Catalytic Allylic Substitution of Simple Alkenes

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Supporting Information

Experimental Procedures, Analytical and Spectroscopic Data for Compounds.

General Information

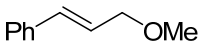
Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of argon with rigorous exclusion of moisture from reagents and glassware. Toluene, dichloromethane, tetrahydrofuran, triethylamine and diethyl ether were obtained from an SG Water solvent purification system. Bis(cyclooctadienyl)nickel(0) ($Ni(cod)_2$) and tris(*o*-methoxylphenyl)-phosphine ($P(o\text{-Anisyl})_3$) were purchased from Strem Chemicals, Inc., stored under nitrogen atmosphere and used without further purification. Ethylene and propylene were purchased from BOC Gases and Aldrich, respectively, and used as received. Methyl iodide was purified by filtration through basic alumina before use. 1-Octene, vinylcyclohexane and styrene were distilled from CaH_2 prior to use. All other reagents and solvents were used as obtained, without further purification. Analytical and preparative thin-layer chromatography were performed using EM Science silica gel 60 F254 plates. The developed chromatogram was visualized by UV lamp or stained using one of the following: aqueous potassium permanganate ($KMnO_4$) and ethanolic phosphomolybdic acid (PMA). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on silica gel (230-400 mesh).

Melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Inova-300 MHz spectrometer, a Bruker AVANCE-400 MHz spectrometer or Varian Inova 500 MHz spectrometers in $CDCl_3$, unless otherwise noted. Chemical shifts in ^1H NMR spectra are reported in parts per million (ppm) on the δ scale from an internal standard of tetramethylsilane in $CDCl_3$ (0.00 ppm) or residual benzene in C_6D_6 (7.16 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, and br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ^{13}C NMR spectra are reported in ppm from the central peak of $CDCl_3$ (77.00 ppm), or C_6D_6 (128.00 ppm) on the δ scale. Infrared (IR) spectra were recorded on a Perkin-Elmer 2000 FT-IR. High-resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXII 3 Fourier Transform Mass Spectrometer by Ms. Li Li of the Massachusetts Institute of Technology, Department of Chemistry Instrumentation Facility. GCMS spectra were obtained on an Agilent 5973N Gas Chromatograph/Mass Spectrometer and the Restek Rtx-1 GC column (30 m x 250 μm x 1 μm) in the Massachusetts Institute of Technology, Department of Chemistry

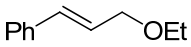
Instrumentation Facility.

Material Information.

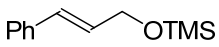
Methyl ether **1d**[1] was synthesized according to the reported procedure.



(E)-(3-Methoxyprop-1-enyl)benzene.[2] To a suspension of NaH (60%, prewashed with pentane, 596 mg, 14.9 mmol, 2 equiv) in THF (20 mL) was added cinnamyl alcohol (1 g, 7.45 mmol, 1 equiv) at rt. The mixture was stirred for 100 min at rt, after which MeI (1.40 mL, 22.4 mmol, 3 equiv) was added in one portion. The mixture was stirred for 1 h at rt, then filtrated through a pad of silica gel. The solid was washed using hexane/AcOEt (1/1) as the eluent, and the filtrate was concentrated and purified by silica gel column chromatography, using hexane/AcOEt (20/1) as the eluent, to afford the title compound (1.05 g, 95% yield).



(E)-(3-Ethoxyprop-1-enyl)benzene.[3] To a suspension of NaH (60%, prewashed with pentane, 596 mg, 14.9 mmol, 2 equiv) in THF (20 mL) was added cinnamyl alcohol (1 g, 7.45 mmol, 1 equiv) at rt. The mixture was stirred for 100 min at rt, after which EtI (1.79 mL, 22.4 mmol, 3 equiv) was added at 0 ^{o}C in one portion. The mixture was stirred for 19 h at rt, then the reaction was quenched by addition of saturated aqueous $NaHCO_3$. The mixture was extracted with AcOEt, washed with brine, dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography, using hexane/AcOEt (20/1) as the eluent, to afford the title compound (1.19 g, 98% yield).



(E)-Cinnamyloxytrimethylsilane.[4] To a mixture of cinnamyl alcohol (1 g, 7.45 mmol, 1 equiv) and triethylamine (1.25 mL, 8.94 mmol, 1.2 equiv) in DCM (5 mL) was

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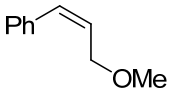
[1] Bischofberger, N.; Waldmann, H.; Saito, T.; Simon, E. S.; Lees, W.; Bednarski, M. D. Whitesides, G. M. *J. Org. Chem.* **1988**, *53*, 3457.

[2] Zhao, H.; Wang, Y.; Sha, J.; Sheng, S.; Cai, M. *Tetrahedron* **2008**, *64*, 7517.

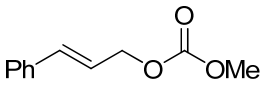
[3] Onodera, G.; Imajima, H.; Yamanashi, M.; Nishibayashi, Y.; Hidai, M.; Uemura, S. *Orgnometallics* **2004**, *23*, 5841.

[4] Fleming, S. A.; Parent, A. A.; Parent, E. E.; Pincock, J. A.; Renault, L. *J. Org. Chem.* **2007**, *72*, 9464.

added TMSCl (1.05 mL, 8.20 mmol, 1.1 equiv) at 0 °C. The mixture was stirred for 15 min at that temperature, warmed to rt, and filtered over celite. The residue after concentration was purified by silica gel column chromatography, using hexane/AcOEt (20/1) as the eluent, to afford the title compound (1.43 g, 93% yield).



(Z)-(3-Methoxyprop-1-enyl)benzene. To a solution of KHMDS (2.554 g, 12.8 mmol, 1.3 equiv) in THF (30 mL) was added 2-methoxyethyltriphenylphosphonium bromide[5] (5.137 g, 12.8 mmol, 1.3 equiv) at 0 °C. The mixture was left to stir for 1 h at 0 °C, after which benzaldehyde (1 mL, 9.85 mmol, 1 equiv) was added. The mixture was allowed to warm to rt, stirred for 16 h at rt, and poured into saturated aqueous NH_4Cl. It was extracted with AcOEt, dried over Na_2SO_4, concentrated, and purified by careful silica gel column chromatography, using hexane/EtOAc (20/1) as the eluent, to afford an yellowish title compound (670.3 mg, 46% yield).
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.19-7.37 (m, 5H), 6.61 (d, *J* = 11.8 Hz, 1H), 5.85 (dt, *J* = 6.3, 11.8 Hz, 1H), 4.21 (dd, *J* = 1.8, 6.3 Hz, 2H), 3.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 136.6, 131.6, 129.0, 128.7, 128.2, 127.1, 69.3, 58.2.



Cinnamyl methyl carbonate.[6] To a mixture of pyridine (7.5 mL, 92.73 mmol, 8.3 equiv), cinnamyl alcohol (1.5 g, 11.2 mmol, 1 equiv) and dichloromethane (15 mL) was added methyl chloroformate (1.88 mL, 25.7 mmol, 2.3 equiv) dropwise at 0 °C. The reaction mixture was allowed to warm to rt and refluxed for 15 h. The reaction was cooled to 0 °C, then 1N HCl aq. (80 mL) and EtOAc (10 mL) were added. The mixture was extracted with AcOEt, washed with water and brine successively, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography, using hexane/AcOEt (20/1) as the eluent, to afford the title compound (2.13 g, 99% yield).

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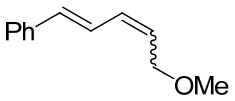
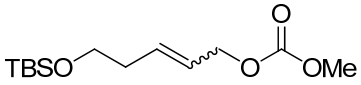
[5] Rao, G. V.; Reddy, C. *Tetrahedron Lett.* **2008**, *49*, 824.
[6] Pan, D.; Chen, A.; Su, Y.; Zhou, W.; Li, S.; Jia, W.; Xiao, J.; Liu, Q.; Zhang, L.; Jiao, N. *Angew. Chem. Int. Ed.* **2008**, *47*, 4729.



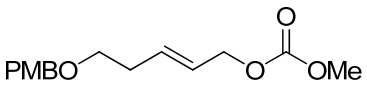
(1E)-(5-Methoxypenta-1,3-dienyl)benzene. To a solution of KO^{t}Bu (1.436 g, 12.8 mmol, 1.3 equiv) in THF (30 mL) was added 2-methoxyethyltriphenylphosphonium bromide (5.137 g, 12.8 mmol, 1.3 equiv) at 0 ^{o}C. The mixture was left to stir for 1 h at 0 ^{o}C, after which *trans*-cinnamaldehyde (1.24 mL, 9.85 mmol, 1 equiv) was added. The mixture was allowed to warm to rt, stirred for 16 h at rt, and poured into saturated aqueous NH_4Cl. It was extracted with AcOEt, dried over Na_2SO_4, concentrated, and purified by silica gel column chromatography, using hexane/EtOAc (20/1) as the eluent, to afford an orange title compound (288.7 mg, 17% yield). The geometric ratio was determined by ^{1}H NMR spectroscopy to be 86:14 (3*Z*:3*E*).
^{1}H NMR (500 MHz, $CDCl_3$, δ): **(1*E*, 3*Z*):** 7.20-7.44 (m, 5H), 7.04 (ddd, *J* = 1.1, 11.3, 15.5, 1H), 6.58 (d, *J* = 15.5 Hz, 1H), 6.32 (tq, *J* = 0.8, 11.3 Hz, 1H), 5.63 (dt, *J* = 6.8, 11.0 Hz, 1H), 4.21 (dd, *J* = 1.5, 6.8 Hz, 2H), 3.38 (s, 3H); **(1*E*, 3*E*):** Distinguishable peaks are shown. 6.79 (dd, *J* = 10.5, 15.7 Hz, 1H), 6.41 (ddd, *J* = 0.7, 10.5, 15.3 Hz, 1H), 5.87 (dt, *J* = 6.2, 15.3 Hz, 1H), 4.02 (dd, *J* = 1.3, 6.2 Hz, 2H), 3.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(1*E*, 3*Z*):**137.1, 134.2, 129.9, 128.6, 127.8, 127.7, 126.5, 123.6, 68.4, 58.1; **(1*E*, 3*E*):** Distinguishable peaks are shown. 137.1, 132.9, 132.7, 129.9, 128.2, 127.6, 126.4, 72.8, 58.0; IR (NaCl plate, thin film, cm^{-1}): 3028, 2984, 2924, 2891, 2816, 1637, 1595, 1492, 1449, 1355, 1189, 1103, 988, 910, 732, 691.



5-(*tert*-Butyldimethylsilyloxy)pent-2-enyl methyl carbonate. To a mixture of pyridine (1.65 mL, 20.8 mmol, 8.3 equiv), 5-(*tert*-butyldimethylsilyloxy)pent-2-en-1-ol[7] (*E* major (86:14), 532.1 mg, 2.5 mmol, 1 equiv) and dichloromethane (3.3 mL) was added methyl chloroformate (437 μL, 5.8 mmol, 2.3 equiv) dropwise at 0 ^{o}C. The reaction mixture was allowed to warm to rt and stirred for 18 h at rt. The reaction was cooled to 0 ^{o}C, then 1N HCl aq. (15 mL) and EtOAc (10 mL) were added. The mixture was extracted with AcOEt, washed with brine and saturated aqueous $NaHCO_3$ successively, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography, using hexane/AcOEt (20/1) as the eluent, to afford the title compound

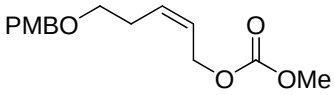
[7] Jensen, T.; Pedersen, H.; Bang-Andersen, B.; Madsen, R.; Jørgensen, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 888.

(622.6 mg, 92% yield). The geometric ratio was determined by ^{1}H NMR spectroscopy to be 88:12 (*E*:*Z*).
^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 5.81 (dt, *J* = 6.9, 15.5 Hz, 1H), 5.66 (dt, *J* = 6.5, 15.5 Hz, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 3.78 (s, 3H), 3.65 (t, *J* = 6.7 Hz, 2H), 2.28 (q, *J* = 7.3 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H); **(*Z*):** Distinguishable peaks are shown. 4.70 (d, *J* = 6.7 Hz, 2H), 2.35 (q, *J* = 7.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**155.6, 133.6, 125.1, 68.5, 62.4, 54.7, 35.8, 25.9, 18.3, 5.3; **(Z):** Distinguishable peaks are shown. 132.1, 124.5; IR (NaCl plate, thin film, cm^{-1}): 2956, 2857, 1750, 1443, 1381, 1267, 1099, 950, 836, 776; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{13}H_{26}O_4SiNa$, 297.1493; found, 297.1501.

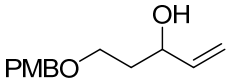


(E)-5-(4-Methoxybenzyloxy)pent-2-enyl methyl carbonate. To a mixture of pyridine (1.51 mL, 18.7 mmol, 8.3 equiv), (E)-5-(4-methoxybenzyloxy)pent-2-en-1-ol[8] (500 mg, 2.25 mmol, 1 equiv) and dichloromethane (3.0 mL) was added methyl chloroformate (400 μL, 5.2 mmol, 2.3 equiv) dropwise at 0 °C. The reaction mixture was allowed to warm to rt and stirred for 17 h at rt. The reaction was cooled to 0 °C, then 1N HCl aq. (15 mL) and EtOAc (10 mL) were added. The mixture was extracted with AcOEt, washed with 1N HCl aq. and saturated aqueous $NaHCO_3$ successively, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography, using hexane/AcOEt (5/1) as the eluent, to afford the title compound (614.1 mg, 97% yield).
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.83 (dtt, *J* = 1.1, 6.8, 15.5 Hz, 1H), 5.67 (dtt, *J* = 1.4, 6.5, 15.5 Hz, 1H), 4.58 (d, *J* = 6.5 Hz, 2H), 4.44 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.49 (t, *J* = 6.7 Hz, 2H), 2.37 (q, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.1, 155.6, 133.5, 130.3, 129.3, 125.1, 113.7, 72.6, 68.9, 68.4, 55.3, 54.7, 32.7; IR (NaCl plate, thin film, cm^{-1}): 2955, 1747, 1612, 1513, 1442, 1247, 1095, 1033, 942, 791; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{15}H_{20}O_5Na$, 303.1203; found, 303.1208.

[8] Banfi, L.; Basso, A.; Guanti, G.; Riva, R. *Tetrahedron* **2006**, *62*, 4331.



(*Z*)-5-(4-Methoxybenzyloxy)pent-2-enyl methyl carbonate. To a mixture of pyridine (3.8 mL, 46.9 mmol, 16.6 equiv), 5-(4-methoxybenzyloxy)pent-2-en-1-ol[9] (*Z* major (96:4), 627.8 mg, 2.82 mmol, 1 equiv) and dichloromethane (3.8 mL) was added methyl chloroformate (502 μL, 6.5 mmol, 2.3 equiv) dropwise at 0 ^{o}C. The reaction mixture was allowed to warm to rt and stirred for 17 h at rt. The reaction was cooled to 0 ^{o}C, then 1N HCl aq. (45 mL) was added. The mixture was extracted with AcOEt, washed with 1N HCl aq. and saturated aqueous $NaHCO_3$ successively, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography, using hexane/AcOEt (5/1) as the eluent, to afford the title compound (729.2 mg, 92% yield). The geometric ratio was determined by ^{1}H NMR spectroscopy to be 95:5 (*Z*:*E*).
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.25 (apparent d, *J* = 8.2 Hz, 2H), 5.69 (apparent d, *J* = 8.7 Hz, 2H), 5.73 (dtt, *J* = 1.3, 7.4, 11.0 Hz, 1H), 5.66 (dtt, *J* = 1.3, 6.8, 11.0 Hz, 1H), 4.70 (d, *J* = 6.7 Hz, 2H), 4.44 (s, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.48 (t, *J* = 6.7 Hz, 2H), 2.43 (q, *J* = 6.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.1, 155.7, 132.0, 130.4, 129.2, 124.6, 113.7, 72.6, 69.0, 63.7, 55.2, 54.7, 28.2; IR (NaCl plate, thin film, cm^{-1}): 2956, 1745, 1612, 1513, 1442, 1358, 1262, 1173, 1093, 1033, 947, 792; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{15}H_{20}O_5Na$, 303.1203; found, 303.1213.



5-(4-Methoxybenzyloxy)pent-1-en-3-ol.[10] To a solution of vinylmagnesiumbromide in THF (1M, 4.92 mL, 4.92 mmol, 1.2 equiv) was added 3-(4-methoxybenzyloxy)propanal[11] (796 mg, 4.1 mmol, 1 equiv) at 0 ^{o}C. The reaction mixture was stirred for 30 min at rt, after which the reaction was quenched with saturated aqueous NH_4Cl at 0 ^{o}C. The mixture was extracted with AcOEt, dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography, to afford the title compound in 92% yield.

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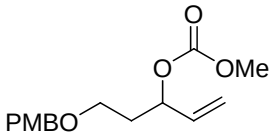
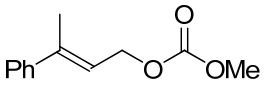
[9] Tang, M.; Pyne, S. G. *Tetrahedron* **2004**, *60*, 5759.
[10] This compound is known and fully characterized in the literature. Paquette, L. A.; Dong, S.; Parker, G. D. *J. Org. Chem.* **2007**, *72*, 7135.
[11] Hayashi, Y.; Yamaguchi, H.; Toyoshima, M.; Okado, K.; Toyo, T.; Shoji, M. *Org. Lett.* **2008**, *10*, 1405.



5-(4-Methoxybenzyloxy)pent-1-en-3-yl methyl carbonate. To a mixture of pyridine (3.3 mL, 40.7 mmol, 8.3 equiv), 5-(4-methoxybenzyloxy)pent-1-en-3-ol (1.09 g, 4.9 mmol, 1 equiv) and dichloromethane (6.5 mL) was added methyl chloroformate (870 μl, 11.3 mmol, 2.3 equiv) dropwise at 0 ^{o}C. The reaction mixture was allowed to warm to rt and stirred for 17 h at rt. The reaction was cooled to 0 ^{o}C, then 1N HCl aq. (35 mL) was added. The mixture was extracted with AcOEt, washed with 1N HCl aq. and saturated aqueous $NaHCO_3$ successively, dried over Na_2SO_4, concentrated, and purified by silica gel chromatography, using hexane/AcOEt (5/1) as the eluent, to afford the title compound (927.2 mg, 68% yield).

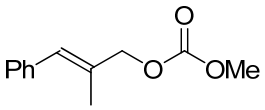
^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.23-7.27 (m, 2H), 6.86-6.90 (m, 2H), 5.80 (ddd, *J* = 6.8, 10.6, 17.3 Hz, 1H), 5.31 (dt, *J* = 1.2, 17.3 Hz, 1H), 5.25 (tq, *J* = 1.0, 6.8 Hz, 1H), 5.21 (dt, *J* = 1.1, 10.6 Hz, 1H), 4.42 (s, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.46-3.55 (m, 2H), 1.86-2.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 159.1, 155.1, 135.7, 130.3, 129.3, 117.6, 113.7, 76.4, 72.7, 65.5, 55.3, 54.6, 34.4; IR (NaCl plate, thin film, cm^{-1}): 2956, 1748, 1613, 1513, 1442, 1265, 1173, 1095, 1034, 942, 791; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{15}H_{20}O_5Na$, 303.1203; found, 303.1206.



(E)-Methyl 3-phenylbut-2-enyl carbonate. The reaction of (E)-3-phenylbut-2-en-1-ol[12] (1.02 g) and methyl chloroformate (1.22 mL), following the above-mentioned procedure for the synthesis of 5-(4-Methoxybenzyloxy)pent-1-en-3-yl methyl carbonate, afforded the title compound (1.38 g, 97% yield).

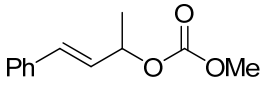
Mp. 36-37 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.24-7.42 (m, 5H), 5.92 (t, *J* = 7.0 Hz, 1H), 4.85 (d, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 155.8, 142.4, 141.0, 128.3, 127.6, 125.8, 120.6, 64.9, 54.8, 16.3; IR (NaCl plate, thin film, cm^{-1}): 2956, 1748, 1652, 1495, 1444, 1379, 1334, 1263, 943, 792, 760, 696; HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{12}H_{15}O_3$, 207.1016; found, 207.1017.

[12] Miller, D. J.; Yu, F.; Young, N. J.; Allemann, R. K. *Org. Biomol. Chem.* **2007**, *5*, 3287.



(E)-Methyl 2-methyl-3-phenylallyl carbonate. The reaction of *trans*-2-methyl-3-phenyl-2-propen-1-ol (Aldrich, 1 mL) and methyl chloroformate (1.17 mL), following the above-mentioned procedure for the synthesis of 5-(4-Methoxybenzyloxy)pent-1-en-3-yl methyl carbonate, afforded the title compound (1.35 g, 99% yield).

Mp. 34-35 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.32-7.37 (m, 2H), 7.22-7.29 (m, 3H), 6.57 (s, 1H), 4.74 (d, *J* = 0.9 Hz, 2H), 3.82 (s, 3H), 1.92 (d, *J* = 1.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 155.7, 136.8, 132.0, 128.9, 128.9, 128.1, 126.9, 73.7, 54.8, 15.4; IR (NaCl plate, thin film, cm^{-1}): 3018, 2961, 2937, 2872, 1752, 1663, 1447, 1399, 1345, 1278, 1013, 956, 849, 794, 745, 701, 518; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{12}H_{14}O_3Na$, 229.0835; found, 229.0841.



(E)-methyl 4-phenylbut-3-en-2-yl carbonate. The reaction of (E)-1-phenylbut-2-en-1-ol[13] (750 mg, 5.06 mmol) and methyl chloroformate (0.9 mL), following the above-mentioned procedure for the synthesis of 5-(4-Methoxybenzyloxy)pent-1-en-3-yl methyl carbonate, afforded the title compound (366.3 mg, 35% yield). The reaction may proceed via carbonate formation and the subsequent 1,3-carbonate transfer.

^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.40 (m, 2H), 7.28-7.34 (m, 2H), 7.23-7.27 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 7.0, 16.0 Hz, 1H), 5.37 (d quint, *J* = 1.1, 6.5 Hz, 1H), 3.78 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 155.1, 136.1, 132.2, 128.5, 128.0, 128.0, 126.6, 75.3, 54.6, 20.5; IR (NaCl plate, thin film, cm^{-1}): 2983, 1744, 1495, 1442, 1328, 1263, 1148, 1036, 967, 941, 871, 791, 750, 693; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{12}H_{14}O_3Na$, 229.0835; found, 229.0846.

[13] Fuchter, M. J.; Levy, J.-N. *Org. Lett.* **2008**, *10*, 4919.

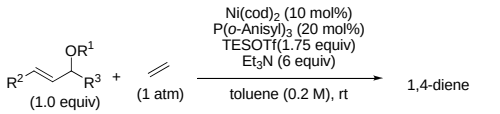
General Procedure for Nickel-Catalyzed Allylic Substitution Reaction Using Ethylene (Table 1).

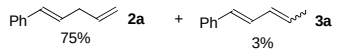
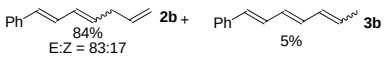
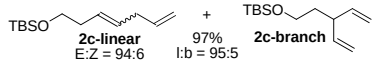
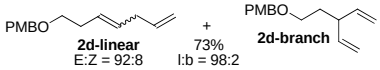
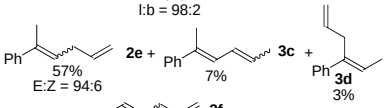
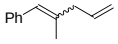
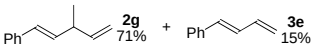
A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15-30 min at rt. The reaction mixture was purged with ethylene for 1 min to remove argon, taken care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), allylalcohol derivative (0.5 mmol, 1 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 15-90 min. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and to the residue was added a certain amount of CH_3CN (10-20 mg) or $(PhCH_2)_2O$ (15-20 mg) as an internal standard. The mixture was completely dissolved in $CDCl_3$ and analyzed by ^1H NMR spectroscopy. The product yield was determined by referring to methyl protons of CH_3CN or methylene protons of $(PhCH_2)_2O$.

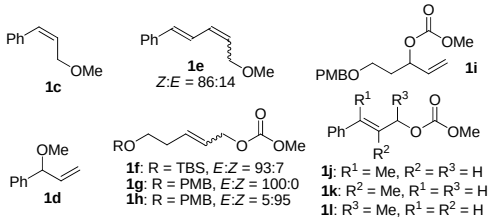
General Procedure for Nickel-Catalyzed Allylic Substitution Reaction Using Ethylene (Table 2).

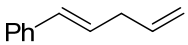
A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol%) were added to the test tube, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15-30 min at rt. The reaction mixture was purged with ethylene for 1 min to remove argon, taken care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), allylalcohol derivative (0.5 mmol, 1 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 20-200 min. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1 v/v). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography or preparative thin layer chromatography. The complete results are summarized in the table shown below. The byproducts (mainly 1,3-dienes) shown in the table are inseparable from the 1,4-diene products. In these cases,

reported yields of the 1,4-diene were determined by ^{1}H NMR spectroscopy of the isolated mixture of 1,3- and 1,4-dienes.

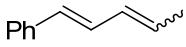


Entry	Substrate	Time (min)	Product
1	**1a**	75	 **2a** 75% + **3a** 3%
2	**1c**	50	**2a** 83% + **3a** 2%
3	**1d**	70	**2a** 74% + **3a** 4%
4	**1e**	60	 **2b** 84% E:Z = 83:17 + **3b** 5%
5	**1f**	70	 **2c-linear** E:Z = 94:6 + 97% l:b = 95:5 **2c-branch**
6	**1g**	45	 **2d-linear** E:Z = 92:8 + 73% l:b = 98:2 **2d-branch**
7	**1h**	20	**2d-linear** E:Z = 92:8 + 82% l:b = 98:2 **2d-branch**
8	**1i**	20	**2d-linear** E:Z = 92:8 + 76% l:b = 98:2 **2d-branch**
9	**1j**	120	 **2e** 57% E:Z = 94:6 + **3c** 7% + **3d** 3%
10	**1k**	200	 **2f** 81% E:Z = 88:12
11	**1l**	165	 **2g** 71% + **3e** 15%

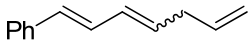




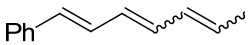
(E)-Penta-1,4-dienylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ):7.16-7.36 (m, 5H), 6.41 (d, *J* = 15.9 Hz, 1H), 6.22 (dt, *J* = 6.7, 15.9 Hz, 1H), 5.90 (dtt, *J* = 6.4, 10.1, 17.0 Hz, 1H), 5.11 (dq, *J* = 1.9, 17.1 Hz, 1H), 5.06 (dq, *J* = 1.4, 10.1 Hz, 1H), 2.96 (dt, *J* = 1.5, 6.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 137.5, 136.4, 130.8, 128.5, 128.1, 127.0, 126.0, 115.6, 37.0; IR (NaCl plate, thin film, cm^{-1}): 3080, 3060, 3026, 2978, 2891, 1944, 1637, 1599, 1495, 1448, 1429, 1305, 992, 965, 914, 742, 692.



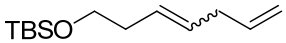
(1E)-Penta-1,3-dienylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. **(1*E*, 3*E*)**: 6.74 (dd, *J* = 10.5, 15.7 Hz, 1H), 1.82 (dd, *J* = 1.1, 6.8 Hz, 3H); **(1*E*, 3*Z*)**: 1.86 (dd, *J* = 1.7, 7.2 Hz, 3H).



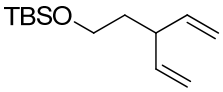
(1E)-Hepta-1,3,6-trienylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(1*E*, 3*E*):** 7.16-7.42 (m, 5H), 6.76 (dd, *J* = 10.5, 15.7 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 10.5, 15.2 Hz, 1H), 5.77-5.91 (m, 2H), 5.07 (dq, *J* = 1.6, 17.2 Hz, 1H), 5.02-5.06 (m, 1H), 2.89 (dt, *J* = 1.3, 6.7 Hz, 2H); **(1*E*, 3*Z*):** Distinguishable peaks are shown. 7.04 (ddd, *J* = 1.2, 11.1, 15.6 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 5.10 (dq, *J* = 1.8, 17.1 Hz, 1H), 5.53 (dt, *J* = 7.7, 10.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(1*E*, 3*E*):**137.5, 136.3, 132.6, 131.5, 130.7, 129.0, 128.5, 127.2, 126.2, 115.6, 36.8; **(1*E*, 3*Z*):** 137.4, 136.3, 132.7, 129.7, 129.4, 128.5, 127.5, 126.3, 124.0, 115.3, 32.1; IR (NaCl plate, thin film, cm^{-1}): 3079, 3060, 3023, 2910, 1944, 1844, 1680, 1637, 1596, 1495, 1448, 1428, 1295, 988, 913, 746, 691; HRMS-DART (m/z): $[M+H]^+$ calculated for $C_{13}H_{15}$, 171.1168; found, 171.1171.



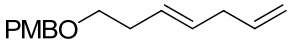
Hepta-1,3,5-trienylbenzene. Distinguishable peaks are shown. 1.79 (dd, *J* = 1.5, 6.8 Hz, 3H).



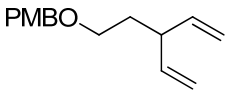
***tert*-Butyl(hepta-3,6-dienyloxy)dimethylsilane.** ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 5.82 (ddt, *J* = 6.4, 10.4, 17.0 Hz, 1H), 5.40-5.55 (m, 2H), 5.02 (dq, *J* = 1.7, 17.1 Hz, 1H), 4.98 (dd, *J* = 1.3, 10.1 Hz, 1H), 3.62 (t, *J* = 6.9 Hz, 2H), 2.75 (t, *J* = 6.1 Hz, 2H), 2.23 (q, *J* = 6.7 Hz, 2H), 0.89 (s, 9H), 0.05 (s, 6H); **(*Z*):** Distinguishable peaks are shown. 2.81 (t, *J* = 6.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**137.1, 129.8, 127.8, 114.9, 63.2, 36.8, 36.3, 25.9, 18.4, -5.2. IR (NaCl plate, thin film, cm^{-1}): 2929, 2858, 1472, 1255, 1102, 968, 912, 836, 775; HRMS-DART (m/z): $[M+H]^+$ calculated for $C_{13}H_{27}OSi$, 227.1826; found, 227.1829.



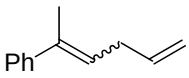
***tert*-Butyldimethyl(3-vinylpent-4-enyloxy)silane.** ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 5.73 (ddd, *J* = 7.5, 10.5, 17.4 Hz, 2H), 2.89 (quint, *J* = 7.3 Hz, 1H).



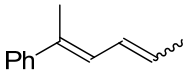
1-((Hepta-3,6-dienyloxy)methyl)-4-methoxybenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 7.26 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.81 (ddt, *J* = 6.4, 10.1, 17.2 Hz, 1H), 5.42-5.55 (m, 2H), 4.96-5.05 (m, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 3.46 (t, *J* = 6.9 Hz, 2H), 2.75 (t, *J* = 5.7 Hz, 2H), 2.32 (dq, *J* = 0.7, 6.9 Hz, 2H); **(*Z*):** Distinguishable peaks are shown. 2.81 (t, *J* = 5.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**159.0, 137.0, 130.5, 129.7, 129.2, 127.6, 114.9, 113.7, 72.4, 69.7, 55.2, 36.7, 33.0; IR (NaCl plate, thin film, cm^{-1}): 3076, 3000, 2934, 2906, 2854, 1637, 1613, 1586, 1513, 1464, 1441, 1361, 1302, 1248, 1208, 1172, 1098, 1037, 993, 971, 913, 821, 756; HRMS-DART (m/z): $[M+H]^+$ calculated for $C_{15}H_{21}O_2$, 233.1536; found, 233.1534.



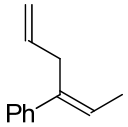
1-Methoxy-4-((3-vinylpent-4-enyloxy)methyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 5.71 (ddd, *J* = 7.5, 10.4, 17.2 Hz, 2H), 2.90 (quint, *J* = 7.4 Hz, 1H).



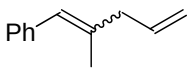
Hexa-2,5-dien-2-ylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 7.38-7.41 (m, 2H), 7.28-7.33 (m, 2H), 7.17-7.26 (m, 1H), 5.89 (ddt, *J* = 10.1, 17.1, 6.2 Hz, 1H), 5.80 (tq, *J* = 7.3, 1.4 Hz, 1H), 5.10 (dq, *J* = 17.1, 1.8 Hz, 1H), 5.02 (dq, *J* = 10.1, 1.9 Hz, 1H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.04 (d, *J* = 1.4 Hz, 3H); **(*Z*):** Distinguishable peaks are shown. 5.49 (tq, *J* = 7.6, 1.5 Hz, 1H), 2.72 (ddq, *J* = 6.1, 6.1, 1.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**143.7, 136.6, 135.9, 128.1, 126.6, 125.6, 125.2, 114.8, 33.0, 15.8; IR (NaCl plate, thin film, cm^{-1}): 3079, 3058, 3031, 2977, 2922, 1637, 1598, 1493, 1444, 1379, 1026, 993, 910, 756, 695; HRMS-EI (m/z): $[M]^+$ calculated for $C_{12}H_{14}$, 158.1090; found, 158.1094.



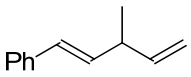
(2E)-Hexa-2,4-dien-2-ylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 1.86 (d, *J* = 6.7 Hz, 3H).



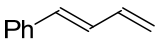
(E)-Hexa-2,5-dien-3-ylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 3.26 (d, *J* = 5.9 Hz, 2H), 1.79 (d, *J* = 6.9 Hz, 3H).



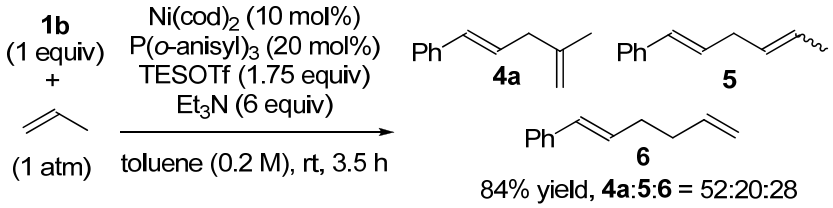
(2-Methylpenta-1,4-dienyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 7.27-7.33 (m, 2H), 7.21-7.26 (m, 2H), 7.16-7.20 (m, 1H), 6.30 (s, 1H), 5.88 (ddt, *J* = 10.1, 17.0, 6.9 Hz, 1H), 5.07-5.15 (m, 2H), 2.90 (d, *J* = 6.9 Hz, 2H), 1.85 (d, *J* = 1.3 Hz, 3H); **(*Z*):** Distinguishable peaks are shown. 6.39 (s, 1H), 2.96 (d, *J* = 6.2 Hz, 2H), 1.88 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**138.4, 137.2, 136.4, 128.8, 128.0, 125.9, 125.7, 116.3, 45.0, 17.8; **(*Z*):** Distinguishable peaks are shown. 115.9, 37.2, 28.0; IR (NaCl plate, thin film, cm^{-1}): 3079, 3023, 2977, 2911, 1653, 1635, 1492, 1441, 1383, 1172, 1073, 993, 915, 830, 742, 698; HRMS-EI (m/z): $[M]^+$ calculated for $C_{12}H_{14}$, 158.1090; found, 158.1092.



(E)-(3-Methylpenta-1,4-dienyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.16-7.36 (m, 5H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 7.1, 16.0 Hz, 1H), 5.86 (ddd, *J* = 6.6, 10.3, 17.0 Hz, 1H), 5.07 (dt, *J* = 17.0, 1.5 Hz, 1H), 5.01 (dt, *J* = 10.3, 1.4 Hz, 1H), 2.97-3.07 (m, 1H), 1.19 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 142.4, 137.6, 134.2, 128.6, 128.4, 127.0, 126.0, 113.3, 40.6, 19.8; IR (NaCl plate, thin film, cm^{-1}): 3081, 3060, 3026, 2966, 2927, 2869, 1635, 1599, 1495, 1448, 1411, 1369, 994, 965, 913, 747, 692; HRMS-EI (m/z): $[M]^+$ calculated for $C_{12}H_{14}$, 158.1090; found, 158.1089.

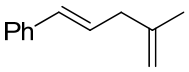


(E)-Buta-1,3-dienylbenzene.[14]



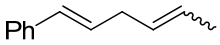
Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with Propene

A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and P(*o*-anisyl)$_3$ (35.2 mg, 0.1 mmol, 20 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 40 min at rt. The reaction mixture was purged with propene for 1 min to remove argon, taken care not to introduce oxygen. The propene atmosphere was maintained with a propene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 3.5 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford a mixture of **4a**, **5**, and **6** (66.7 mg, 84% yield).

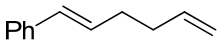


(E)-(4-Methylpenta-1,4-dienyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.31-7.38 (m, 2H), 7.25-7.31 (m, 2H), 7.15-7.22 (m, 1H), 6.34-6.44 (m, 1H), 6.16-6.26 (m, 1H), 4.79 (brs, 1H), 4.78 (brs, 1H), 2.89 (d, *J* = 7.0 Hz, 2H), 1.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 144.5, 137.6, 131.3, 128.5, 128.2, 127.0, 126.0, 111.0, 41.5, 22.5; IR (NaCl plate, thin film, cm^{-1}): 3080, 3026, 2970, 2935, 1646, 1495, 1448, 1373, 965, 889, 740, 691; HRMS-EI (m/z): $[M]^+$ calculated for $C_{12}H_{14}$, 158.1090; found, 158.1096.

[14] Mundal, D. A.; Lutz, K. E.; Thomson, R. J. *Org. Lett.* **2009**, *11*, 465.



(1E)-Hexa-1,4-dienylbenzene. (A mixture of (1*E*, 4*E*) and (1*E*, 4*Z*).) ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 5.45-5.62 (m, 2H), 1.65-1.72 (m, 3H).



(E)-Hexa-1,5-dienylbenzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): Distinguishable peaks are shown. 5.86 (ddt, *J* = 6.6, 10.2, 17.1 Hz, 1H), 5.06 (dq, *J* = 1.6, 17.1 Hz, 1H), 4.99 (ddt, *J* = 1.2, 2.0, 10.2 Hz, 1H), 2.31 (q, *J* = 6.8 Hz, 2H), 2.23 (q, *J* = 6.7 Hz, 2H).

Experimental Procedure for the Reactions in Table 3.

The optimal reaction conditions are dependent on the olefins used. The same reaction conditions can be used in the case of propylene as in the case of ethylene. Higher concentration (1M) and the addition of allylcarbonate prior to olefins are necessary for high yields in the case of olefins other than propylene. The replacement of half amount of PCy_2Ph by $P(OPh)_3$ generally gave higher yield by 10% than that obtained without using $P(OPh)_3$, but in some cases $P(OPh)_3$ was not employed since the byproduct TESOPh derived from $P(OPh)_3$ and TESOTf contaminated the desired products. Slow addition of TESOTf suppresses the formation of the byproducts such as a triethylamine adduct, and gave better yield in case where the desire reaction was so slow that the byproduct formation significantly competes with the desired pathway.

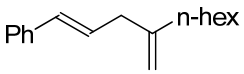
Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with Propene (Entry 1 in Table 3).

A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (27.4 mg, 0.1 mmol, 20 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (2.5 mL) under argon and stirred for 15 min at rt. The reaction mixture was purged with propene for 1 min to remove argon, taken care not to introduce oxygen. The propene atmosphere was maintained with a propene balloon. Triethylamine (418 μL, 3 mmol, 6 equiv), cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 3.5 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were

removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **4a** (61.1 mg, 77% yield, >98% selectivity).

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with 1-Octene (Entry 2 in Table 3).

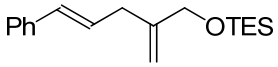
A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (13.7 mg, 0.05 mmol, 10 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at rt. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at rt. $P(OPh)_3$ (13.1 μL, 0.05 mmol, 10 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), 1-octene (393 μL, 2.5 mmol, 5 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 18 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **4b** (90.4 mg, 79% yield, >98% selectivity).



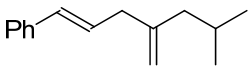
(E)-(4-Methylenedec-1-enyl)benzene. ^1H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.38 (m, 2H), 7.27-7.32 (m, 2H), 7.17-7.22 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.77-4.81 (m, 2H), 2.90 (d, *J* = 7.1 Hz, 2H), 2.05 (t, *J* = 7.6 Hz, 2H), 1.40-1.50 (m, 2H), 1.25-1.35 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 148.7, 137.6, 131.2, 128.5, 127.0, 126.0, 110.0, 39.9, 36.1, 31.8, 29.0, 27.6, 22.6, 14.1; IR (NaCl plate, thin film, cm^{-1}): 3081, 3026, 2955, 2927, 2856, 1644, 1495, 1449, 965, 891, 739, 691; HRMS-EI (m/z): $[M]^+$ calculated for $C_{17}H_{24}$, 228.1873; found, 228.1875.

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with allyloxytriethylsilane or 4-methyl-1-pentene (Entries 3 and 5 in Table 3).

A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (27.4 mg, 0.1 mmol, 20 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at rt. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at rt. $P(OPh)_3$ (26.2 μL, 0.1 mmol, 20 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), allyloxytriethylsilane[15] (Entry 3, 514 μL, 2.5 mmol, 5 equiv) or 4-methyl-1-pentene (Entry 5, 316 μL, 2.5 mmol, 5 equiv), and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 50 min (entry 3) or 21 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **4c** (104.8 mg, 73% yield, >98% selectivity) or **4e** (87.2 mg, 87% yield, >98% selectivity).



(E)-Triethyl(2-methylene-5-phenylpent-4-enyloxy)silane. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.38 (m, 2H), 7.28-7.32 (m, 2H), 7.19-7.23 (m, 1H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 7.1 Hz, 1H), 5.12 (s, 1H), 4.92 (s, 1H), 4.12 (s, 2H), 2.94 (d, *J* = 6.6 Hz, 2H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.63 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 147.1, 137.5, 131.5, 128.5, 127.8, 127.0, 126.0, 110.1, 65.4, 36.4, 6.8, 4.4; IR (NaCl plate, thin film, cm^{-1}): 3026, 2955, 2910, 2876, 1238, 1111, 1078, 1007, 965, 900, 803, 741, 691; HRMS-ESI (m/z): $[M+H]^+$ calculated for $C_{18}H_{29}OSi$, 311.1802; found, 311.1809.

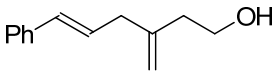


(E)-(6-Methyl-4-methylenehept-1-enyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.38 (m, 2H), 7.27-7.31 (m, 2H), 7.17-7.22 (m, 1H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.83 (d, *J* = 1.7 Hz, 1H), 4.77 (s, 1H), 2.88 (d, *J* = 7.1

[15] Velasco-Torrijos, T.; Murphy, P. V. *Org. Lett.* **2004**, *6*, 3961.

Hz, 2H), 1.94 (d, J = 7.3 Hz, 2H), 1.76-1.85 (m, 1H), 0.89 (d, J = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.3, 137.6, 131.3, 128.5, 128.4, 127.0, 126.0, 111.5, 45.9, 39.5, 25.9, 22.5; IR (NaCl plate, thin film, cm^{-1}): 3081, 3026, 2954, 2924, 2868, 1642, 1496, 1464, 1449, 1383, 1366, 966, 894, 741, 691; HRMS-Dart (m/z): $[M-H]^+$ calculated for $C_{15}H_{19}$, 199.1481; found, 199.1486.

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with 3-buten-1-ol *tert*-butyldimethylsilyl ether (Entry 4 in Table 3). A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (13.8 mg, 0.05 mmol, 10 mol%) and PCy_2Ph (13.7 mg, 0.05 mmol, 10 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at rt. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at rt. $P(OPh)_3$ (13.1 μL, 0.05 mmol, 10 mol%), triethylamine (418 μL, 3 mmol, 6 equiv), 3-buten-1-ol *tert*-butyldimethylsilyl ether[16] (573 μL, 2.5 mmol, 5 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 16 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford a mixture of **4d** and 3-buten-1-ol *tert*-butyldimethylsilyl ether, which were found to be inseparable from each other. The mixture was dissolved in MeOH(3 mL), and 12N HCl aq. (ca. 100 mg) was added at rt. The mixture was stirred for 10 min at rt, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford (E)-3-methylene-6-phenylhex-5-en-1-ol (78.0 mg, 83% yield in 2 steps).



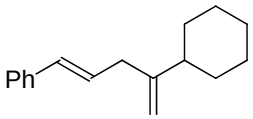
(E)-3-Methylene-6-phenylhex-5-en-1-ol. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 7.34-7.38 (m, 2H), 7.27-7.32 (m, 2H), 7.18-7.23 (m, 1H), 6.43 (d, J = 15.8 Hz, 1H), 6.20 (dt, J = 15.8, 7.1 Hz, 1H), 4.97 (d, J = 1.4 Hz, 1H), 4.91 (s, 1H), 3.75 (t, J = 6.3 Hz, 2H), 2.94 (d, J = 7.0 Hz, 2H), 2.35 (t, J = 6.4 Hz, 2H), 1.55 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 144.6, 137.3, 131.8, 128.5, 127.6, 127.1, 126.0, 113.0, 60.3, 39.6, 39.0; IR (NaCl

[16] Ferrié, L.; Reymond, S.; Capdevielle, P.; Cossy, J. *Org. Lett.* **2007**, *9*, 2461.

plate, thin film, cm^{-1}): 3352, 3080, 3026, 2888, 1644, 1598, 1495, 1448, 1046, 967, 896, 741, 692; HRMS-ESI (m/z): $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$, 211.1093; found, 211.1098.

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with vinylcyclohexane (Entry 6 in Table 3).

A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at rt. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at rt. Triethylamine (418 μL, 3 mmol, 6 equiv) and vinylcyclohexane (342 μL, 2.5 mmol, 5 equiv) were added in that order. TESOTf (198 μL, 0.875 mmol, 1.75 equiv) was then added over 4 h by using a syringe pump. The mixture was stirred at rt for another 12 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **4f** (72.4 mg, 64% yield). Inseparable regioisomers are included (<10% yield) in the reported yield. In GC-MS analysis, major two peaks are detected, both of which has molecular weight of 226 (About the analysis conditions, see Figure 2 shown below). One of them corresponds to the desired 1,4-skipped diene, and the other peak is unambiguously attributable to (E)-(5-cyclohexylidenepent-1-enyl)benzene by comparison with the authentic sample which was synthesized via the route shown below (Scheme 2).



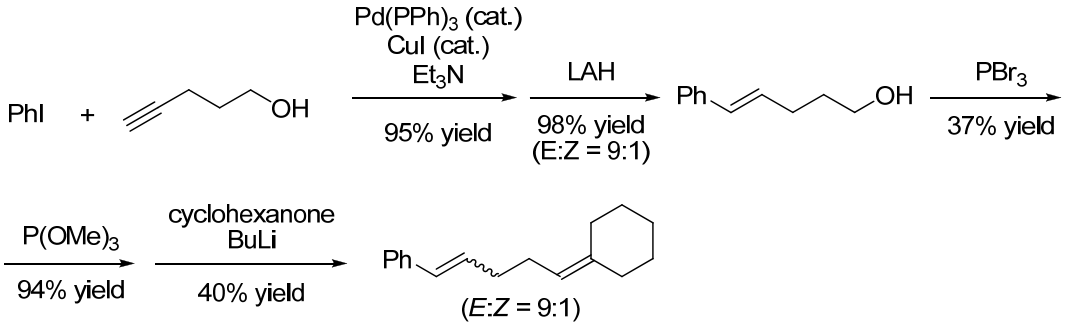
(E)-(4-Cyclohexylpenta-1,4-dienyl)benzene. ^1H NMR (500 MHz, $CDCl_3$, δ): 7.33-7.38 (m, 2H), 7.27-7.31 (m, 2H), 7.17-7.22 (m, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.21 (dt, *J* = 15.8, 7.1 Hz, 1H), 4.80 (s, 1H), 4.76 (d, *J* = 1.5 Hz, 1H), 2.93 (d, *J* = 7.0 Hz, 2H), 1.10-1.93 (m, 11H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): 153.8, 137.7, 131.1, 128.9, 128.5, 126.9, 126.0, 108.4, 44.1, 38.6, 32.3, 26.7, 26.4; IR (NaCl plate, thin film, cm^{-1}): 3081, 3025, 2925, 2851, 1639, 1495, 1448, 965, 887, 742, 691; HRMS-EI (m/z): $[M]^+$ calculated for $C_{17}H_{22}$, 226.1716; found, 226.1711.

Experimental Procedure for Nickel-Catalyzed Reaction of Cinnamyl Methyl Carbonate with styrene (Entry 7 in Table 3).

A test tube (borosilicate glass, 16 x 100 mm) and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (27.5 mg, 0.1 mmol, 20 mol%) and PCy_2Ph (54.9 mg, 0.2 mmol, 40 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (0.5 mL) under argon and stirred for 15 min at rt. Cinnamyl methyl carbonate (96.1 mg, 0.5 mmol, 1 equiv) was added, and the mixture was stirred for 30 min at rt. Triethylamine (418 μL, 3 mmol, 6 equiv) and styrene (286 μL, 2.5 mmol, 5 equiv) and TESOTf (198 μL, 0.875 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 18 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1). The solvents were removed under reduced pressure and the crude mixture was purified by silica gel column chromatography, to afford **7**[17] (27.7 mg, 25% yield).

Synthesis of (E)-(5-cyclohexylidenepent-1-enyl)benzene.

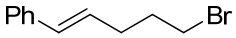
Scheme 2.



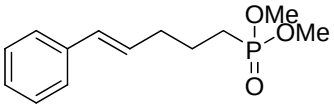
To a solution of 5-phenylpent-4-en-1-ol[18] (550 mg, 3.39 mmol, 1 equiv, *E*:*Z* = 9:1) in DCM (10 mL) was added PBr_3 (319 μL, 3.39 mmol, 1 equiv) over 30 min. The reaction mixture was stirred for 2 h at rt, then $NaHCO_3$ aq. was added at 0 ^oC. The organic layer was partitioned, extracted with DCM, and concentrated *in vacuo*. The

[17] Matsuhashi, H.; Asai, S.; Hirabayashi, K.; Hatanaka, Y.; Mori, A.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1943.
[18] Seiders, II, J.; Wang, L.; Floreancig, P. E. *J. Am. Chem. Soc.* **2003**, *125*, 2406.

crude mixture was purified by silica gel column chromatography, to afford (5-bromopent-1-enyl)benzene (280.7 mg, 37% yield, *E*:*Z* = 9:1).
A mixture of (5-bromopent-1-enyl)benzene (114.2 mg, 0.51 mmol, *E*:*Z* = 9:1) and $P(OMe)_3$ (10 mL) was heated for 62 h under reflux. The reaction mixture was cooled to rt, concentrated *in vacuo*, and purified by silica gel column chromatography, affording dimethyl 5-phenylpent-4-enylphosphonate (121.3 mg, 94% yield, *E*:*Z* = 9:1).
To a solution of dimethyl 5-phenylpent-4-enylphosphonate (20 mg, 0.08 mmol, 1 equiv, *E*:*Z* = 9:1) in THF (0.32 mL) was added n-BuLi (2.5 M hexane solution, 35 μL, 1.1 equiv) at -78 ^{o}C. The reaction mixture was stirred for 10 min at -78 ^{o}C, then cyclohexanone (9 μL, 0.088 mmol, 1.1 equiv) was added to the mixture. After stirred for 5 min at -78 ^{o}C, the reaction mixture was allowed to warm to rt and stirred for 22 h at rt. Concentration of the reaction mixture, followed by purification on silica gel column chromatography afforded (5-cyclohexylidenepent-1-enyl)benzene (7.2 mg, 40% yield, *E*:*Z* = 9:1).

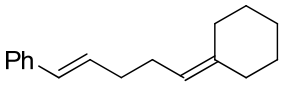


(5-Bromopent-1-enyl)benzene. ^{1}H NMR (500 MHz, $CDCl_3$, δ): **(*E*):** 7.16-7.36 (m, 5H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.16 (dt, *J* = 15.9, 7.0 Hz, 1H), 3.45 (t, *J* = 6.7 Hz, 2H), 2.38 (dq, *J* = 1.4, 7.1 Hz, 2H), 2.03 (quint, *J* = 6.8 Hz, 2H); **(*Z*):** Distinguishable peaks are shown. 5.61 (dt, *J* = 11.6, 7.3 Hz, 1H), 3.41 (t, *J* = 6.9 Hz, 2H), 2.48 (dq, *J* = 1.8, 7.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, δ): **(*E*):**137.4, 131.3, 128.5, 128.4, 127.1, 126.0, 33.2, 32.2, 31.3; **(*Z*):** Distinguishable peaks are shown. 130.5, 130.2, 128.7, 128.2, 126.7, 33.1, 32.9, 27.2; IR (NaCl plate, thin film, cm^{-1}): 3080, 3058, 3025, 2932, 2844, 1597, 1492, 1447, 1265, 1241, 1072, 1028, 965, 741, 692, 561; HRMS-DART (m/z): $[M]^+$ calculated for $C_{11}H_{13}Br$, 224.0195; found, 224.0225.



(E)-Dimethyl 5-phenylpent-4-enylphosphonate. ^{1}H NMR (400 MHz, $CDCl_3$, δ): **(*E*):**7.18-7.38 (m, 5H), 6.40 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.9 Hz, 1H), 3.74 (d, *J* = 10.8 Hz, 6H), 2.30 (q, *J* = 6.8 Hz, 2H), 1.72-1.86 (m, 4H); **(*Z*):** Distinguishable peaks are shown. 6.48 (d, *J* = 11.4 Hz, 1H), 5.60 (dt, *J* = 7.3, 11.6 Hz, 1H), 3.71 (d, *J* = 10.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): **(*E*):**137.4, 131.2, 129.0, 128.5, 127.1, 126.0, 52.3 (d, *J* = 6.6 Hz), 33.5 (d, *J* = 17.1 Hz), 24.8, 23.3, 22.0 (d, *J* = 4.8 Hz); IR

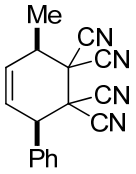
(NaCl plate, thin film, cm^{-1}): 3024, 2953, 2850, 1651, 1598, 1493, 1448, 1236, 1183, 1031, 967, 815, 746, 694. HRMS-DART (m/z): $[M+H]^+$ calculated for $C_{13}H_{19}O_3P$, 255.1145; found, 255.1147.



(5-Cyclohexylidenepent-1-enyl)benzene. ^1H NMR (500 MHz, $CDCl_3$, δ): **(*E*):**7.32-7.36 (m, 2H), 7.26-7.30 (m, 2H), 7.16-7.20 (m, 1H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.5 Hz, 1H), 5.12 (t, *J* = 7.2 Hz, 1H), 2.20-2.26 (m, 2H), 2.11-2.20 (m, 4H), 2.06-2.10 (m, 2H), 1.44-1.56 (m, 6H); **(*Z*):** Distinguishable peaks are shown. 5.67 (dt, *J* = 11.7, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): **(*E*):**140.3, 137.9, 130.7, 129.8, 128.4, 126.7, 125.9, 120.3, 37.1, 33.6, 28.8, 28.7, 27.8, 27.0, 26.9; IR (NaCl plate, thin film, cm^{-1}): 3025, 2925, 2852, 1598, 1494, 1446, 962, 742, 691. HRMS-DART (m/z): $[M-H]^+$ calculated for $C_{17}H_{21}$, 225.1638; found, 225.1646.

Gram-Scale Allylic Substitution Reaction of Ethylene (Scheme 1).

A round-bottomed flask and a stir bar were oven-dried and brought into a glove box. $Ni(cod)_2$ (68.8 mg, 0.25 mmol, 2.5 mol%) and P(*o*-anisyl)$_3$ (352 mg, 1 mmol, 10 mol%) were added to the flask, which was sealed with a septum, and brought out of the glove box and connected to an argon line. The catalyst mixture was dissolved in toluene (50 mL) under argon and stirred for 15 min at rt. The reaction mixture was purged with ethylene for 1 min to remove argon, taken care not to introduce oxygen. The ethylene atmosphere was maintained with an ethylene balloon. Triethylamine (8.4 mL, 60 mmol, 6 equiv), cinnamyl methylcarbonate (10 mmol, 1 equiv) and TESOTf (4.0 mL, 17.5 mmol, 1.75 equiv) were added in that order. The mixture was stirred at rt for 2 h. The mixture was then filtered through a plug of silica gel, and washed with a mixture of hexane-EtOAc (1/1 v/v). The solvents were removed under reduced pressure and the crude mixture was dissolved in benzene (50 mL). Tetracyanoethylene (256 mg, 20 mol%) was added to the reaction mixture, and the reaction mixture was kept stirred for 30 min at rt. After evaporation of the solvent, the crude mixture was purified by silica gel column chromatography, to afford **2a** (1.18 g, >98% purity, 81% yield) along with **12** (134.8 mg, 5% yield). The inseparable impurity was (**3Z)-3a** (<2% yield).



3-Methyl-6-phenylcyclohex-4-ene-1,1,2,2-tetracarbonitrile. Mp. 128-129 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44-7.51 (m, 5H), 6.10 (ddd, *J* = 2.8, 3.6, 10.6 Hz, 1H), 6.00 (dt, *J* = 10.6, 2.1 Hz, 1H), 4.29 (q, *J* = 2.5 Hz, 1H), 3.28-3.37 (m, 1H), 1.73 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 132.8, 130.2, 129.8, 129.2, 128.6, 124.5, 111.6, 111.3, 110.0, 109.7, 46.6, 42.9, 42.8, 37.5, 17.8; IR (NaCl plate, thin film, cm^{-1}): 3036, 2098, 2255, 1495, 1455, 1393, 1379, 1219, 1169, 1115, 1031, 911, 823, 753, 735, 702. HRMS-DART (m/z): $[M+H]^+$ calculated for $C_{17}H_{12}N_4$, 273.1135; found, 273.1130.

GC-MS analysis

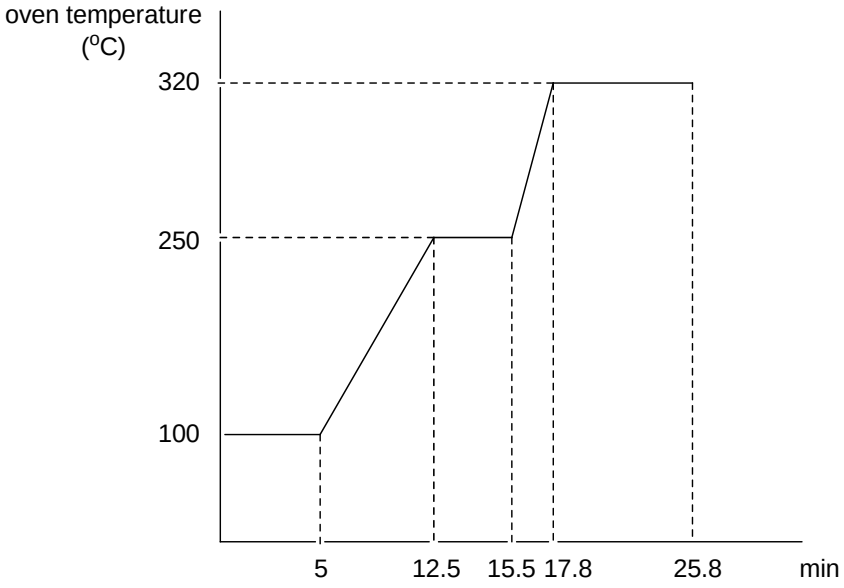


Figure 2. GC-MS analysis conditions.

In the chart of ASR product, three major peaks were observed at 10.3 min, 12.2 min, and 12.4 min. It was found that the peaks at 10.3 min, 12.2 min and 12.4 min are attributable to background, the desired 1,4-diene and a 1,5-diene, respectively.

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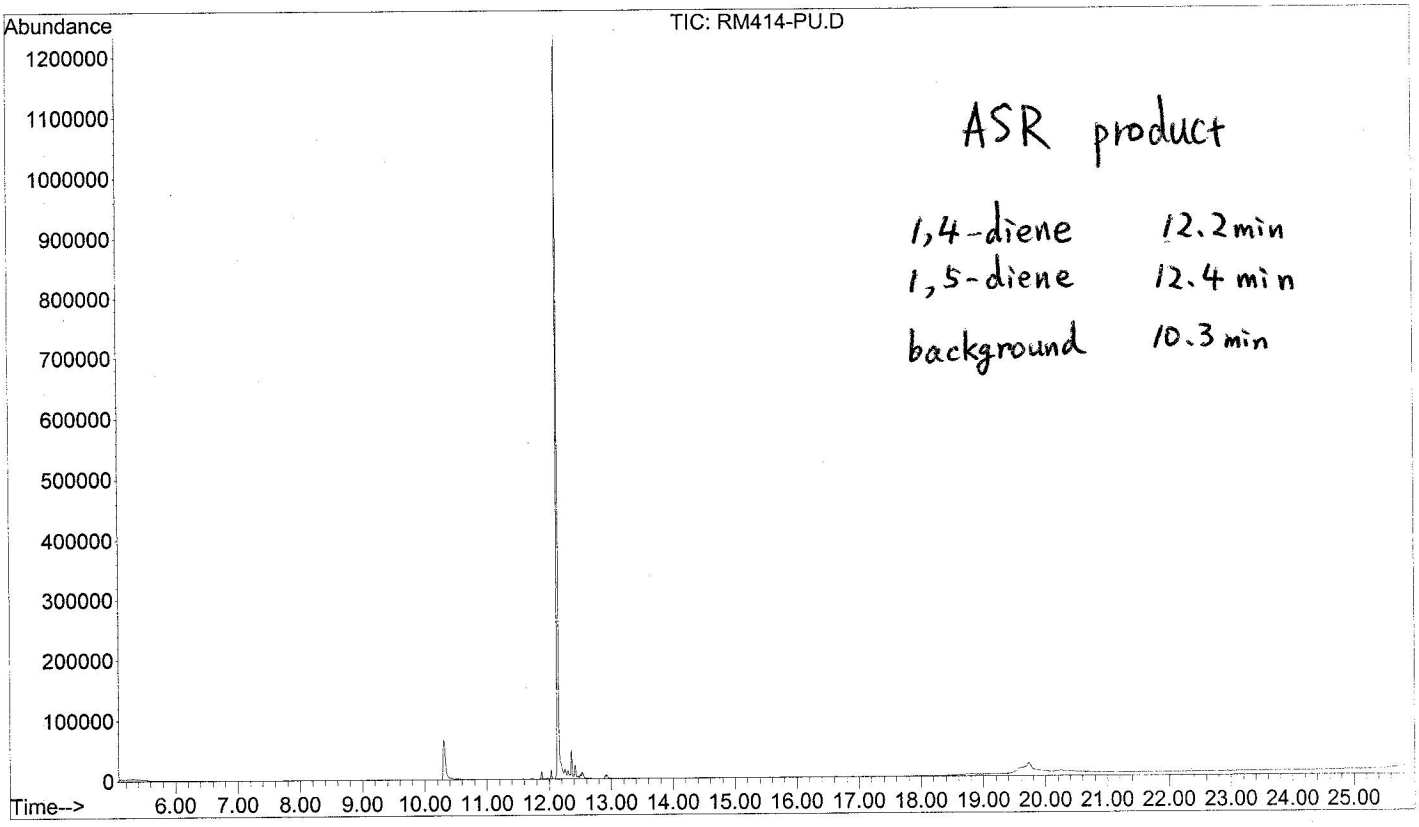
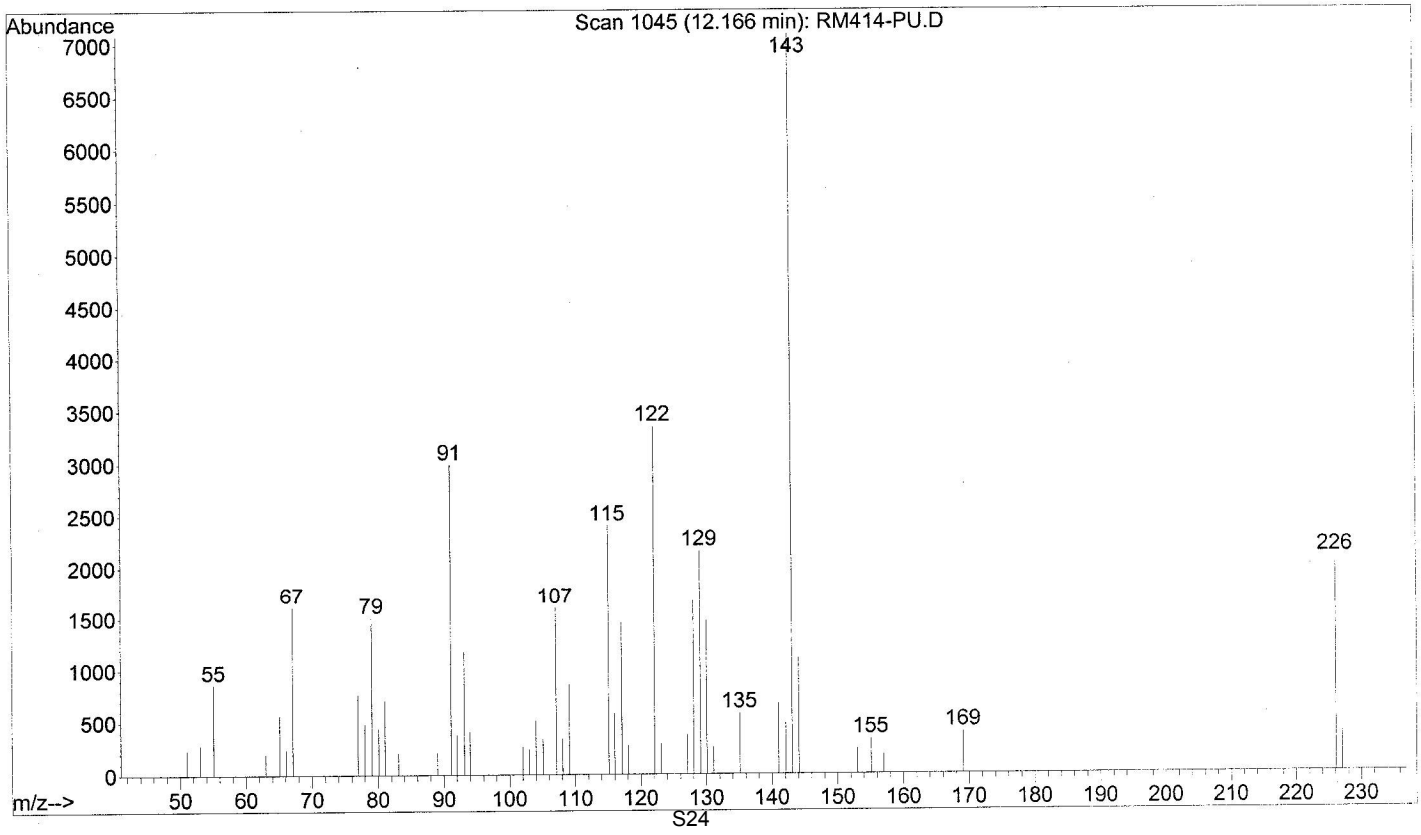


ASR product

1,4-diene 12.2 min
1,5-diene 12.4 min
background 10.3 min



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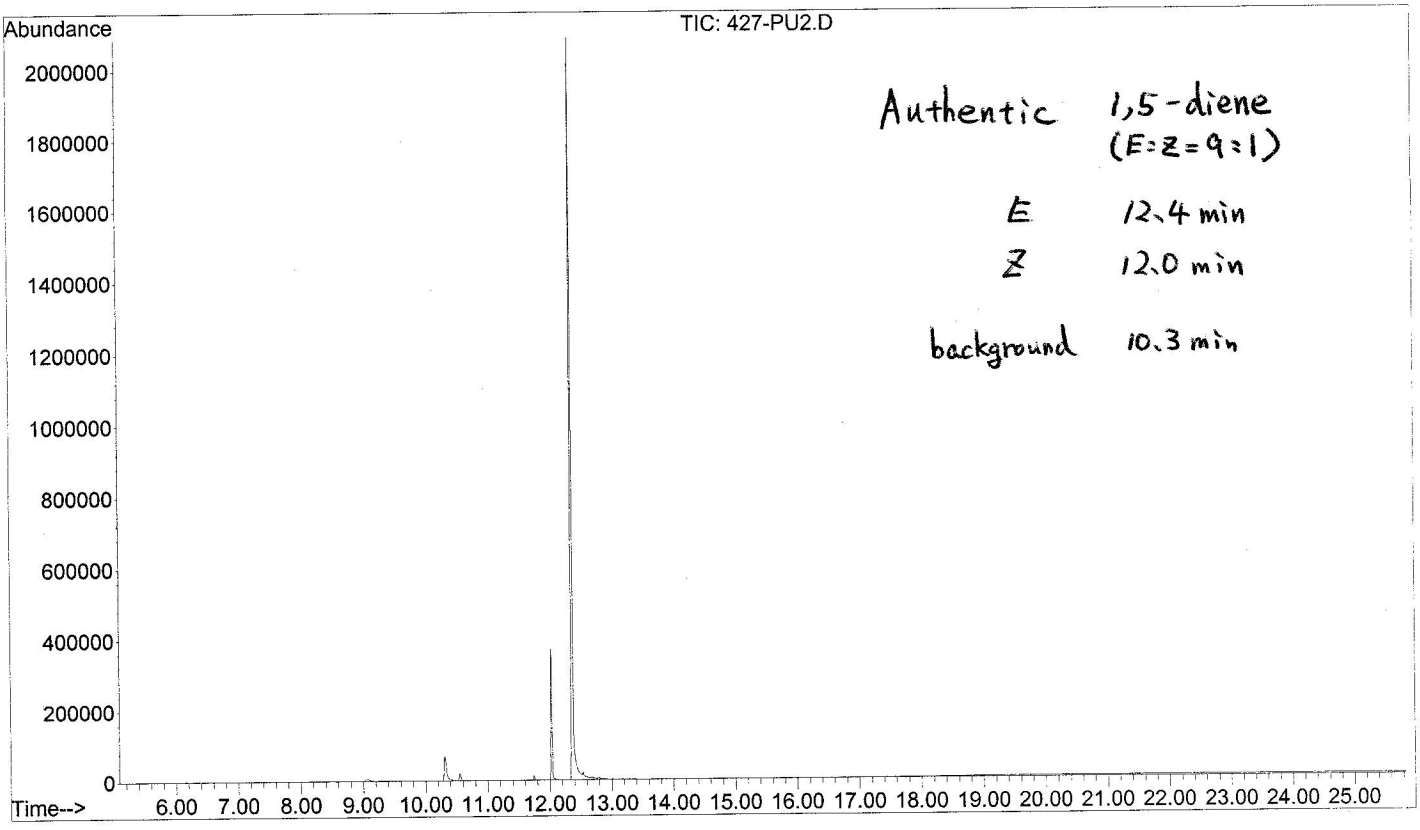

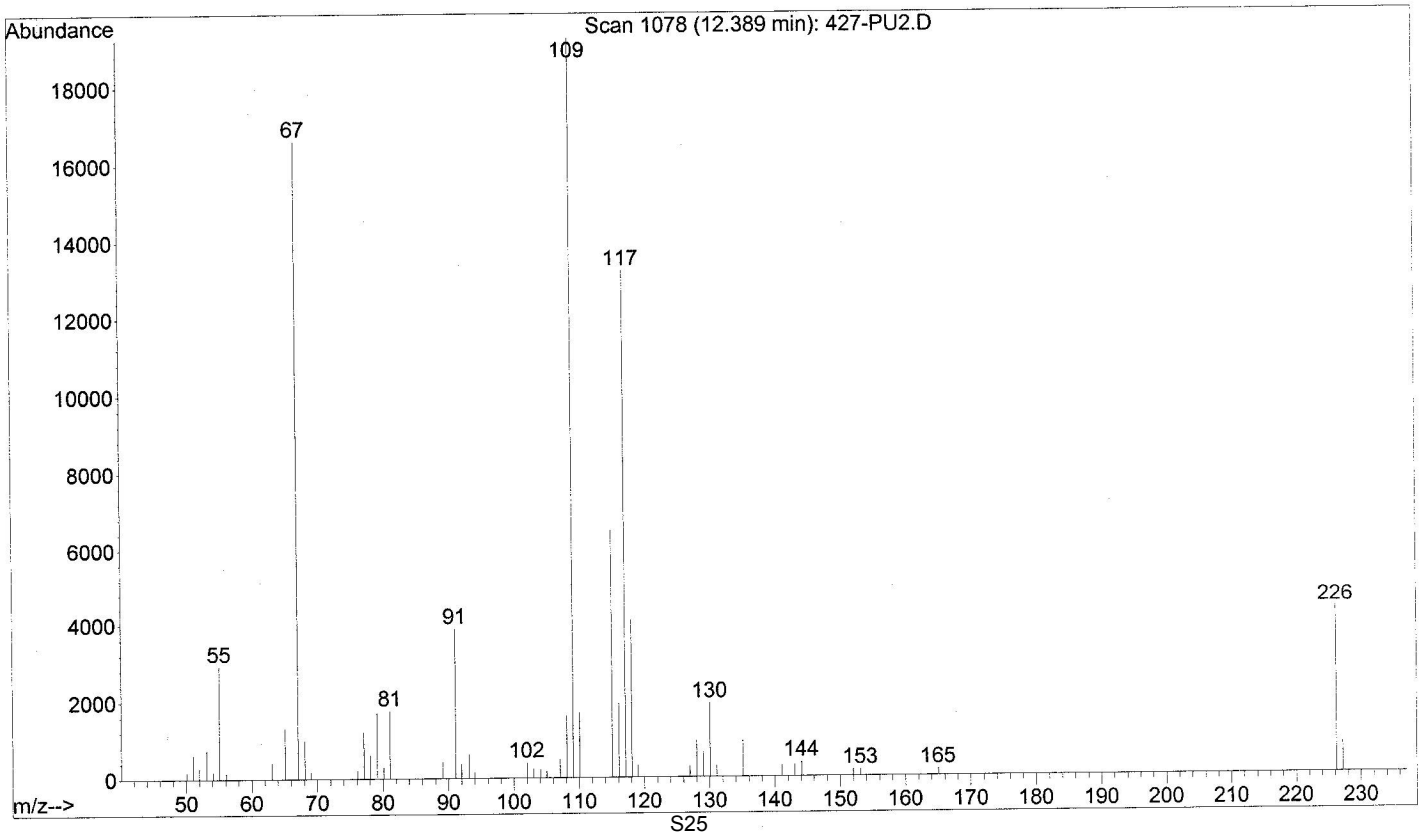

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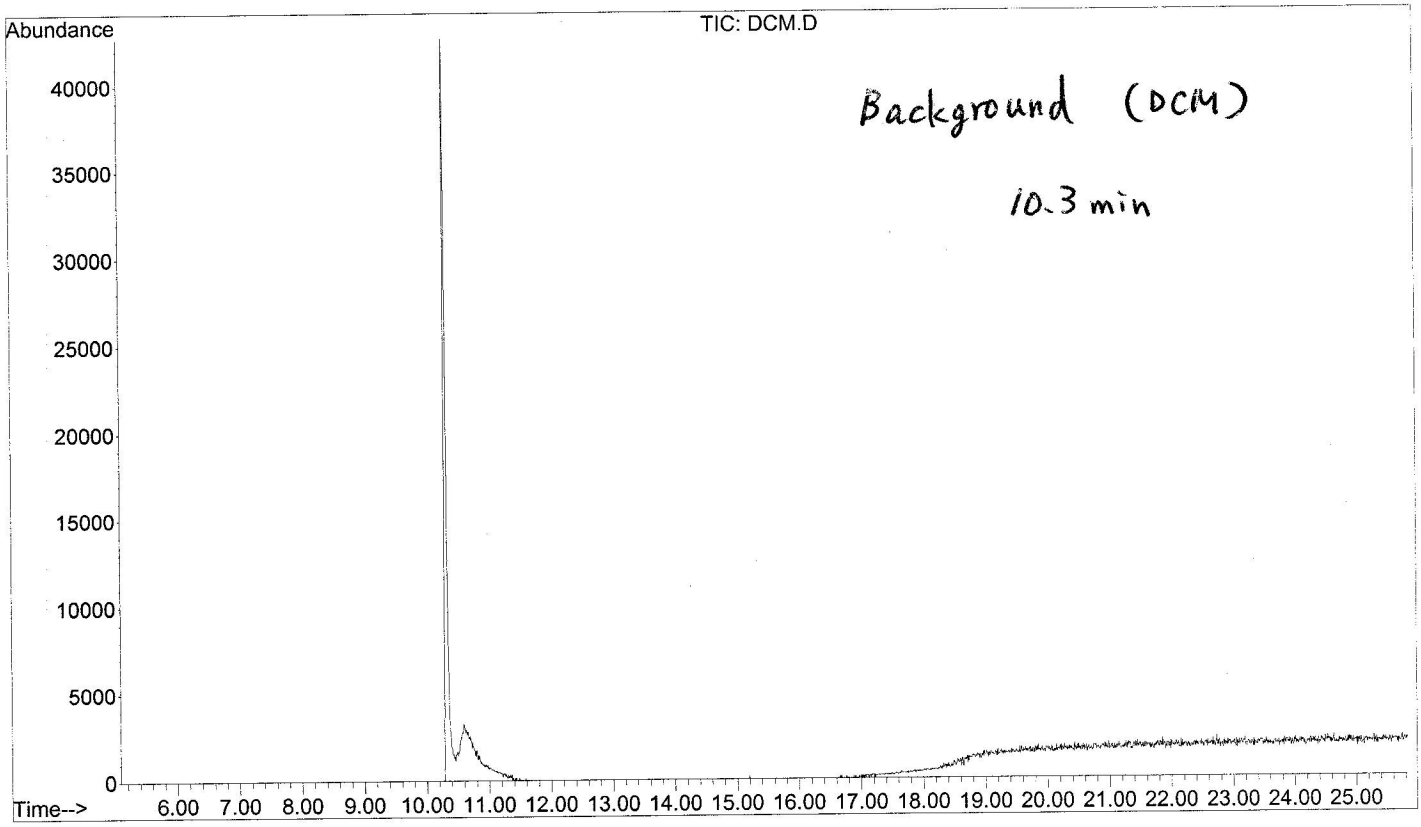

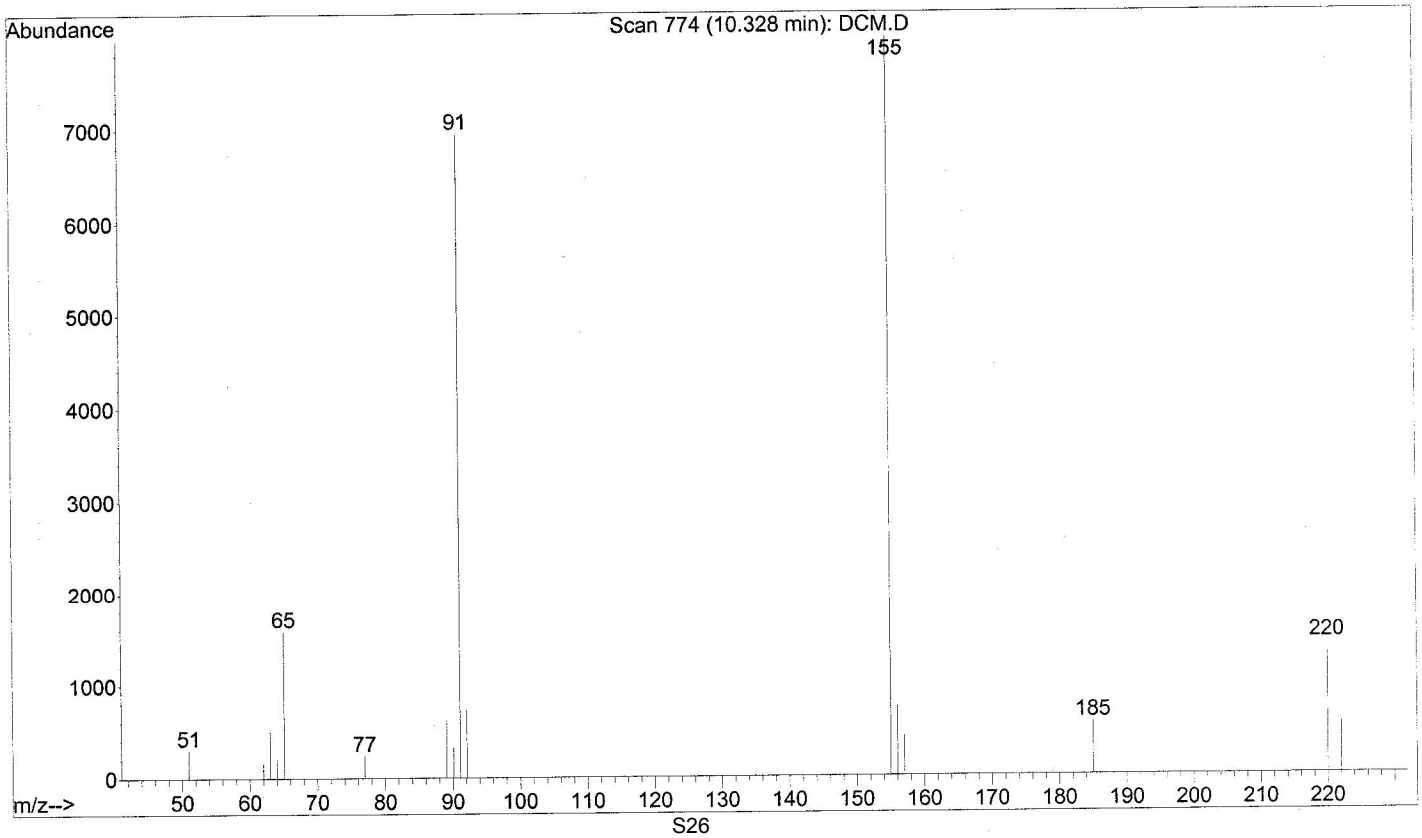

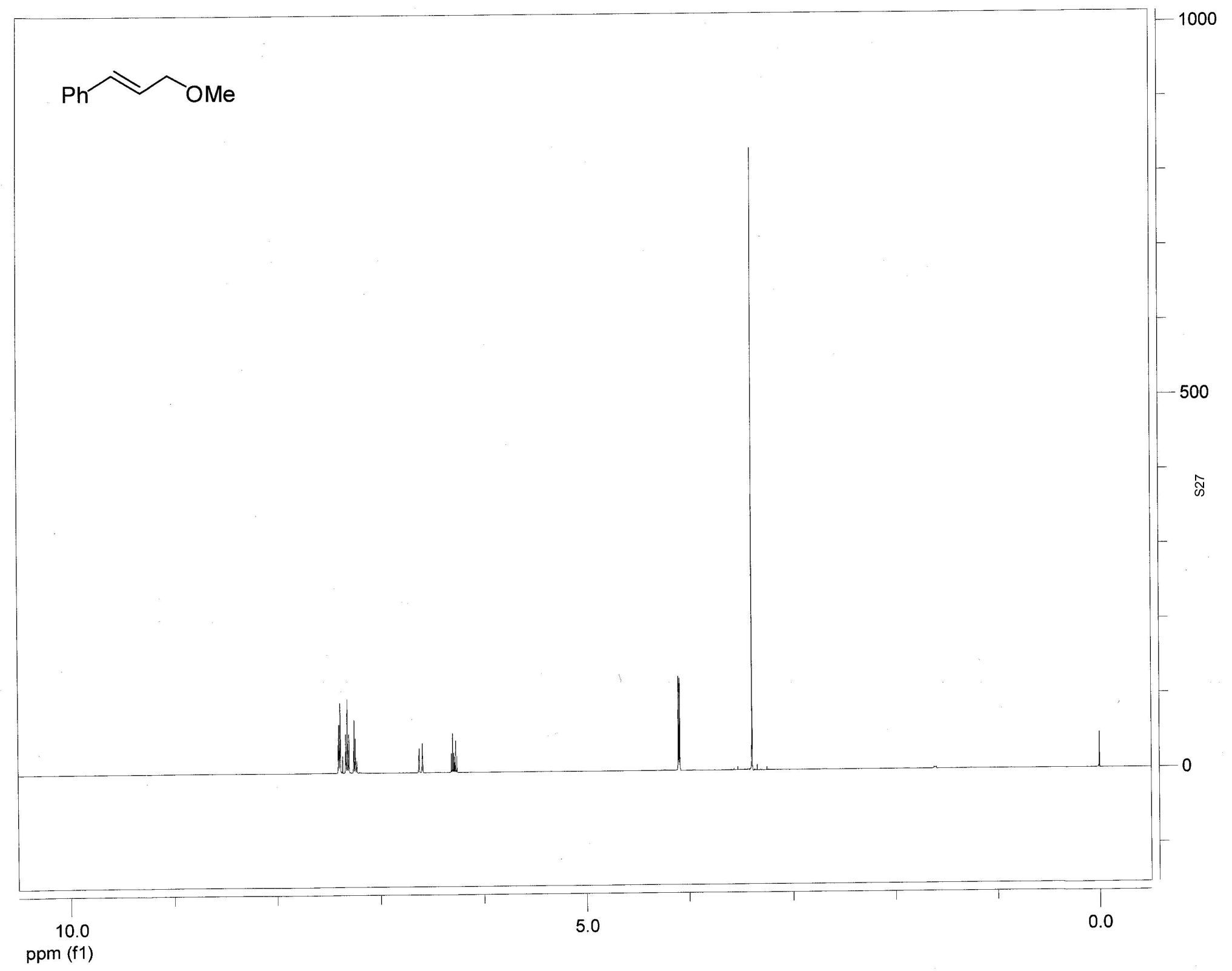
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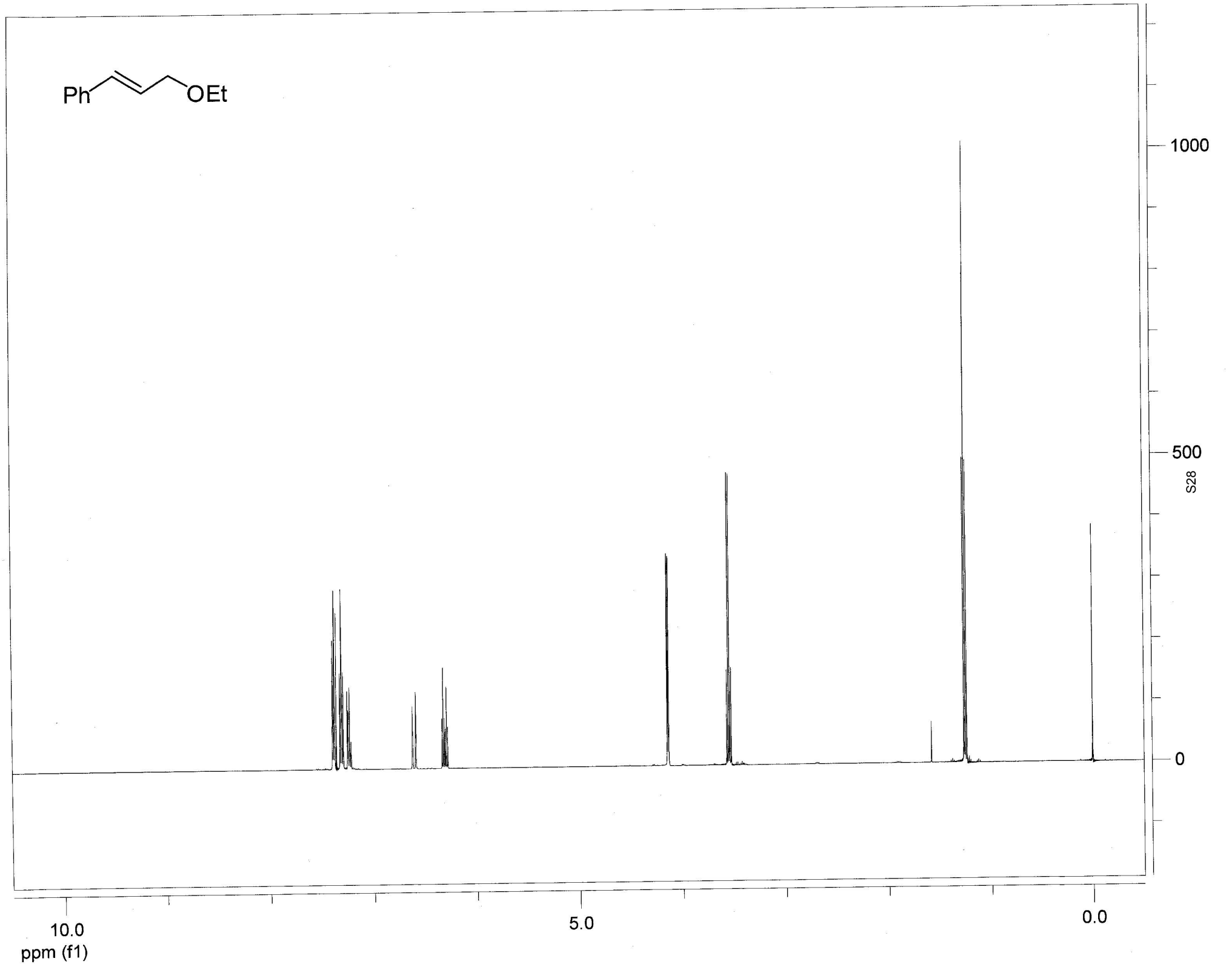
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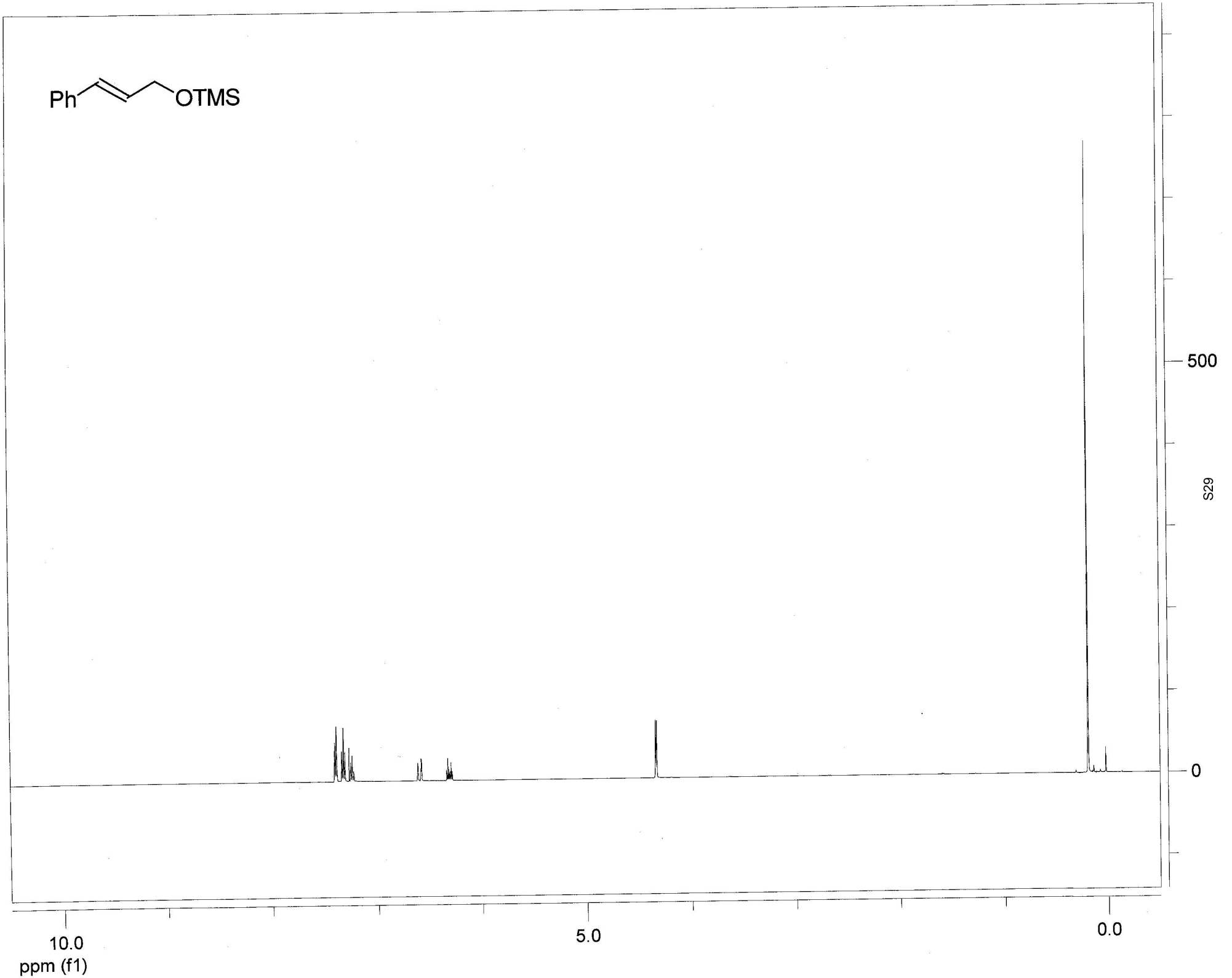
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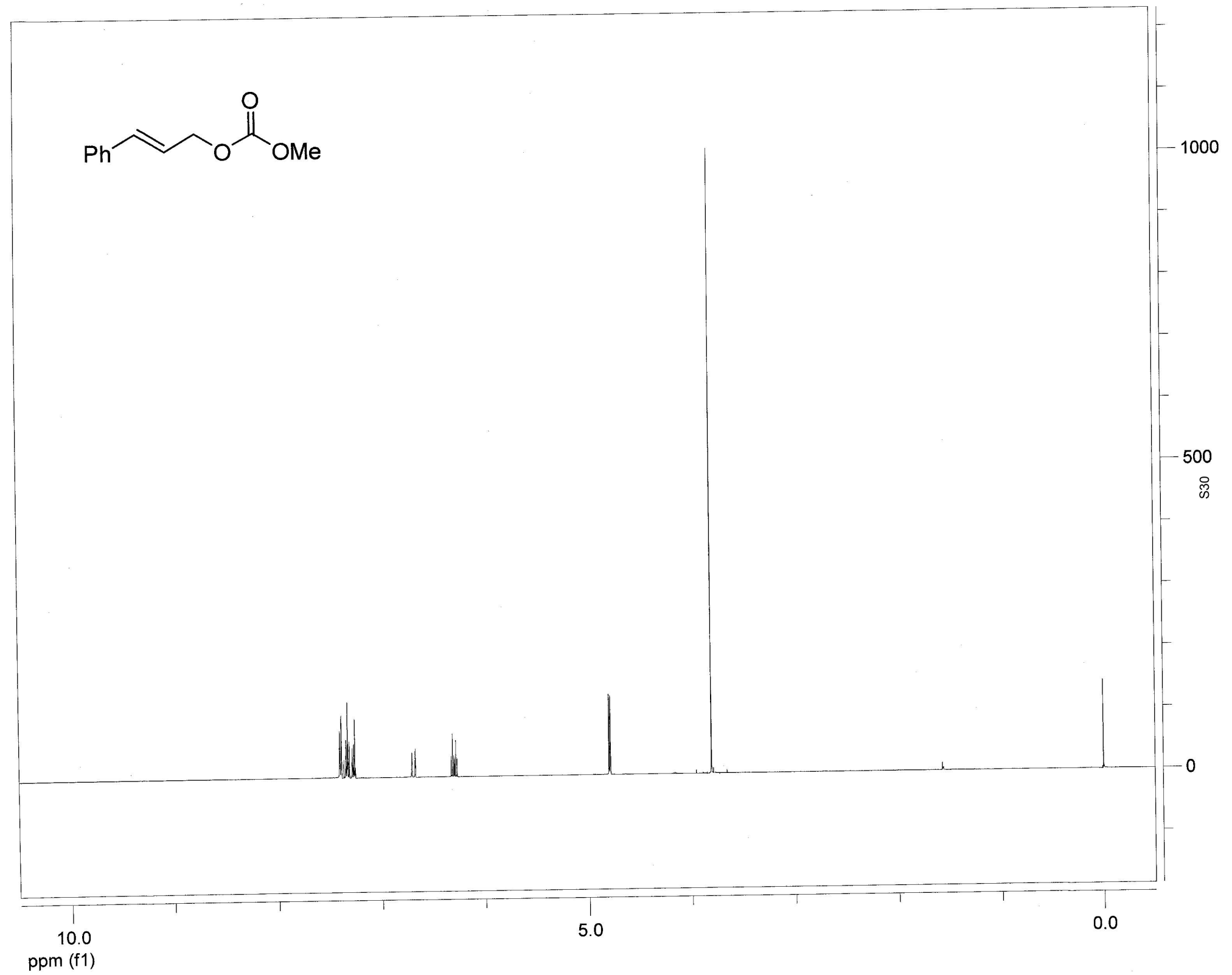
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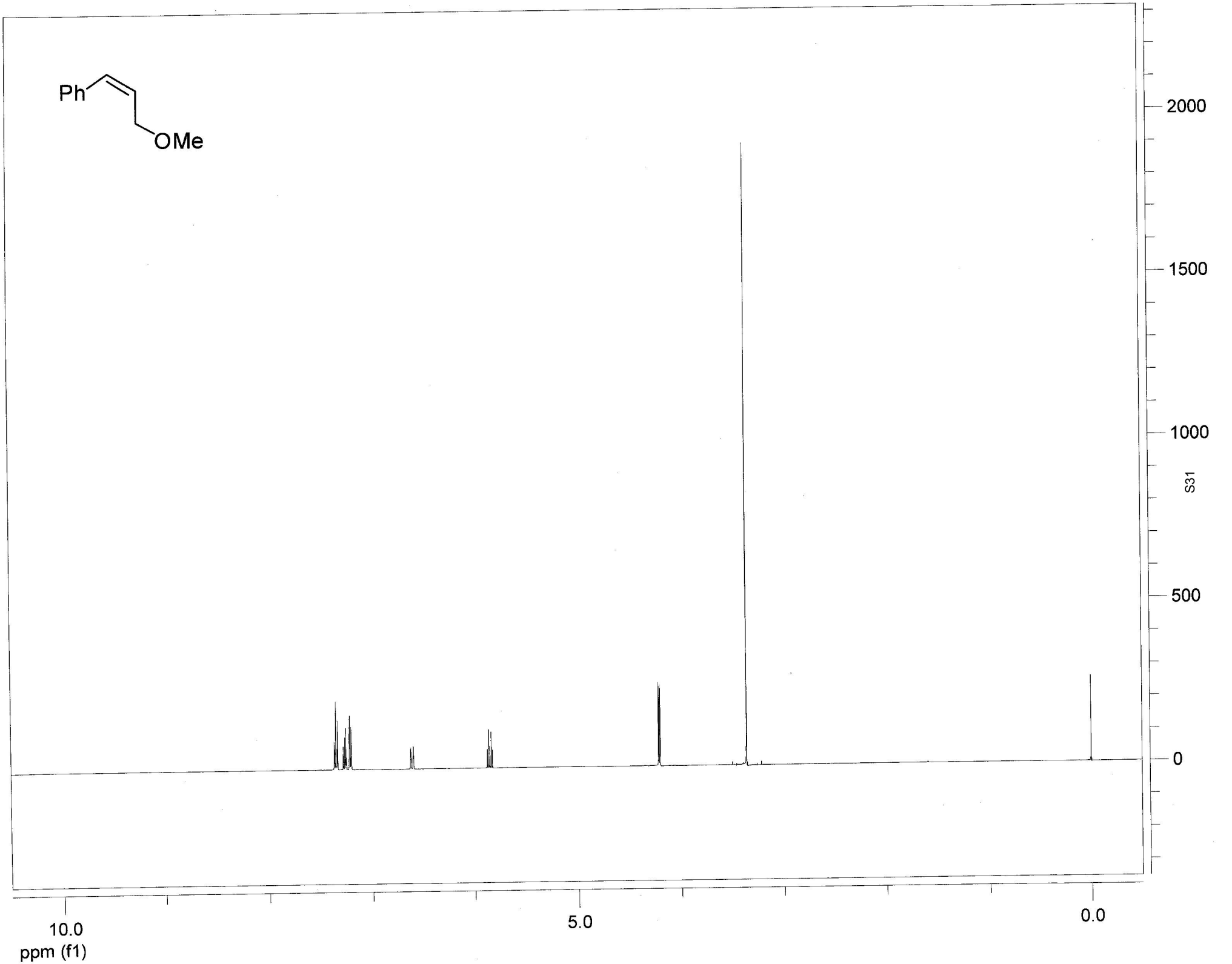
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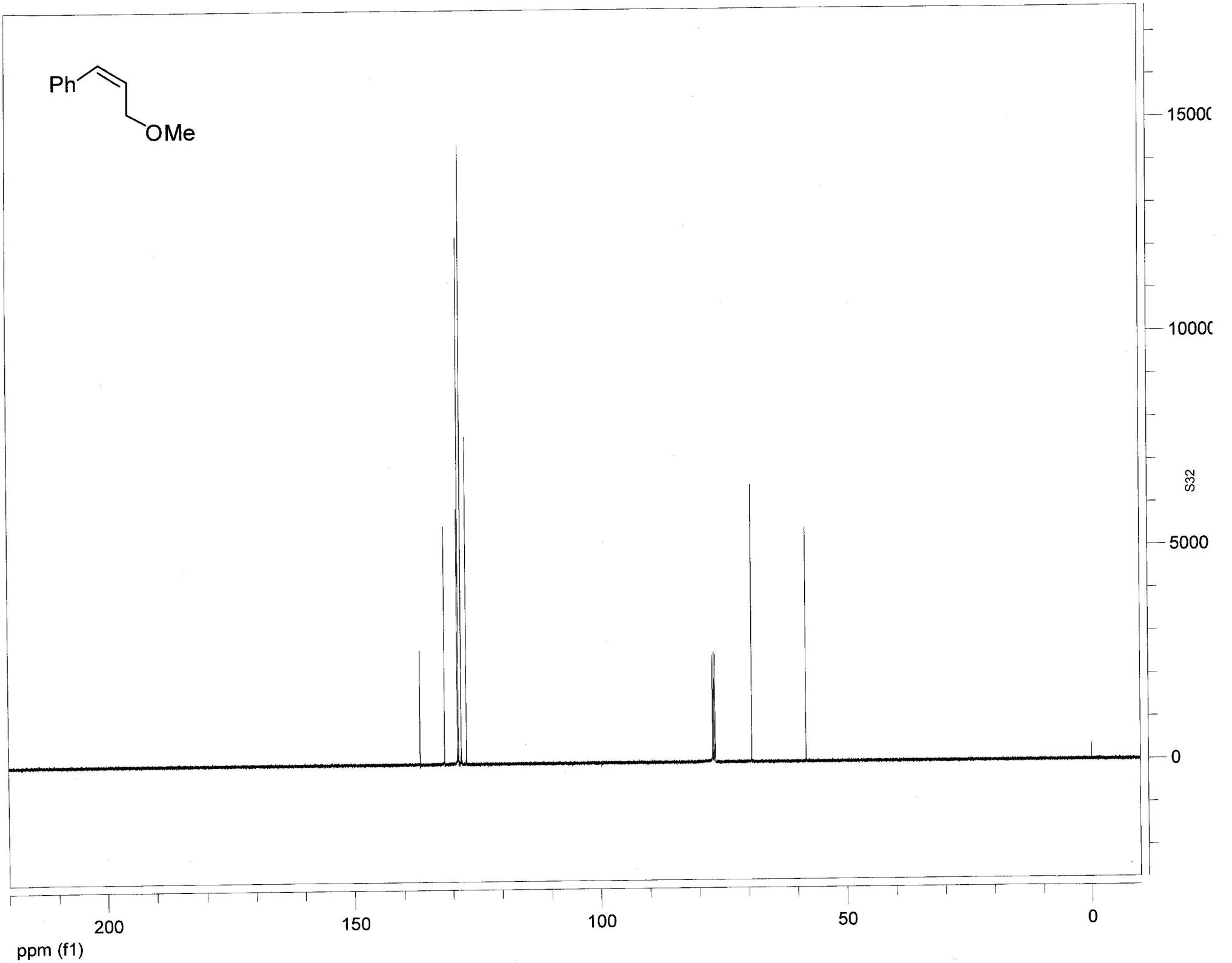
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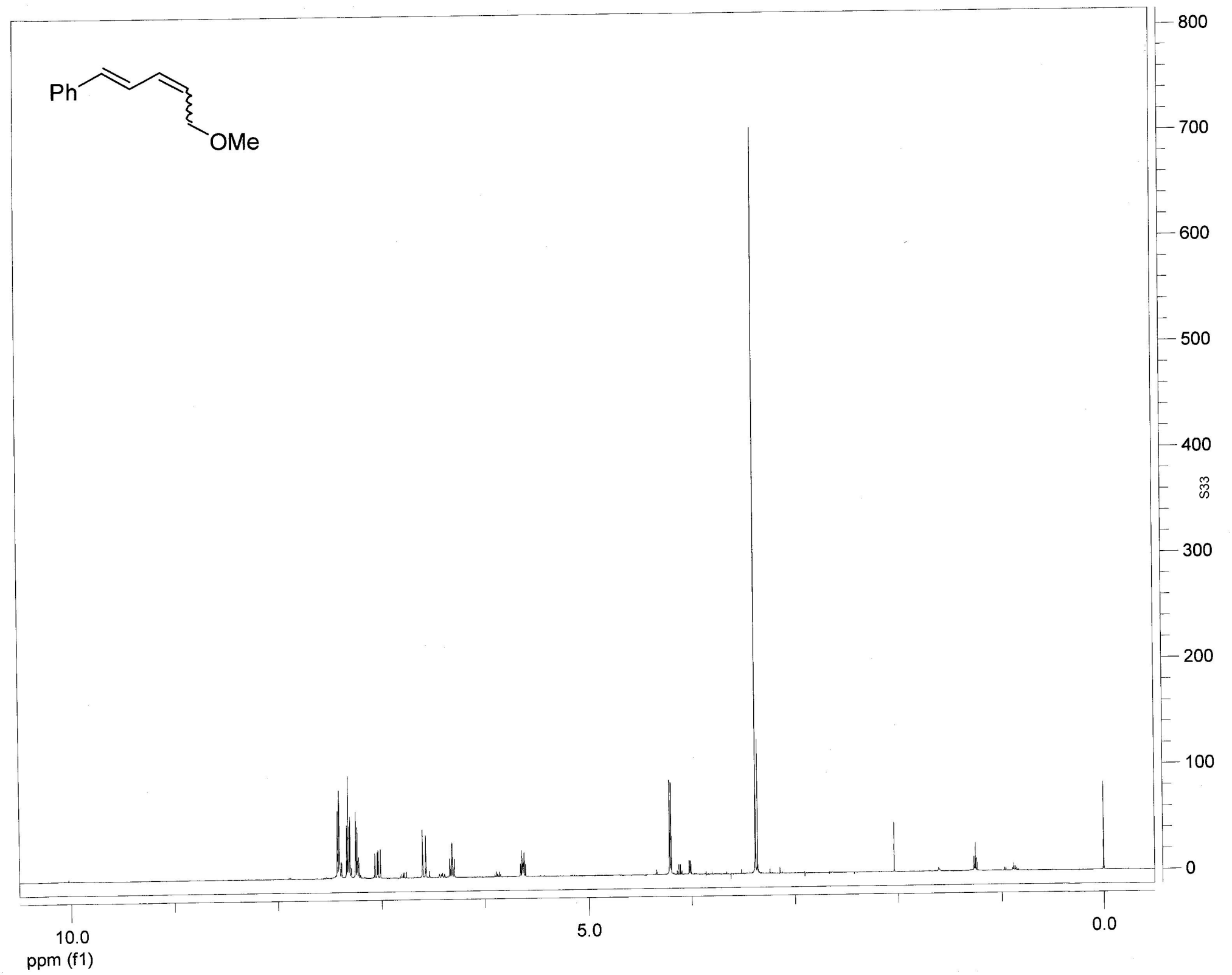
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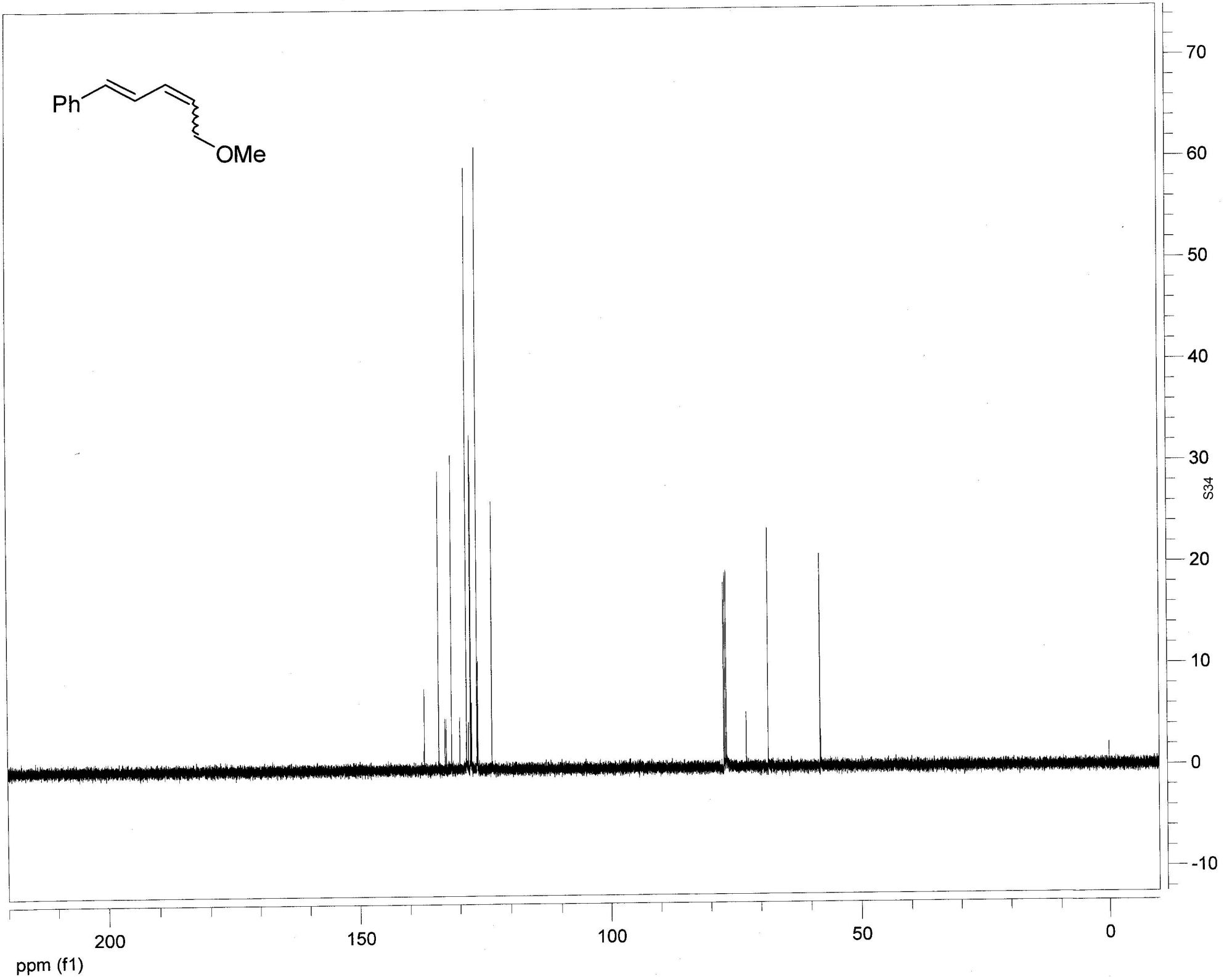
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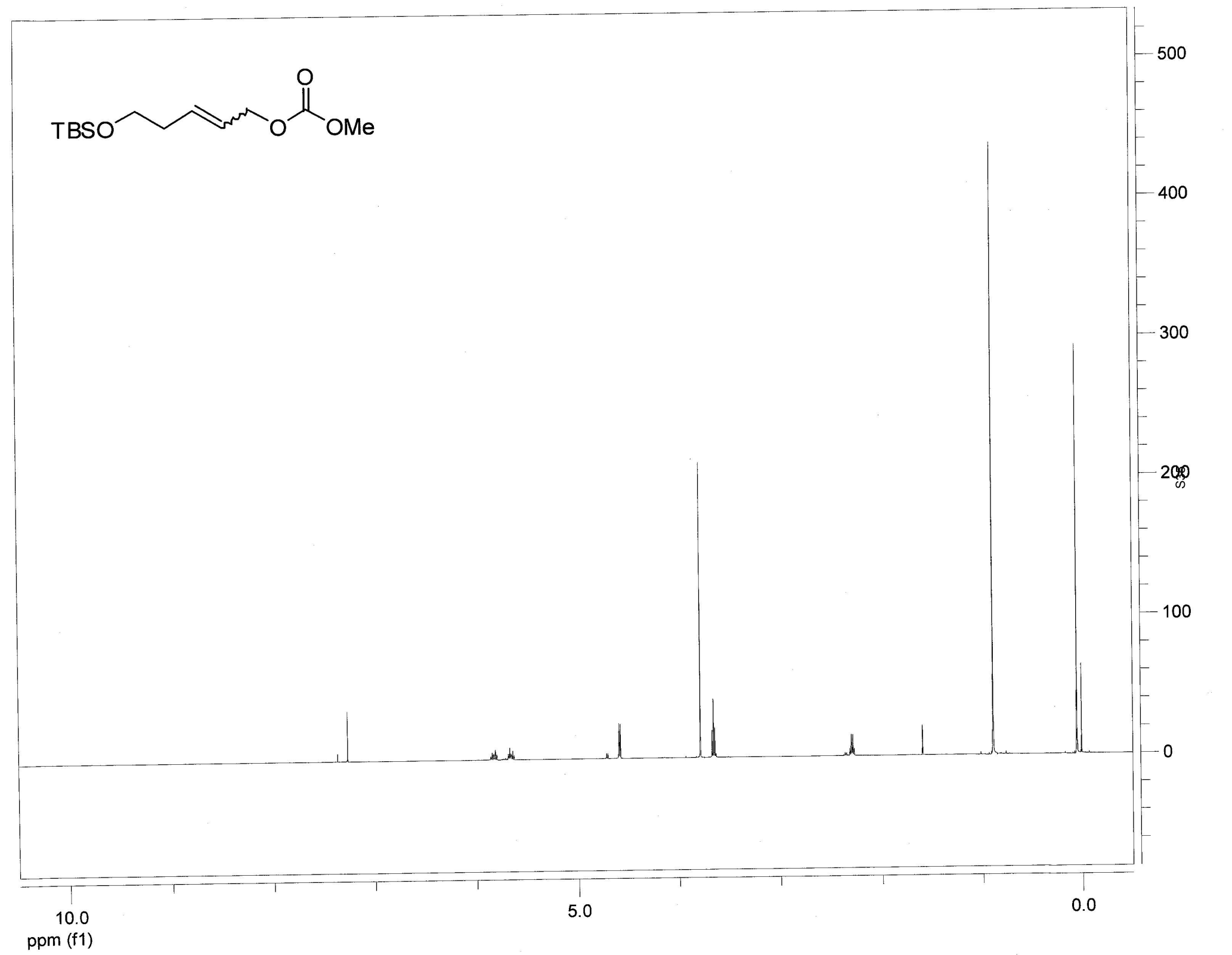
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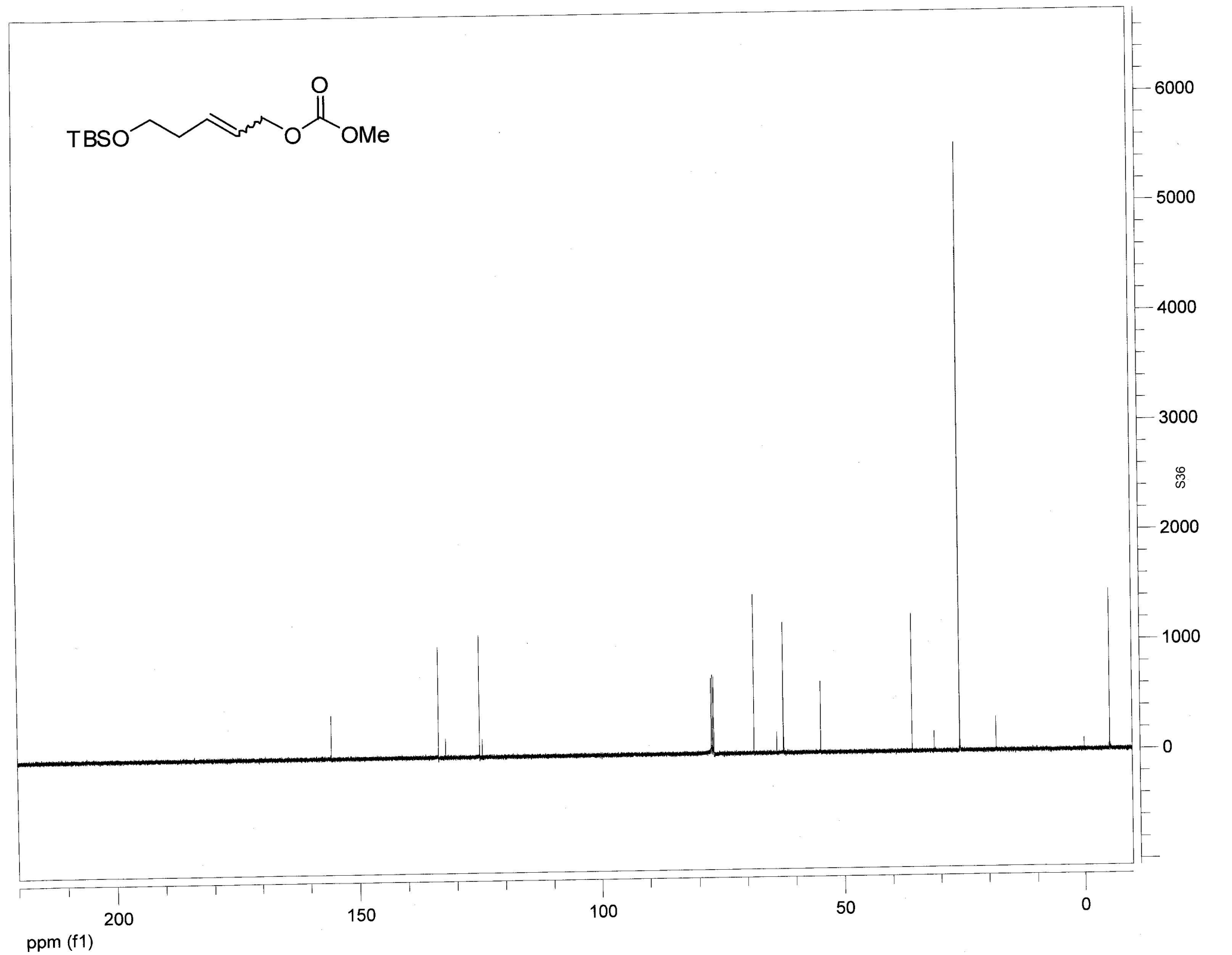
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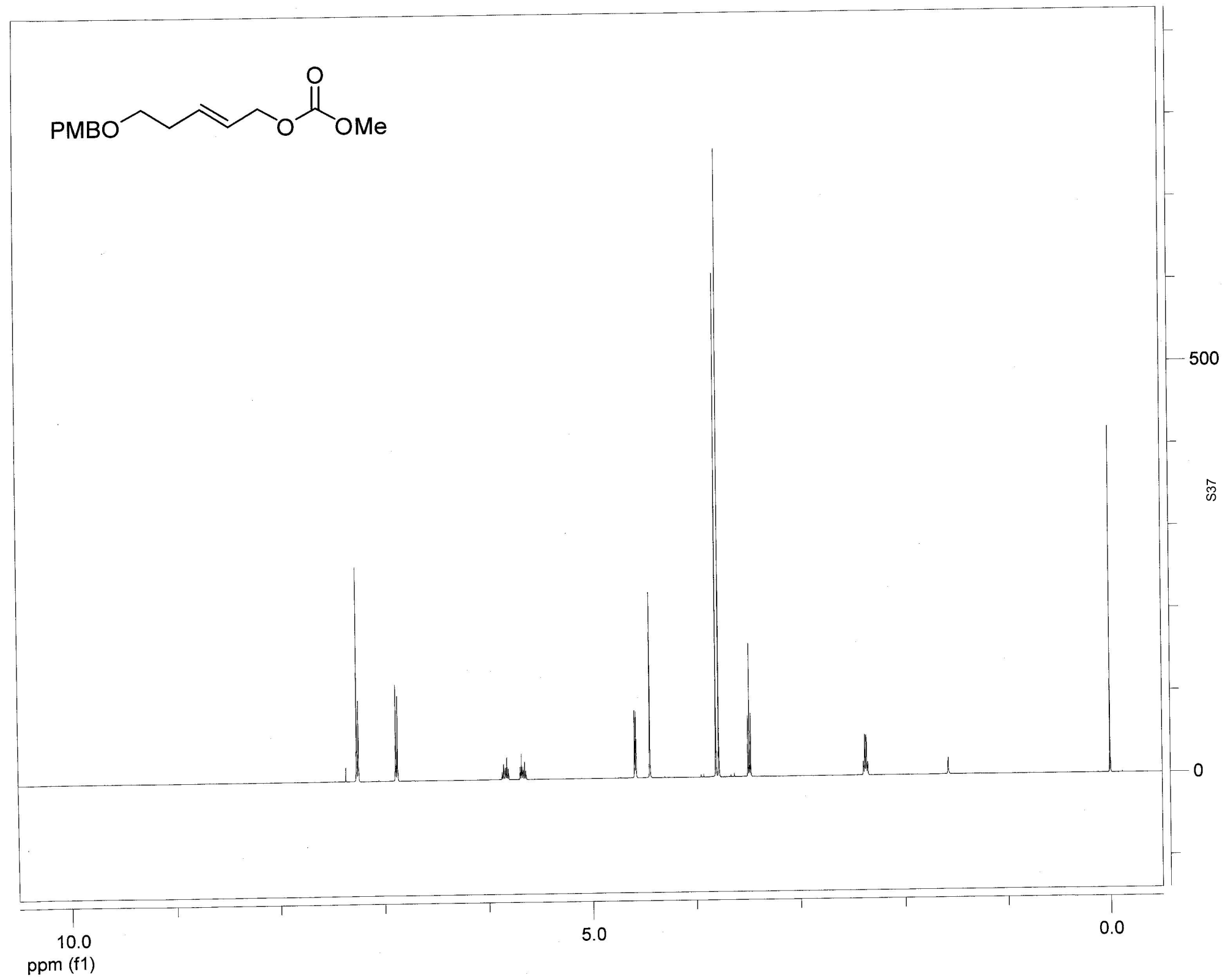
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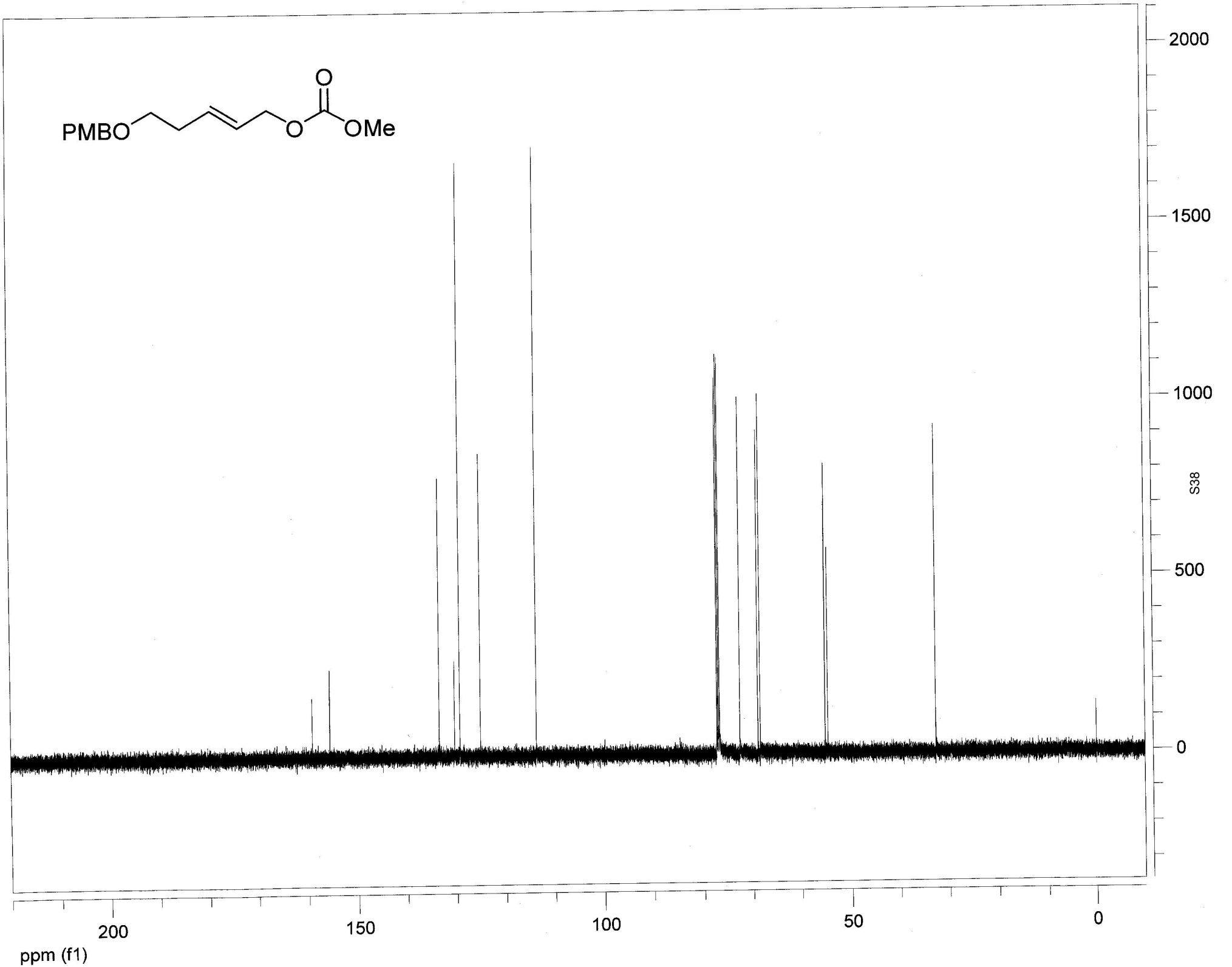
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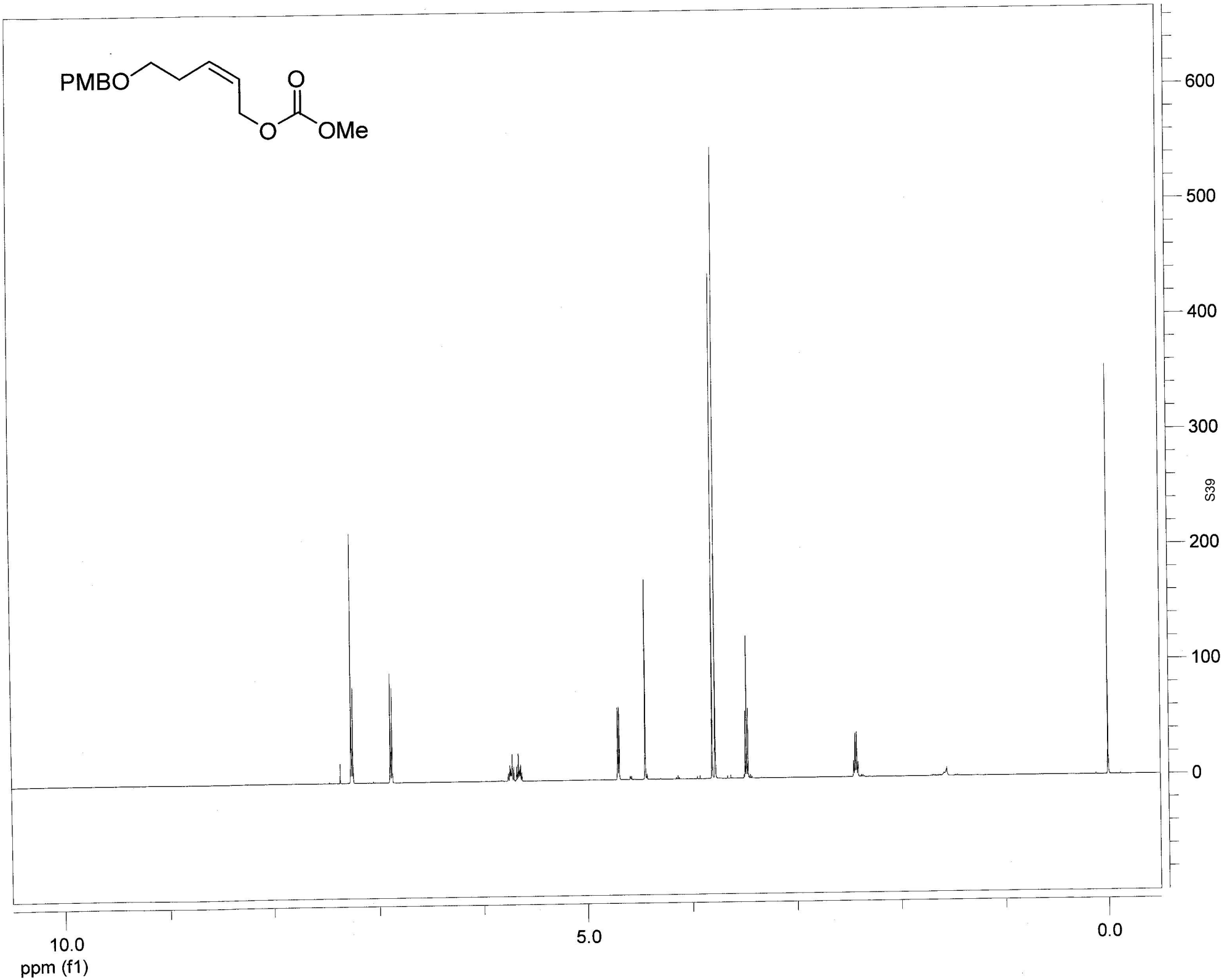
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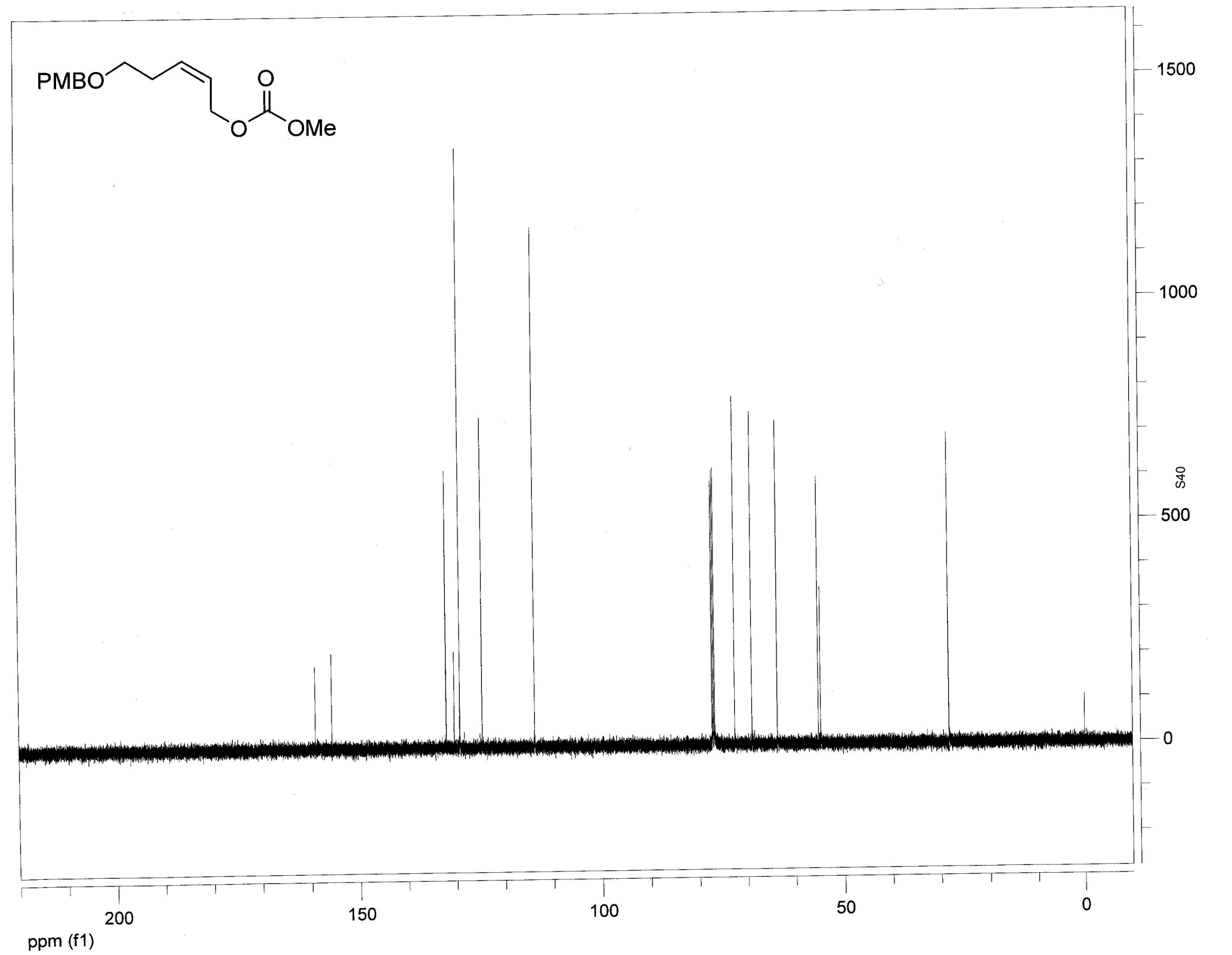
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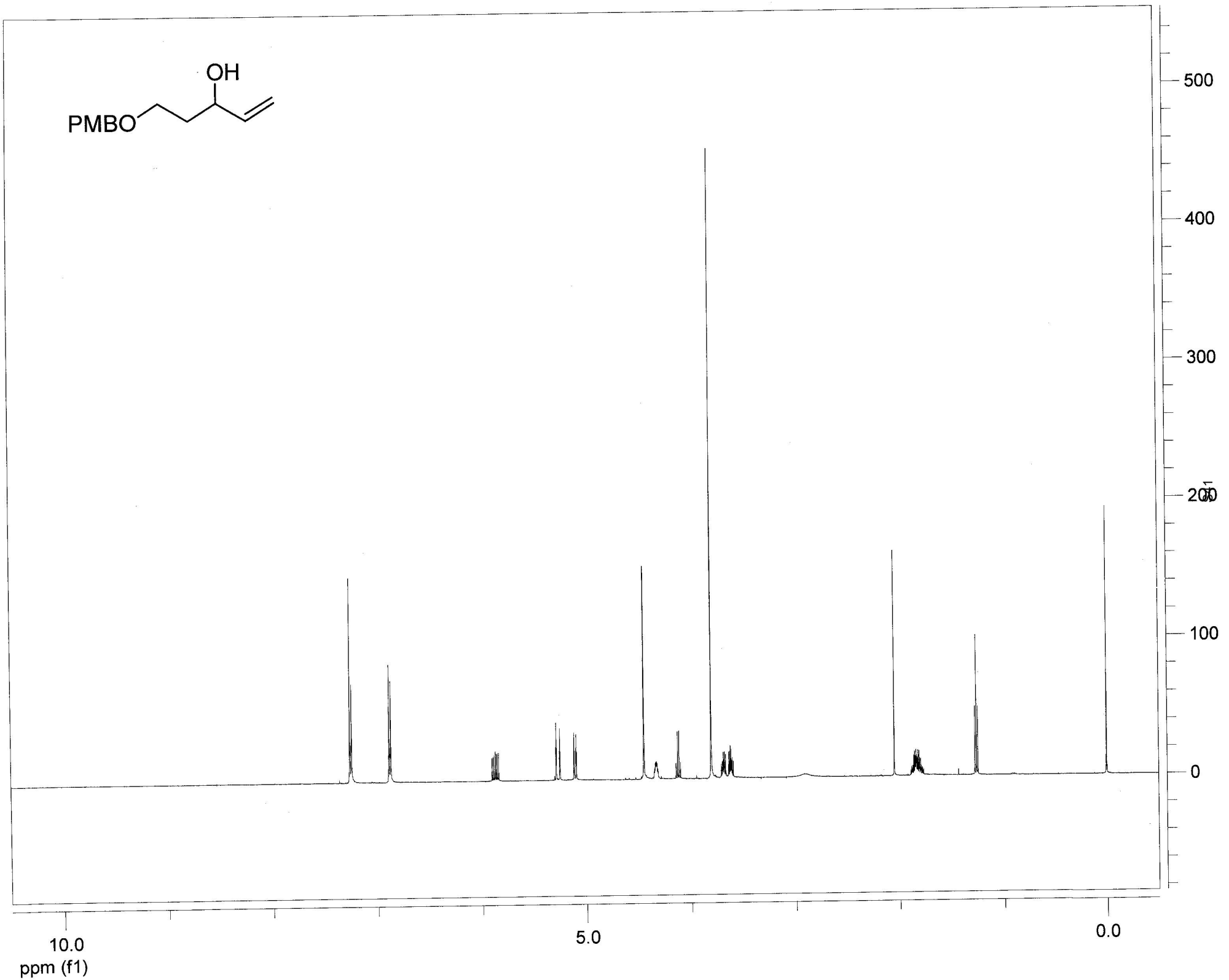
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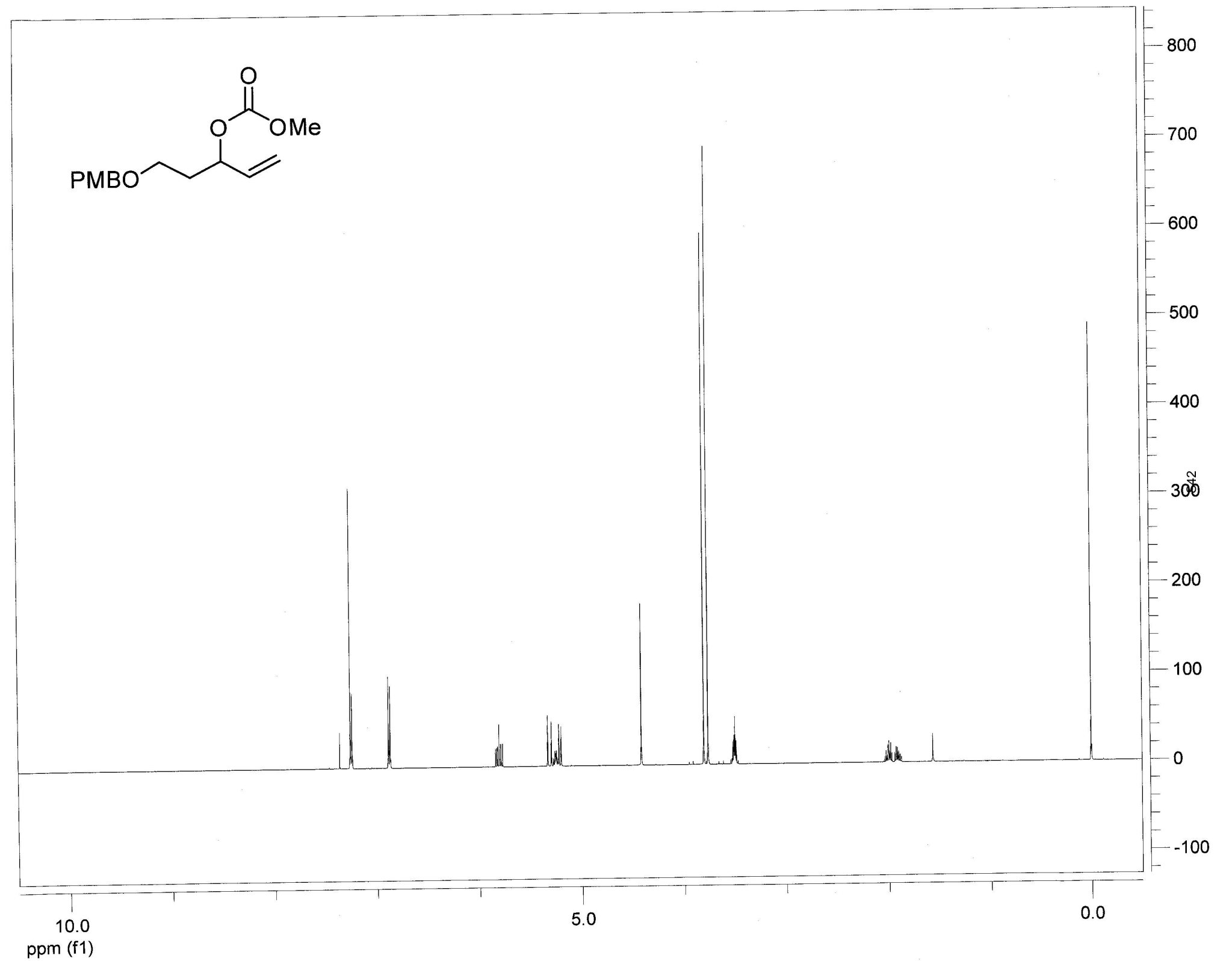
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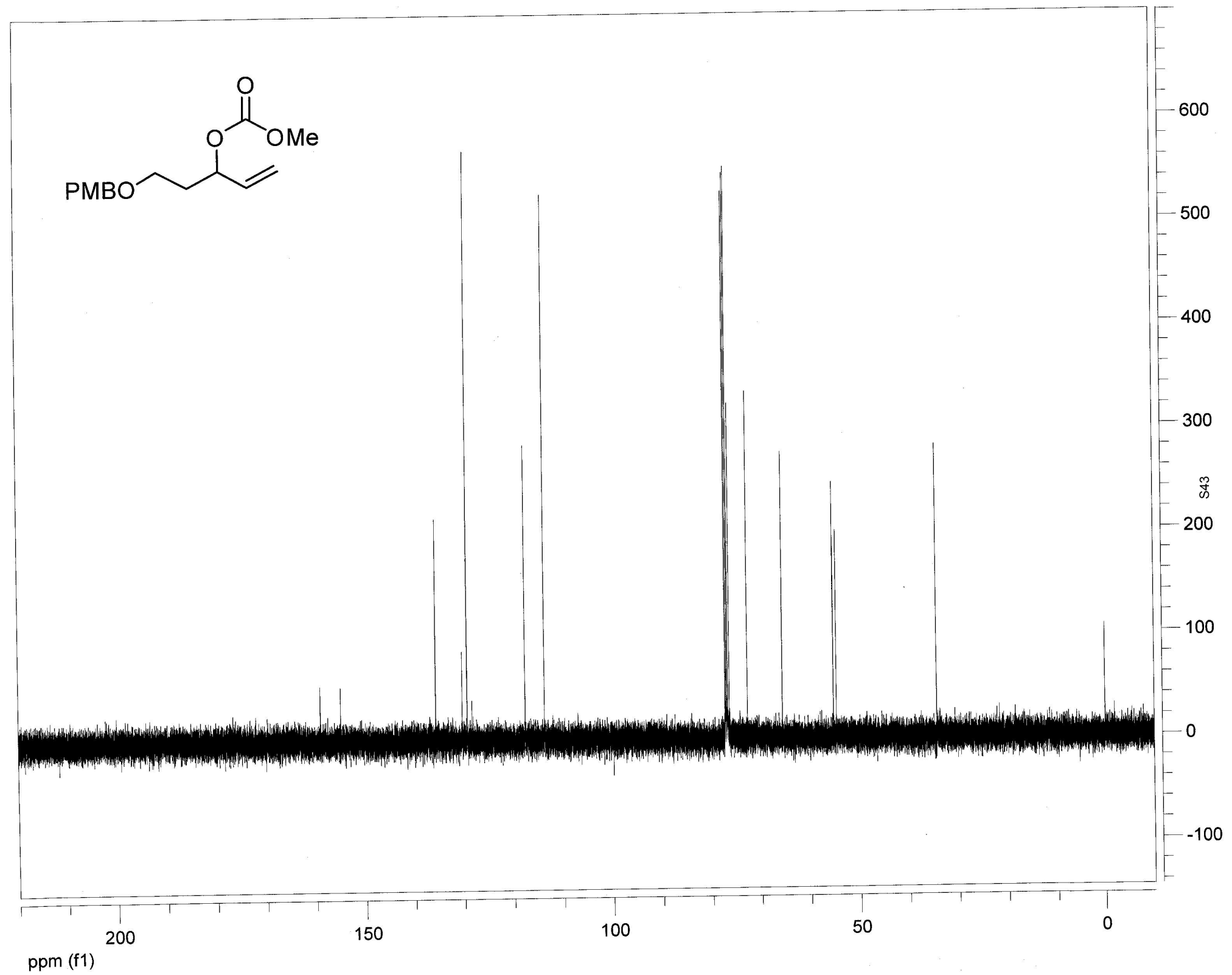
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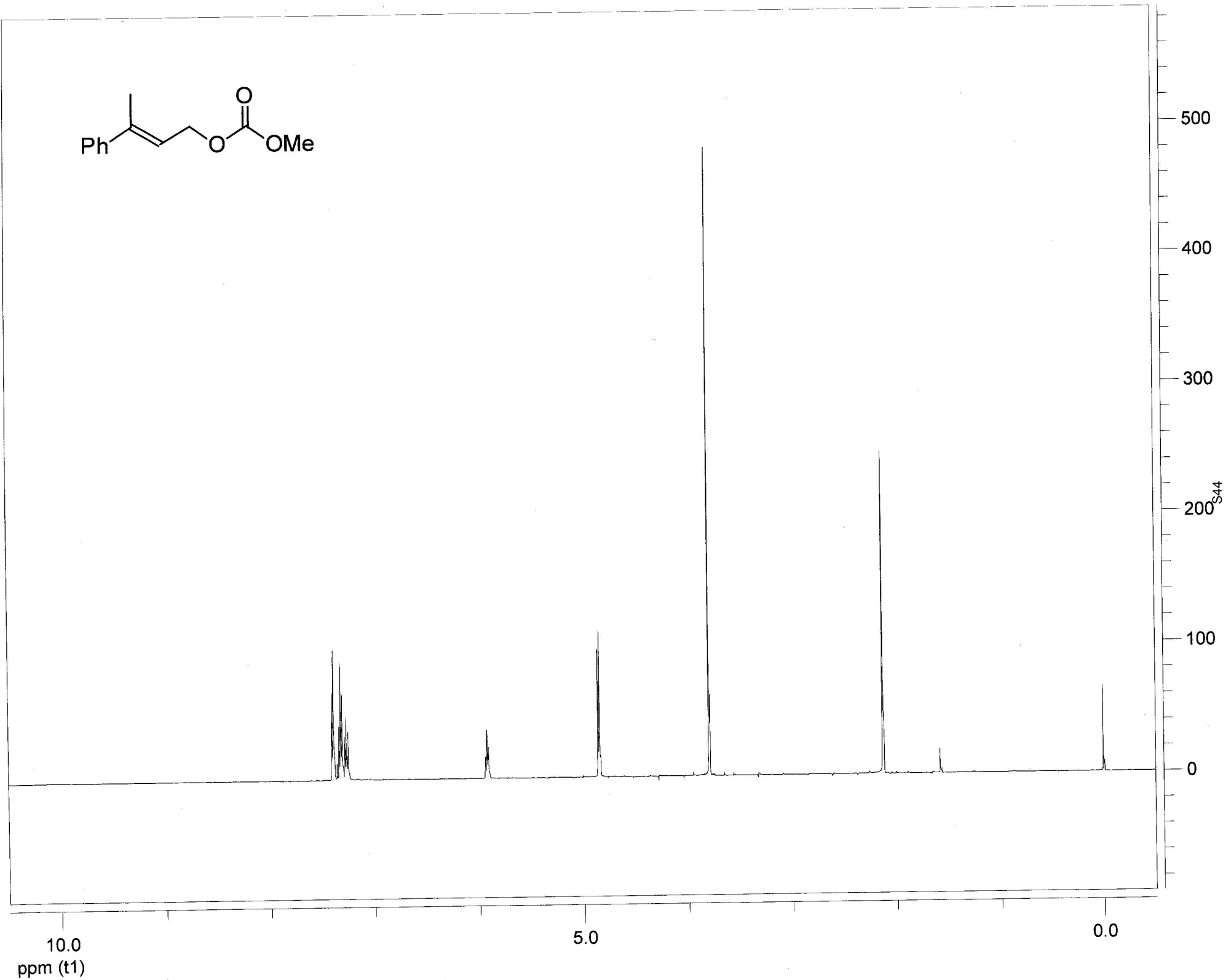
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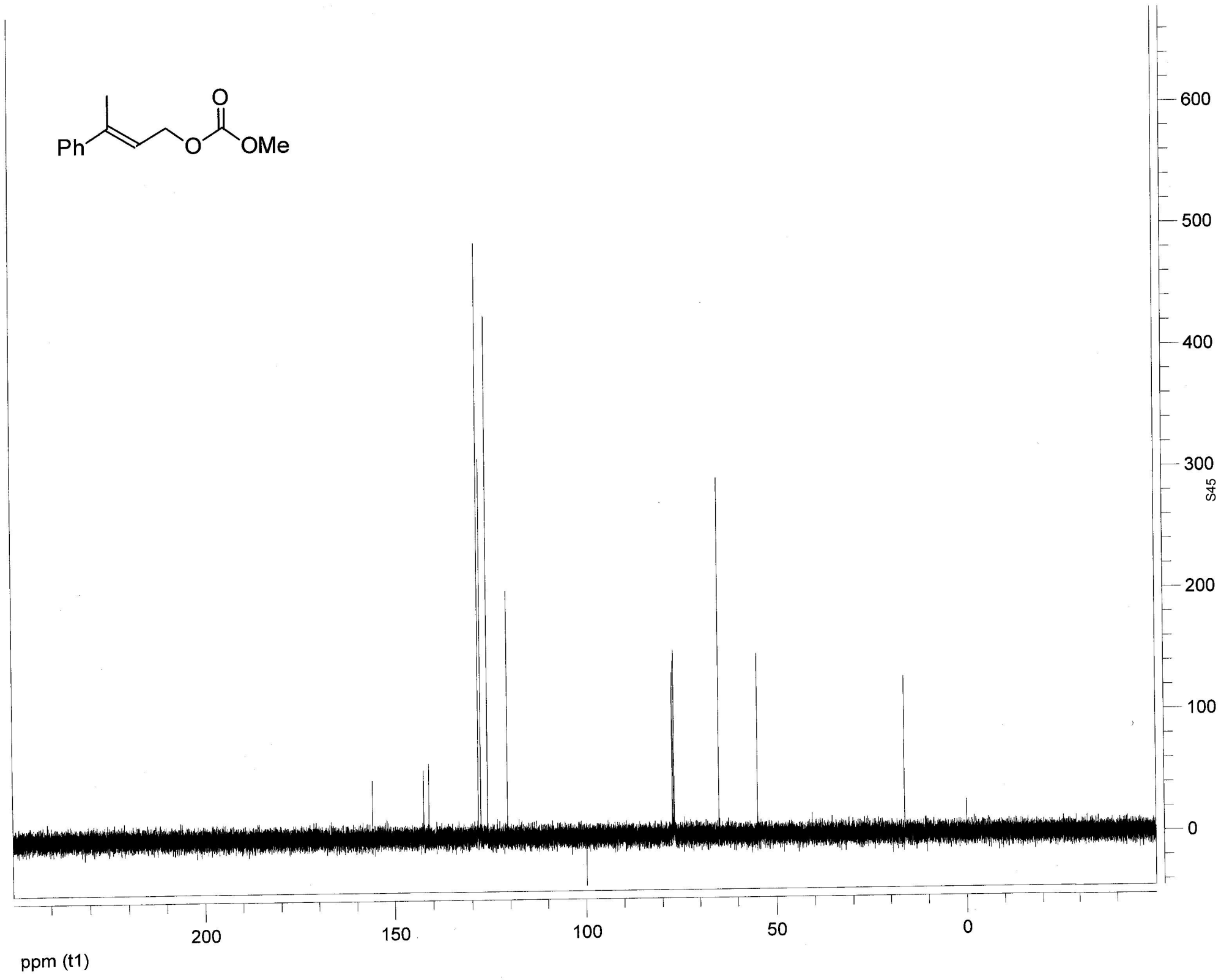
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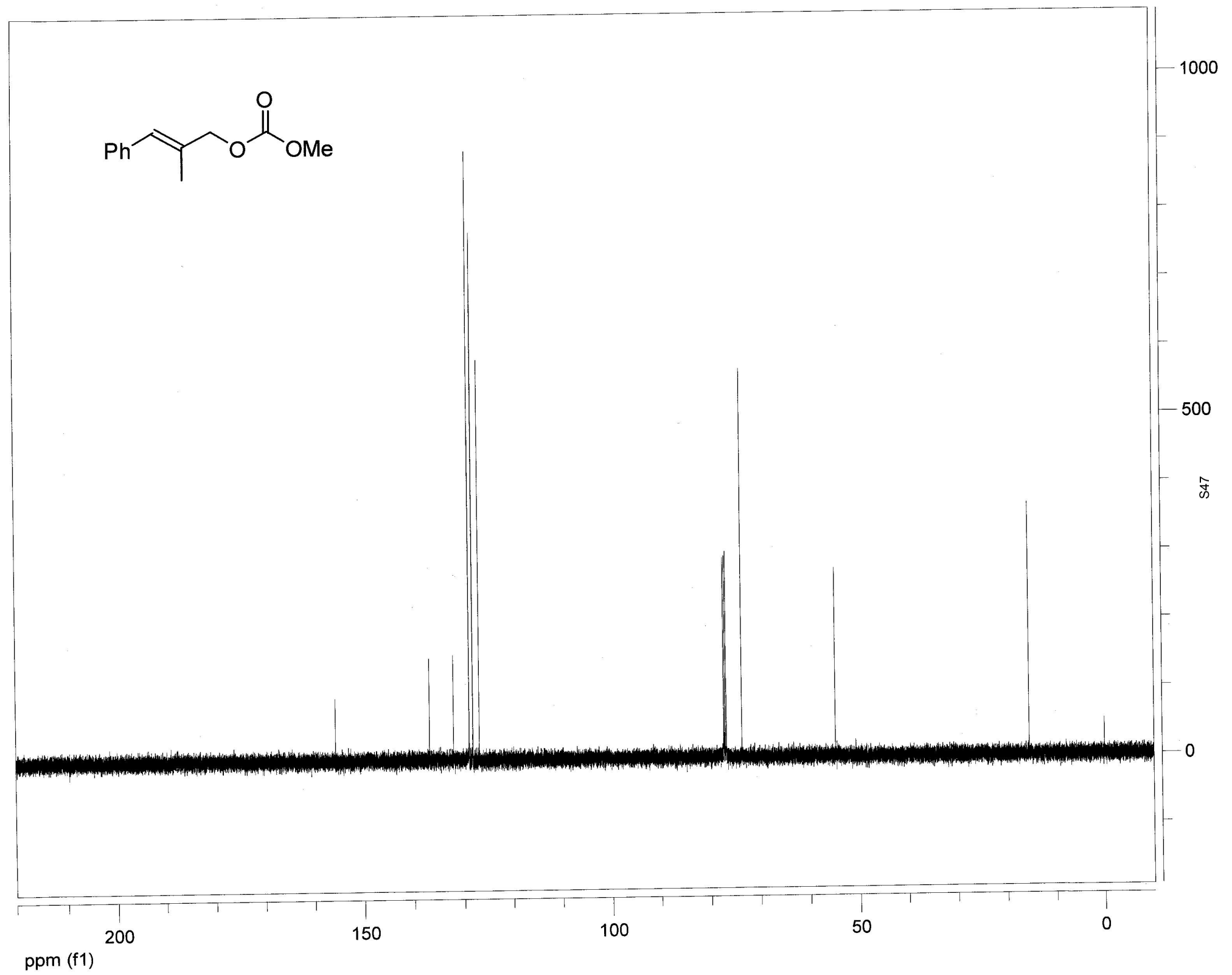
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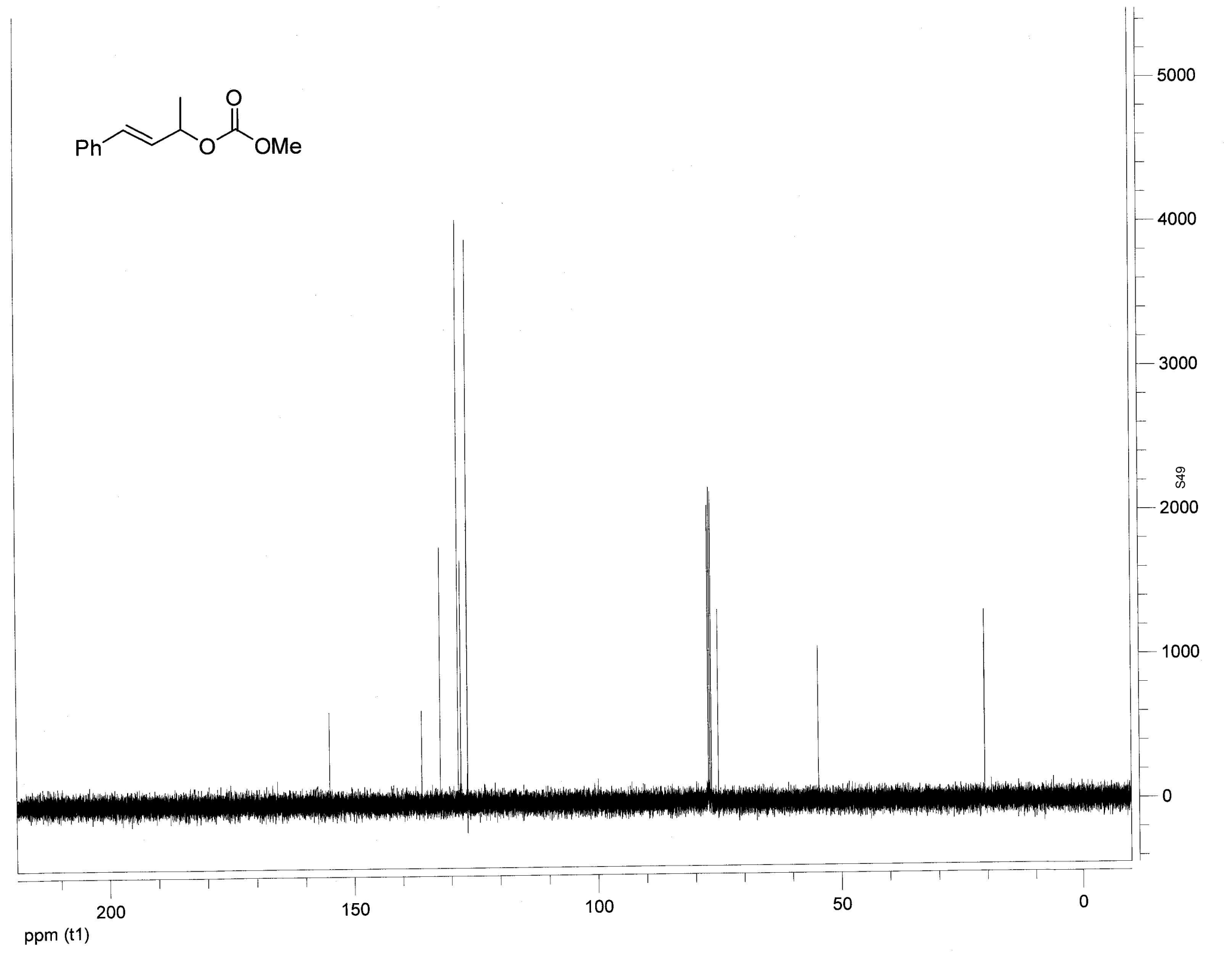
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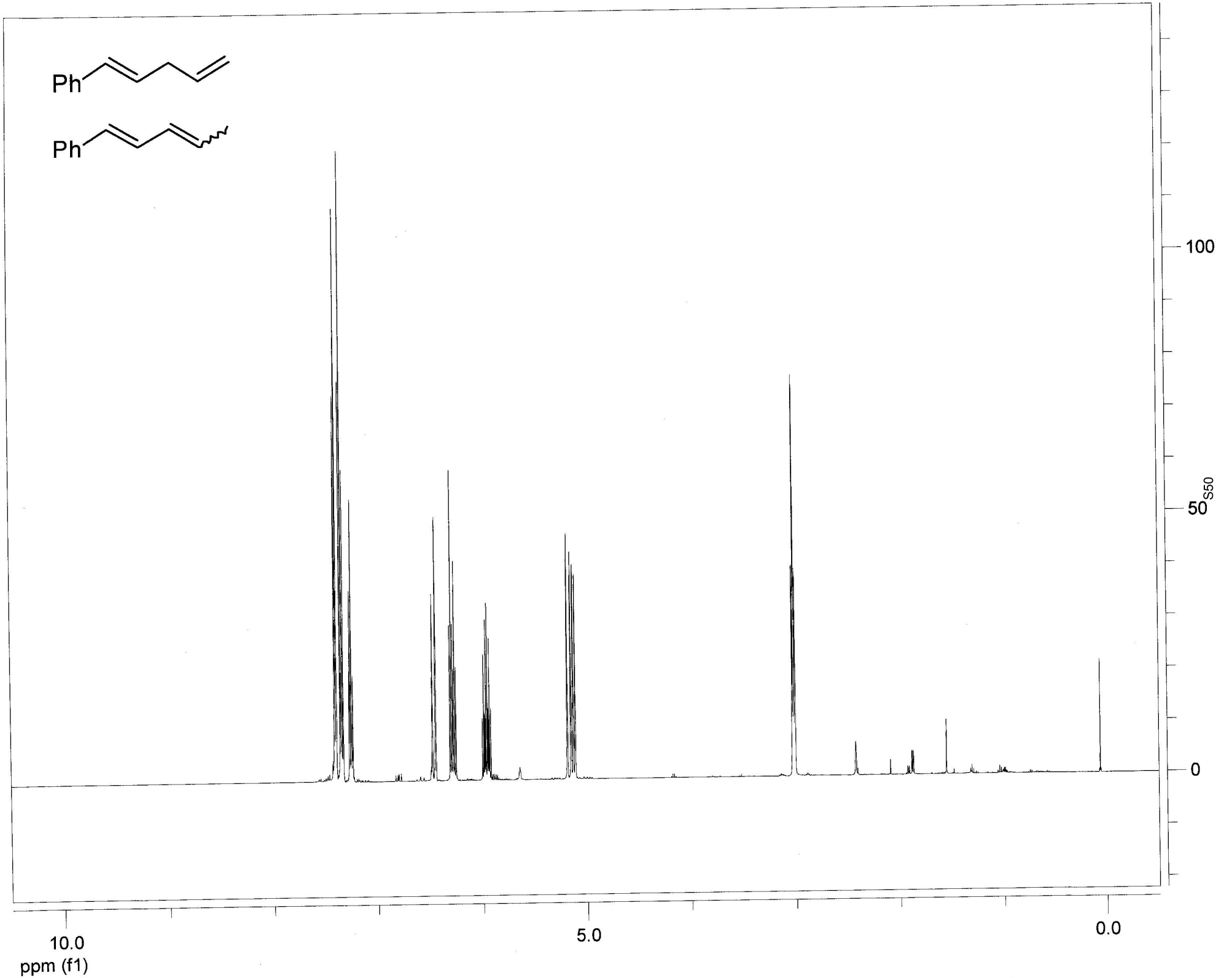
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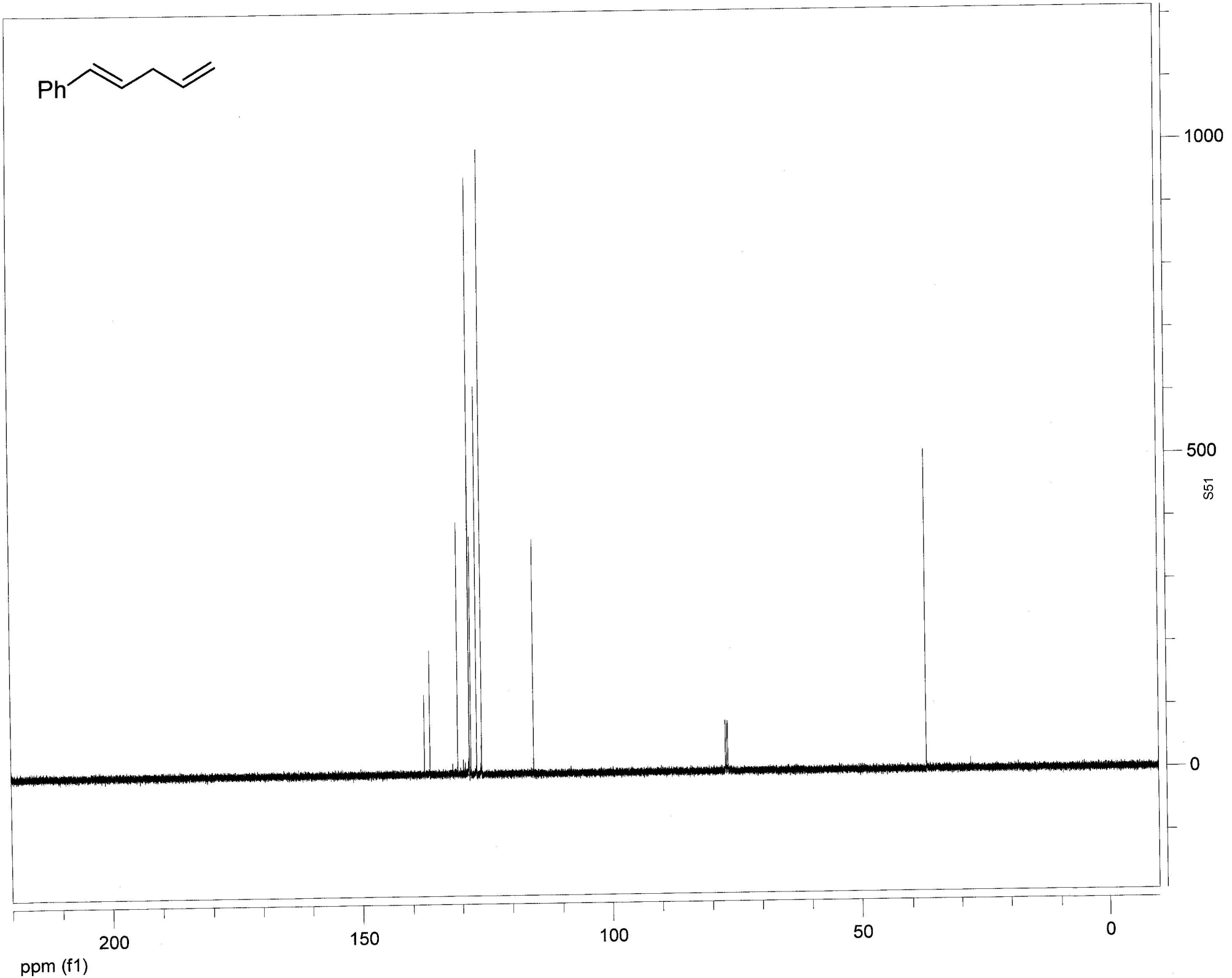
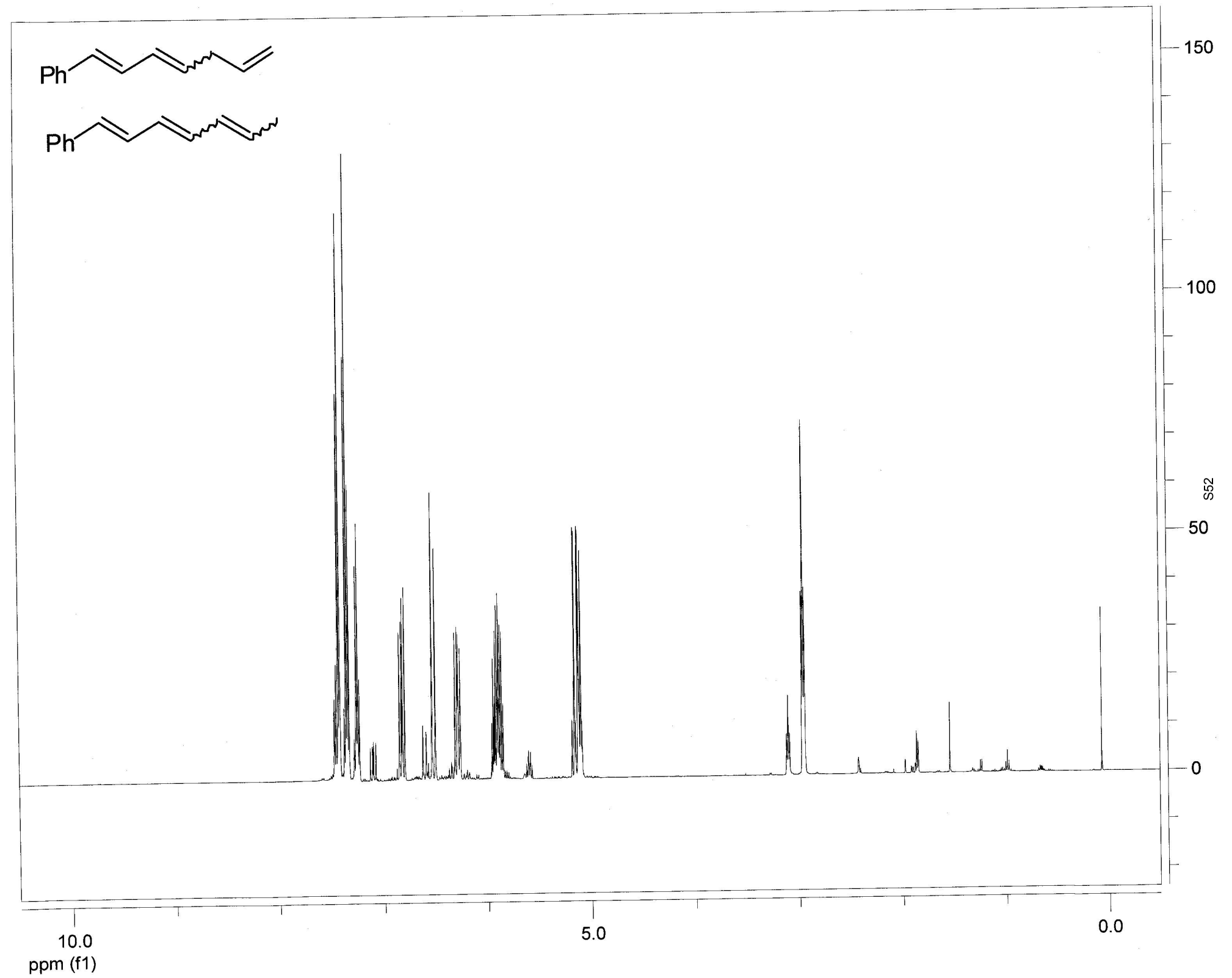
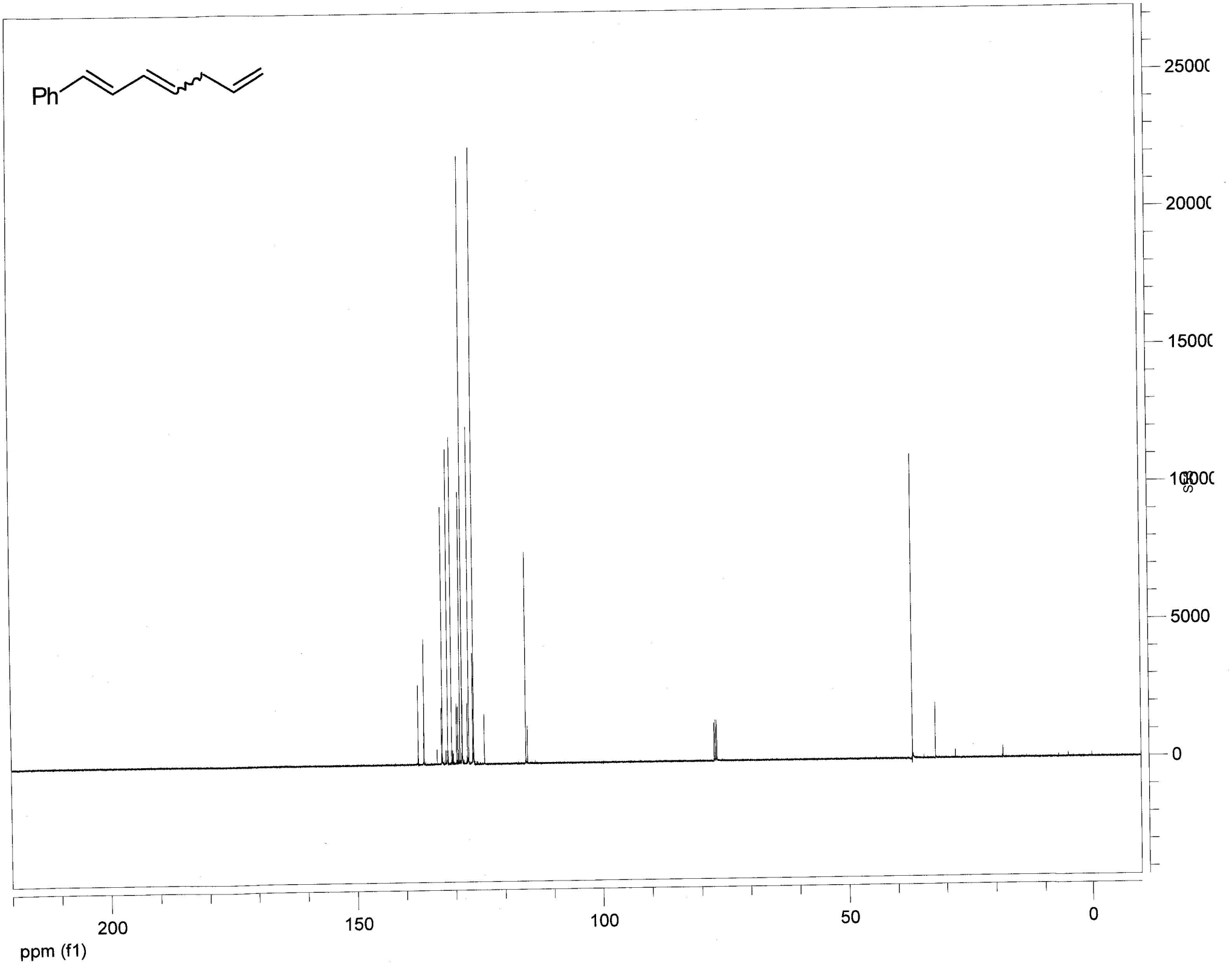
Ph
100
50
0
S50
10.0
5.0
0.0
ppm (f1)


Ph
1000
500
0
S51
200
150
100
50
0
ppm (f1)


Ph
Ph
150
100
50
0
S52
10.0
ppm (f1)
5.0
0.0


Ph
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20000
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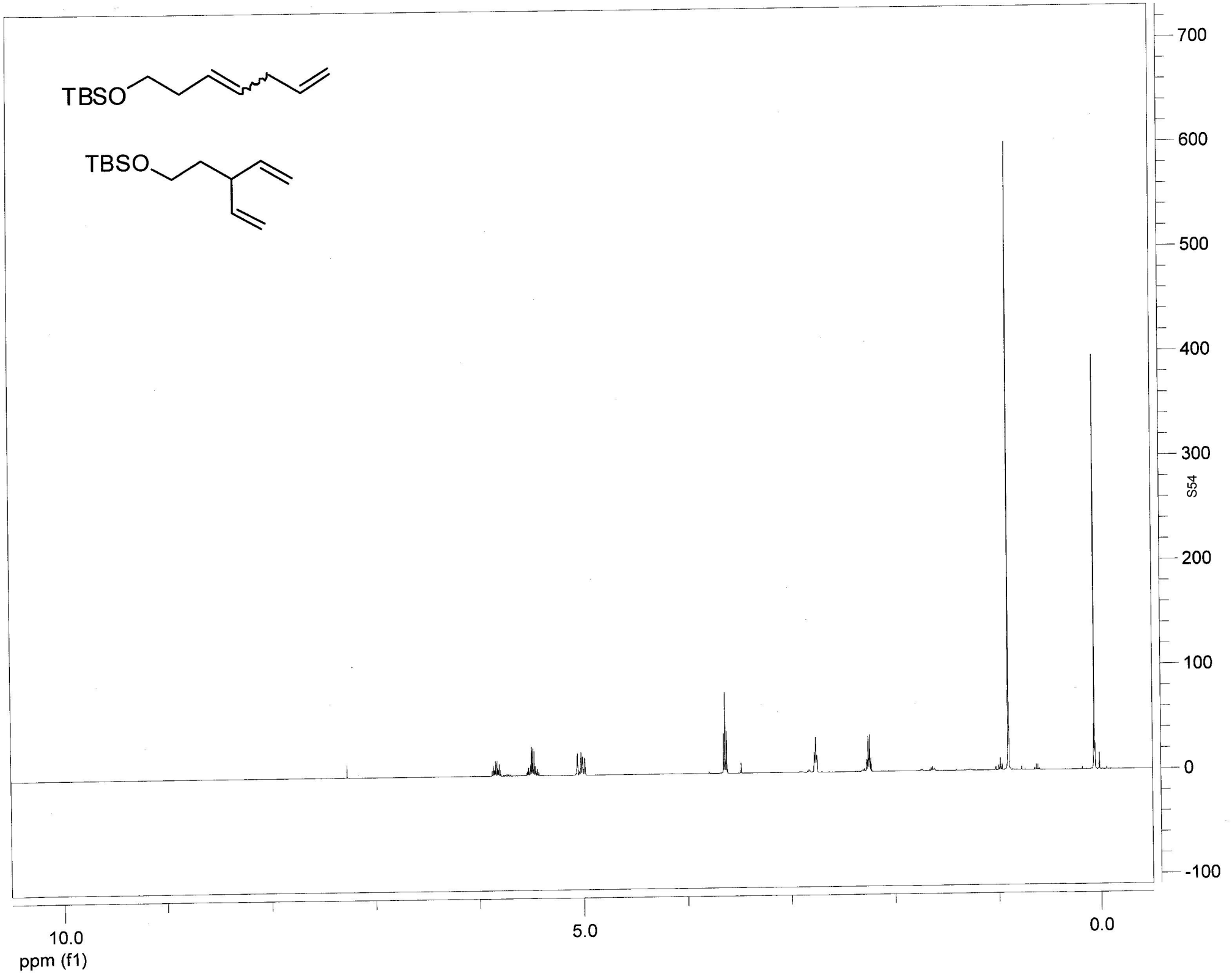
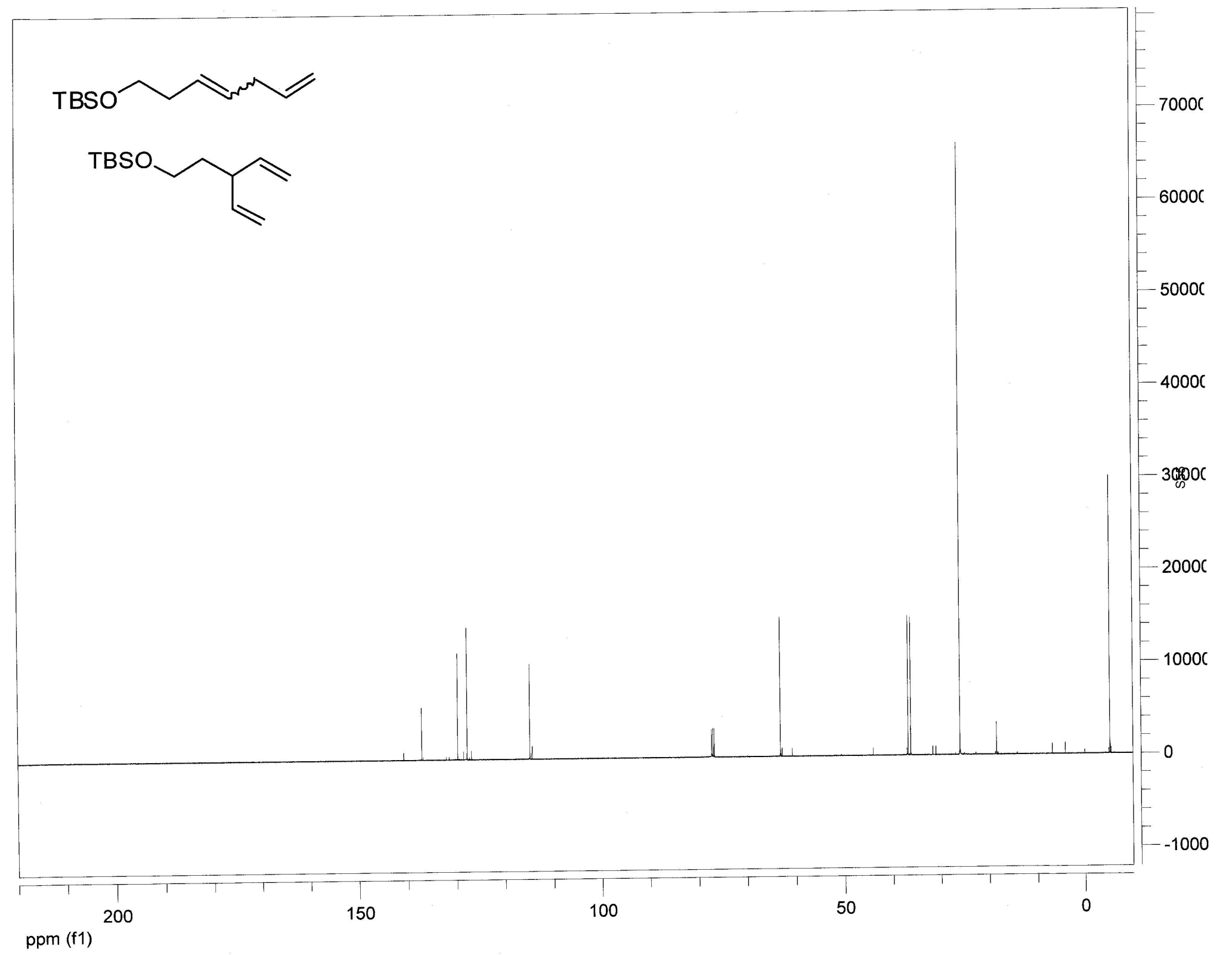
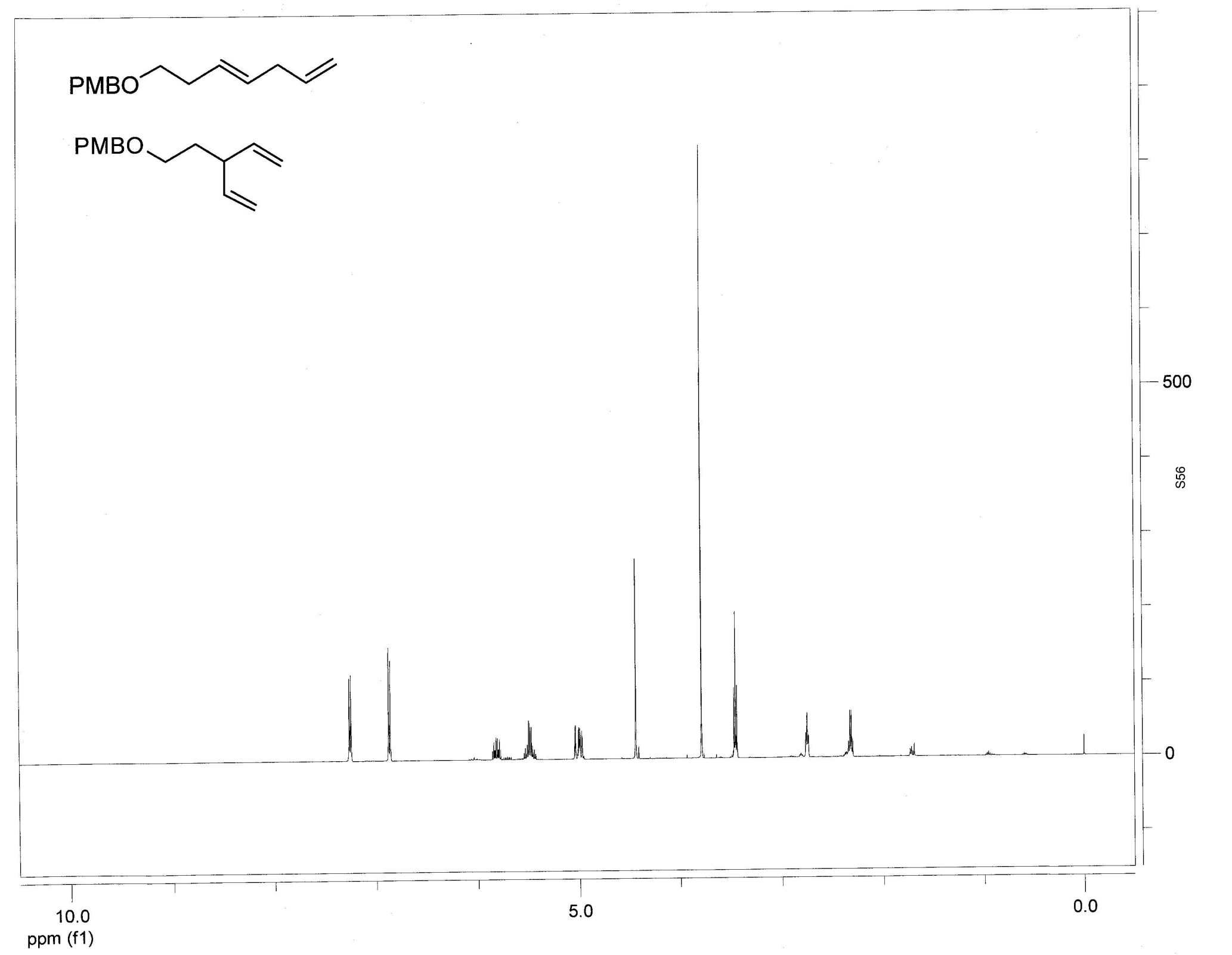
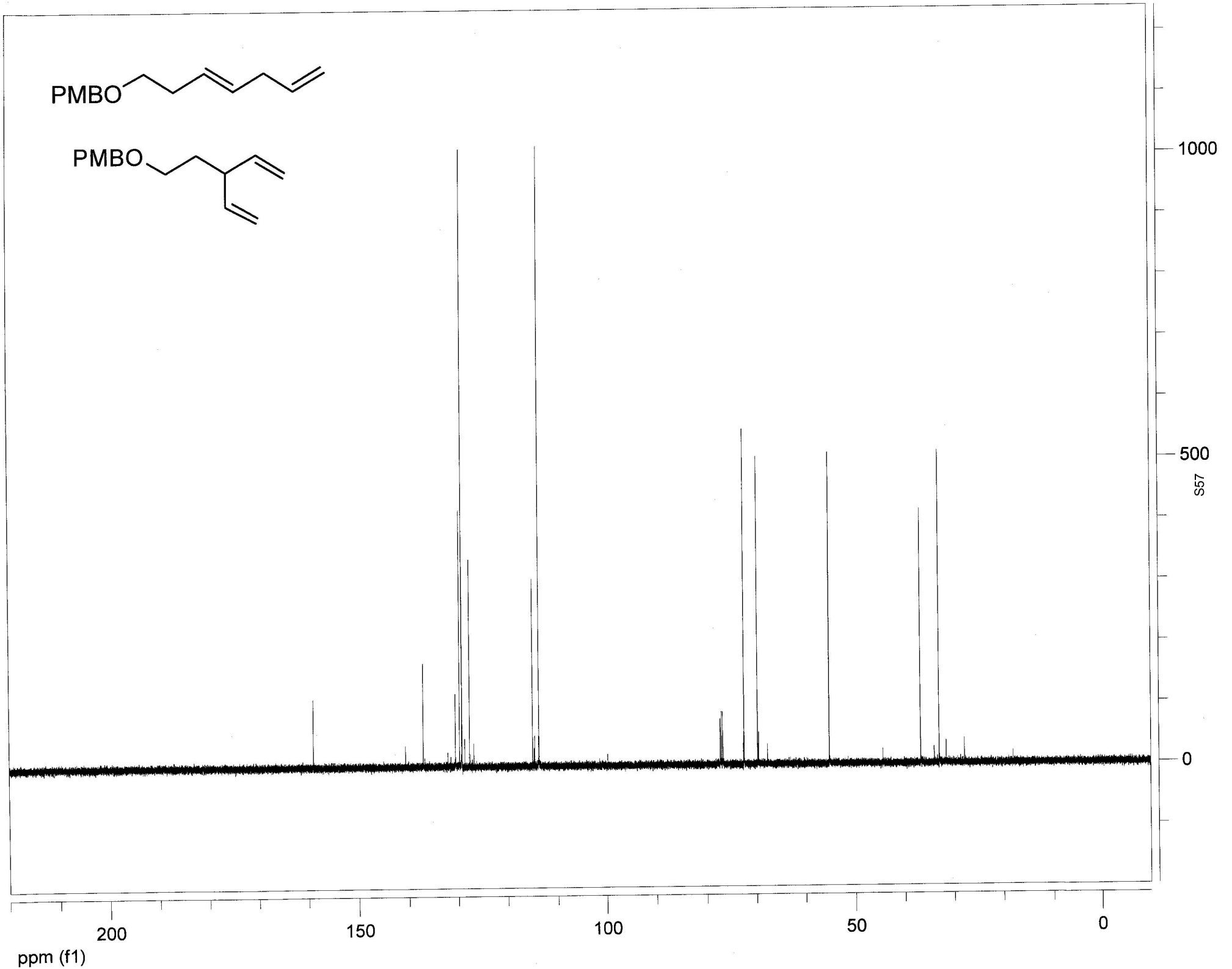
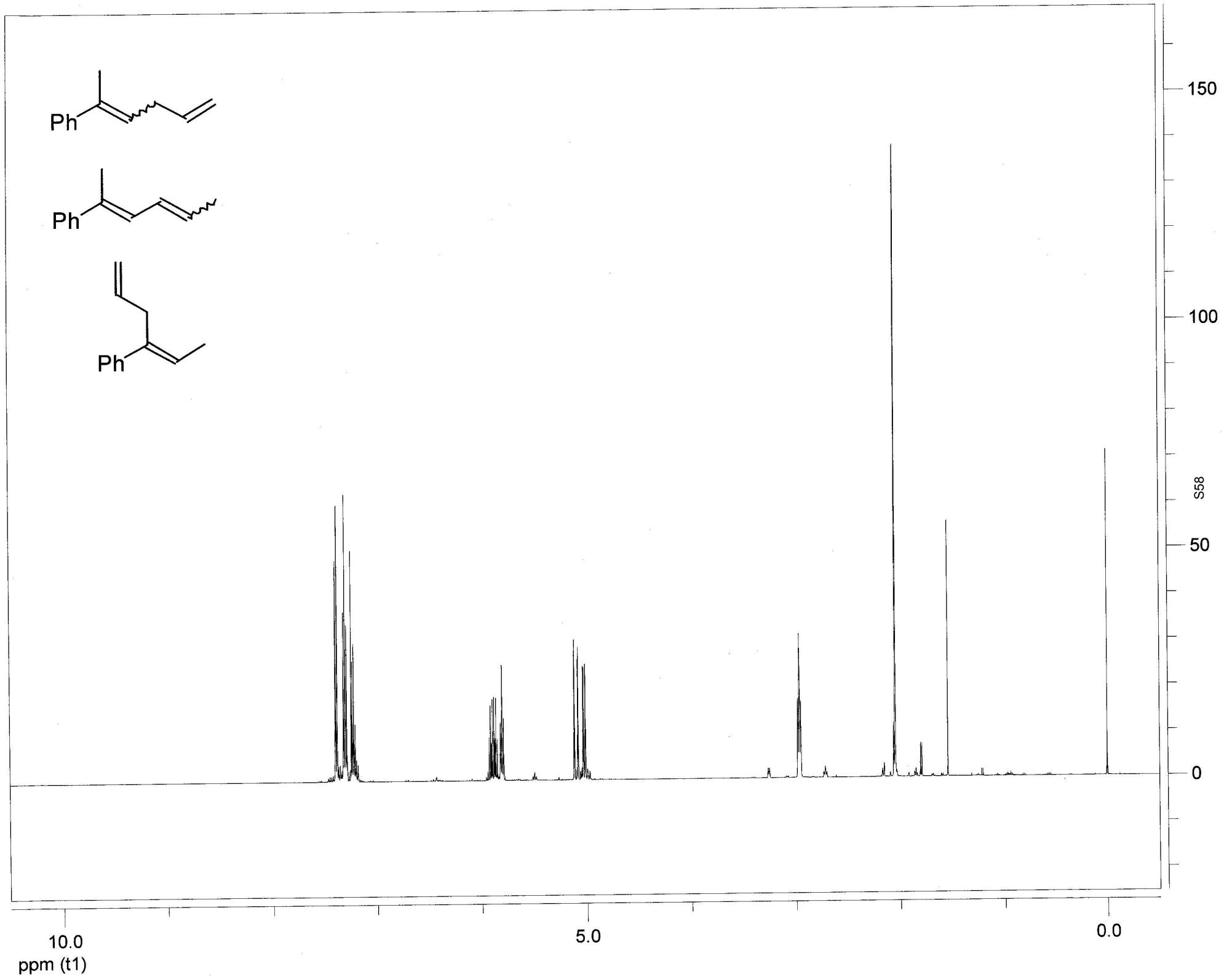
10000
5000
0
200
150
100
50
0
ppm (f1)

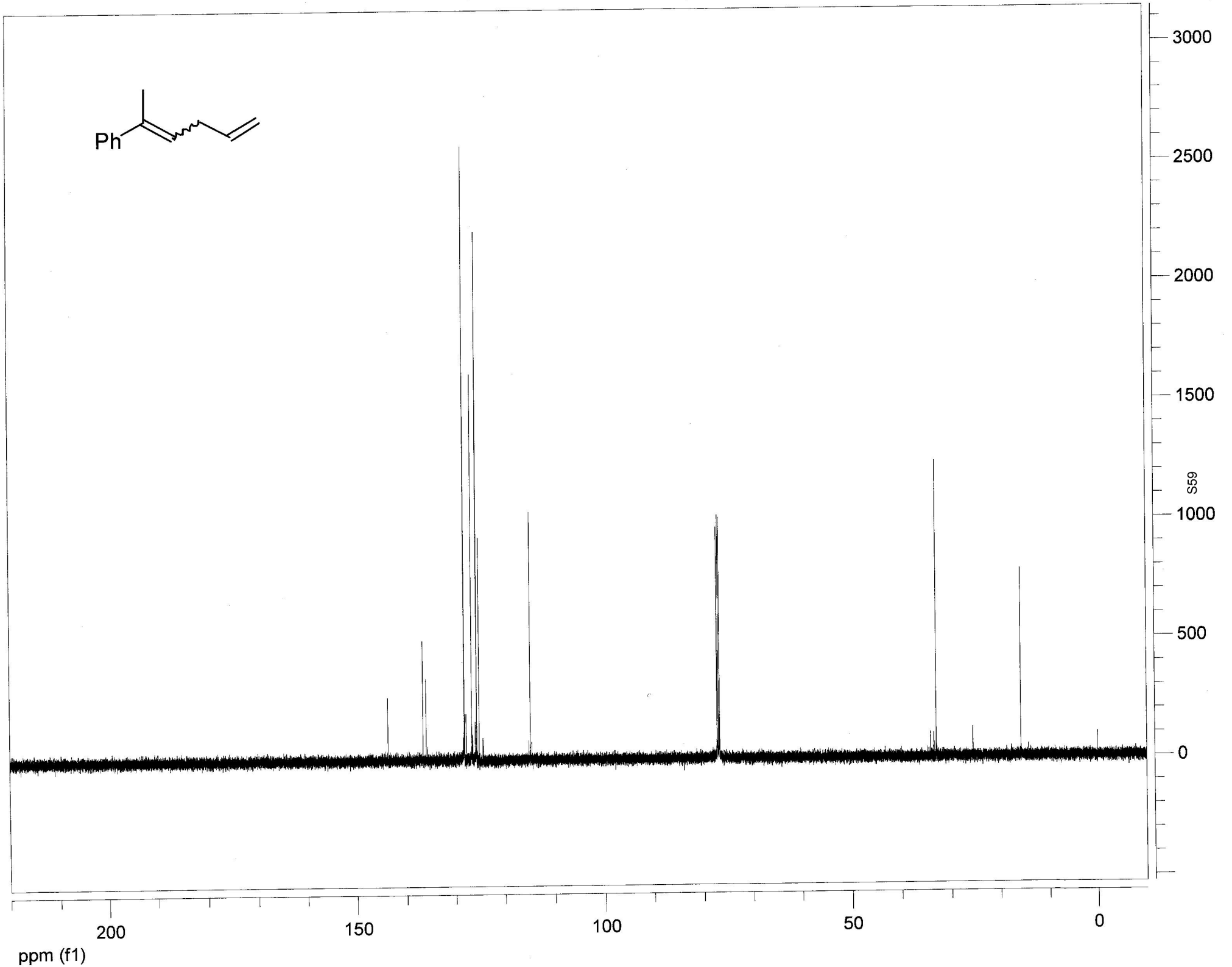

TBSO
TBSO
700
600
500
400
300
200
100
0
-100
S54
10.0
5.0
0.0
ppm (f1)

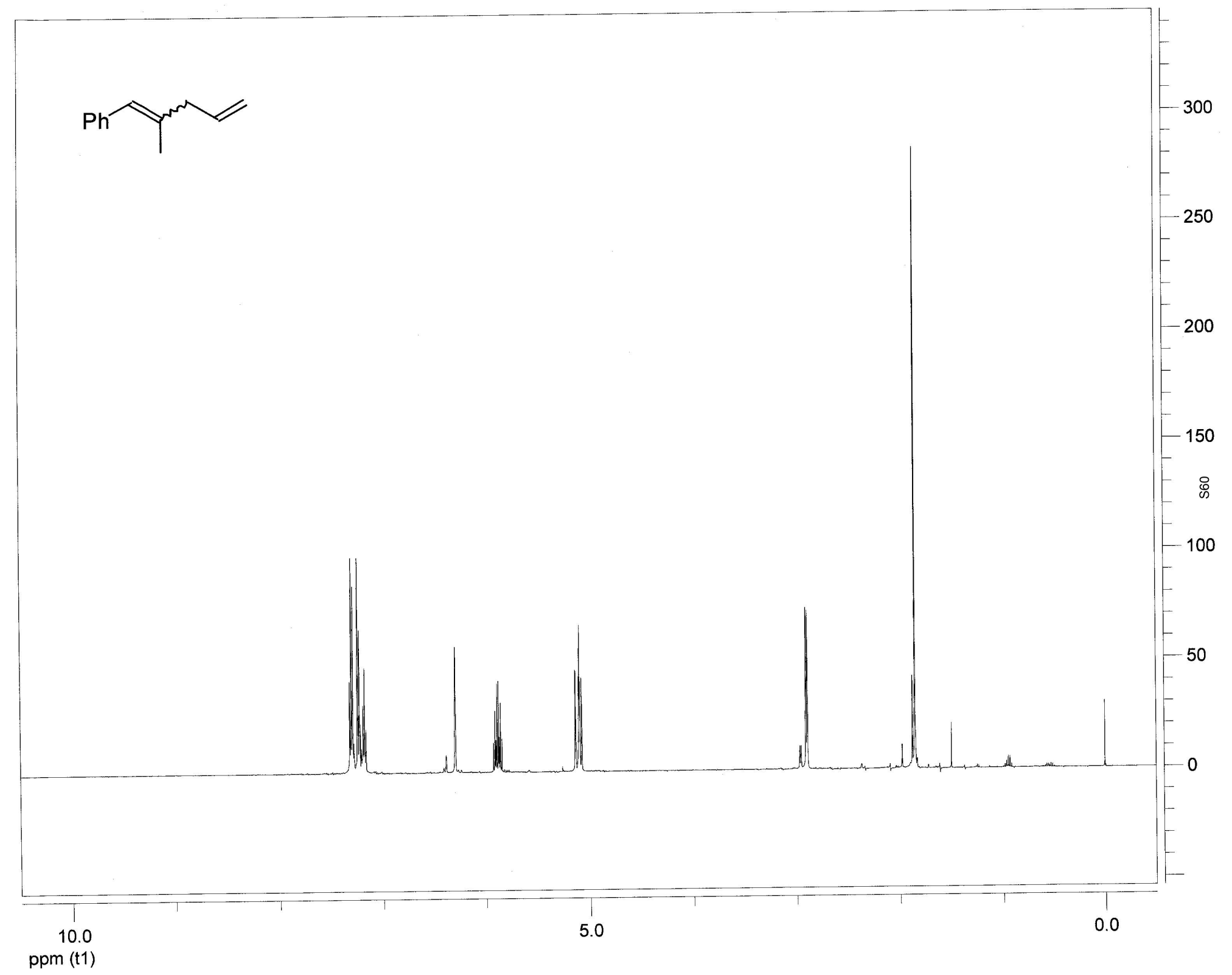

TBSO
TBSO
70000
60000
50000
40000
30000
20000
10000
0
-1000
200
150
100
50
0
ppm (f1)

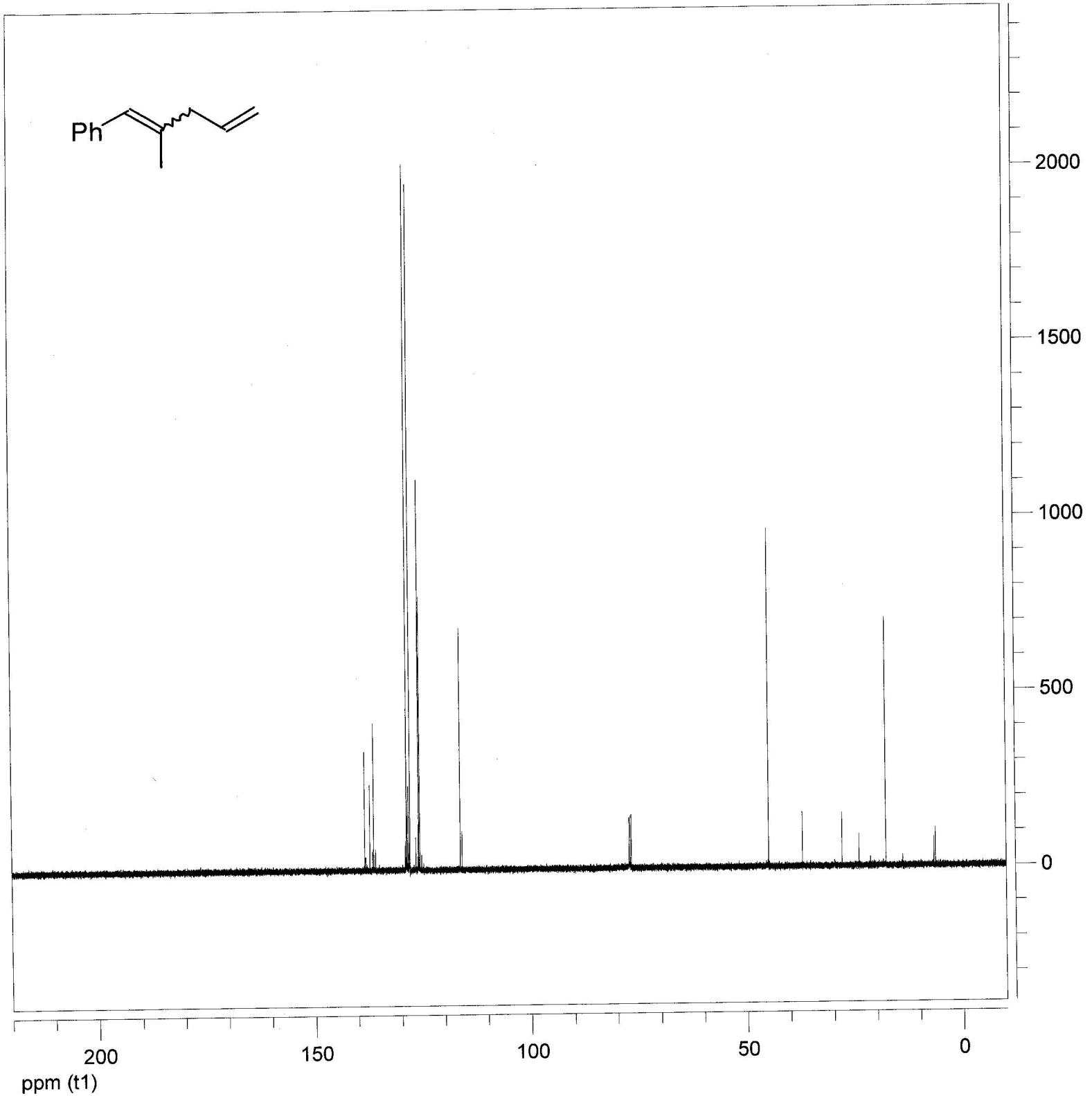

PMBO
PMBO
500
0
S56
10.0
ppm (f1)
5.0
0.0


PMBO
PMBO
1000
500
0
S57
200
150
100
50
0
ppm (f1)


Ph
Ph
Ph
150
100
50
0
S58
10.0
ppm (t1)
5.0
0.0


Ph
3000
2500
2000
1500
1000
500
0
S59
200
150
100
50
0
ppm (f1)


Ph
300
250
200
150
S60
100
50
0
10.0
ppm (t1)
5.0
0.0



Date:
26 Jan 2010
Document's Title:
RM220-13C.fid

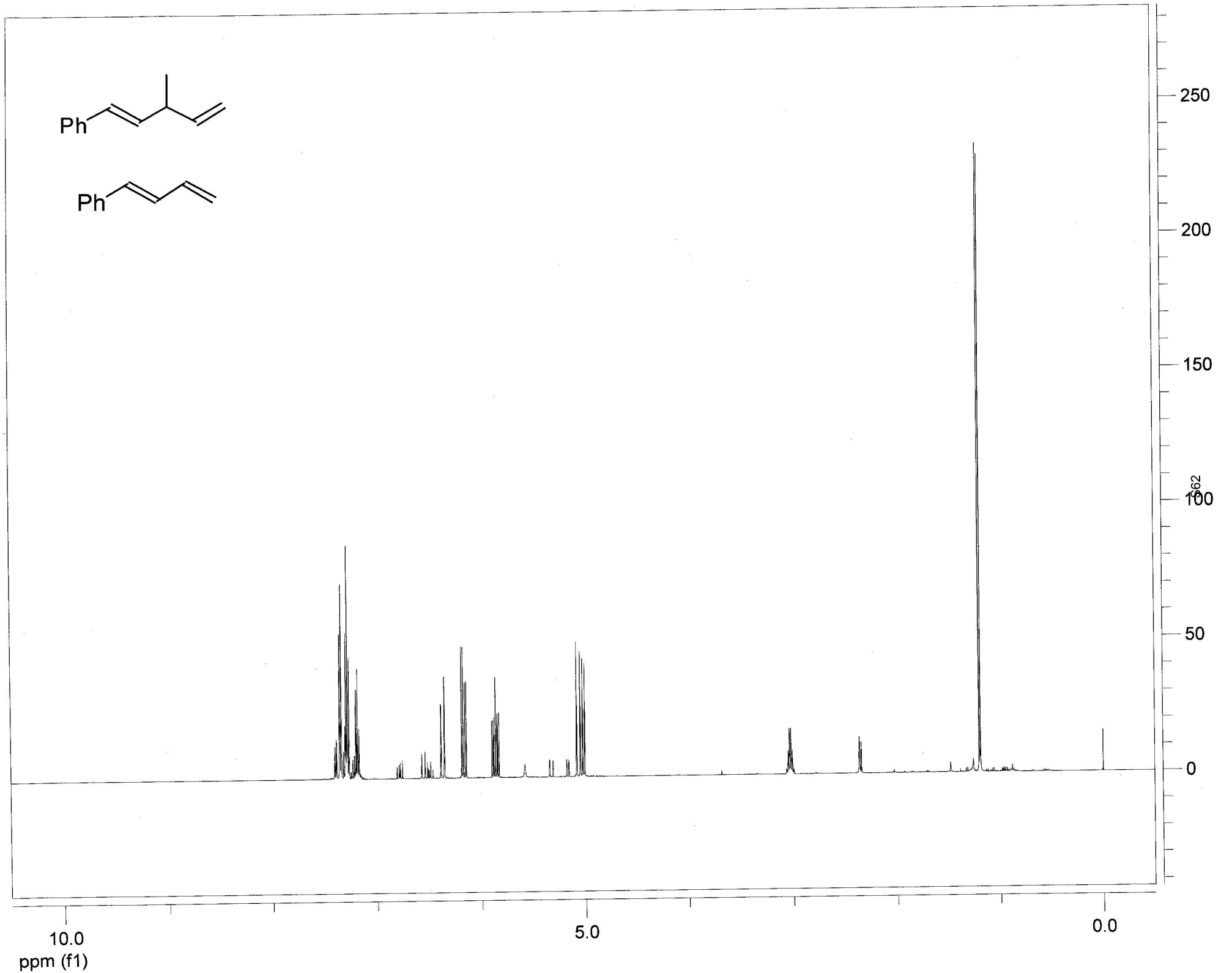
Spectrum Title:
STANDARD CARBON PARAMETERS

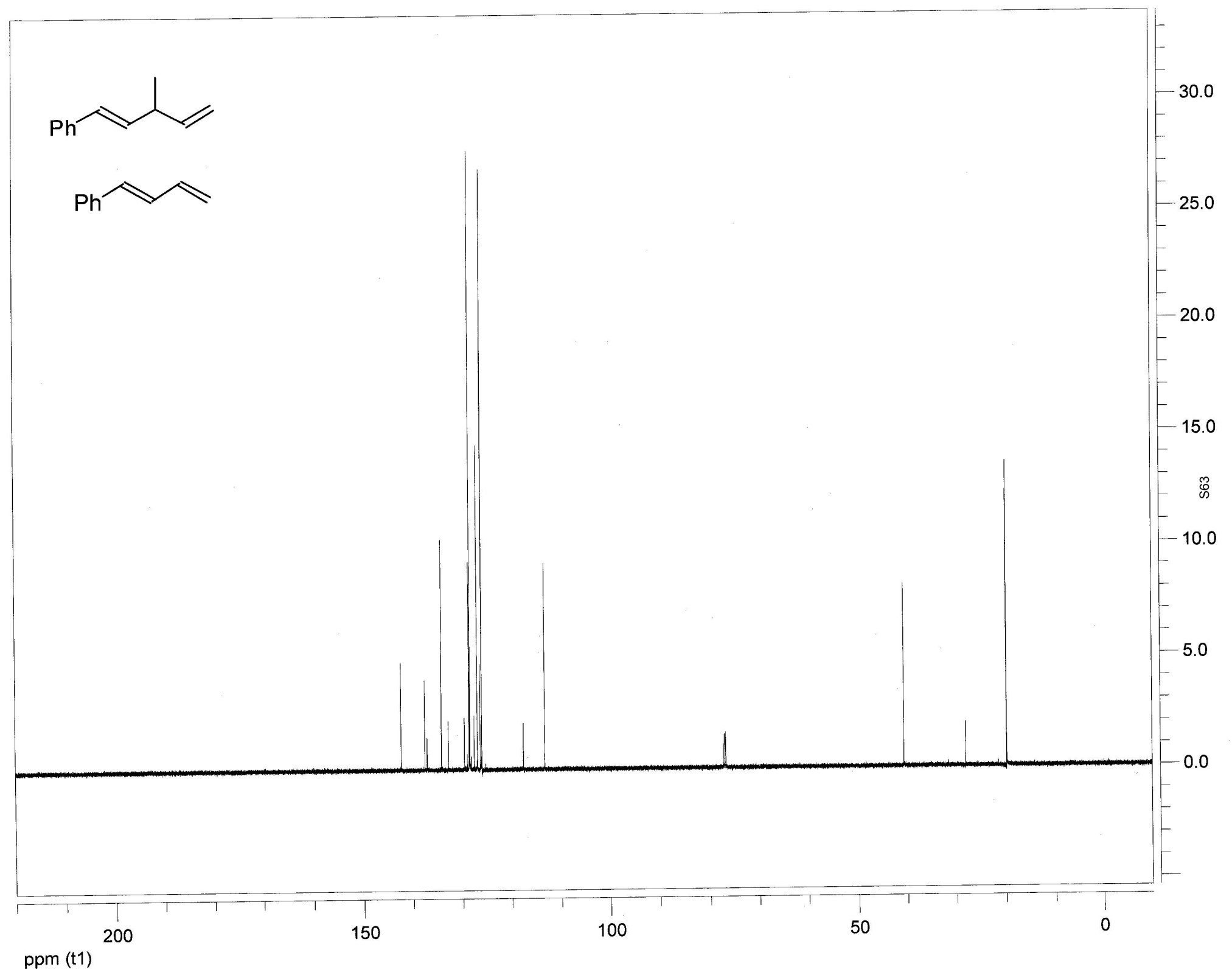
Frequency (MHz):
(f1) 125.795
Original Points Count:
(f1) 65505
Actual Points Count:
(f1) 131072
Acquisition Time (sec):
(f1) 1.7359
Spectral Width (ppm):
(f1) 299.979
Pulse Program:
s2pul
Temperature:
20

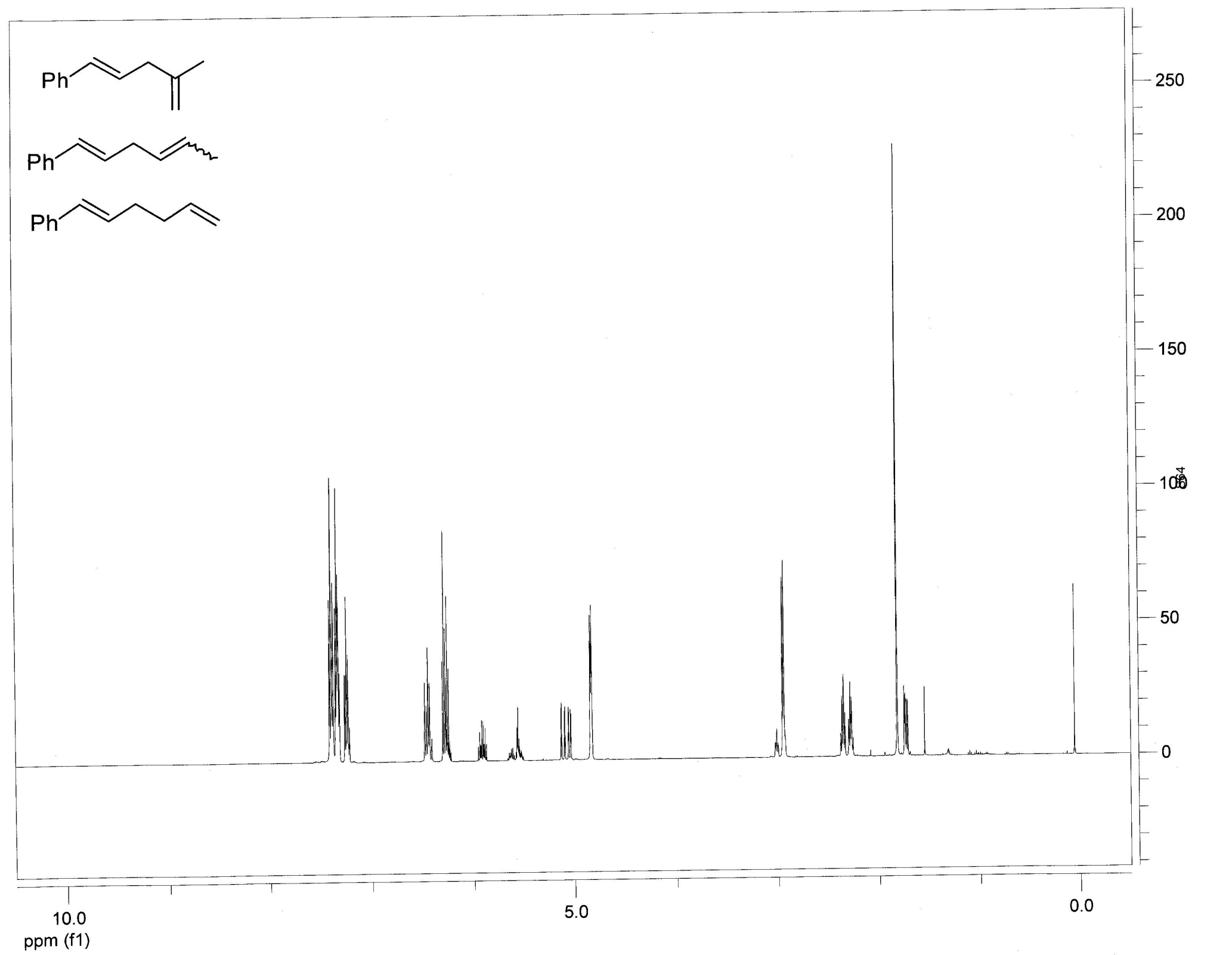
Number of Scans:
64

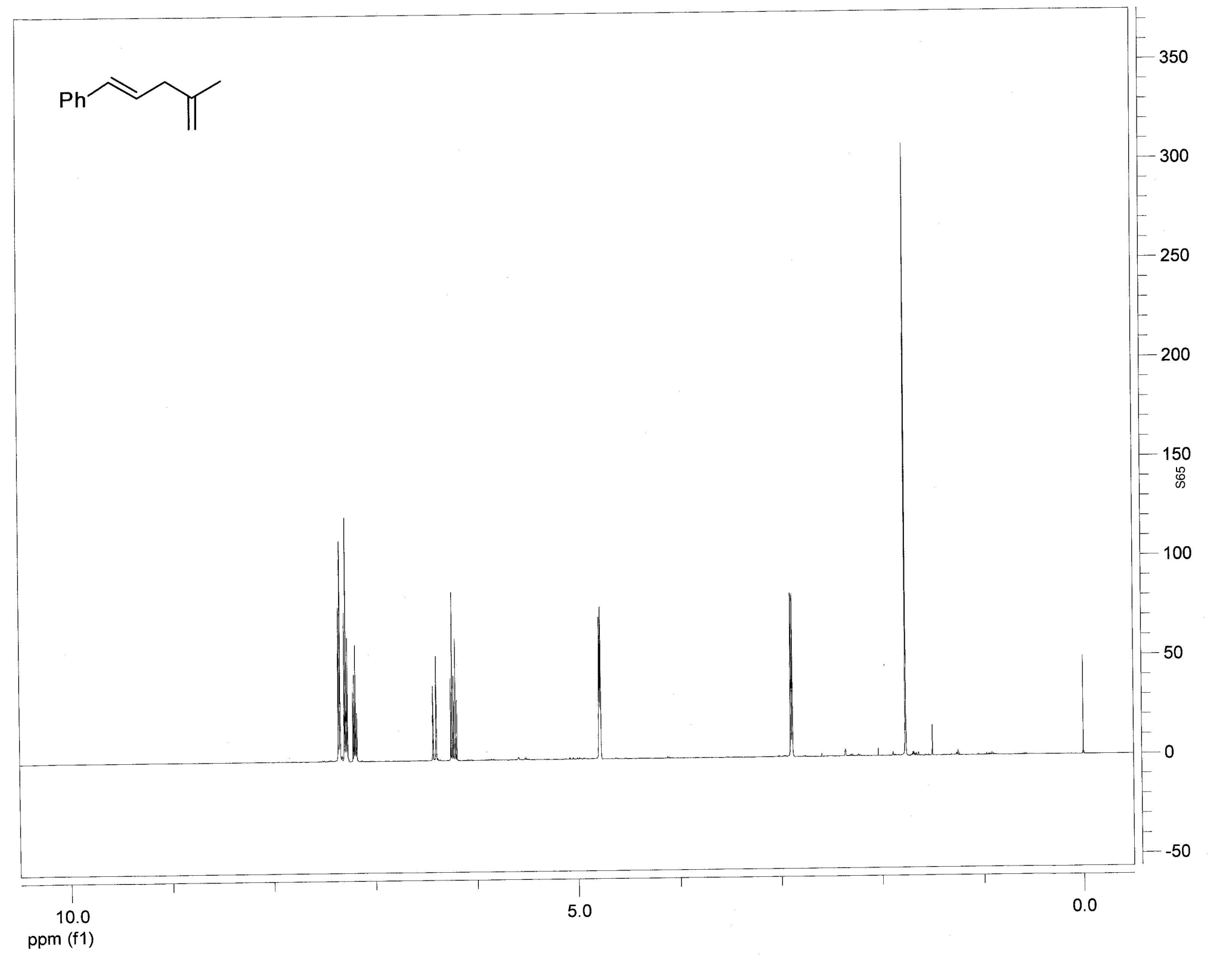
Acq. Date:
Oct 27 2009

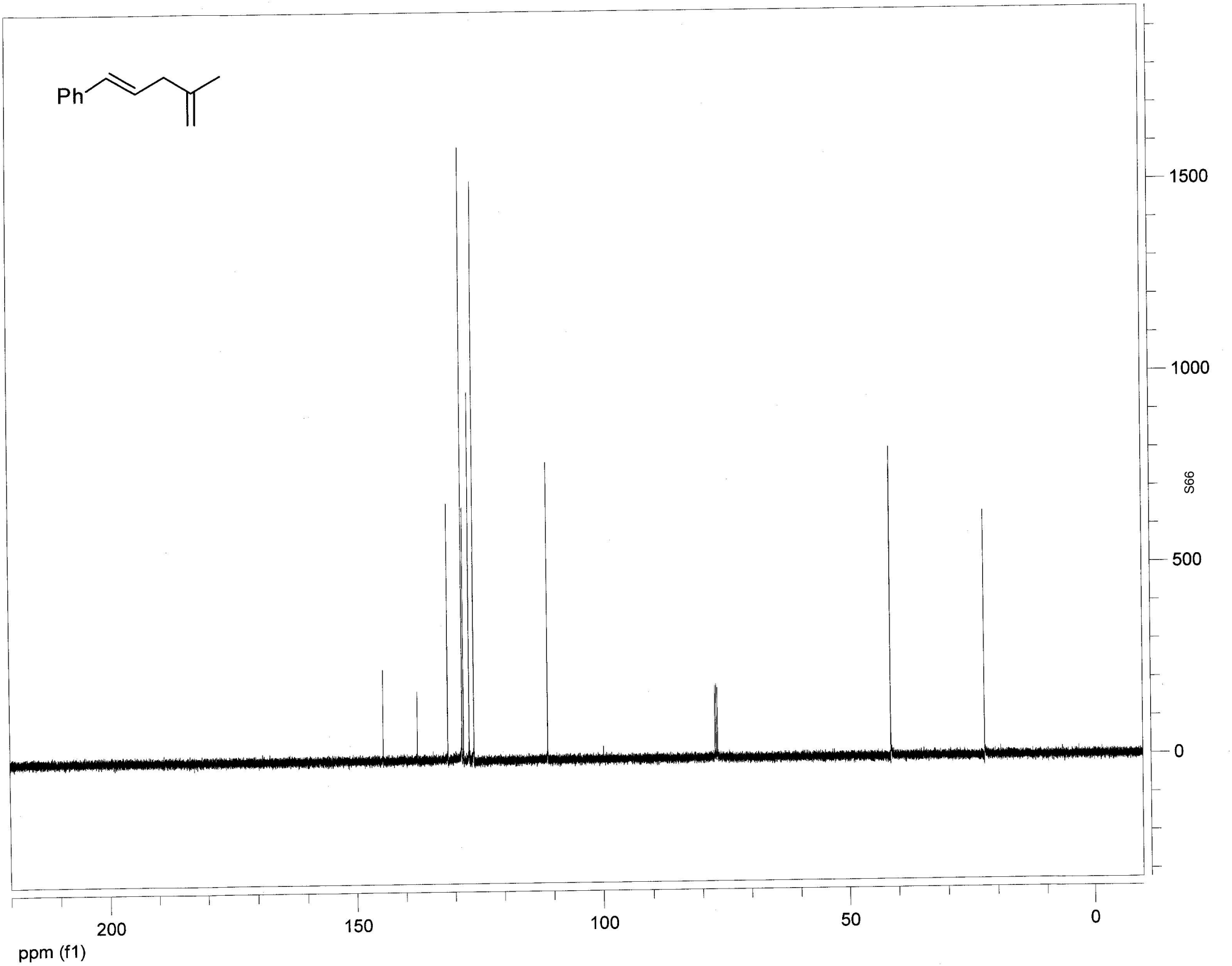
S61


Ph
Ph
250
200
150
100
50
0
162
10.0
ppm (f1)
5.0
0.0

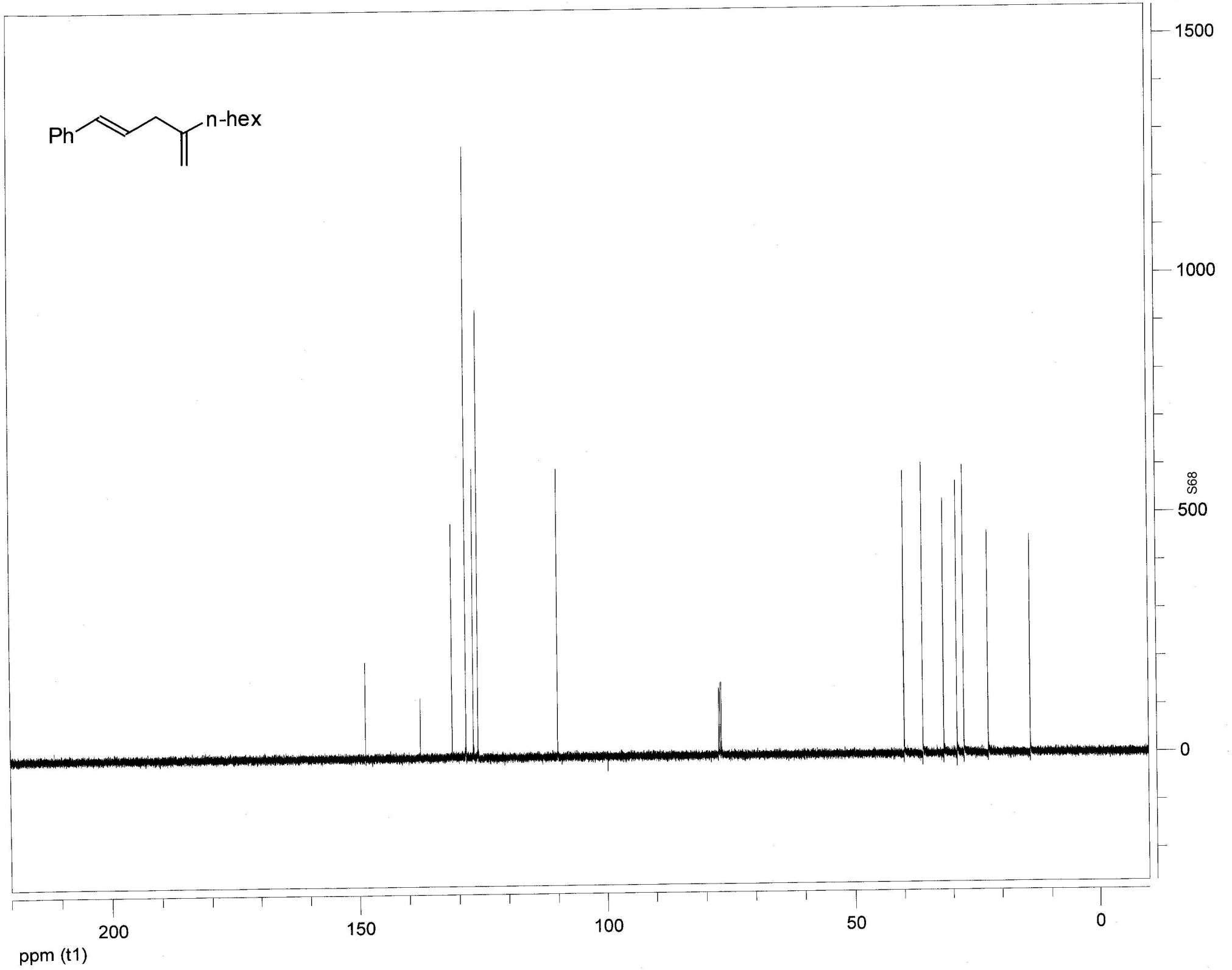

Ph
Ph
30.0
25.0
20.0
15.0
10.0
5.0
0.0
S63
200
150
100
50
0
ppm (t1)

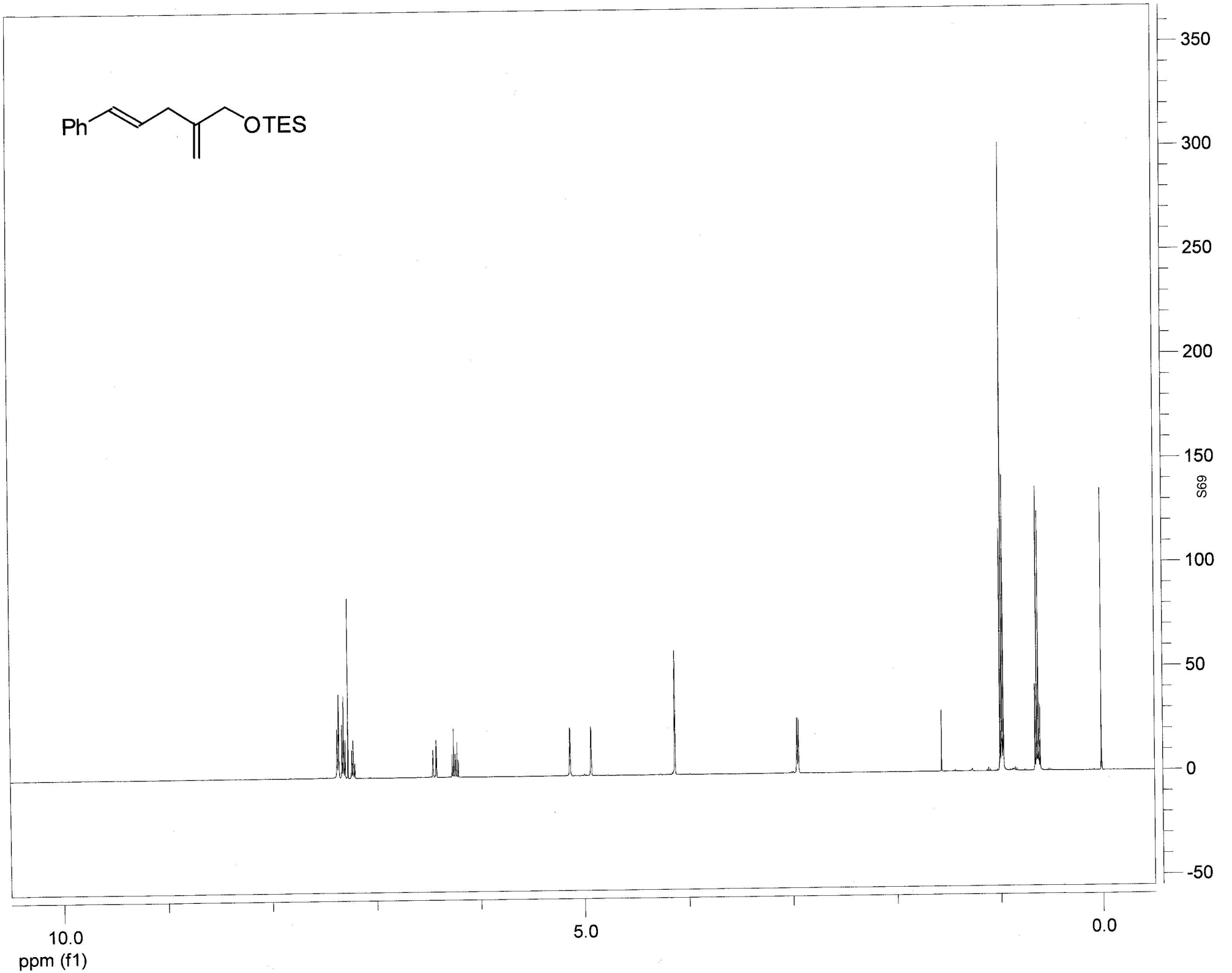

Ph
Ph
Ph
250
200
150
100
50
0
10.0
ppm (f1)
5.0
0.0

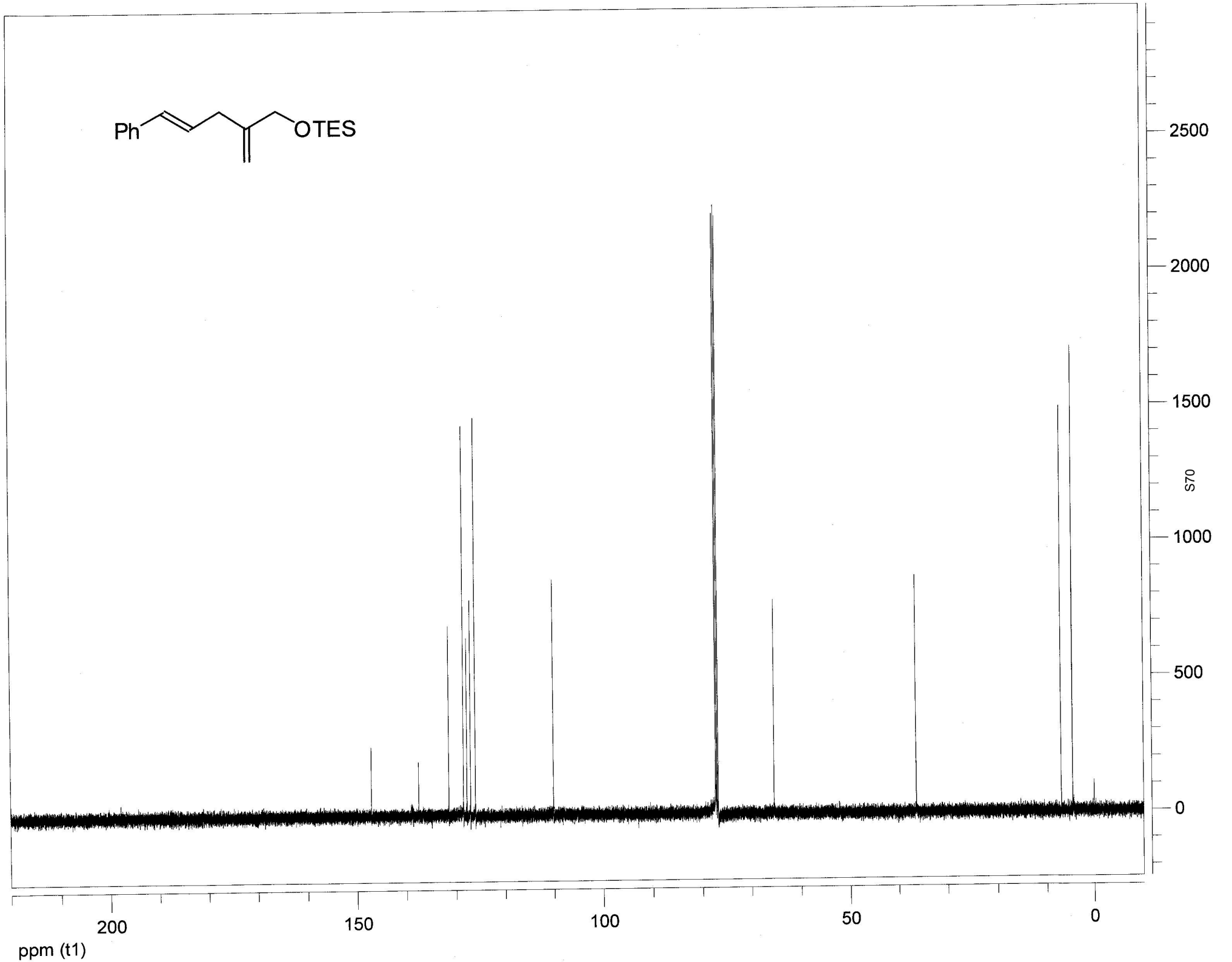

Ph
350
300
250
200
150
100
50
0
-50
S65
10.0
ppm (f1)
5.0
0.0

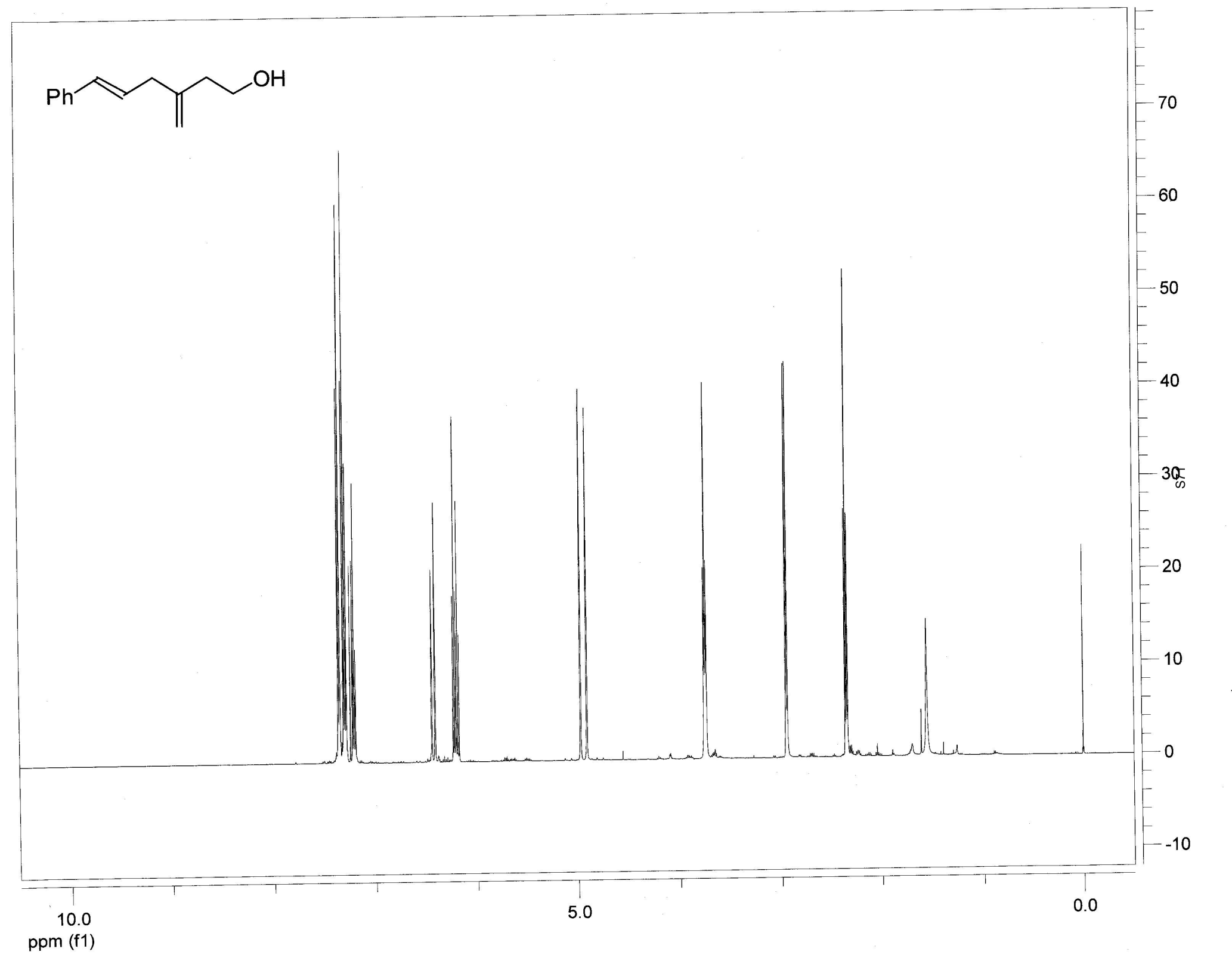

Ph
1500
1000
500
0
S66
200
150
100
50
0
ppm (f1)

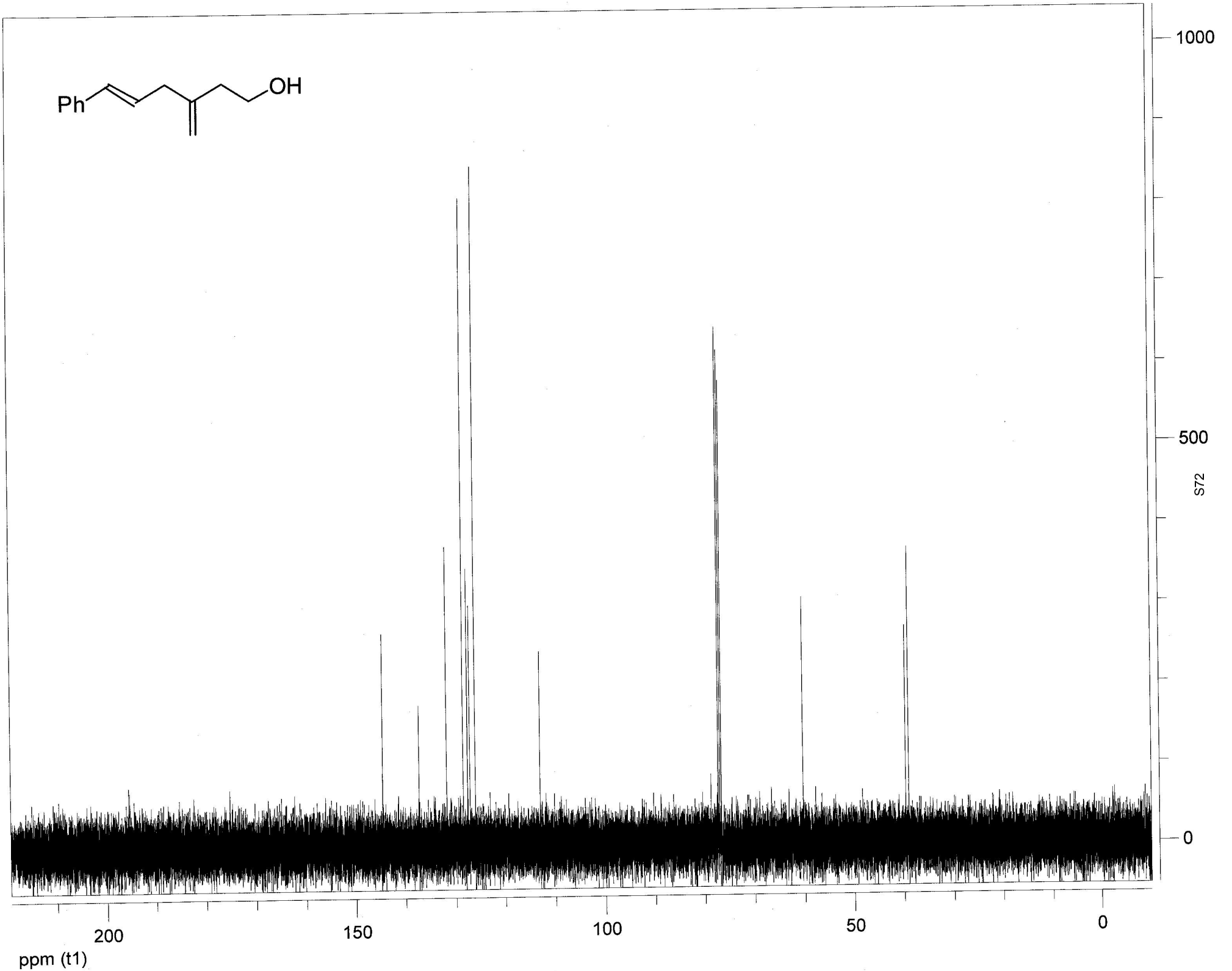
Ph
n-hex
10.0
5.0
0.0
ppm (f1)
0
50
100

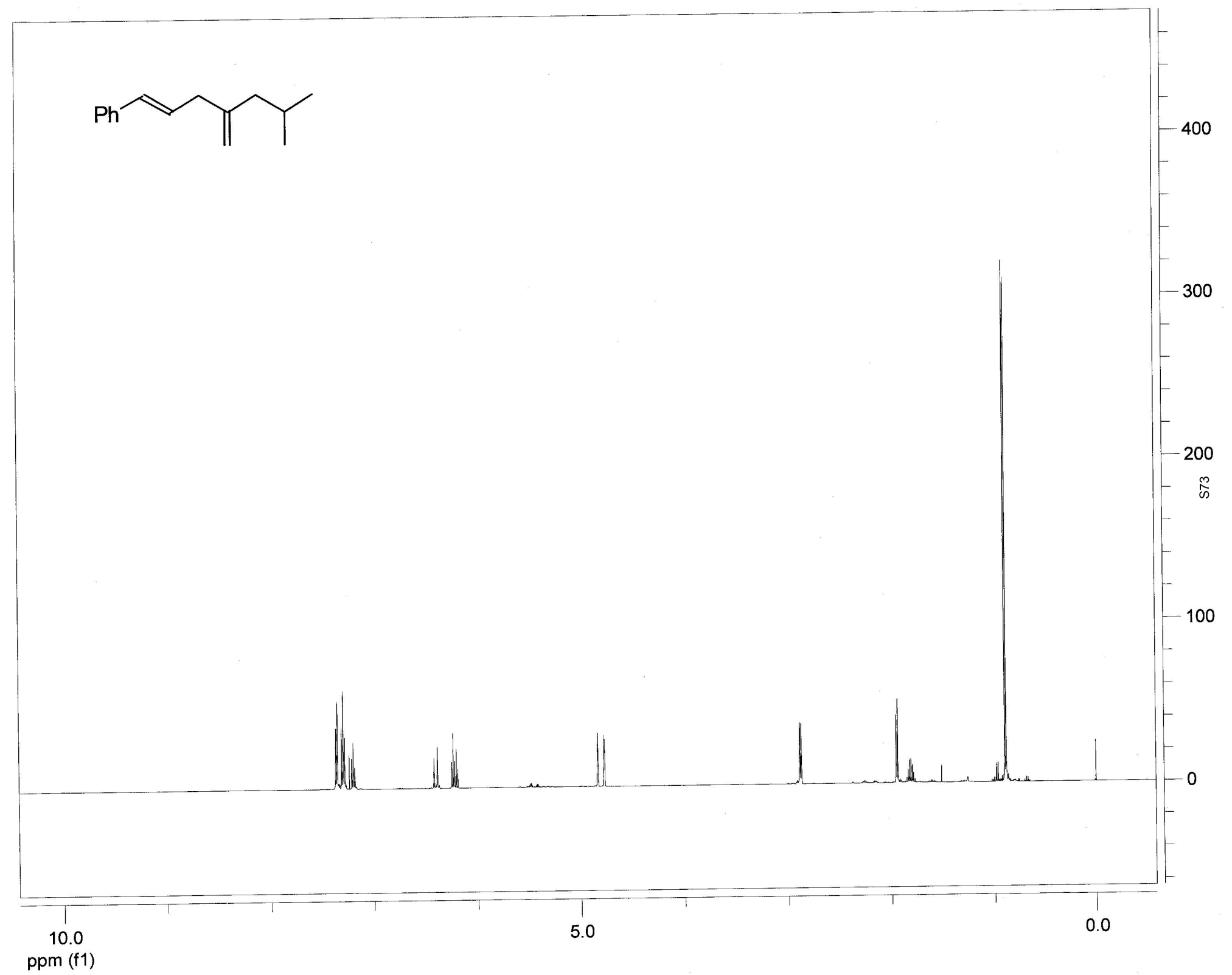

Ph
n-hex
1500
1000
500
0
S68
200
150
100
50
0
ppm (t1)

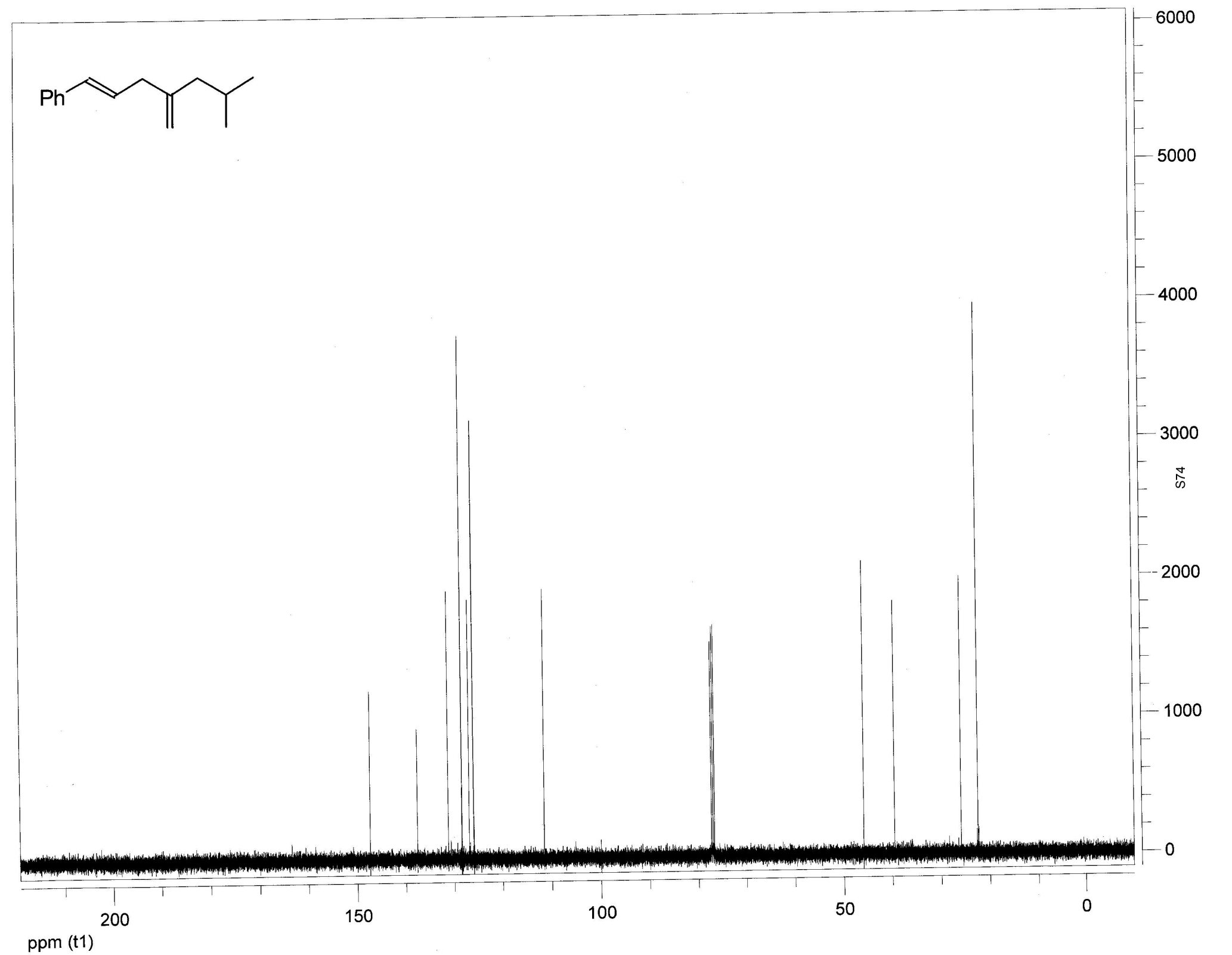

Ph
OTES
350
300
250
200
150
100
50
0
-50
S69
10.0
ppm (f1)
5.0
0.0

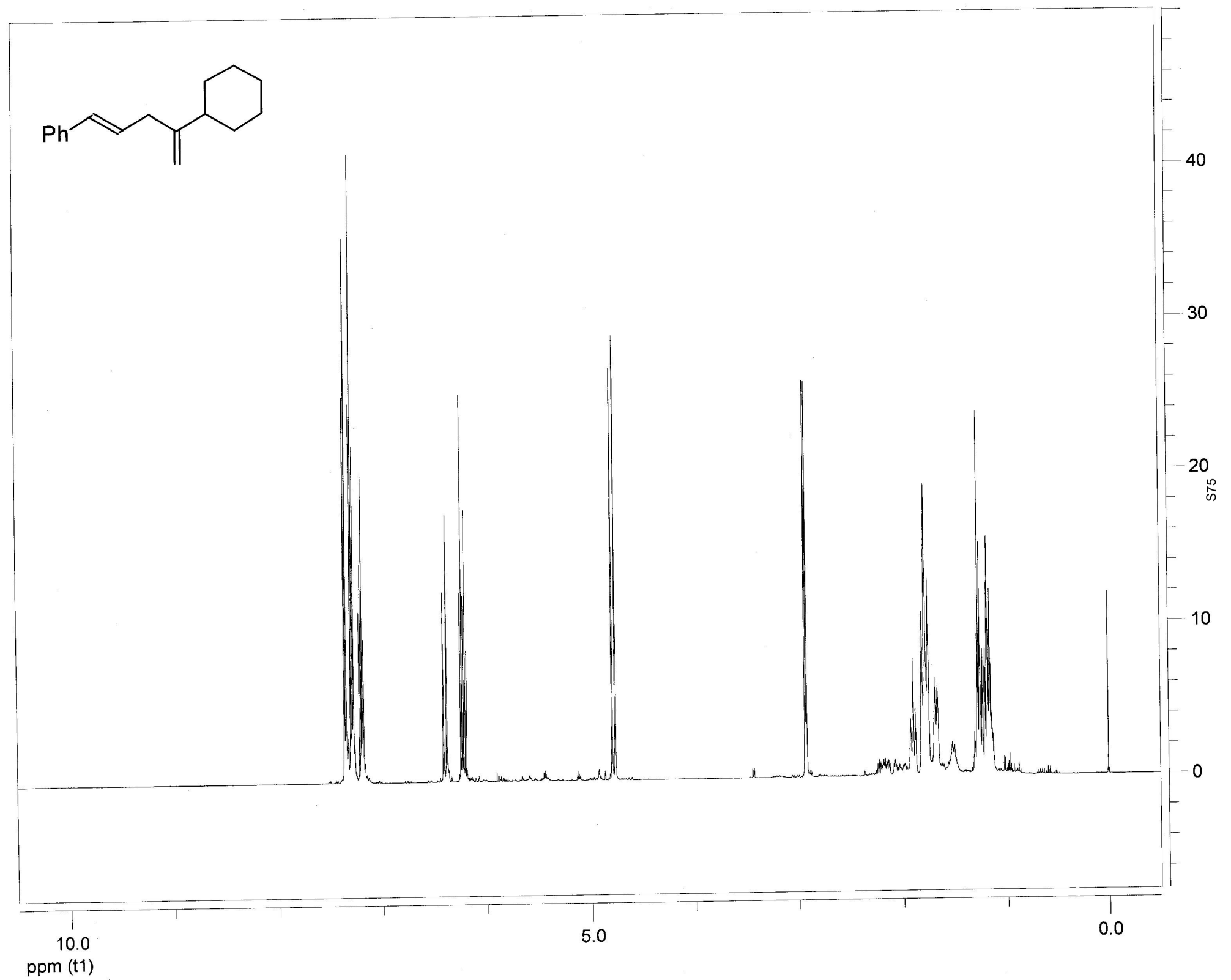

Ph
OTES
2500
2000
1500
S70
1000
500
0
200
150
100
50
0
ppm (t1)

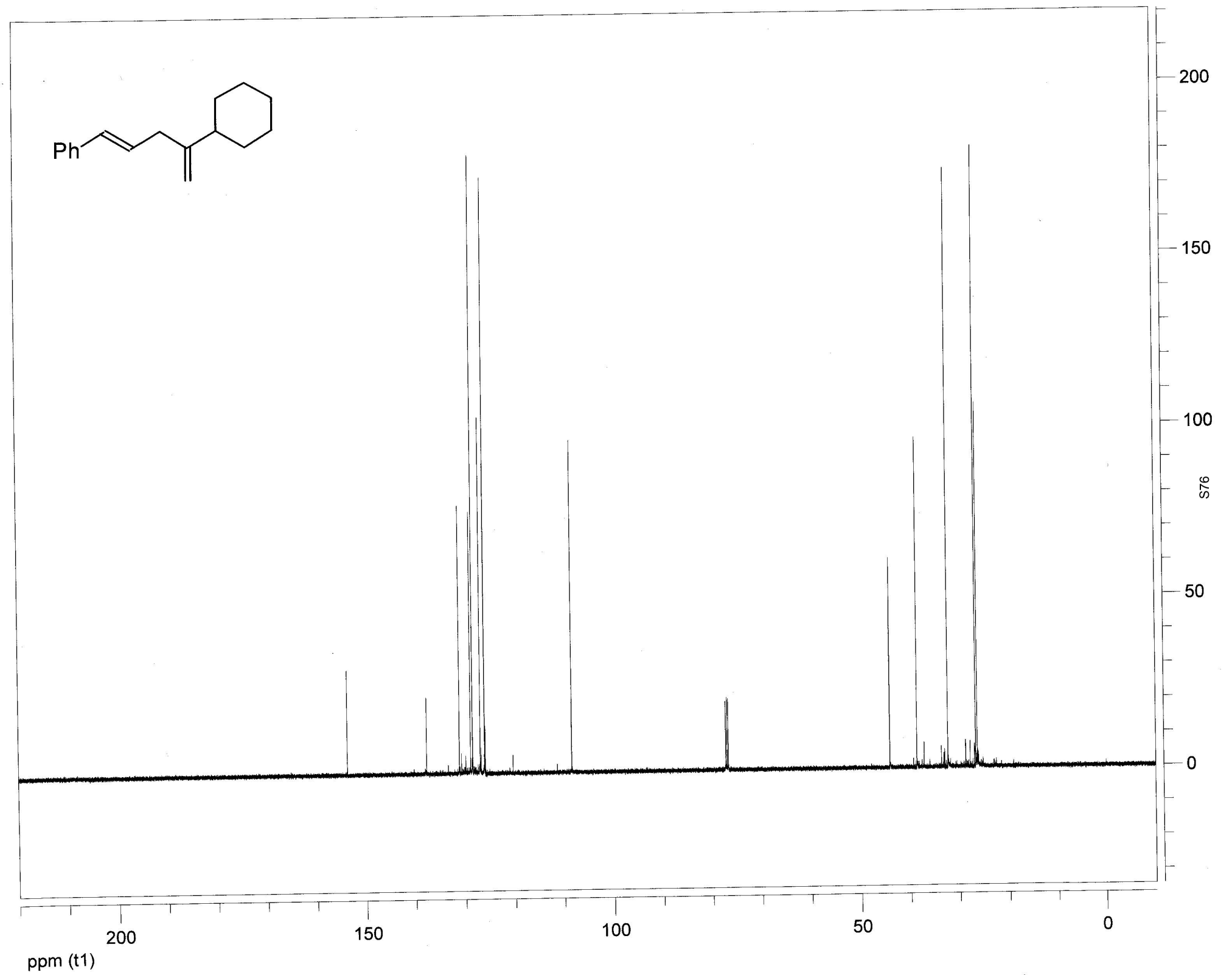

Ph
OH
70
60
50
40
30
20
10
0
-10
10.0
ppm (f1)
5.0
0.0

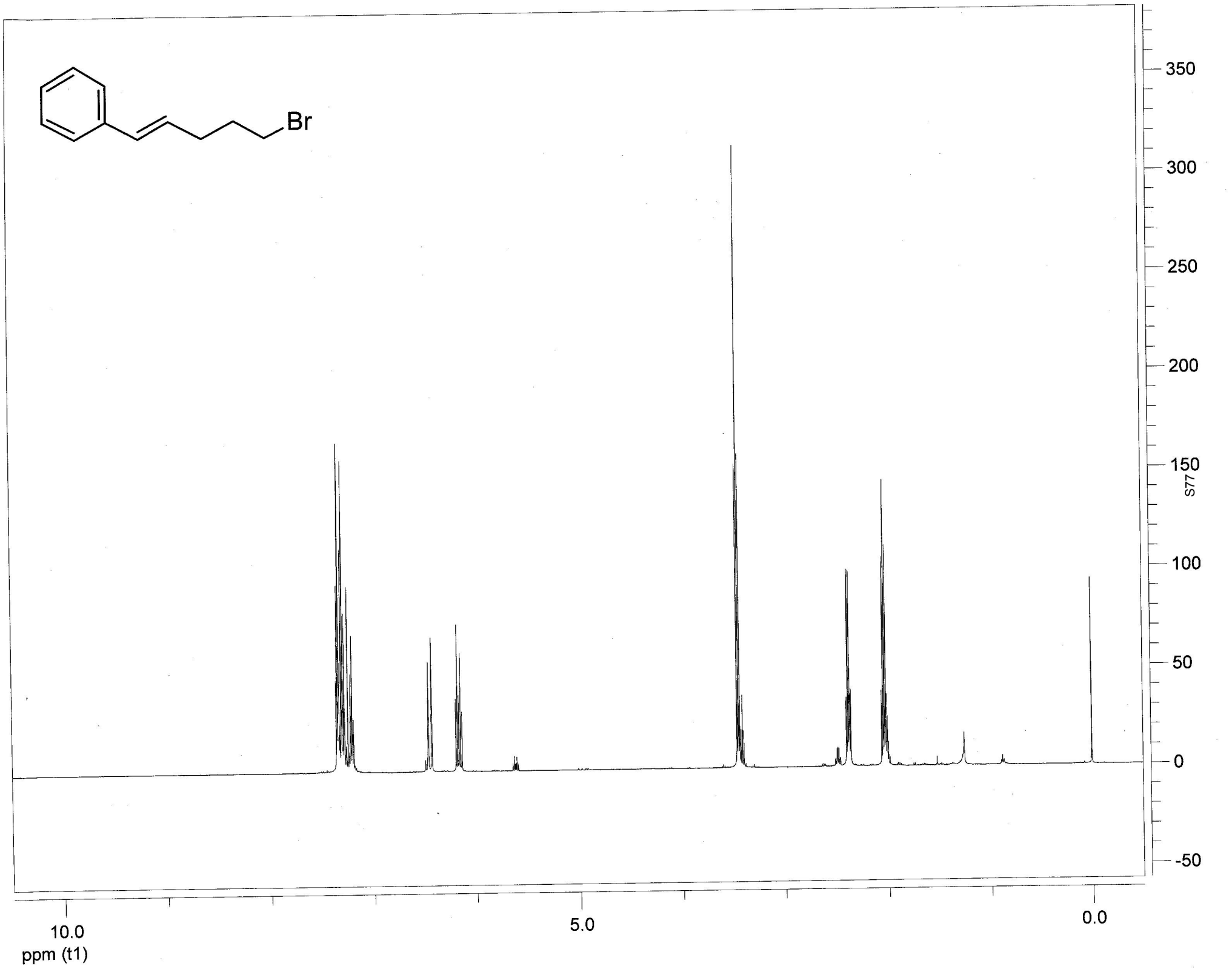

Ph
OH
1000
500
0
S72
200
150
100
50
0
ppm (t1)

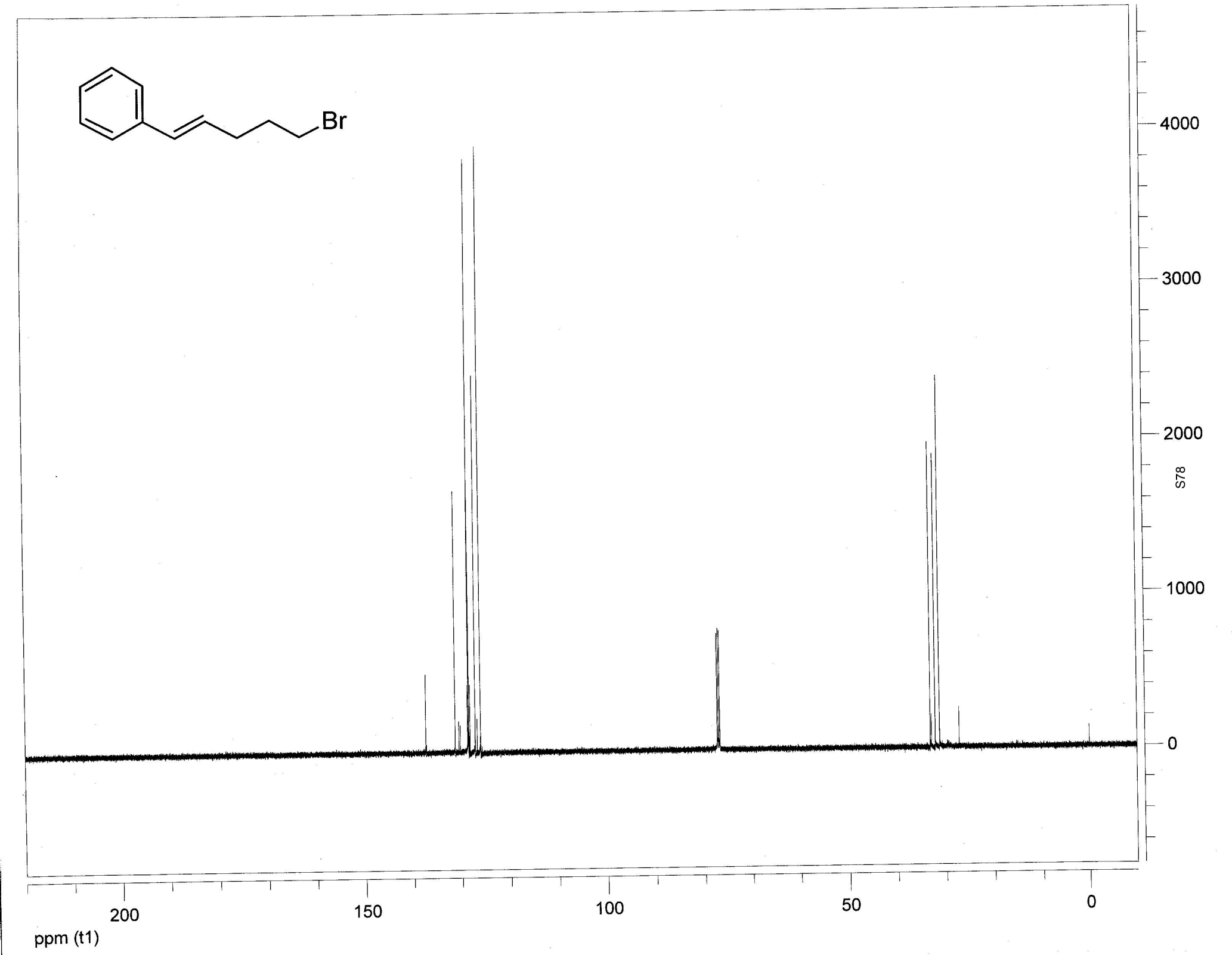

Ph
400
300
200
100
0
S73
10.0
ppm (f1)
5.0
0.0

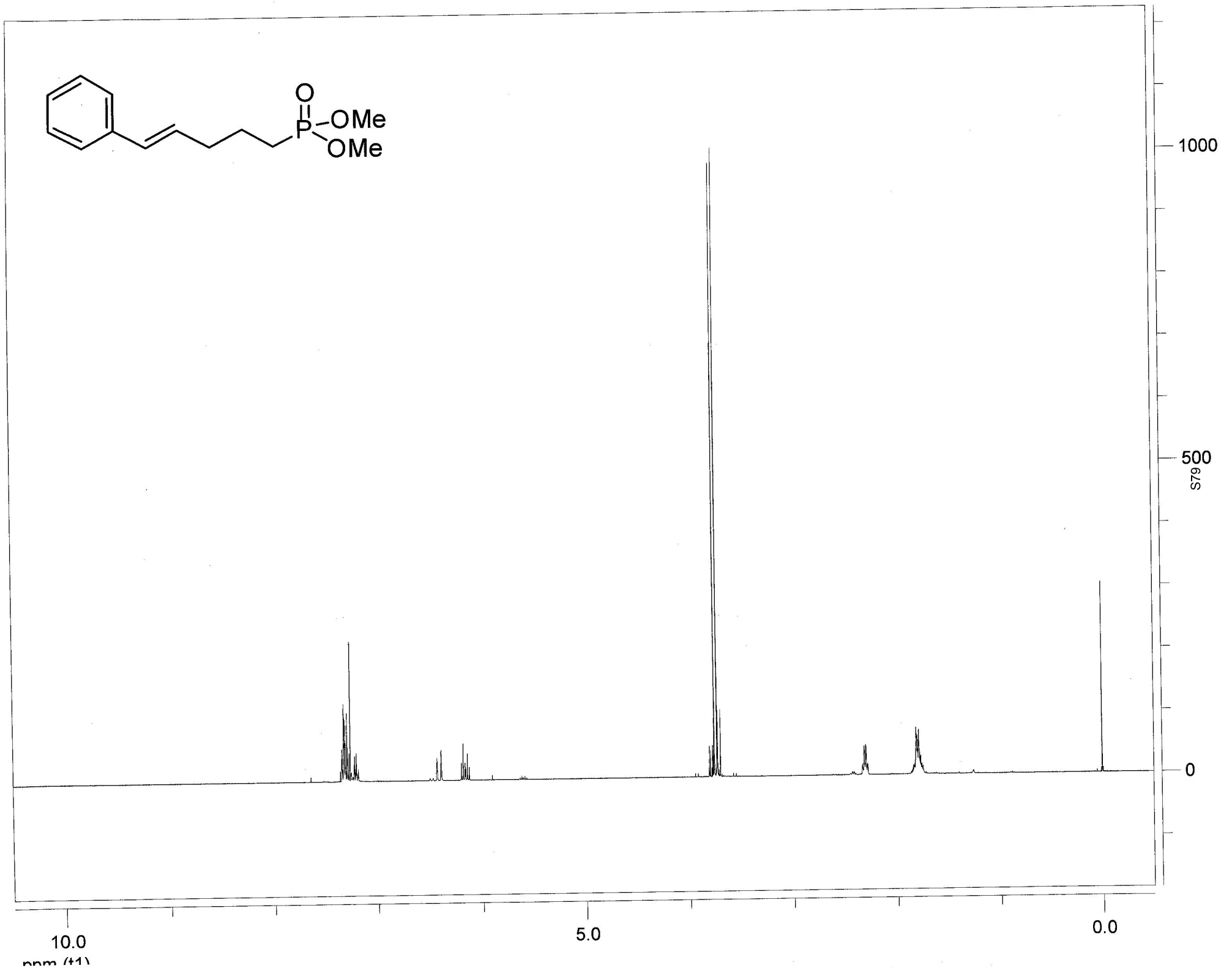

Ph
6000
5000
4000
3000
2000
1000
0
S74
200
150
100
50
0
ppm (t1)

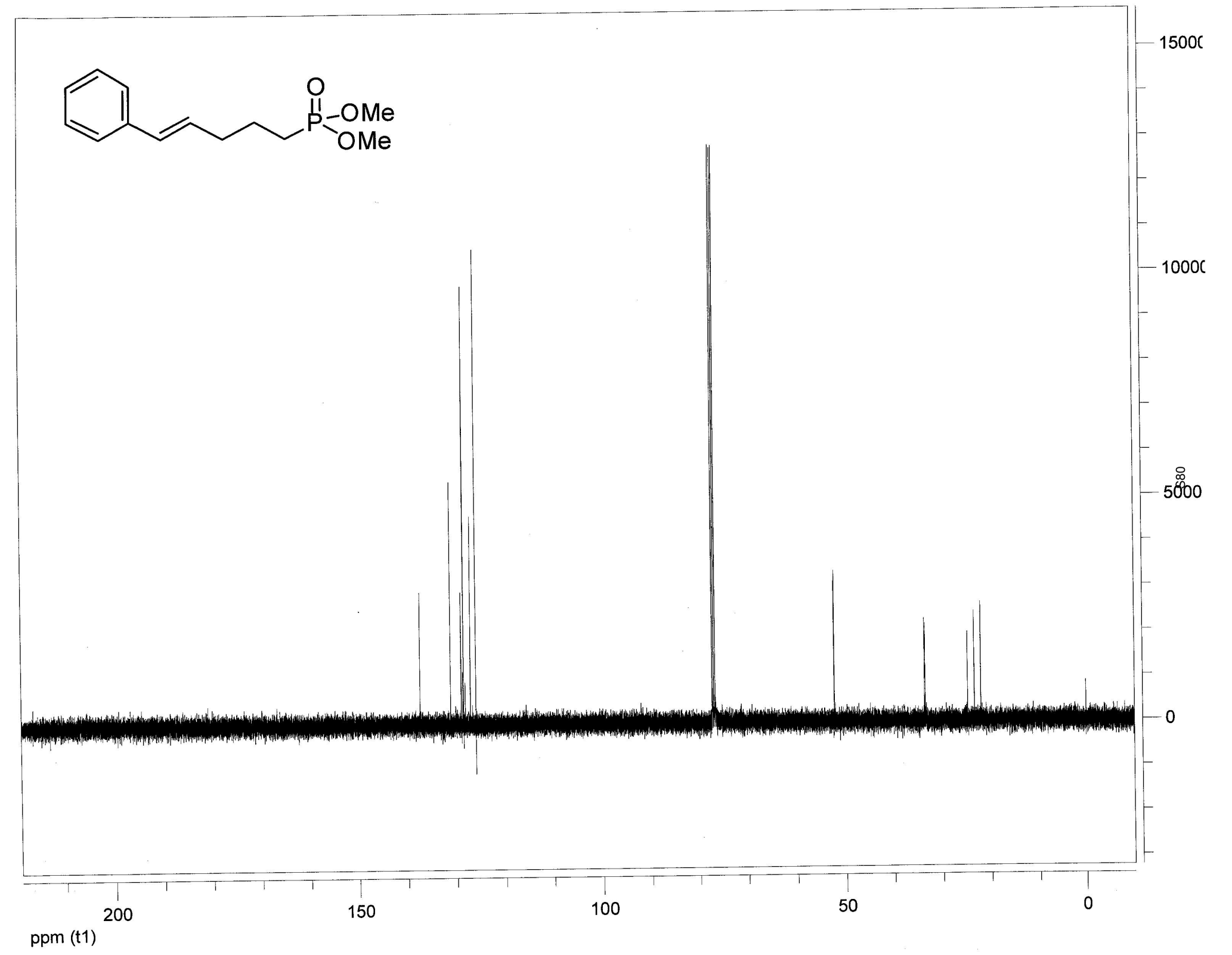

Ph
40
30
20
10
0
S75
10.0
ppm (t1)
5.0
0.0


Ph
200
150
100
50
0
ppm (t1)
S76

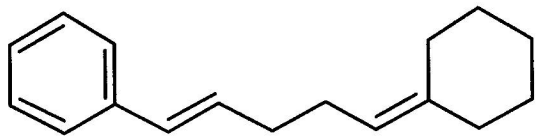

Br
350
300
250
200
150
100
50
0
-50
S77
10.0
ppm (t1)
5.0
0.0


Br
4000
3000
2000
1000
0
S78
200
150
100
50
0
ppm (t1)

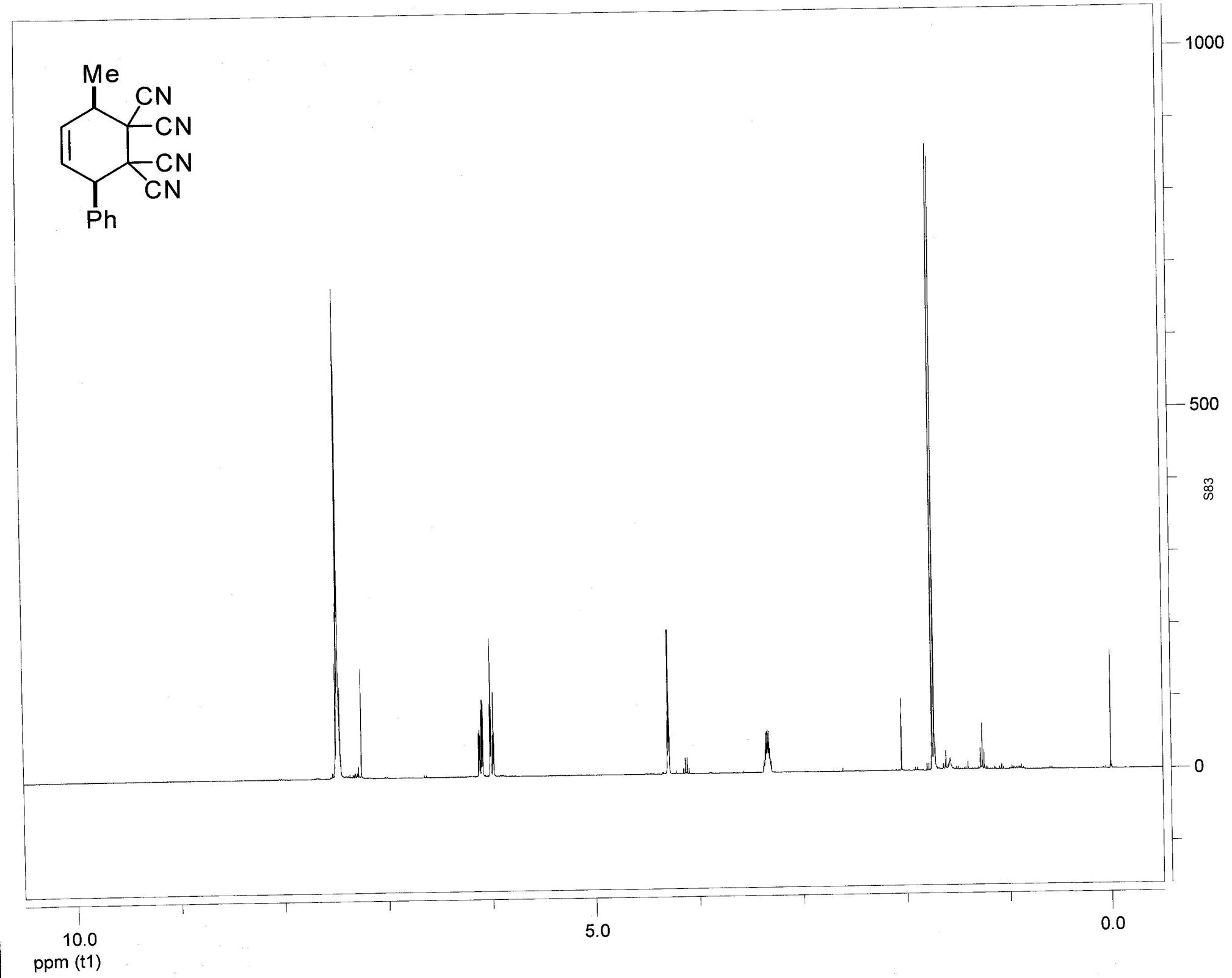

O
P
OMe
OMe
1000
500
0
S79
10.0
5.0
0.0
ppm (t1)

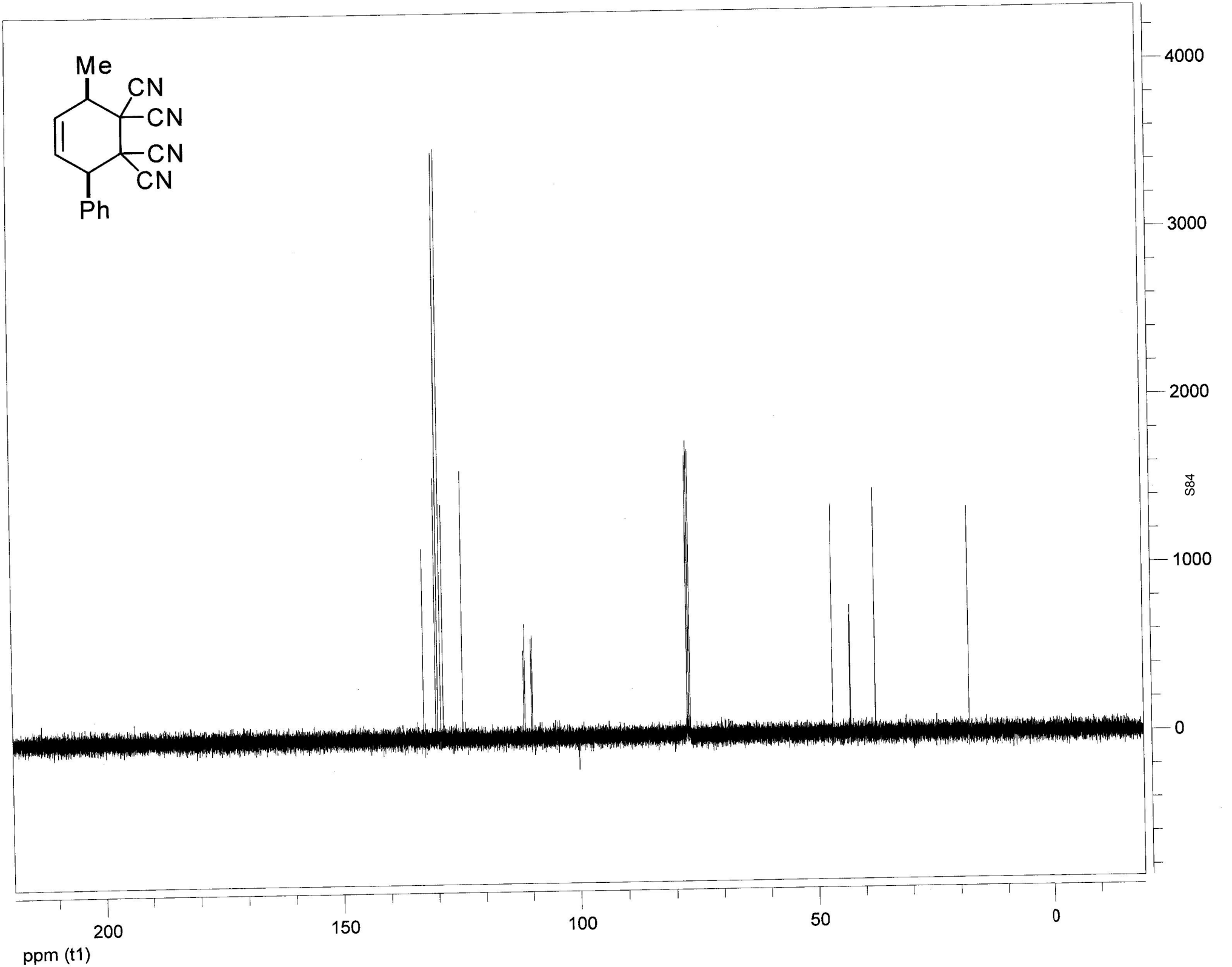

O
P
OMe
OMe
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

ppm (f1)
10.0
5.0
0.0
0
50
100



8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
Sc
200
150
100
50
0
ppm (t1)


Me
CN
CN
CN
CN
Ph
1000
500
0
S83
10.0
ppm (t1)
5.0
0.0


Me
CN
CN
CN
CN
Ph
4000
3000
2000
1000
0
S84
200
150
100
50
0
ppm (t1)