Enantioselective Synthesis of α-tertiary Hydroxy Aldehydes by Palladium-Catalyzed Asymmetric Allylic Alkylation of Enolates

Barry M. Trost*, Jiayi Xu and Markus Reichle

Department of Chemistry, Stanford University, Stanford, California 94305-5080. bmtrost@stanford.edu

Supplemental Information

Experimental

General

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glasswares with magnetic stirring, unless otherwise indicated. 1,4-Dioxane for Pd-catalyzed reactions were freshly distilled from sodium. Solvents for other reactions were from J. C. Meyer's Solvent Purification System. Tris(dibenzylideneacetone)palladium(0) monochloroform complex, $Pd_2dba_3•CHCl_3$ was prepared by the procedure of Ibers.[1] Ligands **L** were prepared by literature procedures[2,3] All other reagents were used as obtained unless otherwise noted.

Flash Chromatography was performed with EM Science silica gel (0.040-0.063µm grade). Analytical thin-layer chromatography was performed with 0.25 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Melting points were obtained on a Thomas-Hoover apparatus in open capillary tubes and are uncorrected. Kugelrohr distillations were performed on a Büchi GKR-50 glass tube oven. Proton nuclear magnetic resonance (^{1}H-NMR) data were acquired on a Mercury 400 (400 MHz) or on a Varian Unity Inova-500 (500 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, in parts per million (ppm) downfield from tetramethylsilane. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; p, pentet, m, multiplet, br, broad. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) data were acquired at 100 MHz on a Mercury 400 or at 125 MHz on a Varian Unity Inova 500 spectrometer. Chemical shifts are reported in ppm relative to the center line of a triplet at 77.1 ppm for chloroform-*d.* Infrared (IR) data were recorded as films on sodium chloride plates or a potassium bromide (KBr) pellets on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm^{-1}). Elemental analyses (Anal.) were performed by M.-H.-W. Laboratories of Pheonix, AZ. Chiral GC analyses were performed on a HP 6890 series GC system using a Cyclosil B chiral column. GC analyses were performed on a HP 6850 series GC system using a Agilent Technologies HP-1 GC column (30 m length, 0.32 mm I.D., 0.25 µm film). Chiral HPLC analyses were performed on a Themo Separation Products Spectra Series P-100 or 200 and UV100 (254 nm) using Chiralcel® columns (OD-H, OB-H, OJ, AD, As, or OC) eluting with heptane / *iso*-propanol mixtures indicated. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm cells and the sodium D line (589 nm) at ambient temperature in the solvent and concentration indicated.

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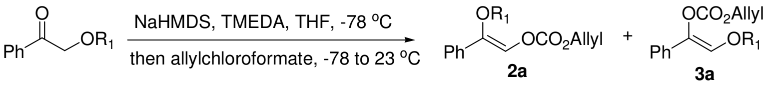
[1] Ukai, T.; Kawazura, H.; Ishii, Y.; Bonnet, J. J.; Ibers, J. A. *J. Organometallic Chem.* **1974**, *65*, 253-266.
[2] Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327-9343.
[3] Trost, B. M.; Bunt, R. C.; Lemoine, R. C.; Calkins, T. L. *J. Am. Chem. Soc.* **2000**, *122*, 5968-5976.

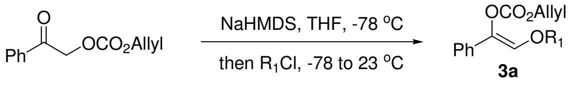
Gereral Procedure for the Preparation of 2a and 3a[5].

Method A:



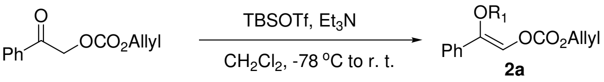
To a clean dry 100 mL flask with a magnetic stirring bar was loaded 1.15 g (6.0 mmol) sodium hexamethyldisilazane (Aldrich, 97%) in a glove box under nitrogen. The flask was cooled in a dry-ice-acetone bath for 5 min and 20 mL dry THF was transferred slowly to this flask with a syringe. The flask was warmed to 0 °C to make a clear solution and 0.91 mL (6.0 mmol) tetramethylethlenediamine (TMEDA) was added. The solution was cooled to -78 °C again and a solution of ketone (5.0 mmol) in 5 mL THF was added slowly in 5 min. The reaction mixture was stirred for 1 h and was added 0.64 mL (6 mmol) allyl chloroformate at -78 °C. After 5 min at -78 °C the reaction was taken out from the bath and allowed to warm to room temperature. The reaction was quenched with 5% KH_2PO_4 aqueous solution and transferred into a separation funnel. Diluted with 50 mL diethyl ether and washed with brine once, the organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The product was purified with column chromatography on silica gel eluted with petroleum ether / diethyl ether.

Method B:



The same procedure as Method A but no TMEDA was added and quenching with R_1Cl instead of allyl chloroformate.

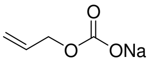
Method C:



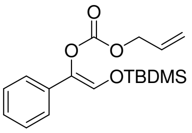
To a clean dry flask under argon was added keto carbonate 3 mmol, 20 mL CH_2Cl_2 and 0.65 mL triethylamine (3.6 mmol). The flask was cooled at -78 °C and was added 0.50 mL TBSOTf. The reaction was stirred at -78 °C for 10 min and was allowed to warm to room temperature. The reaction was monitored by TLC. The reaction solution was transferred with diethyl ether into a separation funnel and washed with water and then brine. Organic layer was dried over magnesium sulfate, filtrated and concentrated. The residue was purified by silica gel column chromatography.

Gereral Procedure for the Pd-catalyzed Reaction of Carbonates.

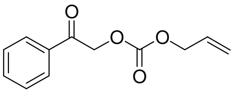
Two test tubes were connected with a double-end needle. One test tube was loaded with 7.8 mg (0.75% mmol) $Pd_2(dba)_3CHCl_3$ and 1.65% mmol ligand and the other one was loaded with 0.30 mmol carbonate. The system was evacuated and flushed with argon three times at which point 1.5 mL dioxane (freshly distilled from sodium) was added to both of the test tubes. After stirred for 20 min the orange solution of catalyst was transferred into the test tube containing carbonate substrate. In most cases, the color of the reaction solution turned to light yellow within a few minutes and then turned back to orange in different time depending on the choice of ligand, substrate, solvent and temperature, indicating the completion of the reaction. The reaction mixture was concentrated *in vacuo* and purified by column chromatography on silica gel eluted with diethyl ether in petroleum ether



Sodium allyl carbonate: A clean dry 250 mL three neck flask was charged with 2.0 g NaH (60%, 50 mmol) and 50 mL THF under nitrogen. To the suspension was added 3.4 mL allyl alcohol and stirred for 15 min at room temperature. The suspension was cooled to -15 °C and a stream of carbon dioxide from the vapor of dry ice was bubbled through the reaction mixture for 30 min. The stream of carbon dioxide was stopped and the reaction flask was allowed to warm to room temperature. The solid was filtrated and washed with 50 mL diethyl ether twice. The solid was further dried by azeotropic distilled with 50 mL benzene and put on high vacuum overnight. 3.7 g white solid (60%) was isolated with greater than 95% purity by proton NMR. ^{1}H NMR (400 MHz, D_2O): δ = 5.86 (m, 1H), 5.14 (d, *J* = 18.1Hz, 1H), 5.04 (d, *J* = 10.4Hz, 1H), 3.96 (d, *J* = 4.0Hz, 2H).

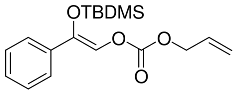


Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-phenyl-vinyl ester (3a-2): Method B: starting from 760 mg 2-(tert-butyldimethylsilyloxy)acetophenone (3.45 mmol), 963 mg product was obtained (83%) as colorless oil. R_f = 0.51 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3059 (m), 2931 (s), 2859 (s), 1766 (s), 1668 (s), 1472 (m), 1448 (m), 1240 (s), 1177 (s), 991 (s), 936 (s), 828 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 4H), 7.15 (m, 1H), 6.68 (s, 1H), 6.00 (m, 1H), 5.33 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.20 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.63 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 0.99 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.8, 134.7, 133.3, 131.5, 130.6, 128.6, 127.3, 123.2, 119.0, 68.9, 25.5, 18.2, -5.21. Anal. Calcd. for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83; Found: C, 64.74; H, 7.68. The structure was further confirmed by HMBC and NOE experiment.

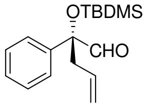


Carbonic acid allyl ester 2-oxo-2-phenyl-ethyl ester: Method I: 1.36 g 2-hydroxyacetophone (10 mmol) was dissolved in 20 mL dichloromethane and was added 1 mL pyridine. The solution was cooled in an ice-water bath and was added 1.28 mL allylchloroformate (12 mmol) dropwise. The reaction solution was stirred for 30 min and was transferred into a separation funnel diluted with 50 mL diethyl ether. It was washed with water twice and brine once. The organic layer was dried over anhydrous magnesium sulfate and dried in *vacuo*. The residue was purified by silica gel column chromatograph eluted with 10 to 15% ethyl acetate in petroleum ether in 1.88 g yield (85%) as a colorless oil.

Method II: 1.99 g 2-bromoacetophone (10 mmol) and 1.24 g sodium allyl carbonate was stirred in 20 mL DMF at room temperature overnight. The reaction mixture was transferred into a separation funnel and diluted with 60 mL water. The aqueous layer was extracted with diethyl ether 40 mL three times. The organic layer was combined and washed with water 50 mL three times and brine once. It was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph eluted with 10 to 15% ethyl acetate in petroleum ether in 1.32 g (60%) as a colorless oil. R_f = 0.52 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3066 (w), 2945 (m), 1756 (s), 1705 (s), 1598 (m), 1451 (m), 1423 (m), 1376 (s), 1277 (s), 1226 (s), 960 (s), 759 (s), 690 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.63 (m, 1H), 7.50 (m, 2H), 5.98 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.38 (s, 2H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.71 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 154.8, 134.1, 134.0, 131.3, 129.0, 127.8, 119.2, 69.1, 68.7. Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49; Found: C, 65.65; H, 5.61.

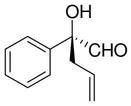


Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-vinyl ester (2a-1): Method C; starting from 1.88 g carbonic acid allyl ester 2-oxo-2-phenyl-ethyl ester (3.45 mmol), 963 mg product was obtained (83%) as colorless oil. R_f = 0.62 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3133 (w), 2931 (s), 2859 (s), 1760 (s), 1667 (m), 1472 (m), 1446 (m), 1344 (s), 1240 (s), 1162 (s), 1086 (s), 1028 (s), 783 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.43 (m, 2H), 7.25 (m, 3H), 7.08 (s, 1H), 5.90 (m, 1H), 5.35 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.25 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.67 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.7, 139.4, 135.7, 131.3, 128.3, 128.2, 125.2, 121.5, 118.9, 68.9, 25.9, 18.6, -4.3. Anal. Calcd. for $C_{18}H_{26}O_4Si$: C, 64.64; H, 7.83; Found: C, 64.81; H, 7.82. The structure was further confirmed by HMBC and NOE experiment.

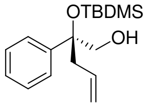


(*S*)-(–)-2-(tert-butyldimethylsilyloxy)-2-phenylpent-4-enal (1a-1): Starting from 100 mg **3a-2** (0.3 mmol), and following the procedure of palladium catalyzed decarboxylation alkylation, 83.4 mg product was isolated (96%); Colorless oil. R_f = 0.66 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -95.3 (c, 1.25; $CHCl_3$, 92% ee); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 6.95 min (minor), t_2 = 8.51 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3079 (w), 2931 (s), 2858 (s), 1732 (s), 1472 (m), 1448 (m), 1259 (s), 1149 (s), 1074 (s), 778 (s), 699 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.55 (s, 1H), 7.5-7.2 (m, 5H), 5.60 (m, 1H), 5.01 (m, 2H), 3.01 (ddt, J_1 = 15.3 Hz, J_2 = 7.2 Hz, J_3 = 1.4 Hz, 1H), 2.71 (ddt, J_1 = 15.3 Hz,

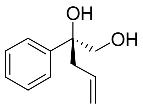
J_2 = 6.4 Hz, J_3 = 1.2 Hz, 1H), 1.01 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 138.5, 132.2, 128.6, 127.9, 126.4, 118.8, 84.6, 41.3, 26.1, 18.8, -2.2. HRMS (EI): $[M]^+$ calcd. For $C_{17}H_{26}O_2$, 290.1702; Found: 290.1701.



(*S*)-(+)-2-Hydroxy-2-phenyl-pent-4-enal:[4] 83 mg **1a-1** (0.28 mmol) in 2 mL THF was treated with 0.35 mL 1.0 M TBAF in THF and was stirred for 5 min. Most solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography eluted with 5% ethyl acetate in petroleum ether to afford 14.4 mg colorless oil (29%). R_f = 0.58 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{22}$ = +123 (c, 1.4; $CHCl_3$, 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3492 (br, s), 3075 (w), 2918 (w), 2835 (w), 1727 (s), 1493 (w), 1448 (m), 1344 (m), 1151 (w), 1105 (m), 995 (m), 923 (m), 758 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.50 (d, J = 0.9 Hz, 1H), 7.5-7.1 (m, 5H), 5.62 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 6.9 Hz, 1H), 5.09 (m, 2H), 3.62 (d, J = 1.1 Hz, 1H), 2.75 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.9, 138.0, 131.2, 128.9, 128.2, 125.9, 120.3, 81.1, 41.6.



(*S*)-(+)-2-(*tert*-Butyl-dimethyl-silanyloxy)-2-phenyl-pent-4-en-1-ol: 77 mg **1a-1** (0.26 mol) in 3 mL methanol at 0 °C was treated with 24 mg sodium borohydride in portions. The reaction mixture was stirred for 10 min and quenched with pH 7 phosphate buffer. It was extracted with 30 mL diethyl ether and the organic layer was dried over magnesium sulfate. After filtration and concentration the residue was purified with silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to afford 68 mg colorless oil (90%). R_f = 0.23 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = +13.5 (c, 2.58; $CHCl_3$, 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3455 (m), 3075 (w), 2956 (s), 2930 (s), 2857 (s), 1641 (w), 1472 (m), 1446 (m), 1253 (s), 1145 (m), 1114 (m), 1076 (s), 995 (m), 914 (m), 836 (s), 776 (s), 701 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35 (m, 2H), 7.26 (m, 2H), 7.17 (m, 1H), 5.55 (ddt, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 6.9 Hz, 1H), 4.92 (m, 2H), 3.80 (dd, J_1 = 11.4 Hz, J_2 = 5.8 Hz, 1H), 3.68 (dd, J_1 = 11.4 Hz, J_2 = 7.3 Hz, 1H), 2.56 (m, 2H), 1.50 (dd, J_1 = 7.2 Hz, J_2 = 5.8 Hz, 1H), 0.87 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.5, 133.7, 128.2, 127.1, 126.4, 118.0, 80.2, 69.5, 44.0, 26.2, 18.9, -2.2, -2.3.



(*S*)-(–)-2-Phenyl-pent-4-ene-1,2-diol:[4] 50 mg 2-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-pent-

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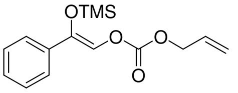
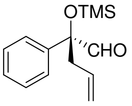
[4] Agami, C.; Couty, F.; Lequesne, C. *Tetrahedron* **1995**, *51*, 4043.

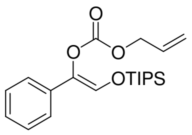
4-en-1-ol (0.17 mmol) in 2 mL THF was treated with 0.34 mL 1.0 M TBAF in THF. The reaction was stirred for 10 min at room temperature and quenched with pH 7 phosphate buffer. It was extracted with diethyl ether. The organic layer was dried over magnesium sulfate and was concentrated *in vacuo*. The residue was purified with 30% ethyl acetate in petroleum ether to afford 28.2 mg (93%) colorless oil. R_f = 0.19 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{24}$ = -45.2 (c, 1.2; $CHCl_3$, 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3418 (s), 3074 (w), 3028 (w), 2932 (w), 1641 (w), 1495 (w), 1447 (m), 1268 (w), 1068 (s), 1000 (m), 917 (m), 702 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (m, 2H), 7.37 (m, 2H), 7.27 (m, 1H), 5.60 (dddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 8.5 Hz, J_3 = 6.3 Hz, 1H), 5.12 (m, 2H), 3.77 (d, J = 11.3 Hz, 1H), 3.69 (d, J = 11.3 Hz, 1H), 2.66 (m, 2H), 3.2-1.8 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 143.3, 132.9, 128.5, 127.3, 125.5, 119.7, 76.3, 70.1, 43.0.



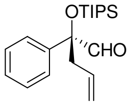
Carbonic acid allyl ester (*Z*)-2-phenyl-2-trimethylsilanyloxy-vinyl ester (**2a-2**): Method C: Starting from 660 mg carbonic acid allyl ester 2-oxo-2-phenyl-ethyl ester (3.0 mmol), 672 mg product was obtained (77%) as colorless oil. R_f = 0.50 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3125 (w), 2959 (s), 1759 (s), 1666 (m), 1447 (m), 1389 (s), 1345 (s), 1239 (s), 1162 (m), 1088 (m), 1028 (m), 959(m), 886 (m), 846 (s), 756 (m), 694 cm^{-1} (m); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.48 (s, 1H), 7.43 (m, 2H), 7.05 (m, 3H), 5.58 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.6 Hz, 1H), 5.07 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 4.91 (dq, J_1 = 10.4 Hz, J_2 = 1.4 Hz, 1H), 4.38 (dt, J_1 = 5.6 Hz, J_2 = 1.4 Hz, 2H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ = 152.8, 139.4, 135.8, 131.6, 128.6, 127.9, 124.9, 122.0, 118.5, 68.7, 0.46. HRMS (EI): $[M]^+$ calcd. For $C_{15}H_{20}O_4Si$, 292.1131; Found: 292.1136. The structure was further confirmed by HMBC experiment.



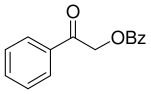
(*S*)-(–)-2-Phenyl-2-trimethylsilanyloxy-pent-4-enal (**1a-2**): Starting from 88 mg **2a-3**, and following the procedure of palladium catalyzed decarboxylation alkylation, 76.3 mg product was isolated (100%); Colorless oil. R_f = 0.56 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{25}$ = -58.5 (c, 2.2; CH_2Cl_2, 92% ee); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2957 (m), 2803 (w), 1738 (s), 1642 (w), 1492 (w), 1448 (m), 1253 (s), 1152 (m), 1076 (m), 994 (m), 918 (m), 844 (s), 756 (s), 700 cm^{-1} (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 9.39 (s, 1H), 7.32 (m, 2H), 7.11 (m, 2H), 7.03 (m, 1H), 5.65 (ddt, J_1 = 17.1 Hz, J_2 = 10.3 Hz, J_3 = 6.9 Hz, 1H), 4.92 (m, 2H), 2.80 (ddt, J_1 = 14.9 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H), 2.62 (ddt, J_1 = 14.9 Hz, J_2 = 7.0 Hz, J_3 = 1.2 Hz, 1H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6): δ = 199.0, 139.4, 132.5, 128.7, 127.9, 126.5, 118.7, 85.2, 42.0, 2.4. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{13}H_{19}OSi$, 219.1205; Found: 219.1204. The absolute configuration was determined by desilylation with HF-water in methanol and comparing the optical rotation of the hydroxy aldehyde ($[\alpha]_D^{24}$ = +129.9 (c, 1.5; CH_2Cl_2)) with (*S*)-2-hydroxy-2-phenyl-pent-4-enal.



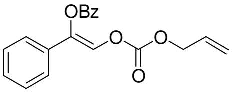
Carbonic acid allyl ester (*Z*)-1-phenyl-2-triisopropylsilanyloxy-vinyl ester (**3a-3**): Method A; starting from 1.1 g 2-(triisopropylsilyloxy)acetophenone (3.76 mmol), 553 mg product was obtained (39%) as colorless oil. R_f = 0.49 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3058 (m), 2946 (s), 2867 (s), 1766 (s), 1668 (s), 1464 (s), 1366 (m), 1302 (s), 1245 (s), 1184 (s), 1071 (m), 992 (s), 922 (m), 882 (s), 764 (s), 690 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (m, 4H), 7.21 (tt, J_1 = 7.2 Hz, J_2 = 1.5 Hz, 1H), 6.84 (s, 1H), 5.96 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.39 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.27 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.69 (dt, J_1 = 5.8 Hz, J_2 = 1.5 Hz, 2H), 1.22 (m, 3H), 1.11 (d, J = 6.9 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.7, 134.2, 133.4, 131.5, 131.1, 128.6, 127.2, 123.1, 119.0, 69.0, 17.6, 11.9. HRMS (EI): M^+ calcd. For $C_{21}H_{32}O_4Si$, 376.2070; Found: 376.2054. The structure was further confirmed by HMBC experiment.



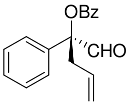
(*S*)-(–)-2-Phenyl-2-triisopropylsilanyloxy-pent-4-enal (**1a-3**): Starting from 75 mg **3a-4** (0.2 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 45 mg product was isolated (67%) as colorless oil. R_f = 0.61 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{22}$ = -81.8 (c, 3.9; CH_2Cl_2, 91% ee); HPLC (Chiralcel® OD-H column; 2000:1 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 6.283 min (minor), t_2 = 7.169 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3078 (m), 2945 (s), 2868 (s), 2715 (w), 1732 (s), 1643 (w), 1493 (m), 1463 (s), 1448 (s), 1384 (m), 1258 (s), 1150 (s), 996 (s), 957 (m), 917 (s), 882 (s), 759 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.63 (s, 1H), 7.43-7.25 (m, 5H), 5.58 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 6.9 Hz, 1H), 4.98 (m, 2H), 2.97 (ddt, J_1 = 15.0 Hz, J_2 = 7.0 Hz, J_3 = 1.8 Hz, 1H), 2.68 (ddt, J_1 = 15.0 Hz, J_2 = 6.7 Hz, J_3 = 1.2 Hz, 1H), 1.16 (m, 3H), 1.09 (d, J = 5.2 Hz, 18 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 138.7, 132.3, 128.5, 127.8, 126.3, 118.7, 84.8, 42.4, 18.5, 13.8. HRMS (EI): $[M-CH(CH_3)_2]^+$ calcd. For $C_{17}H_{25}O_2Si$, 289.1624; Found: 289.1646. The absolute configuration was determined by desilylation with TBAF in THF and comparing the optical rotation of the hydroxy aldehyde with (*S*)-2-hydroxy-2-phenyl-pent-4-enal.



Benzoic acid 2-oxo-2-phenyl-ethyl ester[5]: hydroxyacetophenone 1.36 g (10 mmol), 122 mg DMAP (1 mmol) was dissolved in 10 mL DCM and cooled to 0 °C. To this solution was added 2 mL pyridine and 1.75 mL benzoyl chloride (15 mmol). 100 mL diethyl ether was added to the reaction and transferred into a separation funnel. Washed with 100 mL water twice and brine once, the organic layer was dried over magnesium sulfate. After filtration and concentration, the crude produce was recrystallized from ethanol twice to give a slight yellow solid 1.4 g (58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (m, 2H), 7.98 (m, 2H), 7.61(m, 2H), 7.50 (m, 4H), 5.59 (s, 2H). The ^{1}HNMR spectrum is identical to the literature reported.



Benzoic acid 2-allyloxycarbonyloxy-1-phenyl-vinyl ester (**2a-4**): Method A; Starting from 1.2 g benzoic acid 2-oxo-2-phenyl-ethyl ester (5 mmol), 1.59 g of white solid was obtained (98%). M.p. = 61-63 °C; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3109 (m), 1748 (s), 1684 (m), 1601 (m), 1451 (s), 1366 (s), 1262 (s), 1220 (s), 1166 (s), 1085 (s), 1068 (s), 1026 (s), 953 (s), 760 (s), 708 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22 (m, 2H), 7.65 (m, 1H), 7.64 (s, 1H), 7.52 (m, 2H), 7.47 (m, 2H), 7.34 (m, 3H), 5.92 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 6.0 Hz, 1H), 5.37 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.29 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.5, 152.1, 135.3, 133.8, 132.0, 130.8, 130.5, 128.90, 128.88, 128.83, 128.7, 126.9, 124.4, 120.0, 69.6. MS (ESI): $[M+Na]^+$ for $C_{19}H_{16}O_5$, 347.1. Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.36; H, 4.97; Found: C, 70.12; H, 4.78. The structure was further confirmed by HMBC and NOE experiment.



Benzoic acid (*S*)-(–)-1-formyl-1-phenyl-but-3-enyl ester (**1a-4**): Starting from 97.3 mg **2a-5** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 78 mg product was isolated (93%) as colorless oil. R_f = 0.30 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -69.5 (c, 6.8; CH_2Cl_2, 81% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 5.035 min (minor), t_2 = 5.611 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3072 (m), 2982 (w), 2819 (m), 2711 (w), 1732 (s), 1711 (s), 1643 (w), 1601 (m), 1494 (m), 1451 (s), 1317 (s), 1293 (s), 1251 (s), 1178 (m), 1109 (s), 1070 (s), 1026 (s), 994 (m), 923 (m), 843 (m), 760 (m), 712 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.59 (s, 1H), 8.17 (m, 2H), 7.66 (tt, J_1 = 7.5 Hz, J_2 = 1.4 Hz, 1H), 7.54 (m, 4H), 7.45 (m, 2H), 7.38 (tt, J_1 = 7.3 Hz, J_2 = 1.4 Hz, 1H), 5.54 (dddd, J_1 = 18.2 Hz, J_2 = 10.1 Hz, J_3 = 7.9 Hz, J_4 = 6.4 Hz, 1H), 5.00 (m, 2H), 3.31 (ddt, J_1 = 15.3 Hz, J_2 = 8.1 Hz, J_3 = 0.9 Hz, 1H), 3.20 (ddt, J_1 = 15.1 Hz, J_2 = 6.4 Hz, J_3 = 1.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.5, 165.6, 134.2, 133.9, 130.9, 130.0, 129.2, 129.0, 128.8, 128.6, 126.2, 119.8, 88.1, 38.3. MS (ESI): $[M+Na]^+$ 303.1; HRMS (EI): $[M\text{-}CHO]^+$ calcd. For $C_{17}H_{15}O_2$,

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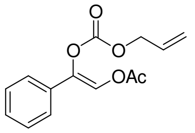
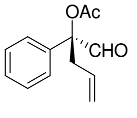
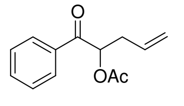
[5] Banerjee, A.; Falvey, D. E.; *J. Org. Chem.* **1997**, *62*, 6245-6251.

251.1072; Found: 251.1068. The absolute configuration was determined by debenzoylation with potassium carbonate in methanol and comparing the optical rotation of the hydroxy aldehyde ($[\alpha]_D^{23}$ = +80.4 (c, 0.9; CH_2Cl_2)) with (*S*)-(+)-2-hydroxy-2-phenyl-pent-4-enal.



Acetic acid (*Z*)-2-allyloxycarbonyloxy-2-phenyl-vinyl ester (**3a-5**): A clean dry flask was charged with 460 mg NaHMDS (2.4 mmol) in dry box and was cooled to -78 °C. 10 mL dry THF and 0.36 mL TMEDA (2.4 mmol) were added to the flask. 400 mg carbonic acid allyl ester 2-oxo-2-phenyl-ethyl ester (2 mmol) in 2 mL dry THF was added slowly into the base solution and stirred for 1h. To the enolate solution was added 0.17 mL acetyl chloride in one portion. After 5 min, the dry-ice bath was removed and the reaction flask was allowed to warm to room temperature. Ammonium chloride saturated aqueous solution was added and the mixture was transferred with 40 mL diethyl ether to a separation funnel. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration the crude product was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether. 400 mg product was afforded as a colorless oil (76%). R_f = 0.25 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3106 (w), 2951 (w), 1769 (s), 1683 (w), 1448 (m), 1371 (s), 1243 (s), 1198 (s), 1131 (s), 1003 (m), 988 (m), 949 (m), 913 (m), 770 (m), 693 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.72 (s, 1H), 7.45 (m, 2H), 7.35 (m, 3H), 5.97 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.6 Hz, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.32 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.73 (dt, J_1 = 5.8 Hz, J_2 = 1.4 Hz, 2H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9, 152.2, 135.8, 131.7, 131.1, 128.9, 128.8, 125.1, 124.4, 119.4, 69.4, 20.7. $[M]^+$ calcd. For $C_{14}H_{14}O_5$, 262.0841; Found: 262.0829. The structure was further confirmed by HMBC experiment.

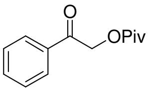




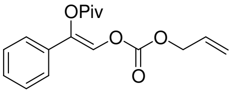
Acetic acid (*S*)-(–)-1-formyl-1-phenyl-but-3-enyl ester (**1a-5**): Starting from 79 mg **3a-6** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 26 mg product was isolated (40%) as colorless oil. R_f = 0.34 (10% ethyl acetate in petroleum ether); $[\alpha]_D^{23}$ = -163.9 (c, 2.0; CH_2Cl_2, 91% ee); HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 7.598 min (major), t_2 = 8.300 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2982 (w), 2819 (w), 2711 (w), 1732 (s), 1643 (w), 1494 (m), 1449 (m), 1371 (s), 1235 (s), 1129 (w), 1057 (m), 1022 (m), 922 (m), 834 (w), 761 (m), 700 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ = 9.44 (s, 1H), 7.42 (m, 4H), 7.34 (m, 1H), 5.47 (dddd, J_1 = 18.4 Hz, J_2 = 10.1 Hz, J_3 = 8.2 Hz, J_4 = 6.1 Hz, 1H), 5.03 (m, 2H), 3.18 (ddt, J_1 = 15.1 Hz, J_2 = 8.2 Hz, J_3 = 1.1 Hz, 1H), 3.08 (ddt, J_1 = 15.1 Hz, J_2 = 6.1 Hz, J_3 = 1.5 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.6, 170.3, 133.9, 131.1, 128.9, 128.6, 126.1, 119.4, 87.6, 38.2, 21.0. MS (ESI):

$[M+H]^+$ 219.1; HRMS (EI): $[M-CHO]^+$ calcd. For $C_{12}H_{13}O_2$, 189.0916; Found: 189.0916. The absolute configuration was determined by deacetylation with potassium carbonate in methanol and comparing the optical rotation of the hydroxy aldehyde ($[\alpha]_D^{25}$ = +119 (c, 0.88; CH_2Cl_2)) with (*S*)-(+)-2-hydroxy-2-phenyl-pent-4-enal.

Acetic acid 1-(1-phenyl-methanoyl)-but-3-enyl ester (**4a-5**): From the same reaction as above 41 mg was isolated from the above reaction (60%) as colorless oil. R_f = 0.28 (10% ethyl acetate in petroleum ether); 21% ee; HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 7.294 min (minor), t_2 = 11.835 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3065 (w), 2982 (w), 1744 (s), 1698 (s), 1621 (m), 1598 (m), 1449 (m), 1371 (m), 1233 (s), 1069 (m), 1002 (m), 923 (m), 769 (w), 700 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.94 (m, 2H), 7.60 (m, 1H), 7.49 (m, 2H), 5.95 (dd, J_1 = 8.3 Hz, J_2 = 4.2 Hz, 1H), 5.82 (dddd, J_1 = 18.4 Hz, J_2 = 10.1 Hz, J_3 = 8.2 Hz, J_4 = 6.1 Hz, 1H), 5.11 (m, 2H), 2.66 (m, 1H), 2.58 (m, 1H), 2.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 194.6, 170.3, 133.9, 131.1, 128.9, 128.6, 126.1, 119.4, 87.6, 38.2, 21.0. MS (ESI): $[M+H]^+$ 219.1, $[M+Na]^+$ 241.1; HRMS (EI): $[M-C_2H_3O]^+$ calcd. For $C_{11}H_{11}O_2$, 175.0759; Found: 175.0755.



2,2-Dimethyl-propionic acid 2-oxo-2-phenyl-ethyl ester[6]: Hydroxyacetophenone 681 mg (5 mmol), was dissolved in 10 mL DCM and cooled to 0 °C. To this solution was added 0.81 mL pyridine (10 mmol) and 0.92 mL pivaloyl chloride (7.5 mmol) and stirred for 4 h. 100 mL diethyl ether was added to the reaction and transferred into a separation funnel. Washed with 100 mL water twice and brine once, the organic layer was dried over magnesium sulfate. After filtration and concentration, the crude produce was purified by silica gel column chromatography eluted with 20-40% diethyl ether gradient to afford 1.12 g product as white crystals (100%). R_f = 0.67 (30% ethyl acetate in petroleum ether); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.61 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.49 (m, 2H), 5.32 (s, 2H), 1.31 (s, 9H). The ^1HNMR spectrum is identical to the literature reported.



2,2-Dimethyl-propionic acid (*Z*)-2-allyloxycarbonyloxy-1-phenyl-vinyl ester (**2a-6**): Method A; Starting from 1.1 g 2,2-dimethyl-propionic acid 2-oxo-2-phenyl-ethyl ester (5 mmol), 1.15 g of white solid was obtained by following the procedure to make enol carbonates (80%). M.p. = 51-52 °C; R_f = 0.22 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3109 (w), 2976 (m), 1761 (s), 1681 (w), 1481 (m), 1448 (m), 1367 (m), 1324 (m), 1277 (s), 1242 (s), 1169 (m), 1108 (s), 955 (m), 758 (m), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (s, 1H), 7.35 (m, 5H), 5.94 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.39 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.71 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 1.39 (s, 9H); ^{13}C

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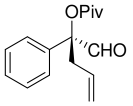
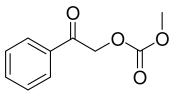
[6] Knochel, P.; Chou, T.-S.; Jubert, C.; Rajagopal, D. *J. Org. Chem.* **1993**, *58*, 588-599.

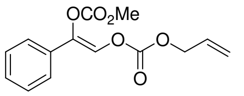
NMR (100 MHz, $CDCl_3$): δ = 175.5, 152.1, 135.6, 132.2, 131.0, 128.8, 126.2, 124.3, 119.5, 69.4, 39.3, 27.2. MS (ESI): $[M+Na]^+$ 327.1; HRMS (EI): $[M-C_5H_9O]^+$ calcd. For $C_{12}H_{12}O_2$, 220.0736; Found: 220.0720. The structure was further confirmed by HMBC and NOE experiment.



2,2-Dimethyl-propionic acid (*S*)-(–)-1-formyl-1-phenyl-but-3-enyl ester (**1a-6**): Starting from 87 mg **2a-7** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 70 mg product was isolated (90%) as white solid. M.p. = 31- 33 °C; R_f = 0.47 (10% diethyl ether in petroleum ether); $[\alpha]_D^{25}$ = -176 (c, 1.9; CH_2Cl_2, 91% ee); HPLC (Chiralcel® OD-H column; 99:1 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 6.946 min (major), t_2 = 7.942 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3078 (w), 2979 (m), 2812 (w), 2707 (w), 1729 (s), 1643 (w), 1479 (m), 1449 (m), 1398 (m), 1293 (m), 1259 (m), 1157 (s), 1132 (s), 1018 (w), 921 (m), 760 (m), 699 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.37 (s, 1H), 7.42 (m, 4H), 7.34 (m, 1H), 5.44 (dddd, J_1 = 18.4 Hz, J_2 = 10.1 Hz, J_3 = 8.2 Hz, J_4 = 6.1 Hz, 1H), 5.02 (m, 2H), 3.18 (ddt, J_1 = 15.1 Hz, J_2 = 8.2 Hz, J_3 = 1.0 Hz, 1H), 3.10 (ddt, J_1 = 15.1 Hz, J_2 = 6.1 Hz, J_3 = 1.5 Hz, 1H), 1.34 (s, 9H); MS (ESI): $[M+H]^+$ 261.2; HRMS (EI): $[M-CHO]^+$ calcd. For $C_{15}H_{19}O_2$, 231.1385; Found: 231.1395.



Carbonic acid methyl ester 2-oxo-2-phenyl-ethyl ester[7]: Hydroxyacetophenone 681 mg (5 mmol), was dissolved in 10 mL DCM and cooled to 0 °C. To this solution was added 0.81 mL pyridine (10 mmol) and 0.58 mL methylchloroformate (7.5 mmol) and stirred for 30 min. 100 mL diethyl ether was added to the reaction and transferred into a separation funnel. Washed with 100 mL water twice and brine once, the organic layer was dried over magnesium sulfate. After filtration and concentration, the crude produce was purified by silica gel column chromatography eluted with 20-40% diethyl ether gradient to afford 0.90 g product as colorless oil (93%). R_f = 0.42 (30% ethyl acetate in petroleum ether); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.61 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.51 (m, 2H), 5.37 (s, 2H), 3.87 (s, 3H). The ^{1}HNMR spectrum is identical to the literature reported.



Carbonic acid (*Z*)-2-allyloxycarbonyloxy-1-phenyl-vinyl ester methyl ester (**2a-7**): Method A: Starting from 0.90 g carbonic acid methyl ester 2-oxo-2-phenyl-ethyl ester (4.6 mmol), 593 mg white solid was obtained by following the procedure to make enol carbonates (46%). M.p. = 48-50 °C; R_f = 0.29 (10% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3110 (m), 2960 (m), 1766 (s),

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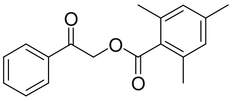
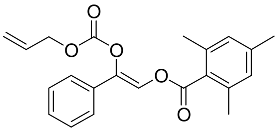
[7] Banerjee, A.; Lee, K.; Falvey, D. E.; *Tetrahedron* **1999**, *55*, 12699-12710.

1689 (m), 1442 (s), 1367 (s), 1265 (s), 1227 (s), 1166 (s), 979 (s), 952 (s), 770 (s), 693 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (s, 1H), 7.44 (m, 2H), 7.36 (m, 3H), 5.97 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.35 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.74 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.9, 151.9, 135.9, 131.5, 130.8, 129.1, 128.9, 126.9, 124.5, 120.1, 69.7, 55.9. HRMS (EI): M$^+$ calcd. For $C_{13}H_{14}O_3$, 278.0790; Found: 278.0780. The structure was further confirmed by HMBC experiment.



2,4,6-Trimethyl-benzoic acid 2-oxo-2-phenyl-ethyl ester:[8] To as flask was charged 995 mg bromoacetophenone (5 mmol), 820 mg 2,4,6-trimethylbenzoic acid (5 mmol), 690 mg potassium carbonate (5 mmol), 200 mg tetrabutylammonium iodide (0.54 mmol), 20 mL DCM and 20 mL water. The reaction mixture was stirred vigorously for 3 h and the organic layer was separated out. The aqueous layer was extracted with 50 mL diethyl ether. The organic layer was combined and dried over magnesium sulfate. After filtration and concentration the residue was purified by silica gel column chromatography eluted with 20% diethyl ether in petroleum ether. 1.57 g white crystals were obtained (93%). M.p. = 79-80 °C (lit. 80 °C) R_f = 0.56 (30% ethyl acetate in petroleum); IR ($CDCl_3$ film): $\tilde{\nu}_{\max}$ = 2928 (w), 1732 (s), 1705 (s), 1612 (m), 1450 (m), 1430 (m), 1370 (m), 1264 (s), 1229 (s), 1167 (s), 1101 (s), 1018 (m), 961 (m), 910 (s), 854 (m), 734 (s), 688 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.97 (m, 2H), 7.63 (m, 1H), 7.51 (m, 2H), 6.89 (s, 2H), 5.56 (s, 2H), 2.42 (s, 6H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.1, 169.5, 139.8, 136.0, 134.4, 134.0, 129.8, 129.0, 128.6, 127.9, 66.3, 21.2, 20.1. HRMS (EI): [M]$^+$ calcd. For $C_{18}H_{18}O_3$, 282.1256; Found: 282.1267.



2,4,6-Trimethyl-benzoic acid (Z)-2-allyloxycarbonyloxy-2-phenyl-vinyl ester (**3a-8**): Method A; Starting from 1.41 g 2,4,6-trimethyl-benzoic acid 2-oxo-2-phenyl-ethyl ester (5 mmol), 1.77 g of colorless oil was obtained by following the procedure to make enol carbonates (95%). R_f = 0.33 (10% diethyl ether in petroleum); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1H), 7.50 (m, 2H), 7.36 (m, 3H), 6.89 (s, 2H), 5.85 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.31 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.19 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.65 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 2.36 (s, 6H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 152.3, 140.6, 136.8, 136.4, 131.8, 131.0, 128.9, 128.8, 128.5, 126.5, 125.3, 124.4, 119.3, 69.4, 21.3, 20.4. MS (ESI): [M+Na]$^+$ 389.1. Anal. Calcd. for $C_{22}H_{22}O_5$: C, 72.12; H, 6.05; Found: C, 71.81; H, 5.88. The structure was further confirmed by HMBC experiment.

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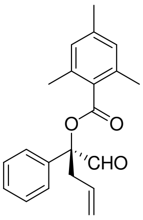
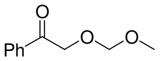
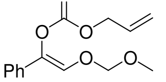
[8] Clark, J. H.; Miller, J. M.; *Tetrahedron Lett.* **1977**, *18*, 599.



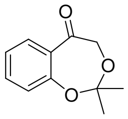
2,4,6-Trimethyl-benzoic acid (*S*)-(–)-1-formyl-1-phenyl-but-3-enyl ester (**1a-8**): Starting from 110 mg **3a-9** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 9.5 mg product was isolated (10%) as colorless oil. $R_f = 0.52$ (10% diethyl ether in petroleum ether); $[\alpha]_D^{24} = -92.9$ (c, 0.9; CH_2Cl_2, 91% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; $t_1 = 4.922$ min (major), $t_2 = 8.346$ min (minor)); IR (film): $\tilde{\nu}_{max} = 2924$ (m), 1792 (m), 1732 (s), 1612 (m), 1494 (w), 1450 (m), 1398 (w), 1246 (s), 1215 (m), 1170 (m), 1077 (s), 989 (s), 761 (w), 700 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 7.5-7.3 (m, 5H), 6.91 (s, 2H), 5.50 (m, 1H), 5.10 (dq, $J_1 = 17.1$ Hz, $J_2 = 1.4$ Hz, 1H), 5.02 (dq, $J_1 = 10.2$ Hz, $J_2 = 1.4$ Hz, 1H), 3.37 (ddt, $J_1 = 15.6$ Hz, $J_2 = 7.8$ Hz, $J_3 = 1.0$ Hz, 1H), 3.26 (ddt, $J_1 = 15.4$ Hz, $J_2 = 6.3$ Hz, $J_3 = 1.7$ Hz, 1H), 2.40 (s, 6H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 194.2, 169.2, 140.3, 136.0, 134.1, 131.1, 129.2, 128.9, 128.6, 126.3, 119.7, 88.8, 38.7, 21.3, 20.4. HRMS (EI): $[M]^+$ calcd. For $C_{21}H_{22}O_3$, 322.1569; Found: 322.1577.



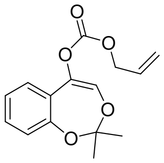
2-Methoxymethoxy-1-phenyl-ethanone: 817 mg hydroxyacetophenone (6 mmol) in 20 mL dichloromethane was cooled in a ice-water bath and was treated with 1.2 mL diisopropylethylamine (7.3 mmol) and then 0.55 mL MOMCl (7.2 mmol). The reaction was allowed to warm to room temperature and stirred for 24 h. The reaction mixture was diluted with ether 50 mL and washed with water 50 mL once and brine 50 mL once. The organic layer was dried over sodium sulfate and concentrated. The residue was purified with silica gel column chromatography eluted with 10-20% ethyl acetate in petroleum ether to afford 0.91 g slight yellow oil (83%). $R_f = 0.33$ (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max} = 3063$ (w), 2950 (m), 2893 (m), 2826 (m), 1703 (s), 1598 (m), 1450 (s), 1287 (m), 1229 (s), 1214 (s), 1151 (s), 1125 (s), 1062 (s), 1015 (s), 976 (s), 921 (s), 757 (s), 691 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.91 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 4.88 (s, 2H), 4.80 (s, 2H), 3.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 195.5, 134.8, 133.6, 128.8, 127.8, 96.6, 69.7, 55.8.



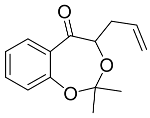
Carbonic acid allyl ester (*Z*)-2-methoxymethoxy-1-phenyl-vinyl ester (**1a-9**): Method A: Starting from 540.6 mg 2-methoxymethoxy-1-phenyl-ethanone (3 mmol), 670 mg colorless oil was isolated (85%). $R_f = 0.55$ (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max} = 3062$ (w), 2960 (m), 2895 (m), 2830 (w), 1767 (s), 1682 (s), 1448 (m), 1367 (m), 1241 (s), 1160 (s), 1056 (s), 1010 (s), 955 (s), 853 (w), 767 (s), 694 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.4-7.2 (m, 5H), 6.81 (s, 1H), 5.98 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.30 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.94 (s, 2H), 4.72 (dt, J_1 = 5.6 Hz, J_2 = 1.4 Hz, 2H), 3.45 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 152.8, 133.3, 132.9, 132.8, 131.3, 128.7, 127.7, 123.3, 119.1, 96.9, 69.2, 56.2. HRMS (EI): $[M]^+$ calcd. For $C_{14}H_{16}O_5$, 264.0998; Found: 264.0998.



6,6-Dimethyl-5,7-dioxa-benzocyclohepten-9-one: 2,2’-dihyroxyacetophenone[9] 1.52 g (10 mmol), 2 mL 2,2-dimethoxypropane, 125 mg pyridinium *p*-toluene sulfonate (0.5 mmol) was dissolved in 20 mL DMF and stirred overnight. The reaction mixture was diluted with 100 mL water and extracted with 50 mL diethyl ether three times. The organic layer was combined and washed with water 50 mL three times and brine 50 mL once. It was dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatography eluted with 5% ethyl acetate in petroleum ether to give a colorless oil. R$_f$ = 0.74 (30% ethyl acetate in petroleum); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.86 (dd, J_1 = 7.8 Hz, J_2 = 1.6 Hz, 1H), 7.54 (td, J_1 = 7.7 Hz, J_2 = 1.3 Hz, 1H), 7.27 (td, J_1 = 8.3 Hz, J_2 = 1.0 Hz, 1H), 7.06 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 4.41 (s, 2H), 1.52 (s, 6H).



Carbonic acid allyl ester 6,6-dimethyl-5,7-dioxa-benzocyclohepten-9-yl ester (**5**): Method A; starting from 457 mg 6,6-Dimethyl-5,7-dioxa-benzocyclohepten-9-one, 505 mg product was isolated (77%) as a colorless oil. R$_f$ = 0.30 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3080 (m), 3000 (s), 2945 (s), 1770 (s), 1715 (s), 1652 (s), 1575 (s), 1488 (s), 1447 (s), 1379 (s), 1258 (s), 1113 (s), 1018 (s), 947 (m), 758 cm^{-1} (s); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.25-6.95 (m, 4H), 6.79 (s, 1H), 5.98 (m, 1H), 5.42 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.33 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 1.56 (s, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 154.9, 151.5, 138.7, 131.2, 130.4, 128.2, 125.6, 123.8, 123.3, 121.5, 119.6, 104.0, 69.4, 25.7. Anal. Calcd. for $C_{15}H_{16}O_5$: C, 65.21; H, 5.84; Found: C, 65.43; H, 5.65.



8-Allyl-6,6-dimethyl-5,7-dioxa-benzocyclohepten-9-one (**6**): Starting from 83 mg **5** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 62.4 mg product was isolated (90%) as a white solid. Mp = 38-39 ^{o}C; R$_f$ = 0.54 (Diethyl ether/petroleum ether 1:9);

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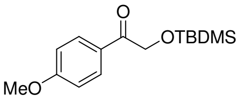
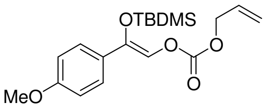
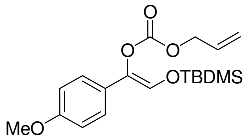
[9] Casiraghi, G.; Salerno, G.; Sartori, G. *Synthesis* **1975**, *3*, 186.

$[\alpha]_D^{23}$ = -32.2 (c, 1.98; CH_2Cl_2, 99% ee); HPLC (Chiralcel® OD column; 98:2 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 5.346 min (major), t_2 = 6.638 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2991 (m), 2941 (w), 1694 (s), 1601 (s), 1474 (m), 1454 (s), 1384 (m), 1288 (s), 1233 (s), 1145 (m), 1083 (m), 906 (m), 690 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$): δ 7.92 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.52 (td, J_1 = 6.6 Hz, J_2 = 1.8 Hz, 1H), 7.25 (td, J_1 = 7.3 Hz, J_2 = 1.1 Hz, 1H), 7.05 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H), 5.90 (m, 1H), 5.20 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.12 (m, 1H), 4.58 (dd, J_1 = 9.4 Hz, J_2 = 3.5 Hz, 1H), 2.90 (m, 1H), 2.42 (m, 1H), 1.61 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 201.1, 154.6, 134.5, 134.4, 130.9, 129.8, 124.9, 124.2, 117.8, 104.4, 77.3, 34.5, 25.5, 24.0. Anal. Calcd. for $C_{14}H_{16}O_3$: C, 65.21; H, 5.84; Found: C, 65.43; H, 5.65.



2-(*tert*-Butyl-dimethyl-silanyloxy)-4'-methoxyacetophenone: 1.6 g (9.6 mmol) 2-hydroxy-4'-methoxyacetophenone prepared from 2-bromo-4'-methoxyacetophenone [10], 1.74 g *tert*-butyldimethylsilylchloride (11.5 mmol) in 40 mL DMF was added 1.31 g imidazole (19.3 mmol) and was stirred for 1h. The reaction was diluted with diethyl ether and transferred into a separation funnel. The solution was washed with water and then brine. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to yield 2.61 g colorless oil (97%). R_f = 0.20 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2954 (s), 2929 (s), 2856 (s), 1698 (s), 1601 (s), 1576 (s), 1512 (s), 1463 (s), 1421 (m), 1313 (s), 1259 (s), 1152 (s), 1114 (s), 1032 (s), 978 (s), 835 (s), 779 cm^{-1} (s); ^1H NMR (400 MHz, C_6D_6): δ = 7.92 (d, J = 9.2 Hz, 2H), 6.92 (d, J = 9.2 Hz, 2H), 4.84 (s, 2H), 3.84 (s, 3H), 0.91 (s, 9H), 0.1 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 196.1, 163.6, 130.3, 128.0, 113.8, 67.4, 55.5, 25.9, 18.6, -5.2. Anal. Calcd. for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.63; Found: C, 64.16; H, 8.72.





Method A; starting from 1.40 g 2-(*tert*-Butyl-dimethyl-silanyloxy)-4'-methoxyacetophenone, 324 mg **2b** (18%) and 1.19 g **3b** (65%) were isolated.

Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-(4-methoxy-phenyl)-vinyl ester (**2b**): Colorless oil. R_f = 0.21 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3120 (w), 2931 (s), 2858 (s), 1758 (s), 1666 (m), 1610 (s), 1513 (s), 1463 (m), 1367 (s), 1342 (s), 1239 (s), 1176 (s), 1085 (s), 1032 (s), 960 (s), 836 (s), 782 cm^{-1} (s); ^1H NMR (400 MHz, C_6D_6): δ = 7.37 (m, 2H), 7.32 (s, 1H), 6.65 (m, 2H), 5.60 (m, 1H), 5.09 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H),

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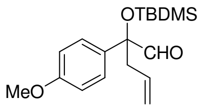
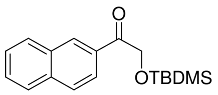
[10] Pirkle, W. H.; Simmons, K. A. *J. Org. Chem.* **1983**, *48*, 2520. Yoshikawa, N.; Suzuki, T.; Shibasaki, M. *J. Org. Chem.* **2002**, *67*, 2556.

4.91 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.35 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 3.23 (s, 3H), 1.06 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 160.2, 153.0, 139.7, 131.7, 128.4, 126.8, 121.0, 118.3, 114.1, 68.6, 54.7, 26.0, 18.8, -4.1. Anal. Calcd. for $C_{19}H_{28}O_5Si$: C, 62.61; H, 7.74; Found: C, 62.48; H, 7.59.

Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-(4-methoxy-phenyl)-vinyl ester (3b): Method A; 65%; Colorless oil. R_f = 0.21 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2932 (s), 2859 (s), 1765 (s), 1674 (m), 1611 (s), 1515 (s), 1464 (m), 1301 (s), 1239 (s), 1174 (s), 990 (s), 832 cm^{-1} (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.34 (m, 2H), 6.70 (m, 2H), 6.59 (s, 1H), 5.70 (m, 1H), 5.14 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 4.94 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.46 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 3.23 (s, 3H), 0.95 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 159.7, 153.2, 135.7, 132.1, 129.5, 126.6, 125.5, 118.2, 114.4, 68.6, 54.7, 25.6, 18.4, -5.3. Anal. Calcd. for $C_{19}H_{28}O_5Si$: C, 62.61; H, 7.74; Found: C, 62.62; H, 7.75.



2-(*tert*-Butyl-dimethyl-silanyloxy)-2-(4-methoxy-phenyl)-pent-4-enal (1b): Starting from 109 mg **2b** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 90.5 mg product was isolated (94%) as a colorless oil. R_f = 0.50 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -92.6 (c, 1.9; CH_2Cl_2, 92% ee); HPLC (Chiralcel® OD column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 7.873 min (minor), t_2 = 9.620 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3079 (w), 2931 (s), 2858 (s), 1732 (s), 1609 (m), 1511 (s), 1253 (s), 1176(m), 830 (s), 778 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.50 (s, 1H), 7.30 (m, 2H), 7.10 (m, 2H), 5.60 (m, 1H), 5.02 (m, 2H), 3.80 (s, 3H), 2.98 (ddt, J_1 = 15.3 Hz, J_2 = 7.2 Hz, J_3 = 1.4 Hz, 1H), 2.68 (ddt, J_1 = 15.3 Hz, J_2 = 6.4 Hz, J_3 = 1.2 Hz, 1H), 0.99 (s, 9H), 0.124 (s, 3H), 0.120 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 159.3, 132.3, 130.3, 127.8, 118.7, 114.0, 84.2, 55.3, 41.1, 26.1, 18.8, -2.25, -2.27. Anal. Calcd. for $C_{18}H_{18}O_3Si$: C, 67.46; H, 8.81; Found: C, 67.27; H, 8.61.



2-(*tert*-Butyl-dimethyl-silanyloxy)-2'-acetonaphthone: 1.9g 2-hydroxy-2'-acetonaphthone (10 mmol) prepared from 2-bromo-2'-acetonaphthone[11], 3.0 g *tert*-butyldimethylsilylchloride (20 mmol) in 20 mL DMF was added 1.36 g imidazole (20 mmol) and was stirred for 1h. The reaction was diluted with diethyl ether and transferred into a separation funnel. The solution was washed with water and then brine. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 5% diethyl ether in petroleum ether to yield 2.71 g colorless oil (90%). R_f = 0.33 (Diethyl

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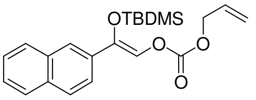
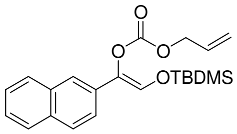
[11] Pirkle, W. H.; Simmons, K. A. *J. Org. Chem.* **1983**, *48*, 2520. Demir, A. S.; Camkerten, N.; Akgun, H.; Tanyeli, C.; Mahasneh, A. S.; Watt, D. S; *Synth. Commun.* **1990**, *20*, 2279.

ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2954 (s), 2929 (s), 2856 (s), 1701 (s), 1628 (m), 1597 (w), 1471 (s), 1256 (s), 1150 (s), 1121 (s), 984 (m), 939 (m), 835 (s), 779 (s), 746 cm^{-1} (m); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.46 (s, 1H), 7.98 (dd, J_1 = 8.6 Hz, J_2 = 1.7 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.87 (t, J = 9.0 Hz, 2H), 7.56 (m, 2H), 5.03 (s, 2H), 0.94 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 197.5, 135.7, 132.5, 132.2, 129.7, 129.6, 128.6, 127.9, 126.9, 123.8, 67.7, 25.9, 18.6, -5.2. Anal. Calcd. for $C_{18}H_{24}O_3Si$: C, 71.95; H, 8.05; Found: C, 71.79; H, 7.87.

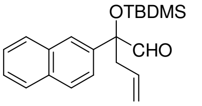




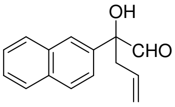
Method A; starting from 1.5 g 2-(*tert*-butyl-dimethyl-silanyloxy)-2'-acetonaphthone (5 mmol), 958 mg **2c** (50%) and 720 mg **3c** (37%) were isolated.

Carbonic acid allyl ester (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-naphthalen-2-yl-vinyl ester (**2c**): Colorless oil. R_f = 0.56 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3120 (w), 2931 (s), 2858 (s), 1760 (s), 1664 (m), 1370 (s), 1337 (s), 1241 (s), 1176 (s), 1079 (s), 1033 (s), 969 (s), 831 (s), 783 cm^{-1} (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 8.01 (s, 1H), 7.56 (m, 2H), 7.52 (s, 1H), 7.48 (d, J = 1 Hz, 2H), 7.20 (m, 2H), 5.60 (m, 1H), 5.10 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 4.93 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.36 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 1.07 (s, 9H), 0.24 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 152.9, 139.7, 133.73, 133.67, 133.4, 131.6, 128.6, 128.4, 127.9, 126.5, 126.3, 124.6, 123.2, 122.6, 118.5, 68.7, 26.0, 18.8, -4.1. Anal. Calcd. for $C_{22}H_{28}O_4Si$: C, 68.71; H, 7.34; Found: C, 68.90; H, 7.21.

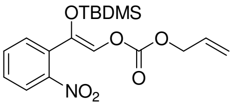
Carbonic acid allyl ester (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-naphthalen-2-yl-vinyl ester (**3c**): Colorless oil. R_f = 0.41 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ =3058 (m), 2955 (s), 2858 (s), 1769 (s), 1668 (s), 1472 (s), 1364 (m), 1243 (s), 1177 (s), 1007 (s), 940 (s), 840 cm^{-1} (s); ^{1}H NMR (400 MHz, C_6D_6): δ = 7.97 (d, J =1.2 Hz, 1H), 7.50 (m, 4H), 7.17 (m, 2H), 6.81 (s, 1H), 5.70 (m, 1H), 5.15 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 5.94 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.49 (dt, J_1 = 5.8 Hz, J_2 = 1.3 Hz, 2H), 0.96 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6): δ = 153.1, 135.8, 134.1, 133.2, 132.0, 131.48, 131.47, 128.7, 128.4, 127.9, 126.6, 126.0, 122.4, 121.8, 118.4, 68.8, 25.6, 18.4, -5.3. Anal. Calcd. for $C_{22}H_{28}O_4Si$: C, 68.71; H, 7.34; Found: C, 68.51; H, 7.29.

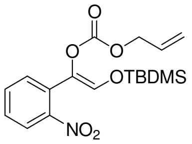


2-(*tert*-Butyl-dimethyl-silanyloxy)-2-naphthalen-2-yl-pent-4-enal (**1c**): Starting from 115 mg **2c** (0.3 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 94.3 mg product was isolated (92%); Colorless oil. R_f = 0.64 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{23}$ = -112.5 (c, 1.7; CH_2Cl_2, 85% ee); IR (film): $\tilde{\nu}_{max}$ = 3059 (w), 2923 (s), 2857 (s), 1733 (s), 1472 (s), 1255 (s), 1145(s), 830 (s), 779 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.61 (s, 1H), 7.91 (d, J = 1.7 Hz, 1H), 7.83 (m, 3H), 7.46 (m, 3H), 5.62 (m, 1H), 5.03 (dq, J_1 = 17.2 Hz, J_2 = 1.4 Hz, 1H), 4.97 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 3.11 (ddt, J_1 = 15.3 Hz, J_2 = 7.2 Hz, J_3 = 1.4 Hz, 1H), 2.78 (ddt, J_1 = 15.3 Hz, J_2 = 6.4 Hz, J_3 = 1.2 Hz, 1H), 1.05 (s, 9H), 0.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.7, 135.9, 133.2, 132.9, 132.1, 128.40, 128.37, 127.7, 126.5, 126.4, 126.0, 123.9, 118.9, 84.8, 41.3, 26.2, 18.9, -2.2. Anal. Calcd. for $C_{21}H_{28}O_2Si$: C, 74.07; H, 8.29; Found: C, 73.86; H, 8.30.



2-Hydroxy-2-naphthalen-2-yl-pent-4-enal: 96 mg **1c** (2.82 mmol) in 2 mL THF was treated with 0.3 mL 1.0 M TBAF in THF and was stirred for 5 min. Most solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to afford 18 mg colorless oil (28%). R_f = 0.70 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{24}$ = +115.8 (c, 1.7; CH_2Cl_2; 85% ee); HPLC (Chiralcel® OJ-H column; UV = 254 nm; 90:10 heptane/isopropanol; flow rate 1 mL/min; t_1 = 17.378 min (minor), t_2 = 18.561 min (major)); IR(neat): $\tilde{\nu}_{max}$ = 3492 (br, s), 1726 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.69 (d, J = 1.0 Hz, 1H), 8.00 (m, 1H), 7.9-7.8 (m, 3H), 7.59 (dd, J_1 = 8.7 Hz, J_2 = 2.0 Hz, 1H), 7.51 (m, 2H), 5.73 (m, 1H), 5.24 (dq, J_1 = 14.5 Hz, J_2 = 1.4 Hz, 1H), 5.18 (ddt, J_1 = 10.3 Hz, J_2 = 1.8 Hz, J_2 = 1.0 Hz, 1H), 3.83 (d, J = 1.1 Hz, 1H), 2.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.8, 135.4, 133.3, 132.9, 131.1, 128.8, 128.3, 127.69, 126.63, 126.59, 125.4, 123.3, 120.5, 81.3, 41.6. Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24; Found: C, 79.46; H, 6.38.

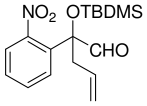




Starting from 640 mg 2-(*tert*-butyl-dimethyl-silanyloxy)-1-(2-nitro-phenyl)-ethanone (2.17 mmol), 138 mg **2d** (17%) and 358 mg **3d** (45%) as yellow oil were obtained.

Carbonic acid allyl ester (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-(2-nitro-phenyl)-vinyl ester (**2d**): R_f = 0.34 (10% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3104 (w), 2957 (m), 2932 (m), 2860 (m), 1760 (s), 1538 (s), 1472 (m), 1360 (s), 1229 (s), 1173 (s), 1034 (m), 951 (m), 861 (s), 842 (s), 784 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.87 (ddd, J_1 = 8.2 Hz, J_2 = 1.2 Hz, J_3 = 0.4 Hz, 1H), 7.58 (m, 2H), 7.47 (ddd, J_1 = 8.2 Hz, J_2 = 7.2 Hz, J_3 = 1.8 Hz, 1H), 7.02 (s, 1H), 5.90 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.35 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.28 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.64 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 0.89 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.2, 148.3, 138.3, 132.4, 131.0, 130.9, 129.7, 129.4, 126.4, 124.4, 119.6, 69.3, 25.5, 18.1, -5.0. HRMS (EI): $[M-C_4H_9]^+$ calcd. For $C_{14}H_{16}NO_6Si$, 322.0747; Found: 322.0742.

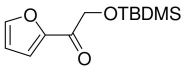
Carbonic acid allyl ester (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-(2-nitro-phenyl)-vinyl ester (3d): R_f = 0.22 (10% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3110 (w), 2956 (s), 2932 (s), 2859 (s), 1760 (s), 1680 (m), 1532 (s), 1472 (m), 1353 (s), 1237 (s), 1167 (s), 1109 (m), 1067 (m), 1036 (m), 958 (s), 861 (s), 842 (s), 783 cm^{-1} (s); ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.80 (ddd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, J_3 = 0.5 Hz, 1H), 7.55 (td, J_1 = 7.6 Hz, J_2 = 1.4 Hz, 1H), 7.47 (m, 2H), 6.93 (s, 1H), 5.96 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 5.8 Hz, 1H), 5.41 (dq, J_1 = 17.2 Hz, J_2 = 1.3 Hz, 1H), 5.31 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.72 (dt, J_1 = 6.0 Hz, J_2 = 1.2 Hz, 2H), 0.85 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 152.4, 148.9, 136.8, 132.5, 131.2, 130.8, 130.4, 129.5, 124.5, 123.0, 119.2, 69.1, 25.5, 18.3, -4.7. HRMS (EI): [M-C_4H_9]$^+$ calcd. For $C_{14}H_{16}NO_6Si$, 322.0747; Found: 322.0750.



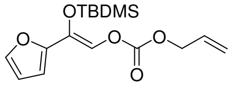
2-(*tert*-Butyl-dimethyl-silanyloxy)-2-(2-nitro-phenyl)-pent-4-enal (1d): Starting from 76 mg **2d** (0.2 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 46 mg product was isolated (69%) as yellow oil. R_f = 0.29 (10% diethyl ether in petroleum ether); 79% ee; HPLC (Chiralcel® OC column; 99:1 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 6.331 min (minor), t_2 = 7.828 min (major)); IR (film): $\tilde{\nu}_{max}$ = 3082 (w), 2957 (s), 2931 (s), 2859 (s), 2712 (w), 1733 (s), 1539 (s), 1472 (s), 1361 (s), 1257 (s), 1155 (m), 1109 (s), 1069 (m), 993 (m), 920 (m), 839 (s), 780 (s), 721 cm^{-1} (m); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 9.66 (s, 1H), 7.87 (dd, J_1 = 7.1 Hz, J_2 = 1.5 Hz, 1H), 7.73 (dd, J_1 = 6.9 Hz, J_2 = 1.4 Hz, 1H), 7.63 (ddd, J_1 = 8.1 Hz, J_2 = 7.3 Hz, J_3 = 1.4 Hz, 1H), 7.47 (ddd, J_1 = 8.1 Hz, J_2 = 7.5 Hz, J_3 = 1.5 Hz, 1H), 5.73 (ddt, J_1 = 16.8 Hz, J_2 = 10.4 Hz, J_3 = 7.0 Hz, 1H), 5.04 (m, 2H), 3.00 (ddt, J_1 = 14.8 Hz, J_2 = 6.9 Hz, J_3 = 1.4 Hz, 1H), 2.92 (ddt, J_1 = 14.8 Hz, J_2 = 7.2 Hz, J_3 = 1.4 Hz, 1H), 0.94 (s, 9H), 0.09 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 197.5, 135.3, 132.7, 131.4, 129.6, 129.2, 125.4, 119.8, 82.0, 41.1, 26.0, 25.6, 18.9, -2.3, -2.7. [M]$^+$ calcd. For $C_{17}H_{25}NO_4Si$, 335.1553; Found: 355.1540.

General Procedure for Formation of *tert*-butyl(dimethyl)silyl enol ether followed by Rubottom-Oxidation:

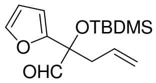
To a solution of the methyl ketone and triethylamine (1.5 eq.) in dichloromethane (20 mL) was added *tert*-butyl(dimethyl)silyl trifluoromethanesulfonate (1.2 eq) at -20 °C over 10 min. After stirring for 30 min. at -20 °C the reaction mixture was warmed up to room temperature continuing stirring for another 30 min. The mixture was poured into sat. aqueous sodium bicarbonate solution (20 mL), extracted with dichloromethane (3 x), washed with brine (10 mL), dried over sodium sulfate, filtered and evaporated. To the crude product was added sodium phosphate monobasic (2.0 eq.) and hexane (20 - 30 mL). After cooling to -20 °C, *m*-CPBA (1.1 eq.) was added portionwise over 10 min. The mixture was slowly warmed up to r.t. and stirring was continued for 2-5 h. The reaction mixture was filtered, the solvent evaporated and the residue purified by column chromatography eluted with petroleum ether / diethyl ether.



2-(*tert*-Butyl-dimethyl-silanyloxy)-1-furan-2-yl-ethanone: To a solution of 2-acetylfuran (1.10 g, 10.0 mmol, 1.2 mL) and triethylamine (1.52 g, 15.0 mmol, 2.1 mL, 1.5 eq.) in dichloromethane (20 mL) was added *tert*-butyl(dimethyl)silyl trifluoromethanesulfonate (2.94 g, 12.0 mmol, 2.6 mL, 1.2 eq) dropwise at -20 °C over 10 min. After stirring for 30 min. at -20 °C the reaction mixture was warmed up to r.t. continuing stirring for another 30 min. The mixture was poured into sat. aqueous sodium bicarbonate solution (20 mL), extracted with dichloromethane (3 x), washed with brine (10 mL), dried over sodium sulfate, filtered and the solvent removed *in vacuo*. To the crude silyl enol ether was added sodium phosphate monobasic (2.4 g, 20.0 mmol, 2.0 eq.) and hexane (30 mL). After cooling to -20 °C, *m*-CPBA (2.71 g, 11.0 mmol, 1.1 eq.) was added portionwise over 10 min. The mixture was slowly warmed up to r.t. and stirring was continued for 4 h. The reaction mixture was filtered, the solvent evaporated and the residue purified by column chromatography eluted with 10% diethyl ether in petroleum ether giving the product as a colorless liquid (882 mg, 37 %). $R_f = 0.21$ (diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 2930 (s), 2858 (s), 2362 (w), 1699 (s), 1572 (m), 1472 (s), 1394 (w), 1362 (w), 1305 (w), 1255 (s), 1224 (w), 1150 (s), 1084 (w), 1016 (m), 982 (w), 896 (w), 838 (s), 778 (m), 719 cm^{-1} (w); ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 7.57 (m, 1H), 7.32-7.31 (m, 1H), 6.54-6.53 (m, 1H), 4.73 (s, 2H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ (ppm) = 187.1, 150.9, 146.4, 118.1, 112.1, 67.2, 25.9, 18.6, -5.3.

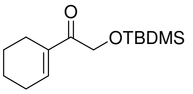


Carbonic acid allyl ester (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-furan-2-yl-vinyl ester (**2e**): Method A; Starting from 601 mg 2-(*tert*-butyl-dimethyl-silanyloxy)-1-furan-2-yl-ethanone (2.5 mmol) colorless oil 575 mg (71 %) was isolated. $R_f = 0.50$ (Diethyl ether/petroleum ether 1:9)); IR (film): $\tilde{\nu}_{max}$ = 2957 (m), 2932 (m), 2860 (m), 1770 (s), 1682 (s), 1472 (m), 1364 (m), 1291 (m), 1243 (s), 1180 (s), 1159 (m), 1025 (m), 1002 (m), 868 (m), 840 (m), 786 (m), 728 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 1H), 6.76 (s, 1H), 6.51 (dd, J_1 = 3.4 Hz, J_2 = 1.8 Hz, 1H), 6.20 (m, 1H), 5.96 (ddt, J_1 = 16.8 Hz, J_2 = 10.4 Hz, J_3 = 7.0 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.40 (dq, J_1 = 10.5 Hz, J_2 = 1.4 Hz, 1H), 4.70 (dt, J_1 = 5.8 Hz, J_2 = 1.2 Hz, 2H), 0.94 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.6, 148.1, 141.3, 131.4, 130.7, 127.8, 119.1, 111.2, 104.8, 69.1, 25.5, 18.2, -5.2. Anal. Calcd. for $C_{16}H_{24}O_5Si$: C, 59.23; H, 7.46; Found: C, 58.97; H, 7.22. The structure was further confirmed by HMBC experiment.

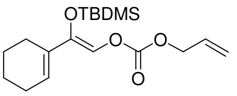


2-(*tert*-Butyl-dimethyl-silanyloxy)-2-furan-2-yl-pent-4-enal (**1e**): Starting from 65 mg **2e** (0.2 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, 45.4 mg product was isolated (81%) as colorless oil. $R_f = 0.53$ (10% diethyl ether in petroleum ether); $[\alpha]_D^{27} = +2.3$ (c, 2.0; CH_2Cl_2, 93% ee determined by the corresponding diol); HPLC of the diol

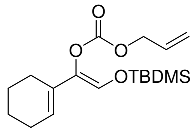
(Chiralcel® AD column; 95:5 Heptane / Isopropanol; flow rate = 1 mL / min; UV = 220 nm; t_1 = 16.957 min (major), t_2 = 19.747 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 2956 (s), 2930 (s), 2858 (s), 1746 (s), 1473 (s), 1254 (s), 1158 (m), 1128 (m), 1080 (m), 1011 (m), 921 (m), 839 (s), 780 (s), 740 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.65 (s, 1H), 7.42 (dd, J_1 = 1.7 Hz, J_2 = 0.7 Hz, 1H), 6.37 (dd, J_1 = 3.4 Hz, J_2 = 1.8 Hz, 1H), 6.35 (dd, J_1 = 3.4 Hz, J_2 = 0.9 Hz, 1H), 5.77 (m, 1H), 5.12 (m, 2H), 2.88 (ddt, J_1 = 14.5 Hz, J_2 = 6.7 Hz, J_3 = 1.4 Hz, 1H), 2.81 (ddt, J_1 = 14.5 Hz, J_2 = 7.3 Hz, J_3 = 1.2 Hz, 1H), 0.91 (s, 9H), -0.07 (s, 3H), -0.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.8, 152.2, 142.7, 131.6, 119.2, 110.7, 109.1, 79.7, 40.7, 25.9, 18.5, -3.57, -3.63. Anal. Calcd. for $C_{15}H_{24}O_3Si$: C, 64.24; H, 8.63; Found: C, 64.04; H, 8.40.



2-(*tert*-Butyl-dimethyl-silanyloxy)-1-cyclohex-1-enyl-ethanone: Starting from 1-acetylcyclohexene (1.1 g, 9.0 mmol, 1.2 mL) the product was obtained as a colorless liquid (1.00 g, 62 %). R_f = 0.47 (diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 2931 (s), 2858 (s), 1689 (s), 1668 (m), 1638 (m), 1472 (m), 1436 (w), 1390 (w), 1361 (w), 1254 (m), 1214 (w), 1146 (s), 989 (m), 938 (w), 899 (m), 837 (s), 779 (s), 734 (w), 700 (w), 657 (w); ^1H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 6.83 (tt, J = 3.9, 2.0 Hz, 1H), 4.61 (s, 2H), 2.23-2.20 (m, 4H), 1.65-1.58 (m, 4H), 0.91 (s, 9H), 0.08 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ(ppm) =198.1, 139.5, 137.2, 66.4, 26.0, 25.9, 23.1, 21.9, 21.6, 18.6, -5.3; HRMS (EI): $[M-C_4H_9]^+$ calcd. For $C_{10}H_{17}O_2Si$, 197.0998; Found: 197.0991.



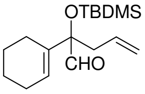
and



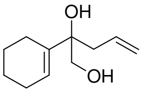
Method A: Starting from 763 mg 2-(*tert*-butyl-dimethyl-silanyloxy)-1-cyclohex-1-enyl-ethanone (3.0 mmol), a mixture of **2f** and **3f** 618 mg (62%, 2.6:1) as colorless oil were obtained.

Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-cyclohex-1-enyl-vinyl ester (2f): R_f = 0.64 (Diethyl ether/petroleum ether 1:9); IR($CDCl_3$): $\tilde{\nu}_{max}$ = 2931 (s), 2859 (s), 1759 (s), 1660 (w), 1633 (w), 1463 (m), 1390 (m), 1364 (m), 1328 (m), 1261 (s), 1157 (m), 1084 (m), 1032 (m), 973 (m), 910 (m), 876 (w), 835 (s), 782 (s), 735 (s), 649 (w) cm^{-1}; ^1H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 6.74 (s, 1H), 6.15-6.13 (m, 1H), 5.93 (ddt, J = 17.2, 10.8, 5.5 Hz, 1H), 5.37 (ddt, J = 17.2, 3.0, 1.5 Hz, 1H), 5.28 (ddt, J = 10.6, 2.6, 1.3 Hz, 1H), 4.68 (ddd, J = 5.5, 1.4, 1.4 Hz, 2H), 2.15-2.04 (m, 4H), 1.69-1.55 (m, 4H), 0.91 (s, 9H), 0.15 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ(ppm) = 152.8, 140.1, 131.4, 130.9, 125.2, 120.3, 118.7, 68.7, 26.0, 25.4, 24.2, 22.5, 22.2, 18.7, -4.3. HRMS (EI): $[M]^+$ calcd. For $C_{18}H_{30}O_4Si$, 338.1913; Found: 338.1903.

Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-cyclohex-1-enyl-vinyl ester (3f): R_f = 0.56 (Diethyl ether/petroleum ether 1:9); IR($CDCl_3$): $\tilde{\nu}_{max}$ = 3048 (w), 2931 (s), 2859 (s), 1765 (s), 1665 (m), 1630 (m), 1473 (m), 1364 (m), 1240 (s), 1191 (s), 1170 (s), 1080 (w), 994 (m), 931 (m), 874 (m), 840 (m), 784 (m), 694 (w), 663 (w) cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 6.26 (m, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.78-5.76 (m, 1H), 5.38 (ddt, *J* = 17.2, 3.0, 1.5 Hz, 1H), 5.27 (ddt, *J* = 10.4, 2.6, 1.2 Hz, 1H), 4.66 (ddd, *J* = 5.7, 1.5, 1.3 Hz, 2H), 2.12-2.03 (m, 4H), 1.67-1.55 (m, 4H), 0.97 (s, 9H), 0.15 (s, 6H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ(ppm) = 152.8, 136.4, 131.7, 128.6, 128.2, 120.9, 118.9, 68.8, 25.5, 25.2, 23.8, 22.3, 22.2, 18.2, -5.2; HRMS (EI): $[M]^+$ calcd. For $C_{18}H_{30}O_4Si$, 338.1913; Found: 338.1914.

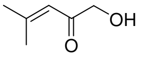


2-(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohex-1-enyl-pent-4-enal (**1f**): Starting from 67.7 mg **2f** (0.2 mmol) 55 mg colorless oil was isolated. R_f = 0.79 (Petroleum ether, diethyl ether 9:1); $[\alpha]_D^{27}$ = -259.2 (c, 3.40; $CHCl_3$); IR(neat): $\tilde{\nu}_{max}$ = 3078 (w), 2931 (s), 2858 (s), 2797 (w), 2707 (w), 1732 (s), 1640 (w), 1472 (m), 1436 (m), 1389 (w), 1361 (m), 1254 (s), 1152 (m), 1078 (m), 993 (m), 967 (m), 911 (m), 838 (s), 777 (s), 670 (w); ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 9.24 (s, 1H), 5.97-5.96 (m, 1H), 5.72 (dddd, *J* = 17.3, 10.3, 7.2, 6.2 Hz, 1H), 5.11-5.06 (m, 2H), 2.73 (dddd, *J* = 15.4, 7.3, 1.4, 1.3 Hz, 1H), 2.33 (dddd, *J* = 15.4, 6.1, 1.5, 1.4 Hz, 1H), 2.13-2.03 (m, 2H), 1.88-1.72 (m, 2H), 1.65-1.47 (m, 4H), 0.94 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 199.8, 133.4, 132.8, 127.4, 118.0, 85.4, 37.9, 26.1, 25.6, 24.0, 22.7, 22.1, 18.7, -2.3, -2.3. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{16}H_{29}OSi$, 265.1988; Found: 265.1979.

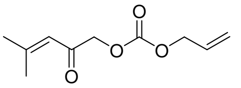


2-Cyclohex-1-enyl-pent-4-ene-1,2-diol: 55 mg **1f** (0.19 mmol) was dissolved in 1 mL ethanol and was treated with 8 mg sodium borohydride (0.21 mmol). After 5 min at room temperature, 1 mL of acetone was added into the reaction mixture and most solvent was evaporate *in vacuo*. The residue was dissolved in 5 mL diethyl ether and washed with brine once. The organic layer was dried over magnesium sulfate and was concentrated. The crude product was dissolved in 2 mL THF and was added 0.3 mL 1.0 M TBAF in THF. 1 mL 5% KH_2PO_4 aqueous was added to the reaction mixture after 5 min and was extracted with 5 mL diethyl ether twice. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 30% ethyl acetate in petroleum ether to give 24.7 mg colorless oil (73%). R_f = 0.24 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{24}$ = -32.3 (c, 2.4; CH_2Cl_2, 98% ee); HPLC (Chiralcel® OD-H column; 97:3 Heptane / Isopropanol; flow rate = 0.8 mL / min; UV = 210 nm; t_1 = 13.882 min (major), t_2 = 15.196 min (minor)); IR(neat): $\tilde{\nu}_{max}$ = 3418 (bs), 3075 (w), 2928 (s), 2857 (s), 1640 (w), 1438 (m), 1389 (w), 1337 (m), 1270 (m), 1068 (s), 997 (m), 920 (s) cm^{-1} (w); ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 5.80 (septet, *J* = 1.7 Hz, 1H), 5.73 (m, 1H), 5.15 (t, *J* = 1.1 Hz, 1H), 5.12 (m, 1H), 3.59 (d, *J* = 11.0 Hz, 1H), 3.47 (d, *J* = 11.0 Hz, 1H), 2.40 (ddt, J_1 = 14.0 Hz, J_2 = 6.1 Hz, J_3 = 1.4 Hz, 1H), 2.30 (ddt, J_1 = 14.0 Hz, J_2 = 8.4 Hz, J_3 = 1.0 Hz, 1H), 2.23 (bs, 1H), 2.09 (m, 2H), 1.95 (m, 3H), 1.60 (m, 4H); ^{13}C-NMR (125

MHz, $CDCl_3$): δ = 138.0, 133.1, 123.5, 119.0, 76.9, 67.7, 40.0, 25.14, 25.06, 22.9, 22.3. HRMS (EI): $[M]^+$ calcd. For $C_{11}H_{18}O_2$, 182.1307.1988; Found: 182.1304.



1-Hydroxy-4-methyl-pent-3-en-2-one:[12] To a solution of mesityl oxide (1.47 g, 15.0 mmol, 1.72 mL) and triethylamine (2.33 g, 23.0 mmol, 3.23 mL, 1.5 eq.) in dichloromethane was added trimethylsilyl trifluoromethanesulfonate (4.00 g, 18.0 mmol, 3.26 mL, 1.2 eq.) at -20 °C dropwise and the mixture was stirred at -20 °C for 30 min. After warming up to r.t., the reaction mixture was poured into a sat. aqueous sodium bicarbonate solution (20 mL), extracted with dichloromethane (3 x), washed with brine, dried over sodium sulfate, filtered and evaporated *in vacuo*. To the crude product was added sodium phosphate monobasic (3.60 g, 30.0 mmol, 2.0 eq.), hexane (40 mL) and, after cooling to -20 °C, *m*-CPBA portionwise over 10 min. The reaction mixture was slowly warmed up to r.t. and stirred for 2 h. Then, the mixture was filtered, the solvent evaporated and the crude product was stirred in methanol for 20 h at r.t. The solvent was evaporated and the residue was filtered through a silica column eluted with petroleum ether. The crude product (346 mg, 21 %) was used in the next step. R_f = 0.08 (diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 3449 (s), 2914 (s), 2360 (w), 1688 (s), 1623 (s), 1445 (s), 1383 (s), 1277 (m), 1217 (m), 1135 (w), 1091 (s), 1029 (s), 969 (w), 911 (m), 818 (m); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 5.96 (m, 1H), 4.19 (s, 2H), 3.52 (br s, 1H), 2.22 (s, 3H), 1.93 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm) = 198.1, 159.4, 119.1, 68.6, 27.9, 21.5.



Carbonic acid allyl ester 4-methyl-2-oxo-pent-3-enyl ester: To a solution of crude 1-hydroxy-4-methyl-pent-3-en-2-one (342 mg, 3.0 mmol) and pyridine (475 mg, 6.0 mmol, 0.5 mL, 2.0 eq) in dichloromethane (20 mL) was added allyl chloroformate (434 mg, 3.6 mmol, 0.4 mL, 1.2 eq.) and the mixture was stirred for 20 h. The mixture was poured into dist. water (20 mL), extracted with dichloromethane (3 x), washed with brine, dried over sodium sulfate and concentrated *in vacuo*. Column chromatography eluting with 10% diethyl ether in petroleum ether afforded the carbonate as a colorless liquid (236 mg, 46 %). R_f = 0.11 (diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 3088 (w), 2940 (s), 1756 (s), 1704 (s), 1622 (s), 1422 (s), 1373 (s), 1258 (s), 1144 (m), 1111 (s), 1048 (m), 982 (s), 913 (s), 819 (m), 789 (s), 734 (w); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 6.01 (m, 1H), 5.90 (m, 1H), 5.36-5.31 (m, 1H), 5.24-5.21 (m, 1H), 4.61 (m, 4H), 2.15 (s, 3H), 1.89 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm) = 192.1, 159.7, 154.6, 131.3, 118.8, 118.5, 71.1, 68.8, 27.9, 21.2. Anal. Calcd. for $C_{10}H_{14}O_2$: C, 60.59; H, 7.12; Found: C, 60.56; H, 6.92.

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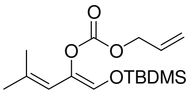
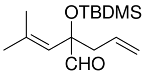
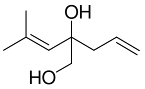
[12] Katritzky, A. R.; Sengupta, S. *Tetrahedron Lett.* **1987**, *28*, 1847-1850.



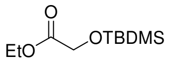
Carbonic acid allyl ester 1-(*tert*-butyl-dimethyl-silanyloxymethylene)-3-methyl-but-2-enyl ester (3g): Method B: Starting from 370 mg carbonic acid allyl ester 4-methyl-2-oxo-pent-3-enyl ester (1.8 mmol), 370 mg colorless oil was isolated (66%). R_f = 0.45 (Diethyl ether/petroleum ether 1:9)); IR (film): $\tilde{\nu}_{max}$ = 2931 (s), 2859 (s), 1765 (s), 1676 (m), 1632 (m), 1482 (m), 1451 (m), 1378 (m), 1364 (m), 1246 (s), 1198 (s), 1162 (s), 842 (s), 783 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.13 (s, 1H), 5.95 (ddt, J_1 = 16.8 Hz, J_2 = 10.4 Hz, J_3 = 7.0 Hz, 1H), 5.52 (m, 1H), 5.38 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.27 (dq, J_1 = 10.5 Hz, J_2 = 1.4 Hz, 1H), 4.67 (dt, J_1 = 5.8 Hz, J_2 = 1.2 Hz, 2H), 1.82 (s, 3H), 1.77 (s, 3H), 0.91 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.7, 134.3, 134.0, 132.4, 131.6, 118.9, 115.7, 68.7, 27.3, 25.5, 19.3, 18.2, -5.3. Anal. Calcd. for $C_{16}H_{28}O_4Si$: C, 61.50; H, 9.03; Found: C, 61.32; H, 8.83.



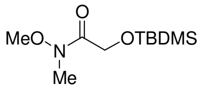
2-Allyl-2-(*tert*-butyl-dimethyl-silanyloxy)-4-methyl-pent-3-enal (1g): Starting from 62.5 mg **3g**, and following the procedure of palladium catalyzed decarboxylation alkylation, 48.0 mg product was isolated (89%); Colorless oil. R_f = 0.64 (Diethyl ether/petroleum ether 1:9); $[\alpha]_D^{24}$ = +0.97 (c, 2.78; CH_2Cl_2, 98% ee); IR (film): $\tilde{\nu}_{max}$ = 3080 (w), 2956 (s), 2931 (s), 2858 (s), 1742 (s), 1473 (m), 1438 (m), 1255 (s), 1149 (m), 1096 (s), 995 (m), 917 (m), 838 (m), 810 (s), 777 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.57 (s, 1H), 5.78 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 7.2 Hz, 1H), 5.25 (t, J = 1.2 Hz, 1H), 5.08 (m, 2H), 2.53 (m, 2H), 1.75 (d, J = 1.5 Hz, 3H), 1.63 (d, J = 1.2 Hz, 3H), 0.92 (s, 9H), 0.12 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.7, 140.1, 132.3, 125.2, 118.8, 81.4, 43.6, 26.6, 26.0, 21.1, 18.5, -2.3 -2.7. Anal. Calcd. for $C_{15}H_{28}O_2Si$: C, 67.11; H, 10.51; Found: C, 66.85; H, 10.25.



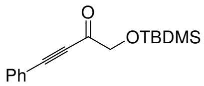
2-Allyl-4-methyl-pent-3-ene-1,2-diol: 23 mg **1g** (0.086 mmol) was dissolved in 1 mL ethanol and was treated with 4 mg sodium borohydride. After 5 min at room temperature, 1 mL of acetone was added into the reaction mixture and most solvent was evaporate *in vacuo*. The residue was dissolved in 5 mL diethyl ether and washed with brine once. The organic layer was dried over magnesium sulfate and was concentrated. The crude product was dissolved in 1 mL THF and was added 0.1 mL 1.0 M TBAF in THF. 1 mL 5% KH_2PO_4 aqueous was added to the reaction mixture after 5 min and was extracted with 5 mL diethyl ether twice. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 30% ethyl acetate in petroleum ether to give 10 mg colorless oil (75%). R_f = 0.21 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{26}$ = -2.1 (c, 0.9; CH_2Cl_2, 98% ee); HPLC (Chiralcel® AD column; 98:2 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 23.577 min (major), t_2 = 28.206 min (minor)); IR(neat): $\tilde{\nu}_{max}$ = 3397 (br, s), 2928 (s), 1668 (w), 1641 (w), 1440 (m), 1376 (m), 1058 (s), 1016 (m), 997 (m), 916 cm^{-1} (s); ^{1}H-NMR (400 MHz, CDCl$_3$): δ(ppm) = 5.85 (m, 1H), 5.15 (m, 3H), 3.59 (d, J = 11.0 Hz, 1H), 3.47 (m, 1H), 2.41 (m, 2H), 2.16 (bs, 1H), 2.02 (bs, 1H), 1.87 (d, J = 1.4 Hz, 3H), 1.74 (d, J = 1.4 Hz, 3H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ = 137.8, 133.8, 126.0, 119.00, 75.1, 69.0, 43.1, 27.6, 19.2.



(*tert*-Butyl-dimethyl-silanyloxy)-acetic acid ethyl ester:[13]
A mixture of ethyl glycolate (6.25 g, 60 mmol), tert-butyldimethylchlorosilane (10.85 g, 72 mmol, 1.2 eq.) and imidazole (5.31 g, 78 mmol, 1.3 eq) was stirred for 2 h. The mixture was filtered and the filtrate was distilled yielding the product as a colorless liquid (12.9 g, 99%, b.p.: 60 °C / 0.2 mbar). IR(neat): $\tilde{\nu}_{\max}$ = 2931 (s), 2858 (s), 1763 (s), 1737 (s), 1473 (m), 1445 (m), 1392 (m), 1382 (m), 1256 (s), 1206 (s), 1189 (s), 1149 (s), 1032 (m), 939 (w), 839 (s), 780 (s), 662 (w) cm^{-1}; ^{1}H-NMR (400 MHz, CDCl$_3$): δ(ppm) = 4.22 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 0.90 (s, 9H), 0.09 (s, 6H); ^{13}C-NMR (100 MHz, CDCl$_3$): δ(ppm) = 171.9, 61.9, 60.8, 25.8, 18.5, 14.3, -5.4. Spectroscopic data are consistent with the literature.



2-(*tert*-Butyl-dimethyl-silanyloxy)-*N*-methoxy-*N*-methyl-acetamide:[14]
To a mixture of N,O-Dimethylhydroxyamine hydrochloride (5.1g, 52 mmol, 1.1 eq.), (*tert*-butyl-dimethyl-silanyloxy)-acetic acid ethyl ester (11 g, 50 mmol) and THF (50 mL) was added isopropylmagnesium chloride (2.0 M solution in THF, 52 mL, 2.1 eq.) dropwise over 20 min. at -20 °C and the mixture was stirred for 4 h. After allowing to warm up to 0 °C, the reaction mixture was poured into ice cooled dist. water (100 mL), extracted with diethyl ether (3 x), washed with brine, dried over sodium sulfate, filtered and the solvent evaporated. The residue was distilled to give a colorless liquid (9.1g, 78 %, b.p.: 82 °C / 0.2 mbar). IR(neat): $\tilde{\nu}_{\max}$ = 2954 (s), 2857 (s), 1694 (s), 1472 (s), 1443 (m), 1390 (m), 1330 (m), 1255 (s), 1159 (s), 1089 (s), 997 (s), 921 (w), 838 (s), 780 (m), 734 (m), 665 (w), 611 cm^{-1} (w); ^{1}H-NMR (400 MHz, CDCl$_3$): δ(ppm) = 4.42 (s, 2H), 3.67 (s, 3H), 3.17 (s, 3H), 0.92 (s, 9H), 0.11 (s, 6H). NMR data are consistent with the literature.



1-(*tert*-Butyl-dimethyl-silanyloxy)-4-phenyl-but-3-yn-2-one: A solution of phenylacetylene (1.53 g, 15 mmol, 2.1 eq.) in THF (10 mL) was cooled to -78 °C. Then, n-BuLi (2.5 M solution in hexane, 6.0 mL, 15 mmol, 2.1 eq.) was added dropwise and the mixture was warmed up to -20 °C and stirred for 3 h. After cooling to -78 °C, a solution of the Weinreb amide (2.33 g, 7 mmol) in

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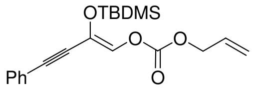
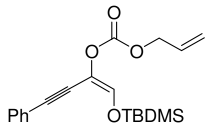
[13] Wissner, A.; Grudzinskas, C. V. *J. Org. Chem.* **1978**, *43*, 3972-3974.

[14] S. Arns, L. Barriault, *J. Org. Chem.* **2006**, *71*, 1809; Evans, D. A.; Glorius, F.; Burch, J. D. *Org. Lett.* **2005**, *7*, 3331.

THF (5 mL) was added and the reaction mixture was stirred for 1 h warming up to -20 °C. The mixture was poured into dist. water (30 mL), extracted with diethyl ether (3 x), washed with brine, dried over sodium sulfate, filtered and the solvent removed *in vacuo*. Flash chromatography eluting with 2 % diethyl ether in petroleum ether afforded the desired product as a yellow oil (1.48 g, 77 %). R_f = 0.62 (diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 2955 (s), 2938 (s), 2858 (s), 2360 (w), 2203 (s), 2133 (w), 1694 (s), 1673 (s), 1490 (m), 1472 (m), 1444 (m), 1431 (w), 1390 (w), 1362 (w), 1287 (m), 1259 (s), 1163 (s), 1118 (s), 1068 (s), 1006 (w), 939 (w), 912 (w), 839 (s), 781 (s), 758 (s), 734 (m), 689 (s), 670 (m) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.59-7.57 (m, 2H), 7.49-7.45 (m, 1H), 7.41-7.37 (m, 2H), 4.43 (s, 2H), 0.95 (s, 9H), 0.14 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm) = 187.0, 133.2, 130.9, 128.7, 119.9, 93.7, 86.0, 70.5, 25.9, 18.5, -5,3; HRMS (EI): $[M-C_4H_9]^+$ calcd. For $C_{12}H_{13}O_2Si$, 217.0684; Found: 217.0683.

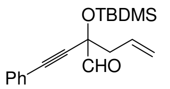




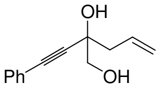
Method A: Starting from 1.28 g 1-(*tert*-butyl-dimethyl-silanyloxy)-4-phenyl-but-3-yn-2-one, 804 mg **2i** (48%) and 240 mg **11** (14%) were isolated.

Carbonic acid allyl ester (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-4-phenyl-but-1-en-3-ynyl ester (2i): Yellow oil; R_f = 0.74 (Diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 3113 (w), 2931 (m), 2859 (m), 2361 (w), 2208 (w), 1763 (s), 1655 (w), 1598 (w), 1491 (w), 1464 (w), 1444 (w), 1368 (m), 1343 (m), 1241 (s), 1160 (s), 1031 (w), 1002 (m), 989 (m), 827 (m), 785 (m), 756, 690 (s) cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.43 (m, 2H), 7.33 (m, 3H), 6.95 (s, 1H), 5.96 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.39 (ddt, J = 17.2, 1.5, 1.5 Hz, 1H), 5.31 (ddt, J = 10.6, 1.3, 1.2 Hz, 1H), 4.71 (ddd, J = 5.7, 1.5, 1.2 Hz, 2H), 0.99 (s, 9H), 0.27 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm) = 152.0, 131.4, 131.1, 128.7, 128.5, 128.4, 123.6, 122.3, 119.3, 90.2, 84.2, 69.2, 25.6, 18.4, -4.4; HRMS (EI): $C_{20}H_{26}O_2Si$: $[M]^+$ calcd. 358.1600, found 358.1601. The structure was further confirmed by HMBC and NOE experiment.

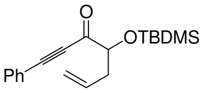
Carbonic acid allyl ester 1-(*tert*-butyl-dimethyl-silanyloxymethylene)-3-phenyl-prop-2-ynyl ester (11): R_f = 0.59 (Diethyl ether/petroleum ether 1:9); IR(neat): $\tilde{\nu}_{max}$ = 3057 (w), 2956 (s), 2931 (s), 2859 (s), 2207 (m), 1808 (m), 1767 (s), 1694 (m), 1651 (m), 1597 (w), 1490 (m), 1444 (m), 1364 (m), 1254 (s), 1209 (s), 1158 (m), 1098 (m), 1043 (m), 995 (m), 941 (m), 839 (s), 786 (s), 757 (s), 690 (m); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.43 (m, 2H), 7.33 (m, 3H), 6.96 (s, 1H), 5.97 (ddt, J = 17.2, 10.6, 5.8 Hz, 1H), 5.41 (ddt, J = 17.2, 1.5, 1.5 Hz, 1H), 5.30 (ddt, J = 10.4, 1.2, 1.2 Hz, 1H), 4.71 (ddd, J = 5.8, 1.4, 1.3 Hz, 2H), 0.98 (s, 9H), 0.22 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ(ppm) = 153.9, 143.5, 131.4, 131.2, 128.5, 128.3, 122.8, 122.6, 119.4, 97.6, 80.1, 69.3, 25.5, 18.3, -5.2; HRMS (EI): $[M]^+$ calcd. For $C_{20}H_{26}O_2Si$, 358.1600; Found 358.1591. The structure was further confirmed by HMBC and NOE experiment.



2-(*tert*-Butyl-dimethyl-silanyloxy)-2-phenylethynyl-pent-4-enal (**1i**): Starting from 71.7 mg **2i**, and following the procedure of palladium catalyzed decarboxylation alkylation 48 mg product was isolated (76%) as a colorless oil; $[\alpha]_D^{28}$ = +48.0 (c, 3.10; $CHCl_3$, 89% ee); IR(neat): $\tilde{\nu}_{max}$ = 3082 (w), 2956 (s), 2930 (s), 2857 (s), 2808 (w), 2227 (w), 1748 (s), 1643 (w), 1599 (w), 1491 (m), 1472 (m), 1444 (w), 1362 (w), 1254 (s), 1172 (m), 1126 (m), 1095 (m), 995 (m), 955 (w), 919 (m), 889 (s), 810 (m), 780 (s), 756 (s), 890 (s); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 9.46 (s, 1H), 7.46-7.43 (m, 2H), 7.38-7.31 (m, 3H), 5.91 (ddt, *J* = 17.7, 9.5, 7.2 Hz, 1H), 5.21-5.16 (m, 2H), 2.79-2.59 (m, 1H), 2.62-2.50 (m, 1H), 0.94 (s, 9H), 0.23 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 196.2, 131.7, 131.5, 129.1, 128.5, 121.9, 119.6, 90.0, 85.8, 76.4, 43.4, 25.8, 18.4, -3.0. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{18}H_{25}OSi$, 285.1675; Found: 285.1666.

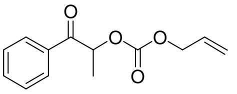


2-Phenylethynyl-pent-4-ene-1,2-diol: 46 mg **1i** (0.144 mmol) was dissolved in 1 mL ethanol and was treated with 5.6 mg sodium borohydride (0.15 mmol). After 5 min at room temperature, 1 mL of acetone was added into the reaction mixture and most solvent was evaporate *in vacuo*. The residue was dissolved in 5 mL diethyl ether and washed with brine once. The organic layer was dried over magnesium sulfate and was concentrated. The crude product was dissolved in 1 mL THF and was added 0.15 mL 1.0 M TBAF in THF. 1 mL 5% KH_2PO_4 aqueous was added to the reaction mixture after 5 min and was extracted with 5 mL diethyl ether twice. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 30% ethyl acetate in petroleum ether to give 25.4 mg white solid (87%). M.p. = 73-75 °C; R_f = 0.16 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{24}$ = -8.3 (c, 2.5; CH_2Cl_2, 89% ee); HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 10.400 min (minor), t_2 = 16.303 min (major)); IR($CDCl_3$ film): $\tilde{\nu}_{max}$ = 3568 (br, s), 3386 (br, s), 2926 (m), 1638 (w), 1599 (w), 1490 (s), 1443 (m), 1388 (m), 1070 cm^{-1} (s); ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 7.43 (m, 2H), 7.32 (m, 3H), 6.04 (m, 1H), 5.25 (m, 2H), 3.79 (d, *J* = 11.1 Hz, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 2.81 (bs, 1H), 2.56 (m, 2H), 2.26 (bs, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 132.6, 131.9, 128.7, 128.4, 122.2, 119.9, 89.1, 86.0, 71.2, 69.3, 42.8. $[M-H]^+$ calcd. For $C_{13}H_{13}O_2$, 201.0916; Found: 201.0915.

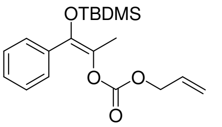


4-(*tert*-Butyl-dimethyl-silanyloxy)-1-phenyl-hept-6-en-1-yn-3-one (**4i**): Starting from 71.2 mg **11** and following the procedure of palladium catalyzed decarboxylation alkylation 60 mg product was obtained as a colorless oil (95 %). R_f = 0.44 (Petroleum ether, diethyl ether 9:1); $[\alpha]_D^{27}$ = +58.2 (c, 2.60; $CHCl_3$, 99% ee); HPLC (Chiralcel® AS column; 99.5:0.5 heptane / isopropanol; flow rate 1 mL/min; t_1 = 3.878 min (major), t_2 = 5.386 min (minor)); IR(neat): $\tilde{\nu}_{max}$ = 3081 (w), 2930 (s), 2958 (s), 2202 (s), 1674 (s), 1490 (m), 1472 (m), 1444 (m), 1362 (w), 1285 (m), 1259 (s), 1159 (s), 1102 (s), 1073 (s), 998 (m), 916 (s), 837 (s), 779 (s), 758 (s), 699 (s), 633 (w); ^{1}H-

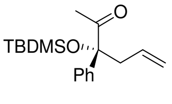
NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.61-7.58 (m, 2H), 7.49-7.45 (m, 1H), 7.42-7.37 (m, 2H), 5.85 (dddd, J = 17.2, 10.1, 7.1, 7.1 Hz, 1H), 5.89-5.78 (m, 1H), 4.26 (dd, J = 6.9, 5.2 Hz, 2H), 2.62-2.50 (m, 2H), 0.94 (s, 9H), 0.13 (s, 3H), 0.09 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 190.0, 133.2, 133.1, 130.9, 128.7, 120.1, 118.5, 94.5, 86.7, 78.8, 39.4, 25.8, 18.4, -4.5, -4.9; HRMS (EI): $[M]^+$ calcd. For $C_{19}H_{26}O_2Si$, 314.1702; Found: 314.1700.



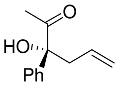
Carbonic acid allyl ester 1-methyl-2-oxo-2-phenyl-ethyl ester: 640 mg 2-bromopropionophenone (3.0 mmol) and 500 mg sodium allyl carbonate (4.0 mmol) were stirred in 15 mL DMF overnight. The reaction mixture was transferred into a separation funnel and diluted with 60 mL water. The aqueous layer was extracted with diethyl ether 40 mL three times. The organic layer was combined and washed with water 50 mL three times and brine once. It was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph eluted with 10% ethyl acetate in petroleum ether in 610 mg (87%) as a colorless oil. R_f = 0.65 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3065 (w), 2991 (m), 2942 (w), 1748 (s), 1702 (s), 1598 (m), 1451 (s), 1373 (s), 1299 (s), 1258 (s), 1230 (s), 1139 (m), 1067 (m), 1021 (s), 972 (s), 948 (m), 889 (m), 787 (m), 701 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.95 (m, 2H), 7.60 (m, 1H), 7.49 (m, 2H), 5.92 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.8 Hz, 1H), 5.87 (d, J = 7.0 Hz, 1H), 5.37 (dq, J_1 = 17.1 Hz, J_2 = 1.5 Hz, 1H), 5.27 (dt, J_1 = 10.5 Hz, J_2 = 1.2 Hz, 1H), 4.64 (dt, J_1 = 5.6 Hz, J_2 = 1.2 Hz, 2H), 1.58 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.5, 154.4, 134.2, 133.8, 131.3, 128.9, 128.5, 119.1, 74.7, 68.9, 17.4. HRMS (EI): $[M]^+$ calcd. For $C_{13}H_{14}O_3$, 234.0892; Found: 234.0900.



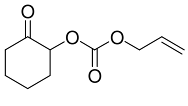
Carbonic acid allyl ester (*E*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-methyl-2-phenyl-vinyl ester (**7**): Method B: Starting from 430 mg carbonic acid allyl ester 1-methyl-2-oxo-2-phenyl-ethyl ester (1.8 mmol), 421 mg **7** (67%) was isolated as colorless oil. R_f = 0.47 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2957 (s), 2931 (s), 2859 (s), 1757 (s), 1472 (m), 1445 (m), 1363 (m), 1296 (s), 1254 (s), 1201 (s), 1154 (s), 1107 (m), 1068 (s), 1008 (m), 939 (m), 891 (m), 861 (s), 840 (s), 782 (s), 700 cm^{-1} (s); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.40-7.20 (m, 5H), 5.83 (m, 1H), 5.22 (m, 2H), 4.56 (dt, J_1 = 5.6 Hz, J_2 = 1.4 Hz, 2H), 2.07 (s, 3H), 0.92 (s, 9H), -0.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 153.5, 142.5, 135.8, 134.1, 131.4, 128.1, 128.0, 118.7, 68.6, 25.7, 18.2, 14.8, -4.3. HRMS (EI): $[M]^+$ calcd. For $C_{19}H_{28}O_4Si$, 348.1757; Found: 348.1765. The structure was further confirmed by HMBC and NOE experiment.



(*R*)-(+)-3-(*tert*-Butyl-dimethyl-silanyloxy)-3-phenyl-hex-5-en-2-one (**8**): Starting from 70 mg **7** and following the procedure of palladium catalyzed decarboxylation alkylation 57 mg product was obtained as a colorless oil (94 %). R_f = 0.58 (Petroleum ether, diethyl ether 9:1); $[\alpha]_D^{23}$ = +39.3 (c, 1.8; CH_2Cl_2, 80% ee); IR(neat): $\tilde{\nu}_{max}$ = 3078 (w), 2958 (s), 2930 (s), 2858 (s), 1716 (s), 1641 (w), 1472 (m), 1448 (m), 1351 (m), 1260 (s), 1204 (m), 1145 (s), 1107 (m), 1075 (m), 915 (m), 830 (s), 777 (s), 700 cm^{-1} (s); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.36-7.23 (m, 5H), 5.63 (ddt, J_1 = 17.1 Hz, J_2 = 10.4 Hz, J_3 = 6.7 Hz, 1H), 4.98 (m, 2H), 3.01 (ddt, J_1 = 15.3 Hz, J_2 = 6.9 Hz, J_3 = 1.5 Hz, 1H), 2.85 (ddt, J_1 = 15.3 Hz, J_2 = 6.7 Hz, J_3 = 1.4 Hz, 1H), 2.07 (s, 3H), 0.99 (s, 9H), 0.08 (s, 3H), 0.01 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 209.5, 141.7, 133.0, 128.4, 127.7, 125.9, 118.4, 85.6, 41.6, 26.20, 26.15, 18.9, -2.2, -3.1. Anal. Calcd. for $C_{18}H_{28}O_2Si$: C, 71.00; H, 9.27; Found: C, 70.85; H, 9.09.



(*R*)-(–)-3-Hydroxy-3-phenyl-hex-5-en-2-one:[15] 50 mg **8** (0.16 mmol) in 1.5 mL THF was treated with 0.17 mL 1.0 M TBAF in THF and was stirred for 5 min. Most solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to afford 26.5 mg colorless oil (87%). R_f = 0.21 (Petroleum ether, diethyl ether 9:1); $[\alpha]_D^{24}$ = -91.3 (c, 1.05; benzene; 80% ee; lit. for *S*-, +124.7; c, 0.635; benzene; 98% ee); HPLC (Chiralcel® OJ-H column; UV = 230 nm; 90:10 heptane/isopropanol; flow rate 1 mL/min; t_1 = 9.007 min (minor), t_2 = 15.771 min (major)); IR(neat): $\tilde{\nu}_{max}$ = 3459 (br, s), 3077 (m), 3026 (m), 2980 (m), 2924 (m), 1711 (s), 1640 (m), 1494 (m), 1448 (s), 1355 (s), 1205 (m), 1180 (s), 1072 (s), 997 (m), 923 (s), 765 (s), 700 cm^{-1} (s); ^{1}H-NMR (400 MHz, $CDCl_3$): δ(ppm) = 7.48 (m, 2H), 7.38 (m, 2H), 7.31 (m, 1H), 5.76 (dddd, J_1 = 17.2 Hz, J_2 = 10.2 Hz, J_3 = 7.9 Hz, J_3 = 6.3 Hz, 1H), 5.20 (m, 2H), 4.26 (s, 1H), 2.96 (m, 2H), 2.09 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 208.8, 140.5, 132.2, 128.8, 128.1, 126.1, 119.8, 82.2, 41.5, 24.1.



Carbonic acid allyl ester 2-oxo-cyclohexyl ester: 2-hydroxycyclohexanone dimer 1.14 g (5 mmol) was suspended in 25 mL dichloromethane and was added 1.20 mL pyridine (15 mmol), then 1.60 mL allylchloroformate (15 mmol). The reaction mixture was stirred at room temperature for 24 h until it turned clear. TLC analysis showed there is very little product. 2 mL pyridine and 2 mL allylchloroformate was added at 0 °C. TLC after 5 min suggested the accomplishment of the reaction. The reaction solution was transferred into a separation funnel with 40 mL diethyl ether and was washed with 60 mL water and then 60 mL brine. The organic layer was dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified with 10% ethyl acetate in petroleum to afford 1.56 g colorless oil (79%). R_f = 0.43 (30% ethyl acetate

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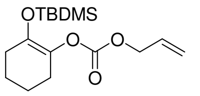
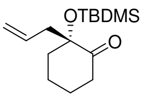
[15] Soai, K.; Ishizaki, M. *J. Org. Chem.* **1986**, *51*, 3290-3295.

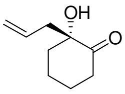
in petroleum); IR(neat): $\tilde{\nu}_{max}$ = 2947 (s), 2958 (s), 2870 (m), 1755 (s), 1728 (s), 1650 (w), 1452 (m), 1377 (s), 1302 (s), 1264 (s), 1219 (s), 1116 (s), 1022 (s), 995 (m), 958 (m), 939 (m), 786 cm^{-1} (m); ^{1}H-NMR (500 MHz, $CDCl_3$): δ(ppm) = 5.95 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.7 Hz, 1H), 5.40 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.29 (dq, J_1 = 10.5 Hz, J_2 = 1.3 Hz, 1H), 5.03 (m, 1H), 4.66 (m, 2H), 2.54 (m, 1H), 2.39 (m, 2H), 2.10 (m, 1H), 2.00 (m, 1H), 1.80 (m, 2H), 1.64 (m, 1H); ^{13}C-NMR (125 MHz, $CDCl_3$): δ = 204.2, 154.2, 131.4, 119.0, 79.5, 68.8, 40.6, 33.0, 27.0, 23.7. HRMS (EI): $[M]^+$ calcd. For $C_{10}H_{14}O_4$, 198.0892; Found: 198.0899.



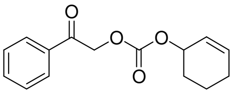
Carbonic acid allyl ester 2-(*tert*-butyl-dimethyl-silanyloxy)-cyclohex-1-enyl ester (**9**): 400 mg carbonic acid allyl ester 2-oxo-cyclohexyl ester (2 mmol) in 10 mL THF was cooled to -78 °C and was treated with the solution of 367 mg NaHMDS in 4 mL THF. The reaction mixture was stirred for 1 h and was added 360 mg TBSCl in 2 mL THF. The reaction was stirred at -78 °C for 30 min and warmed to r.t. for 1 h before the quenching of water. It was transferred into a separation funnel and extracted with 20 mL diethyl ether. The organic layer was washed with brine and dried over magnesium sulfate. After filtration and concentration the residue was purified by silica gel column chromatography eluted with 2% diethyl ether in petroleum ether to afford 417 mg colorless oil (67%). R_f = 0.45 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3087 (w), 2933 (s), 2859 (s), 1749 (s), 1712 (m), 1450 (m), 1375 (m), 1249 (s), 1129 (m), 1038 (m), 995 (m), 968 (s), 933 (s), 839 (s), 784 (s), 701 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.95 (ddt, J_1 = 17.2 Hz, J_2 = 10.5 Hz, J_3 = 5.7 Hz, 1H), 5.37 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.27 (dq, J_1 = 10.5 Hz, J_2 = 1.3 Hz, 1H), 4.63 (m, 2H), 2.22 (m, 2H), 2.12 (m, 2H), 1.68 (m, 4H), 0.91 (s, 9H), 0.12 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 153.1, 138.9, 131.6, 130.8, 119.0, 68.6, 29.6, 26.2, 25.6, 22.83, 22.76, 18.1, -4.3. HRMS (EI): $[M]^+$ calcd. For $C_{16}H_{28}O_4Si$, 312.1757; Found: 312.1764.



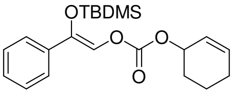
(*R*)-2-Allyl-2-(*tert*-butyl-dimethyl-silanyloxy)-cyclohexanone (**10**): Starting from 62.5 mg **9** and following the procedure of palladium catalyzed decarboxylation alkylation 51.5 mg product was obtained as a colorless oil (96%). R_f = 0.48 (Petroleum ether, diethyl ether 9:1); $[\alpha]_D^{23}$ = -27.7 (c, 2.0; CH_2Cl_2, 64% ee); IR(neat): $\tilde{\nu}_{max}$ = 3078 (w), 2936 (s), 2857 (s), 1725 (s), 1640 (w), 1472 (m), 1431 (m), 1254 (s), 1172 (s), 1126 (s), 1074 (s), 966 (m), 916 (m), 835 (s), 777 cm^{-1} (s); ^{1}H-NMR (400 MHz, $CDCl_3$): 5.77 (m, 1H), 5.03 (m, 2H), 2.55 (m, 1H), 2.47 (m, 2H), 2.35 (m, 1H), 2.0-1.5 (m, 6H), 0.89 (s, 9H), 0.17 (s, 3H), 0.01. (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ = 211.2, 133.2, 117.9, 81.4, 42.6, 40.5, 39.5, 27.4, 26.1, 22.2, 18.7, -2.2, -2.8. HRMS (EI): $[M-C_4H_9]^+$ calcd. For $C_{11}H_{19}O_2Si$, 211.1154; Found: 211.1151.



(*R*)-2-Allyl-2-hydroxy-cyclohexanone:[16] 46 mg **10** (0.17 mmol) in 1 mL THF was treated with 0.17 mL 1.0 M TBAF and stirred for 5 min. Most solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to afford 26.5 mg colorless oil (100%). R_f = 0.54 (30% ethyl acetate in petroleum ether); $[\alpha]_D^{23}$ = -73.4 (c, 2.6; $CHCl_3$; 64% ee; lit. for *S*-, +136.6; c, 2; $CHCl_3$; 86% ee); HPLC (Chiralcel® AD column; UV = 210 nm; 98:2 heptane/isopropanol; flow rate 1 mL/min; t_1 = 12.643 min (minor), t_2 = 13.711 min (major)); ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 5.72 (m, 1H), 5.12 (m, 2H), 3.96 (s, 1H), 2.60 (dd, J_1 = 14.2 Hz, J_2 = 7.3 Hz, 1H), 2.46 (m, 3H), 2.23 (m, 1H), 2.12 (m, 1H), 1.9-1.5 (m, 4H).



Carbonic acid cyclohex-2-enyl ester 2-oxo-2-phenyl-ethyl ester (**16**): A clean dry 250 mL three neck flask was charged with 505 mg NaH (95%, 20 mmol) and 50 mL THF under nitrogen. To the suspension was added 2 g 2-cyclohexen-1-ol (20 mmol). The suspension was heated to 60 °C for 1 h and cooled to -15 °C. A stream of carbon dioxide from the vapor of dry ice was bubbled through the reaction mixture for 30 min. The stream of carbon dioxide was stopped and the reaction flask was allowed to warm to room temperature. The solvent was removed *in vacuo* and to the residue solid was added 3.98 g 2-bromoacetophenone (20 mmol) in 50 mL DMF. The reaction mixture was stirred at room temperature overnight. 200 mL diethyl ether was used to transfer the reaction mixture into a separation funnel and the solution was washed with 100 mL water four times and brine once. The organic layer was dried over magnesium sulfate and concentrated. The residue was purified by silica gel column chromatography eluted with 10% ethyl acetate in petroleum ether to afford 2.4 g slight yellow oil (46%). R_f = 0.14 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3034 (m), 2941 (s), 2870 (m), 2836 (m), 1747 (s), 1712 (s), 1598 (s), 1582 (m), 1450 (s), 1424 (s), 1373 (s), 1337 (s), 1269 (s), 1226(s), 1163 (m), 1050 (m), 1002 (s), 953 (s), 914 (s), 784 (m), 760 (s), 690 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.62 (m, 2H), 7.50 (m, 1H), 6.01 (m, 1H), 5.82 (m, 1H), 5.35 (m, 2H), 5.18 (m, 1H), 2.2-1.5 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 154.6, 134.1, 134.0, 133.7, 129.0, 127.8, 124.7, 72.8, 68.5, 28.2, 24.9, 18.6.



Carbonic acid (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-vinyl ester cyclohex-2-enyl ester (**12b**): To a clean and oven-dried flask was charged with 4.6 mL 20% wt solution of phosgene in toluene (8.75 mmol) and cooled to -35 °C by a dry-ice-acetone bath. A solution of 730 mg 2-cyclohexenol (7.5 mmol) in 5 mL THF was slowly added to the phosgene solution and

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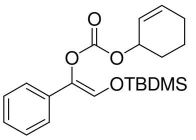
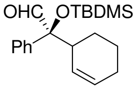
[16] Compain, P.; Goré, J.; Vatèle J. M. *Tetrahedron* **1996**, *52*, 6647-6664.

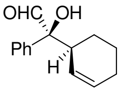
stirred for 20 min. The reaction flask was moved into a ice-water bath and stirred for 30 min. A nitrogen stream was bubbled into the solution for 1 h, with a base trap at the end to absorb the excess phosgene removed by the nitrogen stream. The solution was cooled to -78 °C before use. Meanwhile, 1.15 g (6 mmol) NaHMDS was weighted to a clean oven-dried flask in a dry-box and cooled in a dry-ice-acetone bath. To the solid was added 20 mL dry-THF and 0.91 mL re-distilled TMEDA. 2-(*tert*-butyldimethylsilanyloxy)-acetophenone 1.25 g (5.0 mmol) in 5 mL THF was slowly added into the solution and stirred at -78 °C for 1 h. The enolate solution then was transferred to the chlorocarbonate solution through a cannula and stirred for 5 min before the dry-ice bath was removed and the reaction flask was allowed to warm to room temperature in the air. The reaction mixture was quenched with ammonium chloride aqueous solution and transferred with 50 mL diethyl ether into a separation funnel. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration, the residue was purified by silica gel column chromatography eluted with 2% diethyl ether in petroleum. 580 mg colorless oil was isolated (31%) together with 910 mg **13b** (49%). $R_f = 0.66$ (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max} = 3036$ (w), 2952 (s), 2932 (s), 2859 (m), 1755 (s), 1666 (m), 1472 (m), 1353 (s), 1244 (s), 1155 (s), 1084 (m), 1026 (s), 1002 (m), 916 (s), 842 (s), 783 (s), 734 (m), 696 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$ (m, 2H), 7.30 (3H), 7.12 (s, 1H), 6.01 (m, 1H), 5.80 (m, 1H), 5.19 (m, 1H), 2.2-1.6 (m, 6H), 0.97 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.8$, 139.4, 135.9, 133.9, 128.5, 128.3, 125.3, 124.9, 121.7, 72.8, 28.4, 26.1, 26.0, 25.1, 18.7, -4.1. HRMS (EI): $[M-C_7H_9O_2]^+$ calcd. For $C_{14}H_{19}O_2Si$, 249.1311; Found: 249.1308.



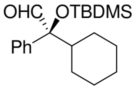
Carbonic acid (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-phenyl-vinyl ester cyclohex-2-enyl ester (**13b**): Method B: Started from 664 mg **16** (2.55 mmol), the crude product was filtrated through a short silica gel column washed with 5% diethyl ether in petroleum ether to afford 794 mg colorless oil (83%). $R_f = 0.49$ (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max} = 3036$ (w), 2932 (s), 2859 (s), 1759 (s), 1668 (s), 1472 (m), 1301 (s), 1245 (s), 1178 (s), 1006 (s), 939 (m), 883 (m), 831 (s), 785 (s), 733 (m), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.4$-7.2 (m, 5H), 6.74 (s, 1H), 6.00 (m, 1H), 5.81 (m, 1H), 5.17 (m, 1H), 2.2-1.6 (m, 6H), 0.96 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 152.7$, 134.8, 133.5, 130.6, 128.7, 128.6, 127.3, 124.9, 123.2, 72.5, 28.2, 25.9, 25.5, 24.9, 18.6, -5.2. HRMS (EI): M^+ calcd. For $C_{21}H_{30}O_4Si$, 374.1913; Found: 374.1925.



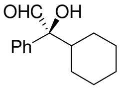
(*S*)-(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohex-2-enyl-2-phenyl-acetaldehyde (**14b**): Starting from 794 mg **13b** (2.12 mol) and following the procedure of palladium catalyzed decarboxylation alkylation, the crude product was dissolved in 5 mL 10% diethyl ether in petroleum ether and passed through a short pipette with 2 mL silica gel to remove the catalyst. 735 mg product contaminated with 10 mol% Dba from $Pd_2(dba)_3CHCl_3$ (a mixture of two diastereomers in 11:1 ratio) was isolated (99%) as a colorless oil. The analytical pure product was purified by silica gel column chromatography eluted with 2% diethyl ether in petroleum ether. R_f = 0.55 (10% diethyl ether in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3028 (w), 2931 (s), 2857 (s), 2710 (w), 1739 (s), 1473 (m), 1447 (m), 1388 (w), 1255 (s), 1190 (m), 1078 (m), 1003 (m), 947 (m), 837 (s), 778 (s), 738 (m), 701 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H), 7.5-7.25 (m, 5H), 5.70 (m, 1H), 5.35 (m, 1H), 3.08 (m, 1H), 1.94 (m, 2H), 1,77 (m, 1H), 1.66 (m, 1H), 1.50 (m, 2H), 0.98 (s, 9H), 0.17 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 138.9, 129.9, 128.5, 127.7, 126.6, 125.9, 87.2, 44.4, 26.3, 25.1, 24.1, 22.2, 19.4, -2.1, -2.2. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{19}H_{29}OSi$, 301.1988; Found: 301.1988.



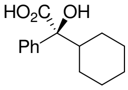
(*S*)-2-(*R*)-Cyclohex-2-enyl-2-hydroxy-2-phenyl-acetaldehyde: 50 mg **14b** (0.15 mmol) was dissolved in 1 mL THF and was added 0.2 mL 1.0 M TBAF in THF. 5% KH_2PO4 aqueous solution was added after 5 min and extracted with 5 mL diethyl ether. The organic layer was dried over anhydrous magnesium sulfate. After concentration the crude product was purified by silica gel column chromatograph. 15 mg product was obtained as a white solid (46%). Major Isomer: M.p. = 84-86 °C; $[\alpha]_D^{23}$ = +151.8 (c, 1.68; CH_2Cl_2; 99% ee); HPLC of the major isomer (Chiralcel® OJ-H column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 9.562 min (minor), t_2 = 14.014 min (major)); HPLC of the minor isomer (Chiralcel® OJ column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 9.711 min (minor), t_2 = 10.527 min (major)). R_f = 0.21 (10% diethyl ether in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3505 (s), 2937 (s), 1721 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ = 9.69 (d, *J* = 1.3 Hz, 1H), 7.56 (m, 2H), 7.43 (m, 2H), 7.34 (m, 1H), 5.85 (m, 1H), 5.24 (d, *J* = 10.3, 1H), 3.71 (d, *J* = 0.9 Hz, 1H), 3.20 (m, 1H), 2.02 (m, 2H), 1.86 (m, 1H), 1.60 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.5, 137.8, 131.6, 129.0, 128.0, 126.2, 124.2, 83.8, 42.0, 24.8, 23.5, 21.8. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{13}H_{15}O$, 187.1123; Found: 187.1119.



(*S*)-(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohexyl-2-phenyl-acetaldehyde (**15b**): 680 mg **14b**, 136 mg 10% Pd on carbon in 20 mL methanol was stirred overnight with 1 atm H_2. The catalyst was removed by filtration through a pad of celite and the solution was concentrated. No further purification required. 639 mg colorless oil was obtained (96%). $[\alpha]_D^{23}$= +38.9 (c, 2.1; CH_2Cl_2); R_f = 0.65 (10% diethyl ether in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 2932 (s), 2855 (s), 1739 (s), 1472 (m), 1447 (m), 1387 (w), 1254 (s), 1204 (s), 1077 (m), 1005 (m), 945 (m), 912 (m), 837 (s), 778 (s), 738 (m), 720 (s), 700 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.69 (s, 1H), 7.5-7.2 (m, 5H), 2.15 (m, 1H), 1.78 (m, 1H), 1.65 (m, 2H), 1.56 (m, 1H), 1.2 (m, 6H), 1.03 (s, 9H), 0.20 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.3, 139.2, 128.4, 127.4, 126.2, 88.4, 45.6, 27.8, 26.6, 26.5, 26.4, 25.6, 19.7, -1.95, -2.1. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{19}H_{31}OSi$, 303.2144; Found: 303.2158.



(*S*)-2-Cyclohexyl-2-hydroxy-2-phenyl-acetaldehyde: 31 mg **15b** (0.093 mmol) in 0.5 mL THF was treated with 0.1 mL 1.0 M TBAF and stirred for 5 min. Most solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to afford 9.0 mg white solid (44%). M.p. = 87-89 ^{o}C; $[\alpha]_D^{25}$ = +180.3 (c, 0.84; CH_2Cl_2; 84% ee); HPLC (Chiralcel® AD column; 98:2 Heptane / Isopropanol; UV = 220 nm; flow rate = 1.0 mL / min; t_1 = 8.438 min (minor), t_2 = 10.025 min (major)). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.64 (d, *J* = 1.5 Hz, 1H), 7.51 (m, 2H), 7.41 (m, 2H), 7.31 (m, 1H), 3.72 (d, *J* = 1.5 Hz, 1H), 2.21 (m, 1H), 1.80 (m, 1H), 1.68 (m, 2H), 1.5-1.1 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2, 138.1, 128.8, 127.7, 125.9, 84.5, 43.5, 26.9, 26.5, 26.3, 26.2, 25.1. HRMS (EI): $[M]^+$ calcd. For $C_{14}H_{18}O_2$, 218.1307; Found: 218.1308.



(*S*)-2-cyclohexyl-2-hydroxy-2-phenylacetic acid (**17**)[17]: 600 mg **15b** (1.8 mmol) in a flask was added 45 mL *t*-BuOH, 18 mL water, 12 mL 2-methyl-2-butene, 1.71 g sodium phosphate monobasic (12.42 mmol) and 1.87 g sodium chlorite (16.56 mmol) in the order. The reaction mixture was stirred at room temperature overnight and transferred into a separation funnel. 100 mL ethyl acetate was used to extracted the product three times. The organic layer combined was combined and washed with 5% KH_2PO_4 aqueous solution two times and brine once. The organic layer was dried over anhydrous sodium sulfate. After filtration and concentration the residue was load on a short silica gel column chromatography (about 50 g silica) and eluted with 10% diethyl ether 200 mL and then 5% methanol in methylene chloride 200 mL. 400 mg glass like material was obtained (95%) with 84% enantiomeric excess by chiral HPLC. The analytic pure material was obtained by recrystallization from 3 mL 5% DCM in hexane. White solid; $[\alpha]_D^{23}$ = +24.0 (c, 1.0; EtOH, >99% ee); HPLC (Chiralcel® AS column; 95:5:0.1 Heptane / Isopropanol / TFA; flow rate = 1.0 mL / min; 230 nm UV; t_1 = 5.535 min (minor, not observed for enantiomeric rich material), t_2 = 7.903 min (major)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63 (m, 2H), 7.34 (m, 2H), 7.27 (m, 1H), 3.47 (brs, 1H), 2.26 (m, 1H), 1.82 (m, 1H), 1.7-1.0 (m, 9H).

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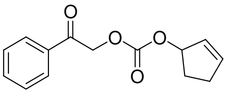
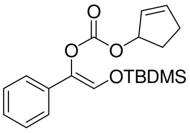
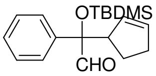
[17] Senanayake, C. H.; Fang K.; Crover, P.; Bakale, R. P.; Vandenbossche, C. R.; Wald, S. A.; *Tetrahedron Lett.* **1999**, *40*, 819-822; Grover, P. T.; Bhongle, N. N.; Wald, S. A.; Senanayake, C. H. *J. Org. Chem.* **2000**, *65*, 6283-6287; Masumoto, S.; Suzuki, M.; Kanai, M. Shibasaki, M. *Tetrahedron Lett.* **2002**, *43*, 8647-8651; Gupta, P. Fernandes, R. A.; Kumar, P. *Tetrahedron Lett.* **2003**, *44*, 4231-4232; Tokuda, O.; Kano, T.; Gao, W. G.; Ikemoto, T.; Maruoka, K. *Org. Lett.* **2005**, *7*, 5103-5105.



Carbonic acid cyclopent-2-enyl ester 2-oxo-2-phenyl-ethyl ester: 119 mg triphosgene (0.4 mmol) was dissolved in 5 mL THF and cooled to -78 °C. To the solution was added a solution of 0.081 mL pyridine (1 mmol), 136 mg hyroxyacetophenone (1 mmol) in 2 mL THF. The reaction was stirred for 15 min and warmed to -25 °C for 10 min, then -15 °C for 30 min. At this point a solution of 84 mg 2-cyclopentenol (1 mmol) and 0.081 mL pyridine in 2 mL THF was added slowly. The reaction was slowly warmed to room temperature. Diluted with 20 mL diethyl ether and washed with brine once, the organic layer was dried over magnesium sulfate and concentrated. Silica gel column chromatography eluted with 15-30% diethyl ether afforded 85.3 mg colorless oil (35%). R_f = 0.69 (30% ethyl acetate in petroleum ether); IR ($CDCl_3$ film): $\tilde{\nu}_{max}$ =3063 (w), 2974 (m), 2942 (m), 2856 (m), 1748 (s), 1705 (s), 1598 (m), 1450 (m), 1424 (m), 1376 (s), 1342 (s), 1269 (s), 1227 (s), 1110 (m), 1029 (s), 951 (s), 884 (m), 759 (s), 690 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.92 (m, 2H), 7.61 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 7.49 (m, 2H), 6.17 (m, 1H), 5.91 (m, 1H), 5.68 (m, 1H), 5.35 (m, 2H), 2.56 (m, 1H), 2.32 (m, 2H), 2.00 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 154.7, 139.0, 134.0, 128.9, 128.4, 127.8, 85.1, 68.5, 31.1, 29.6. HRMS (EI): $[M]^+$ calcd. For $C_{14}H_{14}O_4$, 246.0892; Found: 246.0893.

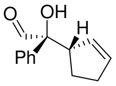


Carbonic acid (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-phenyl-vinyl ester cyclopent-2-enyl ester (**13a**): To a solution of 700 mg NaHMDS in 20 mL THF at -78 °C was added 780 mg carbonic acid cyclopent-2-enyl ester 2-oxo-2-phenyl-ethyl ester (3.17 mmol) in 5 mL THF and stirred for 30 min. To the enolate was added 573 mg TBSCl in 5 mL THF and allow the reaction warmed to room temperature. The reaction was quenched with saturated ammonium chloride aqueous solution and extracted with diethyl ether. The organic layer was separated out and dried over magnesium sulfate. After filtration and concentration, the crude product was purified by silica gel column chromatography eluted with 2% diethyl ether in petroleum ether to afford 832 mg colorless oil (73%). R_f = 0.38 (Diethyl ether/petroleum ether 1:9); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.35 (m, 2H), 7.30 (m, 2H), 7.22 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 6.74 (s, 1H), 6.16 (m, 1H), 5.91 (m, 1H), 5.68 (m, 1H), 2.56 (m, 1H), 2.32 (m, 2H), 1.98 (m, 1H), 0.96 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.8, 138.7, 134.7, 133.5, 130.6, 128.7, 128.6, 127.3, 123.2, 84.9, 31.2, 29.7, 25.5, 18.2, -5.2. HRMS (EI): $[M-C_6H_6O_2]^+$ calcd. For $C_{14}H_{22}O_2Si$, 250.1389; Found: 250.1381.

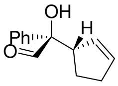


(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclopent-2-enyl-2-phenyl-acetaldehyde (**14a**): Starting from 108 mg **13a** (0.3 mmol), 62 mg product was isolated (98%) as a mixture of two diastereomers in 2.5:1 ratio. Colorless oil; R_f = 0.63 (10% diethyl ether in petroleum ether);

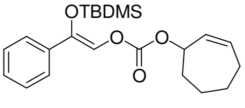
Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 7.5-7.25 (m, 5H), 5.73 (dq, J_1 = 5.9 Hz, J_2 = 2.2 Hz, 1H), 5.57 (m, 1H), 3.53 (m, 1H), 2.22 (m, 1H), 2.04 (m, 1H), 1.94 (m, 1H), 1.70 (m, 1H), 0.97 (s, 9H), 0.13 (s, 3H), 0.05 (s, 3H); Minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 9.74 (s, 1H), 7.5-7.25 (m, 5H), 5.86 (dq, J_1 = 5.9 Hz, J_2 = 2.2 Hz, 1H), 5.57 (m, 1H), 3.66 (m, 1H), 2.22 (m, 1H), 2.04 (m, 1H), 1.94 (m, 1H), 1.70 (m, 1H), 0.95 (s, 9H), 0.11 (s, 6H); HRMS (EI): $[M-CHO]^+$ calcd. For $C_{18}H_{27}OSi$, 287.1831; Found: 287.1829.



Cyclopent-2-enyl-2-hydroxy-2-phenyl-acetaldehyde: R_f = 0.30 (10% ethyl acetate in petroleum ether); $[\alpha]_D^{22}$ = -105.1 (c, 0.75; CH_2Cl_2, 87% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 6.654 min (major), t_2 = 7.627 min (minor)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.70 (d, J = 0.8 Hz, 1H), 7.55 (m, 2H), 7.43 (m, 2H), 7.33 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 6.02 (dq, J_1 = 5.8 Hz, J_2 = 2.2 Hz, 1H), 5.46 (dq, J_1 = 5.8 Hz, J_2 = 2.3Hz, 1H), 3.72 (m, 1H), 3.36 (d, J = 0.9 Hz, 1H), 2.37 (m, 1H), 2.28 (m, 1H), 1.78 (m, 1H), 1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.7, 137.8, 136.6, 128.9, 127.9, 127.7, 126.2, 83.5, 51.7, 32.1, 23.7. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{12}H_{13}O$, 173.0966; Found: 173.0958.

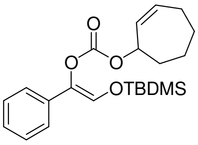


Cyclopent-2-enyl-2-hydroxy-2-phenyl-acetaldehyde: R_f = 0.33 (10% ethyl acetate in petroleum ether); $[\alpha]_D^{23}$ = +17.2 (c, 1.5; CH_2Cl_2, 92% ee); HPLC (Chiralcel® OJ column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 9.571 min (minor), t_2 = 11.305 min (major)); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.68 (d, J = 1.2 Hz, 1H), 7.56 (m, 2H), 7.42 (m, 2H), 7.33 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 5.91 (dq, J_1 = 5.8 Hz, J_2 = 2.3 Hz, 1H), 5.30 (dq, J_1 = 5.8 Hz, J_2 = 2.3Hz, 1H), 3.73 (m, 1H), 3.62 (d, J = 1.2 Hz, 1H), 2.46 (m, 1H), 2.37 (m, 1H), 1.95 (m, 1H), 1.69 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.1, 138.3, 135.0, 128.9, 128.0, 127.8, 126.0, 83.6, 52.0, 33.1, 23.5. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{12}H_{13}O$, 173.0966; Found: 173.0960.

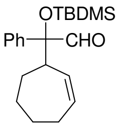


Carbonic acid (Z)-2-(*tert*-butyl-dimethyl-silanyloxy)-2-phenyl-vinyl ester cyclohept-2-enyl ester (**12c**): To a clean and oven-dried flask was charged with 6.0 mL 20% wt solution of phosgene in toluene and cooled to -35 °C by a dry-ice-acetone bath. A solution of 1.12 g 2-cycloheptenol (10 mmol) in 5 mL THF was slowly added to the phosgene solution and stirred for 20 min. The reaction flask was moved into a ice-water bath and stirred for 30 min. A nitrogen stream was bubbled into the solution for 1 h, with a base trap at the end to absorb the excess phosgene removed by the nitrogen stream. The solution was cooled to -78 °C before use. Meanwhile, 1.15 g (6 mmol) NaHMDS was weighted to a clean oven-dried flask in a dry-box and cooled in a dry-ice-acetone bath. To the solid was added 20 mL dry-THF and 0.91 mL re-distilled

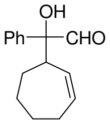
TMEDA. 2-(*tert*-butyldimethylsilanyloxy)-acetophenone 1.25 g (5.0 mmol) in 5 mL THF was slowly added into the solution and stirred at -78 °C for 1 h. The enolate solution then was transferred to the chlorocarbonate solution through a cannula and stirred for 5 min before the dry-ice bath was removed and the reaction flask was allowed to warm to room temperature in the air. The reaction mixture was quenched with ammonium chloride aqueous solution and transferred with 50 mL diethyl ether into a separation funnel. The organic layer was separated and dried over anhydrous magnesium sulfate. After filtration and concentration, the residue was purified by silica gel column chromatography eluted with 2% diethyl ether in petroleum. 241 mg waxy solid was isolated (12.4%). M.p. = 35-42 °C; R_f = 0.53 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 2930 (s), 2858 (m), 1756 (s), 1666 (w), 1472 (w), 1446 (w), 1347 (s), 1252 (s), 1161 (m), 1086 (m), 1025 (m), 973 (m), 840 (m), 784 (m), 695 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.49 (m, 2H), 7.30 (m, 3H), 7.13 (s, 1H), 5.88 (m, 1H), 5.75 (m, 1H), 5.34 (m, 1H), 2.3-1.3 (m, 8H), 0.98 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.4, 139.2, 135.7, 132.6, 132.4, 128.3, 128.1, 125.1, 121.5, 78.7, 32.6, 28.5, 26.6, 26.3, 25.9, 18.6, -4.3. MS (ESI): $[M+H]^+$ 389.2; HRMS (EI): $[M-C_8H_{11}O_2]^+$ calcd. For $C_{22}H_{32}O_4Si$, 249.1311; Found: 249.1301.



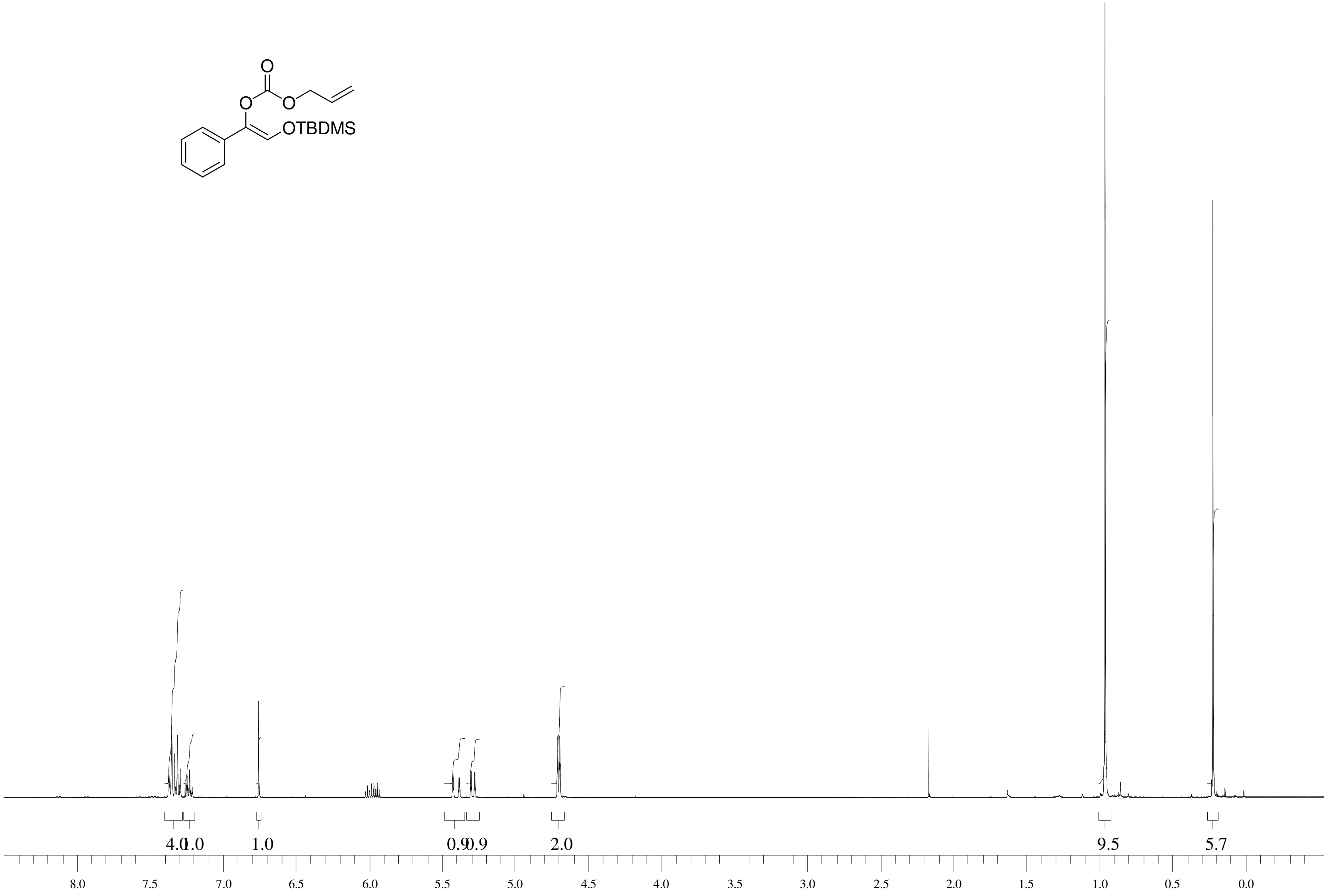
Carbonic acid (*Z*)-2-(*tert*-butyl-dimethyl-silanyloxy)-1-phenyl-vinyl ester cyclohept-2-enyl ester (13c): 776 mg was isolated (40%) as colorless oil. R_f = 0.41 (Diethyl ether/petroleum ether 1:9); IR (film): $\tilde{\nu}_{max}$ = 3033 (w), 2931 (s), 2858 (s), 1760 (s), 1668 (s), 1472 (m), 1448 (m), 1302 (s), 1249 (s), 1177 (s), 1076 (w), 992 (s), 832 (s), 785 (s), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32 (m, 4H), 7.22 (m, 1H), 6.73 (s, 1H), 5.85 (m, 1H), 5.76 (m, 1H), 5.31 (m, 1H), 2.3-1.3 (m, 8H), 0.95 (s, 9H), 0.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.5, 134.7, 133.5, 132.9, 132.0, 130.6, 128.6, 127.3, 123.3, 78.8, 32.8, 28.5, 26.6, 26.4, 25.5, 18.3, -5.1. Anal. Calcd. for $C_{22}H_{32}O_4Si$: C, 68.00; H, 8.30; Found: C, 68.19; H, 8.45.



(*tert*-Butyl-dimethyl-silanyloxy)-2-cyclohept-2-enyl-2-phenyl-acetaldehyde (14c): Starting from 78 mg **12c** (0.2 mmol), 70 mg product was isolated (100%) as colorless oil (50:1 dr). R_f = 0.66 (10% diethyl ether in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3029 (w), 2929 (s), 2856 (s), 1739 (s), 1660 (w), 1472 (m), 1446 (m), 1360 (w), 1254 (s), 1170 (s), 1078 (m), 838 (s), 779 (s), 701 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 9.66 (s, 1H), 7.5-7.25 (m, 5H), 5.73 (m, 1H), 5.50 (m, 1H), 3.25 (m, 1H), 2.1 (m, 3H), 1.8-1.1 (m, 5H), 0.99 (s, 9H), 0.20 (s, 3H), 0.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.6, 139.0, 132.5, 132.1, 128.7, 127.7, 126.7, 89.0, 46.5, 31.5, 29.8, 28.4, 26.4, 26.3, 19.6, -2.09, -2.13. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{20}H_{31}OSi$, 315.2144; Found: 315.2128.



2-Cyclohept-2-enyl-2-hydroxy-2-phenyl-acetaldehyde: white crystals. M.p. = 131-132 °C; R_f = 0.20 (10% diethyl ether in petroleum ether); $[\alpha]_D^{24}$ = +272.5 (c, 0.87; CH_2Cl_2, 99% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 7.216 min (minor), t_2 = 8.270 min (major)); IR ($CDCl_3$ film): $\tilde{\nu}_{max}$ = 3506 (w), 2927 (m), 2857 (m), 1721 (s), 1448 (m), 1383 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$): δ = 9.60 (d, *J* = 1.4 Hz, 1H), 7.50 (m, 2H), 7.41 (m, 2H), 7.32 (tt, J_1 = 7.5 Hz, J_2 = 1.2 Hz, 1H), 5.81 (m, 1H), 5.45 (m, 1H), 3.83 (dd, J_1 = 1.4 Hz, J_2 = 0.5 Hz, 1H), 3.29 (m, 1H), 2.3-2.0 (m, 3H), 1.75 (m, 1H), 1.7-1.4 (m, 3H), 1.3 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 200.3, 137.9, 133.3, 131.1, 129.0, 128.0, 126.5, 85.3, 44.5, 30.9, 28.52, 28.50, 26.3. HRMS (EI): $[M-CHO]^+$ calcd. For $C_{14}H_{17}O$, 201.1279; Found: 201.1276.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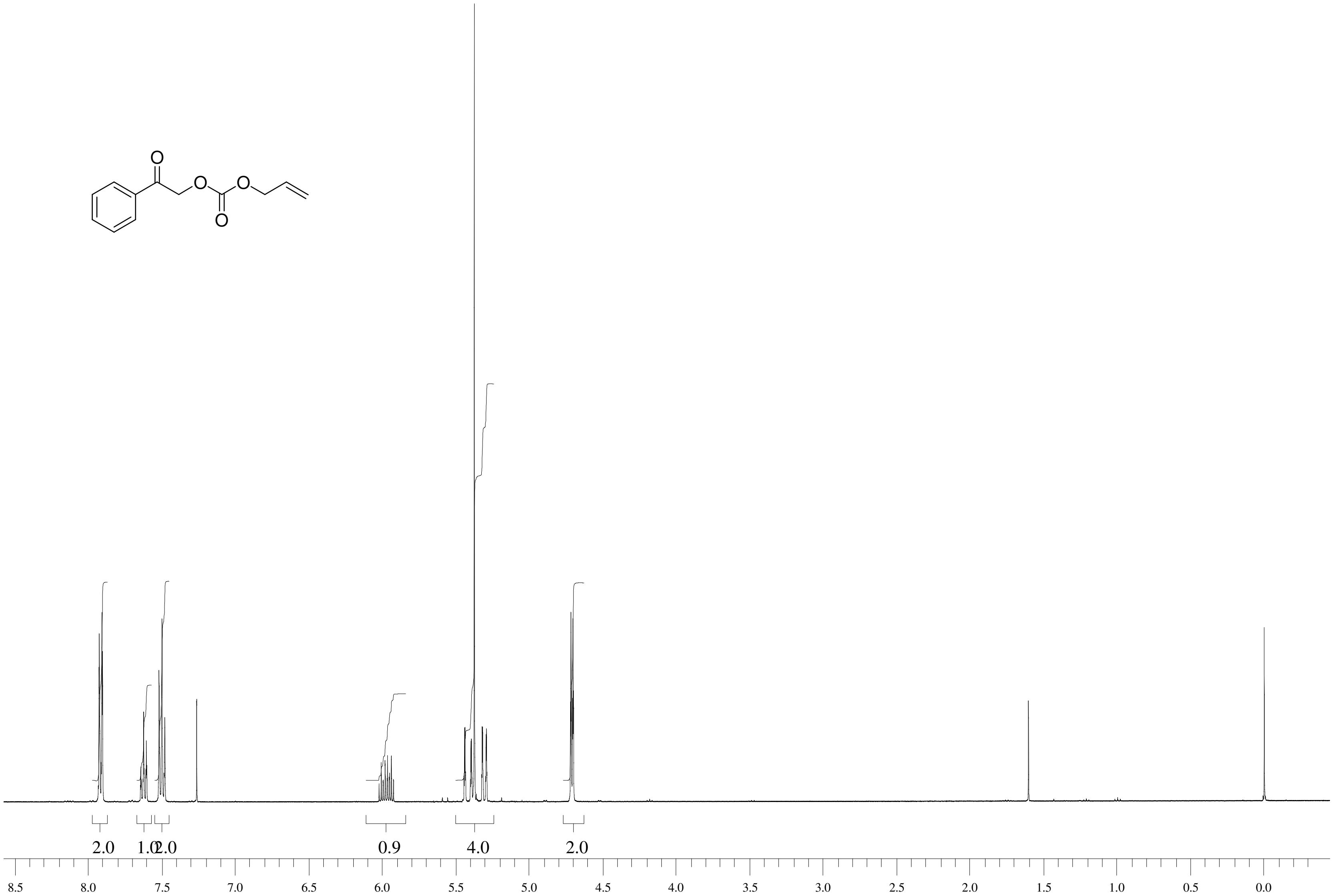
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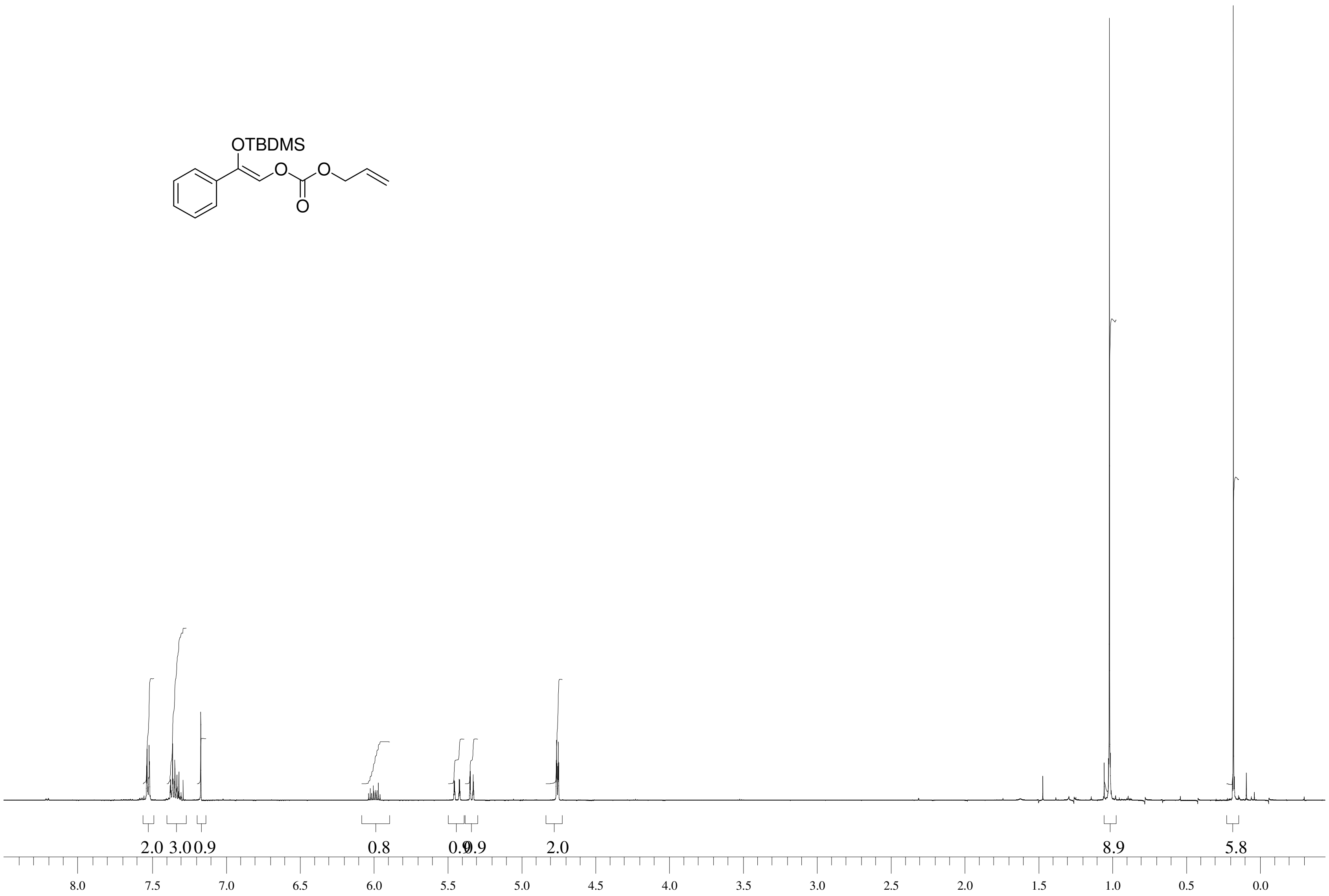
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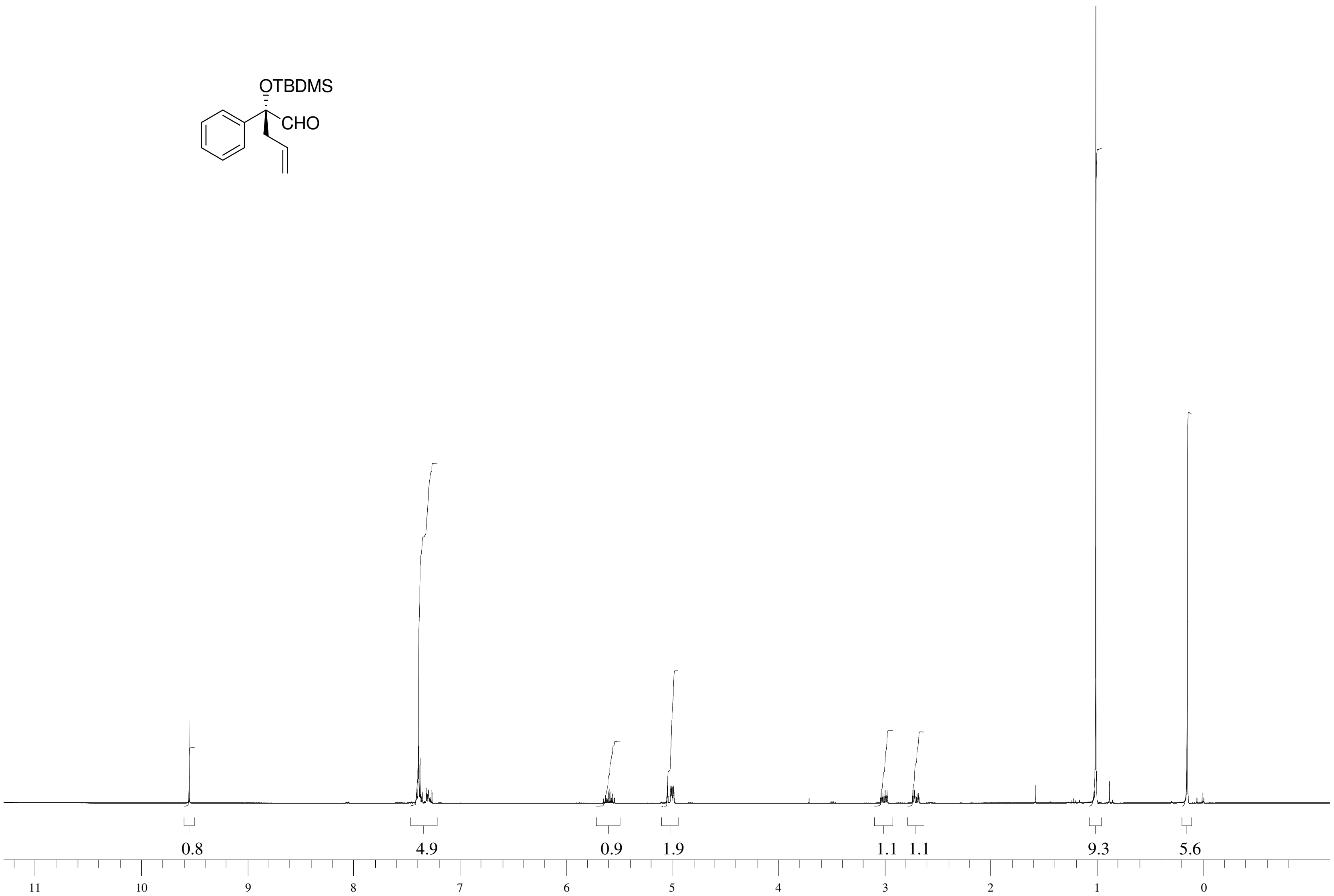
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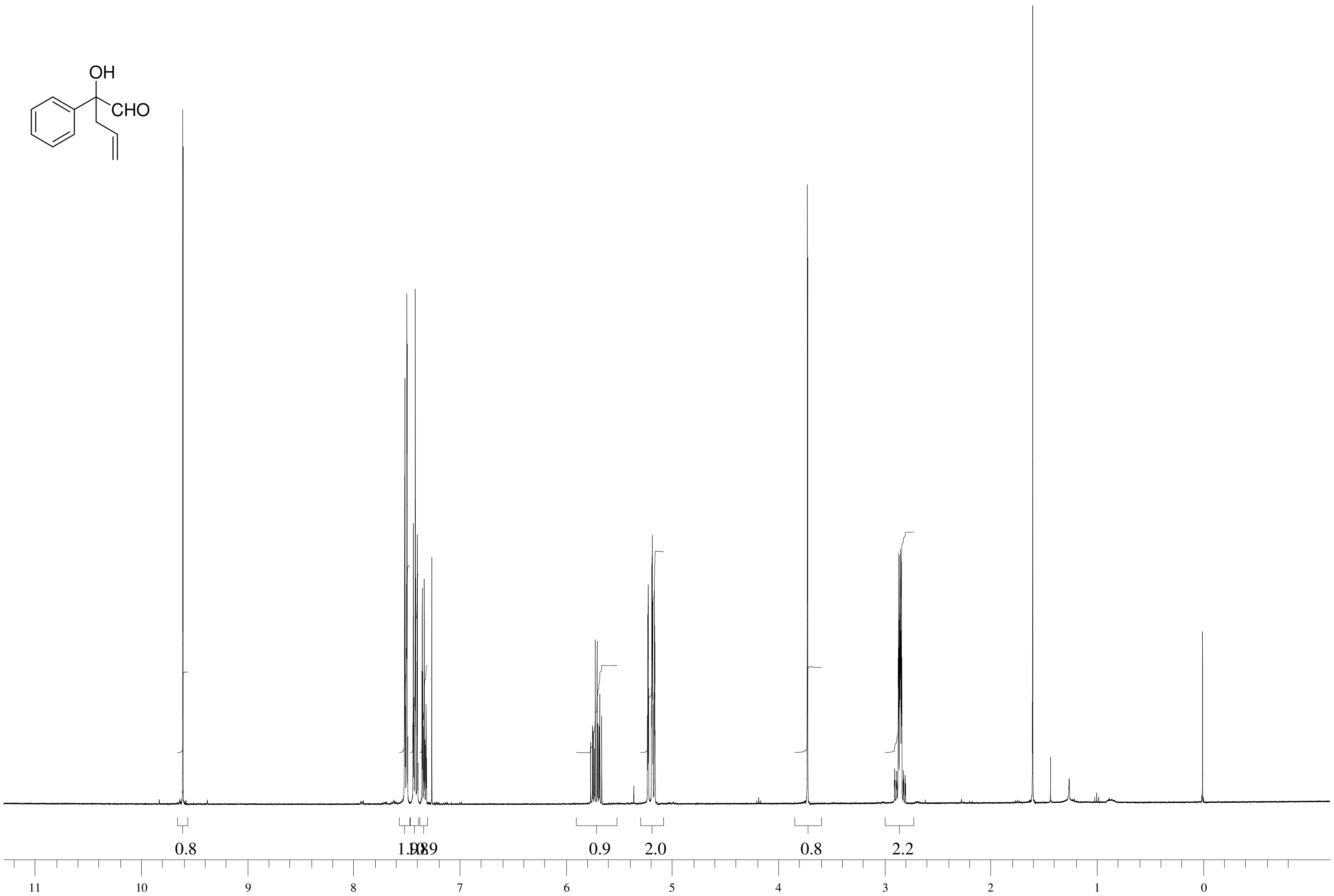
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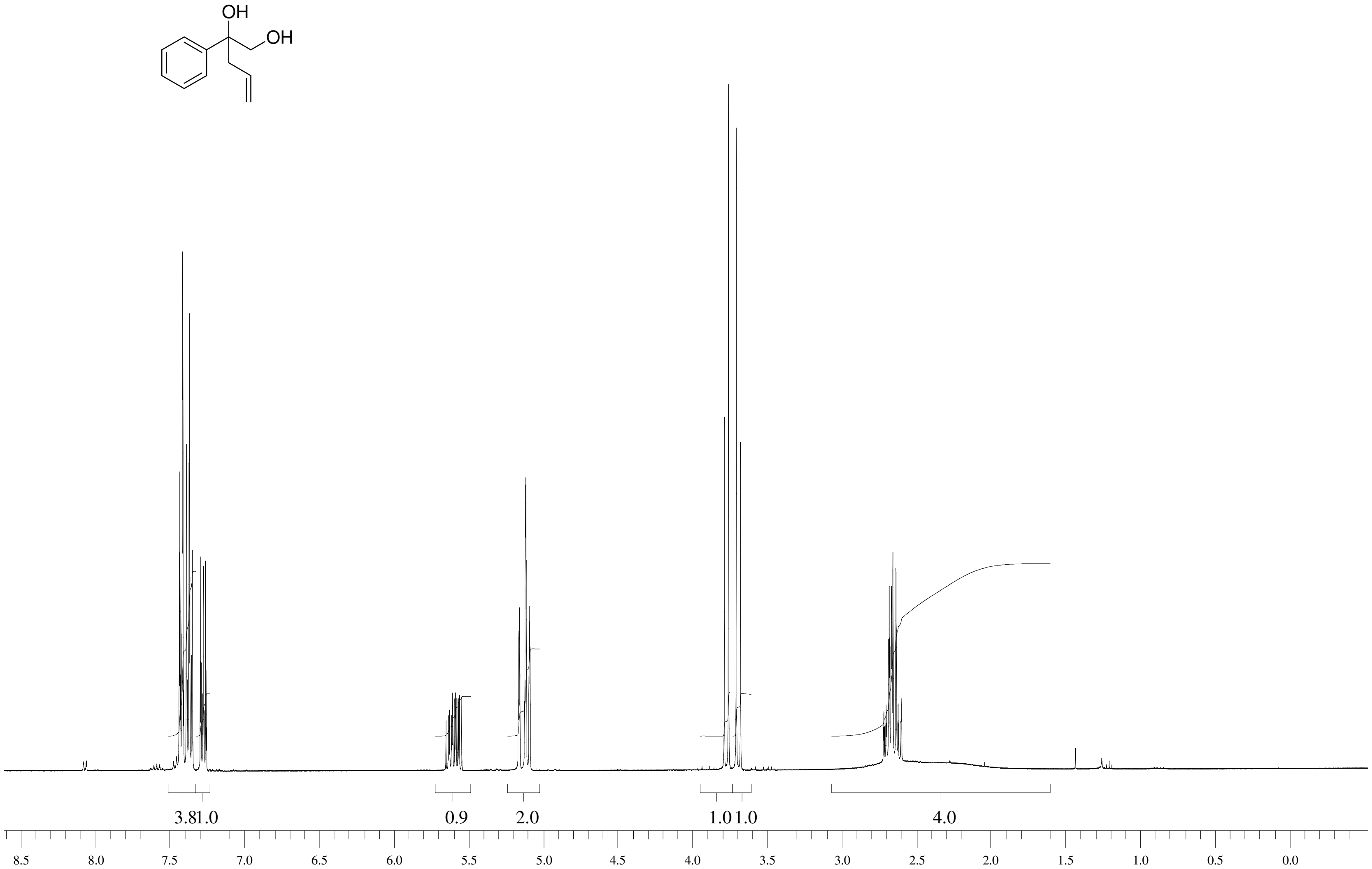
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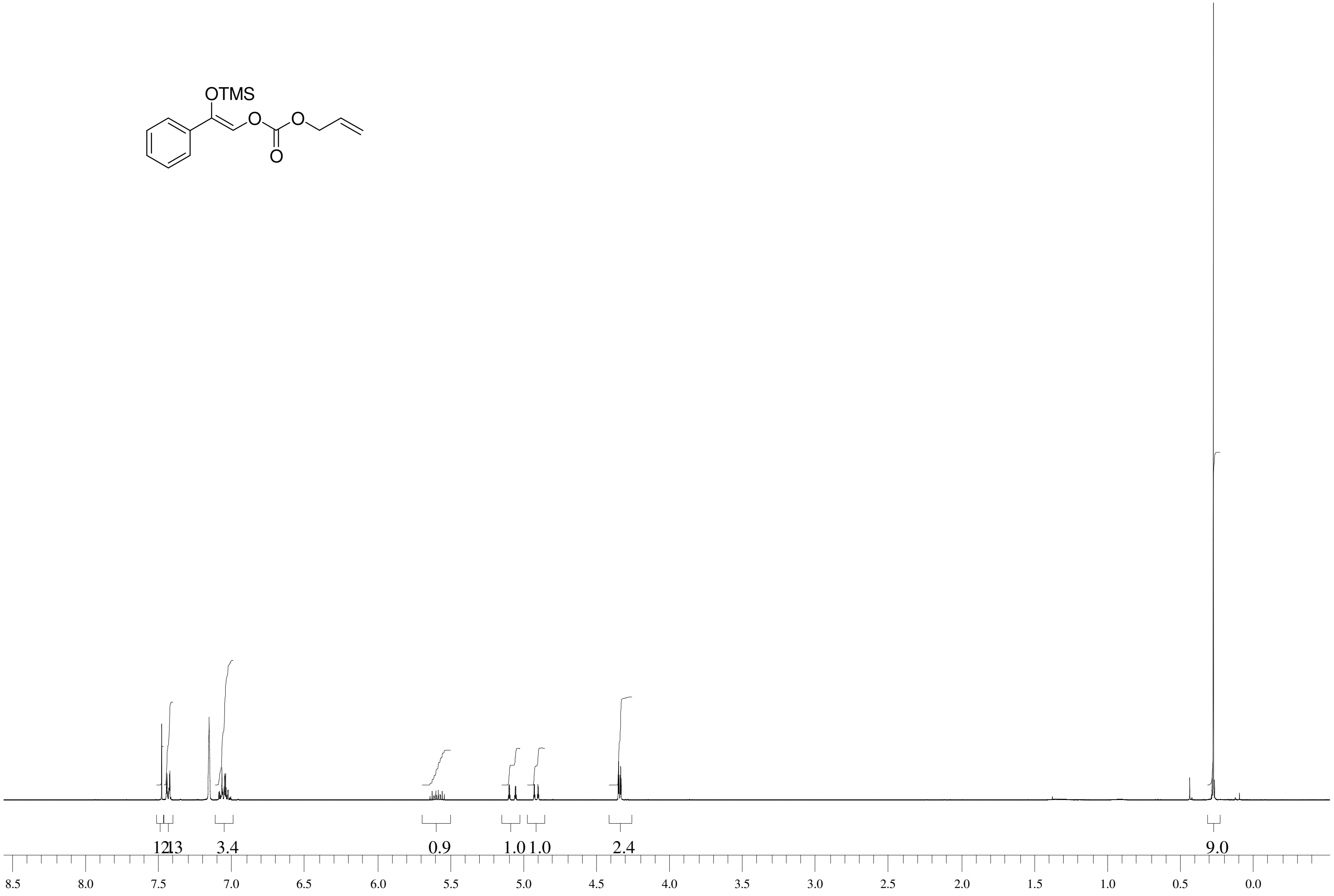
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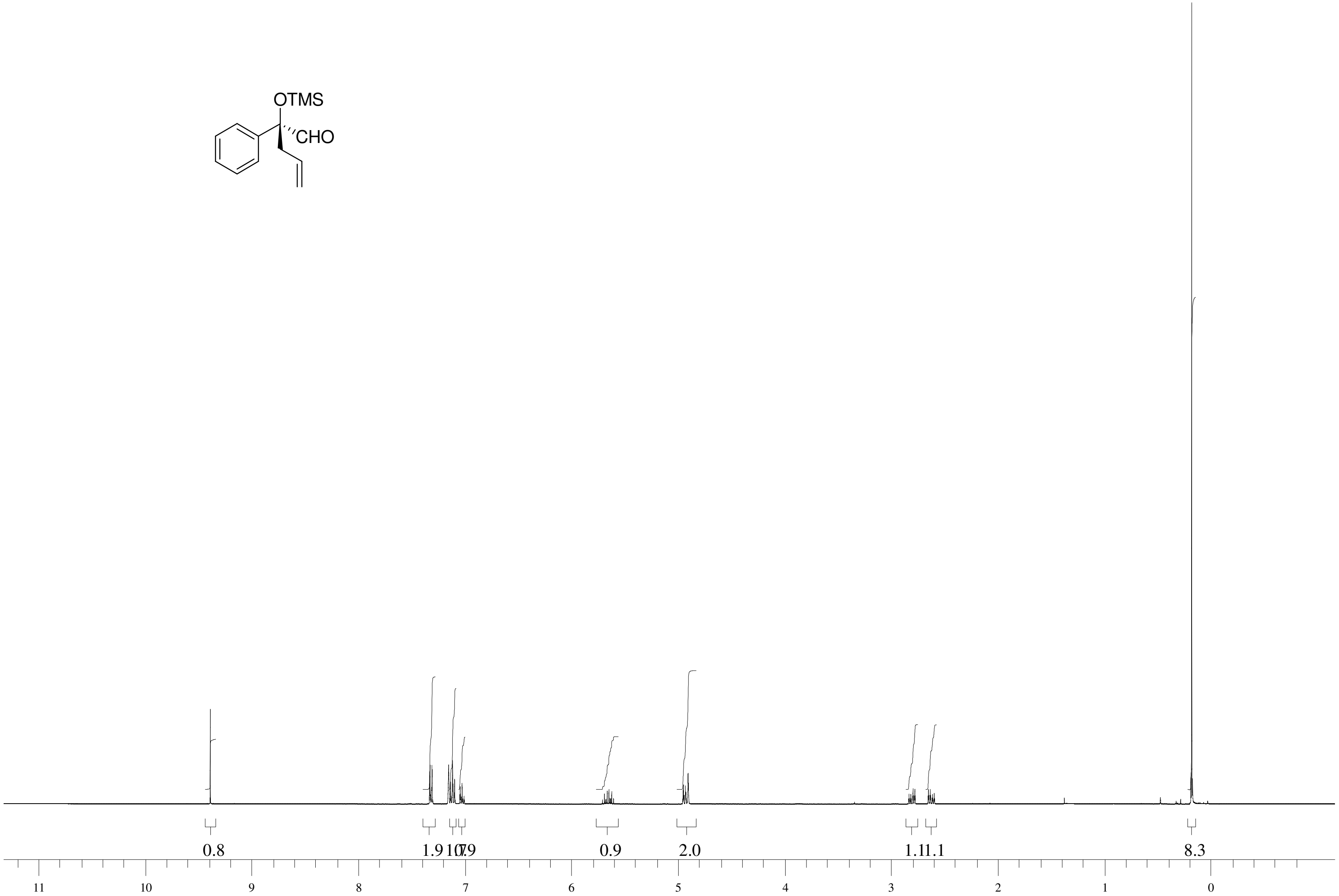
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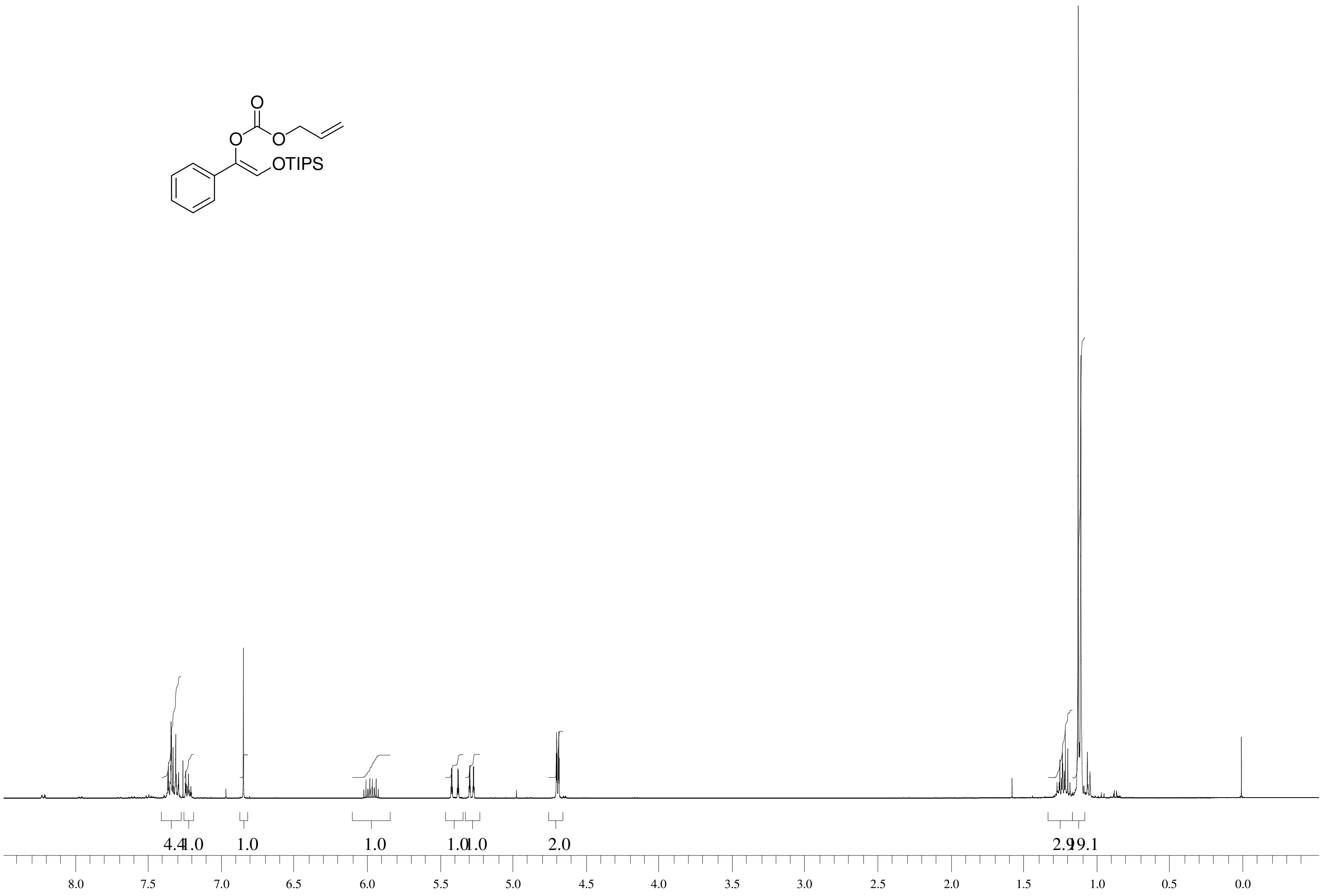
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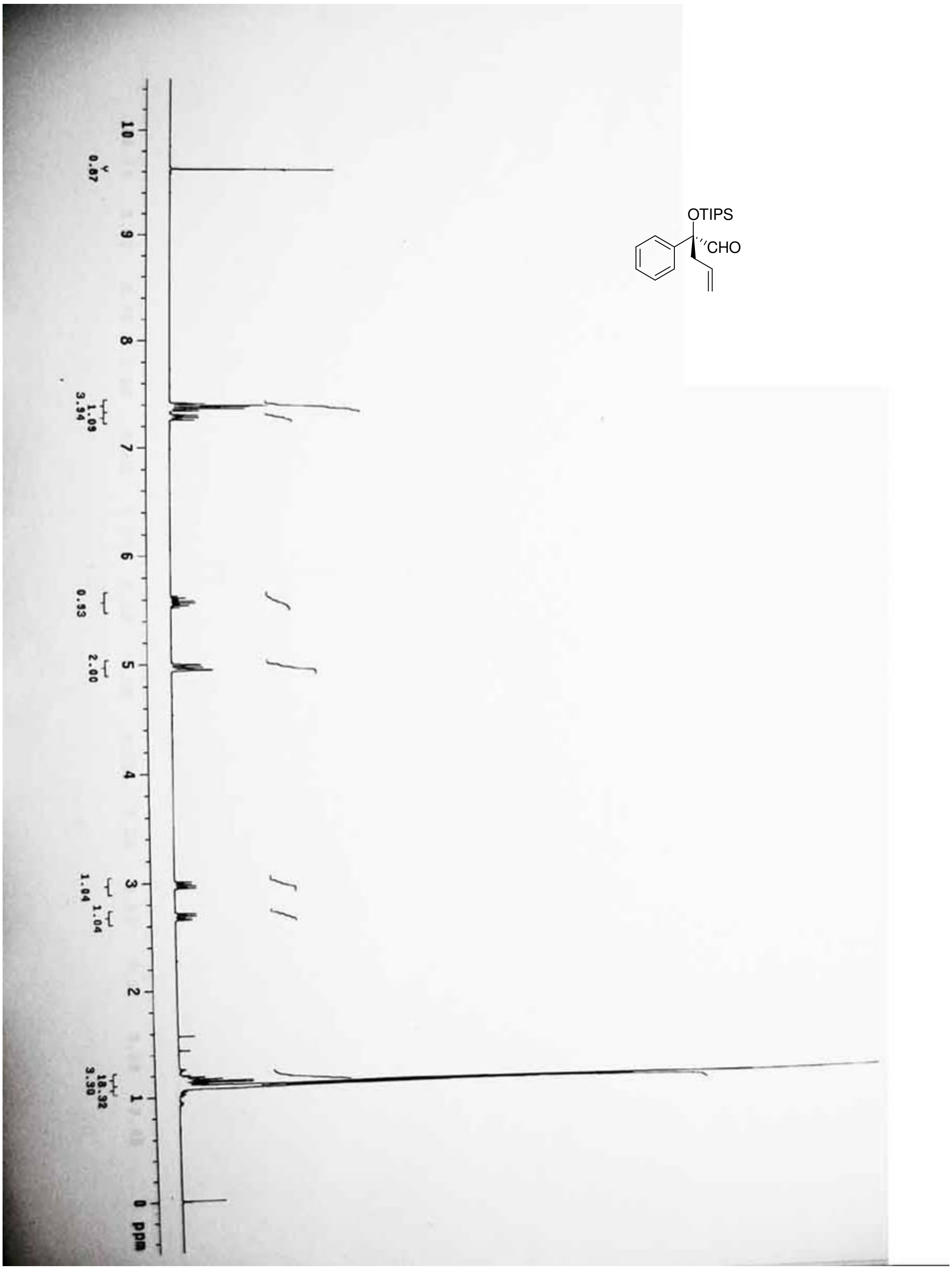
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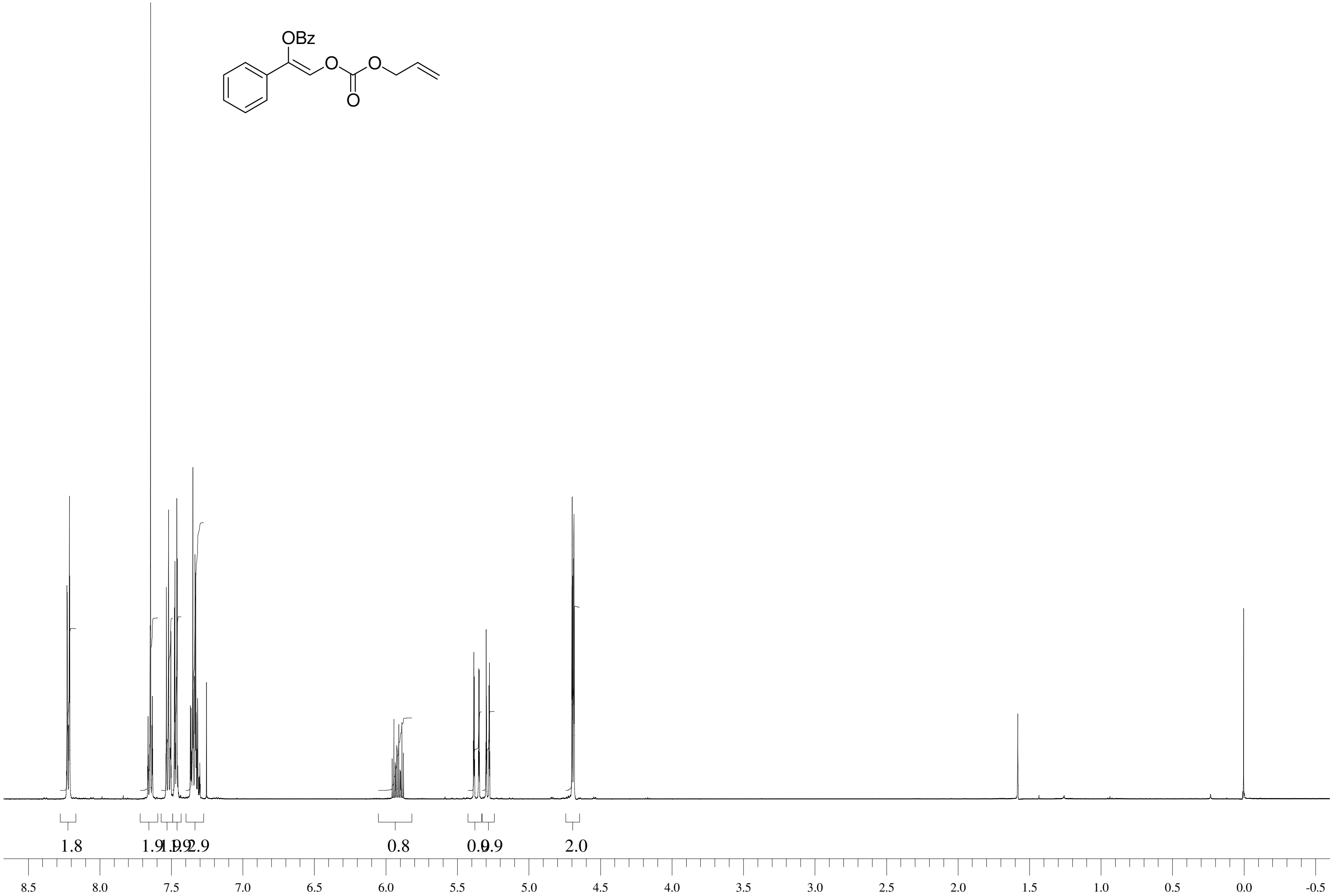
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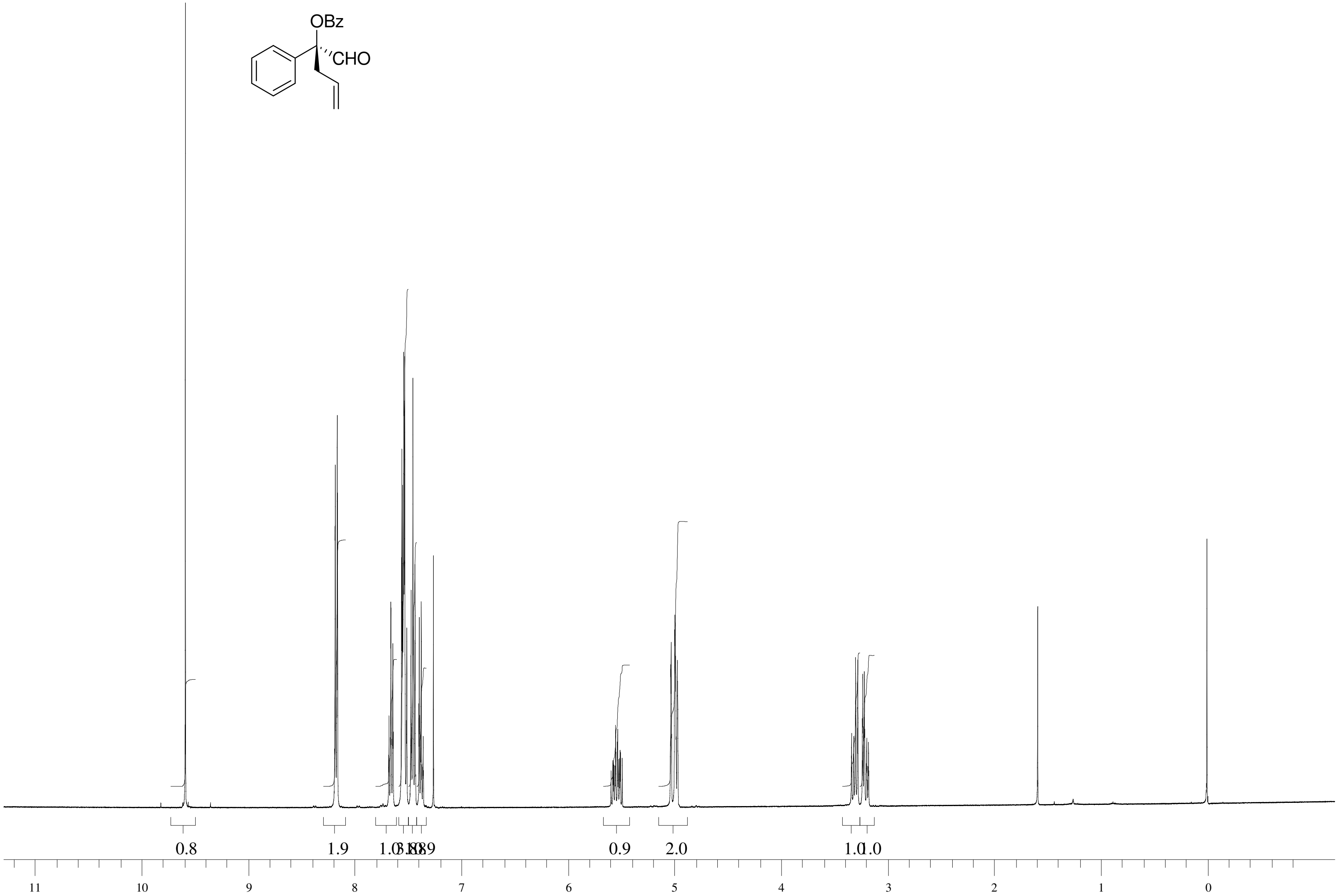
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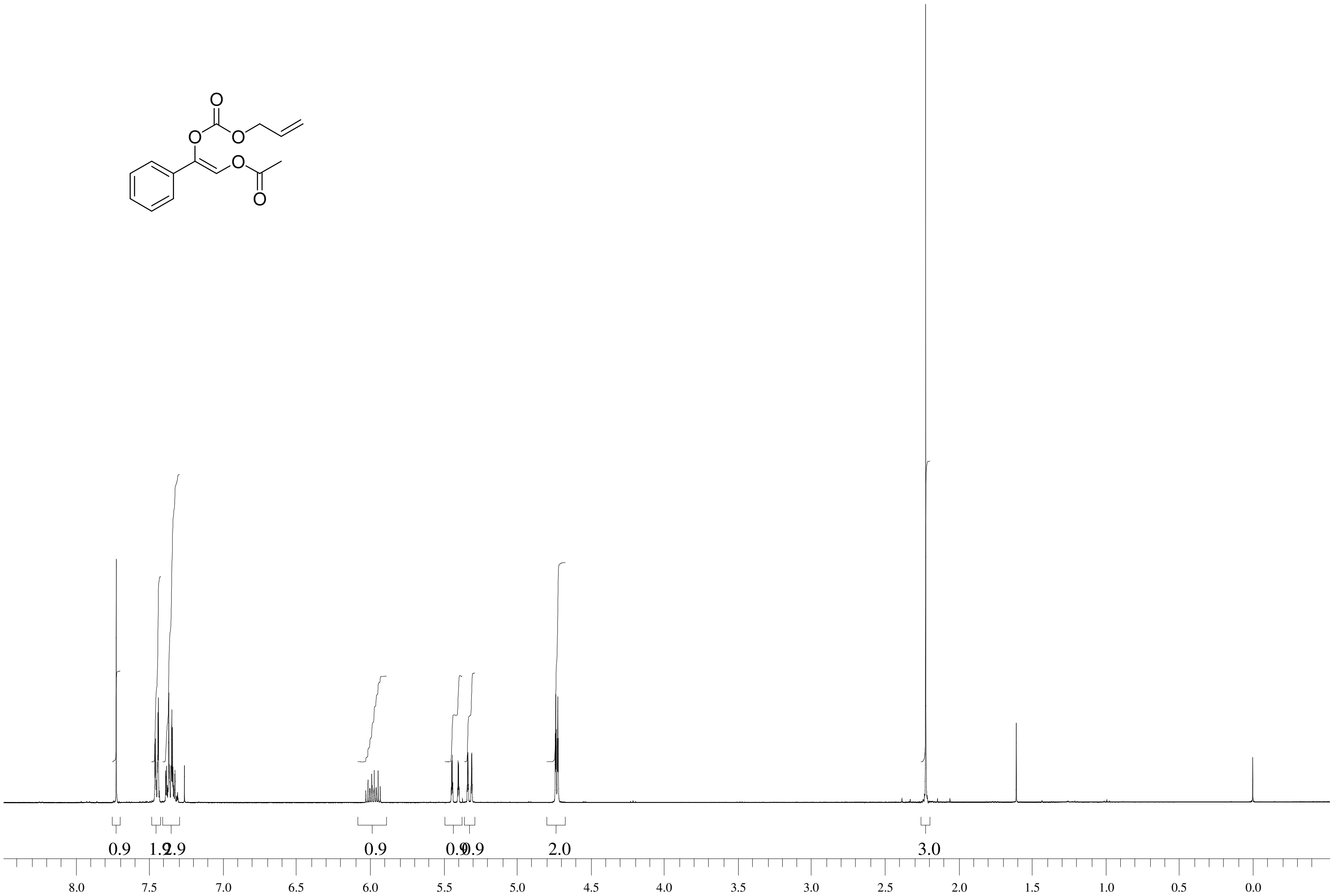
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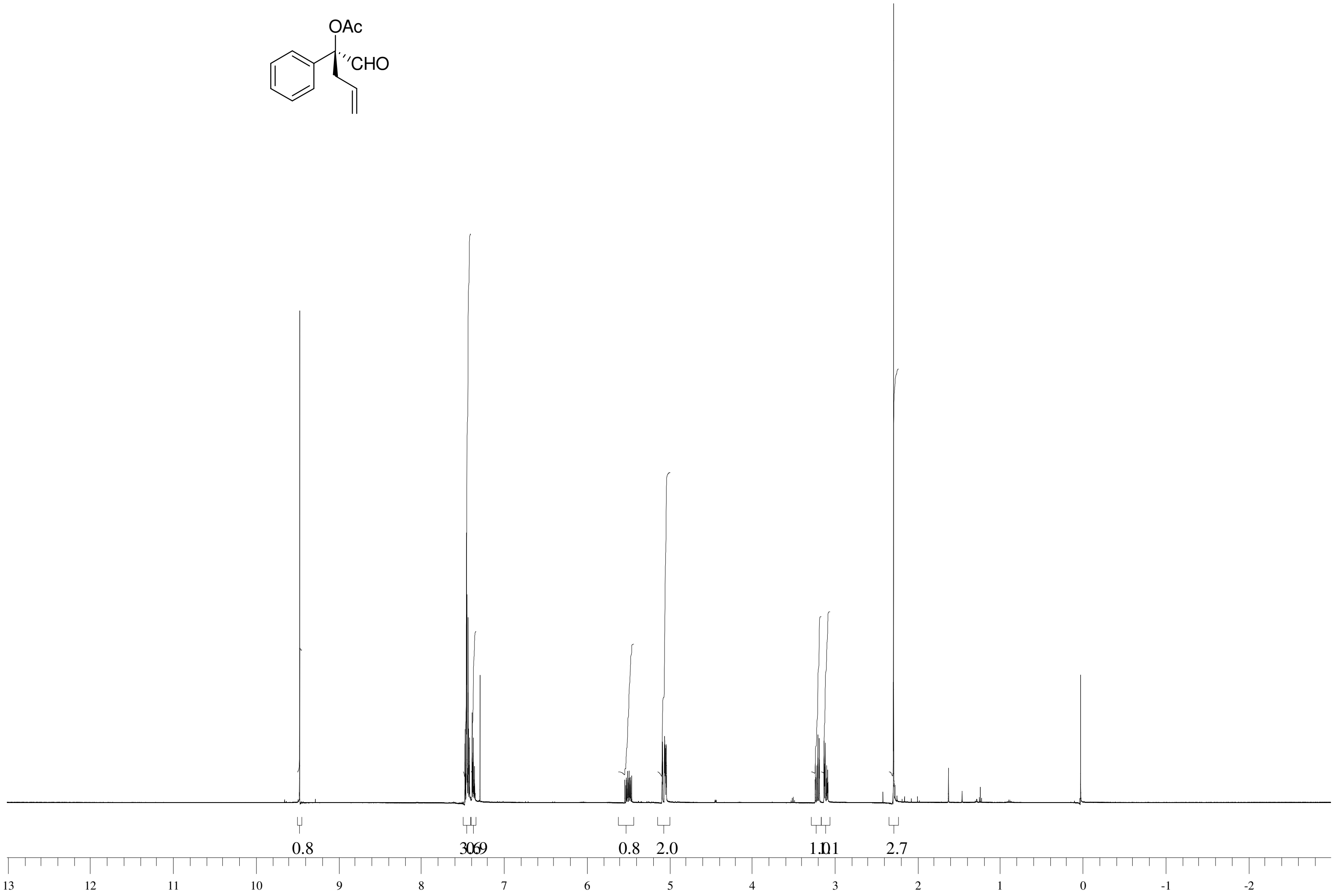
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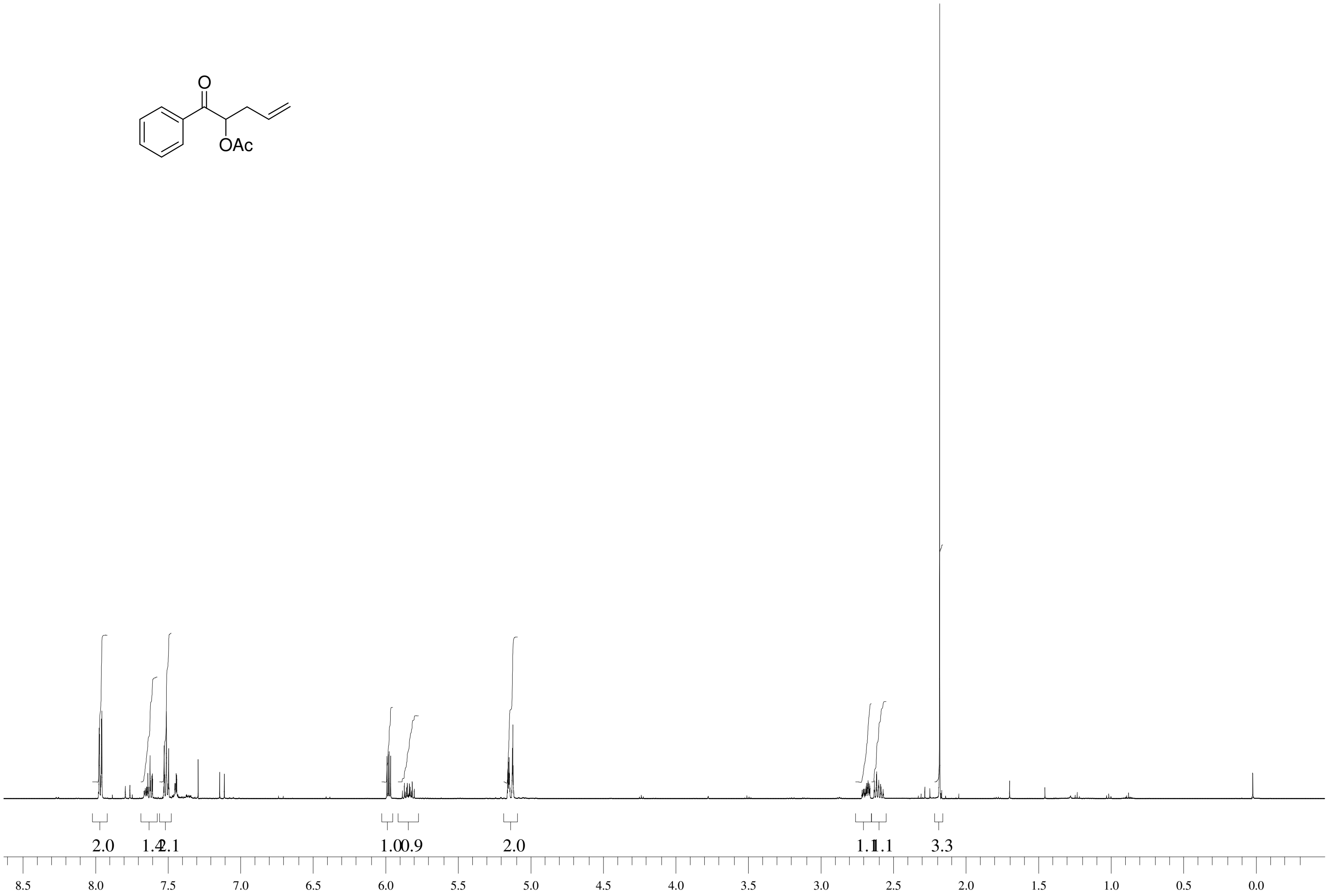
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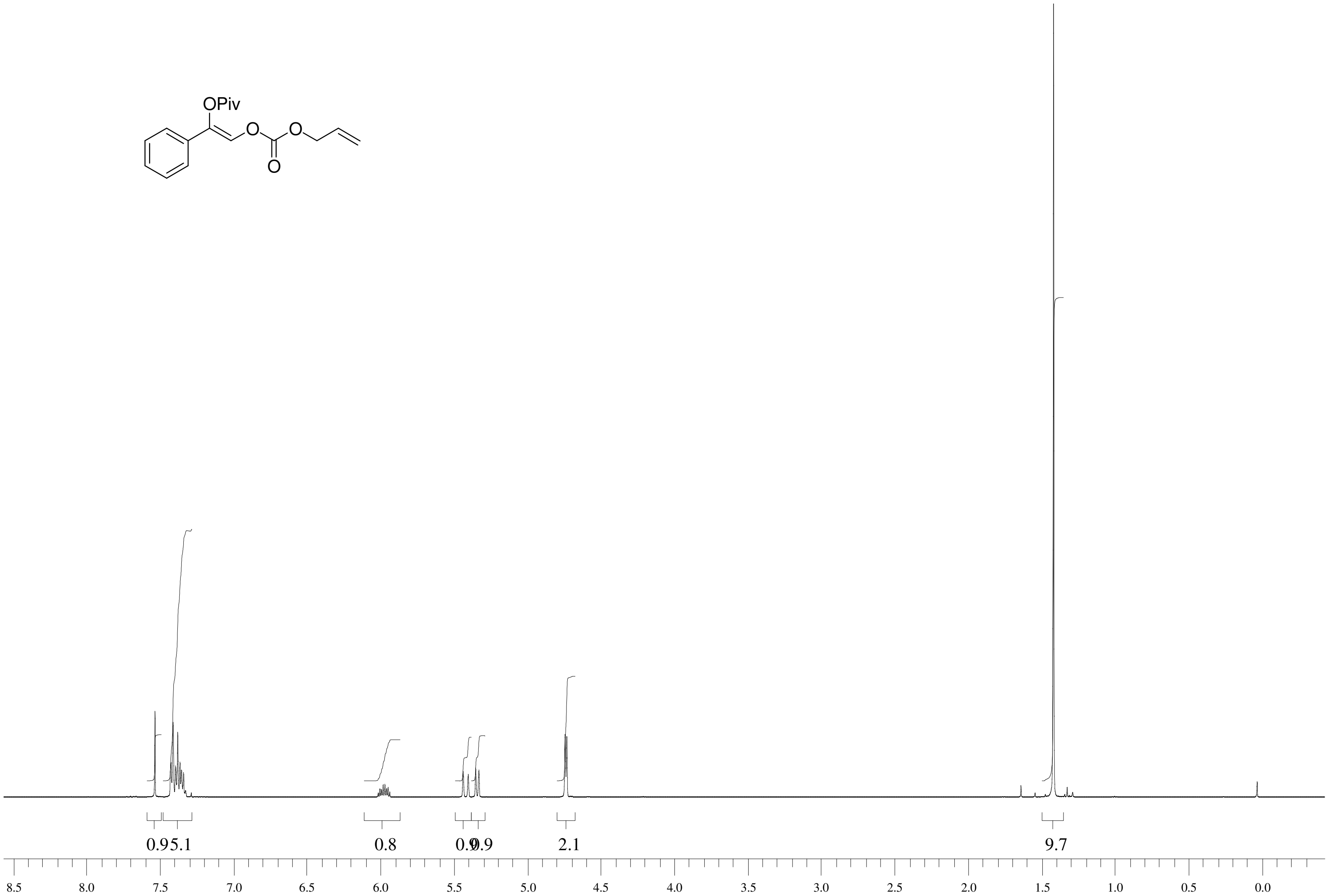
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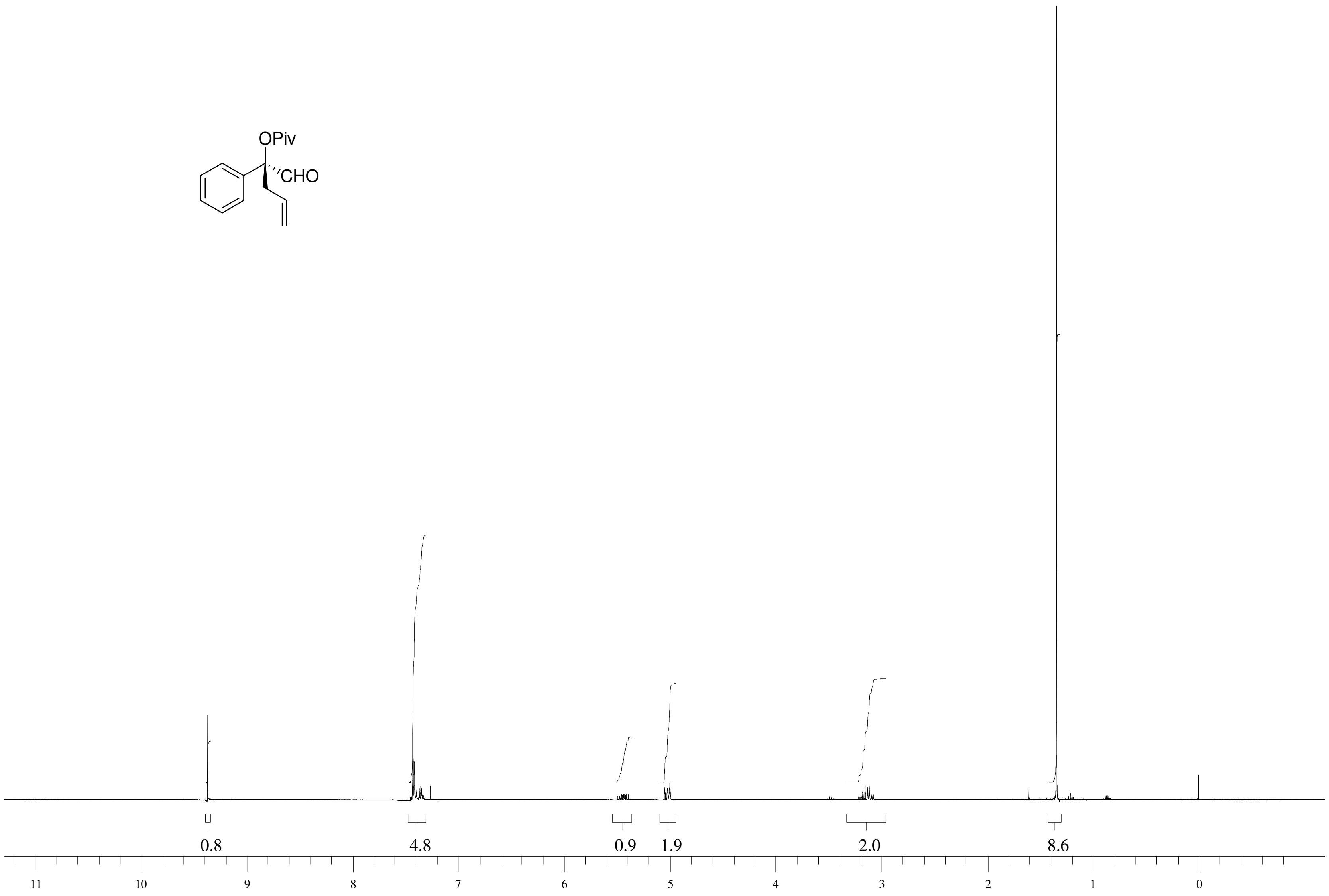
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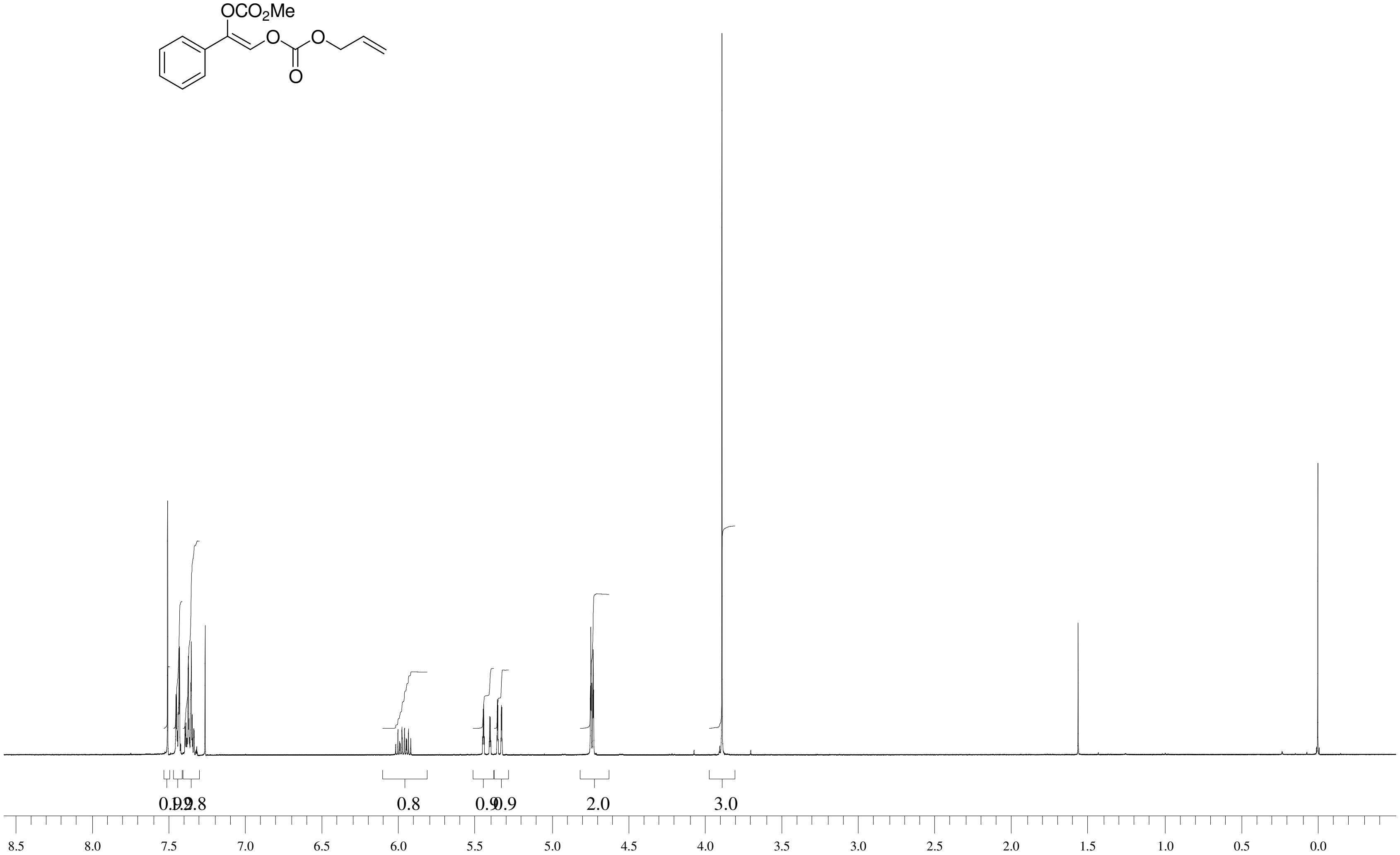
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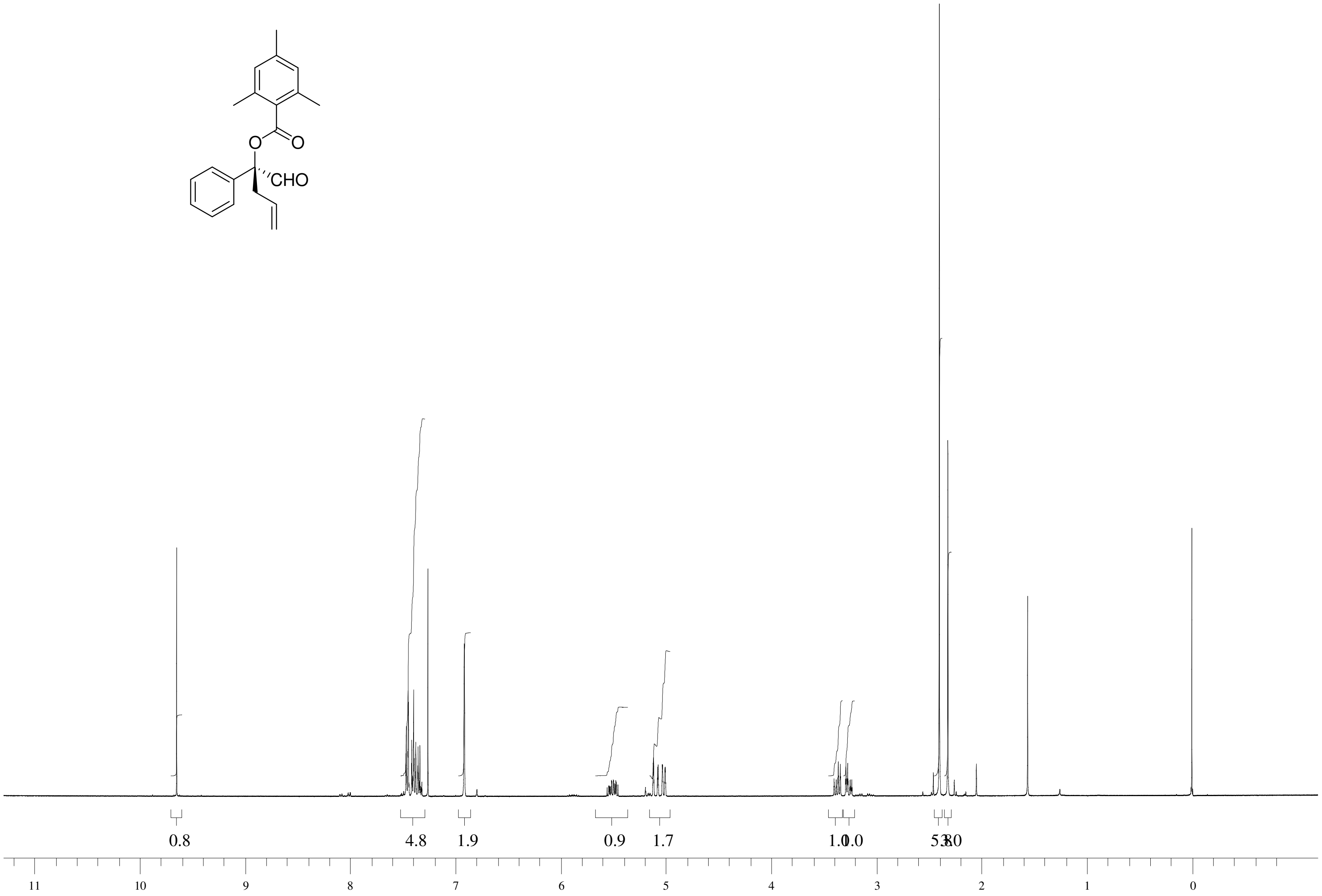O
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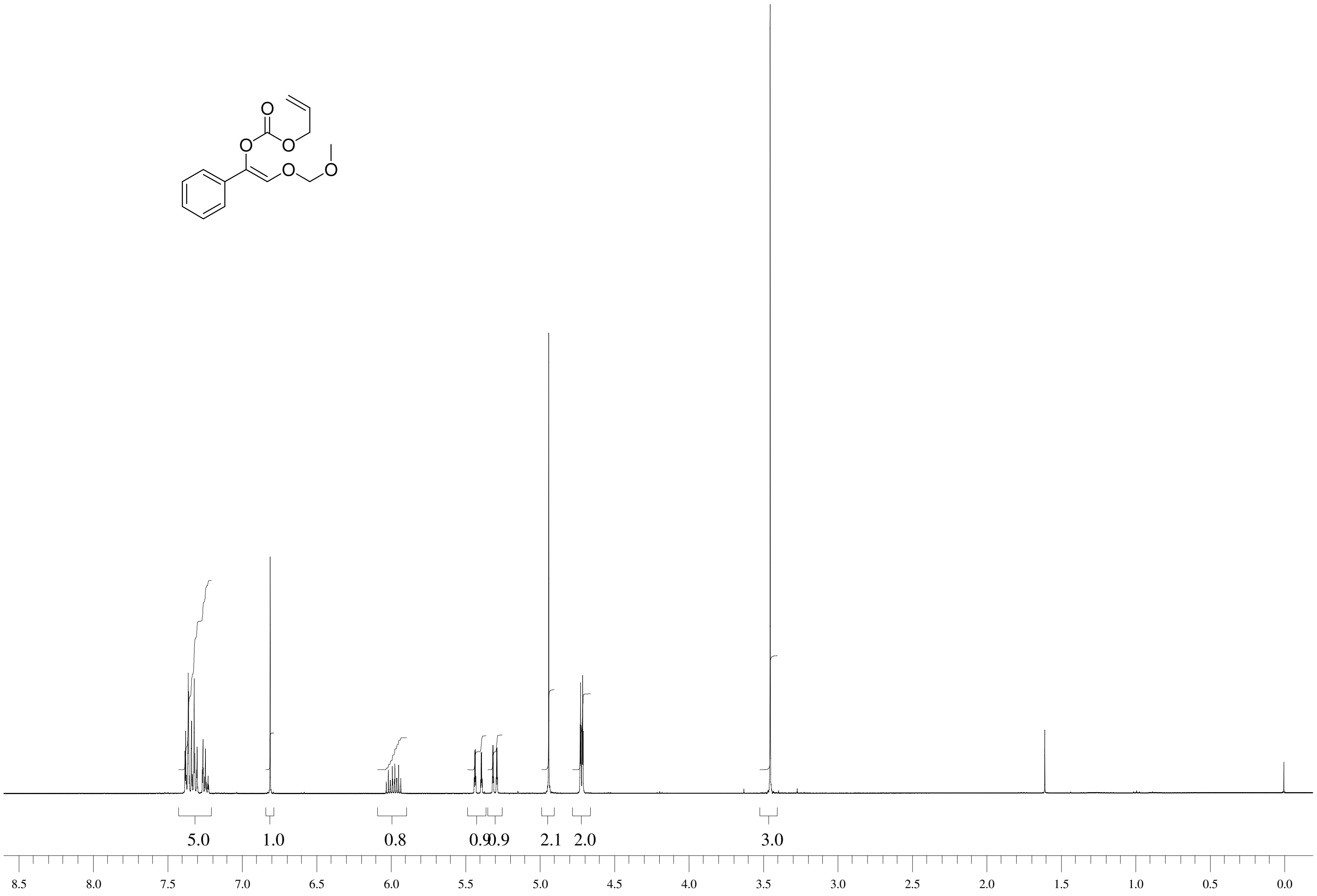
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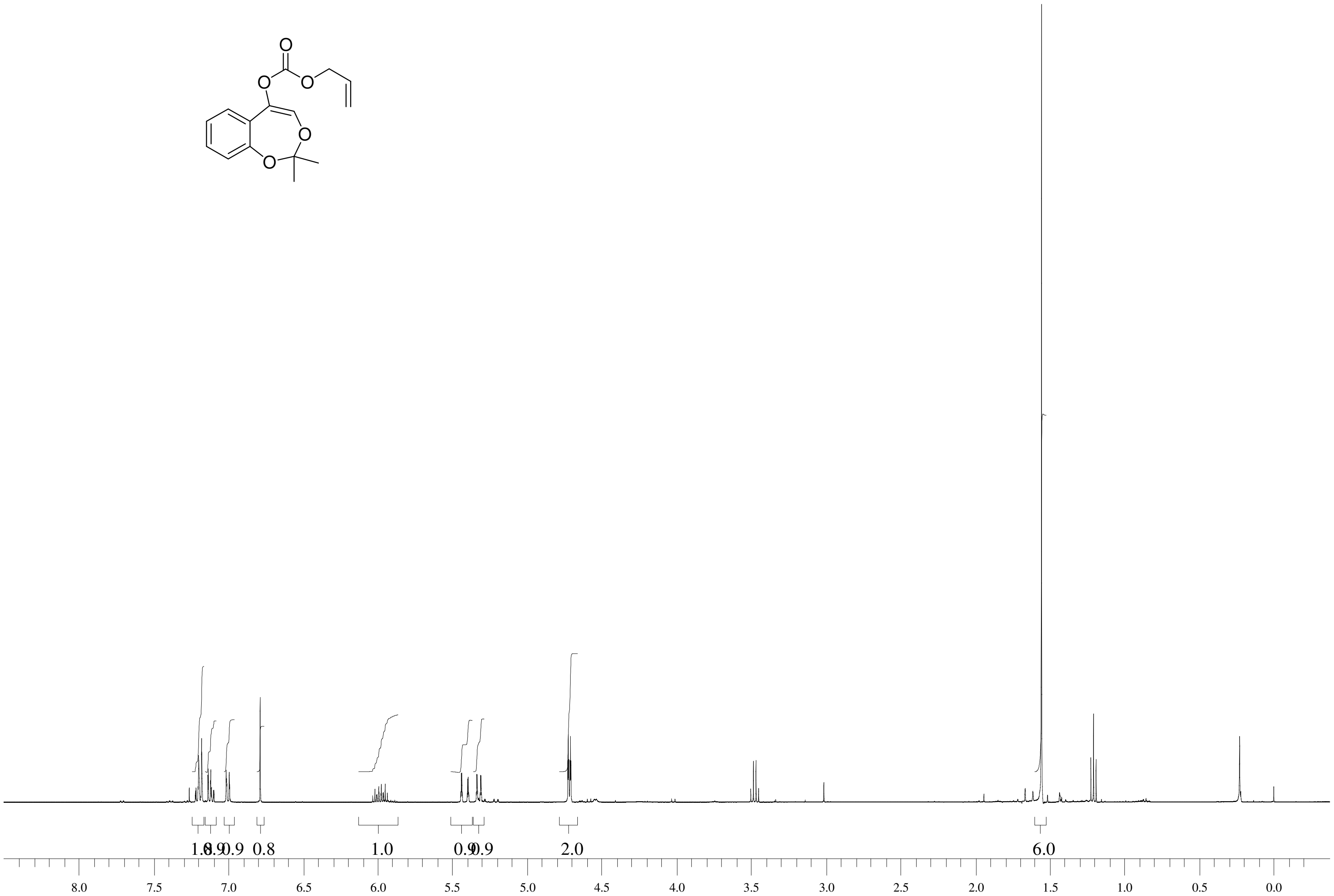
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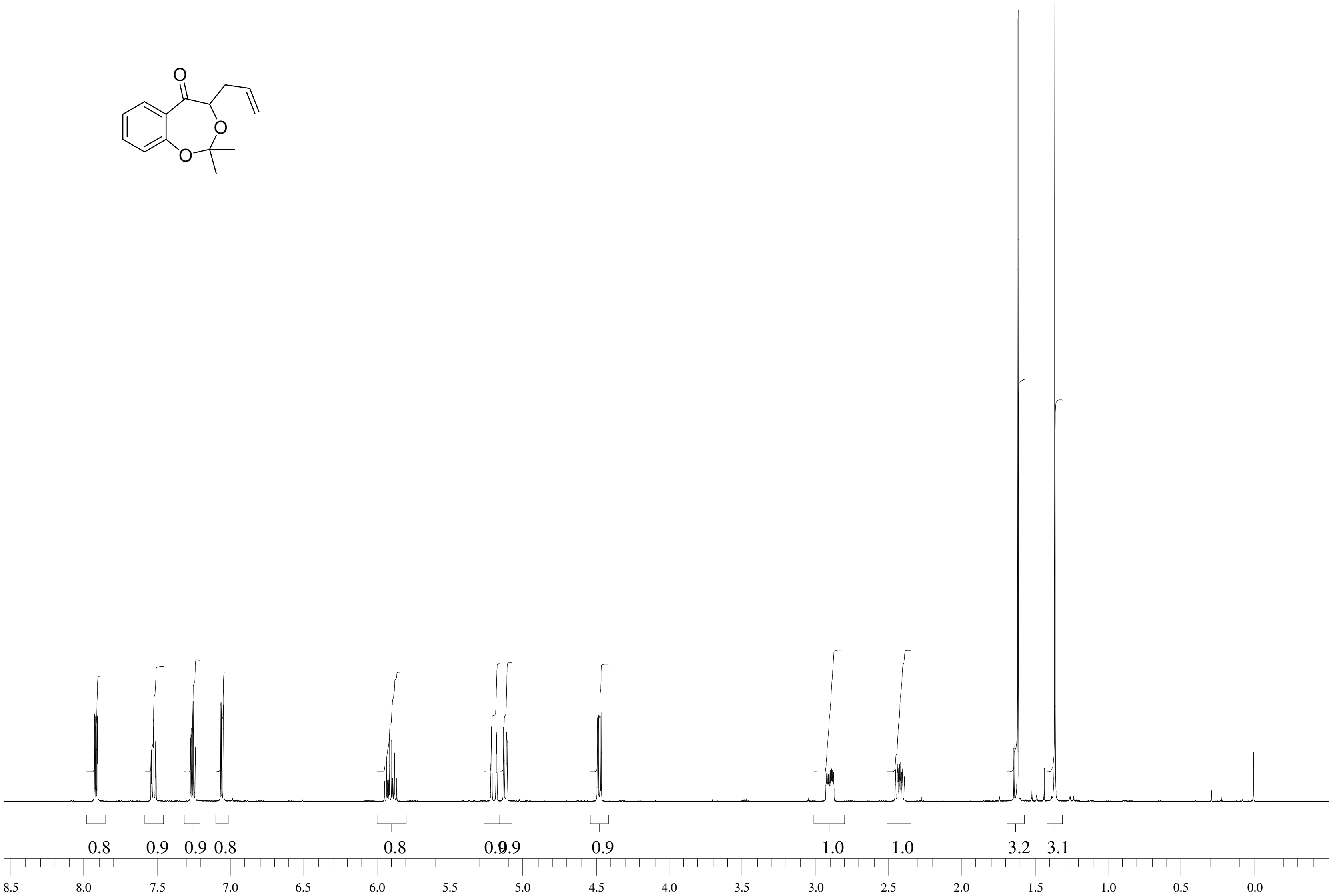
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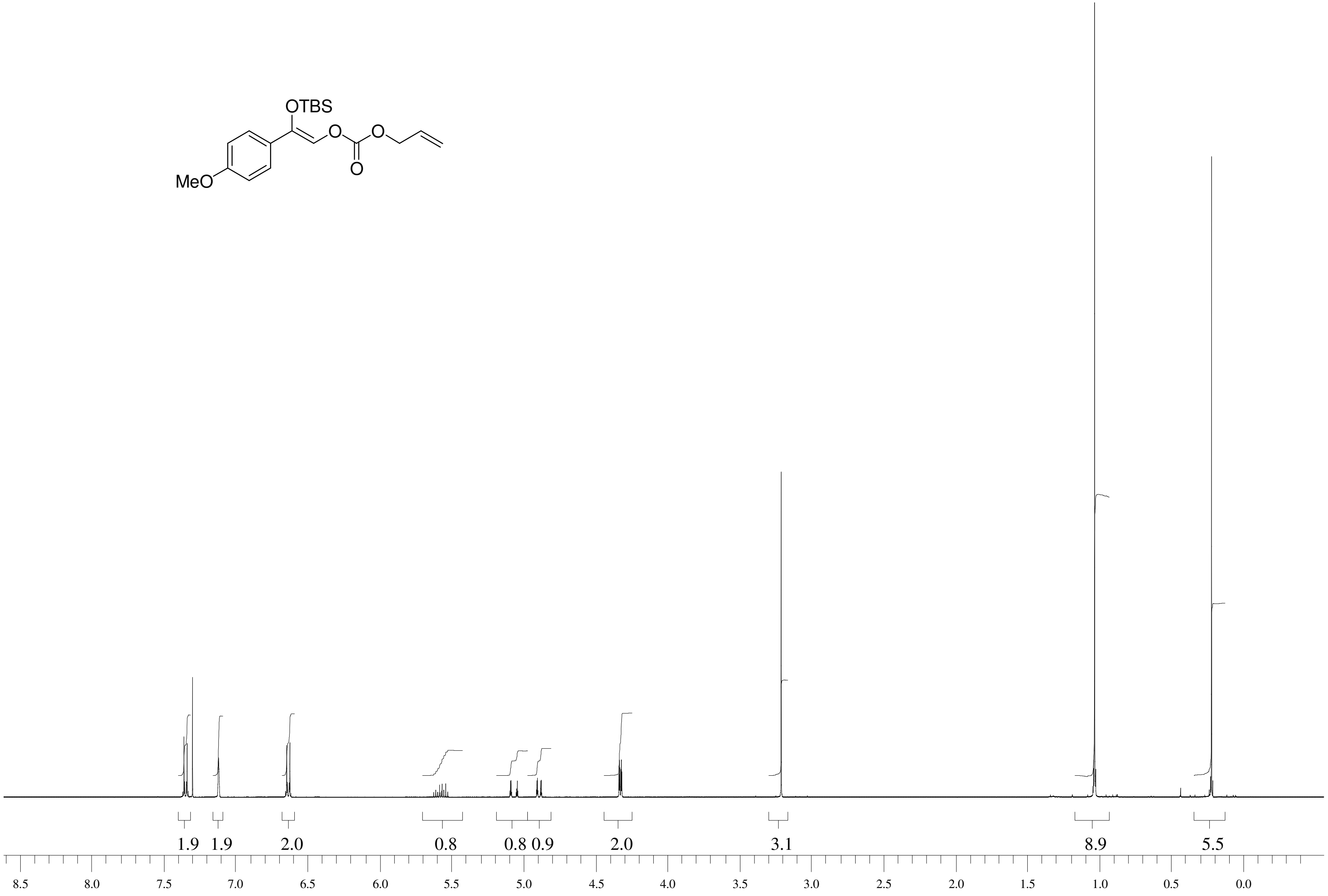
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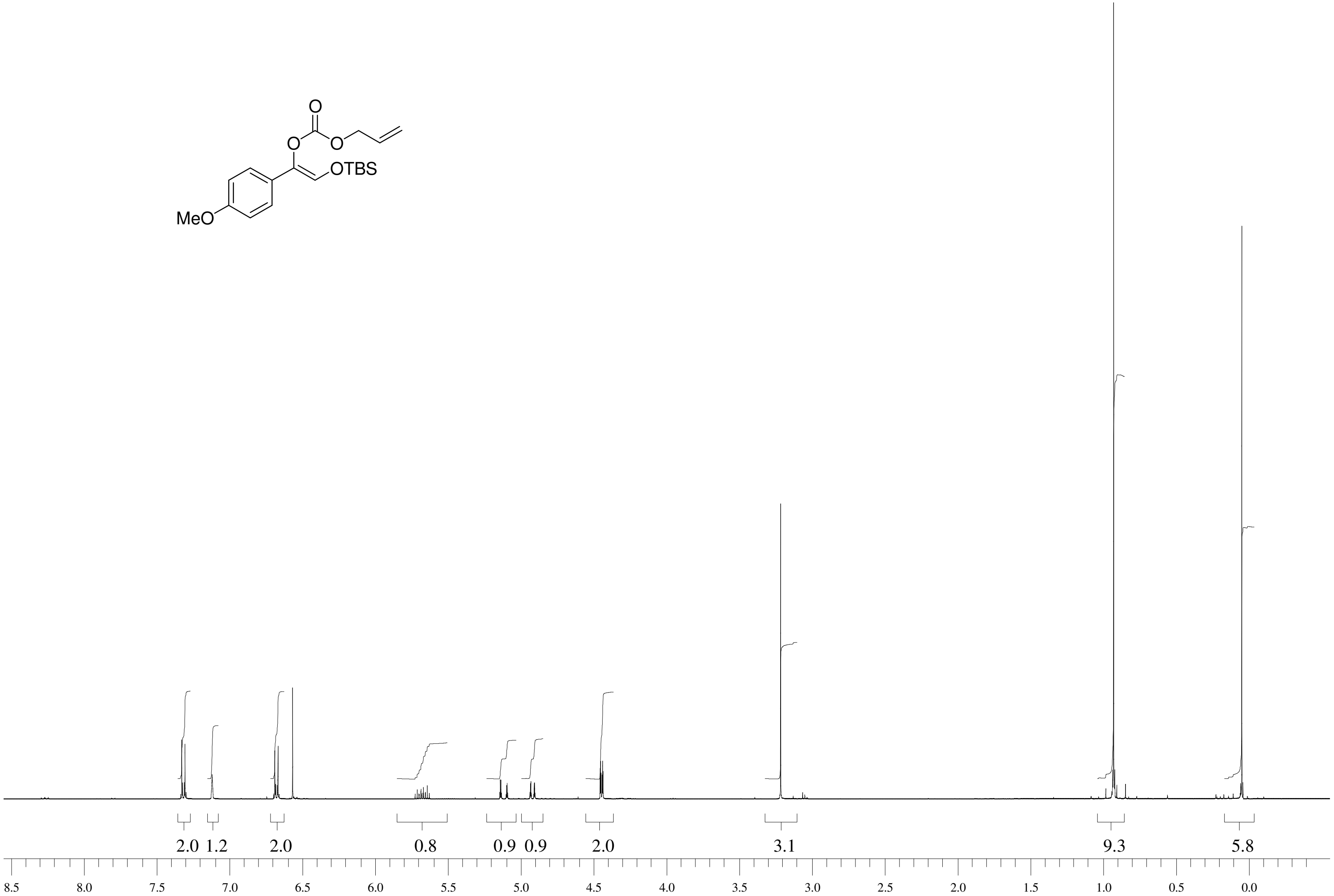
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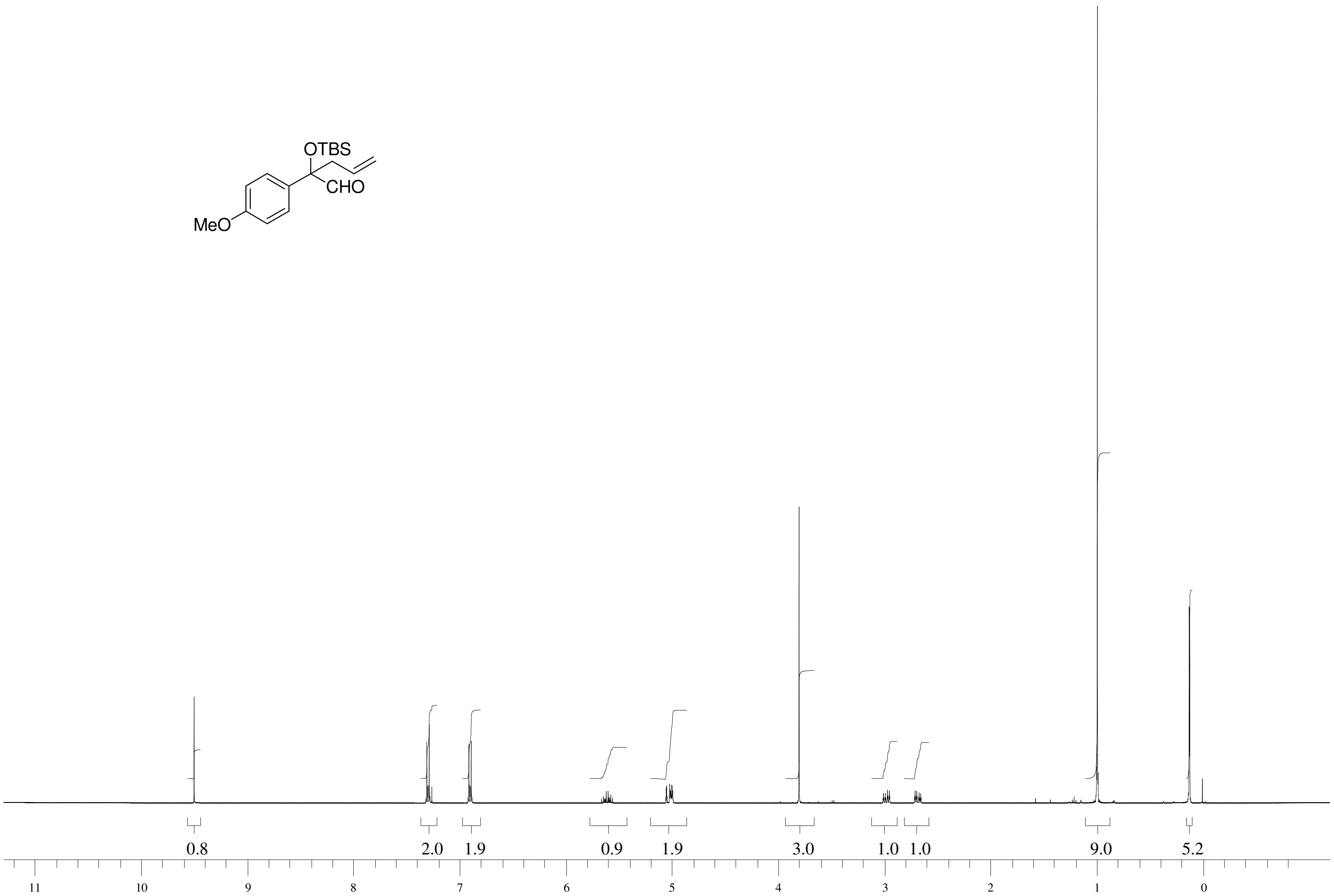
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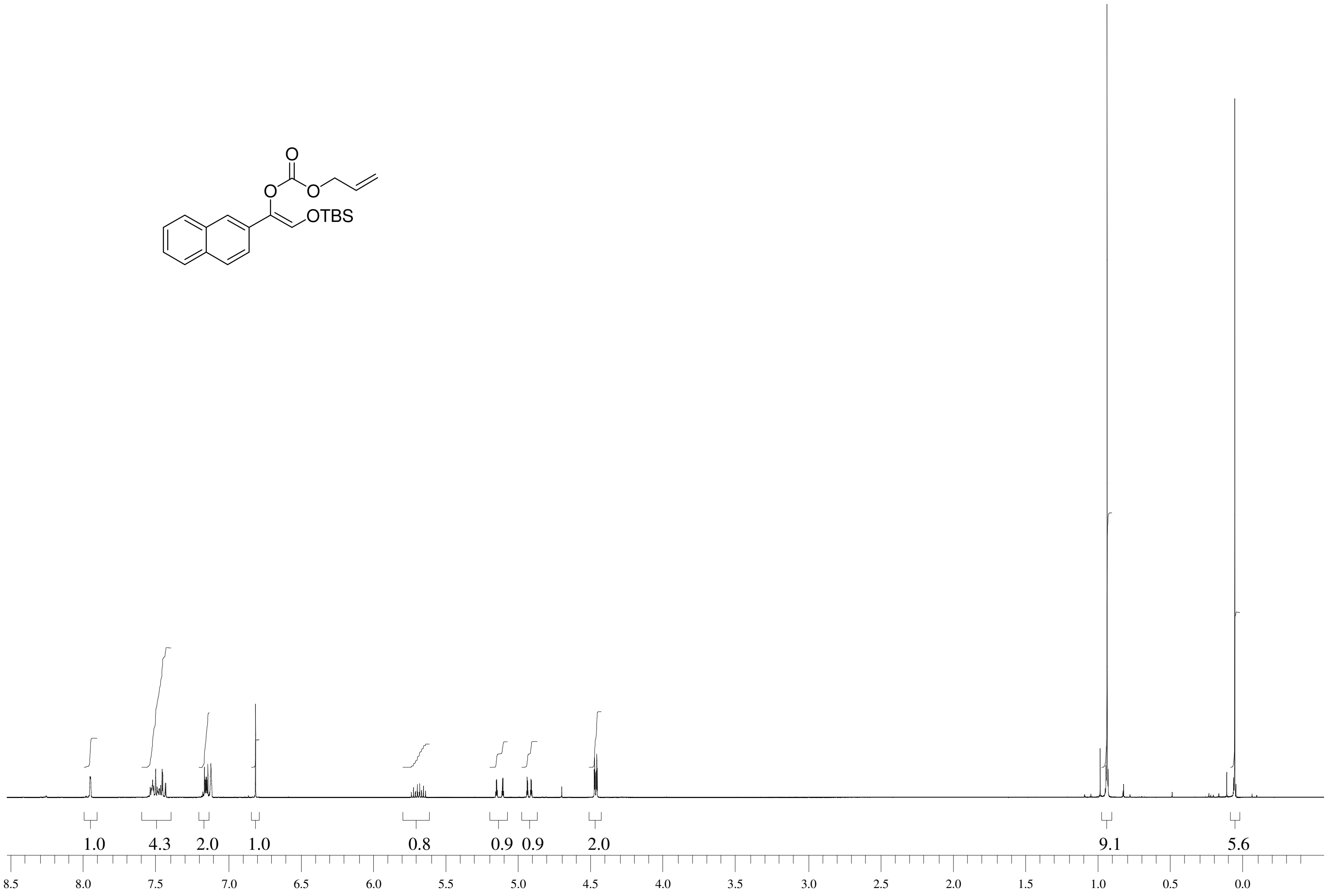
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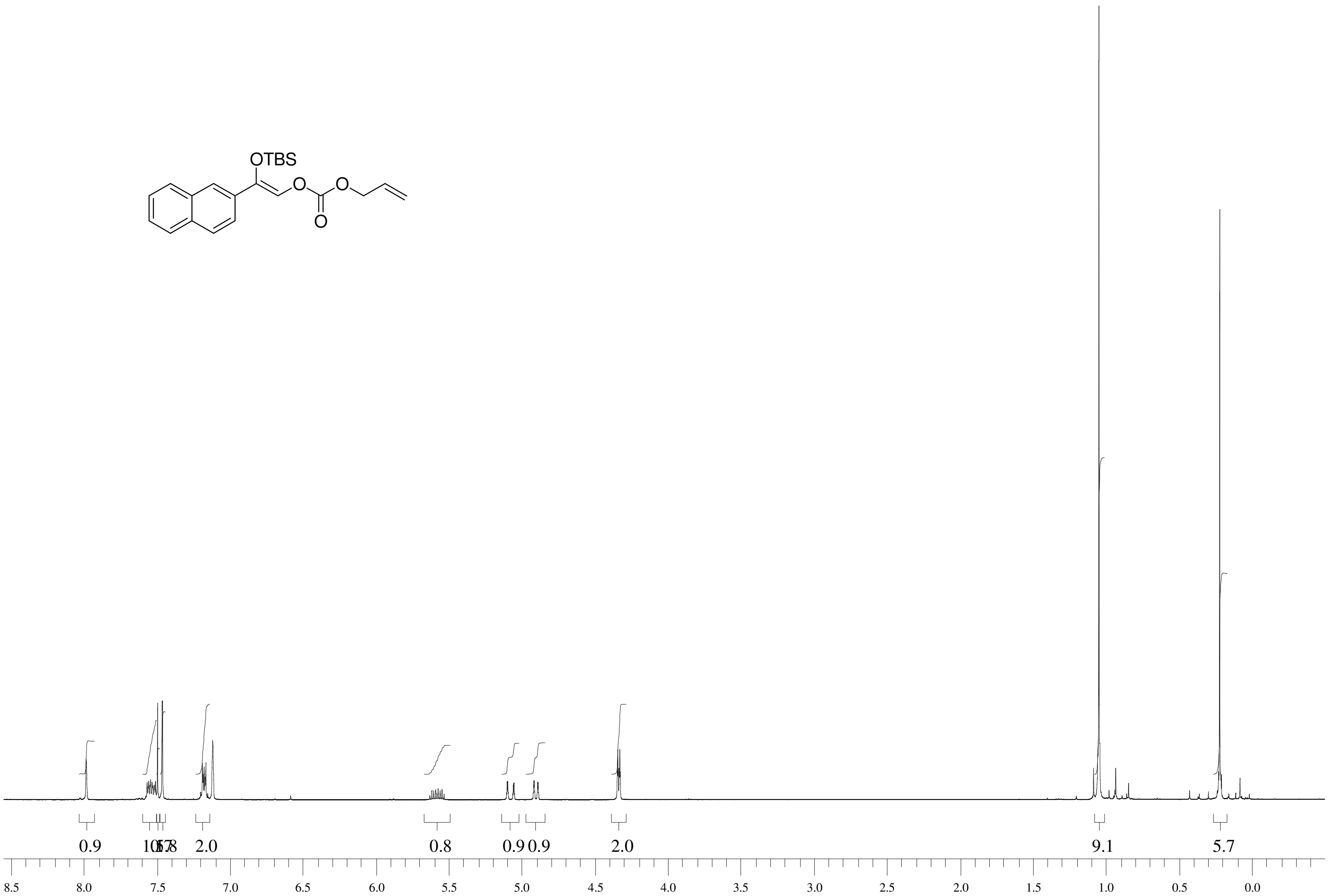
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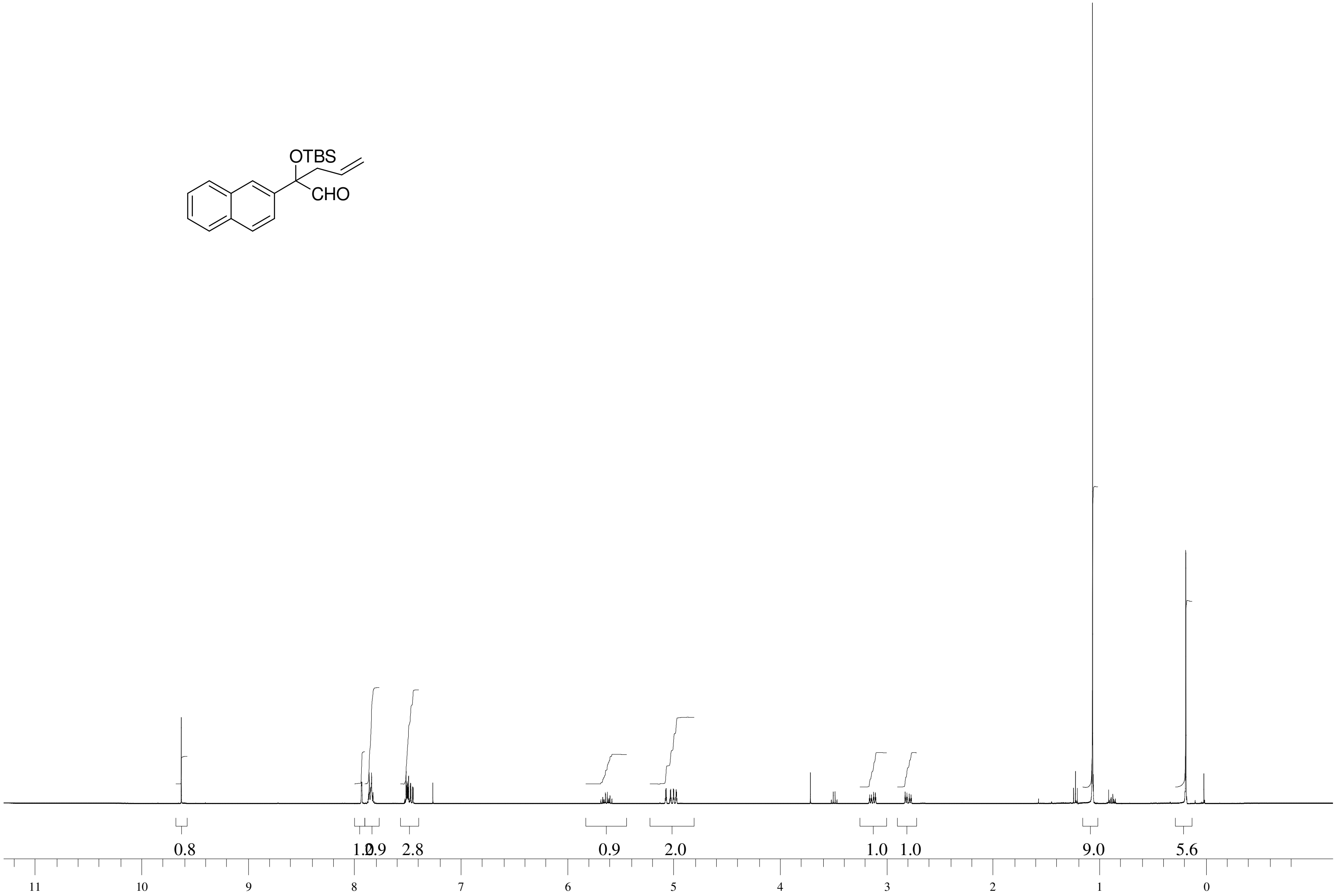
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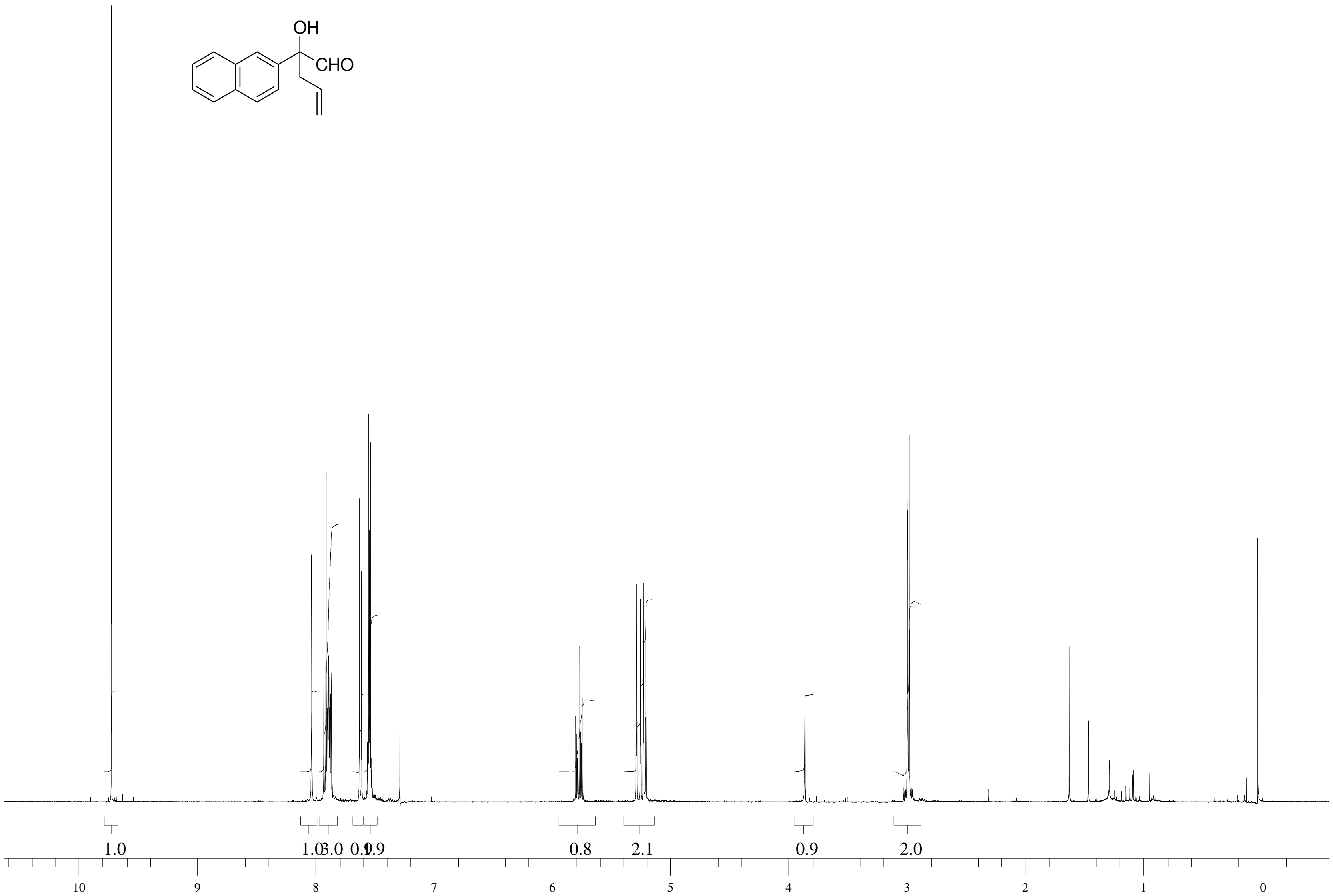
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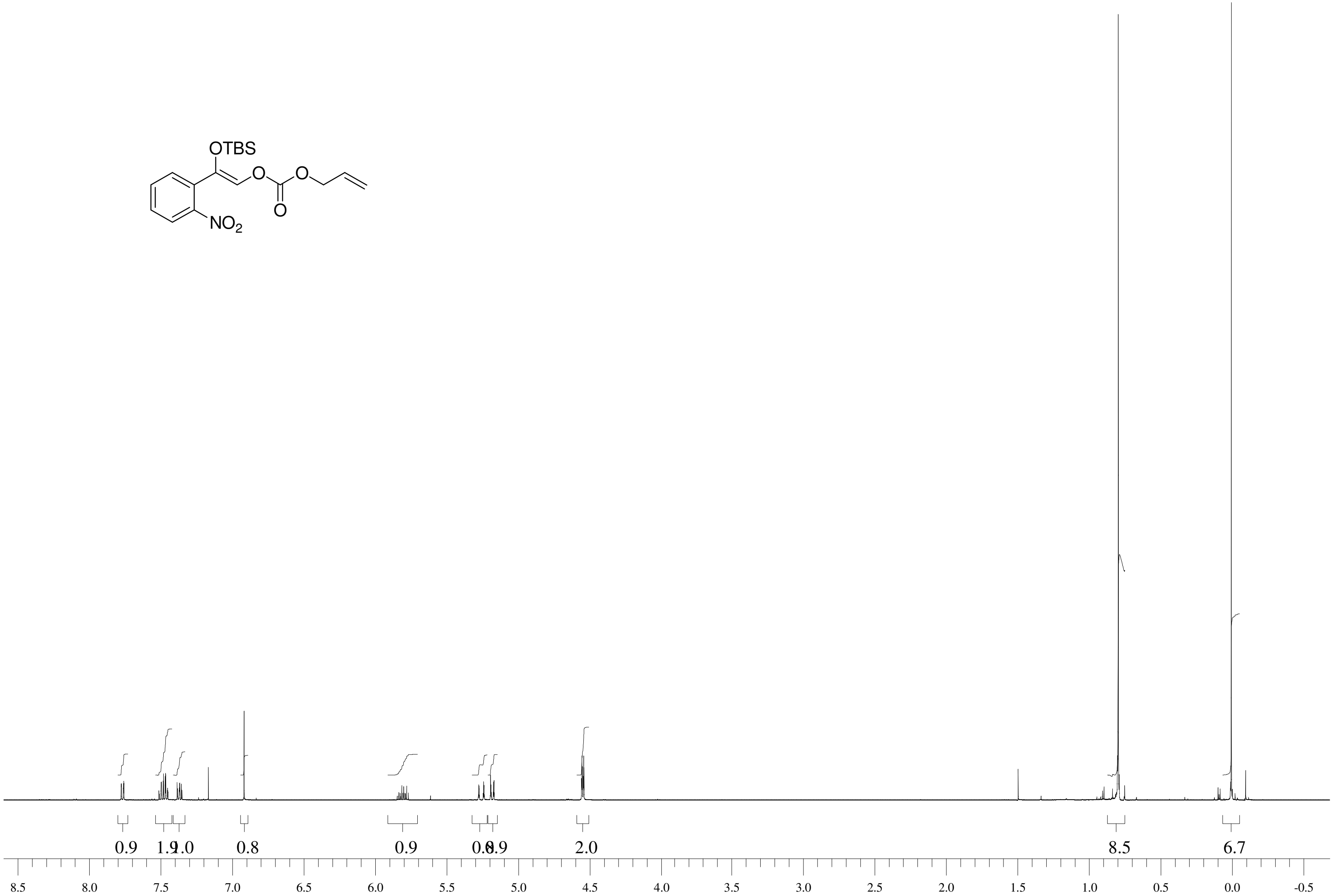
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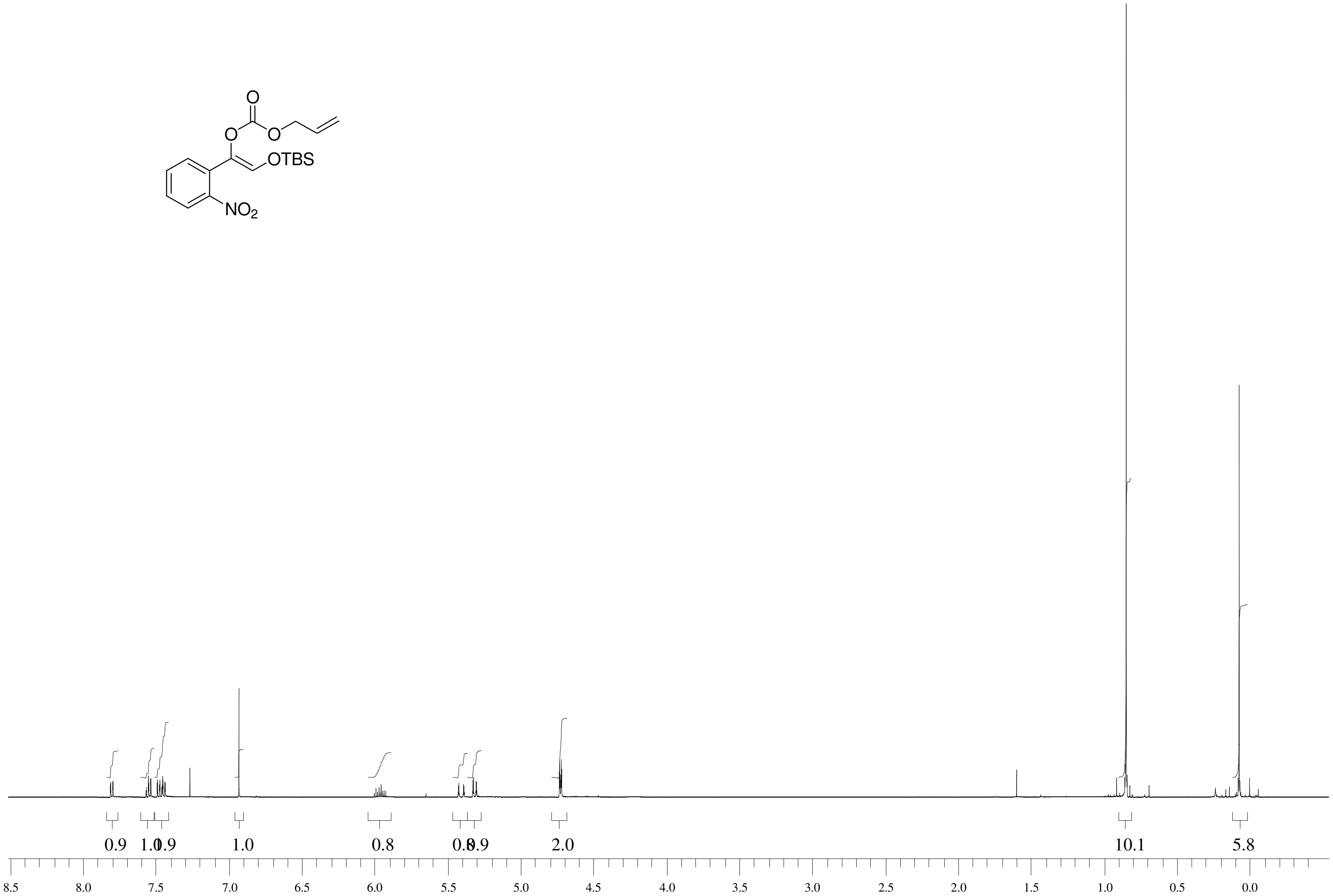
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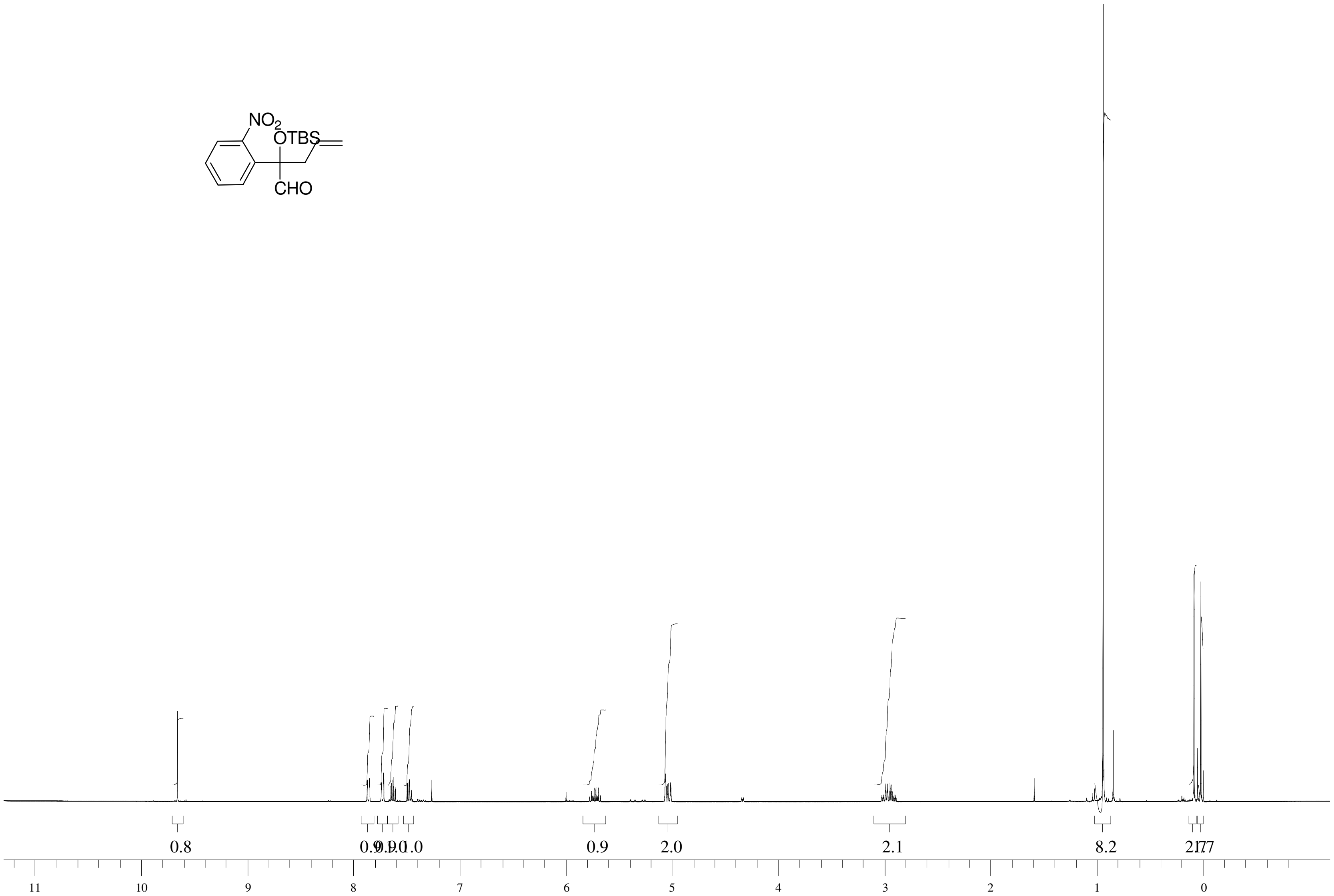
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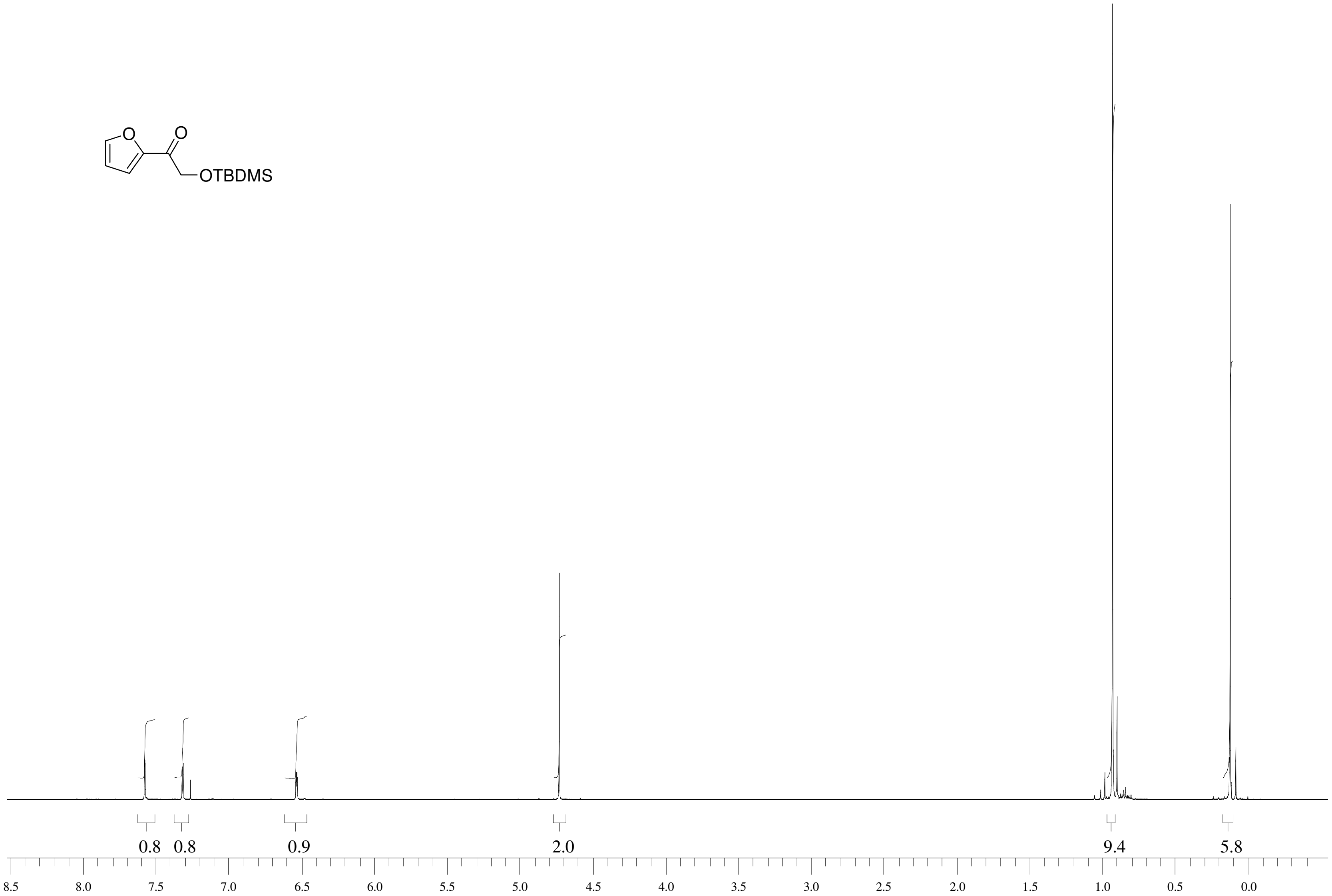
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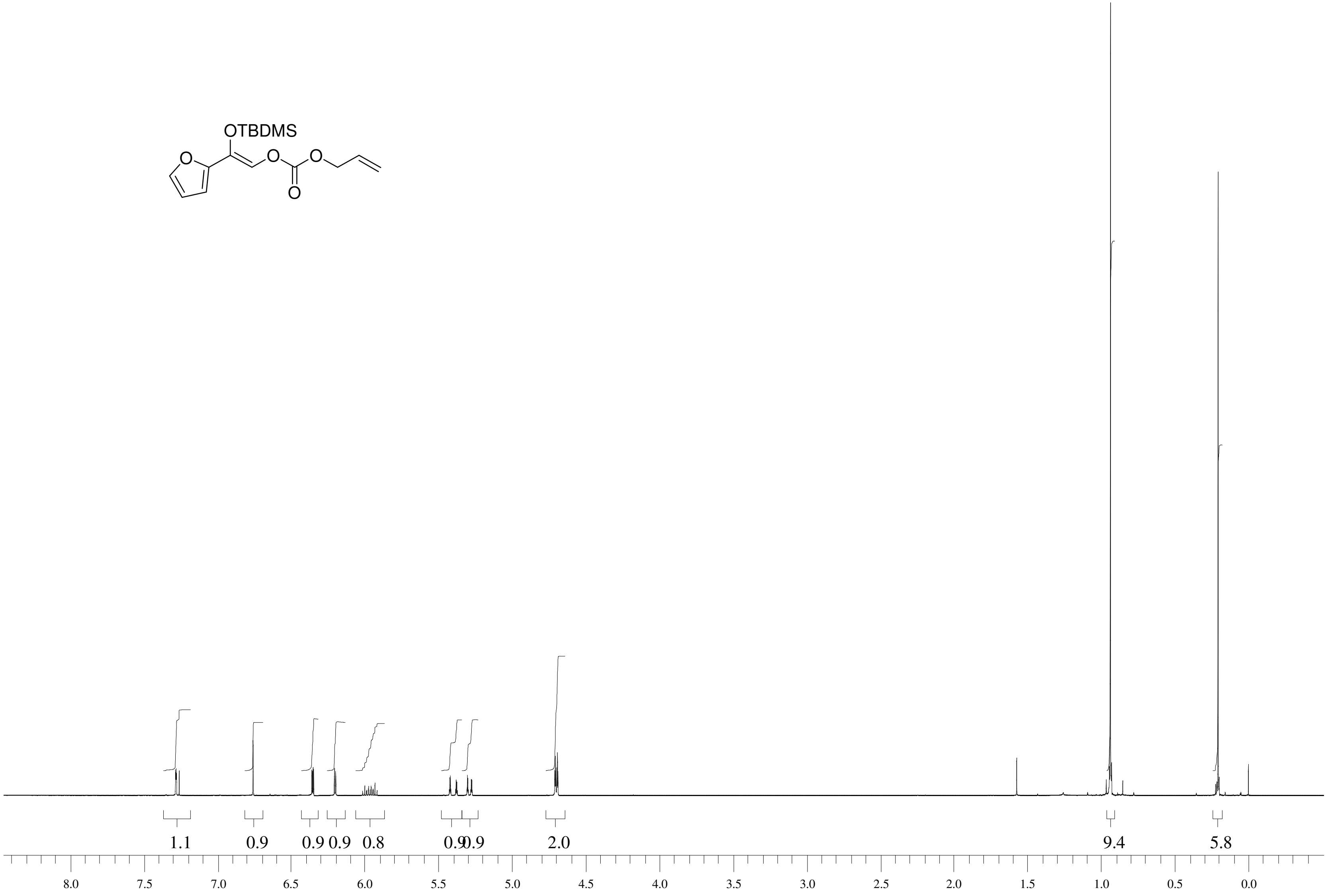
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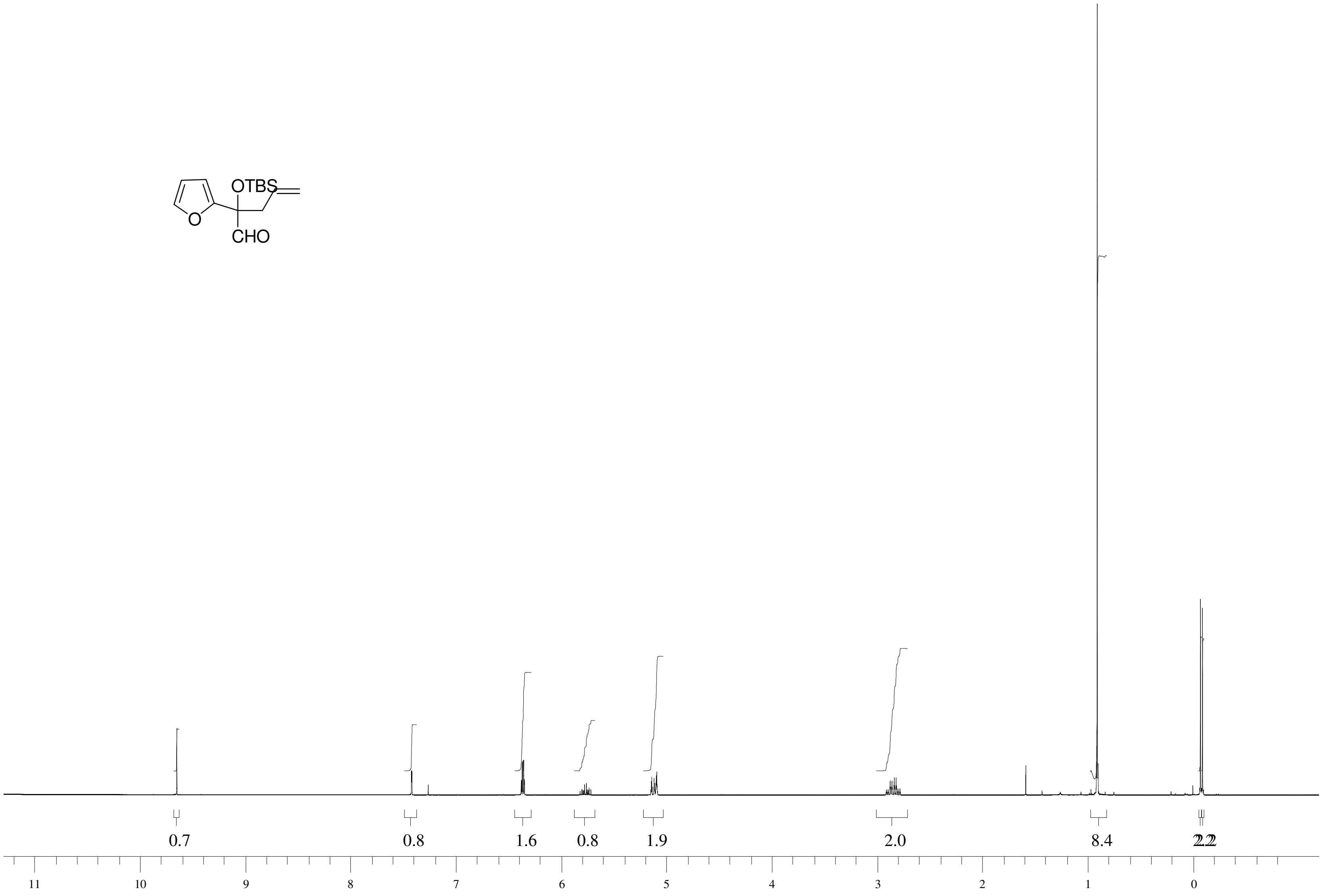
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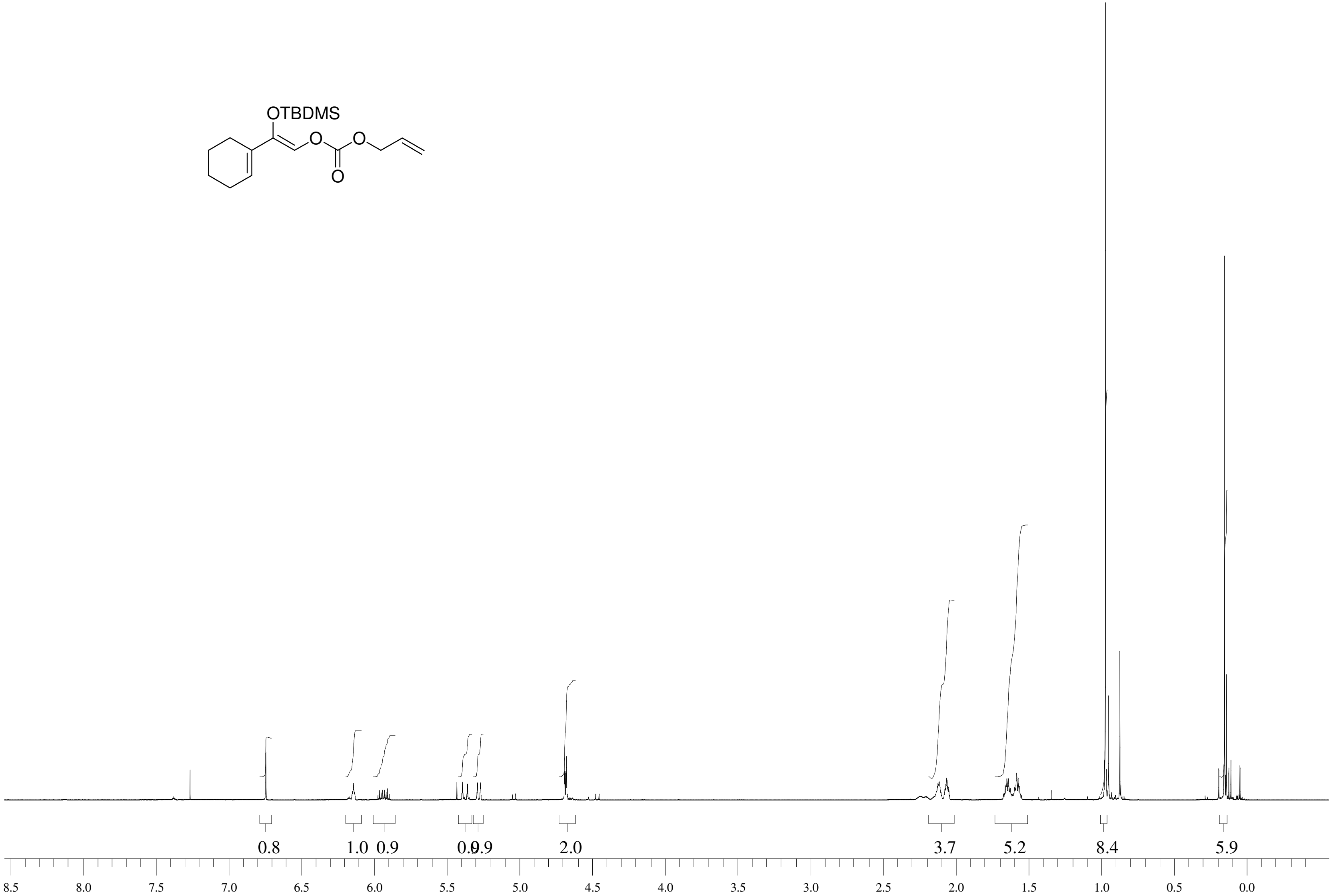
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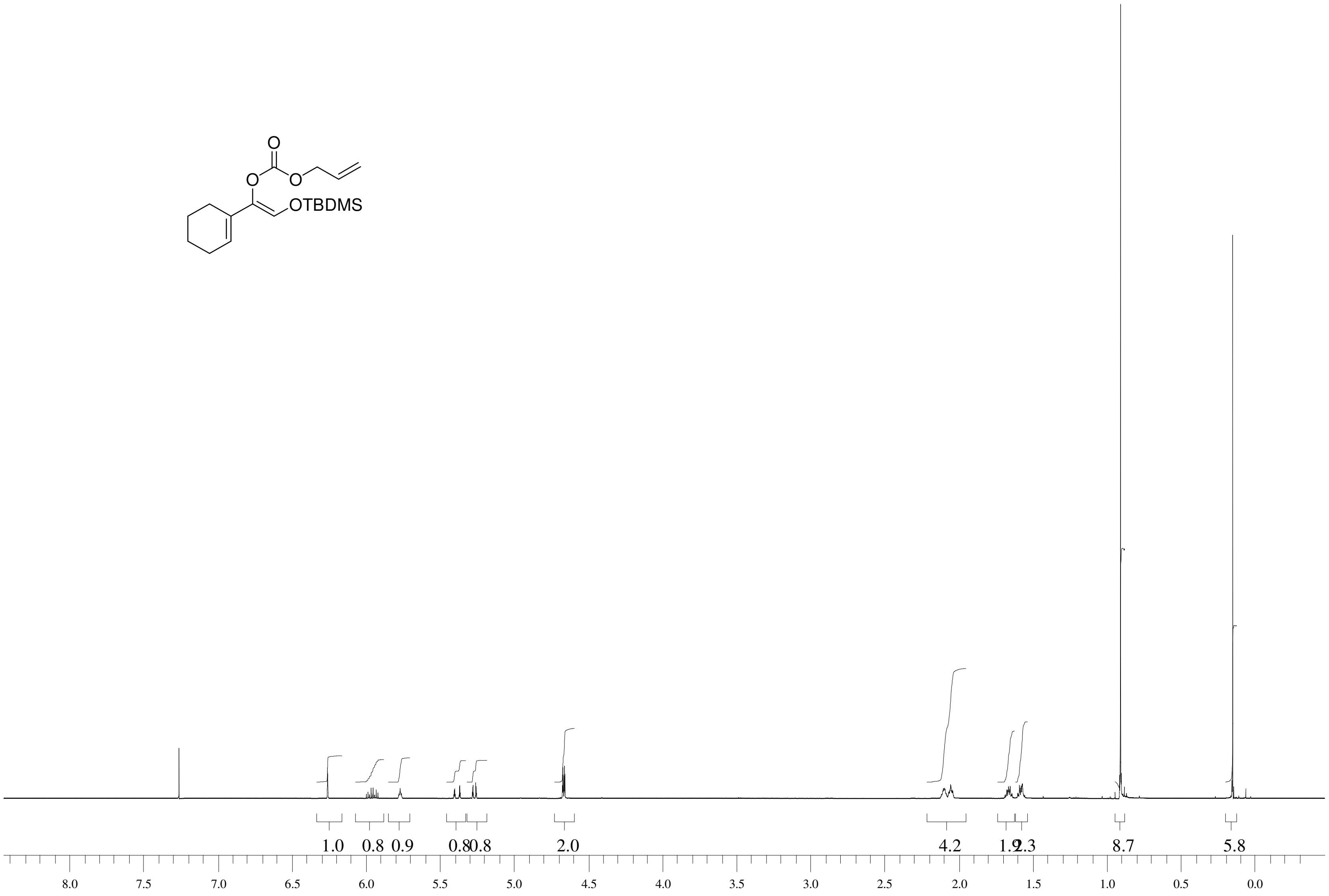
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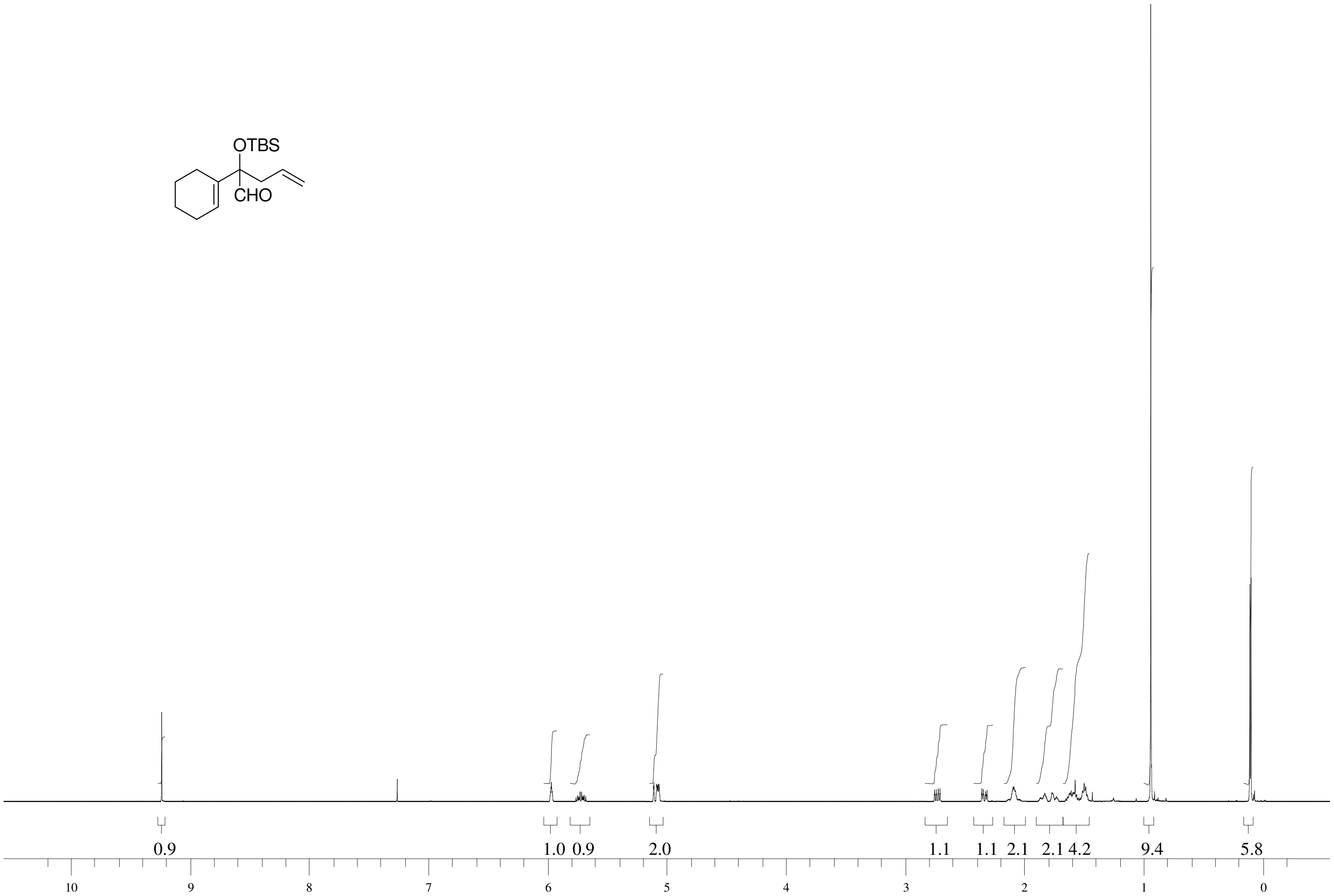
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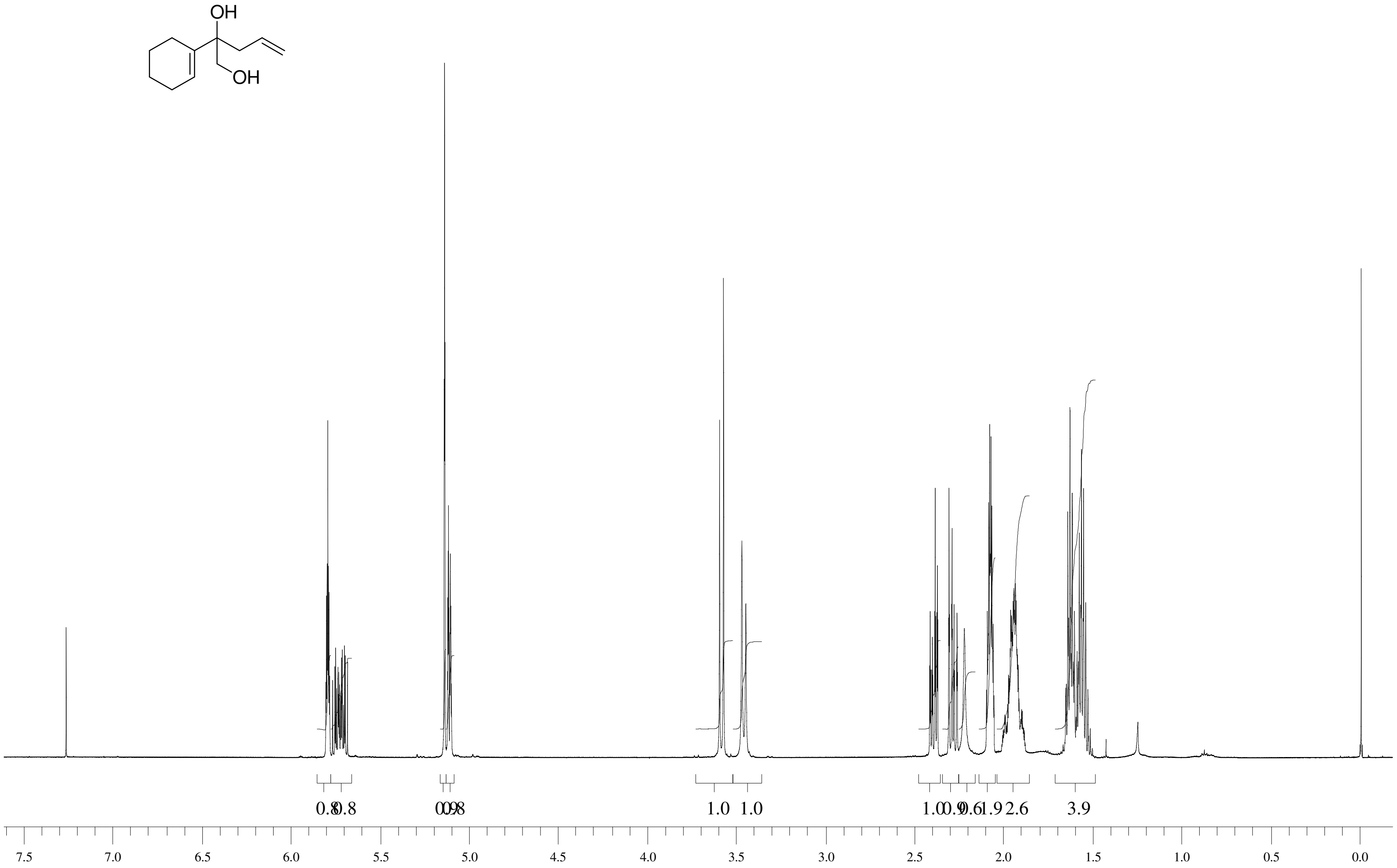
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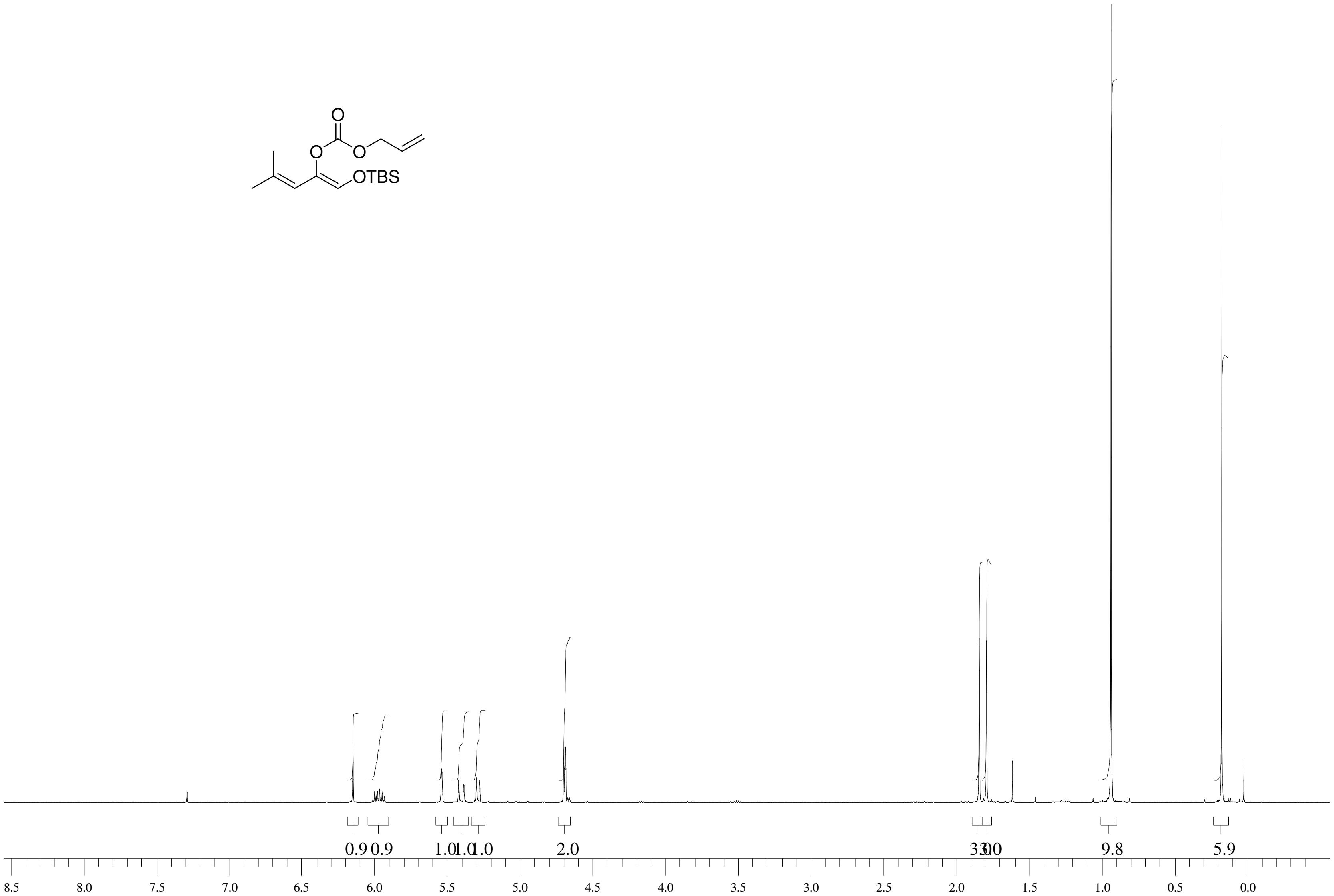
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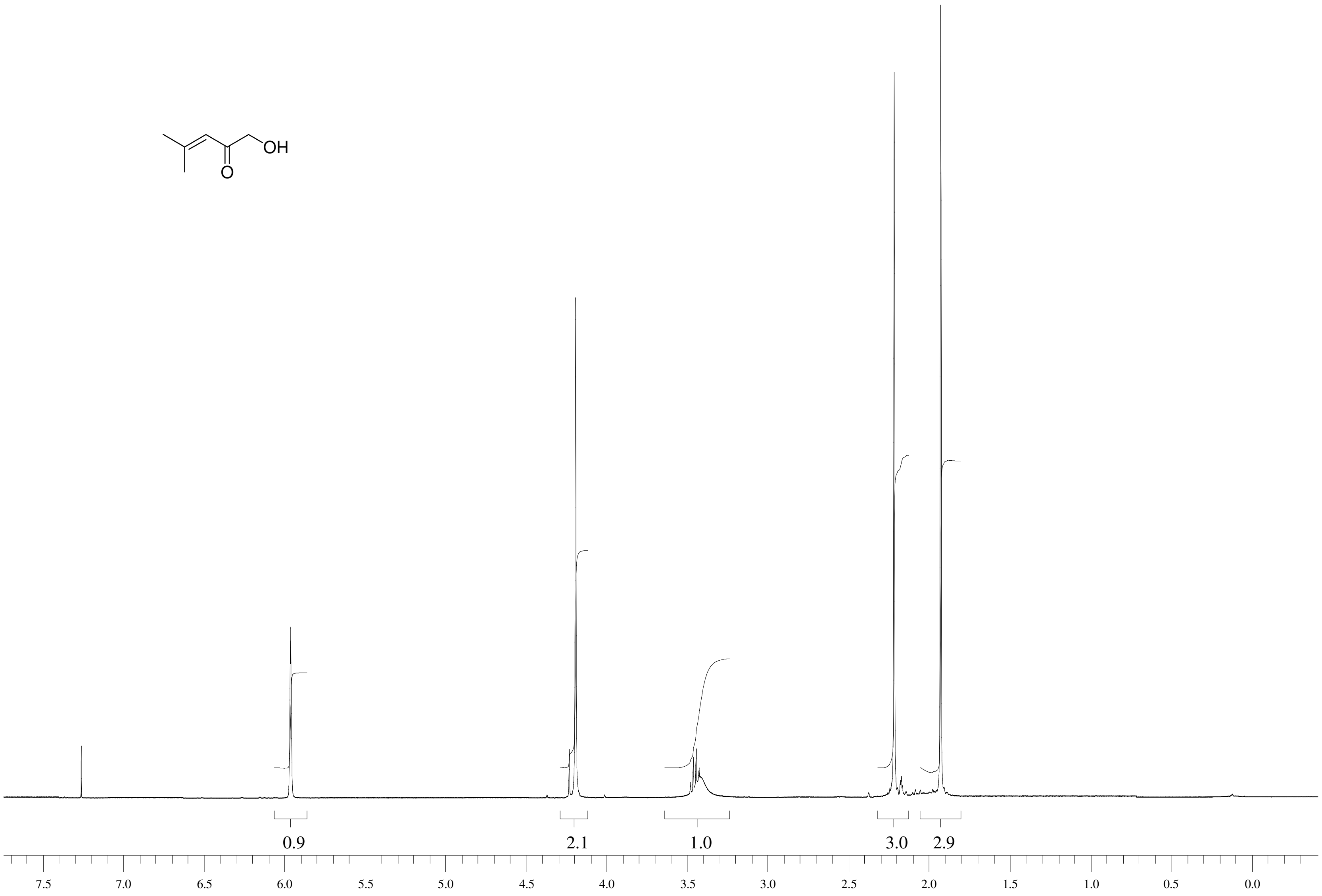
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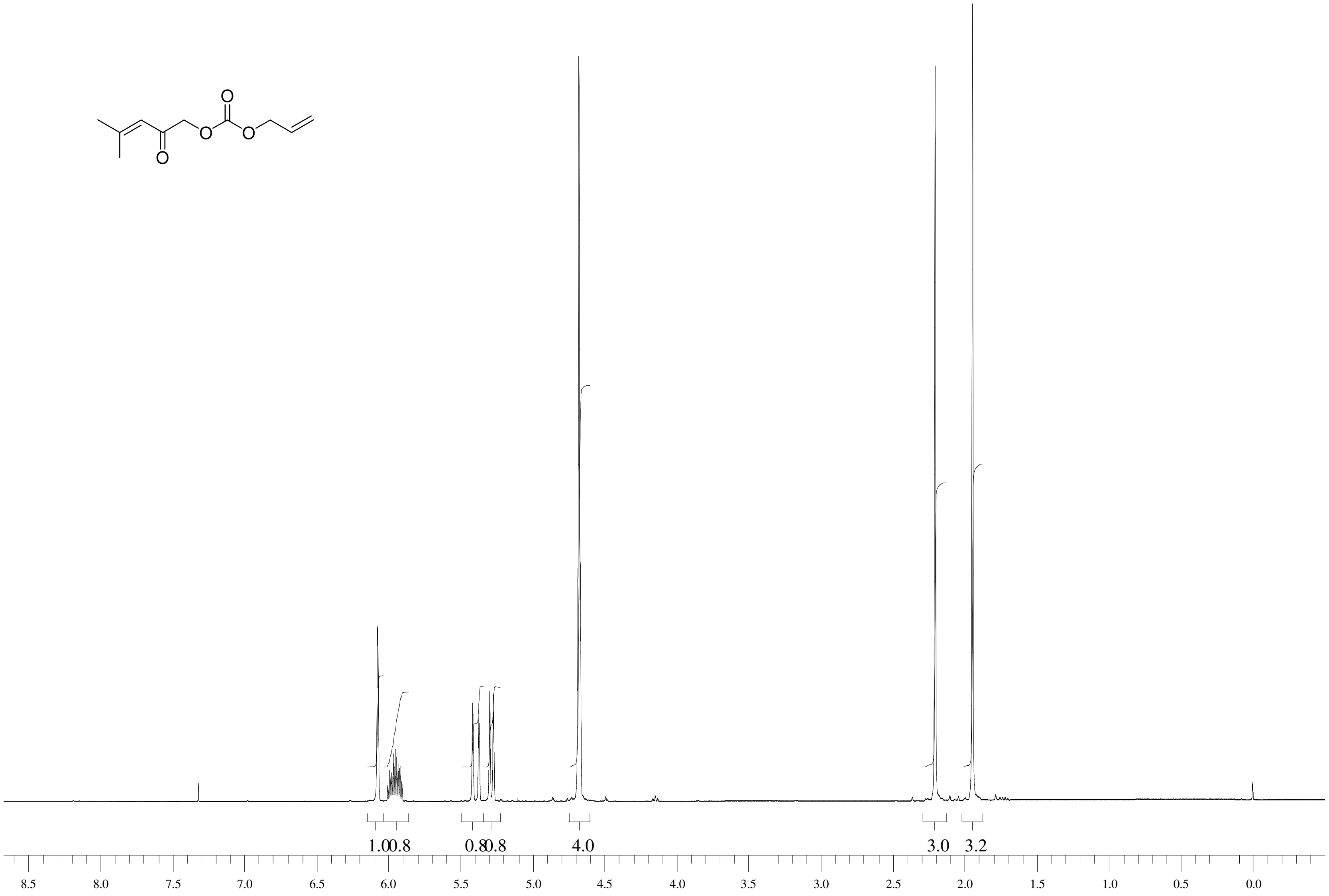
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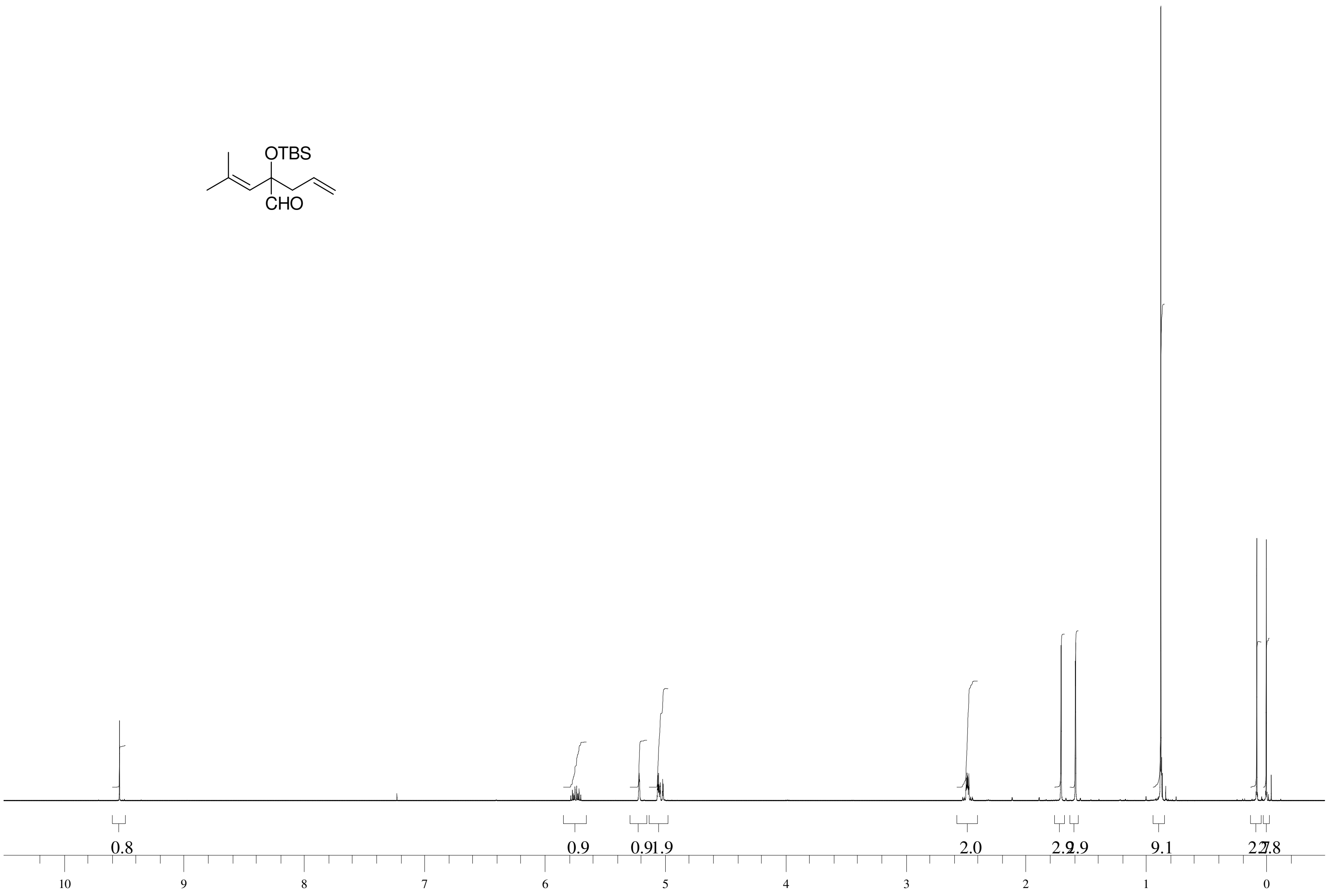
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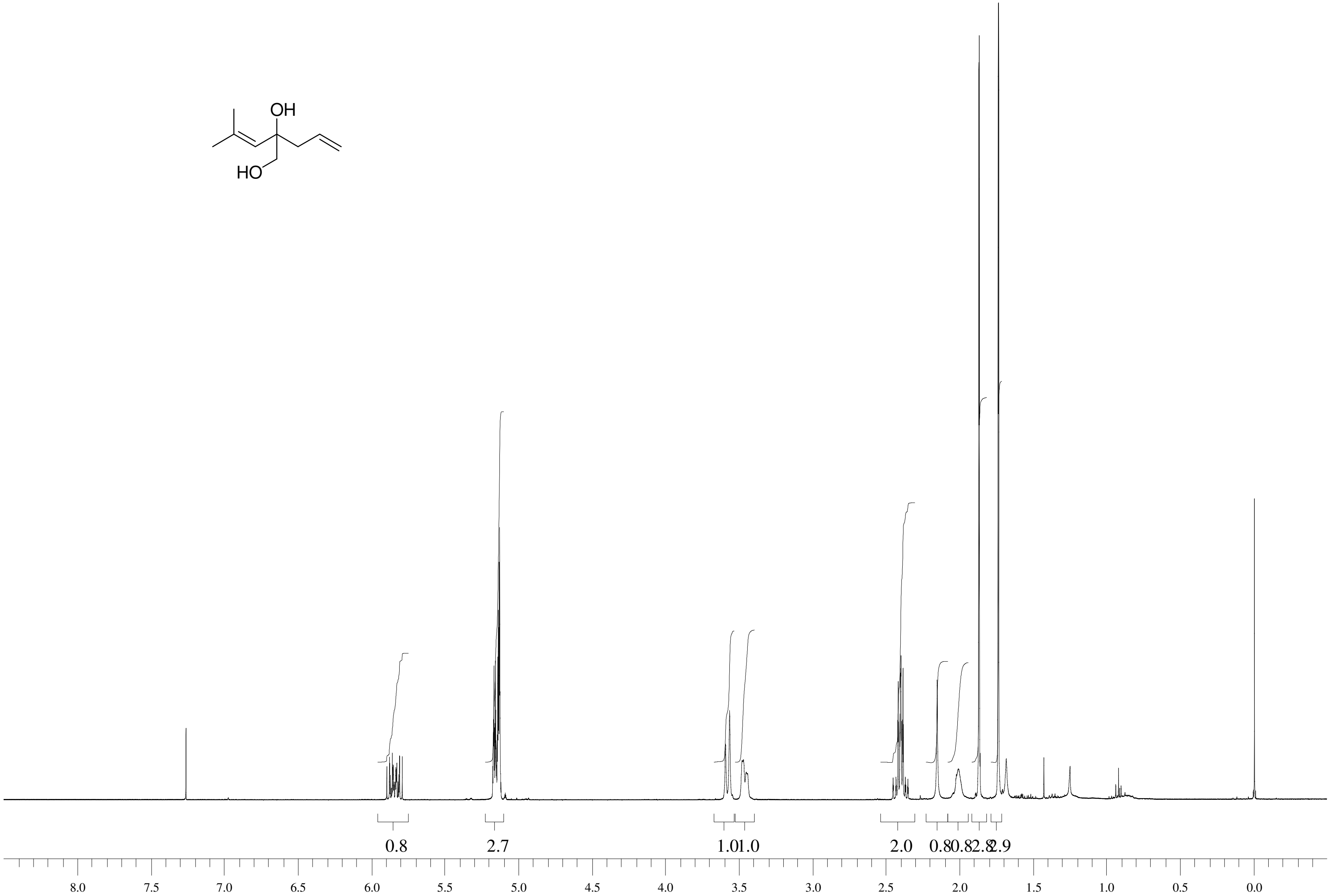
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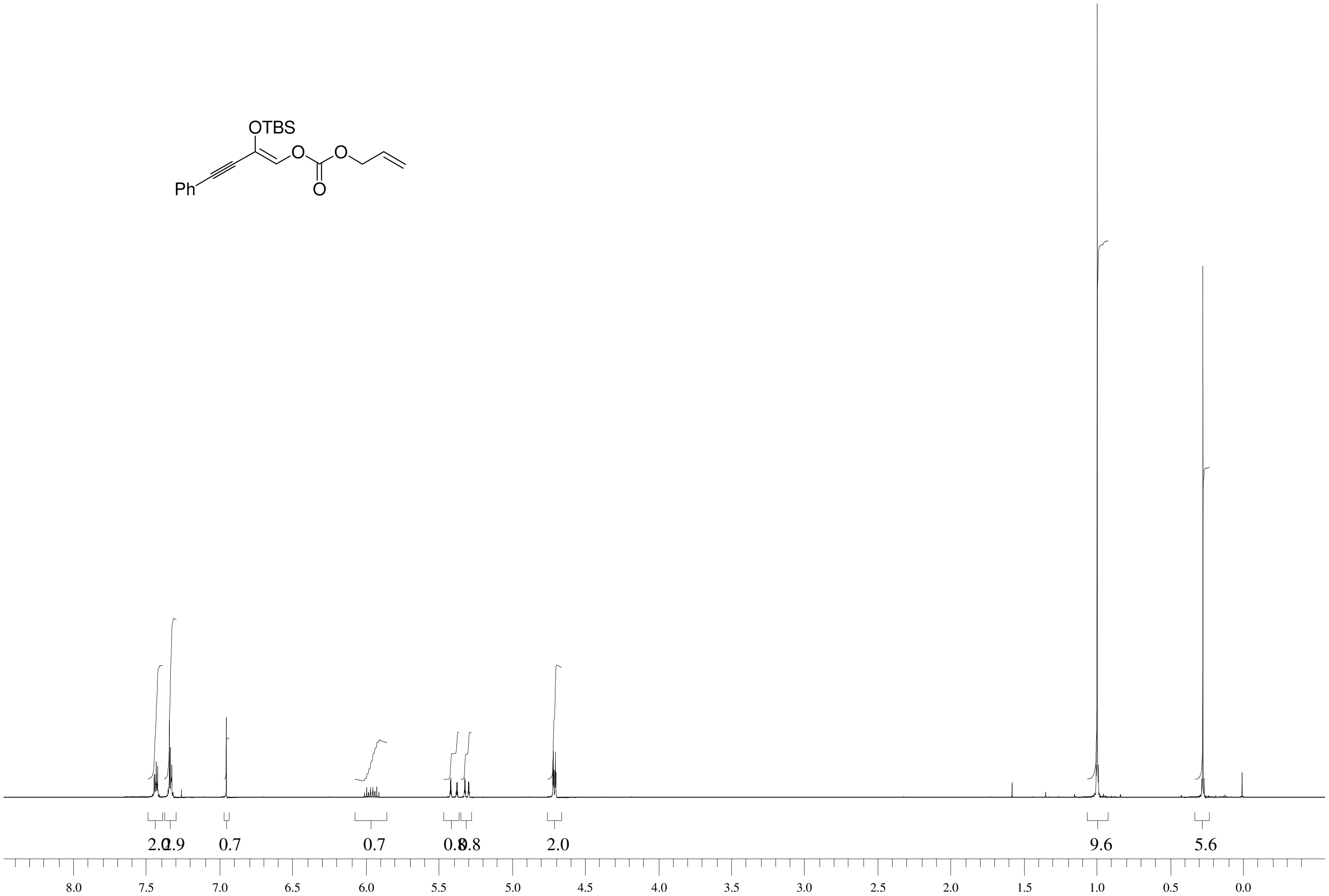
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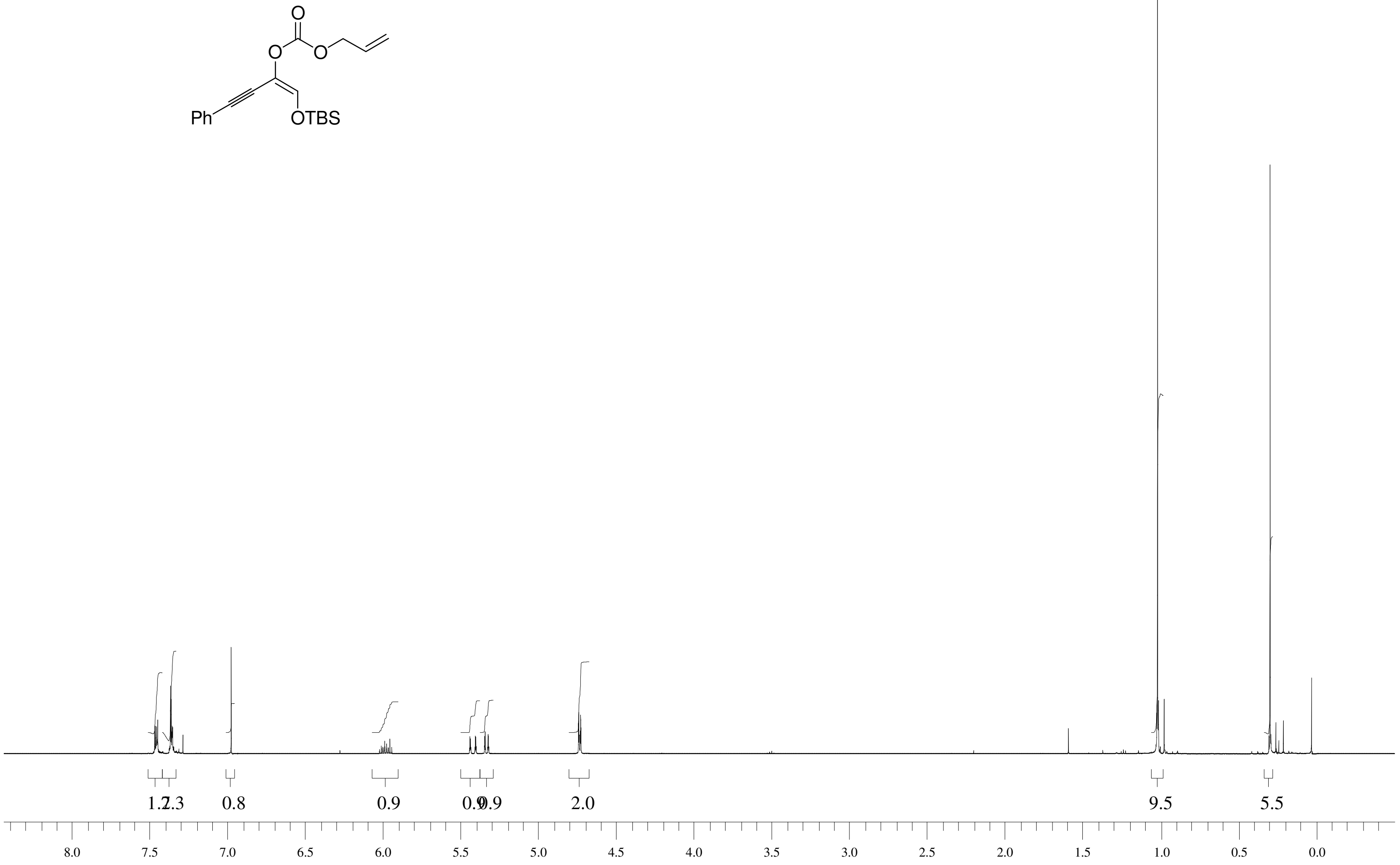
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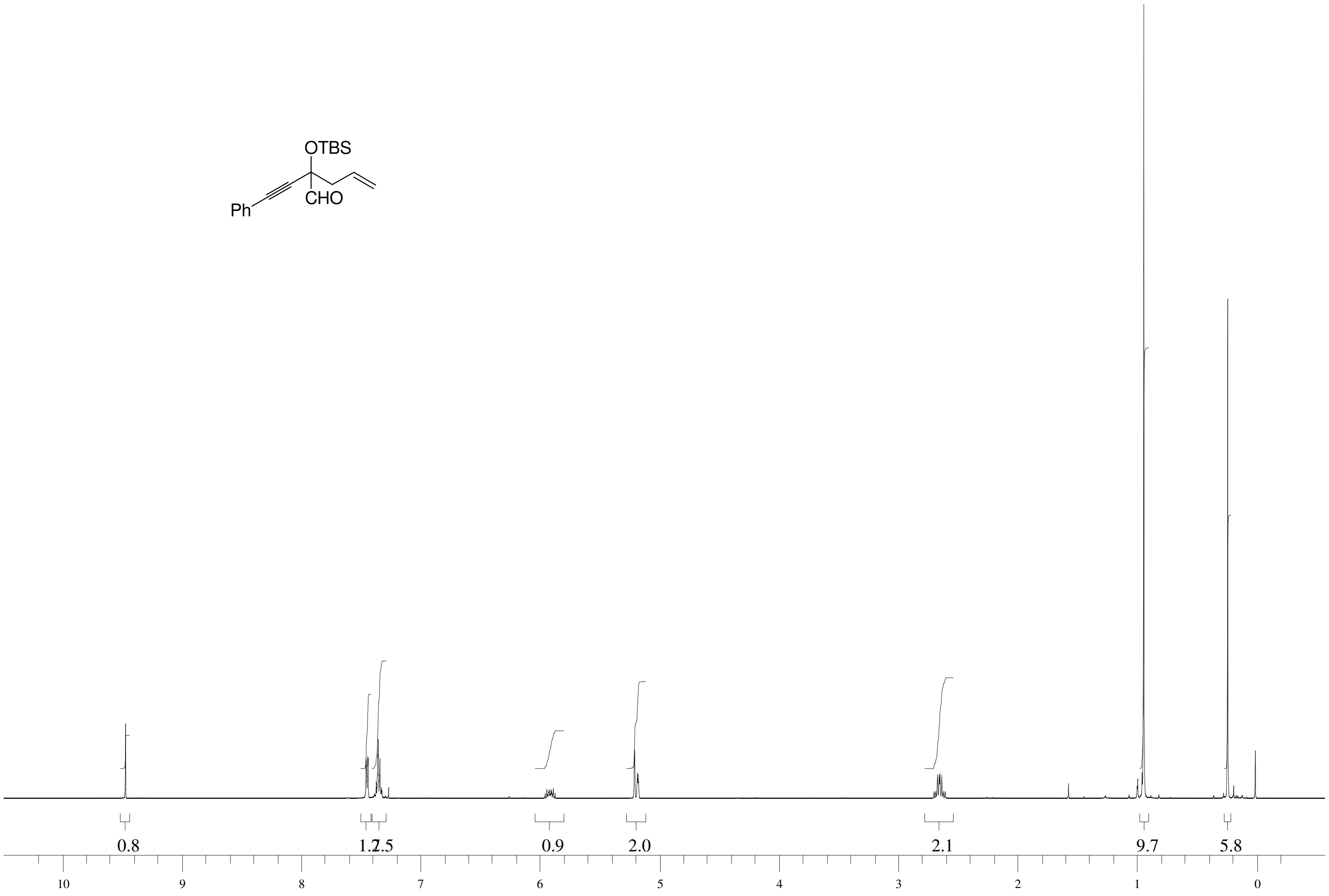
OTBS
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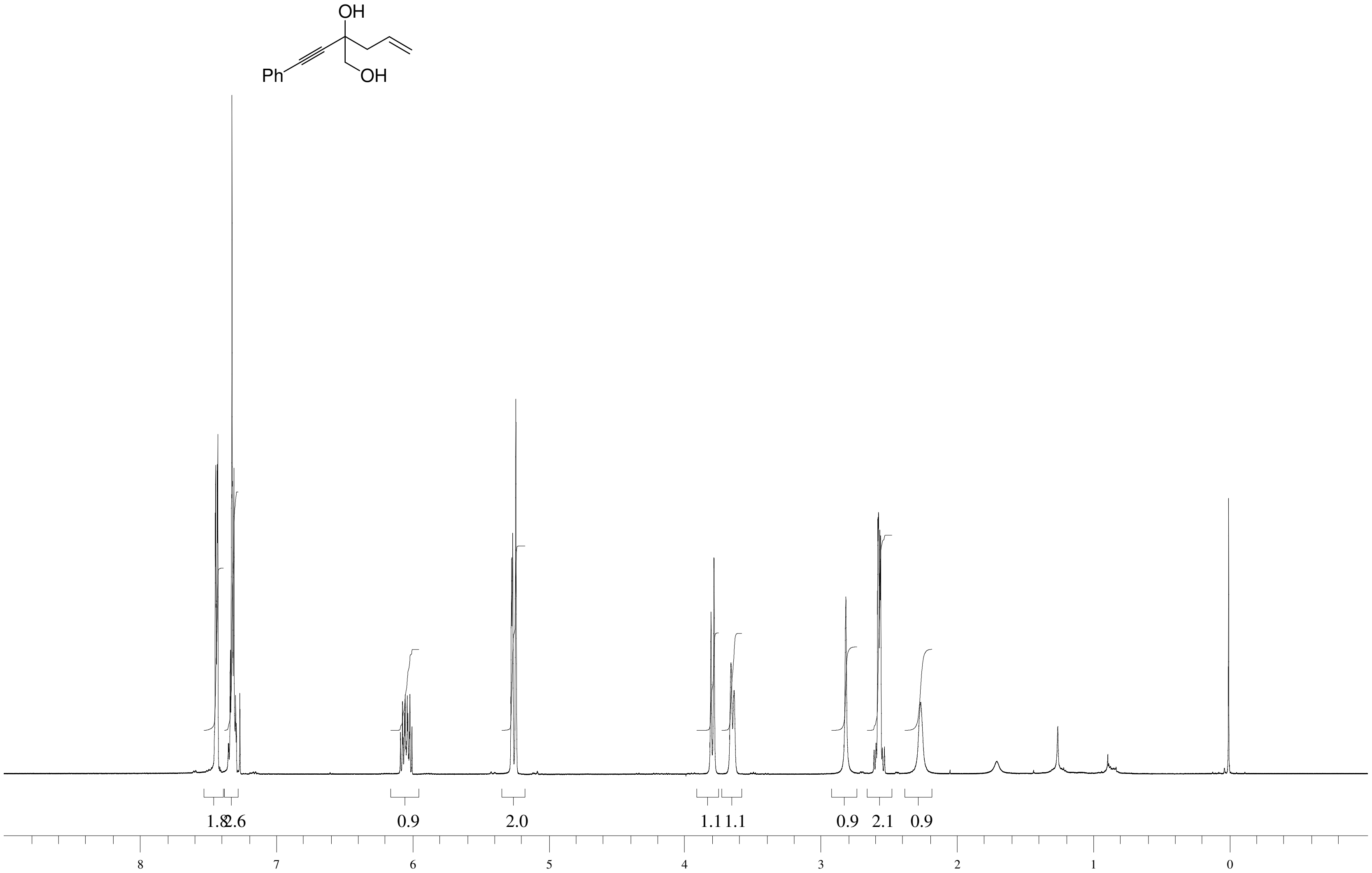
OH
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OH
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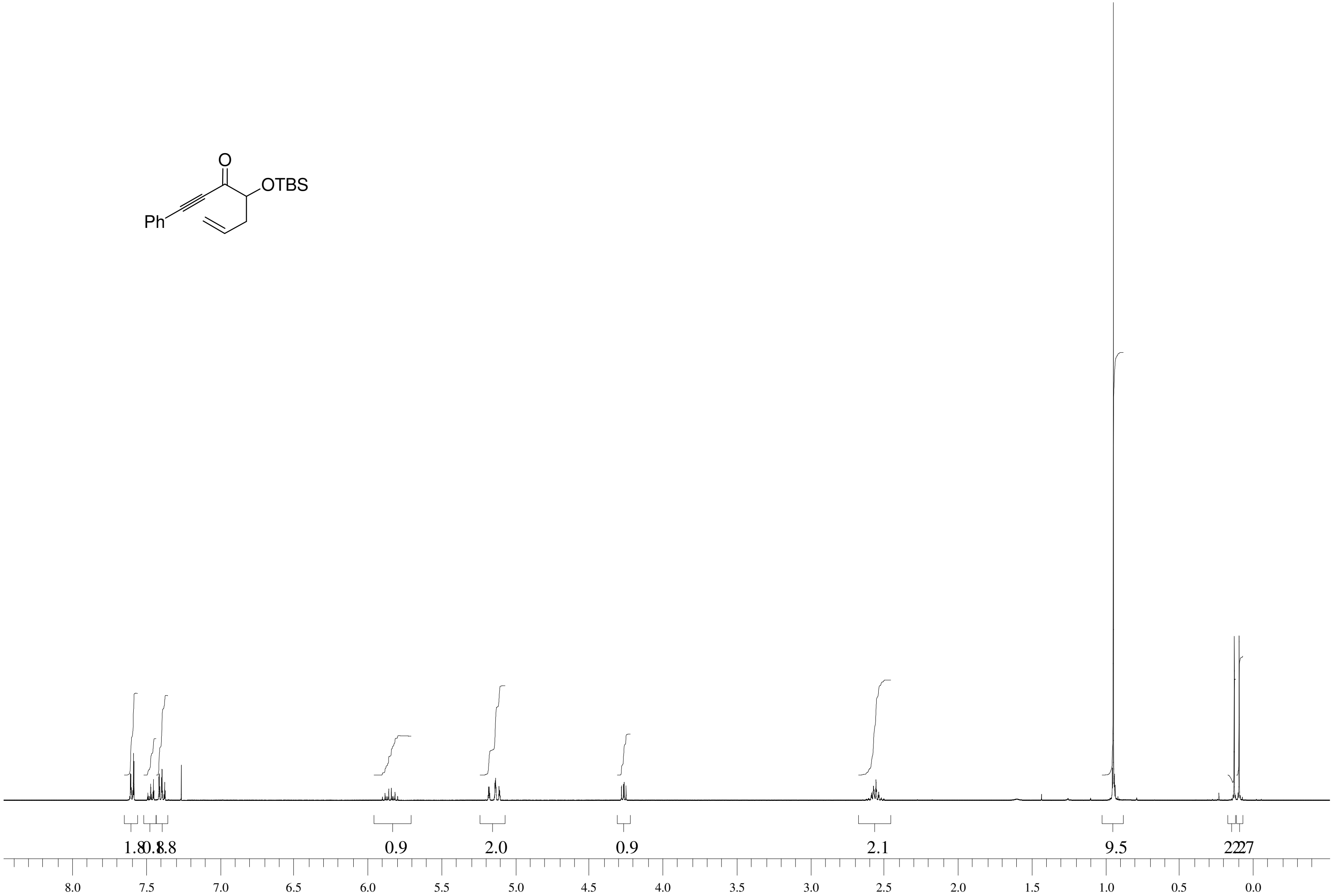
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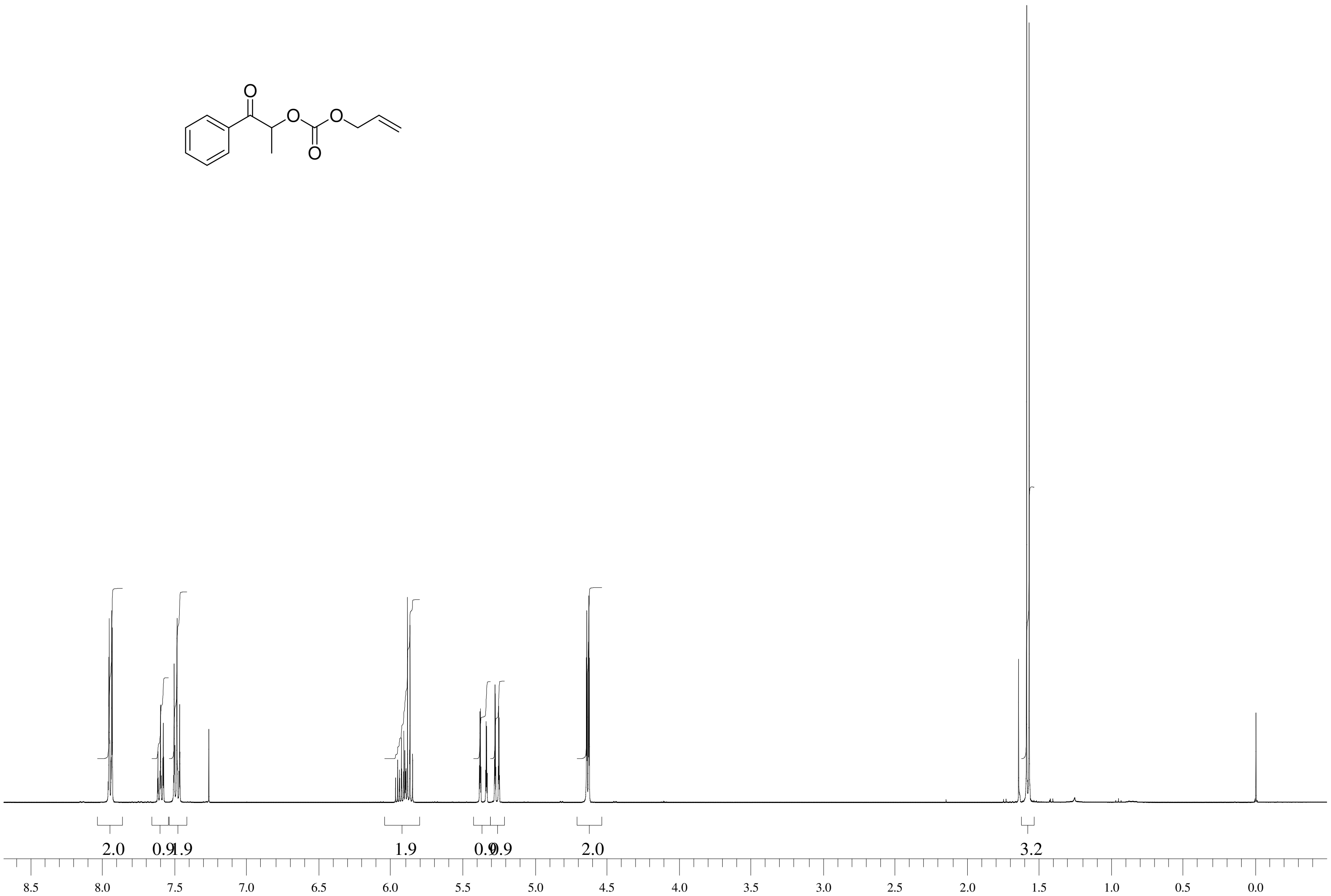
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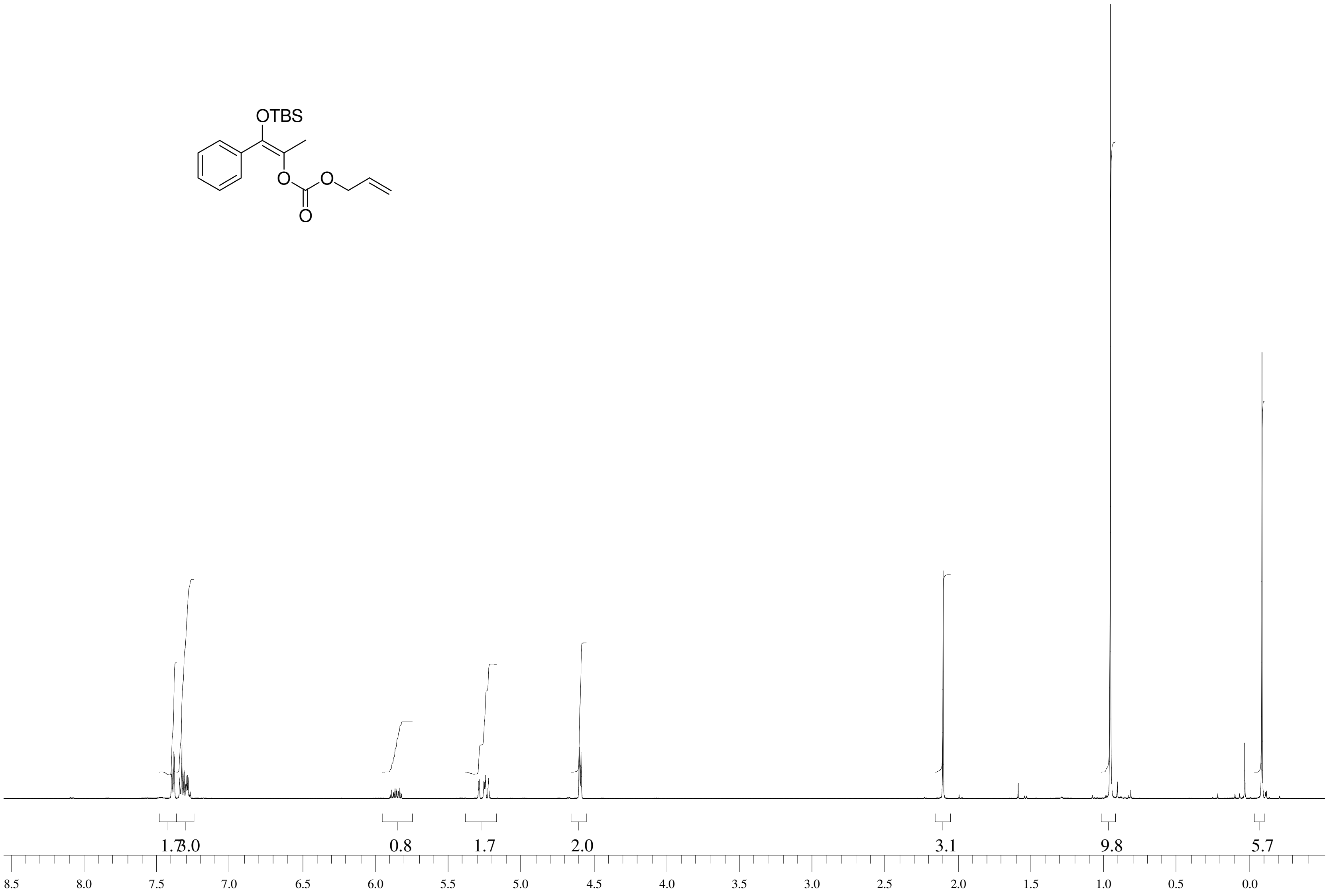
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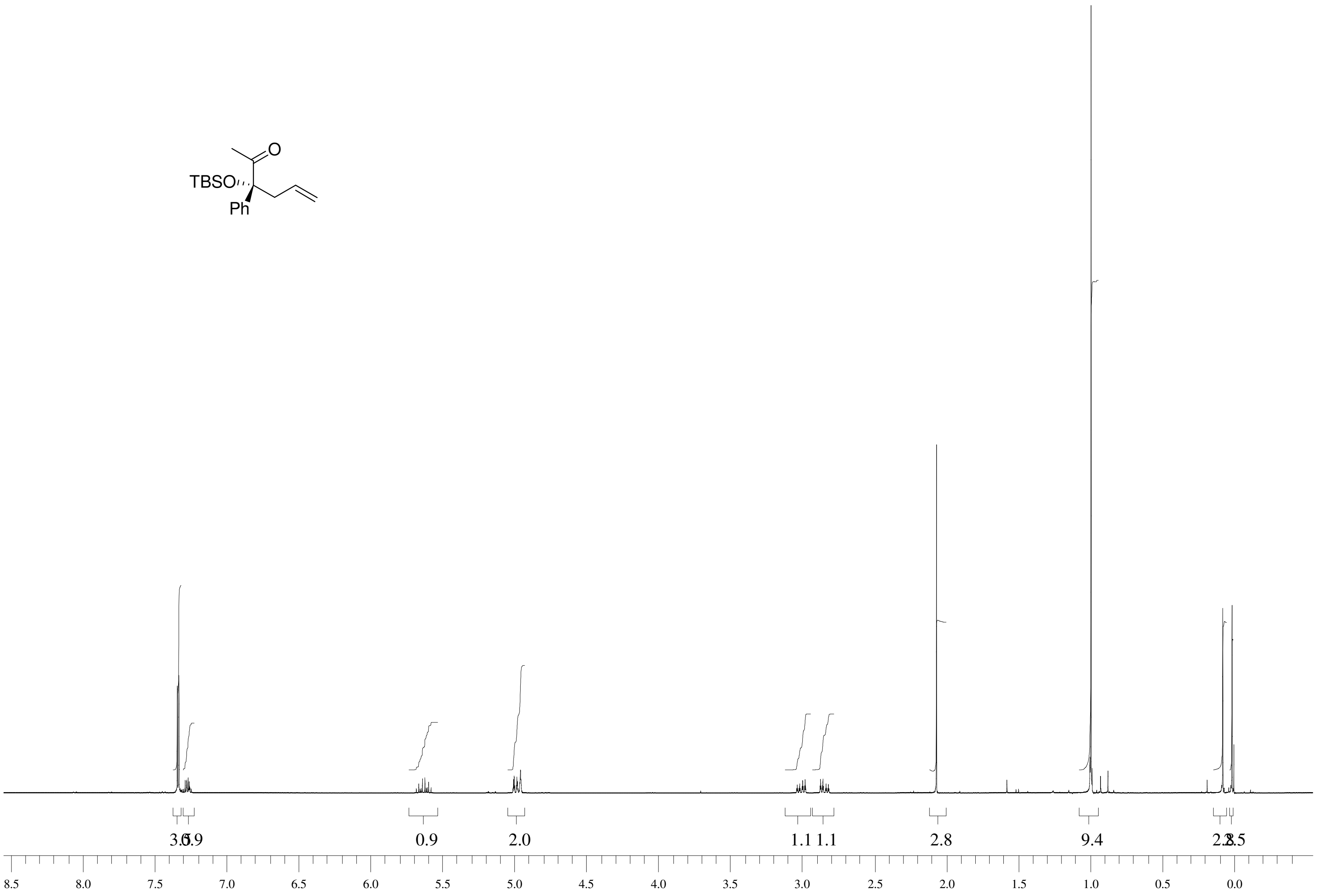
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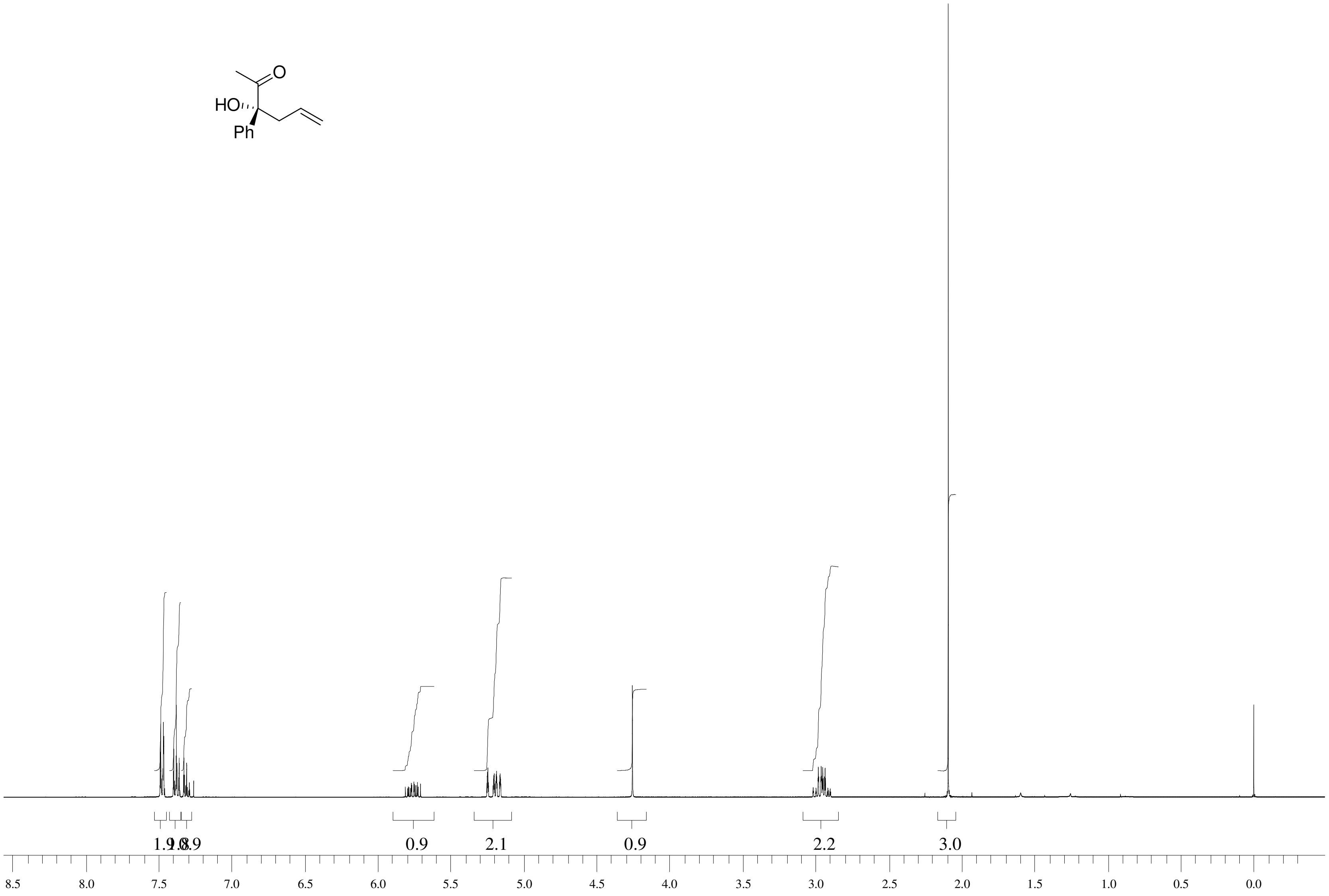
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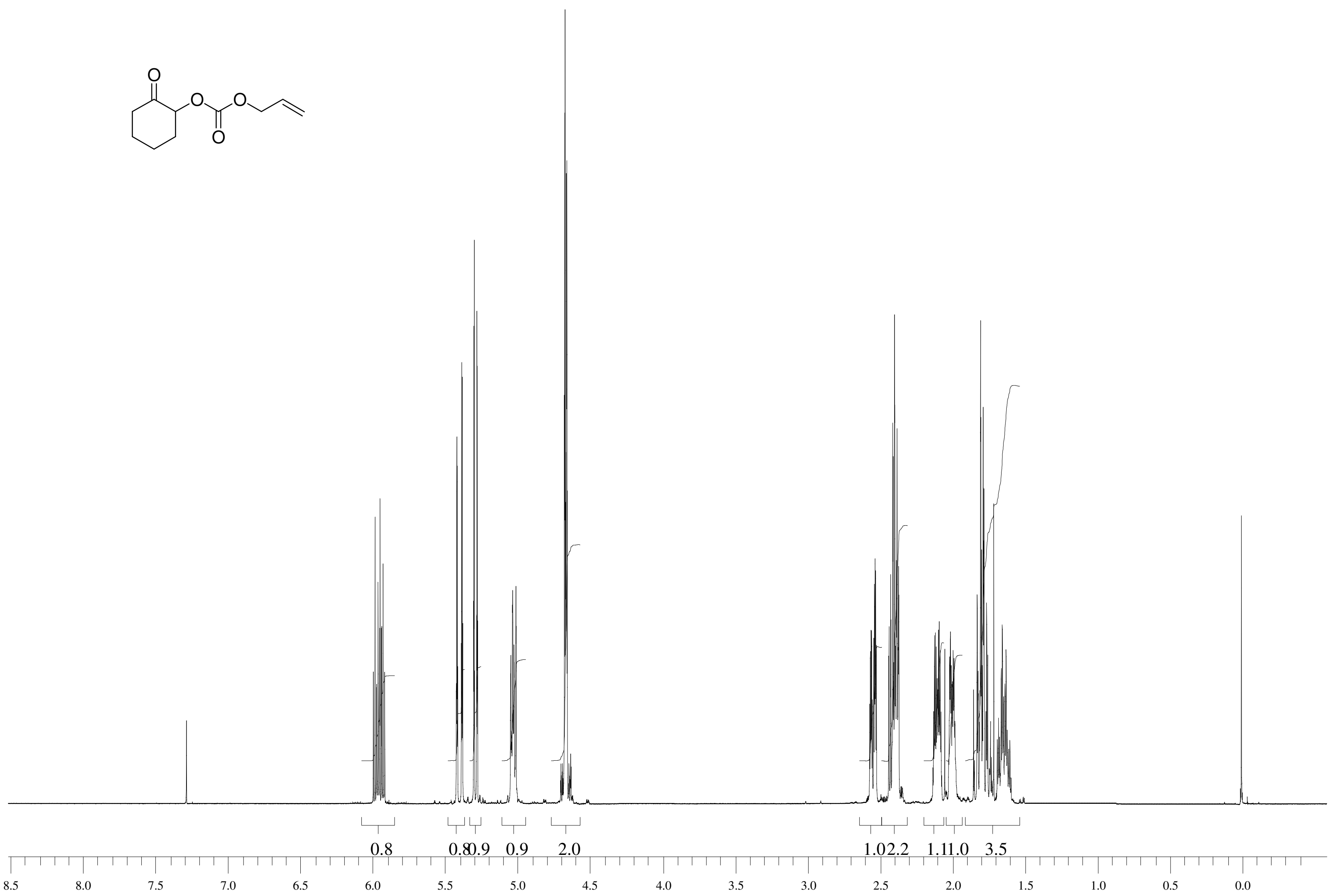
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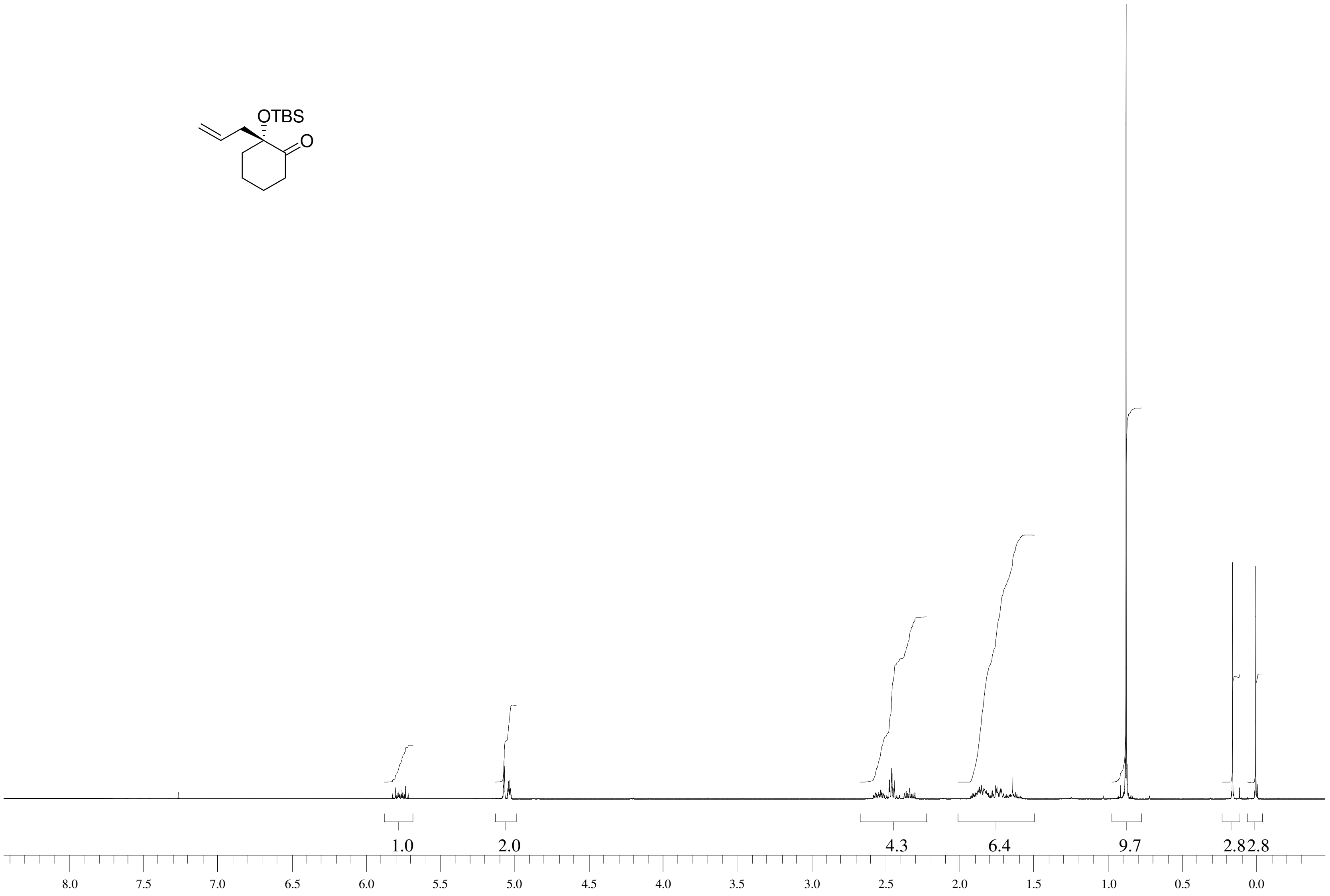
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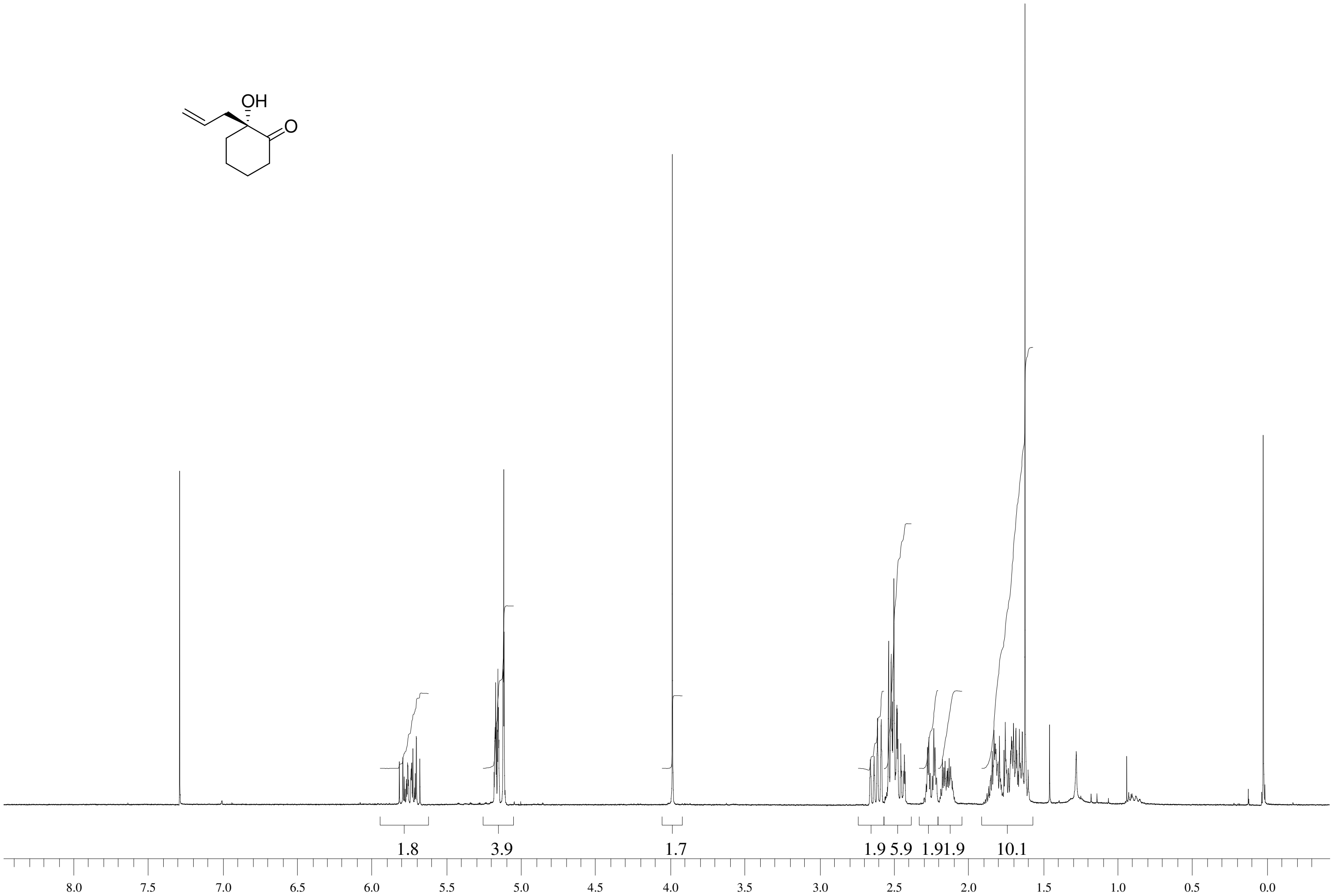
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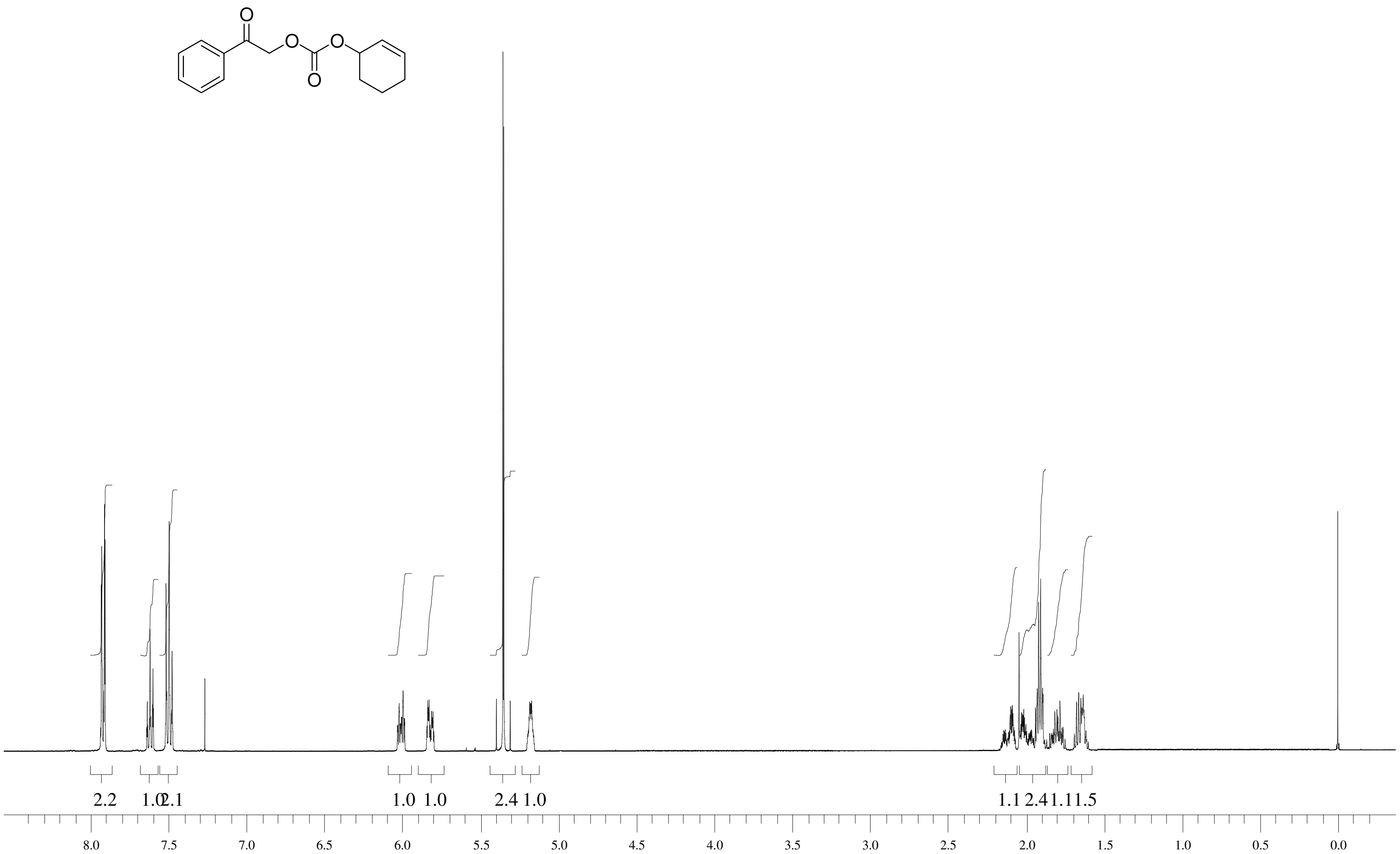
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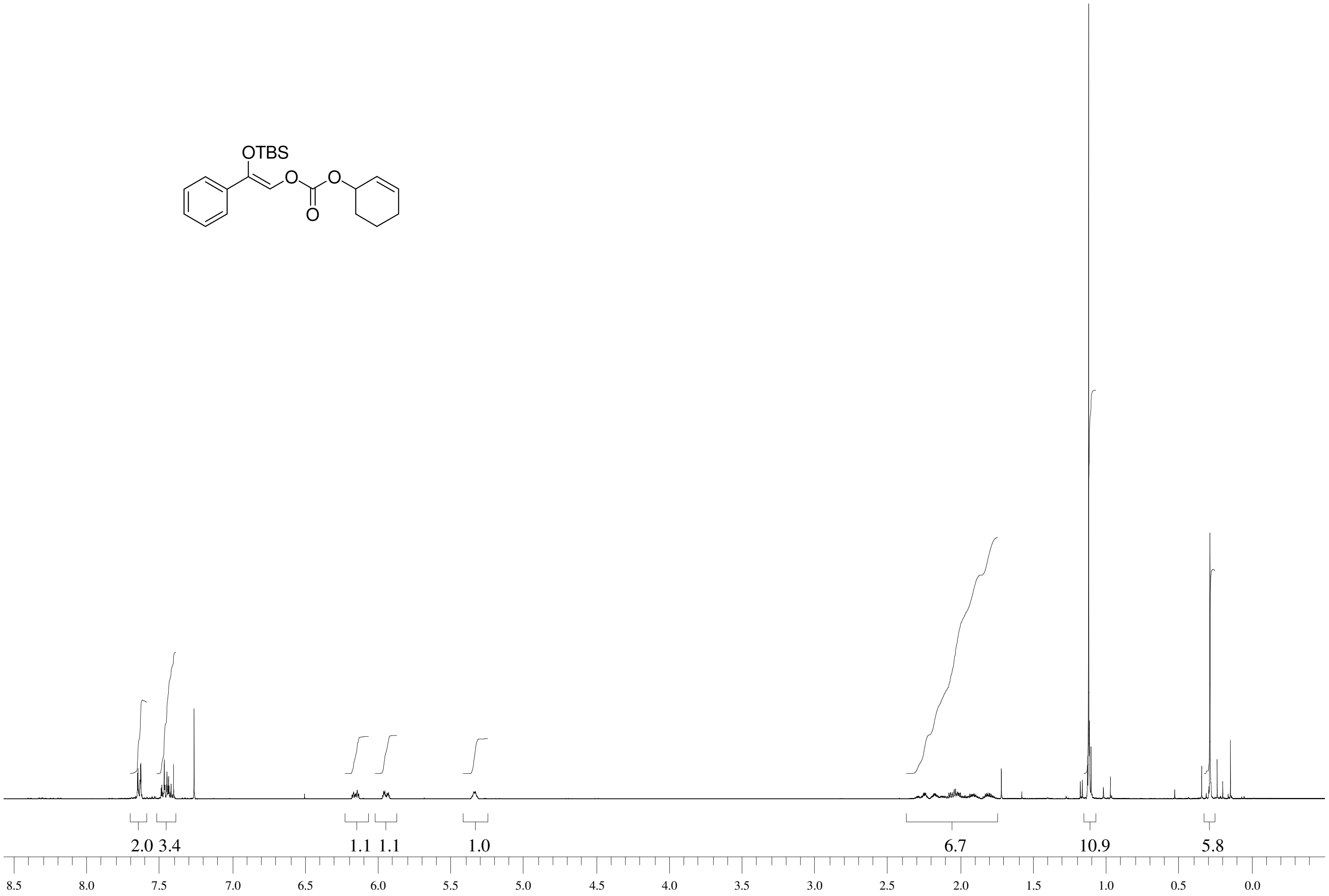
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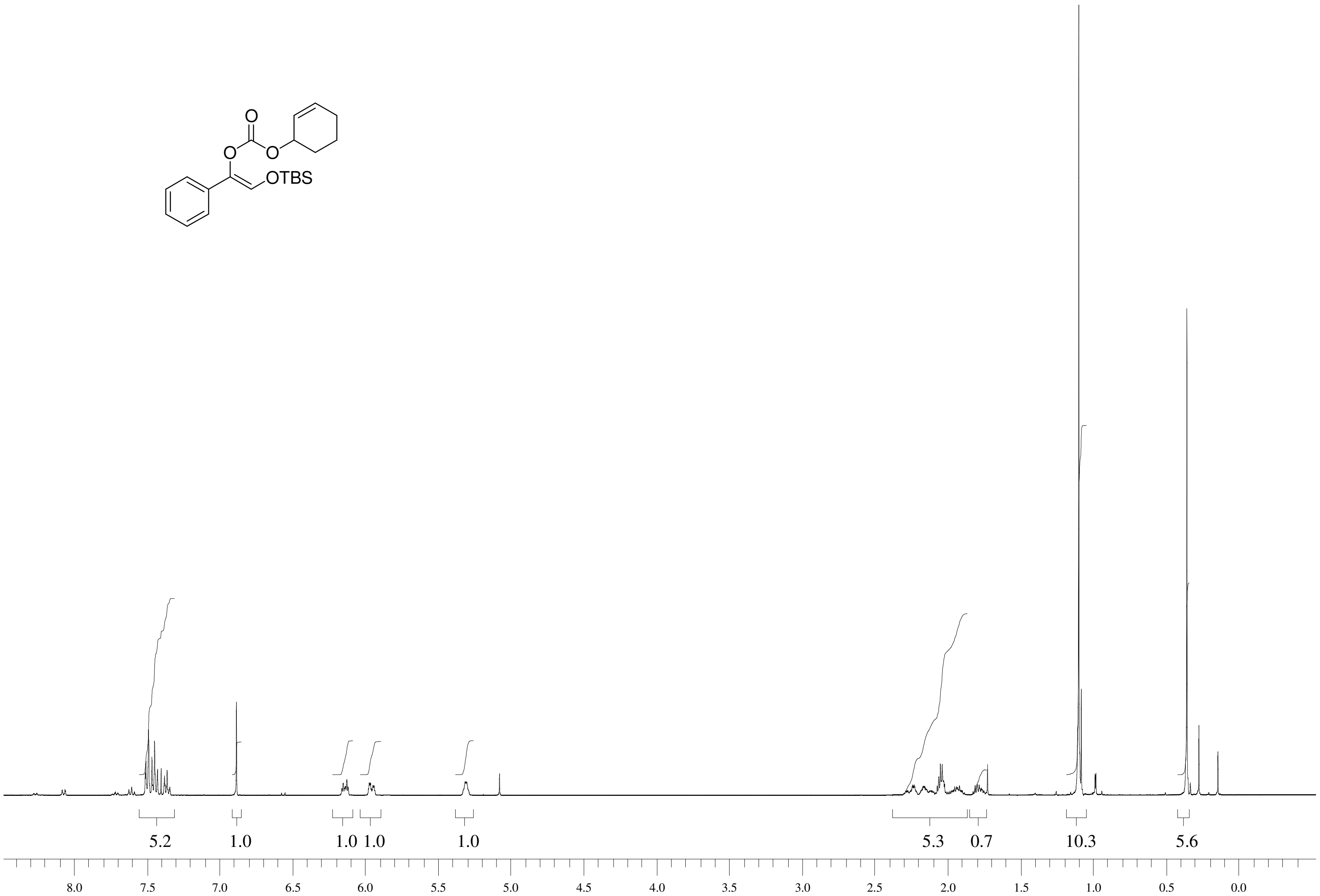
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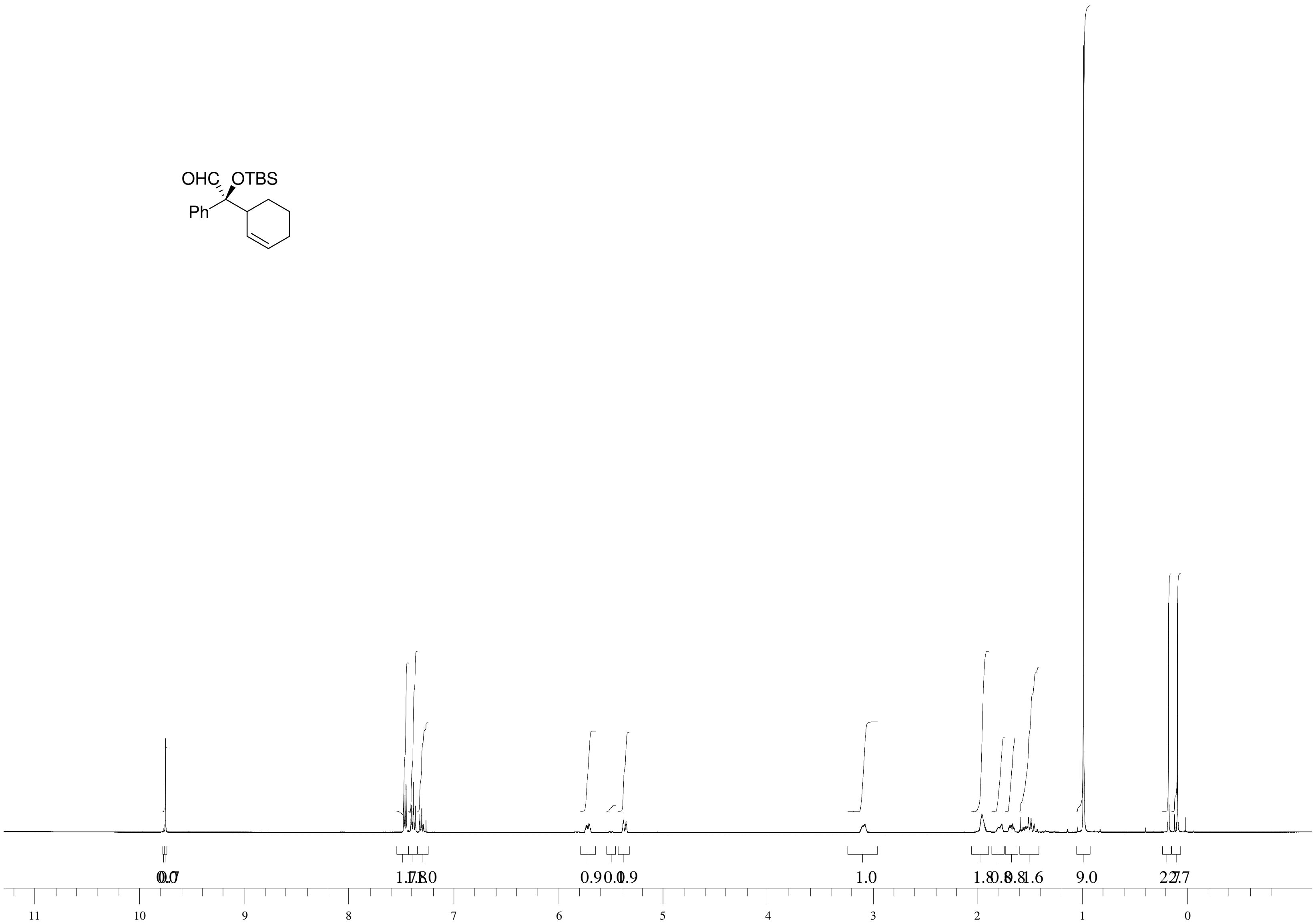
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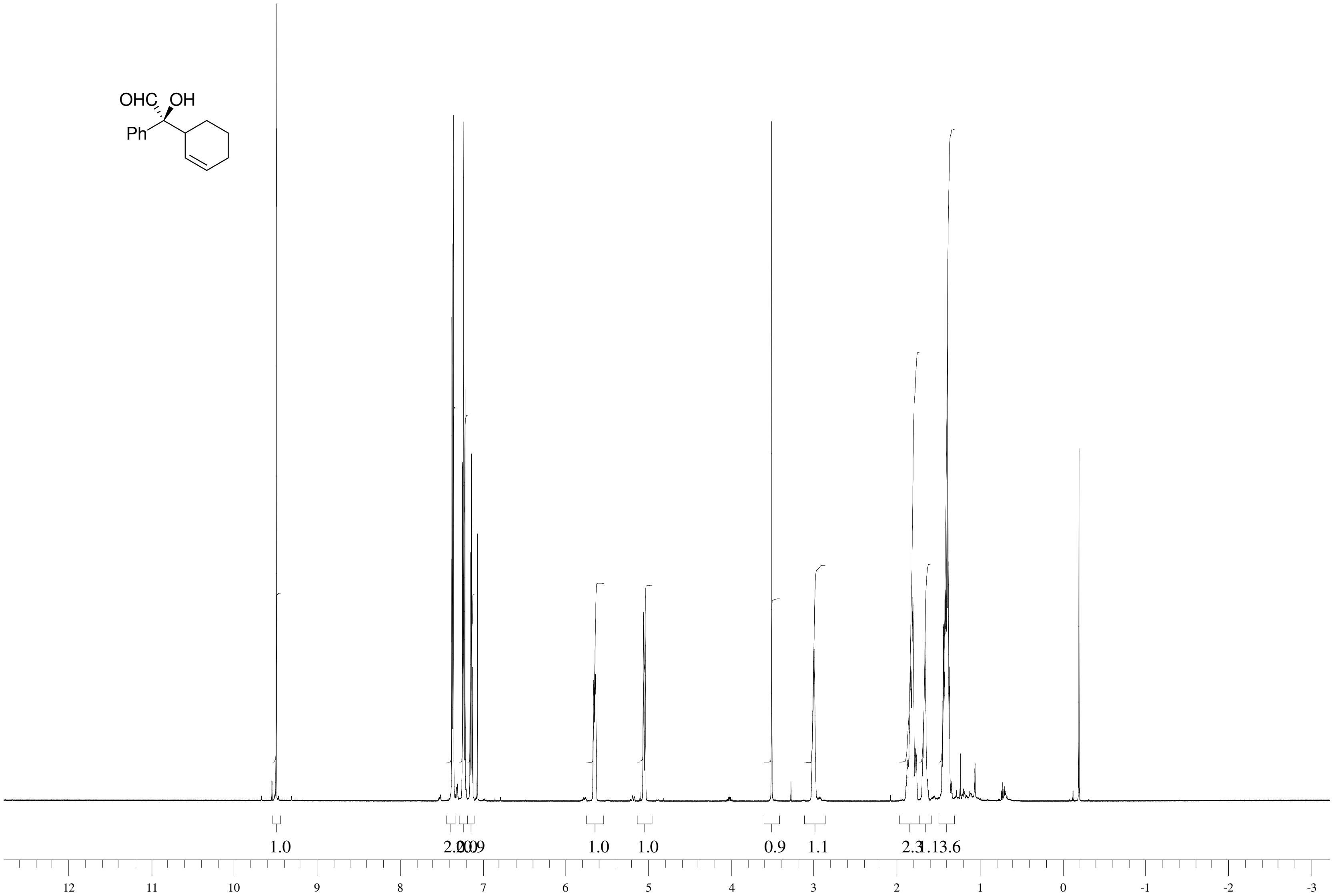
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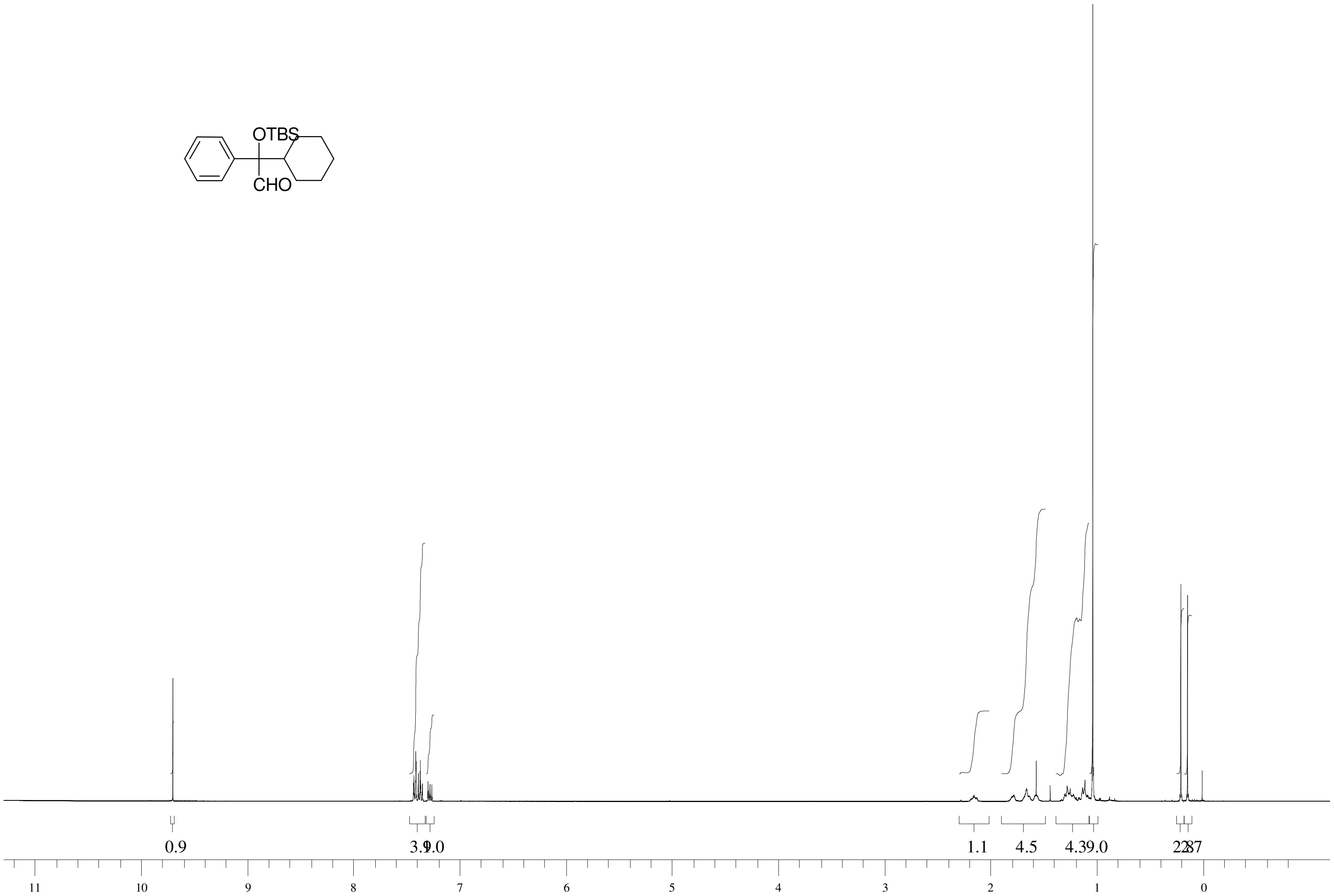
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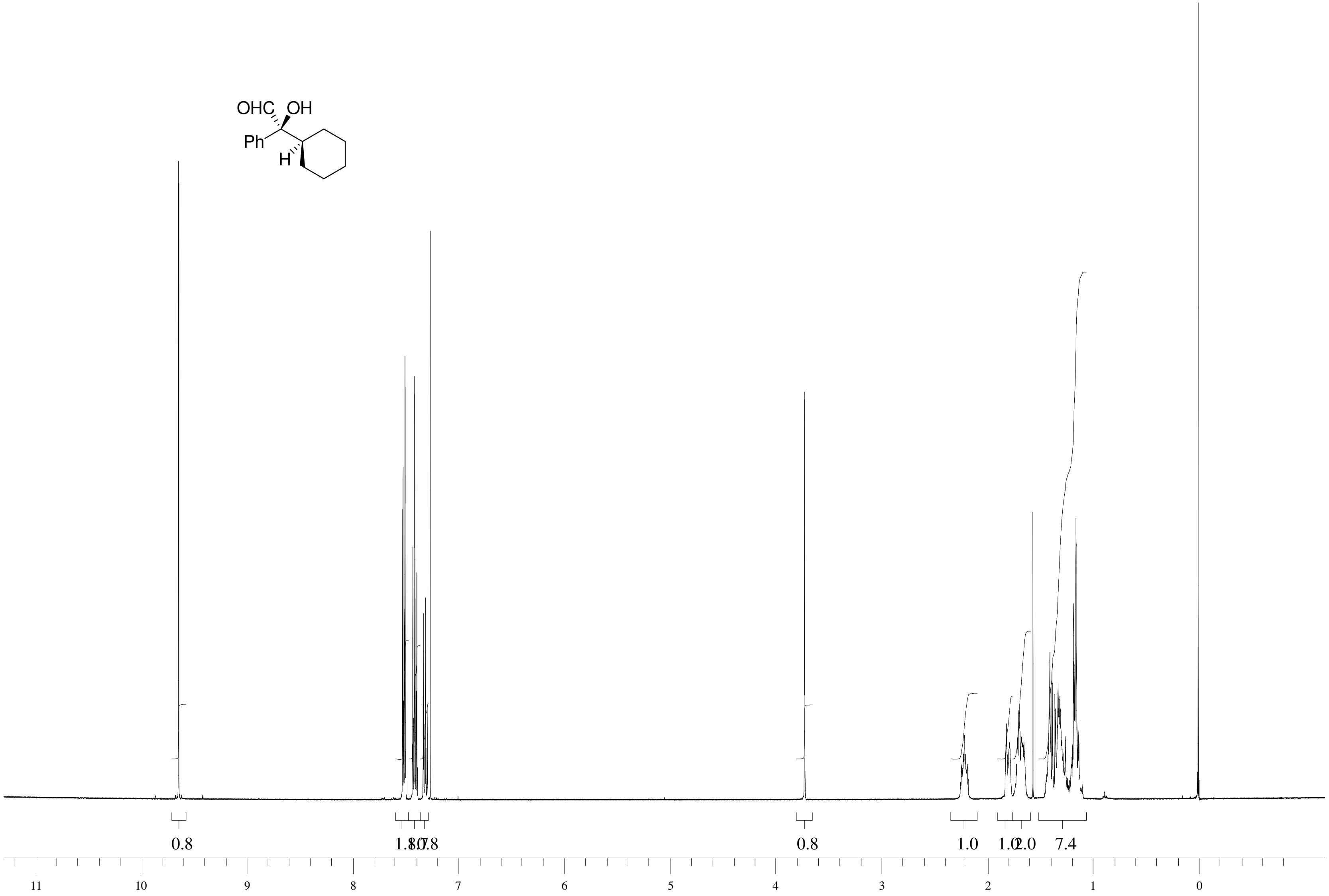
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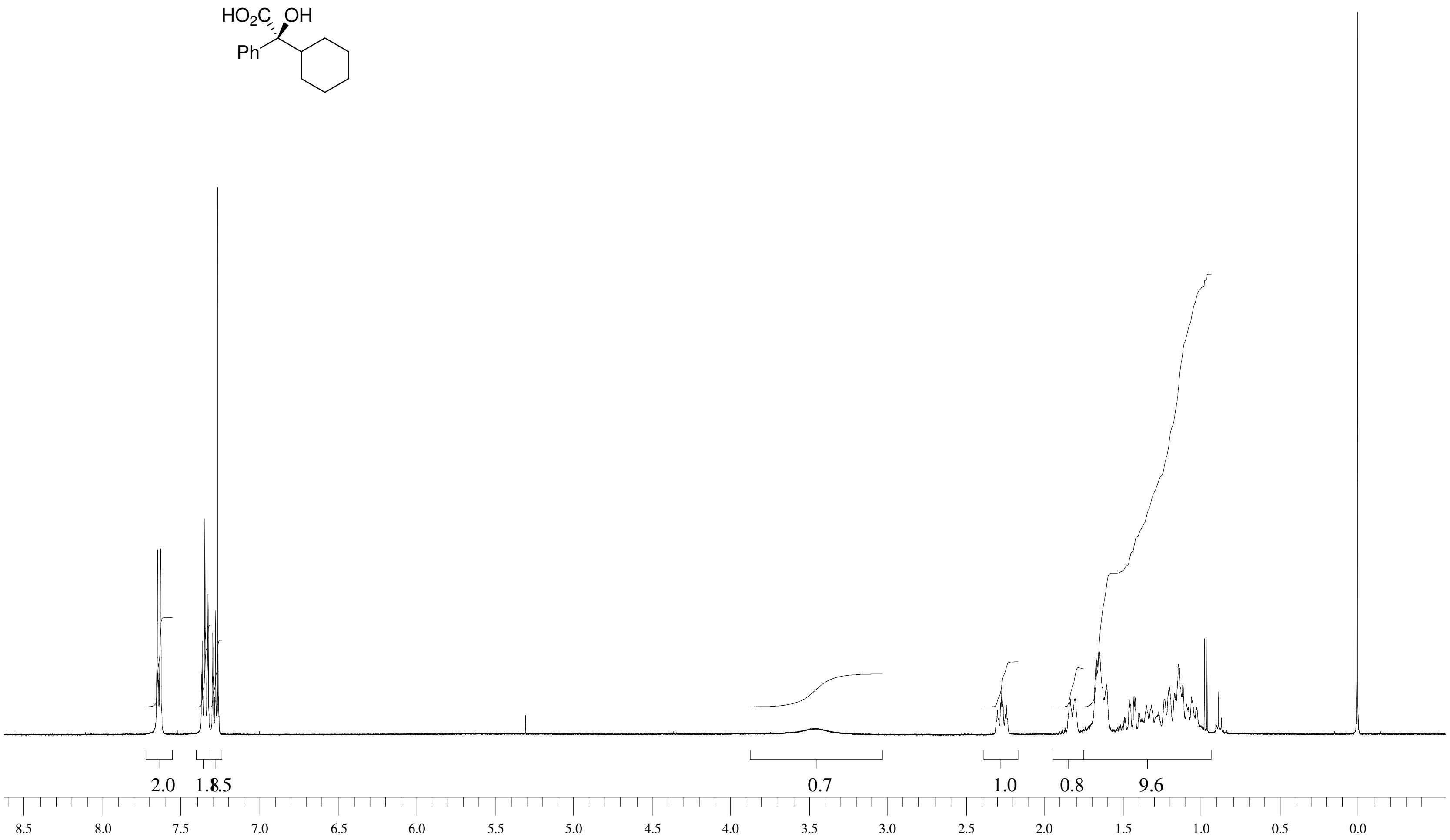
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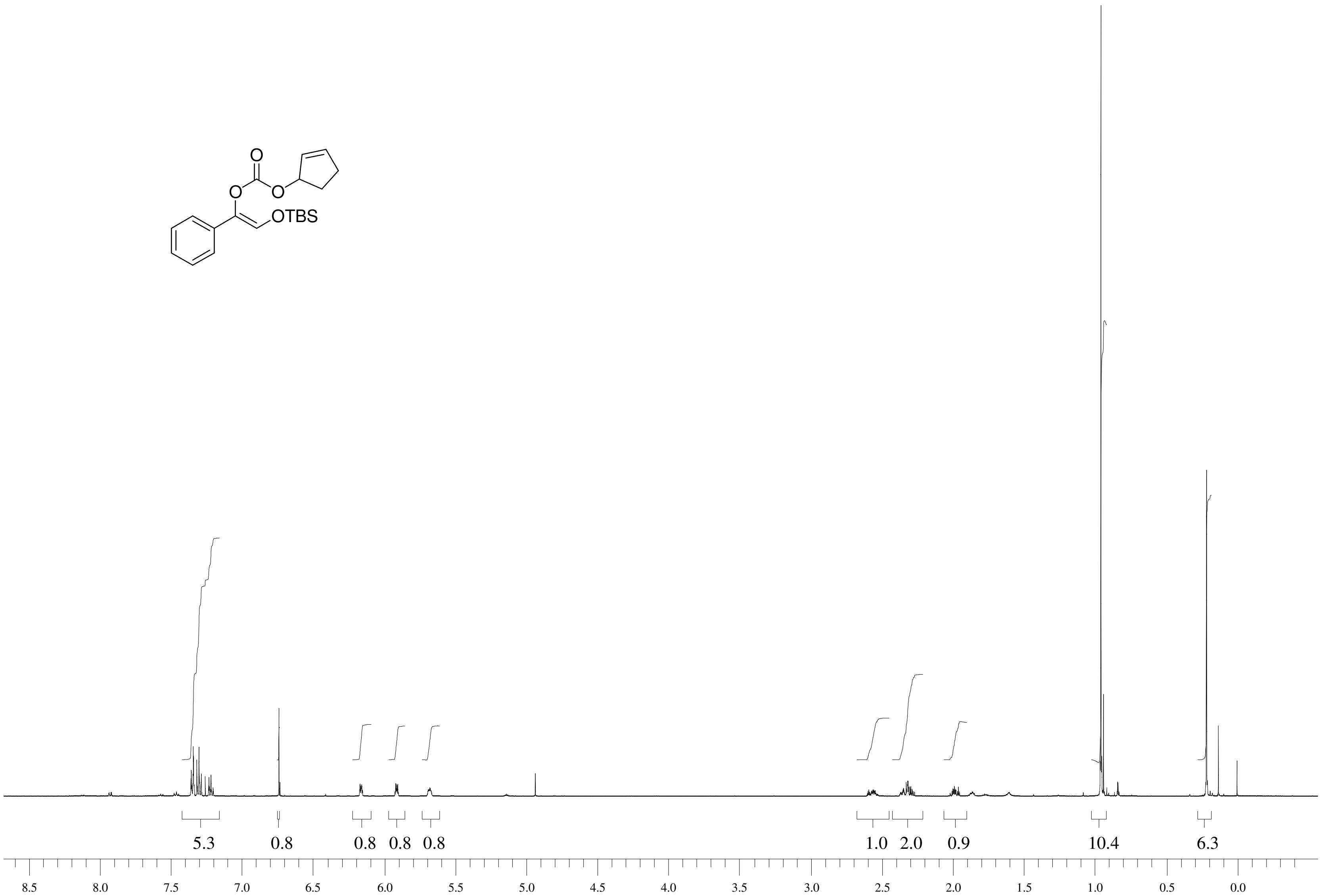
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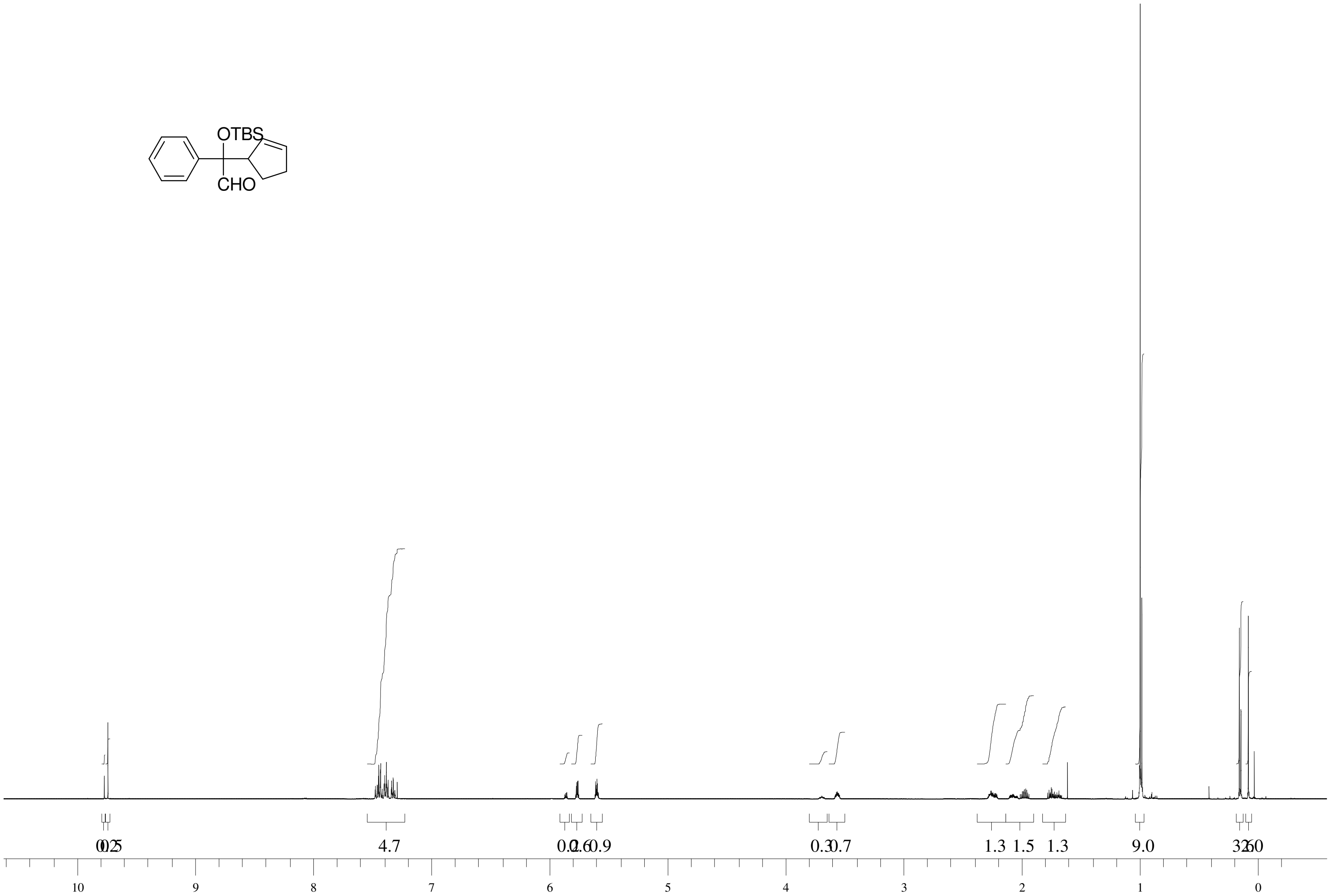
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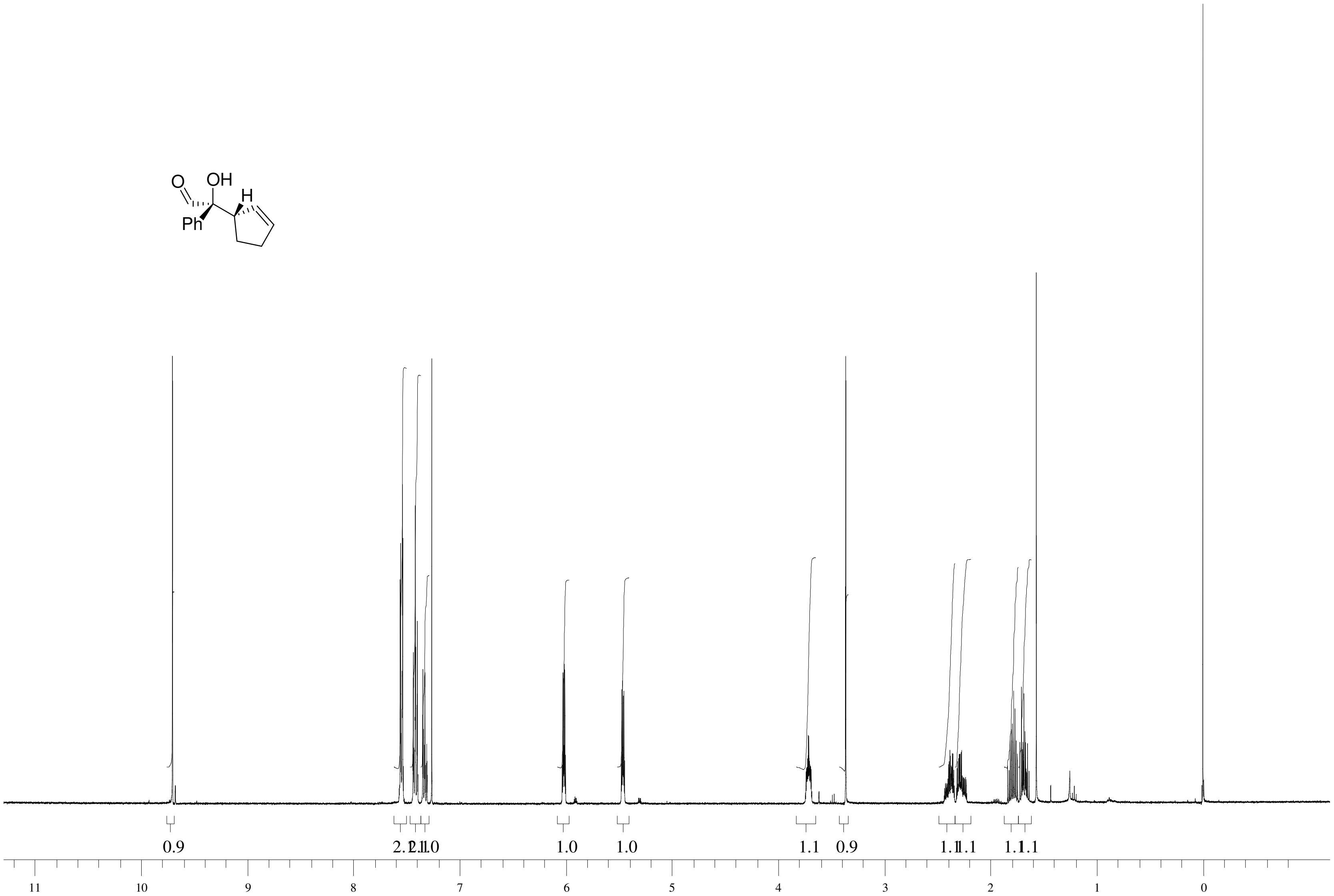
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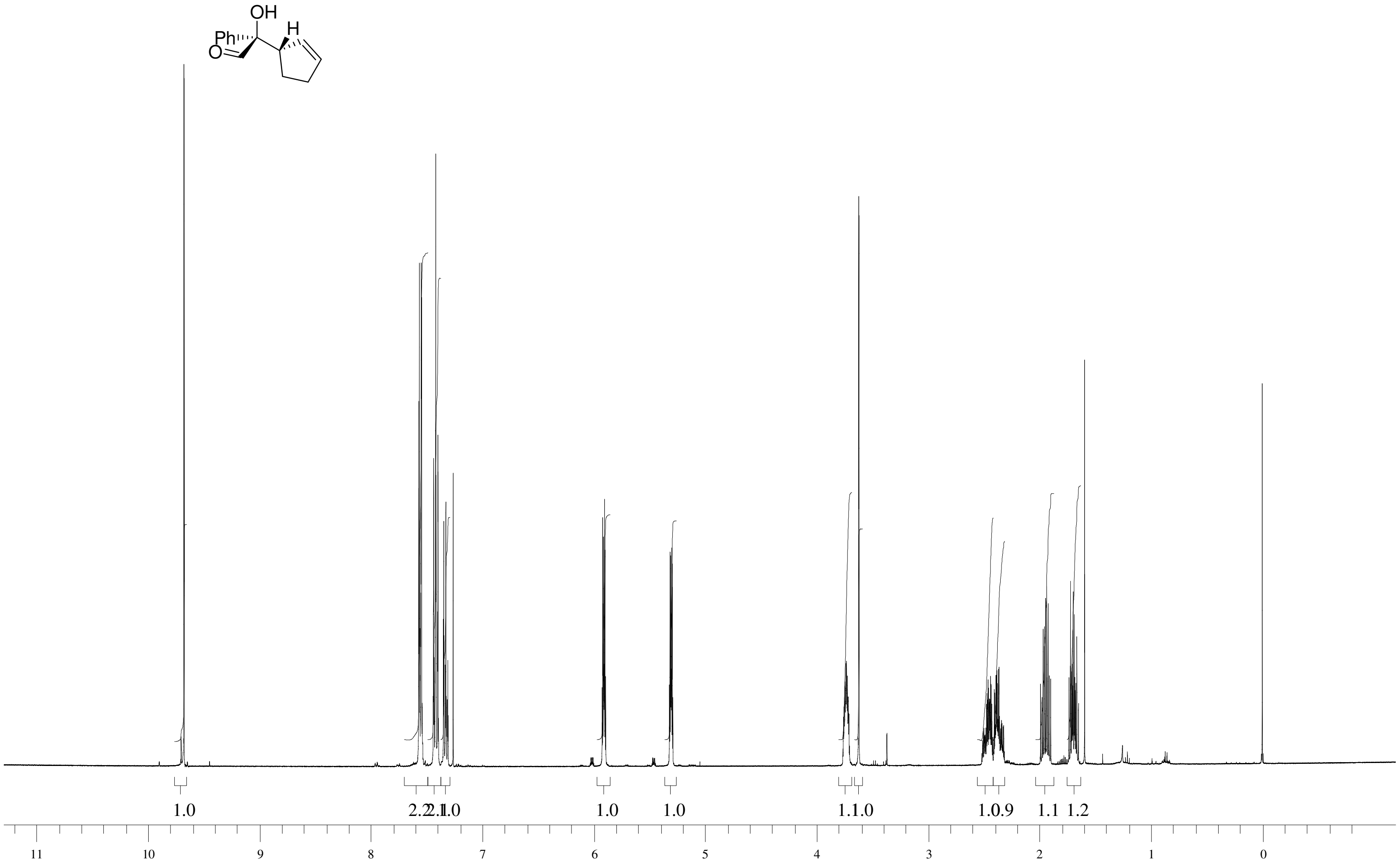
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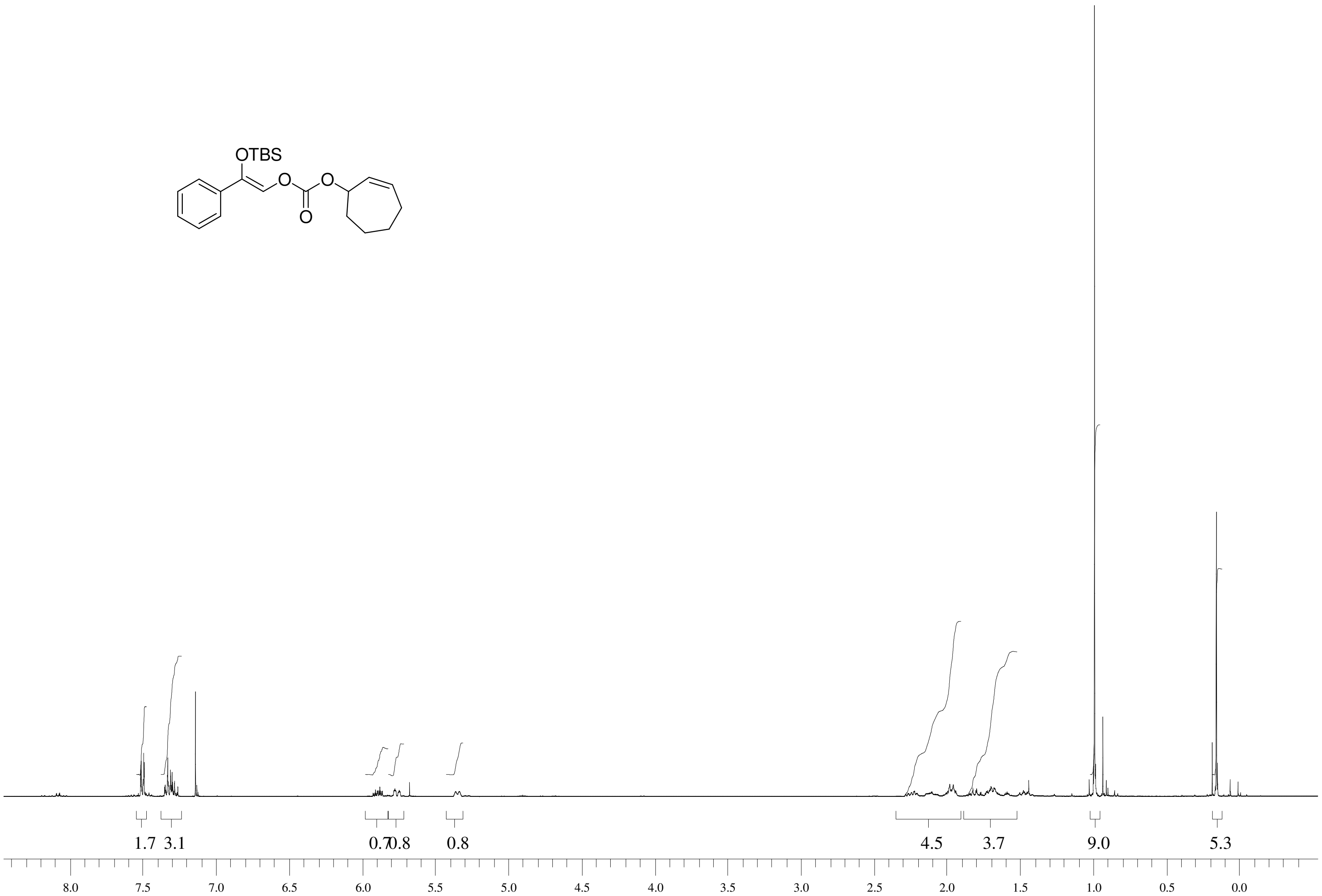
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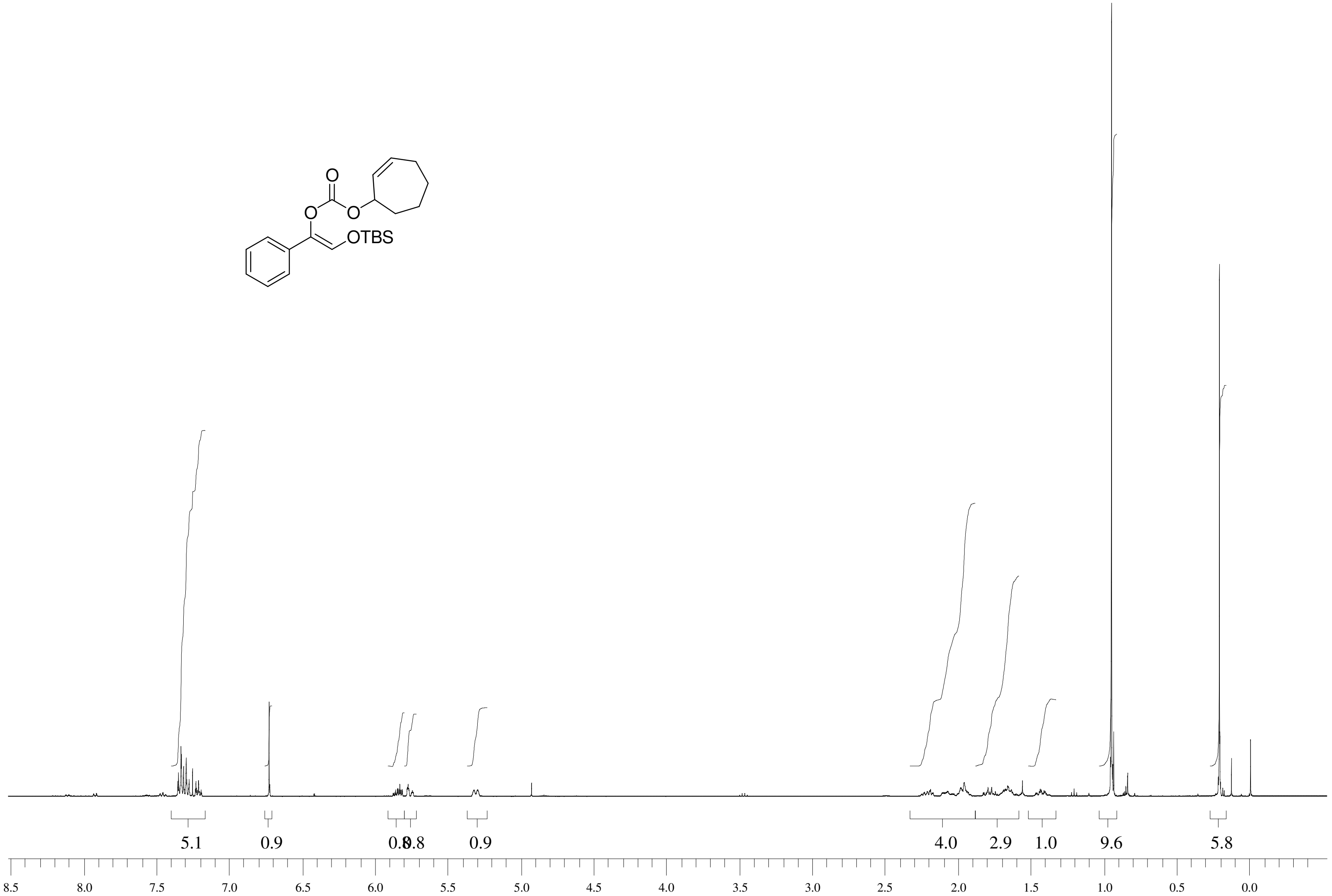
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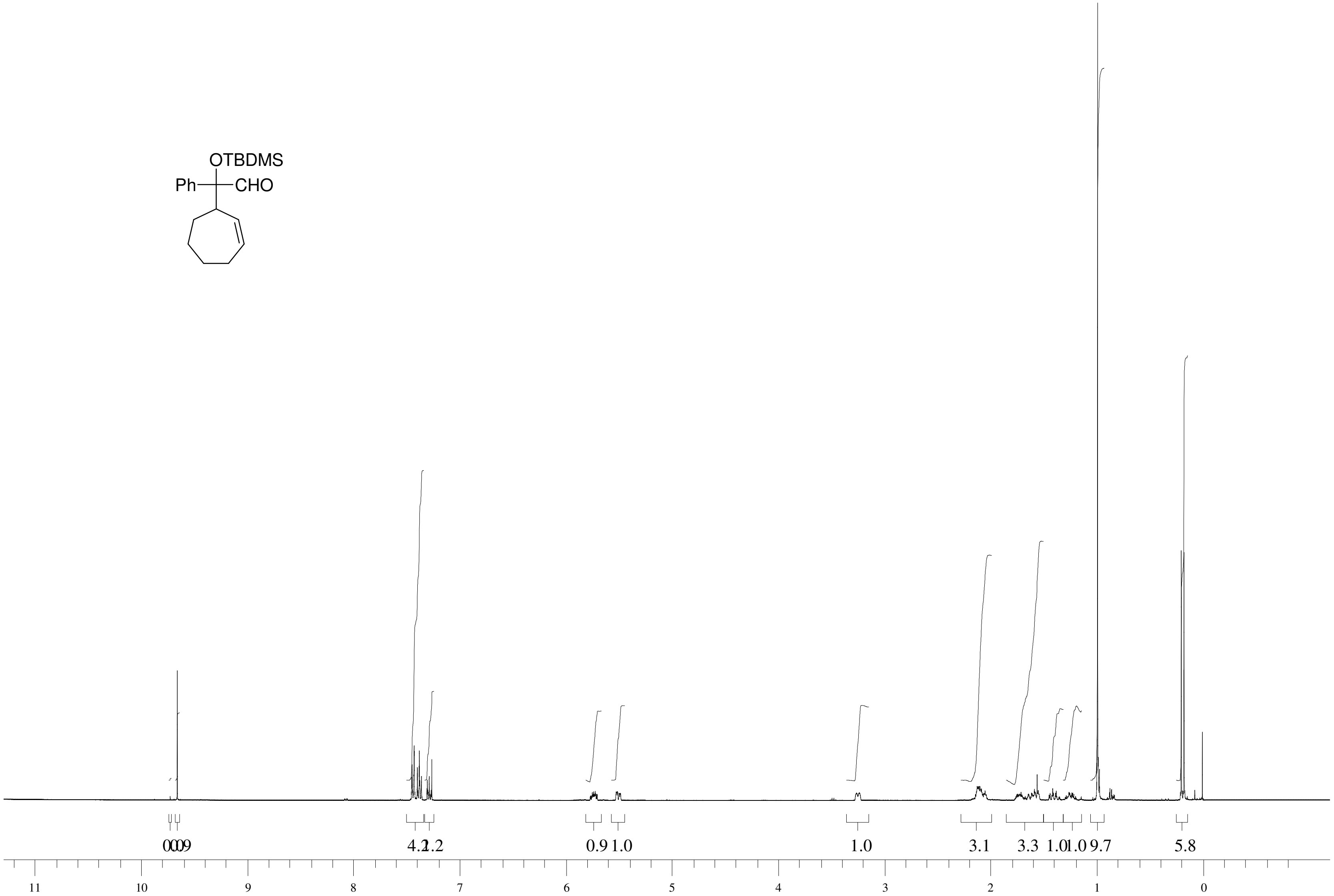
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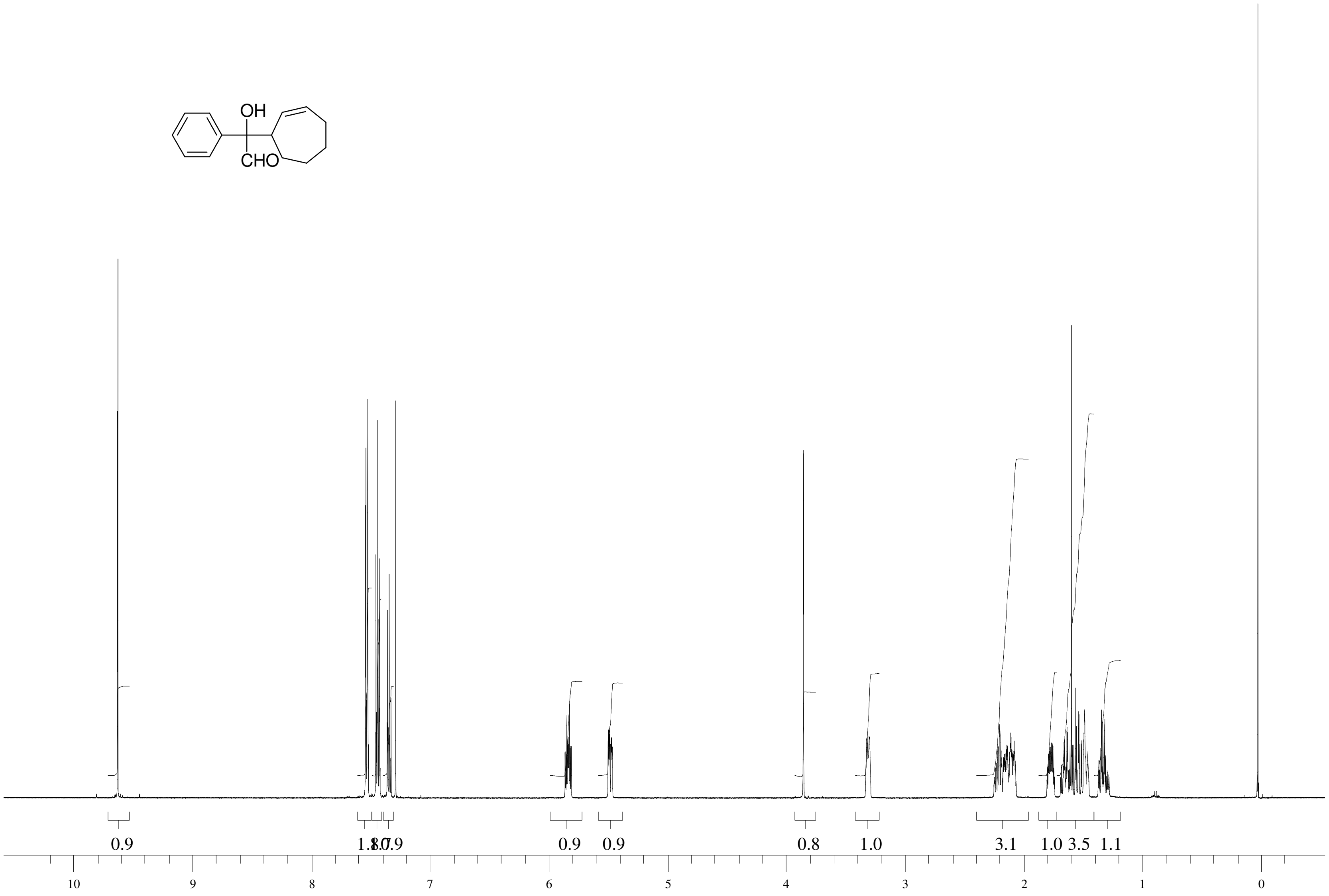
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