Supporting Information

Ligand-free Reductive Coupling of Aldehyde with 1,3-diene Using Sulfur-Modified Au-Supported Nickel Nanoparticle Catalyst

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Contents

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL-300 (300 MHz), JEOL JNM-AL-400 (400 MHz) or JEOL ECA-500 (500 MHz) with tetramethylsilane as an internal standard. Chemistation (TOKYO RIKAKIKAI CO., LTD, PPS-CTRL) was used for heating reactions using SANi. GC-MS analyses were by GCMS-QP2010 SE (Shimadzu corporation). Au mesh was purchased from Sanwa Metal CO. LTD. Column chromatography was carried out with silica gel (Kanto Chemical Co. Inc., Silica Gel 60 N, spherical neutral) unless otherwise stated.

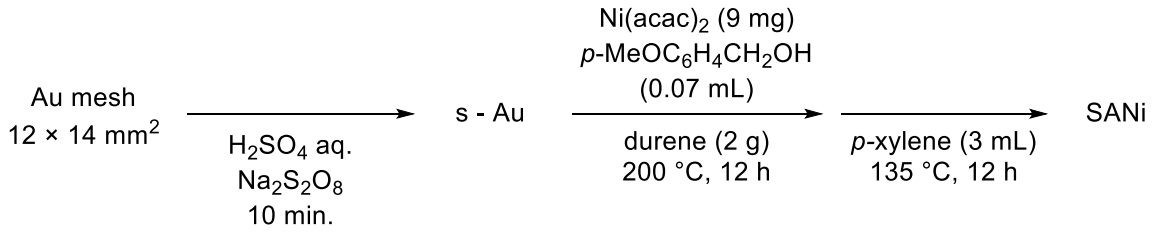
Experiment materials

Solvent were dried by molecular sieves 3A or 4A. Commercial reagents and argon gas were used as received. TLC (Merck silica gel 60 F^{254}) was used for monitoring reactions.

General consideration

Unless otherwise indicated, all reactions were carried out under nitrogen atmosphere. Reactions were monitored by thin layer chromatography.

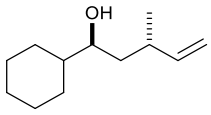
2. Preparation of SANi



$Na_2S_2O_8$ (4 g) was gradually added to 98% H_2SO_4 (4.7 g) in a flask at 0 ℃ with stirring. 17 mL of water cooled in ice bath was added to the solution to maintain the temperture below 15 ℃. After stirring at this temperture, the ice bath was removed and the mixture was stirred at room temperture for 30 min to obtain piranha solution. Au (100 mesh, 12 × 14 mm^2) was placed in piranha solution (3 mL) at 25 ℃ for 10 min, and then rinsed in succession with H_2O (1 mL × 6) and EtOH (1 mL × 6). The sample was placed in a flask and dried under reduced pressure for 10 min. The resulting sulfur-modified Au [s-Au] was placed in a solution of $Ni(acac)_2$ (9 mg) in and 4-methoxybenzylalcohol (0.07 mL) in durene (2 g) and the reaction mixture was stirred at 200 ℃ for 12 h under a N_2 atmosphere. Then the plate was rinsed with *p*-xylene (1 mL × 6) and dried under reduced pressure for 20 min. The obtained mesh was placed in *p*-xylene (3 mL) and heated at 135 ℃ for 12 h. The mesh was rinsed with *p*-xylene (1 mL × 6) and dried under reduced pressure for 20 min to give SANi.

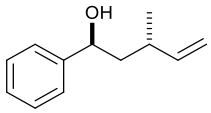
3. General procedure (Table 1)

In a test tube (15 Φ), a mixture of cyclohexanecarboxaldehyde (17 μL, 0.14 mmol) was dissolved in THF (0.62 mL) in the presence of SANi under an argon atmosphere. Isoprene (0.06 mL, 0.60 mmol, 4.3 eq.) and $ZnEt_2$ (1.09 M *n*-hexane solution, 0.32 mL, 0.35 mmol, 2.5 eq.) was added into the reaction mixture and heated at 80 ℃ for 24 h without stirring. After the reaction mixture had been cooled to room temperture, the SANi was removed from the reaction mixture and rinsed several times with THF. Then, HCl aq. (1 N, 5 mL) was added into the reaction mixture, and the reaction mixture was extracted with AcOEt. The organic layer was washed with sat $NaHCO_3$ aq., dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (*n*-hexane : AcOEt = 15 : 1) to afford 1,3-*anti*-1-cyclohexyl-3-metyl-4-pentenol **3aa** (16.9 mg, 0.093 mmol, 66%) as a colorless oil.



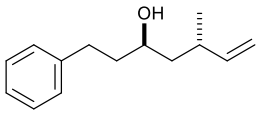
1,3-*anti*-1-Cyclohexyl-3-methyl-4-penten-1-ol (**3aa**) [1,3]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 5.85-5.77 (m, 1H), 5.04 (m, 1H), 4.94 (m, 1H), 3.47 (m, 1H), 2.34 (m, 1H), 1.79-1.72 (m, 3H), 1.67-1.64 (m, 2H), 1.50-1.37 (m, 2H), 1.35-0.96 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 145.6, 112.6, 74.6, 44.0, 41.2, 35.5, 29.3, 27.6, 26.6, 26.4, 26.3, 19.9.



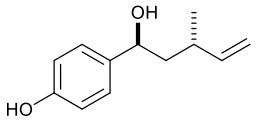
1,3-*anti*-3-Methyl-1-phenyl-4-penten-1-ol (**3ba**) [1,2,3]

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.35-7.26 (m, 6H), 5.78 (m, 1H), 5.03-4.97 (m, 2H), 4.73 (dd, J = 7.7, 6.0 Hz, 1H), 2.25-2.19 (m, 1H), 1.88-1.83 (m, 2H), 1.65 (dt, J = 13.7, 6.3 Hz, 1H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 144.7, 144.6, 128.5, 127.7, 126.1, 113.3, 73.1, 46.0, 35.3, 20.6.



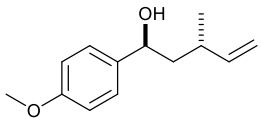
3,5-*anti*-5-Methyl-1-phenyl-6-hepten-3-ol (**3ca**) [1,3]

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.30-7.16 (m, 5H), 5.77 (ddd, J = 17.8, 9.7, 7.4 Hz, 1H), 5.02 (m, 1H), 4.93 (m, 1H), 3.74-3.69 (m, 1H), 2.82-2.76 (m, 1H), 2.70-2.64 (m, 1H), 2.35-2.29 (m, 1H), 1.81-1.70 (m, 2H), 1.60 (s, 1H), 1.56-1.50 (m, 1H), 1.43 (m, 1H), 1.00 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 145.1, 142.2, 128.5, 128.5, 125.8, 113.1, 70.1, 44.6, 39.4, 35.8, 32.0, 20.5.



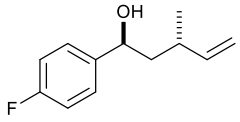
1,3-*anti*-1-(*p*-Hydroxyphenyl)-3-methyl-4-penten-1-ol (**3da**) [3]

Light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.23 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 5.81-5.73 (m, 1H), 5.00 (br d, J = 14.7 Hz, 1H), 4.96 (br d, J = 7.8 Hz, 1H), 4.91 (s, 1H), 4.69-4.66 (m, 1H), 2.21-2.14 (m, 1H), 1.89-1.81 (m, 2H), 1.67-1.62 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H); ^{13}C NMR (MHz, $CDCl_3$) δ : 155.3, 144.6, 136.5, 127.7, 115.4, 113.5, 73.0, 45.7, 35.4, 20.7; mp: 88-90 °C (recrystallized from n-hexane/$CHCl_3$, plate).



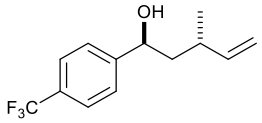
1,3-*anti*-1-(*p*-Methoxyphenyl)-3-methyl-4-penten-1-ol (**3ea**) [4]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.26 (m, 2H), 6.87 (m, 2H), 5.82-5.70 (m, 1H), 4.97 (m, 2H), 4.66 (t, J = 7.1 Hz, 1H), 3.79 (s, 3H), 2.20-2.11 (m, 1H), 1.89-1.79 (m, 2H), 1.63 (m, 1H), 1.00 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 159.1, 144.6, 136.9, 127.4, 113.9, 113.3, 72.7, 55.4, 45.8, 35.3, 20.7.



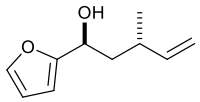
1,3-*anti*-1-(*p*-Fluorophenyl)-3-methyl-4-penten-1-ol (**3fa**) [4]

^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.33-7.29 (m, 2H), 7.06-7.00 (m, 2H), 5.77 (ddd, J = 17.6, 9.8, 7.5 Hz, 1H), 5.03-4.97 (m, 2H), 4.72 (t, J = 6.7 Hz, 1H), 2.26-2.12 (m, 1H), 1.97 (br s, 1H), 1.84 (dt, J = 15.1, 6.9 Hz, 1H), 1.62 (dt, J = 13.6, 6.1 Hz, 1H), 1.03 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ : 162.3 (d, $^1J_{C\text{-}F}$ = 244.7 Hz), 144.5, 140.5 (d, $^4J_{C\text{-}F}$ = 3.6 Hz), 127.8 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 113.6, 72.6, 46.1, 35.4, 20.7.



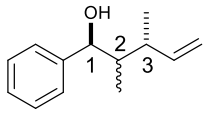
1,3-*anti*-1-(*p*-Trifluoromethylphenyl)-3-methyl-4-penten-1-ol (**3ga**) [4]

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.60 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 5.79 (ddd, J = 18.0, 9.3, 7.2 Hz, 1H), 5.06-4.99 (m, 2H), 4.80 (t, J = 6.6 Hz, 1H), 2.29-2.20 (m, 1H), 2.11 (br s, 1H), 1.88-1.80 (m, 1H), 1.76-1.61 (m, 1H), 1.04 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 148.7, 144.4, 129.8 (q, $^2J_{C\text{-}F}$ = 32.6 Hz), 126.4, 125.5 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 272.2 Hz), 113.8, 72.7, 46.2, 35.5, 20.6.



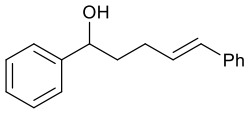
1,3-anti-1-(2-Furyl)-3-metyl-4-penten-1-ol (**3ha**)[3]

Colorless oil; a mixture of 1,3-*anti* and 1,3-*syn* = 5:1; ^{1}H NMR (300 MHz, $CDCl_3$, 1,3-*anti* isomer) δ : 7.39-7.38 (m, 1H), 6.33 (dd, J = 3.3, 1.9 Hz, 1H), 6.23 (d, J = 3.1 Hz, 1H), 5.75 (ddd, J = 17.5, 9.7, 7.5 Hz, 1H), 5.01-4.94 (m, 2H), 4.76-4.71 (m, 1H), 2.29-2.17 (m, 1H), 1.98 (s, 1H), 1.89-1.70 (m, 2H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 1,3-*anti* isomer) δ : 156.5, 144.2, 142.1, 113.4, 110.2, 106.2, 66.3, 42.1, 34.9, 20.3; ^{13}C NMR (100 MHz, $CDCl_3$, 1,3-*syn* isomer) δ : 157.1, 143.6, 142.0, 114.0, 110.5, 105.7, 65.8, 42.1, 34.6, 21.0.



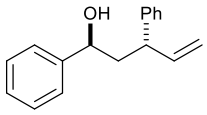
2,3-Dimethyl-1-phenyl-4-penten-1-ol (**3bb**) [2,3]

Colorless oil; a mixture of 1,2-*syn*-1,3-*anti* and 1,2-*anti*-1,3-anti = 10:3; ^{1}H NMR (500 MHz, $CDCl_3$, 1,2-*syn* isomer) δ : 7.36-7.25 (m, 5H), 5.80 (ddd, J = 18.0, 9.5, 7.7 Hz, 1H), 5.08-4.97 (m, 2H), 4.70 (d, J = 5.7 Hz, 1H), 2.22-2.15 (m, 1H), 1.78-1.73 (m, 2H), 1.05 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 1,2-*syn* isomer) δ : 144.1, 141.8, 128.4, 127.3, 126.4, 114.8, 76.7, 45.5, 40.5, 19.3, 9.6; ^{1}H NMR (500 MHz, $CDCl_3$, 1,2-*anti* isomer) δ : 7.36-7.25 (m, 5H) 5.93-5.86 (ddd, J = 18.0, 9.5, 7.7 Hz, 1H), 5.08-4.97 (m, 1H), 4.47 (d, J = 9.2 Hz, 1H), 2.76-2.73 (m, 1H), 1.95-1.88 (m, 1H), 1.62 (br s, 1H), 1.01 (d, J = 6.9 Hz, 1H), 0.53 (d, J = 6.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$, 1,2-*anti* isomer) δ :144.3, 143.8, 128.5, 127.8, 127.0, 113.4, 77.2, 44.3, 37.0, 13.0, 11.0.



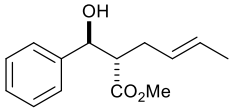
(4E)-1,5-Diphenyl-4-penten-1-ol (**3bc**) [3]

Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ : 7.38-7.17 (m, 10H), 6.41 (d, J = 16.2 Hz, 1H), 6.23 (dt, J = 15.7, 6.8 Hz, 1H), 4.75 (t, J = 6.5 Hz, 1H), 2.29 (m, 2H), 2.06-1.88 (m, 3H): ^{13}C NMR (125 MHz, $CDCl_3$) δ : 144.6, 137.7, 130.5, 130.1, 128.6, 128.6, 127.8, 127.1, 126.1, 126.0, 74.1, 38.6, 29.4.



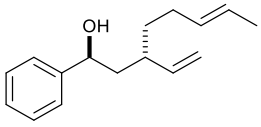
anti-1,3-Diphenyl-4-penten-1-ol (**3bd**) [3]

^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.35-7.21 (m, 10H), 6.03 (ddd, J = 17.4, 9.9, 7.3 Hz, 1H), 5.08-5.06 (m, 1H), 5.04-5.03 (m, 1H), 4.50 (dt, J = 9.0, 4.2 Hz, 1H), 3.55 (dt, J = 15.1, 7.3 Hz, 1H), 2.23 (ddd, J = 14.7, 8.2, 5.7 Hz, 1H), 2.06 (ddd, J = 13.8, 8.8, 4.4 Hz, 1H), 1.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 144.8, 143.4, 142.3, 128.7, 128.6, 127.9, 127.7, 126.6, 125.9, 114.3, 72.3, 46.5, 44.6.



(4E)-1,2-anti-2-Methoxycarbonyl-1-phenyl-4-hexen-1-ol (**3be**) [2,3]

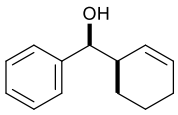
^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.34-7.24 (m, 5H), 5.49-5.41 (m, 1H), 5.36-5.29 (m, 1H), 4.95 (dd, J = 5.7, 2.1 Hz, 1H), 3.57 (s, 3H), 2.88 (d, J = 2.3 Hz, 1H), 2.78 (ddd, J = 10.2, 5.2, 4.2 Hz, 1H), 2.45-2.37 (m, 1H), 2.34-2.27 (m, 1H), 1.60 (br d, J = 7.3 Hz, 3H)
^{13}C NMR (100 MHz, $CDCl_3$) δ : 174.9, 141.5, 128.4, 127.8, 127.7, 127.7, 126.2, 74.0, 53.3, 51.7, 30.5, 18.0.



anti-7-Methyl-1-phenyl-3-vinyl-6-octenol (**3bf**) [2,3]

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.34-7.25 (m, 5H), 5.67 (ddd, J = 18.2, 9.0, 7.9 Hz, 1H), 5.08-4.98 (m, 3H), 4.72 (t, J = 6.9 Hz, 1H), 2.00-1.92 (m, 2H), 1.87-1.77 (m, 3H), 1.65 (s, 3H), 1.55 (s, 3H), 1.40 (dd, J = 20.4, 14.0 Hz, 1H), 1.32-1.22 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 143.2, 131.6, 128.5, 127.7, 126.3, 124.4, 115.4, 73.5, 44.5, 41.3, 35.3, 25.8, 25.5, 17.8.

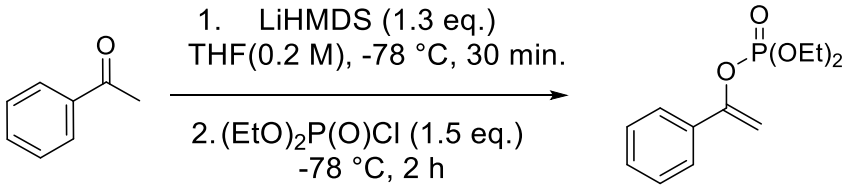


1-(2-Cyclohexenyl)-1-phenylmethanol (**3bg**) [3]

Colorless oil; a mixture of 1,2-*syn* and 1,2-*anti* = 10:3; ^{1}H NMR (300 MHz, $CDCl_3$, 1,2-*syn* isomer) δ : 7.35-7.24 (m, 5H), 5.84-5.78 (m, 1H), 5.38 (dd, J = 10.3, 2.1 Hz, 1H), 4.59 (d, J = 6.5 Hz, 1H), 2.54-2.44 (m, 1H), 1.99 (m, 2H), 1.89 (s, 1H), 1.73 (m, 2H), 1.56-1.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$, 1,2-*syn* isomer) δ : 143.0, 130.5, 128.3, 128.1, 127.5, 126.6, 77.5, 43.1, 25.3, 23.9, 21.2. ^{13}C NMR (125 MHz, $CDCl_3$,1,2-*anti* isomer) δ : 143.6, 130.0, 128.4, 127.6, 127.1, 126.4, 78.1, 42.9, 26.4, 25.4, 21.6.

4. Preparation of diene

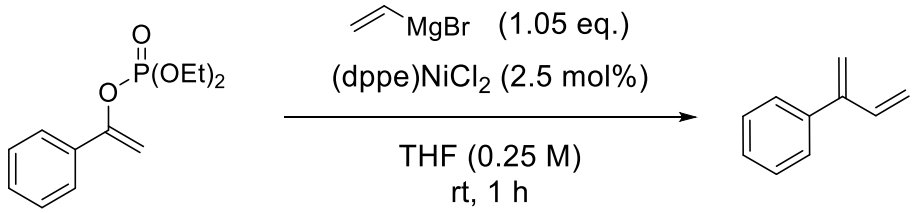
diethyl (1-phenylvinyl) phosphate (**2d'**) [5,6]



To a stirred solution of ketone (20.0 mmol, 1.0 equiv.) in anhydrous THF at –78 °C and under an inert atmosphere of nitrogen, LiHMDS (20 mL of a 1.3 M solution in THF, 26 mmol, 1.3 equiv.) was added dropwise. After 30 min, diethyl chlorophosphate (4.3 mL, 30 mmol, 1.5 equiv.) was added dropwise and the reaction mixture was stirred at –78 °C for 2 h. The reaction mixture was warmed up to room temperature for 15 min, quenched with saturated ammonium chloride solution and then extracted with ethyl acetate (3 x 25 mL). The combined organics were dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexane buffered with 0.1% of Et_3N) affording pure enol phosphate **2d'** (1.6 g, 6.3 mmol, 63% yield) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.57 (m, 2H), 7.38-7.33 (m, 3H), 5.29 (t, J = 2.7 Hz, 1H), 5.23 (t, J = 2.5 Hz, 1H), 4.27-4.16 (m, 4H), 1.34 (t, J = 7.3, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 152.3, 134.4, 134.4, 129.2, 128.5, 125.3, 97.4, 97.3, 64.6, 64.6, 16.2, 16.2.

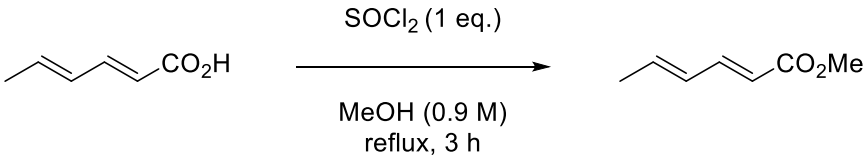
buta-1,3-dien-2-ylbenzene (**2d**) [6,7]



Inside a glovebox, [(dppe)$NiCl_2$] (79 mg, 0.15 mmol, 2.5 mol%) was weighted in a 25 mL Schlenk and suspended in 18 mL of anhydrous and degassed tetrahydrofuran. Outside the glovebox, the heterogeneous mixture was cooled to 0 °C and the enol phosphate **2d'** (6.0 mmol, 1.0 equiv.) was added to the mixture using a syringe. Vinyl magnesium bromide (6.3 mL of a 1.0 M solution in THF, 6.3 mmol, 1.05 equiv.) was added dropwise by syringe at 0 °C (final volume: 24 mL, concentration: 0.25 M). The ice bath was removed, and the reaction mixture was stirred for 1 h at room temperature. The reaction was then quenched by addition of 5.0 mL of a saturated solution of ammonium chloride at 0 °C and extracted with diethyl ether (3 x 25 mL). The organic layers were dried over sodium sulfate, filtered and the solvent removed under vacuum affording the crude residue that, after purification by silica gel flash chromatography (hexane buffered with 0.1% triethylamine), afforded pure diene **2d** (436 mg, 3.3 mmol, 55% yield) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.29 (m, 5H), 6.62 (dd, J = 17.4, 11.0 Hz, 1H), 5.30-5.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 139.8, 138.2, 128.4, 128.2, 127.6, 117.3, 117.0.

Methyl sorbate (**2e**) [8,9]



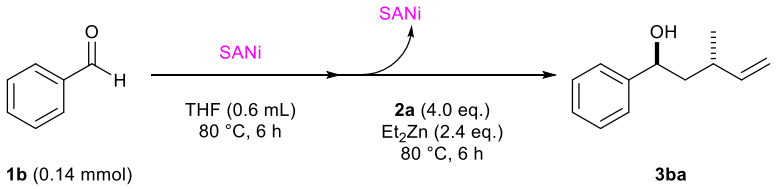
In a test tube (15 Φ), $SOCl_2$ (0.22 mL, 3.0 mmol) was added slowly to a solution of sorbic acid (333 mg, 3.0 mmol) in MeOH (3.3 mL) at 0 °C. The reaction was heated at reflux for 3 h, then cooled to rt before diluting with CH_2Cl_2 (3 mL) and sat. $NaHCO_3$ aq. (3 mL). The reaction mixture was extracted with CH_2Cl_2. The combined organic layer was washed with sat. $NaHCO_3$ aq., dried over Na_2SO_4, and concentrated under reduced pressure. The residual crude product was purified by flash silica gel column chromatography (*n*-hexane : Et_2O = 10 : 1) to afford methyl sorbate **2e** (282 mg, 2.2 mmol, 75%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ : 7.26 (dd, J = 15.2, 10.6 Hz, 1H), 6.23-6.11 (m, 2H), 5.78 (d, J = 15.5 Hz, 1H), 3.74 (s, 3H), 1.86 (d, J = 6.3 Hz, 3H; ^{13}C NMR (125 MHz, $CDCl_3$) δ : 167.8, 145.2, 139.5, 129.7, 118.5, 51.4, 18.7.

5. Reusability of SANi in the ligand-free homoallylation of aldehyde with 1,3-diene

In a test tube (15 Φ), a mixture of benzaldehyde (**1b**) (14 μL, 0.14 mmol, 1.0 eq.) dissolved in THF (0.6 mL) in the presence of SANi was heated at 80 ℃ for 6 h without stirring under a nitrogen atmosphere. After the reaction mixture had been cooled to room temperature, SANi was removed from the reaction mixture and rinsed several times with THF. Isoprene (**2a**) (56 μL, 0.56 mmol, 4.0 eq.) and diethylzinc (0.31 mL of a 1.09 M solution in THF, 0.34 mmol, 2.4 eq.) was added into the reaction mixture and heated at 80 ℃ for 6 h without stirring under a nitrogen atmosphere. The yields of **3ba** were determined by GC-MS. The recovered SANi plate was again subject to the above reaction. This procedure was repeated a total of 5 times (Table S1).

Table S1. 3 sets of the results of Reductive coupling using SANi repeatedly five times.



Set		1st	2nd	3rd	4th	5th
1	Yield (%)[a]	75	62	74	71	54
	leached Ni (μg)	27	14	11	12	3
2	Yield (%)[a]	73	66	65	62	68
	leached Ni (μg)	27	12	24	12	4
3	Yield (%)[a]	76	58	53	62	45
	leached Ni (μg)	15	12	4	5	6

a) GC yield.

GC Method: 50 ℃ hold for 1 min, followed by a temperature increase of 40 ℃/min to 230 ℃, and hold for 4.5 min (total run time: 10 min). Retention time: 5.04 min.

5. References

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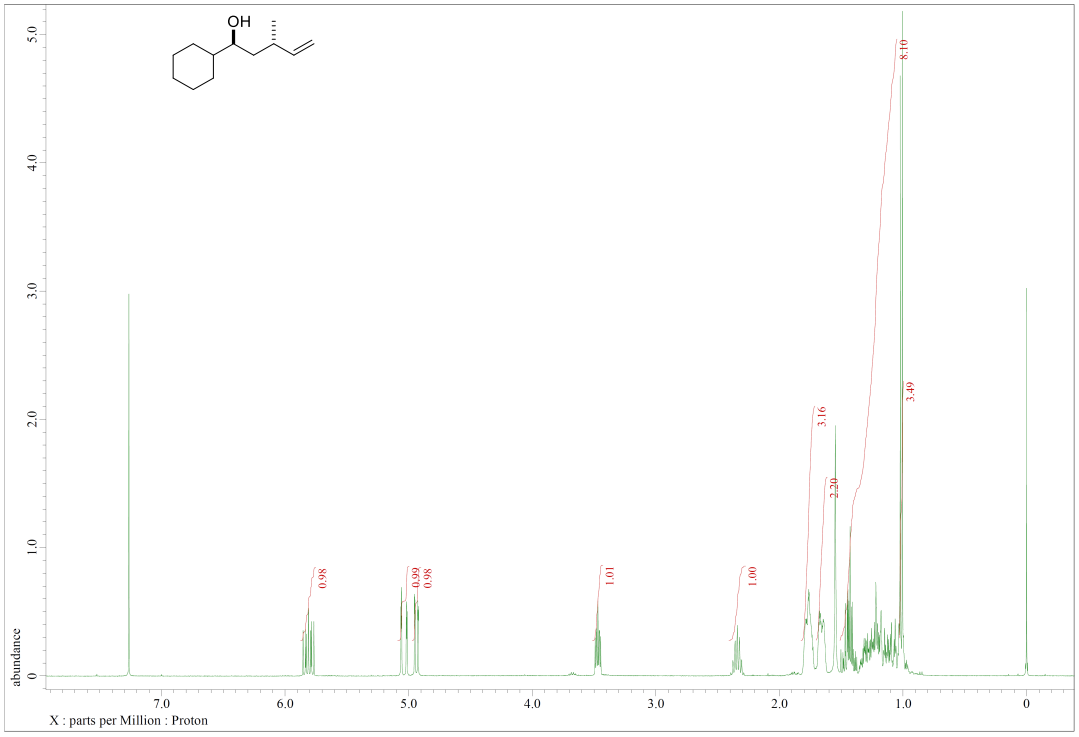

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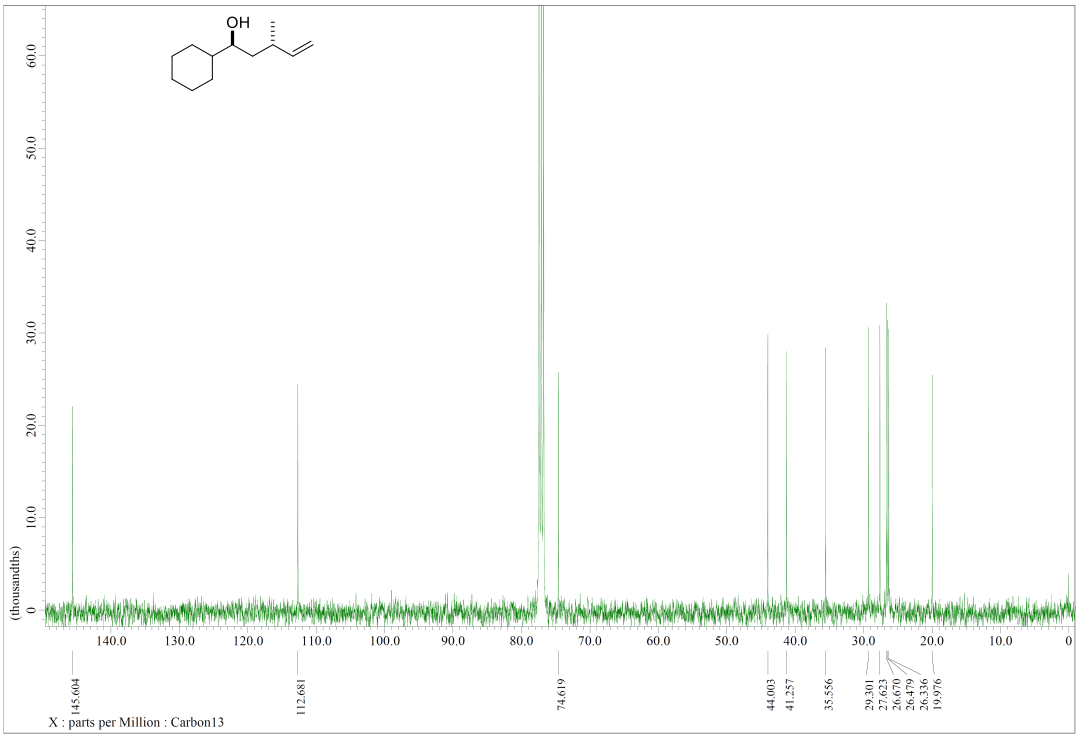

3ba

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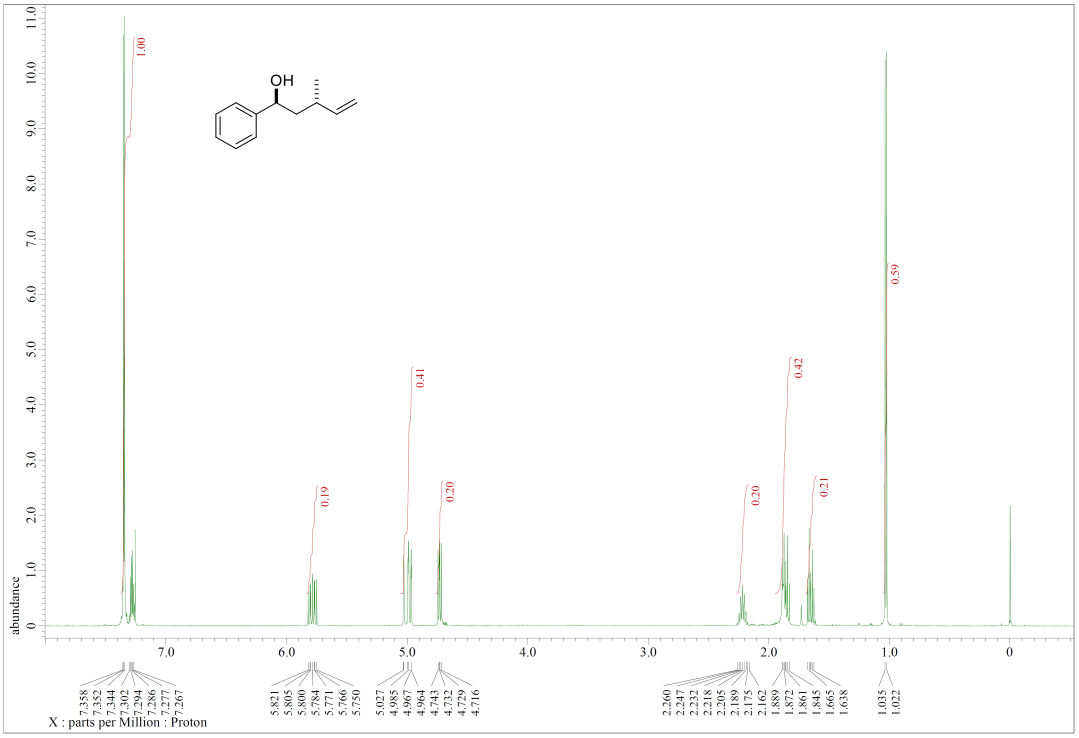

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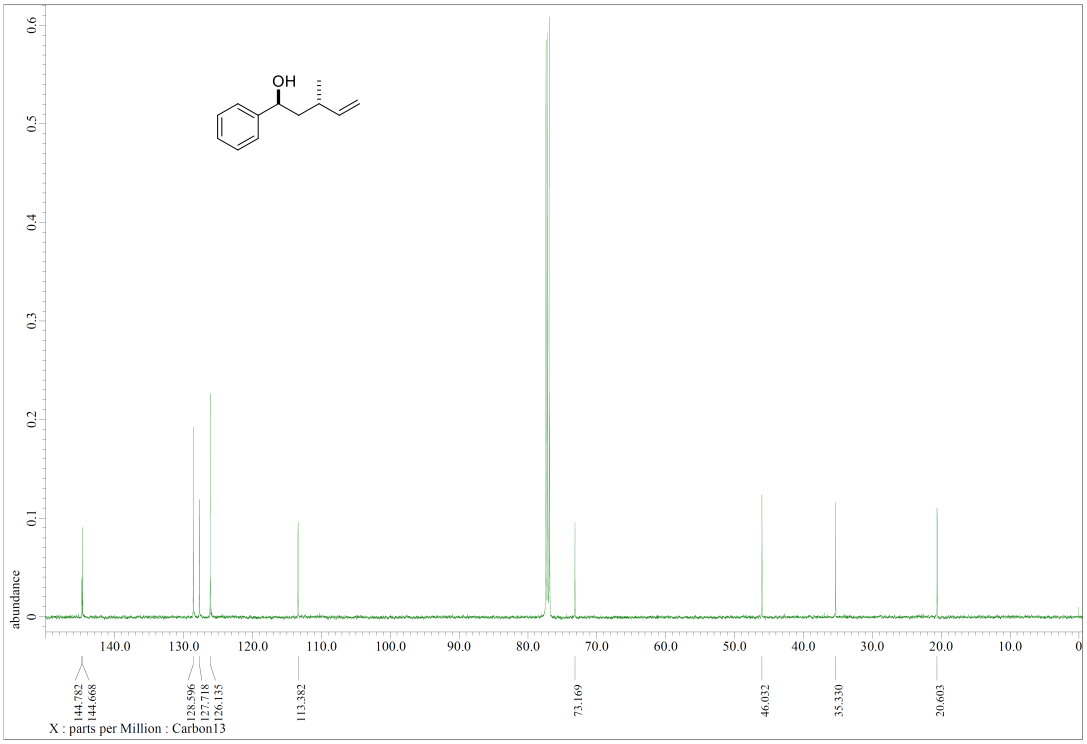

3ca

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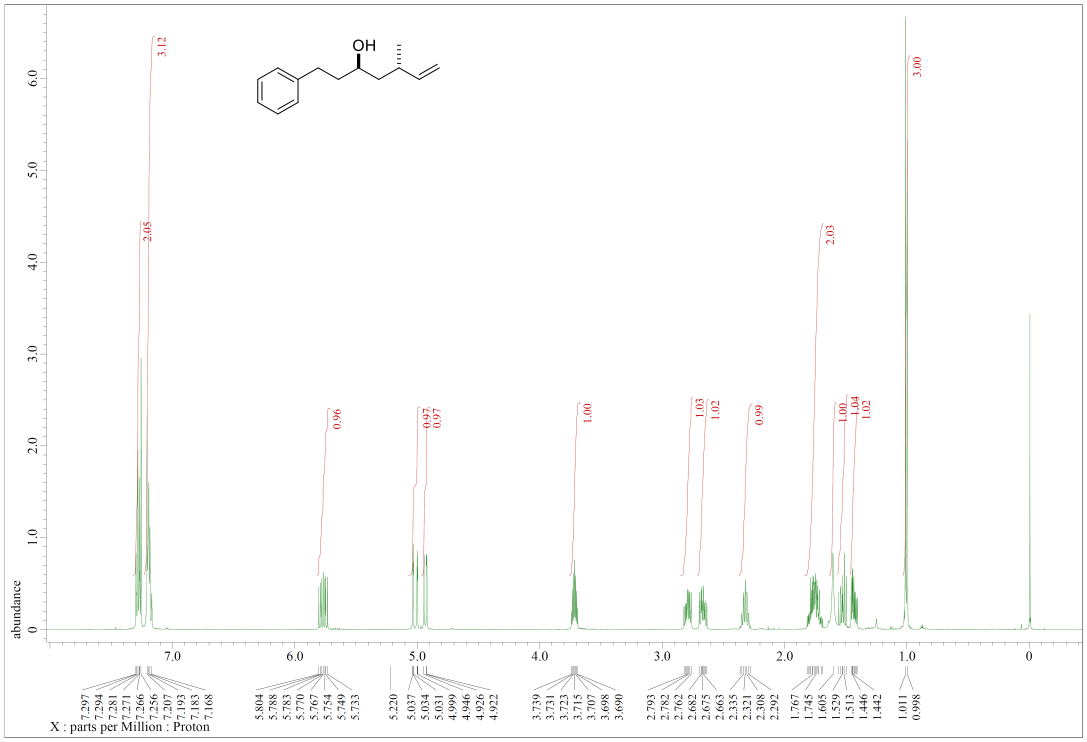

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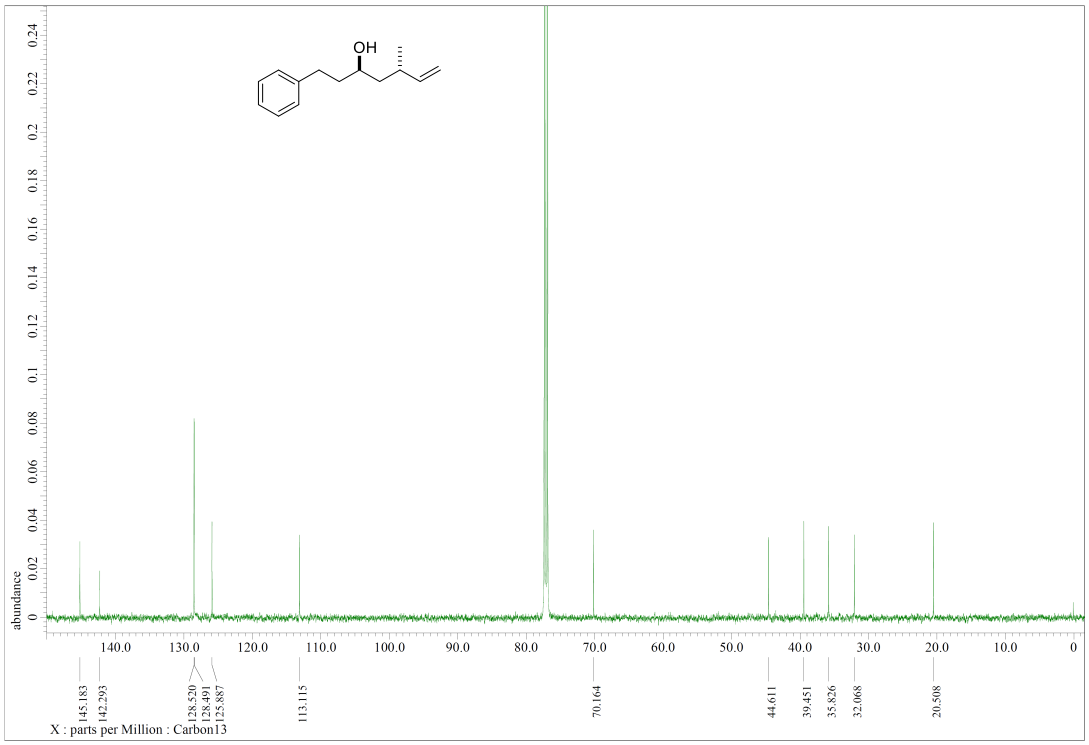

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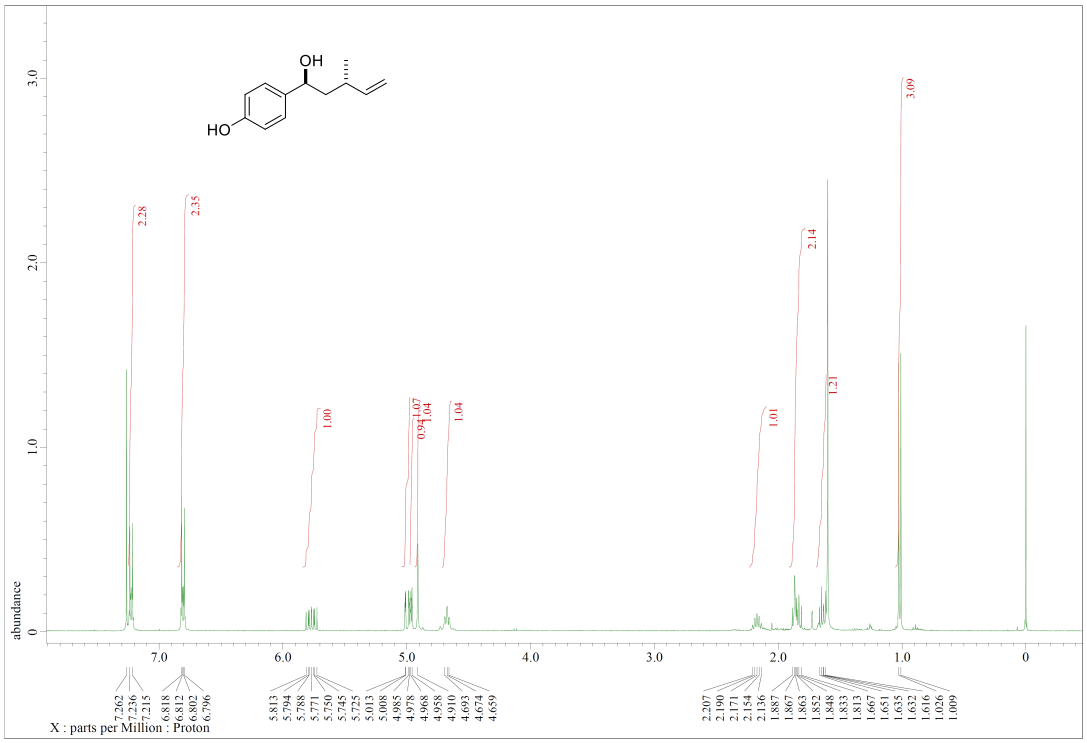

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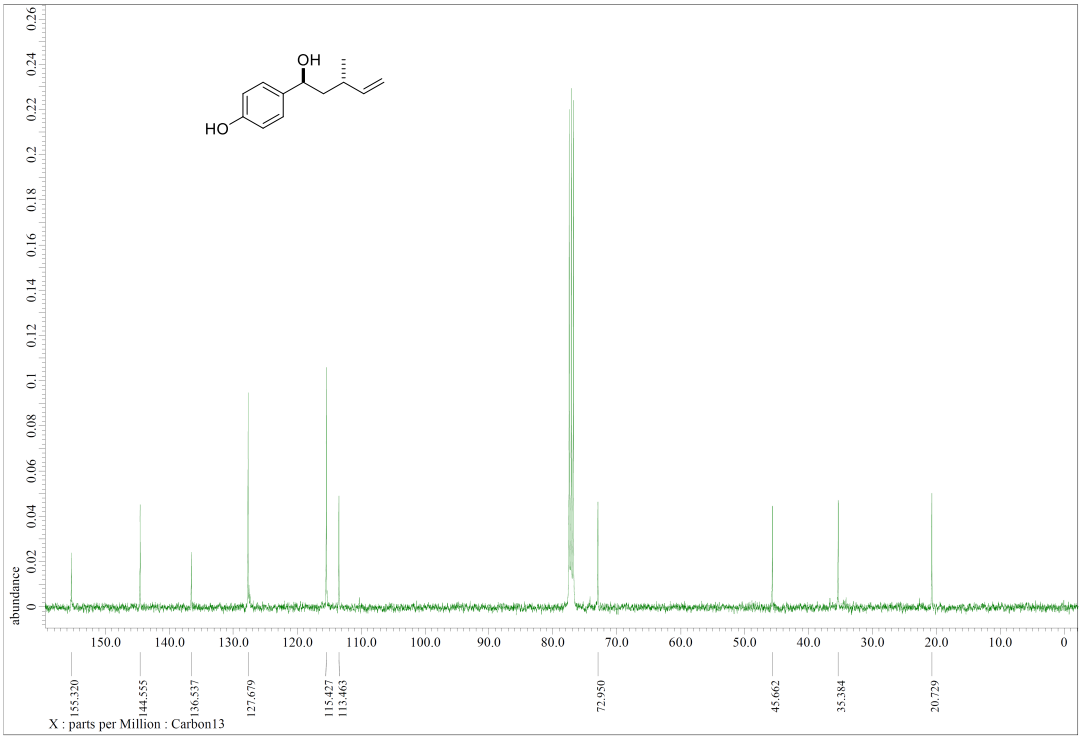

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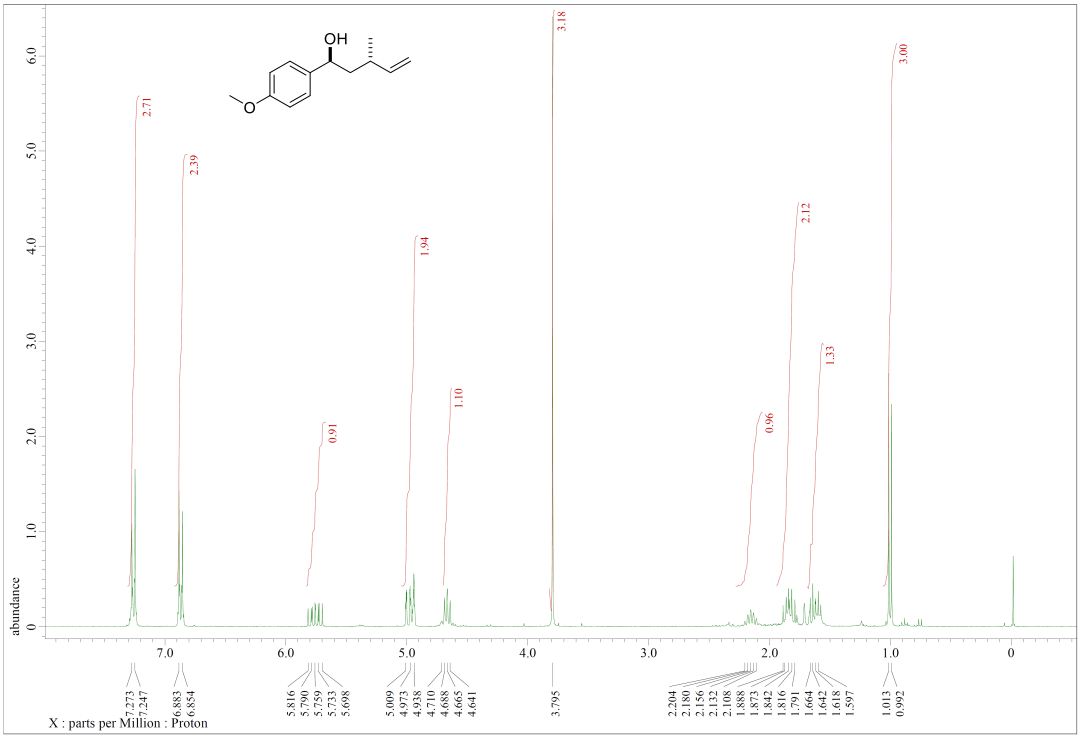

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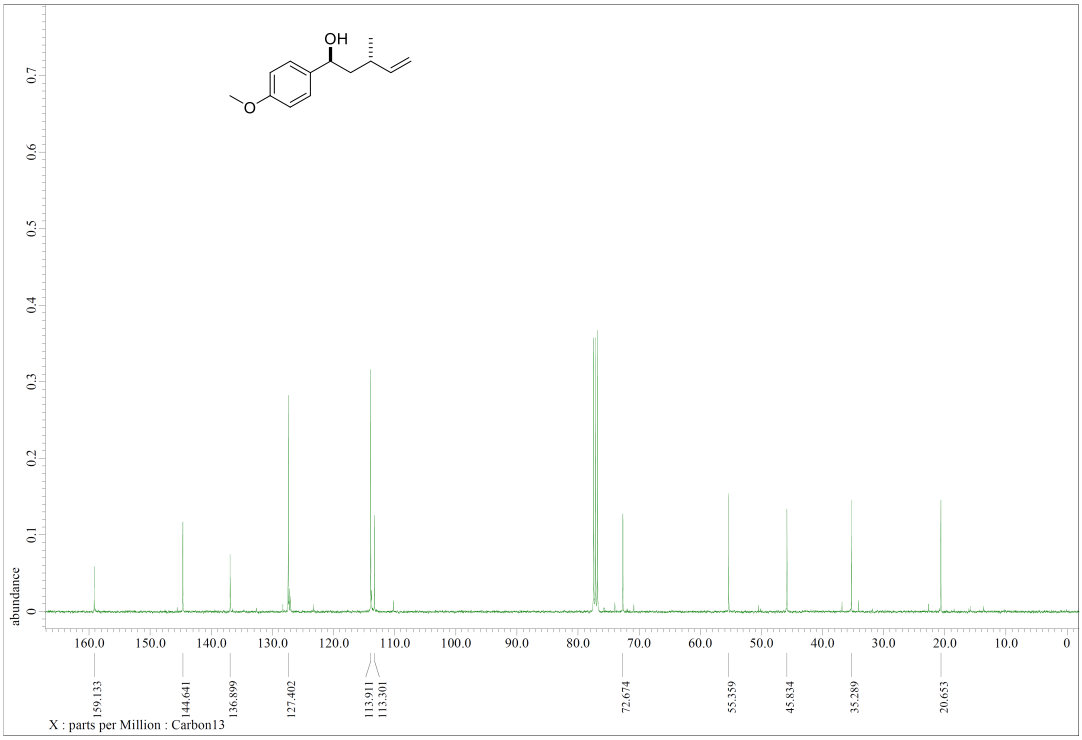

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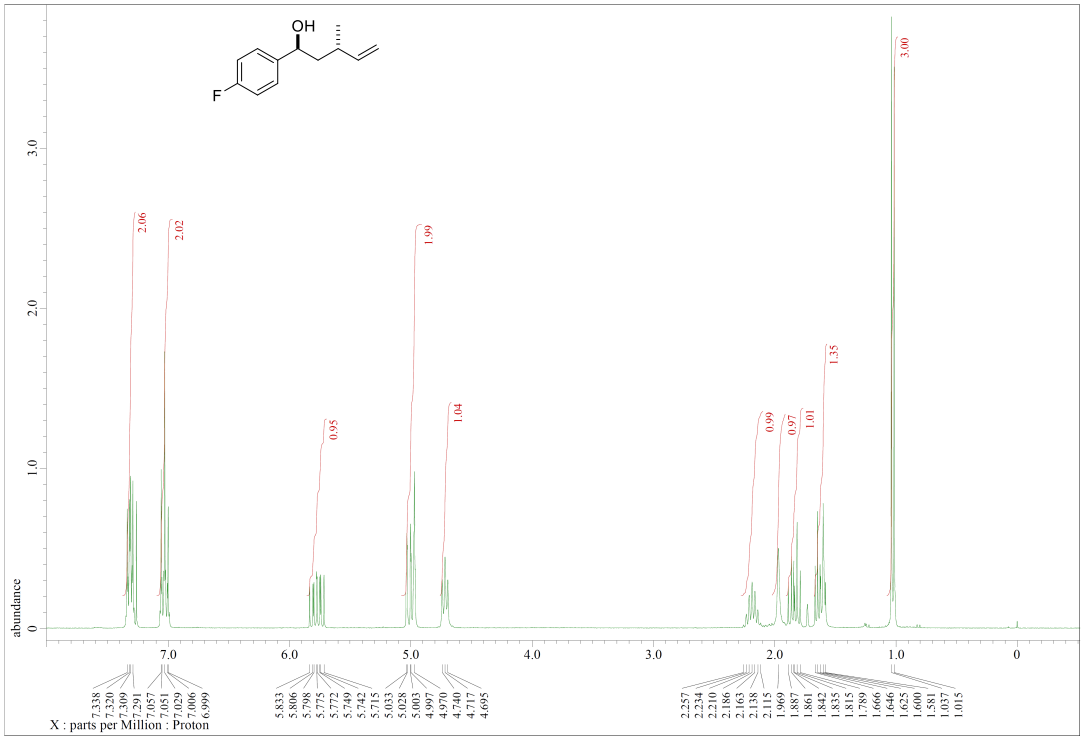

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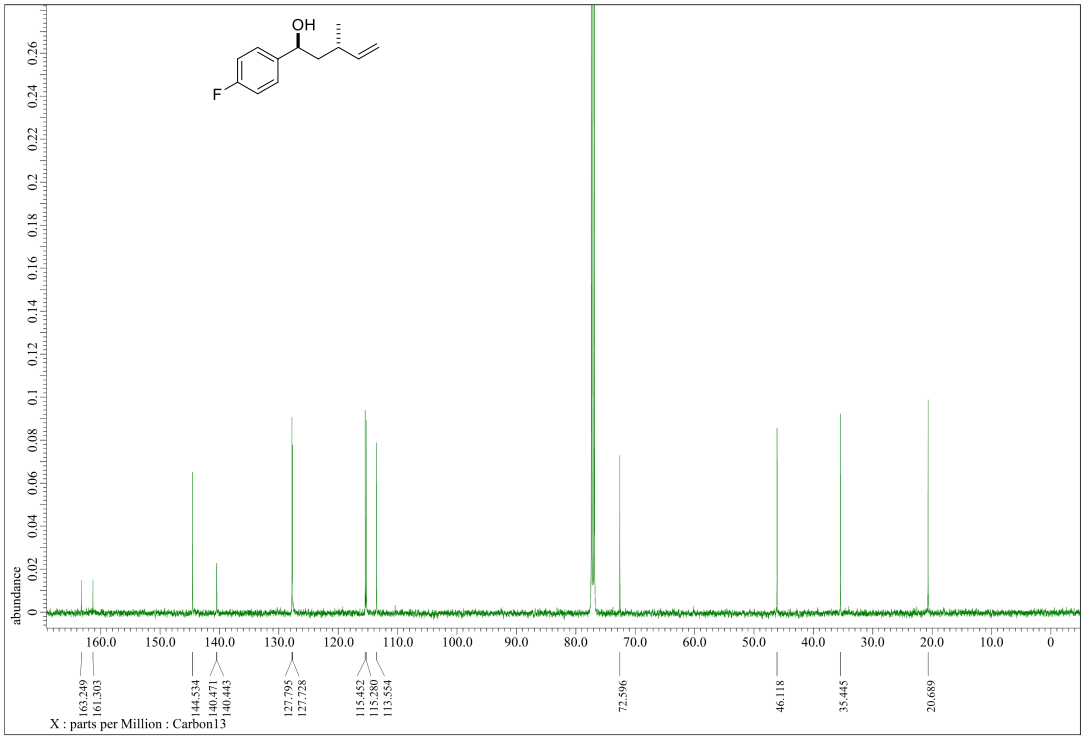

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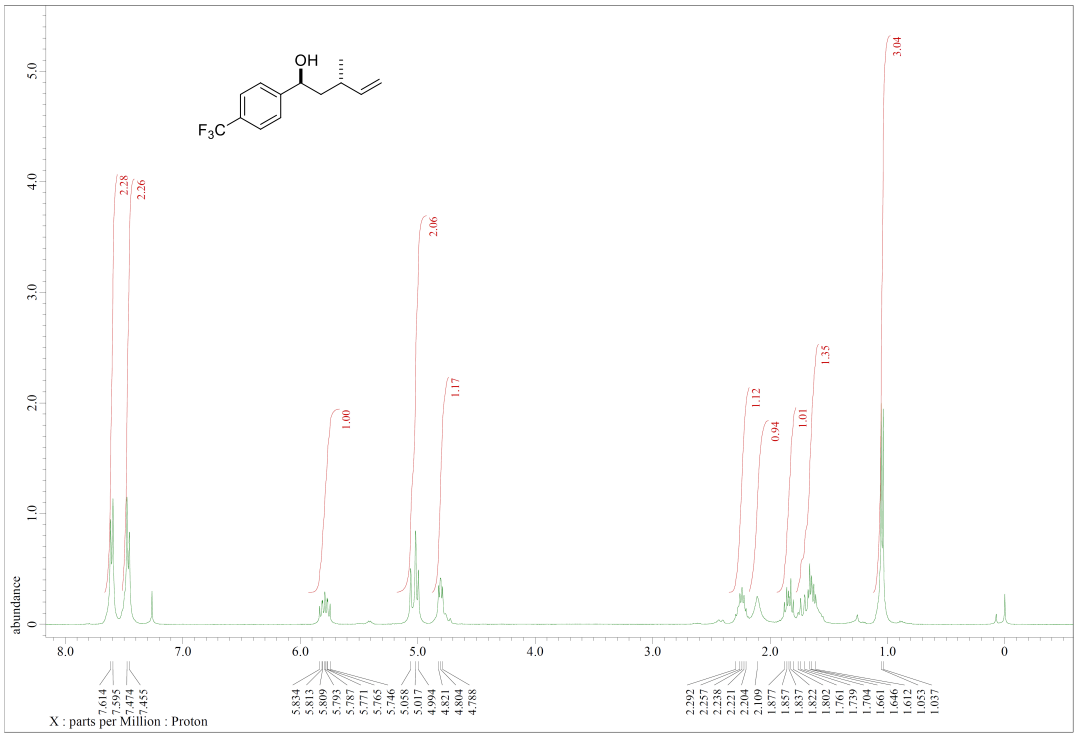

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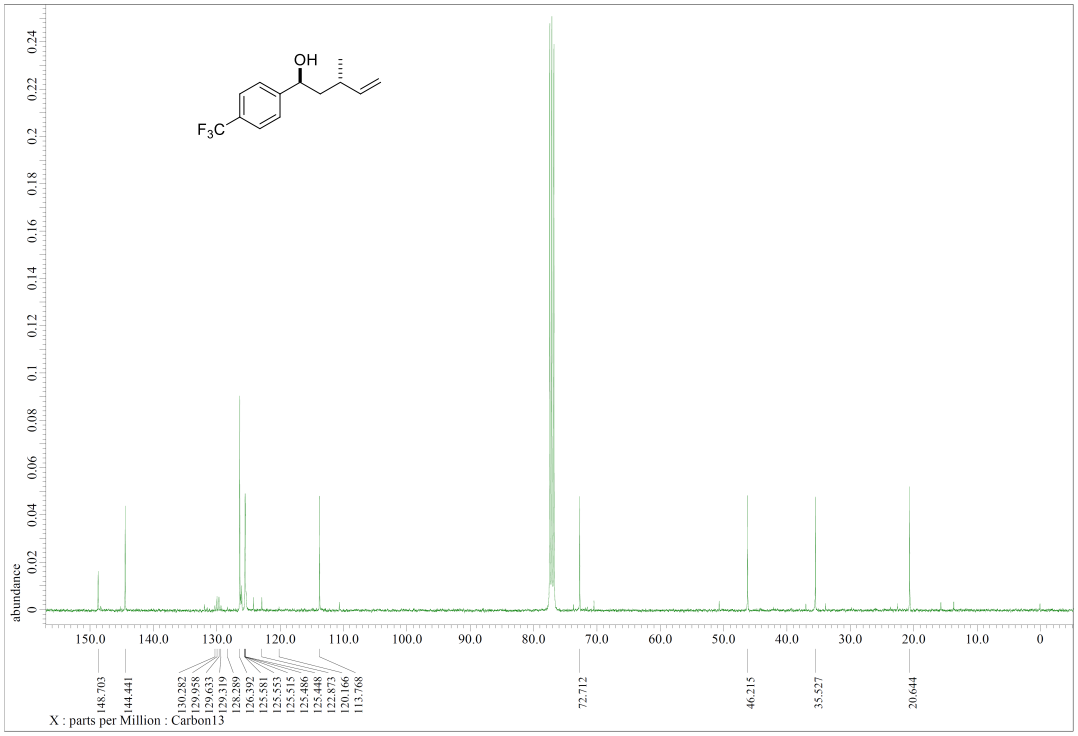

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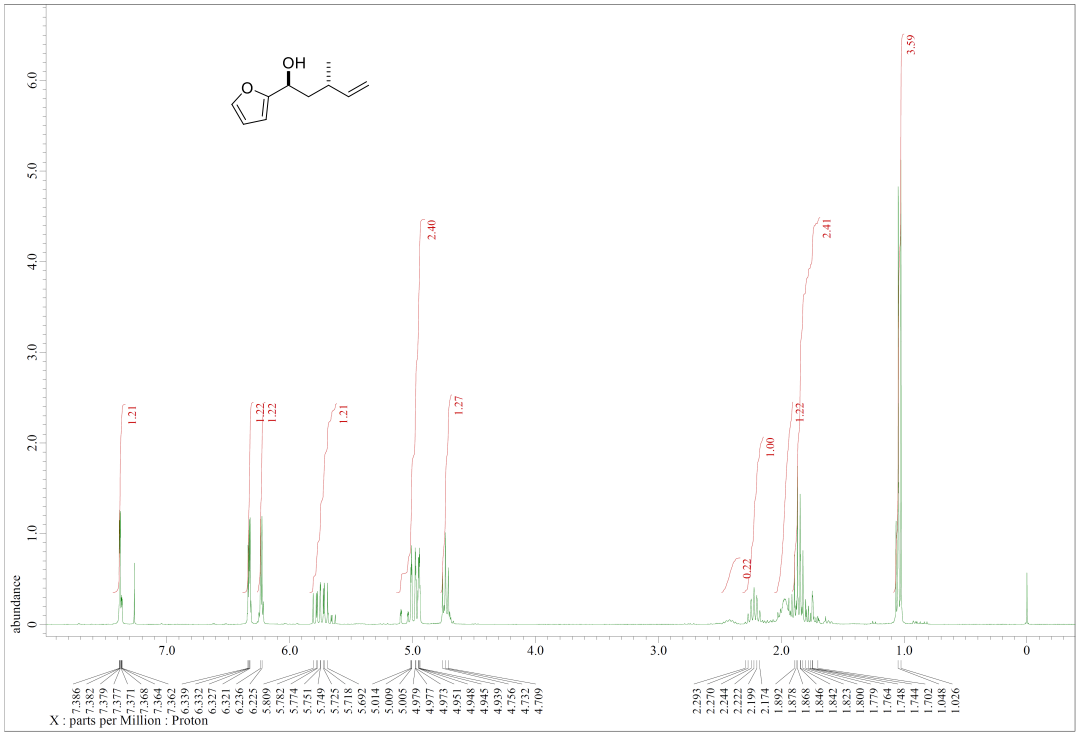

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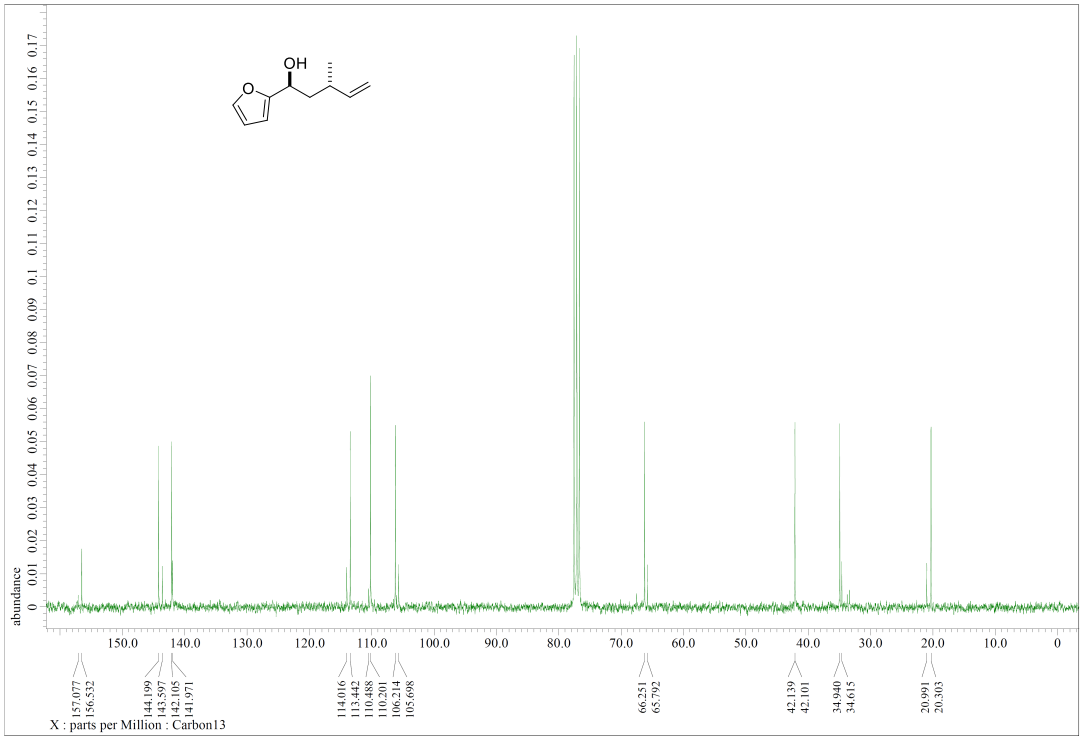

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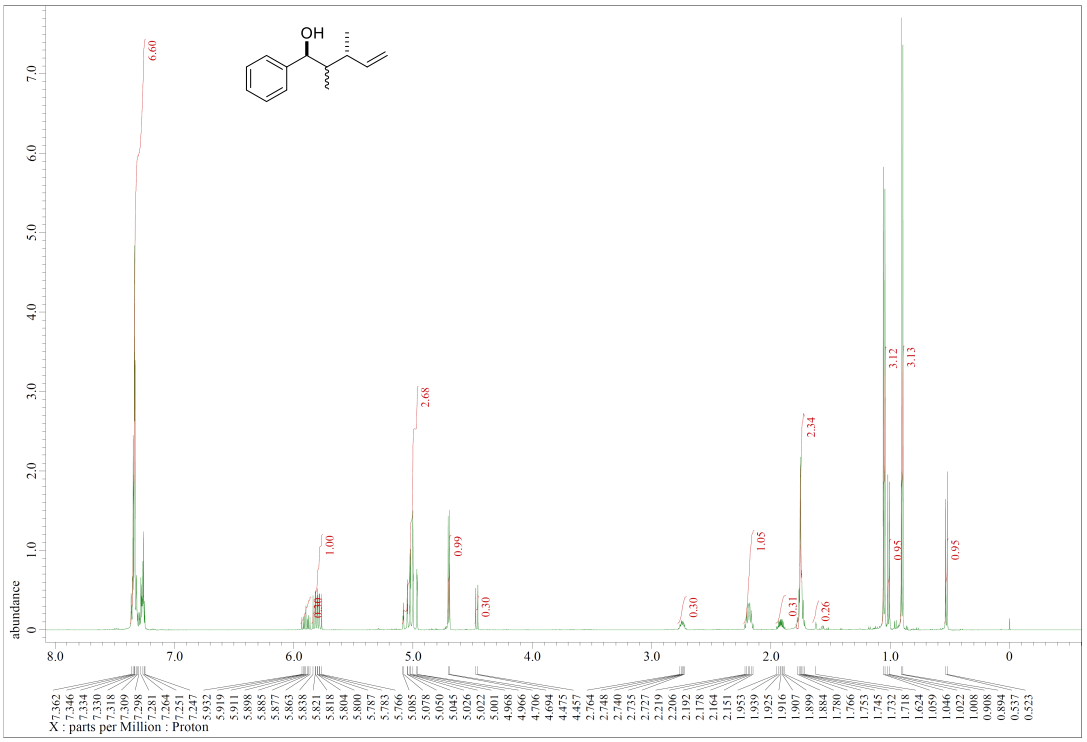

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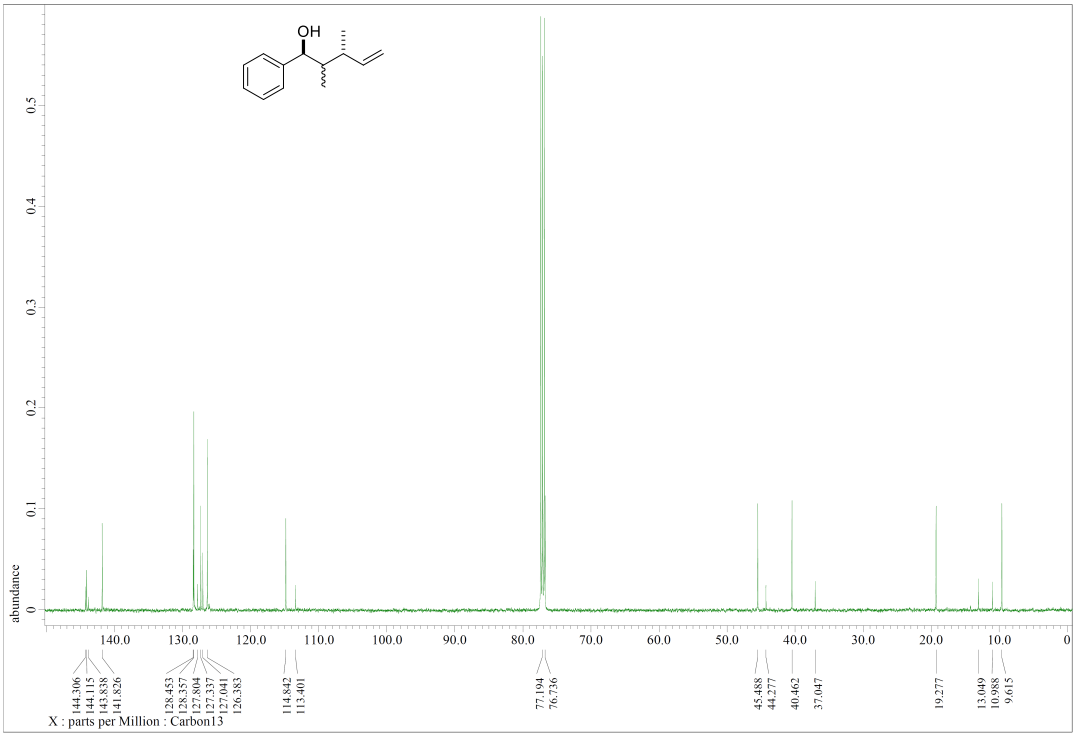

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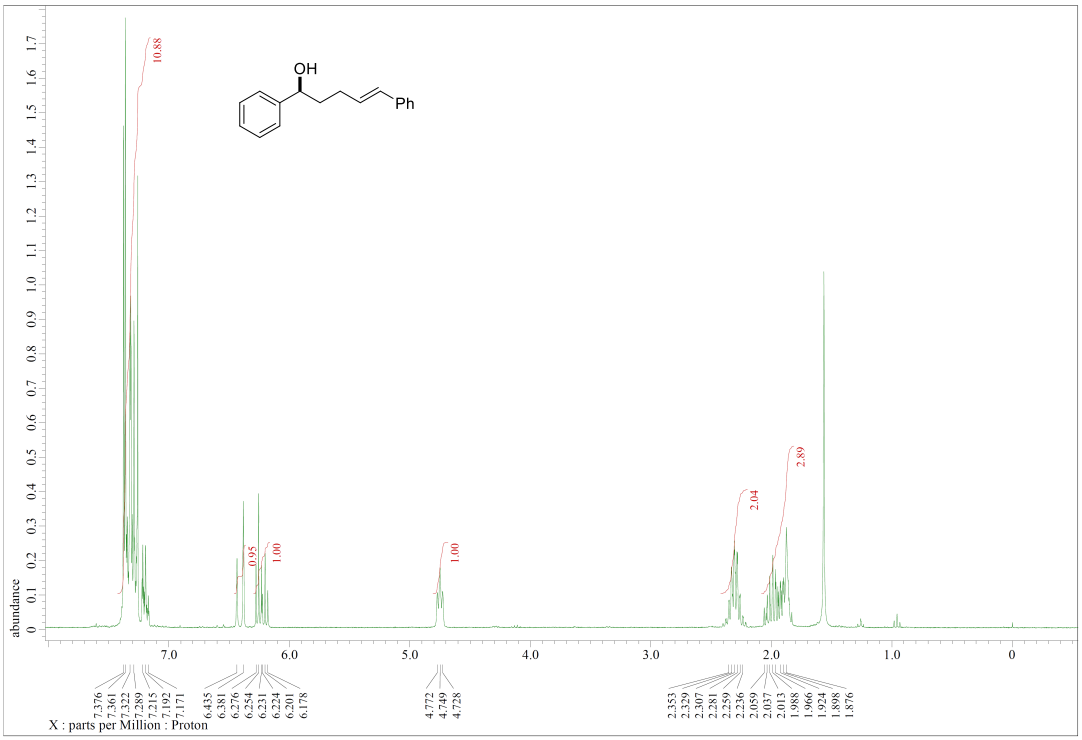

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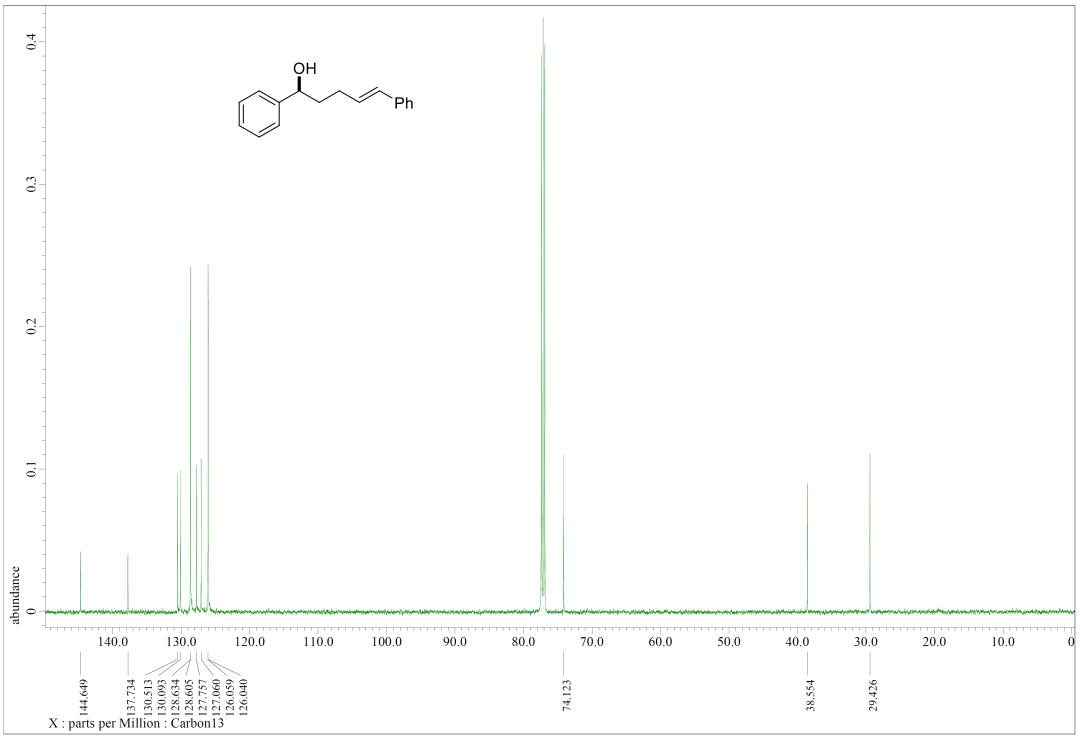

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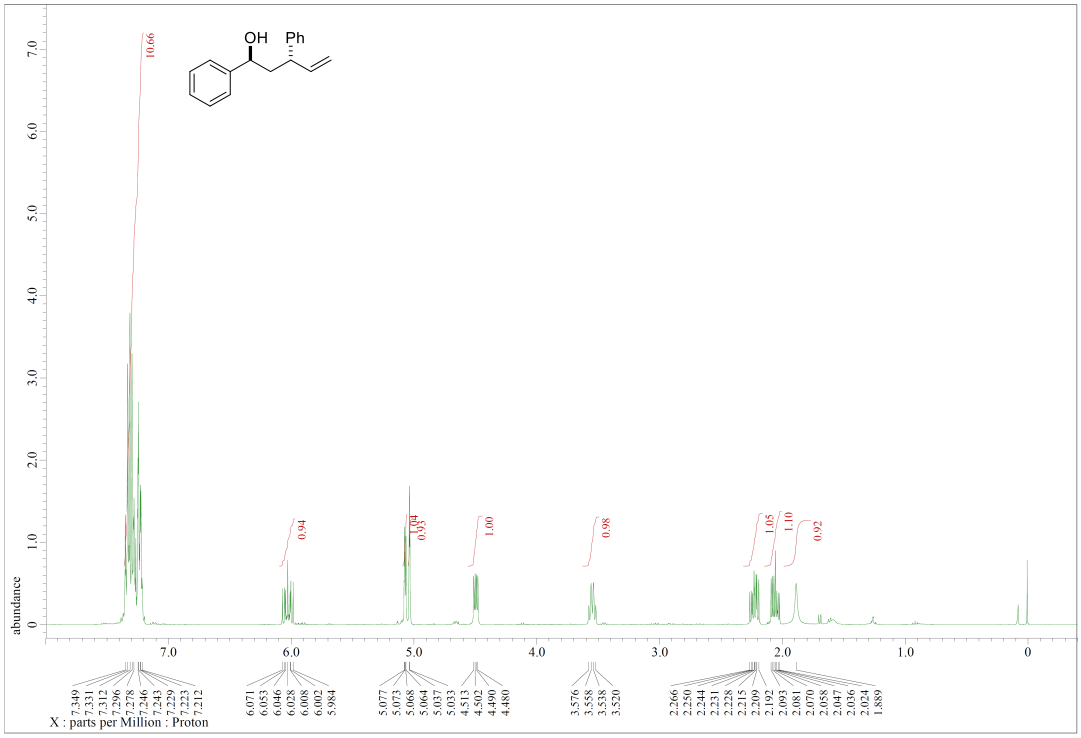

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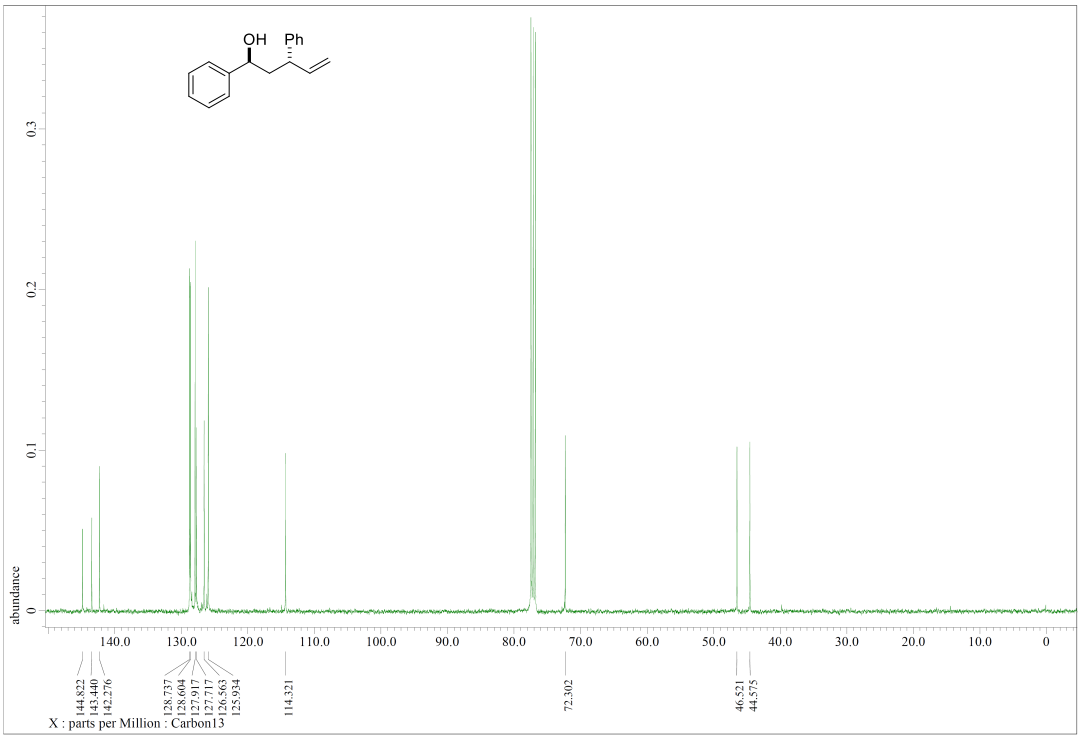

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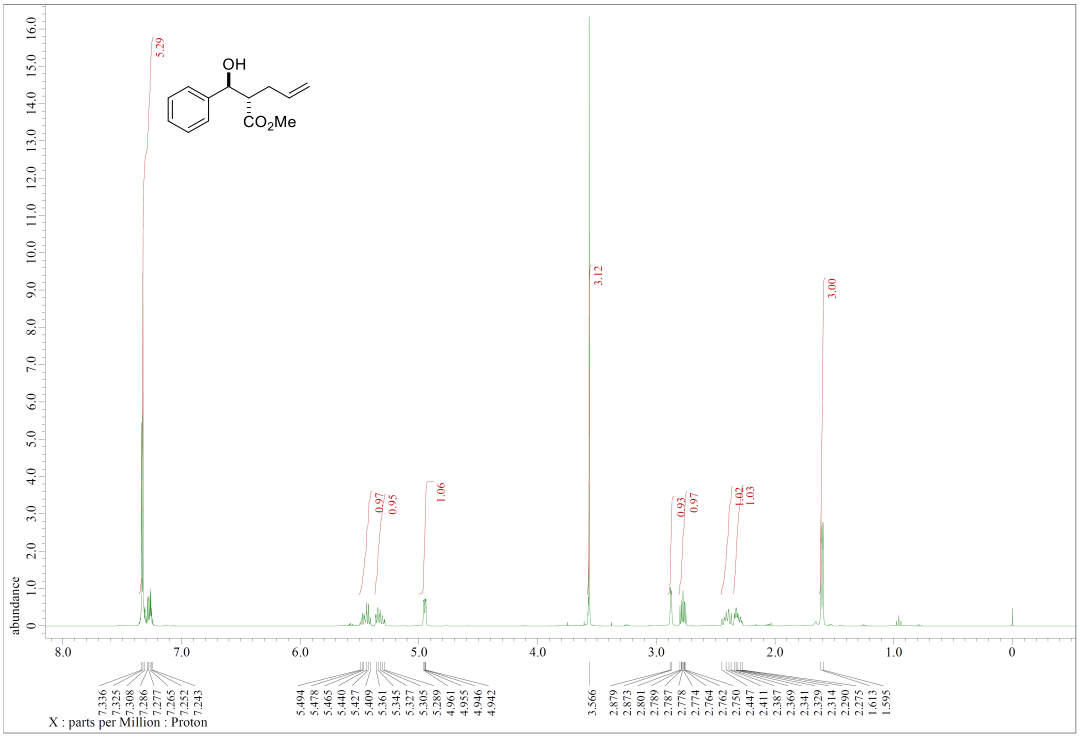

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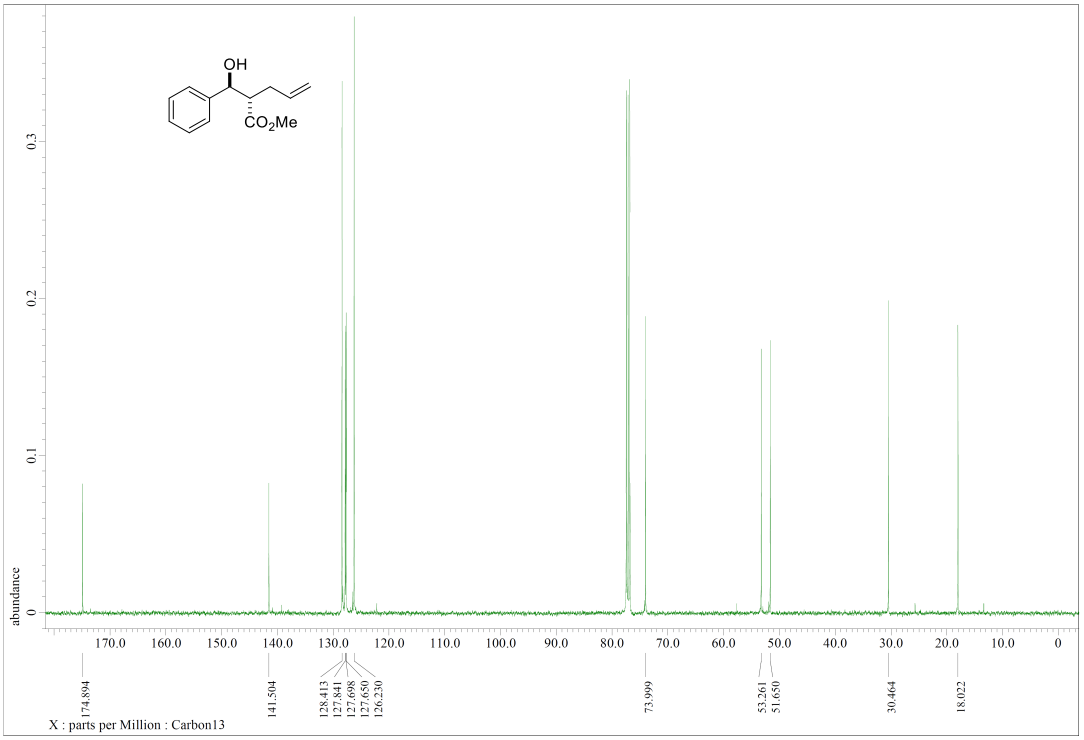

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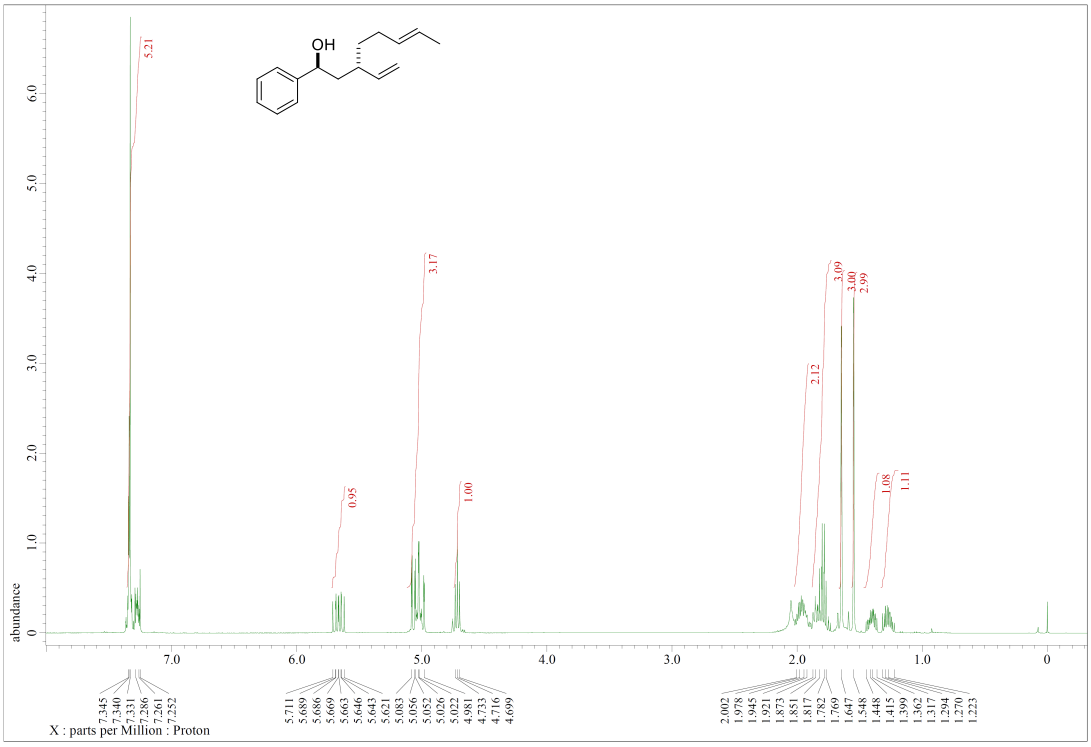

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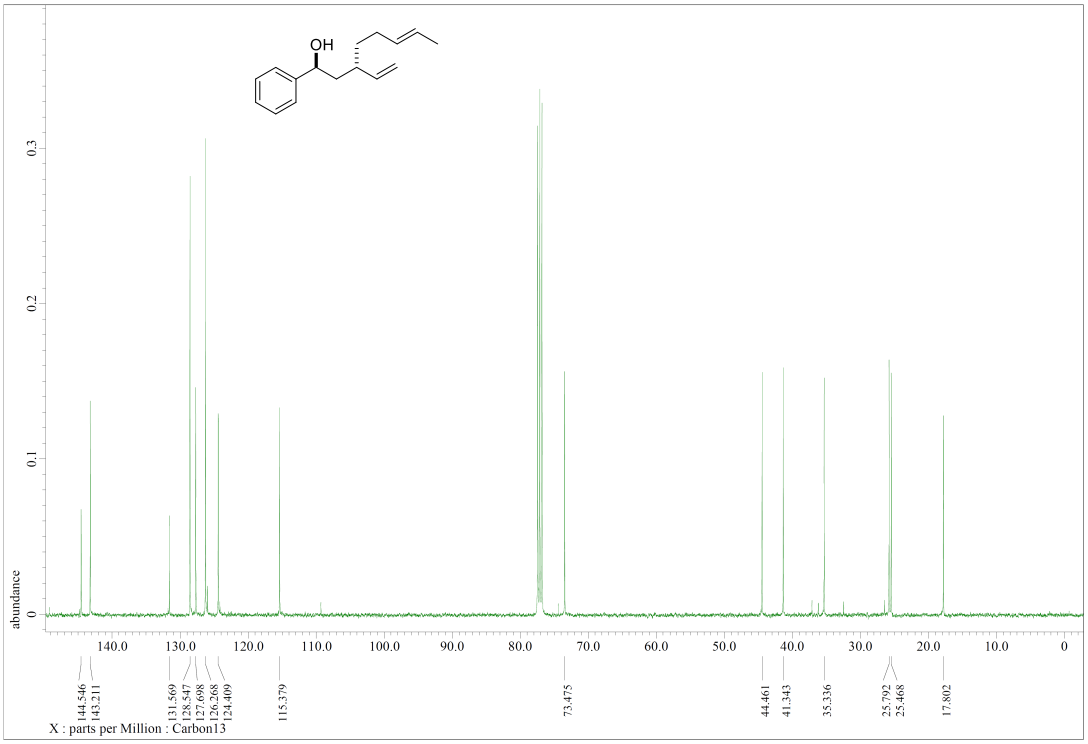

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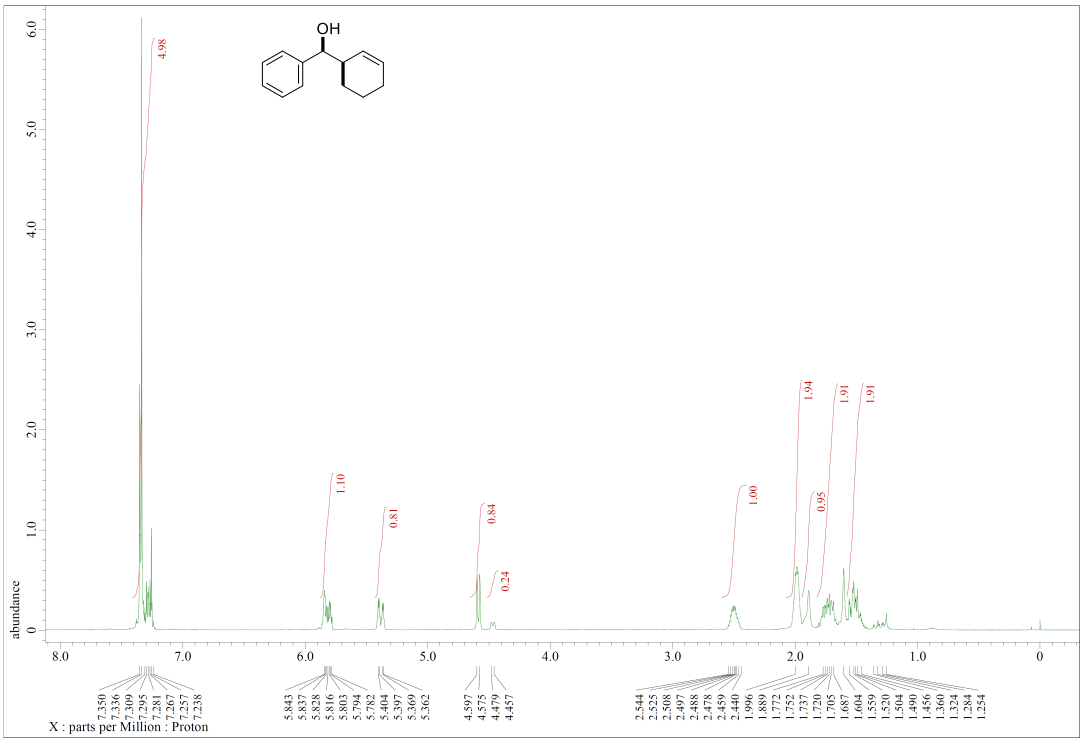

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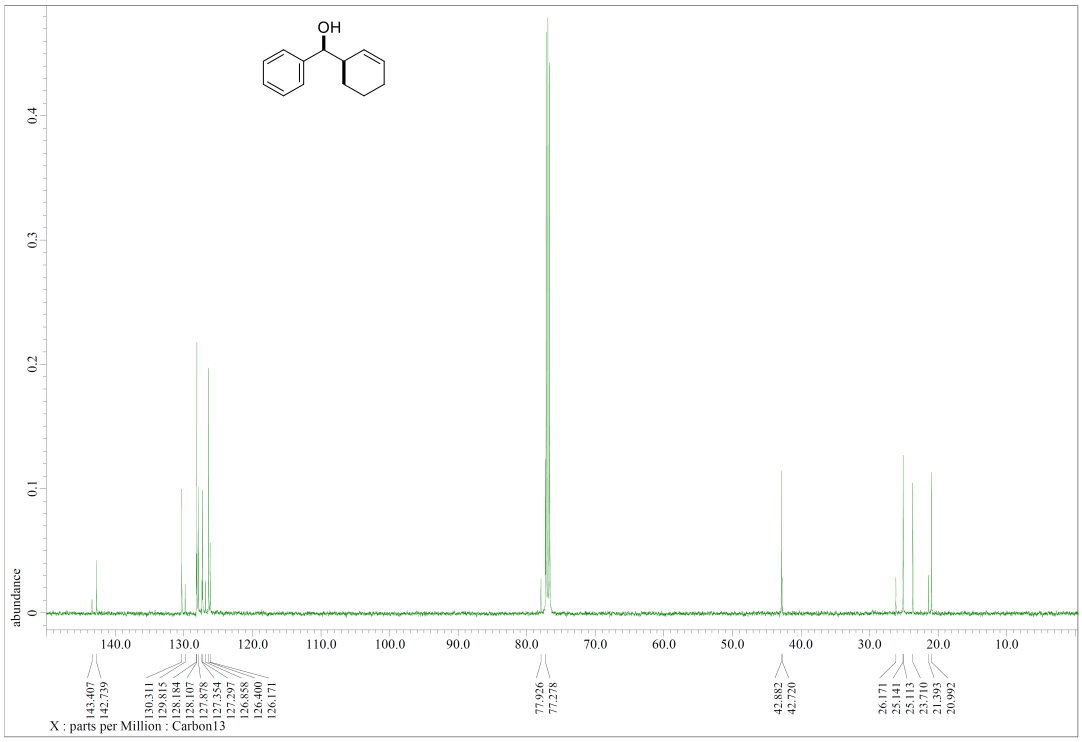

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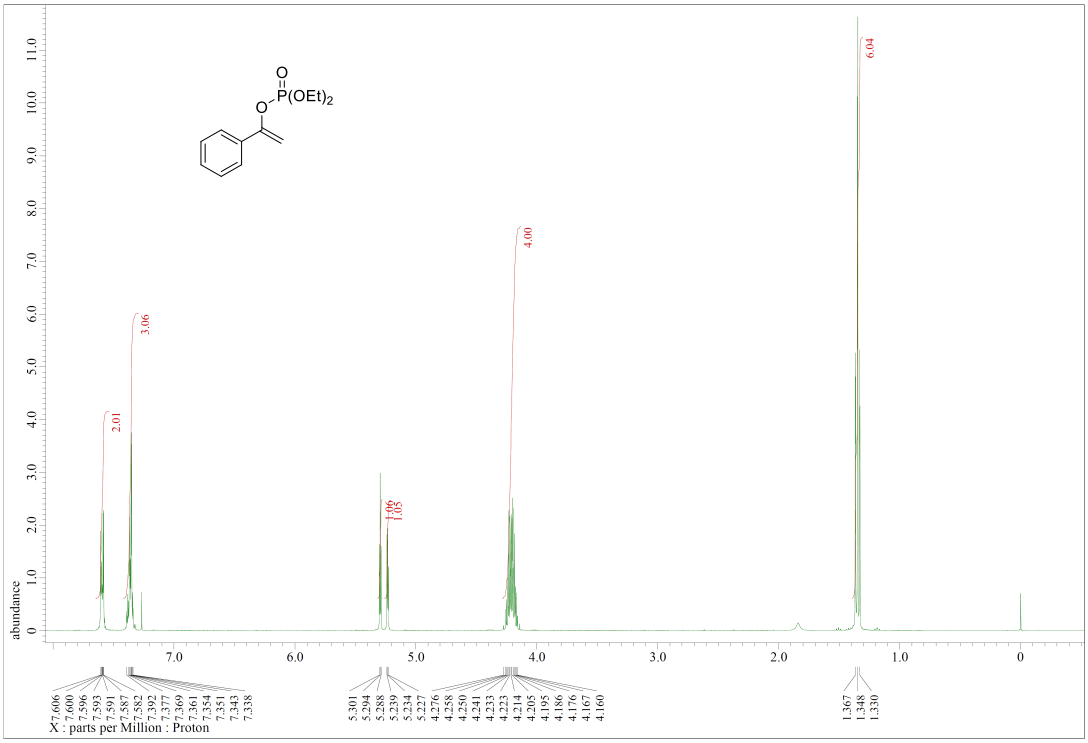

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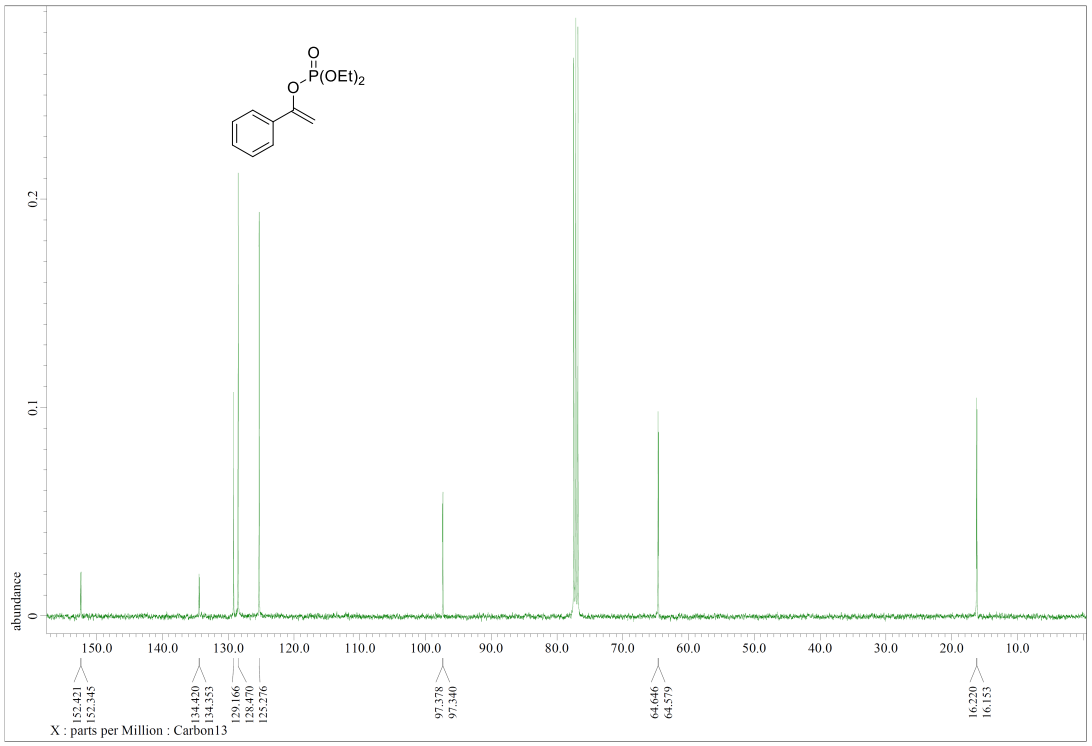

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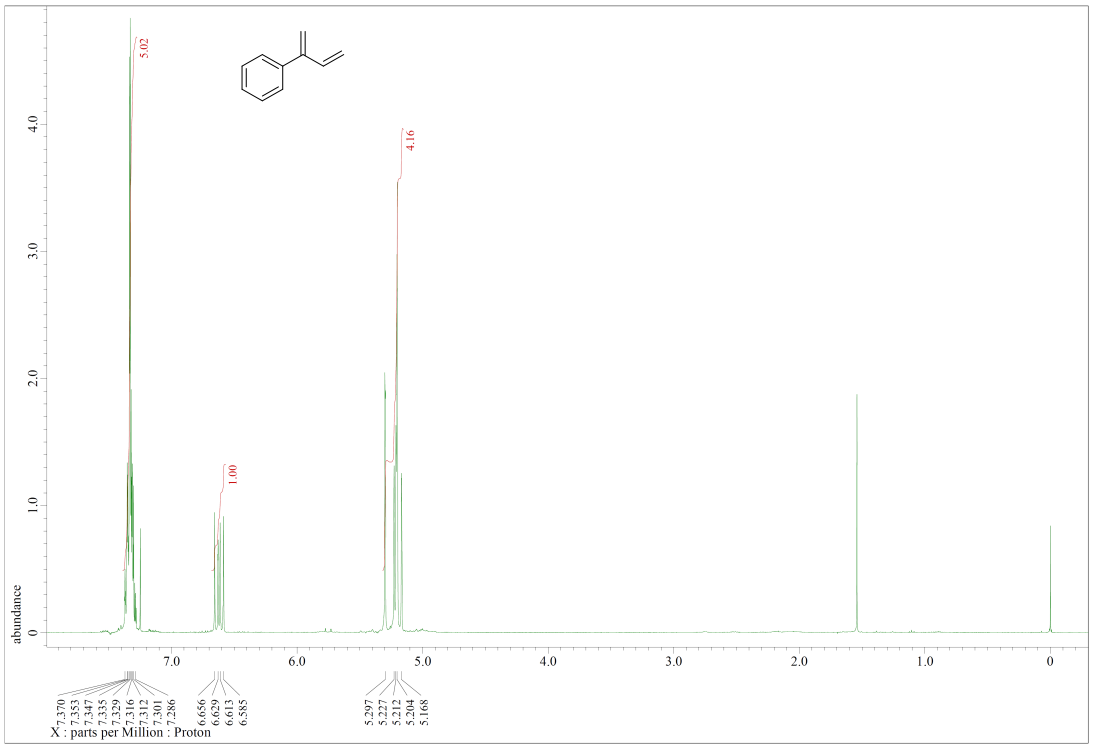

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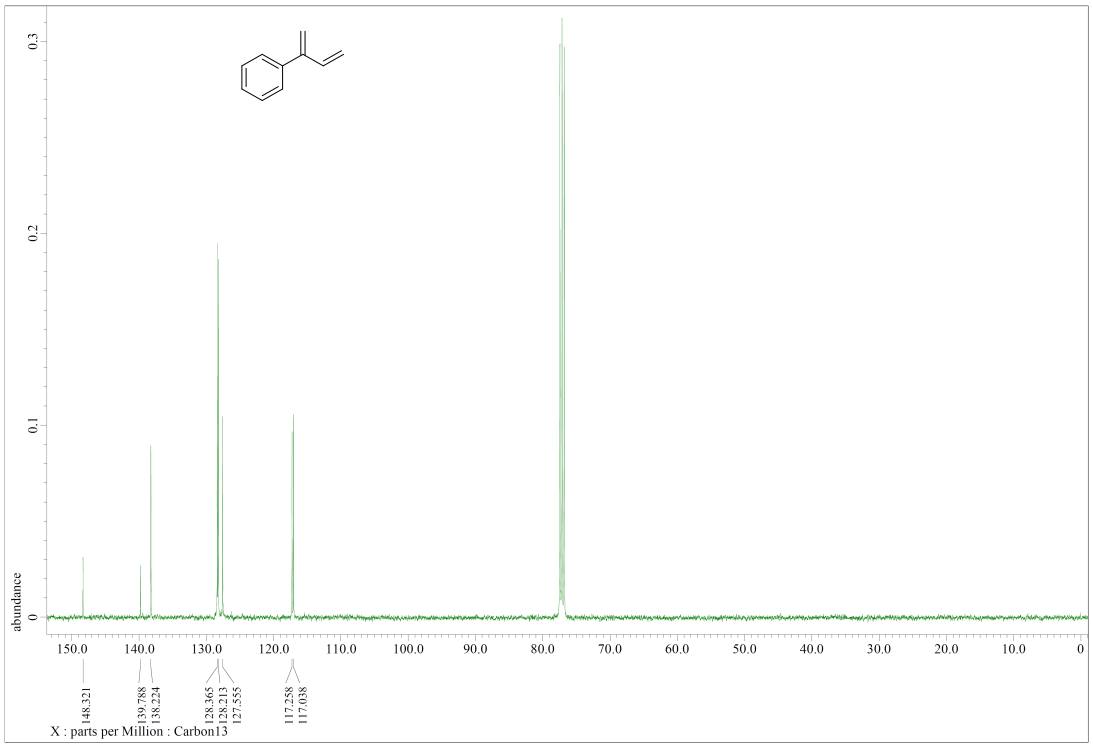

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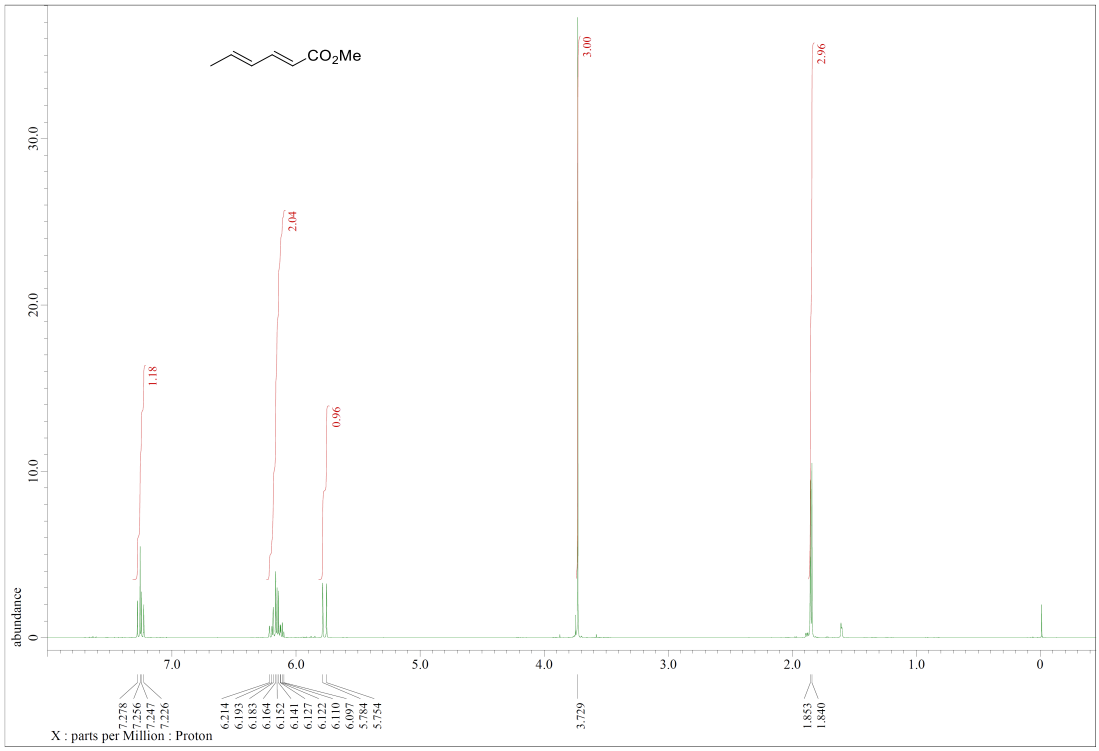

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