Electronic Supplementary Information

TEMPO-Mediated Allylic C-H Amination with Hydrazones

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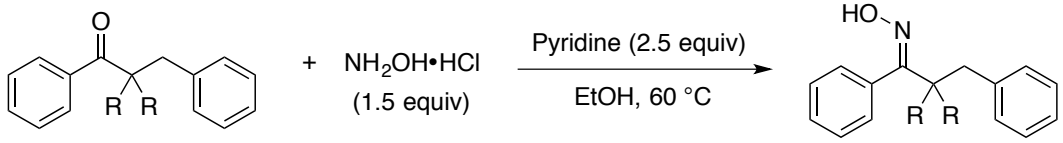
1. General

^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 or 300 spectrometers 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 or 300 spectrometers 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, tt = triplet of triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, tdd = triplet of double of doublet, dddd = doublet of doublet of doublet of doublet, m = multiplet, br = broad. IR spectra were recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer on NaCl plate. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer (Waters). X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractometer. Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using either Merck silica gel 60 or with distilled solvents. DMF (anhydrous), 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), diisopropyl azodicarboxylate (DIAD) and K_2CO_3 were purchased from Sigma-Aldrich Co., Inc. In the case that hydrazones (**3l**, **3m**) were obtained as a mixture of *E/Z*-isomers, the stereochemistry was assigned using ^{13}C NMR (the chemical shift of α-carbon with *syn* to the NH is farther to the higher field than that with *anti* to the NH).[1]

2. Synthesis of oximes 1 and hydrazones 3

2.1 Synthesis of oximes 1

General procedure:[2]



To a solution of corresponding ketone (1.0 equiv) and hydroxylamine hydrochloride (1.5 equiv) in EtOH (1.0 M) was added pyridine (2.5 equiv) under a nitrogen atmosphere. The reaction mixture was warmed to 60 °C and kept stirring until the ketone was consumed. After the mixture was cooled down to room temperature, the solvent was removed under vacuum. The residue was diluted with water and extracted with ethyl acetate. The combined extracts were washed with brine and dried over $MgSO_4$, followed by filtration and evaporation to give the crude oxime product. Purification of the crude product by flash column chromatography (silica gel;ethyl acetate: hexane = 5:95) afforded the oxime.

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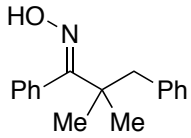
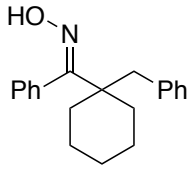
(1) R. M. Silverstein, F. X. Webster, D. J. Kiemle, *Spectrometric Identification of Organic Compounds*; John Wiley & Sons Inc.: New York, 2005.
(2) X. Zhu, Y.-F. Wang, W. Ren, F.-L. Zhang, S. Chiba, *Org. Lett*. 2013, **15**, 3214.

(*Z*)-2,2-Dimethyl-1,3-diphenylpropan-1-one oxime (1a):[2]



57% yield as a white solid (single *Z*-isomer) from 2,2-dimethyl-1,3-diphenylpropan-1-one.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (6H, s), 2.87 (2H, s), 7.09 (2H, d, *J* = 7.6 Hz), 7.15 (2H, d, *J* = 7.2 Hz), 7.20- 7.28 (3H, m), 7.35-7.44 (3H, m), 7.56 (1H, s br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.6, 41.0, 46.1, 126.2, 127.7, 127.8, 128.0, 128.1, 130.9, 133.6, 138.1, 166.6.

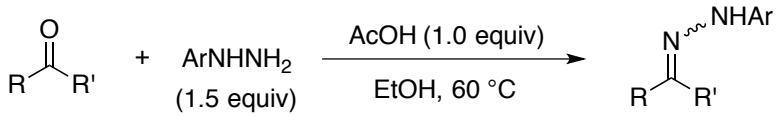
(*Z*)-(1-benzylcyclohexyl)(phenyl)methanone oxime (1b):[2]



81% yield as a white solid (single *Z* isomer) from (1-benzylcyclohexyl)(phenyl)methanone.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24-1.39 (3H, m), 1.45-1.56 (5H, m), 1.73-1.77 (2H, m), 2.93 (2H, s), 7.02 (2H, d, *J* = 7.2 Hz), 7.18-7.39 (8H, m), 8.09 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.5, 25.8, 34.1, 44.8, 45.3, 126.2, 127.7, 127.8, 127.9, 128.0, 131.0, 133.5, 137.9, 163.9.

2.2 Synthesis of hydrazones 3

General procedure: modified by the reported method[1]

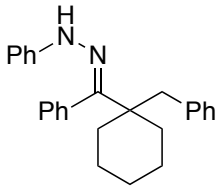


To a solution of ketone (1.0 equiv) and arylhydrazine (1.5 equiv) in EtOH (1.0 M) was added AcOH (1.0 equiv) under nitrogen atmosphere. The reaction mixture was then warmed to 60 °C and kept stirring until the ketone was consumed. After the mixture was cooled down to room temperature, the solvent was removed under vacuum and the resulting crude product was purified immediately by flash column chromatography under N_2 protection (as the hydrazones are unstable and can be oxidized by oxygen to give the peroxide species[4]) afforded the corresponding hydrazones which was used immediately or stored under -20 °C with N_2 protection.

*All the hydrazones were obtained as a pure single isomer except for **3l** and **3m**.*

(3) T. Takuwa, T. Minowa, H. Fujisawa, T. Mukaiyama, *Chem. Pharm. Bull*. 2005**, 53**, 476.
(4) M. Harej, D. Dolenc, *J. Org. Chem*. 2007, **72**, 7214.

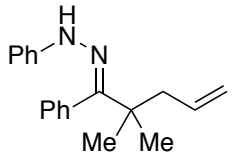
(*Z*)-1-((1-Benzylcyclohexyl)(phenyl)methylene)-2-phenylhydrazine (3a):



68% yield as a yellow viscous liquid (single *Z*-isomer) from (1-benzylcyclohexyl)(phenyl)-methanone.[2]

IR (NaCl) 3337, 3053, 2934, 1647, 1601, 1503, 1452, 1308, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19-1.35 (1H, m), 1.40-1.49 (4H, m), 1.53-1.56 (3H, m), 1.81-1.86 (2H, m), 2.99 (2H, s), 6.78 (1H, t, *J* = 8.0 Hz), 6.90-6.92 (5H, m), 7.17-7.26 (7H, m), 7.35-7.43 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 26.0, 26.9, 34.4, 45.6, 112.5, 119.2, 125.9, 127.8, 128.39, 128.41, 129.0, 129.1, 131.1, 133.7, 138.9, 145.4, 151.5; ESIHRMS: Found: *m/z* 369.2333. Calcd for $C_{26}H_{29}N_2$: $(M+H)^+$ 369.2331.

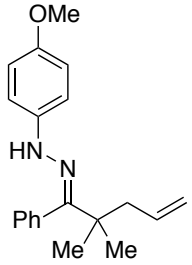
(*Z*)-1-(2,2-Dimethyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3b):



91% yield as a pale yellow oil (single *Z*-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one [5]

IR (NaCl) 3335, 3051, 2968, 2928, 1639, 1601, 1501, 1265, 1252, 1101, 1066, 1016 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (6H, s), 2.33 (2H, d, *J* = 7.2 Hz), 5.06 (1H, d, *J* = 16.8 Hz), 5.07 (1H, d, *J* = 11.2 Hz), 5.94 (1H, tdd, *J* = 7.2, 11.2, 16.8 Hz), 6.73 (1H, s br), 6.76 (1H, t, *J* = 7.6 Hz), 6.91 (2H, d, *J* = 8.4 Hz), 7.13 (2H, d, *J* = 7.6 Hz), 7.18 (2H, t, *J* = 7.6 Hz), 7.42 (1H, dd, *J* = 7.2, 7.6 Hz), 7.48 (1H, d, *J* = 7.6 Hz), 7.50 (1H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 41.0, 44.9, 112.5, 117.0, 119.3, 128.5, 128.6, 129.06, 129.10, 133.5, 135.7, 145.4, 153.2; ESIHRMS: Found: *m/z* 279.1861. Calcd for $C_{19}H_{23}N_2$: $(M+H)^+$ 279.1861.

(*Z*)-1-(2,2-Dimethyl-1-phenylpent-4-en-1-ylidene)-2-(4-methoxyphenyl)hydrazine (3c):

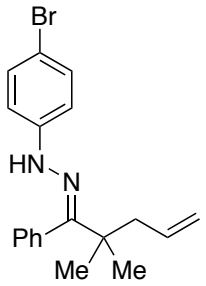


(5) B. Han, X.-L. Yang, R. Fang, W. Yu, C. Wang, X.-Y. Duan, S. Liu, *Angew. Chem. Int. Ed.* 2012, **51**, 8816.

98% yield (purity >95%) as a yellow viscous oil (single *Z*-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one.[5] This compound was easily oxidized by atmospheric oxygen to form peroxide species,[3] and thus should be used immediately after purification.[4]

IR (NaCl) 3333, 3055, 2967, 2932, 1640, 1603, 1512, 1466, 1265, 1233, 1115, 1092 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (6H, s), 2.32 (2H, d, *J* = 7.2 Hz),), 3.74 (3H, s), 5.05 (1H, d, 16.4 Hz), 5.06 (1H, d, *J* = 10.8 Hz), 5.94 (1H, tdd, *J* = 7.2, 10.8, 16.4 Hz), 6.57 (1H, s br), 6.76-6.79 (2H, m), 6.85-6.88 (2H, m), 7.11-7.13 (2H, m), 7.39-7.43 (1H, dd, *J* = 7.2, 7.6 Hz), 7.47 (1H, d, *J* = 7.6 Hz), 7.49 (1H, d, *J* =7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 40.9, 44.9, 55.8, 113.7, 114.6, 117.0, 128.4, 128.7, 129.1, 133.7, 135.8, 139.8, 152.7, 153.2; ESIHRMS: Found: *m/z* 309.1967. Calcd for $C_{20}H_{25}N_2O$: $(M+H)^+$ 309.1967

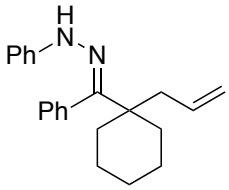
(*Z*)-1-(4-Bromophenyl)-2-(2,2-dimethyl-1-phenylpent-4-en-1-ylidene)hydrazine (3d):



98% yield as a yellow viscous oil (single *Z*-isomer) from 2,2-dimethyl-1-phenylpent-4-en-1-one.[5]

IR (NaCl) 3337, 3075, 2968, 2928, 1638, 1595, 1493, 1250, 1171, 1116, 1069 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.60 (6H, s), 2.32 (2H, d, *J* = 7.2 Hz), 5.06 (1H, dd, *J* =0.8, 17.6 Hz), 5.07 (1H, dd, *J* = 0.8, 9.6 Hz), 5.3 (1H, tdd, *J* = 7.2, 9.6, 17.6 Hz), 6.72 (1H, s br), 6.79 (2H, d, *J* = 8.8 Hz), 7.10-7.13 (2H, m), 7.23-7.27 (2H, m), 7.41-7.51 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 41.1, 44.9, 110.9, 114.2, 117.2, 128.5, 128.7, 129.2, 131.8, 133.2, 135.5, 144.4, 154.1; ESIHRMS: Found: *m/z* 357.0966. Calcd for $C_{19}H_{22}{}^{79}BrN_2$: $(M+H)^+$ 357.0966.

(*Z*)-1-((1-Allylcyclohexyl)(phenyl)methylene)-2-phenylhydrazine (3e):

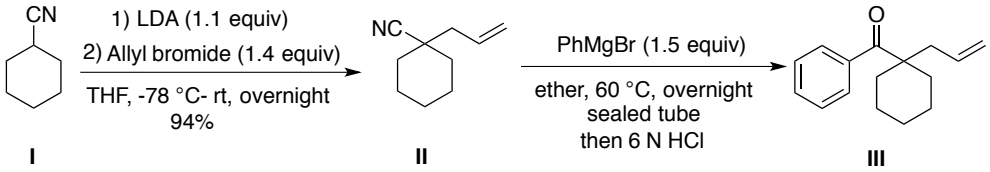


93% yield as a yellow viscous oil (single *Z*-isomer) from (1-allylcyclohexyl)(phenyl)methanone (**III**).

IR (NaCl) 3337, 3074, 2928, 1635, 1601, 1504, 1452, 1254, 1112, 1069 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.35-1.66 (8H, m), 1.86-1.92 (2H, m), 2.29 (2H, d, *J* = 6.9 Hz), 5.04-5.09 (2H, m), 5.84-5.98 (1H, m), 6.74-6.81 (2H, m), 6.91 (2H, d, *J* = 7.5 Hz), 7.15-7.20 (4H, m),

7.39-7.51 (3H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.5, 26.3, 34.1, 42.6, 44.3, 112.5, 116.8, 119.2, 128.5 (overlapped), 129.1 (overlapped), 133.4, 135.2, 145.5, 150.9; ESIHRMS: Found: *m/z* 319.2174. Calcd for $C_{22}H_{27}N_2$: $(M+H)^+$ 319.2174.

Synthesis of (1-allylcyclohexyl)(phenyl)methanone (**III**) (for synthesis of **3e**):

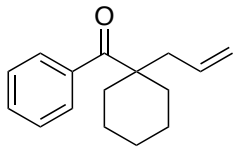


I **II** **III**

To a freshly prepared LDA (from 11.0 mmol *n*-BuLi and 12.0 mmol diisopropyl amine at 0 °C for 30 min) in THF (20 mL) was added cyclohexane carbonitrile **I** (1.2 mL, 10.0 mmol) dropwise at -78 °C. The resulting mixture was stirred at the same temperature for 30 min. Allyl bromide (1.2 mL, 14.0 mmol) was added to the reaction mixture dropwise before allowing the reaction mixture to warm up to room temperature. After stirring for overnight, the reaction mixture was quenched with water at 0 °C and extracted with ethyl acetate. The combined extracts was washed with brine, dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 5: 95) afforded compound **II** (1.40 g, 9.38 mmol) in 94 % yield.

In a flame-dried schlenk tube was placed compound **II** (667 mg, 4.54 mmol) and ether (5 mL) under N_2 atmosphere. After the mixture was cooled down to 0 °C, PhMgBr (2.3 mL, 3.0 M in ether) was added via syringe. The schlenk tube was sealed and the reaction mixture was stirred for overnight at 60 °C. The reaction was quenched with 6 N HCl before cooling down to 0 °C. The resulting mixture was kept stirring and heating until the hydrolysis finished. After dilution with water and ether, the reaction mixture was extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded (1-allylcyclohexyl)(phenyl)methanone (**III**) (580 mg, 2.54 mmol) in 56% yield as a colorless oil.

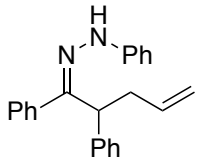
(1-Allylcyclohexyl)(phenyl)methanone (III) (for synthesis of **3e**):



IR (NaCl) 3053, 2936, 1668, 1452, 1265, 1219, 1001 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (6H, s), 1.82-1.86 (2H, m), 1.97-2.03 (2H, m), 4.90-4.99 (2H, m), 5.70-5.80 (1H, m), 7.37-7.41 (2H, m), 7.44-7.48 (1H, m), 7.64-7.66 (2H, m); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 26.1 (overlapped), 29.2, 40.1, 47.7, 114.5, 127.5, 128.1, 130.8, 138.4, 139.1, 209.0; ESIHRMS: Found: *m/z* 229.1590. Calcd for $C_{16}H_{21}O$: $(M+H)^+$ 229.1592.

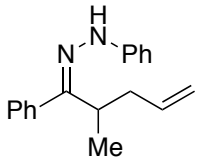
(*E*)-1-(1,2-Diphenylpent-4-en-1-ylidene)-2-phenylhydrazine (3f):



99% yield as a yellow viscous oil (single *E*-isomer) from 1,2-diphenylpent-4-en-1-one.[6]

IR (NaCl) 3339, 3057, 3026, 1639, 1601, 1504, 1310, 1252, 1130, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 2.66 (1H, ddd, *J* = 7.6, 8.4, 14.4 Hz), 3.05 (1H, ddd, *J* = 6.8, 7.6, 14.4 Hz), 3.80 (1H, dd, *J* = 7.6, 7.6 Hz), 4.99 (1H, dd, *J* = 1.2, 10.4 Hz), 5.09 (1H, dd, *J* = 1.2, 16.8 Hz), 5.89 (1H, dddd, *J* = 6.8, 8.4, 10.4, 16.8 Hz), 6.81 (1H, t, *J* = 7.2 Hz), 6.92-6.95 (2H, m), 6.99-7.02 (2H, m), 7.15-7.24 (8H, m), 7.31-7.36 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.0, 53.8, 112.7, 116.1, 119.5, 126.6, 127.8, 128.3, 128.4, 128.6, 129.1, 129.2, 134.5, 137.2, 141.5, 145.3, 147.6; ESIHRMS: Found: *m/z* 327.1860. Calcd for $C_{23}H_{23}N_2$: $(M+H)^+$ 327.1861.

(*E*)-1-(2-Methyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3g):

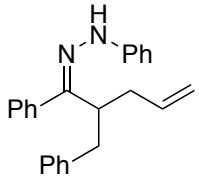


97% yield as a pale yellow viscous oil (single *E*-isomer) from 2-methyl-1-phenylpent-4-en-1-one.[7]

IR (NaCl) 3337, 3053, 2968, 2928, 1639, 1601, 1504, 1309, 1252, 1063 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, d, *J* = 7.2 Hz), 2.13 (1H, ddd, 7.2, 7.2, 14.4 Hz), 2.50 (1H, ddd, *J* = 6.8, 7.2, 14.4 Hz), 2.77 (1H, ddq, *J* = 7.2, 7.2, 7.2 Hz), 5.02 (1H, dd, *J* = 1.2, 10.4 Hz), 5.05 (1H, dd, *J* = 1.2, 17.6 Hz), 5.87 (1H, dddd, *J* = 6.8, 7.2, 10.4, 14.4 Hz), 6.77 (1H, t, *J* = 7.2 Hz), 6.94 (2H, d, *J* = 8.0 Hz), 7.13 (1H, s br), 7.16-7.23 (4H, m), 7.39-7.43 (1H, m),7.47 (1H, d, *J* = 8.0 Hz), 7.49 (1H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 38.6, 41.2, 112.6, 116.1, 119.3, 127.9, 128.7, 129.1, 129.3, 134.2, 137.1, 145.4, 150.4; ESIHRMS: Found: *m/z* 265.1706. Calcd for $C_{18}H_{21}N_2$: $(M+H)^+$ 265.1705

(6) J. M. Cid, J. L. Romera, A. A. Trabanco, *Tetrahedron. Lett*. 2004, **45**, 1133.
(7) B. M. Trost, J. Xu, T. Schmidt, *J. Am. Chem. Soc*. 2009, **131**, 18343.

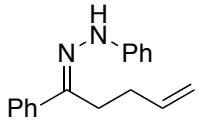
(*E*)-1-(2-Benzyl-1-phenylpent-4-en-1-ylidene)-2-phenylhydrazine (3h):



95% yield as a pale yellow viscous oil (single *E*-isomer) from 2-benzyl-1-phenylpent-4-en-1-one.[6]

IR (NaCl) 3339, 3078, 3053, 3026, 1639, 1601, 1504, 1443, 1265, 1253, 1128 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.26 (1H, ddd, *J* = 6.0, 6.8, 14.0 Hz), 2.46 (1H, ddd, *J* = 7.2, 7.2, 14.0 Hz), 2.80 (1H, dd, *J* = 6.8, 13.2 Hz), 2.97 (1H, dddd, *J* = 6.0, 6.8, 7.2, 7.6 Hz), 3.12 (1H, dd, *J* = 7.6, 13.2 Hz), 5.01-5.07 (2H, m), 5.88 (1H, m), 6.76 (1H, dd, *J* = 7.2, 7.2 Hz), 6.94 (2H, d, *J* = 7.6 Hz), 7.01-7.03 (2H, m), 7.11-7.24 (8H, m), 7.30-7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.1, 38.9, 48.7, 112.6, 116.5, 119.3, 125.8, 127.6, 128.1, 128.6, 129.0, 129.2, 129.3, 134.7, 136.6, 140.7, 145.2, 147.9; ESIHRMS: Found: *m/z* 341.2017. Calcd for $C_{24}H_{25}N_2$: $(M+H)^+$ 341.2018

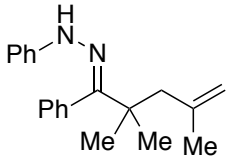
(*E*)-1-Phenyl-2-(1-phenylpent-4-en-1-ylidene)hydrazine (3i):[8]



85% yield as a pale yellow viscous oil (single *E*-isomer) from 2-benzyl-1-phenylpent-4-en-1-one.[6]

^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (2H, td, *J* = 7.2, 7.6 Hz), 2.78 (2H, t, *J* = 7.6 Hz), 5.09 (1H, d, *J* = 10.0 Hz), 5.17 (1H, d, *J* = 18.0 Hz), 5.92 (1H, ddd, *J* = 7.6, 10.0, 18.0 Hz), 6.87 (1H, t, *J* = 7.2 Hz), 7.16-7.18 (2H, m), 7.26-7.31 (3H, m), 7.35-7.39 (3H, m), 7.78-7.80 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 29.8, 113.2, 116.1, 120.2, 125.5, 127.9, 128.4, 129.2, 137.1, 138.1, 144.1, 145.2.

(*Z*)-1-Phenyl-2-(2,2,4-trimethyl-1-phenylpent-4-en-1-ylidene)hydrazine (3j):



99% yield as a pale yellow viscous oil (single *Z*-isomer) from 2,2,4-trimethyl-1-phenylpent-4-en-1-one.

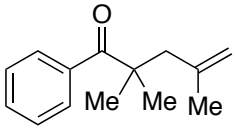
IR (NaCl) 3335, 3051, 2967, 2928, 1639, 1601, 1504, 1468, 1310, 1252, 1101, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (6H, s), 1.79 (3H, s), 2,34 (2H, s), 4.78 (1H, s), 4.89 (1H, s),

(8) M. Tiecco, L. Testaferri, F. Marini, C. Santi, L. Bagnoli, A. Temperini, *Tetrahedron* 1997, **53**, 7311.

6.73-6.77 (2H, m), 6.91 (2H, d, J = 8.0 Hz), 7.14-7.19 (4H, m), 7.40-7.44 (1H, m), 7.46-7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 27.0, 41.1, 47.8, 112.5, 114.3, 119.2, 128.5, 128.6, 129.07, 129.09, 133.7, 143.5, 145.4, 153.6; ESIHRMS: Found: *m/z* 293.2018. Calcd for $C_{20}H_{25}N_2$: $(M+H)^+$ 293.2018.

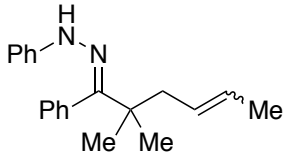
The ketone was synthesized following the above procedure [see synthesis of (1-allylcyclohexyl)(phenyl)methanone (III)] from isobutyronitrile and 3-bromo-2-methylprop-1-ene.

2,2,4-Trimethyl-1-phenylpent-4-en-1-one (for synthesis of **3j**):



IR (NaCl) 3072, 2968, 2936, 1672, 1468, 1445, 1387, 1207 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (6H, s), 1.65 (3H, s), 2.57 (2H, s), 4.66-4.66 (1H, m), 4.82-4.83 (1H, m), 7.37-7.41 (2H, m), 7.43-7.48 (1H, m), 7.68-7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 26.8, 47.5, 48.4, 114.5, 127.9, 128.0, 130.8, 139.0, 142.4, 209.0; ESIHRMS: Found: *m/z* 203.1436. Calcd for $C_{14}H_{19}O$: $(M+H)^+$ 203.1436.

(1*Z*)-1-(2,2-Dimethyl-1-phenylhex-4-en-1-ylidene)-2-phenylhydrazine (3k):

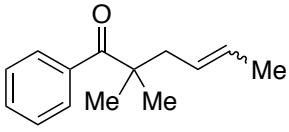


96% yield as a pale yellow viscous oil from 2,2-dimethyl-1-phenylhex-4-en-1-one (*E/Z* ratio of the alkenyl moiety = 6:1)

IR (NaCl) 3335, 3022, 2964, 2928, 1639, 1601, 1502, 1252, 1113 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (6H, s), 1.67-1.69 (3H, m), 2.24 (2H, d, J = 6.8 Hz), 5.41-5.60 (2H, m), 6.72-6.73 (1H, s br), 6.76 (1H, t, J = 7.2 Hz), 6.91 (2H, d, J = 7.6 Hz), 7.12 (2H, d, J = 6.8 Hz), 7.18 (2H, dd, J = 7.6, 8.4 Hz), 7.40-7.43 (1H, m), 7.46-7.50 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 26.3, 41.2, 43.7, 112.5, 119.2, 127.5, 127.9, 128.5, 128.6, 128.7, 129.1, 133.7, 145.5, 153.6; ESIHRMS: Found: *m/z* 293.2016. Calcd for $C_{20}H_{25}N_2$: $(M+H)^+$ 293.2018.

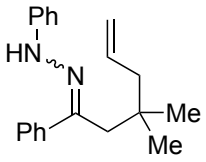
The ketone was synthesized following the above procedure [see synthesis of (1-allylcyclohexyl)(phenyl)methanone (III)] from isobutyronitrile and 1-bromobut-2-ene.

2,2-Dimethyl-1-phenylhex-4-en-1-one (*E/Z* ratio of the alkenyl moiety = 6:1)



Major *E* isomer: IR (NaCl) 3053, 2983, 1670, 1630, 1465, 1423, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (6H, s), 1.62 (3H, dd, *J* = 1.2, 6.0 Hz), 2.41 (2H, d, *J* = 6.8 Hz), 5.29-5.45 (2H, m), 7.36-7.40 (2H, m), 7.42-7.47 (1H, m) 7.63-7.66 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 25.7, 43.7, 47.9, 126.3, 127.6, 128.0, 128.7, 130.6, 139.3, 209.0; ESIHRMS: Found: *m/z* 203.1436. Calcd for $C_{14}H_{19}O$: $(M+H)^+$ 203.1436.

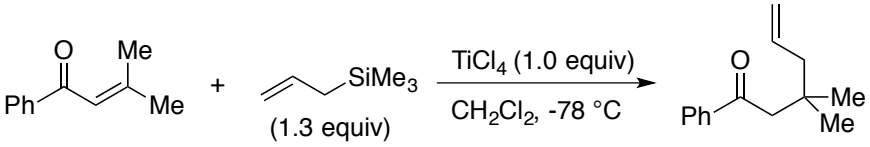
1-(3,3-Dimethyl-1-phenylhex-5-en-1-ylidene)-2-phenylhydrazine (3l):



99% yield as a pale yellow oil (*E/Z* = 1:1) from 3,3-dimethyl-1-phenylhex-5-en-1-one. The stereochemistry of each isomers was not assigned. Spectrum data were shown as a 1:1 mixture.

IR (NaCl) 3335, 3053, 2960, 2932, 1672, 1601, 1495, 1447, 1265, 1153 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, s), 0.91 (6H, s), 2.02 (2H, d, *J* = 7.2 Hz), 2.08 (2H, d, *J* = 7.6 Hz), 2.56 (2H, s), 2.68 (2H, s), 4.89-5.12 (4H, m, overlapped), 5.71-5.96 (2H, m, overlapped), 6.78 (1H, t, *J* = 7.2 Hz), 6.86 (1H, t, *J* = 7.2 Hz), 6.95 (2H, d, *J* = 8.0 Hz), 7.14 (2H, d, *J* = 7.6 Hz), 7.20 (2H, dd, *J* = 7.2, 8.4 Hz), 7.23-7.42 (9H, m, overlapped), 7.45-7.54 (3H, m, overlapped), 7.71 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 28.2, 34.8, 35.9, 36.0, 46.8, 48.3, 49.1, 112.6, 113.0, 117.1, 118.4, 119.4, 120.0, 126.3, 127.7, 127.8, 128.2, 128.7, 129.1, 129.2, 129.3, 134.8, 135.5, 135.8, 140.7, 144.2, 145.0, 145.2, 145.7; ESIHRMS: Found: *m/z* 293.2019. Calcd for $C_{20}H_{25}N_2$: $(M+H)^+$ 293.2018.

Synthesis of **3,3-dimethyl-1-phenylhex-5-en-1-one** (for synthesis of **3l**):

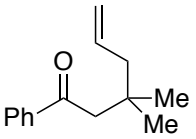


Modified procedure from reported literature[9]: A solution of $TiCl_4$ (4.8 mL, 1.0 M in CH_2Cl_2) was added dropwise to the solution of 3-methyl-1-phenylbut-2-en-1-one (769 mg, 4.80 mmol) in CH_2Cl_2 at -78 °C. After stirring for 5 min, allylsilane (1.0 mL, 6.24 mmol) in 5 mL CH_2Cl_2 was added dropwise and the resulting mixture was kept stirring for 5 min. The reaction was warmed to room temperature and stirred for 30 min followed by cooling down to 0 °C and quenched with H_2O. The reaction

(9) R. B. Miles, C. E. Davis, R. M. Coates, *J. Org. Chem*. 2006, **71**, 1493.

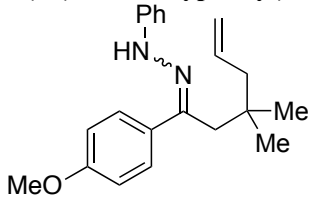
mixture was diluted with ether, the separated organic layer was washed with 10% HCl, satd. $NaHCO_3$, bine. The organic layer was dried over $MgSO_4$ and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded 3,3-dimethyl-1-phenylhex-5-en-1-one (500 mg, 2.47 mmol) in 51% yield as a colorless oil.

3,3-Dimethyl-1-phenylhex-5-en-1-one (for synthesis of **3l**):



IR (NaCl) 3059, 2959, 2930, 1690, 1672, 1638, 1597, 1448, 1359, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (6H, s), 2.18 (2H, d, *J* = 7.6 Hz), 2.85 (2H, s), 5.01-5.06 (2H, m), 5.79-5.90 (1H, m), 7.44 (2H, dd, *J* = 7.6, 7.6 Hz), 7.53 (1H, dd, *J* = 7.2, 7.6 Hz), 7.91-7.93 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 34.1, 46.8, 47.7, 117.7, 128.1, 128.5, 132.7, 135.1, 138.6, 200.3; ESIHRMS: Found: *m/z* 203.1437. Calcd for $C_{14}H_{19}O$: $(M+H)^+$ 203.1436.

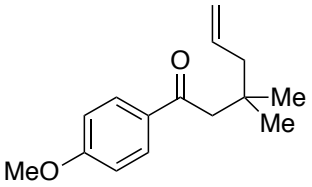
1-(1-(4-Methoxyphenyl)-3,3-dimethylhex-5-en-1-ylidene)-2-phenylhydrazine (3m):



99% yield as a pale yellow oil (*E/Z* = 1:0.8) from 1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one. The mixture of *E/Z* = 0.2:1 was partially isolated and was used in the next step.
IR (NaCl) 3337, 3053, 2959, 2936, 1639, 1601, 1502, 1466, 1292, 1265, 1177, 1032 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$ for major *Z*-isomer): δ 0.87 (6H, s), 2.02 (2H, d, *J* = 7.6 Hz), 2.53 (2H, s), 3.86 (3H, s), 4.94 (1H, dd, *J* = 2.0, 17.2 Hz), 5.01 (1H, *J* = 2.0, 10.4 Hz), 5.84 (1H, tdd, *J* = 7.2, 10.4, 17.2 Hz), 6.78 (1H, t, *J* = 7.2 Hz), 6.95-7.00 (4H, m), 7.20 (2H, dd, *J* = 7.6, 8.0 Hz), 7.24-7.28 (2H, m), 7.45 (1H, s br); ^{13}C NMR (100 MHz, $CDCl_3$ for major *Z*-isomer): δ 27.6, 34.8, 46.9, 49.3, 55.3, 112.6, 114.6, 117.0, 119.3, 129.1, 129.2 (overlapped), 135.6, 145.36, 145.42, 159.6; ESIHRMS: Found: *m/z* 323.2122. Calcd for $C_{21}H_{27}N_2O$: $(M+H)^+$ 323.2123.

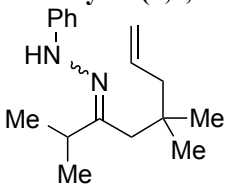
The ketone was synthesized following the above procedure [see synthesis of 3,3-dimethyl-1-phenylhex-5-en-1-one (for synthesis of **3l**)] from 1-(4-methoxyphenyl)-3-methylbut-2-en-1-one and allylsilane.

1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one (for synthesis of **3m):**



24%; colorless oil; IR (NaCl) 3074, 2959, 2932, 1728, 1682, 1660, 1601, 1510, 1462, 1259 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.04 (6H, s), 2.17 (2H, d, *J* = 7.6 Hz), 2.80 (2H, s), 3.87 (3H, s), 5.01-5.07 (2H, m), 5.80-5.89 (1H, m), 6.92 (2H, d, *J* = 8.8 Hz), 7.92 (2H, d, *J* = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.5, 34.1, 46.9, 47.4, 55.4, 113.6, 117.6, 130.4, 131.7, 135.2, 163.2, 198.8; ESIHRMS: Found: *m/z* 233.1542. Calcd for $C_{15}H_{21}O_2$: $(M+H)^+$ 233.1542.

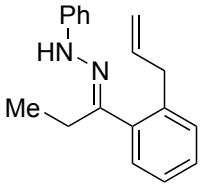
1-Phenyl-2-(2,5,5-trimethyloct-7-en-3-ylidene)hydrazine (3n):



72% yield as a wine red oil (single isomer; the stereochemistry is not assigned) from 2,5,5-trimethyloct-7-en-3-one.[10] This compound was easily oxidized by atmospheric oxygen to form peroxide species,[3] and thus should be used immediately after purification.

IR (NaCl) 3374, 2963, 2930, 1638, 1601, 1503, 1468, 1265, 1142 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.01 (6H, s), 1.16 (6H, d, *J* = 7.2 Hz), 2.09 (2H, d, *J* = 7.2 Hz), 2.18 (2H, s), 2.45 (1H, septet, *J* = 7.2 Hz), 5.06-5.16 (2H, m), 5.84-5.94 (1H, m), 6.79 (1H, t, *J* = 7.2 Hz), 7.01-7.03 (2H, m), 7.17 (1H, s br), 7.20-7.25 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 28.1, 35.8, 36.8, 38.9, 48.3, 112.6, 118.2, 119.2, 129.1, 134.8, 146.0, 152.3; ESIHRMS: Found: *m/z* 259.2172. Calcd for $C_{17}H_{27}N_2$: $(M+H)^+$ 259.2174.

(*E*)-1-(1-(2-Allylphenyl)propylidene)-2-phenylhydrazine (3o):



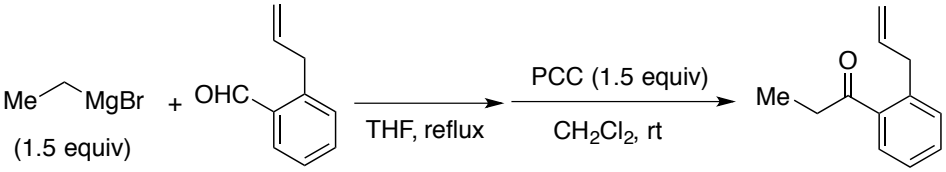
86% yield as a pale yellow oil (single *E* isomer) from 1-(2-allylphenyl)propan-1-one.

IR (NaCl) 3333, 3051, 2974, 1638, 1601, 1503, 1429, 1265, 1126 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, t, *J* = 7.2 Hz), 2.56 (2H, dq, *J* = 2.0, 7.2 Hz), 3.25 (2H, d, *J* = 6.4 Hz), 4.99-5.05 (2H, m), 5.84-5.94 (1H, m), 6.78 (1H, t, *J* = 7.2 Hz), 6.86 (1H, s br), 6.94 (2H, d, *J*

(10) S. Bogen, L. Fensterbank, M. Malacria, *J. Org. Chem*. 1999, **64**, 819.

= 7.6 Hz), 7.09 (1H, d, *J* = 7.6 Hz), 7.19 (2H, dd, *J* = 7.2, 7.6 Hz), 7.31-7.41 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.0, 31.5, 37.0, 112.6, 116.5, 119.3, 127.2, 127.9, 129.0, 129.1, 130.0, 134.4, 136.6, 137.6, 145.3, 148.8; ESIHRMS: Found: *m/z* 265.1704. Calcd for $C_{18}H_{21}N_2$: $(M+H)^+$ 265.1705.

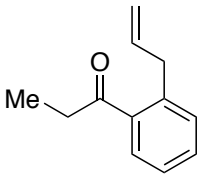
Synthesis of **1-(2-allylphenyl)propan-1-one** (for synthesis of **3o**):



To a solution of 2-allylbenzaldehyde (1.14 g, 7.79 mmol) in THF (15 mL) was added EtMgBr (5.1 mL, 2.3 M in THF, 11.68 mmol) dropwise at 0 °C. The resulting mixture was stirred at 0 °C for 1 hour before quenching with Satd. NH_4Cl at the same temperature. The reaction mixture was extracted with ether. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The resulting crude alcohol was used directly for the next step.

To a solution of obtained crude alcohol (1.13 g, 6.39 mmol) in CH_2Cl_2 (18 mL) was added celite (1.0 g) and then PCC (2.07 g, 9.58 mmol) portionwise at room temperature. The reaction mixture was stirred for 2 hours and filtered. The filtrate was evaporated and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 5: 95) afforded 1-(2-allylphenyl)propan-1-one (0.924 g, 5.30 mmol) in 83% yield.

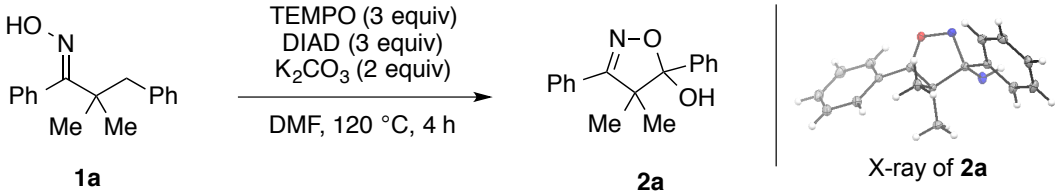
1-(2-Allylphenyl)propan-1-one (for synthesis of **3o):**



IR (NaCl) 3073, 2978, 2938, 1690, 1638, 1599, 1445, 1222 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (3H, t, *J* = 7.2 Hz), 2.90 (2H, q, *J* = 7.2 Hz), 3.60 (2H, d, *J* = 6.8 Hz), 4.97-5.03 (2H, m), 5.92-6.02 (1H, m), 7.26-7.29 (2H, m), 7.37-7.41 (1H, m), 7.55-7.57 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.30, 35.1, 37.8, 115.7, 126.1, 127.9, 131.0, 131.1, 137.5, 138.8, 139.1, 205.6; ESIHRMS: Found: *m/z* 175.1122. Calcd for $C_{12}H_{15}O$: $(M+H)^+$ 175.1123

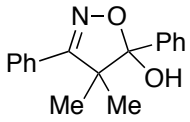
3. TEMPO and DIAD-mediated reactions with oximes 1 (Scheme 1-b) and hydrzaone 3a (Scheme 3)

A typical procedure for synthesis of hemiacetal **2a** from oxime **1a**:



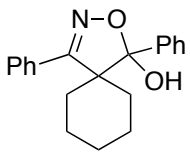
To a solution of oxime **1a** (74.3 mg, 0.293 mmol), TEMPO (137.5 mg, 0.880 mmol), and K_2CO_3 (81.1 mg, 0.587 mmol) in DMF was added DIAD (diisopropyl diazene-1,2-dicarboxylate) (173.0 μL, 0.880 mmol) via a micro syringe under an Ar atmosphere. The reaction mixture was kept stirring at 120 °C for 4 hours before cooling down to room temperature. After dilution with water and ethyl acetate, the mixture was extracted with ethyl acetate. The combined extracts were washed with water for three times (to remove DMF) and brine, dried over $MgSO_4$, and concentrated. Purification of the crude product by flash column chromatography (silica gel;ethyl acete: hexane = 20: 80) afforded hemiacetal **2a** (57.1 mg, 0.214 mmol) in 73% yield as a white solid.

4,4-Dimethyl-3,5-diphenyl-4,5-dihydroisoxazol-5-ol (2a):



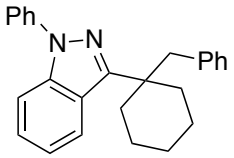
Colourless crystal (CCDC 926979); mp: 162-164 °C; IR (NaCl) 3422, 3053, 2986, 1638, 1551, 1491, 1422, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.89 (3H, s), 1.46 (3H, s), 3.01 (1H, s br), 7.40-7.43 (6H, m), 7.65-7.69 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6, 25.1, 55.4, 110.1, 126.7, 127.7, 128.2, 128.6, 129.0, 129.4, 129.9, 137.8, 166.2; ESIHRMS: Found: *m/z* 268.1339. Calcd for $C_{17}H_{18}NO_2$: $(M+H)^+$ 268.1338.

1,4-Diphenyl-2-oxa-3-azaspiro[4.5]dec-3-en-1-ol (2b):



55%; White solid; mp: 165-167 °C; IR (NaCl) 3421, 3053, 2986, 1639, 1551, 1491, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.30-0.40 (1H, m), 0.99-1.12 (2H, m), 1.21-1.27 (1H, m), 1.43-1.60 (4H, m), 1.74-1.81 (1H, m), 2.29-2.40 (1H, m), 3.05 (1H, s br), 7.38-7.47 (6H, m), 7.49-7.54 (2H, m), 7.74-7.77 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 21.5, 24.9, 26.4, 31.2, 58.9, 109.4, 127.8, 128.1, 128.3, 128.9, 129.0, 129.4, 130.3, 139.0, 167.1; ESIHRMS: Found: *m/z* 308.1644. Calcd for $C_{20}H_{22}NO_2$: $(M+H)^+$ 308.1651.

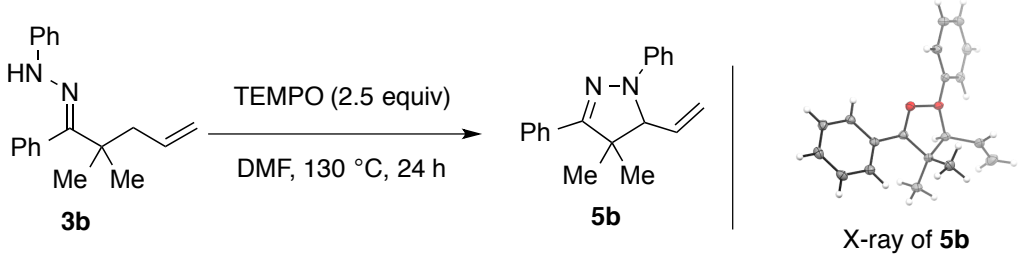
3-(1-Benzylcyclohexyl)-1-phenyl-1*H*-indazole (4a):



54%; Yellow thick viscous liquid; IR (NaCl) 3053, 2986, 1638, 1597, 1506, 1422, 1267 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32-1.38 (1H, m), 1.47-1.56 (3H, m), 1.62-1.73 (4H, m), 2.56-2.59 (2H, m), 3.09 (2H, s), 6.67-7.70 (2H, m), 7.01-7.12 (4H, m), 7.26-7.37 (2H, m), 7.47 (2H, d, *J* = 8.0 Hz), 7.59-7.62 (2H, m), 7.72 (1H, d, *J* = 8.0 Hz), 7.76 (1H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 26.3, 35.8, 42.9, 49.2, 110.4, 120.4, 122.4, 122.8, 123.8, 125.8, 126.0, 126.1, 127.3, 129.2, 130.3, 138.1, 140.2, 140.5, 150.8; ESIHRMS: Found: *m/z* 367.2175. Calcd for $C_{26}H_{27}N_2$: $(M+H)^+$ 367.2174.

4. TEMPO-mediated reactions with hydrozones 3b-3k (Table 1-entry 1, Table 2)

A typical procedure for synthesis of dihydropyrazole **5b** from hydrazone **3b**:

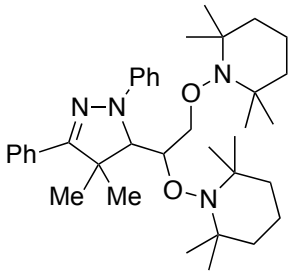


The mixture of hydrazine **3b** (56.0 mg, 0.201 mmol) and TEMPO (78.5 mg, 0.503 mmol) in anhydrous DMF (0.1 M) was heated at 130 °C for 24 hours under an Ar atmosphere. The mixture was then cooled down to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate and the combined extracts were washed with water for 3 times (to remove DMF) and then washed with brine. The organic phase was dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded **5b** (42.8 mg, 0.155 mmol) in 77% yield. (In table 1, entry 4, the byproduct **5b'** was formed in 11% yield.)

4,4-Dimethyl-1,3-diphenyl-5-vinyl-4,5-dihydro-1*H*-pyrazole (5b):

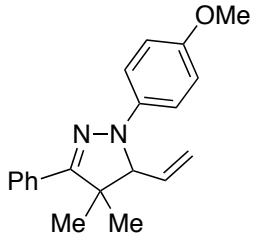
77%; Pale yellow crystal (CCDC 996573); mp: 99-100 °C; IR (NaCl) 3053, 2976, 1636, 1597, 1495, 1265, 1138 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.29 (3H, s), 1.26 (3H, s), 4.13 (1H, d, *J* = 8.4 Hz), 5.36 (1H, d, *J* = 12.4 Hz), 5.37 (1H, d, *J* = 16.4 Hz), 5.86 (1H, ddd, *J* = 8.4, 12.4, 16.4 Hz), 6.85-6.89 (1H, m), 7.23-7.28 (4H, m), 7.30-7.39 (3H, m), 7.76-7.79 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 25.9, 51.3, 76.4, 115.2, 118.9, 120.0, 126.8, 128.3, 128.4, 128.7, 132.5, 134.7, 146.0, 155.4; ESIHRMS: Found: *m/z* 277.1706. Calcd for $C_{19}H_{21}N_2$: $(M+H)^+$ 277.1705.

1,1'-((1-(4,4-dimethyl-1,3-diphenyl-4,5-dihydro-1*H*-pyrazol-5-yl)ethane-1,2-diyl)bis-(oxy))bis(2,2,6,6-tetramethylpiperidine) (5b', Table 1, entry 4):[4]



11%; ^1H NMR (400 MHz, $CDCl_3$) δ 0.78 (3H, s), 0.82 (3H, s), 1.00 (3H, s), 1.09 (3H, s), 1.22-1.26 (14 H, m), 1.31-1.37 (4H, m), 1.46-1.55 (9H, m), 1.73 (3H, s), 3.97-4.02 (1H, m), 4.27-4.30 (2H, m), 4.62 (1H, dd, *J* = 4.0, 10.8 Hz), 6.72-6.76 (1H, m), 7.21-7.29 (4H, m), 7.31-7.38 (3H, m), 7.71-7.73 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.1, 17.2, 20.0, 20.2, 20.3, 26.8, 30.1, 32.9, 33.5, 33.7, 34.2, 39.5, 40.7, 41.1, 49.5, 59.0, 59.7, 60.7, 70.6, 74.5, 79.1, 112.5, 117.6, 127.1, 127.8, 128.0, 129.0, 132.9, 144.1, 155.6.

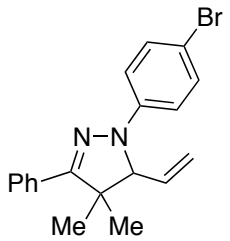
1-(4-Methoxyphenyl)-4,4-dimethyl-3-phenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5c):



73%; Pale yellow solid; mp: 63-65 °C; IR (NaCl) 3053, 2982, 2934, 1636, 1508, 1464, 1265, 1242 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (3H, s), 1.44 (3H, s), 3.77 (3H, s), 3.97 (1H, d, *J* = 8.8 Hz), 5.34 (1H, d, *J* = 18.0 Hz), 5.35 (1H, d, *J* = 10.4 Hz), 5.92 (1H, ddd, *J* = 8.8, 10.4, 18.0 Hz), 6.81-6.86 (2H, m), 7.19-7.24 (2H, m), 7.29-7.38 (3H, m), 7.75-7.78 (2H, m); ^{13}C

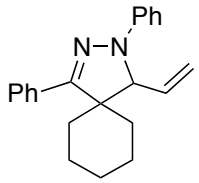
NMR (100 MHz, $CDCl_3$) δ 20.5, 25.3, 51.3, 55.6, 76.7, 114.1, 117.5, 119.2, 126.7, 128.2, 128.3, 132.6, 134.9, 140.6, 154.2, 155.4; ESIHRMS: Found: *m/z* 307.1810. Calcd for $C_{20}H_{23}N_2O$: $(M+H)^+$ 307.1810.

1-(4-Bromophenyl)-4,4-dimethyl-3-phenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5d):



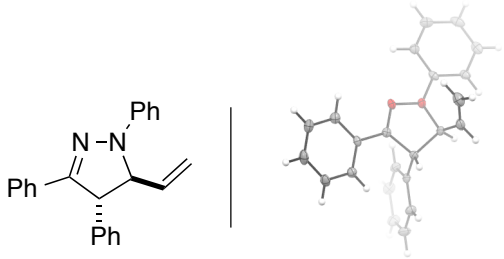
74%; Yellow thick viscous liquid; IR (NaCl) 3051, 2980, 1597, 1572, 1491, 1368, 1265, 1094 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.28 (3H, s), 1.46 (3H, s), 4.09 (1H, d, *J* = 8.4 Hz), 5.35 (1H, d, *J* = 17.2 Hz), 5.37 (1H, d, *J* = 10.0 Hz), 5.82 (1H, ddd, *J* = 8.4, 10.0, 17.2 Hz), 7.11-7.14 (2H, m), 7.31-7.40 (5H, m), 7.74-7.77 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 25.9, 51.5, 76.3, 112.1, 116.7, 119.3, 126.8, 128.4, 128.6, 131.5, 132.2, 134.2, 144.9, 156.0; ESIHRMS: Found: *m/z* 355.0808. Calcd for $C_{19}H_{20}{}^{79}BrN_2$: $(M+H)^+$ 355.0810.

1,3-Diphenyl-4-vinyl-2,3-diazaspiro[4.5]dec-1-ene (5e):



62%; Yellow thick viscous liquid; IR (NaCl) 3053, 2980, 2936, 1630, 1597, 1576, 1501, 1302, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30-1.36 (2H, m), 1.62-1.70 (2H, m), 1.73-1.80 (3H, m), 1.85-1.99 (3H, m), 4.71 (1H, d, *J* = 8.4 Hz), 5.29 (1H, d, *J* = 10.8 Hz), 5.30 (1H, d, *J* = 17.2 Hz), 5.66 (1H, ddd, *J* = 8.4, 10.8, 17.2 Hz), 6.80 (1H, tt, *J* = 0.8, 7.2 Hz), 7.11-7.14 (2H, m), 7.22-7.26 (2H, m), 7.32-7.40 (3H, m), 7.67-7.70 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 23.0, 25.4, 28.2, 31.9, 55.8, 69.7, 113.7, 118.6, 119.3, 127.5, 128.2 (overlapped), 128.8, 131.4, 133.0, 144.4, 155.3; ESIHRMS: Found: *m/z* 317.2019. Calcd for $C_{22}H_{25}N_2$: $(M+H)^+$ 317.2018.

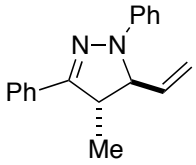
(4S,5S)-1,3,4-Triphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5f):



X-ray of **5f**

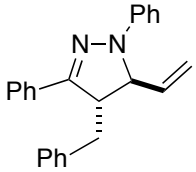
80%; Pale yellow crystal (CCDC 995494); IR (NaCl) 3061, 3028, 1641, 1597, 1553, 1493, 1445, 1387, 1336, 1138 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.38 (1H, d, *J* = 4.8 Hz), 4.59 (1H, dd, *J* = 4.8, 6.8 Hz), 5.24 (1H, d, *J* = 10.4 Hz), 5.25 (1H, d, *J* = 17.2 Hz), 5.96 (1H, ddd, *J* = 6.8, 10.4, 17.2 Hz), 6.84 (1H, t, *J* = 7.2 Hz), 7.18-7.30 (12H, m), 7.63-7.65 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 59.3, 72.9, 113.7, 117.1, 119.3, 126.2, 127.4, 127.5, 128.2, 128.4, 128.9, 129.2, 132.2, 136.4, 140.2, 144.5, 148.9; ESIHRMS: Found: *m/z* 325.1705. Calcd for $C_{23}H_{21}N_2$: $(M+H)^+$ 325.1705.

(4S,5S)-4-Methyl-1,3-diphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5g):



53%; Yellow thick viscous liquid; IR (NaCl) 3053, 2982, 2930, 1641, 1597, 1557, 1504, 1391, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, d, *J* = 7.2 Hz), 3.37 (1H, dq, *J* = 4.0, 7.2 Hz), 4.36 (1H, dd, *J* = 4.0, 6.8 Hz), 5.17 (1H, d, *J* = 10.4 Hz), 5.25 (1H, d, *J* = 17.2), 5.83 (1H, ddd, *J* = 6.8, 10.4, 17.2 Hz), 6.82 (1H, t, *J* = 7.2 Hz), 7.18 (2H, d, *J* = 8.0 Hz), 7.23-7.32 (3H, m), 7.37 (2H, dd, *J* = 7.2, 7.6 Hz), 7.74 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.1, 47.1, 71.0, 113.5, 116.6, 118.9, 126.0, 128.3, 128.6, 128.9, 132.1, 136.2, 144.7, 151.6; ESIHRMS: Found: *m/z* 263.1548. Calcd for $C_{18}H_{19}N_2$: $(M+H)^+$ 263.1548.

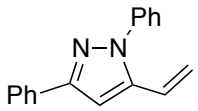
(4S,5S)-4-Benzyl-1,3-diphenyl-5-vinyl-4,5-dihydro-1H-pyrazole (5h):



72%; Yellow thick viscous liquid; IR (NaCl) 3053, 2981, 2928, 1635, 1590, 1546, 1500, 1389, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.64 (1H, dd, *J* = 10.8, 14.0), 3.19 (1H, dd, *J*

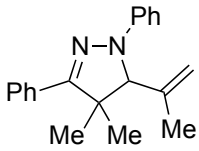
= 3.6, 14.0 Hz), 3.63 (1H, ddd, *J* = 3.2, 3.6, 10.8 Hz), 4.53 (1H, dd, *J* = 3.2, 6.4 Hz), 4.92 (1H, d, *J* = 17.2 Hz), 5.01 (1H, d, *J* = 10.0 Hz), 5.61 (1H, ddd, *J* = 6.4, 10.0, 17.2 Hz), 6.80 (1H, t, *J* = 7.2 Hz), 7.11 (2H, d, *J* = 8.4 Hz), 7.21-7.24 (5H, m), 7.30-7.34 (3H, m), 7.40 (2H, dd, *J* = 7.6, 7.6 Hz), 7.81 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 37.3, 53.8, 66.8, 113.3, 116.4, 118.9, 125.9, 126.6, 128.4, 128.66, 128.69, 128.9, 129.0, 132.1, 135.7, 138.3, 144.2, 149.7; ESIHRMS: Found: *m/z* 339.1861. Calcd for $C_{24}H_{23}N_2$: $(M+H)^+$ 339.1861.

1,3-Diphenyl-5-vinyl-1H-pyrazole (5i):[2]



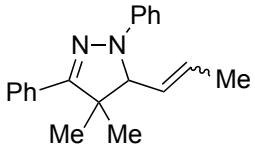
80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (1H, d, *J* = 11.2 Hz), 5.79 (1H, d, *J* = 17.2 Hz), 6.56 (1H, dd, *J* = 17.2, 11.2 Hz), 6.89 (1H, s), 7.30-7.34 (1H, m), 7.39-7.43 (3H, m), 7.47-7.53 (4H, m), 7.89 (2H, d, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 101.3, 117.5, 124.6, 125.5, 125.8, 127.9, 128.6, 129.1 (overlapped), 133.0, 139.5, 142.6, 151.8.

4,4-Dimethyl-1,3-diphenyl-5-(prop-1-en-2-yl)-4,5-dihydro-1H-pyrazole (5j):



86%; Yellow thick viscous liquid; IR (NaCl) 3051, 2978, 2938, 1647, 1595, 1545, 1503, 1465, 1443, 1383, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (3H, s), 1.51 (3H, s), 1.57 (3H, s), 4.28 (1H, s), 5.06 (2H, s), 6.83 (1H, t, *J* = 6.8 Hz), 7.17-7.19 (2H, m), 7.24-7.28 (2H, m), 7.31-7.39 (3H, m), 7.77 (2H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 20.5, 28.3, 50.3, 78.8, 113.6, 115.9, 119.0, 126.8, 128.2, 128.4 (overlapped), 128.8, 132.5, 145.1, 154.7; ESIHRMS: Found: *m/z* 291.1861. Calcd for $C_{20}H_{23}N_2$: $(M+H)^+$ 291.1861.

4,4-Dimethyl-1,3-diphenyl-5-(prop-1-en-1-yl)-4,5-dihydro-1H-pyrazole (5k) (alkene: *E/Z* = 25:1)**:**

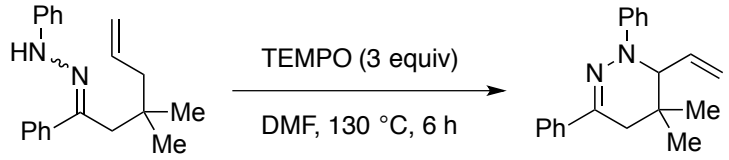


56%; Yellow thick viscous liquid; IR (NaCl) 3053, 2982, 1670, 1595, 1545, 1495, 1464, 1379, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$ for major *E*-isomer) δ 1.28 (3H, s), 1.43 (3H, s),

1.78 (3H, d, *J* = 5.6 Hz), 4.08 (1H, d, *J* = 8.4 Hz), 5.51 (1H, dd, *J* = 8.4, 15.6 Hz), 5.79 (1H, qd, *J* = 5.6, 15.6 Hz), 6.85-6.89 (1H, m), 7.24-7.30 (4H, m), 7.32-7.39 (3H, m), 7.79 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$ for major *E*-isomer) δ 17.9, 20.8, 25.8, 51.1, 75.9, 115.2, 119.7, 126.7, 127.4, 128.2, 128.3, 128.6, 130.0, 132.7, 146.1, 155.4; ESIHRMS: Found: *m/z* 291.1861. Calcd for $C_{20}H_{23}N_2$: $(M+H)^+$ 291.1861.

5. TEMPO-mediated reactions with hydrozones 3l-3o (Scheme 5)

A typical procedure for synthesis of tetrahydropyridazine **5l** from hydrazone **3l**:

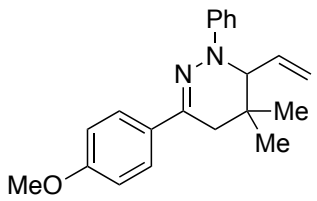


3l **5l**

The mixture of hydrazine **3l** (87.4 mg, 0.299 mmol) and TEMPO (140 mg, 0.897 mmol) in anhydrous DMF (0.1 M) was heated at 130 °C for 6 hours under an Ar atmosphere. The mixture was then cooled down to room temperature and diluted with water. The resulting mixture was extracted with ethyl acetate and the combined extracts were washed with water for 3 times (to remove DMF) and then washed with brine. The organic phase was dried over $MgSO_4$, and concentrated. Purification by flash column chromatography (silica gel; ethyl acetate: hexane = 1: 99) afforded **5l** (79.0 mg, 0.272 mmol) in 91% yield as a yellow thick viscous liquid.

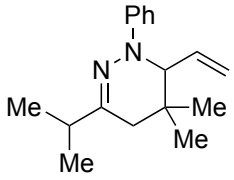
IR (NaCl) 3053, 2970, 2930, 1639, 1589, 1564, 1491, 1445, 1265 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, s), 1.18 (3H, s), 2.34 (2H, s), 4.12 (1H, d, *J* = 6.0 Hz), 5.08 (1H, ddd, *J* = 1.2, 1.2, 17.2 Hz), 5.19 (1H, ddd, *J* = 1.2, 1.2, 10.4 Hz), 5.79 (1H, ddd, *J* = 6.0, 10.4, 17.2 Hz), 6.88 (1H, t, *J* = 7.2 Hz), 7.25-7.32 (3H, m), 7.35-7.39 (4H, m), 7.81-7.84 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 27.6, 29.9, 33.2, 64.3, 114.0, 118.3, 119.7, 124.6, 127.5, 128.2, 128.8, 132.0, 138.1, 138.9, 147.2; ESIHRMS: Found: *m/z* 291.1860. Calcd for $C_{20}H_{23}N_2$: $(M+H)^+$ 291.1861.

3-(4-Methoxyphenyl)-5,5-dimethyl-1-phenyl-6-vinyl-1,4,5,6-tetrahydropyridazine (5m):



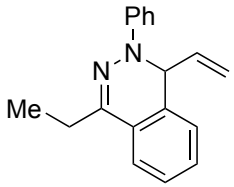
87%; Yellow thick viscous liquid; IR (NaCl) 3053, 2974, 2936, 1625, 1595, 1512, 1495, 1375, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (3H, s), 1.17 (3H, s), 2.31 (2H, s), 3.82 (3H, s), 4.11 (1H, d, *J* = 6.0 Hz), 5.08 (1H, d, *J* = 17.2 Hz), 5.18 (1H, d, *J* = 10.4 Hz), 5.78 (1H, ddd, *J* = 6.0, 10.4, 17.2 Hz), 6.85 (1H, t, *J* = 7.2 Hz), 6.89-6.92 (2H, m), 7.28 (2H, dd, *J* = 7.6, 8.4 Hz), 7.33-7.35 (2H, m), 7.76 (2H, d, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.1, 27.6, 29.9, 33.2, 55.3, 64.2, 113.6, 113.9, 118.2, 119.3, 125.8, 128.8, 131.9, 132.0, 138.1, 147.3, 159.3; ESIHRMS: Found: *m/z* 321.1968. Calcd for $C_{21}H_{25}N_2O$: $(M+H)^+$ 321.1967.

3-Isopropyl-5,5-dimethyl-1-phenyl-6-vinyl-1,4,5,6-tetrahydropyridazine (5n):



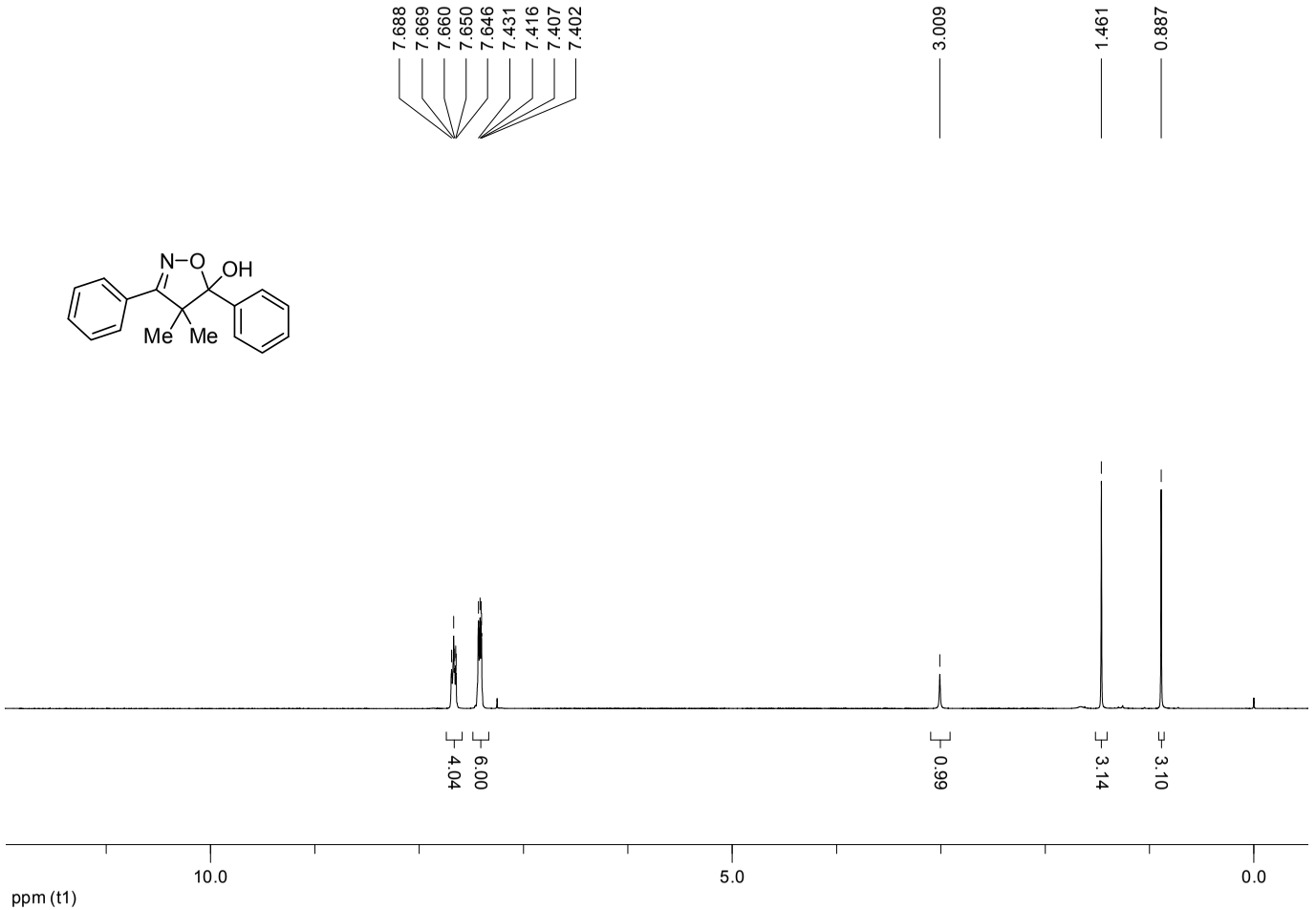
87%; Brown thick viscous liquid; IR (NaCl) 3053, 2965, 2930, 1638, 1595, 1576, 1498, 1467, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, s), 1.07 (3H, s), 1.13 (3H, d, *J* = 7.2 Hz), 1.14 (3H, d, *J* = 7.2 Hz), 1.74 (1H, dd, *J* = 1.6, 17.6 Hz), 1.99 (1H, d, *J* = 17.6 Hz), 2.50 (1H, septet, *J* = 7.2 Hz), 3.98 (1H, dd, *J* = 1.6, 6.0 Hz), 4.99 (1H, ddd, *J* = 0.8, 1.6, 17.2 Hz), 5.15 (1H, ddd, *J* = 0.8, 0.8, 10.4 Hz), 5.71 (1H, ddd, 6.0, 10.4, 17.2 Hz), 6.77 (1H, tt, *J* = 1.6, 6.8 Hz), 7.18-7.25 (4H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.0, 20.7, 27.0, 29.5, 33.3, 35.9, 63.9, 113.2, 117.8, 118.4, 128.7, 132.3, 147.7, 147.9; ESIHRMS: Found: *m/z* 257.2019. Calcd for $C_{17}H_{25}N_2$: $(M+H)^+$ 257.2018.

4-Ethyl-2-phenyl-1-vinyl-1,2-dihydrophthalazine (5o):

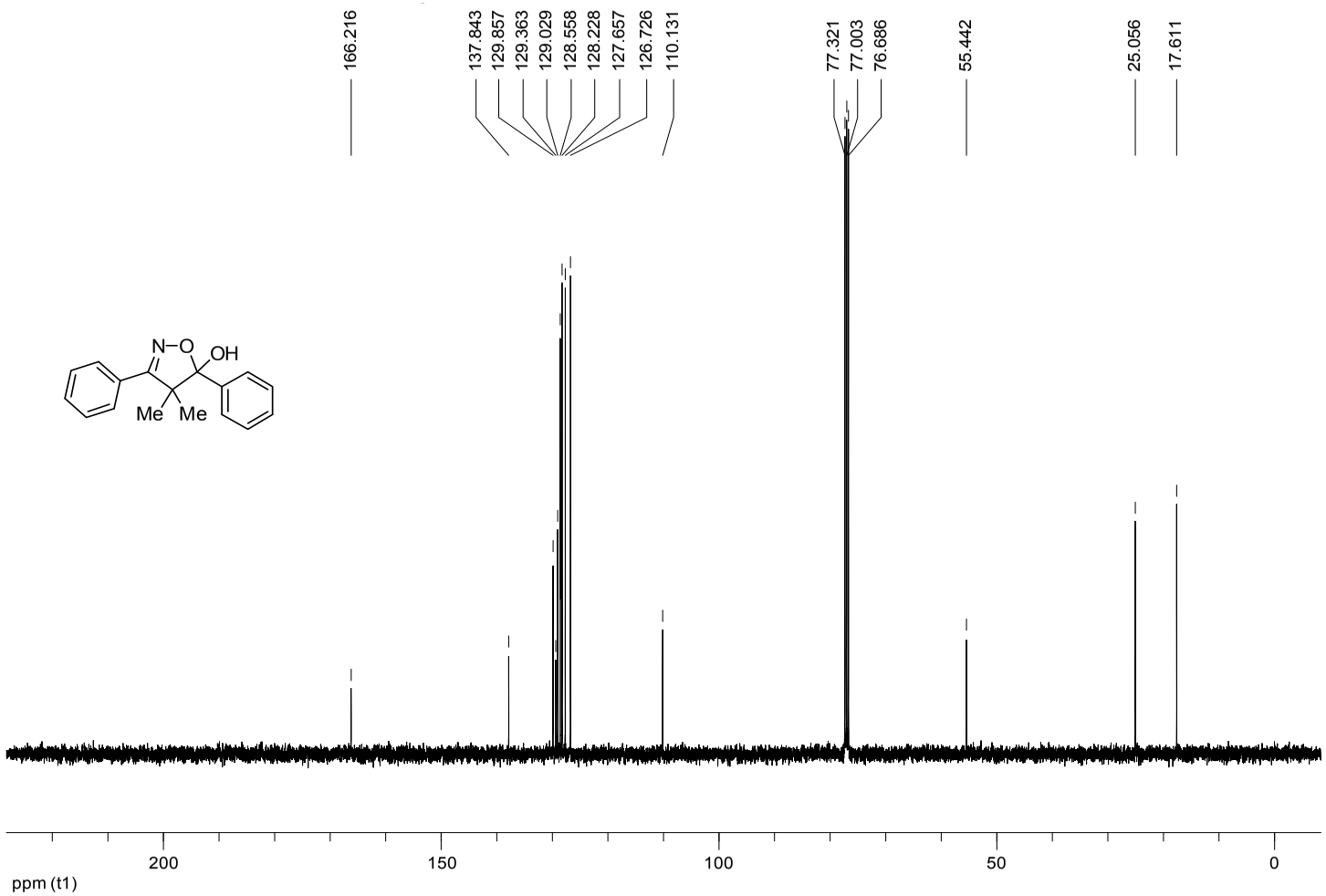


41%; Yellow thick viscous liquid; IR (NaCl) 3061, 2970, 2934, 1636, 1595, 1495, 1454, 1265 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, *J* = 7.2 Hz), 2.80 (1H, qd, *J* = 7.2, 15.2 Hz), 2.83 (1H, qd, *J* = 7.2, 15.2 Hz), 4.94 (1H, ddd, *J* = 1.2, 1.2, 16.8 Hz), 5.06 (1H, ddd, *J* = 1.2, 1.2, 10.4 Hz), 5.70 (1H, d, *J* = 4.8 Hz), 5.80 (1H, ddd, *J* = 4.8, 10.4, 16.8 Hz), 6.92 (1H, t, *J* = 7.2 Hz), 7.19-7.21 (1H, m), 7.29-7.44 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.2, 25.3, 57.9, 114.6, 116.2, 120.2, 122.9, 125.1, 126.3, 128.0, 128.9, 130.1, 132.4, 133.8, 146.5, 146.6; ESIHRMS: Found: *m/z* 263.1548. Calcd for $C_{18}H_{19}N_2$: $(M+H)^+$ 263.1548.

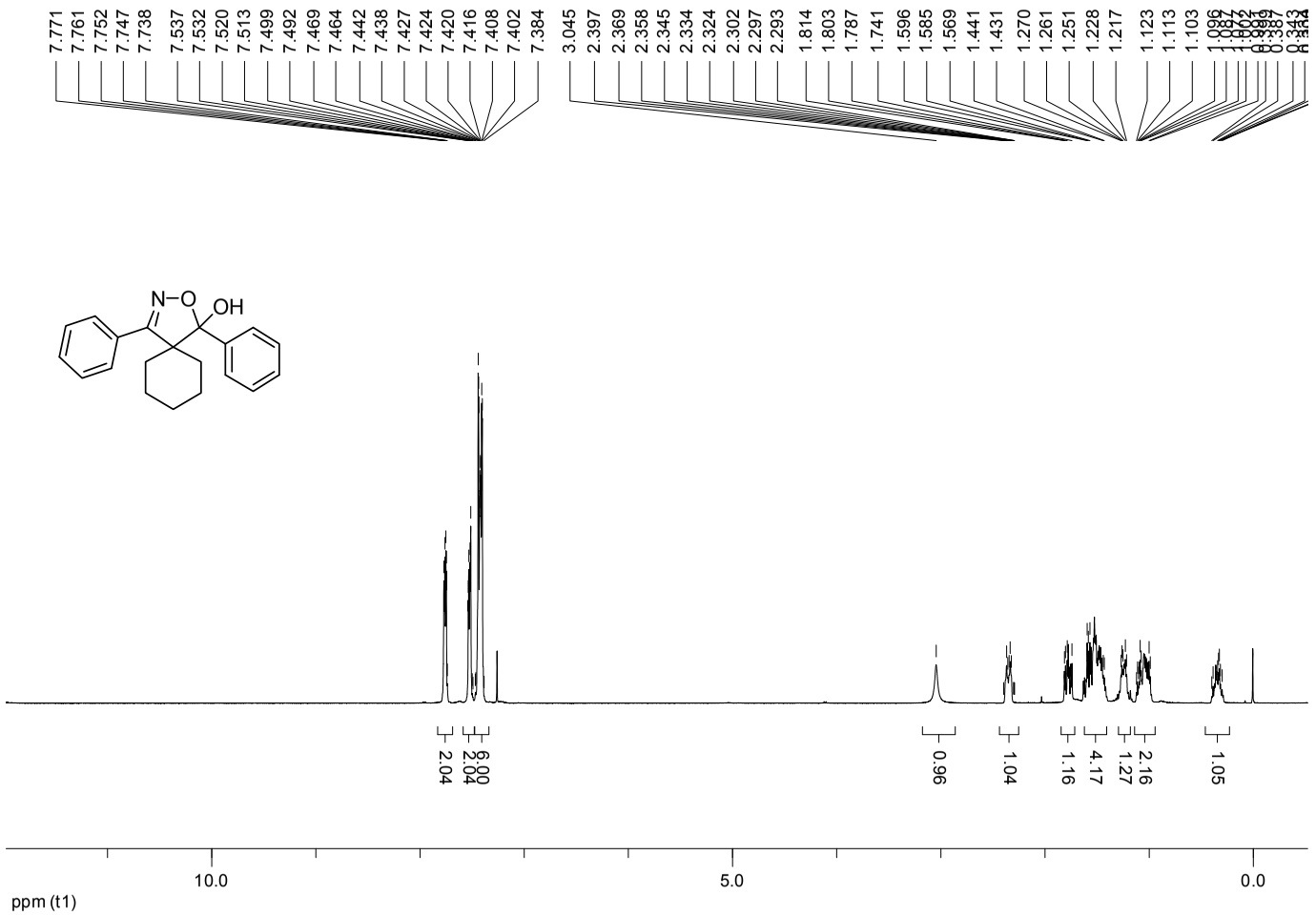
^{1}H NMR spectrum of **2a** (400 MHz, $CDCl_3$)



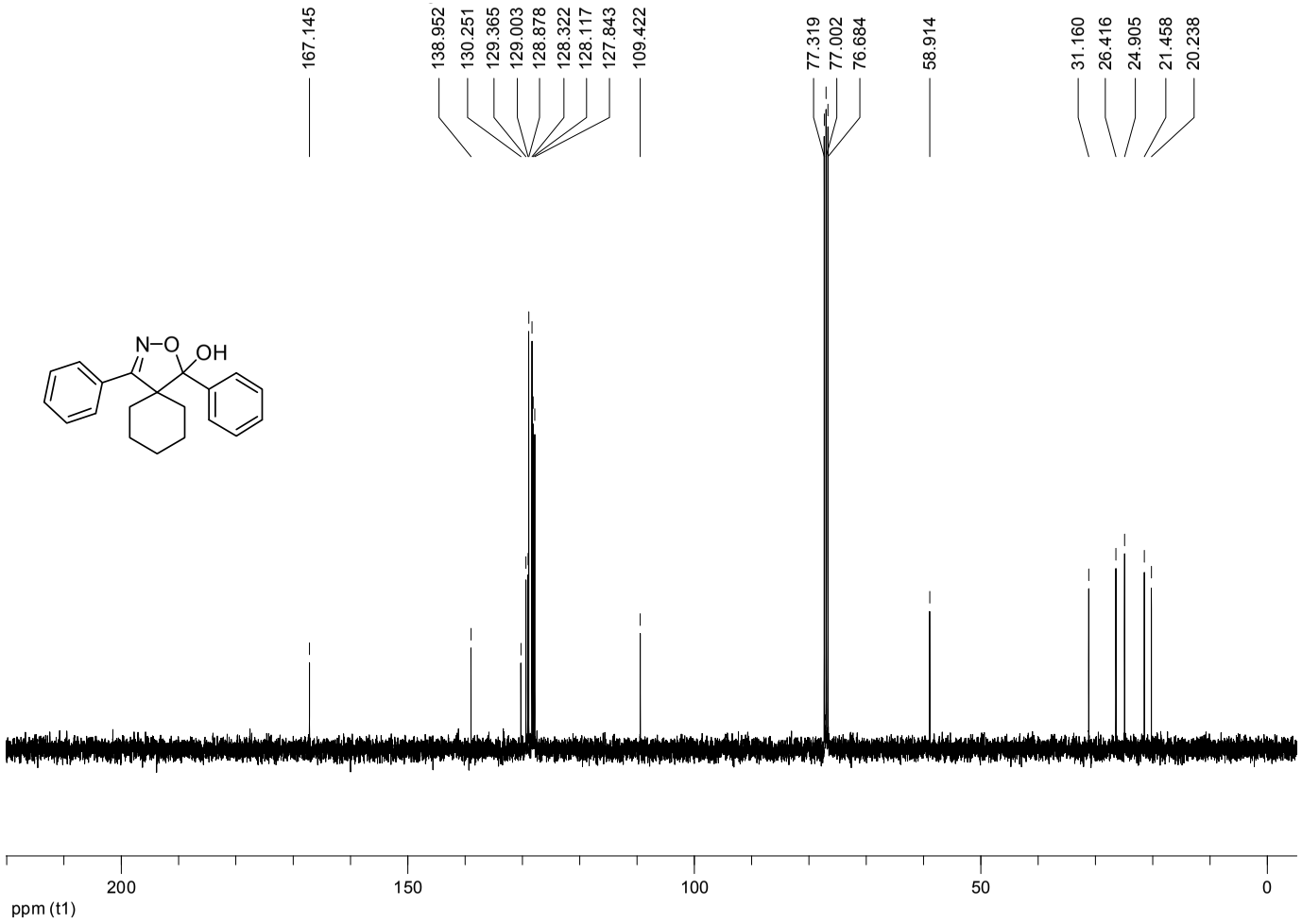
^{13}C NMR spectrum of **2a** (100 MHz, $CDCl_3$)



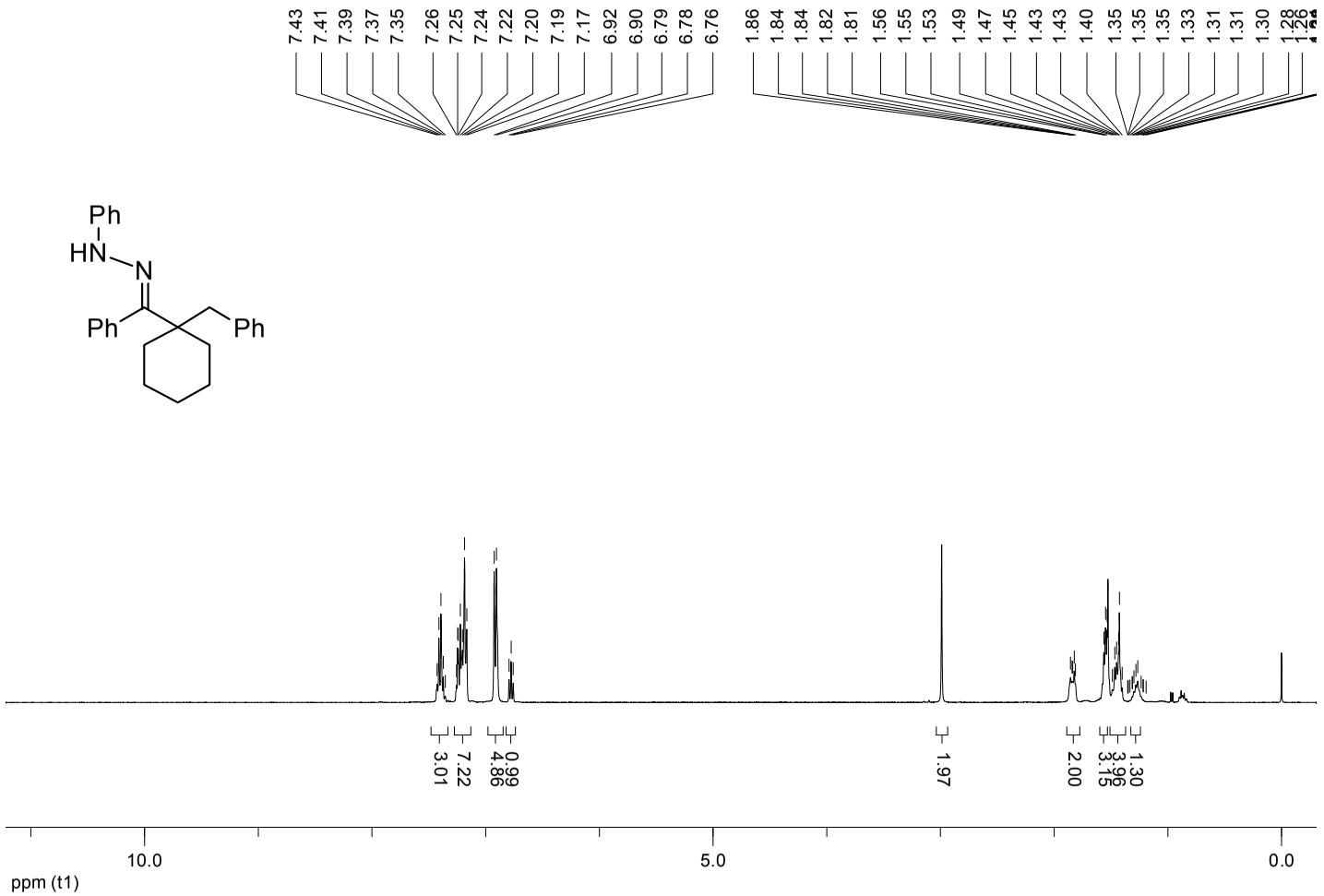
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$)



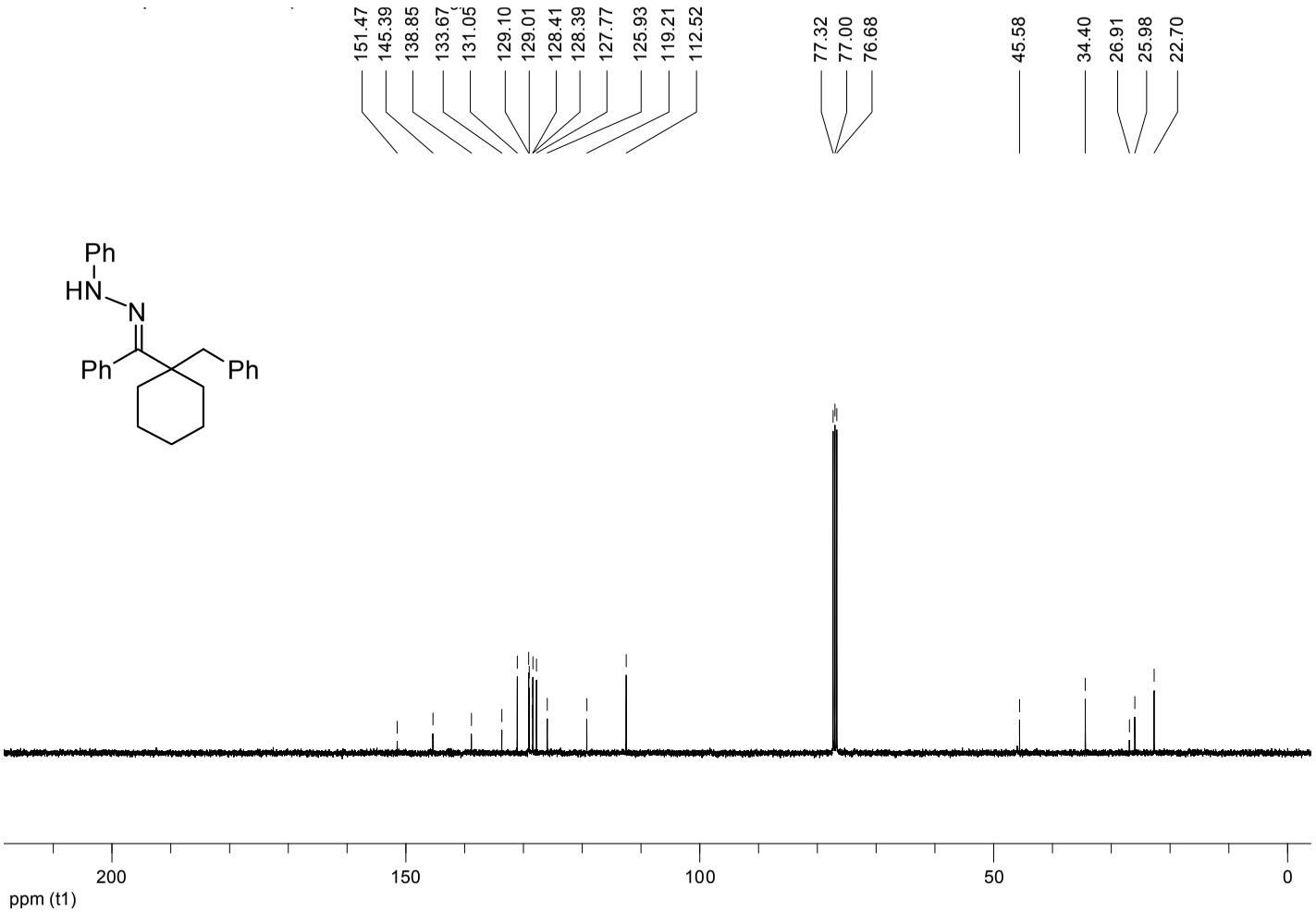
^{13}C NMR spectrum of **2b** (100 MHz, $CDCl_3$)



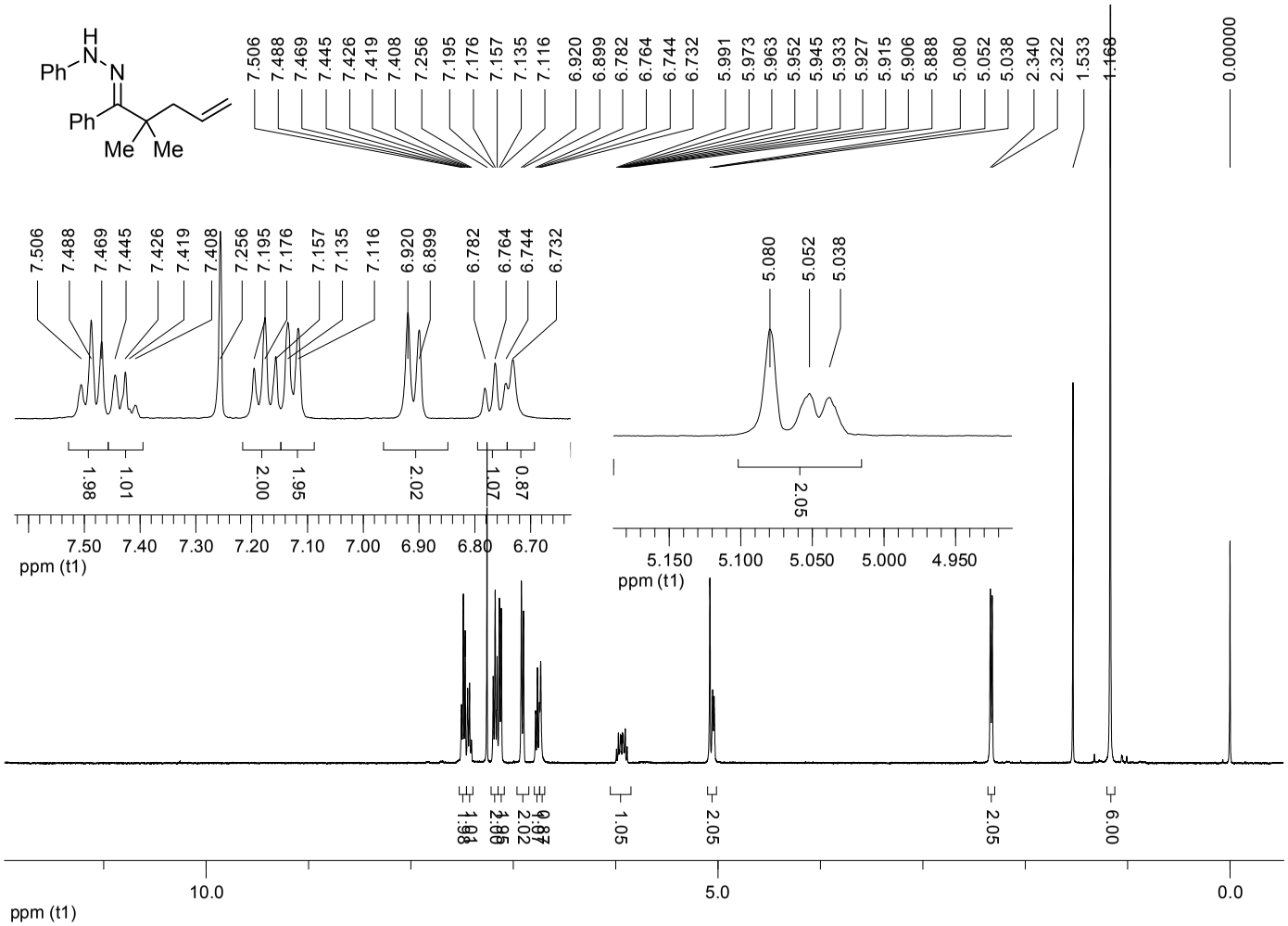
^{1}H NMR spectrum of **3a** (400 MHz, $CDCl_3$)



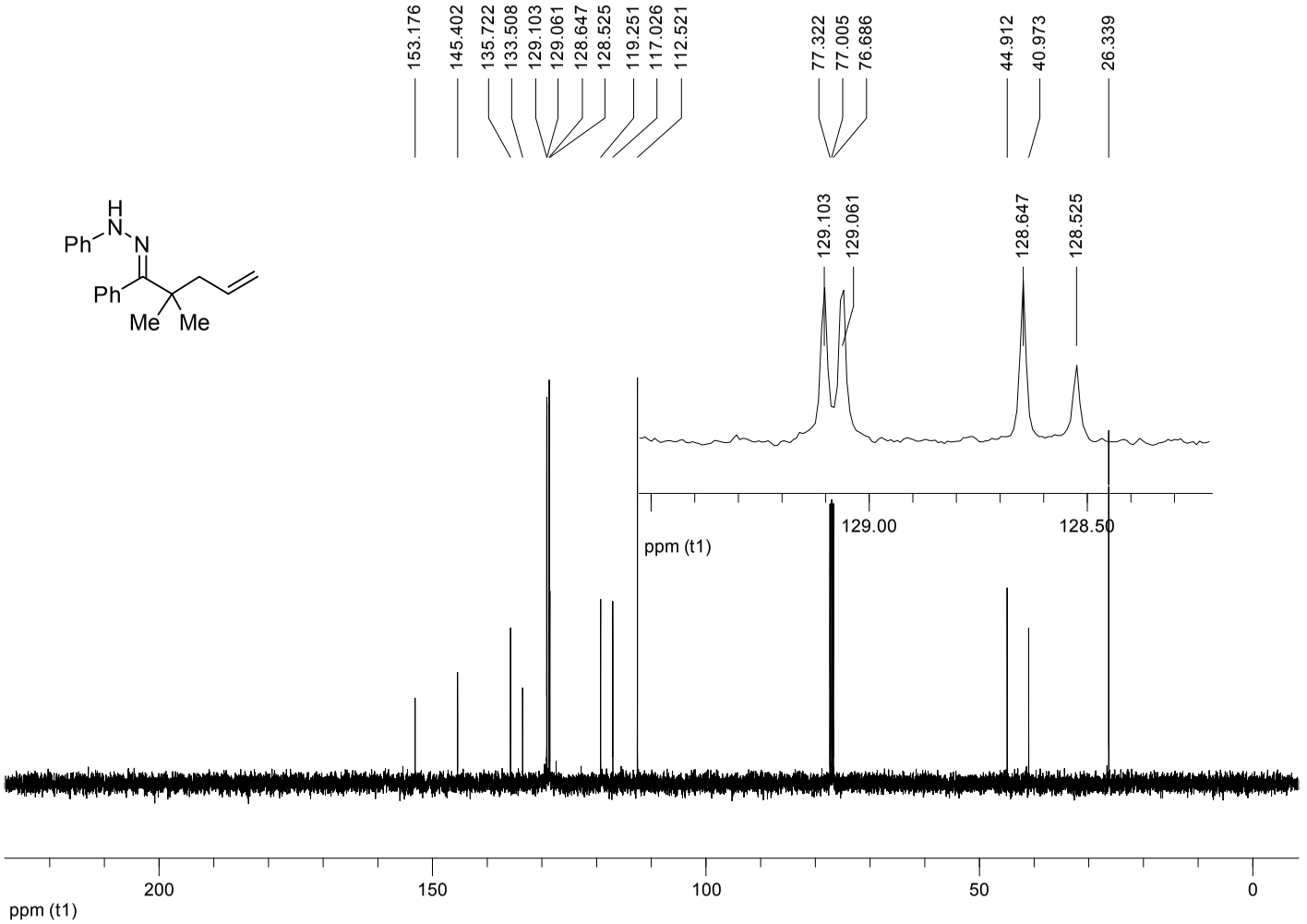
^{13}C NMR spectrum of **3a** (100 MHz, $CDCl_3$)



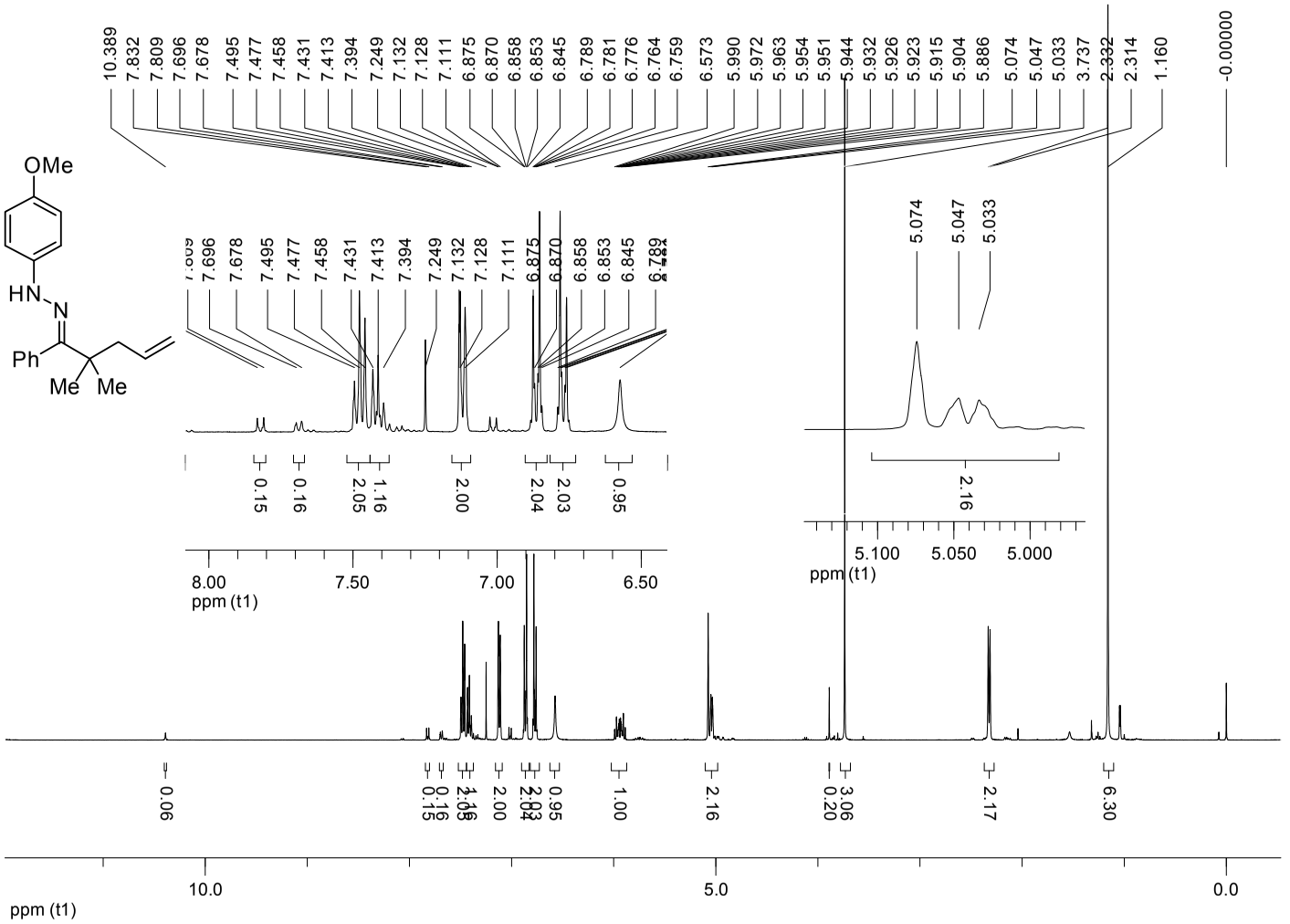
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$)



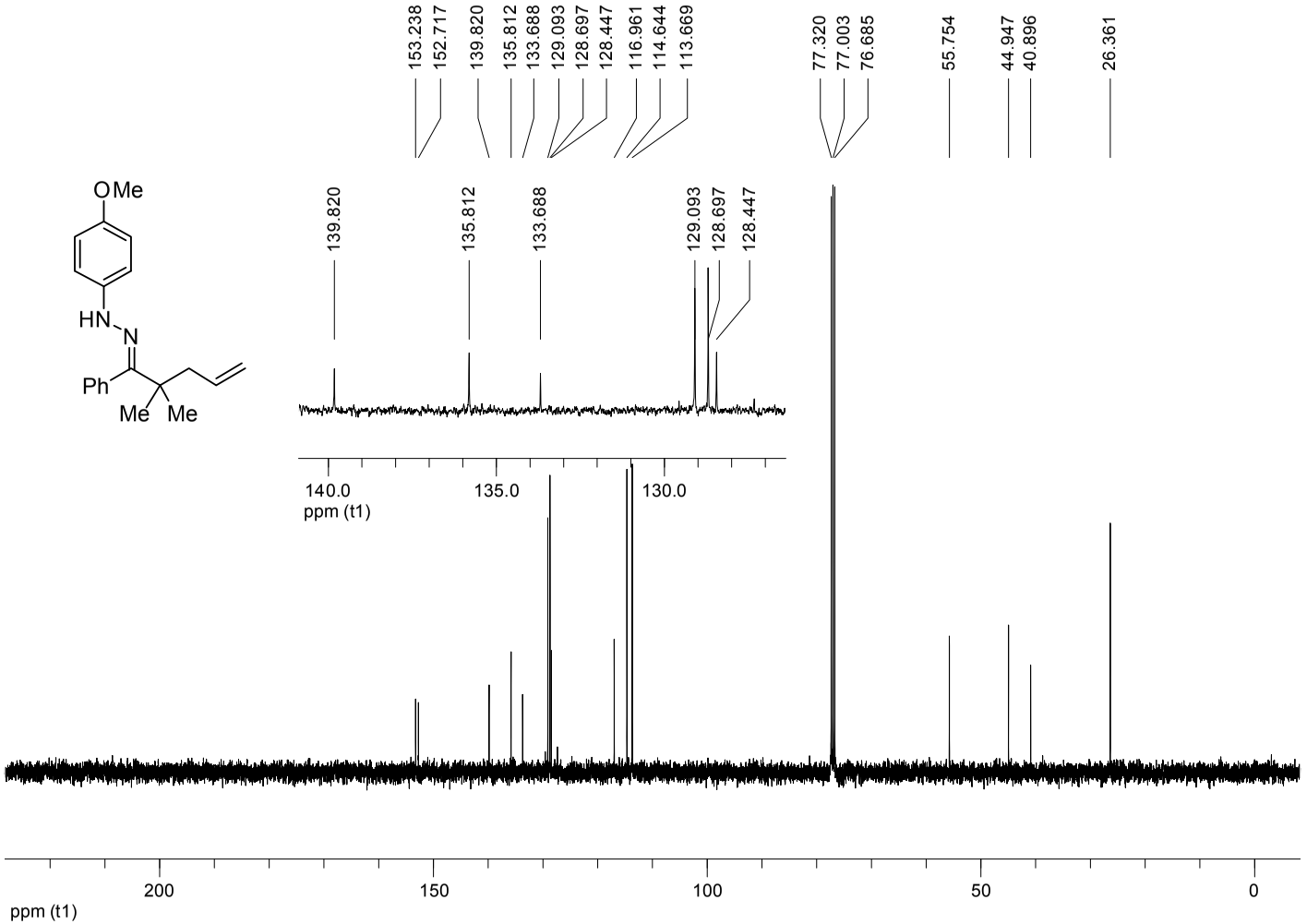
^{13}C NMR spectrum of **3b** (100 MHz, $CDCl_3$)



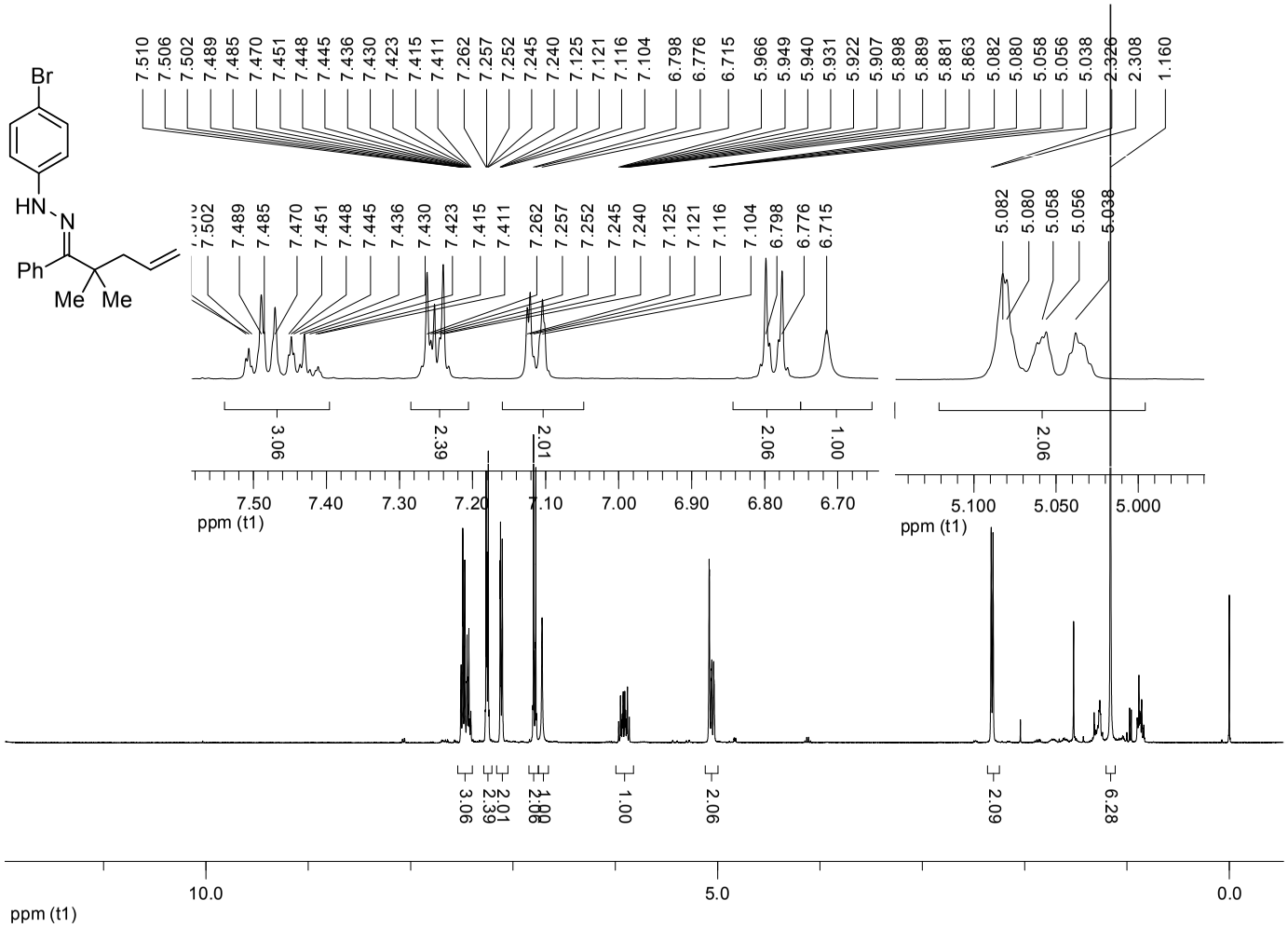
^{1}H NMR spectrum of **3c** (400 MHz, $CDCl_3$)



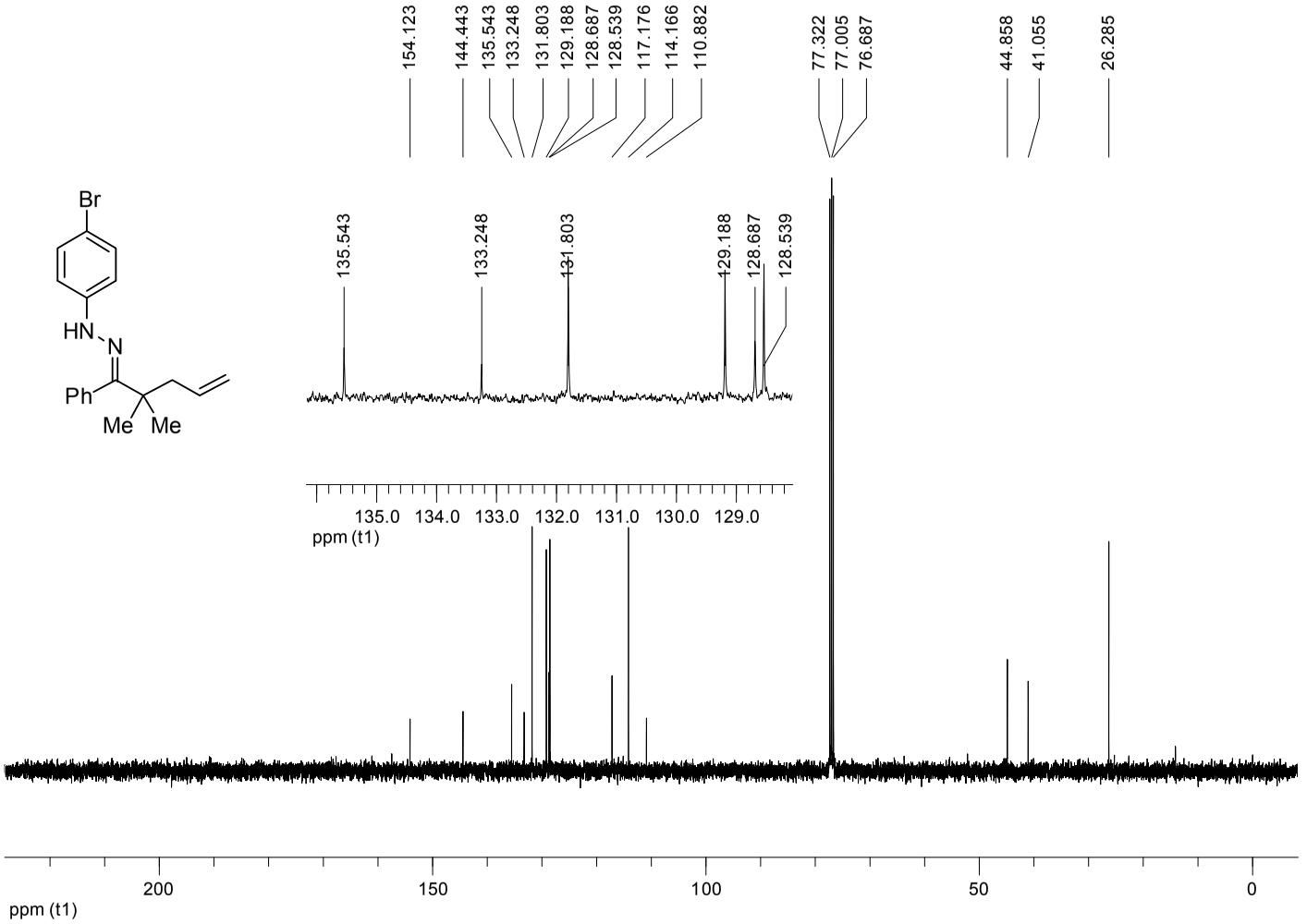
^{13}C NMR spectrum of **3c** (100 MHz, $CDCl_3$)



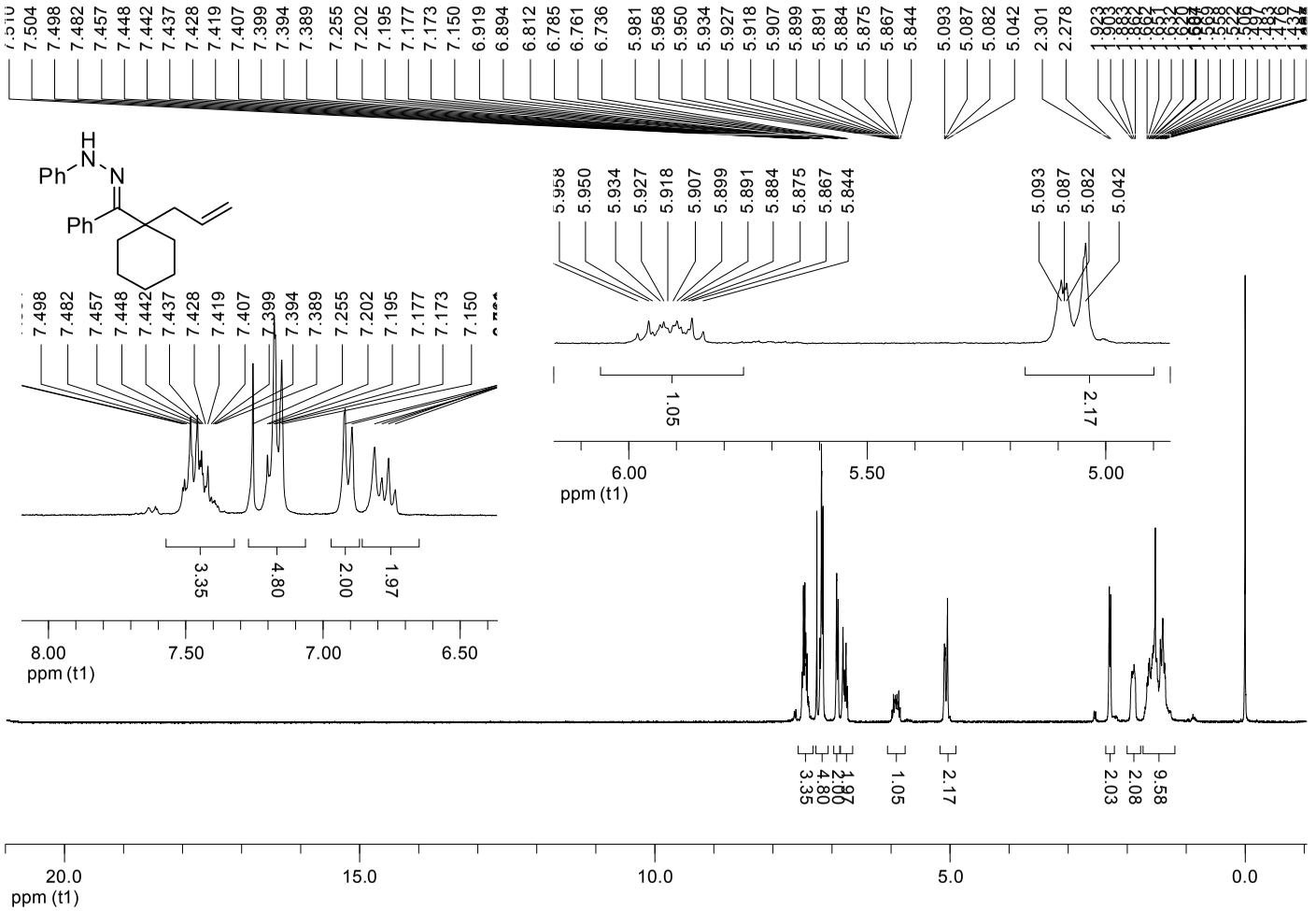
^{1}H NMR spectrum of **3d** (400 MHz, $CDCl_3$)



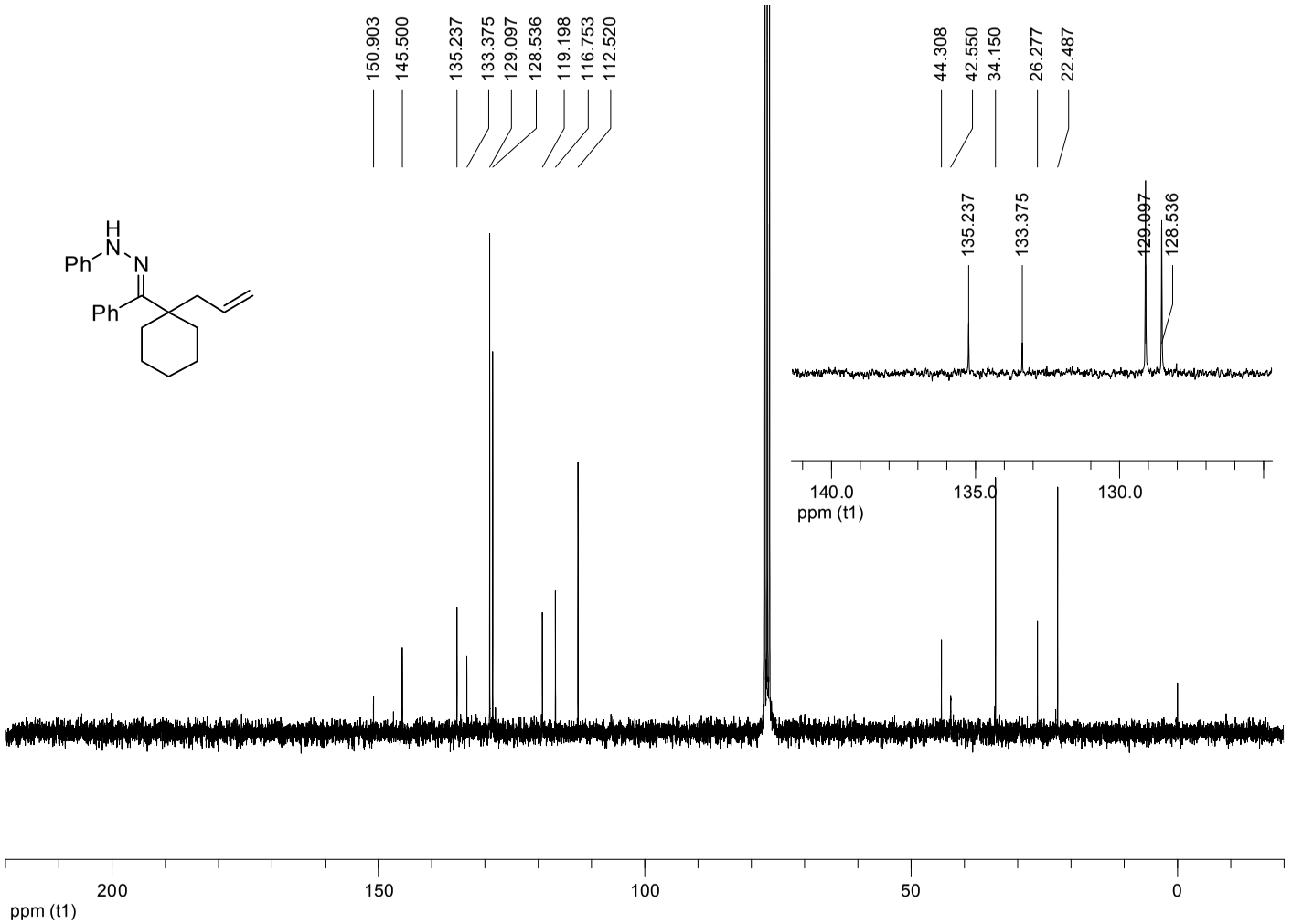
^{13}C NMR spectrum of **3d** (100 MHz, $CDCl_3$)



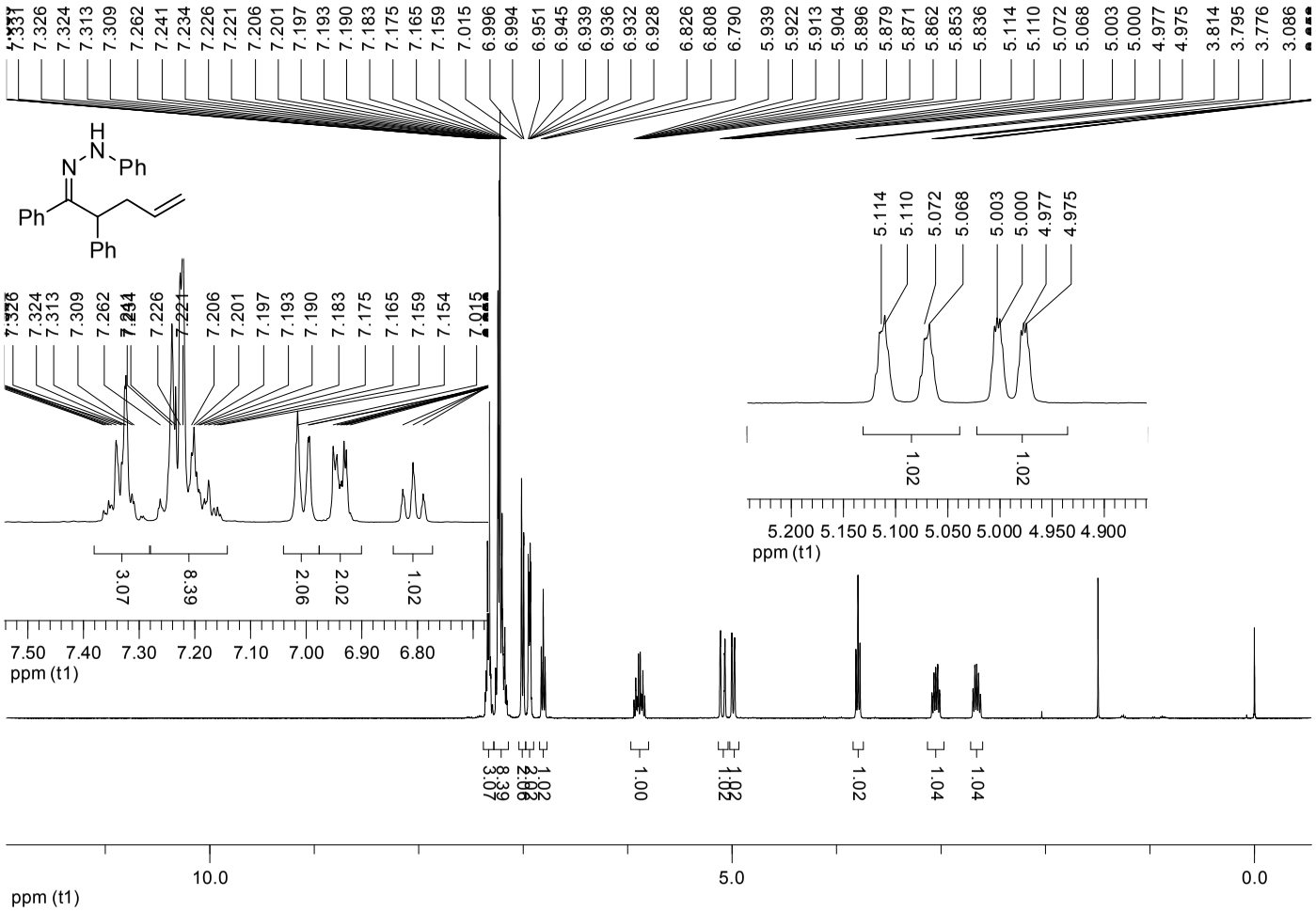
^{1}H NMR spectrum of **3e** (300 MHz, $CDCl_3$)



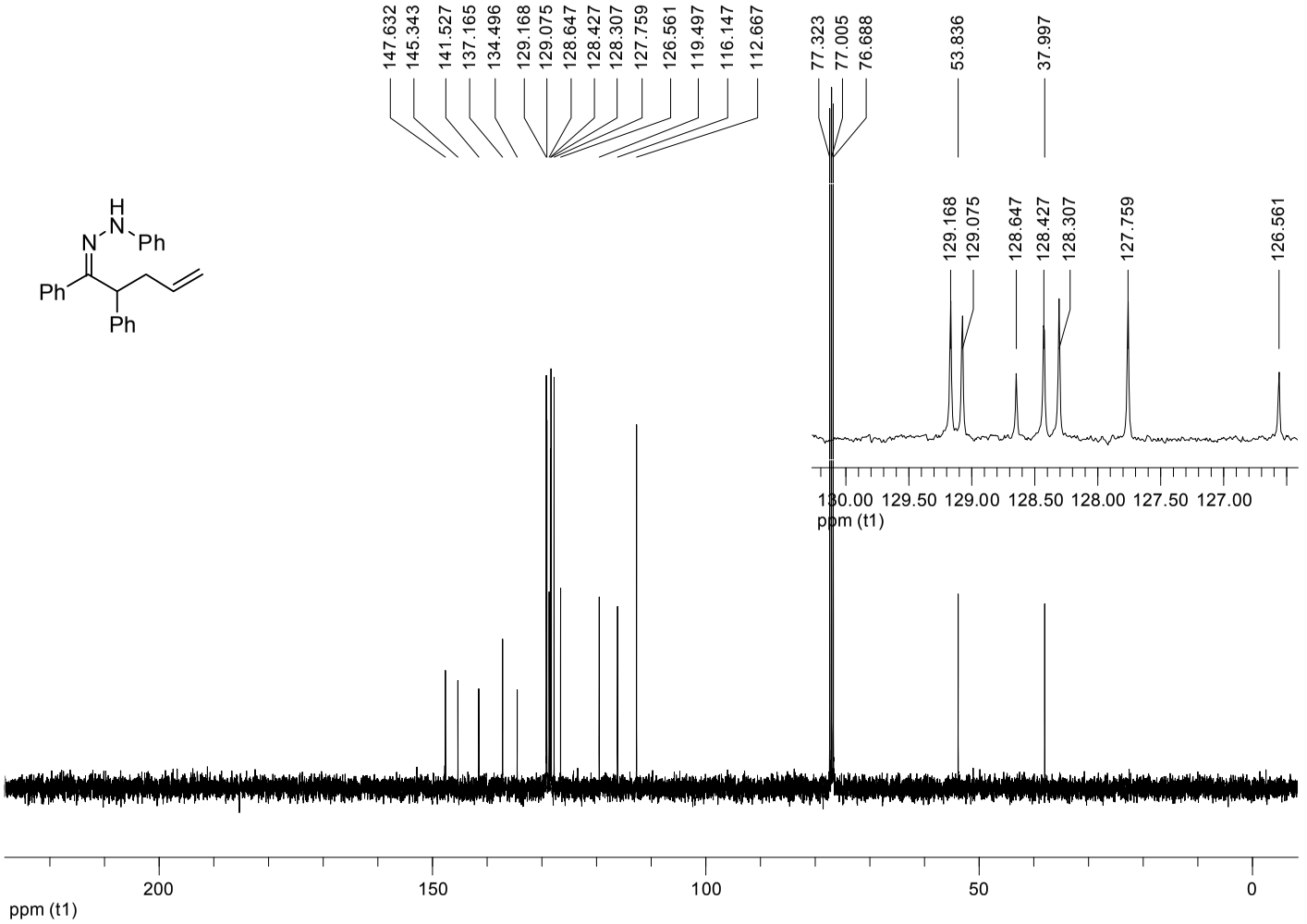
^{13}C NMR spectrum of **3e** (75 MHz, $CDCl_3$)



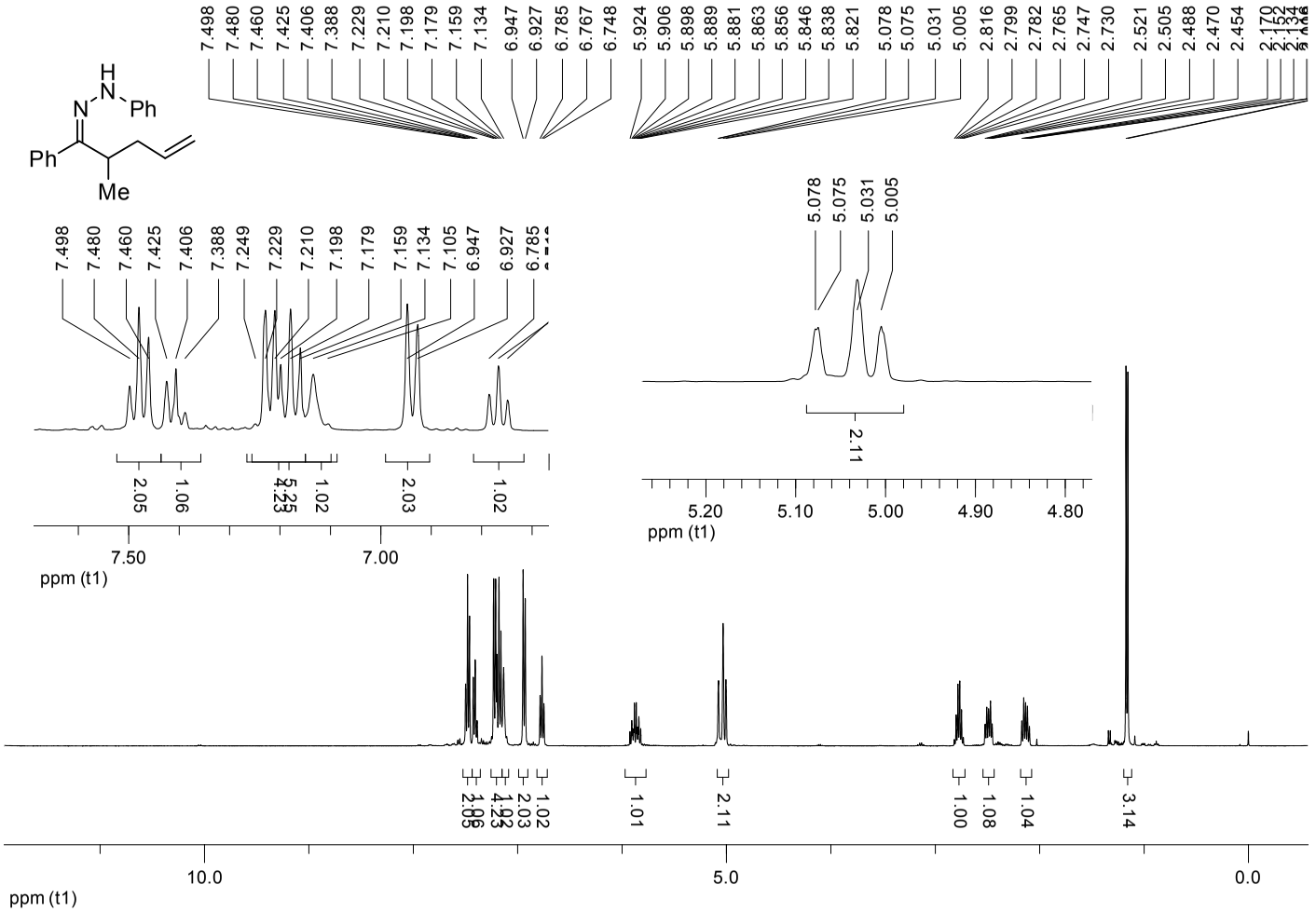
^{1}H NMR spectrum of **3f** (400 MHz, $CDCl_3$)



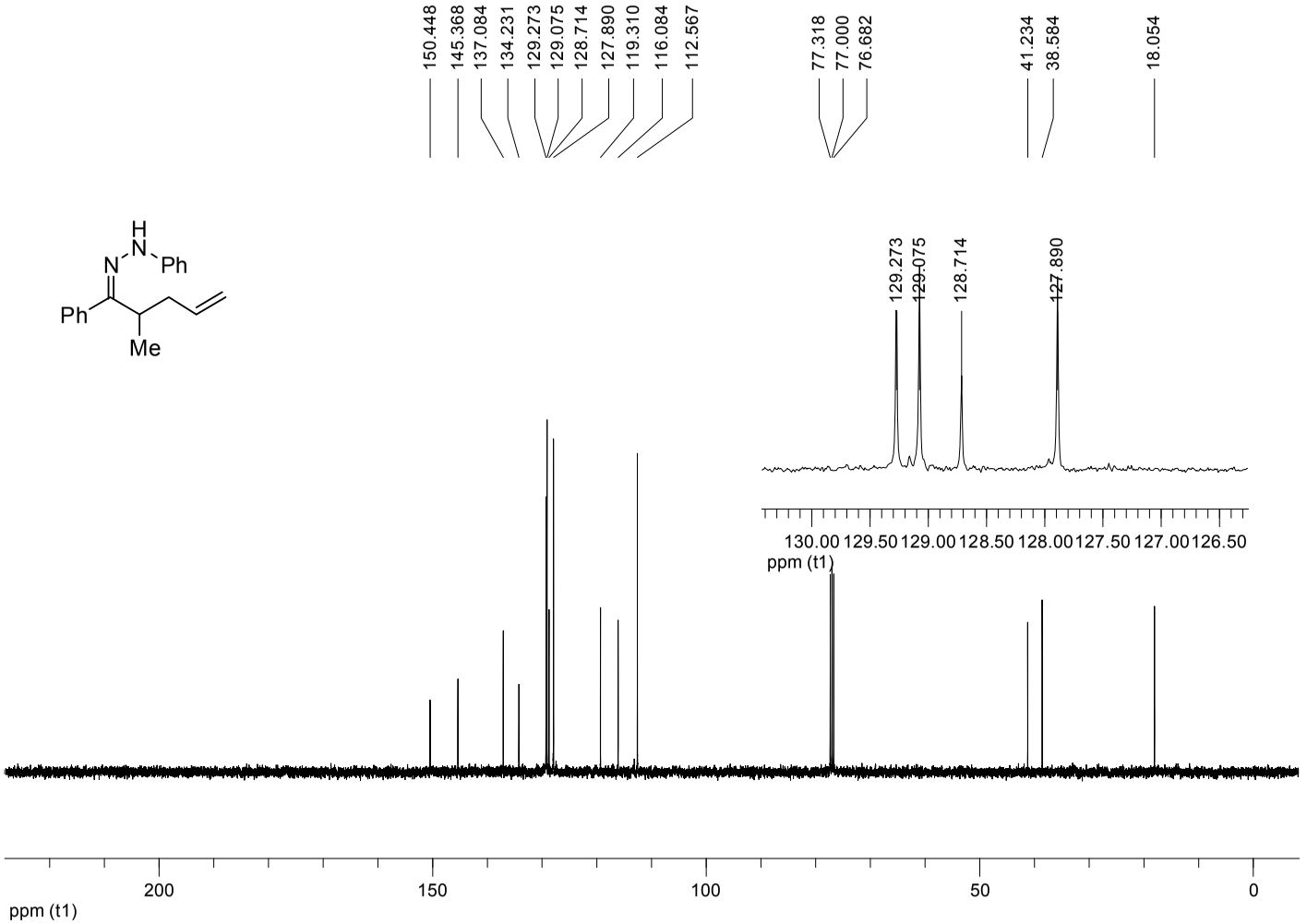
^{13}C NMR spectrum of **3f** (100 MHz, $CDCl_3$)



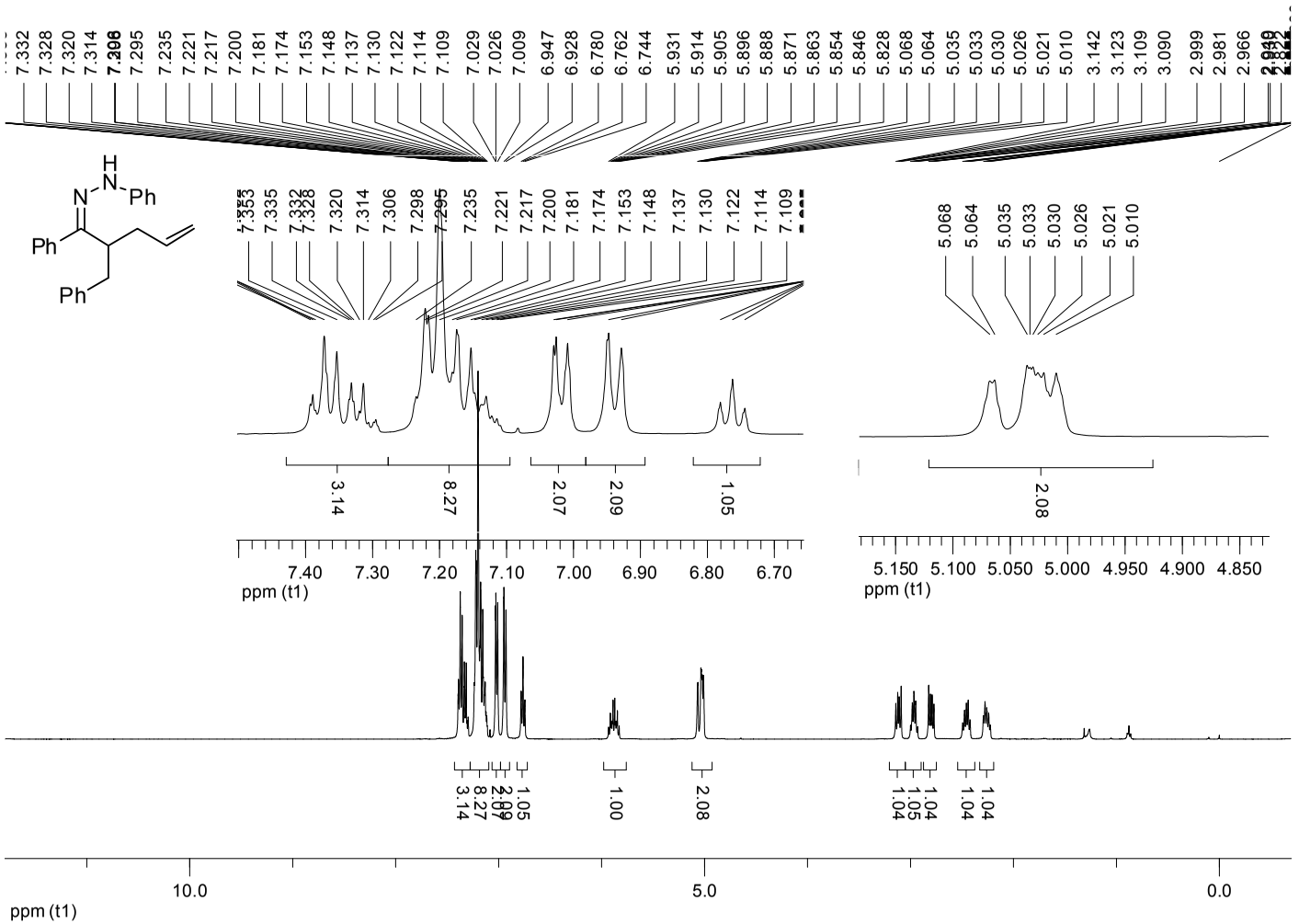
^{1}H NMR spectrum of **3g** (400 MHz, $CDCl_3$)



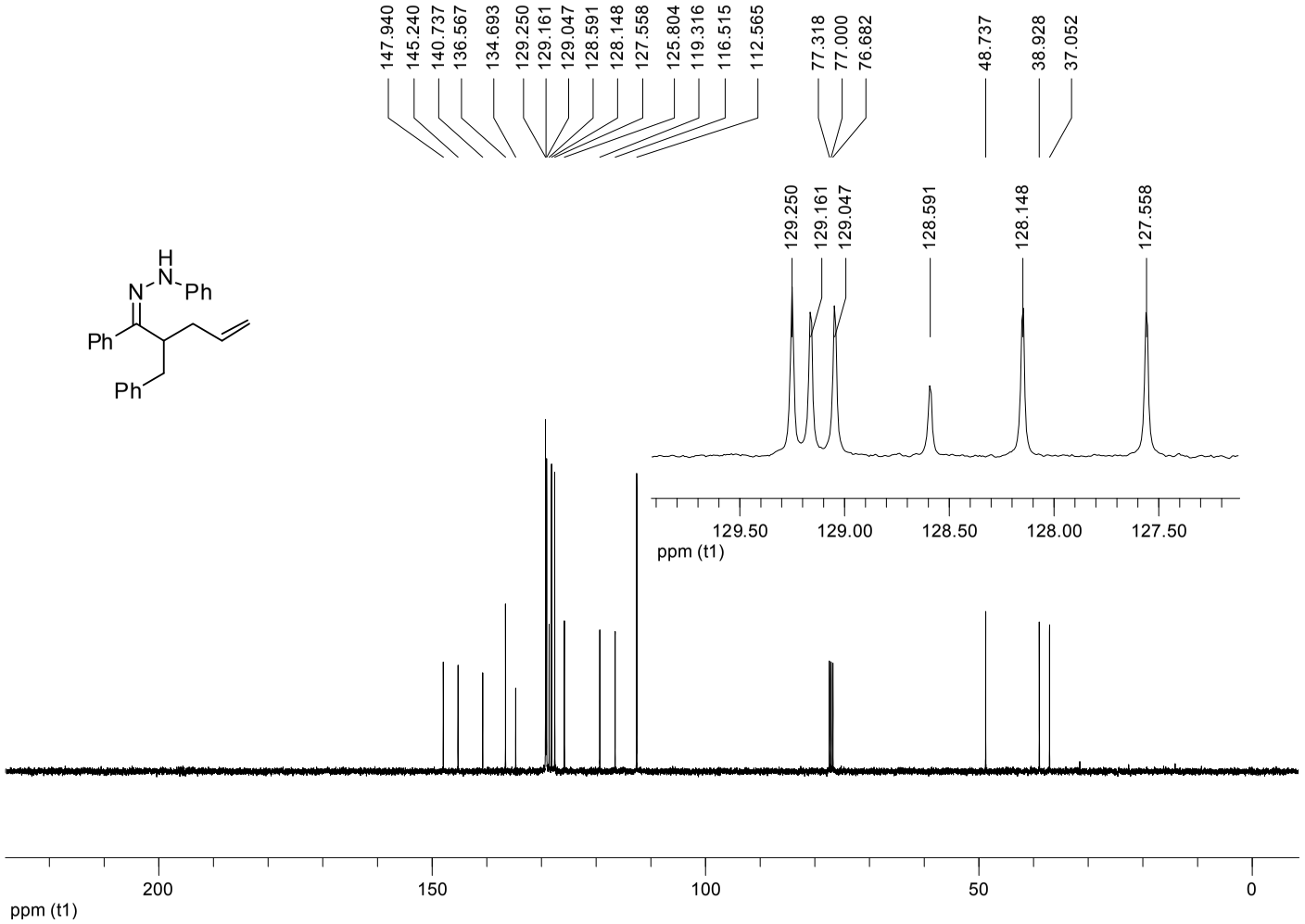
^{13}C NMR spectrum of **3g** (100 MHz, $CDCl_3$)



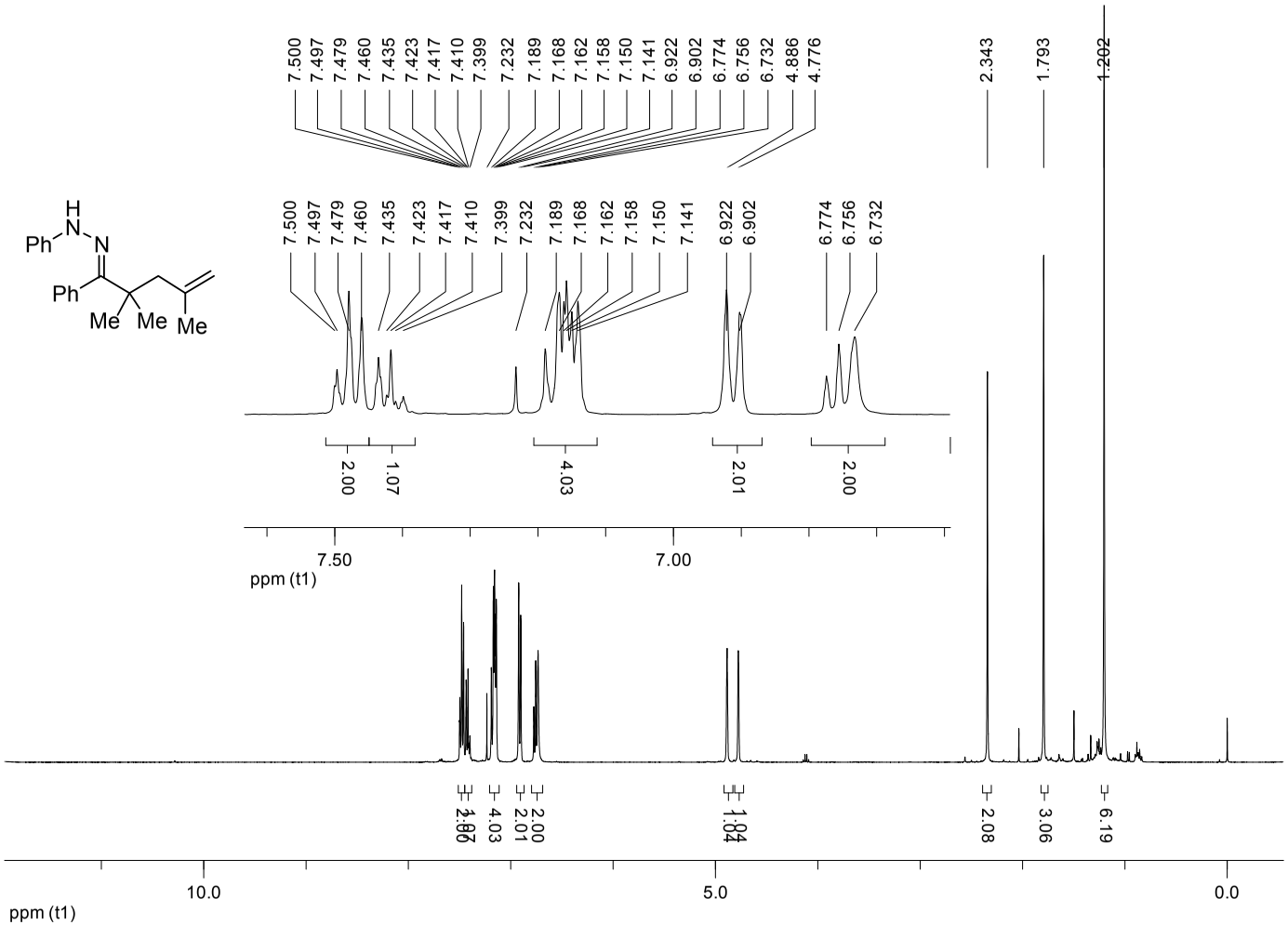
^{1}H NMR spectrum of **3h** (400 MHz, $CDCl_3$)



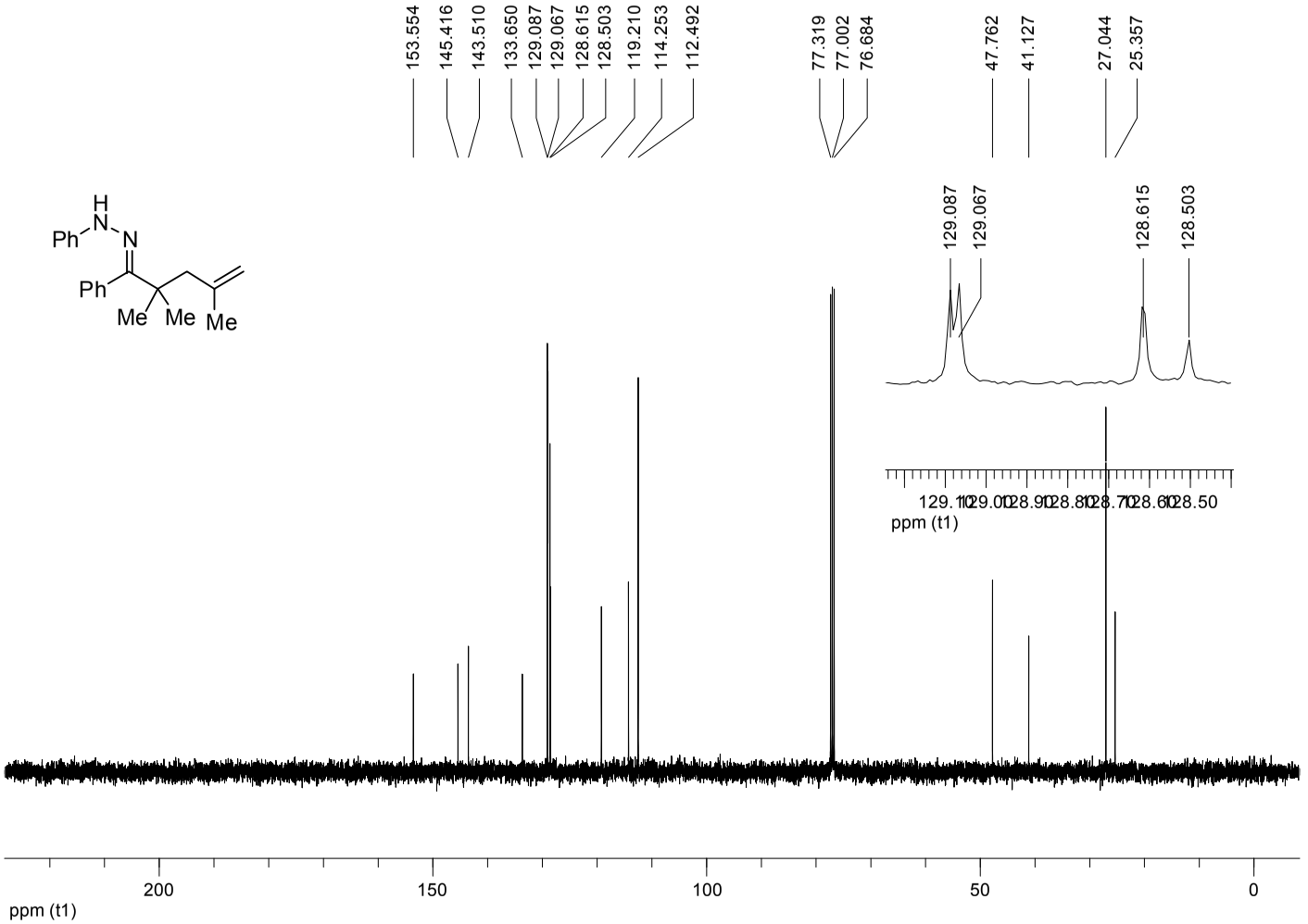
^{13}C NMR spectrum of **3h** (100 MHz, $CDCl_3$)



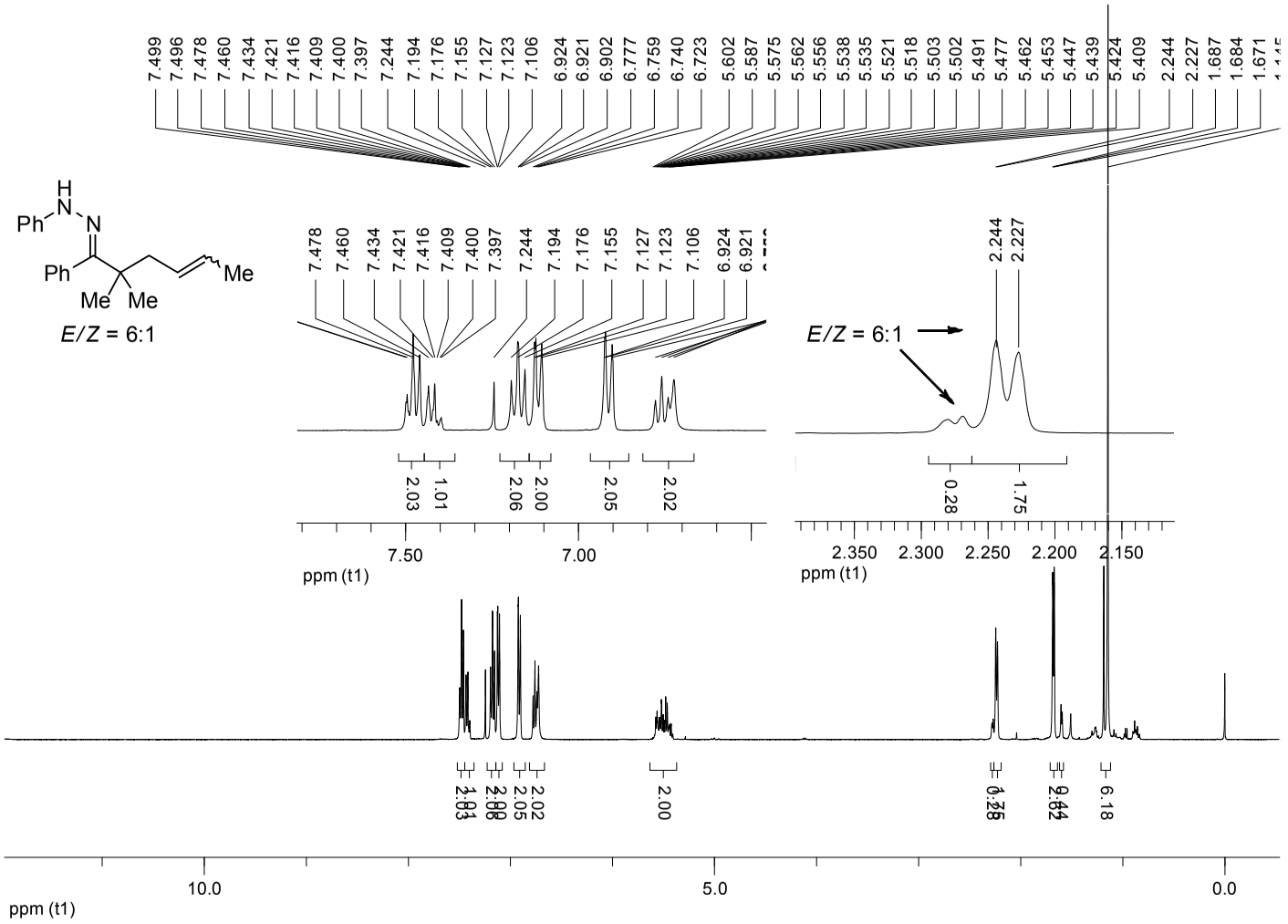
^{1}H NMR spectrum of **3j** (400 MHz, $CDCl_3$)



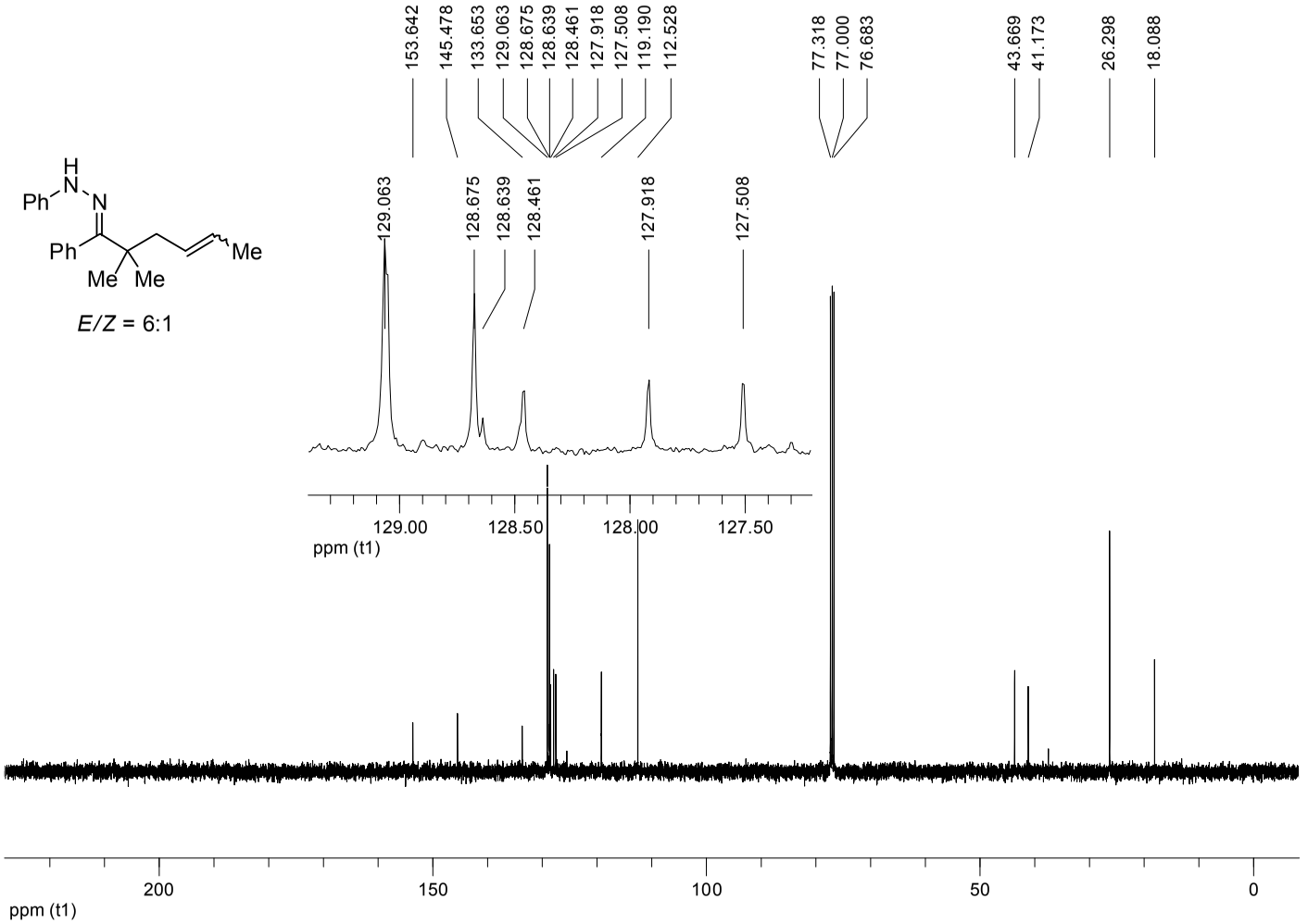
^{13}C NMR spectrum of **3j** (100 MHz, $CDCl_3$)



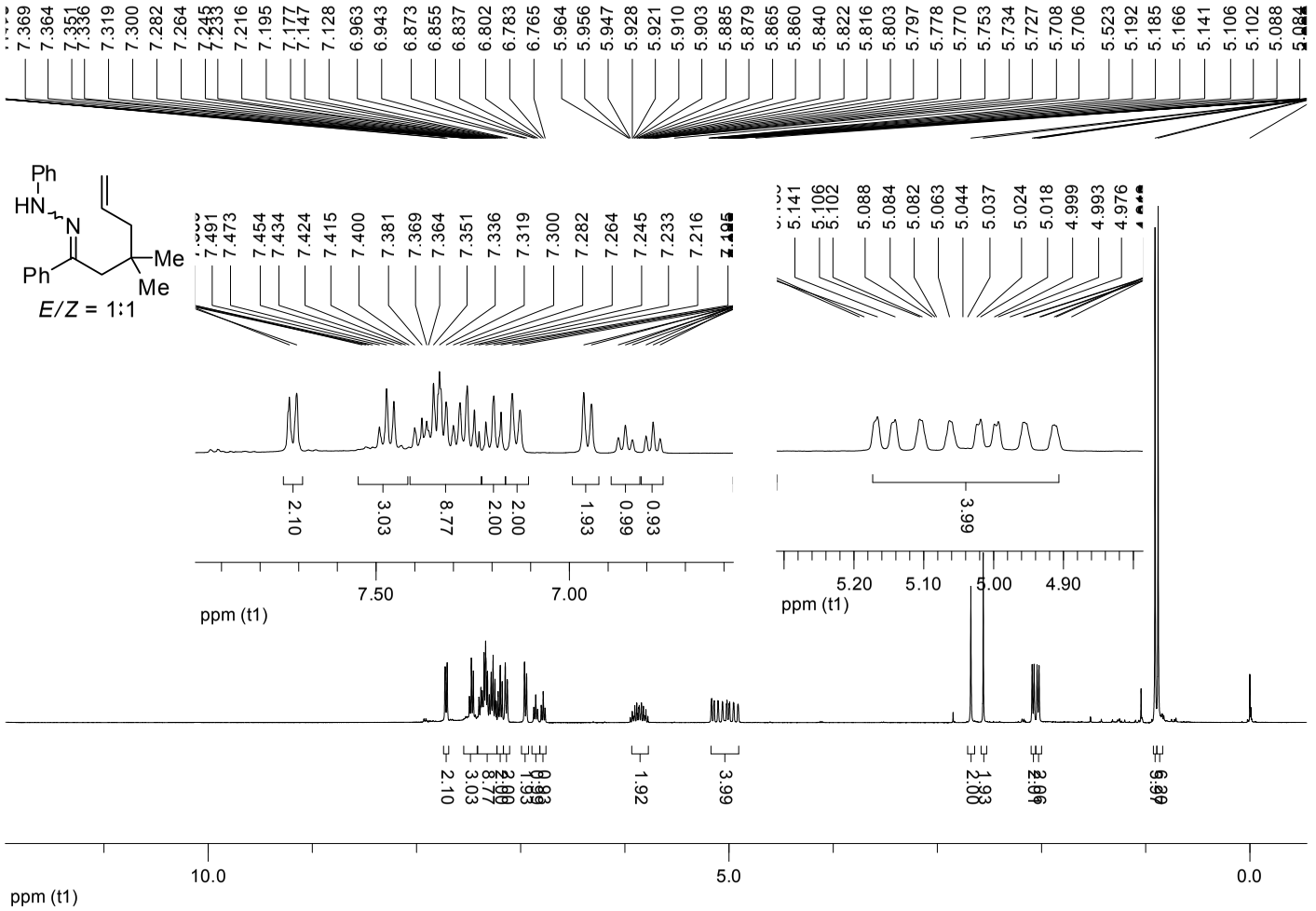
^{1}H NMR spectrum of **3k** (400 MHz, $CDCl_3$)



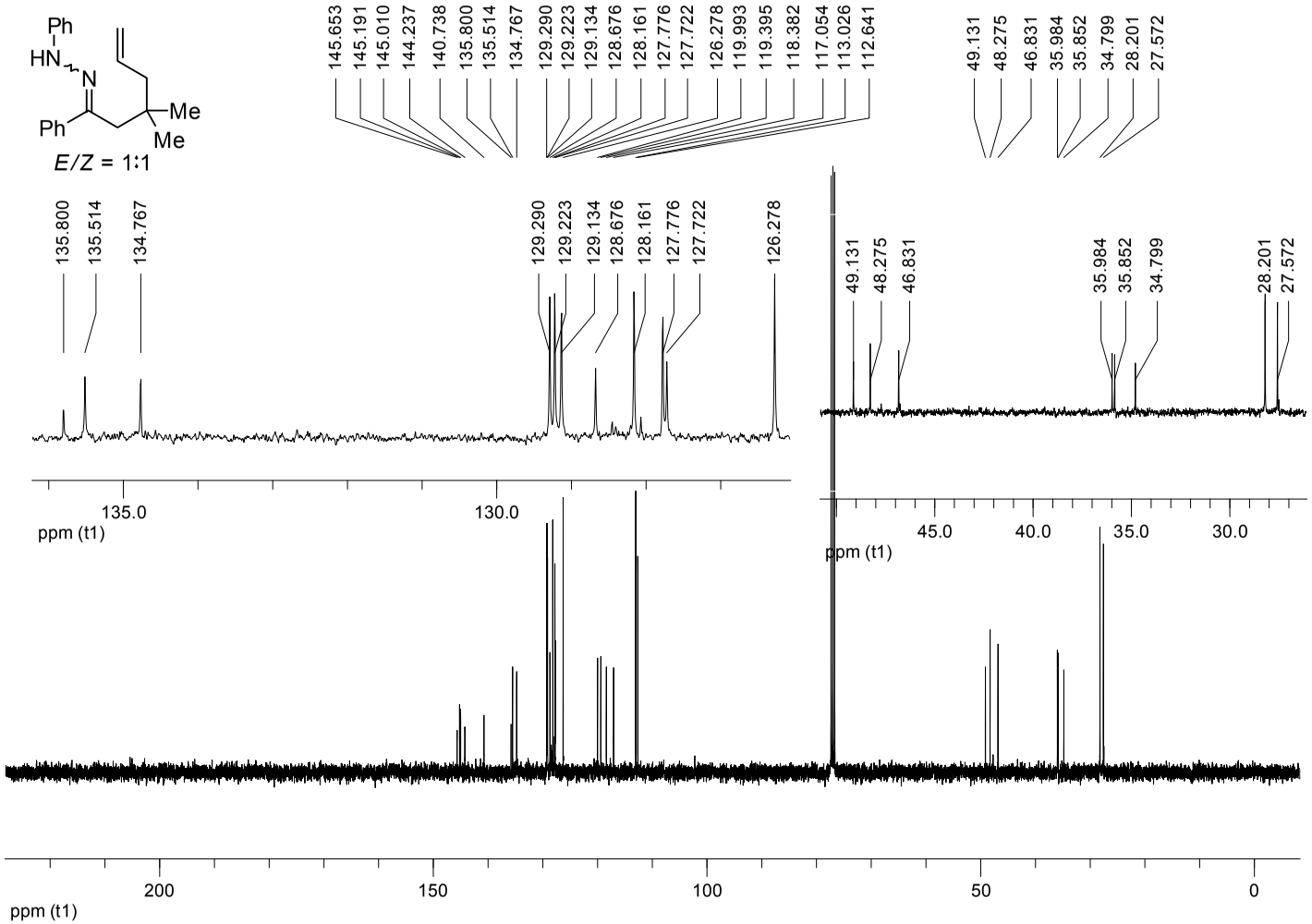
^{13}C NMR spectrum of **3k** (100 MHz, $CDCl_3$)



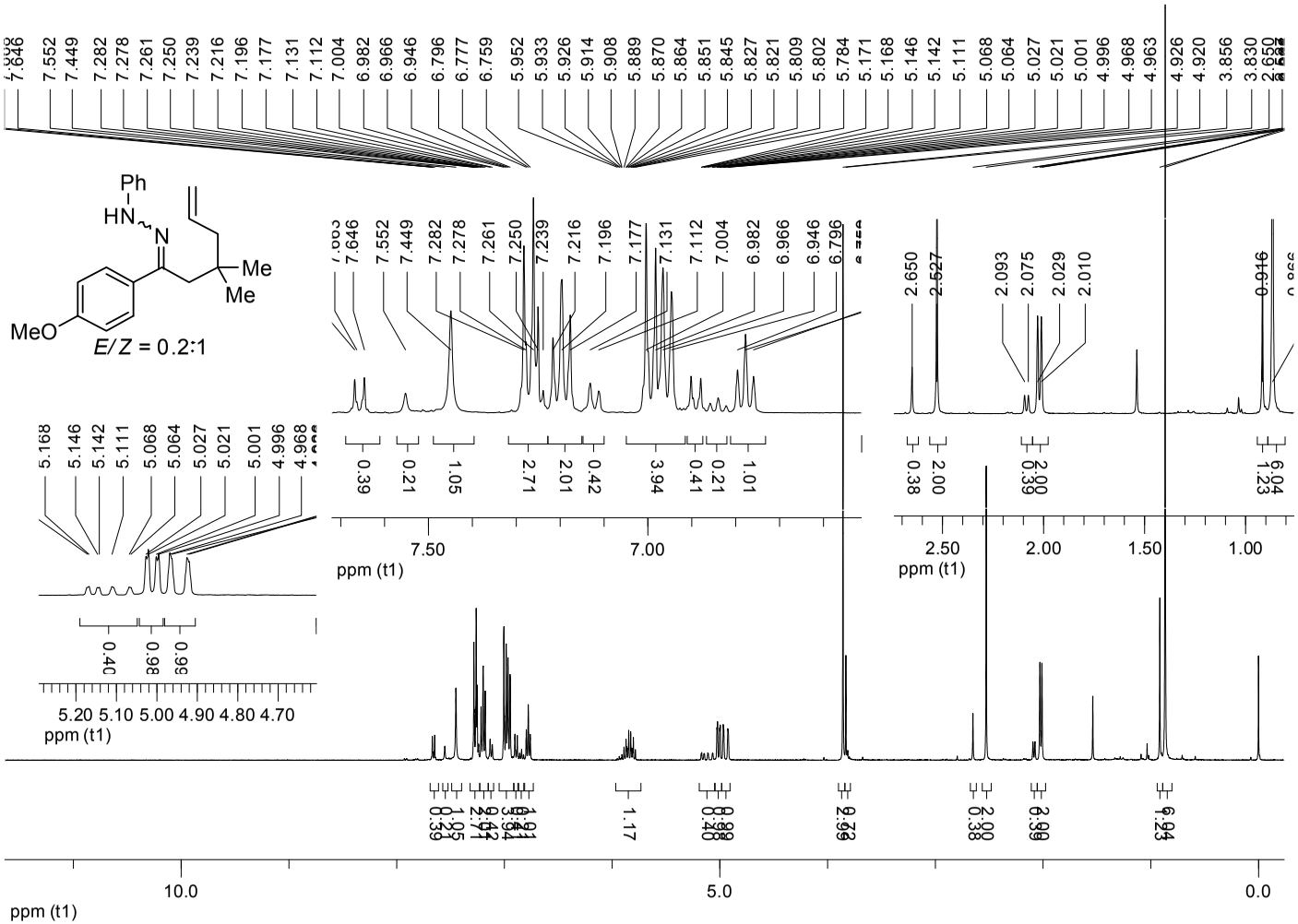
^{1}H NMR spectrum of **3l** (400 MHz, $CDCl_3$)



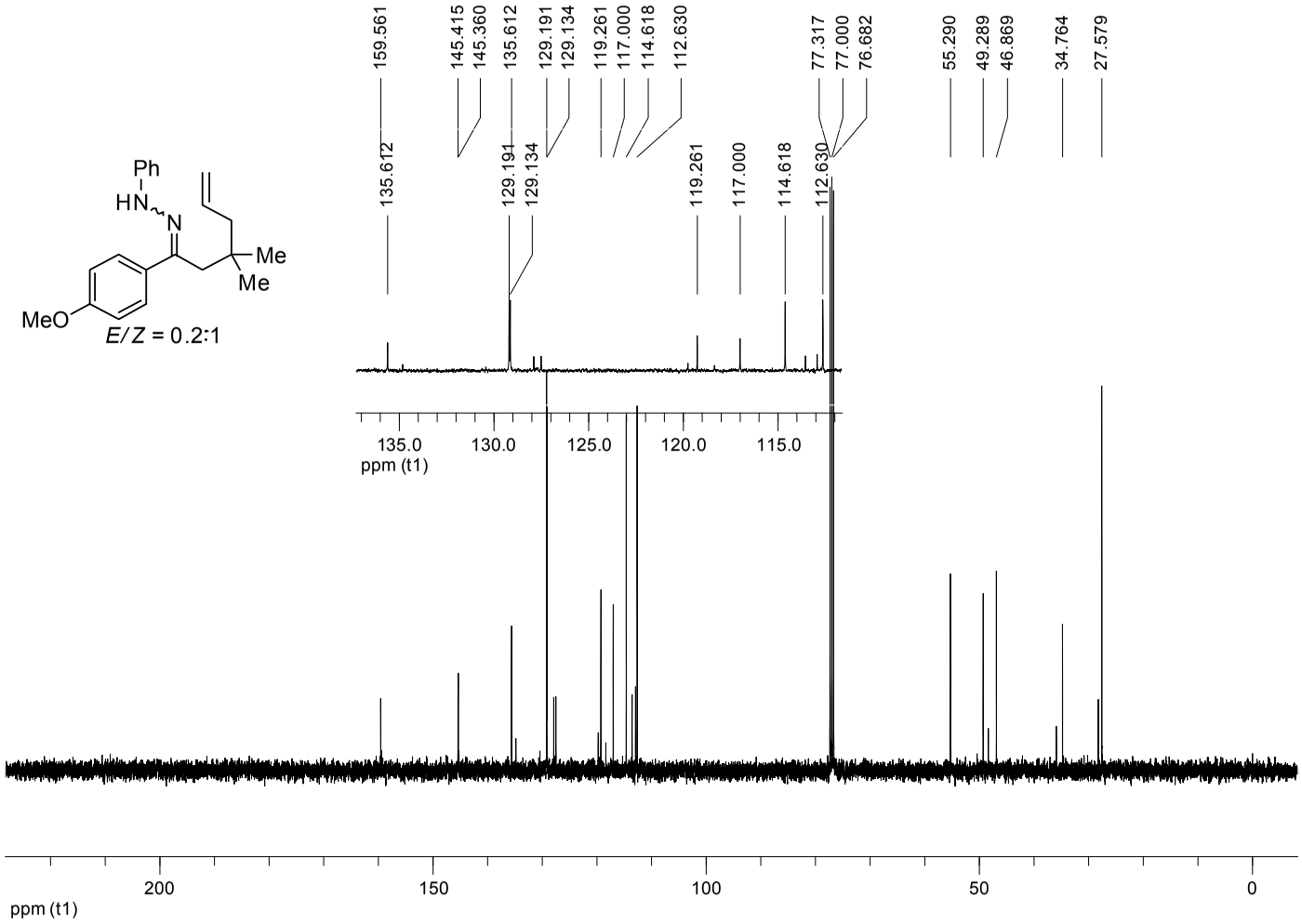
^{13}C NMR spectrum of **3l** (100 MHz, $CDCl_3$)



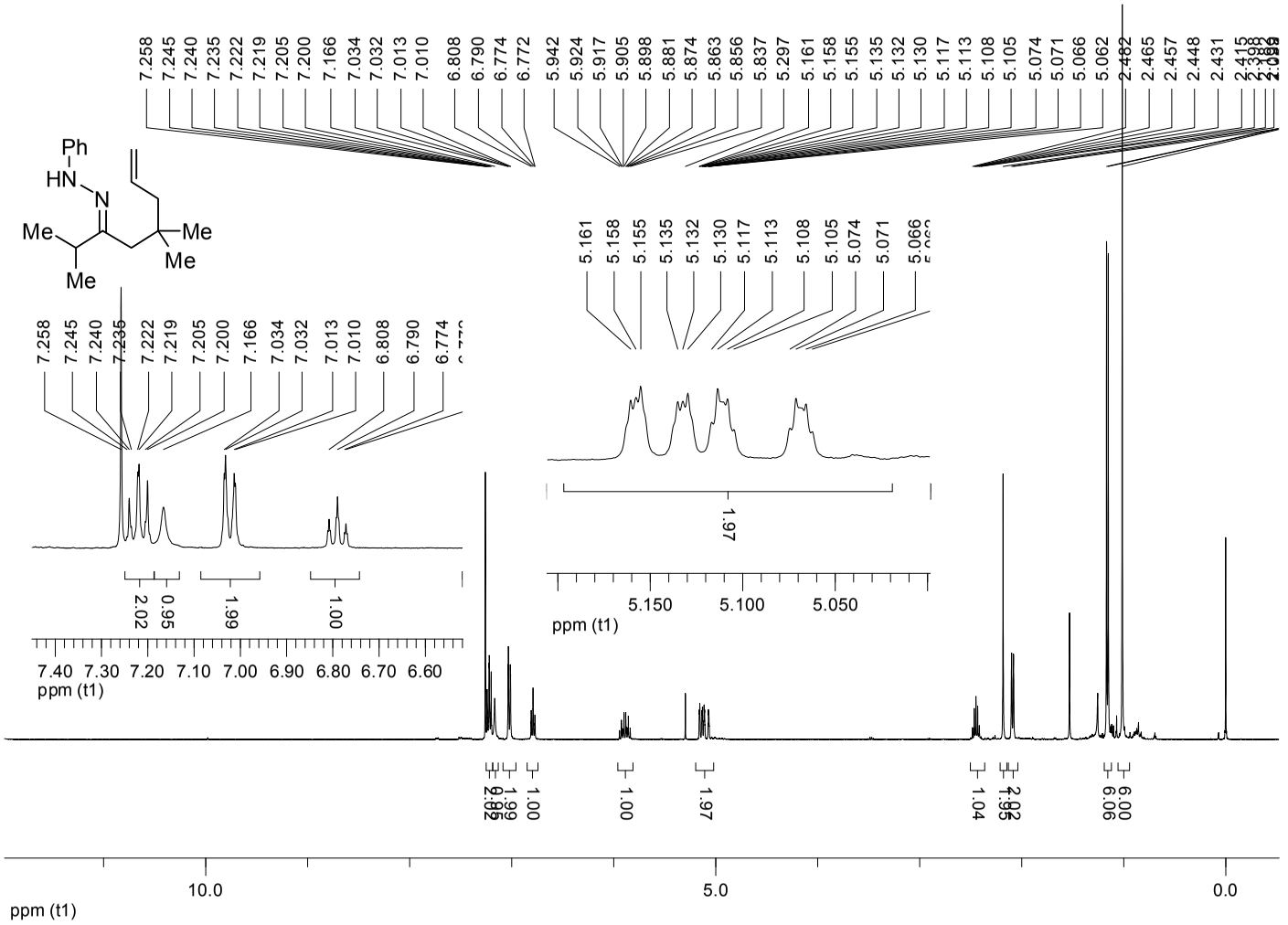
^{1}H NMR spectrum of **3m** (400 MHz, $CDCl_3$)



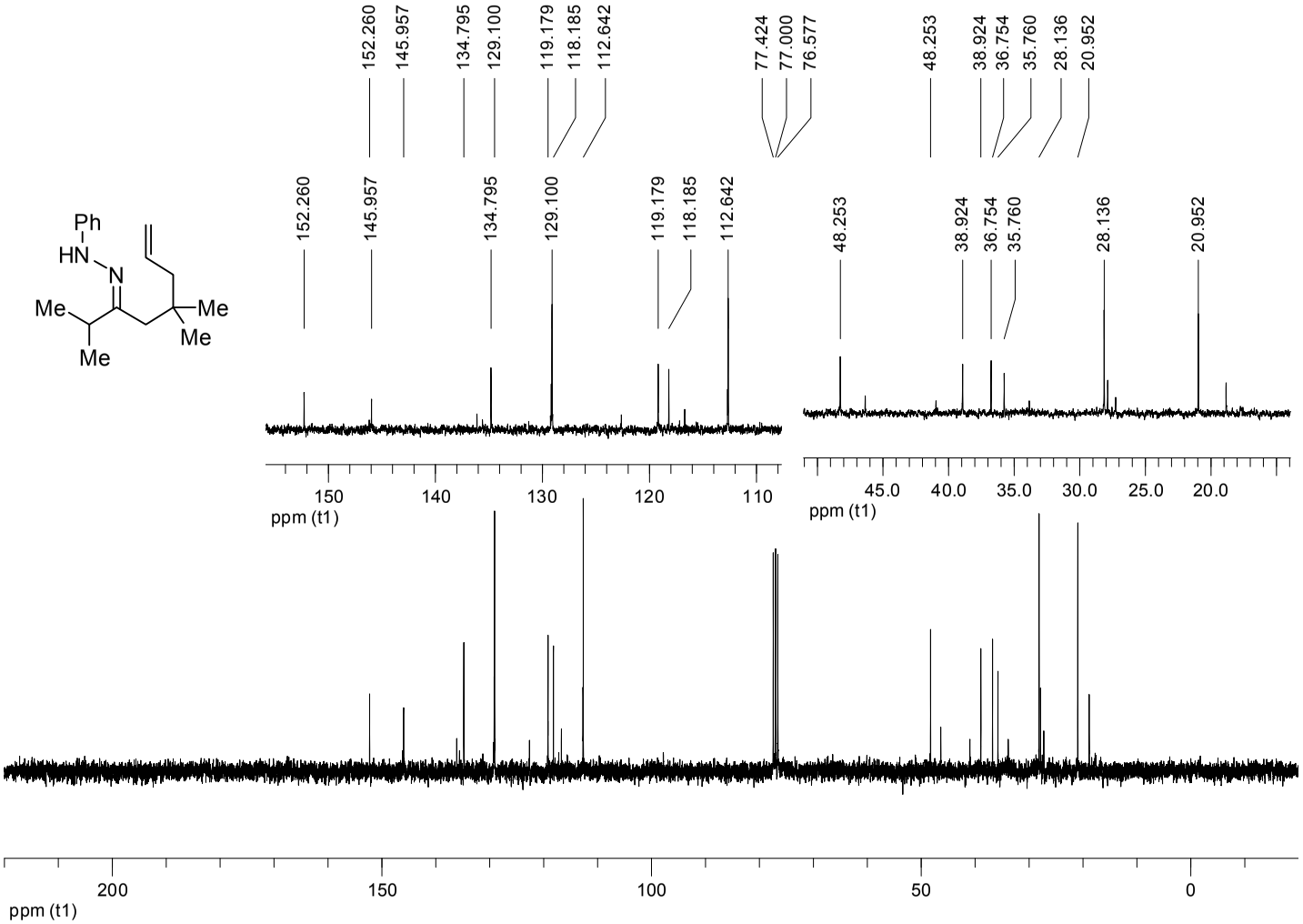
^{13}C NMR spectrum of **3m** (100 MHz, $CDCl_3$)



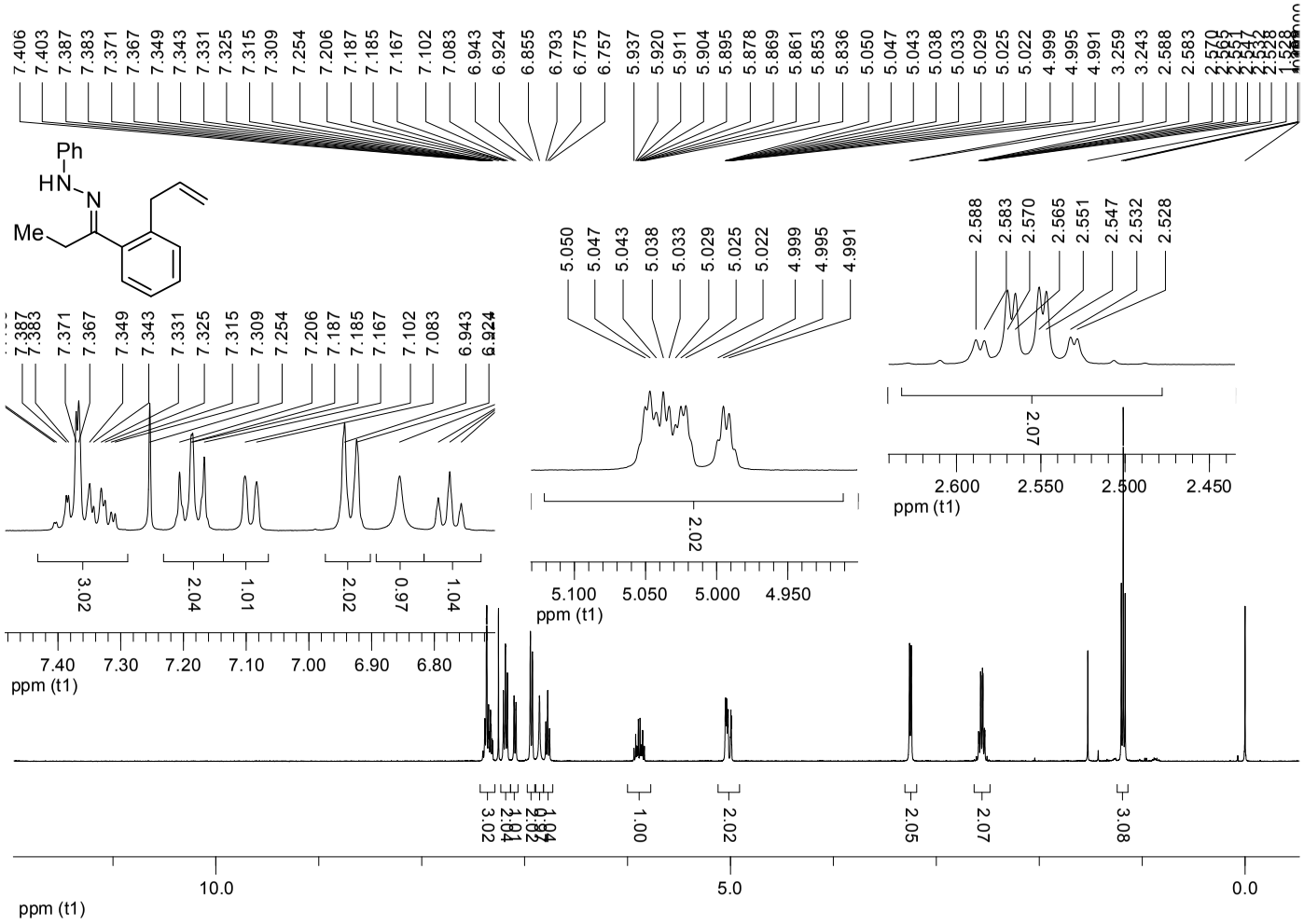
^{1}H NMR spectrum of **3n** (400 MHz, $CDCl_3$)



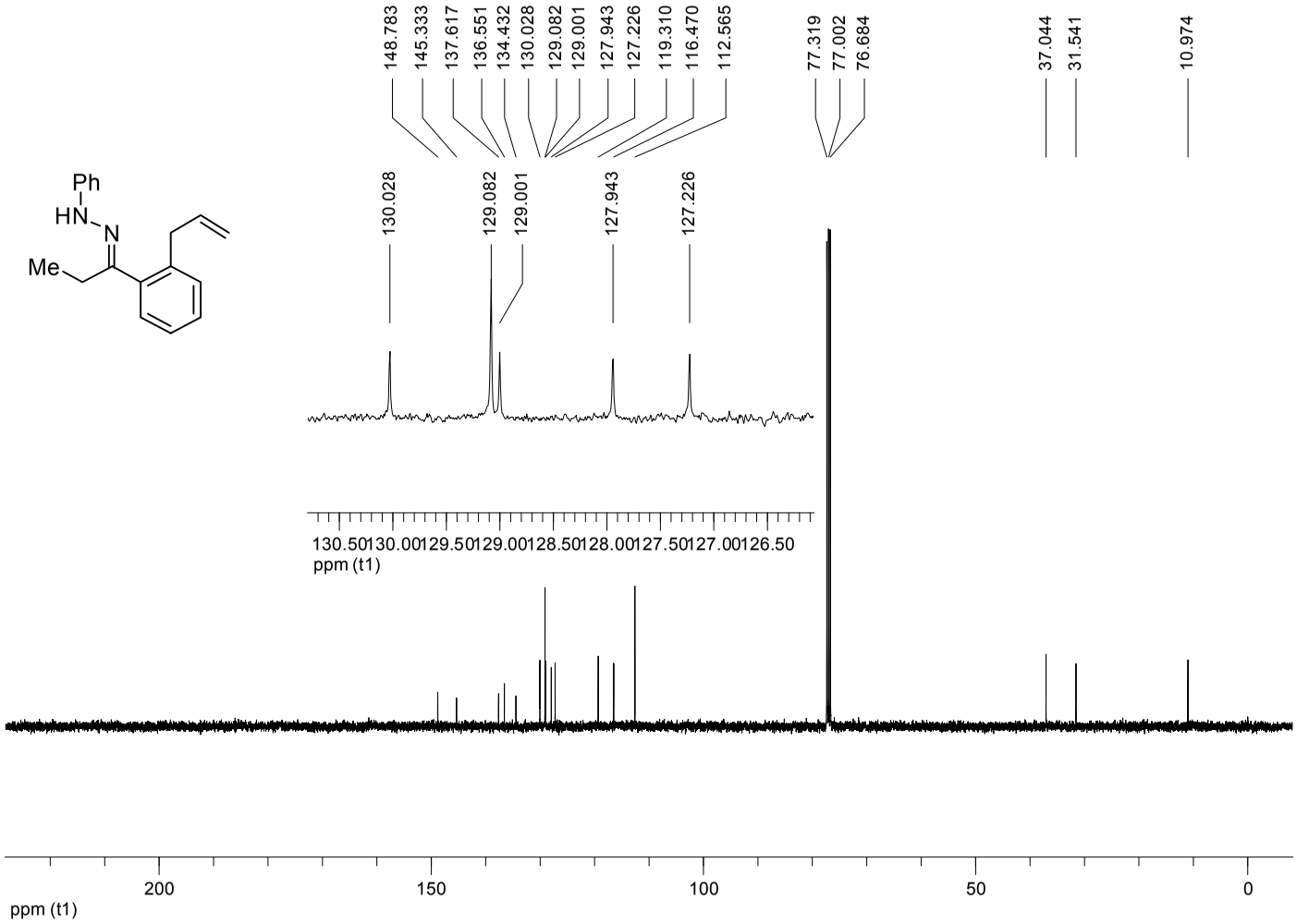
^{13}C NMR spectrum of **3n** (100 MHz, $CDCl_3$)



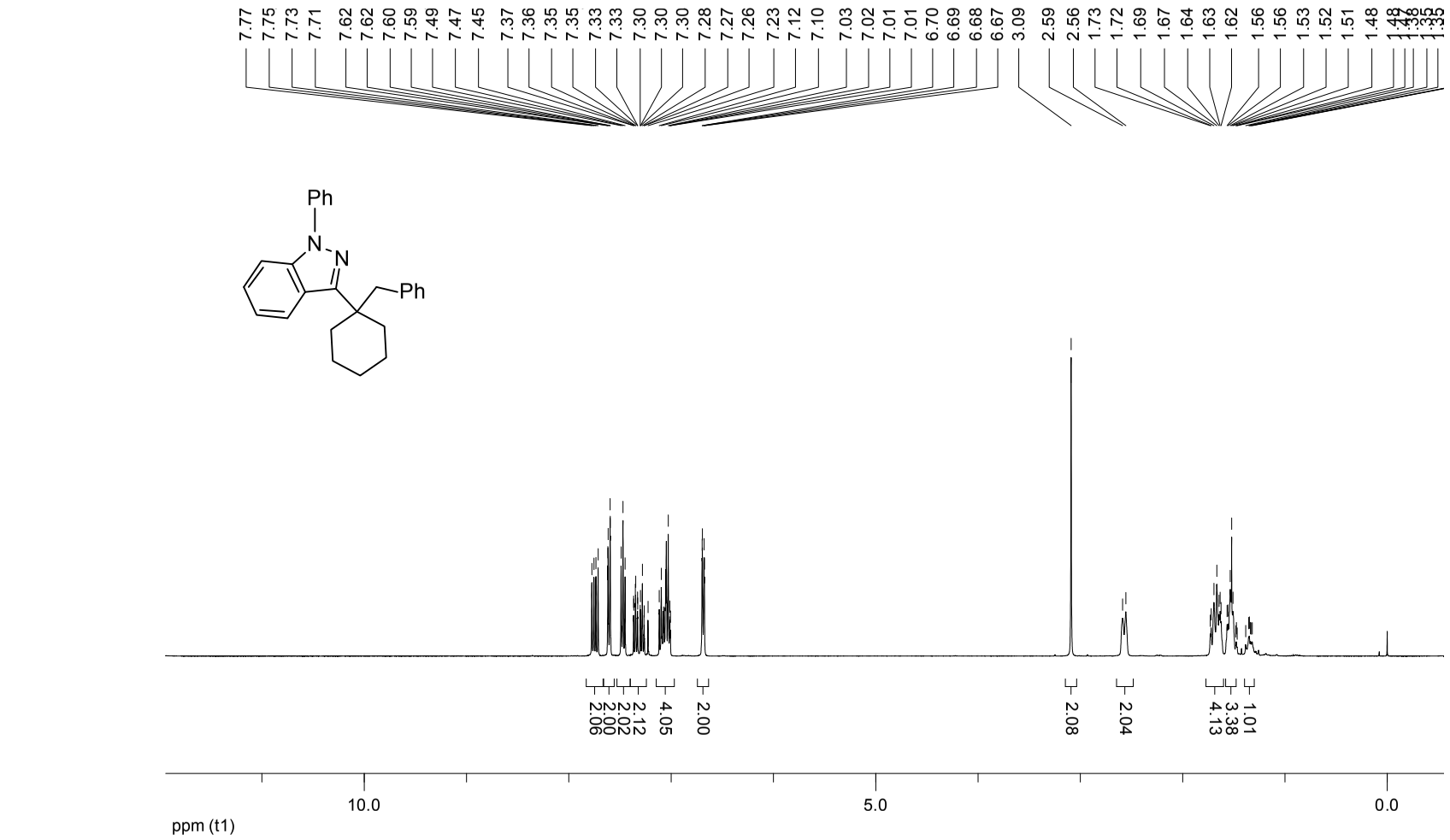
^{1}H NMR spectrum of **3o** (400 MHz, $CDCl_3$)



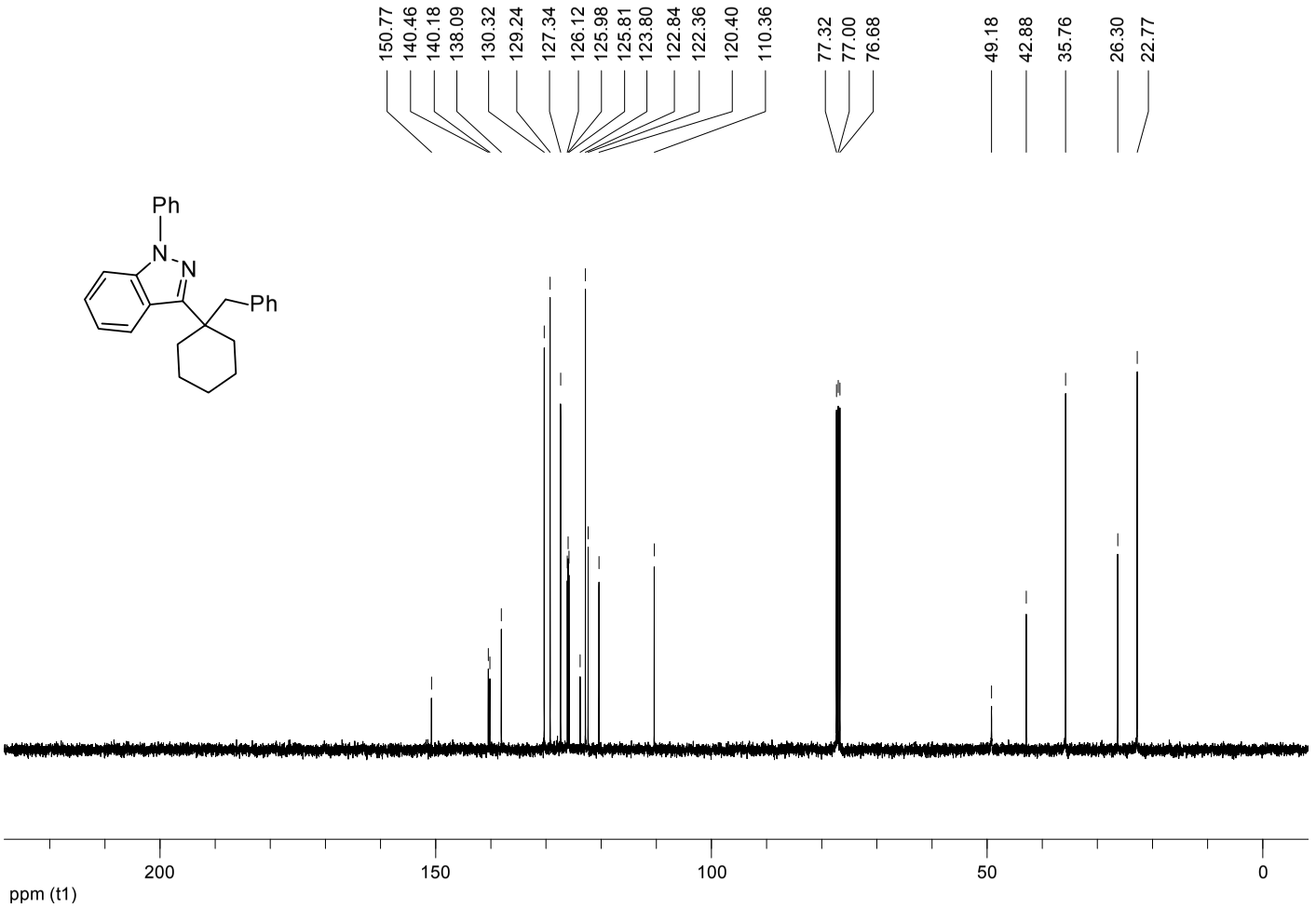
^{13}C NMR spectrum of **3o** (100 MHz, $CDCl_3$)



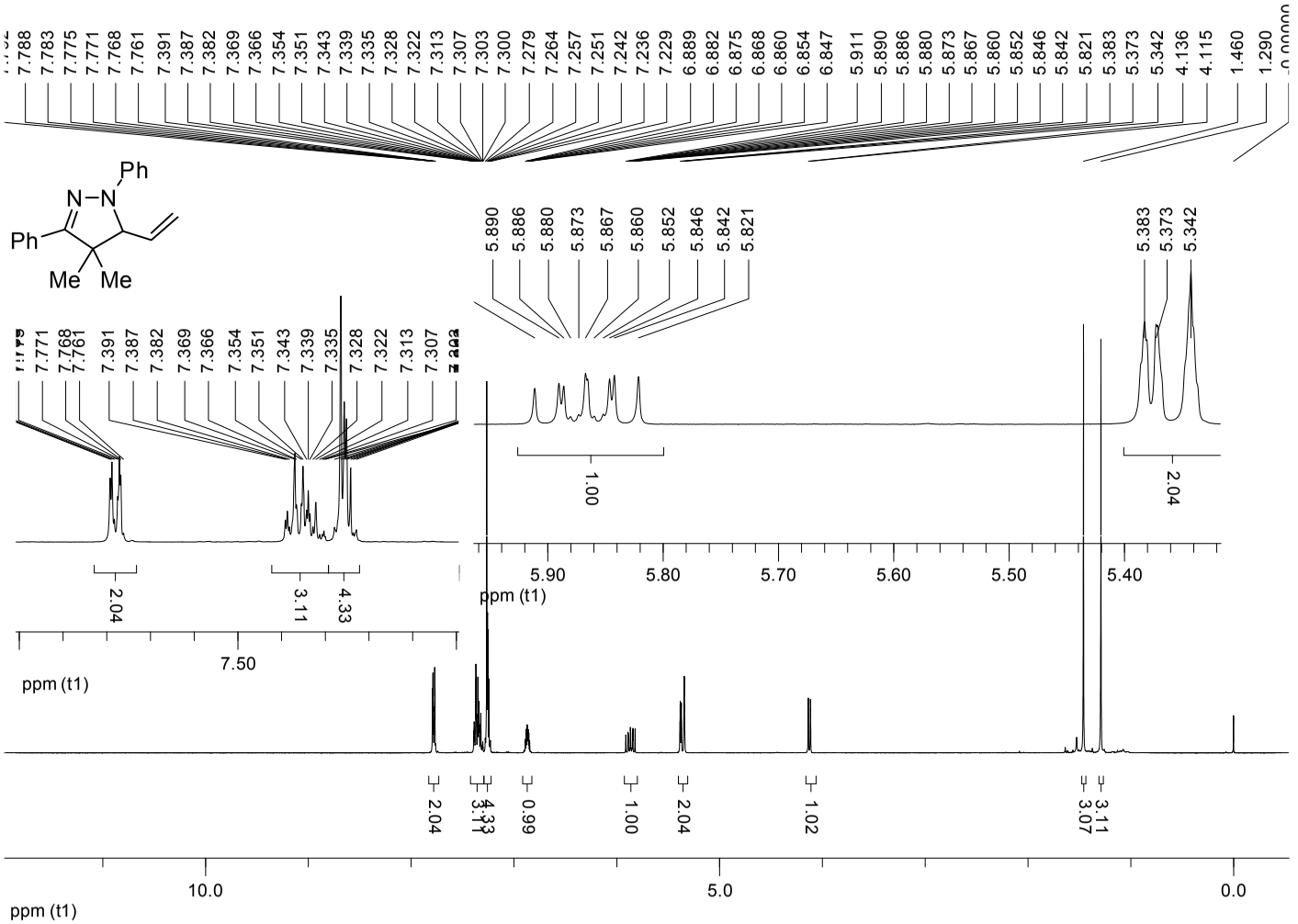
^{1}H NMR spectrum of **4a** (400 MHz, $CDCl_3$)



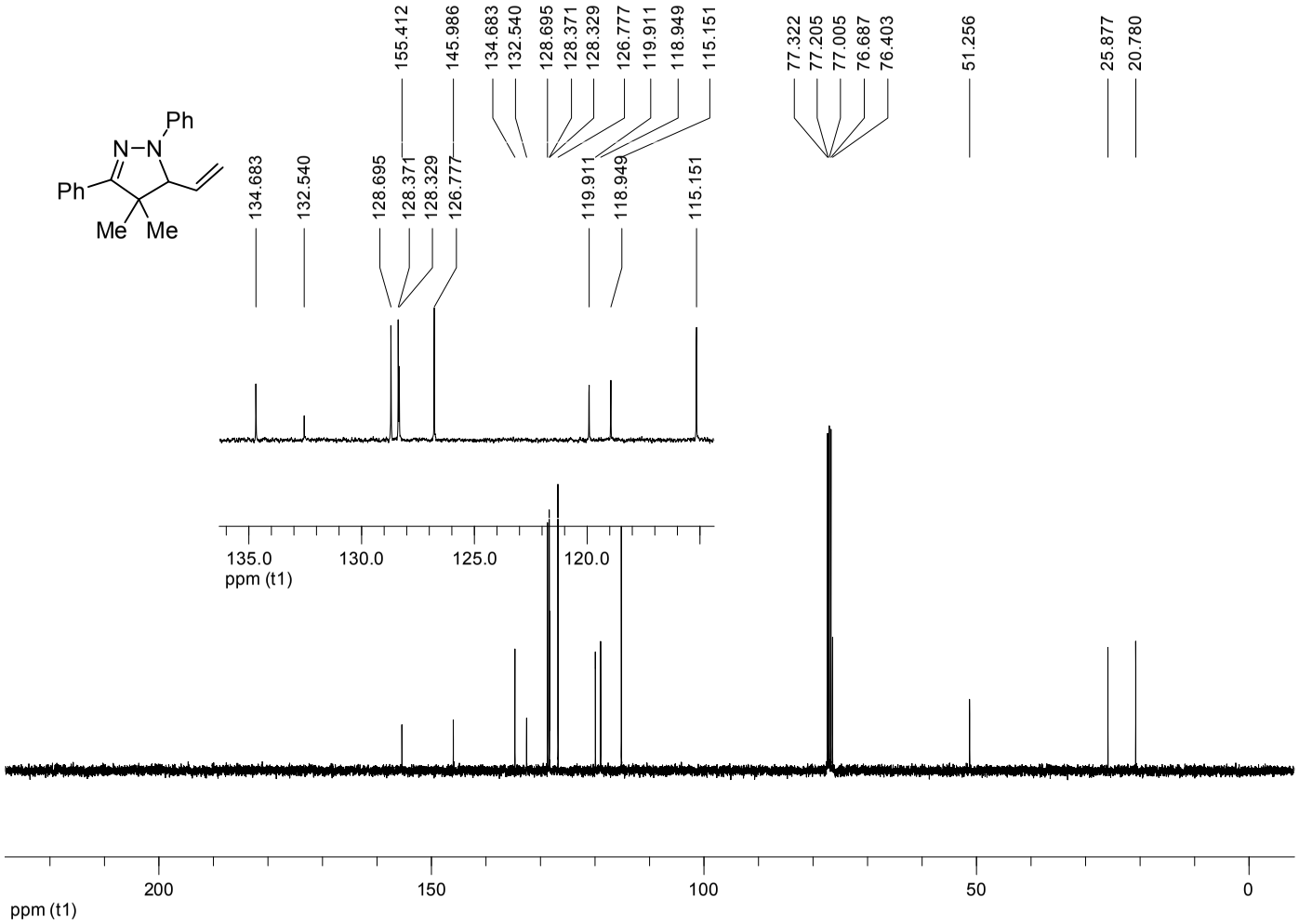
^{13}C NMR spectrum of **4a** (100 MHz, $CDCl_3$)



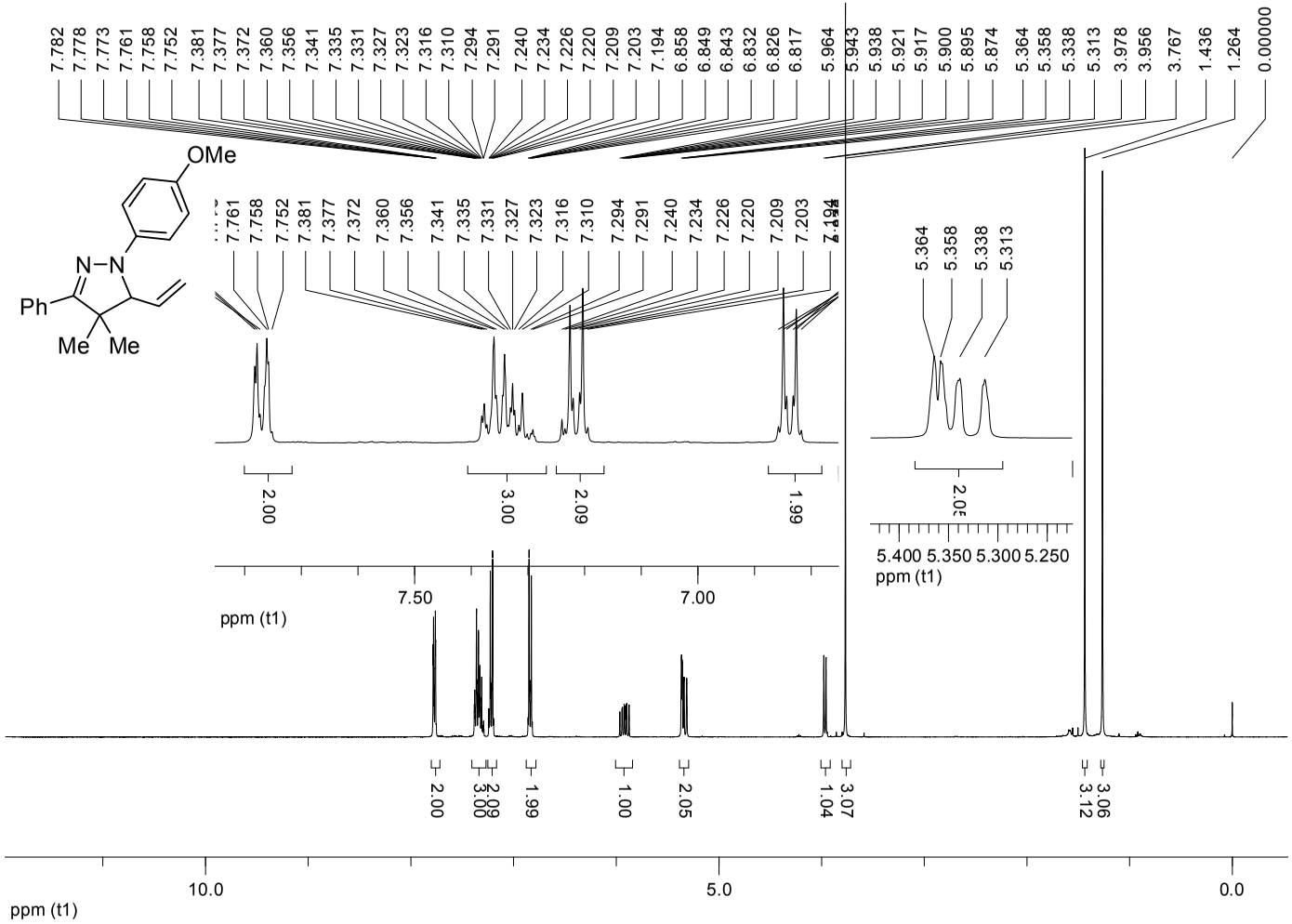
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$)



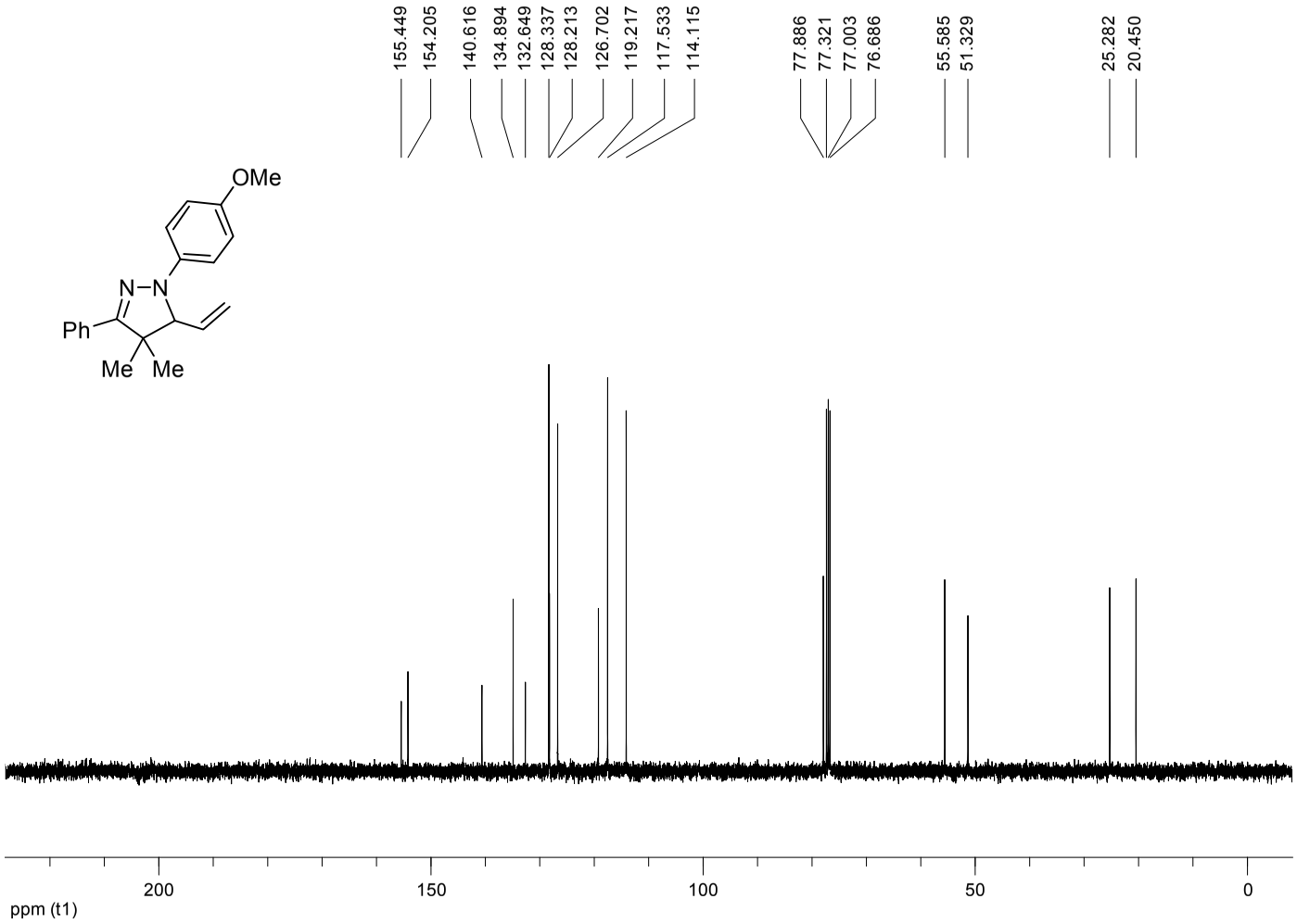
^{13}C NMR spectrum of **5b** (100 MHz, $CDCl_3$)



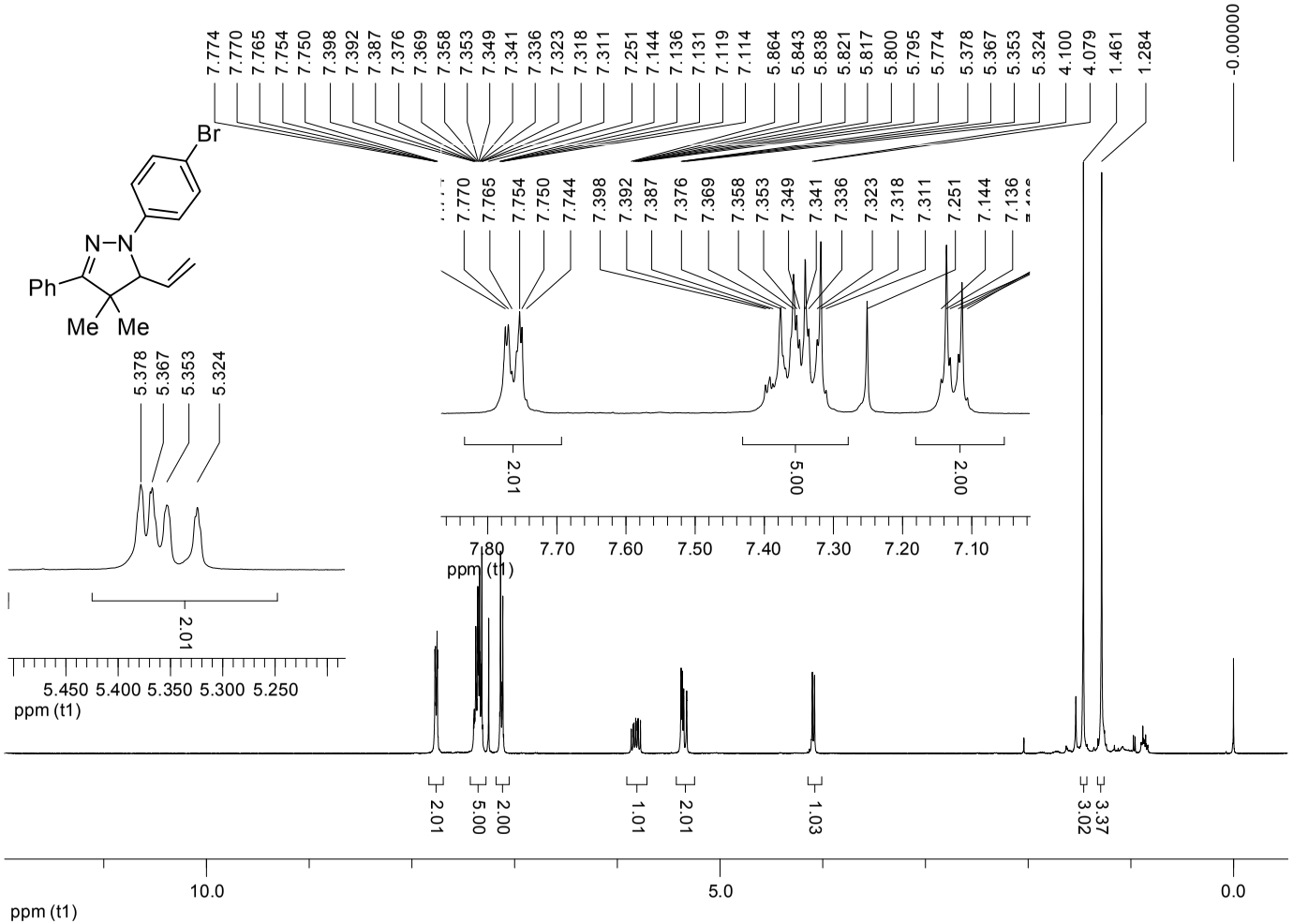
^{1}H NMR spectrum of **5c** (400 MHz, $CDCl_3$)



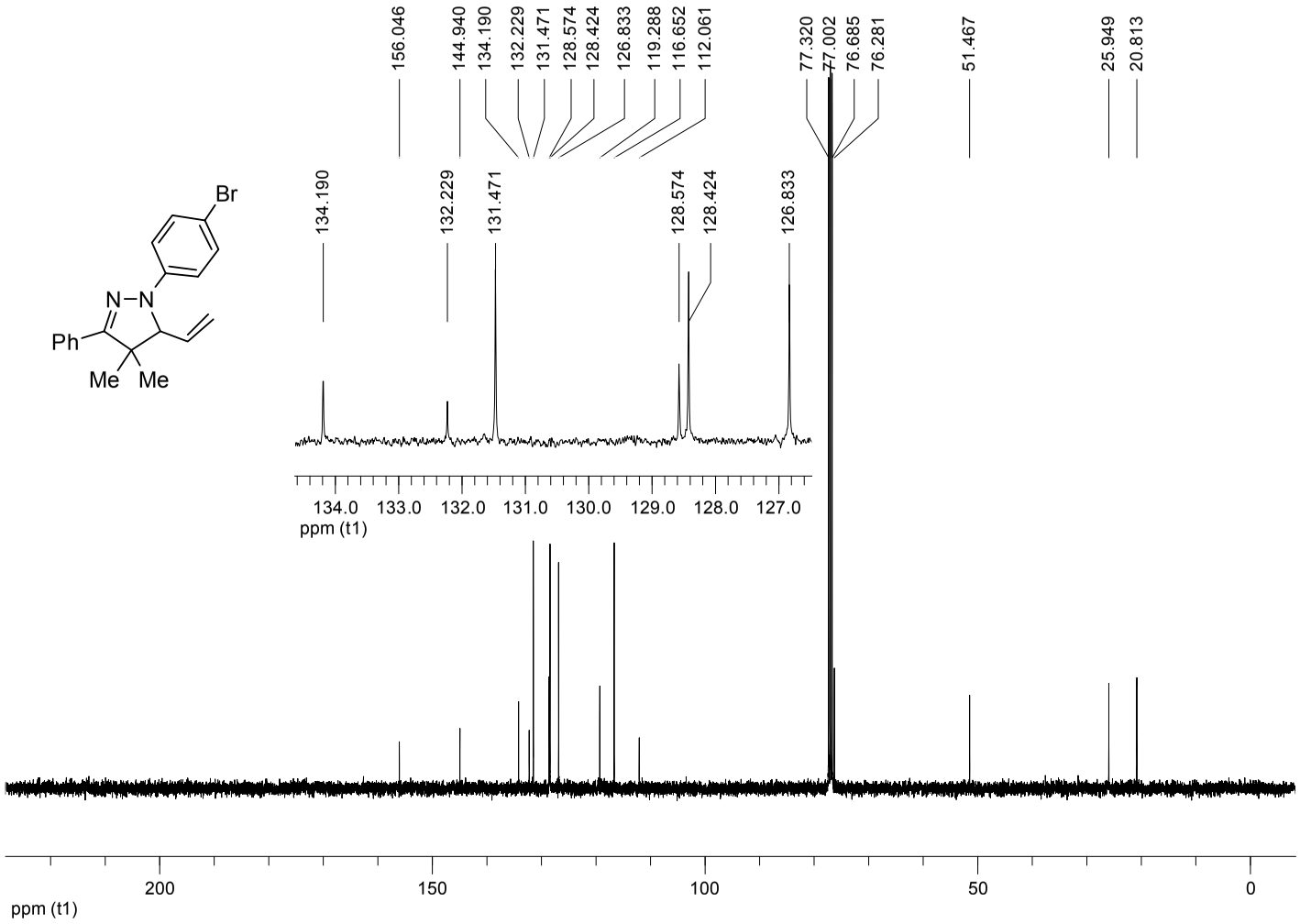
^{13}C NMR spectrum of **5c** (100 MHz, $CDCl_3$)



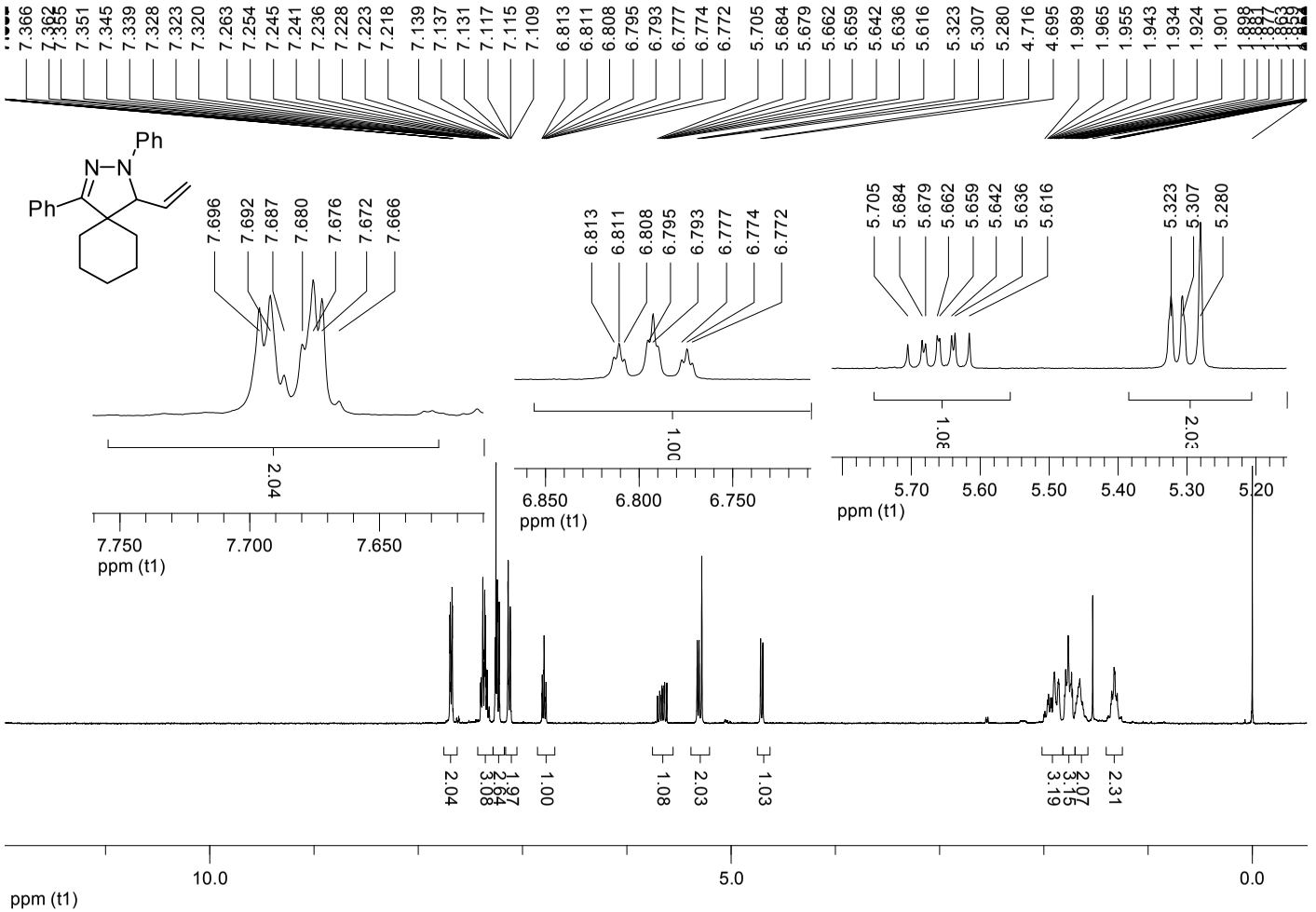
^{1}H NMR spectrum of **5d** (400 MHz, $CDCl_3$)



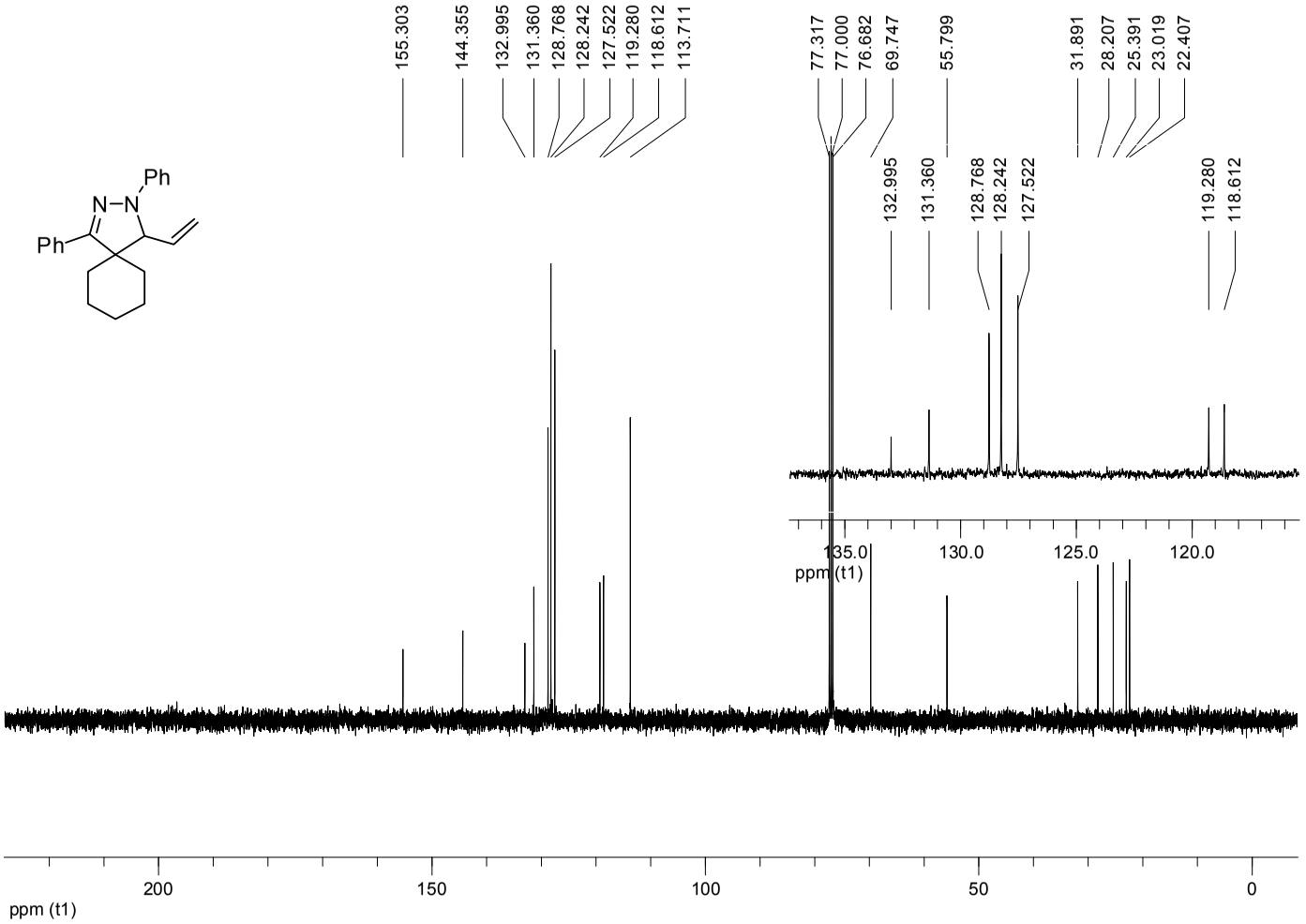
^{13}C NMR spectrum of **5d** (100 MHz, $CDCl_3$)



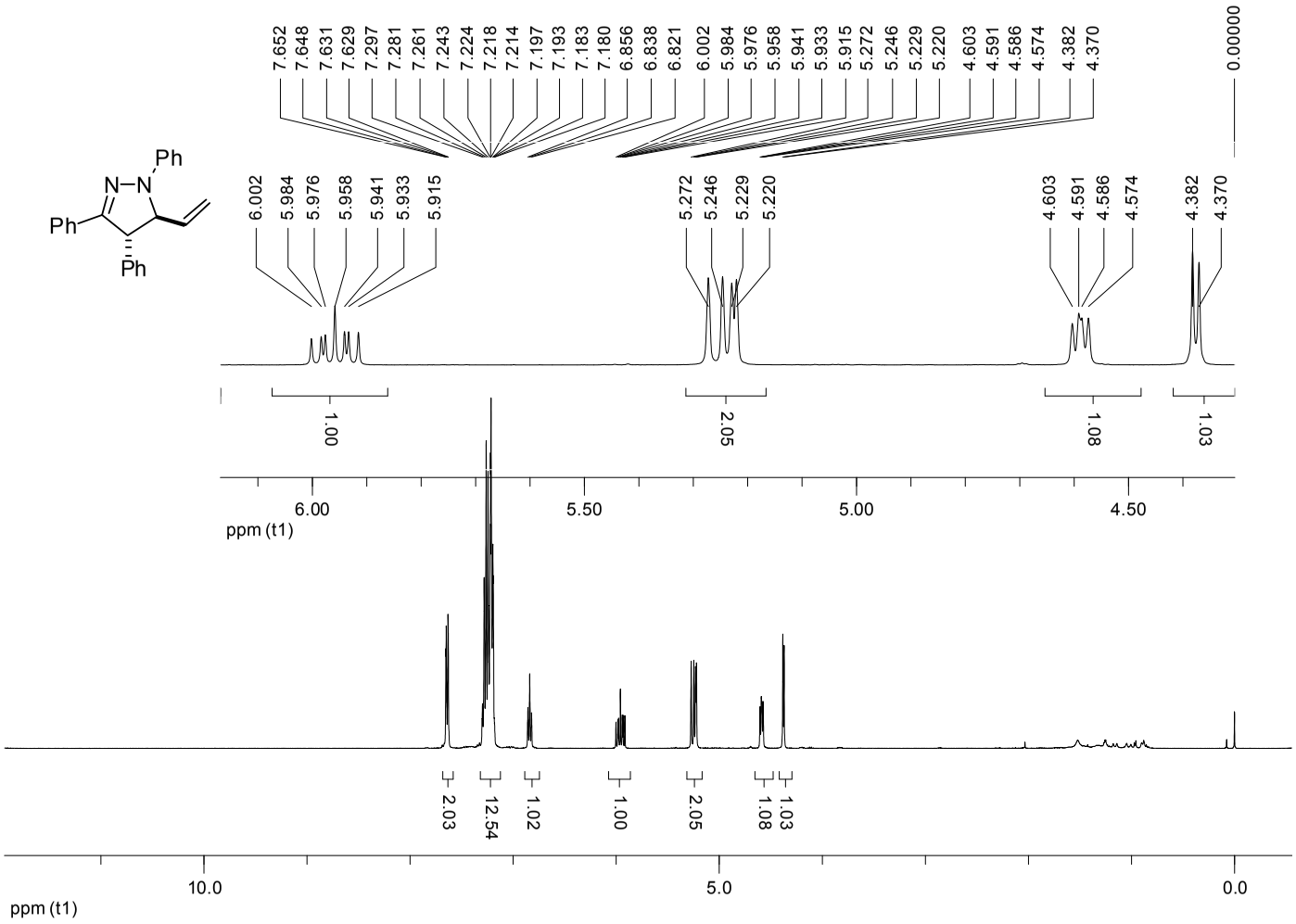
^{1}H NMR spectrum of **5e** (400 MHz, $CDCl_3$)



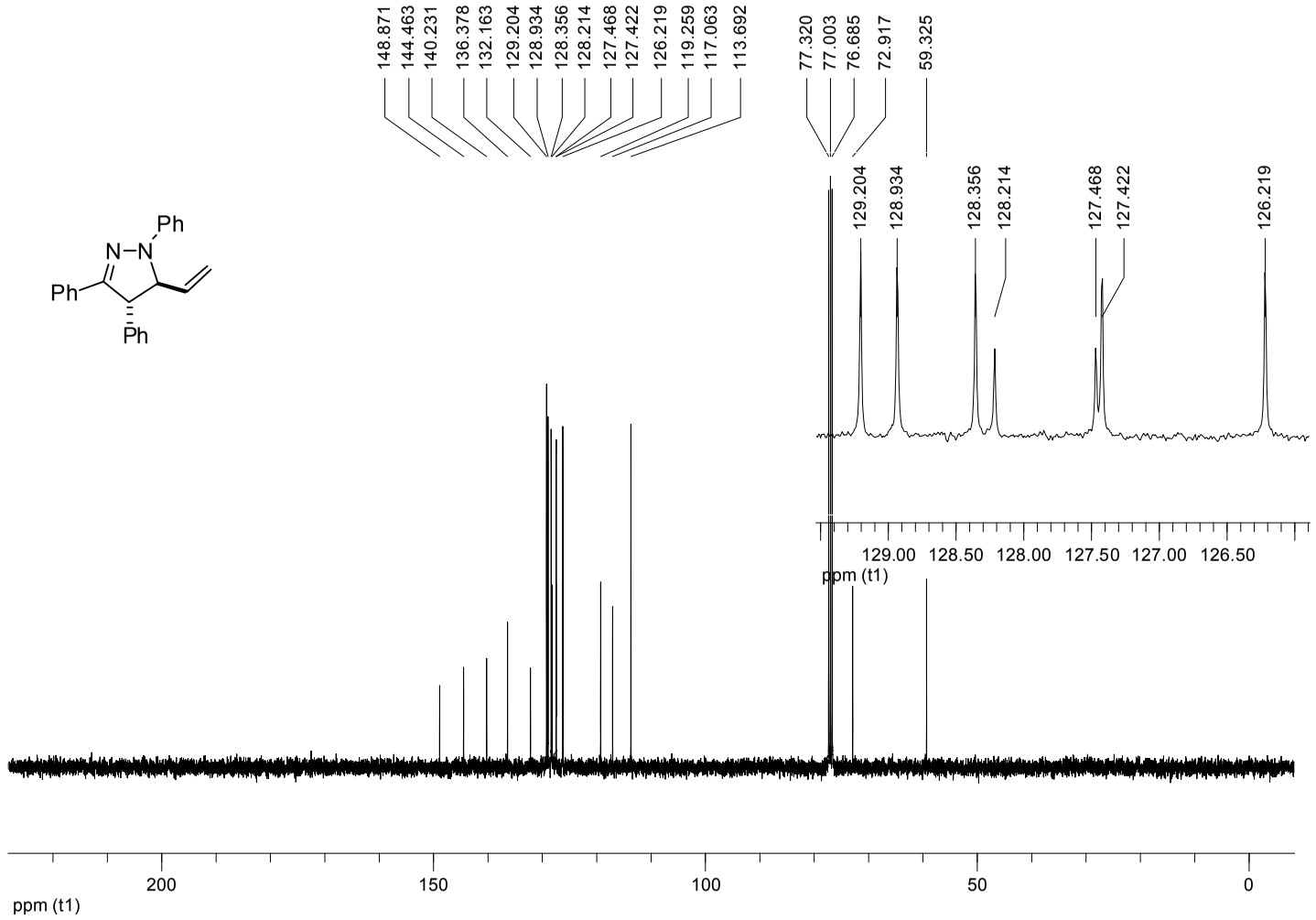
^{13}C NMR spectrum of **5e** (100 MHz, $CDCl_3$)



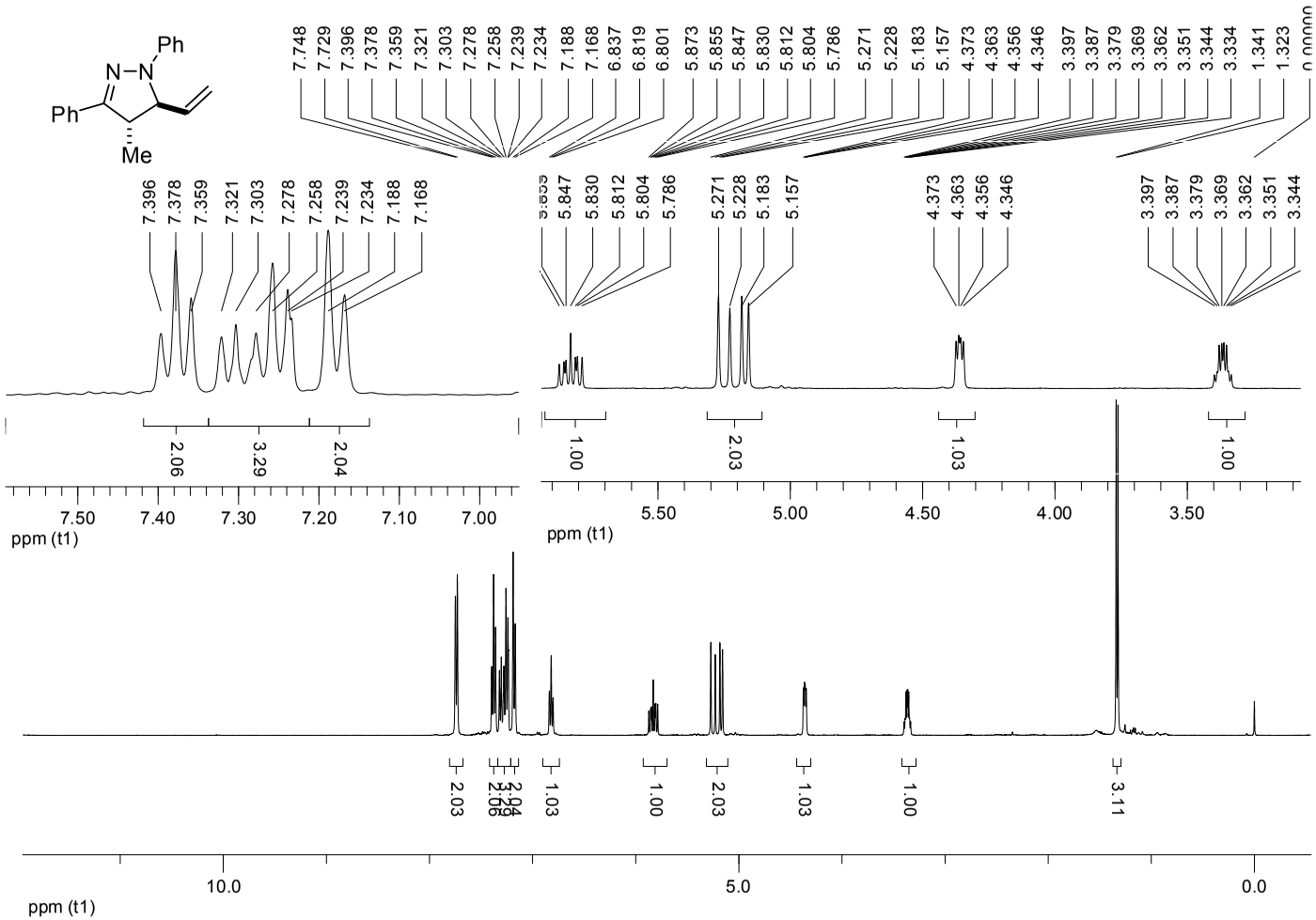
^{1}H NMR spectrum of **5f** (400 MHz, $CDCl_3$)



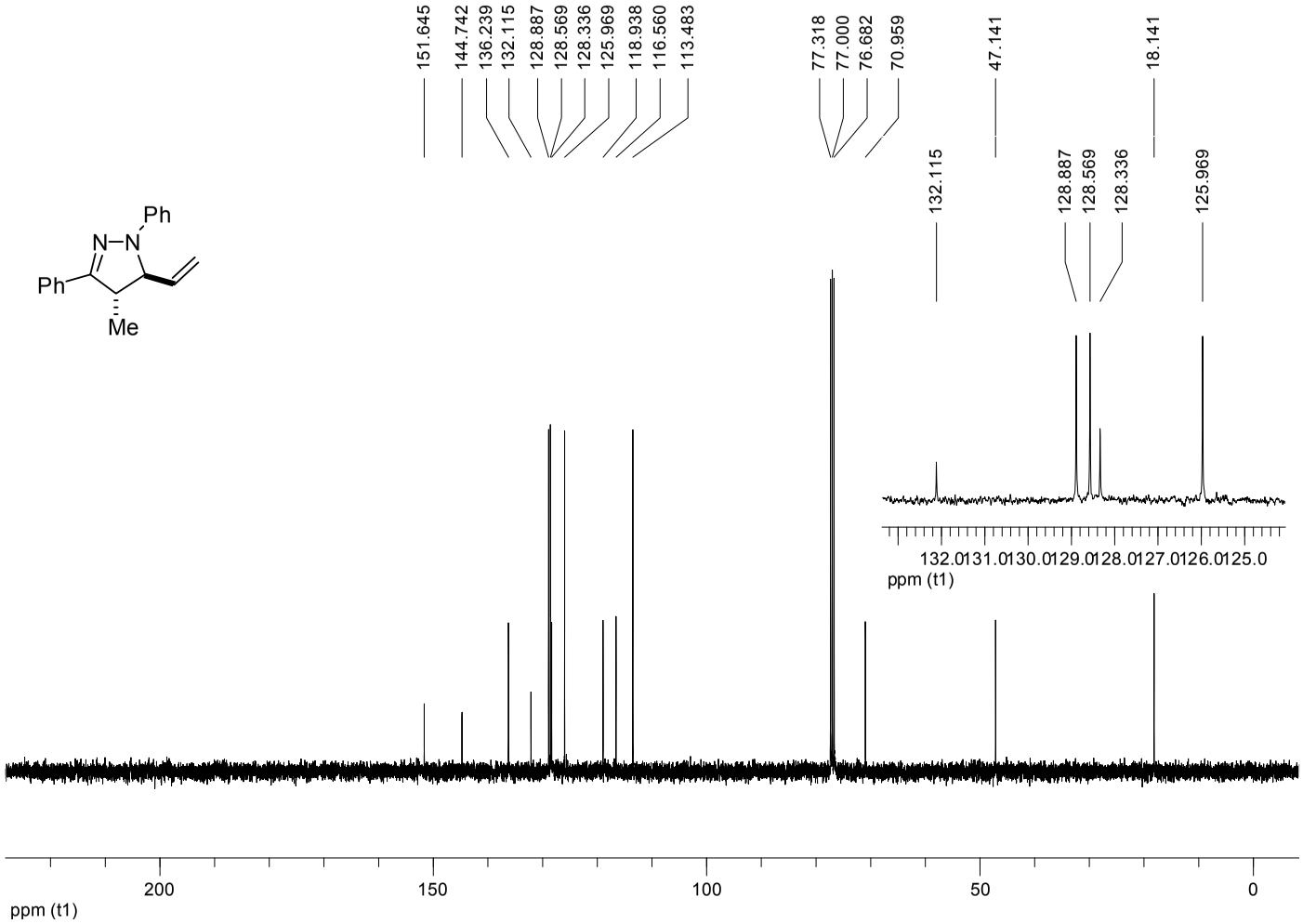
^{13}C NMR spectrum of **5f** (100 MHz, $CDCl_3$)



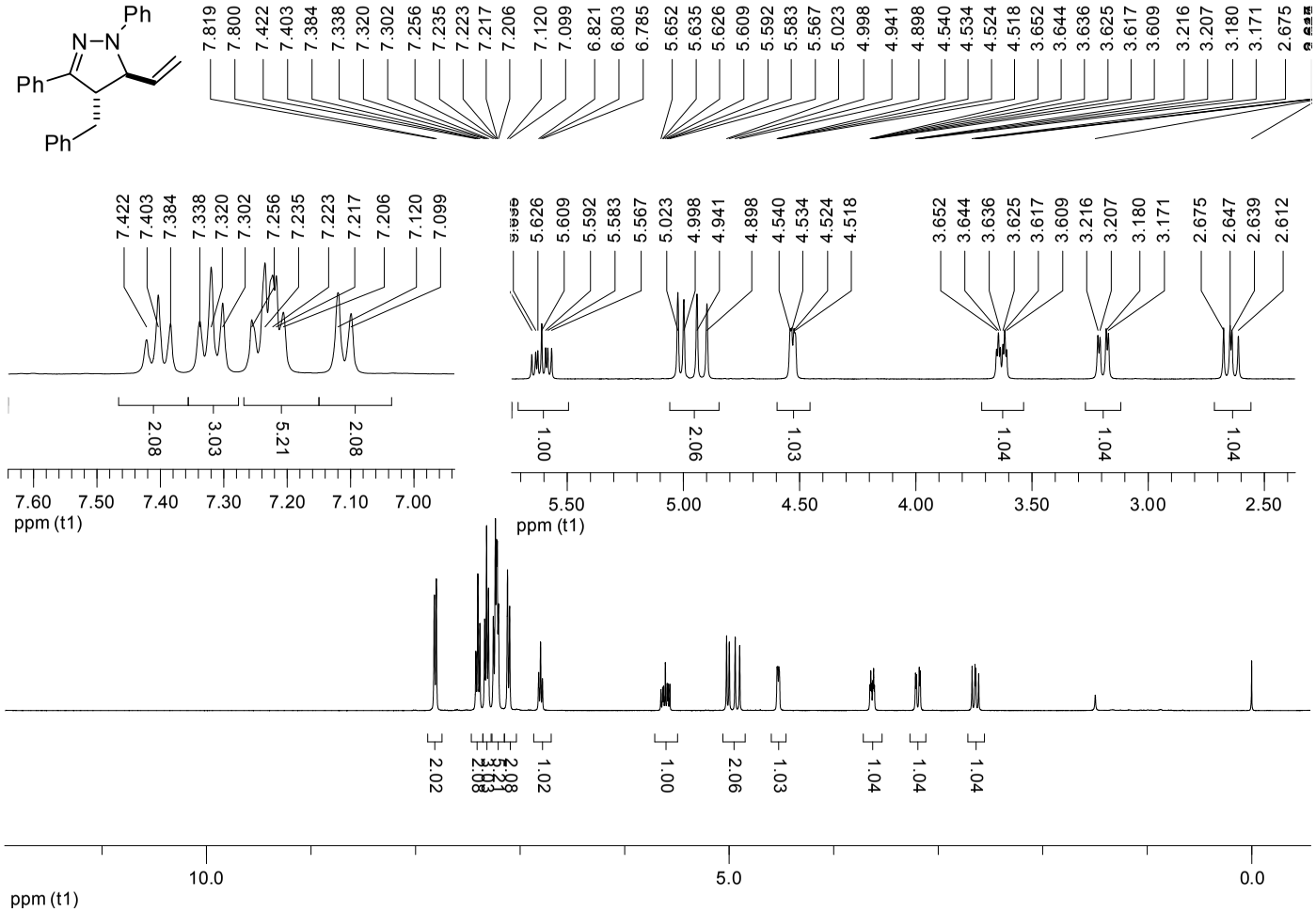
^{1}H NMR spectrum of **5g** (400 MHz, $CDCl_3$)



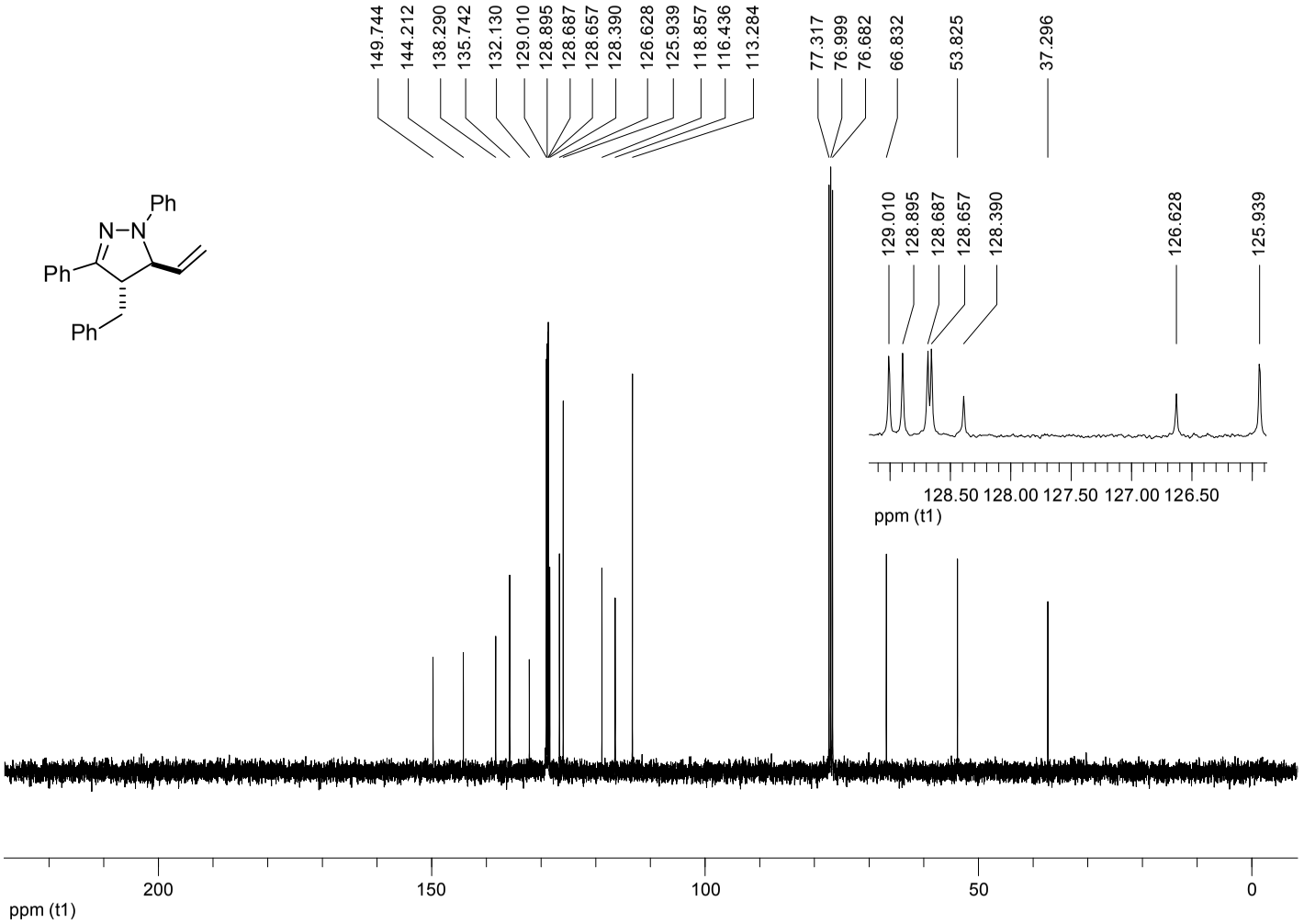
^{13}C NMR spectrum of **5g** (100 MHz, $CDCl_3$)



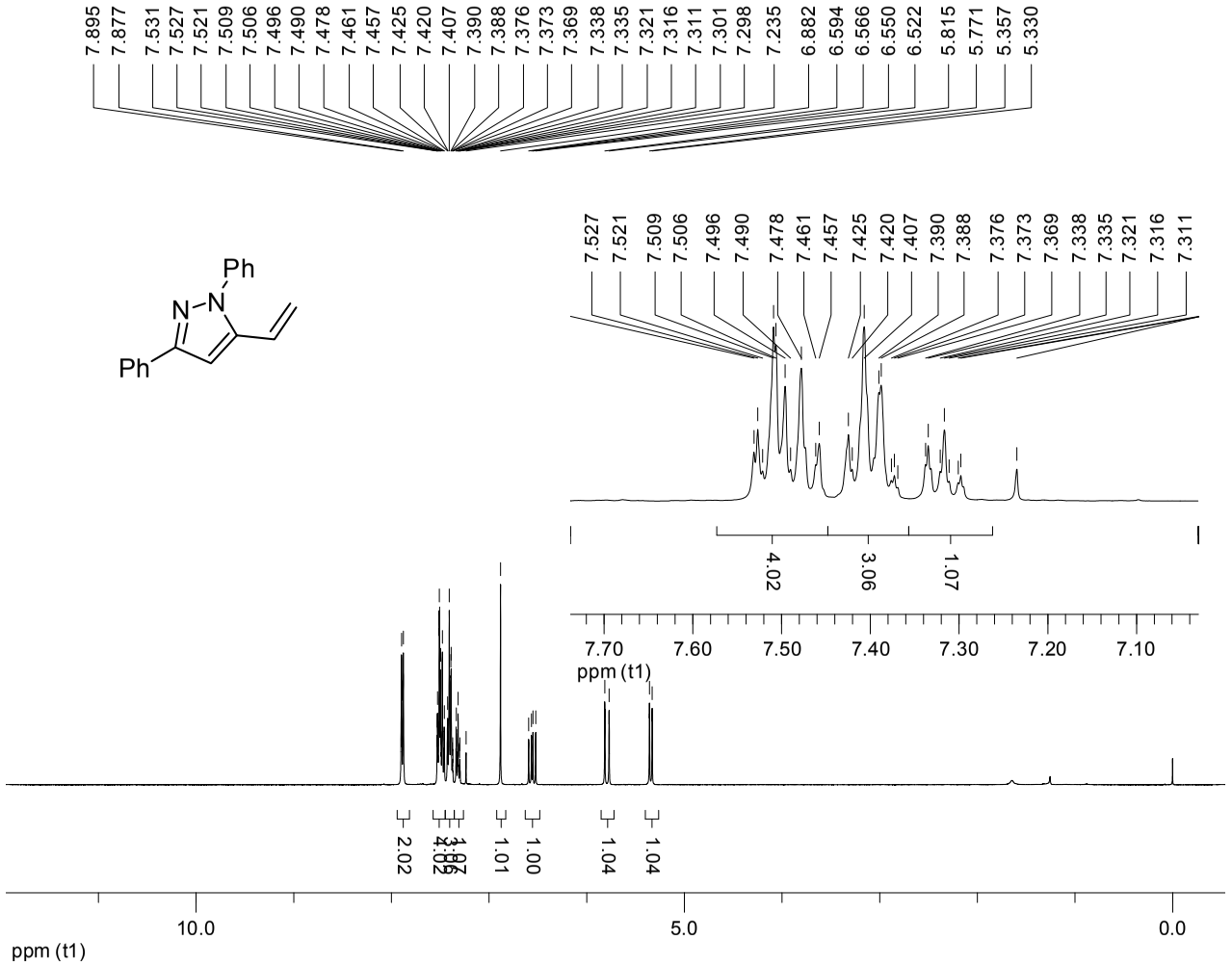
^{1}H NMR spectrum of **5h** (400 MHz, $CDCl_3$)



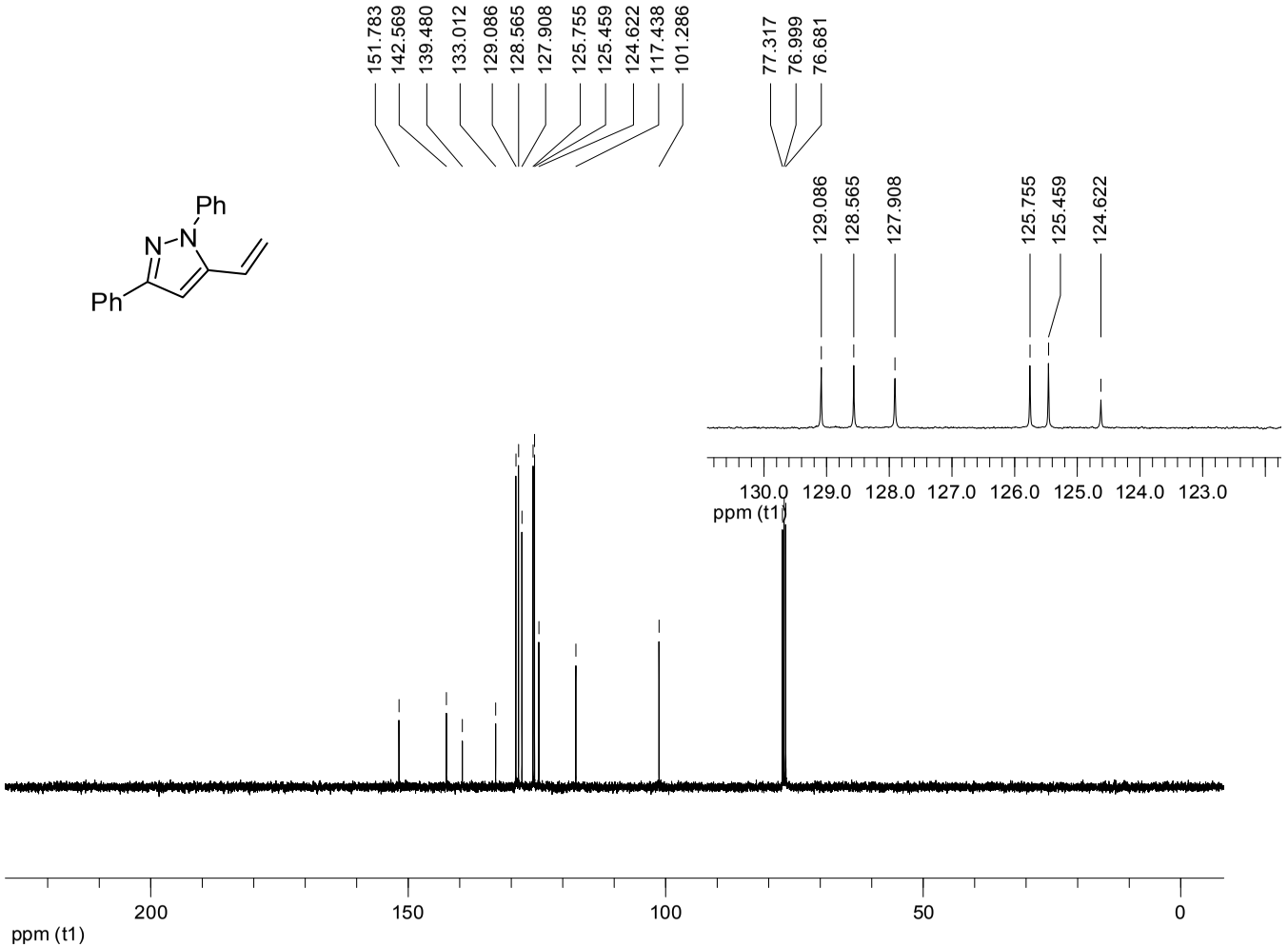
^{13}C NMR spectrum of **5h** (100 MHz, $CDCl_3$)



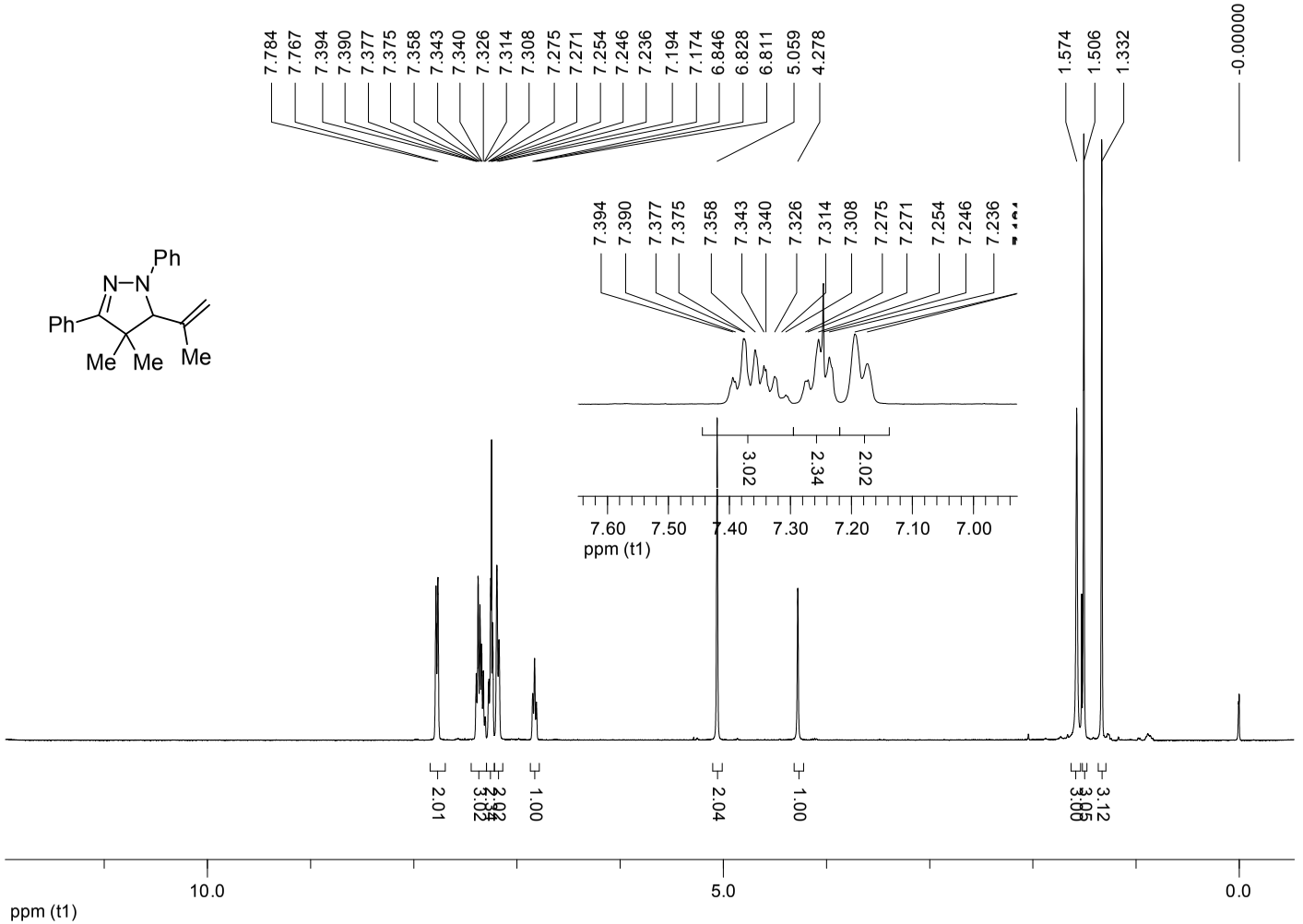
^{1}H NMR spectrum of **5i** (400 MHz, $CDCl_3$)



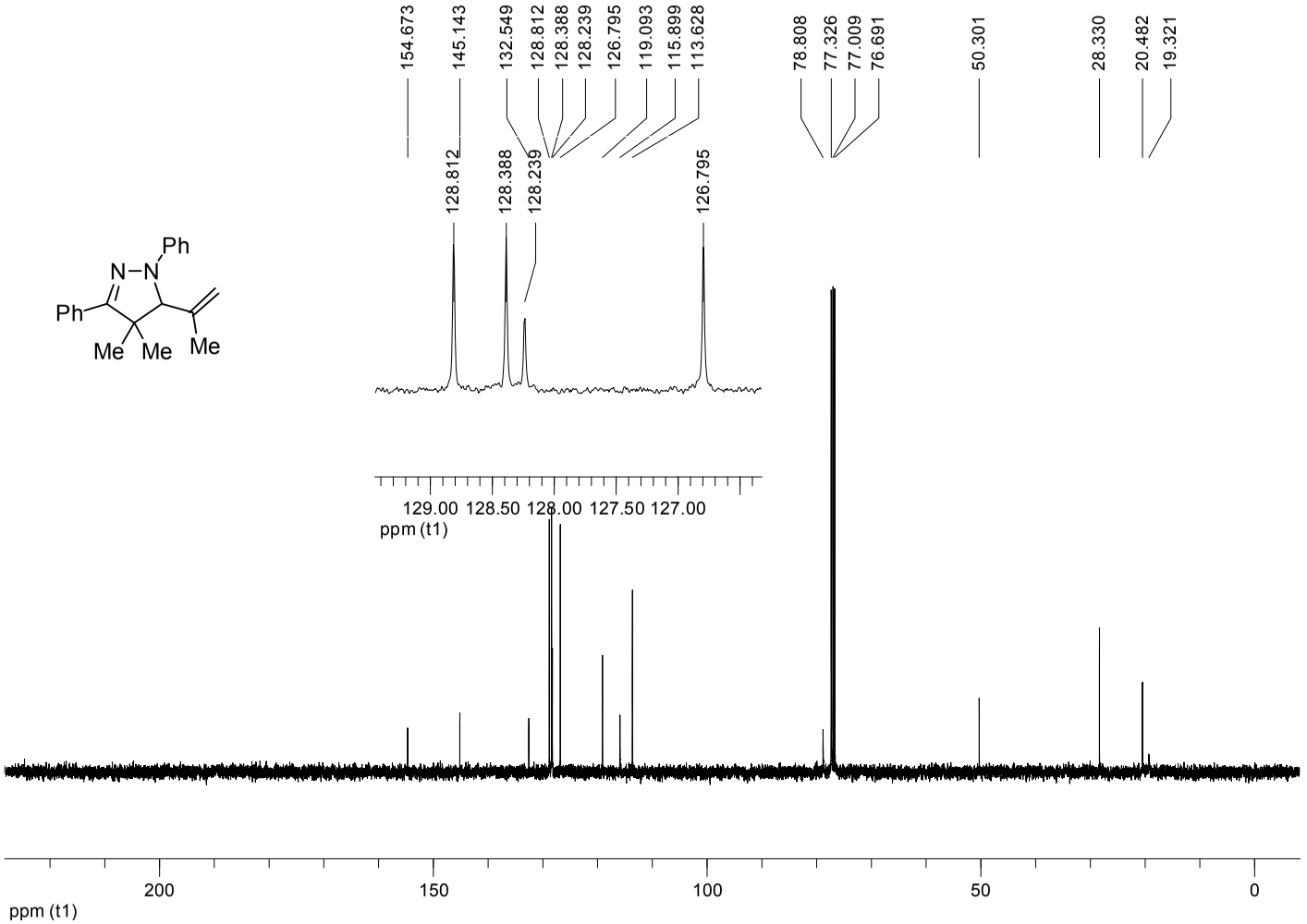
^{13}C NMR spectrum of **5i** (100 MHz, $CDCl_3$)



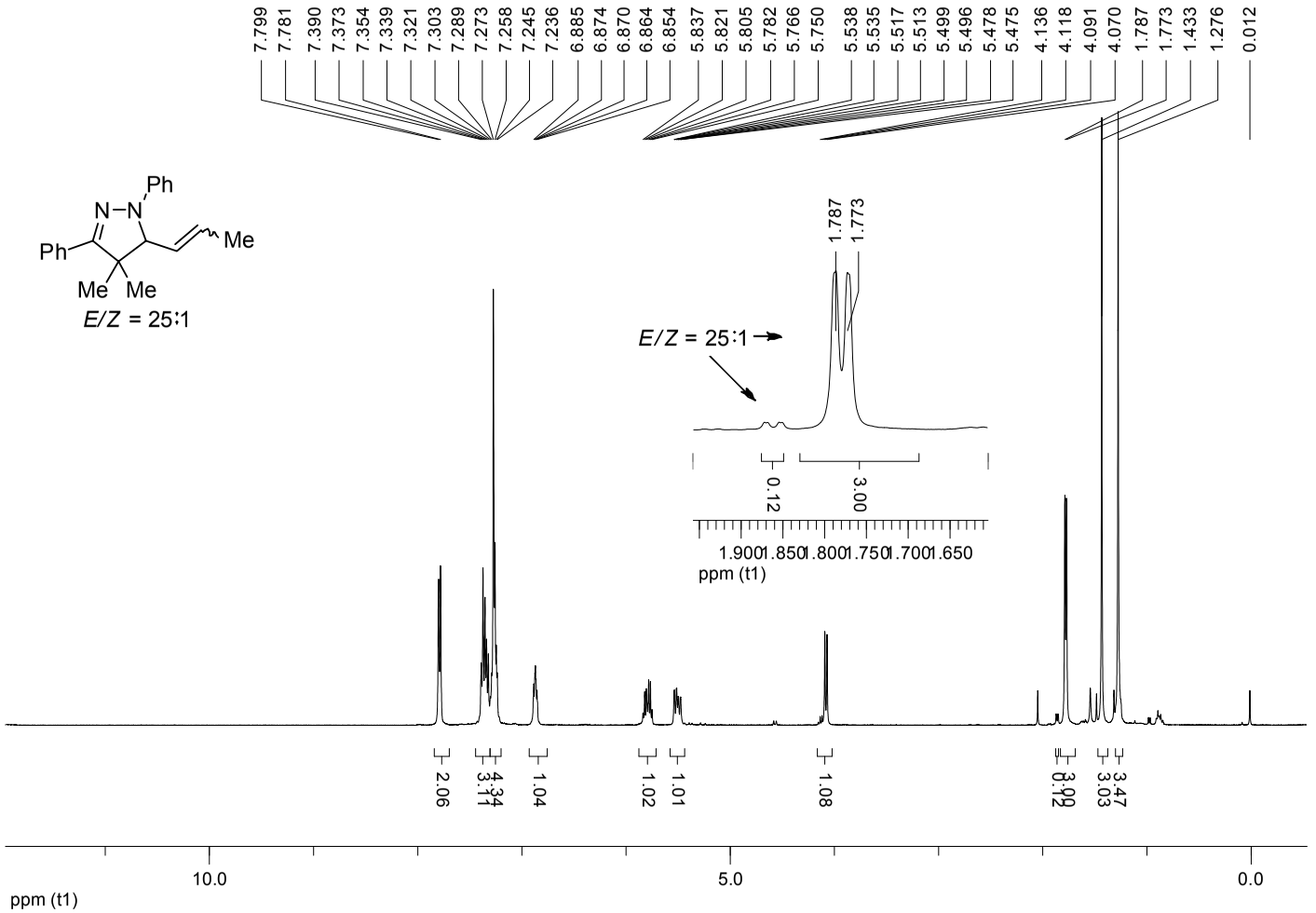
^{1}H NMR spectrum of **5j** (400 MHz, $CDCl_3$)



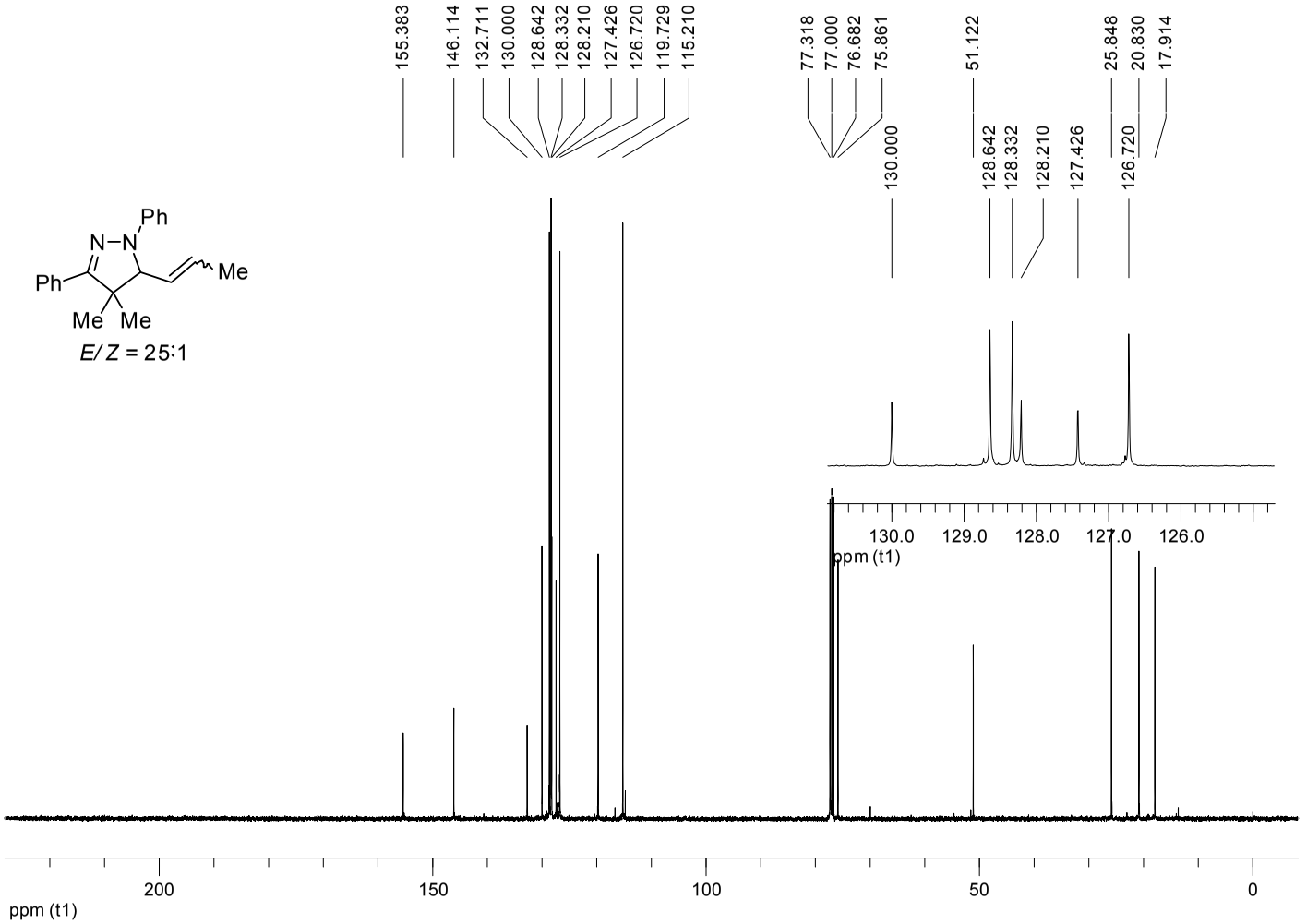
^{13}C NMR spectrum of **5j** (100 MHz, $CDCl_3$)



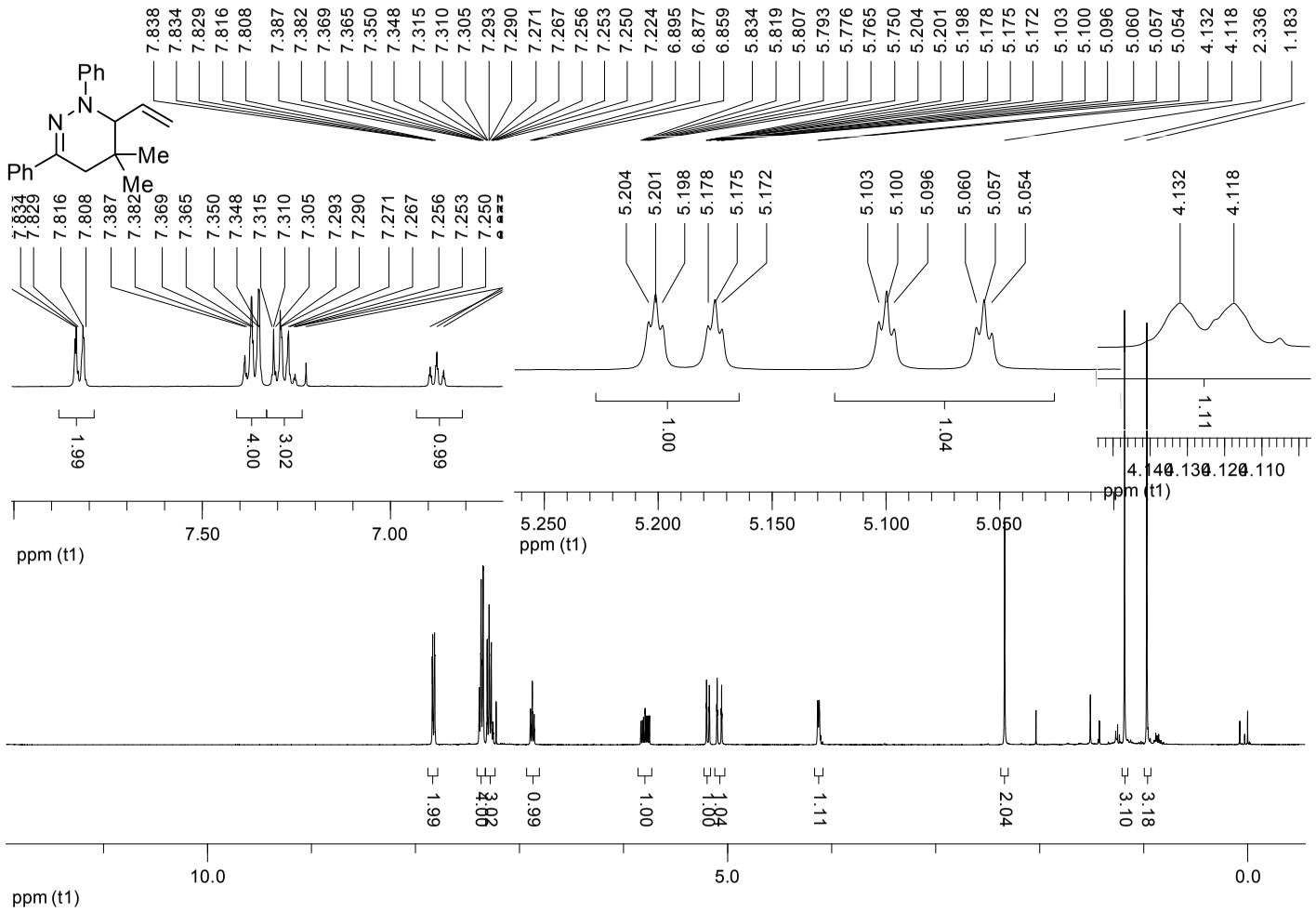
^{1}H NMR spectrum of **5k** (400 MHz, $CDCl_3$)



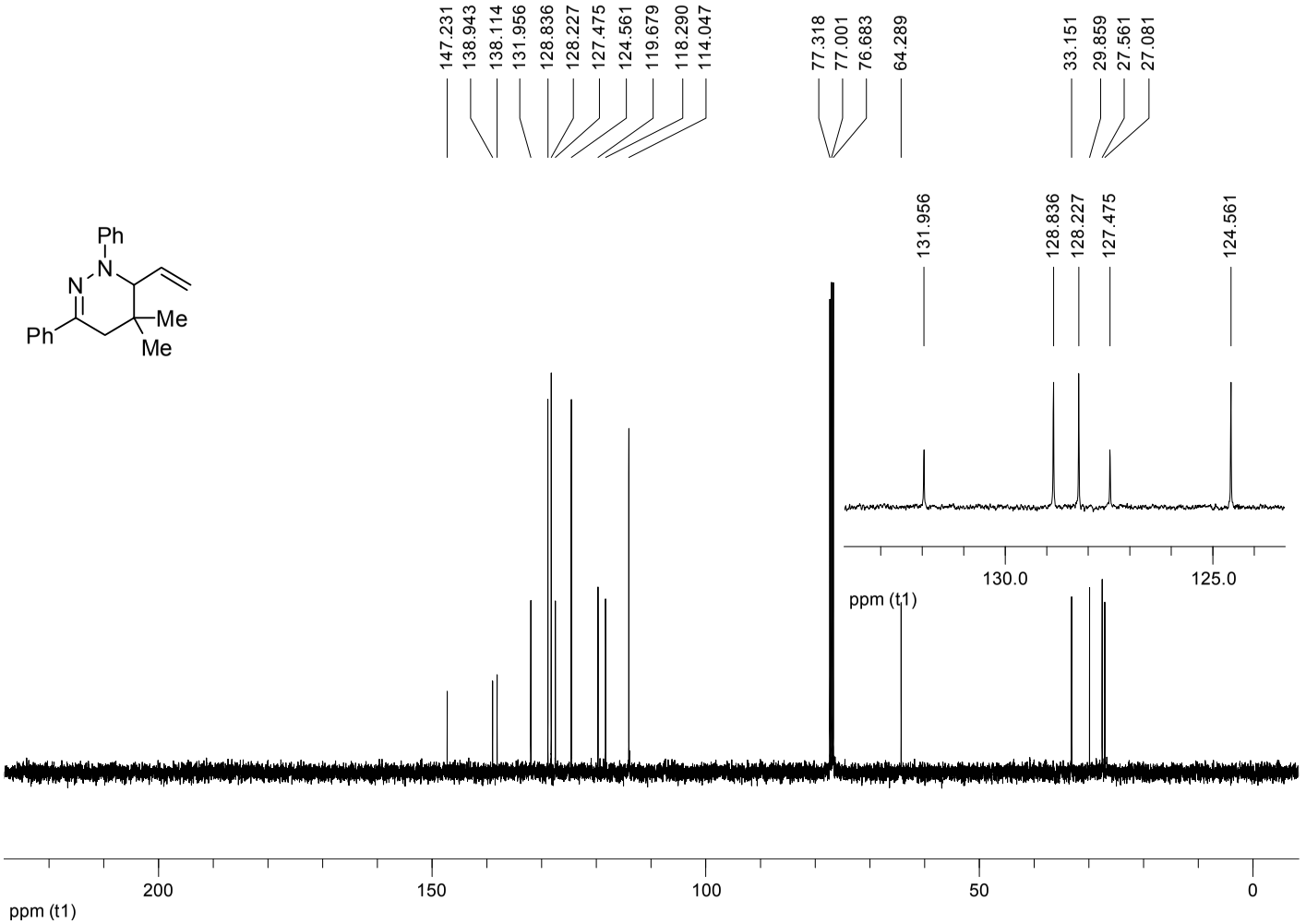
^{13}C NMR spectrum of **5k** (100 MHz, $CDCl_3$)



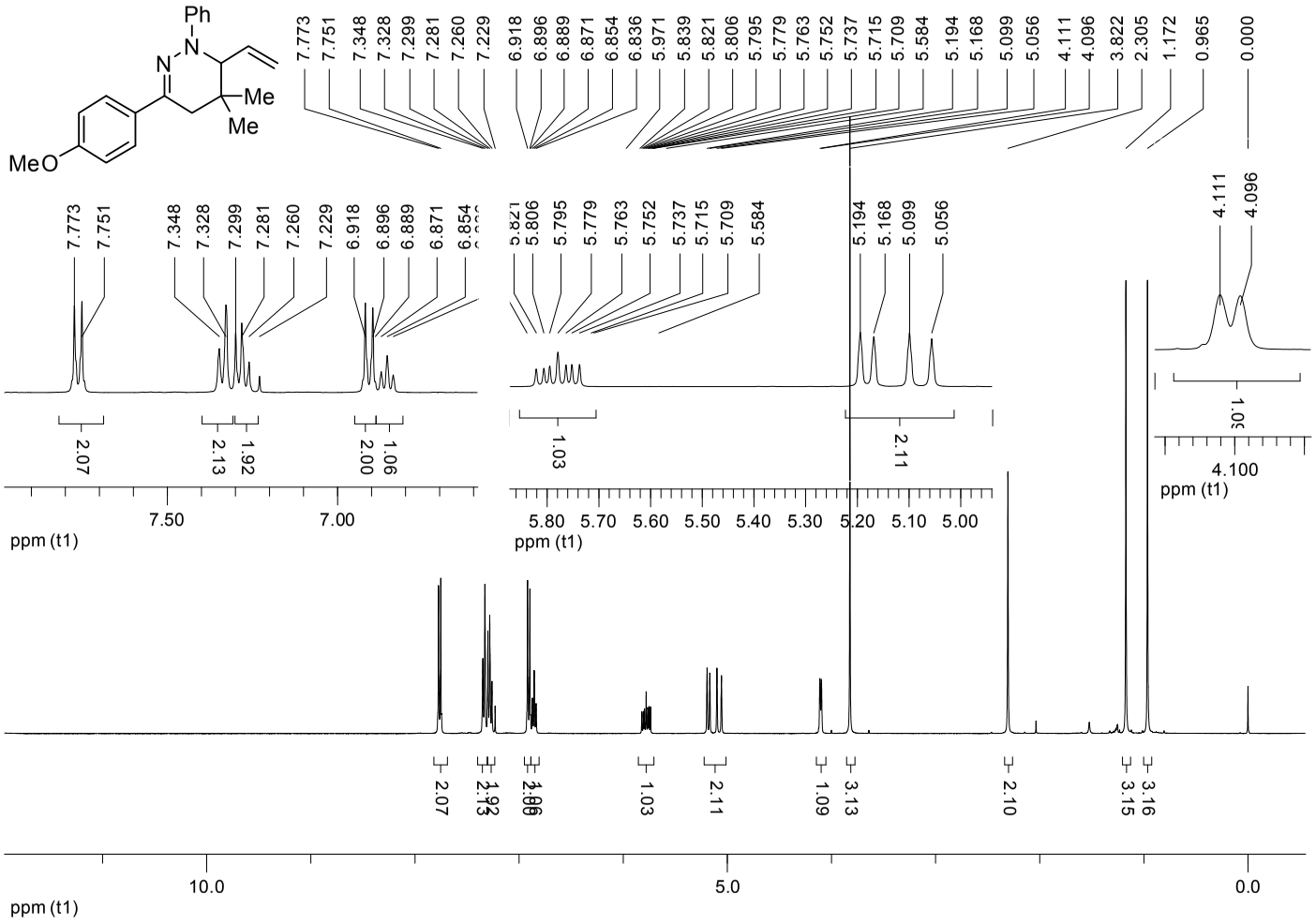
^{1}H NMR spectrum of **5l** (400 MHz, $CDCl_3$)



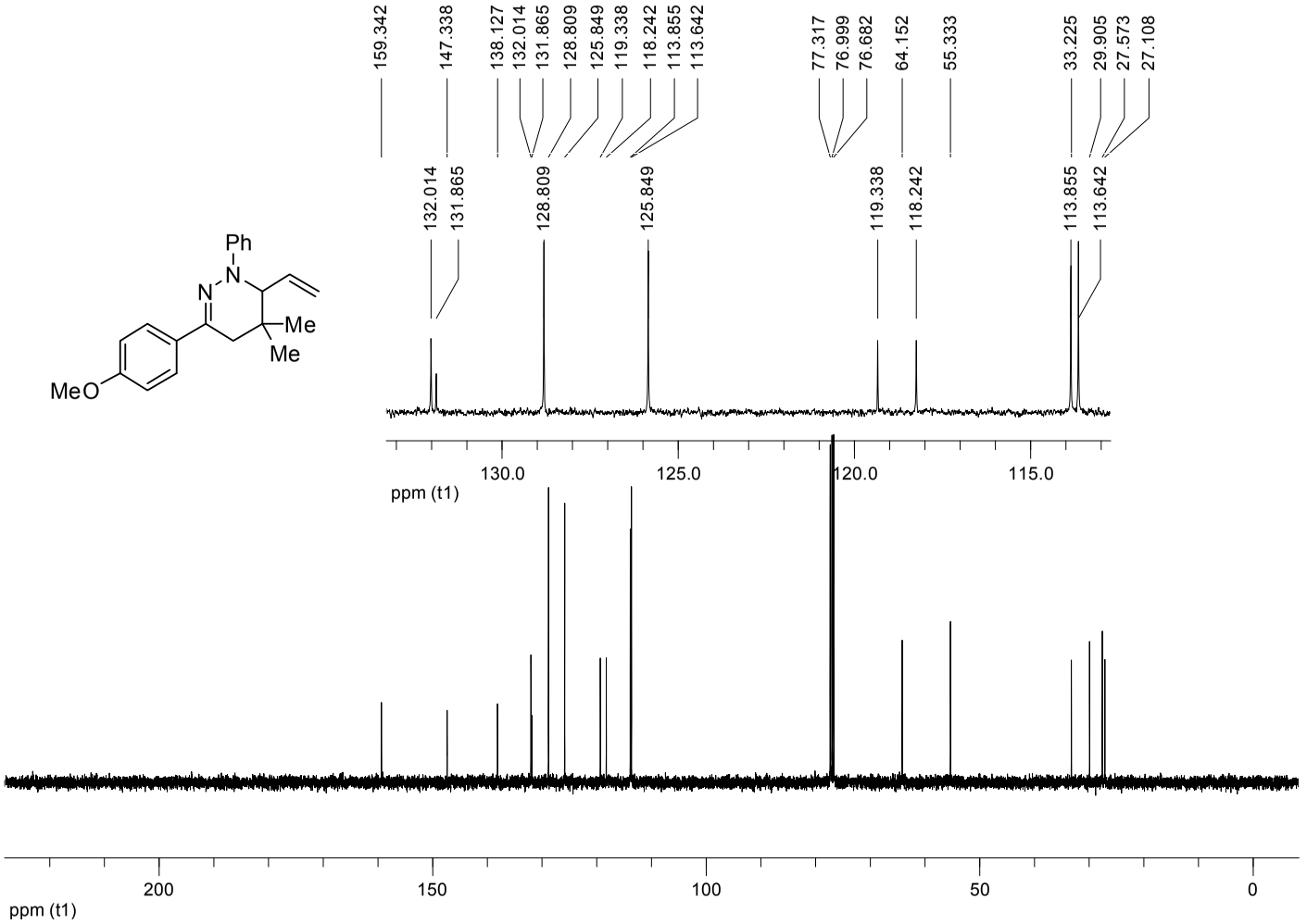
^{13}C NMR spectrum of **5l** (100 MHz, $CDCl_3$)



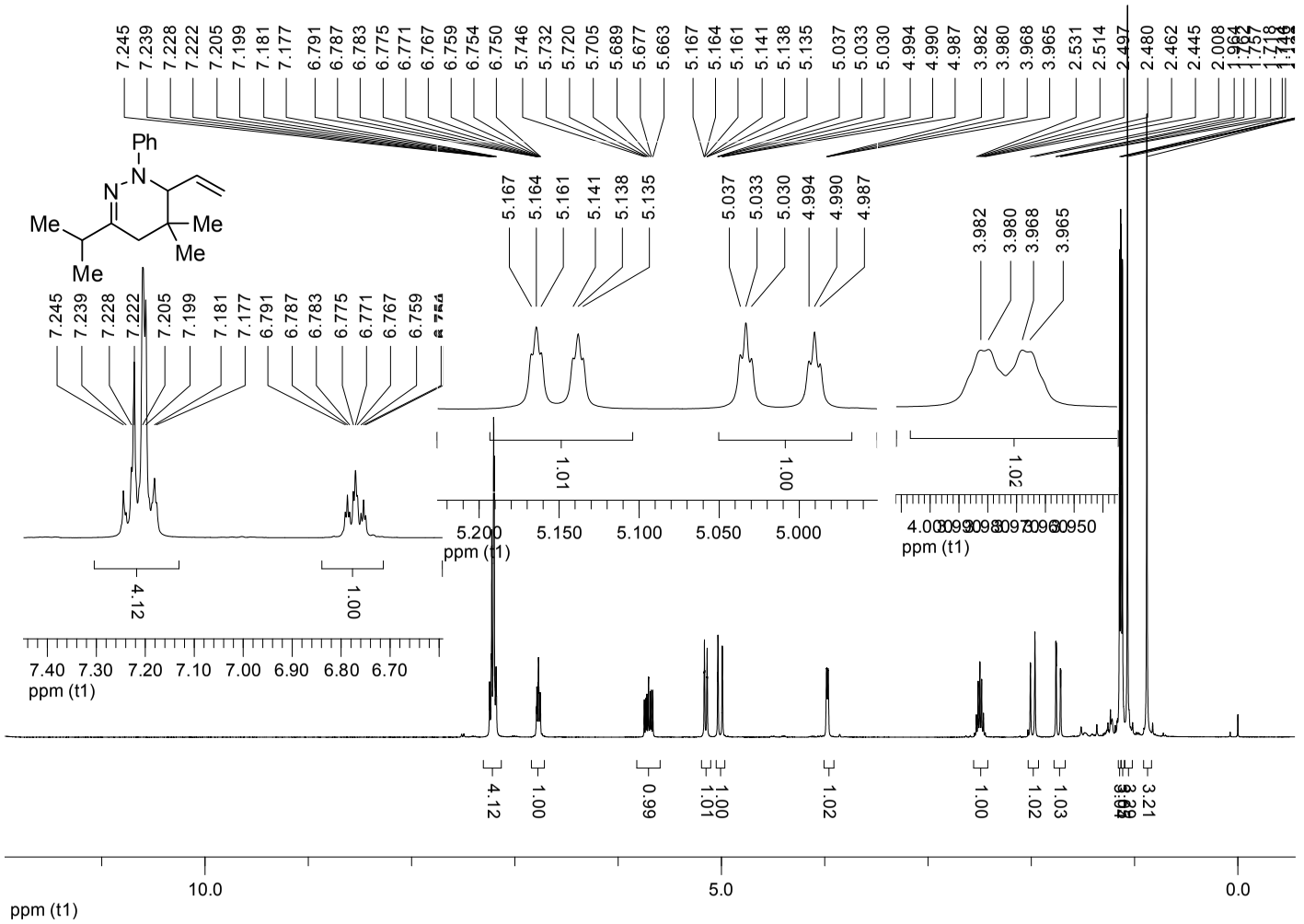
^{1}H NMR spectrum of **5m** (400 MHz, $CDCl_3$)



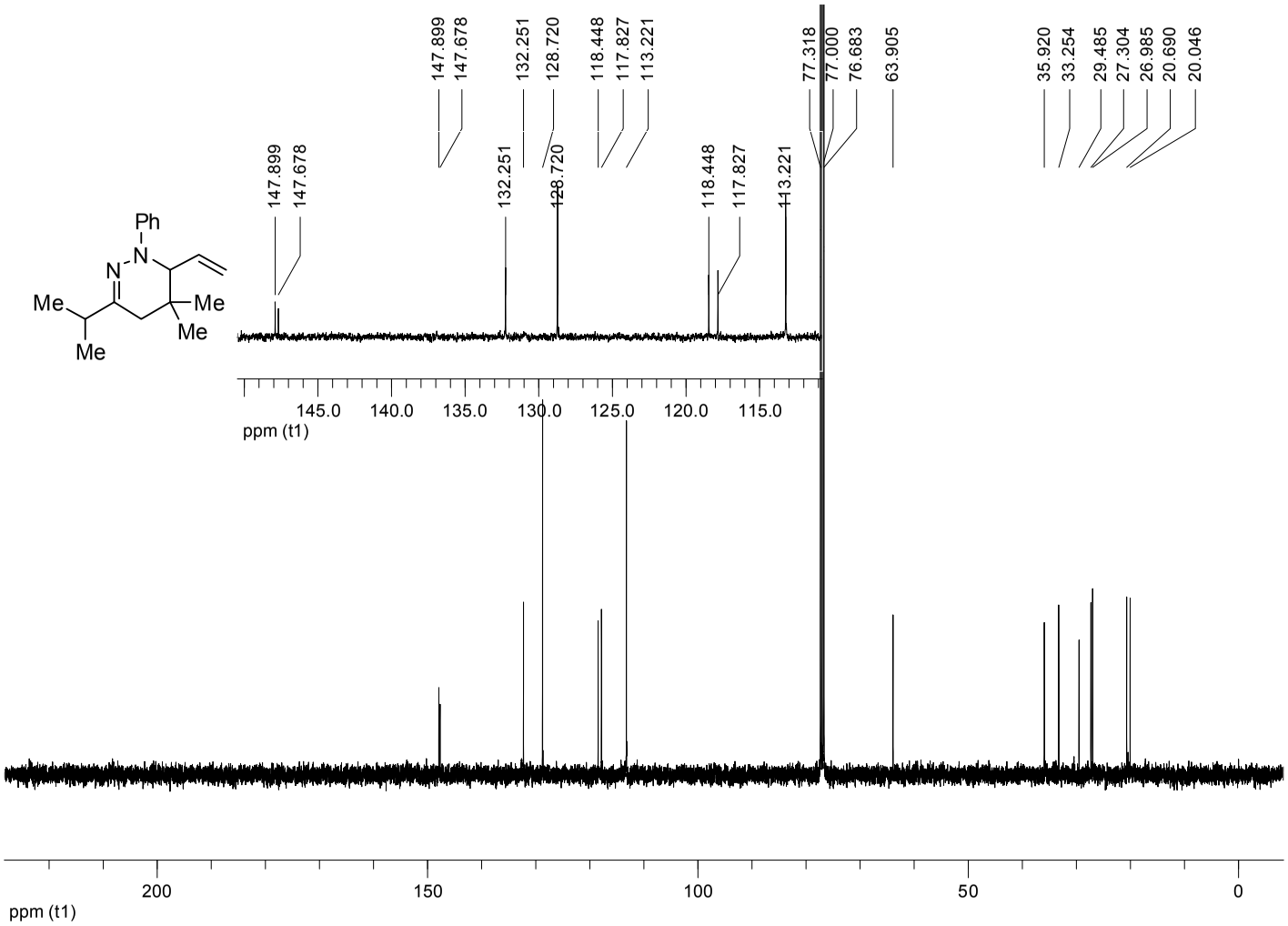
^{13}C NMR spectrum of **5m** (100 MHz, $CDCl_3$)



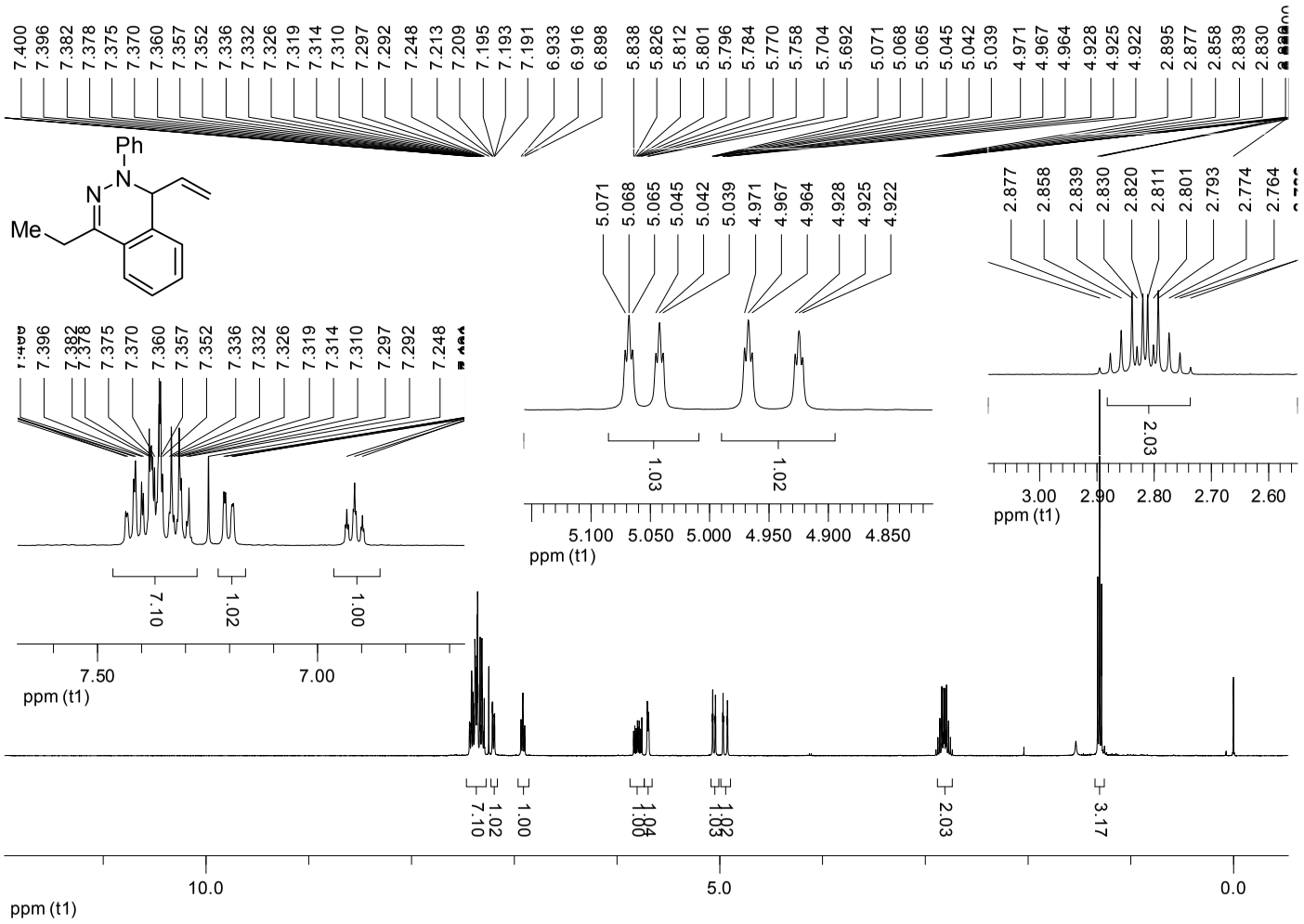
^{1}H NMR spectrum of **5n** (400 MHz, $CDCl_3$)



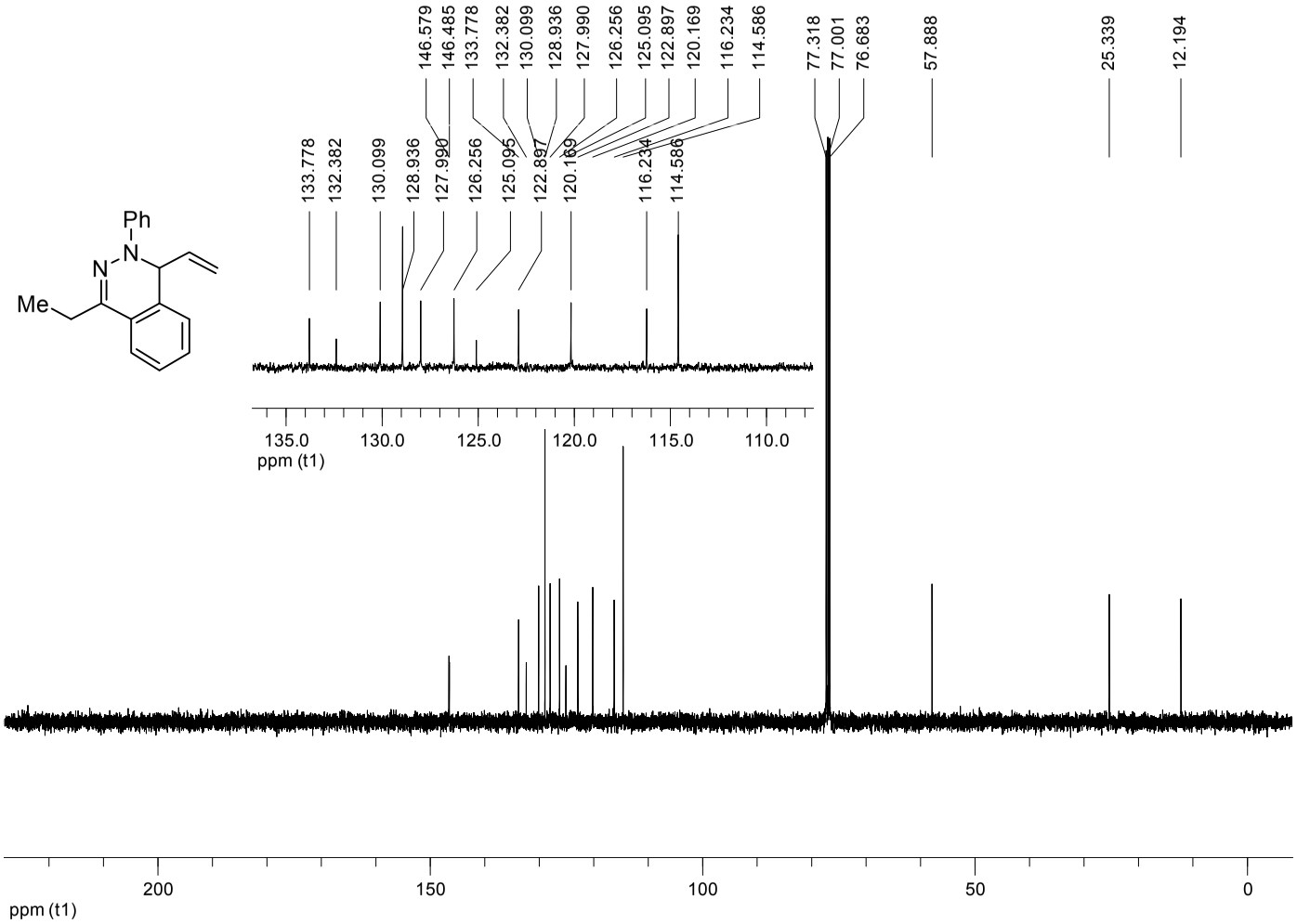
^{13}C NMR spectrum of **5n**(100 MHz, $CDCl_3$)



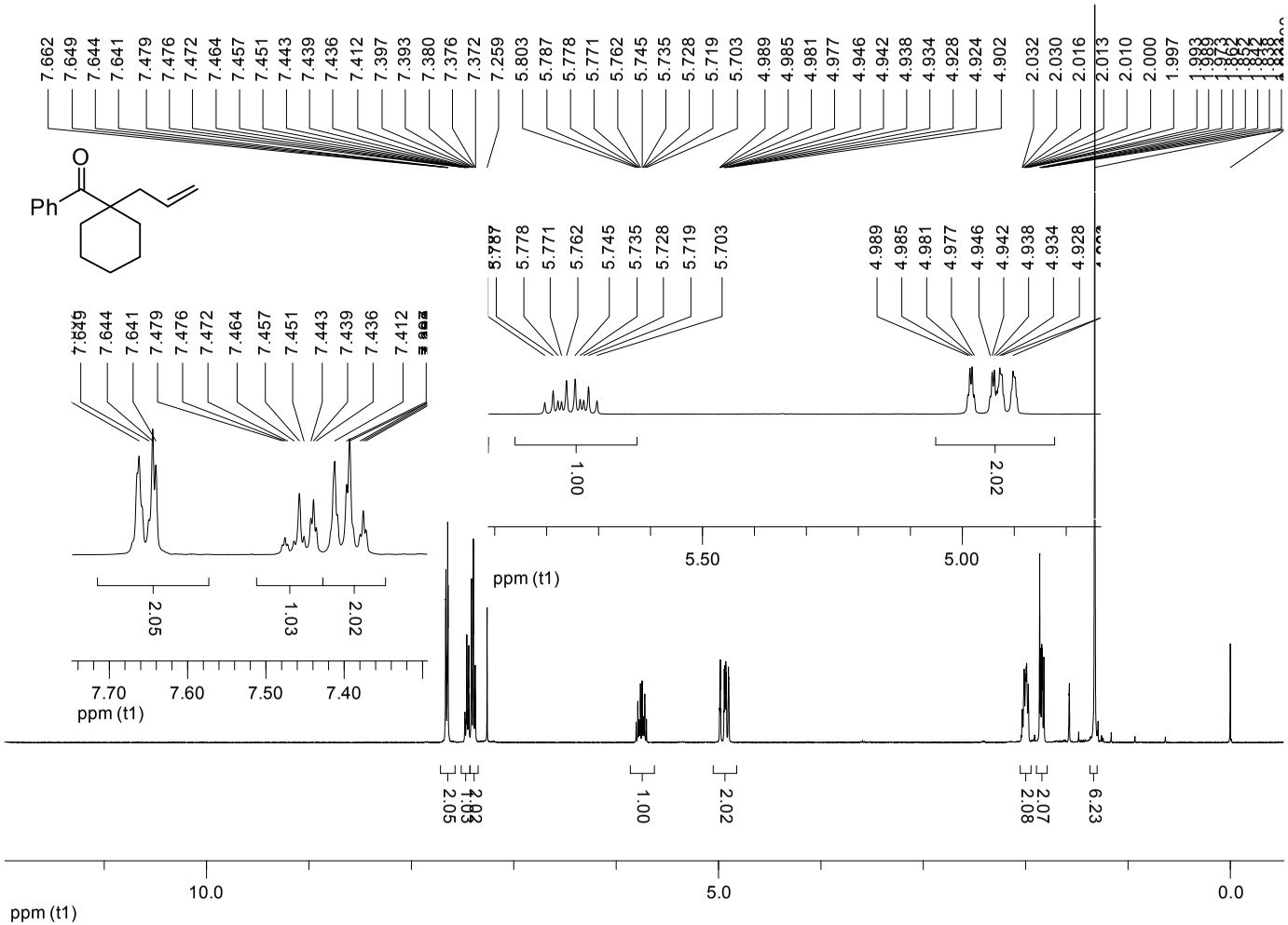
^{1}H NMR spectrum of **5o** (400 MHz, $CDCl_3$)



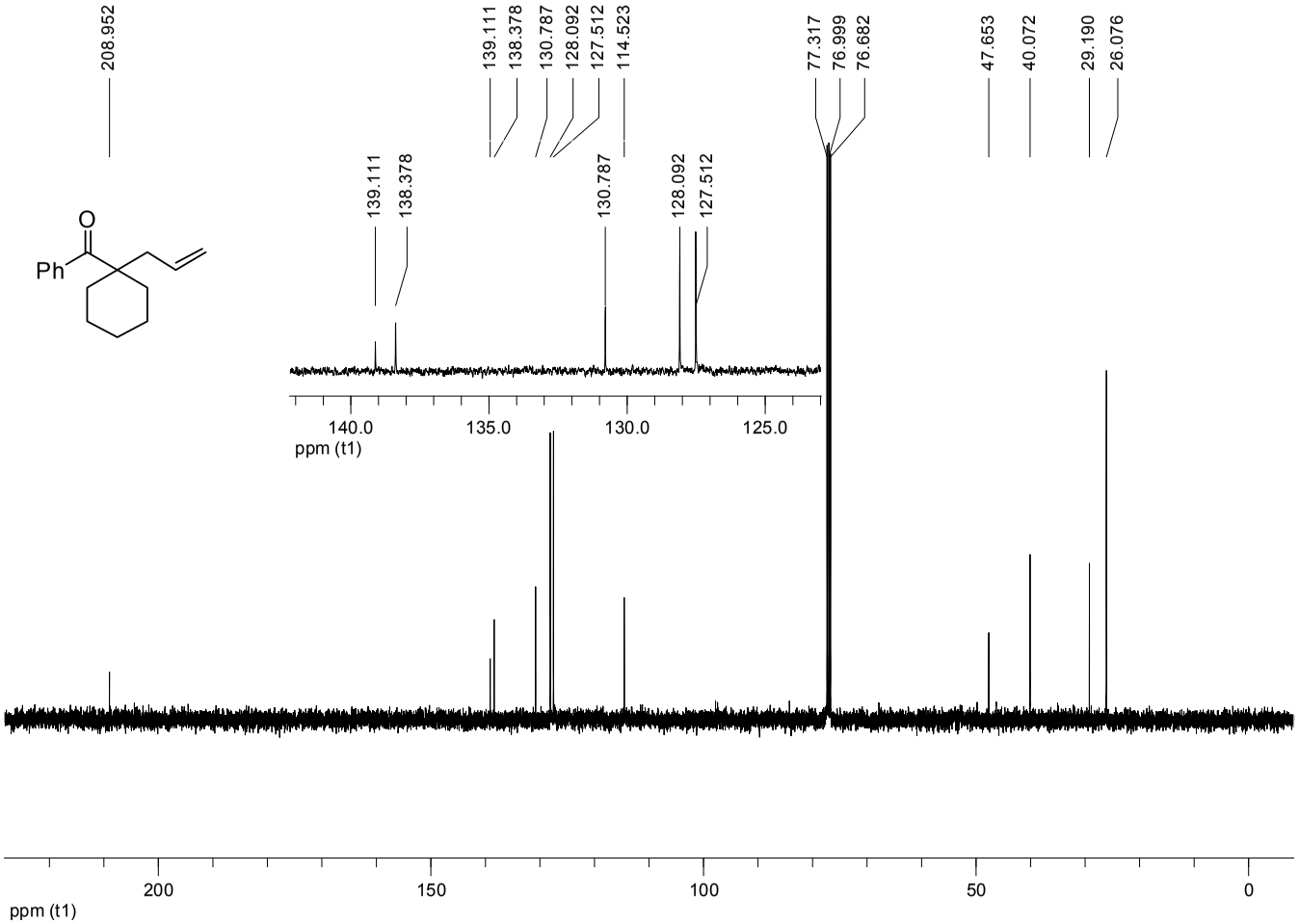
^{13}C NMR spectrum of **5o** (100 MHz, $CDCl_3$)



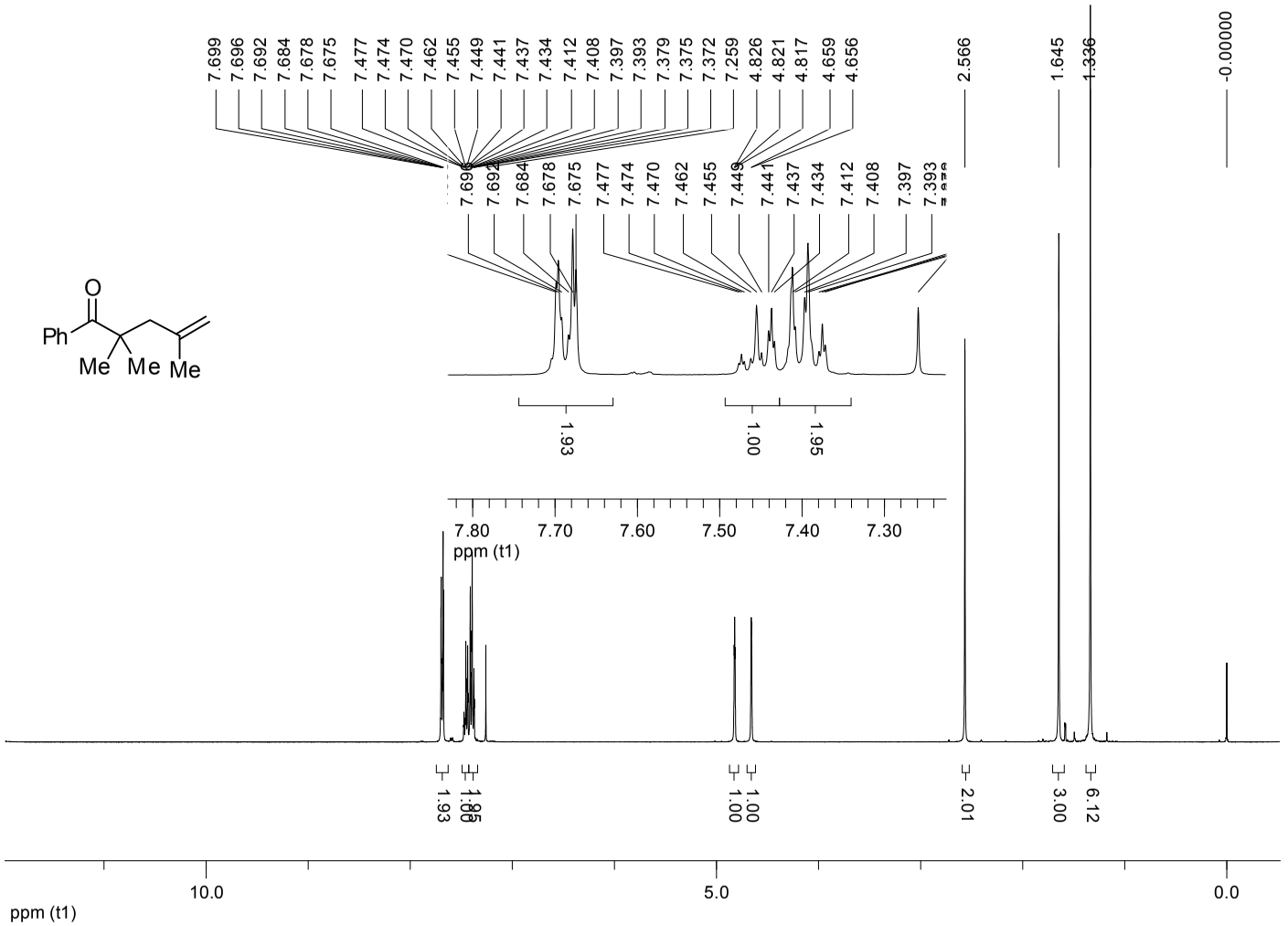
^{1}H NMR spectrum of **(1-allylcyclohexyl)(phenyl)methanone** (for synthesis of **3e**) (400 MHz, $CDCl_3$)



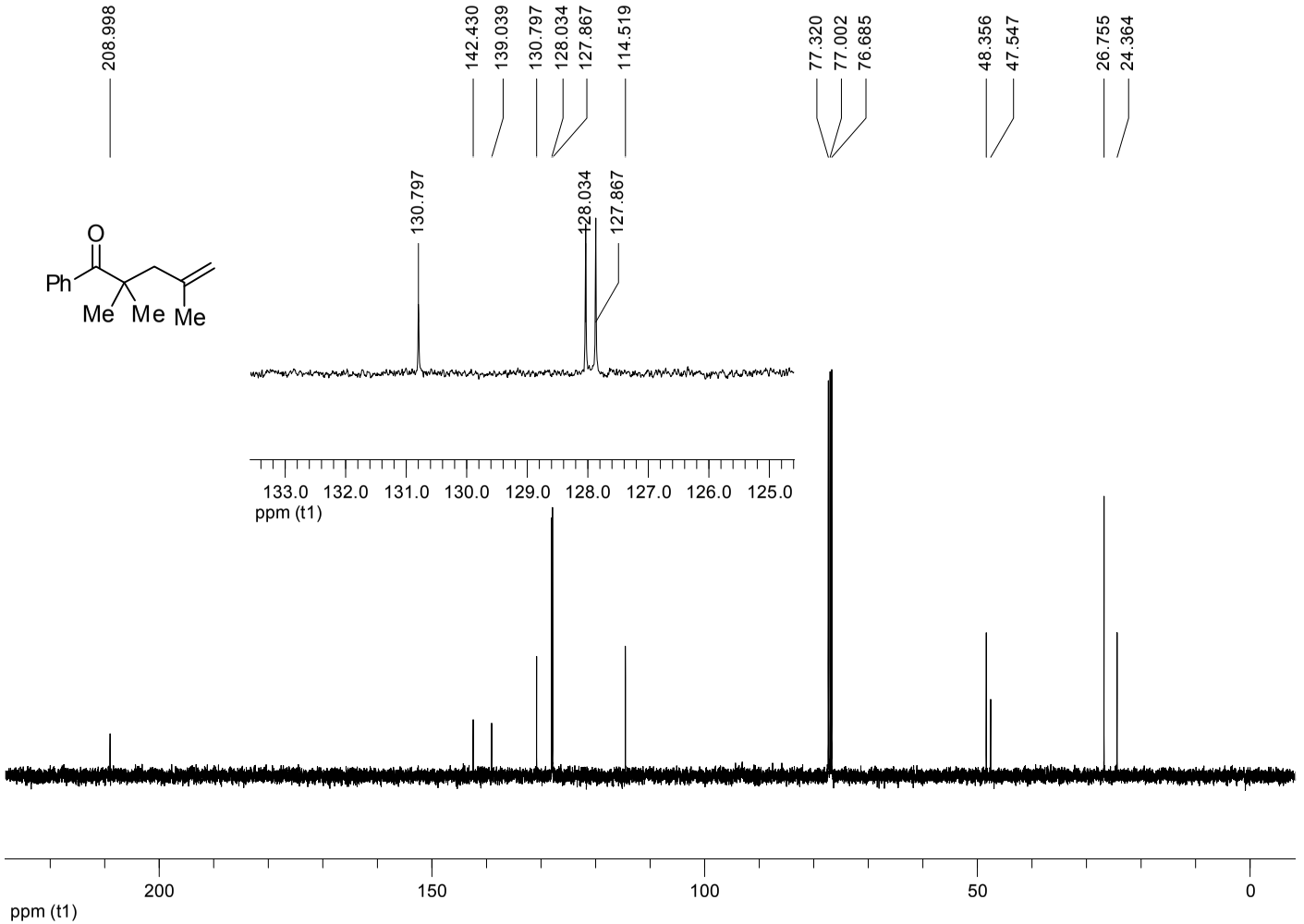
^{13}C NMR spectrum of **(1-allylcyclohexyl)(phenyl)methanone** (for synthesis of **3e**) (100 MHz, $CDCl_3$)



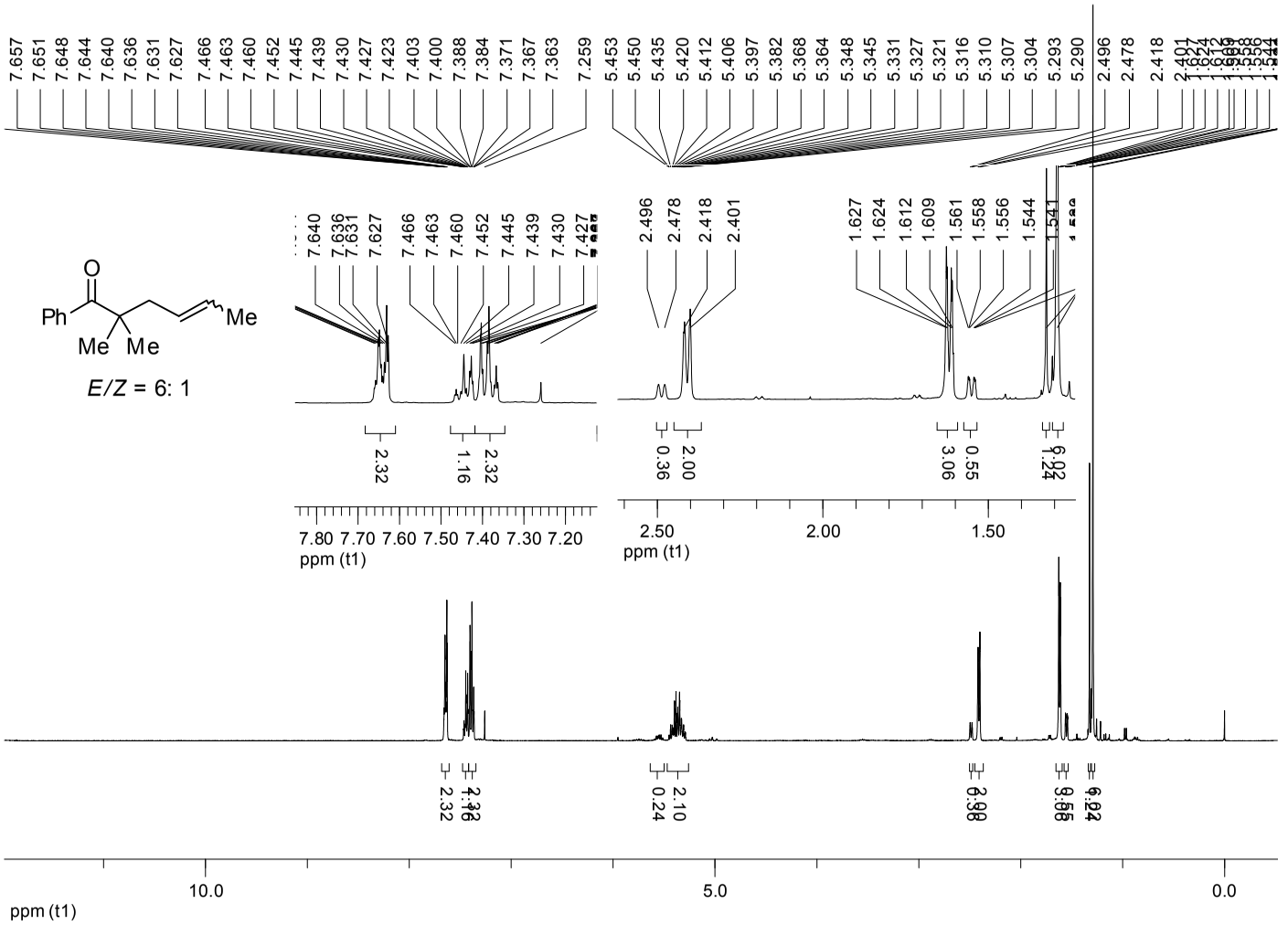
^{1}H NMR spectrum of **2,2,4-trimethyl-1-phenylpent-4-en-1-one** (for synthesis of **3j**) (400 MHz, $CDCl_3$)



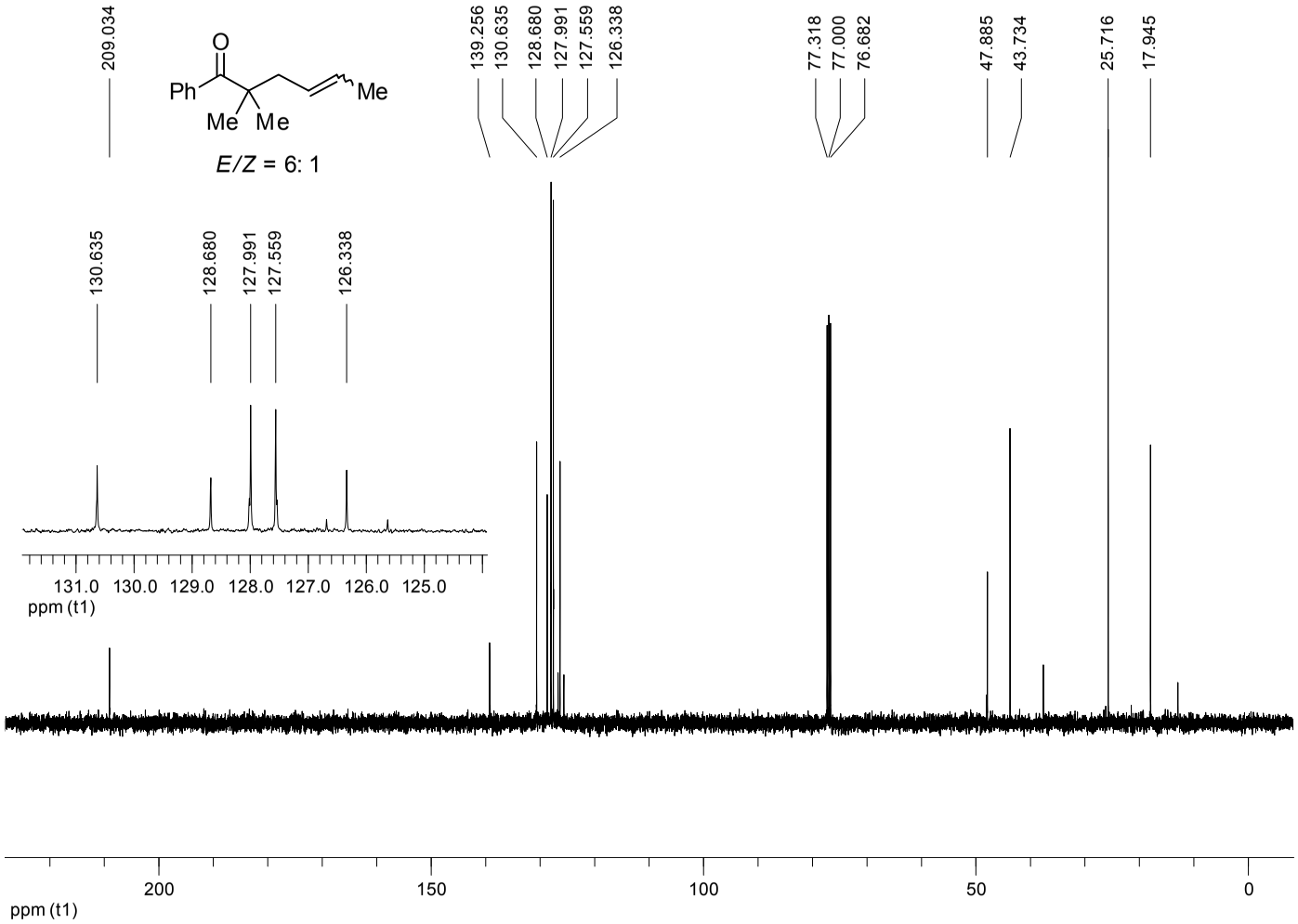
^{13}C NMR spectrum of **2,2,4-trimethyl-1-phenylpent-4-en-1-one** (for synthesis of **3j**) (100 MHz, $CDCl_3$)



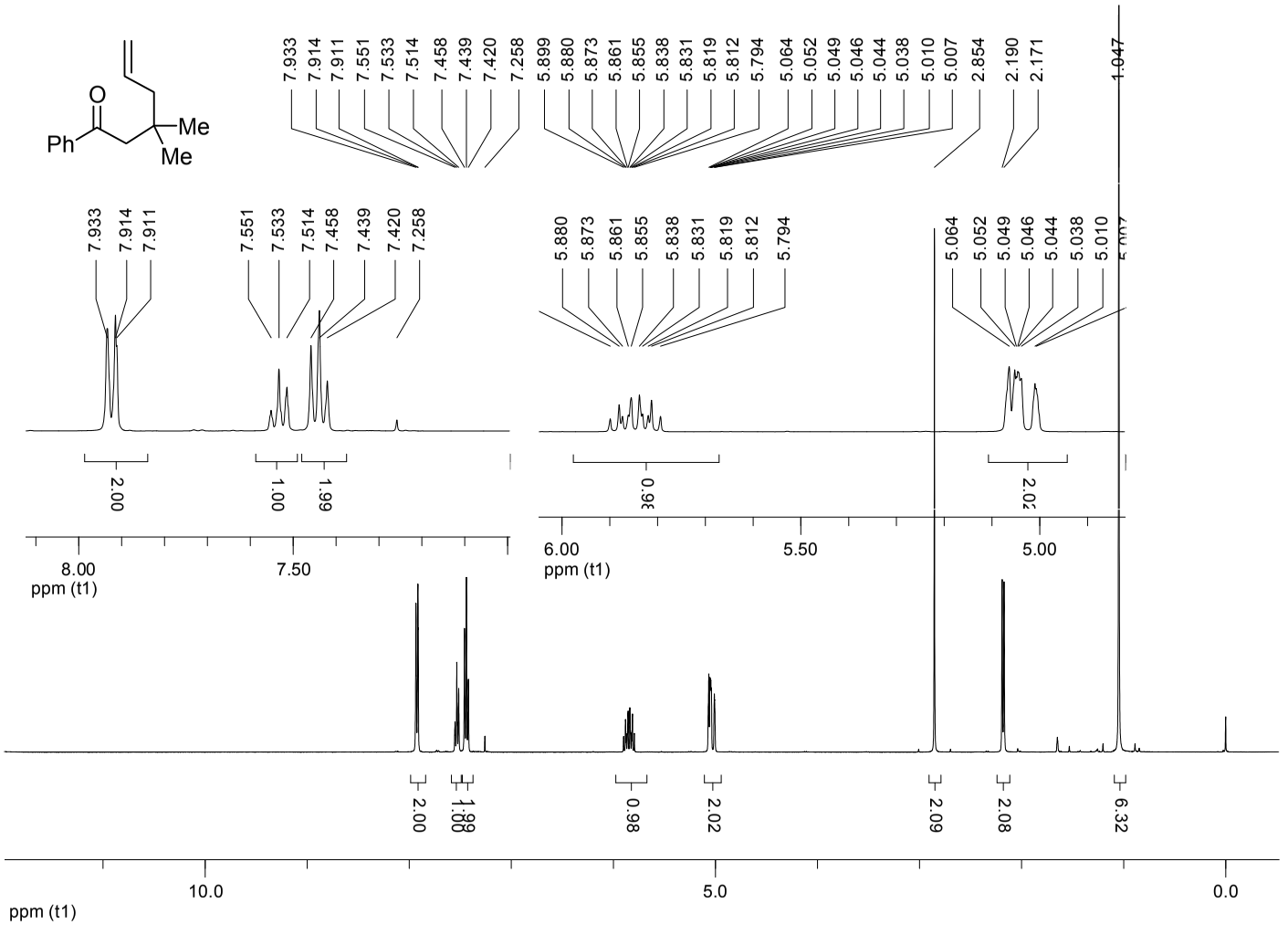
^{1}H NMR spectrum of **2,2-dimethyl-1-phenylhex-4-en-1-one** (for synthesis of **3k**) (400 MHz, $CDCl_3$)



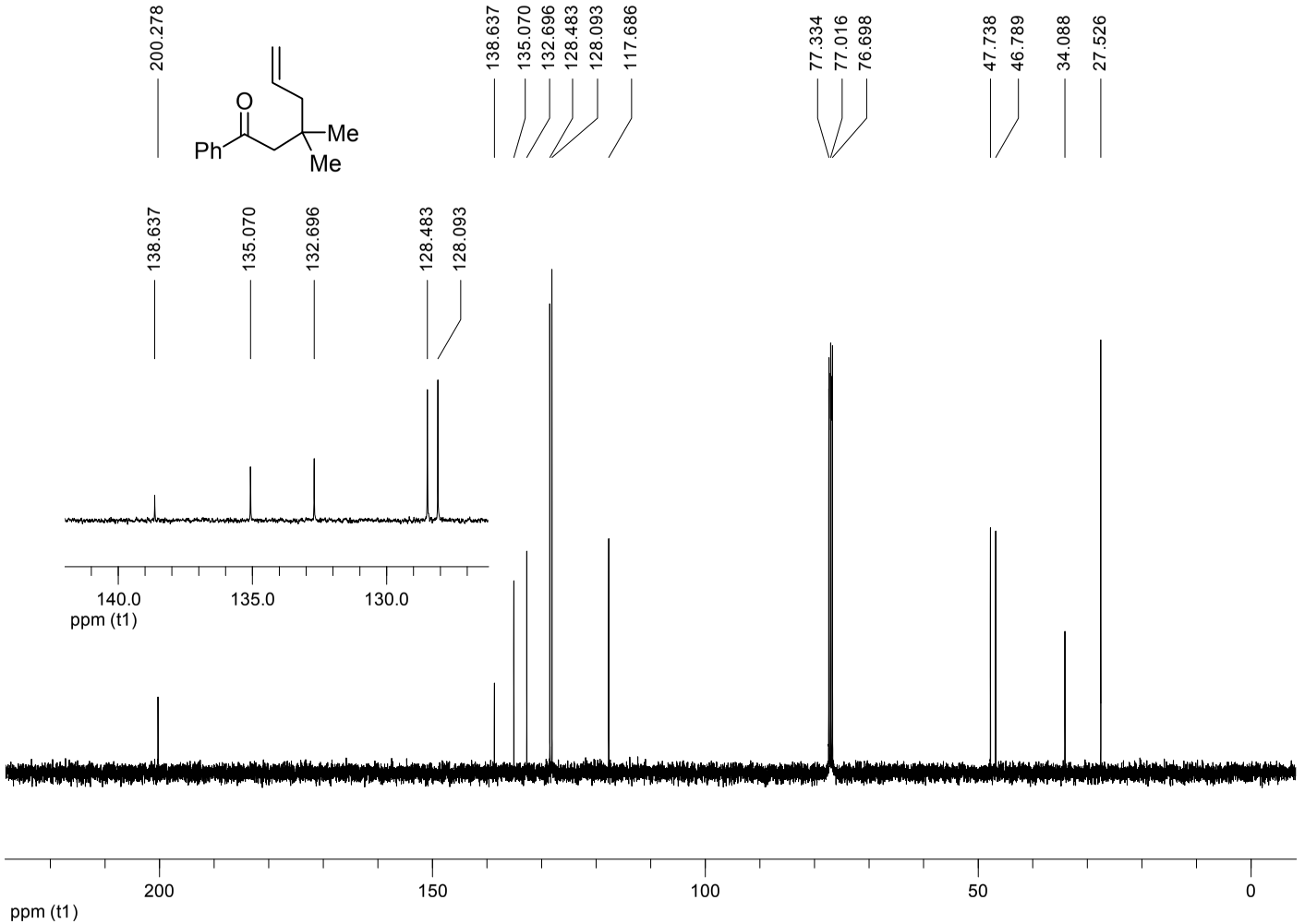
^{13}C NMR spectrum of **2,2-dimethyl-1-phenylhex-4-en-1-one** (for synthesis of **3k**) (100 MHz, $CDCl_3$)



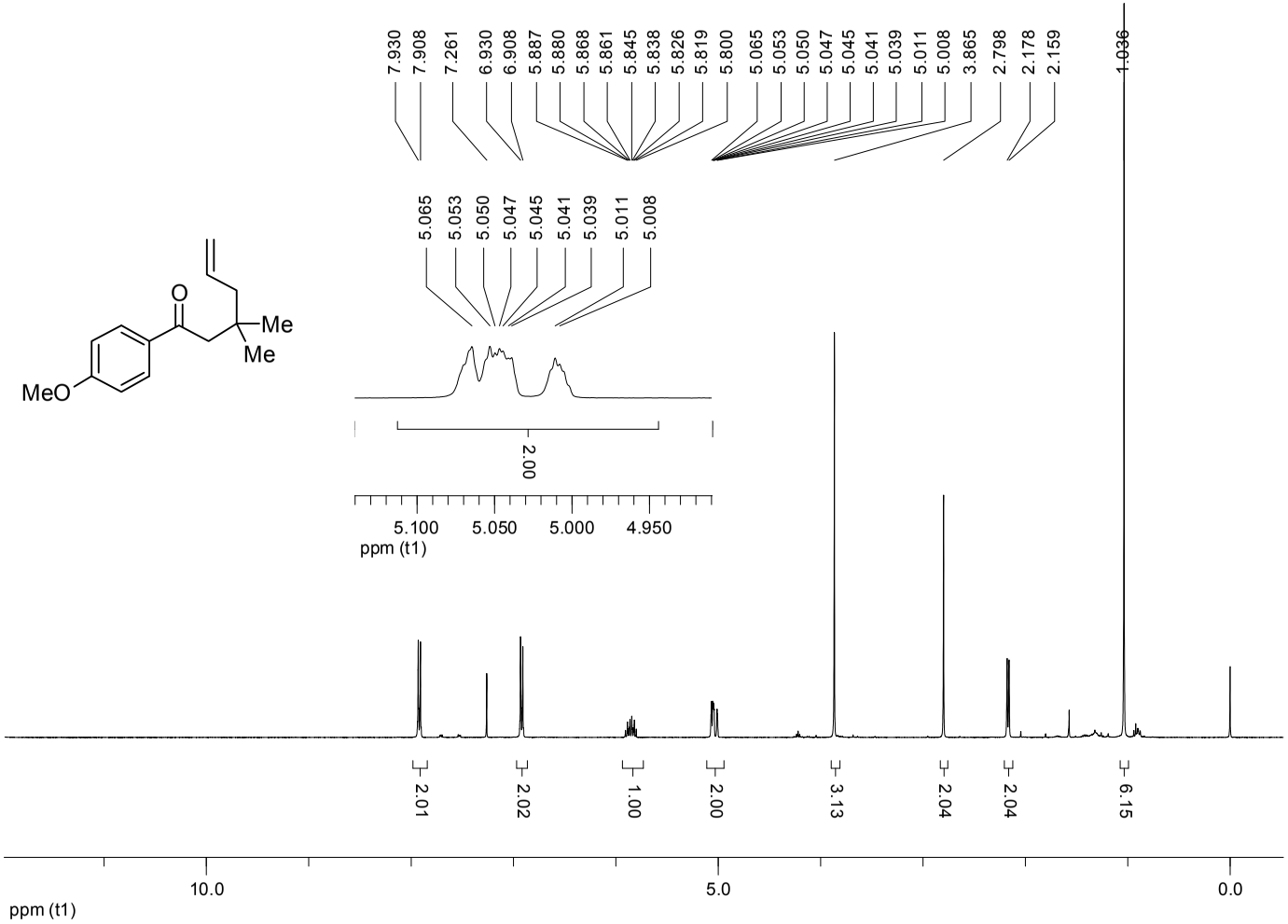
^{1}H NMR spectrum of **3,3-dimethyl-1-phenylhex-5-en-1-one** (for synthesis of **3l**) (400 MHz, $CDCl_3$)



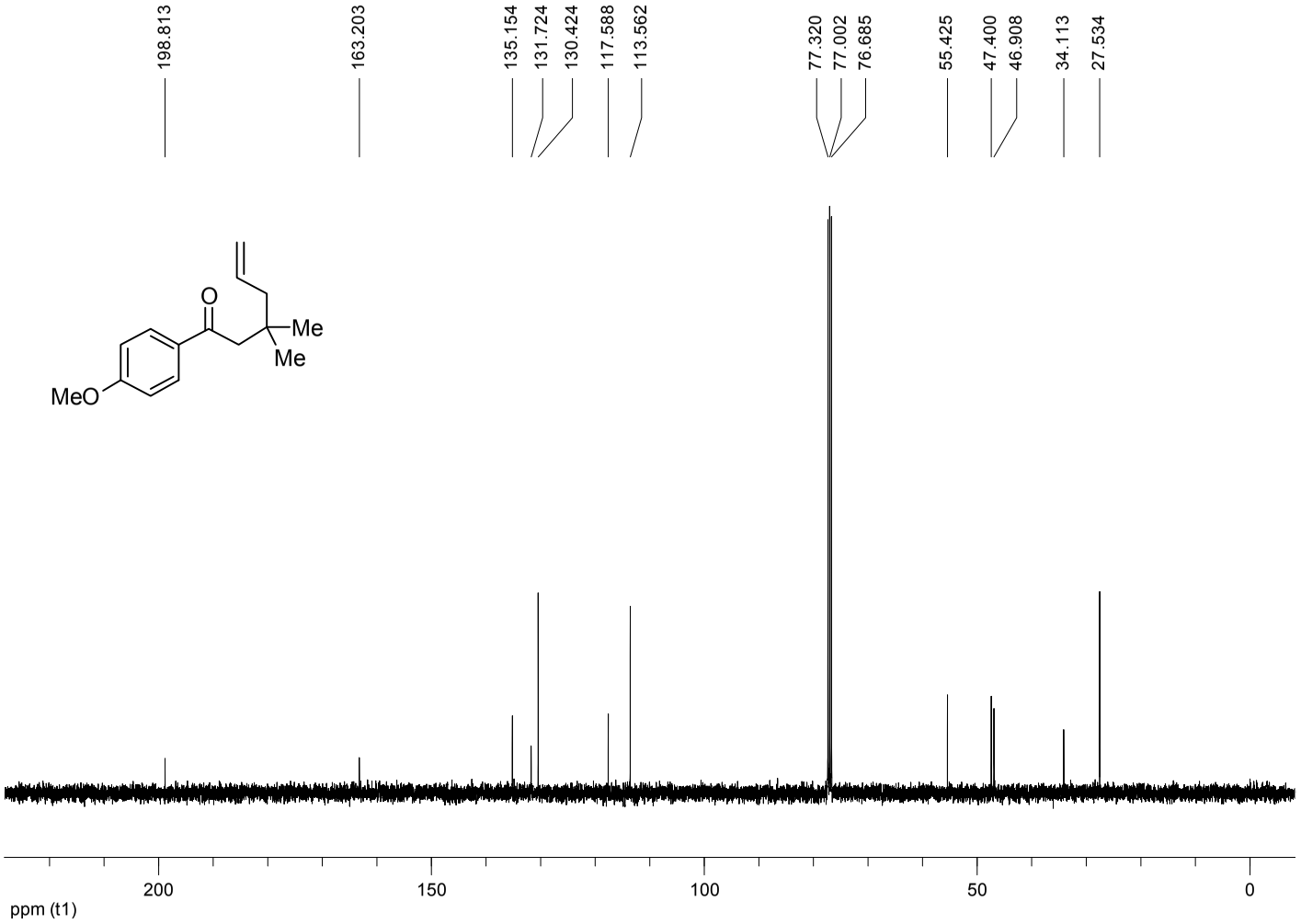
^{13}C NMR spectrum of **3,3-dimethyl-1-phenylhex-5-en-1-one** (for synthesis of **3l**) (100 MHz, $CDCl_3$)



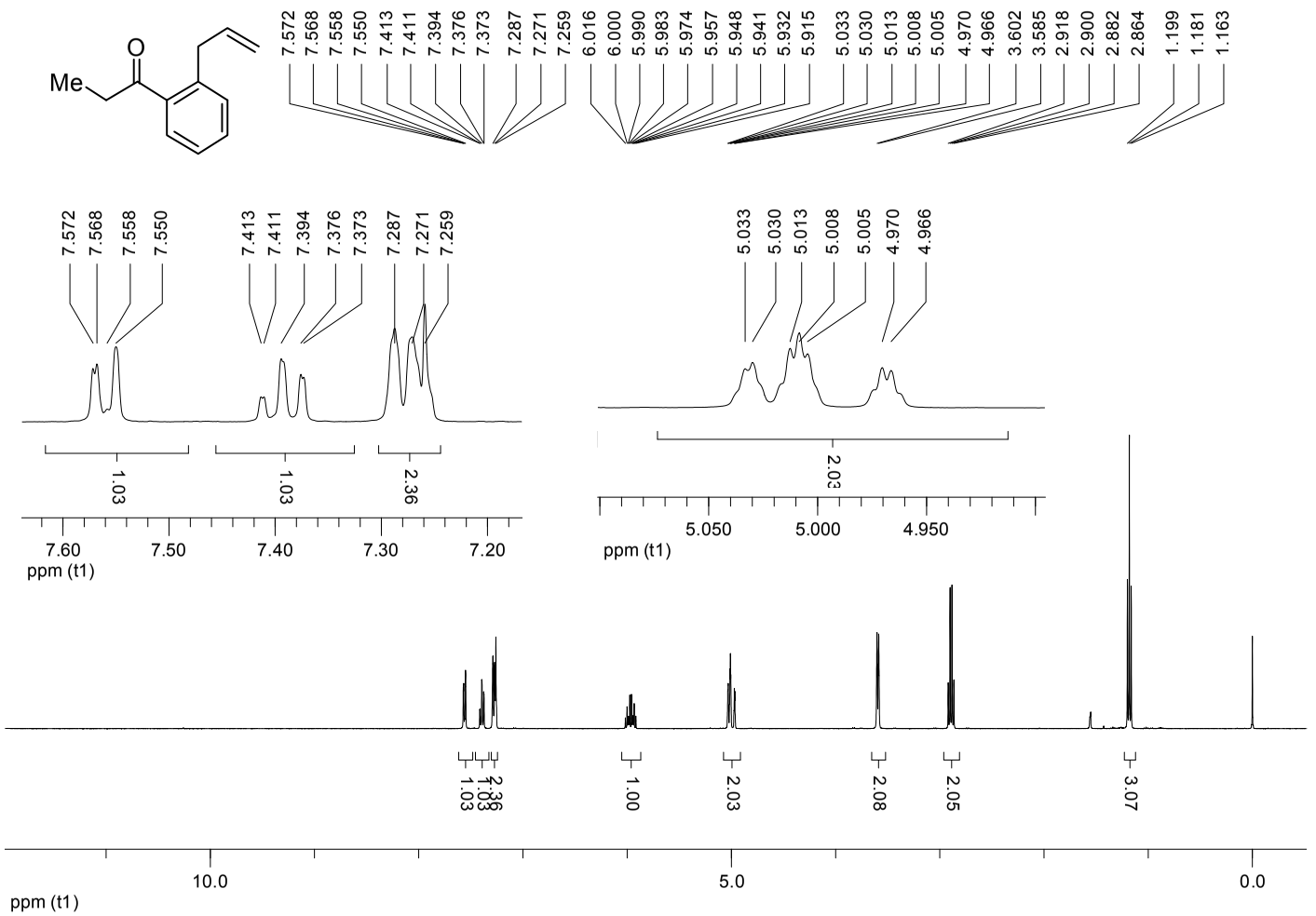
^{1}H NMR spectrum of **1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one** (for synthesis of **3m**) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1-(4-methoxyphenyl)-3,3-dimethylhex-5-en-1-one** (for synthesis of **3m**) (100 MHz, $CDCl_3$)



^{1}H NMR spectrum of **1-(2-allylphenyl)propan-1-one** (for synthesis of **3o**) (400 MHz, $CDCl_3$)



^{13}C NMR spectrum of **1-(2-allylphenyl)propan-1-one** (for synthesis of **3o**) (100 MHz, $CDCl_3$)