Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Synthesis of Highly Functionalized Cyclohexenone Rings: Rhodium-Catalyzed 1,3-Acyloxy Migration and Subsequent [5+1] Cycloaddition**

*Dongxu Shu, Xiaoxun Li, Min Zhang, Patrick J. Robichaux, and Weiping Tang**

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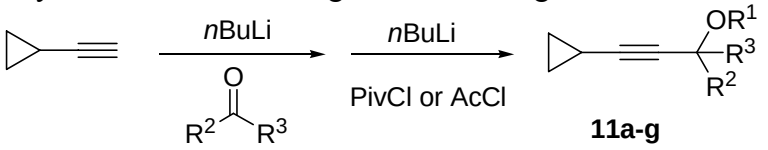
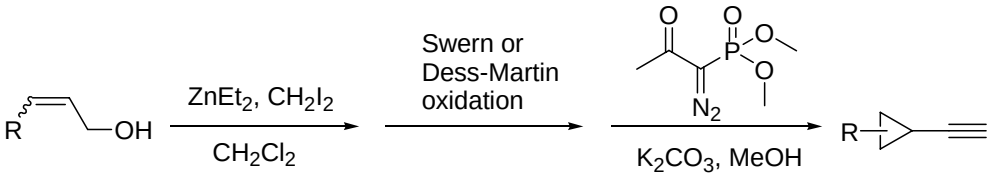
General remarks:
All reactions in non-aqueous media were conducted under a positive pressure of dry argon or carbonmonoxide in glassware that had been oven dried prior to use unless noted otherwise. Anhydrous solutions of reaction mixtures were transferred via an oven dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Reagents were purchased from Aldrich, Acros, TCI, or Alfa unless otherwise noted. Thin layer chromatography was performed using precoated silica gel plates (EMD Chemical Inc. 60,F254). Flash column chromatography was performed with silica gel (Sillicycle, 40-63μm). Infrared spectra (IR) were obtained as neat oils on a Bruker Equinox 55Spectrophotometer. ^{1}H and ^{13}C Nuclear magnetic resonance spectra (NMR) were obtained on a Varian Unity-Inova 400 MHz or 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ or CD_3OD. Signal splitting patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint),or multiplet (m), with coupling constants (*J*) in hertz. High resolution mass spectra (HRMS) were performed by Analytical Instrument Center at the School of Pharmacy or Department of Chemistry on an Electron Spray Injection (ESI) mass spectrometer. Enantiomeric excess was determined by chiral HPLC analysis. The optical rotation was determined by Perkin–Elmer 241 Polarimeter.

General Procedures for the preparation of substrates:

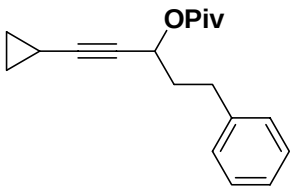
Substrates **11a-g** were synthesized according to Scheme 1.[1,2] More substituted substrates were generally synthesized from allylic alcohols via cyclopropanation[3], oxidation, and Seyfurth-Gilbert Homologation[4] according to Scheme 2.



Scheme 1. Synthesis of Substrates 11a-g

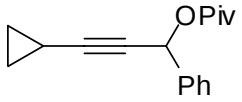


Scheme 2. Synthesis of Substituted Cyclopropyl Alkynes

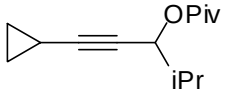


2,2-Dimethyl-propionic acid 3-cyclopropyl-1-phenethyl-prop-2-ynyl ester (11a). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.68 (m, 2H), 0.77 (m, 2H), 1.21 (s, 9H), 1.26 (m, 1H), 2.03 (m, 2H), 2.73 (m, 2H), 5.32 (td, *J* = 5.2, 1.5 Hz, 1H), 7.18 (m, 3H), 7.27 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.3, 8.58, 8.59, 27.2, 31.6, 36.9, 38.9, 63.9, 72.9, 89.5, 126.2, 128.61, 128.67, 141.3, 177.5. IR (film): ν 2963, 2246, 1731, 1479, 1455, 1366,

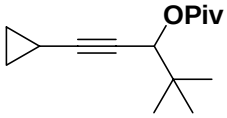
1278, 1146, 1030, 911 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}NaO_2$ $(M+Na)^+$ 307.1668, found 307.1666.



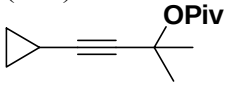
3-cyclopropyl-1-phenylprop-2-ynyl pivalate (11b). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.71 (m, 2 H), 0.78 (m, 2 H), 1.20 (s, 9H), 1.30 (m, 1 H), 6.40 (d, *J*=1.7 Hz, 1 H), 7.34 (m, 3 H), 7.46 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 8.8, 27.4, 39.1, 66.1, 72.5, 91.3, 127.6, 128.78, 128.82, 138.4, 177.6. IR: ν 2976, 2362, 2342, 1732, 1271, 1137 cm^{-1}. HRMS (ESI) for $C_{17}H_{20}NaO_2$ (M+23) 279.1356 (Calc.), found 279.1361.



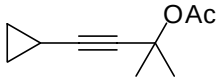
1-cyclopropyl-4-methylpent-1-yn-3-yl pivalate (11c). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.66 (m, 2H), 0.75 (m, 2H), 0.97 (d, *J* = 6.9 Hz, 6H), 1.21 (s, 9H), 1.26 (m, 1H), 1.93 (m, 1H), 5.14 (dd, *J* = 5.6, 1.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 8.85, 18.2, 18.6, 27.6, 33.2, 39.3, 69.6, 72.1, 89.8, 177.9. IR: ν 2968, 2362, 2343, 1781, 1281, 1147 cm^{-1}. HRMS (ESI) for $C_{14}H_{22}O_2$ (M+1) 223.1693 (Calc.), found 223.1691.



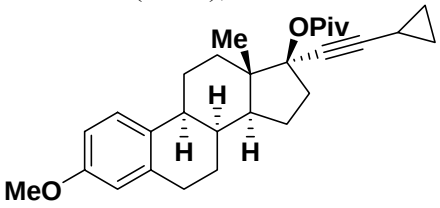
2,2-Dimethyl-propionic acid 1-tert-butyl-3-cyclopropyl-prop-2-ynyl ester (11d). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 0.65 (m, 2H), 0.75 (m, 2H), 0.97 (s, 9H), 1.22 (s, 9H), 1.23 (m, 1H), 5.00 (d, *J* = 1.5Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.3, 8.5, 25.8, 27.2, 35.5, 39.1, 71.7, 72.2, 89.3, 177.5. IR (film): ν 2972, 2245, 1733, 1147 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{24}NaO_2$ $(M+Na)^+$ 259.1668, found 259.1669.



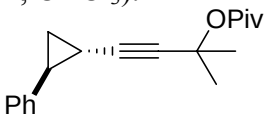
2,2-Dimethyl-propionic acid 3-cyclopropyl-1,1-dimethyl-prop-2-ynyl ester (11e). ^1H NMR (500 MHz, $CDCl_3$, TMS): δ 0.65 (m, 2H), 0.73 (m, 2H), 1.16 (s, 9H), 1.24 (m, 1H), 1.59 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ -0.2, 8.8, 27.5, 29.7, 39.5, 72.5, 77.0, 87.7, 177.1. IR (film): ν 2980, 2240, 1732, 1117, 912, 856, 812 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{13}H_{20}NaO_2$ $(M+Na)^+$ 231.1355, found 231.1360.



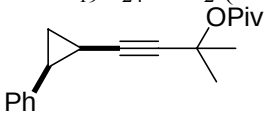
4-cyclopropyl-2-methylbut-3-yn-2-yl acetate (11f). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.63 (m, 2H), 0.71 (m, 2H), 1.21 (m, 1H), 1.58 (s, 6H), 1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 0.0, 8.9, 22.7, 29.8, 73.1, 77.0, 88.2, 169.9. IR: ν 2942, 2361, 2343, 1743, 1365, 1266, 1243, 1138, 1123 cm^{-1}. HRMS (ESI) for $C_{10}H_{14}NaO_2$ $(M+Na)^+$ 189.0886 (Calc.), found 189.0885.



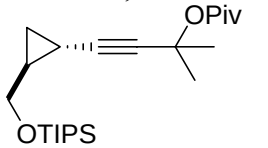
2,2-Dimethyl-propionic acid 17-cyclopropylethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl ester (11g). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.66 (m, 2H), 0.76 (m, 2H), 0.89 (s, 9H), 1.29 (m, 2H), 1.42 (m, 2H), 1.69 (m, 1H), 1.80 (m, 2H), 1.90 (m, 1H), 1.99 (m, 2H), 2.23 (m, 1H), 2.36 (m, 1H), 2.70 (ddd, *J* = 15.2, 9.6, 6.0 Hz, 1H), 2.86 (m, 2H), 3.78 (s, 3H), 6.64 (d, *J* = 3.5 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -0.1, 8.83, 8.85, 13.9, 23.6, 26.6, 27.3, 27.6, 30.1, 33.6, 37.6, 39.3, 39.4, 43.8, 48.1, 48.5, 55.4, 75.0, 84.9, 90.2, 111.7, 114.0, 126.6, 132.7, 126.6, 132.7, 138.1, 157.7, 176.8. IR (film): ν 2937, 2243, 1733, 1500, 1156, 1029, 908, 729 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{29}H_{38}NaO_3$ $(M+Na)^+$ 457.2713, found 457.2714. $[\alpha]_D^{25}$ = -108.6 (*c* 1, $CHCl_3$).



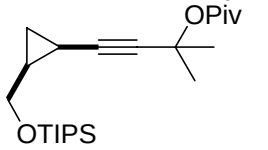
2,2-Dimethyl-propionic acid 1,1-dimethyl-3-(2-phenyl-cyclopropyl)-prop-2-ynyl ester (14). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.18 (s, 9H), 1.20 (m, 1H), 1.28 (m, 1H), 1.53 (ddd, *J* = 6.8, 5.5, 4.5 Hz, 1H), 1.62 (s, 6H), 2.20 (ddd, *J* = 7.2, 6.0, 4.5 Hz, 1H), 7.06 (m, 2H), 7.16 (m, 1H), 7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 18.3, 26.5, 27.3, 29.3, 29.4, 39.2, 72.2, 78.1, 86.0, 126.0, 126.3, 128.5, 141.1, 176.9. IR (film): ν 2981, 2246, 1733, 1479, 1285, 1172, 1117, 860, 748, 697 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}NaO_2$ $(M+Na)^+$ 307.1668, found 307.1678.



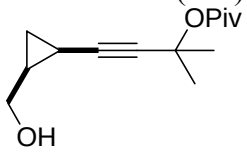
2,2-Dimethyl-propionic acid 1,1-dimethyl-3-(2-phenyl-cyclopropyl)-prop-2-ynyl ester (17). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11 (s, 9H), 1.16 (ddd, *J* = 7.2, 6.4, 5.6 Hz, 1H), 1.32 (td, *J* = 8.4, 5.2 Hz, 1H), 1.39 (s, 6H), 1.78 (td, *J* = 8.4, 6.0 Hz, 1H), 2.27 (td, *J* = 8.4, 6.8 Hz, 1H), 7.16-7.29 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.7, 15.0, 23.8, 27.2, 28.9, 29.1, 39.2, 72.0, 81.3, 83.8, 126.2, 127.8, 128.6, 138.3, 176.7. IR (film): ν 1735, 1288, 1119, 911, 698 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{19}H_{24}NaO_2$ $(M+Na)^+$ 307.1668, found 307.1682.



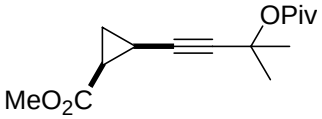
2,2-Dimethyl-propionic acid 1,1-dimethyl-3-(2-triisopropylsilanyloxymethyl-cyclopropyl)-prop-2-ynyl ester (18). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80 (m, 2H), 1.04 (m, 21H), 1.16 (s, 9H), 1.39 (s, 6H), 1.26 (m, 1H), 1.31 (m, 1H), 1.60 (s, 6H), 3.66 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.72 (dd, *J* = 10.4, 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 3.8, 12.2, 12.5, 18.1, 24.2, 27.2, 29.41, 29.42, 39.2, 63.6, 72.3, 76.9, 86.8, 176.8. IR (film): ν 2943, 2244, 1736, 1462, 1286, 1116, 881, 796, 681 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{23}H_{42}SiNaO_3$ $(M+Na)^+$ 417.2795, found 417.2798.



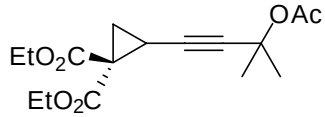
2,2-Dimethyl-propionic acid 1,1-dimethyl-3-(2-triisopropylsilanyloxymethyl-cyclopropyl)-prop-2-ynyl ester (21). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.53 (ddd, *J* = 5.5, 5.5, 5.5 Hz, 1H), 0.98 (m, 1H), 1.08 (m, 21H), 1.16 (s, 9H), 1.27 (m, 1H), 1.46 (m, 1H), 1.59 (s, 6H), 3.62 (dd, *J* = 10.5, 7.0 Hz, 1H), 3.94 (dd, *J* = 10.5, 6.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 4.8, 12.2, 12.5, 13.5, 18.2, 20.6, 27.2, 29.2, 29.3, 39.1, 64.7, 72.1, 79.1, 84.0, 176.5. IR (film): ν 2944, 2868, 1736, 1463, 1286, 1129, 883, 772, 682 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{23}H_{42}SiNaO_3$ $(M+Na)^+$ 417.2795, found 417.2803.



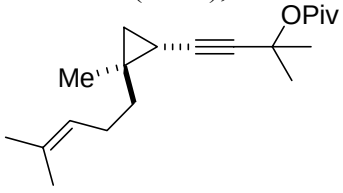
2,2-Dimethyl-propionic acid 3-(2-hydroxymethyl-cyclopropyl)-1,1-dimethyl-prop-2-ynyl ester (22). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.60 (ddd, *J* = 5.2, 5.2, 5.2 Hz, 1H), 0.96 (td, *J* = 7.6, 4.8 Hz,1H), 1.17 (s, 9H), 1.43 (m, 2H), 1.60 (s, 6H), 2.88 (s, 1H), 3.45 (dd, *J* = 11.6, 8.4 Hz, 1H), 3.99 (d, *J* = 12.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.5, 12.6, 21.2, 27.2, 28.8, 29.5, 39.4, 63.5, 72.1, 78.5, 84.9, 177.9. IR (film): ν 2985, 2244, 1723, 1129, 915 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{22}NaO_3$ $(M+Na)^+$ 261.1461, found 261.1473.

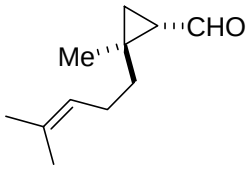


2-[3-(2,2-Dimethyl-propionyloxy)-3-methyl-but-1-ynyl]-cyclopropanecarboxylic acid methyl ester (24). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (s, 9H), 1.19 (m, 1H), 1.41 (ddd, *J* = 6.8, 6.4, 4.8 Hz, 1H), 1.59 (s, 3H), 1.60 (s, 3H), 1.81 (td, *J* = 8.8, 7.2 Hz, 1H), 1.93 (ddd, *J* = 8.4, 7.6, 6.0 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 9.5, 14.5, 21.5, 27.2, 29.1, 29.3, 39.2, 51.9, 71.9, 80.5, 81.4, 170.6, 176.8. IR (film): ν 2981, 2245, 1732, 1197, 1074 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}NaO_4$ $(M+Na)^+$ 289.1410, found 261.1424.



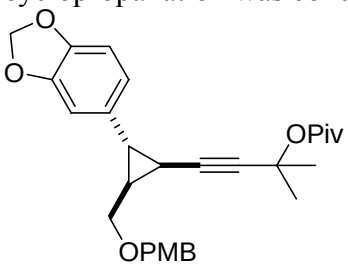
Diethyl 2-(3-acetoxy-3-methylbut-1-ynyl)cyclopropane-1,1-dicarboxylate (26). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (t, *J* = 8.0 Hz, 3H), 1.31 (t, *J* = 8.0 Hz, 3H), 1.53 (dd, *J* = 9.2, 4.5 Hz, 1H), 1.56 (s, 6H), 1.77 (dd, *J* = 7.2, 4.5 Hz, 1H), 1.97 (s, 3H), 2.46 (dd, *J* = 9.2, 7.2 Hz, 1H), 4.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 14.3, 16.7, 22.1, 29.2, 36.4, 61.9, 62.1, 72.1, 80.4, 81.5, 166.5, 168.9, 169.4. IR: ν 2986, 2359, 2344, 1733, 1371, 1321, 1243, 1202, 1137, 1017 cm^{-1}. HRMS (ESI) for $C_{16}H_{22}NaO_6$ $(M+Na)^+$ 333.1309 (Calc.), found 333.1316.



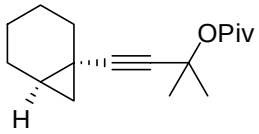


2,2-Dimethyl-propionic acid 1,1-dimethyl-3-[2-methyl-2-(4-methyl-pent-3-enyl)-cyclopropyl]-prop-2-ynyl ester (28). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.46 (dd, *J* =

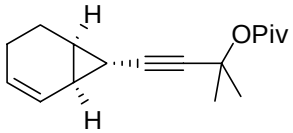
5.0, 5.0 Hz, 1H), 0.73 (dd, *J* = 9.0, 4.0 Hz, 1H), 1.11 (dd, *J* = 8.5, 5.0 Hz, 1H), 1.16 (s, 9H), 1.16 (s, 3H), 1.17-1.31 (m, 2H), 1.60 (s, 3H), 1.62 (s, 6H), 1.67 (s, 3H), 2.03 (m, 2H), 5.07 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.4, 17.8, 18.8, 22.7, 23.4, 25.5, 25.9, 27.3, 29.5, 29.6, 39.3, 40.1, 72.5, 79.2, 85.5, 124.5, 131.6, 176.8. IR (film): ν 2969, 2238, 1736, 1286, 1172, 1114 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{32}NaO_2$ $(M+Na)^+$ 327.2945, found 327.2305. $[\alpha]_D^{25}$ = +73.8 (*c* 1, $CHCl_3$). The enantiomeric excess (87%) of substrate **28** was determined by HPLC analysis of the precursor aldehyde shown above. (Chiralcel OJ-H; eluent: pure hexane; flow rate: 0.7 mL/min; detection: at 210 nm): retention times t_1 = 20.2 min t_2=23.8 min. Compound **28** was prepared according to general procedures in Schemes 1 and 2. The enantioselective cyclopropanation was conducted according to literature procedure.[5]



2,2-Dimethyl-propionic acid 3-[2-benzo[1,3]dioxol-5-yl-3-(4-methoxybenzyloxymethyl)-cyclopropyl]-1,1-dimethyl-prop-2-ynyl ester (30). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (s, 9H), 1.61 (s, 6H), 1.65 (m, 1H), 1.71 (dd, *J* = 8.4, 5.2 Hz, 1H), 1.96 (t, *J* = 5.2 Hz, 1H), 3.70 (dd, *J* = 6.0, 1.6 Hz, 2H), 3.79 (s, 3H), 4.48 (d, *J* = 10.4 Hz, 1H), 4.56 (d, *J* = 10.4 Hz, 1H), 5.90 (s, 2H), 6.52 (d, *J* = 2.0 Hz, 1H), 6.56 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.87 (m, 2H), 7.30 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.1, 27.3, 27.6, 29.3, 31.1, 39.3, 55.5, 70.1, 72.1, 72.7, 80.8, 82.7, 101.1, 106.8, 108.3, 114.0, 119.7, 129.6, 130.9, 134.1, 146.3, 147.9, 159.4, 176.8. IR (film): ν 1731, 1513, 1250, 1038, 756 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{29}H_{34}NaO_6$ $(M+Na)^+$ 501.2247, found 501.2246.

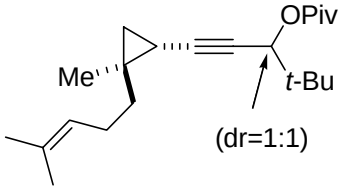


4-((1R,6R)-bicyclo[4.1.0]heptan-1-yl)-2-methylbut-3-yn-2-yl pivalate (32). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.48 (m, 1H), 0.90 (m, 2H), 1.10 (m, 1H), 1.15 (s, 9H), 1.23 (m, 3H), 1.52 (m, 1H), 1.57 (s, 3H), 1.58 (s, 3H), 1.85 (m, 1H), 1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 20.4, 20.5, 21.2, 23.4, 27.3, 29.5, 29.6, 39.3, 72.5, 76.2, 92.2, 176.8. IR: ν 2976, 2935, 2863, 2364, 2234, 1733, 1285, 1172, 1120 cm^{-1}. HRMS (ESI) for $C_{17}H_{26}O_2$ (M+1) 263.2006 (Calc.), found 263.2002.



4-((1S,6R,7S)-bicyclo[4.1.0]hept-2-en-7-yl)-2-methylbut-3-yn-2-yl pivalate (34). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.17 (s, 9H), 1.27 (d, *J* = 1.0 Hz, 1H), 1.46 (m, 1H), 1.51 (m, 1H), 1.60 (s, 6H), 1.61 (m, 1H), 1.71 (m, 1H), 2.00 (m, 2H), 5.46 (m, 1H), 6.01 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.2, 17.9, 20.8, 22.1, 24.9, 26.7, 27.3, 29.4, 39.3, 72.3, 78.3, 86.1, 124.4, 126.4, 176.9. IR: ν 2983, 2935, 2806, 2360, 2244, 1734,

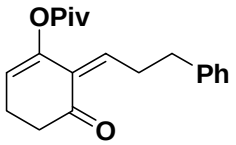
1172, 1126, 1098 cm^{-1}. HRMS (ESI) for $C_{17}H_{24}O_2$ (M+1) 261.1849 (Calc.), found 261.1846.



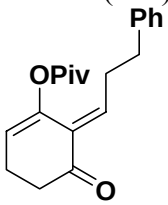
2,2-Dimethyl-propionic acid 1-tert-butyl-3-[2-methyl-2-(4-methyl-pent-3-enyl)-cyclopropyl]-prop-2-ynyl ester (36, 1:1 diastereoisomers). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 0.45 (dd, *J* = 4.5, 4.5Hz, 1H), 0.74 (dd, *J* = 8.5, 4.0 Hz, 1H), 0.99 (s, 9H), 1.13 (m, 1H), 1.16 (m, 3H), 1.21 (s, 9H), 1.23 (m, 2H), 1.60 (s, 3H), 1.67 (s, 3H), 2.04 (m, 2H), 5.04 (d, *J* = 2.0 Hz, 1H), 5.07 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 13.5, 17.8, 19.1, 19.1, 22.73, 22.76, 23.37, 23.43, 25.5, 25.92, 25.94, 25.96, 27.3, 35.56, 35.60, 39.1, 40.03, 40.05, 72.50, 72.57, 74.2, 87.32, 87.37, 124.4, 131.7, 177.5. IR (film): ν 2973, 2239, 1735, 1479, 1279, 1150, 1032 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{22}H_{36}NaO_2$ $(M+Na)^+$ 355.2607, found 355.2610.

General Procedure for the rhodium catalyzed tandem 1,3-acyl migration followed by [5+1] cycloaddition.

To an oven-dried flask was added $[Rh(CO)_2Cl]_2$ (0.005mmol) and anhydrous toluene (1ml) under an CO atmosphere, cyclopropyl propargyl ester (0.1 mmol) was added and the oil bath was heated to 60 ^{o}C. The reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated and the residue was further purified by flash chromatography.

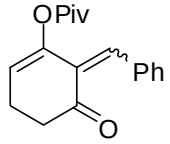


(*Z*)-2,2-Dimethyl-propionic acid 5-oxo-6-(3-phenyl-propylidene)-cyclohex-1-enyl ester (12a). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.23 (s, 9H), 2.49 (td, *J* = 6.5, 5.0 Hz, 2H), 2.60 (t, *J* = 7.0 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.97 (dt, *J* = 7.5, 7.5 Hz,2H), 5.58 (t, 5.0Hz, 1H), 5.92 (t, *J* = 7.5 Hz, 1H), 7.17 (m, 3H), 7.26 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 27.3, 30.5, 35.5, 39.2, 39.8, 115.6, 126.1, 128.5, 128.7, 129.6, 137.1, 141.2, 146.0, 176.4, 199.3. IR (film): ν 2972, 1753, 1702, 1373, 1119, 914, 700 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}NaO_3$ $(M+Na)^+$ 335.1617, found 335.1632.

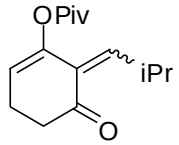


(*E*)-2,2-Dimethyl-propionic acid 5-oxo-6-(3-phenyl-propylidene)-cyclohex-1-enyl ester (12a). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.22 (s, 9H), 2.45 (td, *J* = 6.0, 5.2 Hz, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.68 (dt, *J* = 7.6, 7.6 Hz, 2H), 2.77 (t, *J* = 7.2 Hz, 2H), 5.63 (t, *J* = 5.2Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 7.17 (m, 3H), 7.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.4, 27.3, 30.7, 35.4, 37.1, 39.2, 118.5, 126.3, 128.4, 128.6, 129.7,

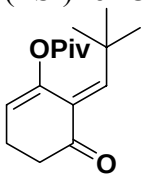
137.7, 141.0, 147.0, 177.0, 198.4. IR (film): ν 2971, 1751, 1705, 1266, 1120, 914, 735 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}NaO_3$ $(M+Na)^+$ 335.1617, found 335.1614.



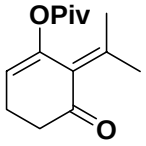
(*E*/*Z*)-6-benzylidene-5-oxocyclohex-1-enyl pivalate (12b). ^1H NMR (400 MHz, $CDCl_3$, TMS): For *E*-isomer: δ 0.76 (s, 9H), 2.53 (m, 2H), 2.63 (t, *J* = 6.2 Hz, 2H), 5.87 (td, *J* = 5.3, 1.2 Hz, 1H, one isomer), 7.31 (m, 4H), 7.43 (m, 1H), 7.58 (s, 1H). For *Z*-isomer: δ 1.35 (s, 9H), 2.58 (m, 2H), 2.73 (t, *J* = 6.4 Hz, 2H), 5.73 (t, *J* = 4.5 Hz, 1H), 6.67 (s, 1H), 7.31 (m, 4H), 7.43 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2, 26.7, 36.7, 40.3, 120.3, 128.2, 129.1, 130.4, 131.6, 134.2, 135.4, 146.5, 176.4, 199.5. IR: ν 2975, 2361, 2342, 1749, 1702, 1162, 1112 cm^{-1}. HRMS (ESI) for $C_{18}H_{20}O_3$ (M+1) 285.1485 (Calc.), found 285.1481.



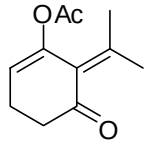
(*E*/*Z*)-6-(2-methylpropylidene)-5-oxocyclohex-1-enyl pivalate (12c). ^1H NMR (400 MHz, $CDCl_3$, TMS): For *E*-isomer: δ 0.98 (d, *J* = 6.6 Hz, 6H), 1.30 (s, 9H), 2.45 (m, 2H), 2.59 (m, 2H), 3.46 (m, 1H), 5.59 (m, 1H), 6.46 (d, *J* = 10.7 Hz, 1H). For *Z*-isomer: δ 0.97 (d, *J* = 6.6 Hz, 6H), 1.28 (s, 9H), 2.45 (m, 2H), 2.59 (m, 2H), 2.96 (m, 1H), 5.58 (m, 1H), 5.70 (d, *J* = 9.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 21.4, 22.7, 22.8, 27.3, 27.4, 27.5, 27.7, 37.3, 39.34, 39.35, 40.0, 115.6, 118.4, 127.0, 127.4, 145.1, 145.2, 146.0, 146.9, 176.4, 177.0, 199.0, 199.3. IR: ν 2973, 2361, 2342, 1751, 1704, 1114 cm^{-1}. HRMS (ESI) for $C_{15}H_{22}O_3$ (M) 251.1642 (Calc.), found 251.1639.



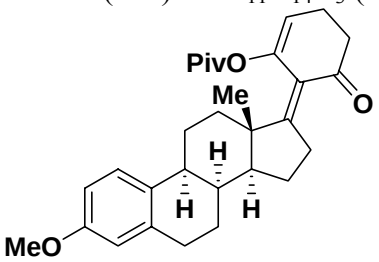
2,2-Dimethyl-propionic acid 6-(2,2-dimethyl-propylidene)-5-oxo-cyclohex-1-enyl ester (12d). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.15 (s, 9H), 1.26 (s, 9H), 2.38 (dt, *J* = 6.0, 6.0Hz, 2H), 2.50 (t, *J* = 6.8Hz, 2H), 5.74 (td, *J* = 5.2, 1.2Hz, 1H), 6.69 (d, *J* = 1.2Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.7, 27.4, 29.9, 33.2, 35.9, 39.2, 119.0, 129.5, 146.2, 148.9, 177.3, 201.4. IR (film): ν 2963, 1749, 1703, 1110 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{24}NaO_3$ $(M+Na)^+$ 287.1617, found 287.1615.



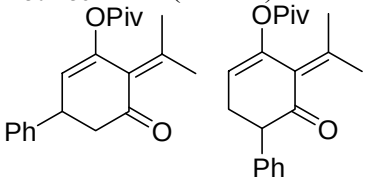
2,2-Dimethyl-propionic acid 6-isopropylidene-5-oxo-cyclohex-1-enyl ester (12e). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 9H), δ 1.97 (s, 3H), δ 2.15 (s, 3H), δ 2.36 (dt, *J* = 6.0, 6.0 Hz, 2H), δ 2.51 (t, *J* = 6.4Hz, 2H), δ 5.62 (t, *J* = 5.2Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 20.2, 24.3, 25.2, 27.4, 38.5, 39.2, 116.7, 128.6, 146.5, 147.3, 176.6, 201.7. IR (film): ν 2974, 1747, 1690, 1267, 1149, 1112 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{14}H_{20}NaO_3$ $(M+Na)^+$ 259.1304, found 259.1302.



5-oxo-6-(propan-2-ylidene)cyclohex-1-enyl acetate (12f). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.99 (s, 3H), 2.15 (s, 3H), 2.16 (s, 3H), 2.39 (m, 2H), 2.53 (t, *J* = 6.5 Hz, 2H), 5.66 (t, *J* = 5.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5, 21.1, 24.8, 38.9, 117.1, 128.1, 146.4, 146.7, 168.7, 201.4. IR: ν 2906, 2361, 2342, 1756, 1689, 1205, 1149 cm^{-1}. HRMS (ESI) for $C_{11}H_{14}O_3$ (M+1) 195.1016 (Calc.), found 195.1015.

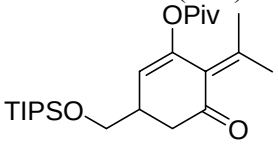


2,2-Dimethyl-propionic acid 6-(3-methoxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-cyclopenta[a]phenanthren-17-ylidene)-5-oxo-cyclohex-1-enyl ester (12g). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.96 (s, 3H), 1.27 (s, 9H), 1.28-1.60 (m, 6H), 1.83 (m, 1H), 1.95 (m, 1H), 2.17-2.50 (m, 6H), 2.63 (m, 2H), 2.87 (m, 2H), 3.00 (dd, *J* = 20.8, 8.0 Hz, 1H), 3.78 (s, 3H), 5.70 (dd, *J* = 7.2, 3.6 Hz, 1H), 6.63 (d, *J* = 2.8 Hz, 1H), 6.71 (dd, *J* = 8.1, 2.8 Hz, 1H), δ 7.20 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.8, 19.8, 23.8, 26.9, 27.5, 27.7, 30.0, 32.6, 33.6, 37.2, 38.7, 39.1, 43.6, 47.2, 54.3, 55.4, 111.7, 113.9, 116.6, 124.6, 126.4, 132.6, 138.0, 147.3, 157.7, 164.9, 177.1, 202.9. IR (film): ν 2937, 1746, 1689, 1500, 1254, 1112, 910, 731 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{30}H_{38}NaO_4$ $(M+Na)^+$ 485.2662, found 457.2656. $[\alpha]_D^{25}$ = -48.0 (*c* 1, $CHCl_3$).



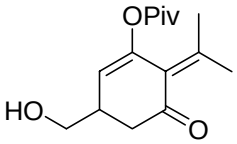
15 **16**

2,2-Dimethyl-propionic acid 6-isopropylidene-5-oxo-3(4)-phenyl-cyclohex-1-enyl ester (15, 16). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.28 (s, 9H, isomer **15**), 1.29 (s, 9H, isomer **16**), 2.00 (s, 3H, isomer **16**), 2.04 (s, 3H, isomer **15**), 2.05 (s, 3H, isomer **16**), 2.16 (s, 3H, isomer **15**), 2.64-2.86 (m, 2H), 3.74 (t, *J* = 8.0 Hz, 1H, isomer 16), 3.84 (m, 1H, isomer **15**), 5.65 (d, *J* = 4.0 Hz, 1H, isomer **15**), 5.66 (t, *J* = 6.0 Hz, 1H, isomer **16**), 7.18-7.35 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 24.6, 25.0, 25.2, 27.4, 28.6, 38.6, 39.3, 47.8, 54.0, 115.9, 121.0, 127.1, 127.2, 127.4, 128.1, 128.7, 128.7, 129.0, 143.0, 147.1, 147.5, 176.6, 200.0. IR (film): ν 2976, 1747, 1690, 1271, 1109, 911, 763, 731, 699 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{20}H_{24}NaO_3$ $(M+Na)^+$ 335.1617, found 335.1627.

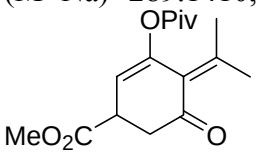


2,2-Dimethyl-propionic acid 6-isopropylidene-5-oxo-3-triisopropylsilanyloxymethyl-cyclohex-1-enyl ester (19). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.04 (m, 21H), 1.23 (s,

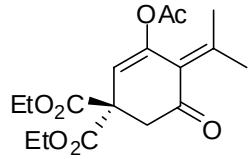
9H), 1.97 (s, 3H), 2.14 (s, 3H), 2.45 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.60 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.75 (m, 1H), 3.63 (dd, *J* = 9.6, 6.8 Hz, 1H), 3.68 (dd, *J* = 9.6, 6.4 Hz, 1H), 5.54 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 18.1, 24.4, 25.2, 27.3, 35.5, 39.2, 41.9, 66.1, 118.5, 128.4, 146.6, 147.6, 176.5, 200.9. IR (film): ν 2944, 1752, 1693, 1463, 1107, 882, 734, 684 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{24}H_{42}SiNaO_4$ $(M+Na)^+$ 445.2744, found 445.2730.



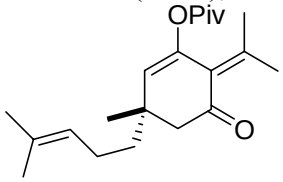
2,2-Dimethyl-propionic acid 3-hydroxymethyl-6-isopropylidene-5-oxo-cyclohex-1-enyl ester (23). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 9H), 1.99 (s, 3H), 2.14 (s, 3H), 2.48 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.62 (dd, *J* = 15.6, 6.0 Hz, 1H), 2.77 (m, 1H), 3.63 (d, *J* = 6.0 Hz, 1H), 5.52 (d, *J* = 4.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 25.2, 27.3, 35.4, 39.2, 41.9, 65.4, 118.0, 128.1, 147.0, 148.0, 176.8, 200.5. IR (film): ν 3500, 2977, 2001, 1747, 1688, 1119, 732 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{15}H_{22}NaO_4$ $(M+Na)^+$ 289.1410, found 261.1416.



3-(2,2-Dimethyl-propionyloxy)-4-isopropylidene-5-oxo-cyclohex-2-enecarboxylic acid methyl ester (25). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.27 (s, 9H), 1.99 (s, 3H), 2.18 (s, 3H), 2.73 (m, 2H), 3.50 (m, 1H), 3.72 (s, 3H), 5.76 (d, *J* = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.3, 25.5, 27.3, 37.6, 39.2, 40.6, 52.6, 114.5, 127.7, 148.5, 149.4, 172.4, 176.2, 198.5. IR (film): ν 2976, 1740, 1693, 1107 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{16}H_{22}NaO_5$ $(M+Na)^+$ 317.1359, found 261.1369.

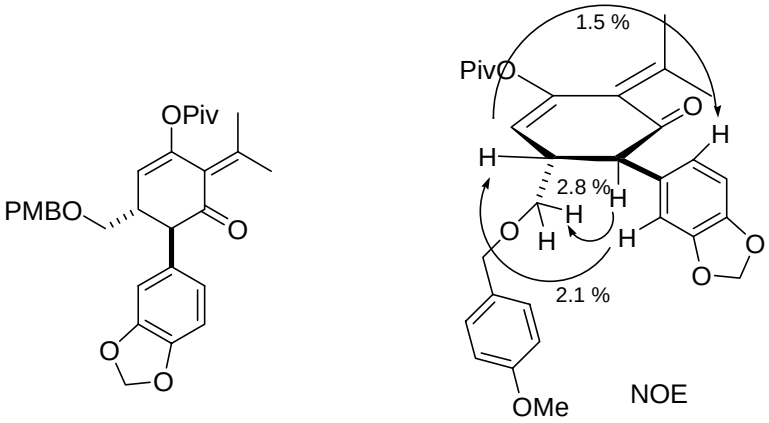


Diethyl 3-acetoxy-5-oxo-4-(propan-2-ylidene)cyclohex-2-ene-1,1-dicarboxylate (27). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.25 (t, *J* = 7.1 Hz, 6H), 1.99 (s, 3H), 2.18 (s, 3H), 2.23 (s, 3H), 2.90 (s, 2H), 4.21 (m, 4H), 6.09 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 20.9, 24.9, 25.3, 44.1, 53.2, 62.5, 114.9, 126.1, 148.9, 151.2, 168.0, 168.8, 195.8. IR: ν 2985, 2361, 2344, 1733, 1697, 1266, 1187 cm^{-1}. HRMS (ESI) for $C_{17}H_{22}O_7$ (M+1) 339.1438 (Calc.), found 339.1437.

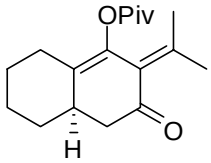


2,2-Dimethyl-propionic acid 6-isopropylidene-3-methyl-3-(4-methyl-pent-3-enyl)-5-oxo-cyclohex-1-enyl ester (29). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.10 (s, 3H), 1.27 (s, 9H), 1.40 (m, 2H), 1.58 (s, 3H), 1.66 (s, 3H), 1.97 (m, 2H), 1.99 (s, 3H), 2.15 (s, 3H), 2.36 (d, *J* = 15.0 Hz, 1H), 2.51 (d, *J* = 15.0 Hz, 1H), 5.06 (t, *J* = 7.0 Hz, 1H), 5.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 17.8, 23.3, 24.8, 25.3, 25.9, 26.8, 27.4, 35.3, 39.2, 42.1,

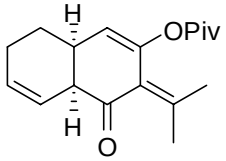
52.3, 124.3, 126.4, 127.6,131.9, 146.0, 146.4, 176.7, 201.0. IR (film): ν 2967, 1751, 1693, 1273, 1111 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{21}H_{32}NaO_3$ $(M+Na)^+$ 355.2243, found 355.2251. $[\alpha]_D^{25}$ = -10.7 (*c* 0.3, $CHCl_3$); The enantiomeric excess (87%) of product **29** was determined by HPLC analysis of an alcohol derived from reduction of ketone group in **29**. (Chiralcel AS-H; eluent: pure hexane; flow rate: 0.7 mL/min; detection: at 210 nm): retention times t_1 = 6.8 min t_2=7.2 min.



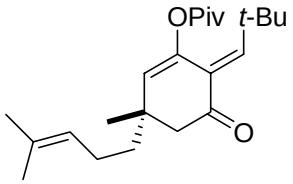
2,2-Dimethyl-propionic acid 4-benzo[1,3]dioxol-5-yl-6-isopropylidene-3-(4-methoxy-benzyloxymethyl)-5-oxo-cyclohex-1-enyl ester (31). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 1.28 (s, 9H), 1.98 (s, 3H), 2.02 (s, 3H), 2.93 (m, 1H), 3.28 (dd, *J* = 9.5, 7.0 Hz, 1H), 3.36 (dd, *J* = 9.0, 4.5 Hz, 1H), 3.58 (d, *J* = 8.5 Hz, 1H), 3.80 (s, 3H), 4.33 (d, *J* = 9.6 Hz, 1H), 4.40 (d, *J* = 9.2 Hz, 1H), 5.63 (d, *J* = 3.0 Hz, 1H), 5.93 (s, 2H), 6.58 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.65 (d, *J* = 1.5 Hz, 1H), 6.74 (d, *J* = 9.0 Hz, 1H), 6.85 (m, 2H), 7.19 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 24.3, 24.9, 27.4, 39.3, 40.3, 55.5, 56.3, 70.9, 73.0, 101.2, 108.5, 109.3, 114.0, 118.6, 122.7, 128.4, 129.5, 130.3, 132.2, 146.5, 146.7, 146.9, 148.0, 159.5, 176.5, 200.5. IR (film): ν 1749, 1513, 1248, 1125, 1037 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{30}H_{34}NaO_7$ $(M+Na)^+$ 529.2196, found 529.2198.



(R)-3-oxo-2-(propan-2-ylidene)-2,3,4,4a,5,6,7,8-octahydronaphthalen-1-yl pivalate (33). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (s, 9H), 1.26 (m, 1H), 1.34 (m, 2H), 1.70 (m, 3H), 1.80 (m, 1H), 1.87 (s, 6H), 2.26 (dd, *J* = 13.4, 7.6 Hz, 1H), 2.44 (m, 2H), 2.61 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.6, 24.0, 25.8, 26.9, 27.7, 35.3, 36.9, 39.3, 47.1, 53.7, 123.8, 129.8, 130.2, 137.8, 175.7, 200.7. IR: ν 2975, 2933, 2860, 2361, 1745, 1704, 1271, 1111 cm^{-1}. HRMS (ESI) for $C_{18}H_{26}O_3$ (M+1) 291.1955 (Calc.), found 291.1967.



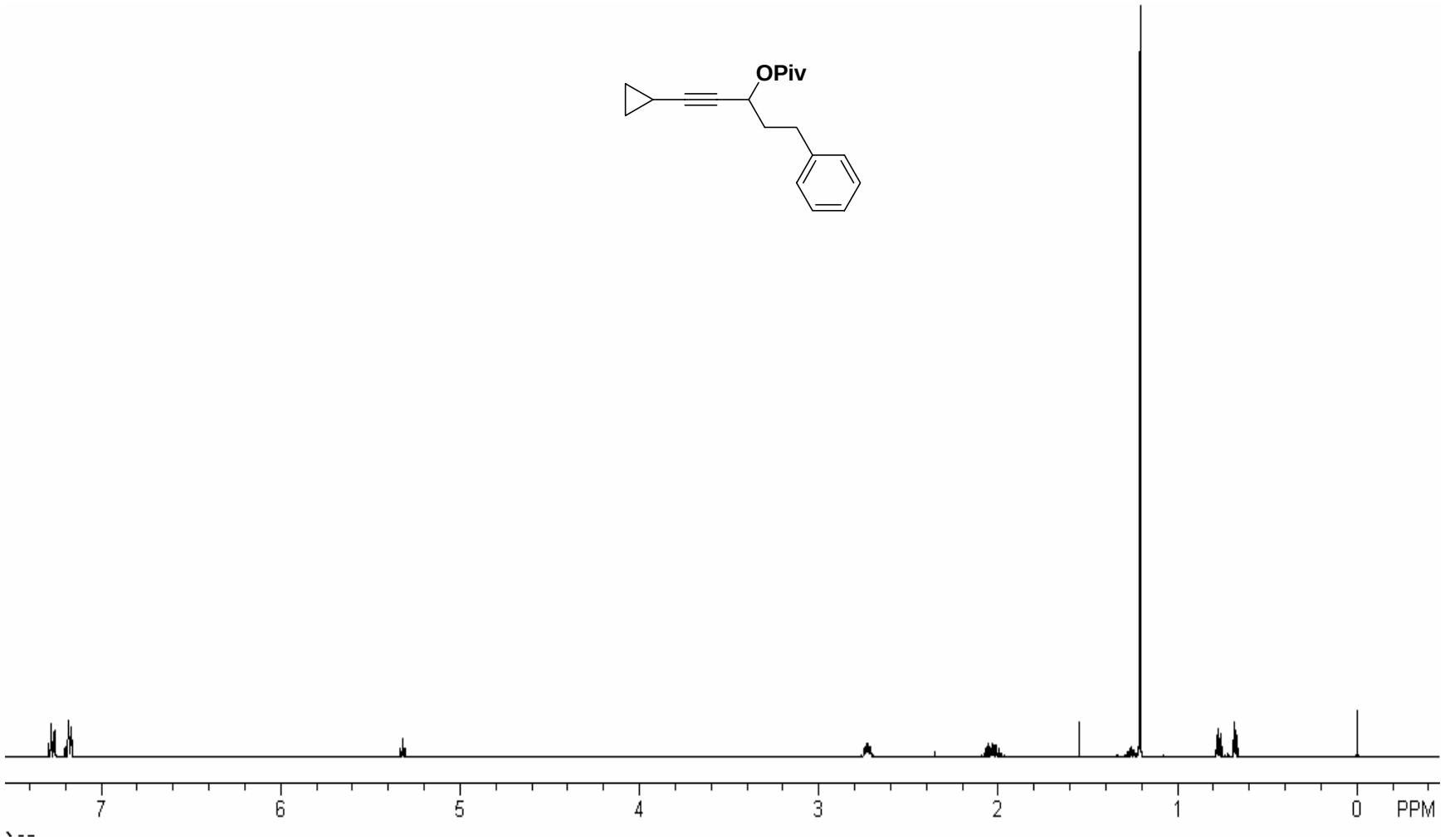
(4aS,8aS)-4-oxo-3-(propan-2-ylidene)-3,4,4a,7,8,8a-hexahydronaphthalen-2-yl pivalate (35). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.24 (s, 9H), 1.43 (m, 1H), 1.74 (m, 1H), 1.94 (s, 3H), 2.02 (s, 3H), 2.03 (m, 2H), 2.70 (m, 1H), 3.15 (m, 1H), 5.46 (d, *J* = 5.6 Hz, 1H), 5.74 (m, 1H), 5.87 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.17, 24.22, 24.5, 26.3, 27.4, 32.6, 39.2, 48.4, 120.3, 124.2, 128.1, 129.3, 144.3, 146.0, 176.5, 201.8. IR: ν 2976, 2922, 2874, 2360, 2343, 1750, 1688, 1159, 1113 cm^{-1}. HRMS (ESI) for $C_{18}H_{24}O_3$ (M+1) 289.1798 (Calc.), found 289.1796.



2,2-Dimethyl-propionic acid 6-(2,2-dimethyl-propylidene)-3-methyl-3-(4-methyl-pent-3-enyl)-5-oxo-cyclohex-1-enyl ester (37). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11 (s, 3H), 1.19 (s, 9H), 1.30 (s, 9H), δ 1.41 (m, 2H), 1.58 (d, *J* = 0.4 Hz, 3H), 1.66 (d, *J* = 1.2 Hz, 3H), 1.97 (m, 2H), 2.37 (d, *J* = 16.0 Hz, 1H), 2.48 (d, *J* = 16.0 Hz, 1H), 5.05 (tqq, *J* = 7.2, 1.2, 0.4 Hz, 1H), 5.51 (d, *J* = 1.2 Hz, 1H), 6.76 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 23.4, 25.8, 26.3, 27.5, 30.1, 33.0, 34.7, 39.3, 41.8, 49.8, 124.1, 128.5, 128.9, 132.0, 144.9, 148.8, 177.4, 200.5. IR (film): ν 2962, 1752, 1703, 1479, 1107 cm^{-1}. HRMS (ESI) *m/z* calcd. For $C_{23}H_{36}NaO_3$ $(M+Na)^+$ 383.2556, found 383.2564.

Reference

1. F. Kleinbeck, F.D. Toste, *J. Am. Chem. Soc*. **2009**, *131*, 9178.
2. M. Uemura, I.D.G. Watson, F. D. Toste, *J. Am. Chem. Soc.* **2009**, *131*, 3464.
3. J. Peitruszka, A.C.M. Rieche, T. Wilhelm, A. Witt, *Adv. Synth. Catal*. **2003**, *345*, 1273.
4. (a) G.J. Roth, B. Liepold, S.G. Muller, H. J. Bestmann. *Synthesis*. **2004**, 59. (b) J. C. Gilbert, U. Weerasooriya, *J. Org. Chem.*, **1982**, *47*, 1837-1845.
5. A. B. Charette, H. Juteau, H. Lebel, C. Molinaro. *J. Am. Chem. Soc*. **1998**, *120*, 11943.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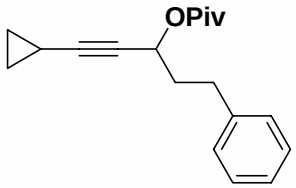
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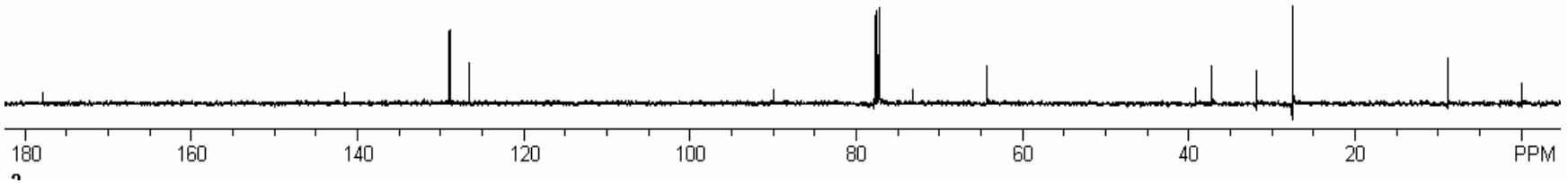
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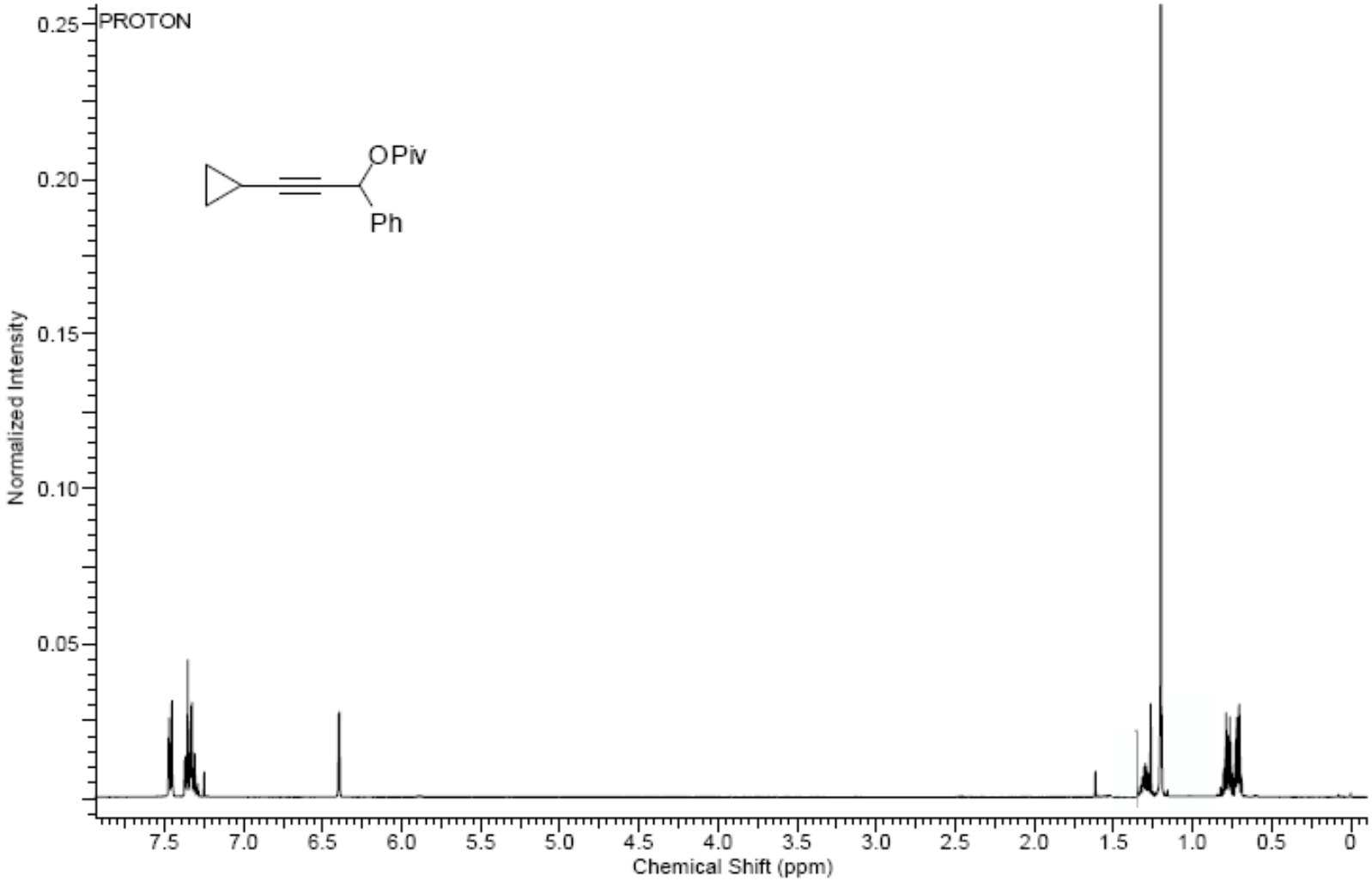
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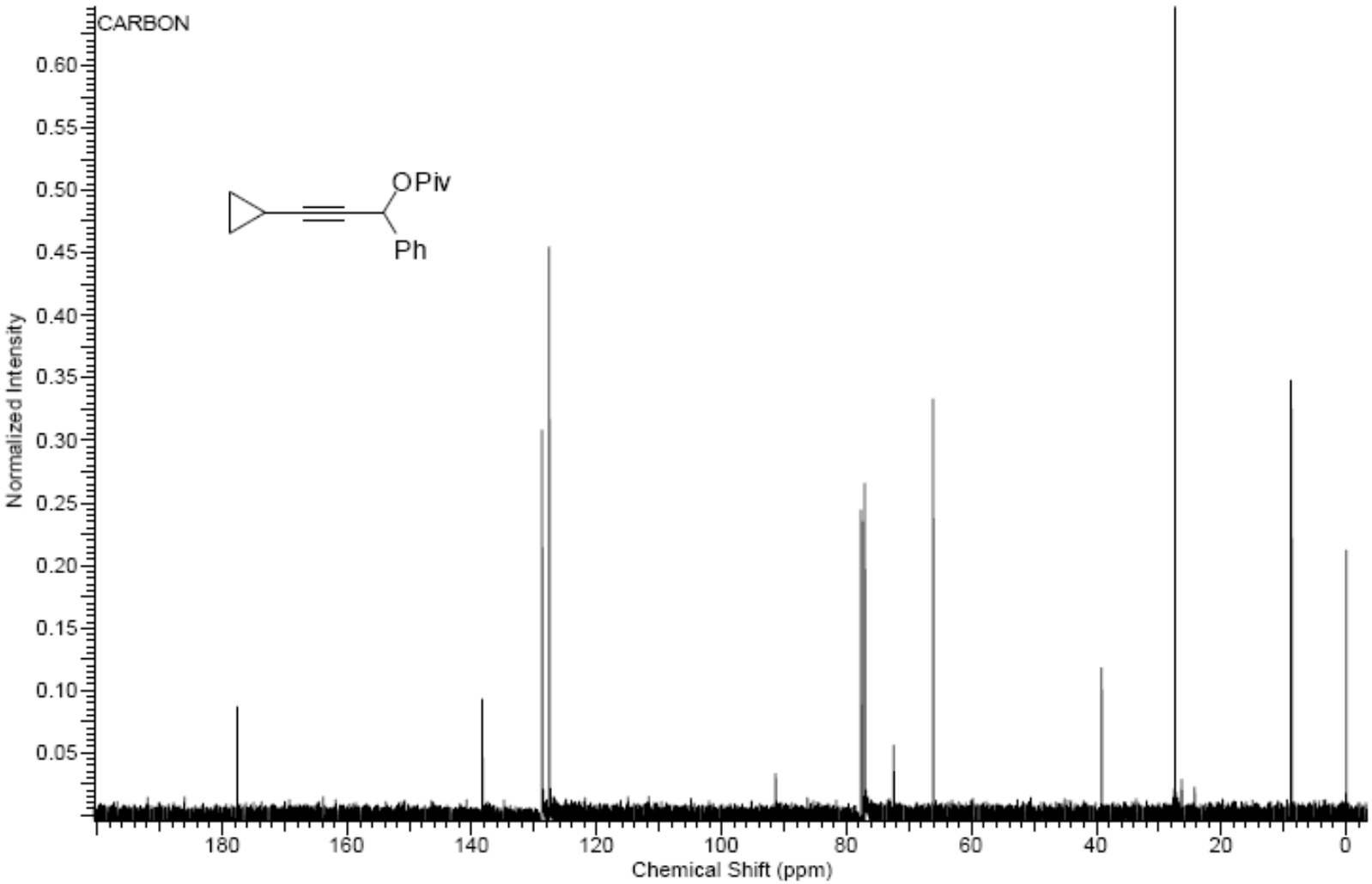
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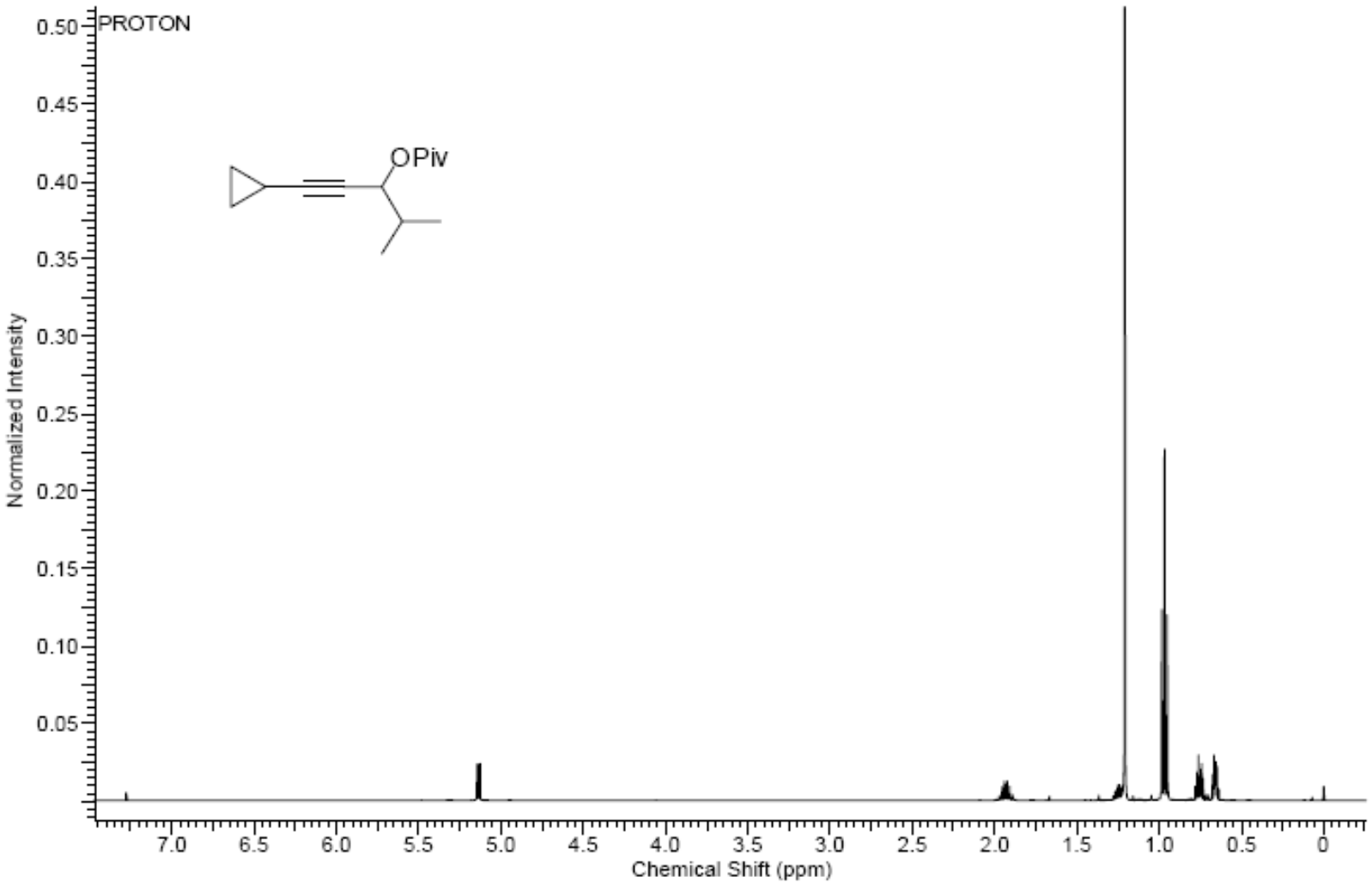
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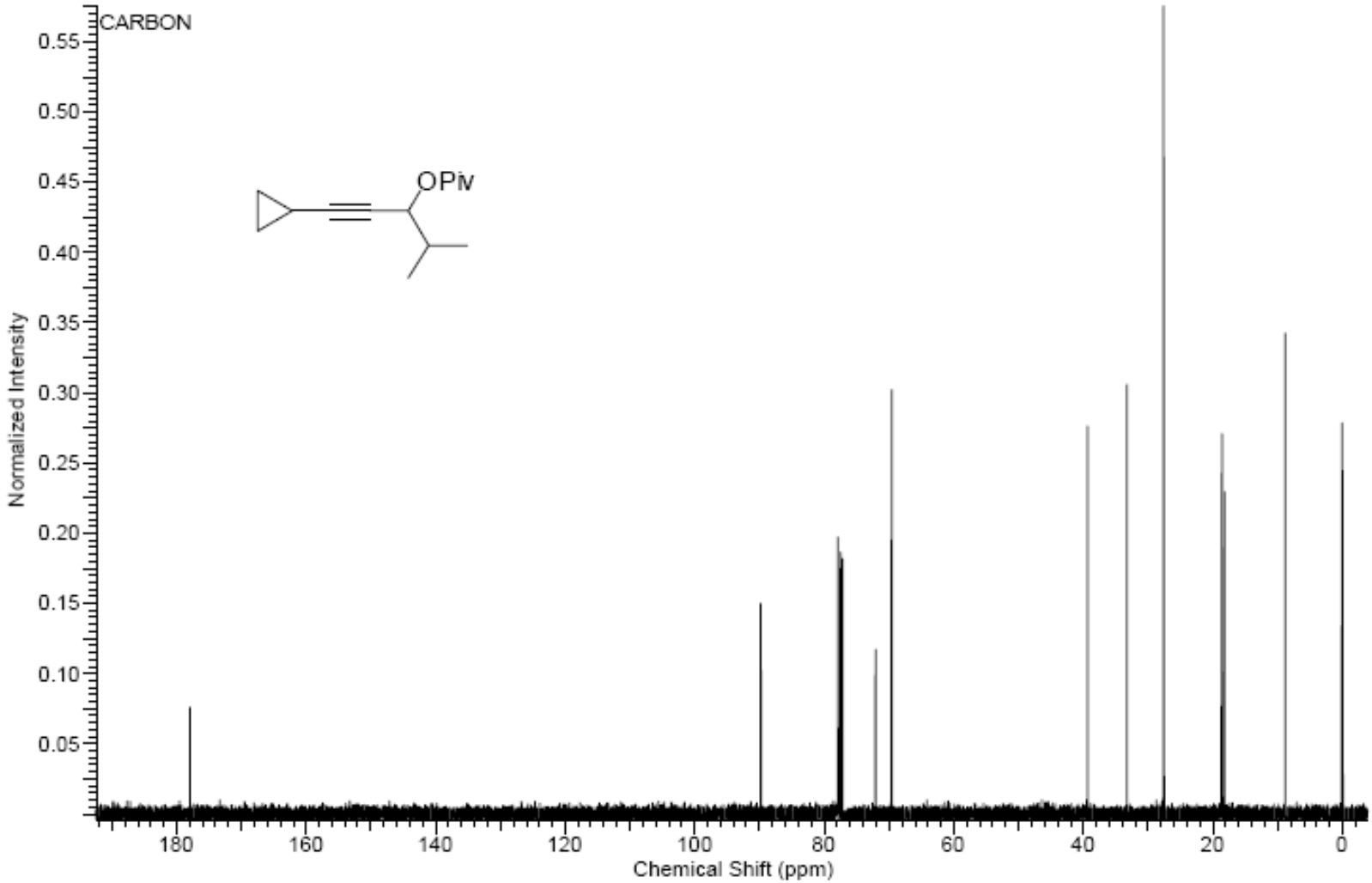
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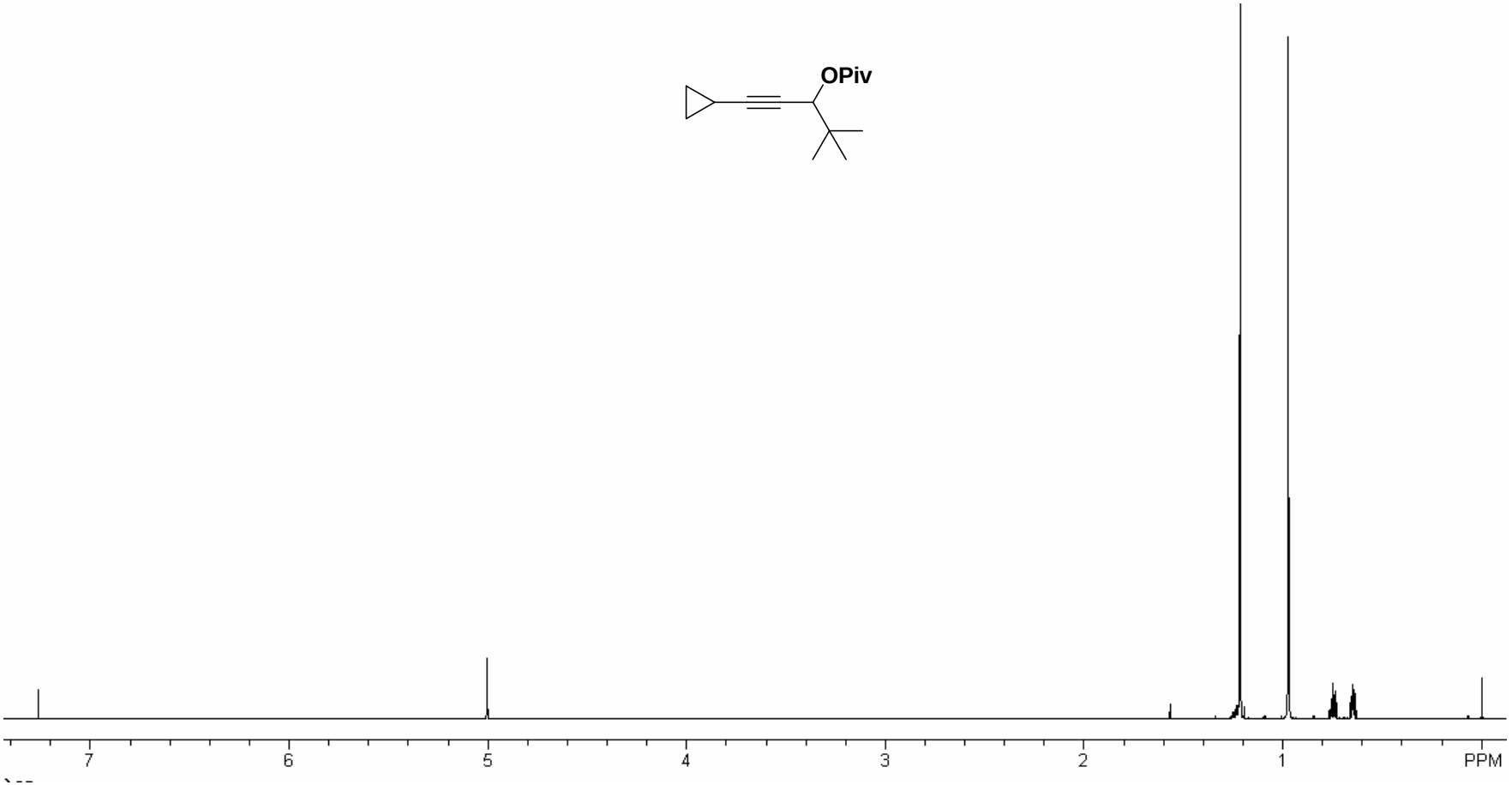
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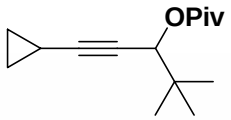
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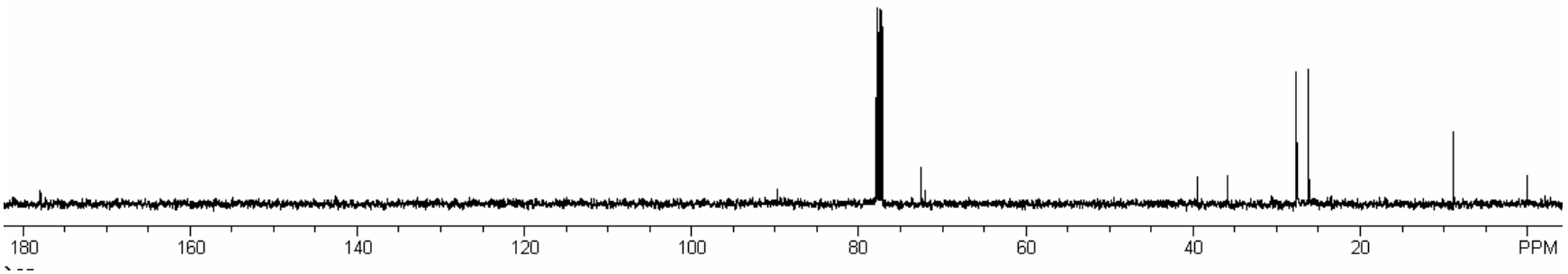
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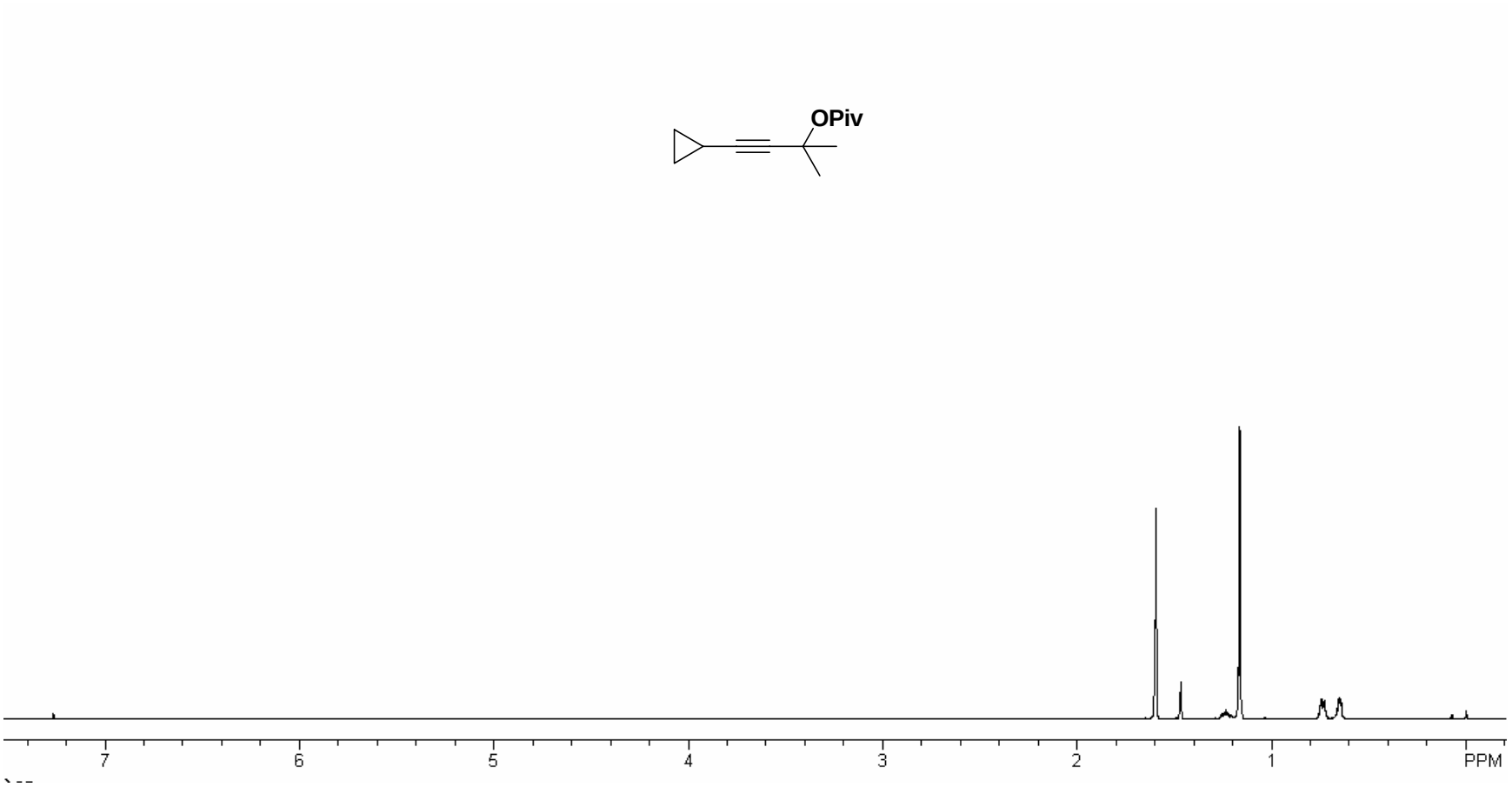
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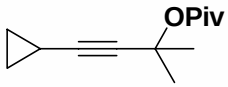
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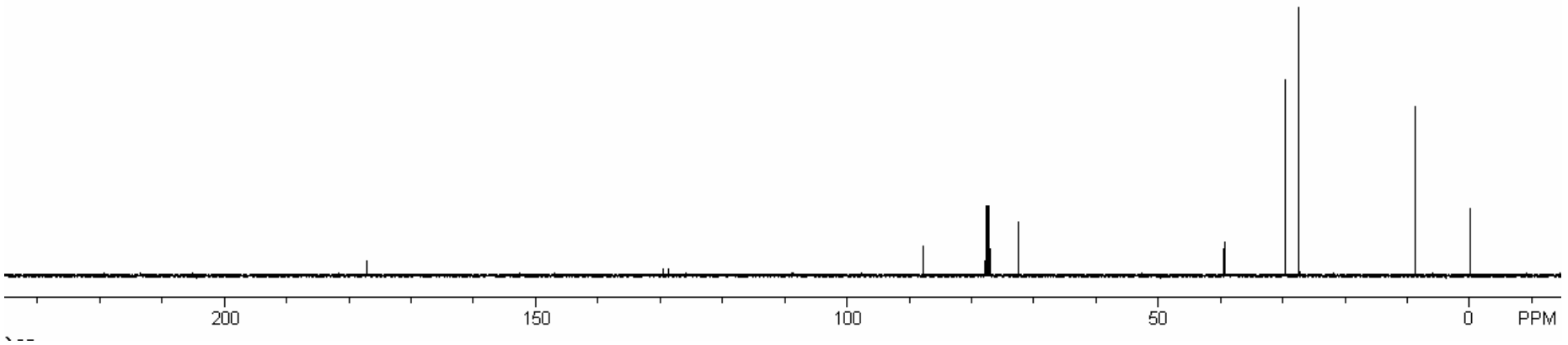
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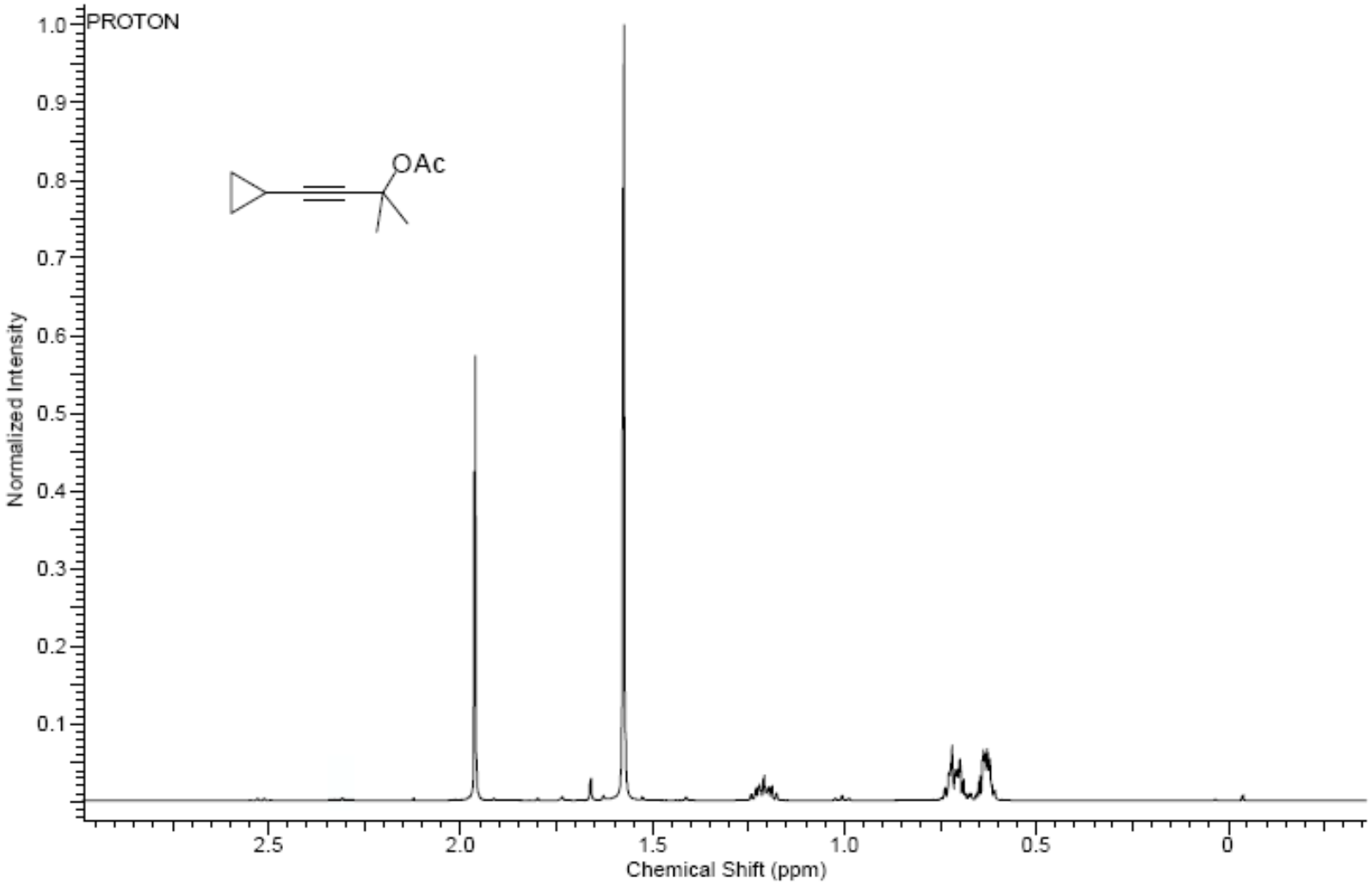
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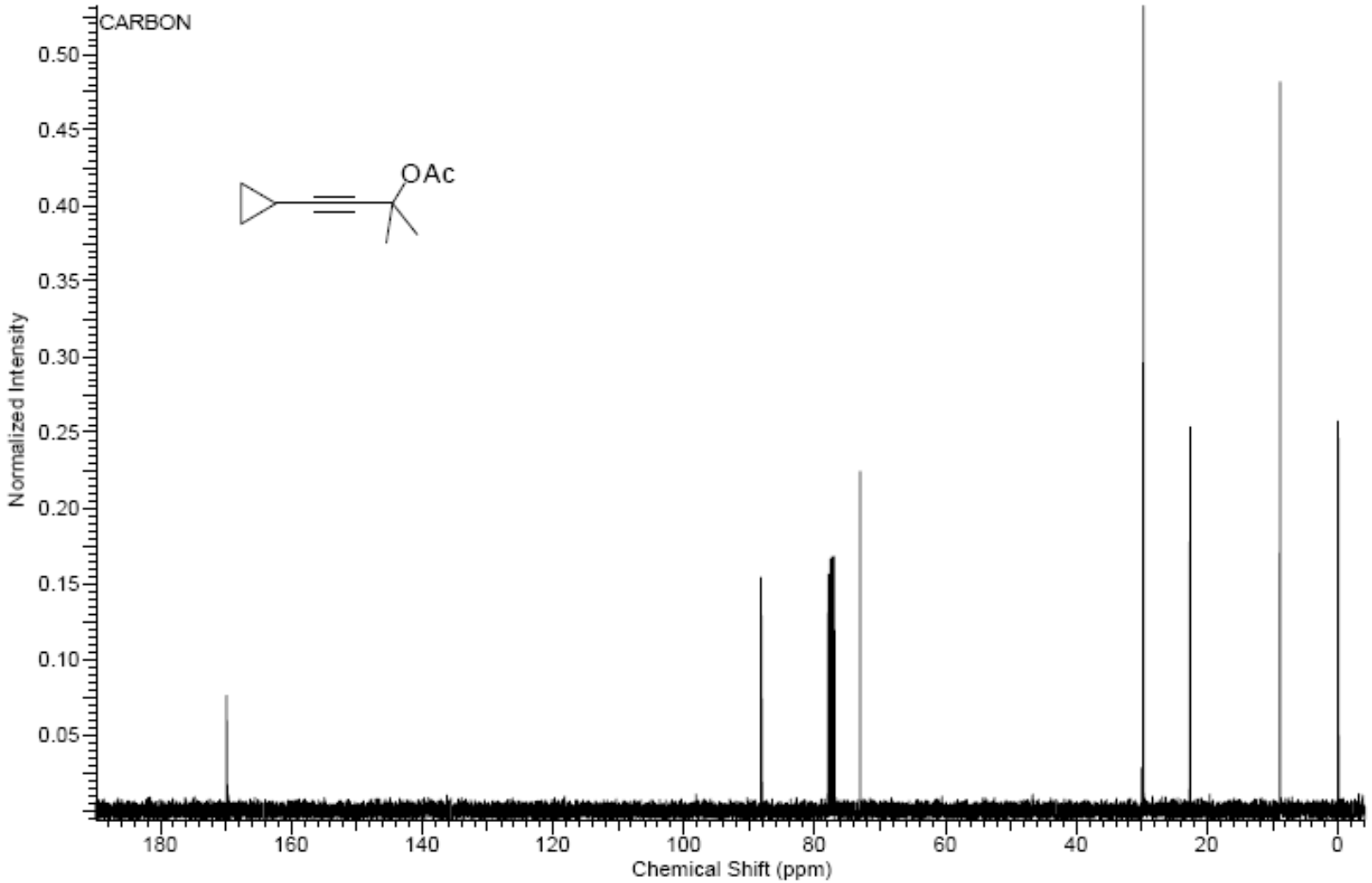
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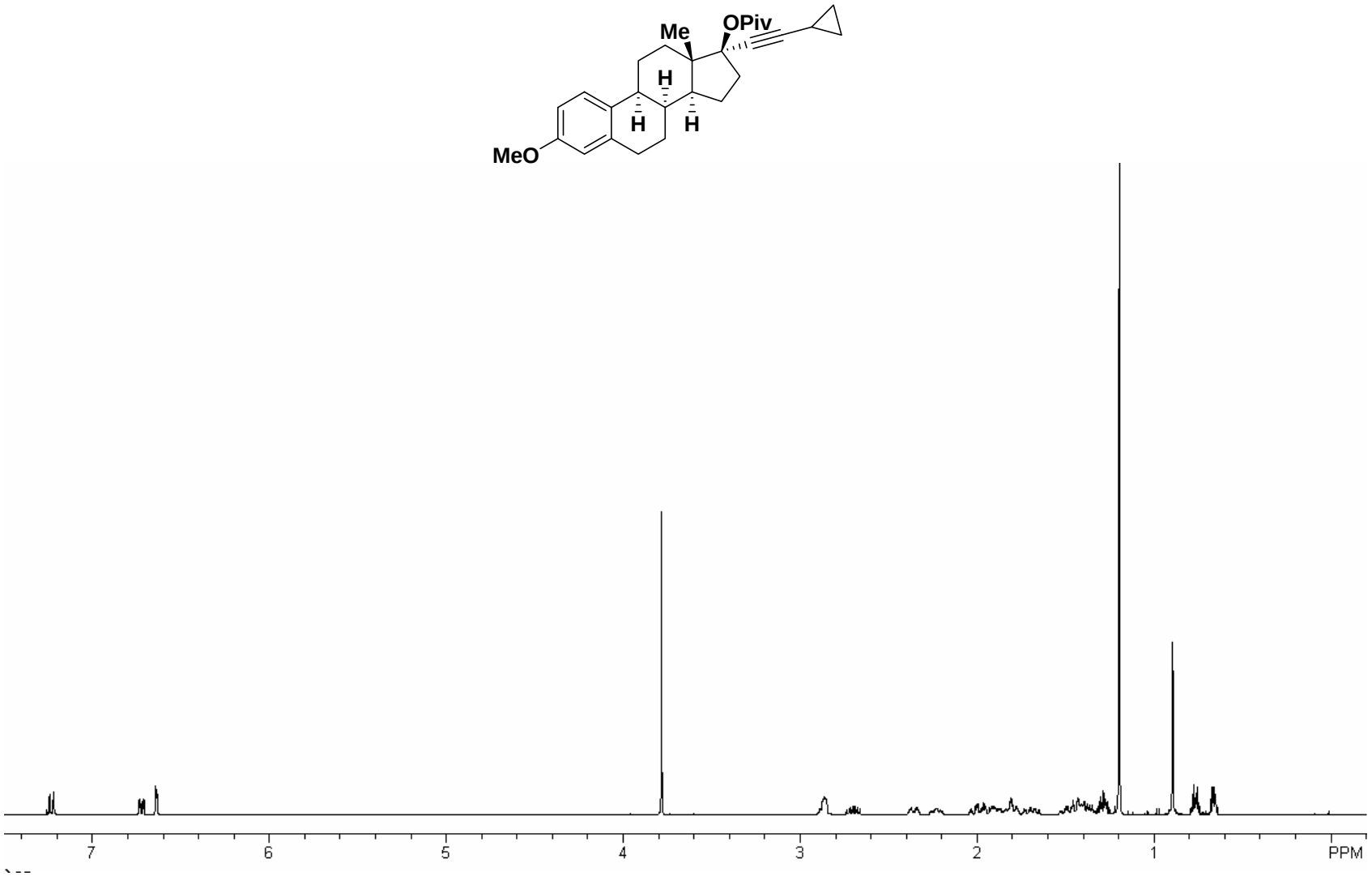
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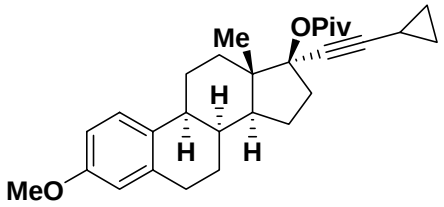
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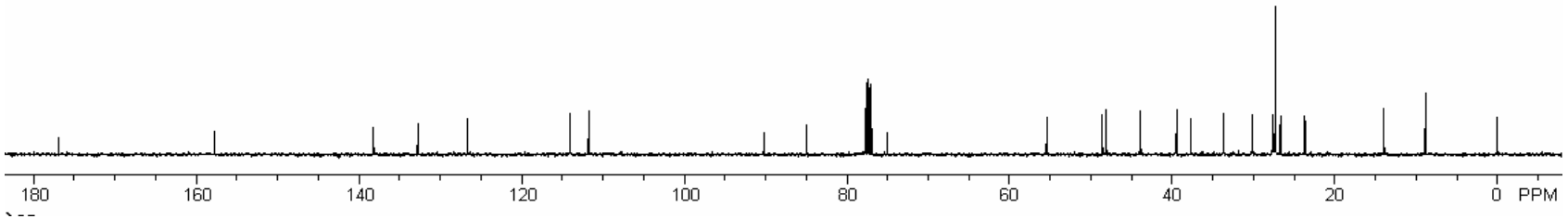
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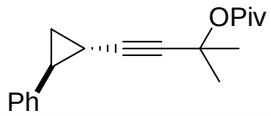
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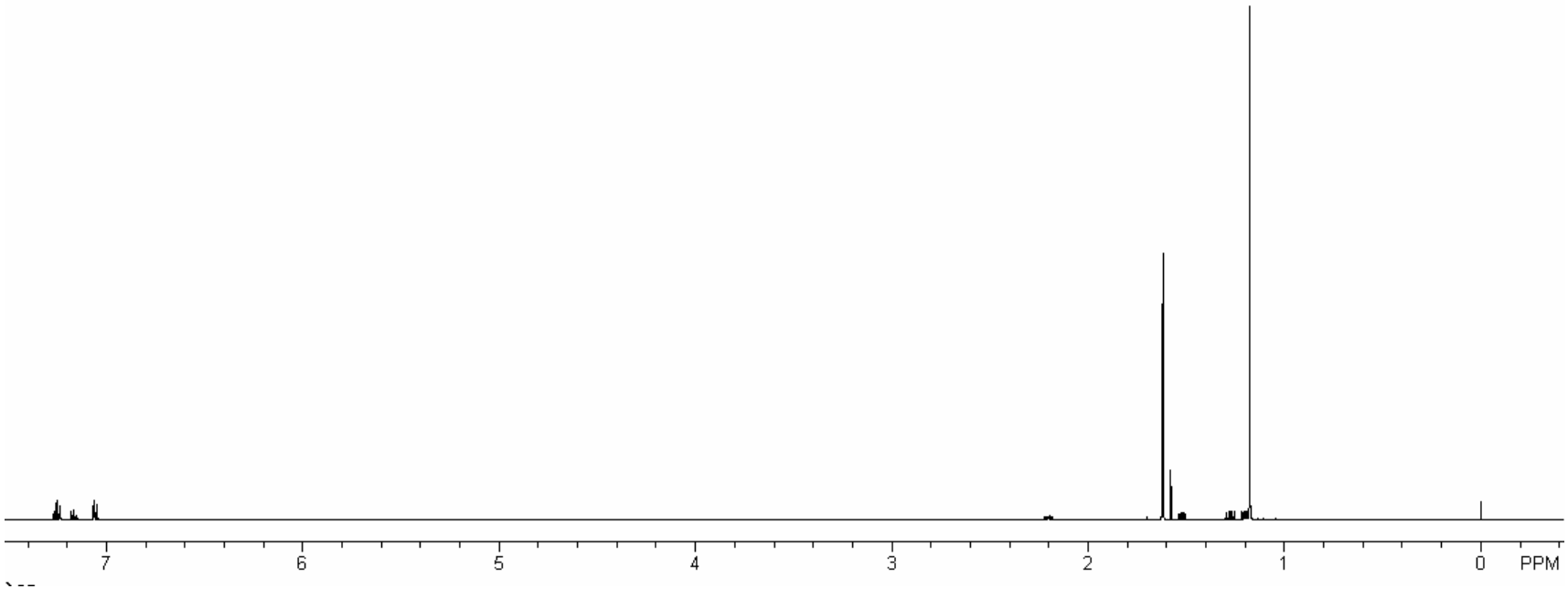
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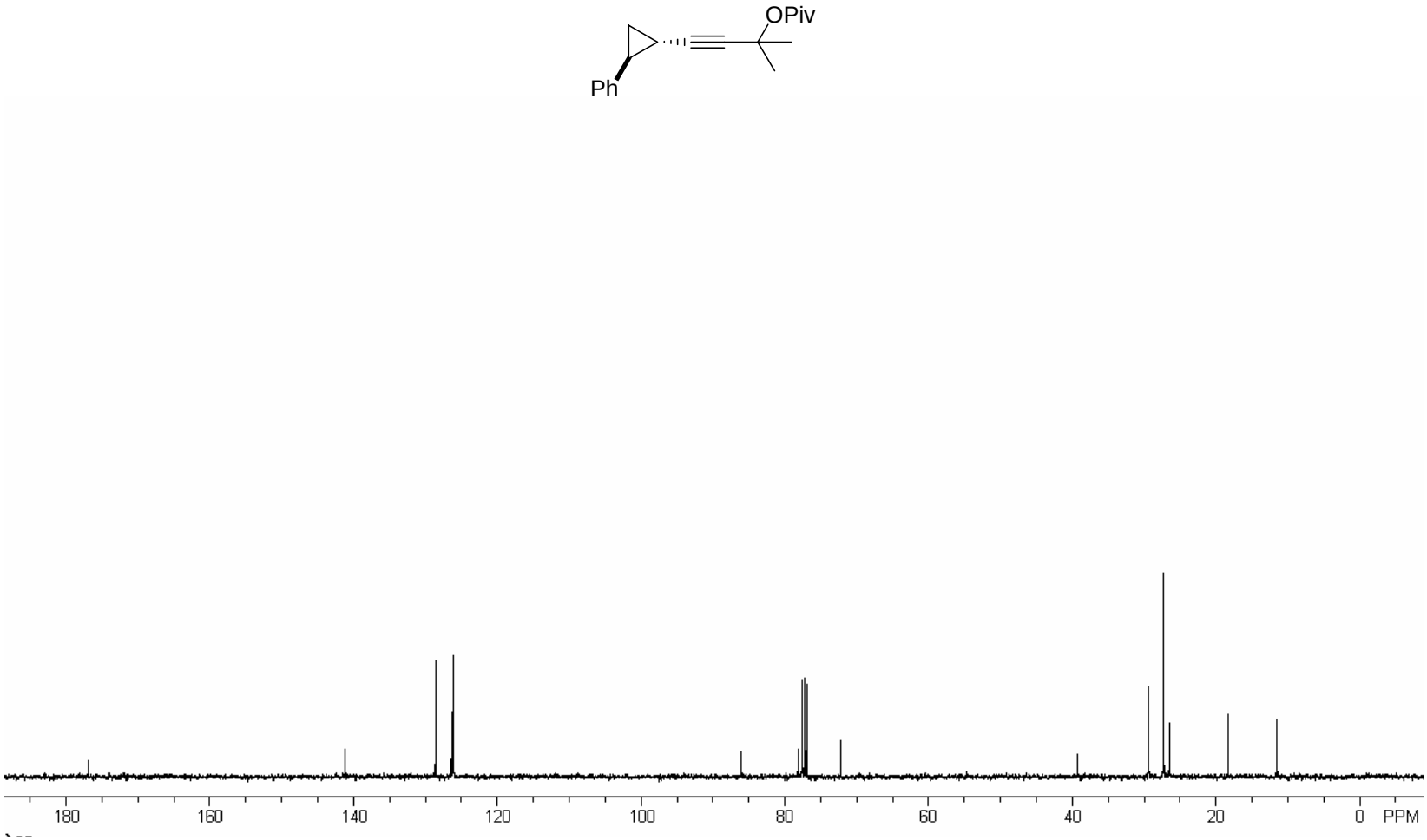
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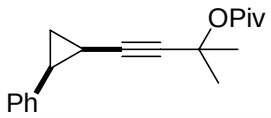
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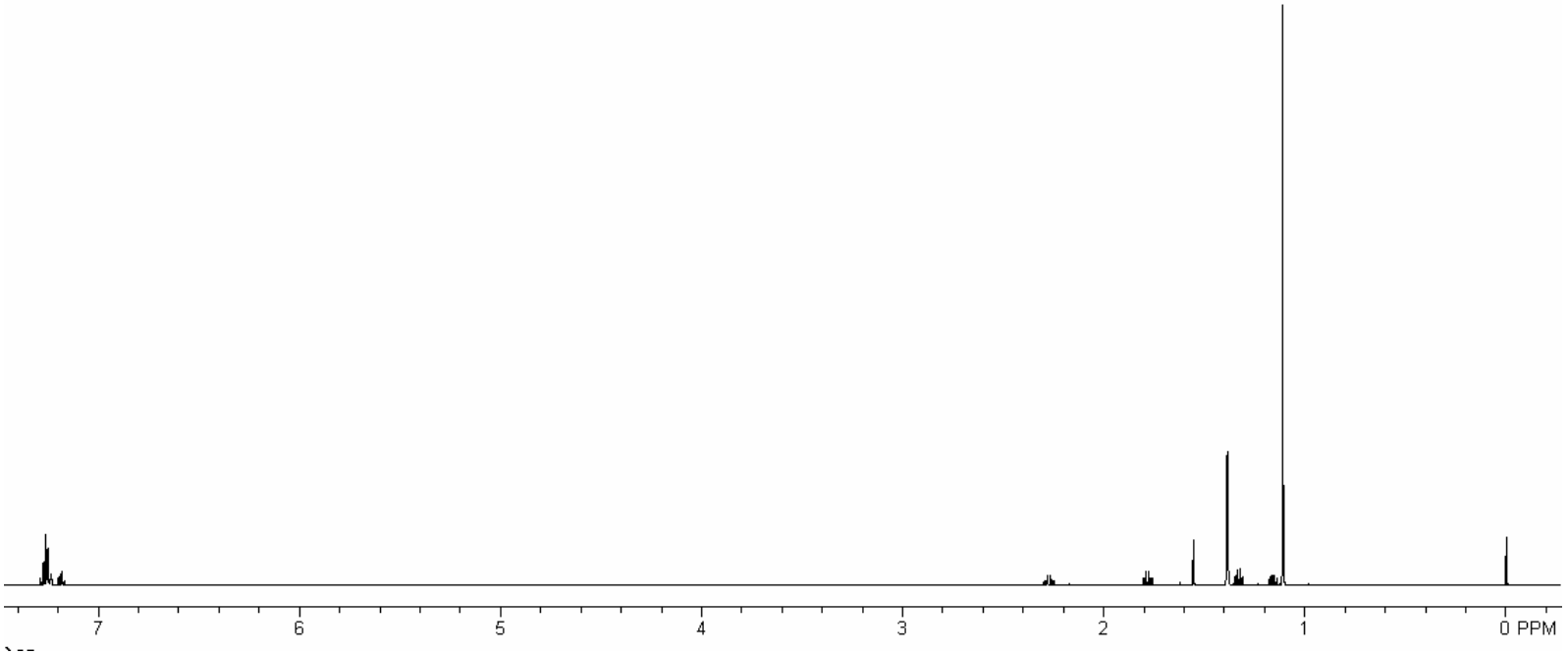
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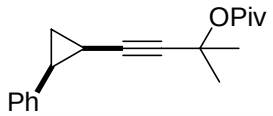
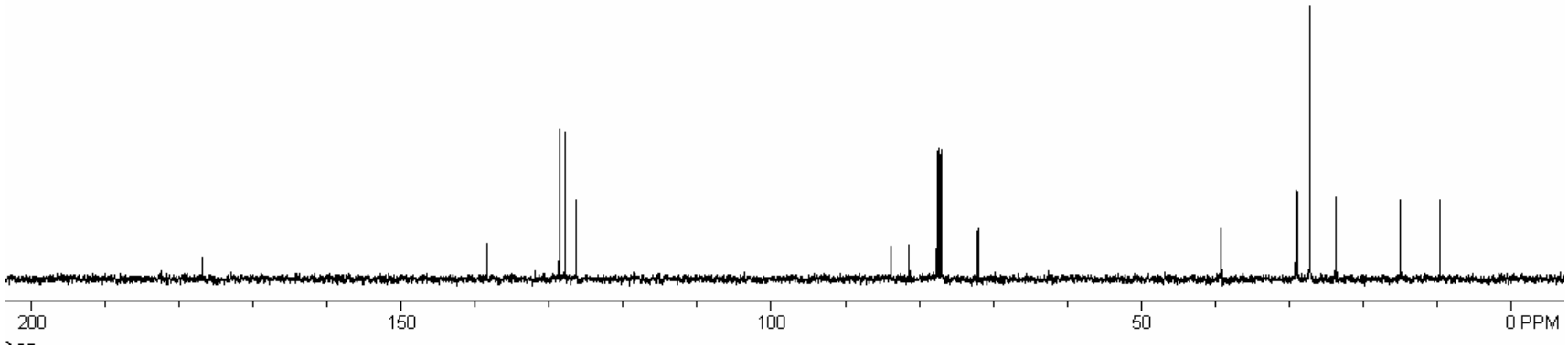

OPiv
Ph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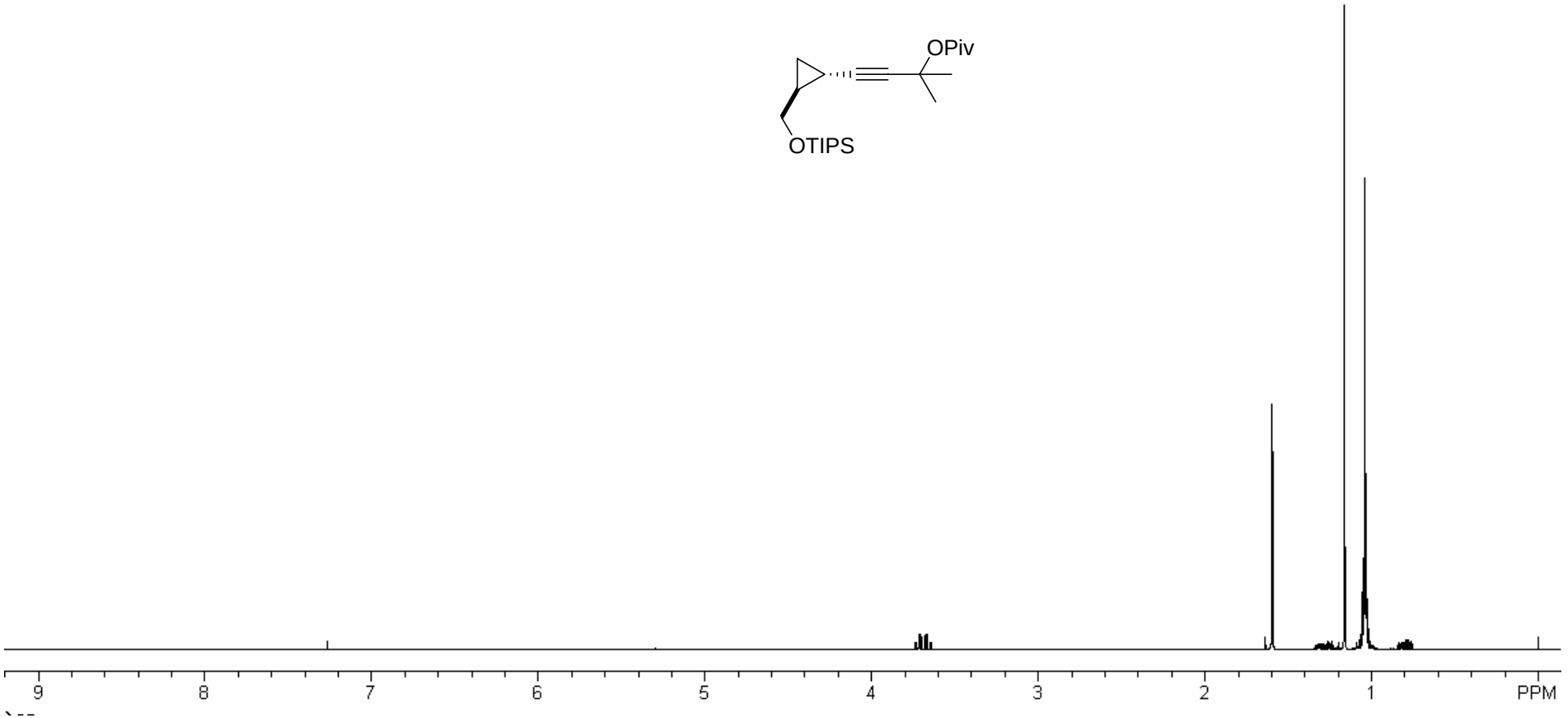
OPiv
OTIPS
9
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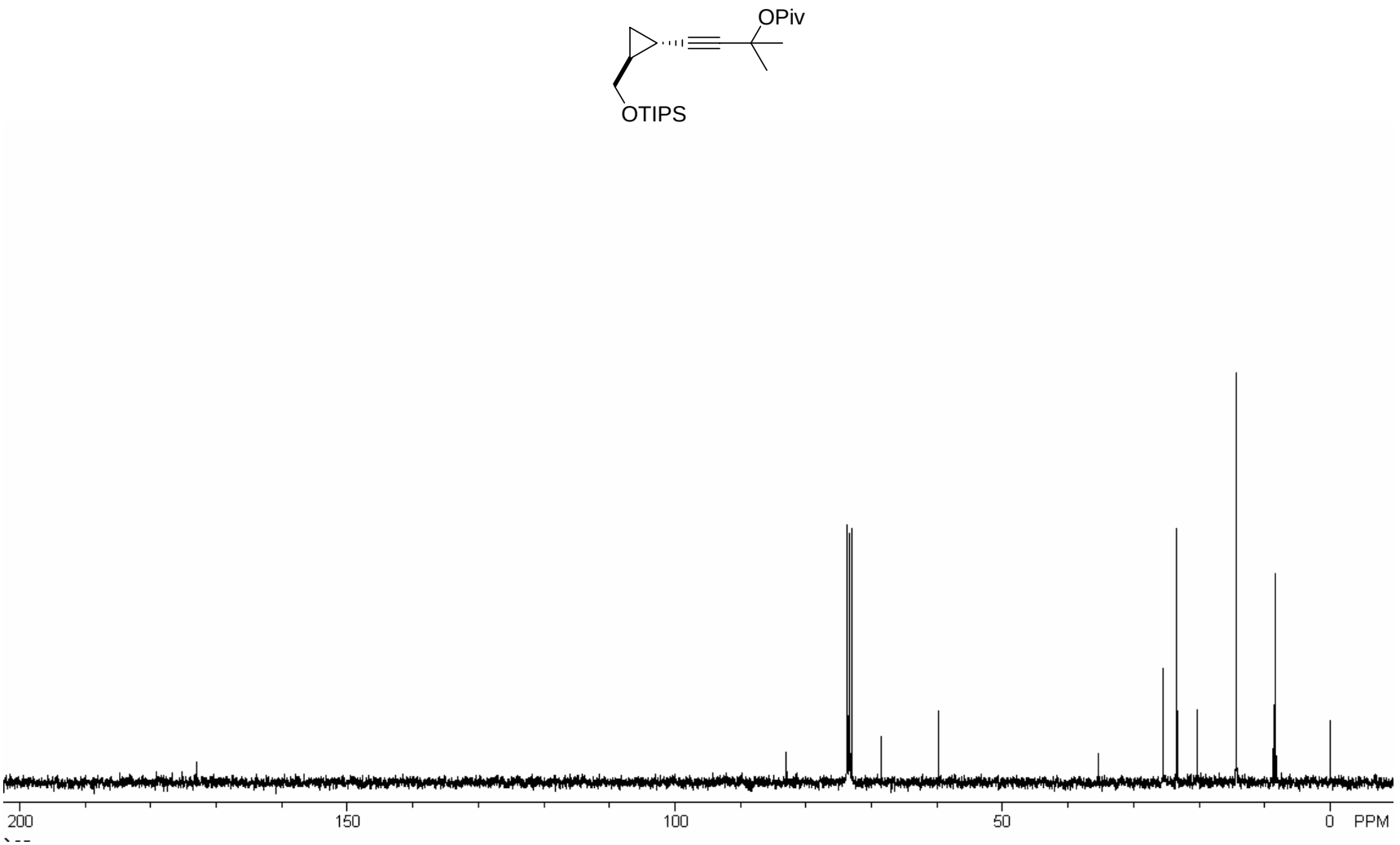
1
PPM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OTIPS
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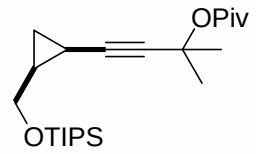
PPM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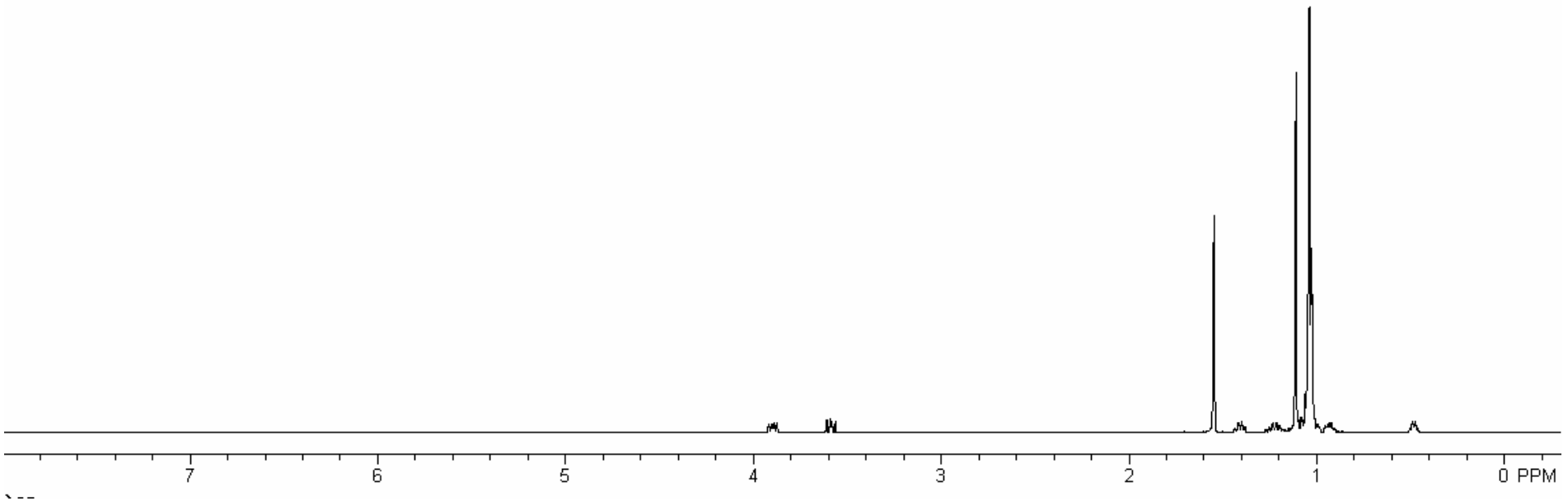
OTIPS


7
6
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2
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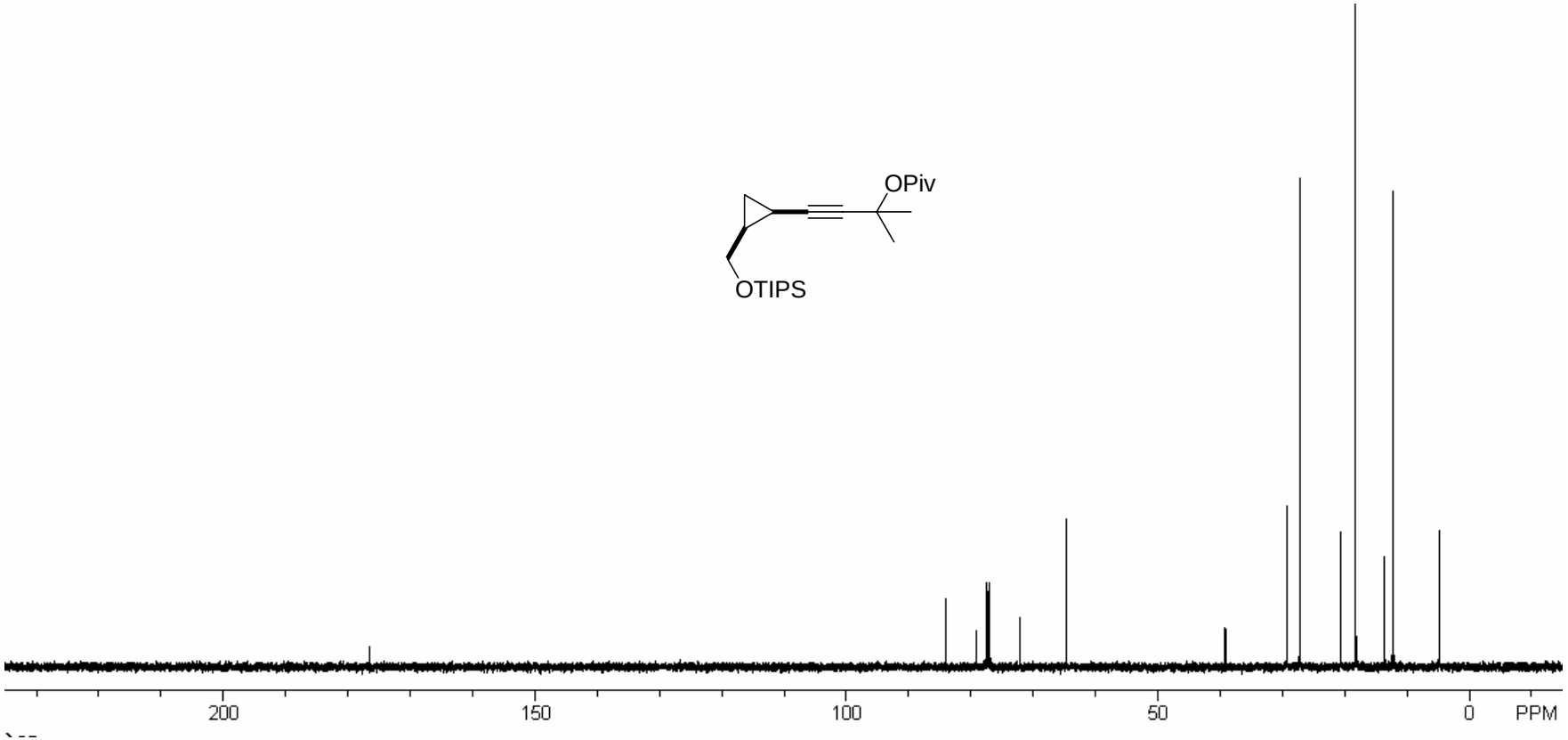
0 PPM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OTIPS
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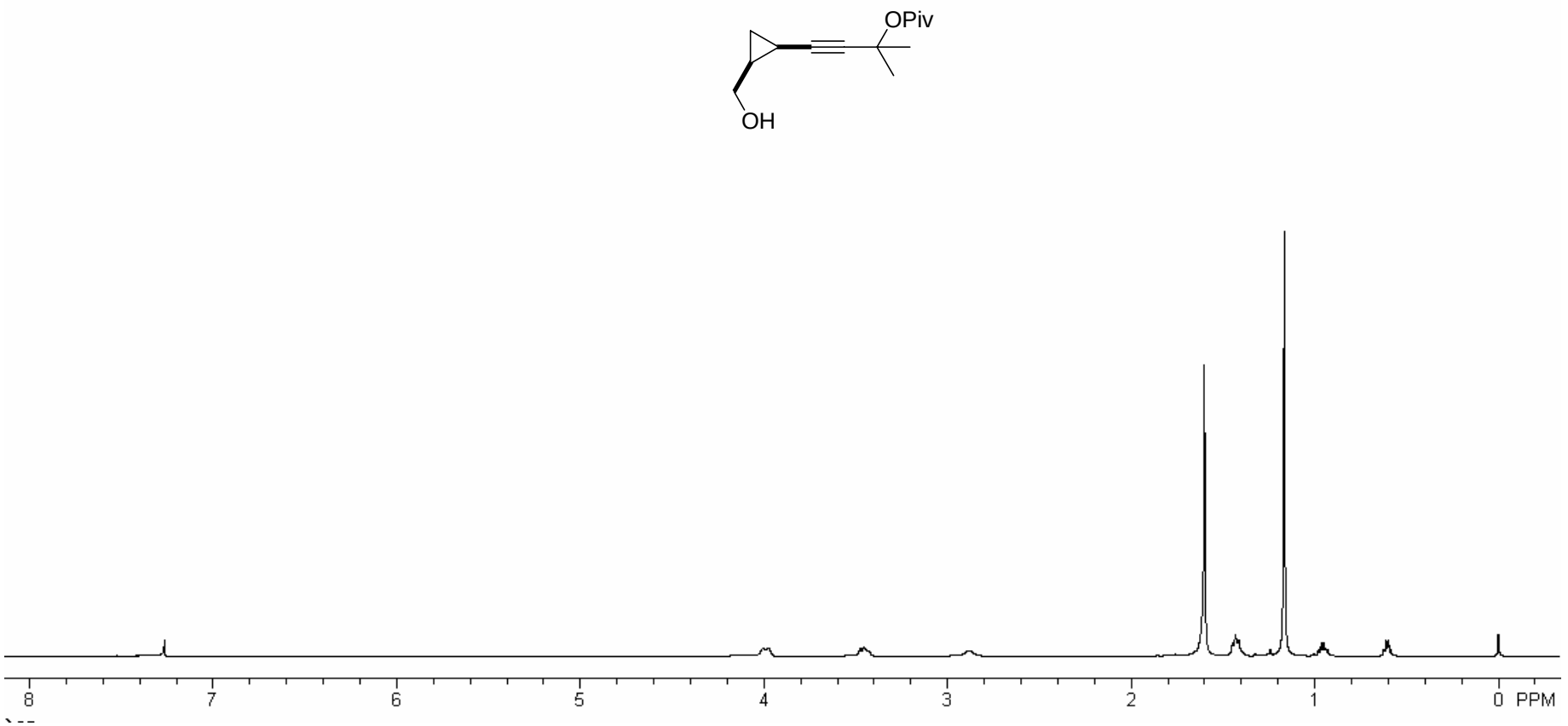
PPM


OPiv
OH
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7
6
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2
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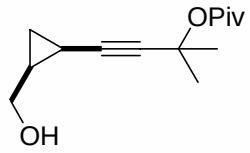
0 PPM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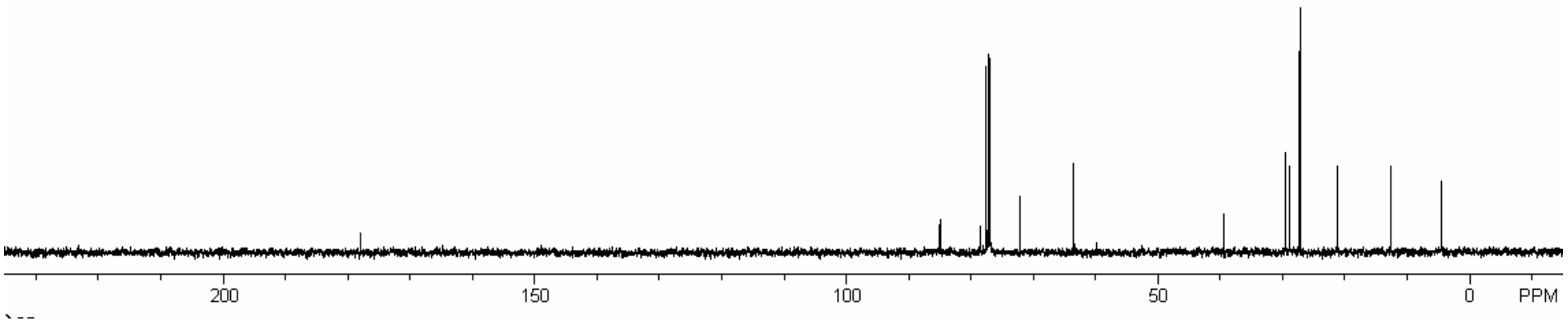
OH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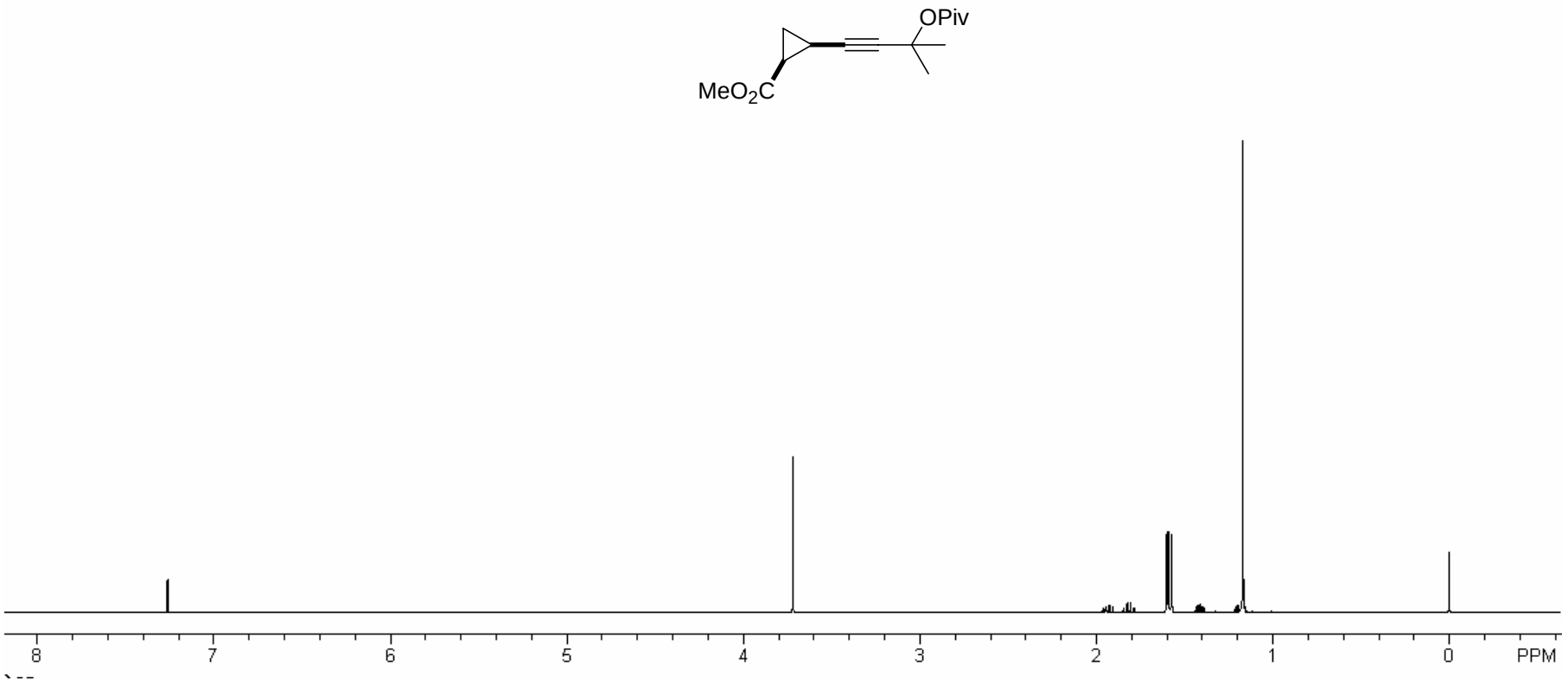
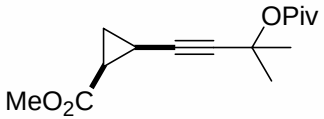

OPiv
MeO2C
8
7
6
5
4
3
2
1
0
PPM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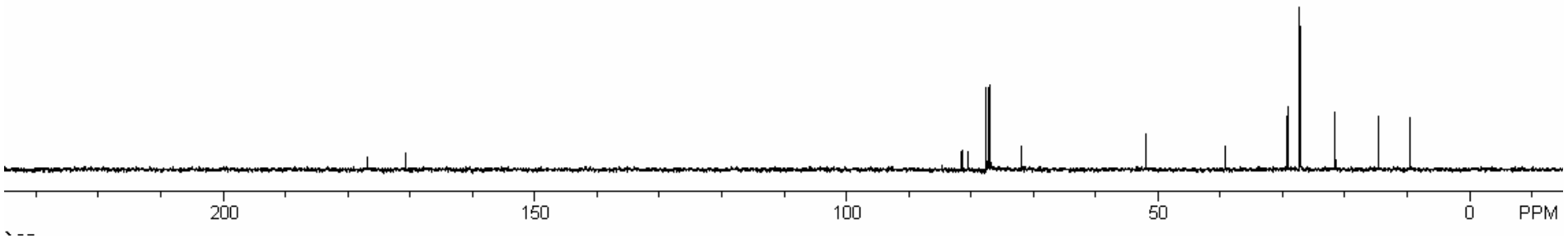
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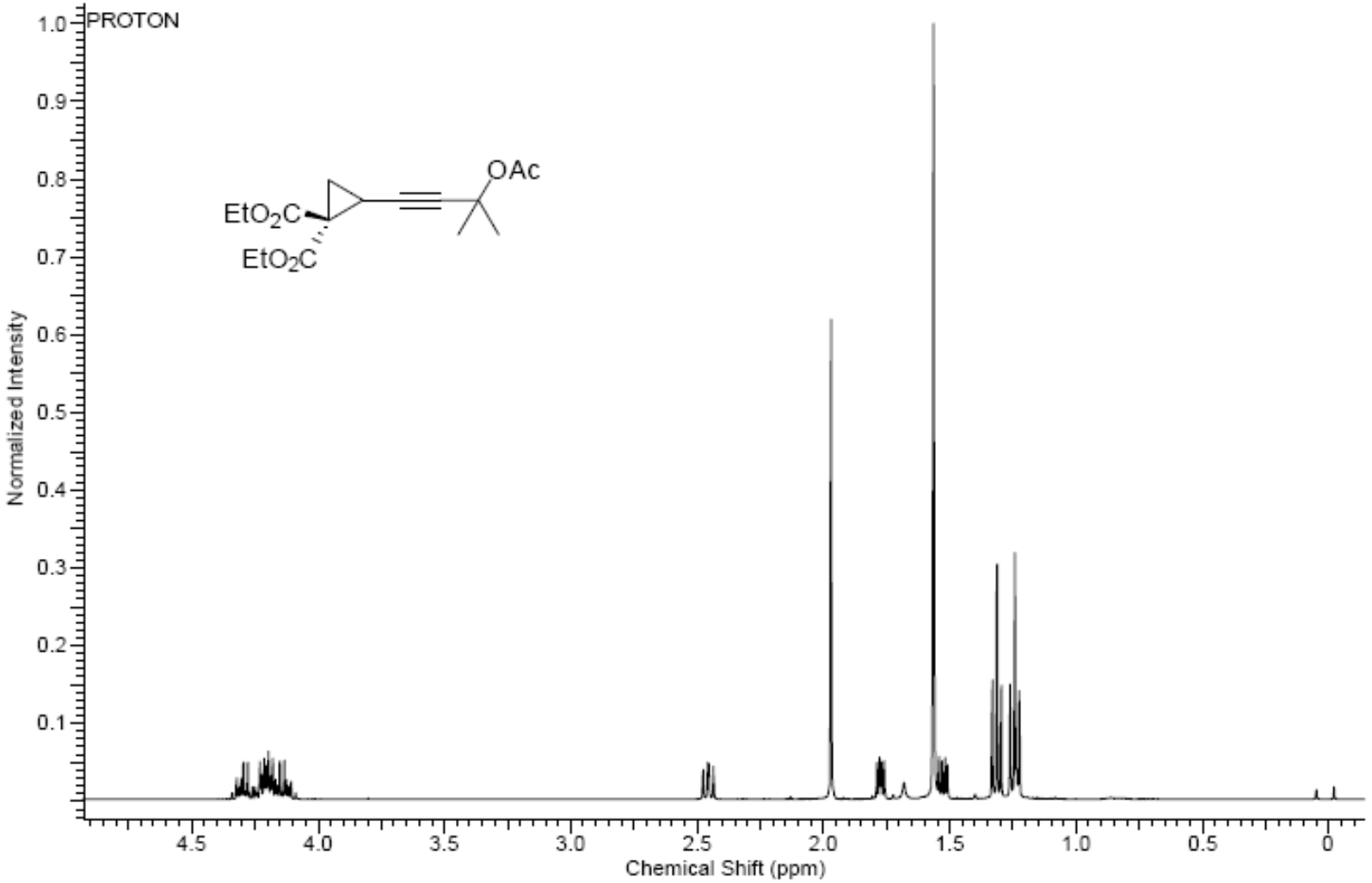
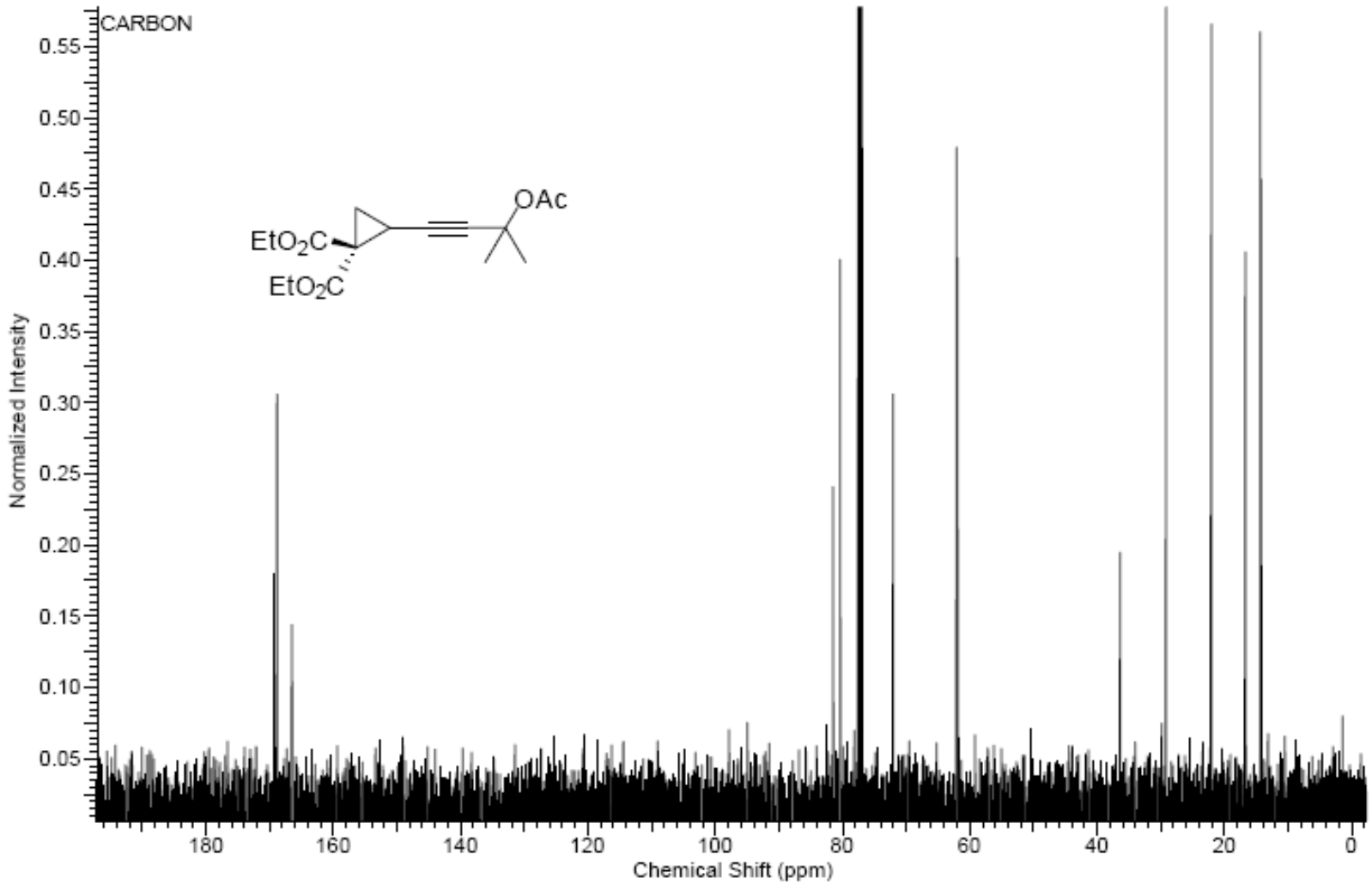
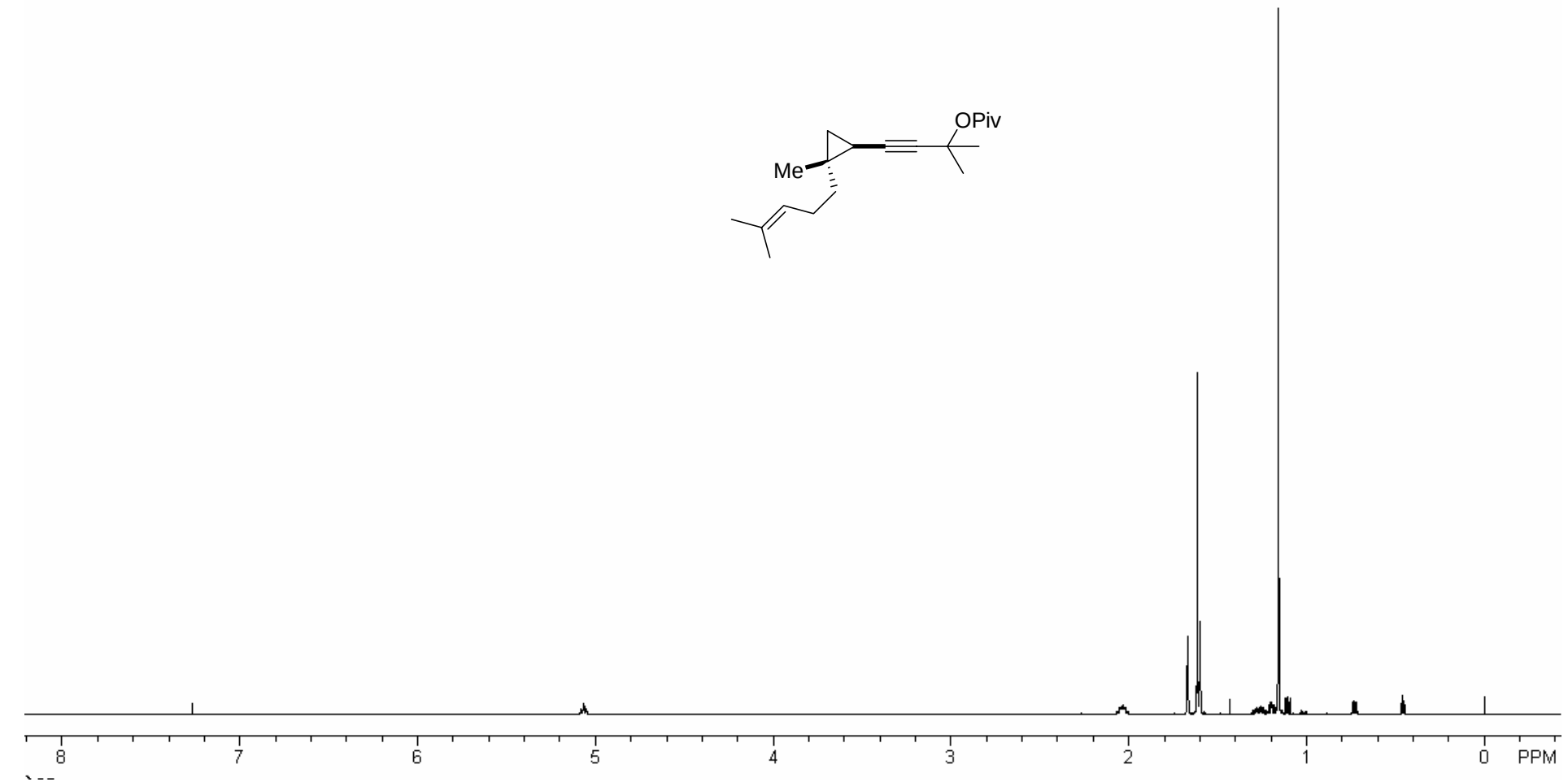
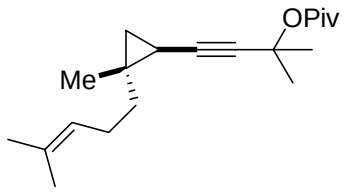
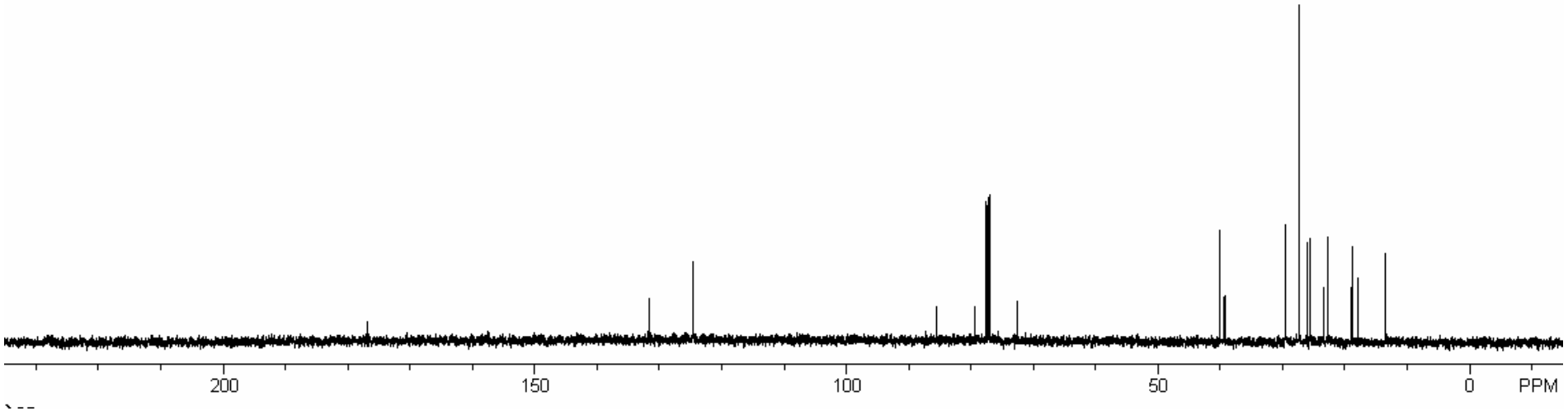
PPM


PROTON
OAc
EtO2C
EtO2C
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
OAc
EtO2C
EtO2C
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OPiv
Me
8
7
6
5
4
3
2
1
0
PPM


OPiv
Me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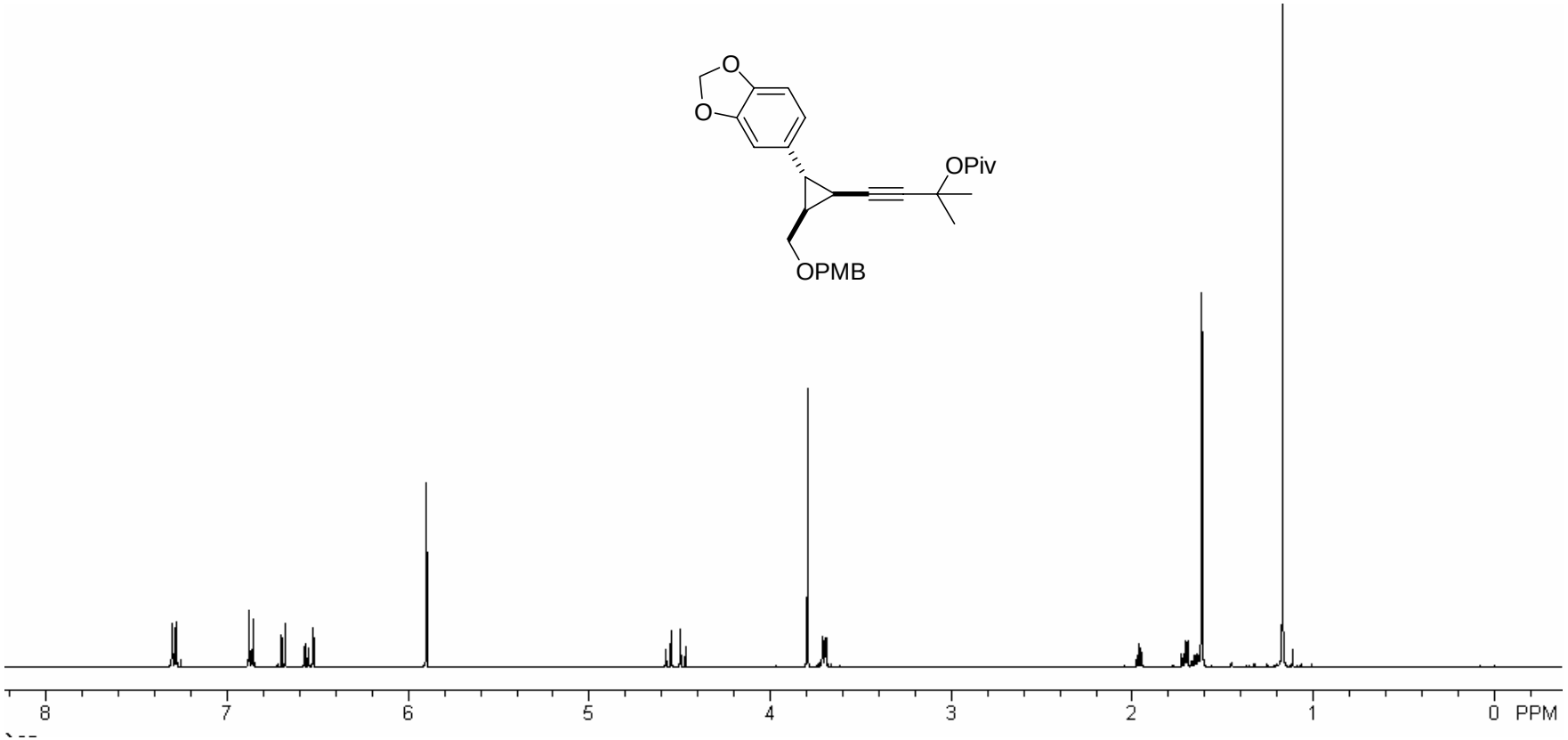
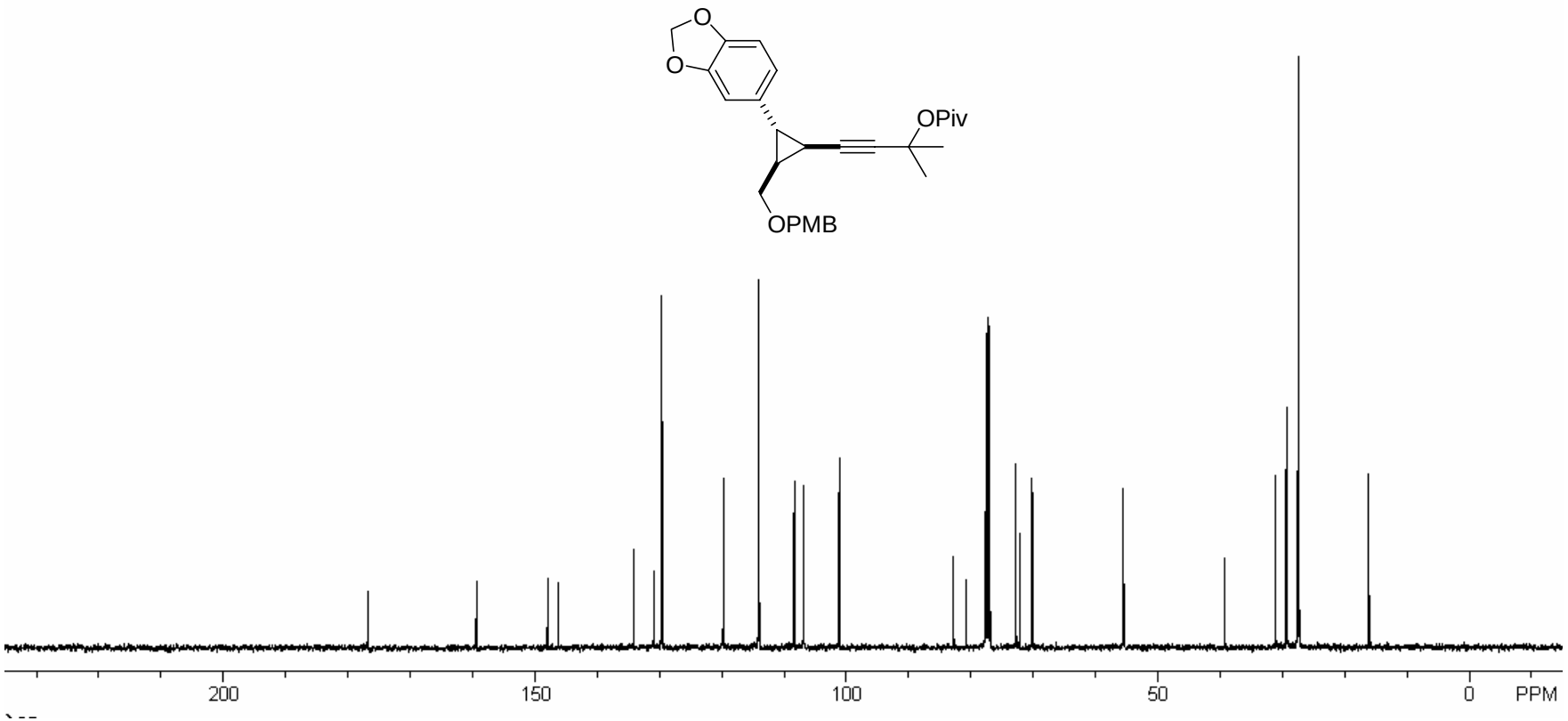
100
50
0
PPM


O
O
OPiv
OPMB
8
7
6
5
4
3
2
1
0
PPM


O
O
OPiv
OPMB
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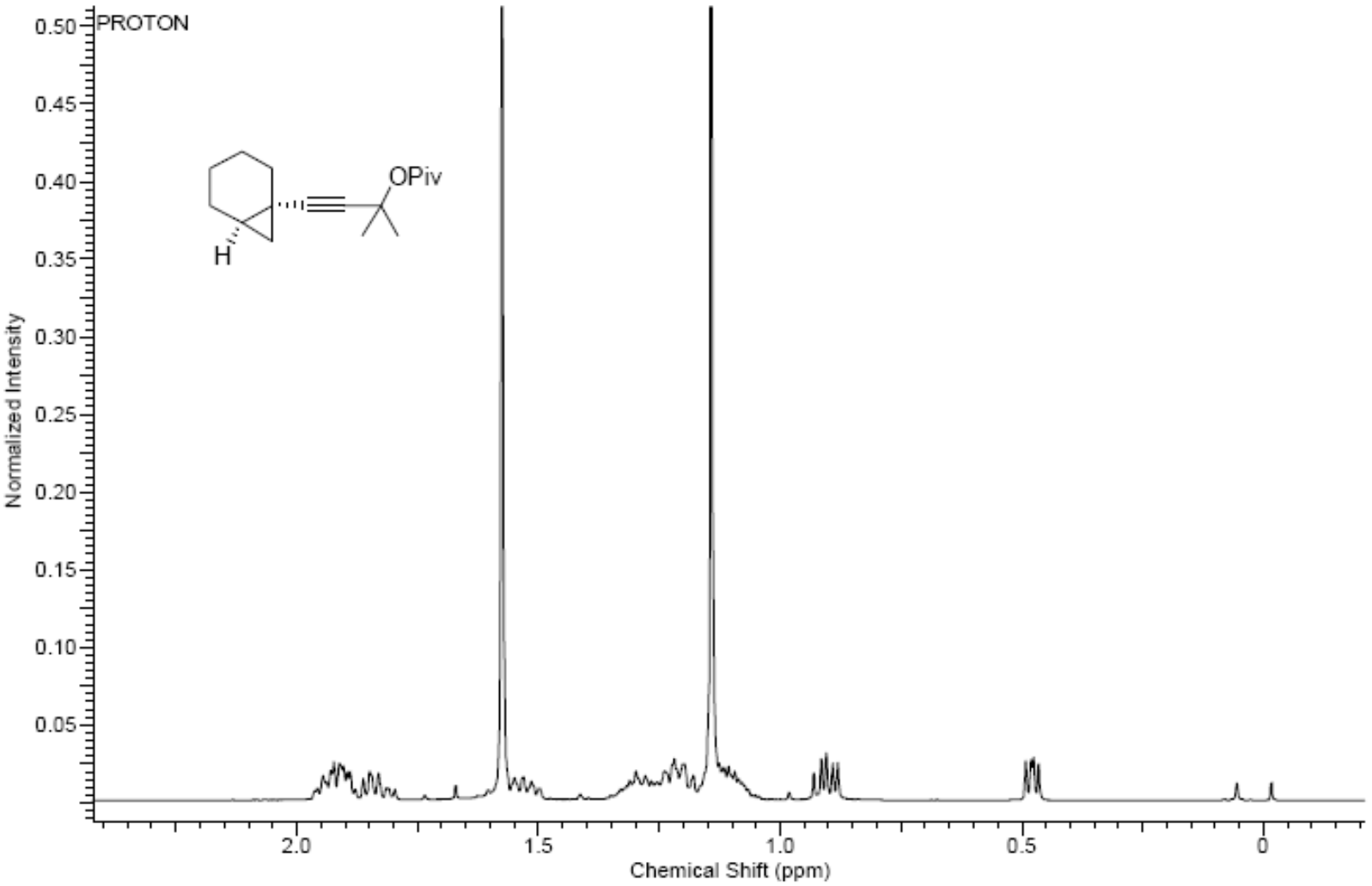
150
100
50
0
PPM


PROTON
OPiv
H
Normalized Intensity
0.50
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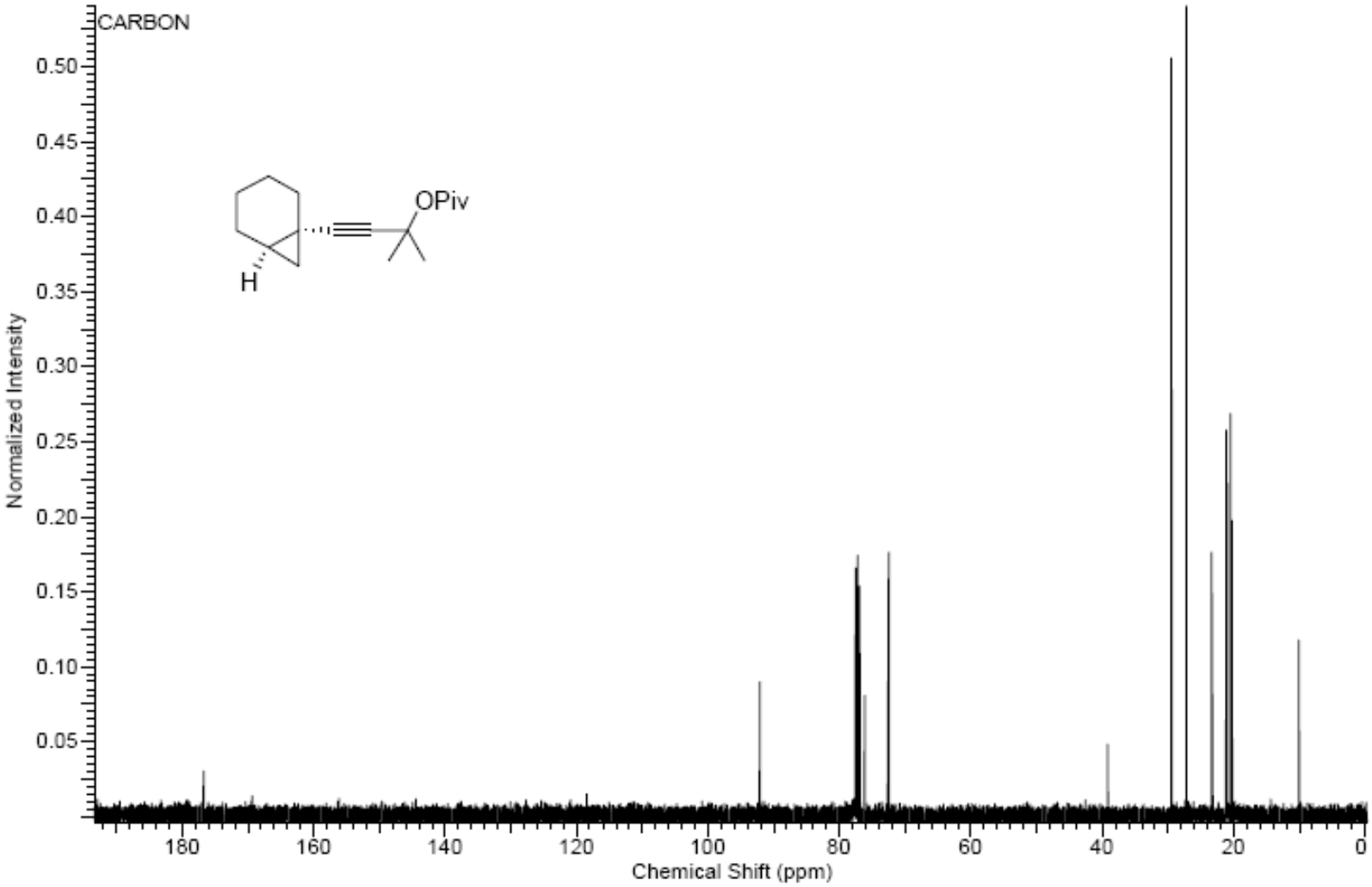
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
OPiv
H
Normalized Intensity
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0.40
0.35
0.30
0.25
0.20
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0.10
0.05
180
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100
80
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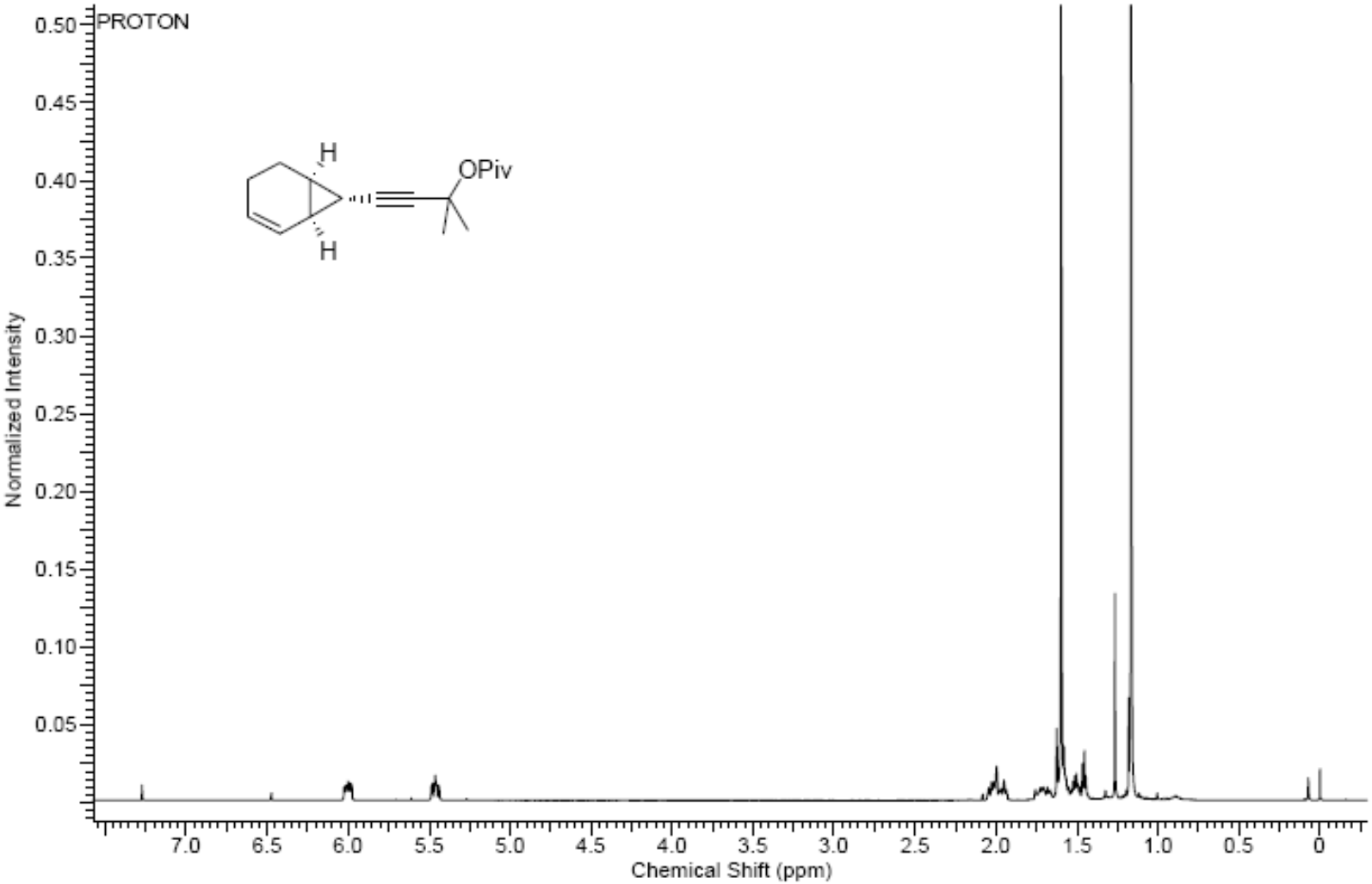
20
0
Chemical Shift (ppm)


PROTON
H
OPiv
H
Normalized Intensity
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0.40
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0.30
0.25
0.20
0.15
0.10
0.05
7.0
6.5
6.0
5.5
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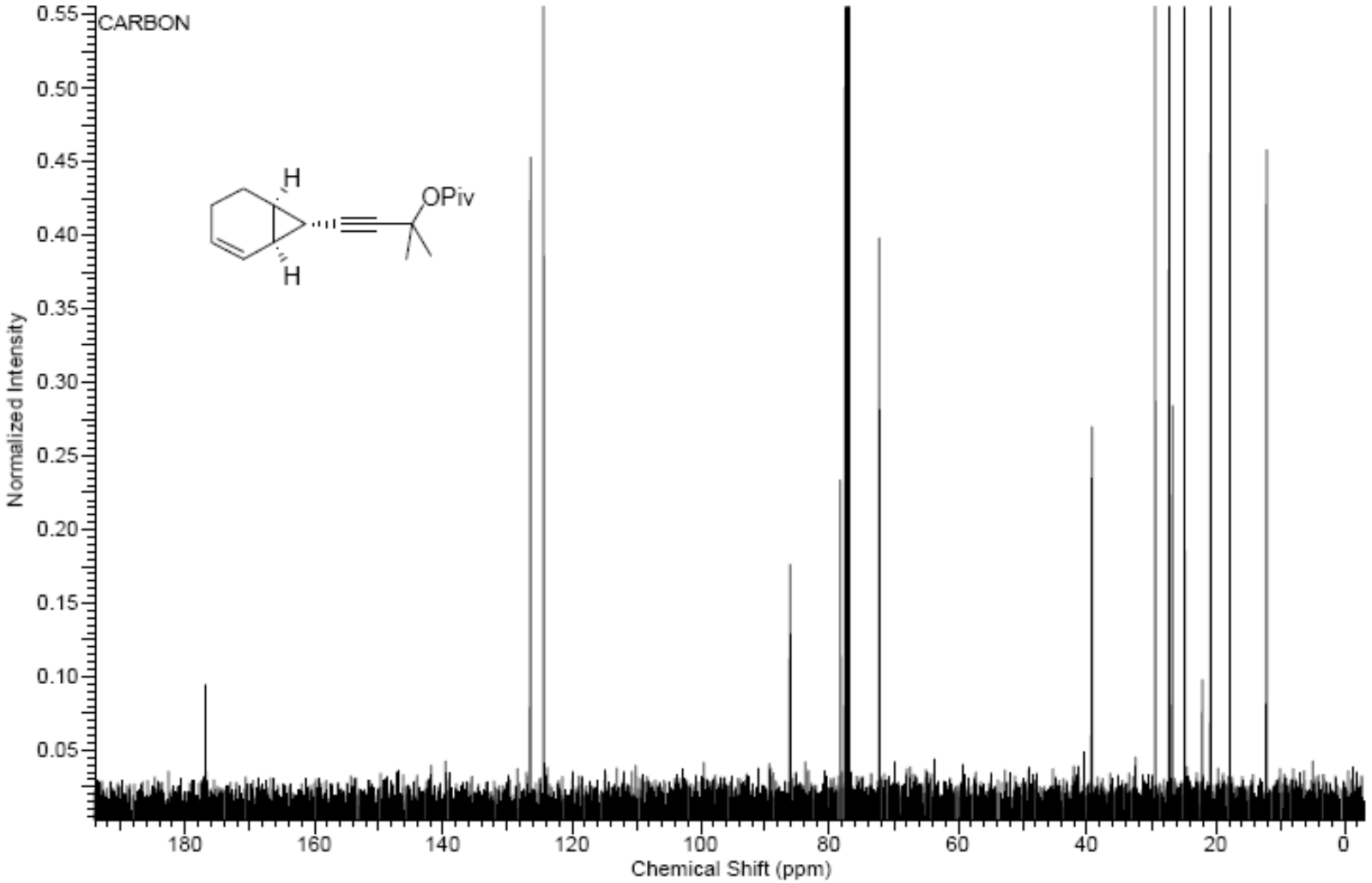
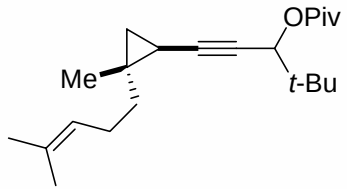
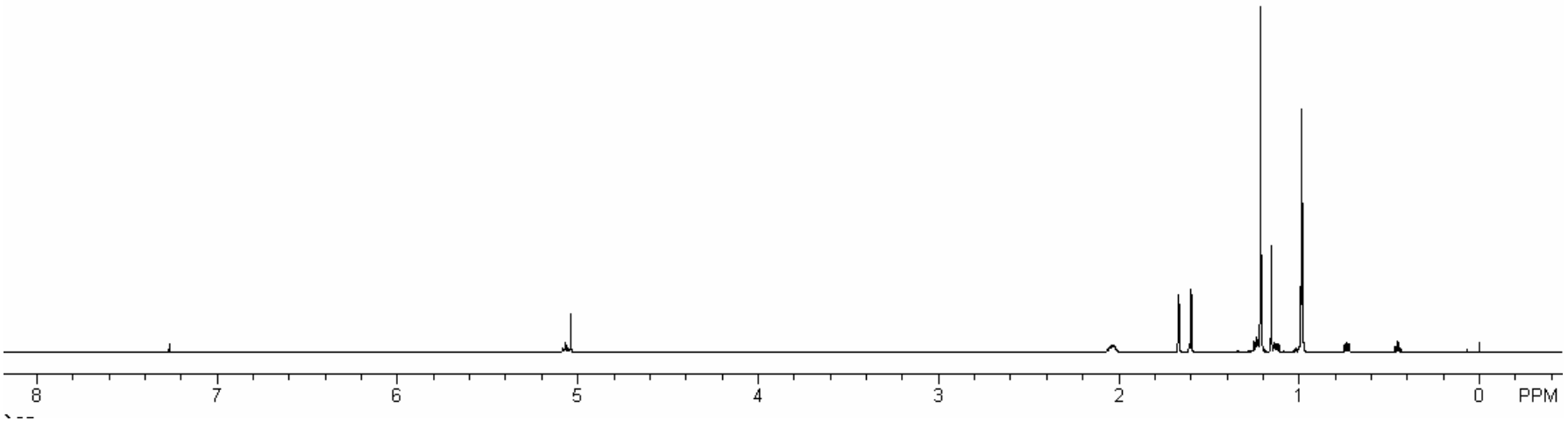
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
H
OPiv
H
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OPiv
Me
t-Bu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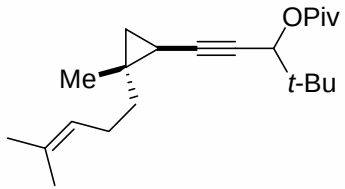
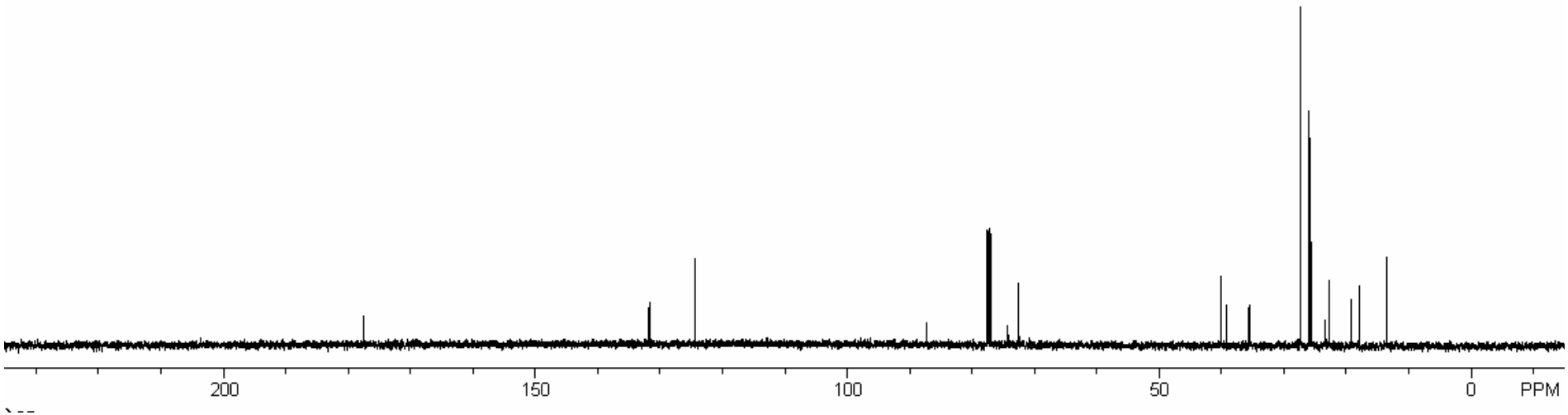
5
4
3
2
1
0
PPM


OPiv
Me
t-Bu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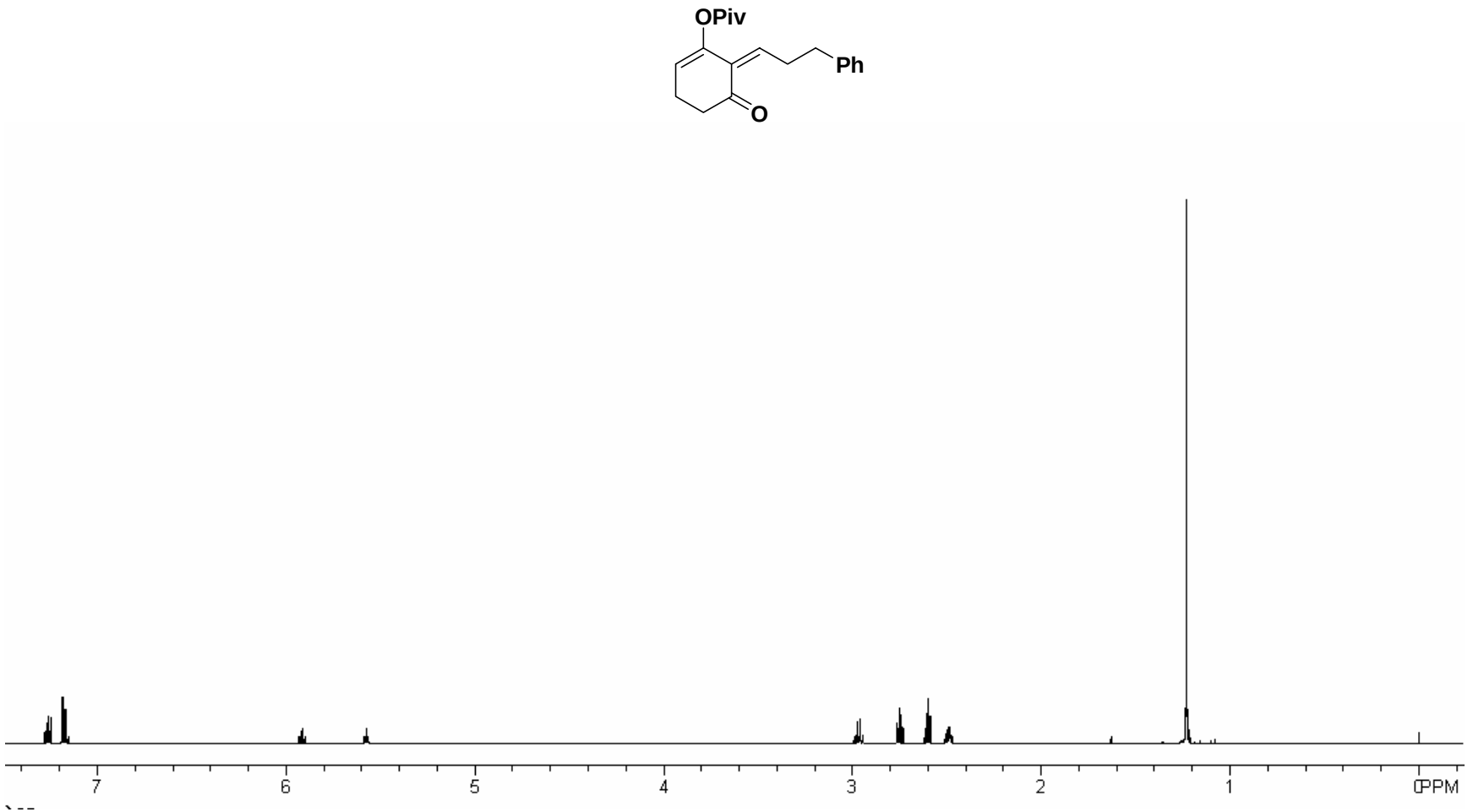
100
50
0
PPM


OPiv
Ph
O
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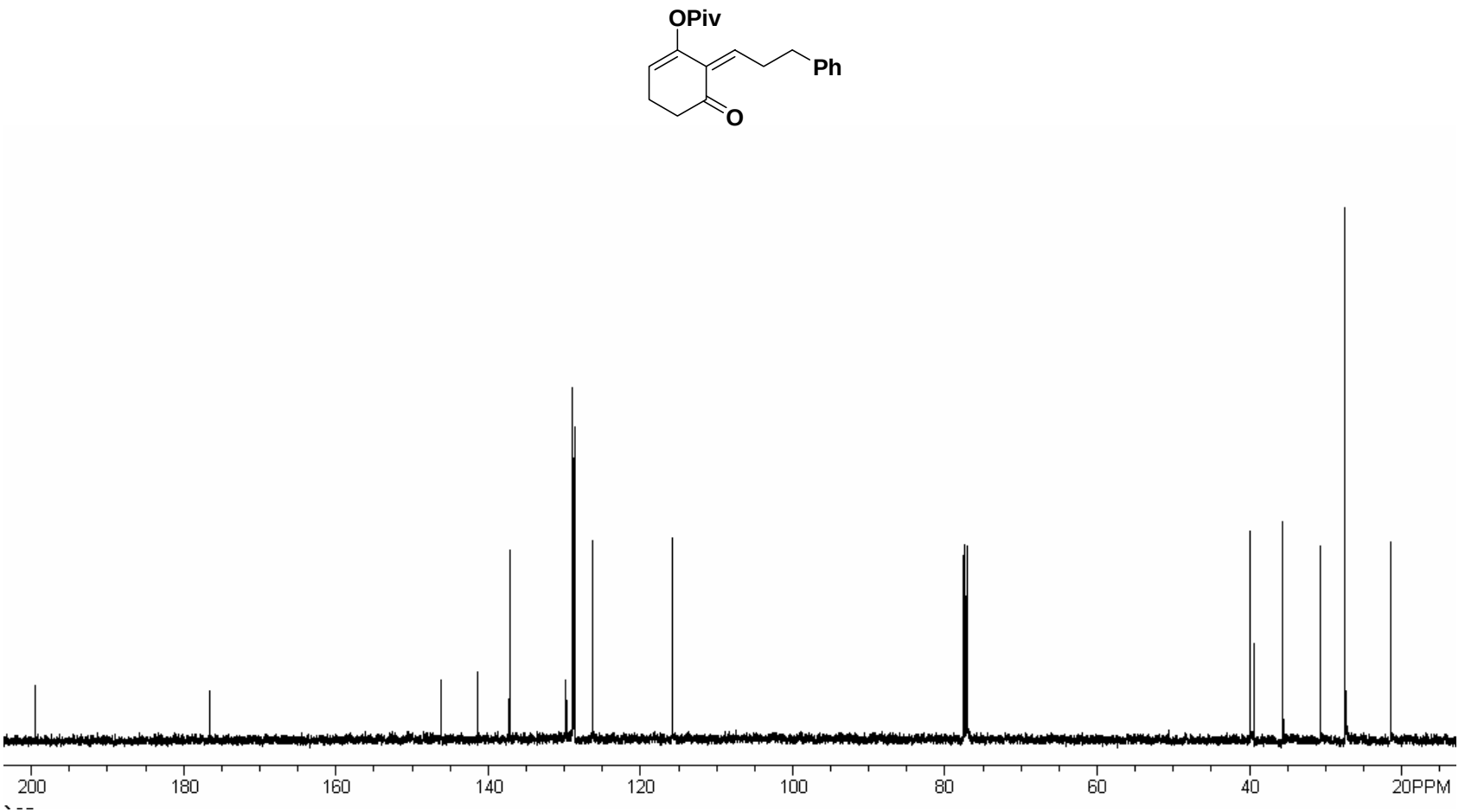
6
5
4
3
2
1
0
PPM


OPiv
Ph
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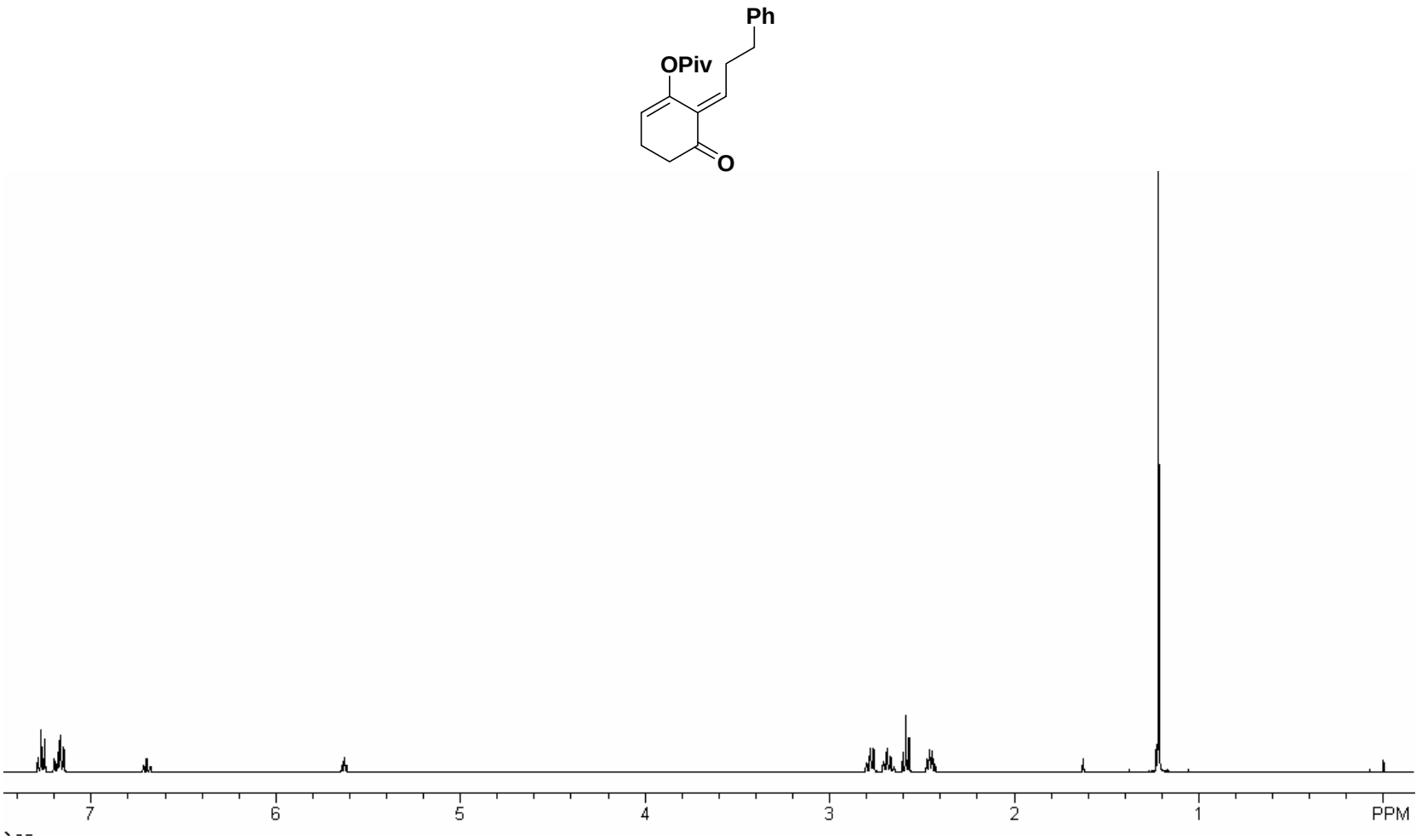
20PPM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OPiv
O
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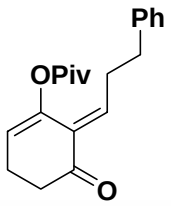
6
5
4
3
2
1
PPM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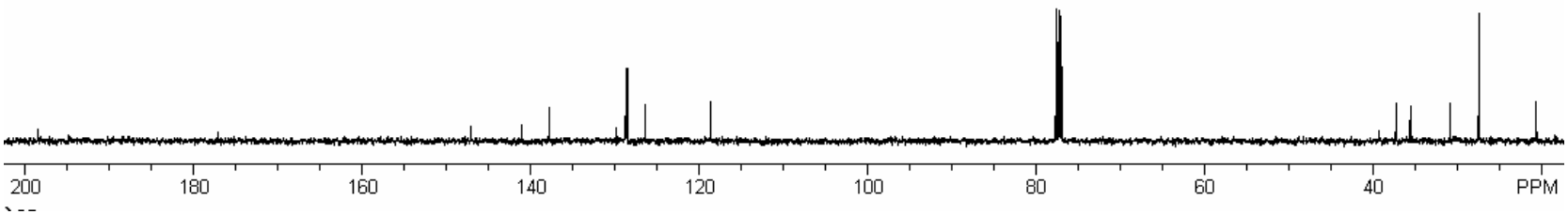
OPiv
O


200
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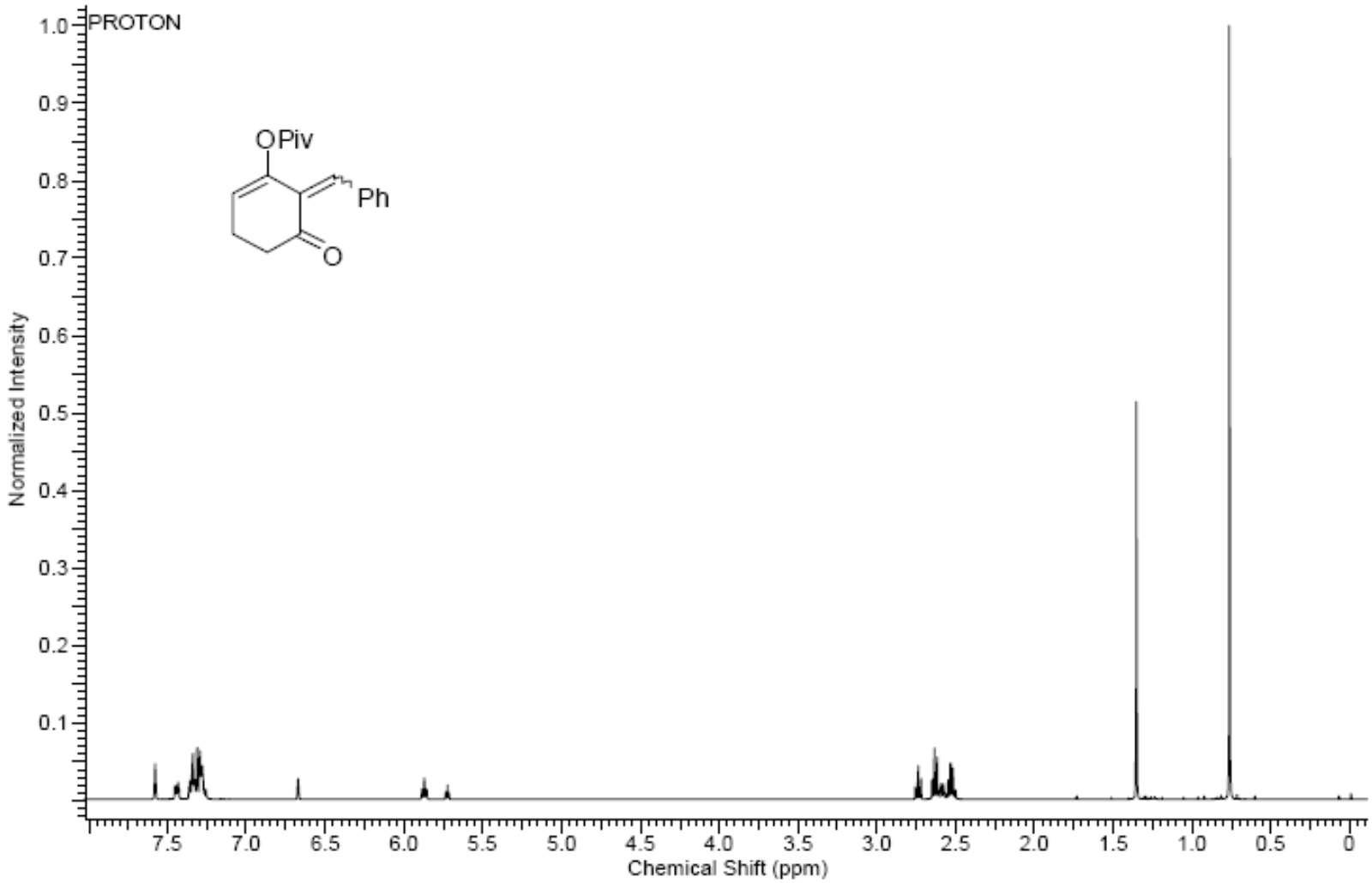
140
120
100
80
60
40
PPM


PROTON
OPiv
Ph
O
Normalized Intensity
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0.7
0.6
0.5
0.4
0.3
0.2
0.1
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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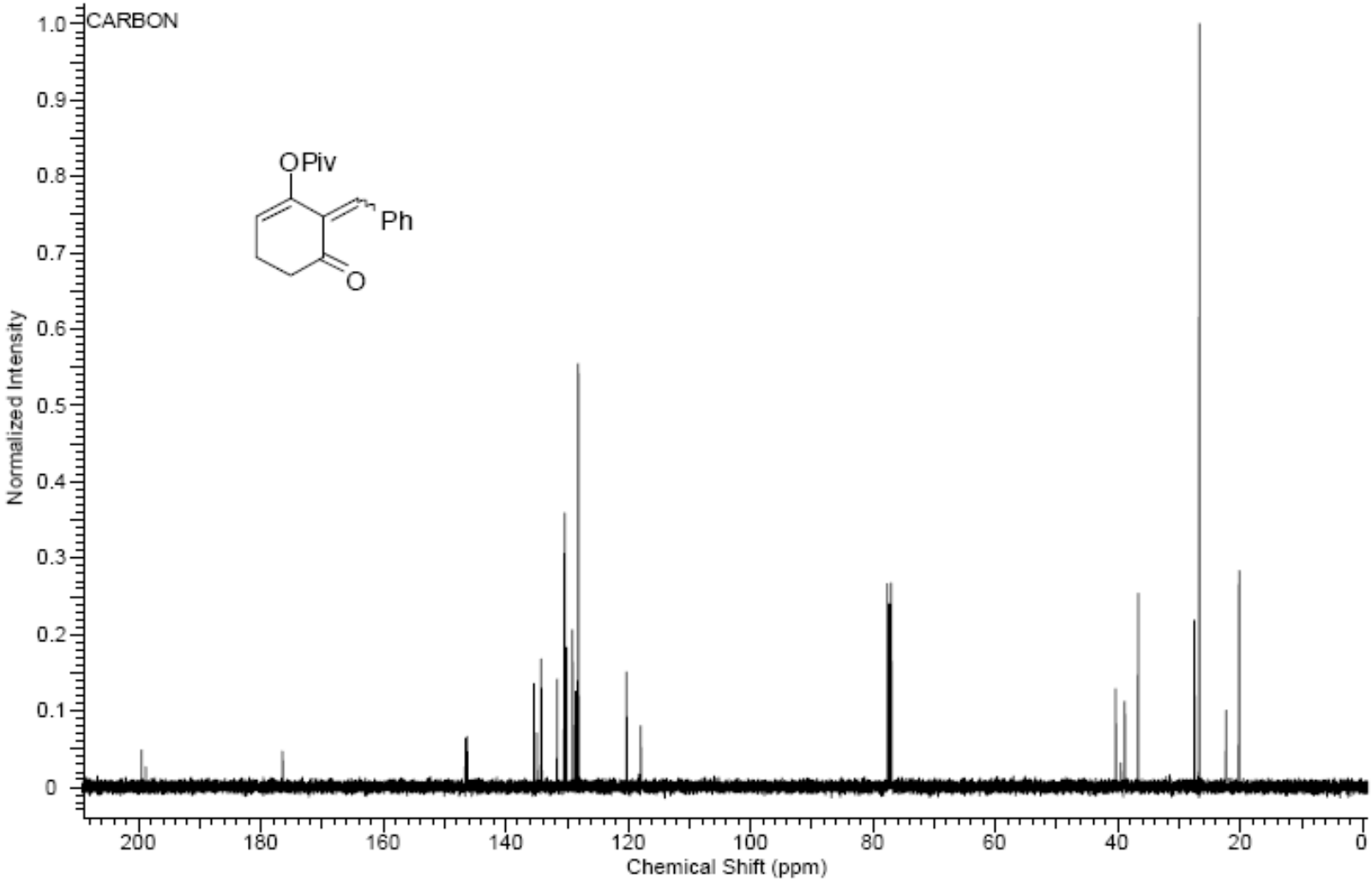
Chemical Shift (ppm)


CARBON
OPiv
Ph
O
Normalized Intensity
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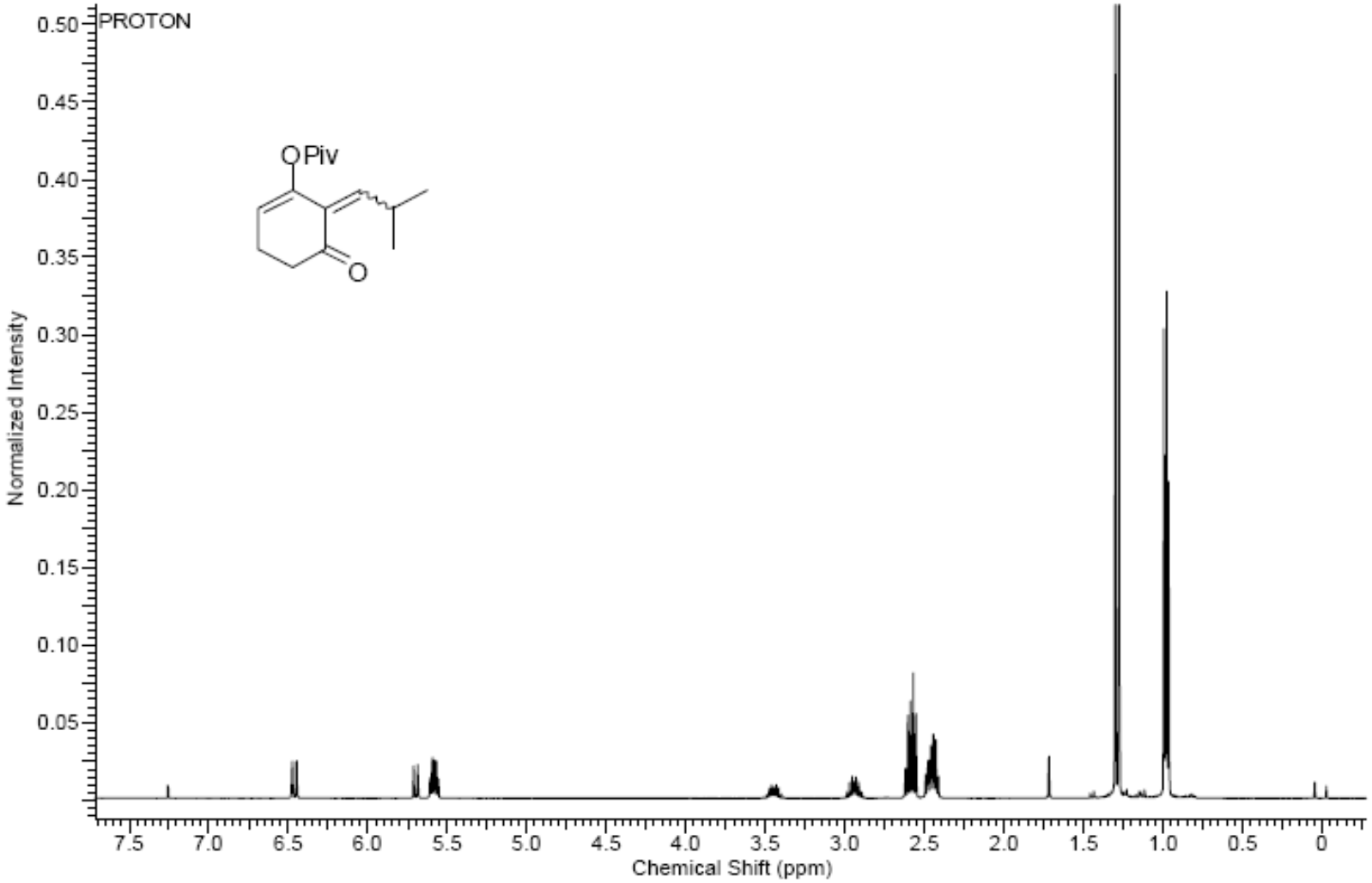
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PROTON
OPiv
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Normalized Intensity
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0.30
0.25
0.20
0.15
0.10
0.05
7.5
7.0
6.5
6.0
5.5
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4.5
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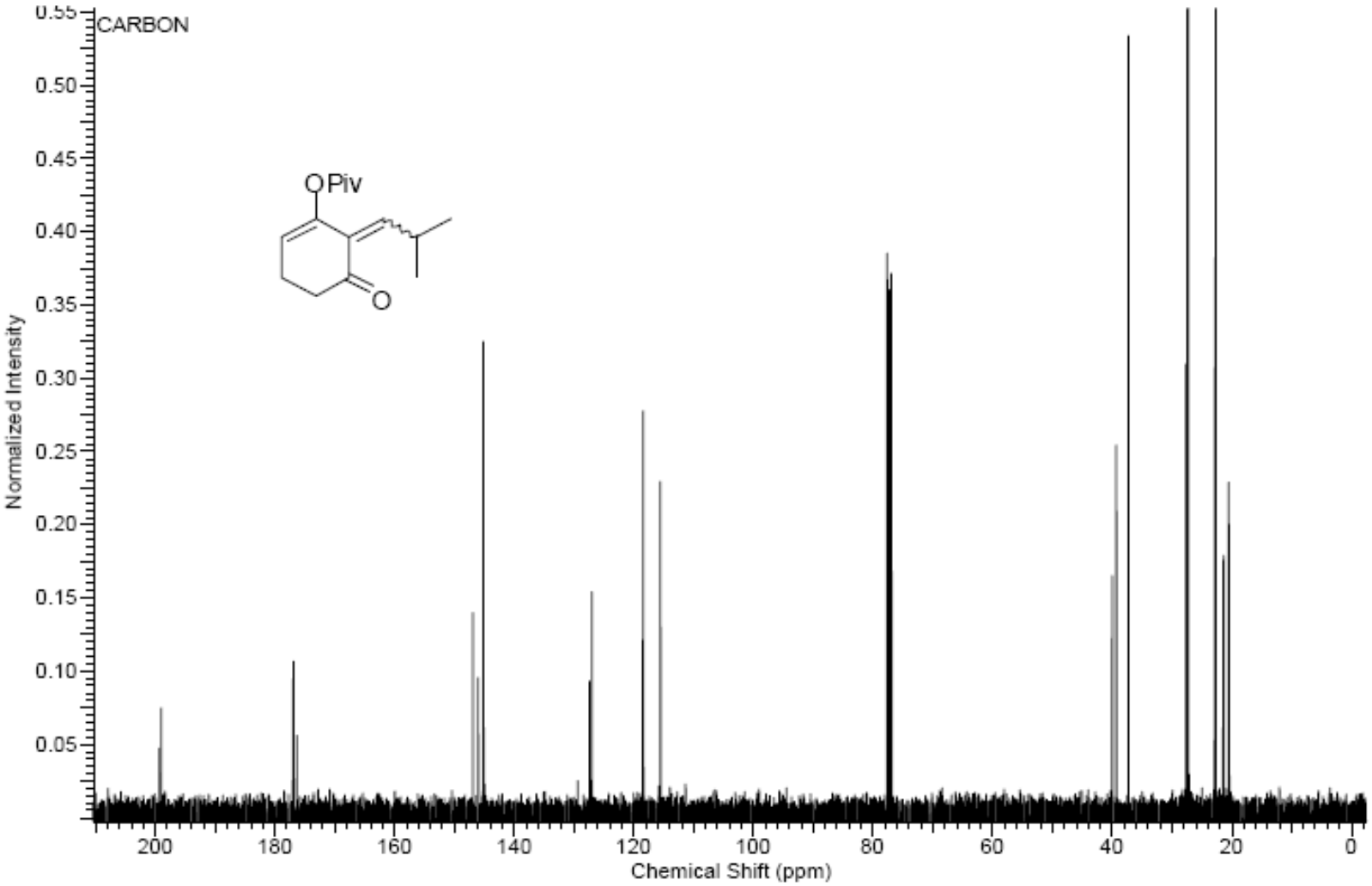
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
OPiv
O
Normalized Intensity
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0.50
0.45
0.40
0.35
0.30
0.25
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0.15
0.10
0.05
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180
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140
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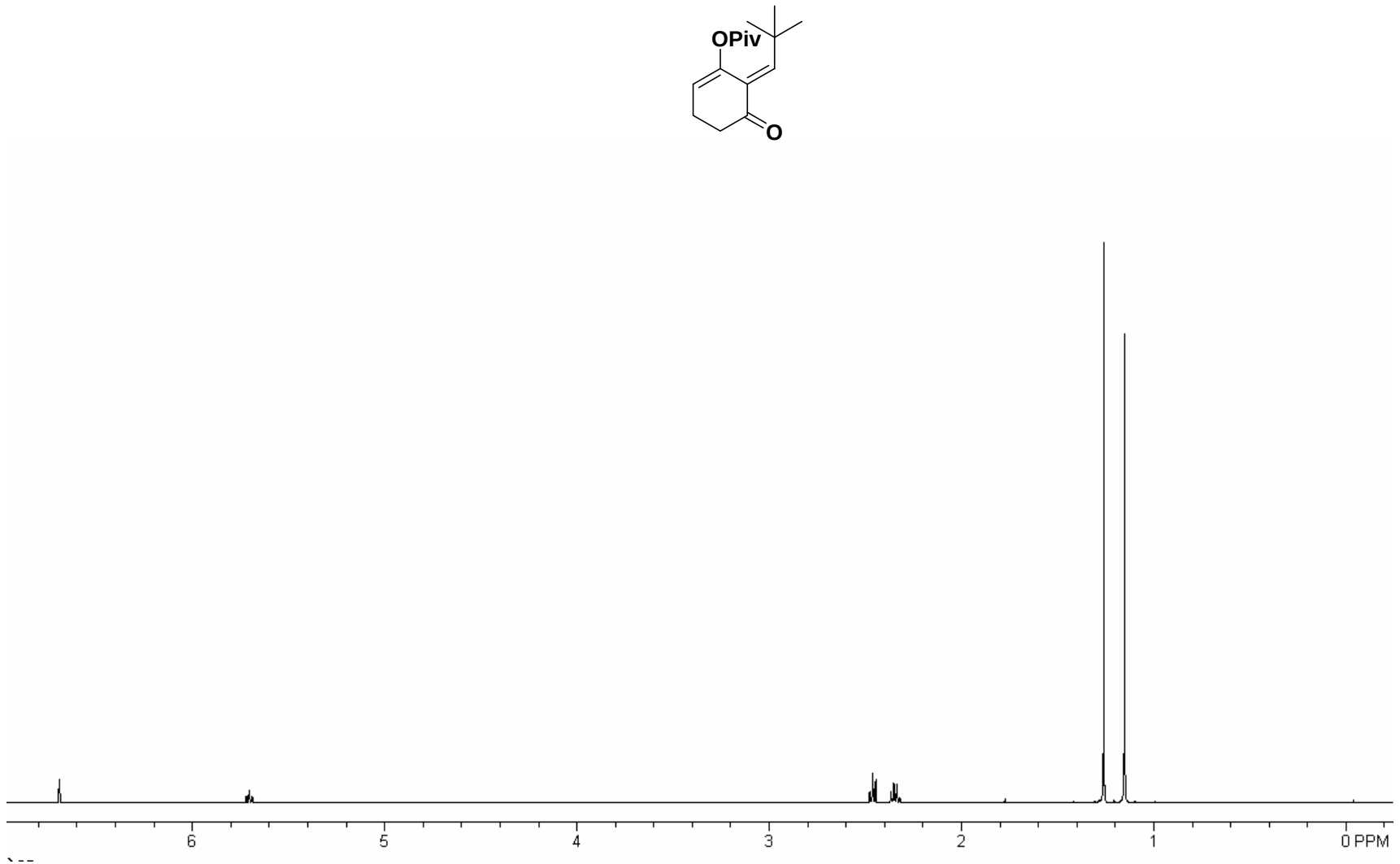
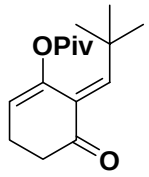
100
80
60
40
20
0
Chemical Shift (ppm)


OPiv
O
6
5
4
3
2
1
0 PPM


OPiv
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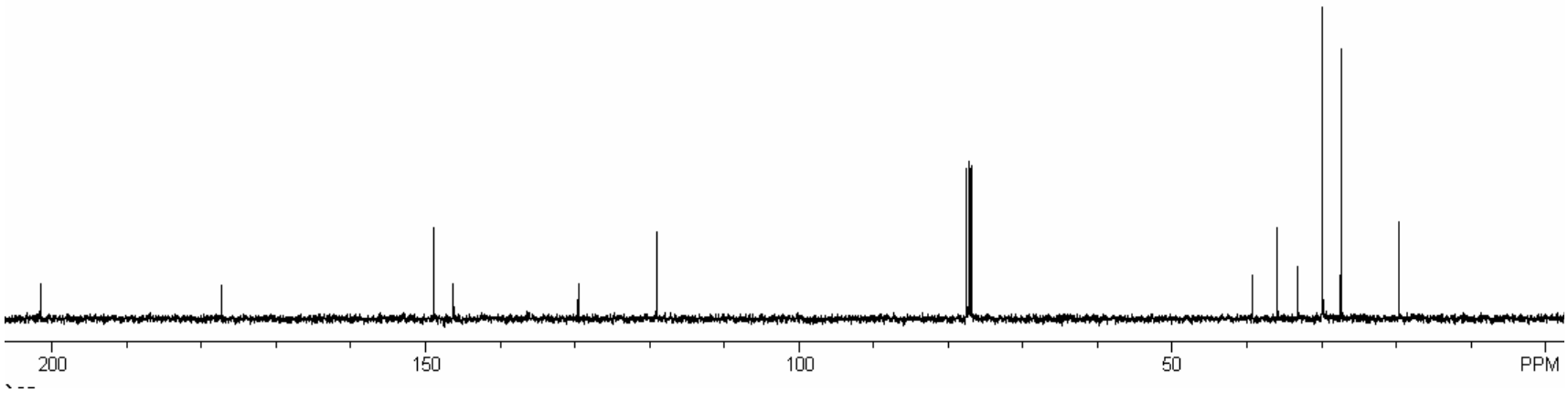
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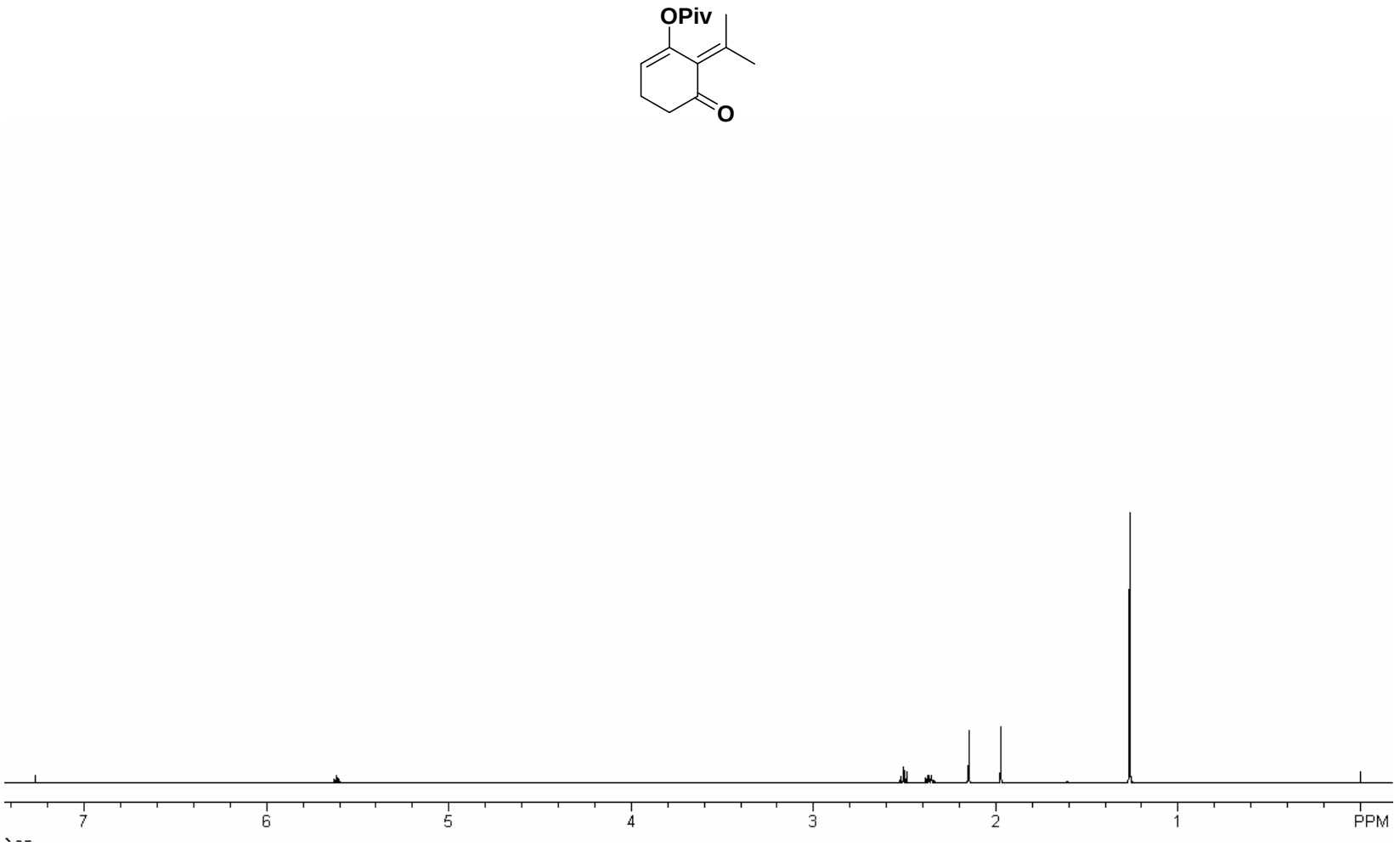
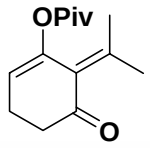
100
50
PPM


OPiv
O
7
6
5
4
3
2
1
PPM


OPiv
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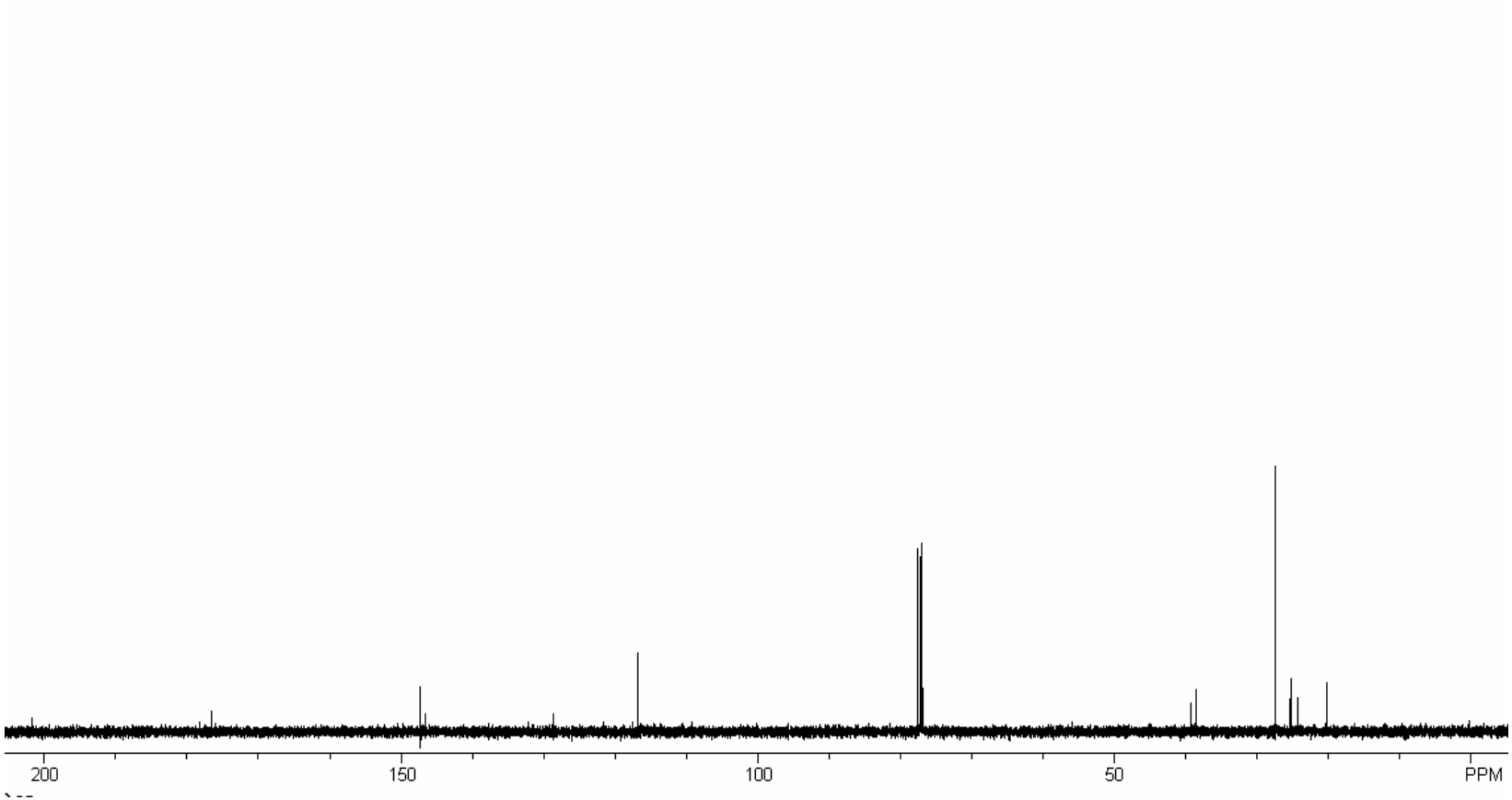
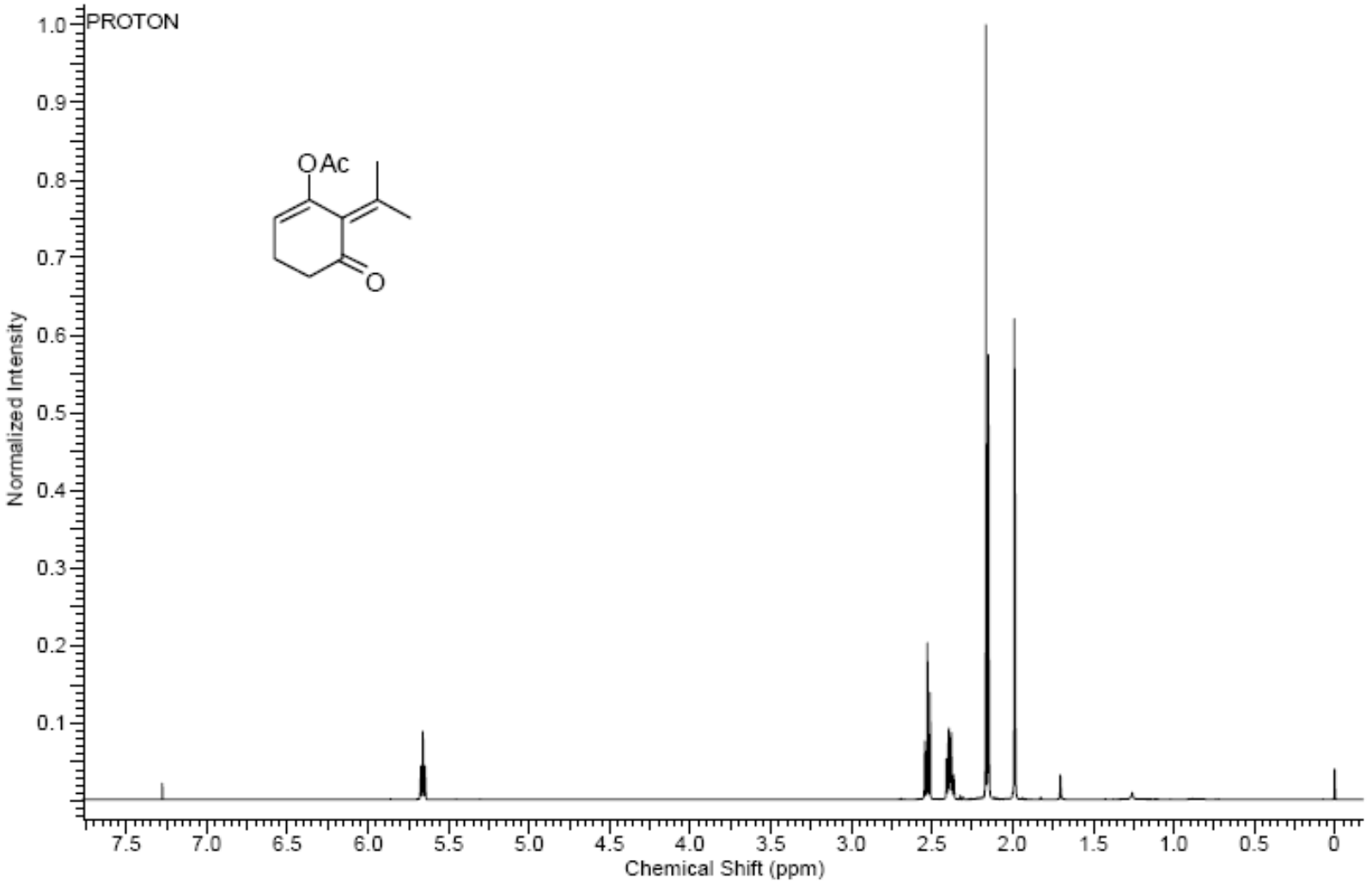

200
150
100
50
PPM


PROTON
OAc
O
Normalized Intensity
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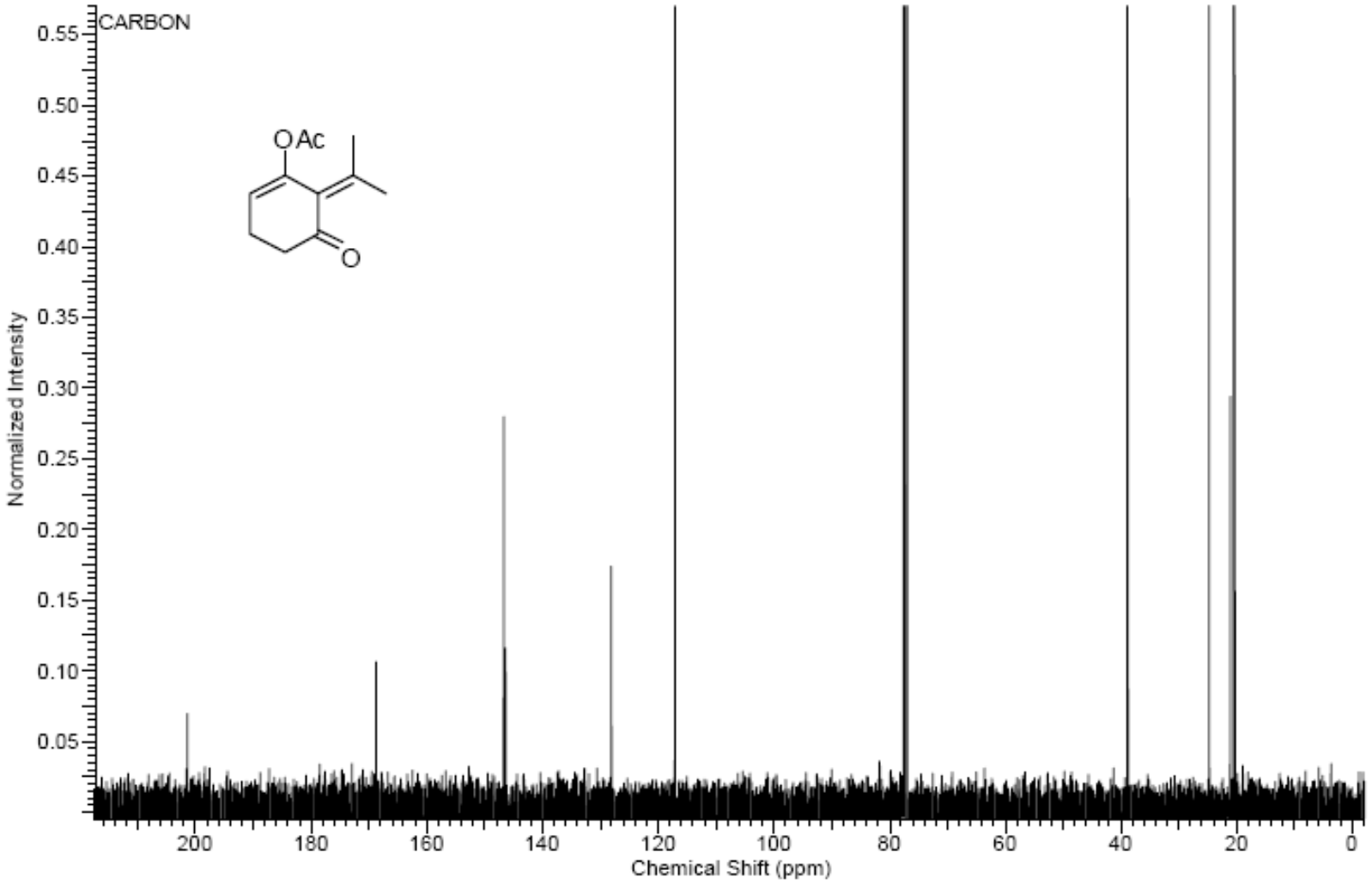
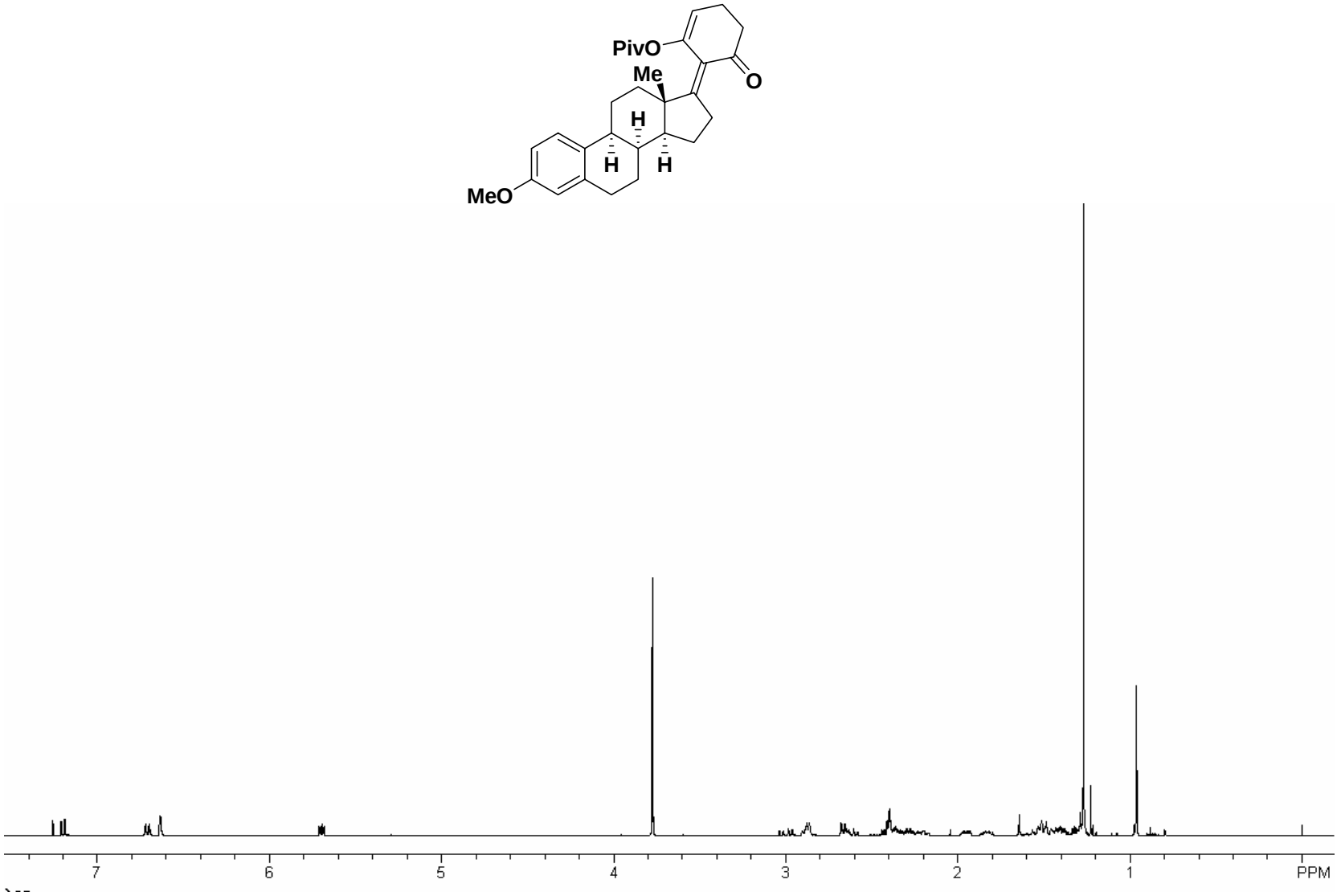
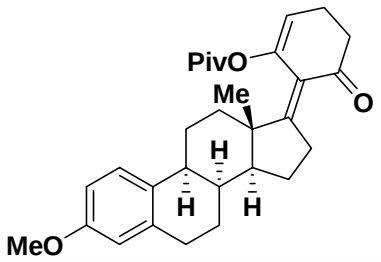
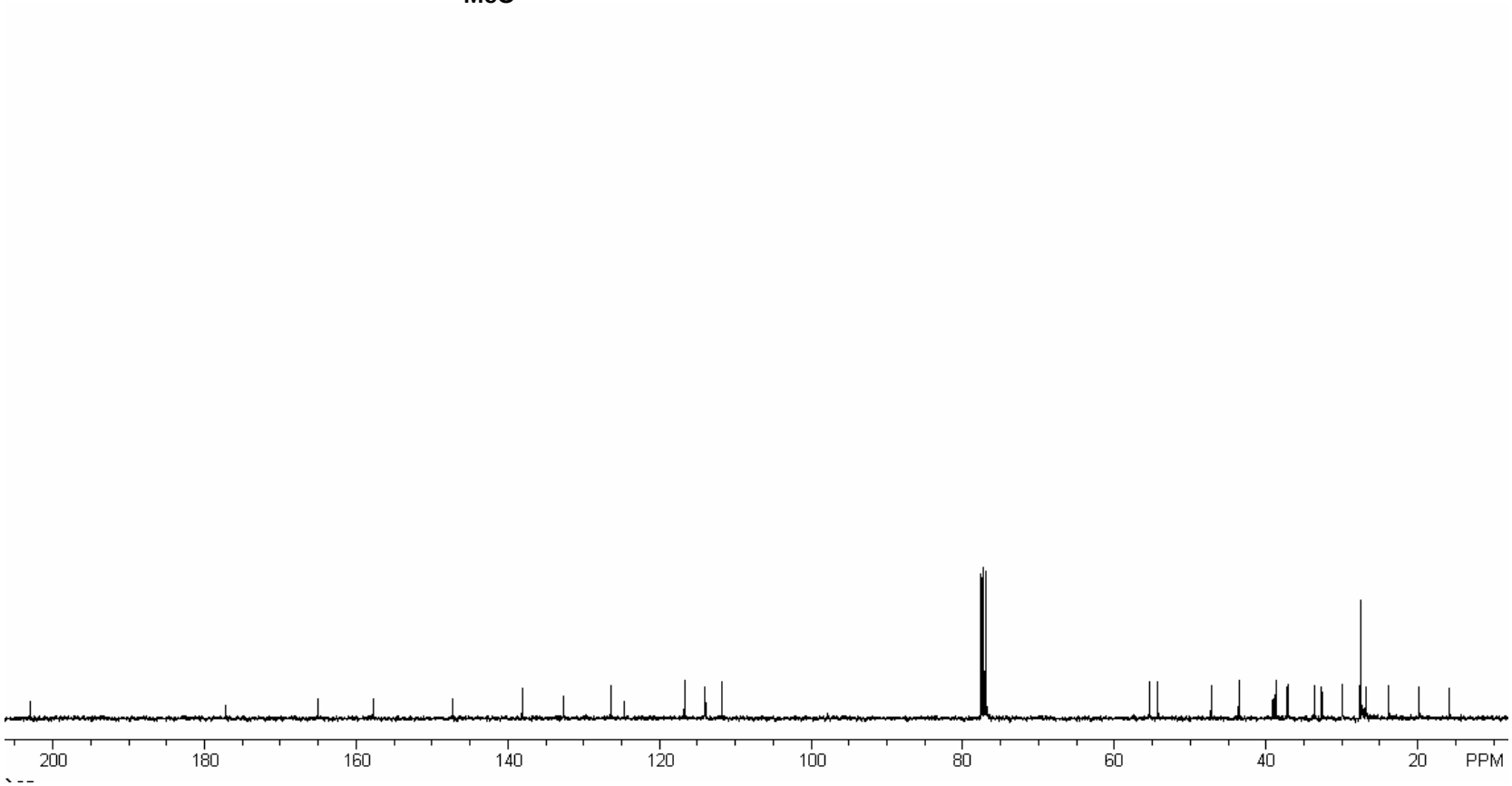
0.7
0.6
0.5
0.4
0.3
0.2
0.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
OAc
O
Normalized Intensity
0.55
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


PivO
Me
O
H
H
H
MeO
7
6
5
4
3
2
1
PPM


PivO
Me
O
H
H
H
MeO


200
180
160
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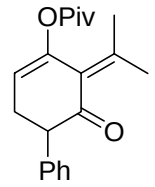
100
80
60
40
20
PPM



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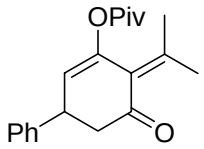

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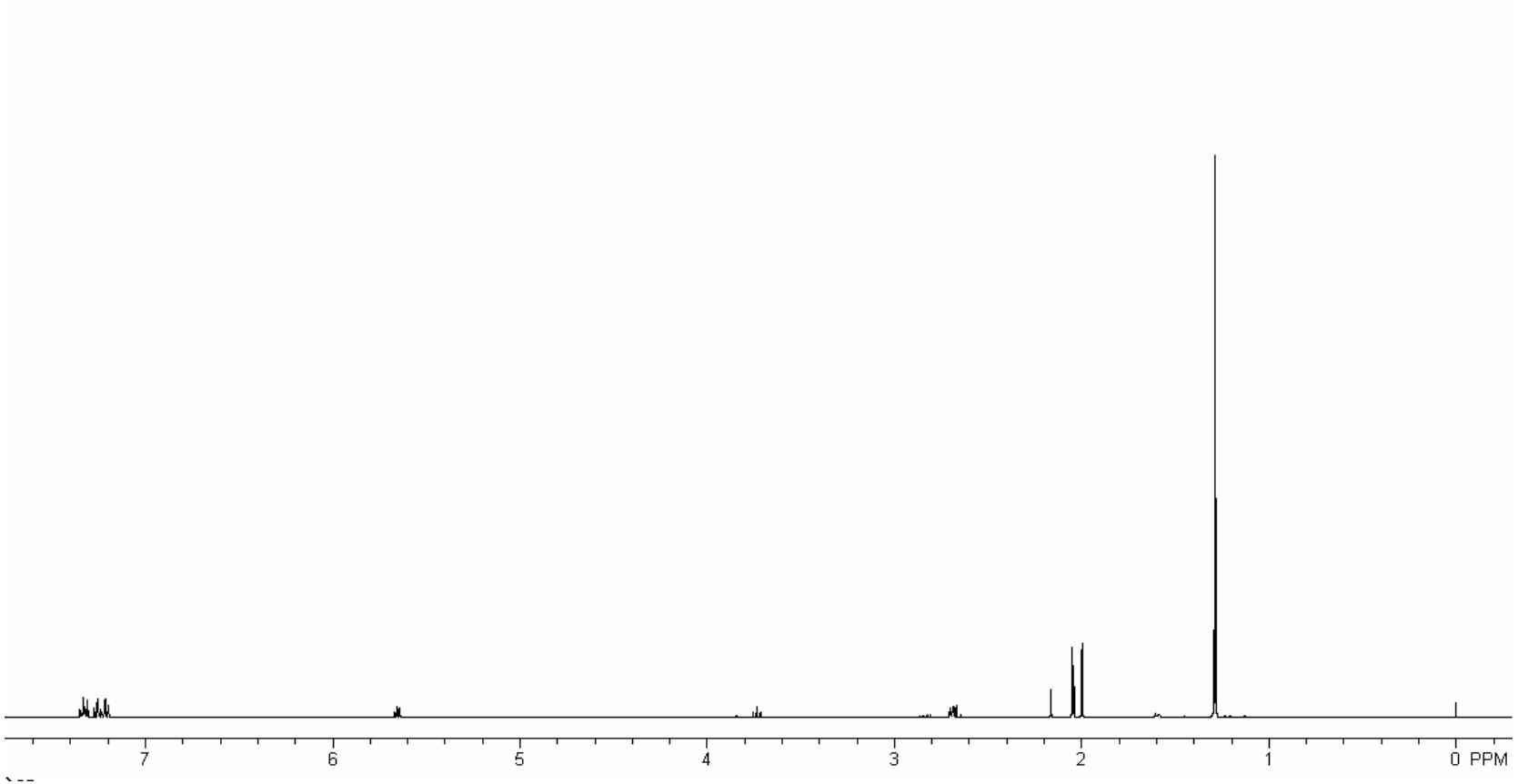

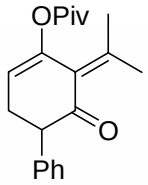

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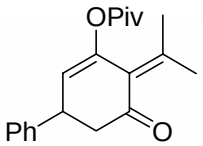

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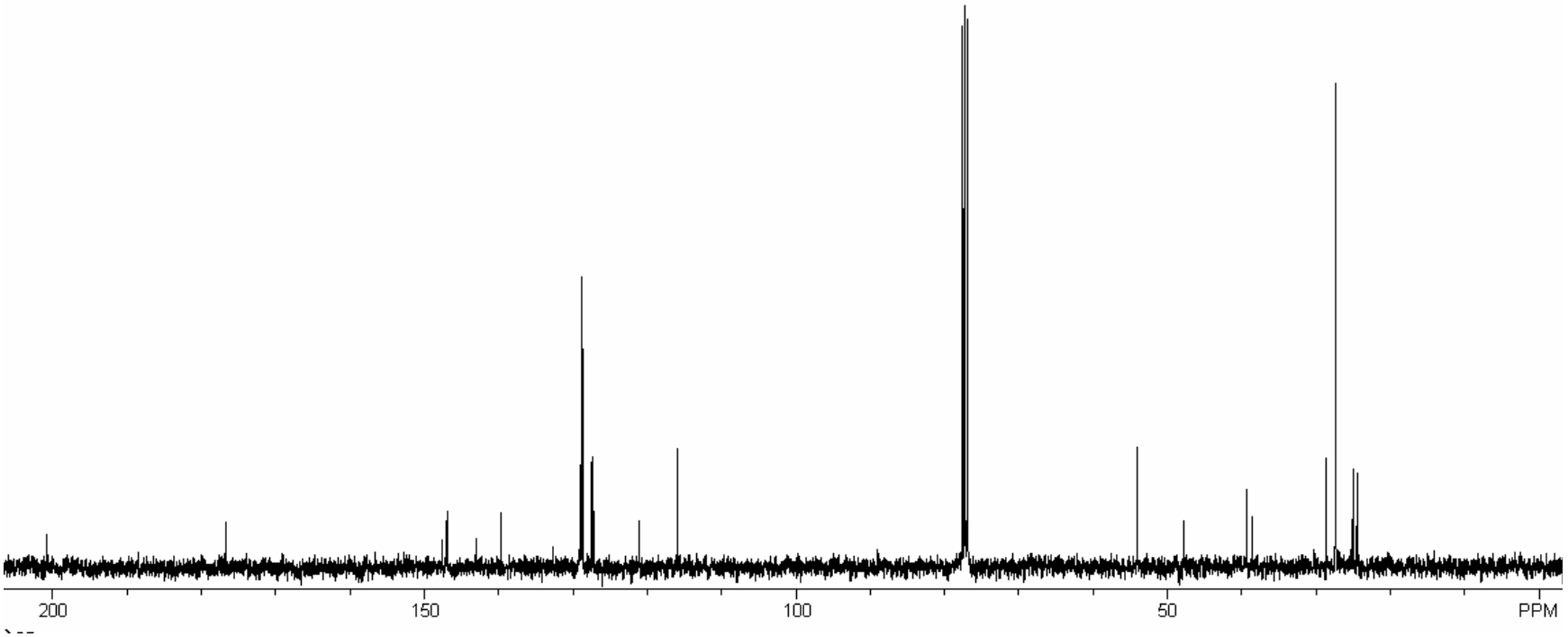
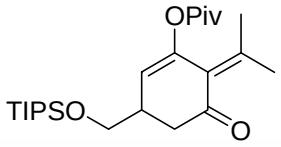
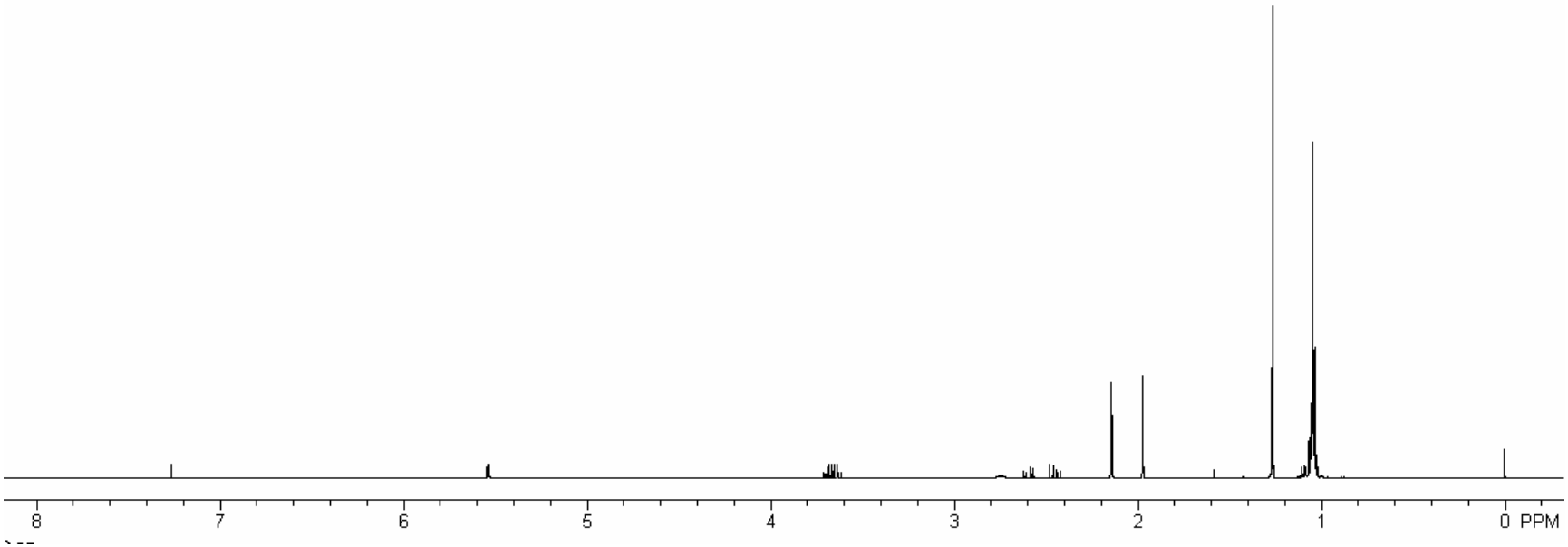
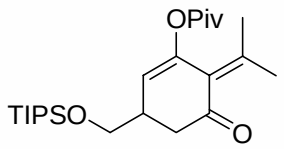



OPiv
TIPSO
O


8
7
6
5
4
3
2
1
0 PPM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TIPSO
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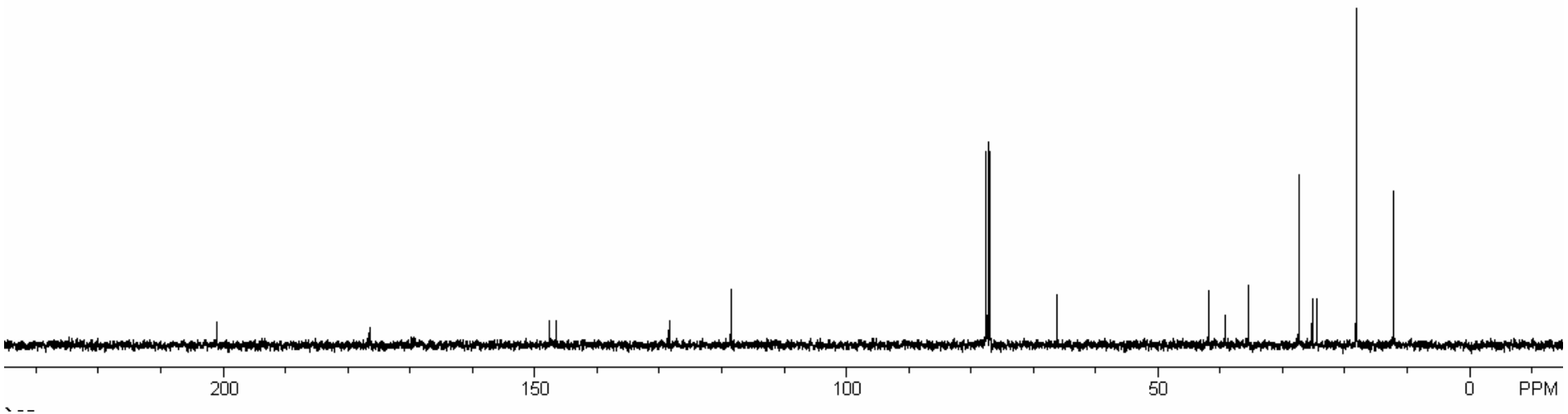
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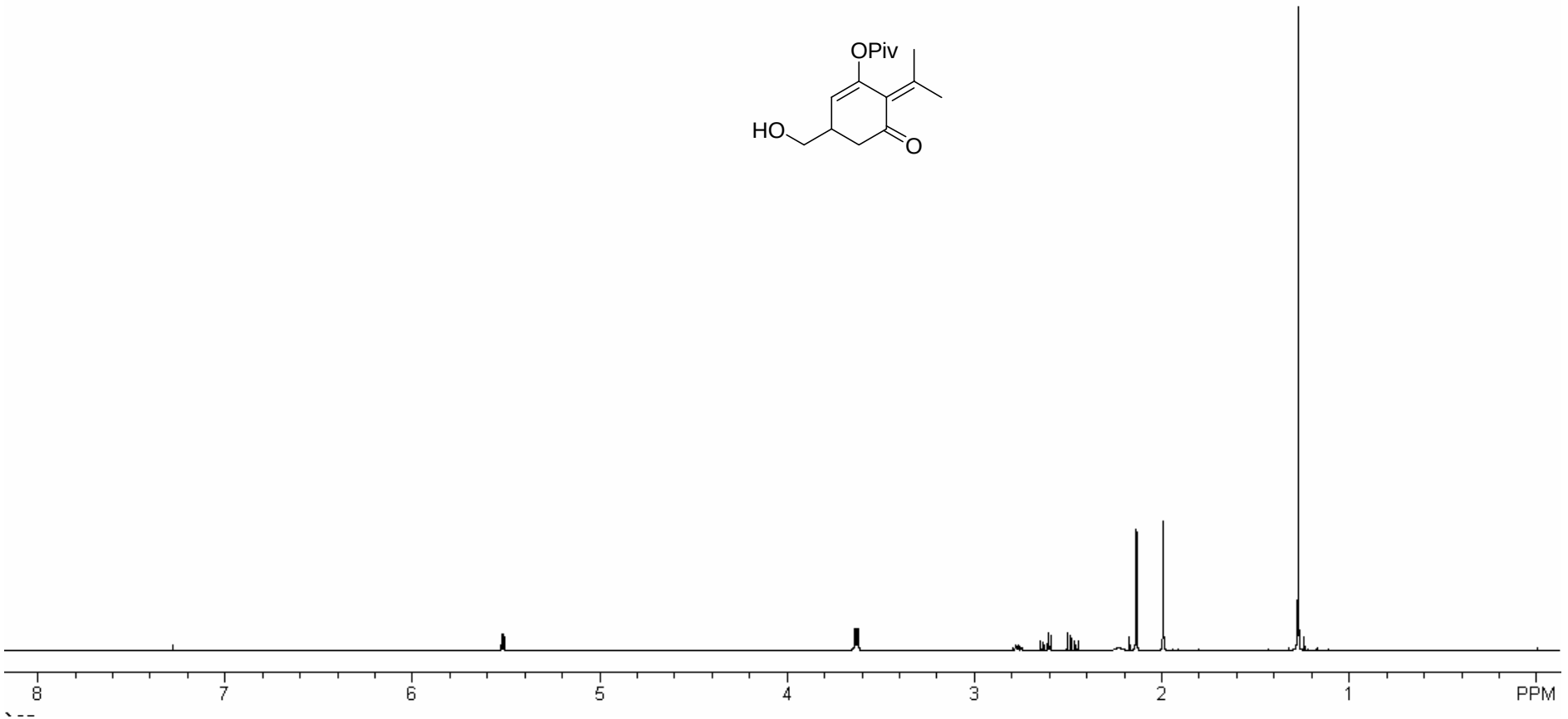
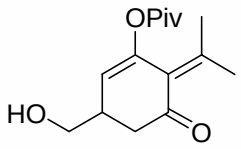
PPM


OPiv
HO
O
8
7
6
5
4
3
2
1
PPM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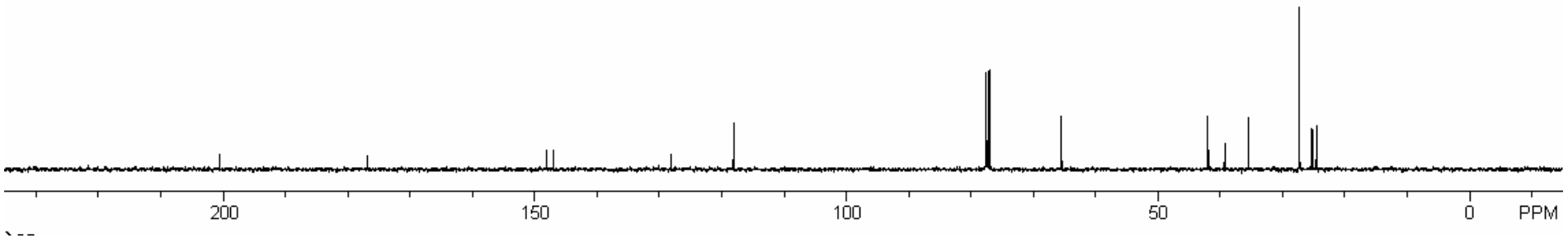
HO
O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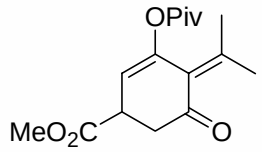
100
50
0
PPM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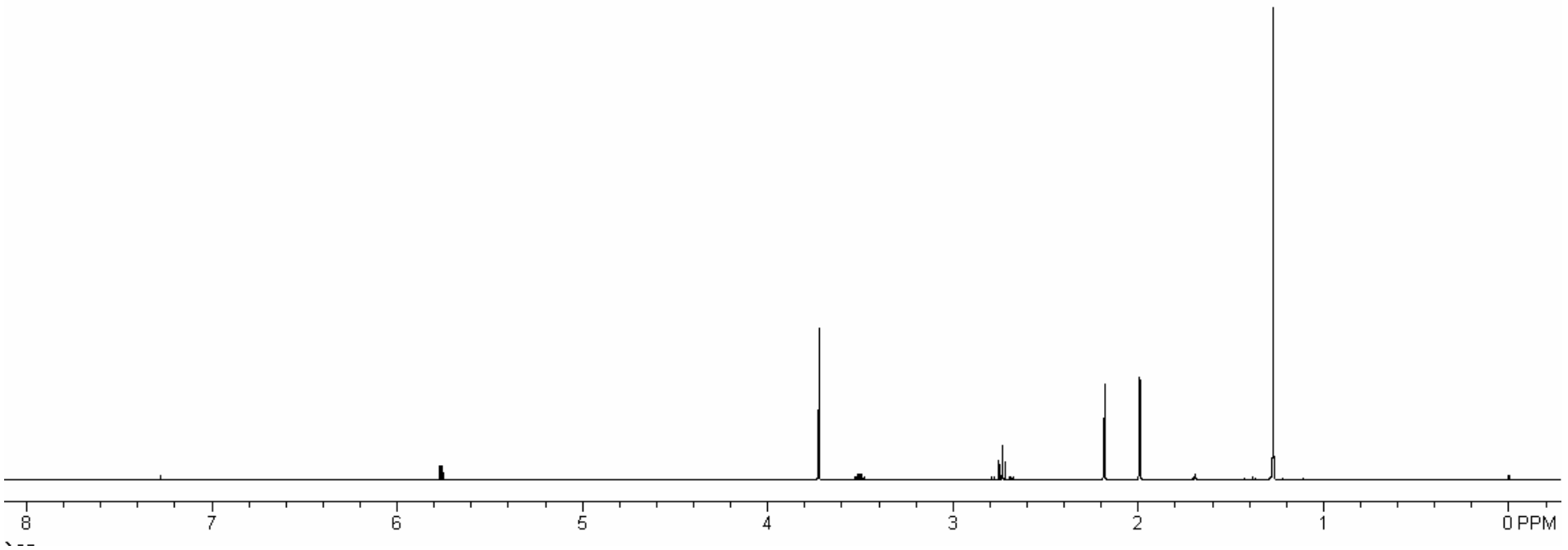
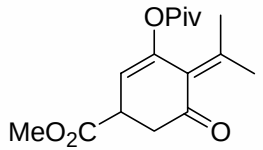
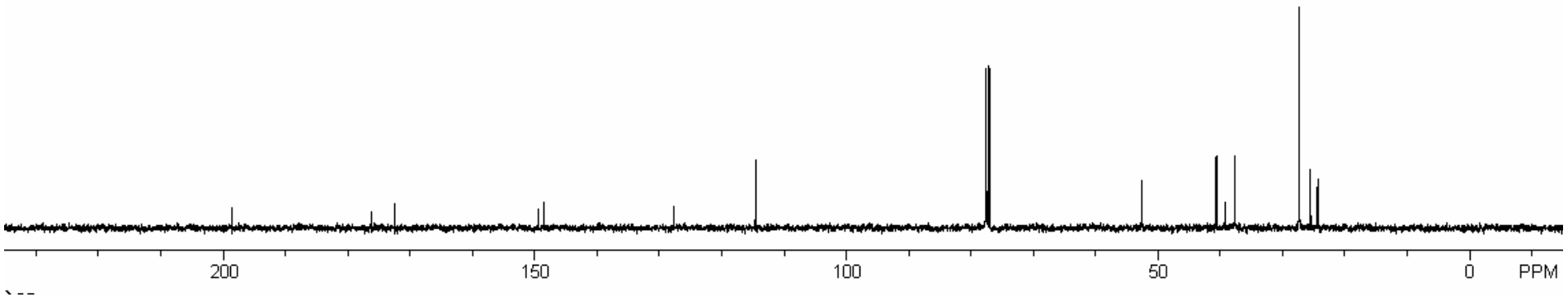
MeO2C
O


8
7
6
5
4
3
2
1
0 PPM


OPiv
MeO2C
O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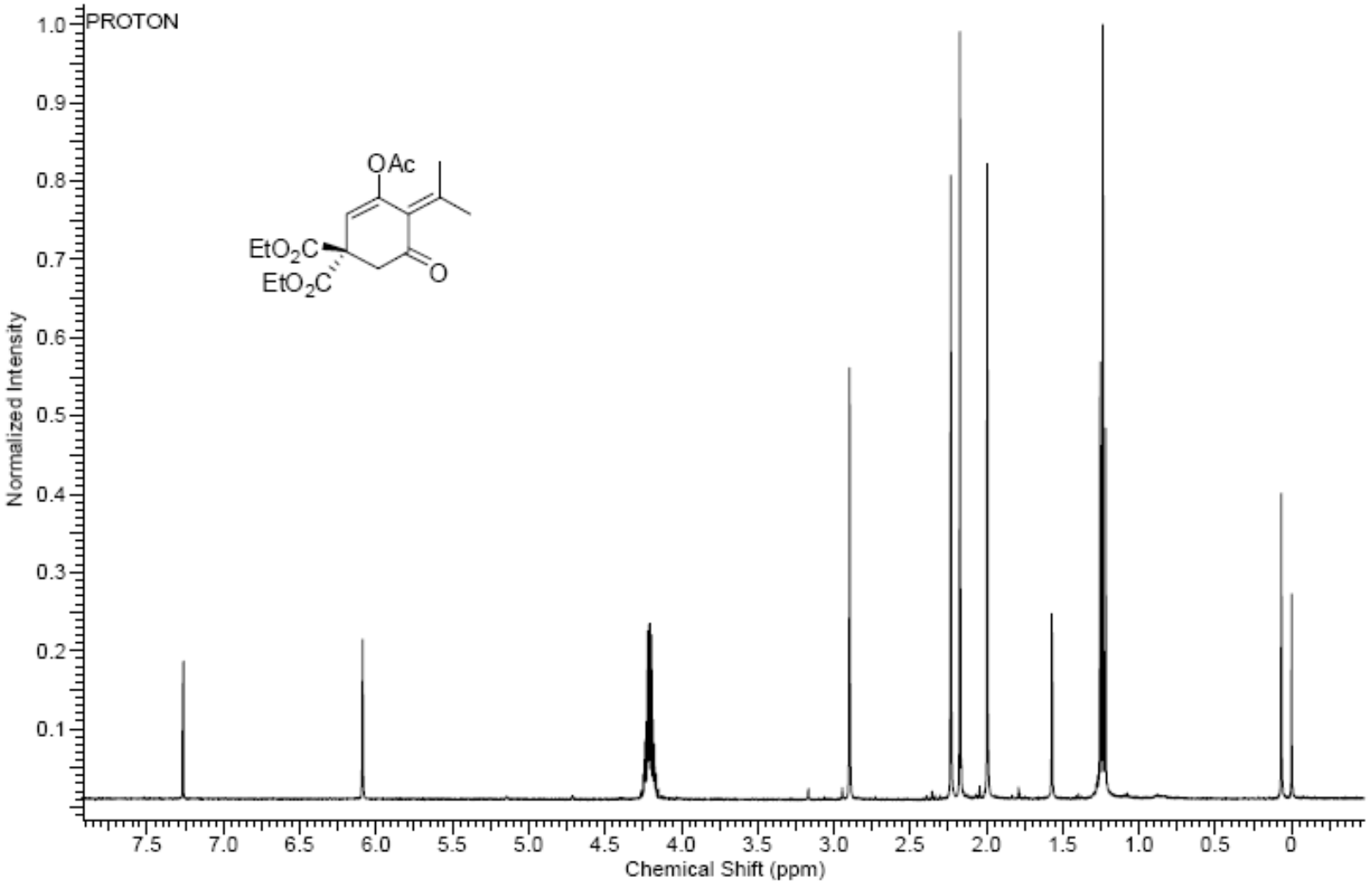
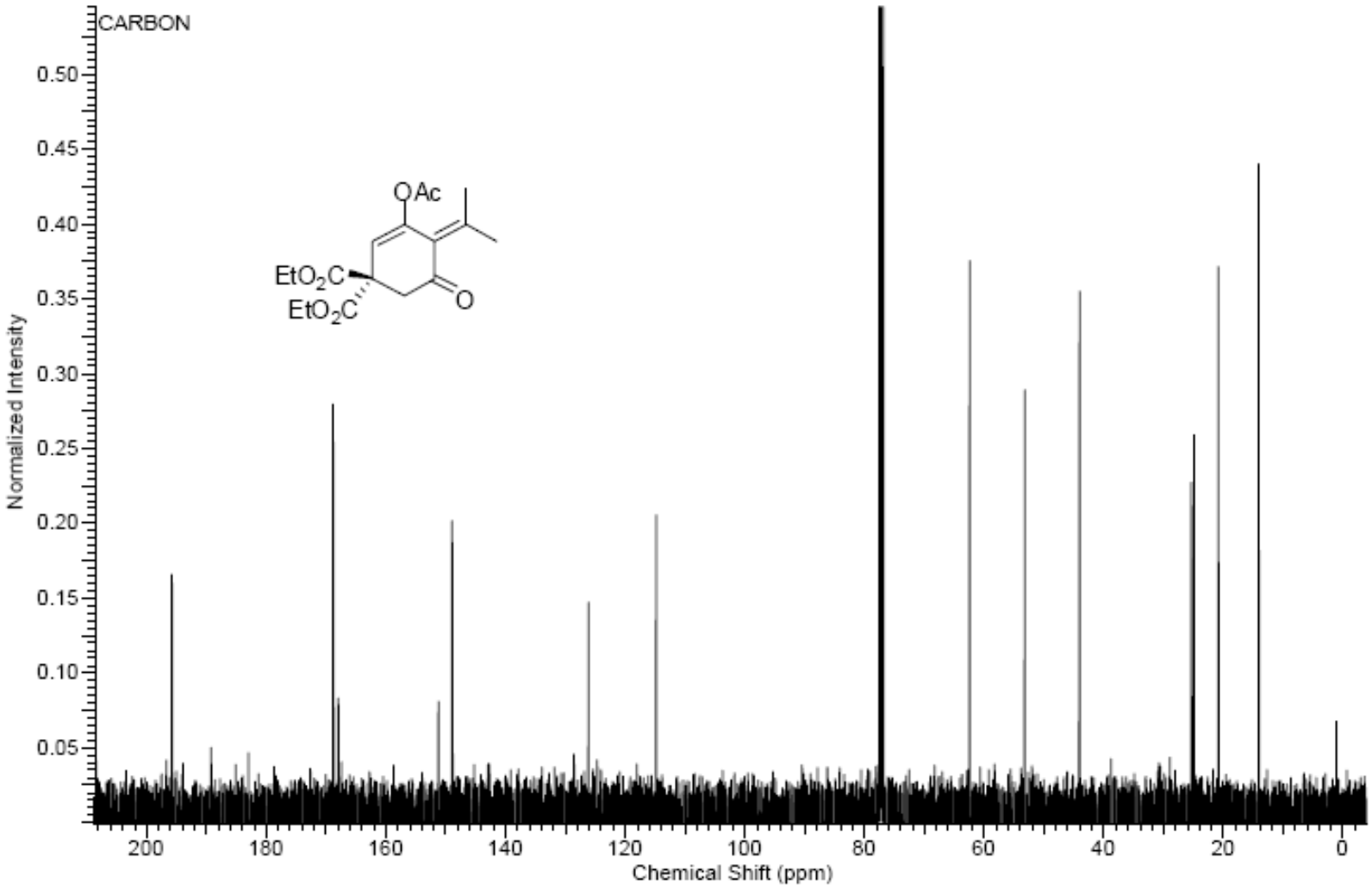
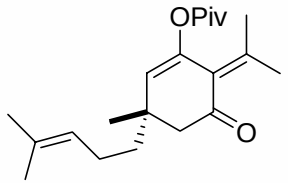
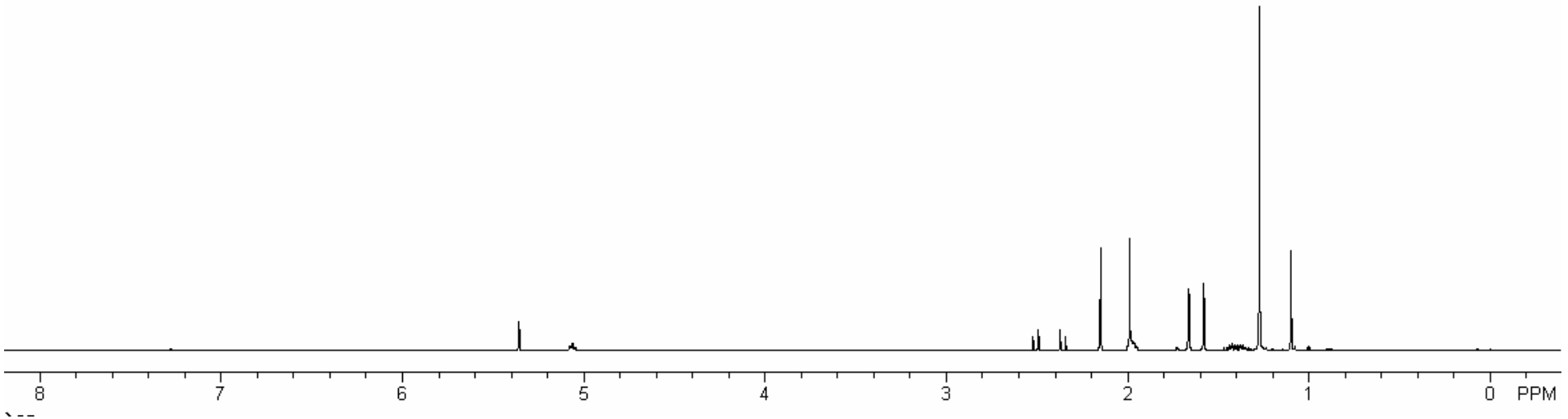
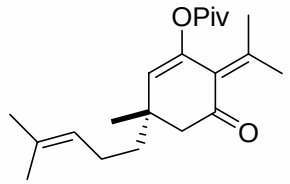
150
100
50
0
PPM

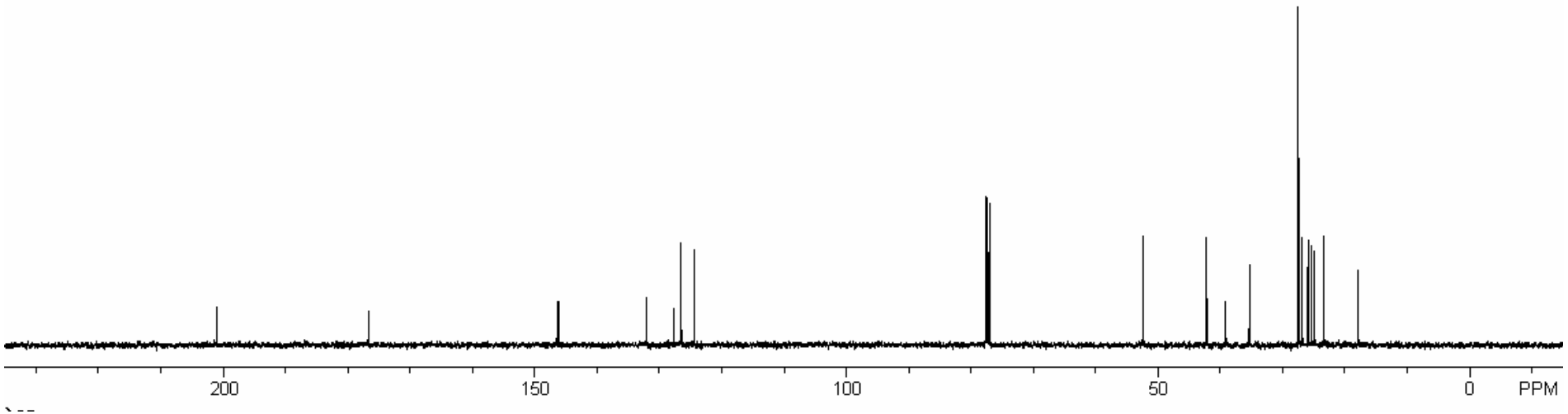

PROTON
OAc
EtO2C
EtO2C
O
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

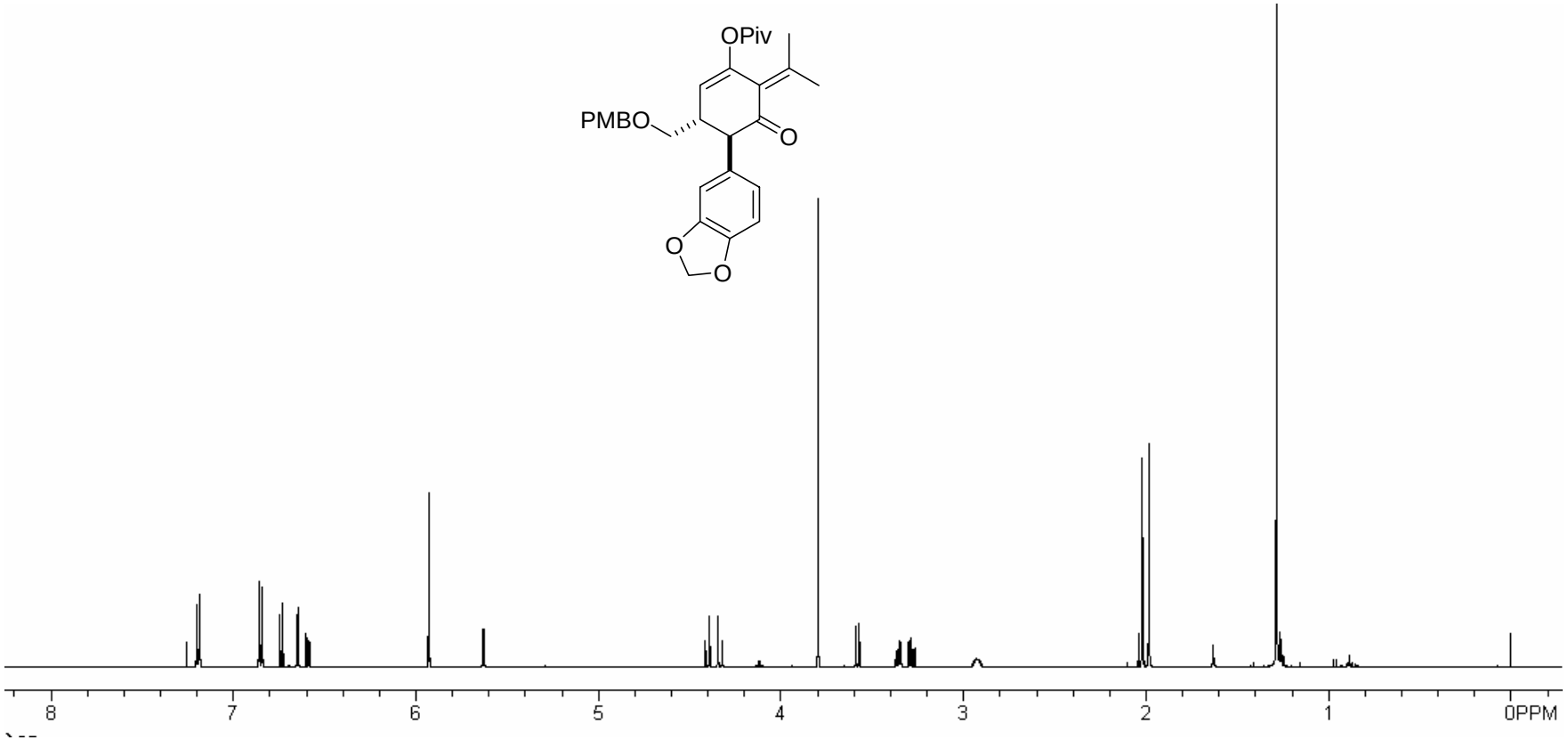

CARBON
Normalized Intensity
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
OAc
EtO2C
EtO2C
O
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

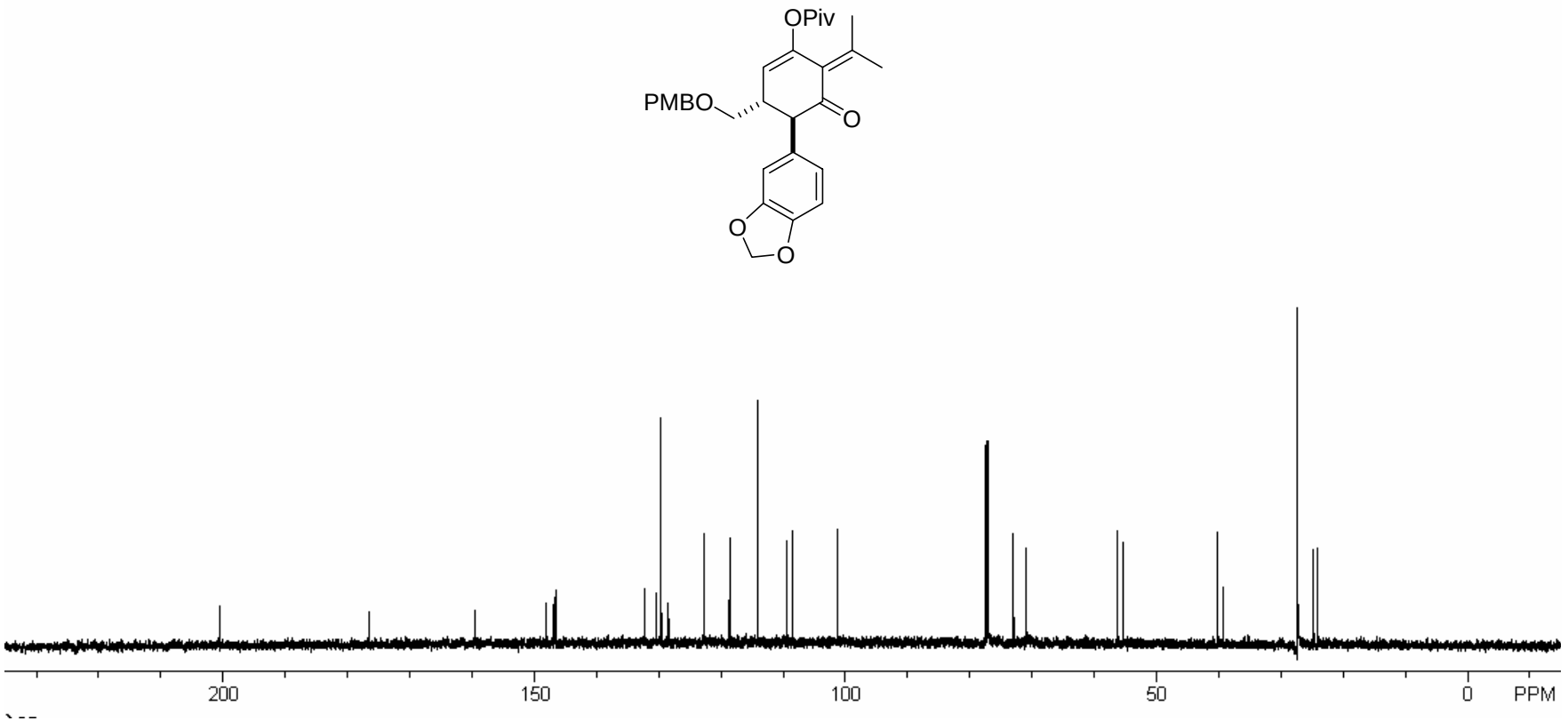

OPiv
O


8
7
6
5
4
3
2
1
0
PPM


OPiv
O


200
150
100
50
0
PPM


OPiv
PMBO
O
O
O
8
7
6
5
4
3
2
1
0PPM


OPiv
PMBO
O
O
O
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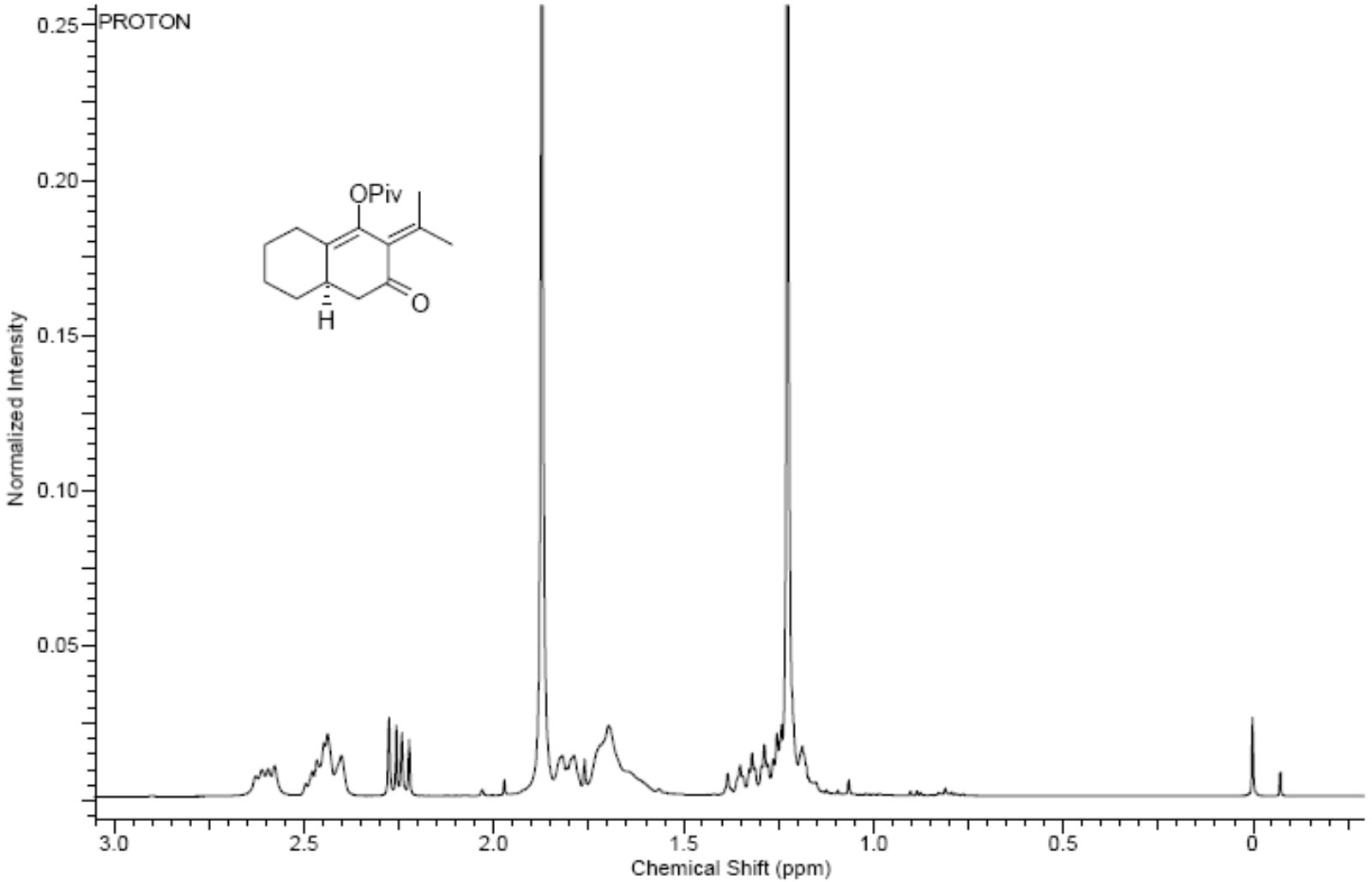
150
100
50
0
PPM


PROTON
OPiv
O
H
0.25
0.20
0.15
0.10
0.05
Normalized Intensity
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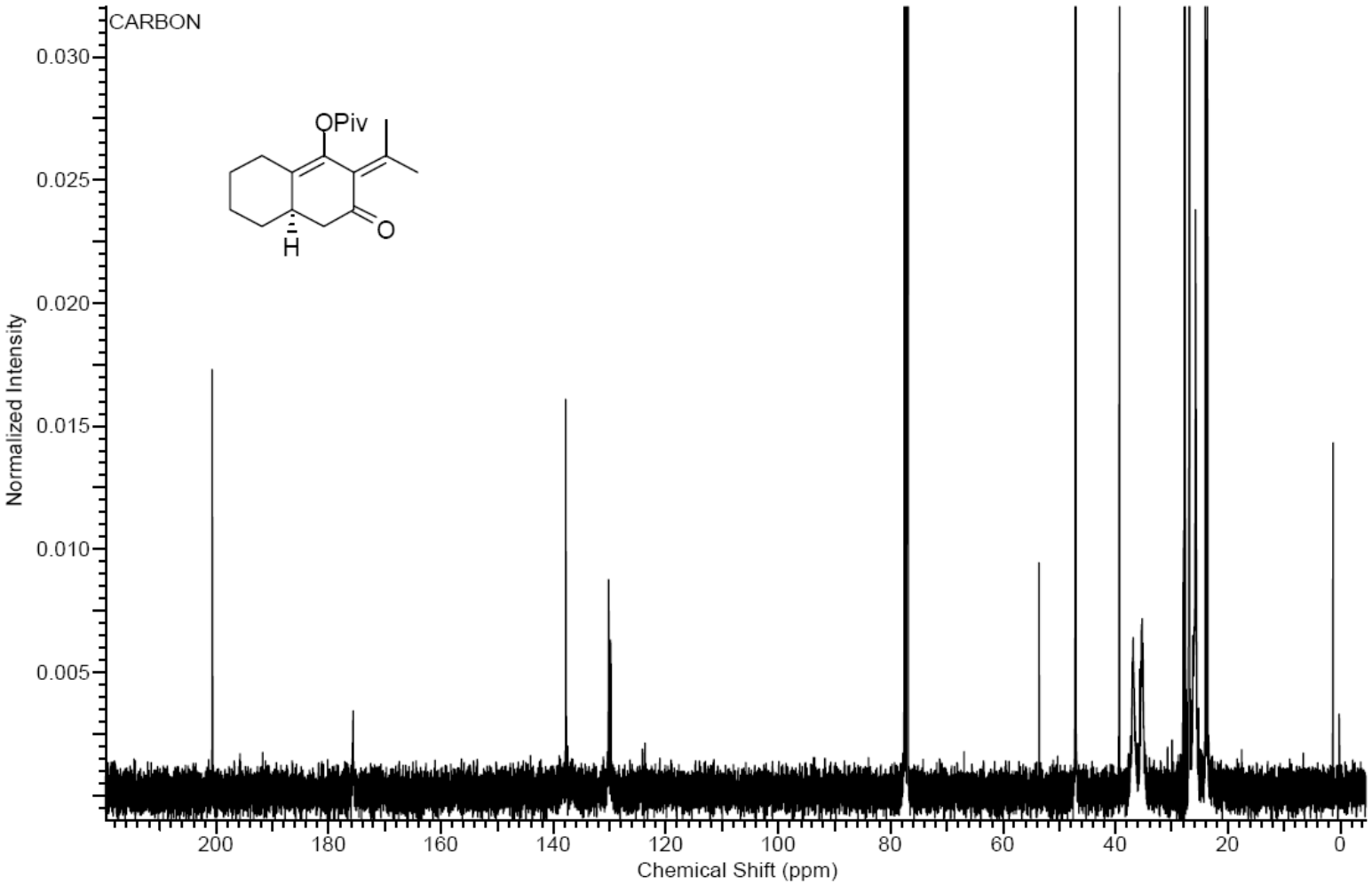
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
OPiv
O
H
Normalized Intensity
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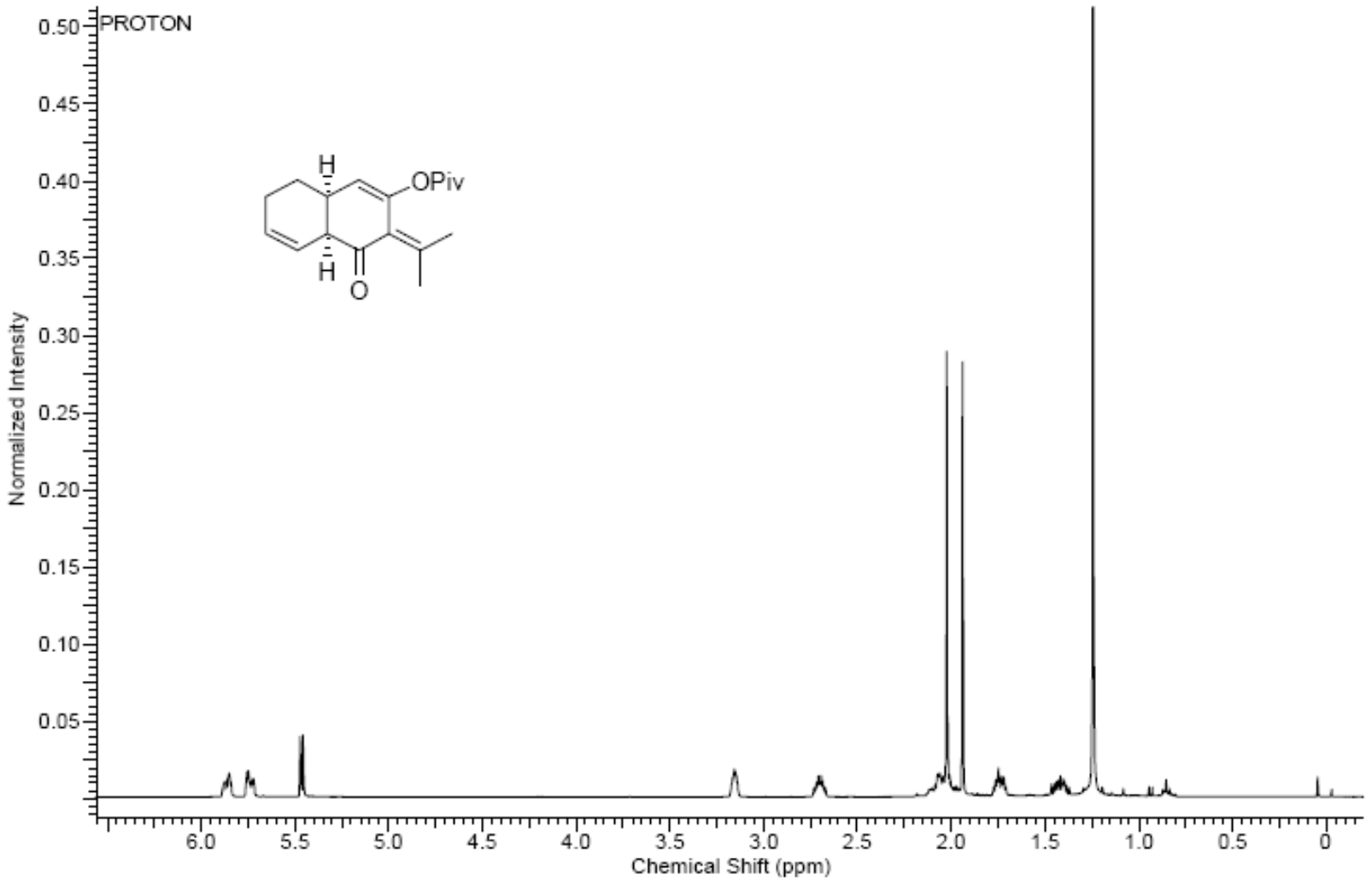
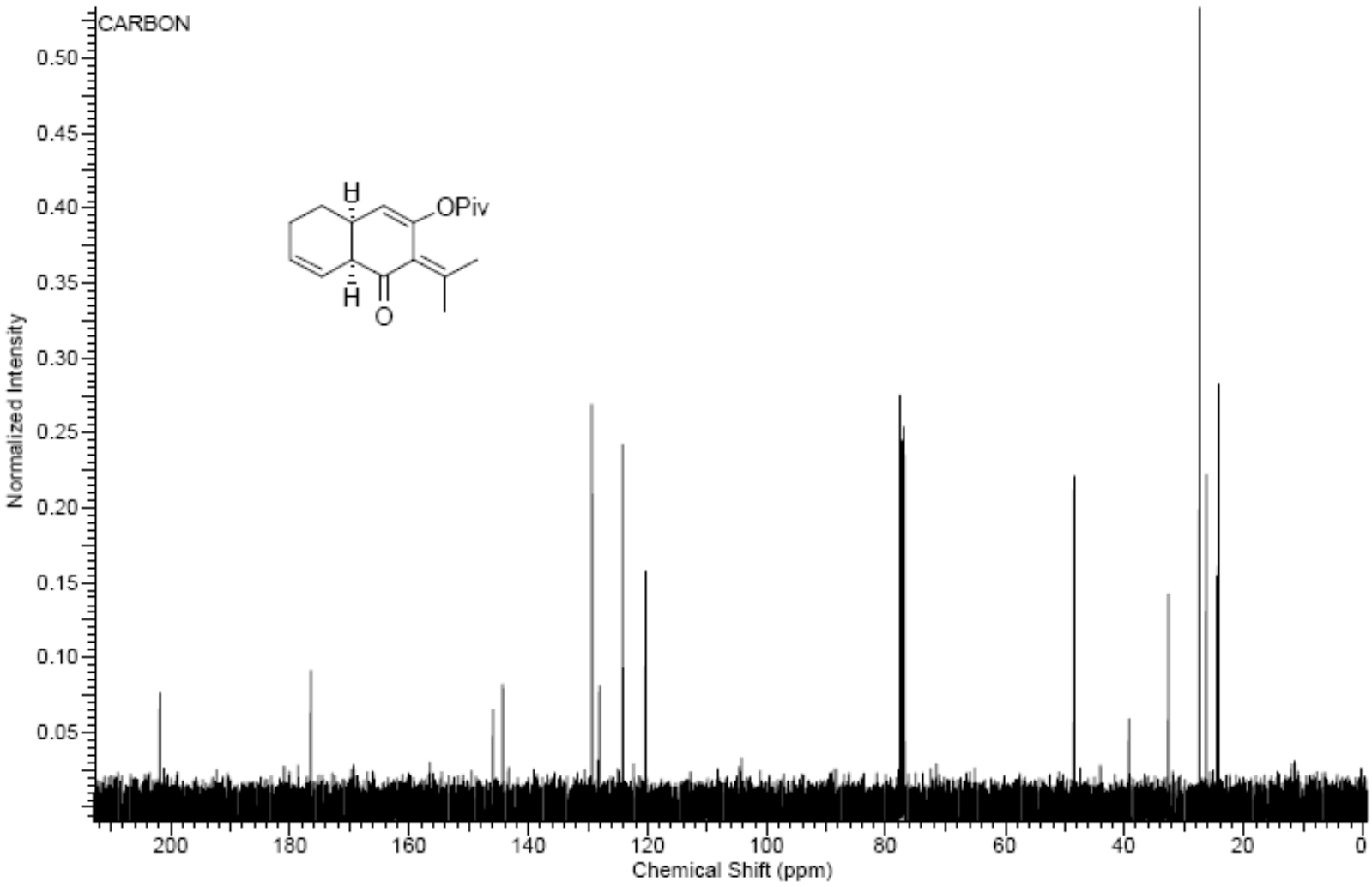
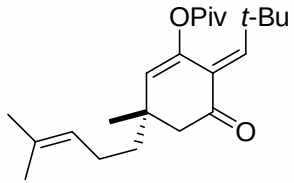
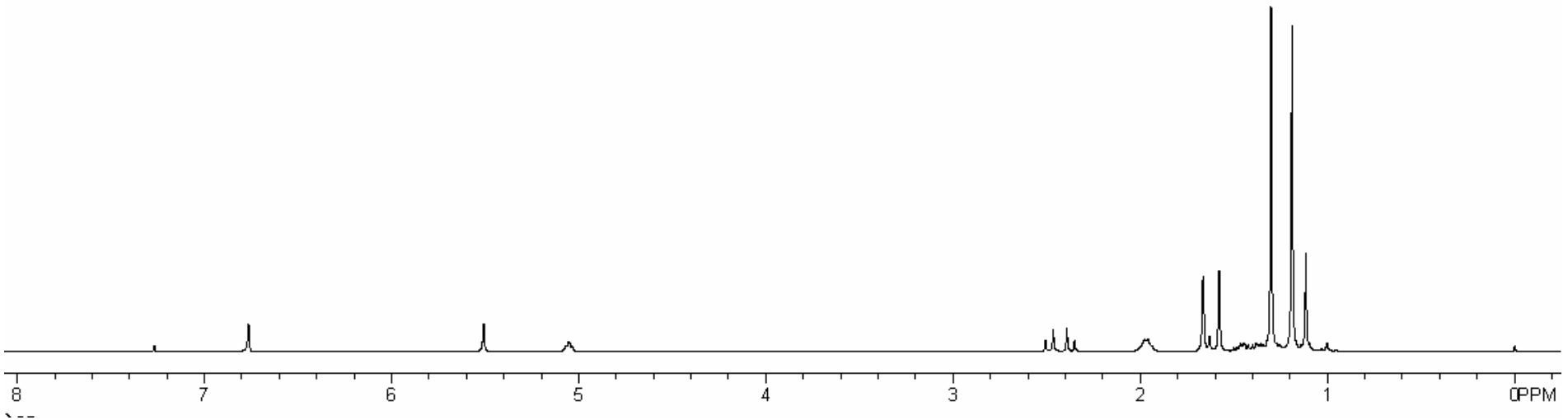
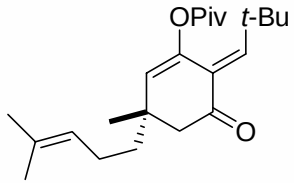
0.025
0.020
0.015
0.010
0.005
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

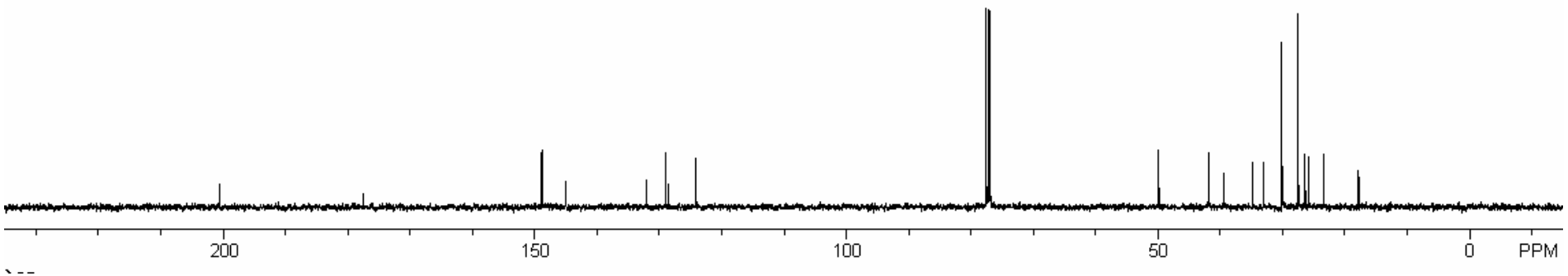

PROTON
H
OPiv
H
O
Normalized Intensity
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


CARBON
Normalized Intensity
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
H
OPiv
H
O
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


OPiv
t-Bu
O


8
7
6
5
4
3
2
1
0PPM


OPiv
t-Bu
O


200
150
100
50
0
PPM