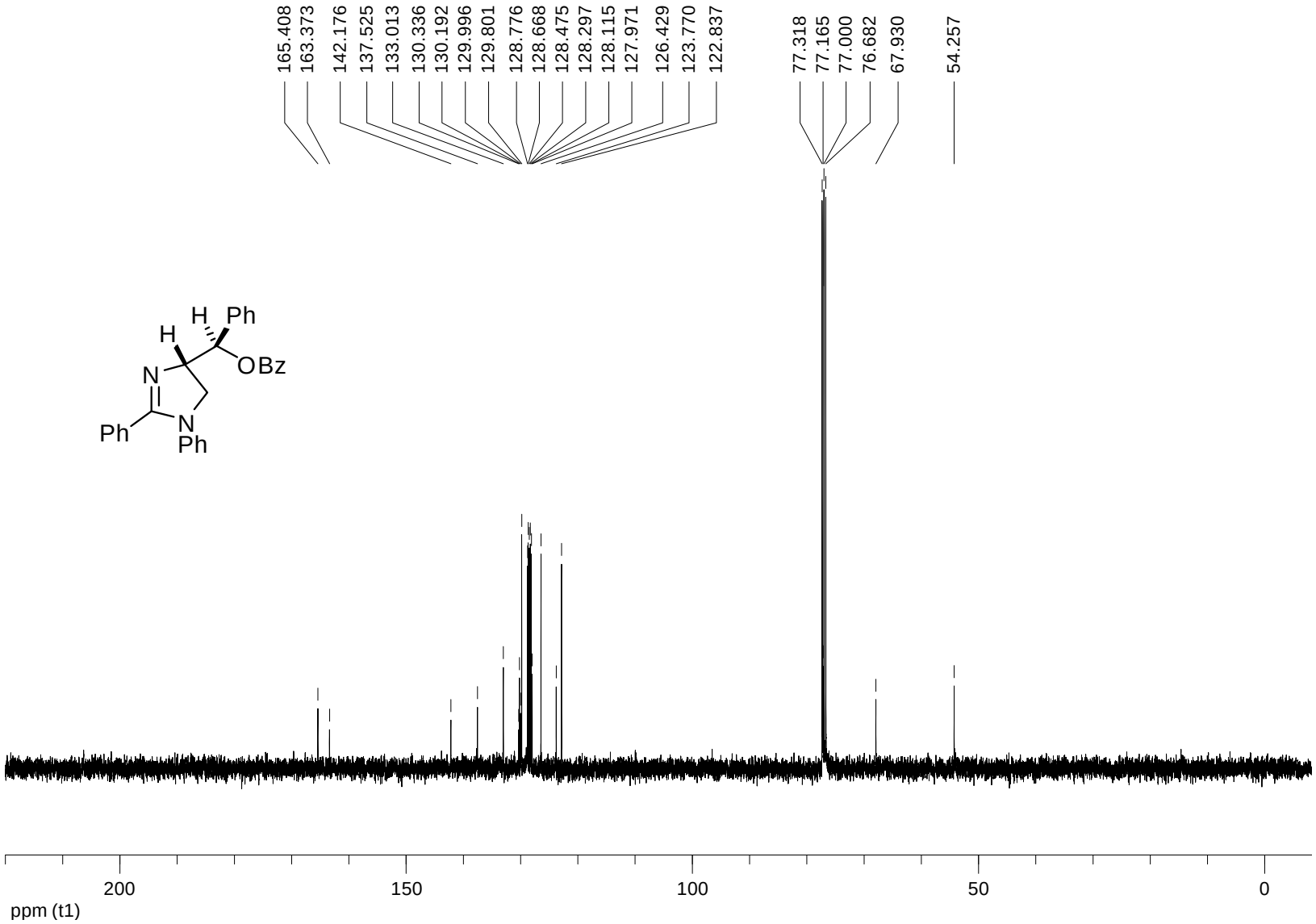
^{13}C NMR spectrum of **3u'** (the minor stereoisomer) (100 MHz, $CDCl_3$)



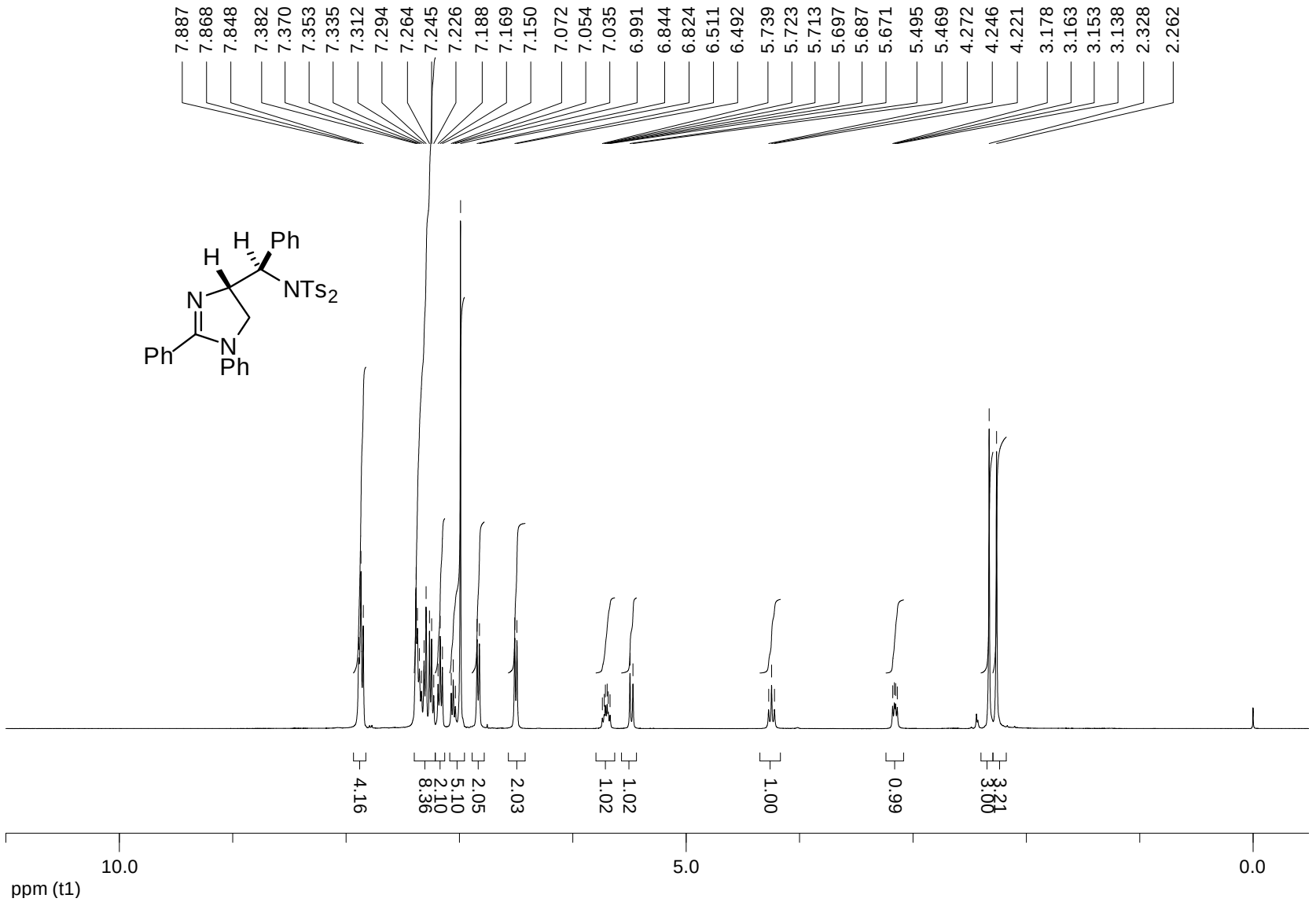
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



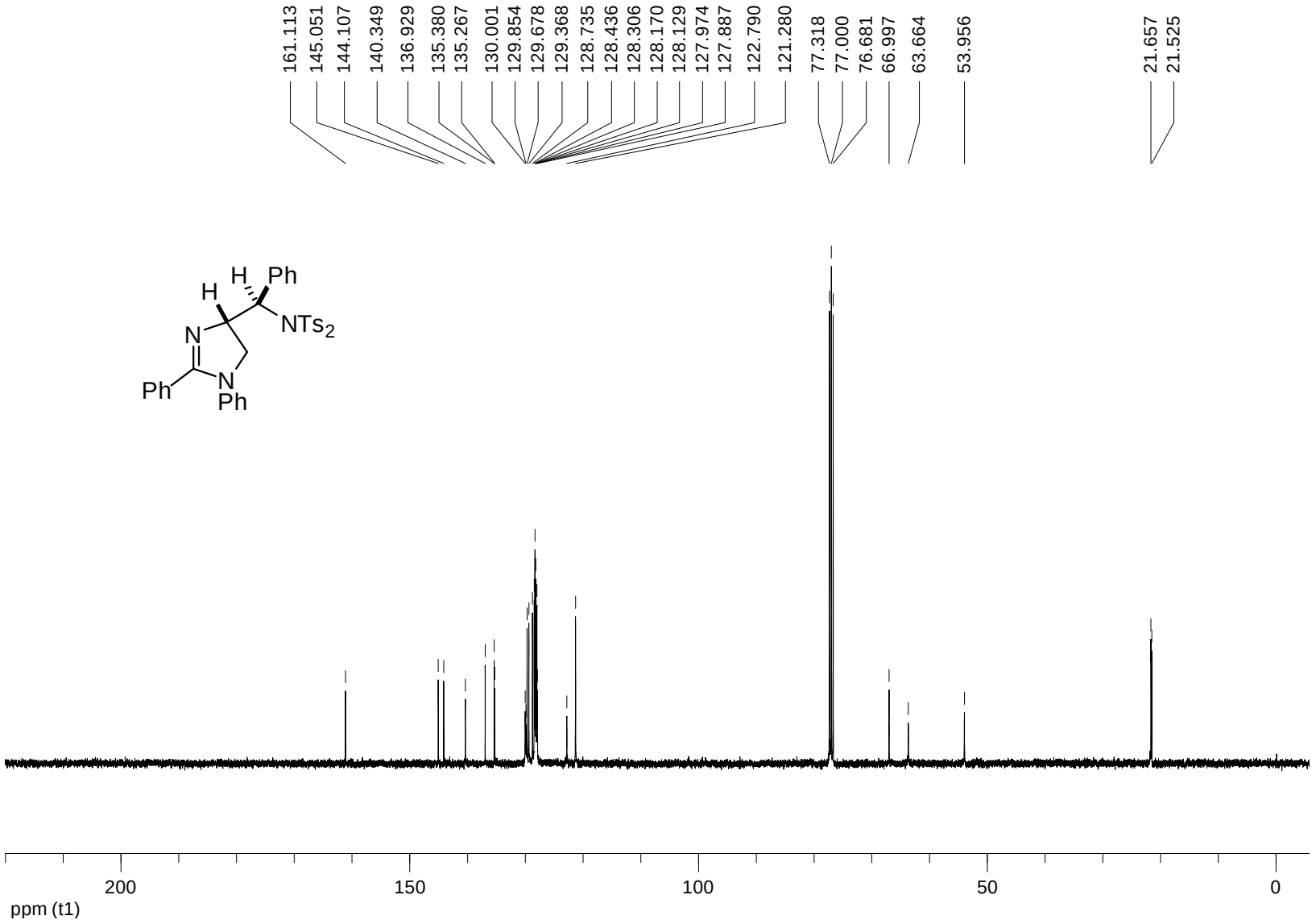
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



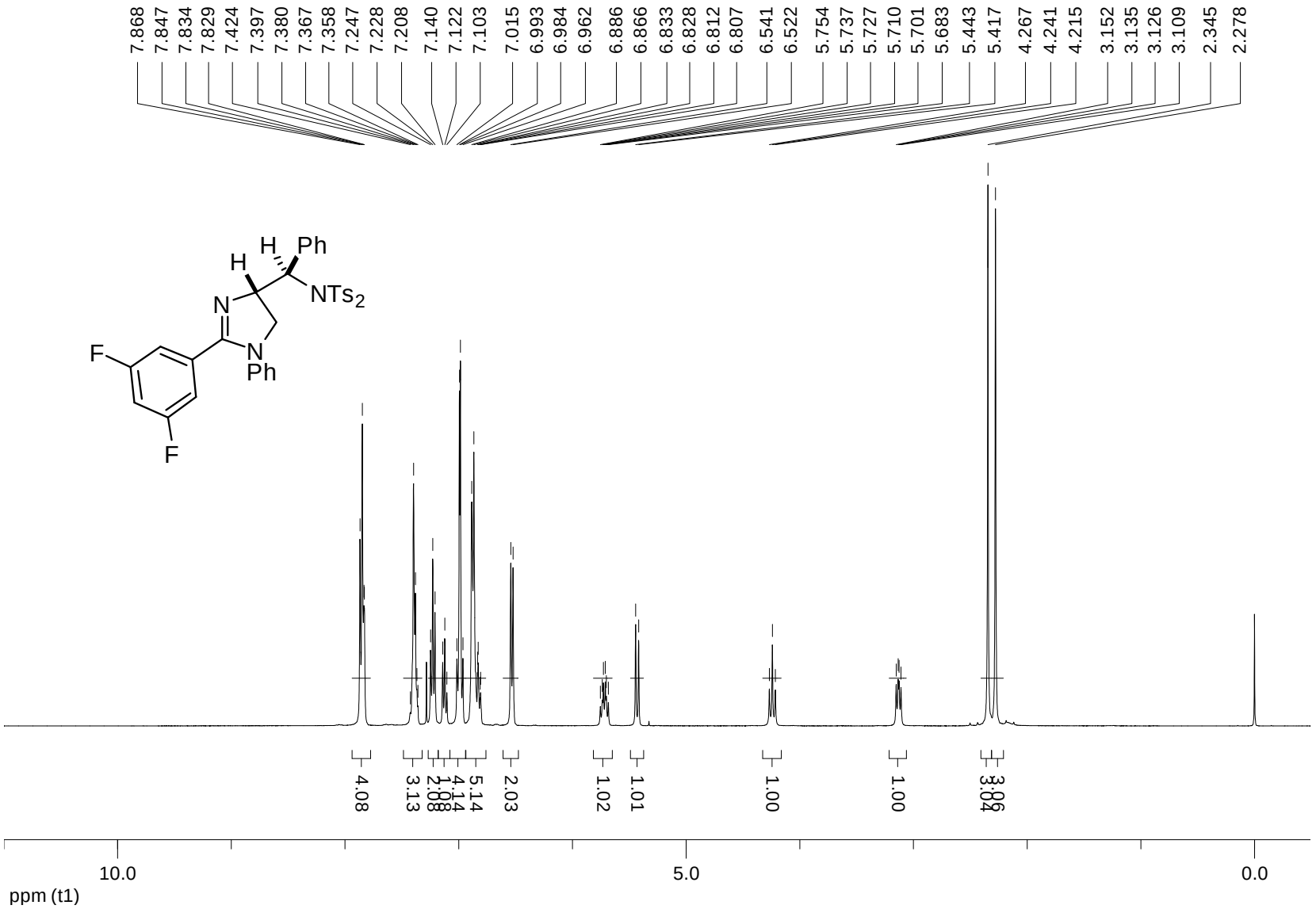
^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



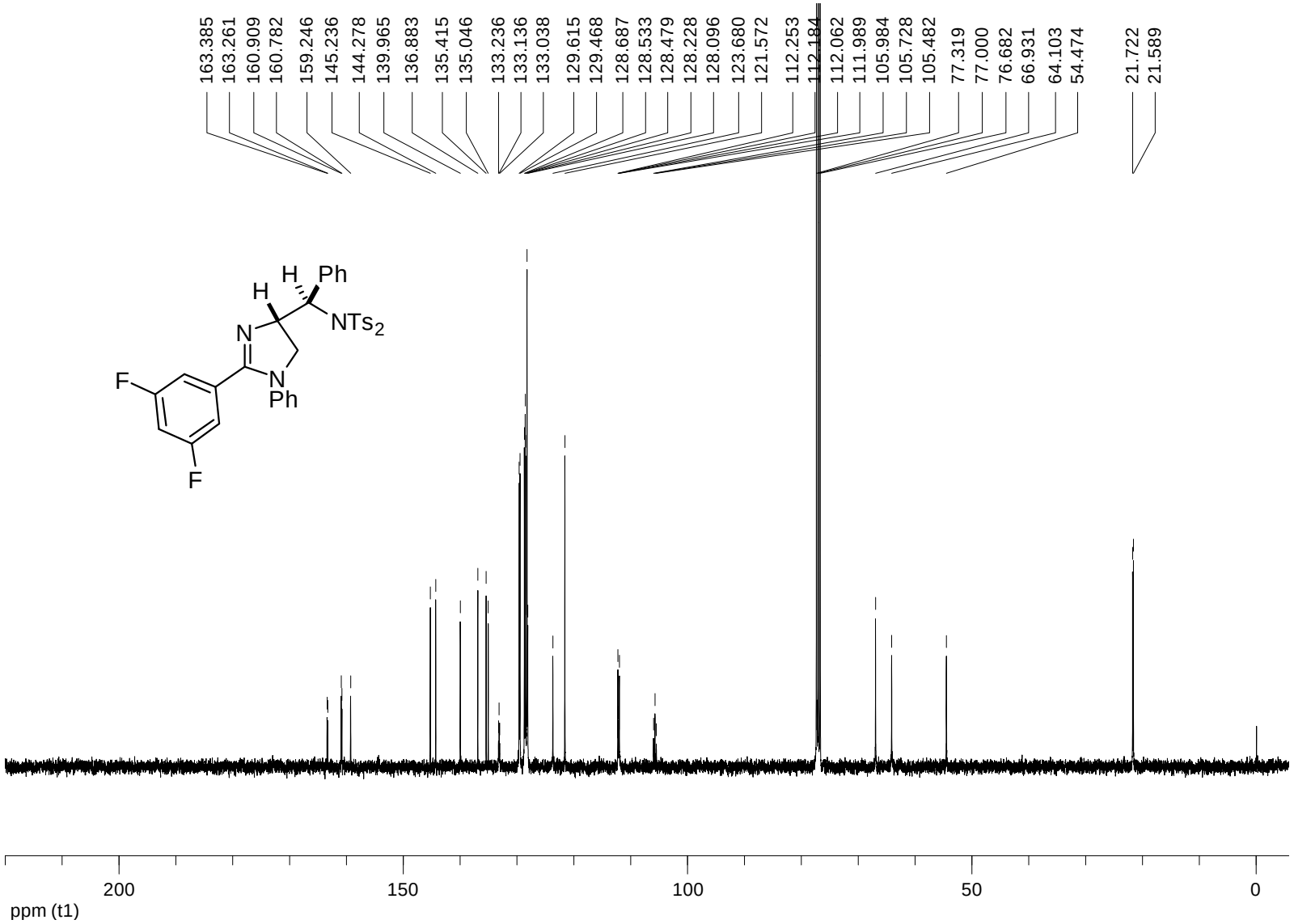
^{13}C NMR spectrum of **6a** (100 MHz, $CDCl_3$)



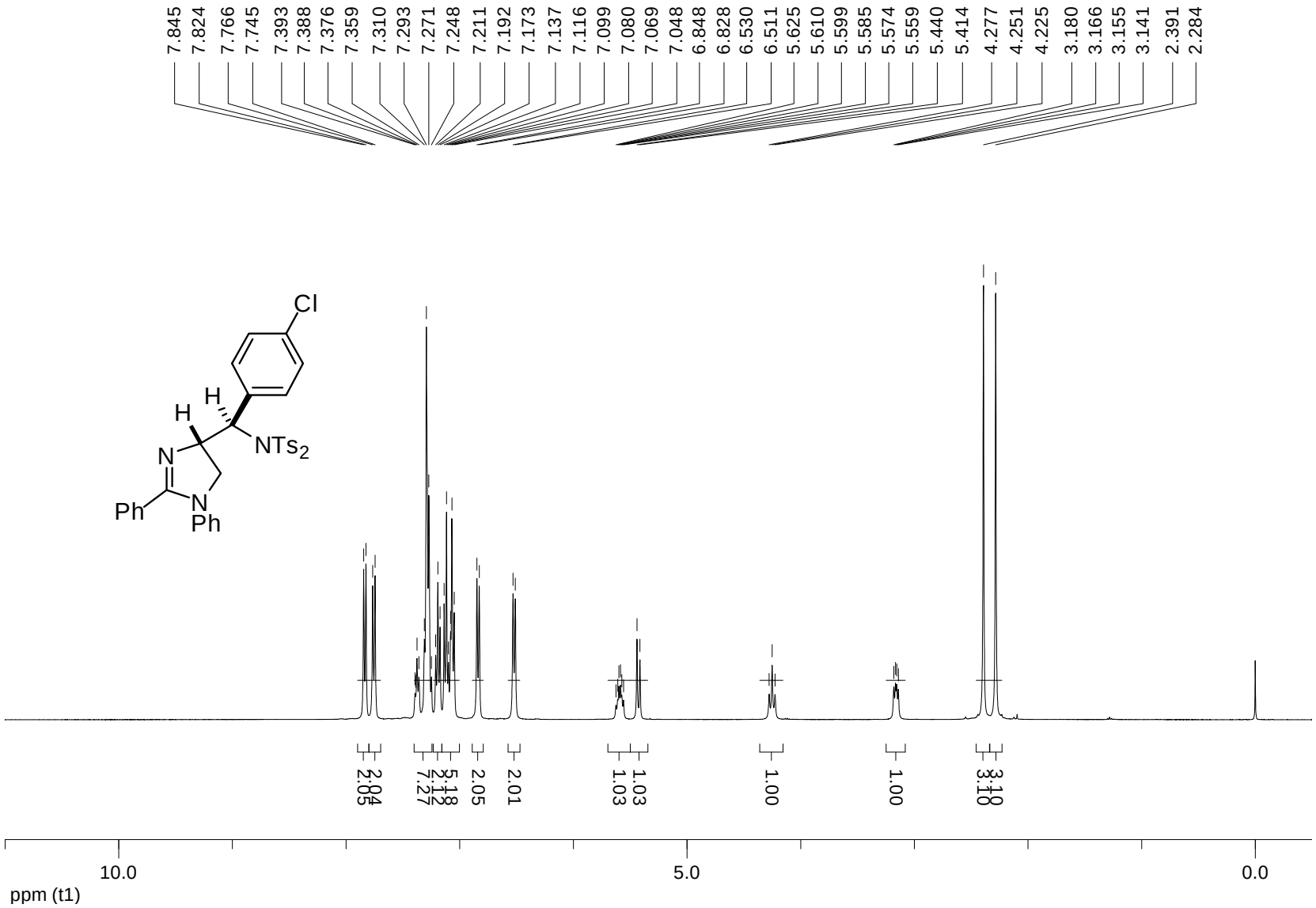
^{1}H NMR spectrum of **6c** (400 MHz, $CDCl_3$)



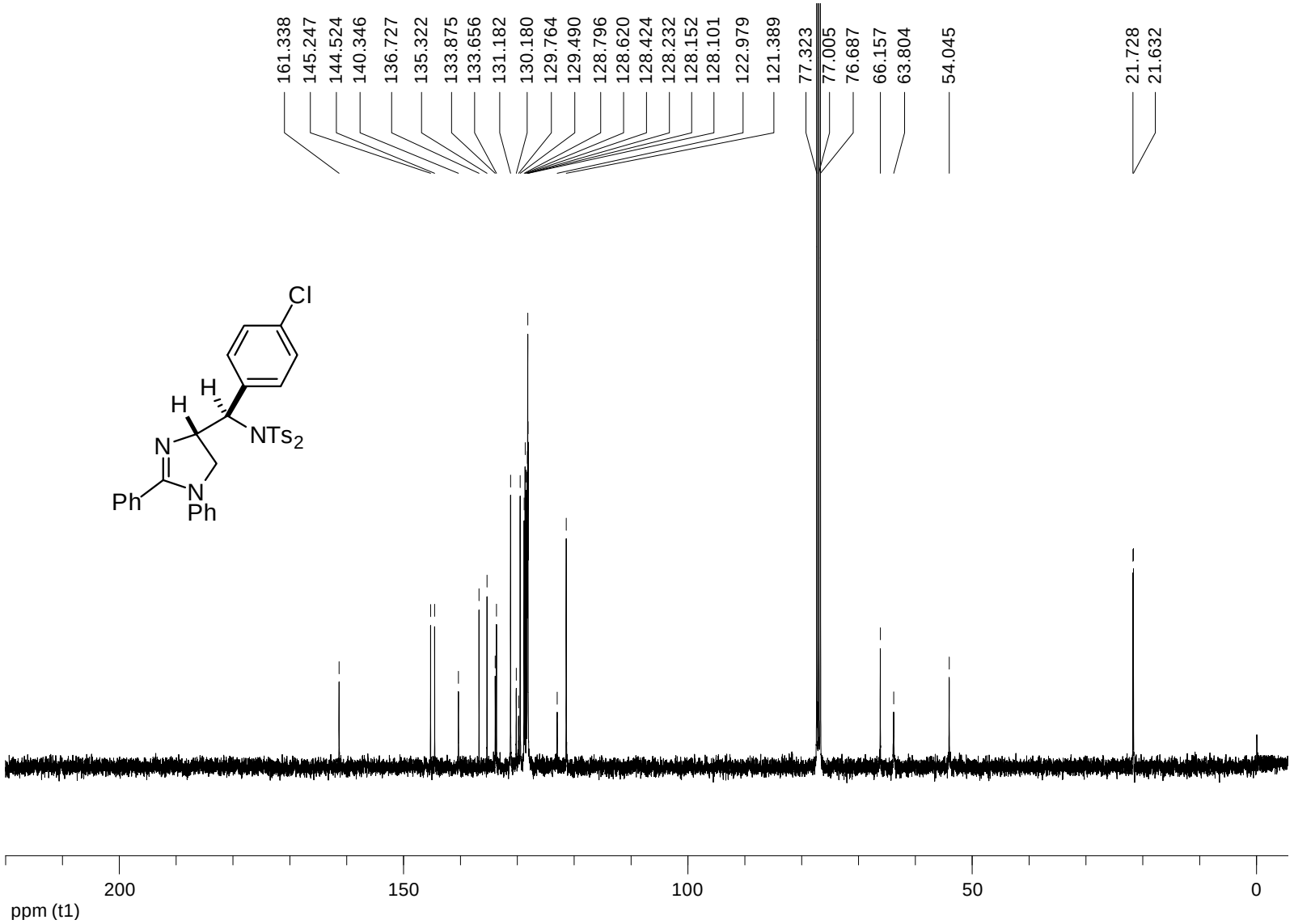
^{13}C NMR spectrum of **6c** (100 MHz, $CDCl_3$)



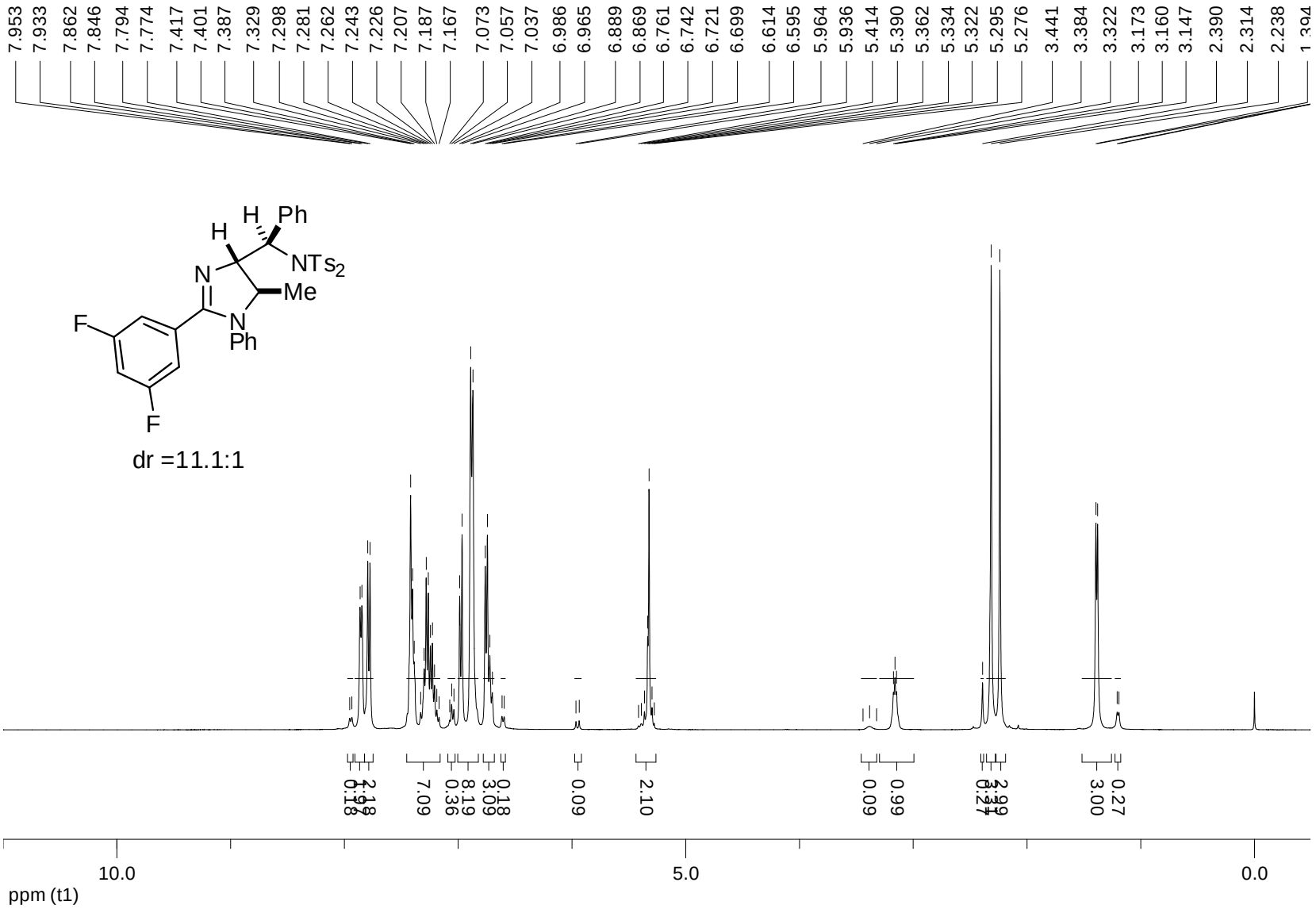
^{1}H NMR spectrum of **6g** (400 MHz, $CDCl_3$)



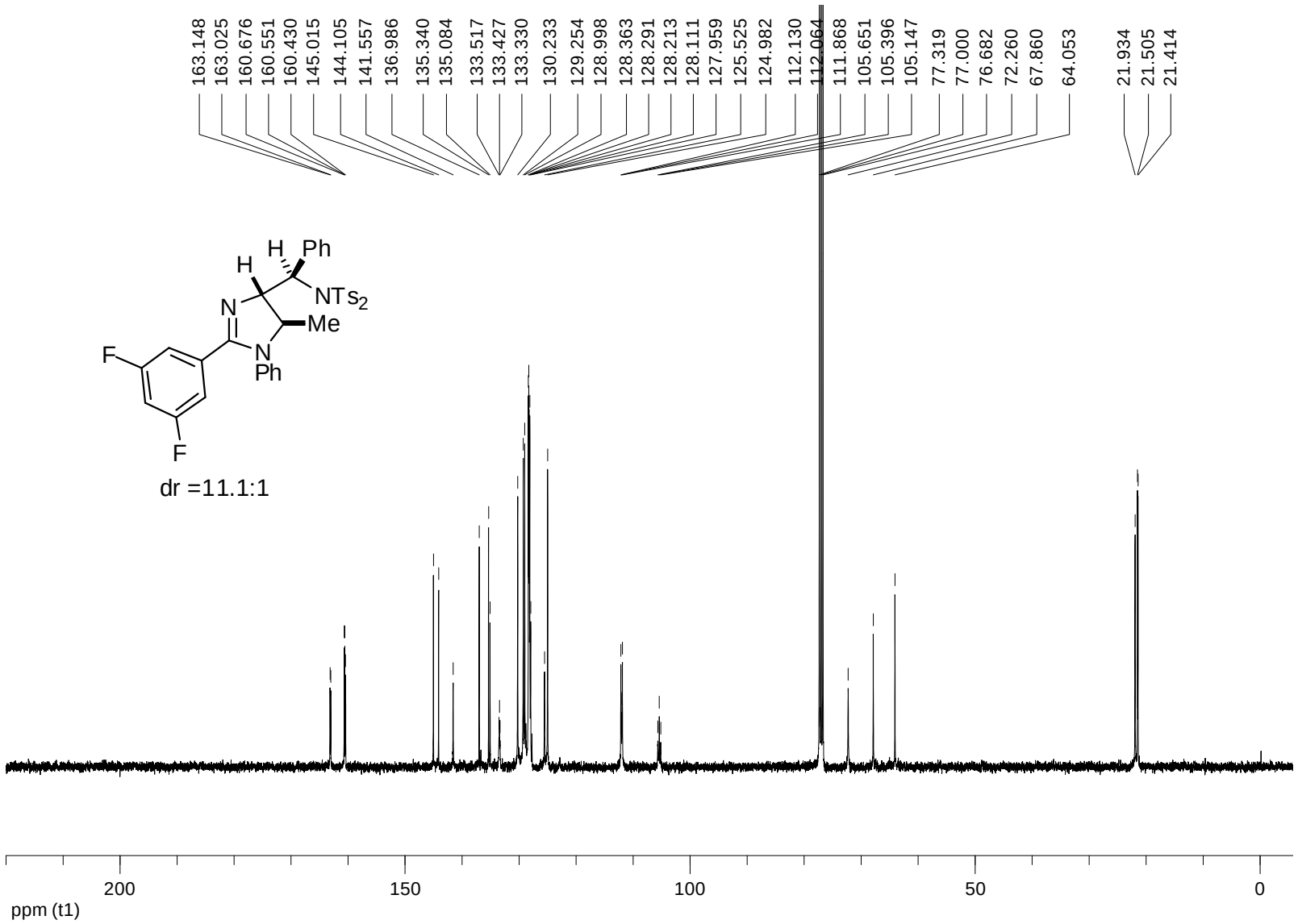
^{13}C NMR spectrum of **6g** (100 MHz, $CDCl_3$)



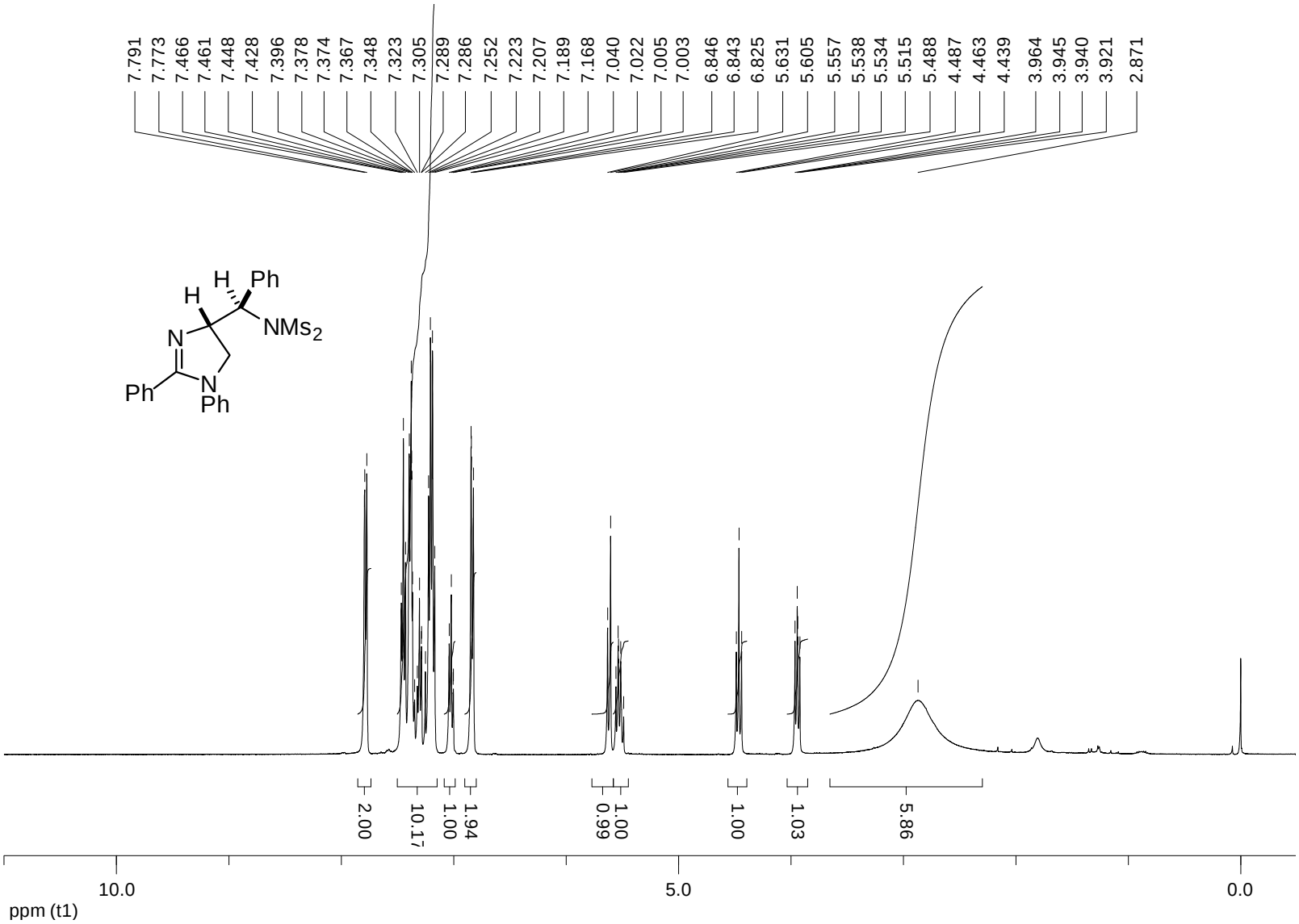
^{1}H NMR spectrum of **6u** (dr =11.1:1) (400 MHz, $CDCl_3$)



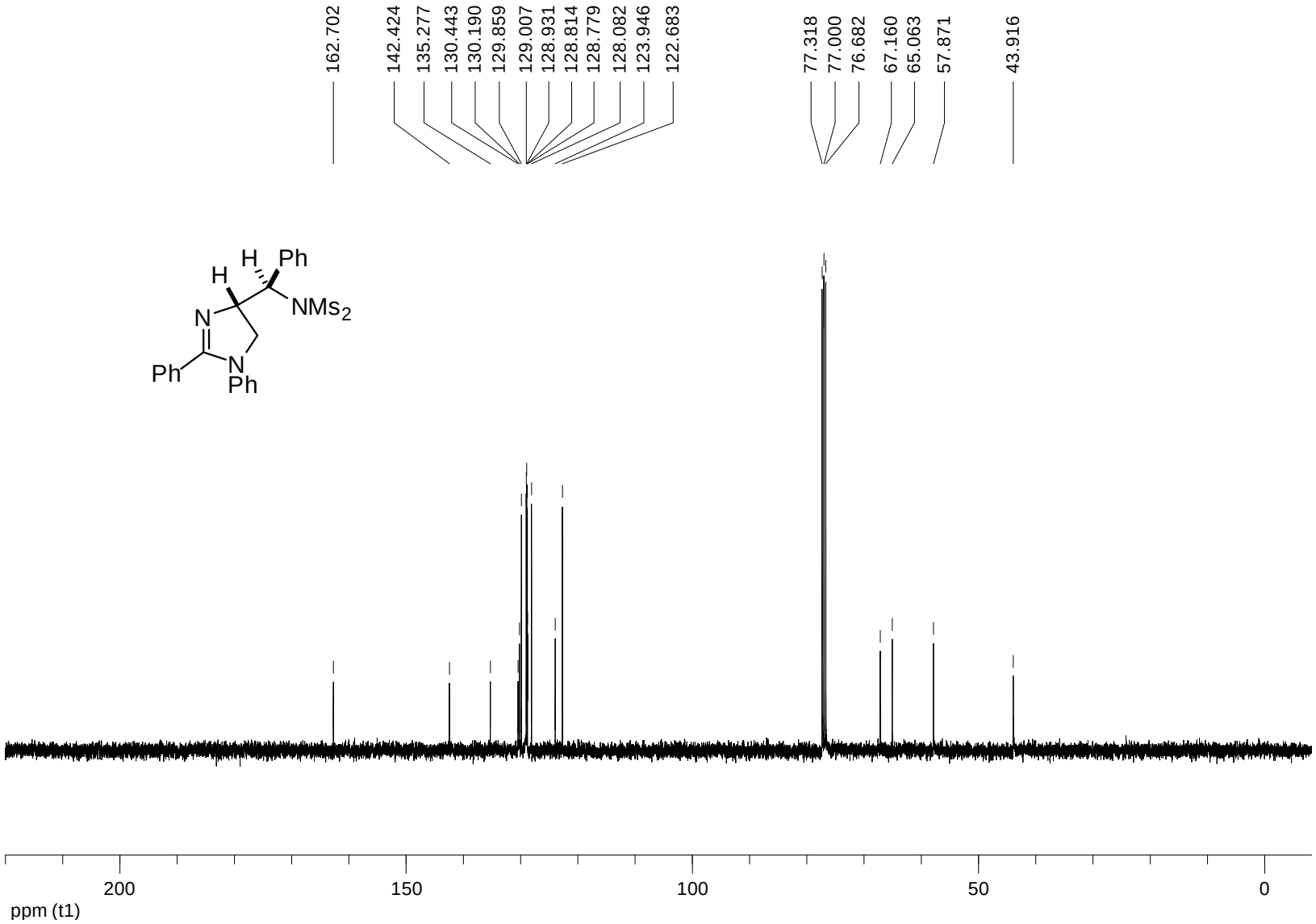
^{13}C NMR spectrum of **6u** (dr =11.1:1) (100 MHz, $CDCl_3$)



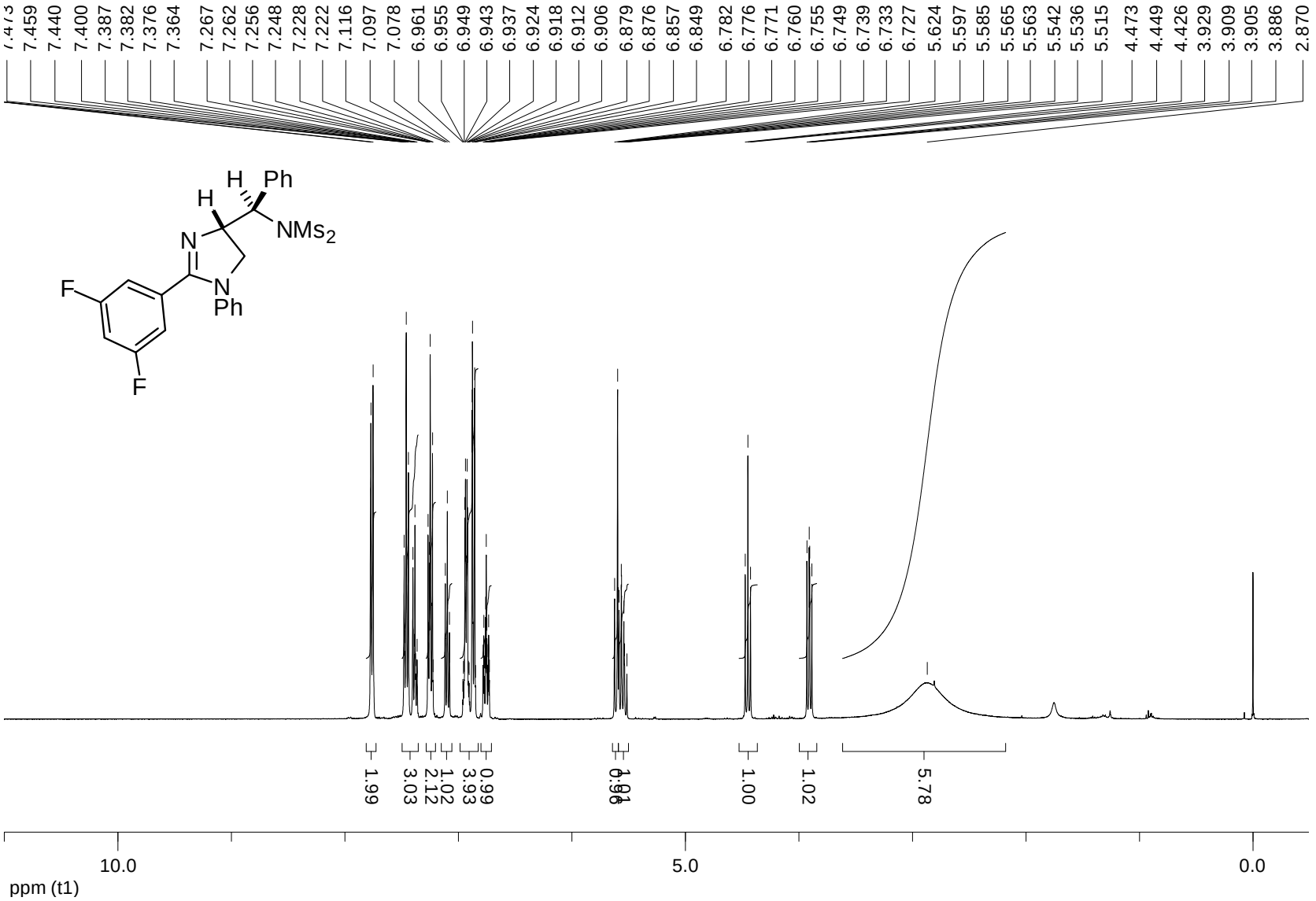
^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$)



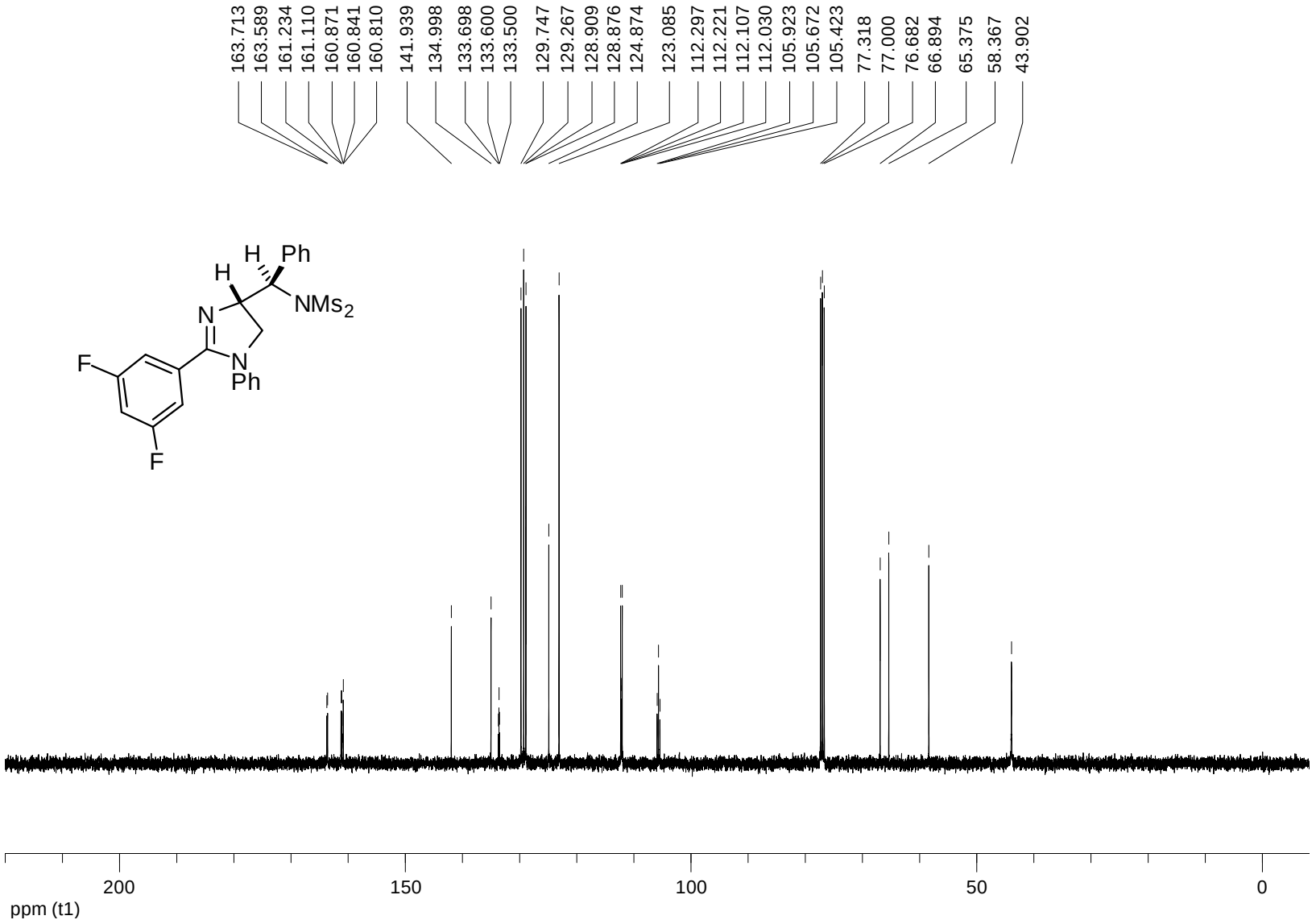
^{13}C NMR spectrum of **7a** (100 MHz, $CDCl_3$)



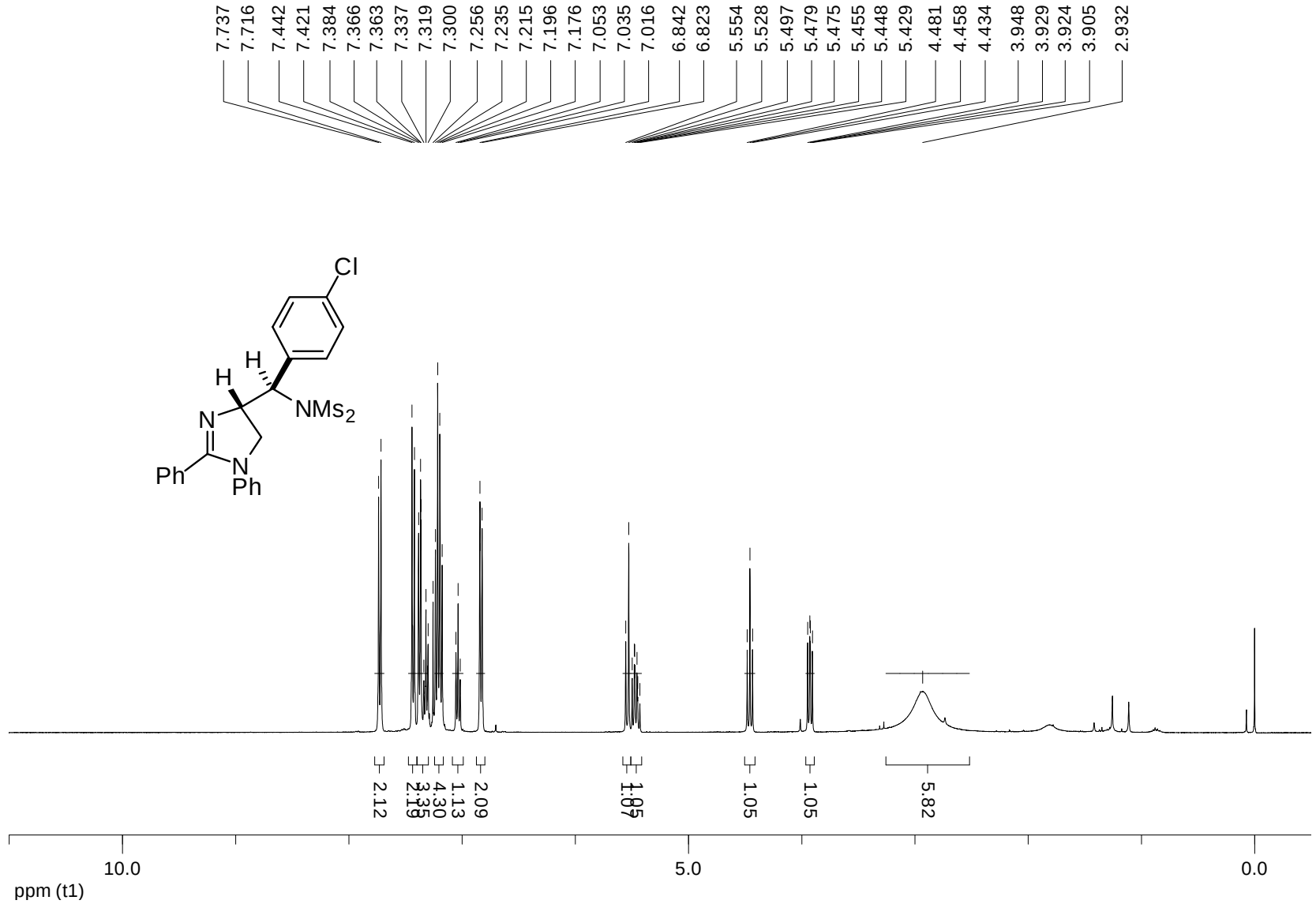
^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$)



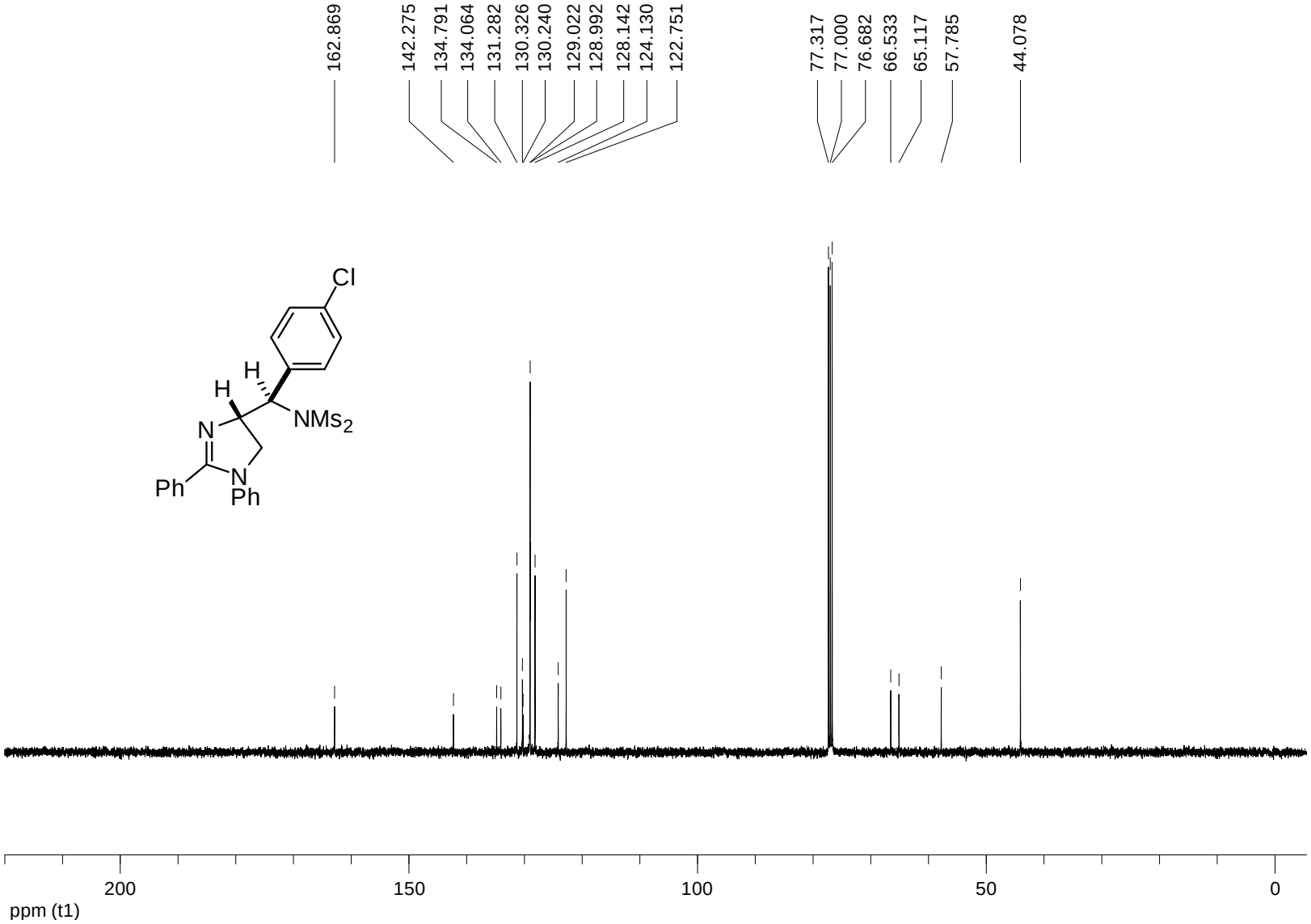
^{13}C NMR spectrum of **7c** (100 MHz, $CDCl_3$)



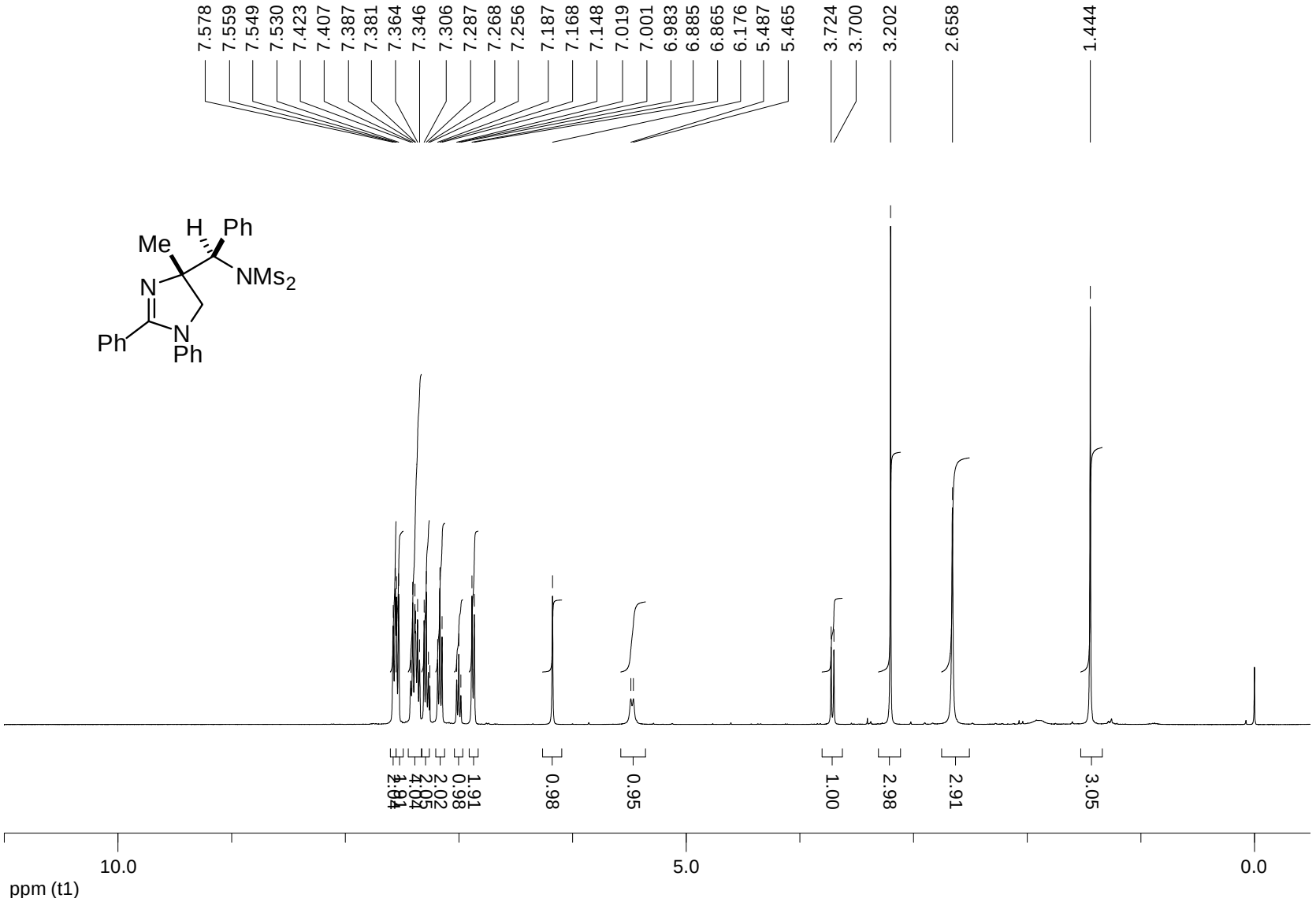
^{1}H NMR spectrum of **7g** (400 MHz, $CDCl_3$)



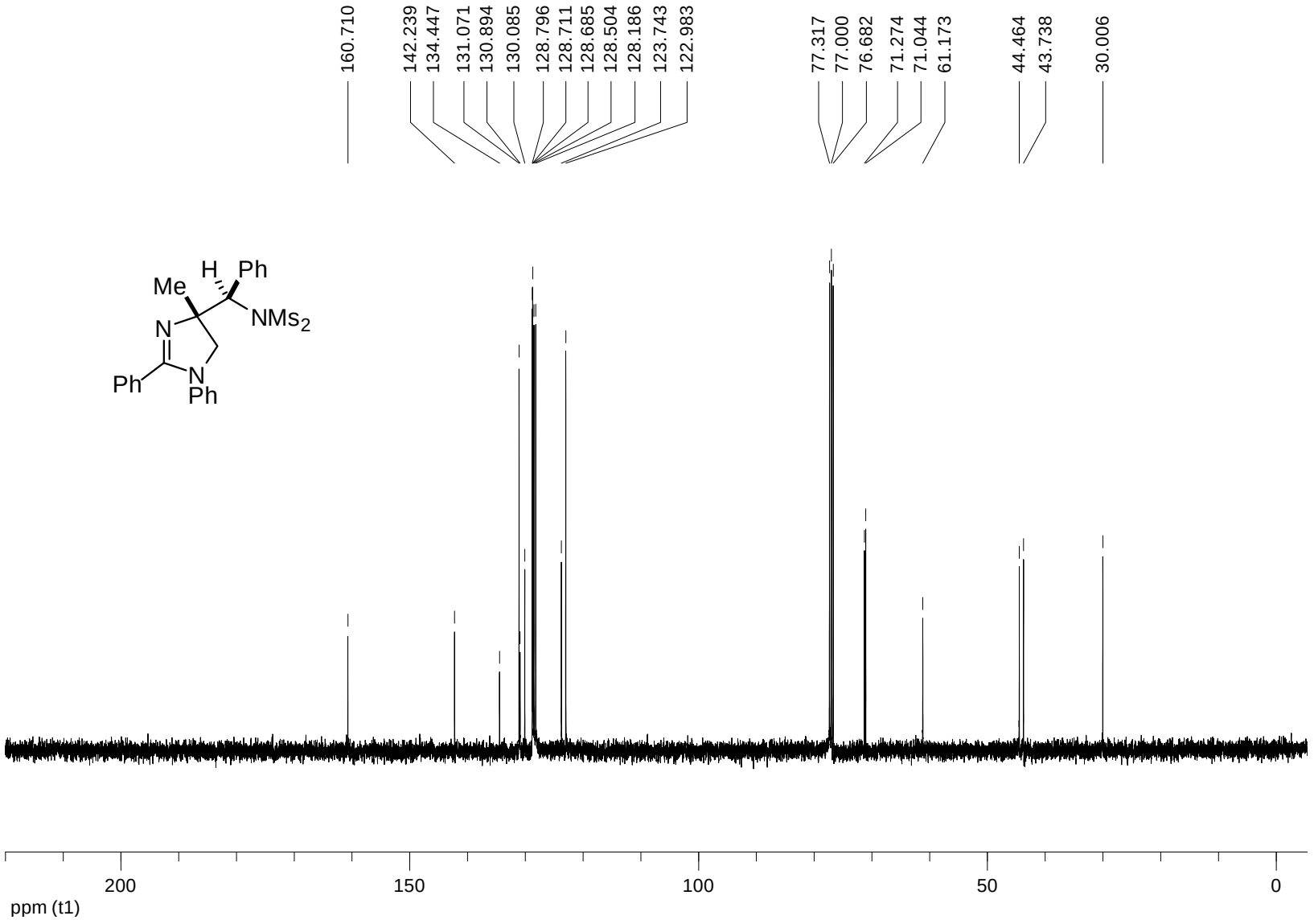
^{13}C NMR spectrum of **7g** (100 MHz, $CDCl_3$)



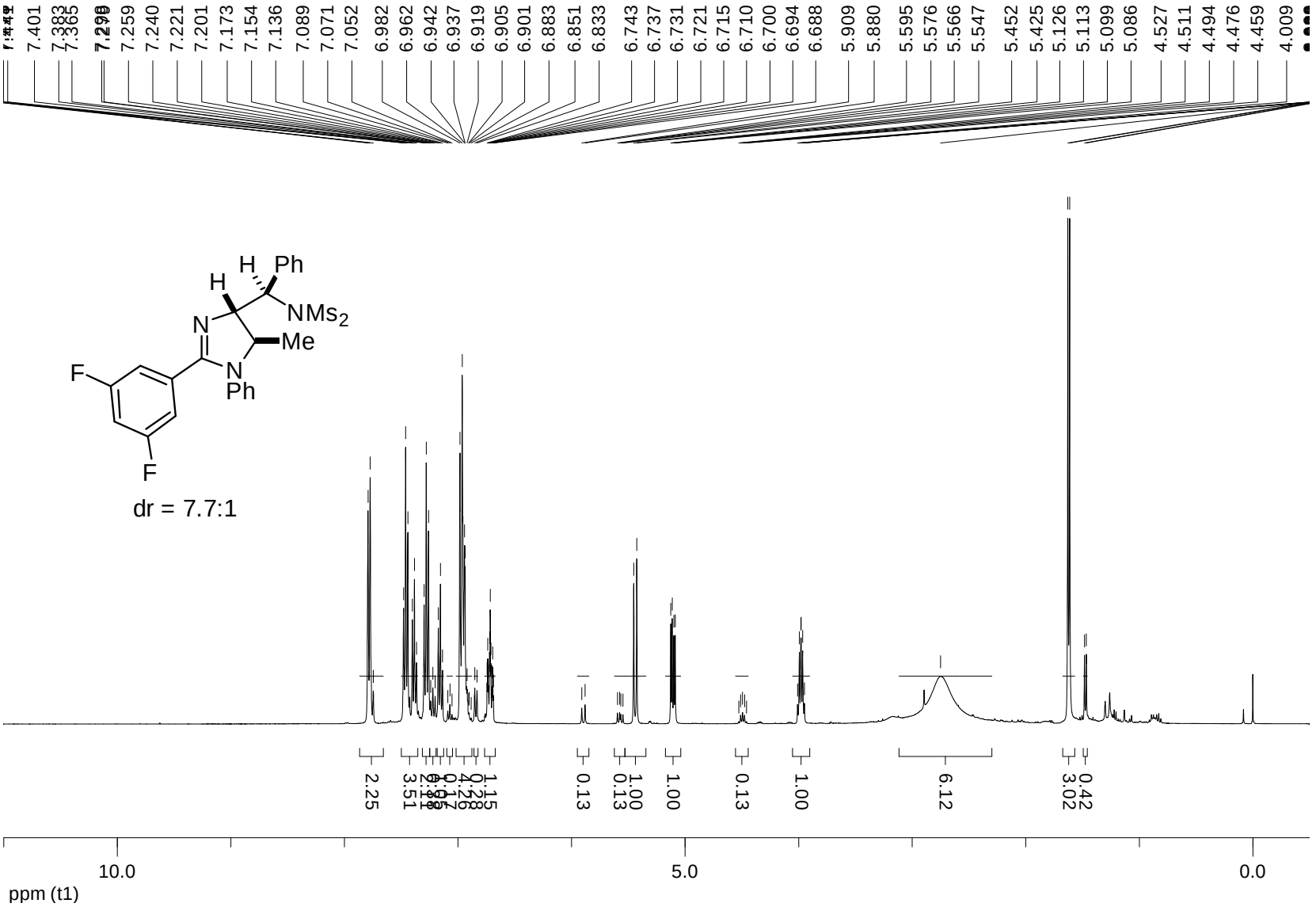
^{1}H NMR spectrum of **7p** (400 MHz, $CDCl_3$)



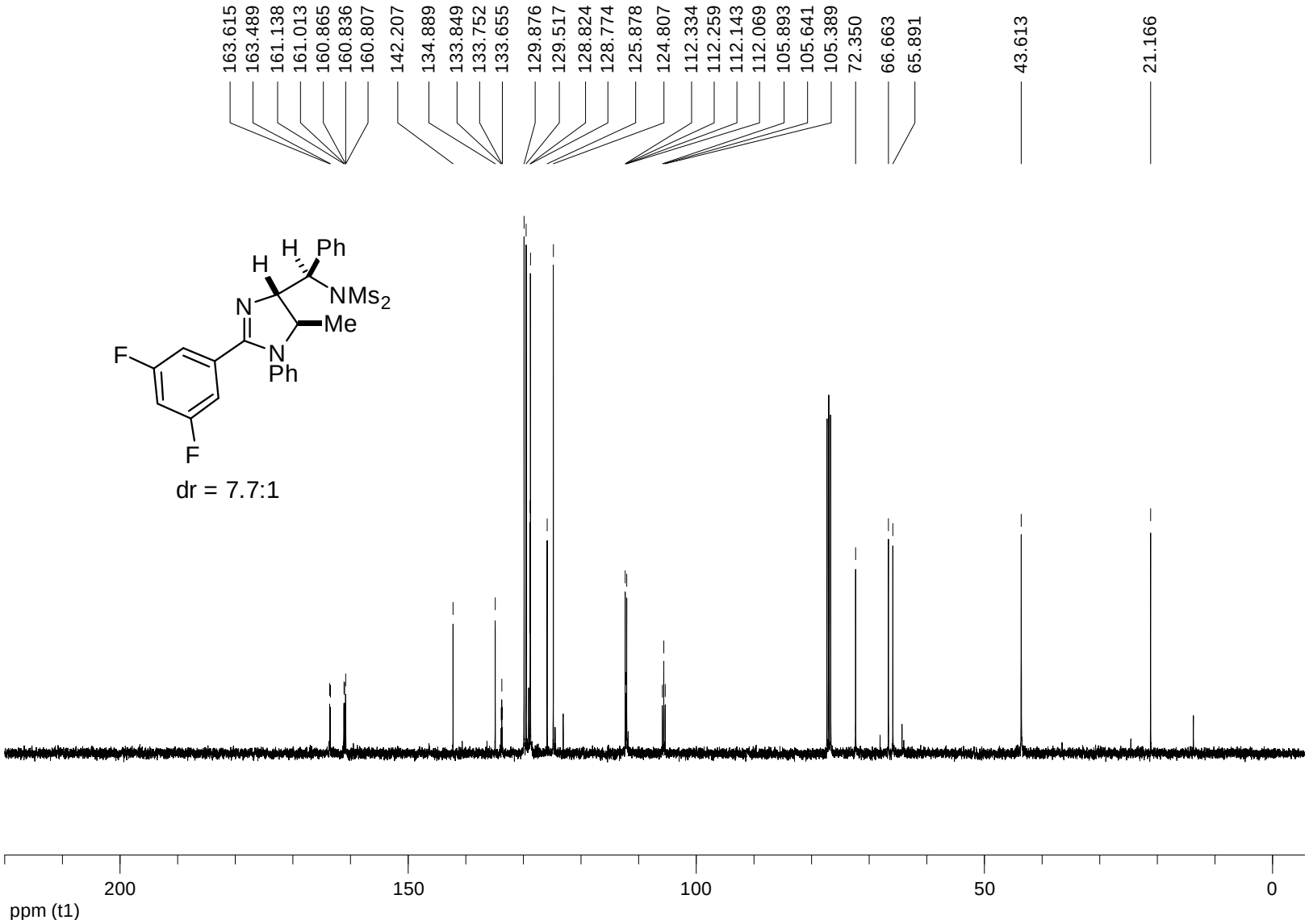
^{13}C NMR spectrum of **7p** (100 MHz, $CDCl_3$)



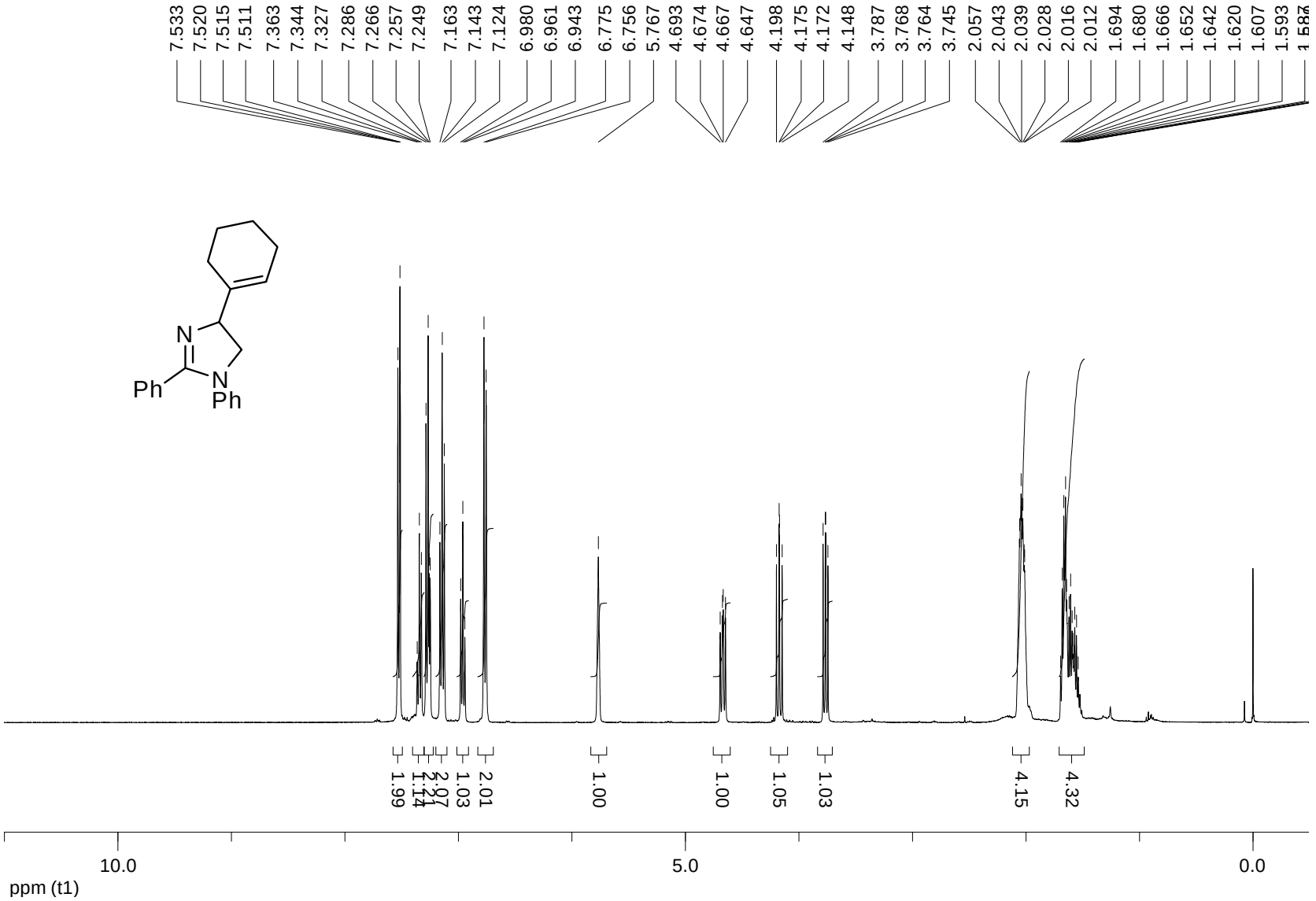
^{1}H NMR spectrum of **7u** (dr = 7.7:1) (400 MHz, $CDCl_3$)



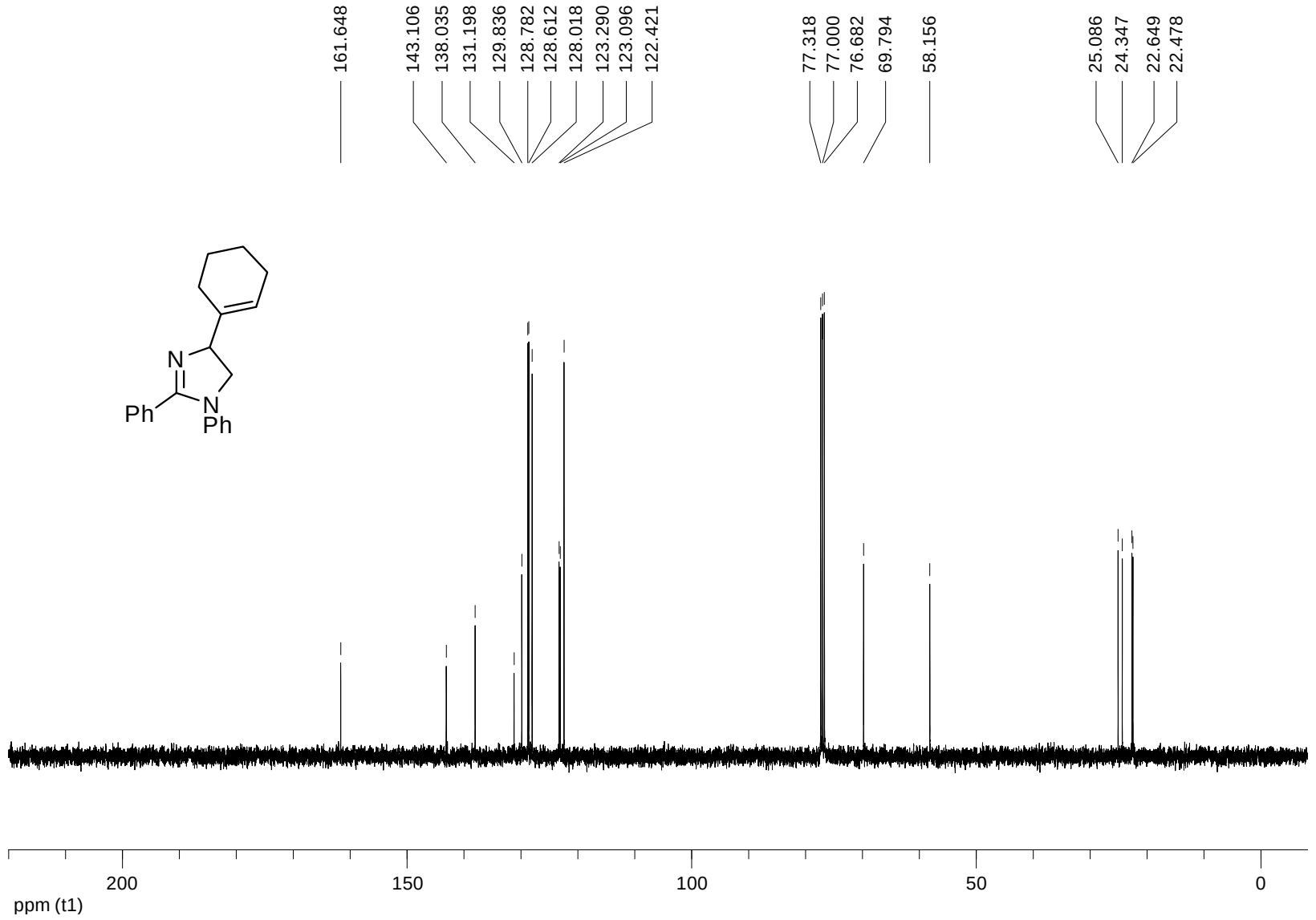
^{13}C NMR spectrum of **7u** (dr = 7.7:1) (100 MHz, $CDCl_3$)



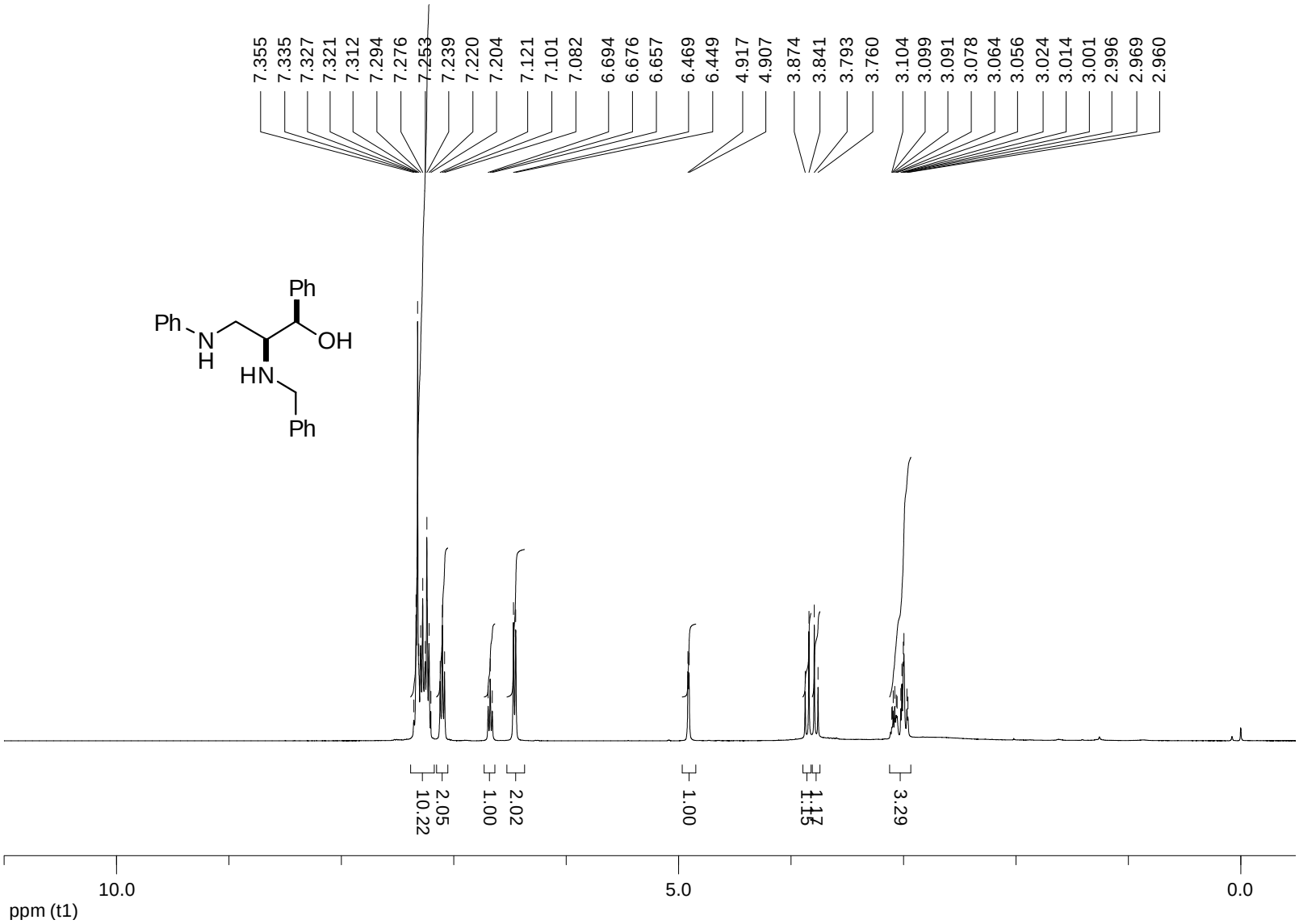
^{1}H NMR spectrum of **8m** (400 MHz, $CDCl_3$)



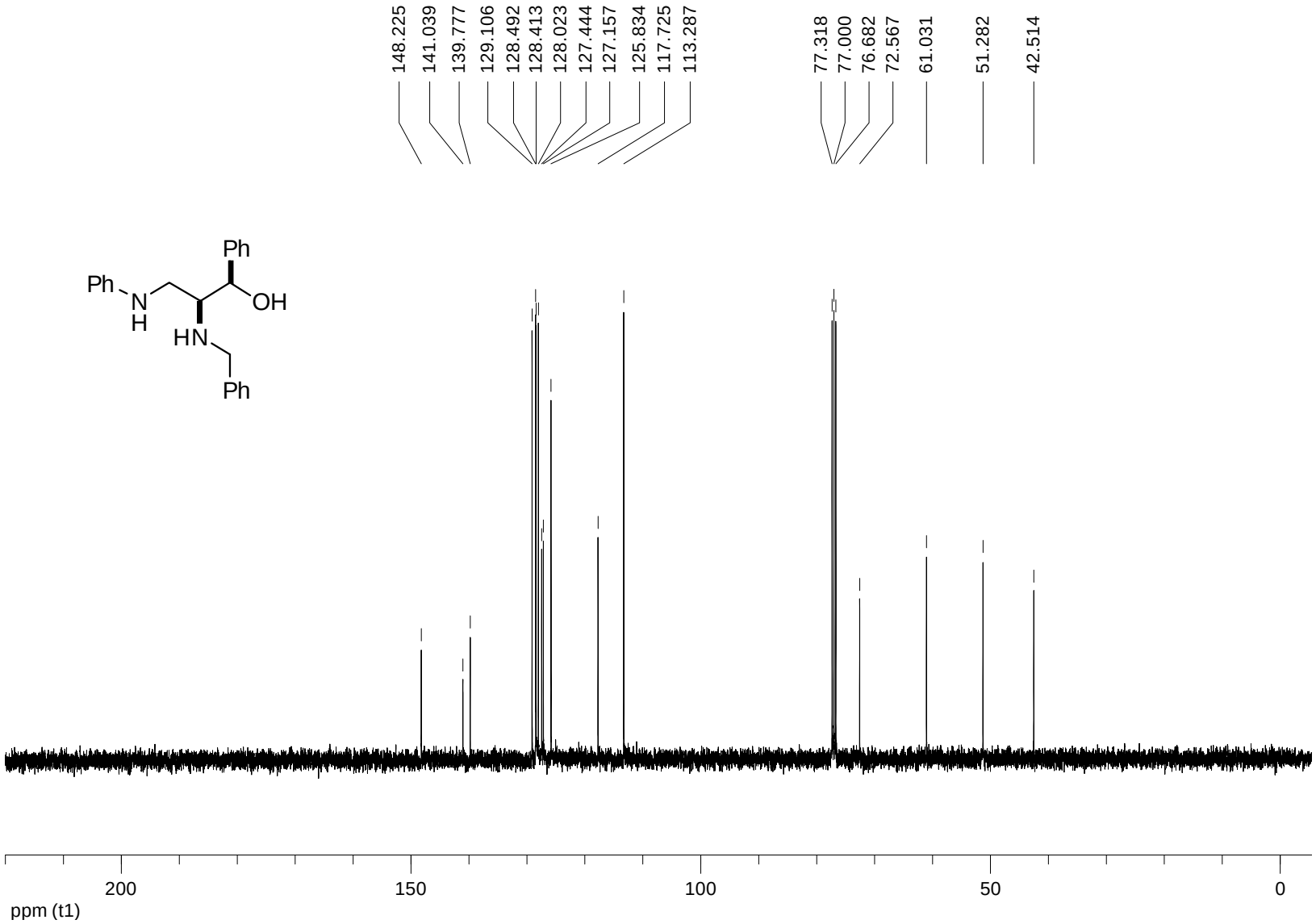
^{13}C NMR spectrum of **8m** (100 MHz, $CDCl_3$)



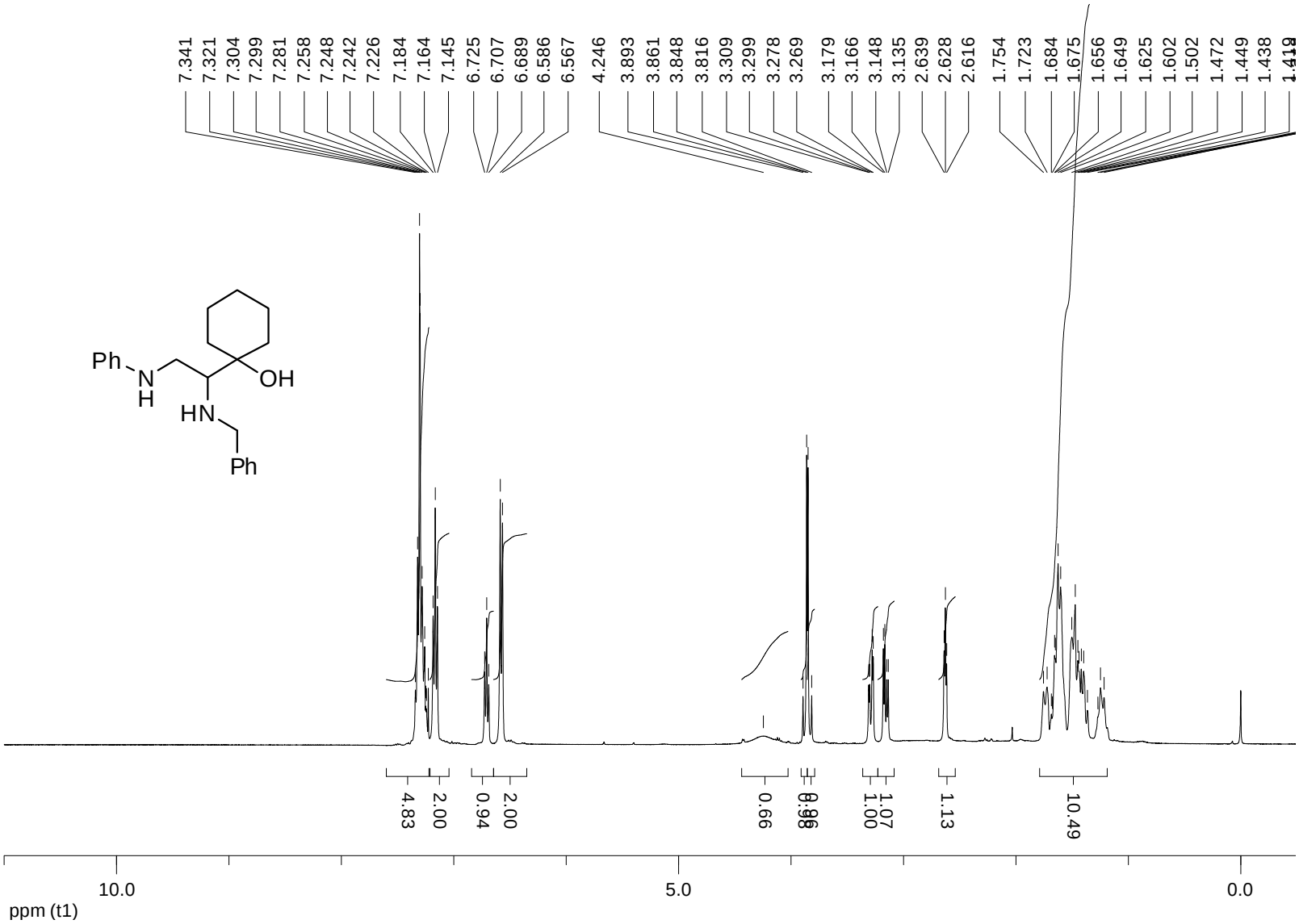
^{1}H NMR spectrum of **9a** (400 MHz, $CDCl_3$)



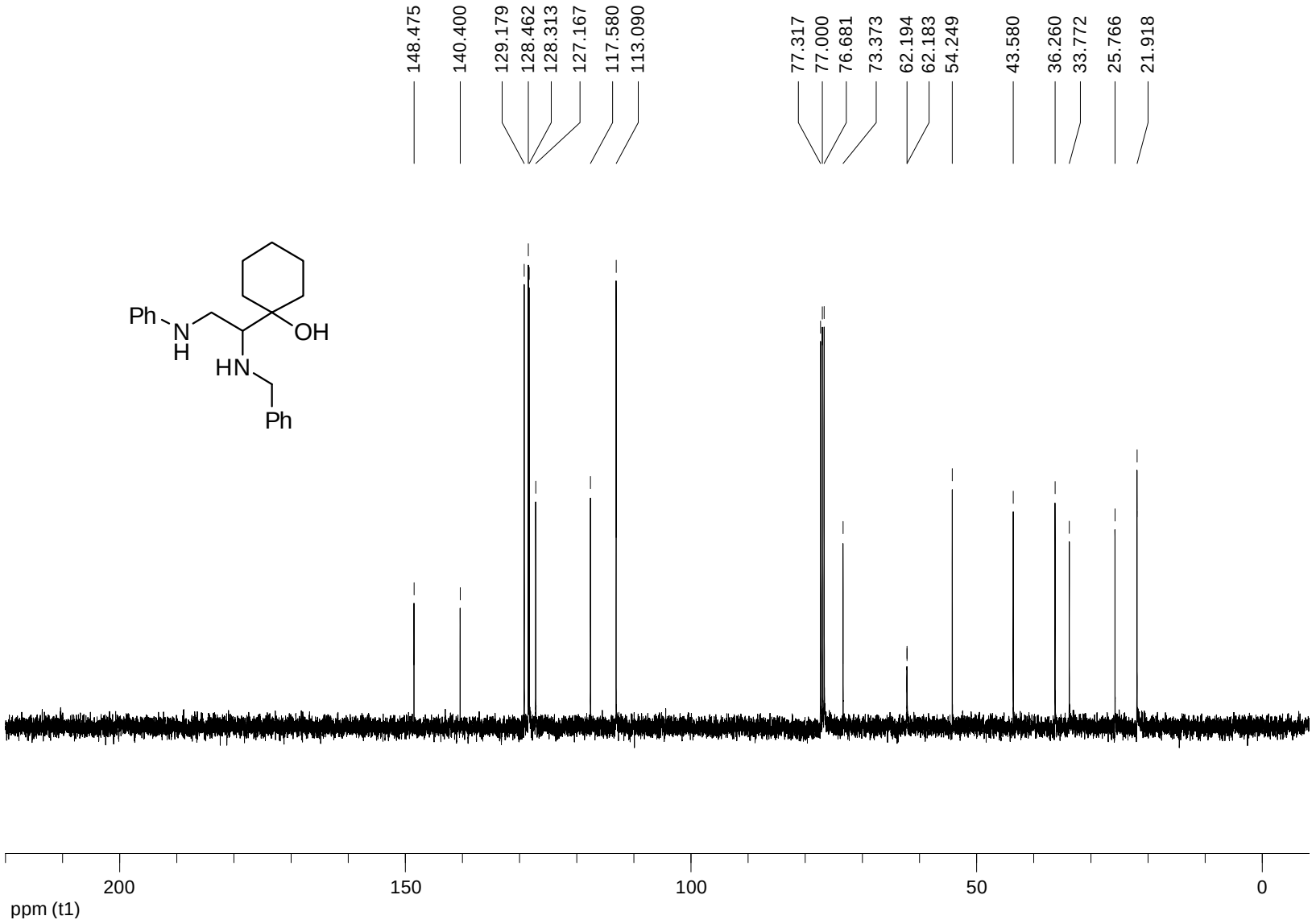
^{13}C NMR spectrum of **9a**(100 MHz, $CDCl_3$)



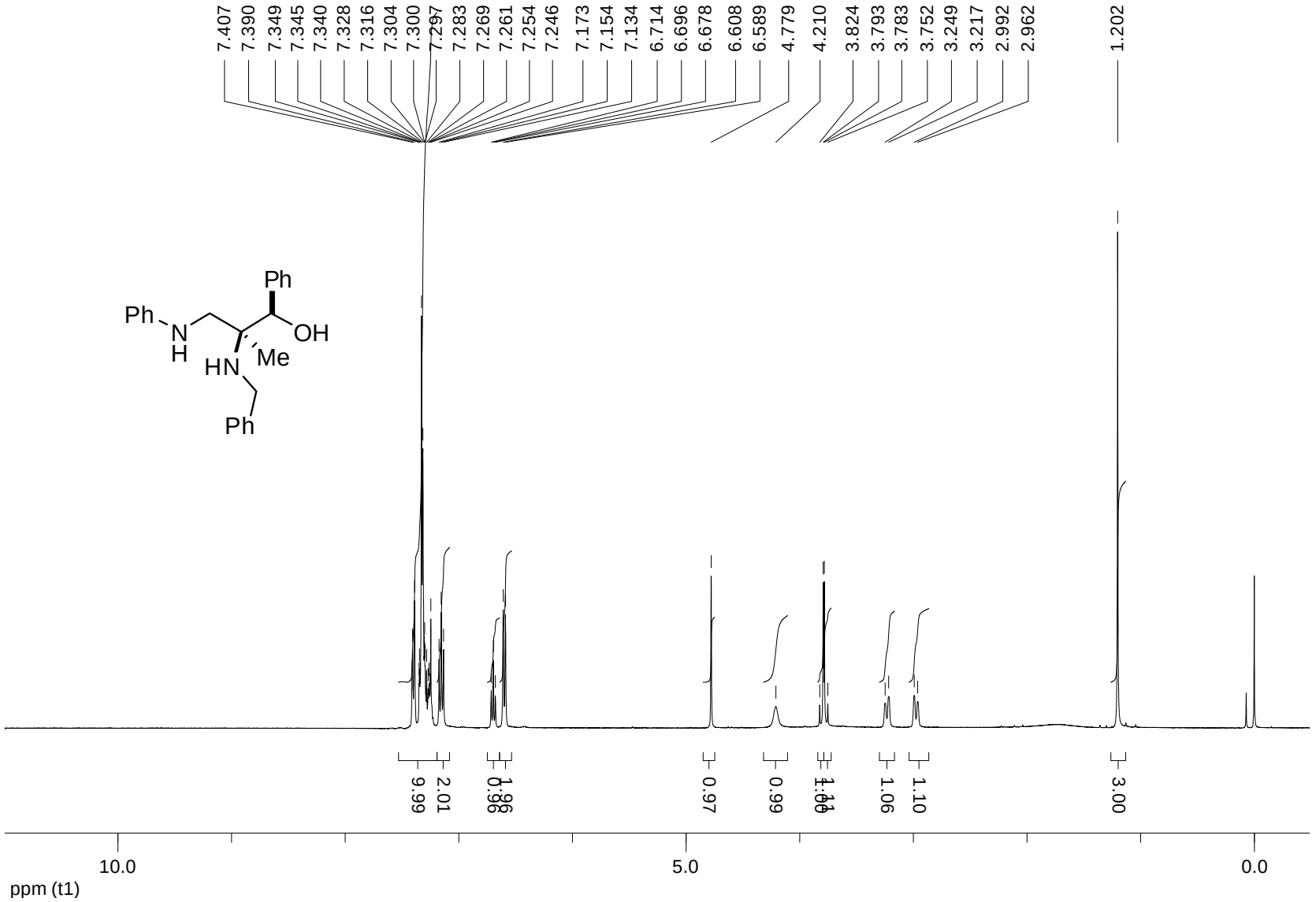
^{1}H NMR spectrum of **9m** (400 MHz, $CDCl_3$)



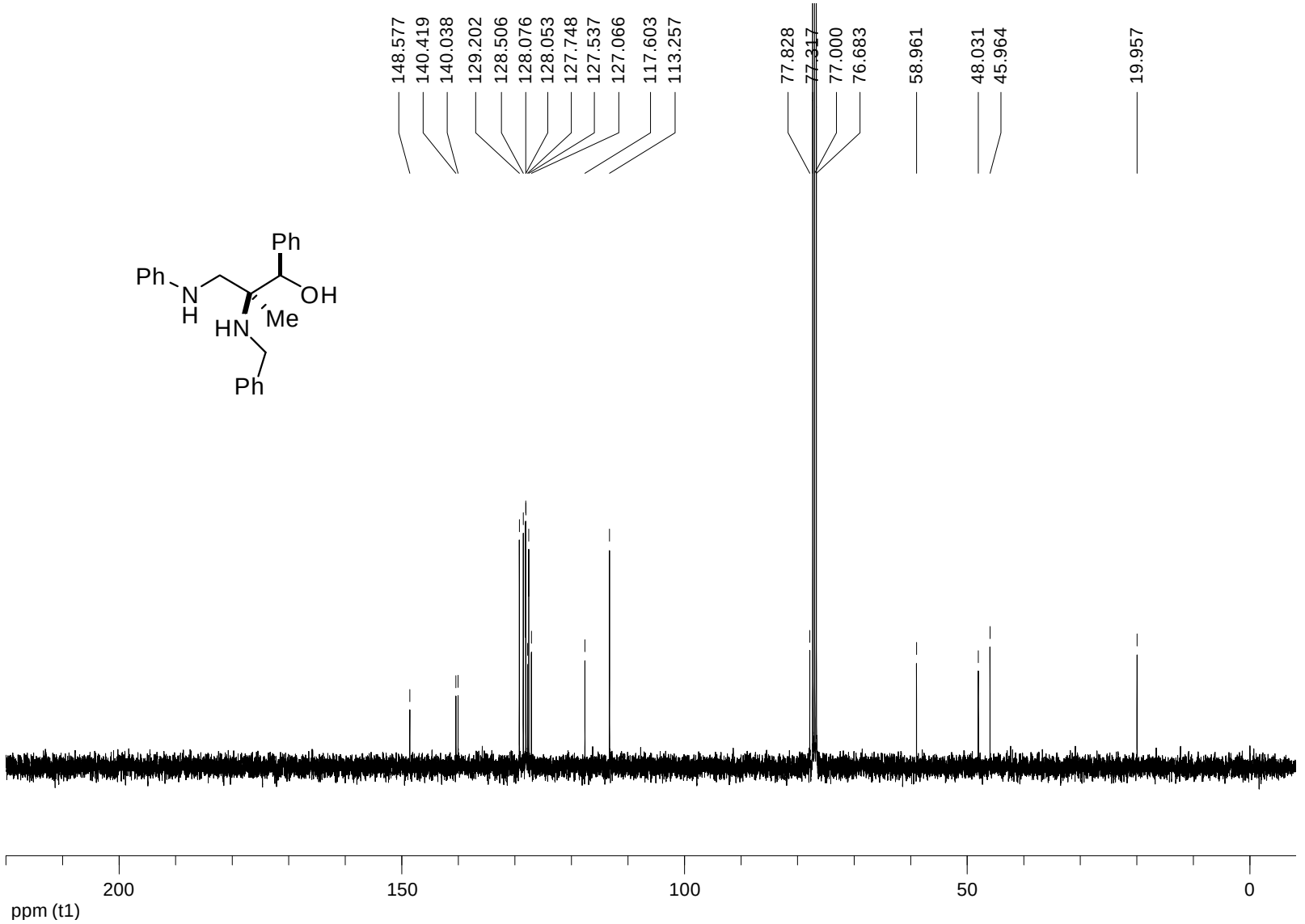
^{13}C NMR spectrum of **9m** (100 MHz, $CDCl_3$)



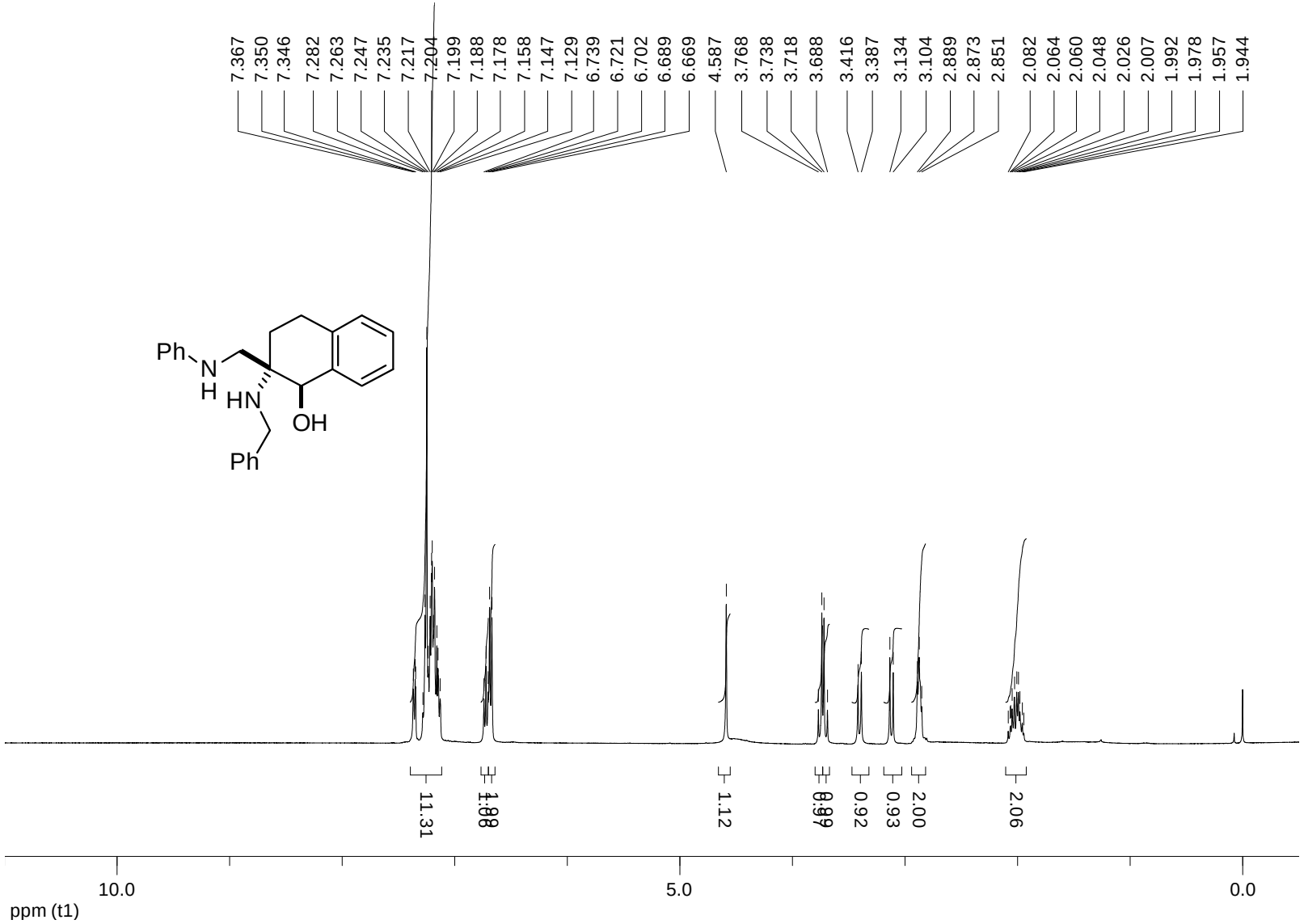
^{1}H NMR spectrum of **9p** (400 MHz, $CDCl_3$)



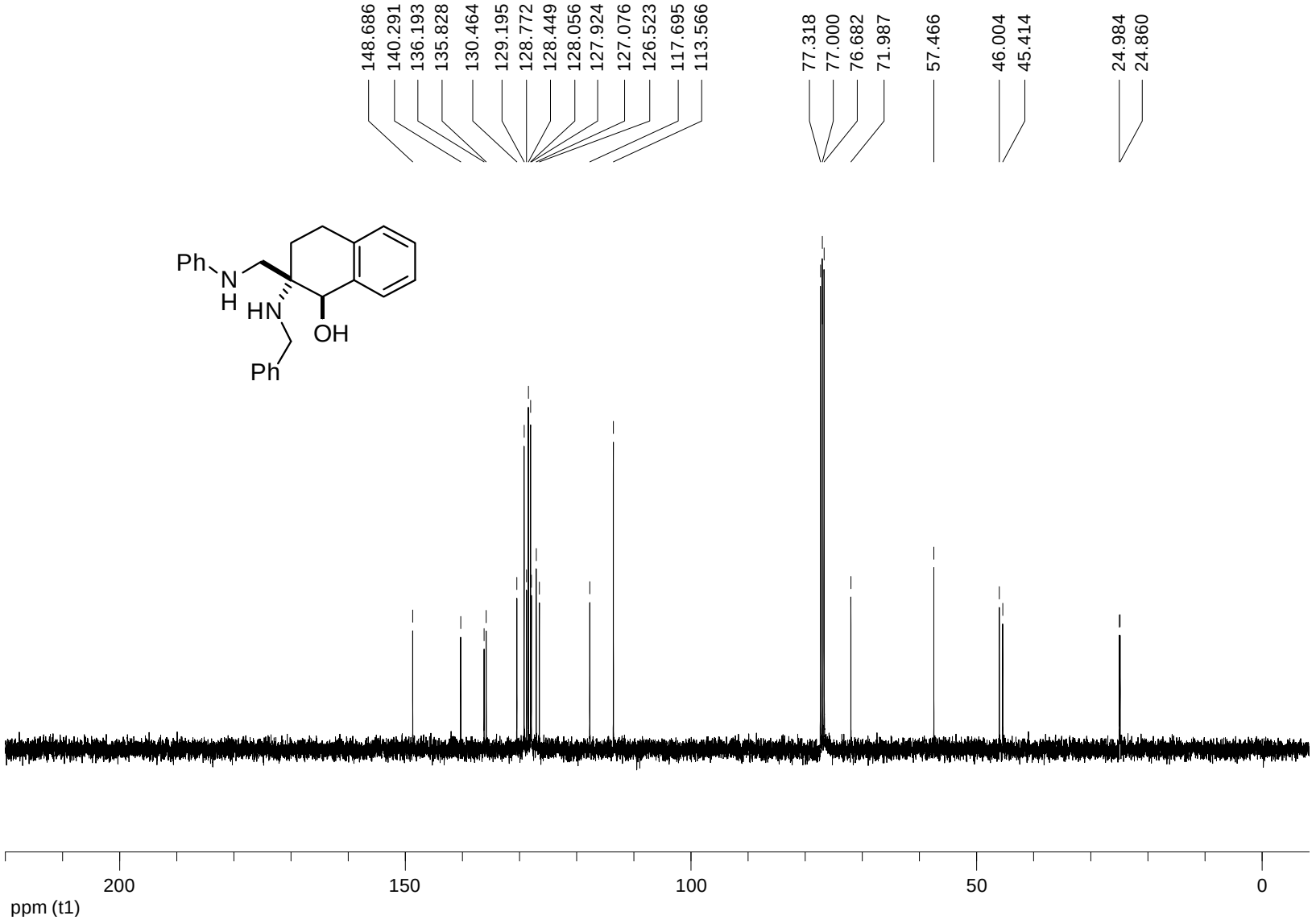
^{13}C NMR spectrum of **9p** (100 MHz, $CDCl_3$)



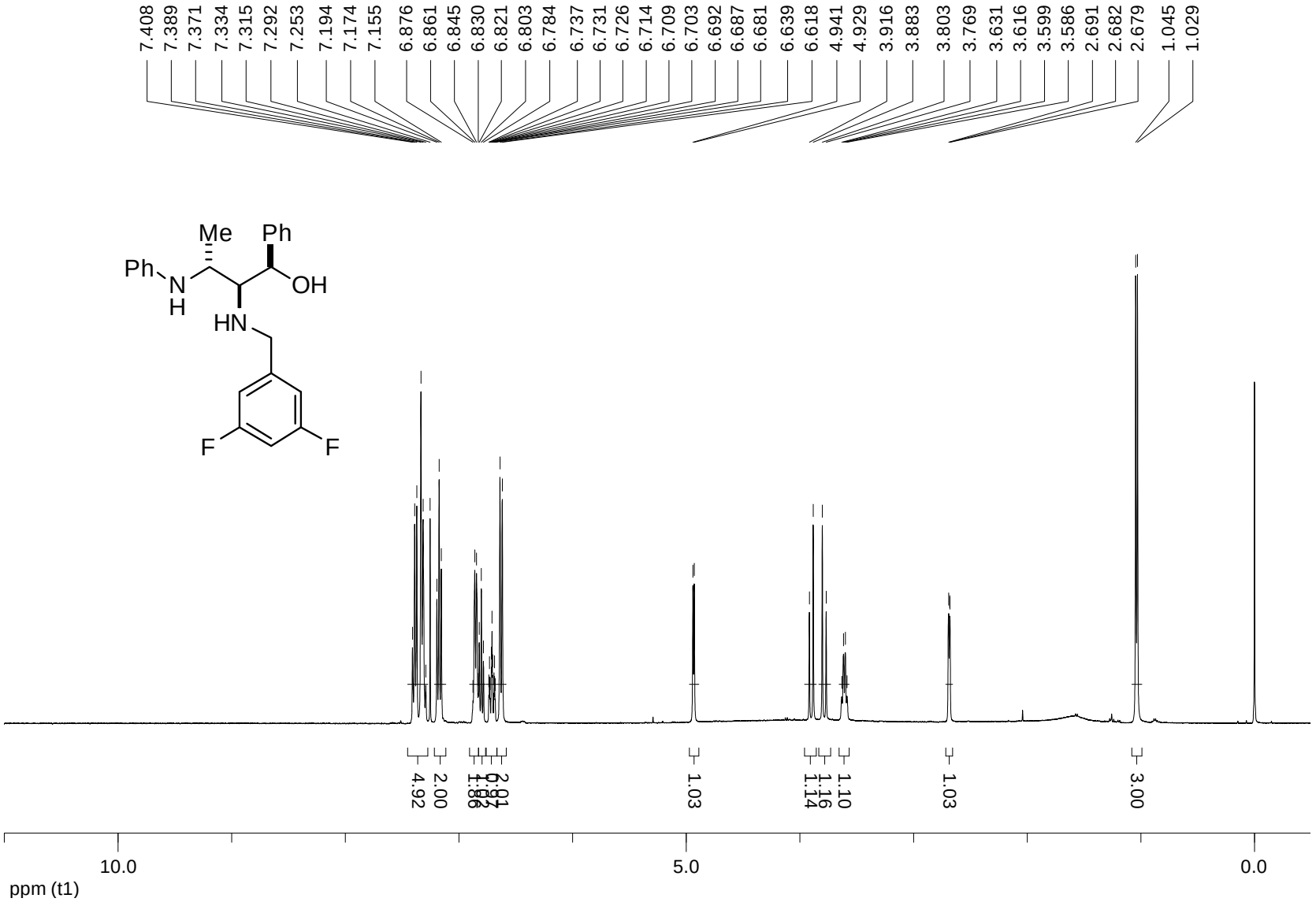
^{1}H NMR spectrum of **9r** (400 MHz, $CDCl_3$)



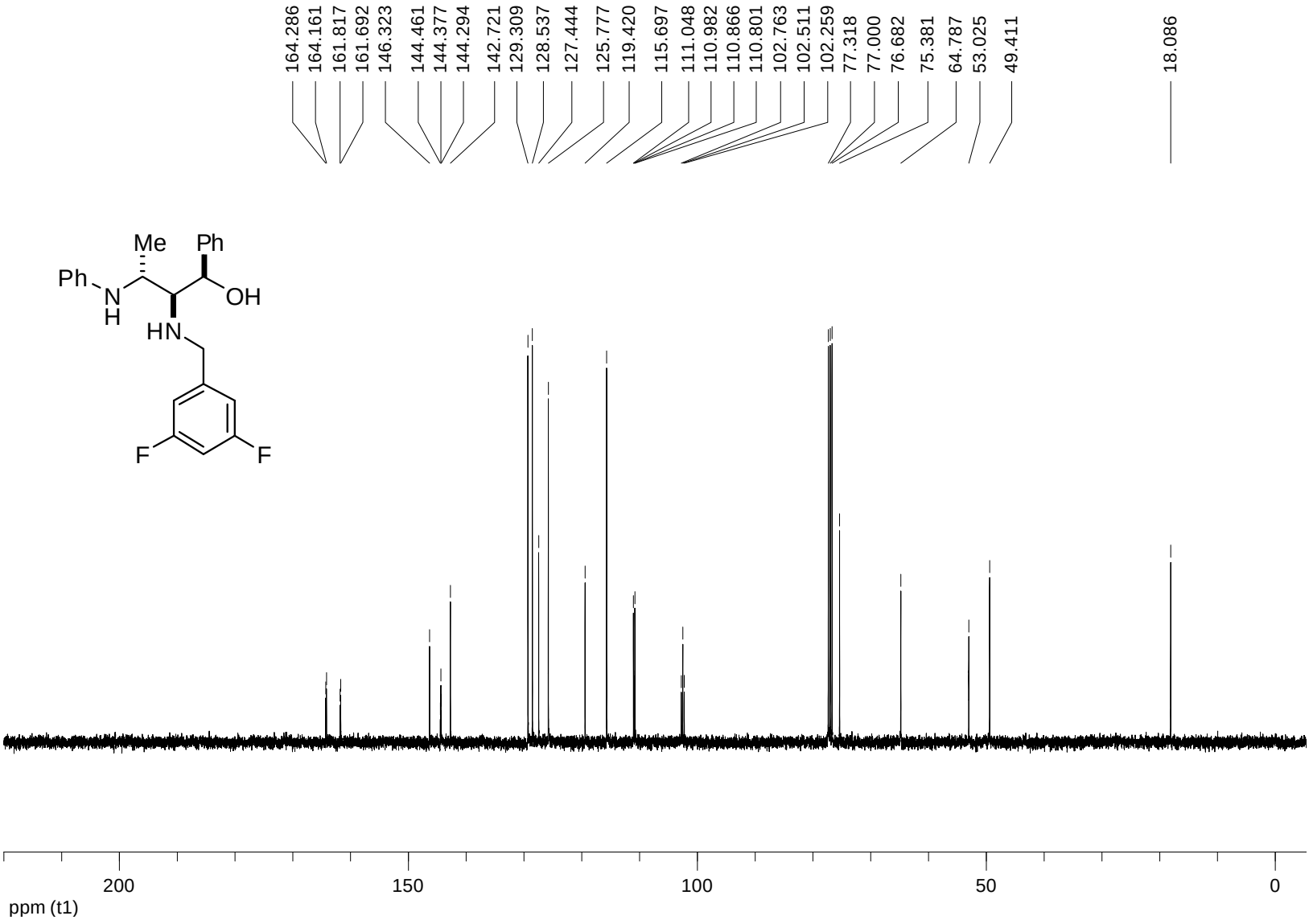
^{13}C NMR spectrum of **9r** (100 MHz, $CDCl_3$)



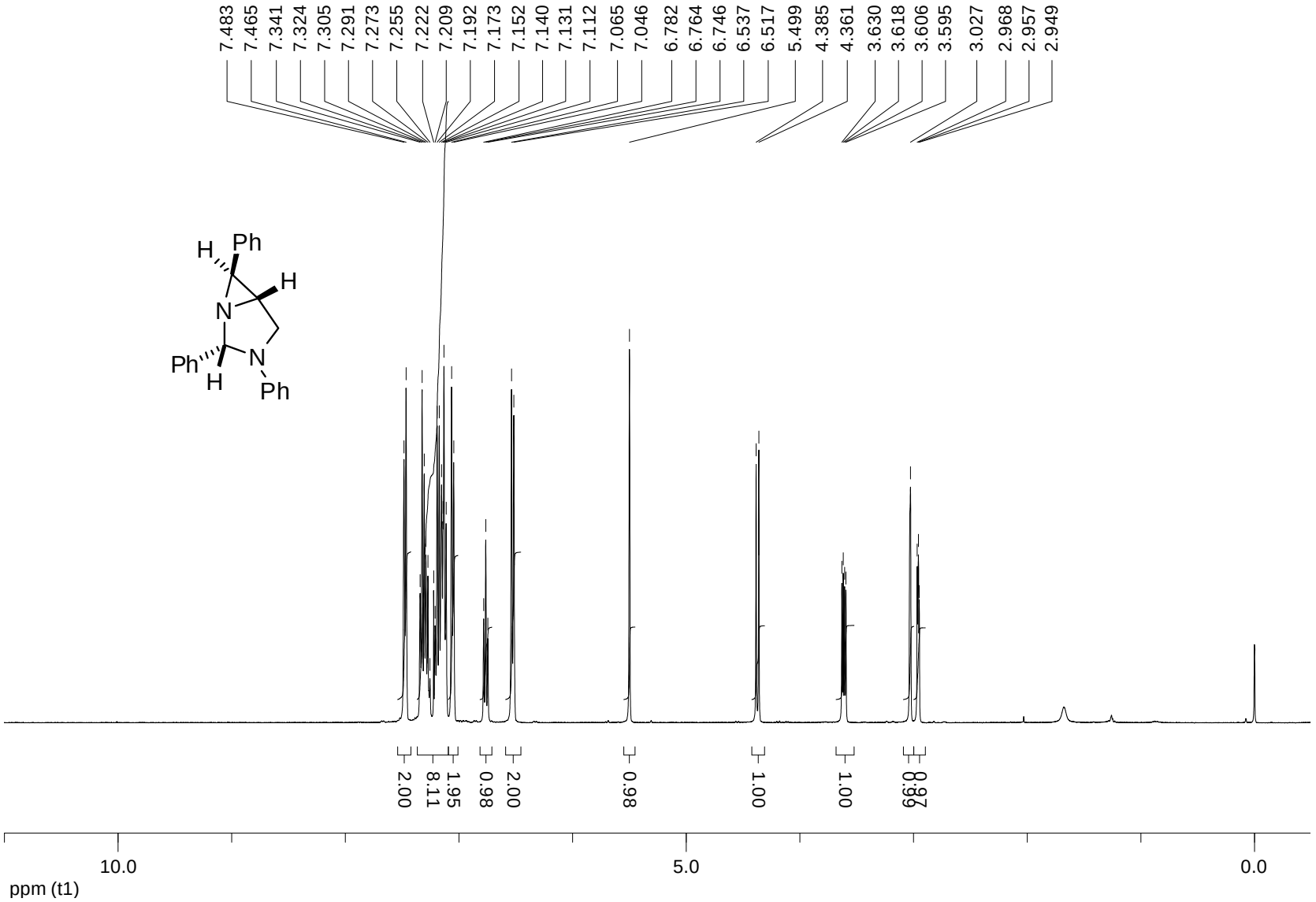
^{1}H NMR spectrum of **9u** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **9u** (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **10a** (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **10a** (100 MHz, $CDCl_3$)