Enantioselective rhodium-catalyzed allylic alkylation of acyclic α-alkoxy substituted ketones using a chiral monodentate phosphite ligand

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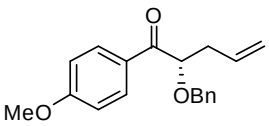
Contents of Supporting Information:

1. General Information

All reactions were carried out under an argon atmosphere with anhydrous solvents and commercially available reagents were purchased and used as received. Compounds were purified by flash chromatography using silica gel 60 (40-63 μm, *FluoroChem*) and gave spectroscopic data consistent with being ≥95% the assigned structure. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick silica gel 60-F_{254} plates (*Whatman PE SIL G/UV*); visualized using UV light and by treatment with a $KMnO_4$ stain followed by heating. Optical rotations ($[\alpha]_D^{20}$) were measured on a *Perkin-Elmer Model 343 plus* polarimeter with a sodium lamp (D line, 589 nm) at ambient temperature (indicated in ºC as superscript) using a 1 mL quartz cell of 100 mm length; solution concentration (*c*) are given in g/100 mL. IR spectra were recorded on a *Perkin-Elmer FT-IR Spectrum 100* (ATR)

spectrometer; wavenumbers (ν) are given in cm^{-1}; and the abbreviations w (weak, <25%), m (medium, 25-50%), s (strong, 51-75%), vs (very strong, >75%) and br (broad) are used to describe the relative intensities of the IR absorbance bands. Mass spectra were obtained through the Chemistry Department Mass Spectrometry Service, University of Liverpool. High resolution chemical ionization (CI) and electrospray ionization (ESI) mass spectra were recorded on a *Fisons Trio-1000* or *LTQ Orbitrap*, and *Micromass LTC* mass spectrometers, respectively. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on a *Bruker Avance DRX-500* spectrometer in $CDCl_3$ or C_6D_6 at ambient temperature; chemical shifts (δ) are given in ppm and calibrated using the signal of residual undeuterated solvent as internal reference (δ_H = 7.26 ppm and δ_C = 77.16 ppm for $CDCl_3$, δ_H = 7.16 ppm and δ_C = 128.06 ppm for C_6D_6). ^{1}H NMR data are reported as follows: chemical shift (multiplicity, first order spin system if available, coupling constant, integration). Coupling constants (*J*) are reported in Hz and apparent splitting patterns are designated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quintet, m (multiplet), br (broad), app. (apparent) and the appropriate combinations. ^{13}C NMR spectra with complete proton decoupling were described with the aid of an APT sequence, separating methylene and quaternary carbons (e, even), from methyl and methine carbons (o, odd).

2. Spectral Data for the Allylic Alkylation Products



(2*S*)-2-(Benzyloxy)-1-(4-methoxyphenyl)pent-4-en-1-one (4a).

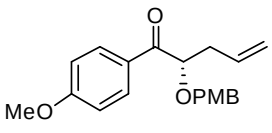
$[\alpha]_D^{20}$ –57.5 (*c* = 1.01, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column), 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 11.2 min., t_R (*minor*) 19.7 min., 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.34-7.26 (m, 5H), 6.95-6.92 (m, 2H), 5.87 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.10-5.06 (m, 2H), 4.65 (d, A of AB, J_{AB} = 11.8 Hz, 1H), 4.65-4.62 (m, 1H), 4.41 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 3.88 (s, 3H), 2.68-2.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.55 (e), 163.88 (e), 137.75 (e), 133.69 (o), 131.38 (o), 128.52 (o), 128.26 (e), 128.12 (o), 127.95 (o), 117.84 (e), 113.94 (o), 82.30 (o), 71.86 (e), 55.63 (o), 37.95 (e).

IR (neat) 3068 (w), 3028 (w), 3008 (w), 2977 (w), 2948 (w), 2836 (w), 1765 (m), 1642 (w), 1597 (w), 1505 (s), 1455 (m), 1441 (m), 1191 (s), 1166 (m), 1118 (s), 1101 (s), 1033 (m) cm^{-1}.

HRMS (EI, $[M+H]^+$) calcd for $C_{19}H_{20}O_3$ 296.1407, found 296.1401.



(2*S*)-2-[(4-Methoxybenzyl)oxy]-1-(4-methoxyphenyl)pent-4-en-1-one (4b).

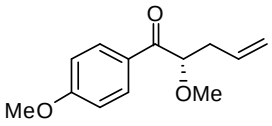
$[\alpha]_D^{20}$ –39.7 (*c* = 1.18, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column), 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 17.0 min., t_R (*minor*) 35.4 min., 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.23-7.20 (m, 2H), 6.94-6.91 (m, 2H), 6.86-6.83 (m, 2H), 5.89-5.80 (m, 1H), 5.08-5.05 (m, 2H), 4.61 (dd, *J* = 7.8, 5.4 Hz, 1H), 4.58 (d, A of AB, J_{AB} = 11.3 Hz, 1H), 4.34 (d, B of AB, J_{AB} = 11.3 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 2.65-2.54 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.70 (e), 163.83 (e), 159.42 (e), 133.72 (o), 131.34 (o), 129.82 (o), 129.76 (e), 128.24 (e), 117.73 (e), 113.88 (o), 81.88 (o), 71.50 (e), 55.60 (o), 55.38 (o), 37.91 (e).

IR (neat) 3008 (w), 2962 (w), 2937 (w), 2966 (w), 2838 (w), 1680 (m), 1598 (s), 1511 (s), 1463 (m), 1421 (m), 1304 (m), 1246 (s), 1171 (s), 1093 (m), 1032 (s), 751 (s) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{20}H_{23}O_4$ 327.1591, found 327.1600.



(2*S*)-2-Methoxy-1-(4-methoxyphenyl)pent-4-en-1-one (4c).

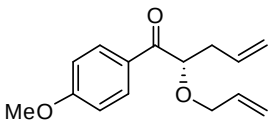
$[\alpha]_D^{20}$ –46.7 (*c* = 0.97, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column), 7% isopropanol/hexane at 0.8 mL/min. flow rate, 280 nm; t_R (*major*) 8.6 min., t_R (*minor*) 9.8 min., 92% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 6.96-6.93 (m, 2H), 5.89-5.81 (m, 1H), 5.11-5.07 (m, 2H), 4.48 (t, *J* = 6.5 Hz, 1H), 3.88 (s, 3H), 3.37 (s, 3H), 2.57 (tt, *J* = 6.7, 1.2 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.39 (e), 163.88 (e), 133.62 (o), 131.25 (o), 128.23 (e), 117.82 (e), 113.96 (o), 84.40 (o), 57.75 (o), 55.61 (o), 37.69 (e).

IR (neat) 3078 (w), 2982 (w), 2933 (w), 2828 (w), 1681 (m), 1641 (w), 1598 (s), 1574 (m), 1509 (m), 1459 (m), 1420 (m), 1309 (m), 1253 (s), 1171 (s), 1115 (m), 1028 (m), 840 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{13}H_{17}O_3$ 221.1172, found 221.1173.



(2*S*)-2-(Allyloxy)-1-(4-methoxyphenyl)pent-4-en-1-one (4d).

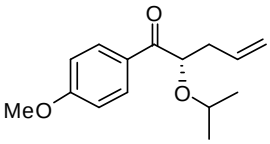
$[\alpha]_D^{20}$ –31.9 (*c* = 1.10, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column), 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 8.2 min., t_R (*minor*) 10.8 min., 87% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09-8.06 (m, 2H), 6.95-6.93 (m, 2H), 5.93-5.82 (m, 2H), 5.25 (app. dq, *J* = 17.2, 1.6 Hz, 1H), 5.17 (app. dq, *J* = 10.4, 1.3 Hz, 1H), 5.10-5.06 (m, 2H), 4.61 (dd, *J* = 7.5, 5.6 Hz, 1H), 4.10 (ddt, A of $ABMX_2$, J_{AB} = 12.7 Hz, J_{AM} = 5.3 Hz, J_{AX} = 1.4 Hz, 1H), 3.91 (ddt, B of $ABMX_2$, J_{AB} = 12.7 Hz, J_{BM} = 6.0 Hz, J_{BX} = 1.3 Hz, 1H), 3.88 (s, 3H), 2.63-2.54 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.58 (e), 163.85 (e), 134.36 (o), 133.70 (o), 131.33 (o), 128.30 (e), 117.81 (e), 117.76 (e), 113.93 (o), 82.26 (o), 71.02 (e), 55.62 (o), 37.96 (e).

IR (neat) 3079 (w), 3008 (w), 2981 (w), 2937 (w), 2840 (w), 1677 (m), 1599 (s), 1574 (m), 1509 (m), 1421 (m), 1310 (m), 1257 (s), 1172 (s), 1100 (m), 1031 (m), 921 (m), 841 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{15}H_{19}O_3$ 247.1329, found 247.1339.



(2*S*)-2-Isopropoxy-1-(4-methoxyphenyl)pent-4-en-1-one (4e).

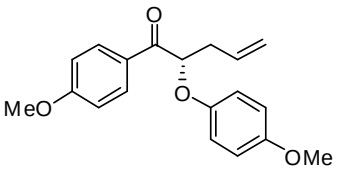
$[\alpha]_D^{20}$ –50.5 (*c* = 0.99, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 280 nm; t_R (*major*) 7.7 min., t_R (*minor*) 10.2 min., 89% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14-8.11 (m, 2H), 6.95-6.92 (m, 2H), 5.85 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.09-5.04 (m, 2H), 4.52 (dd, *J* = 8.2, 5.3 Hz, 1H), 3.88 (s, 3H), 3.59 (septet, *J* = 6.1 Hz, 1H), 2.59-2.48 (m, 2H), 1.17 (d, *J* = 6.0 Hz, 3H), 1.11 (d, *J* = 6.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.79 (e), 163.70 (e), 134.03 (o), 131.60 (o), 128.11 (e), 117.56 (e), 113.76 (o), 81.76 (o), 71.83 (o), 55.60 (o), 38.65 (e), 23.08 (o), 21.65 (o).

IR (neat) 3078 (w), 2972 (w), 2932 (w), 2841 (w), 1687 (m), 1668 (m), 1598 (s), 1574 (m), 1509 (m), 1310 (m), 1254 (s), 1171 (s), 1117 (m), 1088 (m), 1028 (m), 916 (m), 841 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{15}H_{21}O_3$ 249.1485, found 249.1495.



(2*S*)-2-(4-Methoxyphenoxy)-1-(4-methoxyphenyl)pent-4-en-1-one (4f).

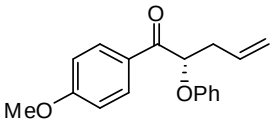
$[\alpha]_D^{20}$ –13.5 (*c* = 1.11, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 23.9 min., t_R (*minor*) 36.5 min., 90% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10-8.07 (m, 2H), 6.95-6.92 (m, 2H), 6.82-6.79 (m, 2H), 6.76-6.73 (m, 2H), 5.94 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.19 (dd, *J* = 7.9, 5.1 Hz, 1H), 5.18-5.11 (m, 2H), 3.87 (s, 3H), 3.71 (s, 3H), 2.83-2.70 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 197.23 (e), 164.04 (e), 154.42 (e), 151.98 (e), 133.21 (o), 131.47 (o), 127.56 (e), 118.33 (e), 116.60 (o), 114.78 (o), 114.07 (o), 81.81 (o), 55.76 (o), 55.63 (o), 37.90 (e).

IR (neat) 3073 (w), 3008 (w), 2936 (w), 2906 (w), 2838 (w), 1680 (m), 1597 (s), 1510 (s), 1462 (m), 1304 (m), 1245 (s), 1171 (s), 1094 (m), 1029 (m), 918 (m), 840 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{19}H_{21}O_4$ 313.1434, found 313.1427.



(2*S*)-1-(4-Methoxyphenyl)-2-phenoxypent-4-en-1-one (4g).

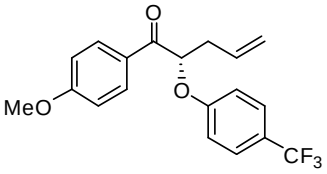
$[\alpha]_D^{20}$ +4.7 (*c* = 1.14, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 16.0 min., t_R (*minor*) 23.6 min., 87% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11-8.08 (m, 2H), 7.23-7.19 (m, 2H), 6.95-6.90 (m, 3H), 6.87-6.85 (m, 2H), 5.95 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.29 (dd, *J* = 7.9, 5.1 Hz, 1H), 5.18-5.12 (m, 2H), 3.87 (s, 3H), 2.85-2.73 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 196.85 (e), 164.08 (e), 157.80 (e), 133.11 (o), 131.45 (o), 129.68 (o), 127.44 (e), 121.57 (o), 118.38 (e), 115.35 (o), 114.10 (o), 80.82 (o), 55.63 (o), 37.83 (e).

IR (neat) 3073 (w), 3013 (w), 2918 (w), 2850 (w), 1686 (m), 1597 (s), 1573 (m), 1509 (m), 1493 (m), 1421 (m), 1309 (m), 1258 (m), 1227 (s), 1171 (s), 1071 (m), 1027 (m), 841 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{18}H_{19}O_3$ 283.1329, found 283.1323.



(2*S*)-1-(4-Methoxyphenyl)-2-[4-(trifluoromethyl)phenoxy]pent-4-en-1-one (4h).

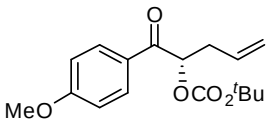
$[\alpha]_D^{20}$ +19.0 (*c* = 1.11, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 230 nm; t_R (*major*) 15.9 min., t_R (*minor*) 23.4 min., 78% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08-8.05 (m, 2H), 7.47 (d, *J* = 8.8 Hz, 2H), 6.97-6.94 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.93 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1H), 5.36 (dd, *J* = 7.7, 5.1 Hz, 1H), 5.20-5.14 (m, 2H), 3.88 (s, 3H), 2.86-2.76 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 195.77 (e), 164.34 (e), 160.20 (e), 132.64 (o), 131.34 (o), 127.14 (o, q, $^3J_{CF}$ = 3.7 Hz), 124.38 (e, q, $^1J_{CF}$ = 271.3 Hz), 123.68 (e, q, $^2J_{CF}$ = 32.4 Hz), 118.73 (e), 115.24 (o), 114.28 (o), 80.63 (o), 55.65 (o), 37.71 (e).

IR (neat) 3078 (w), 3013 (w), 2957 (w), 2936 (w), 2841 (w), 1686 (m), 1615 (m), 1598 (s), 1573 (w), 1512 (m), 1422 (w), 1326 (s), 1239 (s), 1171 (s), 1161 (s), 1109 (s), 1063 (s), 834 (s) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{19}H_{18}O_3F_3$ 351.1203, found 351.1202.



***tert*-Butyl (2*S*)-1-(4-methoxyphenyl)-1-oxypent-4-en-2-yl carbonate (4i).**

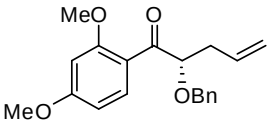
$[\alpha]_D^{20}$ +42.5 (*c* = 0.55, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 7% isopropanol/hexane at 0.8 mL/min. flow rate, 270 nm; t_R (*minor*) 12.8 min., t_R (*major*) 42.8 min., 94% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.92 (m, 2H), 6.96-6.93 (m, 2H), 5.84 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 5.72 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.13-5.09 (m, 2H), 3.87 (s, 3H), 2.67-2.56 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 194.54 (e), 164.00 (e), 153.10 (e), 132.41 (o), 130.93 (o), 127.67 (e), 118.72 (e), 114.12 (o), 83.07 (e), 76.77 (o), 55.65 (o), 36.10 (e), 27.81 (o).

IR (neat) 3079 (w), 3013 (w), 2981 (w), 2937 (w), 2840 (w), 1677 (m), 1599 (s), 1574 (m), 1509 (m), 1421 (m), 1310 (m), 1257 (s), 1172 (s), 1100 (m), 1031 (m), 921 (m), 841 (m) cm^{-1}.

HRMS (EI, M^+) calcd for $C_{17}H_{22}O_5$ 306.1462, found 306.1464.



(2S)-2-(Benzyloxy)-1-(2,4-dimethoxyphenyl)pent-4-en-1-one (4j).

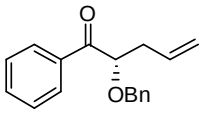
$[\alpha]_D^{20}$ –57.7 (c = 1.04, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (major) 20.2 min., t_R (minor) 25.4 min., 98% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.28-7.25 (m, 1H), 6.55 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.43 (d, *J* = 2.0 Hz, 1H), 5.96-5.88 (m, 1H), 5.06-5.03 (m, 2H), 4.97 (dd, *J* = 8.1, 3.5 Hz, 1H), 4.75 (d, A of AB, J_{AB} = 11.8 Hz, 1H), 4.41 (d, B of AB, J_{AB} = 11.8 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.55-2.50 (m, 1H), 2.38 (dt, B of ABX_2, J_{AB} = 14.7 Hz, J_{BX} = 7.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.47 (e), 164.83 (e), 160.42 (e), 138.56 (e), 134.91 (o), 133.32 (o), 128.32 (o), 128.03 (o), 127.59 (o), 119.74 (e), 116.92 (e), 105.66 (o), 98.41 (o), 83.37 (o), 71.94 (e), 55.71 (o), 55.54 (o), 37.10 (e).

IR (neat) 3068 (w), 3008 (w), 2977 (w), 2942 (w), 2839 (w), 1670 (m), 1598 (s), 1572 (m), 1498 (m), 1455 (m), 1417 (m), 1295 (m), 1252 (m), 1211 (s), 1162 (m), 1103 (s), 1025 (m), 914 (m), 834 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{20}H_{23}O_4$ 327.1591, found 327.1590.



(2*S*)-2-(Benzyloxy)-1-phenylpent-4-en-1-one (4k).

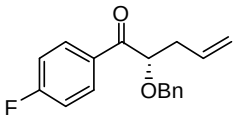
$[\alpha]_D^{20}$ –58.4 (*c* = 1.02, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 7.9 min., t_R (*minor*) 11.0 min., 90% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05-8.03 (m, 2H), 7.60-7.57 (m, 1H), 7.48-7.45 (m, 2H), 7.35-7.28 (m, 5H), 5.92-5.84 (m, 1H), 5.10-5.07 (m, 2H), 4.72 (dd, *J* = 7.0, 5.9 Hz, 1H), 4.68 (d, A of AB, J_{AB} = 11.7 Hz, 1H), 4.43 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 2.68-2.59 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.07 (e), 137.59 (e), 135.30 (e), 133.57 (o), 133.45 (o), 128.87 (o), 128.77 (o), 128.52 (o), 128.12 (o), 127.98 (o), 117.99 (e), 81.99 (o), 71.94 (e), 37.66 (e).

IR (neat) 3065 (w), 3030 (w), 2922 (w), 2856 (w), 1693 (s), 1676 (s), 1641 (w) 1597 (m), 1578 (w), 1448 (m), 1242 (m), 1207 (m), 1098 (s), 1077 (m), 1027 (m), 1001 (m), 917 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{18}H_{19}O_2$ 267.1380, found 267.1393.



(2*S*)-2-(Benzyloxy)-1-(4-fluorophenyl)pent-4-en-1-one (4l).

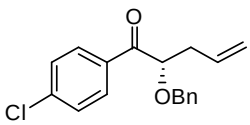
$[\alpha]_D^{20}$ –46.3 (*c* = 1.14, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 7.6 min., t_R (*minor*) 10.3 min., 87% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12-8.08 (m, 2H), 7.34-7.27 (m, 5H), 7.14-7.10 (m, 2H), 5.89-5.81 (m, 1H), 5.10-5.06 (m, 2H), 4.63 (d, A of AB, J_{AB} = 11.6 Hz, 1H), 4.61 (dd, *J* = 7.6, 5.5 Hz, 1H), 4.43 (d, B of AB, J_{AB} = 11.6 Hz, 1H), 2.68-2.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.63 (e), 165.99 (e, d, $^1J_{CF}$ = 255.6 Hz), 137.41 (e), 133.27 (o), 131.79 (o, d, $^3J_{CF}$ = 9.3 Hz), 131.59 (e, d, $^4J_{CF}$ = 3.3 Hz), 128.56 (o), 128.14 (o), 128.08 (o), 118.14 (e), 115.88 (o, d, $^2J_{CF}$ = 21.9 Hz), 82.62 (o), 72.06 (e), 37.69 (e).

IR (neat) 3084 (w), 3013 (w), 2925 (w), 2861 (w), 1691 (m), 1676 (m), 1642 (w), 1598 (s), 1506 (m), 1455 (w), 1410 (w), 1233 (s), 1157 (m), 1097 (m), 1014 (w), 920 (m), 846 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{18}H_{18}O_2F$ 285.1285, found 285.1293.



(2*S*)-2-(Benzyloxy)-1-(4-chlorophenyl)pent-4-en-1-one (4m).

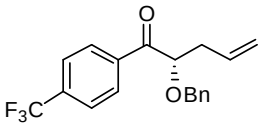
$[\alpha]_D^{20}$ –22.7 (*c* = 1.08, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate; t_R (*major*) 7.7 min., t_R (*minor*) 10.9 min., 90% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.44-7.41 (m, 2H), 7.35-7.27 (m, 5H), 5.88-5.80 (m, 1H), 5.10-5.05 (m, 2H), 4.63 (d, A of AB, J_{AB} = 12.0 Hz, 1H), 4.61 (dd, J = 7.8, 5.7 Hz, 1H), 4.43 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 2.68-2.56 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.10 (e), 140.06 (e), 137.36 (e), 133.48 (e), 133.19 (o), 130.50 (o), 129.09 (o), 128.60 (o), 128.17 (o), 128.13 (o), 118.24 (e), 82.63 (o), 72.12 (e), 37.66 (e).

IR (neat) 3067 (w), 3033 (w), 2922 (w), 2867 (w), 1680 (s), 1641 (w), 1587 (s), 1488 (m), 1455 (m), 1400 (m), 1271 (m), 1208 (m), 1176 (m), 1091 (s), 1013 (m), 918 (m), 839 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{18}H_{18}O_2Cl$ 301.0990, found 301.0992.



(2*S*)-2-(Benzyloxy)-1-[4-(trifluoromethyl)phenyl]pent-4-en-1-one (4n).

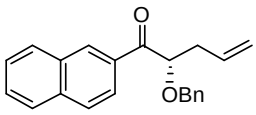
$[\alpha]_D^{20}$ –35.3 (*c* = 1.00, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 4% isopropanol/hexane at 0.8 mL/min. flow rate, 230 nm; t_R (*major*) 7.6 min., t_R (*minor*) 10.3 min., 79% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.35-7.27 (m, 5H), 5.85 (ddt, J = 17.0, 10.2, 6.9 Hz, 1H), 5.11-5.07 (m, 2H), 4.65 (dd, J = 5.3, 2.1 Hz, 1H), 4.64 (d, A of AB, J_{AB} = 11.4 Hz, 1H), 4.47 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 2.67 (dt, A of ABX_2, J_{AB} = 14.5 Hz, J_{AX} = 7.2 Hz, 1H), 2.61 (dt, B of ABX_2, J_{AB} = 14.0 Hz, J_{BX} = 6.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.44 (e), 137.94 (e), 137.19 (e), 134.67 (e, q, $^2J_{CF}$ = 32.7 Hz), 132.95 (o), 129.38 (o), 128.61 (o), 128.19 (o), 125.75 (o, q, $^3J_{CF}$ = 3.6 Hz), 123.66 (e, q, $^1J_{CF}$ = 273.0 Hz), 118.42 (e), 82.71 (o), 72.25 (e), 37.45 (e).

IR (neat) 2962 (m), 2924 (m), 2856 (m), 1699 (m), 1687 (m), 1644 (w), 1456 (m), 1410 (m), 1324 (s), 1270 (m), 1169 (s), 1130 (s), 1112 (s), 1067 (s), 1016 (m), 919 (m), 852 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{19}H_{18}O_2F_3$ 335.1253, found 335.1250.



(2*S*)-2-(Benzyloxy)-1-(2-naphthyl)pent-4-en-1-one (4o).

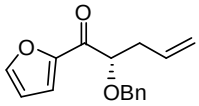
$[\alpha]_D^{20}$ –46.9 (*c* = 1.19, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 7% isopropanol/hexane at 0.8 mL/min. flow rate, 210 nm; t_R (*major*) 10.1 min., t_R (*minor*) 12.5 min., 89% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.89 (t, J = 8.9 Hz, 2H), 7.64-7.60 (m, 1H), 7.58-7.54 (m, 1H), 7.33-7.27 (m, 5H), 5.94-5.87 (m, 1H), 5.12-5.08 (m, 2H), 4.83 (dd, J = 7.5, 5.6 Hz, 1H), 4.72 (d, A of AB, J_{AB} = 11.7 Hz, 1H), 4.48 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 2.76-2.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.07 (e), 137.62 (e), 135.85 (e), 133.50 (o), 132.62 (e), 132.59 (e), 130.80 (o), 129.89 (o), 128.86 (o), 128.65 (o), 128.57 (o), 128.22 (o), 128.04 (o), 127.92 (o), 126.95 (o), 124.51 (o), 118.07 (e), 82.23 (o), 72.02 (e), 37.88 (e).

IR (neat) 3062 (w), 3028 (w), 2923 (m), 2855 (m), 1686 (s), 1627 (m), 1597 (w), 1464 (m), 1455 (m), 1278 (m), 1188 (m), 1098 (s), 917 (m), 825 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{22}H_{21}O_2$ 317.1536, found 317.1534.



(2*S*)-2-(Benzyloxy)-1-(2-furyl)pent-4-en-1-one (4p).

$[\alpha]_D^{20}$ –51.1 (*c* = 1.20, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column, 7% isopropanol/hexane at 0.8 mL/min. flow rate, 280 nm; t_R (*major*) 9.0 min., t_R (*minor*) 11.7 min., 85% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.63 (m, 1H), 7.43 (d, *J* = 3.5 Hz, 1H), 7.35-7.27 (m, 5H), 6.55 (dd, *J* = 3.5, 1.6 Hz, 1H), 5.85 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1H), 5.12-5.07 (m, 2H), 4.67 (d, A of AB, J_{AB} = 11.7 Hz, 1H), 4.48-4.45 (m, 1H), 4.45 (d, B of AB, J_{AB} = 11.8 Hz, 1H), 2.65-2.56 (m, 2H).

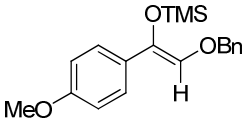
^{13}C NMR (125 MHz, $CDCl_3$) δ 189.23 (e), 150.92 (e), 147.16 (o), 137.50 (e), 133.25 (o), 128.54 (o), 128.07 (o), 128.03 (o), 119.80 (o), 118.15 (e), 112.43 (o), 82.19 (o), 72.31 (e), 37.92 (e).

IR (neat) 3134 (w), 3068 (w), 3032 (w), 2925 (w), 2861 (w), 1668 (s), 1567 (m), 1463 (s), 1391 (m), 1100 (m), 1084 (m), 1014 (s), 914 (m) cm^{-1}.

HRMS (CI, $[M+H]^+$) calcd for $C_{16}H_{17}O_3$ 257.1172, found 257.1181.

3. Preparation of the Silyl Enol Ether (*Z*)-5a

The aryl ketone **1a** (156.5 mg, 0.61 mmol) was dissolved in tetrahydrofuran (2.4 mL) and cooled with stirring to –10 °C under an atmosphere of argon. Lithium bis(trimethylsilyl)amide (611 μL, 0.61 mmol) was added slowly and the mixture was stirred for 10 minutes. Trimethylsilyl chloride (156 μL, 1.22 mmol) was then added and the mixture was stirred for 2 hours at –10 °C. The reaction was quenched with saturated aqueous sodium bicarbonate solution (2 ml) and then partitioned between diethyl ether and saturated aqueous sodium bicarbonate. The combined organic layers were dried using anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography (eluting with 6% ethyl acetate/hexanes) provided the *enol ether* (***Z*)-5a** (179.0 mg, 89%) as a colorless oil.



[(*Z*)-2-(Benzyloxy)-1-(4-methoxyphenyl)vinyl]oxy}(trimethyl)silane ((*Z*)-5a)

^{1}H NMR (500 MHz, C_6D_6) δ 7.44-7.42 (m, 2H), 7.25 (d, *J* = 7.3 Hz, 2H), 7.16-7.13 (m, 2H), 7.09-7.06 (m, 1H), 6.79-6.76 (m, 2H), 6.20 (s, 1H), 4.49 (s, 2H), 3.30 (s, 3H), 0.32 (s, 9H).

^{13}C NMR (125 MHz, C_6D_6) δ 159.32 (e), 137.92 (e), 135.37 (e), 130.13 (e), 129.45 (o), 128.71 (o), 128.14 (o), 127.89 (o), 125.39 (o), 114.10 (o), 74.15 (e), 54.81 (o), 0.93 (o).

IR (neat) 3035 (w), 2956 (w), 2901 (w), 2836 (w), 1661 (m), 1608 (m), 1510 (s), 1455 (m), 1344 (m), 1299 (m), 1247 (vs), 1153 (s), 1136 (s), 1081 (s), 1033 (s), 893 (m), 845 (s) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{19}H_{24}NaO_3Si$ 351.1392, found 351.1404.

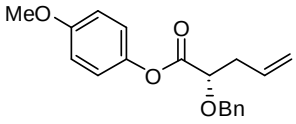
4. Representative Experimental Procedure for the Rhodium-Catalyzed Allylic Alkylation using the Silyl Enol Ether (*Z*)-5a

The trimethylsilyl enol ether ***(Z)*-5a** (188.0 mg, 0.57 mmol) was dissolved in tetrahydrofuran (1.4 mL) and cooled with stirring to –10 °C under an atmosphere of argon. Methyllithium (335 μL, 0.54 mmol) was added dropwise and the solution was stirred at –10 °C for *ca*. 1 hour. A suspension of BINOL-***Me***OP (33.0 mg, 0.095 mmol) and Wilkinson's catalyst (22.1 mg, 0.024 mmol) in anhydrous tetrahydrofuran (1.0 mL) was stirred at room temperature under an atmosphere of argon for *ca*. 10 minutes resulting in a light yellow homogeneous solution. The catalyst solution was then added to the enolate solution *via* Teflon® cannula, followed by the addition of allyl benzoate **2d** (38.8 mg, 0.24 mmol) *via* a tared gastight syringe. The reaction mixture was allowed to stir for *ca*. 15 hours and then quenched with saturated aqueous ammonium chloride solution (2 mL). The resulting mixture was partitioned between diethyl ether and saturated aqueous ammonium chloride, and the combined organic phases were dried using anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography (eluting with 4% diethyl ether/hexanes) furnished the *α-benzyloxy aryl ketone* **4a** (60.8 mg, 86%; 93% *ee*) as a colorless oil.

5. Baeyer-Villiger Oxidation of the α-Benzyloxy Aryl Ketone 4a to the Aryl Ester 8

Potassium carbonate (69.1 mg, 0.50 mmol) was flame dried *in vacuo* and placed under an atmosphere of argon. N,N'-((1S,2S)-cyclohexane-1,2-diyl)bis(4-methylbenzenesulfonamide) **7** (26.4 mg, 0.063 mmol) was then added to the flask. The solids were dissolved in dichloromethane (2.5 mL) and a 1M solution of tin(IV) chloride (62.3 μL, 0.063 mmol) was

added dropwise. The flask was cooled to 0 °C and bis(trimethylsilyl)peroxide (107.6 μL, 0.50 mmol) was added dropwise. The reaction was stirred for 10 minutes and (*S*)-2-(benzyloxy)-1-(4-methoxyphenyl)pent-4-en-1-one **4a** (74.0 mg, 0.25 mmol) was added *via* tared gastight syringe. The mixture was stirred at 0 °C for 1 hour, quenched with saturated aqueous sodium sulfite solution and then partitioned between dichloromethane and saturated aqueous sodium sulfite. The combined organic layers were dried using anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography (eluting with 7% ethyl acetate/hexanes) furnished the *aryl ester* **8** (62.9 mg, 81%) as a colorless oil.



4-Methoxyphenyl (2*S*)-2-(benzyloxy)pent-4-enoate (8)

$[\alpha]_D^{20}$ –55.1 (*c* = 1.00, $CHCl_3$); Chiral HPLC analysis (25 cm x 4.6 mm Chiralcel OJ-H column), 20% isopropanol/hexane at 1.0 mL/min. flow rate, 210 nm; t_R (*major*) 26.9 min., t_R (*minor*) 32.2 min., 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5H), 7.00-6.96 (m, 2H), 6.90-6.87 (m, 2H), 5.93 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.22 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.18-5.15 (m, 1H), 4.81 (d, A of AB, J_{AB} = 11.7 Hz, 1H), 4.56 (d, B of AB, J_{AB} = 11.7 Hz, 1H), 4.25 (t, *J* = 6.2 Hz, 1H), 3.80 (s, 3H), 2.74-2.65 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.10 (e), 157.54 (e), 143.98 (e), 137.43 (e), 132.92 (o), 128.61 (o), 128.23 (o), 128.12 (o), 122.28 (o), 118.50 (e), 114.63 (o), 77.77 (o), 72.65 (e), 55.73 (o), 37.58 (e).

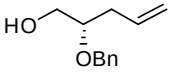
IR (neat) 3073 (w), 2942 (w), 2912 (w), 2866 (w), 2835 (w), 1765 (m), 1642 (w), 1597 (w), 1505 (s), 1455 (m), 1248 (m), 1191 (s), 1167 (m), 1115 (s), 1102 (s), 1030 (m), 916 (m), 737 (m) cm^{-1}.

HRMS (ESI, $[M+Na]^+$) calcd for $C_{19}H_{20}O_4Na$ 335.1259, found 335.1254.

6. Baeyer-Villiger Oxidation/Reduction of the α-Benzyloxy Aryl Ketone 4a to the Primary Alcohol 9

Potassium carbonate (63.5 mg, 0.46 mmol) was flame dried *in vacuo* and placed under an atmosphere of argon. N,N'-((1S,2S)-cyclohexane-1,2-diyl)bis(4-methylbenzenesulfonamide) **7** (24.3 mg, 0.058 mmol) was then added to the flask. The solids were dissolved in dichloromethane (2.3 mL) and a 1M solution of tin(IV) chloride in dichloromethane (57.3 μL, 0.058 mmol) was added dropwise. The flask was cooled to 0 °C and bis(trimethylsilyl)peroxide (99.0 μL, 0.46 mmol) was added dropwise. The reaction was stirred for *ca.* 10 minutes and (*S*)-2-(benzyloxy)-1-(4-methoxyphenyl)pent-4-en-1-one **4a** (65.6 mg, 0.23 mmol) was added *via* tared

gastight syringe. The mixture was stirred at 0 °C for 1 hour and then cooled to –78 °C. A 1M solution of diisobutylaluminium hydride in hexanes (810 μL, 0.81 mmol) was then slowly injected. The reaction was stirred for *ca*. 45 minutes, quenched with 1M hydrochloric acid solution (2 mL) and partitioned between dichloromethane and dilute hydrochloric acid solution. The combined organic phases were dried using anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to afford a crude oil. Purification by flash chromatography (eluting with 15% ethyl acetate/hexanes) furnished the *primary alcohol* **9** (39.3 mg, 89%) as a colorless oil.



(2*S*)-2-(Benzyloxy)pent-4-en-1-ol (9).

$[\alpha]_D^{20}$ +24.3 (*c* = 0.55, CH_2Cl_2), Lit.[1] $[\alpha]_D^{24}$ +21.7 (*c* = 0.55, CH_2Cl_2); Chiral HPLC analysis (25 cm x 4.6 mm Chiralpak AD-H column), 4% isopropanol/hexane at 0.8 mL/min. flow rate, 254 nm; t_R (*major*) 12.09 min., t_R (*minor*) 13.13 min., 93% *ee*.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 5.82 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.13 (dq, *J* = 17.1, 1.6 Hz, 1H), 5.09 (ddt, *J* = 10.2, 1.9, 1.0 Hz, 1H), 4.68 (d, A of AB, J_{AB} = 11.5 Hz, 1H), 4.55 (d, B of AB, J_{AB} = 11.5 Hz, 1H), 3.71-3.66 (m, 1H), 3.61-3.54 (m, 2H), 2.45-2.39 (m, 1H), 2.35-2.29 (m, 1H), 1.89 (br s, 1H).

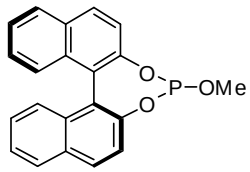
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.44 (e), 134.19 (o), 128.64 (o), 127.95 (o), 127.92 (o), 117.73 (e), 79.27 (o), 71.72 (e), 64.23 (e), 35.50 (e).

IR (neat) 3360 (br), 3078 (w), 3033 (w), 2938 (w), 1641 (w), 1509 (vs), 1454 (m), 1440 (m), 1232 (s), 1100 (m), 1071 (m), 1035 (s), 917 (m), 826 (m) cm^{-1}.

HRMS (CI, M^+) calcd for $C_{12}H_{16}O_2$ 192.1145, found 192.1143.

7. Preparation of the Chiral Phosphite Ligand 3a

S-(–)-1,1'-Bi-2-naphthol (1.09 g, 3.76 mmol) was suspended in anhydrous dichloromethane (10 mL) and stirred at room temperature under an atmosphere of argon. Triethylamine (1.31 mL, 9.40 mmol) was added slowly and the reaction was then cooled to 0 °C and then neat methyldichlorophosphite (436 μL, 4.5 mmol) was added slowly *via* tared syringe. The reaction mixture was then allowed to warm to room temperature and stirred for *ca*. 30 minutes. The reaction mixture was concentrated *in vacuo* and filtered through a plug of silica gel (eluting with 20% dichloromethane/hexanes) to afford BINOL-***Me***OP **3a** (1.00 g, 77%) as a white crystalline solid, which was further purified by crystallization from dichloromethane/hexanes.



(*S*)-4-Methoxydinaphtho[1,2-*f*:2',1'-*d*][1,3,2]dioxaphosphepine (3a).

$[\alpha]_D^{20}$ +705 (*c* = 1.10, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.8 Hz, 1H), 7.95 (d, *J* = 8.6 Hz, 1H), 7.92 (t, *J* = 7.4 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.46-7.41 (m, 3H), 7.38-7.34 (m, 2H), 7.28-7.25 (m, 2H), 3.55 (d, $^3J_{HP}$ = 9.8 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.95 (e, d, $^2J_{CP}$ = 5.0 Hz), 147.60 (e, d, $^2J_{CP}$ = 2.3 Hz), 132.91 (e), 132.69 (e), 131.61 (e), 131.08 (e), 130.56 (o), 130.24 (o), 128.48 (o), 128.41 (o), 127.05 (o), 126.40 (o), 126.38 (o), 125.17 (o), 125.03 (o), 124.12 (e, d, $^3J_{CP}$ = 5.3 Hz), 122.72 (e, d, $^3J_{CP}$ = 2.2 Hz), 121.93 (o), 121.64 (o), 52.09 (o, d, $^2J_{CP}$ = 4.1 Hz).

^{31}P NMR (212 MHz, $CDCl_3$) δ 140.02 (q, $^3J_{PH}$ = 9.6 Hz).

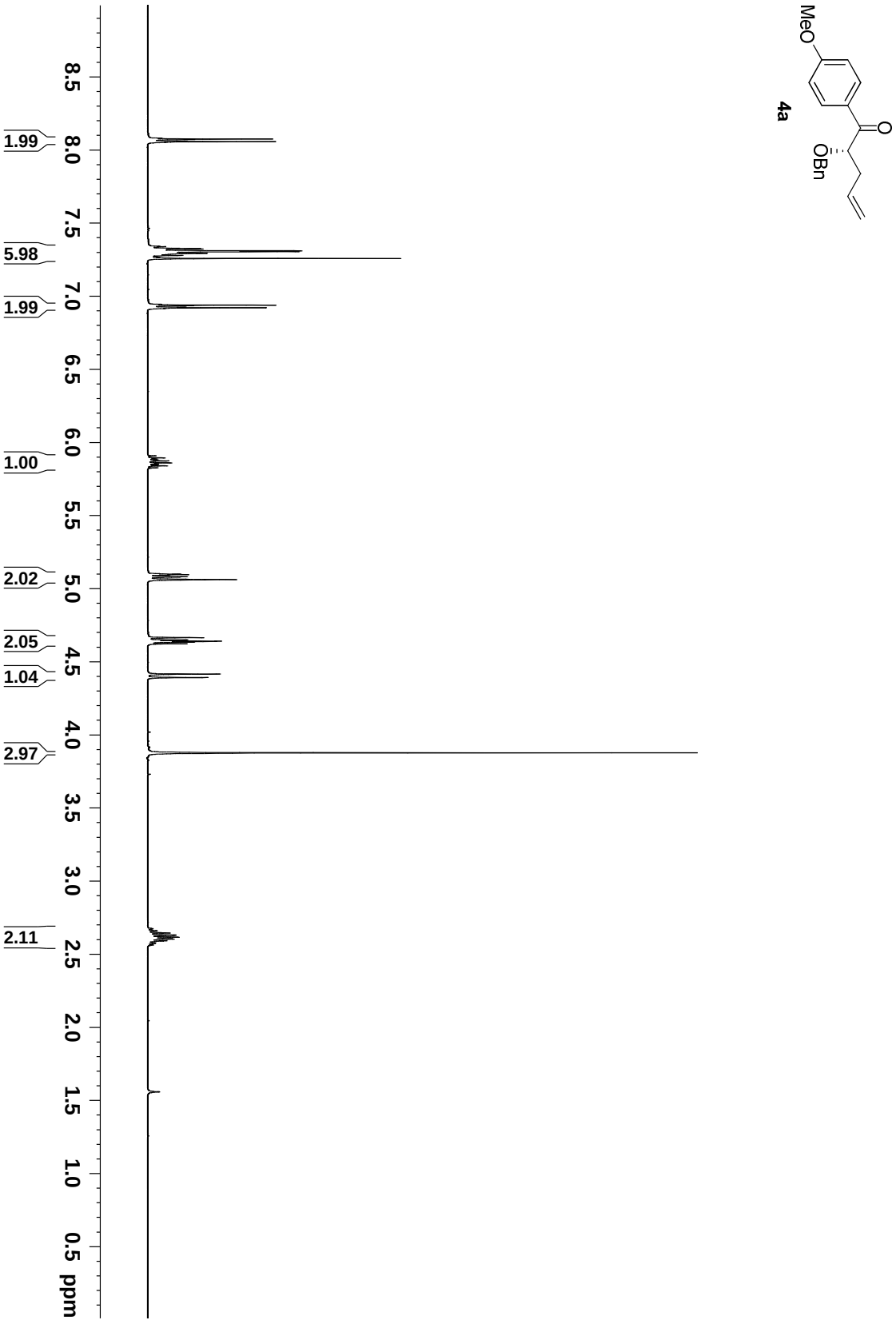
IR (neat) 3058 (w), 3008 (w), 2947 (w), 2846 (w), 1618 (w), 1590 (m), 1505 (m), 1460 (m), 1325 (m), 1227 (s), 1199 (m), 1030 (s), 947 (s), 820 (s) cm^{-1}.

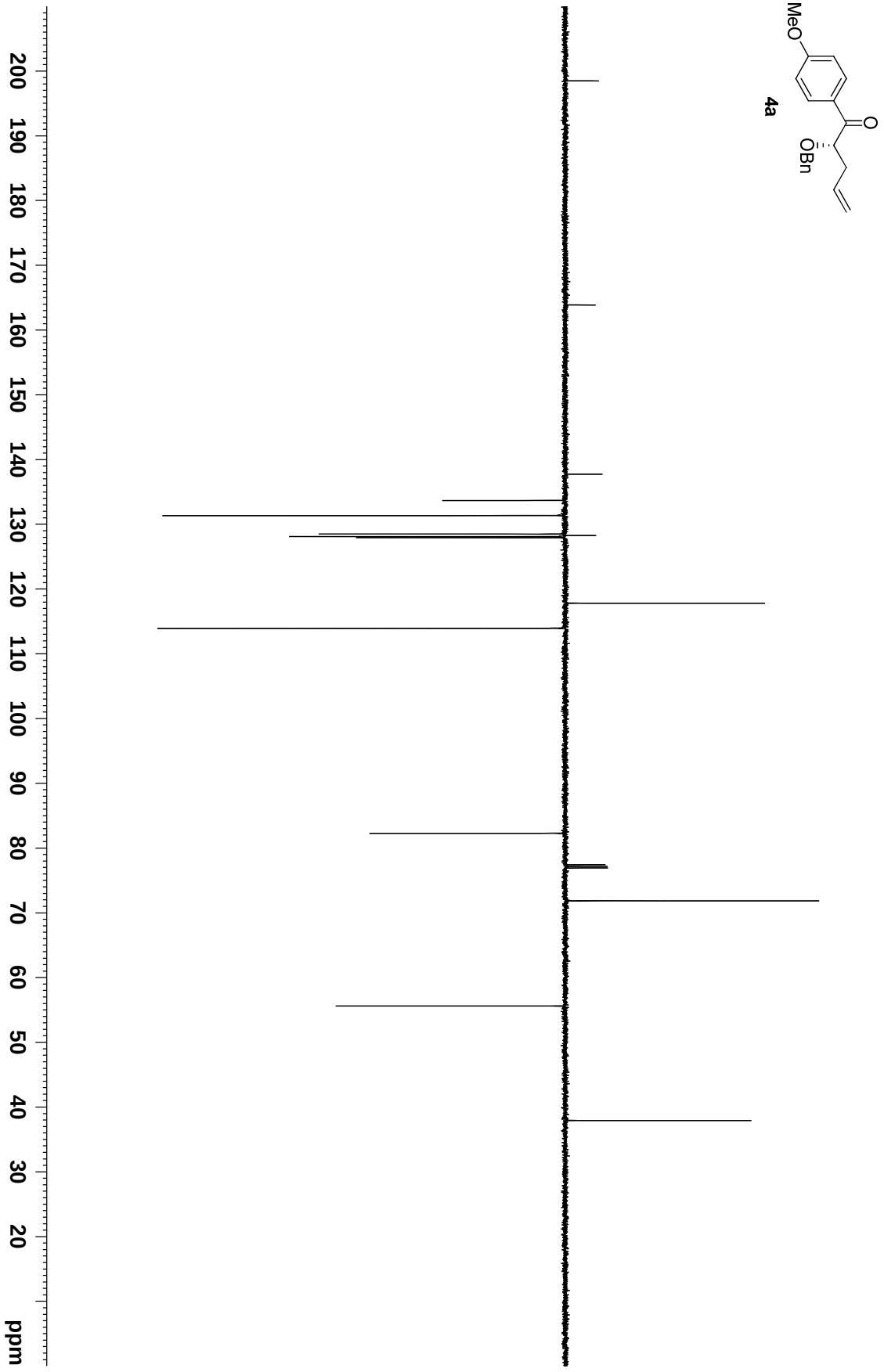
HRMS (CI, M^+) calcd for $C_{21}H_{15}O_3P$ 346.0753, found 346.0760.

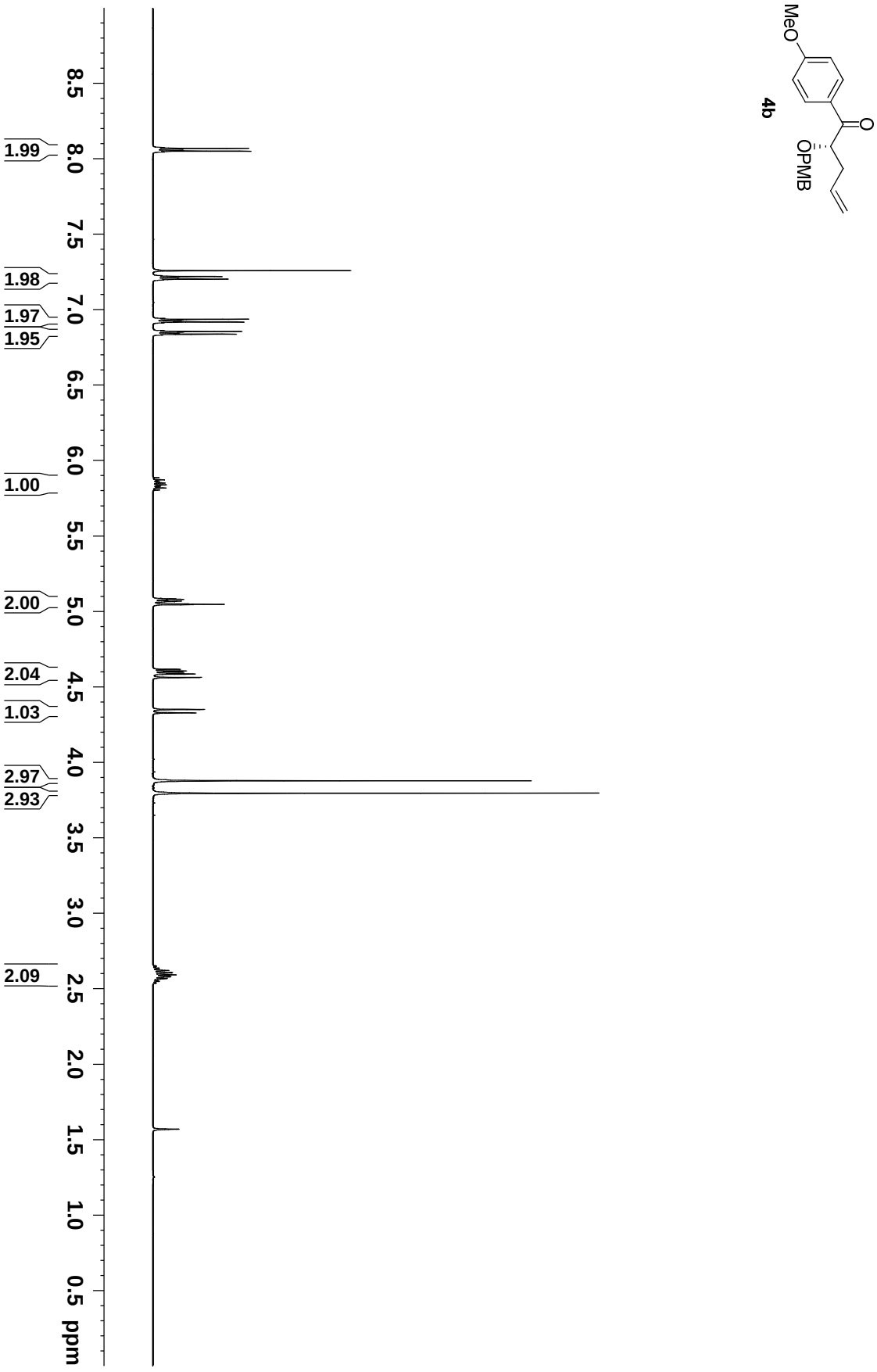
8. References

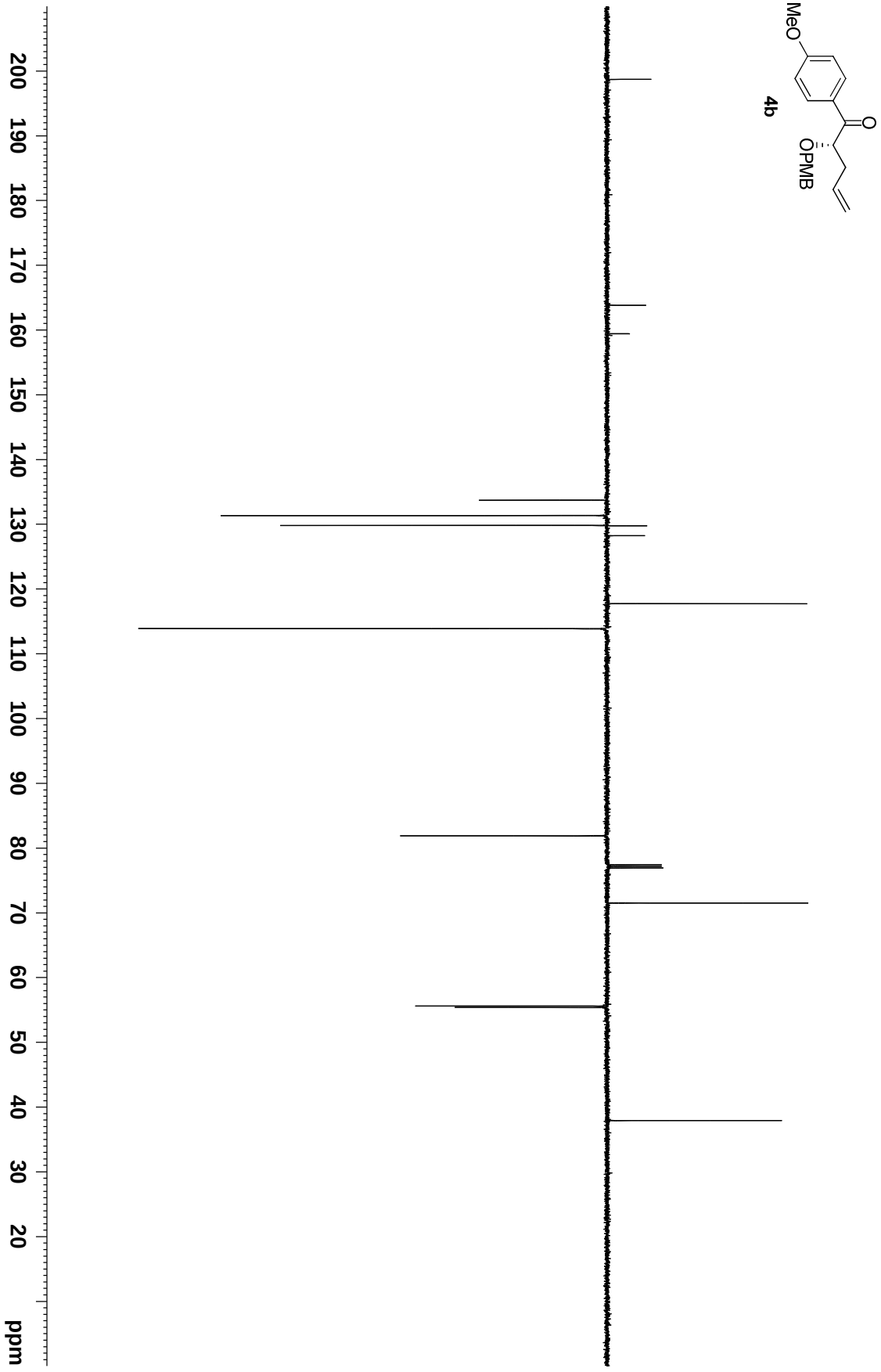
1. M. T. Crimmins and A. C. DeBaillie, *J. Am. Chem. Soc.* 2006, **128**, 4936.

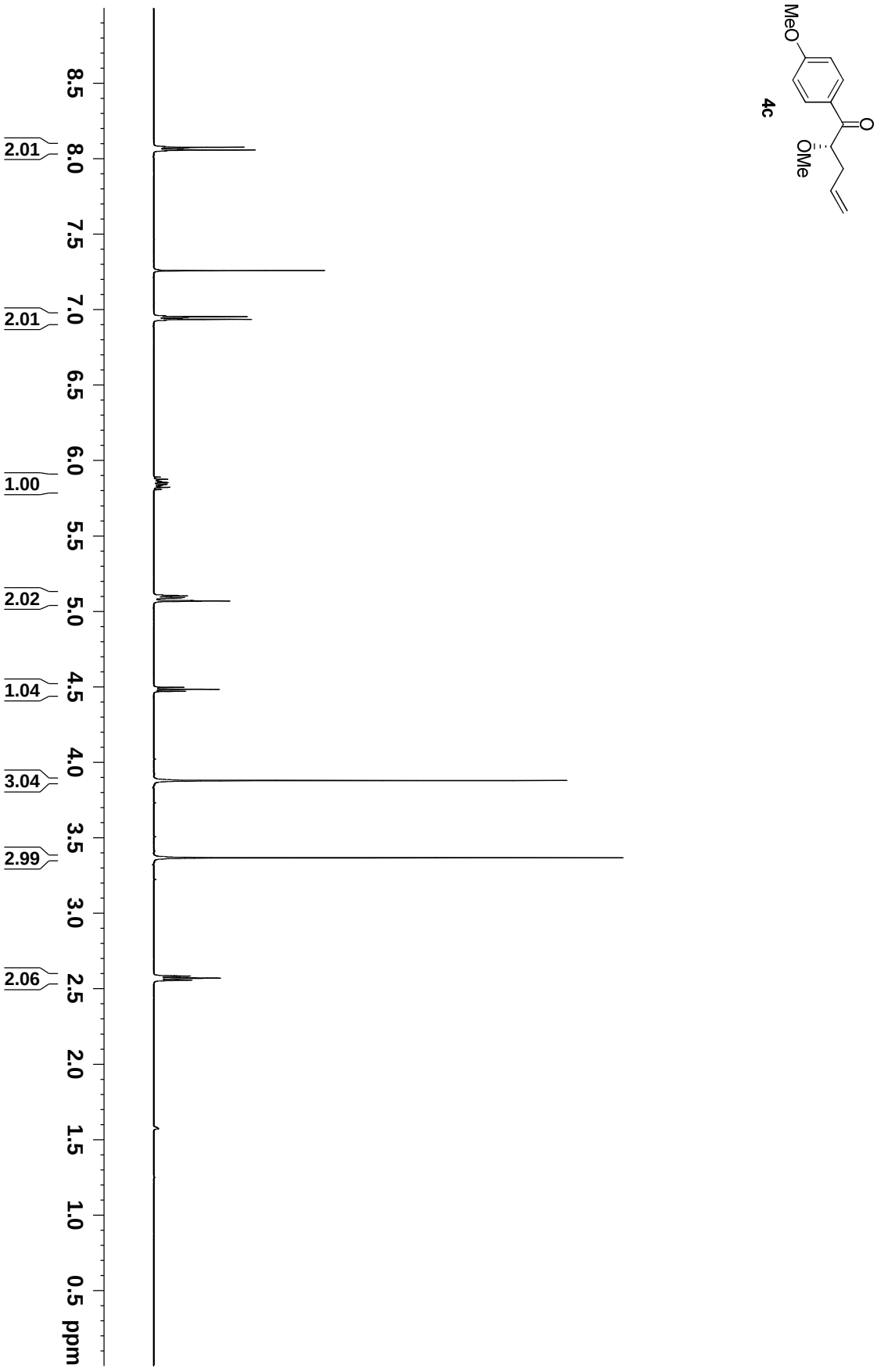
9. Proton and Carbon NMR Spectra, including nOe Data

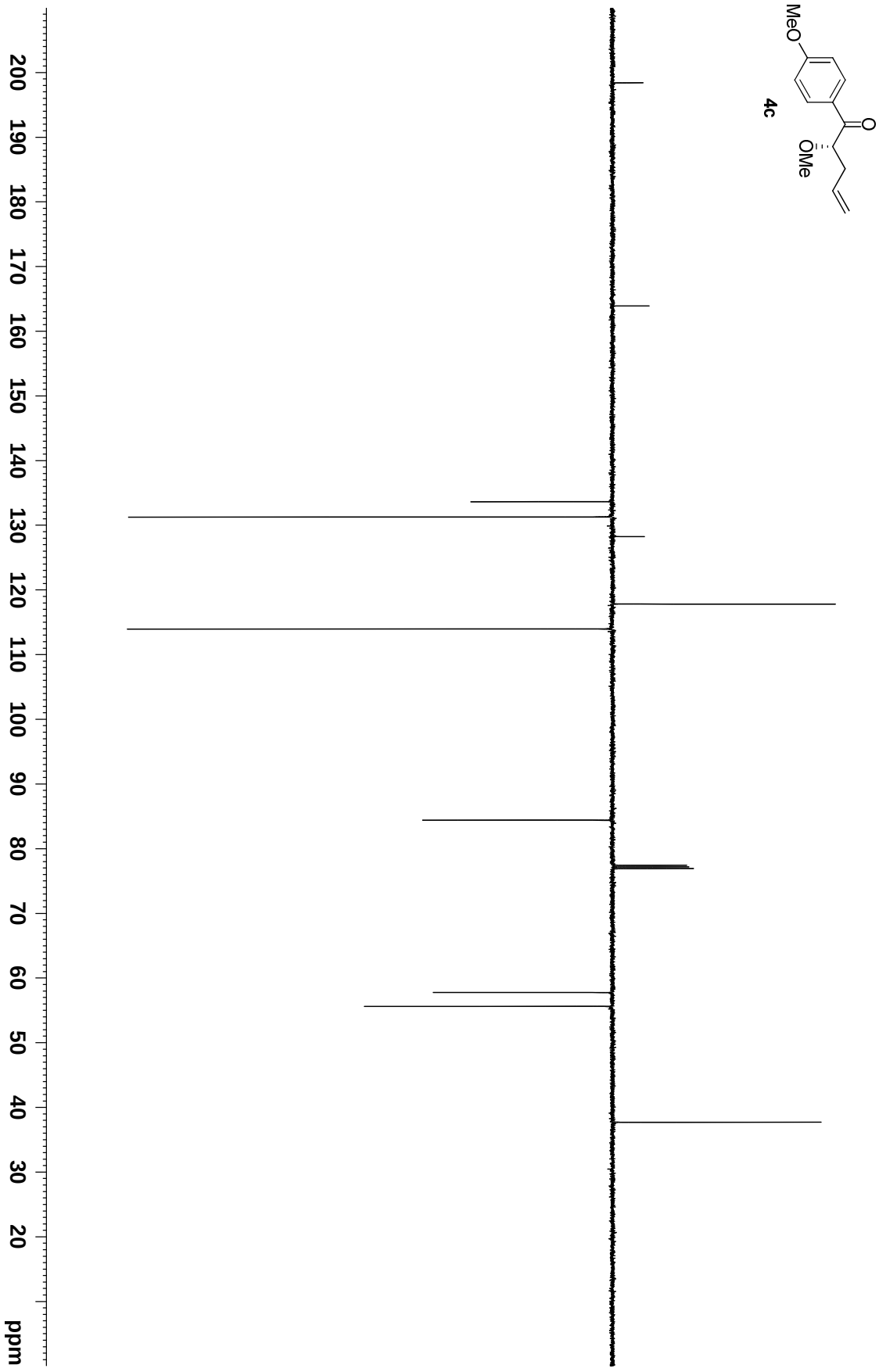


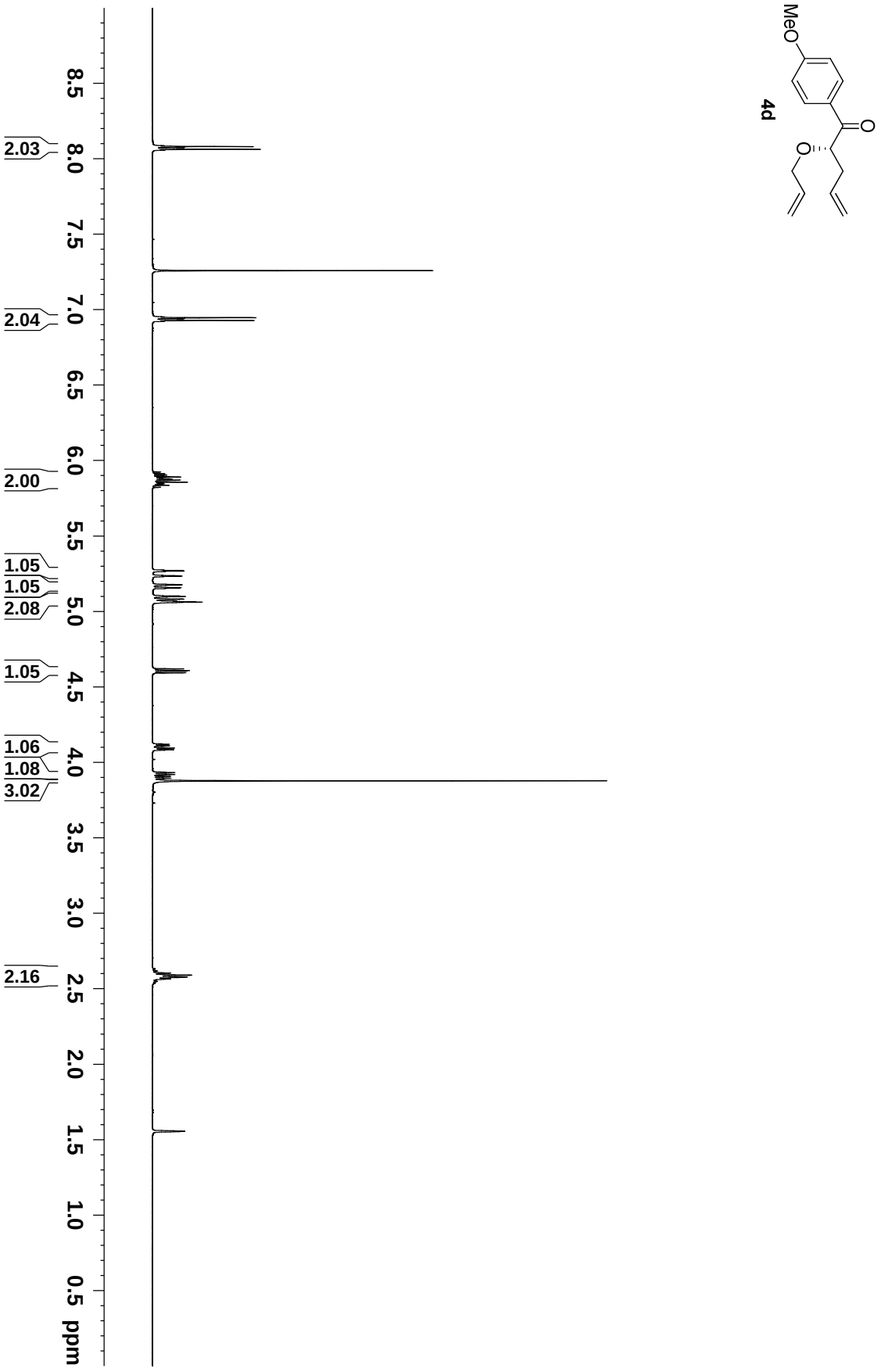


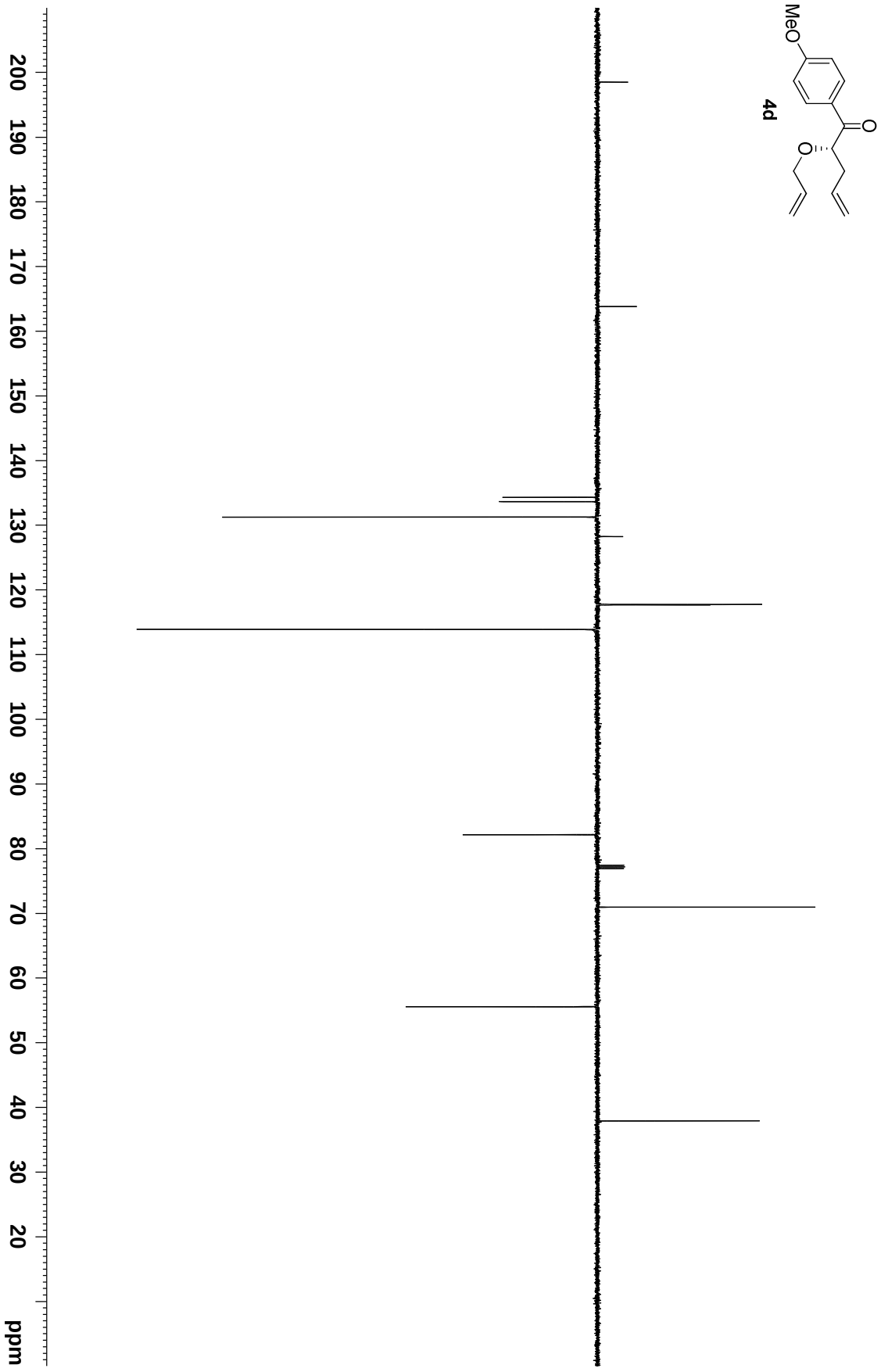


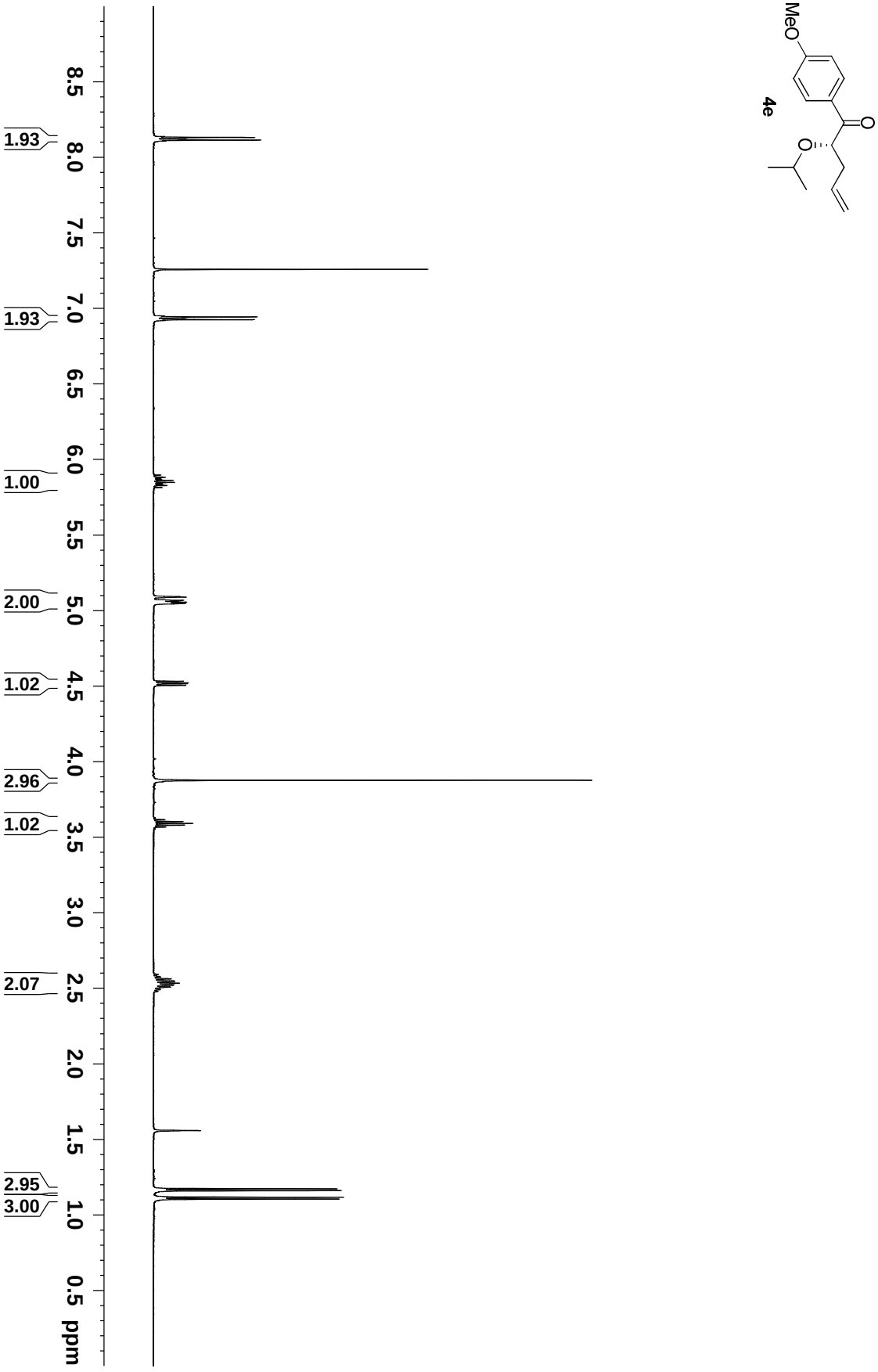








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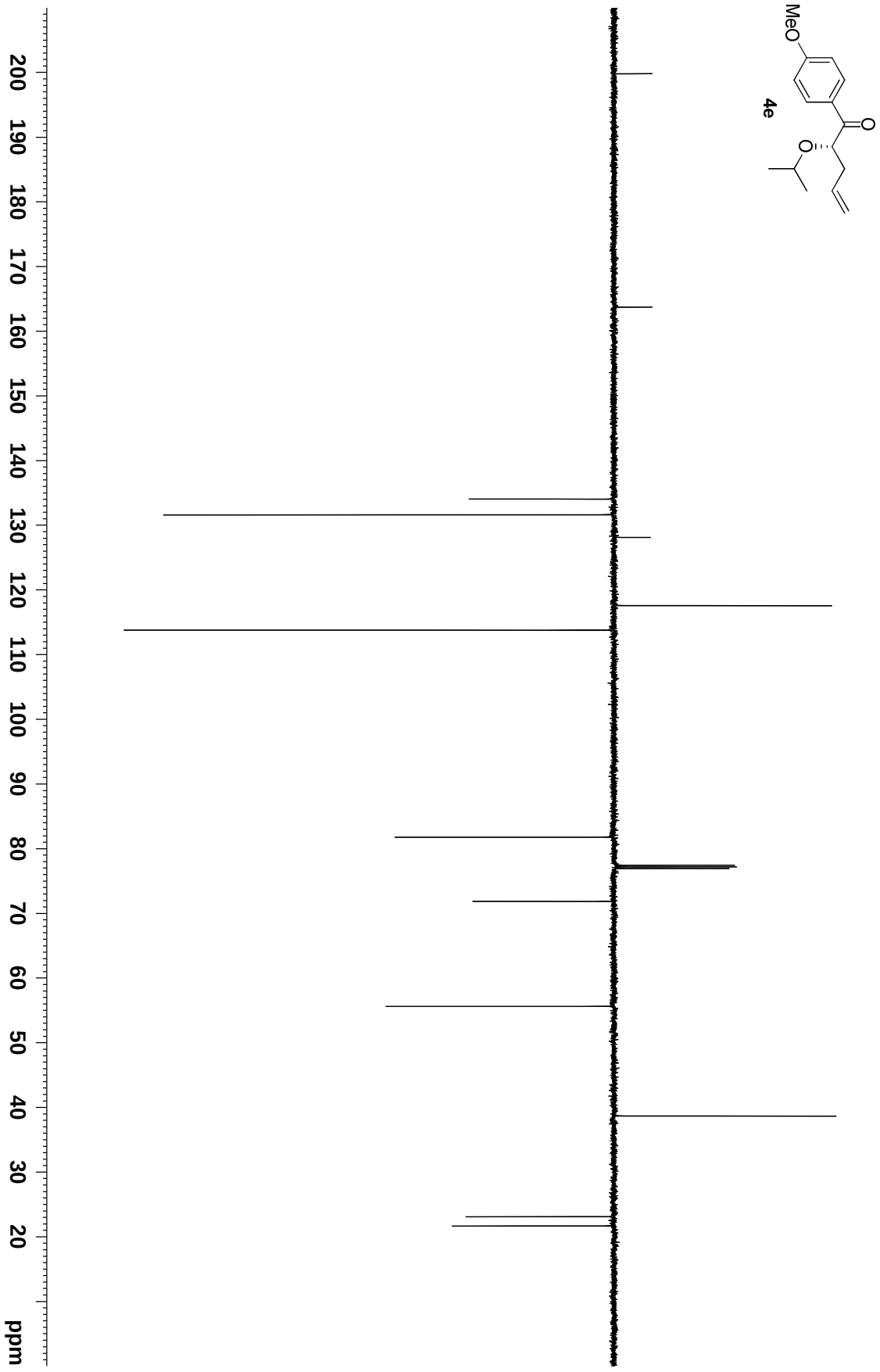

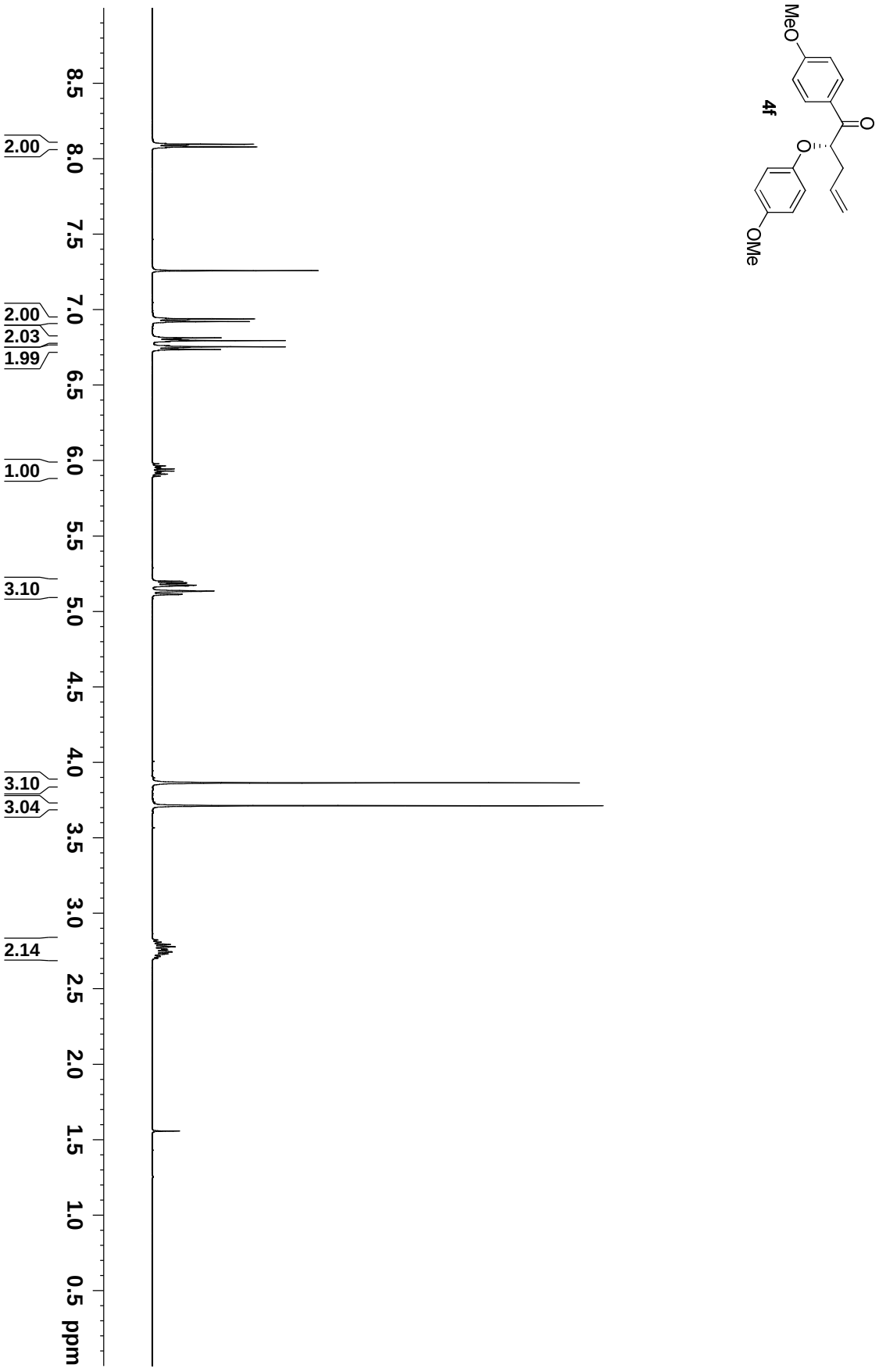
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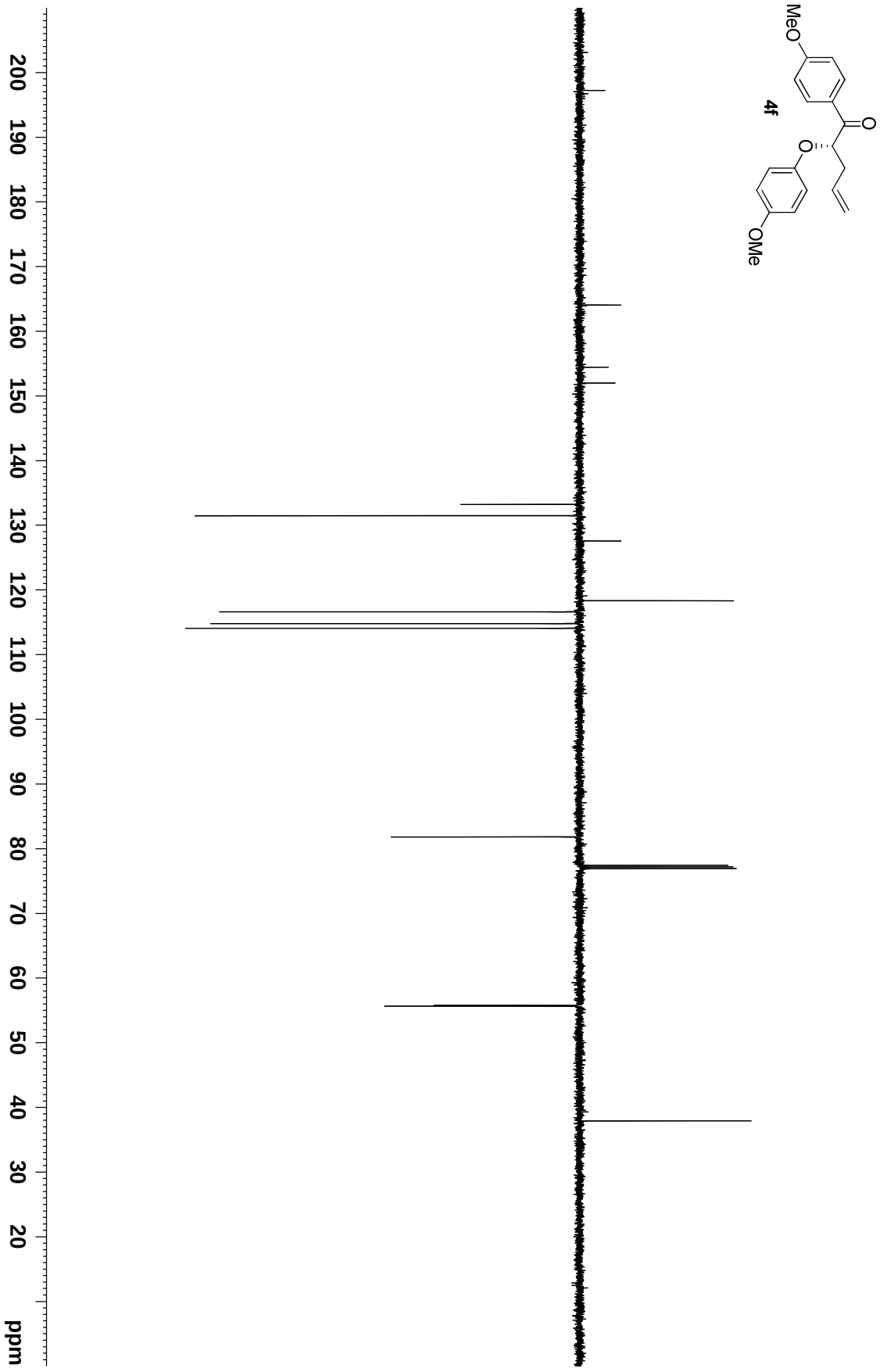

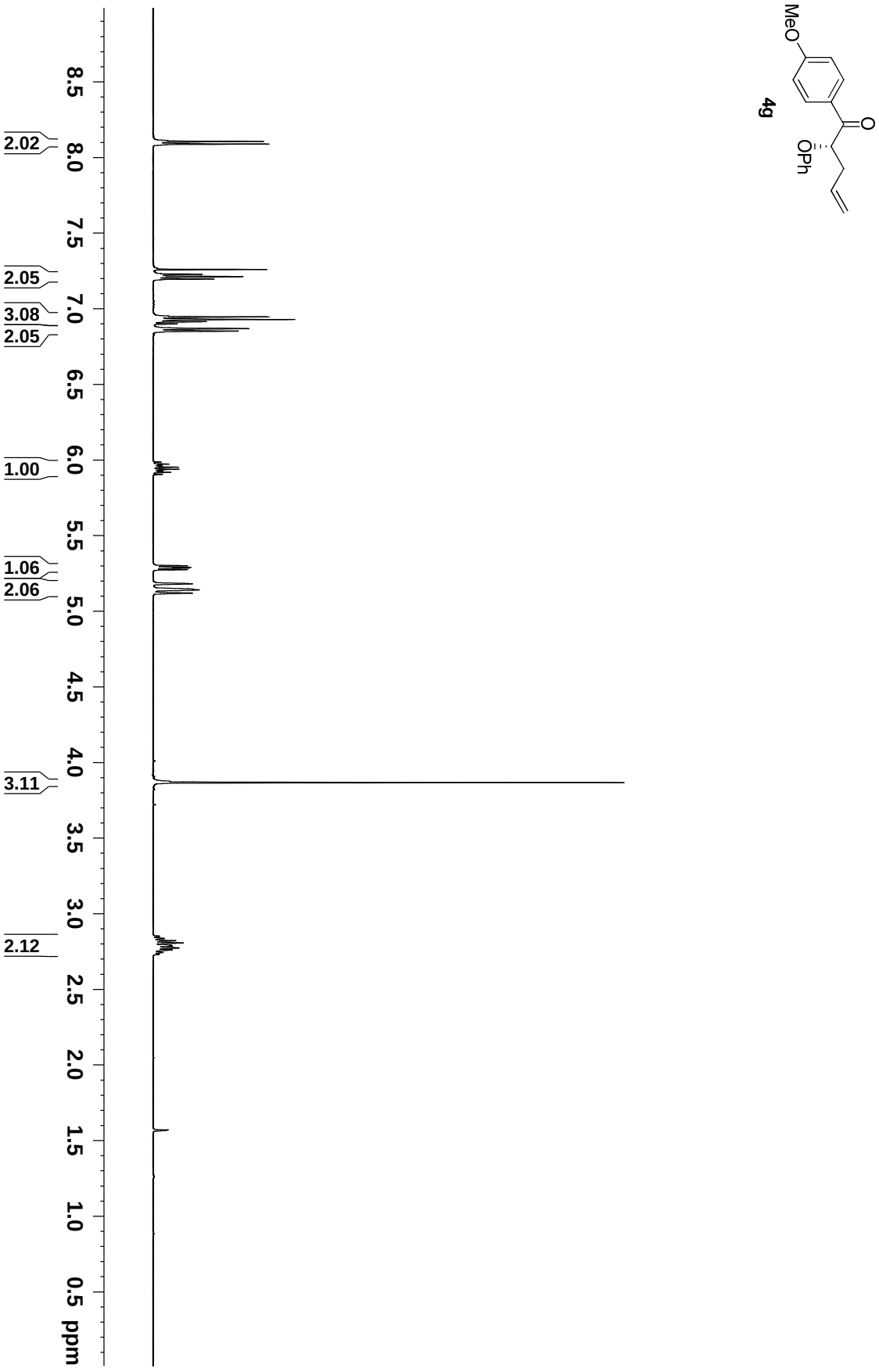
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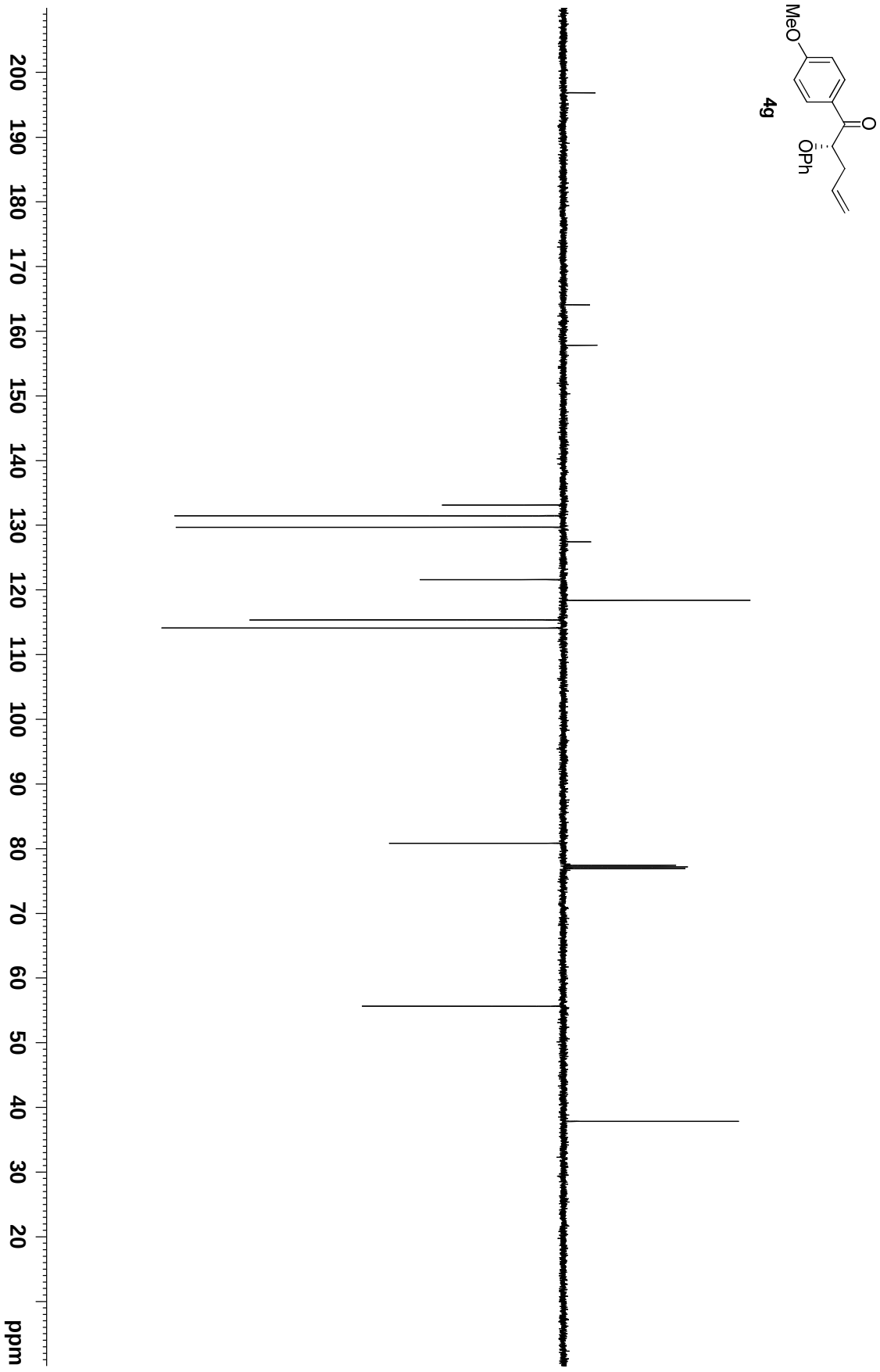

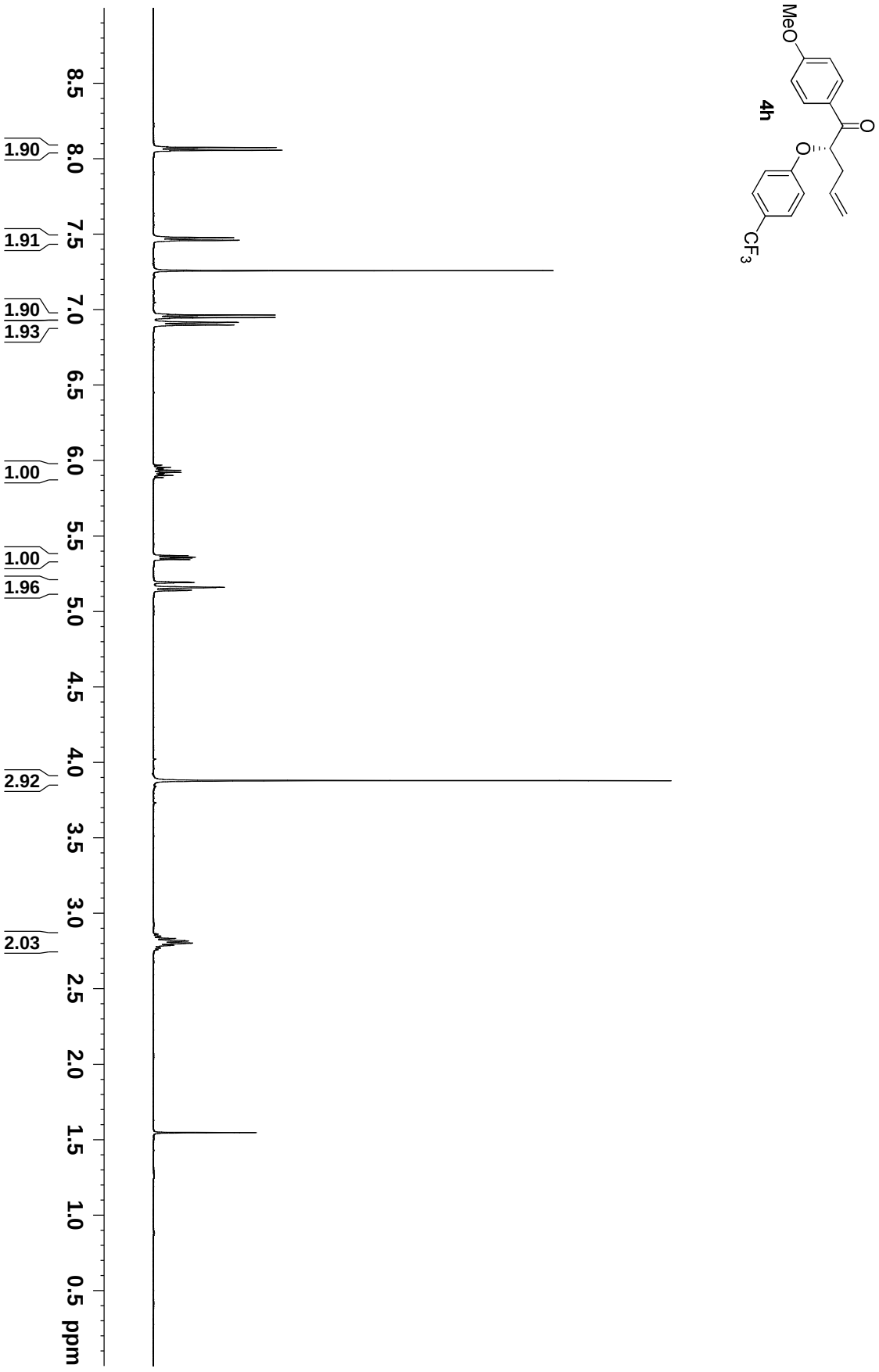

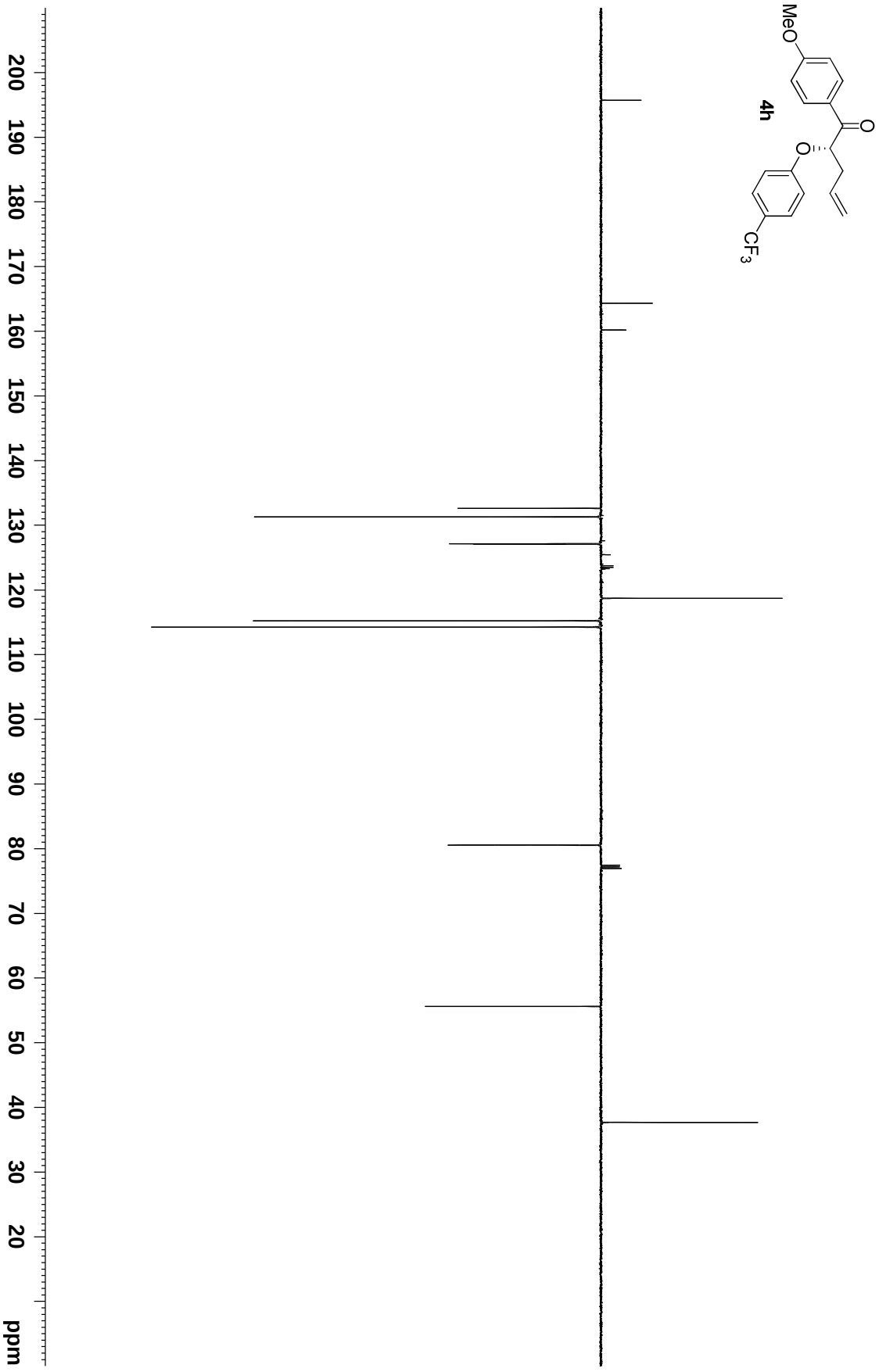

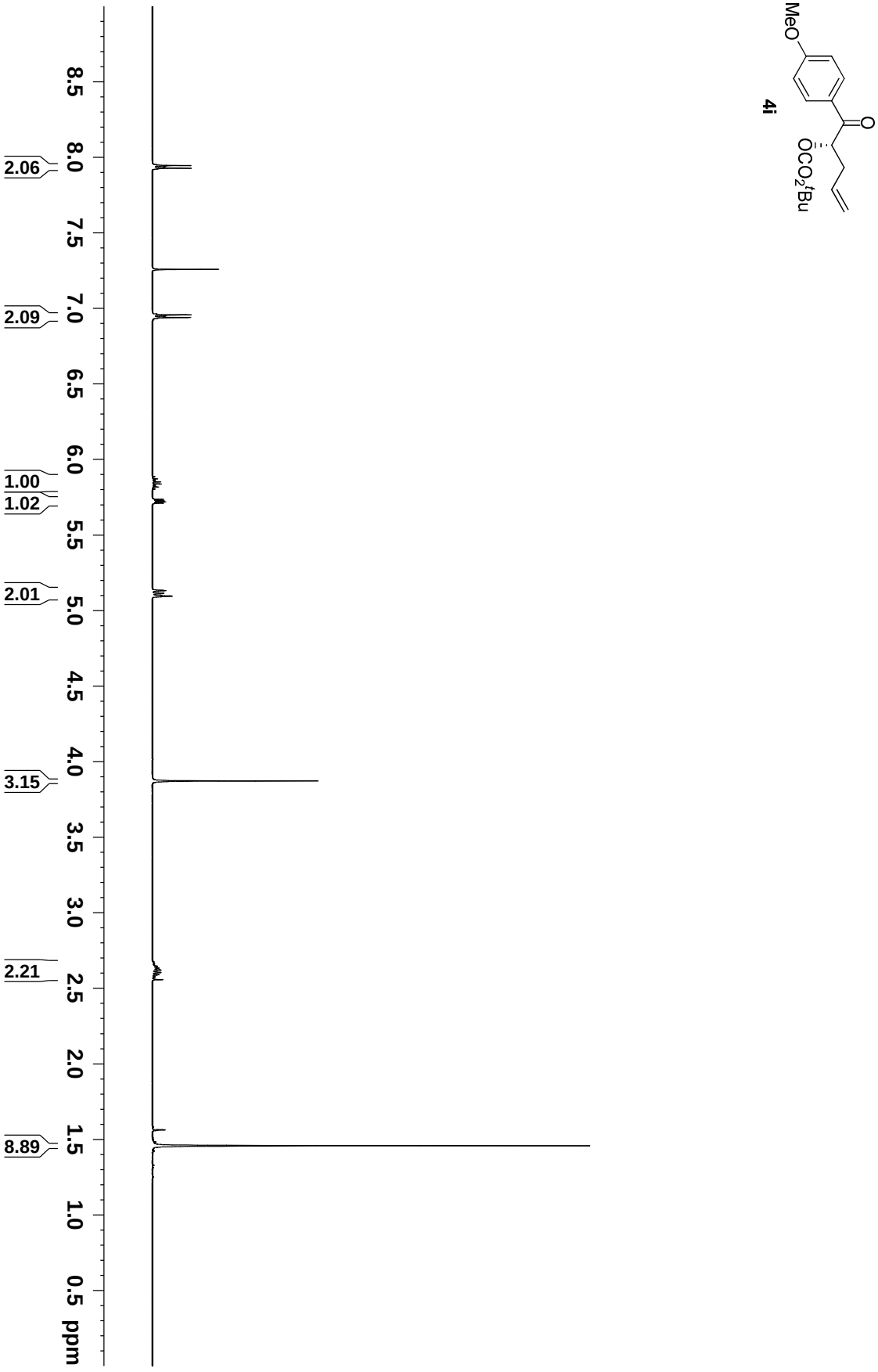

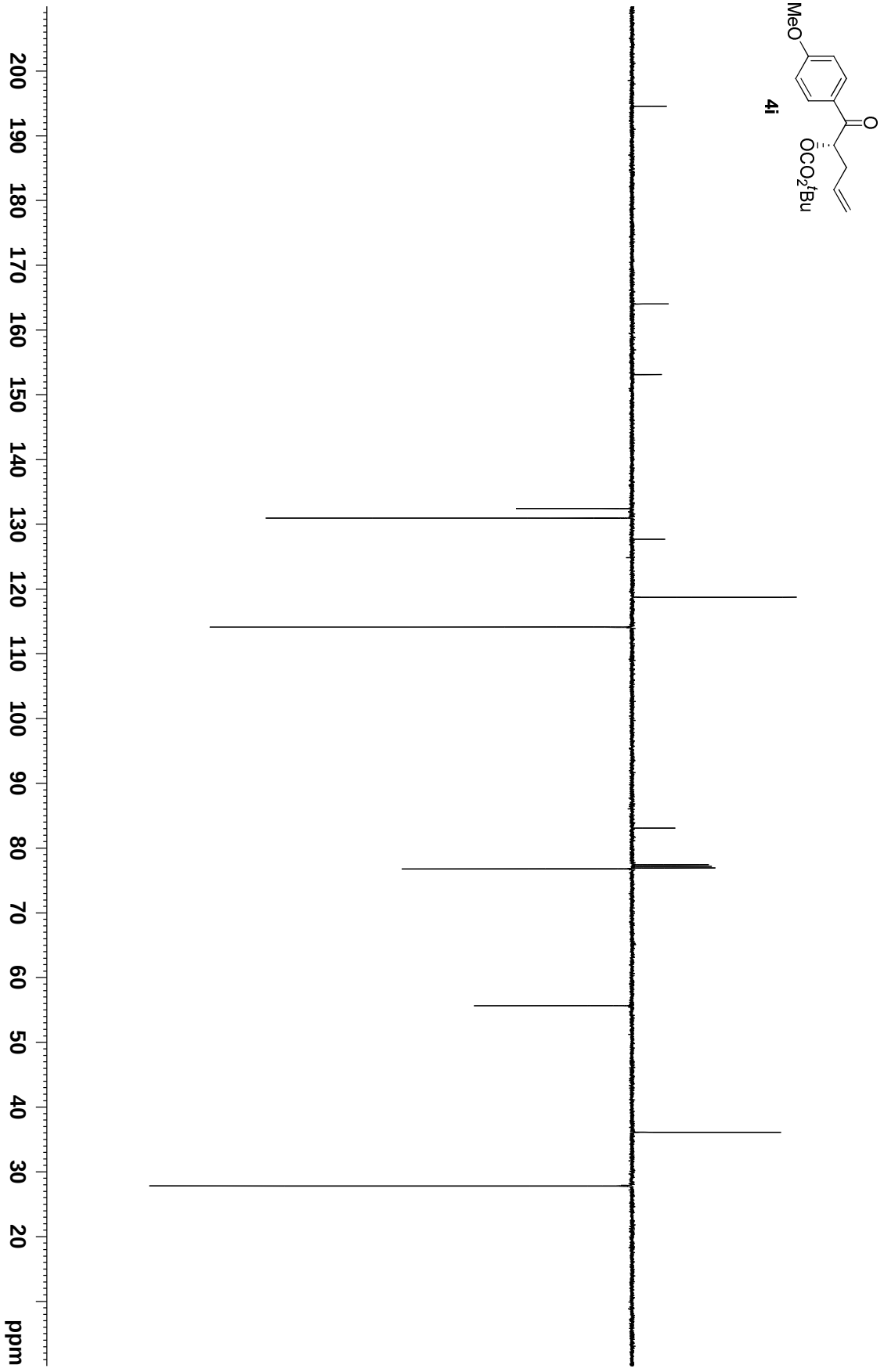

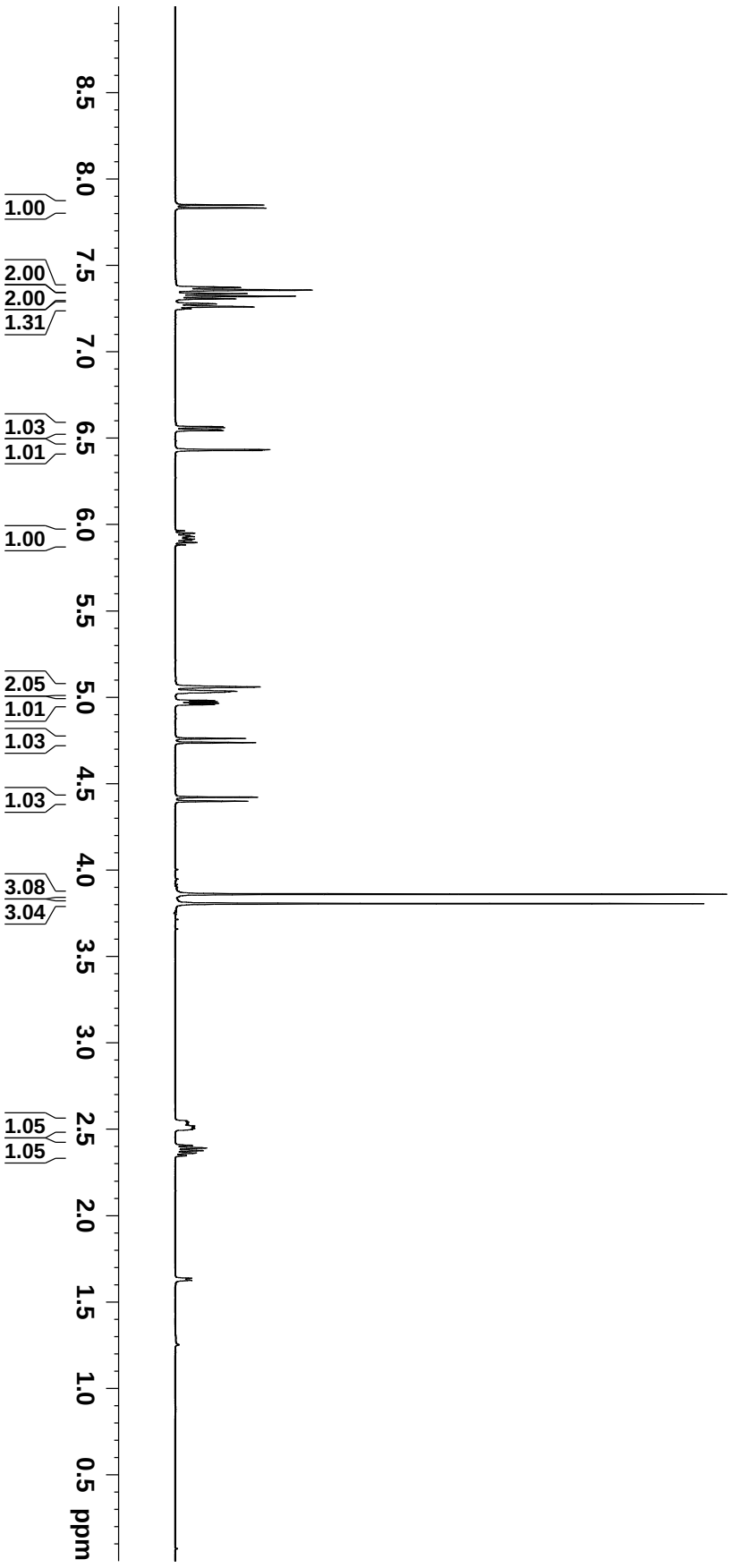
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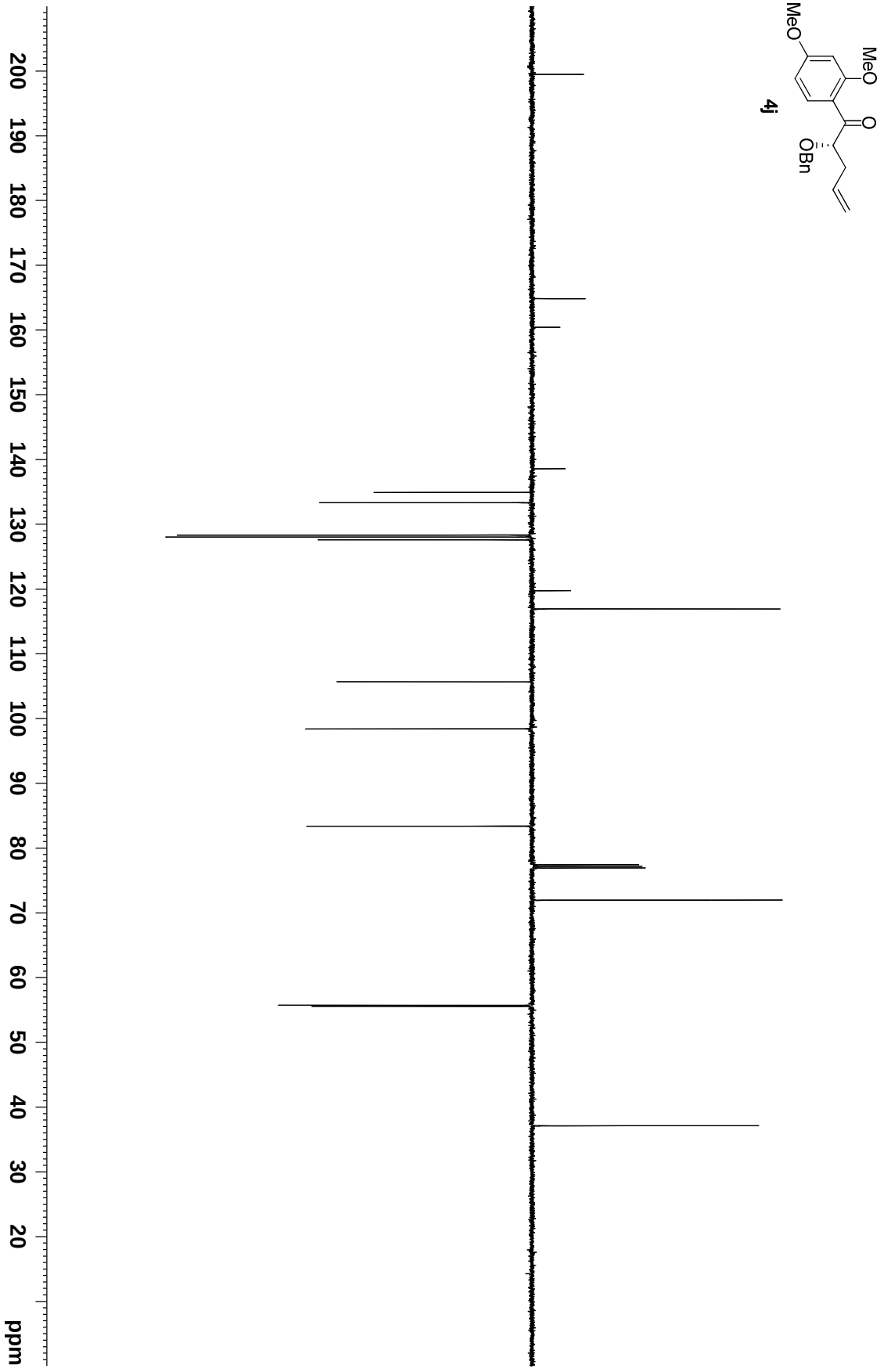

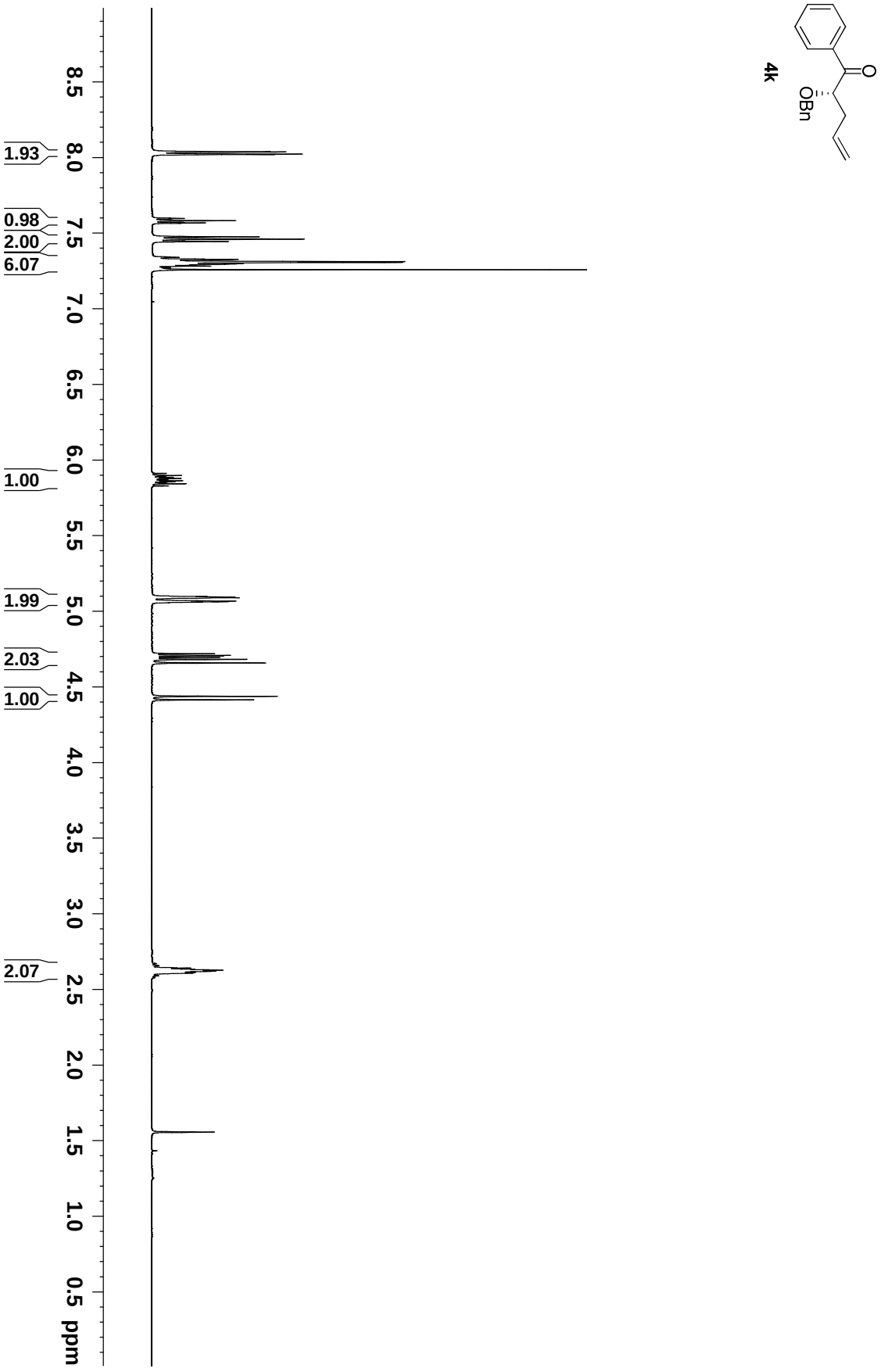

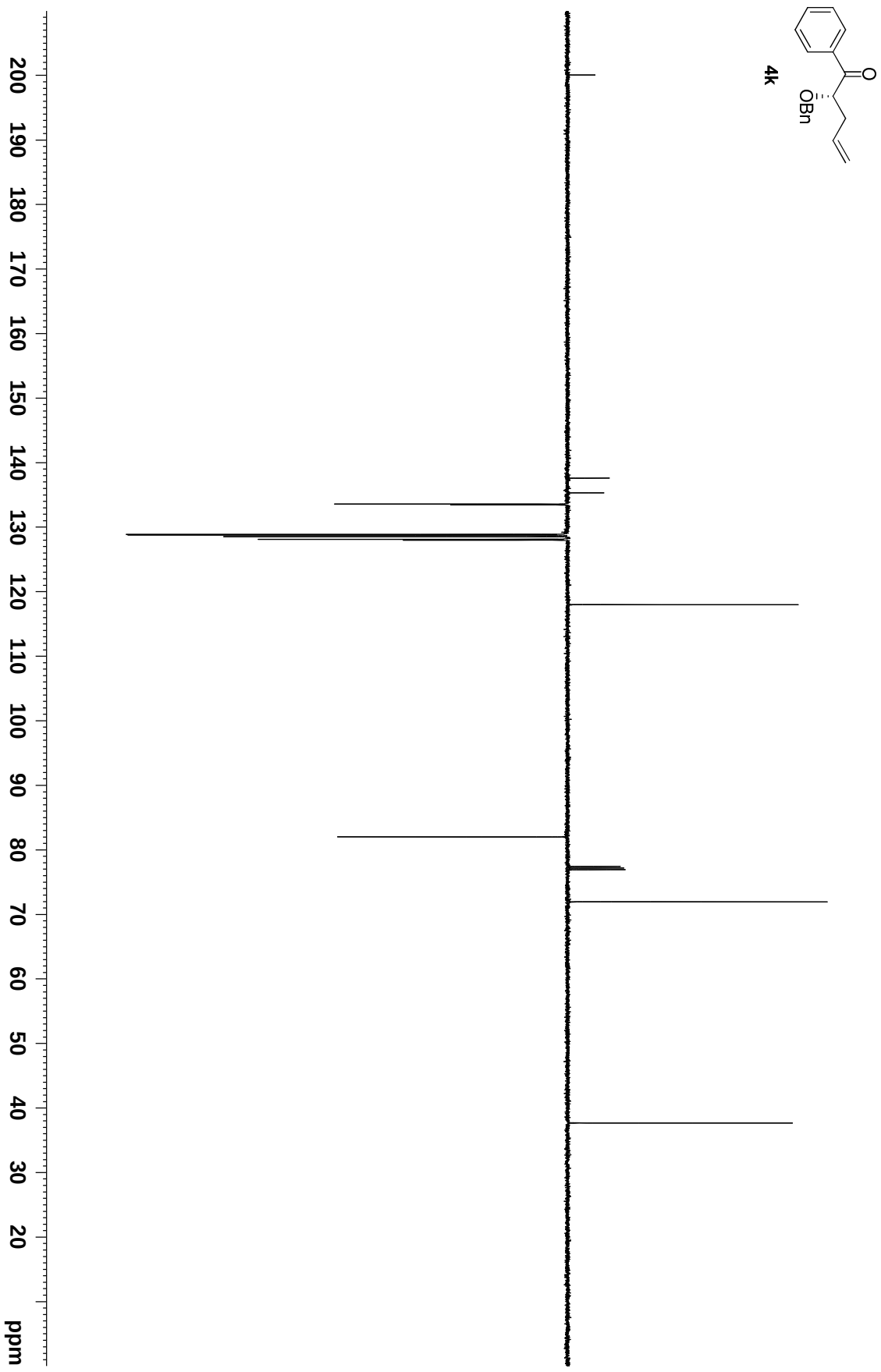

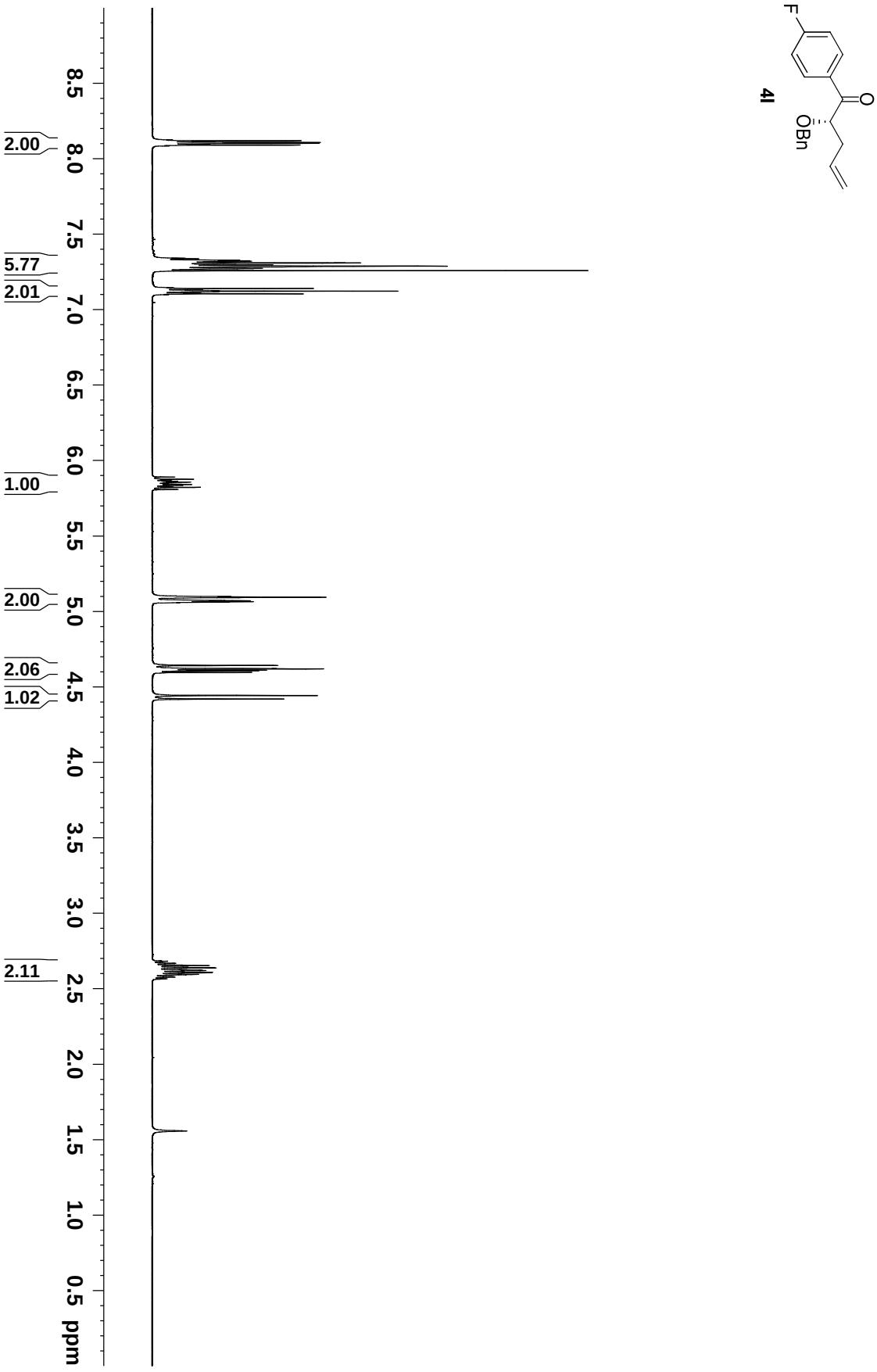
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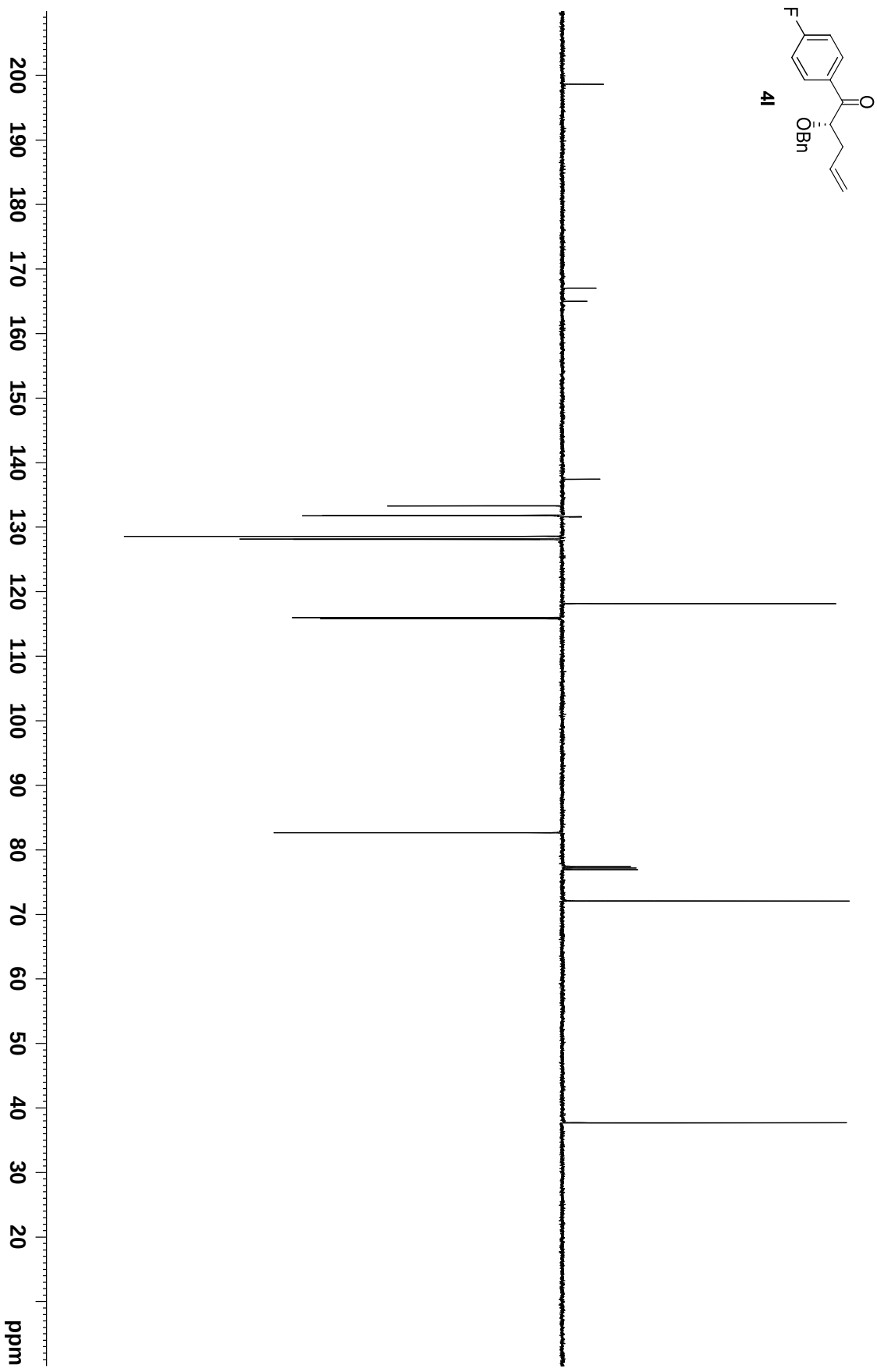

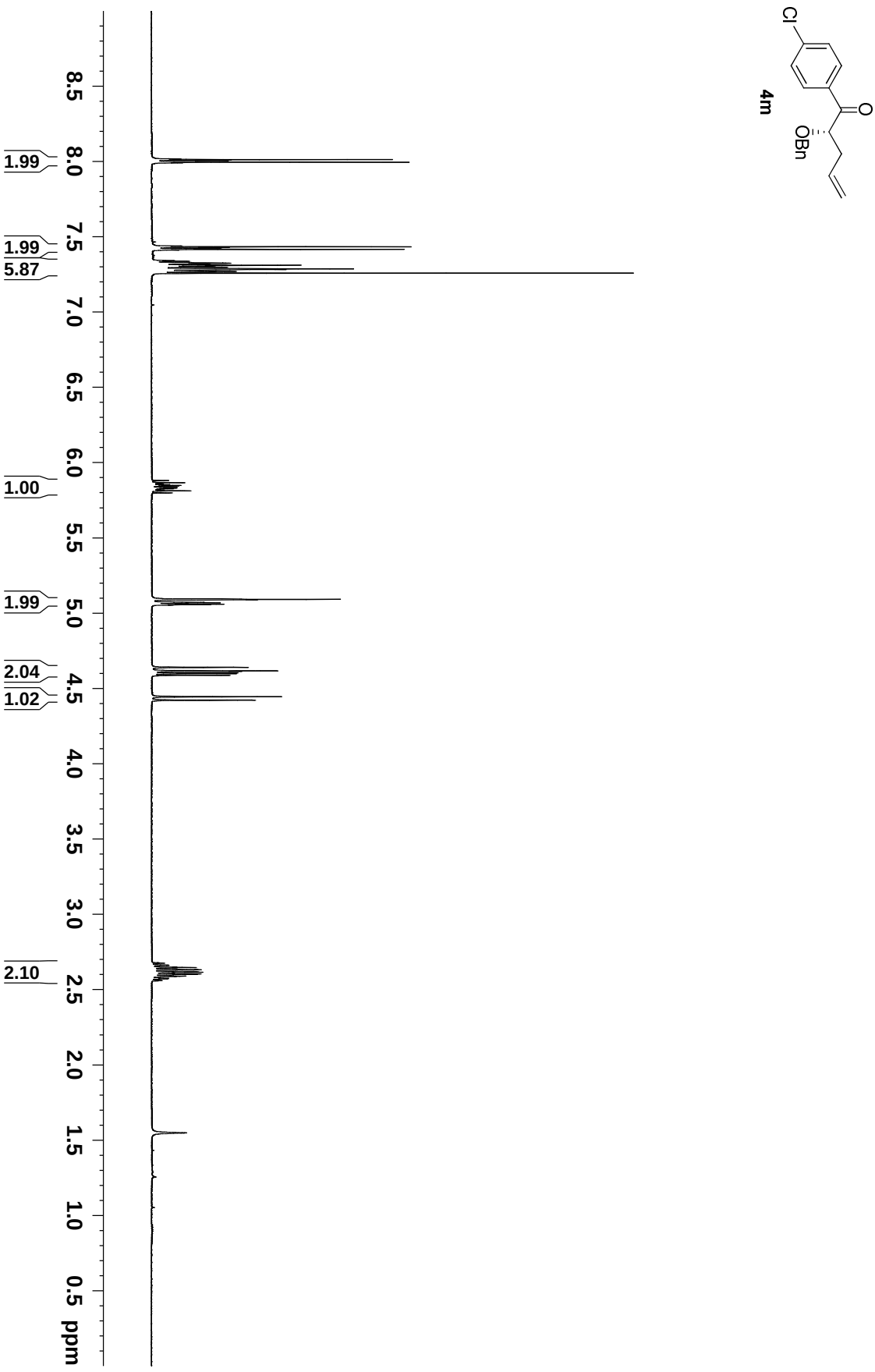
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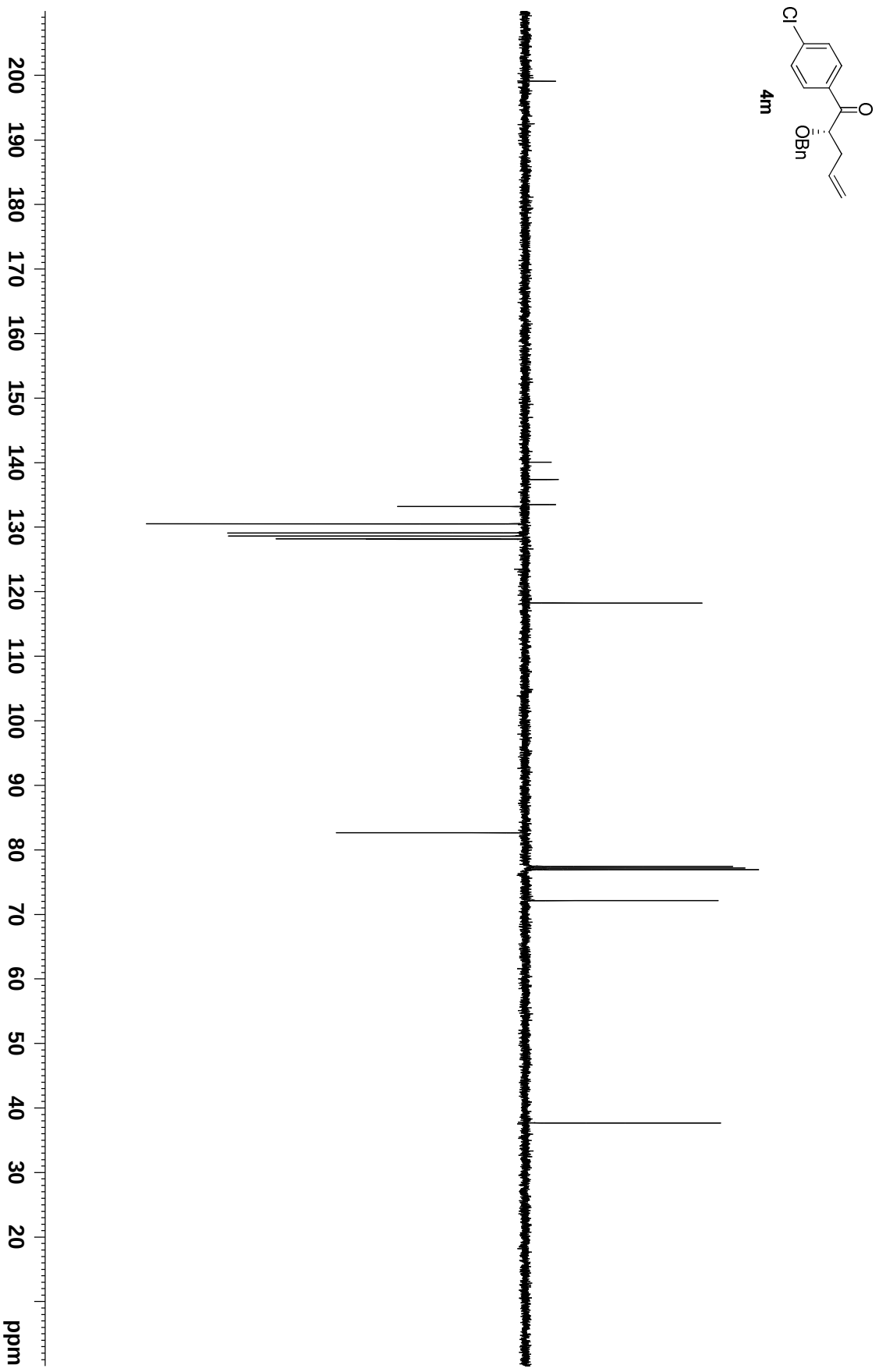

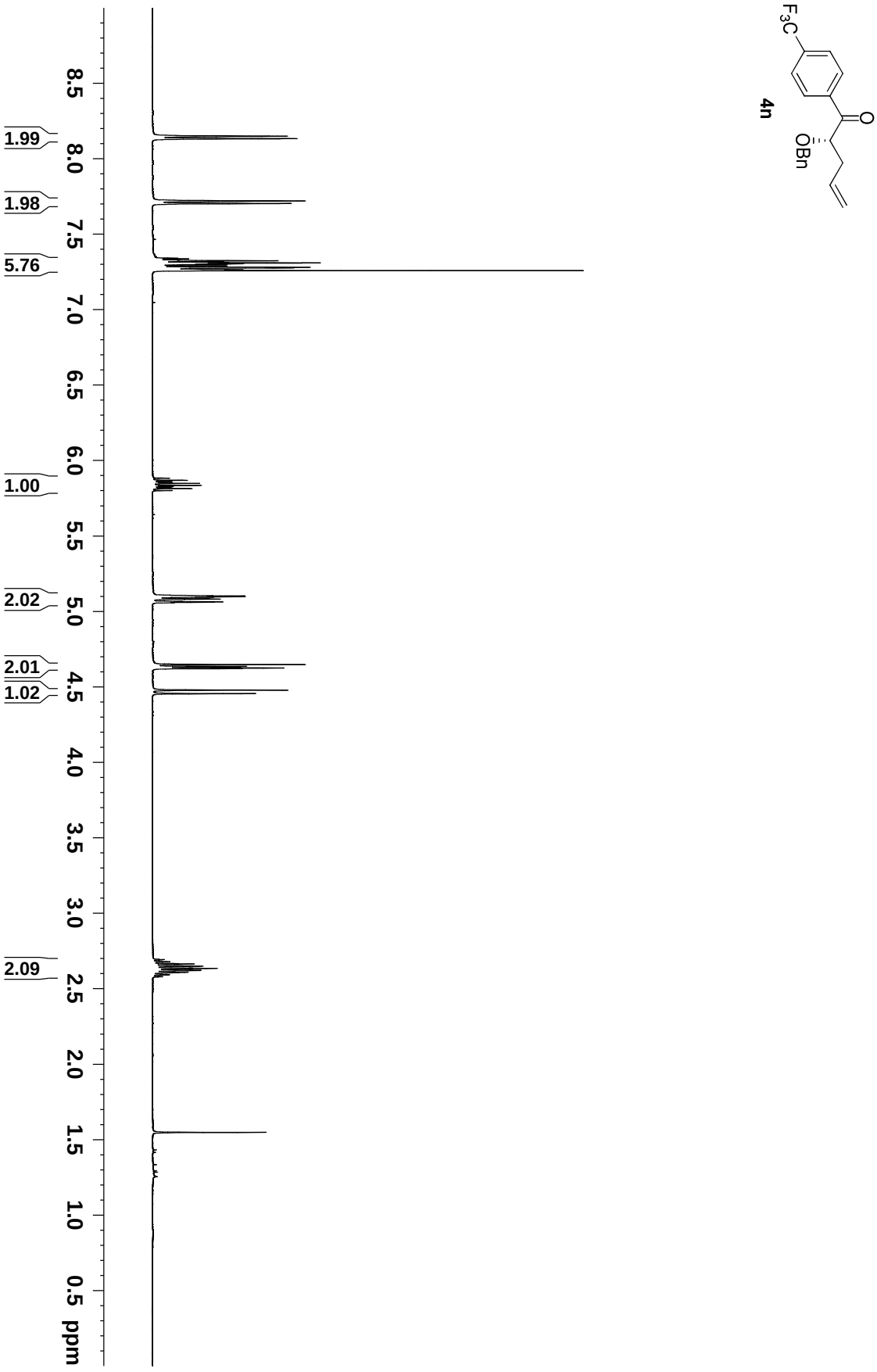

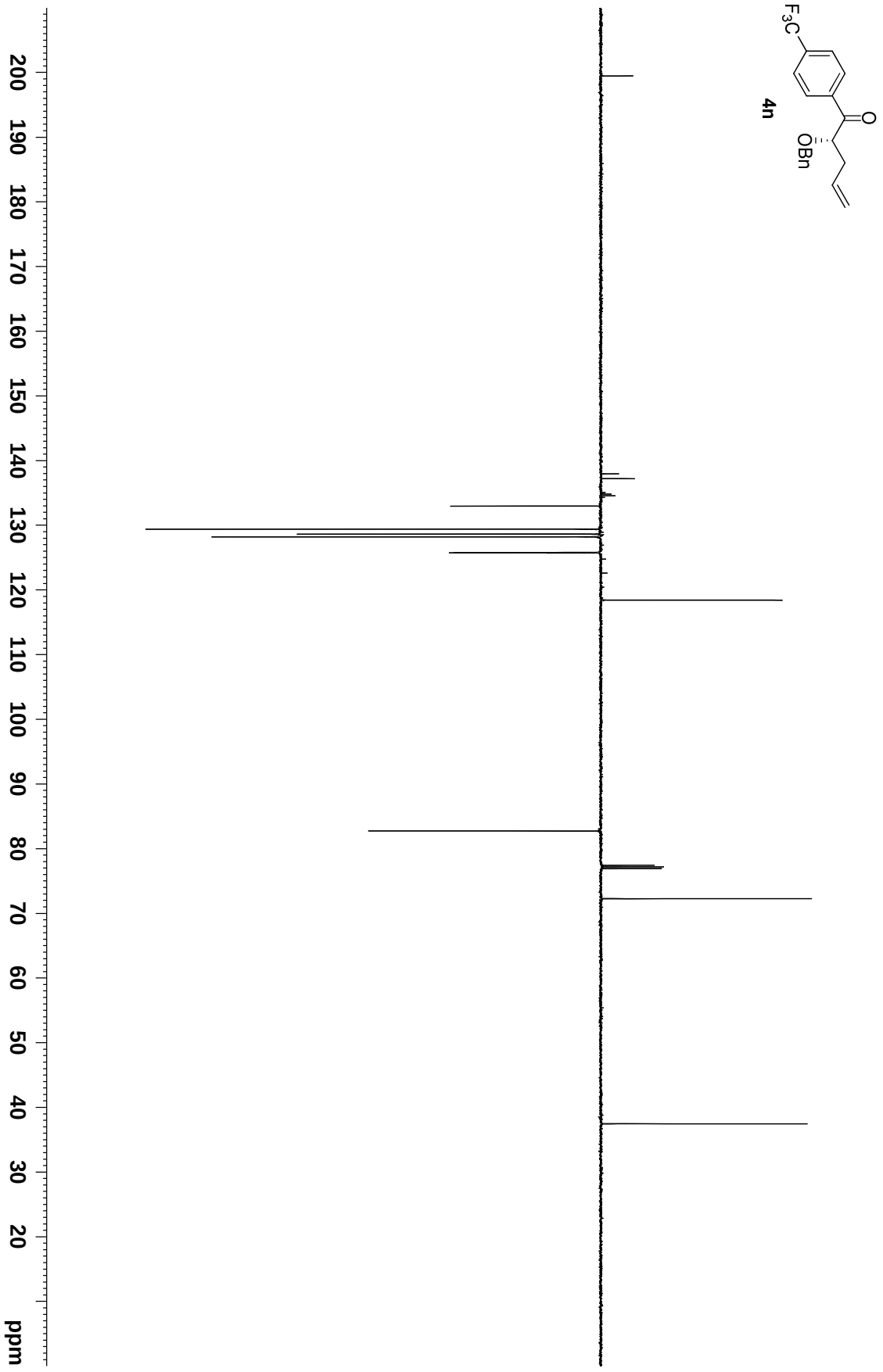

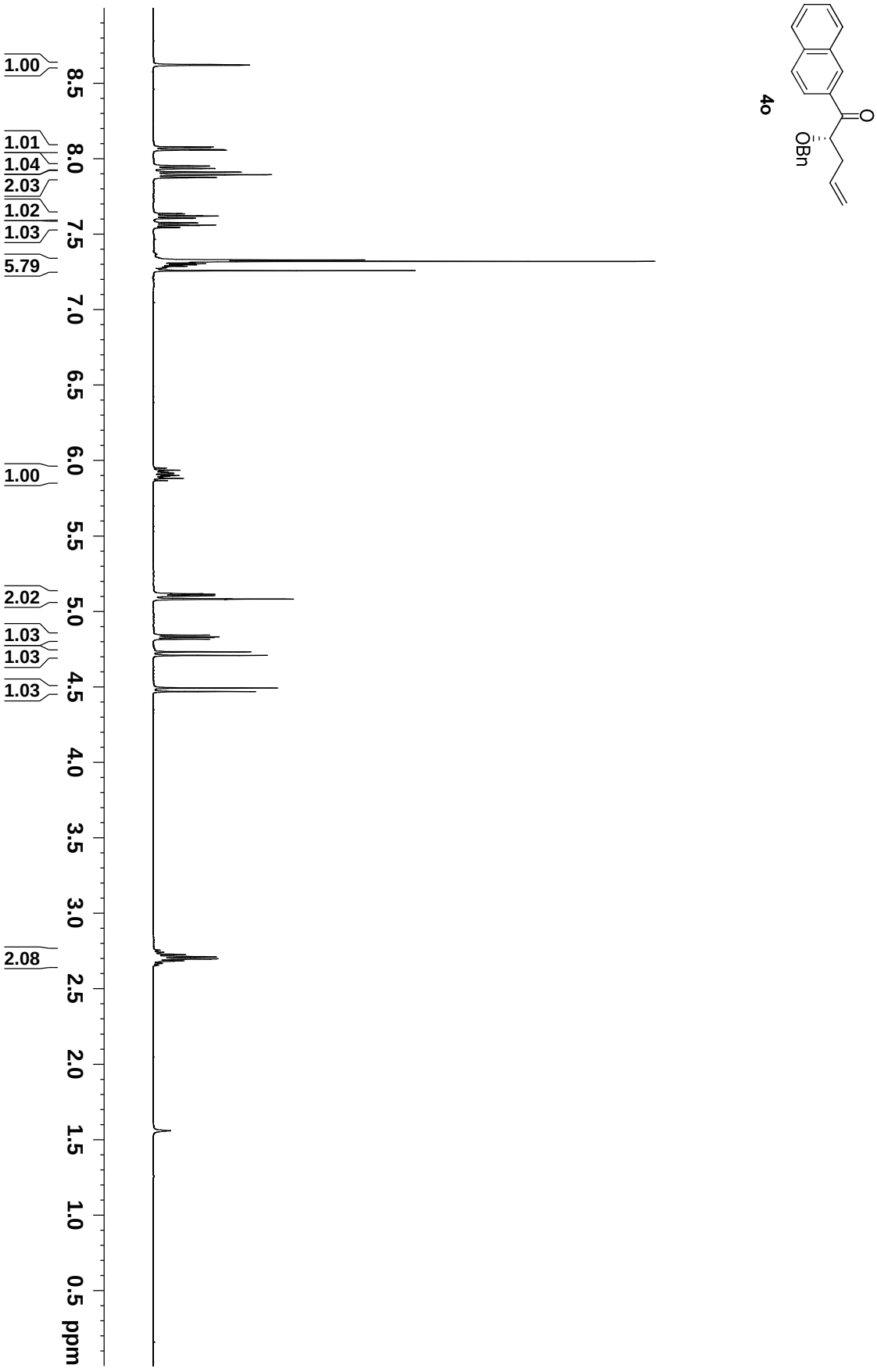

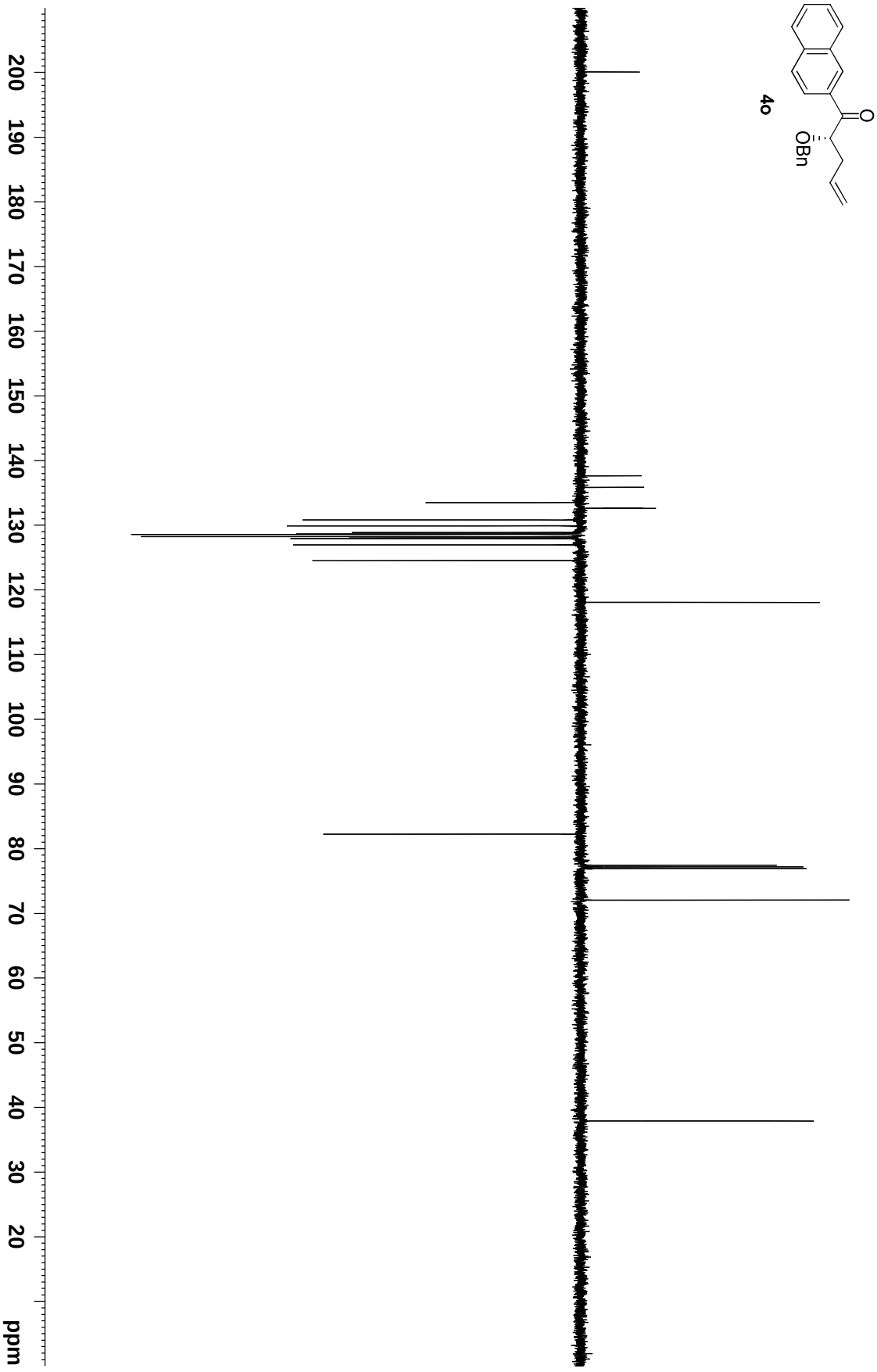
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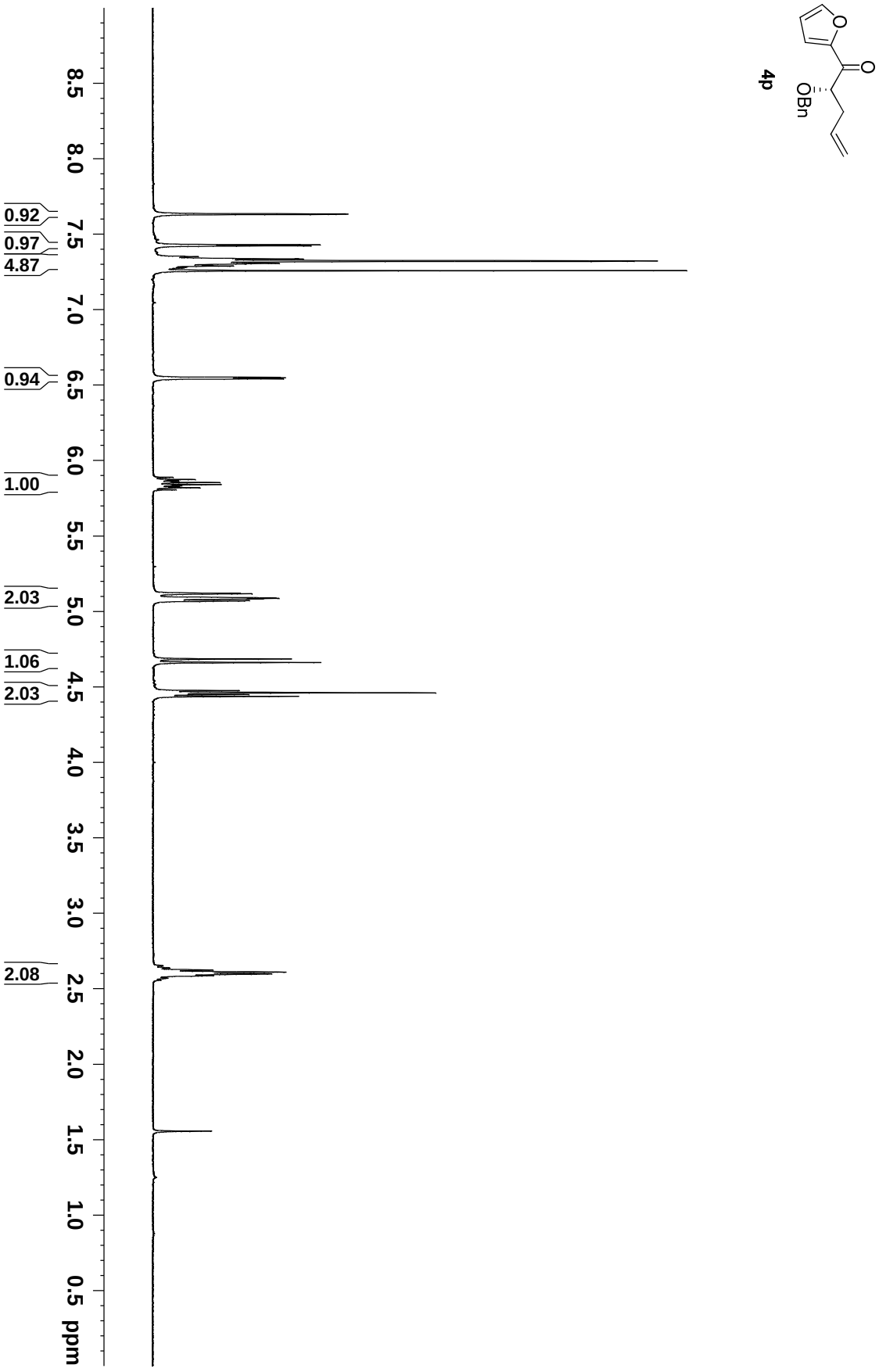

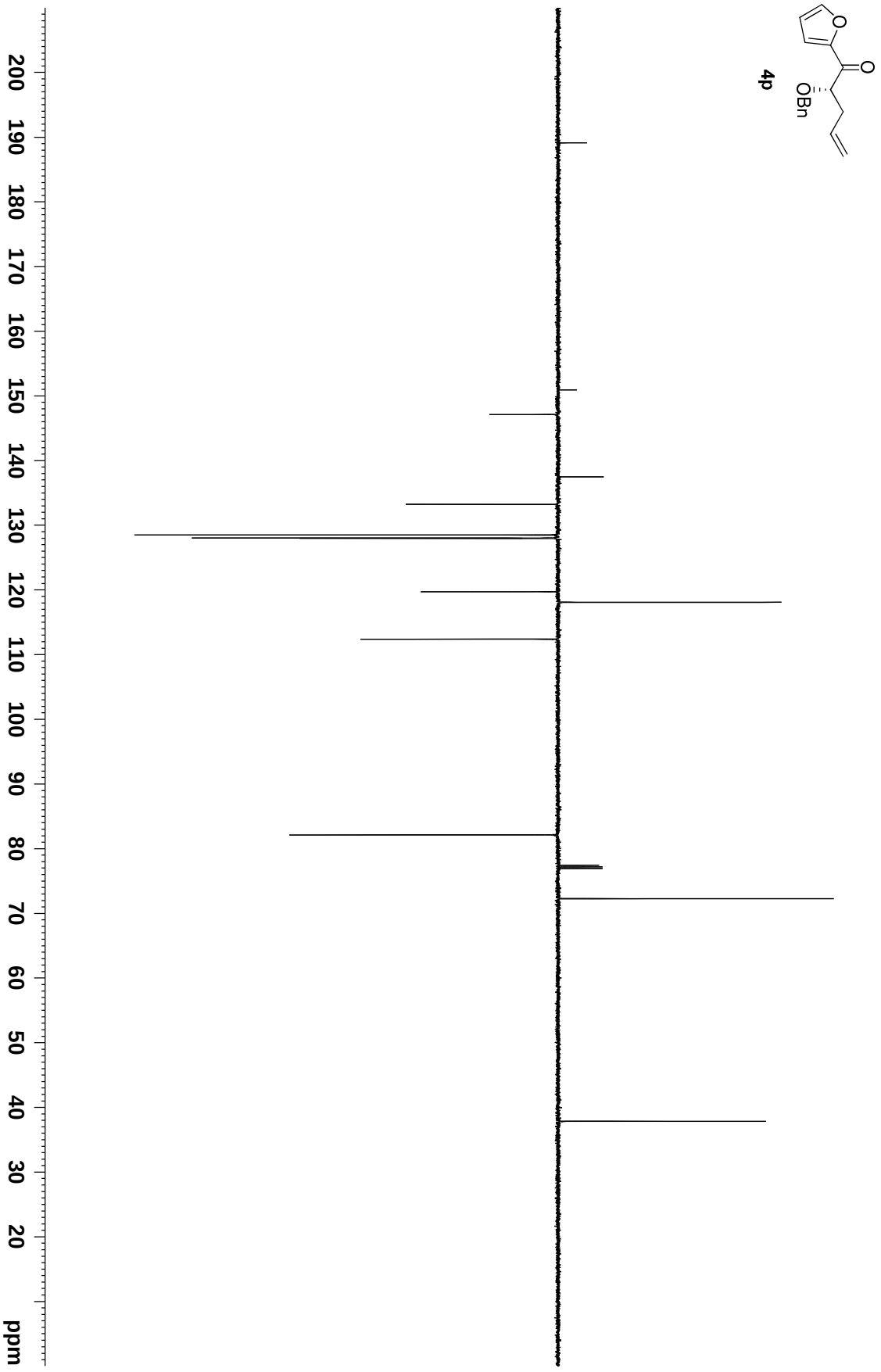

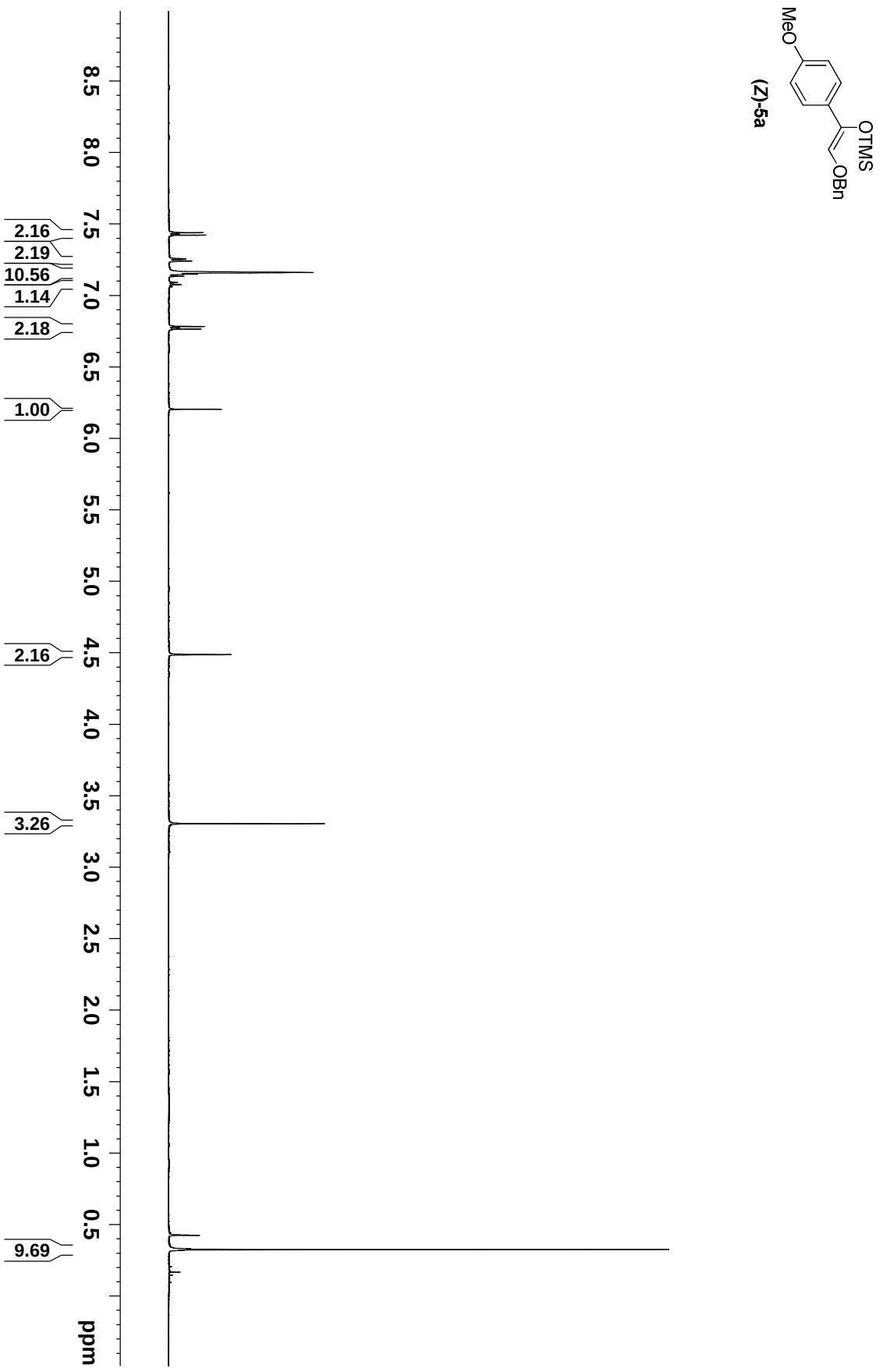

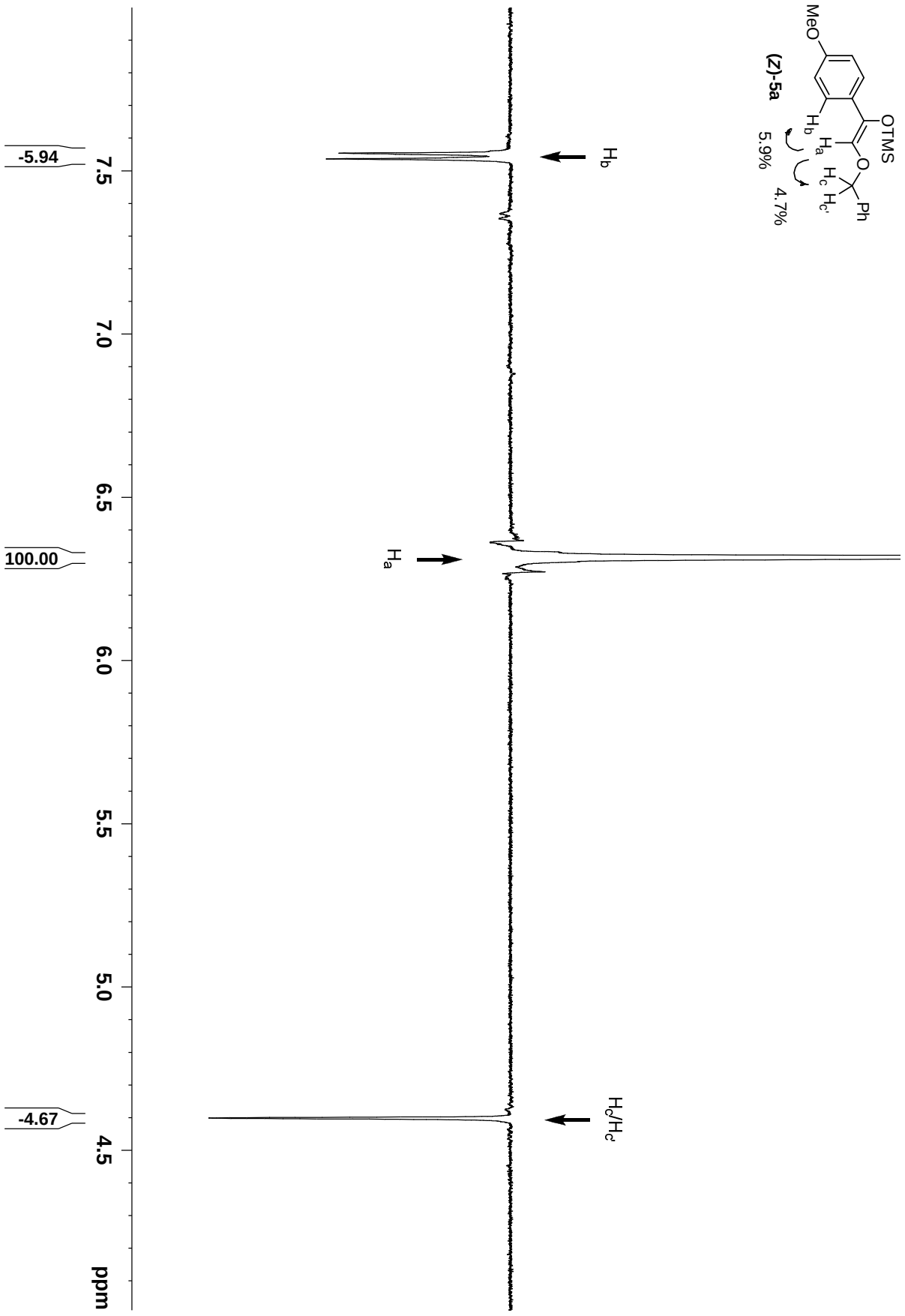

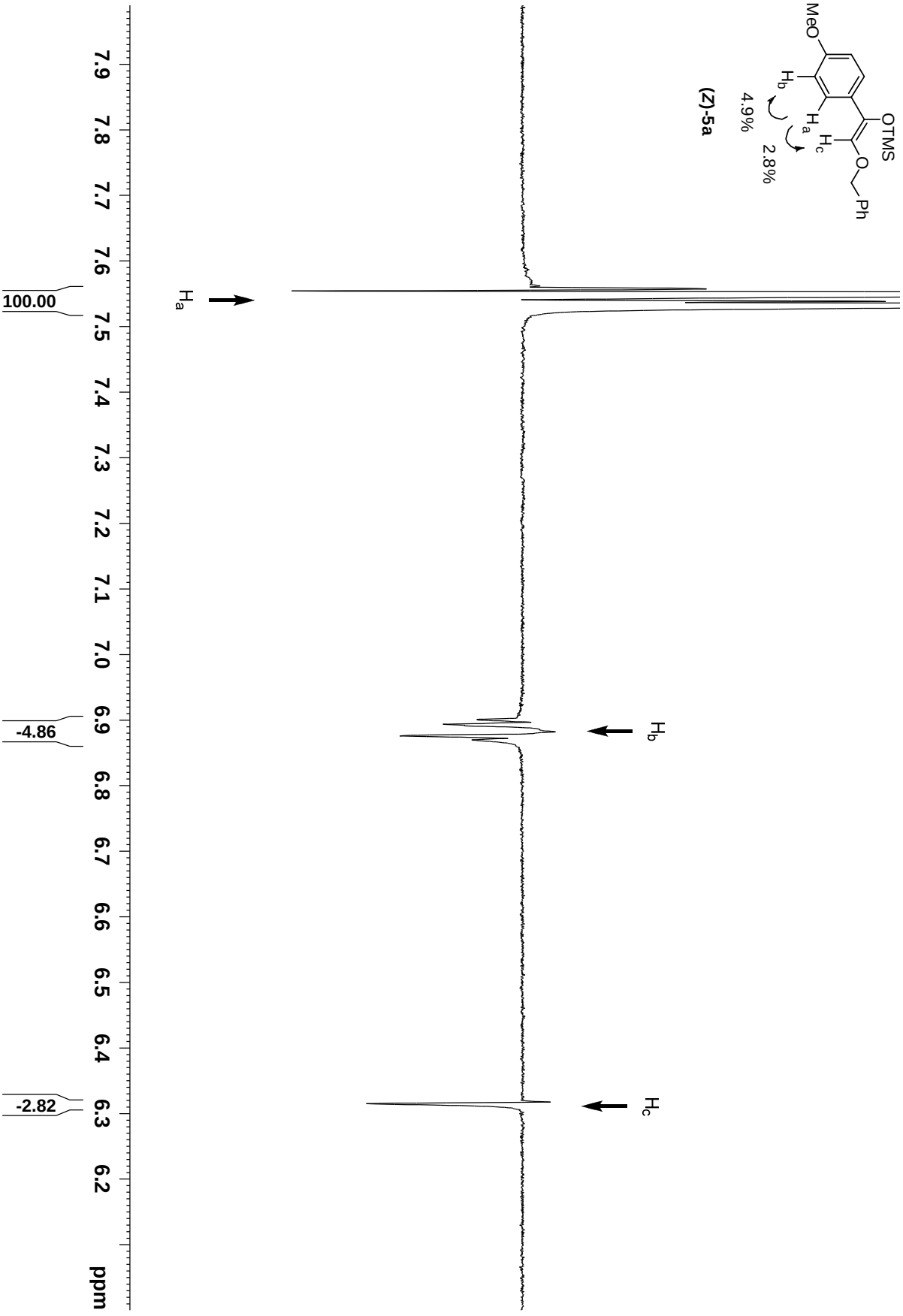

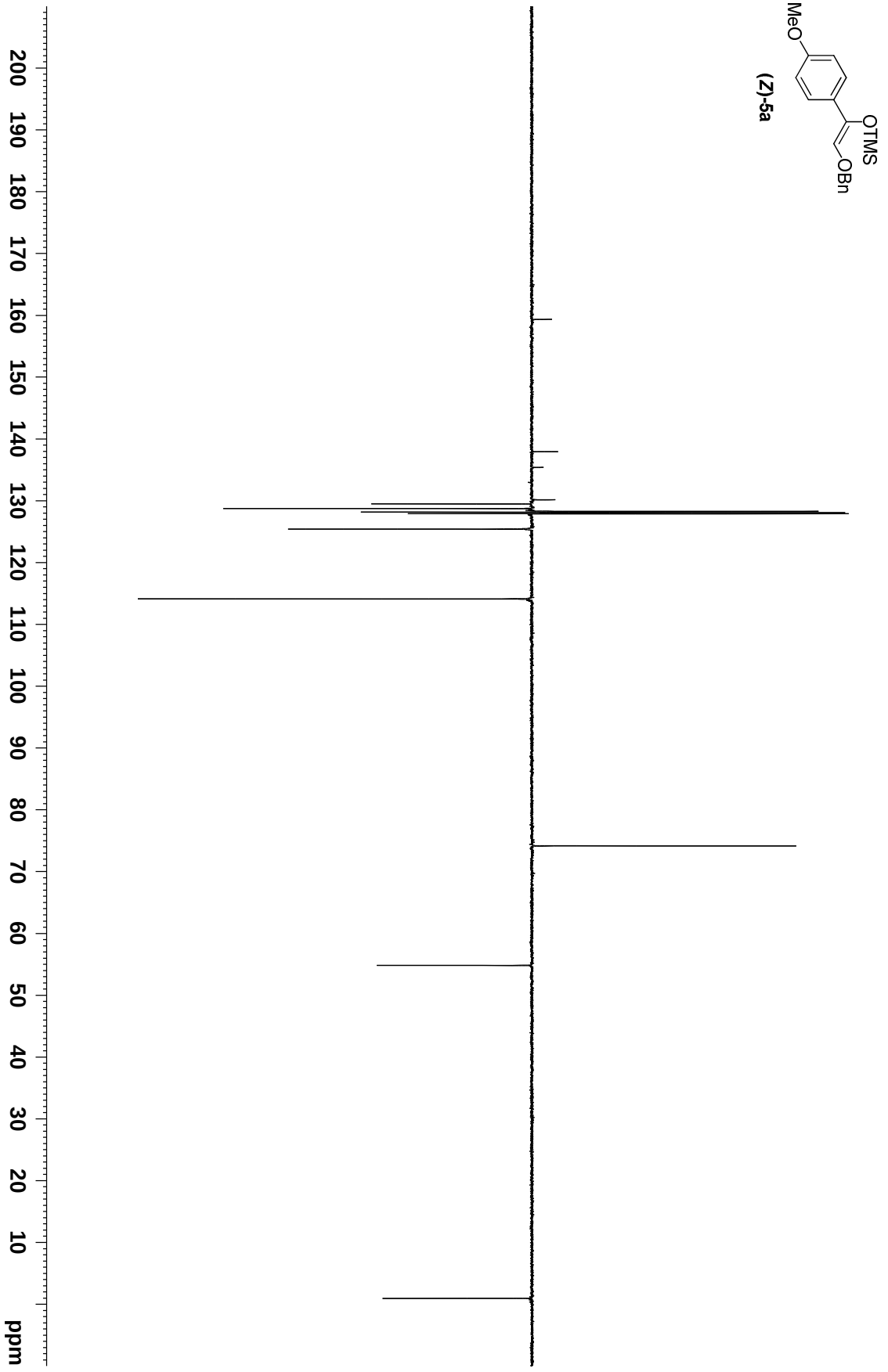
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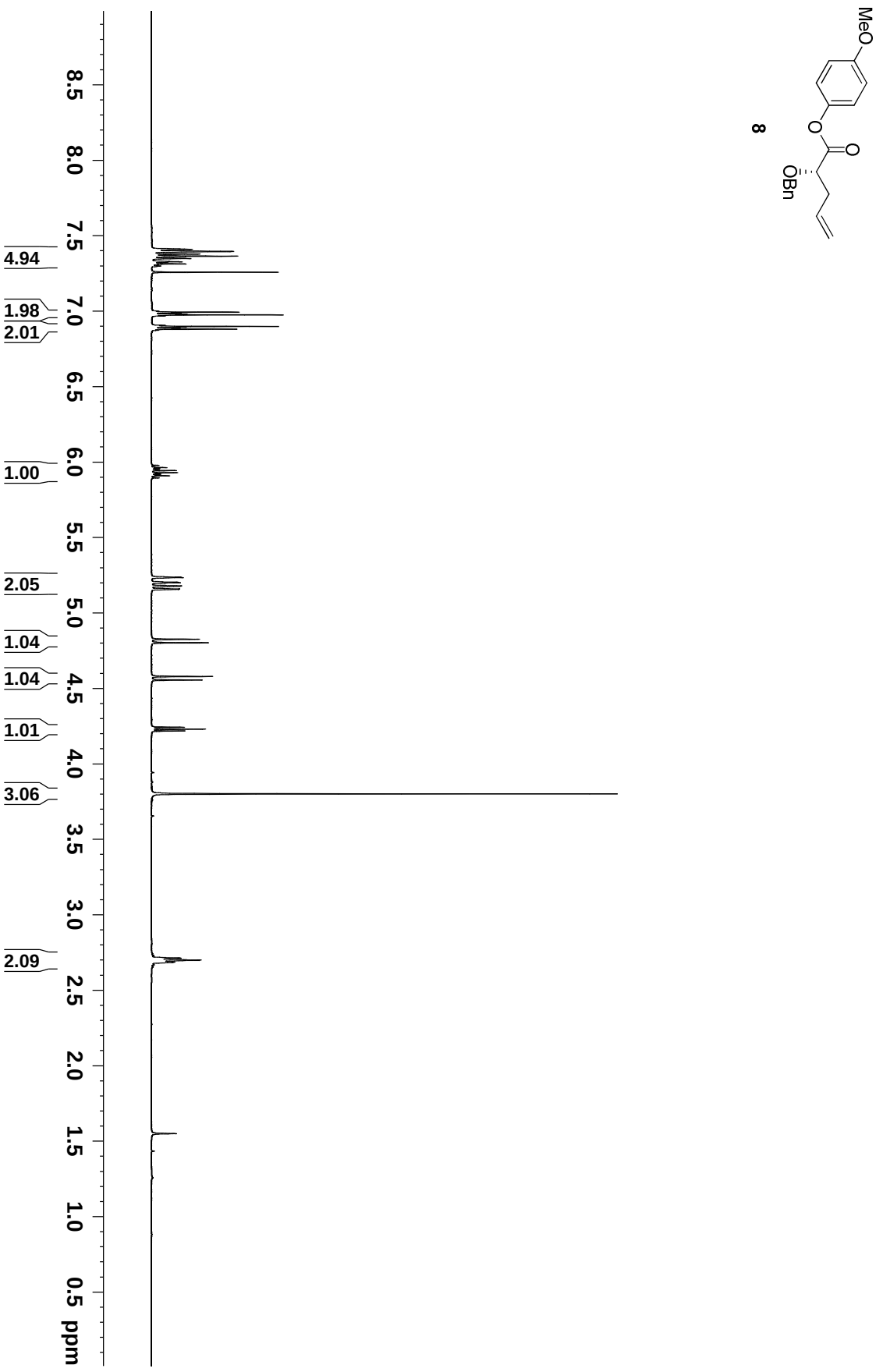

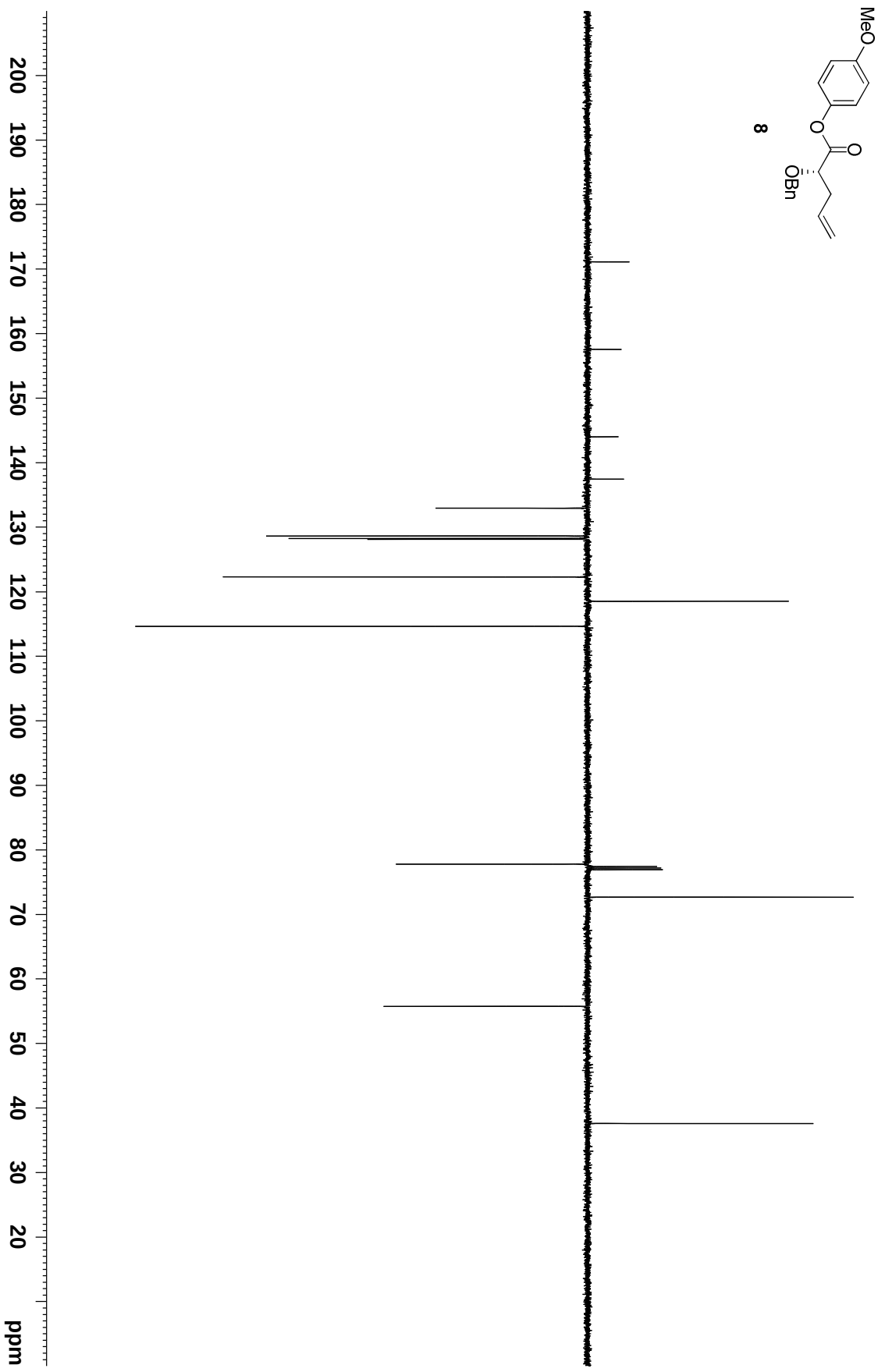

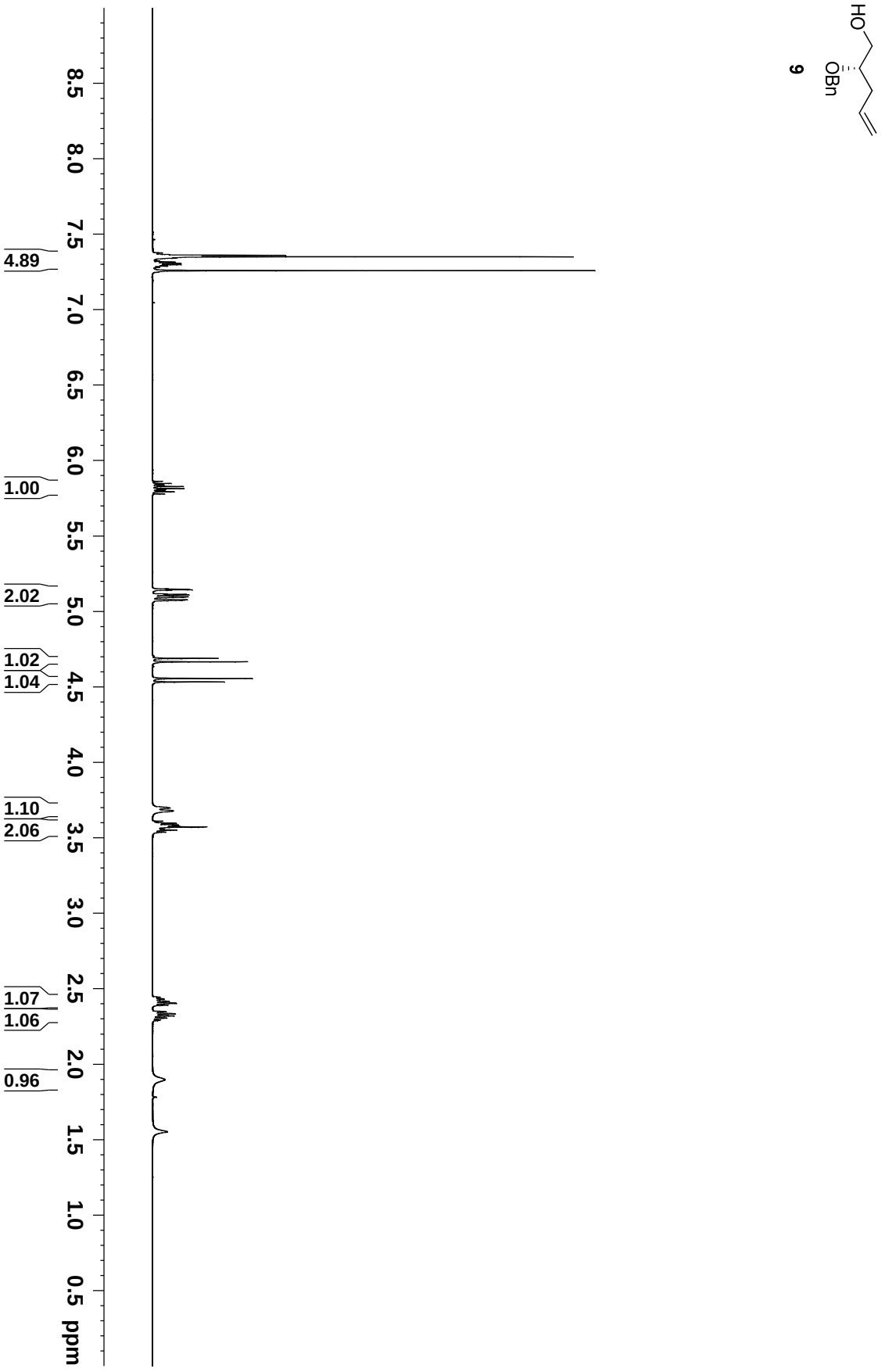

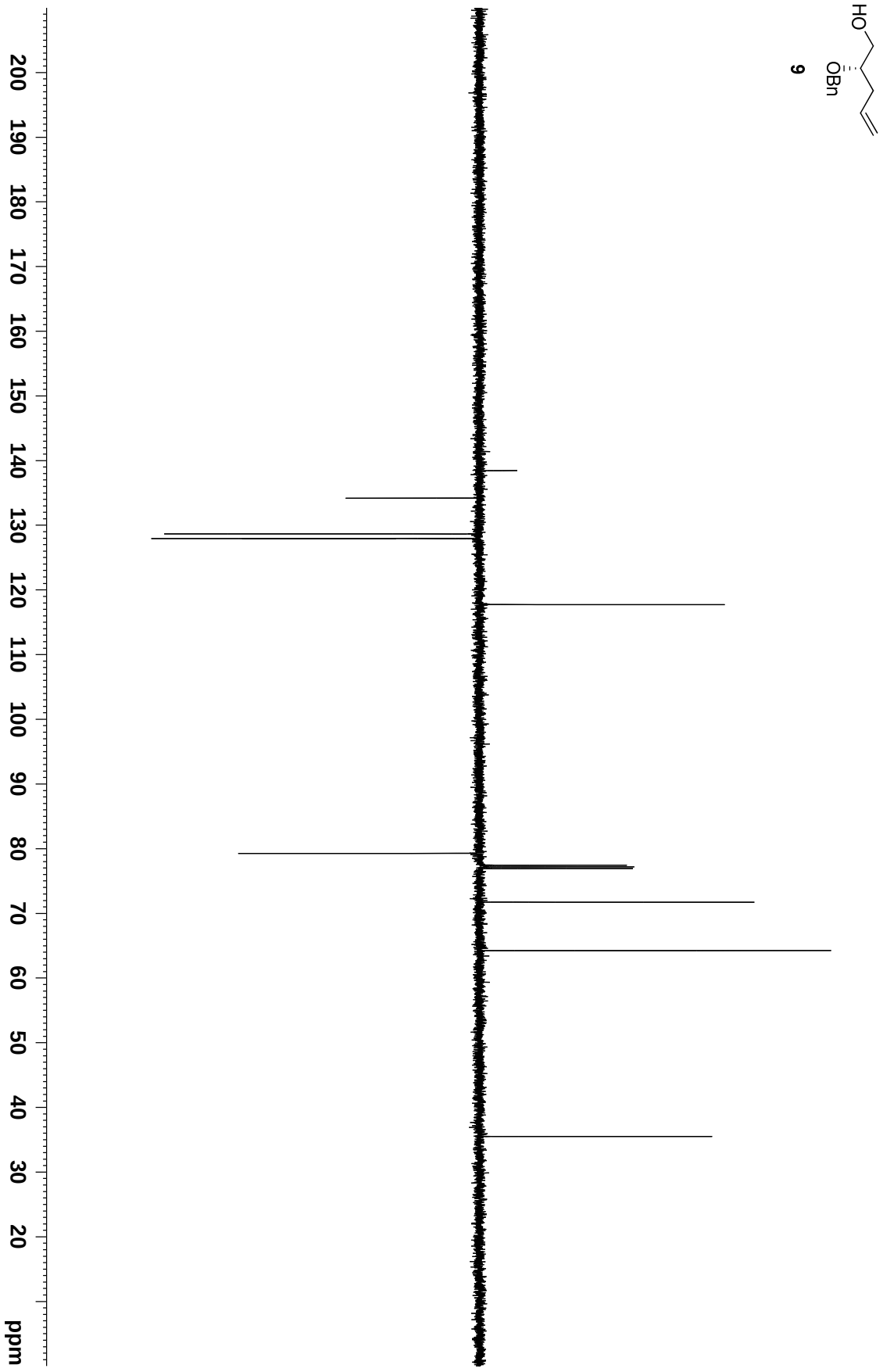

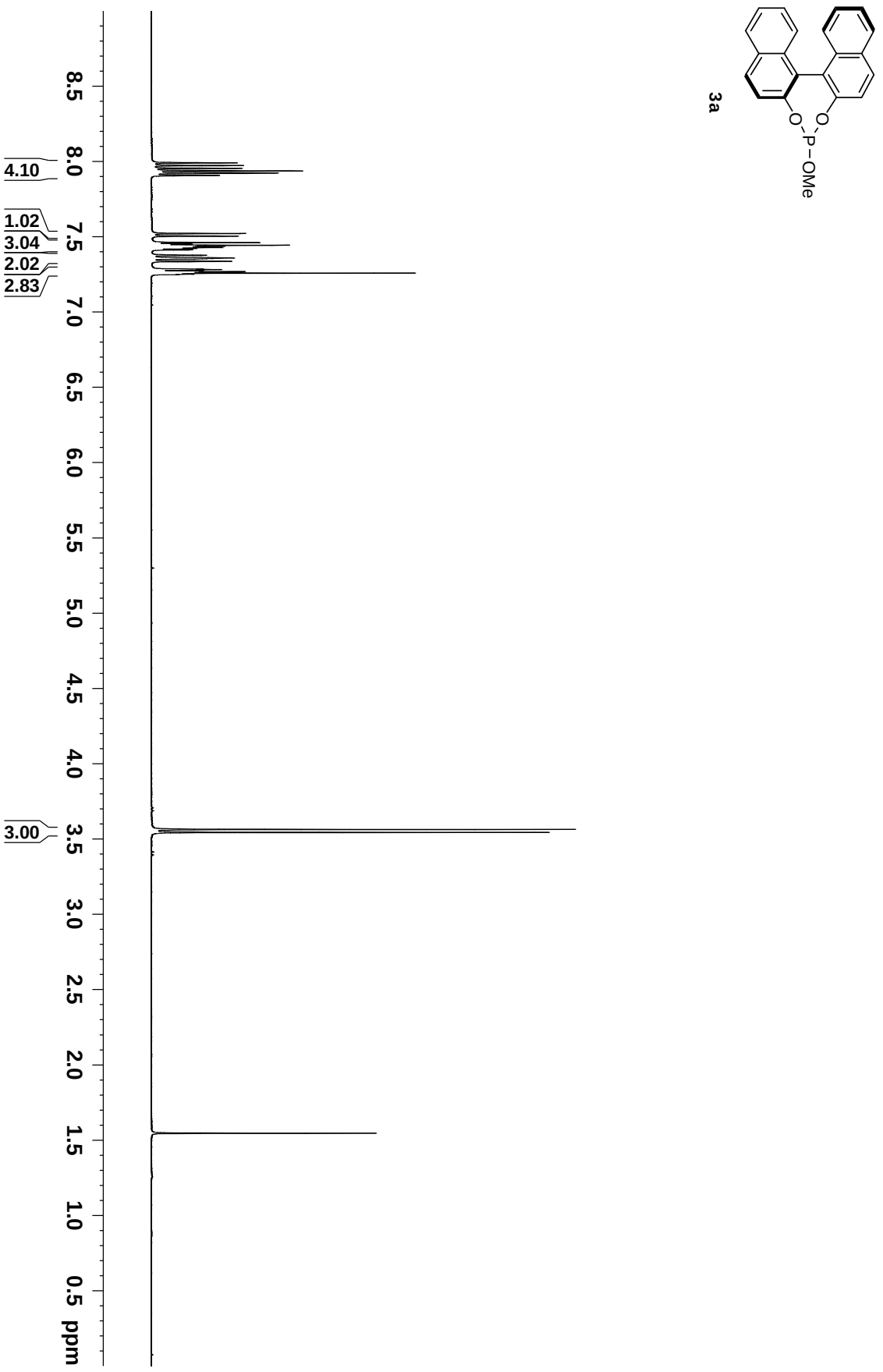

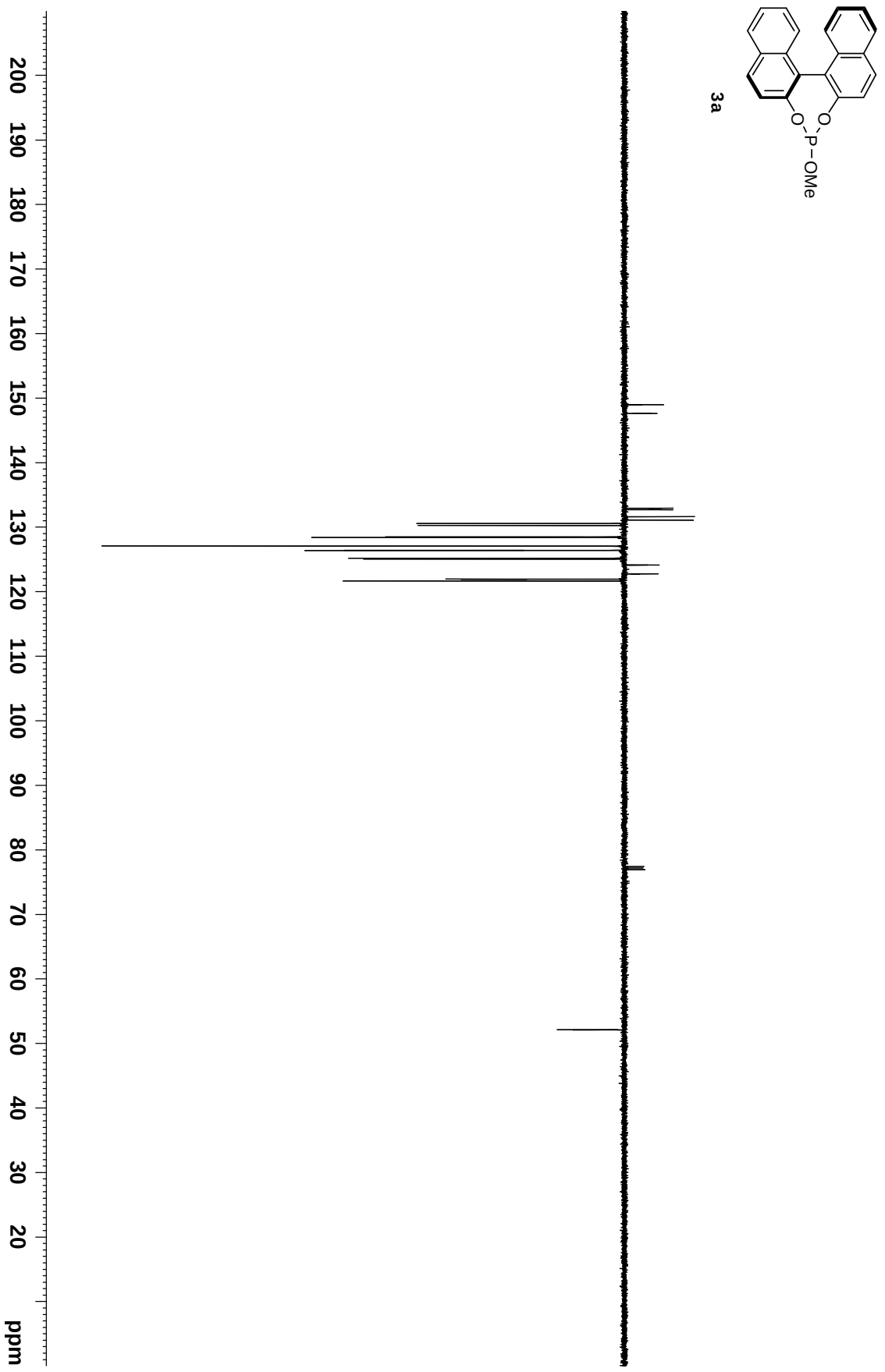

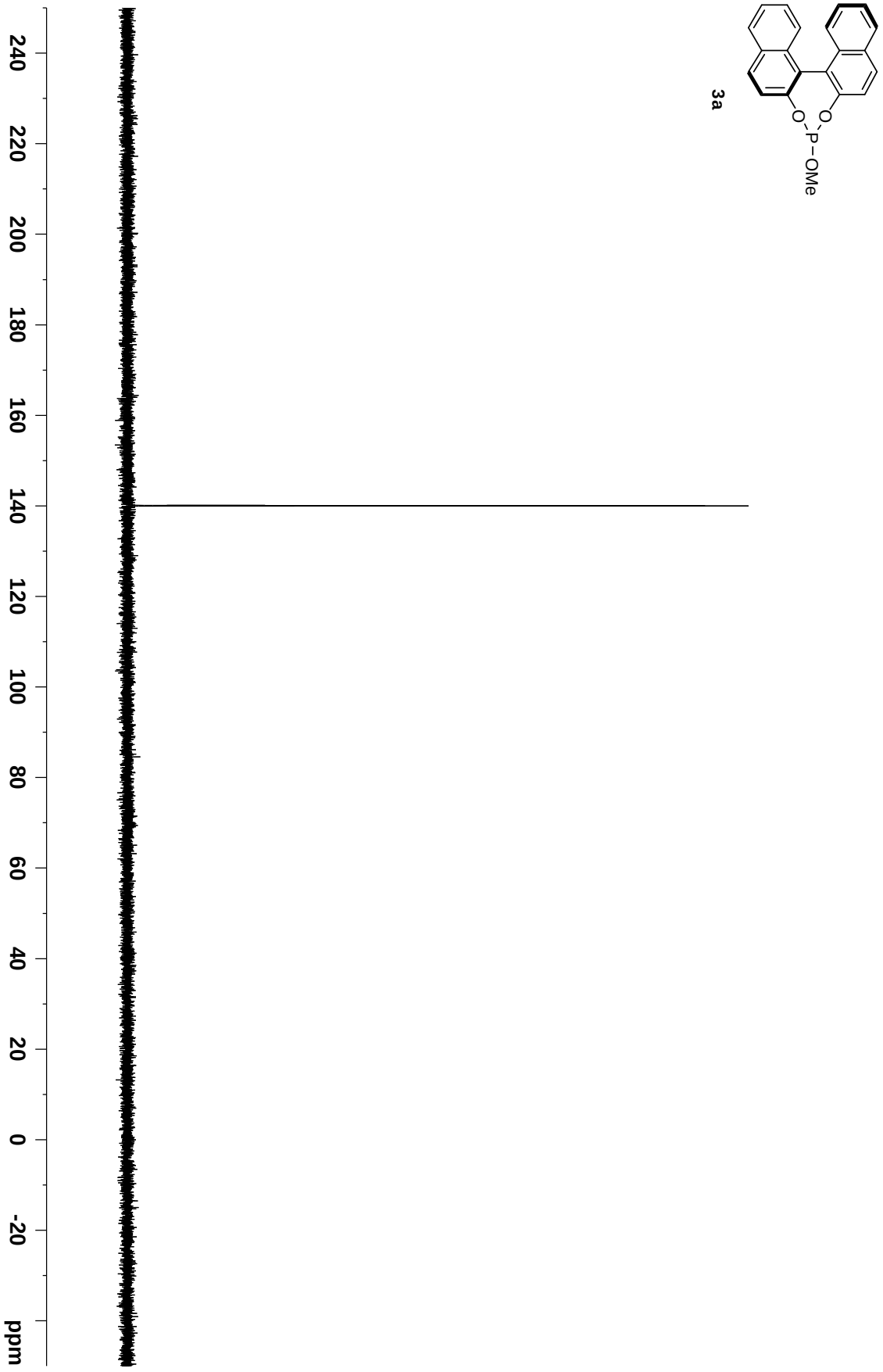
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