SUPPORTING INFORMATION

Total Regio- and Diastereocontrol in the Aldol Reactions of Dienolborinates

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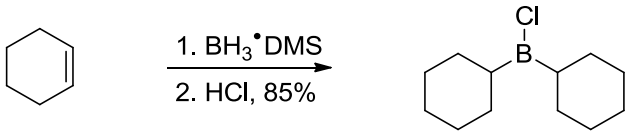
General Supporting Information

All reagents were purchased from Sigma-Aldrich, Fisher-Acros, Strem Chemical, or Alfa-Aesar, and were used without further purification unless otherwise noted. All solvents were distilled prior to use unless otherwise noted: DCM and Pentanes from CaH_2, Toluene from Na, and Et_2O and THF from Na/Benzophenone. All reactions were performed at room temperature and under a nitrogen atmosphere in either flame or oven-dried glassware unless otherwise noted. All TLC analysis was performed using 60Å, Glass-backed Thin-Layer Chromatography Plates (250 μm thickness, F-254 indicator). All solvent systems are given as volume : volume ratios. Flash chromatography was performed using 230-400 mesh, 60Å pore diameter flash chromatography gel. All chromatography elutions were gradient in nature, eluting first with hexanes, followed by incorporating more polar solvents as appropriate. Any volatile products were eluted with appropriate mixtures of Et_2O and pentanes. ^{1} H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded at room temperature, on either Varian INOVA 300 MHz, Bruker ARX400, or Bruker DRX500 spectrometers. Chemical shifts (δ values) are reported in parts per million, and are referenced to either the deuterated residual solvent peak, or to tetramethylsilane. ^{11}B, ^{19}F, and ^{31}P NMR are referenced internal to the spectrometer. Data are reported as: δ value, multiplicity, and integration, (s=singlet, d=doublet, t=triplet, q=quartet, p=pentet, h=hextet, g=heptet, br=broad). ^{1}H NMR was used as a measurement of the diastereomeric ratios of aldol products, and were made by comparing the relative integration values of the secondary vinylic protons of the respective aldol products. Products which were rotameric and displayed such peaks in the NMR spectra were confirmed as such by both VT ^{1}H NMR and 1D-NOE measurements. Optical rotations were measured on a Perkin Elmer 341 Polarimeter, and are reported against the “Sodium D” line at 25 °C ($[\alpha]_D^{25}$). Melting points were measured Mel-Temp II melting point apparatus, and are uncorrected.

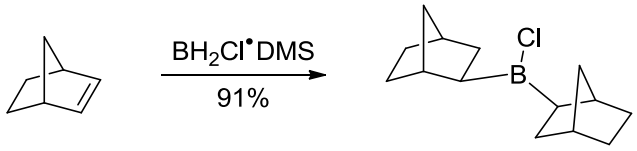
Preparation of Reagents

Preparation of Boron Reagents



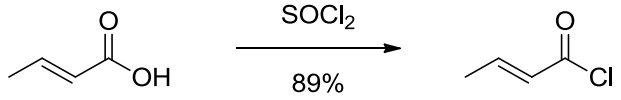
Dicyclohexylchloroborane. Into a 250 round-bottom flask charged with cyclohexene (24.7 mL, 0.243 mol, 2.0 eq.) was added 90 mL diethyl ether. After cooling the solution to 0 °C with an ice-water bath, borane-dimethyl sulfide complex (11.5 mL, 0.122 mol, 1.0 eq.) was added drop-wise over 10 minutes. The solution was stirred for 4 hours at the same temperature, whereafter the stirring was stopped and the white solid was allowed to settle. The supernatent solvent was then entirely removed *via* cannula. A 20 mL aliquot of diethyl ether was added to the reaction mixture, which was stirred for 5 minutes. In the same manner, the solvent was removed, and the product was again washed with an additional volume of ether. Residual solvent was removed at room temperature *in vacuo* over a period of 12 hours to provide dicyclohexylborane in excellent yield.

The dicyclohexylborane thus obtained was solvated in 26 mL diethyl ether, and the suspension was cooled to 0 °C with an ice-water bath. Etheric hydrogen chloride (previously produced from the reaction of sulfuric acid and sodium chloride; variable molarity, 1.1 eq.) was then slowly added over a 10 minute span. The reaction was allowed to stir for 5 hours while warming to room temperature, during which time the white suspension dissappeared. The reaction progress could be confirmed by this dissappearance, the evolution of hydrogen gas, and with the coincidental appearance of the product's signal in the ^{11}B NMR, δ = 82 ppm. The solvent was removed *via* cannula distillation *in vacuo* to provide 22.1 g (85%) analytically pure chlorodicyclohexylborane, which was stored as a 1M solution in dichloromethane.

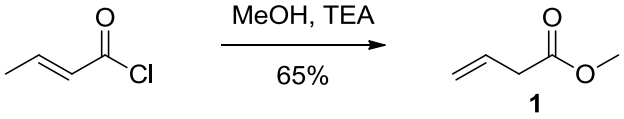


Di(bicyclo[2.2.1]heptan-2-yl)chloroborane. Into a 250 round-bottom flask charged with bicyclo[2.2.1]hept-2-ene (20.0 g, 0.212 mol, 2.0 eq.) was added 90 mL diethyl ether. After cooling the solution to 0 °C with an ice-water bath, monochloroborane-dimethyl sulfide complex (11.1 mL, 0.106 mol, 1.0 eq.) was added drop-wise over 5 minutes. The solution was stirred for 4 hours at the same temperature, whereafter the solvent was removed *via* cannula distillation *in vacuo*. The product was purified *via* careful distillation (oil bath temperature = 180 °C, head temperature = 133-136 °C, 1.5 torr) to provide 22.8 g (91%) analytically pure di(bicyclo[2.2.1]heptan-2-yl)chloroborane. (^{11}B NMR δ = 71).

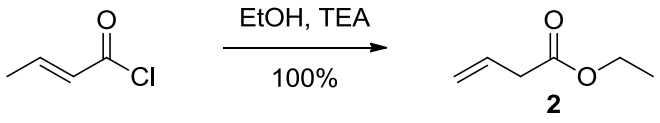
Preparation of But-3-enoate Esters



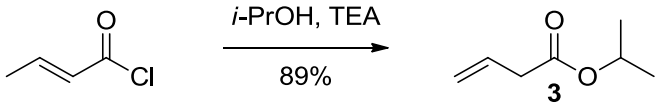
But-2*E*-enoyl chloride. A 250 mL round-bottom flasked was charged with crotonic acid (100.0 g, 1.16 mol, 1.0 eq.). An addition funnel containing thionyl chloride (84.3 mL, 1.16 mol, 1.0 eq) was attached to the flask, then the whole apparatus was flushed with nitrogen. The thionyl chloride was added to the crotonic acid at a rate of roughly 3-5 drops per second; the whole addition took place over 1 hour, during which time the escape of the evolved gas cooled the solution sufficiently to control the rate of reaction. After the addition was complete, the mixture was heated to 80 °C until no further gas evolution took place (roughly 2 hours). The light orange-colored solution was then allowed to cool to room temperature. The product was directly distilled from the reaction flask (oil bath temperature = 200 °C, head temperature = 115-120 °C, 1 atm.) to obtain 107.9 g (89%) but-2*E*-enoyl chloride. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (dq, *J* = 15.1, 6.9 Hz, 1H), 6.10 (d, *J* = 15.1 Hz, 1H), 2.00 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.6, 152.6, 127.8, 18.3.



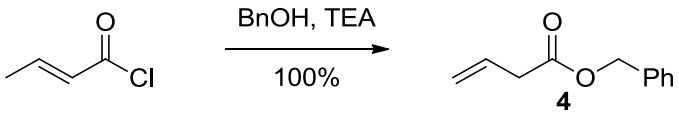
Methyl but-3-enoate (1). A 500 mL round-bottom flask charged with methanol (12.6 mL, 310 mmol, 1.5 eq.), 275 mL *n*-pentane, and triethylamine (28.8 mL, 207 mmol, 1.0 eq.) was cooled to 0 °C. Crotonoyl chloride (19.8 mL, 207 mmol, 1.0 eq.) was then added dropwise over 20 minutes. The solution, which instantly formed a white-colored precipitate, was allowed to warm to room temperature after the addition. After stirring for 1 hour, 10 mL of a saturated aqueous $NaHCO_3$ solution was added to the reaction mixture, followed by 50 mL deionized H_2O. The reaction mixture was then poured into a separatory funnel, and the layers were separated. The residual product was extracted out of the aqueous layer with an organic mixture consisting of 40 mL diethyl ether and 10 mL *n*-pentane. After combining the organic layers and washing with brine, the crude product was carefully concentrated without the aid of any external heating. The product was then distilled through a Vigreux column (oil bath temperature = 180 °C, head temperature = 103-107 °C, 1 atm.) to obtain 13.5 g (65.1%) of **1**. R_f = 0.44, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (m, 1H), 5.18 (d, 1H, 6.0 Hz) 5.14 (s, 1H), 3.69 (s, 3H), 3.09 (d, 2H, *J*=6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 130.4, 118.5, 51.8, 39.0.



Ethyl but-3-enoate (2). A 500 mL round-bottom flask charged with ethanol (4.18 mL, 71.7 mmol, 1.5 eq.), 95 mL *n*-pentane, and triethylamine (6.67 mL, 47.8 mmol, 1.0 eq.) was cooled to 0 °C. Crotonoyl chloride (4.58 mL, 47.8 mmol, 1.0 eq.) was then added dropwise over 20 minutes. The solution, which instantly formed a white-colored precipitate, was allowed to warm to room temperature after the addition. After stirring for 3 hours, 5 mL of a saturated aqueous $NaHCO_3$ solution was added to the reaction mixture, followed by 50 mL deionized H_2O. The reaction mixture was then poured into a separatory funnel, and the layers were separated. The residual product was extracted out of the aqueous layer with an organic mixture consisting of 60 mL diethyl ether and 10 mL *n*-pentane. After combining the organic layers and washing with brine, the crude product was dried with sodium sulfate then carefully concentrated without the aid of any external heating. The product was purified *via* column chromatography to provide 5.45 g (100%) of **2**. R_f = 0.47, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (m, 1H), 5.17 (d, *J* = 15.9 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.09 (d, *J* = 7.5 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 130.4, 118.5, 51.8, 39.0.

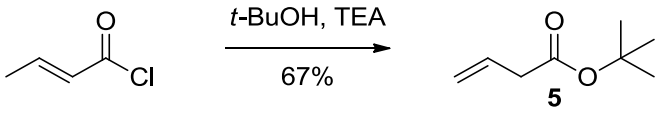


Isopropyl but-3-enoate (3). A 500 mL round-bottom flask charged with isopropanol (5.45 mL, 71.7 mmol, 1.5 eq.), 95 mL *n*-pentane, and triethylamine (6.67 mL, 47.8 mmol, 1.0 eq.) was cooled to 0 °C. Crotonoyl chloride (4.58 mL, 47.8 mmol, 1.0 eq.) was then added dropwise over 20 minutes. The solution, which instantly formed a white-colored precipitate, was allowed to warm to room temperature after the addition. After stirring for 3 hours, 8 mL of a saturated aqueous $NaHCO_3$ solution was added to the reaction mixture, followed by 10 mL deionized H_2O. The reaction mixture was then poured into a separatory funnel, and the layers were separated. The residual product was extracted out of the aqueous layer with an organic mixture consisting of 25 mL diethyl ether and 25 mL *n*-pentane. After combining the organic layers and washing with brine, the crude product was dried with sodium sulfate then carefully concentrated without the aid of any external heating. The product was purified *via* column chromatography to provide 5.48 g (89%) of **3**. R_f = 0.50, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (m, 1H), 5.17 (d, *J* = 6.0 Hz, 2H), 5.13 (s, *J* = 7.1 Hz, 2H), 5.01 (g, *J* = 6.2 Hz, 1H), 3.05 (d, *J* = 9.6 Hz, 2H), 1.25 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 130.7, 118.2, 67.9, 39.5, 21.8.



4

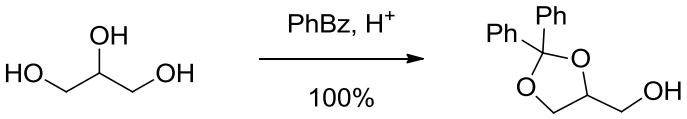
Benzyl but-3-enoate (4). A 500 mL round-bottom flask charged with benzyl alcohol (7.42 mL, 71.7 mmol, 1.5 eq.), 190 mL *n*-pentane, and triethylamine (6.67 mL, 47.8 mmol, 1.0 eq.) was cooled to 0 °C. Crotonoyl chloride (4.58 mL, 47.8 mmol, 1.0 eq.) was then added dropwise over 20 minutes. The solution, which instantly formed a white-colored precipitate, was allowed to warm to room temperature after the addition. After stirring for 30 minutes, 15 mL of a saturated aqueous $NaHCO_3$ solution was added to the reaction mixture. The reaction mixture was then poured into a separatory funnel, and the layers were separated. The organic layer was washed with 50 mL deionized water then brine. The crude product was then dried with sodium sulfate then concentrated *in vacuo*. The product was purified *via* column chromatography to provide 8.42 g (100%) of **4**. R_f = 0.48, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.27 (m, 5H), 5.92 (m, 1H), 5.20-5.11 (m, 4H), 3.11 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.2, 135.9, 130.2, 128.6, 128.2, 128.1, 118.6, 66.4, 39.1.



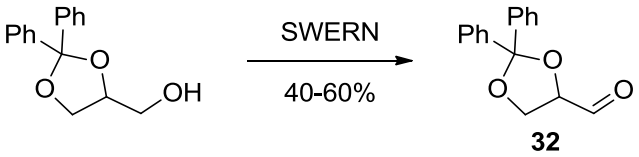
5

***t*-Butyl but-3-enoate (5)**. A 500 mL round-bottom flask charged with *tert*-butanol (6.81 mL, 71.7 mmol, 1.5 eq.), 95 mL *n*-pentane, and triethylamine (6.67 mL, 47.8 mmol, 1.0 eq.) was cooled to 0 °C. Crotonoyl chloride (4.58 mL, 47.8 mmol, 1.0 eq.) was then added dropwise over 20 minutes. The solution, which instantly turned yellow and formed a white-colored precipitate, was allowed to warm to room temperature after the addition. After stirring for 3 hours, 10 mL of a saturated aqueous $NaHCO_3$ solution was added to the reaction mixture, followed by 25 mL deionized H_2O. The reaction mixture was then poured into a separatory funnel, and the layers were separated. The residual product was extracted out of the aqueous layer with an organic mixture consisting of 10 mL diethyl ether and 90 mL *n*-pentane. After combining the organic layers and washing with brine, the crude product was dried with sodium sulfate then concentrated *in vacuo*. The product was purified *via* column chromatography to provide 4.56 g (67%) of **5**. R_f = 0.54, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (m, 1H), 5.15 (s, 1H), 5.11 (s, 1H), 3.00 (d, *J* = 6.8 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.9, 131.0, 118.0, 80.5, 40.5, 28.1.

Preparation of Aldehydes



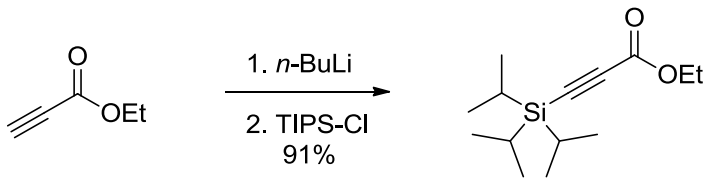
(2,2-Diphenyl-1,3-dioxolan-4-yl)methanol. A 100 mL round-bottom flask was fitted with a Dean-Stark trap. The latter's trap was filled with toluene, then a reflux condenser was attached to the top of the trap. The round-bottom flask was then charged with glycerol (3.24 mL, 44.0 mmol, 1.1 eq.) and 50 mL toluene. Benzophenone (7.29 g, 40.0 mmol. 1.0 eq.) and *p*-toluenesulfonic acid monohydrate (380 mg, 2.0 mmol, 0.05 eq.) were then added sequentially to the solution. The reaction mixture was heated to reflux for 36 hours, whereafter the solution was cooled to room temperature, and 20 mL diethyl ether were added, followed by 5 mL saturated aqueous sodium bicarbonate and 50 mL deionized water. The reaction mixture was then poured into a separatory funnel, and the layers were separated. Residual product was extracted out of the aqueous layer with an additional 50 mL diethyl ether. The combined organic layers were washed with brine, then concentrated *in vacuo*. The product was purified *via* column chromatography to provide 12.65 g (100%) of (2,2-Diphenyl-1,3-dioxolan-4-yl)methanol. R_f = 0.31, 70 : 30 = Hex : EtOAc, stain = $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (dd, *J* = 18.8, 7.6 Hz, 4H), 7.31-7.24 (m, 6H), 4.21 (m, 1H), 3.97-3.87 (m, 2H), 3.67-3.54 (m, 2H), 2.60-2.40 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.9, 128.3, 128.2, 128.15, 128.1, 126.2, 126.1, 110.0, 76.9, 66.3, 63.1. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ 279.1, found 279.1; calcd for $[M+K]^+$ 295.1, found 295.1.



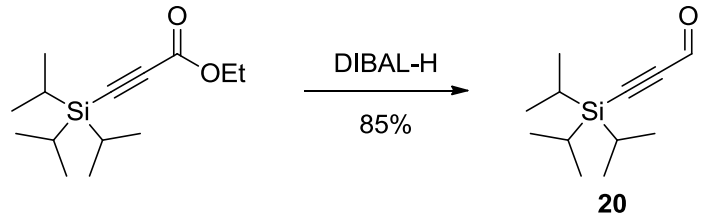
32

2,2-Diphenyl-1,3-dioxolane-4-carbaldehyde (32). A 100 mL round-bottom flask was charged with dimethyl sulfoxide (2.4 eq.) and dichloromethane (≈0.5 M in DMSO). After cooling to -78 °C, a solution of oxalyl chloride (1.1 eq.) in dichloromethane (≈2.7 M in $C_2Cl_2O_2$) was added drop-wise over 5 minutes. After stirring for 30 minutes, a solution of (2,2-Diphenyl-1,3-dioxolan-4-yl)methanol (1.0 eq.) in dichloromethane (≈2.0 M in alcohol) was added drop-wise over 5 minutes. After stirring for 1 hour, a solution of triethylamine (5.0 eq.) in dichloromethane (≈5.0 M in TEA) was slowly added. After stirring for 45 minutes at -78 °C, the cold bath was removed and the solution was allowed to stir for an additional hour. The mixture was then transferred to a seperatory funnel and was partitioned between 100 mL deionized water and dichloromethane (1 : 1). The organic layer was removed, and the residual product was extracted from the aqueous layer with an additional 50 mL dichloromethane. The combined organic layers were washed with brine then concentrated; column chromatographic purification provided **32** in 40-60% yield. R_f = 0.55, 50 : 50 = Hex : EtOAc, stain = 2,4-dinitrophenylhydrazine. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (d, *J* = 1.8 Hz, 1H), 7.53-7.49 (m, 4H), 7.32-7.23

(m, 6H), 4.42 (ddd, *J* = 8.0, 4.8, 1.9 Hz, 1H), 4.17 (dd, *J* = 8.7, 4.8 Hz, 1H), 4.09 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.0, 141.0, 140.9, 128.5, 128.3, 128.25, 128.2, 128.15, 128.1, 126.3, 126.2, 111.6, 80.1, 66.2.



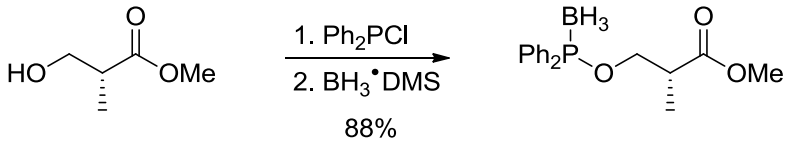
Ethyl 3-(triisopropylsilyl)prop-2-ynoate. Ethyl propiolate (1.04 mL, 10.2 mmol, 1.0 eq.) were added to a 100 mL round-bottom flask, followed by 25.5 mL THF. After cooling to -78 °C, *n*-BuLi (6.44 mL, 10.3 mmol, 1.01 eq., 1.6 M in hexanes) was added down the side of the round-bottom flask over 5 minutes. After stirring for 15 minutes, TIPS-Cl (2.38 mL, 11.2 mmol, 1.1 eq.) were added over a 5 minute period. After stirring the reaction mixture for 25 minutes, the cold bath was removed, and the reaction was stirred overnight. A 10 mL aliquot of saturated aqueous NH_4Cl was added to quench the reaction. After separating the organic layer, the residual product was extracted from the aqueous layer with an additional 25 mL diethyl ether. The combined organic layers were washed with brine, then dried over $MgSO_4$. After filtration and concentration, the product was purified *via* column chromatography to yield 2.36 g (91%) ethyl 3-(triisopropylsilyl)prop-2-ynoate. R_f = 0.41, 80 : 20 = Hex : DCM, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.23 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.11 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 153.1, 97.0, 90.8, 62.0, 18.5, 14.1, 11.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+H]^+$ 255.2, found 255.3; for $[M+Na]^+$ 277.2, found 277.2; calcd for $[M+K]^+$ 293.1, found 293.1.



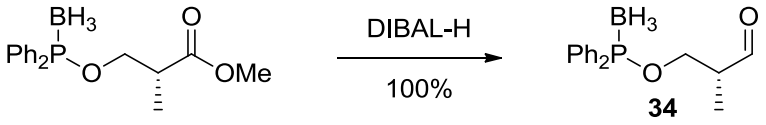
20

3-(Triisopropylsilyl)prop-2-ynal (20). A 250 mL round-bottom flask was charged with ethyl 3-(triisopropylsilyl)prop-2-ynoate (2.0 g, 7.86 mmol, 1.0 eq.) and 80 mL dichloromethane, and the flask was cooled to -78 °C. DIBAL-H (1.54 mL, 8.65 mmol, 1.1 eq.) was then added drop-wise over 5 minutes. After stirring for 20 minutes, 20 mL saturated aqueous Rochelle's salt was added, then the cold bath was removed. An additional 2 hours stirring time, the reaction was partitioned between a mixture consisting of 100 mL deionized water, 100 mL dichloromethane, and 50 mL chloroform. The organic layer was removed, then the residual product was extracted from the aqueous layer with an additional 100 mL dichloromethane. The combined organic layers were washed with brine, then concentrated. The product was purified *via* column chromatography to provide 1.41 g (85%) **20**. R_f = 0.47, 80 : 20 = Hex :

DCM, stain = I_2, *p*-anisaldehyde, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 1.18 (g, *J* = 7.9 Hz, 3H), 1.12 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.2, 104.6, 100.2, 18.4, 11.0.



Methyl (R)-3-((diphenylphosphino)oxy)-2-methylpropanoate(P-B)borane. A 250 mL round-bottom flask was charged with Roche ester (9.25 mL, 84.7 mmol, 1.0 eq.) and 40 mL THF. DMAP (3.1 g, 25.4 mmol, 0.3 eq.) and TEA (14.2 mL, 101.6 mmol, 1.2 eq.) were then added to the reaction mixture. After cooling to 0 °C, chlorodiphenylphosphine (17.1 mL, 93.1 mmol, 1.1 eq.) was added over a 30 minute period. The solution, which instantly formed a white-colored precipitate, was stirred for 3 hours, then allowed to warm to room temperature. While carefully maintining the mixture under an inert atmosphere, the solution was transferred to a separatory funnel, and 25 mL saturated aqueous $(NH_4)_2SO_4$, 400 mL deionized H_2O, and 250 mL EtOAc were added. The organic layer was removed and stored under nitrogen, and the residual product was extracted from the aqueous layer with an additional 250 mL EtOAc. The two organic layers were combined, and washed with brine, then concentrated *in vacuo*. The organic residue was taken up in 280 mL THF, then borane-dimethyl sulfide adduct (16.8 mL, 169.4 mmol, 2.0 eq.) was added at 0 °C. After stirring for 1 hour, approximately 200 g of ice were slowly added to quench the excess borane. The reaction was allowed to warm to room temperature over 1 hour while monitoring the evolution of hydrogen gas with a bubbler. After the quenching completed, the reaction mixture was partitioned between 400 mL EtOAc and 400 mL deionized H_2O in a separatory funnel. The organic layer was removed, and the residual product was extracted from the aqueous layer with an additional 400 mL EtOAc. The combined organic layers washed with brine then concentrated. The product was then purified *via* column chromatography to provide 23.6 g (88%) methyl (R)-3-((diphenylphosphino)oxy)-2-methylpropanoate(P-B)borane. $[\alpha]_D^{25}$ = +548 (*c* 3.0, $CHCl_3$). R_f = 0.44, 75 : 25 = Hex : EtOAc, stain = I_2, Vanillin, Dragendorff-Munier, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.67 (m, 4H), 7.53-7.42 (m, 6H), 4.17-4.05 (ddt, *J* = 10.8, 8.6, 7.4 Hz, 2H), 3.65 (s, 3H), 2.87 (m, 1H), 1.46-0.59 [q(br), 3H], 1.21 (d, *J* = 7.1 Hz, 3H). ^{11}B NMR (96 MHz, $CDCl_3$): δ -40.31 [d(m), *J* = 57.6 Hz]. ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.0, 132.2, 132.0, 131.9, 131.6, 131.4, 131.25, 131.2, 131.13, 131.1, 128. 7, 128.6, 68.4, 51.8, 40.9, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 106.8 [d(m), *J* = 77.8 Hz]. Mass: LRMS (ESI+) *m*/*z* calcd for $[M-H]^+$ 315.1, found 314.7; for $[M+Na]^+$ 339.1, found 338.8.

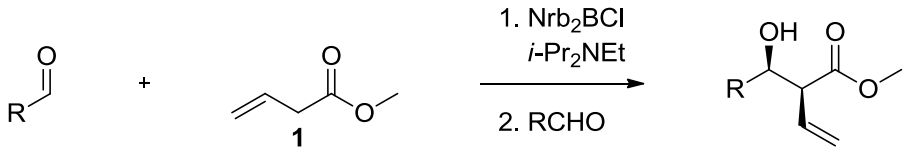


34

Methyl (R)-3-((diphenylphosphino)oxy)-2-methylpropanoate(P-B)borane (34). A 250 mL round-bottom flask was charged with methyl (R)-3-((diphenylphosphino)oxy)-2-methylpropanoate(P-B)borane (3.0 g, 9.49 mmol, 1.0 eq.) and 95 mL dichloromethane, and the flask was cooled to -78 °C. DIBAL-H (1.78 mL, 9.96 mmol, 1.05 eq.) The reaction, which was completed within 1 minute, was quenched by the careful addition of 200 mL saturated aqueous Rochelle's salt. The cold bath was removed, and the reaction mixture was stirred for 3 hours. The solution was then partitioned between 100 mL deionized water and 100 mL dichloromethane. The organic layer was removed, then the residual product was extracted from the aqueous layer with an additional 100 mL dichloromethane. The combined organic layers were washed with brine, then concentrated to provide 2.74 g (100%) **34** which had no need for further purification. The product was stored as a 0.4 M solution in dichloromethane. $[\alpha]_D^{25}$ = +337 (*c* 11.4, CH_2Cl_2). R_f = 0.34, 75 : 25 = Hex : EtOAc, stain = I_2, 2,4-dinitrophenylhydrazine, PMA, Dragendorff-Munier, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (d, *J* = 1.4 Hz, 1H), 7.73-7.43 (m, 10H), 4.19 (m, 2H), 2.76 (m, 1H), 1.44-0.62 [q(br), 3H], 1.17 (d, *J* = 7.2 Hz, 3H). ^{11}B NMR (96 MHz, $CDCl_3$): δ -40.28 (m). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 131.9, 131.7, 131.1, 130.9, 128.6, 128.5, 66.2, 47.0, 10.2. ^{31}P NMR (121 MHz, $CDCl_3$): δ 107.4 [d(m), *J* = 89.5 Hz]. Mass: LRMS (ESI+) *m/z* calcd for $[M-H]^+$ 285.1, found 285.0; for $[M+Na]^+$ 309.1, found 309.1.

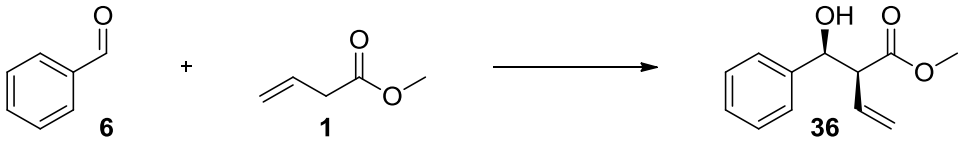
Syn-aldol Procedure and Data

General Procedure for the *Syn*-aldol Reaction

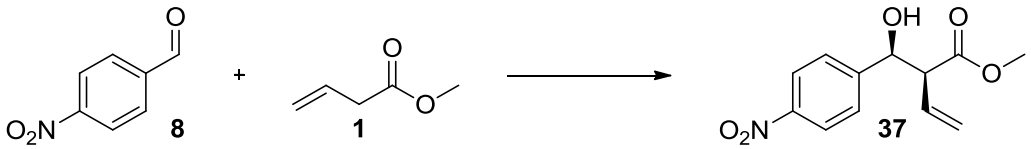


General procedure for the preparation of *syn*-aldol products: Into a 25 mL round-bottom flask was added methyl but-3-enoate **1** (107 µL, 1.0 mmol, 1.0 eq.), 3.5 mL dichloromethane, then Hünig's base (260 µL, 1.5 mmol, 1.5 eq.). After cooling the solution to 0 °C, di(bicyclo[2.2.1]heptan-2-yl)chloroborane (1.3 mL, 1.3 mmol, 1.3 eq., 1.0 M in CH_2Cl_2) was added drop-wise over 5 minutes. The solution was stirred for 2 hours, then was cooled to -78 °C, whereat the aldehyde was added slowly over 5 minutes (solid aldehydes were added in small portions while maintaining an inert atmosphere; aldehyde **34** was added as a 0.4 M solution in CH_2Cl_2). After stirring for 10 minutes, the cold bath was removed, and the solution was stirred for 14 hours. (A small aliquot of the reaction mixture was set aside here for measurement of the diastereomeric ratio by ^{1}H NMR.) After cooling to 0 °C, 10 mL MeOH then 1 mL *p*H = 7 phosphate buffer were added to the solution. Very slowly, 1 mL 30% aqueous H_2O_2 was added (rapid addition resulted in a local exotherm which rapidly degraded the aldol product). After stirring at 0 °C for 10 minutes, the cold bath was removed, and the solution was stirred for an additional 2 hours. Thereafter, the mixture was transferred to a separatory funnel, and 25 mL CH_2Cl_2 and 25 mL H_2O were then added. After removing the organic layer, the residual product was extracted from the aqueous layer with an additional 25 mL CH_2Cl_2. The organic layers were combined, washed with brine, then concentrated. The product was purified by column chromatography to provide the desired aldol product.

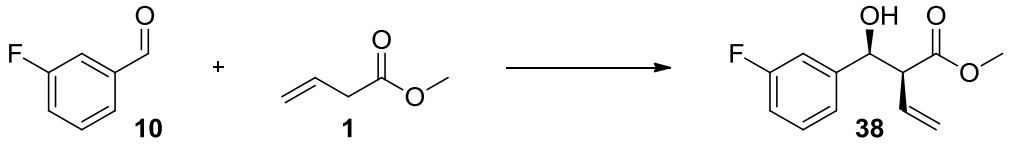
Characterization Data for *Syn*-aldol Products



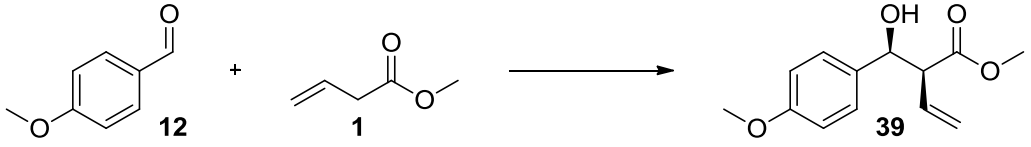
Methyl *syn*-2-(hydroxy(phenyl)methyl)but-3-enoate (36). R_f = 0.44, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.24 (m, 5H), 5.96 (m, 1H), 5.27-5.25 (d, *J* = 8.0 Hz , 2H), 5.17-5.13 (d, *J* = 16.0 Hz, 1H), 5.13 (d, *J* = 8.0 Hz, 1H), 3.60 (s, 3H), 3.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 140.7, 131.7, 128.2, 127.9, 126.3, 120.7, 73.9, 58.2, 52.0. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 229.1, found 229.2.



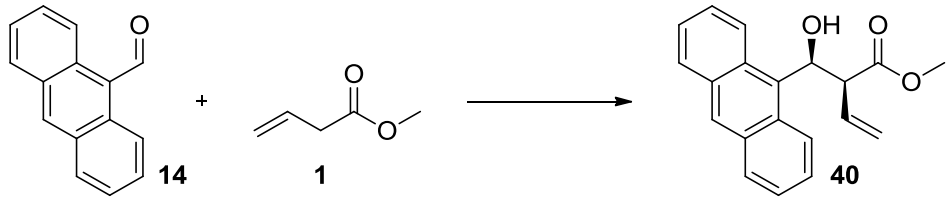
Methyl *syn*-2-(hydroxy(4-nitrophenyl)methyl)but-3-enoate (37). R_f = 0.28, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 5.74 (ddd, *J* = 17.1, 10.2, 8.6 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 4.98 (d, *J* = 6.9 Hz, 1H), 3.78 (s, 1H), 3.29 (t, *J* = 8.0 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 148.2, 147.4, 130.3, 127.3, 123.5, 121.6, 72.9, 57.6, 52.4. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+K]^+$ 290.0, found 290.2.



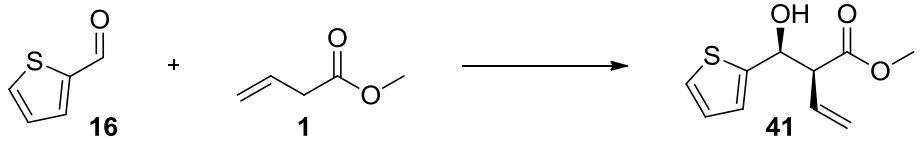
Methyl *syn*-2-((3-fluorophenyl)hydroxymethyl)but-3-enoate (38). R_f = 0.44, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-6.92 (m, 5H), 5.91 (m, 1H), 5.25 (d, *J* = 8.0 Hz, 1H), 5.12 (d, *J* = 19.7 Hz, 1H), 5.03 (dd, *J* = 4.0, 2.0 Hz, 1H), 3.62 (s, 3H), 3.31 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.23 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.0, 162.8 (d, *J* = 244 Hz), 143.5 (d, *J* = 7.0 Hz), 131.2, 129.8, 121.9, 121.0, 114.(d, *J* = 21.0 Hz), 113.4 (d, *J* = 22.0 Hz), 73.2, 58.0, 52.2. ^{19}F (376.5 MHz, $CDCl_3$): δ -114.5. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 247.1, found 247.1.



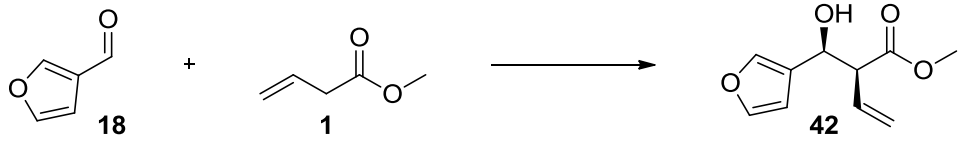
Methyl *syn*-2-(hydroxy(4-methoxyphenyl)methyl)but-3-enoate (39). R_f = 0.35, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.2 (d, *J* = 8.6 Hz 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.91 (m, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 5.16 (d, *J* = 17.1 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.42 (t, *J* = 8.5 Hz, 1H), 2.78 (d, *J* = 4.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 159.0, 133.4, 132.1, 127.9, 120.2, 113.5, 73.6, 58.1, 55.1, 52.0. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ 259.1, found 259.1.



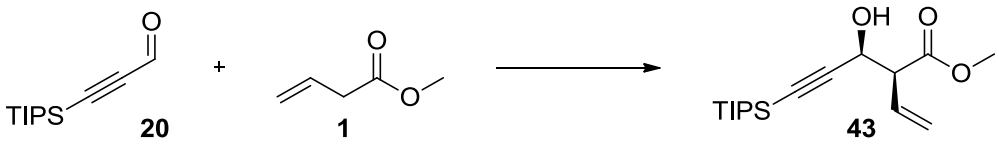
Methyl *syn*-2-((anthracen-9-yl)(hydroxy)methyl)but-3-enoate (40). R_f = 0.39, 70 : 30 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 2H), 8.33 (s, 1H), 7.91 (m, 2H), 7.42 (dddd, *J* = 22.4, 8.0, 6.5, 1.3 Hz, 4H), 6.38 (dd, *J* = 9.2, 2.3 Hz, 1H), 6.17 (ddd, *J* = 17.1, 10.2, 9.1 Hz, 1H), 5.36-5.31 (m, 2H), 4.15 (t, *J* = 9.1 Hz, 1H), 3.02 (d, *J* = 4.7 Hz, 3H), 3.00 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 133.7, 131.6, 131.1, 129.8, 129.3, 129.0, 125.8, 124.8, 120.6, 70.5, 57.7, 51.6. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ = 329.1, found 328.8; for $[M+K]^+$ 345.1, found 345.4.



Methyl *syn*-2-(hydroxy(thiophen-2-yl)methyl)but-3-enoate (41). R_f = 0.43, 70 : 30 = Hex : EtOAc & R_f = 0.50 DCM : EtOAc = 95 : 5, stain = I_2, Vanillin, $KMnO_4$, PMA. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 4.6, 1.7 Hz, 1H), 6.94-6.92 (m, 2H), 5.96 (ddd, *J* = 17.2, 10.3, 8.9 Hz, 1H), 5.31-5.21 (m, 3H), 3.62 (s, 3H), 3.41 (dd, *J* = 8.8, 6.3 Hz, 1H), 3.34 (d, *J* = 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 144.6, 131.6, 126.5, 124.9, 124.4, 120.9, 70.3, 58.5, 52.1. Mass: LRMS (ESI+) *m/z* calcd for $[M+H]^+$ = 213.1, found 213.1; for $[M+K]^+$ 345.1, found 345.4.

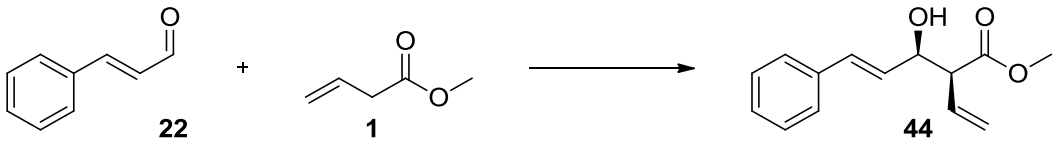


Methyl *syn*-2-((furan-3-yl)(hydroxy)methyl)but-3-enoate (42). R_f = 0.31, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, PMA, $KMnO_4$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 1.4 Hz, 2H), 6.63 (m, 1H), 6.00 (ddd, *J* = 17.2, 10.4, 8.5 Hz, 1H), 5.45-5.39 (m, 2H), 5.17 (dd, *J* = 7.7, 5.7 Hz, 1H), 3.98 (s, 3H), 3.66 (t, *J* = 8.0, 1H), 3.22 (d, *J* = 5.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.5, 143.7, 140.1, 132.3, 126.4, 120.1, 108.9, 68.2, 57.0, 52.5. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 219.1, found 219.1.

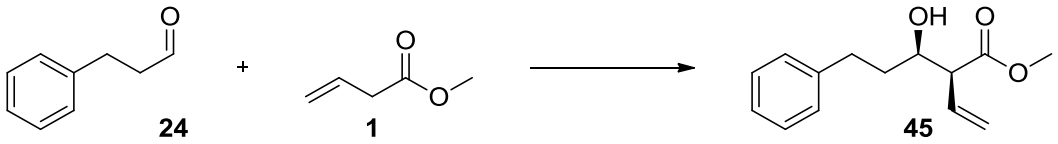


Rotameric Mixture, Roughly 1 : 0.49. ^1H rotameric peaks are integrated on spectra, but are not marked. ^{13}C rotameric peaks are neither marked nor integrated.

Methyl *syn*-2-ethenyl-3-hydroxy-5-(triisopropylsilyl)pent-4-ynoate (43). R_f = 0.18, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, PMA, *p*-anisaldehyde, $KMnO_4$. ^1H NMR (400 MHz, $CDCl_3$): δ 5.96 (ddd, *J* = 17.2, 10.3, 9.0 Hz, 2H), 5.35-5.32 (m, 2H), 4.64-4.61 (m, 1H), 3.74 (s, 3H), 3.36 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.07 (d, *J* = 7.2 Hz, 1H), 1.06 (s, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.2, 131.4, 120.7, 105.4, 87.4, 64.0, 56.5, 52.3, 18.6, 11.2. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 333.2, found 332.7; for $[M+K]^+$ 349.2, found 349.1.

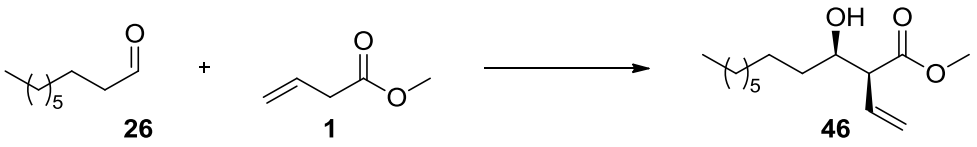


Methyl *syn*-2-ethenyl-3-hydroxy-5-phenylpent-4-enoate (44). R_f = 0.39, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.22 (m, *5*H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.27-6.10 (m, 1H), 5.96 (dt, *J* = 16.9, 9.6 Hz, 1H), 5.32-5.18 (m, 2H), 4.60-4.56 (m, 1H), 3.68 (s, 3H), 3.26 (dd, *J* = 9.4, 4.7 Hz, 1H), 3.00 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 136.4, 131.8, 128.9, 128.6, 128.3, 127.9, 126.6, 120.5, 72.9, 56.5, 52.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+K]^+$ 271.37, found 271.06, calcd for $[M-H_2O]^+$ 214.3, found 214.9.

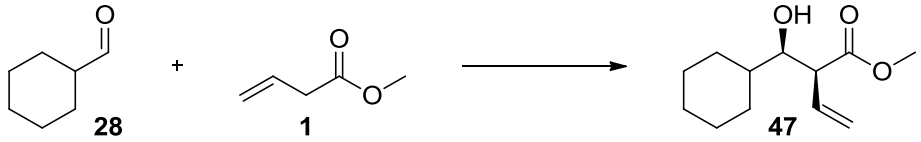


Methyl *syn*-2-ethenyl-3-hydroxy-5-phenylpentanoate (45). R_f = 0.44, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^1H NMR (300 MHz, $CDCl_3$): δ 7.29 – 7.15 (m, 5H), 5.94 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 3.95 (dt, *J* = 8.6, 4.1 Hz, 1H), 3.68 (s, 3H), 3.08 (dd, *J* = 9.3, 4.3 Hz,

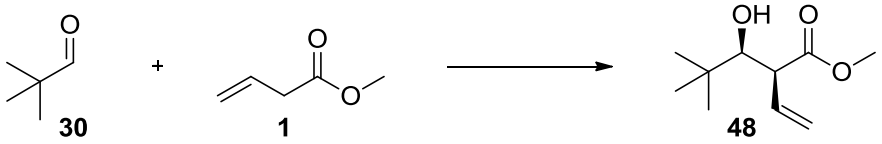
1H), 2.88-2.79 (m, 1H), 2.70-2.60 (m, 1H), 1.87-1.65 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8, 141.8, 131.6, 128.5, 128.4, 125.9, 120.7, 70.7, 55.8, 52.2, 36.0, 32.0. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ 257.3, found 257.6.



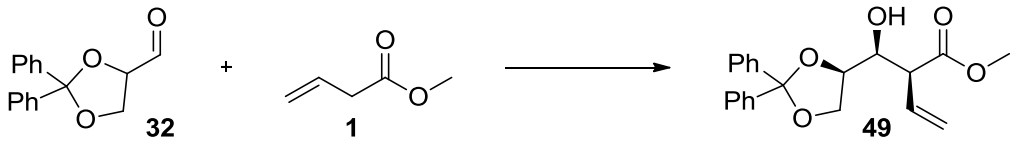
Methyl *syn*-2-ethenyl-3-hydroxyundecanoate (46). R_f = 0.55, 70 : 30 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.94 (ddd, *J* = 17.1, 10.3, 9.3 Hz, 1H), 5.32-5.21 (m, 2H), 3.94-3.90 (m, 1H), 3.72 (s, 3H), 3.08 (dd, *J* = 9.3, 4.4 Hz, 1H), 2.67 (d, *J* = 3.5 Hz, 1H), 1.50-1.36 (m, 3H), 1.36-1.24 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9, 131.7, 120.4, 71.4, 55.8, 52.1, 34.1, 31.9, 29.5 (2C), 29.3, 25.6, 22.7, 14.1. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ = 265.2, found 265.8; for $[M+K]^+$ 281.4, found 281.2.



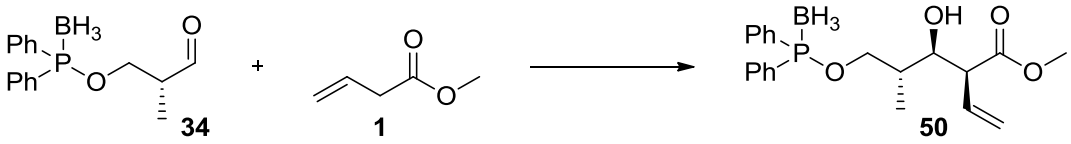
Methyl *syn*-2-((cyclohexyl)(hydroxy)methyl)but-3-enoate (47). R_f = 0.53, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, PMA, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (dt, *J* = 19.6, 10.0 Hz, 1H), 5.32-5.22 (m, 2H), 3.72 (s, 3H), 3.66 (m, 1H), 3.27 (dd, *J* = 9.3, 4.2 Hz, 1H), 2.71 (d, *J* = 3.3 Hz, 1H), 2.03-1.96 (m, 1H), 1.78-1.58 (m, 2H), 1.36 (dtd, *J* = 11.4, 7.8, 3.7 Hz, 1H), 1.28-1.11 (m, 4H), 1.09-0.97 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.2, 131.7, 120.1, 75.4, 52.8, 52.1, 40.3, 29.0, 28.3, 26.4, 26.0, 25.9. Mass: LRMS (ESI+) *m/z* calcd for $[M+K]^+$ = 293.5, found 293.2.



Methyl *syn*-2-ethenyl-3-hydroxy-4,4-dimethylpentanoate (48). R_f = 0.58, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, PMA, *p*-anisaldehyde, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (m, 1H), 5.28-5.24 (m, 2H), 3.69 (s, 3H), 3.31 (dd, *J* = 9.6, 4.8 Hz, 1H), 2.57 (d, *J* = 3.7 Hz, 1H), 0.94 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.4, 133.3, 119.8, 77.9, 52.7, 52.2, 35.6, 26.4. Mass: LRMS (ESI+) *m/z* calcd for $[M+H]^+$ = 187.1, found 187.1.



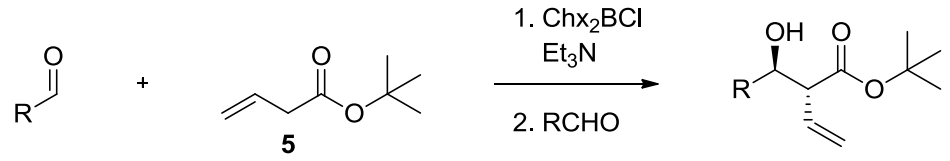
Methyl (2,3-*syn*, 2,4-*anti*)-2-((hydroxy)(2,2-diphenyl-1,3-dioxolan-4-yl)methyl)but-3-enoate (49). R_f = 0.63, 60 : 40 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.44 (m, 4H), 7.31-7.21 (m, 6H), 5.95 (dt, *J* = 17.2, 9.8 Hz, 1H), 5.37-5.31 (m, 2H), 4.10-4.03 (m, 4H), 3.61 (s, 3H), 3.49-3.45 (m, 1H), 3.22 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.7, 142.0, 141.9, 130.7, 128.3, 128.2, 128.1, 128.0, 126.3, 126.2, 126.2, 126.1, 126.0, 121.0, 109.9, 76.0, 72.6, 67.7, 52.5, 52.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 377.1, found 377.1; for $[M+K]^+$ 393.1, found 393.2.



Methyl (2S,3R,4R)-2-ethenyl-3-hydroxy-4-methyl-5-((diphenylphospino)oxy)pentanoate(P-B)borane (50). $[\alpha]_D^{25}$ = +1,760 (± 15%) (*c* 1.8 $CHCl_3$). R_f = 0.44, 70 : 30 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.70 (m, 4H), 7.53-7.43 (m, 6H), 5.95 (ddd, *J* = 17.2, 10.3, 9.5 Hz, 1H), 5.33-5.23 (m, 2H), 4.14-4.02 (m, 2H), 3.93 (dt, *J* = 9.1, 3.1 Hz, 1H), 3.71 (s, 3H), 3.23 (dd, *J* = 9.5, 3.1 Hz, 1H), 2.97 (d, *J* = 3.3 Hz, 1H), 1.88 (m, 1H), 1.52-0.60 [q(br), 3H], 0.98 (d, *J* = 6.9 Hz, 3H). ^{11}B NMR (96 MHz, $CDCl_3$): δ -40.65 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ 174.1, 132.3, 132.20, 131.9, 131.7, 131.6, 131.4, 131.3, 130.7, 128.7, 128.6, 120.7, 72.2, 69.0, 52.5, 52.3, 37.0, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.8 [d(m), *J* = 92.3 Hz]. Mass: LRMS (ESI+) *m*/*z* calcd for $[M-H]^+$ = 385.2, found 385.4; for $[M+Na]^+$ 409.2, found 409.3.

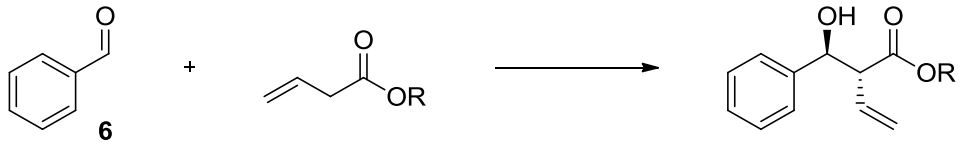
Anti-aldol Procedure and Data

General Procedure for the *Anti*-aldol Reaction



General procedure for the preparation of *anti*-aldol products: Into a 25 mL round-bottom flask was added *t*-butyl but-3-enoate **5** (150 µL, 1.0 mmol, 1.0 eq.), 3.5 mL dichloromethane, then triethylamine (210 µL, 1.5 mmol, 1.5 eq.). After cooling the solution to 0 °C, dicyclohexylchloroborane (1.3 mL, 1.3 mmol, 1.3 eq., 1.0 M in CH_2Cl_2) was added drop-wise over 5 minutes. The solution was stirred for 2 hours, then was cooled to -78 °C, whereat the aldehyde was added slowly over 5 minutes (solid aldehydes were added in small portions while maintaining an inert atmosphere; aldehyde **34** was added as a 0.4 M solution in CH_2Cl_2). After stirring for 10 minutes, the cold bath was removed, and the solution was stirred for 14 hours. (A small aliquot of the reaction mixture was set aside here for measurement of the diastereomeric ratio by ^{1}H NMR.) After cooling to 0 °C, 10 mL MeOH then 1 mL *p*H = 7 phosphate buffer were added to the solution. Very slowly, 1 mL 30% aqueous H_2O_2 was added (rapid addition resulted in a local exotherm which rapidly degraded the aldol product). After stirring at 0 °C for 10 minutes, the cold bath was removed, and the solution was stirred for an additional 2 hours. Thereafter, the mixture was transferred to a separatory funnel, and 25 mL CH_2Cl_2 and 25 mL H_2O were then added. After removing the organic layer, the residual product was extracted from the aqueous layer with an additional 25 mL CH_2Cl_2. The organic layers were combined, washed with brine, then concentrated. The product was purified by column chromatography to provide the desired aldol product.

Characterization Data for *Anti*-aldol Products

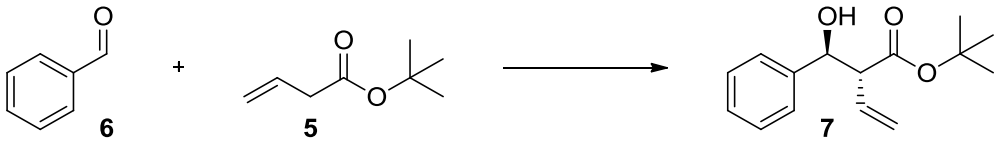


Methyl *anti*-2-(hydroxy(phenyl)methyl)but-3-enoate. R_f = 0.46, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.12 (m, 5H), 5.62 (dt, *J* = 17.9, 9.6 Hz, 1H), 4.99 (m, 2H), 4.89 (m, 1H), 3.67 (s, 3H), 3.40 (t, *J* = 8.0 Hz, 1H), 3.34 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.4, 141.1, 132.0, 128.3, 127.9, 126.7, 119.5, 75.2, 58.0, 52.1.

Ethyl *anti*-2-(hydroxy(phenyl)methyl)but-3-enoate. R_f = 0.52, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.23 (m, 5H), 5.67 (ddd, *J* = 17.0, 10.3, 8.5 Hz, 1H), 5.04 (d, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.90 (dd, *J* = 8.4, 3.5 Hz, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 8.4 Hz, 1H), 3.23 (s, 1H), 1.22 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 141.2, 132.2, 128.3, 127.9, 126.7, 119.4, 75.2, 61.0, 57.9, 14.1.

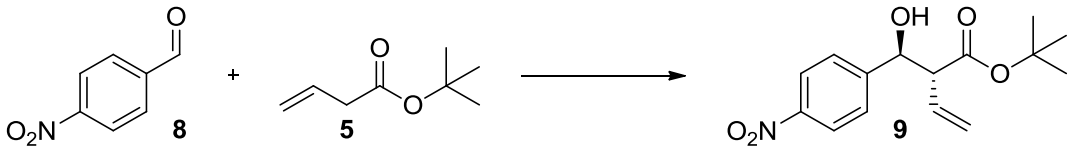
Isopropyl *anti*-2-(hydroxy(phenyl)methyl)but-3-enoate. R_f = 0.62, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.21 (m, 5H), 5.68 (ddd, *J* = 17.1, 10.3, 8.4 Hz, 1H), 5.15-4.97 (m, 3H), 4.89 (dd, *J* = 8.1, 3.9 Hz, 1H), 3.37 (t, *J* = 8.2 Hz, 1H), 3.31 (d, *J* = 5.3 Hz, 1H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.2 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 141.3, 132.4, 128.2, 127.8, 126.6, 119.1, 75.2, 68.5, 57.9, 21.7, 21.6.

Benzyl *anti*-2-(hydroxy(phenyl)methyl)but-3-enoate. R_f = 0.43, 75 : 25 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.24 (m, 10H), 5.68 (ddd, *J* = 17.1, 10.3, 8.5 Hz, 1H), 5.13 (s, 2H), 5.05 (d, *J* = 10.2 Hz, 1H), 5.00 (d, *J* = 17.2 Hz, 1H), 4.92 (dd, *J* = 8.3, 4.7 Hz, 1H), 3.48 (t, *J* = 8.4 Hz, 1H), 3.09 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6, 141.1, 135.6, 132.0, 128.5, 128.3, 128.2, 128.0, 127.9, 126.6, 119.6, 75.2, 66.6, 57.9.

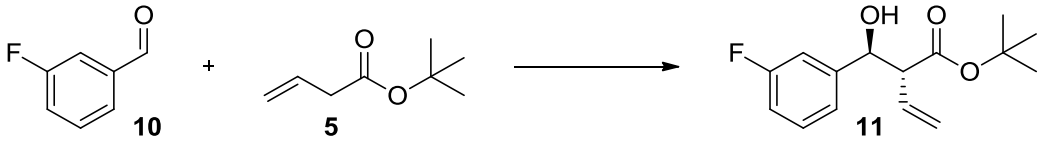


***t*-Butyl *anti*-2-(hydroxy(phenyl)methyl)but-3-enoate (7)**. R_f = 0.46, 75 : 25 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 5H), 5.71 (m, 1H), 5.09-5.5.03 (dd, *J* = 16.0, 8.0 Hz , 2H), 4.87 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.33 (t, *J* = 8.0 Hz, 1H), 3.28 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (101

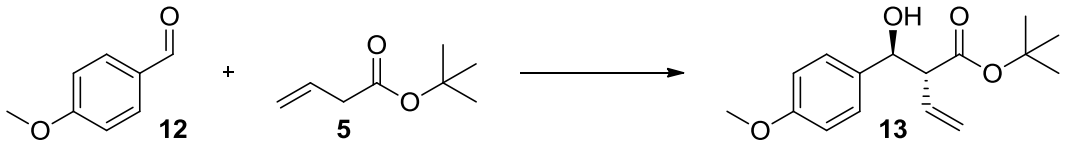
MHz, $CDCl_3$): δ 172.3, 141.4, 132.8, 128.2, 127.8, 126.6, 118.9, 81.6, 75.3, 58.4, 27.9. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+H]^+$ = 249.1, found 249.8; for $[M+Na]^+$ 271.1, found 271.7.



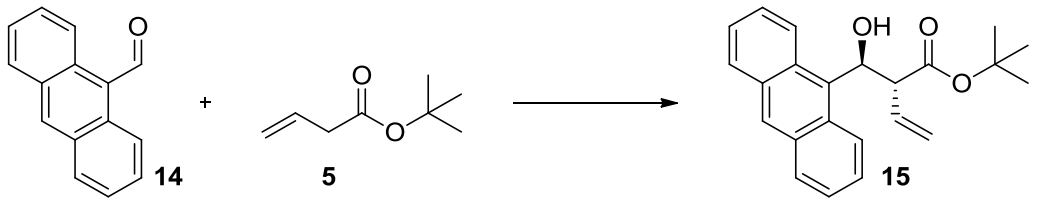
***t*-Butyl *anti*-2-(hydroxy(4-nitrophenyl)methyl)but-3-enoate (9)**. R_f = 0.47, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz 2H), 7.51 (d, *J* = 8.7 Hz, 2H), 5.74 (ddd, *J* = 17.1, 10.2, 8.6 Hz, 1H), 5.15 (d, *J* = 10.3 Hz, 1H), 5.07 (d, *J* = 17.2 Hz, 1H), 4.98 (d, *J* = 6.9 Hz, 1H), 3.78 (s, 1H), 3.29 (t, *J* = 8.0 Hz, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 149.0, 147.5, 132.1, 127.6, 123.5, 120.0, 82.4, 74.4, 58.2, 28.0. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 316.1, found 316.2; for $[M+K]^+$ 332.1, found 332.2.



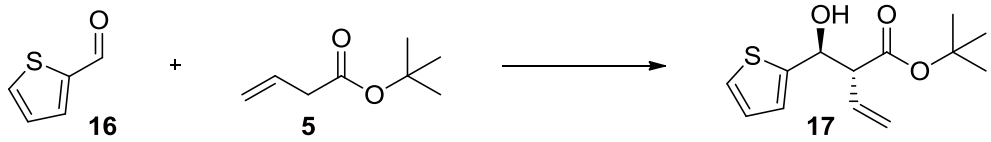
***t*-Butyl *anti*-2-((3-fluorophenyl)(hydroxy)methyl)but-3-enoate (11)**. R_f = 0.64, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.25 (m, 1H), 7.04 (m, 2H), 6.92 (m, 1H), 5.68 (ddd, *J* = 17.2, 10.3, 8.4 Hz, 1H), 5.05 (m, 2H), 4.83 (d, *J* = 7.7 Hz, 1H), 3.81 (s, 1H), 3.26 (t, *J* = 8.1 Hz, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 162.7 (d, *J* = 247.5 Hz), 144.3 (d, *J* = 6.0 Hz), 132.5, 129.6 (d, *J* = 8.1 Hz), 122.3 (d, *J* = 3.0 Hz), 119.2, 114.6 (d, *J* = 21.2 Hz), 113.7 (d, *J* = 23.2 Hz), 81.7, 74.6, 58.4, 27.9. ^{19}F (376.5 MHz, $CDCl_3$): δ -114.6. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+H]^+$ 267.14, found 267.16; for $[M+Na]^+$ 289.1, found 289.2; for $[M+K]^+$ 305.1, found 305.2.



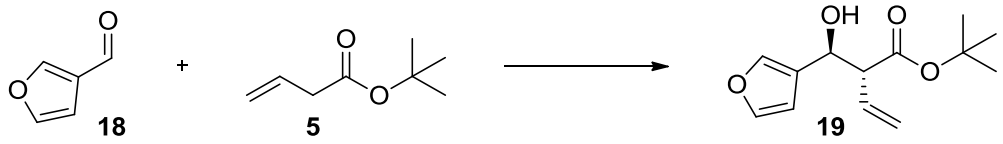
***t*-Butyl *anti*-2-(hydroxy(4-methoxyphenyl)methyl)but-3-enoate (13)**. R_f = 0.49, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.64 (ddd, *J* = 17.1, 10.5, 8.4 Hz, 1H), 5.04-4.98 (m, 2H), 4.80 (d, *J* = 8.3 Hz, 1H), 3.75 (s, 3H), 3.28 (t, *J* = 8.0 Hz, 1H), 3.28 (br, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.3, 159.0, 133.7, 132.9, 127.9, 118.6, 113.5, 81.3, 74.8, 58.7, 55.1, 27.9. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 301.14, found 301.14; for $[M+K]^+$ 317.1, found 317.2.



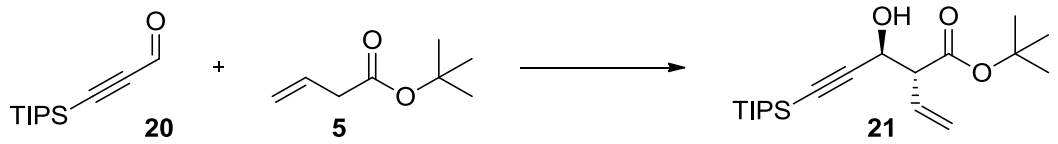
***t*-Butyl *anti*-2-((anthracen-9-yl)(hydroxy)methyl)but-3-enoate (15)**. R_f = 0.13, 85 : 15 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (s, 2H), 8.34 (s, 1H), 7.95-7.91 (m, 2H), 7.43 (dddd, *J* = 23.9, 7.9, 6.5, 1.3 Hz, 4H), 6.57 (dd, *J* = 10.5, 3.5 Hz, 1H), 5.36 (ddd, *J* = 17.1, 10.2, 8.3 Hz, 1H), 4.63 (dt, *J* = 17.1, 1.1 Hz, 1H), 4.54 (dd, *J* = 10.2, 1.3 Hz, 1H), 4.22 (dd, *J* = 10.6, 8.3 Hz, 1H), 3.14 (s, 1H), 1.56 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 132.1, 131.3, 130.1, 129.4, 128.7, 125.8, 124.8, 118.5, 81.7, 70.8, 58.0, 28.2. Mass: LRMS (ESI+) *m/z* calcd for $[M+Na]^+$ = 371.2, found 371.2.



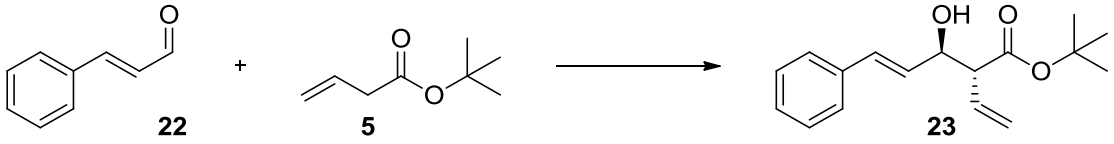
***t*-Butyl *anti*-2-(hydroxy(thiophen-2-yl)methyl)but-3-enoate (17)**. R_f = 0.54, 70 : 30 = Hex : EtOAc & R_f = 0.35 DCM, stain = I_2, Vanillin, $KMnO_4$, PMA, *p*-anisaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (dd, *J* = 4.6, 1.6 Hz, 1H), 6.94-6.90 (m, 2H), 5.75 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 5.17-5.08 (m, 3H), 3.68 (d, *J* = 6.4 Hz, 1H), 3.37 (t, *J* = 8.0 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 145.7, 132.4, 126.4, 124.9, 124.6, 119.3, 81.7, 71.2, 58.5, 27.9. Mass: LRMS (ESI+) *m/z* calcd for $[M+H]^+$ = 255.1, found 255.2.



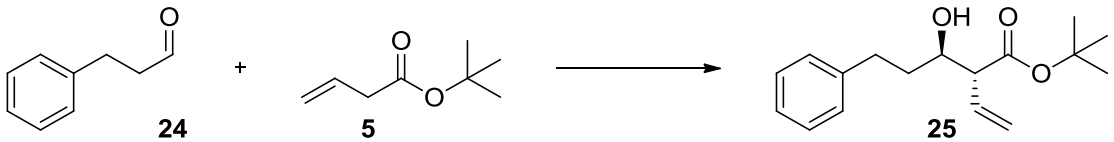
***t*-Butyl *anti*-2-((furan-3-yl)(hydroxy)methyl)but-3-enoate (19)**. R_f = 0.50, 70 : 30 = Hex : EtOAc & R_f = 0.61 DCM : EtOAc = 90 :10, stain = I_2, Vanillin, $KMnO_4$, PMA, *p*-anisaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (m, 2H), 6.38 (m, 1H), 5.82-5.73 (m, 1H), 5.18-5.14 (m, 2H), 4.84 (t, *J* = 7.0 Hz, 1H), 3.36 (d, *J* = 6.7 Hz, 1H), 3.28 (ddt, *J* = 8.2, 7.4, 0.9 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.1, 143.1, 139.7, 132.8, 126.7, 119.0, 108.9, 81.6, 68.1, 57.5, 27.9. Mass: LRMS (ESI+) *m/z* calcd for $[M-H_2O]^+$ = 220.3, found 220.5.



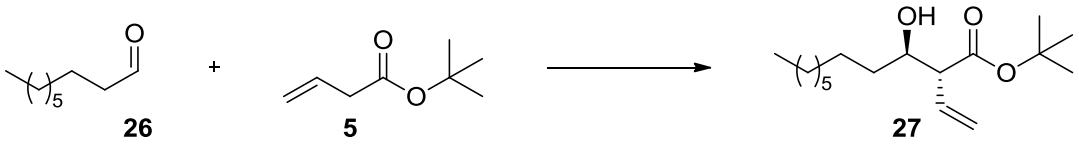
***t*-Butyl *anti*-2-ethenyl-3-hydroxy-5-(triisopropylsilyl)pent-4-ynoate (21)**. R_f = 0.51, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, PMA, *p*-anisaldehyde, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (ddd, *J* = 17.5, 10.1, 8.5 Hz, 1H), 5.30 – 5.22 (m, 2H), 4.59 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.24-3.20 (m, 2H), 1.47 (s, 9H), 1.06 (m, 21H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.0, 132.0, 119.9, 106.1, 86.8, 81.7, 63.7, 57.6, 28.0, 18.6, 11.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 375.2, found 375.9; for $[M+K]^+$ 391.2, found 391.8.



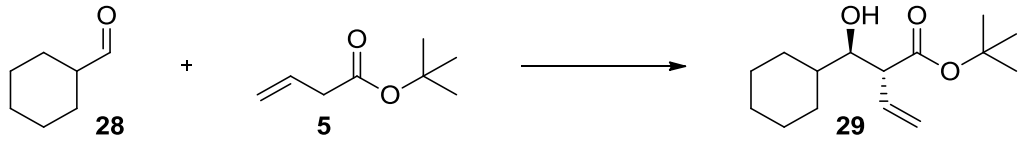
***t*-Butyl *anti*-2-ethenyl-3-hydroxy-5-phenylpent-4-enoate (23)**. R_f = 0.62, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.18 (m, 5H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.19 (dd, *J* = 15.9, 6.2 Hz, 1H), 5.84 (ddd, *J* = 17.1, 10.3, 8.7 Hz, 1H), 5.23-5.17 (m, 2H), 4.52 (t, *J* = 8.0 Hz, 1H), 3.43 (s, 1H), 3.17 (t, *J* = 8.0 Hz, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.9, 136.5, 132.7, 131.2, 129.3, 128.4, 127.6, 126.4, 119.1, 81.4, 73.1, 57.5, 27.9. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 297.1, found 297.8.



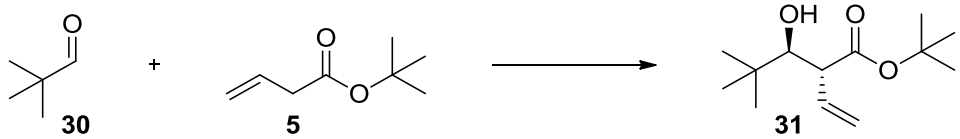
***t*-Butyl *anti*-2-ethenyl-3-hydroxy-5-phenylpentanoate (25)**. R_f = 0.63, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.11 (m, 5H), 5.78 (ddd, *J* = 17.2, 10.2, 9.0 Hz, 1H), 5.20-5.13 (m, 2H), 3.83 (ddd, *J* = 10.0, 7.6, 3.0 Hz, 1H), 3.26 (s, 1H), 3.04-3.00 (t, *J* = 8.0 Hz, 1H), 2.86 (ddd, *J* = 14.3, 10.1, 5.0 Hz, 1H), 2.66 (ddd, *J* = 13.7, 9.9, 6.8 Hz, 1H), 1.84 (dddd, *J* = 13.4, 9.9, 6.7, 3.0 Hz, 1H), 1.68 (ddt, *J* = 14.1, 9.3, 4.8 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 141.9, 133.2, 128.3, 128.2, 125.7, 118.8, 81.1, 71.5, 57.7, 36.3, 31.7, 27.8. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ 299.16, found 299.65; for $[M+K]^+$ 315.14, found 315.78.



***t*-Butyl *anti*-2-ethenyl-3-hydroxyundecanoate (27)**. R_f = 0.40, 85 : 15 = Hex : EtOAc, stain = I_2, Vanillin, PMA, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (ddd, *J* = 17.1, 10.3, 8.9 Hz, 1H), 5.22-5.17 (m, 2H), 3.78 (qd, *J* = 7.1, 2.5 Hz, 1H), 2.99 (m, 1H), 2.79 (d, *J* = 7.0 Hz, 1H), 1.53-1.49 (m, 2H), 1.46 (s, 9H), 1.40-1.24 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.7, 133.6, 118.7, 81.3, 72.6, 57.6, 34.7, 31.9, 29.6, 29.3, 28.1 (2C), 25.6, 22.7, 14.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 307.2, found 307.1; for $[M+K]^+$ 323.2, found 323.2.

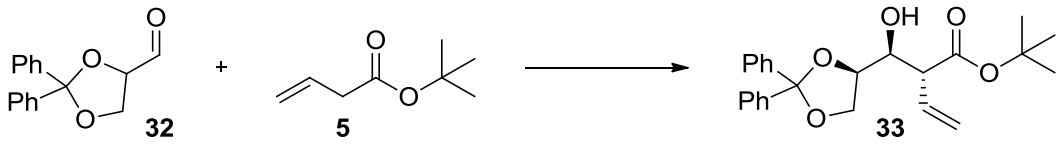


***t*-Butyl *anti*-2-((cyclohexyl)(hydroxy)methyl)but-3-enoate (29)**. R_f = 0.35, 85 : 15 = Hex : EtOAc, stain = I_2, PMA, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (ddd, *J* = 17.1, 10.2, 8.7 Hz, 1H), 5.22-5.16 (m, 2H), 3.54 (m, 1H), 3.17 (t, *J* = 8.0 Hz, 1H), 2.81 (d, *J* = 7.3 Hz, 1H), 1.83-1.57 (m, 6H), 1.46 (s, 9H), 1.40-1.33 (m, 1H), 1.26-1.05 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.9, 134.0, 118.1, 76.8, 54.2, 41.0, 30.1, 28.0 (2C), 26.6, 26.4, 26.1. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 235.3, found 235.1.

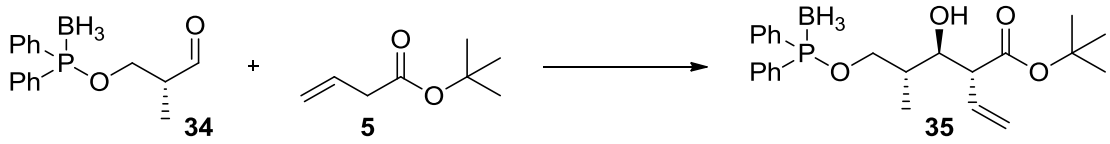


Rotameric Mixture, Roughly 1 : 0.24. ^{1}H rotameric peaks are integrated on spectrum, but are not marked. ^{13}C rotameric peaks are neither marked nor integrated.

***t*-Butyl *anti*-2-ethenyl-3-hydroxy-4,4-dimethylpentanoate (31)**. R_f = 0.41, 85 : 15 = Hex : EtOAc, stain = I_2, PMA, *p*-anisaldehyde, Vanillin, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (ddd, *J* = 17.3, 10.1, 8.3 Hz, 1H), 5.19 (m, 2H), 3.99 (d, *J* = 8.8 Hz, 1H), 3.34 (dd, *J* = 8.8, 3.2 Hz, 1H), 3.18 (dd, *J* = 8.3, 3.3 Hz, 1H), 1.46 (s, 9H), 0.93 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.9, 136.0, 117.3, 81.7, 81.5, 50.6, 36.2, 27.9, 26.4. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 251.2, found 251.1; for $[M+K]^+$ 267.1, found 267.0.



***t*-Butyl (2,3-*anti*, 2,4-*syn*)-2-((hydroxy)(2,2-diphenyl-1,3-dioxolan-4-yl)methyl)but-3-enoate (33)**. MP = 92.4-94.6 °C. R_f = 0.63, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, PMA, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.45 (ddt, *J* = 22.2, 6.1, 1.6 Hz, 4H), 7.33-7.22 (m, 6H), 5.88 (ddd, *J* = 17.3, 10.2, 8.4 Hz, 1H), 5.23-5.16 (m, 2H), 4.15-4.08 (m, 2H), 3.93-3.87 (m, 1H), 3.33-3.28 (dd, *J* = 14.1, 6.4 Hz, 2H), 1.45 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.4, 142.1, 142.0, 132.8, 128.2, 128.16, 128.1, 126.2, 126.1, 119.0, 110.1, 81.9, 77.3, 73.5, 66.9, 52.8, 28.0. Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 419.2, found 419.1.

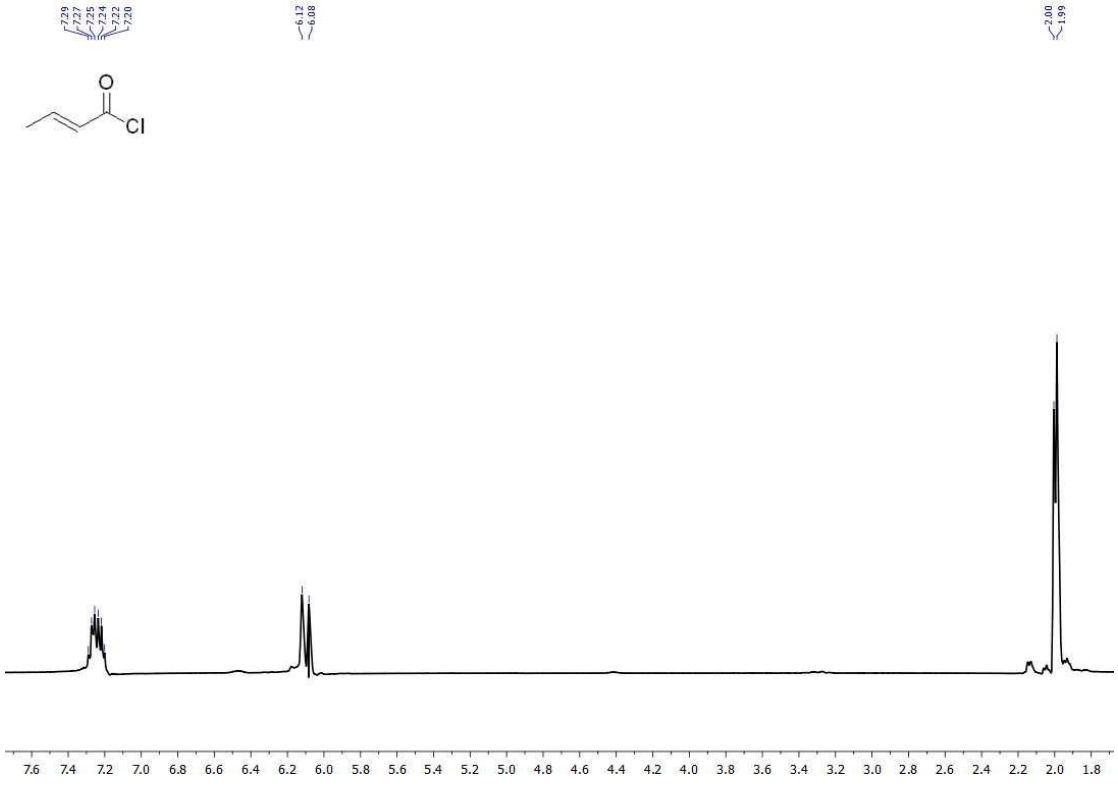


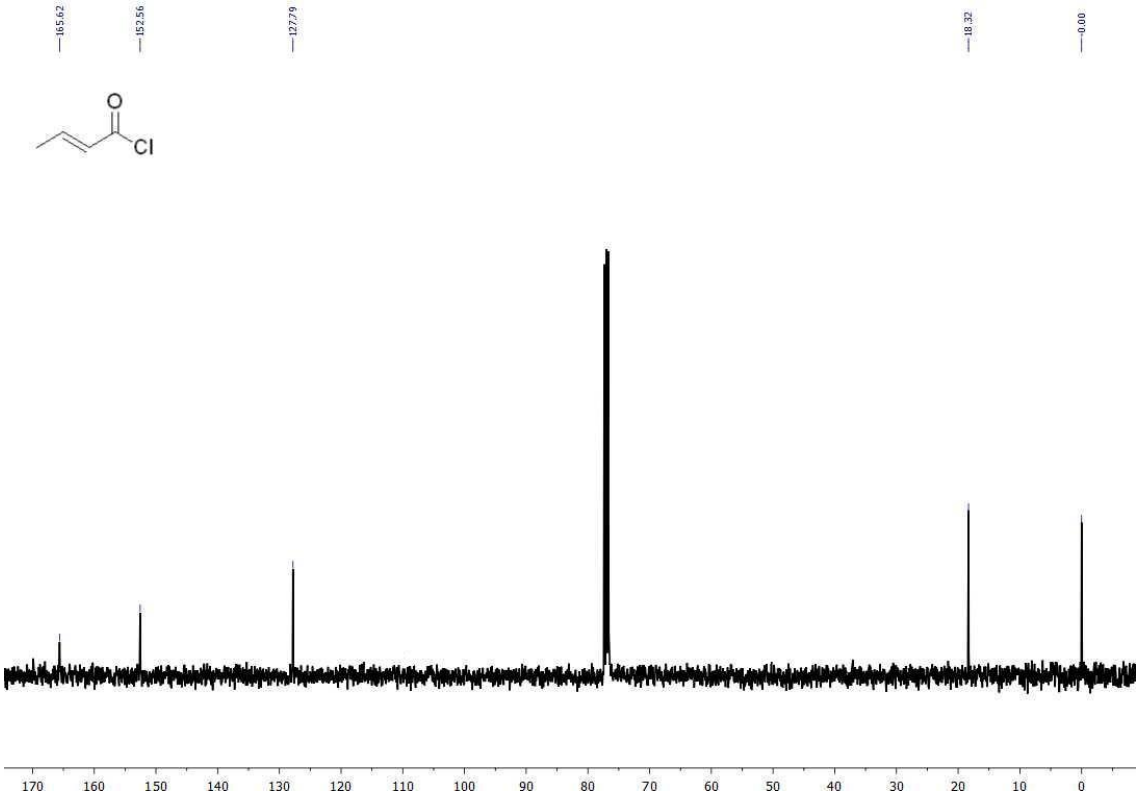
Rotameric Mixture, Roughly 1 : 0.7. ^{1}H rotameric peaks are integrated on spectrum, but are not marked. ^{13}C rotameric peaks are neither marked nor integrated.

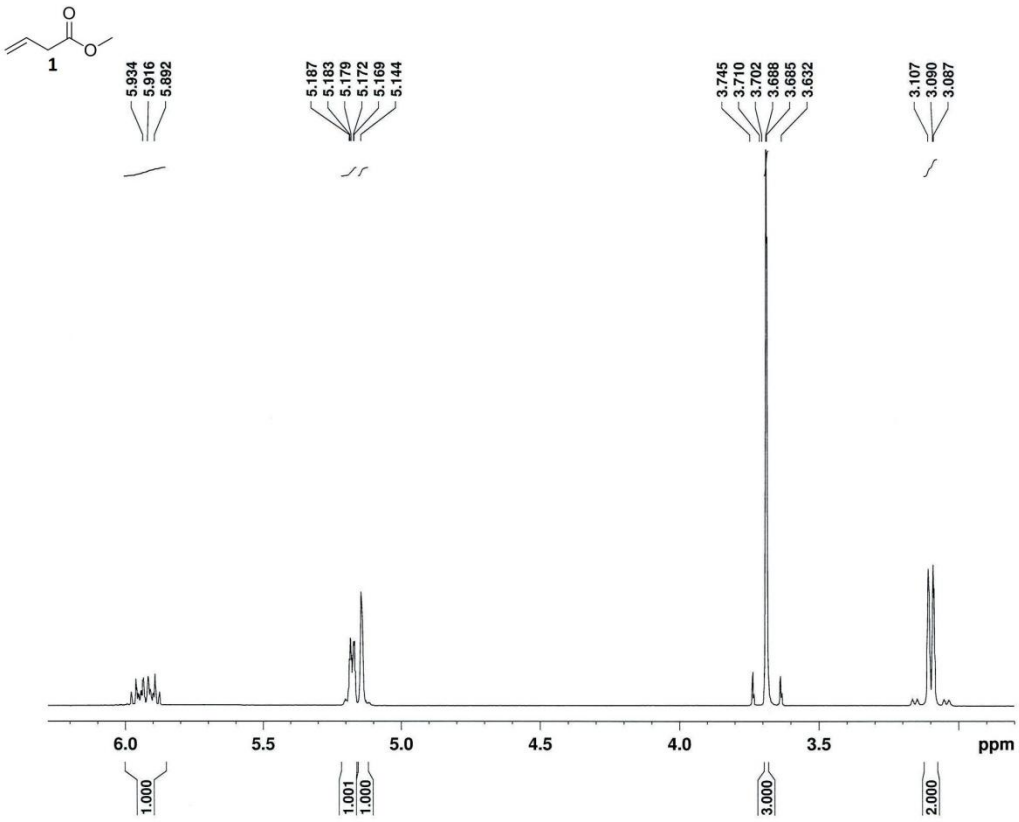
***t*-Butyl (2R,3R,4R)-2-ethenyl-3-hydroxy-4-methyl-5-((diphenylphospino)oxy)pentanoate(P-B)borane (35)**. $[\alpha]_D^{25}$ = +913 (± 10%) (*c* 1.6, $CHCl_3$). R_f = 0.64, 70 : 30 = Hex : EtOAc, stain = I_2, Vanillin, PMA, $KMnO_4$. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.70 [m, (4H x 1.7)], 7.50-7.41 [m, (6H x 1.7)], 5.87 (ddd, *J* = 18.0, 9.9, 8.5 Hz, 1H), 5.23-5.13 [m, (2H x 1.7)], 4.15-4.07 (m, 2H), 3.69 (q, *J* = 7.9 Hz, 1H), 3.21 (dd, *J* = 8.5, 6.1 Hz, 1H), 3.01 (d, *J* = 8.1 Hz, 1H), 2.00 [m, (1H x 1.7)], 1.74-0.63 [q(br), (3H x 1.8)], 1.45 [s, (9H x 1.8)], 1.08 (d, *J* = 6.9 Hz, 3H). ^{11}B NMR (96 MHz, $CDCl_3$): δ -40.2 (m). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.6, 133.4, 132.2, 132.16, 131.8, 131.7, 131.6, 131.3, 131.2, 128.7, 128.6, 118.8, 81.8, 74.7, 68.7, 53.8, 38.0, 28.0, 14.6. ^{31}P NMR (162 MHz, $CDCl_3$): δ 106.0 (m). Mass: LRMS (ESI+) *m*/*z* calcd for $[M+Na]^+$ = 451.2, found 451.1.

^{1}H, ^{11}B, ^{13}C, ^{19}F, and ^{31}P NMR Spectra

NMR Spectra of But-3-enoate Esters



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5.0
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4.0
3.5
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1.000
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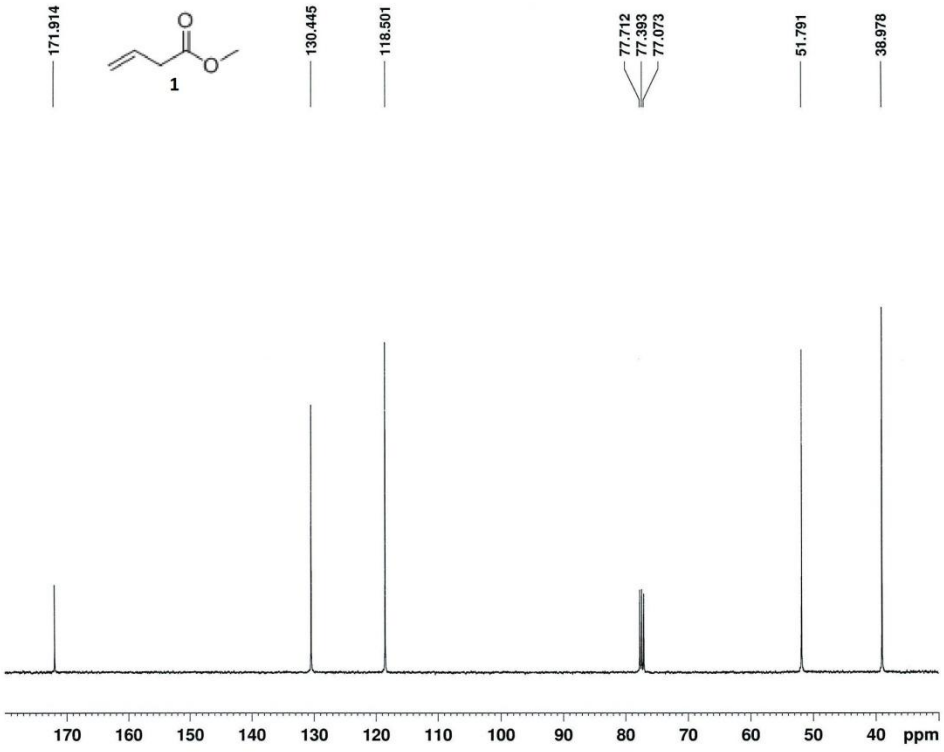
2.000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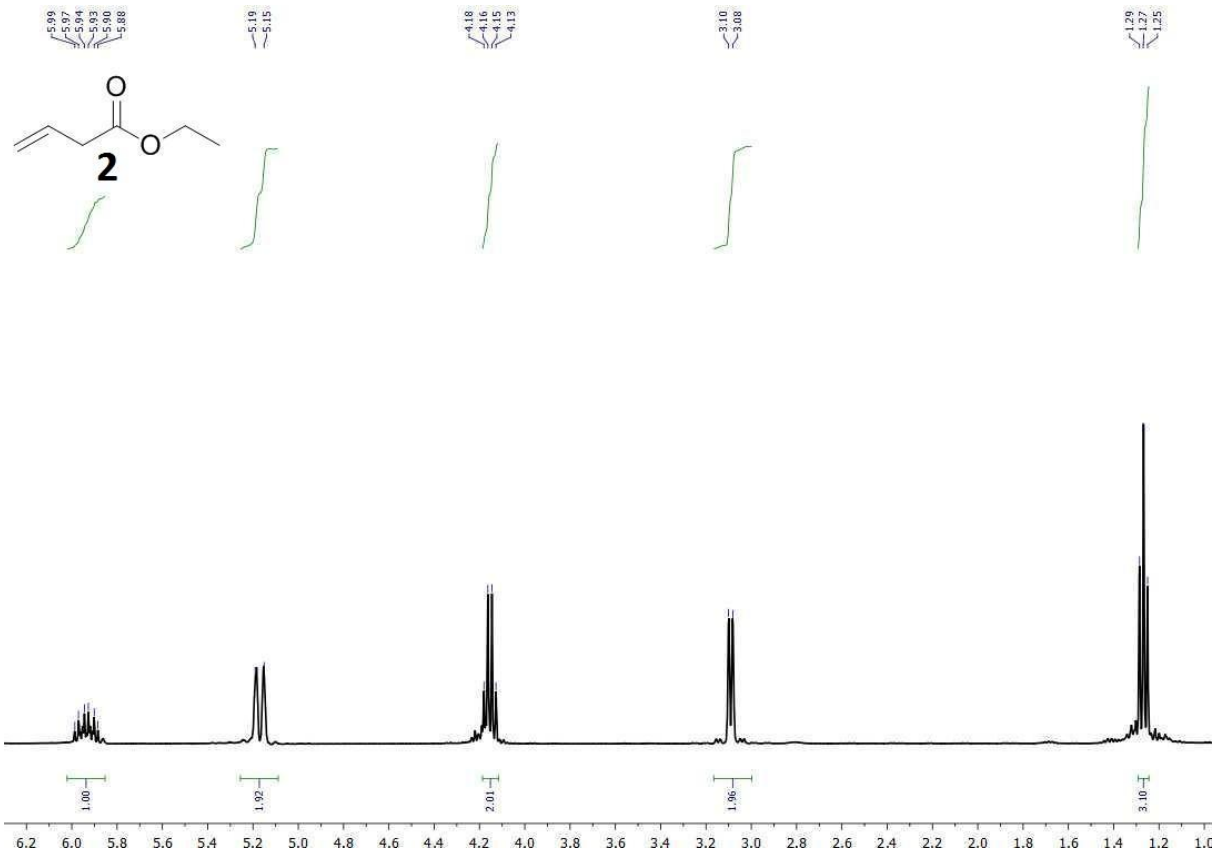
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4.13
3.10
3.08
1.29
1.27
1.25
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O
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1.92
2.01
1.96
3.10
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6.0
5.8
5.6
5.4
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5.0
4.8
4.6
4.4
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4.0
3.8
3.6
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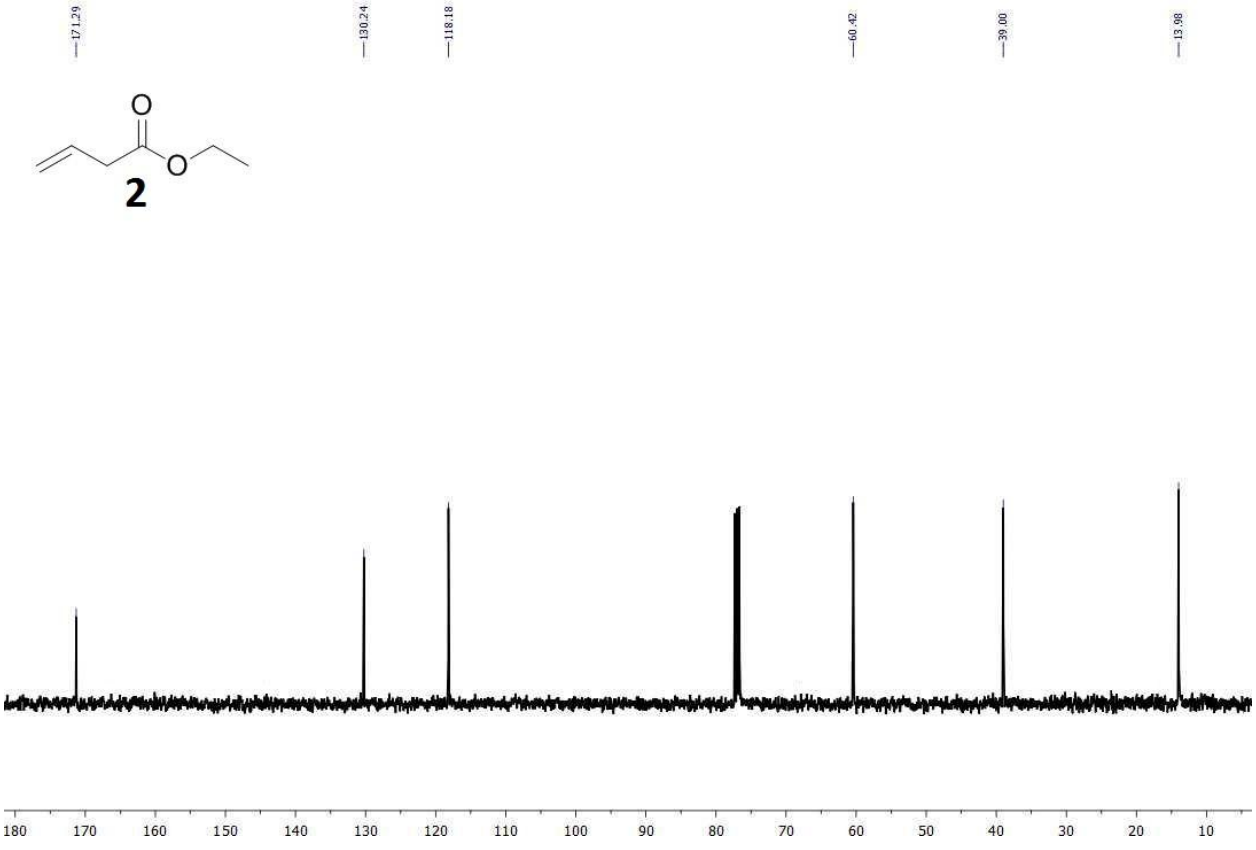
1.2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30
20
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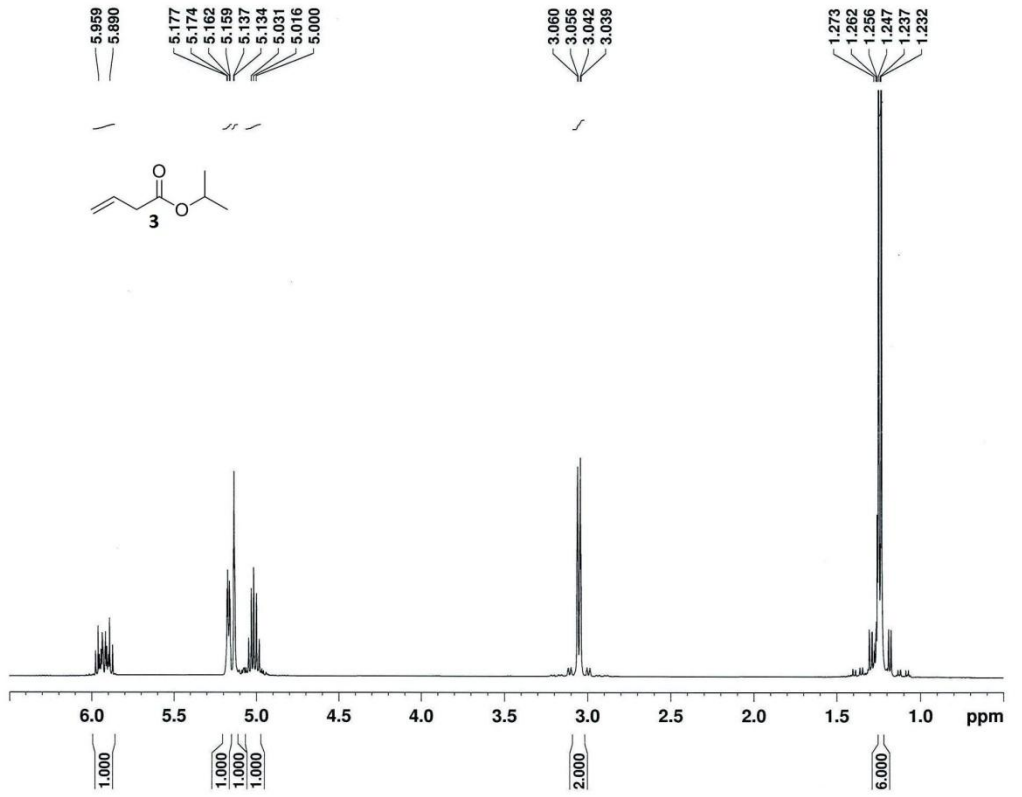
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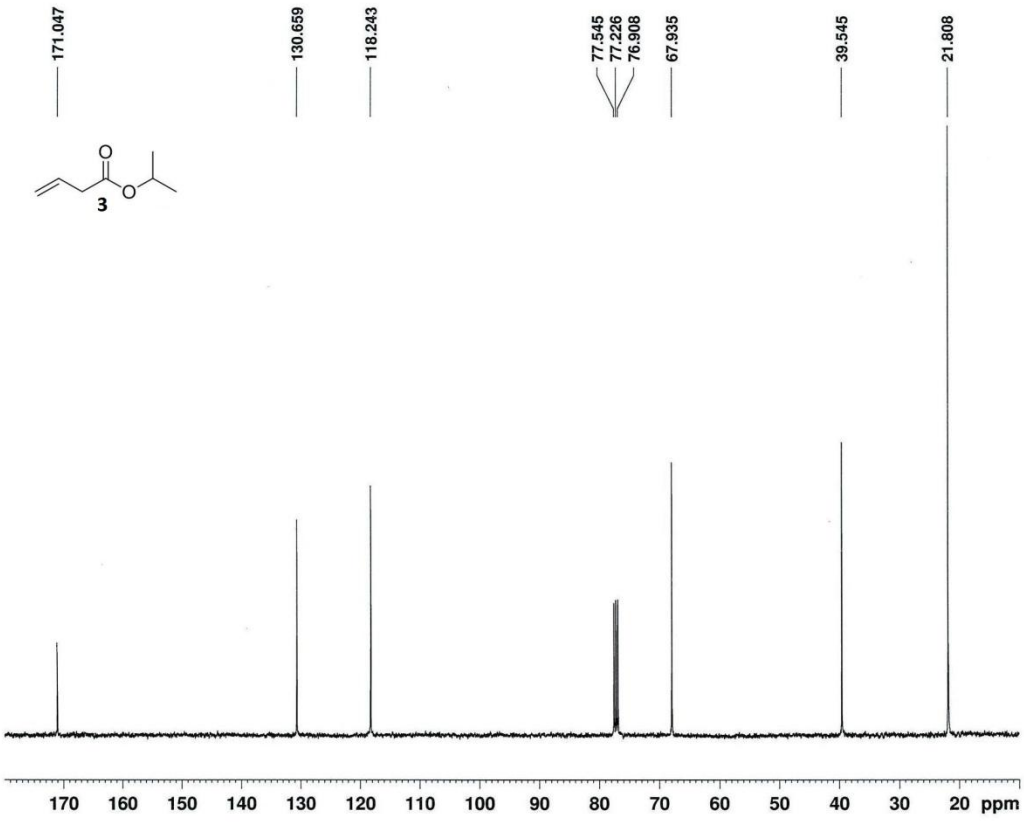
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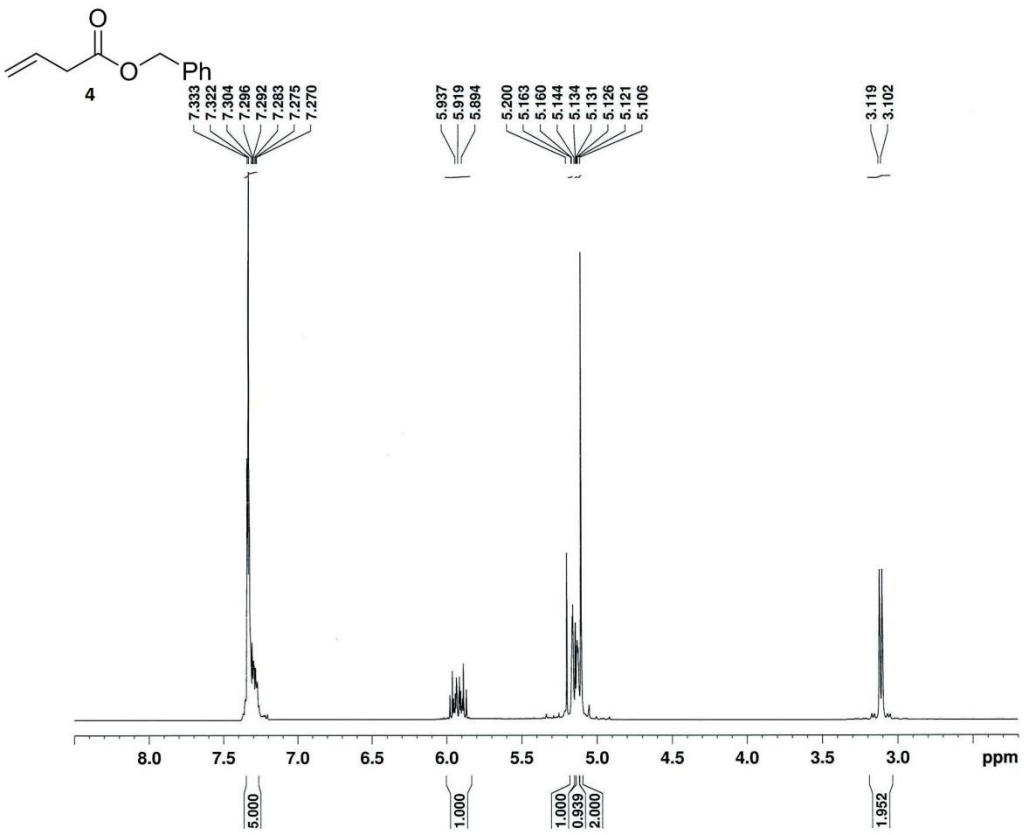
ppm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5.160
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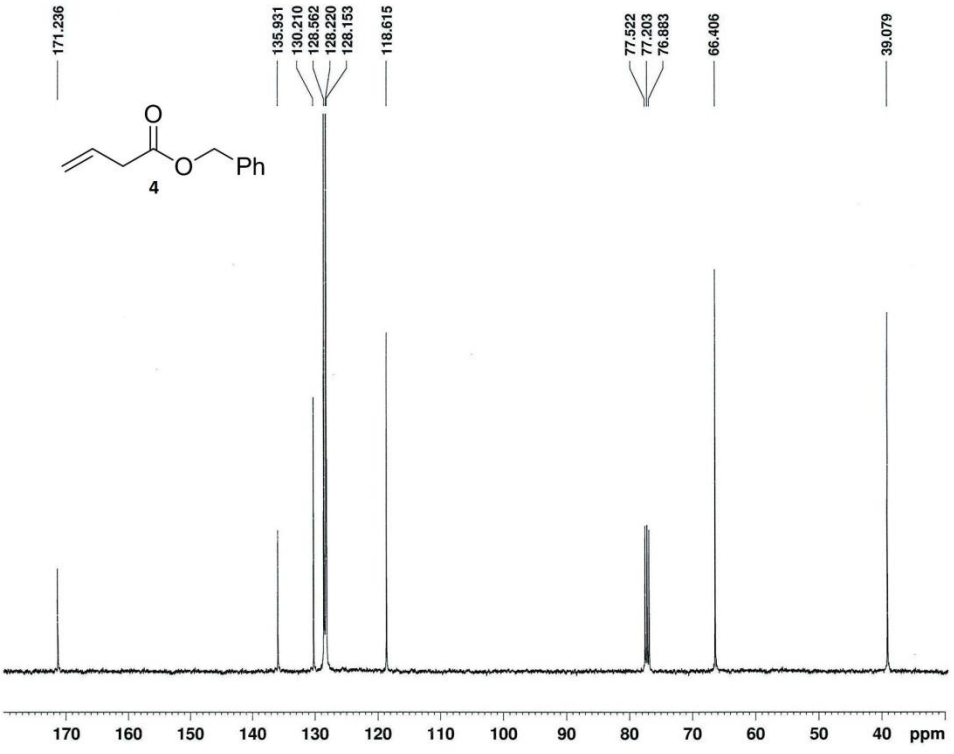
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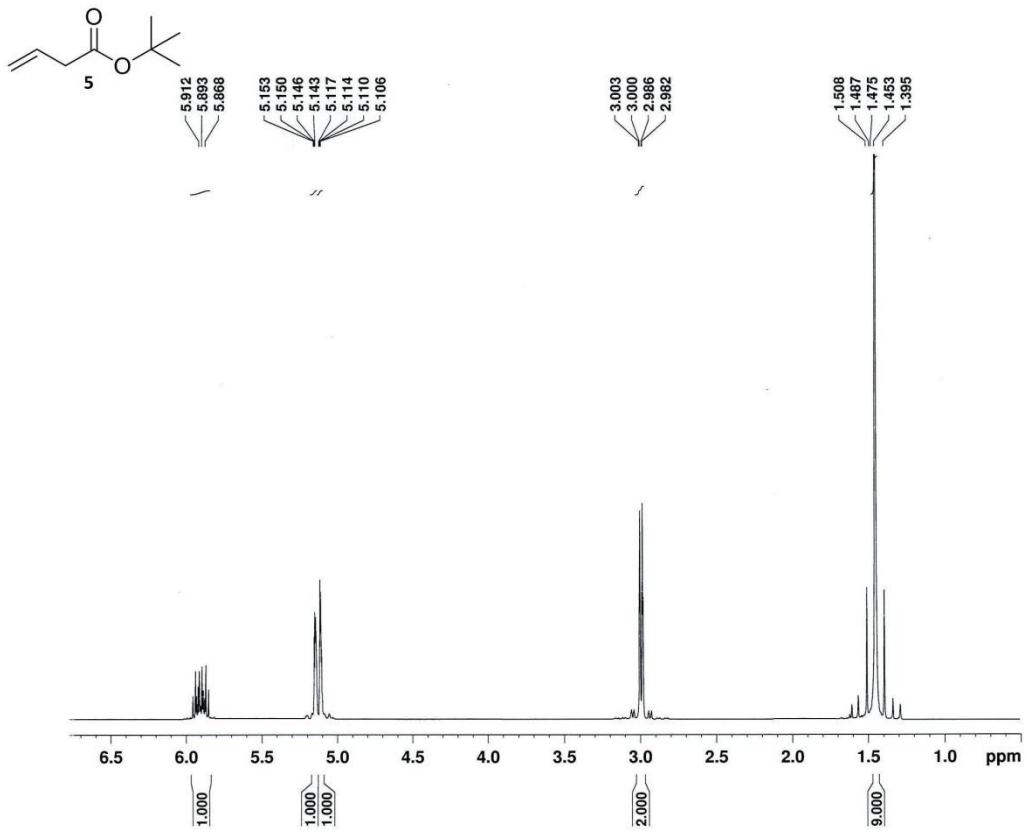
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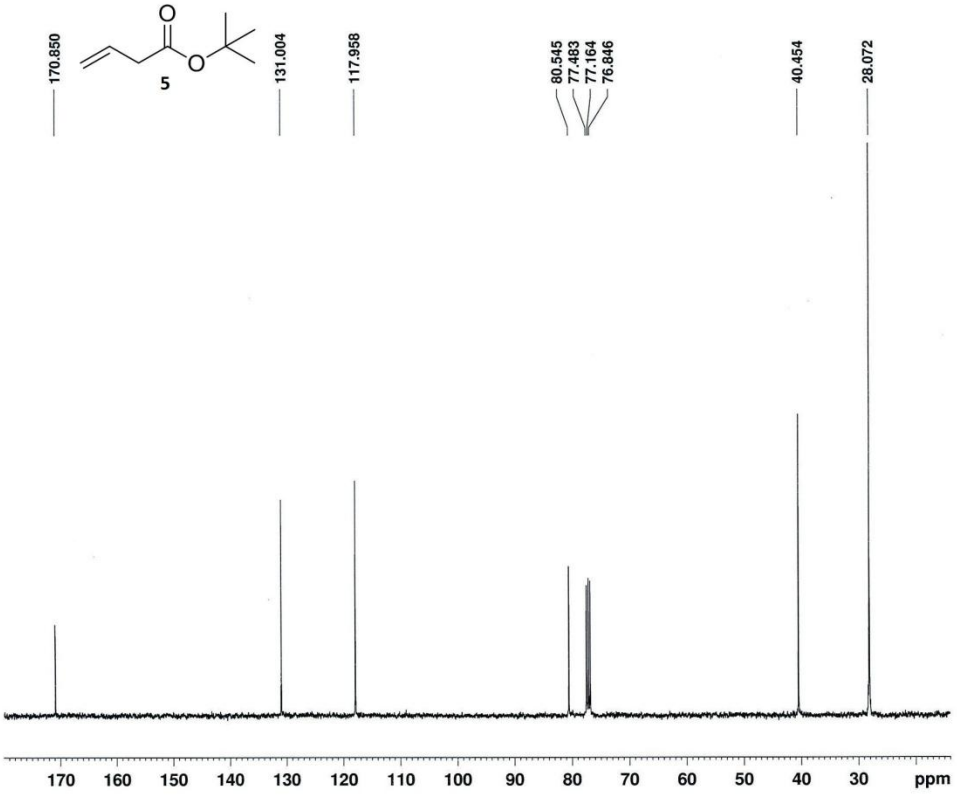
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40
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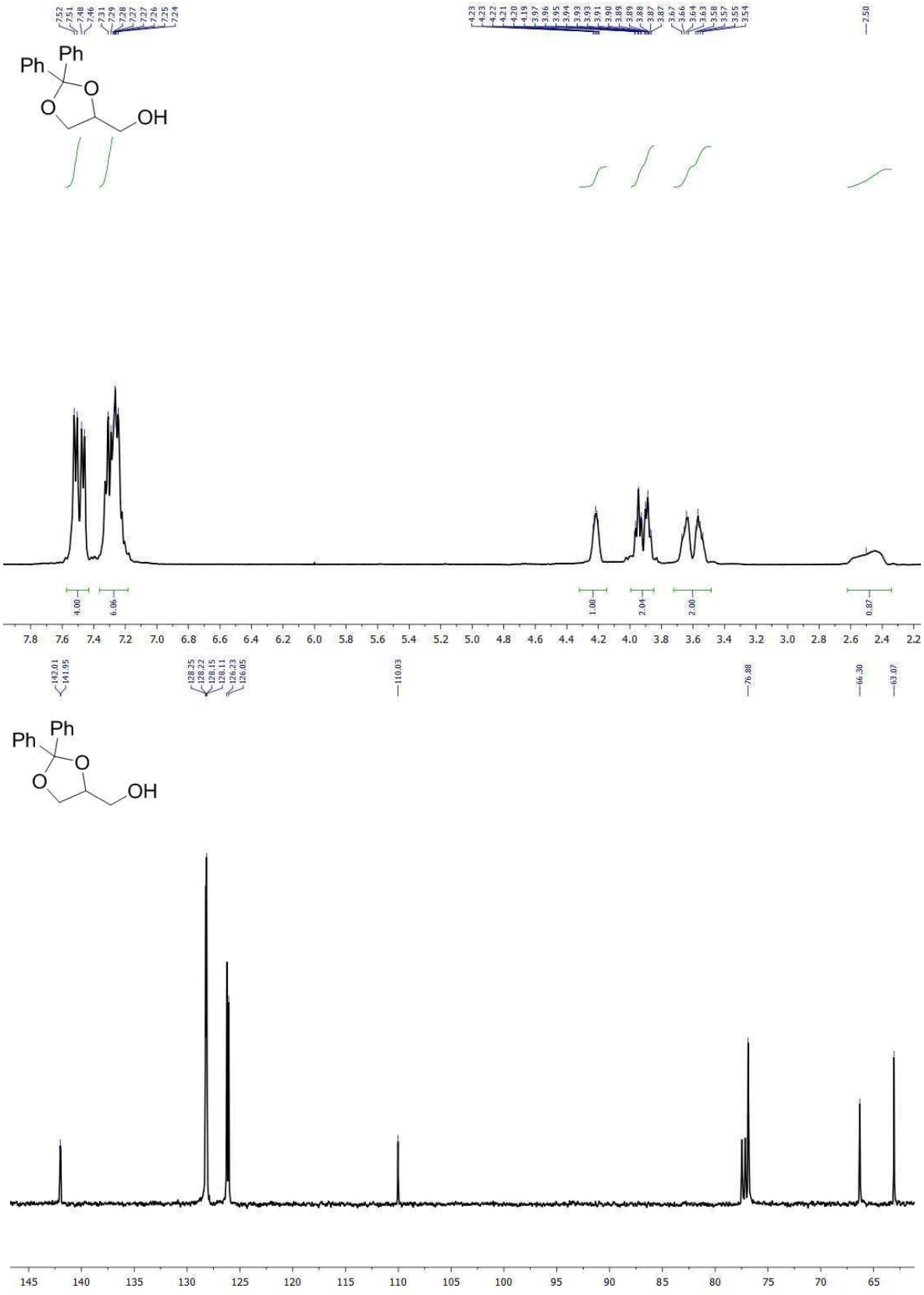
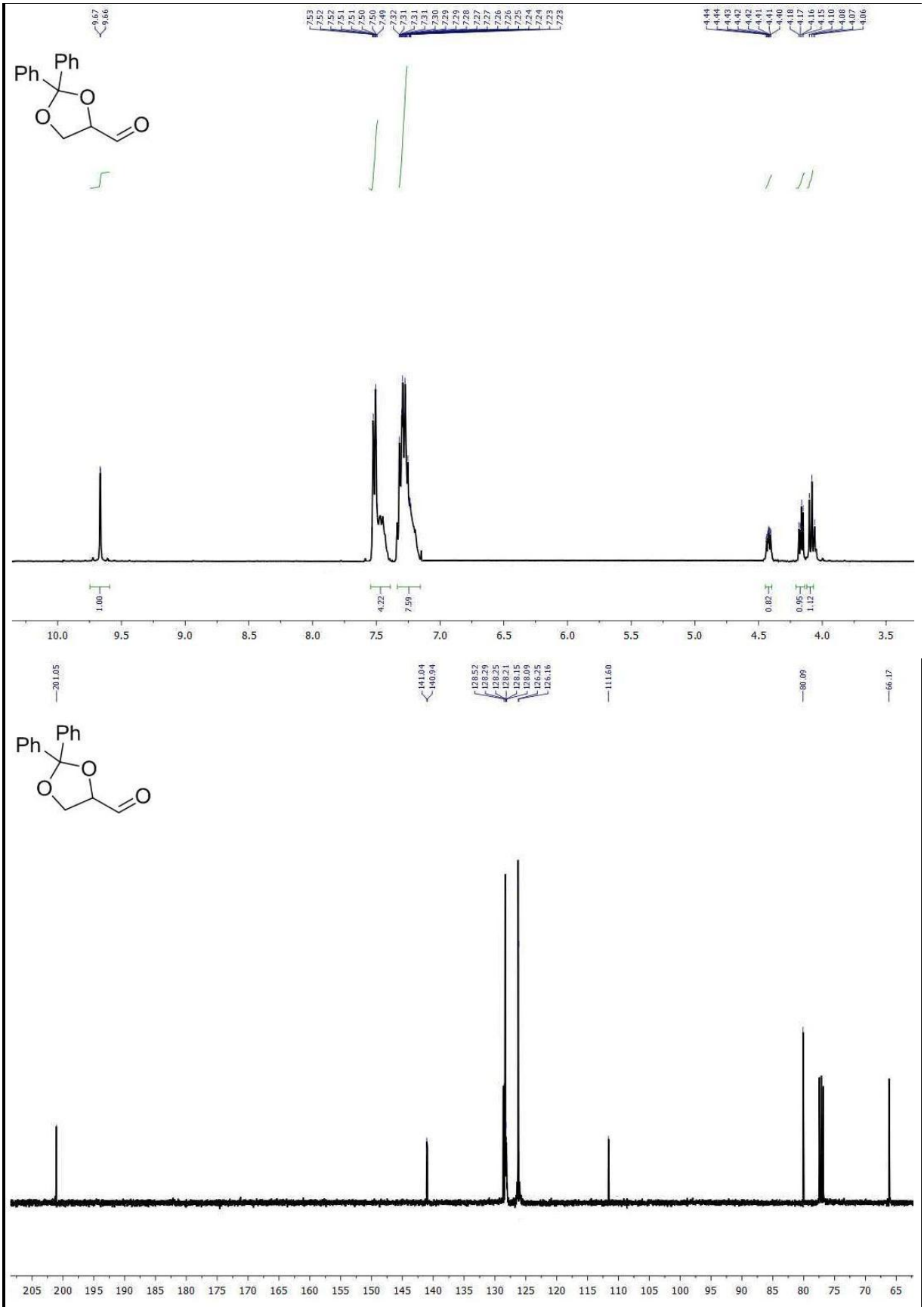
ppm

NMR Spectra of Aldehydes and their Precursors

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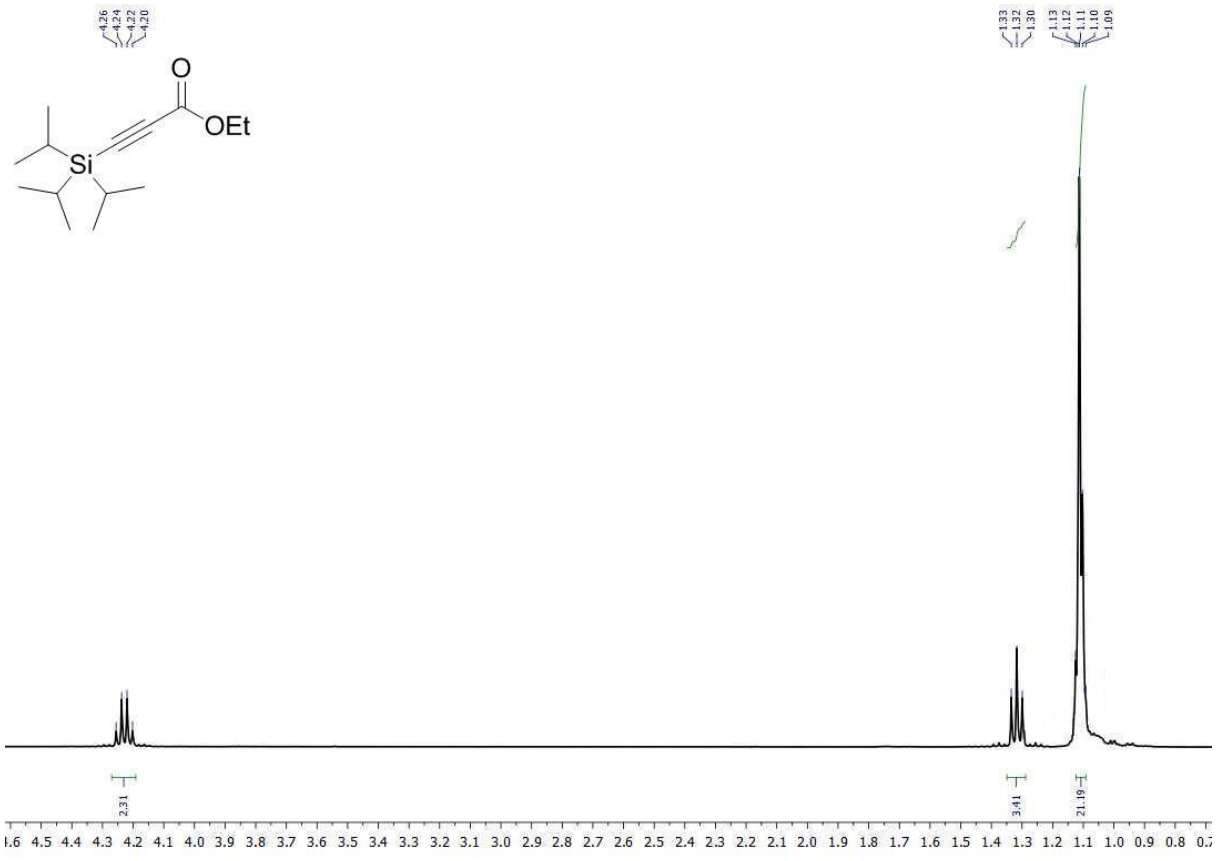
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Si
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3.41
21.19
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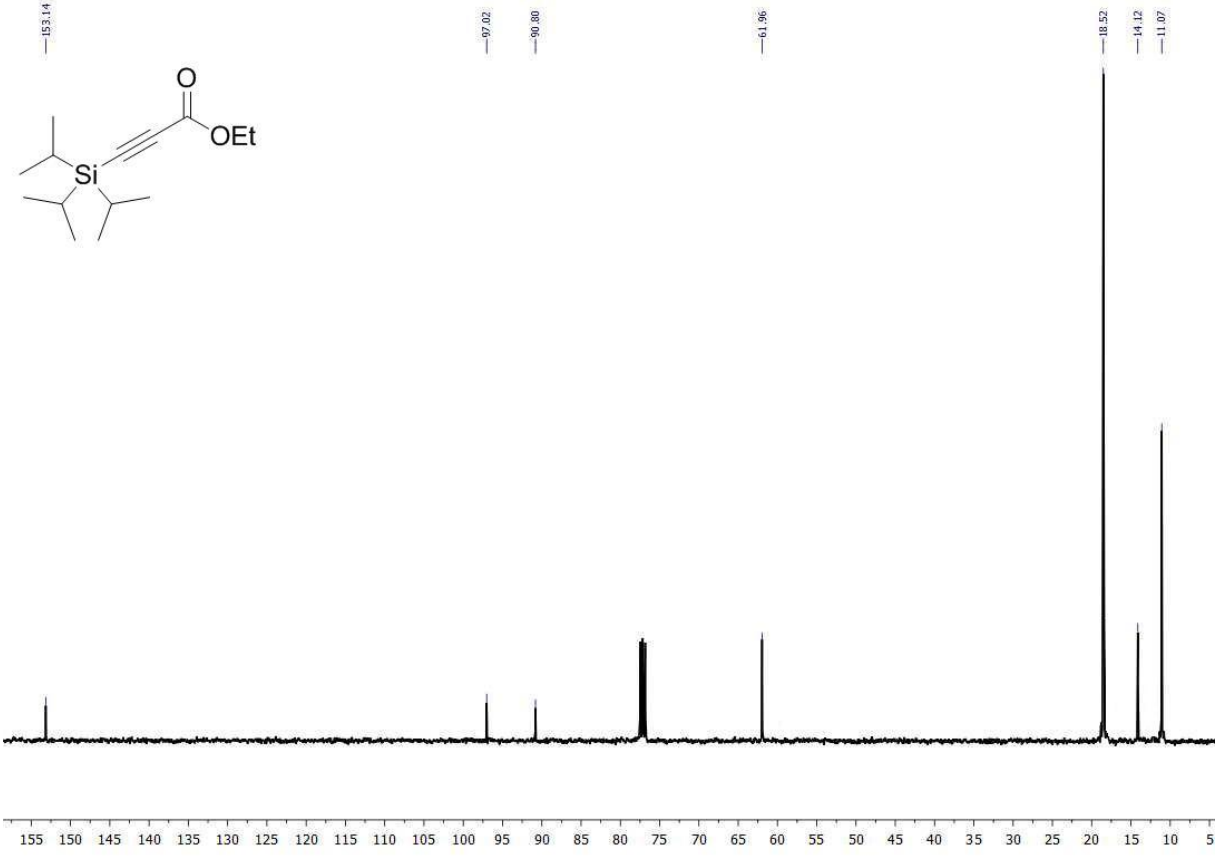
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OEt
Si
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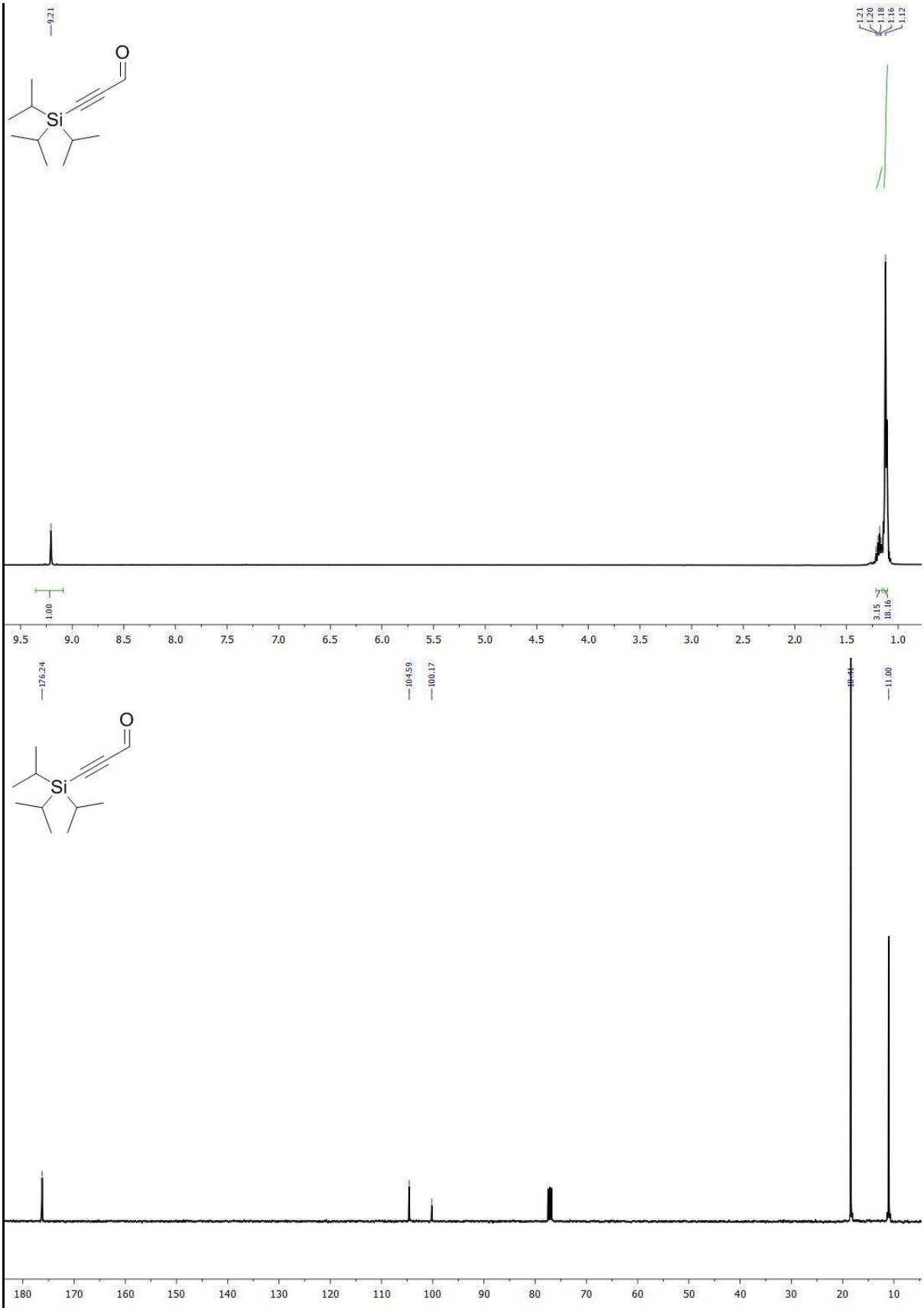
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1.20
1.18
1.16
1.12
O
Si
1.00
3.15
18.16
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
176.24
104.59
100.17
18.41
11.00
O
Si
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170
160
150
140
130
120
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100
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80
70
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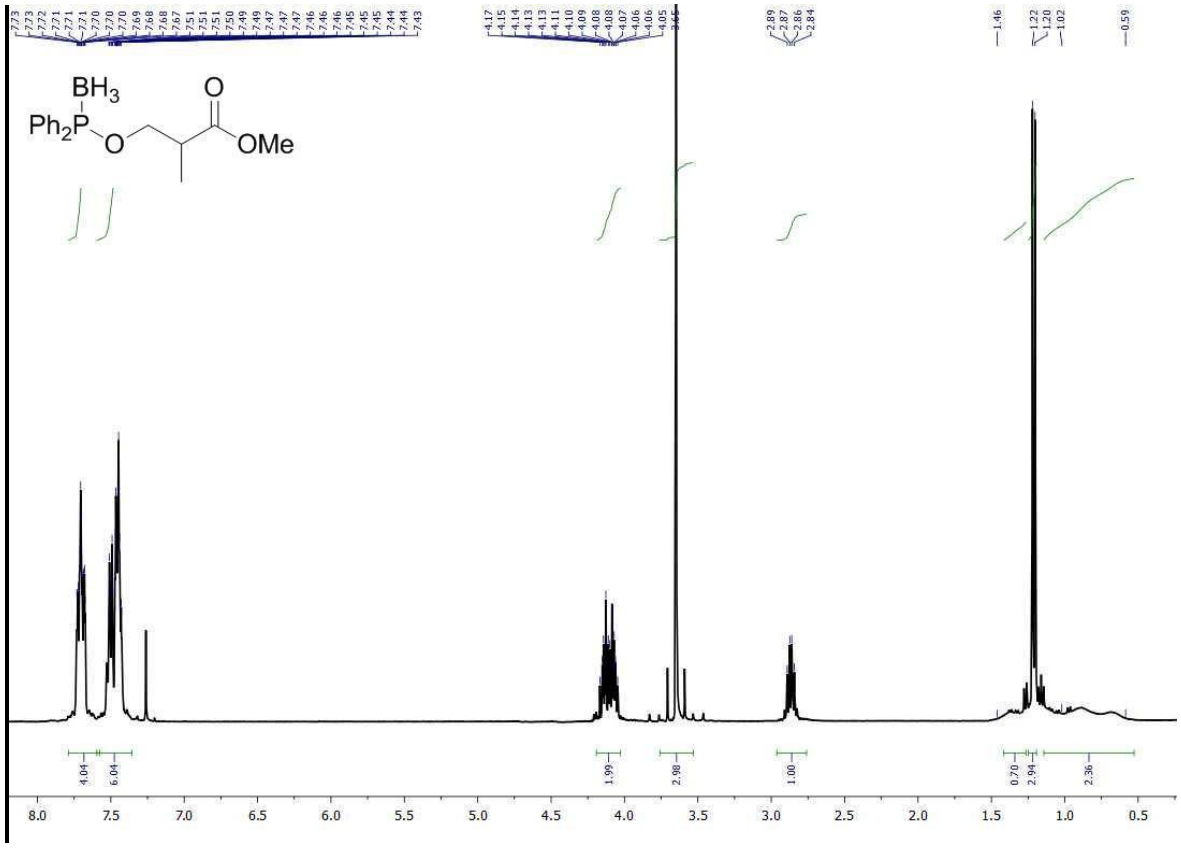
40
30
20
10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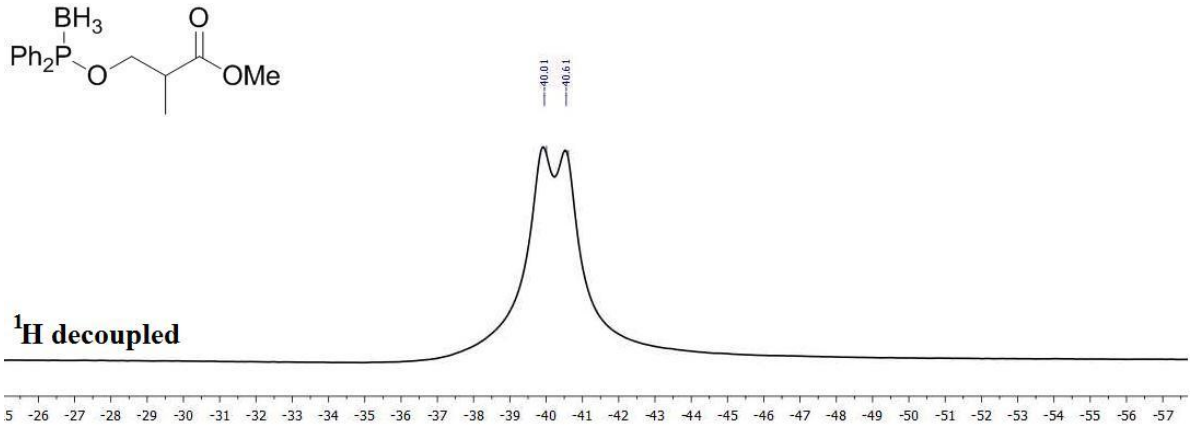
Ph2P
O
OMe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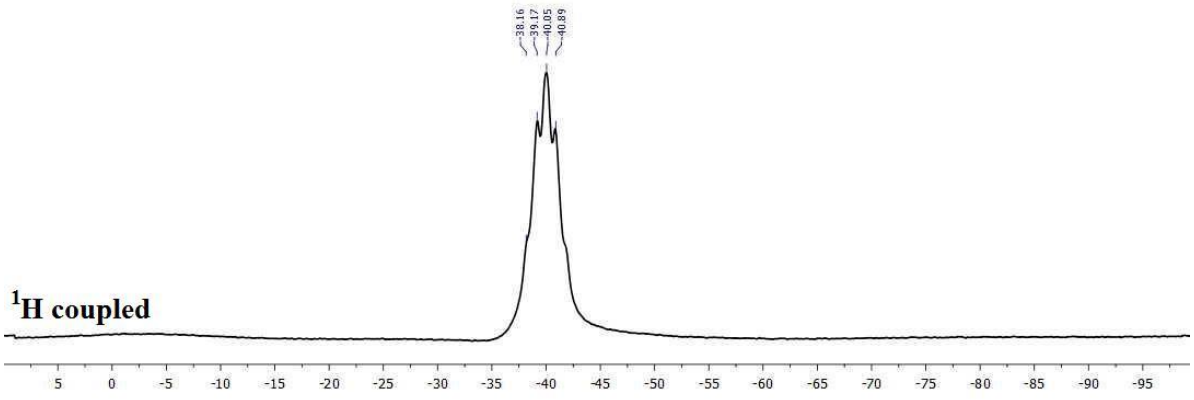
Ph2P
O
OMe
40.01
40.61
1H decoupled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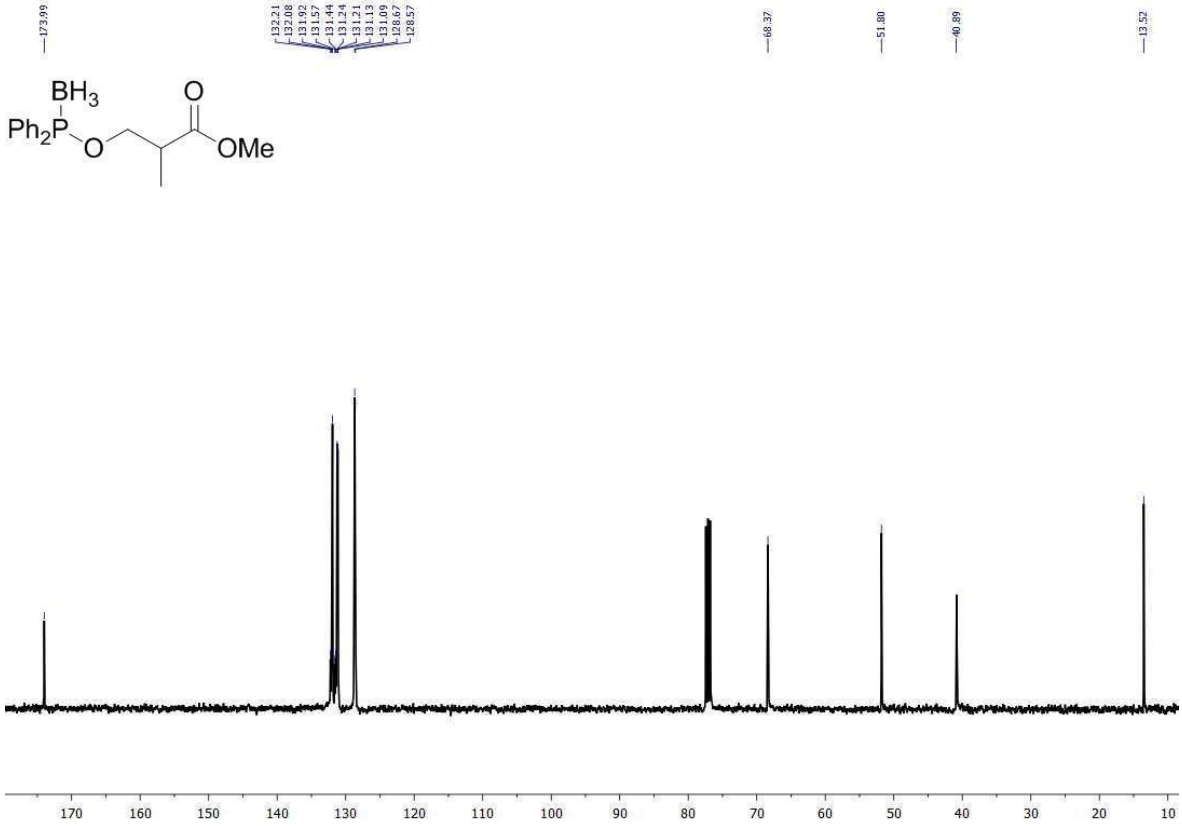
39.17
40.05
40.89
1H coupled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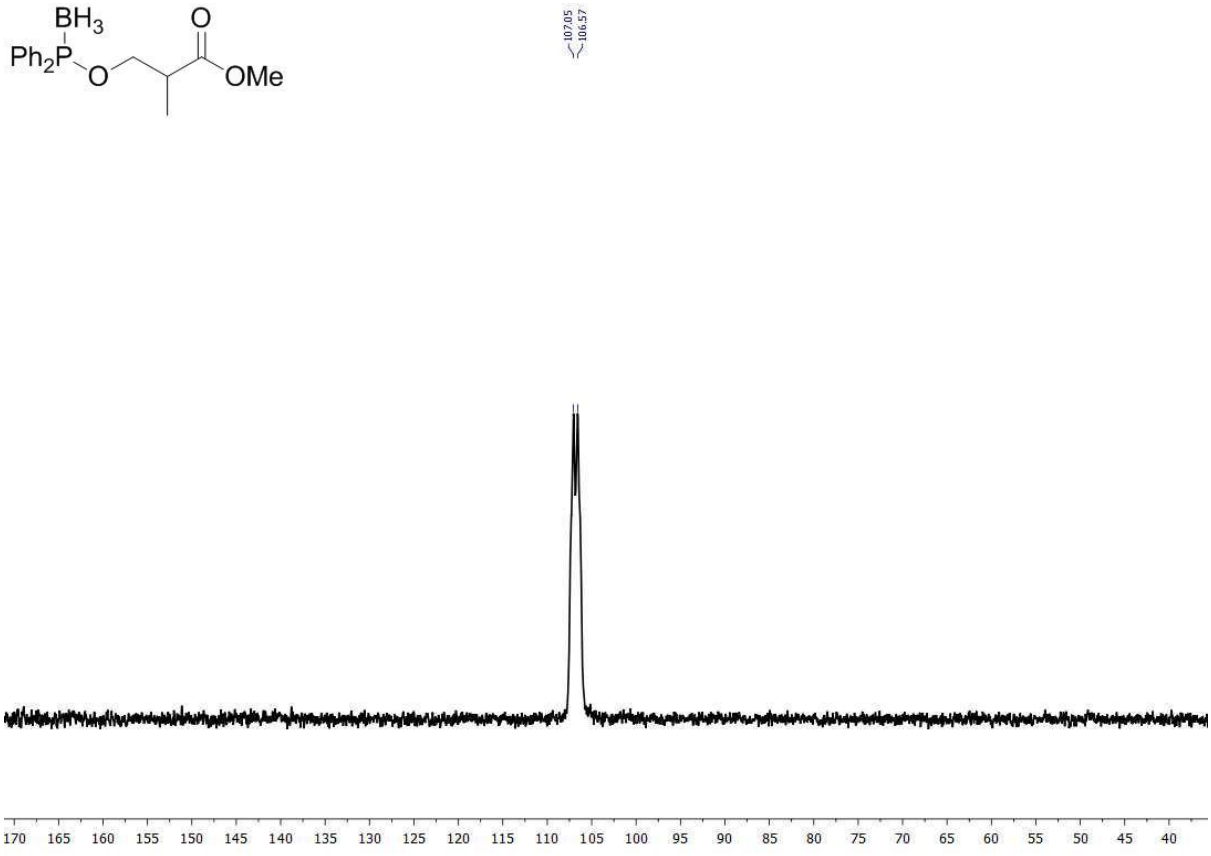
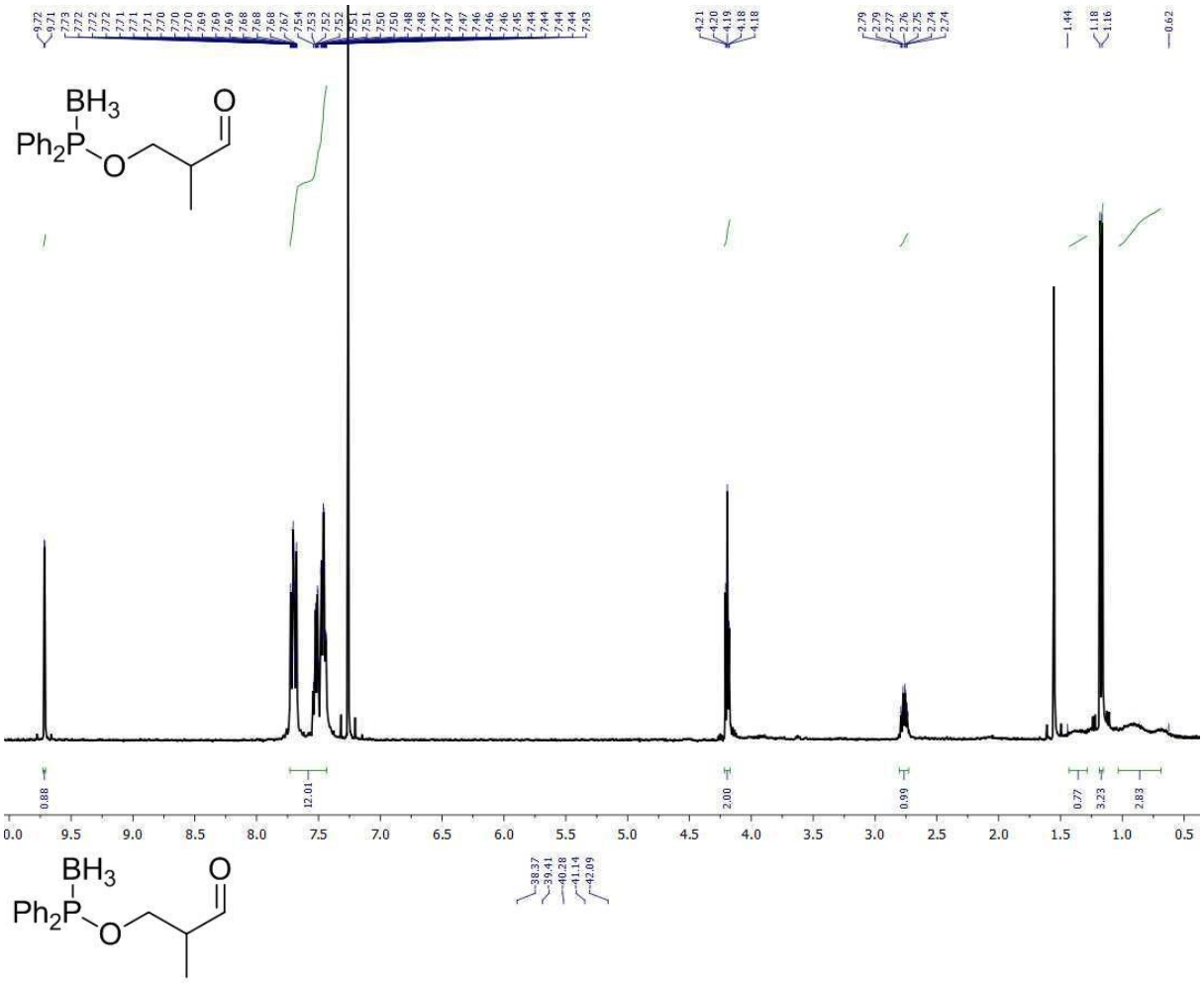
132.21
132.08
131.92
131.57
131.44
131.24
131.21
131.13
131.09
128.67
128.57
68.37
51.80
40.89
13.52
BH3
Ph2P
O
O
OMe
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


107.05
106.57
BH3
Ph2P
O
O
OMe
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40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Ph2P
O
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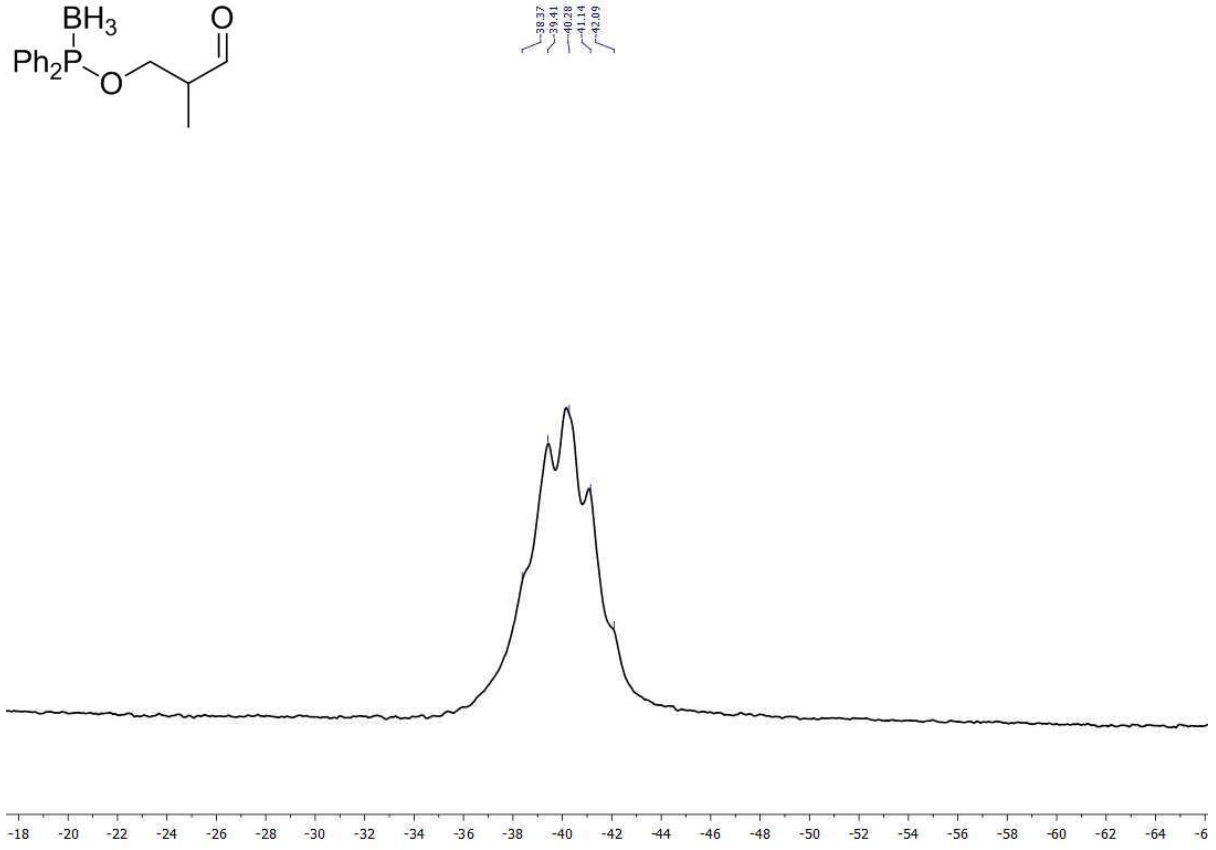
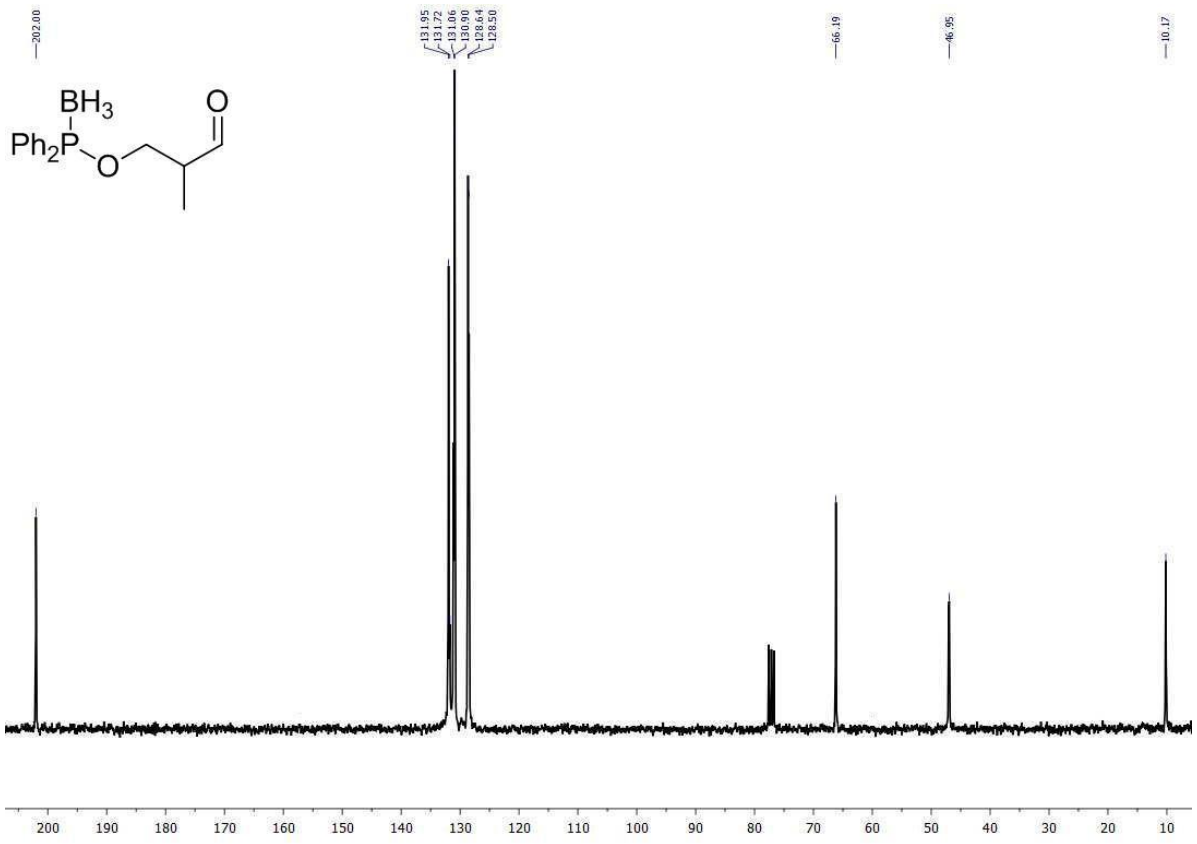
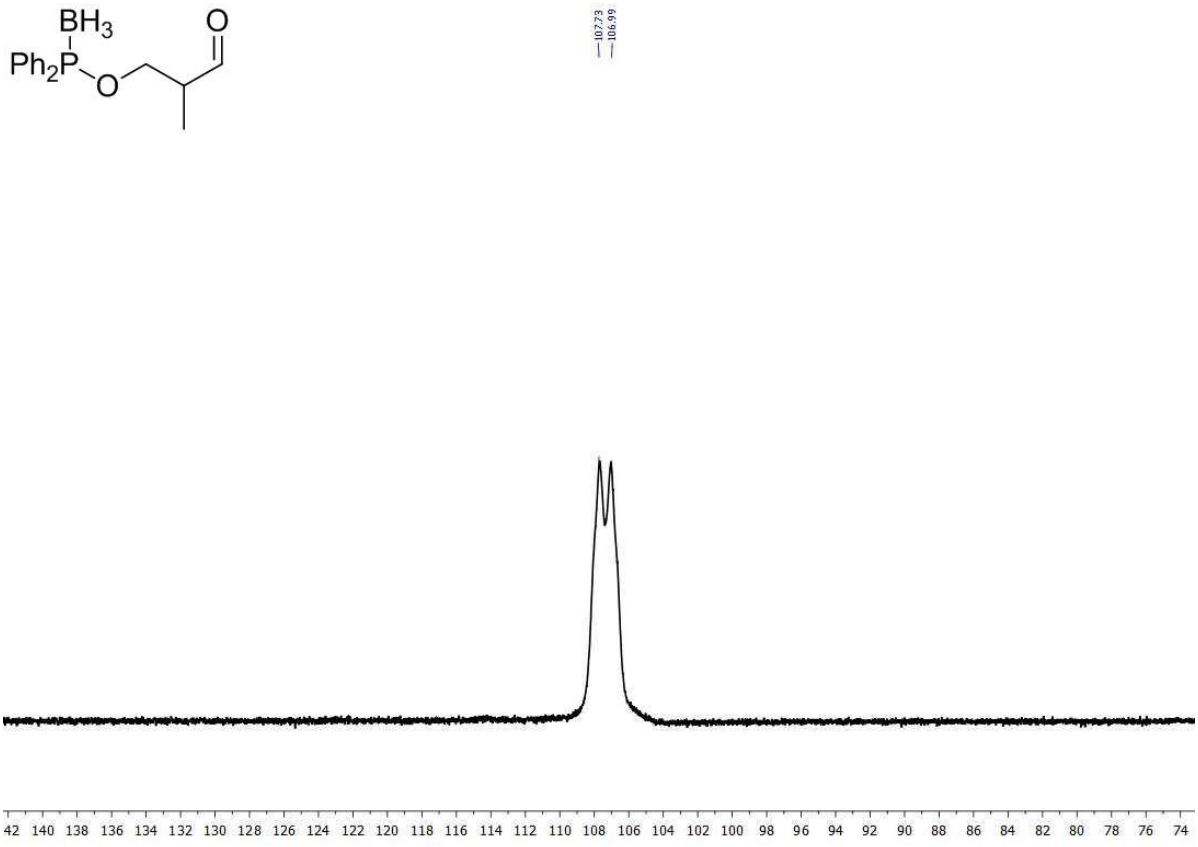

BH3
Ph2P
O
O


202.00
131.95
131.72
131.66
130.90
128.64
128.50
66.19
46.95
10.17
BH3
Ph2P
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


107.73
106.99
BH3
Ph2P
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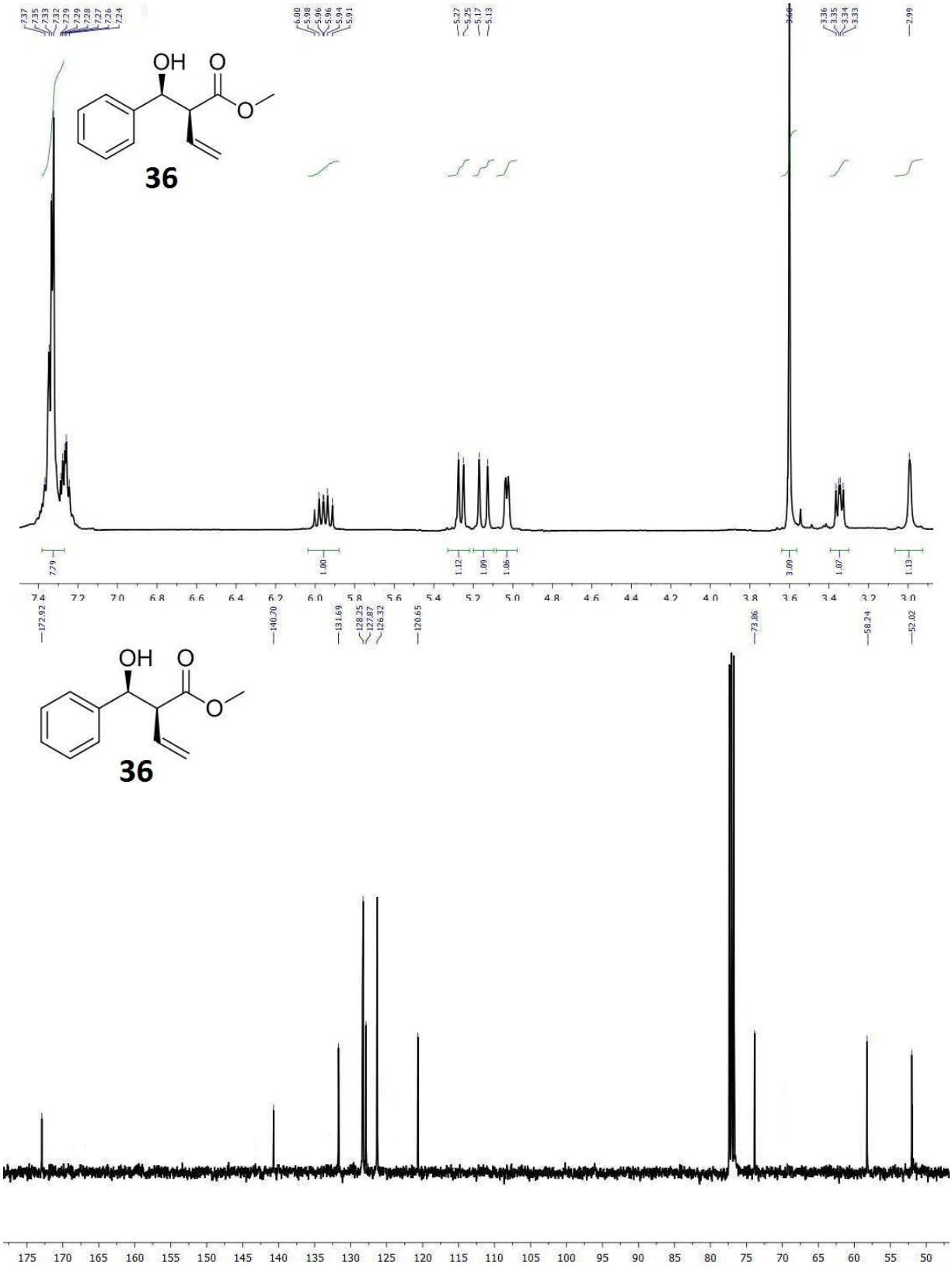
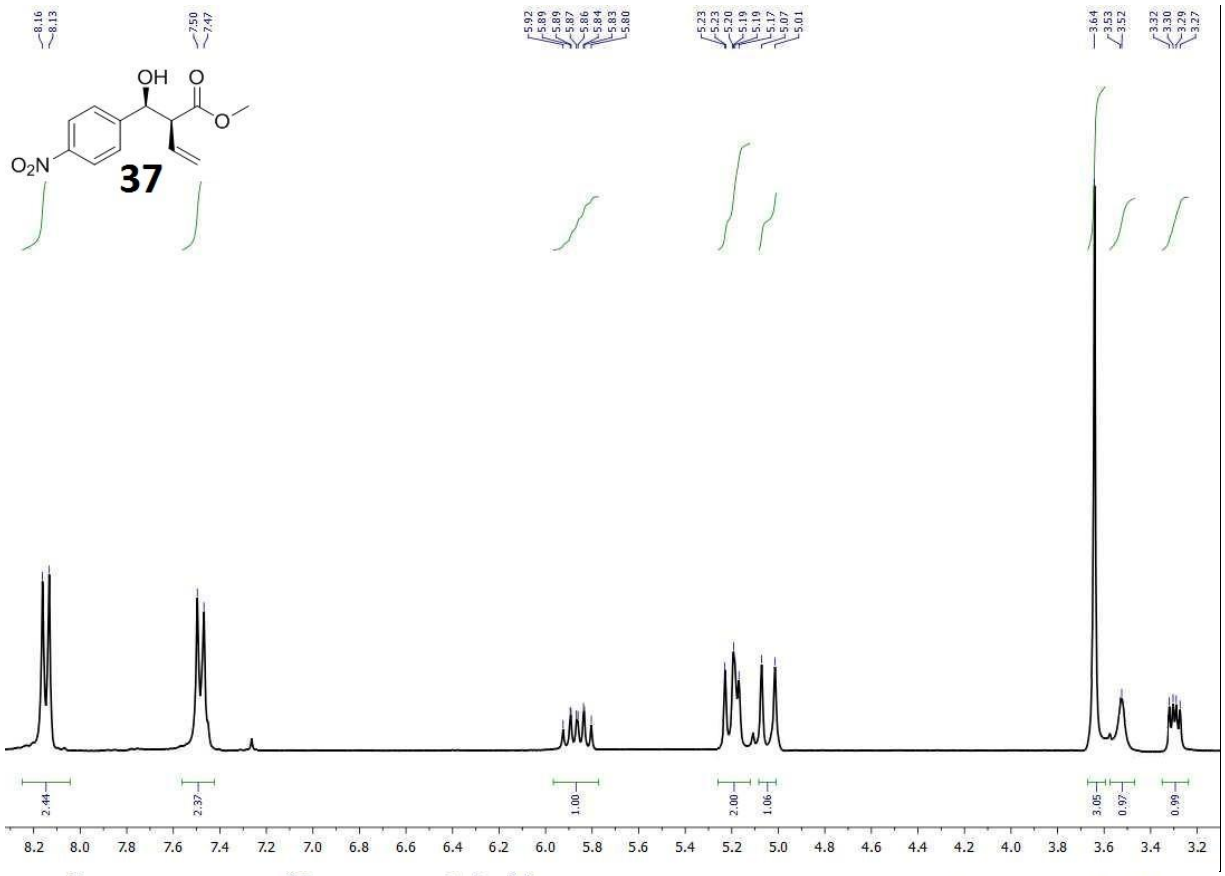
O
42 140 138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94 92 90 88 86 84 82 80 78 76 74

NMR Spectra of *Syn*-aldol Products




8.16
8.13
7.50
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5.92
5.89
5.89
5.87
5.86
5.84
5.83
5.80
5.23
5.23
5.20
5.19
5.19
5.17
5.07
5.01
3.64
3.53
3.52
3.32
3.30
3.30
3.29
3.27
OH
O
O
O2N
37
2.44
2.37
1.00
2.00
1.06
3.05
0.97
0.99
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
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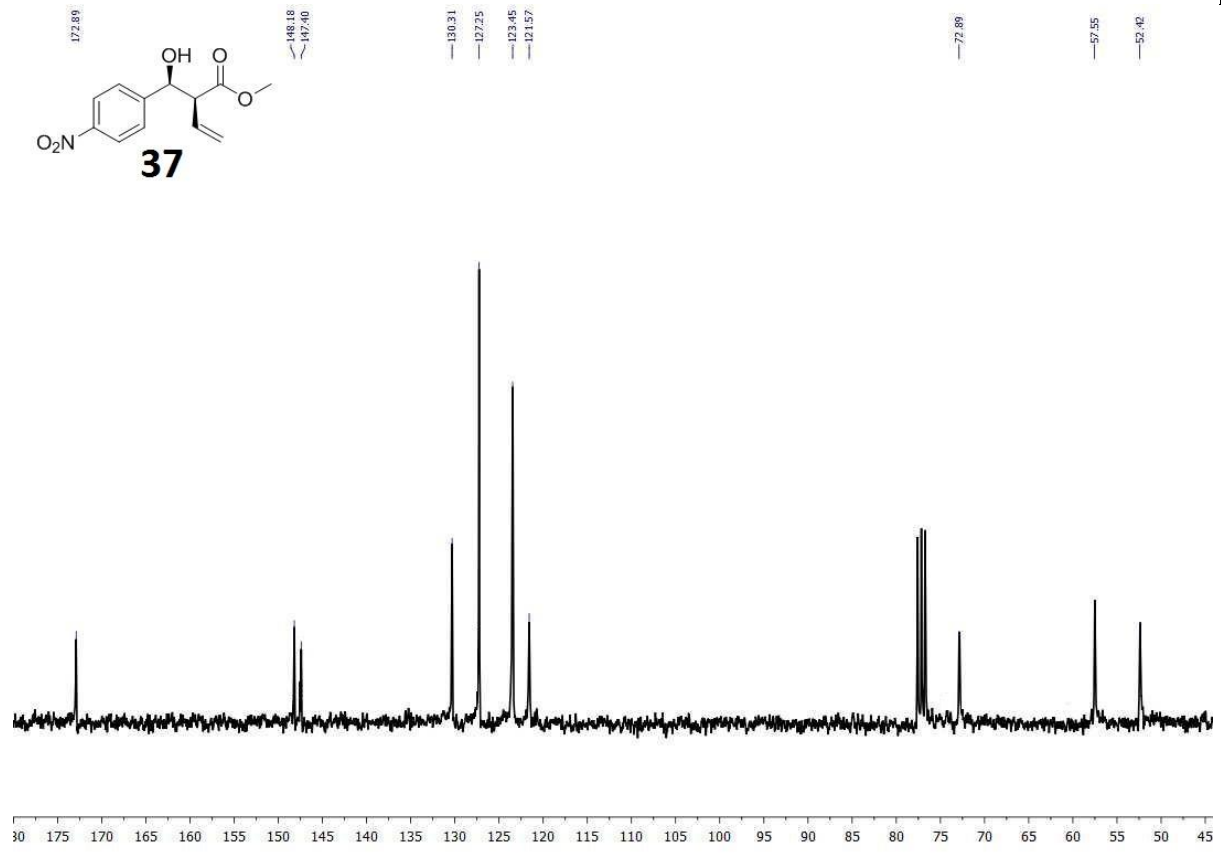
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2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148.18
147.40
130.31
127.25
123.45
121.57
72.89
57.55
52.42
OH
O
O
O2N
37
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
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90
85
80
75
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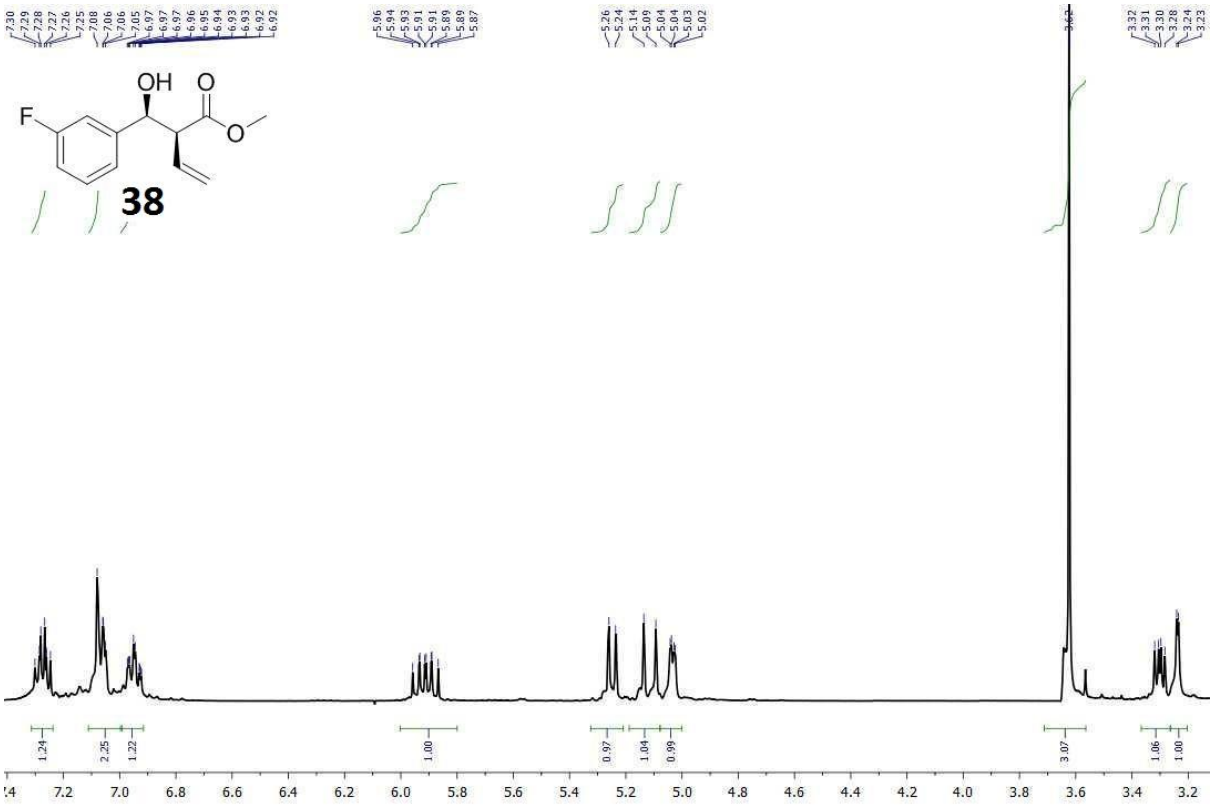
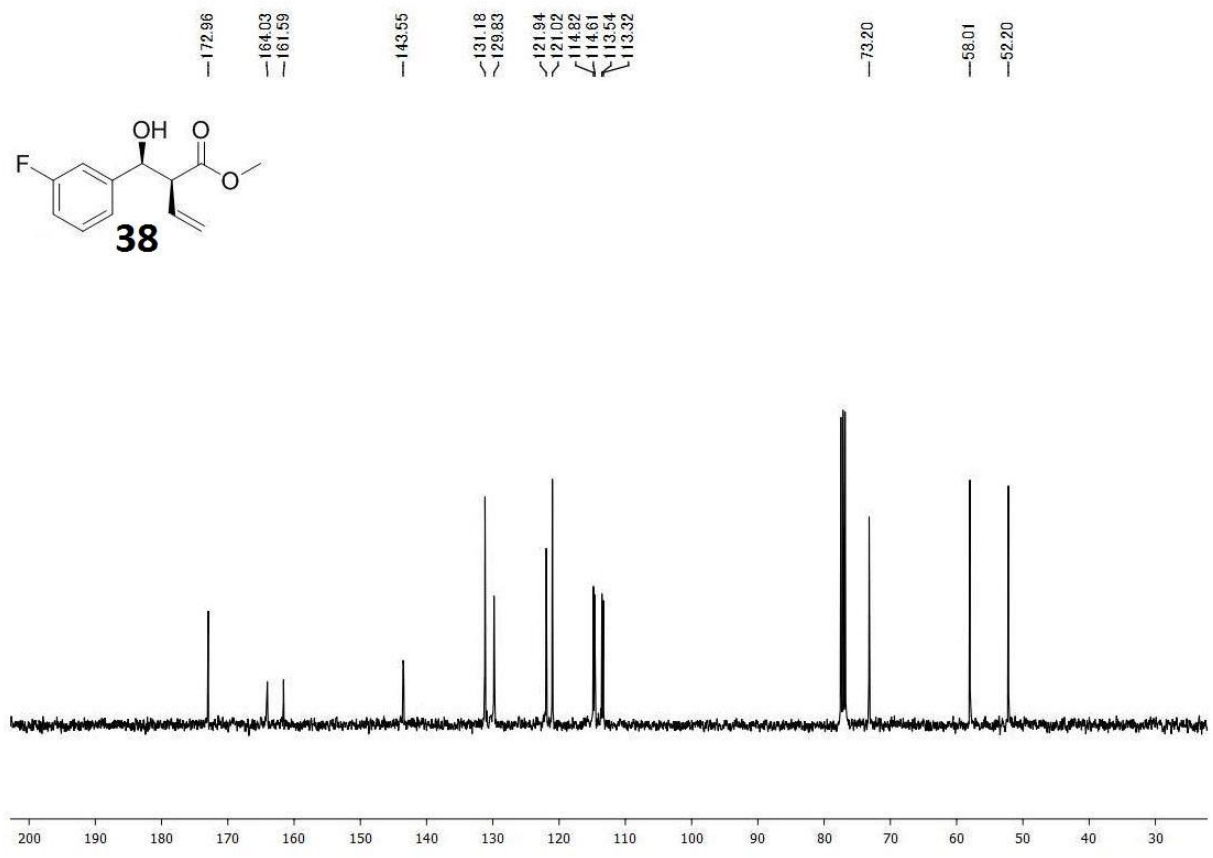
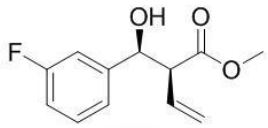
65
60
55
50
45


OH
O
F
O
38


OH
O
F
O
38


OH
O
F
O

38

-114.49
-10
-20
-30
-40
-50
-60
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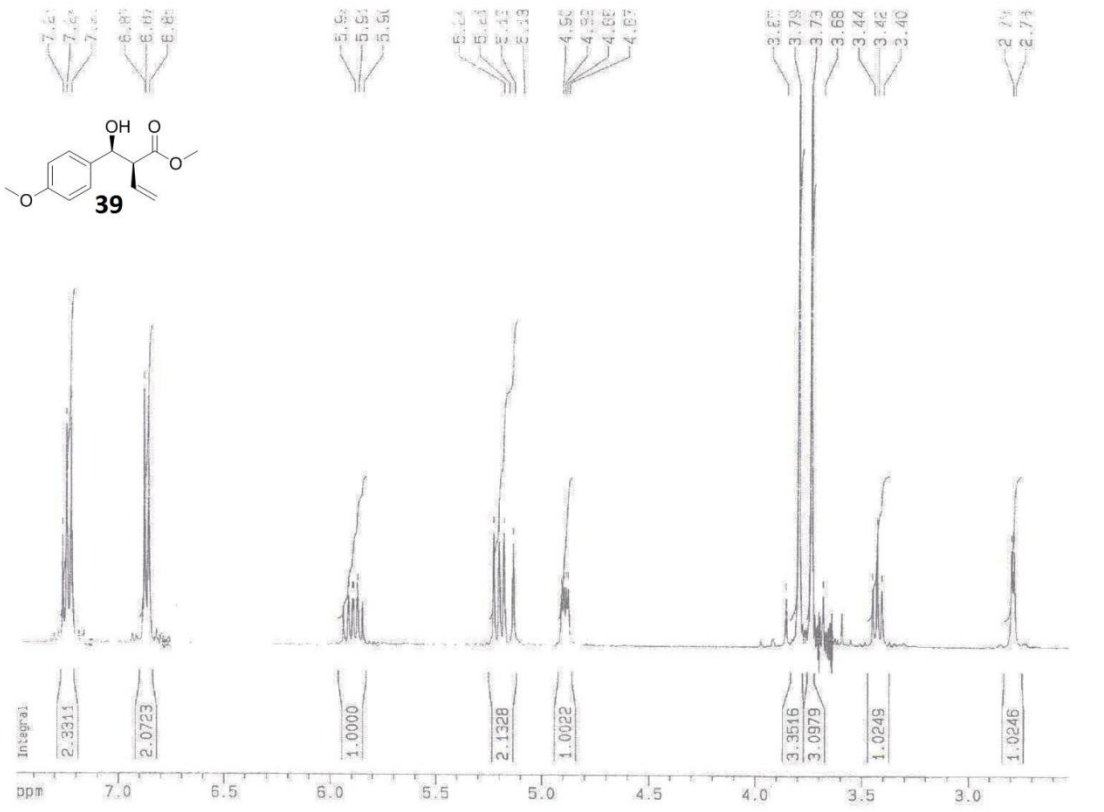
-160
-170
-180
-190
-200
-210
-22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O
O
O
39
Integral
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1.0000
2.1328
1.0022
3.3516
3.0979
1.0249
1.0246
ppm
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6.0
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5.0
4.5
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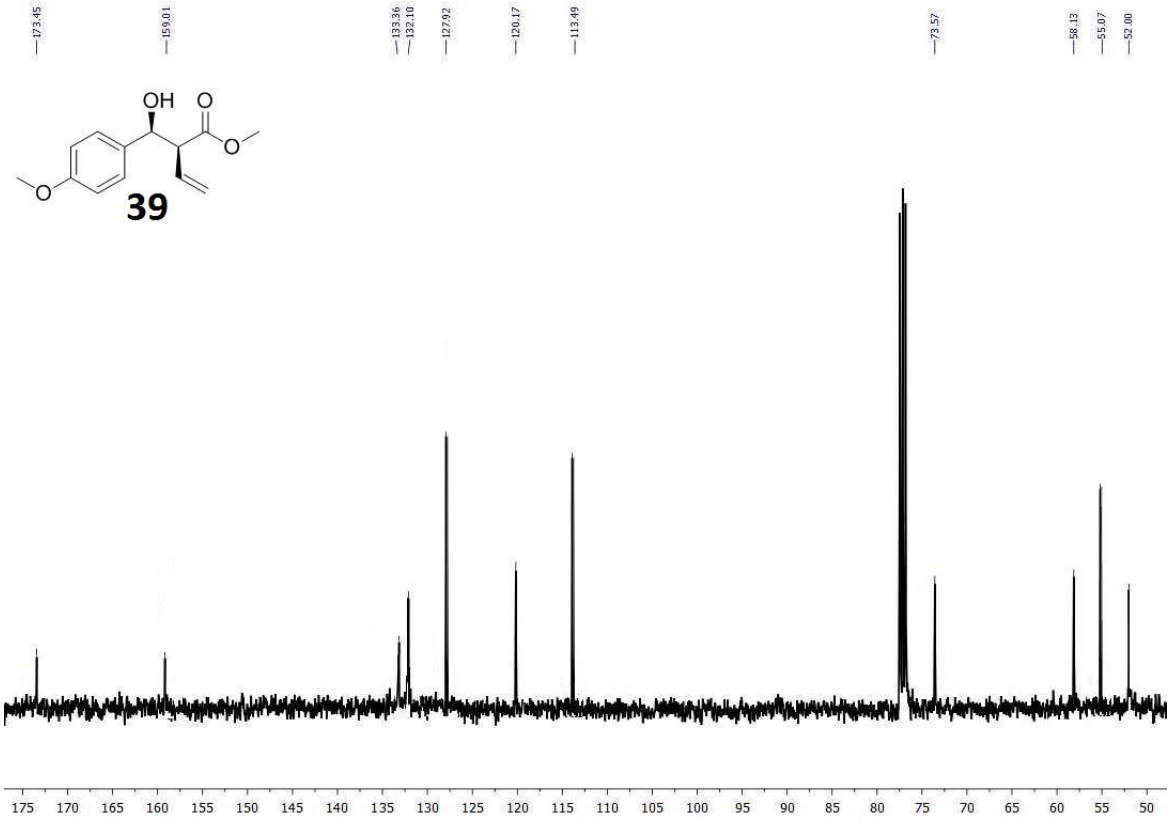
3.5
3.0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159.01
133.36
132.10
127.92
120.17
113.49
73.57
58.13
55.07
52.00
OH
O
O
O
39
175
170
165
160
155
150
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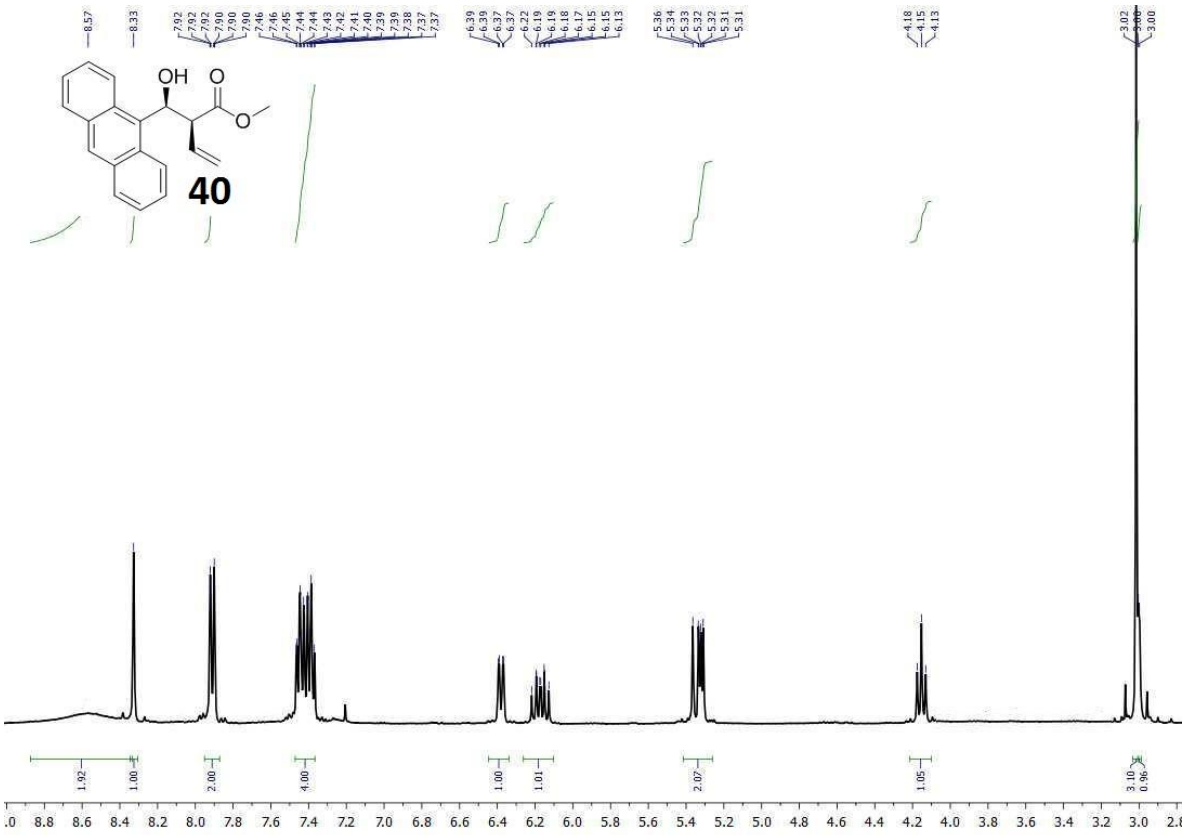
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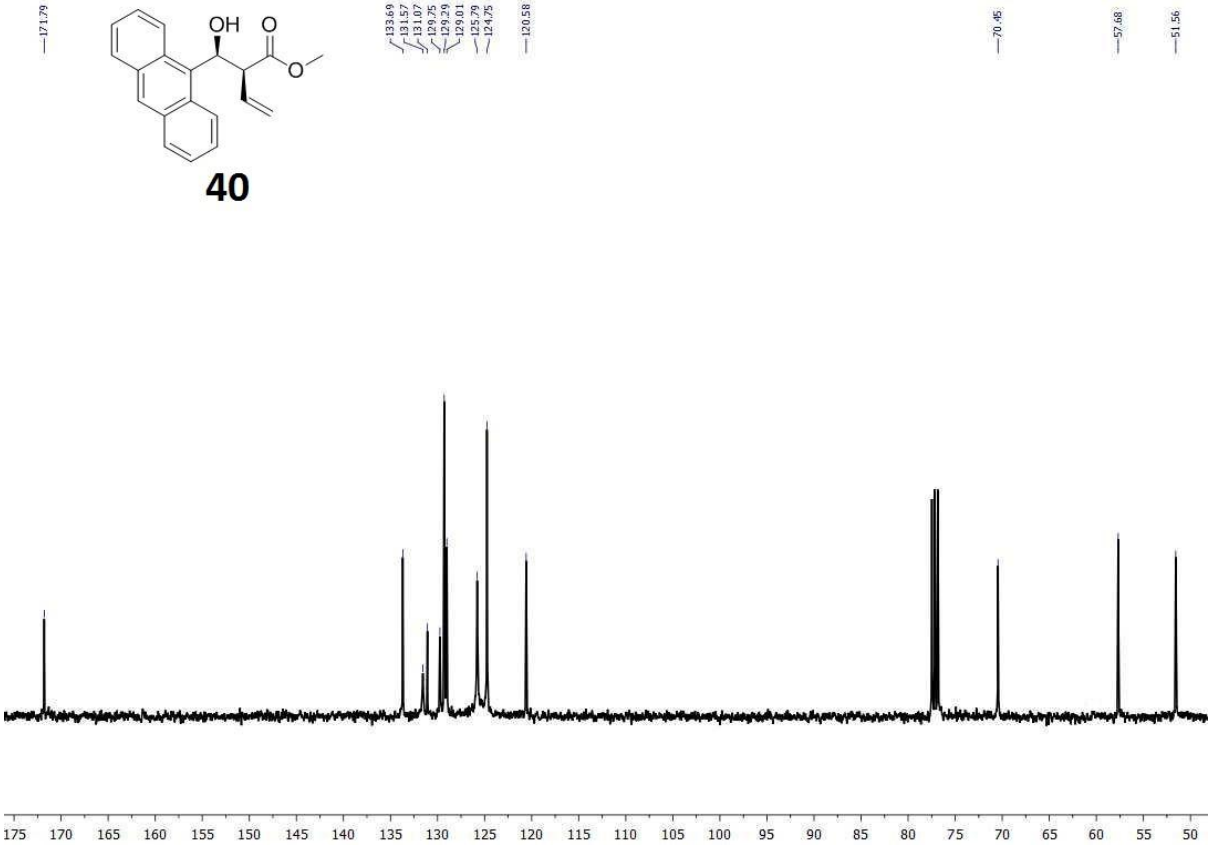
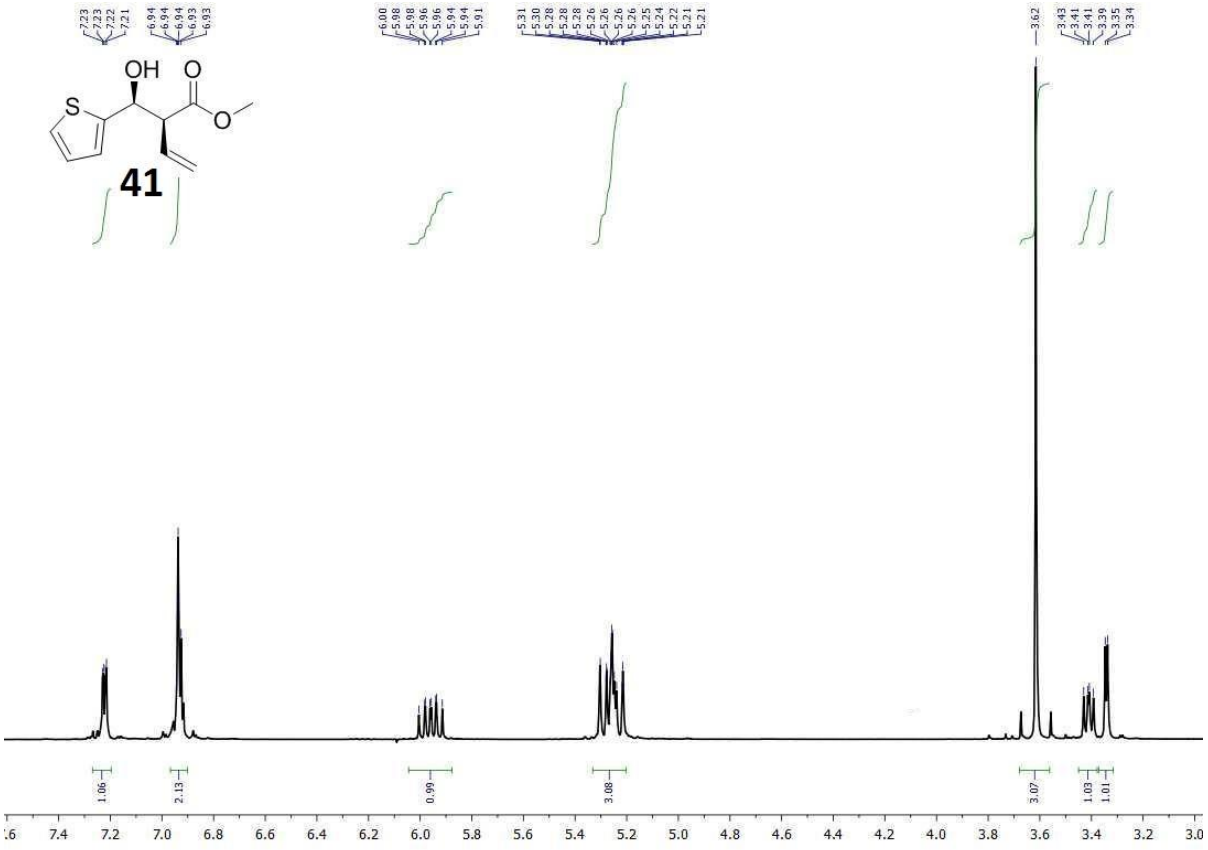

OH
O
O
40


OH
O
S
O
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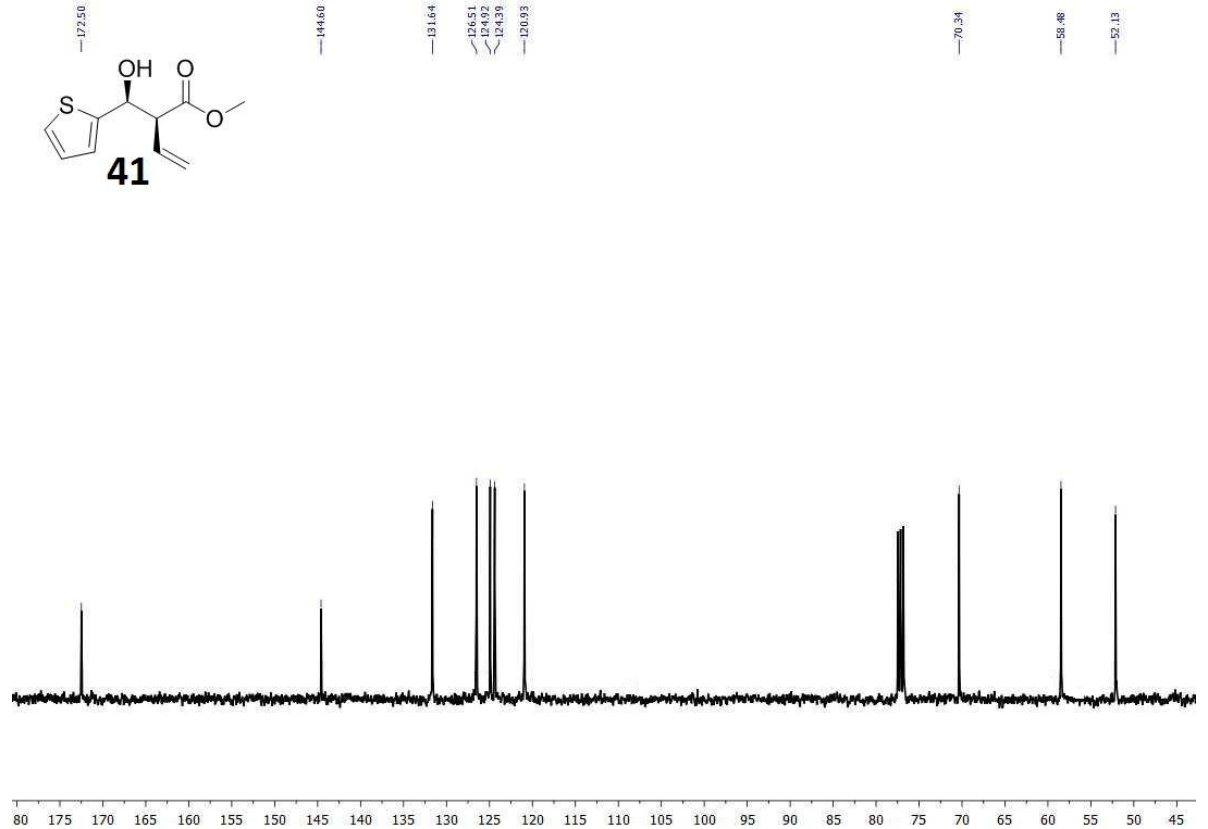
OH
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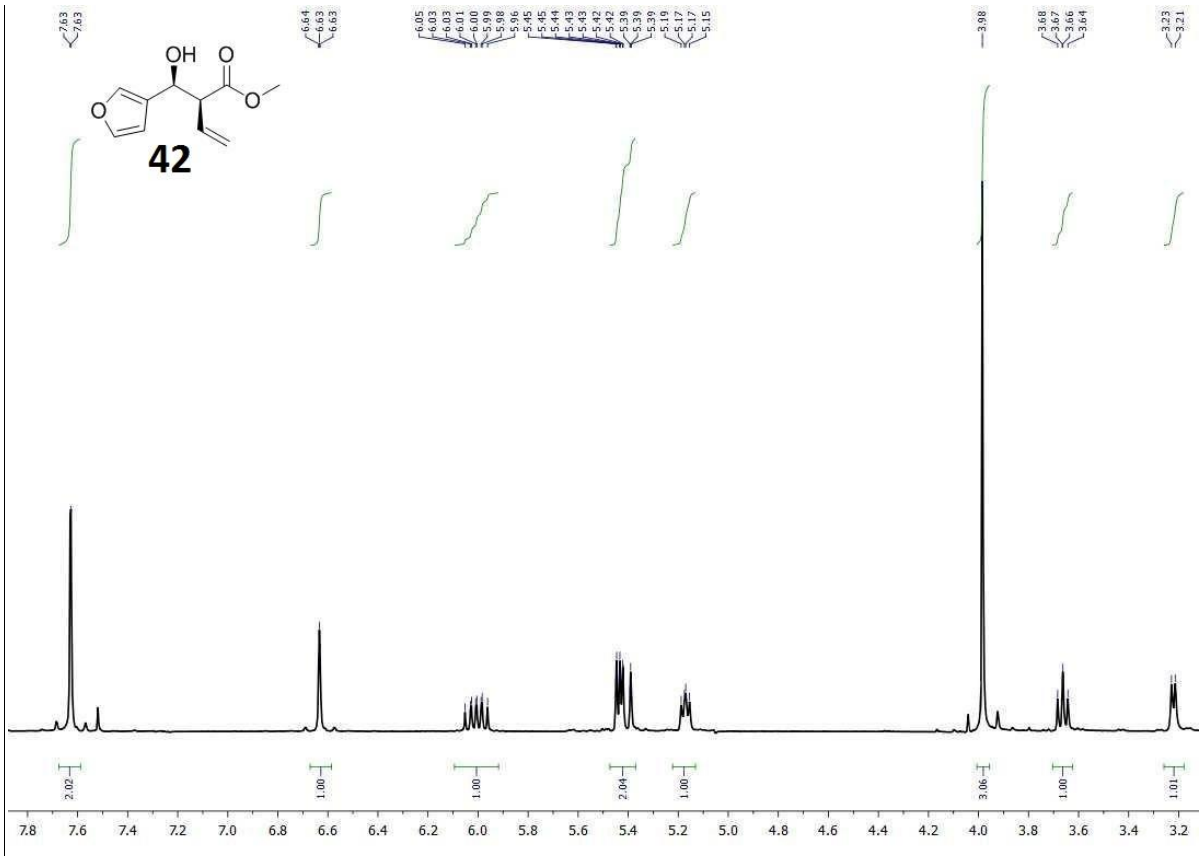
S
O
41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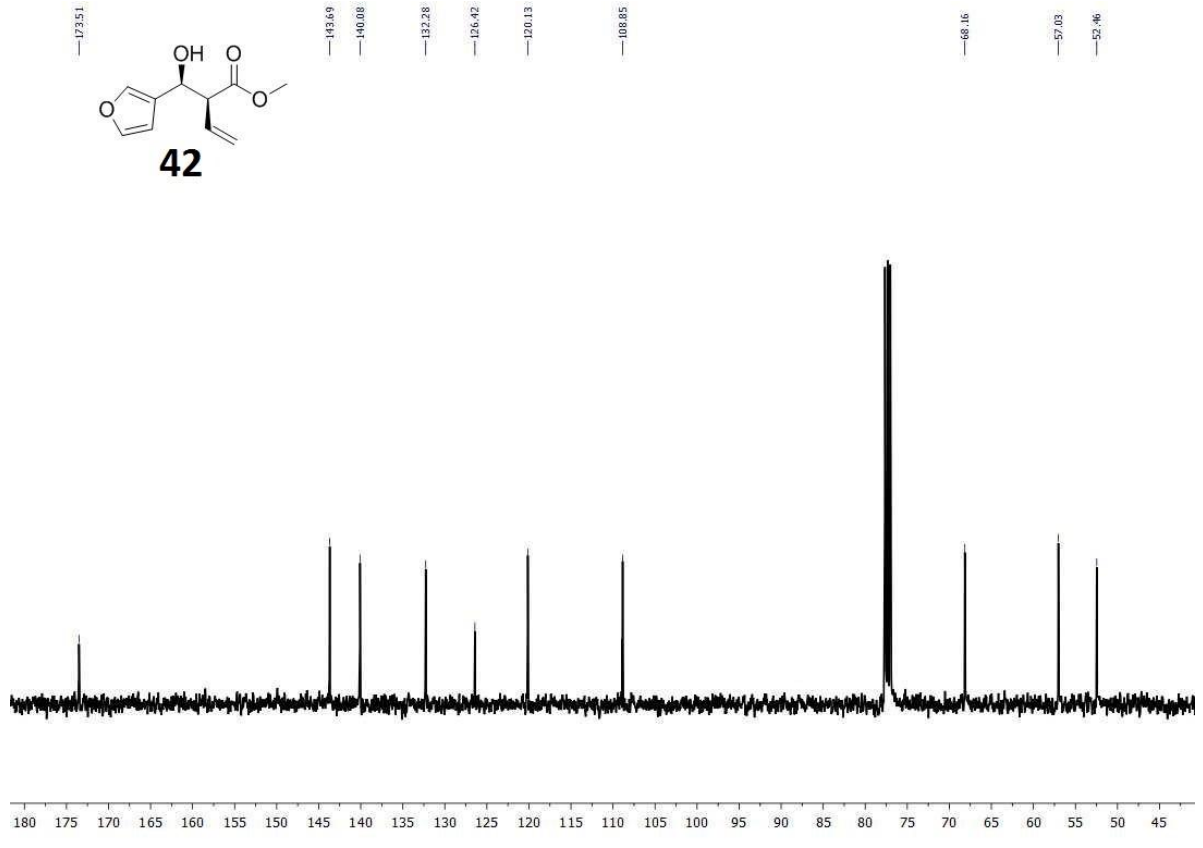
OH
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O
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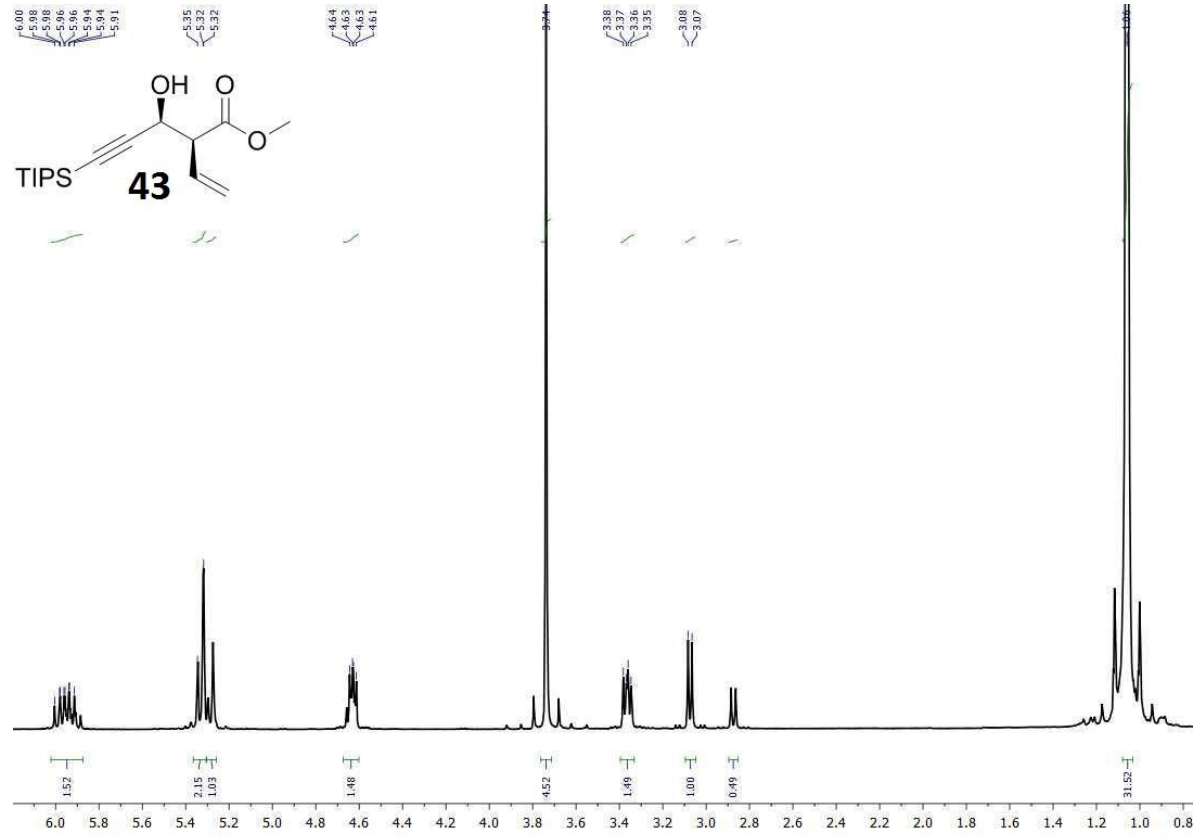
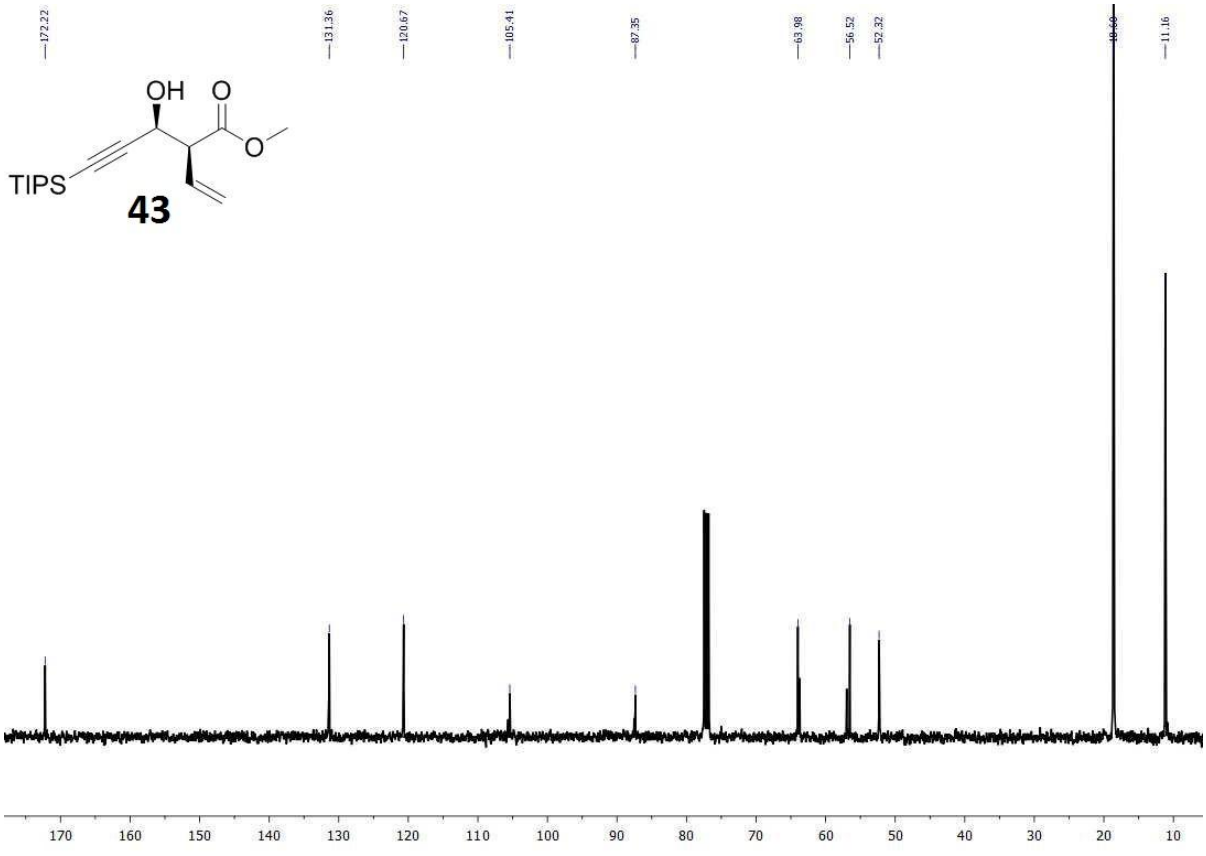

OH
O
O
TIPS
43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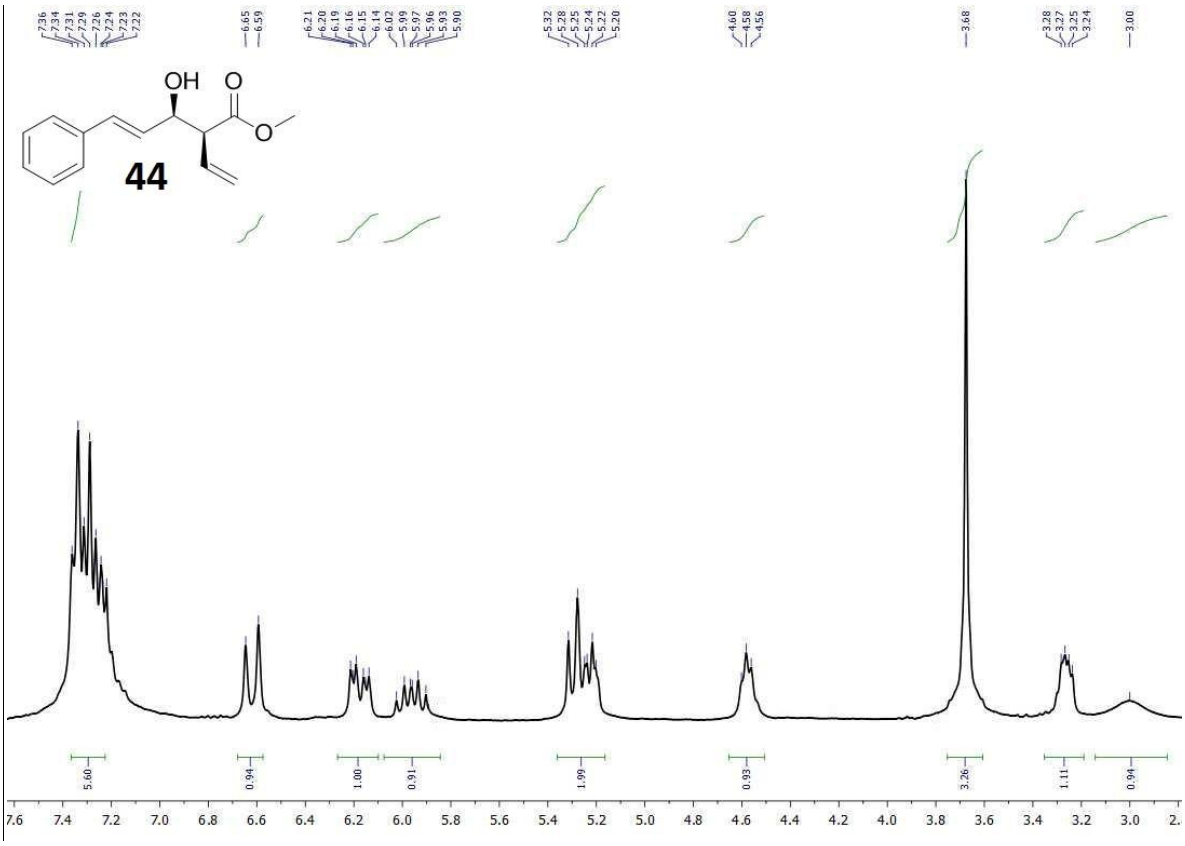
O
TIPS
43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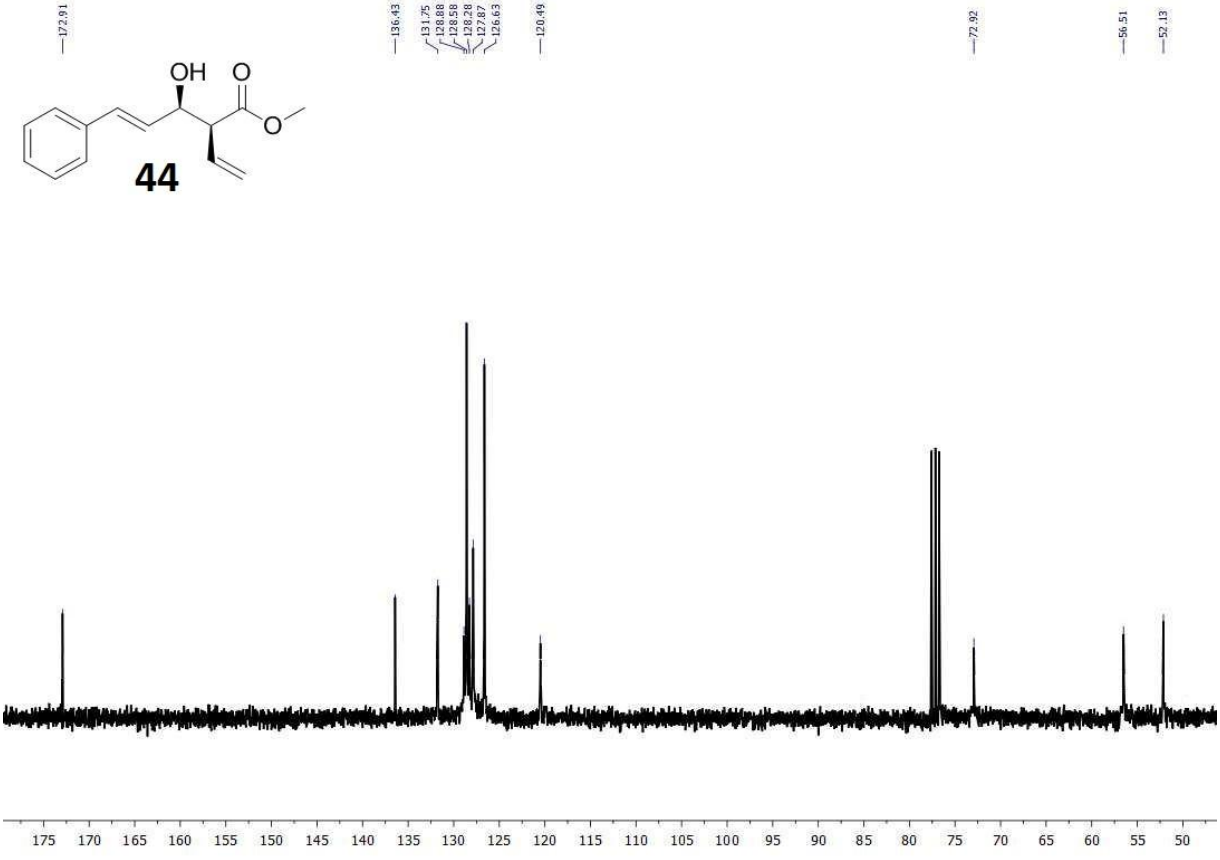
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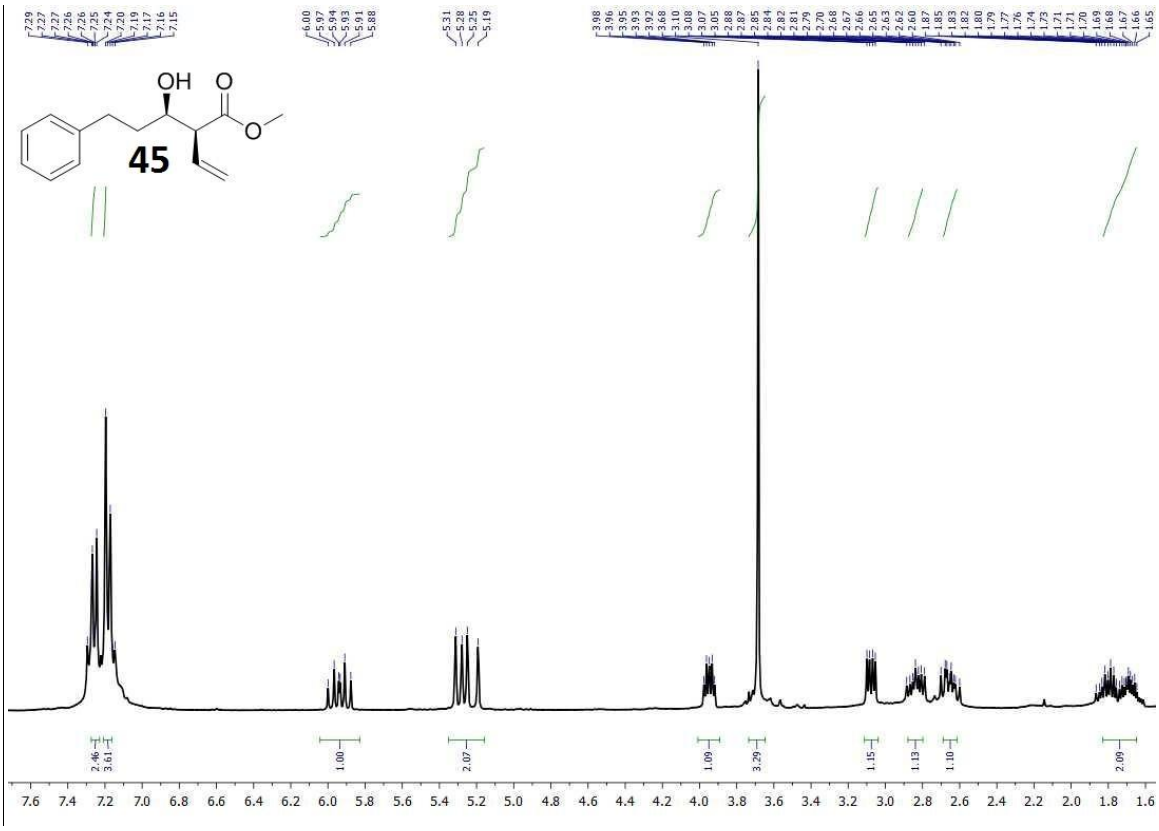
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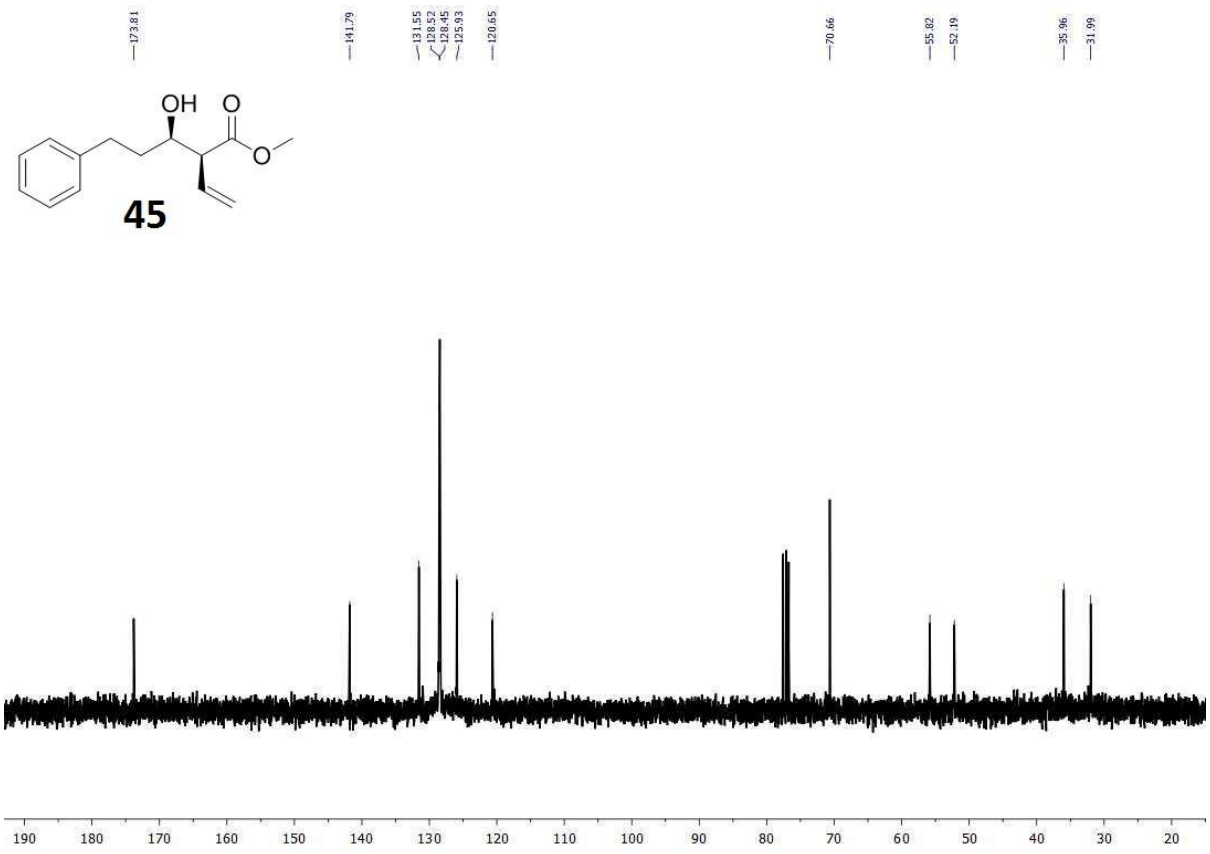
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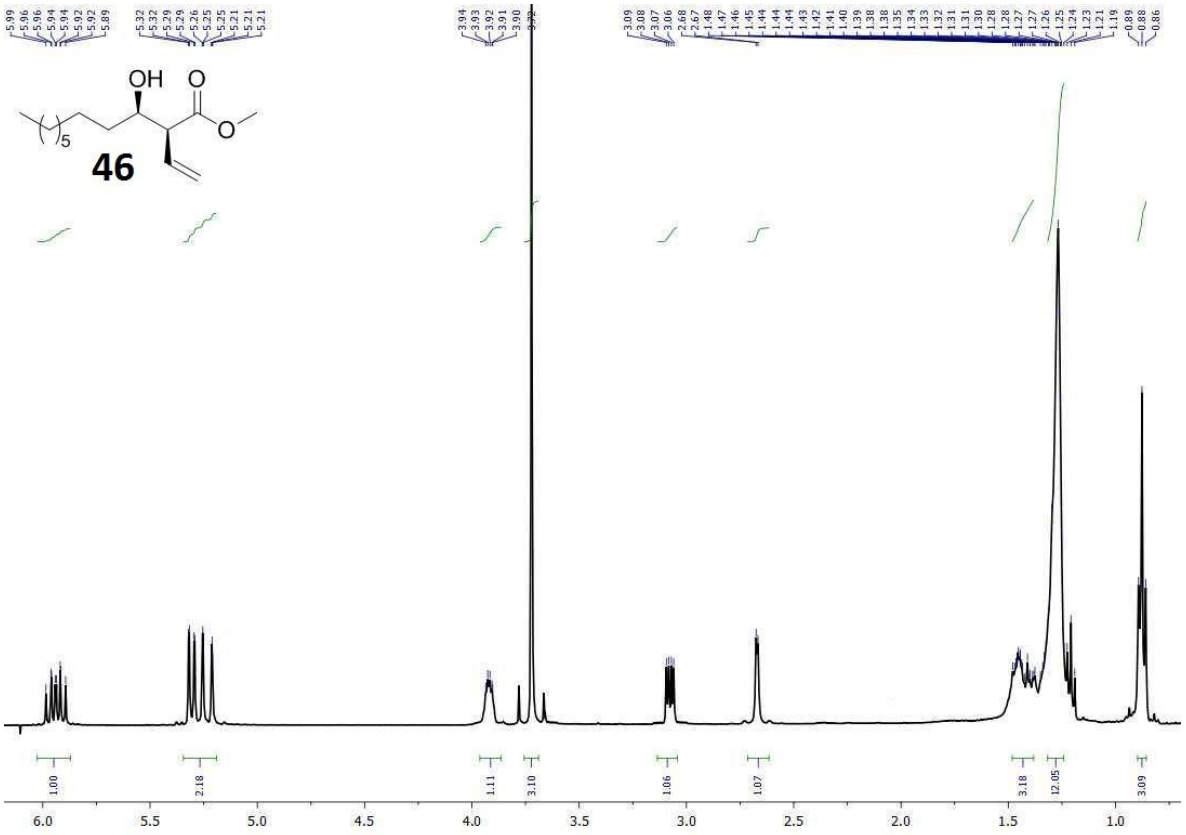
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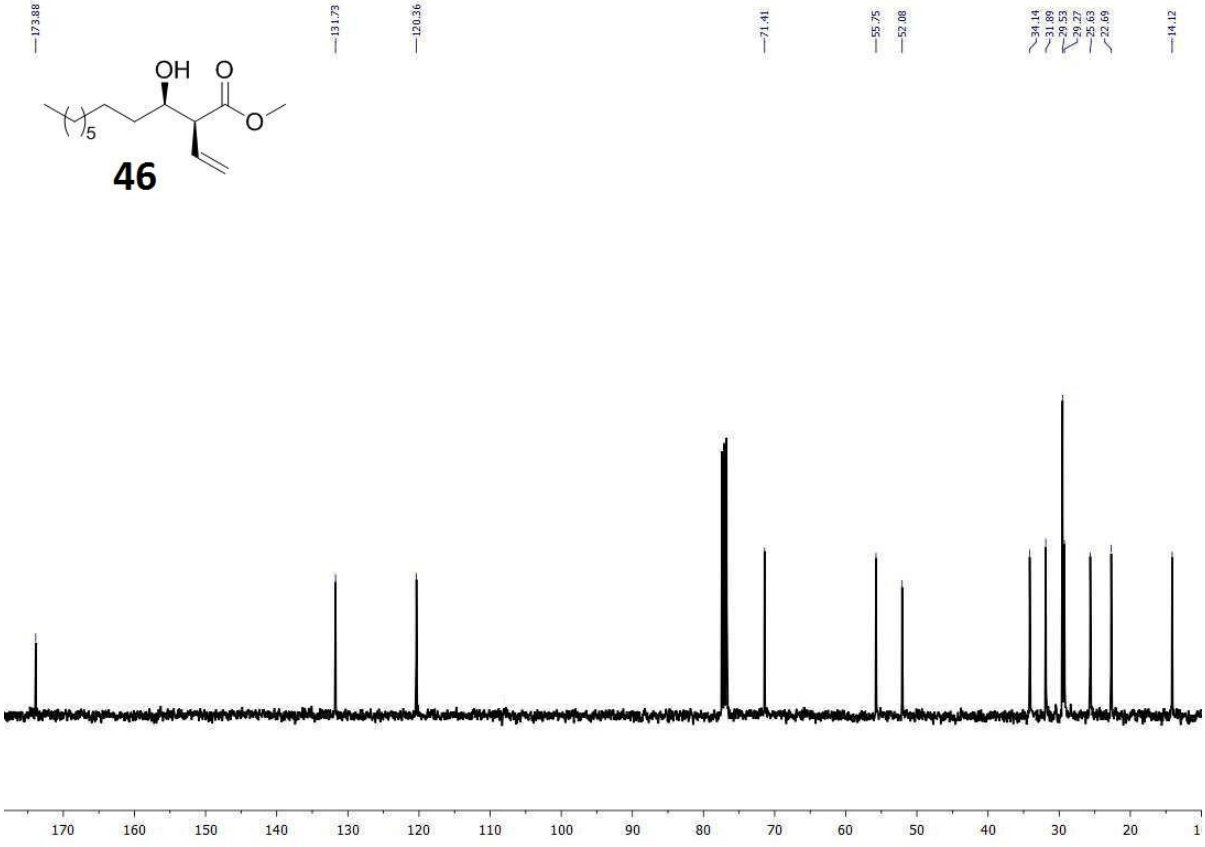
1.5
1.0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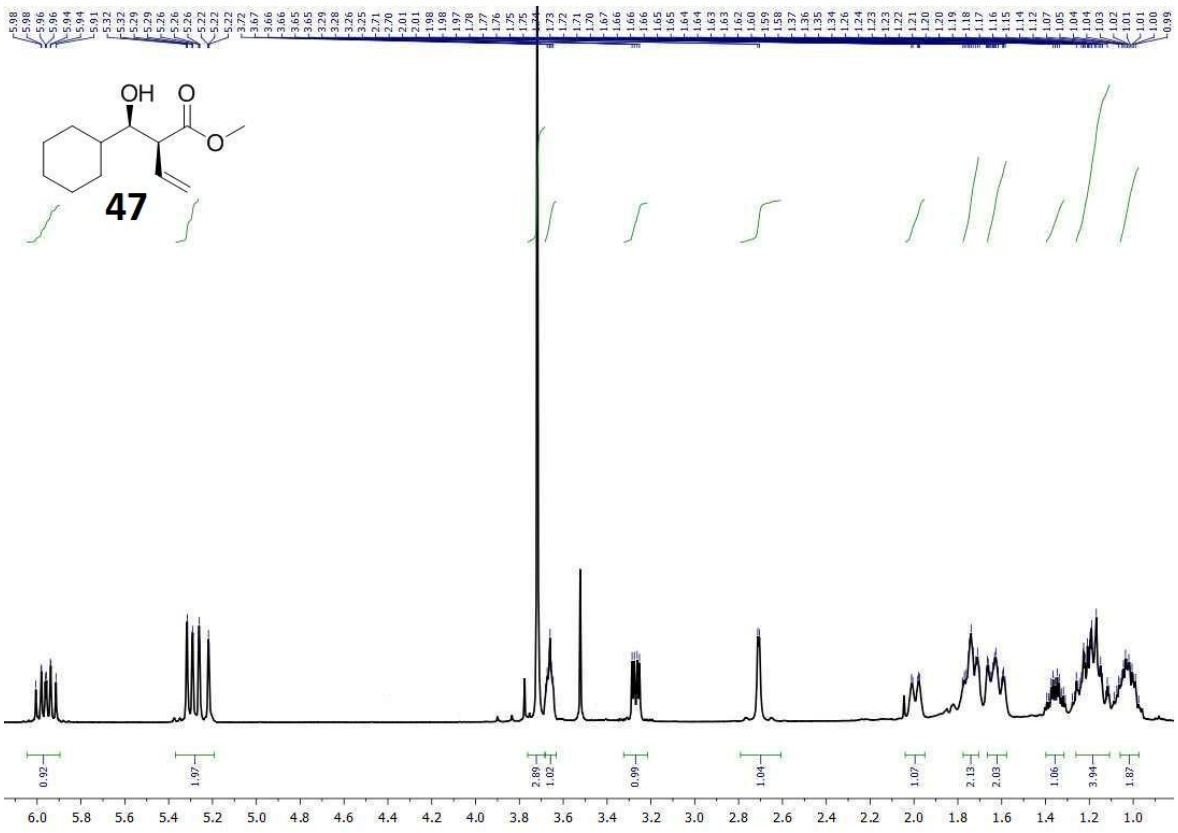
OH
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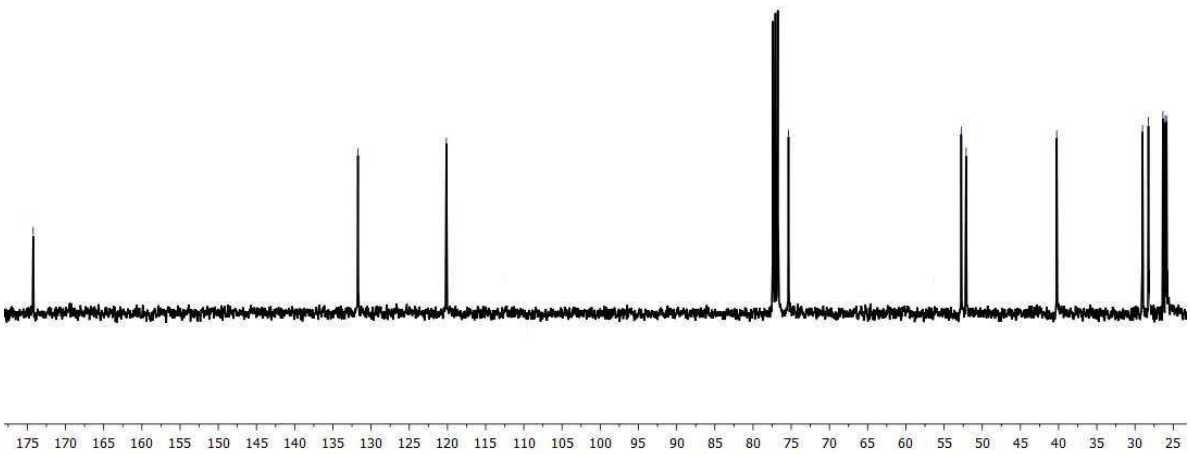
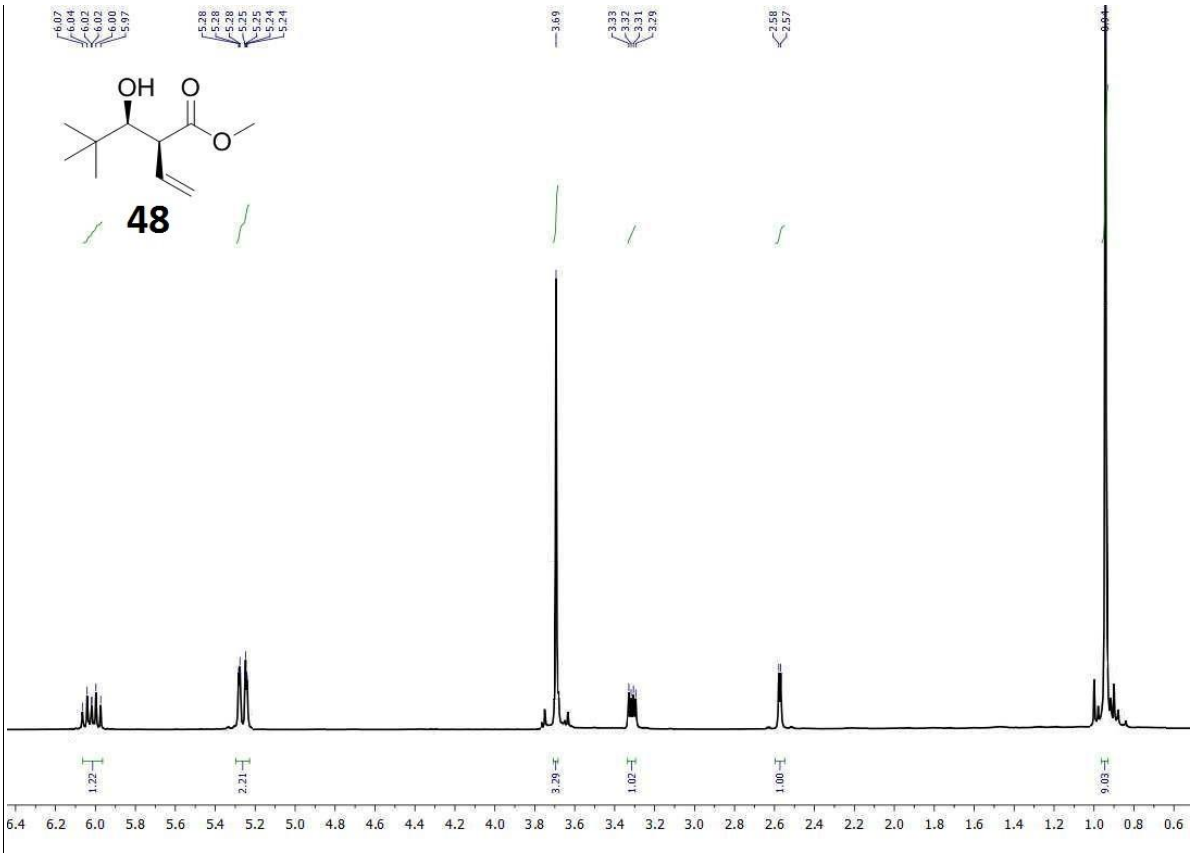
O
47


OH
O
O
47

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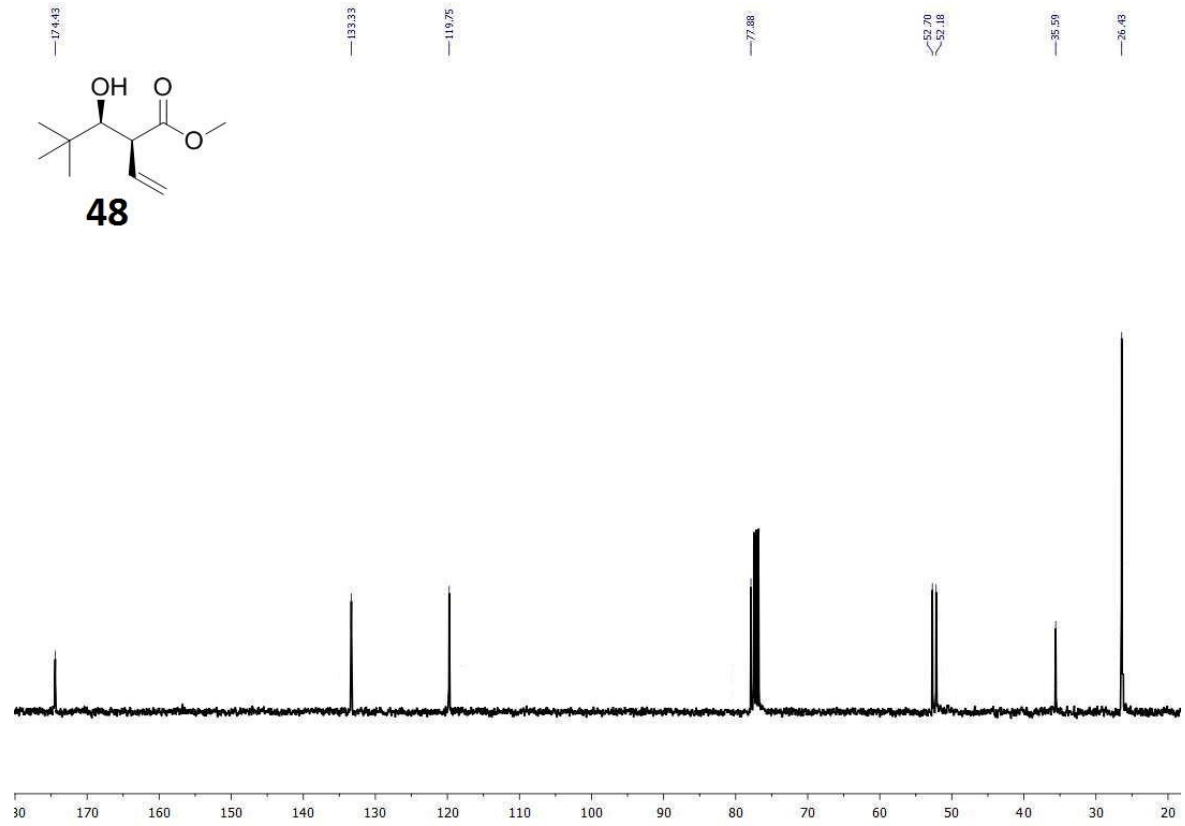
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O
O
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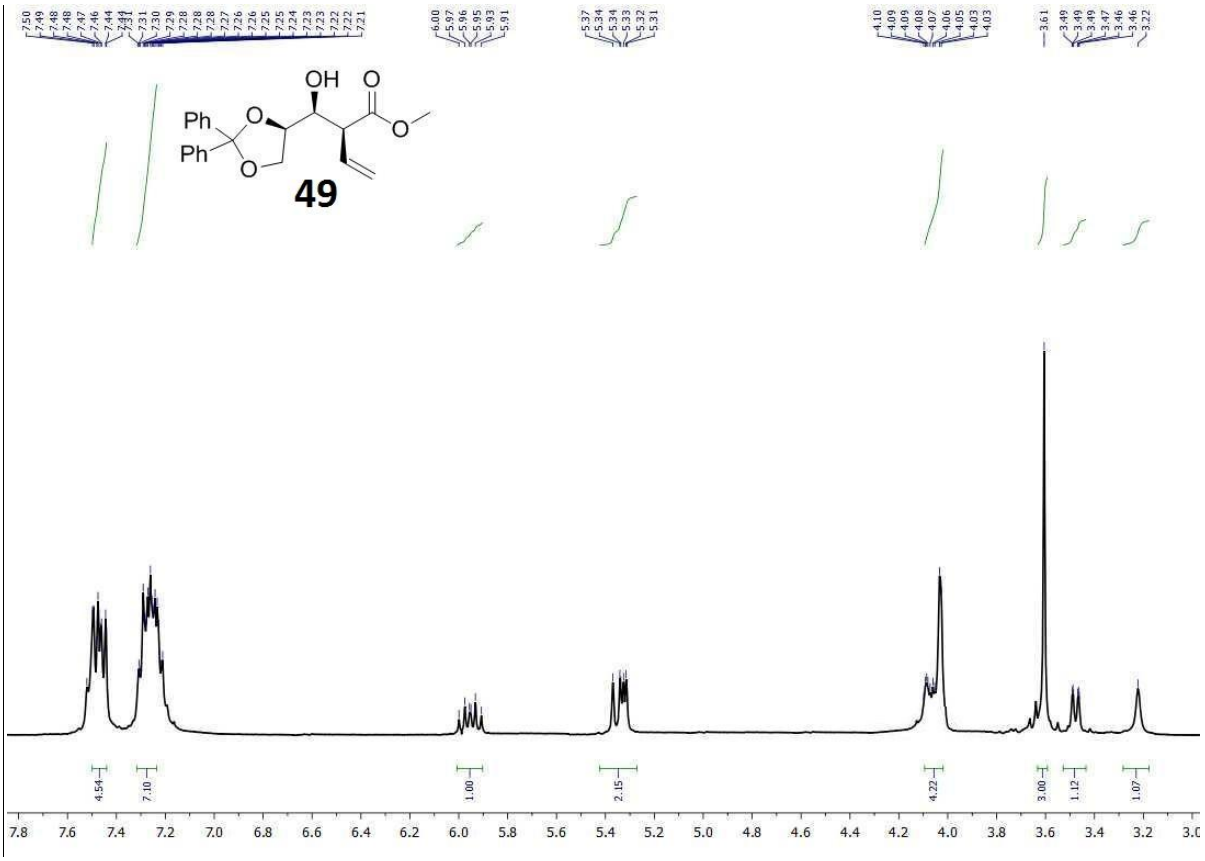
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Ph
Ph
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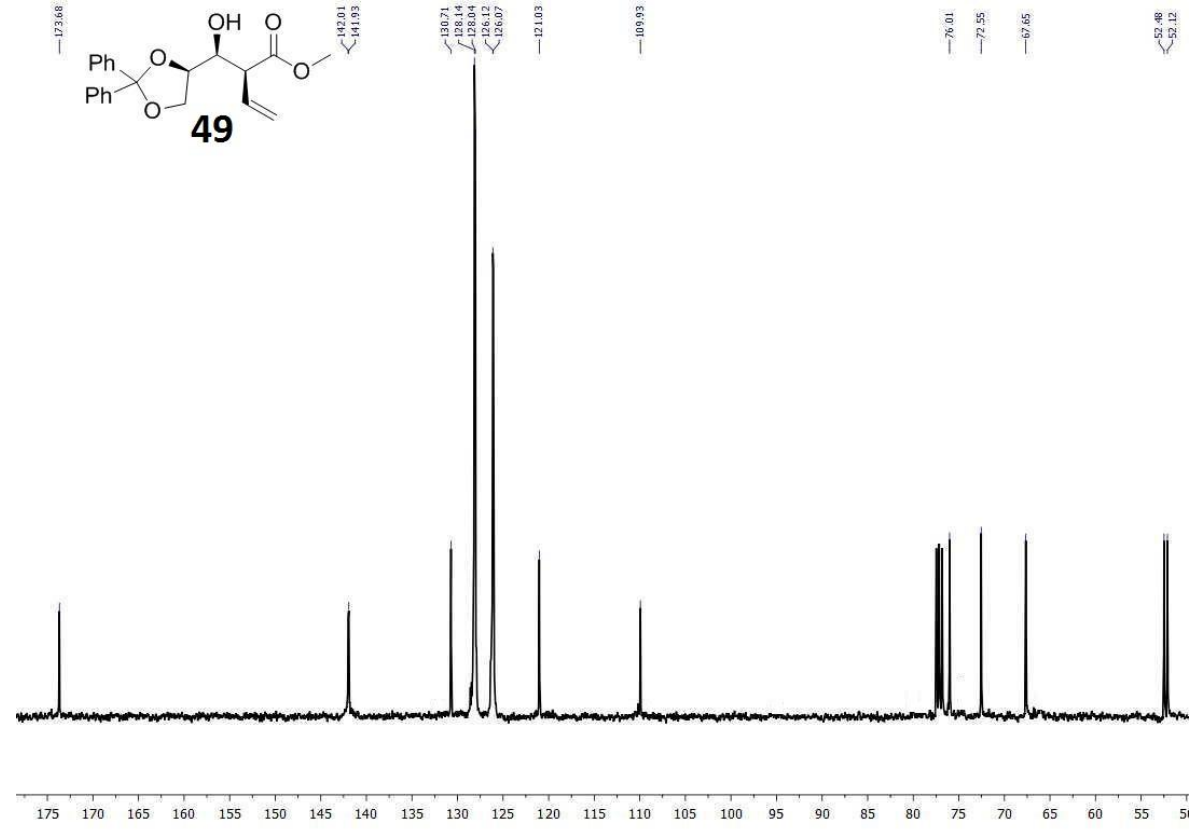
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Ph
Ph
O
O
O
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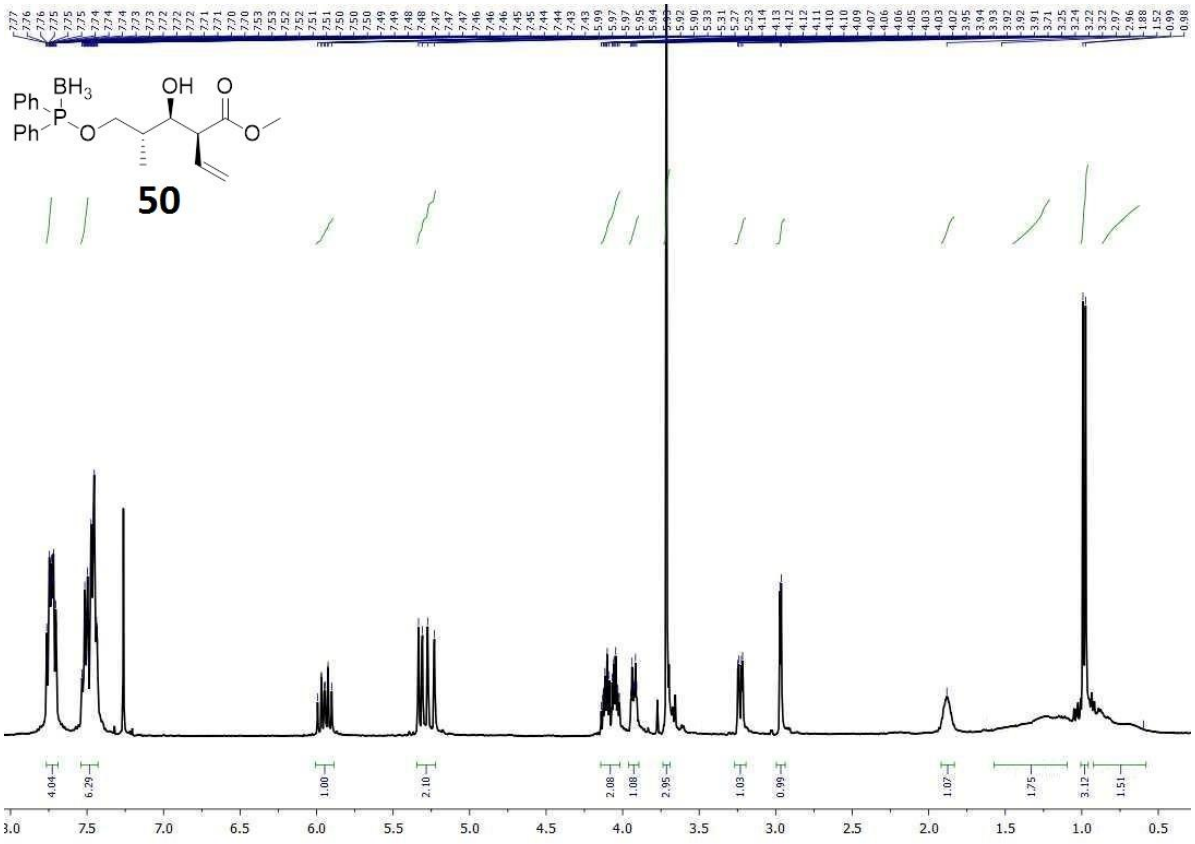

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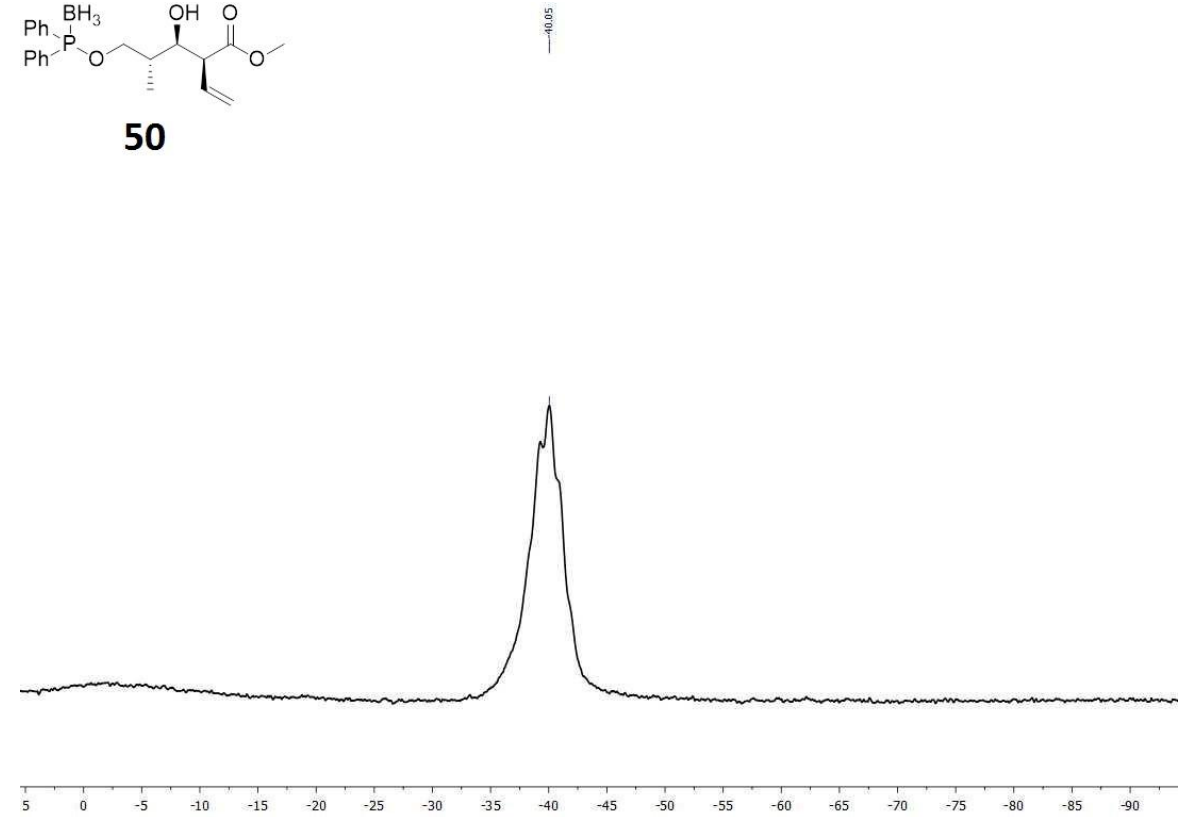

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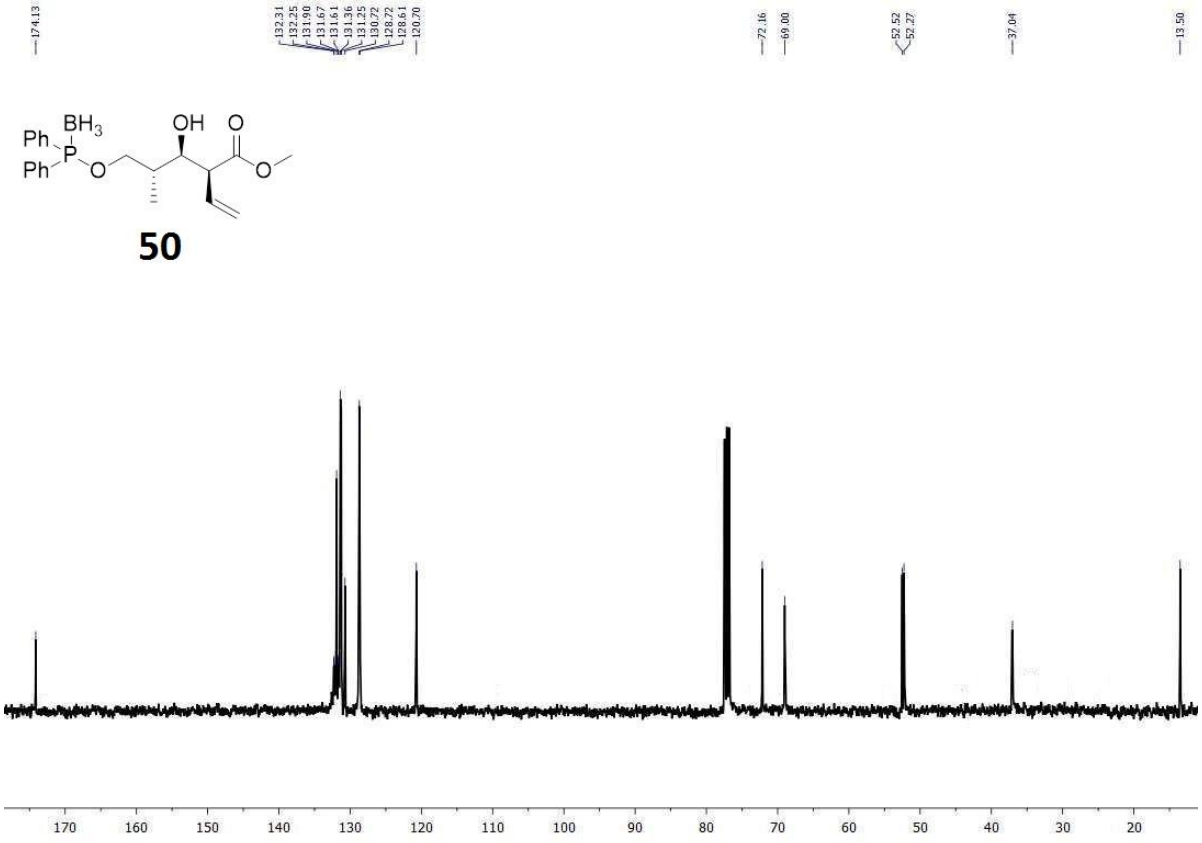
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131.61
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131.25
130.72
128.72
128.61
120.70
72.16
69.00
52.52
52.27
37.04
13.50
Ph
BH3
P
Ph
O
OH
O
O
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170
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150
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130
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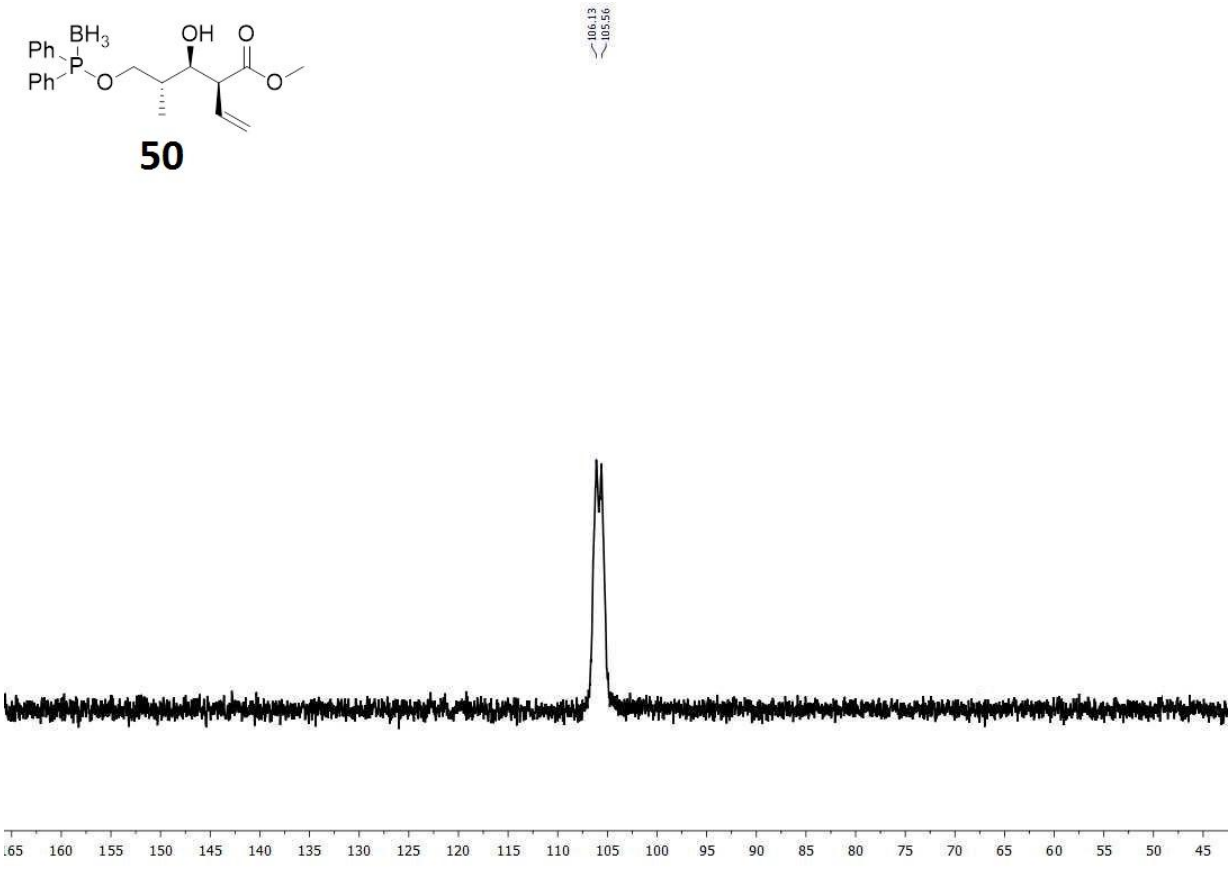
20


106.13
105.56
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BH3
P
Ph
O
OH
O
O
50
165
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155
150
145
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135
130
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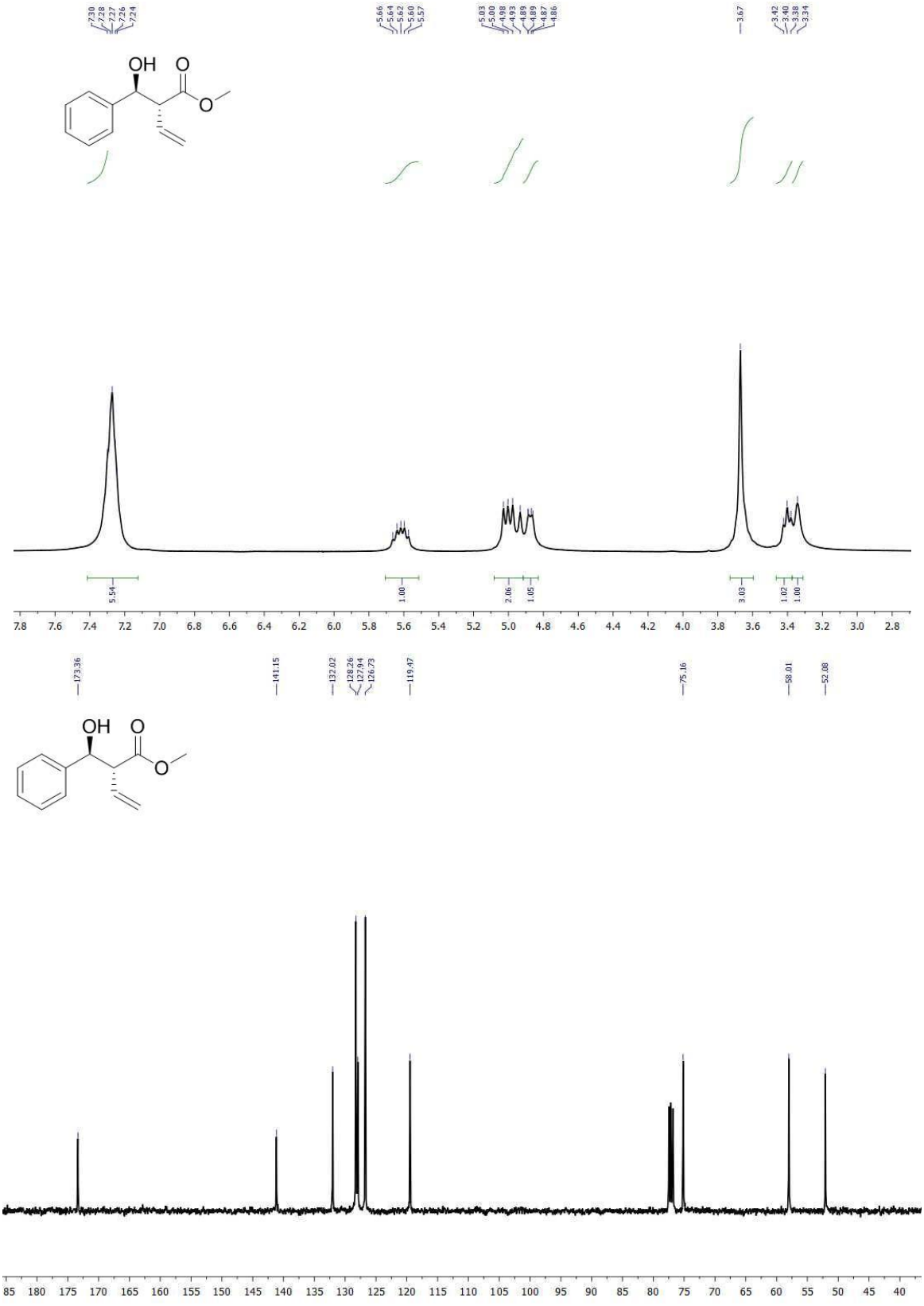
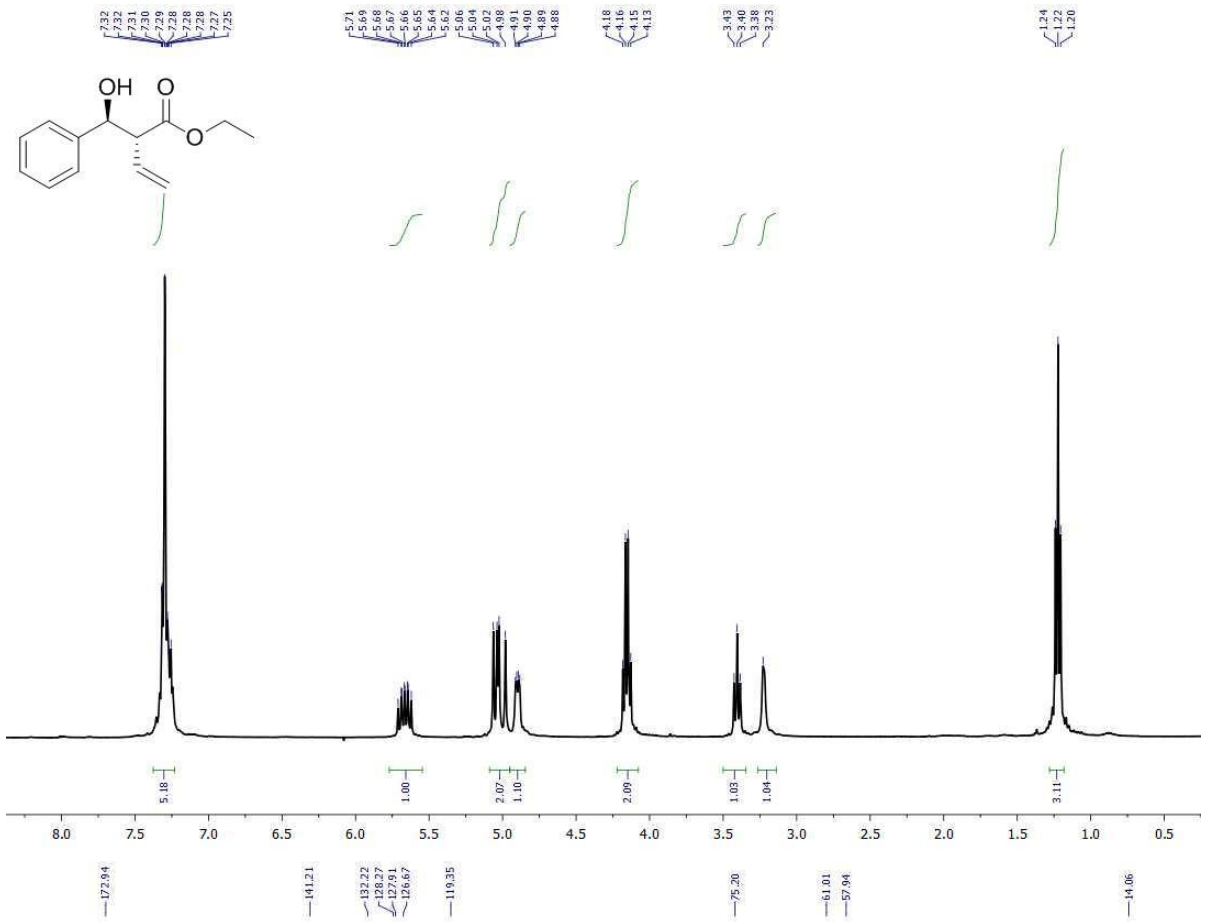
70
65
60
55
50
45

NMR Spectra of *Anti*-aldol Products

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5.69
5.68
5.67
5.66
5.65
5.64
5.62
5.06
5.04
5.02
4.98
4.91
4.90
4.89
4.88
4.18
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4.15
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1.22
1.20
5.18
1.00
2.07
1.10
2.09
1.03
1.04
3.11
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7.5
7.0
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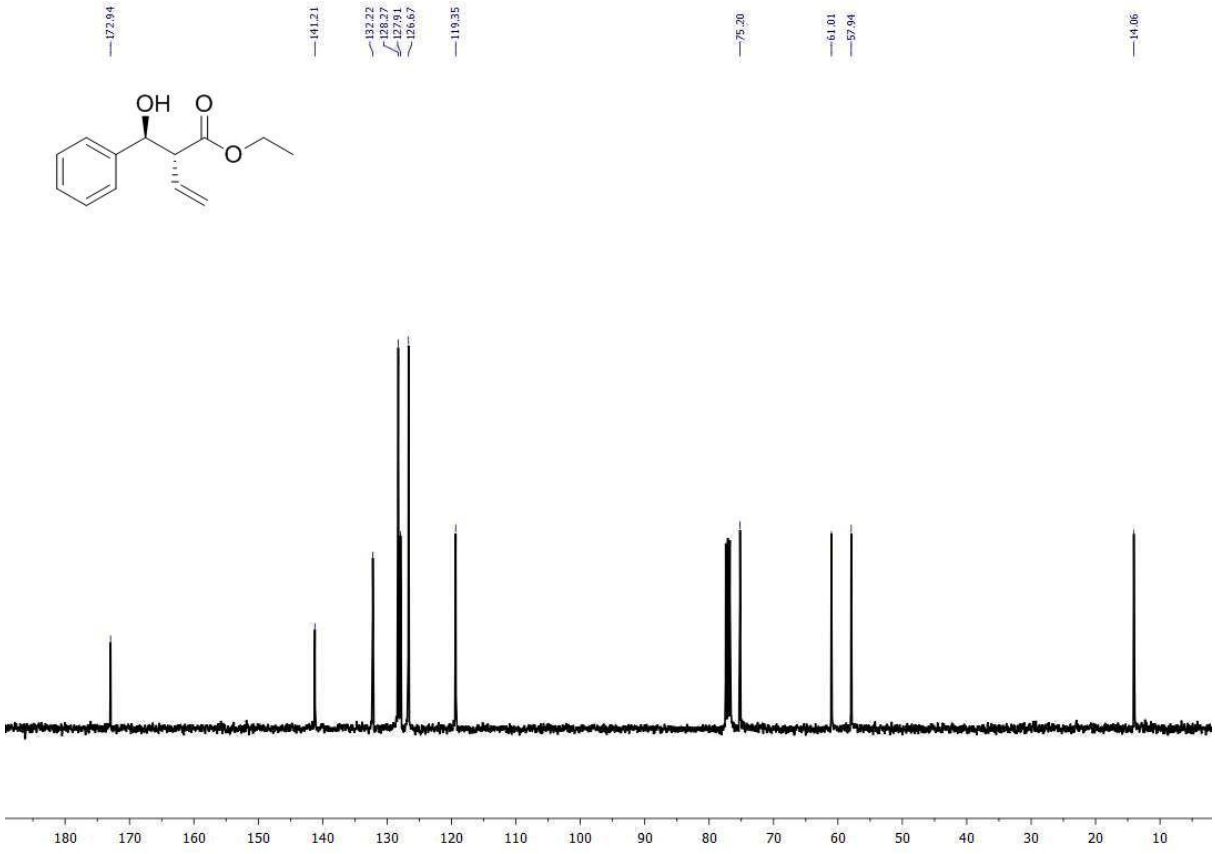
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14.06
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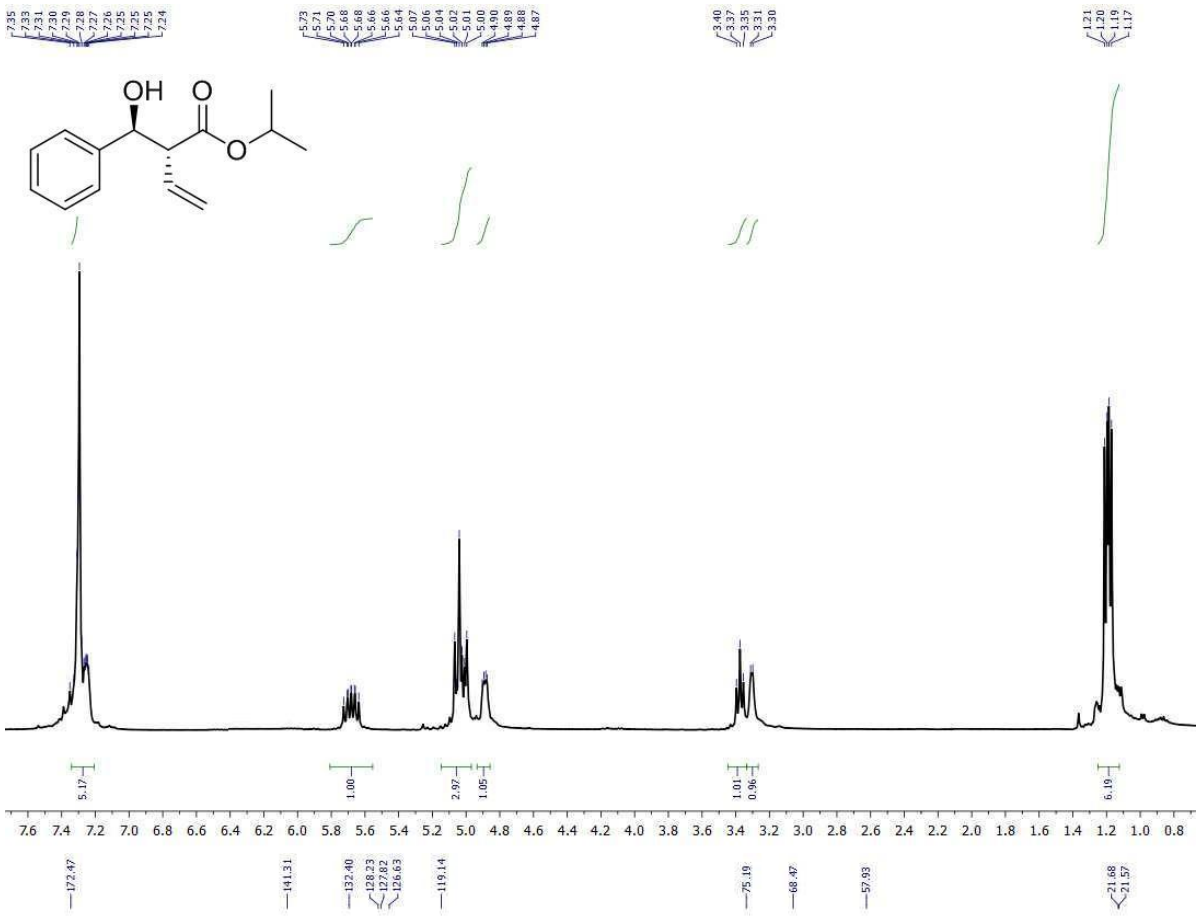
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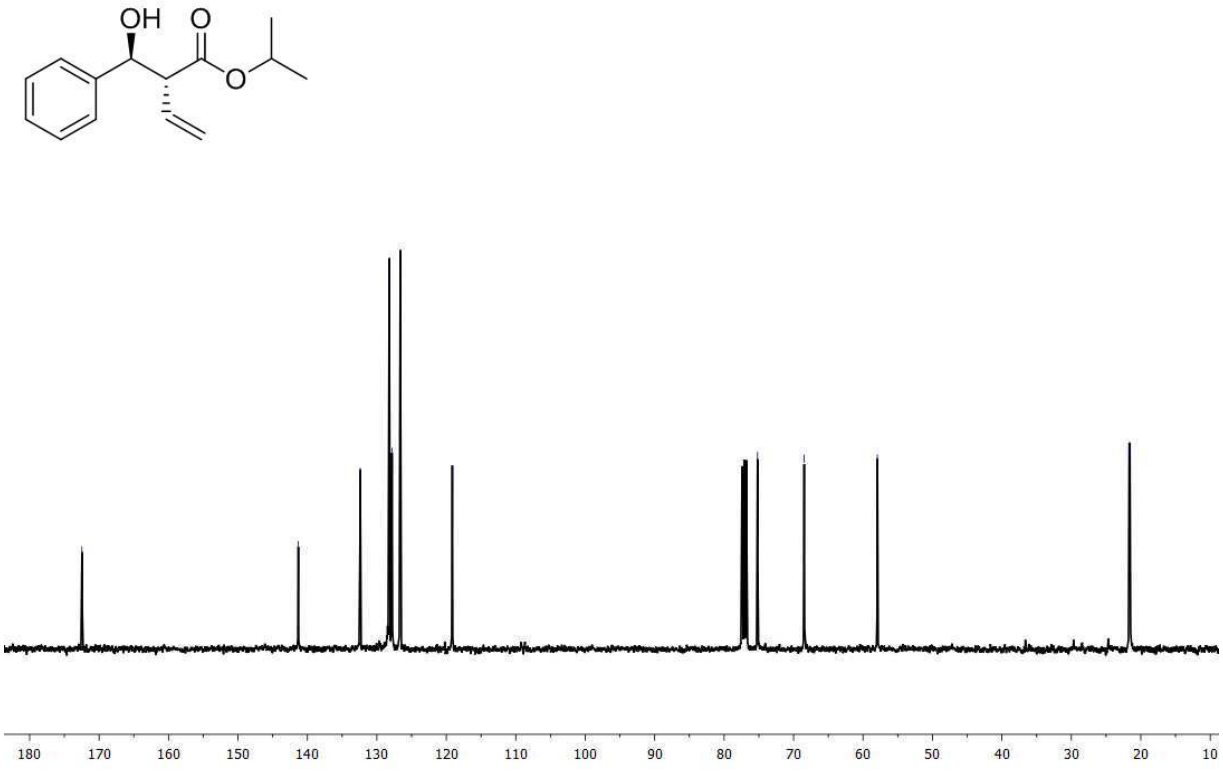
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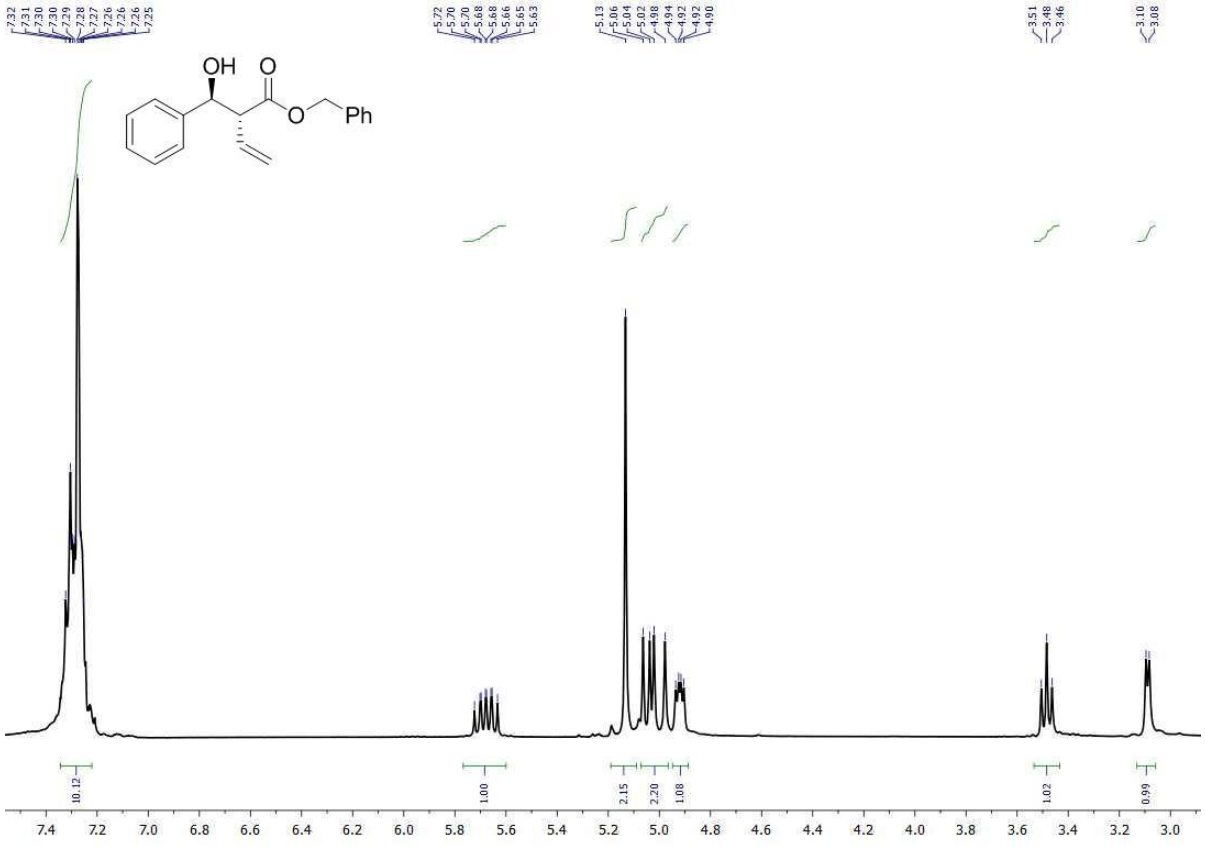
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5.70
5.70
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5.68
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5.65
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5.04
5.02
4.98
4.94
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3.46
3.10
3.08
10.12
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2.15
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1.08
1.02
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6.2
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5.8
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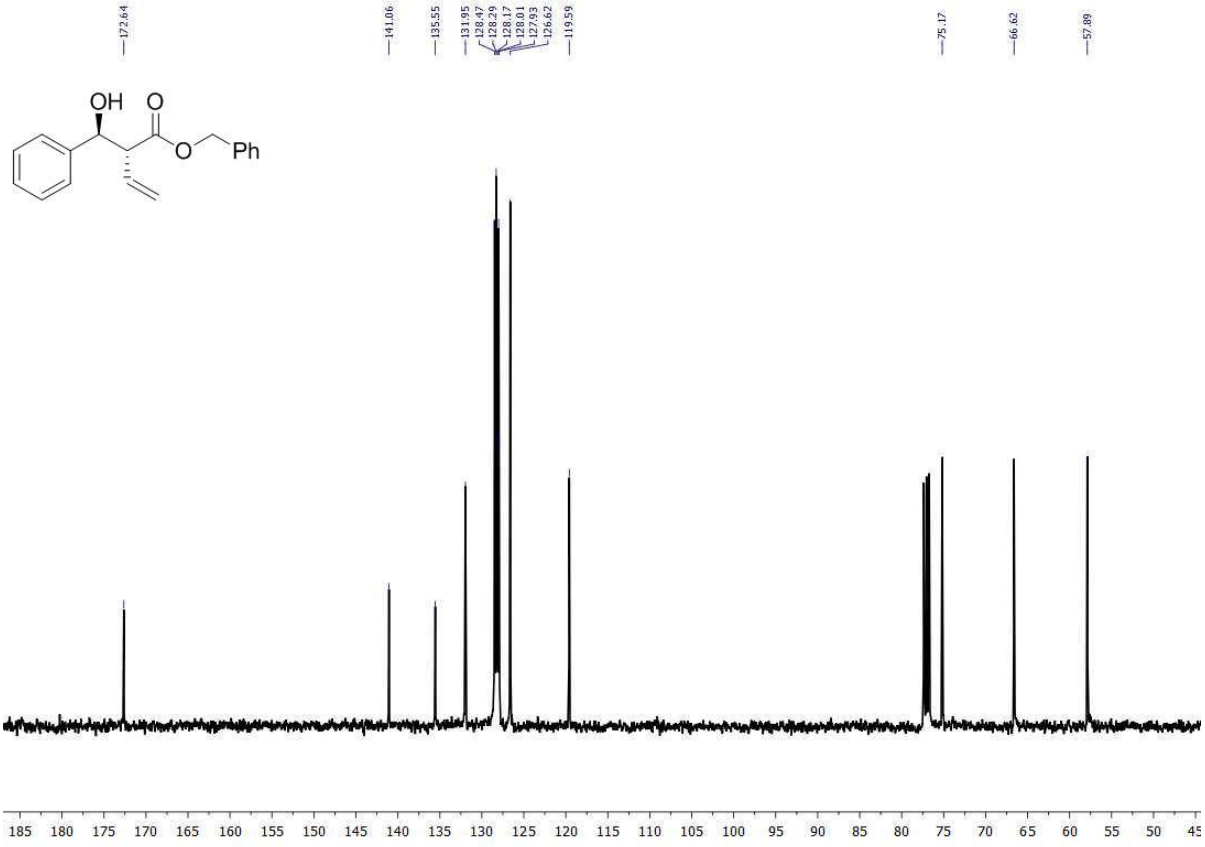
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57.89
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O
O
Ph
185
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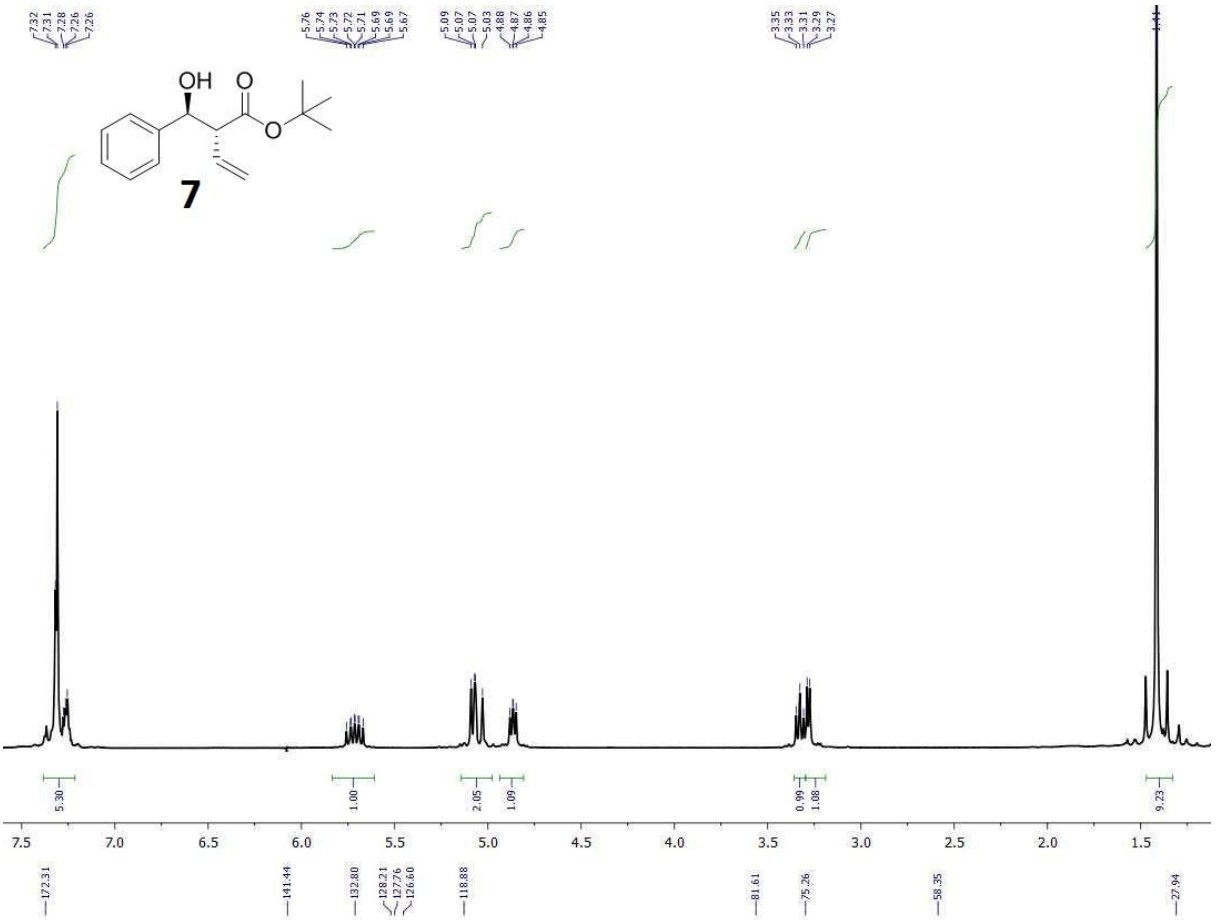
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5.69
5.67
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5.07
5.07
5.03
4.88
4.87
4.86
4.85
3.35
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3.31
3.29
3.27
1.41
5.30
1.00
2.05
1.09
0.99
1.08
9.23
7.5
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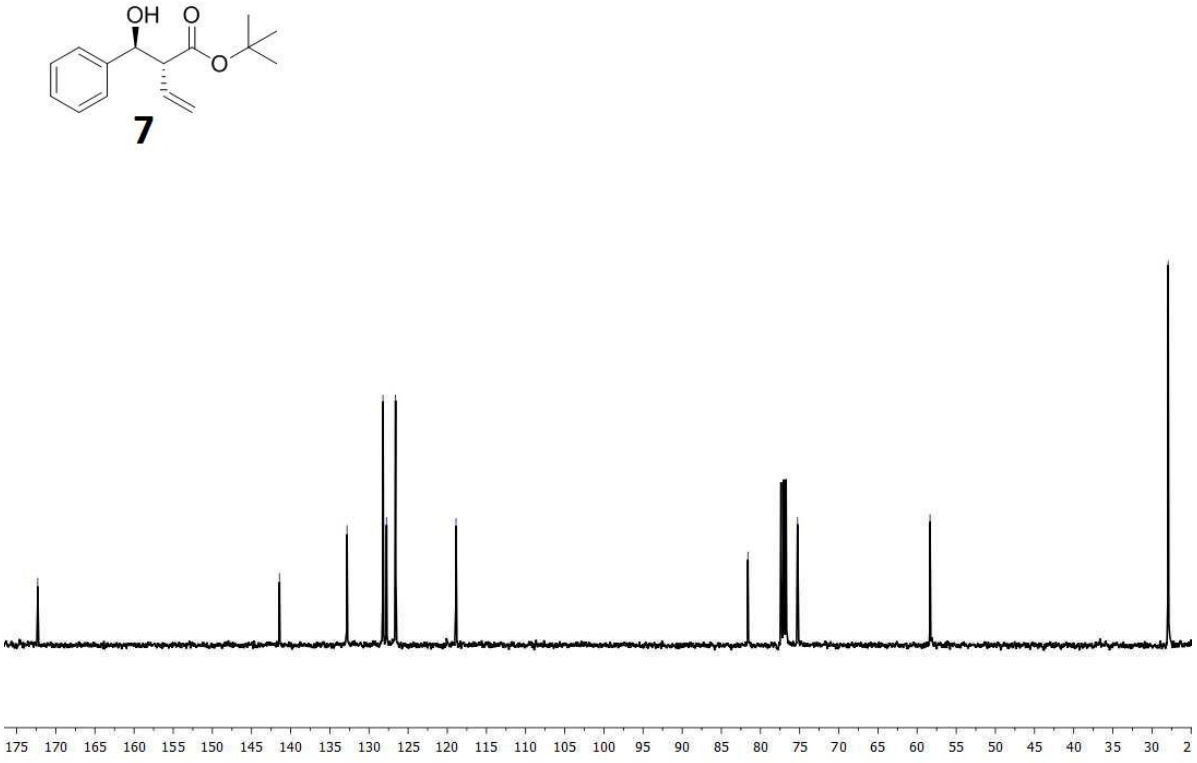
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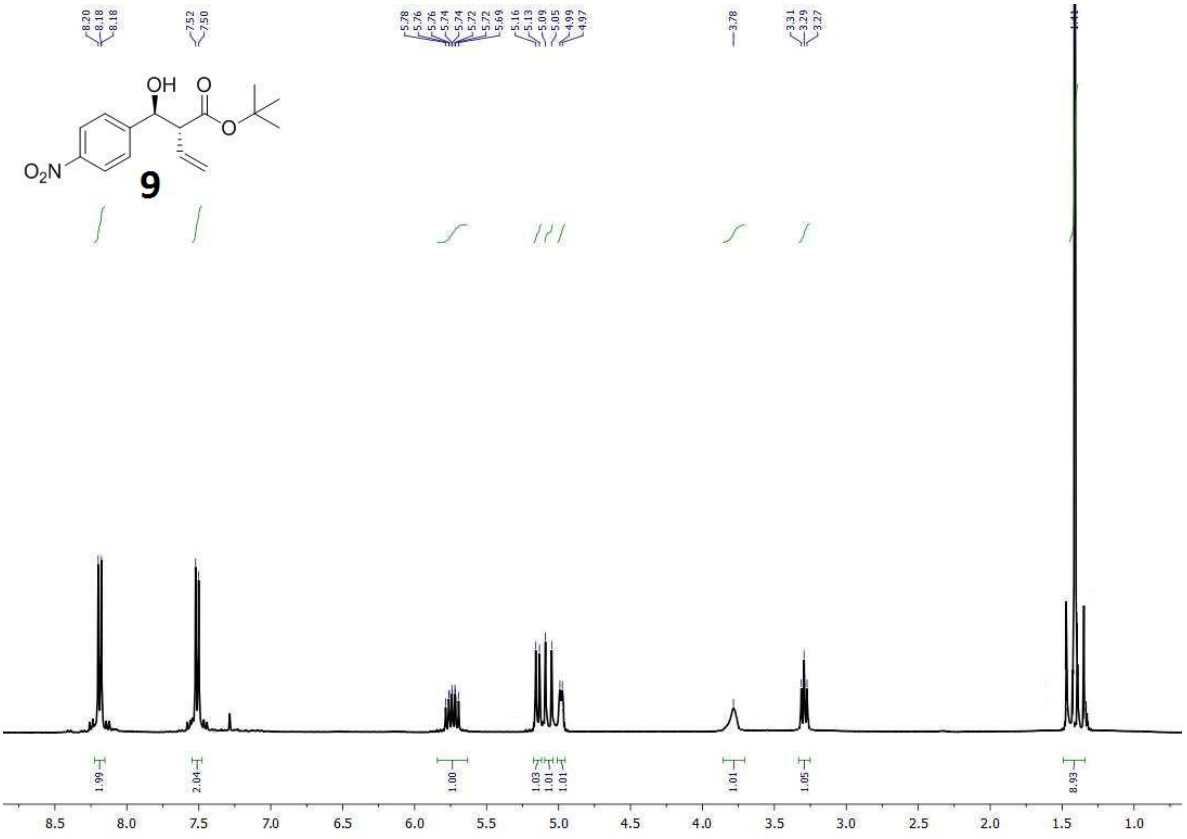
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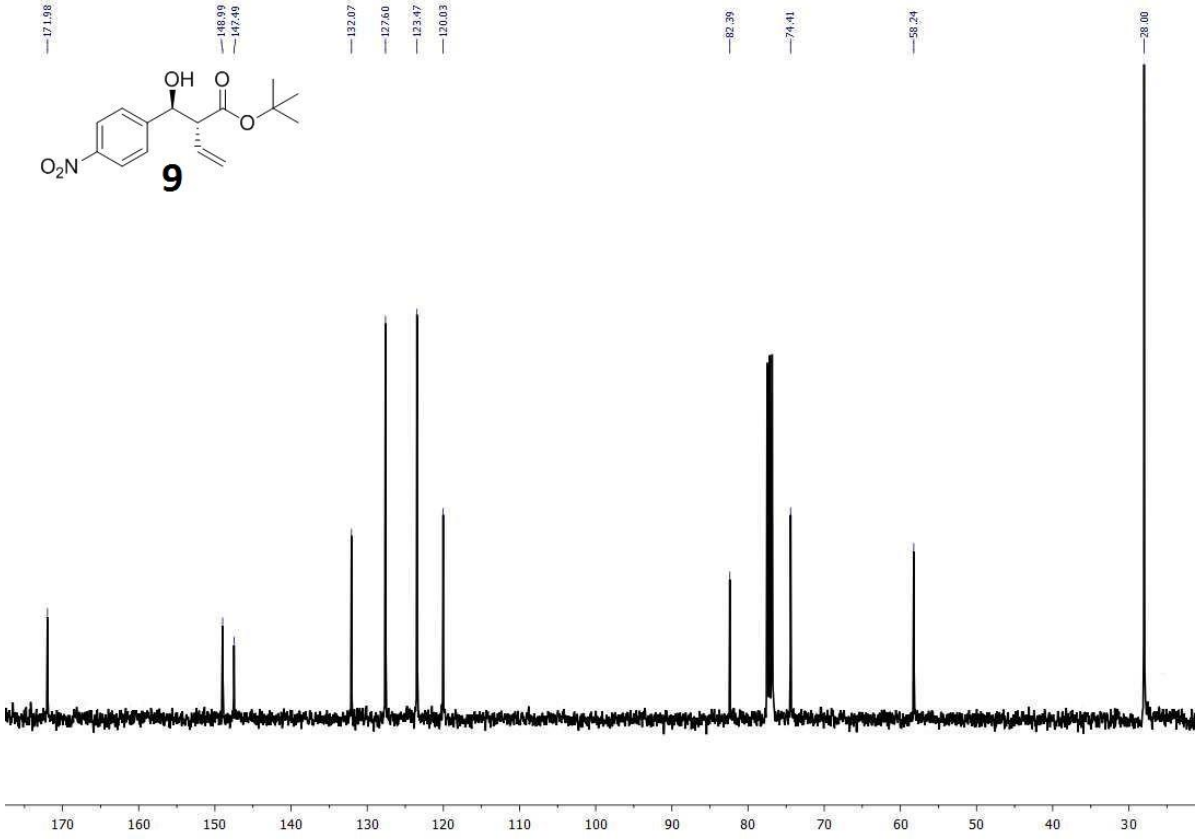
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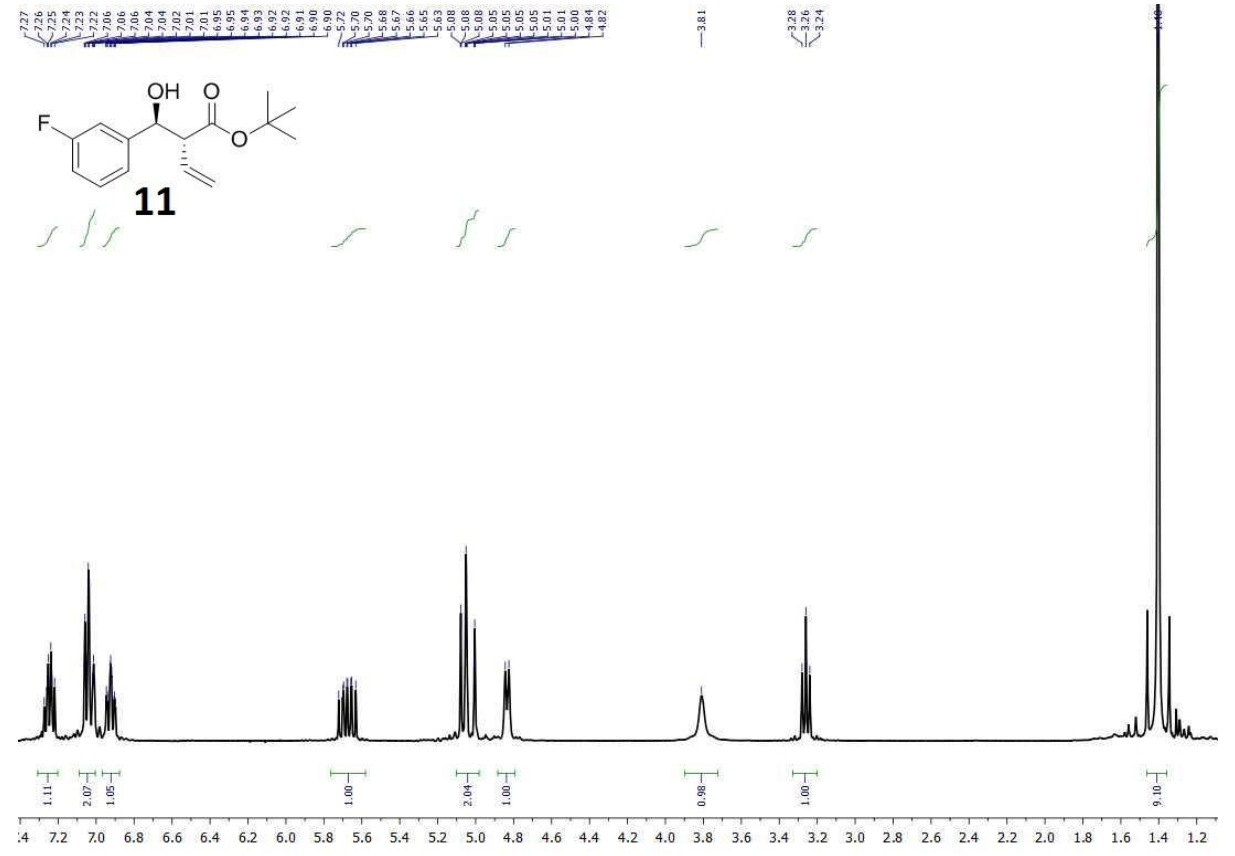
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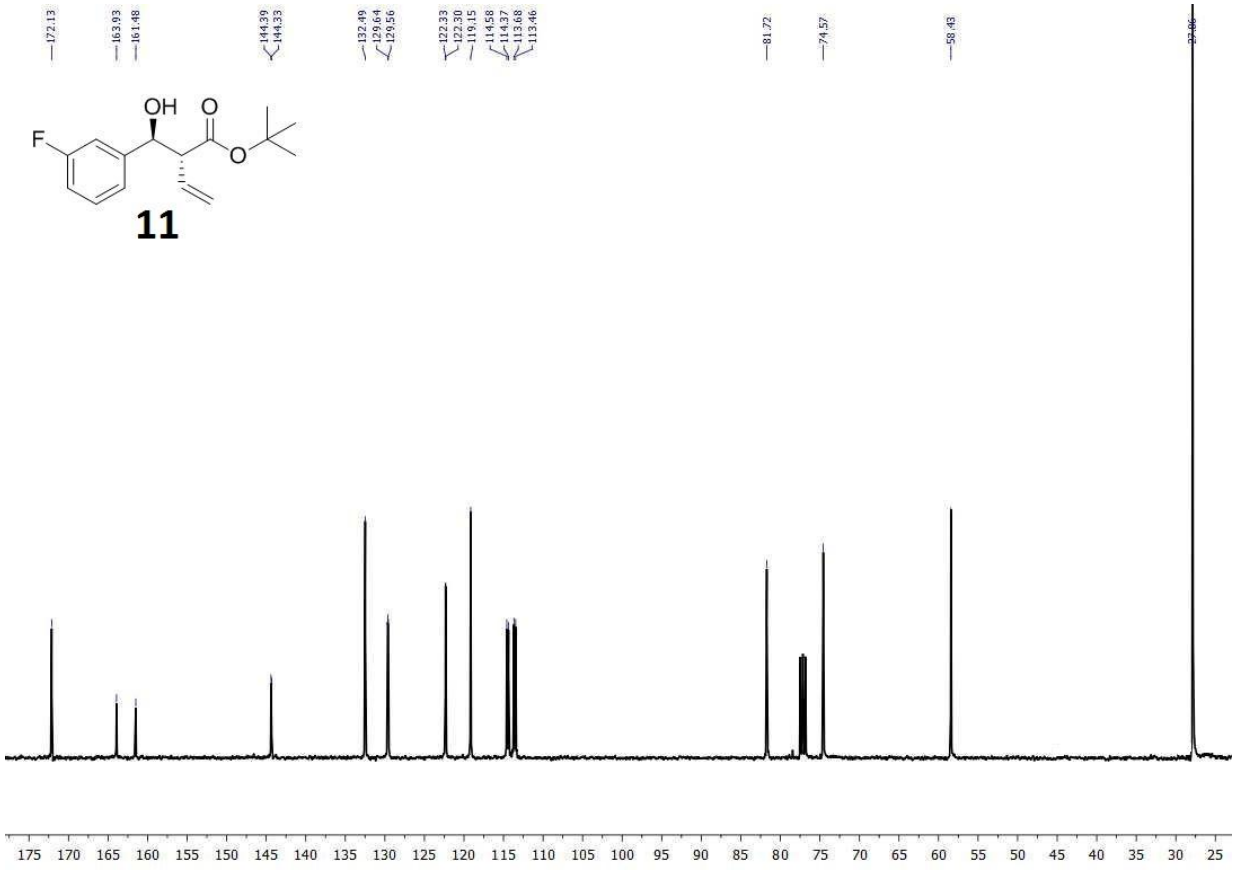
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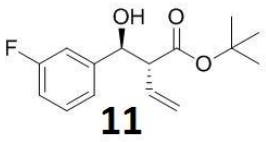
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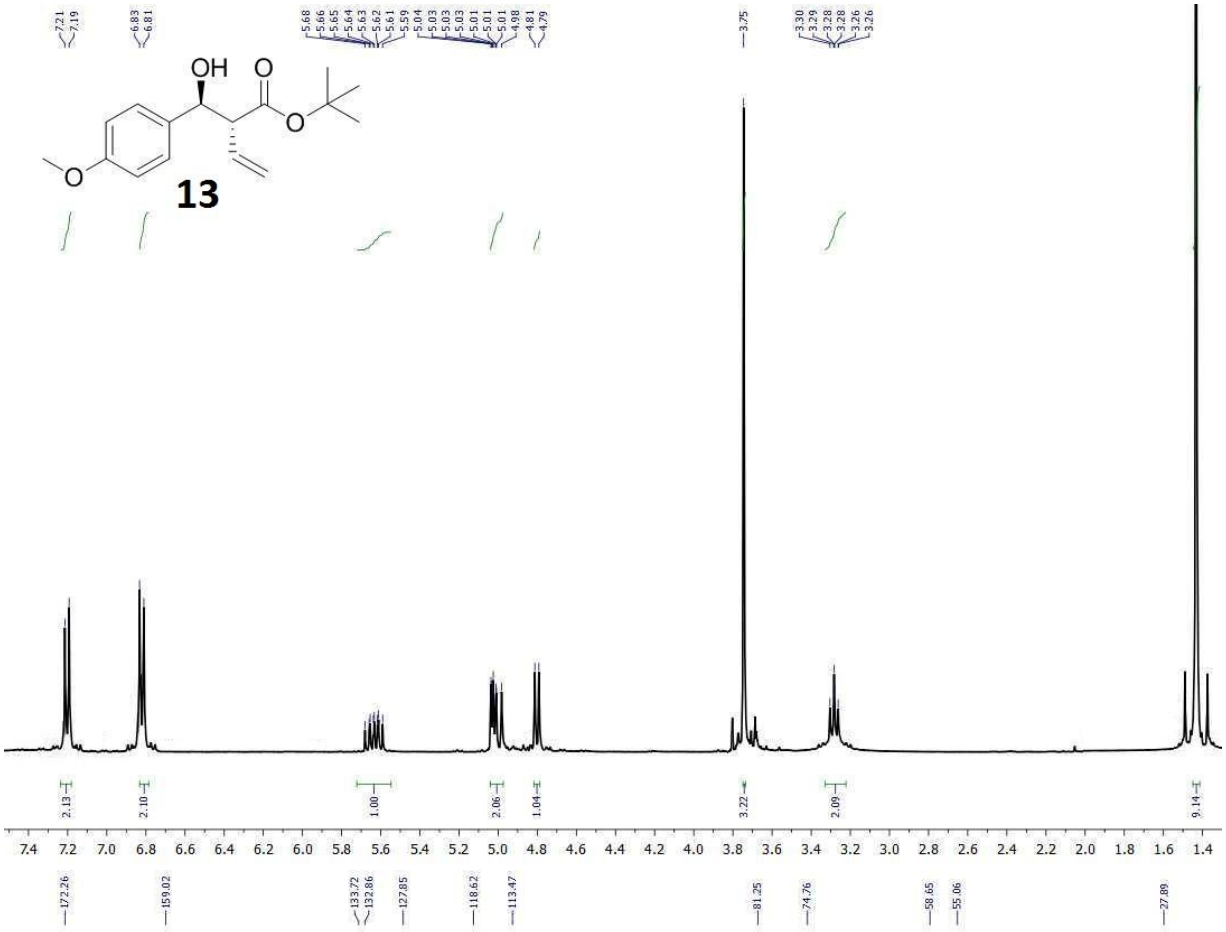
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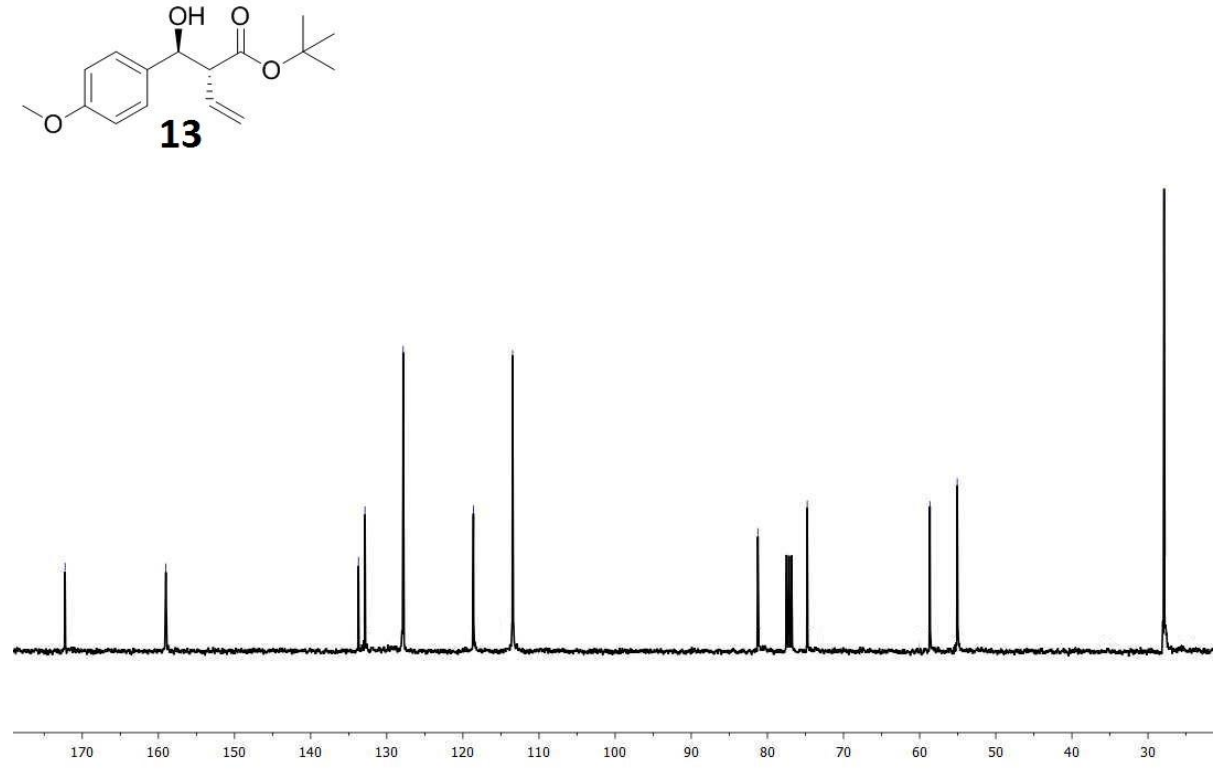
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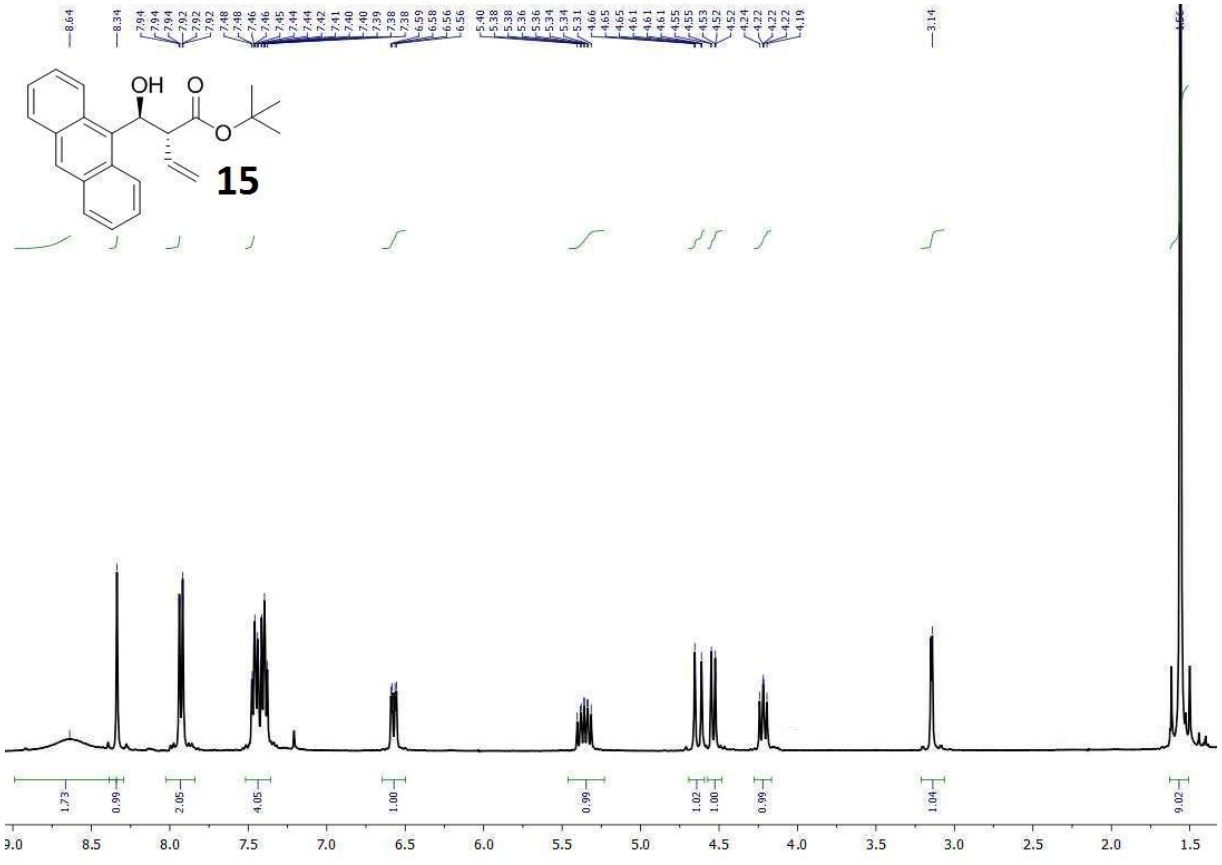
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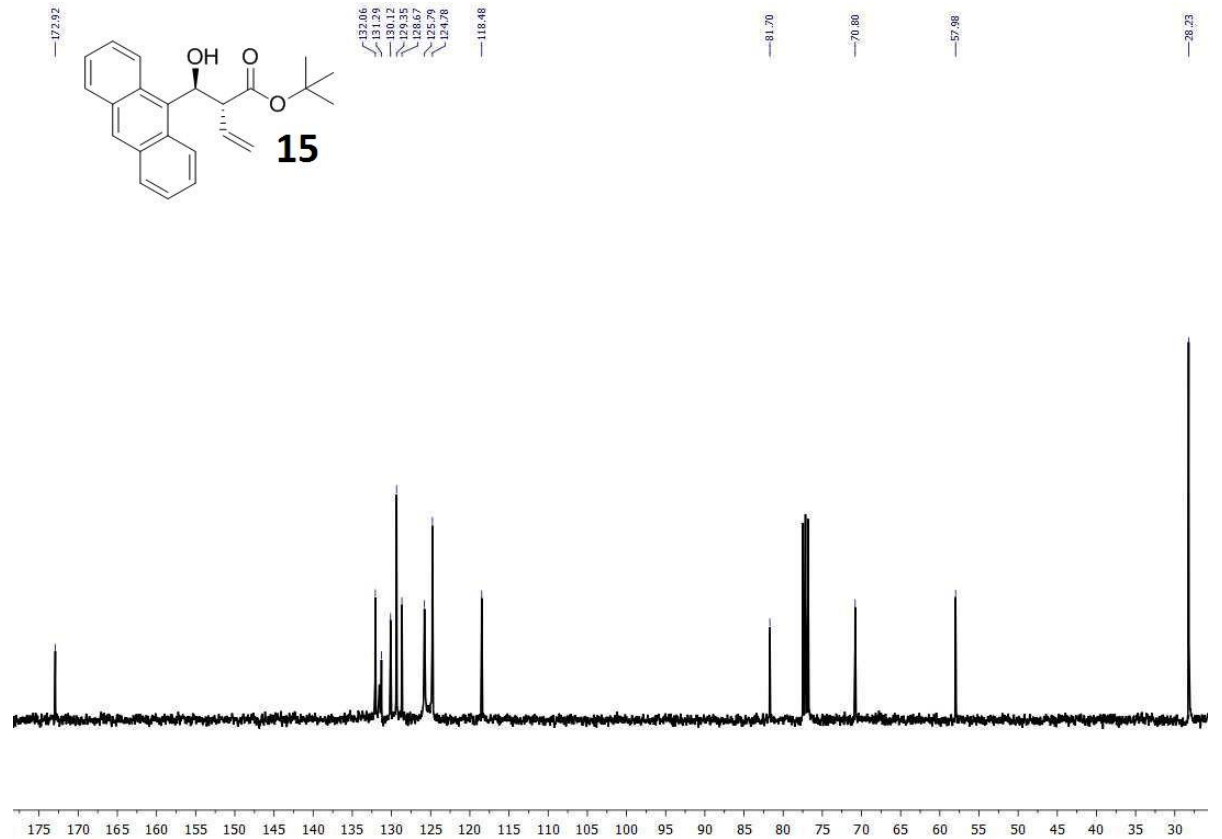
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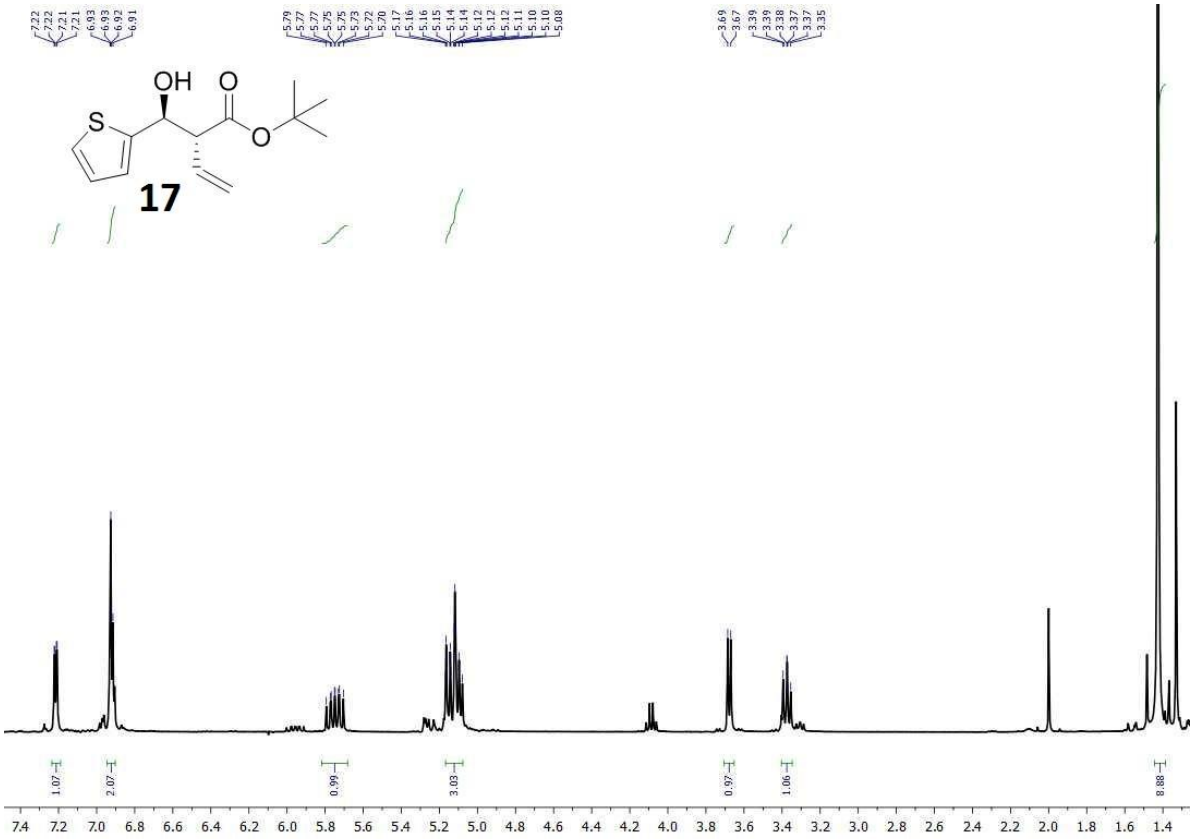
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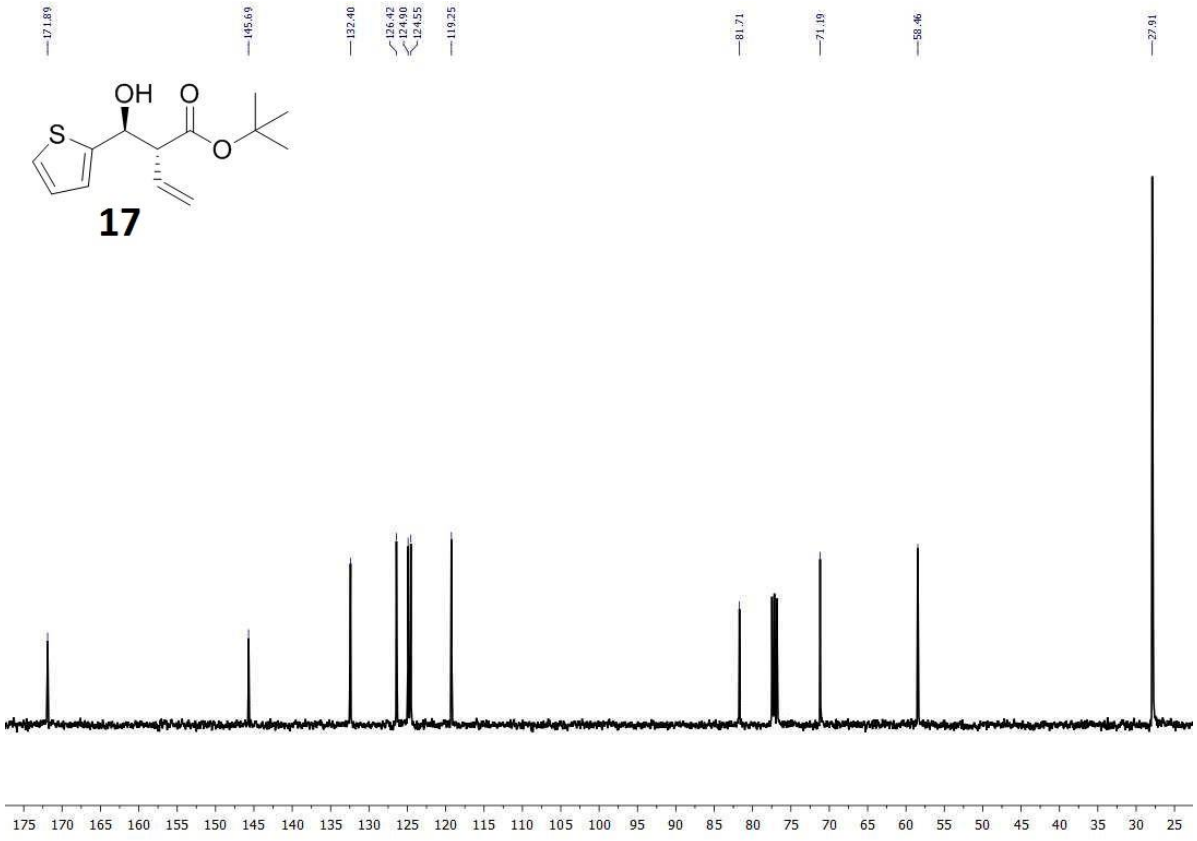
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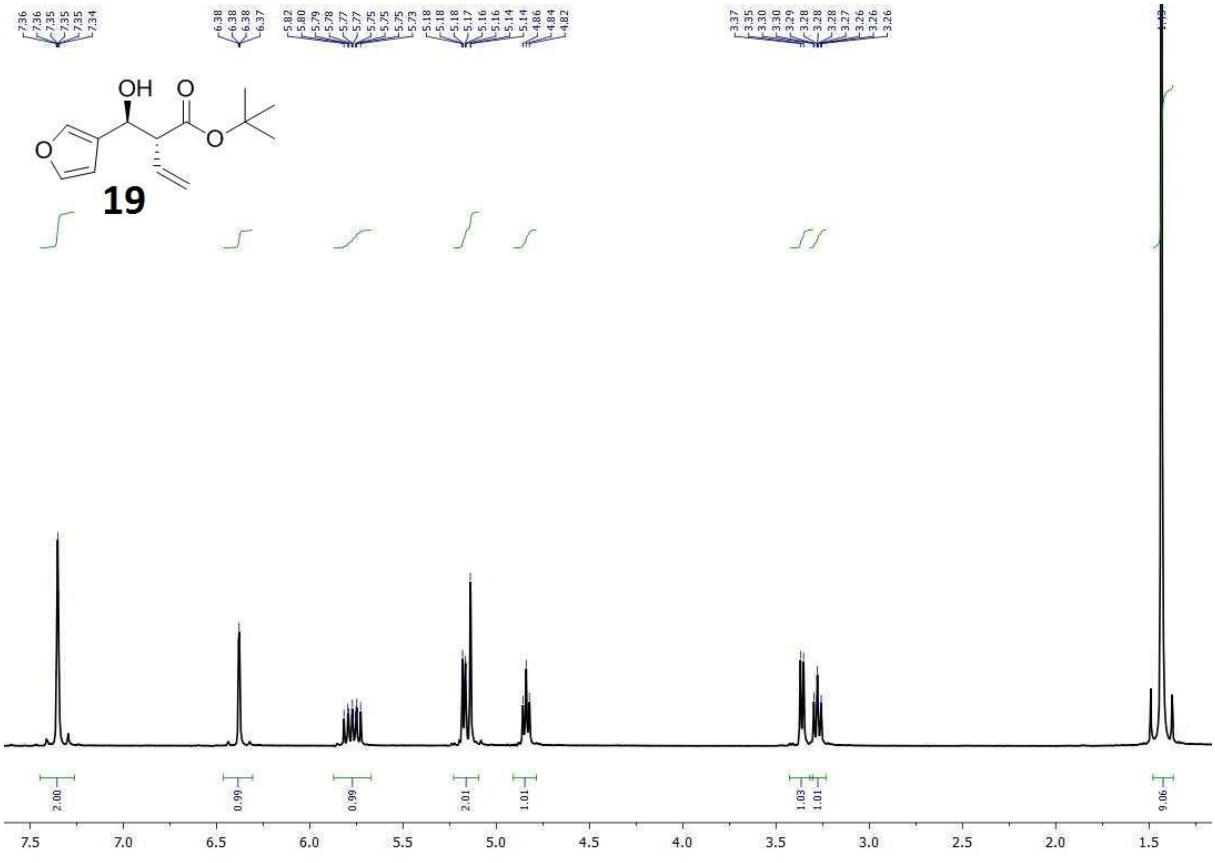
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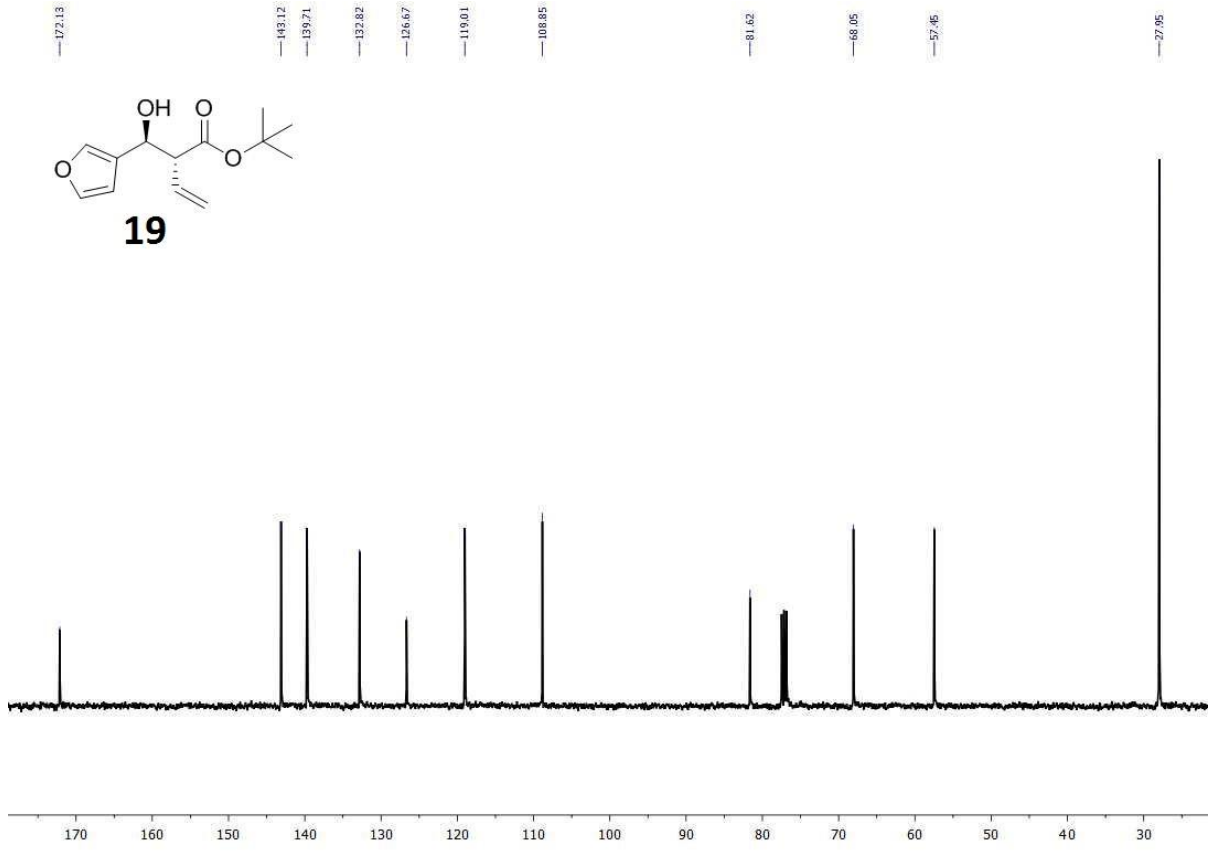
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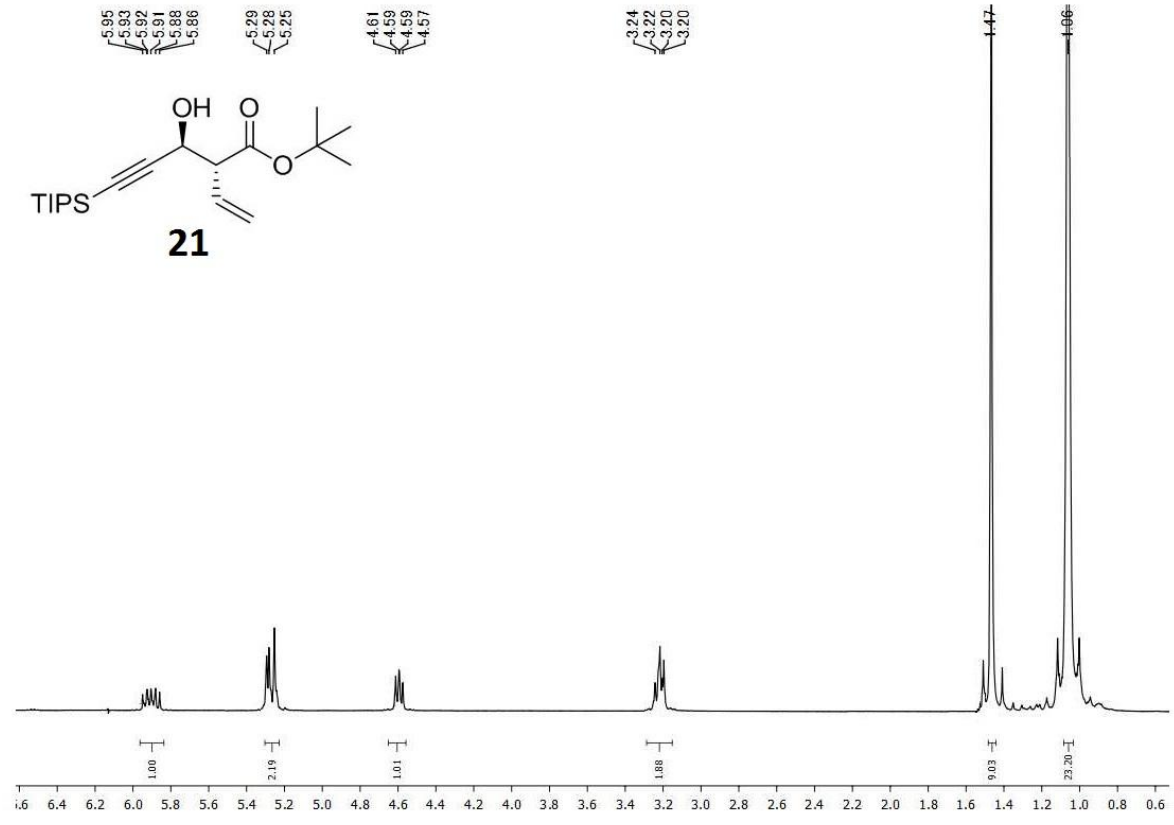
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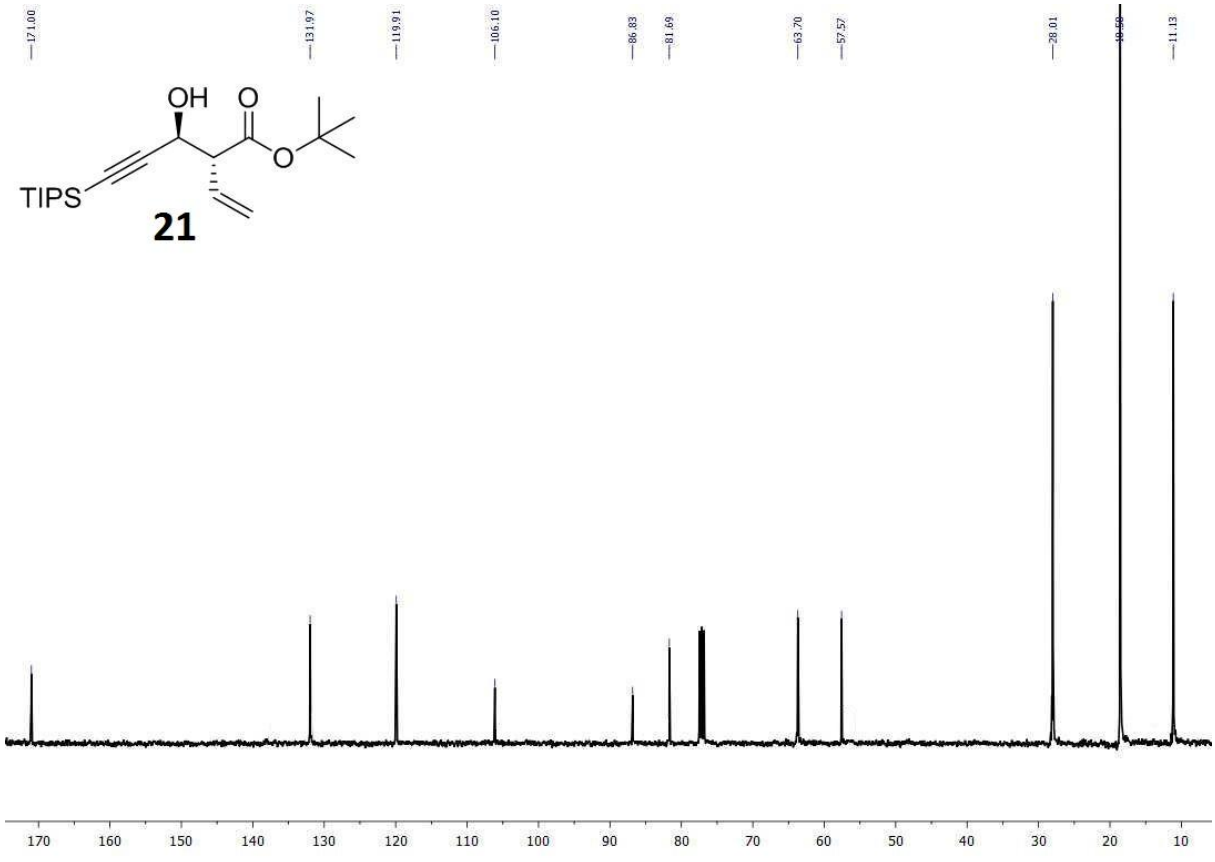
4.57
3.24
3.22
3.20
3.20
1.47
1.06
OH
O
O
TIPS
21
1.00
2.19
1.01
1.88
9.03
23.20
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6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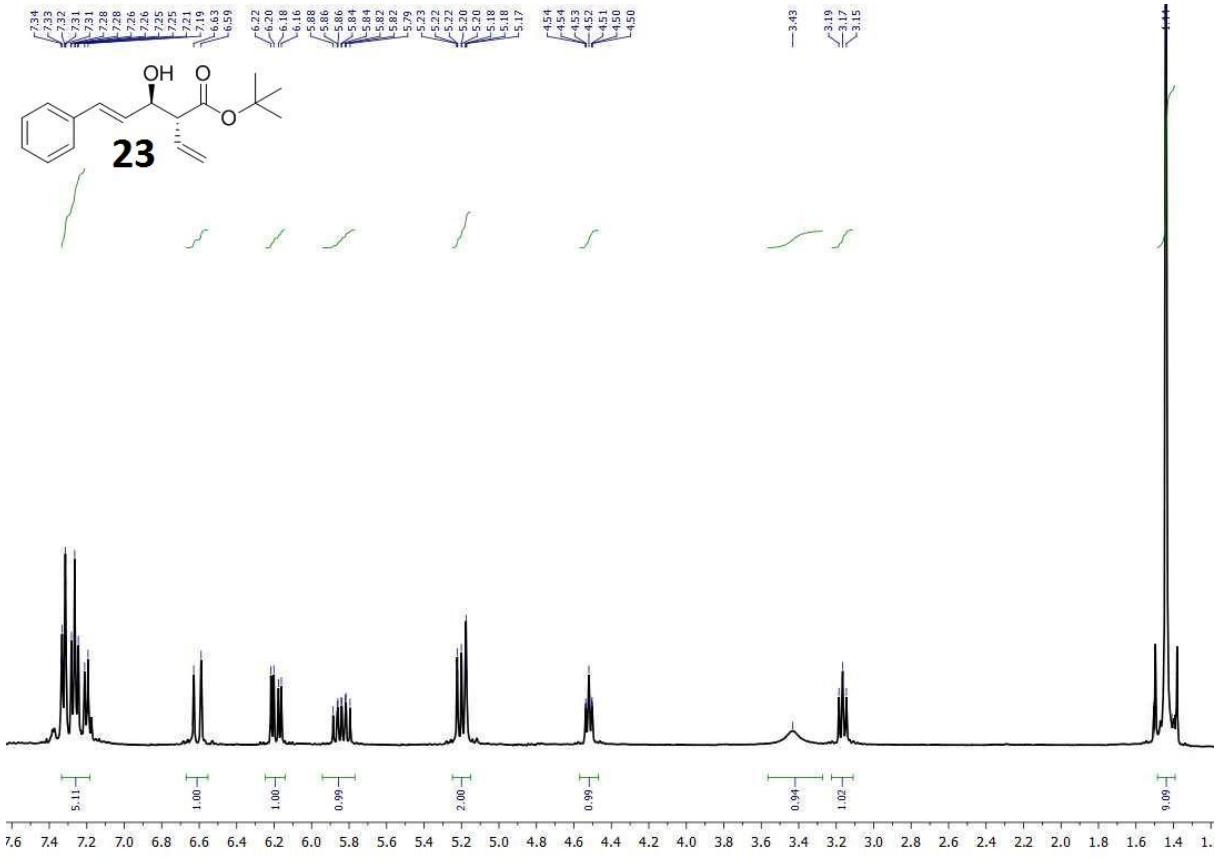
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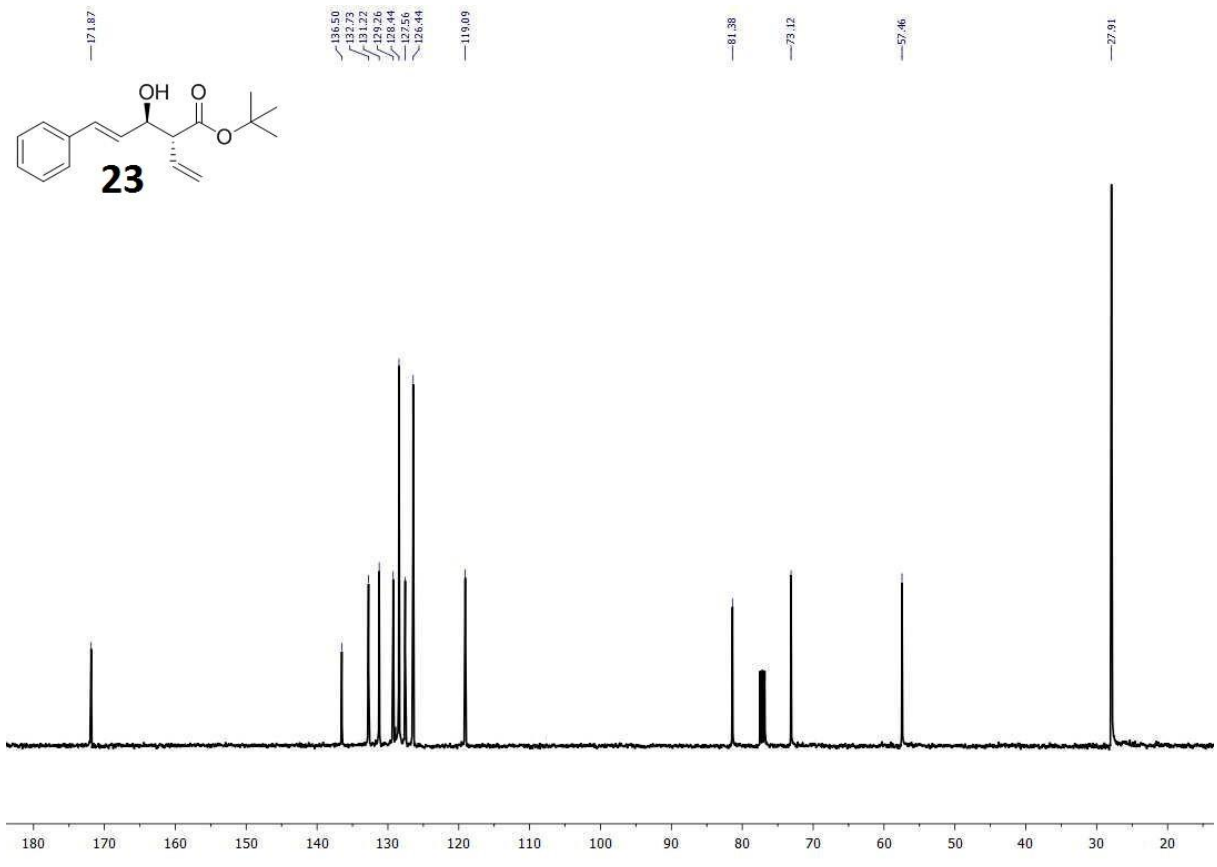
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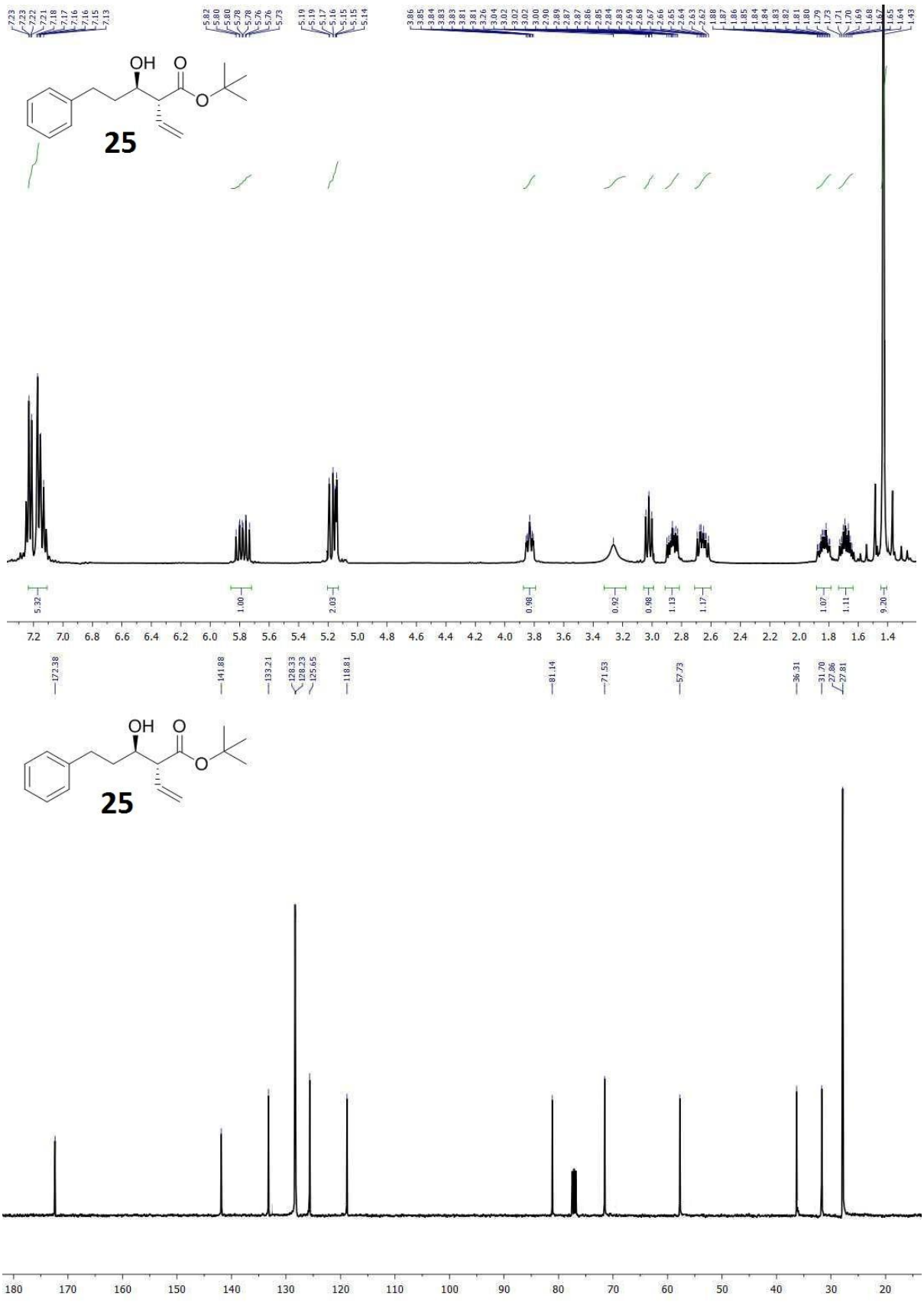
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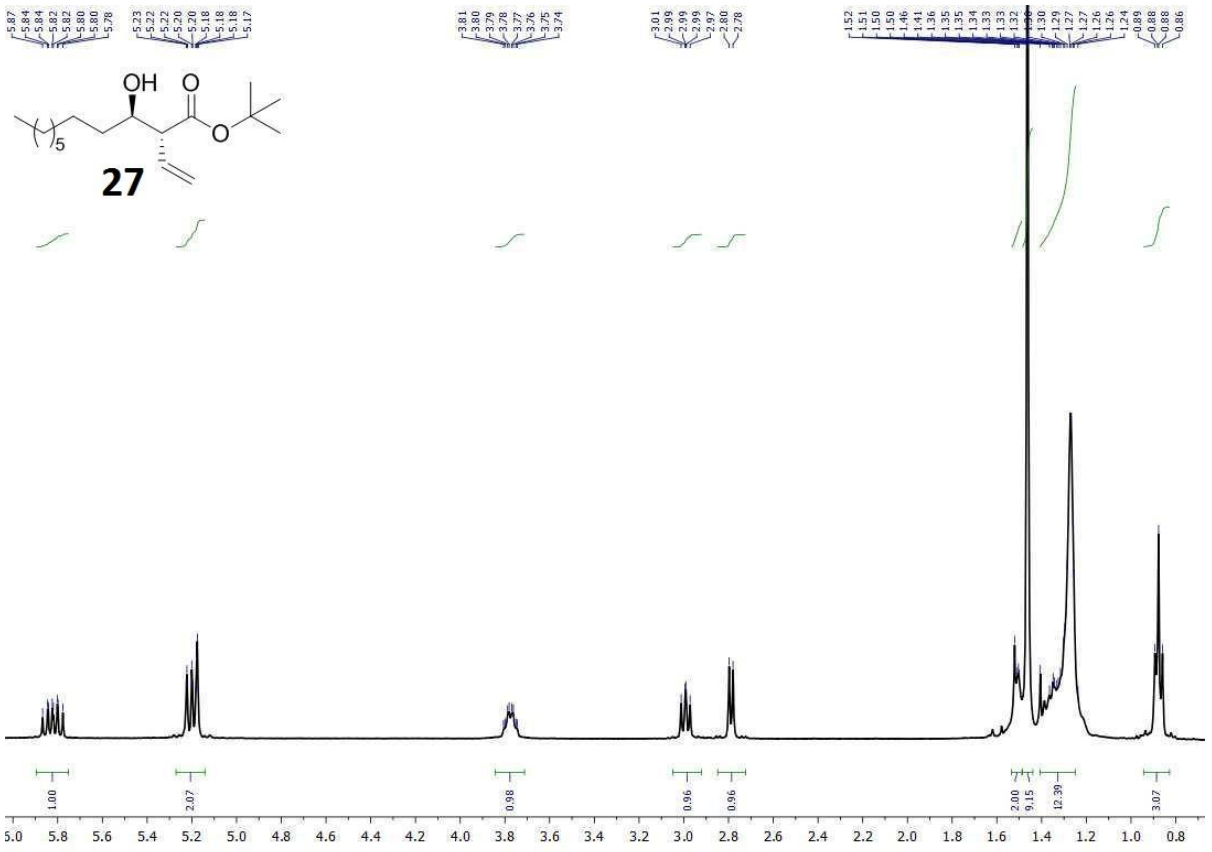
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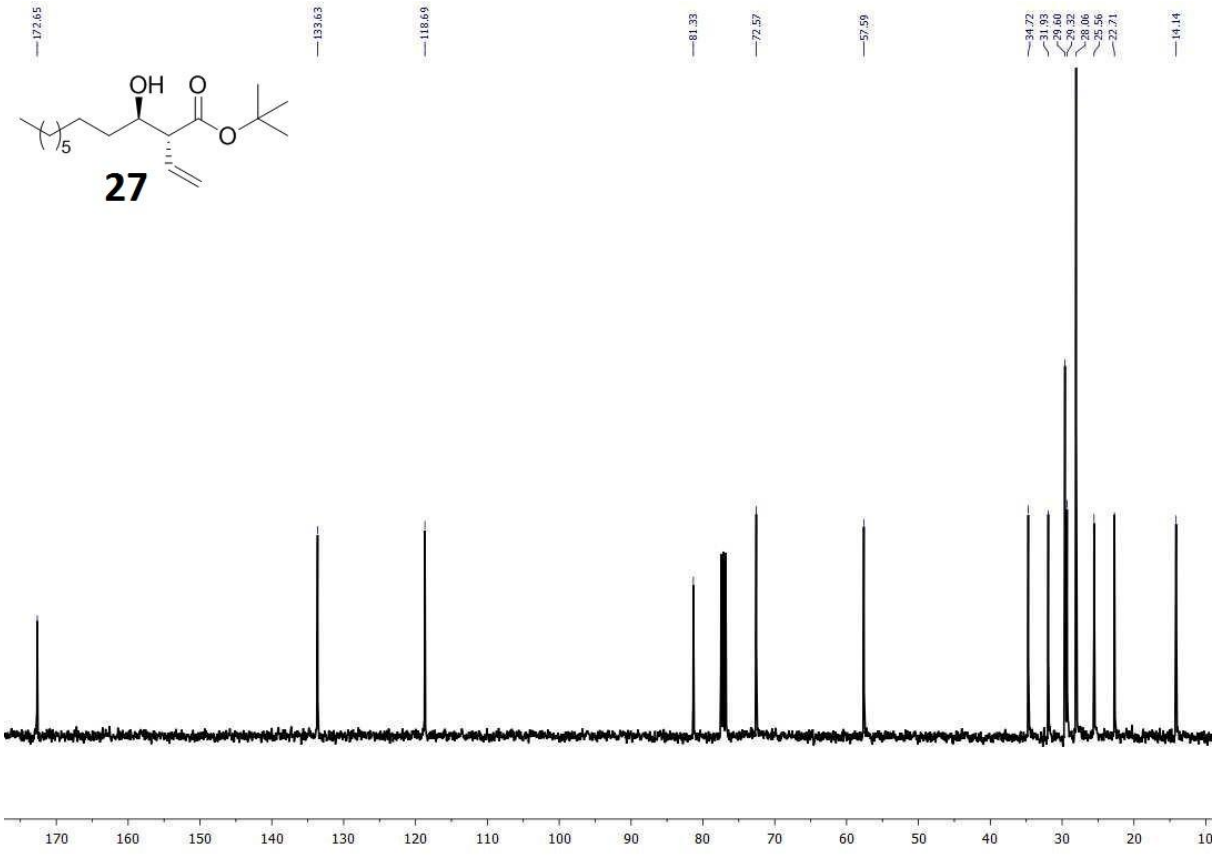
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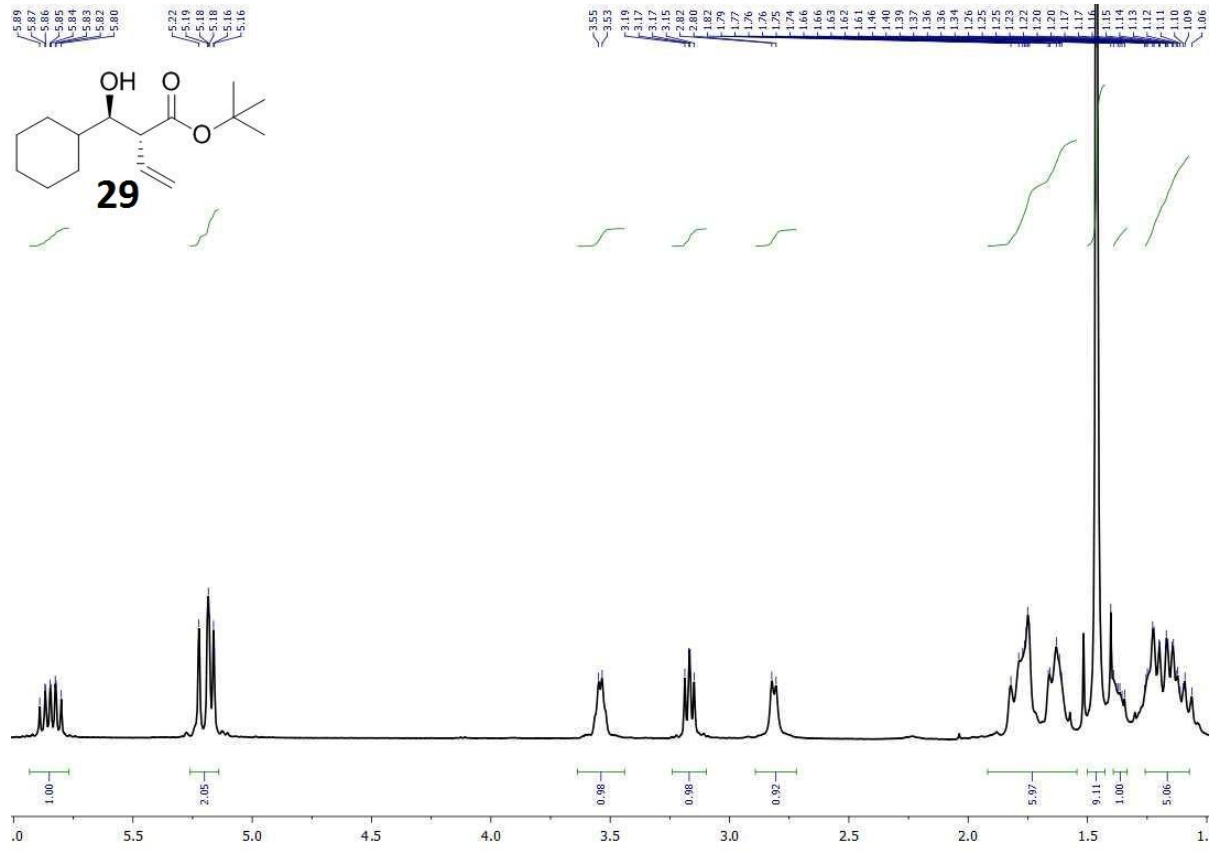
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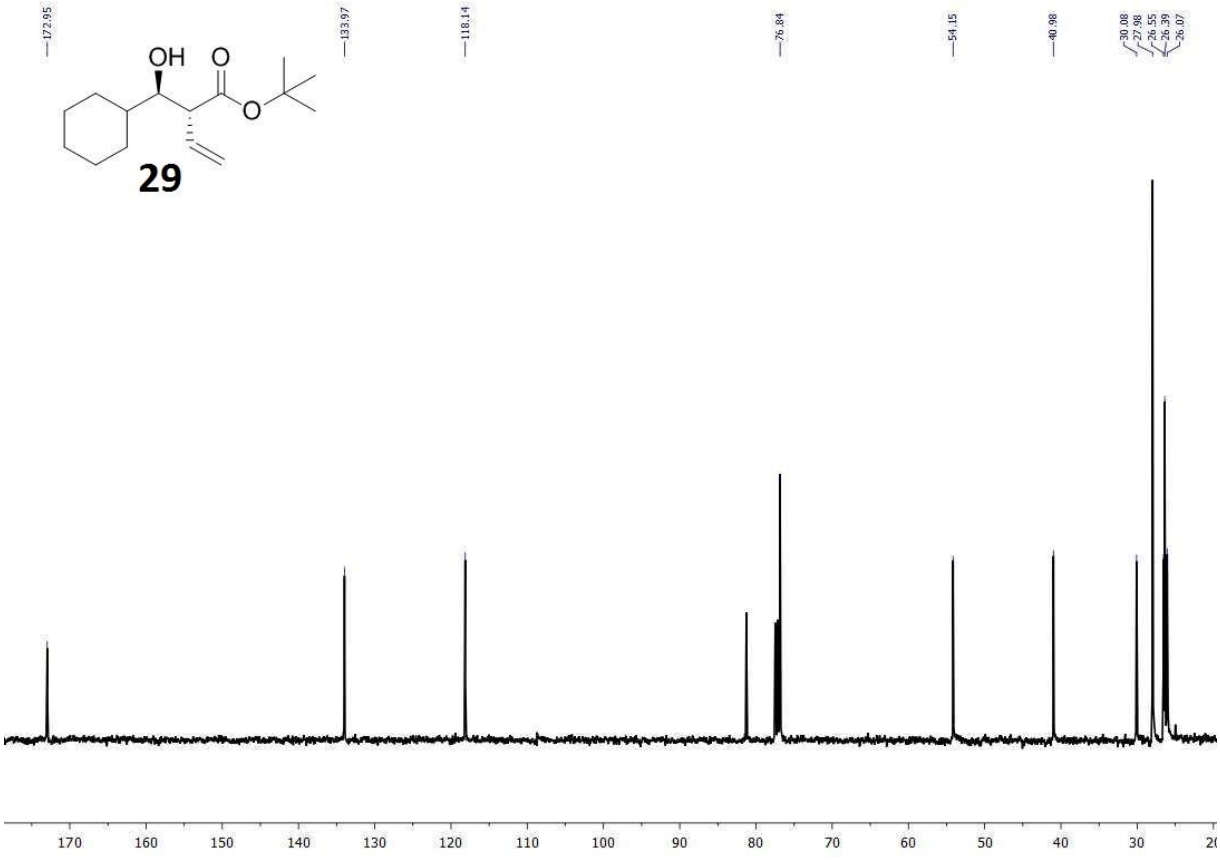
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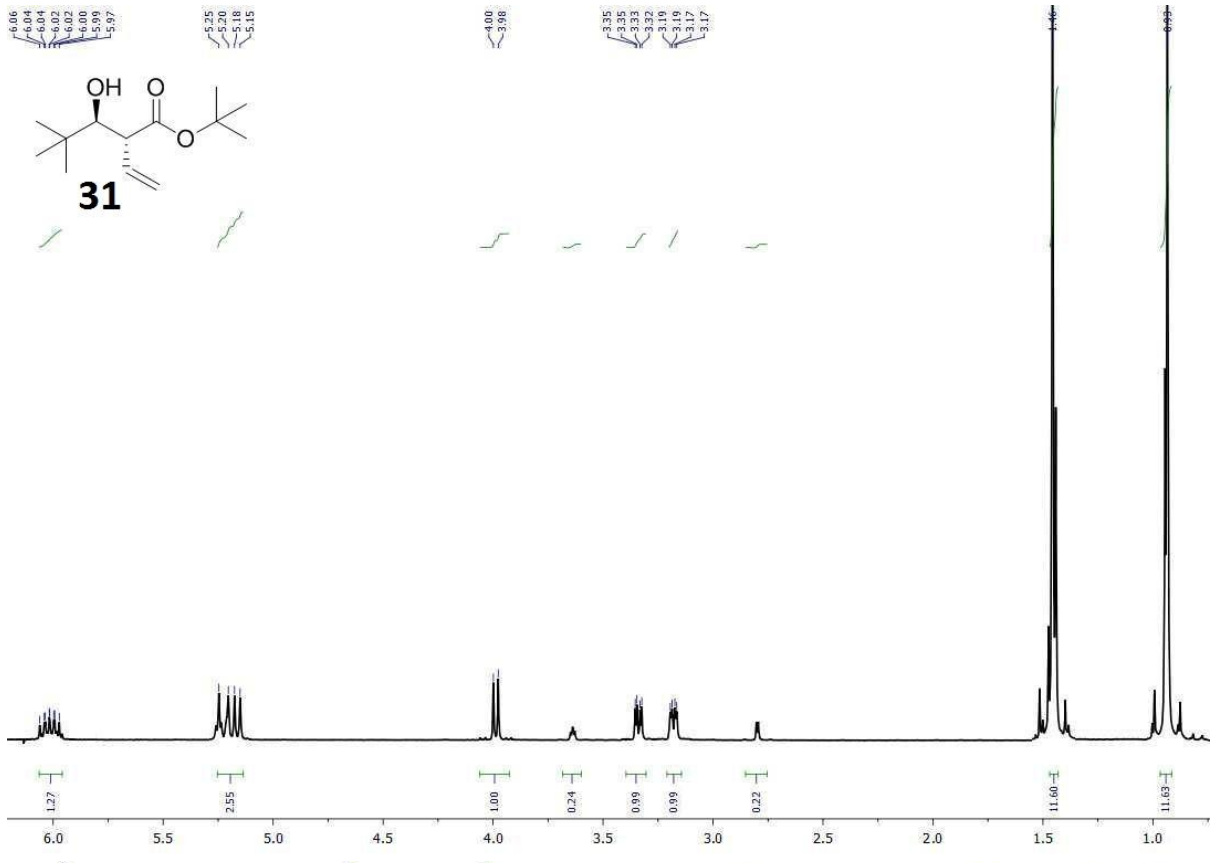
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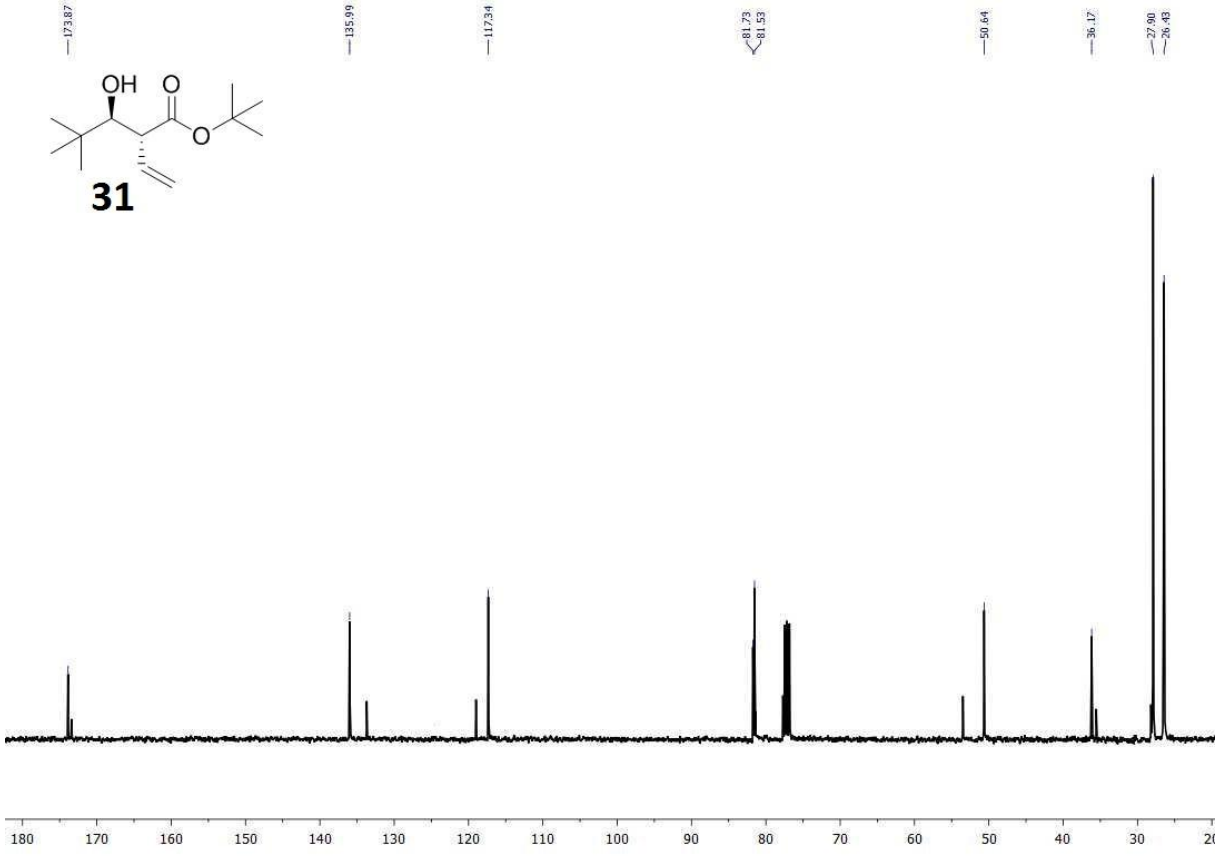
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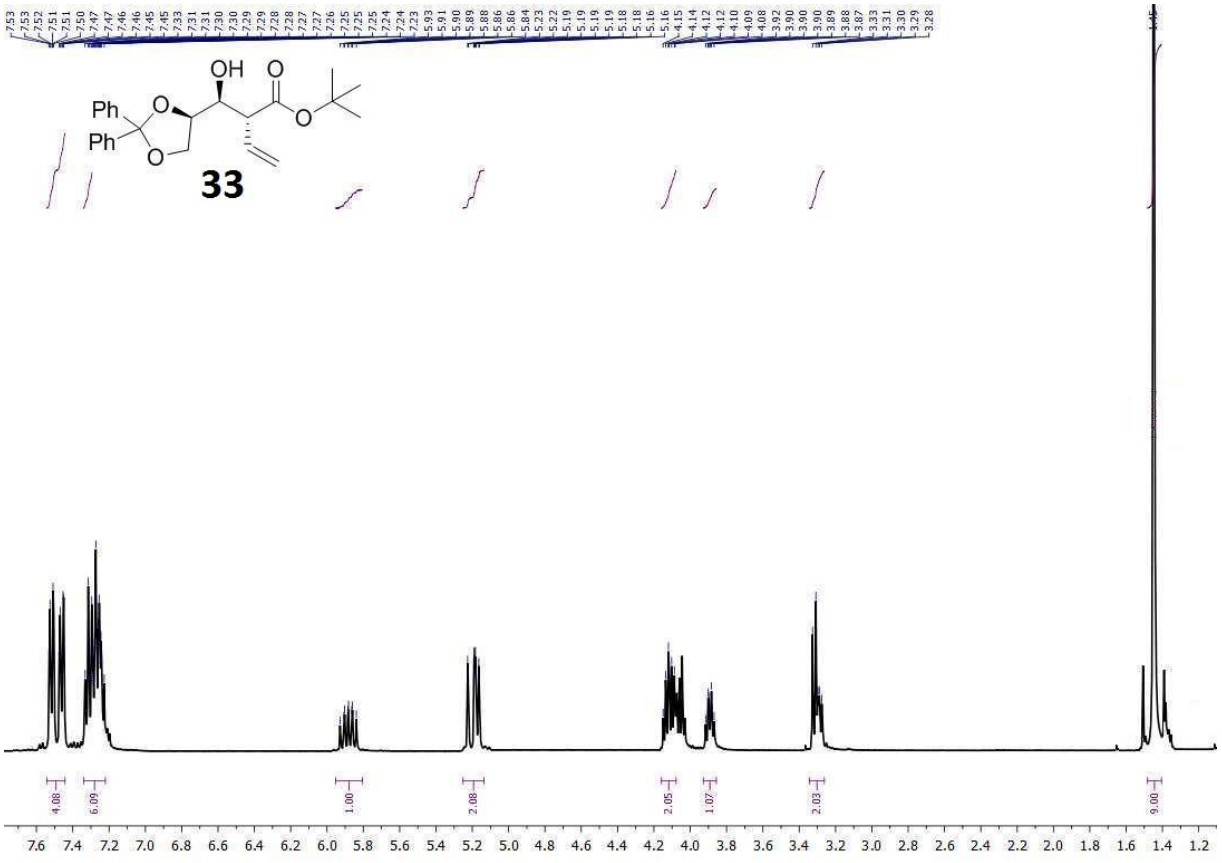
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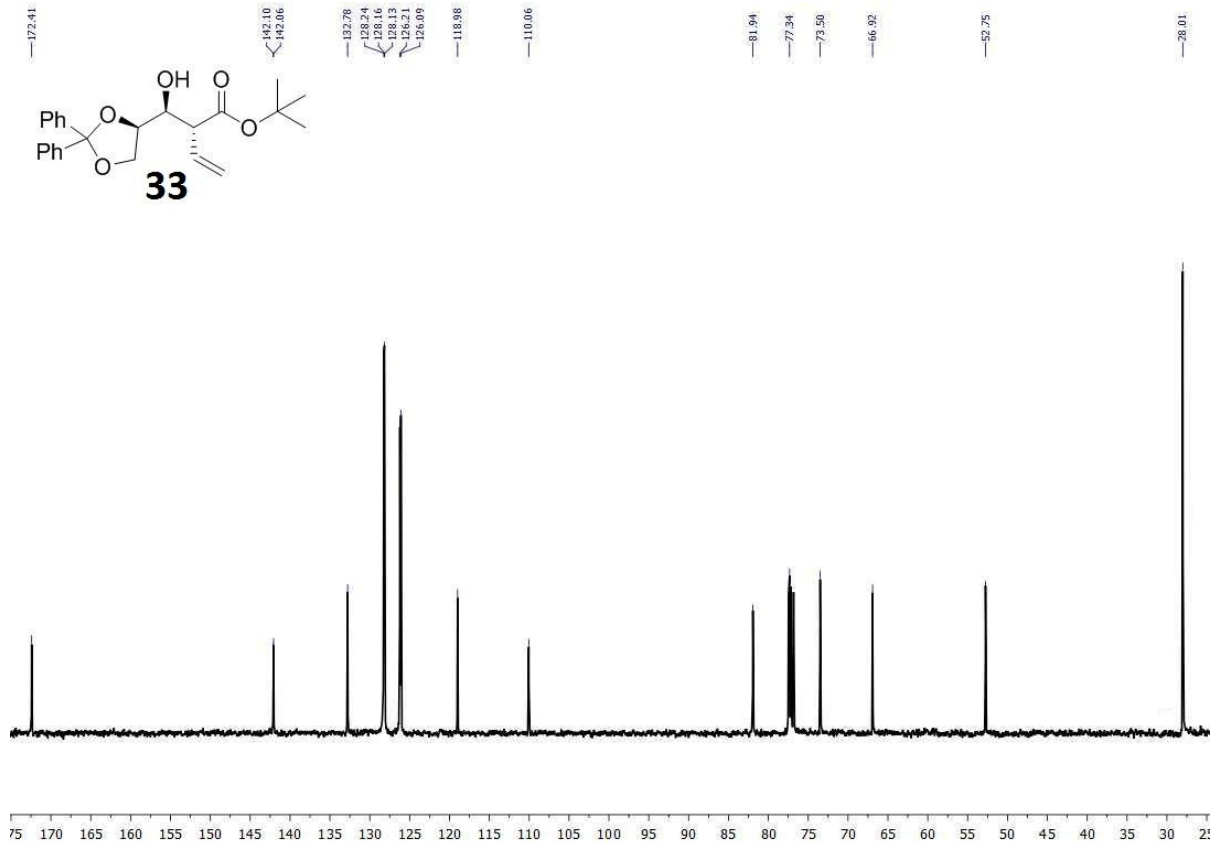
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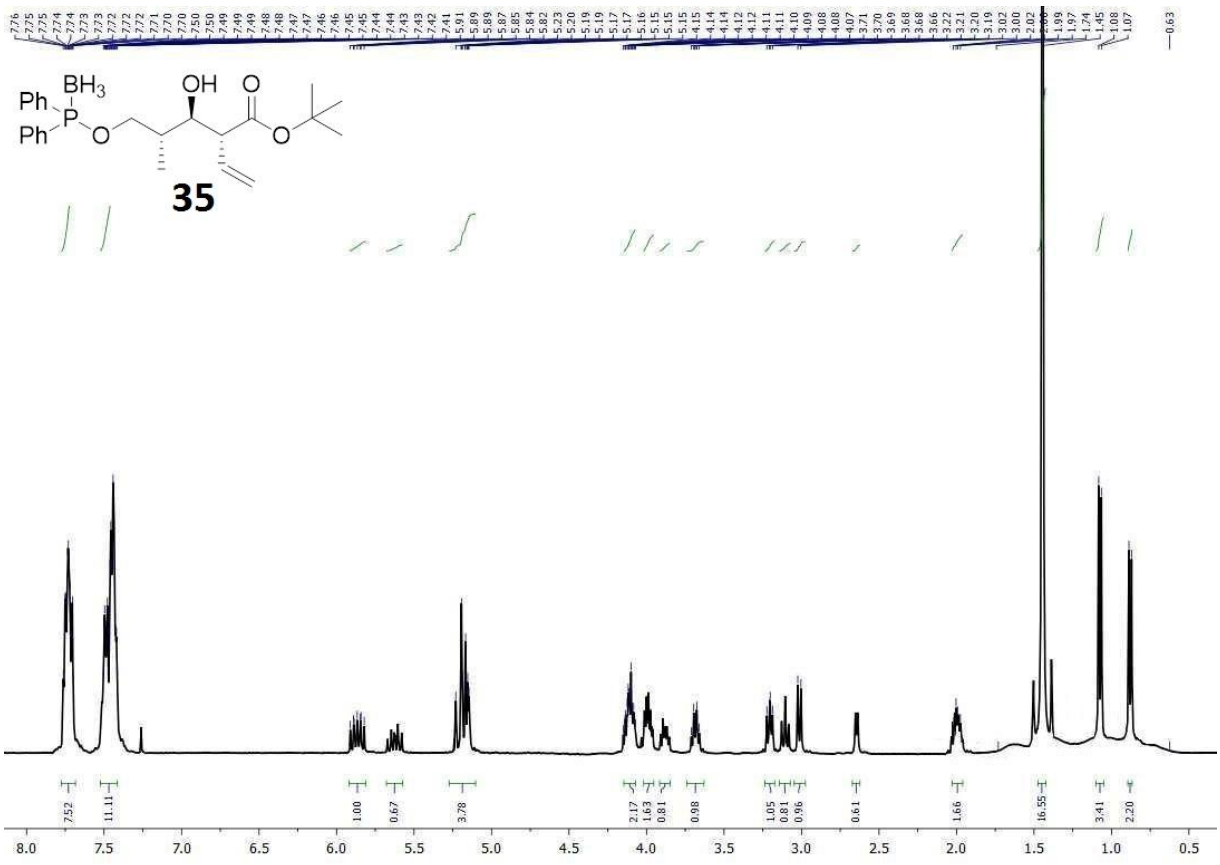
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Ph
Ph
BH3
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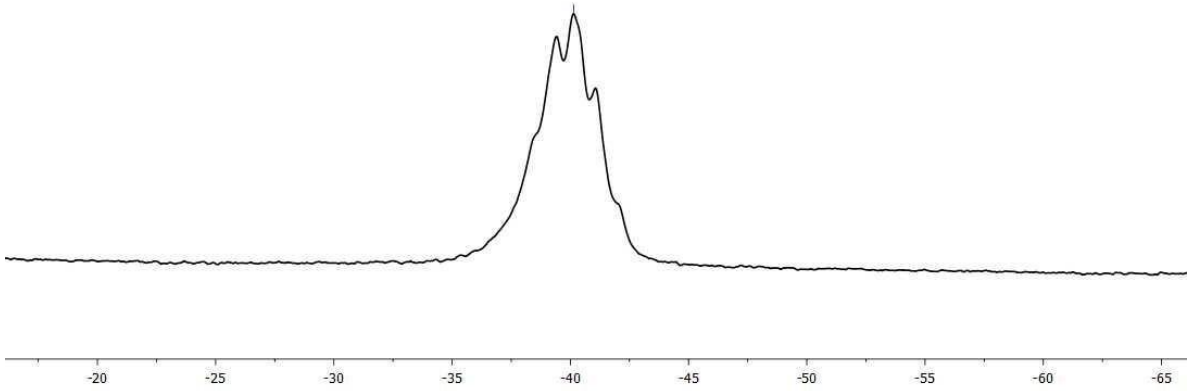

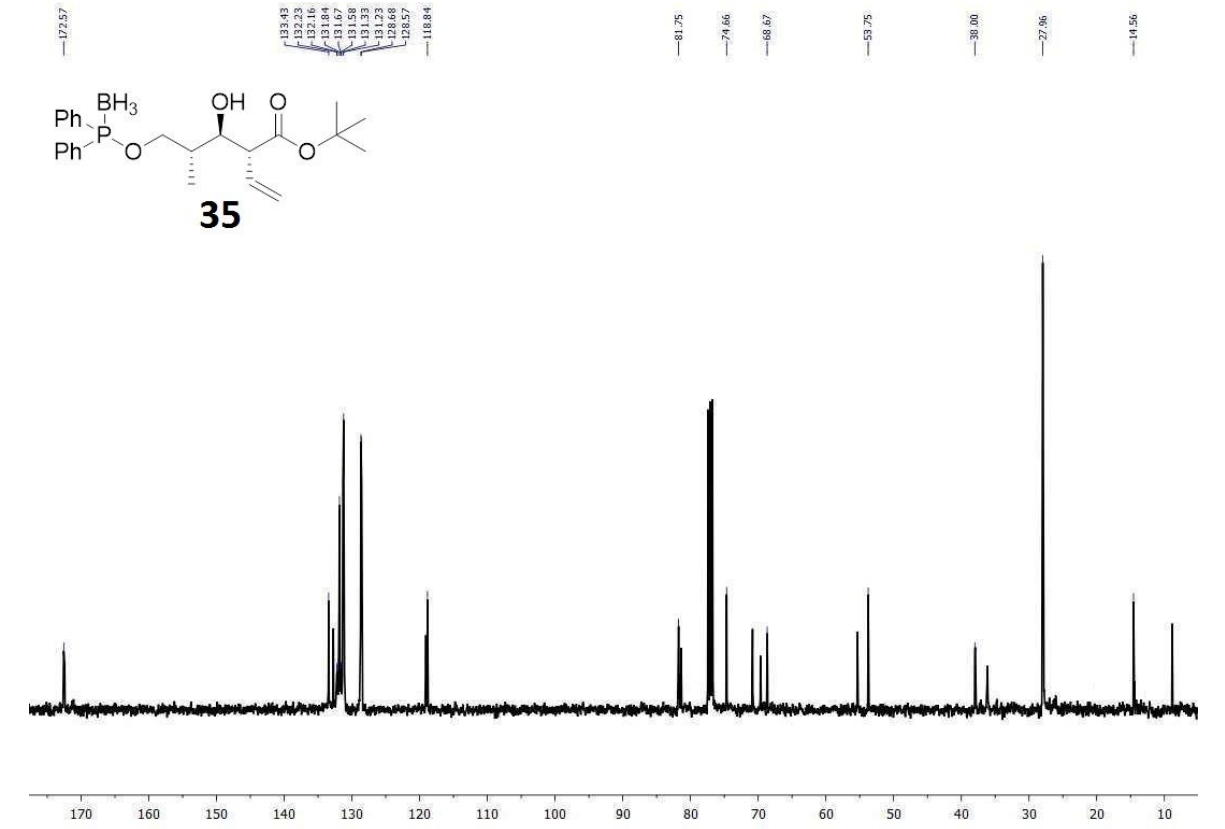
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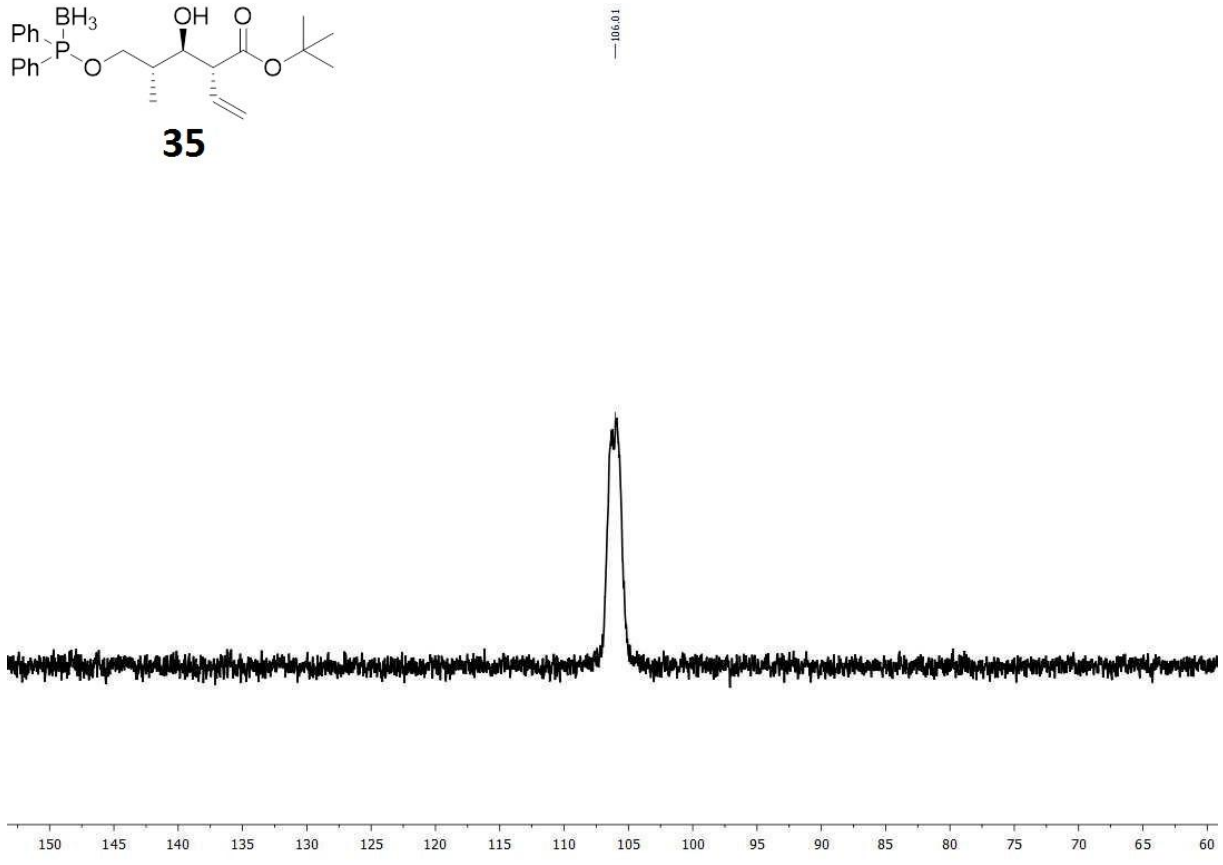
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