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Supporting Information

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Asymmetric Allylic Alkylation of Cyclic Vinylogous Esters and Thioesters Affords Highly Enantioenriched γ,γ-Disubstituted Cycloalkenones

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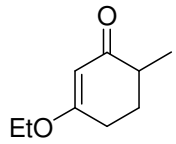
Experimental

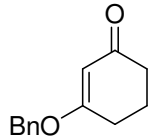
General

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. Solvents for Pd-catalyzed reactions were distilled from sodium-benzophenone and degassed by freeze-pump-thaw techniques under vaccum[1]. Solvents for other reactions were freshly purified by passage through an aluminum column before use. Tris(dibenzylideneacetone)palladium(0) monochloroform complex, Pd_2dba_3•$CHCl_3$ was prepared by the procedure of Ibers[2]. Ligands (*R,R*)-**6** were prepared by literature procedures[3,4] All other reagents were used as obtained unless otherwise noted.

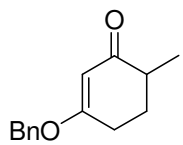
Flash Chromatography was performed with EM Science silica gel (0.040-0.063μm grade). Analytical thin-layer chromatography was performed with 0.2 mm coated commercial silica gel plates (E. Merck, DC-Plasrikfolien, kieselgel 60 F254). Melting points were obtained on a Thomas-Hoover apparatus in open capillary 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 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-H, 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.



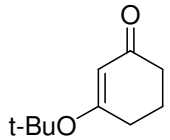
3-Ethoxy-6-methylcyclohex-2-enone *n*-BuLi (2.5 M solution in hexanes, 10.5 ml, 26.2 mmol), was added to a solution of diisopropylamine (4.00 ml, 2.89 g, 28.5 mmol) in THF (15 ml) at –78 °C and the solution allowed to warm to 0 °C over 1 hour, before cannulating into a solution of 3-ethoxy-2-cyclohexen-1-one (3.46 ml, 3.33 g, 23.8 mmol) in THF (25 ml) at –78 °C. After stirring for 1 hour, methyl iodide (1.78 ml, 4.05 g, 28.5 mmol) was added and the solution warmed to 25 °C over 1 hour. Saturated aqueous ammonium chloride (200 ml) was added and extracted with Et_2O (3 x 100 ml), the organics dried ($MgSO_4$) and the solvent removed *in vacuo* (water bath <30 °C, volatile!). Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded 3-ethoxy-6-methylcyclohex-2-enone (3.66 g, 23.8 mmol, 100%) as a colourless oil. IR (thin film) ν_{max} (cm^{-1}) 2936, 1660 (C=O), 1608, 1456, 1377, 1359, 1233, 1192, 1113, 1039, 897, 844, 815; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.29 (1H, d, *J* = 2.5 Hz), 3.86 (2H, m), 2.44 (1H, dddd, *J* = 17.5, 10.5, 5.0, 1.0 Hz), 2.37 (1H, dt, *J* = 17.5, 5.0 Hz), 2.26 (1H, m), 2.02 (1H, dq, *J* = 13.5, 5.0 Hz), 1.67 (1H, m), 1.33 (3H, t, *J* = 7.0 Hz), 1.12 (3H, d, *J* = 6.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 176.9, 102.0, 64.1, 40.0, 29.2, 28.4, 15.3, 14.1. HRMS (EI): M^+ calcd. for $C_9H_{14}O_2$ 154.0994, found 154.0987.



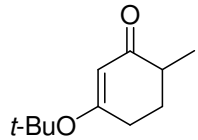
3-Benzyloxycyclohex-2-enone: Benzyl alcohol (20 ml) was added to a solution of cyclohexane-1,3-dione (3.42 g, 30.5 mmol) and *p*-TSA·H_2O (290 mg, 1.53 mmol) in benzene (60 ml) and heated at reflux for 16 hours. After cooling, saturated aqueous sodium bicarbonate (100 ml) was added and the mixture extracted with Et_2O (3 x 100 ml), the combined organics dried ($MgSO_4$). The solvent and excess benzyl alcohol were removed *in vacuo*. Purification by flash column chromatography (1:1 petroleum:Et2O) afforded 3-benzyloxycyclohex-2-enone (4.12 g, 20.4 mmol, 67% (89% on 3 mmol scale)). IR (thin film) ν_{max} (cm^{-1}) 3065, 2959, 2892, 1652 (C=O), 1605, 1499, 1455, 1426, 1401, 1350, 1331, 1244, 1227, 1184, 1136, 996, 984; ^{1}H NMR (500 MHz, d^8-toluene) δ 2.00 (2H, qn, *J* = 6.5 Hz), 2.36 (2H, t, *J* = 6.5 Hz), 2.47 (2H, t, *J* = 6.5 Hz), 4.88 (2H, s), 5.48 (1H, s), 7.35-7.39 (5H, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 21.2, 29.0, 36.7, 70.4, 103.3, 127.8, 128.5, 128.7, 134.9, 177.5, 199.7. HRMS (EI): M^+ calcd. for $C_{13}H_{14}O_2$ 202.0994, found 202.0993.



3-Benzyloxy-6-methylcyclohex-2-enone: ^{n}BuLi (8.96 ml, 2.5 M in hexanes, 22.4 mmol) was added dropwise to a solution of diisopropylamine 3.14 ml, 2.27 g, 22.4 mmol) in THF (20 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-benzyloxycyclohex-2-enone (4.12 g, 20.4 mmol) in THF (30 ml) at –78 ^{o}C. After stirring for 30 mins, methyl iodide (1.39 ml, 3.18 g, 22.4 mmol) was added and the yellow solution warmed to –20 ^{o}C. After 1 hour, the reaction was quenched by addition of 1:1 H_2O:brine (100 ml) and extracted with Et_2O (3 x 80 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded 3-benzyloxy-6-methylcyclohex-2-enone (3.88 g, 17.9 mmol, 88%) as a white crystalline solid. M. P. 43-44 ^{o}C; IR (thin film) ν_{max} (cm^{-1}) 2934, 2872, 1659 (C=O), 1608, 1499, 1456, 1364, 1235, 1186, 1115, 1035, 836, 740, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, d, *J* = 6.8 Hz), 1.67-2.59 (5H, m), 4.86 (1H, d, *J* = 13.6 HZ), 4.88 (1H, d, *J* = 13.6 Hz), 5.45 (1H, d, *J* = 0.8 Hz), 7.34-7.40 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 28.4, 29.2, 40.1, 70.4, 102.7, 127.8, 128.5, 128.6, 135.1, 176.5, 201.9.

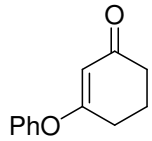


3-^{t}Butoxy-cyclohex-2-enone: A solution of *O*-^{t}Butyltrichloroacetimidate (2.46 g, 2.01 ml, 11.2 mmol) in cyclohexane (20 ml) was added *via* cannula to a solution of cyclohexane-1,3-dione (1.05 g, 9.36 mmol) in DCM (10 ml) followed by borontrifluoride diethyletherate (178 µl, 199 mg, 1.40 mmol) and stirred for 2 hours. Sodium bicarbonate (20 g) was added and the mixture stirred for 30 minutes, then filtered and condensed *in vacuo*. Petroleum (20 ml) was added and the white solid removed by filtration. Purification by flash column chromatography (2:2:1 petroleum:Et_2O:DCM) afforded 3-^{t}butoxy-cyclohex-2-enone (1.57 g, 9.33 mmol, 100%) as a colourless oil. IR (thin film) ν_{max} (cm^{-1}) 2947, 1652 (C=O), 1597, 1370, 1252, 1162, 1135; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (9H, s), 1.93 (2H, qn, *J* = 6.0 Hz), 2.30 (4H, t, *J* = 6.0 Hz), 5.49 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 28.2, 30.6, 36.4, 81.1, 106.0, 175.4, 200.0; HRMS (EI): M^+ calcd. for $C_{10}H_{16}O_2$ 168.1150, found 168.1149.

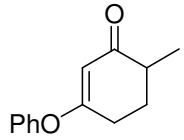


3-^{t}butoxy-6-methylcyclohex-2-enone: ^{n}BuLi (5.57 ml, 2.5 M in hexanes, 13.9 mmol) was added dropwise to a solution of diisopropylamine (1.95 ml, 1.41 g, 13.9 mmol) in THF (10 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-^{t}butoxy-cyclohex-2-enone (2.13 g, 12.7 mmol) in THF (20 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of methyl iodide (788 µl, 1.80 g, 13.9 mmol) in THF (2 ml) at –20 ^{o}C. After 1 hour, the reaction was quenched by addition of saturated aqueous ammonium chloride (50 ml). The mixture was extracted with Et_2O (3 x 50 ml), dried ($MgSO_4$) and condensed *in vacuo*.

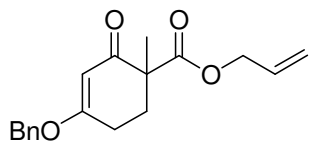
Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded 3-^{t}butoxy-6-methylcyclohex-2-enone (1.65 g, 9.05 mmol, 72 %) as an oily crystalline solid. IR (thin film) ν_{max} (cm^{-1}) 2934, 1655 (C=O), 1601, 1370, 1250, 1200, 1160; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (3H, d, *J* = 6.9 Hz), 1.45 (9H, s), 1.59-2.44 (5H, m), 5.47 (1H, d, *J* = 0.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.5, 28.2, 29.3, 30.0, 39.7, 80.9, 105.4, 174.4, 202.2.



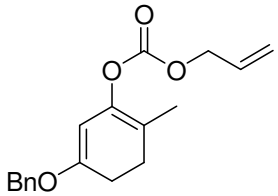
3-Phenoxycyclohex-2-enone: Phenol (1.73 g, 18.4 mmol) was added to a solution of cyclohexane-1,3-dione (1.03 g, 9.19 mmol) and *p*-TSA·H_2O (87 mg, 0.46 mmol) in benzene (40 ml) and heated at reflux for 16 hours. After cooling, saturated aqueous sodium carbonate (80 ml) was added and the mixture was extracted with Et_2O (2 x 80 ml); the combined organics was dried ($MgSO_4$) and evaporated. Purification by flash column chromatography (1:1 petroleum:Et_2O) afforded 3-phenoxycyclohex-2-enone (299 mg, 1.59 mmol, 17 %) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.07 (2H, qn, *J* = 6.4 Hz), 2.36 (2H, t, *J* = 6.4 Hz), 2.65 (2H, t, *J* = 6.4 Hz), 5.11 (1H, s), 7.02 (2H, d, *J* = 8.4 Hz), 7.23 (1H, t, *J* = 8.4 Hz), 7.38 (2H, t, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 28.5, 36.6, 106.0, 121.3, 126.1, 130.0, 152.6, 178.3, 199.6.



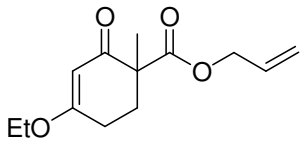
6-Methyl-3-phenoxycyclohex-2-enone: ^{n}BuLi (592 µl, 2.5 M in hexanes, 1.48 mmol) was added dropwise to a solution of diisopropylamine (207 µl, 150 mg, 1.48 mmol) in THF (2 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-phenoxycyclohex-2-enone (232 mg, 1.23 mmol) in THF (2 ml) at –78 ^{o}C. After stirring for 30 mins, methyl iodide (92.1 µl, 210 mg, 1.48 mmol) was added and the yellow solution warmed to –20 ^{o}C. After 1 hour, the reaction was quenched by addition of 1:1 H_2O:brine (15 ml) and extracted with Et_2O (2 x 20 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded 6-methyl-3-phenoxycyclohex-2-enone (187 mg, 0.925 mmol, 75%) as a white solid. M.P. 59-60 ^{o}C; IR (thin film) ν_{max} (cm^{-1}) 3050, 2988, 2960, 2924, 2868, 1651 (C=O), 1614, 1588, 1489, 1454, 1417, 1372, 1199, 1156, 1114, 1068, 1030, 926, 854, 840, 812, 772, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (3H, d, *J* = 6.8 Hz), 1.73-2.75 (5H, m), 5.08 (1H, s), 7.01 (2H, d, *J* = 7.6 Hz), 7.22 (1H, t, *J* = 7.6 Hz), 7.37 (2H, t, *J* = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2, 27.9, 29.1, 40.0, 105.3, 121.3, 126.0, 129.9, 152.8, 177.3, 201.7.



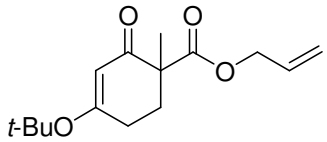
Allyl 4-benzyloxy-1-methyl-2-oxocyclohex-3-ene carboxylate: ^{n}BuLi (2.79 ml, 2.35 M in hexanes, 6.56 mmol) was added dropwise to a solution of diisopropylamine (920 µl, 664 mg, 6.56 mmol) in THF (5 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-benzyloxy-6-methylcyclohex-2-enone (1.29 g, 5.96 mmol) in THF (15 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of allyl chloroformate (696 µl, 791 mg, 6.56 mmol) in THF (2 ml) at –78 ^{o}C. After 30 minutes, the reaction was quenched by addition of saturated aqueous sodium bicarbonate (50 ml). The mixture was extracted with Et_2O (3 x 50 ml), dried (Na_2SO_4) and condensed *in vacuo*. Purification by flash column chromatography (2:1 petroleum:Et_2O) afforded allyl 4-benzyloxy-1-methyl-2-oxocyclohex-3-ene carboxylate (1.55 g, 5.16 mmol, 87%) as a colourless oil. IR (thin film) ν_{max} (cm^{-1}) 2938, 1734 (C=O), 1656 (C=O ketone), 1608 (C=C), 1499, 1456, 1426, 1366, 1318, 1250, 1183, 1113, 1030, 986, 838, 745, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, s), 1.87-2.66 (4H, m), 4.61 (2H, d, *J* = 5.2 Hz), 4.89 (2H, s), 5.21 (1H, d, *J* = 10.4 Hz), 5.29 (1H, d, *J* = 17.2 Hz), 5.51 (1H, s), 5.87 (1H, ddt, *J* = 17.2, 10.4, 5.2 Hz), 7.33-7.41 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 26.4, 31.7, 52.3, 65.6, 70.6, 102.3, 118.1, 127.8, 128.6, 128.7, 131.7, 134.8, 172.4, 176.2, 196.5. HRMS (EI): M^+ calcd. for $C_{18}H_{20}O_4$, 300.1362, found 300.1364.



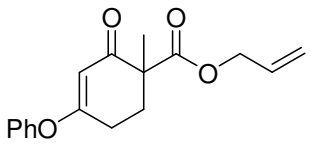
Allyl 5-benzyloxy-2-methylcyclohexa-1,5-dienyl carbonate: ^{n}BuLi (222 µl, 2.5 M in hexanes, 0.555 mmol) was added dropwise to a solution of hexamethyldisilazide (117 µl, 89.6 mg, 0.555 mmol) in THF (1 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. *N*,*N*,*N*,*N*-tetramethylethylenediamine (84.0 µl, 64.1 mg, 0.555 mmol) was added and the mixture added *via* cannula to a solution of 3-benzyloxy-6-methylcyclohex-2-enone (100 mg, 0.462 mmol) in THF (2 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to allyl chloroformate (59.0 µl, 66.9 mg, 0.555 mmol) –50 ^{o}C. After 30 minutes, the reaction was quenched by addition of saturated aqueous sodium bicarbonate (10 ml). The mixture was extracted with Et_2O (2 x 20 ml), dried (Na_2SO_4) and condensed *in vacuo*. Purification by flash column chromatography (Florosil, 5:1 petroleum:Et_2O) afforded allyl 5-benzyloxy-2-methylcyclohexa-1,5-dienyl carbonate (42.5 mg, 0.142 mmol, 31%) as a colourless oil. ^{1}H NMR (400 MHz, d_8-toluene) δ 1.73 (3H, s), 2.11 (2H, t, *J* = 9.4 Hz), 2.36 (2H, t, *J* = 9.4 Hz), 4.48 (2H, s), 4.57 (2H, dt, *J* = 5.6, 1.6 Hz), 5.09 (2H, dt, *J* = 10.4, 1.6 Hz), 5.28 (1H, dt, *J* = 17.2, 1.6 Hz), 5.84 (1H, ddt, *J* = 17.2, 10.4, 5.6 Hz), 7.17-7.23 (5H, m); ^{13}C NMR (100 MHz, d_8-toluene) δ 15.2, 27.4, 28.5, 68.5, 69.7, 111.5, 118.3, 124.9, 125.2, 125.4, 132.2, 137.0, 137.5, 141.4, 153.6, 157.8.



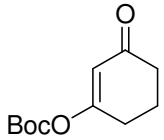
Allyl 4-ethoxy-1-methyl-2-oxocyclohex-3-enecarboxylate: ^{n}BuLi (695 µl, 2.5 M in hexanes, 1.63 mmol) was added dropwise to a solution of diisopropylamine (229 µl, 165 mg, 1.63 mmol) in THF (1 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-ethoxy-6-methylcyclohex-2-enone (229 mg, 1.48 mmol) in THF (3 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of allyl chloroformate (173 µl, 197 mg, 1.63 mmol) in THF (1 ml) at –78 ^{o}C. After 30 minutes, the reaction was quenched by addition of saturated aqueous sodium bicarbonate (10 ml). The mixture was extracted with Et_2O (3 x 15 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (20:1 → 10:1 petroleum:Et_2O) afforded allyl 4-ethoxy-1-methyl-2-oxocyclohex-3-enecarboxylate (301 mg, 1.26 mmol, 85%). IR (thin film) ν_{max} (cm^{-1}) 2984, 2940, 1732 (C=O ester), 1660 (m, C=O ketone), 1607 (C=C), 1456, 1428, 1380, 1362, 1320, 1250, 1196, 1111, 1042, 1022, 990, 929, 902, 847, 815; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35 (3H, t, *J* = 6.9 Hz), 1.41 (3H, s), 1.82-2.60 (4H, m), 3.90 (2H, q, *J* = 6.9 Hz), 4.60 (2H, d, *J* = 5.4 Hz), 5.20 (1H, d, *J* = 10.5, Hz), 5.28 (1H, d, *J* = 17.4 Hz), 5.36 (1H, s), 5.87 (1H, ddt, *J* = 17.4, 10.5, 5.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 20.5, 26.4, 31.7, 52.3, 64.4, 65.6, 101.6, 118.1, 131.8, 172.5, 176.6, 196.7. HRMS (EI): M^+ calcd. for $C_{13}H_{18}O_4$, 238.1205, found 238.1208.



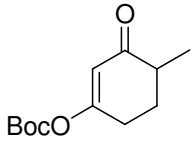
Allyl 4-^{t}butoxy-1-methyl-2-oxocyclohex-3-ene carboxylate: ^{n}BuLi (3.54 ml, 2.5 M in hexanes, 8.33 mmol) was added dropwise to a solution of diisopropylamine (1.17 ml, 843 mg, 8.33 mmol) in THF (7 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of 3-^{t}butoxy-6-methylcyclohex-2-enone (1.38 g, 7.57 mmol) in THF (11 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of allyl chloroformate (884 µl, 1.00 g, 8.33 mmol) in THF (2 ml) at –78 ^{o}C. After 30 minutes, the reaction was quenched by addition of saturated aqueous sodium bicarbonate (50 ml). The mixture was extracted with Et_2O (3 x 50 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (20:1 → 10:1 petroleum:Et_2O) afforded allyl 4-^{t}butoxy-1-methyl-2-oxocyclohex-3-ene carboxylate (1.72 g, 6.46 mmol, 85%) as a pale yellow oil. IR (thin film) ν_{max} (cm^{-1}) 2982, 2934, 1732 (C=O ester), 1652 (C=O ketone), 1601 (C=C), 1459, 1427, 1372, 1319, 1252, 1160, 1115, 990, 927, 895, 851; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.39 (3H, s), 1.45 (9H, s), 1.78-2.50 (4H, m), 4.56 (1H, dd, *J* = 13.5, 5.4 Hz), 4.63 (1H, dd, *J* = 13.5, 5.4 Hz), 5.19 (1H, d, *J* = 10.5 Hz), 5.27 (1H, d, *J* = 16.2 Hz), 5.50 (1H, s), 5.86 (1H, ddt, *J* = 16.2, 10.5, 5.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 27.9, 28.2, 31.6, 51.9, 65.5, 81.4, 105.0, 118.0, 131.8, 172.7, 174.0, 196.7. HRMS (EI): M^+ calcd. for $C_{15}H_{22}O_4$, 266.1518, found 266.1529.



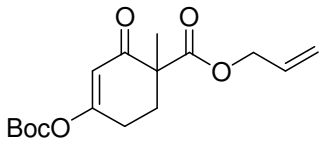
Allyl 1-methyl-2-oxo-4-phenoxycyclohex-3-ene carboxylate: ^{n}BuLi (280 µl, 2.5 M in hexanes, 0.700 mmol) was added dropwise to a solution of diisopropylamine (98.0 µl, 70.8 mg, 0.700 mmol) in THF (1 ml) at –78 °C and warmed to 0 °C over 1 hour. This was then added *via* cannula to a solution of 6-methyl-3-phenoxycyclohex-2-enone (118 mg, 0.583 mmol) in THF (1 ml) at –78 °C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of allyl chloroformate (74.0 µl, 84.4 mg, 49.3 mmol) in THF (0.2 ml) at –78 °C. After 30 minutes, the reaction was quenched by addition of saturated aqueous ammonium chloride (10 ml). The mixture was extracted with Et_2O (3 x 10 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded allyl 1-methyl-2-oxo-4-phenoxycyclohex-3-ene carboxylate (152 mg, 0.531 mmol, 91%) as a colourless oil. IR (thin film) ν_{max} (cm^{-1}) 3071, 2938, 1732 (C=O ester), 1652 (m, C=O ketone), 1616 (C=C), 1587, 1557, 1539, 1488, 1456, 1427, 1374, 1317, 1250, 1199, 1166, 1111, 988, 918, 853, 774, 694; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (3H, s), 1.92 (1H, ddd, *J* = 13.5, 8.5, 5.0 Hz), 2.60 (2H, m), 2.81 (1H, dddd, *J* = 18.0, 9.0, 5.0, 1.0 Hz), 4.60 (1H, dd, *J* = 13.5, 5.5 Hz), 4.64 (1H, dd, *J* = 13.5, 5.5 Hz), 5.14 (1H, d, *J* = 1.0 Hz), 5.22 (1H, d, *J* = 10.5 Hz), 5.29 (1H, d, *J* = 17.0 Hz), 5.88 (1H, ddt, *J* = 17.0, 10.5, 5.5 Hz), 7.01 (2H, d, *J* = 8.5 Hz), 7.24 (2H, t, *J* = 8.5 Hz), 7.38 (1H, t, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5, 26.0, 31.6, 52.3, 65.7, 105.0, 118.2, 121.3, 126.2, 130.0, 131.7, 152.6, 172.3, 176.9, 196.4. HRMS (EI): M^+ calcd. for $C_{17}H_{18}O_4$, 286.1205, found 286.1210.



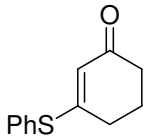
***t*-Butyl 3-oxocyclohex-1-enyl carbonate**: *N*,*N*-Dimethylaminopyridine (50 mg, 0.45 mmol) was added to a suspension of cyclohexane-1,3-dione (1.00g, 8.92 mmol) and di*t*-butyldicarbonate (2.14 g, 9.81 mmol) in hexane (15 ml) and DCM (20 ml) and stirred for 6 hours. 5% Aqueous potassium bisulfate was added and the mixture extracted with Et_2O (2 x 50 ml). The organics were dried ($MgSO_4$) and condensed *in vacuo* to afford ^{t}butyl 3-oxocyclohex-1-enyl carbonate (1.89 g, 8.92 mmol, 100%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.52 (9H, s), 2.04 (2H, qn, *J* = 6.3 Hz), 2.38 (2H, t, *J* = 6.3 Hz), 2.54 (2H, t, *J* = 6.3 Hz), 6.00 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 27.5, 28.0, 36.6, 84.7, 116.1, 149.0, 169.4, 199.6.



***t*-Butyl 4-methyl-3-oxocyclohex-1-enyl carbonate**: ^{n}BuLi (4.27 ml, 2.5 M in hexanes, 10.7 mmol) was added dropwise to a solution of diisopropylamine (1.50 ml, 1.08 g, 10.7 mmol) in THF (5 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of ^{t}butyl 3-oxocyclohex-1-enyl carbonate (1.89 g, 8.91 mmol) in THF (15 ml) at –78 ^{o}C. After stirring for 30 mins, methyl iodide (788 µl, 1.80 g, 13.9 mmol) was added and the yellow solution warmed to –20 ^{o}C. After 1 hour, the reaction was quenched by addition of 5% aqueous potassium carbonate (50 ml) and extracted with Et_2O (2 x 50 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (5:1 petroleum:Et2O) afforded ^{t}butyl 4-methyl-3-oxocyclohex-1-enyl carbonate (1.15 g, 5.08 mmol, 57%) as a colourless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.13 (3H, d, *J* = 6.8 Hz), 1.50 (9H, s), 1.66-2.69 (5H, m), 5.95 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.8, 27.5, 27.5, 29.1, 40.2, 84.5, 115.5, 149.1, 168.5, 201.7.

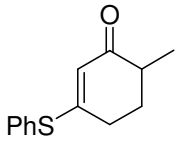


Allyl 4-^{t}butoxycarbonyloxy-1-methyl-2-oxocyclohex-3-ene carboxylate: ^{n}BuLi (2.24 ml, 2.5 M in hexanes, 5.59 mmol) was added dropwise to a solution of diisopropylamine (784 µl, 566 mg, 5.59 mmol) in THF (4 ml) at –78 ^{o}C and warmed to 0 ^{o}C over 1 hour. This was then added *via* cannula to a solution of ^{t}butyl 4-methyl-3-oxocyclohex-1-enyl carbonate (1.15 g, 5.08 mmol) in THF (8 ml) at –78 ^{o}C. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of allyl chloroformate (593 µl, 674 mg, 5.59 mmol) in THF (2 ml) at –78 ^{o}C. After 30 minutes, the reaction was quenched by addition of 2% aqueous potassium bisulfate (50 ml). The mixture was extracted with Et_2O (3 x 50 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (10:1 → 3:1 petroleum:Et2O) afforded allyl 4-^{t}butoxycarbonyloxy-1-methyl-2-oxocyclohex-3-ene carboxylate **2.65** (505 mg, 1.63 mmol, 32%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (3H, s), 1.51 (9H, s), 1.89-2.74 (4H, m), 4.60 (2H, d, *J* = 5.6 Hz), 5.20 (1H, d, *J* = 10.4 Hz), 5.27 (1H, d, *J* = 17.2 Hz), 5.85 (1H, ddt, *J* = 17.2, 10.4, 5.6 Hz), 6.07 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.2, 25.6, 27.5, 31.6, 52.4, 65.8, 84.8, 115.0, 118.4, 131.5, 148.8, 168.1, 171.8, 196.5. LRMS (+ESI) MNa^{+} 333.1.

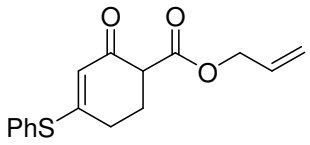


3-Phenylsulfanyl-cyclohex-2-enone: Methanesulfonyl chloride (732 µl, 1.08 g, 9.45 mmol) was added to a solution of cyclohexane-1,3-dione (1.00 g, 8.92 mmol) and triethylamine (1.39 ml, 1.01 g, 9.99 mmol) in acetonitrile (10 ml) at 0 ^{o}C and warmed to 25 ^{o}C over 1 hour. After cooling to 0 ^{o}C, triethylamine (1.39 ml, 1.01 g, 9.99 mmol) and benzenethiol (943 µl, 1.01 mg, 9.19 mmol) were added sequentially and the mixture warmed to 25 ^{o}C over 14 hours. The reaction was quenched with saturated aqueous sodium carbonate (30 ml) and the mixture extracted with Et_2O (3 x 50 ml), the combined

organics dried ($MgSO_4$) and evaporated. Purification by flash column chromatography (2:1 petroleum:Et2O) afforded 3-phenylsulfanyl-cyclohex-2-enone (1.54 g, 7.54 mmol, 85%) as a pale yellow solid. M.P. 44-46 ^oC; IR (thin film) ν_{max} (cm^{-1}) 3058, 2989, 1654, 1577, 1476, 1441, 1427, 1341, 1324, 1293, 1241, 1186, 1136, 1059, 1024, 997, 960, 878, 838, 815, 752, 706, 692; ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (2H, qn, *J* = 6.3 Hz), 2.38 (2H, t, *J* = 6.3 Hz), 2.53 (2H, t, *J* = 6.3 Hz), 5.48 (1H, s), 7.41-7.49 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 30.2, 37.2, 120.8, 127.9, 129.8, 130.1, 135.5, 166.8, 196.1.

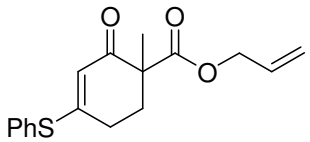


6-Methyl-3-phenylsulfanyl-cyclohex-2-enone: ^{n}BuLi (21.4 ml, 2.5 M in hexanes, 53.4 mmol) was added dropwise to a solution of diisopropylamine (7.49 ml, 5.40 g, 53.4 mmol) in THF (40 ml) at –78 ^oC and warmed to 0 ^oC over 1 hour. This was then added *via* cannula to a solution of 3-phenylsulfanyl-cyclohex-2-enone (10.6 g, 48.6 mmol) in THF (40 ml) at –78 ^oC. After stirring for 30 mins, the yellow solution was added *via* cannula to a solution of methyl iodide (3.32 ml, 7.58 g, 53.4 mmol) at –78 ^oC. After 1 hour, the reaction was quenched by addition of saturated aqueous ammonium chloride (100 ml). The mixture was extracted with Et_2O (3 x 100 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (5:1 → 4:1 petroleum:Et2O) afforded 6-methyl-3-phenylsulfanyl-cyclohex-2-enone (9.78 g, 44.8 mmol, 86%) as a pale yellow solid. M.P. 77-81 ^oC; IR (solid film) ν_{max} (cm^{-1}) 3061, 2931, 1736, 1646 (C=O), 1579 (C=C), 1441, 1208, 1114, 857, 787, 749, 691; ^1H NMR (300 MHz, $CDCl_3$) δ 1.13 (3H, d, *J* = 6.9 Hz), 1.71-2.66 (5H, m), 5.45 (1H, d, *J* = 1.2 Hz), 7.40-7.49 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.1, 29.6, 30.9, 40.7, 120.4, 128.1, 129.8, 130.0, 135.4, 165.5, 198.6.

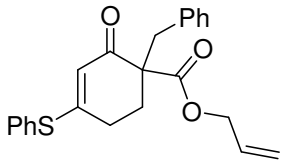


Allyl 2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate (12): To a clean dry 100 ml flask with a magnetic stirring bar was loaded 0.72 ml (5.07 mmol) diisopropylamine and 20 ml toluene under argon. The solution was cooled to -78 ^oC and was added 2.03 ml 2.5 M *n*-BuLi (5.07 mmol). The flask was taken out the dry-ice-acetone bath and put into a ice-water bath stirring for 10 min and then was cooled to -78 ^oC before the addition of 517 mg 3-(phenylthio)cyclohex-2-enone **8** (2.53 mmol) in 5 ml toluene. The enolate solution was stirred for 30 min and 0.27 ml (2.53 mmol) allyl chloroformate was added dropwise. The reaction mixture was warmed to ambient temperature and stirred for 20 min. 10 ml 1N $KHSO_4$ aqueous solution was added to quench the reaction and the organic layer was separated. The aqueous layer was extracted with 30 ml Et_2O and the organic layer was combined washed with brine and dried over anhydride magnesium sulfate; filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatograph eluted with 10-30% EtOAc in petroleum ether to afford 548 mg product

as colorless oil (75%). R_f = 0.52 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2940 (m), 1738 (s), 1660 (s), 1574 (s), 1475 (m), 1441 (s), 1307 (s), 1210 (s), 1149 (s), 1044 (s), 934 (m), 866 (m), 751 (s), 692 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.5-7.4 (m, 5H), 5.90 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.51 (t, J = 1.5 Hz, 1H), 5.33 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.24 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.65 (m, 2H), 3.40 (dd, J_1 = 9.3 Hz, J_2 = 5.0 Hz, 1H), 2.69 (m, 1H), 2.56 (m, 1H), 2.43 (m, 1H), 2.27 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.1, 169.8, 167.4, 135.6, 131.8, 130.4, 130.0, 127.6, 120.0, 118.5, 65.8, 52.8, 28.5, 26.0. HRMS (EI): M^+ calcd. for $C_{16}H_{16}O_3S$, 288.0820; found 288.0817.

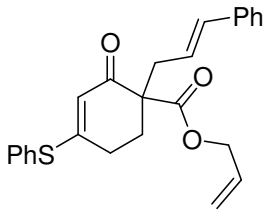


Allyl 1-methyl-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate: To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.2 mmol) was transferred in one portion to this flask. After 10 min stirring, 75 µl methyl iodide was added in to the reaction mixture. The flask was warmed to room temperature and stirred for another 2 h, followed by TLC. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20% diethyl ether in petroleum to yield 240 mg (79%) colorless oil. R_f = 0.70 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2981 (m), 2936 (m), 1732 (s), 1660 (s), 1580 (s), 1475 (m), 1441 (s), 1304 (s), 1251 (s), 1213 (s), 1171 (s), 1113 (s), 984 (m), 864 (m), 752 (s), 692 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.5-7.4 (m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.51 (d, J = 1.5 Hz, 1H), 5.28 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.22 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.68 (m, 2H), 2.67 (m, 1H), 2.53 (m, 2H), 1.96 (m, 1H), 1.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 172.4, 165.9, 135.6, 131.8, 130.3, 130.0, 127.8, 119.8, 118.2, 65.7, 52.8, 33.6, 27.6, 20.5. HRMS (EI): M^+ calcd. for $C_{17}H_{18}O_3S$, 302.0977; found 302.0980.



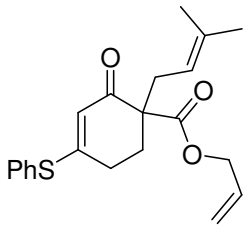
Allyl 1-benzyl-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml THF. The

flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.2 mmol) was transferred in one portion to this flask. After 10 min stirring, 142 µl benzyl bromide was added in to the reaction mixture. The flask was warmed to room temperature and stirred for another 2 h, followed by TLC. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to yield 372 mg (98%) colorless oil. R_f = 0.31 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3063 (w), 2934 (m), 1730 (s), 1661 (s), 1579 (s), 1475 (m), 1441 (m), 1292 (m), 1210 (s), 1176 (s), 1068 (m), 911 (s), 733 (s), 704 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (m, 5H), 7.3-7.1 (m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.52 (d, J = 1.8 Hz, 1H), 5.28 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.61 (m, 2H), 3.27 (m, 2H), 2.72 (m, 1H), 2.38 (m, 2H), 1.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2, 170.7, 166.4, 136.4, 135.5, 131.6, 130.6, 130.3, 129.9, 128.2, 127.7, 126.8, 120.3, 118.5, 65.9, 57.5, 39.8, 29.9, 27.7. HRMS (EI): M^+ calcd. for $C_{23}H_{22}O_3S$, 378.1290; found 378.1289.

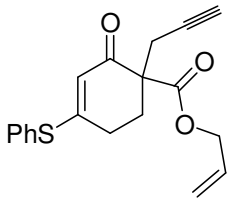


Allyl 1-cinnamyl-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.2 mmol) was transferred in one portion to this flask. After 10 min stirring, 236 mg cinnamyl bromide was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum ether to yield 380 mg (94%) colorless oil. R_f = 0.26 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (m), 3026 (m), 2974 (m), 2934 (m), 2869 (m), 1732 (s), 1652 (s), 1581 (s), 1476 (m), 1442 (s), 1289 (s), 1210 (s), 1185 (s), 1070 (m), 971 (s), 749 (s), 692 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 7.3-7.1 (m, 5H), 6.45 (d, J = 15.7 Hz, 1H), 6.12 (dt, J_1 = 15.7 Hz, J_2 = 7.5 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.6 Hz, 1H), 5.52 (d, J = 1.5 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.22 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.62 (m, 2H), 2.76 (m, 3H), 2.49 (m, 2H), 2.10 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.9, 171.0, 166.5, 137.1, 135.6, 134.1, 131.7, 130.4, 130.0, 128.6, 127.8,

127.4, 126.3, 125.0, 120.1, 118.5, 65.9, 56.6, 37.8, 30.3, 27.6. HRMS (EI): M^+ calcd. for $C_{25}H_{24}O_3S$, 404.1446; found 404.1440.

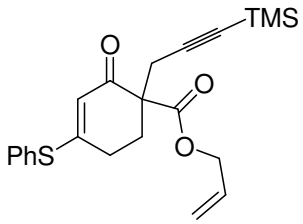


Allyl 1-(3-methylbut-2-enyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 306 mg (1.06 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 72 mg 60% NaH suspension in mineral oil (1.8 mmol) was transferred in one portion to this flask. After 10 min stirring, 233 µl 3,3-dimethylallyl bromide (90%, 1.8 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10-20% diethyl ether in petroleum ether to yield 340 mg (90%) colorless oil. R_f = 0.26 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2969 (m), 2929 (m), 1732 (s), 1661 (s), 1580 (s), 1475 (m), 1441 (s), 1280(m), 1230 (s), 1175 (s), 1066 (m), 916 (m), 750 (m), 733 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.42 (m, 5H), 5.84 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.48 (d, J = 1.5 Hz, 1H), 5.25 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.19 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 5.0 (m, 1H), 4.57 (m, 2H), 2.80-2.60 (m, 2H), 2.55-2.35 (m, 3H), 2.00 (m, 1H), 1.65 (d, J = 1.0 Hz, 3H), 1.59 (d, J = 0.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.0, 171.0, 166.1, 135.5, 135.3, 131.7, 130.2, 129.8, 127.8, 120.2, 118.6, 118.1, 65.6, 56.6, 32.7, 29.9, 27.6, 26.0, 18.0. HRMS (EI): M^+ calcd. for $C_{21}H_{24}O_3S$, 356.1446; found 356.1431.

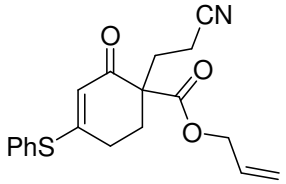


Allyl 2-oxo-4-(phenylthio)-1-(prop-2-ynyl)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.2 mmol) was transferred in one portion to this flask. After 10 min stirring, 130 µl propargyl bromide (80%, 1.2 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10-20% diethyl ether in petroleum ether

to yield 330 mg (100%) colorless oil. R_f = 0.25 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3301 (m), 3061 (w), 2938 (w), 1732 (s), 1660 (s), 1579 (s), 1475 (m), 1442 (m), 1291(m), 1212 (s), 1183 (s), 1068 (m), 914 (m), 733 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.86 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.53 (d, J = 1.2 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.63 (m, 2H), 2.88 (dd, J_1 = 16.9 Hz, J_2 = 2.7 Hz, 1H), 2.89-2.78 (m, 1H), 2.72 (dd, J_1 = 16.9 Hz, J_2 = 2.7 Hz, 1H), 2.65-2.50 (m, 2H), 2.33 (m, 1H), 2.02 (t, J = 2.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.4, 170.0, 167.3, 135.6, 131.5, 130.4, 130.0, 127.7, 119.7, 118.5, 79.6, 71.5, 66.1, 55.5, 30.2, 27.6, 24.3. HRMS (EI): M^+ calcd. for $C_{19}H_{18}O_3S$, 326.0977; found: 325.0896 $(M-H)^+$.

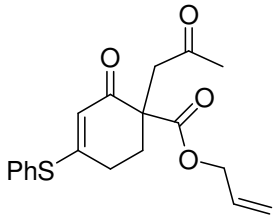


Allyl 2-oxo-4-(phenylthio)-1-(3-(trimethylsilyl)prop-2-ynyl)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 240 mg (0.83 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 40 mg 60% NaH suspension in mineral oil (1 mmol) was transferred in one portion to this flask. After 10 min stirring, 142 µl 3-(Trimethylsilyl)propargyl bromide (80%, 1 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10-20% diethyl ether in petroleum ether to yield 214 mg (65%) colorless oil. R_f = 0.52 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3062 (w), 2959 (s), 2179 (s), 1732 (s), 1668 (s), 1581 (s), 1476 (m), 1442 (s), 1320 (s), 1250 (s), 1181 (s), 1068 (s), 1033 (s), 844 (s), 753 (s), 682 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.86 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.50 (d, J = 1.2 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.63 (m, 2H), 2.97 (d, J = 17.0 Hz, 1H), 2.82 (m, 1H), 2.66 (d, J = 17.0 Hz, 1H), 2.60 (m, 2H), 2.25 (m, 1H), 0.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.5, 169.9, 167.2, 135.6, 131.6, 130.7, 130.0, 127.7, 119.6, 118.3, 102.0, 88.2, 66.0, 55.7, 30.2, 27.6, 25.7, 0.1. HRMS (EI): M^+ calcd. for $C_{22}H_{26}O_3SSi$, 398.1372; found: 398.1389.

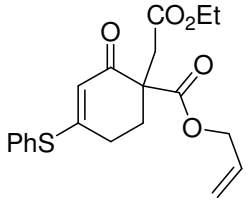


Allyl 1-(2-cyanoethyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml KOH saturated *tert*-butanol. After 10 min stirring, 79 µl acrylonitrile (1.2 mmol) was

added in to the reaction mixture and stirred for 2 h. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 30-50% diethyl ether in petroleum ether to yield 308 mg (90%) colorless oil. R_f = 0.27 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2938 (w), 2249 (w), 1732 (s), 1660 (s), 1580 (s), 1476 (m), 1442 (s), 1345 (m), 1298 (s), 1193 (s), 1075 (s), 983 (m), 752 (s), 692 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.50 (d, J = 0.9 Hz, 1H), 5.28 (m, 2H), 4.64 (m, 2H), 2.70 (m, 1H), 2.52 (m, 4H), 2.20 (m, 2H), 2.06 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 170.5, 166.8, 135.5, 131.3, 130.5, 130.1, 127.4, 119.8, 119.5, 119.1, 66.2, 55.3, 31.1, 29.8, 27.3, 13.3. HRMS (EI): M^+ calcd. for $C_{19}H_{19}NO_3S$, 341.1086; found: 341.1082.

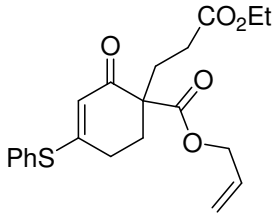


Allyl 2-oxo-1-(2-oxopropyl)-4-(phenylthio)cyclohex-3-enecarboxylate: To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12**, 652 mg Cs_2CO_3 (2 mmol), 320 µl chloroacetone (2.4 mmol), 64 mg tetrabutylammonium iodide (0.2 mmol) and 5 ml DMF and stirred 2 days. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water three times and 25 ml brine once. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20-50% diethyl ether in petroleum to yield 213 mg (62%) colorless oil. R_f = 0.29 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3061 (w), 2950 (m), 1732 (s), 1660 (s), 1580 (s), 1476 (m), 1442 (m), 1362 (m), 1293 (m), 1210 (s), 1171 (s), 1068 (m), 917 (m), 732 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45(m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.53 (d, J = 1.7 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.62 (m, 2H), 3.04 (d, J = 17.7 Hz, 1H), 2.94 (d, J = 17.7 Hz, 1H), 2.80 (m, 1H), 2.44 (m, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 205.3, 191.3, 170.8, 166.5, 135.5, 131.6, 130.3, 129.9, 127.7, 119.8, 118.4, 66.0, 54.9, 46.7, 30.61, 30.56, 27.7. HRMS (EI): M^+ calcd. for $C_{19}H_{20}O_4S$, 344.1082; found: 344.1081.

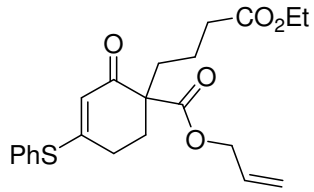


Allyl 1-(2-ethoxy-2-oxoethyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 204 mg (0.71 mmol) **12** and

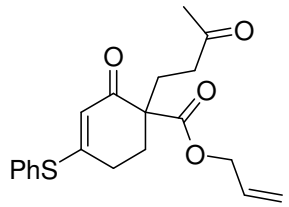
5 ml THF. The flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.7 mmol) was transferred in one portion to this flask. After 10 min stirring, 133 µl ethyl bromoacetate (1.7 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 30% diethyl ether in petroleum ether to yield 300 mg (100%) colorless oil. R_f = 0.52 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3061 (w), 2981 (m), 1732 (s), 1662 (s), 1580 (s), 1475 (m), 1442 (m), 1373 (m), 1345 (m), 1180 (s), 1067 (m), 1026 (m), 916 (m), 753 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45(m, 5H), 5.88 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.54 (d, J = 1.7 Hz, 1H), 5.30 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.24 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.64 (m, 2H), 4.12 (qd, J_1 = 7.2 Hz, J_2 = 0.9 Hz, 2H), 2.89 (d, J = 16.6 Hz, 1H), 2.83 (d, J = 16.6 Hz, 1H), 2.80 (m, 1H), 2.50 (m, 2H), 2.39 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 170.7, 170.5, 166.5, 135.5, 131.6, 130.3, 129.9, 127.7, 119.9, 118.4, 66.1, 60.7, 54.6, 38.7, 30.9, 27.7, 14.1. HRMS (EI): M^+ calcd. for $C_{20}H_{22}O_5S$, 374.1188; found 374.1190.



Allyl 1-(3-ethoxy-3-oxopropyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 276 mg (0.96 mmol) **12** and 10 ml THF. The flask was cooled in an ice-water bath for 5 min and 65 mg 60% NaH suspension in mineral oil (1.62 mmol) was transferred in one portion to this flask. After 10 min stirring, 208 µl ethyl 3-bromopropionate (1.62 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20-30% diethyl ether in petroleum to yield 365 mg (98%) colorless oil. R_f = 0.48 (30% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3061 (w), 2982 (m), 2938 (m), 1732 (s), 1661 (s), 1580 (s), 1476 (m), 1442 (s), 1378 (m), 1341 (m), 1288 (s), 1184 (s), 1079 (s), 1025 (m), 986 (m), 752 (m), 692 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.45(m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.49 (d, J = 0.7 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.23 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.61 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.66 (m, 1H), 2.52 (m, 2H), 2.38 (m, 2H), 2.24 (m, 1H), 2.15 (m, 1H), 2.05 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 192.0, 173.0, 171.0, 166.0, 135.5, 131.6, 130.3, 129.9, 127.7, 120.0, 118.5, 65.8, 60.5, 55.7, 30.7, 29.8, 28.6, 27.4, 14.2. HRMS (EI): M^+ calcd. for $C_{21}H_{24}O_5S$, 388.1344; found 388.1335.

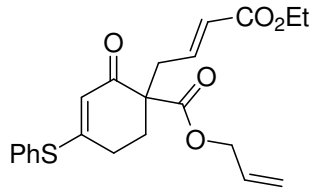


Allyl 1-(4-ethoxy-4-oxobutyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12**, 652 mg Cs_2CO_3 (2 mmol), 172 µl ethyl 4-bromobutanoate (1.2 mmol), 37 mg tetrabutylammonium iodide (0.1 mmol) and 5 ml DMF and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water three times and 25 ml brine once. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20-30% diethyl ether in petroleum ether to yield 246 mg (61%) colorless oil. R_f = 0.35 (30% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3061 (w), 2939 (m), 1732 (s), 1660 (s), 1580 (s), 1476 (m), 1442 (s), 1342 (m), 1291 (s), 1176 (s), 1096 (s), 1024 (m), 922 (m), 752 (m), 692 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45(m, 5H), 5.85 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.49 (d, J = 0.7 Hz, 1H), 5.28 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.22 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.62 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.72 (m, 1H), 2.52 (m, 2H), 2.35 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 2.06 (m, 1H), 1.94 (m, 1H), 1.78 (m, 1H), 1.61 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 173.2, 171.1, 166.2, 135.6, 131.2, 130.3, 130.0, 127.8, 120.0, 118.4, 65.8, 60.4, 56.4, 34.4, 33.1, 29.9, 27.5, 20.1, 14.3. HRMS (EI): M^+ calcd. for $C_{22}H_{26}O_5S$, 402.1501; found: 402.1509.



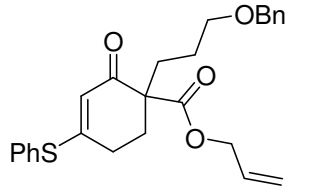
Allyl 2-oxo-1-(3-oxobutyl)-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml KOH saturated *tert*-butanol. After 10 min stirring, 98 µl methyl vinyl ketone (1.2 mmol) was added in to the reaction mixture and stirred for 2 h. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20-30% diethyl ether in petroleum to yield 240 mg (67%) colorless oil. R_f = 0.21 (30% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2936 (s), 1732 (s), 1660 (s), 1581 (s), 1475 (s), 1441 (s), 1357 (s), 1287 (s), 1172 (s), 1085 (s), 1000 (s), 934 (s), 866 (m), 753 (s), 692 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.48 (s, 1H), 5.26 (m, 2H), 4.62 (m, 2H), 2.70-2.45 (m, 5H), 2.20-2.05 (m, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 207.9, 192.4, 171.4, 166.1, 135.6, 131.6, 130.4, 130.0, 127.7, 120.0,

118.6, 65.8, 55.6, 39.0, 31.3, 30.0, 27.3, 27.2. HRMS (EI): M^+ calcd. for $C_{20}H_{22}O_4S$, 358.1239; found: 358.1247.



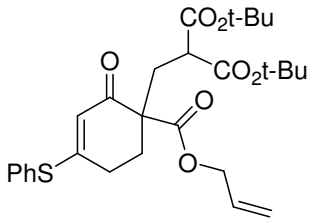
(*E*)-Allyl 1-(4-ethoxy-4-oxobut-2-enyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate

To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml THF. The flask was cooled in an ice-water bath for 5 min and 48 mg 60% NaH suspension in mineral oil (1.2 mmol) was transferred in one portion to this flask. After 10 min stirring, 216 µl *E*- ethyl bromocrotonate (1.2 mmol) was added in to the reaction mixture. The flask was warmed to room temperature and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10% diethyl ether in petroleum to yield 373 mg (93%) colorless oil. R_f = 0.39 (30% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2980 (m), 2937 (m), 1732 (s), 1660 (s), 1581 (s), 1476 (m), 1442 (m), 1368 (m), 1269 (s), 1177 (s), 1097 (m), 1042 (m), 986 (m), 752 (m), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 6.83 (dt, J_1 = 15.6 Hz, J_2 = 7.6 Hz, 1H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.6 Hz, 1H), 5.51 (d, J = 1.1 Hz, 1H), 5.29 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.24 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.62 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.76 (m, 3H), 2.47 (m, 3H), 2.02 (m, 1H), 1.27 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0, 170.5, 166.8, 165.9, 143.3, 135.5, 131.4, 130.4, 130.0, 127.6, 125.3, 119.8, 118.7, 66.1, 60.4, 55.9, 36.7, 30.3, 27.4, 14.3. HRMS (EI): M^+ calcd. for $C_{22}H_{24}O_5S$, 400.1344; found: 400.1349.



Allyl 1-(3-(benzyloxy)propyl)-2-oxo-4-(phenylthio)cyclohex-3-enecarboxylate To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12**, 652 mg Cs_2CO_3 (2 mmol), 275 mg 1-((3-bromopropoxy)methyl)benzene[5] (1.2 mmol), 37 mg tetrabutylammonium iodide (0.1 mmol) and 5 ml DMF and stirred overnight. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water three times and 25 ml brine once. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 20-30% diethyl ether in petroleum to yield 172 mg (39%) colorless oil. R_f = 0.48 (30% ethyl acetate in petroleum); IR (film): $\tilde{\nu}_{max}$ = 3063 (w), 2937 (m), 2859 (m), 1732 (s), 1660 (s), 1580 (s),

1476 (m), 1442 (m), 1361 (m), 1292 (m), 1191 (s), 1102 (s), 1025 (m), 913 (m), 734 (s), 693 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.6-7.2 (m, 10H), 5.86 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.49 (d, J = 0.7 Hz, 1H), 5.25 (m, 2H), 4.60 (m, 2H), 4.48 (s, 2H), 3.47 (m, 2H), 2.70 (m, 1H), 2.50 (m, 2H), 2.02 (m, 2H), 1.86 (m, 1H), 1.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.4, 171.3, 166.0, 138.5, 135.5, 131.7, 130.3, 130.0, 129.9, 128.4, 127.8, 127.6, 120.1, 118.3, 72.8, 70.3, 65.7, 56.3, 30.5, 30.1, 27.5, 24.9. HRMS (EI): M^+ calcd. for $C_{26}H_{28}O_4S$, 436.1708; found 436.1705.

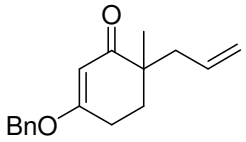


2-(1-Allyloxycarbonyl-2-oxo-4-phenylsulfanyl-cyclohex-3-enylmethyl)-malonic acid di-*tert*-butyl ester To a clean dry 25 ml flask with a magnetic stirring bar was loaded 288.4 mg (1.0 mmol) **12** and 5 ml KOH saturated *tert*-butanol. After 10 min stirring, 474 mg *tert*-butyl acrylate (2 mmol) was added in to the reaction mixture and stirred for 1 h. The reaction mixture diluted with 25 ml diethyl ether was transferred into a 100 ml separation funnel; washed with 10 ml water and 25 ml brine. The organic layer was dried over anhydrous magnesium sulfate, filtrated and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography eluted with 10-20% diethyl ether in petroleum ether to yield 485 mg (94%) sticky colorless oil. R_f = 0.67 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3061 (w), 2979 (s), 2935 (s), 1733 (s), 1662 (s), 1581 (s), 1476 (s), 1442 (s), 1369 (s), 1252 (s), 1167 (s), 1088 (s), 846 (m), 751 (s), 692 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.87 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.5 Hz, 1H), 5.48 (s, 1H), 5.27 (dq, J_1 = 17.2 Hz, J_2 = 1.5 Hz, 1H), 5.21 (dq, J_1 = 10.4 Hz, J_2 = 1.2 Hz, 1H), 4.60 (m, 2H), 3.35 (t, J = 5.8 Hz, 1H), 2.60 (m, 4H), 2.31 (dd, J_1 = 14.8 Hz, J_2 = 5.5 Hz, 1H), 1.96(m, 1H), 1.45 (s, 9H), 1.43 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.8, 170.9, 168.9, 168.5, 165.8, 135.5, 131.7, 130.3, 129.9, 127.8, 120.1, 118.3, 81.7, 81.6, 65.9, 55.8, 50.3, 31.6, 30.6, 27.9, 27.4, 15.3. HRMS (EI): M^+ calcd. for $C_{28}H_{36}O_7S$, 516.2182; found 516.2162.

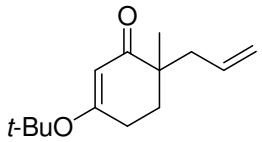
Gereral Procedure for the Pd-catalyzed Reaction of Carbonates.

Two test tubes were connected with a double-end needle. One test tube was loaded with 5.2 mg $Pd_2(dba)_3CHCl_3$ and 9.2 mg ligand and the other one was loaded with 0.20 mmol substrate. The system was evacuated and flushed with argon three times at which point 1.0 ml dry 1,4-dioxane 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 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, 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.

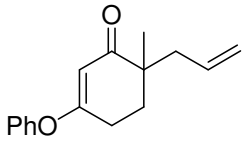
The racemic compounds were prepared thought the same procedure but using 1,2-bis(diphenylphosphino)ethane as the ligand.



6-Allyl-3-benzyloxy-6-methylcyclohex-2-enone: 30.0 mg (0.100 mmol) substrate afforded 13.1 mg product, 0.051 mmol, 51%. Purified by flash column chromatography (3:1 petroleum:Et_2O). Separation of enantiomers: hplc, OD column, 95:5 heptane:^{i}PrOH, R_T = 10.6 min., 12.2 maj.; IR (thin film) ν_{max} (cm^{-1}) 2932, 1654 (C=O), 1611 (C=C), 1499, 1457, 1364, 1239, 1187, 915, 698; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.72 (1H, dt, *J* = 13.6, 6.4 Hz), 1.94 (1H, dt, *J* = 13.6, 6.4 Hz), 2.19 (1H, dd, *J* = 14.0, 7.6 Hz), 2.37 (1H, dd, *J* = 14.0, 7.0 Hz), 2.48 (2H, t, *J* = 6.4 Hz), 4.87 (2H, s), 5.06 (1H, d, *J* = 16.4 Hz), 5.07 (1H, d, *J* = 10.0 Hz), 5.39 (1H, s), 5.74 (1H, dddd, *J* = 16.4, 10.0, 7.6, 7.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 25.9, 31.6, 41.4, 43.2, 70.4, 101.9, 117.9, 127.8, 128.5, 128.6, 134.1, 135.0, 175.5, 203.4. HRMS (EI): M^+ calcd. for $C_{17}H_{20}O_2$, 256.1463; found, 256.1476.

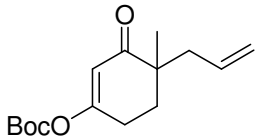


6-Allyl-3-^{t}butoxy-6-methylcyclohex-2-enone: 26.6 mg (0.100 mmol) substrate afforded 11.8 mg product, 0.053 mmol, 53%. Purified by flash column chromatography (4:1 petroleum:Et_2O). Separation of enantiomers: hplc, OD column, 99.5:0.5 heptane:^{i}PrOH, R_T = 9.8 min., 11.7 maj.; IR (thin film) ν_{max} (cm^{-1}) 3075, 2979, 2934, 1651 (C=O), 1603 (C=C), 1461, 1428, 1370, 1327, 1250, 1201, 1162, 909, 854; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04 (3H, s), 1.42 (9H, s), 1.63 (dt, *J* = 13.2, 6.3 Hz), 1.84 (dt, *J* = 13.2, 6.3 Hz), 2.14 (1H, dd, *J* = 13.5, 7.5 Hz), 2.29 (2H, t, *J* = 6.3 Hz), 2.31 (1H, dd, *J* = 13.5, 7.5 Hz), 5.01 (1H, d, *J* = 15.6 Hz), 5.02 (1H, d, *J* = 11.4 Hz), 5.37 (1H, s), 5.71 (1H, ddt, *J* = 15.6, 11.4, 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.1, 27.4, 28.2, 31.5, 41.5, 42.5, 80.8, 104.6, 117.7, 134.3, 173.2, 203.6.

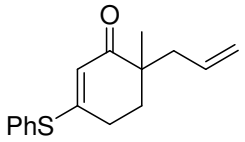


6-Allyl-6-methyl-3-phenoxycyclohex-2-enone: 28.6 mg (0.100 mmol) substrate afforded 17.0 mg product, 0.070 mmol, 70%. Purified by flash column chromatography (5:1 petroleum:Et_2O). Separation of enantiomers: hplc, AS column, 98:2 heptane:^{i}PrOH, R_T = 18.9 maj., 24.5 min; IR (thin film) ν_{max} (cm^{-1}) 3074, 2931, 1656 (C=O), 1621 (C=C), 1588, 1490, 1458, 1373, 1327, 1306, 1229, 1200, 1168, 1003, 914, 855, 764, 694; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.79 (1H, dt, *J* = 13.6, 6.4 Hz), 2.01 (1H, dt, *J* = 13.6, 6.4 Hz), 2.37 (1H, dd, *J* = 13.8, 7.4 Hz), 2.66 (2H, t, *J* = 6.4 Hz), 5.04 (1H, d, *J* =

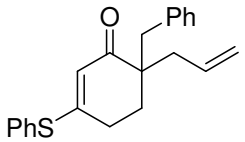
9.6 Hz), 5.05 (1H, d, *J* = 14.8 Hz), 5.09 (1H, s), 5.73 (1H, ddt, *J* = 14.8, 9.6, 7.4 Hz), 7.02 (1H, d, *J* = 8.0 Hz), 7.22 (1H, t, *J* = 8.0 Hz), 7.37 (1H, t, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 25.5, 31.6, 41.4, 43.2, 104.5, 118.1, 121.3, 126.0, 129.9, 134.1, 152.8, 176.2, 203.4. HRMS (EI): M^+ calcd. for $C_{16}H_{18}O_2$, 242.1307; found, 242.1308.



4-Allyl-4-methyl-3-oxo-cyclohex-1-enyl *t*butyl carbonate: 31.0 mg (0.100 mmol) substrate afforded 17.6 mg product, 0.066 mmol, 66%. Purified by flash column chromatography (10:1 petroleum:Et_2O). Separation of enantiomers: hplc, OJ column, 99.5:0.5 heptane:*i*PrOH, R_T = 11.4 maj., 15.4, min.; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.53 (9H, s), 1.77 (1H, dt, *J* = 13.6, 6.4 Hz), 1.97 (1H, dt, *J* = 13.6, 6.4 Hz), 2.20 (1H, dd, *J* = 14.0, 8.0 Hz), 2.36 (1H, dd, *J* = 14.0, 7.0 Hz), 2.58 (1H, t, *J* = 6.4 Hz), 5.07 (1H, d, *J* = 17.2 Hz), 5.08 (1H, d, *J* = 10.0 Hz), 5.73 (1H, dddd, *J* = 17.2, 10.0, 8.0, 7.0 Hz), 5.92 (1H, s).

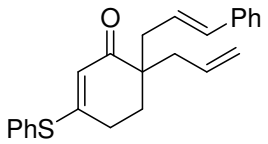


6-Allyl-6-methyl-3-(phenylthio)cyclohex-2-enone From 60.5 mg starting material, after 16 h 39 mg product was isolated (75%) as colorless oil. $[\alpha]_D^{22}$ = +38.6 (c = 3.9, CH_2Cl_2, 100% ee); HPLC (Chiralcel® AS column; 99.5:0.5 Heptane / Isopropanol; flow rate = 1 mL / min; t_1 = 20.1 min (major), t_2 = 25.6 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 2929 (s), 1732 (s), 1652 (s), 1581 (s), 1475 (m), 1441 (s), 1343 (m), 1205 (s), 1140 (m), 1000 (m), 916 (s), 750 (s), 732 (s), 691 cm^{-1} (s); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.5-7.4 (m, 5H), 5.71 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.41 (t, *J* = 1.1 Hz, 1H), 5.06 (m, 2H), 2.54 (t, *J* = 5.6 Hz, 2H), 2.36 (dd, J_1 = 13.9 Hz, J_2 = 7.3 Hz, 1H), 2.16 (dd, J_1 = 13.9 Hz, J_2 = 7.6 Hz, 1H), 1.99 (dt, J_1 = 13.9 Hz, J_2 = 6.6 Hz, 1H), 1.78 (dt, J_1 = 13.9 Hz, J_2 = 6.1 Hz, 1H), 1.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.2, 164.6, 135.5, 134.0, 130.1, 129.8, 128.1, 119.7, 118.2, 43.6, 41.2, 33.3, 27.1, 21.9. HRMS (EI): M^+ calcd. for $C_{16}H_{18}OS$, 258.1078; found 258.1088.

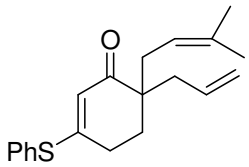


6-Allyl-6-benzyl-3-(phenylthio)cyclohex-2-enone From 75.7 mg starting material, after 16 h 52.4 mg product was isolated (78%) as colorless oil. $[\alpha]_D^{23}$ = -47.7 (c = 5.15, CH_2Cl_2, 92% ee); HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow

rate = 0.8 mL / min; t_1 = 6.8 min (minor), t_2 = 8.0 min (major)); R_f = 0.43 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3062 (w), 2923 (m), 1651 (s), 1580 (s), 1495 (m), 1475 (m), 1441 (m), 1345 (m), 1285 (m), 1208 (s), 912 (s), 733 (s), 704 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 7.23 (m, 3H), 7.1 (m, 2H), 5.73 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.44 (t, J = 1.0 Hz, 1H), 5.06 (m, 2H), 3.14 (d, J = 13.6 Hz, 1H), 2.60 (d, J = 13.6 Hz, 1H), 2.50 (m, 3H), 2.08 (dd, J_1 = 13.9 Hz, J_2 = 7.8 Hz, 1H), 1.90 (m, 1H), 1.80 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.7, 164.8, 137.5, 135.5, 133.9, 130.7, 130.1, 129.9, 128.0, 126.3, 120.4, 118.5, 48.3, 40.8, 40.1, 29.7, 27.1. HRMS (EI): M^+ calcd. for $C_{22}H_{22}OS$, 334.1391; found 334.1388.

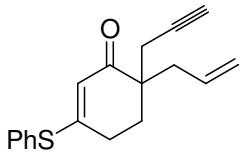


6-Allyl-6-cinnamyl-3-(phenylthio)cyclohex-2-enone From 81.3 mg starting material, after 2 h 71 mg product was isolated (98%) as colorless oil. $[\alpha]_D^{24}$ = -24.6 (c = 4.9, CH_2Cl_2, 95% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 8.3 min (major), t_2 = 10.3 min (minor)); R_f = 0.27 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3060 (w), 2926 (m), 1652 (s), 1580 (s), 1495 (m), 1475 (m), 1441 (m), 1343 (m), 1283 (m), 1208 (s), 969 (m), 912 (s), 733 (s), 692 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.5-7.1 (m, 10H), 6.39 (d, J = 15.7 Hz, 1H), 6.10 (m, 1H), 5.73 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 5.0 Hz, 1H), 5.44 (t, J = 1.0 Hz, 1H), 5.07 (m, 2H), 2.57 (m, 3H), 2.43 (ddt, J_1 = 13.9 Hz, J_2 = 7.8 Hz, J_3 = 1.2 Hz, 1H), 2.28 (ddd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, J_3 = 1.2 Hz, 1H), 2.21 (dd, J_1 = 13.9 Hz, J_2 = 7.6 Hz, 1H), 1.97 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.9, 165.0, 137.4, 135.6, 133.9, 133.3, 130.2, 129.9, 128.6, 128.1, 127.2, 126.2, 125.9, 120.2, 118.5, 47.5, 39.8, 38.8, 30.6, 27.1. HRMS (EI): M^+ calcd. for $C_{24}H_{24}OS$, 360.1548; found 360.1531.

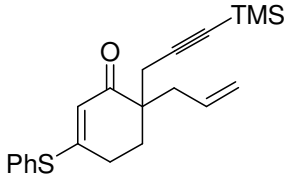


6-Allyl-6-(3-methylbut-2-enyl)-3-(phenylthio)cyclohex-2-enone From 71.3 mg starting material, after 16 h 52.6 mg product was isolated (84%) as colorless oil. $[\alpha]_D^{24}$ = -14.9 (c = 3.8, CH_2Cl_2, 91% ee); HPLC (Chiralcel® AS column; 95:5 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 8.6 min (major), t_2 = 13.3 min (minor)); R_f = 0.27 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 2926 (s), 1657 (s), 1580 (s), 1441 (m), 1342 (m), 1283 (m), 1208 (m), 915 (m), 749 (m), 691 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.70 (m, 1H), 5.41 (t, J = 1.0 Hz, 1H), 5.04 (m, 3H), 2.55 (t, J

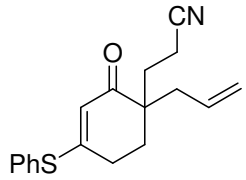
= 6.1 Hz, 2H), 2.40 (ddt, J_1 = 13.9 Hz, J_2 = 7.8 Hz, J_3 = 1.2 Hz, 1H), 2.28 (dd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, 1H), 2.14 (m, 2H), 1.92 (t, J = 6.2 Hz, 2H), 1.69 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.5, 164.5, 135.6, 134.4, 134.3, 130.2, 129.9, 128.2, 120.4, 119.3, 118.1, 47.7, 39.6, 33.4, 30.5, 27.1, 26.1, 18.1. HRMS (EI): M^+ calcd. for $C_{20}H_{24}OS$, 312.1548; found 312.1553.



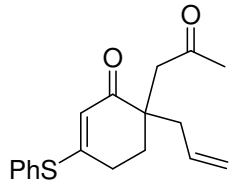
6-Allyl-3-(phenylthio)-6-(prop-2-ynyl)cyclohex-2-enone From 66 mg starting material, after 4 h 47 mg product was isolated (83%) as colorless oil. $[\alpha]_D^{25}$ = +32.7 (c = 3.6, CH_2Cl_2, 72% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 6.6 min (major), t_2 = 7.4 min (minor)); R_f = 0.33 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3300 (m), 3076 (w), 2918 (m), 2117 (w), 1652 (s), 1580 (s), 1476 (m), 1441 (m), 1345 (m), 1286 (m), 1208 (s), 919 (m), 750 (m), 691 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.66 (m, 1H), 5.43 (t, J = 1.0 Hz, 1H), 5.09 (m, 2H), 2.64 (m, 1H), 2.55 (m, 1H), 2.41 (m, 3H), 2.29 (dd, J_1 = 13.9 Hz, J_2 = 7.3 Hz, 1H), 2.18 (m, 1H), 2.08 (m, 1H), 2.00 (t, J = 2.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.5, 165.3, 135.6, 133.1, 130.3, 130.0, 128.0, 119.7, 118.8, 80.8, 71.1, 46.6, 38.7, 30.8, 27.0, 25.0. HRMS (EI): M^+ calcd. for $C_{18}H_{18}OS$, 282.1078; found 282.1072.



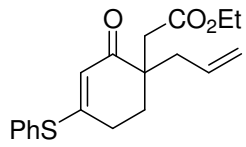
6-Allyl-3-(phenylthio)-6-(3-(trimethylsilyl)prop-2-ynyl)cyclohex-2-enone From 80 mg starting material, after 1 h 63.4 mg product was isolated (89%) as colorless oil. $[\alpha]_D^{23}$ = -12.7 (c = 5.1, CH_2Cl_2, 91% ee); HPLC (Chiralcel® AD column; 98:2 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 5.5 min (major), t_2 = 6.5 min (minor)); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2959 (m), 2175 (w), 1657 (s), 1580 (s), 1476 (w), 1441 (m), 1343 (m), 1285 (m), 1249 (s), 1208 (s), 1034 (m), 916 (s), 843 (s), 733 (s), 691 cm^{-1} (m); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.66 (m, 1H), 5.41 (s, 1H), 5.06 (m, 2H), 2.59 (m, 2H), 2.42 (m, 3H), 2.27 (dd, J_1 = 13.9 Hz, J_2 = 7.3 Hz, 1H), 2.10 (t, J = 6.2 Hz, 1H), 0.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.7, 165.2, 135.6, 133.4, 130.2, 129.9, 128.0, 119.7, 118.6, 103.4, 87.8, 46.6, 38.9, 31.0, 27.1, 26.5, 0.2. HRMS (EI): M^+ calcd. for $C_{21}H_{26}OSSi$, 354.1474; found: 354.1484.



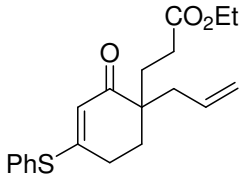
3-(1-Allyl-2-oxo-4-(phenylthio)cyclohex-3-enyl)propanenitrile From 68.3 mg starting material, after 30 min 58 mg product was isolated (98%) as colorless oil. $[\alpha]_D^{25}$ = +9.8 (c = 5.48, CH_2Cl_2, 83% ee); HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 16.8 min (minor), t_2 = 21.5 min (major)); R_f = 0.38 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2931 (m), 2248 (m), 1650 (s), 1580 (s), 1475 (m), 1441 (s), 1347 (m), 1288 (m), 1212 (s), 918 (s), 732 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.65 (ddt, J_1 = 17.2 Hz, J_2 = 10.4 Hz, J_3 = 7.4 Hz, 1H), 5.40 (s, 1H), 5.13 (m, 2H), 2.59 (m, 2H), 2.27 (m, 4H), 1.98 (m, 3H), 1.80 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.6, 165.7, 135.5, 132.4, 130.4, 130.0, 127.6, 120.1, 119.6, 119.5, 46.1, 38.7, 30.7, 30.3, 26.6, 12.3. HRMS (EI): M^+ calcd. for $C_{18}H_{19}NOS$, 297.1187; found: 297.1177.



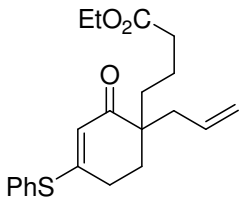
6-Allyl-6-(2-oxopropyl)-3-(phenylthio)cyclohex-2-enone: From 69 mg starting material, reaction finished in 2 h; 58 mg product was isolated (97%) as colorless oil. $[\alpha]_D^{23}$ = +144 (c = 5.0, CH_2Cl_2, 85% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 9.0 min (minor), t_2 = 10.3 min (major)); R_f = 0.33 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (m), 2922 (s), 1712 (s), 1659 (s), 1643 (s), 1588 (s), 1476 (m), 1442 (s), 1347 (s), 1289 (s), 1210 (s), 1165 (s), 1113 (m), 1068 (m), 1000 (m), 917 (s), 750 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.50 (m, 2H), 7.43 (m, 3H), 5.69 (m, 1H), 5.45 (d, J = 2.0 Hz, 1H), 5.12 (m, 2H), 3.02 (d, J = 17.7 Hz, 1H), 2.67 (m, 1H), 2.50-2.30 (m, 3H), 2.40 (d, J = 17.4 Hz, 1H), 2.17 (dd, J_1 = 13.9 Hz, J_2 = 6.9 Hz, 1H), 2.09 (s, 3H), 1.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 206.8, 198.4, 164.5, 135.6, 133.0, 130.1, 129.9, 128.0, 119.6, 119.1, 48.2, 45.9, 39.2, 31.1, 29.8, 26.8. HRMS (EI): M^+ calcd. for $C_{18}H_{20}O_2S$, 300.1184; found: 300.1170.



Ethyl 2-(1-allyl-2-oxo-4-(phenylthio)cyclohex-3-enyl)acetate From 75 mg starting material, after 2 h 53 mg product was isolated (80%) as colorless oil. $[\alpha]_D^{25}$ = +87.8 (c = 2.9, CH_2Cl_2, 92% ee); HPLC (Chiralcel® OD-H column; 90:10 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 7.4 min (major), t_2 = 9.0 min (minor)); R_f = 0.20 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2980 (m), 2928 (m), 1732 (s), 1660 (s), 1582 (s), 1475 (m), 1442 (m), 1344 (s), 1207 (s), 1178 (s), 1027 (m), 920 (m), 750 (m), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.69 (m, 1H), 5.46 (d, *J* = 1.6 Hz, 1H), 5.11 (m, 2H), 4.08 (qd, J_1 = 7.2 Hz, J_2 = 1.1 Hz, 2H), 2.81 (d, *J* = 15.2 Hz, 1H), 2.67 (m, 1H), 2.48 (m, 1H), 2.40 (m, 2H), 2.30 (d, *J* = 15.2 Hz, 1H), 2.22 (dd, J_1 = 13.9 Hz, J_2 = 7.2 Hz, 1H), 1.94 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.0, 171.7, 164.9, 135.8, 133.1, 130.4, 130.1, 128.2, 119.8, 119.4, 60.6, 46.0, 39.7, 39.3, 30.3, 27.0, 14.4. HRMS (EI): M^+ calcd. for $C_{19}H_{22}O_3S$, 330.1290; found 330.1289.

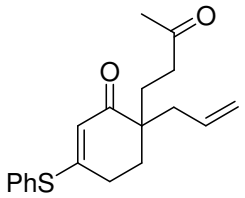


Ethyl 3-(1-allyl-2-oxo-4-(phenylthio)cyclohex-3-enyl)propanoate From 78 mg starting material, after 4 h 62 mg product was isolated (90%) as colorless oil. $[\alpha]_D^{25}$ = -0.8 (c = 4.7, CH_2Cl_2, 73% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 10.5 min (minor), t_2 = 12.2 min (major)); R_f = 0.27 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 2979 (m), 2934 (m), 1732 (s), 1652 (s), 1581 (s), 1475 (m), 1442 (m), 1345 (m), 1285 (m), 1208 (s), 1180 (s), 918 (m), 750 (m), 733 cm^{-1} (s); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.68 (m, 1H), 5.39 (s, 1H), 5.08 (m, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 2.57 (m, 2H), 2.36 (dd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, 1H), 2.29 (m, 1H), 2.21 (m, 2H), 1.98 (m, 1H), 1.87 (m, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.8, 173.9, 165.0, 135.8, 133.7, 130.4, 130.1, 128.2, 120.2, 118.8, 60.7, 46.4, 39.2, 31.4, 29.5, 29.3, 27.0, 14.5. HRMS (EI): M^+ calcd. for $C_{20}H_{24}O_3S$, 344.1446; found 344.1457.

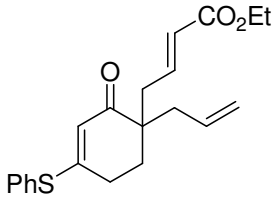


Ethyl 4-(1-allyl-2-oxo-4-(phenylthio)cyclohex-3-enyl)butanoate From 80.5 mg starting material, after 2 h 62 mg product was isolated (86%) as colorless oil. $[\alpha]_D^{23}$ = -9.0 (c =

4.88, CH_2Cl_2, 94% ee); HPLC (Chiralcel® AS column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 8.6 min (major), t_2 = 12.0 min (minor)); R_f = 0.45 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3075 (w), 2935 (s), 1732 (s), 1652 (s), 1582 (s), 1475 (m), 1442 (s), 1346 (m), 1286 (s), 1207 (s), 1172 (s), 1024 (m), 917 (m), 750 (s), 692 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.68 (m, 1H), 5.40 (s, 1H), 5.06 (m, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.55 (t, J = 7.0 Hz, 2H), 2.37 (dd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, 1H), 2.26 (t, J = 7.0 Hz, 2H), 2.20 (dd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, 1H), 1.95 (t, J = 6.2 Hz, 2H), 1.65-1.40 (m, 4H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.2, 173.5, 164.6, 135.6, 134.0, 130.2, 129.9, 128.1, 120.1, 118.2, 60.4, 46.8, 39.3, 34.7, 34.0, 30.8, 27.0, 19.4, 14.3. HRMS (EI): M^+ calcd. for $C_{21}H_{26}O_3S$, 358.1603; found: 358.1654.

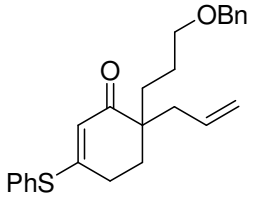


6-Allyl-6-(3-oxobutyl)-3-(phenylthio)cyclohex-2-enone From 71.7 mg starting material, after 6 h 48 mg product was isolated (76%) as colorless oil. $[\alpha]_D^{25}$ = +9.0 (c = 3.9, CH_2Cl_2, 57% ee); HPLC (Chiralcel® OD-H column; 95:5 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 12.7 min (minor), t_2 = 13.8 min (major)); R_f = 0.32 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2978 (s), 2931 (s), 1732 (s), 1652 (s), 1582 (s), 1475 (m), 1442 (s), 1367 (s), 1285 (s), 1209 (s), 1151 (s), 918 (m), 750 (m), 692 cm^{-1} (m); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45 (m, 5H), 5.67 (m, 1H), 5.38 (s, 1H), 5.07 (m, 2H), 2.70-2.25 (m, 5H), 2.18 (dd, J_1 = 13.9 Hz, J_2 = 7.1 Hz, 1H), 2.11 (s, 3H), 1.96 (m, 1H), 1.90-1.70 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 208.6, 198.9, 165.1, 135.6, 133.6, 130.2, 129.9, 128.0, 119.9, 118.6, 46.0, 39.1, 38.3, 31.5, 30.1, 27.8, 26.8. HRMS (EI): M^+ calcd. for $C_{19}H_{22}O_2S$, 314.1341; found: 314.1328.

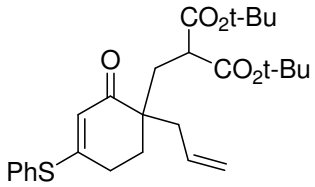


(*E*)-Ethyl 4-(1-allyl-2-oxo-4-(phenylthio)cyclohex-3-enyl)but-2-enoate From 80 mg starting material, after 30 min 62 mg product was isolated (87%) as colorless oil. $[\alpha]_D^{24}$ = +15.6 (c = 5.0, CH_2Cl_2, 95% ee); HPLC (Chiralcel® OD-H column; 98:2 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 19.0 min (minor), t_2 = 22.0 min (major)); R_f = 0.47 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2979 (m), 2931

(m), 1717 (s), 1653 (s), 1580 (s), 1475 (w), 1442 (m), 1368 (m), 1271 (s), 1208 (s), 1178 (s), 1044 (m), 917 (m), 732 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (m, 5H), 6.83 (dt, J_1 = 15.7 Hz, J_2 = 7.2 Hz, 1H), 5.83 (d, J = 15.5 Hz, 1H), 5.67 (ddt, J_1 = 17.1 Hz, J_2 = 10.1 Hz, J_2 = 7.3 Hz, 1H), 5.42 (s, 1H), 5.08 (m, 2H), 4.17 (q, J = 7.2 Hz, 2H), 2.70-2.44 (m, 3H), 2.38 (dd, J_1 = 13.9 Hz, J_2 = 7.2 Hz, 1H), 2.24 (m, 2H), 1.96 (m, 1H), 1.93 (t, J = 5.7 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 197.9, 166.2, 165.2, 144.6, 135.6, 133.2, 130.3, 130.0, 127.9, 124.6, 119.8, 118.9, 60.3, 47.1, 39.4, 37.7, 30.7, 26.9, 14.3. HRMS (EI): M^+ calcd. for $C_{21}H_{24}O_3S$, 356.1446; found: 356.1435.

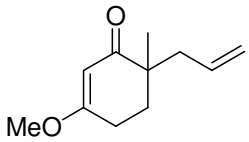


6-Allyl-6-(3-(benzyloxy)propyl)-3-(phenylthio)cyclohex-2-enone: From 44 mg starting material, after 16 h 25.4 mg product was isolated (65%) as colorless oil. $[\alpha]_D^{24}$ = -20.3 (c = 2.18, CH_2Cl_2, 93% ee); HPLC (Chiralcel® AD column; 90:10 Heptane / Isopropanol; flow rate = 1.0 mL / min; t_1 = 7.8 min (minor), t_2 = 10.2 min (major)); R_f = 0.52 (30% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3064 (w), 2933 (s), 2857 (s), 1652 (s), 1581 (s), 1475 (m), 1441 (s), 1345 (m), 1285 (m), 1206 (s), 1101 (s), 1026 (m), 913 (s), 734 (s), 693 cm^{-1} (s); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.5-7.2 (m, 10H), 5.69 (m, 1H), 5.40 (s, 1H), 5.05 (m, 2H), 4.47 (s, 2H), 3.43 (t, J = 5.6 Hz, 2H), 2.54 (m, 2H), 2.38 (dd, J_1 = 13.9 Hz, J_2 = 7.2 Hz, 1H), 2.19 (dd, J_1 = 13.9 Hz, J_2 = 7.6 Hz, 1H), 1.93 (m, 2H), 1.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 199.4, 164.5, 138.6, 135.6, 134.1, 130.2, 129.9, 128.4, 128.1, 127.7, 127.6, 120.2, 118.2, 72.8, 70.7, 46.6, 39.4, 31.1, 31.0, 29.0, 24.2. HRMS (EI): M^+ calcd. for $C_{25}H_{28}O_2S$, 392.1810; found: 392.1823.

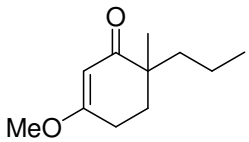


2-(1-Allyl-2-oxo-4-phenylsulfanyl-cyclohex-3-enylmethyl)-malonic acid di-*tert*-butyl ester: From 103 mg starting material, after 2 h, 92 mg product was isolated (97%) as colorless oil. HPLC (Chiralcel® OD-H column; 98:2 Heptane / Isopropanol; flow rate = 0.8 mL / min; t_1 = 7.8 min (minor), t_2 = 8.9 min (major)); R_f = 0.26 (10% ethyl acetate in petroleum ether); IR (film): $\tilde{\nu}_{max}$ = 3076 (w), 2979 (s), 2933 (s), 1732 (s), 1652 (s), 1581 (s), 1475 (m), 1441 (m), 1369 (s), 1286 (s), 1252 (s), 1209 (s), 1138 (s), 917 (m), 849 (m) 750 (m), 734 (s), 693 cm^{-1} (m); ^1H NMR (500 MHz, $CDCl_3$): δ = 7.48 (m, 2H), 7.41 (m,

3H), 5.66 (m, 1H), 5.38 (s, 1H), 5.05 (m, 2H), 3.22 (dd, J_1 = 6.6 Hz, J_2 = 5.0 Hz, 1H), 2.63 (m, 1H), 2.49 (dt, J_1 = 18.3 Hz, J_2 = 5.6 Hz, 1H), 2.42 (dd, J_1 = 13.9 Hz, J_2 = 6.8 Hz, 1H), 2.20 (dd, J_1 = 14.6 Hz, J_2 = 6.8 Hz, 1H), 2.11 (m, 2H), 1.97 (m, 1H), 1.81 (m, 1H), 1.44 (s, 9H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 198.4, 169.5, 169.1, 164.7, 135.7, 133.8, 130.3, 130.0, 128.4, 120.5, 118.9, 81.8, 81.7, 49.7, 46.5, 39.5, 32.8, 31.3, 28.1, 27.0. HRMS (EI): M^+ calcd. for $C_{27}H_{36}O_5S$, 472.2283; found 472.2294.

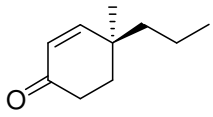


6-Allyl-3-methoxy-6-methylcyclohex-2-enone (17): MeOH (50 ml) was added to sodium pieces washed with hexanes (3 x 20 ml, 1.14 g, 49.7 mmol) at 0 °C and warmed slowly to 25 °C. After all the sodium had dissolved (1 hour) the solution was added *via cannula* to 6-allyl-6-methyl-3-phenylsulfanylcyclohex-2-enone **14** (2.57 g, 9.95 mmol) and heated at reflux for 4 hours. After cooling and evaporation of most of the solvent, the reaction was quenched with saturated aqueous sodium carbonate (50 ml) and extracted with Et_2O (3 x 50 ml). The combined organics were dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (4:1 → 2:1 petroleum:Et_2O) afforded 6-allyl-3-methoxy-6-methylcyclohex-2-enone **17** (1.58 g, 8.77 mmol, 88%) as an orange oil. $[\alpha_D]^{24.3}$ (c. = 1.04 mg/ml in $CHCl_3$) –16.21 ±0.21; IR (thin film) ν_{max} (cm^{-1}) 3075, 2937, 1653 (C=O), 1616 (C=C), 1458, 1374, 1329, 1308, 1246, 1197, 1173, 1034, 988, 916, 842; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.07 (3H, s), 1.69 (1H, dt, *J* = 13.6, 6.4 Hz), 1.91 (1H, dt, *J* = 13.6, 6.4 Hz), 2.17 (1H, dd, *J* = 14.4, 7.2 Hz), 2.34 (1H, dd, *J* = 14.4, 7.2 Hz), 2.41 (2H, t, *J* = 6.4 Hz), 3.67 (3H, s), 5.04 (1H, d, *J* = 16.8 Hz), 5.05 (1H, d, *J* = 10.0 Hz), 5.27 (1H, s), 5.72 (1H, ddt, *J* = 16.8, 10.0, 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 25.7, 31.6, 41.4, 43.2, 55.6, 100.9, 117.9, 134.2, 176.6, 203.5. HRMS (EI): M^+ calcd. for $C_{11}H_{16}O_2$ 180.1150, found 180.1151.

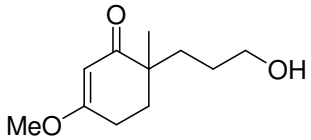


3-Methoxy-6-methyl-6-propyl-cyclohex-2-enone: A solution of 6-allyl-3-methoxy-6-methylcyclohex-2-enone **17** (102 mg, 0.566 mmol) and Wilkinson's catalyst (20.8 mg, 0.0225 mmol) in benzene (2 ml) and EtOH (1 ml) was stirred under a hydrogen atmosphere. After 14 hrs, the solvent was removed *in vacuo*. Purification by flash column chromatography (3:1 petroleum:Et_2O) afforded 3-methoxy-6-methyl-6-propyl-cyclohex-2-enone (97.8 mg, 0.537 mmol, 95%) as a colourless oil. IR (thin film) ν_{max} (cm^{-1}) 2959, 2985, 2872, 1657 (C=O), 1614, 1454, 1374, 1319, 1244, 1195, 1173, 1029, 986, 840; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (3H, t, *J* = 7.2 Hz), 1.04 (3H, s), 1.17-1.53 (4H, m), 1.70 (1H, ddd, *J* = 13.6, 7.6, 5.6 Hz), 1.88 (1H, ddd, *J* = 13.6, 6.8, 5.6 Hz), 2.31-2.48 (2H, m), 3.65 (3H, s), 5.23 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.2, 22.2, 25.8, 32.1,

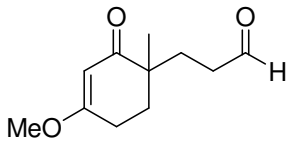
39.1, 43.3, 55.5, 100.9, 176.3, 204.2. Anal. Calcd. for $C_{11}H_{18}O_2$, C, 72.49, H, 9.95; found C 74.01, H, 9.96.



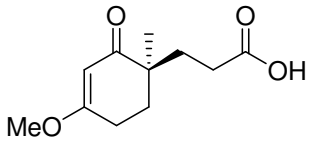
(*S*)-4-Methyl-4-propylcyclohex-2-enone (15)[6]: A solution of diisobutylaluminium hydride in toluene (1.0 M, 721 µl, 0.721 mmol) was added to a solution of 3-methoxy-6-methyl-6-propyl-cyclohex-2-enone (87.6 mg, 0.481 mmol) in Et_2O (2 ml) at 0 °C. After 1 hour, HCl (2M, 15 ml) was added and the mixture stirred for 1 hour. The mixture was extracted with Et_2O (3 x 15 ml), the combined organics washed with saturated aqueous sodium bicarbonate (15 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (5:1 petroleum:Et_2O) afforded 4-methyl-4-propylcyclohex-2-enone (60.0 mg, 0.394 mmol, 82%) as a colourless oil. $[\alpha_D]^{23.0}$ (c = 1.13 mg/ml in MeOH) -47.55 ±0.61; IR (thin film) ν_{max} (cm^{-1}) 2959, 2933, 2873, 1683 (C=O), 1617 (C=C), 1458, 1420, 1390, 1374, 1223, 1123, 804; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (3H, t, *J* = 7.2 Hz), 1.11 (3H, s), 1.24-1.47 (4H, m), 1.74 (1H, dddd, *J* = 13.4, 6.8, 5.6, 1.2 Hz), 1.94 (1H, ddd, *J* = 13.4, 8.8, 5.6 Hz), 2.38-2.49 (2H, m), 5.85 (1H, d, *J* = 10.2 Hz), 6.67 (1H, d, *J* = 10.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.7, 17.4, 24.8, 33.5, 34.1, 35.6, 43.3, 127.9, 159.6, 199.8. HRMS (EI): M^+ calcd. for $C_{10}H_{16}O$ 150.1045, found 150.1041; Anal. Calcd. for $C_{10}H_{16}O$, C, 78.90, H, 10.59, found C, 79.13, H, 10.46.



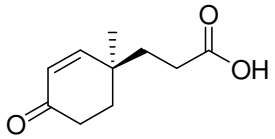
6-(3-Hydroxypropyl)-3-methoxy-6-methylcyclohex-2-enone: Catecholborane (134 µl, 151 mg, 1.26 mmol) was added to a solution of 6-allyl-3-methoxy-6-methylcyclohex-2-enone **17** (189 mg, 1.05 mmol) and Wilkinson's catalyst (29.1 mg, 0.031 mmol) in THF (2 ml) and stirred for 30 minutes. A mixture of THF (1 ml), EtOH (1 ml), pH7 phosphate buffer (2 ml) and 30% H_2O_2 (2 ml) was added and the mixture stirred for 14 hours. The reaction was quenched at 0 °C by careful dropwise addition of saturated aqueous sodium thiosulfate (15 ml, exothermic!!) over 30 minutes. The mixture was extracted with EtOAc (3 x 20 ml) and the combined organics washed with 1M NaOH (30 ml), brine (20 ml), dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (Et_2O → 1:1 EtOAc:Et_2O) afforded 6-(3-hydroxypropyl)-3-methoxy-6-methylcyclohex-2-enone (168 mg, 0.847 mmol, 81%) as a colourless oil. $[\alpha_D]^{22.9}$ (c. = 1.14 mg/ml in $CHCl_3$) +18.49 ± 0.25; IR (thin film) ν_{max} (cm^{-1}) 3418 (br, O-H), 2941, 2970, 1652 (C=O), 1634, 1614, 1456, 1386, 1325, 1250, 1198, 1121, 1060, 1026, 985, 842, 723; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.46-1.56 (2H, m), 1.66-1.74 (3H, m), 1.94 (2H, dt, *J* = 13.4, 6.4 Hz), 2.44 (2H, t, *J* = 6.4 Hz), 3.57-3.61 (2H, m), 3.67 (3H, s), 5.27 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 25.8, 27.3, 32.0, 32.9, 43.0, 55.6, 63.0, 101.0, 176.7, 204.1. HRMS (EI): M^+ calcd. for $C_{11}H_{18}O_3$ 198.1256, found 198.1262.



3-(4-Methoxy-1-methyl-2-oxocyclohex-3-enyl)-propionaldehyde: Dess-Martin periodinane (159 mg, 0.375 mmol) was added to a solution of 6-(3-hydroxypropyl)-3-methoxy-6-methylcyclohex-2-enone (24.8 mg, 0.125 mmol) in CH_2Cl_2 (1 ml) and stirred for 2 hours. Saturated aqueous sodium thiosulfate (15 ml) was added and the mixture extracted with CH_2Cl_2 (2 x 15 ml) and Et_2O (10 ml). The combined organics were dried ($MgSO_4$) and condensed *in vacuo*. Purification by flash column chromatography (1:1 petroleum:EtOAc) afforded 3-(4-methoxy-1-methyl-2-oxocyclohex-3-enyl)-propionaldehyde (18.6 mg, 0.0948 mmol, 76%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s), 1.72-1.91 (4H, m), 2.41-2.48 (4H, m), 3.68 (3H, s), 5.27 (1H, s), 9.76 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 25.7, 28.9, 32.5, 39.2, 42.5, 55.7, 101.0, 176.7, 202.2, 203.0.

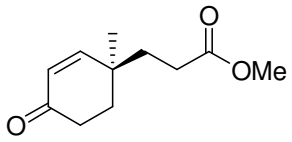


3-(4-Methoxy-1-methyl-2-oxo-cyclohex-3-enyl)-propionic acid: A solution of sodium chlorite (52.5 mg, 0.464 mmol) in pH7 phosphate buffer (0.8 ml) was added to a solution of 3-(4-methoxy-1-methyl-2-oxocyclohex-3-enyl)-propionaldehyde (18.6 mg, 0.948 mmol) and 2-methyl-2-butene (2.0 M in THF, 194 µl, 0.387 mmol) in ^{t}BuOH (0.8 ml) and stirred for 1 hour. The mixture was quenched with saturated aqueous ammonium chloride (15 ml) and extracted with CH_2Cl_2 (2 x 15 ml) and EtOAc (15 ml). The combined organics were dried ($MgSO_4$) and condensed *in vacuo* to afford 3-(4-methoxy-1-methyl-2-oxo-cyclohex-3-enyl)-propionic acid, (19.4 mg, 0.0914 mmol, 96%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, s), 1.76 (1H, dt, J = 13.6, 7.8 Hz), 1.81-1.93 (3H, m), 2.37-2.50 (4H, m), 3.68 (3H, s), 5.29 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 25.7, 29.1, 31.5, 32.4, 42.7, 55.7, 100.9, 176.8, 179.1, 203.3.



3-(1-Methyl-4-oxo-cyclohex-2-enyl)-propionic acid: A solution of diisobutylaluminium hydride in toluene (1.0 M, 229 µl, 0.229 mmol) was added to a solution of 3-(4-methoxy-1-methyl-2-oxo-cyclohex-3-enyl)-propionic acid (19.4 mg, 0.0914 mmol) in THF (0.5 ml) at 0 ^{o}C. After 1 hour, HCl (2M, 15 ml) was added and the mixture stirred for 1 hour. The mixture was extracted with CH_2Cl_2 (3 x 15 ml), the combined organics dried ($MgSO_4$) and condensed *in vacuo* to afford 3-(1-methyl-4-oxo-cyclohex-2-enyl)-propionic acid (16.2 mg, 0.889 mmol, 97%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, s),

1.20-2.49 (8H, m), 5.92 (1H, d, J = 10.2 Hz), 6.65 (1H, d, J = 10.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.5, 29.0, 29.6, 33.1, 33.9, 35.2, 128.1, 157.6, 178.3, 199.3.



(*R*)-Methyl 3-(1-methyl-4-oxo-cyclohex-2-enyl)-propionate (17)[6a]: A solution of trimethylsilyldiazomethane in hexanes (2.0 M, 67 µl, 0.133 mmol) was added to a solution of 3-(1-methyl-4-oxo-cyclohex-2-enyl)-propionic acid (16.2 mg, 0.889 mmol) in benzene (0.8 ml) and stirred for 1 hour. After condensation *in vacuo*, purification by flash column chromatography (1:1 petroleum:Et_2O) afforded methyl 3-(1-methyl-4-oxo-cyclohex-2-enyl)-propionate **17** (6.9 mg, 0.0352 mmol, 40%) as a colourless oil. $[\alpha_D]^{22.5}$ (c. = 0.69 mg/ml in MeOH) –45.09 ±0.52; IR (thin film) ν_{max} (cm^{-1}) 2928, 2865, 1736 (C=O ester), 1684 (C=O ketone), 1438, 1375, 1301, 1201, 1171, 1118, 1090, 1019, 992, 806; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (3H, s), 1.78 (1H, dddd, J = 13.6, 6.8, 5.6, 0.8 Hz), 1.83 (2H, dd, J = 8.4, 7.6 Hz), 1.93 (1H, ddt, J = 13.6, 8.8, 6.0 Hz), 2.32-2.49 (4H, m), 3.68 (3H, s), 5.90 (1H, d, J = 10.0 Hz), 6.63 (1H, dd, J = 10.0, 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 29.2, 33.1, 34.0, 35.2, 35.5, 51.8, 128.0, 157.7, 173.8, 199.2. HRMS (EI): M^+ calcd. for $C_{11}H_{16}O_3$ 196.1099, found 196.1096.

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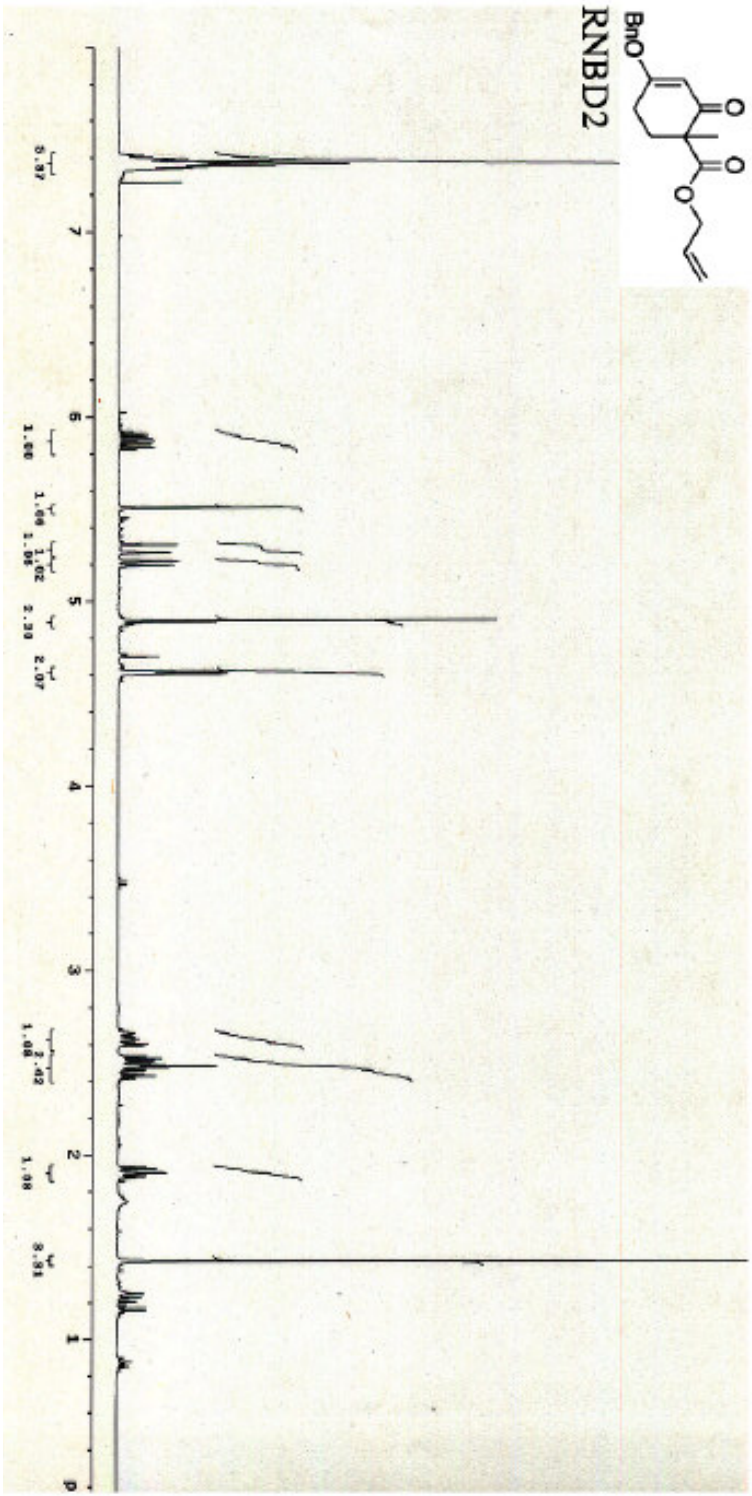
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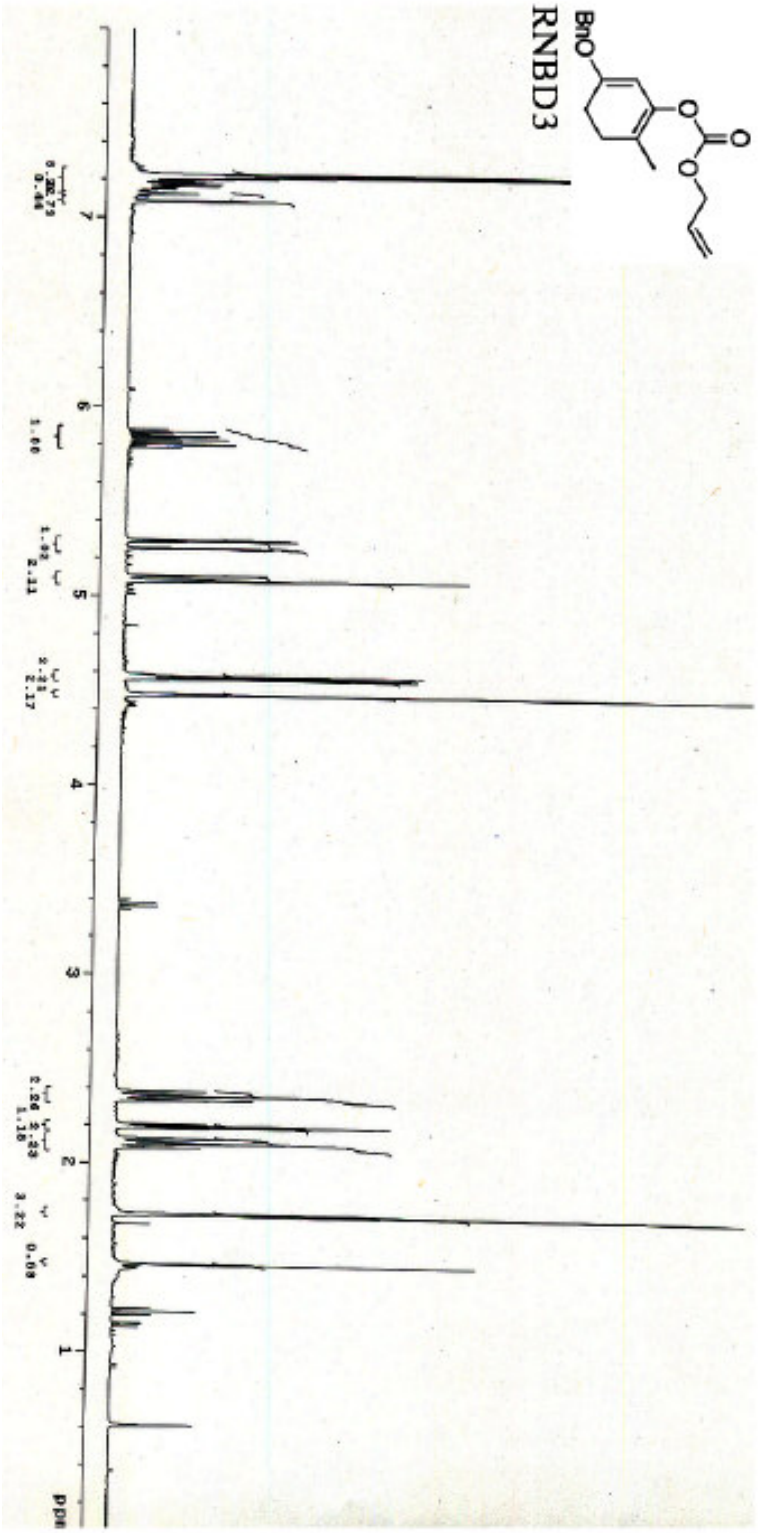
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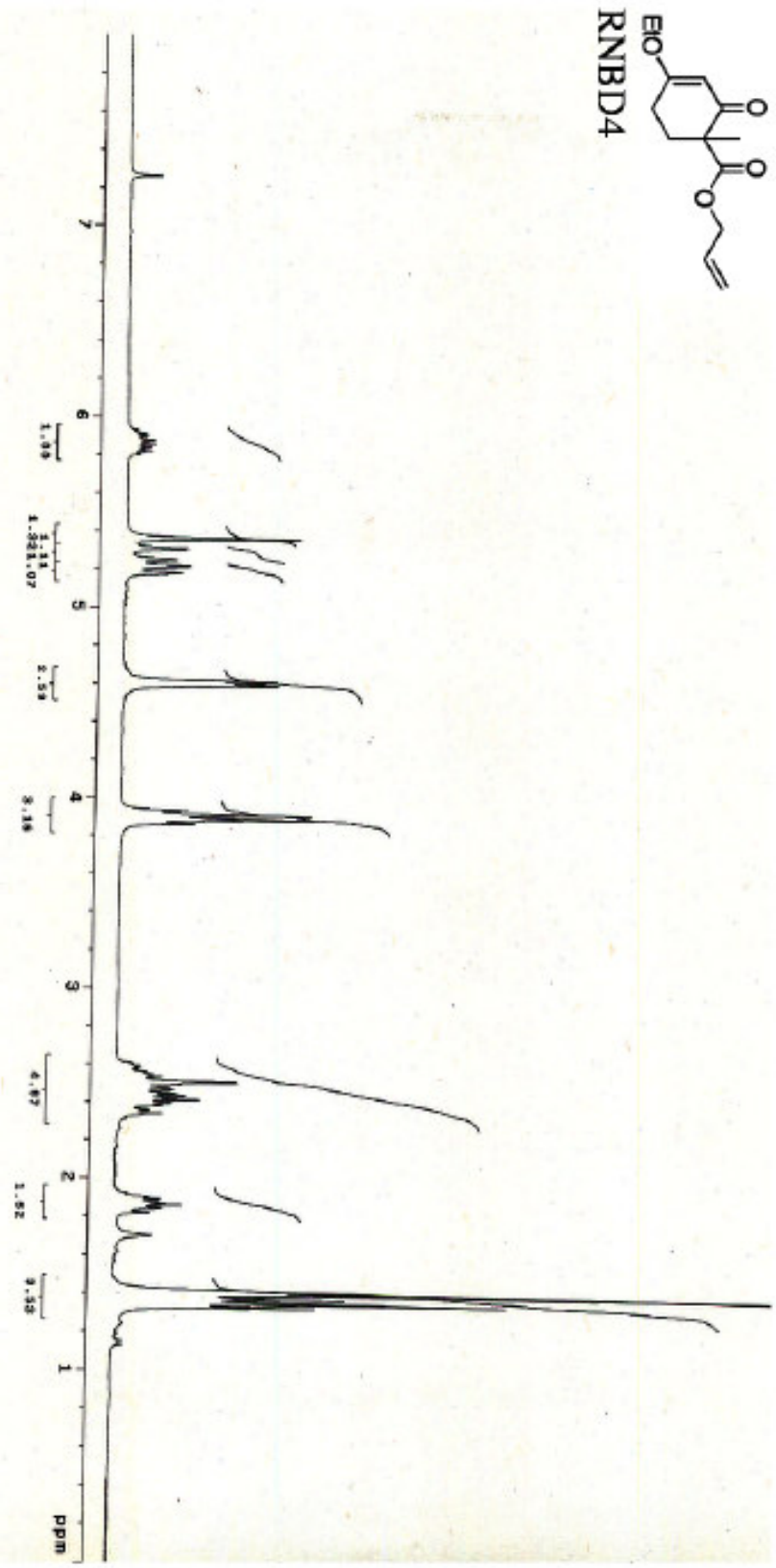
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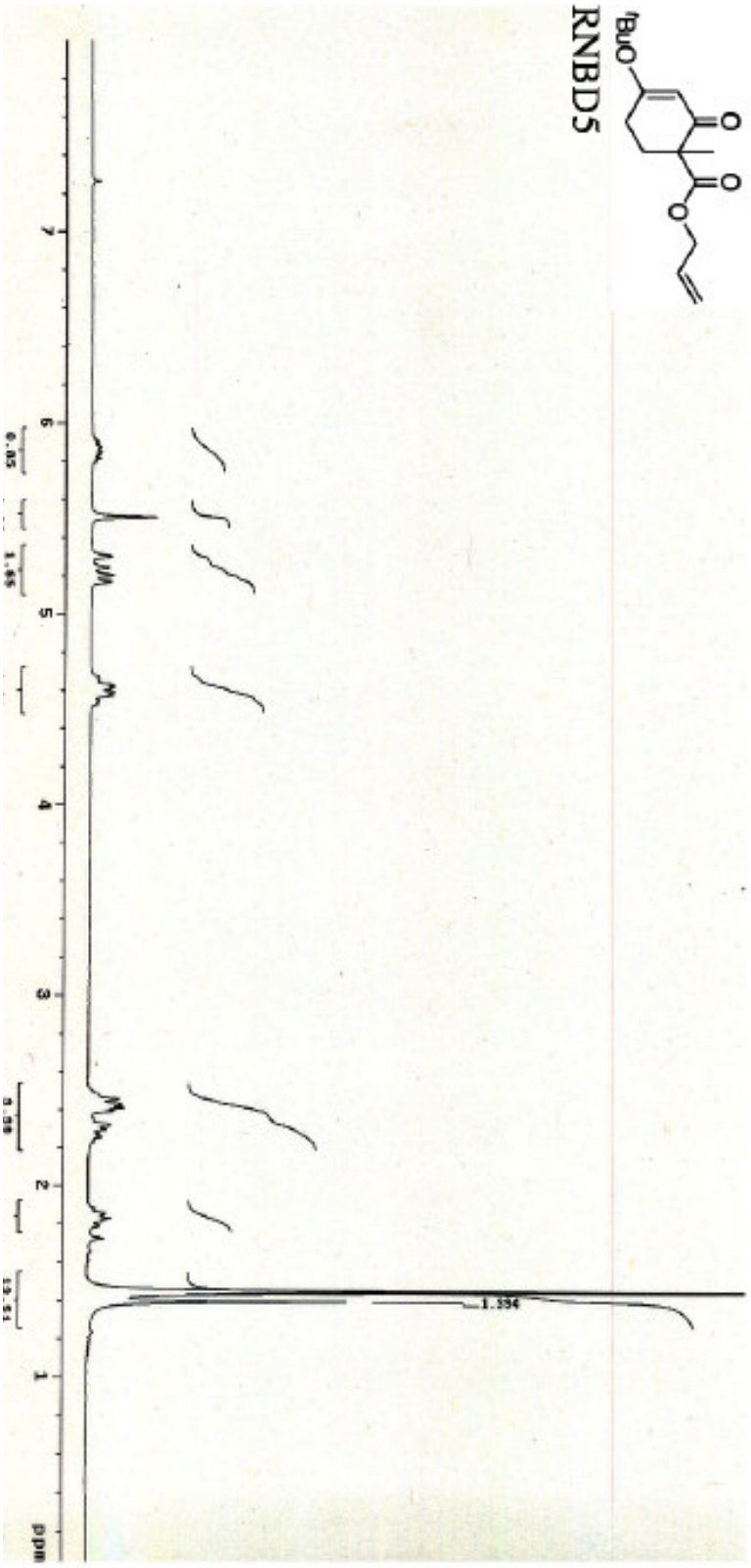
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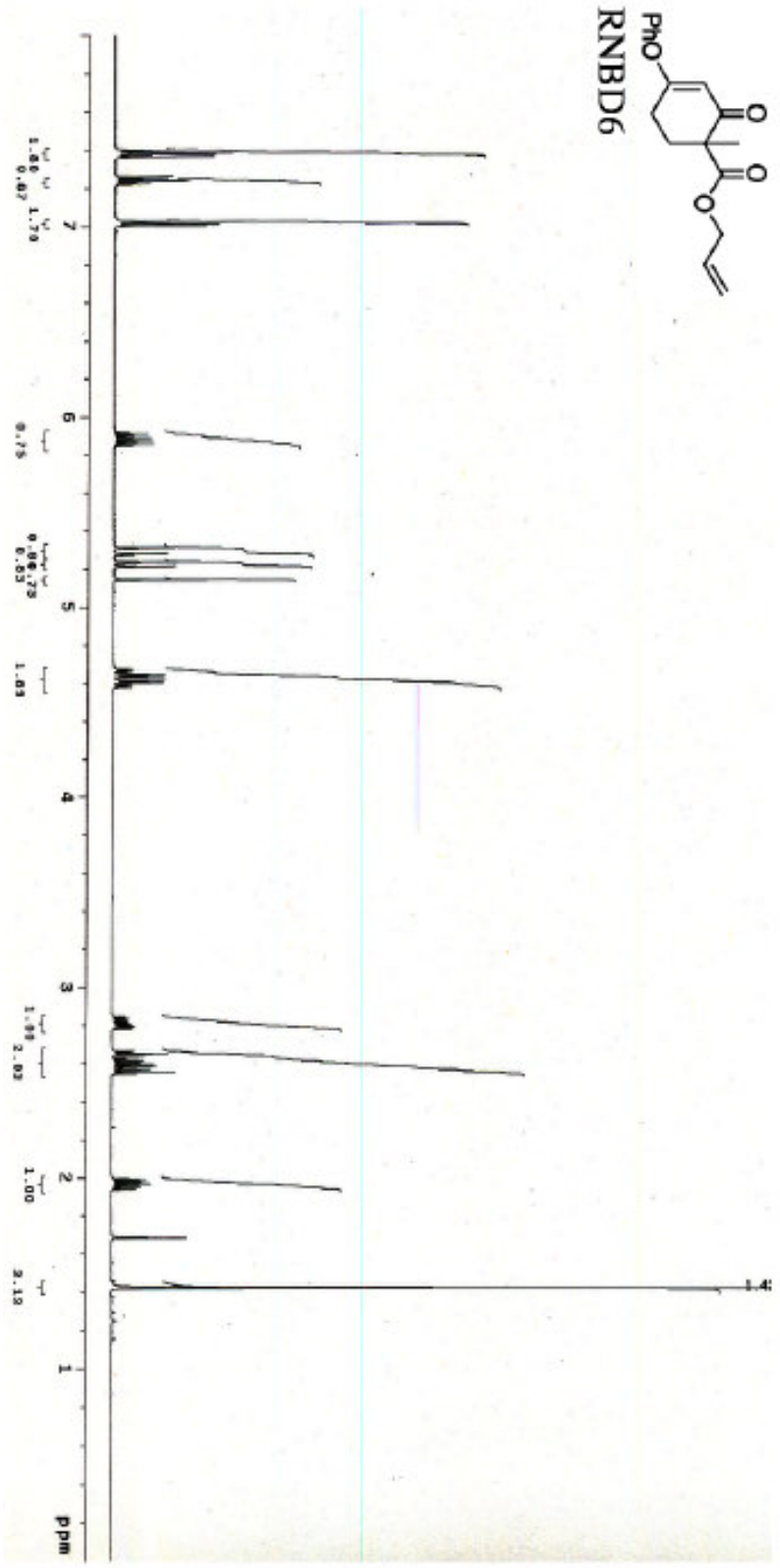
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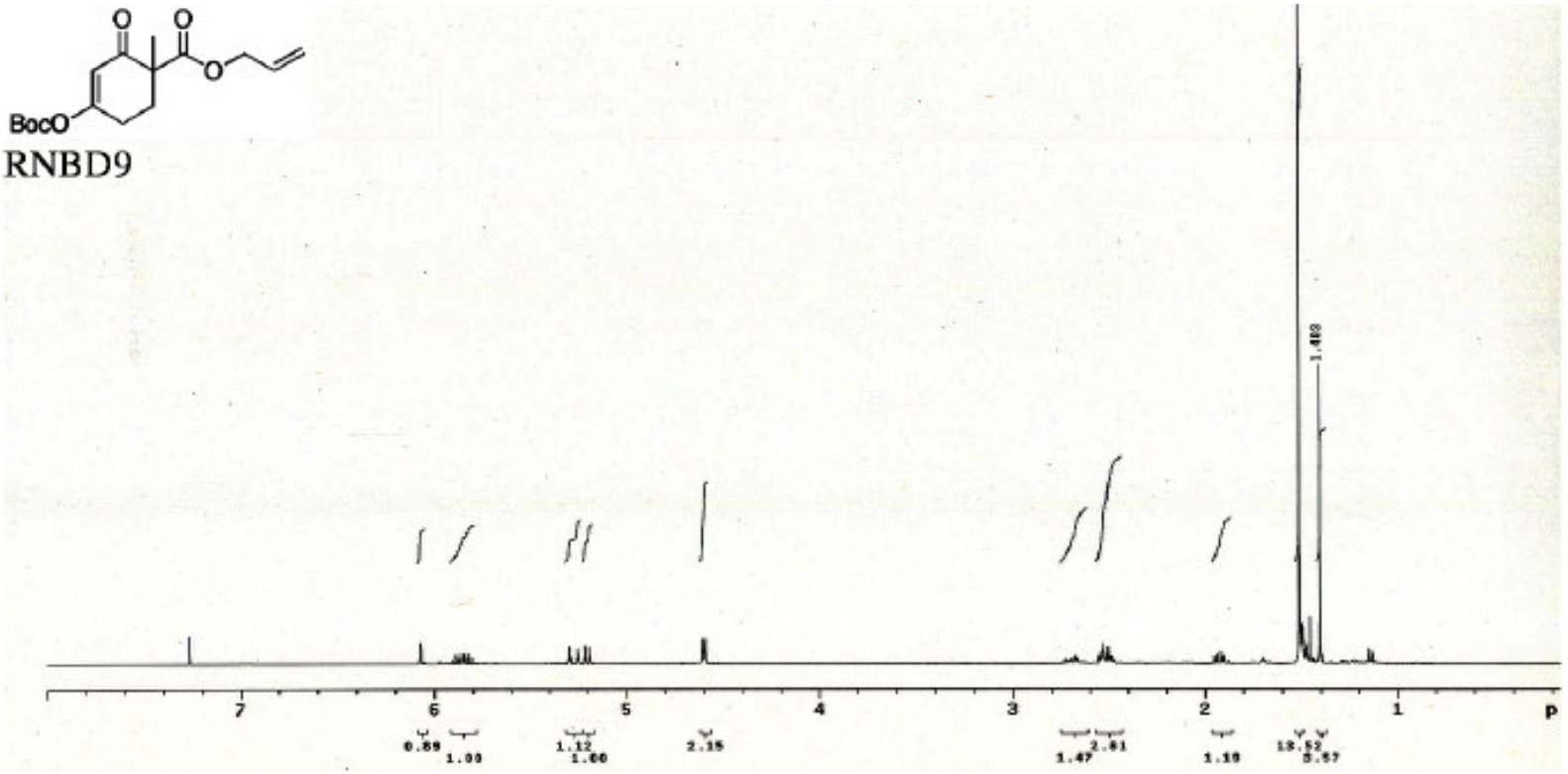
BocO
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6
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2
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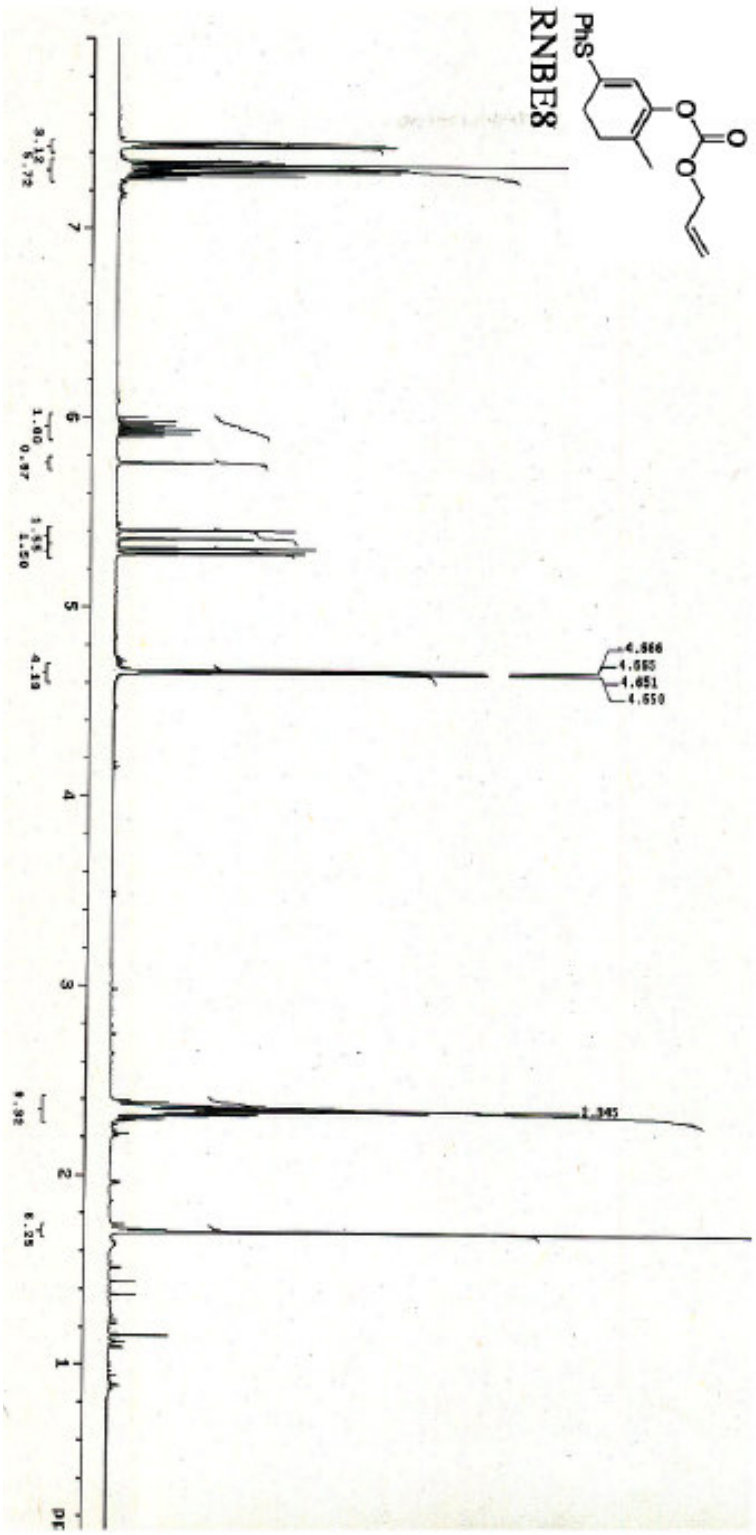
1.488


RNB E8
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4.650
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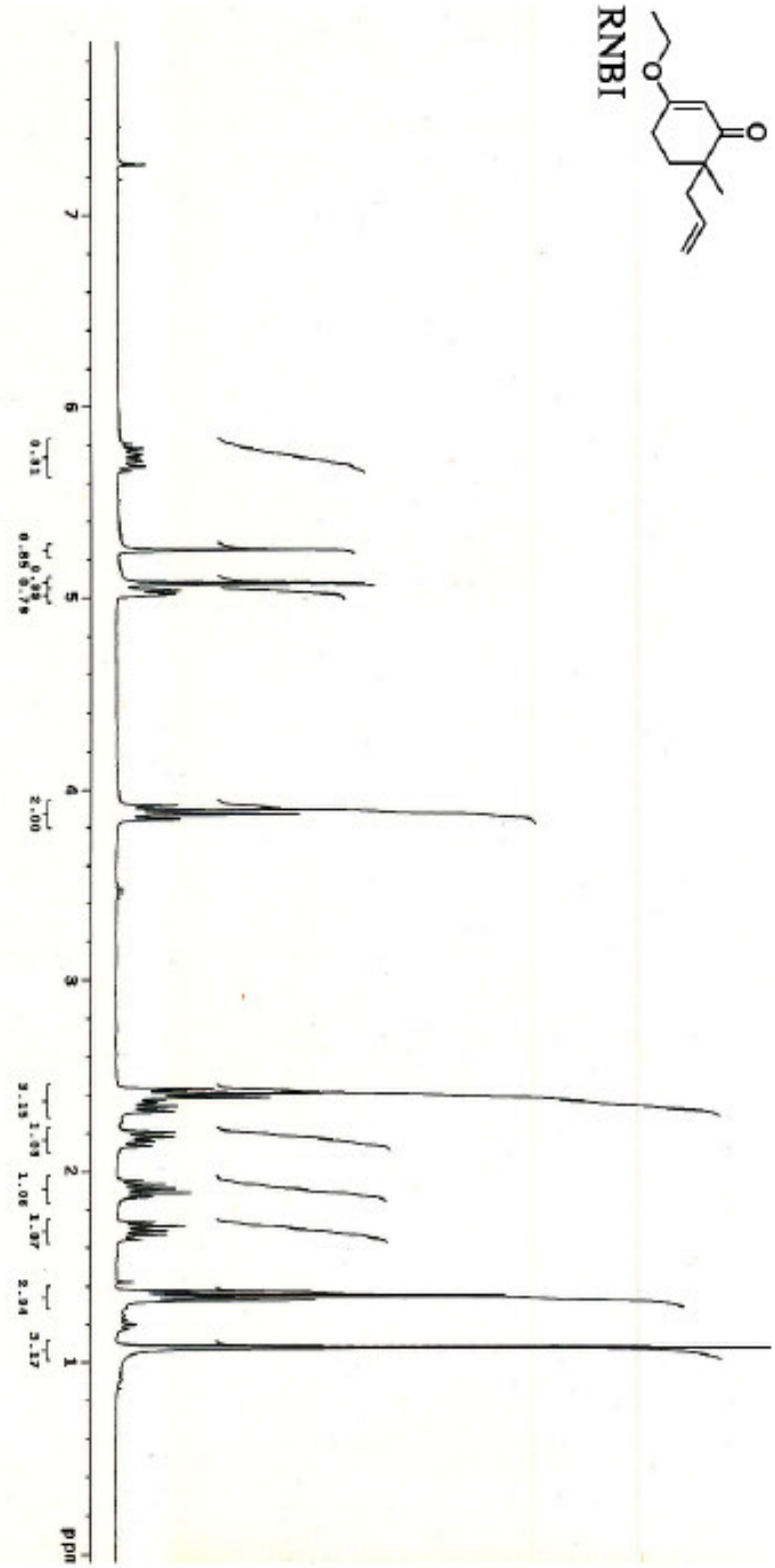
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O
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6
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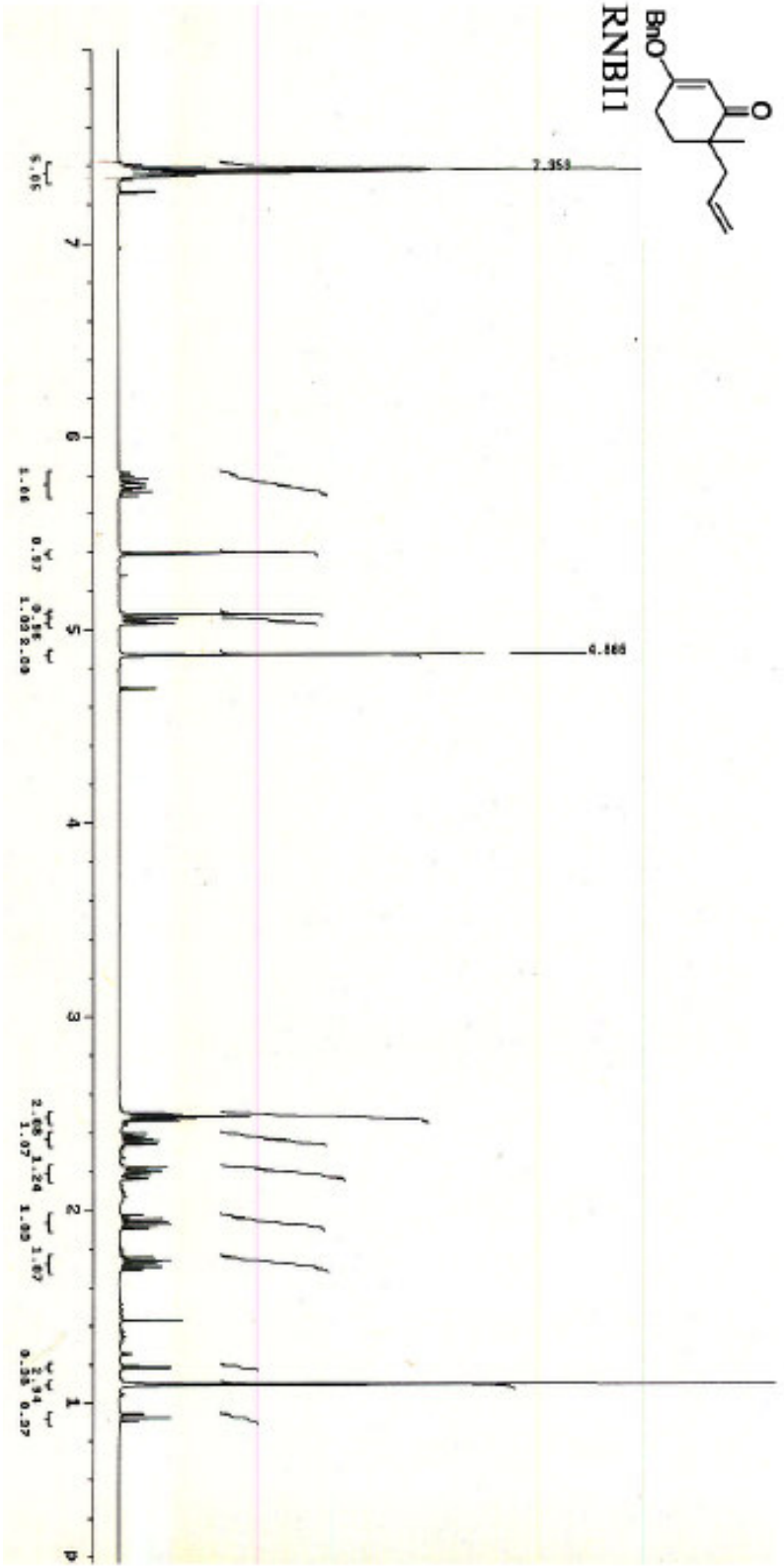
1.07
2.34
3.17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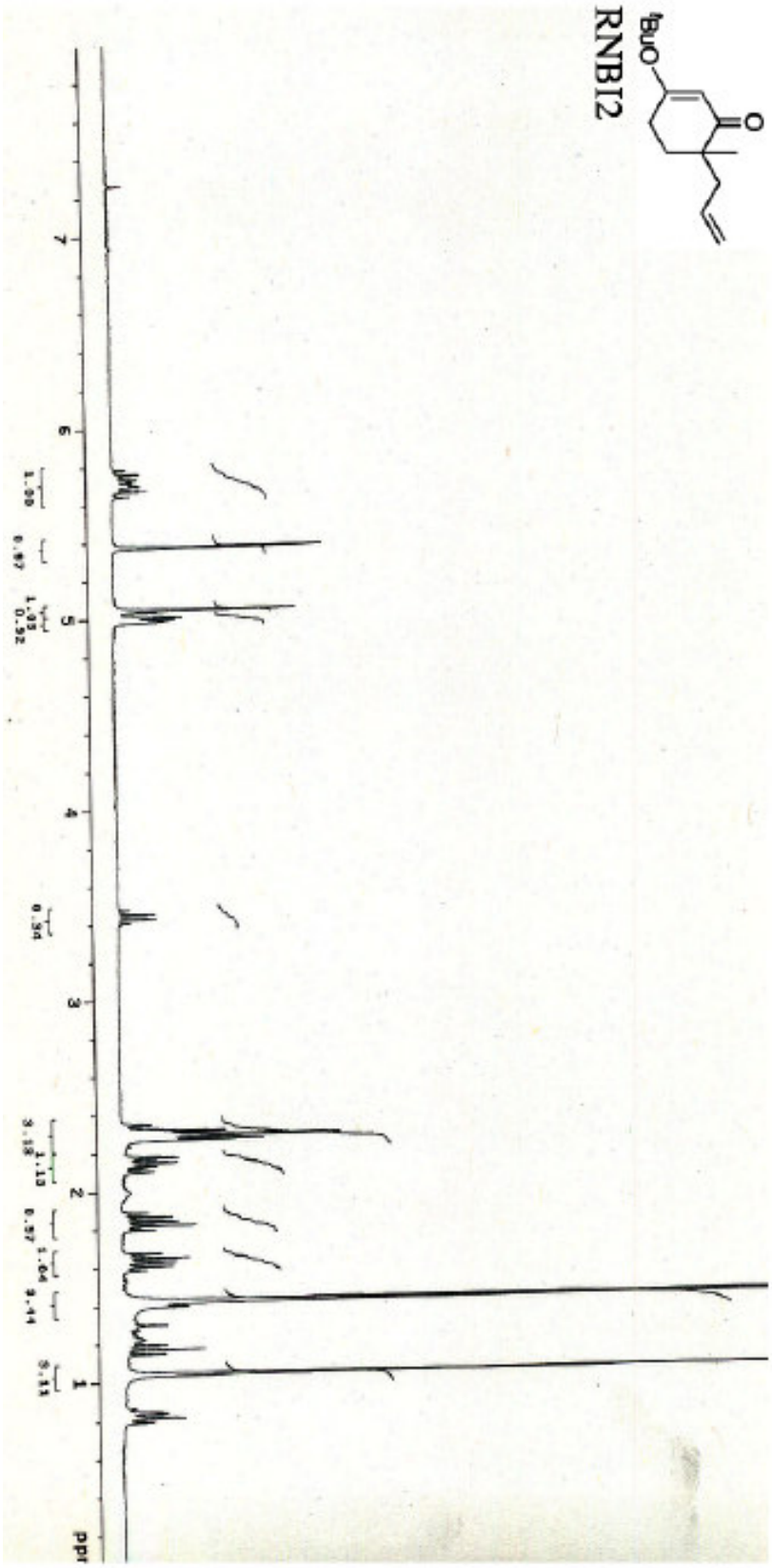
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tBuO
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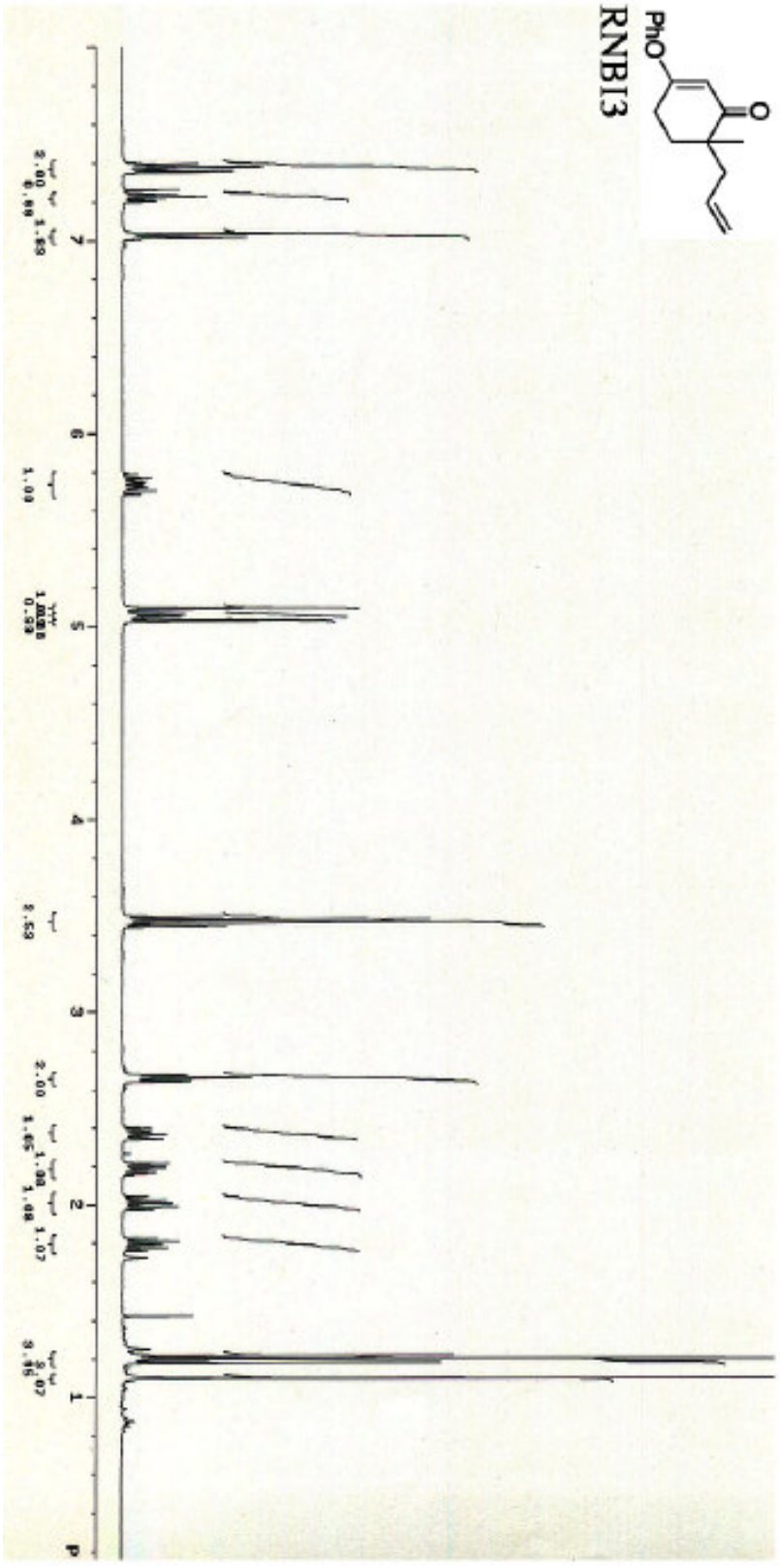
ppm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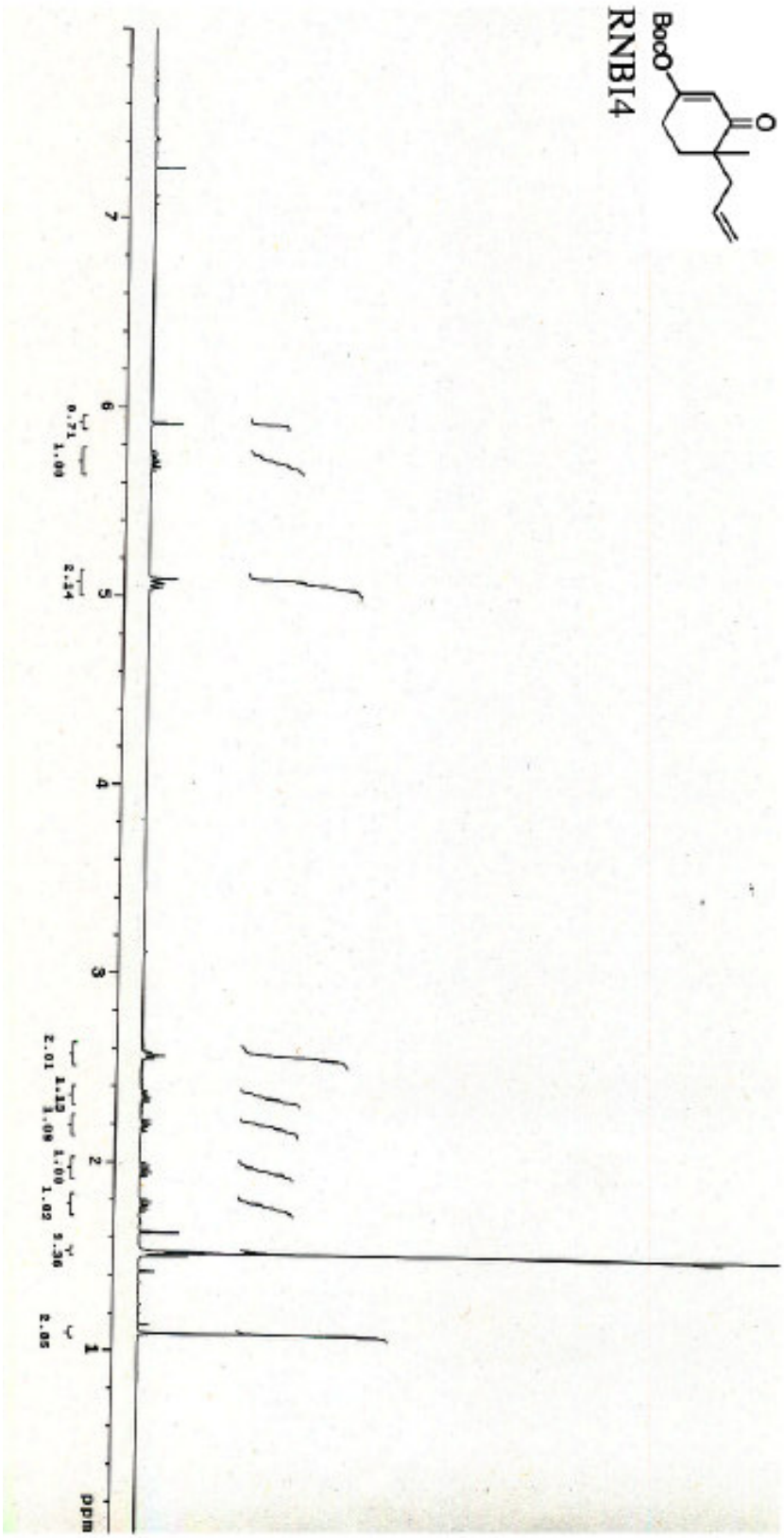
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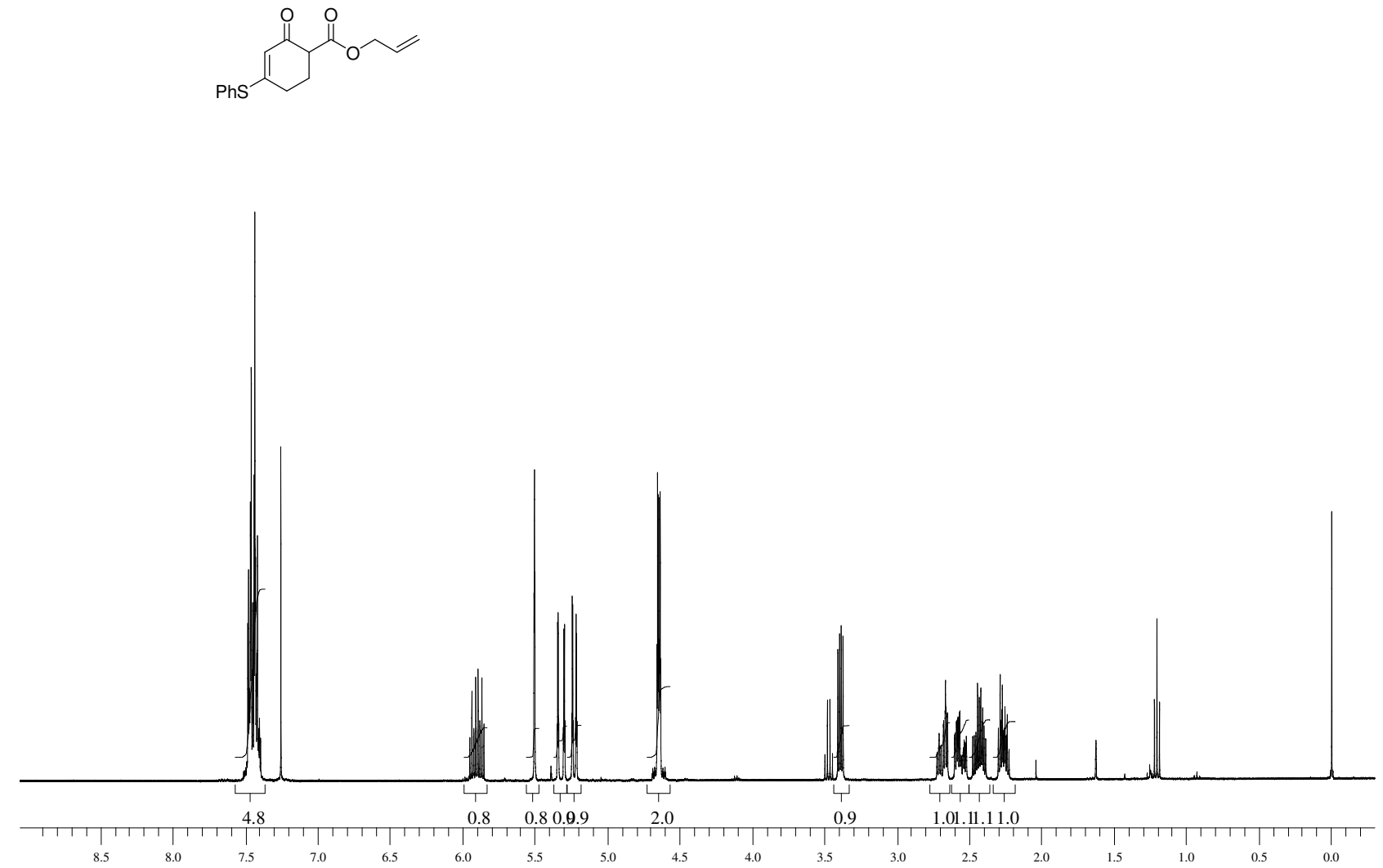
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O
O
PhS
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2.0
0.9
1.0
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1.1
1.0
8.5
8.0
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7.0
6.5
6.0
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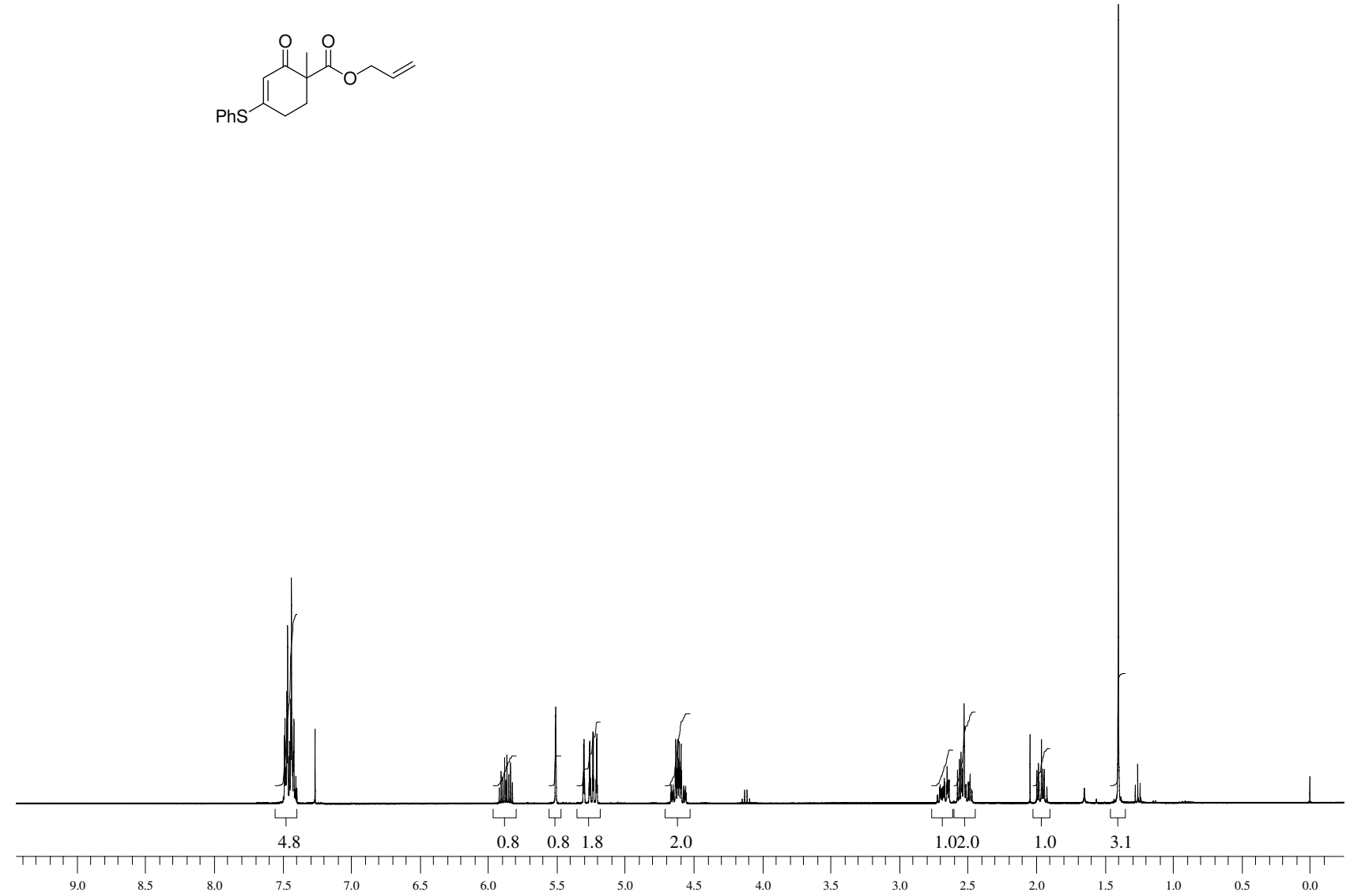
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1.02.0
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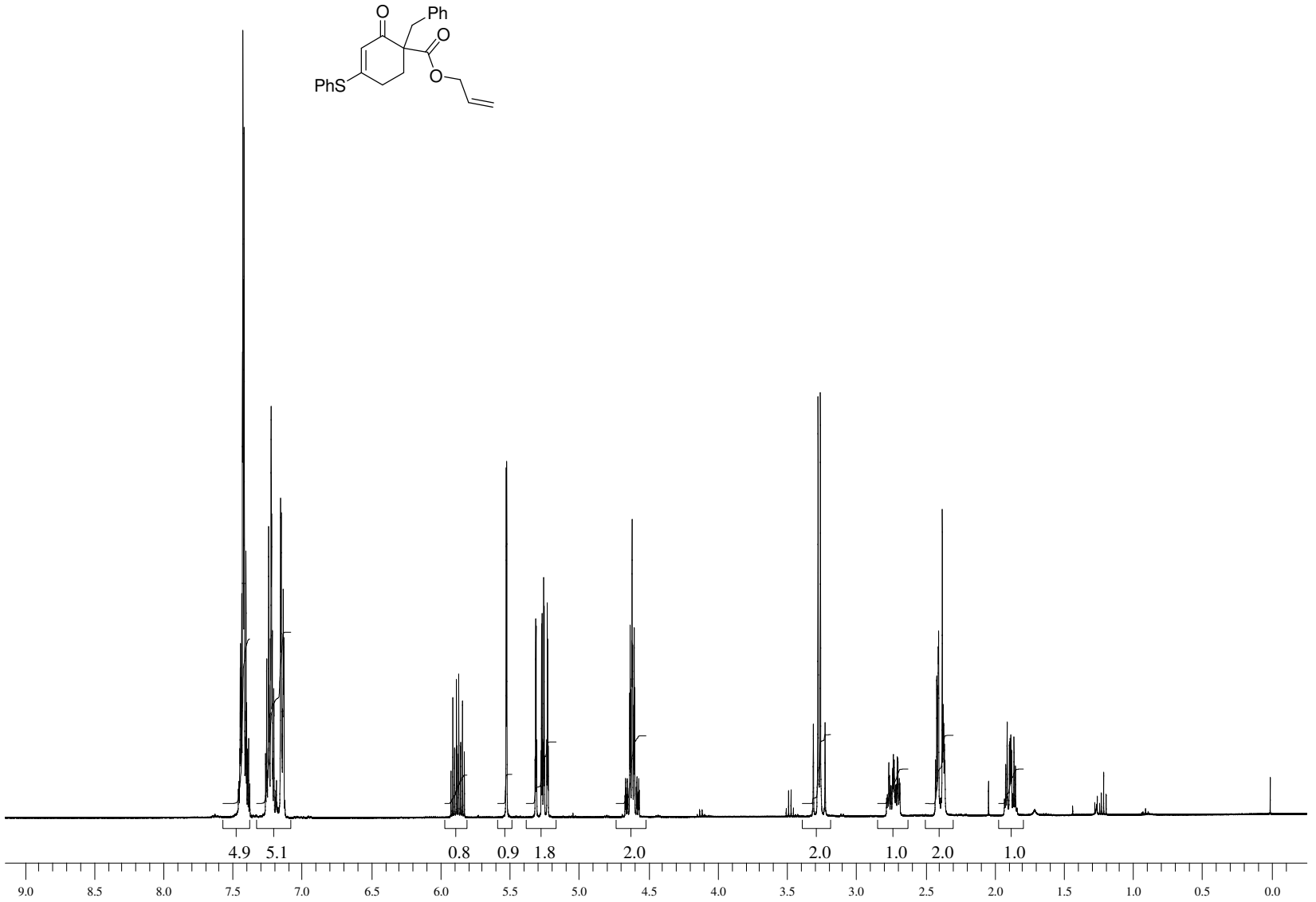
O
Ph
O
PhS
O
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1.8
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2.0
1.0
9.0
8.5
8.0
7.5
7.0
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6.0
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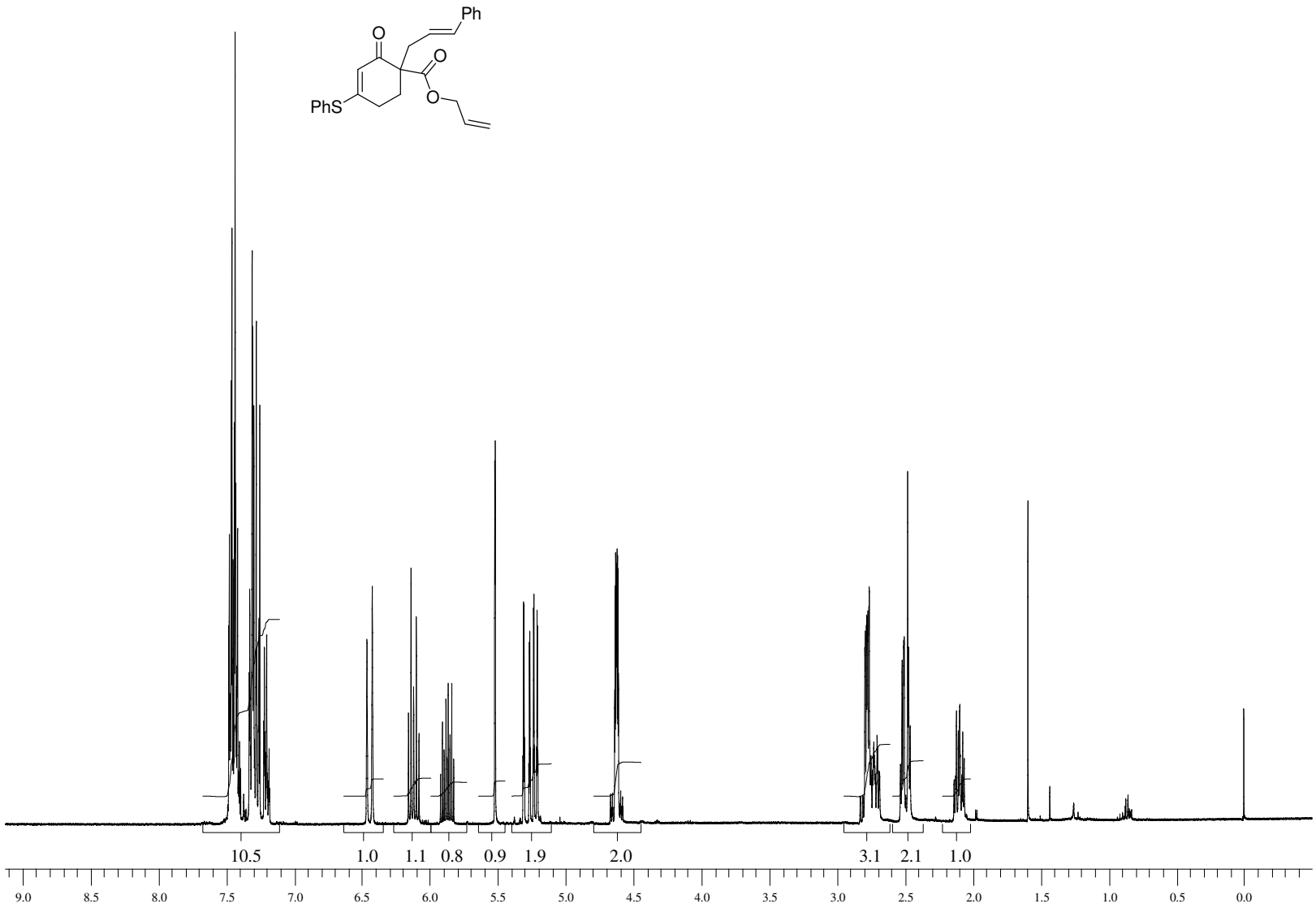
Ph
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O
O
PhS
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1.1
0.8
0.9
1.9
2.0
3.1
2.1
1.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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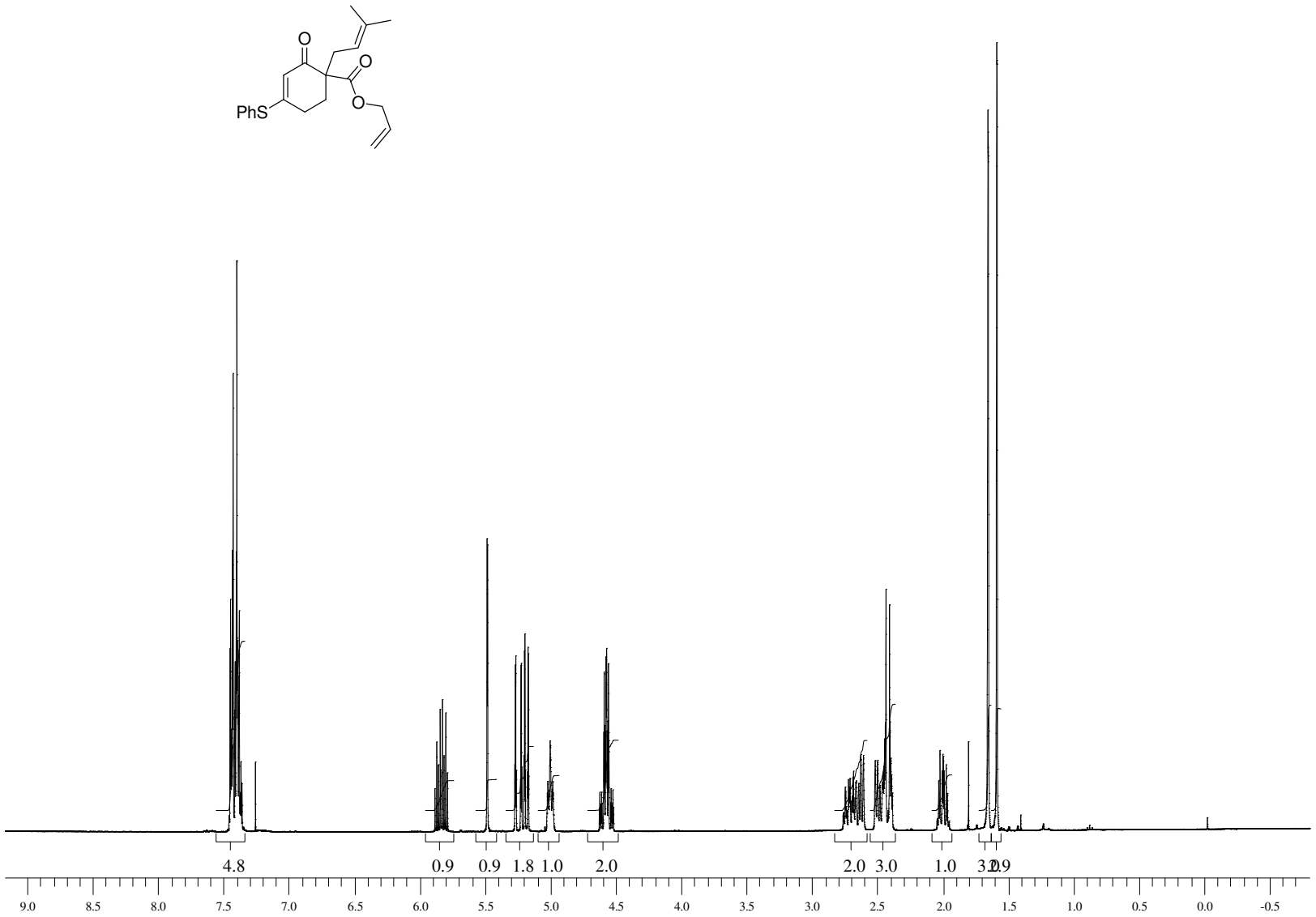
O
O
O
PhS
4.8
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0.9
1.8
1.0
2.0
2.0
3.0
1.0
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9.0
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6.5
6.0
5.5
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1.5
1.0
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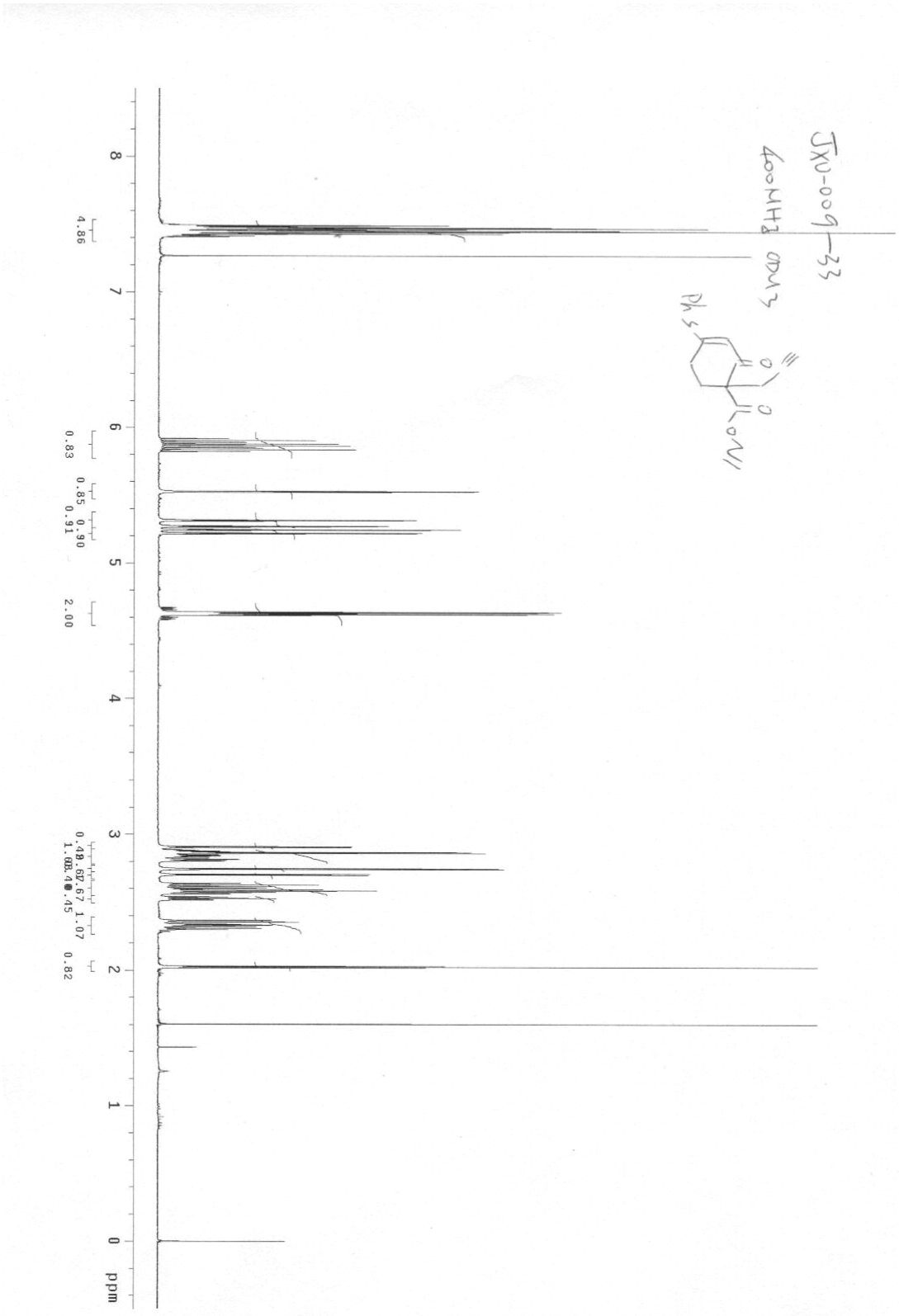
JXD-009-33
400MHz CDCl3
Ph
O
O
OAll
8
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3
2
1
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0.85
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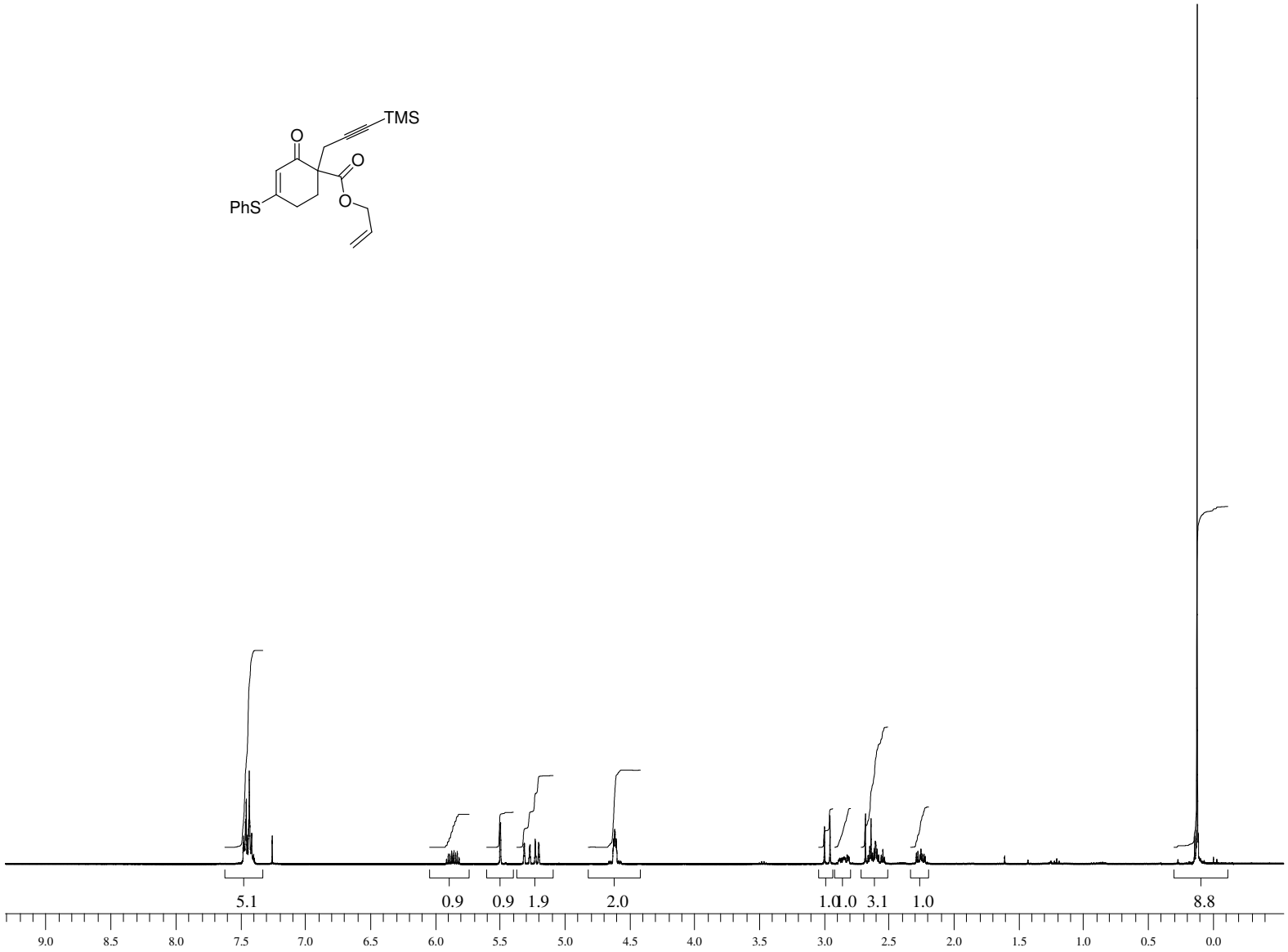
2.00
0.82


TMS
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O
PhS
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1.9
2.0
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1.0
3.1
1.0
8.8
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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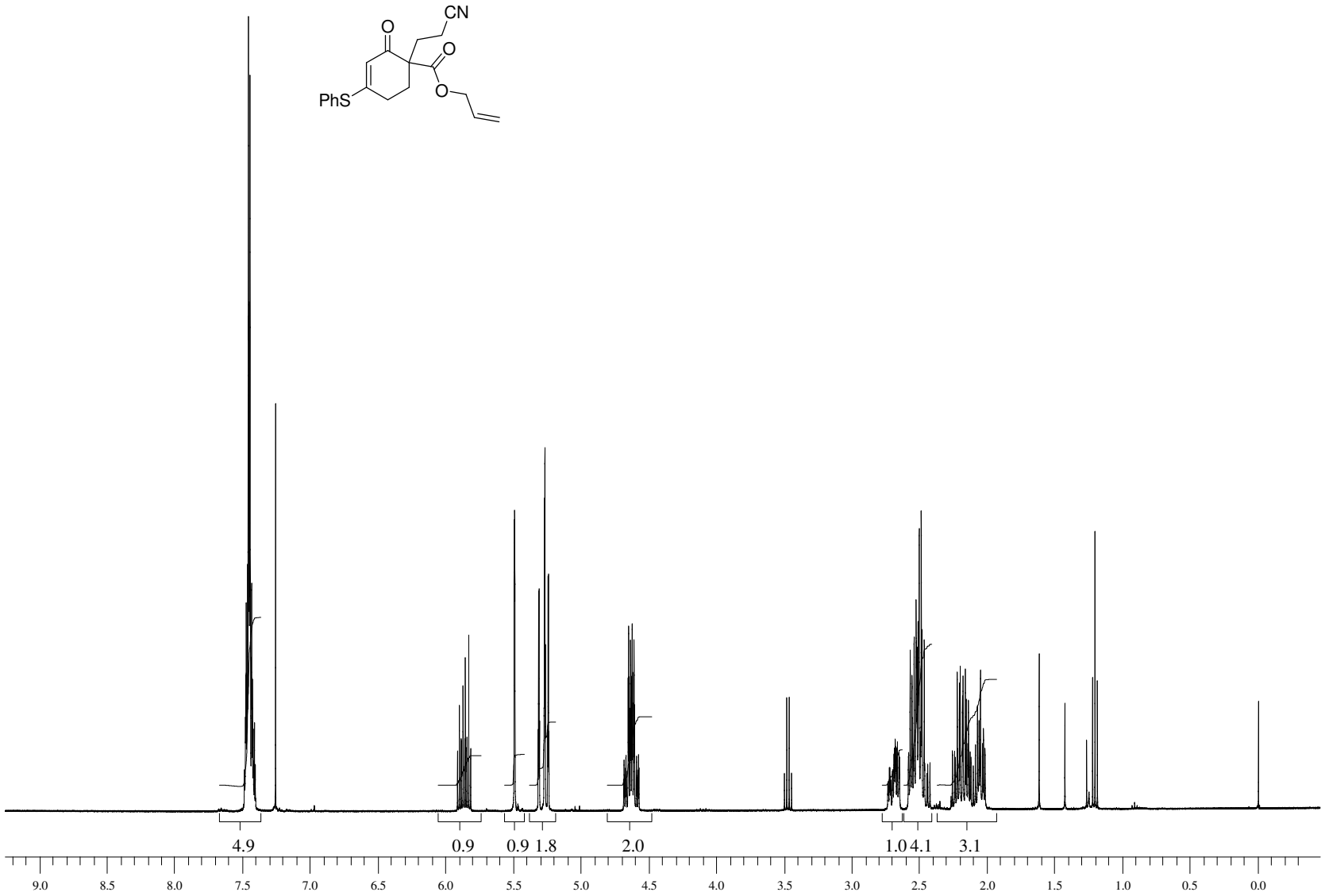
2.0
1.5
1.0
0.5
0.0


CN
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PhS
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0.9
1.8
2.0
1.0
4.1
3.1
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8.0
7.5
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6.5
6.0
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3.0
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2.0
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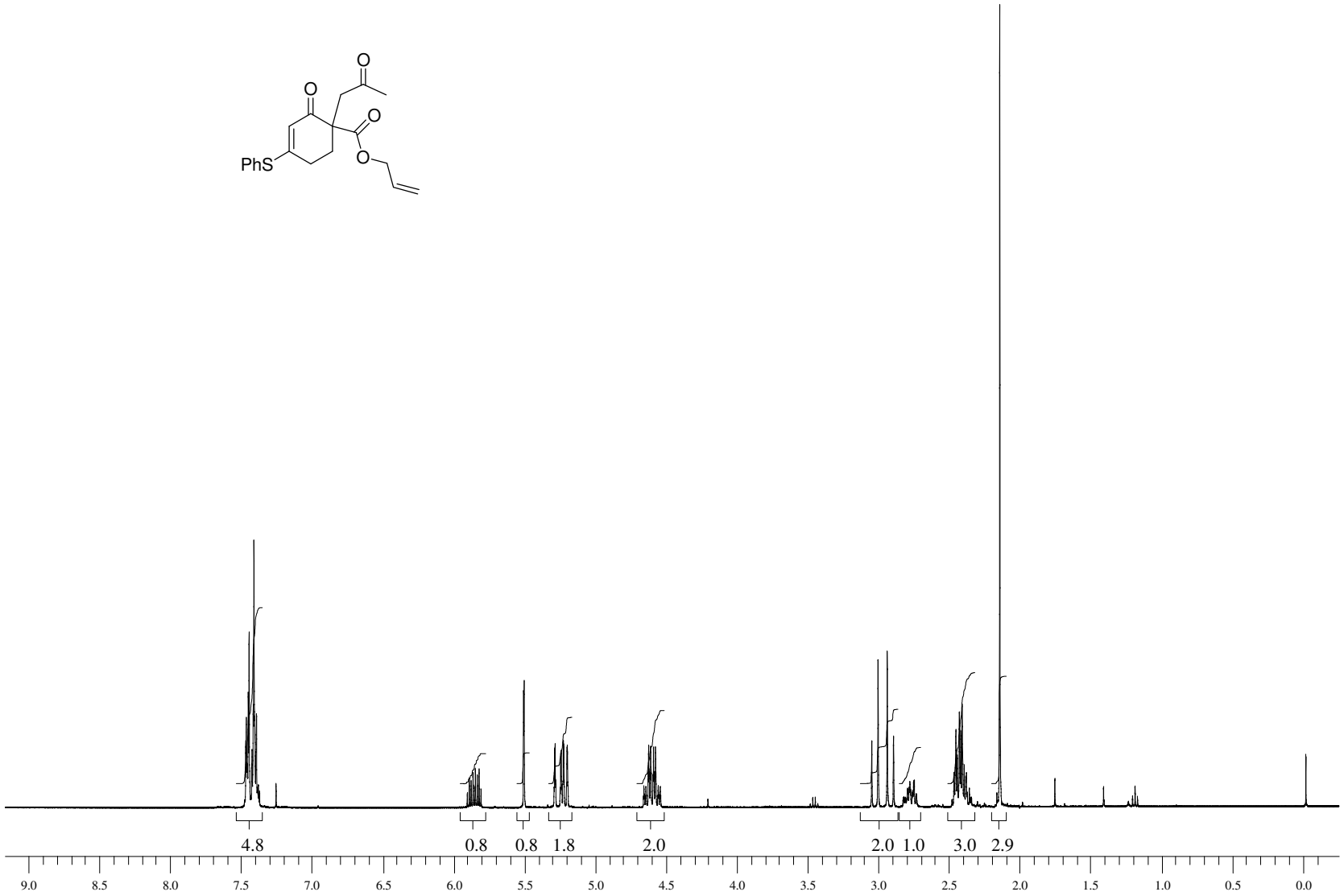
0.0


O
O
O
O
PhS
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0.8
0.8
1.8
2.0
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1.0
3.0
2.9
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
2.5
2.0
1.5
1.0
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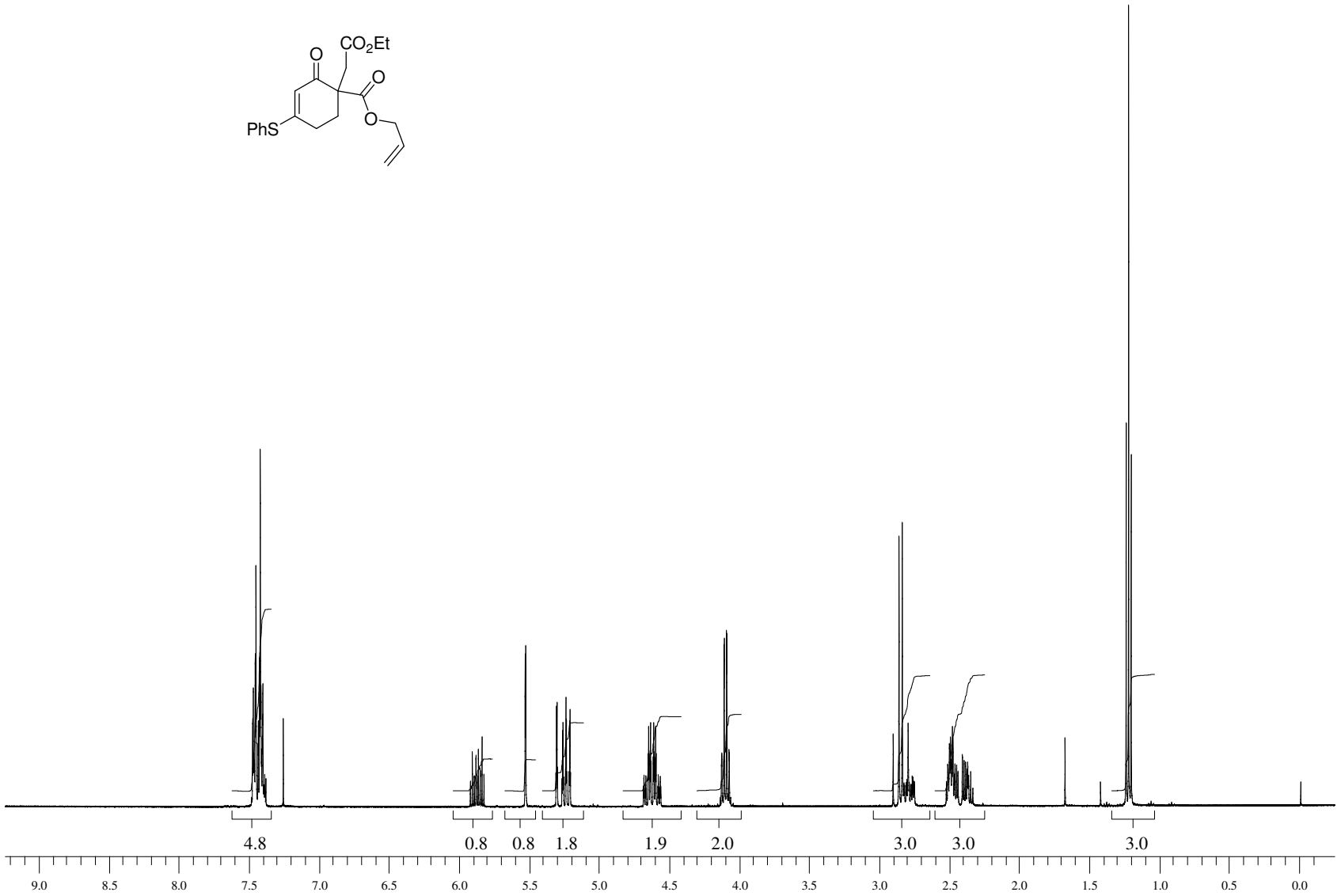
0.0


CO2Et
O
O
O
PhS
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1.8
1.9
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3.0
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6.5
6.0
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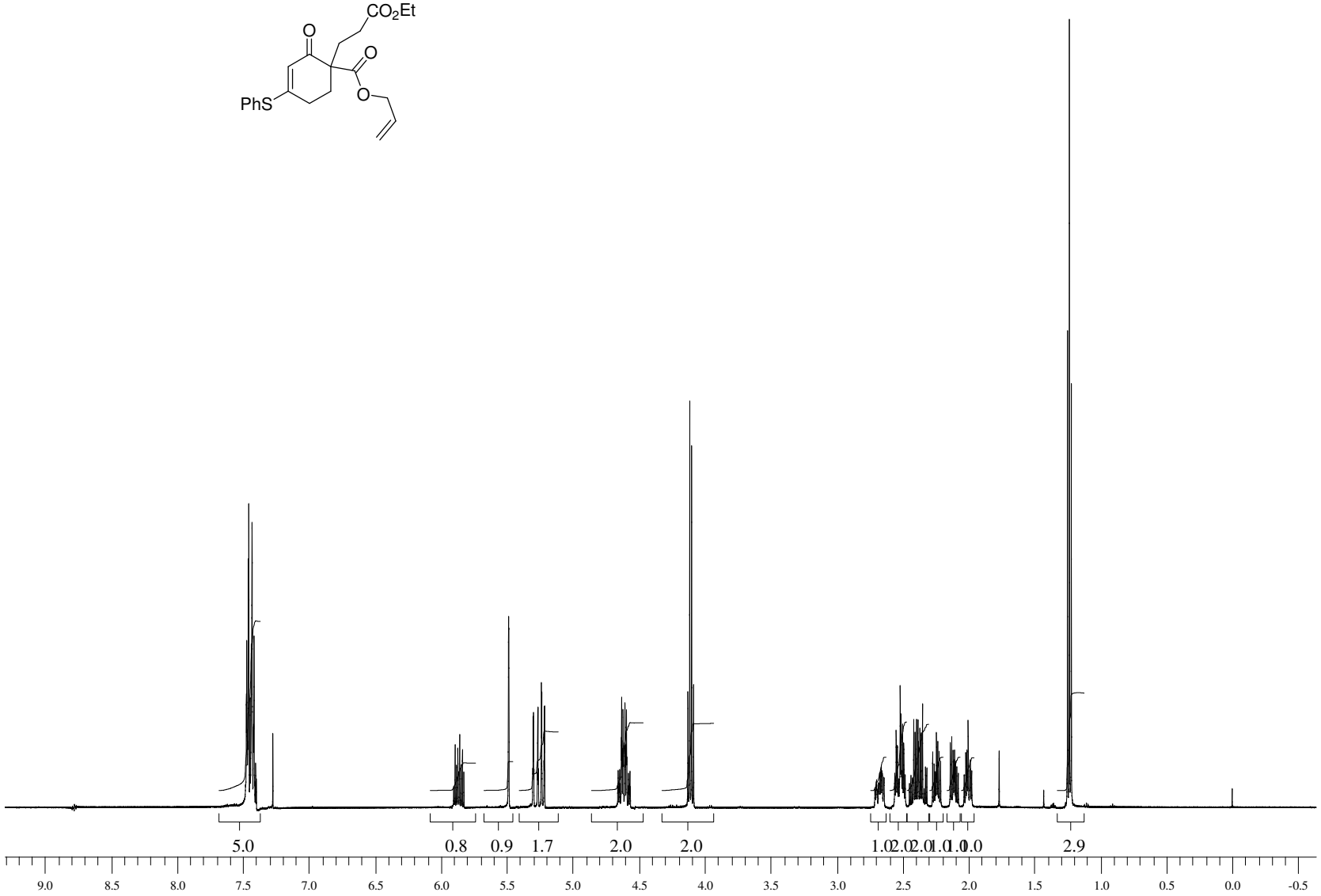
CO2Et
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O
O
PhS
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0.9
1.7
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2.0
2.0
1.0
1.0
2.9
9.0
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8.0
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6.0
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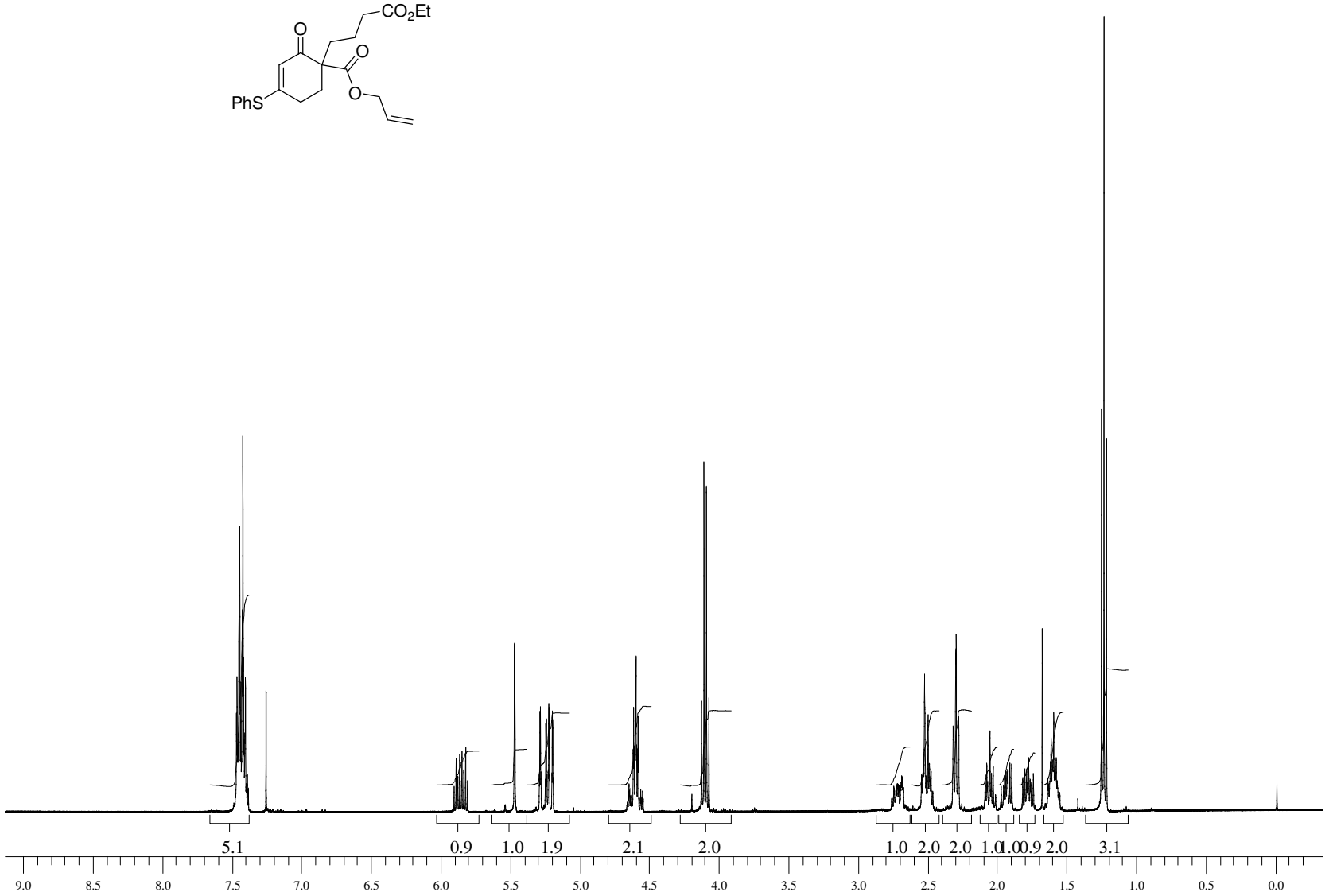
CO2Et
O
O
O
PhS
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1.0
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2.0
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7.0
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6.0
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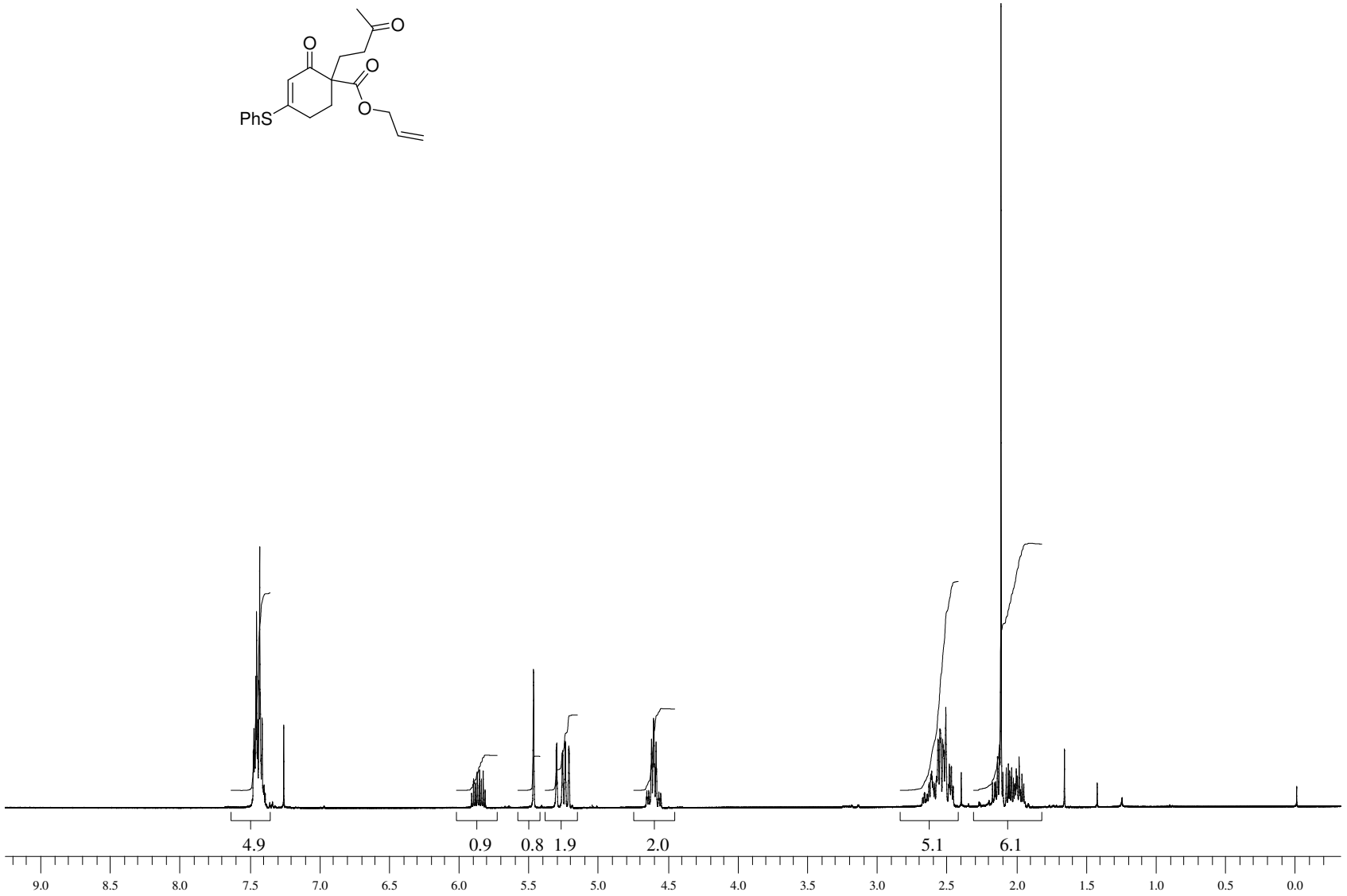
O
O
O
O
PhS
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2.0
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6.1
9.0
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8.0
7.5
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6.5
6.0
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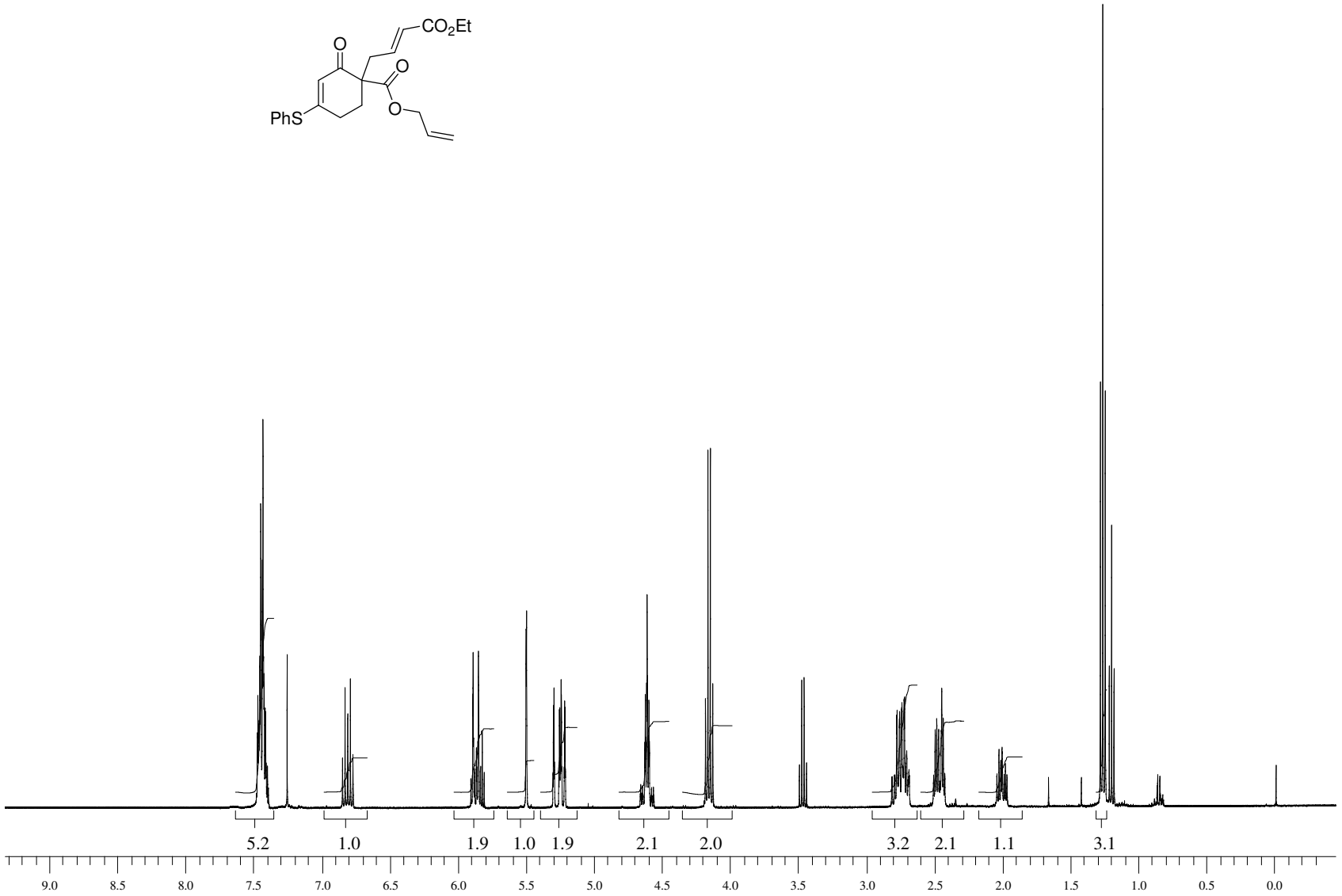
CO2Et
O
O
O
PhS
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3.1
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7.5
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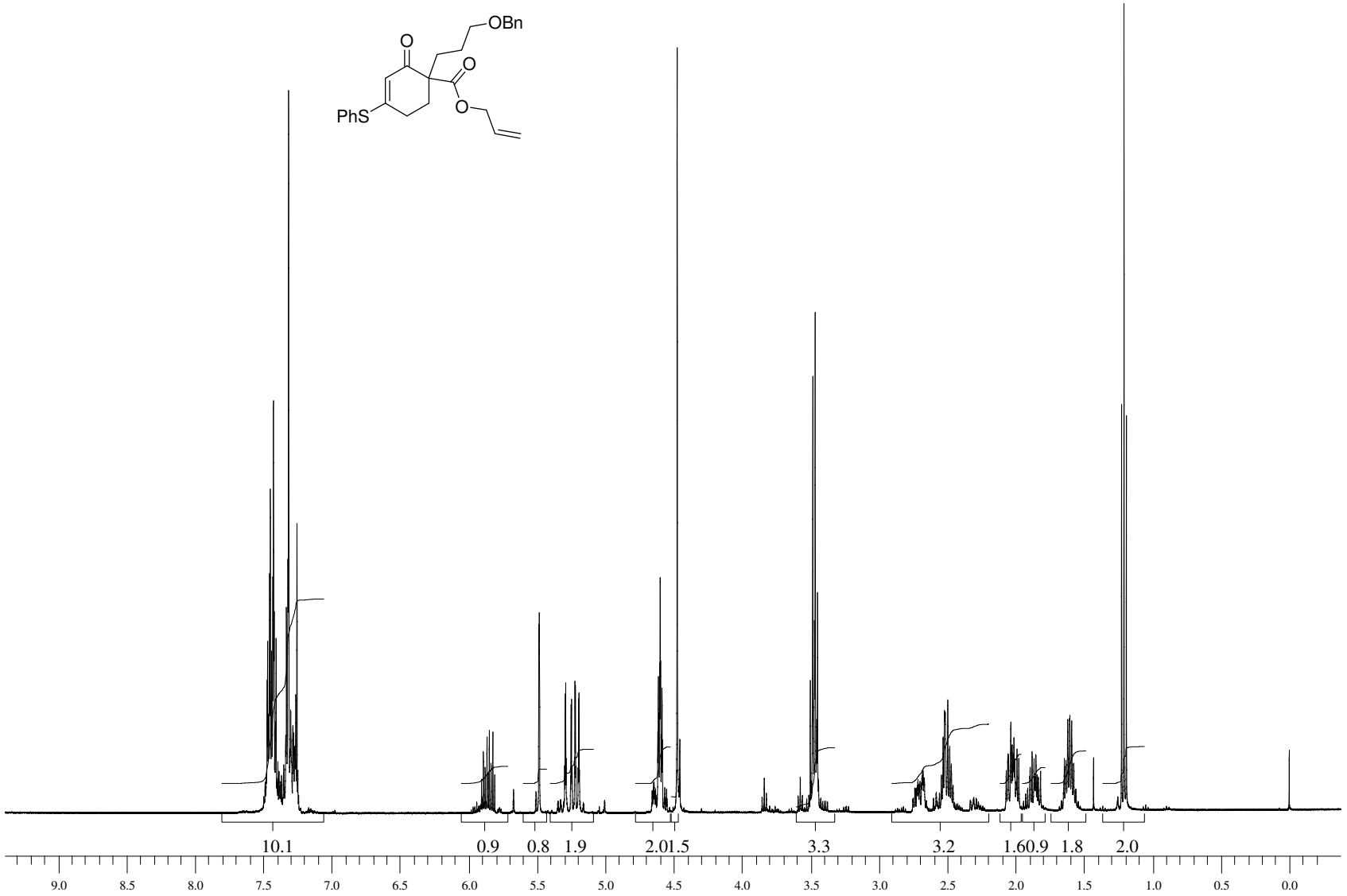
OBn
O
O
O
PhS
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2.01.5
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3.2
1.60.9
1.8
2.0
9.0
8.5
8.0
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7.0
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6.0
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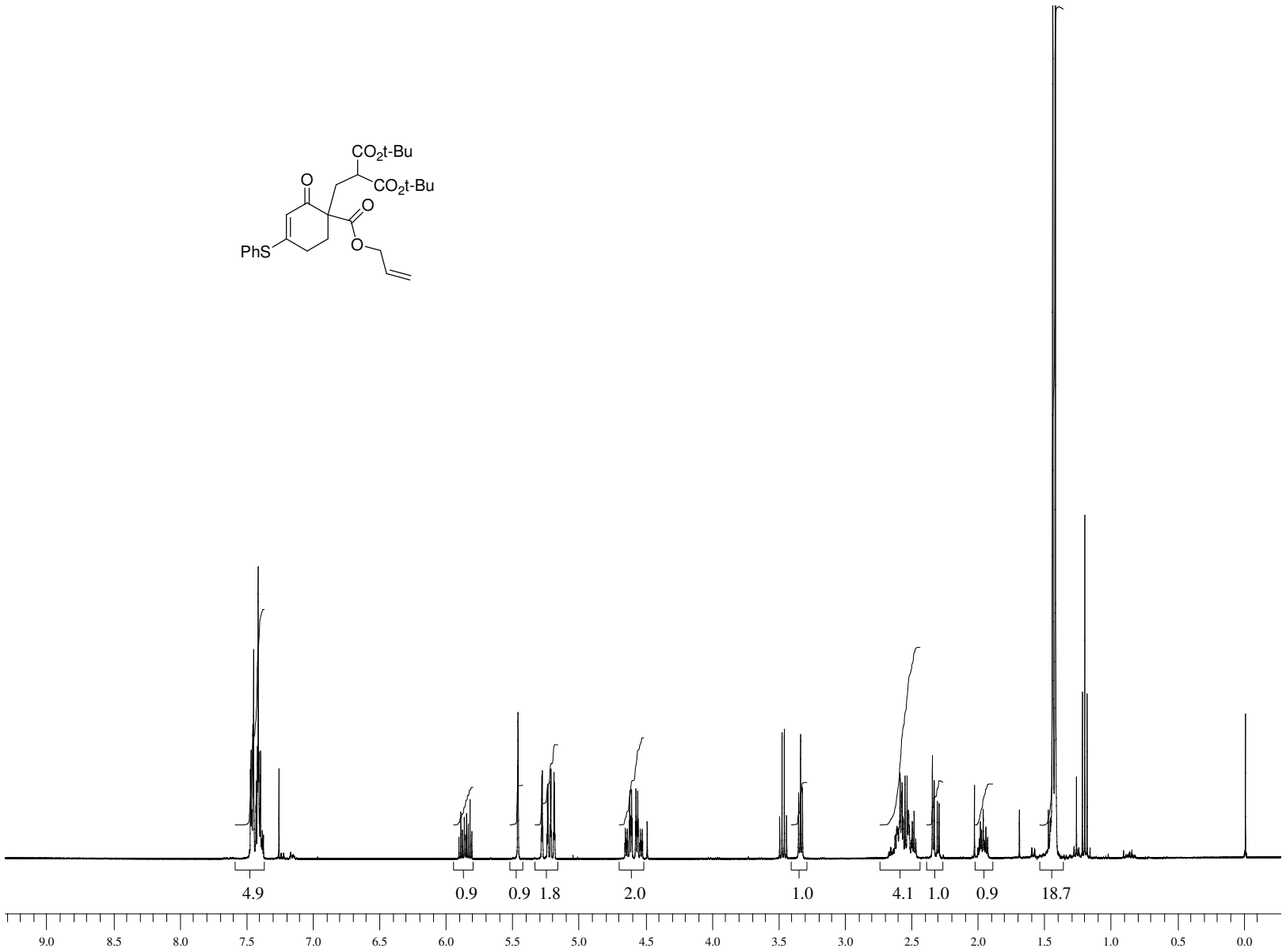
CO2t-Bu
CO2t-Bu
O
O
O
PhS
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1.0
0.9
18.7
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6.5
6.0
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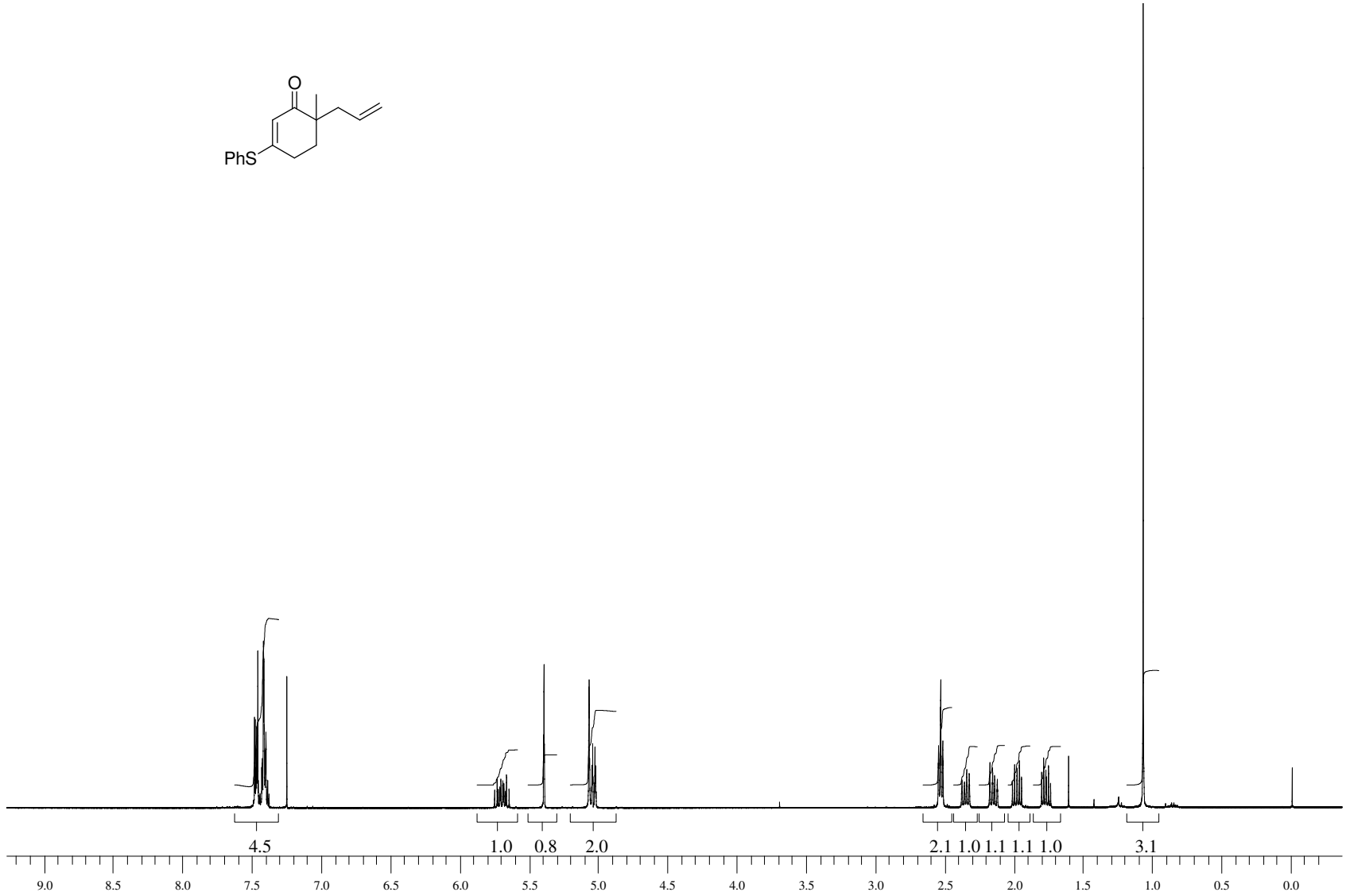
O
PhS
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2.1
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1.1
1.1
1.0
3.1
9.0
8.5
8.0
7.5
7.0
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6.0
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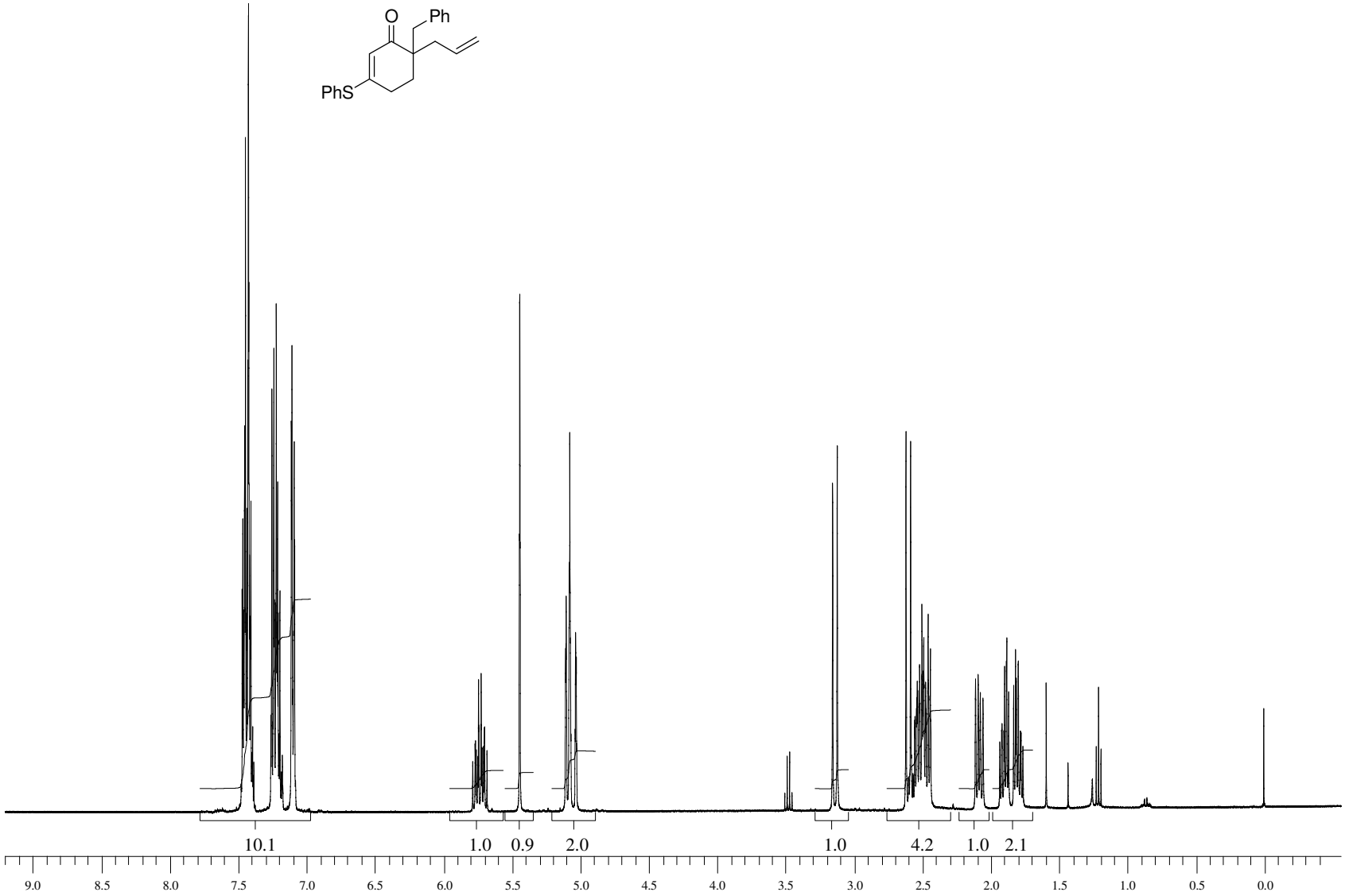
O
Ph
PhS
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2.1
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8.5
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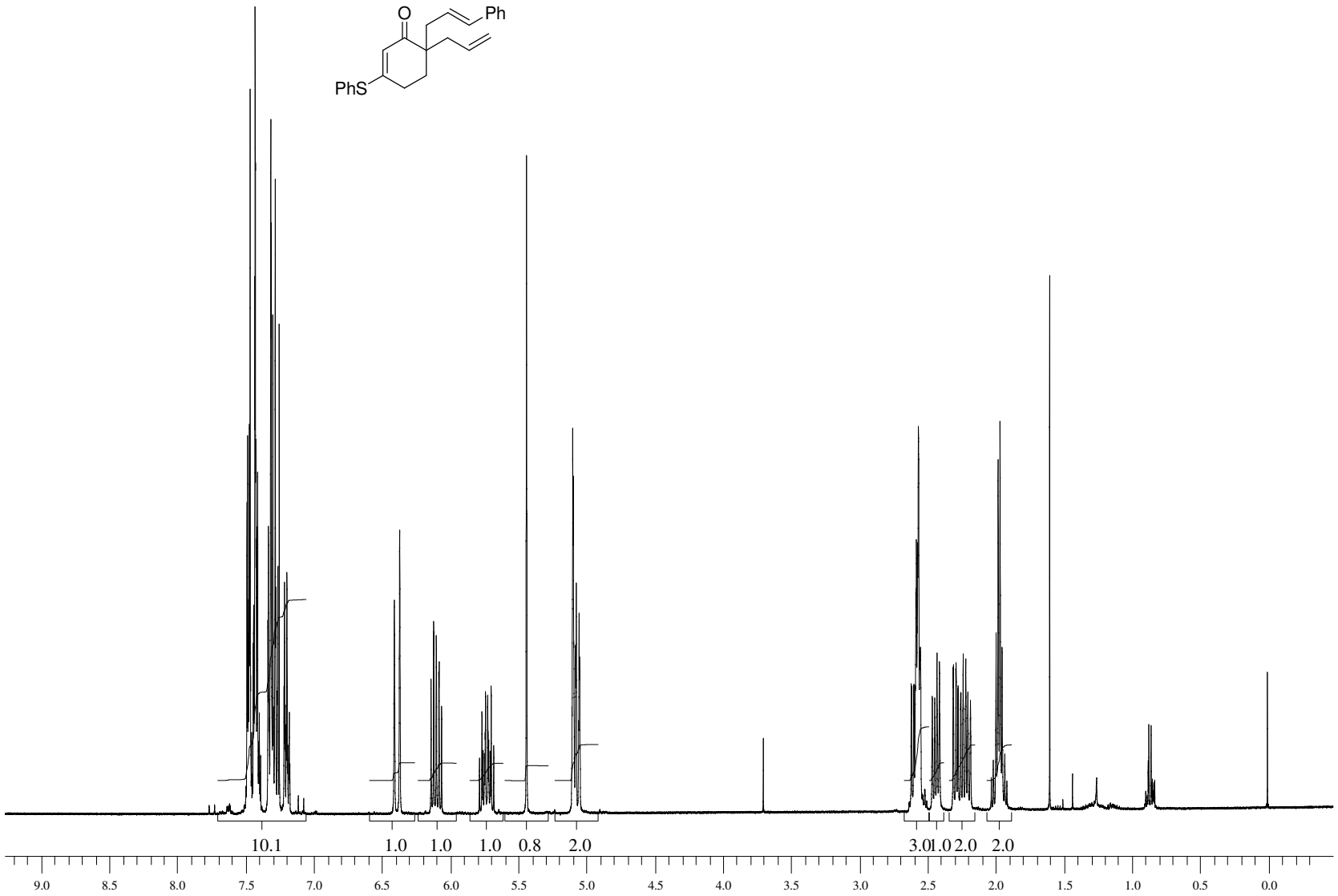
O
Ph
PhS
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9.0
8.5
8.0
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7.0
6.5
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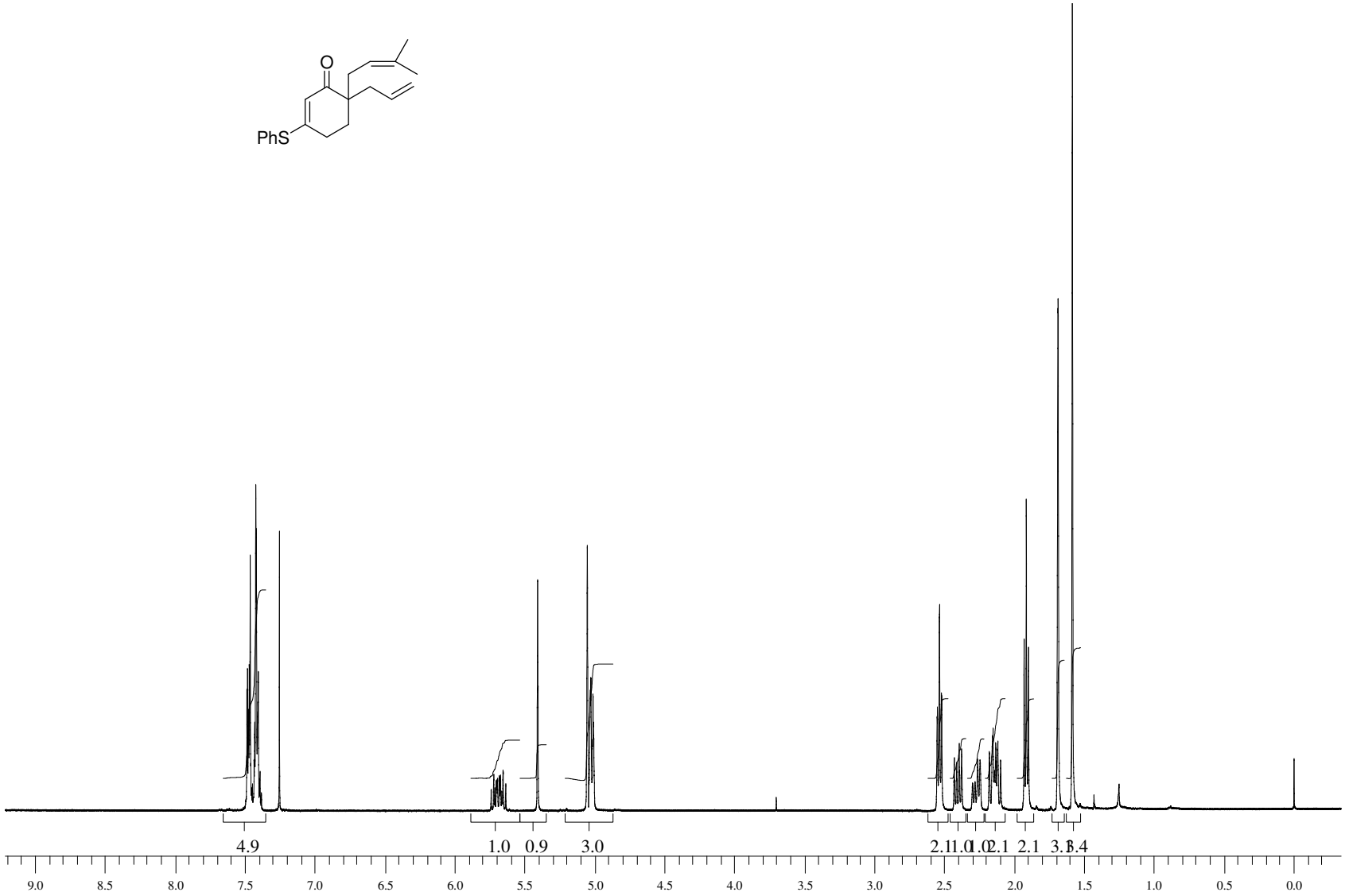
O
PhS
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1.0
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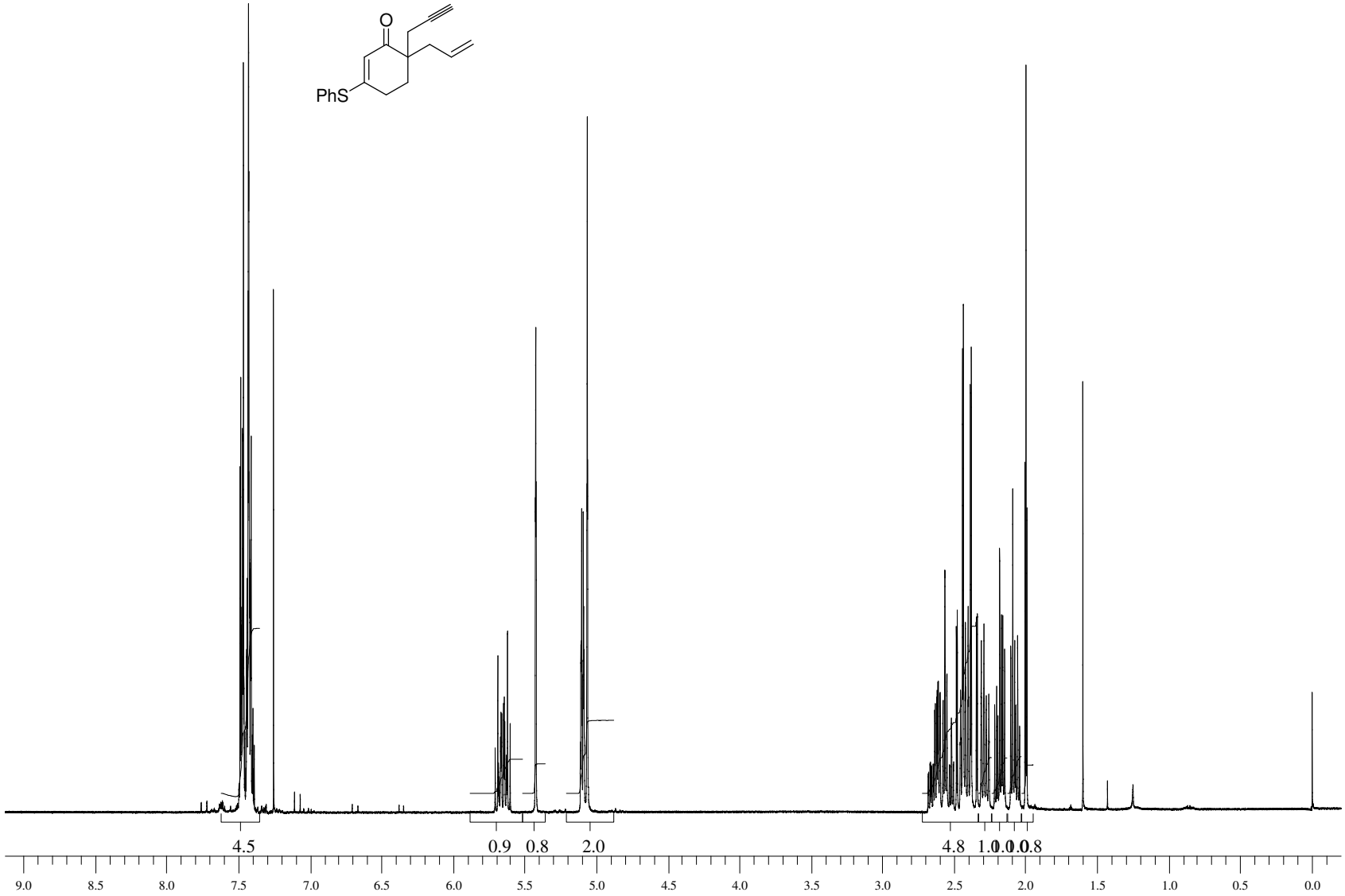
O
PhS
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4.8
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9.0
8.5
8.0
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6.5
6.0
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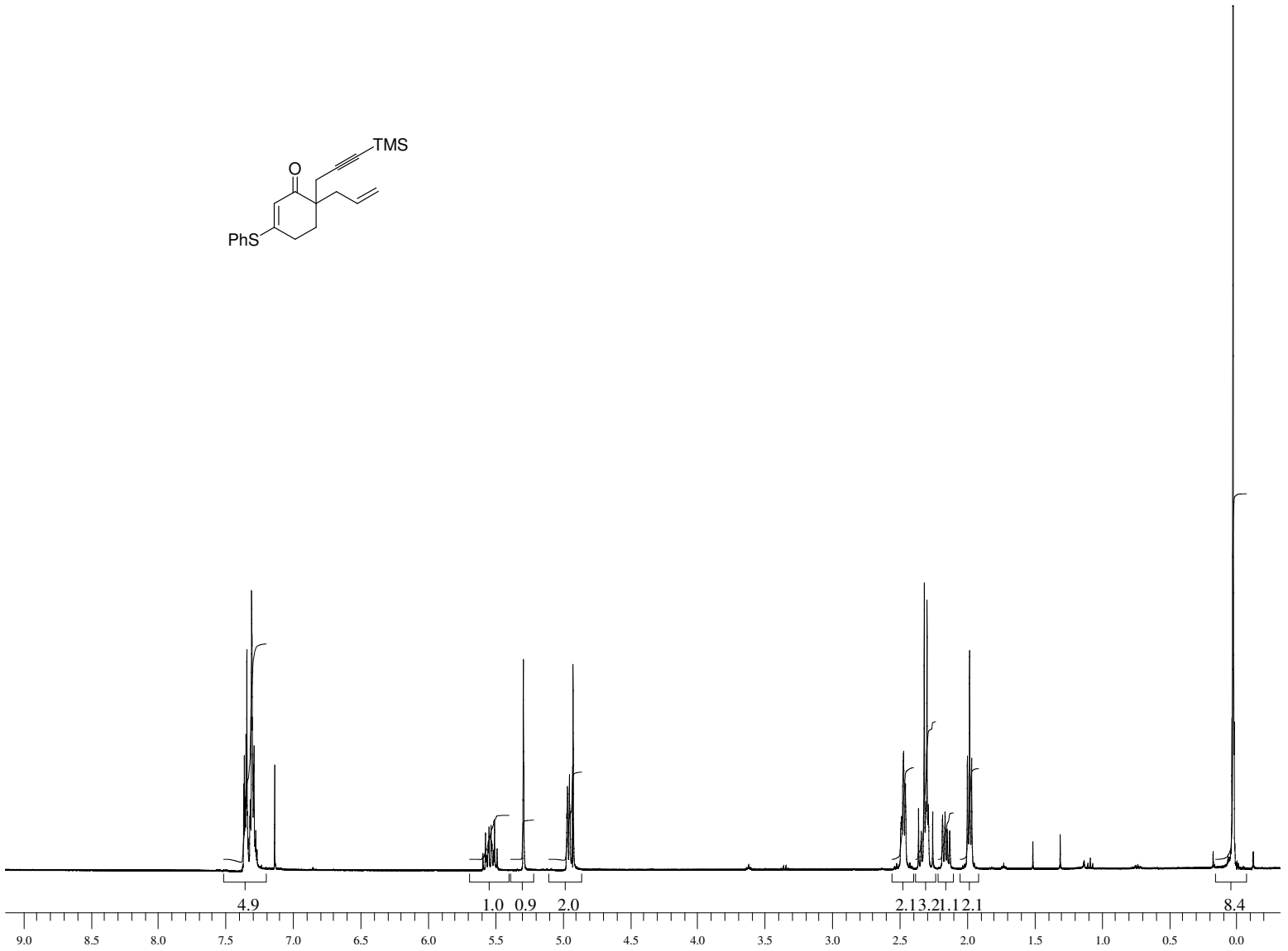
TMS
O
PhS
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2.1
8.4
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6.5
6.0
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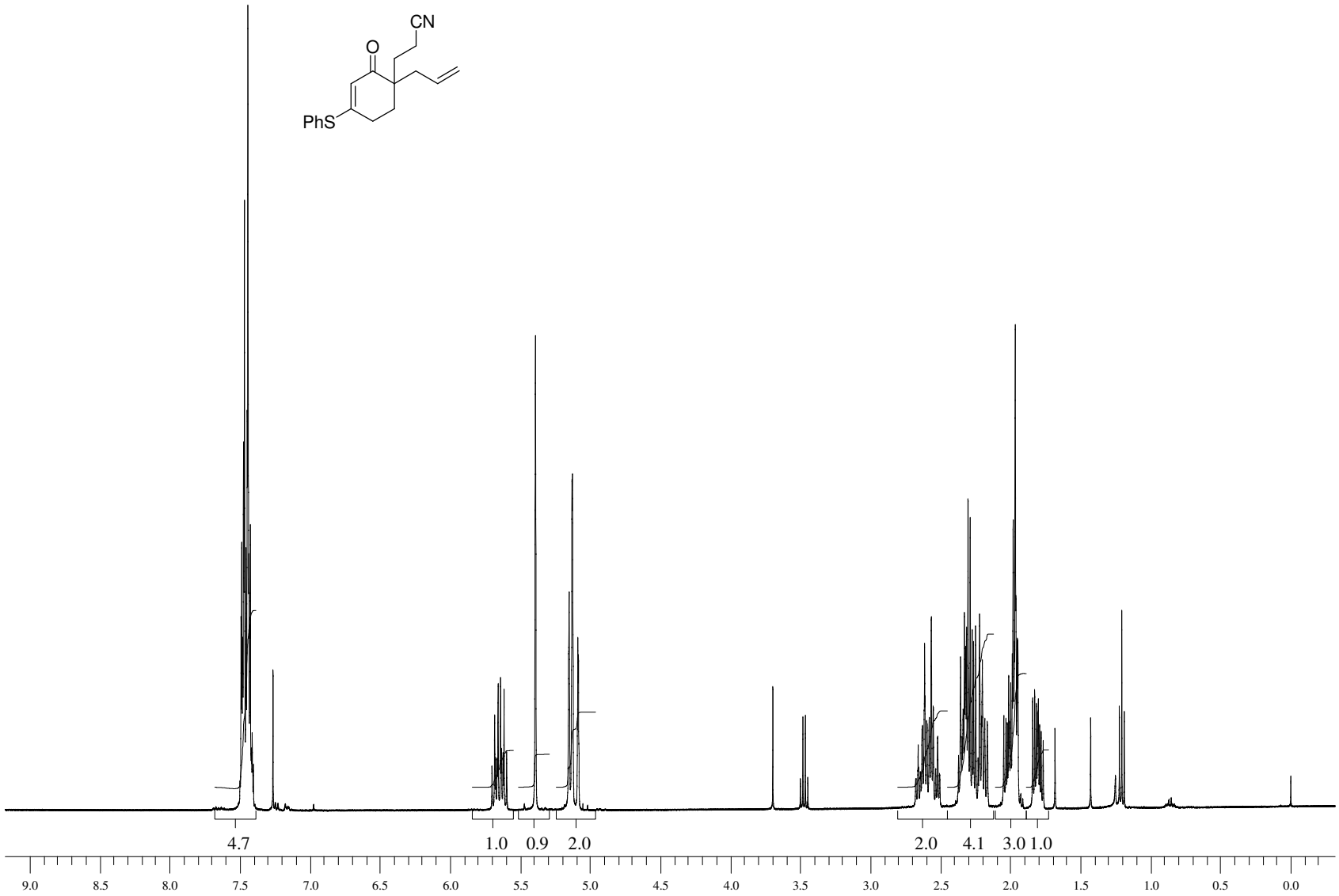
CN
O
PhS
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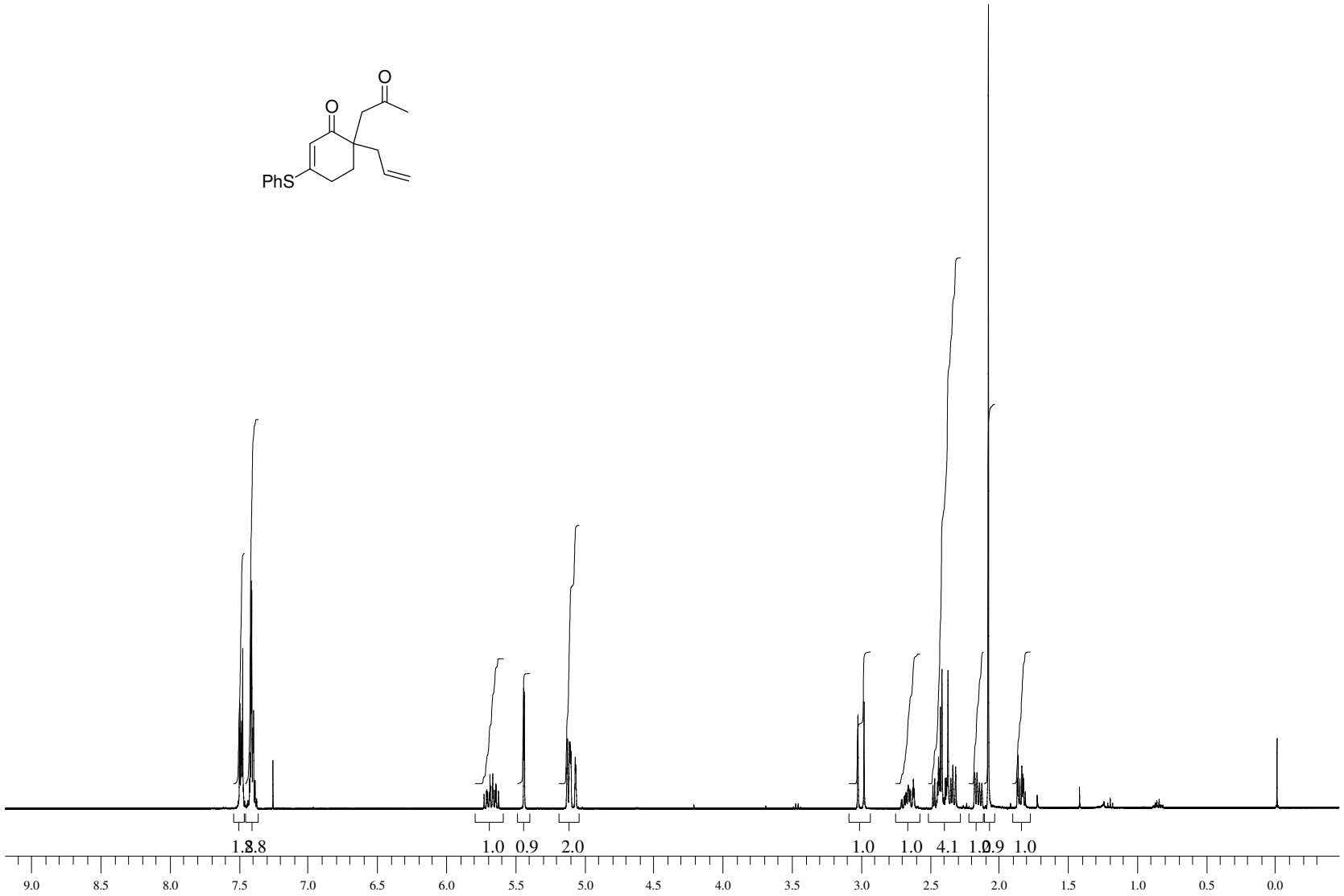
O
O
PhS
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1.0
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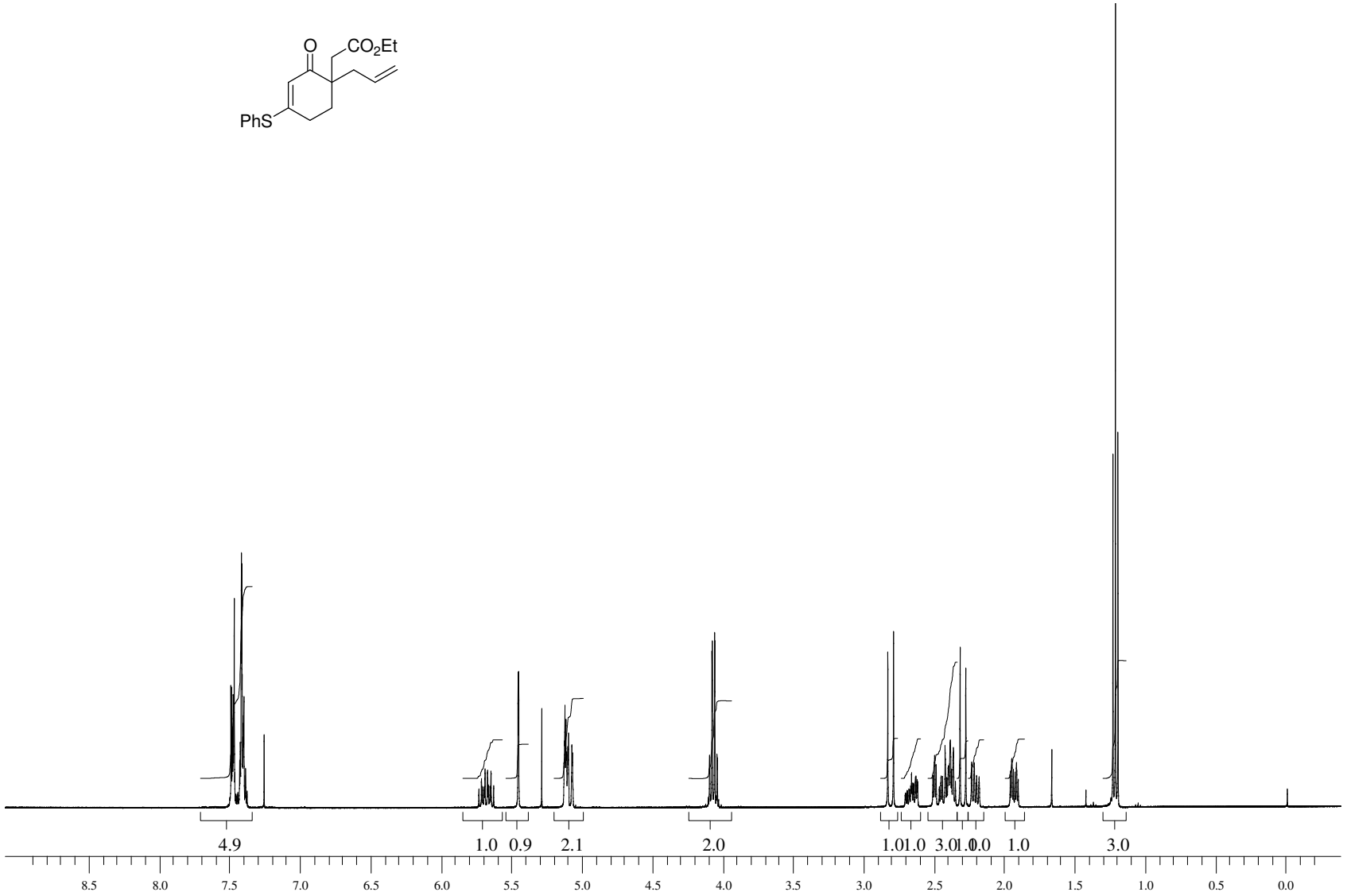
O
CO2Et
PhS
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1.0
0.9
2.1
2.0
1.0
1.0
3.0
1.0
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8.5
8.0
7.5
7.0
6.5
6.0
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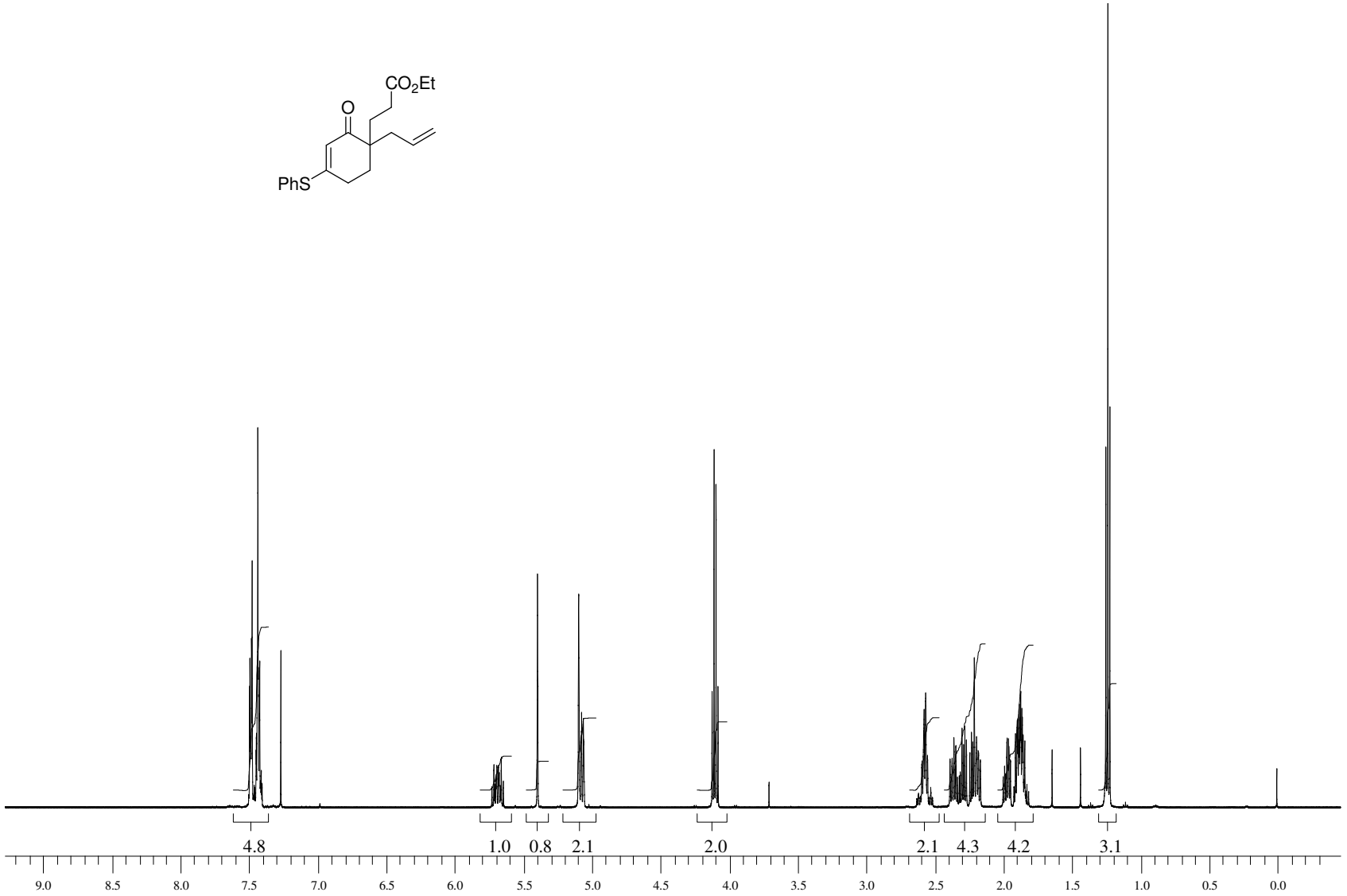
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O
PhS
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2.1
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4.2
3.1
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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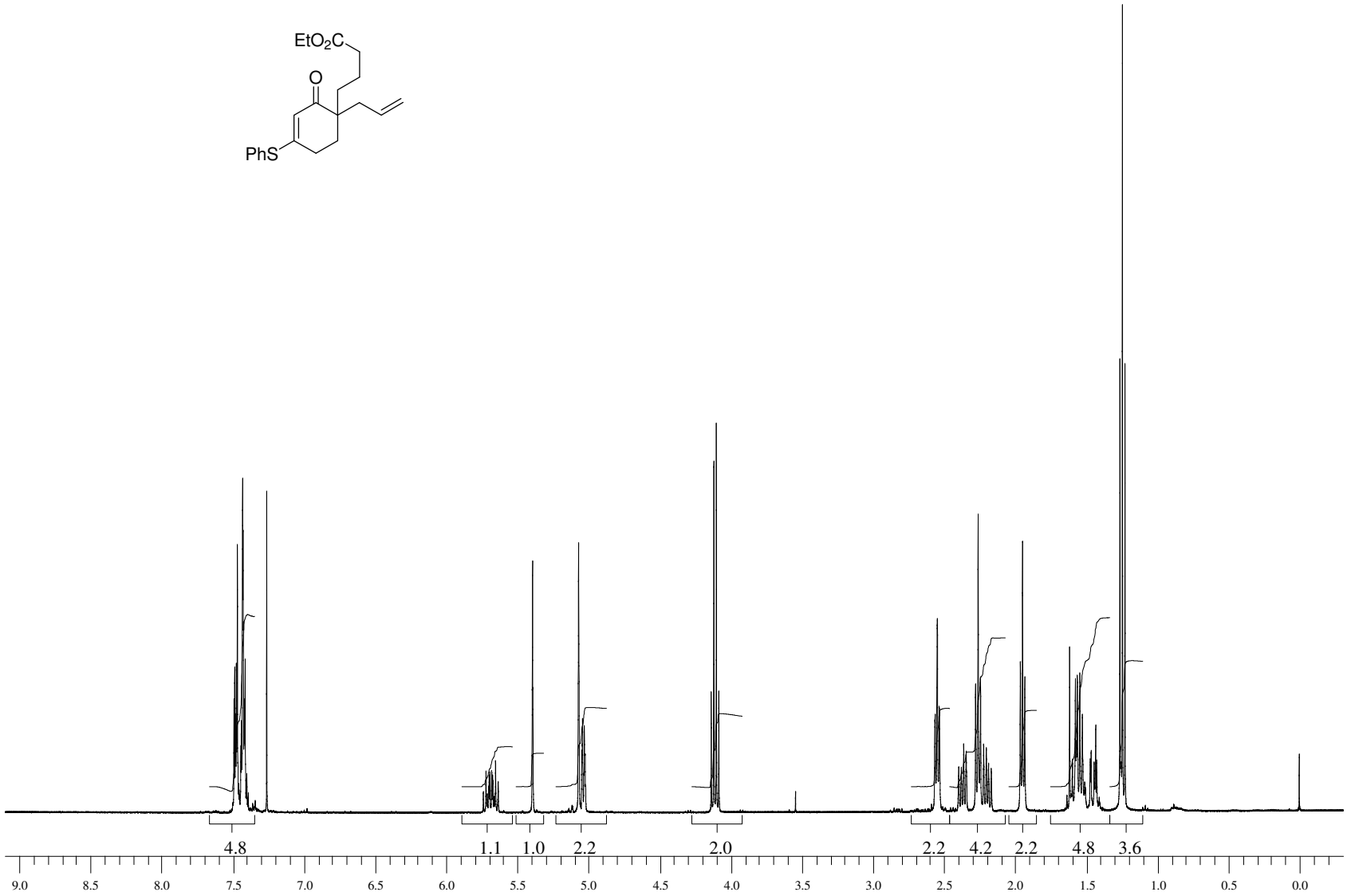
EtO2C
O
PhS
4.8
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1.0
2.2
2.0
2.2
4.2
2.2
4.8
3.6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
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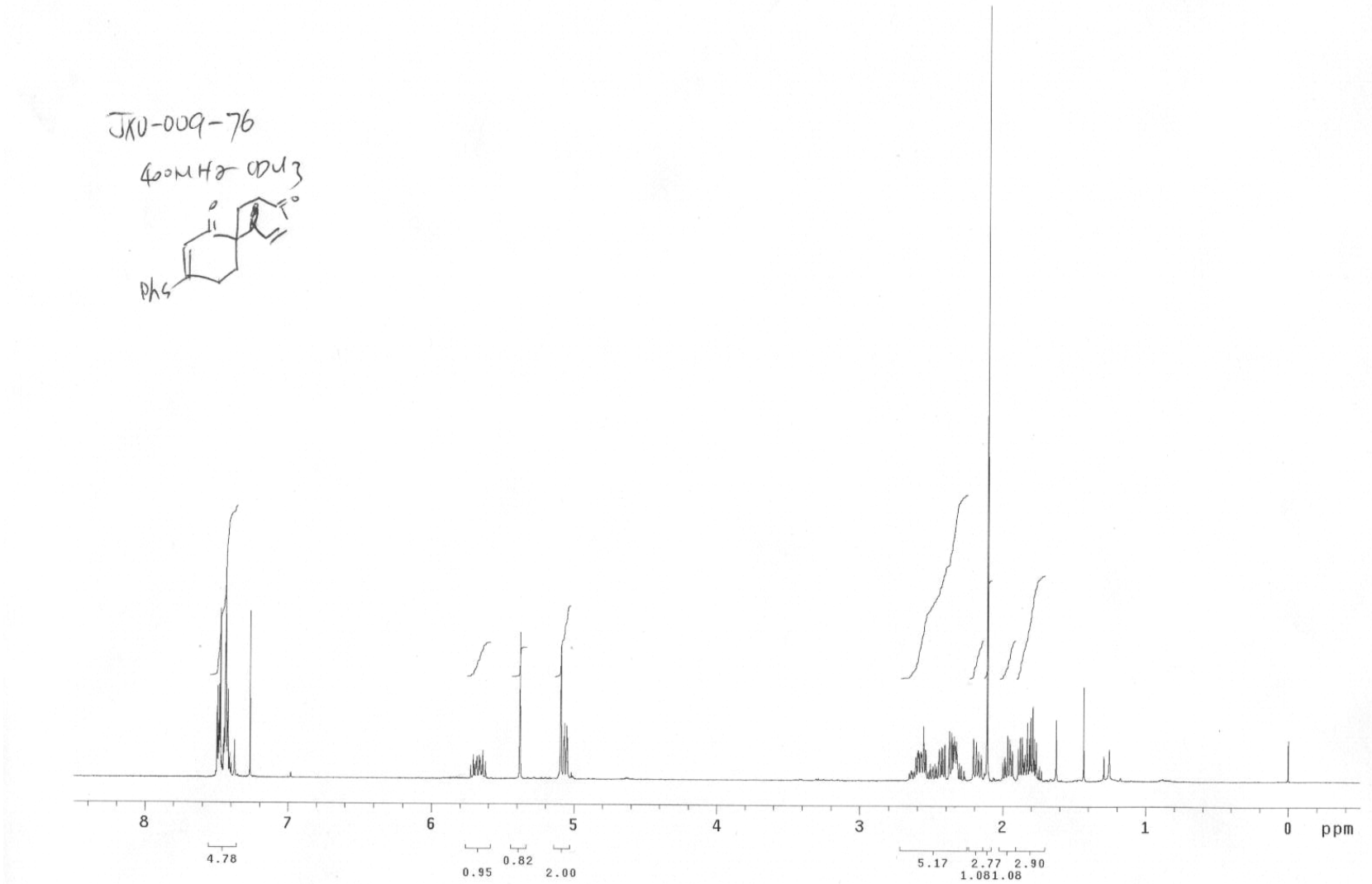
JKU-009-76
400MHz CDCl3
Ph
8
7
6
5
4
3
2
1
0
ppm
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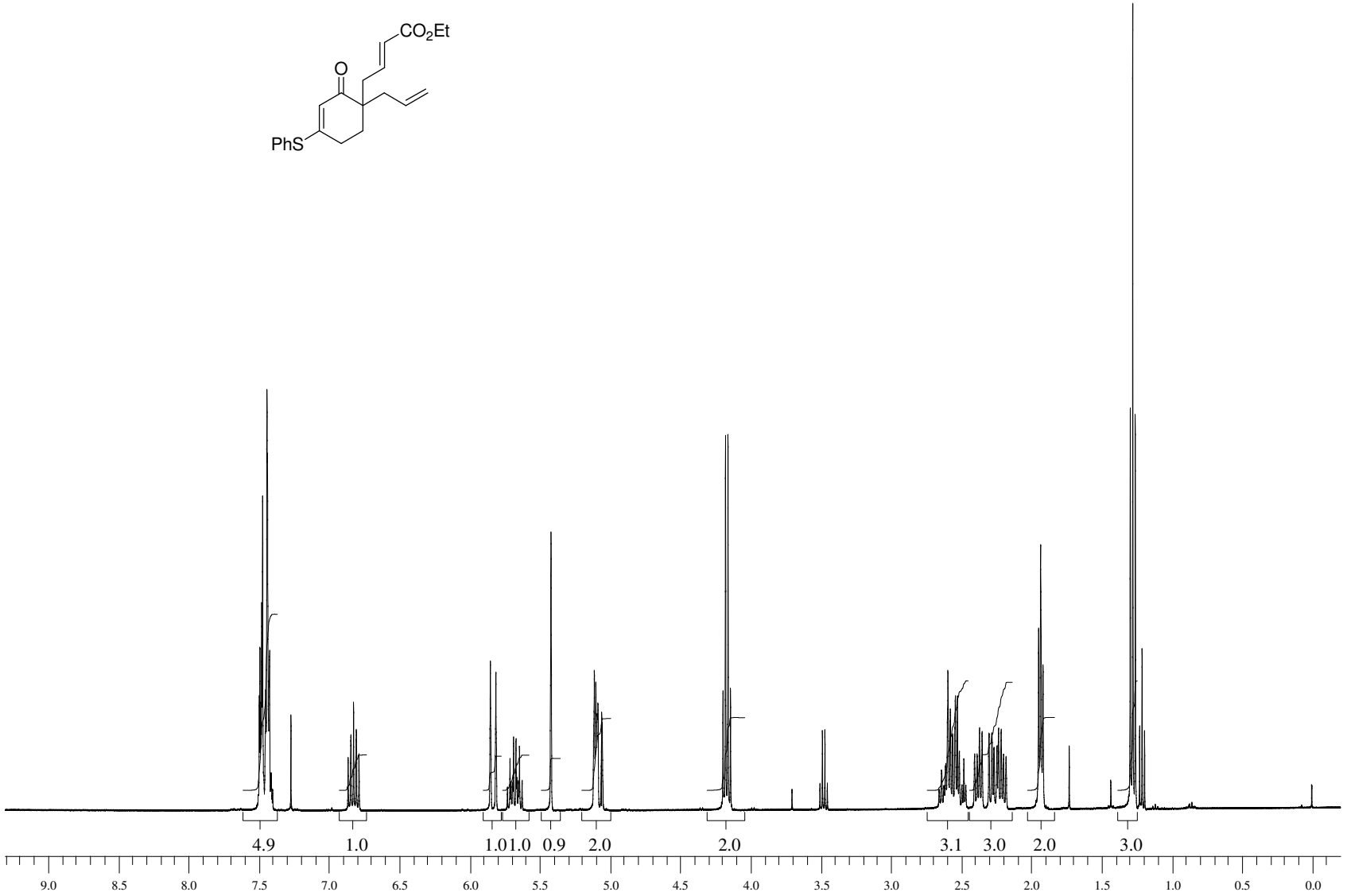
0.95
0.82
2.00
5.17
2.77
2.90
1.08
1.08


CO2Et
O
PhS
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1.01.0
0.9
2.0
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3.1
3.0
2.0
3.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
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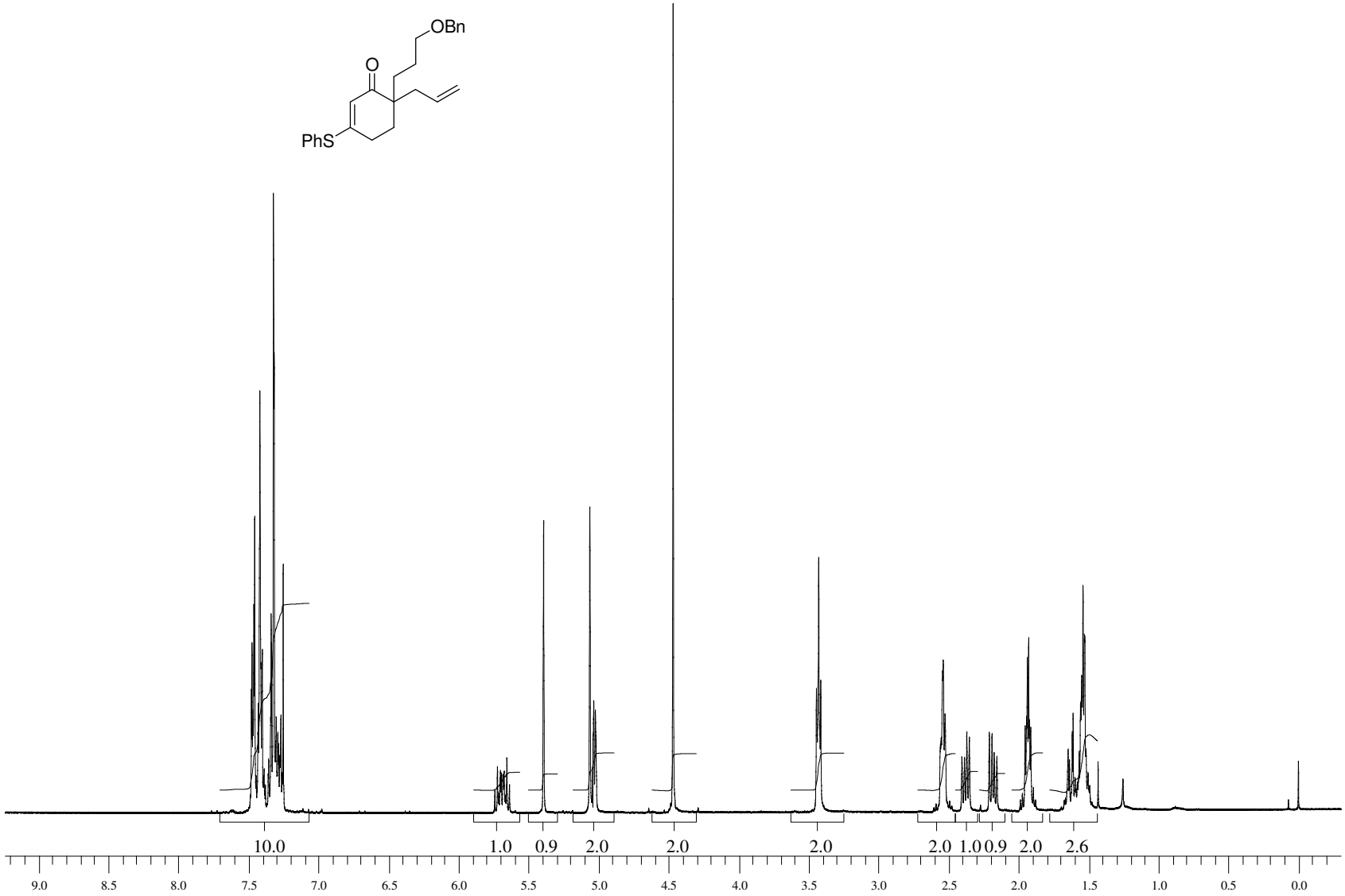
2.0
1.5
1.0
0.5
0.0


OBn
O
PhS
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1.0
0.9
2.0
2.0
2.0
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1.0
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2.0
2.6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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3.0
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2.0
1.5
1.0
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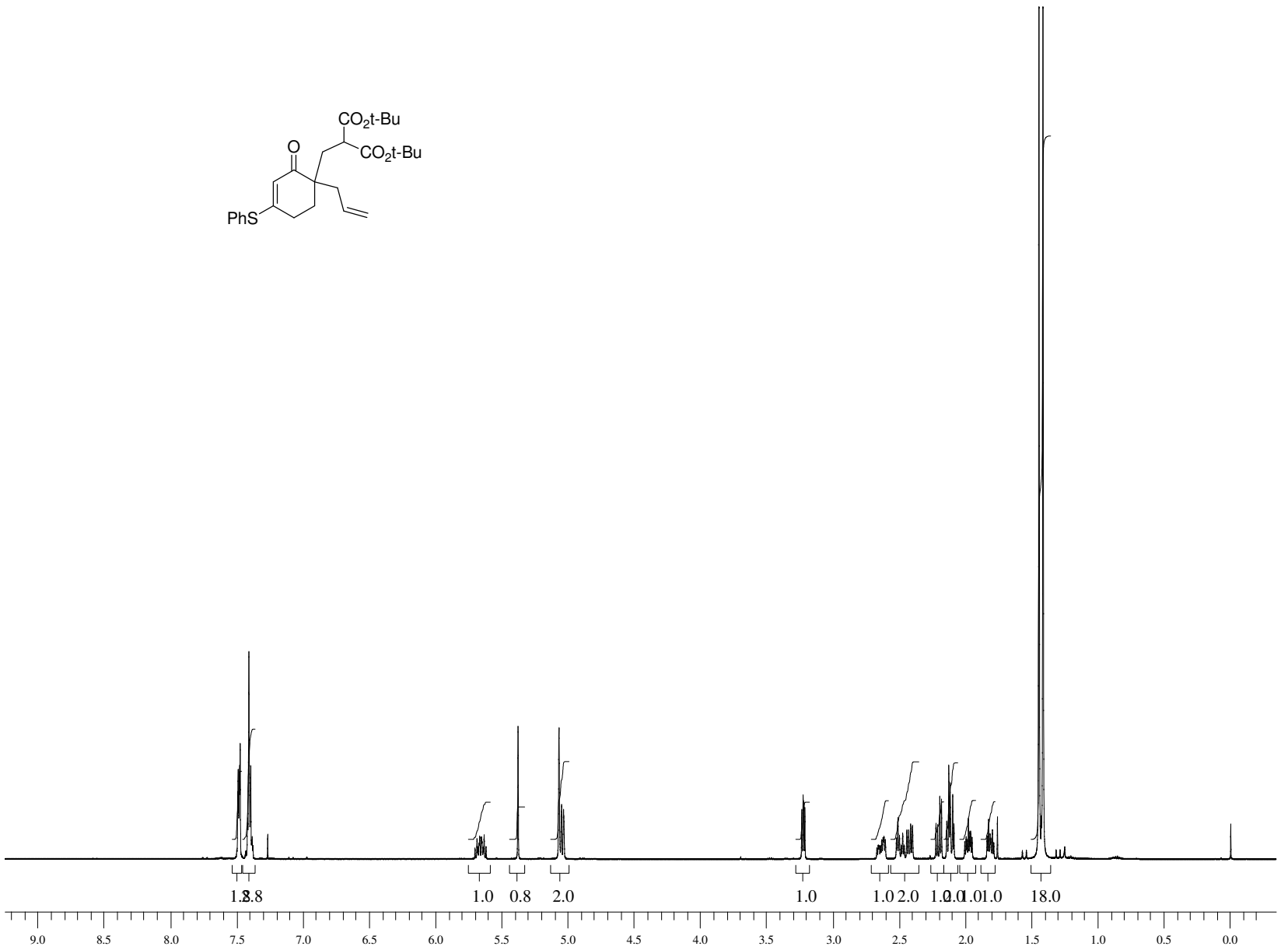
CO2t-Bu
CO2t-Bu
O
PhS
1.2
2.8
1.0
0.8
2.0
1.0
1.0
2.0
1.0
1.0
1.0
1.0
18.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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3.0
2.5
2.0
1.5
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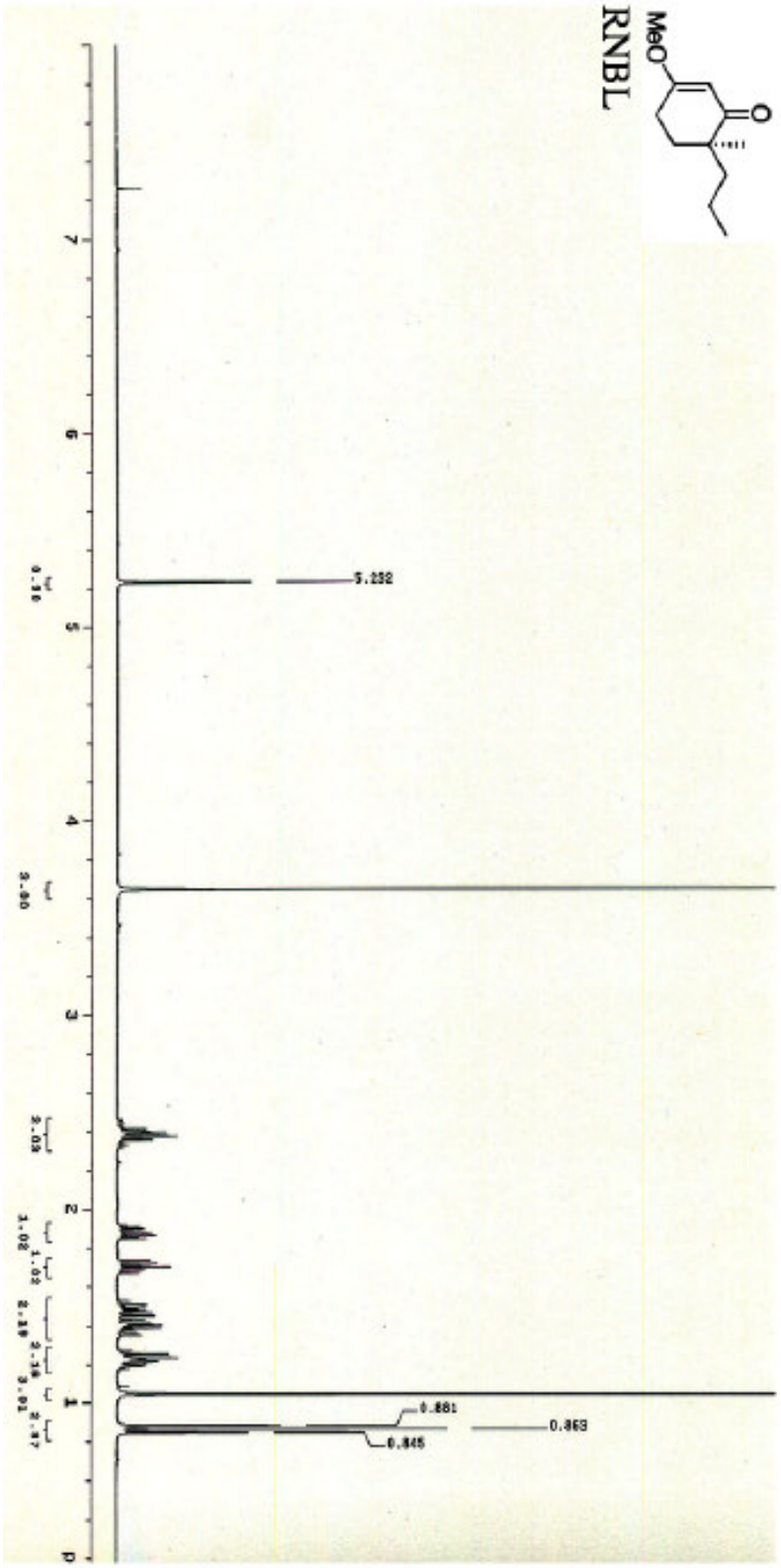
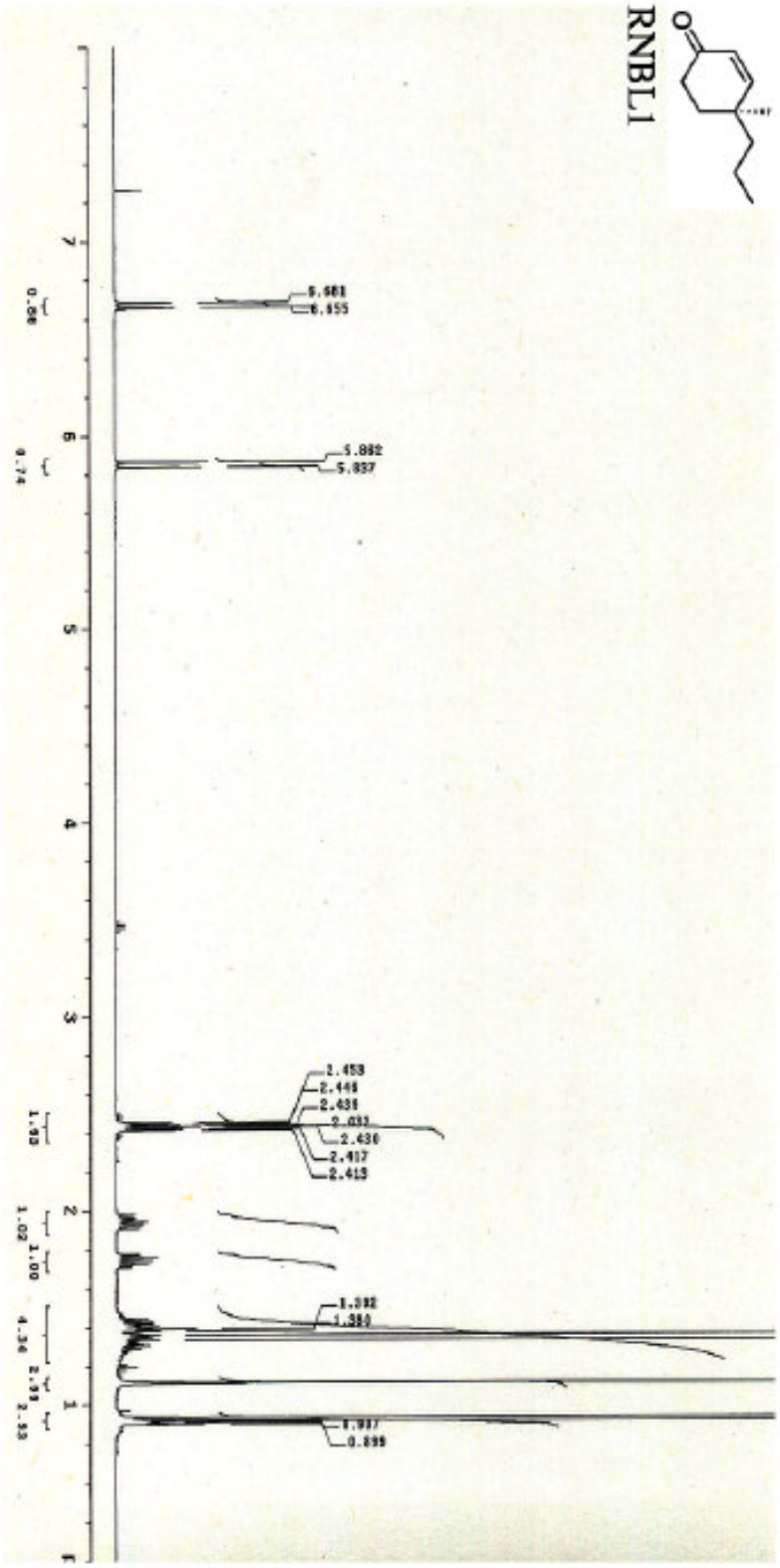
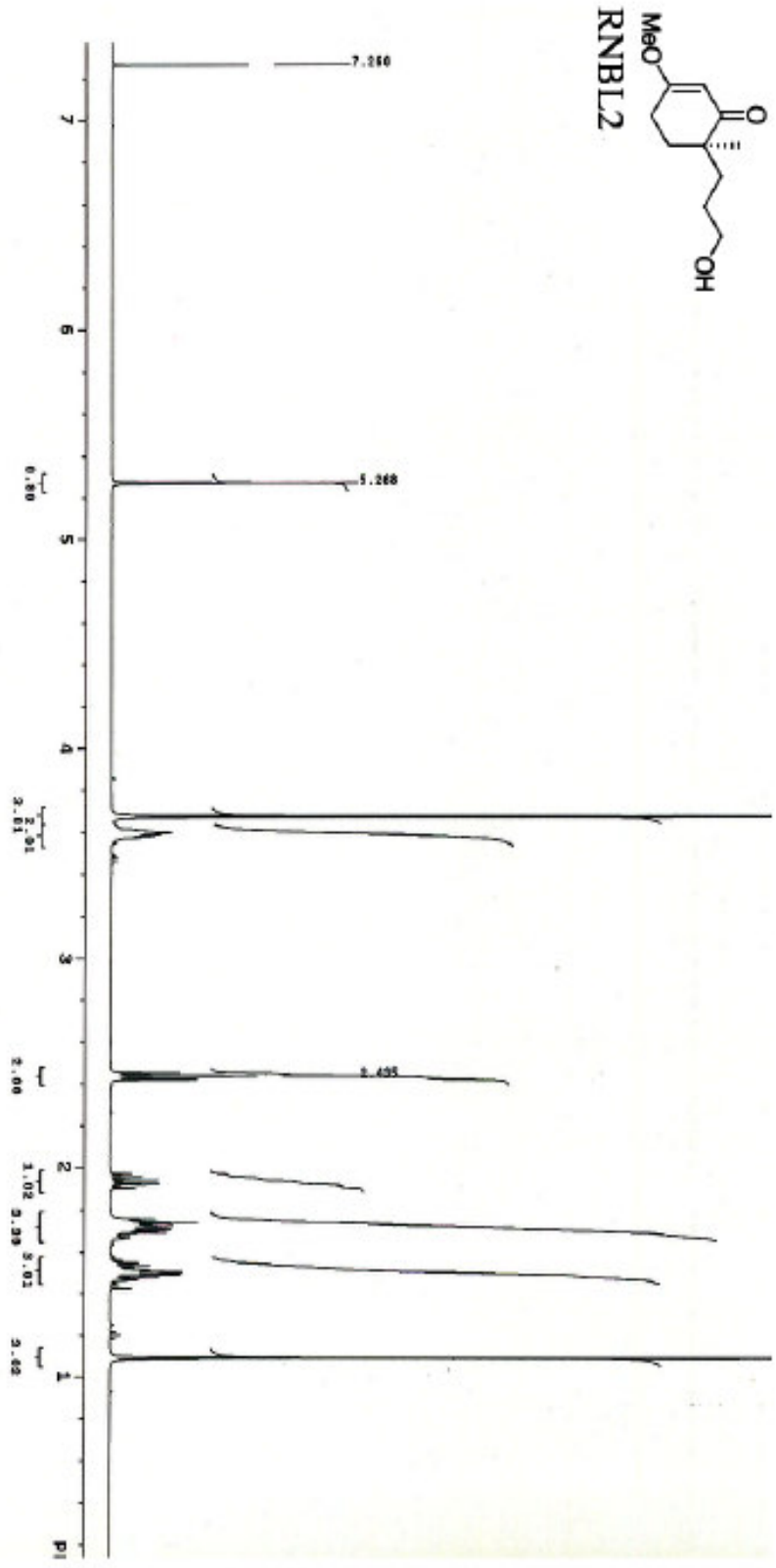
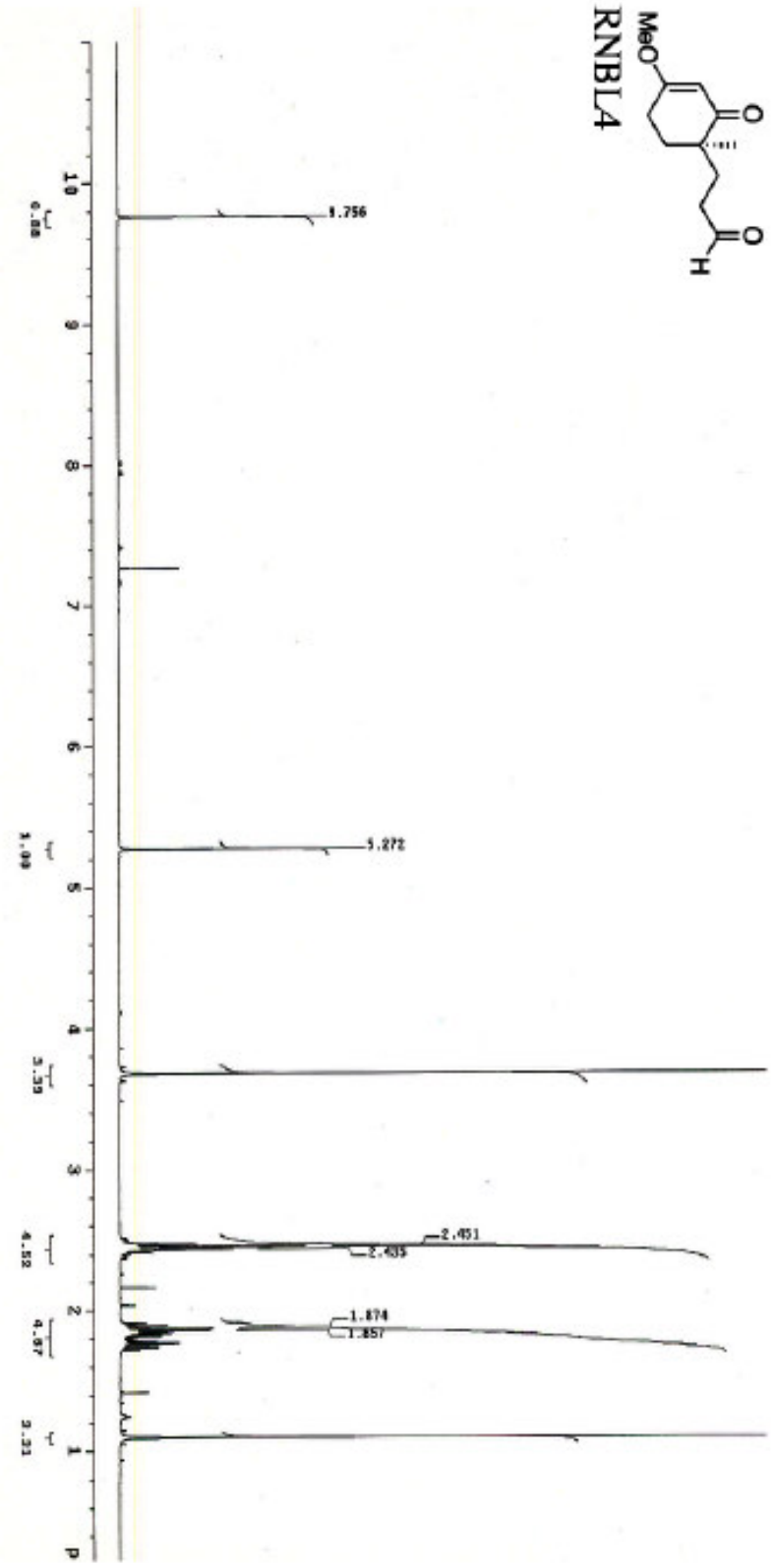
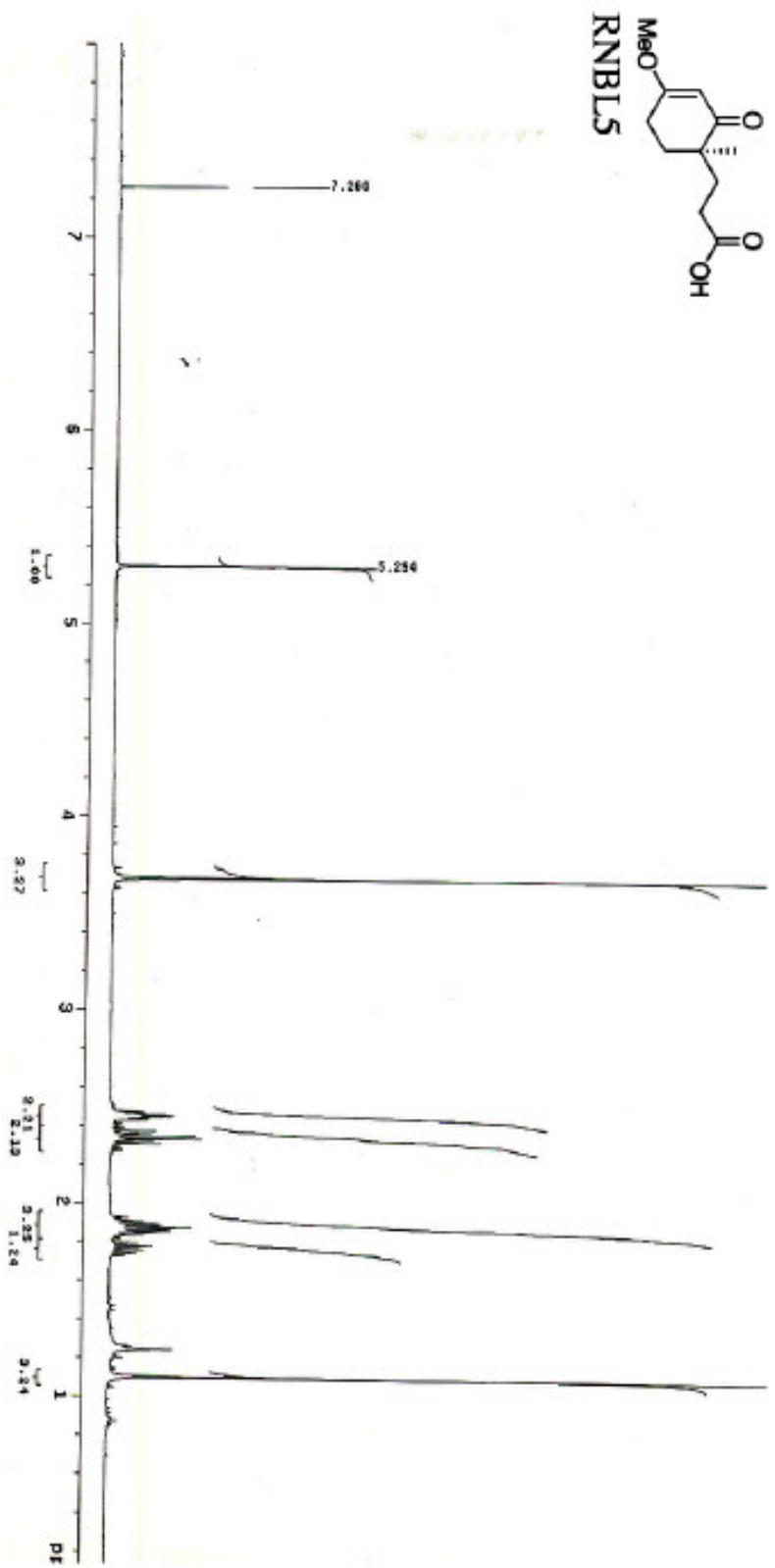
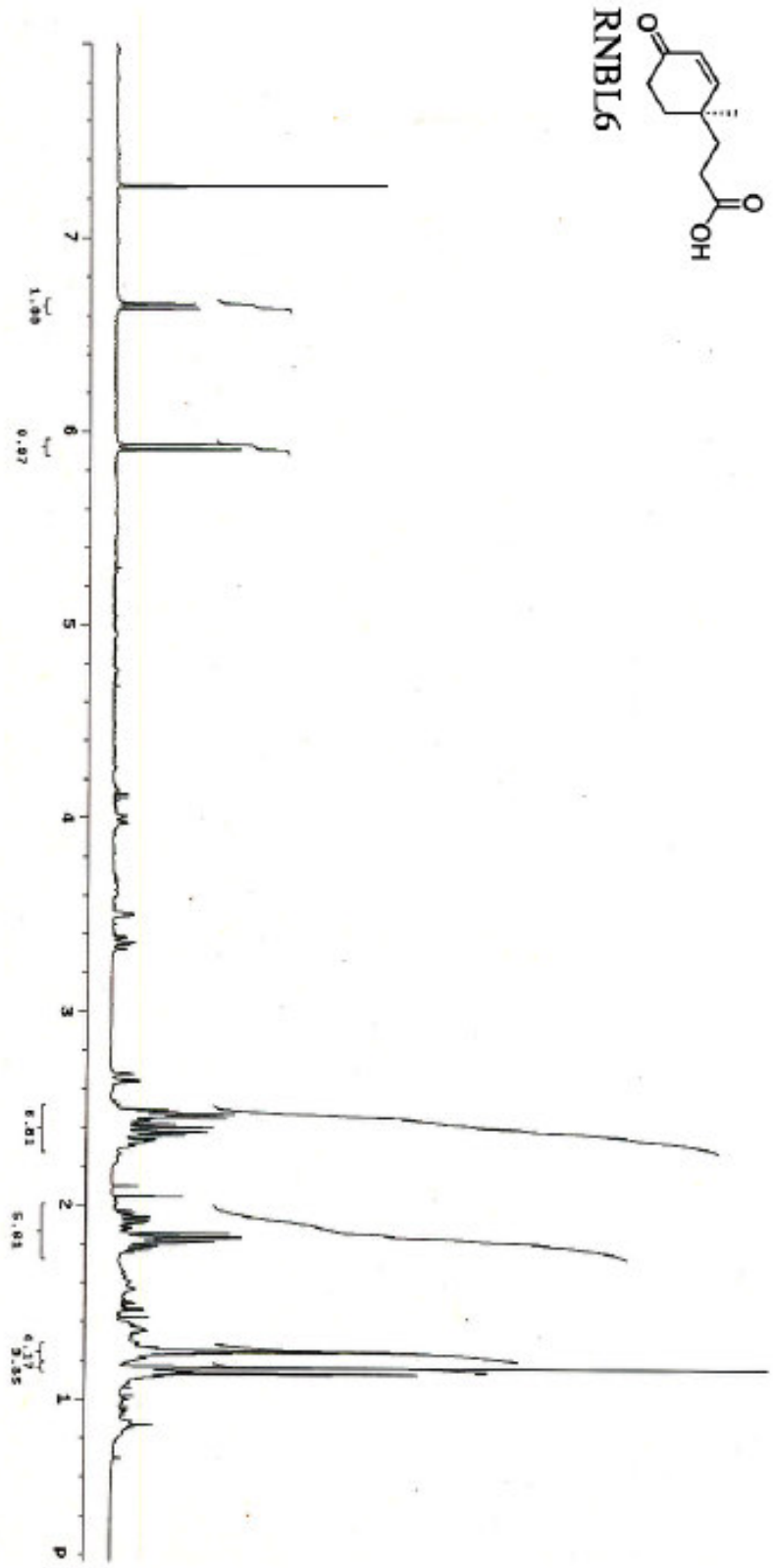

RNBL
MeO
O
5.232
0.881
0.869
0.845

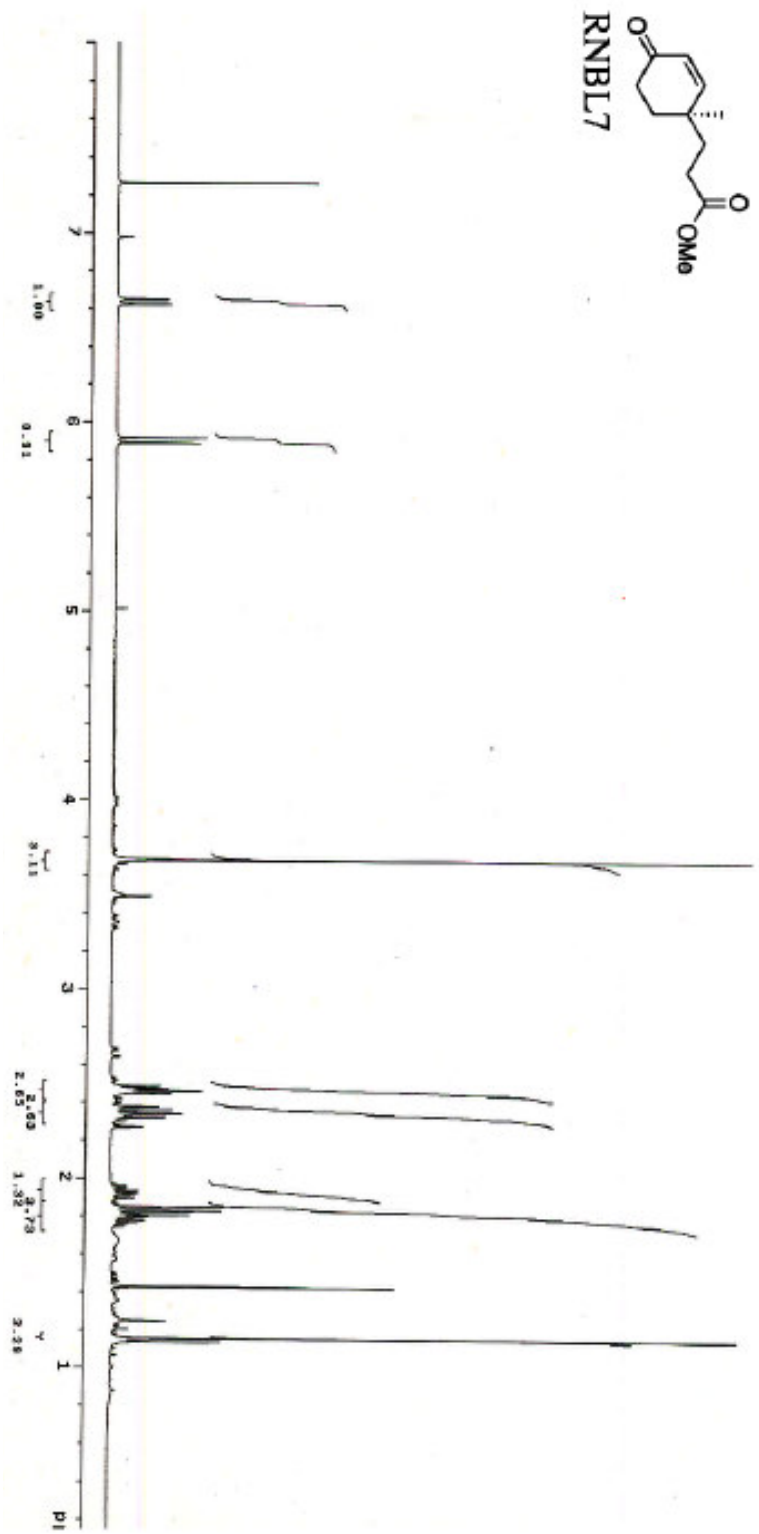

RNBL1
5.861
5.855
5.882
5.837
2.453
2.446
2.436
2.033
2.430
2.417
2.413
1.382
1.360
1.027
0.899


RNBL2
MeO
O
OH
7.250
5.268
3.435
0.80
2.91
2.81
2.00
1.02
3.39
3.01
3.02
7
6
5
4
3
2
1
pi


RNBL4
MeO
O
O
H
9.756
5.272
2.451
2.435
1.874
1.857


RNBL5
MeO
O
O
OH
7.260
5.256
1.00
3.07
2.01
2.19
3.05
1.24
3.24
7
6
5
4
3
2
1
PP


RNBL6
O
O
OH
7
6
5
4
3
2
1
0
1.00
0.97
3.03
5.03
3.35
5.17


RNBL7
O
O
OMe