Electronic Supplementary Information

Copper-Catalyzed Redox-Neutral C-H Amination with Amidoximes

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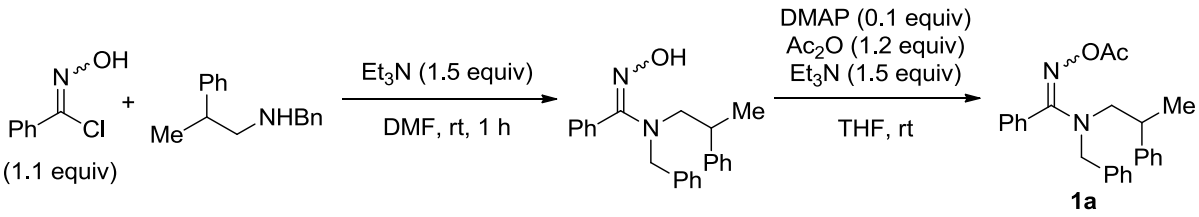
1. General

^{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, sep = septet, 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. CuI, *m*-xylene (anhydrous) and K_3PO_4 were purchased from Sigma-Aldrich Co., Inc.

2. Synthesis of *O*-acetyl amidoxime 1

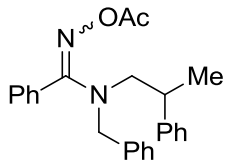
A typical procedure for synthesis of amidoxime 1a:



To a 50 mL two-neck round-bottomed flask (fitted with a water bath) was added *N*-benzyl-2-phenylpropan-1-amine[1] (4.074 g, 18.1 mmol) and triethylamine (3.78 mL, 27.1 mmol) in DMF (12 mL). *N*-Hydroxybenzimidoyl chloride[2] (3.094 g, 19.9 mmol) in DMF (8 mL) was added dropwise to the stirred mixture. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water, 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 = 85:15) to afford *N*-benzyl-*N*'-hydroxy-*N*-(2-phenylpropyl)benzimidamide (4.444 g, 12.9 mmol, *E*/*Z* mixture, *E*/*Z* not determined, ratio 5:1) in 71% yield as a yellow oil. This amidoxime was unstable and used immediately in the next acetylation. For amidoximes **1b**, **1c**, **1e-1h**, **1j**, **1m**, **1q-1r**, the corresponding crude amidoximes was directly used for the next acetylation without further purification.

To a 50 mL two-neck round-bottomed flask was added *N*-benzyl-*N*'-hydroxy-*N*-(2-phenylpropyl)benzimidamide (4.444 g, 12.9 mmol), triethylamine (2.70 mL, 19.4 mmol) and *N*,*N*-dimethylpyridin-4-amine (0.158 g, 0.13 mmol) in THF (30 mL). Acetic anhydride (1.46 mL, 15.5 mmol) was added in a dropwise manner. The reaction mixture was stirred at room temperature for 2 h. The reaction was quenched with water, 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 = 90:10 then 85:15) to afford **1a** in 93% combined yield (4.644 g, 12.0 mmol, *E*/*Z* not determined, major:minor = 1.7:1). The *E*/*Z* mixture could be partially separated by column chromatography to give the less polar major stereoisomer (1.689 g, 4.37 mmol) in 34% yield, the *E*/*Z* mixture (2.185 g, 5.65 mmol, major:minor = 1.3:1) in 44% yield and the polar minor stereoisomer (0.770 g, 1.99 mmol) in 15% yield.

***N*'-Acetoxy-*N*-benzyl-*N*-(2-phenylpropyl)benzimidamide (1a):**



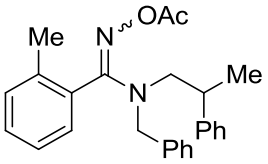
The major stereoisomer:

Colorless oil. IR (NaCl) 2964, 2930, 1748, 1557, 1495, 1452, 1425, 1363, 1219, 1003 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, d, *J* = 6.8 Hz), 1.82 (3H, s), 3.22-3.29 (1H, m), 3.48 (2H, s br), 3.83 (1H, s br), 4.17 (1H, s br), 7.05-7.11 (4H, m), 7.21-7.34 (11H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 19,6, 36.9, 52.7, 54.5, 126.6, 127.3, 127.4, 127.5, 127.7, 128.3, 128.5, 128.6, 129.3, 131.4, 137.5, 144.6, 166.9, 169.5; ESIHRMS: Found: m/z 387.2074. Calcd for $C_{25}H_{27}N_2O_2$: $(M+H)^+$ 387.2073.

The minor stereoisomer:

Colorless oil. IR (NaCl) 3028, 2965, 2930, 1748, 1589, 1557, 1454, 1402, 1366, 1209, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, d, *J* = 6.8 Hz), 2.14 (3H, s), 3.04-3.13 (1H, m), 3.25 (1H, dd, *J* = 9.2, 14.0 Hz), 3.38 (1H, dd, *J* = 6.0, 14.0 Hz), 4.17 (1H, d, *J* = 15.2 Hz), 4.35 (1H, d, *J* = 15.2 Hz), 7.14 (2H, d, *J* = 6.8 Hz), 7.23-7.39 (13H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 19,9, 38.5, 56.3, 57.4, 126.7, 127.3, 127.5, 127.7, 128.2, 128.5, 128.6, 130.0, 130.4, 132.5, 137.6, 144.0, 159.5, 168.6; ESIHRMS: Found: m/z 387.2060. Calcd for $C_{25}H_{27}N_2O_2$: $(M+H)^+$ 387.2073.

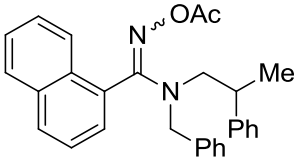
***N*'-Acetoxy-*N*-benzyl-2-methyl-*N*-(2-phenylpropyl)benzimidamide (1b):**



44% yield (two steps) as a pale yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxy-2-methylbenzimidoyl chloride[3] and *N*-benzyl-2-phenylpropan-1-amine.

IR (NaCl) 3028, 2965, 2928, 1755, 1732, 1591, 1568, 1485, 1454, 1362, 1215, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (3H, d, *J* = 7.2 Hz), 2.09 (3H, s), 2.29 (3H, s), 3.07-3.16 (1H, m), 3.34 (1H, dd, *J* = 8.0, 14.0 Hz), 3.48 (1H, dd, *J* = 6.4, 14.0 Hz), 4.06 (1H, d, *J* = 15.6 Hz), 4.32 (1H, d, *J* = 15.6 Hz), 6.98 (1H, d, *J* = 7.2 Hz), 7.07 (1H, t, *J* = 7.6 Hz), 7.11-7.14 (3H, m), 7.17-7.35 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.56, 19,64, 20.0, 39.3, 56.6, 57.9, 125.6, 126.7, 127.3, 127.5 (overlapped), 128.56, 128.59, 129.5, 130.2, 130.4, 132.3, 137.6, 137.8, 144.1, 157.2, 168.6; ESIHRMS: Found: m/z 401.2221. Calcd for $C_{26}H_{29}N_2O_2$: $(M+H)^+$ 401.2229.

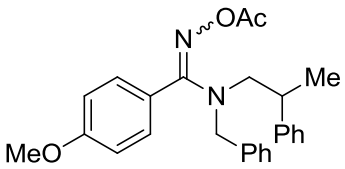
***N*'-Acetoxy-*N*-benzyl-*N*-(2-phenylpropyl)-1-naphthimidamide (1c):**



51% yield (two steps) as a pale yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxy-1-naphthimidoyl chloride[4] and *N*-benzyl-2-phenylpropan-1-amine.

IR (NaCl) 2965, 2930, 1749, 1574, 1495, 1454, 1366, 1219, 1250, 1193 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (3H, d, *J* = 6.8 Hz), 2.14 (3H, s), 3.17-3.22 (1H, m), 3.35-3.41 (1H, m), 3.50-3.53 (1H, m), 4.09 (1H, d, *J* = 15.2 Hz), 4.34 (1H, d, *J* = 15.6 Hz), 7.15 (2H, d, *J* = 7.6 Hz), 7.21 (2H, d, *J* = 7.6 Hz), 7.25-7.45 (10H, m), 7.77-7.80 (1H, m), 7.82 (1H, d, *J* = 8.0 Hz), 7.98 (1H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 20.0, 39.4, 56.8, 58.1, 124.9 (overlapped), 126.0, 126.8, 126.9, 127.4, 127.52, 127.54, 128.1, 128.60, 128.62, 128.8, 130.07, 130.14, 132.1, 133.4, 137.5, 144.1, 156.8, 168.6; ESIHRMS: Found: m/z 436.2225. Calcd for $C_{29}H_{29}N_2O_2$: $(M+H)^+$ 436.2229.

***N*'-Acetoxy-*N*-benzyl-4-methoxy-*N*-(2-phenylpropyl)benzimidamide (1d):**



93% combined yield (*E*/*Z* not determined, major:minor = 1.3:1) from acetic anhydride and *N*-benzyl-*N*'-hydroxy-4-methoxy-*N*-(2-phenylpropyl)benzimidamide (unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxy-4-methoxybenzimidoyl chloride[5] and *N*-benzyl-2-phenylpropan-1-amine in 78% yield. The *E*/*Z* mixture could be partially separated by column chromatography to give the less polar major stereoisomer in 47% yield, the *E*/*Z* mixture (major:minor = 1:5.9) in 34% yield and the polar minor stereoisomer in 12% yield.

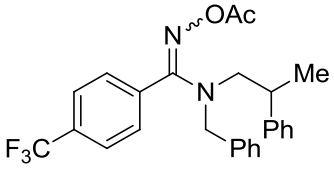
The major stereoisomer:

Pale yellow oil. IR (NaCl) 2962, 2932, 1748, 1611, 1557, 1513, 1423, 1364, 1296, 1250, 1175 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (3H, d, *J* = 6.4 Hz), 1.86 (3H, s), 3.22-3.29 (1H, m), 3.46-3.48 (2H, m), 3.79 (3H, s), 3.86 (1H, d, *J* = 15.6 Hz), 4.22 (1H, d, *J* = 15.2 Hz), 6.84 (2H, d, *J* = 8.8 Hz), 7.00 (2H, d, *J* = 8.0 Hz), 7.11 (2H, d, *J* = 7.2 Hz), 7.19-7.32 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 19,6, 36.8, 52.6, 54.4, 55.1, 113.6, 123.2, 126.4, 127.2, 127.3, 127.4, 128.3, 128.5, 129.3, 137.5, 144.5, 160.1, 166.6, 169.4; ESIHRMS: Found: m/z 439.2005. Calcd for $C_{26}H_{28}N_2O_3Na$: $(M+Na)^+$ 439.1998.

The minor stereoisomer:

Pale yellow oil. IR (NaCl) 3028, 2963, 2932, 1755, 1732, 1607, 1557, 1514, 1362, 1254, 1215, 1172 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (3H, d, *J* = 6.8 Hz), 2.14 (3H, s), 3.04-3.13 (1H, m), 3.23 (1H, dd, *J* = 8.8, 14.0 Hz), 3.36 (1H, dd, *J* = 6.4, 14.0 Hz), 3.79 (3H, s), 4.17 (1H, d, *J* = 15.2 Hz), 4.34 (1H, d, *J* = 14.8 Hz), 6.78 (2H, d, *J* = 8.8 Hz), 7.14-7.17 (4H, m), 7.23-7.36 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 20.0, 38.4, 55.3, 56.2, 57.2, 113.7, 124.5, 126.7, 127.4, 127.6, 127.8, 128.5, 128.7, 131.6, 137.8, 144.1, 159.7, 161.5, 168.8; ESIHRMS: Found: m/z 417.2173. Calcd for $C_{26}H_{29}N_2O_3$: $(M+H)^+$ 417.2178.

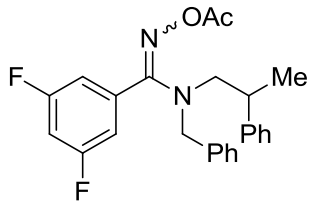
_N_'-Acetoxy-_N_-benzyl-_N_-(2-phenylpropyl)-4-(trifluoromethyl)benzimidamide (1e):



59% yield (two steps) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxy-1-naphthimidoyl chloride[6] and *N*-benzyl-2-phenylpropan-1-amine.

mp: 49-51 °C; IR (NaCl) 2932, 1761, 1593, 1566, 1454, 1366, 1323, 1207, 1167, 1128 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, d, *J* = 7.2 Hz), 2.17 (3H, s), 3.06-3.15 (1H, m), 3.26 (1H, dd, *J* = 9.6, 14.0 Hz), 3.46 (1H, dd, *J* = 5.6, 14.0 Hz), 4.15 (1H, d, *J* = 15.2 Hz), 4.31 (1H, d, *J* = 14.8 Hz), 7.17 (2H, d, *J* = 7.2 Hz), 7.21-7.37 (10H, m), 7.51 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.8, 38.6, 56.2, 57.5, 123.7 (q, *J* = 270.7 Hz), 125.2 (q, *J* = 3.7 Hz), 126.9, 127.3, 127.6, 127.7, 128.6, 128.7, 130.3, 132.2 (q, *J* = 32.3 Hz), 136.4, 137.2, 143.8, 158.1, 168.2; ESIHRMS: Found: m/z 455.1943. Calcd for $C_{26}H_{26}F_3N_2O_2$: $(M+H)^+$ 455.1946.

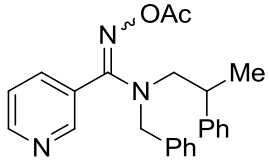
_N_'-Acetoxy-_N_-benzyl-3,5-difluoro-_N_-(2-phenylpropyl)benzimidamide (1f):



72% yield (two steps) as a colorless oil (single stereoisomer, *E*/*Z* not determined) from 3,5-difluoro-*N*-hydroxybenzimidoyl chloride[7] and *N*-benzyl-2-phenylpropan-1-amine.

IR (NaCl) 3028, 2965, 2930, 1769, 1755, 1620, 1402, 1362, 1331, 1200, 1121, 1001 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, d, *J* = 7.2 Hz), 2.16 (3H, s), 3.04-3.13 (1H, m), 3.24 (1H, dd, *J* = 9.6, 14.0 Hz), 3.44 (1H, dd, *J* = 5.6, 14.0 Hz), 4.14 (1H, d, *J* = 14.8 Hz), 4.30 (1H, d, *J* = 14.8 Hz), 6.61-6.65 (2H, m), 6.81 (1H, tt, *J* = 2.4, 8.8 Hz), 7.16-7.38 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 19.8, 38.5, 56.1, 57.4, 105.9 (t, *J* = 25.2 Hz), 113.0 (dd, *J* = 7.5, 19.0 Hz), 127.0, 127.3, 127.6, 127.8, 128.6, 128.8, 136.1 (t, *J* = 9.5 Hz), 137.0, 143.6, 157.4 (t, *J* = 2.8 Hz), 162.5 (dd, *J* = 2.3, 248.1 Hz), 168.1; ESIHRMS: Found: m/z 423.1880. Calcd for $C_{25}H_{25}F_2N_2O_2$: $(M+H)^+$ 423.1884.

_N_'-Acetoxy-_N_-benzyl-_N_-(2-phenylpropyl)nicotinimidamide (1g):

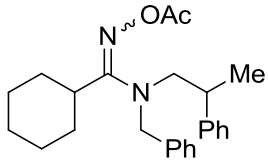


72% yield (two steps) as a yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxynicotinimidoyl chloride[5] and *N*-benzyl-2-phenylpropan-1-amine.

IR (NaCl) 3028, 2965, 1759, 1591, 1495, 1454, 1398, 1366, 1207, 1192, 1155 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, d, *J* = 6.8 Hz), 2.17 (3H, s), 3.05-3.14 (1H, m), 3.26 (1H, dd,

J = 9.6, 14.0 Hz), 3.45 (1H, dd, *J* = 5.6, 14.0 Hz), 4.18 (1H, d, *J* = 14.8 Hz), 4.33 (1H, d, *J* = 14.8 Hz), 7.15-7.37 (11H, m), 7.42 (1H, d, *J* = 8.0 Hz), 8.35 (1H, d, *J* = 2.0 Hz), 8.59 (1H, d, *J* = 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 19.8, 38.5, 56.2, 57.5, 123.1, 126.9, 127.2, 127.5, 127.7, 128.6, 128.70, 128.74, 137.0, 137.4, 143.6, 150.6, 151.1, 156.9, 168.2; ESIHRMS: Found: m/z 388.2022. Calcd for $C_{24}H_{26}N_3O_2$: $(M+H)^+$ 388.2025.

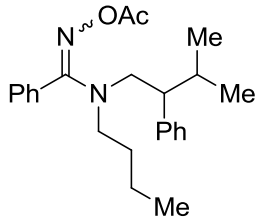
_N_'-Acetoxy-_N_-benzyl-_N_-(2-phenylpropyl)cyclohexanecarboximidamide (1h):



81% yield (two steps) as a colorless oil (inseparable *E*/*Z* mixture, *E*/*Z* not determined, major:minor = 5:1) from *N*-hydroxycyclohexanecarbimidoyl chloride[5] and *N*-benzyl-2-phenylpropan-1-amine.

IR (NaCl) 2959, 2930, 2853, 1748, 1732, 1557, 1454, 1421, 1364, 1221 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03-1.25 (6H × 1 + 6H × 0.2 , m), 1.51-1.93 (7H × 1 + 7H × 0.2 , m), 2.03 (3H × 0.2, s), 2.14 (3H × 1, s), 2.29-2.45 (1H × 1 + 1H × 0.2 , m), 2.98-3.50 (3H × 1 + 3H × 0.2 , m), 4.07-4.46 (2H × 1 + 2H × 0.2 , m), 7.10-7.31 (10H × 1 + 10H × 0.2 , m); ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 18.7, 20.0, 25.9, 26.70, 26.71, 28.26, 28.32, 37.7, 40.9, 53.8, 57.4, 126.4, 126.96, 127.0, 127.4, 128.36, 128.44, 138.4, 144.7, 167.4, 169.3; ESIHRMS: Found: m/z 415.2363. Calcd for $C_{25}H_{32}N_2O_2Na$: $(M+Na)^+$ 415.2361.

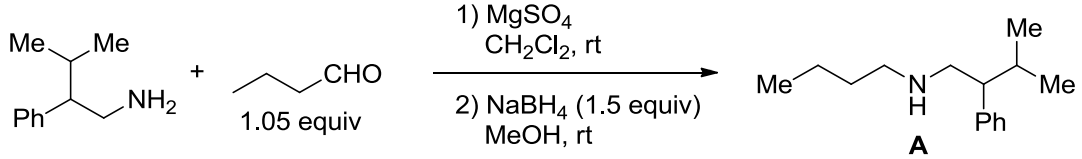
_N_'-Acetoxy-_N_-benzyl-_N_-(3-methyl-2-phenylbutyl)benzimidamide (1i):



86% combined yield (*E*/*Z* not determined, major:minor = 11.4:1) from acetic anhydride and *N*-benzyl-*N*'-hydroxy-4-methoxy-*N*-(2-phenylpropyl)benzimidamide (unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-butyl-3-methyl-2-phenylbutan-1-amine **A** (preparation method was shown below) in 79% yield. The *E*/*Z* mixture could be partially separated by column chromatography to give the less polar major stereoisomer in 5% yield and the *E*/*Z* mixture (major:minor = 10.6:1) in 81% yield. Only the major stereoisomer was characterized.

Colorless oil. IR (NaCl) 2959, 2930, 2872, 1749, 1557, 1498, 1470, 1427, 1364, 1221 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.71-0.74 (6H, m), 0.98-1.06 (5H, m), 1.30-1.33 (2H, m), 1.74-1.88 (4H, m), 2.50 (1H, s br), 2.77 (1H, s br), 2.96 (1H, s br), 3.49-3.55 (1H, m), 3.82-3.84 (1H, m), 6.84 (2H, s br), 7.19-7.33 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.6, 19.7, 20.8, 21.0, 29.6, 31.6, 48.8, 50.1, 50.6, 126.2, 127.7, 128.0 (overlapped), 128.8, 128.9, 131.6, 142.4, 166.4, 169.5; ESIHRMS: Found: m/z 381.2542. Calcd for $C_{24}H_{33}N_2O_2$: $(M+H)^+$ 381.2542.

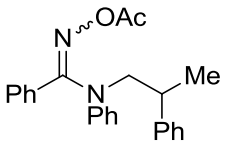
Preparation of *N*-butyl-3-methyl-2-phenylbutan-1-amine A.



To a 50 mL two-neck round-bottomed flask under a nitrogen atmosphere was added 3-methyl-2-phenylbutan-1-amine[8] (1.572 g, 9.62 mmol), butyraldehyde (0.91 mL, 10.10 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 4 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. $NaBH_4$ (0.546 g, 14.43 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 (15 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 = 75:25) to give amine **A** (0.578 g, 2.63 mmol) in 27% yield as a colorless oil.

IR (NaCl) 3312, 2955, 2928, 2870, 1493, 1452, 1385, 1366, 1130 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (3H, d, J = 6.8 Hz), 0.84 (3H, t, J = 7.2 Hz), 0.98 (3H, d, J = 6.4 Hz), 1.16-1.39 (5H, m), 1.79-1.88 (1H, m), 2.44-2.60 (3H, m), 2.79-2.84 (1H, m), 2.99 (1H, dd, J = 4.0, 11.2 Hz), 7.15-7.32 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 20.3, 20.9, 21.0, 31.9, 32.0, 49.7, 52.7, 53.1, 126.2, 128.2, 128.4, 142.8; ESIHRMS: Found: m/z 220.2064. Calcd for $C_{15}H_{26}N$: $(M+H)^+$ 220.2065.

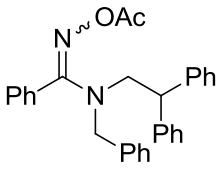
***N*'-Acetoxy-*N*-phenyl-*N*-(2-phenylpropyl)benzimidamide (1j):**



17% yield (two steps) as a yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and *N*-(2-phenylpropyl)aniline[9]. For this substrate, the intermediate *N*'-hydroxy-*N*-phenyl-*N*-(2-phenylpropyl)benzimidamide (used for the next acetylation without purification) was prepared at elevated temperature (50 °C) and the *N*-hydroxybenzimidoyl chloride was added through a syringe pump over 0.5 h.

IR (NaCl) 3028, 2965, 2932, 1765, 1749, 1587, 1557, 1495, 1366, 1205, 1159 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, d, *J* = 6.8 Hz), 1.72 (3H, s), 3.12-3.21 (1H, m), 3.68-3.79 (2H, m), 6.92 (2H, d, *J* = 8.0 Hz), 6.97 (1H, t, *J* = 7.2 Hz), 7.06-7.08 (2H, m), 7.20-7.43 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.9, 19.0, 40.2, 59.6, 119.9, 122.6, 126.8, 127.4, 128.38, 128.43, 128.8, 129.8, 130.7, 131.9, 143.5, 146.5, 158.0, 167.8; ESIHRMS: Found: m/z 373.1917. Calcd for $C_{24}H_{25}N_2O_2$: $(M+H)^+$ 373.1916.

_N_'-Acetoxy-_N_-benzyl-_N_-(2,2-diphenylethyl)benzimidamide (1k):



96% combined yield (*E*/*Z* not determined, major:minor = 7.7:1) from acetic anhydride and *N*-benzyl-*N*-(2,2-diphenylethyl)-*N*'-hydroxybenzimidamide (recrystallized from CH_2Cl_2/hexane, unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-benzyl-2,2-diphenylethanamine[10] in 61% yield. The *E*/*Z* mixture could be separated by column chromatography to give polar major stereoisomer in 85% yield and the less polar minor stereoisomer in 11% yield.

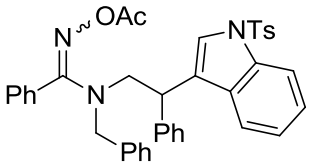
The major stereoisomer:

White solid. mp: 118-119 °C; IR (NaCl) 3063, 3028, 3005, 1765, 1748, 1591, 1557, 1495, 1454, 1366, 1209, 1144 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (3H, s), 3.88 (2H, d, *J* = 8.0 Hz), 4.22 (2H, s), 4.37 (1H, d, *J* = 8.0 Hz), 7.13 (2H, d, *J* = 7.2 Hz), 7.23-7.38 (18H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 49.2, 55.2, 56.6, 126.8, 127.5, 127.6, 128.0, 128.2, 128.6, 128.7, 130.0, 130.5, 132.4, 137.5, 141.5, 159.4, 168.4; ESIHRMS: Found: m/z 449.2228. Calcd for $C_{30}H_{29}N_2O_2$: $(M+H)^+$ 449.2229.

The minor stereoisomer:

Sticky colorless oil. IR (NaCl) 3061, 3028, 2926, 1755, 1748, 1603, 1557, 1495, 1452, 1364, 1219, 1150 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.83 (3H, s), 3.90 (2H, s), 3.94 (2H, d, *J* = 7.6 Hz), 4.87 (1H, s br), 6.99-7.00 (2H, m), 7.09 (2H, d, *J* = 7.2 Hz), 7.19-7.31 (16H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 47.3, 52.1, 52.9, 126.5, 127.1, 127.3, 127.7, 128.3, 128.4 (overlapped), 128.6, 129.2, 131.1, 137.4, 142.1, 166.6, 169.3; ESIHRMS: Found: m/z 449.2237. Calcd for $C_{30}H_{29}N_2O_2$: $(M+H)^+$ 449.2229.

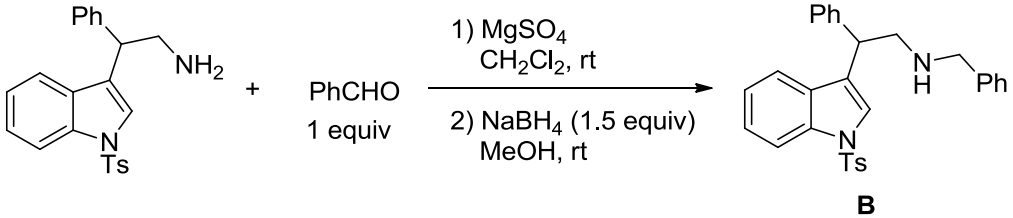
***N*'-Acetoxy-*N*-benzyl-*N*-(2-phenyl-2-(1-tosyl-1*H*-indol-3-yl)ethyl)benzimidamide (1l):**



95% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from acetic anhydride and *N*-benzyl-*N*'-hydroxy-*N*-(2-phenyl-2-(1-tosyl-1*H*-indol-3-yl)ethyl)benzimidamide (recrystallized from CH_2Cl_2/hexane, unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-benzyl-2-phenyl-2-(1-tosyl-1*H*-indol-3-yl)ethanamine **B** (preparation method was shown below) in 41% yield as a white solid.

mp: 76-77 °C; IR (NaCl) 3009, 2962, 1755, 1591, 1566, 1447, 1368, 1211, 1173, 1132 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.92 (3H, s), 2.31 (3H, s), 3.65 (1H, dd, *J* = 9.6, 14.4 Hz), 3.95 (1H, dd, *J* = 6.0, 14.0 Hz), 4.14 (1H, d, *J* = 15.2 Hz), 4.33 (1H, d, *J* = 14.8 Hz), 4.44 (1H, dd, *J* = 6.4, 8.8 Hz), 6.99 (1H, d, *J* = 7.6 Hz), 7.04 (1H, t, *J* = 8.0 Hz), 7.15 (2H, d, *J* = 8.0 Hz), 7.20-7.40 (17H, m), 7.68 (2H, d, *J* = 8.0 Hz), 7.89 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.7, 21.5, 41.2, 54.6, 56.5, 113.6, 119.7, 122.8, 123.09. 123.14, 124.8, 126.7, 127.3, 127.80, 127.83, 128.2, 128.4, 128.7, 128.8, 129.8, 129.99, 130.03, 130.6, 132.3, 135.0, 135.1, 137.3, 140.1, 144.9, 159.5, 168.4; ESIHRMS: Found: m/z 642.2426. Calcd for $C_{39}H_{36}N_3O_4S$: $(M+H)^+$ 642.2427.

Preparation of *N*-benzyl-2-phenyl-2-(1-tosyl-1*H*-indol-3-yl)ethanamine B.

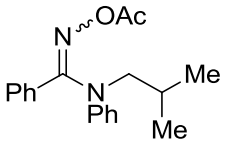


B

Amine **B** was prepared in a similar way to amine **A** from 2-phenyl-2-(1-tosyl-1*H*-indol-3-yl)ethanamine[11] and benzaldehyde (1 equiv was used).

Yield: 88%; Pale yellow oil; IR (NaCl) 3331, 2920, 2824, 1599, 1447, 1368, 1277, 1173, 1123, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.46 (1H, s br), 2.29 (3H, s), 3.18 (1H, dd, *J* = 7.6, 11.6 Hz), 3.29 (1H, dd, *J* = 6.4, 11.6 Hz), 3.79 (1H, d, *J* = 13.6 Hz), 3.83 (1H, d, *J* = 13.2 Hz), 4.34 (1H, t, *J* = 7.2 Hz), 7.08 (1H, t, *J* = 7.6 Hz), 7.13 (2H, d, *J* = 8.0 Hz), 7.19-7.32 (12H, m), 7.46 (1H, s), 7.69 (2H, d, *J* = 8.0 Hz), 7.94 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 42.8, 53.6, 53.8, 113.7, 120.0, 123.0, 123.1, 124.5, 124.7, 126.7, 126.87, 126.94, 127.9, 128.0, 128.4, 128.6, 129.7, 130.5, 135.1, 135.5, 140.1, 141.3, 144.7; ESIHRMS: Found: m/z 481.1951. Calcd for $C_{30}H_{29}N_2O_2S$: $(M+H)^+$ 481.1950.

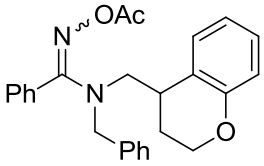
***N*'-Acetoxy-*N*-isobutyl-*N*-phenylbenzimidamide (1m):**



25% yield (two steps) as a yellow oil (inseparable *E*/*Z* mixture, *E*/*Z* not determined, major:minor = 5:1) from *N*-hydroxybenzimidoyl chloride and *N*-isobutylaniline[12]. For this substrate, the intermediate *N*'-hydroxy-*N*-isobutyl-*N*-phenylbenzimidamide (used for the next acetylation without purification) was prepared at elevated temperature (50 °C). *N*-Hydroxybenzimidoyl chloride (2.5 equiv) was added through a syringe pump over 0.5 h and triethylamine (3.5 equiv) was used.

IR (NaCl) 2961, 2934, 2870, 1765, 1759, 1587, 1557, 1495, 1385, 1366, 1207 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.90 (6H × 1, d, *J* = 6.4), 1.01 (6H × 0.2, d, *J* = 6.4), 1.71 (3H × 1, s), 1.88 (3H × 0.2, s), 2.00-2.10 (1H × 1, m), 2.18-2.29 (1H × 0.2, m), 3.38 (2H × 1, d, *J* = 7.2), 3.71 (2H × 0.2, d, *J* = 7.6), 6.97-7.02 (3H × 1 + 3H × 0.2 , m), 7.10 (2H × 0.2, t, *J* = 8.0), 7.18-7.27 (2H × 1 + 5H × 0.2 , m), 7.38-7.48 (3H × 1, m), 7.63-7.65n (2H × 1, m); ^{13}C NMR (100 MHz, $CDCl_3$) major: δ 18.9, 20.0, 29.2, 59.3, 119.6, 122.3, 128.5, 128.8, 129.7, 130.7, 132.2, 146.4, 158.7, 167.9; ESIHRMS: Found: m/z 311.1762. Calcd for $C_{19}H_{23}N_2O_2$: $(M+H)^+$ 311.1760.

***N*'-Acetoxy-*N*-benzyl-*N*-(chroman-4-ylmethyl)benzimidamide (1n):**



90% combined yield (*E*/*Z* not determined, ratio 1.7:1) from acetic anhydride and *N*-benzyl-*N*-(chroman-4-ylmethyl)-*N*'-hydroxybenzimidamide (unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-benzyl-1-(chroman-4-yl)methanamine **D** (preparation method was shown below) in 77% yield. The *E*/*Z* mixture could be separated by column chromatography to give the polar major stereoisomer in 57% yield and the less polar minor stereoisomer in 33% yield.

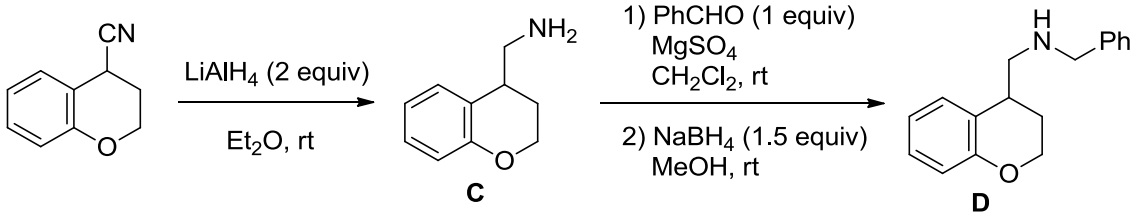
The major stereoisomer:

Colorless oil. IR (NaCl) 3063, 3028, 2945, 1748, 1607, 1582, 1557, 1427, 1364, 1269, 1223, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-1.94 (1H, m), 2.07-2.16 (1H, m), 2.23 (3H, s), 3.08-3.16 (2H, m), 3.29-3.36 (1H, m), 3.71-3.77 (1H, m), 4.09-4.14 (1H, m), 4.59 (1H, d, *J* = 14.8 Hz), 4.72 (1H, d, *J* = 14.4 Hz), 6.67-6.75 (3H, m), 7.01-7.06 (1H, m), 7.25-7.45 (8H, m), 7.51 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 24.0, 32.2, 54.8, 55.8, 62.3, 116.9, 120.2, 122.4, 127.9, 128.1, 128.3, 128.7, 128.9, 129.0, 129.9, 130.8, 132.3, 137.2, 154.7, 160.0, 168.8; ESIHRMS: Found: m/z 415.2018. Calcd for $C_{26}H_{27}N_2O_3$: $(M+H)^+$ 415.2022.

The minor stereoisomer:

Colorless oil. IR (NaCl) 3063, 3028, 2945, 2882, 1748, 1607, 1582, 1557, 1489, 1427, 1364, 1221, 1152 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (3H, s), 1.86-1.89 (1H, m), 2.02-2.08 (1H, m), 3.39-3.41 (3H, m), 3.80 (1H, s br), 4.07-4.10 (1H, m), 4.32-4.35 (1H, m), 4.47 (1H, s br), 6.73-6.80 (2H, m), 6.93 (1H, s br), 7.04 (1H, t, *J* = 7.6 Hz), 7.23-7.39 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 24.2, 30.7, 52.1, 52.7, 62.2, 116.6, 120.0, 122.7, 127.4, 127.54 (overlapped), 127.56, 128.3, 128.5, 129.3, 129.5, 130.9, 136.9, 154.5, 166.6, 168.9; ESIHRMS: Found: m/z 437.1837. Calcd for $C_{26}H_{26}N_2O_3Na$: $(M+H)^+$ 437.1841.

Preparation of *N*-benzyl-1-(chroman-4-yl)methanamine D:



To a suspension of $LiAlH_4$ (0.285 g, 7.50 mmol) in diethyl ether (5 mL) under an

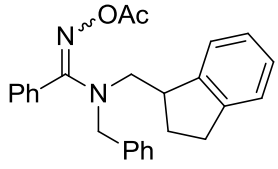
inert atmosphere was added chroman-4-carbonitrile[13] (0.597 g, 3.75 mmol) as a solution in the same solvent (5 mL). The mixture was stirred for 18 h at room temperature. The reaction was quenched by slow addition of 20% aqueous KOH solution (1 mL) at 0 °C. The solid was filtered, and washed with diethyl ether. The combined filtrates were washed with H_2O, dried over $MgSO_4$ and concentrated. Purification of the crude materials by flash column chromatography (silica gel; ethyl acetate:triethylamine = 95:5) afforded chroman-4-ylmethanamine **C** (0.406 g, 2.49 mmol) in 66 % yield as a colorless oil.

IR (NaCl) 3374, 3306, 2924, 2870, 1605, 1580, 1489, 1452, 1306, 1269, 1223, 1117 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (2H, s), 1.97-2.11 (2H, m), 2.81-2.86 (1H, m), 2.91 (1H, dd, *J* = 8.8, 12.8 Hz), 3.07 (1H, dd, *J* = 4.8, 12.8 Hz), 4.17-4.20 (2H, m), 6.81-6.89 (2H, m), 7.10-7.16 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.9, 36.8, 47.0, 63.4, 117.0, 120.2, 123.7, 127.6, 129.0, 155.0; ESIHRMS: Found: m/z 164.1077. Calcd for $C_{10}H_{14}NO$: $(M+H)^+$ 164.1075.

Amine **D** was prepared in a similar way to amine **A** from amine **C** and benzaldehyde.

Yield: 80%; Colorless oil; IR (NaCl) 3333, 3026, 2924, 2879, 1607, 1580, 1489, 1454, 1308, 1269, 1225, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.47 (1H, s br), 2.03-2.08 (2H, m), 2.81 (1H, dd, *J* = 10.0, 12.8 Hz), 2.93-2.99 (2H, m), 3.79 (1H, d, *J* = 13.2), 3.86 (1H, d, *J* = 13.2), 4.14-4.17 (2H, m), 6.79-6.86 (2H, m), 7.07-7.14 (2H, m), 7.23-7.33 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.5, 33.8, 54.0, 54.4, 63.4, 116.9, 120.1, 124.1, 127.0, 127.5, 128.0, 128.4, 129.1, 140.4, 154.9; ESIHRMS: Found: m/z 254.1549. Calcd for $C_{17}H_{20}NO$: $(M+H)^+$ 254.1545.

_N_'-Acetoxy-_N_-benzyl-_N_-((2,3-dihydro-1 -inden-1-yl)methyl)benzimidamide (1o):



90% combined yield (*E*/*Z* not determined, ratio 1.2:1) from acetic anhydride and *N*-benzyl-*N*-((2,3-dihydro-1*H*-inden-1-yl)methyl)-*N*'-hydroxybenzimidamide (unstable, used immediately for the next acetylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-benzyl-1-(2,3-dihydro-1*H*-inden-1-yl)methanamine[14] in 78% yield. The *E*/*Z* mixture could be

partially separated by column chromatography to give the less polar major stereoisomer in 42% yield, the *E*/*Z* mixture (major:minor = 1:5.5) in 46% yield and the polar minor stereoisomer in 2% yield.

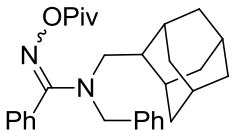
The major stereoisomer:

Colorless oil. IR (NaCl) 3028, 2941, 2849, 1748, 1557, 1497, 1427, 1364, 1223 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72-1.78 (1H, m), 1.81 (3H, s), 2.21-2.30 (1H, m), 2.76-2.79 (2H, m), 3.25 (1H, s br), 3.32-3.35 (1H, m), 3.67 (1H, s br), 4.50 (2H, s br), 7.07-7.37 (14H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 30.1, 30.9, 42.5, 51.4, 52.0, 124.3, 124.5, 126.1, 126.8, 127.3, 127.65, 127.72, 128.3, 128.6, 129.3, 131.3, 137.3, 144.0, 144.4, 166.9, 169.3; ESIHRMS: Found: m/z 399.2067. Calcd for $C_{26}H_{27}N_2O_2$: $(M+H)^+$ 399.2073.

The minor stereoisomer:

Colorless oil. IR (NaCl) 3065, 3028, 2941, 1765, 1748, 1591, 1574, 1557, 1447, 1402, 1366, 1211 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74-1.82 (1H, m), 2.20 (3H, s), 2.29-2.37 (1H, m), 2.78-2.86 (2H, m), 3.00-3.06 (1H, m), 3.48-3.54 (2H, m), 4.57 (1H, d, *J* = 14.8 Hz), 4.62 (1H, d, *J* = 14.8 Hz), 7.00 (1H, d, *J* = 7.2 Hz), 7.07-7.19 (3H, m), 7.29-7.43 (8H, m), 7.52 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.1, 30.0, 30.9, 43.6, 54.9, 56.0, 123.7, 124.7, 126.2, 126.9, 127.7, 128.0, 128.5, 128.8, 130.0, 130.5, 132.8, 137.6, 144.0, 144.1, 159.8, 168.8; ESIHRMS: Found: m/z 421.1898. Calcd for $C_{26}H_{26}N_2O_2Na$: $(M+Na)^+$ 421.1892.

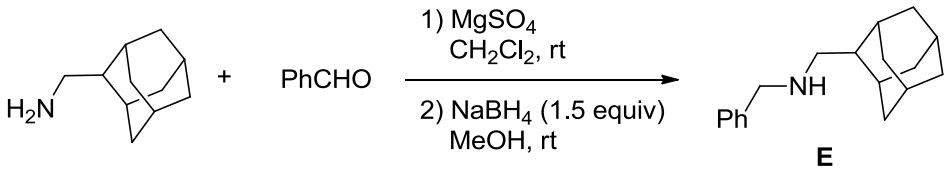
_N_-(Adamantan-2-ylmethyl)-_N_-benzyl-_N_'-(pivaloyloxy)benzimidamide (1p):



97% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from pivalic anhydride (1 equiv was used) and *N*-(adamantan-2-ylmethyl)-*N*-benzyl-*N*'-hydroxybenzimidamide (recrystallized from ethyl acetate/hexane, unstable, used immediately for the next acylation), which was prepared from *N*-hydroxybenzimidoyl chloride and *N*-(adamantan-2-ylmethyl) benzylamine **E** (preparation method was shown below) in 48% yield as a white solid.

mp: 66-67 °C. IR (NaCl) 2972, 2905, 2853, 1748, 1589, 1557, 1476, 1454, 1402, 1271, 1121 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s), 1.43-1.52 (4H, m), 1.68-1.90 (10H, m), 2.07-2.11 (1H, m), 3.16 (2H, d, *J* = 7.6 Hz), 4.44 (2H, s), 7.31-7.43 (8H, m), 7.59-7.61 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 27.7, 28.2, 29.8, 31.6, 38.0, 38.6, 39.0, 42.2, 51.6, 55.0, 127.6, 128.2, 128.4, 128.7, 130.2, 130.7, 133.0, 137.9, 161.1, 175.3; ESIHRMS: Found: m/z 459.3012. Calcd for $C_{30}H_{39}N_2O_2$: $(M+H)^+$ 459.3012.

Preparation of *N*-(adamantan-2-ylmethyl) benzylamine:

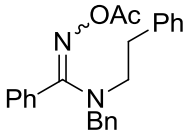


E

Amine **E** was prepared in a similar way to amine **A** from adamantan-2-ylmethanamine[16] and benzaldehyde.

Yield: 84%; Colorless oil; IR (NaCl) 3308, 3026, 2903, 2849, 1495, 1452, 1346, 1123, 1099 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50-1.53 (2H, m), 1.72-1.89 (14H, m), 2.72 (2H, d, *J* = 7.2 Hz), 3.81 (2H, s), 7.21-7.36 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 28.4, 30.6, 31.9, 38.3, 39.1, 44.6, 51.9, 54.2, 126.8, 128.0, 128.3, 140.6; ESIHRMS: Found: m/z 254.2064. Calcd for $C_{18}H_{26}N_2$: $(M+H)^+$ 254.2065.

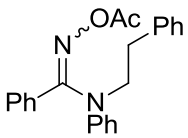
***N*'-Acetoxy-*N*-benzyl-*N*-phenethylbenzimidamide (1q):**



51% yield (two steps) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and *N*-benzyl-2-phenylethanamine[15].

mp: 75-77 °C. IR (NaCl) 3026, 2930, 2860, 1761, 1659, 1572, 1557, 1495, 1447, 1418, 1366, 1209, 1136; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.83 (3H, s), 2.88 (2H, s br), 3.36 (2H, s br), 4.32 (2H, s br), 7.02-7.26 (9H, m), 7.28-7.41 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 33.3, 49.4, 52.1, 126.3, 127.4, 127.6, 127.7, 128.4 (overlapped), 128.6, 128.9, 129.3, 131.4, 137.4, 139.0, 166.5, 169.4; ESIHRMS: Found: m/z 373.1917. Calcd for $C_{24}H_{25}N_2O_2$: $(M+H)^+$ 373.1916.

***N*'-Acetoxy-*N*-phenethyl-*N*-phenylbenzimidamide (1r):**

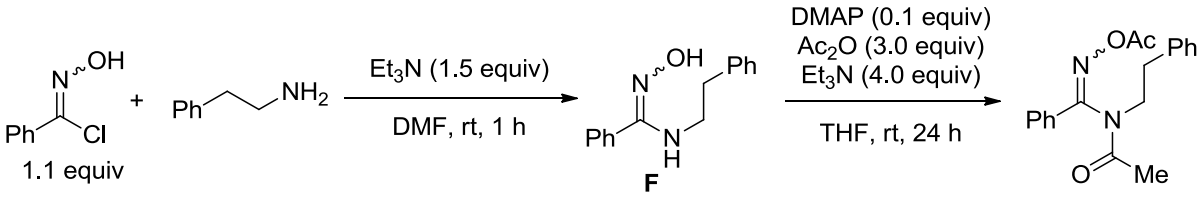


21% yield (two steps) as a yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and *N*-(2-phenylpropyl)aniline[9]. For this substrate, the intermediate *N*'-hydroxy-*N*-phenyl-*N*-(2-phenylpropyl)benzimidamide (used for the next

acetylation without purification) was prepared at elevated temperature (50 °C) and the *N*-hydroxybenzimidoyl chloride was added through a syringe pump over 0.5 h.

IR (NaCl) 3062, 3028, 2936, 1776, 1748, 1601, 1587, 1557, 1495, 1393, 1368, 1204; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (3H, s), 2.93 (2H, t, *J* = 8.0 Hz), 3.85 (2H, t, *J* = 8.0 Hz), 7.00-7.06 (5H, m), 7.21-7.28 (5H, m), 7.34-7.45 (3H, m), 7.54-7.56 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 35.5, 53.2, 120.7, 123.0, 126.6, 128.5, 128.6, 128.8, 129.0, 129.7, 130.7, 132.3, 138.2, 145.5, 158.2, 168.0; ESIHRMS: Found: m/z 359.1762. Calcd for $C_{23}H_{23}N_2O_2$: $(M+H)^+$ 359.1760.

3. Synthesis of *N*-acetyl amidoxime 1s



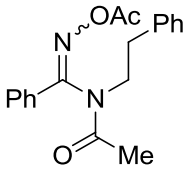
To a 150 mL two-neck round-bottomed flask (fitted with a water bath) was added 2-phenylethanamine (5.03 mL, 40.0 mmol) and triethylamine (8.36 mL, 60.0 mmol) in DMF (40 mL). *N*-Hydroxybenzimidoyl chloride (6.846 g, 44.0 mmol) in DMF (20 mL) was added dropwise to the stirred mixture. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water, 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 = 85:15 then 80:20) to afford *N*'-hydroxy-*N*-phenethylbenzimidamide **F** (7.559 g, 31.5 mmol, single stereoisomer, *E*/*Z* not determined) in 79% yield as a pale yellow oil.

IR (NaCl) 3385, 3061, 2941, 1627, 1494, 1454, 1392, 1145 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (2H, t, *J* = 7.2 Hz), 3.22 (2H, t, *J* = 6.8 Hz), 5.43 (1H, s br), 7.03-7.05 (2H, m), 7.15-7.40 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.8, 45.0, 126.3, 128.2, 128.4, 128.5, 128.7, 129.3, 131.4, 138.5, 156.2; ESIHRMS: Found: *m/z* 241.1336. Calcd for $C_{15}H_{17}N_2O$: $(M+H)^+$ 241.1341.

To a 50 mL two-neck round-bottomed flask was added **F** (1.813 g, 7.55 mmol), triethylamine (4.21 mL, 30.2 mmol) and *N*,*N*-dimethylpyridin-4-amine (0.092 g, 0.75 mmol) in THF (10 mL). Acetic anhydride (2.14 mL, 22.7 mmol) was added in a dropwise manner. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched

with water, 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 = 85:15) to afford **1s** (2.159 g, 6.66 mmol, single stereoisomer, *E*/*Z* not determined) in 88% yield as a yellow oil.

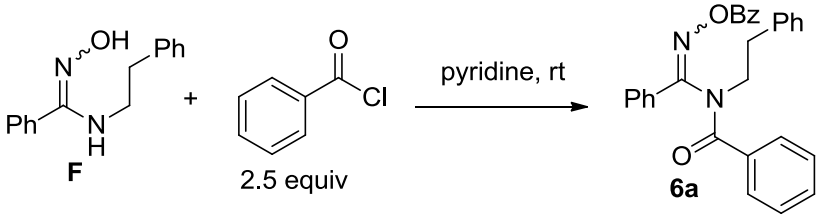
***N*-((Acetoxyimino)(phenyl)methyl)-*N*-phenethylacetamide (1s):**



IR (NaCl) 3028, 2938, 1782, 1682, 1601, 1568, 1447, 1385, 1371, 1296, 1190, 1142; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (3H, s), 2.20 (3H, s), 2.81 (1H, s br), 2.96 (1H, s br), 3.32 (1H, s br), 4.16 (1H, s br), 7.12-7.26 (5H, m), 7.46 (2H, t, *J* = 7.6 Hz), 7.55 (1H, t, *J* = 7.6 Hz), 7.72-7.74 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 21.9, 34.4, 47.6, 126.5, 128.0, 128.4, 128.6, 129.1, 129.8, 132.2, 137.9, 155.4, 167.1, 169.7; ESIHRMS: Found: m/z 325.1555. Calcd for $C_{19}H_{21}N_2O_3$: $(M+H)^+$ 325.1552.

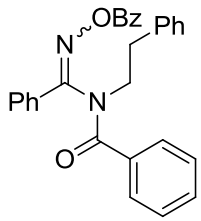
4. Synthesis of *N*-bezoyl amidoxime 6

Preparation of *N*-bezoyl amidoxime 6a:



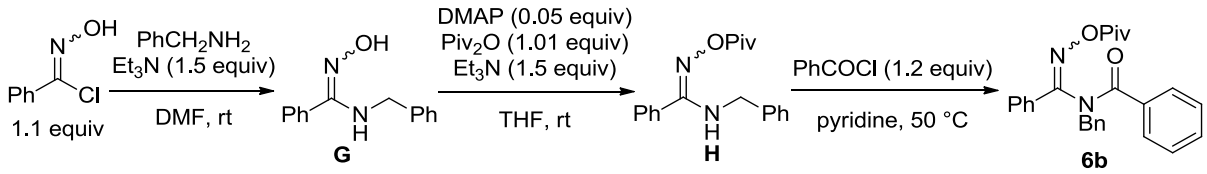
To a 50 mL two-neck round-bottomed flask was added **F** (1.076 g, 4.48 mmol) in pyridine (8 mL). Benzoyl chloride (1.30 mL, 11.2 mmol) was added in a dropwise manner. The reaction mixture was stirred at room temperature for 18 h. The solvent was evaporated and quenched with 1M citric acid, the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with 2M Na_2CO_3 and water, dried over $MgSO_4$, and concentrated. The resulting residue was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 91:9 then 85:15) to afford **6a** as the major compound, which could be repurified by flash column chromatography (silica gel; hexane:CH_2Cl_2 = 50:50 then ethyl acetate) to give pure **6a** (1.364 g, 3.04 mmol, single stereoisomer, *E*/*Z* not determined) in 68% yield as a sticky colorless oil.

***N*-(((Benzoyloxy)imino)(phenyl)methyl)-*N*-phenethylbenzamide (6a):**



IR (NaCl) 3026, 2953, 1748, 1667, 1601, 1493, 1449, 1368, 1331, 1277, 1242, 1134, 1082, 1061; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (2H, t, *J* = 7.6 Hz), 4.30 (2H, t, *J* = 7.6 Hz), 7.15-7.38 (17H, m), 7.52 (1H, t, *J* = 7.2 Hz), 7.80 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.9, 50.8, 126.4, 127.8, 128.1, 128.2, 128.4, 128.46, 128.48, 129.0, 129.2, 129.6, 130.55, 130.63, 131.0, 133.3, 136.6, 138.4, 162.7, 163.2, 172.2; ESIHRMS: Found: m/z 449.1872. Calcd for $C_{29}H_{25}N_2O_3$: $(M+H)^+$ 449.1865.

A typical procedure for synthesis of *N*-bezoyl amidoxime 6b:



To a 150 mL two-neck round-bottomed flask (fitted with a water bath) was added benzylamine (5.50 mL, 50.4 mmol) and triethylamine (10.5 mL, 75.6 mmol) in DMF (40 mL). *N*-Hydroxybenzimidoyl chloride (8.627 g, 55.5 mmol) in DMF (10 mL) was added dropwise to the stirred mixture. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with water, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed three times with water, dried over $MgSO_4$, and concentrated. The resulting residue was recrystallized from ethyl acetate/hexane to afford *N*-benzyl-*N*'-hydroxybenzimidamide **G** (8.873 g, 39.2 mmol, single stereoisomer, *E*/*Z* not determined) in 78% yield as a white solid.
mp: 117-118 °C; IR (NaCl) 3392, 3053, 2986, 1628, 1576, 1497, 1477, 1146 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.24 (2H, s), 5.70 (1H, s), 7.19-7.48 (10H, m), 8.68 (1H, s br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.4, 126.8, 127.2, 128.4, 128.5, 128.6, 129.6, 131.2, 139.5, 156.5; ESIHRMS: Found: *m/z* 227.1183. Calcd for $C_{14}H_{15}N_2O$: $(M+H)^+$ 227.1184.

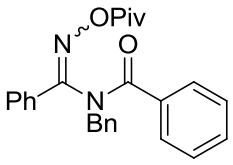
To a 150 mL two-neck round-bottomed flask was added **G** (8.873 g, 39.2 mmol), triethylamine (8.20 mL, 58.8 mmol) and *N*,*N*-dimethylpyridin-4-amine (0.240 g, 1.96 mmol) in THF (50 mL). Pivalic anhydride (7.378 g, 39.6 mmol) was added in a dropwise manner. The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched

with water, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, dried over $MgSO_4$, and concentrated to give analytically pure *N*-benzyl-*N*'-(pivaloyloxy)benzimidamide **H** (11.289 g, 36.4 mmol, single stereoisomer, *E*/*Z* not determined) in 93% yield as a white solid.

mp: 121-122 °C; IR (NaCl) 3424, 3017, 2976, 1746, 1609, 1574, 1477, 1271, 1125, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (9H, s), 4.28 (2H, d, *J* = 6.4 Hz), 5.48 (1H, t, *J* = 6.0 Hz), 7.18 (2H, d, *J* = 6.8 Hz), 7.26-7.45 (6H, m), 7.51-7.53 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 38.8, 47.8, 126.5, 127.6, 128.4, 128.8, 128.9, 129.6, 130.3, 138.6, 160.3, 174.7; ESIHRMS: Found: m/z 311.1765. Calcd for $C_{19}H_{23}N_2O_2$: $(M+H)^+$ 311.1760.

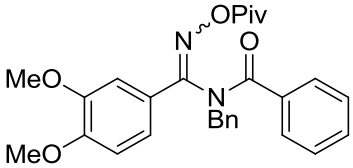
To a 50 mL two-neck round-bottomed flask was added **H** (3.116 g, 10.0 mmol) in pyridine (10 mL). Benzoyl chloride (1.39 mL, 12.0 mmol) was added in a dropwise manner. The reaction mixture was stirred at 55 °C for 12 h. The solvent was evaporated and quenched with 1M citric acid, the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with 2M Na_2CO_3 and water, dried over $MgSO_4$, and concentrated. The resulting residue was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 91:9 then 85:15) to afford **6b** (4.008 g, 9.67 mmol, single stereoisomer, *E*/*Z* not determined) in 97% yield as a white solid.

***N*-Benzyl-*N*-(phenyl((pivaloyloxy)imino)methyl)benzamide (6b):**



mp: 82-83 °C; IR (NaCl) 3063, 2974, 1765, 1759, 1682, 1667, 1601, 1495, 1447, 1360, 1323, 1238, 1105, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (9H, s), 5.31 (2H, s), 6.82-6.84 (2H, m), 7.05 (2H, t, *J* = 7.6 Hz), 7.10-7.31 (7H, m), 7.36 (2H, t, *J* = 7.6 Hz), 7.64-7.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 38.3, 52.8, 127.7 (overlapped), 127.8, 128.0, 128.4, 128.7, 129.7, 130.1, 130.4, 131.2, 136.8, 136.9, 162.5, 172.0, 174.7; ESIHRMS: Found: m/z 415.2024. Calcd for $C_{26}H_{27}N_2O_3$: $(M+H)^+$ 415.2022.

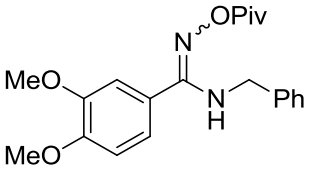
***N*-Benzyl-*N*-((3,4-dimethoxyphenyl)((pivaloyloxy)imino)methyl)benzamide (6c):**



97% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-3,4-dimethoxy-*N*'-(pivaloyloxy)benzimidamide and benzoyl chloride.

mp: 52-53 °C; IR (NaCl) 2972, 2836, 2872, 1748, 1674, 1599, 1514, 1454, 1418, 1312, 1265, 1225, 1138, 1105, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (9H, s), 3.52 (3H, s), 3.78 (3H, s), 5.32 (2H, s), 6.20 (1H, d, *J* = 2.0 Hz), 6.45 (1H, dd, *J* = 2.0, 8.4 Hz), 6.52 (1H, d, *J* = 1.6 Hz), 7.12-7.37 (8H, m), 7.65-7.67 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 38.3, 53.0, 55.5, 55.8, 109.8, 111.7, 122.6, 123.9, 127.6, 127.8, 127.9, 128.5, 129.9, 130.3, 136.9, 137.0, 147.8, 150.3, 162.1, 171.9, 174.8; ESIHRMS: Found: m/z 497.2049. Calcd for $C_{28}H_{30}N_2O_5Na$: $(M+H)^+$ 497.2052.

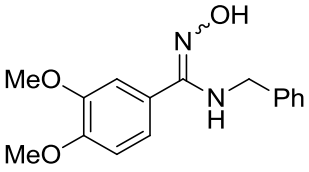
_N_-Benzyl-3,4-dimethoxy-_N_'-(pivaloyloxy)benzimidamide



67% yield (recrystallized from ethyl acetate/diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-*N*'-hydroxy-3,4-dimethoxybenzimidamide and pivalic anhydride.

mp: 130-131 °C; IR (NaCl) 3356, 3015, 2972, 1738, 1732, 1614, 1582, 1520, 1462, 1422, 1261, 1217, 1138, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (9H, s), 3.77 (3H, s), 3.89 (3H, s), 4.31 (2H, d, *J* = 6.4), 5.48 (1H, t, *J* = 6.0), 6.87 (1H, d, *J* = 8.4 Hz), 6.97 (1H, d, *J* = 1.6 Hz), 7.12 (1H, dd, *J* = 1.6, 8.4 Hz), 7.20 (2H, d, *J* = 7.2 Hz), 7.27-7.36 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 38.9, 47.9, 55.8, 55.9, 110.8, 111.9, 122.0, 124.9, 126.4, 127.5, 128.8, 139.0, 148.8, 150.7, 160.4, 174.8; ESIHRMS: Found: m/z 371.1972. Calcd for $C_{21}H_{27}N_2O_4$: $(M+H)^+$ 371.1971.

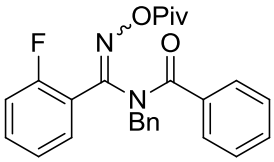
_N_-benzyl-_N_'-hydroxy-3,4-dimethoxybenzimidamide



67% yield (recrystallized from ethyl acetate/diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxy-3,4-dimethoxybenzimidoyl chloride[17] and benzylamine.

mp: 82-83 °C; IR (NaCl) 3400, 3208, 3022, 2938, 2839, 1643, 1607, 1522, 1425, 1258, 1231, 1140, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (3H, s), 3.86 (3H, s), 4.25 (2H, s), 5.77 (1H, s br), 6.83 (1H, d, *J* = 8.4 Hz), 6.92 (1H, d, *J* = 2.0 Hz), 7.05 (1H, dd, *J* = 2.0, 8.4 Hz), 7.19-7.31 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.3, 55.7, 55.8, 110.7, 111.5, 121.2, 123.5, 126.6, 127.0, 128.5, 139.9, 148.6, 150.0, 156.4; ESIHRMS: Found: m/z 287.1395. Calcd for $C_{16}H_{19}N_2O_3$: $(M+H)^+$ 287.1396.

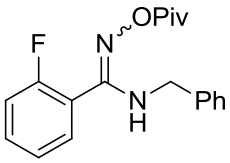
_N_-Benzyl-_N_-((2-fluorophenyl)((pivaloyloxy)imino)methyl)benzamide (6d):



45% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-2-fluoro-*N*'-(pivaloyloxy)benzimidamide and benzoyl chloride.

mp: 74-75 °C; IR (NaCl) 3028, 2974, 1759, 1668, 1595, 1493, 1449, 1366, 1323, 1269, 1240, 1103, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (9H, s), 5.38 (2H, s), 6.58-6.64 (2H, m), 6.89 (1H, t, *J* = 7.6 Hz), 7.11-7.16 (3H, m), 7.21 (1H, d, *J* = 7.6 Hz), 7.25-7.27 (2H, m), 7.31 (1H, d, *J* = 7.2 Hz), 7.37 (2H, t, *J* = 7.2 Hz), 7.68-7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 38.3, 53.0, 115.2 (d, *J* = 21.5 Hz), 120.3 (d, *J* = 14.5 Hz), 123.8 (d, *J* = 3.3 Hz), 127.4, 127.6 (d, *J* = 2.5 Hz), 127.8, 128.0, 128.5, 129.8, 130.6, 132.5 (d, *J* = 8.7 Hz), 136.4, 137.0, 157.6 (d, *J* = 1.7 Hz), 158.7 (d, *J* = 254.3 Hz), 171.9, 174.4; ESIHRMS: Found: m/z 433.1925. Calcd for $C_{26}H_{26}FN_2O_3$: $(M+H)^+$ 433.1927.

_N_-Benzyl-2-fluoro-_N_'-(pivaloyloxy)benzimidamide

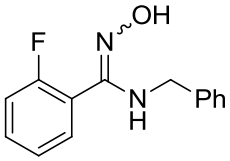


83% yield (recrystallized from ethyl acetate/diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-2-fluoro-*N*'-hydroxybenzimidamide and pivalic anhydride.

mp: 112-113 °C; IR (NaCl) 3364, 2972, 1736, 1612, 1584, 1501, 1456, 1406, 1269, 1221, 1134; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (9H, s), 4.23 (2H, d, *J* = 6.0 Hz), 5.53 (1H, s br), 7.10-7.48 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 38.9, 47.5, 115.7 (d, *J* = 20.8 Hz), 117.9 (d, *J* = 15.1 Hz), 124.4 (d, *J* = 3.5 Hz), 126.8, 127.7, 128.8,

131.7 (d, *J* = 2.6 Hz), 132.3 (d, *J* = 8.1 Hz), 138.1, 155.6, 160.3 (d, *J* = 249.4 Hz), 174.5; ESIHRMS: Found: m/z 329.1667. Calcd for $C_{19}H_{22}FN_2O_2$: $(M+H)^+$ 329.1665.

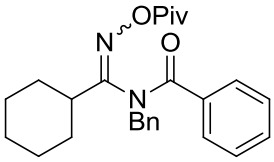
***N*-Benzyl-2-fluoro-*N*'-hydroxybenzimidamide**



95% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from 2-fluoro-*N*-hydroxybenzimidoyl chloride[18] and benzylamine.

mp: 116-117 °C; IR (NaCl) 3404, 3229, 3017, 2870, 1636, 1618, 1497, 1454, 1410, 1348; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.13 (2H, s), 5.77 (1H, s br), 7.04-7.38 (9H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 47.1, 115.7 (d, *J* = 21.3 Hz), 119.1 (d, *J* = 15.1 Hz), 124.2 (d, *J* = 3.6 Hz), 127.0, 127.2, 128.4, 131.4 (d, *J* = 2.5 Hz), 131.5 (d, *J* = 8.2 Hz), 139.0, 151.6, 160.2 (d, *J* = 248.9 Hz); ESIHRMS: Found: m/z 245.1088. Calcd for $C_{14}H_{14}FN_2O$: $(M+H)^+$ 245.1090.

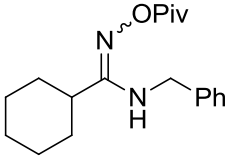
***N*-Benzyl-*N*-(cyclohexyl((pivaloyloxy)imino)methyl)benzamide (6e):**



38% yield as a colorless oil (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-*N*'-(pivaloyloxy)cyclohexanecarboximidamide and benzoyl chloride.

IR (NaCl) 2972, 2934, 2855, 1767, 1759, 1608, 1479, 1447, 1360, 1321, 1269, 1115, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84-0.99 (3H, m), 1.12-1.33 (13H, m), 1.53-1.56 (3H, m), 2.23 (1H, tt, *J* = 3.2, 12.0 Hz), 5.04 (2H, s), 7.23-7.49 (8H, m), 7.61-7.63 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 26.2, 27.2, 27.4, 38.6, 46.2, 54.0, 127.6, 128.35, 128.44, 128.5, 129.1, 131.0, 136.1, 137.1, 168.2, 171.5, 174.2; ESIHRMS: Found: m/z 421.2492. Calcd for $C_{26}H_{33}N_2O_3$: $(M+H)^+$ 421.2491.

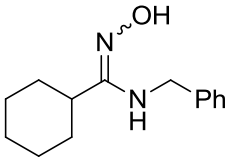
***N*-Benzyl-*N*'-(pivaloyloxy)cyclohexanecarboximidamide**



63% yield (recrystallized from diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-benzyl-*N*'-hydroxycyclohexanecarboximidamide and pivalic anhydride.

mp: 112-113 °C; IR (NaCl) 3429, 2931, 2934, 2855, 1742, 1616, 1452, 1273, 1130; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17-1.30 (12H, m), 1.57-1.92 (7H, m), 2.35 (1H, tt, *J* = 3.2, 12.0 Hz), 4.40 (2H, d, *J* = 6.0 Hz), 5.13 (1H, t, *J* = 5.2 Hz), 7.26-7.39 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.2, 27.4, 30.2, 38.2, 38.8, 46.1, 126.5, 127.7, 128.9, 138.5, 162.8, 174.9; ESIHRMS: Found: m/z 317.2228. Calcd for $C_{19}H_{29}N_2O_2$: $(M+H)^+$ 317.2229.

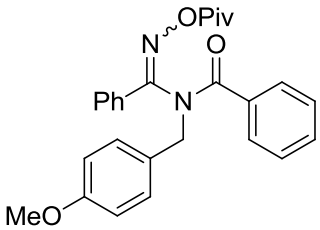
_N_-Benzyl-_N_'-hydroxycyclohexanecarboximidamide



70% yield (recrystallized from ethyl acetate/diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxycyclohexanecarbimidoyl chloride and benzylamine.

mp: 120-121 °C; IR (NaCl) 3395, 3246, 3015, 2934, 2855, 1655, 1495, 1452, 1416, 1339; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15-1.44 (5H, m), 1.64-1.89 (5H, m), 2.26 (1H, tt, *J* = 3.2, 12.0 Hz), 4.34 (2H, d, *J* = 6.0 Hz), 5.51 (1H, t, *J* = 5.6 Hz), 7.25-7.36 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.3, 30.6, 37.4, 45.8, 126.8, 127.3, 128.6, 139.4, 158.1; ESIHRMS: Found: m/z 233.1652. Calcd for $C_{14}H_{21}N_2O$: $(M+H)^+$ 233.1654.

_N_- _N_-(4-Methoxybenzyl)-N-(phenyl((pivaloyloxy)imino)methyl)benzamide (6f):

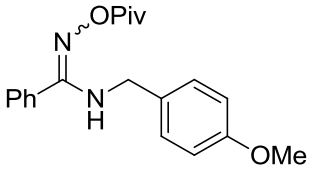


86% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-(4-methoxybenzyl)-*N*'-(pivaloyloxy)benzimidamide and benzoyl chloride.

mp: 132-133 °C; IR (NaCl) 3063, 3017, 2974, 1755, 1667, 1603, 1513, 1449, 1366, 1319, 1250, 1107, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (9H, s), 3.79 (3H, s), 5.26 (2H, s),

6.81-6.90 (4H, m), 7.03-7.26 (8H, m), 7.57-7.61 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 38.3, 52.3, 55.1, 113.8, 127.6, 127.7, 128.0, 128.7, 129.2, 130.0, 130.4, 131.2, 131.4, 137.0, 159.2, 162.5, 172.0, 174.7; ESIHRMS: Found: m/z 445.2130. Calcd for $C_{27}H_{29}N_2O_4$: $(M+H)^+$ 445.2127.

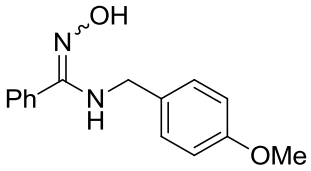
***N*-(4-Methoxybenzyl)-*N*'-(pivaloyloxy)benzimidamide**



73% yield (recrystallized from CH_2Cl_2/hexane) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*'-hydroxy-*N*-(4-methoxybenzyl)benzimidamide and pivalic anhydride.

mp: 134-135 °C; IR (NaCl) 3401, 2970, 2934, 2872, 1732, 1603, 1574, 1510, 1362, 1246, 1142, 1034; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (9H, s), 3.79 (3H, s), 4.20 (2H, d, *J* = 6.4), 5.38 (1H, t, *J* = 6.0), 6.84-6.86 (2H, m), 7.09 (2H, d, *J* = 8.4 Hz), 7.36-7.53 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.4, 38.9, 47.4, 55.2, 114.2, 127.9, 128.4, 129.0, 129.8, 130.3, 130.6, 159.0, 160.3, 174.7; ESIHRMS: Found: m/z 341.1864. Calcd for $C_{20}H_{25}N_2O_3$: $(M+H)^+$ 341.1865.

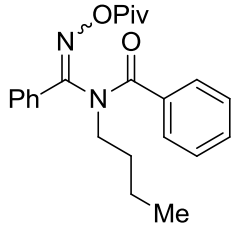
***N*'-Hydroxy-*N*-(4-methoxybenzyl)benzimidamide**



84% yield as a yellow oil (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and 4-methoxylbenzylamine.

IR (NaCl) 3383, 3188, 3061, 2953, 2835, 1628, 1612, 1512, 1408, 1348, 1248, 1175, 1034; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76 (3H, s), 4.14 (2H, s), 5.66 (1H, s br), 6.79-6.83 (2H, m), 7.08 (2H, d, *J* = 8.8 Hz), 7.32-7.47 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 46.9, 55.2, 113.9, 128.0, 128.3, 128.5, 129.5, 131.2, 131.6, 156.4, 158.7; ESIHRMS: Found: m/z 257.1288. Calcd for $C_{15}H_{17}N_2O_2$: $(M+H)^+$ 257.1290.

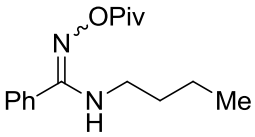
***N*-Butyl-*N*-(phenyl((pivaloyloxy)imino)methyl)benzamide (6g):**



96% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-butyl-*N*'-(pivaloyloxy)benzimidamide and benzoyl chloride.

mp: 101-102 °C; IR (NaCl) 3017, 2961, 2934, 1757, 1670, 1591, 1576, 1449, 1369, 1333, 1288, 1231, 1101, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, t, *J* = 7.2), 1.06 (9H, s), 1.39-1.50 (2H, m), 1.85-1.93 (2H, m), 4.03 (2H, t, *J* = 8.0), 7.14-7.32 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 20.2, 26.8, 30.8, 38.3, 49.5, 127.7, 127.9, 128.0, 128.9, 130.3, 131.1 (overlapped), 136.9, 163.0, 172.1, 174.6; ESIHRMS: Found: m/z 381.2181. Calcd for $C_{23}H_{29}N_2O_3$: $(M+H)^+$ 381.2178.

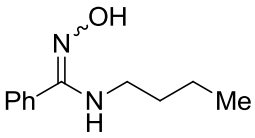
_N_-Butyl-_N_'-(pivaloyloxy)benzimidamide



73% yield (recrystallized from diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-butyl-*N*'-hydroxybenzimidamide and pivalic anhydride.

mp: 109-110 °C; IR (NaCl) 3352, 2963, 2932, 2872, 1738, 1607, 1574, 1479, 1414, 1366, 1273, 1130; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 7.2), 1.25-1.49 (13H, m), 3.03-3.08 (2H, m), 5.10 (1H, s br), 7.38-7.51 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.5, 27.5, 33.2, 38.9, 43.6, 128.3, 128.9, 130.07, 130.10, 160.5, 174.7 ESIHRMS: Found: m/z 277.1912. Calcd for $C_{16}H_{25}N_2O_2$: $(M+H)^+$ 277.1916.

_N_-Butyl-_N_'-hydroxybenzimidamide

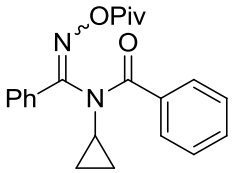


82% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and butan-1-amine.

mp: 51-52 °C; IR (NaCl) 3383, 3206, 2957, 2932, 2872, 1628, 1574, 1464, 1408, 1364, 1219, 1153; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2), 1.22-1.43 (4H,

m), 2.99 (2H, t, *J* = 6.4), 5.31 (1H, s br), 7.35-7.48 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 19.5, 33.3, 43.3, 128.2, 128.5, 129.3, 131.6, 156.5; ESIHRMS: Found: m/z 193.1343. Calcd for $C_{11}H_{17}N_2O$: $(M+H)^+$ 193.1341.

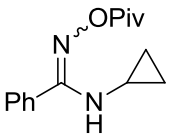
***N*-Cyclopropyl-*N*-(phenyl((pivaloyloxy)imino)methyl)benzamide (6h):**



69% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-cyclopropyl-*N*'-(pivaloyloxy)benzimidamide and benzoyl chloride.

mp: 107-108 °C; IR (NaCl) 3063, 3013, 2974, 1759, 1667, 1601, 1447, 1337, 1217, 1109, 1088, 1082; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91-0.93 (4H, m), 1.09 (9H, s), 3.08-3.13 (1H, m), 7.21-7.43 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.5, 26.9, 31.3, 38.3, 127.5, 127.9, 128.2, 128.8, 130.1, 130.8, 130.9, 136.5, 161.3, 172.4, 174.4; ESIHRMS: Found: m/z 365.1862. Calcd for $C_{22}H_{25}N_2O_3$: $(M+H)^+$ 365.1865.

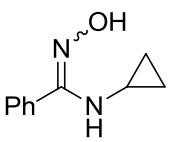
***N*-Cyclopropyl-*N*'-(pivaloyloxy)benzimidamide**



91% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-cyclopropyl-*N*'-hydroxybenzimidamide and pivalic anhydride.

mp: 134-135 °C; IR (NaCl) 3431, 3011, 2972, 1744, 1609, 1574, 1479, 1404, 1364, 1273, 1119, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.44-0.57 (4H, m), 1.31 (9H, s), 2.51-2.53 (1H, m), 5.36 (1H, s br), 7.38-7.45 (3H, m), 7.58 (2H, t, *J* = 7.6); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.9, 25.8, 27.4, 38.8, 128.0, 128.8, 129.8, 130.6, 160.5, 174.6; ESIHRMS: Found: m/z 261.1601. Calcd for $C_{15}H_{21}N_2O_2$: $(M+H)^+$ 261.1603.

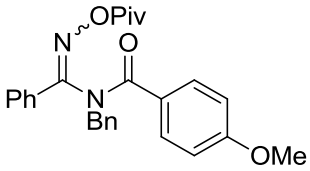
***N*-Cyclopropyl-*N*'-hydroxybenzimidamide**



68% yield (recrystallized from diethyl ether) as a white solid (single stereoisomer, *E*/*Z* not determined) from *N*-hydroxybenzimidoyl chloride and cyclopropanamine.

mp: 93-94 °C; IR (NaCl) 3406, 3231, 3013, 1630, 1576, 1466, 1400, 1350; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39-0.50 (4H, m), 2.42-2.47 (1H, m), 5.55 (1H, s br), 7.35-7.56 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.6, 25.5, 128.0, 128.5, 129.2, 132.1, 156.5; ESIHRMS: Found: m/z 177.1029. Calcd for $C_{10}H_{13}N_2O$: $(M+H)^+$ 177.1028.

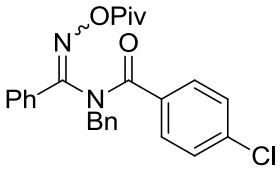
_N_-Benzyl-4-methoxy-_N_-(phenyl((pivaloyloxy)imino)methyl)benzamide (6i):



94% yield as a pale yellow oil (single stereoisomer, *E*/*Z* not determined) from **H** and 4-methoxybenzoyl chloride.

IR (NaCl) 3063, 2972, 2936, 1767, 1748, 1682, 1591, 1504, 1454, 1360, 1306, 1258, 1172, 1119, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (9H, s), 3.72 (3H, s), 5.30 (2H, s), 6.63 (2H, d, *J* = 8.8 Hz), 6.87 (2H, d, *J* = 7.6 Hz), 7.07 (2H, t, *J* = 7.6 Hz), 7.15 (1H, t, *J* = 7.6 Hz), 7.26-7.30 (3H, m), 7.35 (2H, t, *J* = 7.6 Hz), 7.66 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 38.2, 53.1, 55.2, 113.3, 127.6, 127.7, 128.4, 128.5, 129.2, 129.7, 129.9, 130.0, 131.4, 137.1, 161.5, 162.8, 171.6, 174.7; ESIHRMS: Found: m/z 445.2122. Calcd for $C_{27}H_{29}N_2O_4$: $(M+H)^+$ 445.2127.

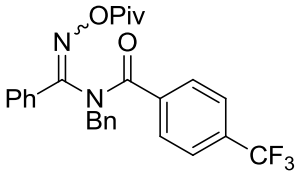
_N_-Benzyl-4-chloro-_N_-(phenyl((pivaloyloxy)imino)methyl)benzamide (6j):



95% yield as a sticky colorless oil (single stereoisomer, *E*/*Z* not determined) from **H** and 4-chlorobenzoyl chloride.

IR (NaCl) 3030, 2974, 1759, 1667, 1593, 1489, 1449, 1366, 1323, 1240, 1105; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (9H, s), 5.28 (2H, s), 6.85-6.87 (2H, m), 7.10-7.38 (10H, m), 7.61-7.63 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.9, 38.3, 52.9, 127.89, 127.94, 128.3, 128.6, 128.8, 129.1, 129.8, 130.4, 131.1, 135.2, 136.7, 136.8, 162.1, 171.0, 174.7; ESIHRMS: Found: m/z 449.1633. Calcd for $C_{26}H_{26}{}^{35}ClN_2O_3$: $(M+H)^+$ 449.1632.

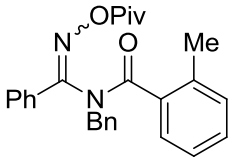
_N_-Benzyl-_N_-(phenyl((pivaloyloxy)imino)methyl)-4-(trifluoromethyl)benzamide (6k):



86% yield as a white solid (single stereoisomer, *E*/*Z* not determined) from **H** and 4-(trifluoromethyl)benzoyl chloride.

mp: 96-97 °C; IR (NaCl) 3021, 2976, 1765, 1755, 1682, 1672, 1605, 1574, 1362, 1323, 1238, 1169, 1109; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.05 (9H, s), 5.27 (2H, s), 6.87 (2H, d, *J* = 7.6 Hz), 7.11 (2H, t, *J* = 8.0 Hz), 7.22 (1H, t, *J* = 7.6 Hz), 7.31-7.41 (7H, m), 7.59 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 38.3, 52.5, 123.5 (q, *J* = 270.9 Hz), 125.0 (q, *J* = 3.7 Hz), 127.5, 127.8, 128.0, 128.6, 128.8, 129.7, 130.6, 130.7, 131.9 (q, *J* = 32.5 Hz), 136.5, 140.2, 161.6, 170.7, 174.5; ESIHRMS: Found: m/z 483.1904. Calcd for $C_{27}H_{26}F_3N_2O_3$: $(M+H)^+$ 483.1896.

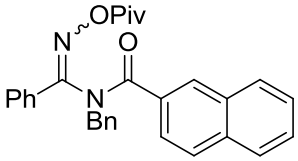
_N_-Benzyl-2-methyl-_N_-(phenyl((pivaloyloxy)imino)methyl)benzamide (6l):



41% yield as a colorless oil (single stereoisomer, *E*/*Z* not determined) from **H** and 2-methylbenzoyl chloride.

IR (NaCl) 3021, 2974, 1759, 1672, 1605, 1591, 1447, 1366, 1321, 1237, 1105, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (9H, s), 2.00 (3H, s), 5.36 (2H, s), 6.65-6.67 (2H, m), 6.81 (1H, d, *J* = 7.6 Hz), 6.97-7.16 (6H, m), 7.29-7.40 (3H, m), 7.67-7.69 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 26.8, 38.3, 52.2, 125.2, 127.0, 127.5, 127.7, 127.8, 128.5, 129.7, 129.8, 129.9, 130.4, 131.5, 136.26, 136.31, 137.2, 162.3, 171.7, 174.7; ESIHRMS: Found: m/z 451.1996. Calcd for $C_{27}H_{28}N_2O_3Na$: $(M+H)^+$ 451.1998.

_N_-Benzyl-_N_-(phenyl((pivaloyloxy)imino)methyl)-2-naphthamide (6m):

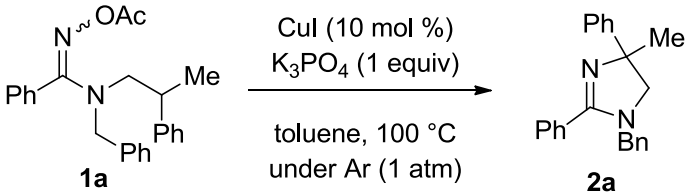


84% yield as a sticky colorless oil (single stereoisomer, *E*/*Z* not determined) from **H** and 2-naphthoyl chloride.

IR (NaCl) 3015, 2974, 1759, 1667, 1593, 1449, 1368, 1323, 1310, 1229, 1107, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (9H, s), 5.40 (2H, s), 6.77-7.05 (5H, m), 7.25-7.48 (6H, m), 7.53 (1H, d, *J* = 8.4 Hz), 7.67-7.76 (4H, m), 7.88 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 38.2, 52.9, 124.2, 126.5, 127.4, 127.46, 127.53, 127.8, 127.9, 128.2, 128.45 (overlapped), 128.48, 129.8, 130.0, 131.2, 132.0, 133.7, 134.0, 137.0, 162.6, 172.0, 174.7; ESIHRMS: Found: m/z 465.2175. Calcd for $C_{30}H_{29}N_2O_3$: $(M+H)^+$ 465.2178.

5. Copper-catalyzed synthesis of dihydroimidazoles 2

Typical Procedure:

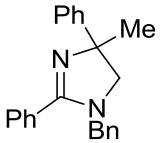


To a solution of *N*'-acetoxy-*N*-benzyl-*N*-(2-phenylpropyl)benzimidamide (the major stereoisomer) (**1a**) (136.1 mg, 0.352 mmol) in toluene (3.5 mL) was added CuI (6.7 mg, 0.035 mmol) and K_3PO_4 (74.7 mg, 0.352mmol). The reaction mixture was then stirred for 4 h at 100 °C under an Ar atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with ethyl acetate, dried over $MgSO_4$ and removed in vacuo to afford a crude residue, which was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 50:50 then ethyl acetate) to provide **2a** (87.3 mg, 0.267 mmol) in 76% yield.

The reaction of the minor stereoisomer of **1a** (104.0 mg, 0.269 mmol) with CuI (5.1 mg, 0.027 mmol) and K_3PO_4 (57.1 mg, 0.269 mmol) in toluene (2.7 mL) under Ar atmosphere at 100 °C for 4 h gave **2a** (67.7 mg, 0.207 mmol) in 77% yield.

The reaction of the *E*/*Z* mixture (major/minor = 1.3:1) of **1a** (128.2 mg, 0.332 mmol) with CuI (6.3 mg, 0.033 mmol) and K_3PO_4 (70.4 mg, 0.332 mmol) in toluene (3.3 mL) under Ar atmosphere at 100 °C for 4 h gave **2a** (80.1 mg, 0.245 mmol) in 74% yield.

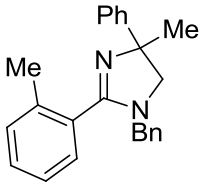
1-Benzyl-4-methyl-2,4-diphenyl-4,5-dihydro-1*H*-imidazole (2a):[19]



Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (3H, s), 3.44 (1H, d, *J* = 9.2 Hz), 3.61 (1H, d, *J* = 9.6 Hz), 4.11 (1H, d, *J* = 15.6 Hz), 4.51 (1H, d, *J* = 15.6 Hz), 7.22-7.49 (13H, m), 7.67-

7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.2, 52.4, 64.2, 69.8, 125.2, 126.2, 126.8, 127.2, 128.1, 128.2, 128.4, 128.5, 129.9, 130.8, 137.5, 148.8, 164.6.

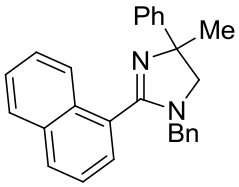
1-Benzyl-4-methyl-4-phenyl-2-(*o*-tolyl)-4,5-dihydro-1*H*-imidazole (2b):



Reaction time: 6 h.

Yield: 78%; Yellow oil; IR (NaCl) 3061, 3026, 2963, 2922, 1614, 1595, 1578, 1495, 1445, 1362, 1315, 1260, 1138; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (3H, s), 2.44 (3H, s), 3.39 (1H, d, *J* = 9.2 Hz), 3.55 (1H, d, *J* = 8.8 Hz), 3.93 (1H, d, *J* = 15.2 Hz), 4.21 (1H, d, *J* = 15.2 Hz), 7.14 (2H, d, *J* = 6.8 Hz), 7.19-7.34 (9H, m), 7.40 (1H, d, *J* = 7.6 Hz), 7.49 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 30.5, 51.5, 62.9, 70.4, 125.4, 125.8, 126.3, 127.3, 127.4, 128.2, 128.6, 128.7, 129.3, 130.4, 131.1, 136.7, 137.5, 149.1, 163.9; ESIHRMS: Found: m/z 341.2021. Calcd for $C_{24}H_{25}N_2$: $(M+H)^+$ 341.2018.

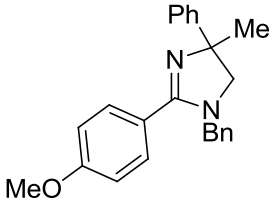
1-Benzyl-4-methyl-2-(naphthalen-1-yl)-4-phenyl-4,5-dihydro-1*H*-imidazole (2c):



Reaction time: 2 h.

Yield: 72%; Yellow oil; IR (NaCl) 3059, 3028, 2963, 2922, 1607, 1574, 1495, 1445, 1416, 1362, 1315, 1250, 1198, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.73 (3H, s), 3.52 (1H, d, *J* = 9.2 Hz), 3.63 (1H, d, *J* = 9.2 Hz), 3.91 (1H, d, *J* = 14.8 Hz), 4.16 (1H, d, *J* = 15.2 Hz), 7.11 (2H, d, *J* = 6.8 Hz), 7.19-7.28 (4H, m), 7.35 (2H, t, *J* = 7.6 Hz), 7.50-7.56 (5H, m), 7.70 (1H, d, *J* = 6.0 Hz), 7.87 (1H, d, *J* = 7.6 Hz), 7.91 (1H, d, *J* = 8.4 Hz), 8.21 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.8, 51.9, 63.1, 70.7, 125.1, 125.2, 125.4, 126.2, 126.3, 126.8, 127.1, 127.3, 127.5, 128.30, 128.33, 128.5, 129.0, 129.8, 131.3, 133.5, 137.3, 149.1, 163.4; ESIHRMS: Found: m/z 377.2021. Calcd for $C_{27}H_{25}N_2$: $(M+H)^+$ 377.2018.

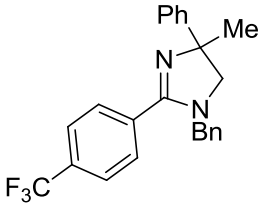
1-Benzyl-2-(4-methoxyphenyl)-4-methyl-4-phenyl-4,5-dihydro-1*H*-imidazole (2d):



This reaction was carried out using the major stereoisomer of **1d** as starting material. Reaction time: 12 h.

Yield: 74%; Yellow oil; IR (NaCl) 3061, 3026, 2963, 2930, 1620, 1607, 1514, 1454, 1360, 1317, 1254, 1173, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (3H, s), 3.41 (1H, d, *J* = 9.6 Hz), 3.60 (1H, d, *J* = 9.2 Hz), 3.81 (3H, s), 4.11 (1H, d, *J* = 16.0 Hz), 4.53 (1H, d, *J* = 16.0 Hz), 6.93 (2H, d, *J* = 8.8 Hz), 7.19-7.35 (8H, m), 7.47 (2H, d, *J* = 7.2 Hz), 7.64 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 52.8, 55.3, 64.6, 69.8, 113.9, 123.3, 125.3, 126.2, 126.9, 127.3, 128.2, 128.6, 129.9, 138.0, 149.2, 160.9, 164.4; ESIHRMS: Found: m/z 357.1962. Calcd for $C_{24}H_{25}N_2O$: $(M+H)^+$ 357.1967.

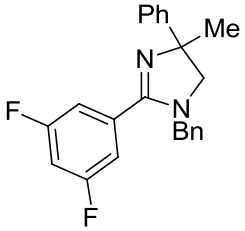
1-Benzyl-4-methyl-4-phenyl-2-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazole (2e):



Reaction time: 1.5 h.

Yield: 76%; Yellow oil; IR (NaCl) 3061, 3028, 2967, 2924, 1601, 1520, 1495, 1416, 1360, 1315, 1173, 1138, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (3H, s), 3.46 (1H, d, *J* = 9.6 Hz), 3.63 (1H, d, *J* = 9.2 Hz), 4.10 (1H, d, *J* = 15.6 Hz), 4.46 (1H, d, *J* = 16.0 Hz), 7.21-7.36 (8H, m), 7.46 (2H, d, *J* = 7.6 Hz), 7.68 (2H, d, *J* = 8.0 Hz), 7.81 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 52.5, 64.4, 70.5, 123.8 (q, *J* = 270.7 Hz), 125.2, 125.5 (q, *J* = 3.7 Hz), 126.4, 126.9, 127.5, 128.3, 128.7, 128.8, 131.9 (q, *J* = 32.5 Hz), 134.9, 137.3, 148.7, 163.4; ESIHRMS: Found: m/z 395.1736. Calcd for $C_{24}H_{22}F_3N_2$: (M+H)+ 395.1735.

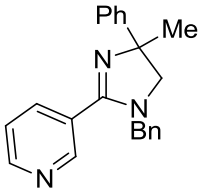
1-Benzyl-2-(3,5-difluorophenyl)-4-methyl-4-phenyl-4,5-dihydro-1*H*-imidazole (2f):



Reaction time: 3 h.

Yield: 62%; Yellow oil; IR (NaCl) 3086, 3061, 3028, 2965, 2924, 1587, 1574, 1495, 1435, 1402, 1362, 1337, 1233, 1121, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (3H, s), 3.44 (1H, d, *J* = 9.6 Hz), 3.61 (1H, d, *J* = 9.6 Hz), 4.11 (1H, d, *J* = 15.6 Hz), 4.47 (1H, d, *J* = 15.6 Hz), 6.88 (1H, tt, *J* = 2.4, 8.8 Hz), 7.20-7.36 (10H, m), 7.43 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.3, 52.5, 64.3, 70.4, 105.5 (t, *J* = 24.9 Hz), 111.6 (dd, *J* = 7.7, 18.9 Hz), 125.2, 126.5, 127.0, 127.6, 128.3, 128.8, 134.4 (t, *J* = 9.5 Hz), 137.1, 148.5, 162.5 (t, *J* = 2.8 Hz), 162.9 (dd, *J* = 12.4, 248.5 Hz); ESIHRMS: Found: m/z 363.1676. Calcd for $C_{23}H_{21}F_2N_2$: (M+H)+ 363.1673.

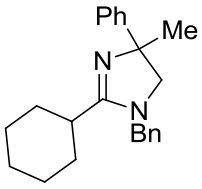
3-(1-Benzyl-4-methyl-4-phenyl-4,5-dihydro-1*H*-imidazol-2-yl)pyridine (2g):



Reaction time: 3 h.

Yield: 72%; Yellow oil; IR (NaCl) 3028, 2965, 2922, 2859, 1612, 1587, 1487, 1445, 1400, 1362, 1317, 1263, 1132, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65 (3H, s), 3.48 (1H, d, *J* = 9.6 Hz), 3.64 (1H, d, *J* = 9.2 Hz), 4.13 (1H, d, *J* = 15.6 Hz), 4.48 (1H, d, *J* = 16.0 Hz), 7.21-7.38 (9H, m), 7.46 (2H, d, *J* = 7.2 Hz), 8.00 (1H, d, *J* = 7.6 Hz), 8.69 (1H, d, *J* = 3.6 Hz), 8.94 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.4, 52.5, 64.3, 70.5, 123.4, 125.2, 126.5, 126.9, 127.4, 127.5, 128.3, 128.8, 136.0, 137.2, 148.7, 149.2, 151.0, 162.0; ESIHRMS: Found: m/z 328.1809. Calcd for $C_{22}H_{22}N_3$: $(M+H)^+$ 328.1814.

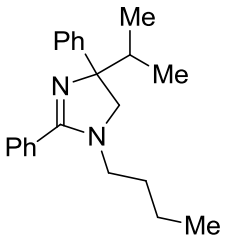
1-Benzyl-2-cyclohexyl-4-methyl-4-phenyl-4,5-dihydro-1*H*-imidazole (2h):



Reaction time: 8 h.

Yield: 40%; Yellow oil; IR (NaCl) 3026, 2930, 2853, 1605, 1578, 1495, 1447, 1418, 1358, 1319, 1279, 1215, 1136, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26-1.34 (3H, m), 1.53 (3H, s), 1.65-1.97 (7H, m), 2.32 (1H, tt, *J* = 3.2, 11.6 Hz), 3.20 (1H, d, *J* = 8.8 Hz), 3.28 (1H, d, *J* = 9.2 Hz), 4.19 (1H, d, *J* = 15.6 Hz), 4.43 (1H, d, *J* = 15.6 Hz), 7.15-7.40 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.9, 26.23, 26.25, 29.6, 30.8, 31.2, 36.2, 50.2, 64.0, 68.4, 125.4, 126.1, 127.0, 127.3, 128.1, 128.7, 137.9, 149.4, 168.1; ESIHRMS: Found: m/z 333.2329. Calcd for $C_{23}H_{29}N_2$: $(M+H)^+$ 333.2331.

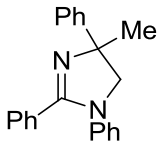
1-Butyl-4-isopropyl-2,4-diphenyl-4,5-dihydro-1*H*-imidazole (2i):



This reaction was carried out using the *E*/*Z* mixture (major/minor = 10.6:1) of **1i** as starting material. Reaction time: 5 h.

Yield: 72%; Yellow oil; IR (NaCl) 3059, 2961, 2928, 2872, 1614, 1595, 1574, 1499, 1445, 1408, 1317, 1304, 1238; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.86 (6H, m), 0.95 (3H, d, *J* = 6.8 Hz), 1.18-1.51 (4H, m), 2.12 (1H, sep, *J* = 6.8 Hz), 2.81-2.88 (1H, m), 3.03-3.10 (1H, m), 3.50 (1H, d, *J* = 9.6 Hz), 3.78 (1H, d, *J* = 9.6 Hz), 7.20 (1H, t, *J* = 7.6 Hz), 7.33 (2H, t, *J* = 7.6 Hz), 7.39-7.55 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 17.1, 17.7, 19.9, 31.1, 39.4, 48.3, 59.9, 76.7, 125.9, 126.3, 127.9, 128.3, 128.4, 129.4, 132.0, 149.0, 164.9; ESIHRMS: Found: m/z 321.2338. Calcd for $C_{22}H_{29}N_2$: $(M+H)^+$ 321.2331.

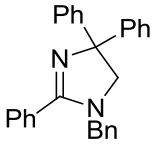
4-Methyl-1,2,4-triphenyl-4,5-dihydro-1*H*-imidazole (2j):[19]



Reaction time: 5 h.

Yield: 92%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (3H, s), 4.12 (1H, d, *J* = 9.2 Hz), 4.16 (1H, d, *J* = 9.2 Hz), 6.77 (2H, d, *J* = 8.0 Hz), 6.95 (1H, t, *J* = 7.6 Hz), 7.13 (2H, d, *J* = 7.6 Hz), 7.21-7.39 (6H, m), 7.53-7.59 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 67.2, 69.8, 122.4, 123.3, 125.4, 126.5, 128.1, 128.3, 128.7, 128.9, 129.9, 131.2, 142.8, 148.4, 160.2.

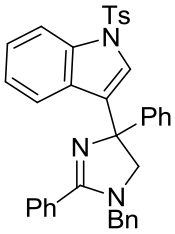
1-Benzyl-2,4,4-triphenyl-4,5-dihydro-1*H*-imidazole (2k):



This reaction was carried out using the major stereoisomer of **1k** as starting material. Reaction time: 3 h.

Yield: 77%; Yellow solid; mp: 146-147 °C; IR (NaCl) 3084, 3019, 2940, 1614, 1595, 1572, 1495, 1445, 1402, 1319, 1215, 1132, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (2H, s), 4.33 (2H, s), 7.18-7.43 (18H, m), 7.68-7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.9, 63.8, 76.4, 126.5, 126.7, 127.1, 127.4, 128.2, 128.46, 128.53, 128.7, 130.0, 131.1, 137.7, 148.0, 164.8; ESIHRMS: Found: m/z 389.2016. Calcd for $C_{28}H_{25}N_2$: $(M+H)^+$ 389.2018.

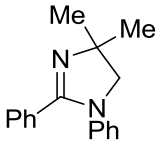
3-(1-Benzyl-2,4-diphenyl-4,5-dihydro-1*H*-imidazol-4-yl)-1-tosyl-1*H*-indole (2l):



Reaction time: 5 h.

Yield: 69%; Sticky yellow oil; IR (NaCl) 3028, 2930, 1612, 1595, 1568, 1495, 1447, 1371, 1217, 1175, 1126, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 3.96 (1H, d, *J* = 10.0 Hz), 4.00 (1H, d, *J* = 10.0 Hz), 4.36 (1H, d, *J* = 15.6 Hz), 4.41 (1H, d, *J* = 16.0 Hz), 7.03 (1H, t, *J* = 7.6 Hz), 7.18-7.44 (17H, m), 7.52 (1H, s), 7.67-7.69 (2H, m), 7.74 (2H, d, *J* = 8.4 Hz), 7.95 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.7, 62.6, 72.3, 113.7, 121.5, 123.0, 123.7, 124.4, 126.4, 126.8, 126.9, 127.1, 127.5, 128.3, 128.5, 128.6, 128.8, 129.0, 129.1, 129.7, 130.2, 130.8, 135.2, 136.0, 137.4, 144.7, 146.0, 165.0; ESIHRMS: Found: m/z 582.2211. Calcd for $C_{37}H_{32}N_3O_2S$: $(M+H)^+$ 582.2215.

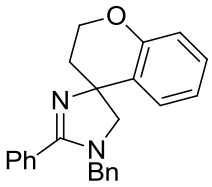
4,4-Dimethyl-1,2-diphenyl-4,5-dihydro-1*H*-imidazole (2m):[19]



Reaction time: 5 h.

Yield: 50%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (6H, s), 3.79 (2H, s), 6.74 (2H, d, *J* = 7.6 Hz), 6.95 (1H, t, *J* = 7.2 Hz), 7.14 (2H, t, *J* = 8.0 Hz), 7.27 (2H, t, *J* = 7.6 Hz), 7.34 (1H, t, *J* = 7.2 Hz), 7.48-7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.0, 64.5, 65.9, 121.9, 122.8, 128.0, 128.6, 128.8, 129.8, 131.2, 143.1, 159.3.

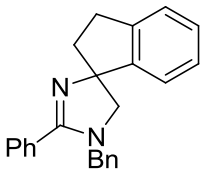
1'-Benzyl-2'-phenyl-1',5'-dihydrospiro[chroman-4,4'-imidazole] (2n):



This reaction was carried out using the major stereoisomer of **1n** as starting material. Reaction time: 3 h.

Yield: 69%; Yellow oil; IR (NaCl) 3063, 3030, 2951, 2874, 1574, 1487, 1454, 1360, 1317, 1254, 1223, 1059, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97-2.03 (1H, m), 2.27-2.34 (1H, m), 3.46 (1H, d, *J* = 10.0 Hz), 3.59 (1H, d, *J* = 10.0 Hz), 4.10-4.16 (1H, m), 4.33 (1H, d, *J* = 15.6 Hz), 4.41-4.47 (2H, m), 6.78 (1H, d, *J* = 8.4 Hz), 6.89 (1H, t, *J* = 7.6 Hz), 7.08-7.12 (1H, m), 7.21-7.43 (9H, m), 7.69-7.71 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.3, 52.6, 63.4, 64.6, 65.6, 116.5, 120.9, 127.2, 127.5, 127.9, 128.3, 128.4, 128.55, 128.60, 128.7, 130.2, 130.7, 137.4, 153.7, 165.5; ESIHRMS: Found: m/z 355.1808. Calcd for $C_{24}H_{23}N_2O$: $(M+H)^+$ 355.1810.

1-Benzyl-2-phenyl-1,2',3',5-tetrahydrospiro[imidazole-4,1'-indene] (2o):

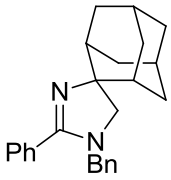


This reaction was carried out using the *E*/*Z* mixture (major/minor = 1:5.5) of **1o** as starting material. Reaction time: 3 h.

Yield: 73%; Brown oil; IR (NaCl) 3063, 3028, 2936, 2847, 1611, 1591, 1570, 1495, 1447, 1402, 1360, 1325, 1254, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02-2.09 (1H, m), 2.36-2.43 (1H, m), 2.74-2.82 (1H, m), 2.98-3.05 (1H, m), 3.44 (1H, d, *J* = 10.0 Hz), 3.48 (1H, d, *J* = 10.0 Hz), 4.25-4.33 (2H, m), 7.10-7.32 (12H, m), 7.58-7.60 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 30.1, 44.4, 52.8, 62.6, 78.0, 123.1, 124.4, 126.8, 127.2, 127.4, 127.5, 128.46,

128.49, 128.7, 130.0, 130.9, 137.7, 143.0, 148.2, 165.1; ESIHRMS: Found: m/z 339.1859. Calcd for $C_{24}H_{23}N_2$: $(M+H)^+$ 339.1861.

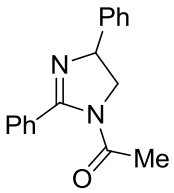
1'-Benzyl-2'-phenyl-1',5'-dihydrospiro[adamantane-2,4'-imidazole] (2p):



Reaction time: 9 h.

Yield: 43%; Yellow oil; IR (NaCl) 3028, 2911, 2851, 1620, 1593, 1495, 1360, 1325, 1298, 1279, 1179, 1074, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.56-1.57 (11H, m), 1.90 (1H, s br), 2.54-2.57 (2H, m), 3.30 (2H, s), 4.29 (2H, s), 7.20 (2H, d, *J* = 7.2 Hz), 7.25-7.41 (6H, m), 7.60-7.63 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.8, 27.4, 33.1, 34.3, 38.0, 38.4, 52.2, 60.0, 73.1, 127.0, 127.3, 128.4, 128.6, 128.7, 129.9, 130.6, 137.6, 163.4; ESIHRMS: Found: m/z 357.2337. Calcd for $C_{25}H_{29}N_2$: $(M+H)^+$ 357.2331.

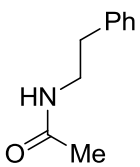
1-(2,4-Diphenyl-4,5-dihydro-1*H*-imidazol-1-yl)ethanone (2s):



Reaction time: 47 h.

Yield: 24%; Yellow oil; IR (NaCl) 3061, 3009, 1694, 1661, 1622, 1495, 1447, 1379, 1339, 1296, 1261, 1153, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (3H, s), 3.99 (1H, dd, *J* = 8.0, 11.2 Hz), 4.53 (1H, dd, *J* = 10.0, 10.8 Hz), 5.26 (1H, dd, *J* = 8.0, 10.0 Hz), 7.28-7.49 (8H, m), 7.60-7.62 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 55.8, 67.3, 126.5, 127.7, 128.39, 128.44, 128.8, 130.6, 131.8, 141.6, 159.4, 168.2; ESIHRMS: Found: m/z 265.1341. Calcd for $C_{17}H_{17}N_2O$: $(M+H)^+$ 265.1341.

***N*-Phenethylacetamide (5):**[20]

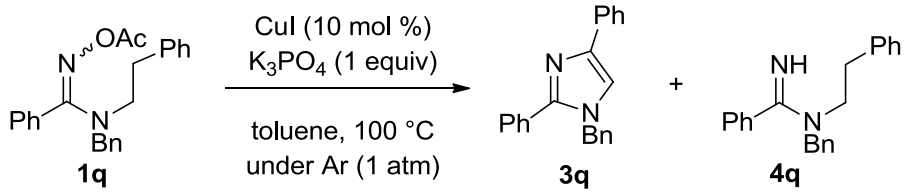


Reaction time: 47 h.

Yield: 57%; Brown solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (3H, s), 2.80 (2H, t, *J* = 7.2), 3.46-3.51 (2H, m), 5.77 (1H, s br), 7.17-7.24 (3H, m), 7.30 (2H, t, *J* = 7.2); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 35.5, 40.6, 126.4, 128.5, 128.6, 138.8, 170.1.

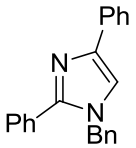
6. Copper-catalyzed synthesis of imidazoles 3

Typical Procedure:



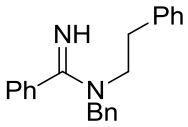
To a solution of *N*'-Acetoxy-*N*-benzyl-*N*-phenethylbenzimidamide **1q** (114.0 mg, 0.306 mmol) in toluene (3.1 mL) was added CuI (5.8 mg, 0.031 mmol) and K_3PO_4 (64.9 mg, 0.306 mmol). The reaction mixture was then stirred for 6 h at 100 °C under an Ar atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with ethyl acetate, dried over $MgSO_4$ and 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:triethylamine = 98:2) to provide **3q** (28.8 mg, 0.093 mmol) in 30% yield and **4q** (39.0 mg, 0.124 mmol) in 41% yield.

1-Benzyl-2,4-diphenyl-1*H*-imidazole (3q):[21]



Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (2H, s), 7.15 (2H, d, *J* = 7.2 Hz), 7.23-7.45 (10H, m), 7.62-7.64 (2H, m), 7.86 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.4, 116.8, 124.9, 126.6, 126.8, 127.9, 128.5, 128.6, 128.96 (overlapped), 128.98, 130.4, 134.0, 136.8, 141.5, 148.6.

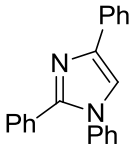
***N*-Benzyl-*N*-phenethylbenzimidamide (4q):**



Yellow oil; IR (NaCl) 3316, 3061, 3026, 2924, 1585, 1568, 1495, 1452, 1425, 1368, 1182, 1128, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85 (2H, t, *J* = 7.6), 3.47 (2H, t, *J* = 7.6), 4.48 (2H, s), 7.03 (2H, d, *J* = 7.2), 7.15-7.35 (13H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.8, 49.1,

51.4, 126.2, 126.5, 127.1, 127.3, 128.3, 128.5 (overlapped), 128.7, 128.8, 138.4, 138.9, 139.3, 169.4; ESIHRMS: Found: m/z 315.1865. Calcd for $C_{22}H_{23}N_2$: $(M+H)^+$ 315.1861.

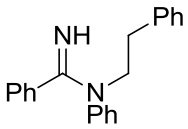
1,2,4-Triphenyl-1*H*-imidazole (3r):[22]



Reaction time: 2 h.

Yield: 36%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.28 (6H, m), 7.38-7.47 (8H, m), 7.89-7.91 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.5, 125.0, 125.8, 127.0, 128.14, 128.17, 128.4, 128.6, 128.8, 129.4, 130.3, 133.8, 138.5, 141.7, 147.0.

***N*-Phenethyl-*N*-phenylbenzimidamide (4r):**[19]



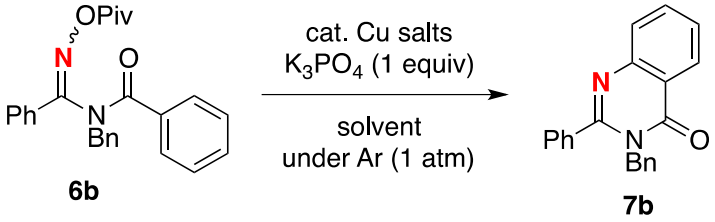
Reaction time: 2 h.

Yield: 42%; Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.07 (2H, t, J = 8.0), 4.13-4.17 (2H, m), 6.80-6.83 (2H, m), 6.95-6.99 (1H, m), 7.08-7.31 (12H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.4, 53.6, 124.9, 126.1, 127.0, 127.6, 128.0, 128.3, 128.66, 128.69, 129.0, 138.9, 139.8, 145.6, 167.7.

7. Copper-catalyzed synthesis of quinazolinones 7

Optimization of the reaction conditions using 6b:

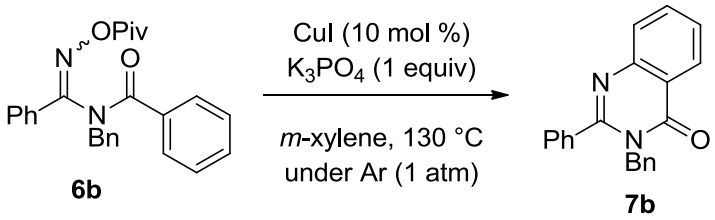
Table S1. Optimization of reaction conditions[a]



entry	Cu salts (mol %)	solvent	temp (°C)	time (h)	yield (%)[b]
1	CuI (10)	toluene	110	62	80
2	CuI (10)	DMSO	120	18	48
3	CuI (10)	DMF	120	18	43[c]
4	CuI (10)	DMA	120	18	30[c]
5	CuI (10)	*m*-xylene	120	41	77
6	CuI (10)	*m*-xylene	130	32	81
7	$(CuOTf)_2 \bullet C_6H_5$ (5)	*m*-xylene	130	32	73[c]
8	$Cu(MeCN)_4PF_6$ (10)	*m*-xylene	130	24	71[c]

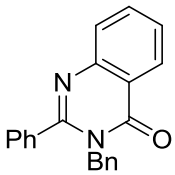
[a] Unless otherwise noted, the reactions were carried out using 0.3 mmol of amidoxime **6b** with Cu salts (10 mol %) and K_3PO_4 (1 equiv) in solvent (0.1 M) under an Ar atmosphere. [b] Isolated yields. [c] ^1H NMR yields.

Typical Procedure:



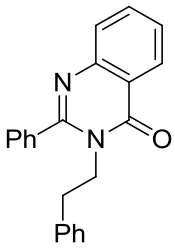
To a solution of *N*-benzyl-*N*-(phenyl((pivaloyloxy)imino)methyl)benzamide **6b** (126.4 mg, 0.305 mmol) in *m*-xylene (3.1 mL) was added CuI (5.8 mg, 0.031 mmol) and K_3PO_4 (64.9 mg, 0.305 mmol). The reaction mixture was then stirred for 32 h at 130 °C under an Ar atmosphere. The mixture was quenched with pH 9 ammonium buffer solution. The organic compounds were then extracted three times with ethyl acetate, dried over $MgSO_4$ and removed in vacuo to afford a crude residue, which was purified by flash column chromatography (silica gel; hexane:ethyl acetate = 85:15 then 80:20) to provide **7b** (77.2 mg, 0.247 mmol) in 81% yield as a pale yellow solid.

3-Benzyl-2-phenylquinazolin-4(3*H*)-one (7b):[23]



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (2H, s), 6.91-6.94 (2H, m), 7.18-7.21 (3H, m), 7.34 (2H, d, *J* = 6.8 Hz), 7.39 (2H, d, *J* = 7.6 Hz), 7.46 (1H, d, *J* = 7.2 Hz), 7.50-7.54 (1H, m), 7.76-7.80 (2H, m), 8.38 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.7, 120.8, 126.9, 127.0, 127.1, 127.4, 127.5, 127.9, 128.4, 128.5, 129.8, 134.5, 135.2, 136.5, 147.2, 156.3, 162.4.

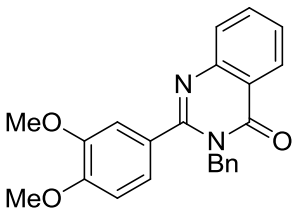
3-Phenethyl-2-phenylquinazolin-4(3*H*)-one (7a):



This reaction was carried in toluene at 100 °C for 40h.

Yield: 60%; White solid; mp: 179-180 °C; IR (NaCl) 3019, 2959, 1676, 1605, 1585, 1566, 1474, 1377, 1333; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.94 (2H, t, *J* = 8.0 Hz), 4.22 (2H, t, *J* = 8.0 Hz), 6.90-6.92 (2H, m), 7.20-7.23 (3H, m), 7.41-7.58 (6H, m), 7.76-7.82 (2H, m), 8.40 (1H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.6, 47.5, 120.9, 126.6, 126.7, 127.0, 127.5, 127.7, 128.5, 128.7 (overlapped), 129.8, 134.3, 135.3, 137.7, 147.1, 156.1, 162.1; ESIHRMS: Found: m/z 327.1500. Calcd for $C_{22}H_{19}N_2O$: $(M+H)^+$ 327.1497.

3-Benzyl-2-(3,4-dimethoxyphenyl)quinazolin-4(3*H*)-one (7c):

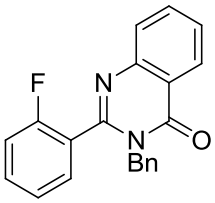


Reaction time: 16 h.

Yield: 81%; White solid; mp: 142-143 °C; IR (NaCl) 3019, 2963, 2837, 1678, 1605, 1589, 1566, 1514, 1474, 1375, 1263, 1173, 1142, 1026; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (3H, s), 3.91 (3H, s), 5.27 (2H, s), 6.71 (1H, d, *J* = 1.2 Hz), 6.90 (1H, d, *J* = 8.4 Hz), 7.00 (2H, d, *J* =

7.2 Hz), 7.04 (1H, d, *J* = 8.4 Hz), 7.19-7.28 (3H, m), 7.49-7.53 (1H, m), 7.77-7.80 (2H, m), 8.37 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.2, 55.4, 55.9, 110.9, 111.0, 120.6, 120.7, 126.6, 127.0 (overlapped), 127.2, 127.4, 127.6, 128.5, 134.5, 136.9, 147.2, 148.5, 150.2, 156.2, 162.5; ESIHRMS: Found: m/z 373.1555. Calcd for $C_{23}H_{21}N_2O_3$: $(M+H)^+$ 373.1552.

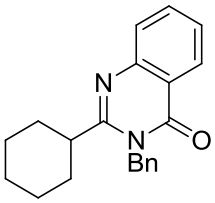
3-Benzyl-2-(2-fluorophenyl)quinazolin-4(3*H*)-one (7d):



Reaction time: 45 h.

Yield: 75%; Pale yellow solid; mp: 139-140 °C; IR (NaCl) 3017, 1678, 1620, 1607, 1589, 1568, 1495, 1474, 1454, 1379, 1246; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (1H, d, *J* = 15.2 Hz), 5.67 (1H, d, *J* = 15.6 Hz), 6.86-6.88 (2H, m), 7.12-7.18 (6H, m), 7.43-7.56 (2H, m), 7.74-7.80 (2H, m), 8.39 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.1, 116.0 (d, *J* = 20.5), 121.1, 123.5 (d, *J* = 15.8), 124.5 (d, *J* = 3.3), 127.1, 127.2, 127.4, 127.5, 127.6, 128.3, 130.4 (d, *J* = 2.2), 131.9 (d, *J* = 8.0), 134.5, 136.2, 147.2, 151.6, 159.0 (d, *J* = 247.1), 162.1; ESIHRMS: Found: m/z 331.1246. Calcd for $C_{21}H_{16}FN_2O$: $(M+H)^+$ 331.1247.

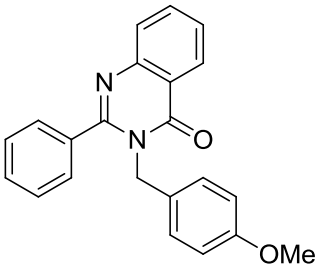
3-Benzyl-2-cyclohexylquinazolin-4(3*H*)-one (7e):[23]



Reaction time: 30 h.

Yield: 54%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18-1.31 (3H, m), 1.67-1.80 (7H, m), 2.72-2.80 (1H, m), 5.44 (2H, s), 7.18 (2H, d, *J* = 7.2 Hz), 7.23-7.45 (4H, m), 7.65-7.74 (2H, m), 8.30 (1H, dd, *J* = 0.8, 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 26.0, 31.5, 42.4, 46.0, 120.3, 126.2, 126.3, 126.9, 127.1, 127.5, 128.8, 134.1, 136.8, 147.5, 160.8, 162.7;

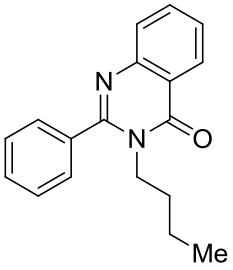
3-(4-Methoxybenzyl)-2-phenylquinazolin-4(3*H*)-one (7f): [23]



Reaction time: 20 h.

Yield: 66%; White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.73 (3H, s), 5.21 (2H, s), 6.72 (2H, d, *J* = 8.8 Hz), 6.85 (2H, d, *J* = 8.4 Hz), 7.35-7.53 (6H, m), 7.73-7.78 (2H, m), 8.37 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.1, 55.1, 113.7, 120.9, 126.98, 126.99, 127.5, 128.0, 128.50, 128.53, 128.6, 129.8, 134.4, 135.3, 147.2, 156.3, 158.8, 162.4;

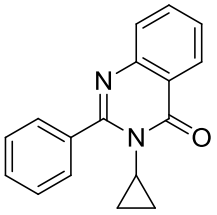
3-Butyl-2-phenylquinazolin-4(3*H*)-one (7g):



Reaction time: 30 h.

Yield: 77%; White solid; mp: 115-116 °C; IR (NaCl) 3013, 2961, 2932, 1682, 1672, 1607, 1585, 1557, 1472, 1385, 1337, 1175, 1080; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (3H, t, *J* = 7.2 Hz), 1.13-1.22 (2H, m), 1.56-1.63 (2H, m), 3.98 (2H, t, *J* = 7.6 Hz), 7.48-7.55 (6H, m), 7.72-7.77 (2H, m), 8.33 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 19.8, 30.6, 45.6, 120.8, 126.6, 126.8, 127.3, 127.7, 128.7, 129.7, 134.2, 135.5, 147.1, 156.2, 162.0; ESIHRMS: Found: m/z 279.1494. Calcd for $C_{18}H_{19}N_2O$: $(M+H)^+$ 279.1497.

3-Cyclopropyl-2-phenylquinazolin-4(3*H*)-one (7h):

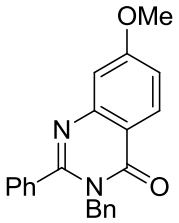


Reaction time: 22 h.

Yield: 94%; Pale yellow oil; IR (NaCl) 3063, 3013, 1688, 1605, 1566, 1557, 1472, 1368, 1333, 1273, 1159, 1036; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47-0.51 (2H, m), 0.90-0.95 (2H, m),

3.11-3.16 (1H, m), 7.45-7.50 (4H, m), 7.69-7.75 (4H, m), 8.30 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.2, 30.2, 120.8, 126.4, 126.8, 127.3, 128.1, 128.3, 129.7, 134.1, 136.1, 147.0, 156.8, 163.8; ESIHRMS: Found: m/z 263.1182. Calcd for $C_{17}H_{15}N_2O$: $(M+H)^+$ 263.1184.

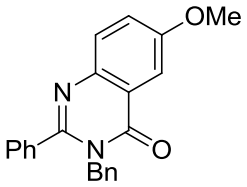
3-Benzyl-7-methoxy-2-phenylquinazolin-4(3*H*)-one (7i): [23]



Reaction time: 7 h.

Yield: 51%; Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.89 (3H, s), 5.25 (2H, s), 6.91-6.93 (2H, m), 7.09 (1H, dd, *J* = 2.4, 8.8 Hz), 7.15-7.20 (4H, m), 7.31-7.34 (2H, m), 7.38 (2H, t, *J* = 8.0 Hz), 7.45 (1H, t, *J* = 7.6 Hz), 8.26 (1H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.5, 55.6, 108.0, 114.3, 117.3, 126.9, 127.3, 127.8, 128.4, 128.5, 128.6, 129.8, 135.3, 136.7, 149.4, 157.1, 161.9, 164.7;

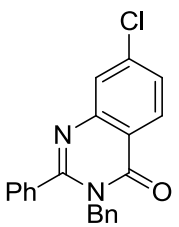
3-Benzyl-6-methoxy-2-phenylquinazolin-4(3*H*)-one (7i'): [23]



Reaction time: 7 h.

Yield: 9%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.95 (3H, s), 5.28 (2H, s), 6.92-6.94 (2H, m), 7.19-7.21 (3H, m), 7.32-7.47 (6H, m), 7.69 (1H, d, *J* = 8.8 Hz), 7.74 (1H, d, *J* = 2.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.9, 55.8, 106.3, 121.6, 124.9, 127.0, 127.4, 128.2, 128.48, 128.54, 129.2, 129.7, 135.4, 136.7, 142.0, 154.1, 158.7, 162.3.

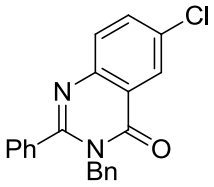
3-Benzyl-7-chloro-2-phenylquinazolin-4(3*H*)-one (7j):



Reaction time: 22 h.

Yield: 69%; White solid; mp: 98-99 °C; IR (NaCl) 3028, 2976, 1682, 1674, 1601, 1585, 1560, 1462, 1423, 1377, 1333, 1250, 1167, 1074; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (2H, s), 6.90-6.92 (2H, m), 7.19-7.21 (3H, m), 7.32-7.49 (6H, m), 7.74 (1H, d, *J* = 2.0 Hz), 8.28 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.8, 119.3, 126.9, 127.1, 127.5, 127.7, 127.9, 128.51, 128.54, 128.6, 130.0, 134.9, 136.3, 140.7, 148.2, 157.6, 161.8; ESIHRMS: Found: m/z 347.0949. Calcd for $C_{21}H_{16}{}^{35}ClN_2O$: $(M+H)^+$ 347.0951.

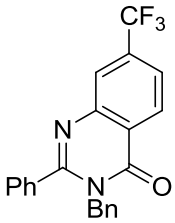
3-Benzyl-6-chloro-2-phenylquinazolin-4(3*H*)-one (7j'):



Reaction time: 22 h.

Yield: 21%; White solid; mp: 125-126 °C; IR (NaCl) 3063, 2978, 1682, 1605, 1585, 1560, 1470, 1447, 1373, 1329, 1234, 1130, 1072; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.27 (2H, s), 6.90-6.92 (2H, m), 7.20-7.21 (3H, m), 7.32-7.50 (5H, m), 7.68-7.73 (2H, m), 8.33 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 48.9, 121.9, 126.4, 127.0, 127.5, 128.0, 128.5, 128.6, 129.3, 130.0, 132.9, 134.9, 135.0, 136.3, 145.7, 156.6, 161.5; ESIHRMS: Found: m/z 347.0947. Calcd for $C_{21}H_{16}{}^{35}ClN_2O$: $(M+H)^+$ 347.0951.

3-Benzyl-2-phenyl-7-(trifluoromethyl)quinazolin-4(3*H*)-one (7k):

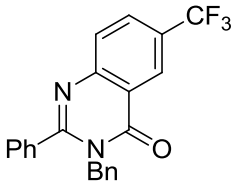


Reaction time: 22 h.

Yield: 60%; White solid; mp: 107-108 °C; IR (NaCl) 3019, 2982, 1682, 1589, 1557, 1497, 1433, 1352, 1317, 1252, 1233, 1165, 1126, 1061; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (2H, s), 6.91-6.93 (2H, m), 7.20-7.22 (3H, m), 7.35-7.51 (5H, m), 7.71 (1H, dd, *J* = 1.2, 8.4 Hz), 8.05 (1H, s), 8.47 (1H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.0, 123.0 (q, *J* = 3.4 Hz), 123.1, 123.4 (q, *J* = 271.4 Hz), 125.2 (q, *J* = 4.1 Hz), 126.9, 127.6, 127.9, 128.3, 128.55,

128.61, 130.2, 134.8, 136.06 (q, *J* = 32.8 Hz), 136.10, 147.2, 157.7, 161.7; ESIHRMS: Found: m/z 381.1212. Calcd for $C_{22}H_{16}F_3N_2O$: $(M+H)^+$ 381.1215.

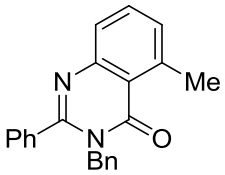
3-Benzyl-2-phenyl-6-(trifluoromethyl)quinazolin-4(3*H*)-one (7k'):



Reaction time: 22 h.

Yield: 28%; White solid; mp: 147-148 °C; IR (NaCl) 3065, 2984, 1694, 1682, 1626, 1587, 1566, 1497, 1377, 1350, 1315, 1294, 1234, 1173, 1130; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.29 (2H, s), 6.91-6.93 (2H, m), 7.21-7.22 (3H, m), 7.35-7.52 (5H, m), 7.85 (1H, d, *J* = 8.8 Hz), 7.97 (1H, dd, *J* = 2.0, 8.8 Hz), 8.67 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.0, 120.7, 123.7 (q, *J* = 270.5 Hz), 125.1(q, *J* = 4.2 Hz), 127.0, 127.6, 127.9, 128.6 (overlapped), 128.7, 129.0 (q, *J* = 33.1 Hz), 130.2, 130.6 (q, *J* = 3.3 Hz), 134.8, 136.1, 149.3, 158.4, 161.8; ESIHRMS: Found: m/z 381.1216. Calcd for $C_{22}H_{16}F_3N_2O$: $(M+H)^+$ 381.1215.

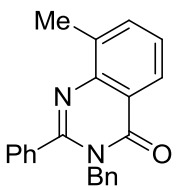
3-Benzyl-5-methyl-2-phenylquinazolin-4(3*H*)-one (7l): [23]



Reaction time: 7 h.

Yield: 9%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (3H, s), 5.22 (2H, s), 6.94-6.96 (2H, m), 7.20-7.23 (3H, m), 7.27-7.47 (6H, m), 7.58-7.63 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.2, 48.6, 119.5, 125.8, 126.8, 127.3, 127.9, 128.5, 128.6, 129.7, 129.8, 133.6, 135.4, 136.8, 141.4, 148.8, 156.2, 162.8.

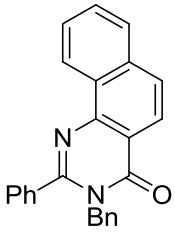
3-Benzyl-8-methyl-2-phenylquinazolin-4(3*H*)-one (7l'): [23]



Reaction time: 7 h.

Yield: 66%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59 (3H, s), 5.28 (2H, s), 6.92-6.94 (2H, m), 7.18-7.19 (3H, m), 7.37-7.46 (6H, m), 7.61 (1H, d, *J* = 6.8 Hz), 8.22 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 48.8, 120.8, 124.7, 126.6, 126.9, 127.3, 128.3 (overlapped), 128.4, 129.7, 135.0, 135.7, 136.2, 136.7, 145.9, 154.8, 162.9;

3-Benzyl-2-phenylbenzo[*h*]quinazolin-4(3*H*)-one (7m): [23]



Reaction time: 20 h.

Yield: 79%; Pale yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.38 (2H, s), 6.96-6.98 (2H, m), 7.19-7.22 (3H, m), 7.40-7.52 (5H, m), 7.60-7.70 (2H, m), 7.86 (1H, d, *J* = 8.8 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 8.29 (1H, d, *J* = 8.8 Hz), 9.00 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 49.0, 117.1, 122.2, 125.3, 126.8, 126.9, 127.3, 127.4, 127.8, 128.38, 128.41, 128.5, 129.2, 129.89, 129.93, 135.6, 136.2, 136.6, 146.0, 156.4, 162.5;

8. References

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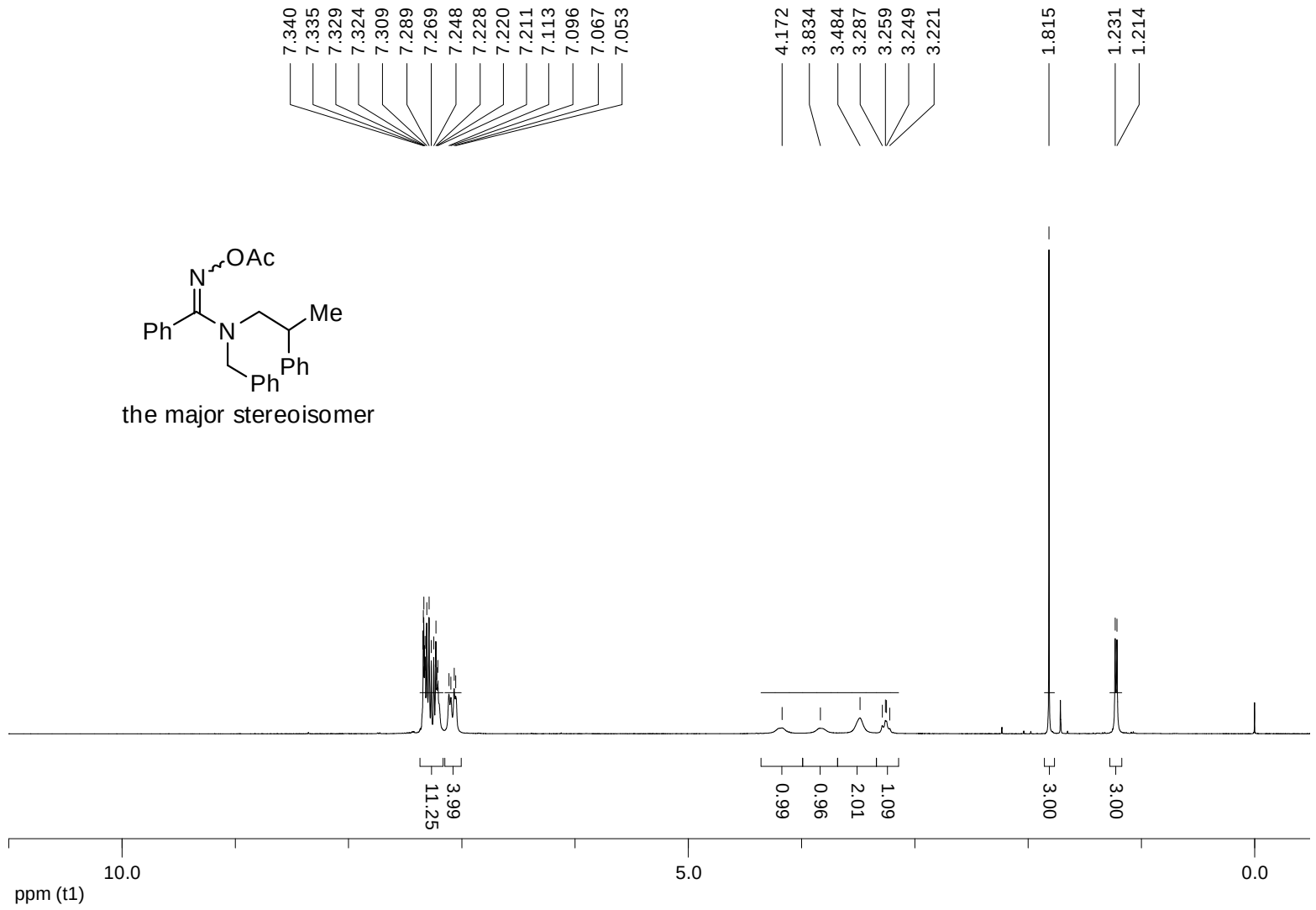
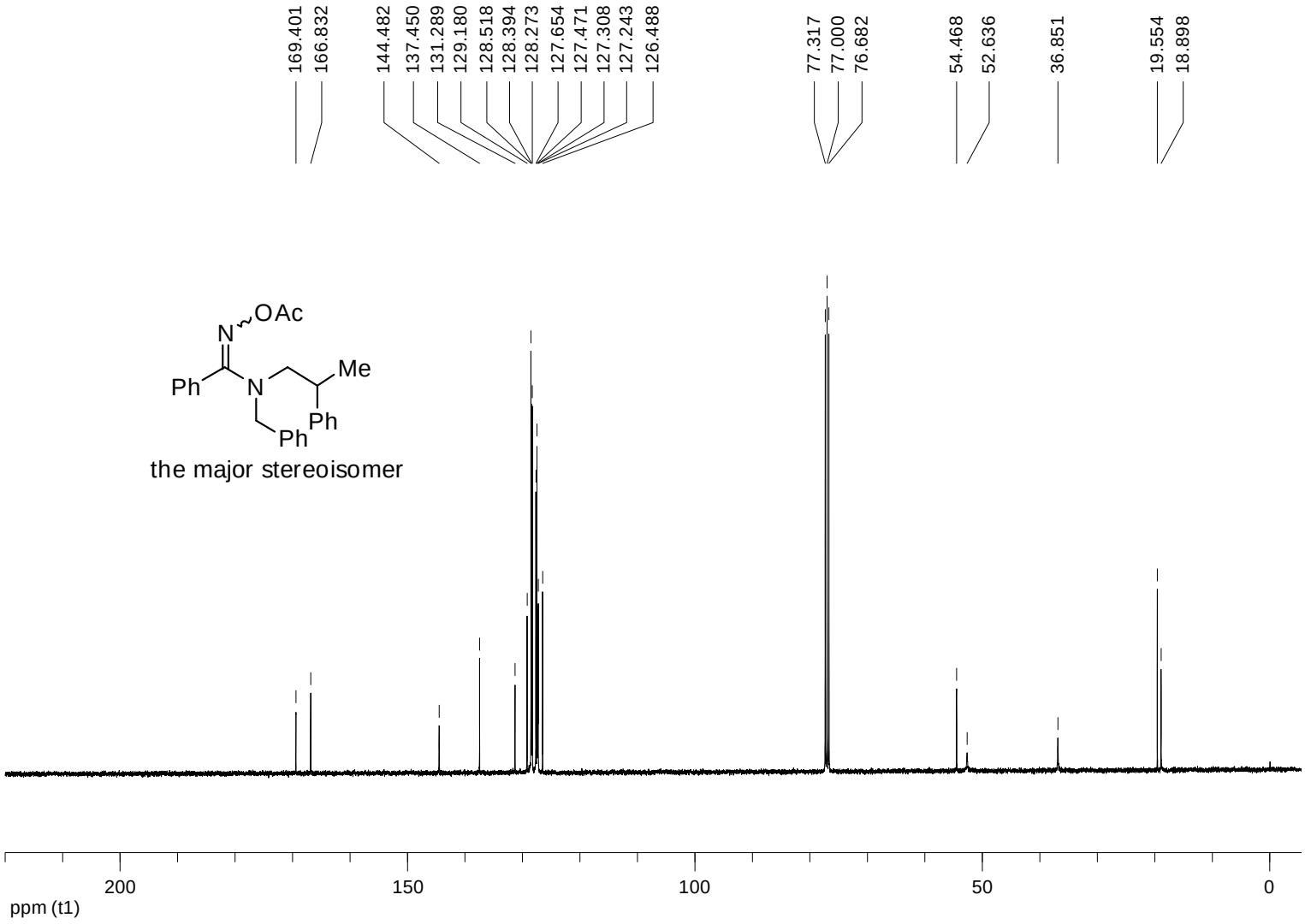
^{1}H NMR spectrum of **1a** (the major stereoisomer) (400 MHz, $CDCl_3$)

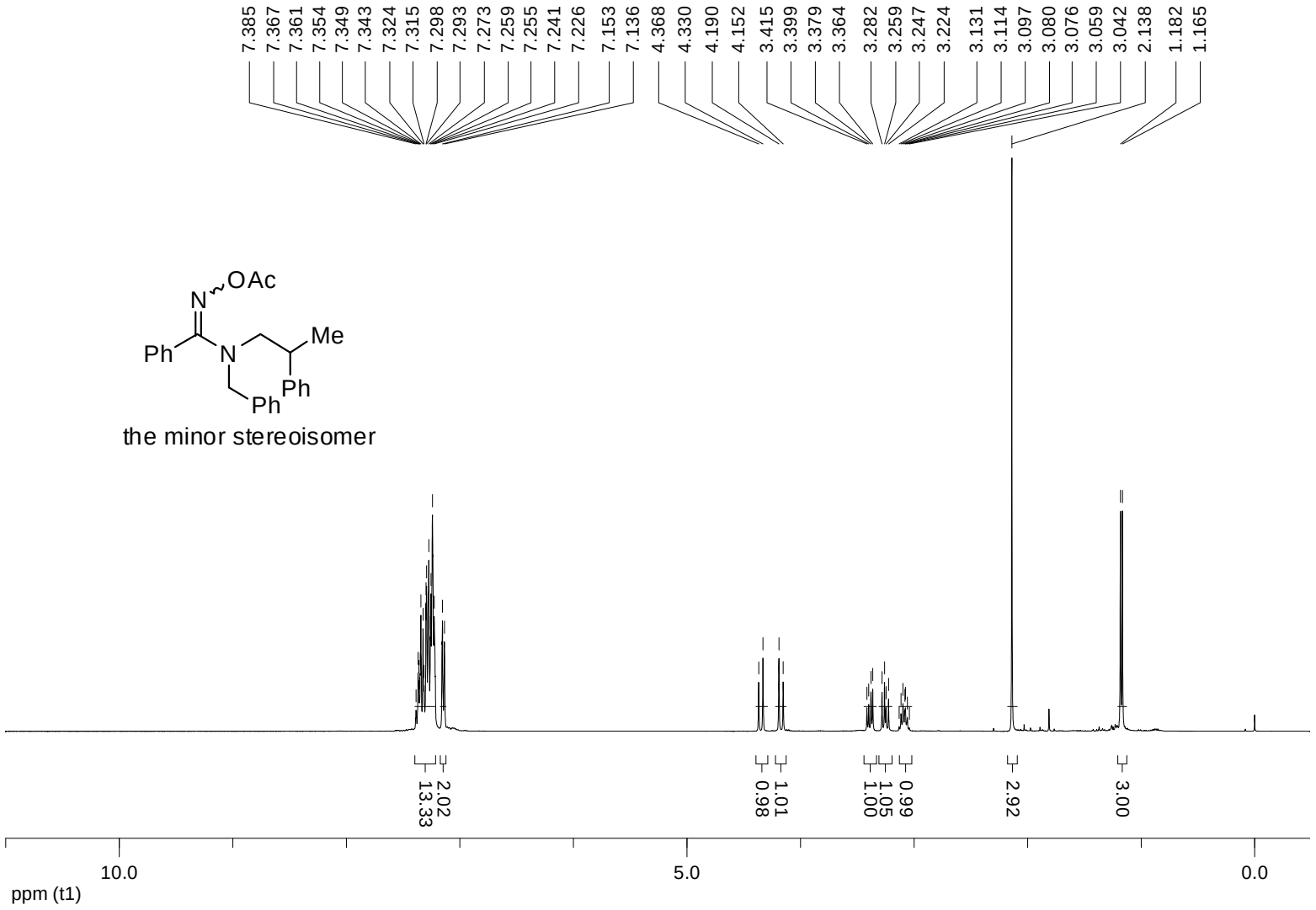


the major stereoisomer

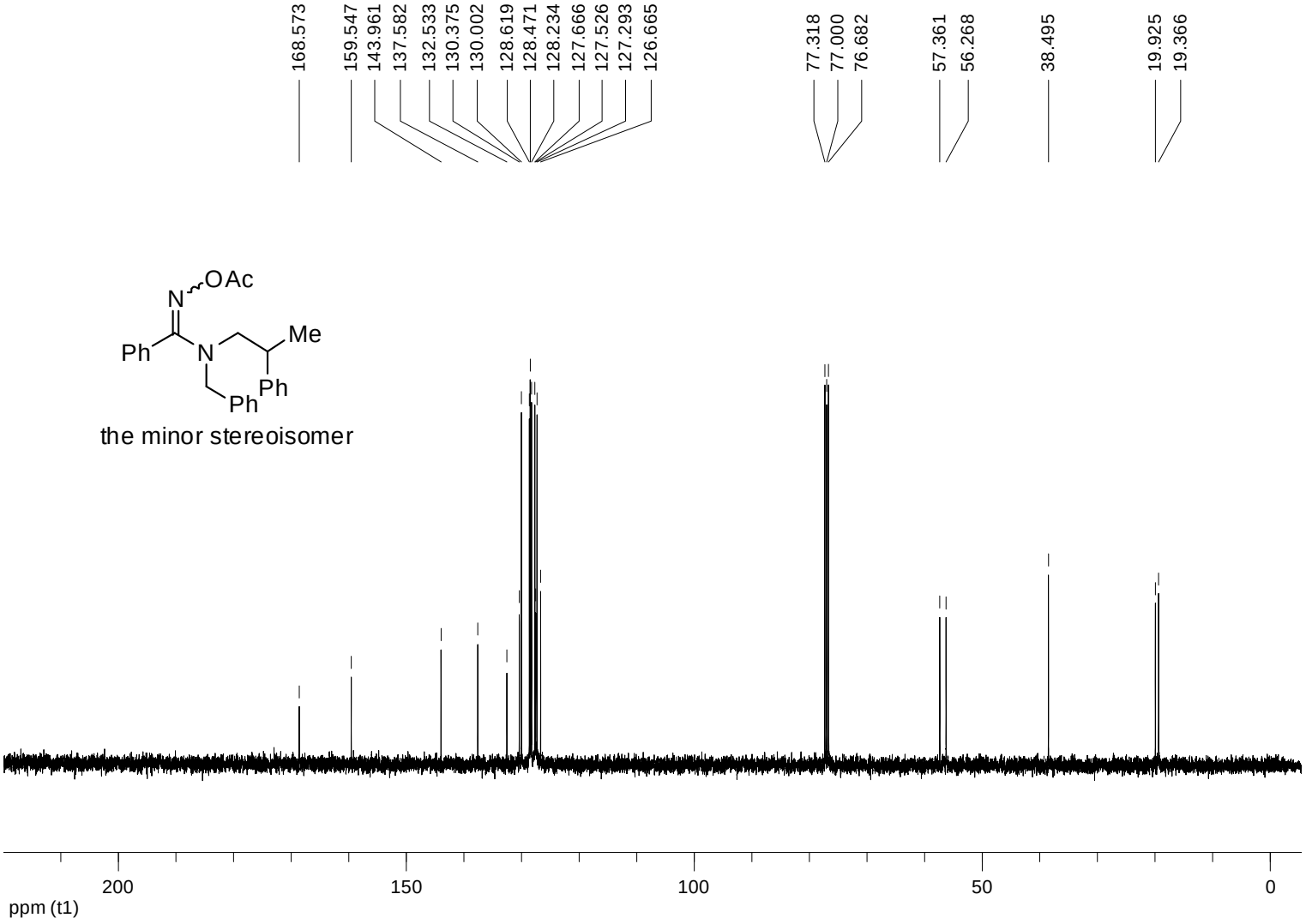
^{13}C NMR spectrum of **1a** (the major stereoisomer) (100 MHz, $CDCl_3$)



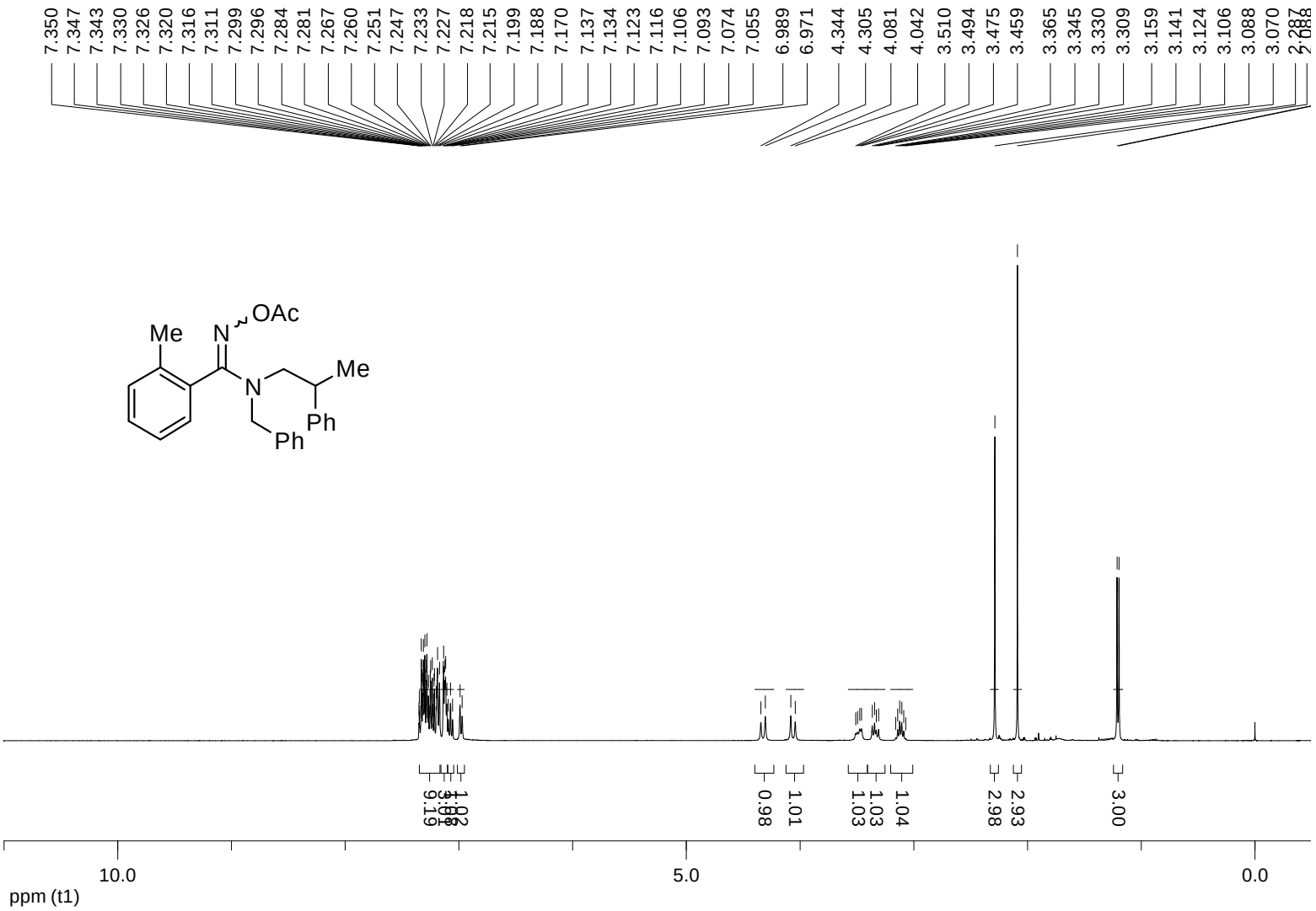
^{1}H NMR spectrum of **1a** (the minor stereoisomer) (400 MHz, $CDCl_3$)



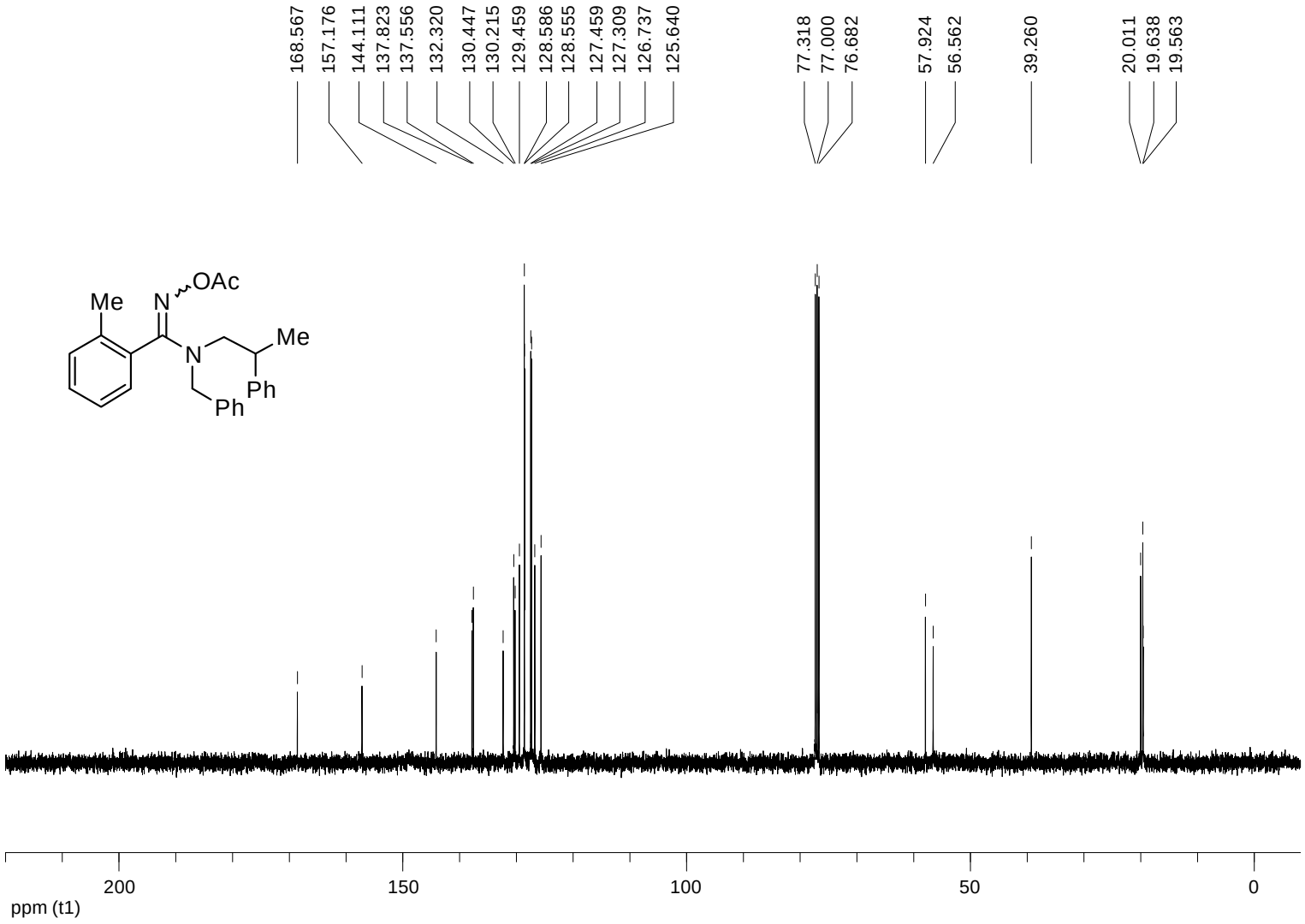
^{13}C NMR spectrum of **1a** (the minor stereoisomer) (100 MHz, $CDCl_3$)



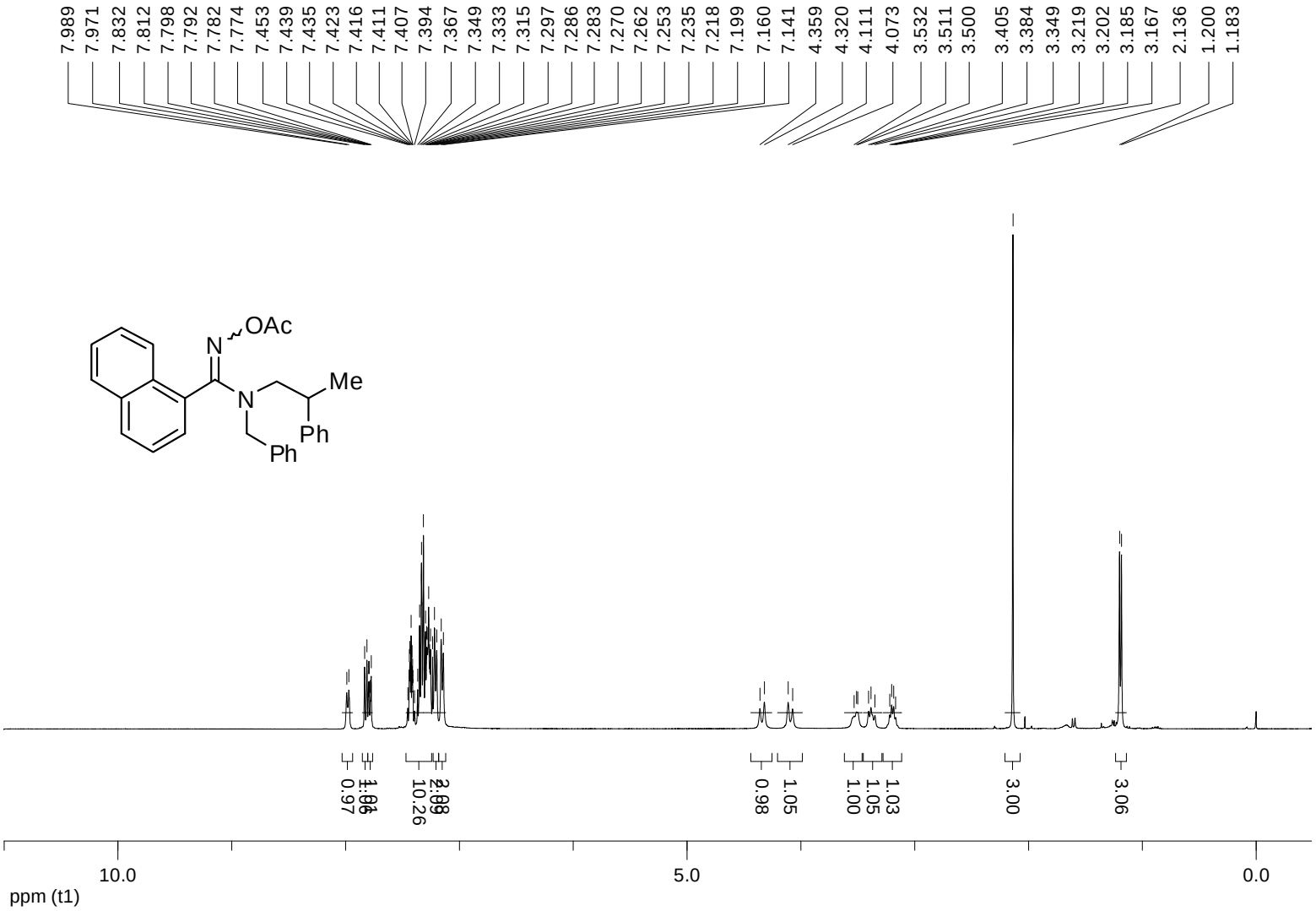
^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$)



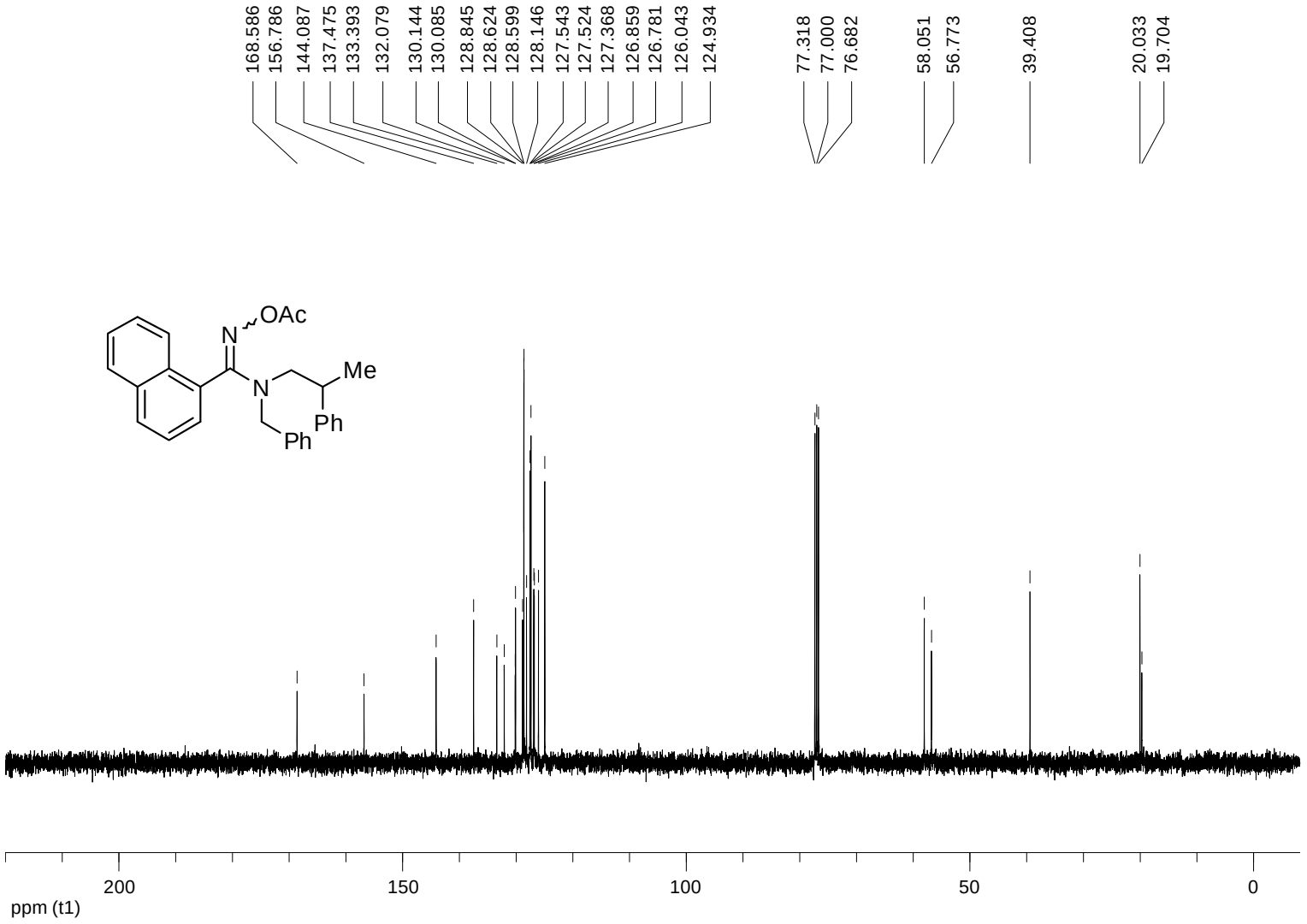
^{13}C NMR spectrum of **1b** (100 MHz, $CDCl_3$)



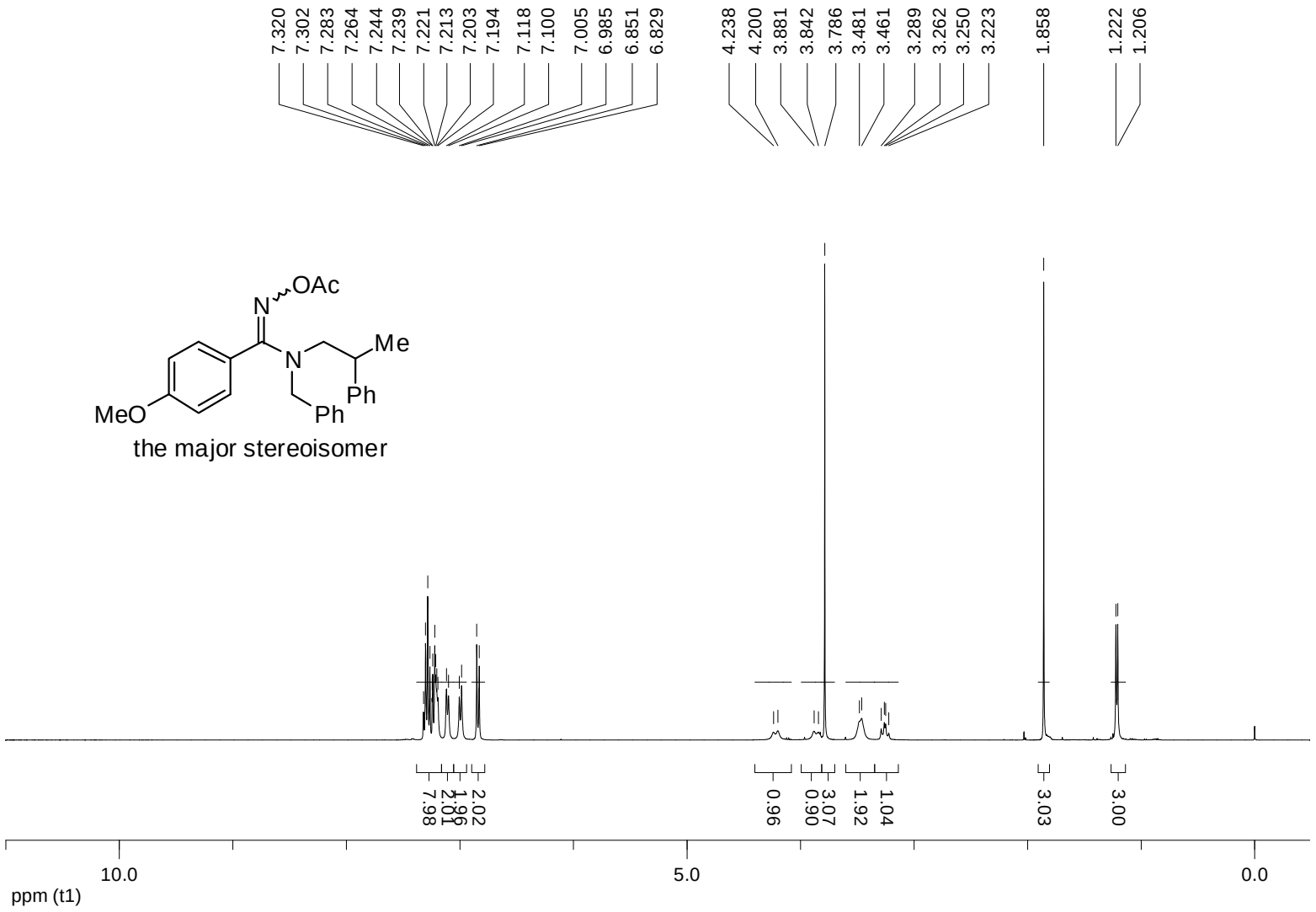
^{1}H NMR spectrum of **1c** (400 MHz, $CDCl_3$)



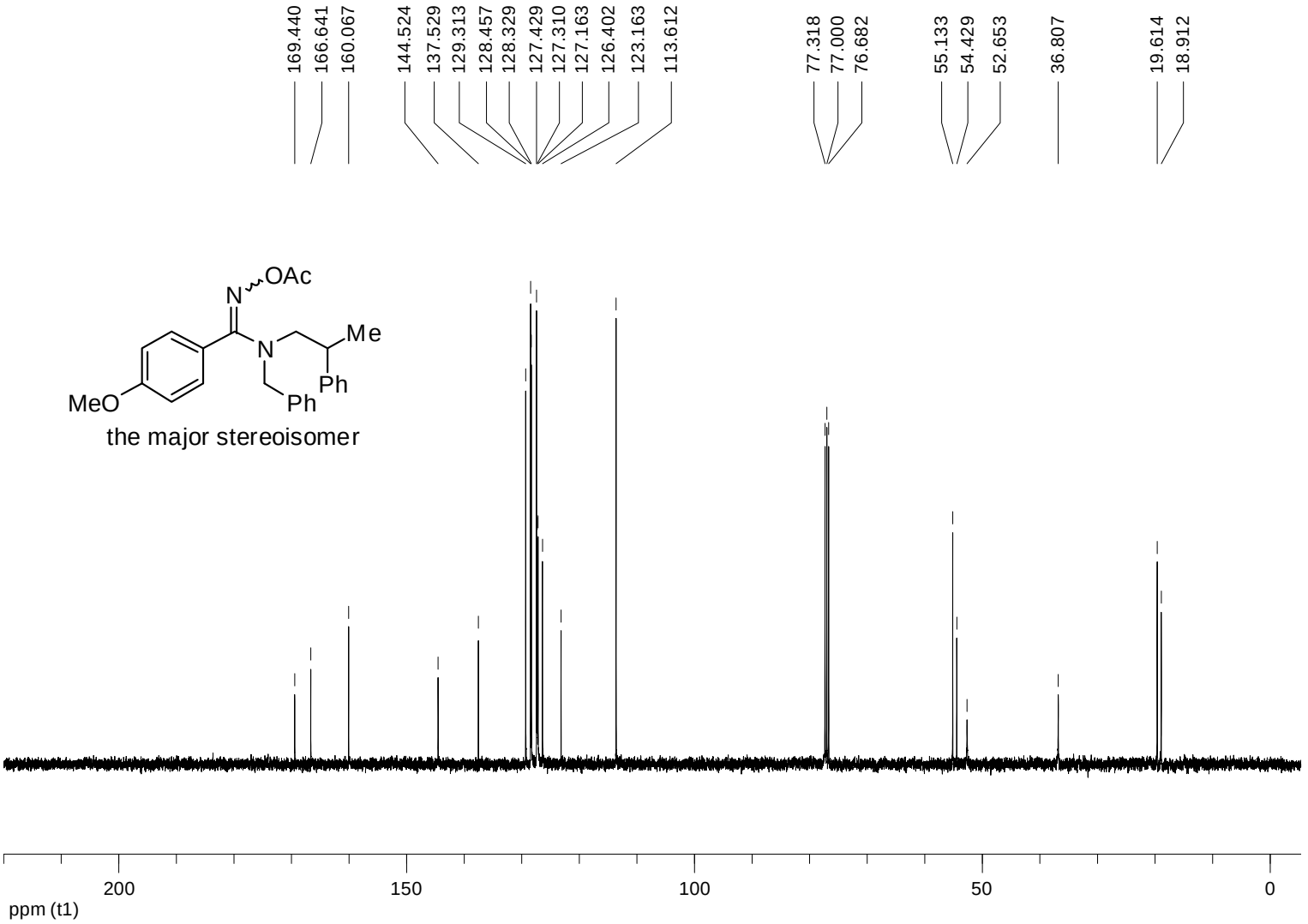
^{13}C NMR spectrum of **1c** (100 MHz, $CDCl_3$)



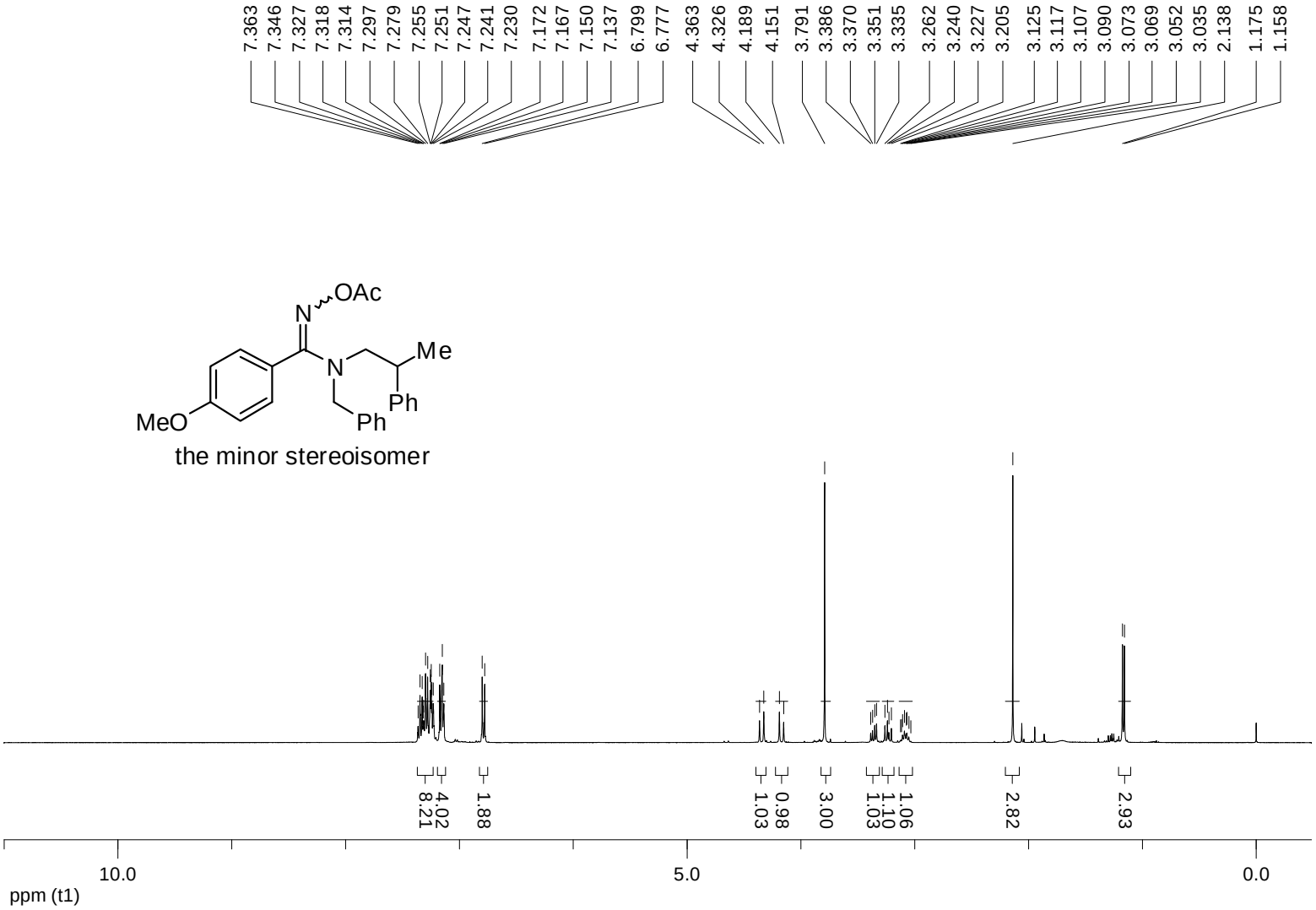
^{1}H NMR spectrum of **1d** (the major stereoisomer) (400 MHz, $CDCl_3$)



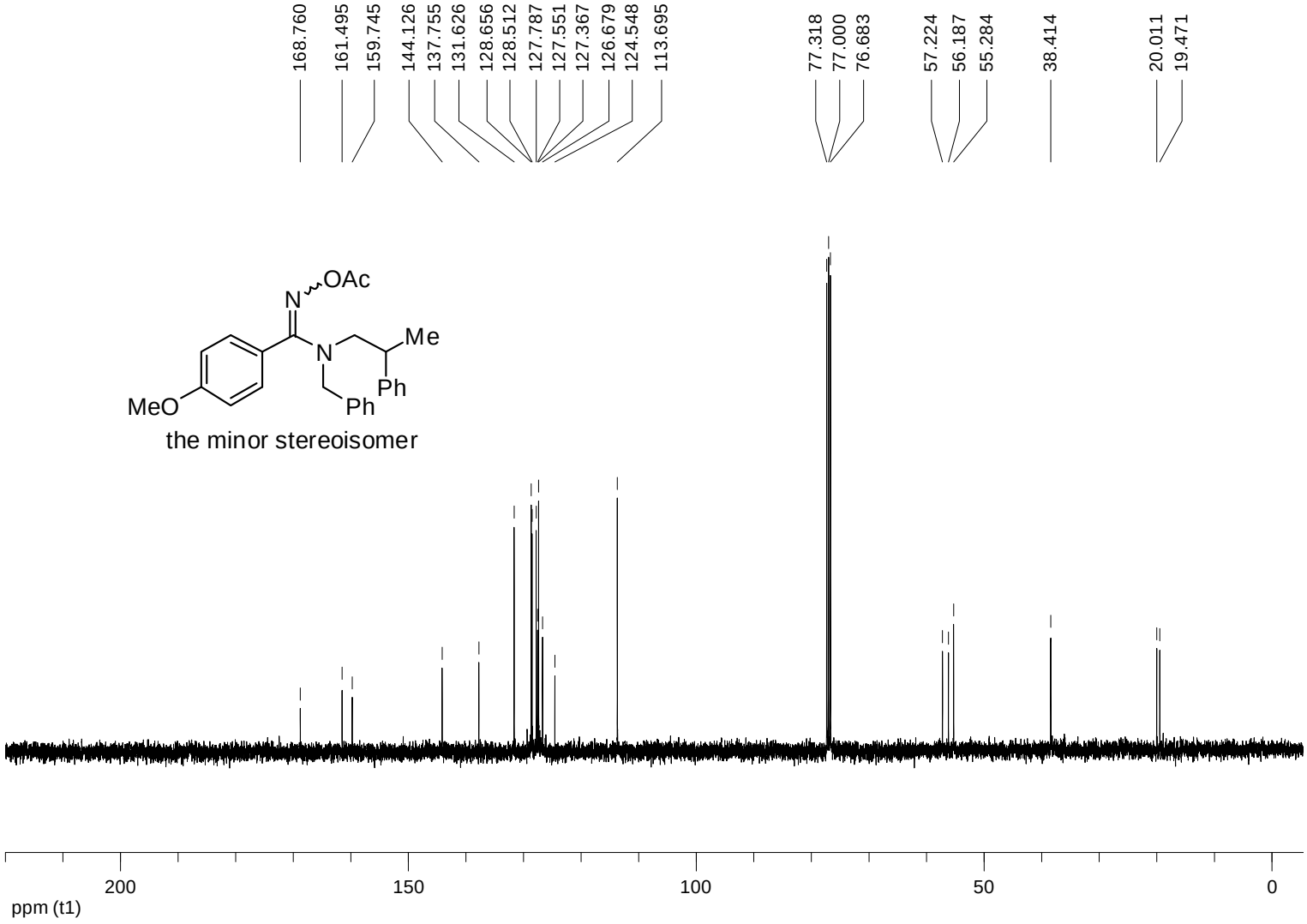
^{13}C NMR spectrum of **1d** (the major stereoisomer) (100 MHz, $CDCl_3$)



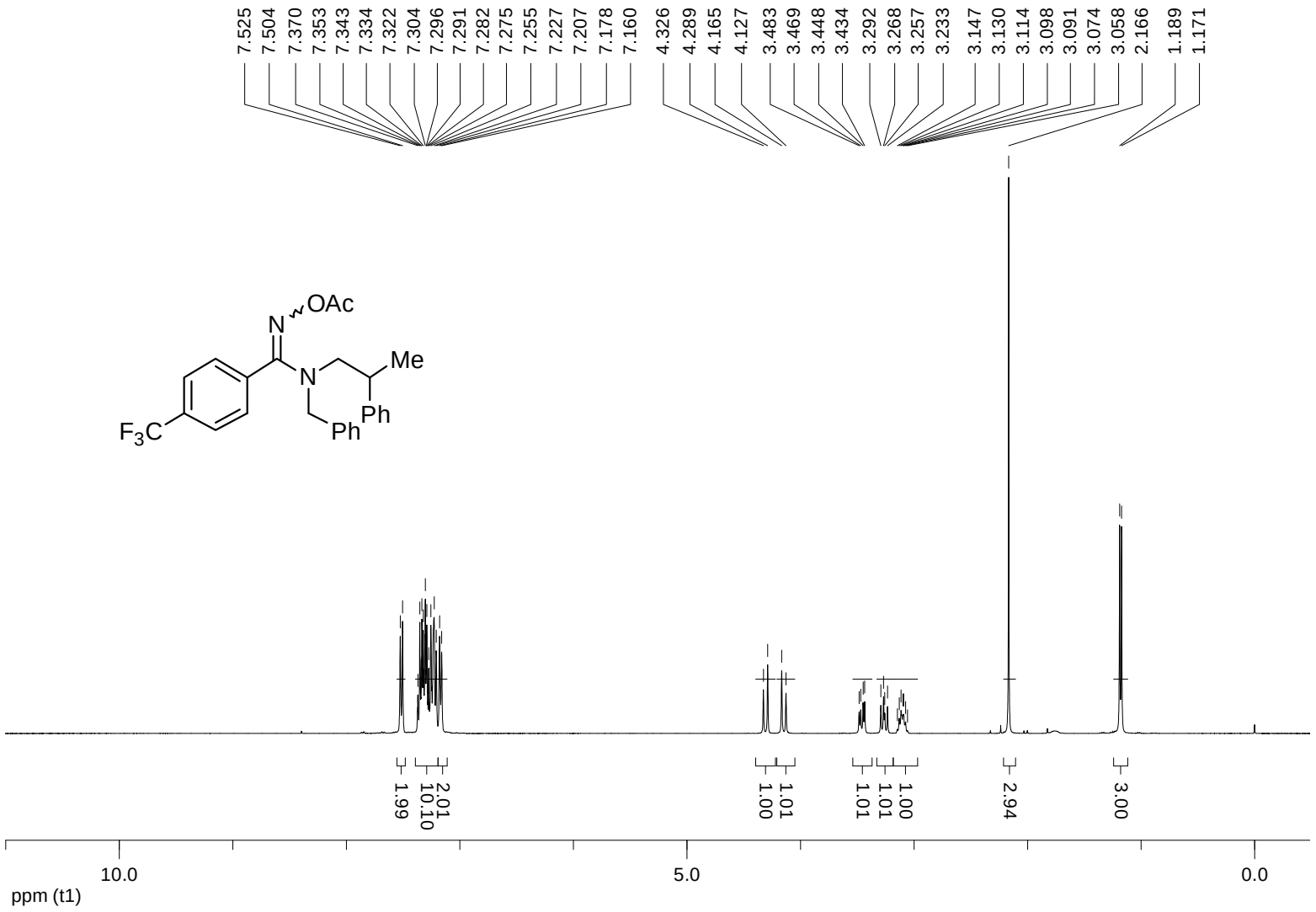
^{1}H NMR spectrum of **1d** (the minor stereoisomer) (400 MHz, $CDCl_3$)



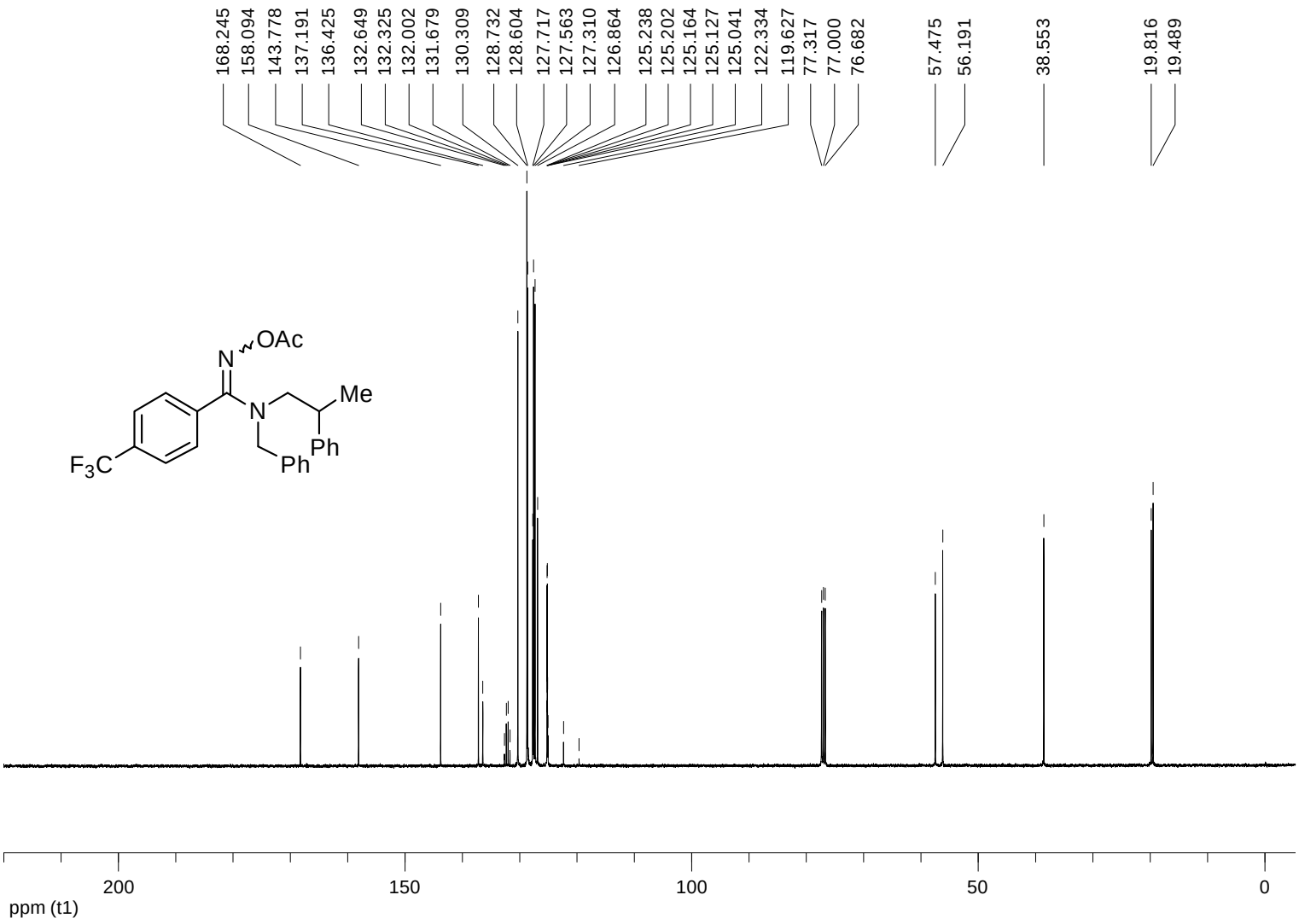
^{13}C NMR spectrum of **1d** (the minor stereoisomer) (100 MHz, $CDCl_3$)



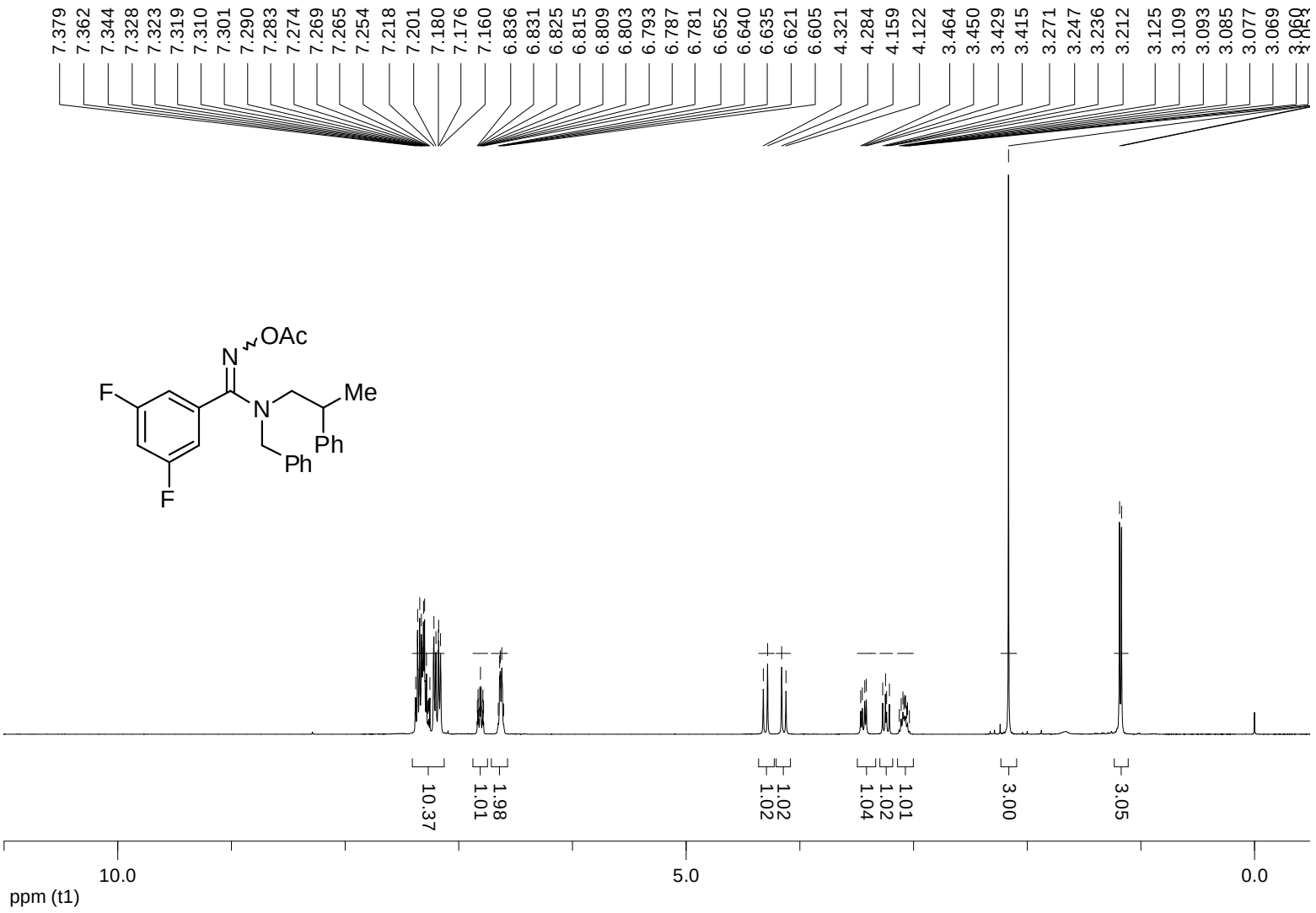
^{1}H NMR spectrum of **1e** (400 MHz, $CDCl_3$)



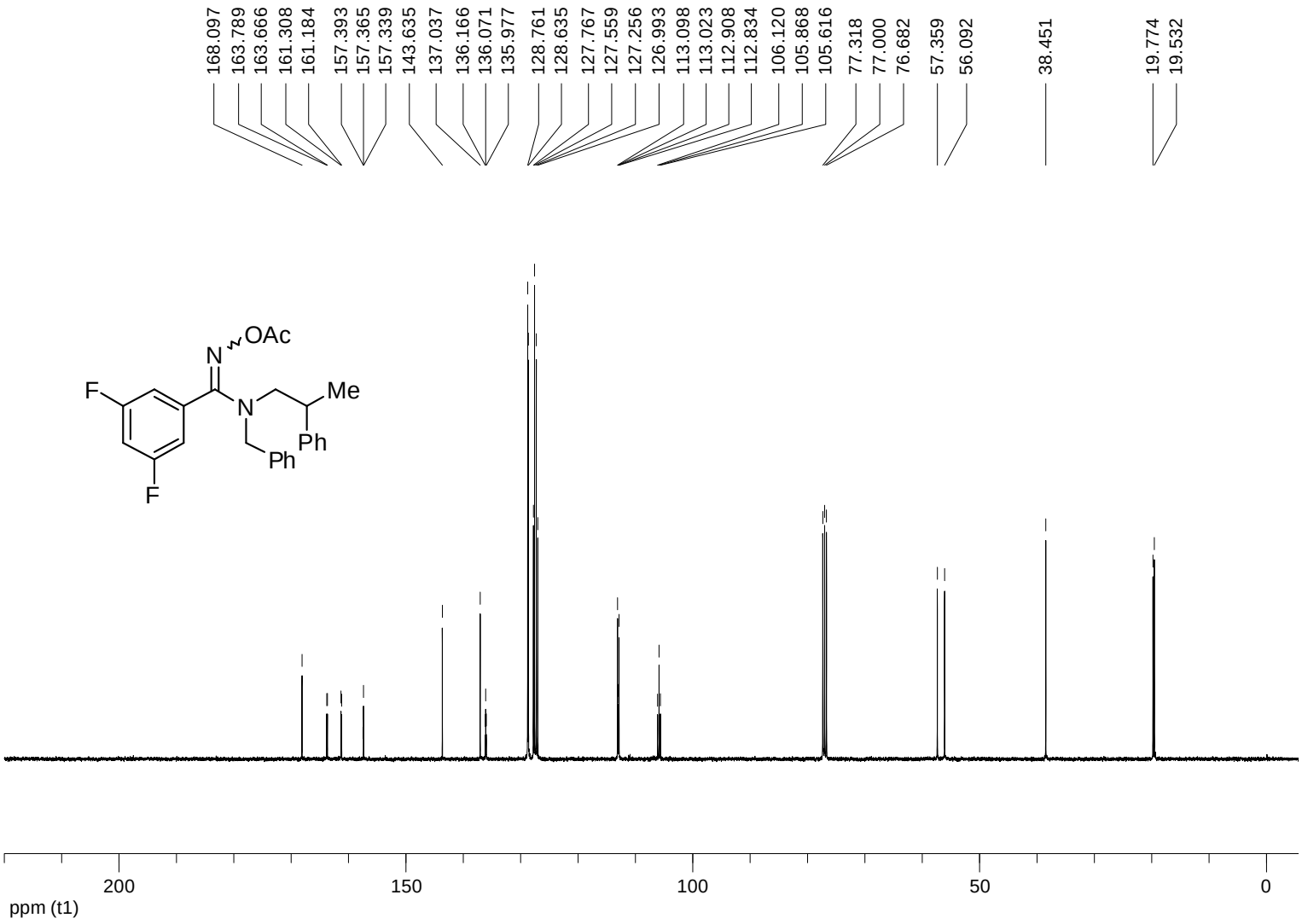
^{13}C NMR spectrum of **1e** (100 MHz, $CDCl_3$)



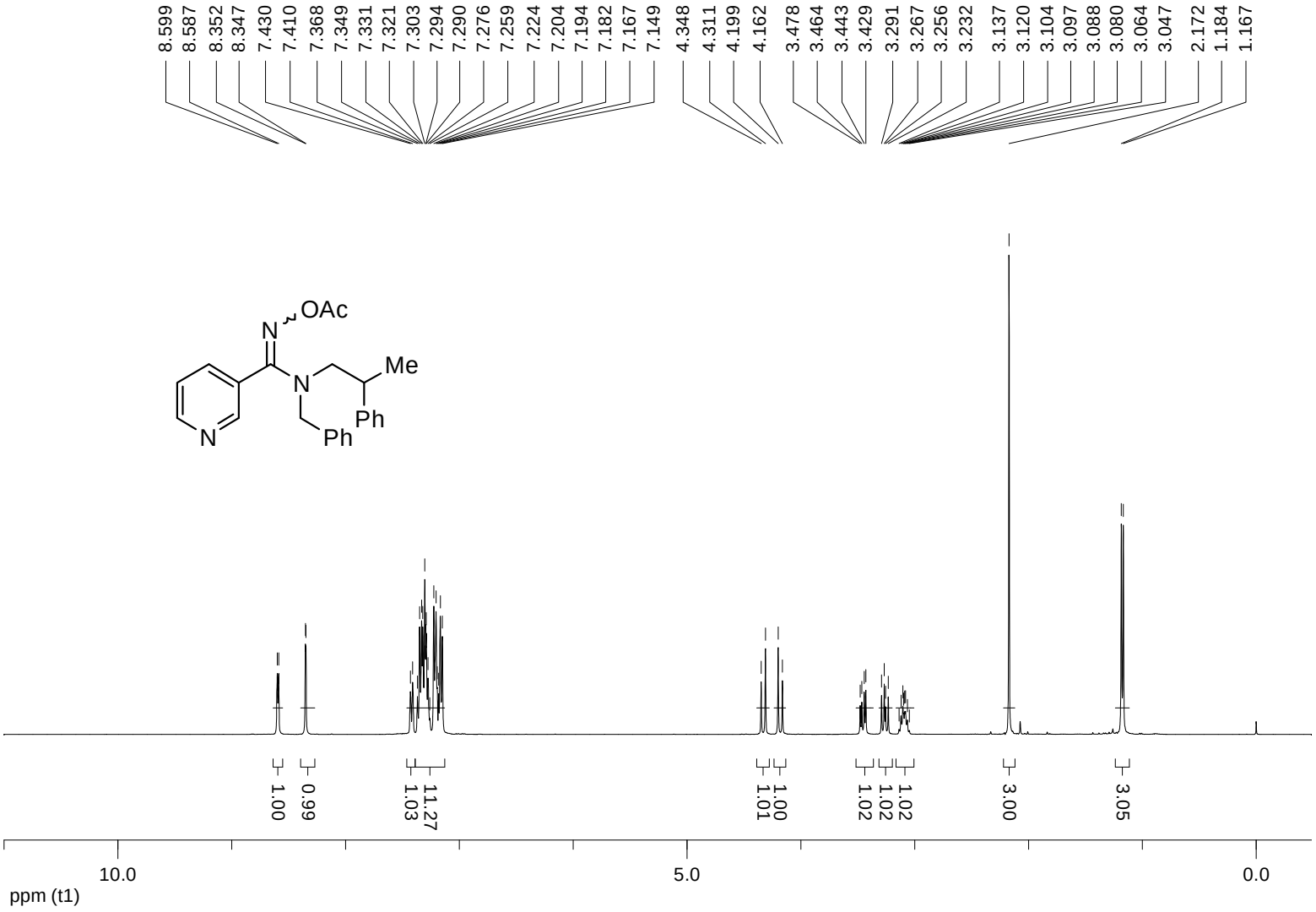
^{1}H NMR spectrum of **1f** (400 MHz, $CDCl_3$)



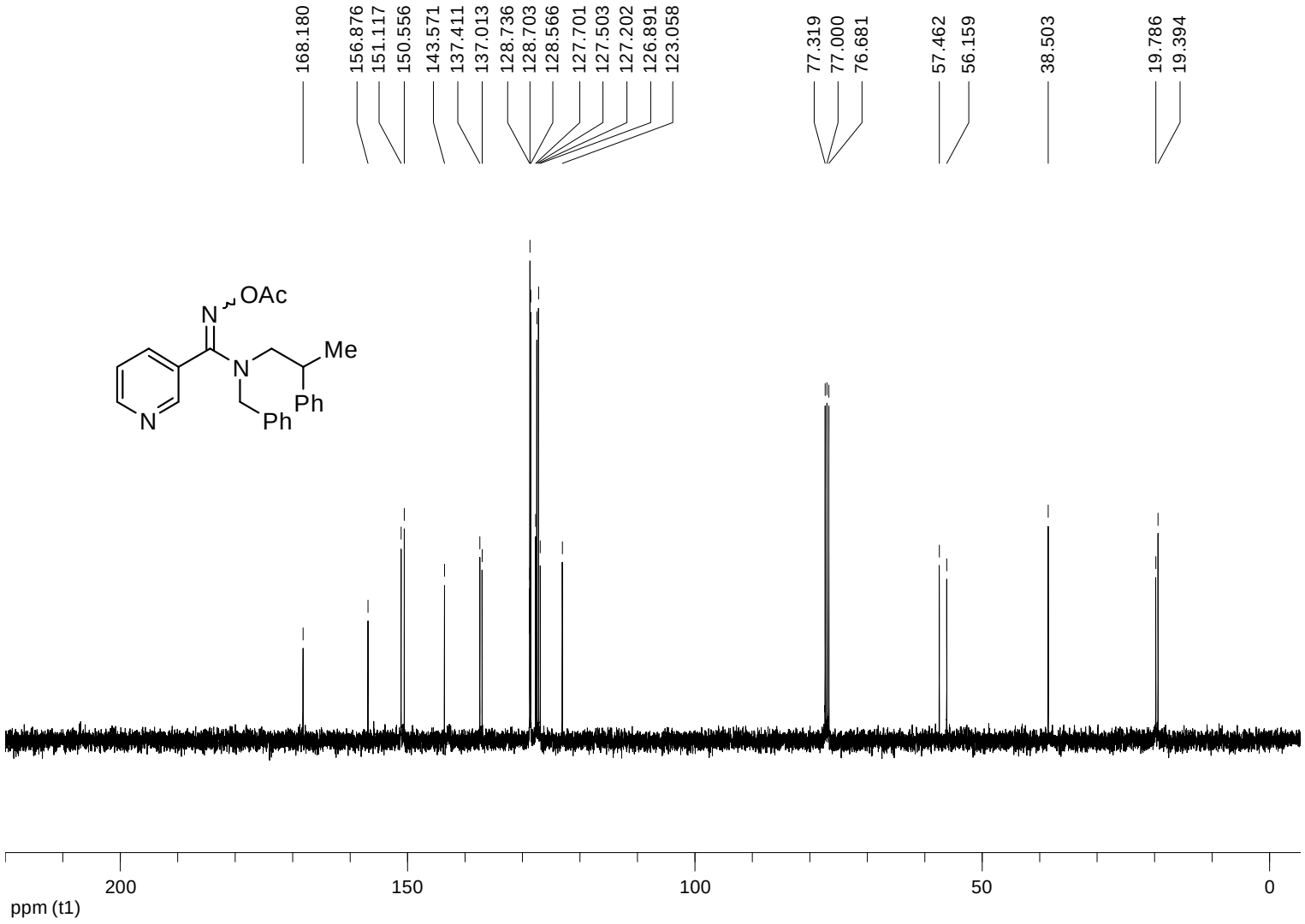
^{13}C NMR spectrum of **1f** (100 MHz, $CDCl_3$)



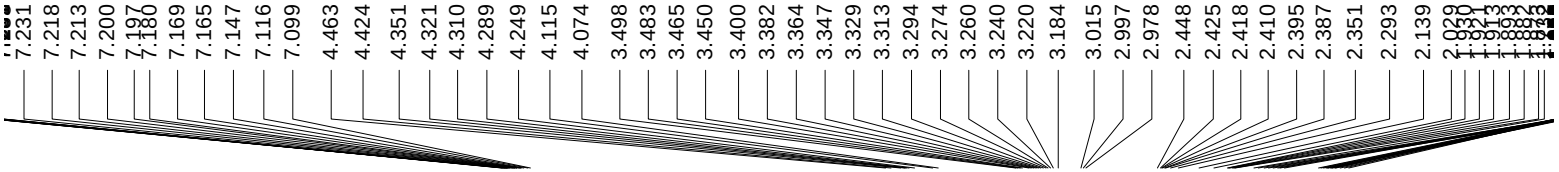
^{1}H NMR spectrum of **1g** (400 MHz, $CDCl_3$)

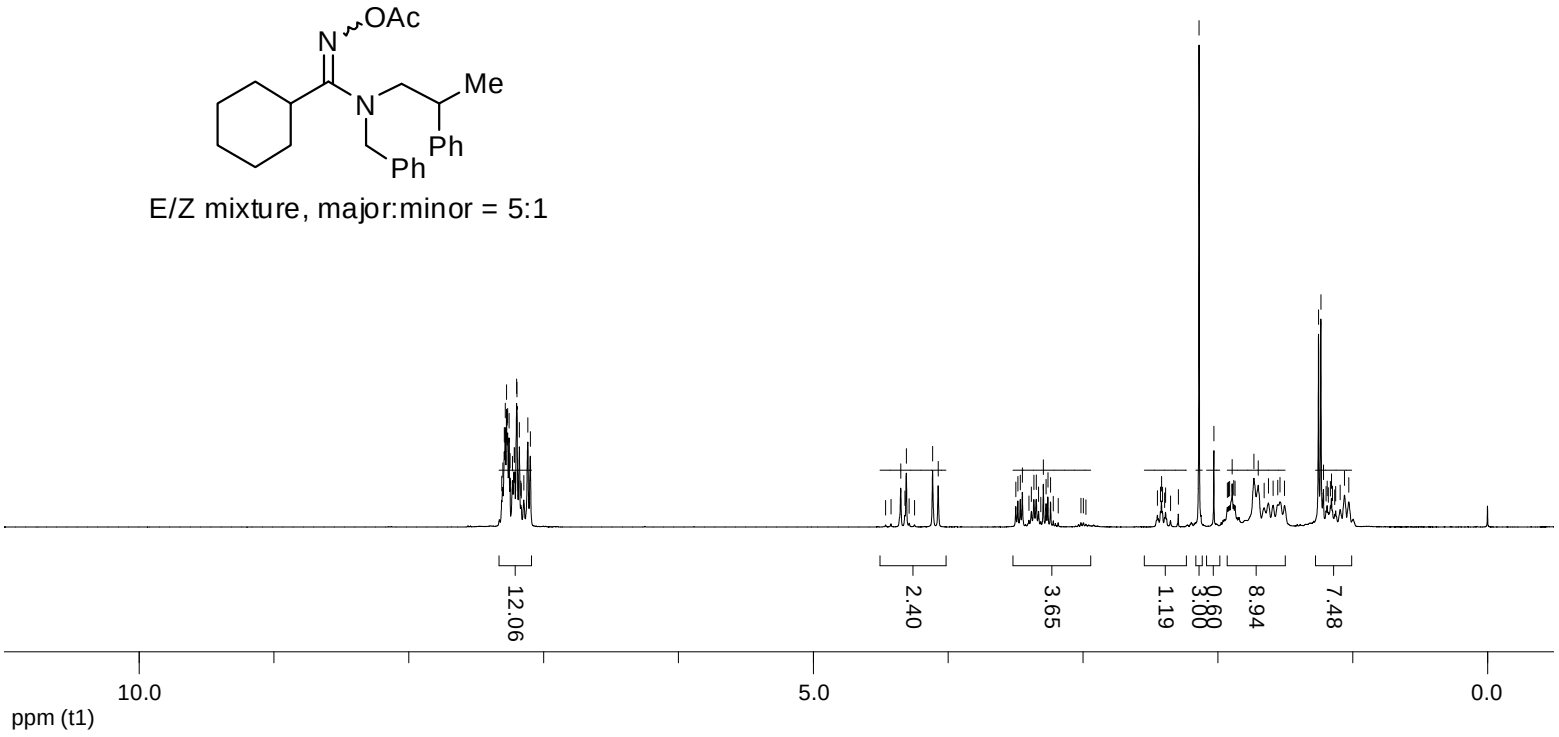


^{13}C NMR spectrum of **1g** (100 MHz, $CDCl_3$)

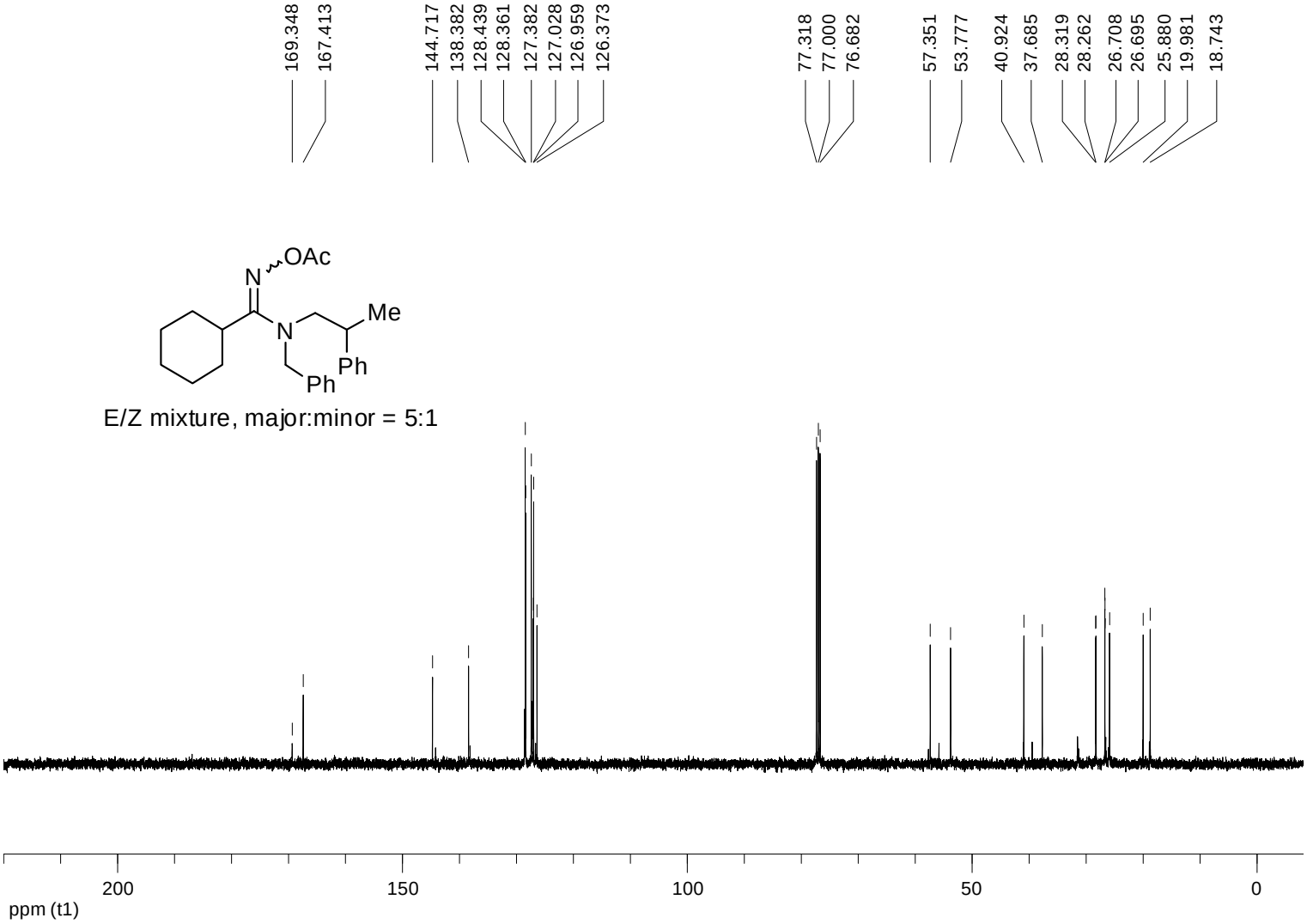


^{1}H NMR spectrum of **1h** (E/Z mixture, major:minor = 5:1) (400 MHz, $CDCl_3$)

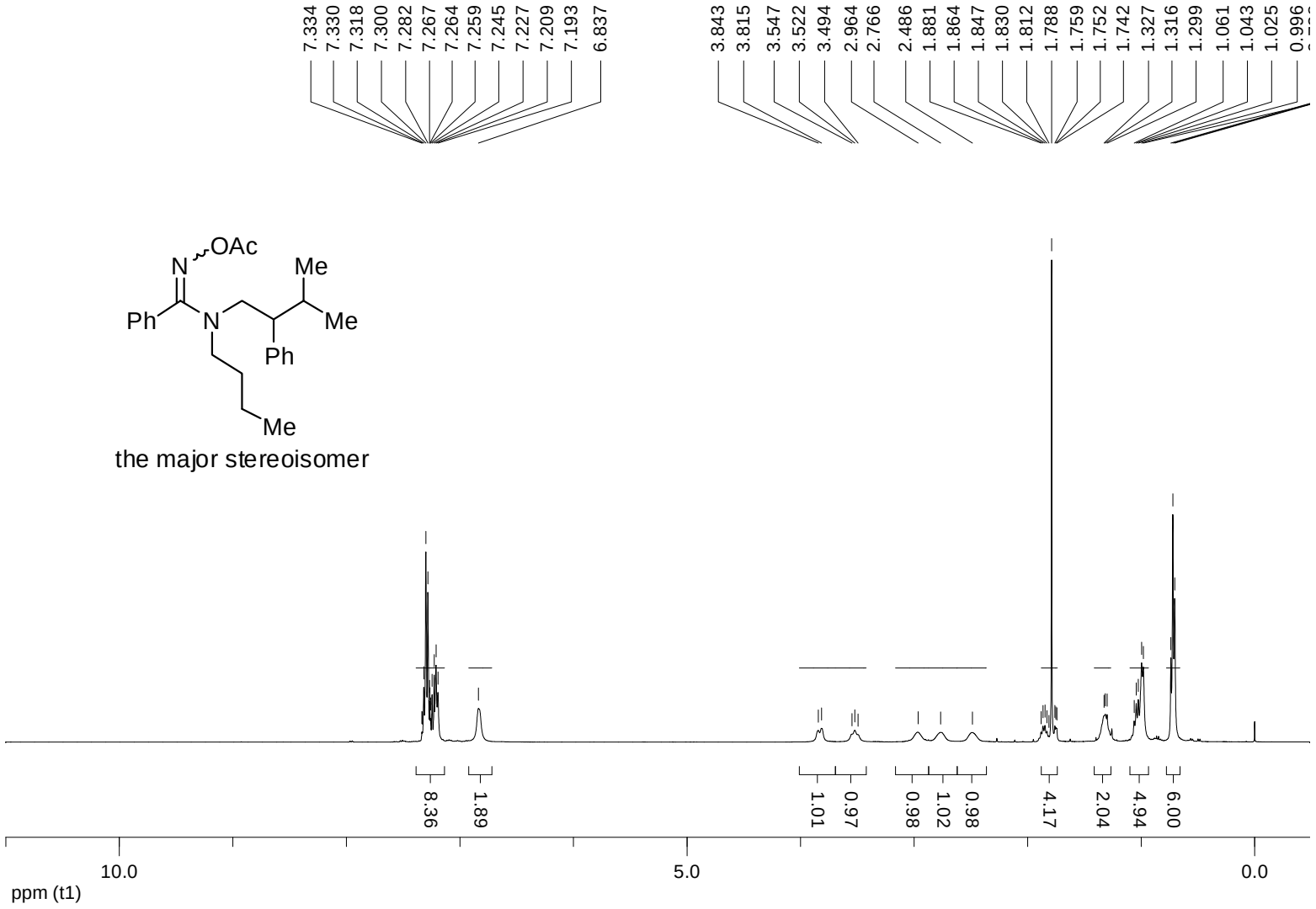




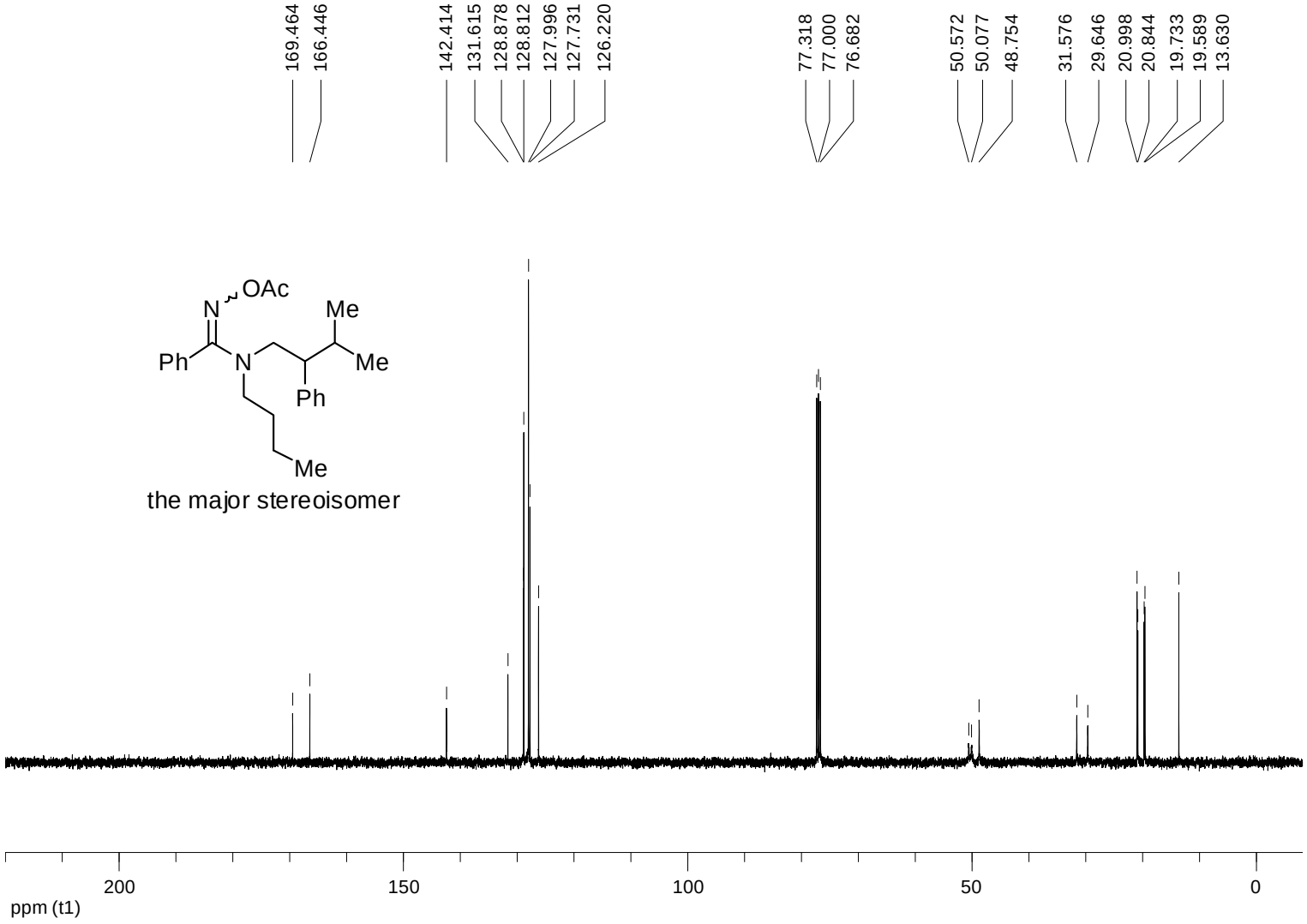
^{13}C NMR spectrum of **1h** (E/Z mixture, major:minor = 5:1) (100 MHz, $CDCl_3$)



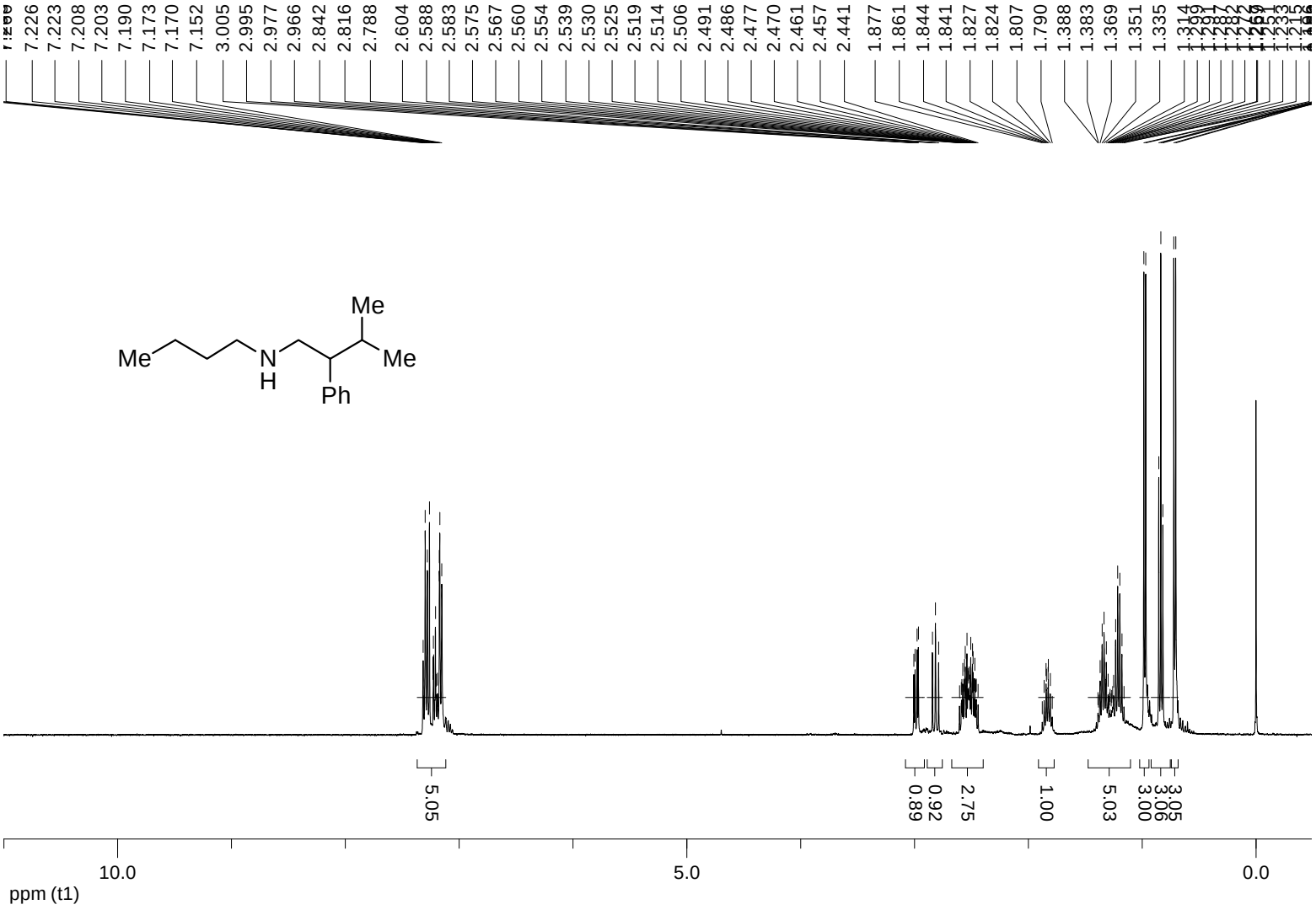
^{1}H NMR spectrum of **1i** (the major stereoisomer) (400 MHz, $CDCl_3$)



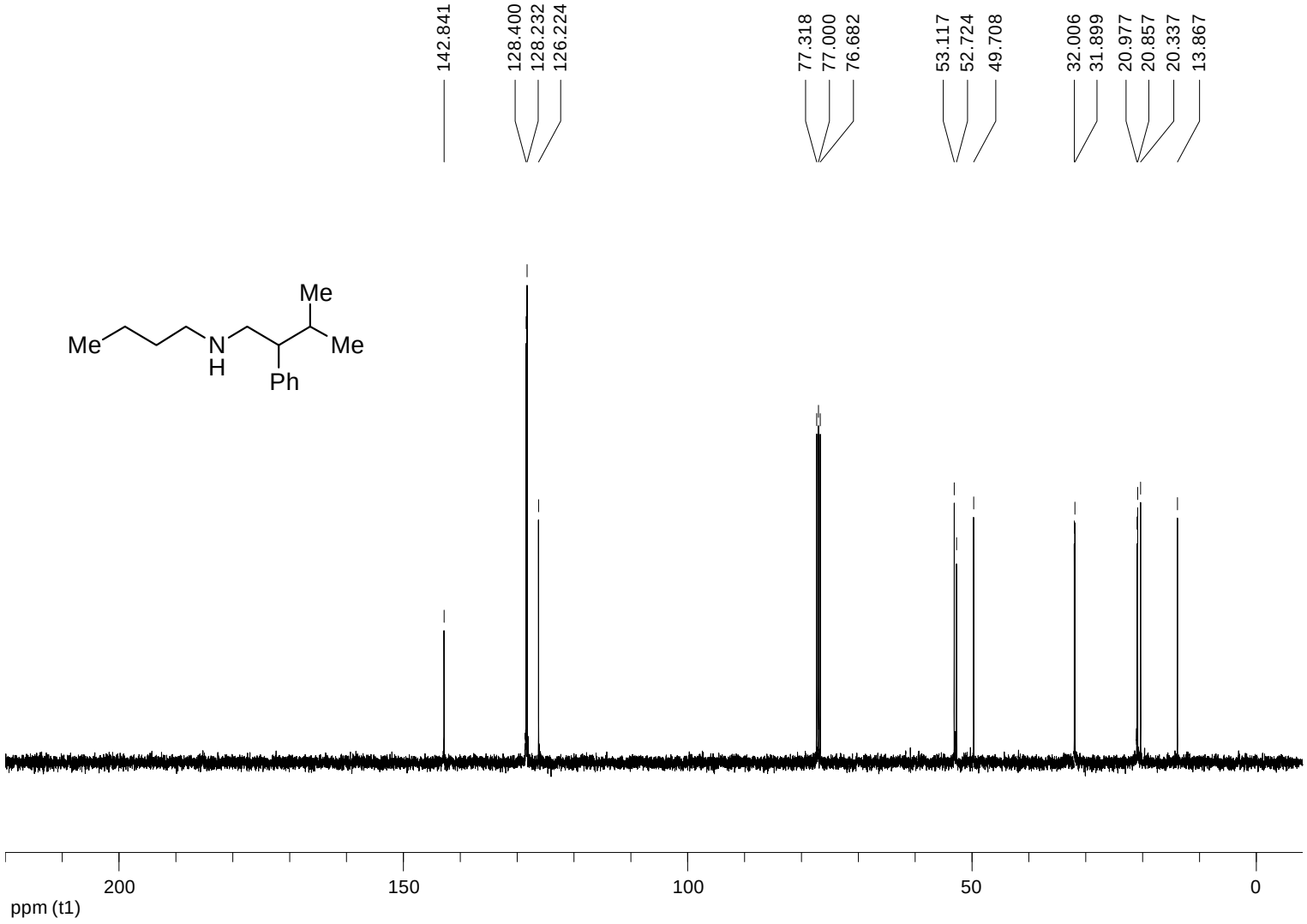
^{13}C NMR spectrum of **1i** (the major stereoisomer) (100 MHz, $CDCl_3$)



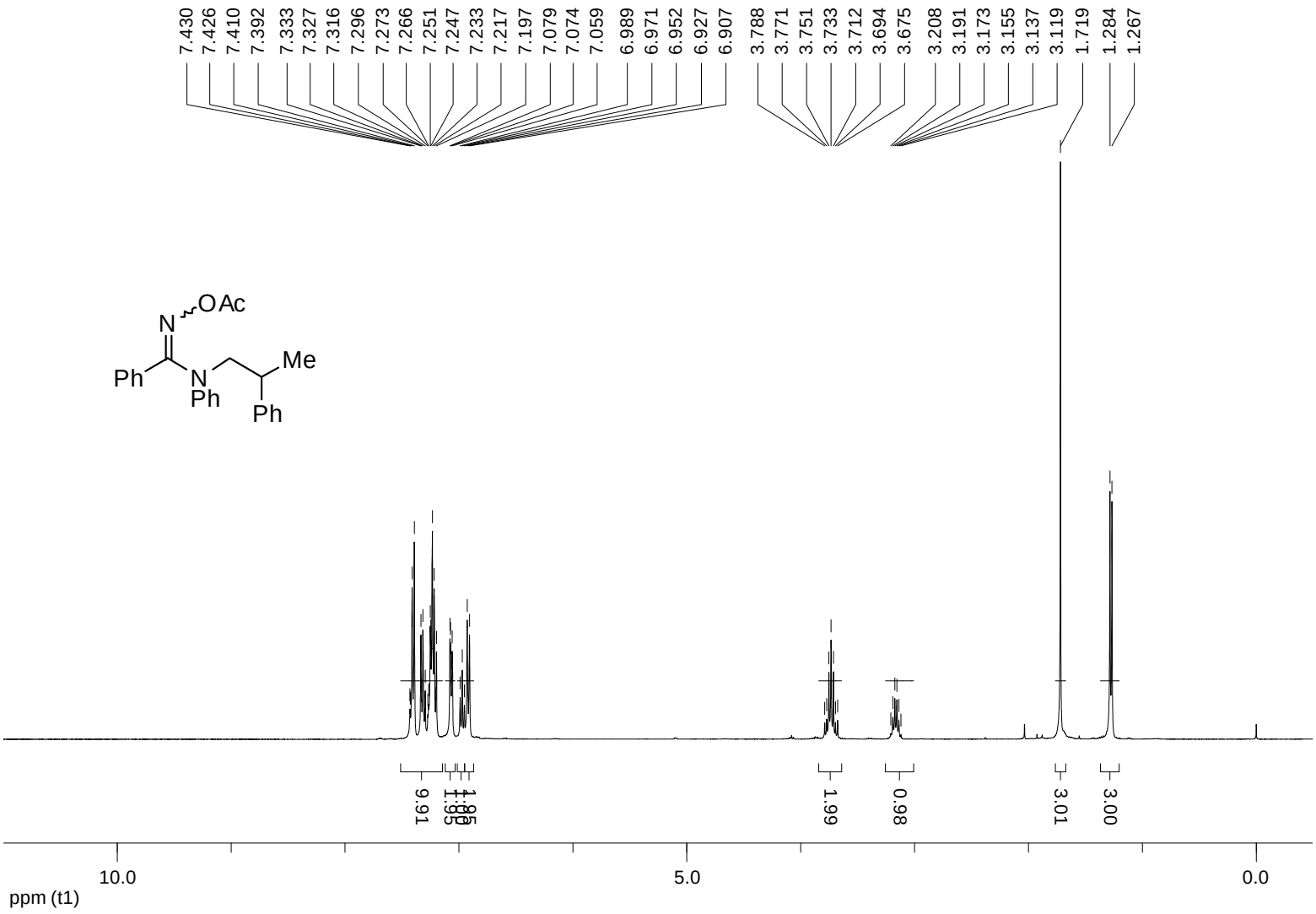
^{1}H NMR spectrum of **A** (400 MHz, $CDCl_3$)



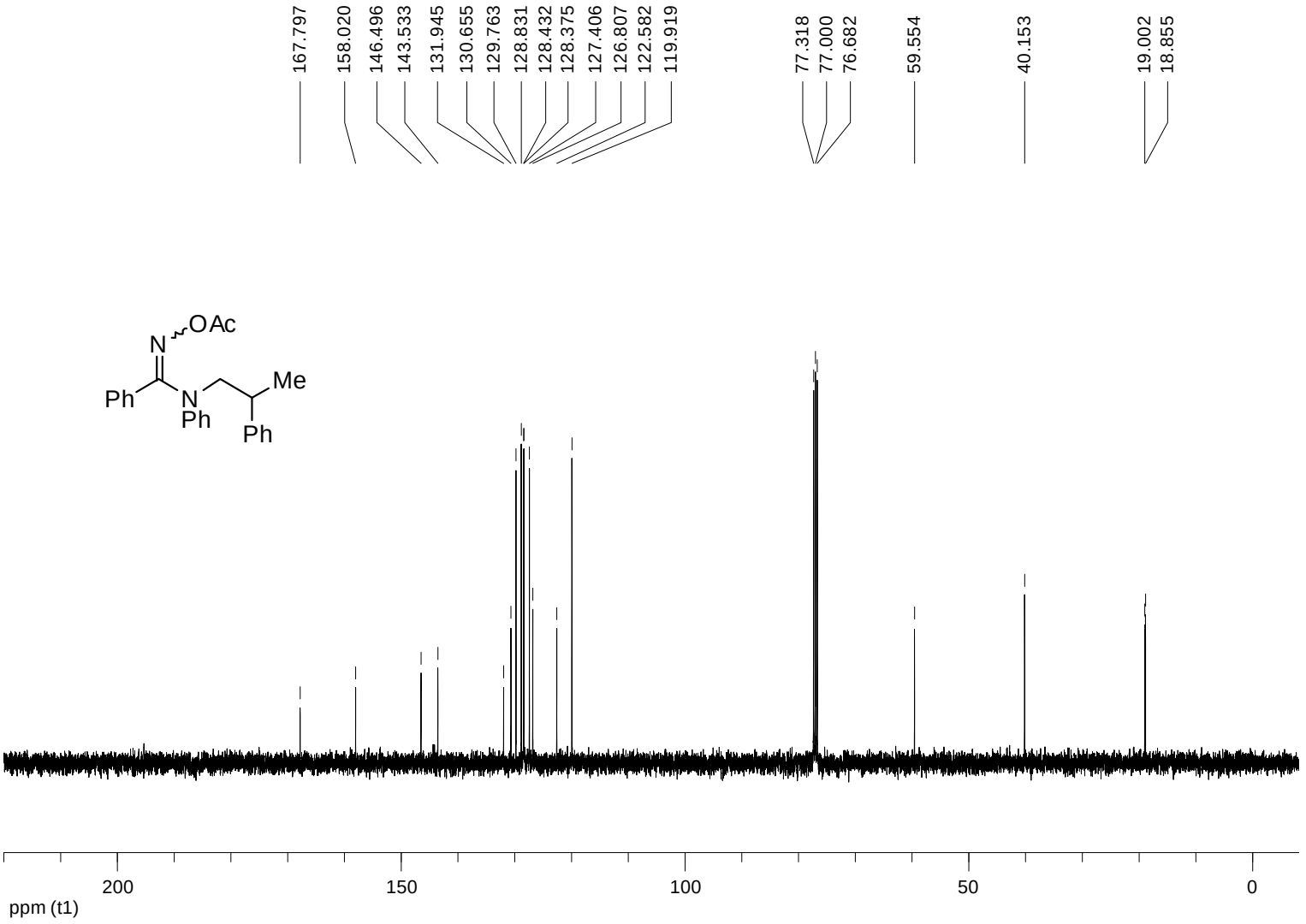
^{13}C NMR spectrum of **A** (100 MHz, $CDCl_3$)



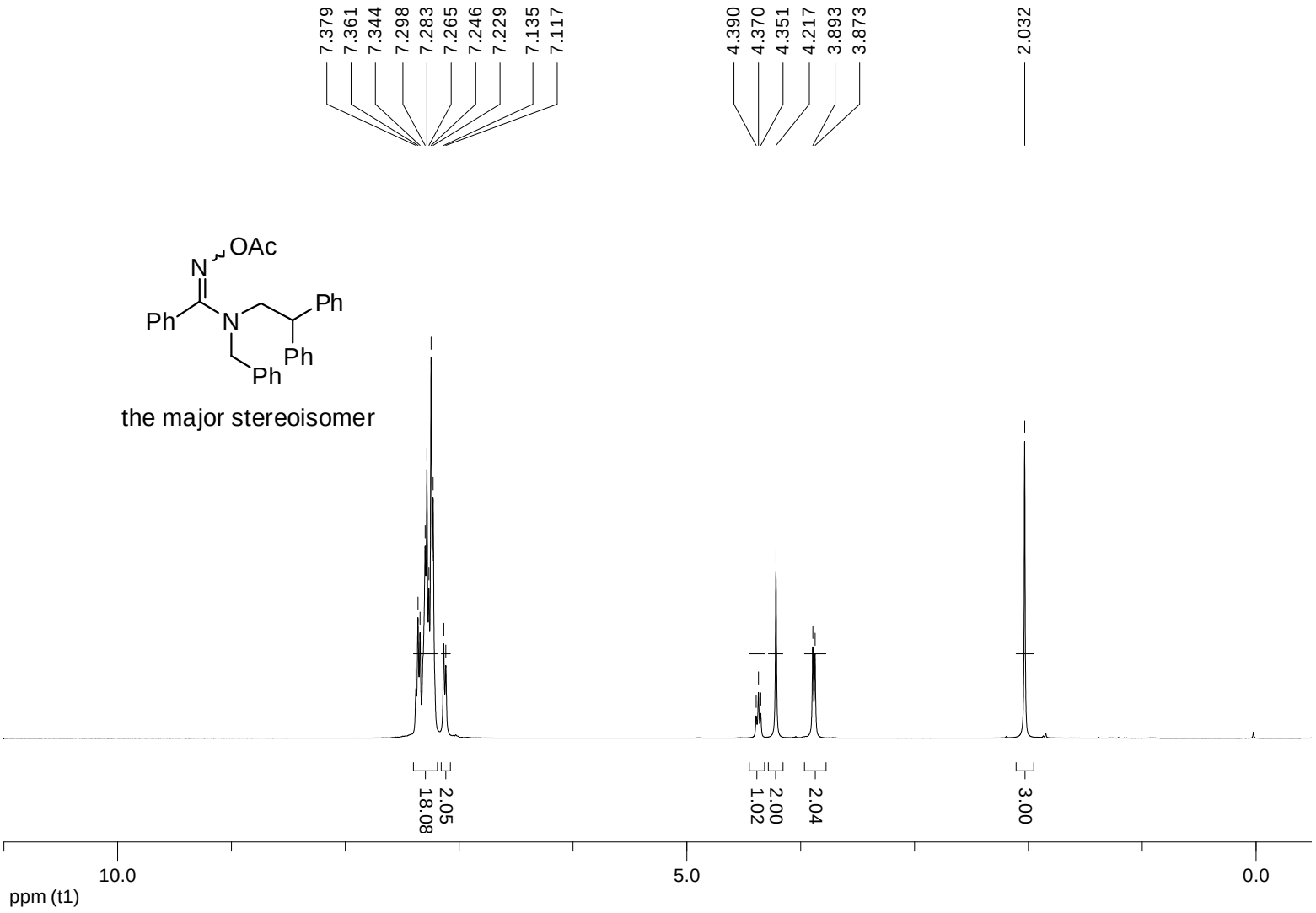
^{1}H NMR spectrum of **1j** (400 MHz, $CDCl_3$)



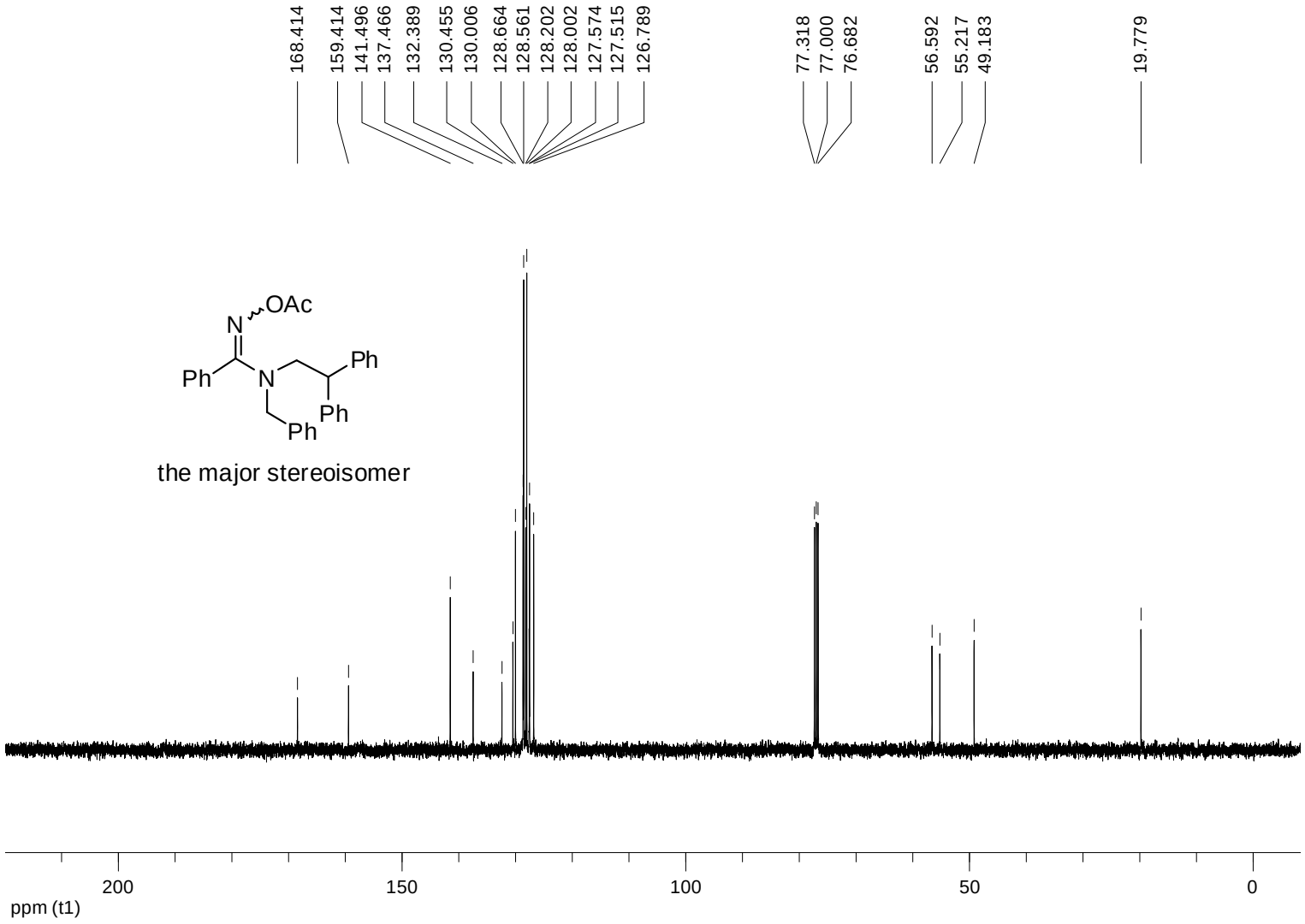
^{13}C NMR spectrum of **1j** (100 MHz, $CDCl_3$)



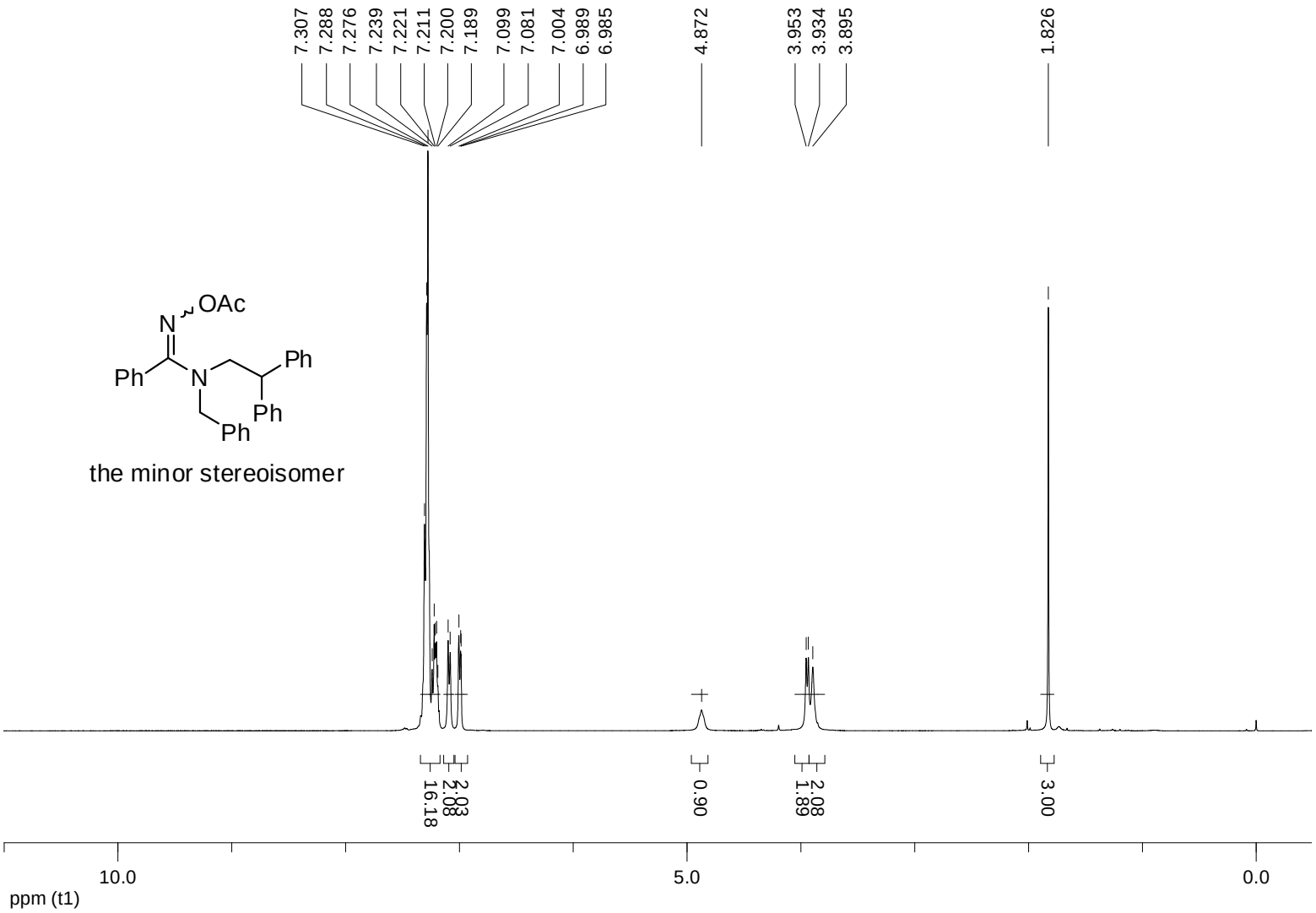
^{1}H NMR spectrum of **1k** (the major stereoisomer) (400 MHz, $CDCl_3$)



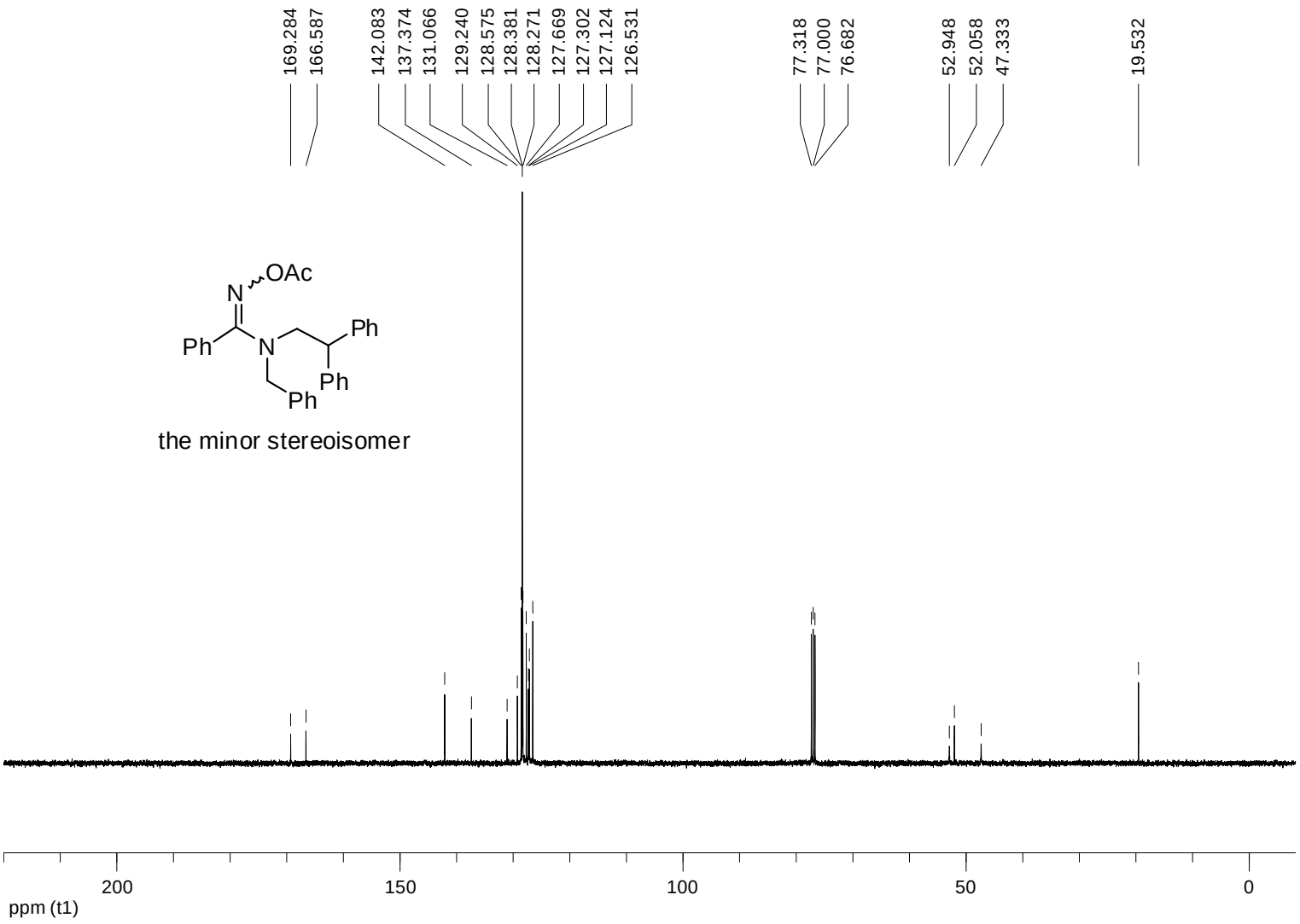
^{13}C NMR spectrum of **1k** (the major stereoisomer) (100 MHz, $CDCl_3$)



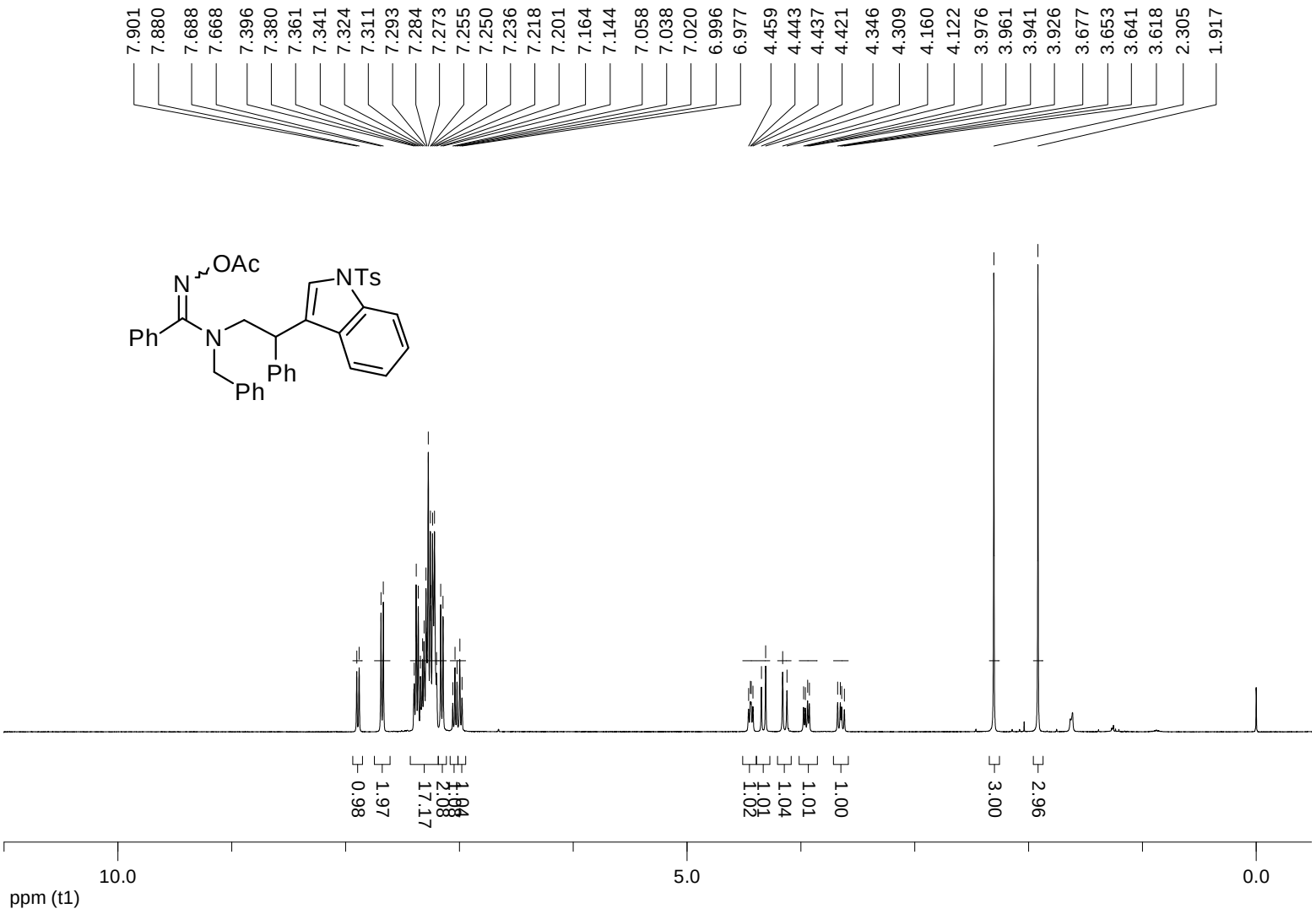
^{1}H NMR spectrum of **1k** (the minor stereoisomer) (400 MHz, $CDCl_3$)



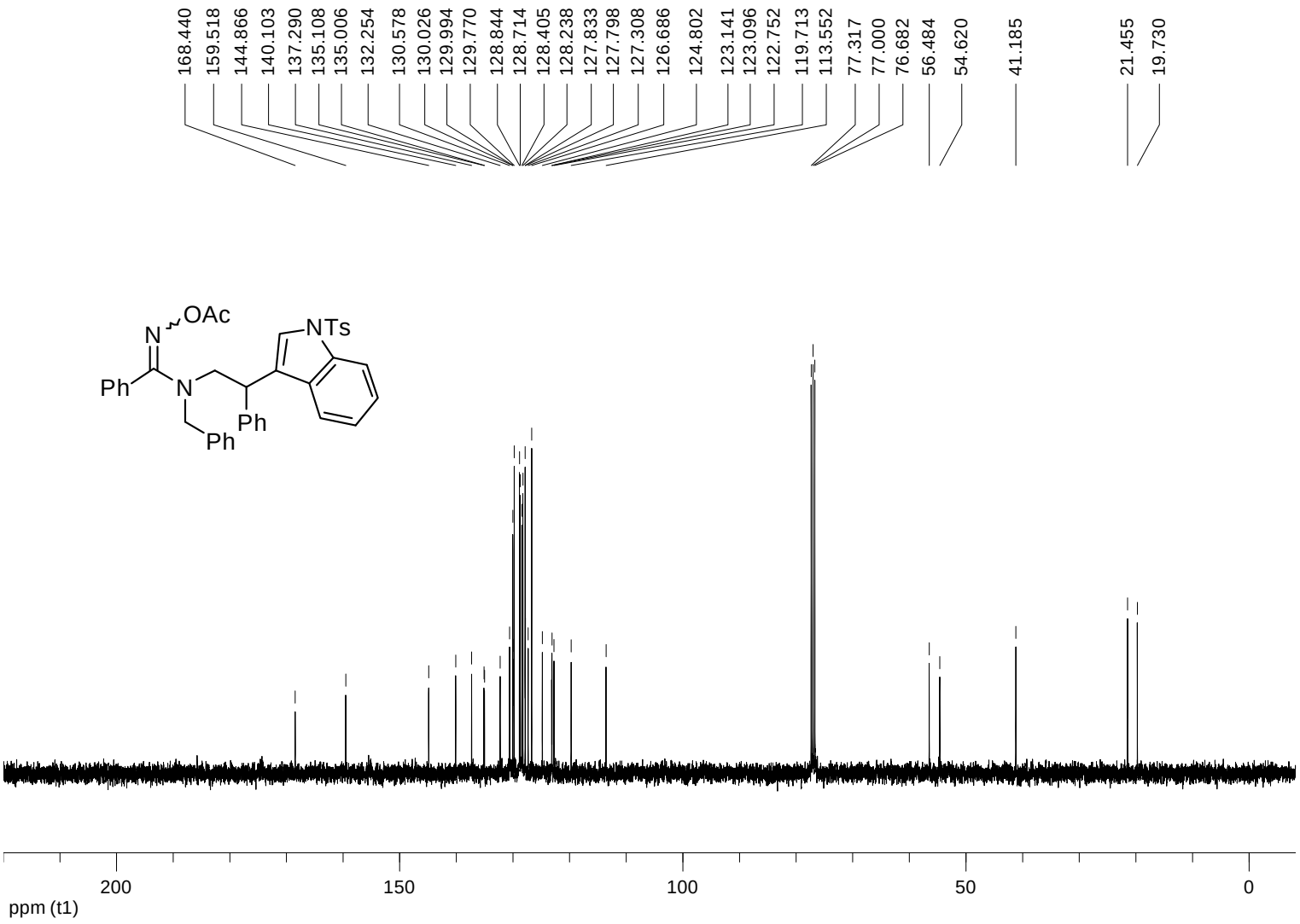
^{13}C NMR spectrum of **1k** (the minor stereoisomer) (100 MHz, $CDCl_3$)



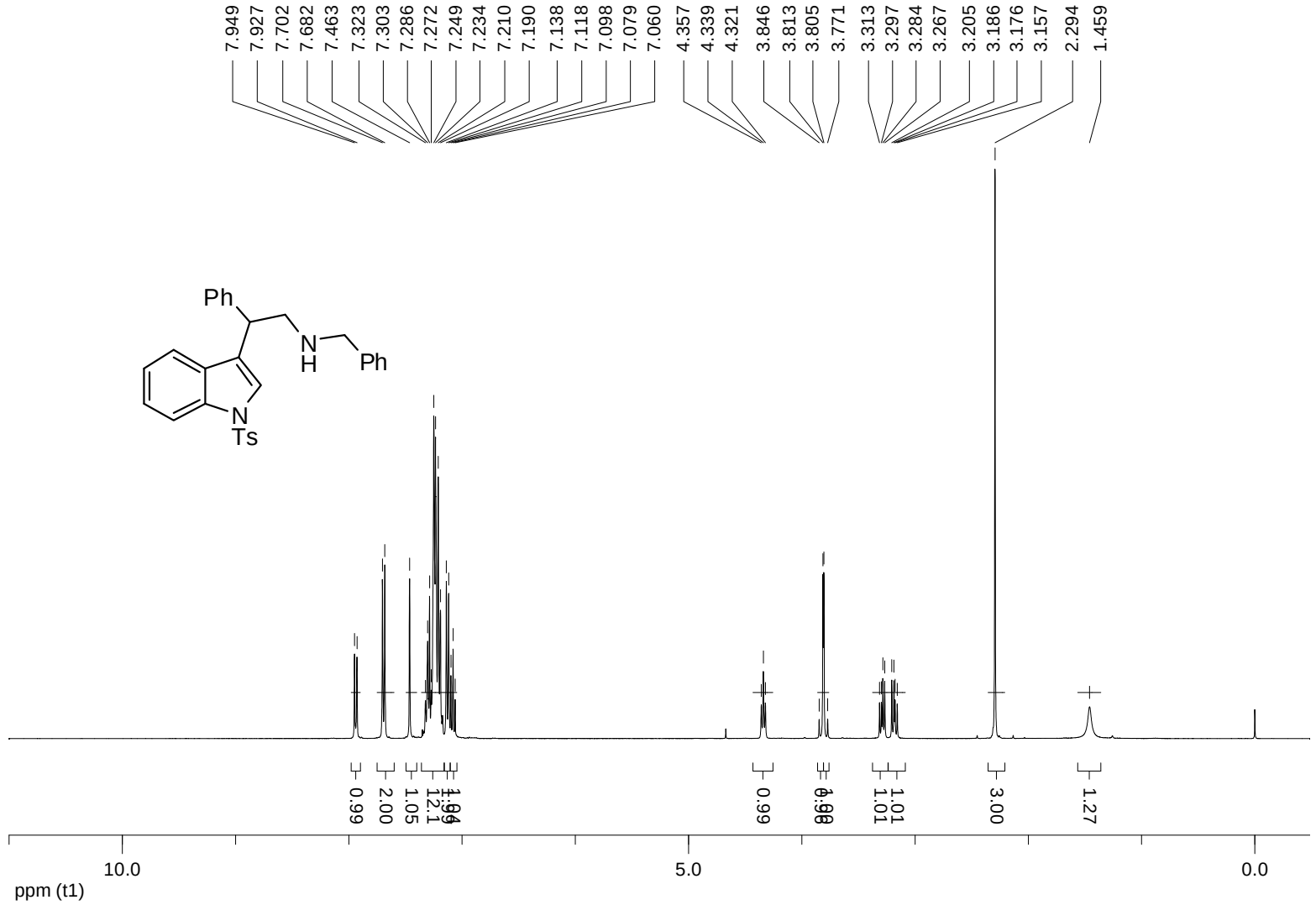
^{1}H NMR spectrum of **1l** (400 MHz, $CDCl_3$)



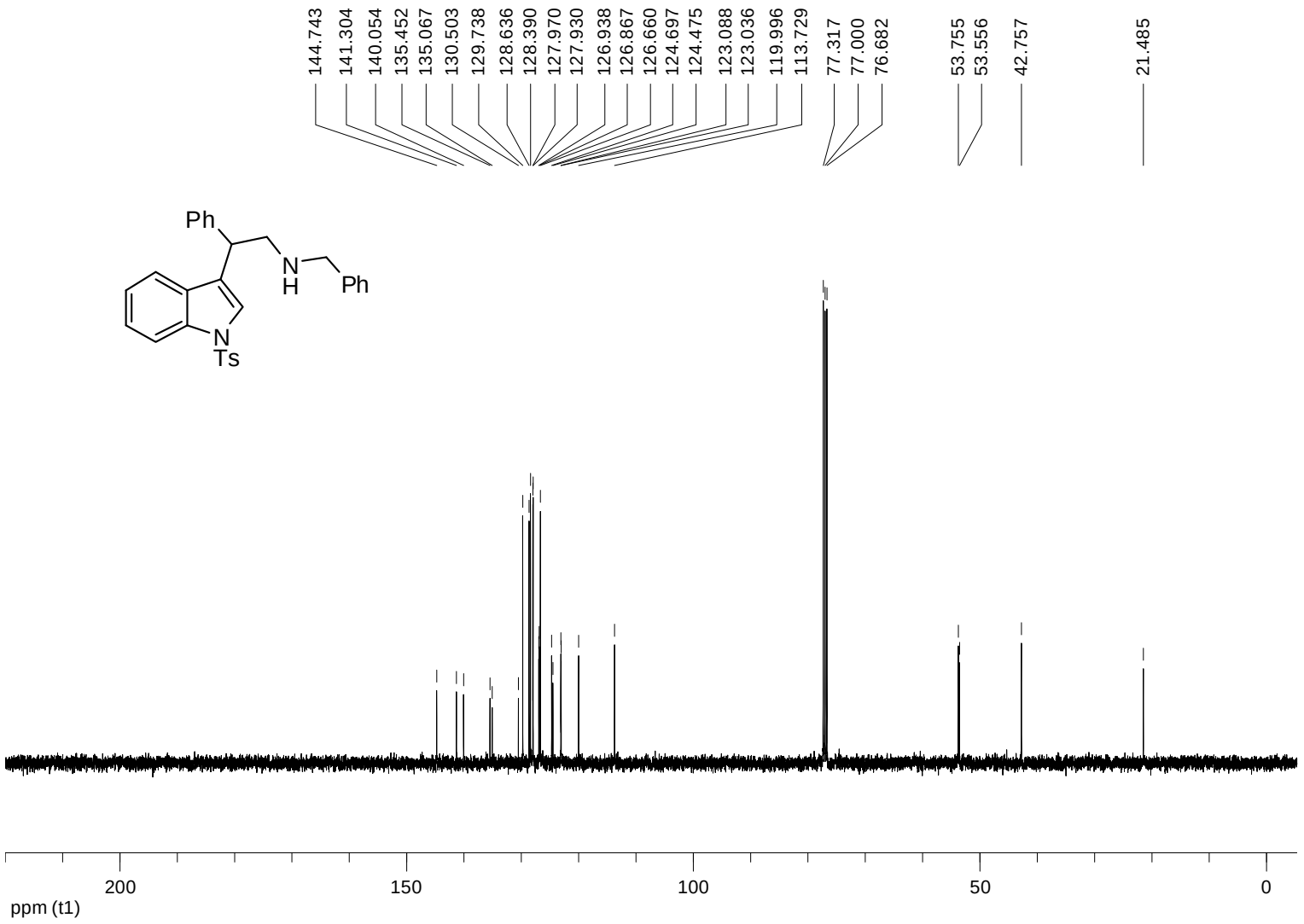
^{13}C NMR spectrum of **1l** (100 MHz, $CDCl_3$)



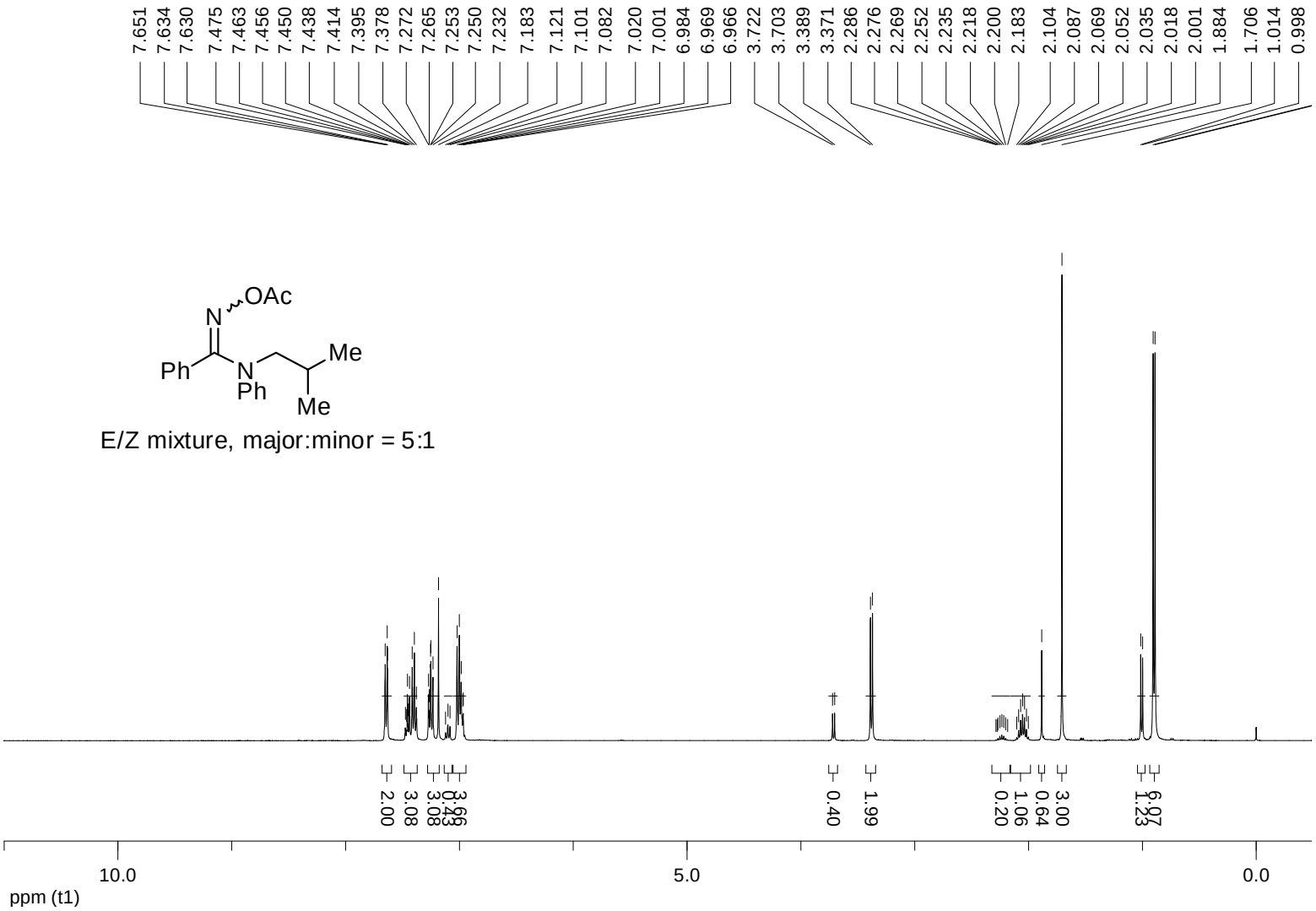
^{1}H NMR spectrum of **B** (major stereoisomer) (400 MHz, $CDCl_3$)



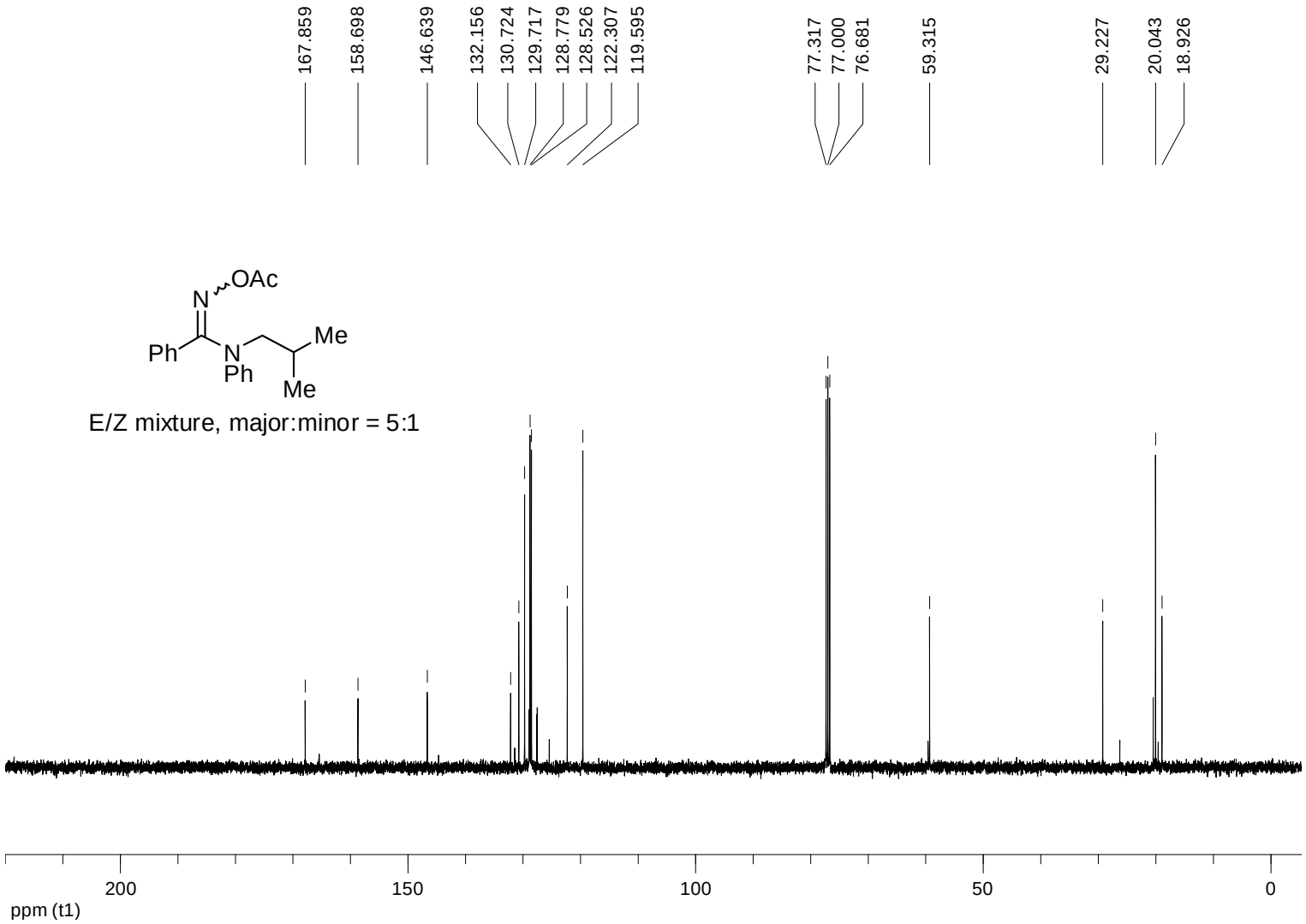
^{13}C NMR spectrum of **B** (major stereoisomer) (100 MHz, $CDCl_3$)



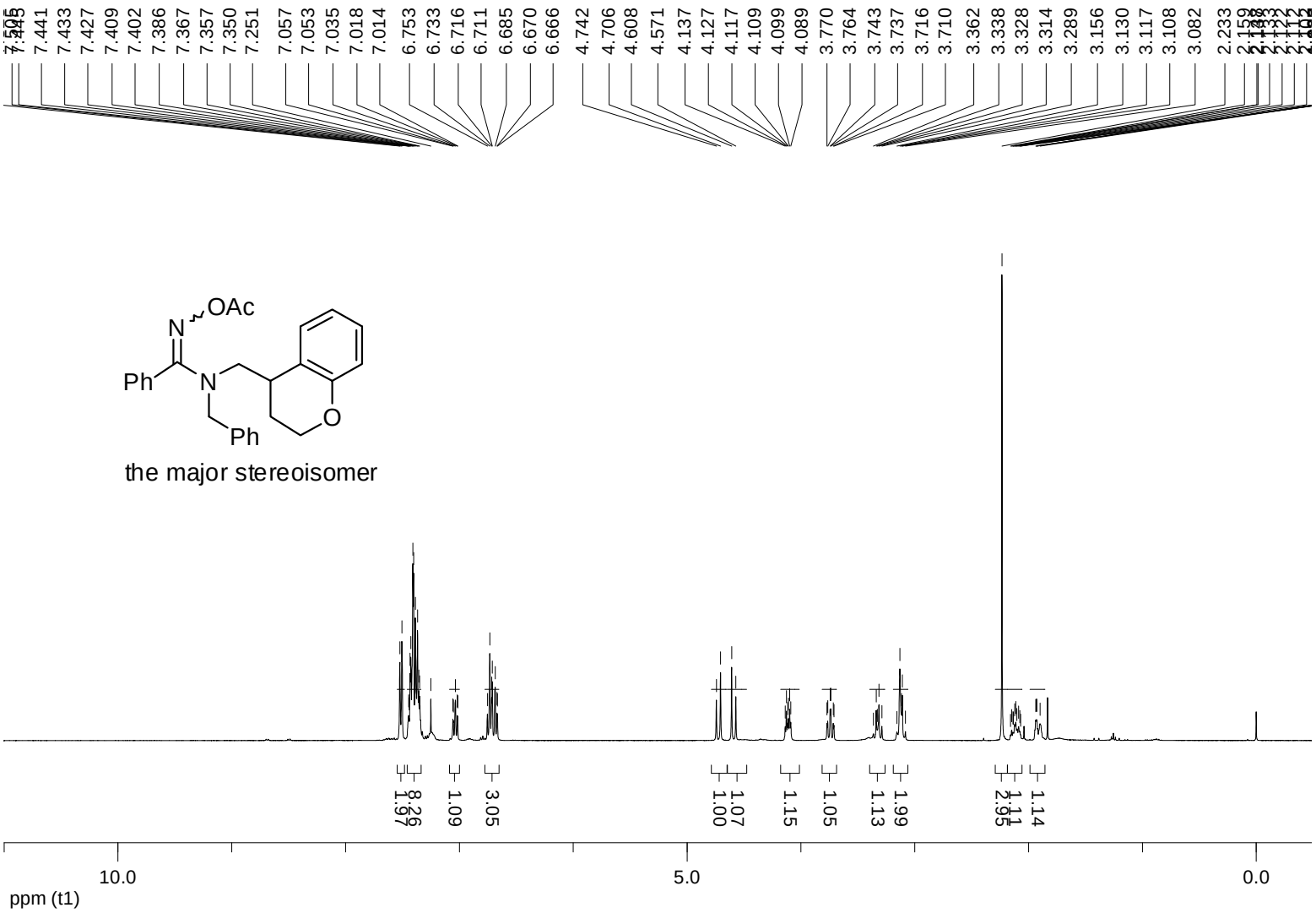
^{1}H NMR spectrum of **1m** (*E*/*Z* mixture, major:minor = 5:1) (400 MHz, $CDCl_3$)



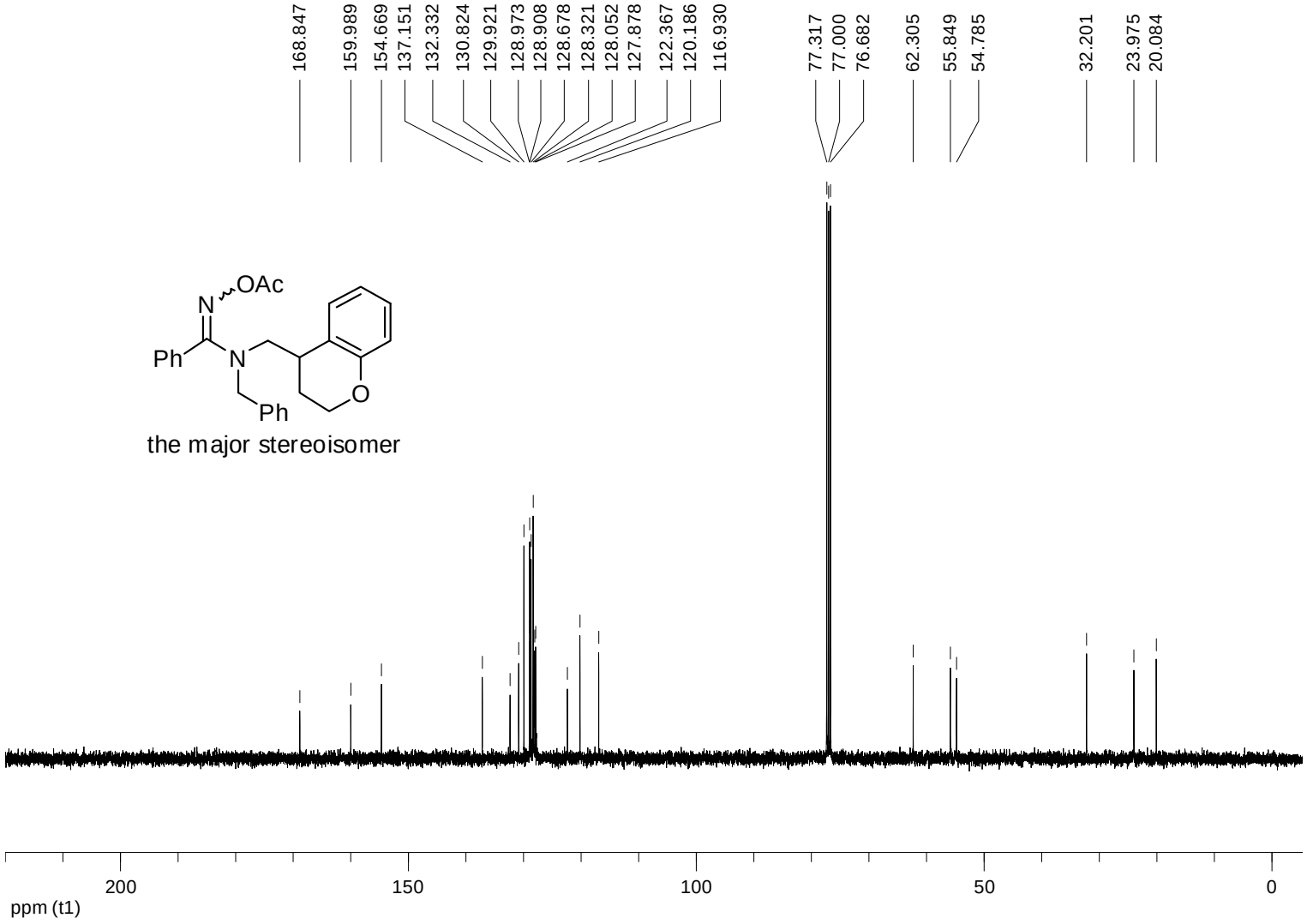
^{13}C NMR spectrum of **1m** (*E*/*Z* mixture, major:minor = 5:1) (100 MHz, $CDCl_3$)



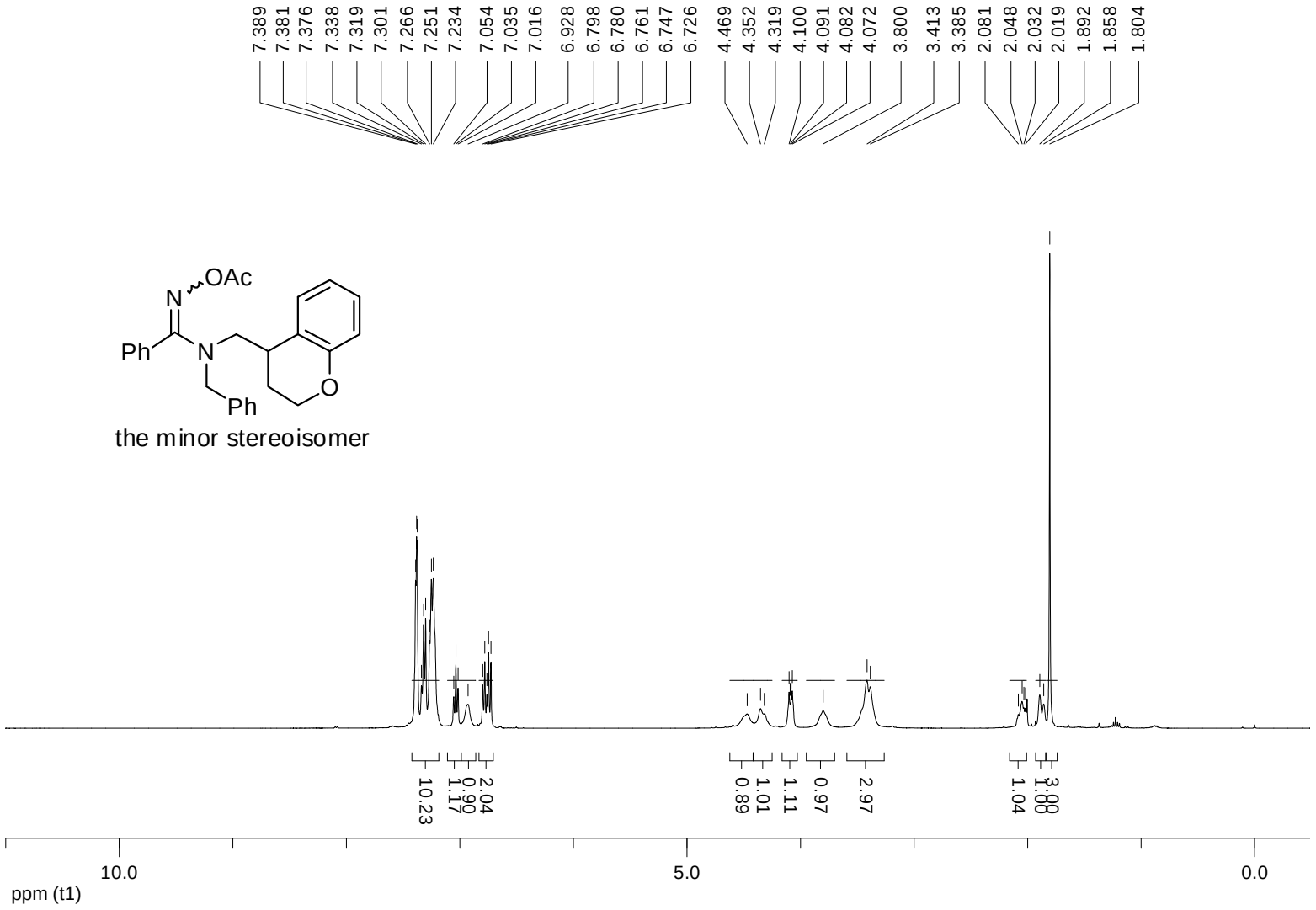
^{1}H NMR spectrum of **1n** (the major stereoisomer) (400 MHz, $CDCl_3$)



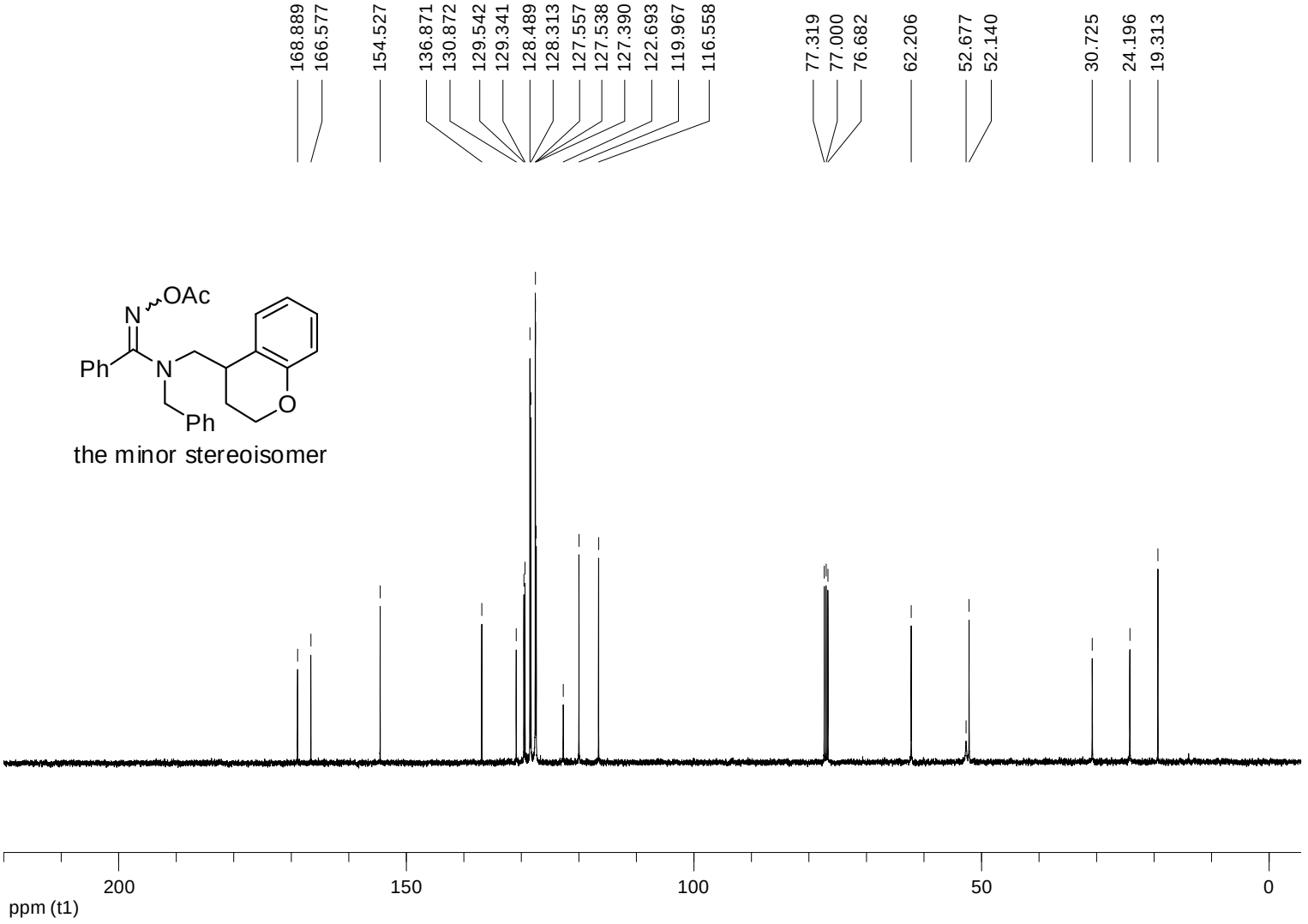
^{13}C NMR spectrum of **1n** (the major stereoisomer) (100 MHz, $CDCl_3$)



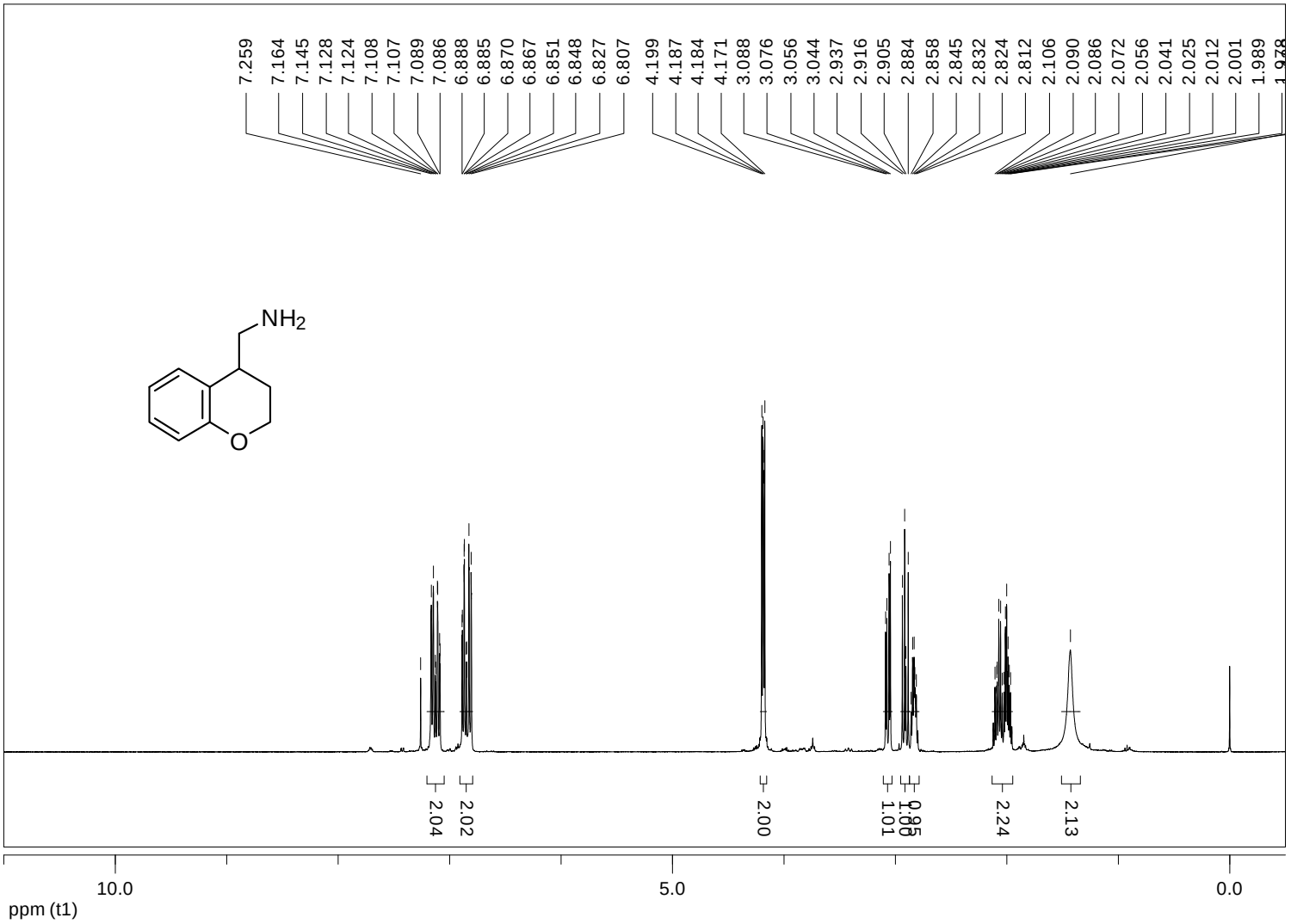
^{1}H NMR spectrum of **1n** (the minor stereoisomer) (400 MHz, $CDCl_3$)



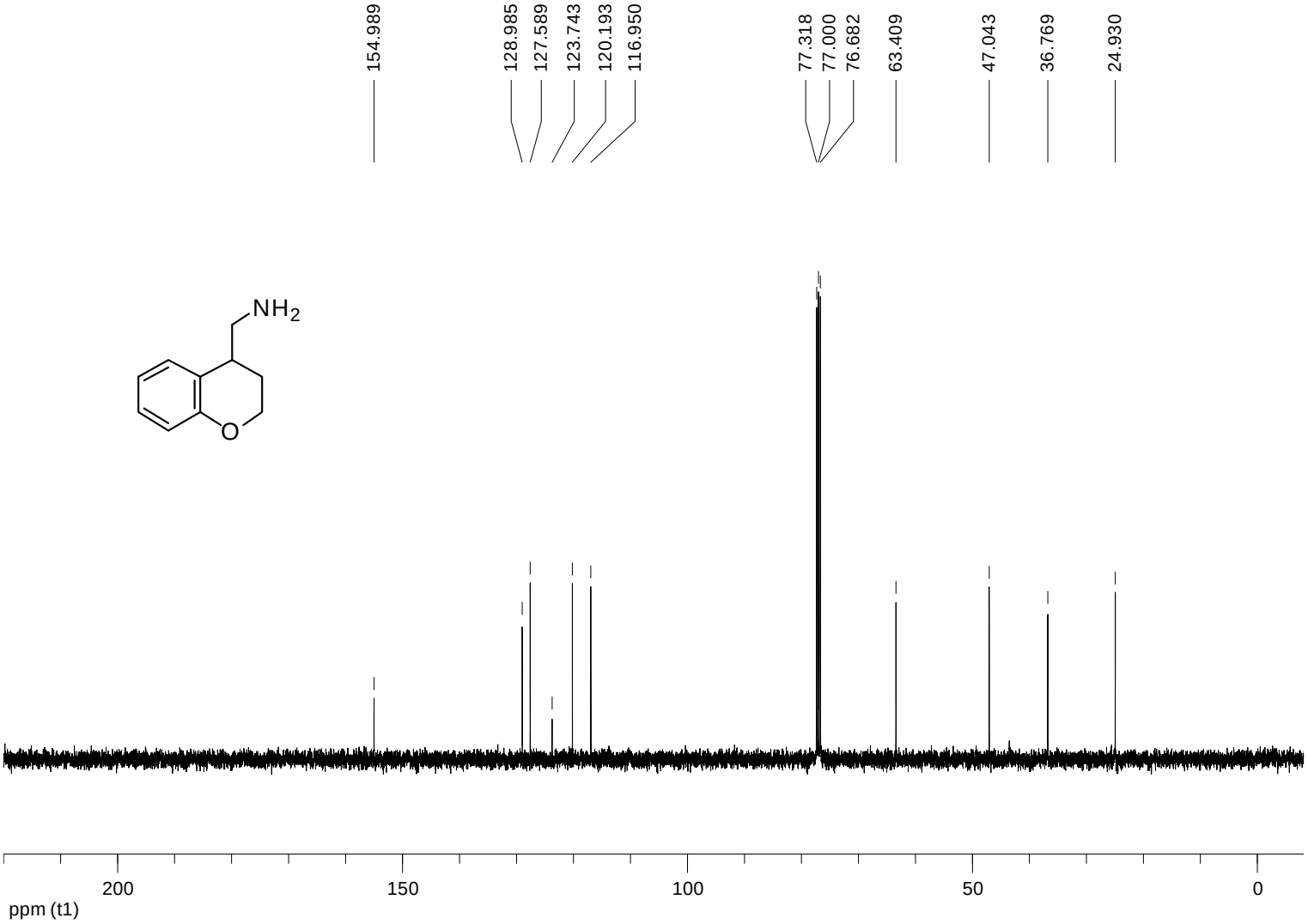
^{13}C NMR spectrum of **1n** (the minor stereoisomer) (100 MHz, $CDCl_3$)



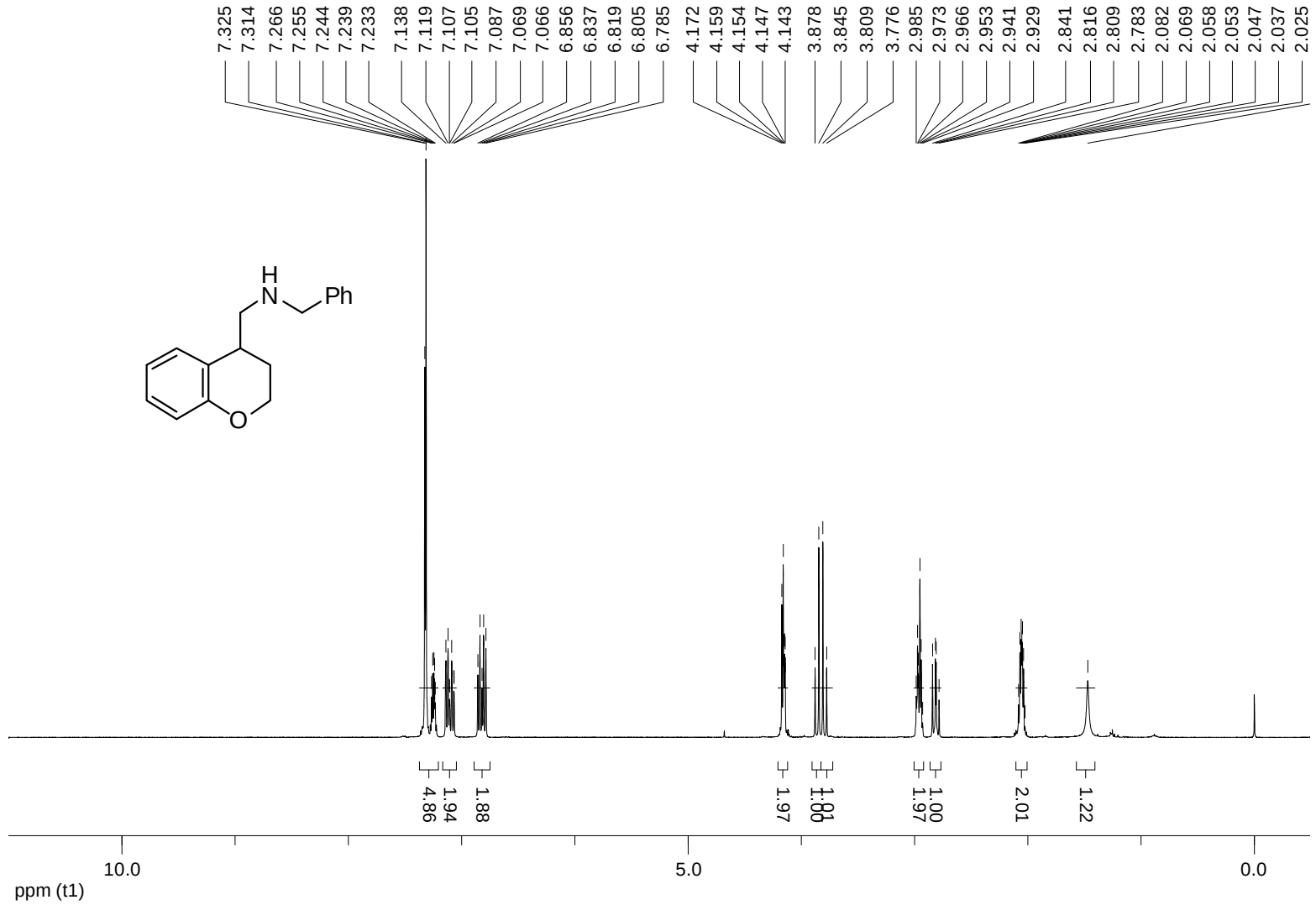
^{1}H NMR spectrum of **C** (400 MHz, $CDCl_3$)



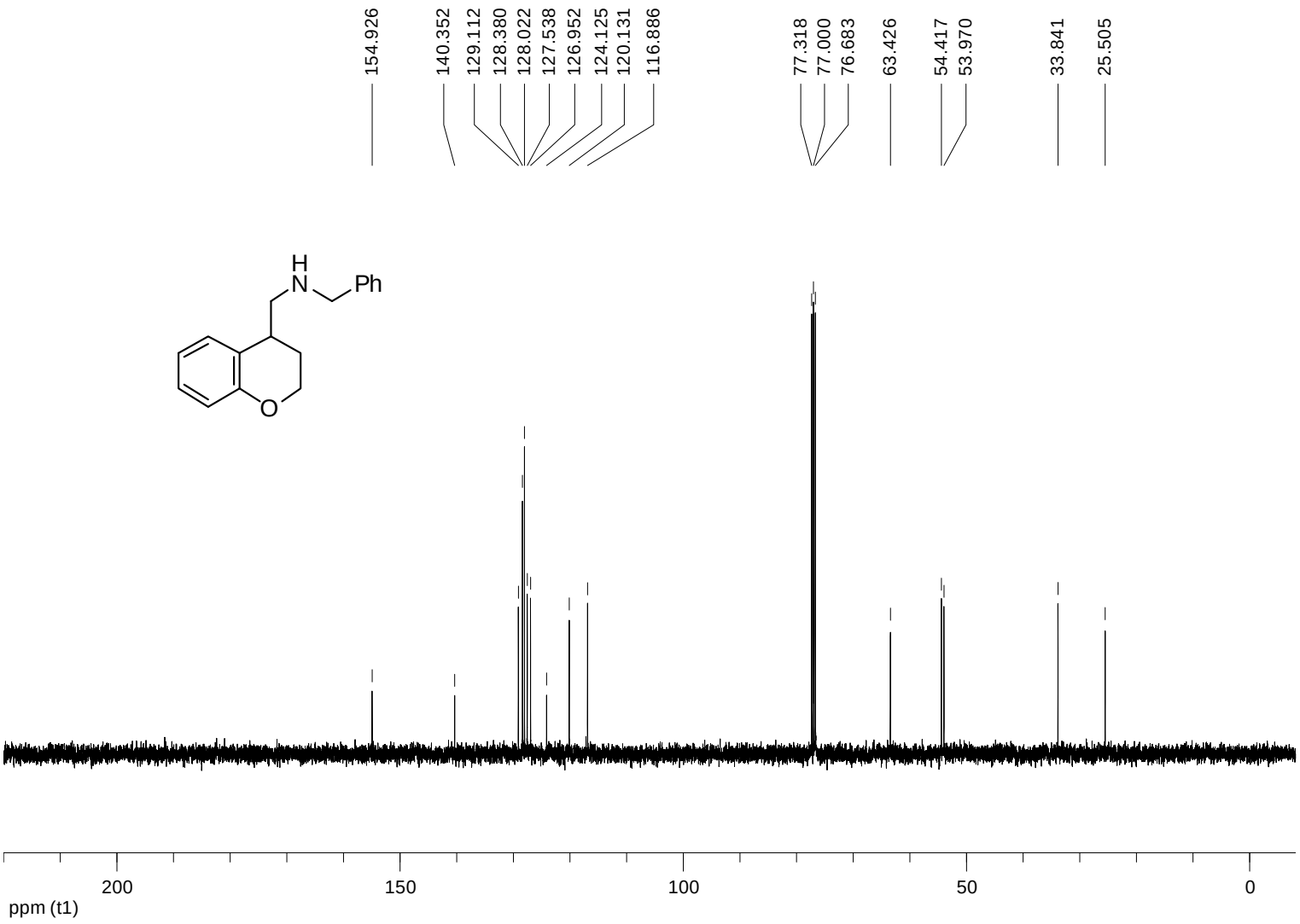
^{13}C NMR spectrum of **C** (100 MHz, $CDCl_3$)



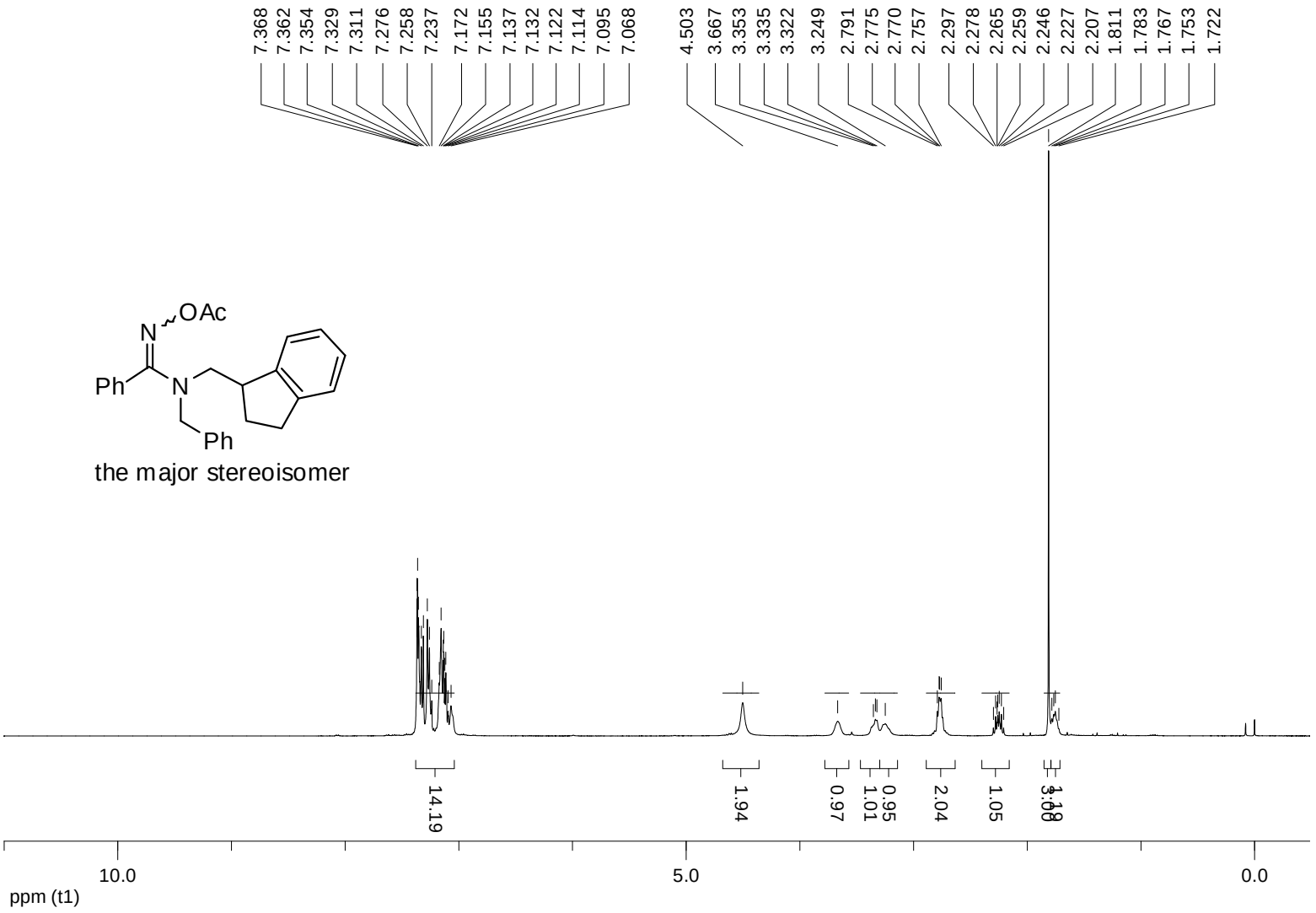
^{1}H NMR spectrum of **D** (400 MHz, $CDCl_3$)



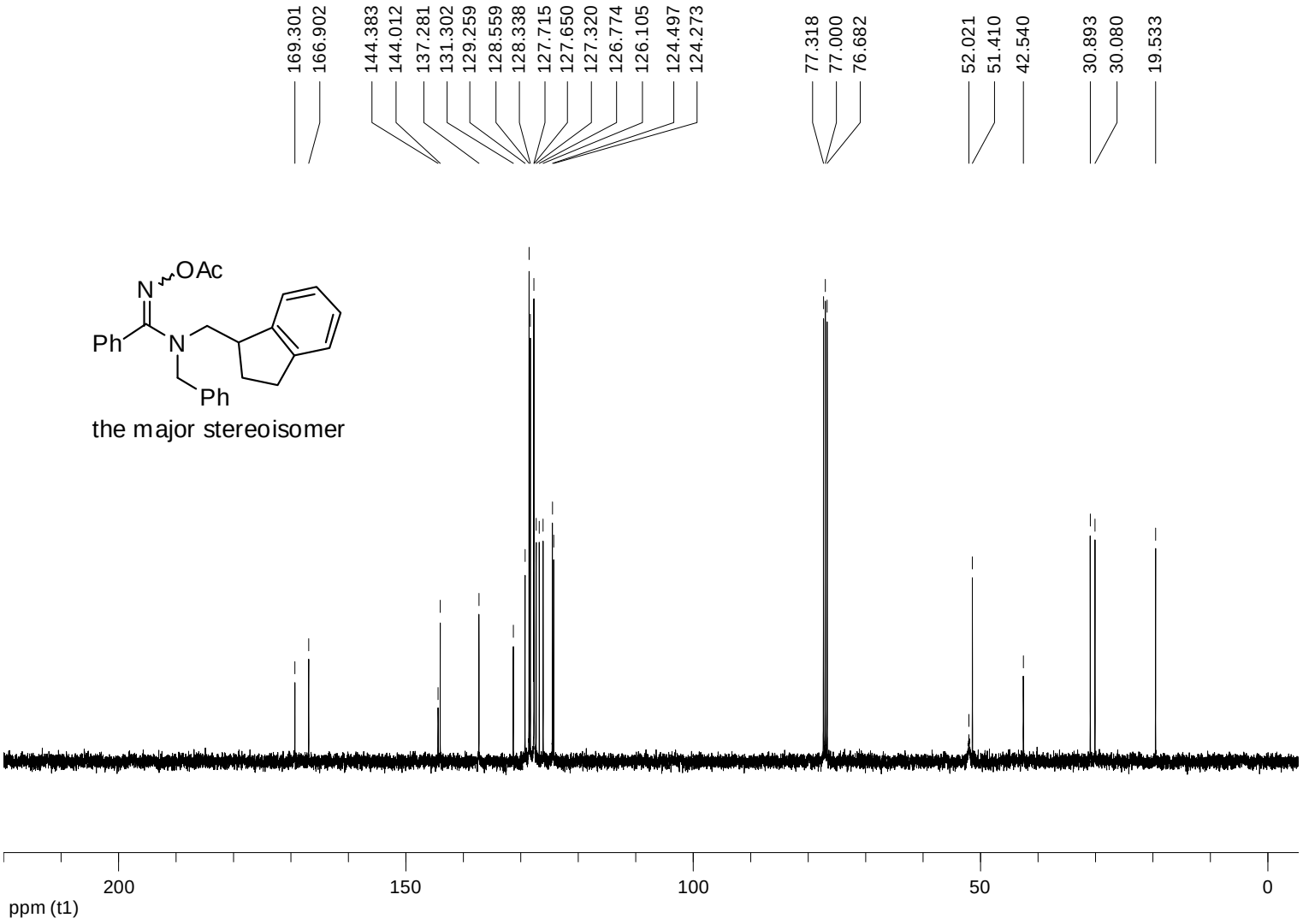
^{13}C NMR spectrum of **D** (100 MHz, $CDCl_3$)



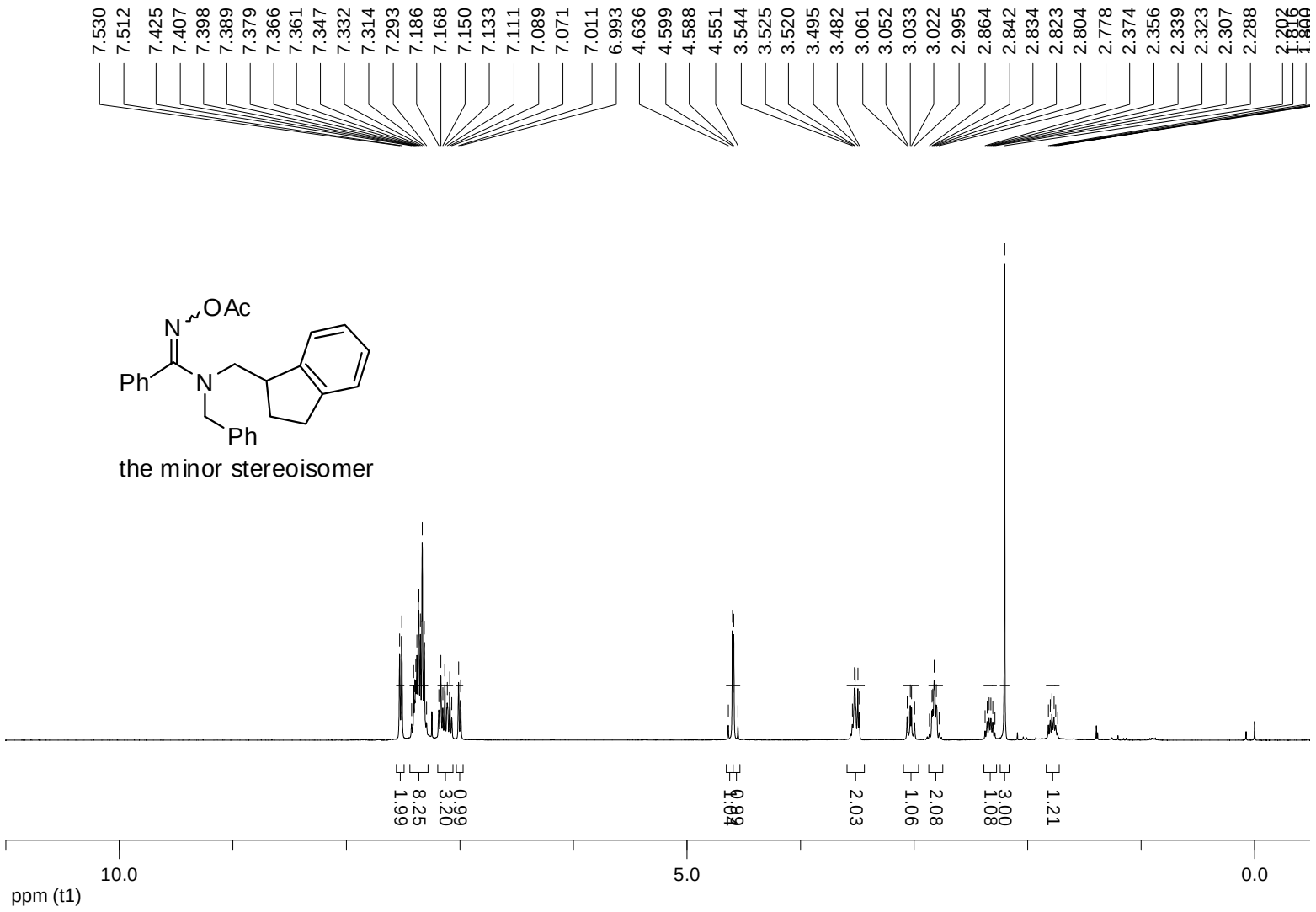
^{1}H NMR spectrum of **1o** (the major stereoisomer) (400 MHz, $CDCl_3$)



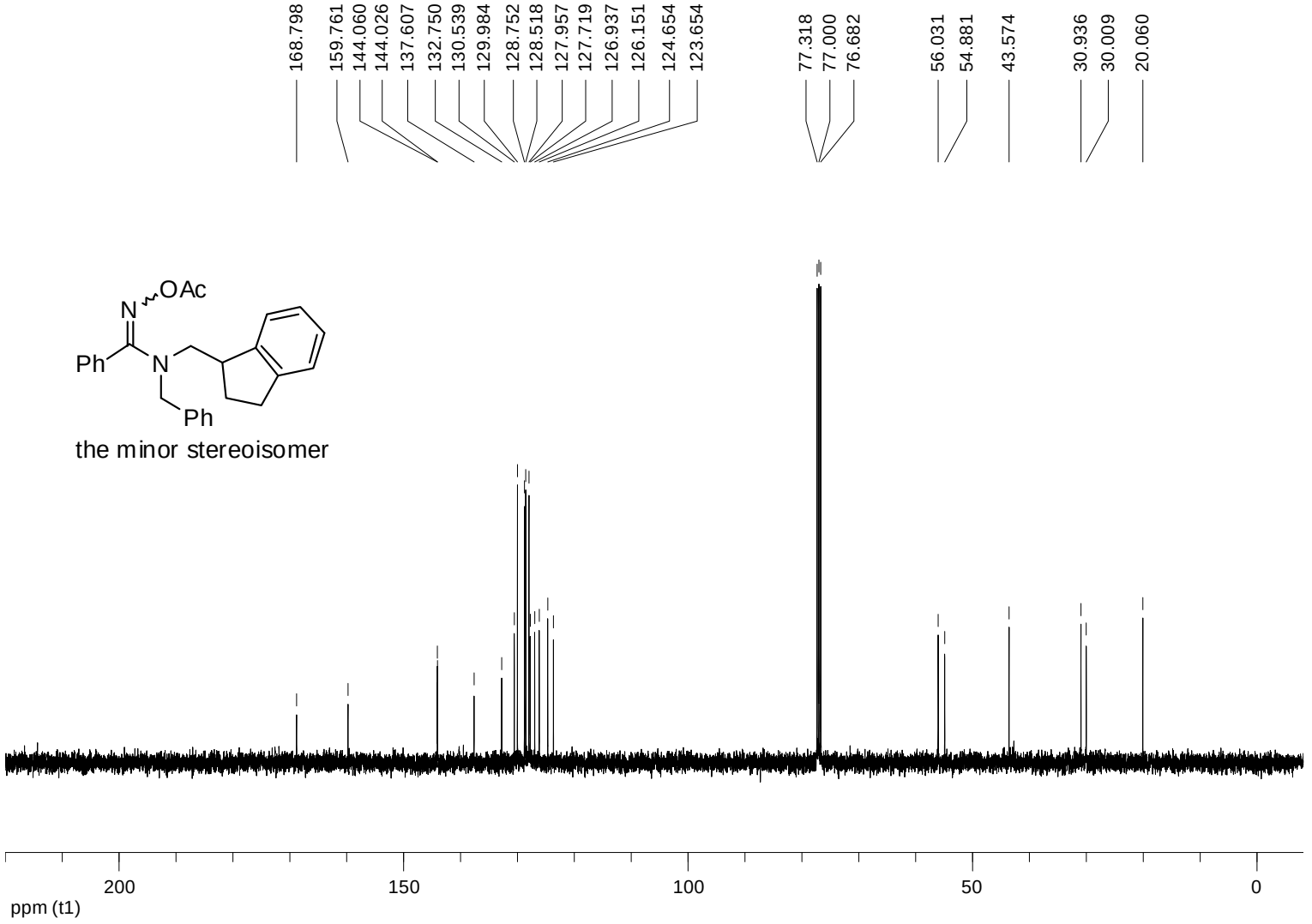
^{13}C NMR spectrum of **1o** (the major stereoisomer) (100 MHz, $CDCl_3$)



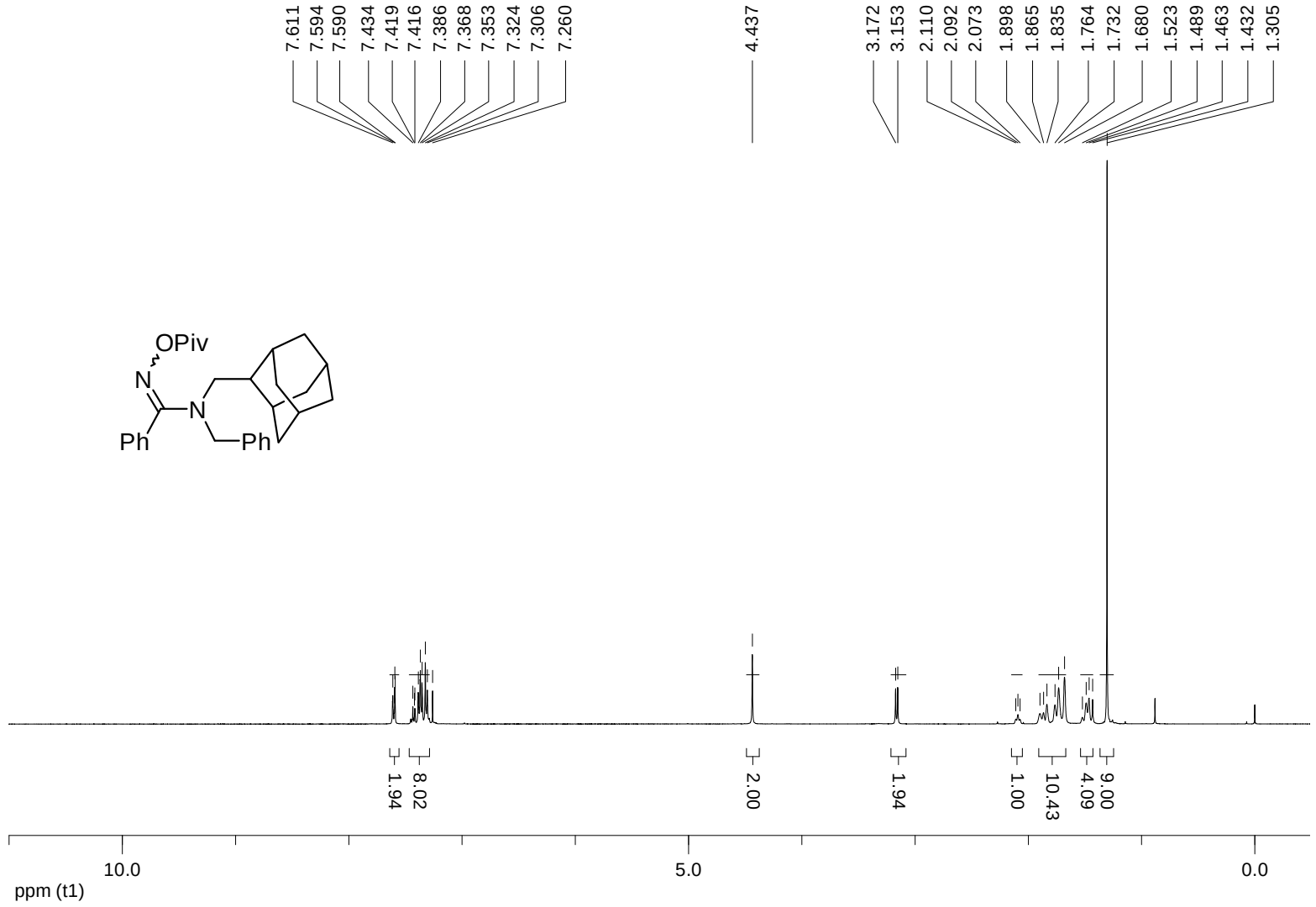
^{1}H NMR spectrum of **1o** (the minor stereoisomer) (400 MHz, $CDCl_3$)



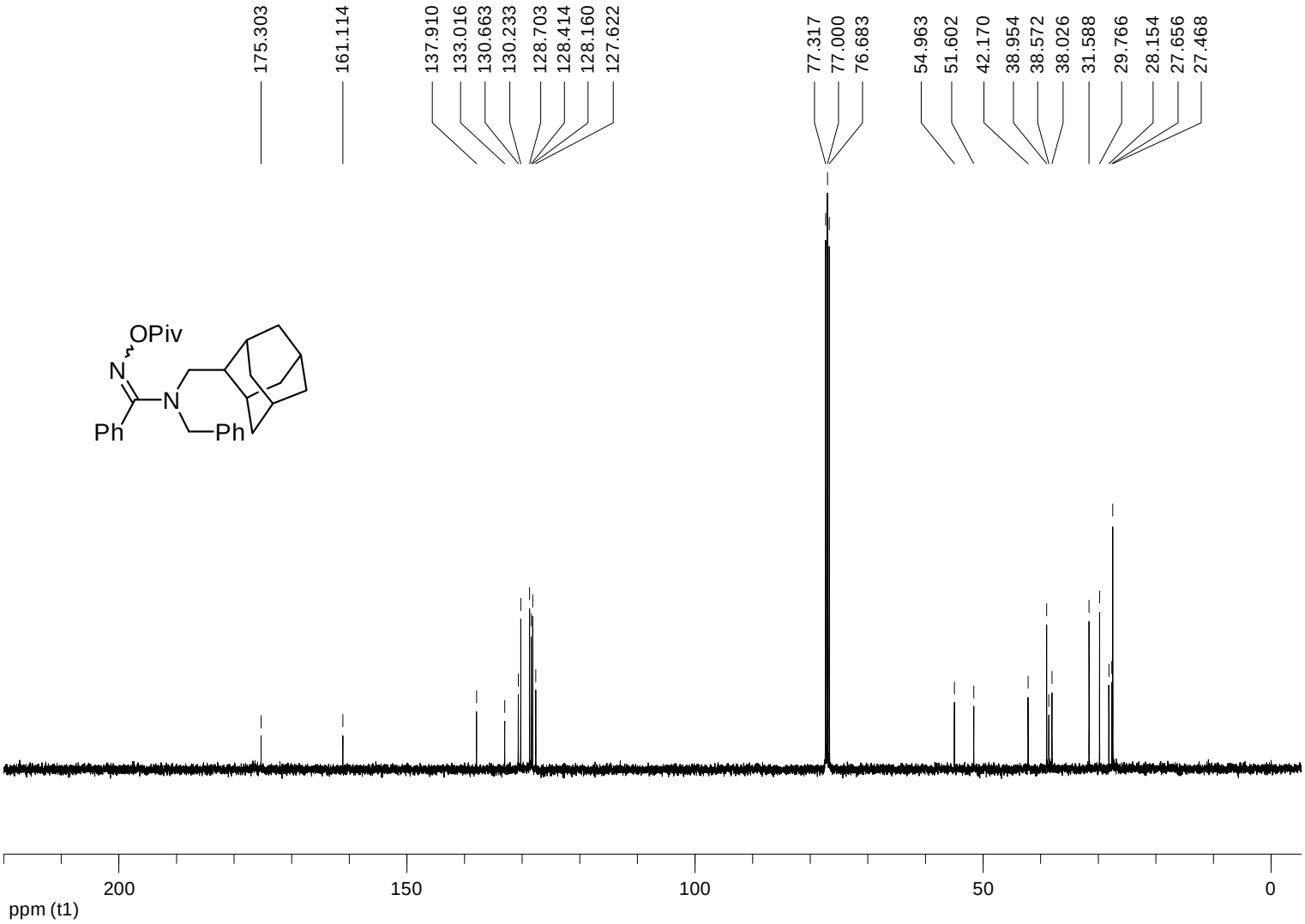
^{13}C NMR spectrum of **1o** (the minor stereoisomer) (100 MHz, $CDCl_3$)



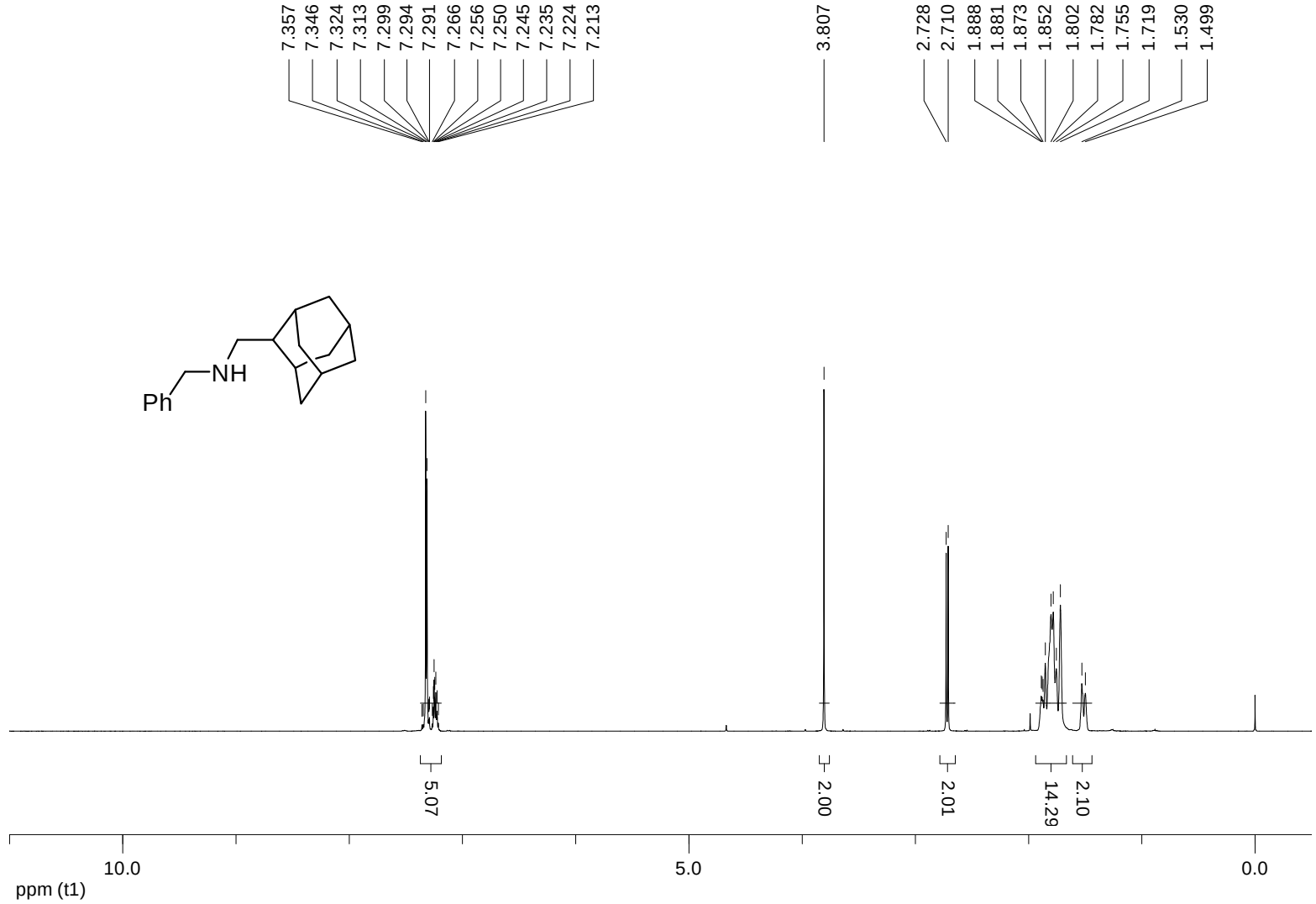
^{1}H NMR spectrum of **1p** (400 MHz, $CDCl_3$)



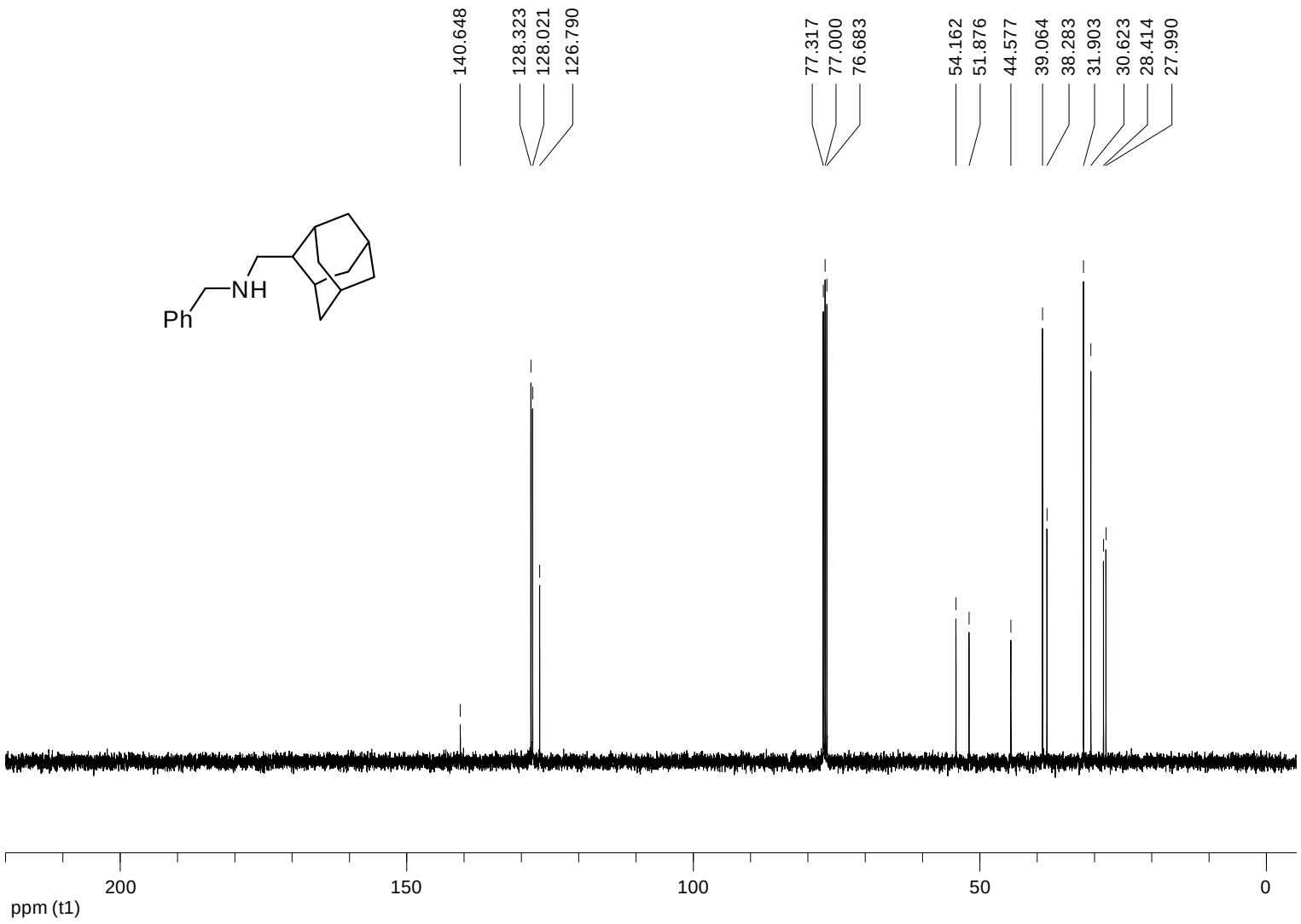
^{13}C NMR spectrum of **1p** (100 MHz, $CDCl_3$)



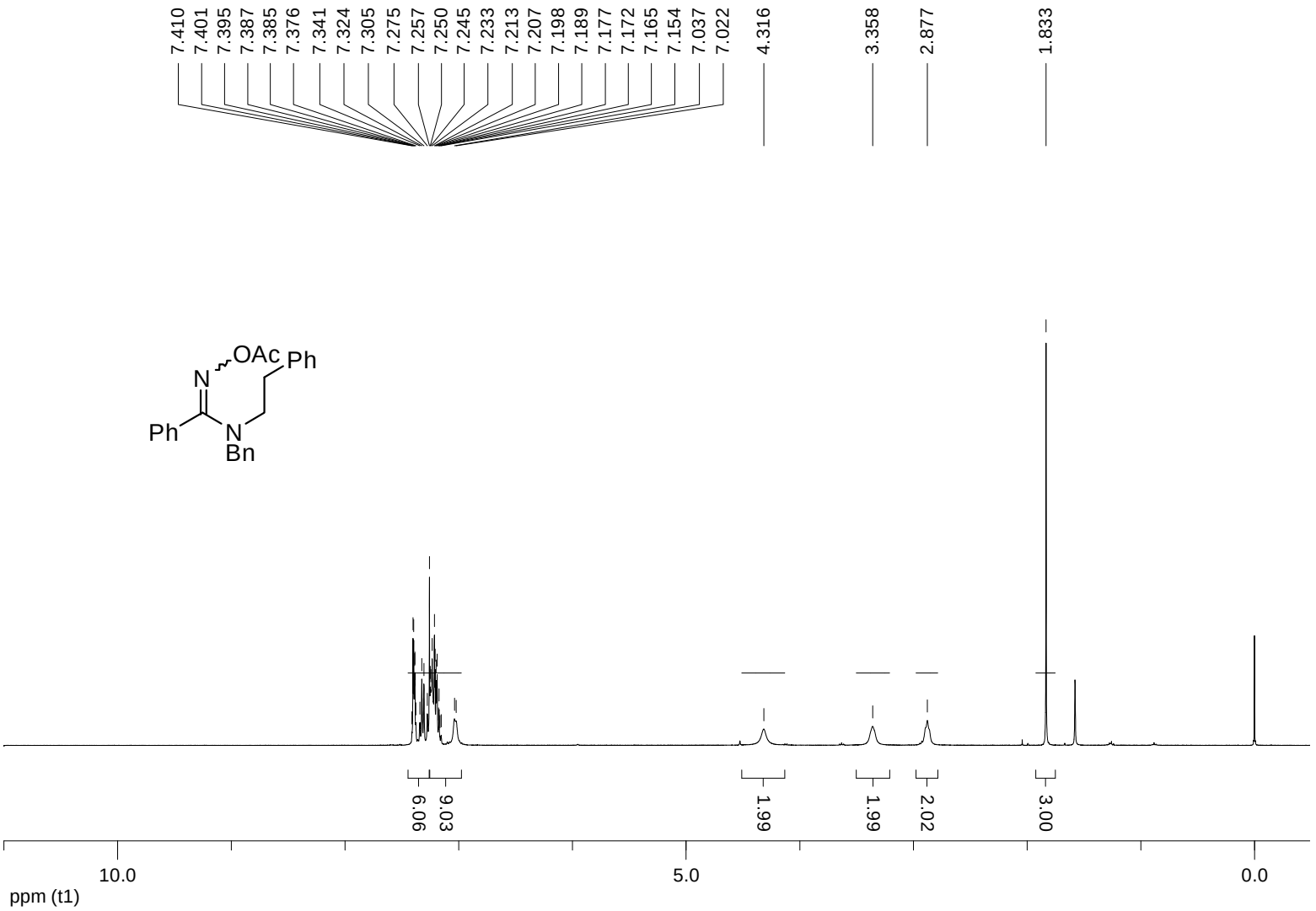
^{1}H NMR spectrum of **E** (400 MHz, $CDCl_3$)



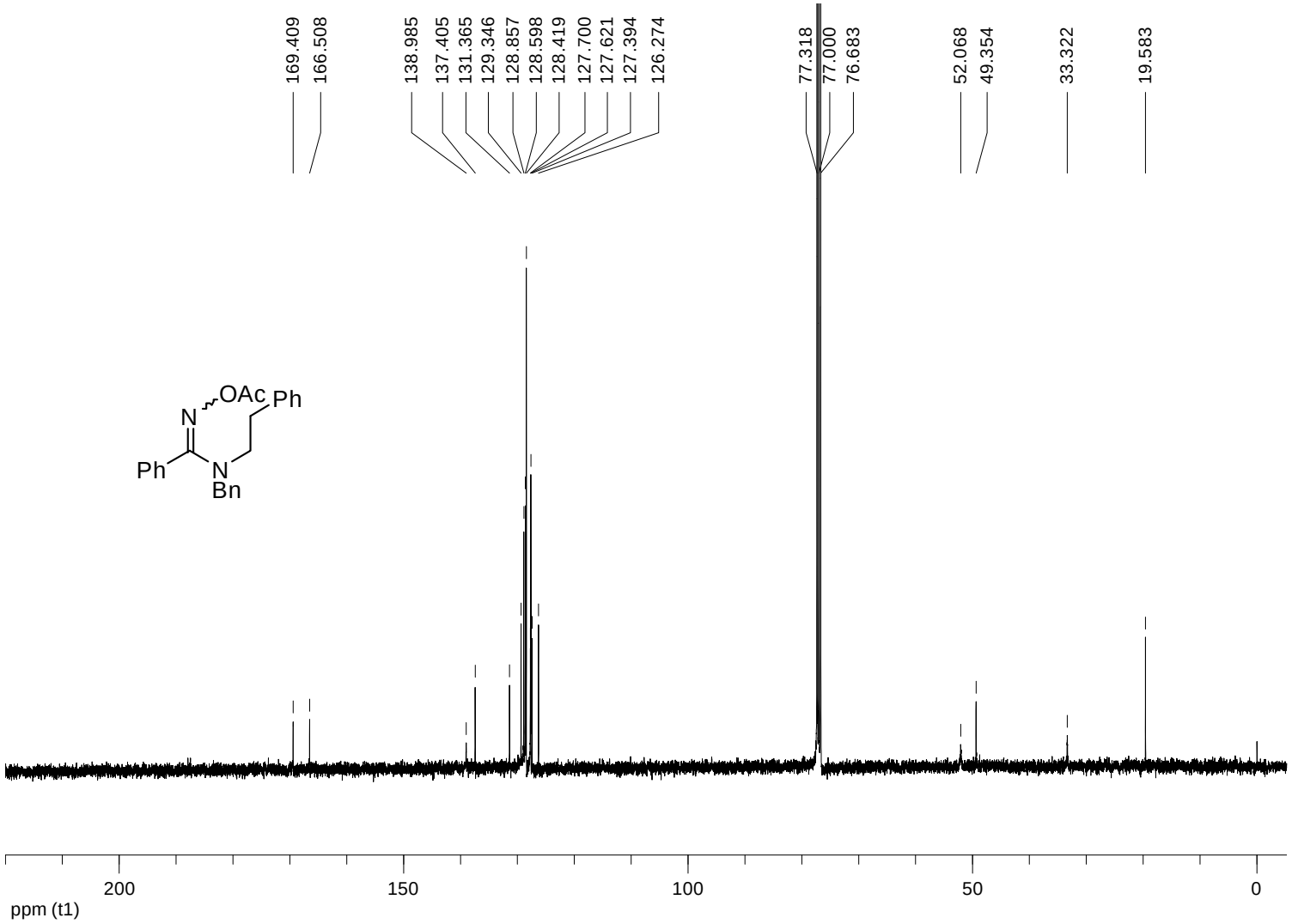
^{13}C NMR spectrum of **E** (100 MHz, $CDCl_3$)



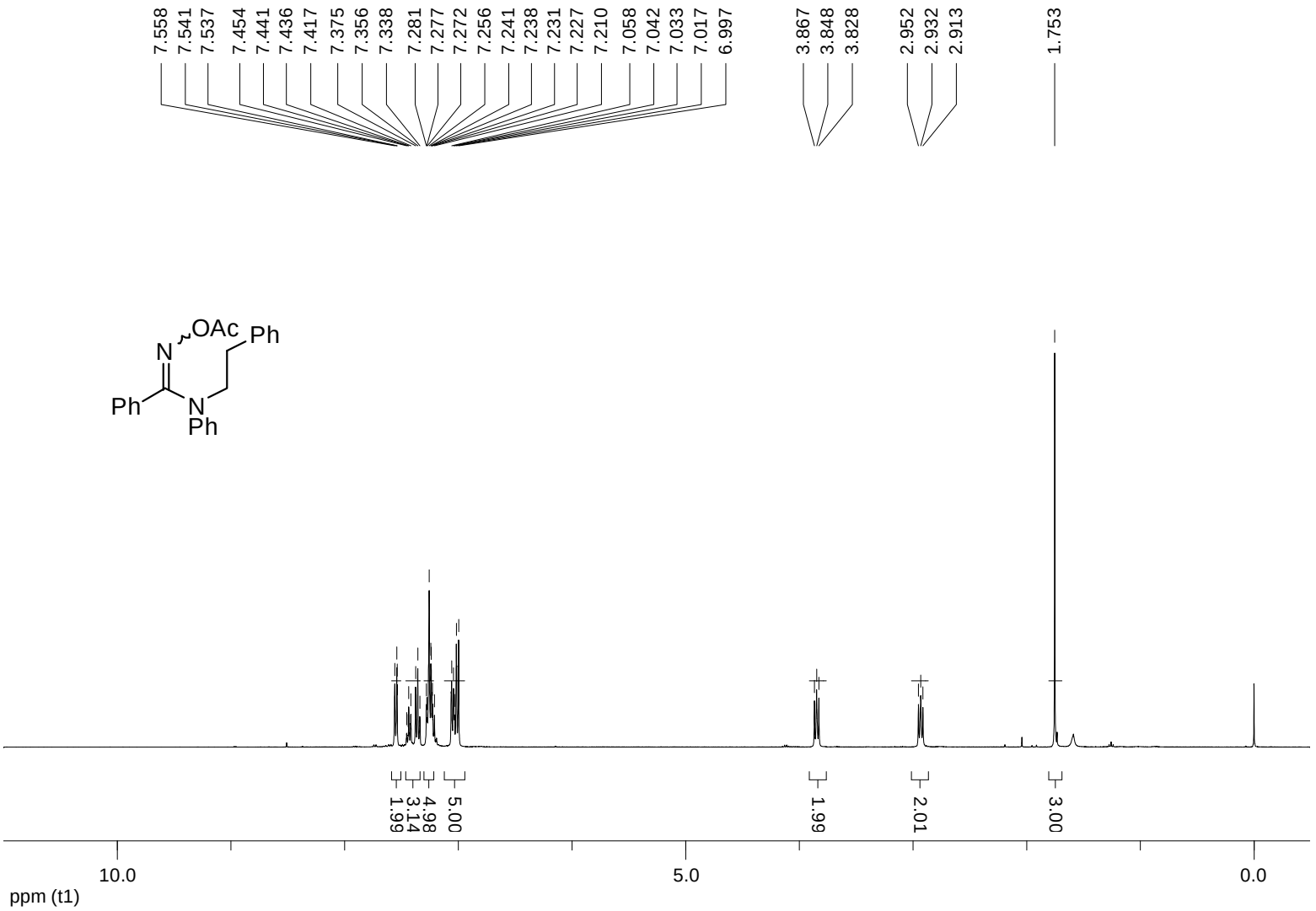
^{1}H NMR spectrum of **1q** (400 MHz, $CDCl_3$)



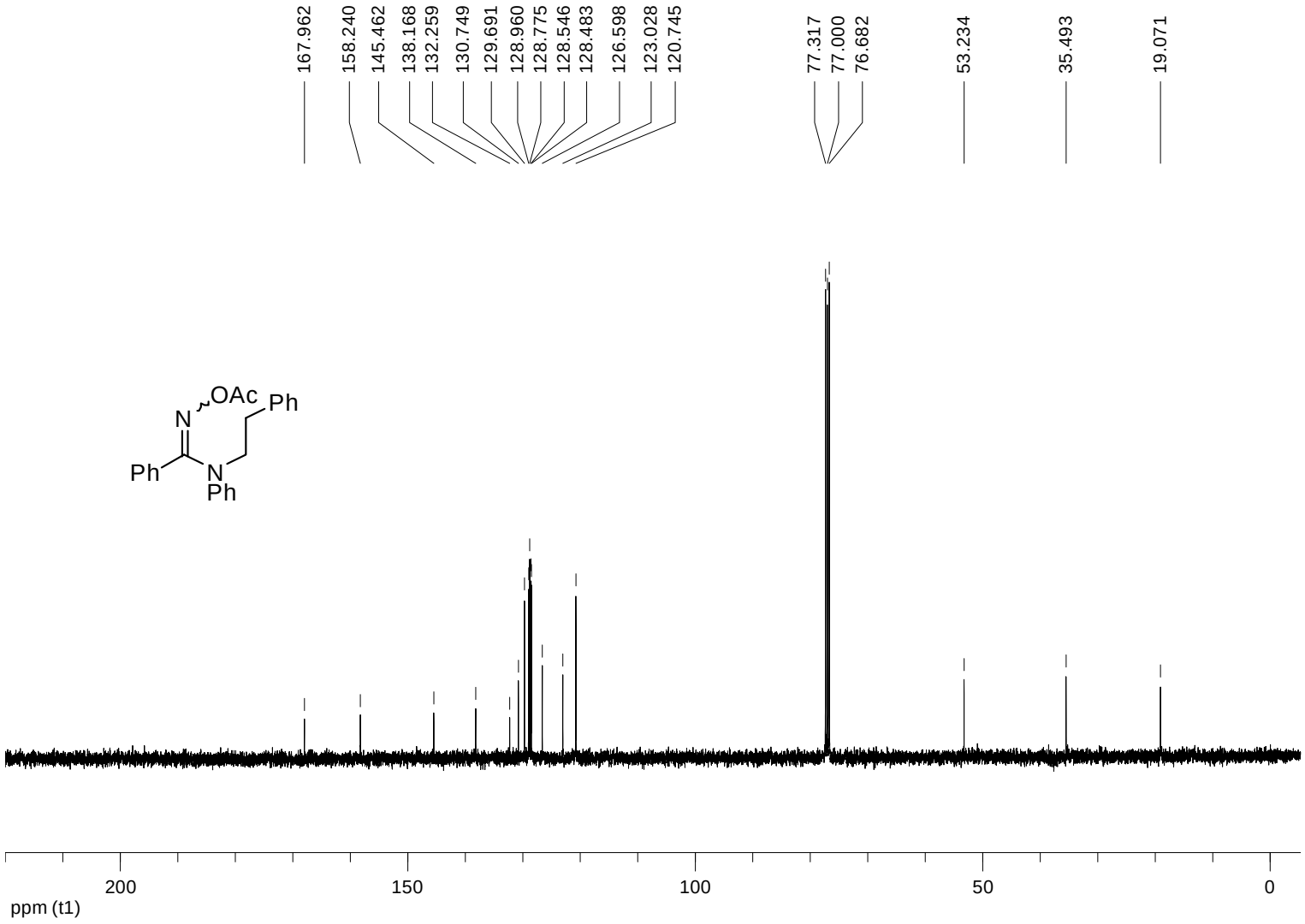
^{13}C NMR spectrum of **1q** (100 MHz, $CDCl_3$)



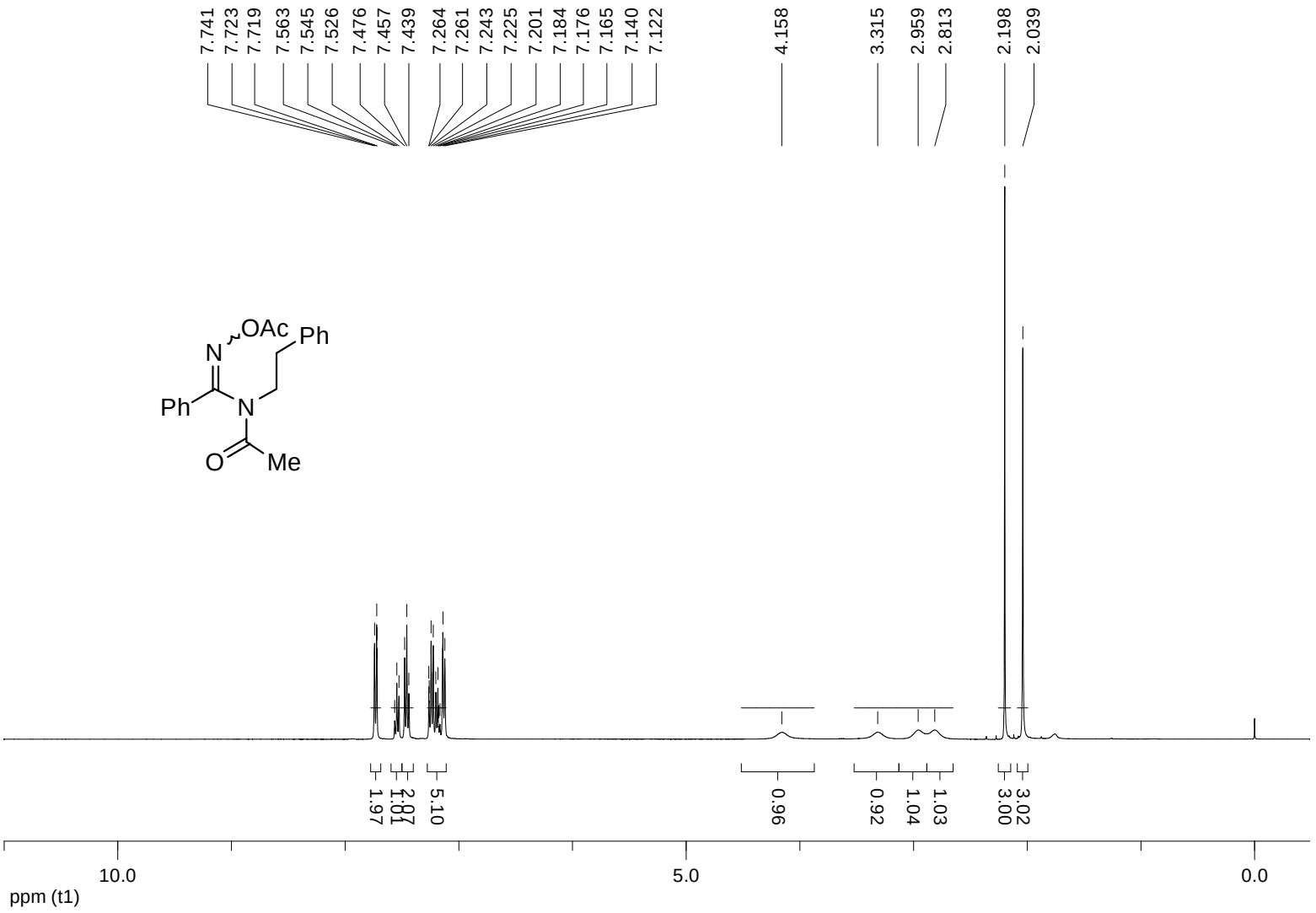
^{1}H NMR spectrum of **1r** (400 MHz, $CDCl_3$)



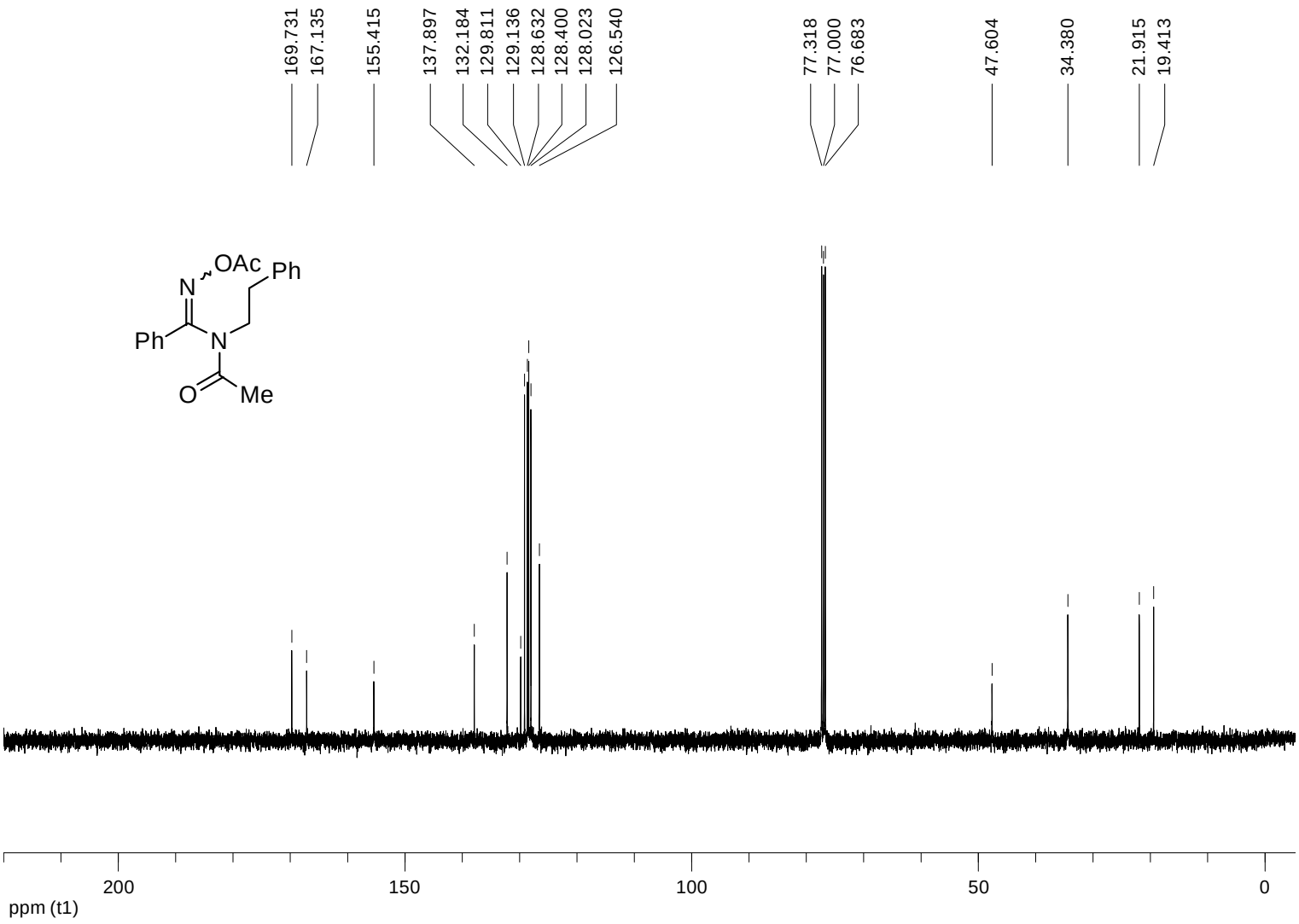
^{13}C NMR spectrum of **1r** (100 MHz, $CDCl_3$)



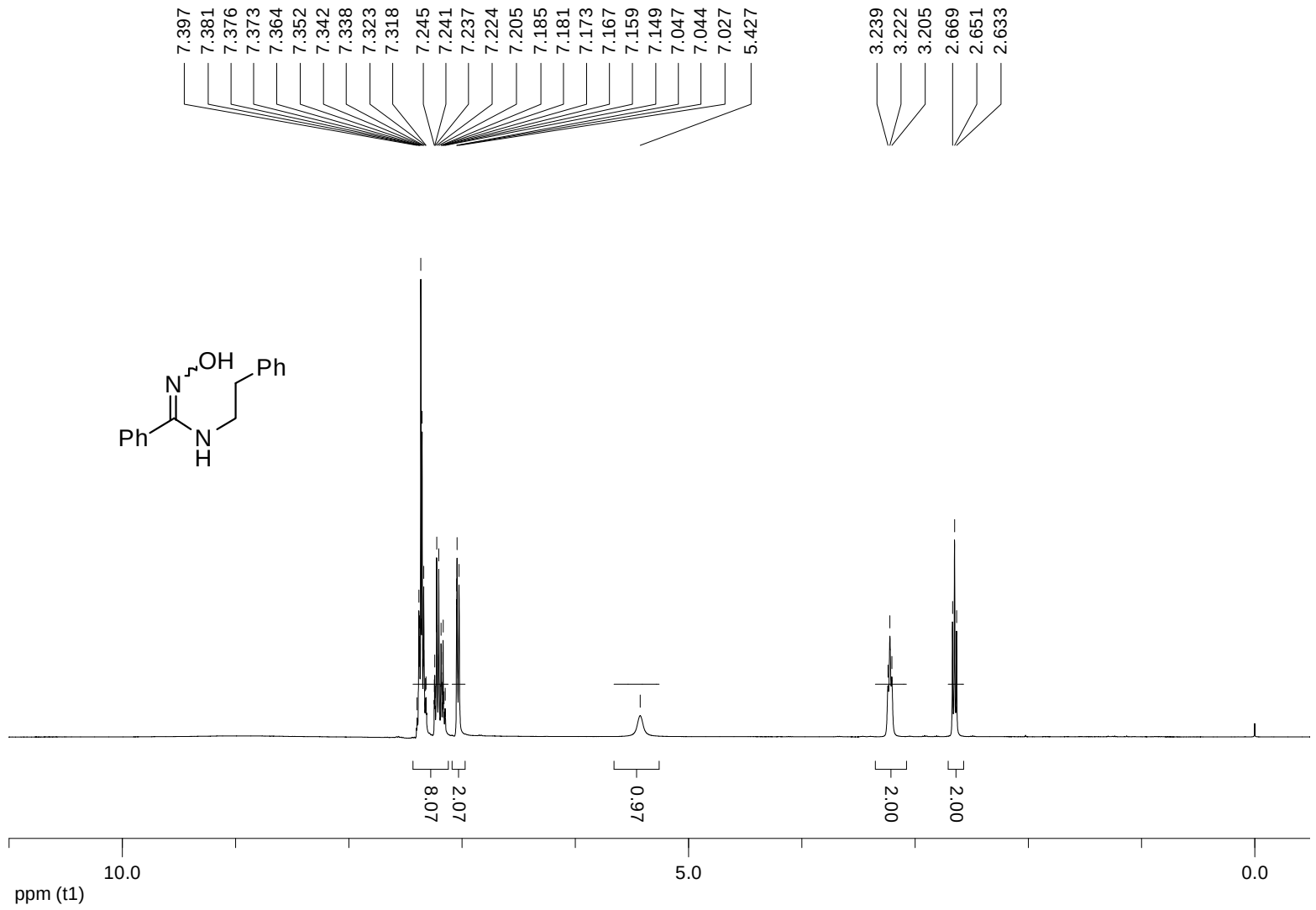
^{1}H NMR spectrum of **1s** (400 MHz, $CDCl_3$)



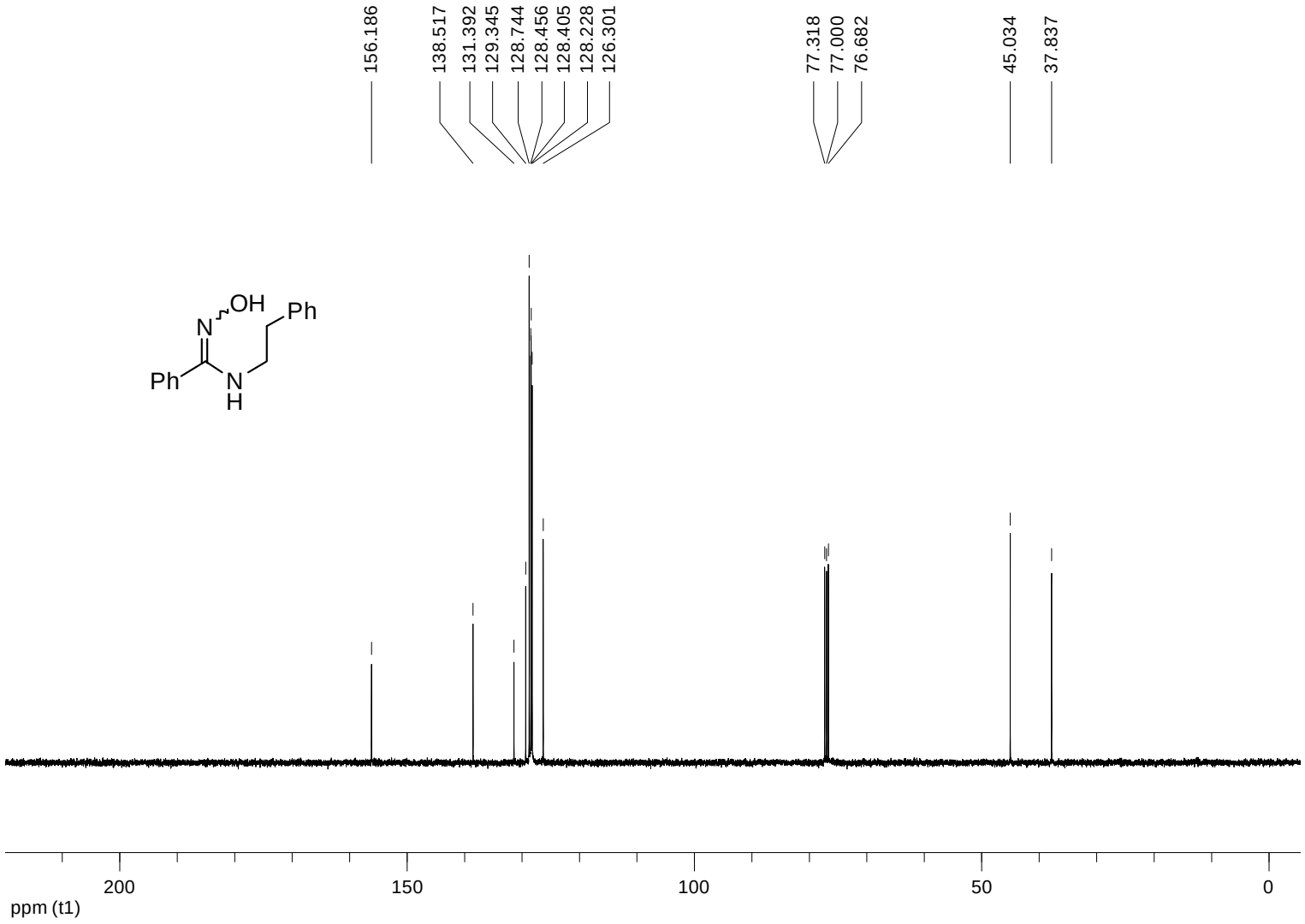
^{13}C NMR spectrum of **1s** (100 MHz, $CDCl_3$)



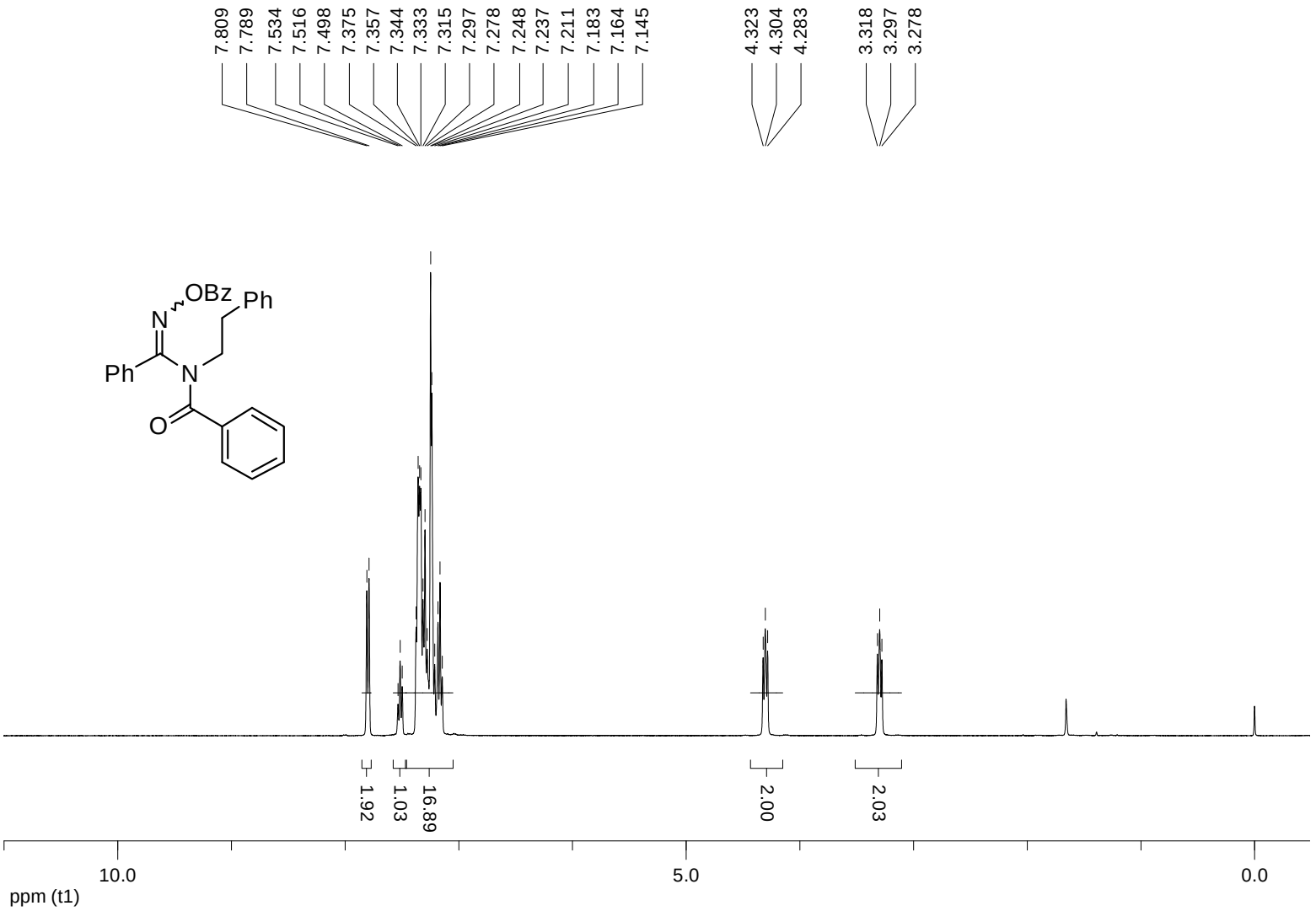
^{1}H NMR spectrum of **F** (400 MHz, $CDCl_3$)



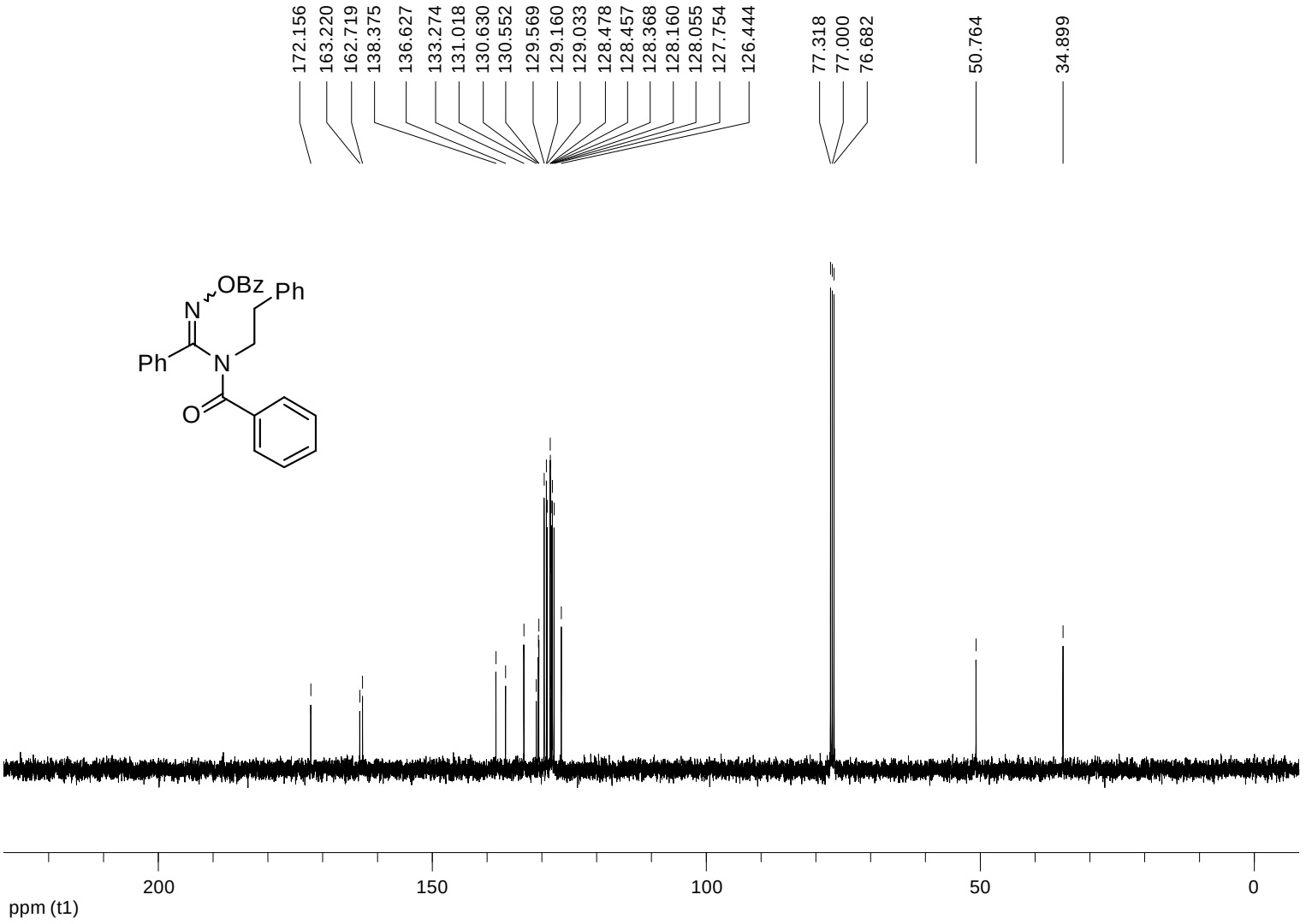
^{13}C NMR spectrum of **F** (100 MHz, $CDCl_3$)



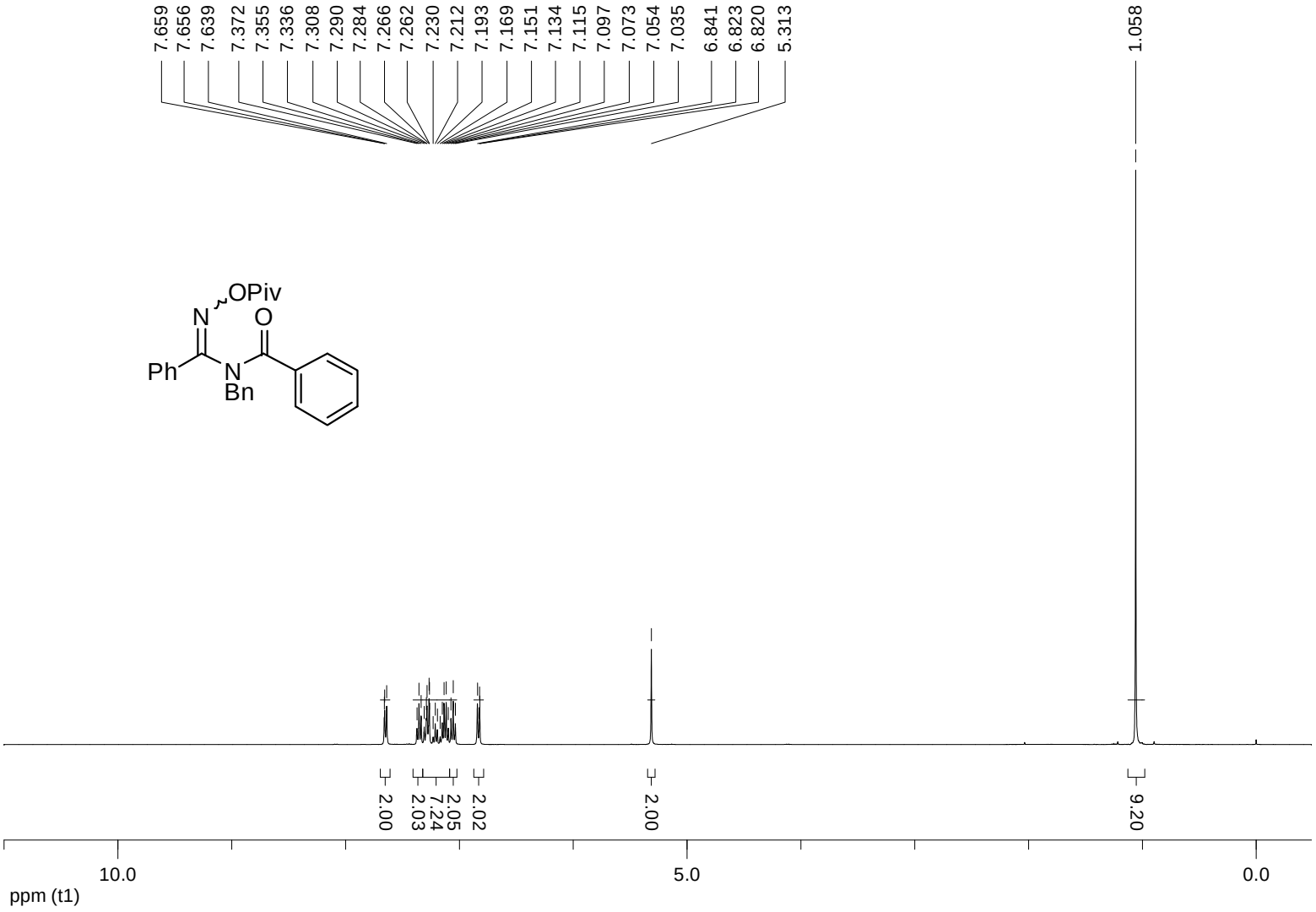
^{1}H NMR spectrum of **6a** (400 MHz, $CDCl_3$)



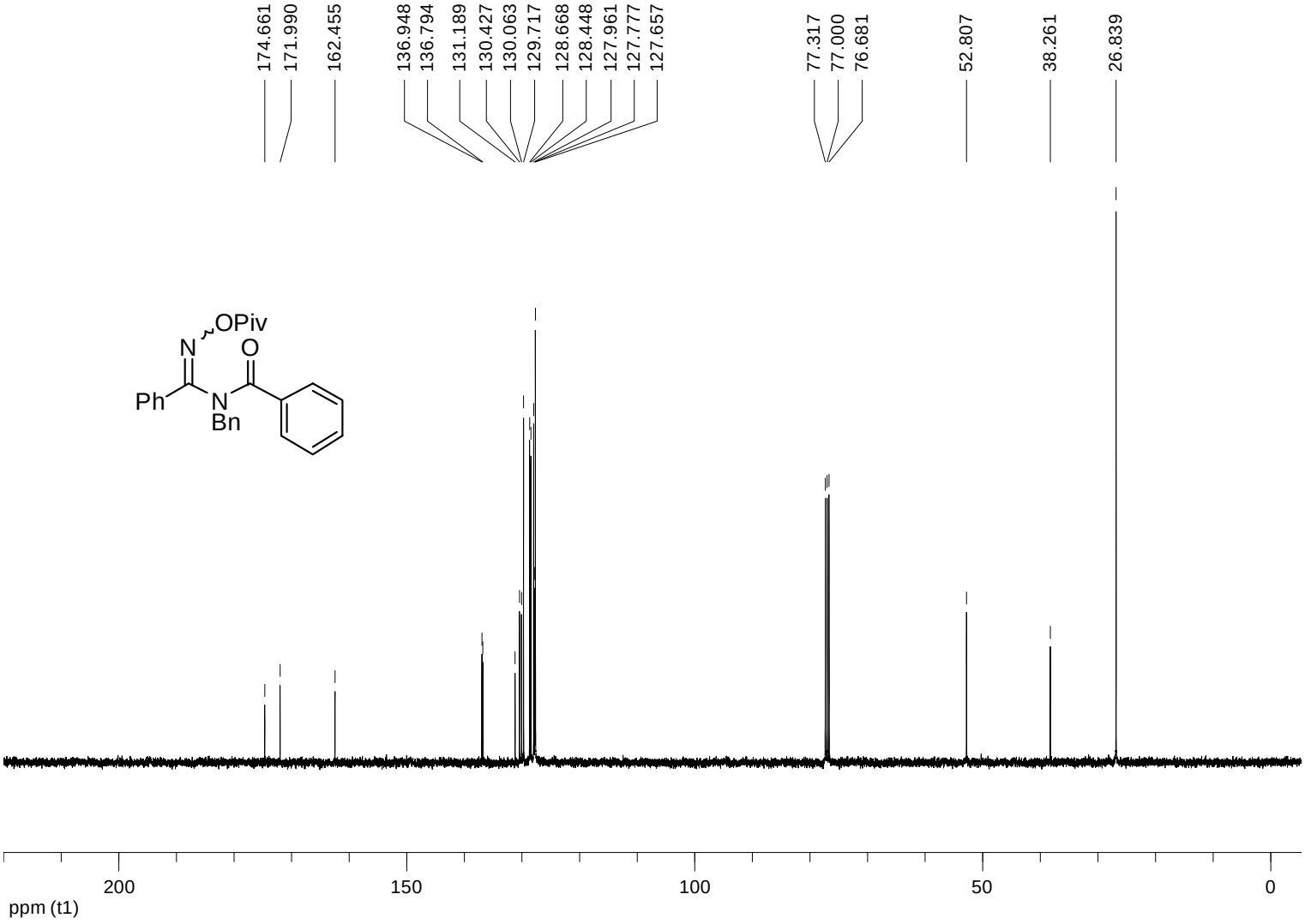
^{13}C NMR spectrum of **6a** (100 MHz, $CDCl_3$)



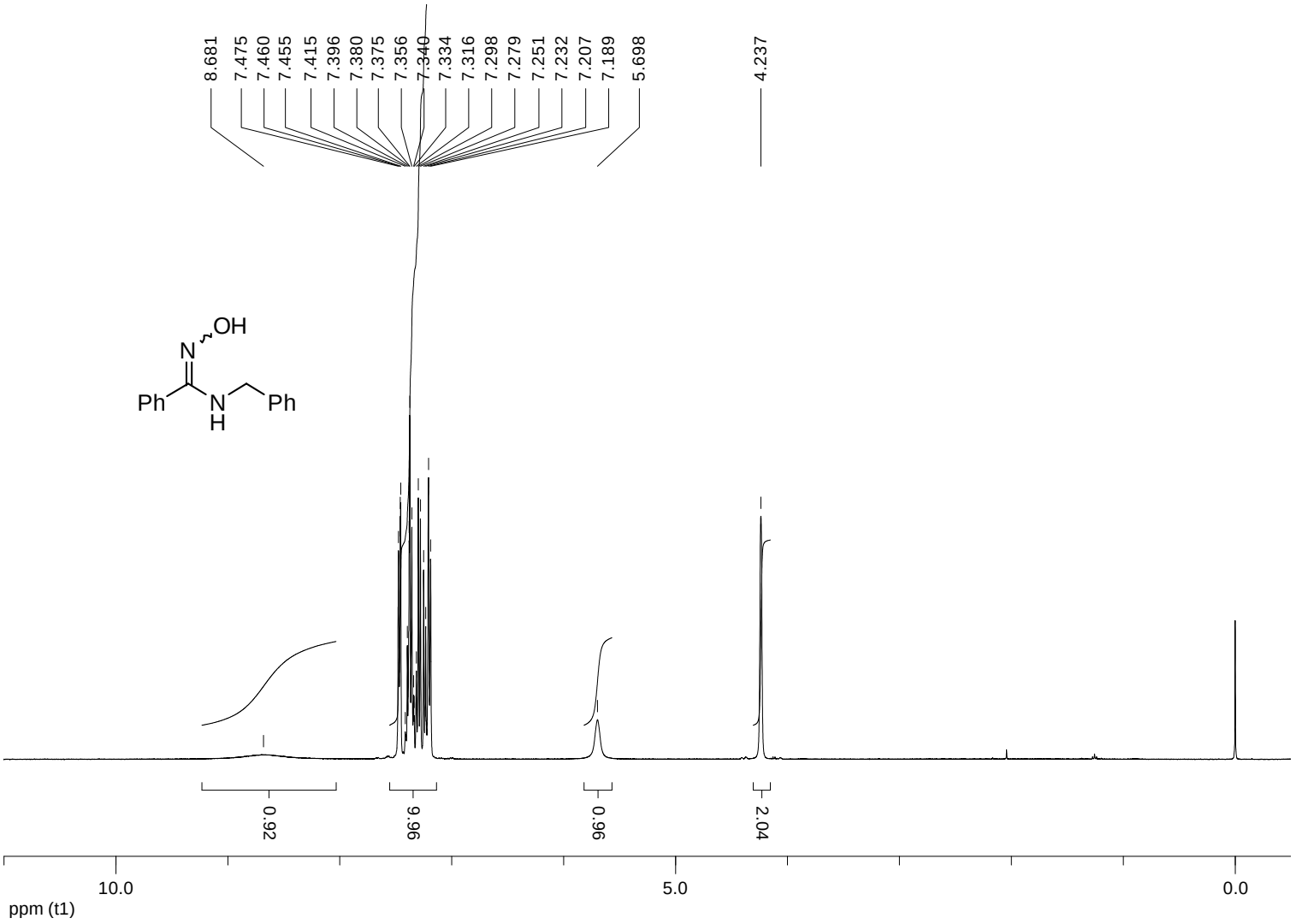
^{1}H NMR spectrum of **6b** (400 MHz, $CDCl_3$)



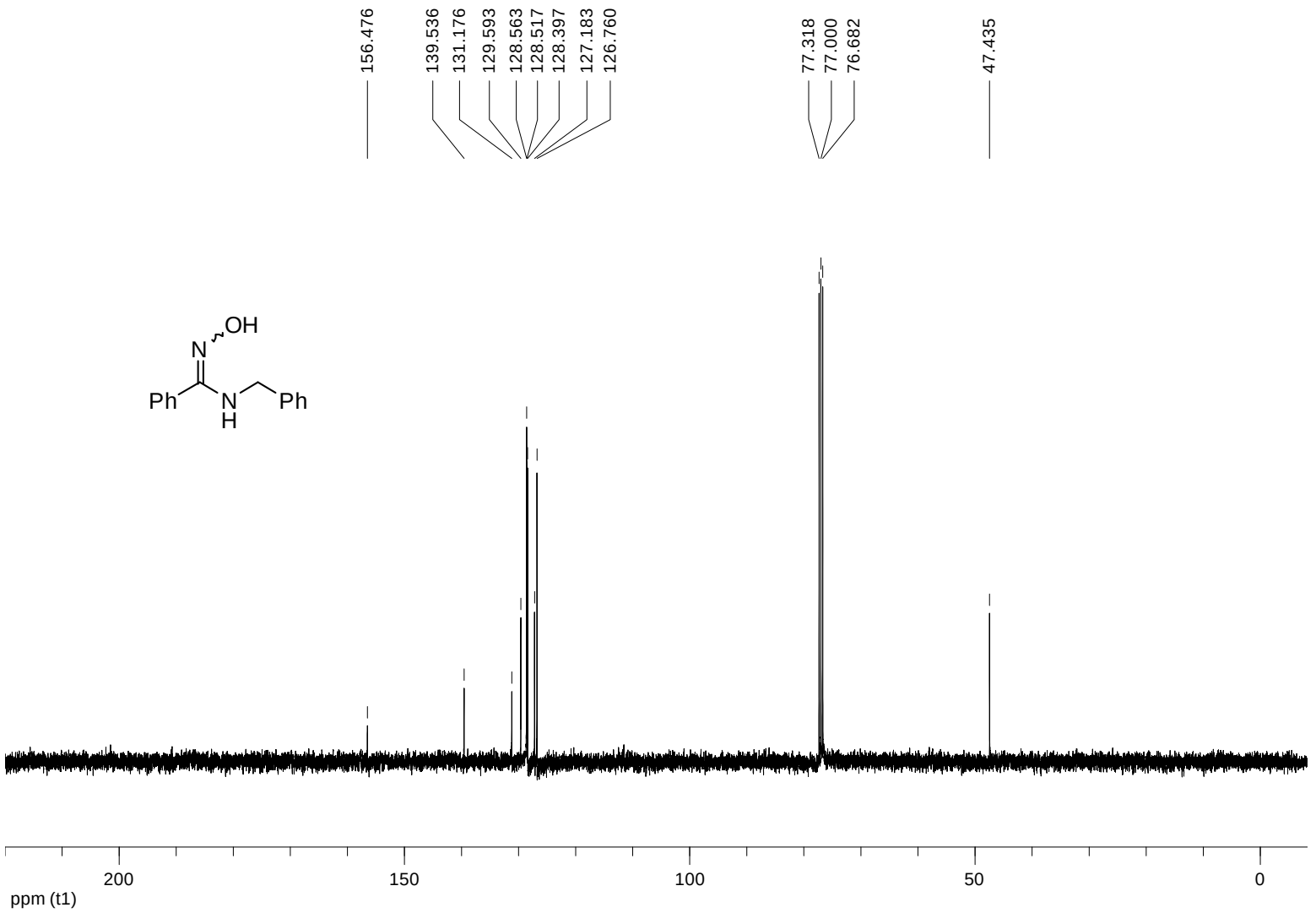
^{13}C NMR spectrum of **6b** (100 MHz, $CDCl_3$)



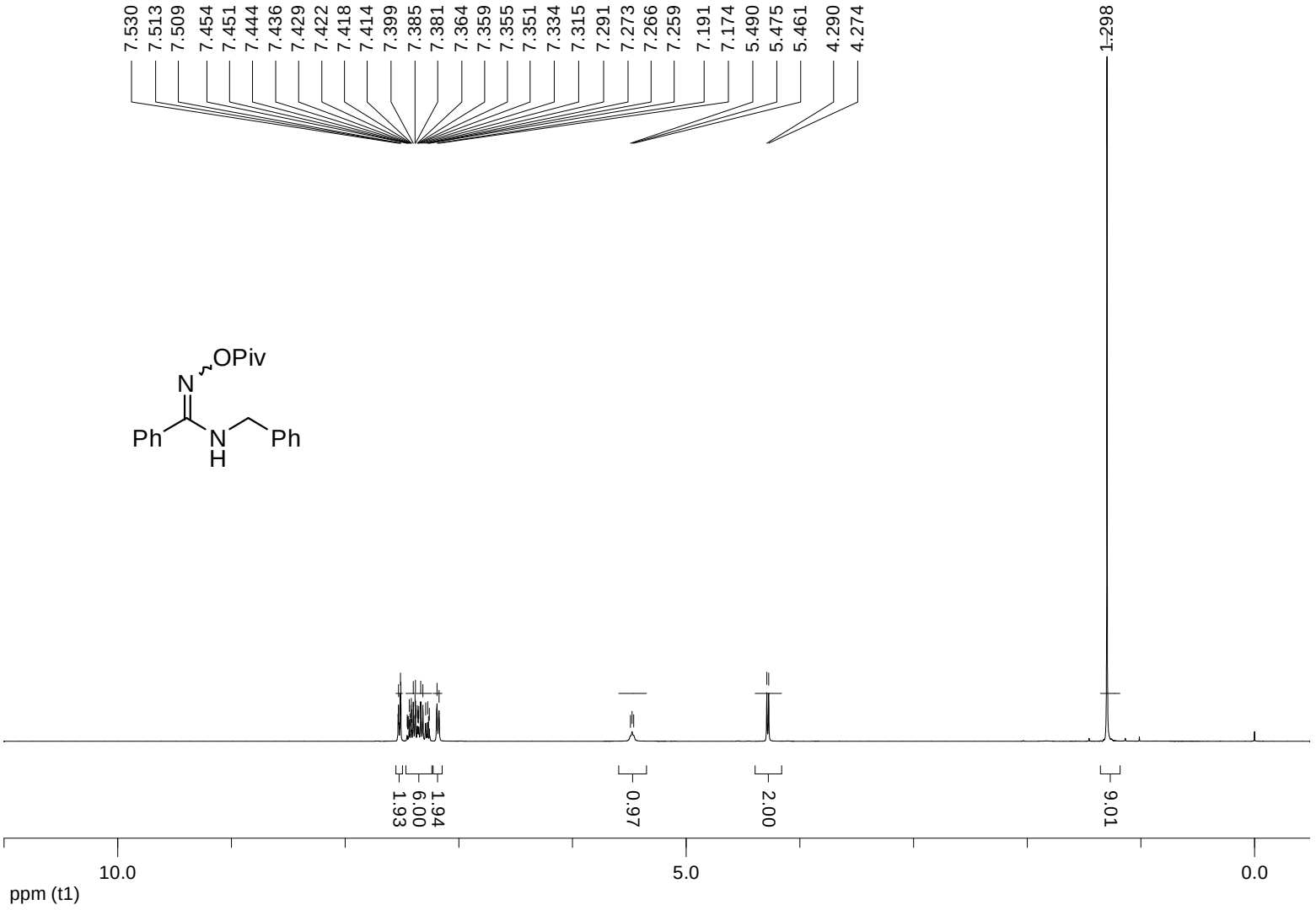
^{1}H NMR spectrum of **G** (400 MHz, $CDCl_3$)



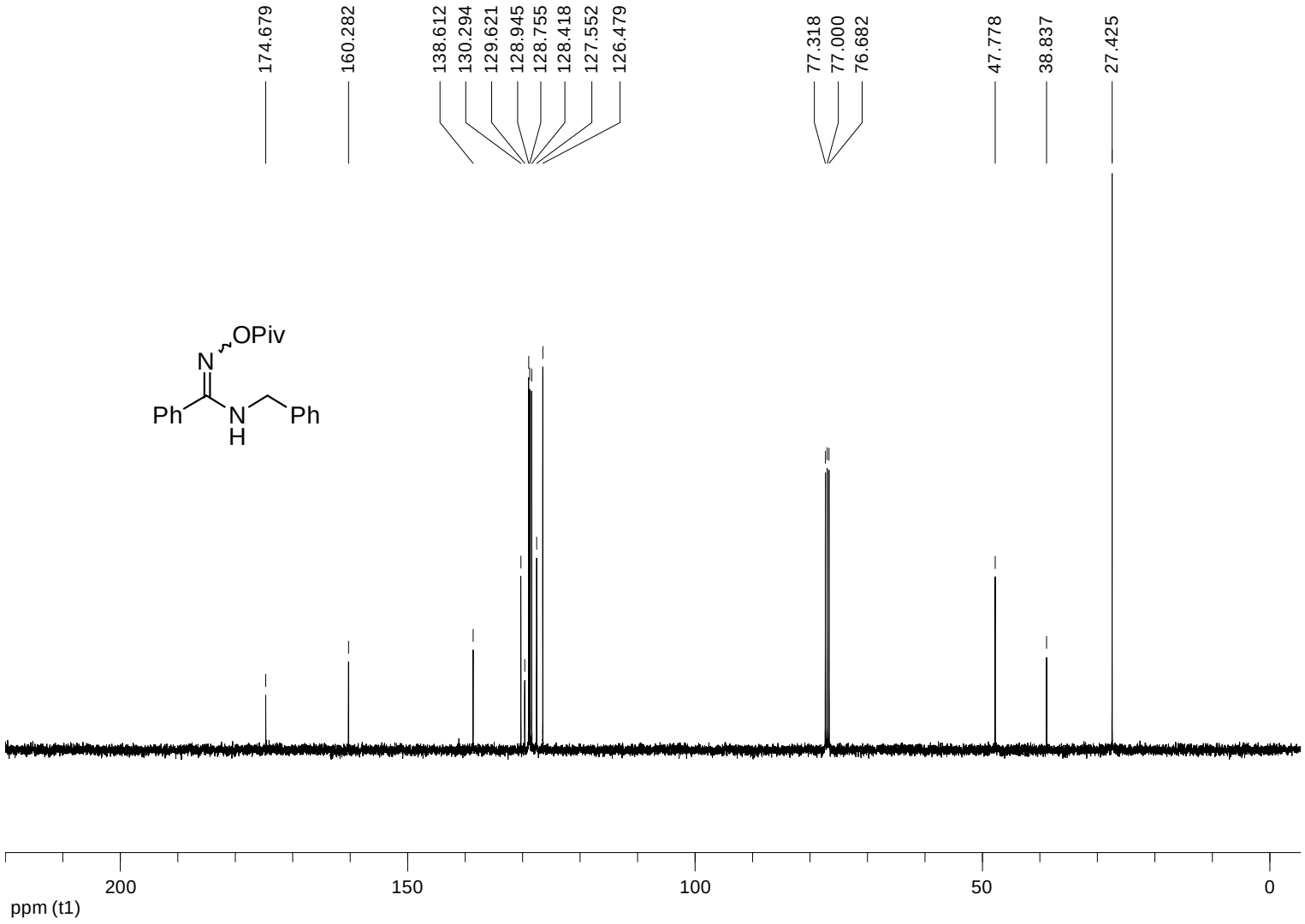
^{13}C NMR spectrum of **G** (100 MHz, $CDCl_3$)



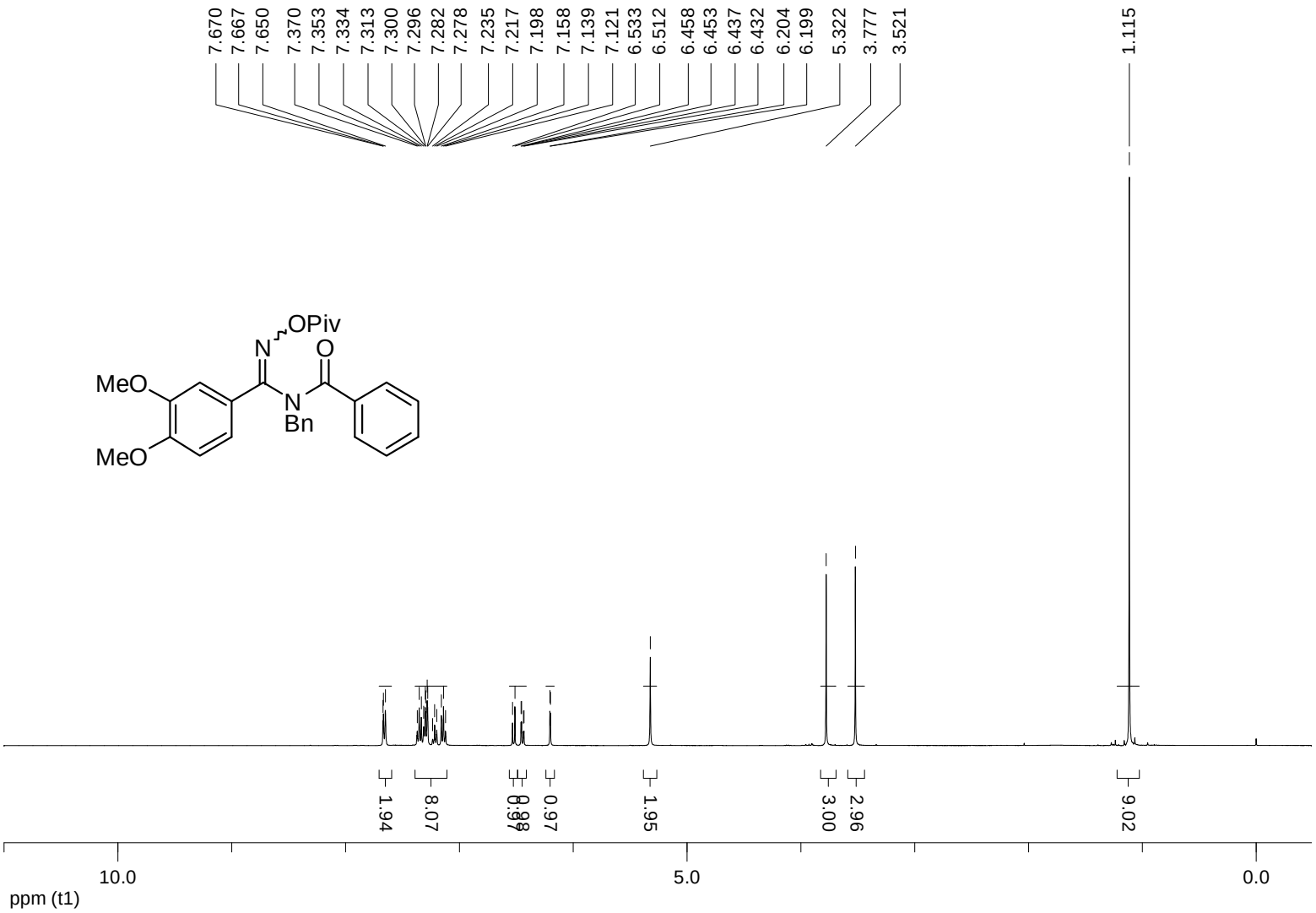
^{1}H NMR spectrum of **H** (400 MHz, $CDCl_3$)



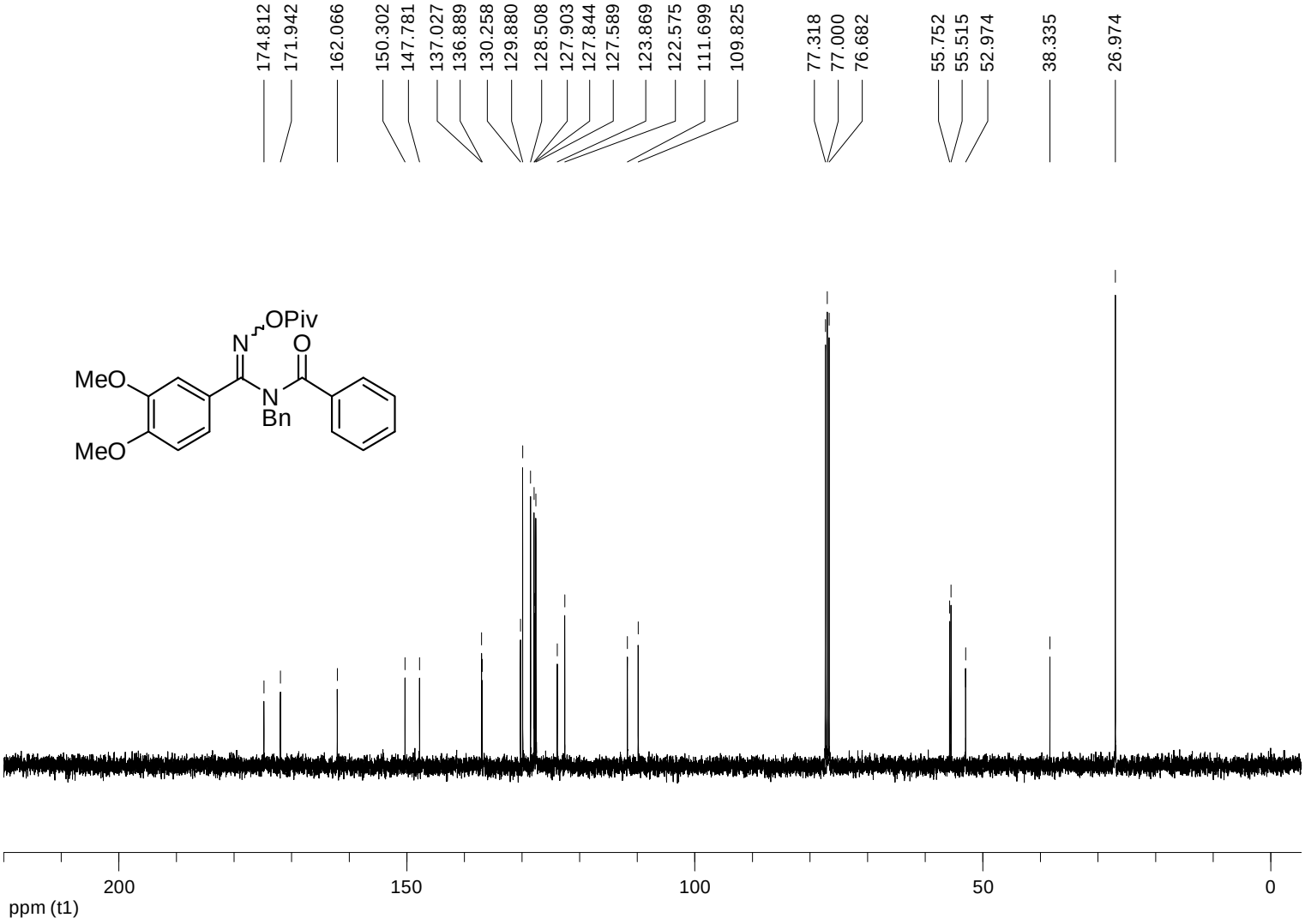
^{13}C NMR spectrum of **H** (100 MHz, $CDCl_3$)



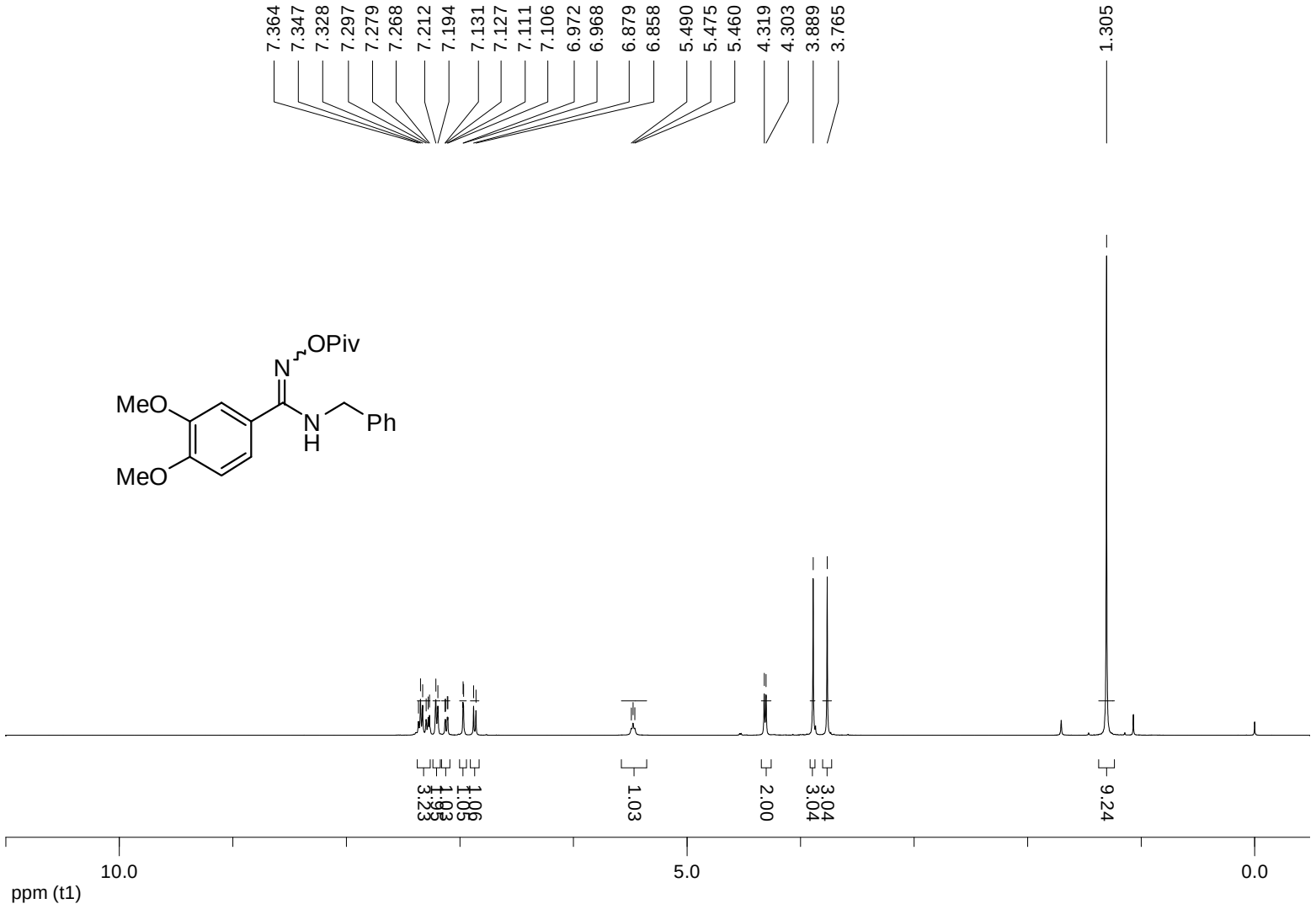
^{1}H NMR spectrum of **6c** (400 MHz, $CDCl_3$)



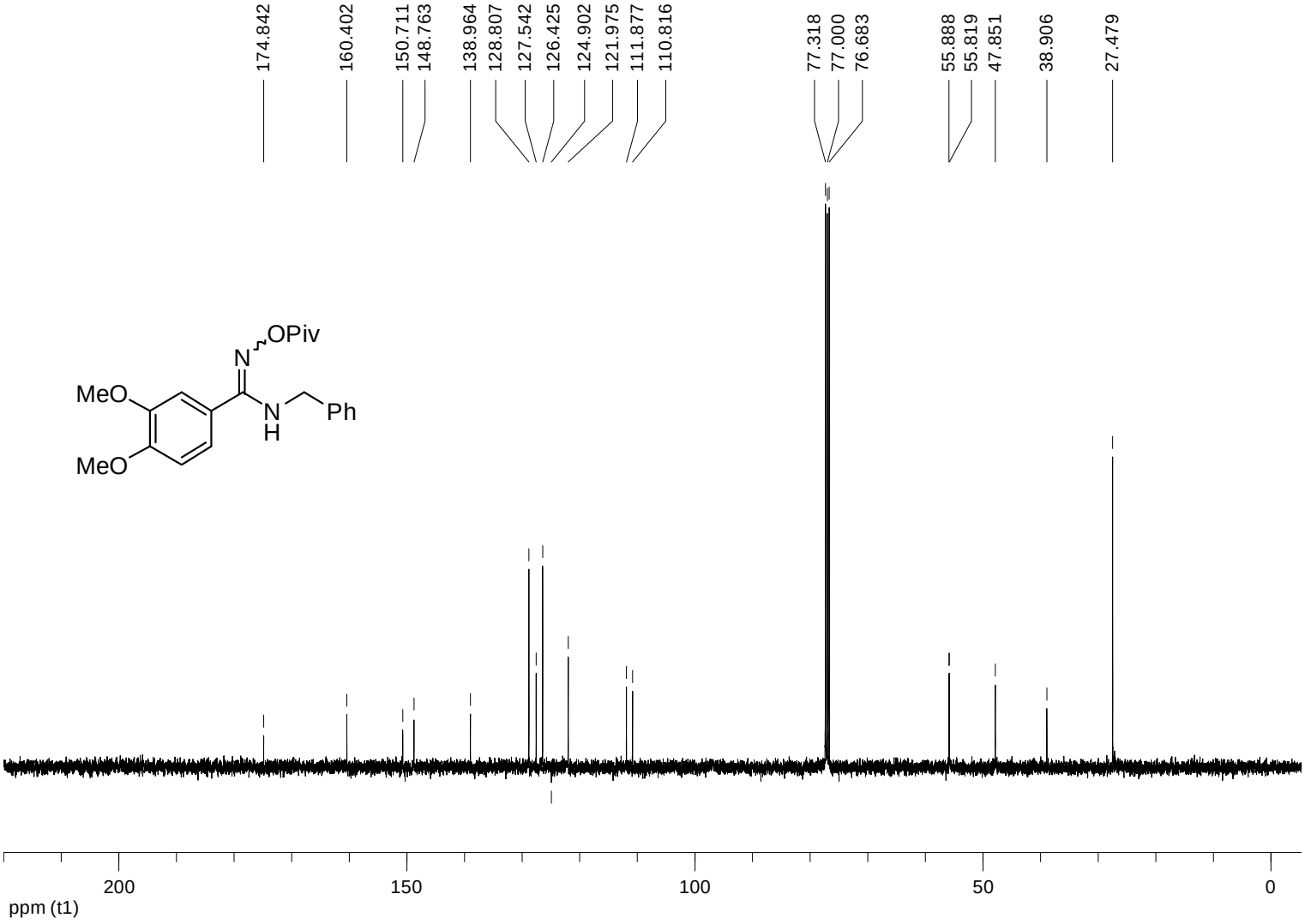
^{13}C NMR spectrum of **6c** (100 MHz, $CDCl_3$)



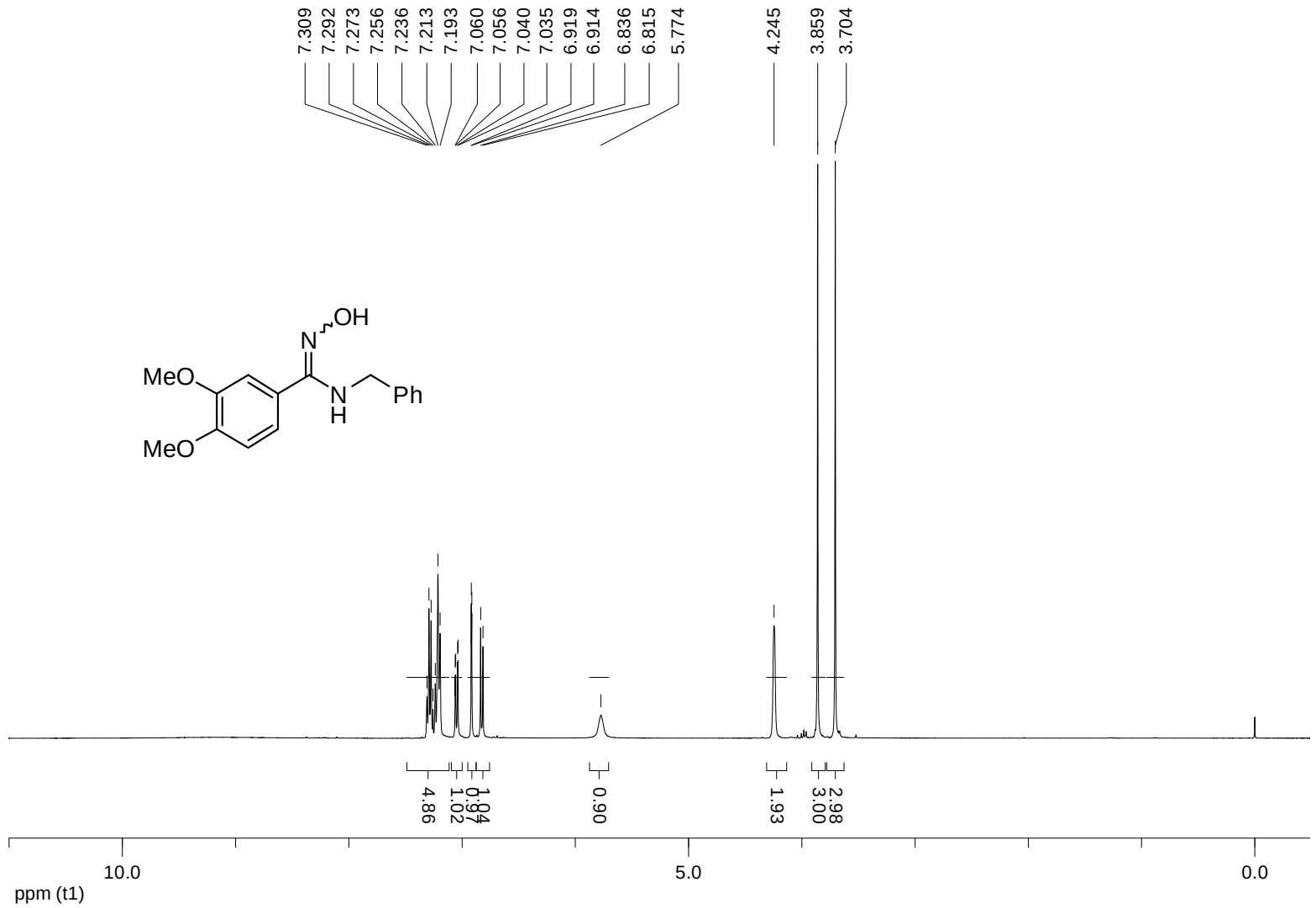
^{1}H NMR spectrum of *N*-benzyl-3,4-dimethoxy-*N*'-(pivaloyloxy)benzimidamide (400 MHz, $CDCl_3$)



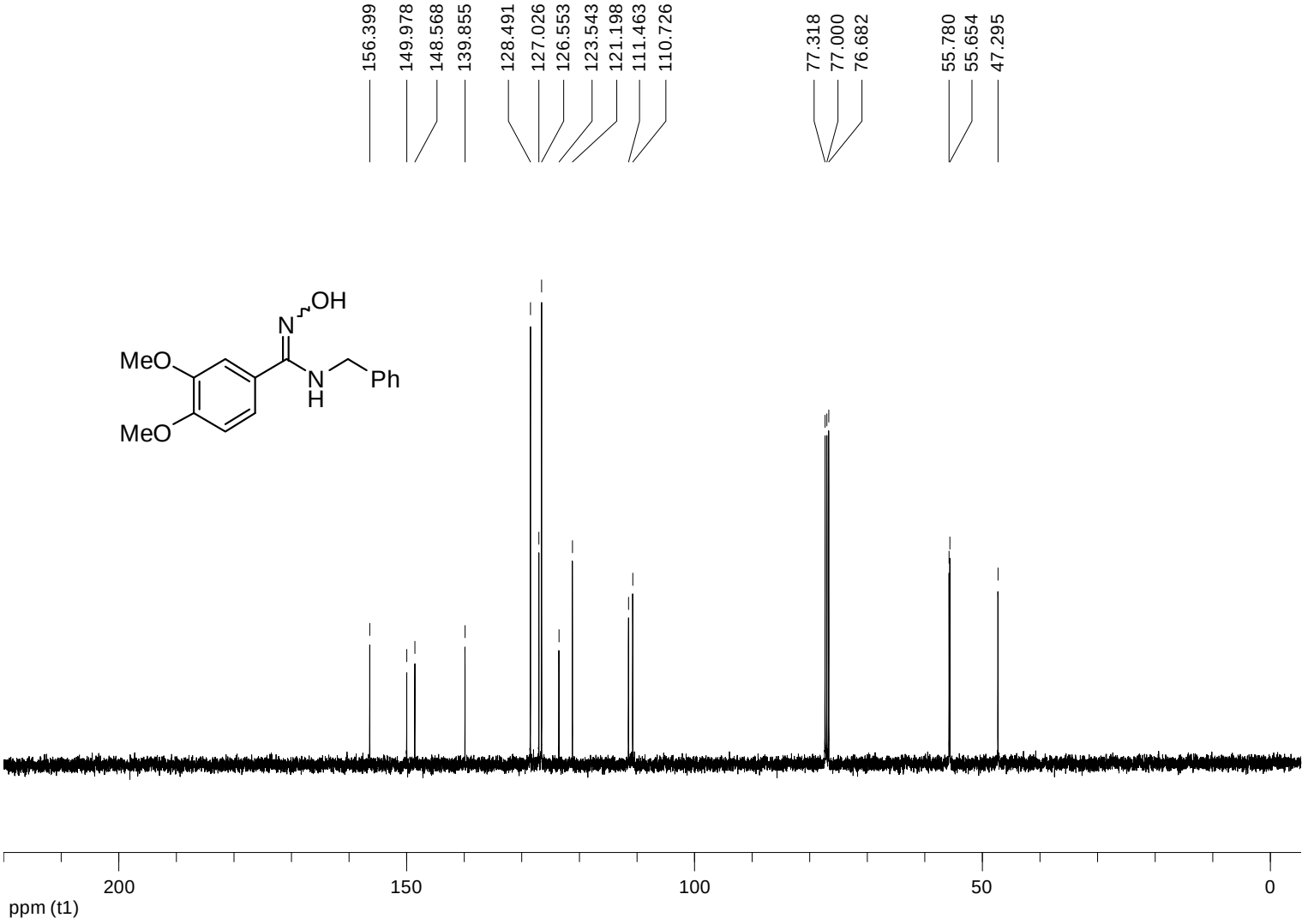
^{13}C NMR spectrum of *N*-benzyl-3,4-dimethoxy-*N*'-(pivaloyloxy)benzimidamide (100 MHz, $CDCl_3$)



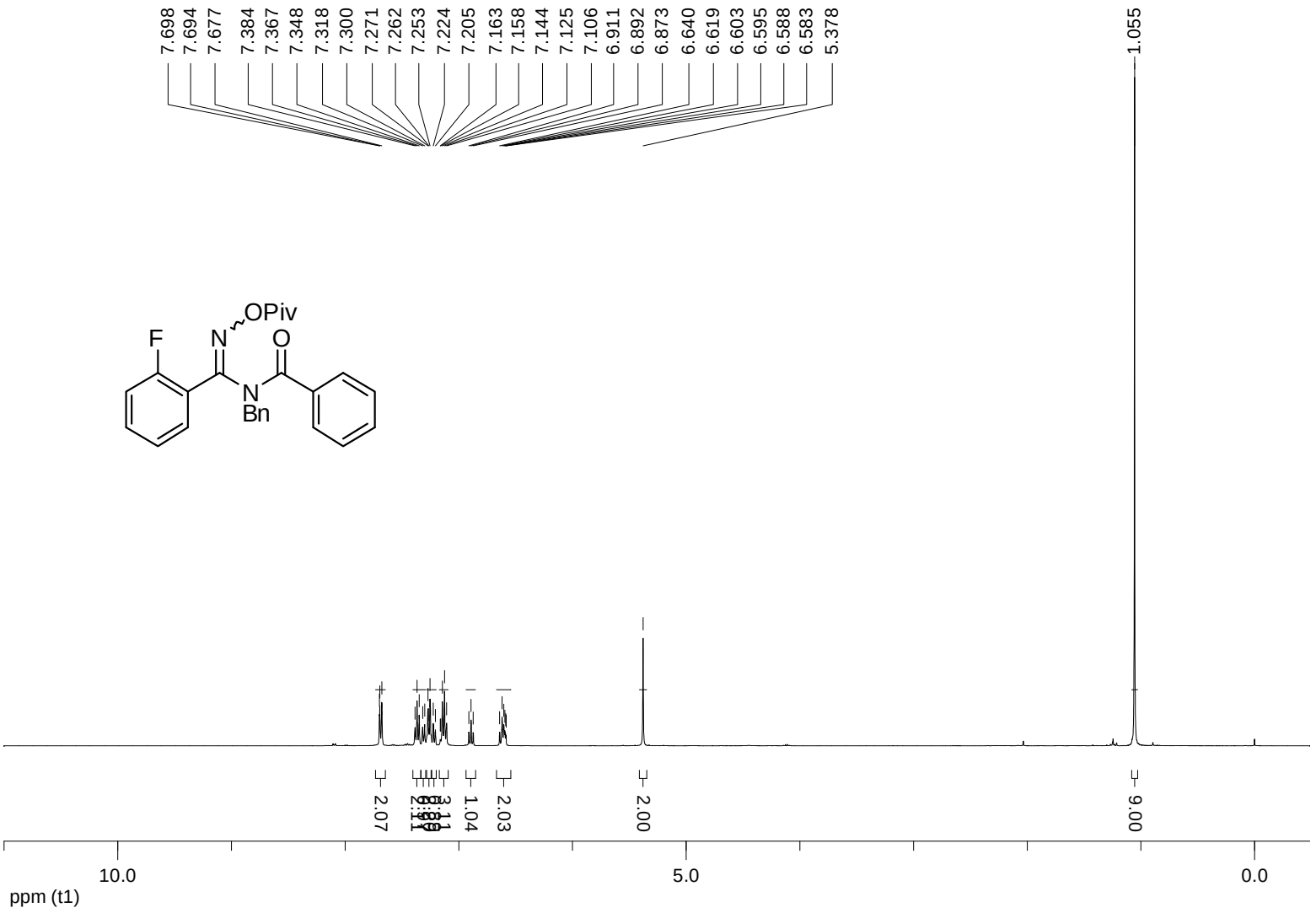
^{1}H NMR spectrum of *N*-benzyl-*N*'-hydroxy-3,4-dimethoxybenzimidamide (400 MHz, $CDCl_3$)



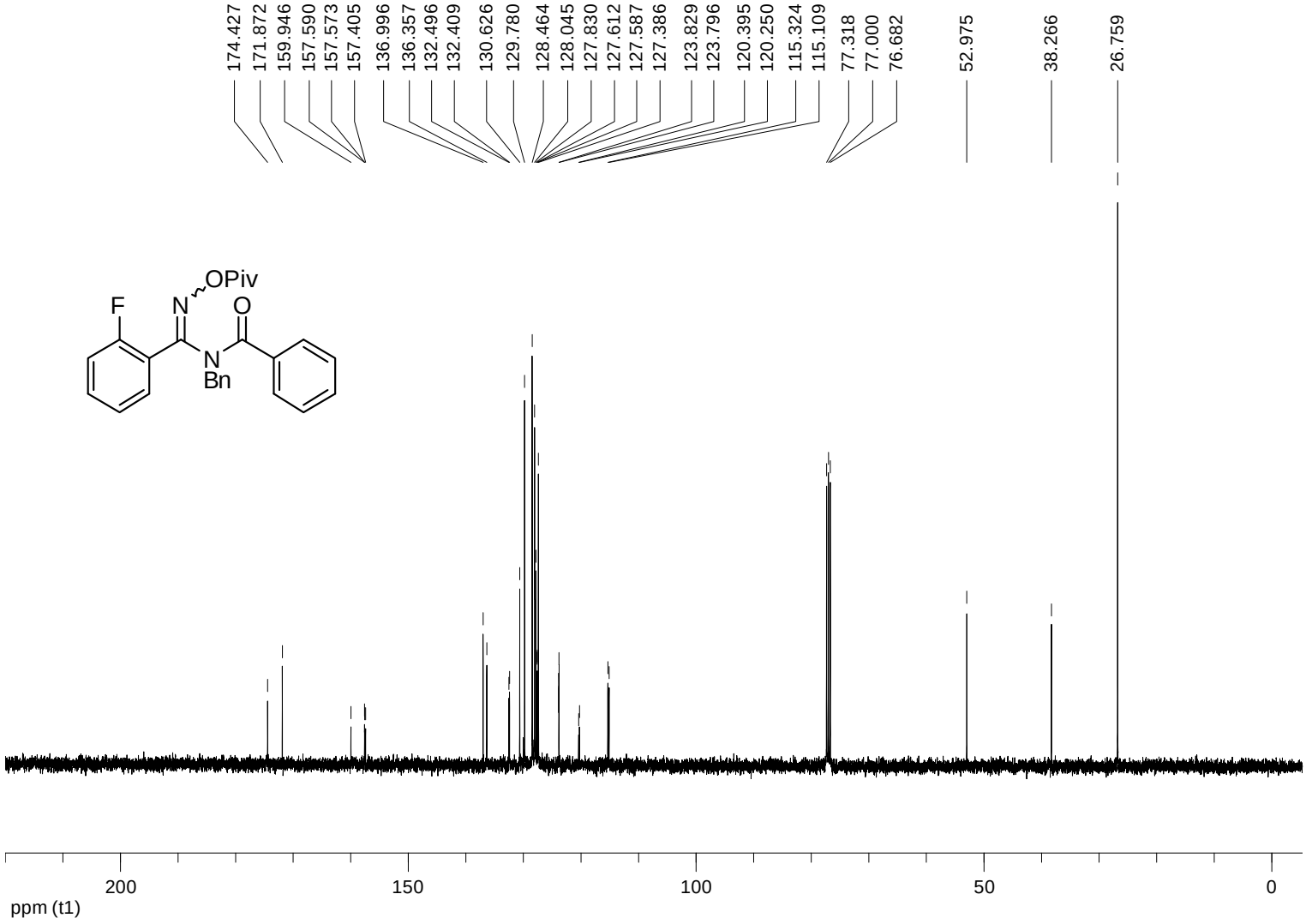
^{13}C NMR spectrum of *N*-benzyl-*N'*-hydroxy-3,4-dimethoxybenzimidamide (100 MHz, $CDCl_3$)



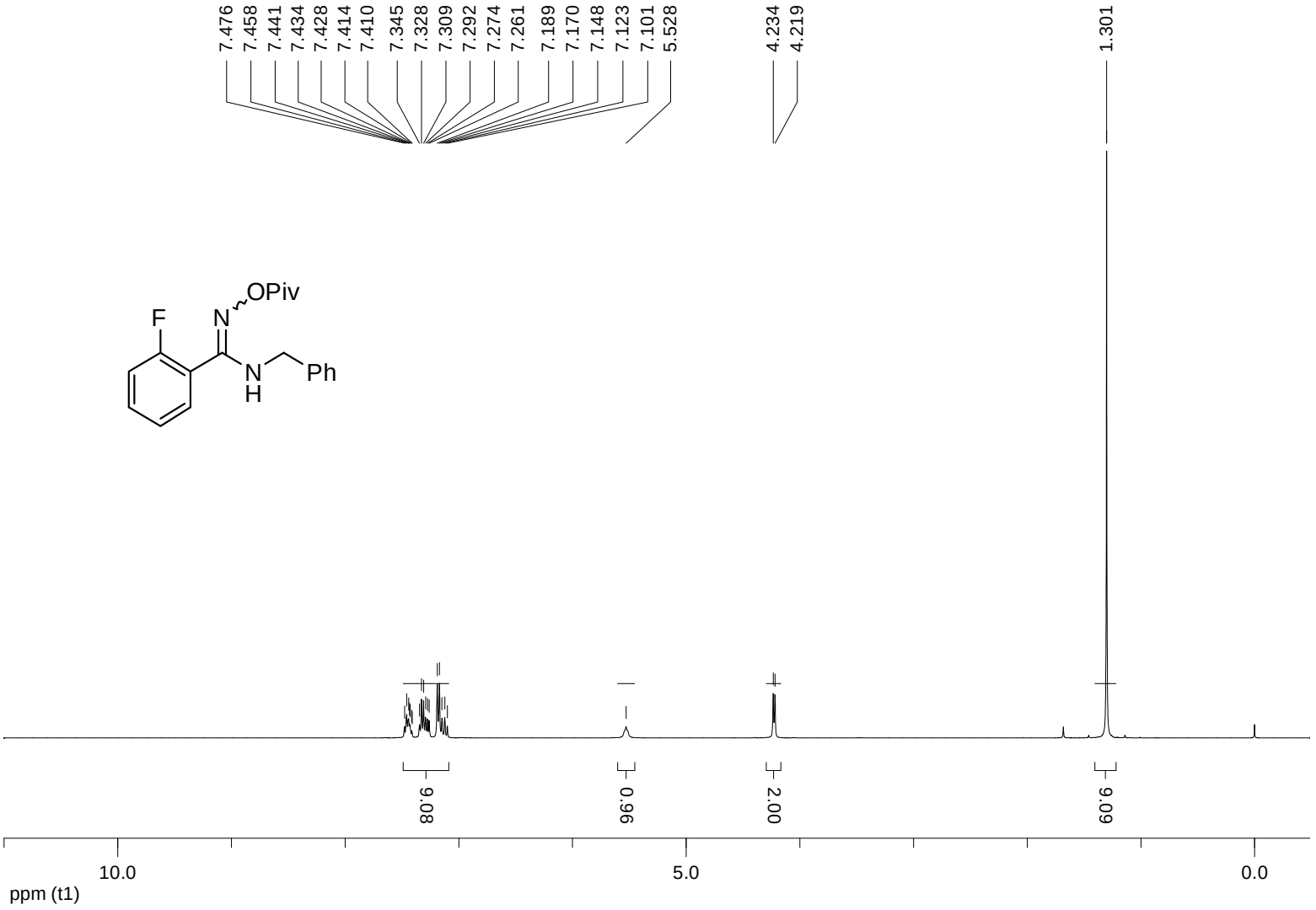
^{1}H NMR spectrum of **6d** (400 MHz, $CDCl_3$)



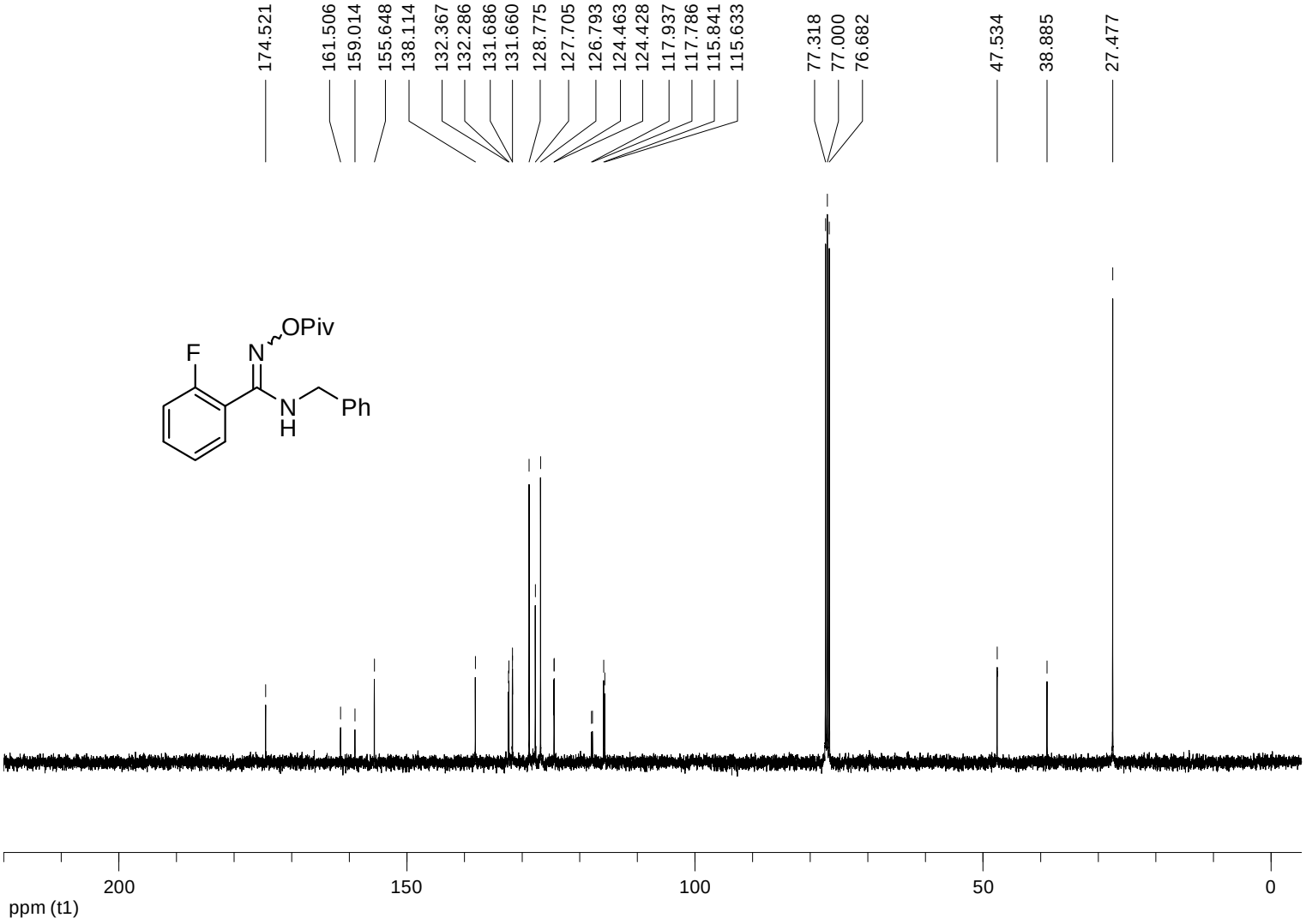
^{13}C NMR spectrum of **6d** (100 MHz, $CDCl_3$)



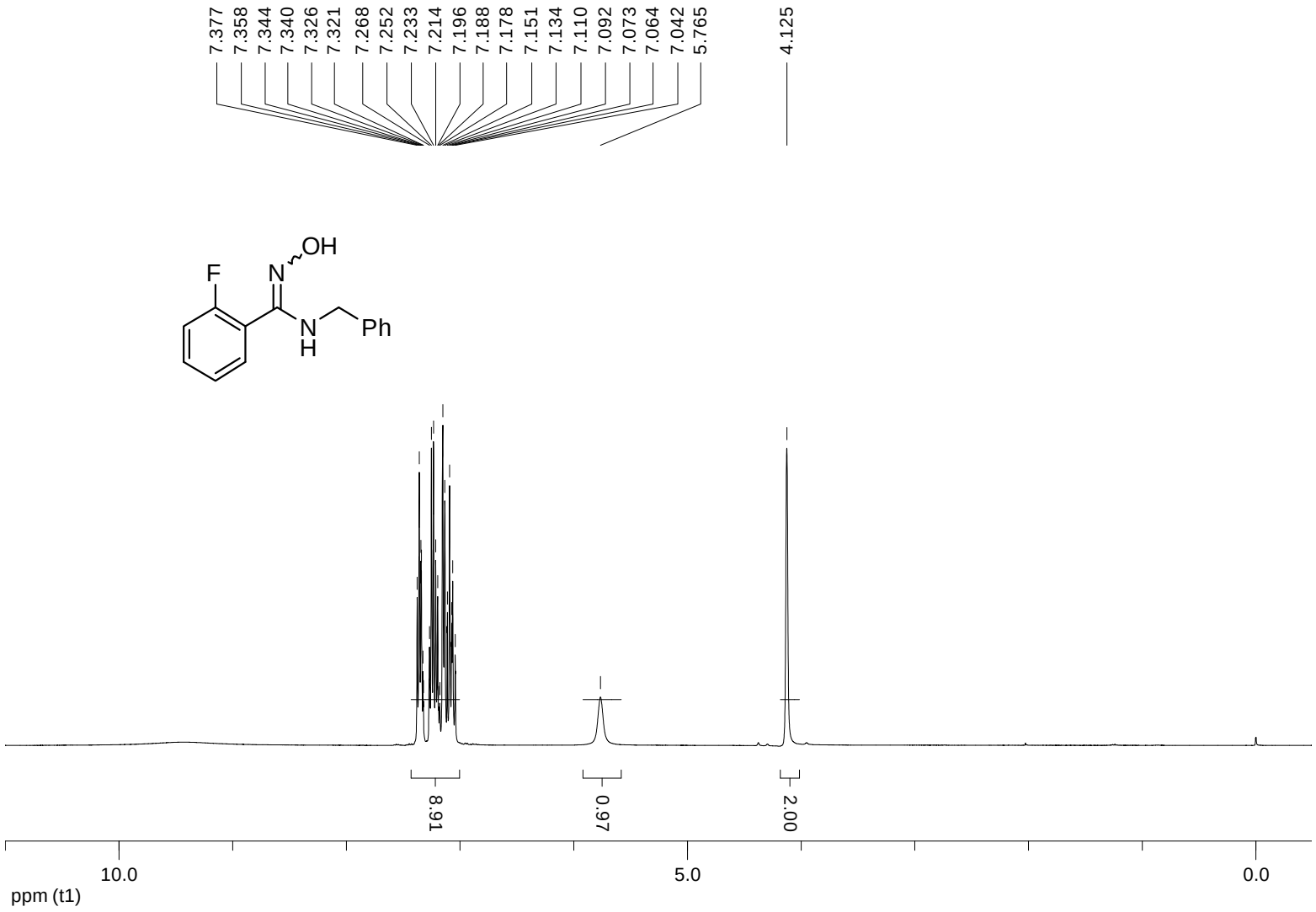
^{1}H NMR spectrum of *N*-benzyl-2-fluoro-*N*'-(pivaloyloxy)benzimidamide (400 MHz, $CDCl_3$)



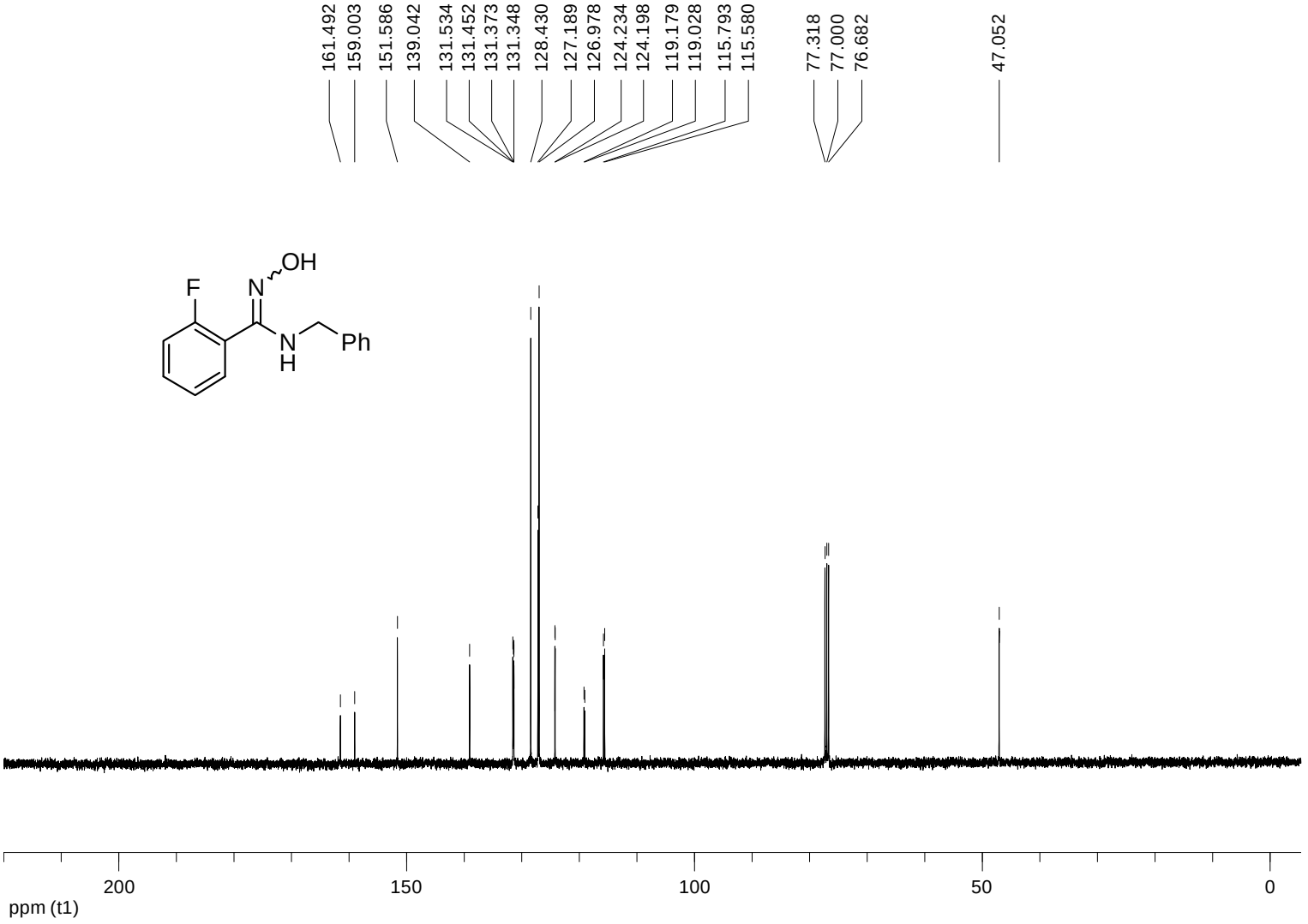
^{13}C NMR spectrum of *N*-benzyl-2-fluoro-*N*'-(pivaloyloxy)benzimidamide (100 MHz, $CDCl_3$)



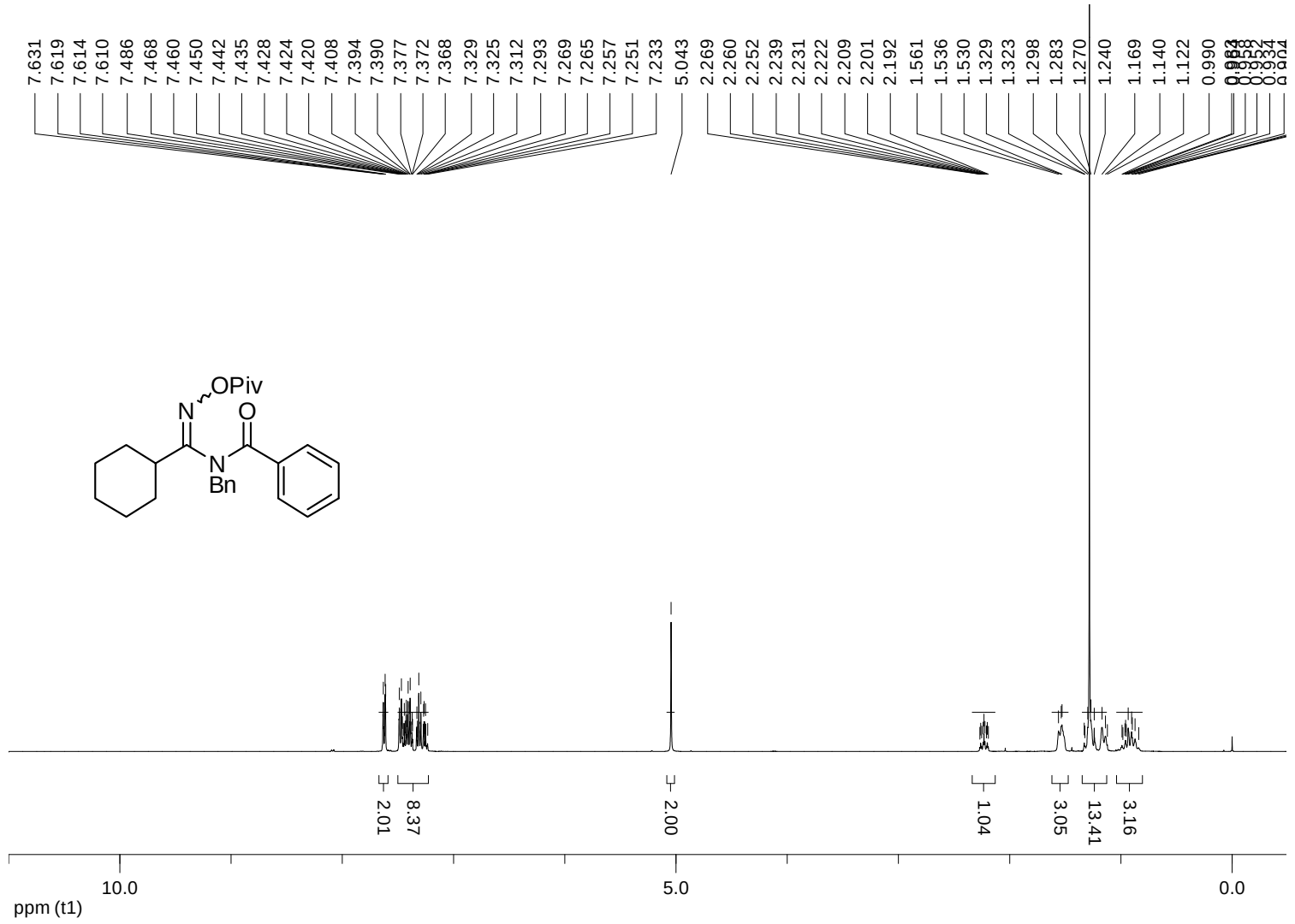
^{1}H NMR spectrum of *N*-benzyl-2-fluoro-*N*'-hydroxybenzimidamide (400 MHz, $CDCl_3$)



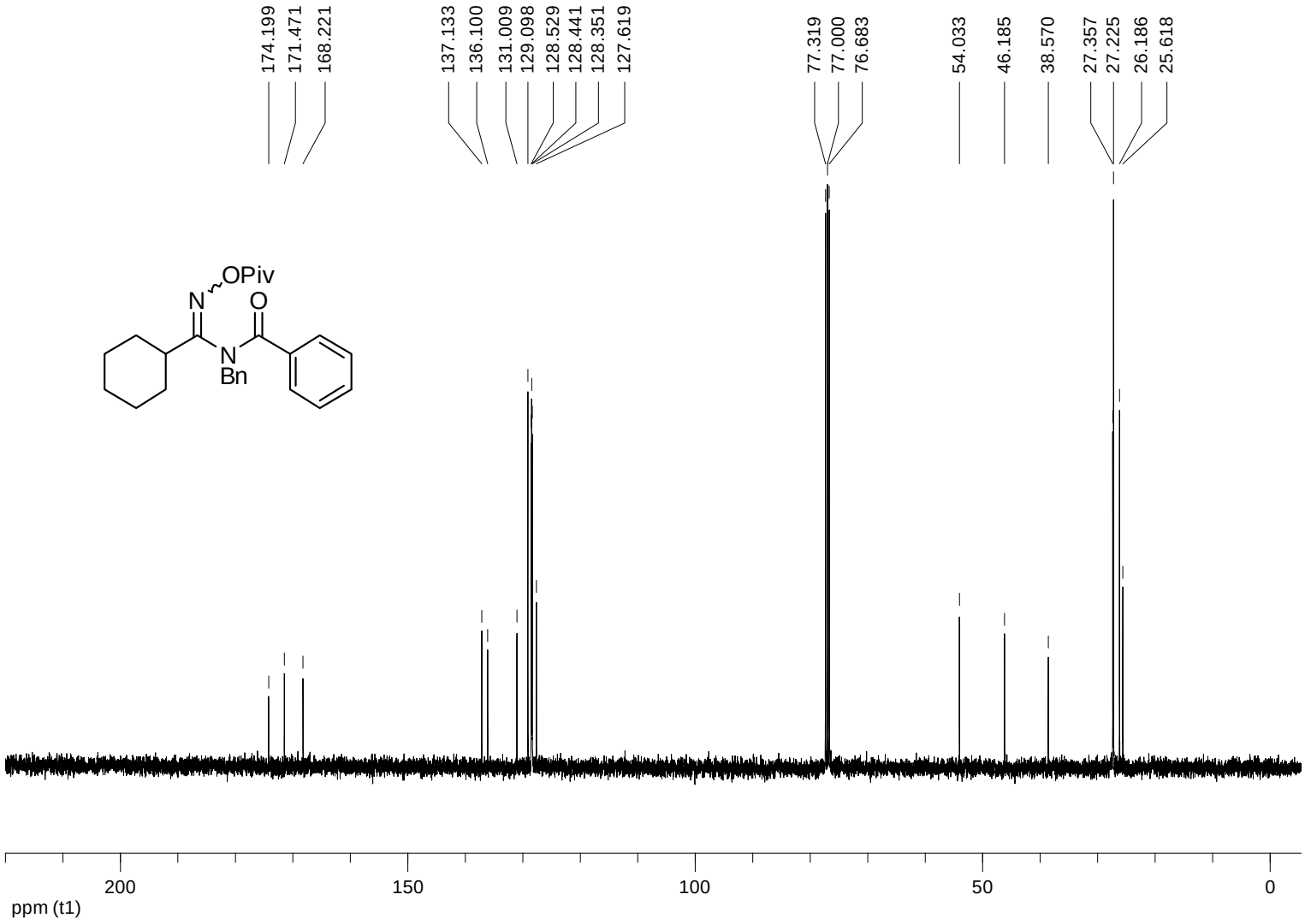
^{13}C NMR spectrum of *N*-benzyl-2-fluoro-*N*'-hydroxybenzimidamide (100 MHz, $CDCl_3$)



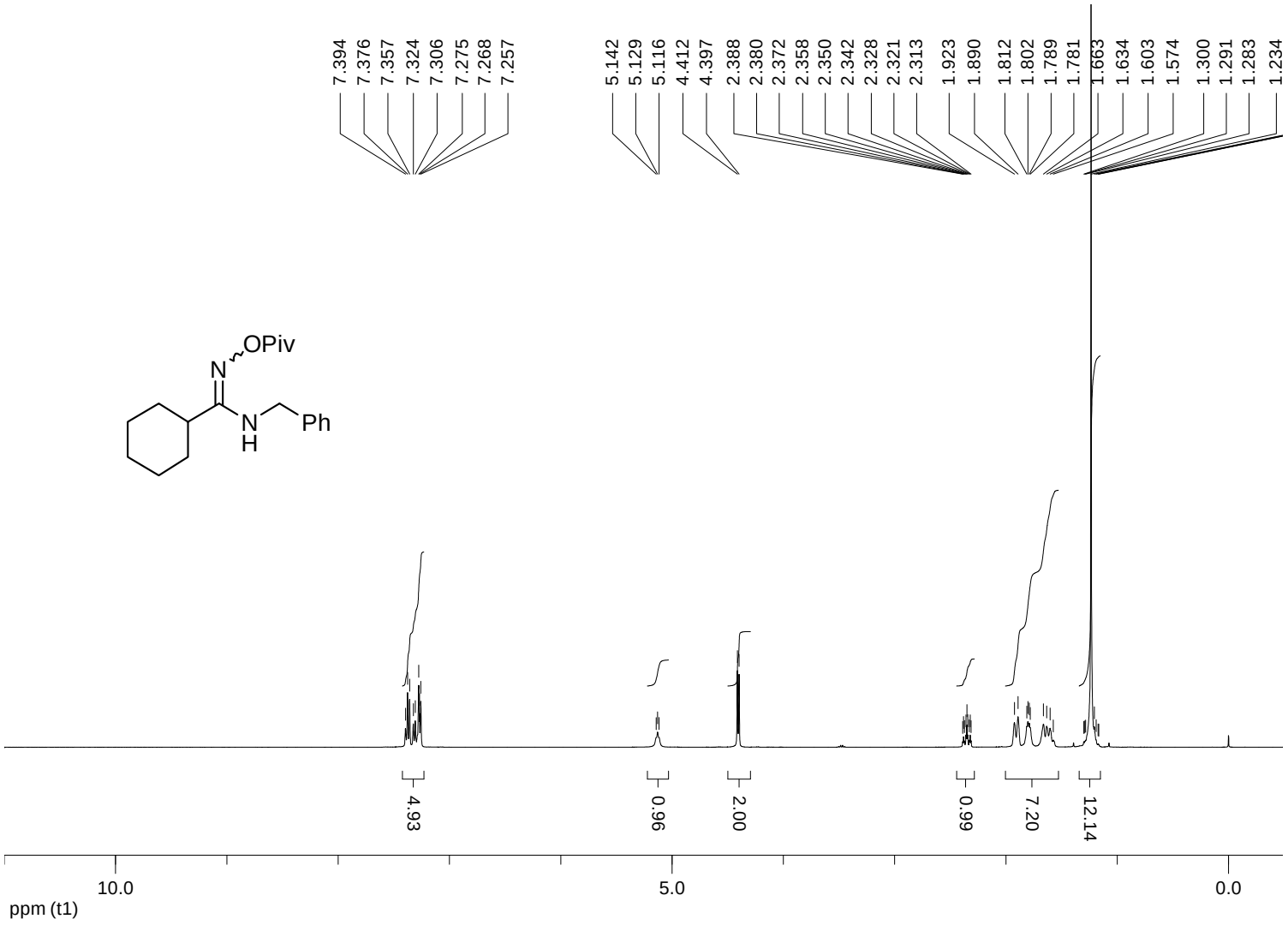
^{1}H NMR spectrum of **6e** (400 MHz, $CDCl_3$)



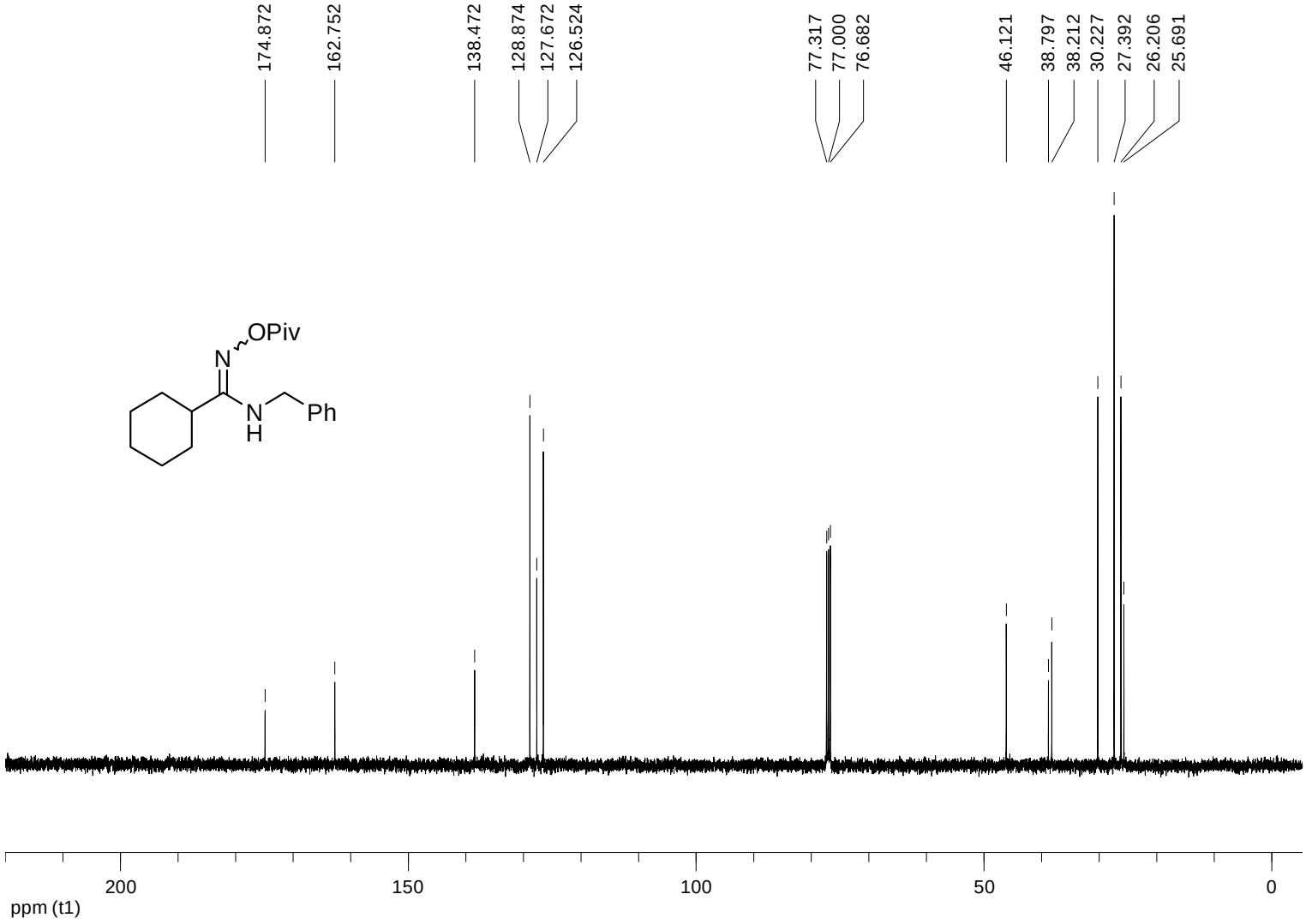
^{13}C NMR spectrum of **6e** (100 MHz, $CDCl_3$)



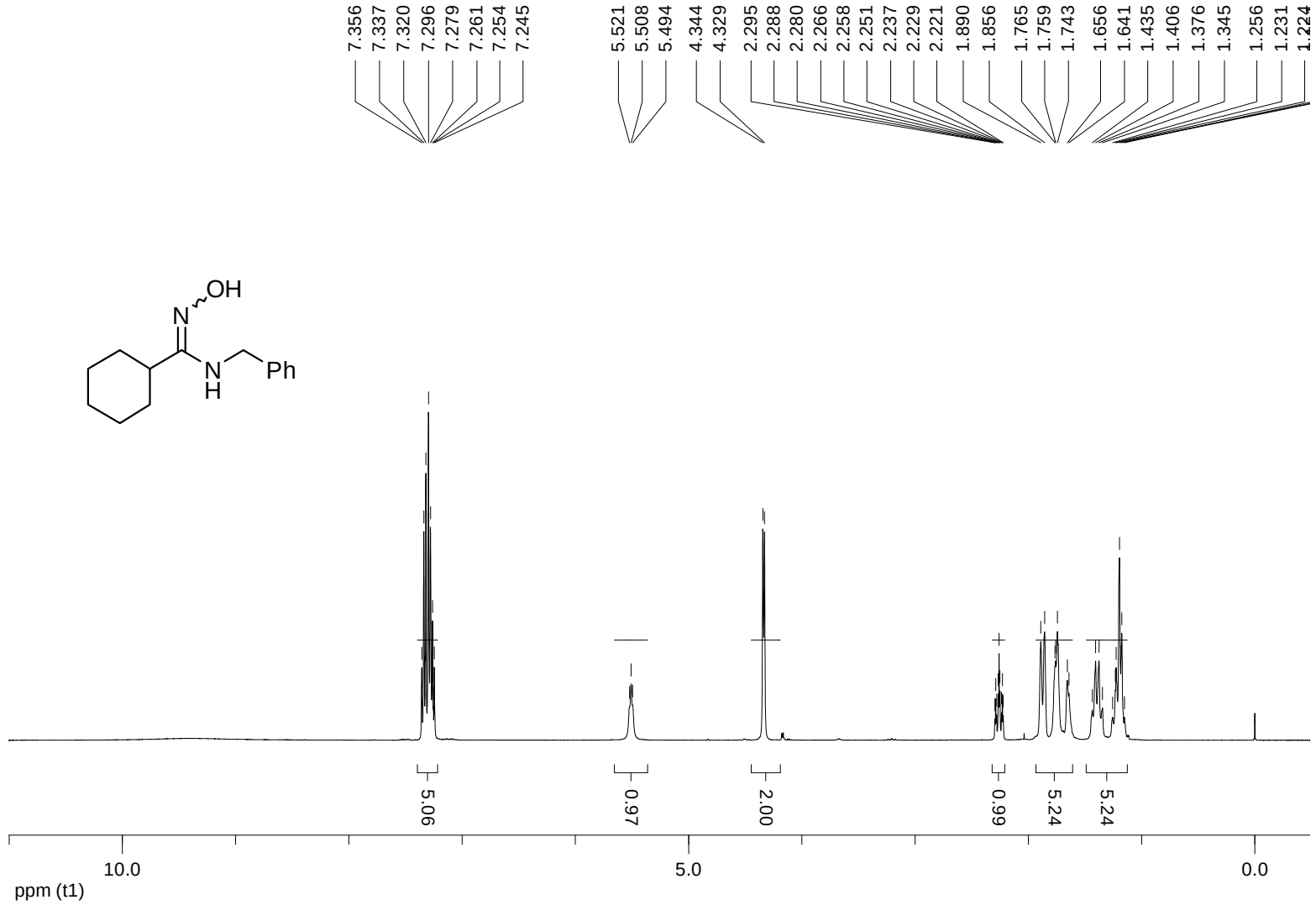
^{1}H NMR spectrum of *N*-benzyl-*N*'-(pivaloyloxy)cyclohexanecarboximidamide (400 MHz, $CDCl_3$)



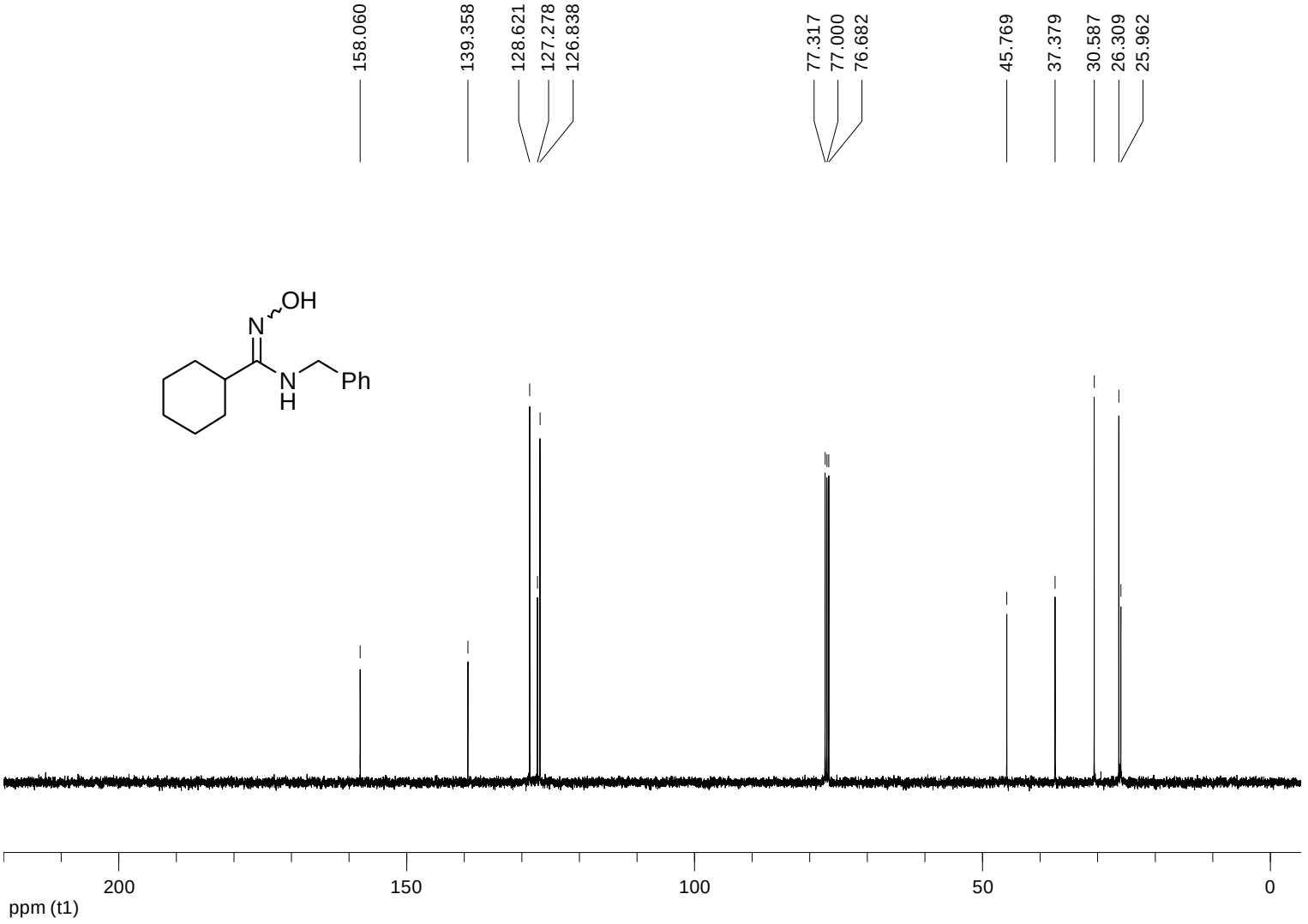
^{13}C NMR spectrum of *N*-benzyl-*N*'-(pivaloyloxy)cyclohexanecarboximidamide (100 MHz, $CDCl_3$)



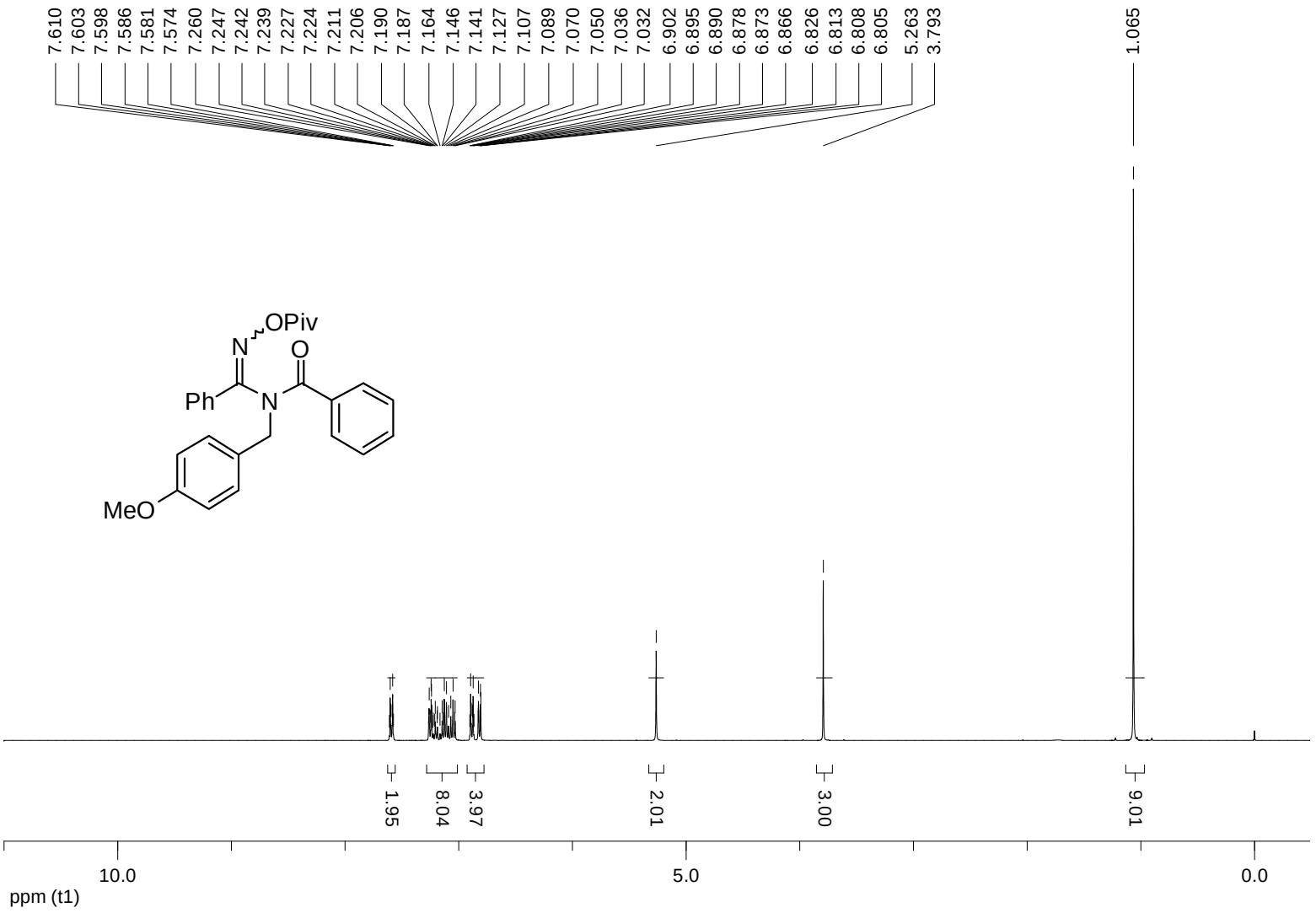
^{1}H NMR spectrum of *N*-benzyl-*N*'-hydroxycyclohexanecarboximidamide (400 MHz, $CDCl_3$)



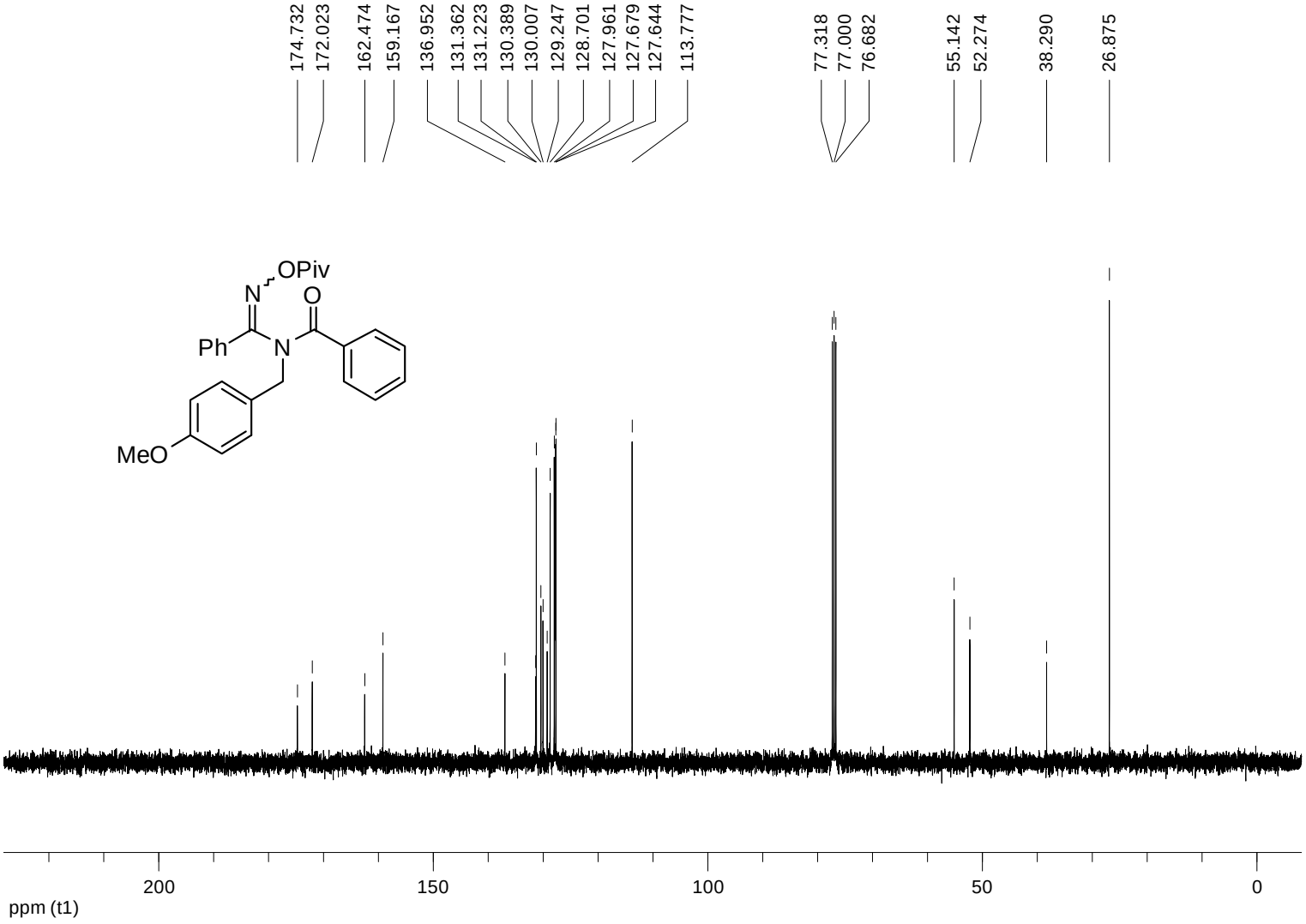
^{13}C NMR spectrum of *N*-benzyl-*N'*-hydroxycyclohexanecarboximidamide (100 MHz, $CDCl_3$)



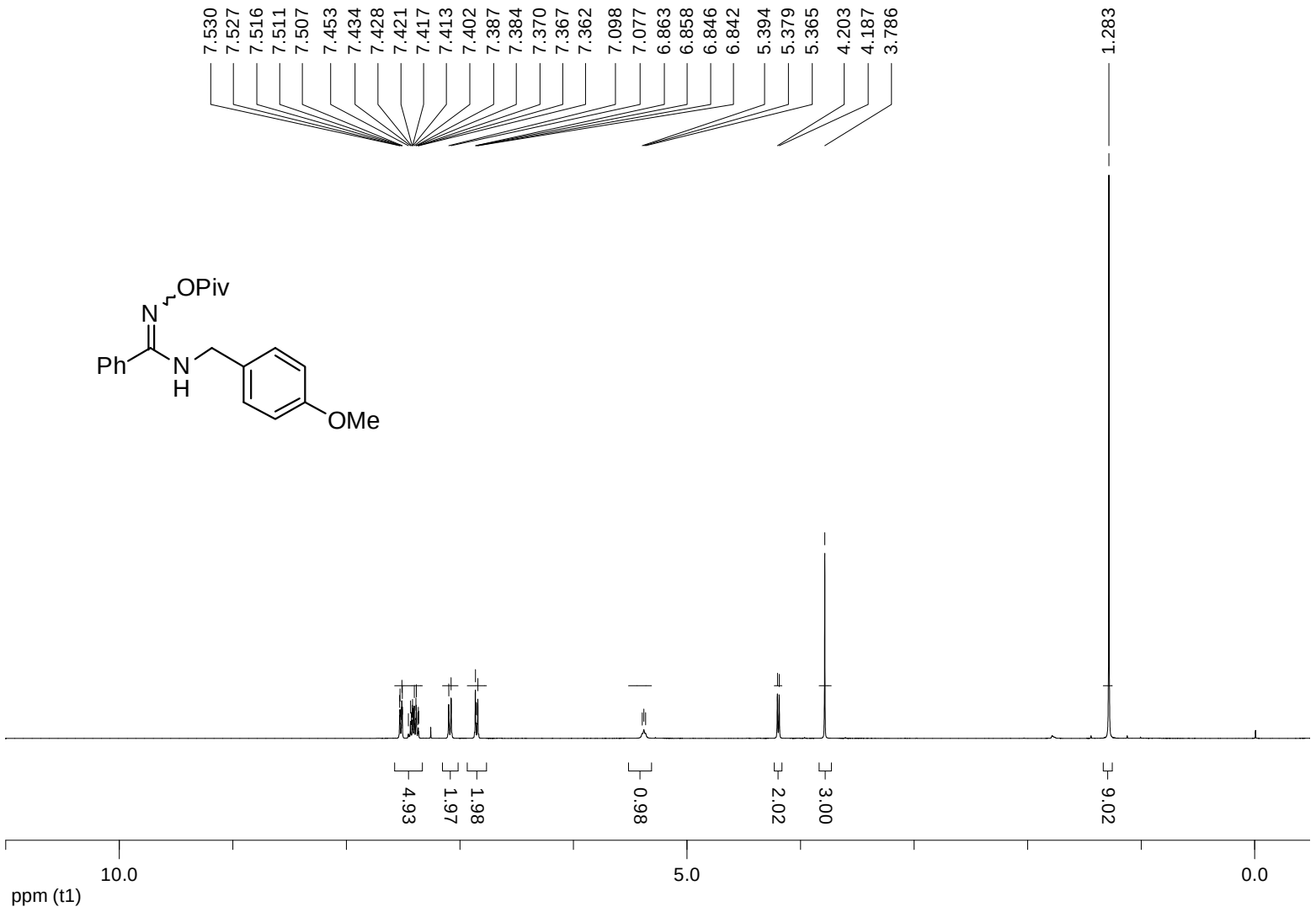
^{1}H NMR spectrum of **6f** (400 MHz, $CDCl_3$)



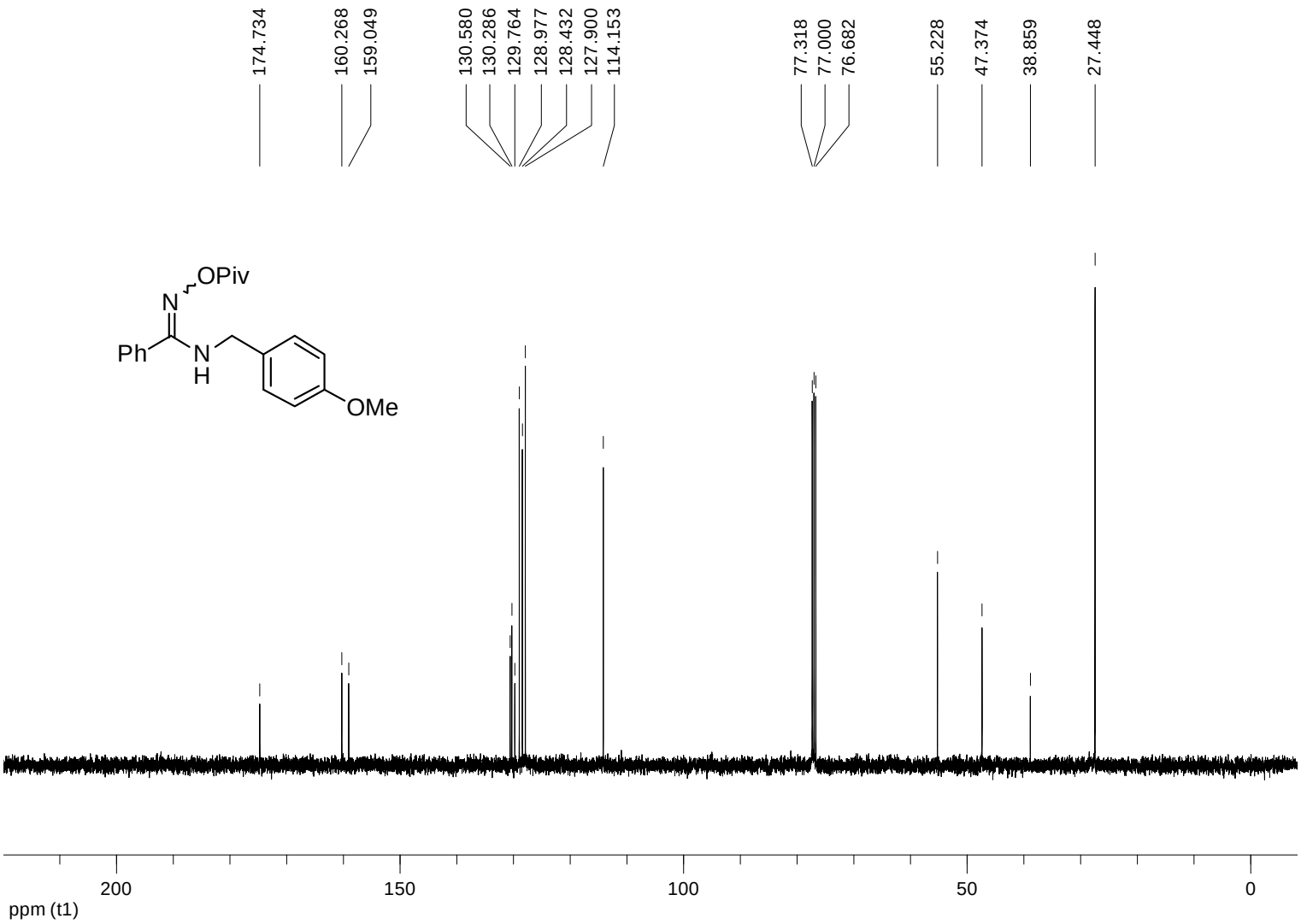
^{13}C NMR spectrum of **6f** (100 MHz, $CDCl_3$)



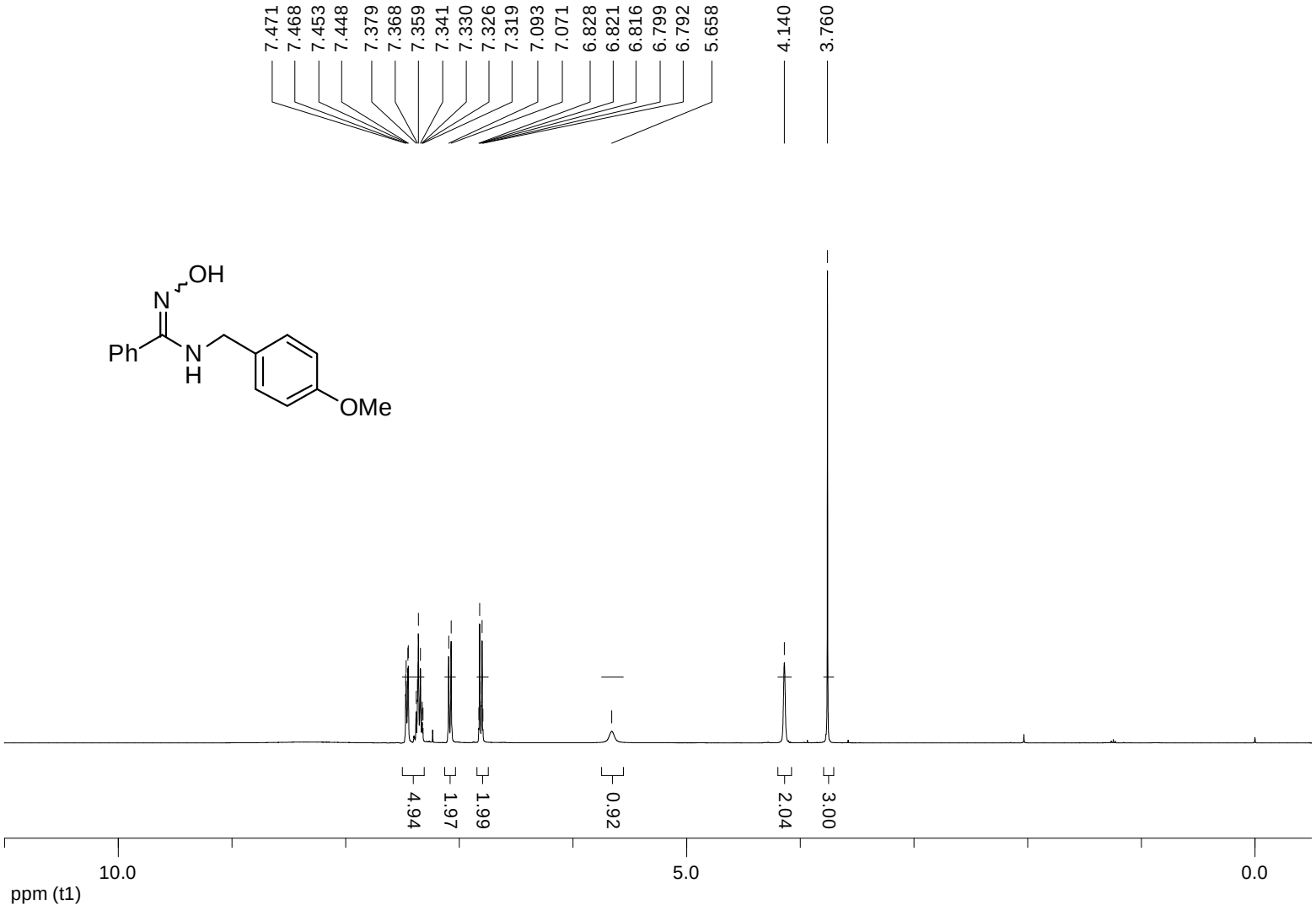
^{1}H NMR spectrum of *N*-(4-methoxybenzyl)-*N'*-(pivaloyloxy)benzimidamide (400 MHz, $CDCl_3$)



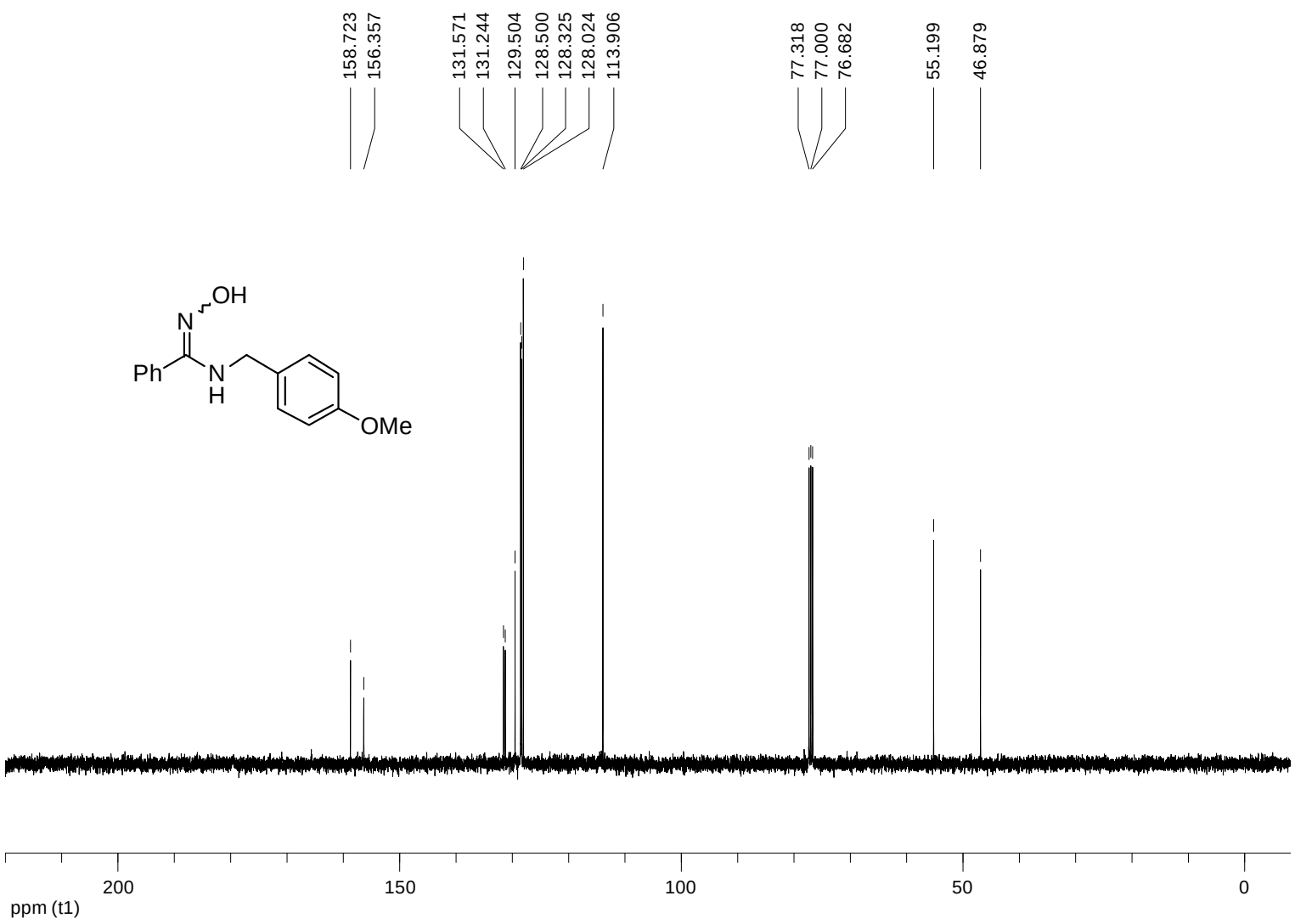
^{13}C NMR spectrum of *N*-(4-methoxybenzyl)-*N'*-(pivaloyloxy)benzimidamide (100 MHz, $CDCl_3$)



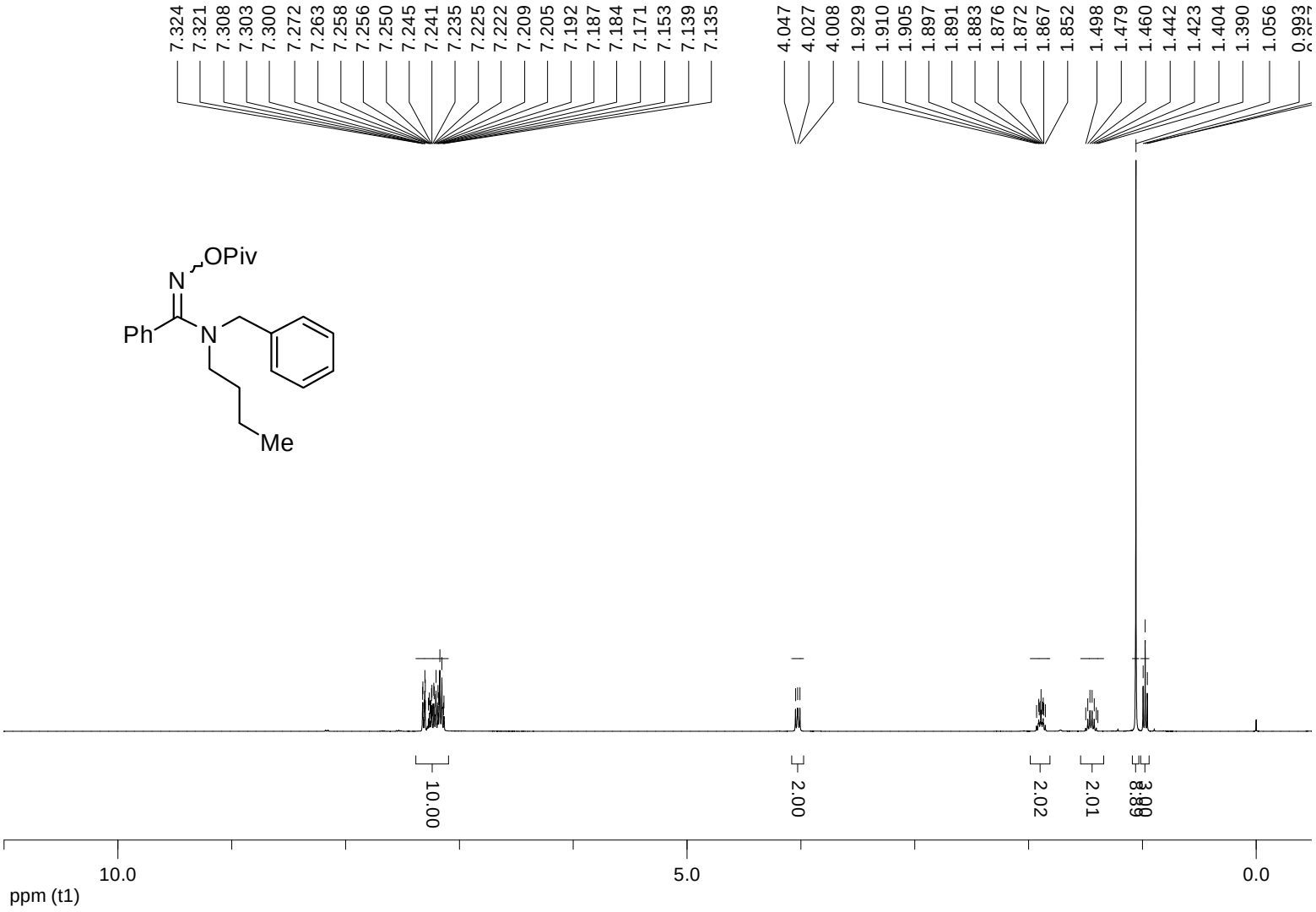
^{1}H NMR spectrum of *N*'-hydroxy-*N*-(4-methoxybenzyl)benzimidamide (400 MHz, $CDCl_3$)



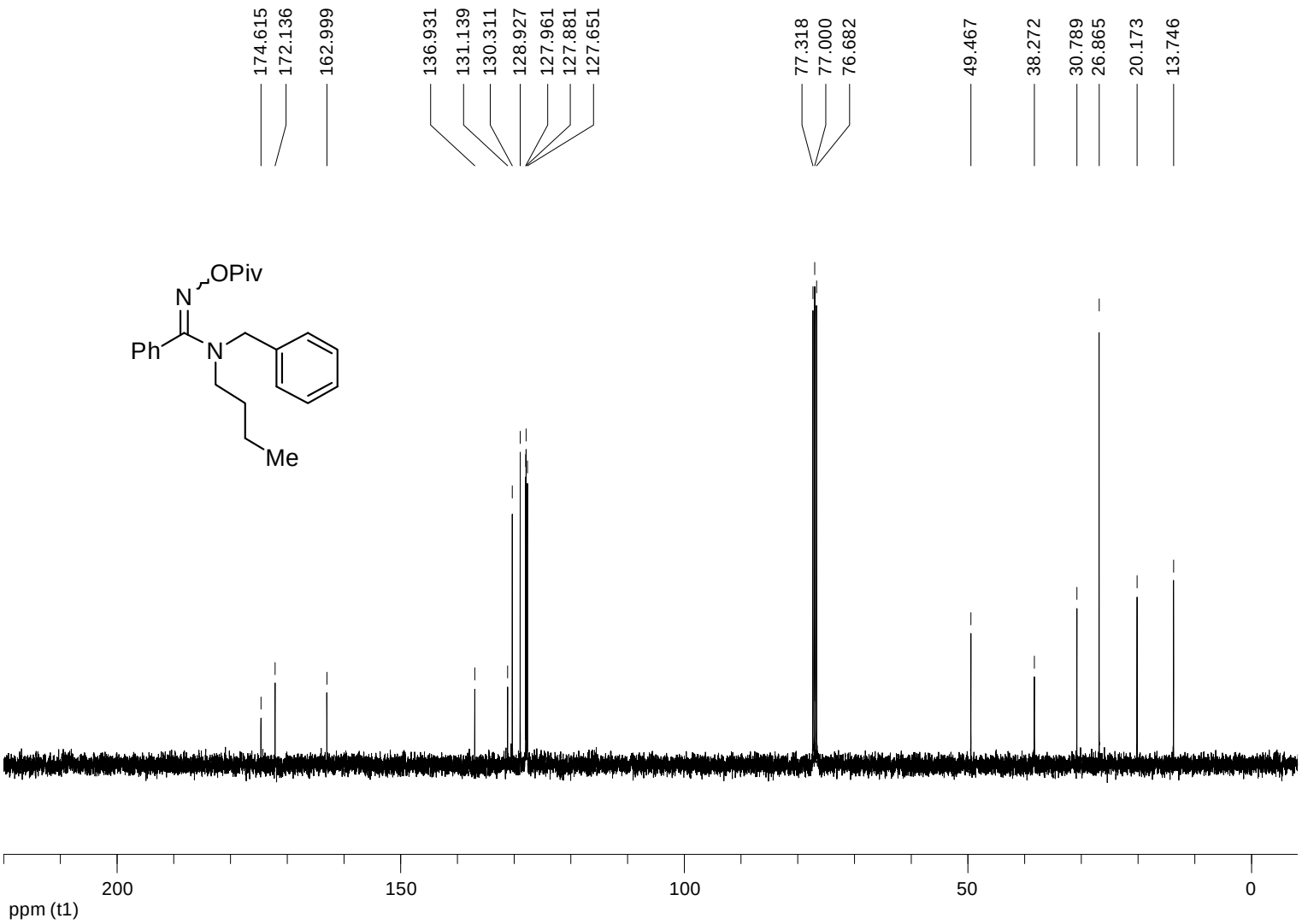
^{13}C NMR spectrum of *N*'-hydroxy-*N*-(4-methoxybenzyl)benzimidamide (100 MHz, $CDCl_3$)



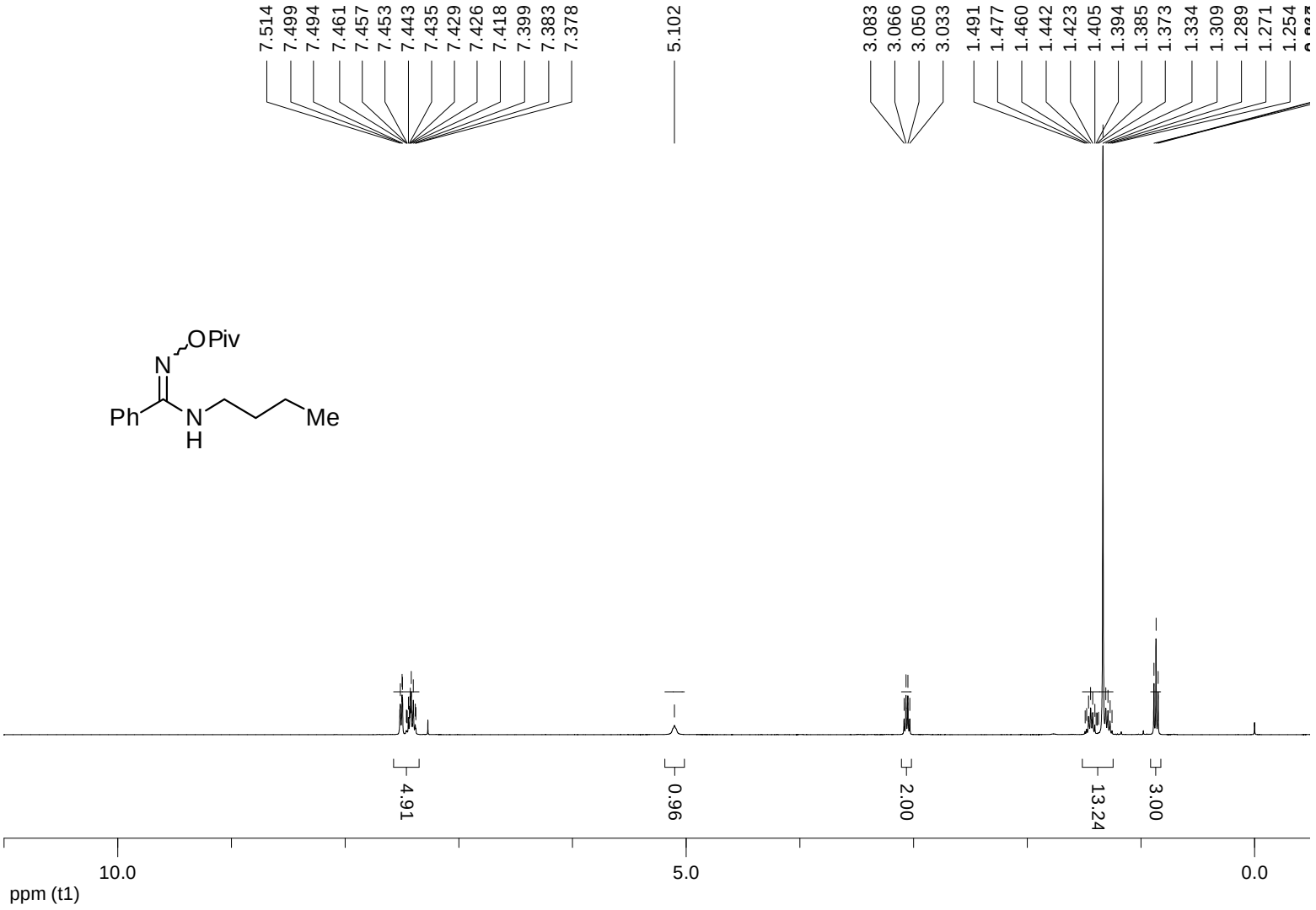
^{1}H NMR spectrum of **6g** (400 MHz, $CDCl_3$)



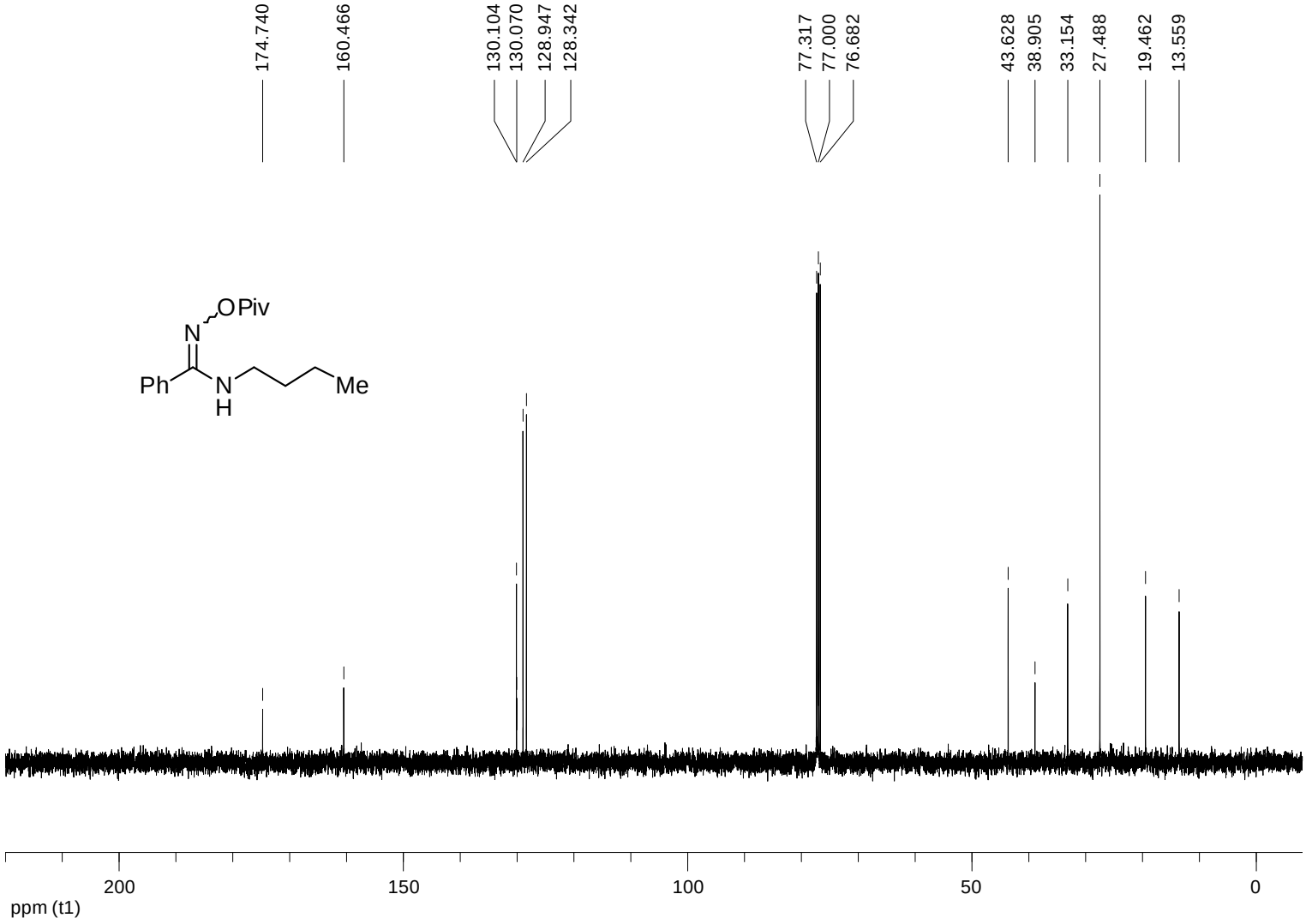
^{13}C NMR spectrum of **6g** (100 MHz, $CDCl_3$)



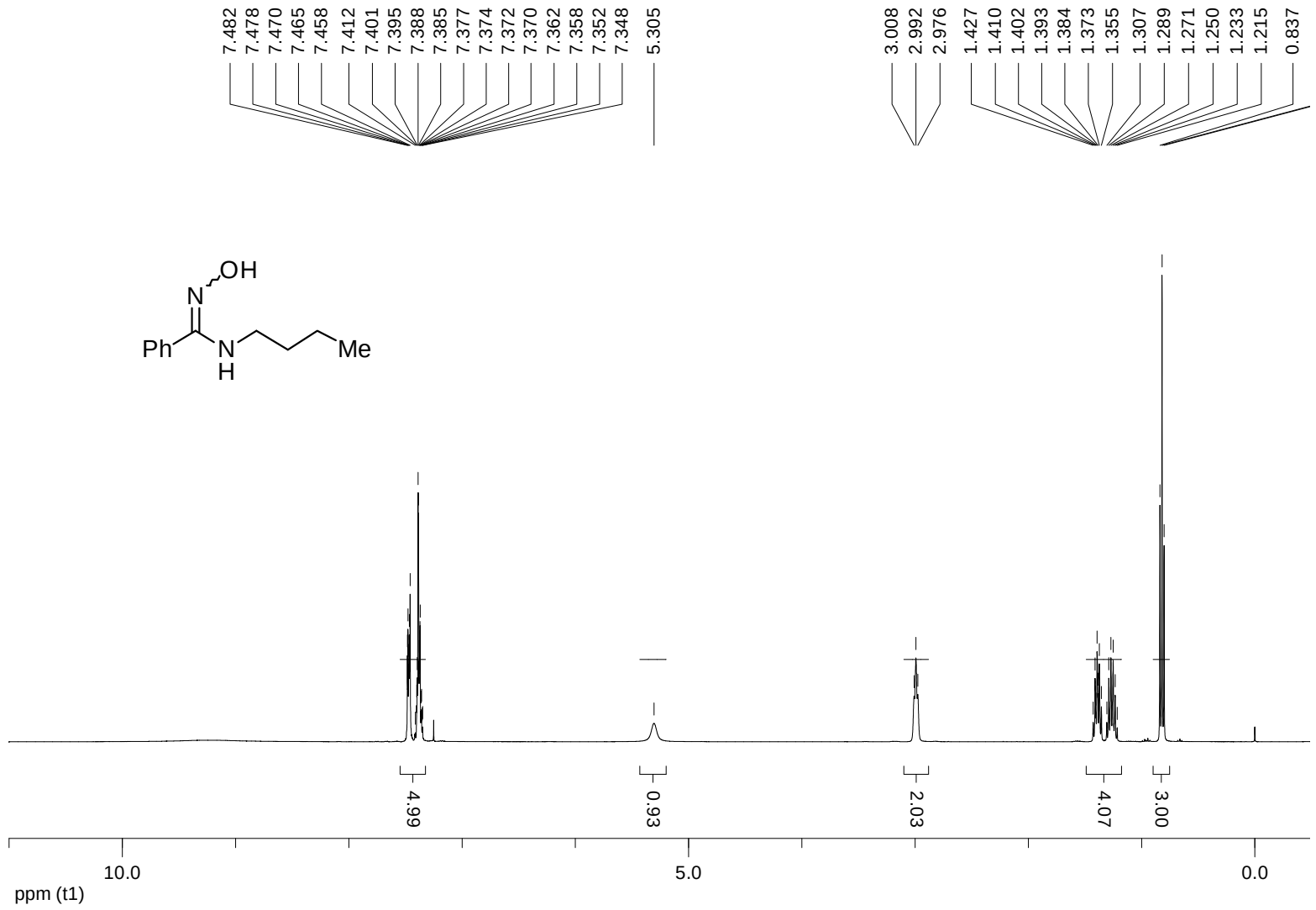
^{1}H NMR spectrum of *N*-butyl-*N*'-(pivaloyloxy)benzimidamide (400 MHz, $CDCl_3$)



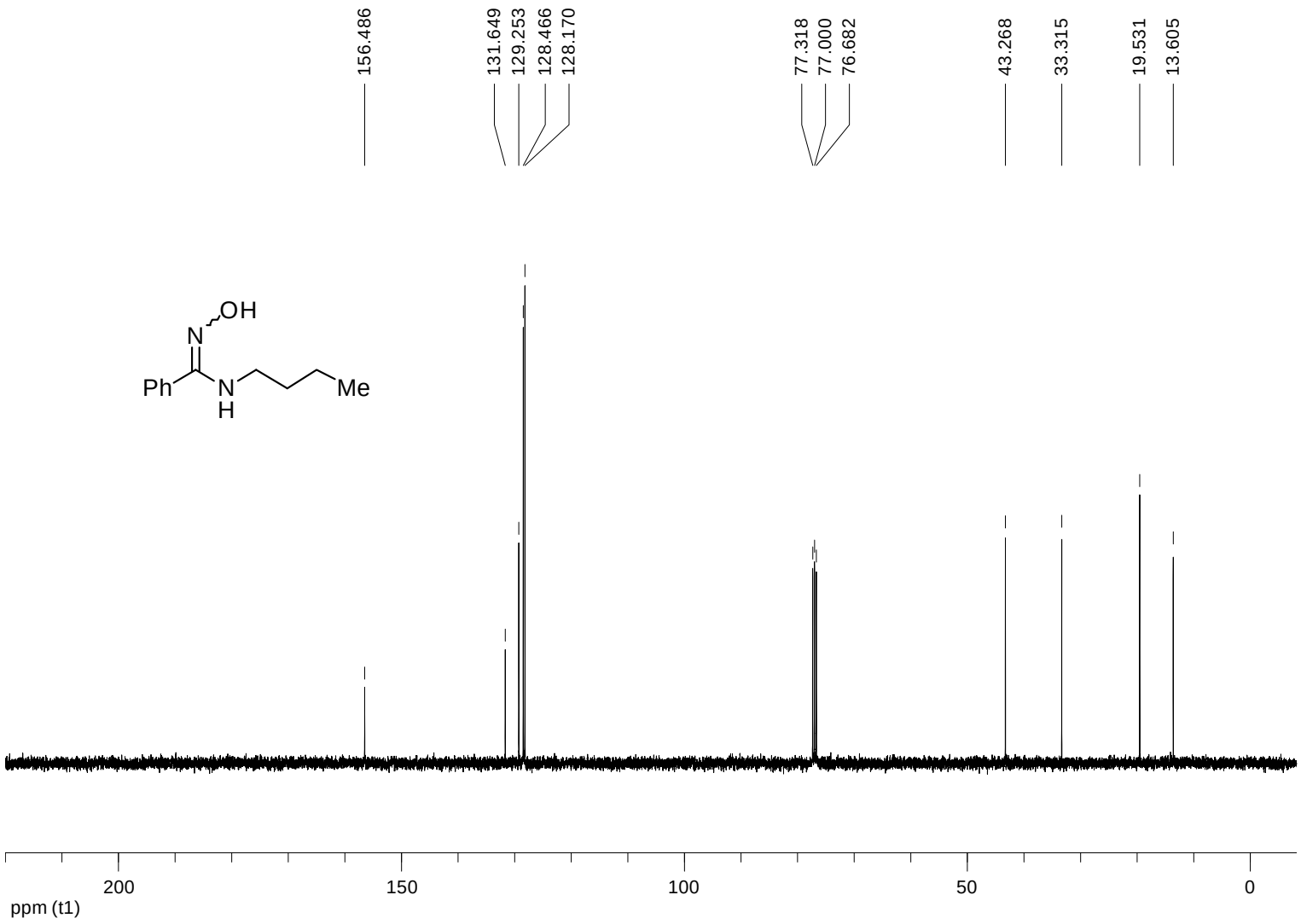
^{13}C NMR spectrum of *N*-butyl-*N*'-(pivaloyloxy)benzimidamide (100 MHz, $CDCl_3$)



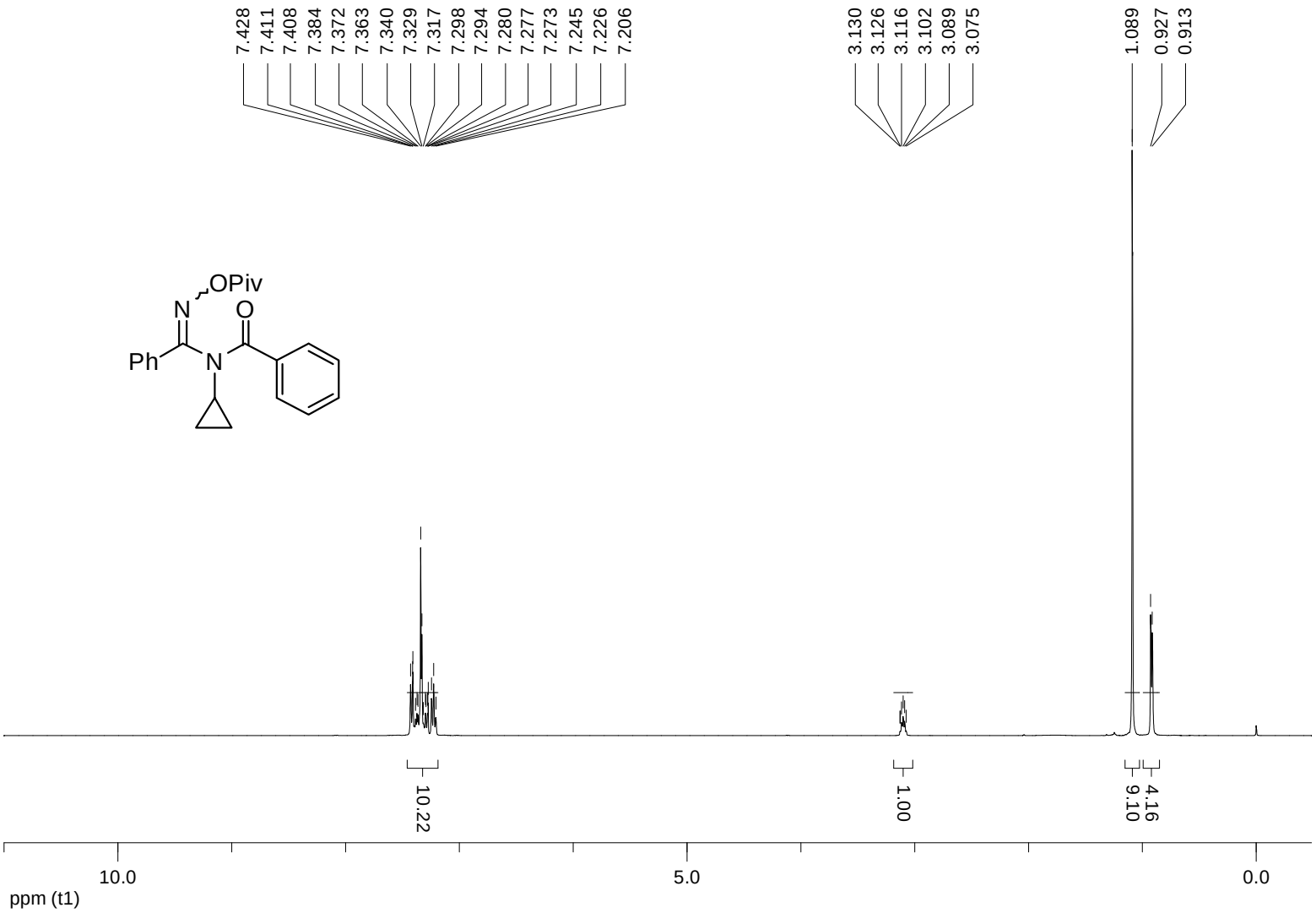
^{1}H NMR spectrum of *N*-butyl-*N'*-hydroxybenzimidamide (400 MHz, $CDCl_3$)



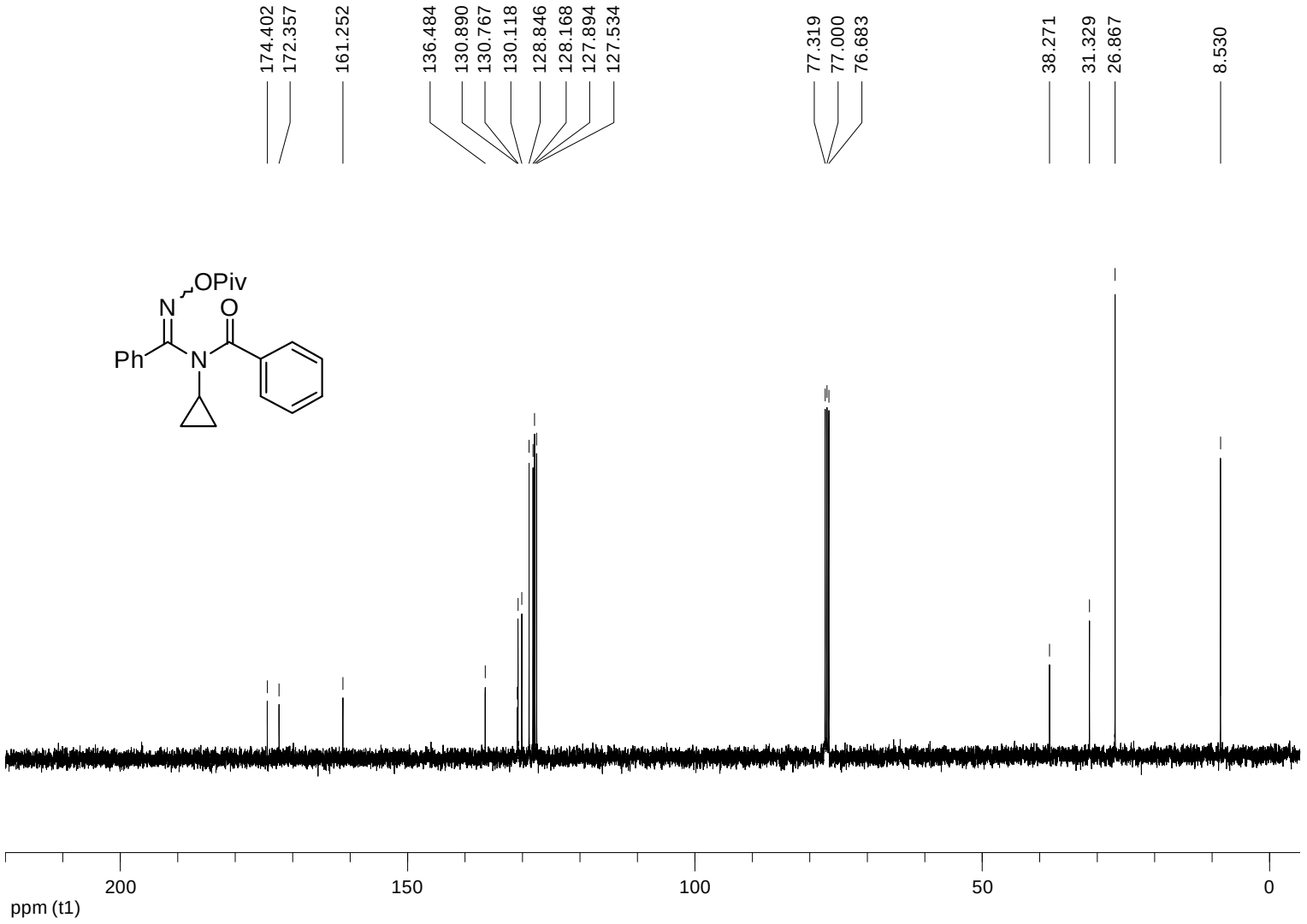
^{13}C NMR spectrum of *N*-butyl-*N*'-hydroxybenzimidamide (100 MHz, $CDCl_3$)



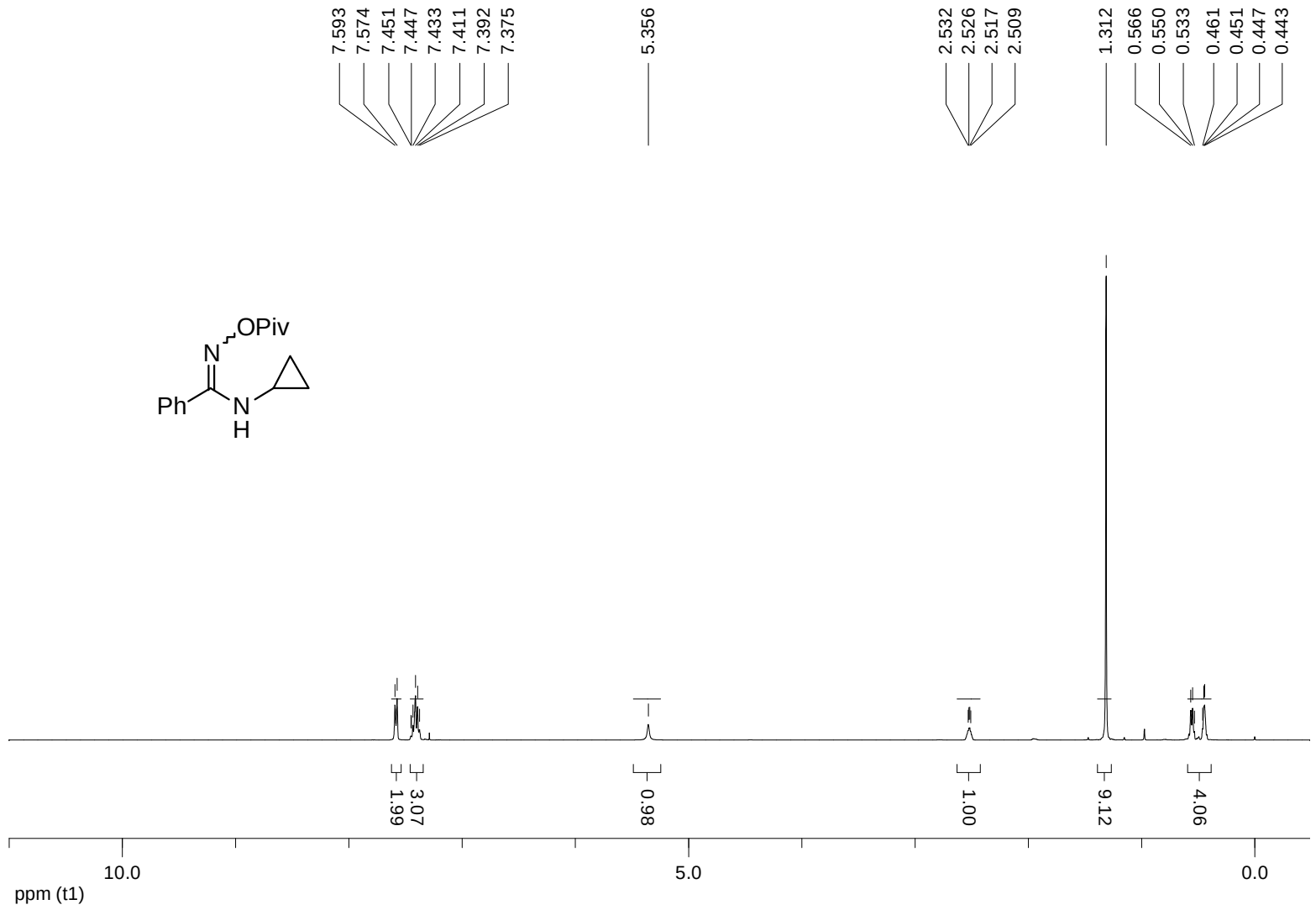
^{1}H NMR spectrum of **6h** (400 MHz, $CDCl_3$)



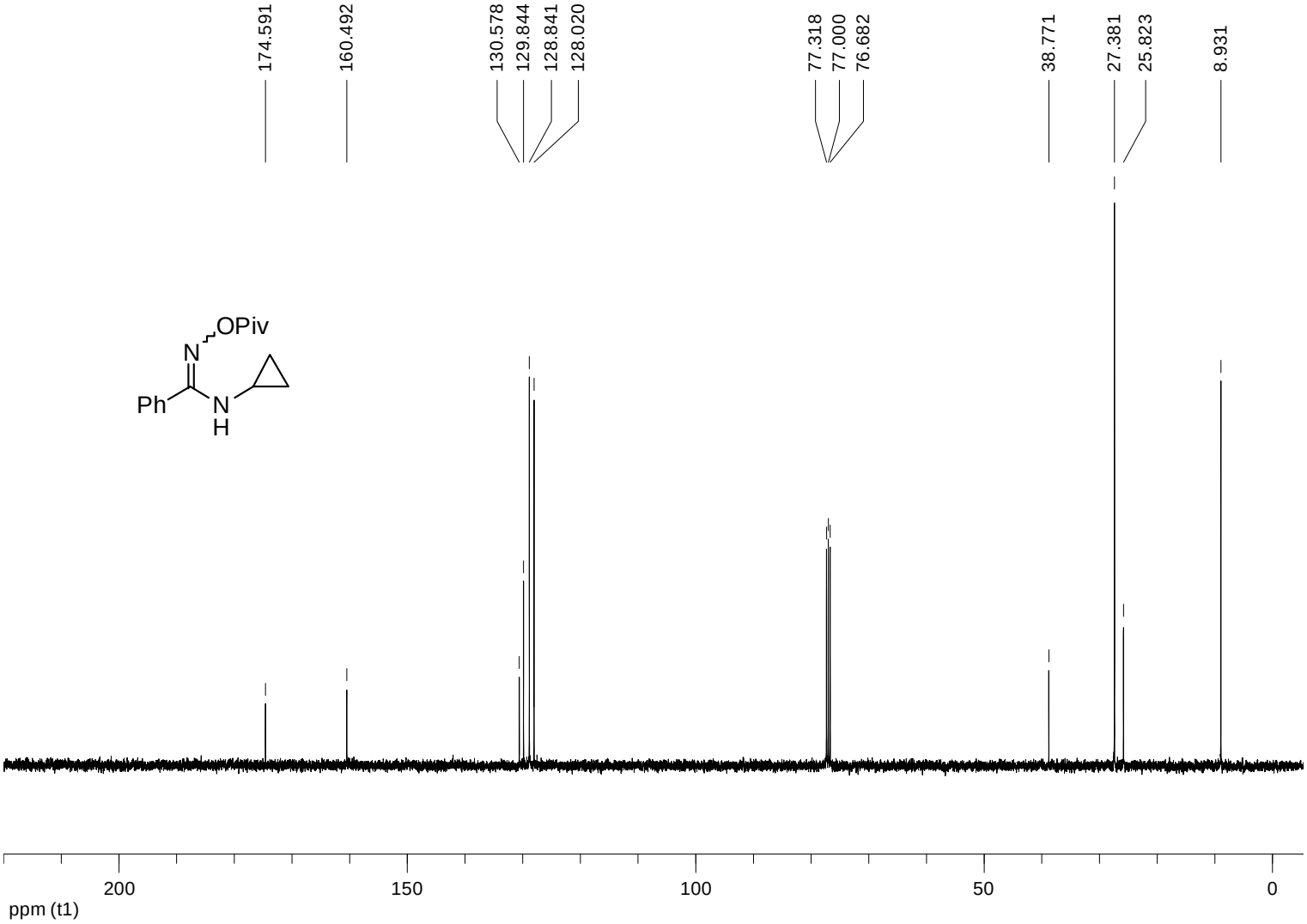
^{13}C NMR spectrum of **6h** (100 MHz, $CDCl_3$)



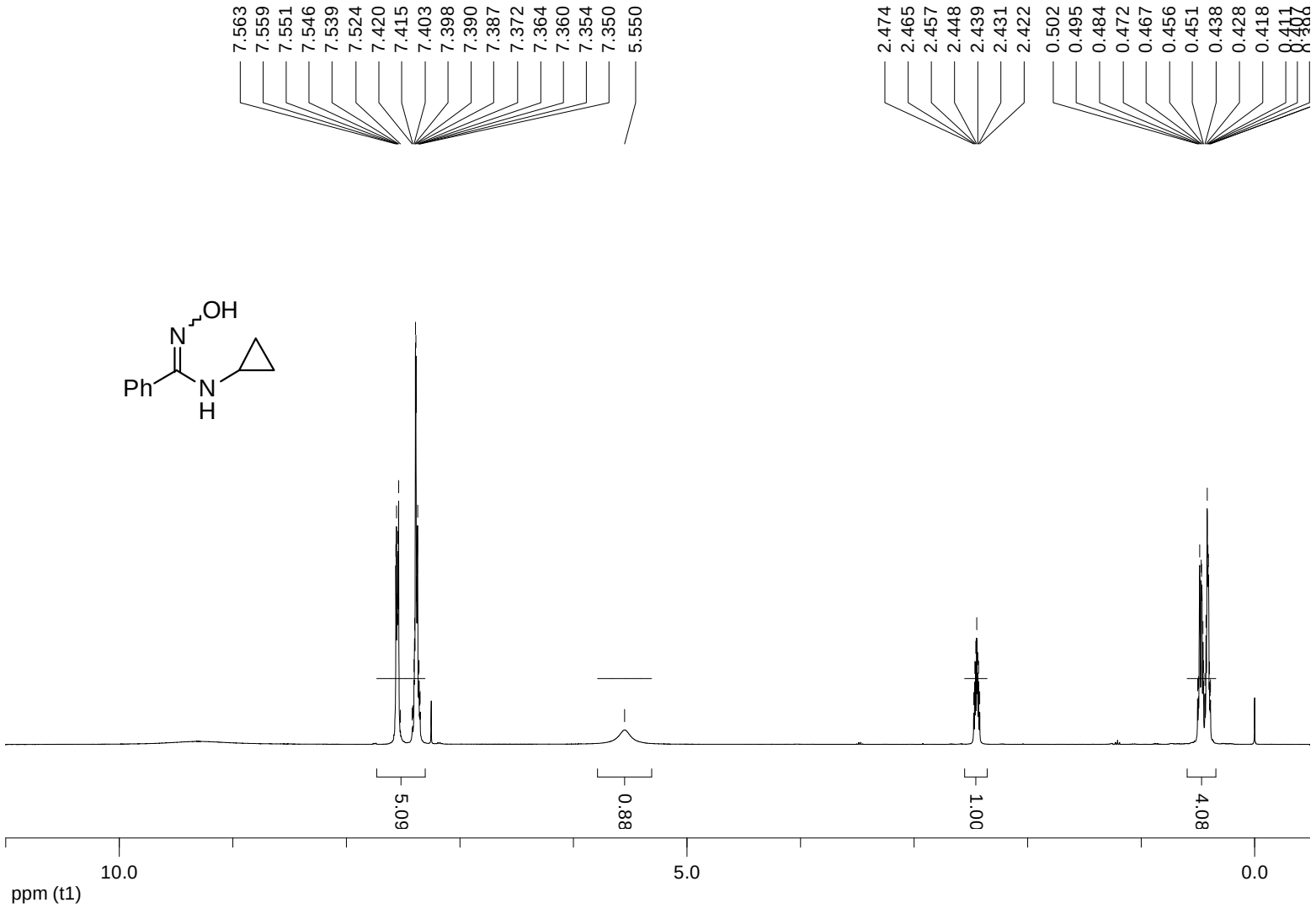
^{1}H NMR spectrum of *N*-cyclopropyl-*N*'-(pivaloyloxy)benzimidamide (400 MHz, $CDCl_3$)



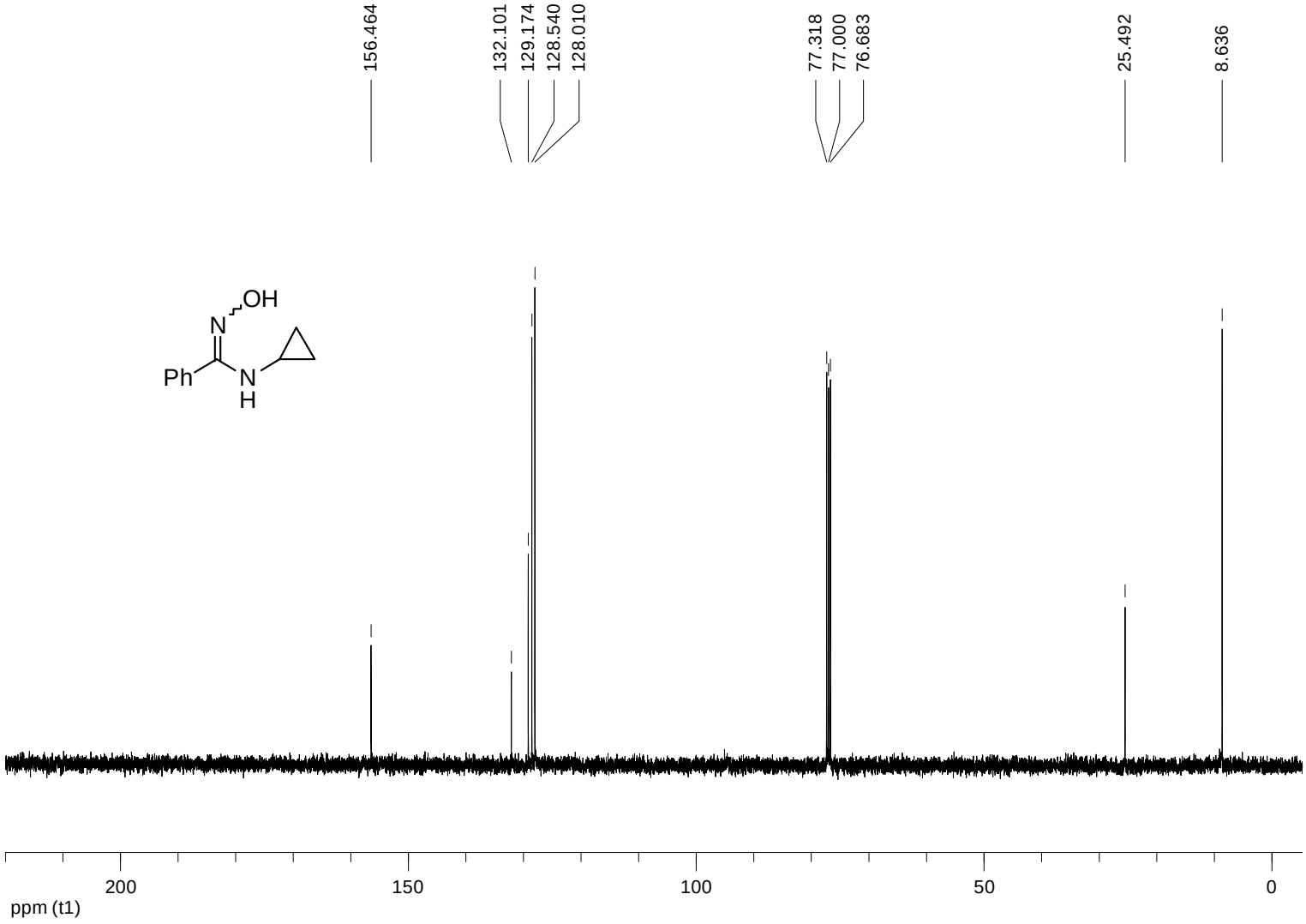
^{13}C NMR spectrum of *N*-cyclopropyl-*N*'-(pivaloyloxy)benzimidamide (100 MHz, $CDCl_3$)



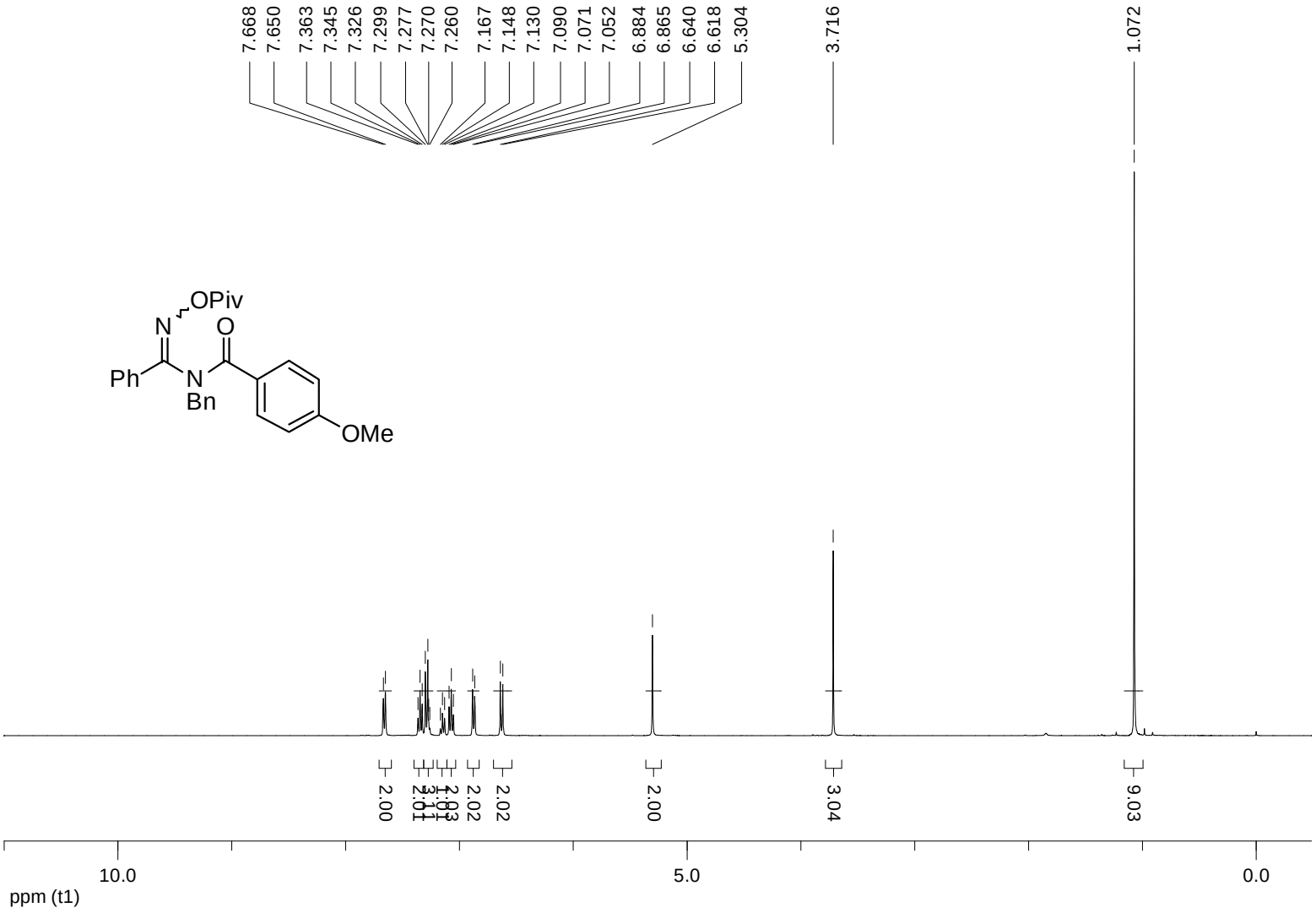
^{1}H NMR spectrum of *N*-cyclopropyl-*N*'-hydroxybenzimidamide (400 MHz, $CDCl_3$)



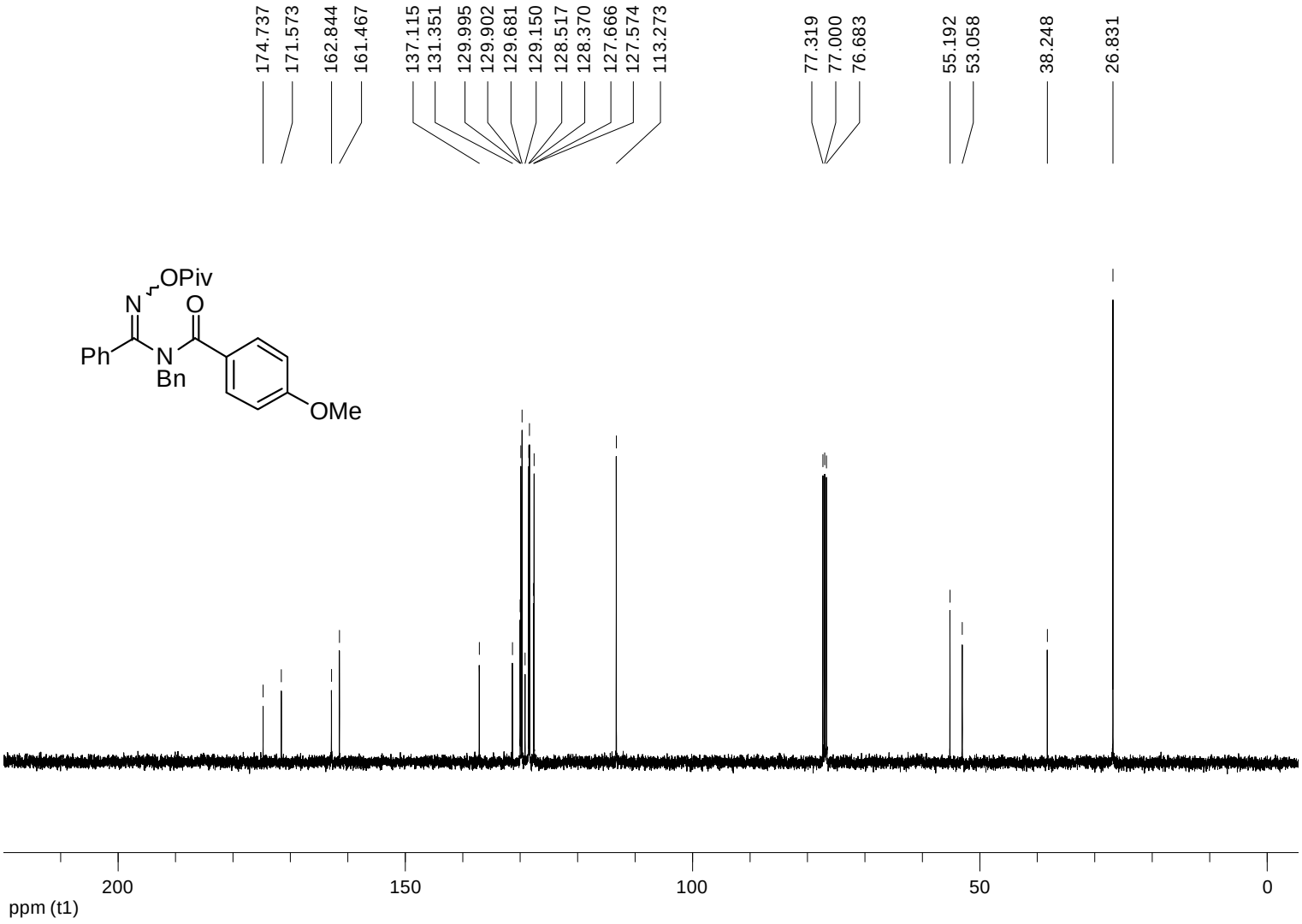
^{13}C NMR spectrum of *N*-cyclopropyl-*N*'-hydroxybenzimidamide (100 MHz, $CDCl_3$)



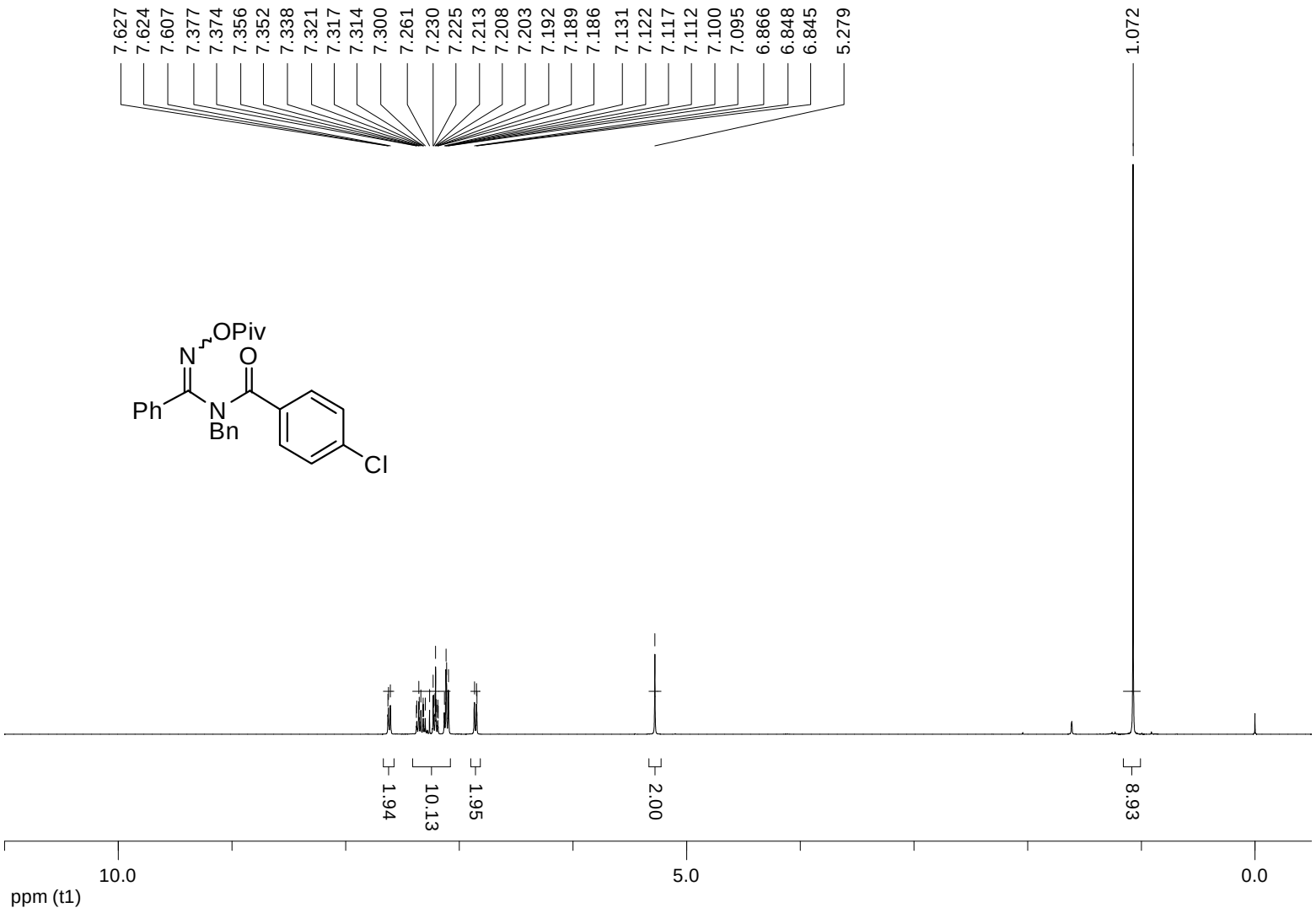
^{1}H NMR spectrum of **6i** (400 MHz, $CDCl_3$)



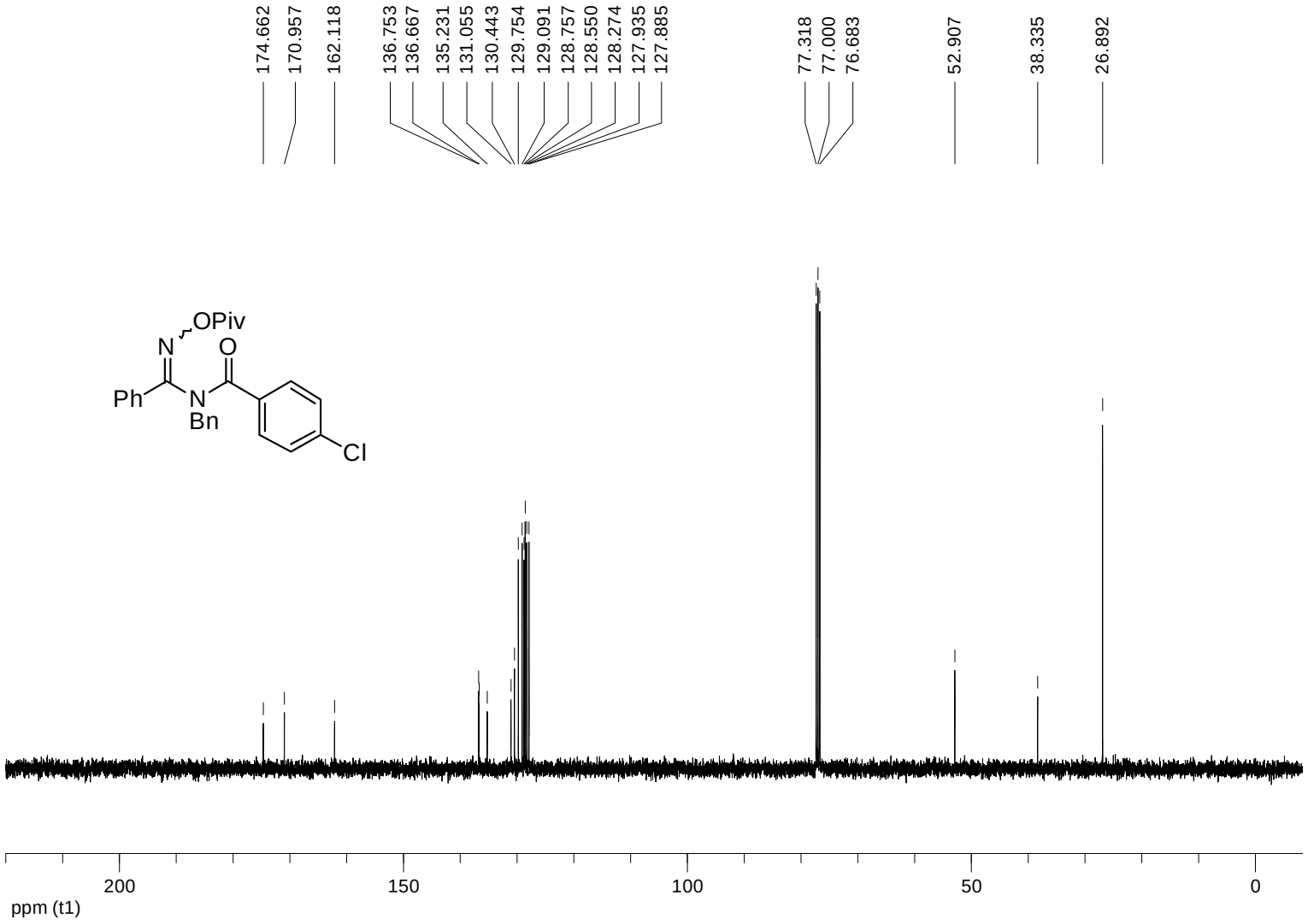
^{13}C NMR spectrum of **6i**100 MHz, $CDCl_3$)



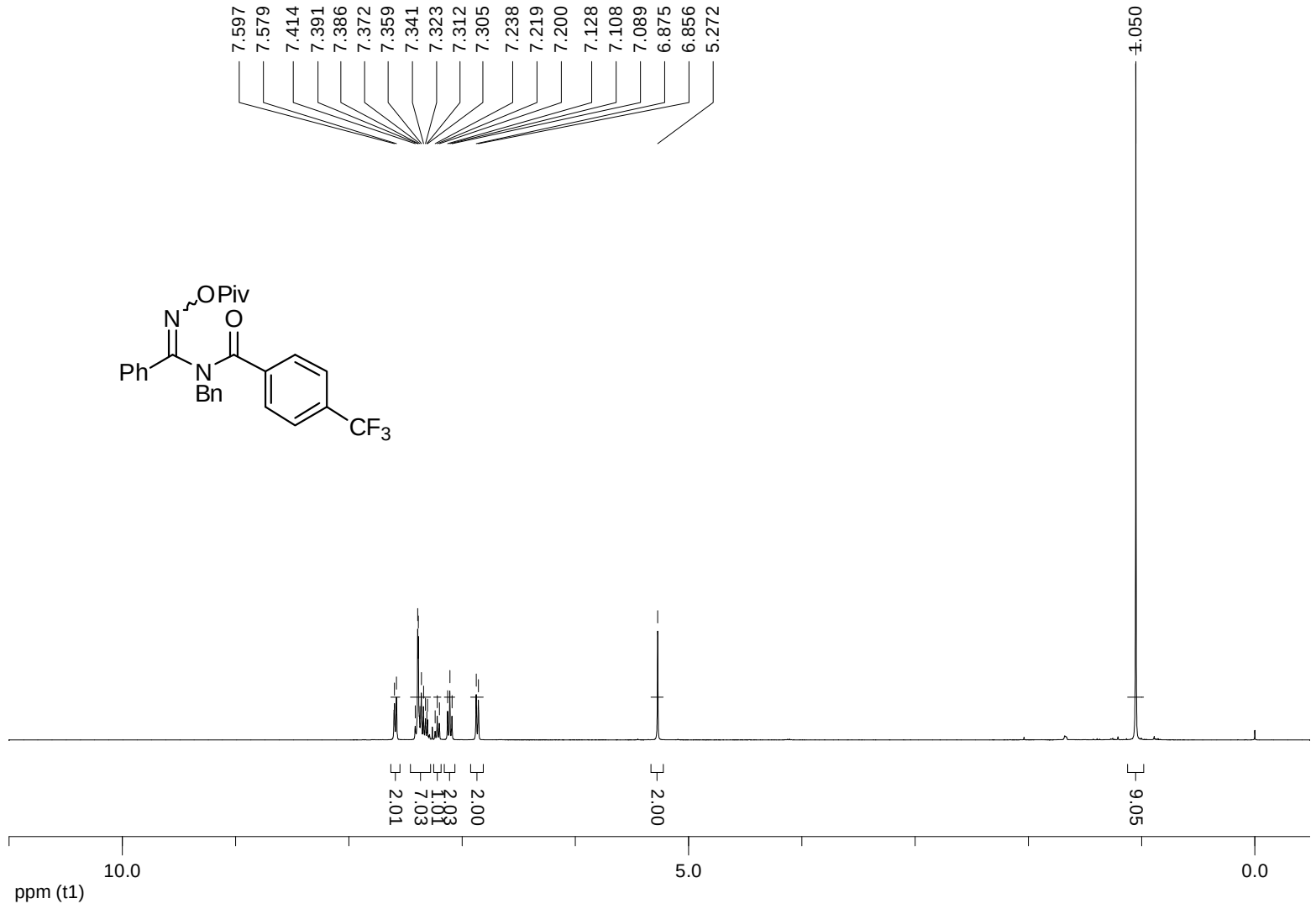
^{1}H NMR spectrum of **6j** (400 MHz, $CDCl_3$)



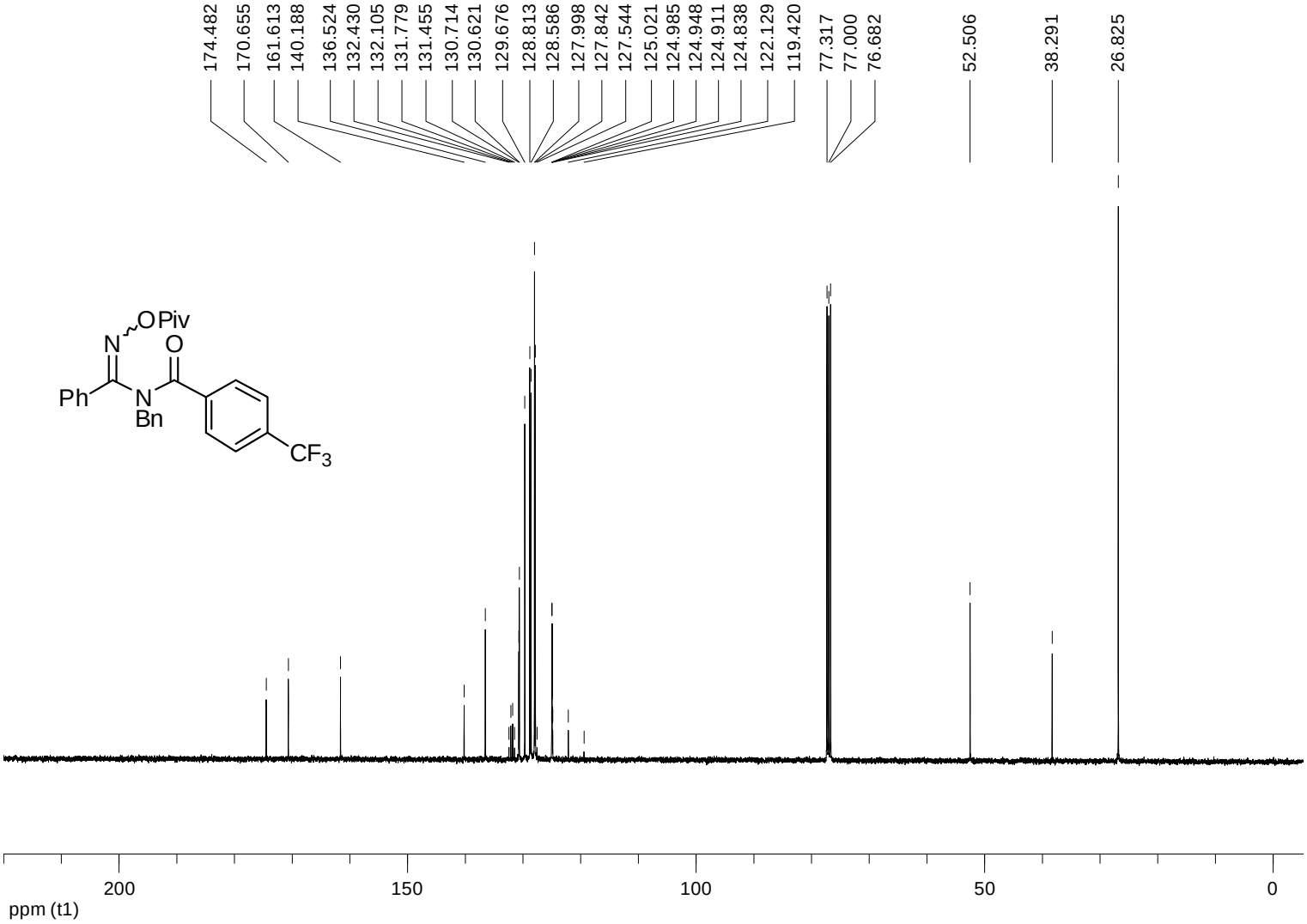
^{13}C NMR spectrum of **6j** (100 MHz, $CDCl_3$)



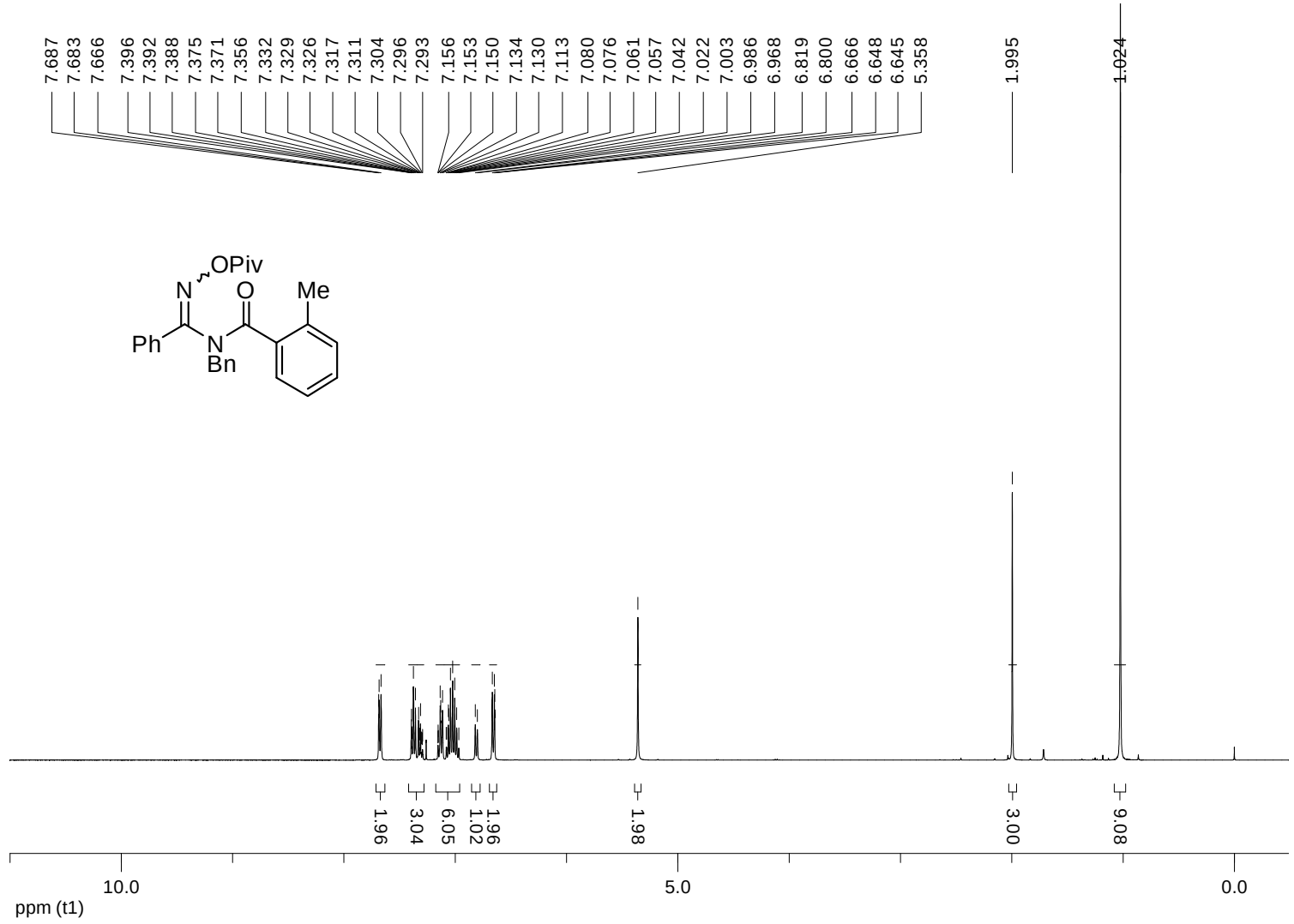
^{1}H NMR spectrum of **6k** (400 MHz, $CDCl_3$)



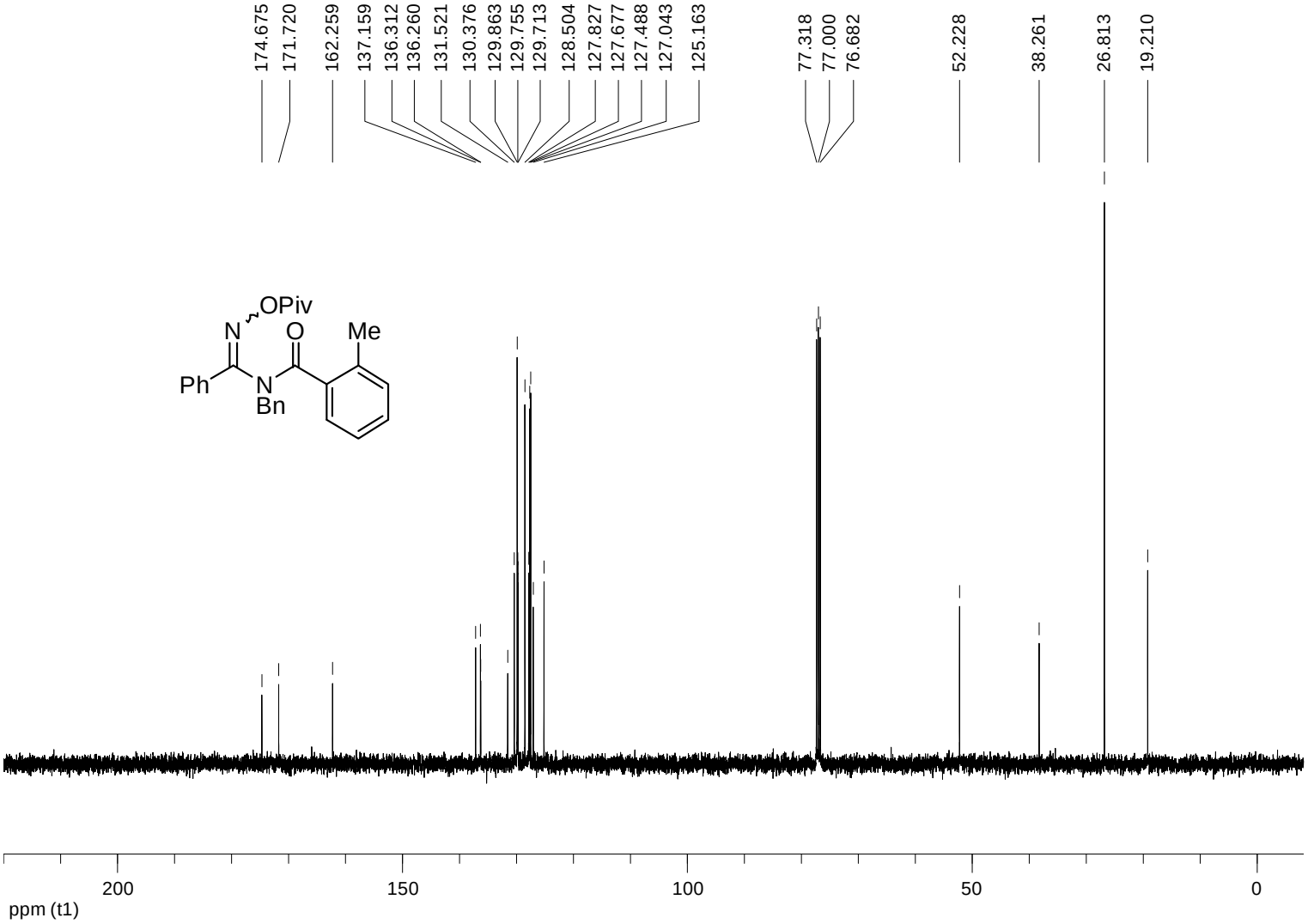
^{13}C NMR spectrum of **6k** (100 MHz, $CDCl_3$)



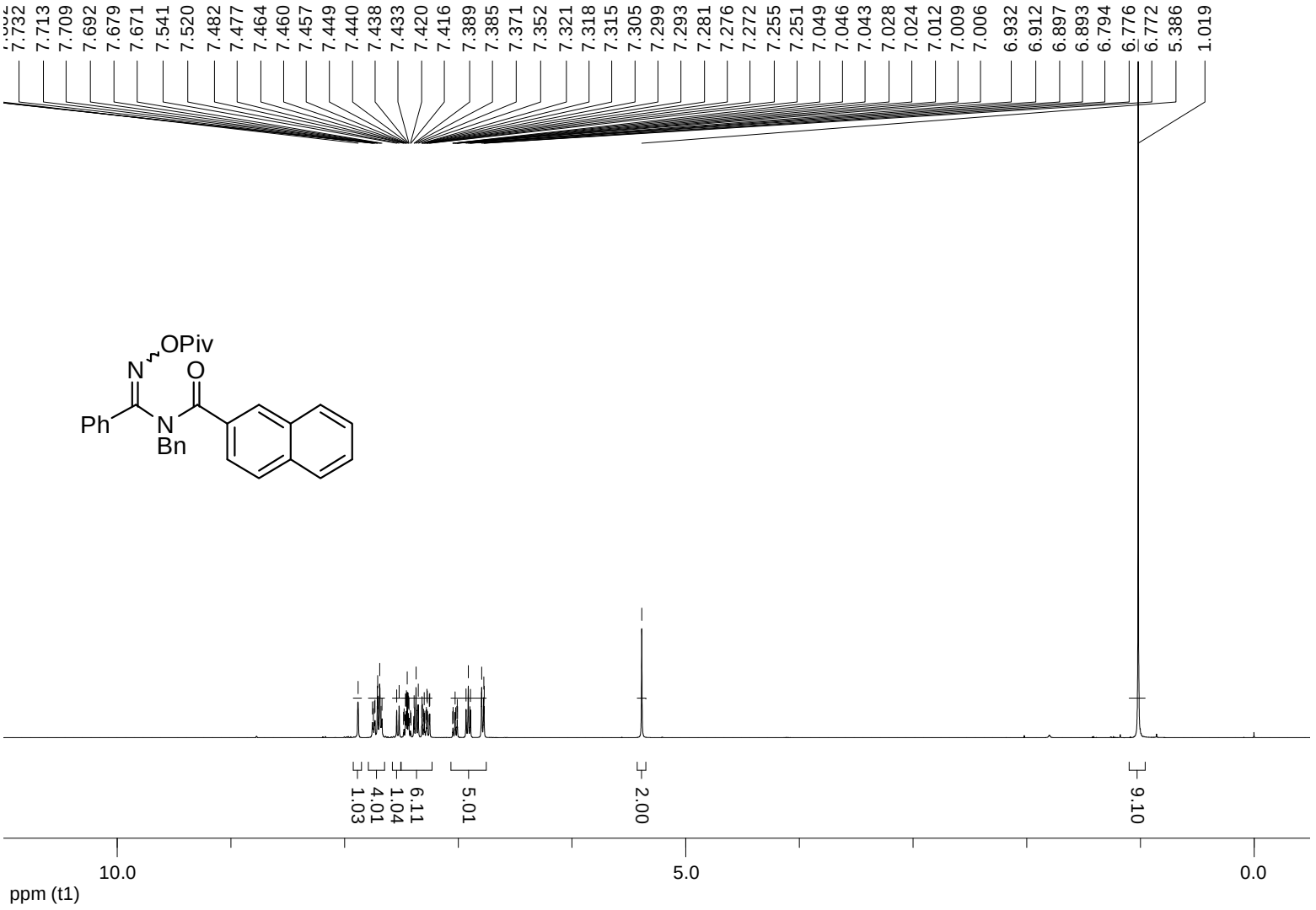
^{1}H NMR spectrum of **6l** (400 MHz, $CDCl_3$)



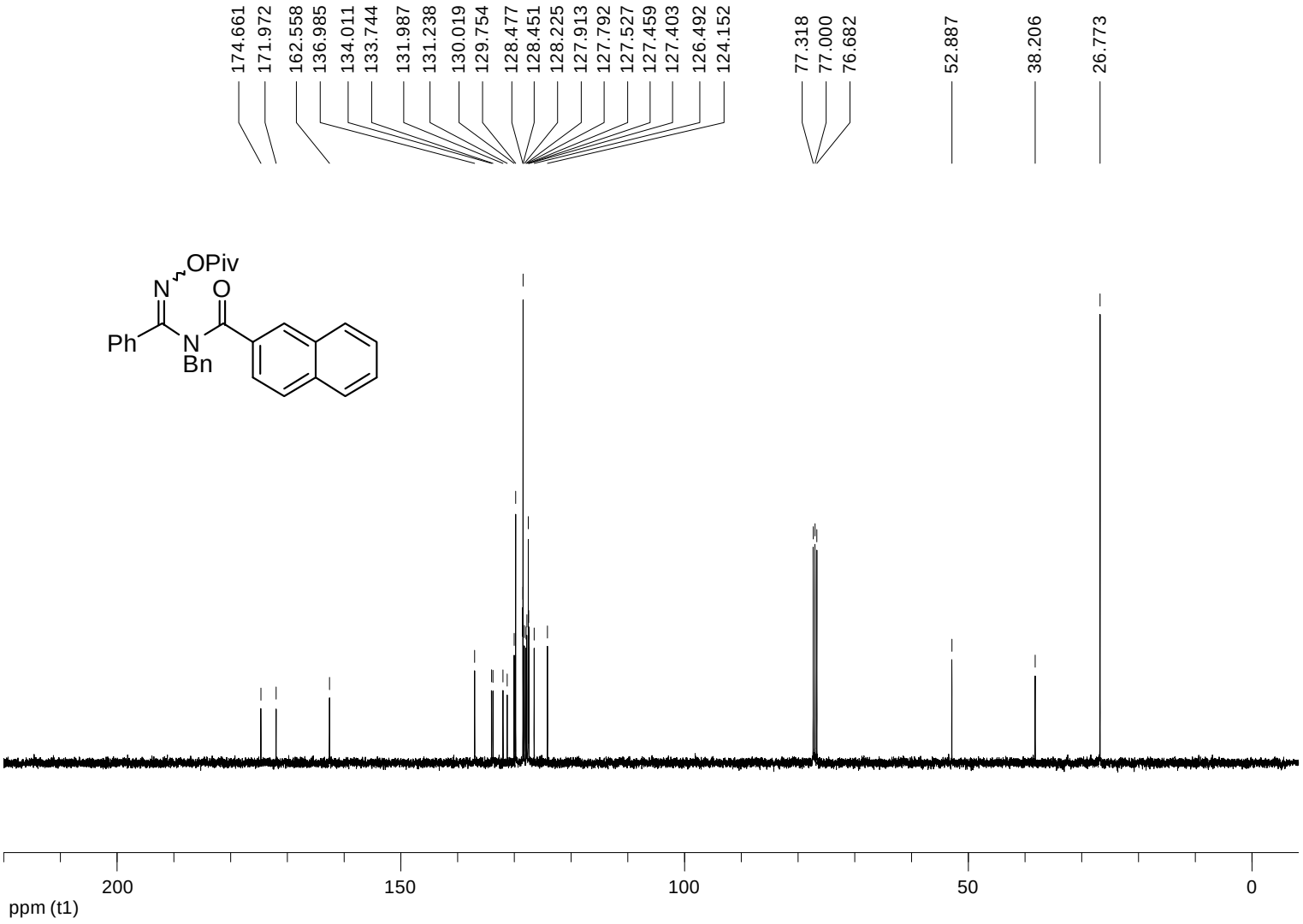
^{13}C NMR spectrum of **6l** (100 MHz, $CDCl_3$)



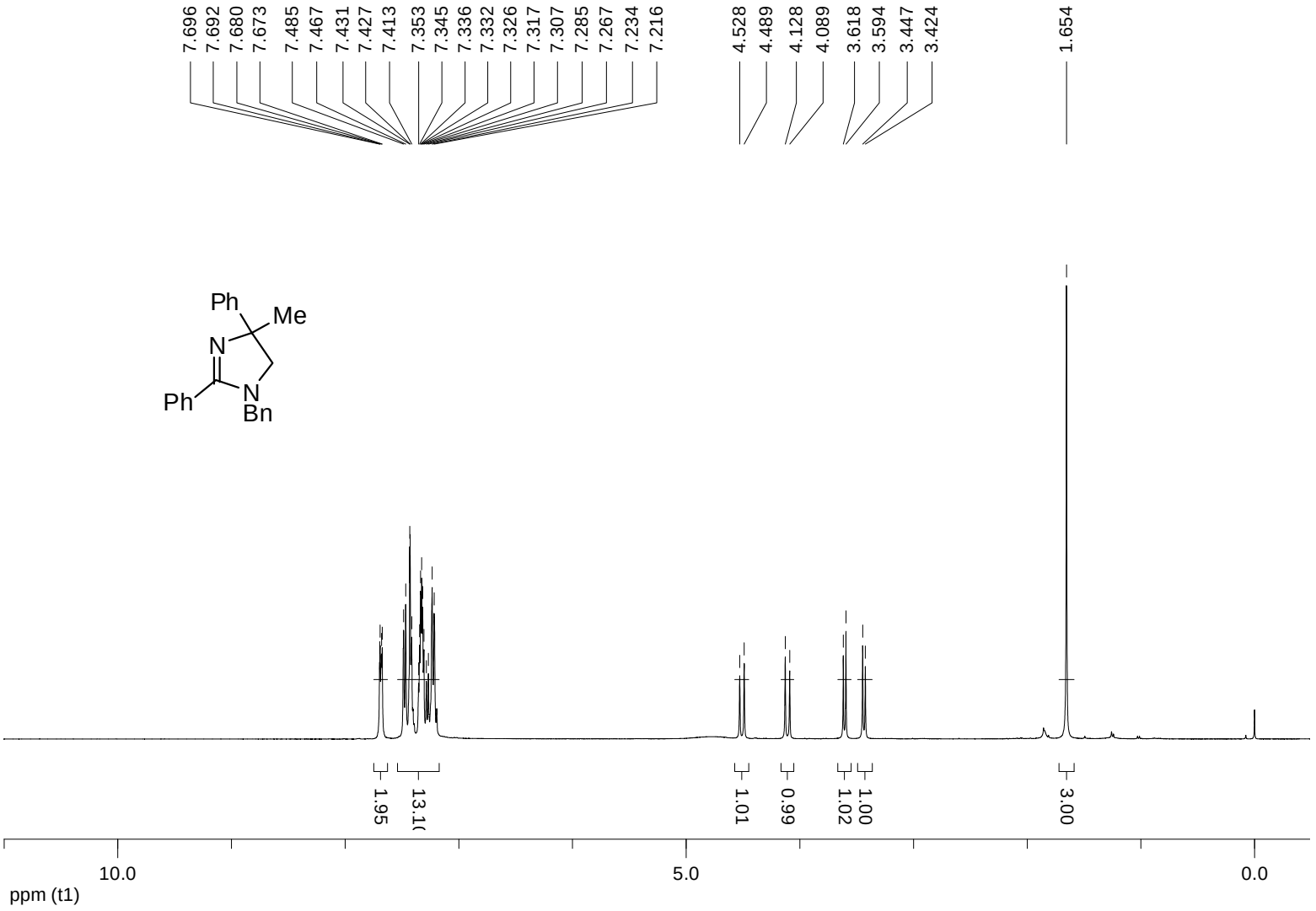
^{1}H NMR spectrum of **6m** (400 MHz, $CDCl_3$)



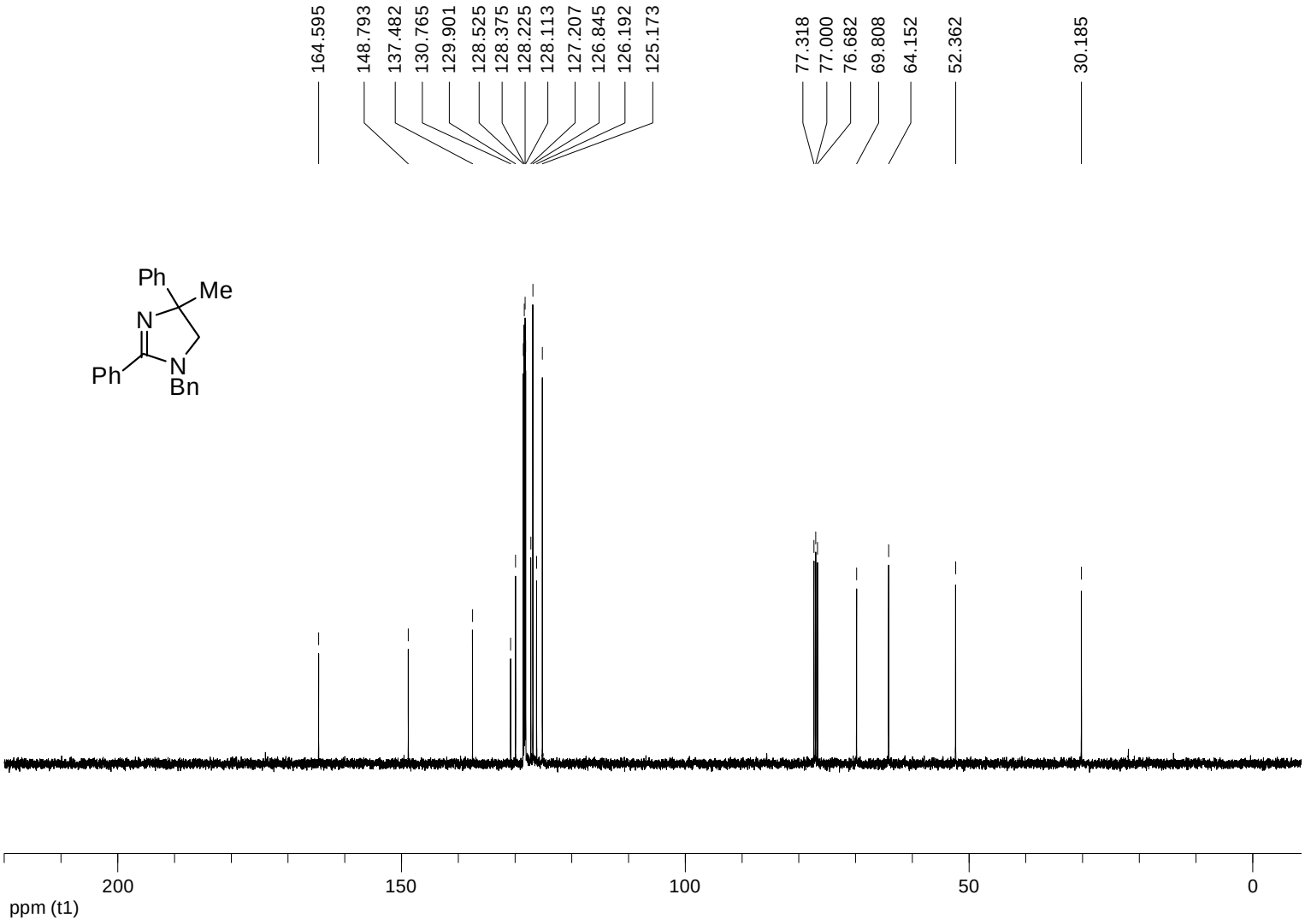
^{13}C NMR spectrum of **6m** (100 MHz, $CDCl_3$)



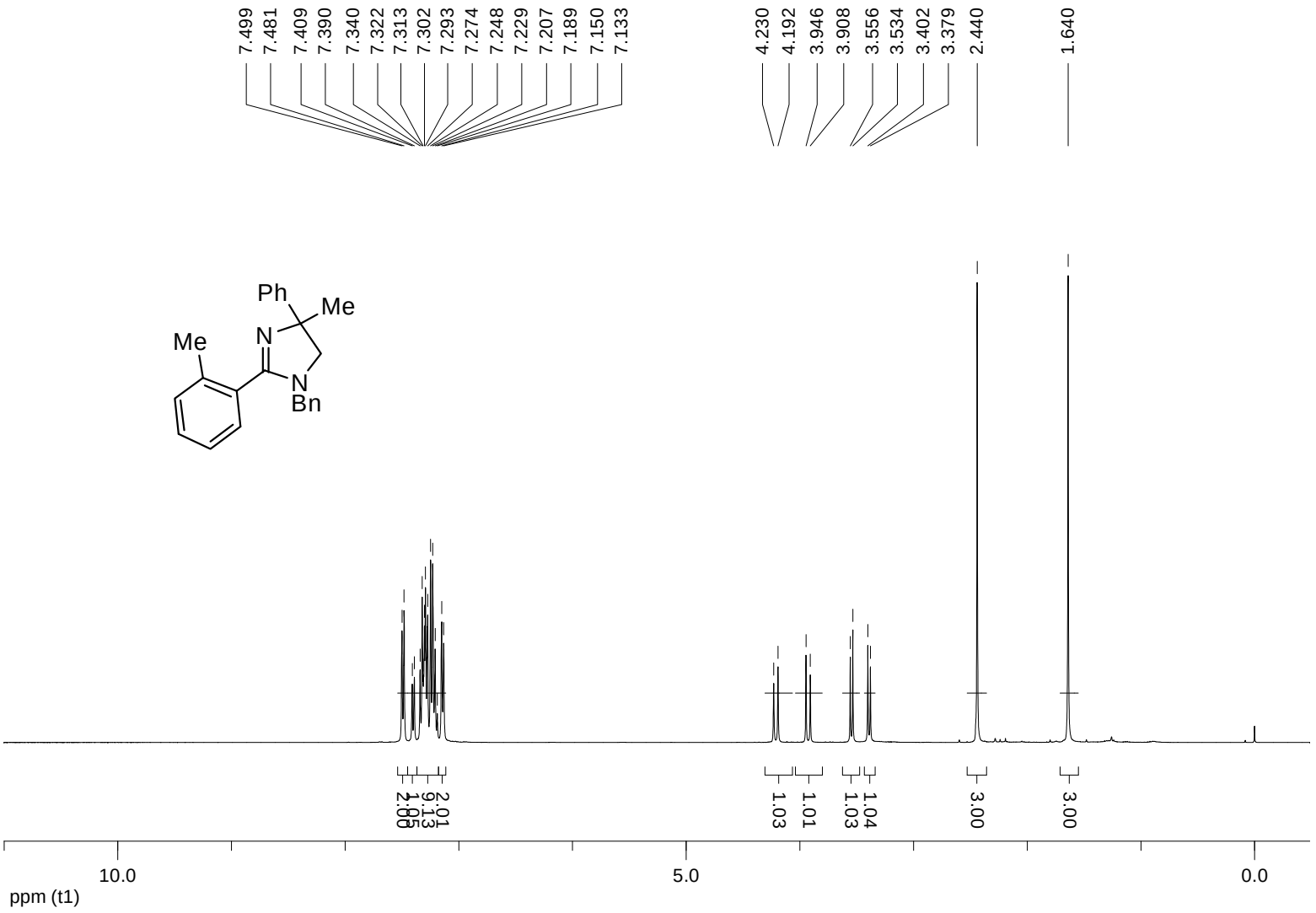
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



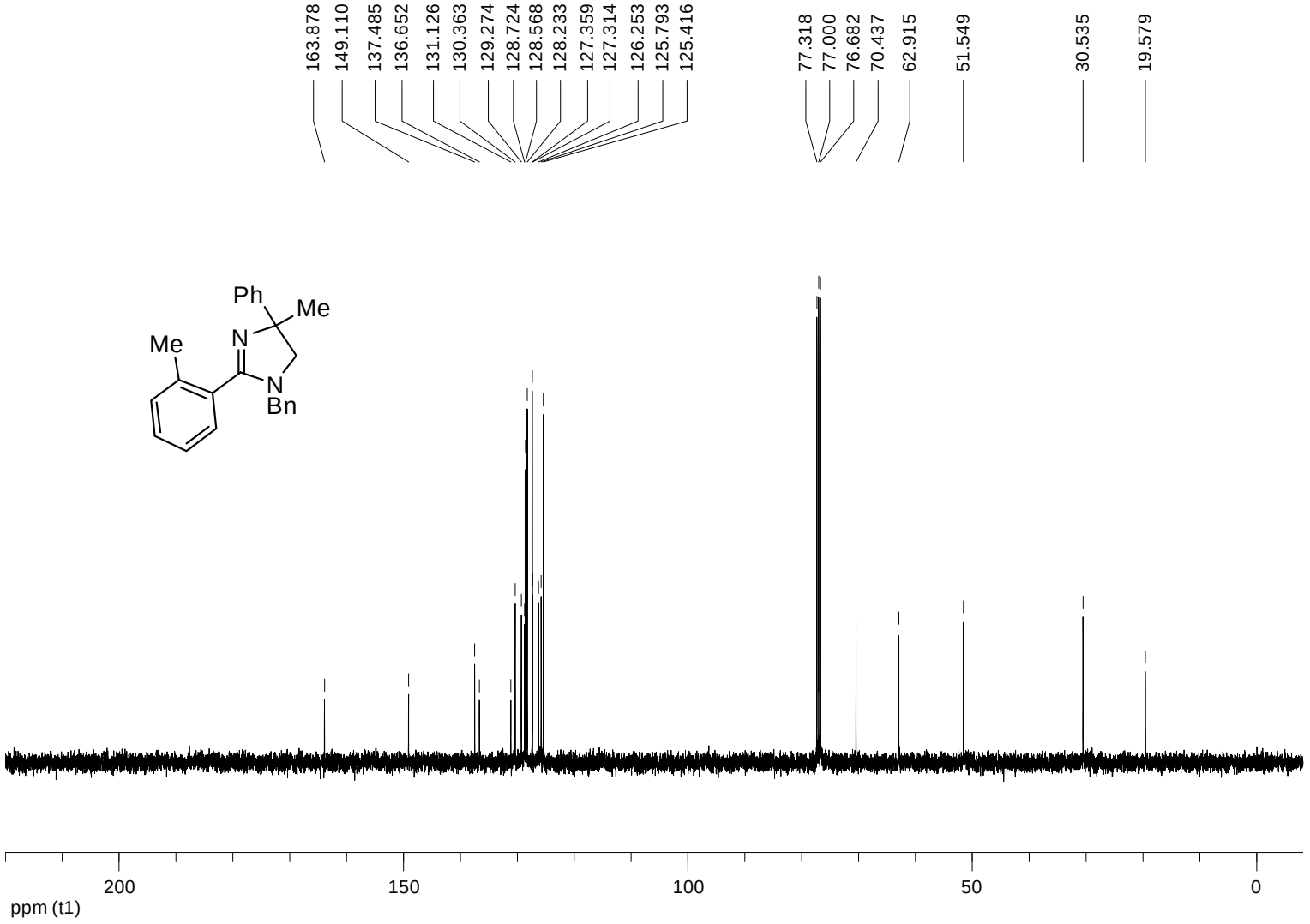
^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)



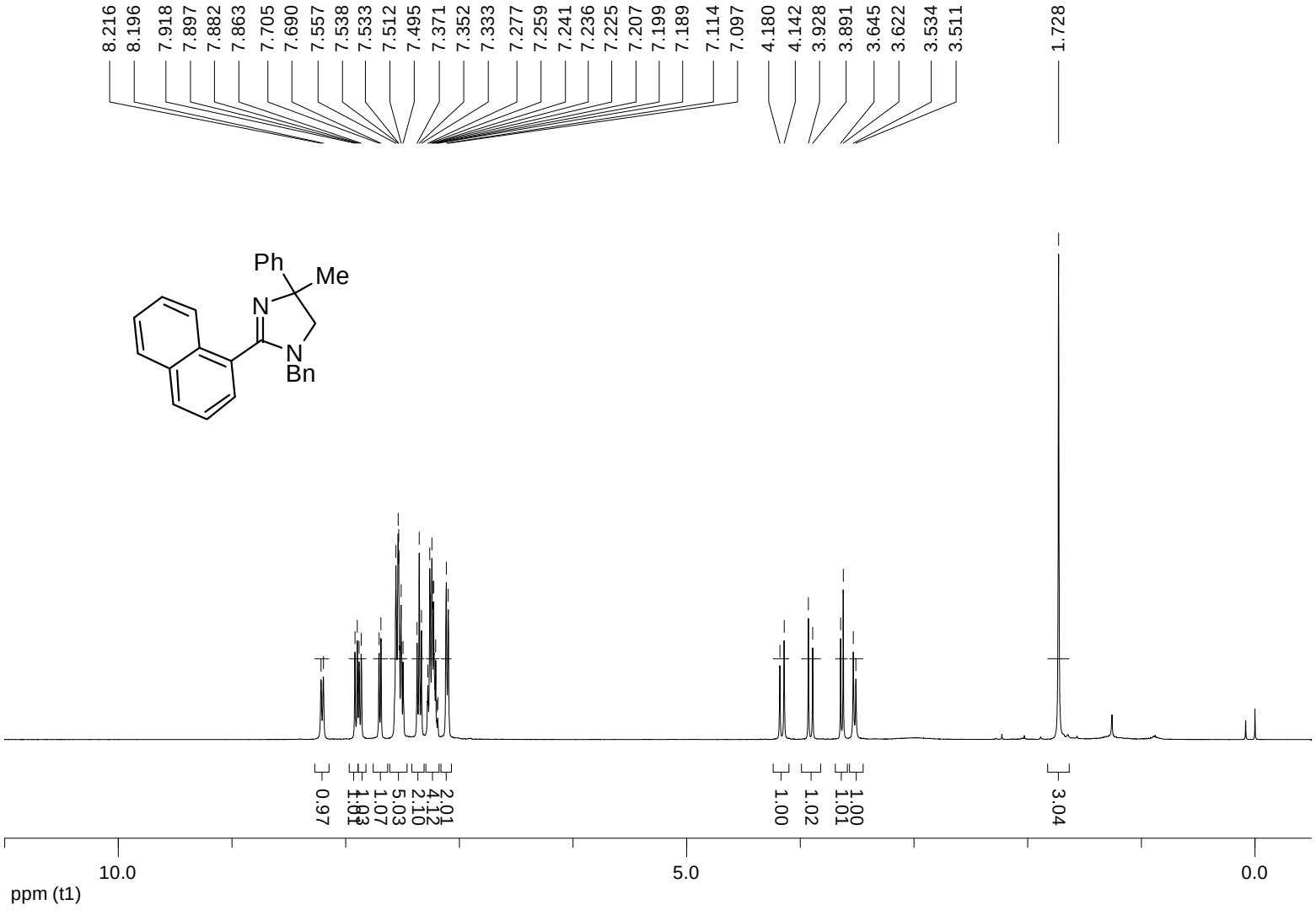
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



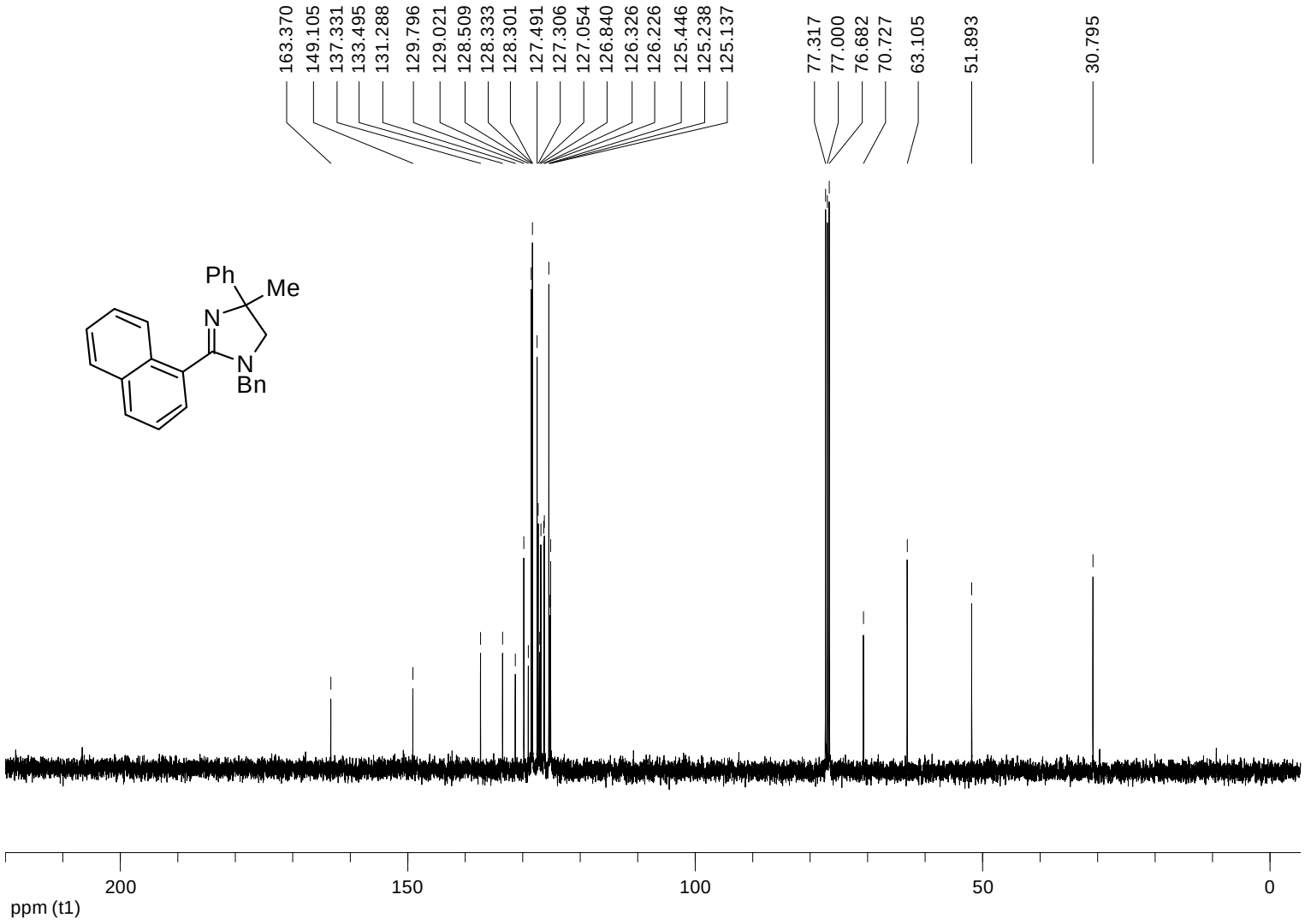
^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)



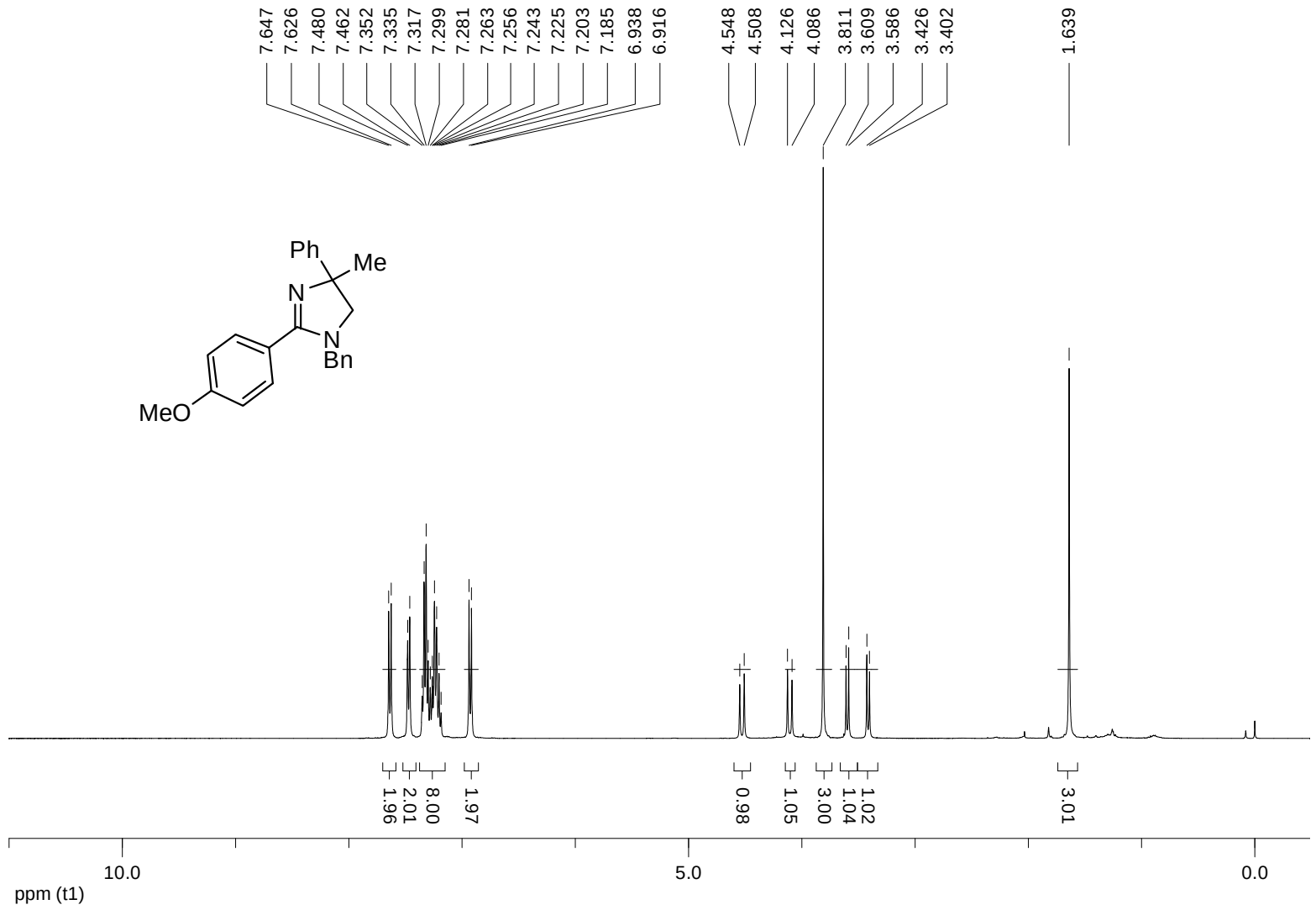
^{1}H NMR spectrum of **2c** (400 MHz, $CDCl_3$)



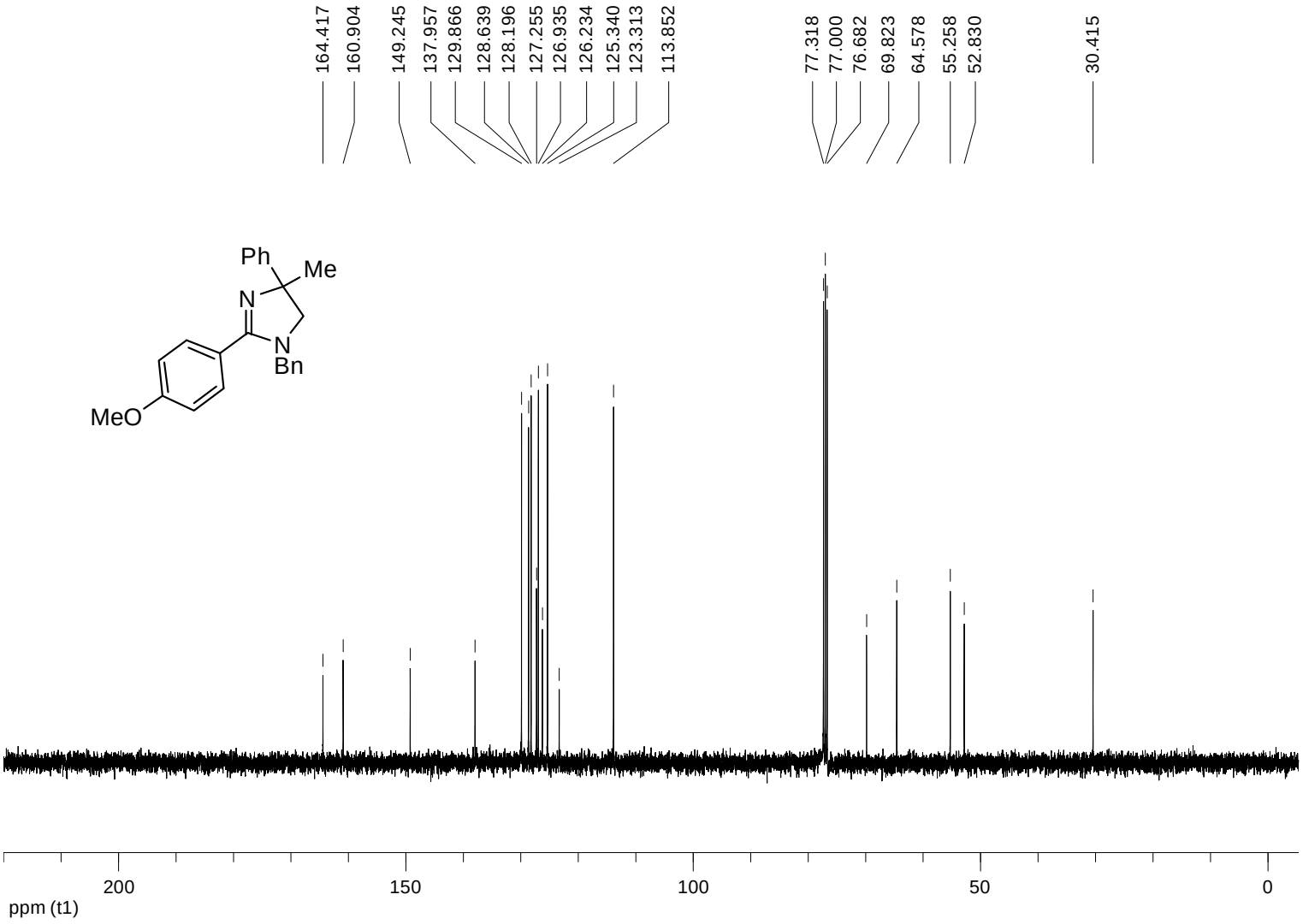
^{13}C NMR spectrum of **2c** (100 MHz, $CDCl_3$)



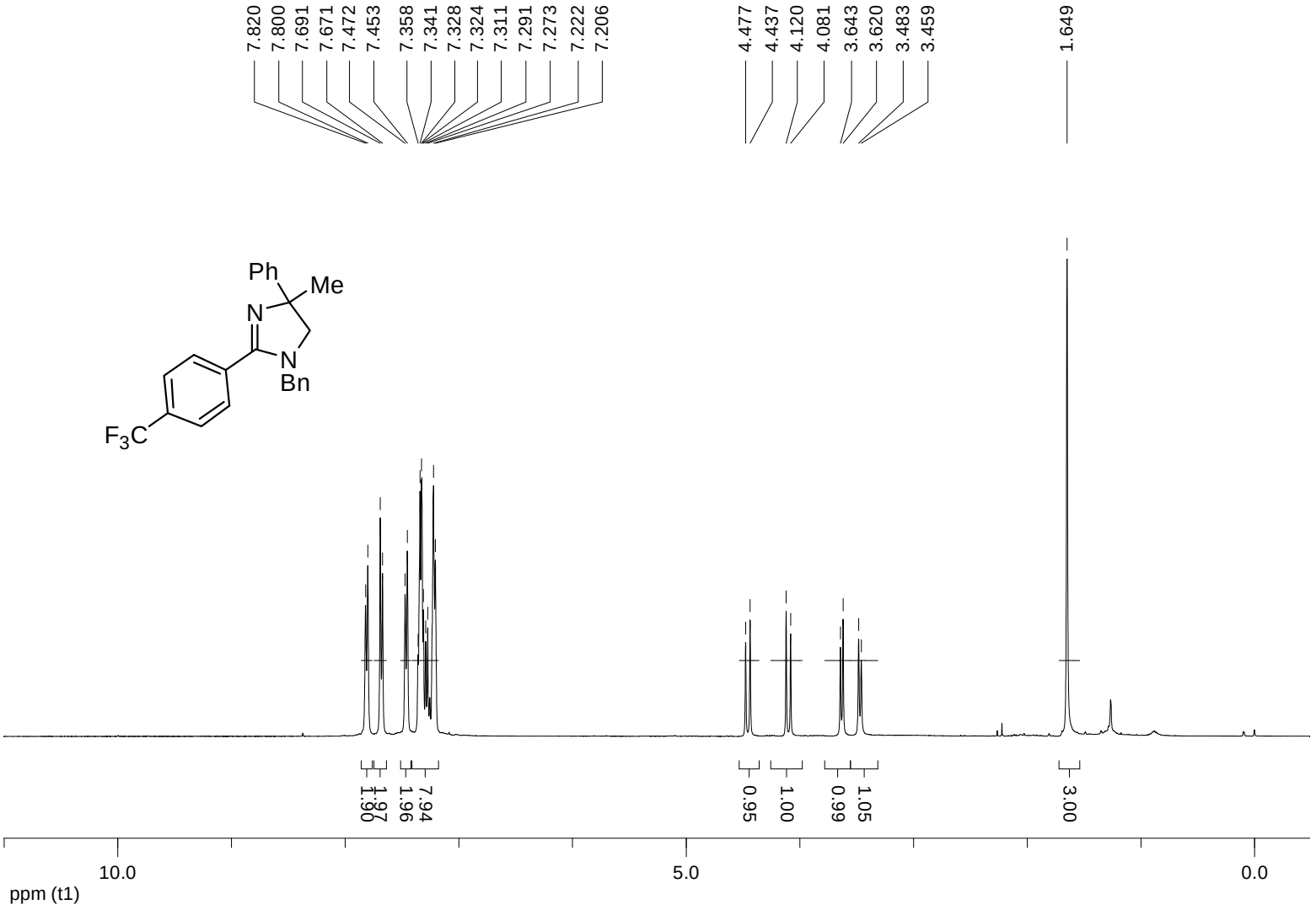
^{1}H NMR spectrum of **2d** (400 MHz, $CDCl_3$)



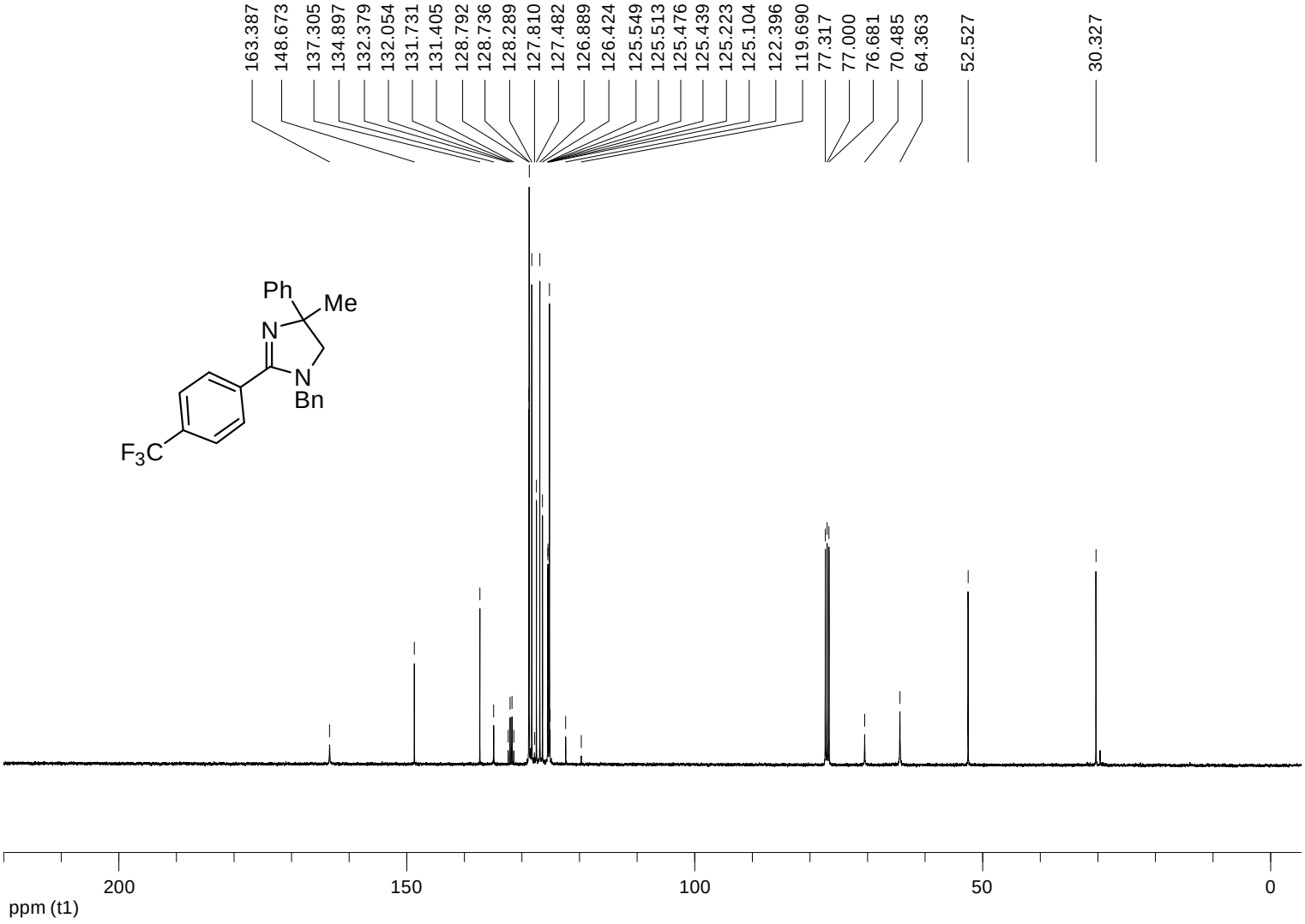
^{13}C NMR spectrum of **2d** (100 MHz, $CDCl_3$)



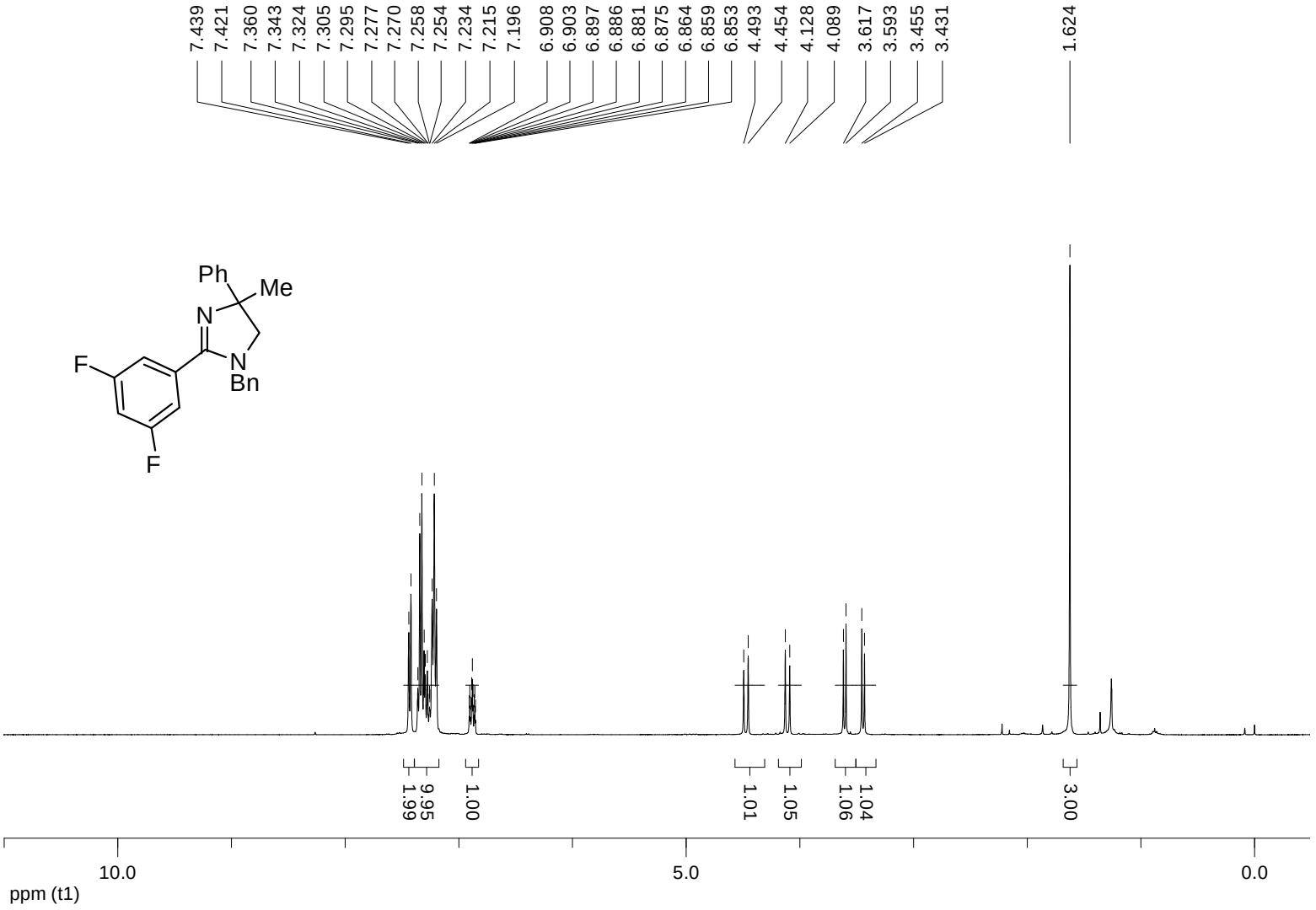
^{1}H NMR spectrum of **2e** (400 MHz, $CDCl_3$)



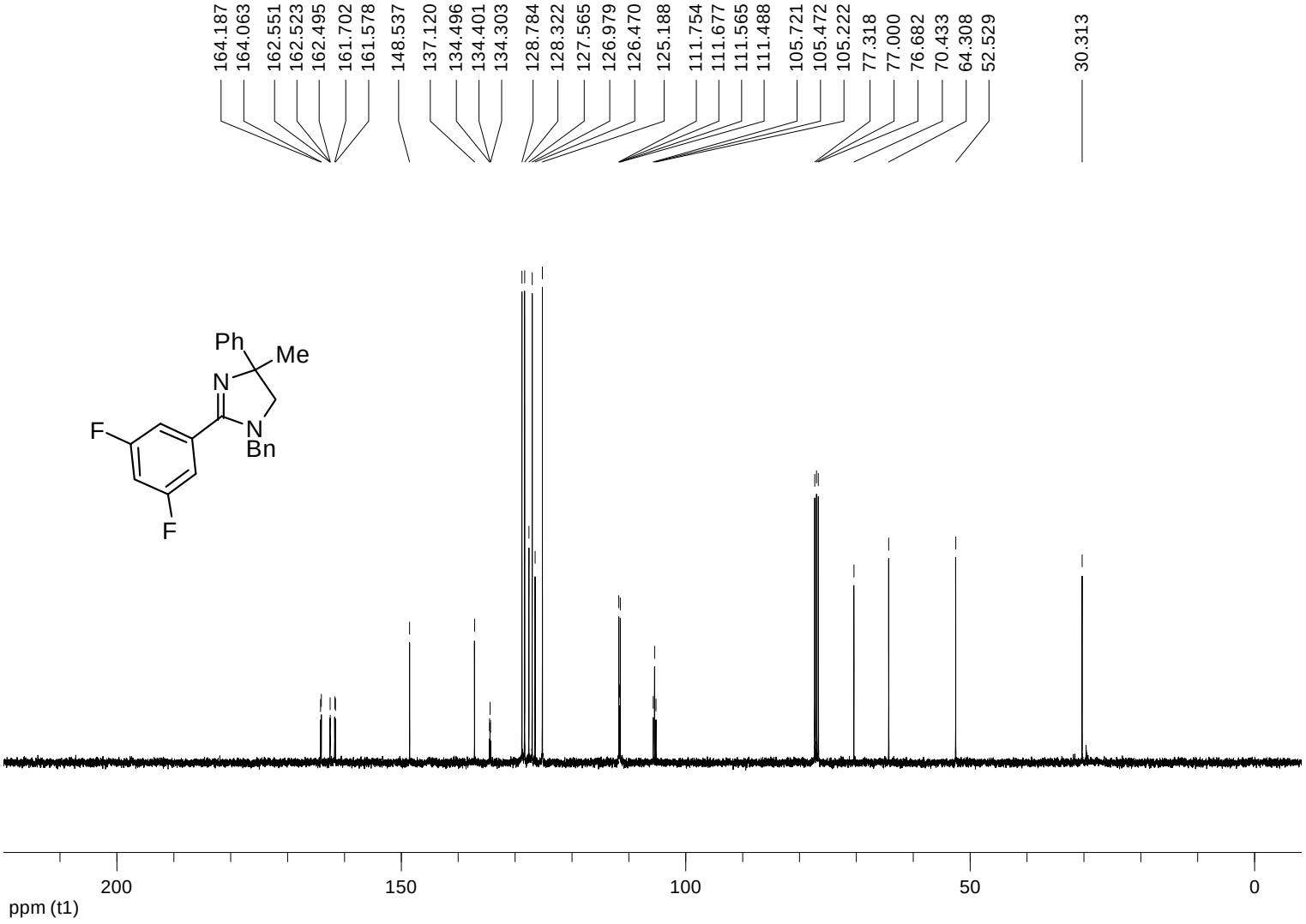
^{13}C NMR spectrum of **2e** (100 MHz, $CDCl_3$)



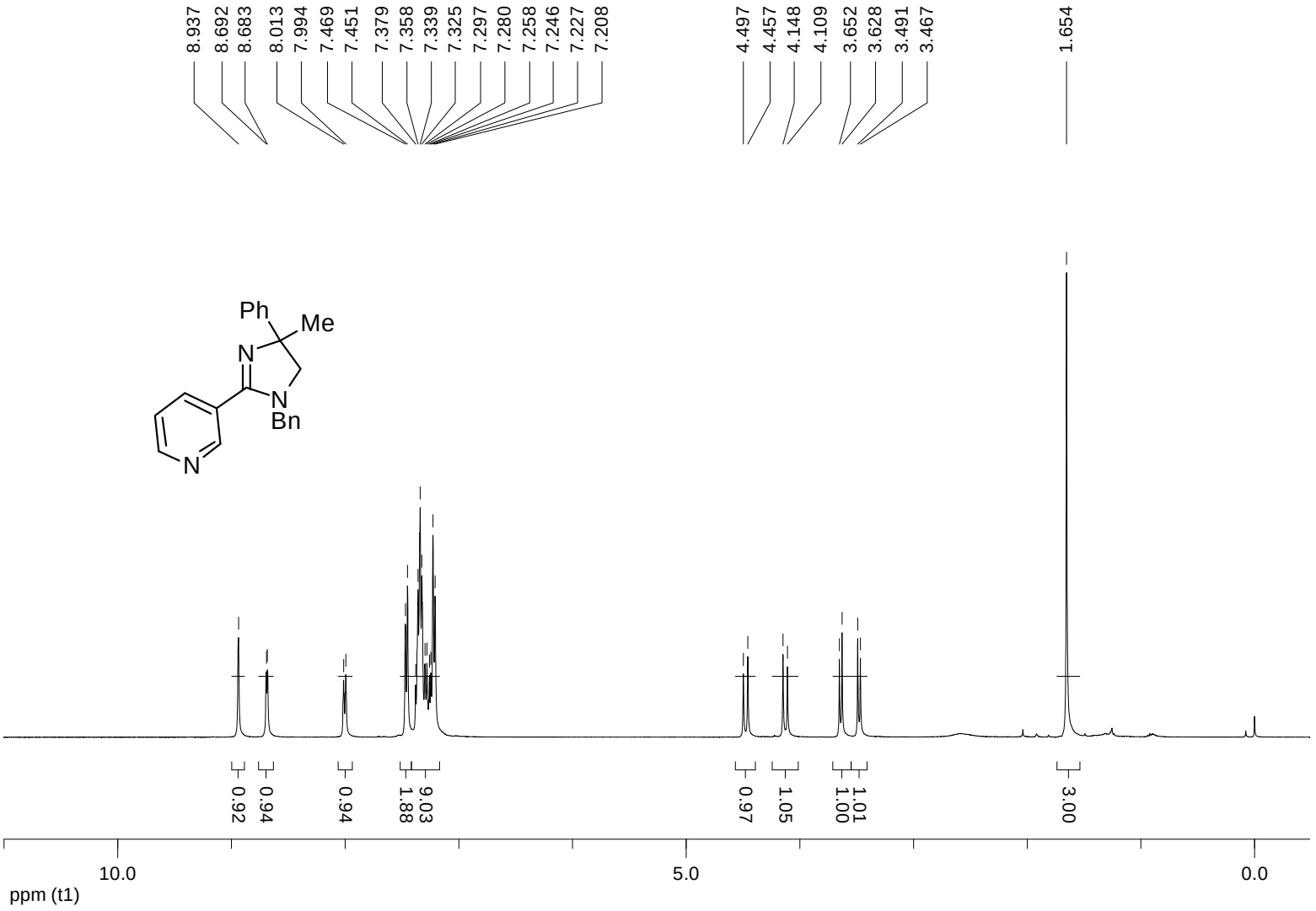
^{1}H NMR spectrum of **2f** (400 MHz, $CDCl_3$)



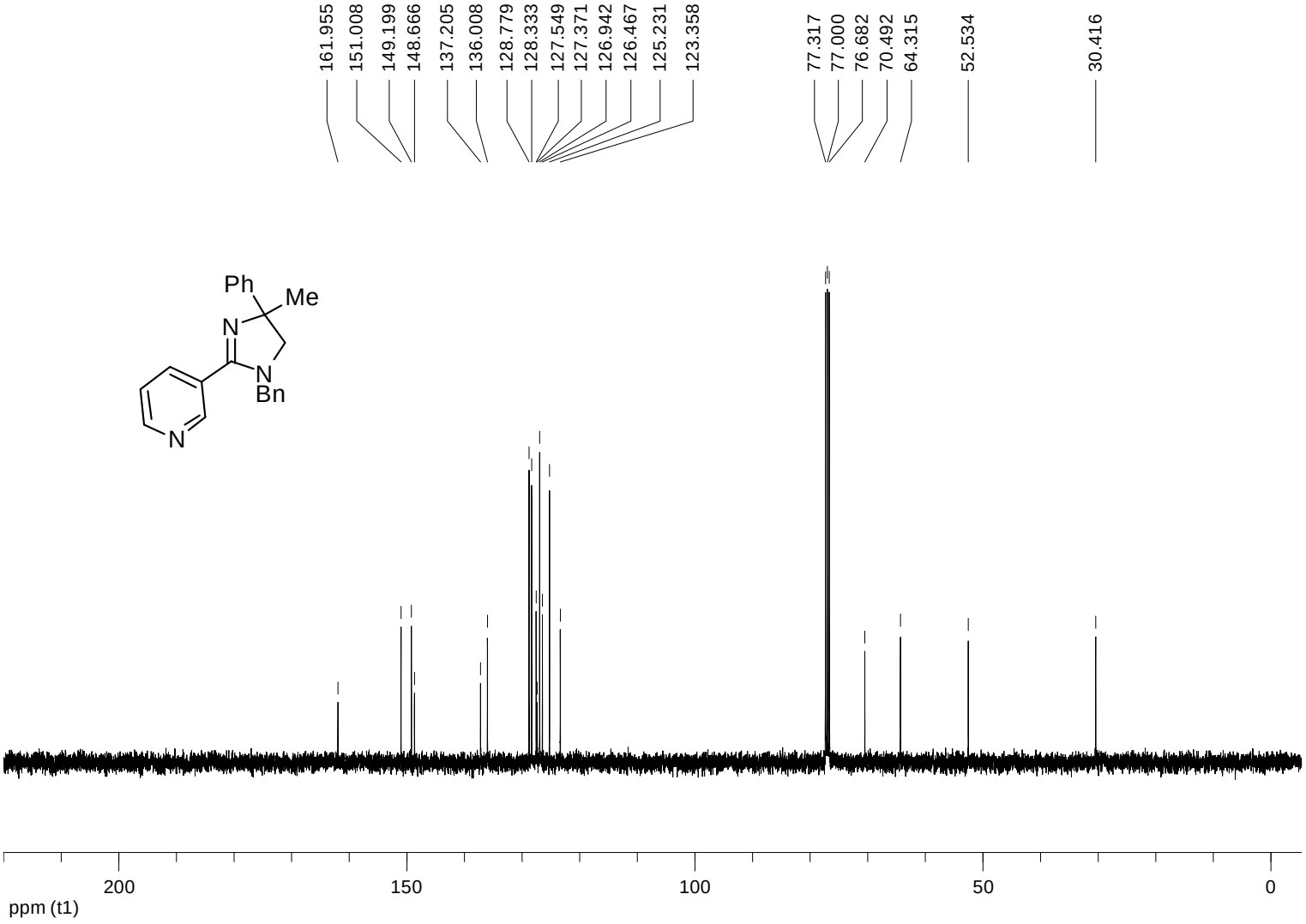
^{13}C NMR spectrum of **2f** (100 MHz, $CDCl_3$)



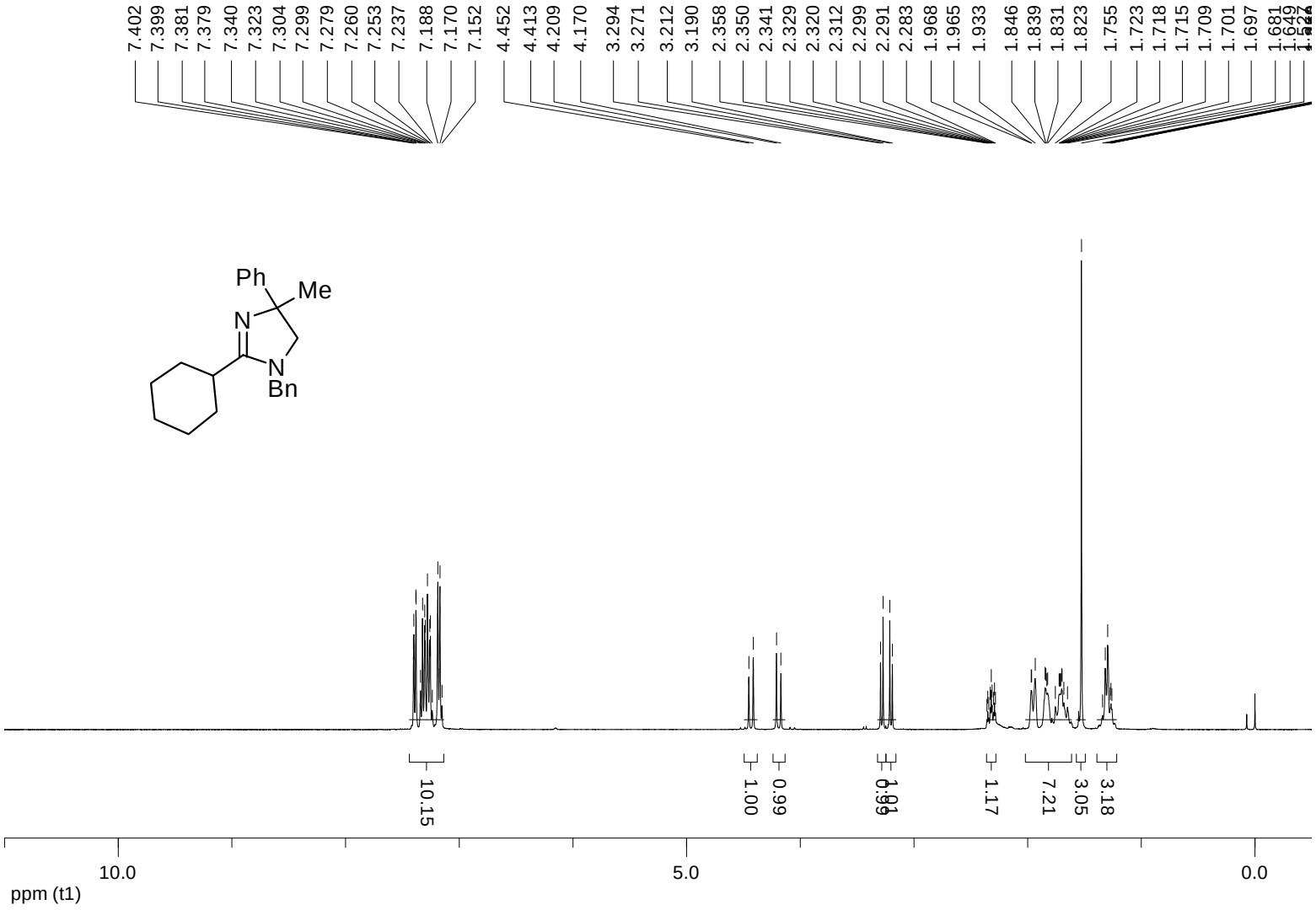
^{1}H NMR spectrum of **2g** (400 MHz, $CDCl_3$)



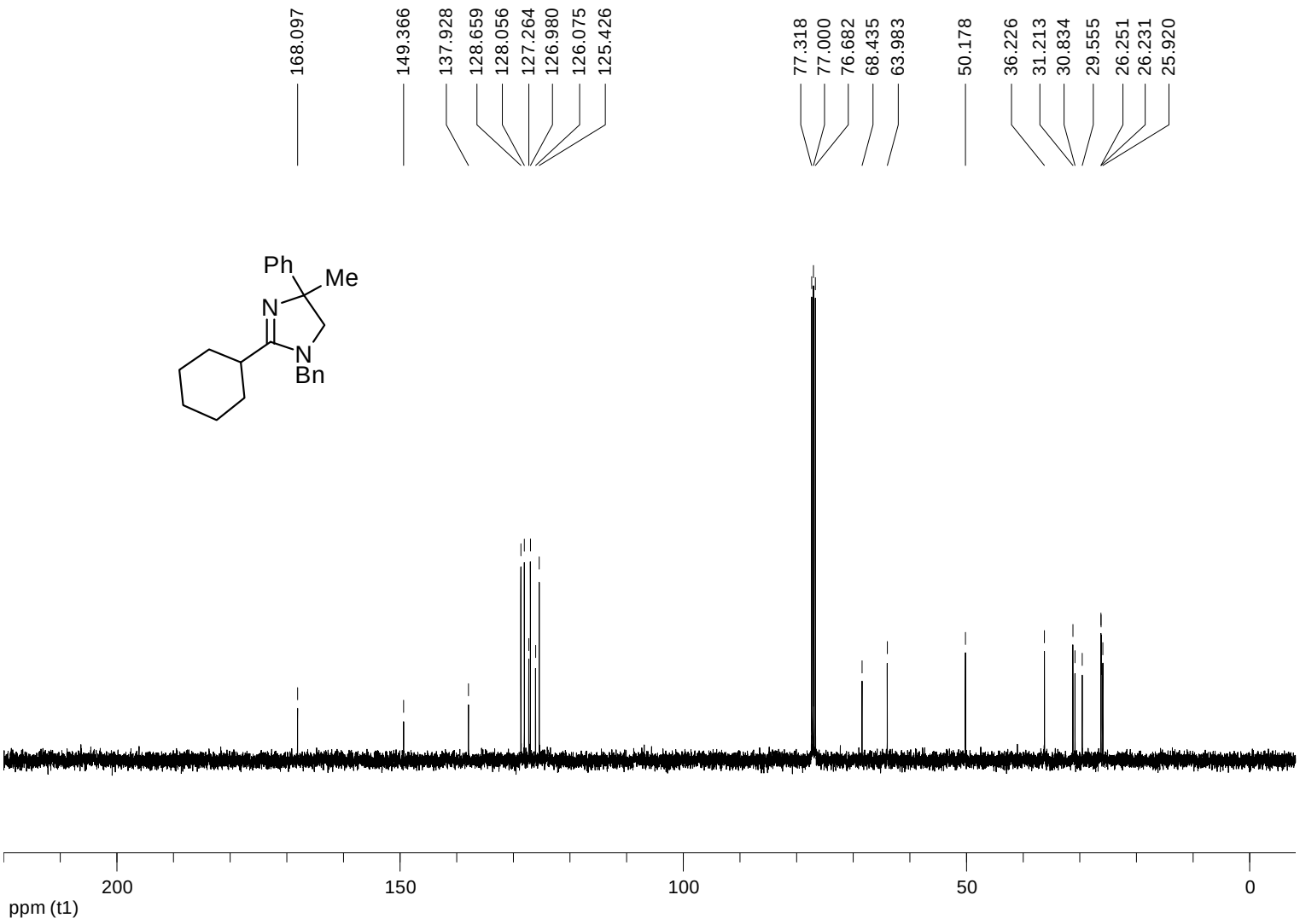
^{13}C NMR spectrum of **2g** (100 MHz, $CDCl_3$)



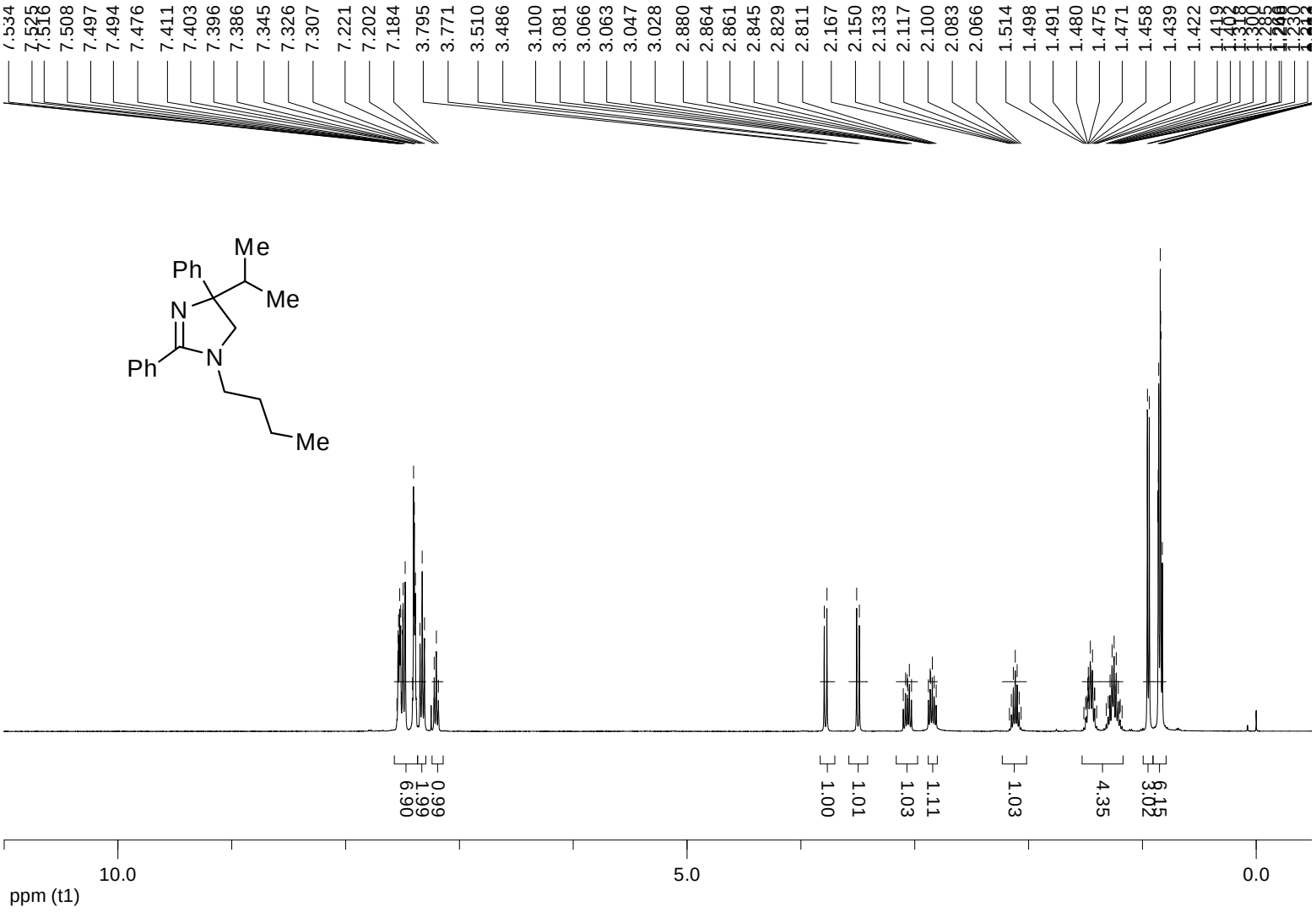
^{1}H NMR spectrum of **2h** (400 MHz, $CDCl_3$)



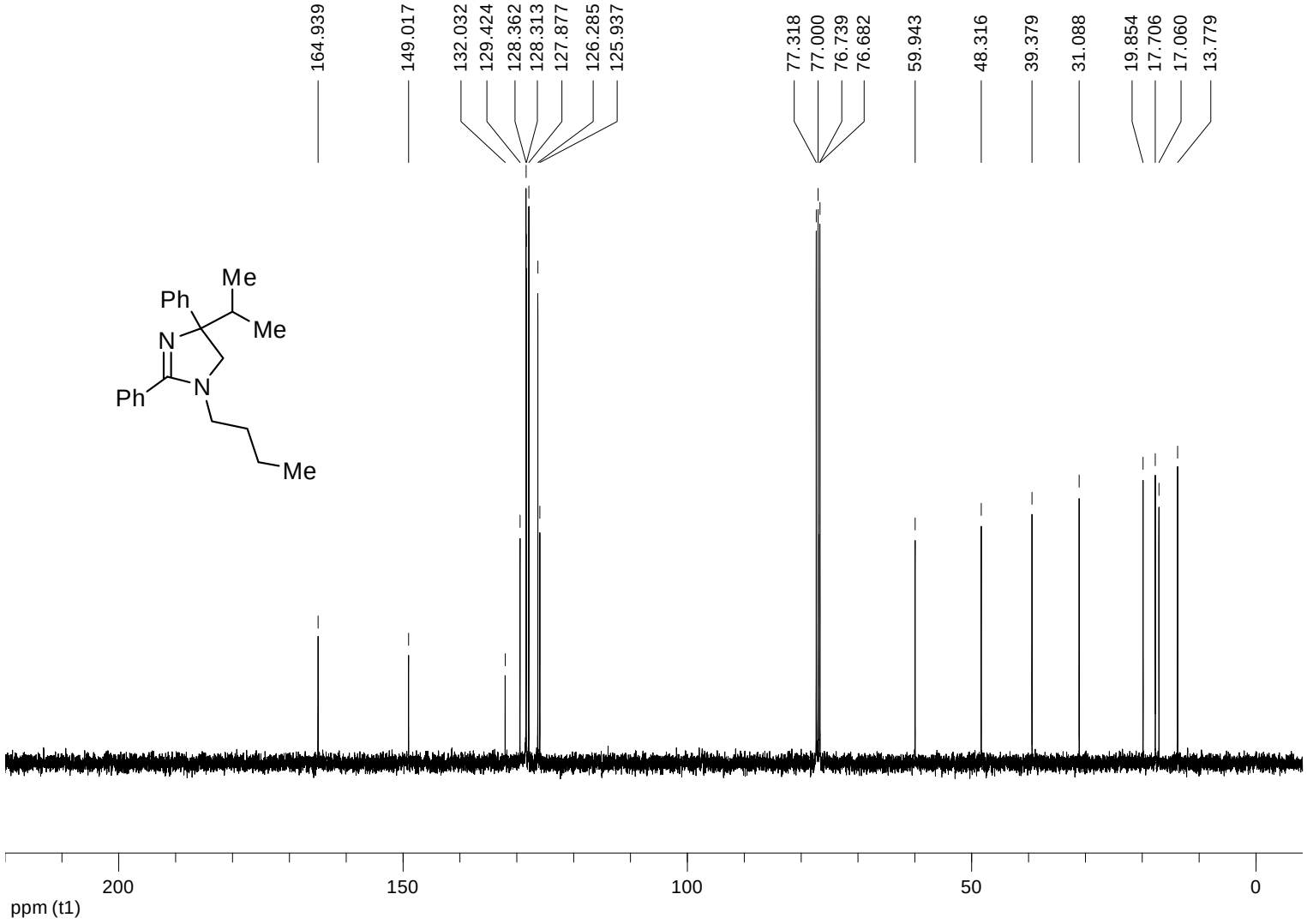
^{13}C NMR spectrum of **2h** (100 MHz, $CDCl_3$)



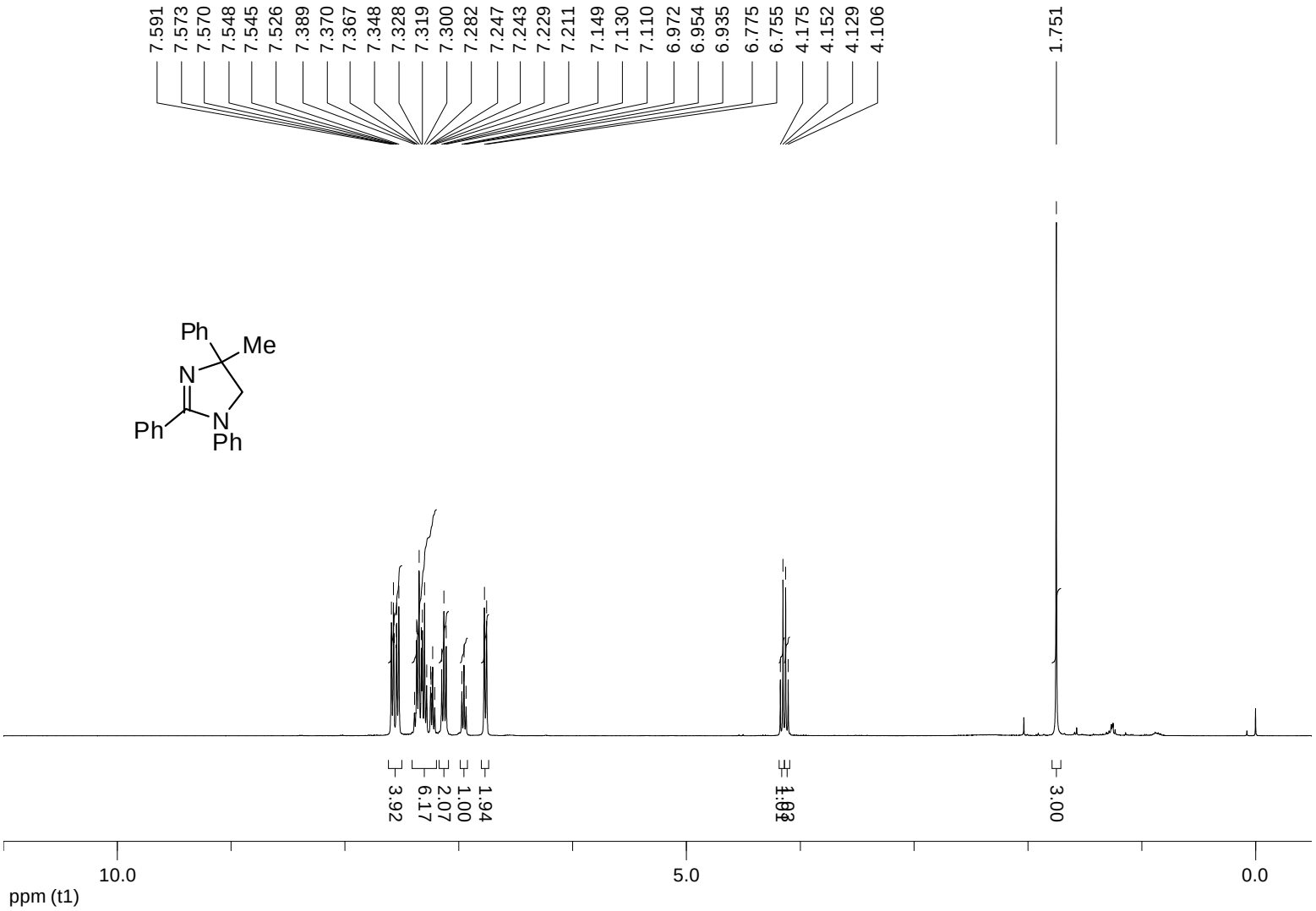
^{1}H NMR spectrum of **2i** (400 MHz, $CDCl_3$)



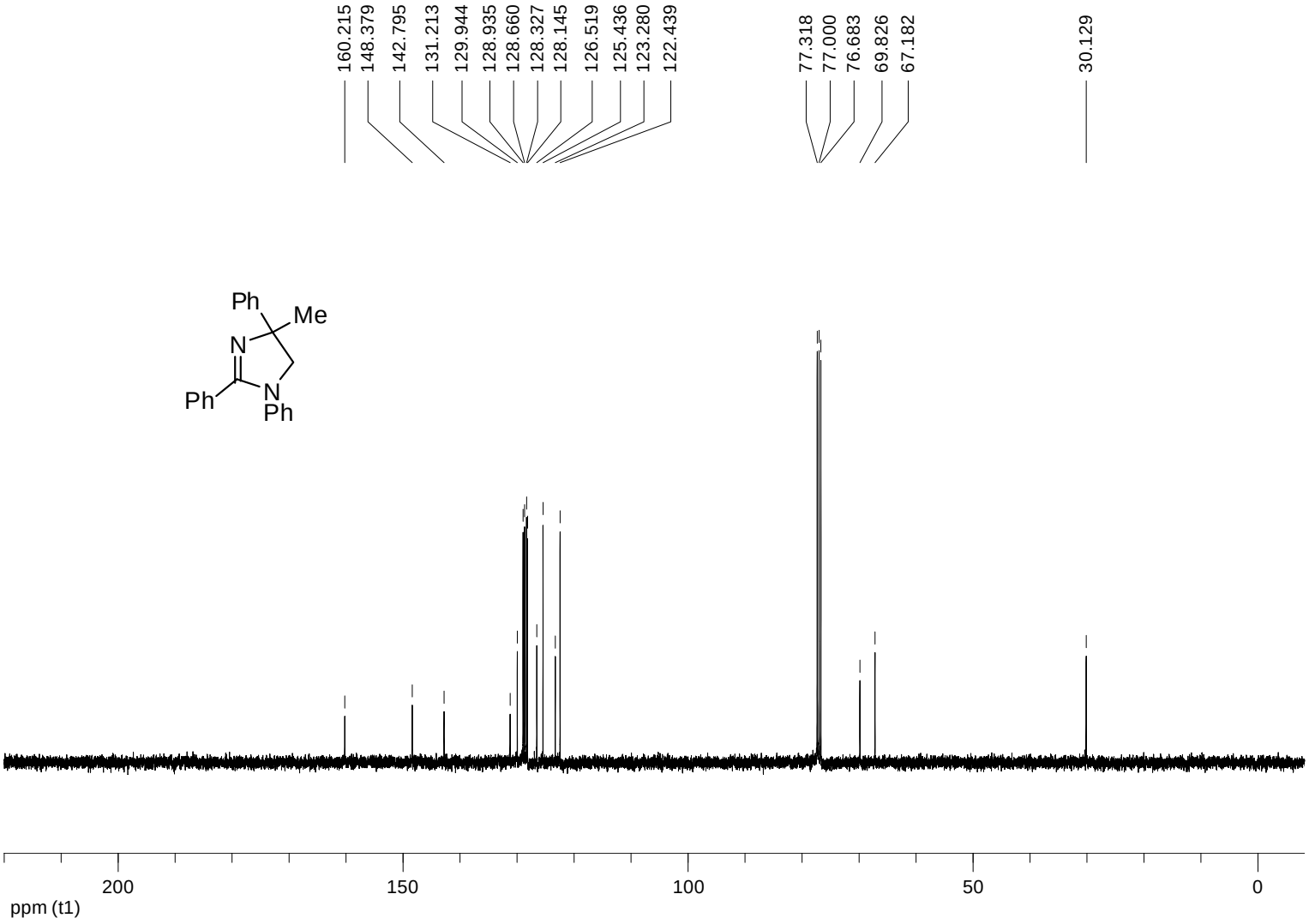
^{13}C NMR spectrum of **2i** (100 MHz, $CDCl_3$)



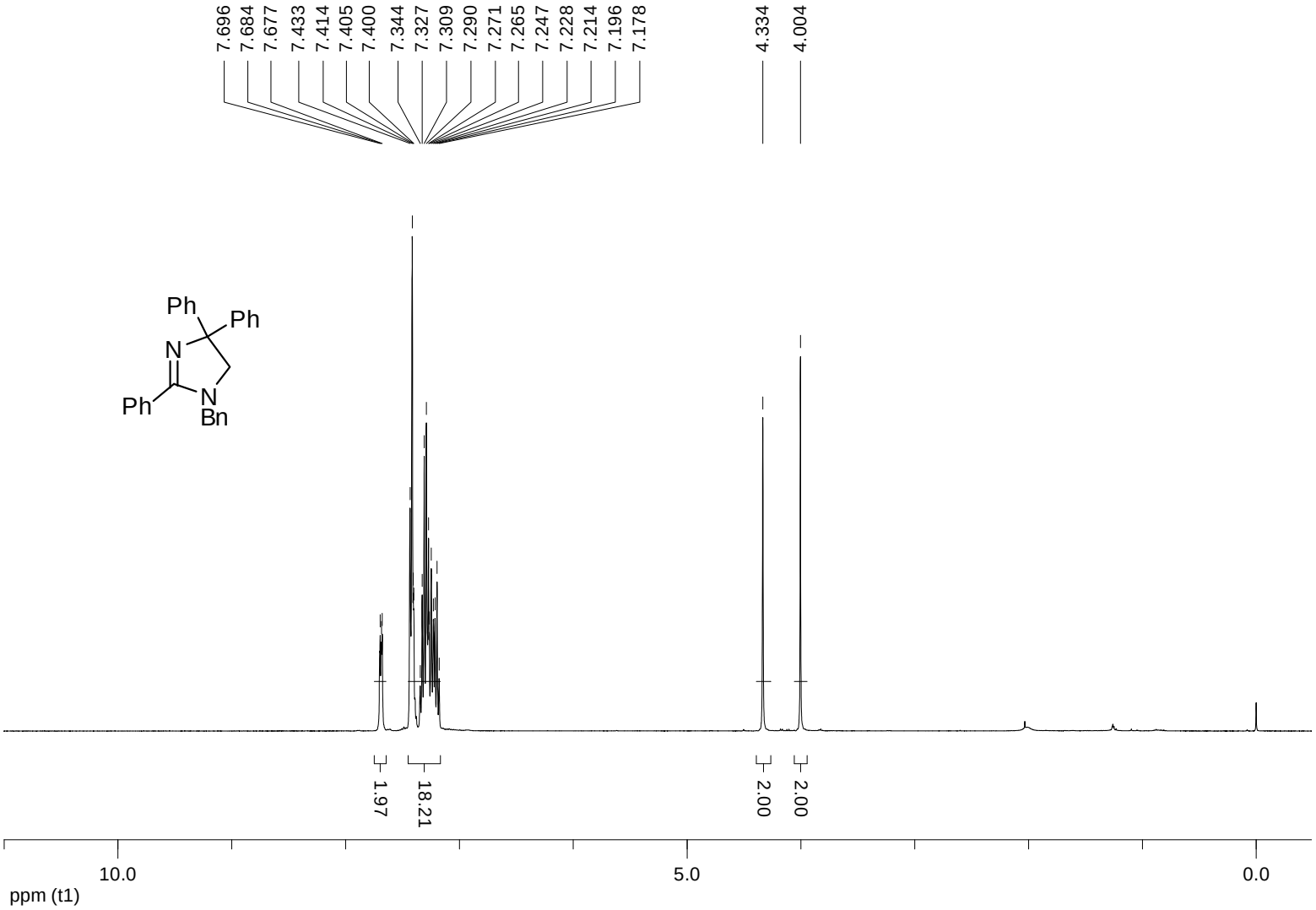
^{1}H NMR spectrum of **2j** (400 MHz, $CDCl_3$)



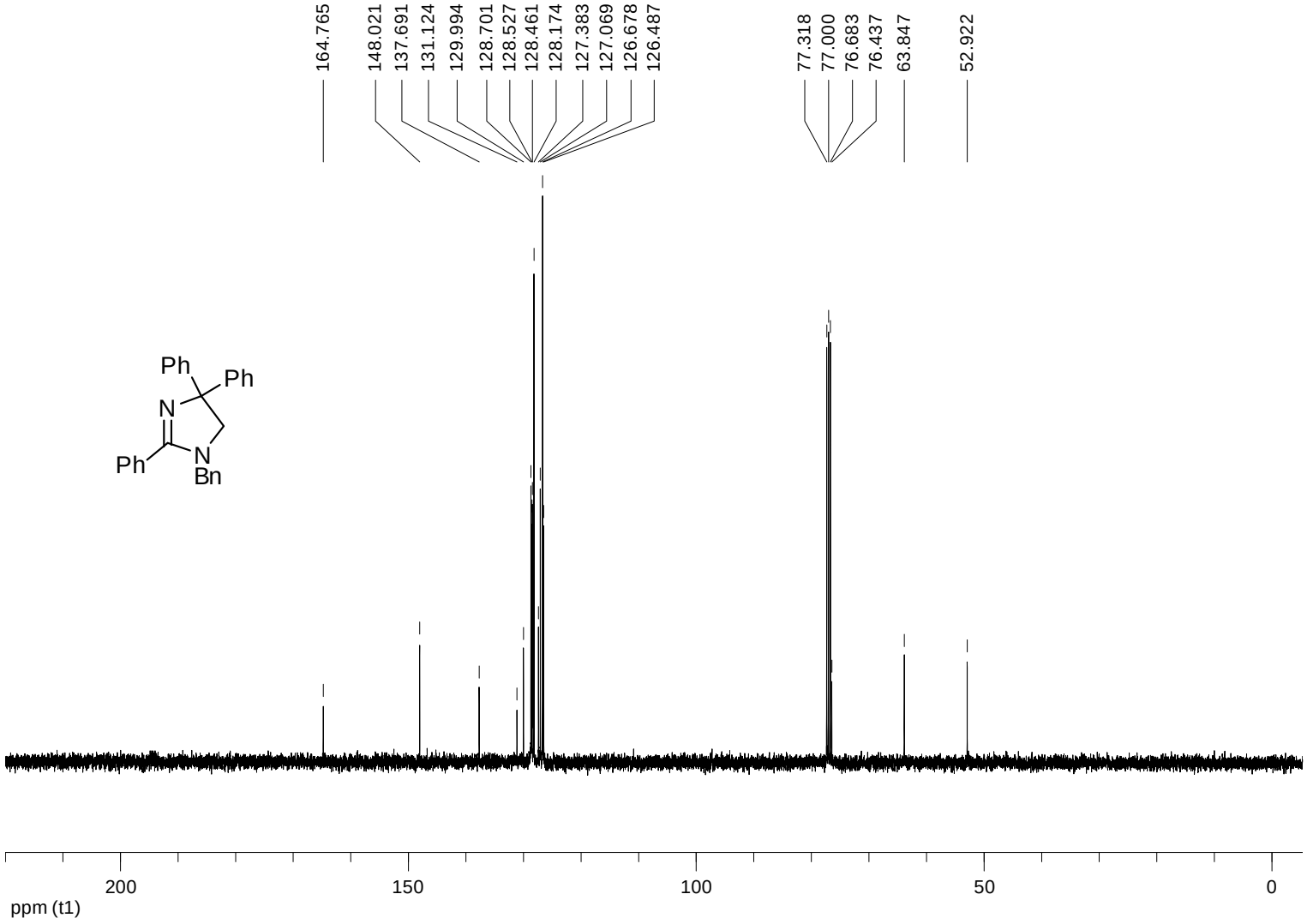
^{13}C NMR spectrum of **2j** (100 MHz, $CDCl_3$)



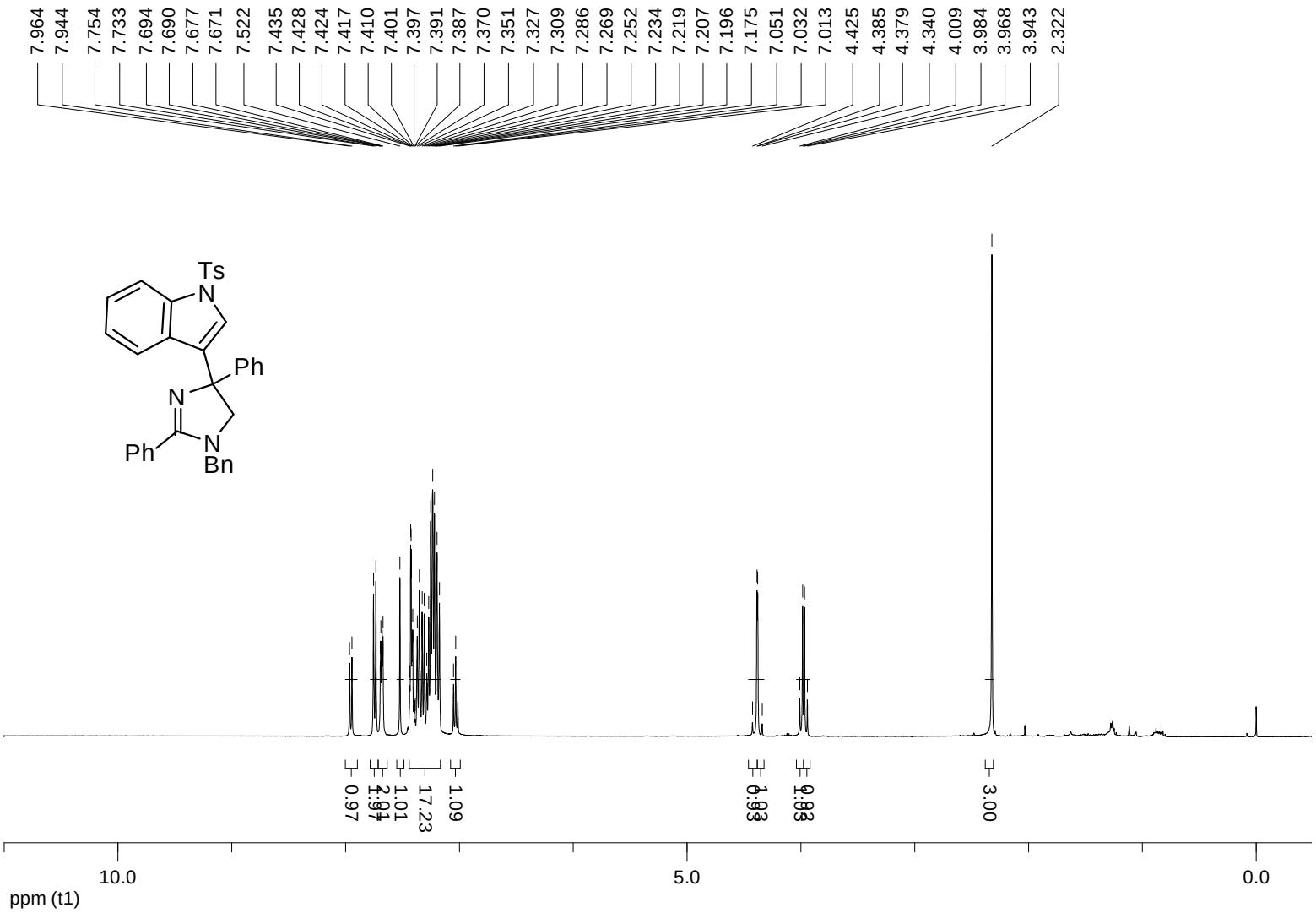
^{1}H NMR spectrum of **2k** (400 MHz, $CDCl_3$)



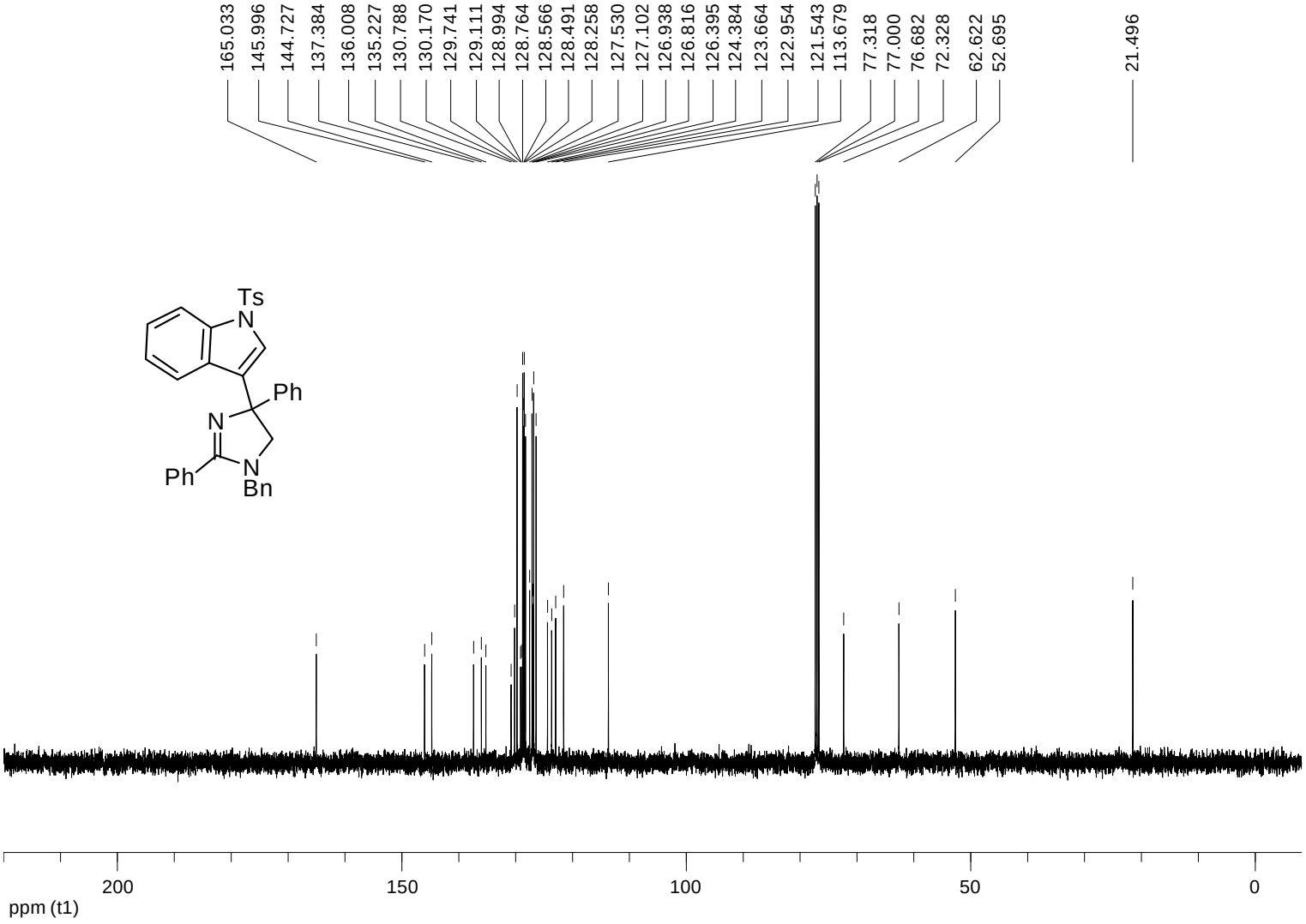
^{13}C NMR spectrum of **2k** (100 MHz, $CDCl_3$)



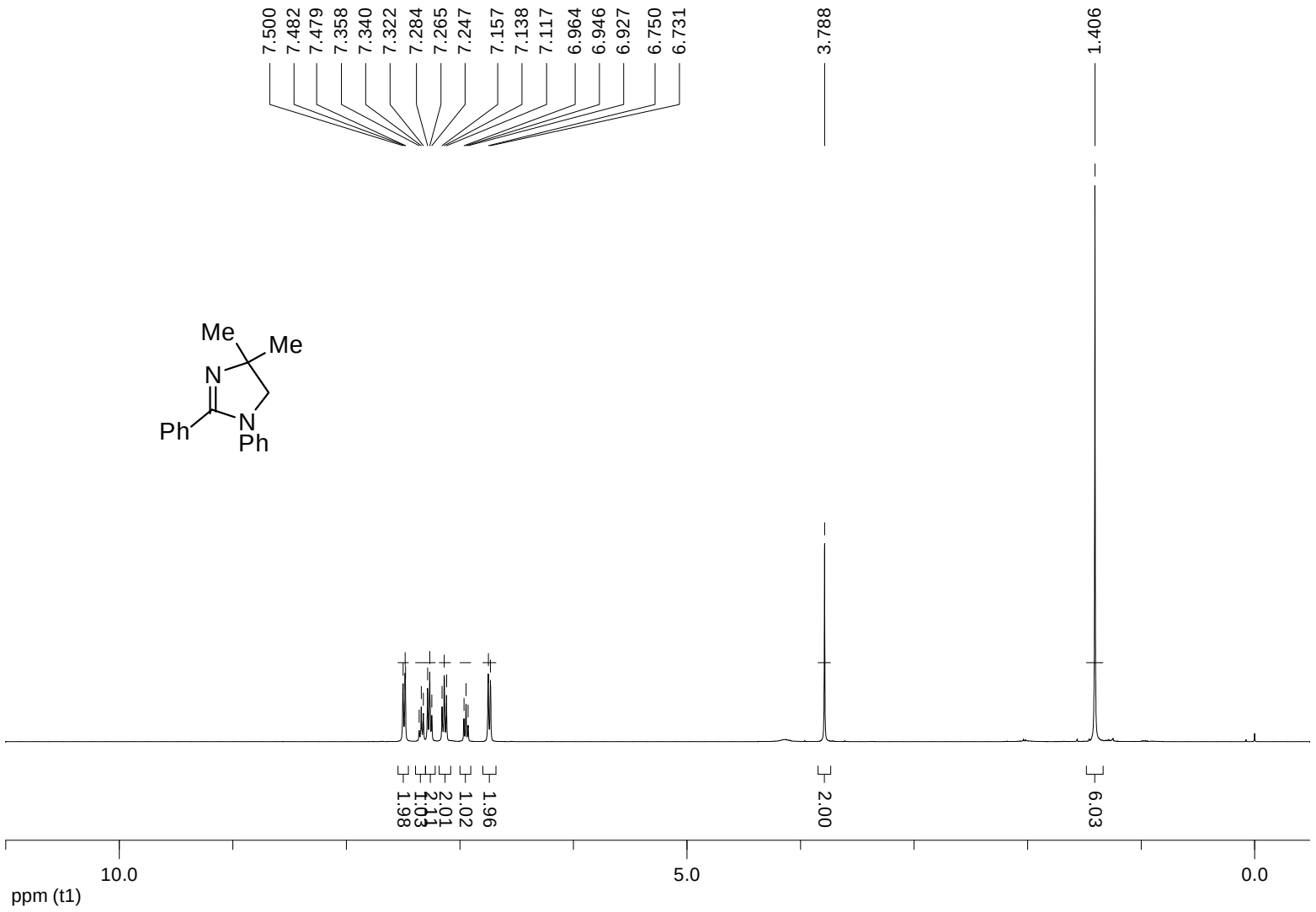
^{1}H NMR spectrum of **2l** (400 MHz, $CDCl_3$)



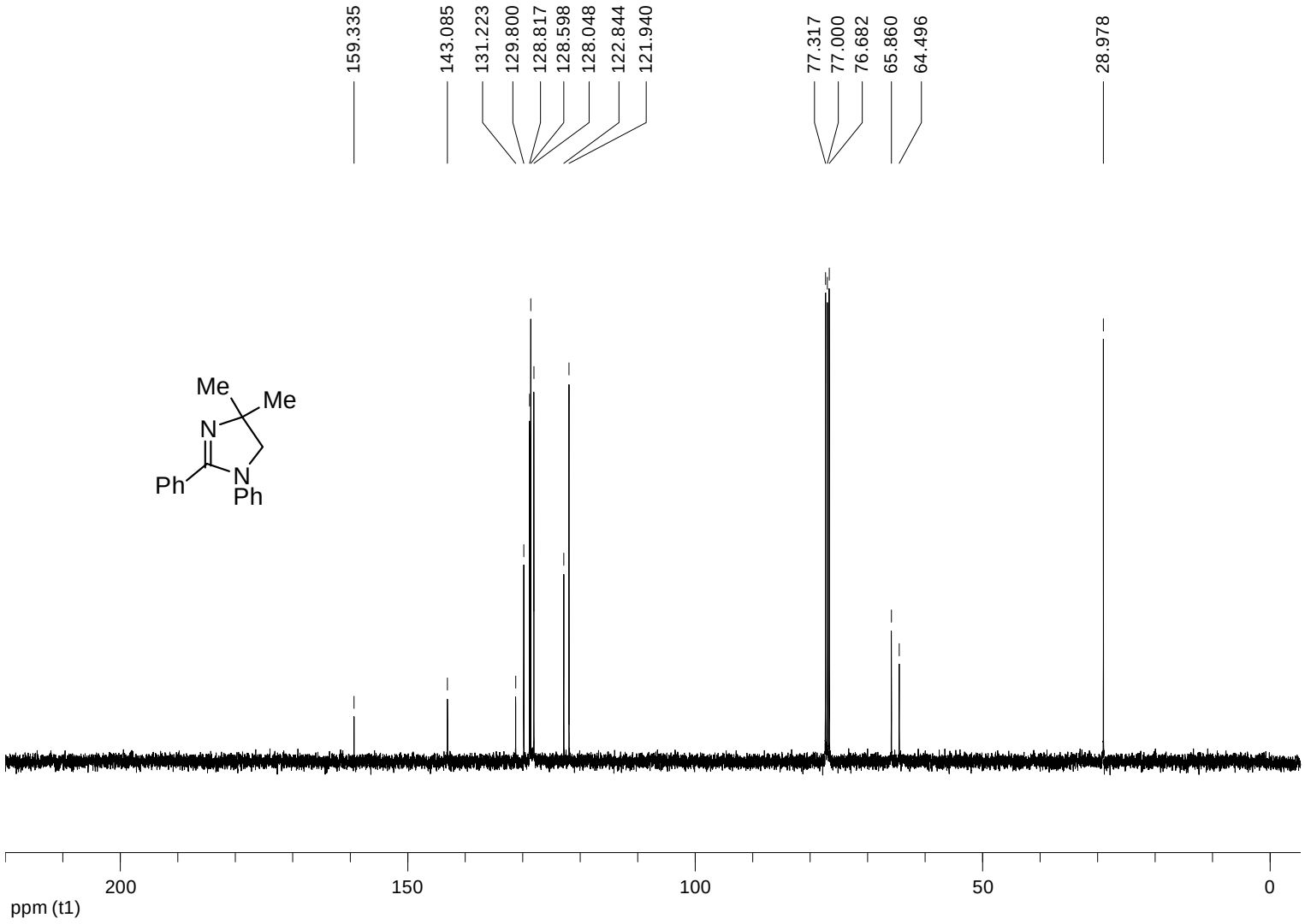
^{13}C NMR spectrum of **2l** (100 MHz, $CDCl_3$)



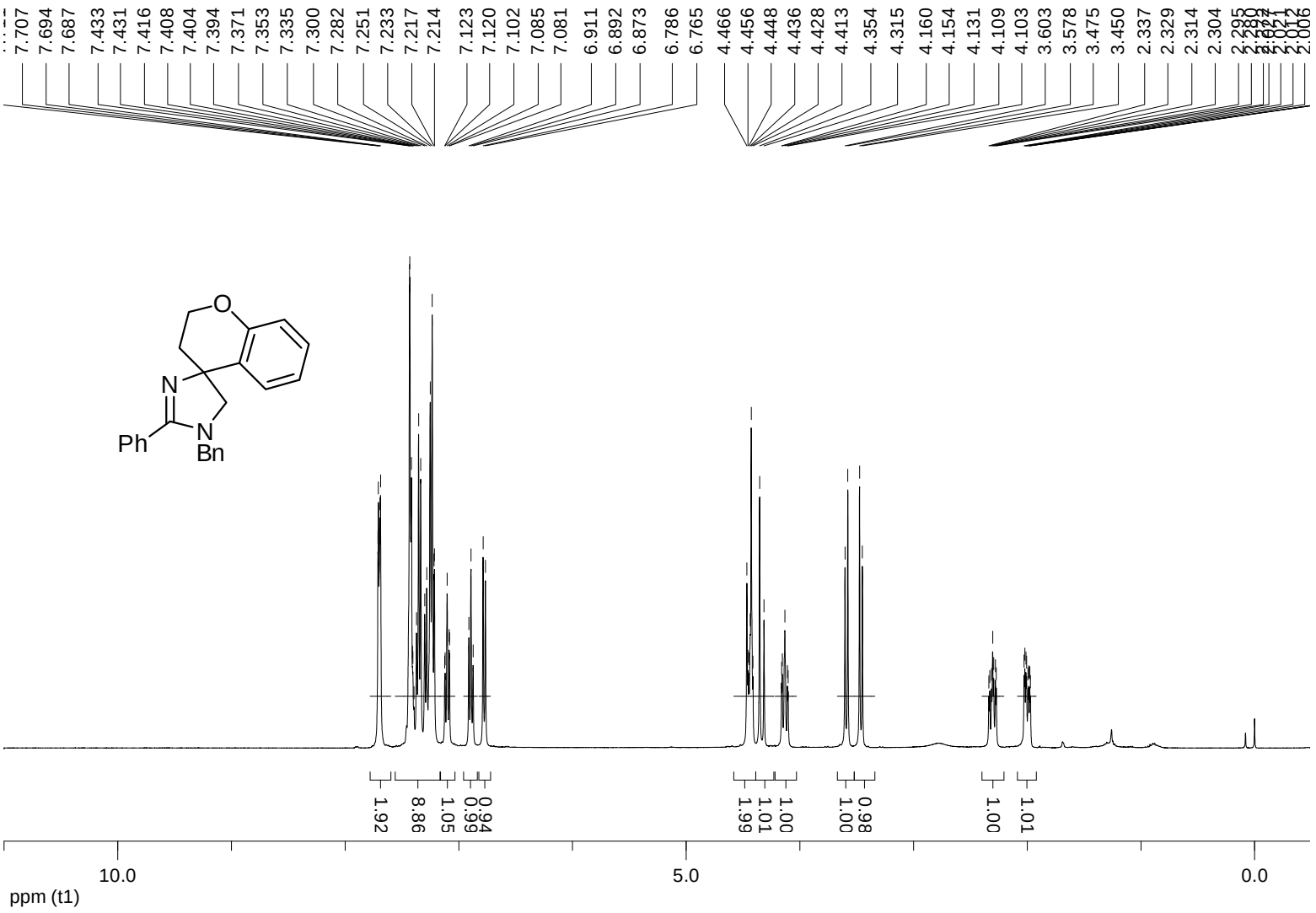
^{1}H NMR spectrum of **2m** (400 MHz, $CDCl_3$)



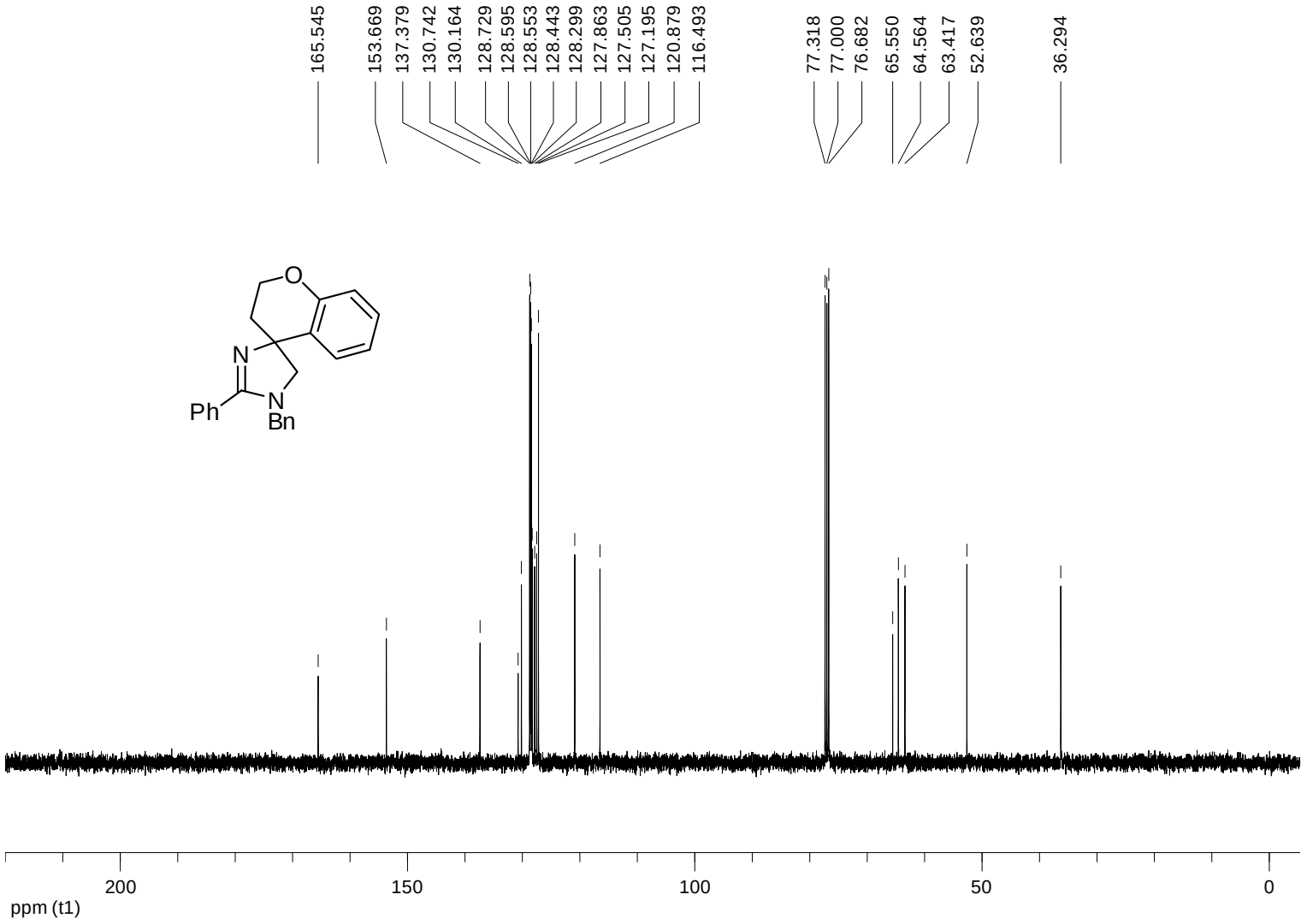
^{13}C NMR spectrum of **2m** (100 MHz, $CDCl_3$)



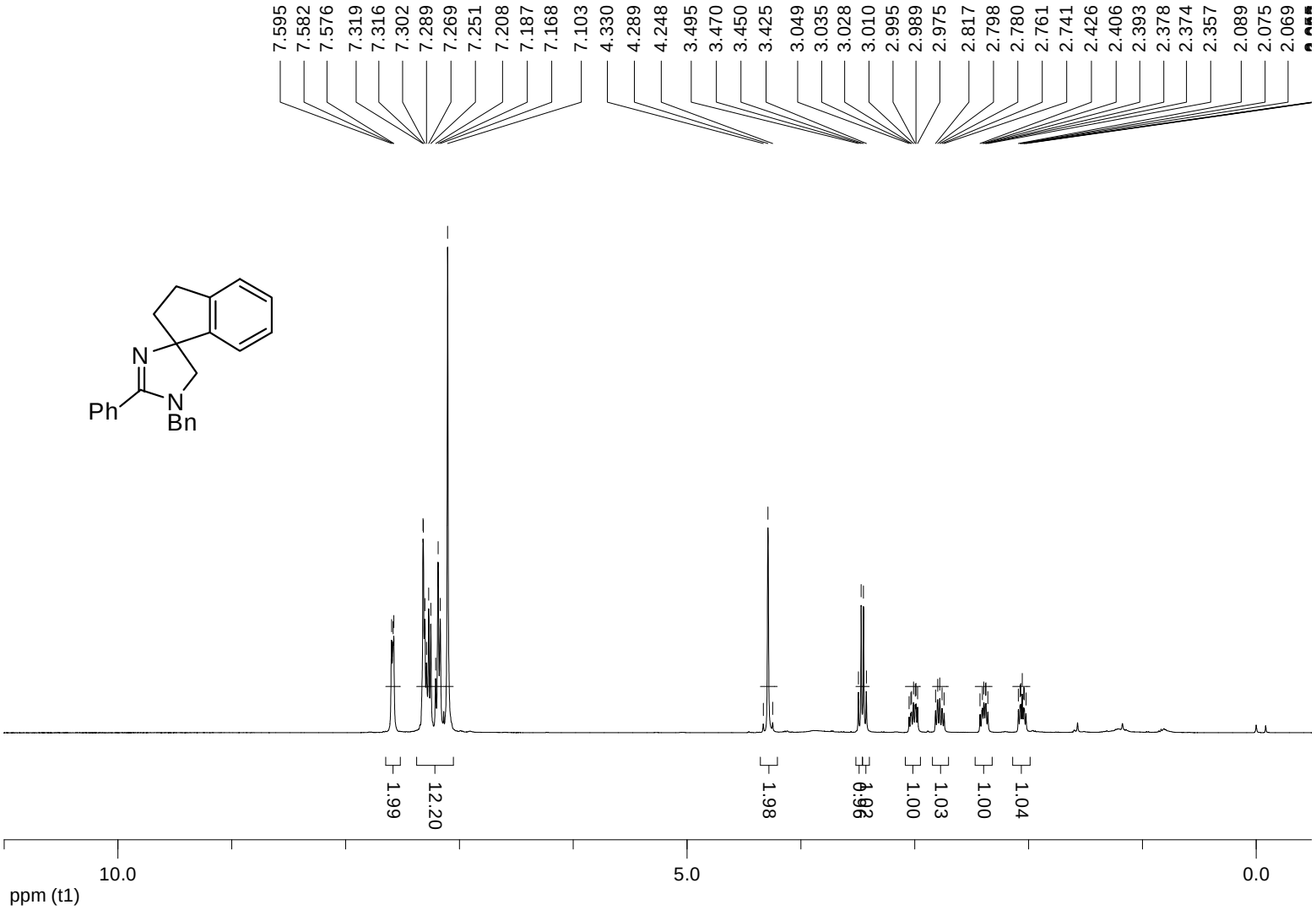
^{1}H NMR spectrum of **2n** (400 MHz, $CDCl_3$)



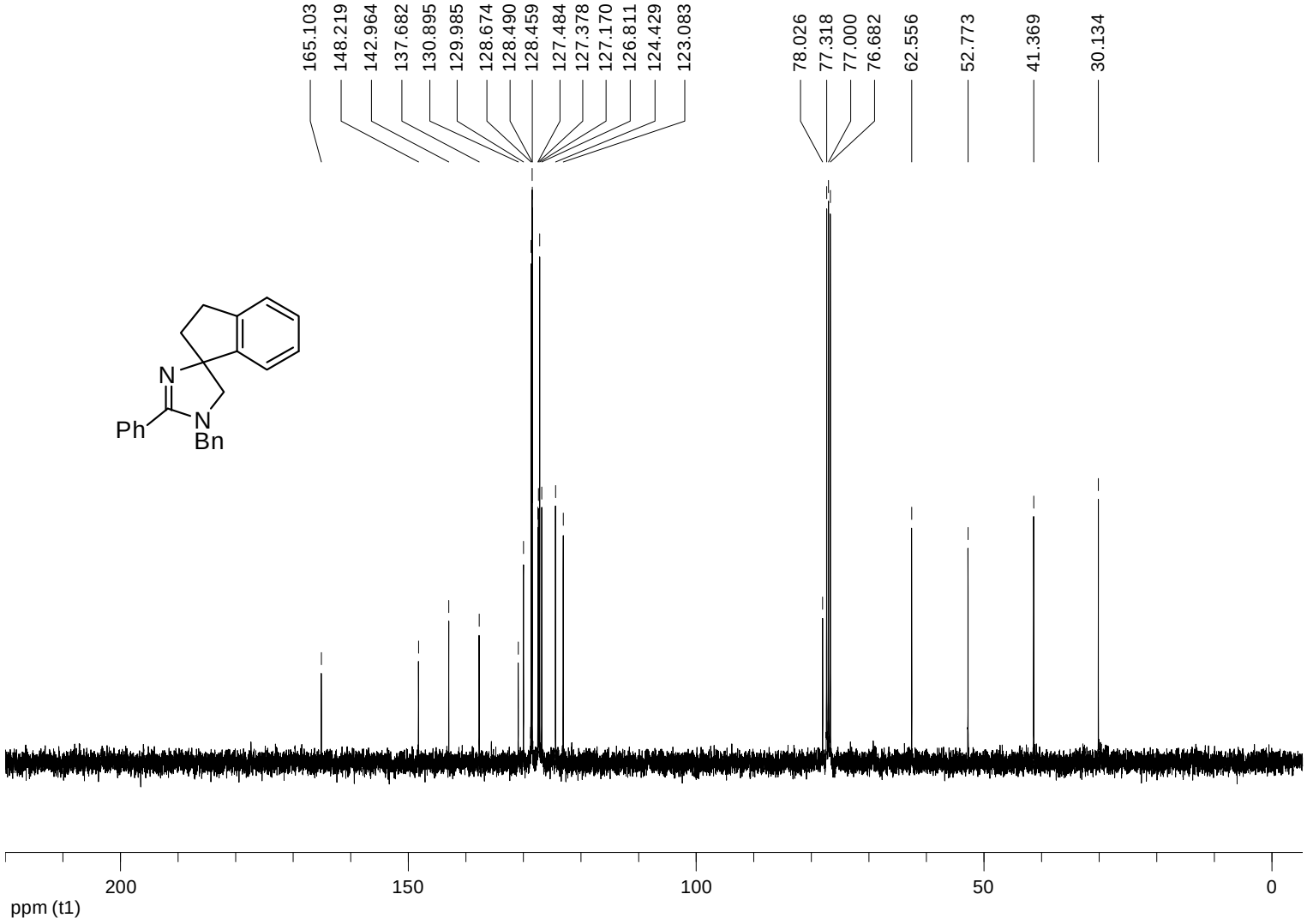
^{13}C NMR spectrum of **2n** (100 MHz, $CDCl_3$)



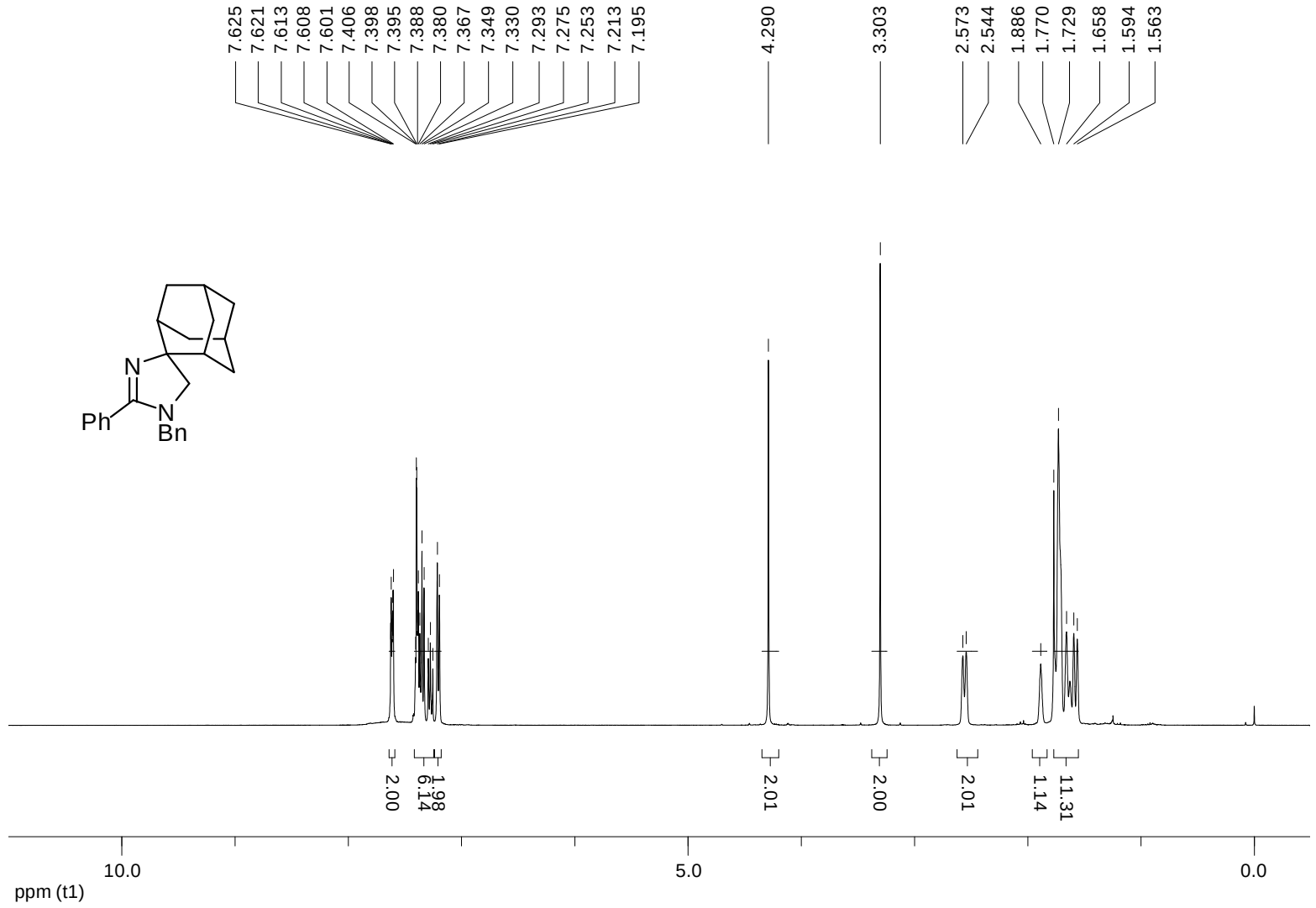
^{1}H NMR spectrum of **2o** (400 MHz, $CDCl_3$)



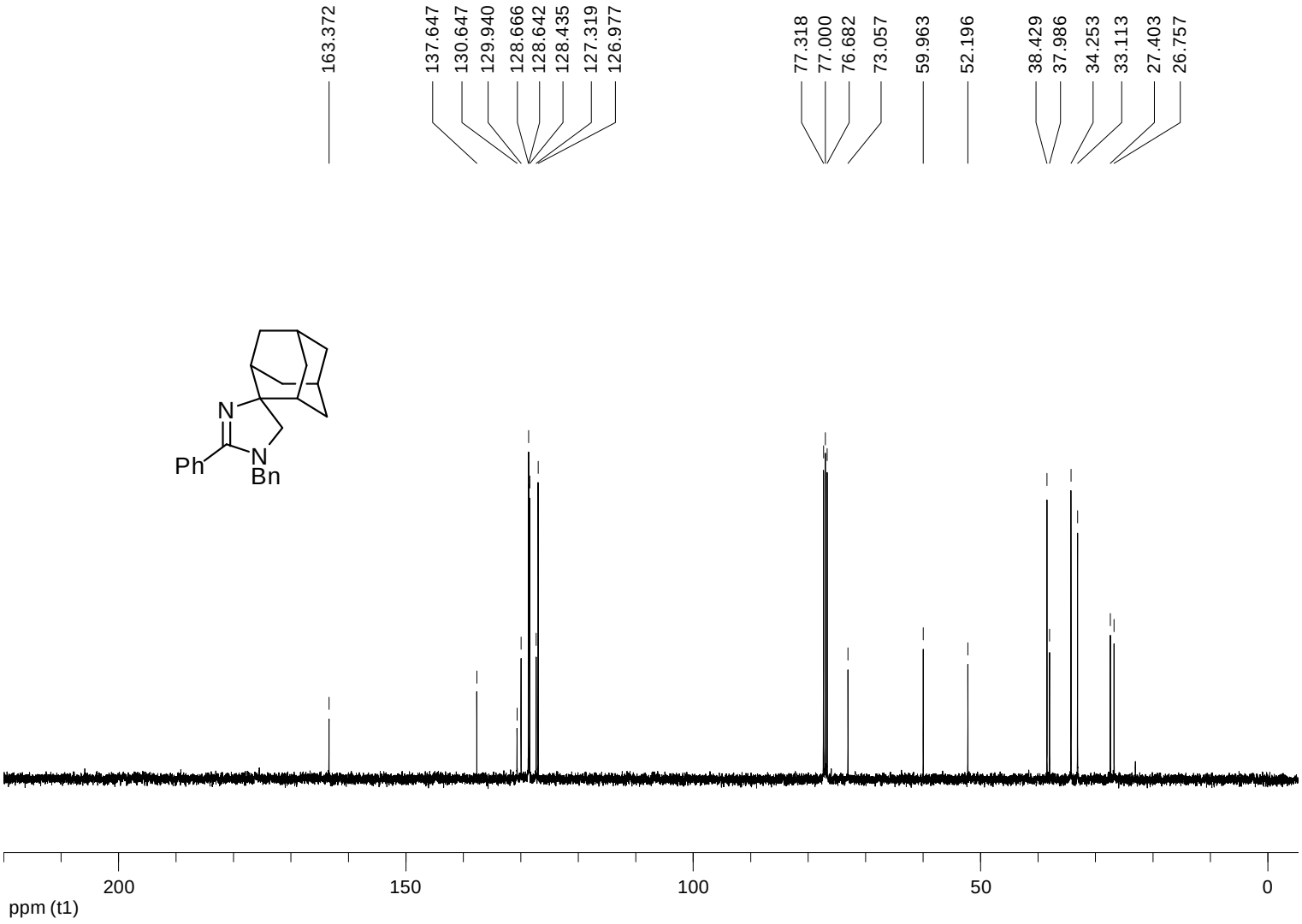
^{13}C NMR spectrum of **2o** (100 MHz, $CDCl_3$)



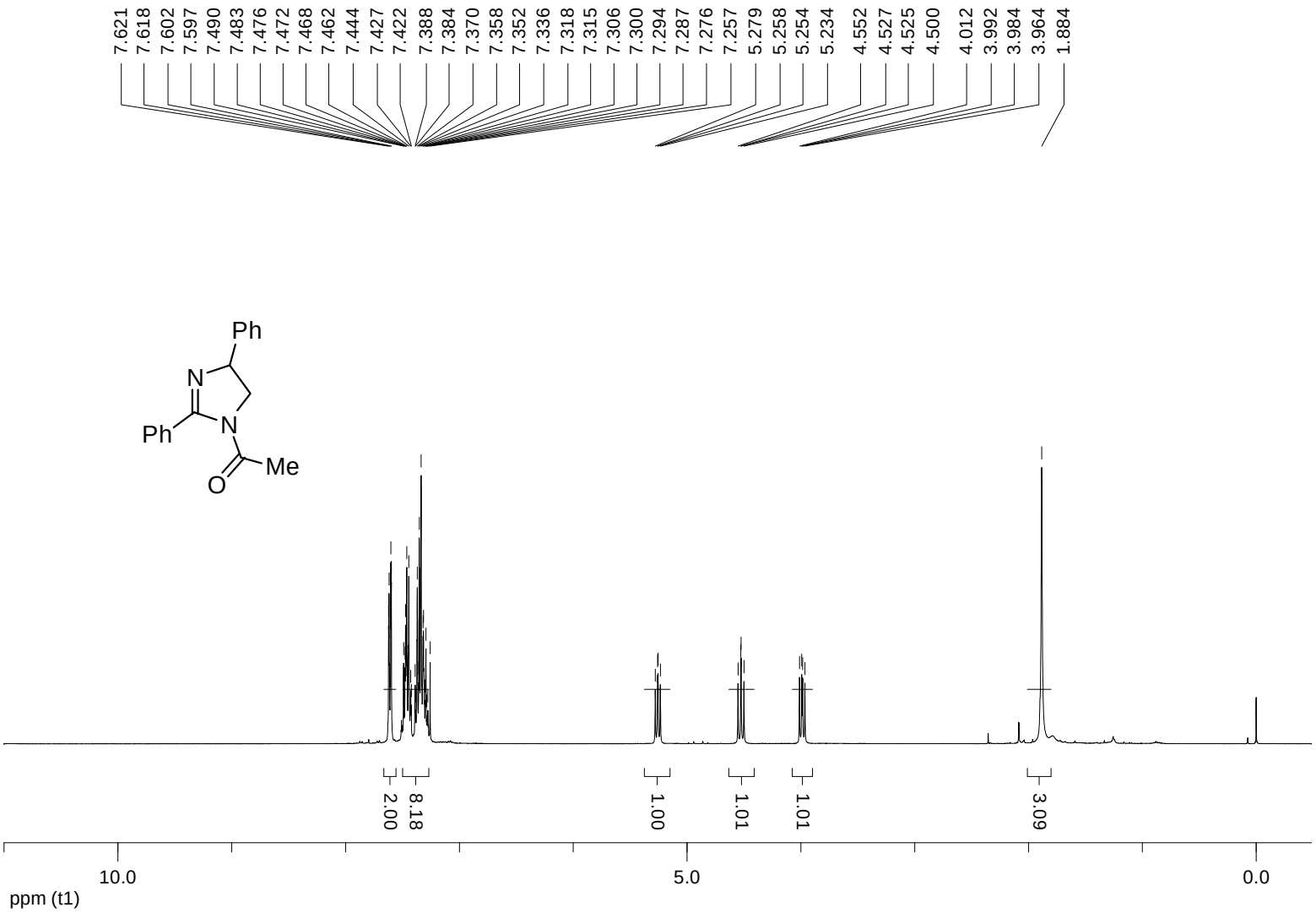
^{1}H NMR spectrum of **2p** (400 MHz, $CDCl_3$)



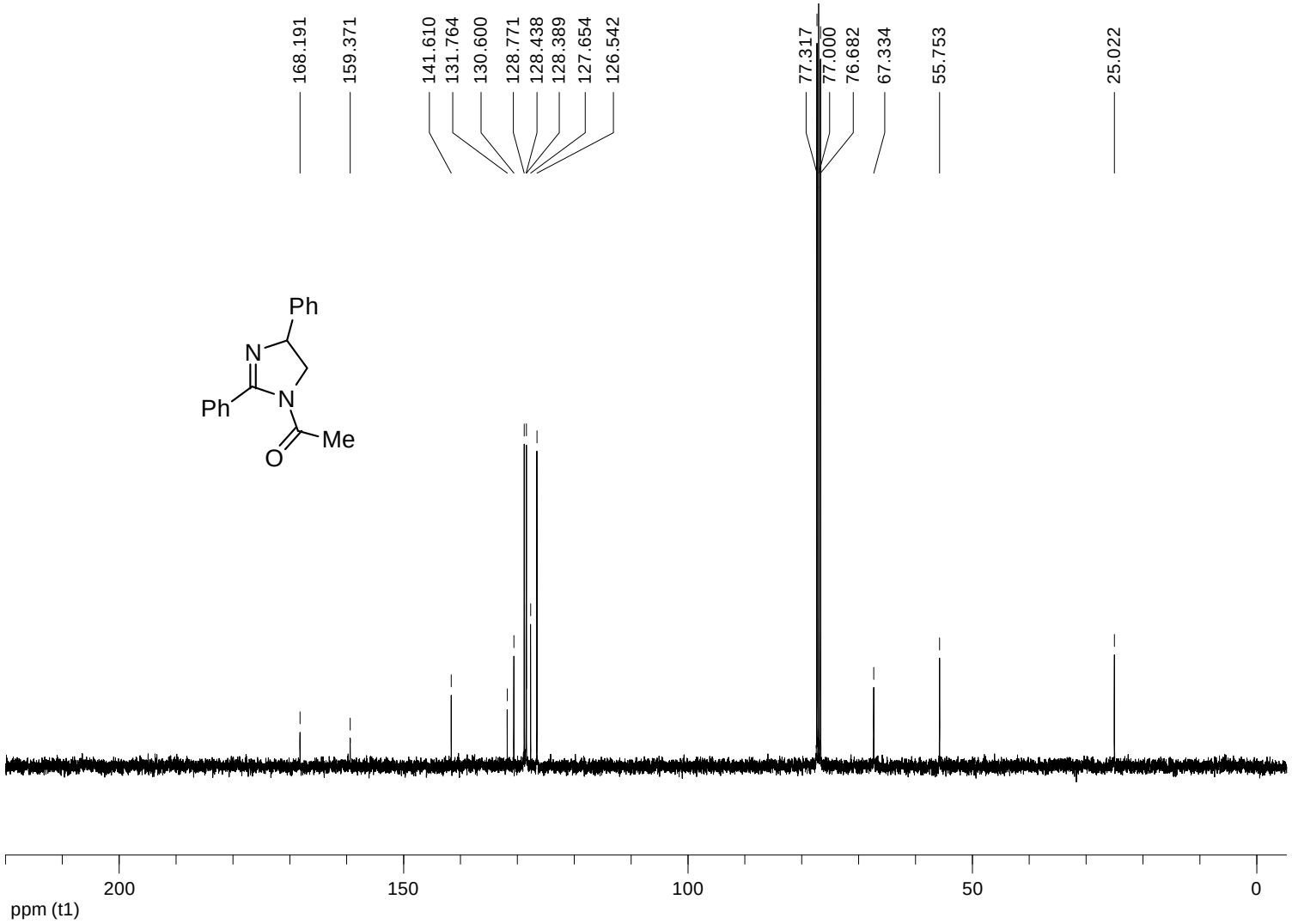
^{13}C NMR spectrum of **2p** (100 MHz, $CDCl_3$)



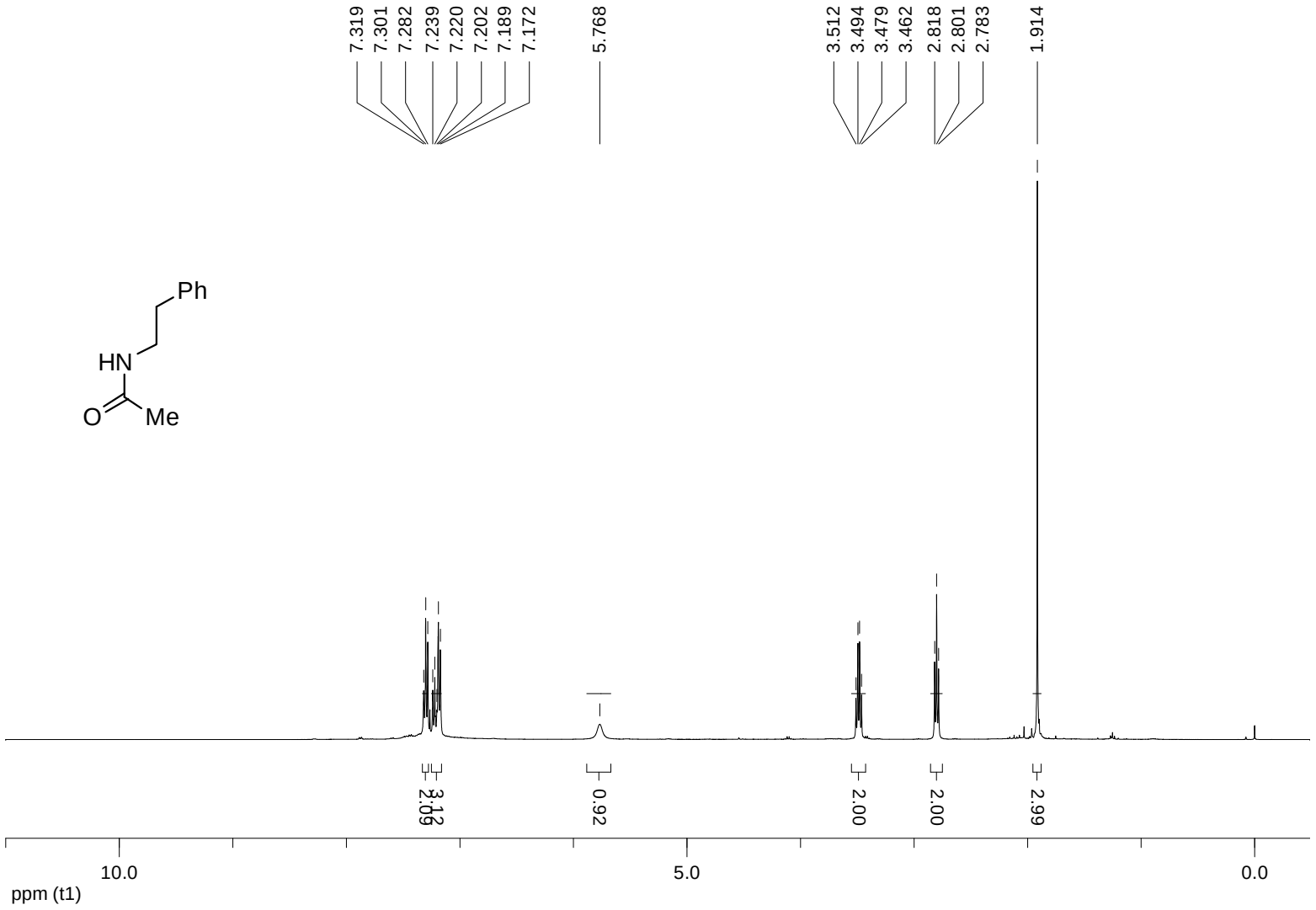
^{1}H NMR spectrum of **2s** (400 MHz, $CDCl_3$)



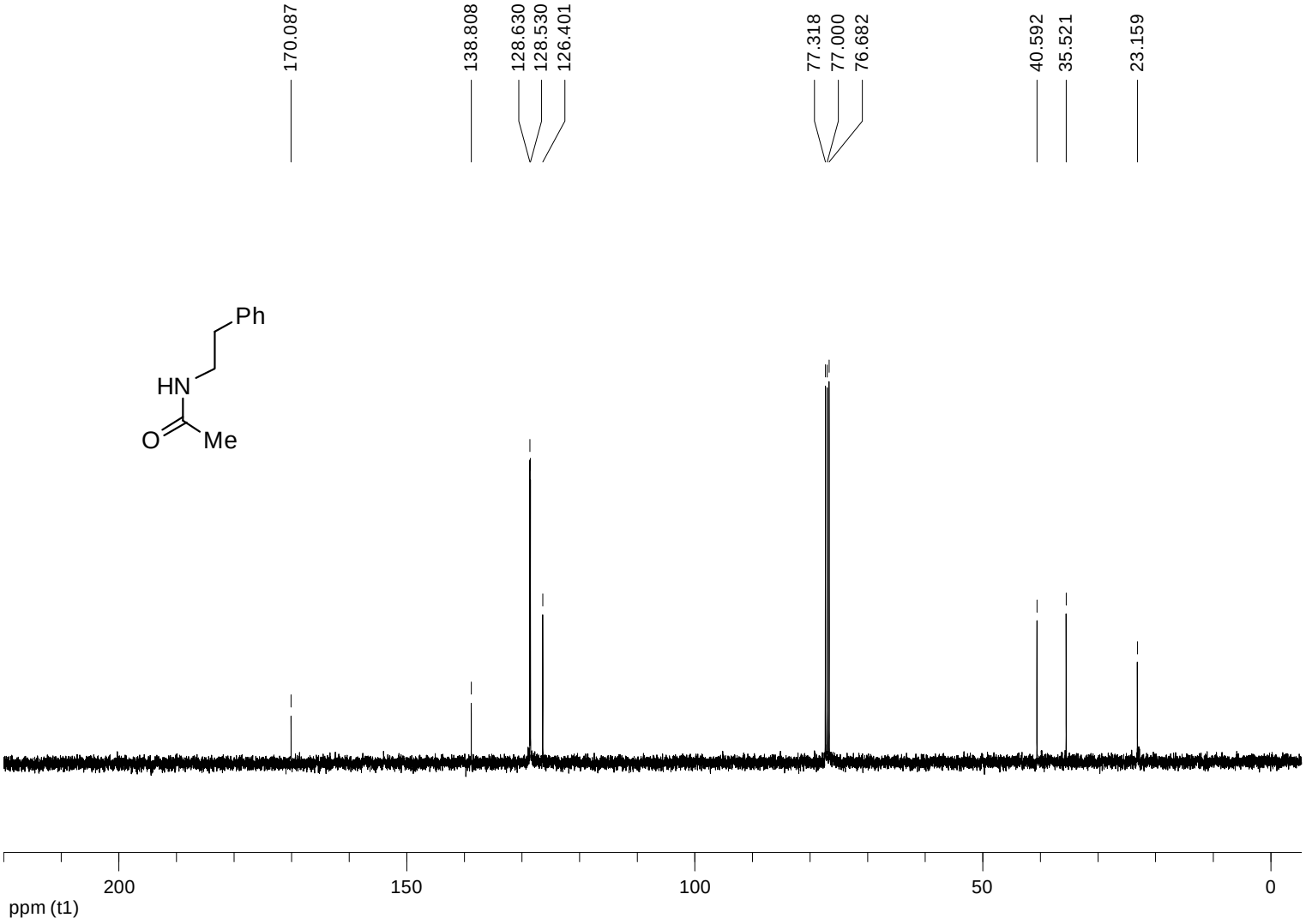
^{13}C NMR spectrum of **2s** (100 MHz, $CDCl_3$)



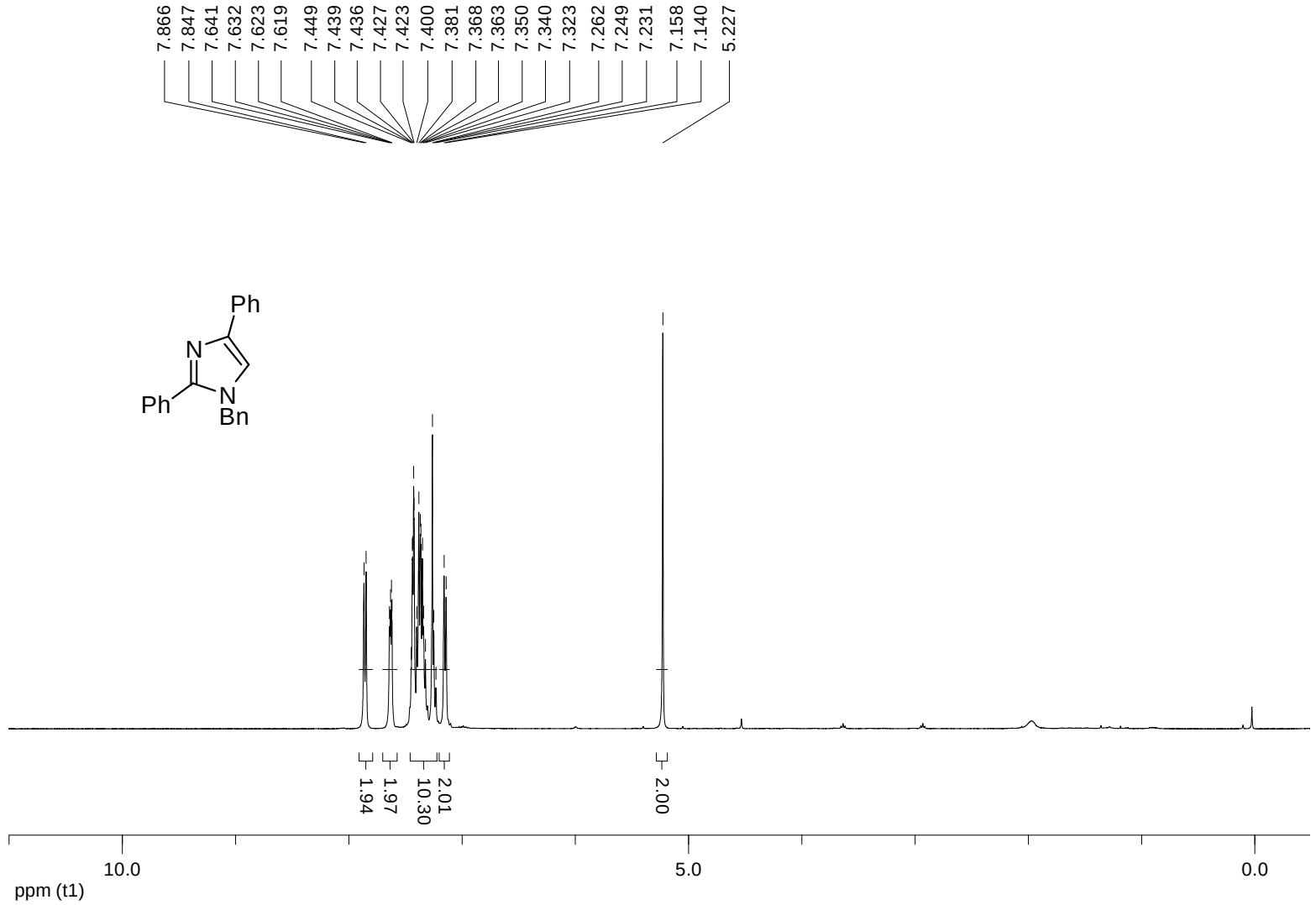
^{1}H NMR spectrum of **5** (400 MHz, $CDCl_3$)



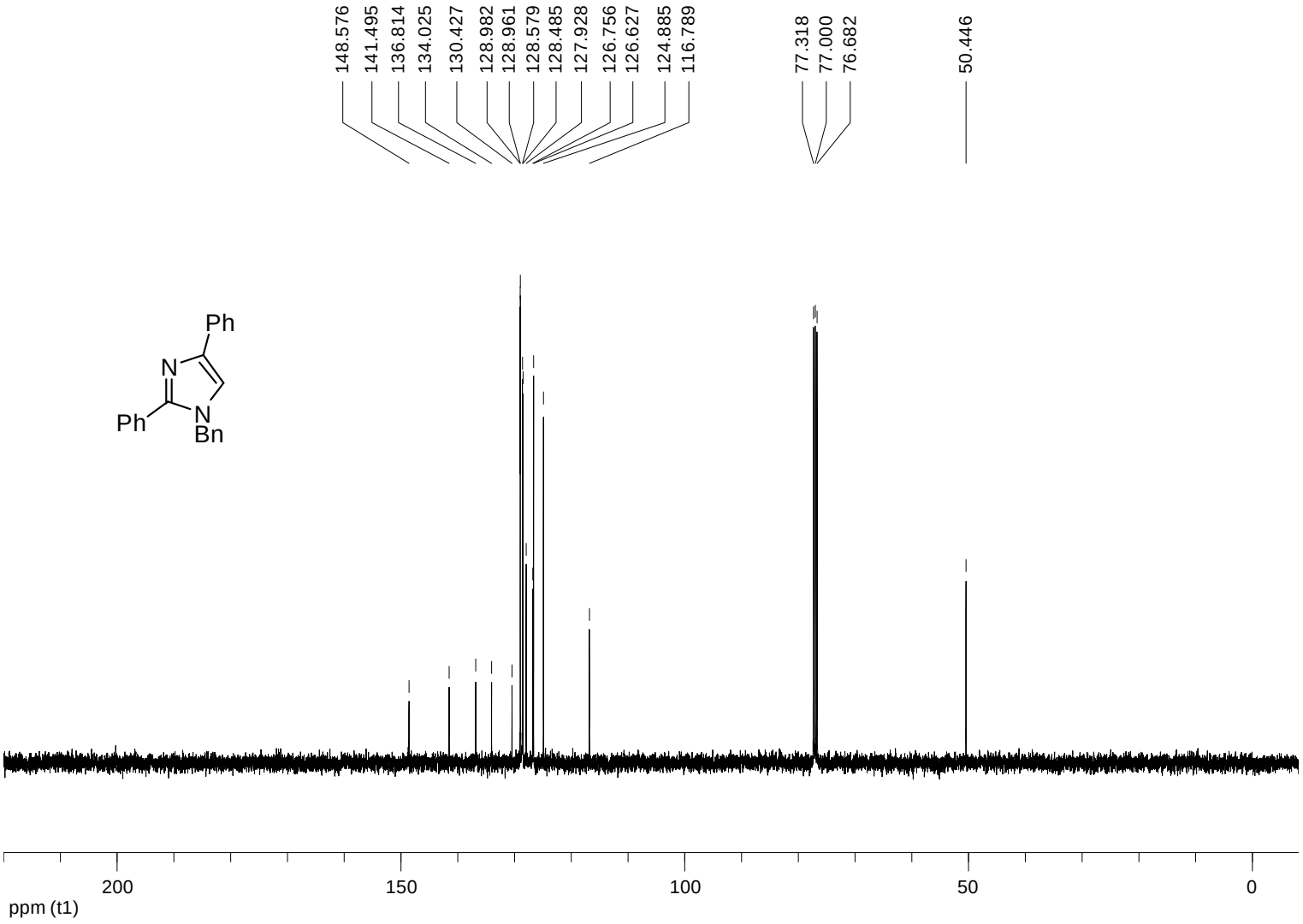
^{13}C NMR spectrum of **5** (100 MHz, $CDCl_3$)



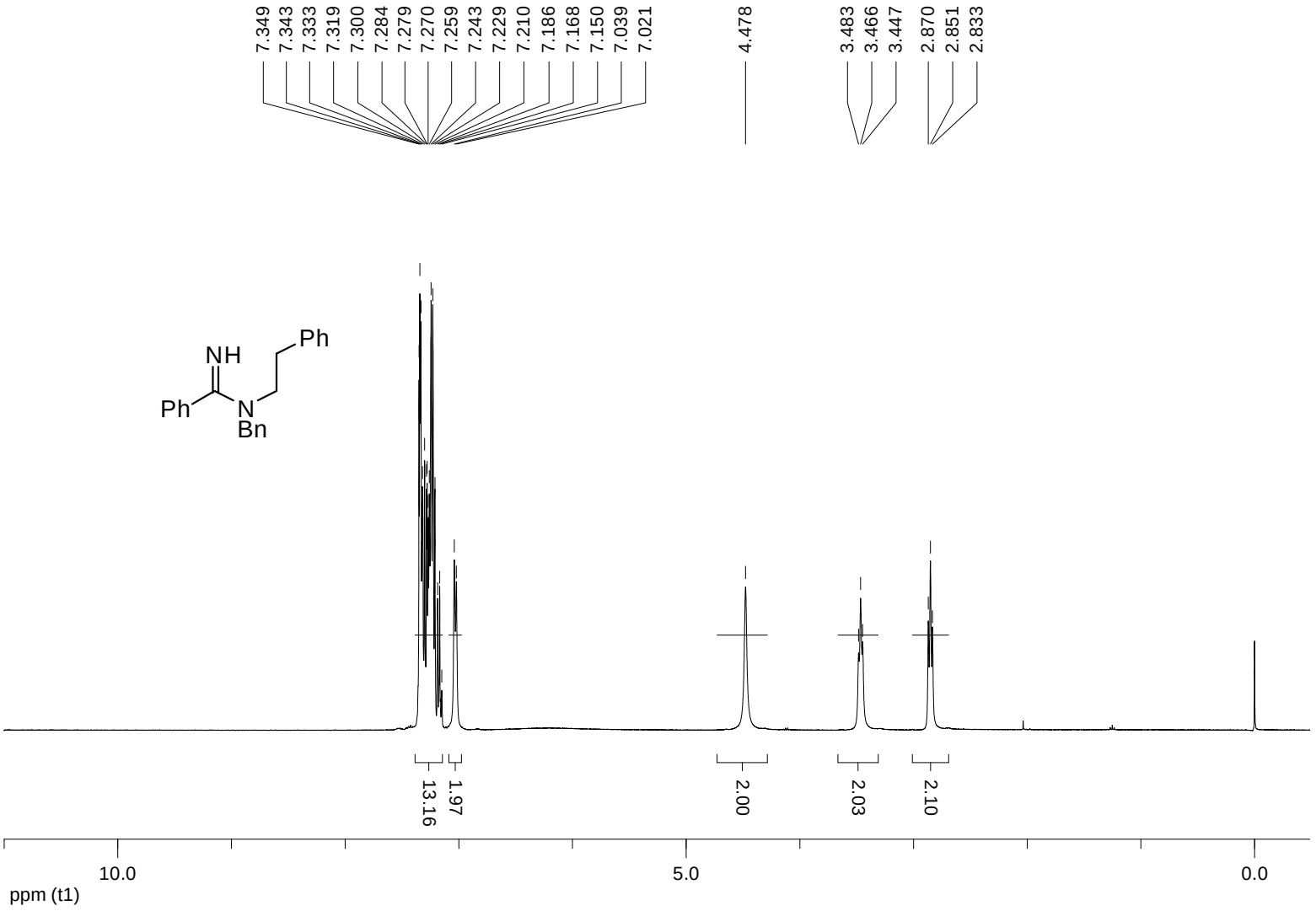
^{1}H NMR spectrum of **3q**(400 MHz, $CDCl_3$)



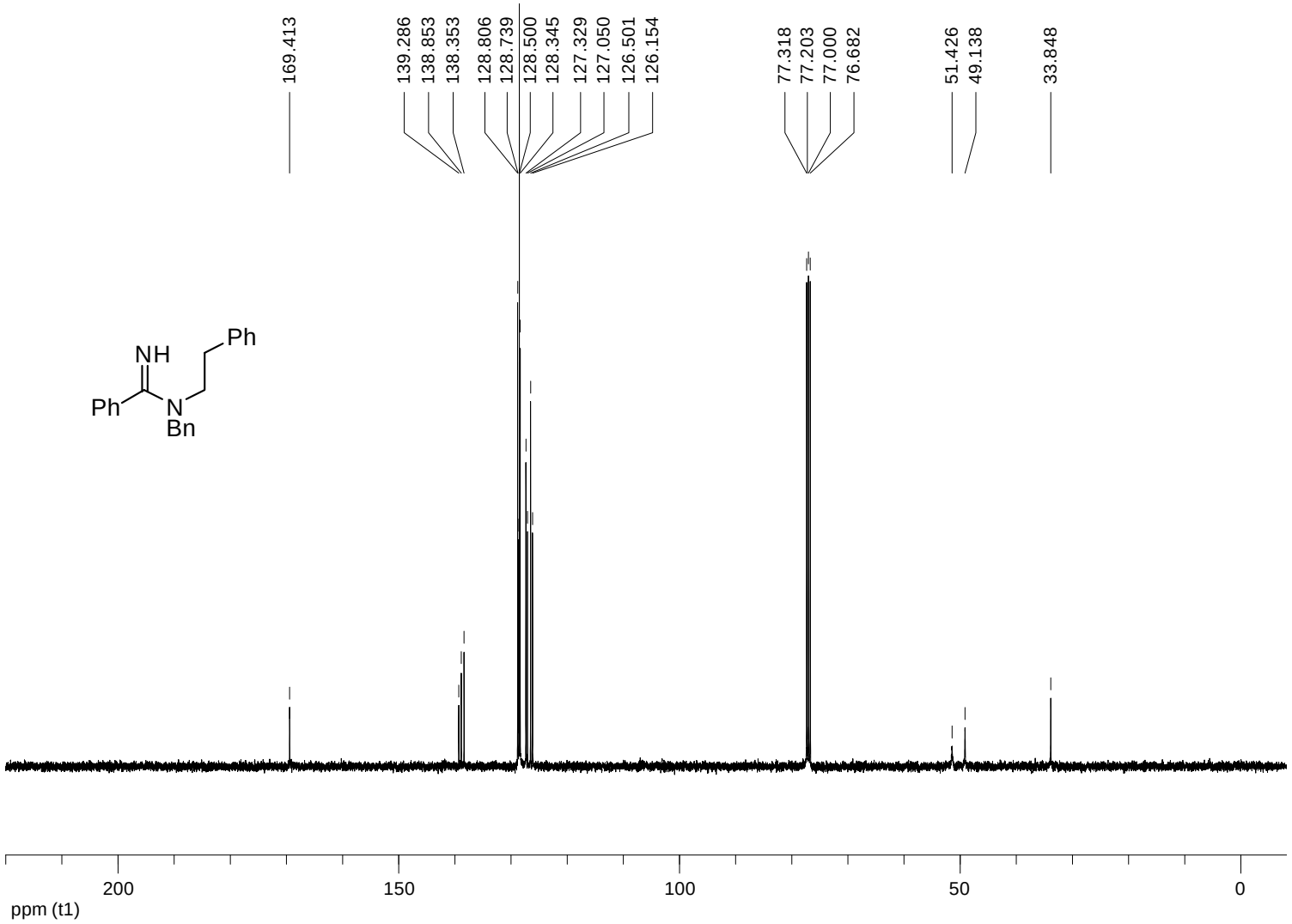
^{13}C NMR spectrum of **3q** (100 MHz, $CDCl_3$)



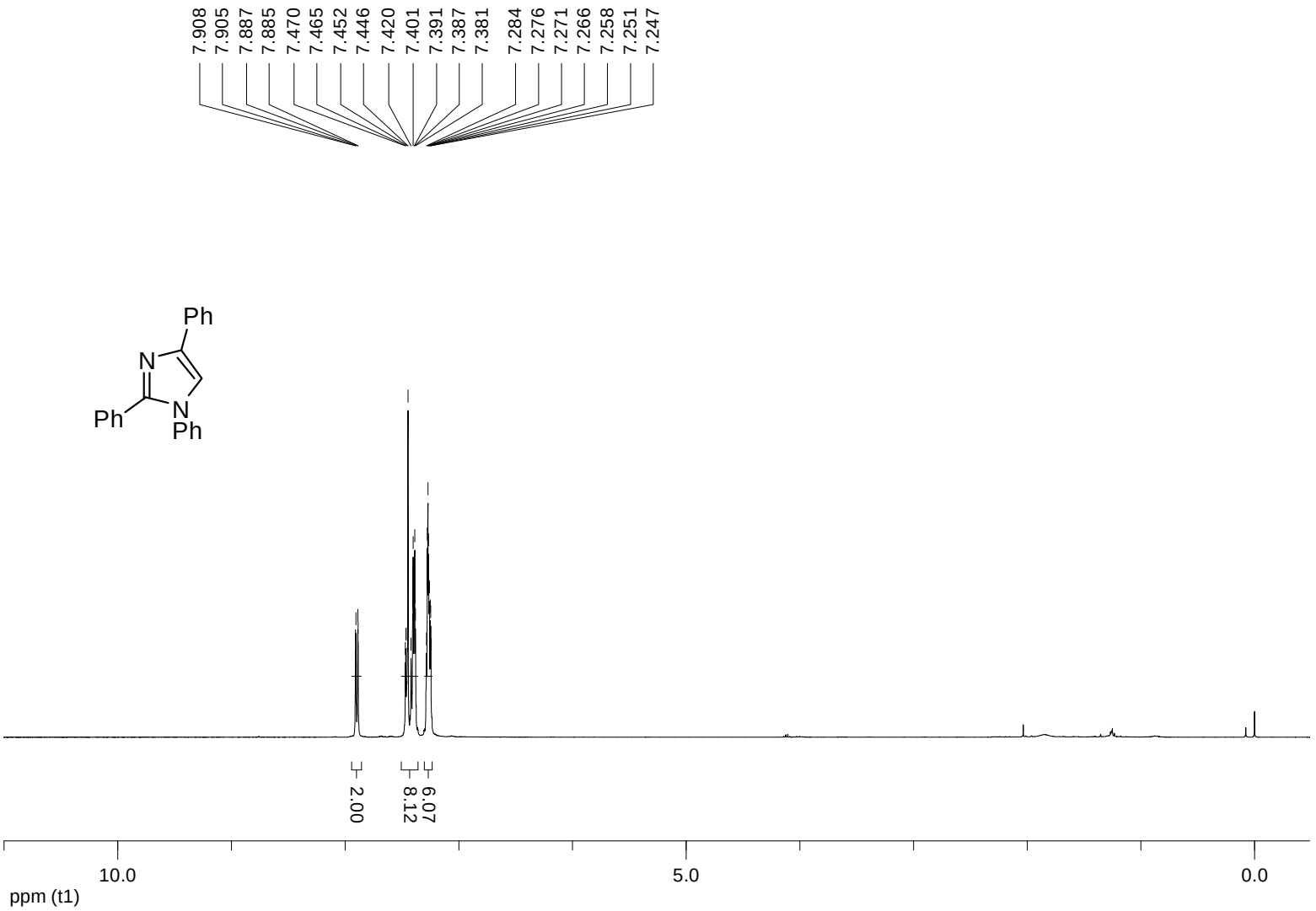
^{1}H NMR spectrum of **4q** (400 MHz, $CDCl_3$)



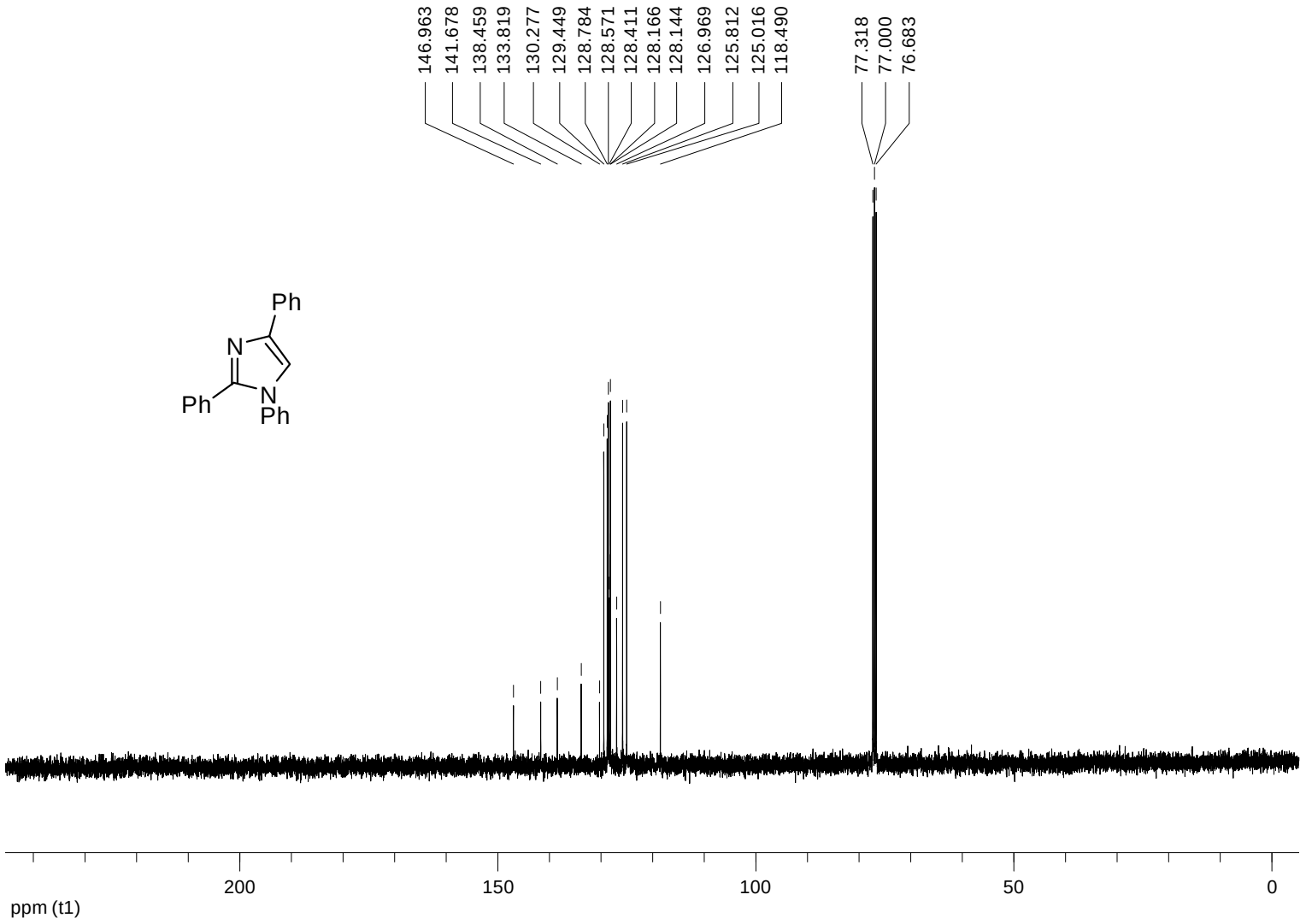
^{13}C NMR spectrum of **4q** (100 MHz, $CDCl_3$)



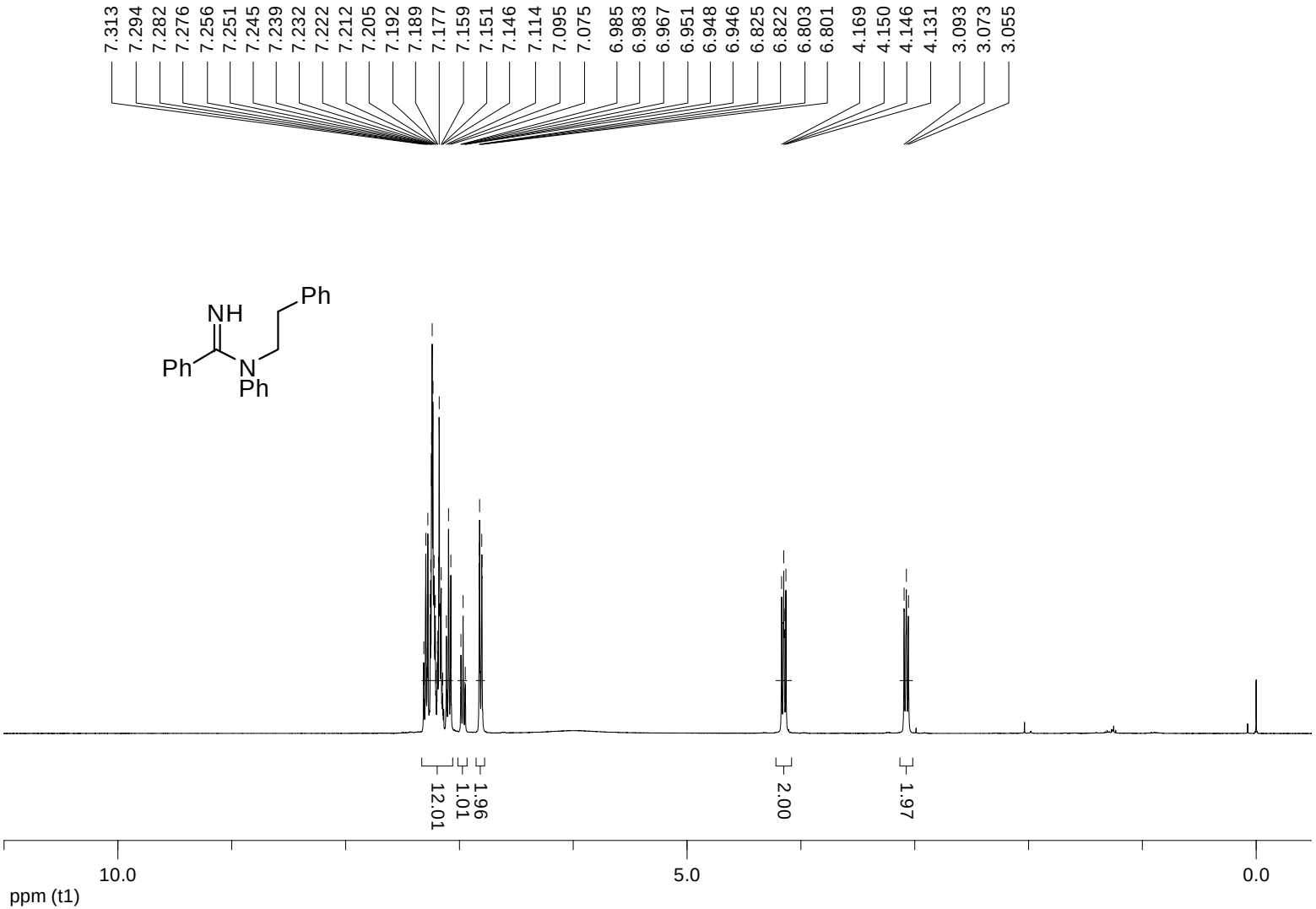
^{1}H NMR spectrum of **3r** (400 MHz, $CDCl_3$)



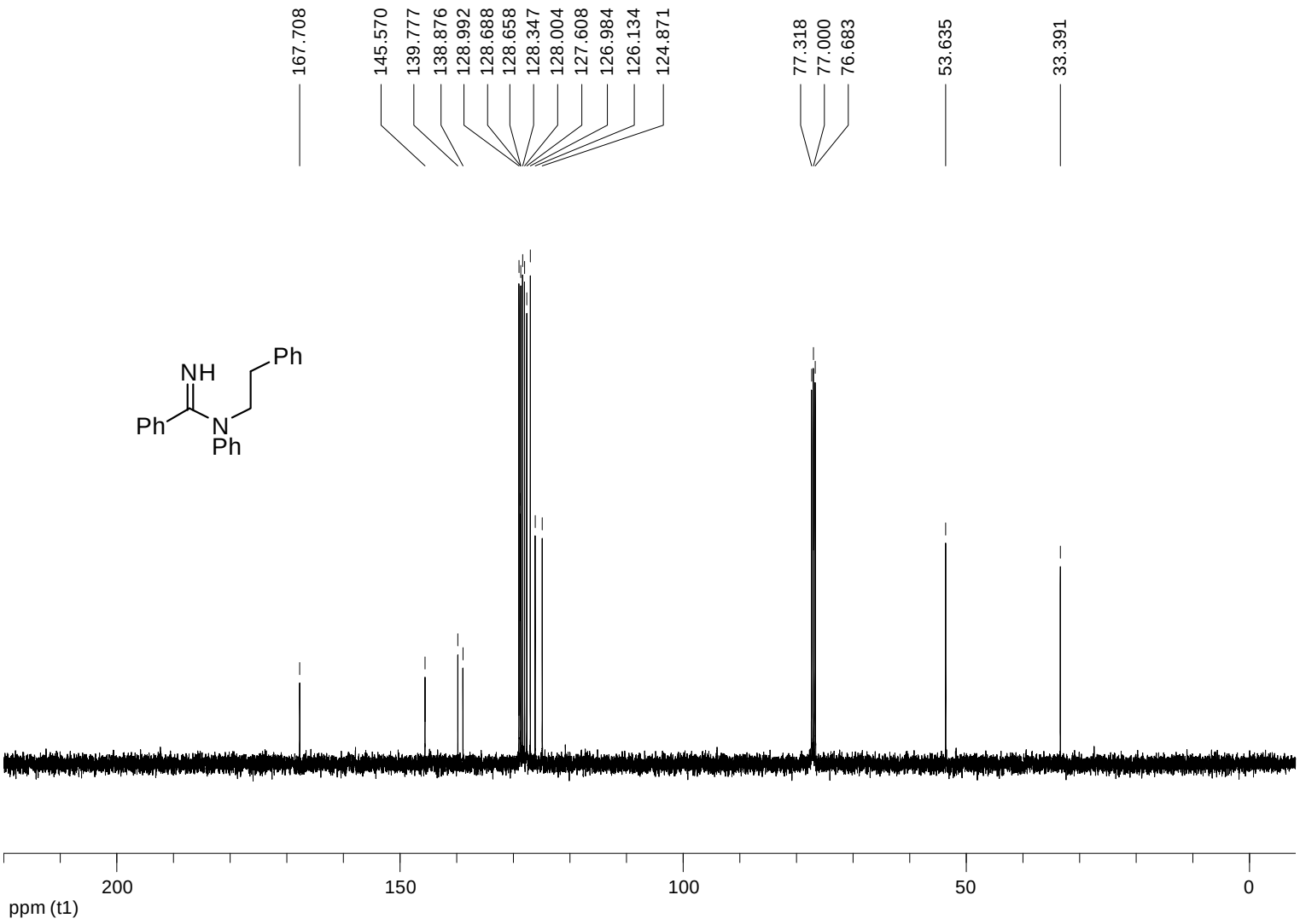
^{13}C NMR spectrum of **3r**(100 MHz, $CDCl_3$)



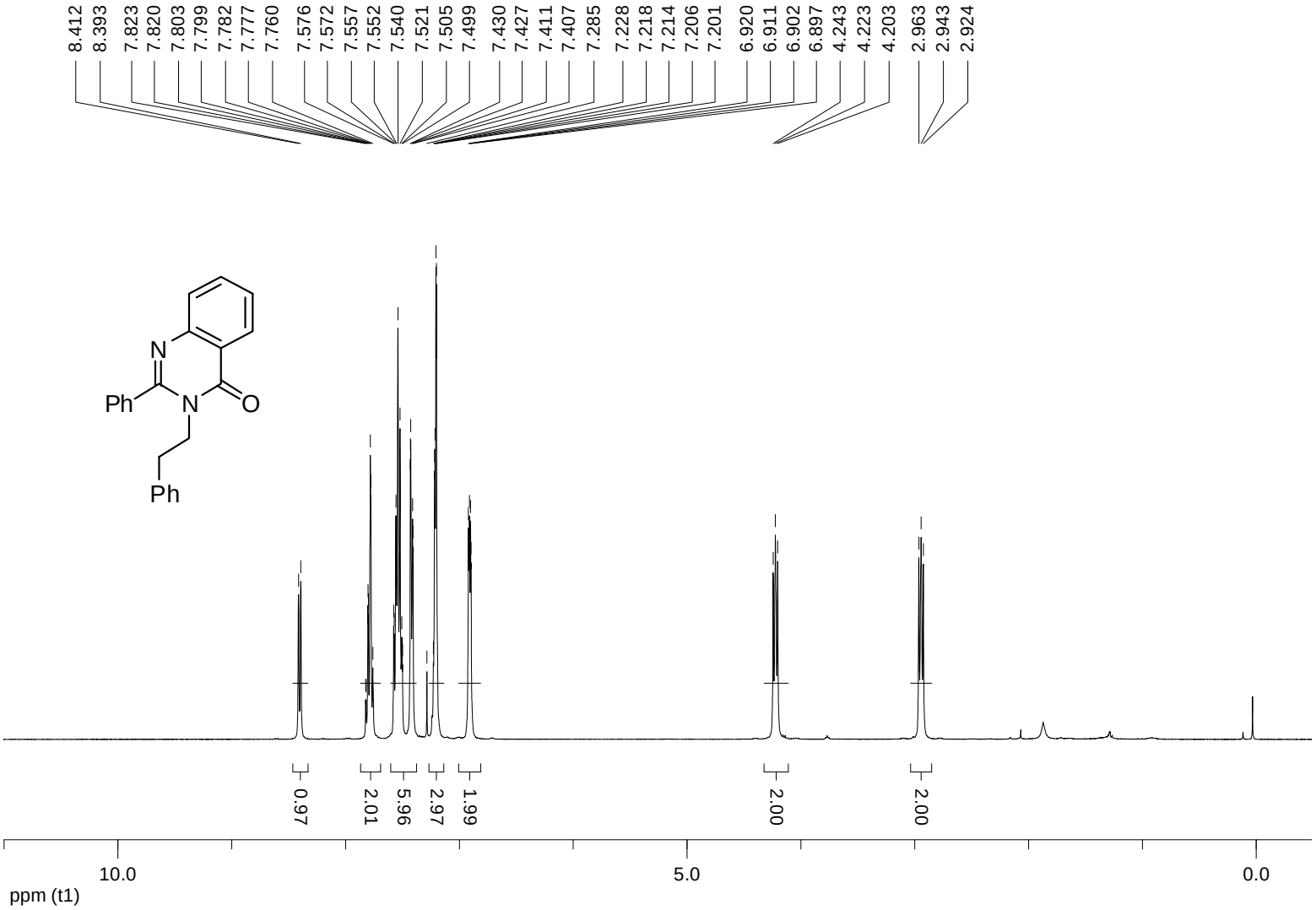
^{1}H NMR spectrum of **4r** (400 MHz, $CDCl_3$)



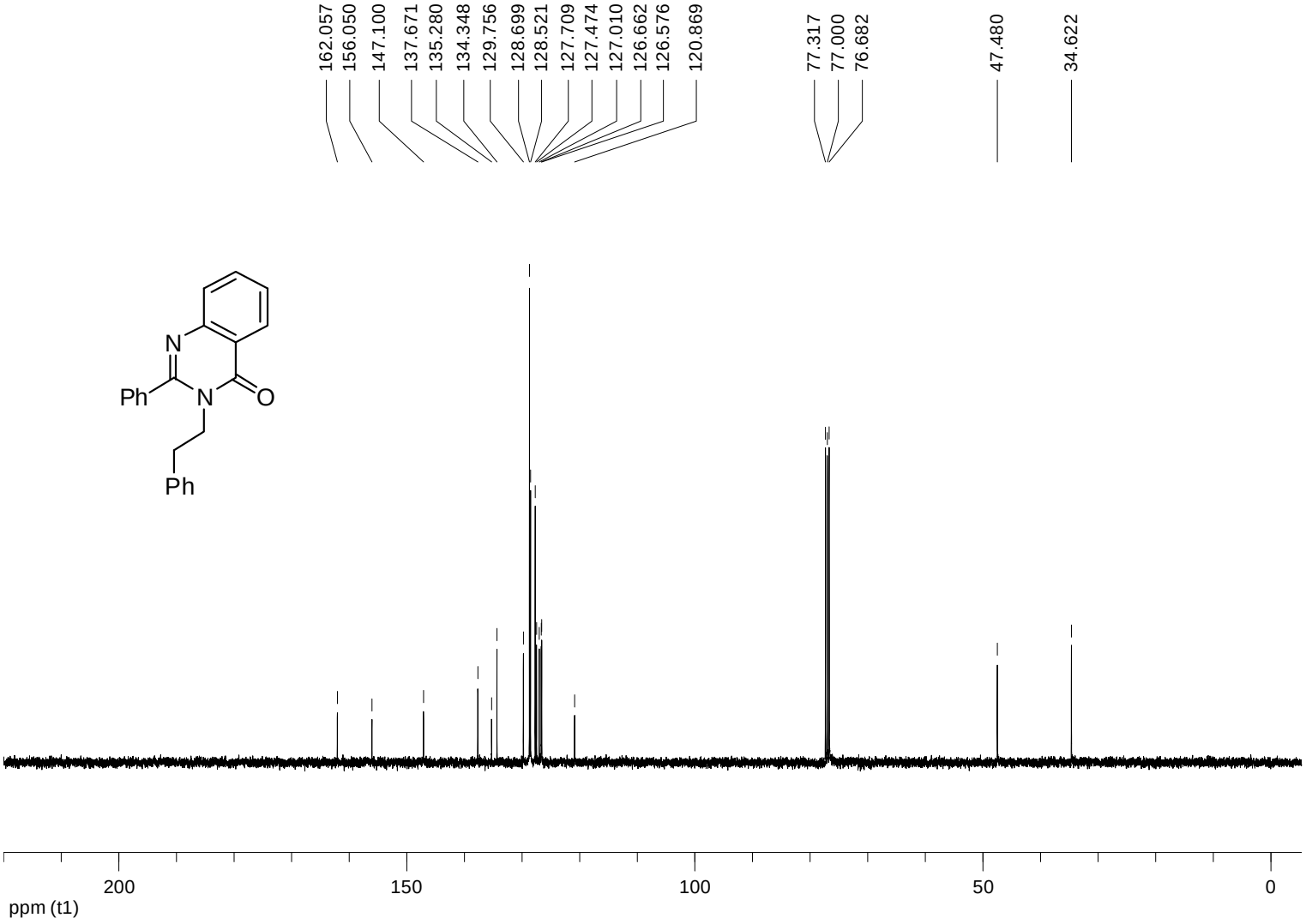
^{13}C NMR spectrum of **4r** (100 MHz, $CDCl_3$)



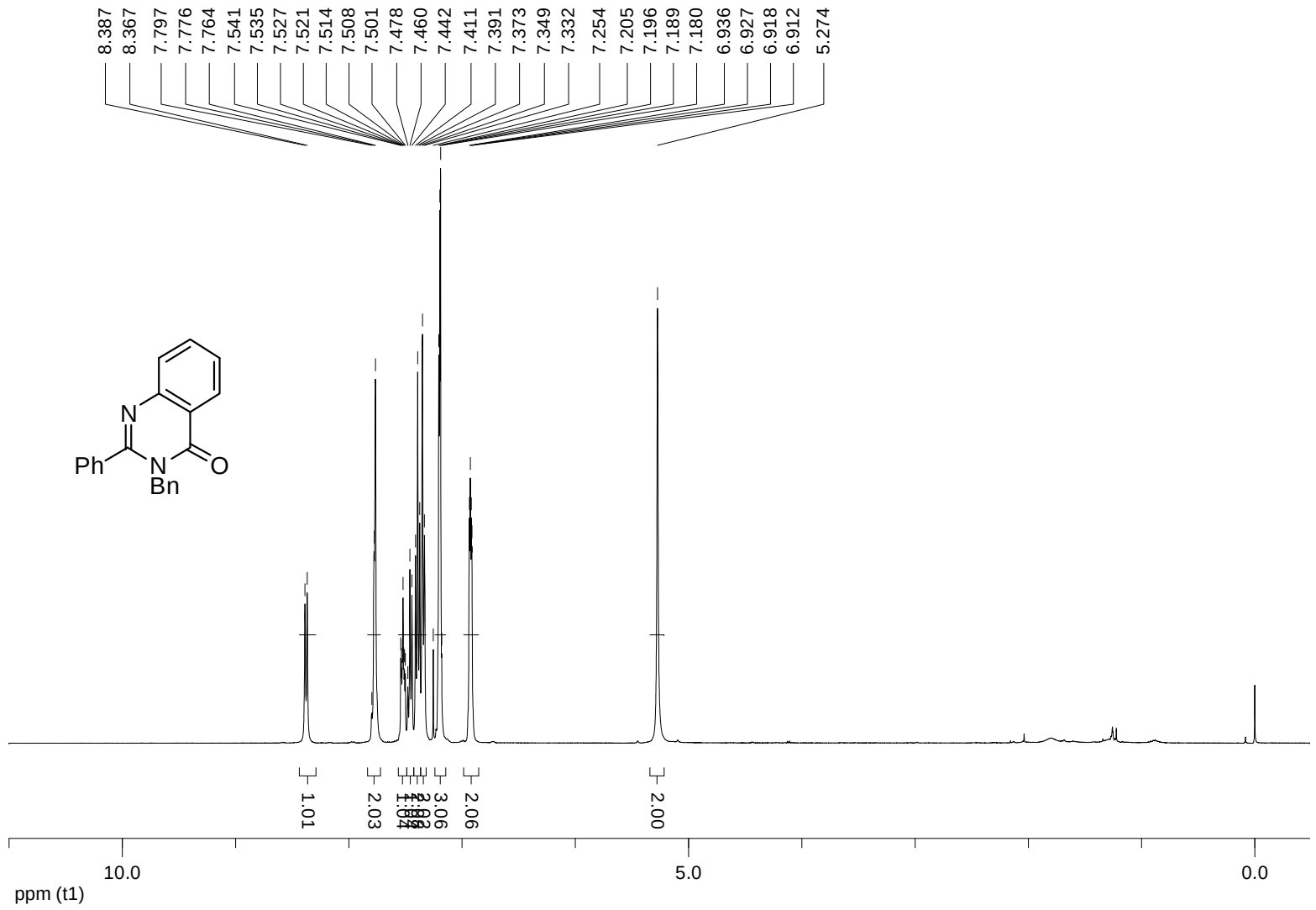
^{1}H NMR spectrum of **7a** (400 MHz, $CDCl_3$)



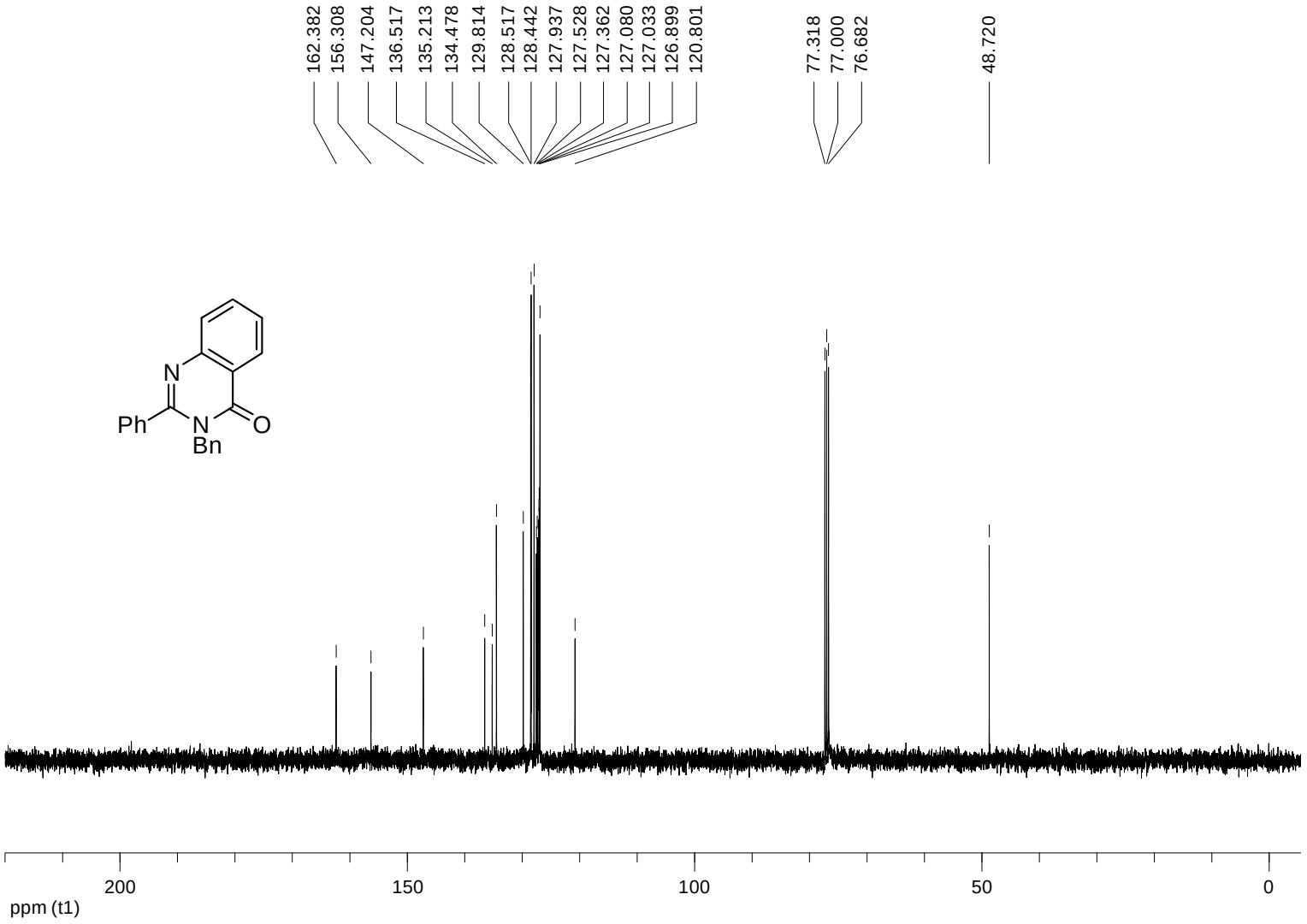
^{13}C NMR spectrum of **7a** (100 MHz, $CDCl_3$)



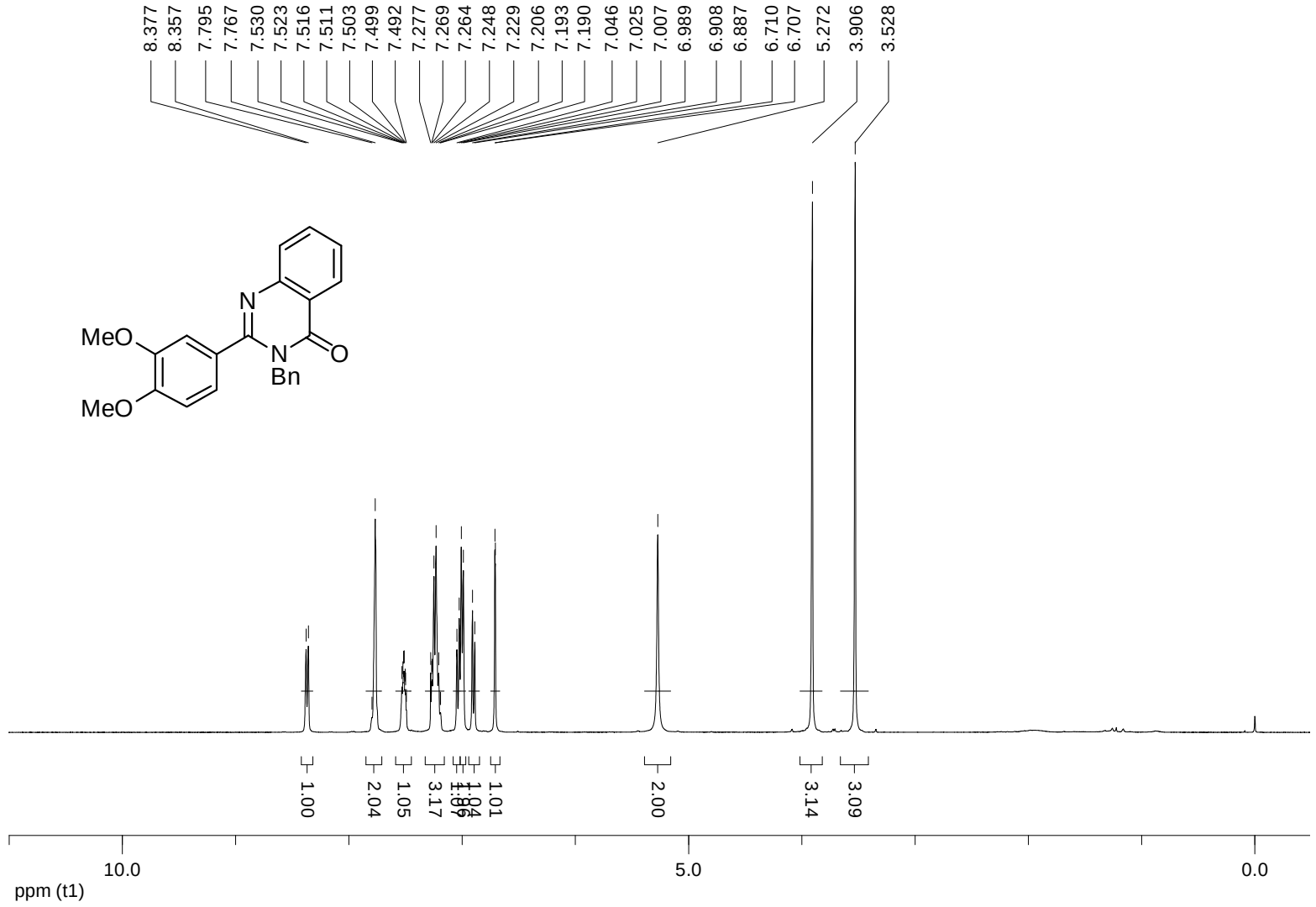
^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$)



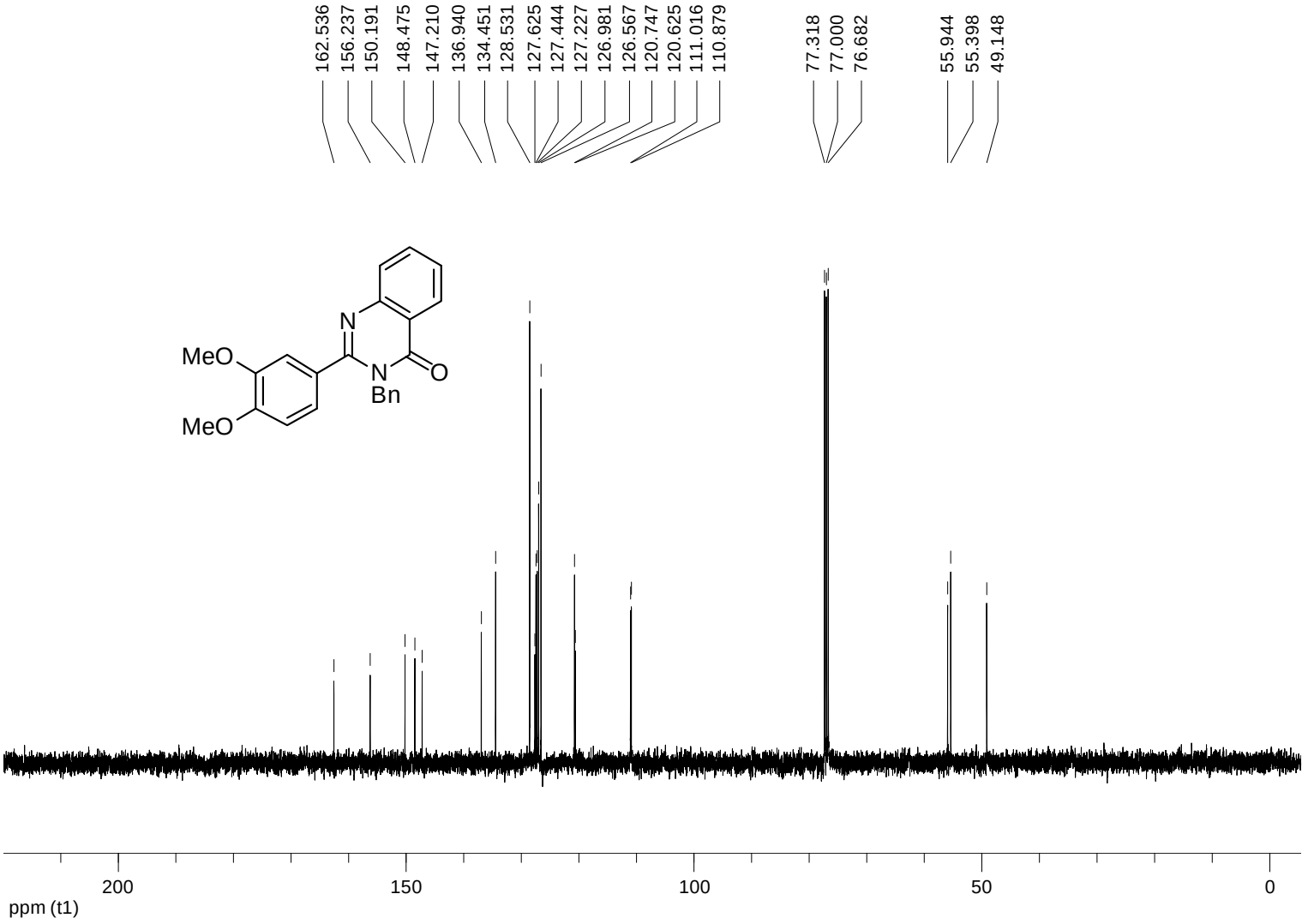
^{13}C NMR spectrum of **7b** (100 MHz, $CDCl_3$)



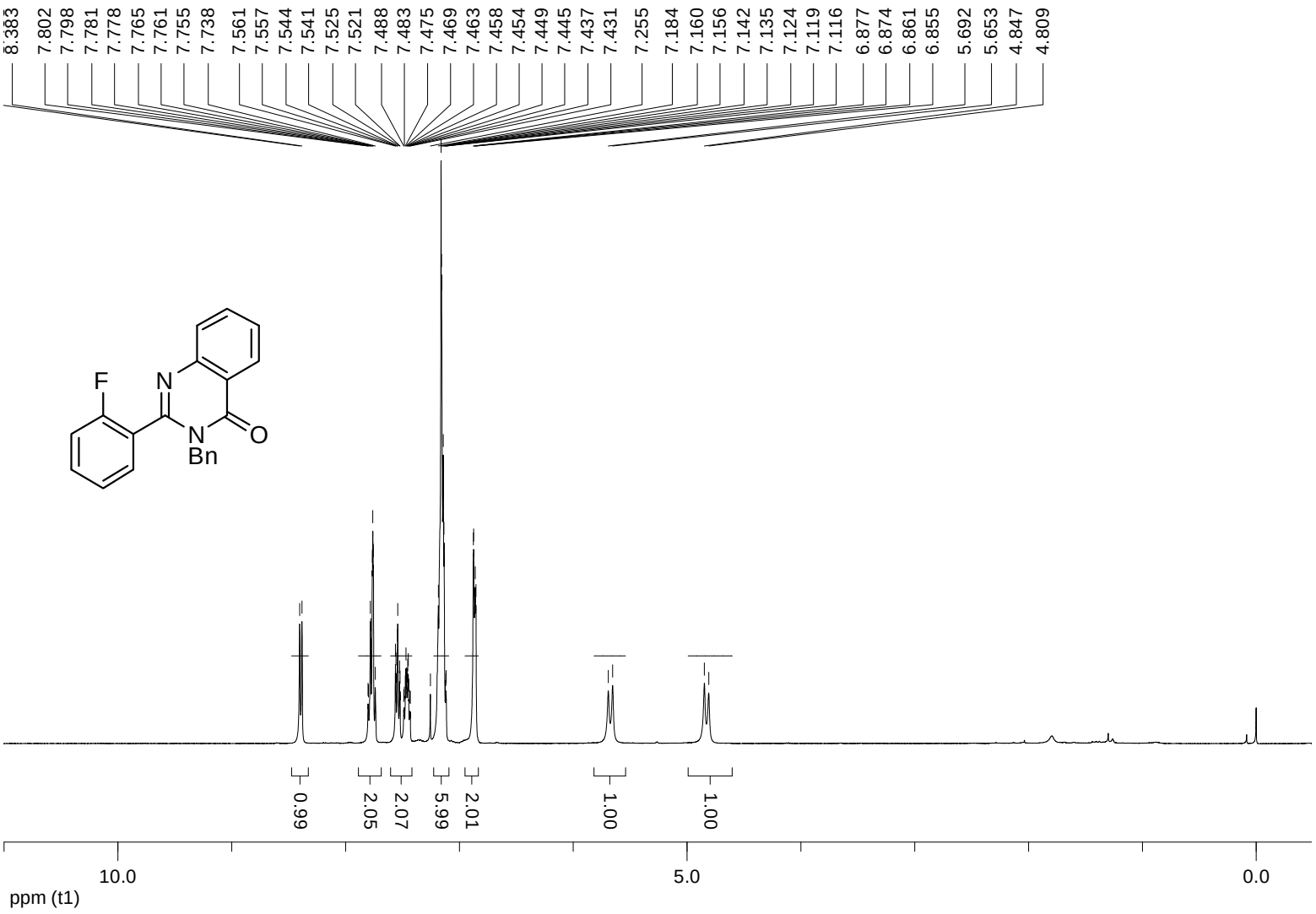
^{1}H NMR spectrum of **7c** (400 MHz, $CDCl_3$)



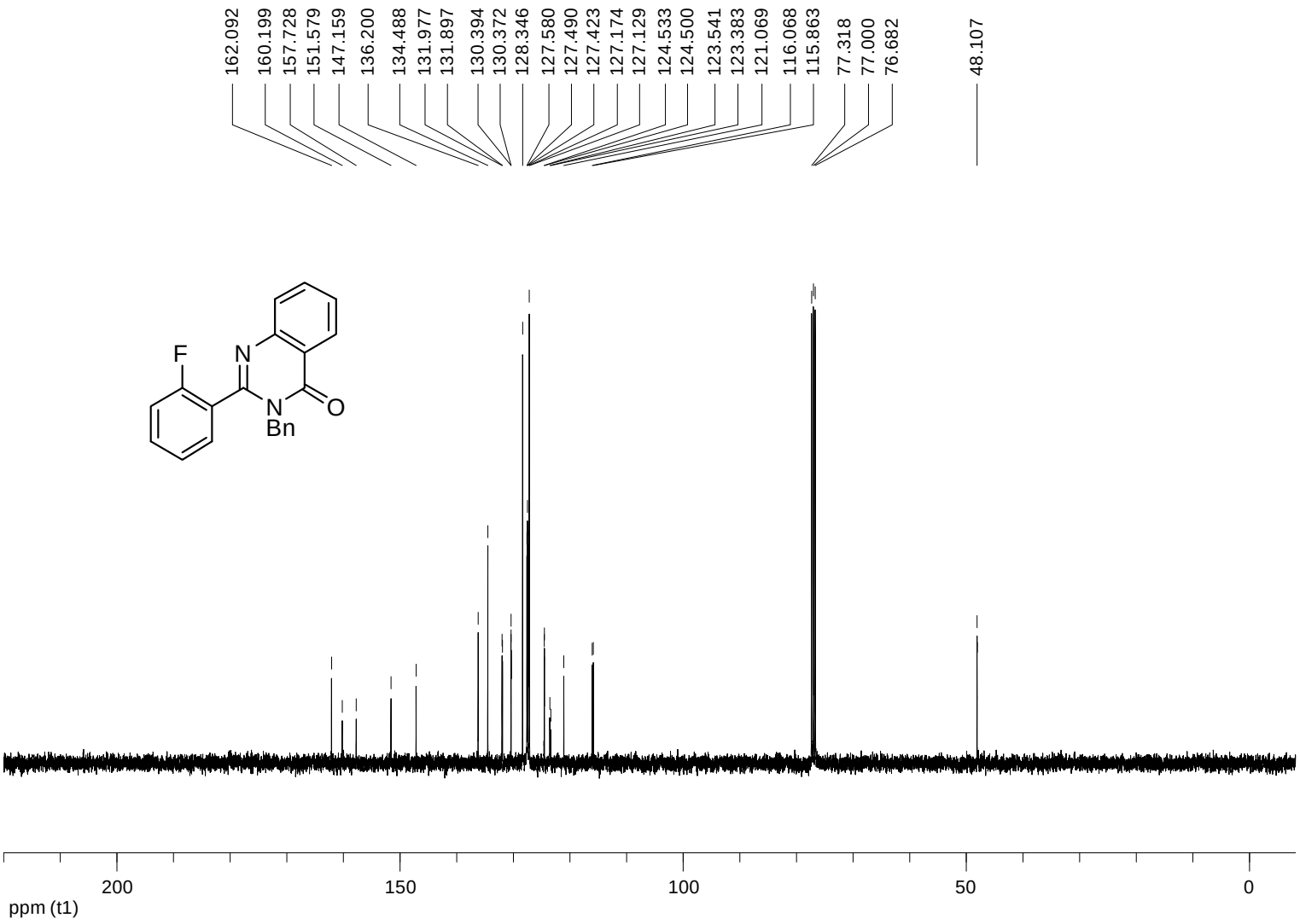
^{13}C NMR spectrum of **7c** (100 MHz, $CDCl_3$)



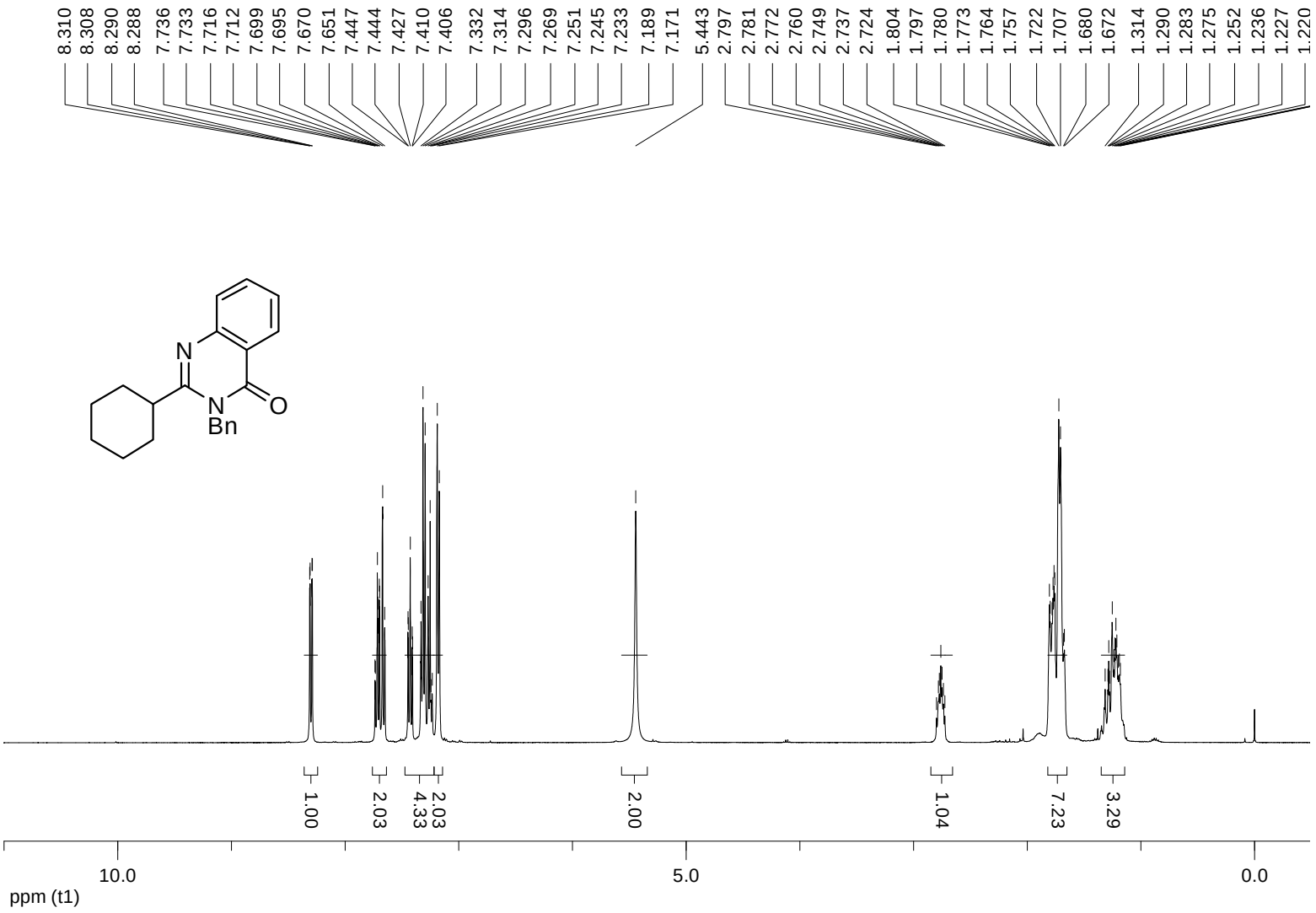
^{1}H NMR spectrum of **7d** (400 MHz, $CDCl_3$)



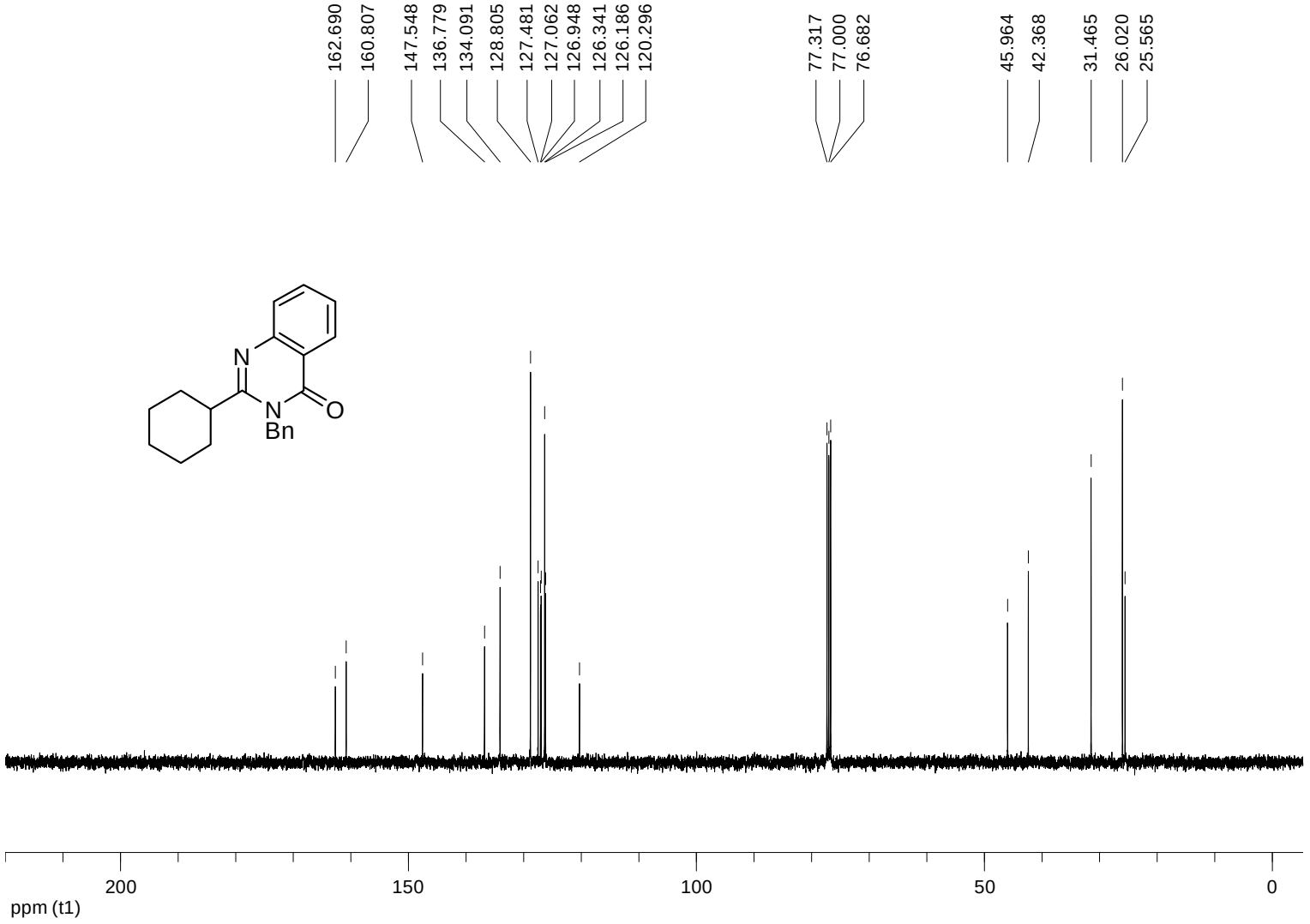
^{13}C NMR spectrum of **7d** (100 MHz, $CDCl_3$)



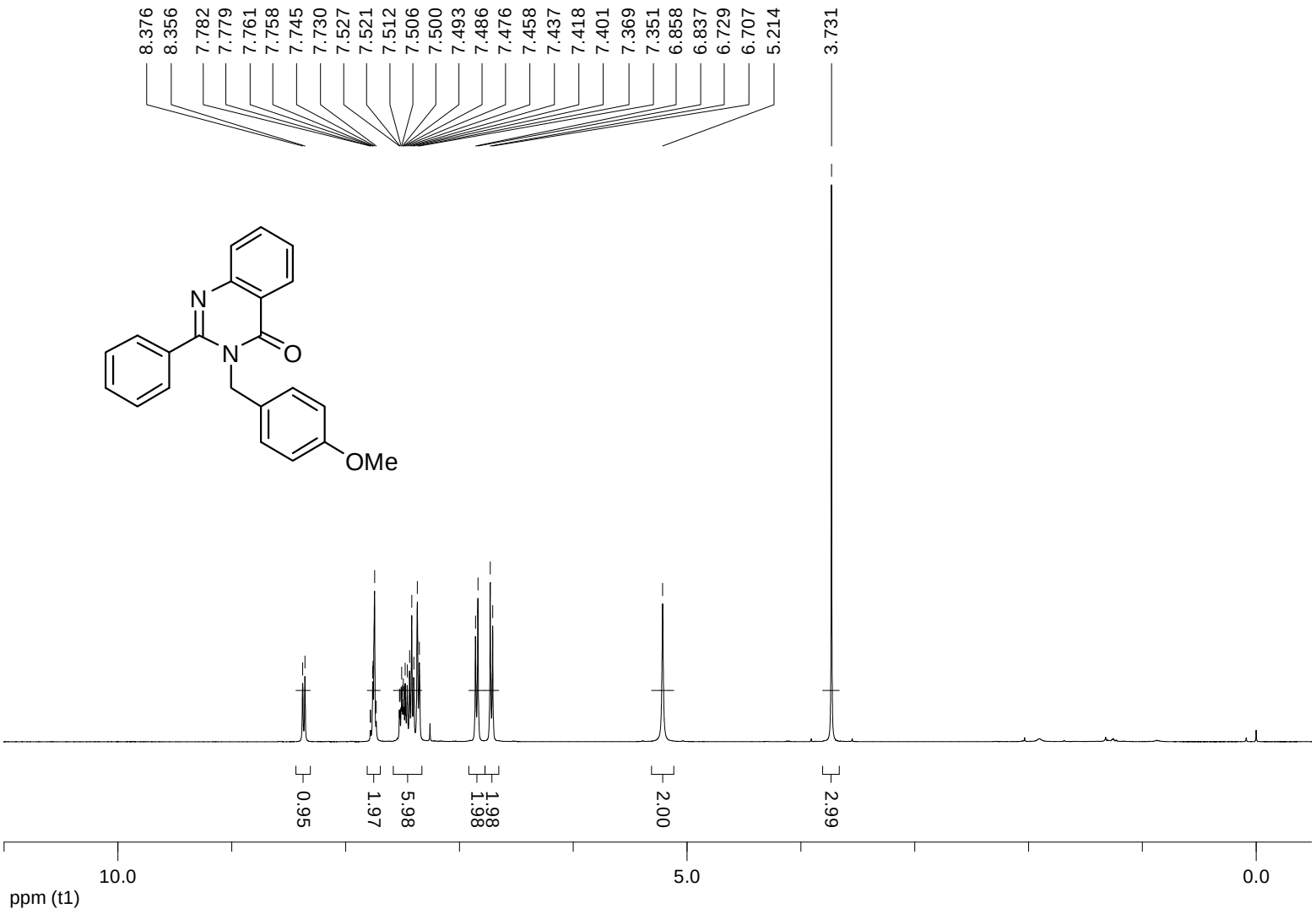
^{1}H NMR spectrum of **7e** (400 MHz, $CDCl_3$)



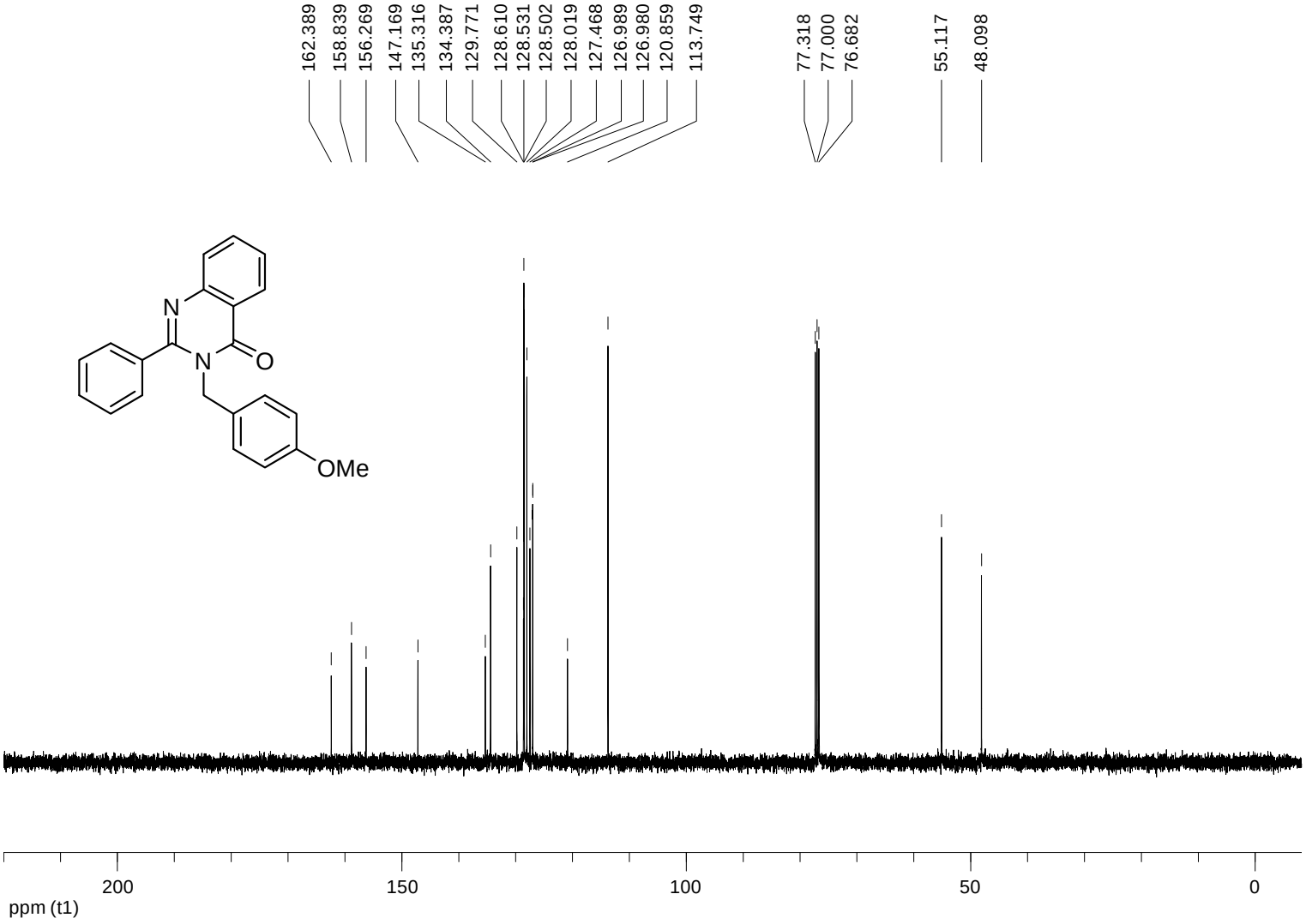
^{13}C NMR spectrum of **7e** (100 MHz, $CDCl_3$)



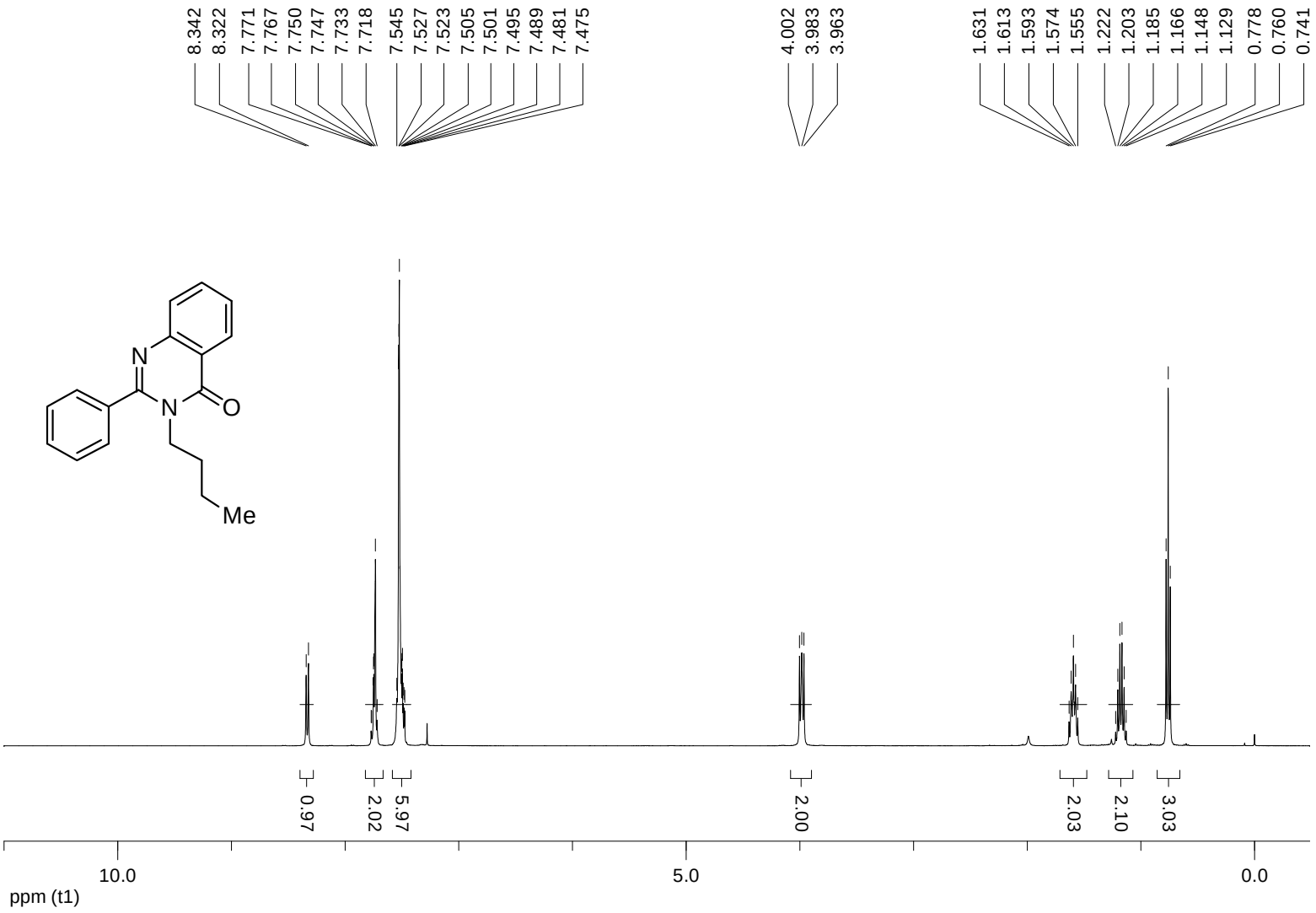
^{1}H NMR spectrum of **7f** (400 MHz, $CDCl_3$)



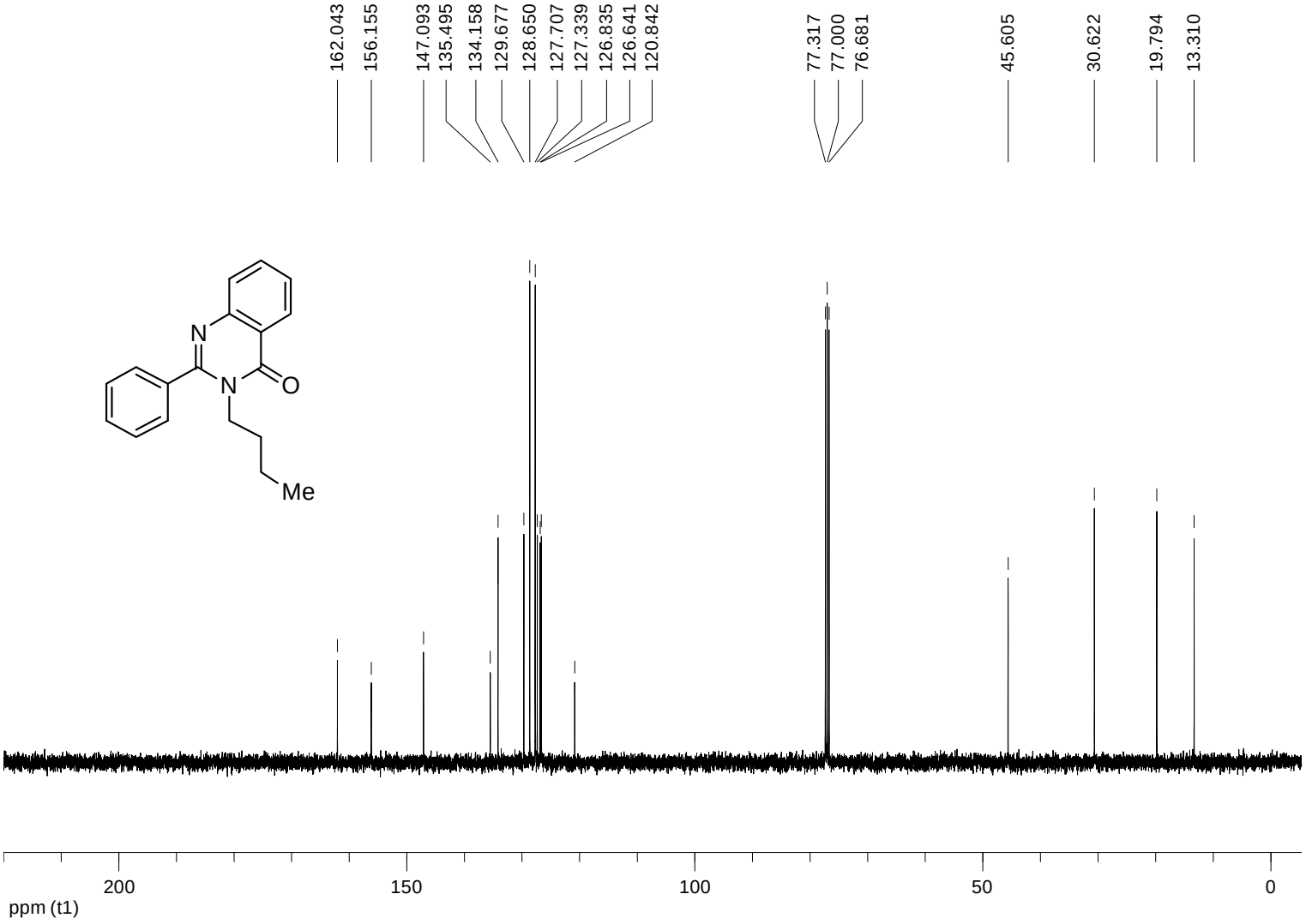
^{13}C NMR spectrum of **7f** (100 MHz, $CDCl_3$)



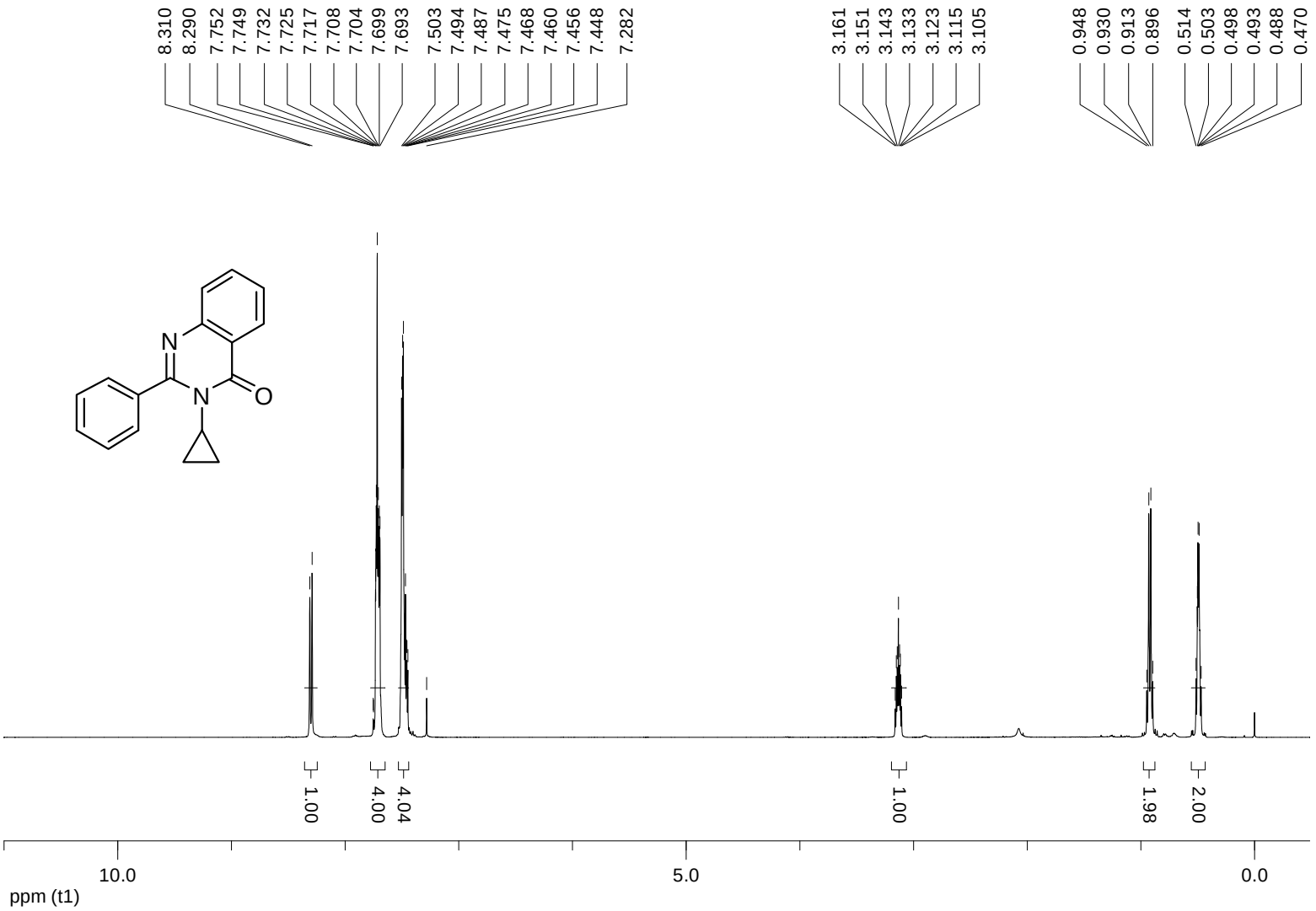
^{1}H NMR spectrum of **7g** (400 MHz, $CDCl_3$)



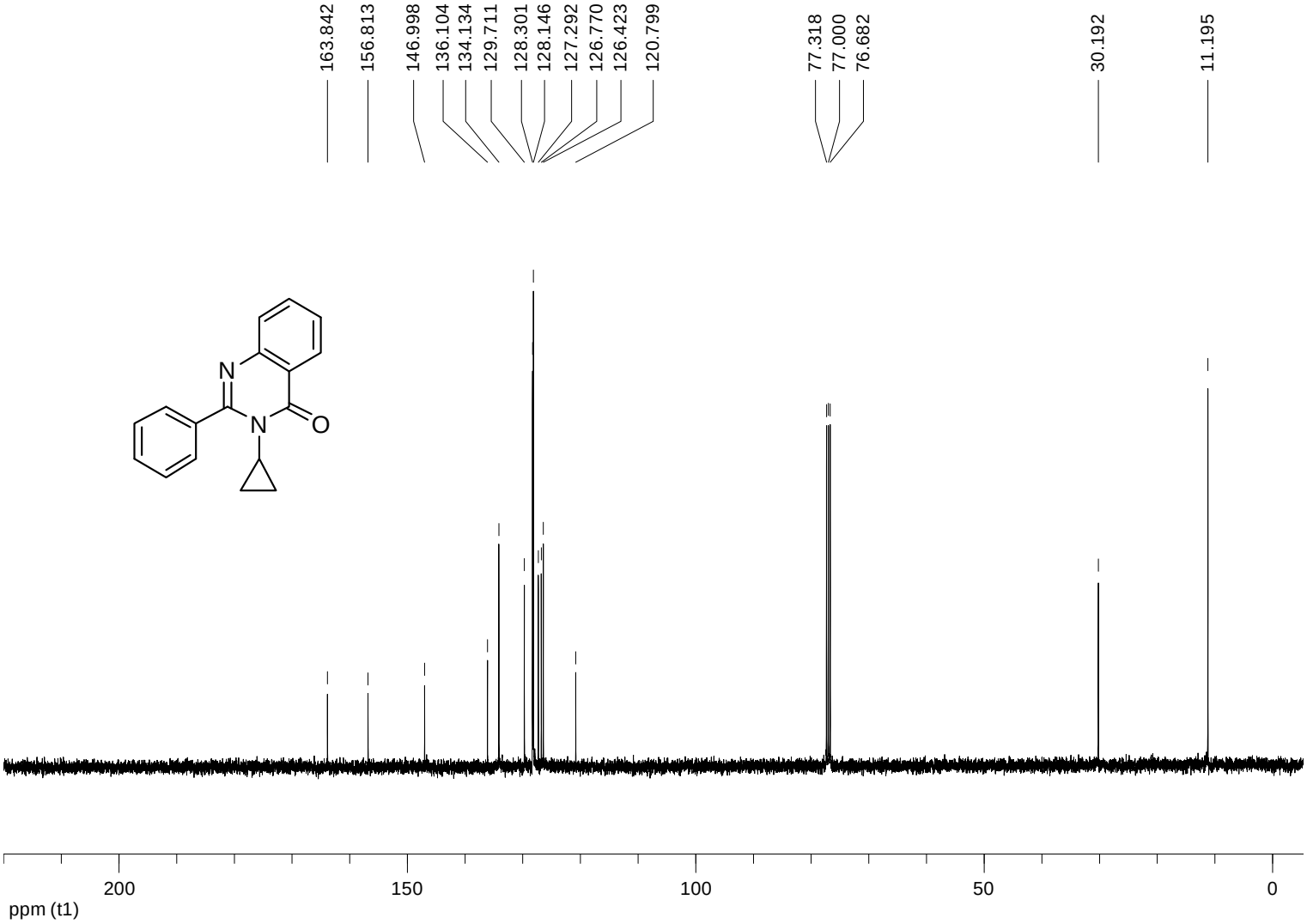
^{13}C NMR spectrum of **7g** (100 MHz, $CDCl_3$)



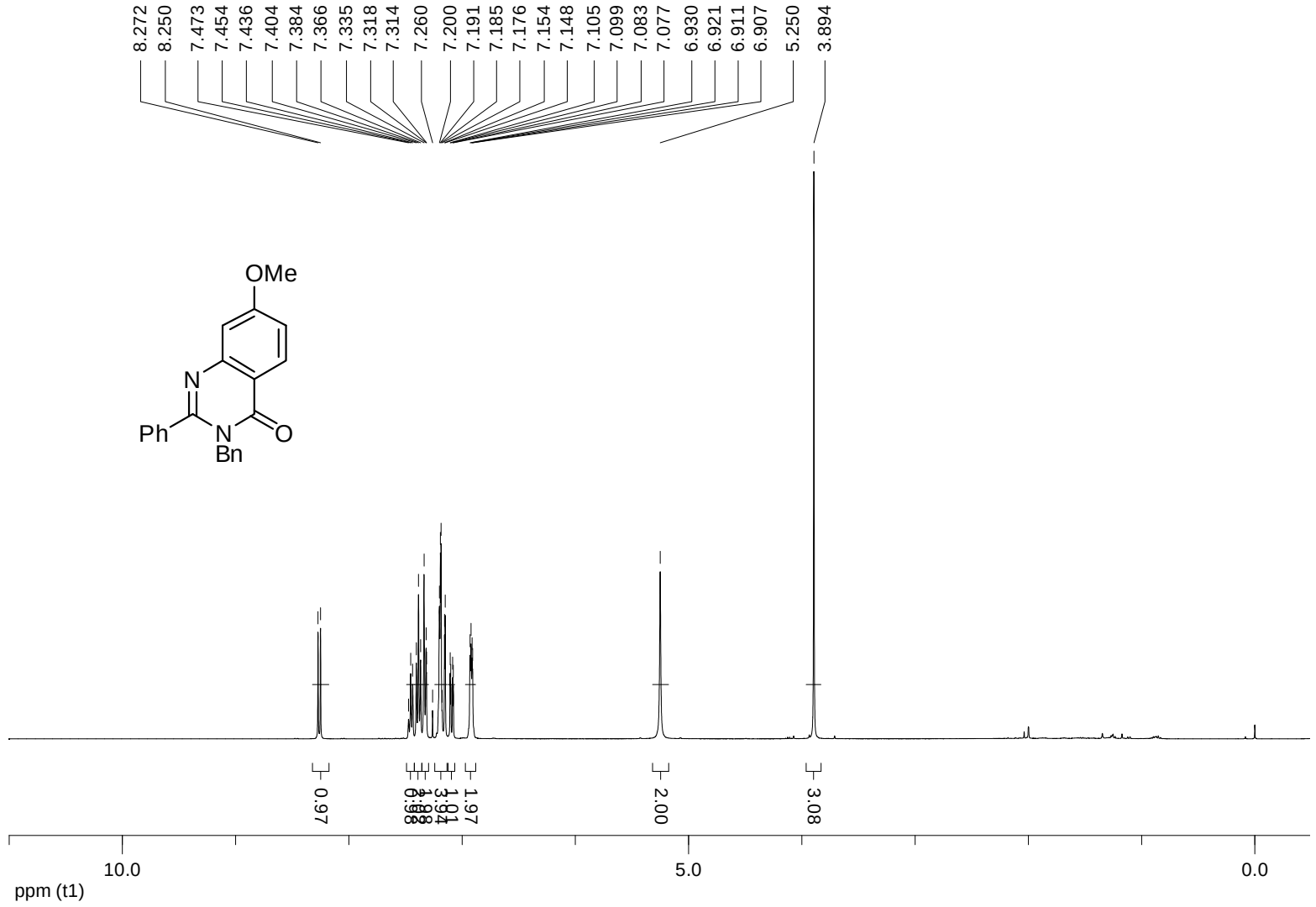
^{1}H NMR spectrum of **7h** (400 MHz, $CDCl_3$)



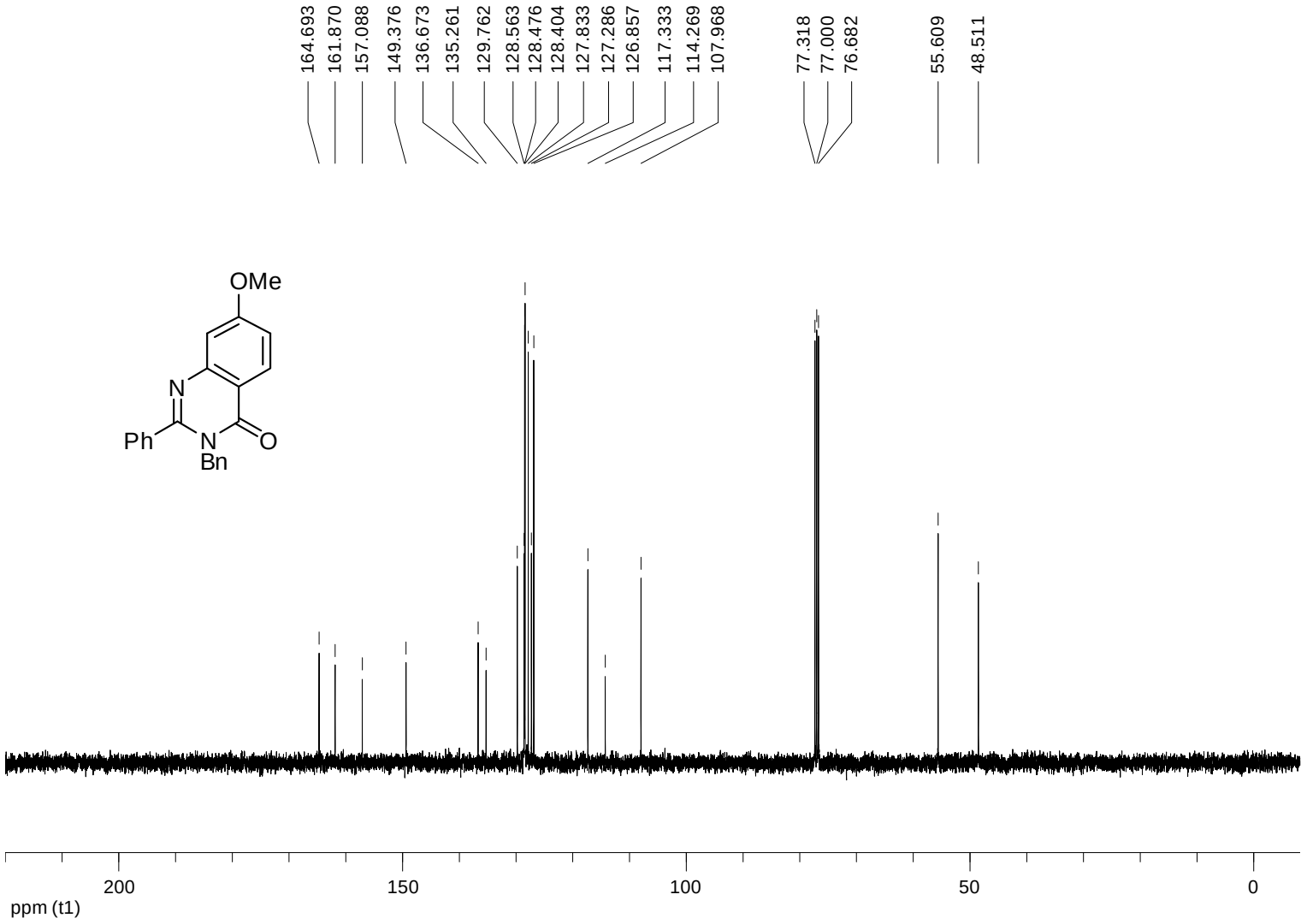
^{13}C NMR spectrum of **7h** (100 MHz, $CDCl_3$)



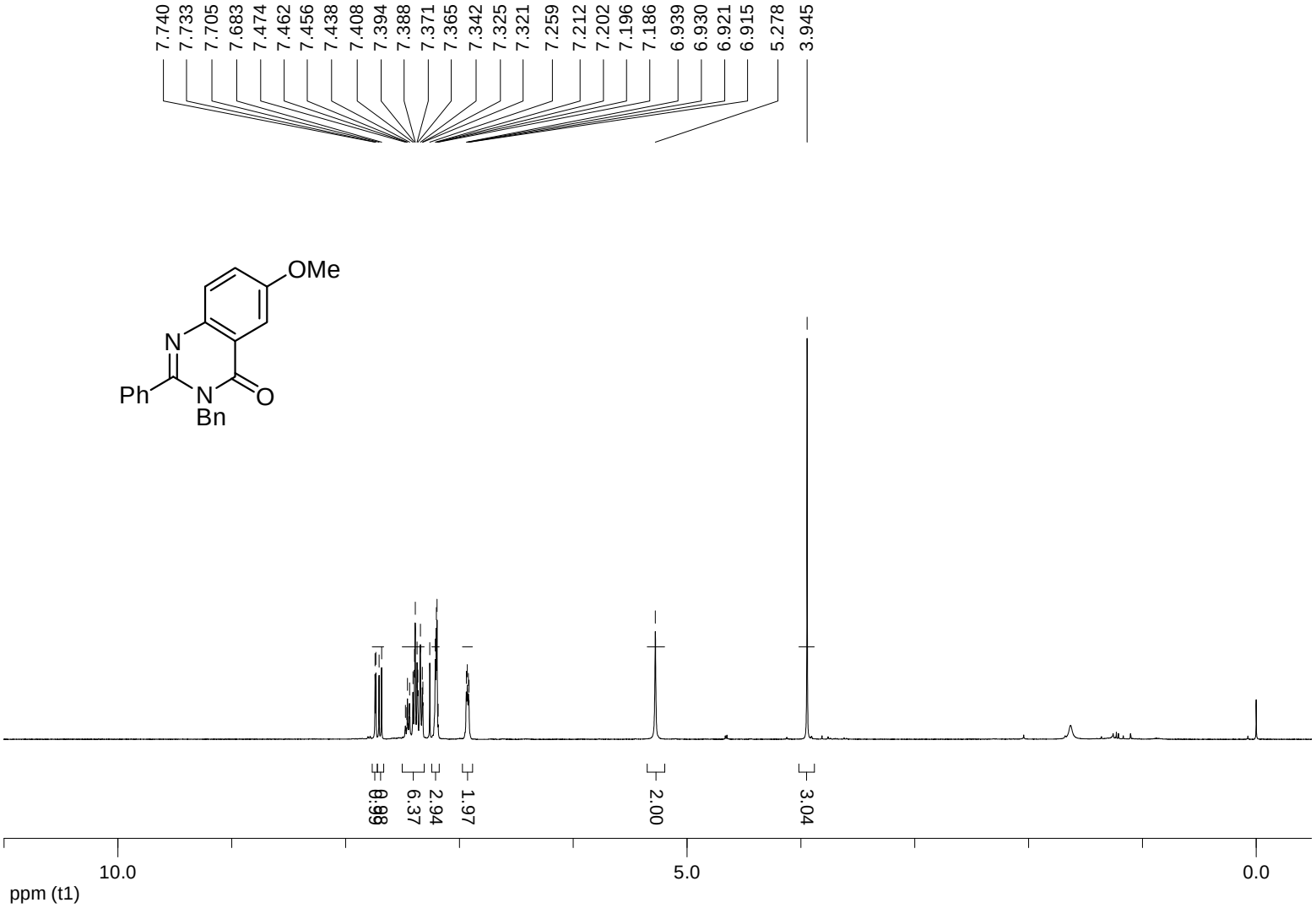
^{1}H NMR spectrum of **7i** (400 MHz, $CDCl_3$)



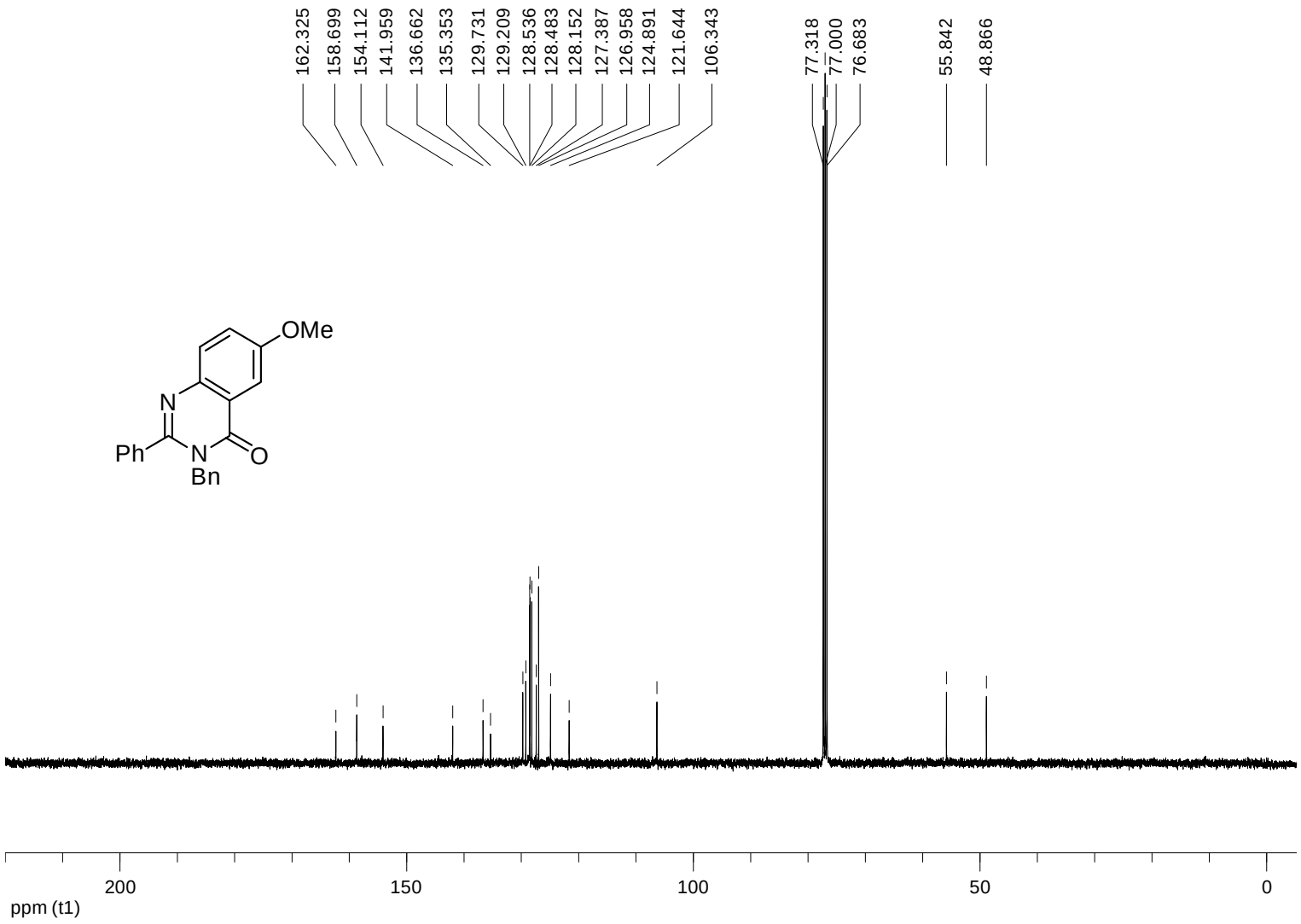
^{13}C NMR spectrum of **7i** (100 MHz, $CDCl_3$)



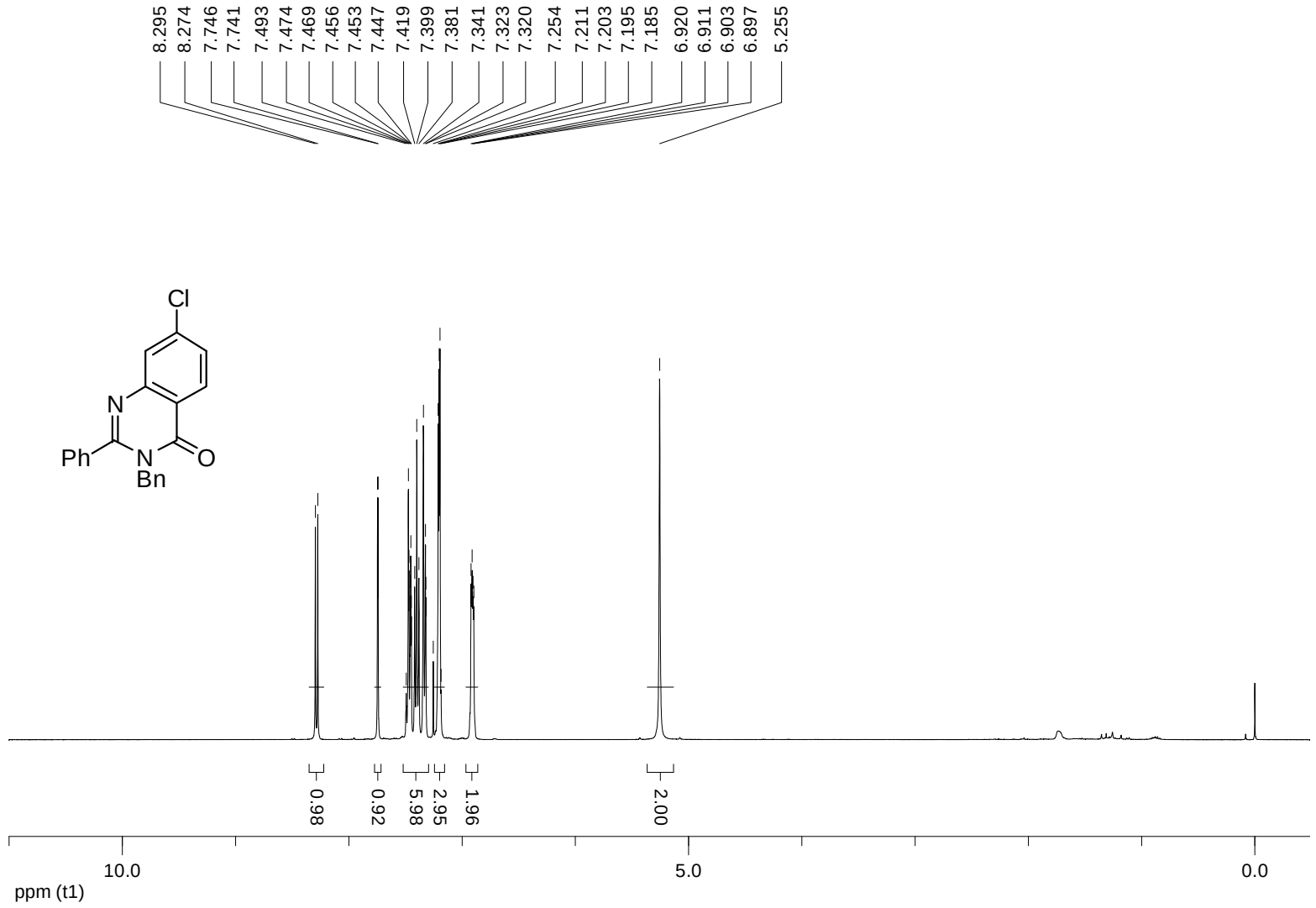
^{1}H NMR spectrum of **7i'** (400 MHz, $CDCl_3$)



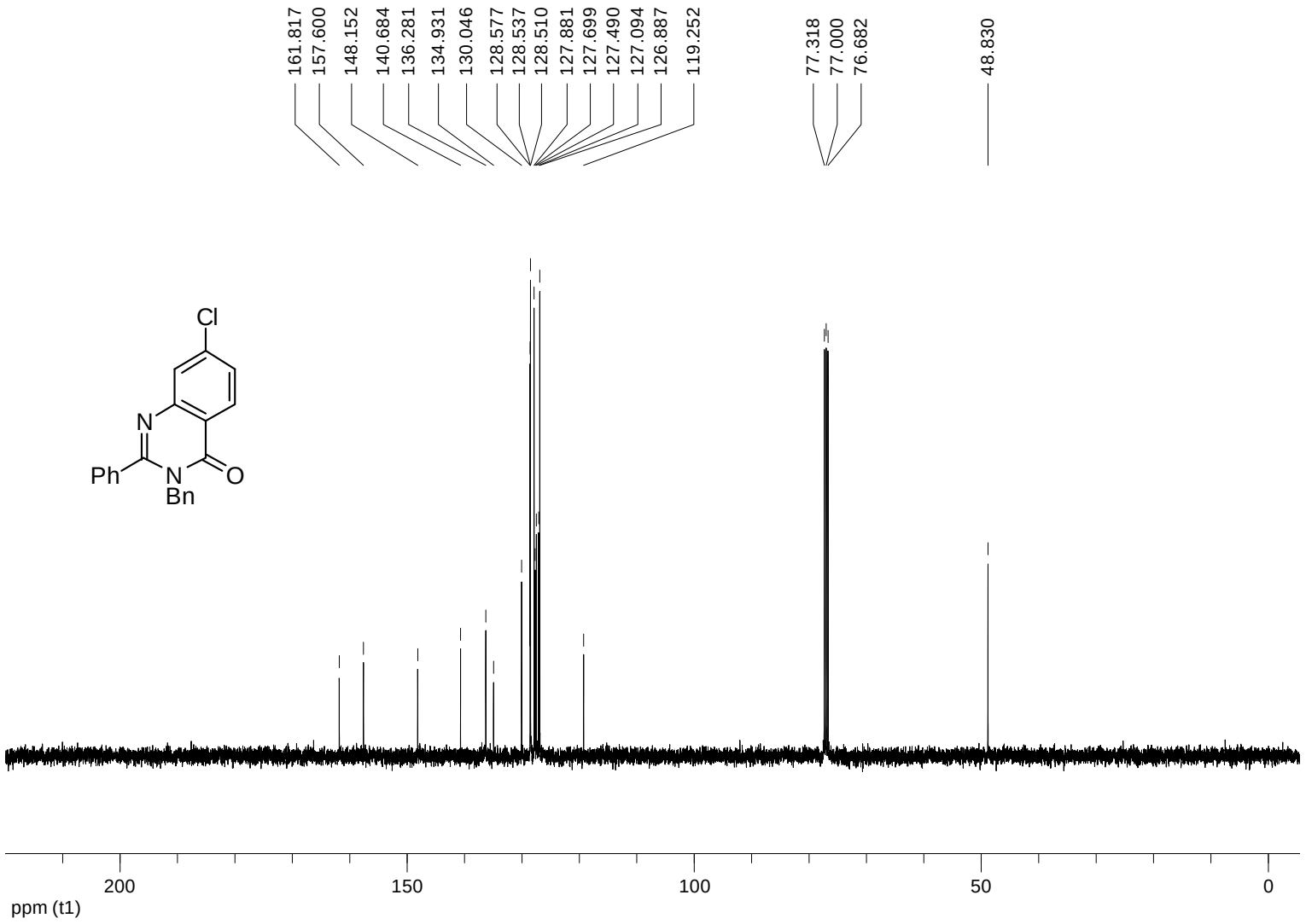
^{13}C NMR spectrum of **7i'** (100 MHz, $CDCl_3$)



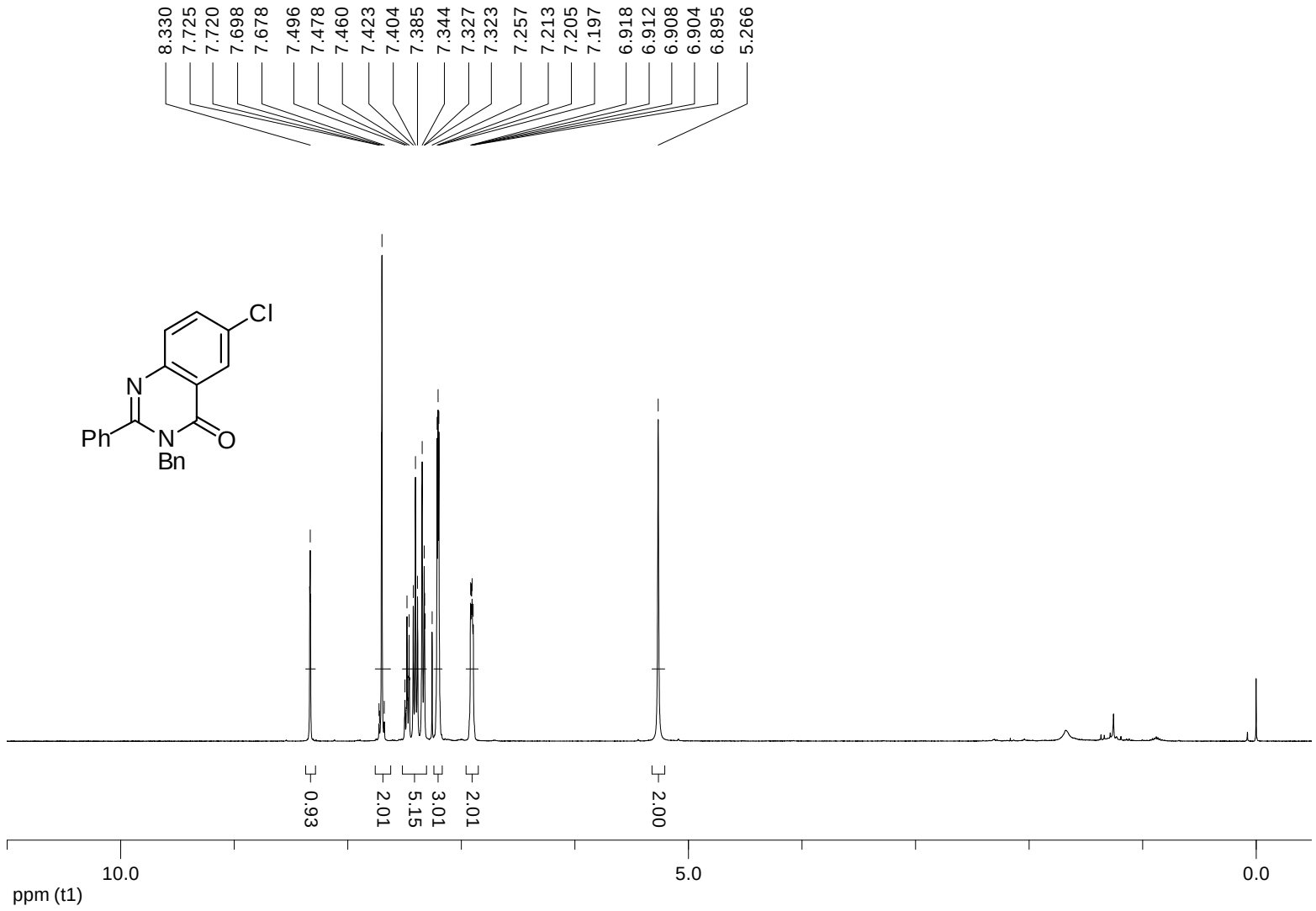
^{1}H NMR spectrum of **7j** (400 MHz, $CDCl_3$)



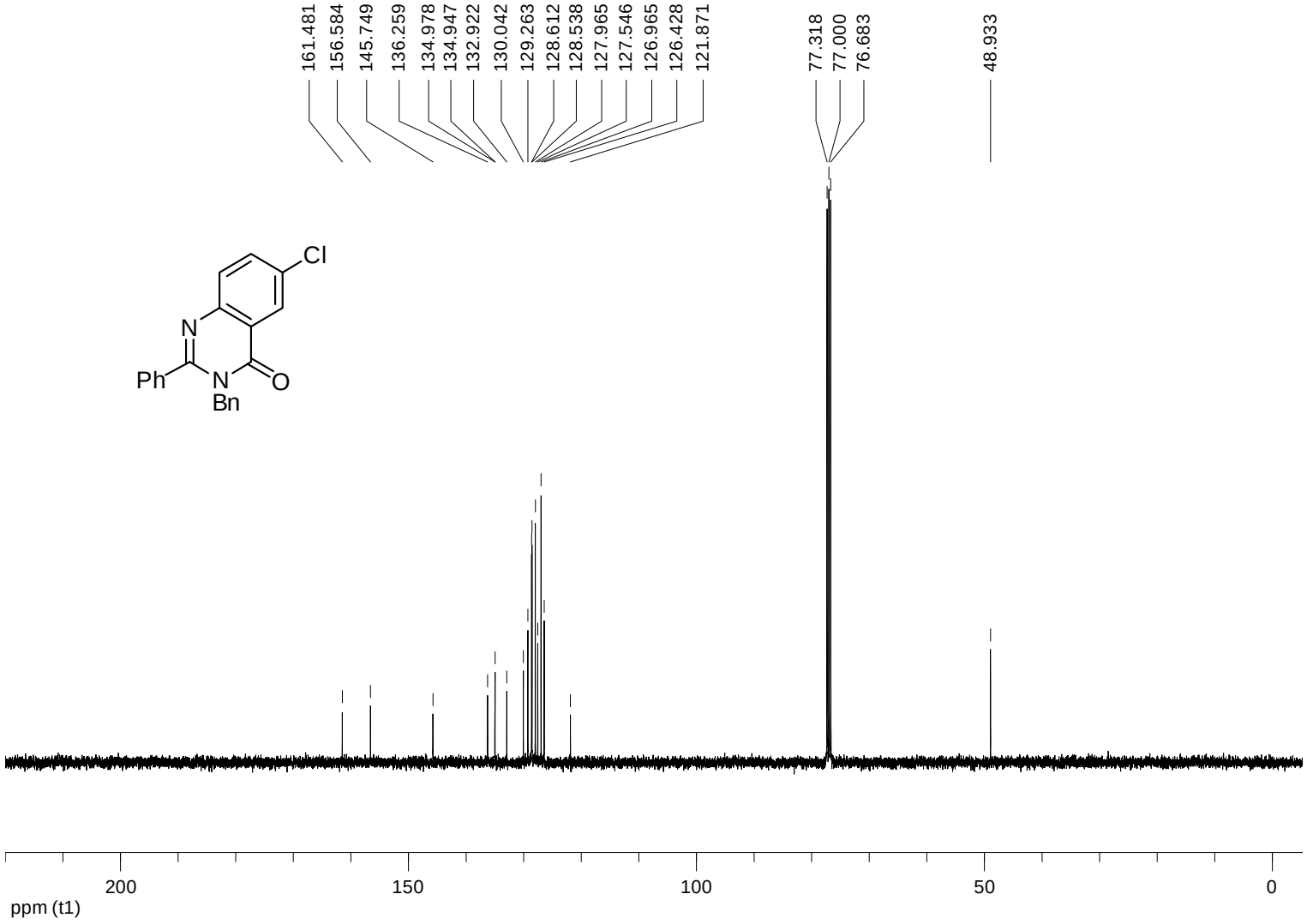
^{13}C NMR spectrum of **7j** (100 MHz, $CDCl_3$)



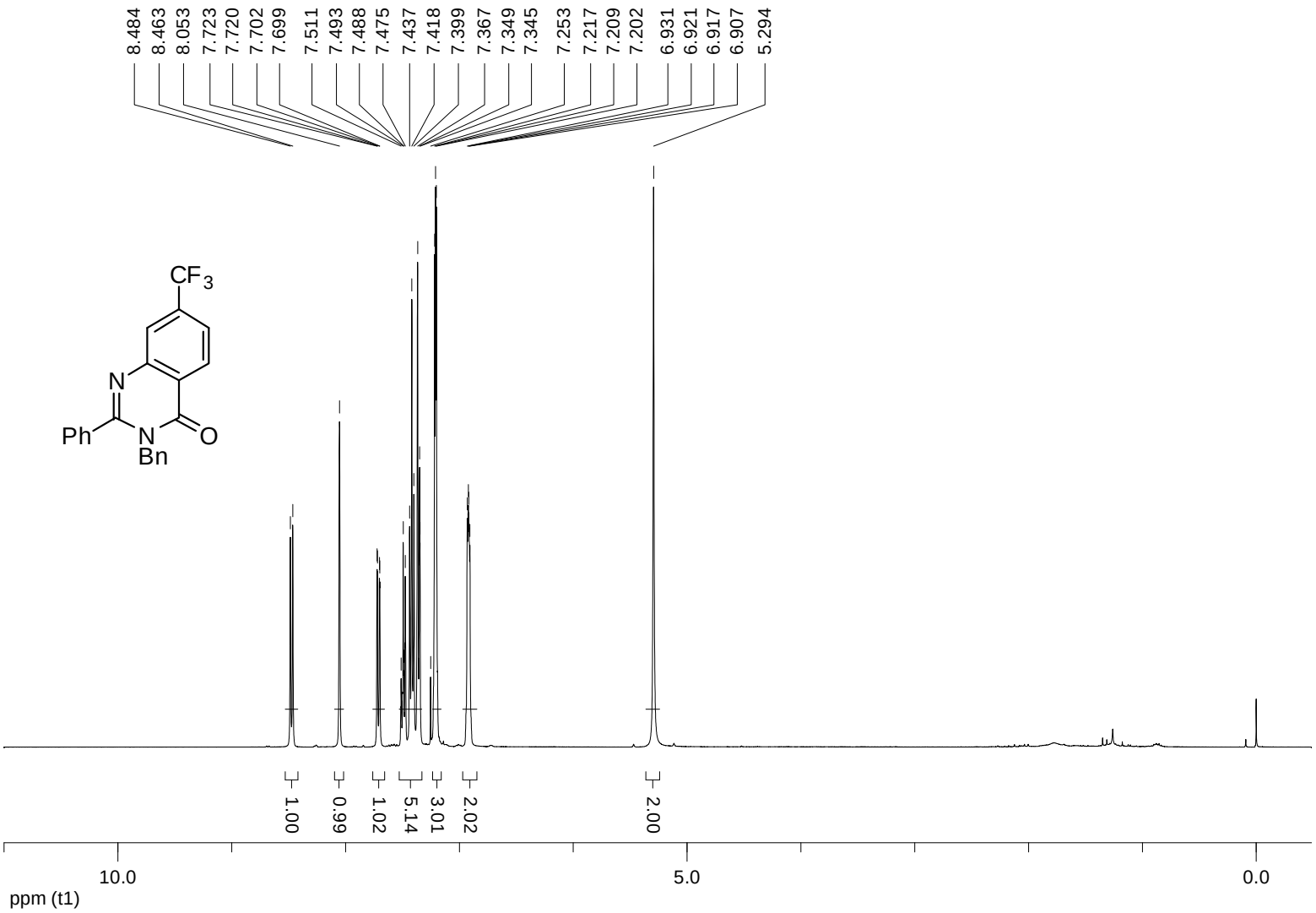
^{1}H NMR spectrum of **7j'** (400 MHz, $CDCl_3$)



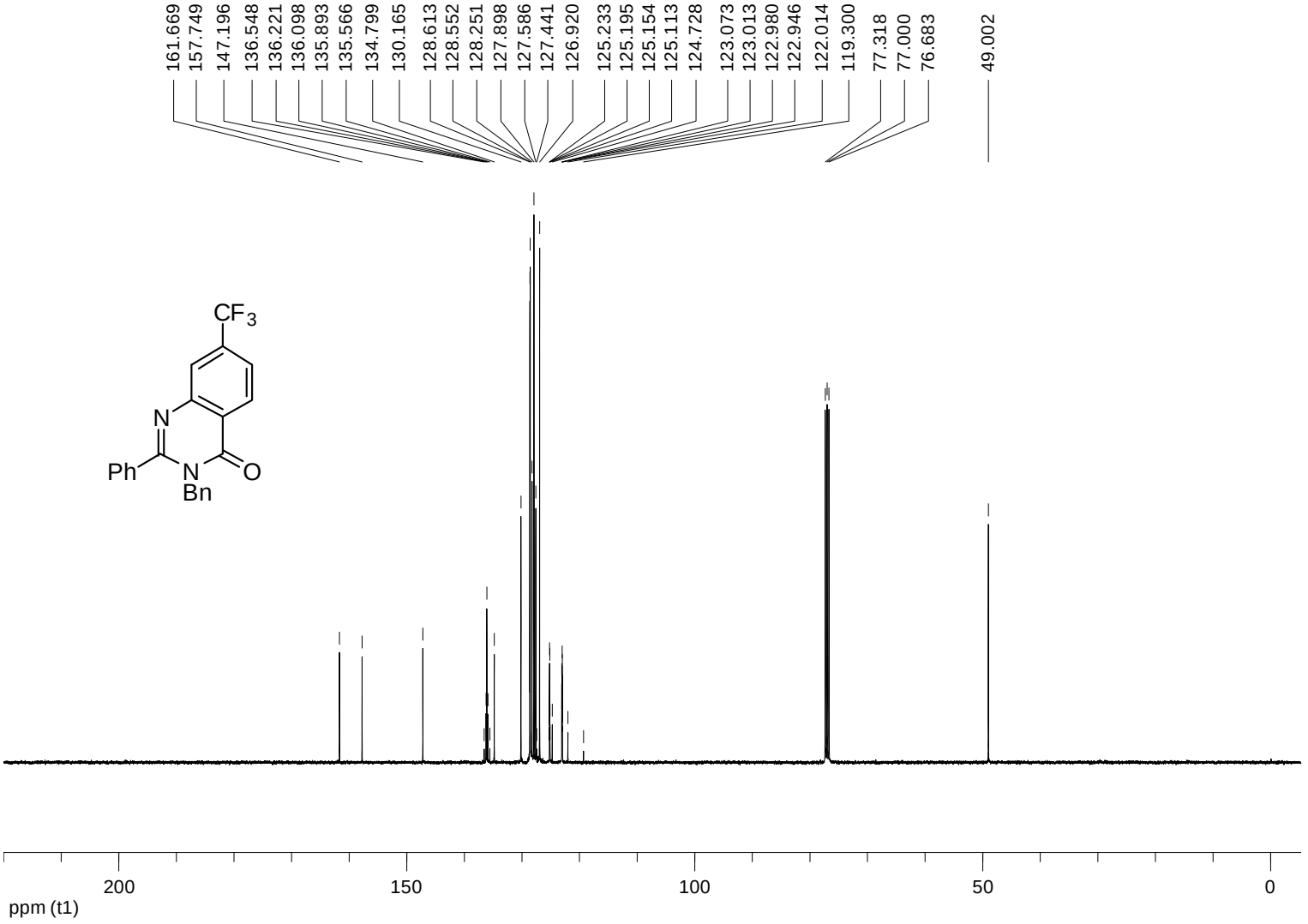
^{13}C NMR spectrum of **7j'** (100 MHz, $CDCl_3$)



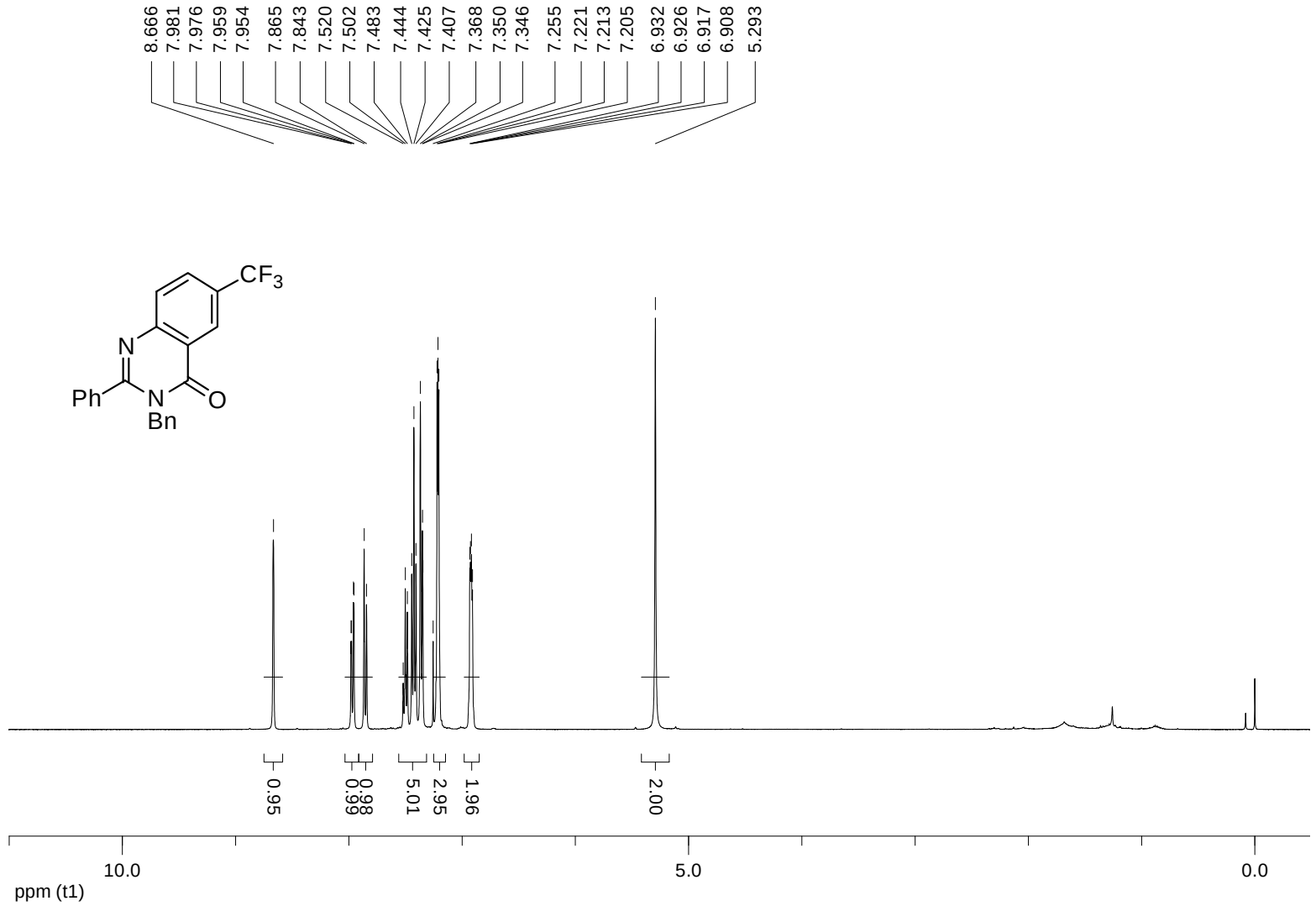
^{1}H NMR spectrum of **7k** (400 MHz, $CDCl_3$)



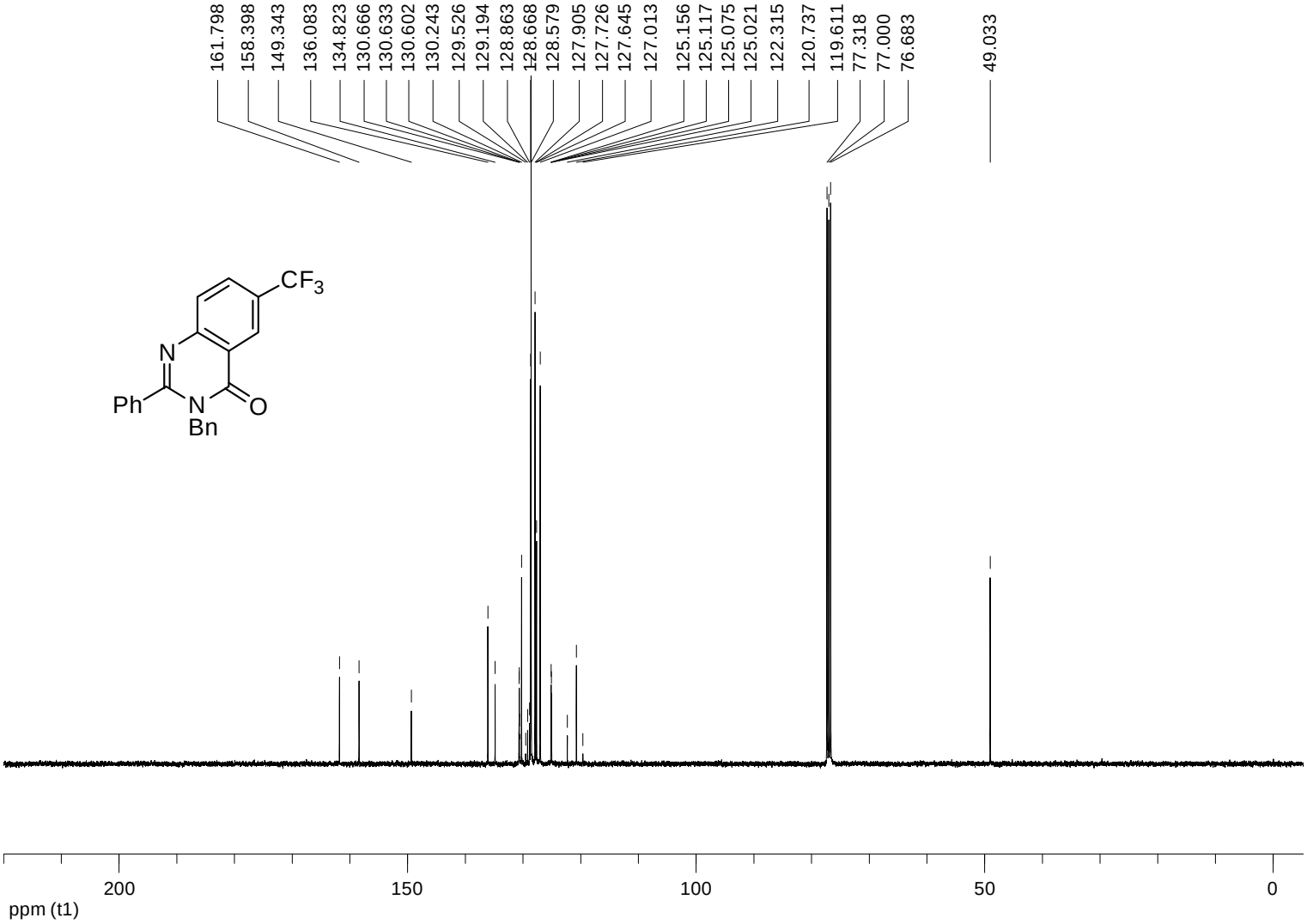
^{13}C NMR spectrum of **7k** (100 MHz, $CDCl_3$)



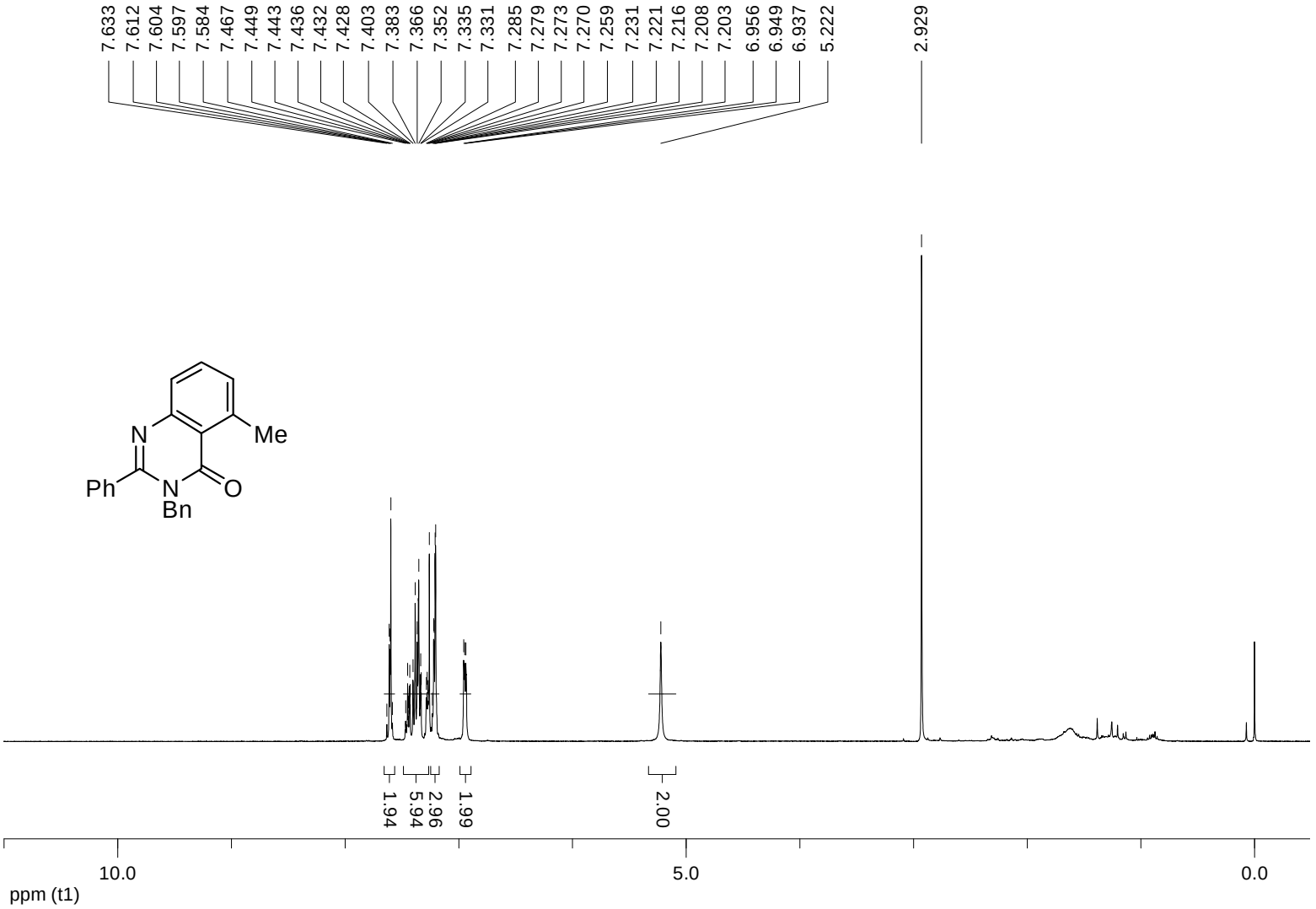
^{1}H NMR spectrum of **7k'** (400 MHz, $CDCl_3$)



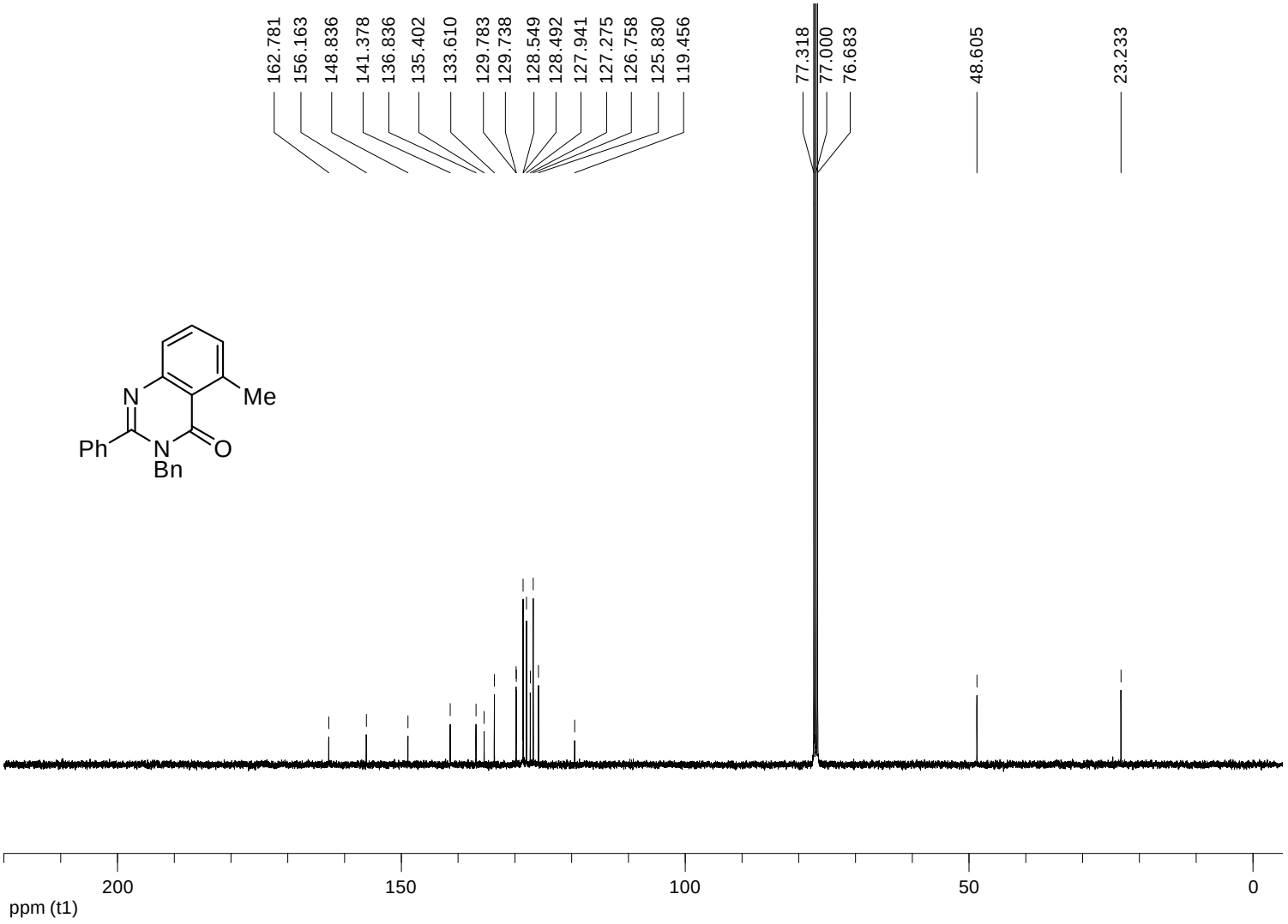
^{13}C NMR spectrum of **7k'** (100 MHz, $CDCl_3$)



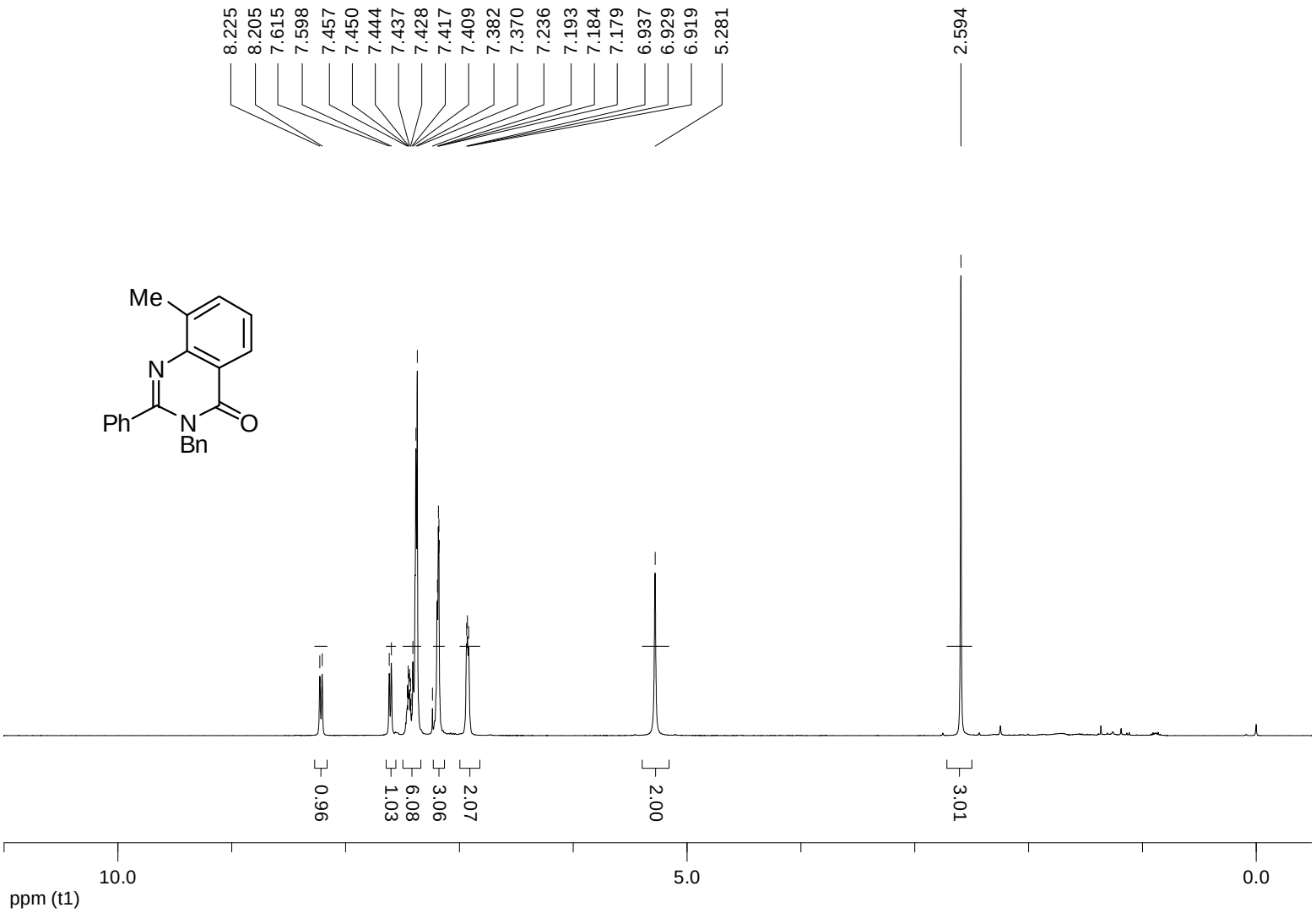
^{1}H NMR spectrum of **7l** (400 MHz, $CDCl_3$)



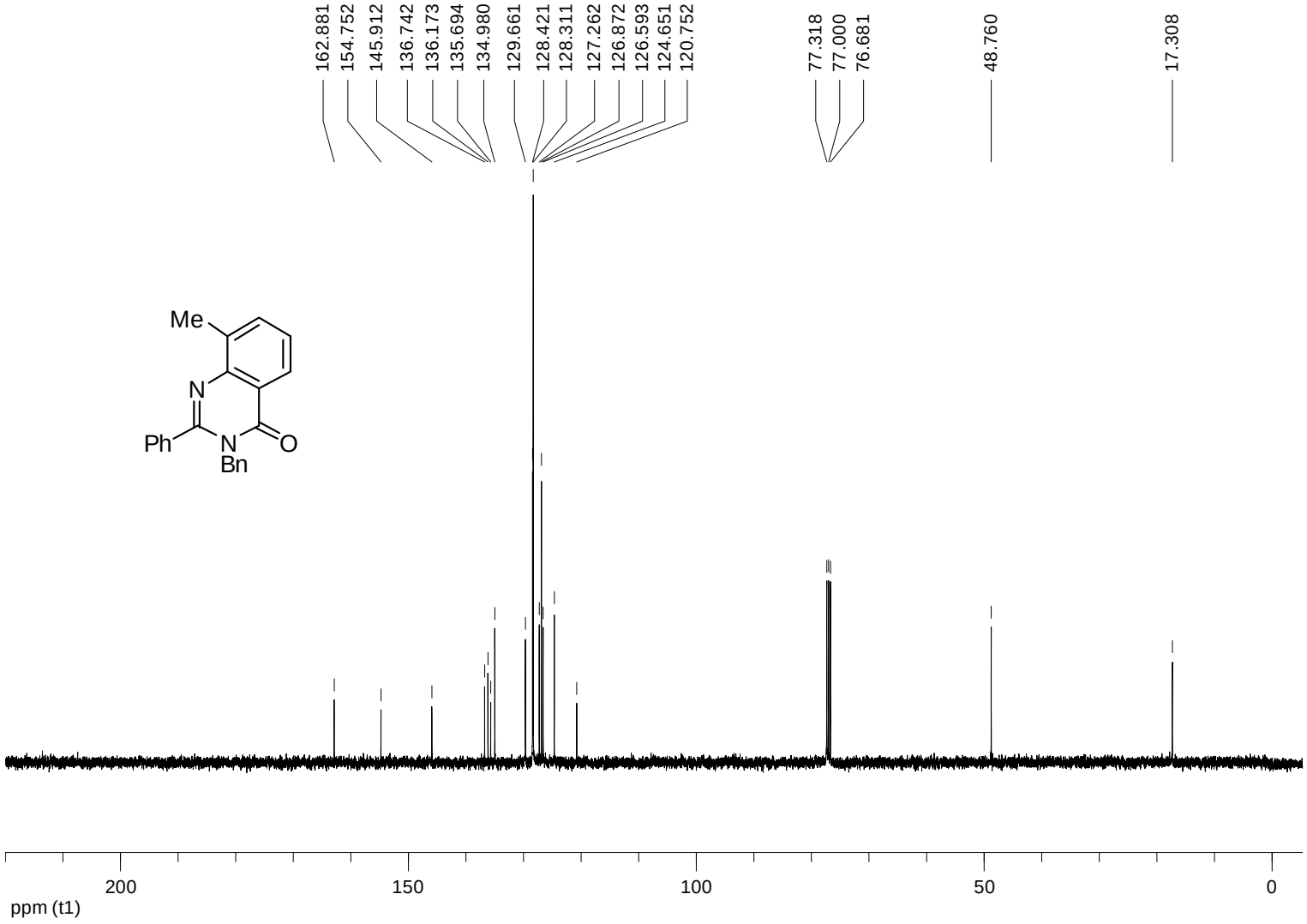
^{13}C NMR spectrum of **7l** (100 MHz, $CDCl_3$)



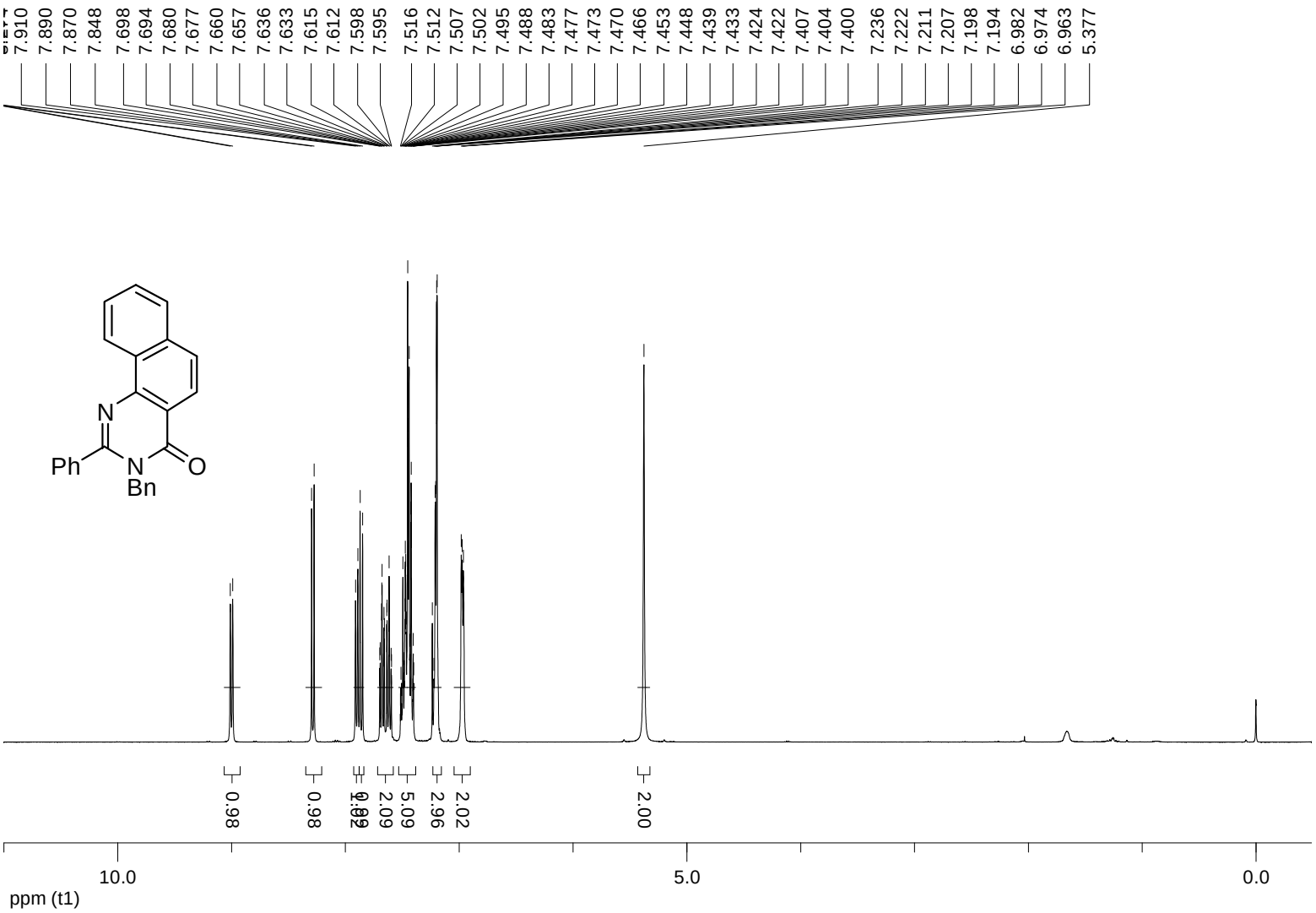
^{1}H NMR spectrum of **7l'** (400 MHz, $CDCl_3$)



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



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



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