Supporting Information for

3,3'-Anisyl-Substituted BINOL, H_4BINOL and H_8BINOL Ligands: Asymmetric Synthesis of Diverse Propargylic Alcohols and Their Ring-Closing Metathesis to Chiral Cycloalkenes

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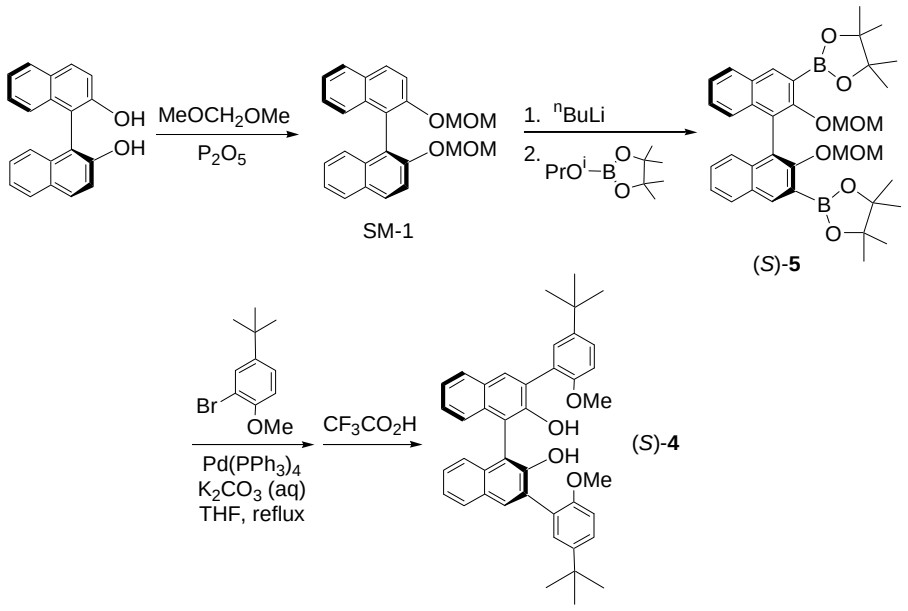
General Data:
Toluene, THF, and 1,4-dioxane were distilled over sodium and benzophenone under nitrogen atmosphere. Methylene chloride and diethyl ether were dried by passing through activated alumina columns under nitrogen. Solvents were stored over 4 Å molecular sieves.

Methyl propiolate was distilled under reduced pressure from 4 Å molecular sieves prior to use. All aldehydes were passed through a plug of alumina and distilled from 4 Å molecular sieves prior to use.

Preparation of the Chiral Ligands

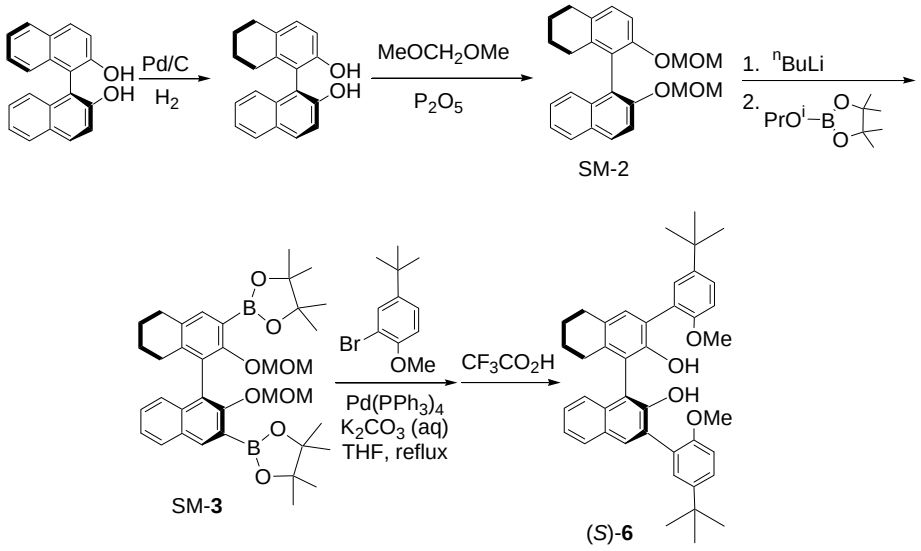


Preparation of (S)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl, SM-1. To a 250 mL flask, (*S*)-BINOL (6.0 g, 21 mmol), $CH_3OCH_2OCH_3$ (21.0 g, 271 mmol) and 150 mL CH_2Cl_2 were added. P_2O_5 (25 g) was then added to the reaction mixture with 5 potions. After the mixture was stirred for 1 h, the reaction was quenched with Na_2CO_3 (saturated, aqueous 100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The resulting organic layers were dried and concentrated. The residue was purified by flash chromatography on silica gel eluted with 10% EtOAc/hexanes to yield the product as a white solid in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.15 (s, 6H), 4.98 (d, 2H, J = 6.9 Hz), 5.09 (d, 2H, J = 6.6 Hz), 7.15-7.25 (m, 4H), 7.32-7.37 (m, 2H), 7.58 (d, 2H, J = 9.0 Hz), 7.88 (d, 2H, J = 8.1 Hz), 7.96 (d, 2H, J = 9.0 Hz).

Preparation of 2-((1'S)-2,2'-bis(methoxymethoxy)-3'-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)-1,1'-binaphthyl-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, (*S*)-5. (*S*)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl (5.0 g, 13 mmol) was dissolved in hexanes and cooled to 0 °C under nitrogen. ^{n}BuLi (2.4 M, 22 mL, 52 mmol) was added and the

reaction mixture was allowed to warm to room temperature over 3 h, during which a white precipitate formed. The reaction mixture was cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15 mL, 73.6 mmol) in THF (30 mL) was added via cannula. The mixture was allowed to warm to room temperature and stirred for 16 h. The generated salts were removed by filtration through a Buchner funnel and rinsed with CH_2Cl_2. The combined organic layer was concentrated and purified by flash chromatography over a short silica gel column (10% EtOAc/hexanes), yielding (*S*)-**5** as a white solid in 80% yield. (Extended time on the column would result in partial hydrolysis to the boronic acid.) ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.42 (s, 24H), 2.30 (s, 6H), 4.91 (s, 4H), 7.22 (d, 2H, J = 8.4 Hz), 7.26-7.32 (m, 2H), 7.39-7.43 (m, 2H), 7.93 (d, 2H, J = 8.1 Hz), 8.49 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.2, 55. 8, 84.1, 100.3, 124.9, 126.1, 127.0, 127.4, 128.5, 130.4, 136.4, 139.4, 157.3.

Preparation of (*S*)-3,3'-bis(5-tert-butyl-2-methoxyphenyl)-1,1'-binaphthyl-2,2'-diol, (*S*)-4. Under nitrogen, (*S*)-**5** (3.15 g, 5 mmol), 2-bromo-4-tert-butyl-1-methoxybenzene (4.86 g, 20 mmol, 4 equiv), and $Pd(PPh_3)_4$ (410 mg, 0.5 mmol, 10 mol%) were placed in a 2-neck flask equipped with a reflux condenser that was connected with a vacuum adaptor. Degassed THF (50 mL) and 2M K_2CO_3 (40 mL) were transferred into the flask via cannula. To ensure the removal of oxygen, the reaction vessel was freeze-pumped at -78 °C and refilled with nitrogen three times. The reaction mixture was then heated at 95 °C for 24 h. After cooled to room temperature, the mixture was extracted with CH_2Cl_2 (3 x 40 mL). The combined organic layer was washed with 2M HCl (3 x 40 mL), dried, and concentrated. The crude product was dissolved in CH_2Cl_2 (25 mL) and trifluoroacetic acid (5 mL) was added. After the reaction mixture was stirred at room temperature for 10 h, it was concentrated and purified by column chromatography on silica gel eluted with 10% EtOAc/hexanes to afforded (*S*)-**4** as a white solid in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.37 (s, 18H), 3.81 (s, 6H), 5.95 (s, 2H), 6.97 (d, 2H, J = 8.7 Hz), 7.26-7.44 (m, 8H), 7.53 (d, 2H, J = 2.4 Hz), 7.90-7.94 (m, 4H). These data are consistent with those reported.[1]



1 Moore, D.; Huang, W. -S.; Pu, L. *Tetrahedron Lett.* **2002**, *43*, 8831-8834.

Preparation of (*S*)-H_4BINOL and (S)-H_8BINOL. The reaction was carried out by slightly modifying a literature procedure.[2] (*S*)-BINOL (5.0 g, 17.5 mmol), 5% Pd/C (0.75 g) and ethanol (95%, 50 mL) were placed in a parr reactor and stirred under 700 psi hydrogen pressure at 70 ^{o}C. The reaction was monitored by TLC. Usually (*S*)-BINOL disappeared in 6 h. A longer reaction time and higher temperature will generate more (*S*)-H_8BINOL. The mixture was then cooled down to room temperature. After the catalyst was removed by filtration and rinsed with ethanol (3 x 50 mL), the combined filtrates were concentrated in vacuum. The residue was purified by flash chromatography on silica gel eluted with 10% EtOAc/hexanes to give (*S*)-H_4BINOL[3] [~60% yield, more polar than (*S*)-H_8BINOL and less polar than (*S*)-BINOL] and (*S*)-H_8BINOL(~40% yield).

Preparation of (*S*)-2,2'-bis(methoxymethoxy)-5,6,7,8-tetrahydro-1,1'-binaphthyl, SM-2. To a 250 mL flask, (*S*)-H_4BINOL (6 g, 21 mmol), $CH_3OCH_2OCH_3$ (21 g, 271 mmol) and 150 mL CH_2Cl_2 were added. P_2O_5 (25 g) was then added to the reaction mixture with 5 potions. After the reaction mixture was stirred for 1 h, it was quenched with Na_2CO_3 (saturated, aqueous, 100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 50 mL). The resulting organic layers were dried and concentrated. The residue was purified by flash chromatography on silica gel eluted with 10% EtOAc/hexanes to yield the product as a white solid in 84% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56-1.63 (m, 2H), 1.72-1.75 (m, 2H), 2.02-2.12 (m, 1H), 2.26-2.36 (m, 1H), 2.83 (t, 2H, J = 6.0 Hz), 3.08 (s, 3H), 3.35 (s, 3H), 4.84 (d, 1H, J = 6.9 Hz), 4.93 (d, 1H, J = 6.6 Hz), 5.09 (d, 1H, J = 6.9 Hz), 5.17 (d, 1H, J = 6.9 Hz), 7.05 (d, 1H, J = 8.4 Hz), 7.14 (d, 1H, J = 8.4 Hz), 7.29-7.38 (m, 3H), 7.51. (d, 1H, J = 9.0 Hz), 7.81-7.87 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 27.4, 29.7, 55.8, 56.2, 95.0, 95.6, 113.2, 117.5, 124.2, 125.3, 126.5, 128.1, 129.1, 129.6, 130.1, 131.3, 133.6, 138.2, 152.0, 153.2.

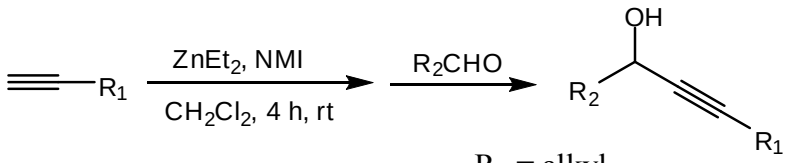
Preparation of 2-((1'S)-2,2'-bis(methoxymethoxy)-3'-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)-5',6',7',8'-tetrahydro-1,1'-binaphthyl-3-yl)-4,4,5,5-tetramethyl-1, 3,2-dioxaborolane, SM-3. Under nitrogen, (*S*)-2,2'-bis(methoxymethoxy)-5,6,7,8-tetrahydro-1,1'-binaphthyl (5.0 g, 13 mmol) was dissolved in hexanes and cooled to 0 °C. ^{n}BuLi (2.4 M, 22 mL, 52 mmol) was added and the reaction mixture was allowed to warm to room temperature over 3 h, during which a white precipitate formed. It was then cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15 mL, 73.6 mmol) in THF (30 mL) was added via cannula. The mixture was allowed to warm to room temperature and stirred for 16 h. The generated salts were removed by filtration through a Buchner funnel and rinsed with CH_2Cl_2. The combined organic layer was concentrated and purified by flash chromatography over a short silica gel column (10% EtOAc/hexanes), yielding SM-**3** as a white solid in 80% yield. (Extended time on the column would result in partial hydrolysis to the boronic acid.) ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (s, 12H), 1.37 (s, 12H), 1.53-1.59 (m, 2H), 1.66-1.76 (m, 2H), 2.07-2.15 (m, 1H), 2.17 (s, 3H), 2.36-2.46 (m, 1H), 2.76 (s, 3H), 2.79-2.85 (m, 2H), 4.72 (d, 1H, J = 6.0 Hz), 4.79 (d, 1H, J = 5.7 Hz), 4.95 (d, 1H, J = 6.3

[2] Korostyleve, A.; Tararov, V. I.; Fischer, C.; Monsees, A.; Brner, A. *J. Org. Chem.* **2004**, 69, 3220-3221.
[3] Heumann, L. V.; Keck, G. E. *J. Org. Chem.* **2008**, *73*, 4725-4727.

Hz), 5.05 (d, 1H, J = 6.3 Hz), 7.35-7.36 (m, 3H), 7.57 (s, 1H), 7.82-7.85 (m, 1H), 8.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.3, 25.1, 28.2, 29.8, 55.6, 56.3, 83.7, 84.0, 100.4, 100.6, 124.8, 126.4, 127.4, 128.6, 130.4, 132.7, 135.6, 137.4, 139.0, 142.7, 156.5, 159.2.

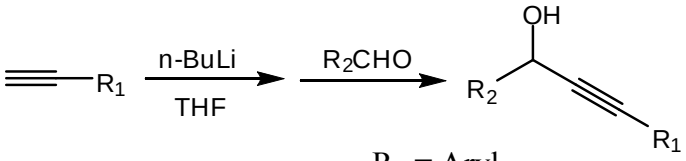
Partial racemization of (*S*)-4, (*S*)-6, and (*S*)-8 for determination of the enantiomeric purity. Under nitrogen, (*S*)-**4**, (*S*)-**6**, and (*S*)-**8** (10 mg) were stirred in NMP (2 mL) at 190 °C for 40 h. After cooled, the mixture was diluted with diethyl ether and washed three times with water. The aqueous layer was extracted once with diethyl ether. The combined organic layers were dried, concentrated, and purified by flash chromatography over a short silica gel column (10% EtOAc/hexanes). The purity of the racemized ligands was confirmed by ^{1}H NMR spectroscopy, and the partially racemized ligands were separated by HPLC (OD column, 99:1 hexanes:^{i}PrOH, flow rate = 0.3 mL/min).

Preparation of Racemic Propargylic Alcohols



R_2 = alkyl

Alkyne (0.5 mmol) was dissolved in CH_2Cl_2. $ZnEt_2$ (51.5 μL, 0.5 mmol) and N-methylimidazole (2 μL, 0.025 mmol) were added and the mixture was stirred for 4 h. An aldehyde (0.25 mmol) was added, and the reaction mixture was stirred overnight. The reaction was quenched with saturated aqueous ammonium chloride (5 mL), extracted with CH_2Cl_2 (3 x 10 mL), dried, and concentrated. The racemic alcohols were purified by flash chromatography over silica gel (10-20% EtOAc/hexanes).[4]

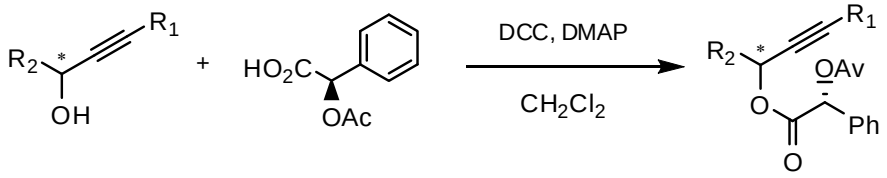


R_2 = Aryl

Under nitrogen, a solution of alkyne (0.75 mmol) in THF (3 mL) in a 10 mL round bottom flask was cooled to -78 ^{o}C by a dry ice/acetone bath, and ^{n}BuLi (0.12 mL, 2.5 M in hexane) was added. The mixture was stirred for 15 min. An aldehyde (0.25 mmol) was then added and the reaction mixture was continuously stirred for another 15 min. Ice was added to quench the reaction and methylene chloride was used for extraction. The extract was dried over magnesium sulfate. After the volatile solvent was removed by roto-evaporation, the residue was passed through a short silica gel eluted with petroleum ether/ethyl acetate (9/1) to afford the product.

[4] Yue, Y.; Yu, X.-Q.; Pu, L. *Chem. Eur. J.* **2009**, 15, 5104-5107.

Preparation of the Mandelic Acetate Derivatives of the Propargylic Alcohols for ^{1}H NMR Analysis



A propargylic alcohol (20 mg), DCC (2 equiv), DMAP (2 equiv), and (*R*)-O-acetylmandelic acid (2 equiv) were dissolved in CH_2Cl_2 (5 mL). The reaction was monitored by TLC. After consumption of the starting material (about 20 min), the crude mixture was passed through a short silica gel column eluted with 30% EtOAc/hexanes. The ee determination was based on the proton signal at δ~5.9 ppm in the ^{1}H NMR spectrum.

Characterization of the New Optically Active Propargylic Alcohol Products:

1-Phenylnon-3-yn-5-ol, P-1. 78% yield. 84% ee determined by HPLC analysis: AD column, 99:1 hexanes:^{i}PrOH, flow rate = 0.3 mL/min, λ = 221 nm, retention time: t_{major} = 51.43 min t_{minor} = 54.968 min. $[\alpha]_D$ = -6.20 (c = 0.34, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93-0.98 (t, 3H, J = 7.2 Hz), 1.37-1.48 (m, 4H), 1.65-1.74 (m, 2H), 2.02 (b, 1H), 2.55 (td, 2H, J_t = 8.4 Hz, J_d = 2.1 Hz), 2.87 (t, 2H, J = 7.5 Hz), 4.37 (tt, 1H, J_1 = 6.6 Hz, J_2 = 2.1 Hz), 7.25-7.37 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 21.2, 22.7, 27.6, 35.3, 38.1, 63.0, 82.5, 84.9, 126.6, 128.6, 128.7, 140.9. HRMS ($M\text{-}H^+$) for $C_{15}H_{19}O$ Calcd: 215.1430. Found: 215.1434.

9-Phenylnon-1-en-6-yn-5-ol, P-2. 67% yield. 80% ee determined by HPLC analysis: AD column, 99:1 hexanes:^{i}PrOH, flow rate = 0.3 mL/min, λ = 254 nm, retention time: t_{major} = 58.59 min t_{minor} = 62.91 min. $[\alpha]_D$ = -2.58 (c = 1.09, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.76-1.84 (m, 2H), 2.10 (b, 1H), 2.19-2.27 (m, 2H), 2.57 (t, 2H, J = 7.5 Hz), 2.88 (t, 2H, J = 7.5 Hz), 4.41 (b, 1H), 5.03-5.14 (m, 2H), 5.81-5.95 (m, 1H), 7.28-7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.2, 29.7, 35.3, 37.3, 62.4, 82.2, 85.2, 115.4, 126.6, 128.7, 128.8, 138.1, 140.8. HRMS (MH^+) for $C_{15}H_{19}O$ Calcd: 215.1430. Found: 215.1429.

Ethyl 4-hydroxynon-8-en-2-ynoate, P-3. 63% yield. 94% ee by HPLC analysis: OD column, 98:2 hexanes:^{i}PrOH, flow rate = 1.0 **mL**/min, λ = 221 nm, retention time: t_{major} = 20.36 min t_{minor} = 16.53 min. $[\alpha]_D$ = -7.35 (c = 1.10, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 3H, J = 7.0 Hz), 1.57-1.62 (m, 2H), 1.74-1.81 (m, 2H), 2.09 (q, 2H, J = 7.1 Hz), 2.26 (b, 1H), 4.23 (q, 1H, J = 7.1 Hz), 4.49 (t, 2H, J = 6.6 Hz), 4.96-5.05 (m, 2H), 5.72-5.85 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 24.3, 29.9, 33.4, 36.4, 62.2, 62.4, 87.9, 115.3, 138.2, 153.6. HRMS (MH^+) for $C_{11}H_{17}O_3$ Calcd: 197.1172. Found: 197.1171.

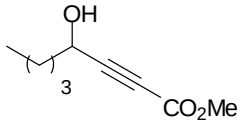
1-Phenyloct-7-en-1-yn-3-ol, P-4. 84% yield. 87% ee determined by analyzing the ^{1}H

NMR spectrum of the (*R*)-mandalate ester derivative. $[\alpha]_D$ = -2.11 (c = 1.09, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64-1.72 (m, 2H), 1.83-1.90 (m, 2H), 2.13-2.20 (m, 2H), 2.45 (bs, 1H), 4.66 (q, 2H, J = 5.1 Hz), 5.00-5.12 (m, 2H), 5.75-5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.76, 33.61, 37.54, 63.05, 85.17, 90.44, 115.13, 122.92, 128.56, 128.65, 131.96, 138.71. HRMS (MH^+) for $C_{14}H_{17}O$ Calcd: 201.1279. Found: 201.1284.

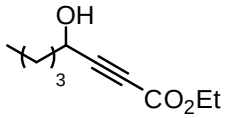
1-Phenyldec-9-en-3-yn-5-ol, P-5. 74% yield. 81% ee determined by analyzing the ^{1}H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D$ = -4.07 (c = 1.01, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (q, 2H, J = 6.0 Hz), 1.63-1.72 (m, 2H), 2.00 (d, 1H, J = 5.1 Hz), 2.09 (q, 2H, J = 6.6 Hz), 2.52 (t, 2H, J = 7.5 Hz), 2.83 (t, 2H, J = 7.5 Hz), 4.34 (d, 1H, J = 5.7 Hz), 4.99-5.08 (m, 2H), 5.75-5.89 (m, 1H), 7.21-7.31 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 24.6, 33.6, 35.3, 37.7, 62.7, 82.3, 84.9, 115.0, 126.6, 128.6, 128.7, 138.8, 140.8. HRMS (MH^+) for $C_{16}H_{21}O$ Calcd: 229.1587. Found: 229.1592.

1-(4-Chlorophenyl)-5-phenylpent-2-yn-1-ol, P-6. 72% yield. 80% ee determined by analyzing the ^{1}H NMR spectrum of the (*R*)-mandalate ester derivative. $[\alpha]_D$ = -19.24 (c = 1.01, THF). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (d, 2H, J = 6.1 Hz), 2.58 (td, 2H, J_t = 7.5 Hz, J_d = 1.8 Hz), 2.86 (t, 2H, J = 7.5 Hz), 5.38 (dt, 2H, J_d = 6.0 Hz, J_t = 1.8 Hz), 7.20-7.39 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 35.0, 64.3, 80.7, 87.4, 126.6, 128.3, 128.7, 128.8, 128.8, 134.2, 139.7, 140.6. HRMS $(M-H)^-$ for $C_{17}H_{14}OCl$ Calcd: 269.0728. Found: 269.0725.

Characterization of the Known Propargylic Alcohols



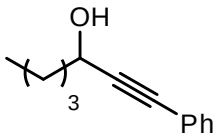
Methyl 4-hydroxyoct-2-ynoate, SM-aa. Reaction time: 10 h. 84% yield. 94% ee determined by HPLC analysis: Chiracel OD column, 98:2 hexanes:^{i}PrOH, flow rate = 0.5 mL/min, λ = 221 nm, retention time: t_{major} = 16.44 min t_{minor} = 14.97 min. $[\alpha]_D$ = -4.30 (c = 1.01, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 7.2 Hz), 1.32-1.39 (m, 4H), 1.73-1.79 (m, 2H), 1.94-1.96 (m, 1H), 3.79 (s, 3H), 4.5 (t, 1H, J = 6.2 Hz). These data are consistent with those reported.[5]



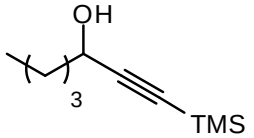
Ethyl 4-hydroxyoct-2-ynoate, SM-ab. 60% yield. 94% ee determined by HPLC analysis: Chiracel OD column, 98:2 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: t_{major} = 17.24 min t_{minor} = 14.93 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz), 1.33 (t, 3H, J = 7.2 Hz), 1.42-1.52 (m, 4H), 1.75-1.82 (m, 2H), 2.66 (d, 1H, J = 5.4 Hz), 4.22-4.29 (m, 2H), 4.47-4.53 (m, 1H). These data are

[5] Rajaram, A.R.; Pu, L. *Org. Lett*. **2006**, *8*, 2019-2021.

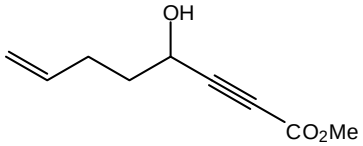
consistent with those reported.[6]



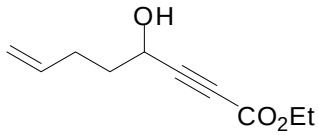
1-Phenylhept-1-yn-3-ol, SM-ac. 88% yield. 81% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 18.55 min t_{minor} = 7.05 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz), 1.38-1.51 (m, 4H), 1.79-1.82 (m, 2H), 1.94 (d, 1H, J = 5.4 Hz), 4.59 (q, 1H, J = 6.2 Hz), 7.29-7.31 (m, 3H), 7.41-7.44 (m, 2H). These data are consistent with those reported.[7]



1-(Trimethylsilyl)hept-1-yn-3-ol, SM-ae. 65% yield. 97% ee determined by analyzing the ^{1}H NMR spectrum of the (R)-mandalate ester derivative. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.91 (t, 3H, J = 7.2 Hz), 1.29-1.47 (m, 4H), 1.66-1.71 (m, 2H), 1.77 (d, 1H J = 5.4 Hz), 4.34 (q, 1H, J = 6.3 Hz). These data are consistent with those reported.[8]



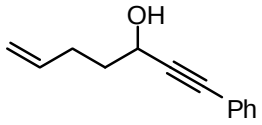
Methyl 4-hydroxyoct-7-en-2-ynoate, SM-ba. 63% yield. 95% ee determined by HPLC analysis: Chiracel OD column, 98:2 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: t_{major} = 14.88 min t_{minor} = 12.84 min. $[\alpha]_D$ = 9.99 (c = 1.06, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.84-1.91 (m, 2H), 1.97 (bs, 1H), 2.26 (q, 2H, J = 7.8 Hz), 3.79 (s, 3H), 4.53 (q, 1H, J = 5.7 Hz), 5.01-5.12 (m, 2H), 5.75-5.88 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.04, 35.71, 52.84, 61.38, 76.32, 87.97, 115.81, 136.92, 153.82. HRMS (MH^+) for $C_9H_{13}O_3$ Calcd: 169.0859. Found: 169.0863.



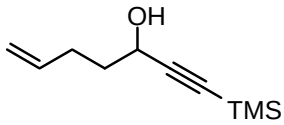
Ethyl 4-hydroxyoct-7-en-2-ynoate, SM-bb. 60% yield. 95% ee determined by HPLC analysis: Chiracel OD column, 98:2 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: t_{major} = 18.47 min t_{minor} = 16.27 min. $[\alpha]_D$ = 13.57 (c = 1.04, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.32 (t, 3H, J = 7.1 Hz), 1.84-1.95 (m, 3H), 2.26 (q, 2H, J= 7.5 Hz), 4.25 (q, 2H, J = 7.2 Hz), 4.52 (q, 1H, J = 6.3 Hz), 5.03 (d, 1H, J

[6] Herrmann, J. L.; Berger, M. H. ; Schlessinger, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 1544-1549.
[7] Gao, G.; Moore, D. ; Xie, R.-G. ; Pu, L. *Org. Lett.* **2002**, *4*, 4143-4146.
[8] Ivanov, I. V.; Romanov, S. G.: Groza, N. V.; Nigam, S.; Kuhn, H.; Myagkova, G. I. *Bioorg. Med. Chem.* **2002**, *10*, 2335-2343.

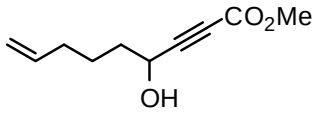
= 10.2 Hz), 5.09 (d, 1H, J= 17.1 Hz), 5.75-5.86 (m, 1H). These data are consistent with those reported.[9]



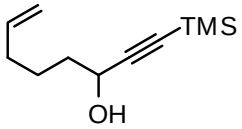
1-Phenylhept-6-en-1-yn-3-ol, SM-bc. 97% yield. 81% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 21.33 min t_{minor} = 7.57 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.89-1.95 (m, 2H), 1.99 (bs, 1H), 2.27-2.35 (m, 2H), 4.63 (t, 1H, J = 6.3 Hz), 5.00-5.14 (m, 2H), 5.81-5.94 (m, 1H), 7.30-7.32 (m, 3H), 7.42-7.45 (m, 2H). These data are consistent with those reported.[10]



1-(Trimethylsilyl)hept-6-en-1-yn-3-ol, SM-be. 69% yield. 94.5% ee determined by analyzing the ^{1}H NMR spectrum of the (*R*)-mandalate ester derivative. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 1.69-1.87 (m, 2H), 1.94 (d, 1H, J = 5.4 Hz), 2.23-2.30 (m, 2H), 4.41 (q, 1H, J = 6.0 Hz), 5.01-5.14 (m, 2H), 5.80-5.94 (m, 1H). These data are consistent with those reported.[11]

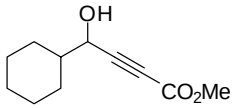


Methyl 4-hydroxynon-8-en-2-ynoate, SM-ca. 67% yield. 95% ee determined by HPLC analysis: Chiracel OD column, 98:2 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: t_{major} = 25.96 min t_{minor} = 20.31 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57-1.65 (m, 2H), 1.77-1.84 (m, 2H), 2.09-2.16 (m, 2H), 2.47 (bs, 1H), 3.81 (s, 3H), 4.53 (d, 1H, J = 4.5 Hz), 4.99-5.08 (m, 2H), 5.75-5.89 (m, 1H). These data are consistent with those reported.[12]

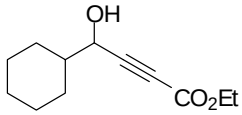


1-(Trimethylsilyl)oct-7-en-1-yn-3-ol, SM-ce. 68% yield. 94% ee determined by analyzing the ^{1}H NMR spectrum of the (*R*)-mandalate ester derivative. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.19 (s, 9H), 1.51-1.60 (m, 2H), 1.66-1.73 (m, 2H), 2.04-2.12 (m, 3H), 4.35 (q, 1H, J = 5.4 Hz), 4.94-5.05 (m, 2H), 5.73-5.86 (m, 1H). These data are consistent with those reported.[13]

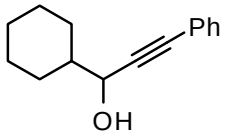
[9] Johansson, M.; Kopcke, B.; Anke, H.; Sterner, O. *Tetrahedron* **2002**, 58, 2523-2528.
[10] Weber, B.; Seebach, D. *Tetrahedron* **1994**, 50, 7473-7484.
[11] Frstner, A.; Nevado, C.; Waser, M.; Tremblay, M.; Chevrier, C.; Tepl, F.; Assa, C.; Moulin, E.; Mller, O. *J. Am. Chem. Soc.* **2007**, 129, 9150-9161.
[12] Albert, B. J.; Koide, K. *J. Org. Chem.* **2008**, 73, 1093-1098.
[13] Satcharoen, V.; Mclean, N. J.; Kemp, S. C.; Camp, N. P.; Brown, R. C.D. *Org. Lett.* **2007**, 9, 1867-1869.



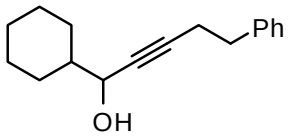
Methyl 4-cyclohexyl-4-hydroxybut-2-ynoate, SM-da. 84% yield. 95% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:^{i}PrOH, flow rate = 0.3 mL/min, λ = 221 nm, retention time: t_{major} = 73.66 min t_{minor} = 78.68 min. $[\alpha]_D$ = 5.04 (c = 1.01, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06-1.33 (m, 5H), 1.57-1.70 (m, 2H), 1.76-1.88 (m, 5H), 3.78 (s, 3H), 4.28 (t, 1H, J = 6.2 Hz). These data are consistent with those reported.[1]



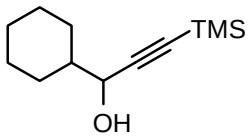
Ethyl 4-cyclohexyl-4-hydroxybut-2-ynoate, SM-db. 81% yield. 99.4% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:^{i}PrOH, flow rate = 0.3 mL/min, λ = 221 nm, retention time: t_{major} = 48.83 min t_{minor} = 52.78 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.04-1.23 (m, 5H), 1.30 (t, 3H, J = 7.2 Hz), 1.62-1.68 (m, 2H), 1.75-1.86 (m, 4H), 2.31 (d, 1H, J = 6.0 Hz), 4.19-4.28 (m, 3H). These data are consistent with those reported.[14]



1-Cyclohexyl-3-phenylprop-2-yn-1-ol, SM-dc. 94% yield. 82% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: t_{major} = 15.98 min t_{minor} = 7.09 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11-1.35 (m, 5H), 1.67-1.95 (m, 6H), 2.33 (d, 1H, J = 5.7 Hz), 4.38 (t, 1H, J = 6.0 Hz), 7.28-7.31 (m, 3H), 7.43-7.46 (m, 2H). These data are consistent with those reported. [6]

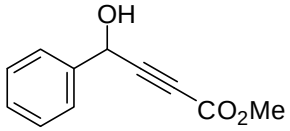


1-Cyclohexyl-5-phenylpent-2-yn-1-ol, SM-dd. 83% yield. 77% ee determined by analyzing the ^{1}H NMR spectrum of the (R)-mandalate ester derivative. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97-1.32 (m, 5H), 1.59-1.80 (m, 7H), 2.52 (td, 2H, J_t = 7.5 Hz, J_d = 1.5 Hz), 2.83 (t, 2H, J = 7.5 Hz), 4.10 (d, 1H, J = 6.0 Hz), 7.21-7.32 (m, 5H). These data are consistent with those reported. [15]

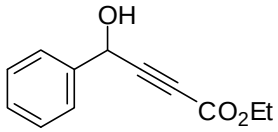


[14] Villeneuve, K.; Tam, W. *Organometallics.*. **2007**, 26, 6082-6090.
[15] Takita, R.; Yakura, K.; Ohshima, T.; Shibasaki, M. *J. Am. Chem. Soc.* **2005**, 127, 13760-13761.

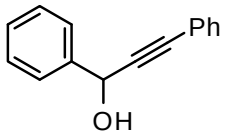
1-Cyclohexyl-3-(trimethylsilyl)prop-2-yn-1-ol, SM-de. 81% yield. 92% ee determined by analyzing the ^{1}H NMR spectrum of the (R)-mandalate ester derivative. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9H), 1.02-1.32 (m, 5H), 1.66-1.87 (m, 7H), 4.13 (t, 1H, J = 5.7 Hz). These data are consistent with those reported.[6]



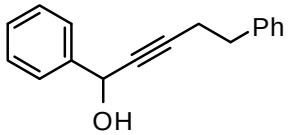
Methyl 4-phenyl-4-hydroxybut-2-ynoate, SM-ea. 64% yield. 90% ee determined by HPLC analysis: Chiracel OD column, 95:5 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 24.30 min t_{minor} = 29.45 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.29 (bs, 1H), 3.80 (s, 3H), 5.58 (d, 1H, J = 6.3 Hz), 7.39-7.41 (m, 3H), 7.51-7.54 (m, 2H). These data are consistent with those reported.[16]



Ethyl 4-phenyl-4-hydroxybut-2-ynoate, SM-eb. 52% yield. 88% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 10.99 min t_{minor} = 13.65 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3H, J = 7.2 Hz), 2.61 (d, 1H, J = 6.3 Hz), 4.24 (q, 2H, J = 7.2 Hz), 5.57 (d, 1H, J = 6.3Hz), 7.34-7.43 (m, 3H), 7.50-7.53 (m, 2H). These data are consistent with those reported.[13]

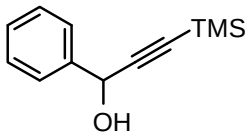


1,3-Diphenylprop-2-yn-1-ol, SM-ec. 91% yield. 83% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 25.28 min t_{minor} = 13.43 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (bs, 1H), 5.74 (bs, 1H), 7.37-7.53 (m, 8H), 7.65-7.67 (m, 2H). These data are consistent with those reported.[6]

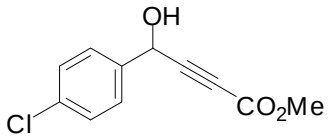


1,5-Diphenylpent-2-yn-1-ol, SM-ed. 61% yield. 92% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 34.07 min t_{minor} = 16.76 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (d, 1H, J = 5.7 Hz), 2.63-2.68 (m, 2H), 2.90-2.96 (m, 2H), 5.49 (bs, 1H), 7.30-7.54 (m, 10H). These data are consistent with those reported.[14]

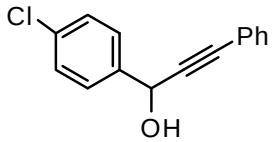
[16] Gao, G.; Wang Q.; Yu, X.-Q.; Xie, R.-G.; Pu, L. *Angew. Chem. Int. Ed.* **2006**, 45, 122-125.



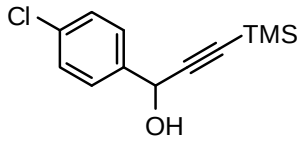
1-Phenyl-3-(trimethylsilyl)prop-2-yn-1-ol, SM-ee. 50% yield. 97% ee determined by HPLC analysis: Chiracel OD column, 95:5 hexanes:^{i}PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 7.41 min t_{minor} = 10.41 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.25 (s, 9H), 2.29 (d, 1H, J = 6.3 Hz), 5.49 (d, 1H, J = 6.3 Hz), 7.37-7.46 (m, 3H), 7.58-7.60 (m, 2H). These data are consistent with those reported.[17]



Methyl 4-(4-chlorophenyl)-4-hydroxybut-2-ynoate, SM-fa. 83% yield. 92% ee determined by HPLC analysis: Chiracel OD column, 95:5 hexanes:^{i}PrOH, flow rate = 1 mL/min, λ = 221 nm, retention time: t_{major} = 19.97 min t_{minor} = 18.47 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.80 (bs, 1H), 3.80 (s, 3H), 5. 55 (bs, 1H), 7.34-7.38 (m, 2H), 7.43-7.46 (m, 2H). These data are consistent with those reported.[15]



1-(4-Chlorophenyl)-3-phenylprop-2-yn-1-ol, SM-fc. 87% yield. 84% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1 mL/min, λ = 254 nm, retention time: t_{major} = 40.32 min t_{minor} = 11.01 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.82 (d, 1H, J = 6.0 Hz), 5.66 (d, 1H, J = 5.7 Hz), 7.32-7.37 (m, 5H), 7.45-7.48 (m, 2H), 7.52-7.55 (m, 2H). These data are consistent with those reported. [6]



1-(4-Chlorophenyl)-3-(trimethylsilyl)prop-2-yn-1-ol, SM-fe: 61% yield. 94% ee determined by HPLC analysis: Chiracel OD column, 90:10 hexanes:^{i}PrOH, flow rate = 1 mL/min, λ = 254 nm, retention time: t_{major} = 14.28 min t_{minor} = 17.18 min. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.20 (s, 9H), 2.24 (d, 1H, J = 6.0 Hz), 5.42 (d, 1H, J = 5.7 Hz), 7.33-7.36 (m, 2H), 7.45-7.48 (m, 2H). These data are consistent with those reported. [18]

Characterization of the Ring-Closing Metathesis Products:

2-(1-Phenylvinyl)cyclopent-2-enyl acetate, P-7. 94% yield. $[\alpha]_D$ = -19.67 (c = 1.73, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92-1.98 (m, 1H), 2.05 (s, 3H), 2.36-2.45 (m,

[17] Asano, Y.; Hara, K.; Ito, H.; Sawamura, M. *Org. Lett.* **2007**, 9, 3901-3904.
[18] Qiu, L.; Wang, Q.; Lin, L.; Liu, X.; Jiang, X.; Zhao, Q.; Hu, G.; Wang, R. *Chirality.* **2009**, 21, 316-323.

2H), 2.57-2.61 (m, 1H), 5.15 (s, 1H), 5.22 (s, 1H), 5.92 (t, 1H, J = 2.7 Hz), 6.07-6.10 (m, 1H), 7.30-7.33 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 31.2, 31.8, 79.3, 114.9, 127.6, 128.3, 128.5, 137.4, 141.8, 141.9, 144.2, 171.4. HRMS (M-H) for $C_{15}H_{15}O_2$ Calcd: 227.1067 Found: 227.1070.

2-(4-Phenylbutan-2-yl)cyclopent-2-enyl acetate, P-8. 85% yield. $[\alpha]_D$ = -3.95 (c = 1.66, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.85-1.93 (m, 1H), 2.05 (s, 3H), 2.29-2.47 (m, 2H), 2.56-2.61 (m, 3H), 2.80-2.85 (m, 2H), 4.97 (s, 1H), 4.99 (s, 1H), 6.01-6.03 (m, 1H), 6.15 (t, 1H, J = 2.4 Hz), 7.19-7.22 (m, 3H), 7.27-7.32 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.6, 31.2, 31.7, 35.1, 36.5, 79.2, 113.0, 126.1, 128.5, 128.7, 133.6, 141.3, 141.7, 142.3, 171.3. EI-HRMS (M-AcOH) for $C_{15}H_{16}$ Calcd: 196.1252. Found: 196.1260.

2-(1-Phenylvinyl)cyclohex-2-enyl acetate, P-9. 97% yield. $[\alpha]_D$ = -140.17 (c = 1.95, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.65-1.83 (m, 3H), 1.92-1.95 (m, 1H), 1.99 (s, 3H), 2.14-2.27 (m, 2H), 5.08 (s, 1H), 5.19 (s, 1H), 5.65 (t, 1H, J = 3.6 Hz), 5.94 (t, 1H, J = 3.9 Hz), 7.26-7.34 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.7, 21.5, 25.9, 29.1, 67.2, 113.0, 127.6, 128.3, 128.6, 134.1, 136.4, 141.7, 149.3, 170.8. HRMS (MH+) for $C_{16}H_{19}O_2$ Calcd: 243.1380. Found: 243.1389

2-(4-Phenylbutan-2-yl)cyclohex-2-enyl acetate, P-10. 87% yield. $[\alpha]_D$ = -77.02 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.66-1.69 (m, 3H), 1.98-2.00 (m, 1H), 2.05 (s, 3H), 2.09-2.17 (m, 1H), 2.26-2.33 (m, 1H), 2.49-2.55 (m, 2H), 2.74-2.80 (m, 2H), 4.88 (s, 1H), 4.97 (s, 1H), 5.70 (b, 1H), 6.17-6.20 (m, 1H), 7.18-7.29 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2, 21.7, 26.0, 29.1, 35.3, 36.1, 66.6, 111.0, 125.9, 126.1, 128.7, 128.7, 130.5, 134.7, 142.4, 145.6, 171.0. EI-HRMS (M-AcOH) for $C_{16}H_{18}$ Calcd: 210.1408. Found: 210.1412.

2-(2-Oxo-2,5-dihydrofuran-3-yl)cyclopent-2-enyl acetate, P-11. 61% yield. ^{1}H NMR (300 MHz,C_6D_6) δ 1.58-1.63 (m, 1H), 1.68 (s, 3H), 1.92-2.04 (m, 2H), 2.26-2.33 (m, 1H), 3.79 (s, 2H), 5.93-5.96 (m, 1H), 6.42 (b, 1H), 7.32 (b, 1H). ^{13}C NMR (75 MHz, C_6D_6) δ 20.8, 30.8, 31.5, 69.1, 79.4, 126.0, 139.2, 142.8, 170.1, 171.6. HRMS (MNH_4+) for $C_{11}H_{16}NO_4$ Calcd: 226.1074. Found: 226.1075

Characterization of the Tandem Ring-Closing Metathesis and Hydrogenation Products.

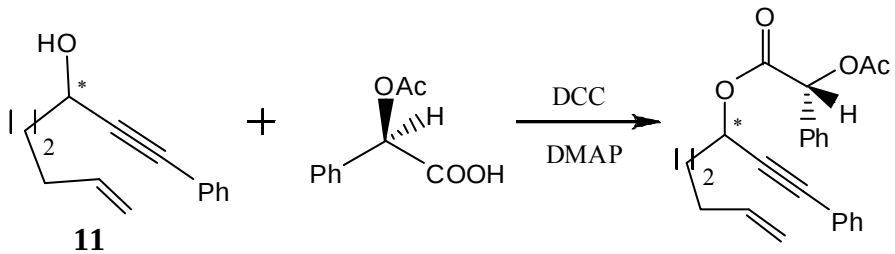
Methyl 2-(5-acetoxycyclopent-1-enyl)propanoate, P-12. 88% yield. The ratio of the two diastereomers is 2:1 determined by analyzing the ^{1}H NMR spectrum. $[\alpha]_D$ = -1.77 (c = 1.10, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.34 (d, 3H, J = 7.2 Hz), 1.72-1.90 (m, 2H), 2.02 (s, 3H), 2.31-2.51 (m, 2H), 3.20-3.30 (m, 1H), 3.66 (s, 3H), 5.70-5.73 (m, 1H), 5.90 (bs, 1H). Following are the resolved signals of another diastereomer: δ 1.29 (d, 3H, J = 7.2 Hz), 3.68 (s, 3H), 5.86 (b, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0, 21.5, 30.4, 31.2, 38.6, 52.2, 80.5, 132.9, 141.0, 171.2, 174.6. Following are the resolved signals of another diastereomer: δ 16.8, 39.6, 80.6, 132.7, 174.9. HRMS (MNa+) for

$C_{11}H_{16}O_4Na$ Calcd: 235.0946. Found: 235.0949.

Ethyl 2-(5-acetoxycyclopent-1-enyl)propanoate, P-13. 89% yield. The ratio of the two diastereomers is 2:1 determined by analyzing the ^{1}H NMR spectrum. $[\alpha]_D$ = -0.44 (c = 1.70, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.22 (t, 3H, J = 7.2 Hz), 1.33 (d, 3H, J = 7.2 Hz), 1.72-1.90 (m, 1H), 2.02 (s, 3H), 2.26-2.51 (m, 3H), 3.17-3.27 (m, 1H), 4.07-4.15 (m, 2H), 5.70-5.73 (m, 1H), 5.89 (b, 1H). Following are the resolved signals of another diastereomer: δ 1.28 (d, 3H, J = 7.2 Hz), 2.01 (s, 3H), 5.86 (bs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 15.9, 21.4, 30.4, 31.3, 38.7, 60.9, 80.6, 132.6, 141.1, 171.2, 174.1. Following are the resolved signals of another diastereomer: δ 16.9, 21.5, 30.4, 39.8, 60.8, 132.6, 171.2, 174.5. HRMS (MNa+) for $C_{12}H_{18}O_4Na$ Calcd: 249.1103 Found: 249.1094.

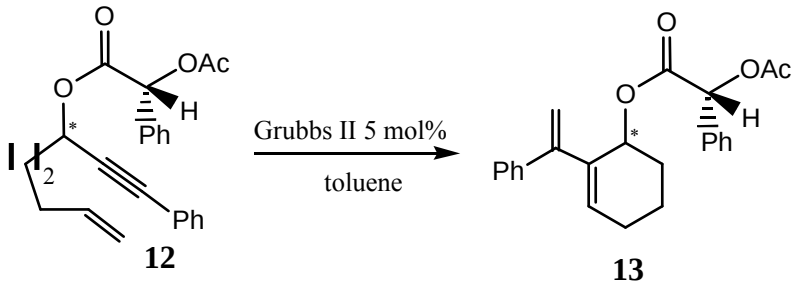
Methyl 2-(6-acetoxycyclohex-1-enyl)propanoate, P-14. 90% yield. The ratio of the two diastereomers is 2:1 determined by analyzing the ^{1}H NMR spectrum. $[\alpha]_D$ = -42.64 (c = 0.61, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, 3H, J = 7.2 Hz), 1.57-1.70 (m, 2H), 1.76-1.88 (m, 3H), 2.01 (s, 3H), 2.09-2.20 (m, 1H), 3.02-3.14 (m, 1H), 3.64 (s, 3H), 5.33 (t, 1H, J = 4.5 Hz), 5.89 (t, 1H, J = 3.9 Hz). Following are the resolved signals of another diastereomer: δ 2.02 (s, 3H), 3.65 (s, 3H), 5.85 (t, 1H, J = 3.9 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.8, 18.3, 21.5, 25.4, 29.1, 43.2, 52.1, 68.8, 130.1, 134.9, 170.9, 175.2. Following are the resolved signals of another diastereomer: δ 17.1, 18.0, 44.0, 69.2, 171.0, 175.3. HRMS (MNH_4+) for $C_{12}H_{22}NO_4$ Calcd: 244.1543 Found: 244.1546.

Ethyl 2-(6-acetoxycyclohex-1-enyl)propanoate, P-15. 91% yield. The ratio of the two diastereomers is 3:1 determined by analyzing the ^{13}C NMR spectrum. $[\alpha]_D$ = -59.92 (c = 1.05, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20-1.26 (m, 6H), 1.60-1.66 (m, 2H), 1.76-1.80 (m, 2H), 2.03 (s, 3H), 2.12-2.26 (m, 2H), 3.01-3.14 (m, 1H), 4.10 (q, 2H, J = 7.2Hz), 5.34 (t, 1H, J = 4.5 Hz), 5.86-5.91 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.4, 15.8, 18.3, 21.5, 25.4, 29.1, 43.1, 60.8, 69.1, 129.8, 135.0, 170.9, 174.8. The following are the resolved signals of another diastereomer: δ 17.2, 18.0, 21.6, 44.2, 69.2, 171.0, 174.9. HRMS (MNa+) for $C_{13}H_{20}O_4Na$ Calcd: 263.1259. Found: 263.1263.



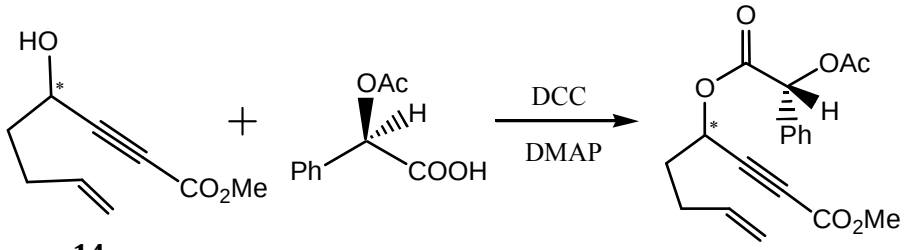
11 **12**

1-Phenyloct-7-en-1-yn-3-ol (**11**) (1.0 equiv) was dissolved in CH_2Cl_2 and cooled to 0 °C. (*R*)-(-)–α-Acetylmandalic acid (1.5 equiv), DCC (1.5 equiv) and DMAP (0.1 equiv) were added in one portion. After 20 min the reaction mixture was passed through a short silica gel column eluted with 20% EtOAc/hexanes to give **12**.



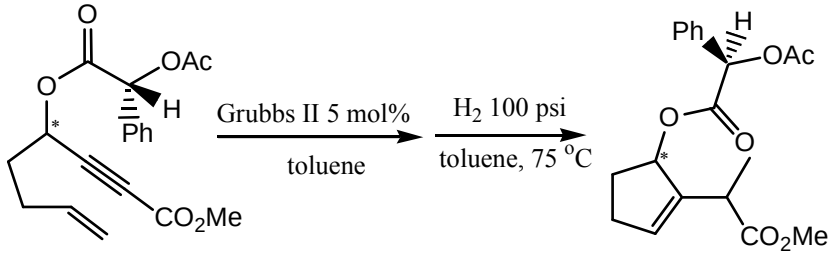
12 **13**

(R)-((S)-1-phenyloct-7-en-1-yn-3-yl) 2-acetoxy-2-phenylacetate (**12**) (1 equiv) was dissolved in toluene (0.14 M) and combined with Grubbs II (5 mol%) under nitrogen. After the mixture was stirred at room temperature for 1 h, it was passed through a short silica gel column eluted with 20% EtOAc/hexanes to give **13**. The ee was determined by analyzing the ^{1}H NMR spectrum. It shows that the enantiomeric purity of the products generated from the asymmetric methyl propiolate addition to the aldehydes is maintained in the subsequent RCM reaction.



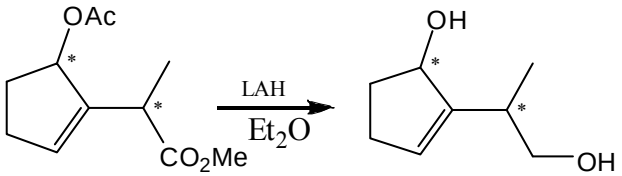
14 **15b**

Methyl 4-hydroxyoct-7-en-2-ynoate (**14**) (1.0 equiv) was dissolved in CH_2Cl_2 and cooled to 0 °C. (*R*)-(-)–α-Acetylmandalic acid (1.5 equiv), DCC (1.5 equiv) and DMAP (0.1 equiv) were added in one portion. After 20 min the reaction mixture was passed through a short silica gel column eluted with 20% EtOAc/hexanes to give **15b**.



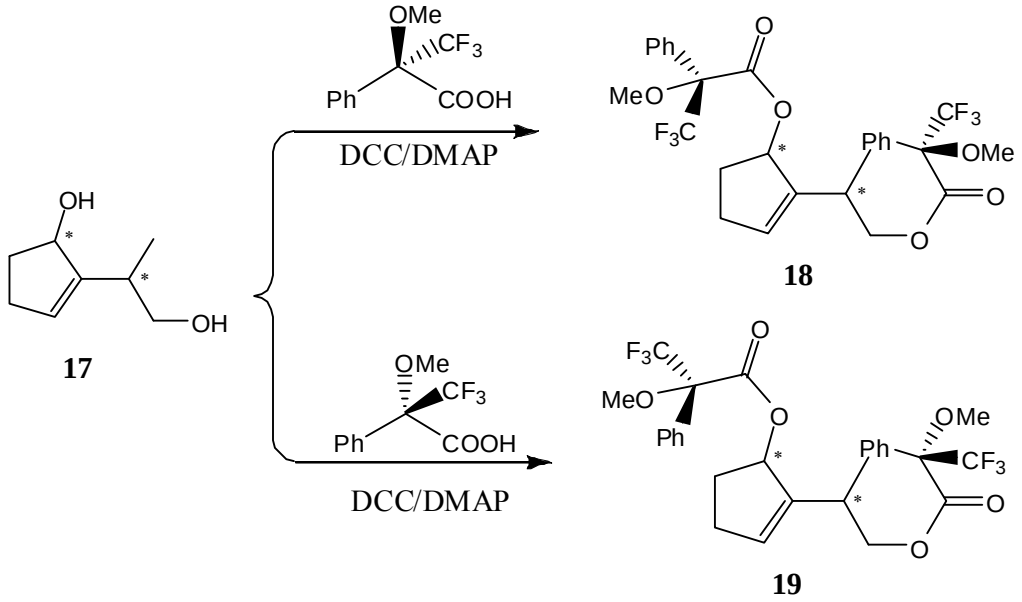
15b **16b**

To a 50 mL round bottom flask, methyl 4-((R)-2-acetoxy-2-phenylacetoxy)oct-7-en-2-ynoate (**15b**) (1 equiv) was dissolved in toluene (0.14 M) and Grubbs II (5 mol%) was added under nitrogen. After stirring 1 h at room temperature, the mixture was transferred to a parr reactor. Hydrogen (100 psi) was introduced and the reactor was heated at 75 ^{o}C with stirring for 10 h. The crude mixture was passed through a short silica gel column eluted with 20% EtOAc/hexanes. The ee was determined by analyzing its ^{1}H NMR spectrum. The enantiomeric purity of the product generated from the asymmetric methyl propiolate addition to the aldehydes is maintained in **16b**.

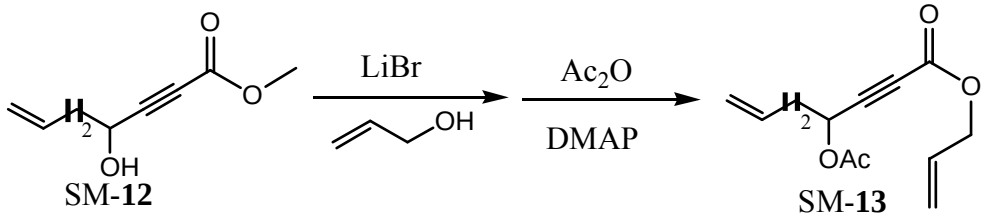


16a **17**

To a 10 mL flask, **16a** (1.0 equiv) and LAH (3 equiv) were dissolved in Et_2O under nitrogen. After the mixture was stirred for 30 min, it was passed through a short silica gel column eluted with 50% EtOAc/hexanes to give **17** in 92% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (d, 3H, J = 7.2 Hz), 1.73-1.82 (m, 1H), 2.18-2.25 (m, 2H), 2.43-2.53 (m, 1H), 2.66-2.77 (m, 1H), 3,21 (bs, 2H), 3.59 (d, 2H, J = 5.4 Hz), 4.77-4.79 (m, 1H), 5.68-5.70 (m, 1H). The following are the resolved signals of another diastereomer: δ 1.07 (d, 3H, J = 7.2 Hz), 3.43 (dd, 1H, J_1 = 8.7 Hz, J_2 = 10.5 Hz), 3.69 (dd, 1H, J_1 = 10.5 Hz, J_2 = 4.5 Hz), 4.63-4.65 (m, 1H).



To a 10 mL flask, **17** (1.0 equiv) was dissolved in CH_2Cl_2 and cooled to 0 °C. (R)-(+)-α-Methoxy-α-trifluoromethyl-phenylacetic acid or (S)-(−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (3.0 equiv), DCC (3.0 equiv) and DMAP (0.1 equiv) were added in one portion. After 1 h the reaction mixture was passed through a short silica gel column eluted with 10% EtOAc/hexanes to give the product **18** or **19**.



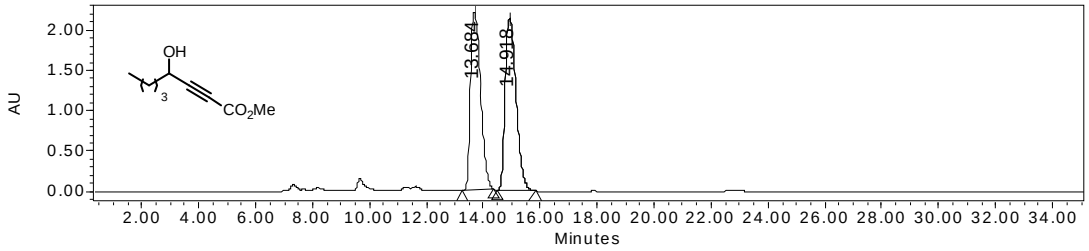
SM-**12** SM-**13**

Preparation of allyl 4-acetoxyoct-7-en-2-ynoate, SM-13. To a 25 mL flask, methyl 4-hydroxyoct-7-en-2-ynoate (SM-**12**) (84 mg, 0.5 mmol), LiBr (86 mg, 1 mmol) and allyl alcohol (15 mL) were added. After the mixture was stirred at 50 °C for 2 d, the solvent

was removed under vacuum. The crude product was dissolved in CH_2Cl_2 (25 mL), and DMAP (12.2 mg, 0.1 mmol) and Ac_2O (0.5 mL) were added. The reaction mixture was stirred at room temperature for 10 min and then concentrated. The residue was purified by column chromatography on silica gel eluted with 10% EtOAc/hexanes to give SM-**13** as a white solid in 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93-2.00 (m, 2H), 2.13 (s, 1H), 2.22-2.29 (m, 2H), 4.70 (d, 2H, J = 6.0 Hz), 5.04-5.13 (m, 2H), 5.31-5.43 (m, 2H), 5.49 (t, 1H, J = 6.6 Hz), 5.75-6.02 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.0, 29.2, 33.3, 62.8, 66.9, 77.7, 84.6, 116.3, 119.8, 131.2, 136.5, 152.9, 169.9. HRMS (MH^+) for $C_{11}H_{15}O_3$ Calcd: 195.1016. Found: 195.1020.

HPLC Plots

SM-**aa:**



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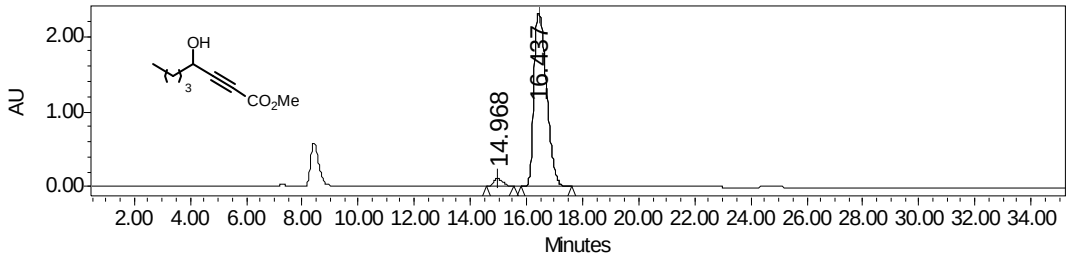

Name	Retention Time	Area	% Area
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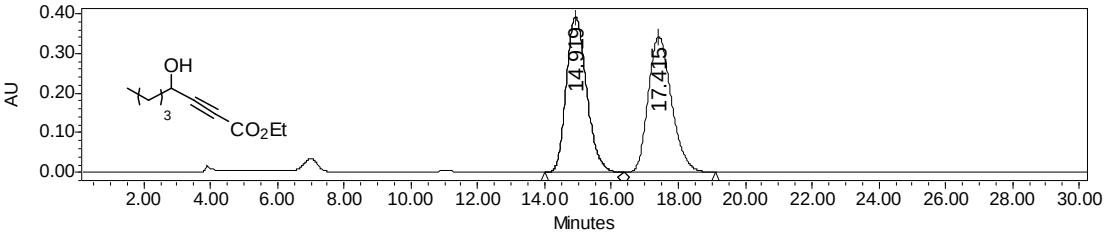
SM-**ab:**



Name	Retention Time	Area	% Area
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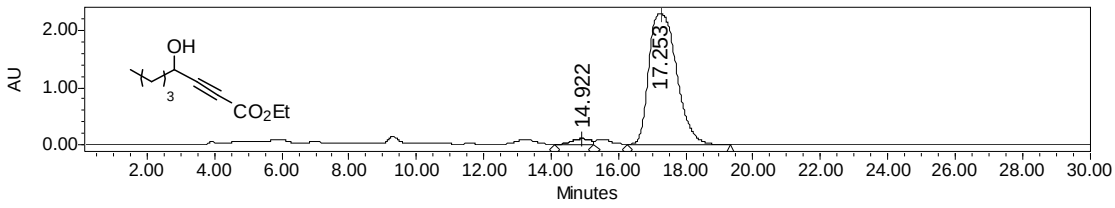
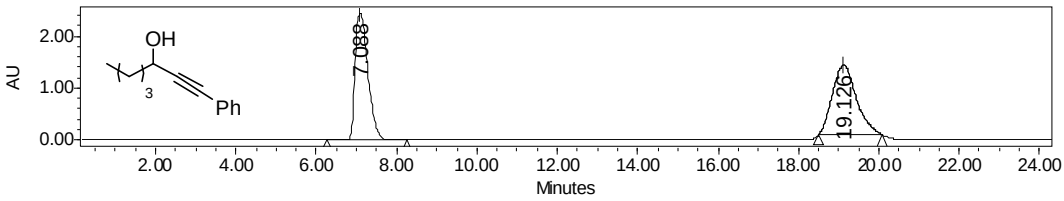


Name	Retention Time	Area	% Area
1	14.922	3899368	2.86
2	17.253	132522065	97.14

SM-**ac:**



Name	Retention Time	Area	% Area
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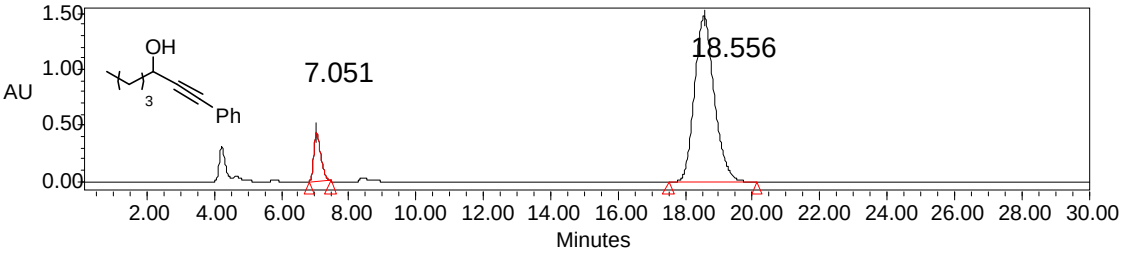
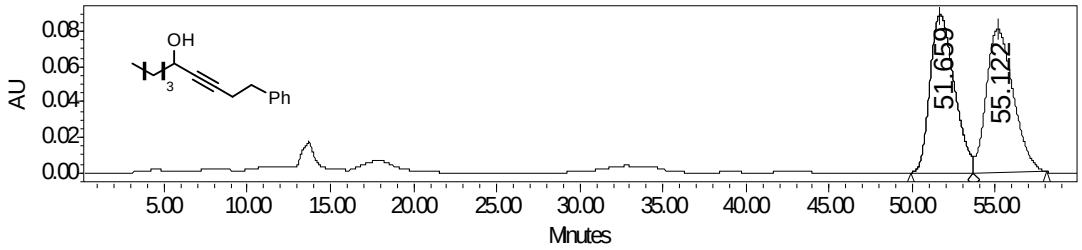


Name	Retention Time	Area	% Area
1	7.051	6203572	9.37
2	18.556	60024037	90.63

SM-**ad (= P-1):**



Name	Time	Area	% Area
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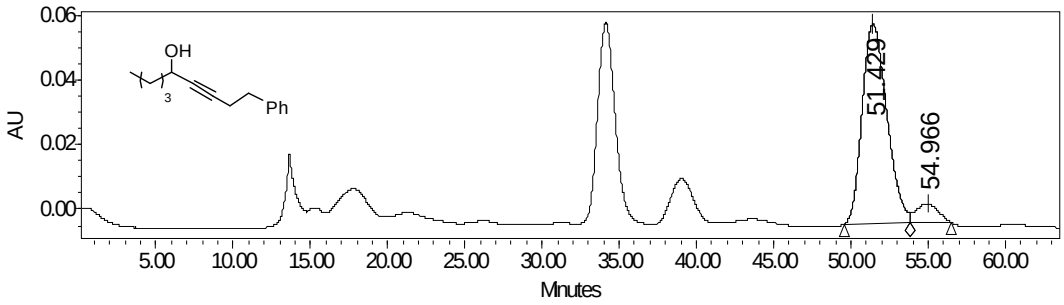

Name	Time	Area	% Area
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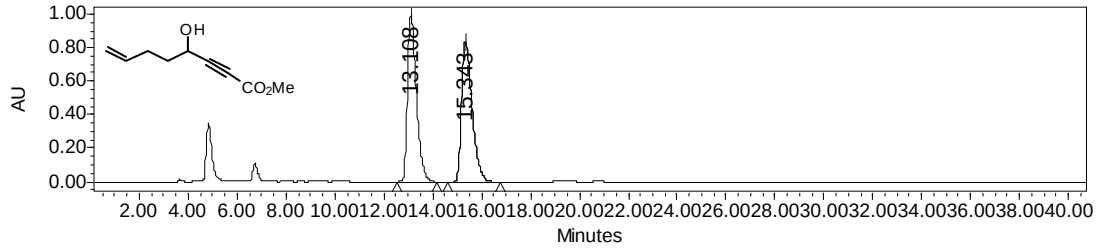
2	54.966	608784	8.08

SM-**ba:**



Name	Retention Time	Area	% Area
1	13.108	24899891	49.82
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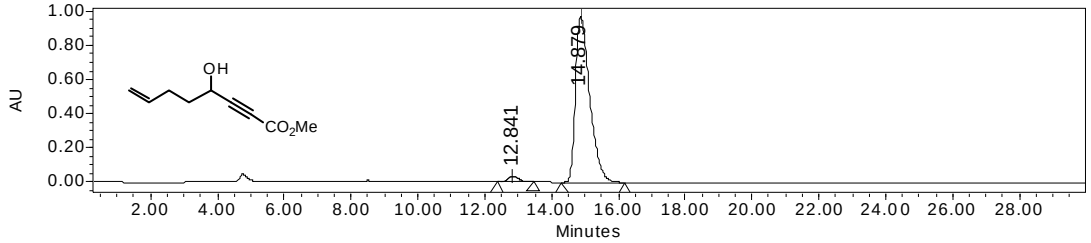

Name	Retention Time	Area	% Area
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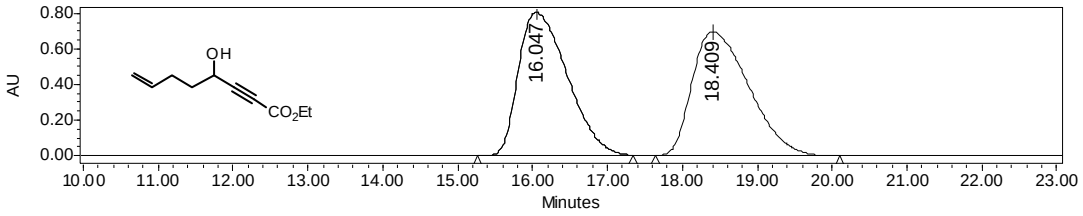
SM-**bb:**



Name	Retention Time	Area	% Area
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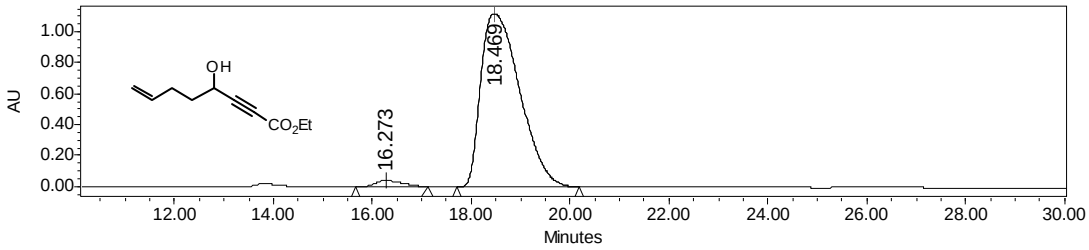

Name	Retention Time	Area	% Area
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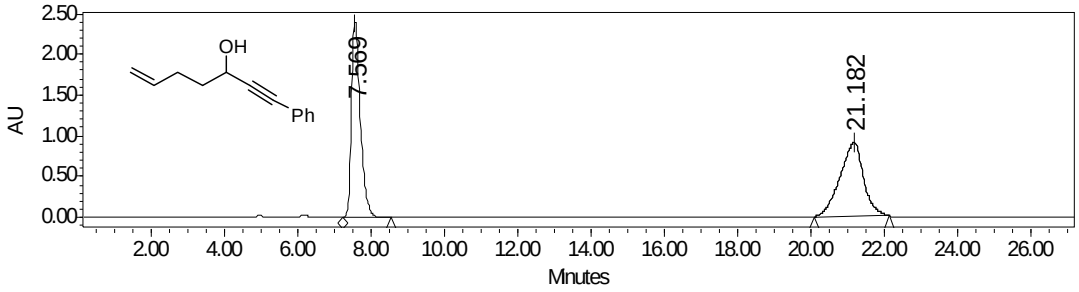
SM-**bc:**



Name	Retention Time	Area	% Area
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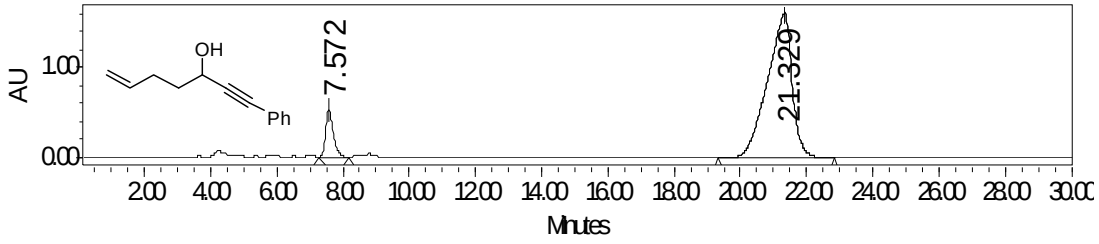

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1	7.572	8574269	9.29
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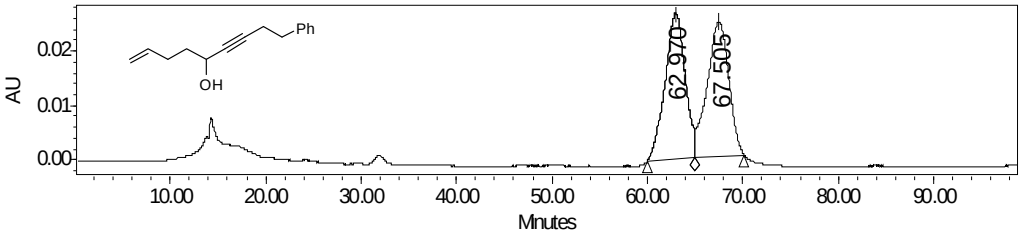
SM-**bd (= P-2):**



Name	Retention Time	Area	% Area
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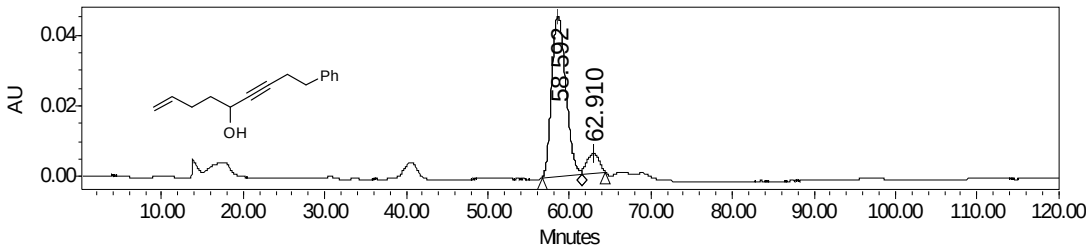

Name	Retention Time	Area	% Area
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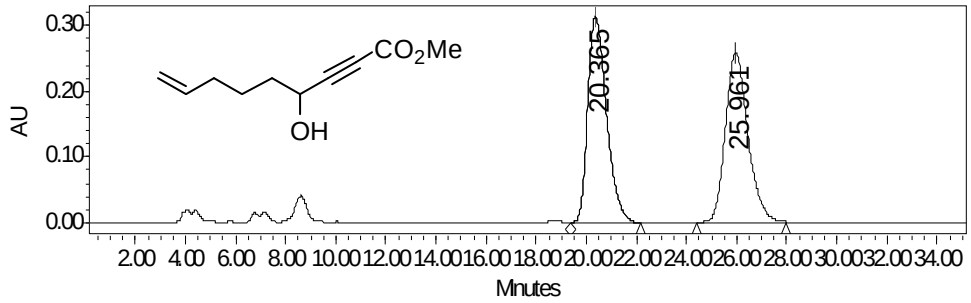
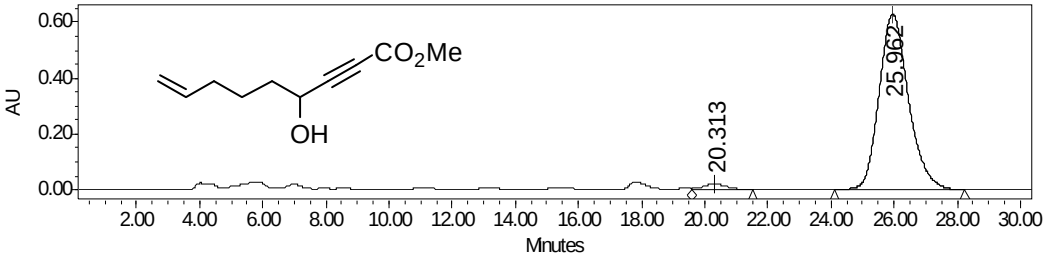
SM-**ca:**

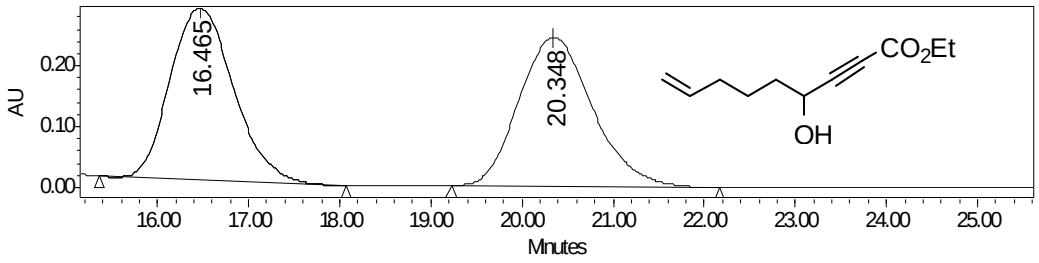


Name	Retention Time	Area	% Area
1	20.365	16409530	50.40
2	25.961	16147458	49.60

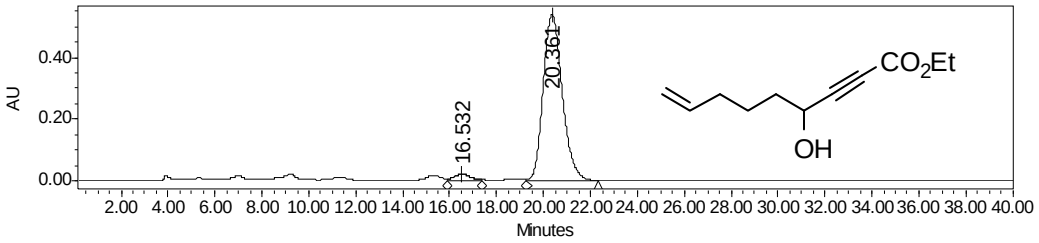


Name	Retention Time	Area	% Area
1	20.313	1021514	2.45
2	25.962	40742263	97.55

SM-**cb (= P-3):**

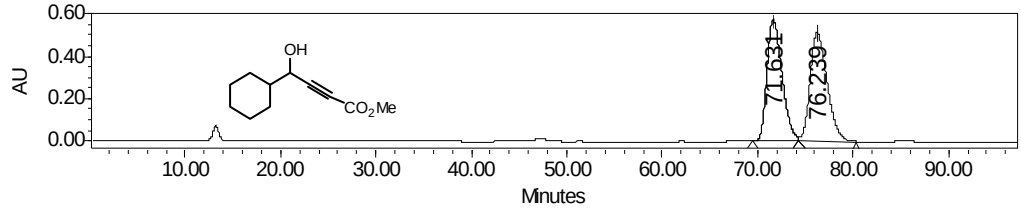


Name	Retention Time	Area	% Area
1	16.465	13654426	49.84
2	20.348	13744620	50.16

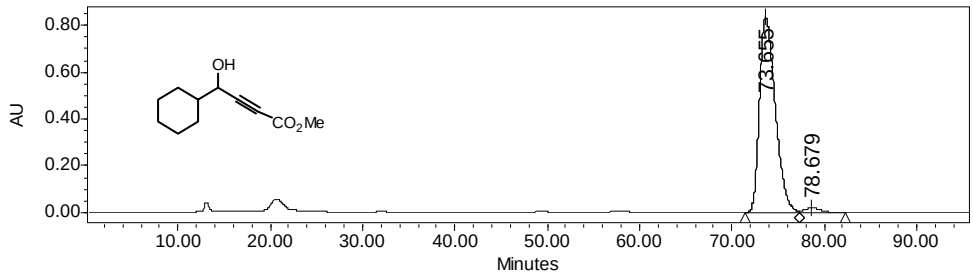


Name	Retention Time	Area	% Area
1	16.532	980870	3.12
2	20.361	30418112	96.88

SM-**da:**

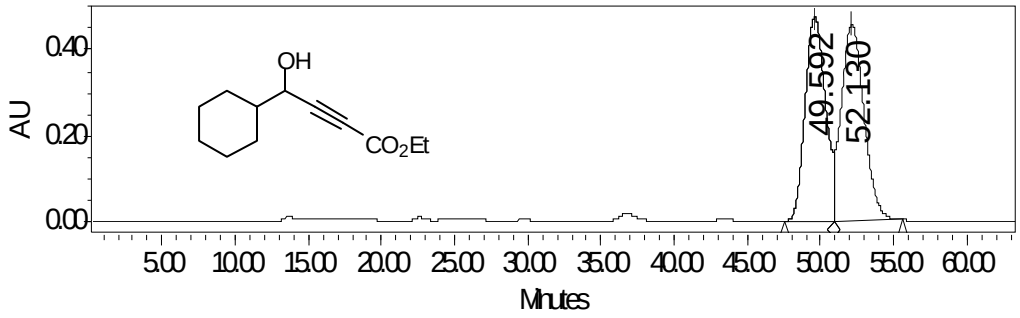


Name	Retention Time	Area	% Area
1	71.631	63675367	49.92
2	76.239	63880927	50.08

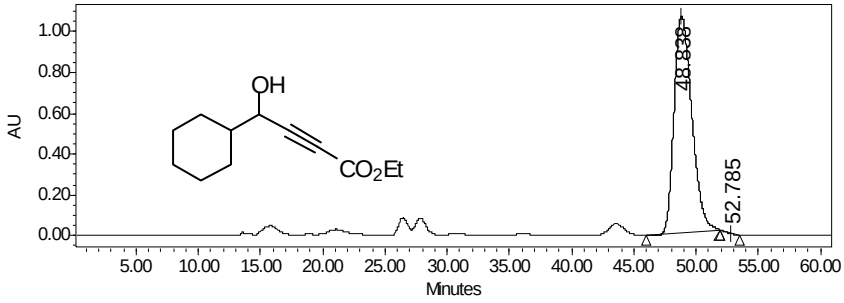


Name	Retention Time	Area	% Area
1	73.655	99728514	97.36
2	78.679	2705025	2.64

SM-**db**:

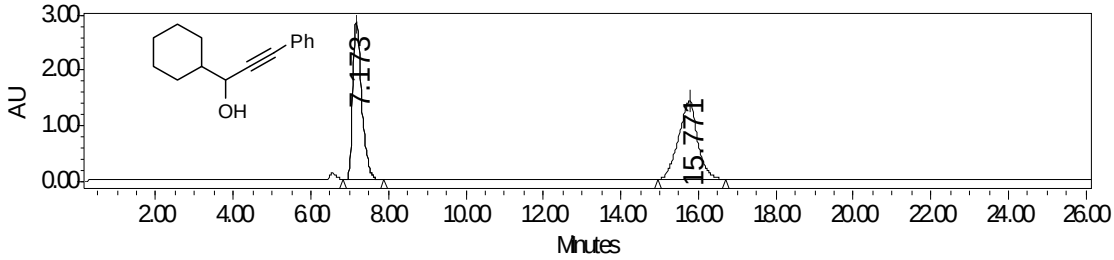


Name	Retention Time	Area	% Area
1	49.592	47746772	49.71
2	52.130	48308387	50.29

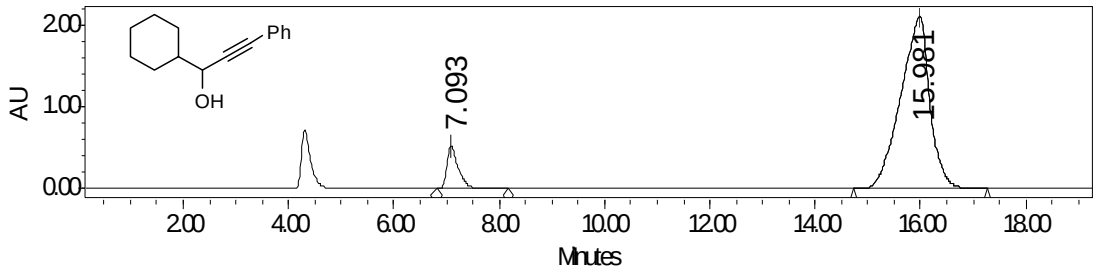


Name	Retention Time	Area	% Area
1	48.838	105122240	99.70
2	52.785	320249	0.30

SM-**dc:**

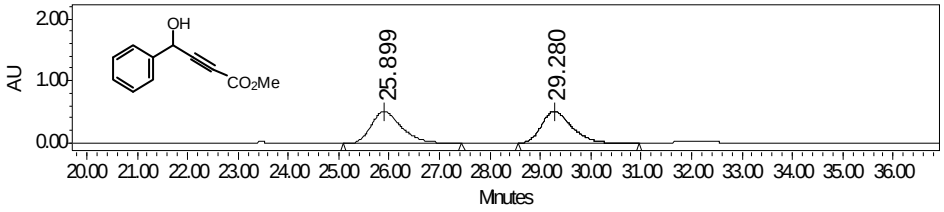


Name	Retention Time	Area	% Area
1	7.173	46556220	48.80
2	15.771	48843347	51.20

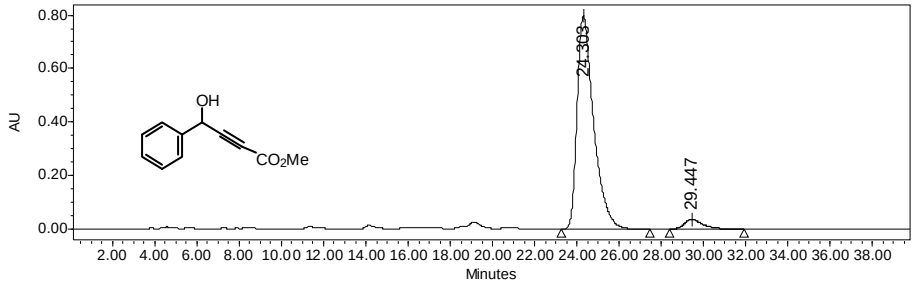


Name	Retention Time	Area	% Area
1	7.093	7916130	8.84
2	15.981	81618006	91.16

SM-**ea:**

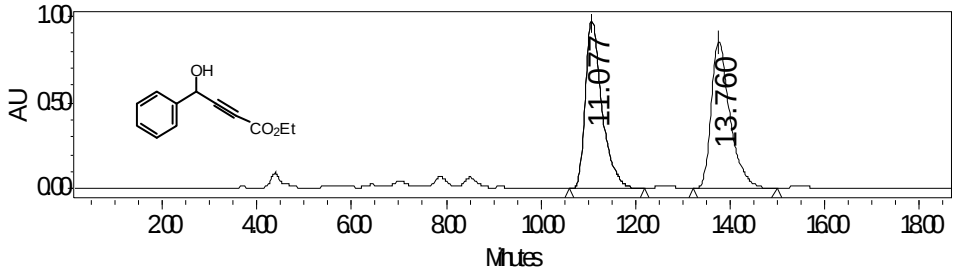


Retention Time	Area	% Area
25.899	21903551	50.20
29.280	21731884	49.80

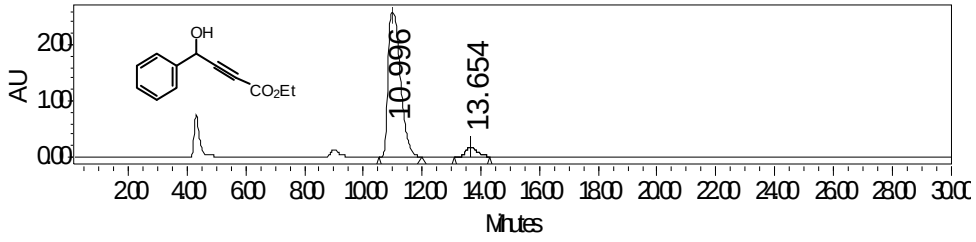


Retention Time	Area	% Area
24.303	43379467	95.13
29.447	2221559	4.87

SM-**eb:**

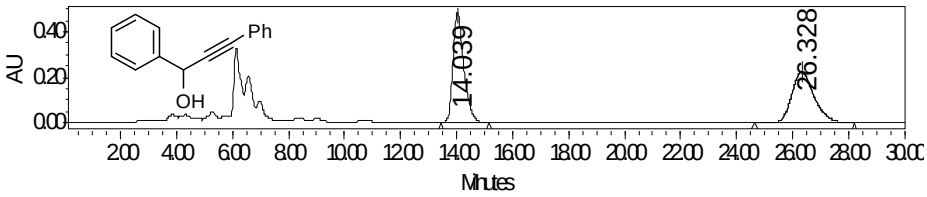


Name	Retention Time	Area	% Area
1	11.077	24191565	50.25
2	13.760	23948441	49.75

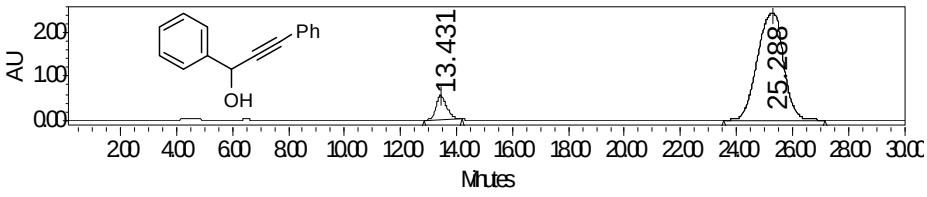


Name	Retention Time	Area	% Area
1	10.996	75247293	94.32
2	13.654	4535437	5.68

SM-**ec:**

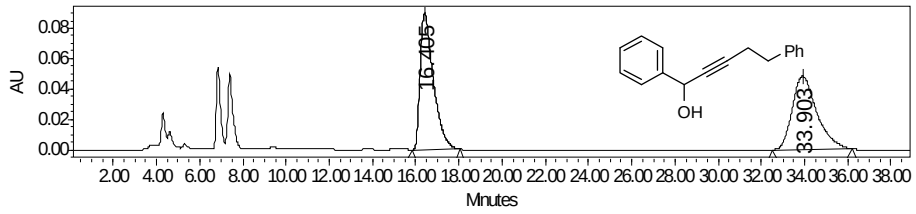


Name	Retention Time	Area	% Area
1	14.039	12881844	50.48
2	26.328	12637699	49.52

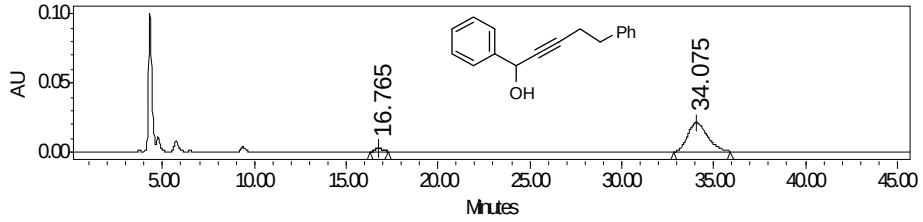


Name	Retention Time	Area	% Area
1	13.431	15453516	8.78
2	25.288	160539328	91.22

SM-**ed:**

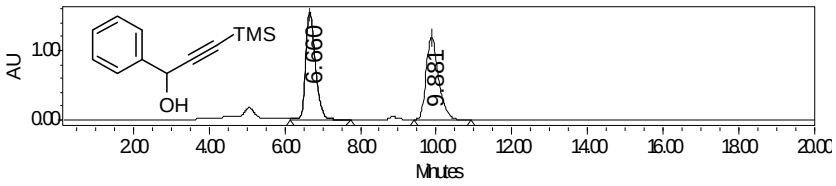


Name	Retention Time	Area	% Area
1	16.405	3835258	50.10
2	33.903	3820121	49.90

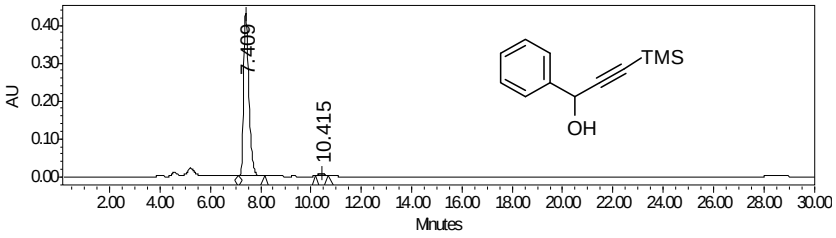


Name	Retention Time	Area	% Area
1	16.765	66450	4.04
2	34.075	1576547	95.96

SM-**ee:**

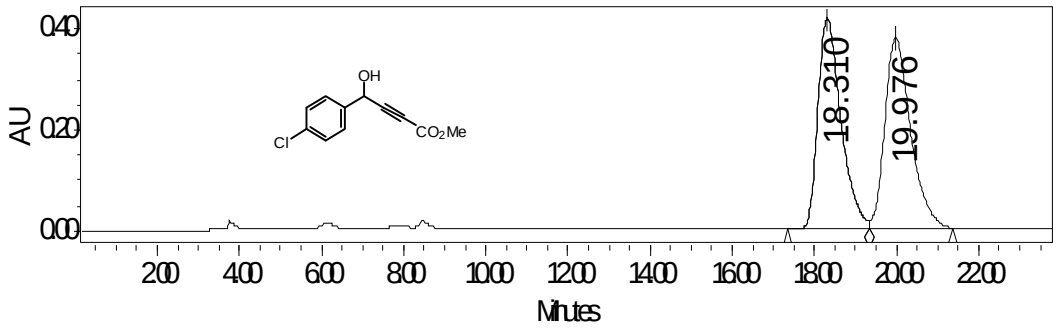


Name	Retention Time	Area	% Area
1	6.660	28021123	50.14
2	9.881	27865086	49.86

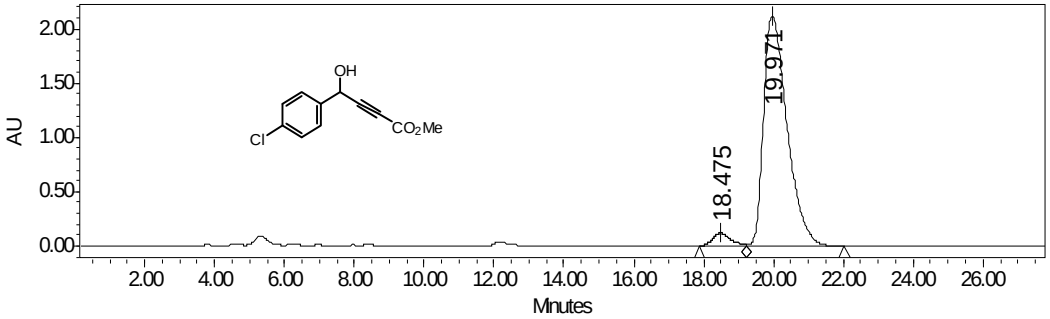


Name	Retention Time	Area	% Area
1	7.409	6157853	98.43
2	10.415	98374	1.57

SM-**fa:**

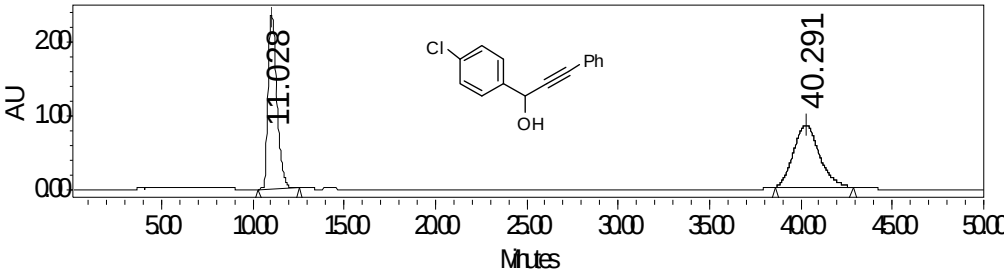


Name	Retention Time	Area	% Area
1	18.310	16463402	49.84
2	19.976	16569596	50.16

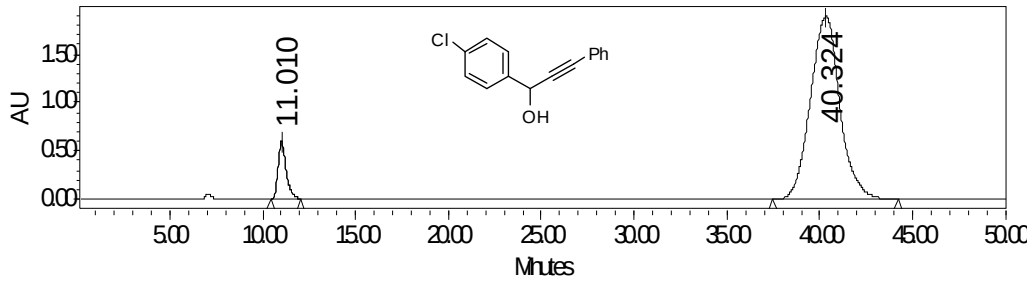


Name	Retention Time	Area	% Area
1	18.475	4246562	4.10
2	19.971	99225708	95.90

SM-**fc:**

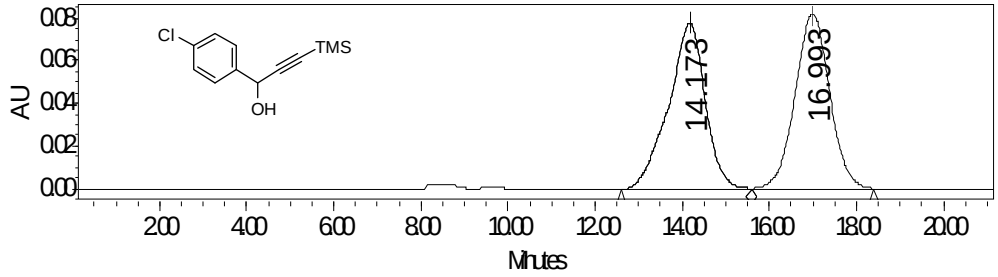


Name	Retention Time	Area	% Area
1	11.028	81629826	49.22
2	40.291	84205753	50.78

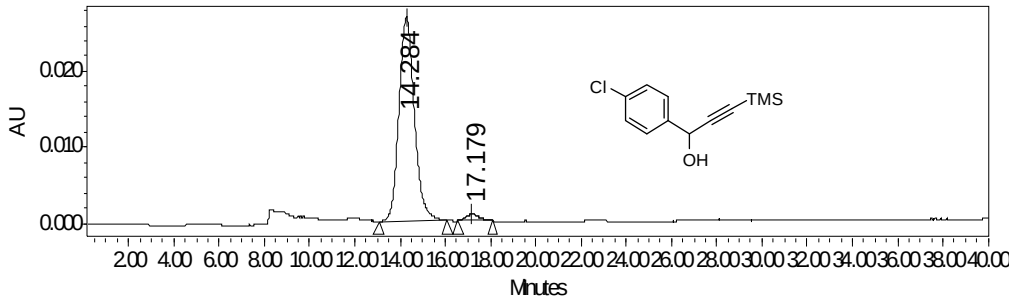


Name	Retention Time	Area	% Area
1	11.010	17816482	7.88
2	40.324	208423689	92.12

SM-**fe:**

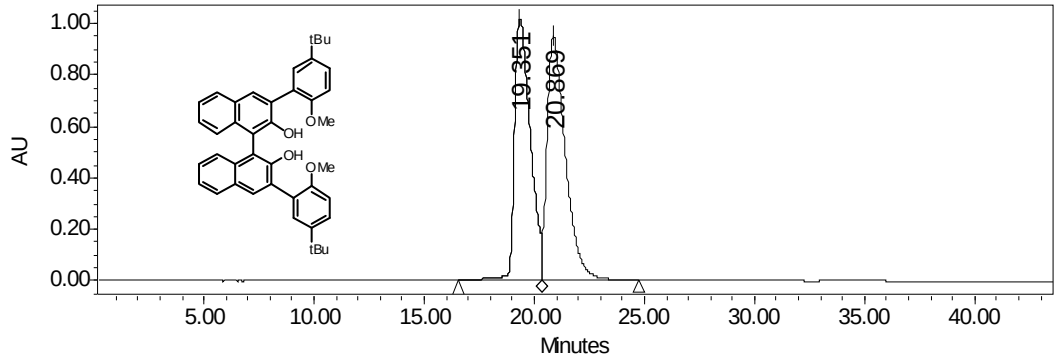


Name	Retention Time	Area	% Area
1	14.173	4595271	50.18
2	16.993	4562491	49.82



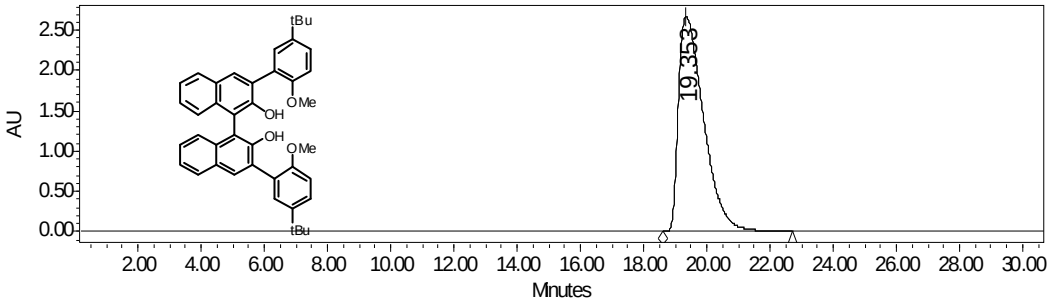
Name	Retention Time	Area	% Area
1	14.284	1270145	97.07
2	17.179	38350	2.93

Partially racemized (*S*)-**4**



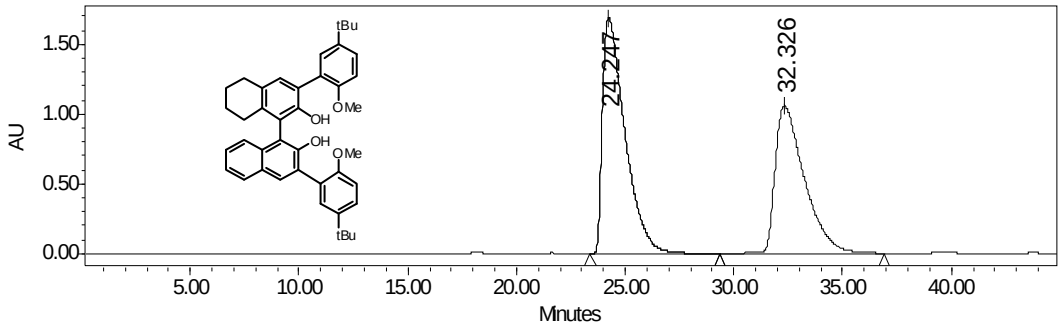
Name	Retention Time	Area	% Area
1	19.351	50853031	48.08
2	20.869	54923355	51.92

(*S*)-**4**



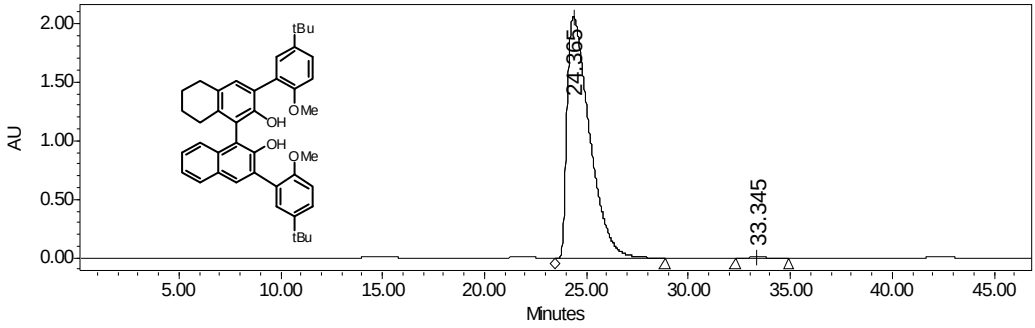
Name	Retention Time	Area	% Area
1	19.353	147518173	100.00

Partially racemized (*S*)-**6**



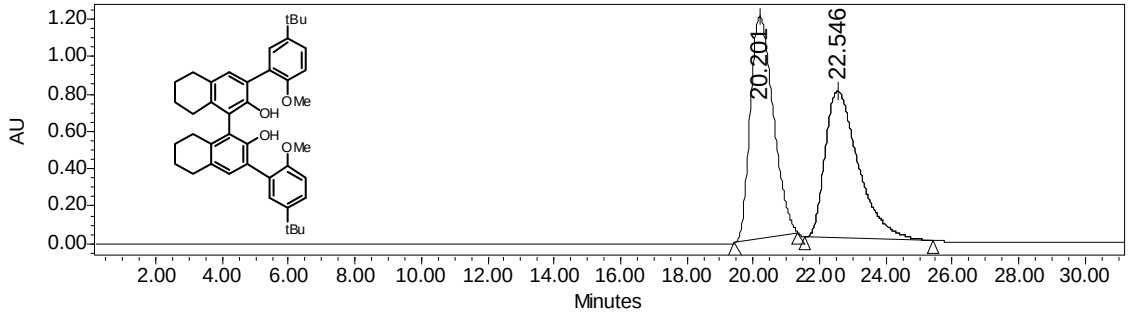
Name	Retention Time	Area	% Area
1	24.247	121721919	55.14
2	32.326	99031814	44.86

(*S*)-**6**



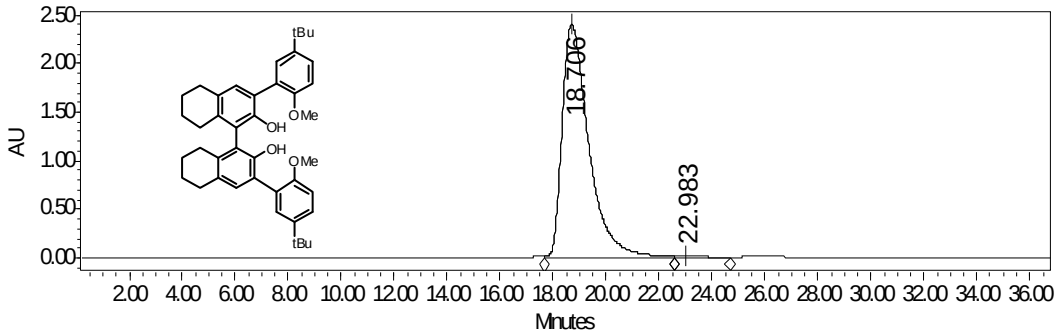
Name	Retention Time	Area	% Area
1	24.365	157558152	99.62
2	33.345	600295	0.38

Racemic **7**



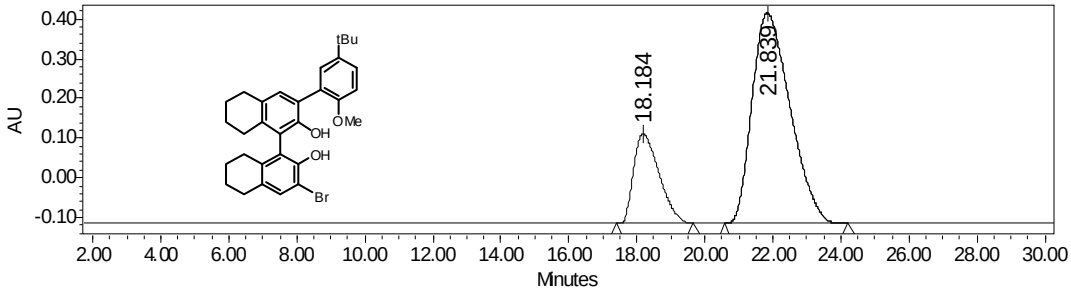
Name	Retention Time	Area	% Area
1	20.201	57158610	50.79
2	22.546	55378818	49.21

(*S*)-**7**



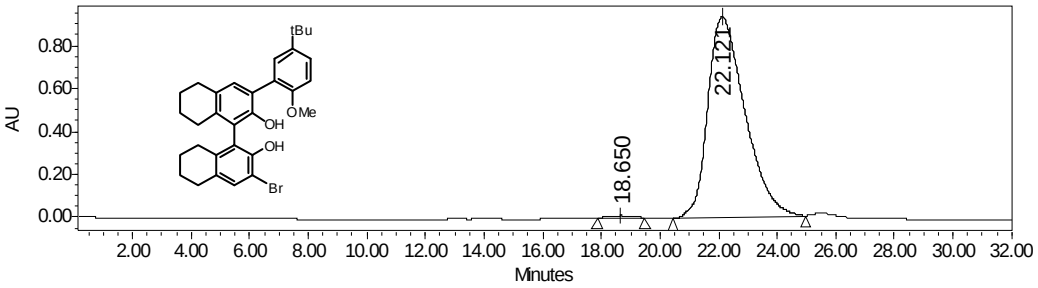
Name	Retention Time	Area	% Area
1	18.706	169810183	99.10
2	22.983	1544576	0.90

Partially racemized (*S*)-**8**



Name	Retention Time	Area	% Area
1	18.184	11658394	22.11
2	21.839	41076770	77.89

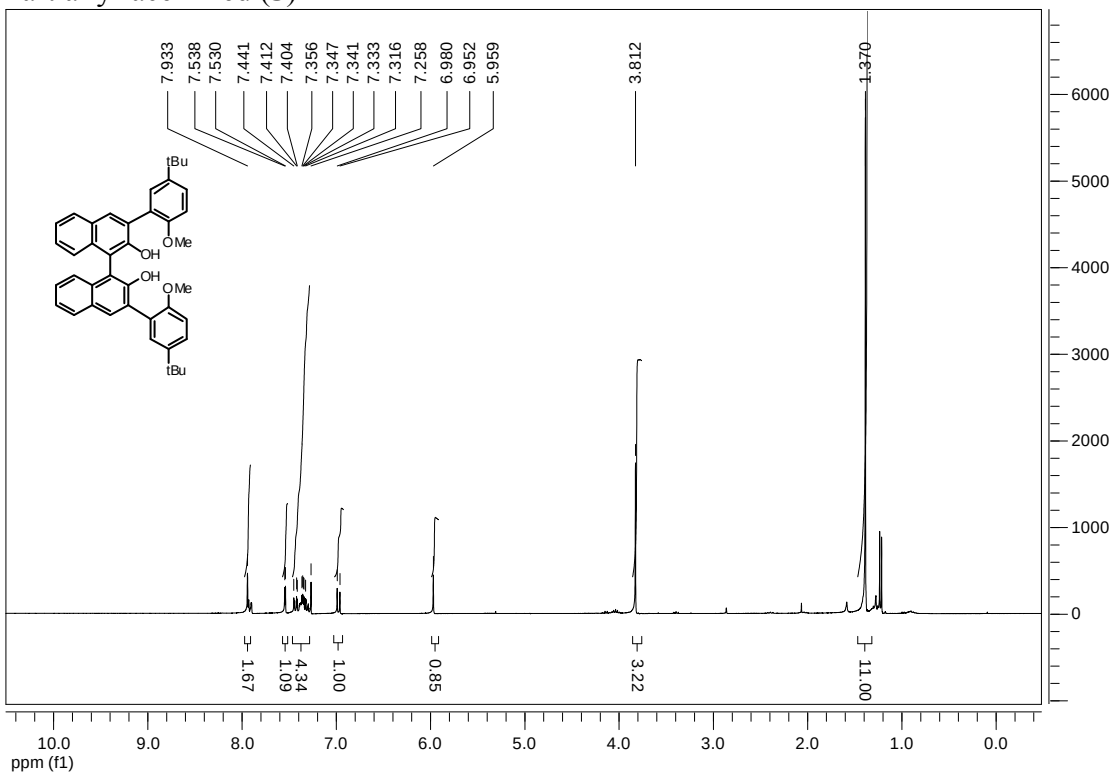
(*S*)-**8**



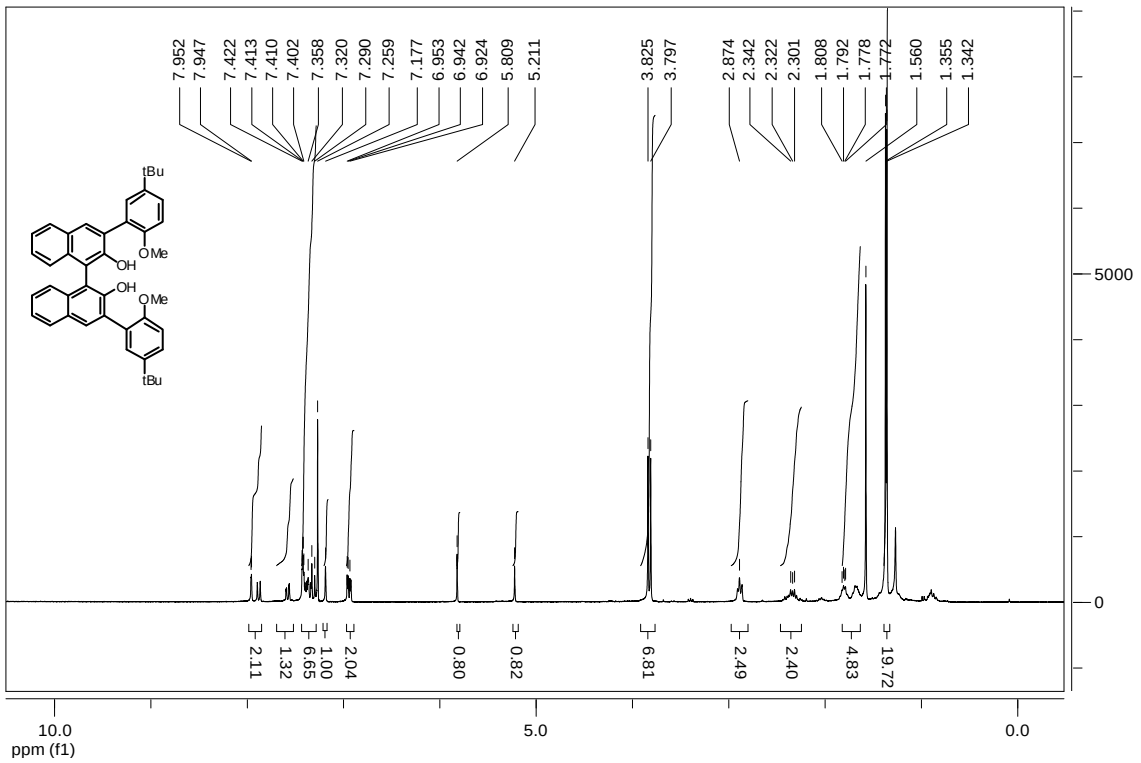
Name	Retention Time	Area	% Area
1	18.650	541518	0.65
2	22.121	82555238	99.35

^{1}H NMR Spectra of Partially Racemized Ligands to Determine Purity

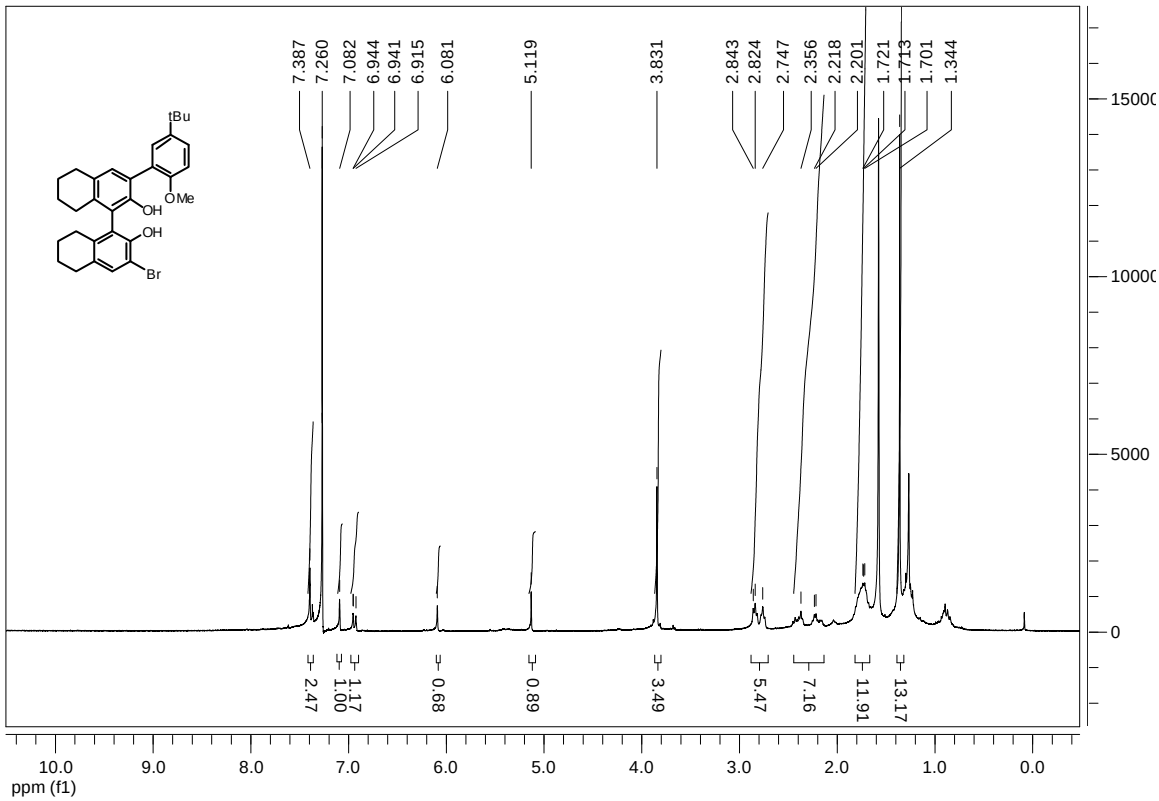
Partially racemized (*S*)-**4**



Partially racemized (*S*)-**6**

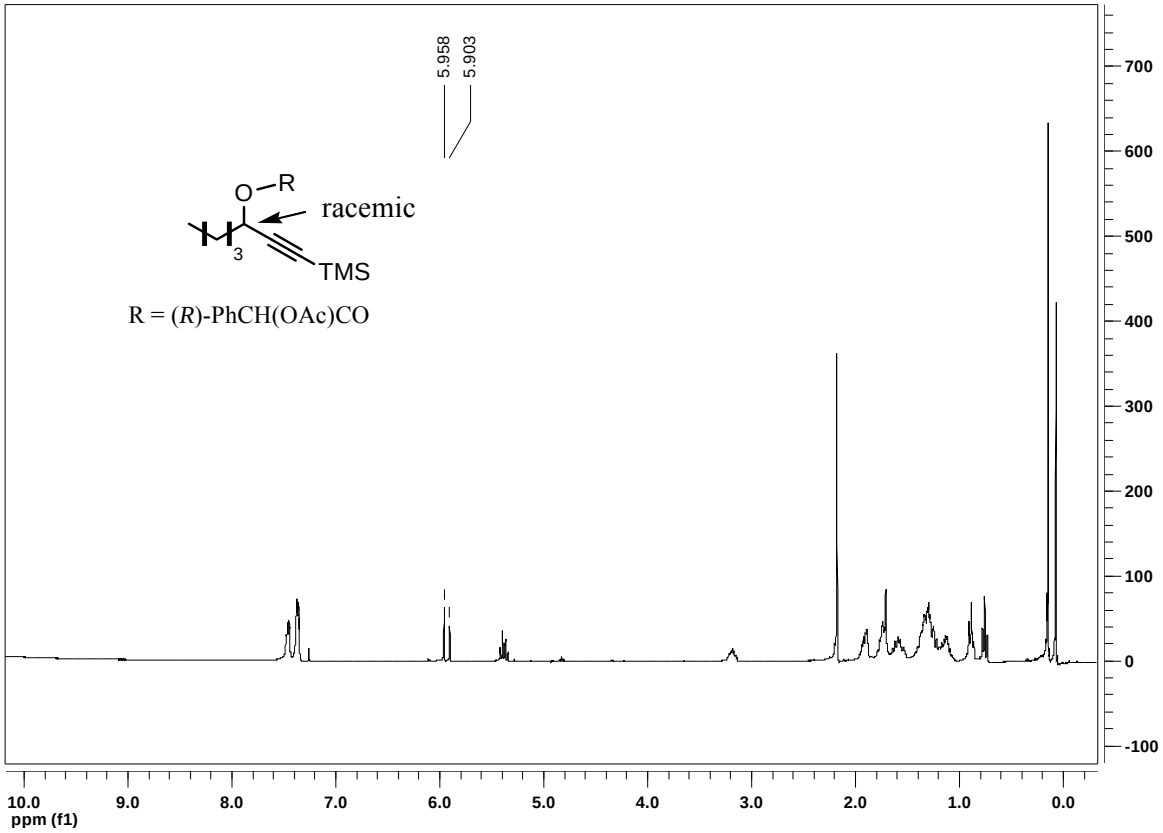


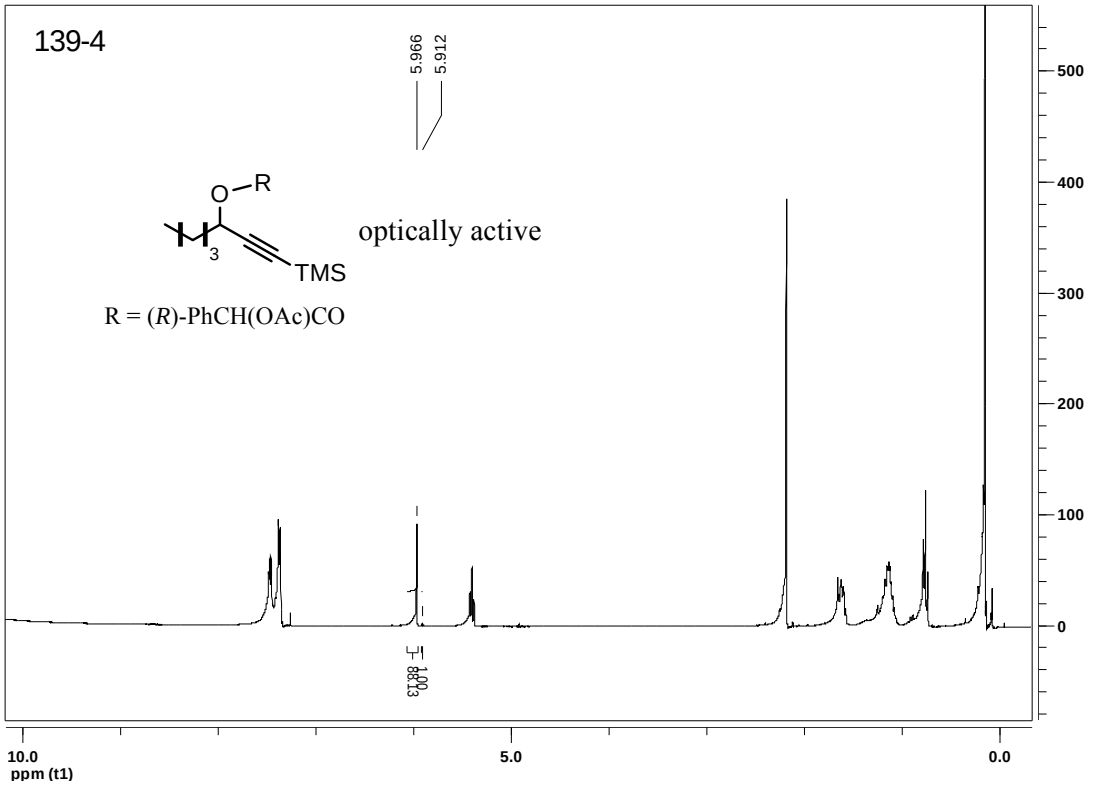
Partially racemized (*S*)-**8**



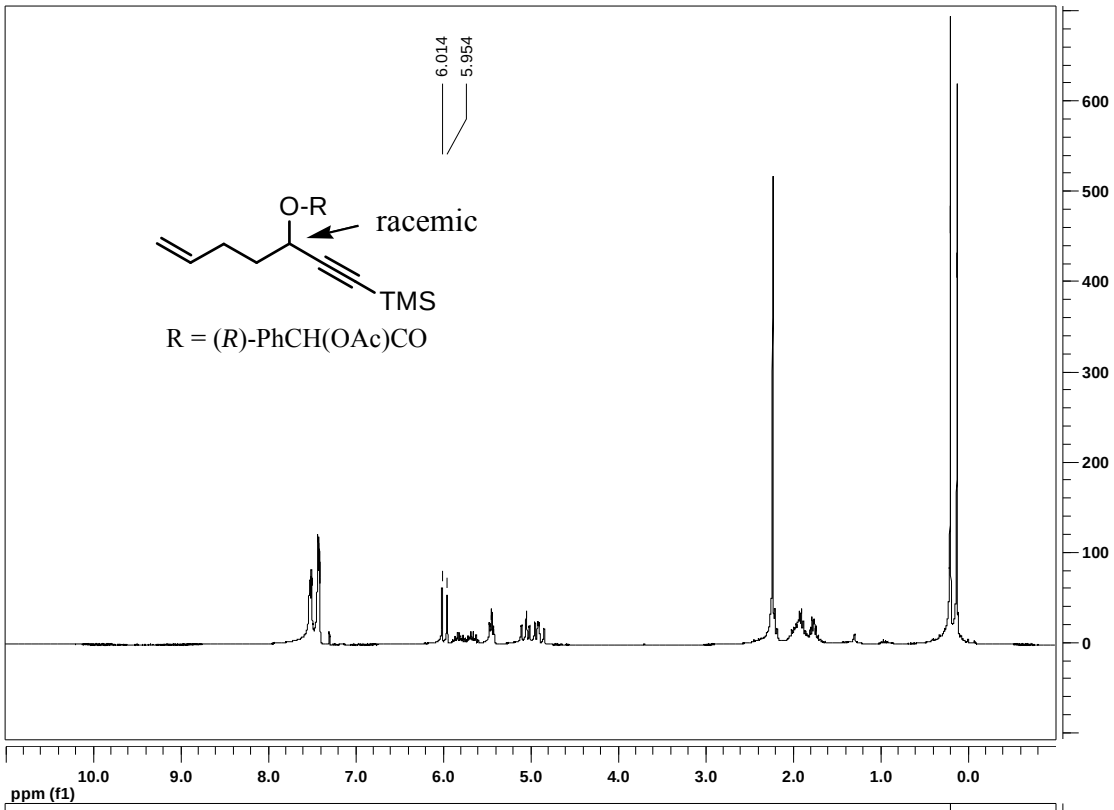
^{1}H NMR Spectra of the Esters Prepared from the Propargylic Alcohols and (*R*)-PhCH(OAc)CO_2H for ee Determination

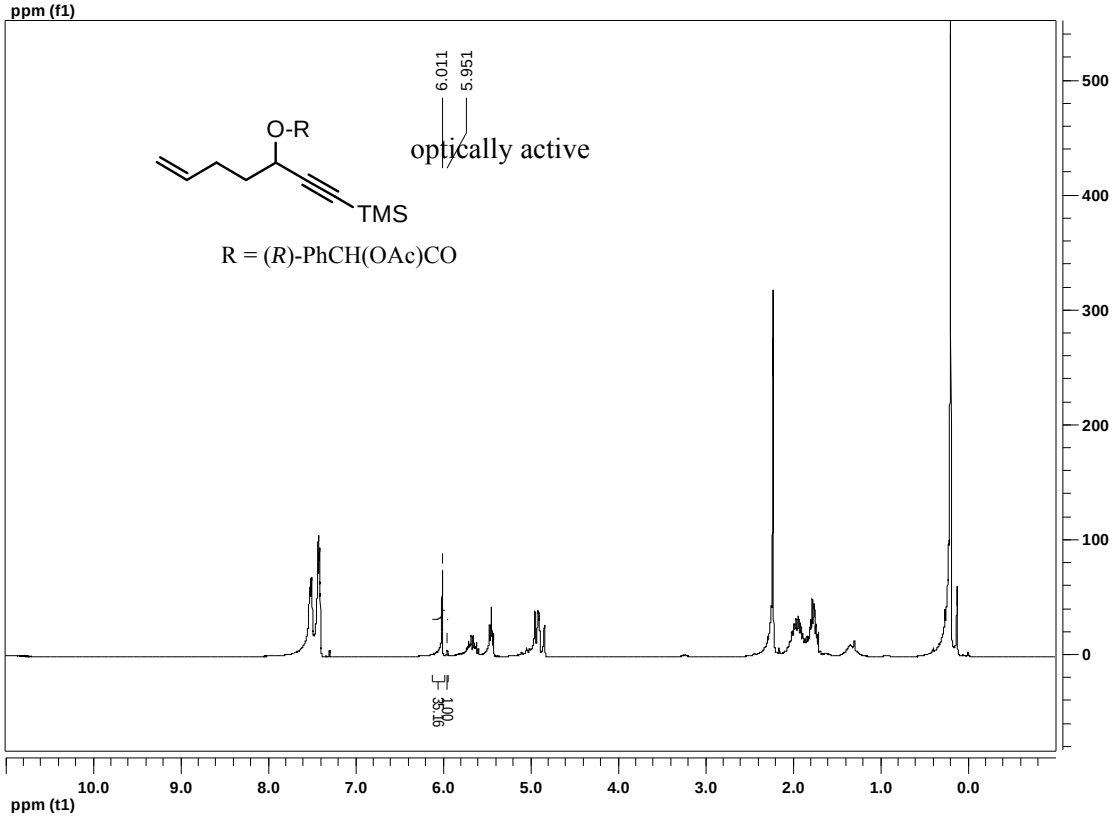
SM-**ae:**



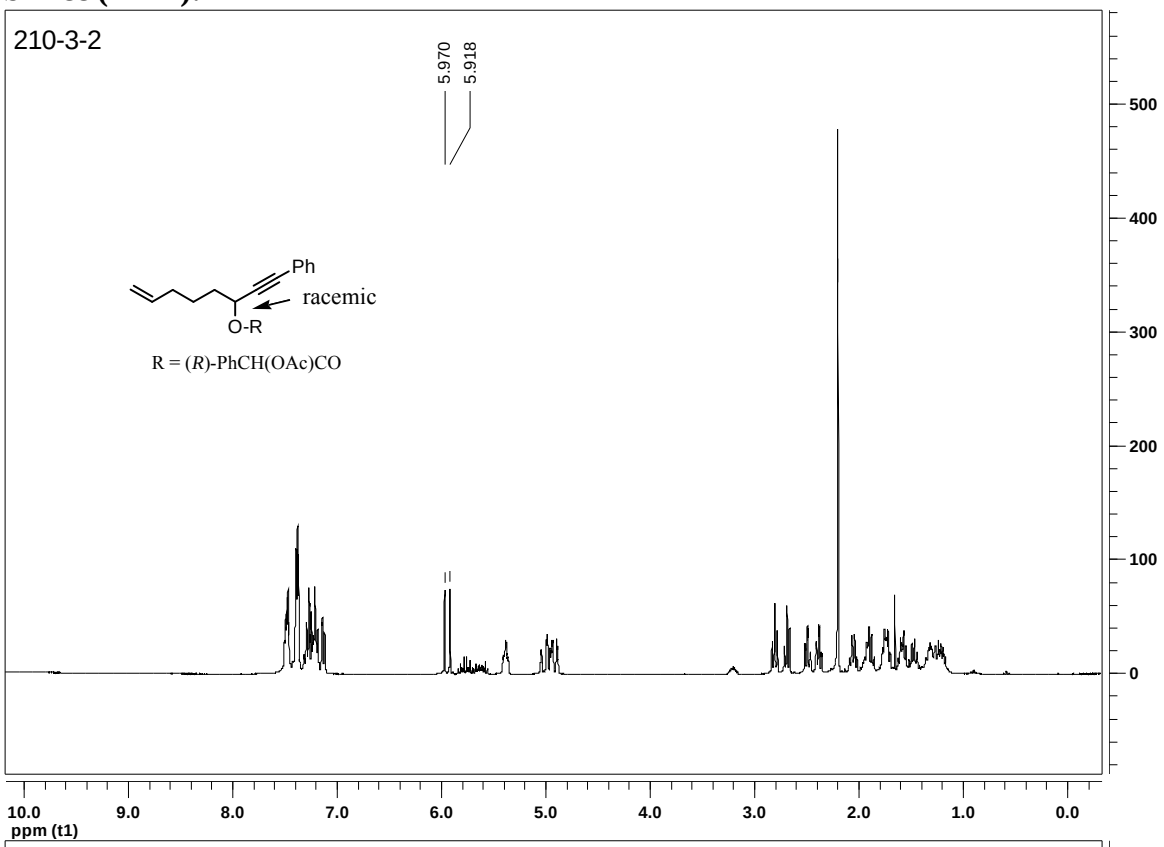

139-4
5.966
5.912
O
R
3
TMS
optically active
R = (R)-PhCH(OAc)CO
1.00
8813
500
400
300
200
100
0
10.0
ppm (t1)
5.0
0.0

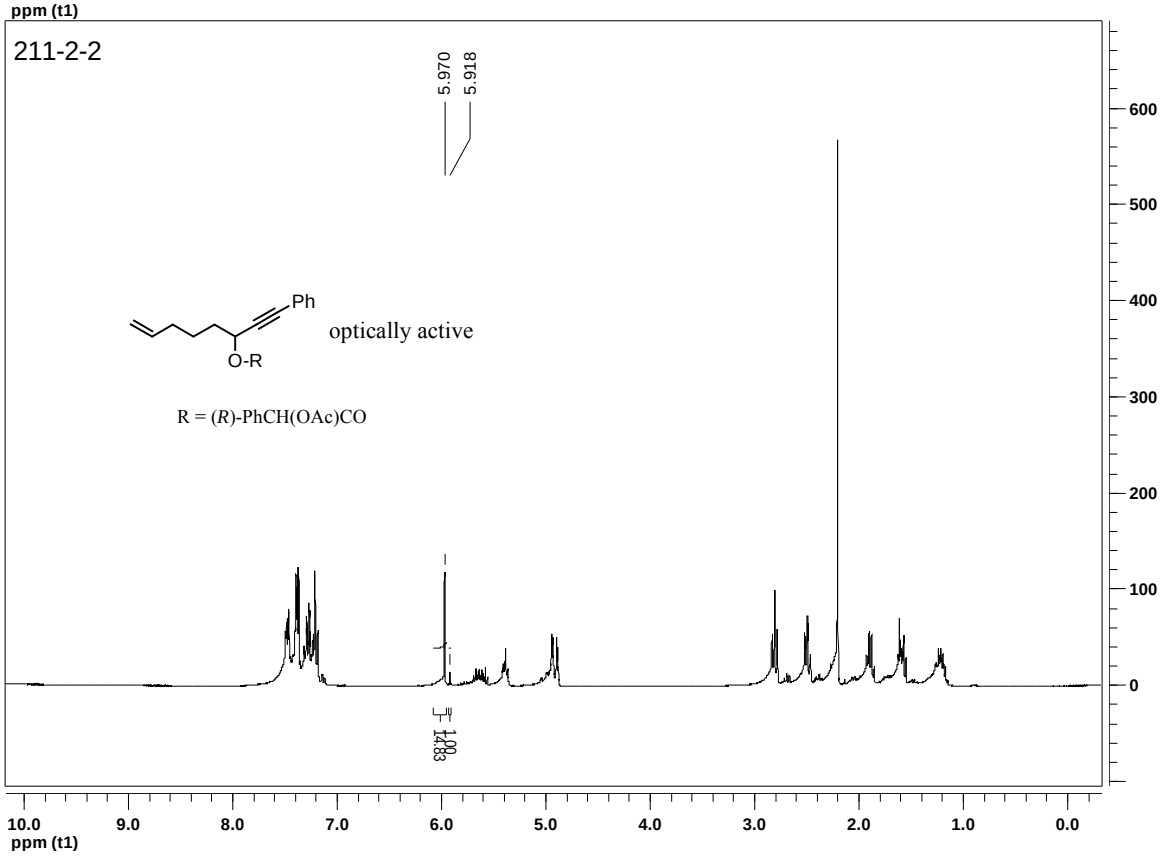
SM-**be**:


6.014
5.954
O-R
racemic
TMS
R = (R)-PhCH(OAc)CO
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

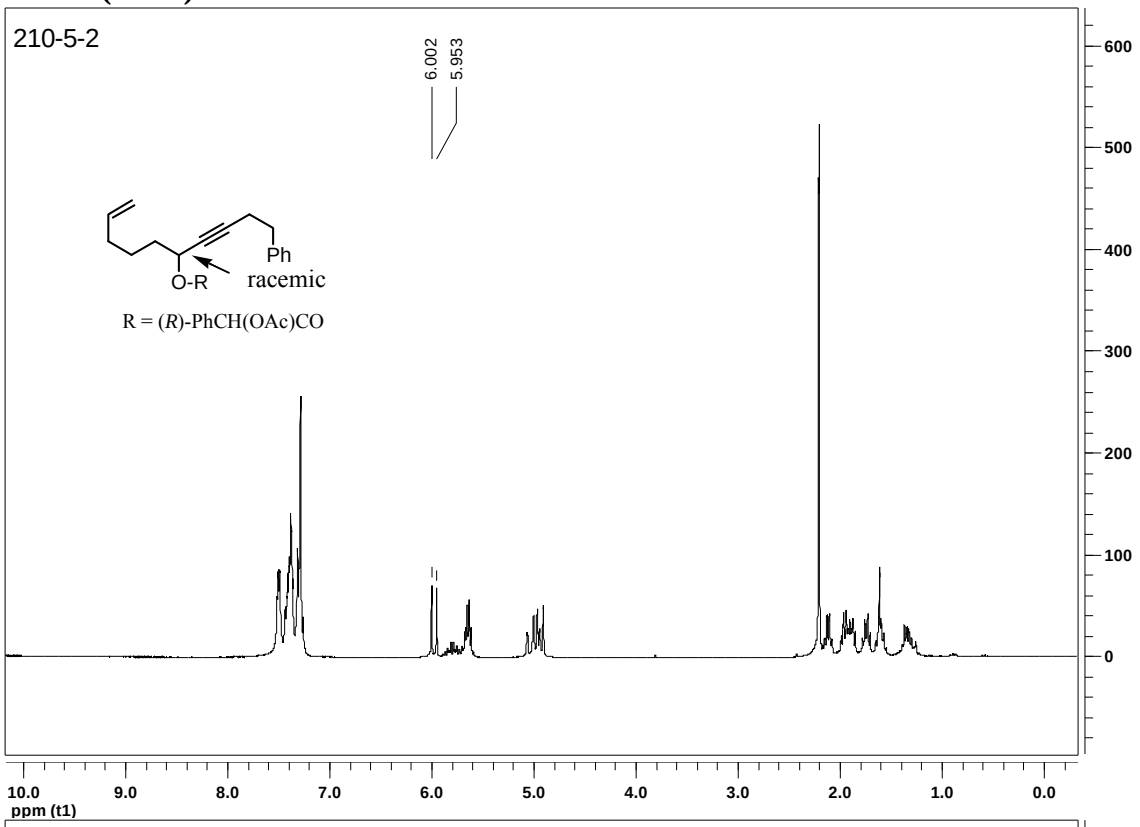

6.011
5.951
O-R
optically active
TMS
R = (R)-PhCH(OAc)CO
1.00
3.06
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

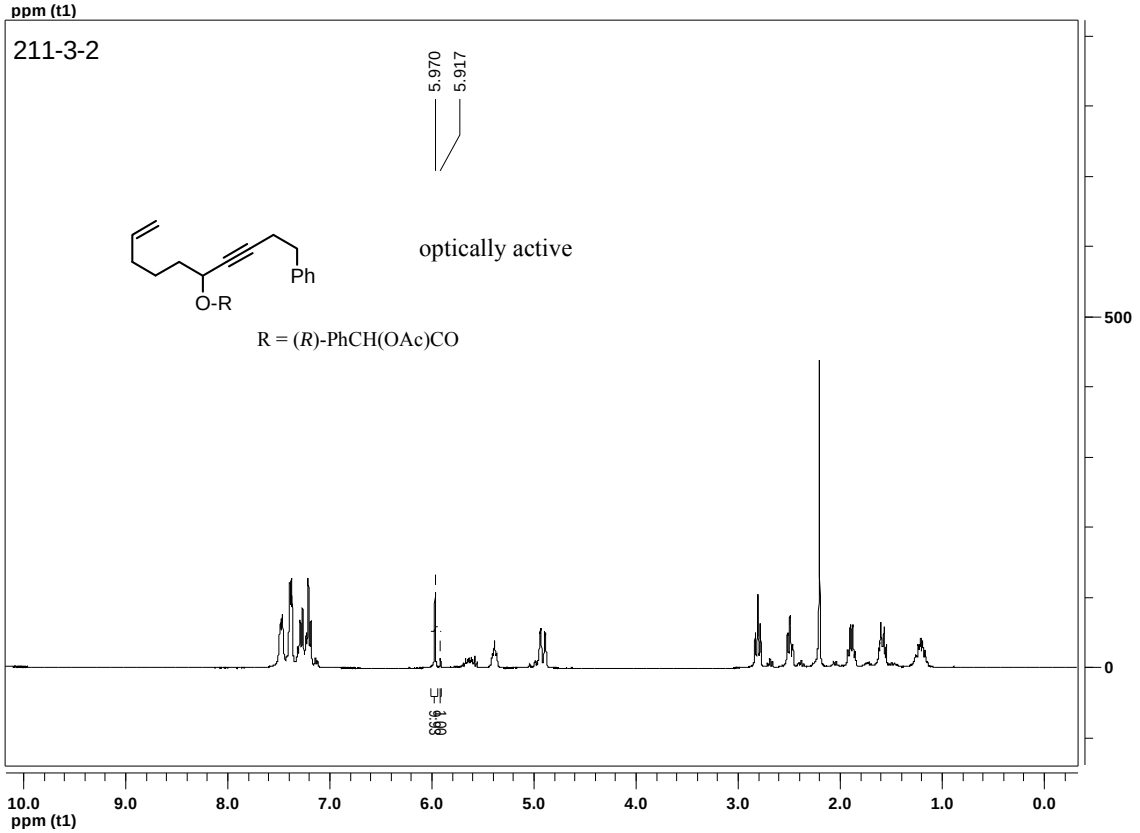
SM-**cc (= P-4):**


210-3-2
5.970
5.918
Ph
racemic
O-R
R = (R)-PhCH(OAc)CO
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

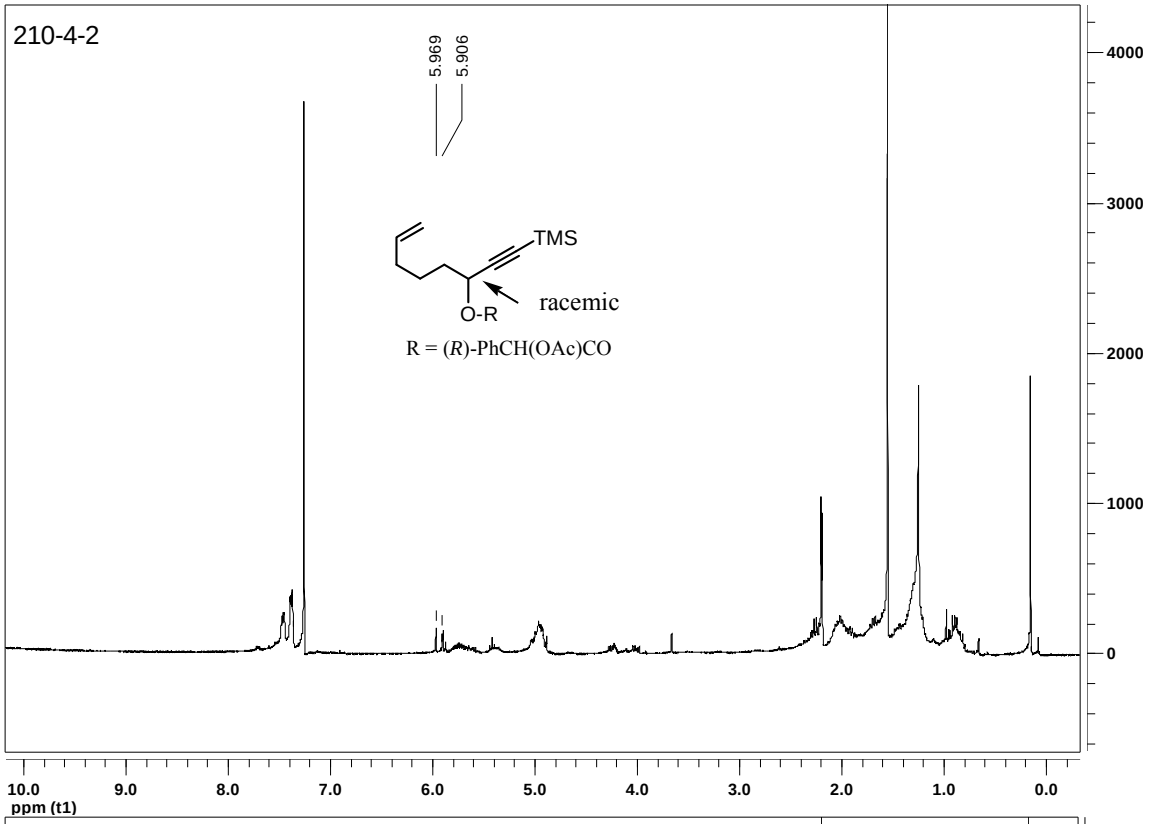

211-2-2
5.970
5.918
Ph
optically active
O-R
R = (R)-PhCH(OAc)CO
1.00
1.83
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

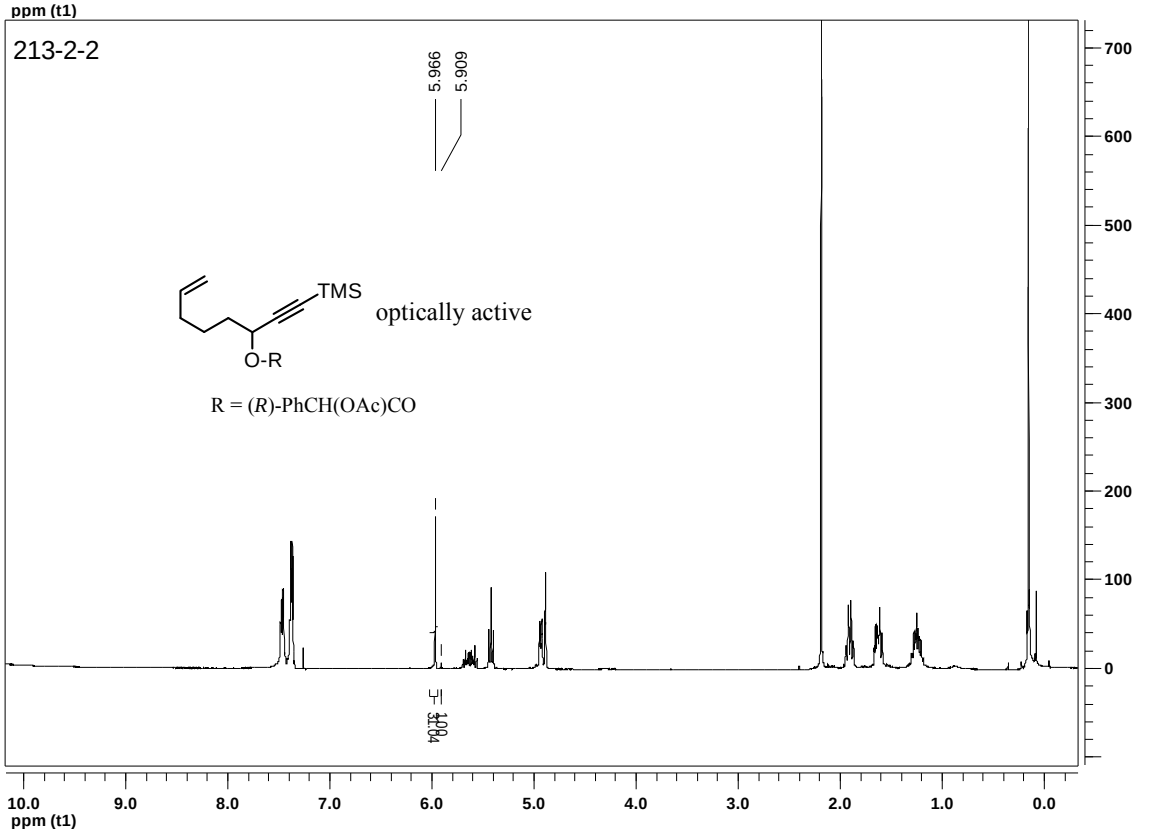
SM-**cd (= P-5)**


210-5-2
6.002
5.953
Ph
racemic
O-R
R = (R)-PhCH(OAc)CO
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

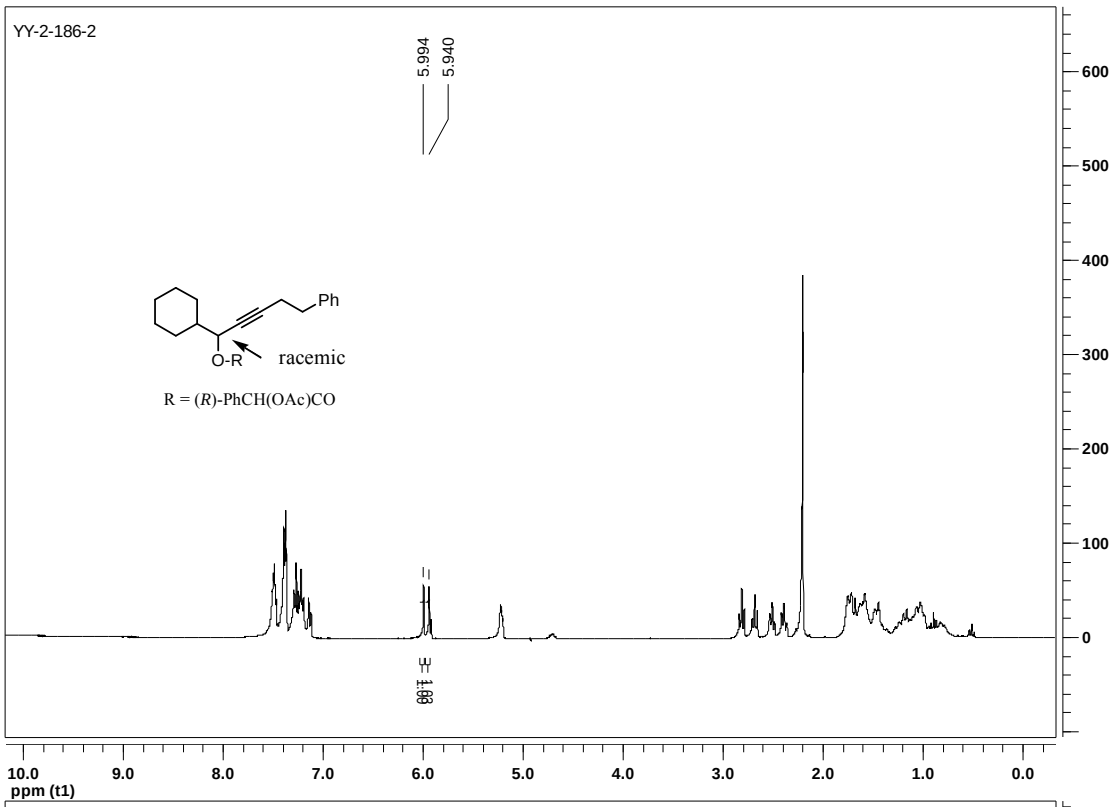

211-3-2
5.970
5.917
optically active
Ph
O-R
R = (R)-PhCH(OAc)CO
500
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

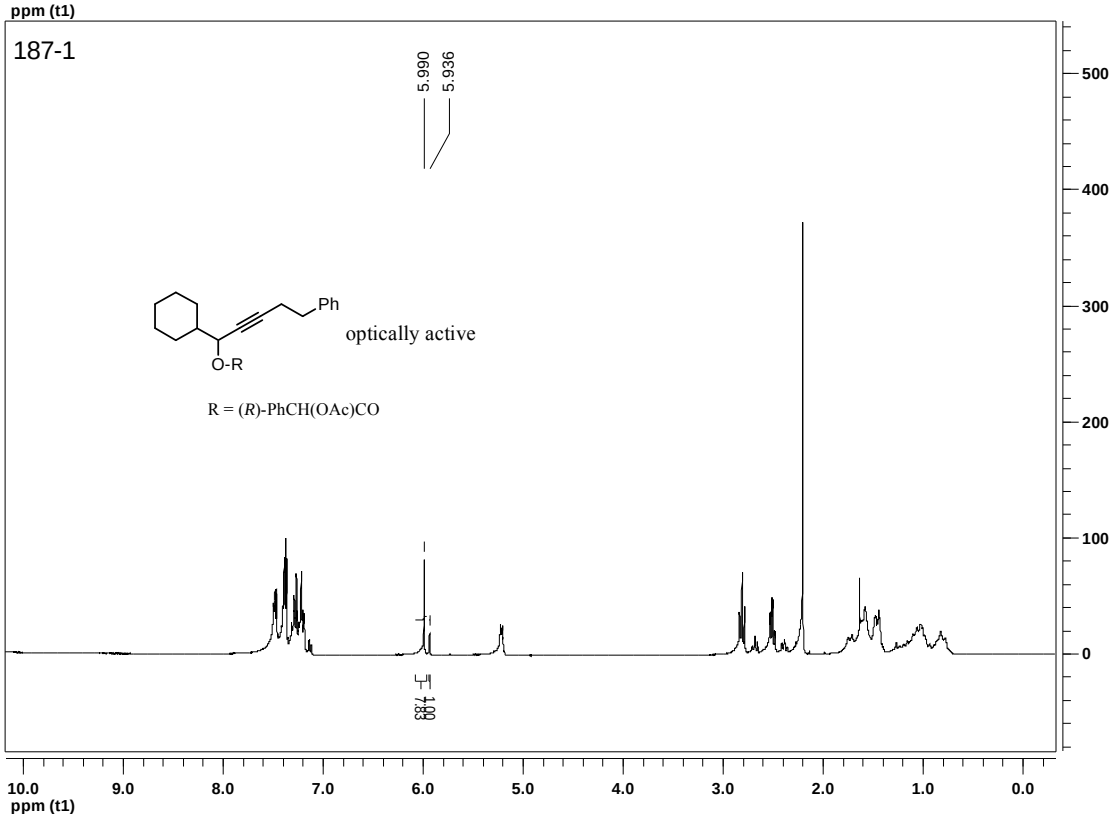
SM-**ce:**


210-4-2
5.969
5.906
TMS
O-R
racemic
R = (R)-PhCH(OAc)CO
4000
3000
2000
1000
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

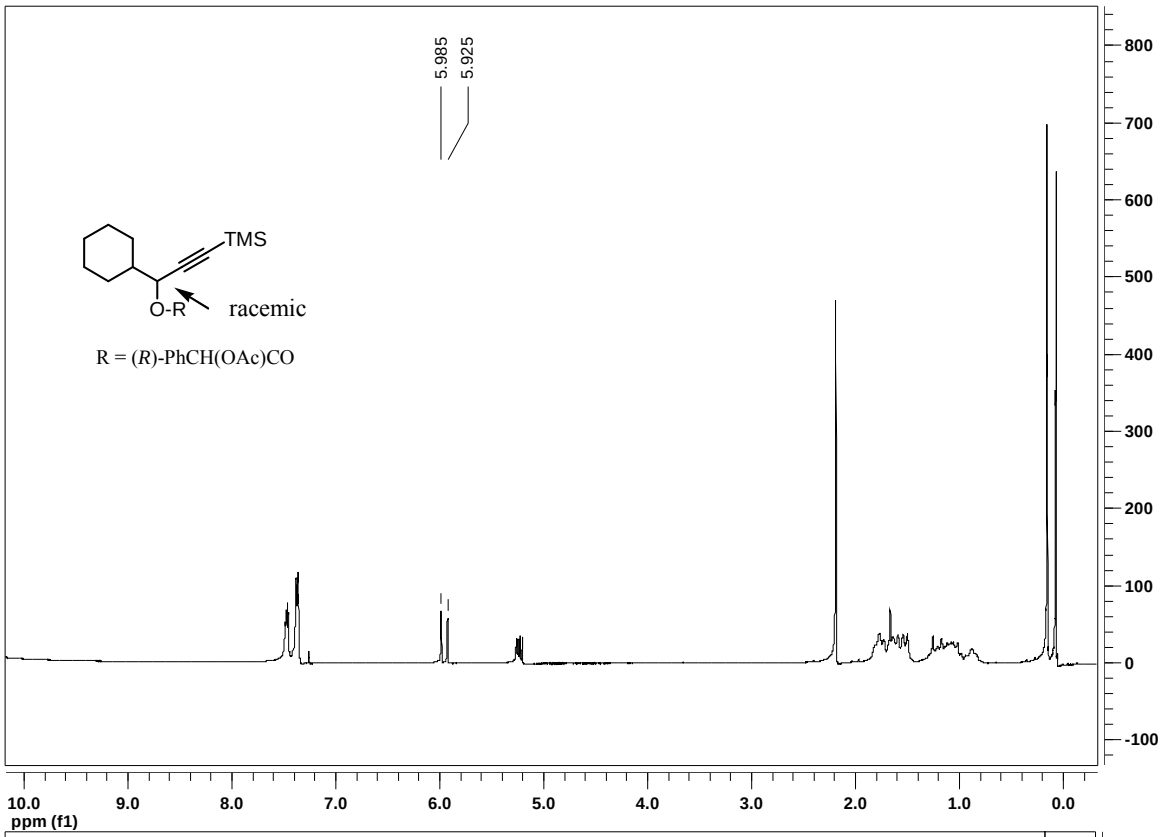

213-2-2
5.966
5.909
TMS
O-R
optically active
R = (R)-PhCH(OAc)CO
3.00
1.04
700
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

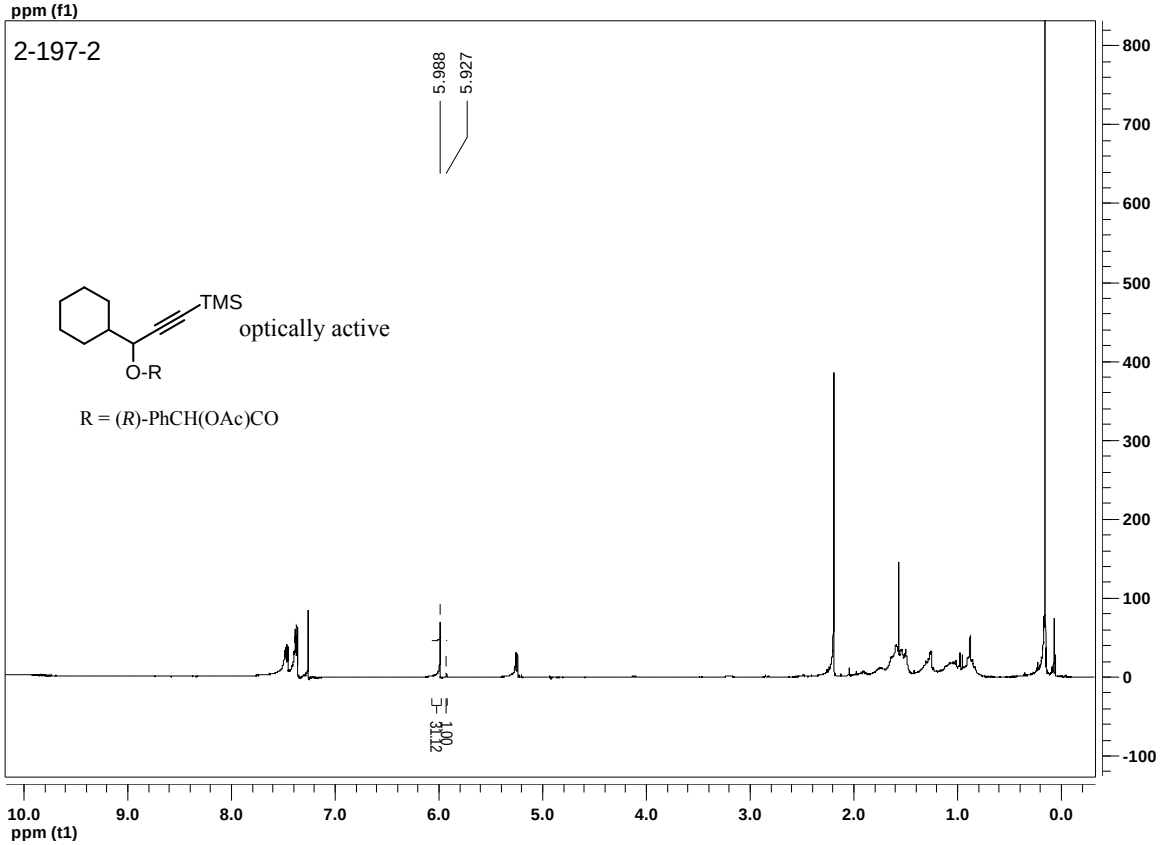
SM-**dd:**


YY-2-186-2
5.994
5.940
Ph
O-R
racemic
R = (R)-PhCH(OAc)CO
1.00
1.88
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

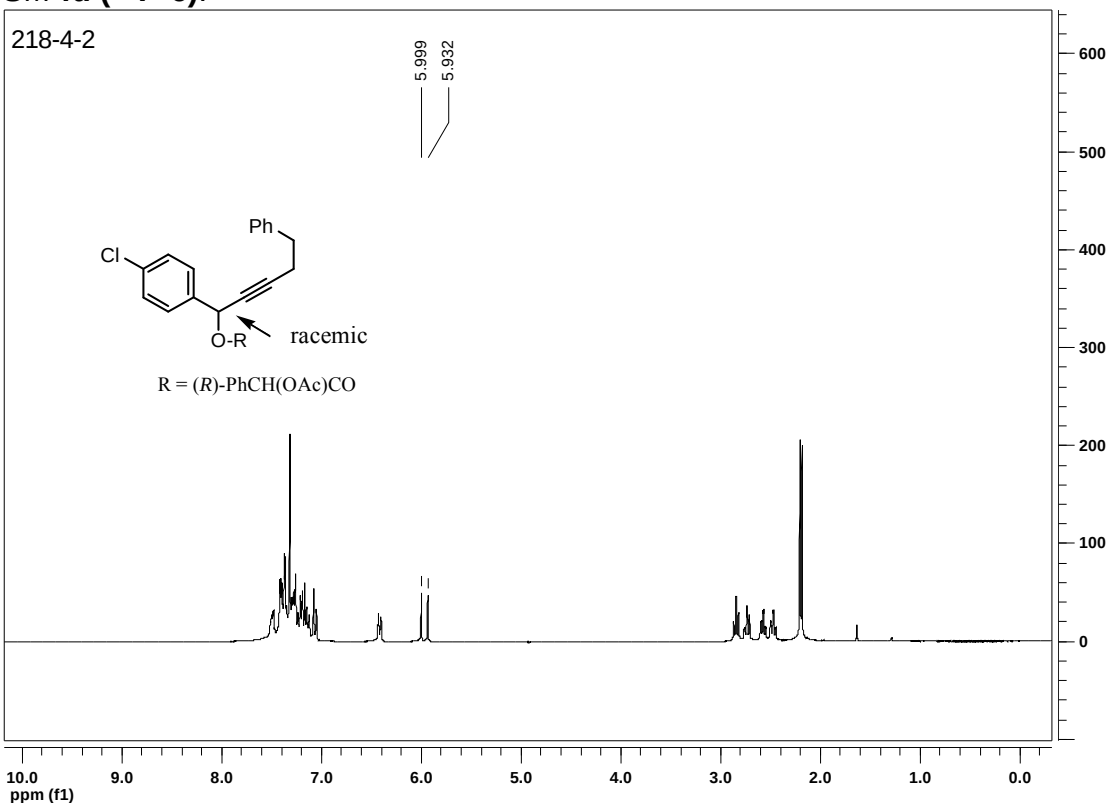

187-1
5.990
5.936
Ph
O-R
optically active
R = (R)-PhCH(OAc)CO
1.00
1.83
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

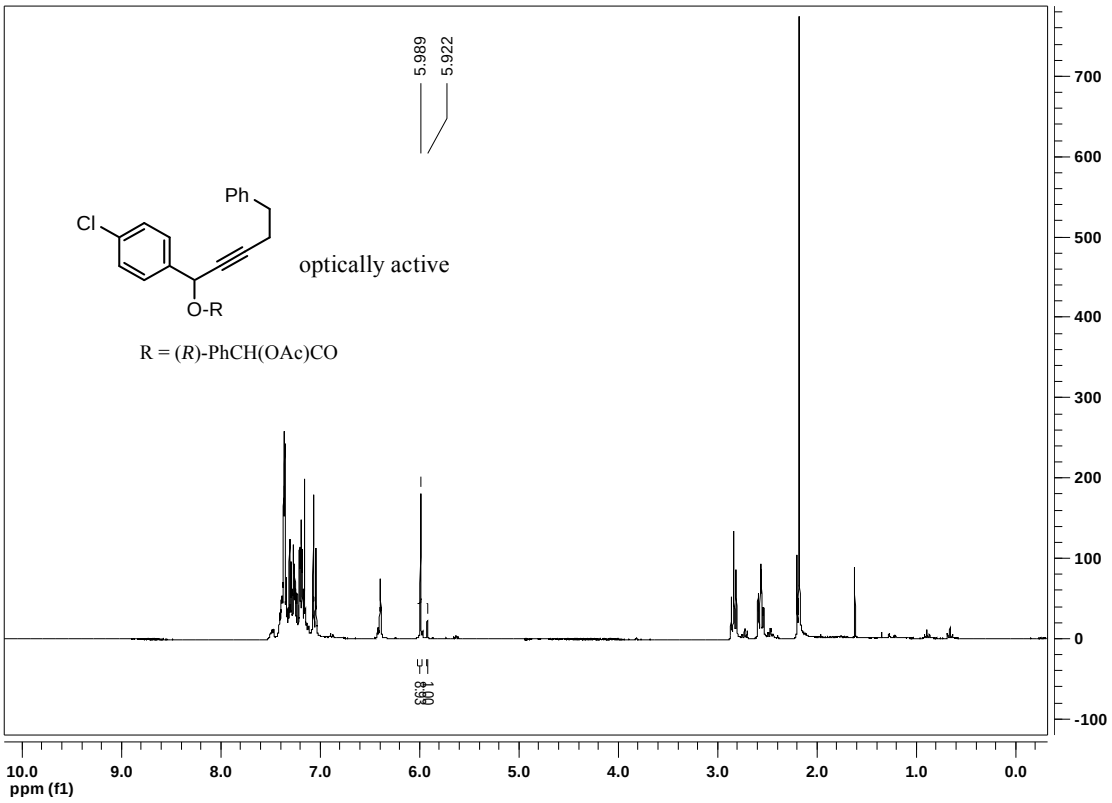
SM-**de:**


5.985
5.925
TMS
O-R
racemic
R = (R)-PhCH(OAc)CO
ppm (f1)

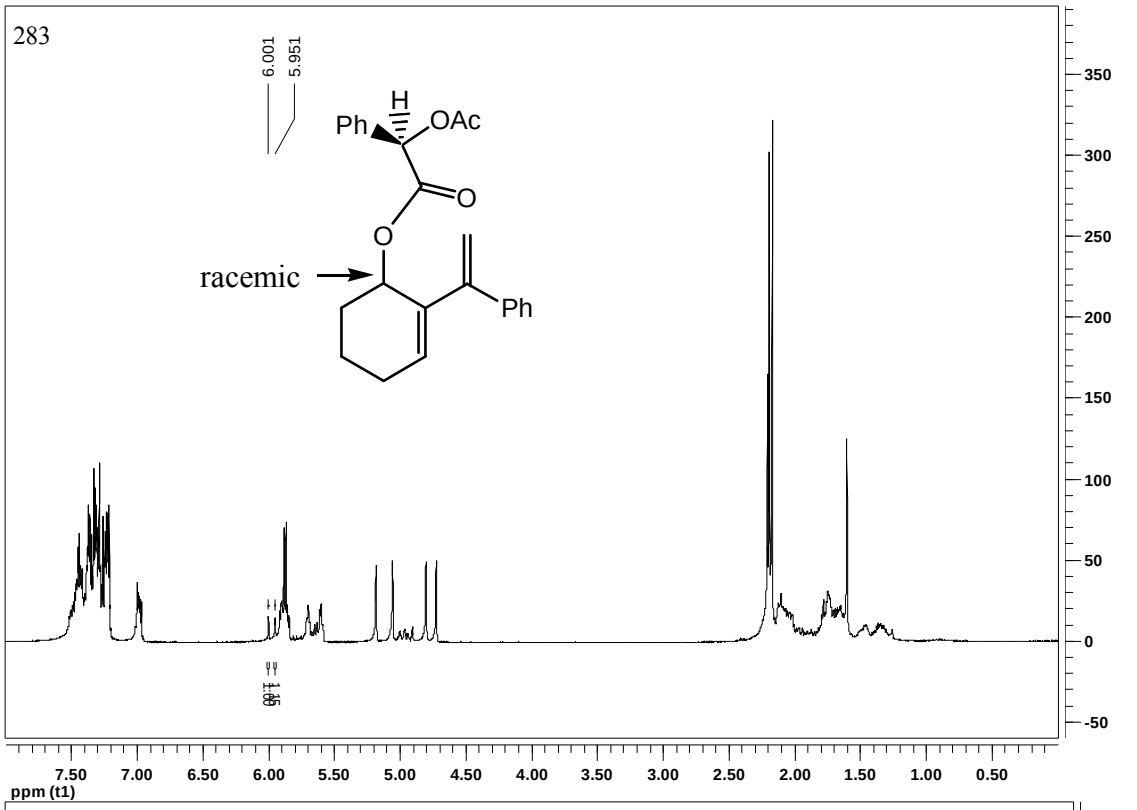

2-197-2
5.988
5.927
TMS
O-R
optically active
R = (R)-PhCH(OAc)CO
3.112
1.000
ppm (t1)

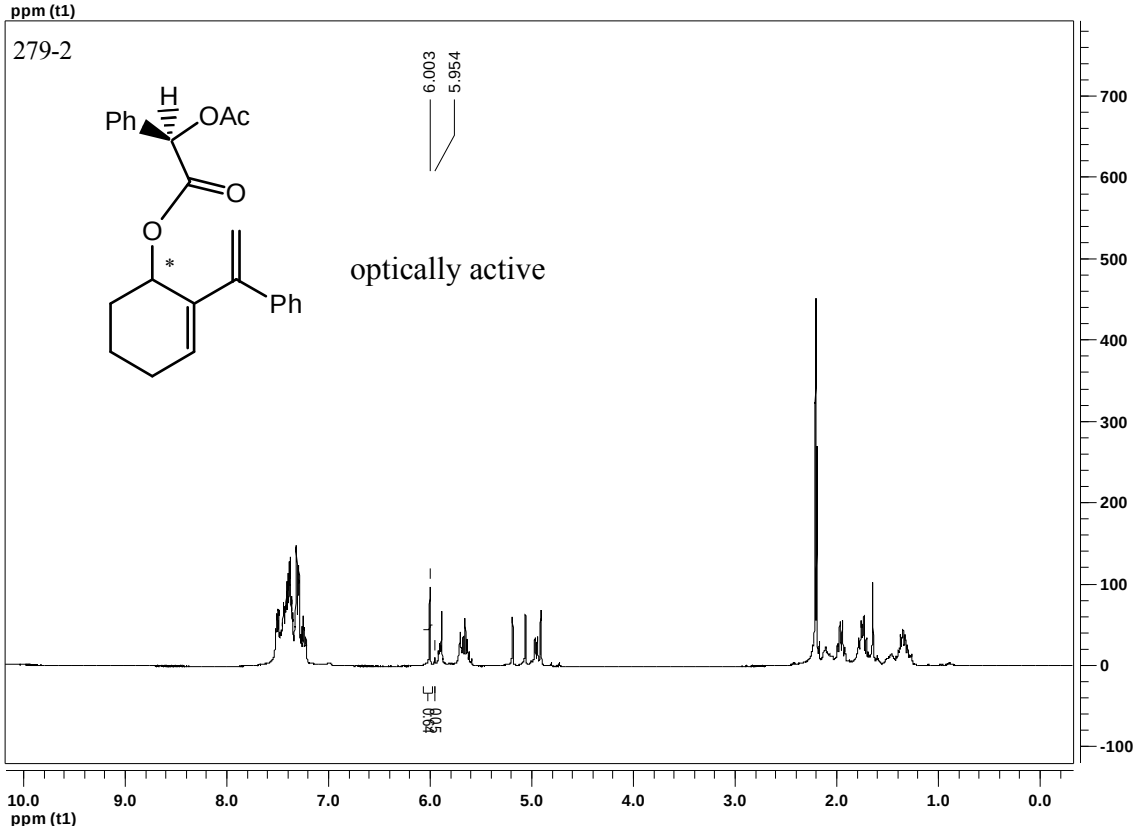
SM-**fd (= P-6)**:


218-4-2
5.999
5.932
Ph
Cl
O-R
racemic
R = (R)-PhCH(OAc)CO
600
500
400
300
200
100
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

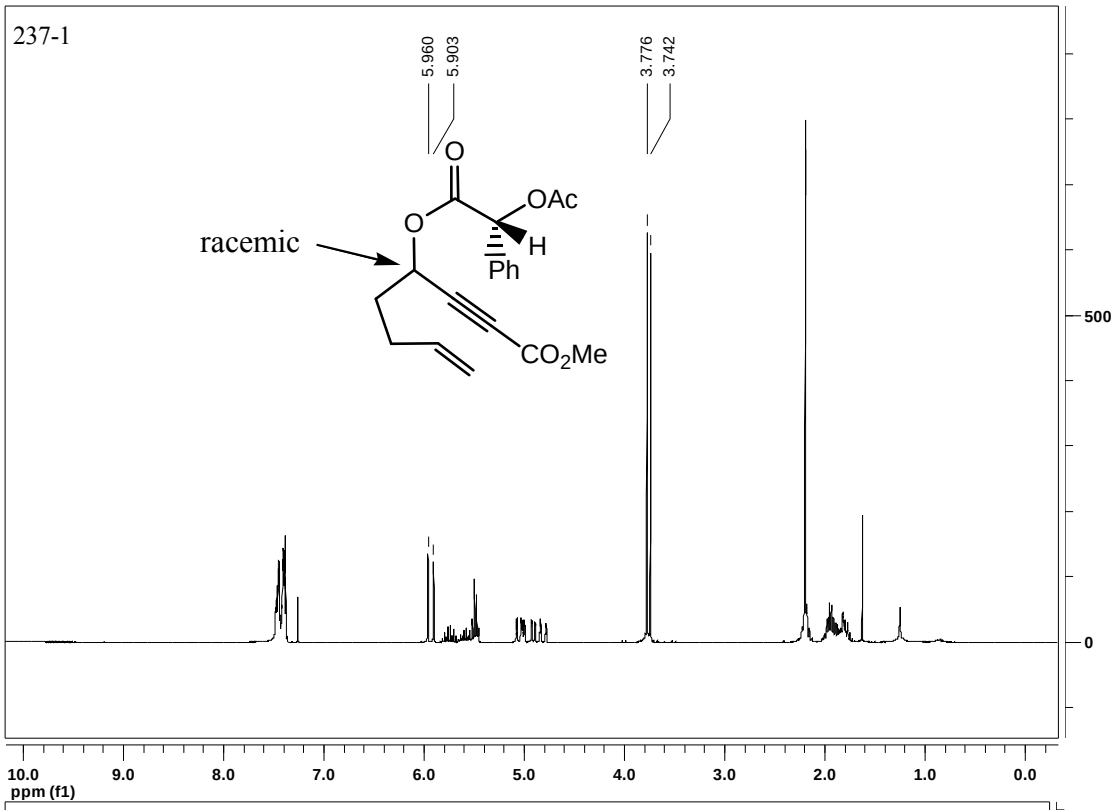

5.989
5.922
Ph
Cl
O-R
optically active
R = (R)-PhCH(OAc)CO
700
600
500
400
300
200
100
0
-100
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

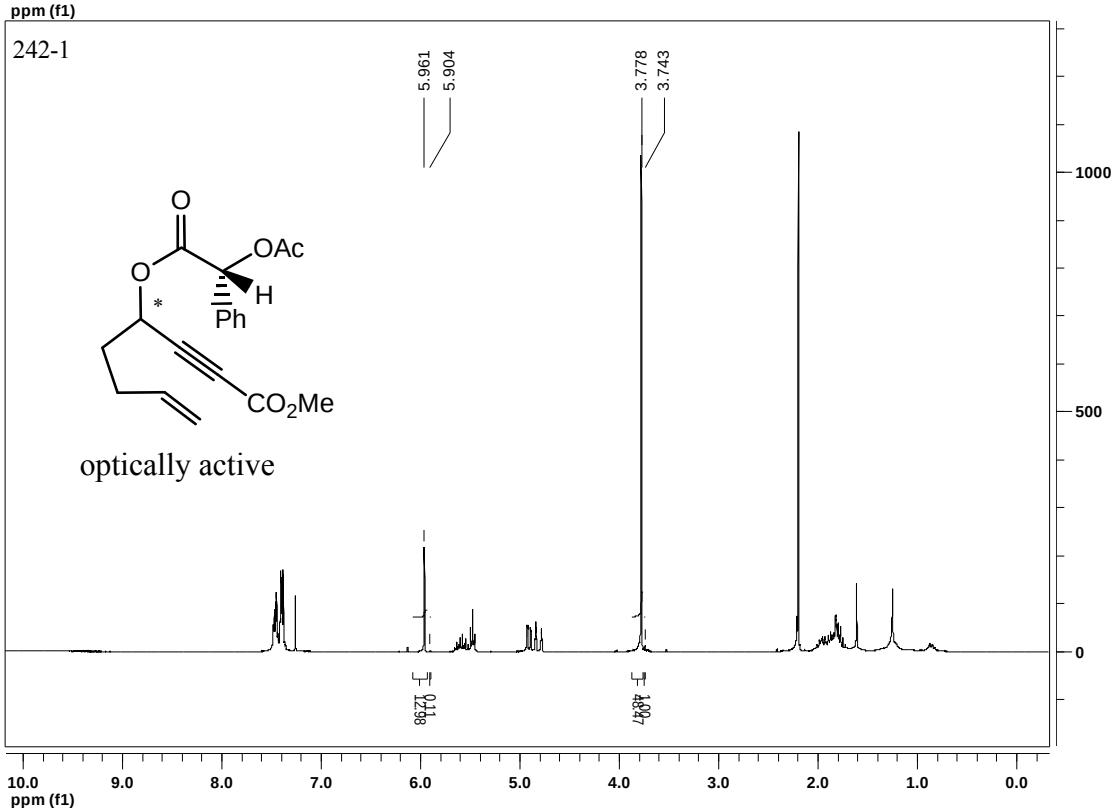
13:


283
6.001
5.951
H
Ph
OAc
O
O
racemic
Ph
1.00
1.45
350
300
250
200
150
100
50
0
-50
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)

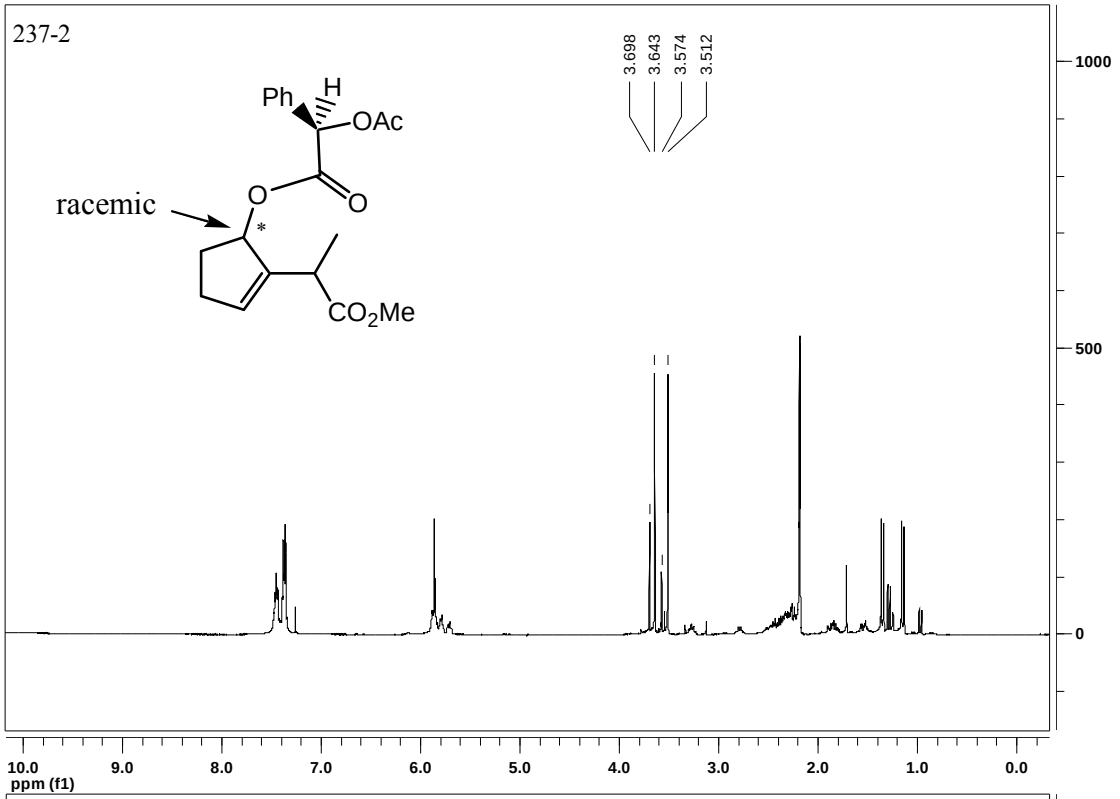

279-2
6.003
5.954
H
Ph
OAc
O
O
*
Ph
optically active
1.00
5.00
700
600
500
400
300
200
100
0
-100
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

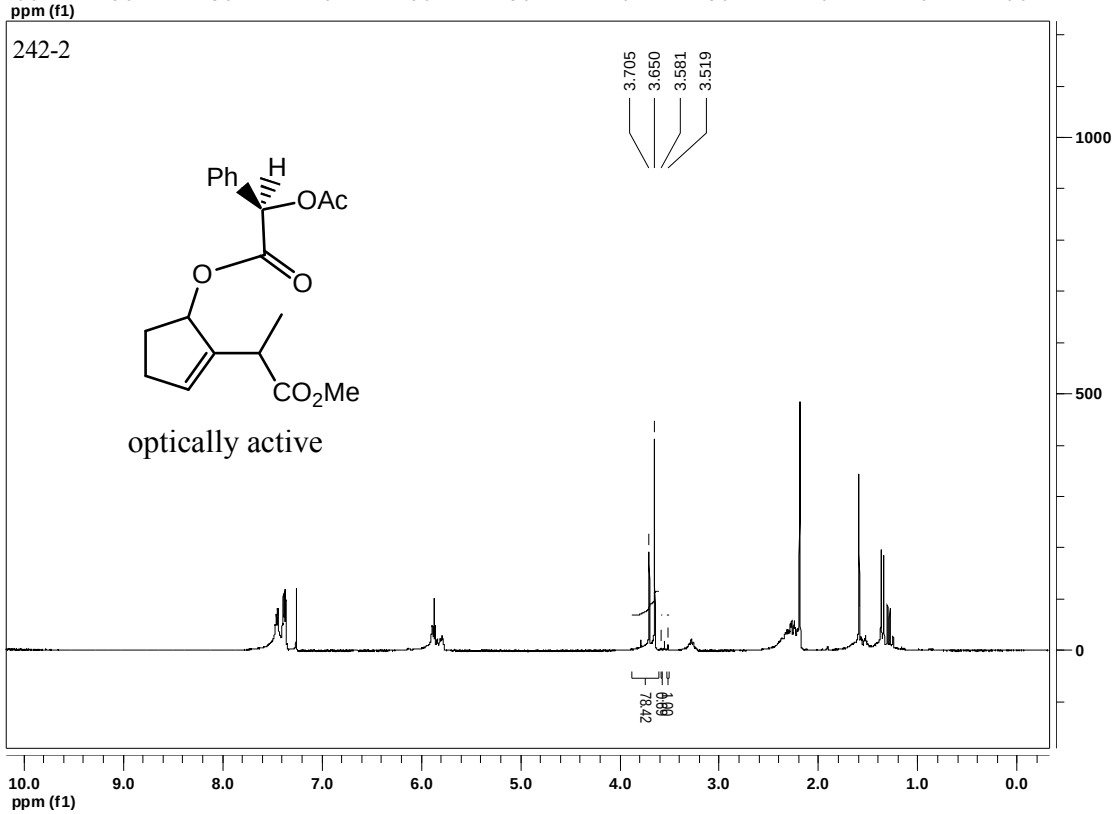
15b:


237-1
5.960
5.903
3.776
3.742
racemic
O
OAc
O
H
Ph
CO2Me
500
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

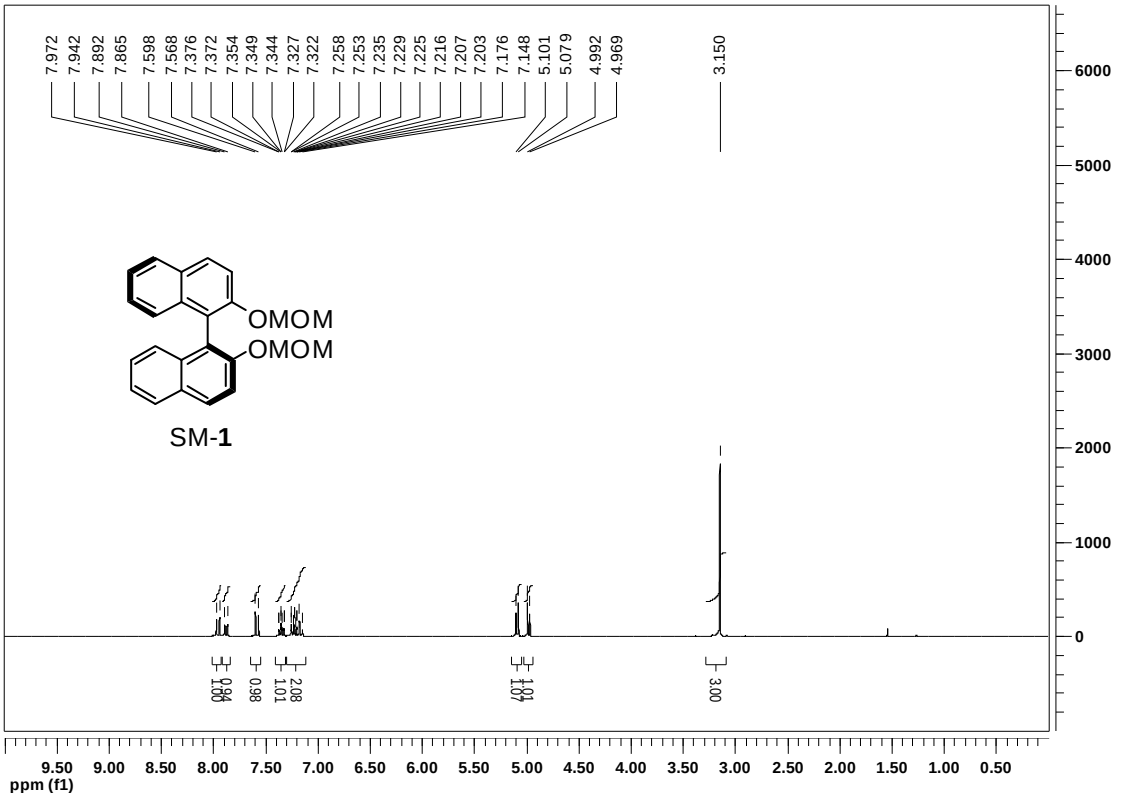

242-1
5.961
5.904
3.778
3.743
O
OAc
O
*
H
Ph
CO2Me
optically active
1.0000
1.2986
4.8947
1000
500
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

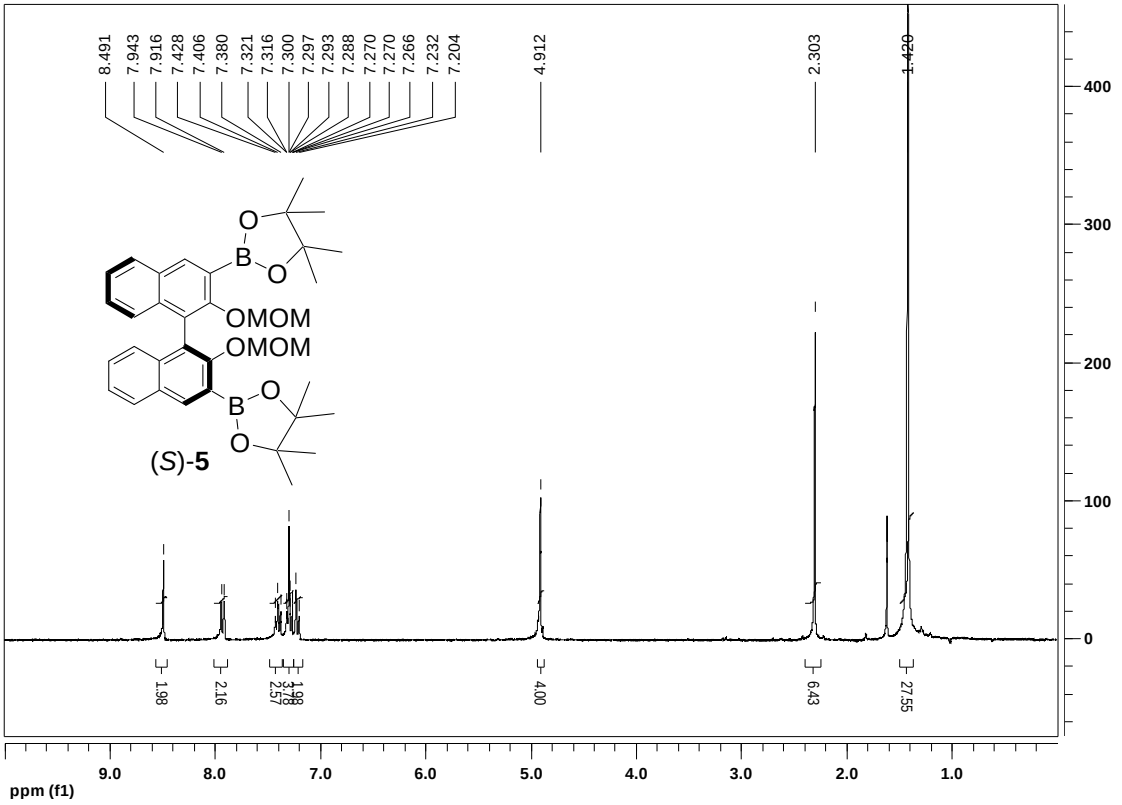
16b:

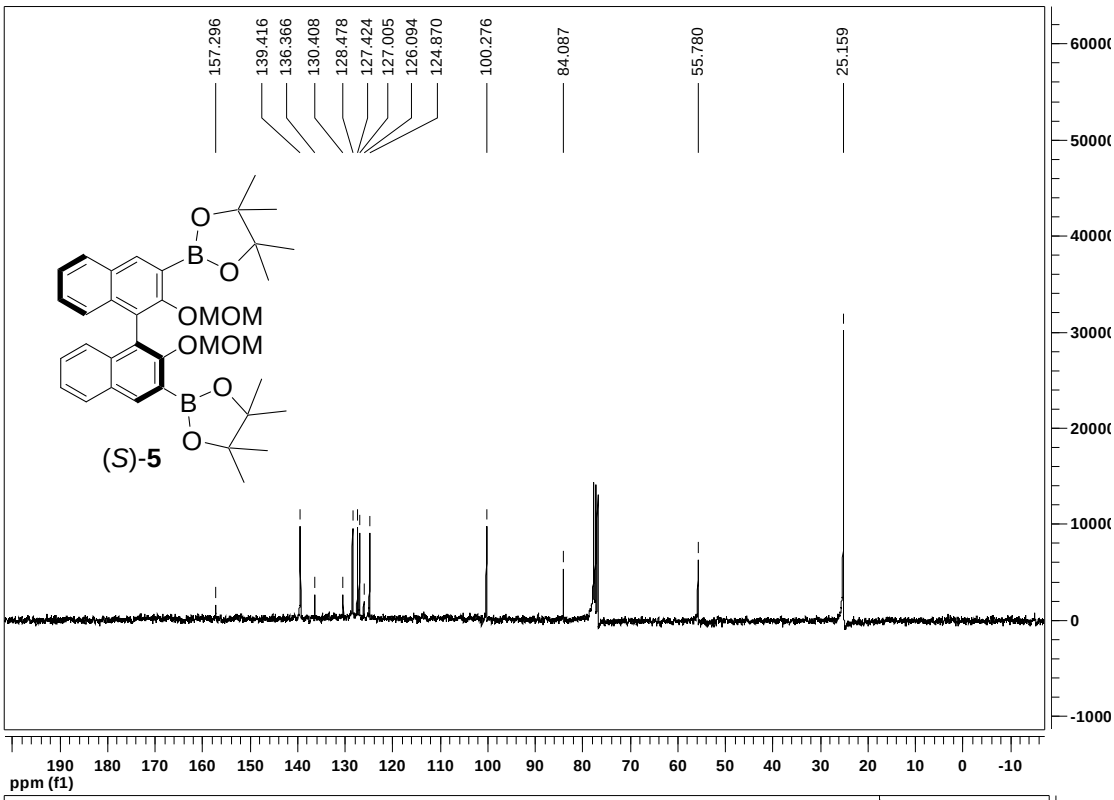

237-2
3.698
3.643
3.574
3.512
Ph
H
OAc
O
O
racemic
*
CO2Me
1000
500
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

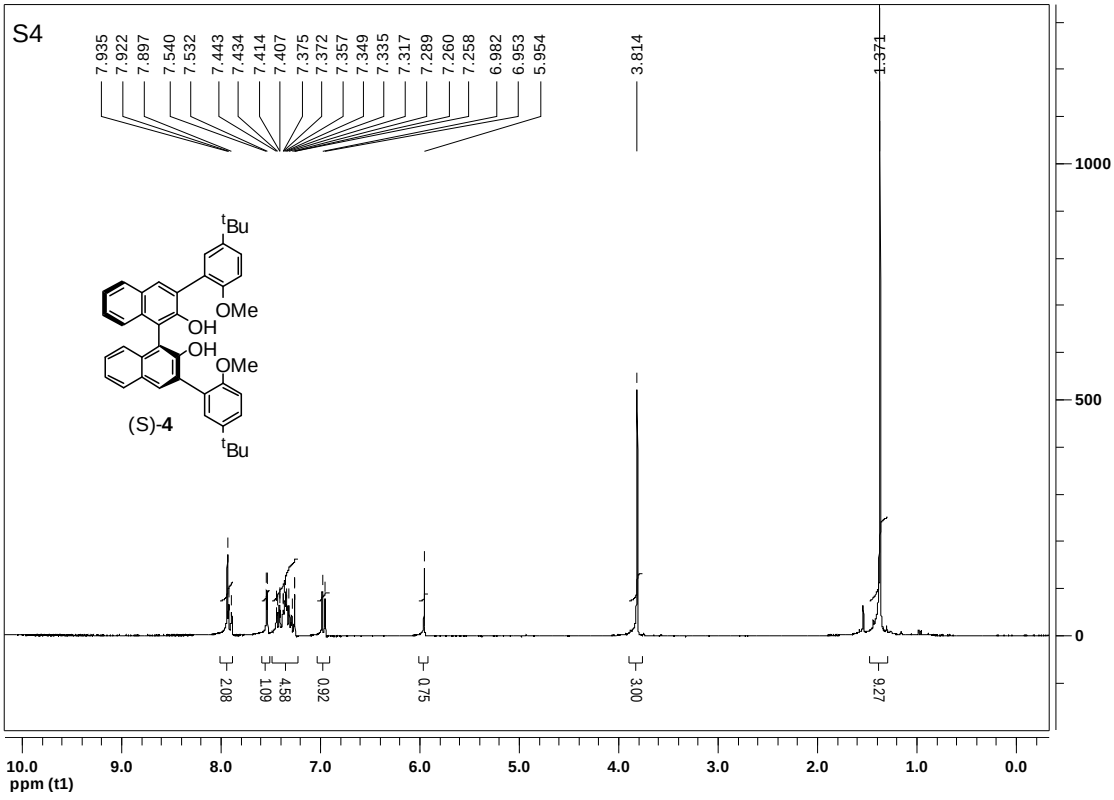

242-2
3.705
3.650
3.581
3.519
Ph
H
OAc
O
O
CO2Me
optically active
7.842
1000
500
0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

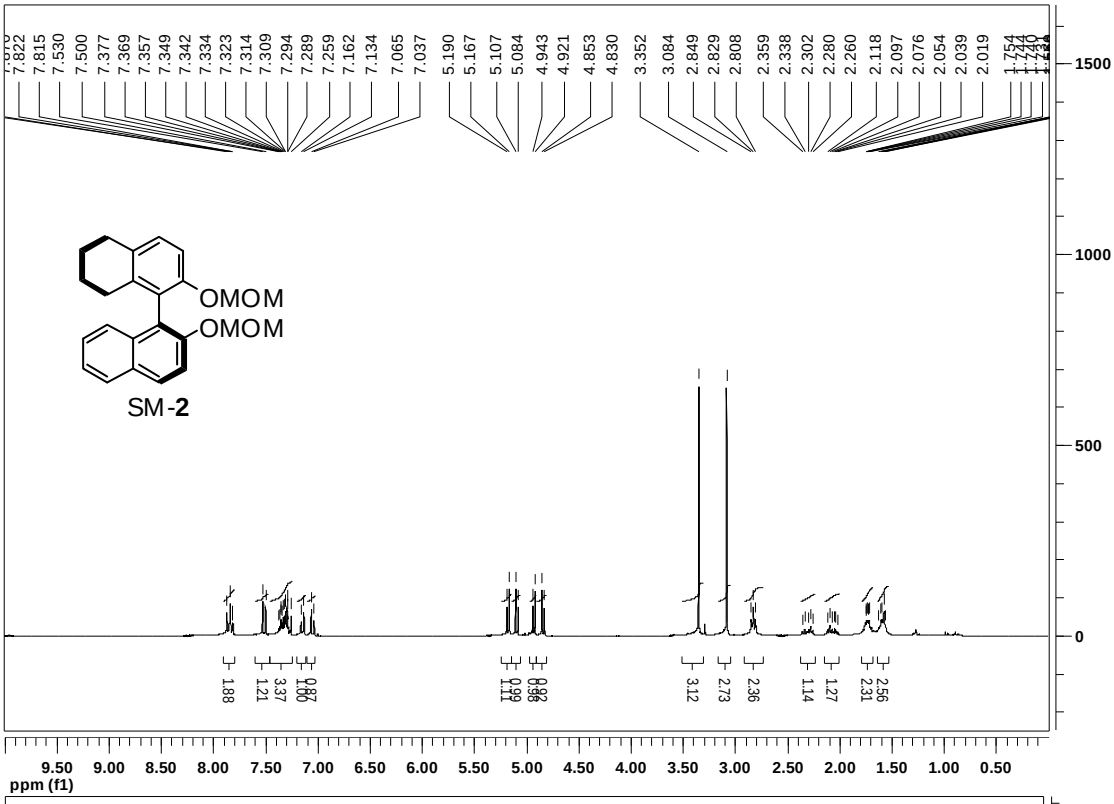
^{1}H and ^{13}C NMR Spectra

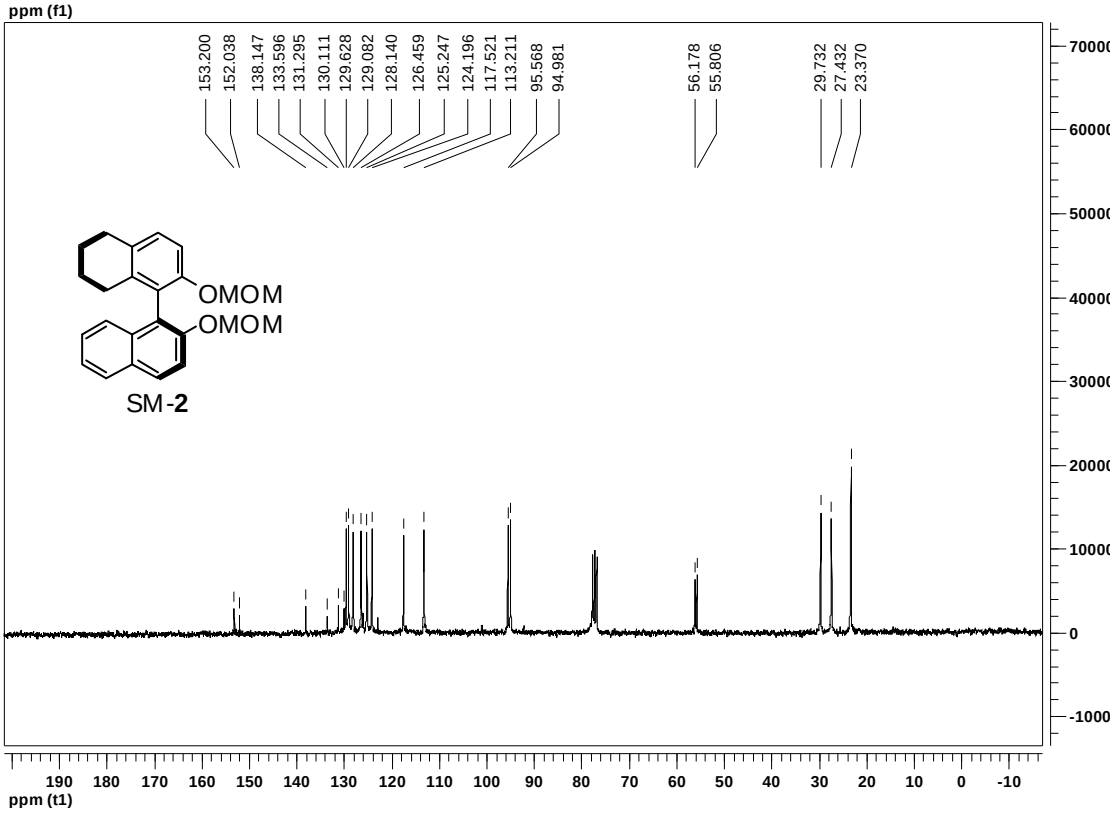


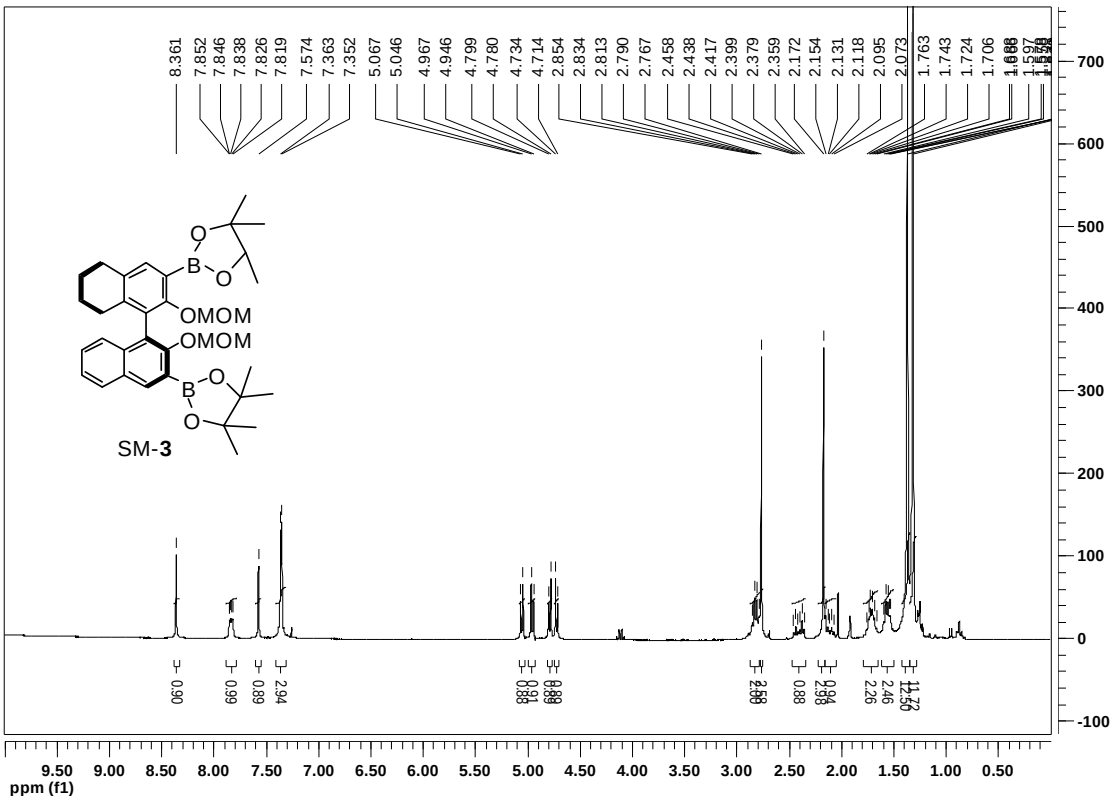


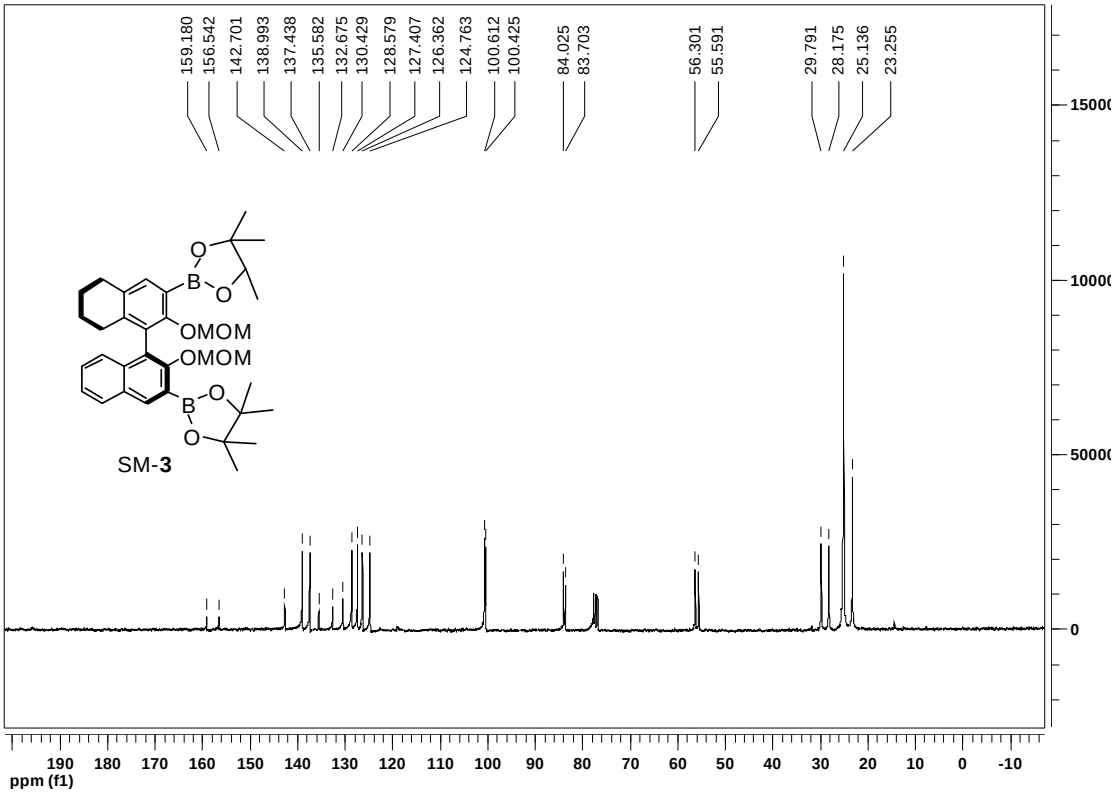

157.296
139.416
136.366
130.408
128.478
127.424
127.005
126.094
124.870
100.276
84.087
55.780
25.159
OMOM
OMOM
(S)-5
ppm (f1)

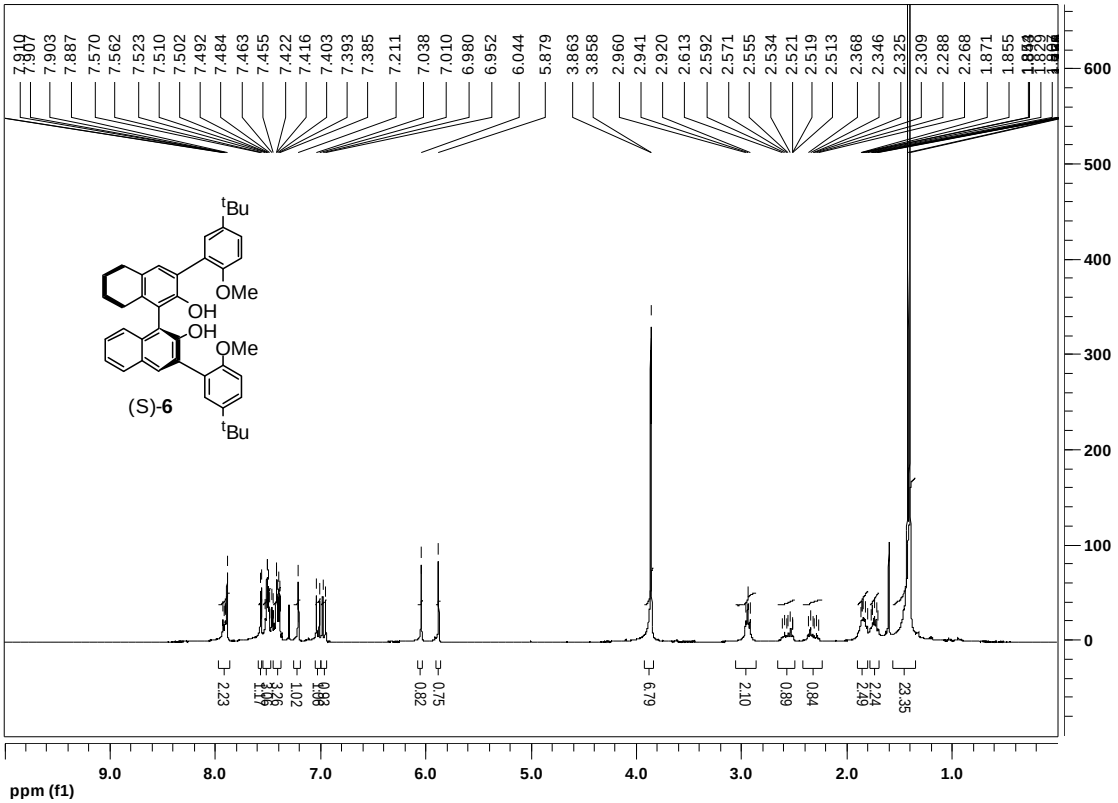

S4
7.935
7.922
7.897
7.540
7.532
7.443
7.434
7.414
7.407
7.375
7.372
7.357
7.349
7.335
7.317
7.289
7.260
7.258
6.982
6.953
5.954
3.814
1.371
tBu
OMe
OH
OH
OMe
tBu
(S)-4
2.08
1.09
4.58
0.92
0.75
3.00
9.27
ppm (t1)

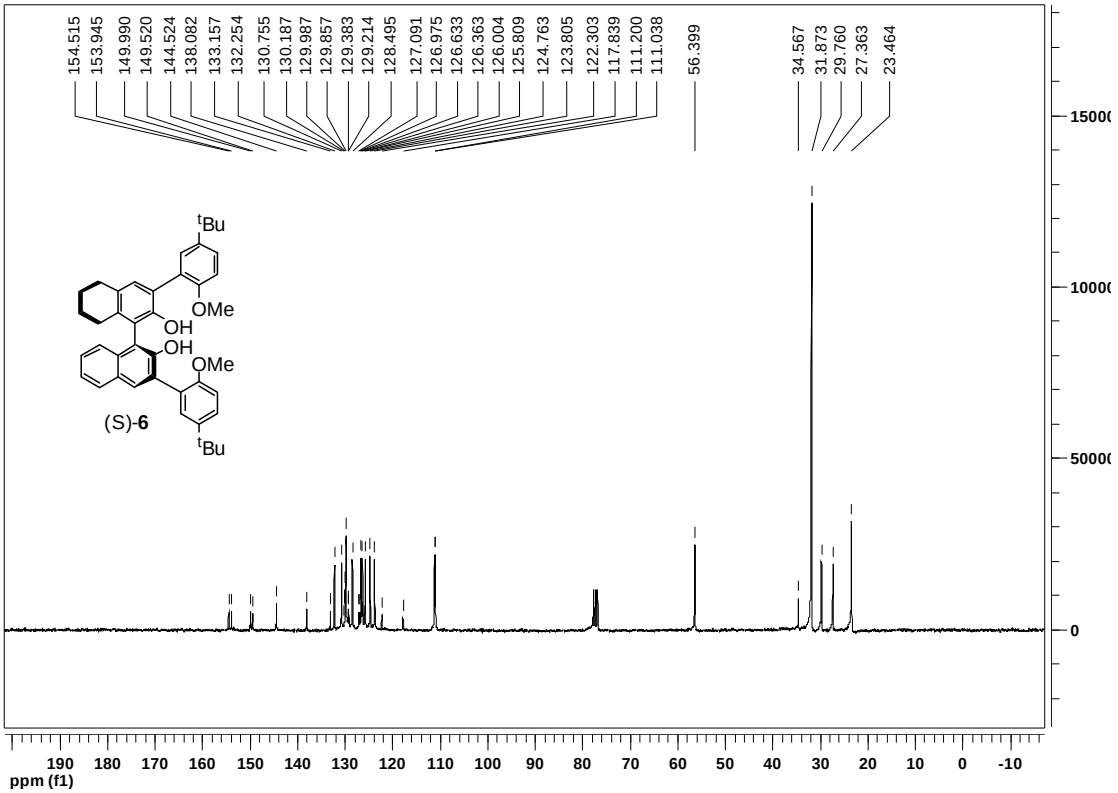

7.822
7.815
7.530
7.500
7.377
7.369
7.357
7.349
7.342
7.334
7.323
7.314
7.309
7.294
7.289
7.259
7.162
7.134
7.065
7.037
5.190
5.167
5.107
5.084
4.943
4.921
4.853
4.830
3.352
3.084
2.849
2.829
2.808
2.359
2.338
2.302
2.280
2.260
2.118
2.097
2.076
2.054
2.039
2.019
1.754
OMOM
OMOM
SM-2
1.88
1.21
3.27
0.87
1.00
1.11
0.99
0.98
0.98
3.12
2.73
2.36
1.14
1.27
2.31
2.56
1500
1000
500
0
9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50
ppm (f1)

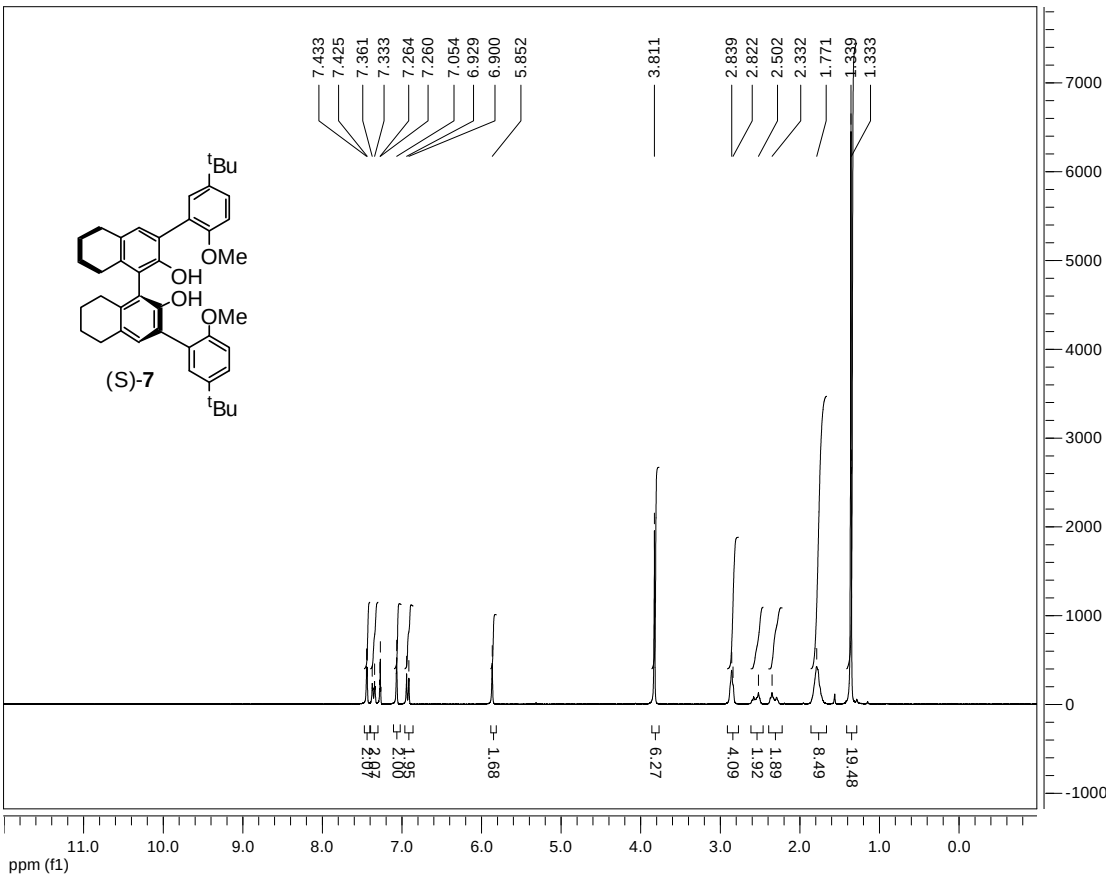

153.200
152.038
138.147
133.596
131.295
130.111
129.628
129.082
128.140
126.459
125.247
124.196
117.521
113.211
95.568
94.981
56.178
55.806
29.732
27.432
23.370
OMOM
OMOM
SM-2
70000
60000
50000
40000
30000
20000
10000
0
-10000
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

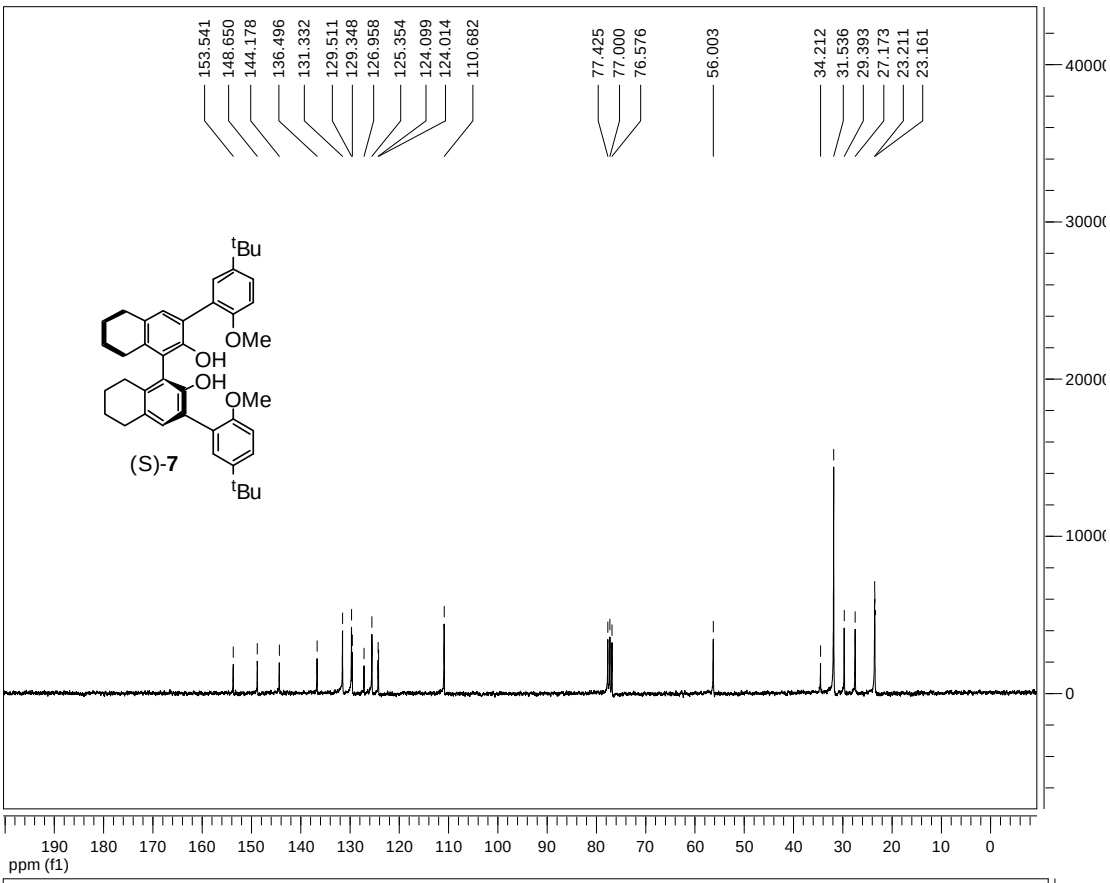

8.361
7.852
7.846
7.838
7.826
7.819
7.574
7.363
7.352
5.067
5.046
4.967
4.946
4.799
4.780
4.734
4.714
2.854
2.834
2.813
2.790
2.767
2.458
2.438
2.417
2.399
2.379
2.359
2.172
2.154
2.131
2.118
2.095
2.073
1.763
1.743
1.724
1.706
OMOM
OMOM
SM-3
ppm (f1)

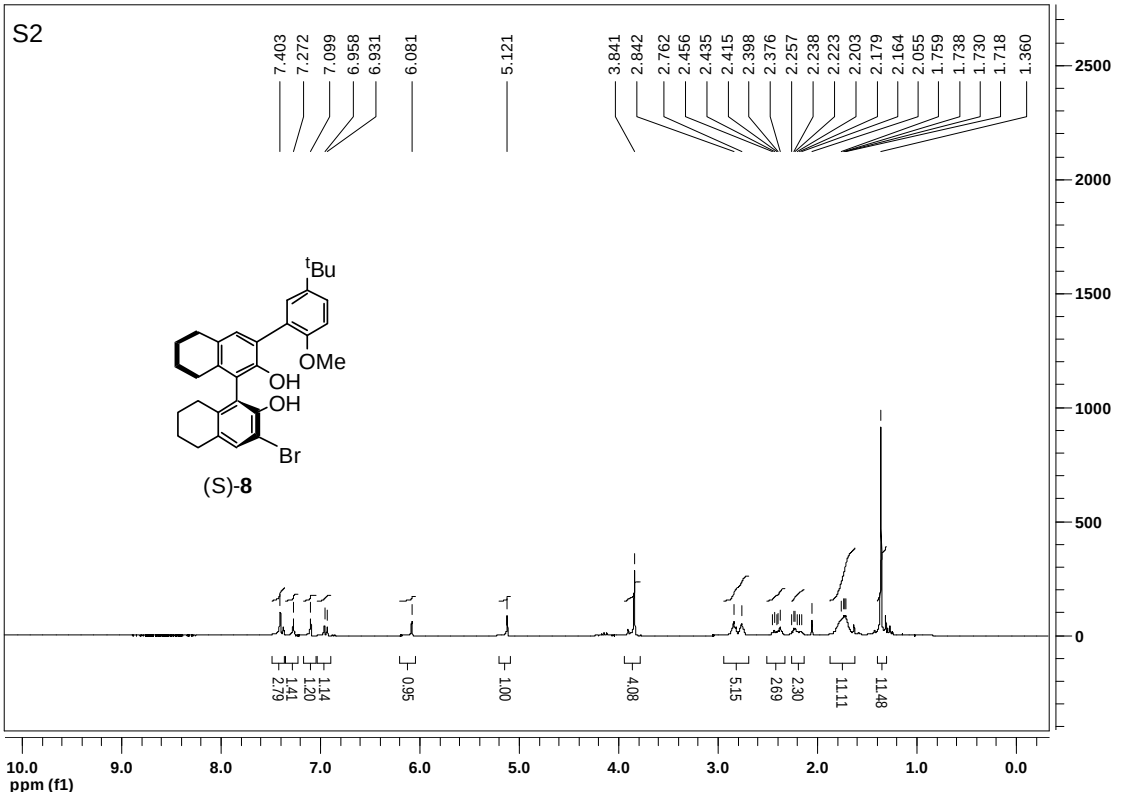

159.180
156.542
142.701
138.993
137.438
135.582
132.675
130.429
128.579
127.407
126.362
124.763
100.612
100.425
84.025
83.703
56.301
55.591
29.791
28.175
25.136
23.255
OMOM
OMOM
SM-3
ppm (f1)

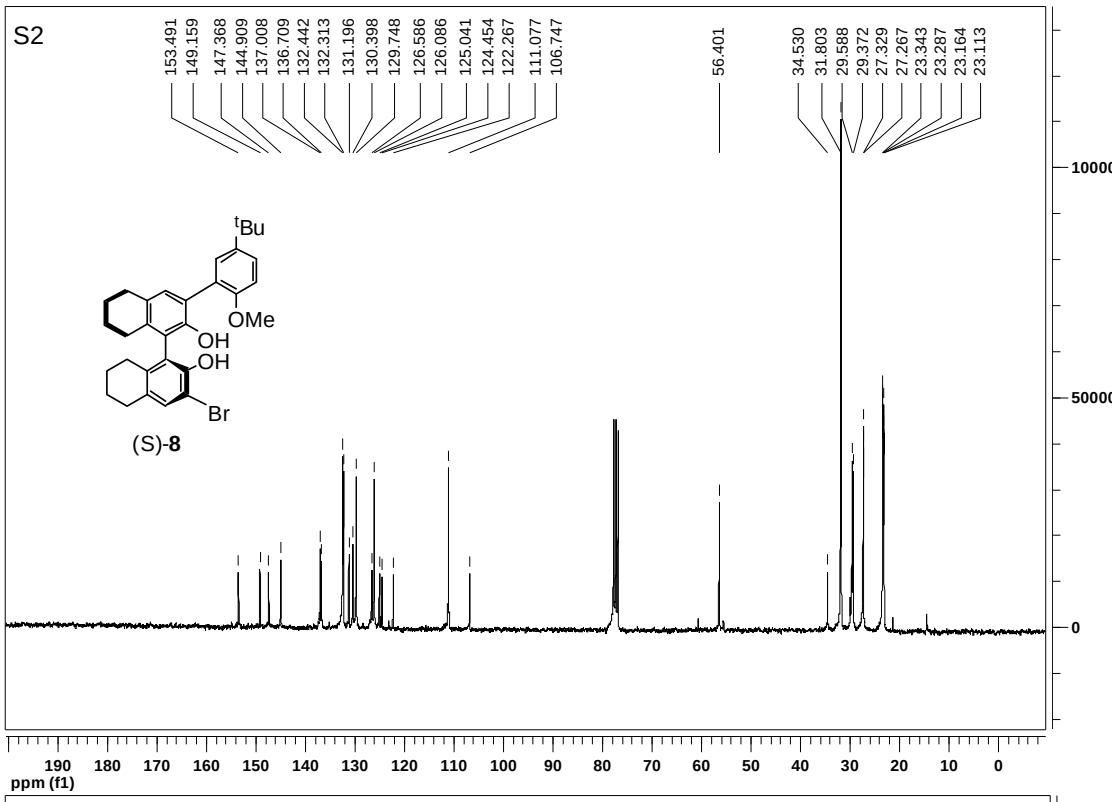

7.910
7.907
7.903
7.887
7.570
7.562
7.523
7.510
7.502
7.492
7.484
7.463
7.455
7.422
7.416
7.403
7.393
7.385
7.211
7.038
7.010
6.980
6.952
6.044
5.879
3.863
3.858
2.960
2.941
2.920
2.613
2.592
2.571
2.555
2.534
2.521
2.519
2.513
2.368
2.346
2.325
2.309
2.288
2.268
1.871
1.855
tBu
OMe
OH
OH
OMe
tBu
(S)-6
2.23
1.02
0.82
0.75
9.79
2.10
0.89
0.84
2.24
2.49
23.35
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

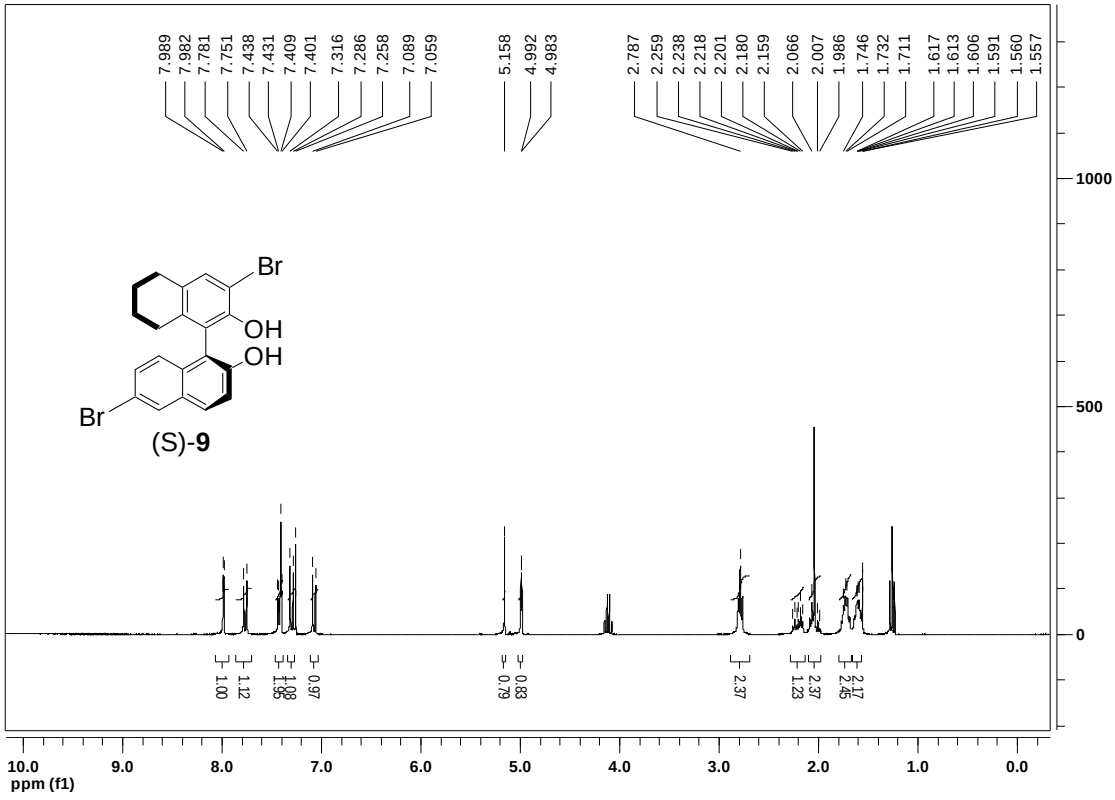

154.515
153.945
149.990
149.520
144.524
138.082
133.157
132.254
130.755
130.187
129.987
129.857
129.383
129.214
128.495
127.091
126.975
126.633
126.363
126.004
125.809
124.763
123.805
122.303
117.839
111.200
111.038
56.399
34.567
31.873
29.760
27.363
23.464
tBu
OMe
OH
OH
OMe
tBu
(S)-6
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)

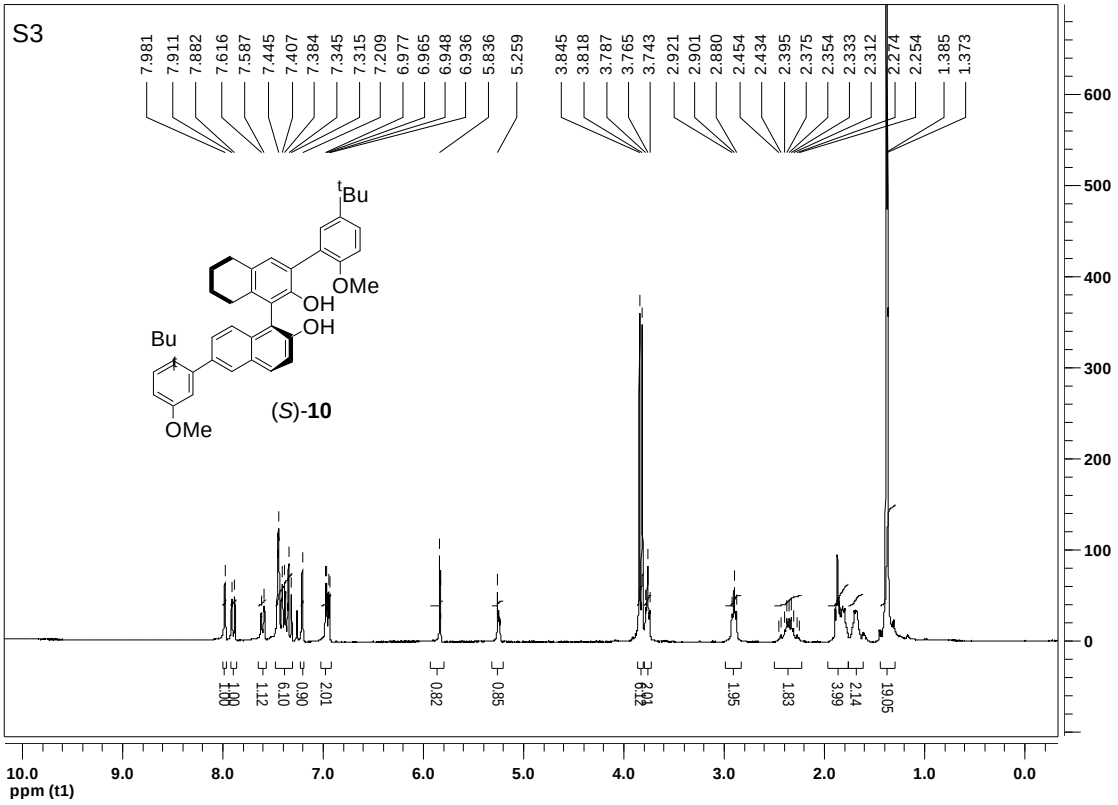

7.433
7.425
7.361
7.333
7.264
7.260
7.054
6.929
6.900
5.852
3.811
2.839
2.822
2.502
2.332
1.771
1.339
1.333
tBu
OMe
OH
OH
OMe
tBu
(S)-7
2.07
2.00
1.95
1.68
6.27
4.09
1.92
1.89
8.49
19.48
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

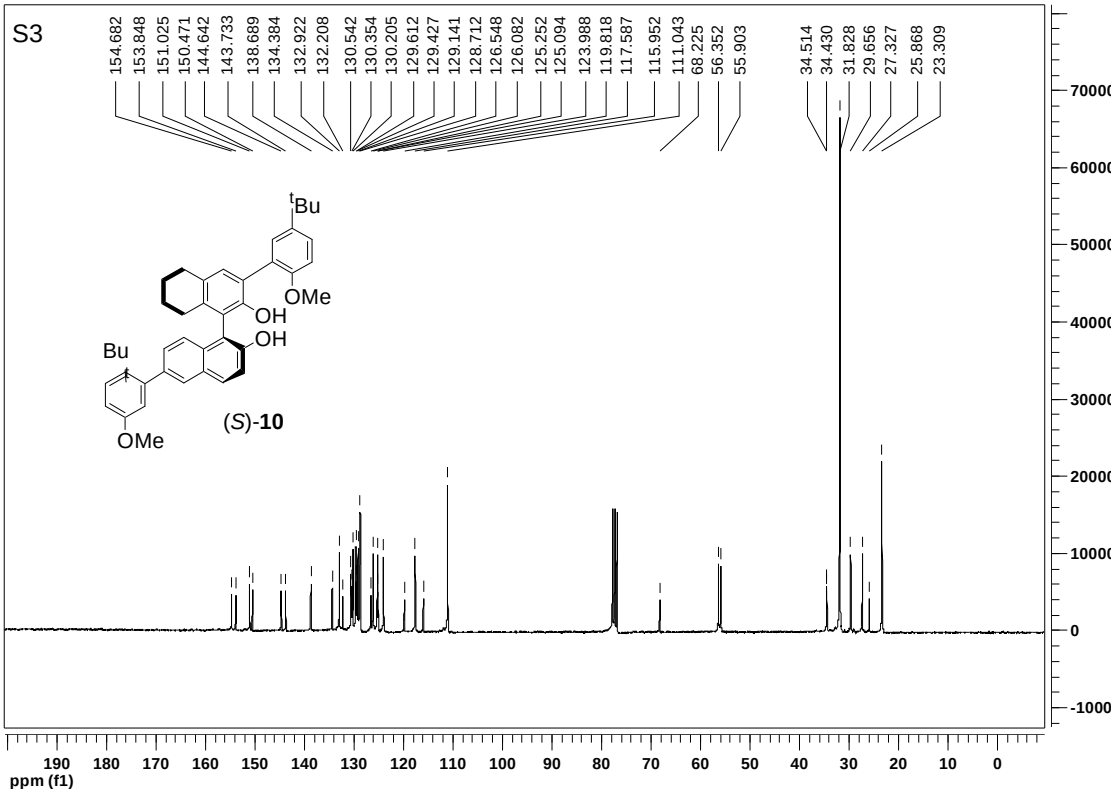

153.541
148.650
144.178
136.496
131.332
129.511
129.348
126.958
125.354
124.099
124.014
110.682
77.425
77.000
76.576
56.003
34.212
31.536
29.393
27.173
23.211
23.161
tBu
OMe
OH
OH
OMe
tBu
(S)-7
ppm (f1)

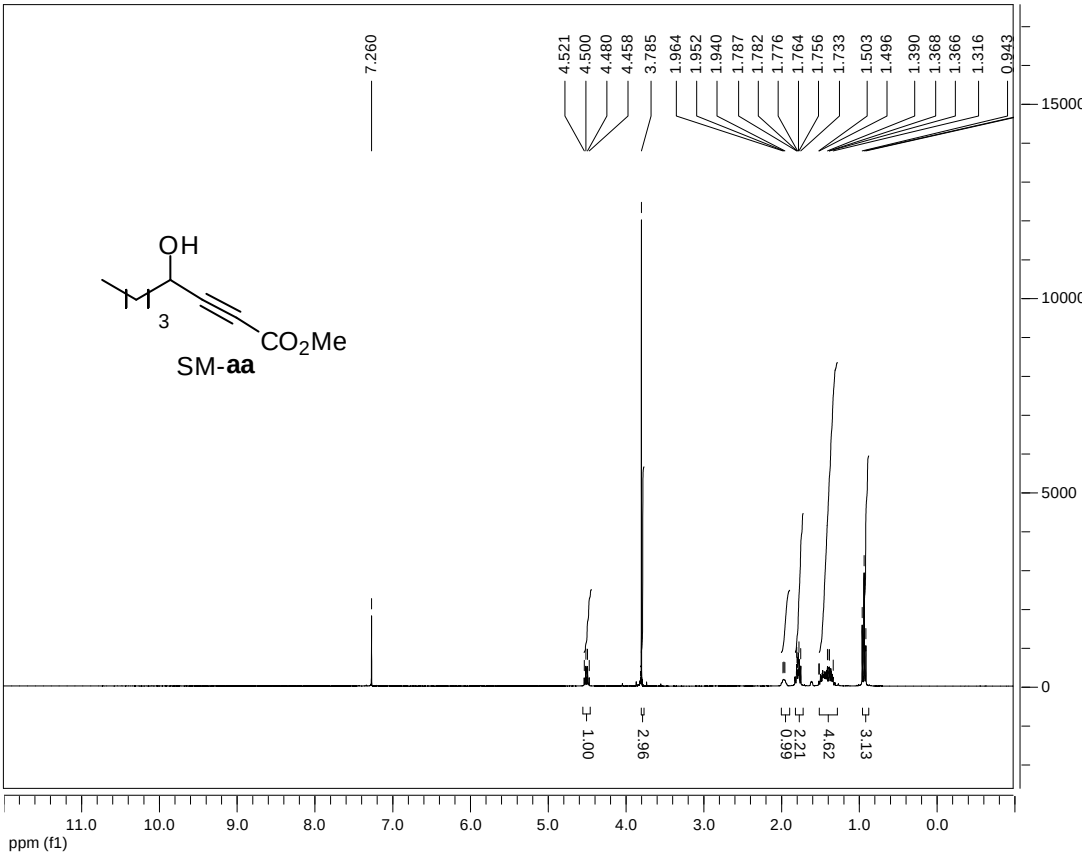

S2
7.403
7.272
7.099
6.958
6.931
6.081
5.121
3.841
2.842
2.762
2.456
2.435
2.415
2.398
2.376
2.257
2.238
2.223
2.203
2.179
2.164
2.055
1.759
1.738
1.730
1.718
1.360
tBu
OMe
OH
OH
Br
(S)-8
2.79
1.41
1.20
1.14
0.95
1.00
4.08
5.15
2.69
2.30
11.11
11.48
ppm (f1)

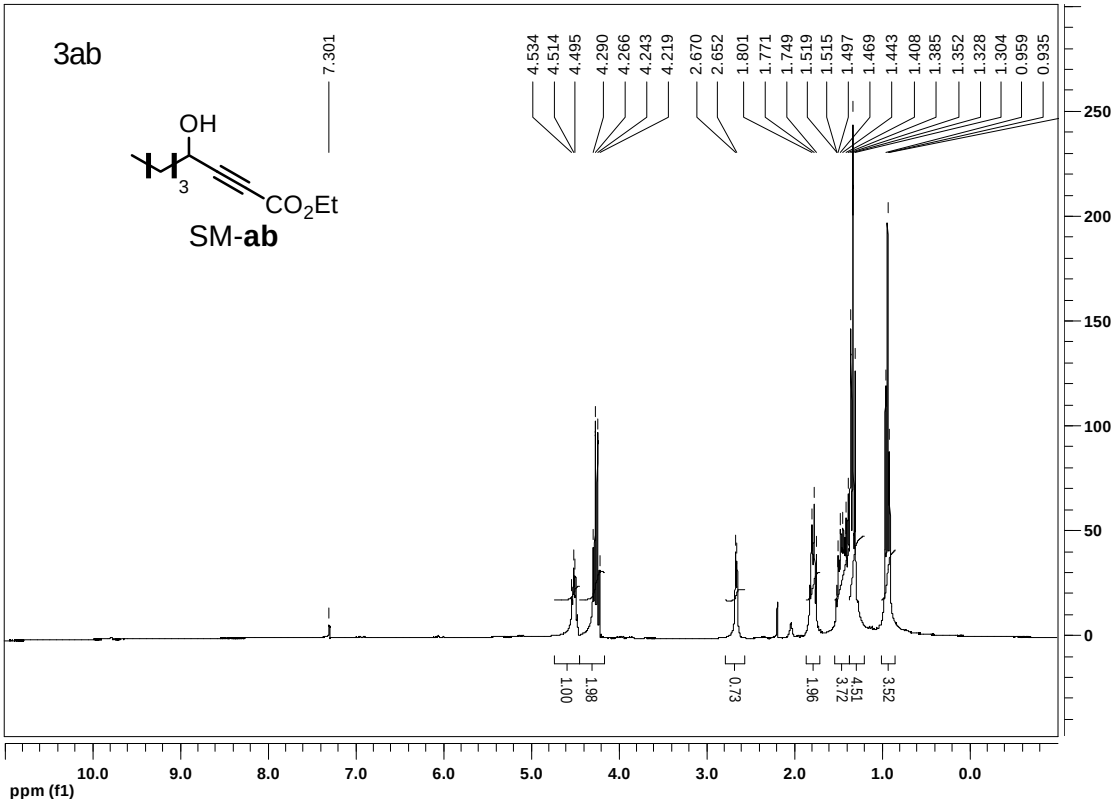

S2
153.491
149.159
147.368
144.909
137.008
136.709
132.442
132.313
131.196
130.398
129.748
126.586
126.086
125.041
124.454
122.267
111.077
106.747
56.401
34.530
31.803
29.588
29.372
27.329
27.267
23.343
23.287
23.164
23.113
tBu
OMe
OH
OH
Br
(S)-8
10000
5000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

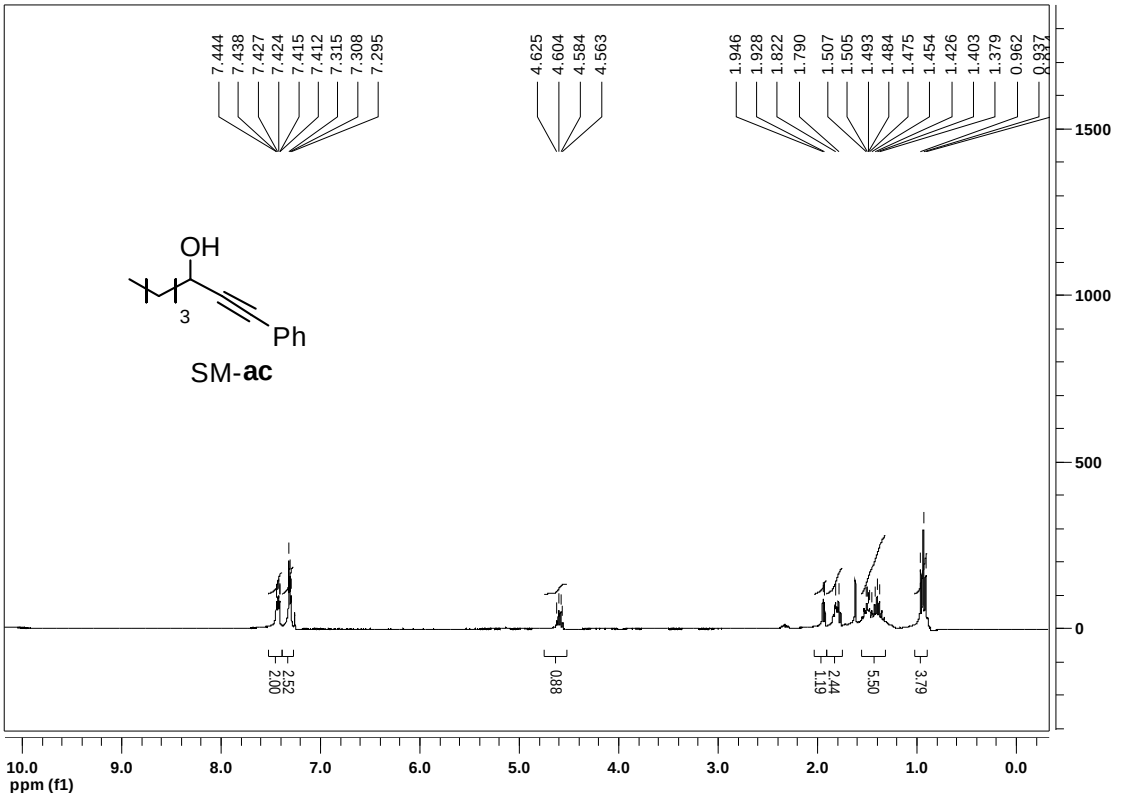

7.989
7.982
7.781
7.751
7.438
7.431
7.409
7.401
7.316
7.286
7.258
7.089
7.059
5.158
4.992
4.983
2.787
2.259
2.238
2.218
2.201
2.180
2.159
2.066
2.007
1.986
1.746
1.732
1.711
1.617
1.613
1.606
1.591
1.560
1.557
Br
OH
OH
Br
(S)-9
1.00
1.12
1.08
1.06
0.97
0.83
0.79
2.37
2.37
1.23
2.17
2.45
1000
500
0
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)

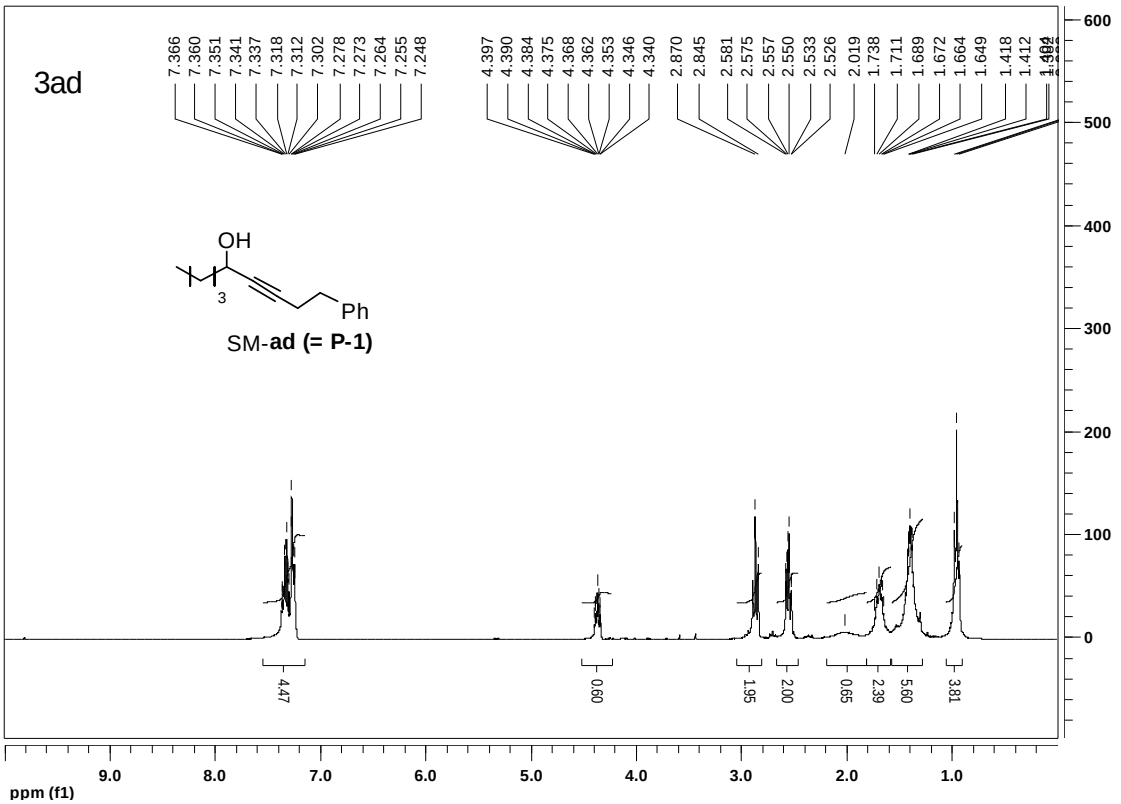

S3
7.981
7.911
7.882
7.616
7.587
7.445
7.407
7.384
7.345
7.315
7.209
6.977
6.965
6.948
6.936
5.836
5.259
3.845
3.818
3.787
3.765
3.743
2.921
2.901
2.880
2.454
2.434
2.395
2.375
2.354
2.333
2.312
2.274
2.254
1.385
1.373
tBu
OMe
OH
OH
Bu
OMe
(S)-10
1.00
1.12
0.90
0.60
2.01
0.82
0.85
6.14
1.95
1.83
3.99
2.14
19.05
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

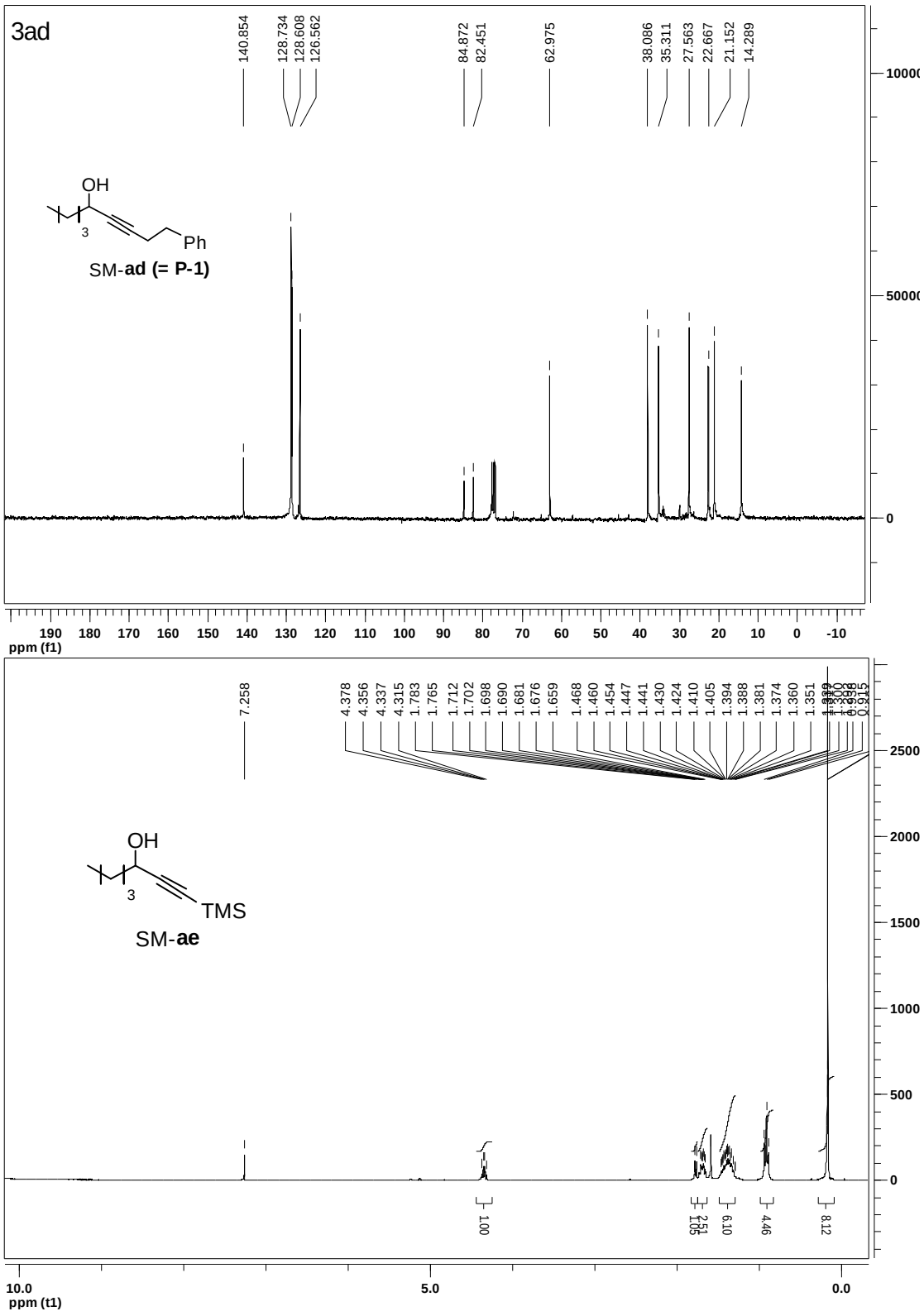

S3
154.682
153.848
151.025
150.471
144.642
143.733
138.689
134.384
132.922
132.208
130.542
130.354
130.205
129.612
129.427
129.141
128.712
126.548
126.082
125.252
125.094
123.988
119.818
117.587
115.952
111.043
68.225
56.352
55.903
34.514
34.430
31.828
29.656
27.327
25.868
23.309
tBu
OMe
OH
OH
Bu
OMe
(S)-10
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

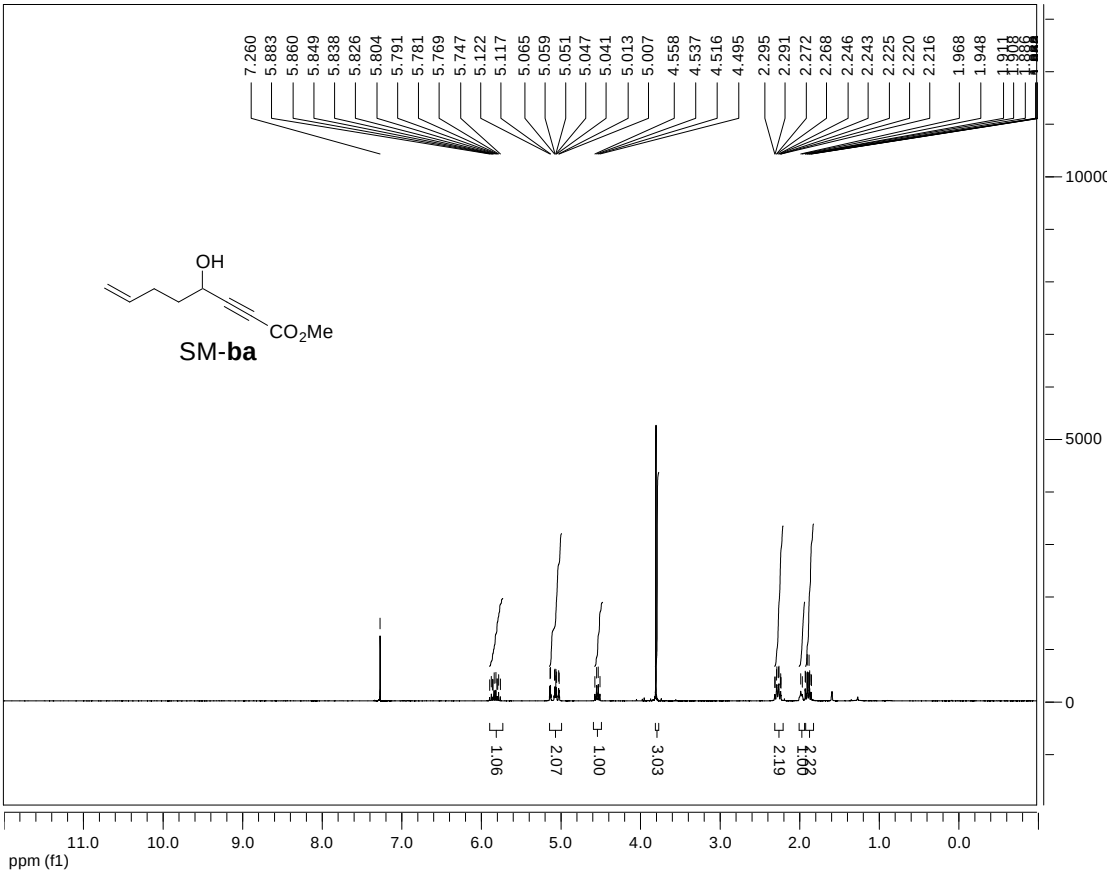

7.260
4.521
4.500
4.480
4.458
3.785
1.964
1.952
1.940
1.787
1.782
1.776
1.764
1.756
1.733
1.503
1.496
1.390
1.368
1.366
1.316
0.943
OH
3
CO2Me
SM-aa
1.00
2.96
2.21
0.99
4.92
3.13
ppm (f1)

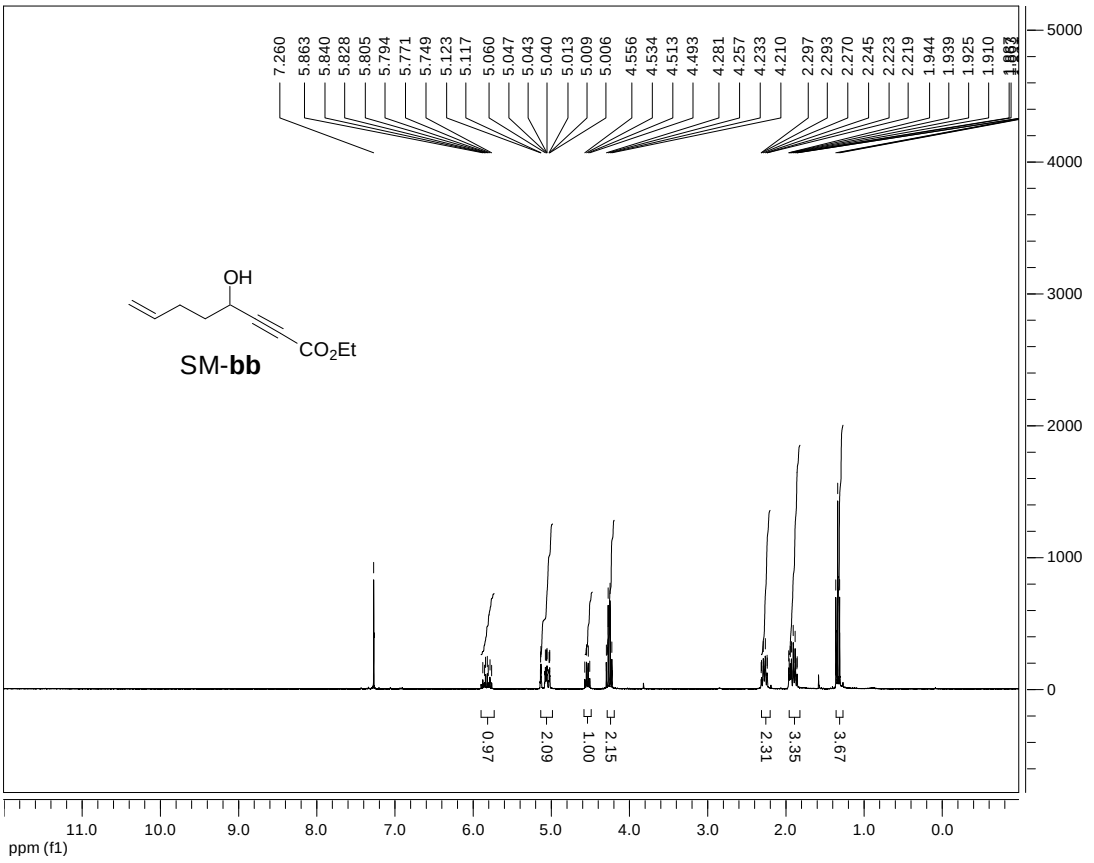

3ab
7.301
4.534
4.514
4.495
4.290
4.266
4.243
4.219
2.670
2.652
1.801
1.771
1.749
1.519
1.515
1.497
1.469
1.443
1.408
1.385
1.352
1.328
1.304
0.959
0.935
OH
3
CO2Et
SM-ab
1.00
1.98
0.73
1.96
4.51
3.72
3.52
ppm (f1)

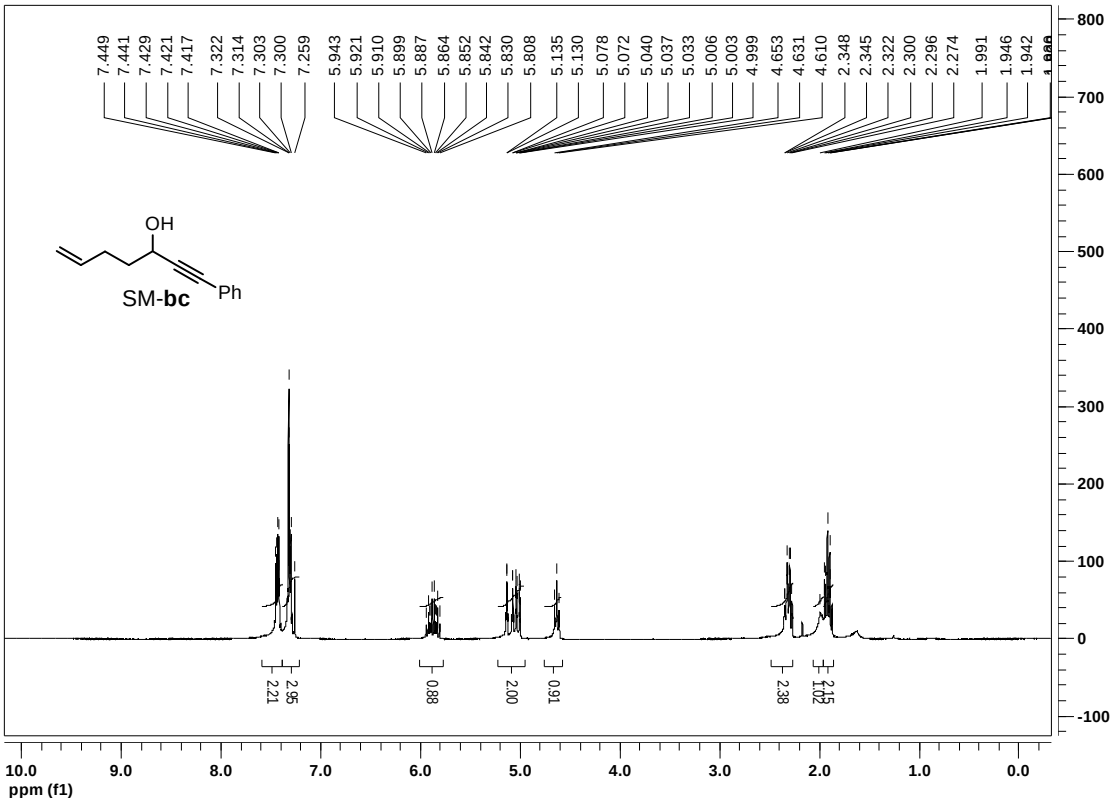

7.444
7.438
7.427
7.424
7.415
7.412
7.315
7.308
7.295
4.625
4.604
4.584
4.563
1.946
1.928
1.822
1.790
1.507
1.505
1.493
1.484
1.475
1.454
1.426
1.403
1.379
0.962
0.937
OH
3
Ph
SM-ac
2.00
2.52
0.88
1.19
2.44
5.50
3.79
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
1500
1000
500
0

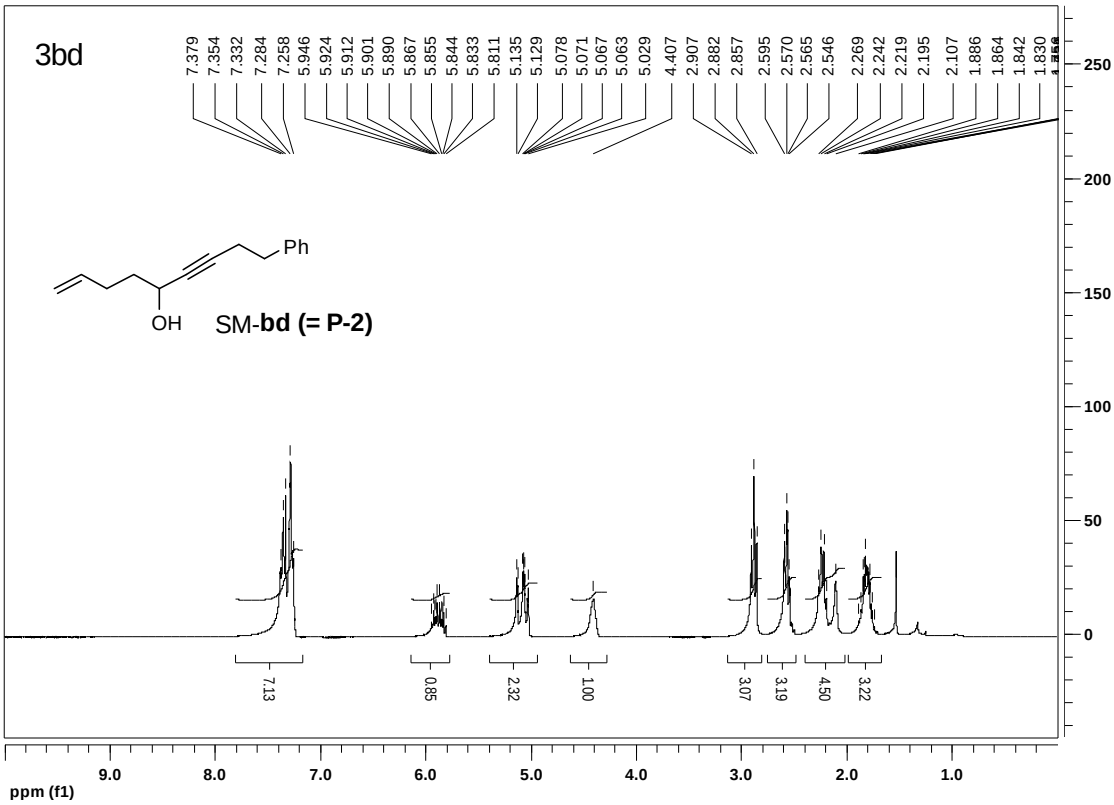

3ad
7.366
7.360
7.351
7.341
7.337
7.318
7.312
7.302
7.278
7.273
7.264
7.255
7.248
4.397
4.390
4.384
4.375
4.368
4.362
4.353
4.346
4.340
2.870
2.845
2.581
2.575
2.557
2.550
2.533
2.526
2.019
1.738
1.711
1.689
1.672
1.664
1.649
1.418
1.412
OH
3
Ph
SM-ad (= P-1)
4.47
0.60
1.95
2.00
0.65
2.39
5.60
3.81
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
600
500
400
300
200
100
0

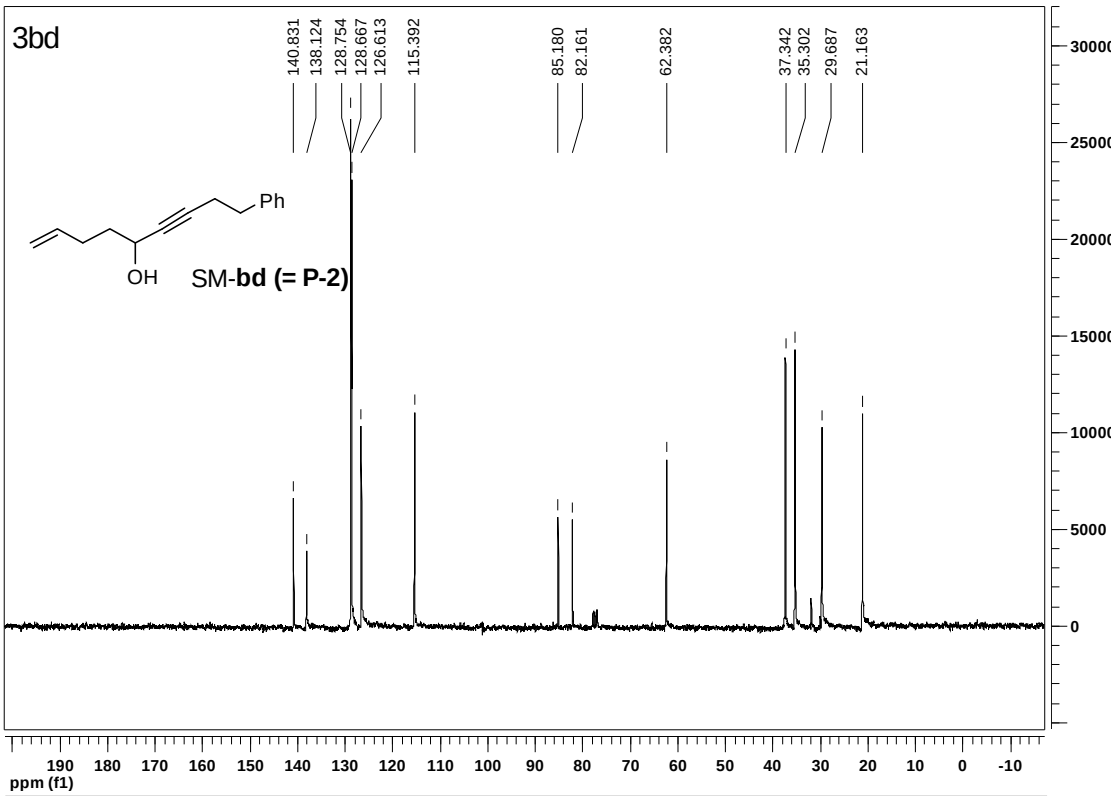

3ad
140.854
128.734
128.608
126.562
84.872
82.451
62.975
38.086
35.311
27.563
22.667
21.152
14.289
OH
3
Ph
SM-ad (= P-1)
ppm (f1)
7.258
4.378
4.356
4.337
4.315
1.783
1.765
1.712
1.702
1.698
1.690
1.681
1.676
1.659
1.468
1.460
1.454
1.447
1.441
1.430
1.424
1.410
1.405
1.394
1.388
1.381
1.374
1.360
1.351
OH
3
TMS
SM-ae
1.00
2.51
6.10
4.46
8.12
10.0
5.0
0.0
ppm (t1)

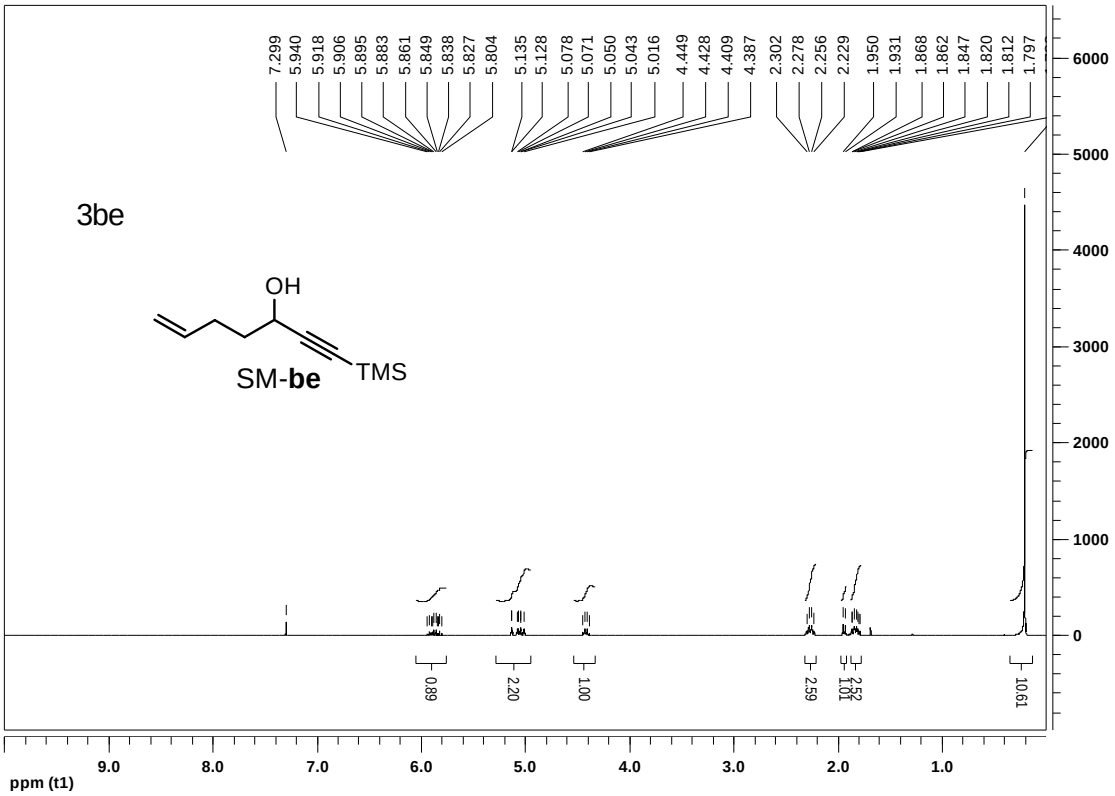

7.260
5.883
5.860
5.849
5.838
5.826
5.804
5.791
5.781
5.769
5.747
5.122
5.117
5.065
5.059
5.051
5.047
5.041
5.013
5.007
4.558
4.537
4.516
4.495
2.295
2.291
2.272
2.268
2.246
2.243
2.225
2.220
2.216
1.968
1.948
OH
CO2Me
SM-ba
10000
5000
0
1.06
2.07
1.00
3.03
2.19
2.22
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

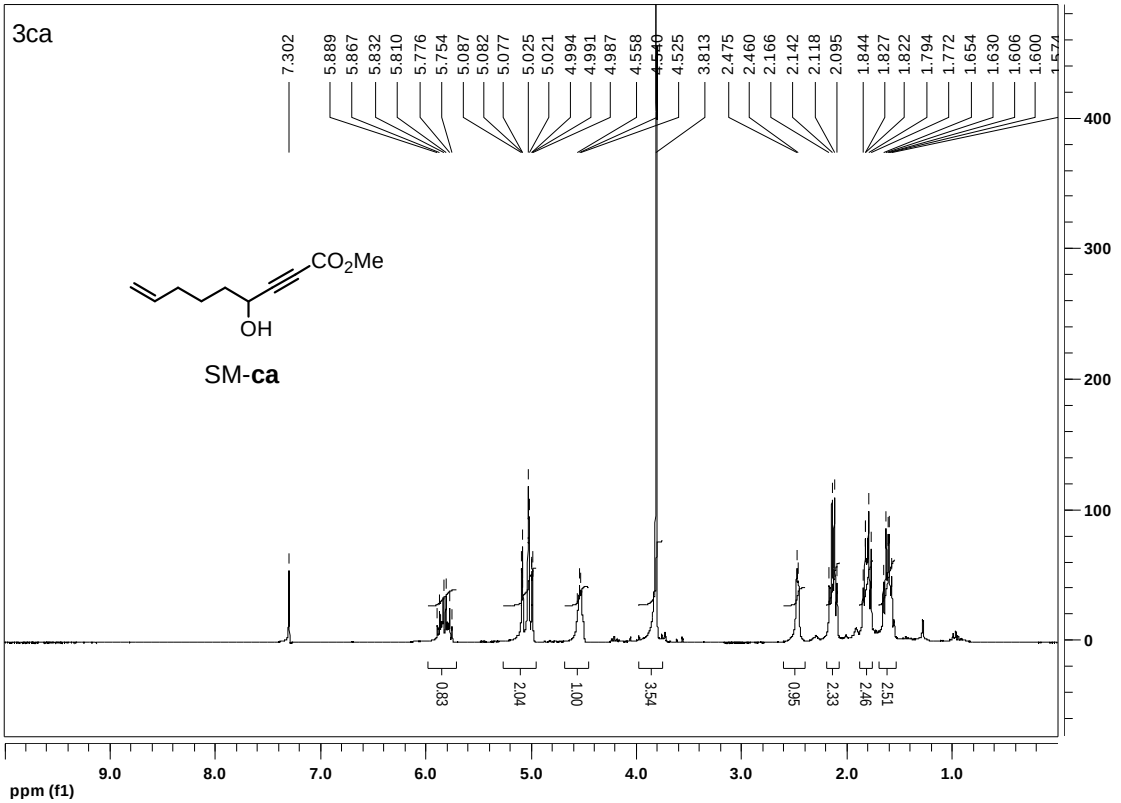

7.260
5.863
5.840
5.828
5.805
5.794
5.771
5.749
5.123
5.117
5.060
5.047
5.043
5.040
5.013
5.009
5.006
4.556
4.534
4.513
4.493
4.281
4.257
4.233
4.210
2.297
2.293
2.270
2.245
2.223
2.219
1.944
1.939
1.925
1.910
OH
CO2Et
SM-bb
5000
4000
3000
2000
1000
0
0.97
2.09
1.00
2.15
2.31
3.35
3.67
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

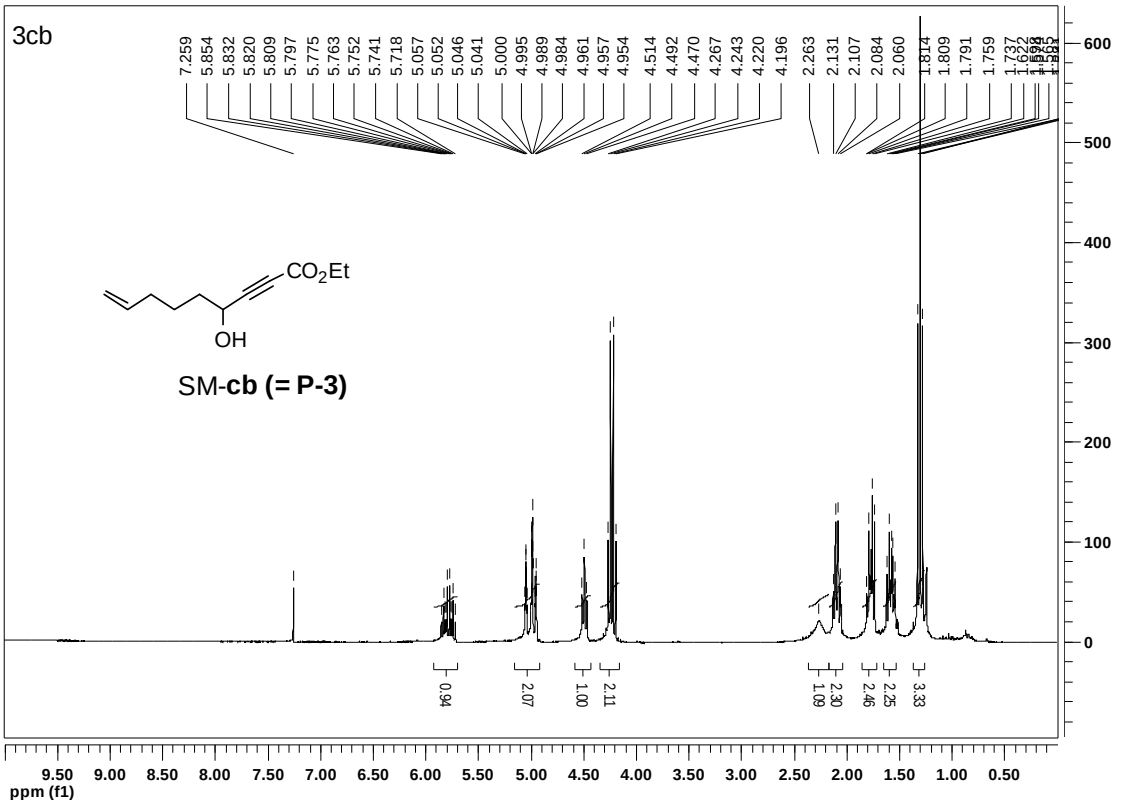

7.449
7.441
7.429
7.421
7.417
7.322
7.314
7.303
7.300
7.259
5.943
5.921
5.910
5.899
5.887
5.864
5.852
5.842
5.830
5.808
5.135
5.130
5.078
5.072
5.040
5.037
5.033
5.006
5.003
4.999
4.653
4.631
4.610
2.348
2.345
2.322
2.300
2.296
2.274
1.991
1.946
1.942
OH
Ph
SM-bc
2.21
2.95
0.88
2.00
0.91
2.38
2.15
1.02
ppm (f1)

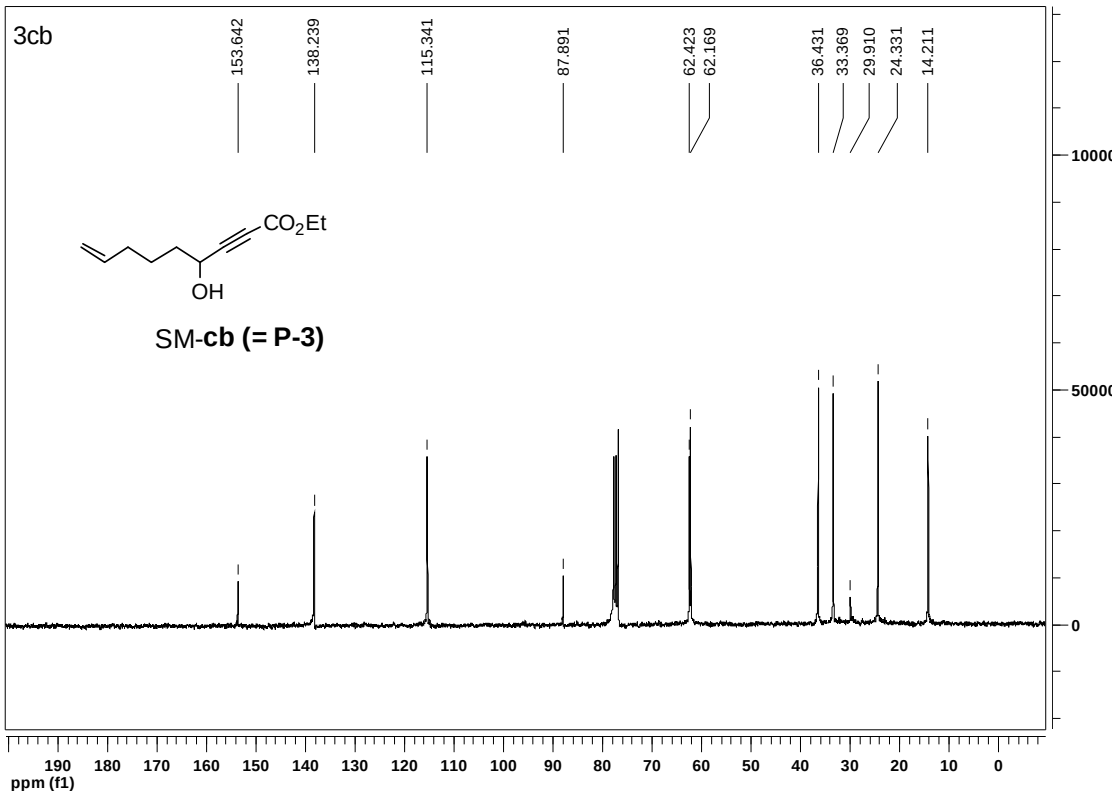

3bd
7.379
7.354
7.332
7.284
7.258
5.946
5.924
5.912
5.901
5.890
5.867
5.855
5.844
5.833
5.811
5.135
5.129
5.078
5.071
5.067
5.063
5.029
4.407
2.907
2.882
2.857
2.595
2.570
2.565
2.546
2.269
2.242
2.219
2.195
2.107
1.886
1.864
1.842
1.830
Ph
OH
SM-bd (= P-2)
7.13
0.85
2.32
1.00
3.07
3.19
4.50
3.22
ppm (f1)

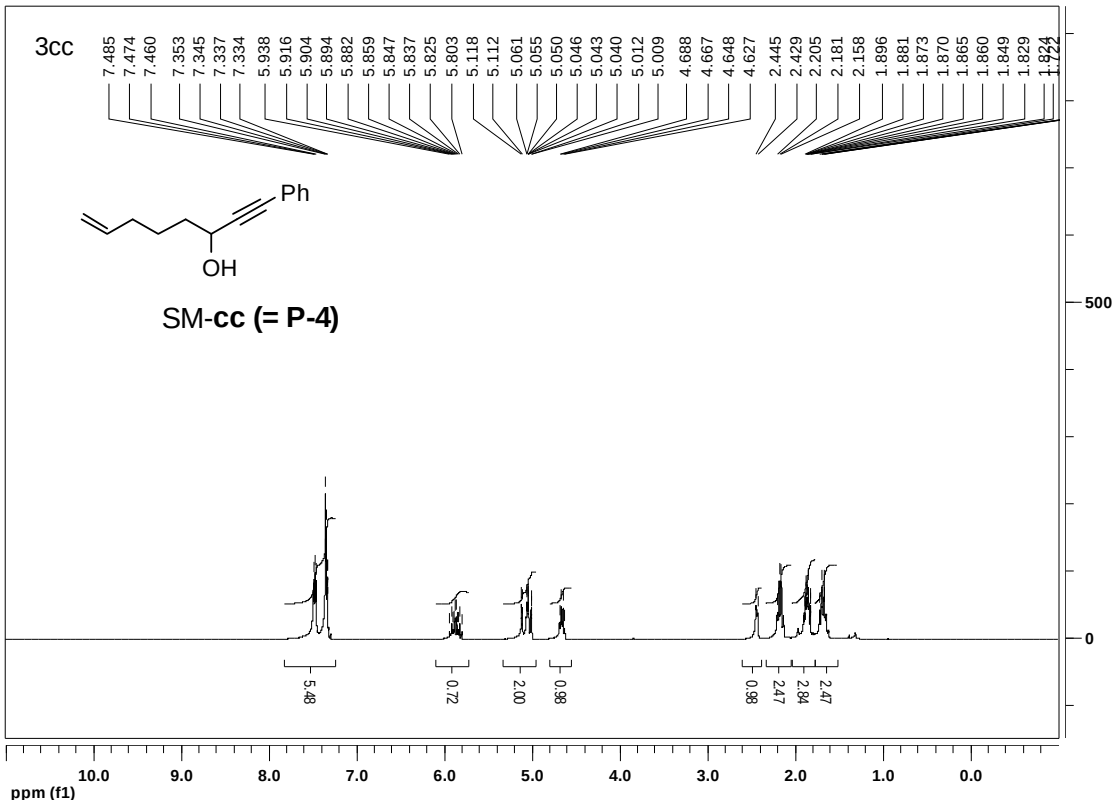

3bd
140.831
138.124
128.754
128.667
126.613
115.392
85.180
82.161
62.382
37.342
35.302
29.687
21.163
Ph
OH
SM-bd (= P-2)
ppm (f1)

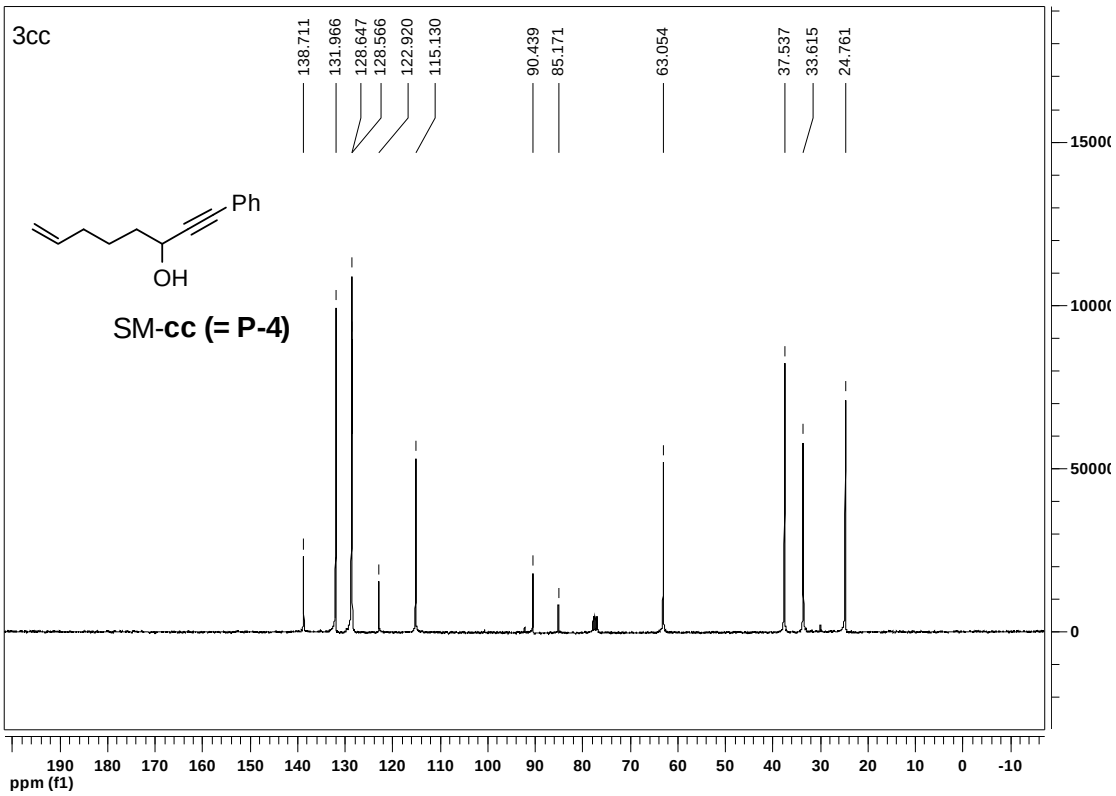

7.299
5.940
5.918
5.906
5.895
5.883
5.861
5.849
5.838
5.827
5.804
5.135
5.128
5.078
5.071
5.050
5.043
5.016
4.449
4.428
4.409
4.387
2.302
2.278
2.256
2.229
1.950
1.931
1.868
1.862
1.847
1.820
1.812
1.797
3be
OH
SM-be
TMS
0.89
2.20
1.00
2.59
2.52
1.01
10.61
ppm (t1)

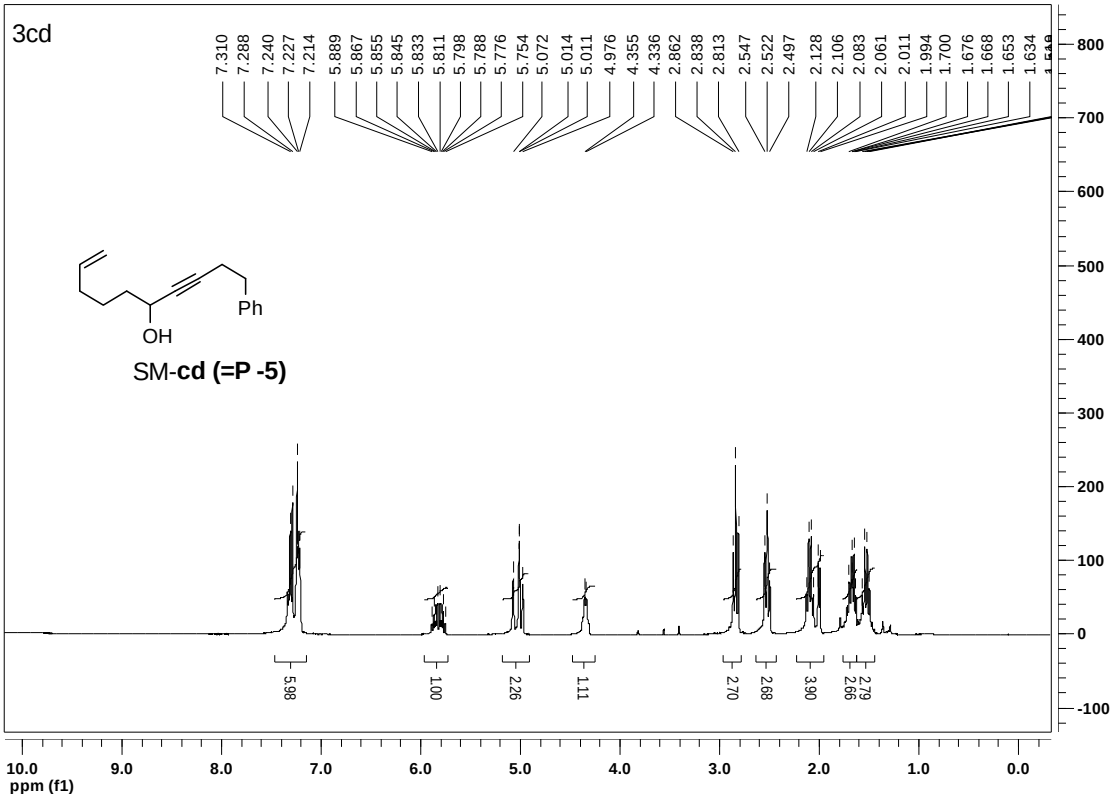

3ca
7.302
5.889
5.867
5.832
5.810
5.776
5.754
5.087
5.082
5.077
5.025
5.021
4.994
4.991
4.987
4.558
4.540
4.525
3.813
2.475
2.460
2.166
2.142
2.118
2.095
1.844
1.827
1.822
1.794
1.772
1.654
1.630
1.606
1.600
CO2Me
OH
SM-ca
0.83
2.04
1.00
3.54
0.95
2.33
2.46
2.51
ppm (f1)

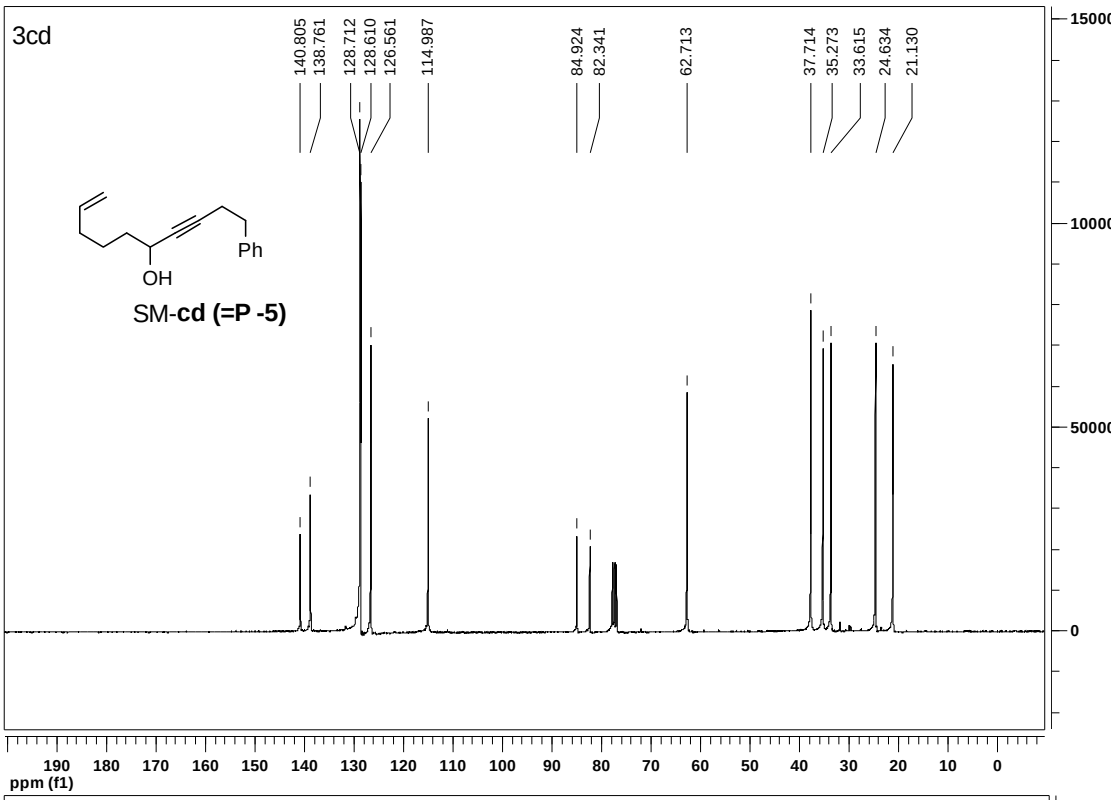

3cb
7.259
5.854
5.832
5.820
5.809
5.797
5.775
5.763
5.752
5.741
5.718
5.057
5.052
5.046
5.041
5.000
4.995
4.989
4.984
4.961
4.957
4.954
4.514
4.492
4.470
4.267
4.243
4.220
4.196
2.263
2.131
2.107
2.084
2.060
1.814
1.809
1.791
1.759
CO2Et
OH
SM-cb (= P-3)
0.94
2.07
1.00
2.11
1.09
2.30
2.46
2.25
3.33
ppm (f1)

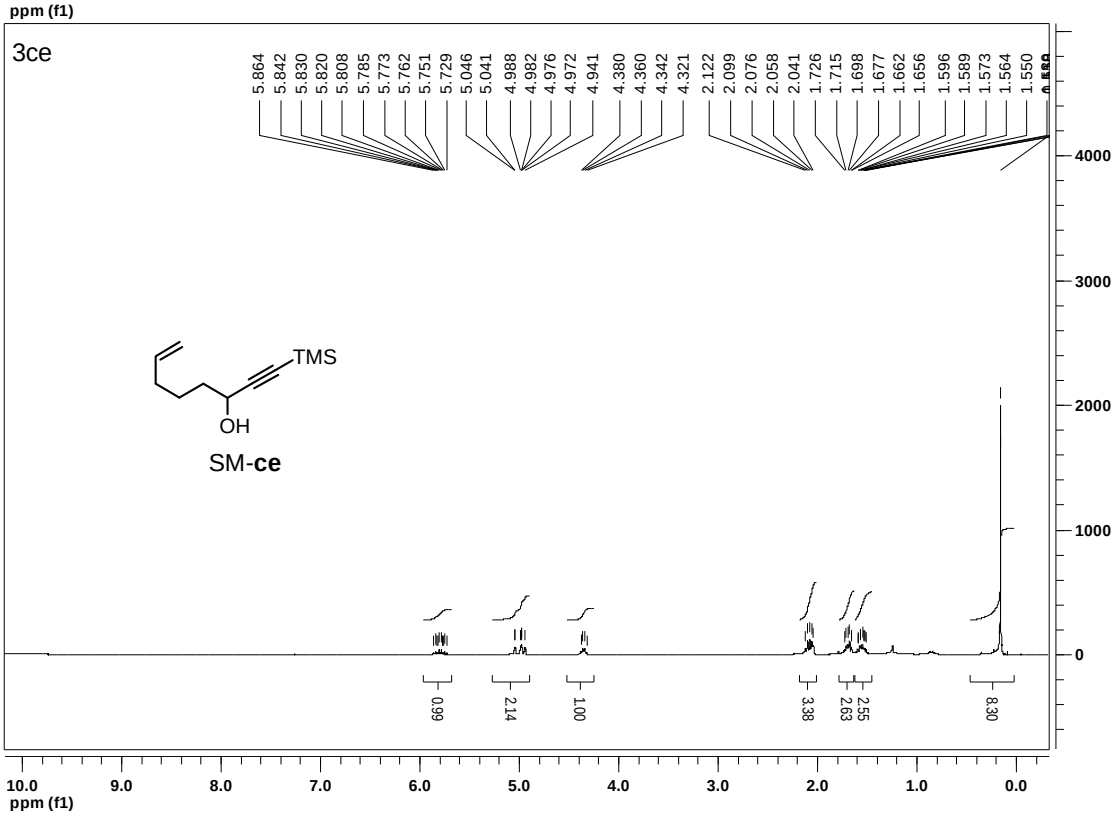

3cb
153.642
138.239
115.341
87.891
62.423
62.169
36.431
33.369
29.910
24.331
14.211
CO2Et
OH
SM-cb (= P-3)
10000
50000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

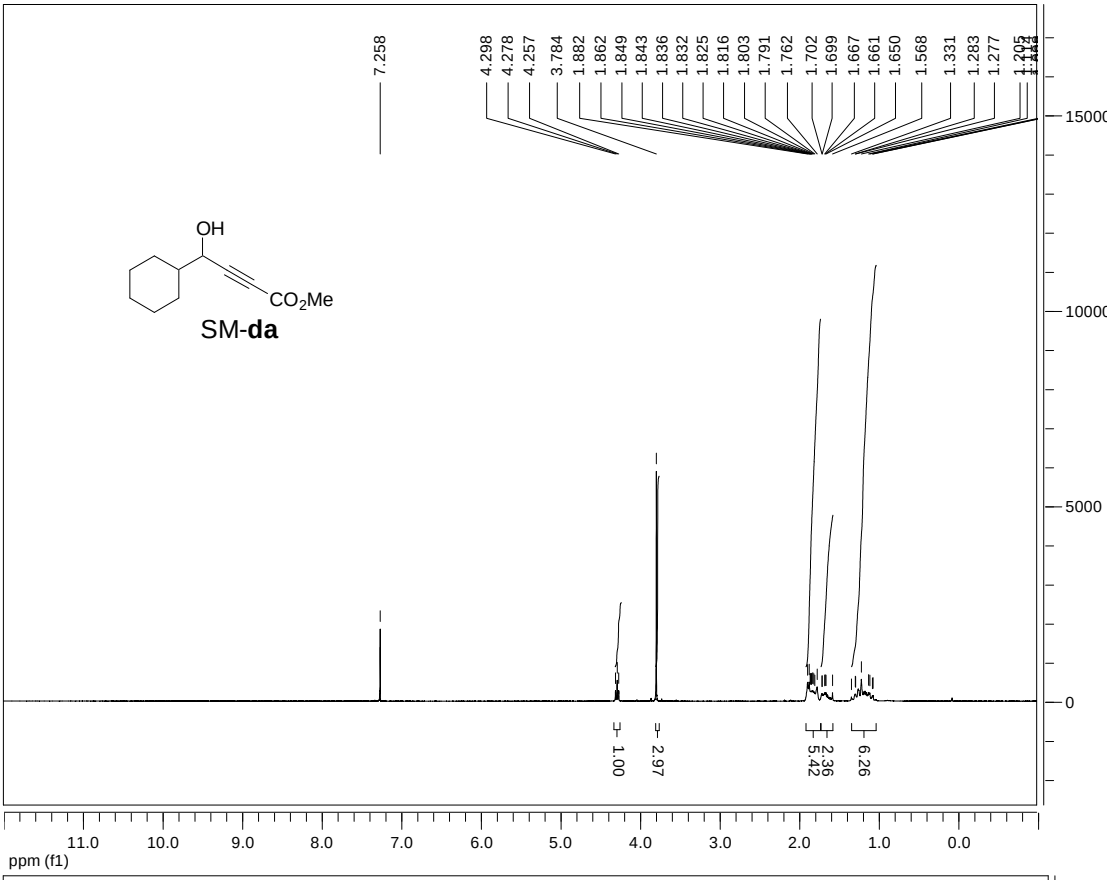

3cc
7.485
7.474
7.460
7.353
7.345
7.337
7.334
5.938
5.916
5.904
5.894
5.882
5.859
5.847
5.837
5.825
5.803
5.118
5.112
5.061
5.055
5.050
5.046
5.043
5.040
5.012
5.009
4.688
4.667
4.648
4.627
2.445
2.429
2.205
2.181
2.158
1.896
1.881
1.873
1.870
1.865
1.860
1.849
1.829
1.824
1.722
Ph
OH
SM-cc (= P-4)
500
0
5.48
0.72
2.00
0.98
0.98
2.47
2.84
2.47
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)

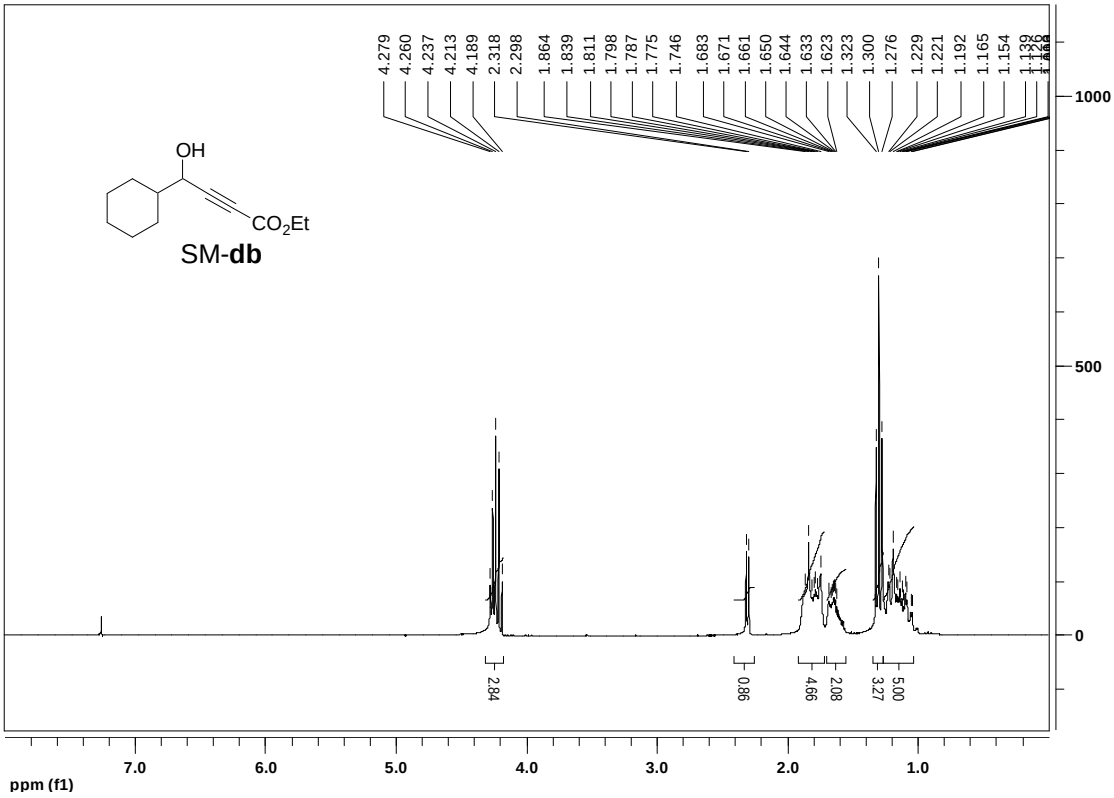

3cc
138.711
131.966
128.647
128.566
122.920
115.130
90.439
85.171
63.054
37.537
33.615
24.761
Ph
OH
SM-cc (= P-4)
ppm (f1)

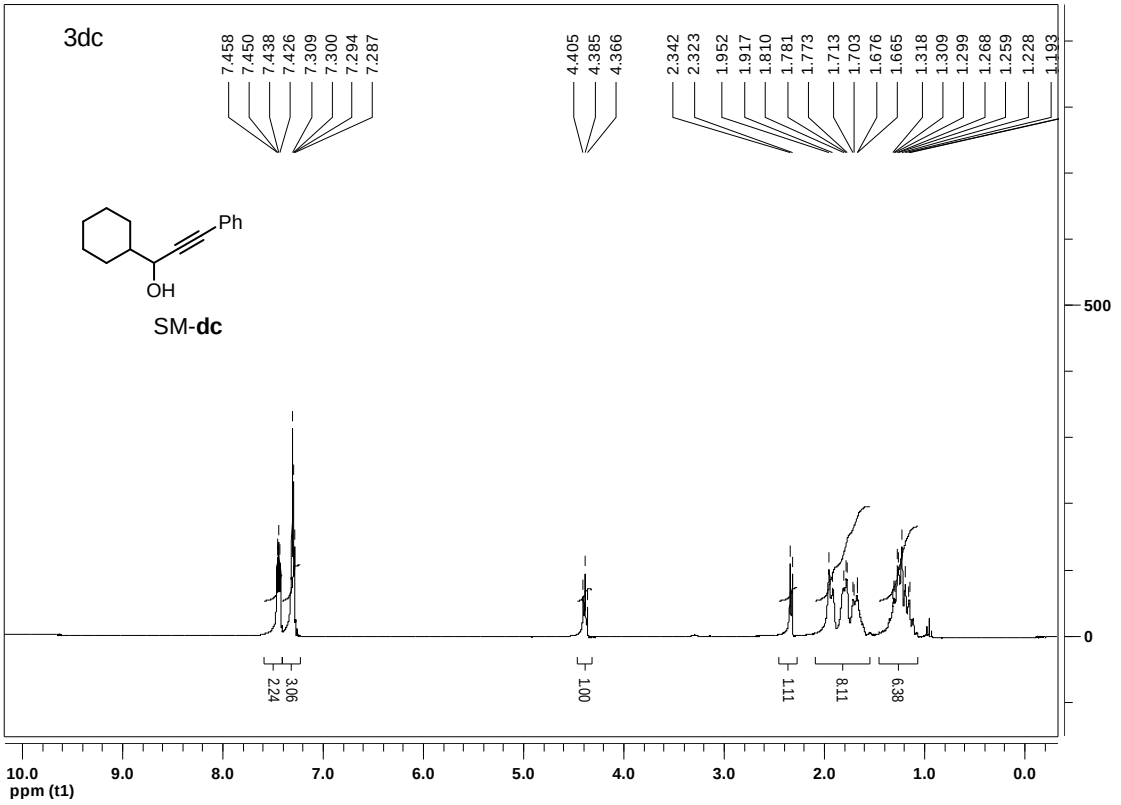

3cd
7.310
7.288
7.240
7.227
7.214
5.889
5.867
5.855
5.845
5.833
5.811
5.798
5.788
5.776
5.754
5.072
5.014
5.011
4.976
4.355
4.336
2.862
2.838
2.813
2.547
2.522
2.497
2.128
2.106
2.083
2.061
2.011
1.994
1.700
1.676
1.668
1.653
1.634
Ph
OH
SM-cd (=P -5)
5.98
1.00
2.26
1.11
2.70
2.68
3.90
2.96
2.79
ppm (f1)

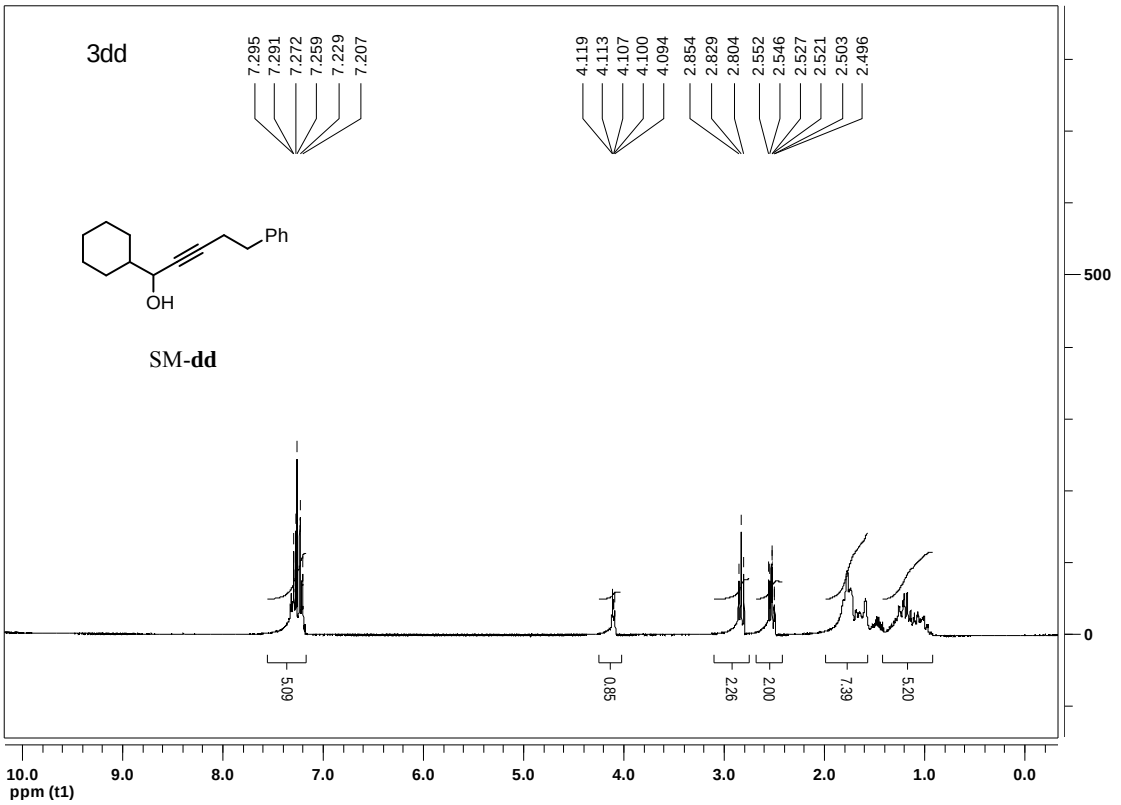

3cd
140.805
138.761
128.712
128.610
126.561
114.987
84.924
82.341
62.713
37.714
35.273
33.615
24.634
21.130
Ph
OH
SM-cd (=P -5)
ppm (f1)

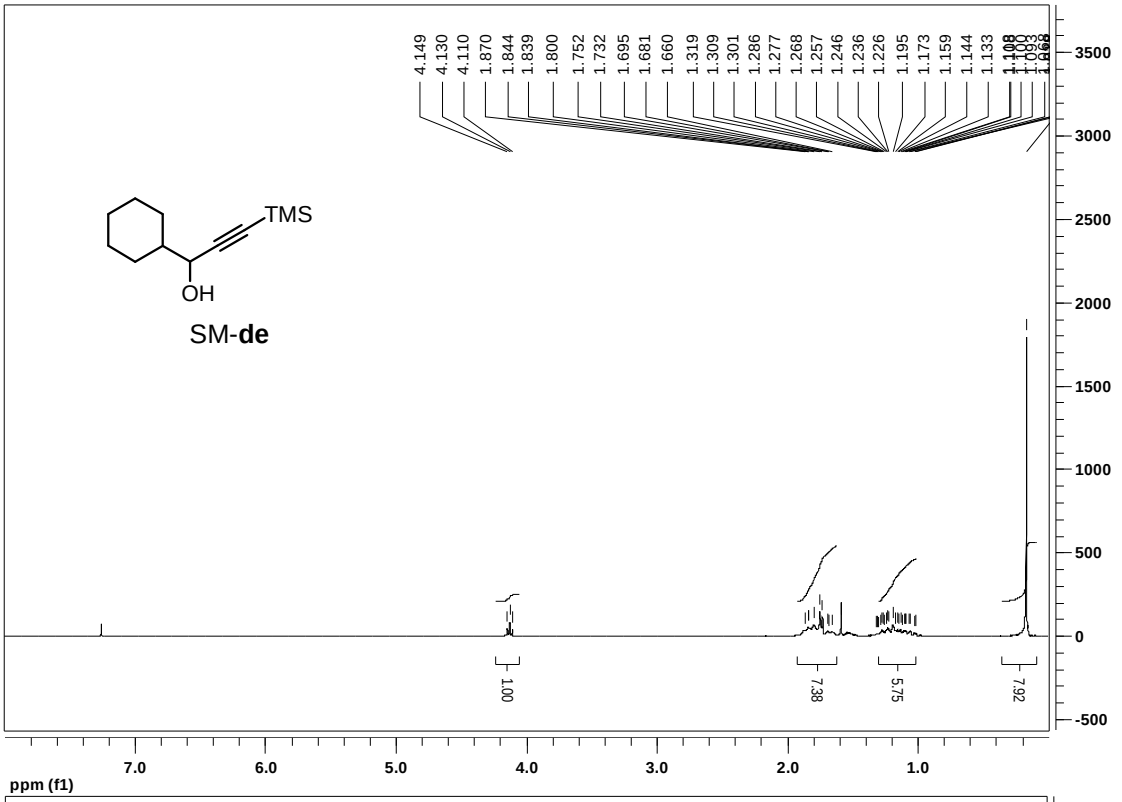

3ce
5.864
5.842
5.830
5.820
5.808
5.785
5.773
5.762
5.751
5.729
5.046
5.041
4.988
4.982
4.976
4.972
4.941
4.380
4.360
4.342
4.321
2.122
2.099
2.076
2.058
2.041
1.726
1.715
1.698
1.677
1.662
1.656
1.596
1.589
1.573
1.564
1.550
TMS
OH
SM-ce
0.99
2.14
1.00
3.38
2.63
2.55
8.30
ppm (f1)

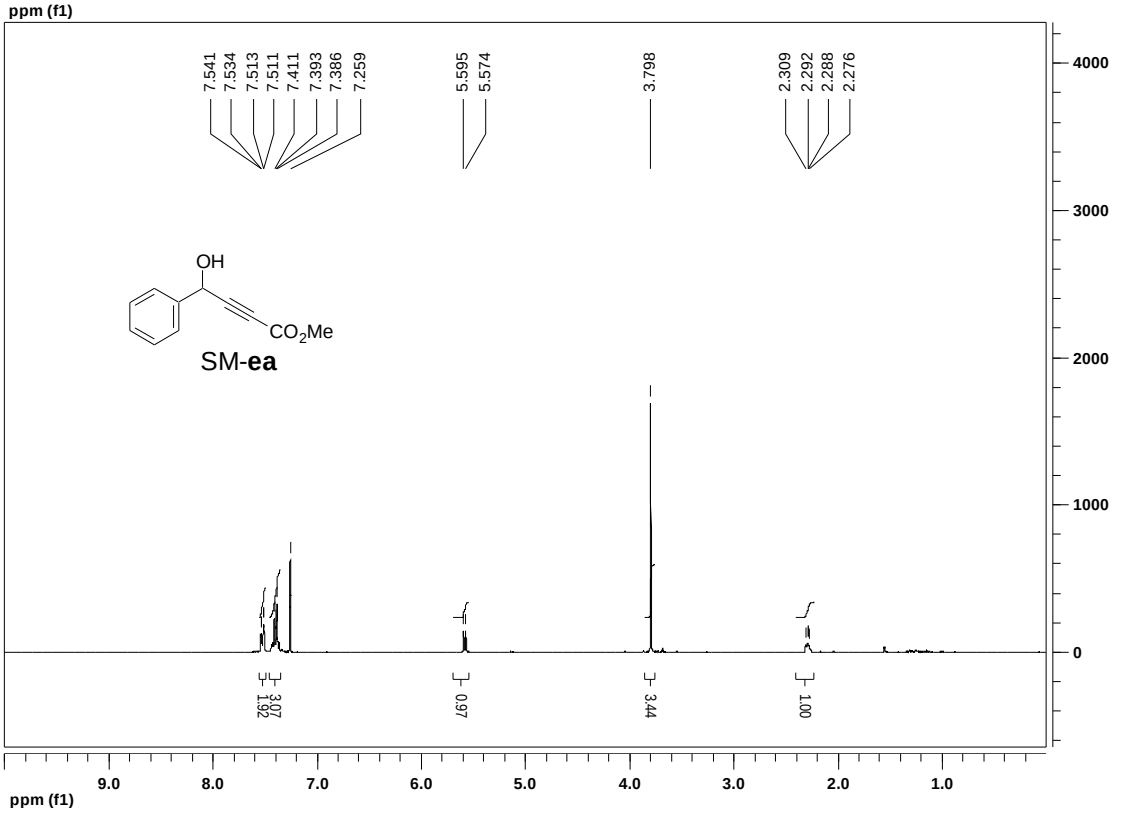

7.258
4.298
4.278
4.257
3.784
1.882
1.862
1.849
1.843
1.836
1.832
1.825
1.816
1.803
1.791
1.762
1.702
1.699
1.667
1.661
1.650
1.568
1.331
1.283
1.277
1.205
OH
CO2Me
SM-da
1.00
2.97
2.36
5.42
9.26
ppm (f1)

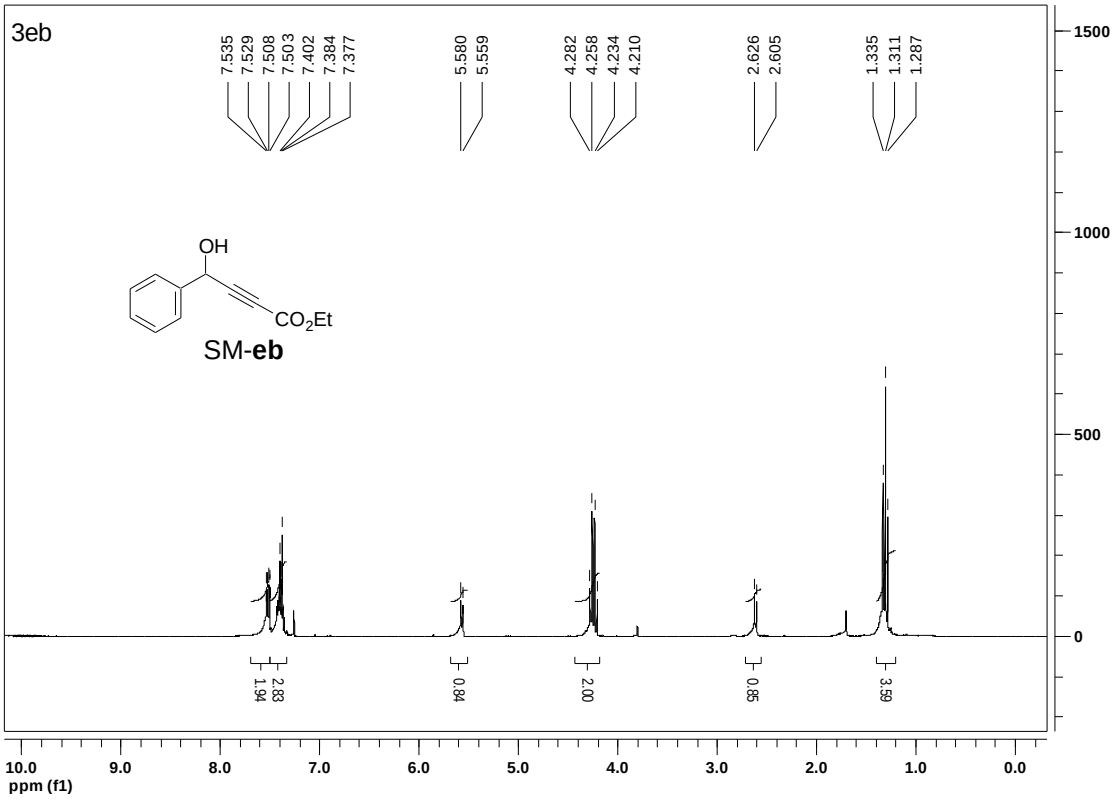

4.279
4.260
4.237
4.213
4.189
2.318
2.298
1.864
1.839
1.811
1.798
1.787
1.775
1.746
1.683
1.671
1.661
1.650
1.644
1.633
1.623
1.323
1.300
1.276
1.229
1.221
1.192
1.165
1.154
OH
CO2Et
SM-db
2.84
0.86
4.66
2.08
3.27
5.00
ppm (f1)

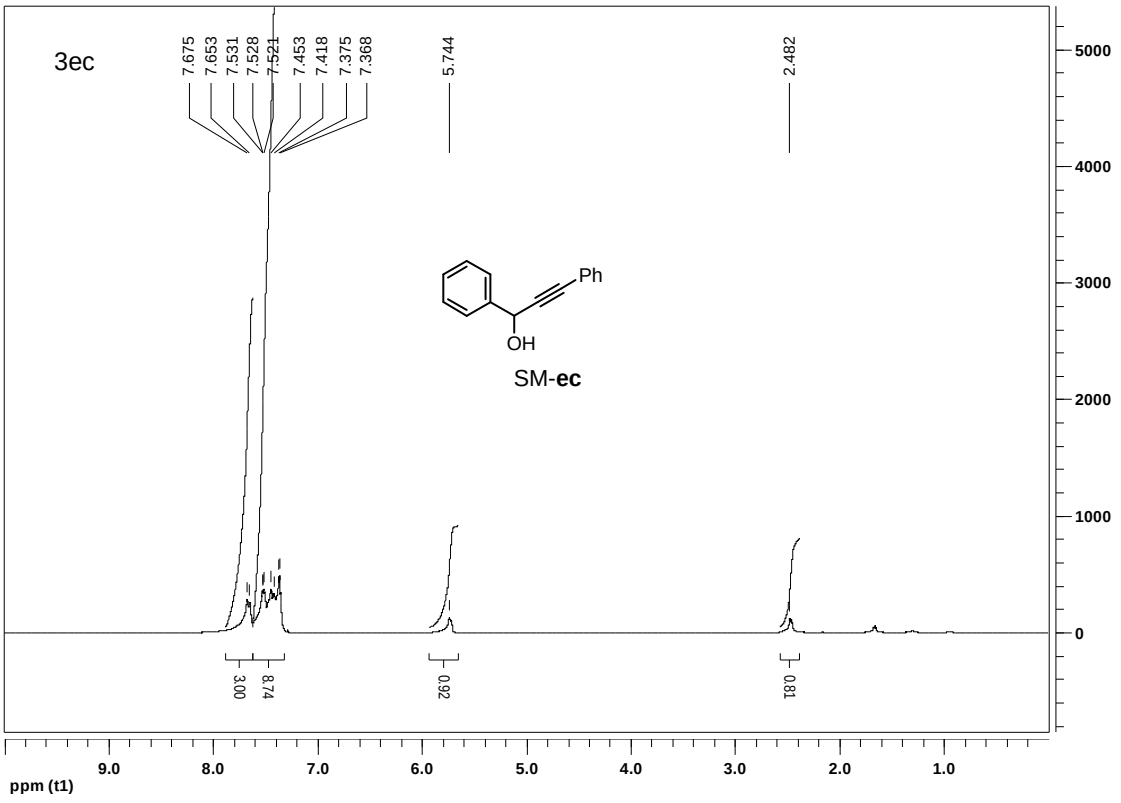

3dc
7.458
7.450
7.438
7.426
7.309
7.300
7.294
7.287
4.405
4.385
4.366
2.342
2.323
1.952
1.917
1.810
1.781
1.773
1.713
1.703
1.676
1.665
1.318
1.309
1.299
1.268
1.259
1.228
1.193
Ph
OH
SM-dc
500
0
2.24
3.06
1.00
1.11
8.11
6.38
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

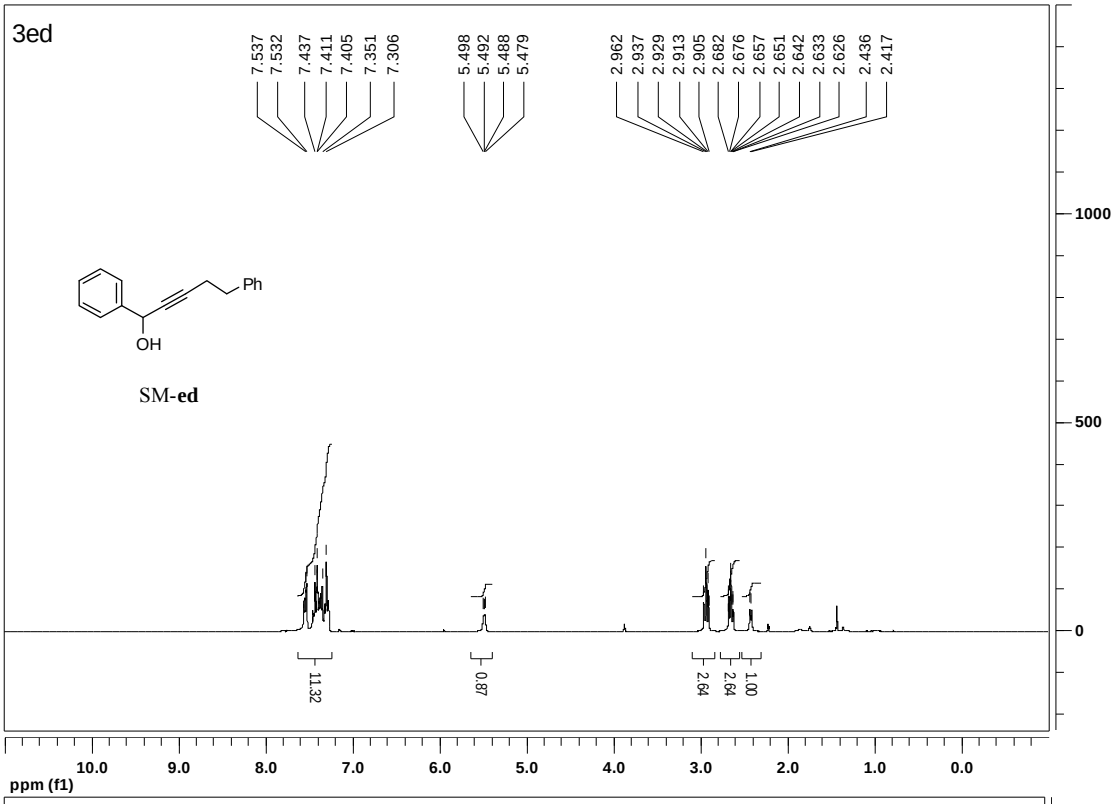

3dd
7.295
7.291
7.272
7.259
7.229
7.207
4.119
4.113
4.107
4.100
4.094
2.854
2.829
2.804
2.552
2.546
2.527
2.521
2.503
2.496
Ph
OH
SM-dd
500
0
5.09
0.85
2.26
2.00
7.39
5.20
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

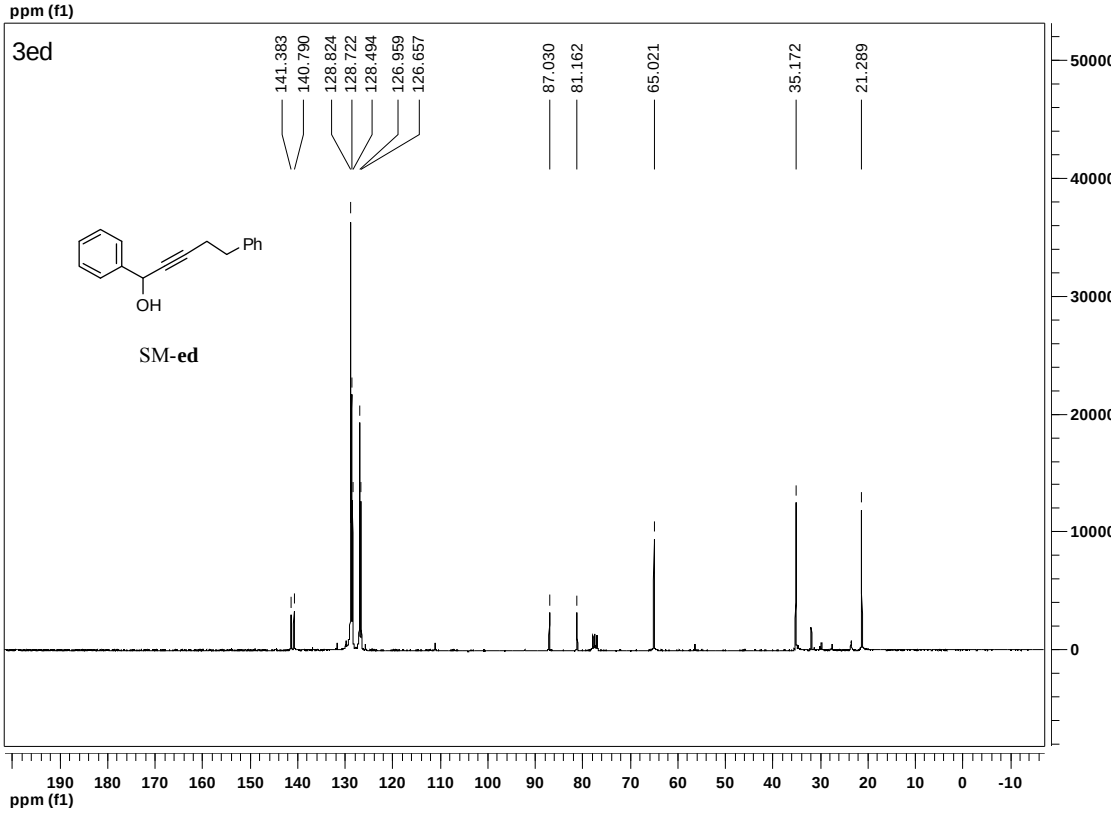

4.149
4.130
4.110
1.870
1.844
1.839
1.800
1.752
1.732
1.695
1.681
1.660
1.319
1.309
1.301
1.286
1.277
1.268
1.257
1.246
1.236
1.226
1.195
1.173
1.159
1.144
1.133
TMS
OH
SM-de
1.00
7.38
5.75
7.92
ppm (f1)

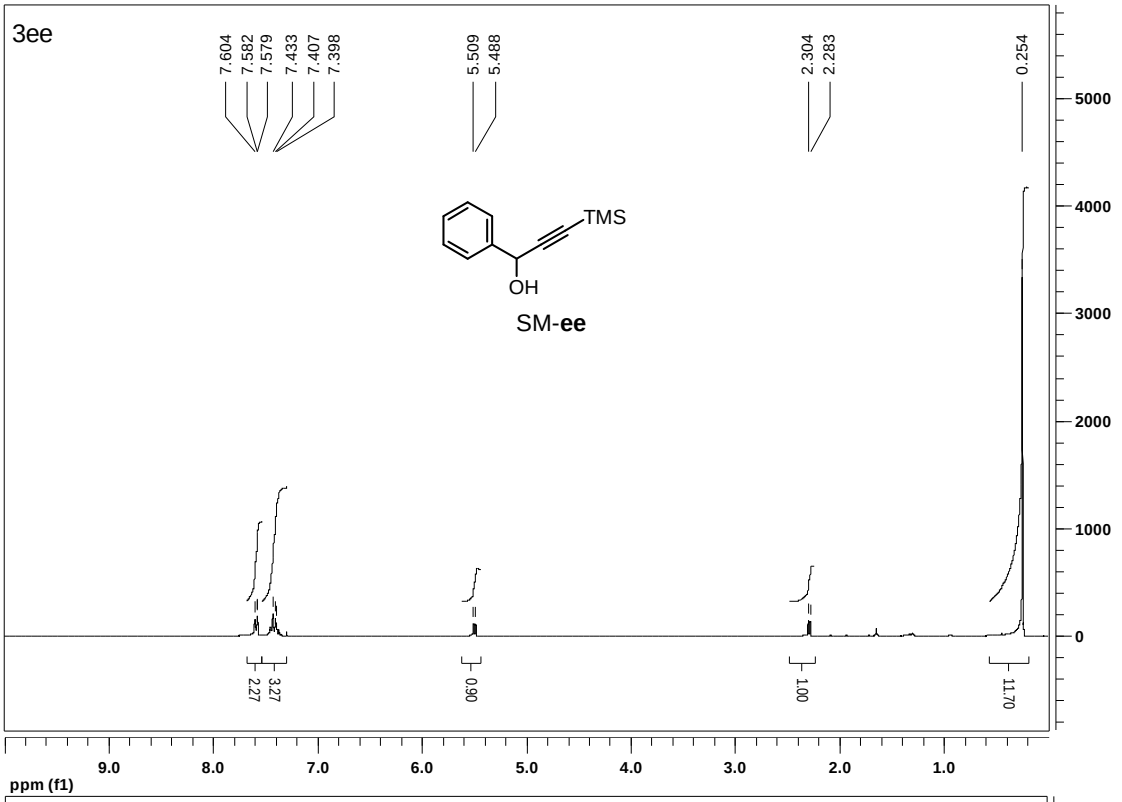

7.541
7.534
7.513
7.511
7.411
7.393
7.386
7.259
5.595
5.574
3.798
2.309
2.292
2.288
2.276
OH
CO2Me
SM-ea
3.07
1.62
0.97
3.44
1.00
ppm (f1)

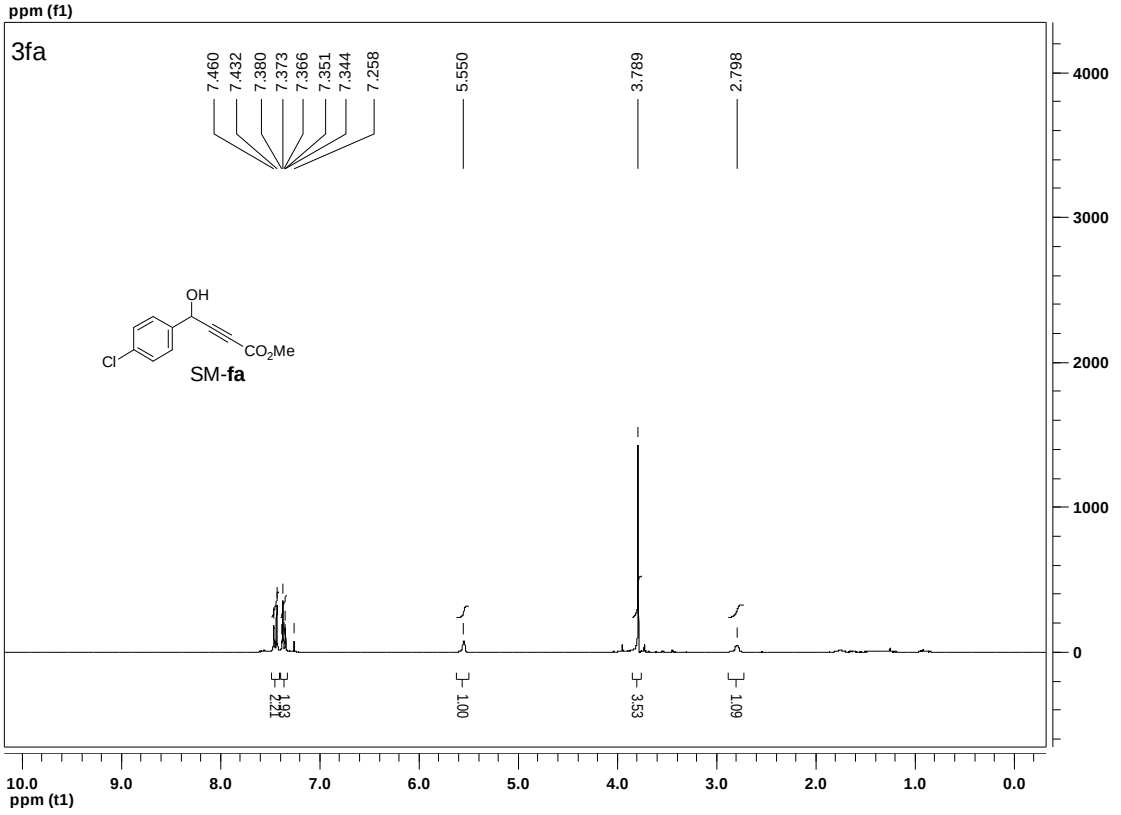

3eb
7.535
7.529
7.508
7.503
7.402
7.384
7.377
5.580
5.559
4.282
4.258
4.234
4.210
2.626
2.605
1.335
1.311
1.287
OH
CO2Et
SM-eb
1.94
2.83
0.84
2.00
0.86
3.59
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)
1500
1000
500
0

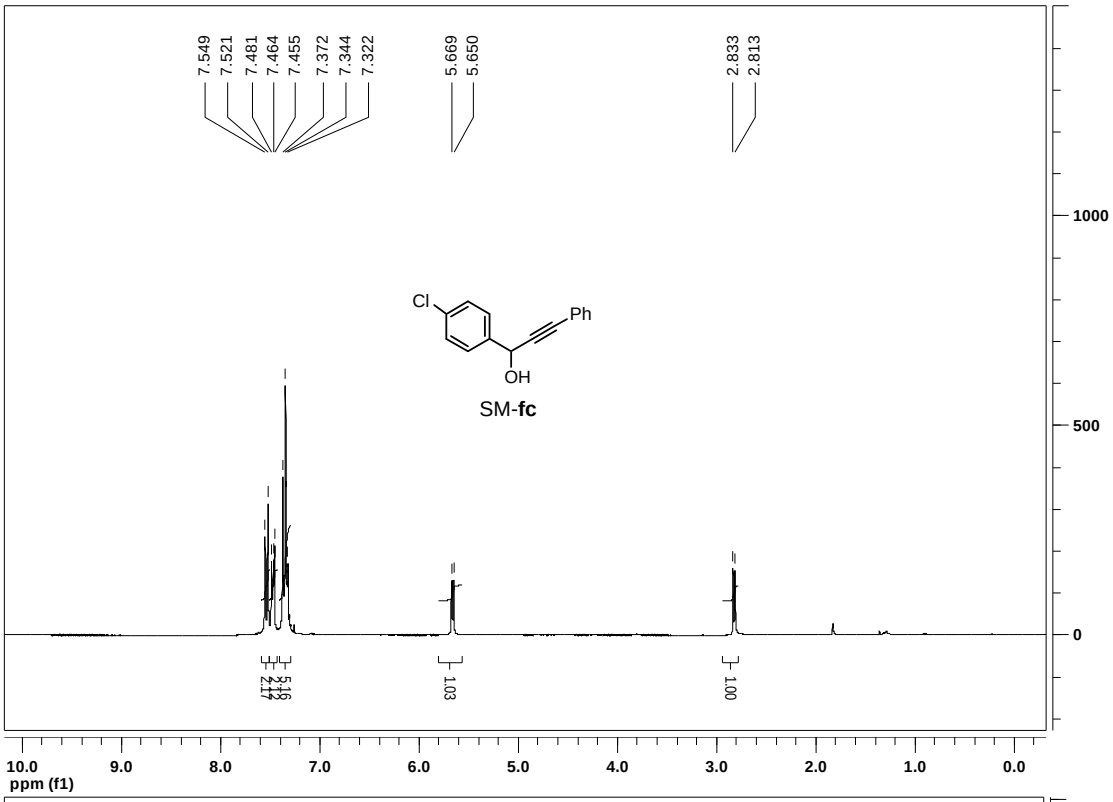

3ec
7.675
7.653
7.531
7.528
7.521
7.453
7.418
7.375
7.368
5.744
2.482
Ph
OH
SM-ec
3.00
8.74
0.92
0.81
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)
5000
4000
3000
2000
1000
0

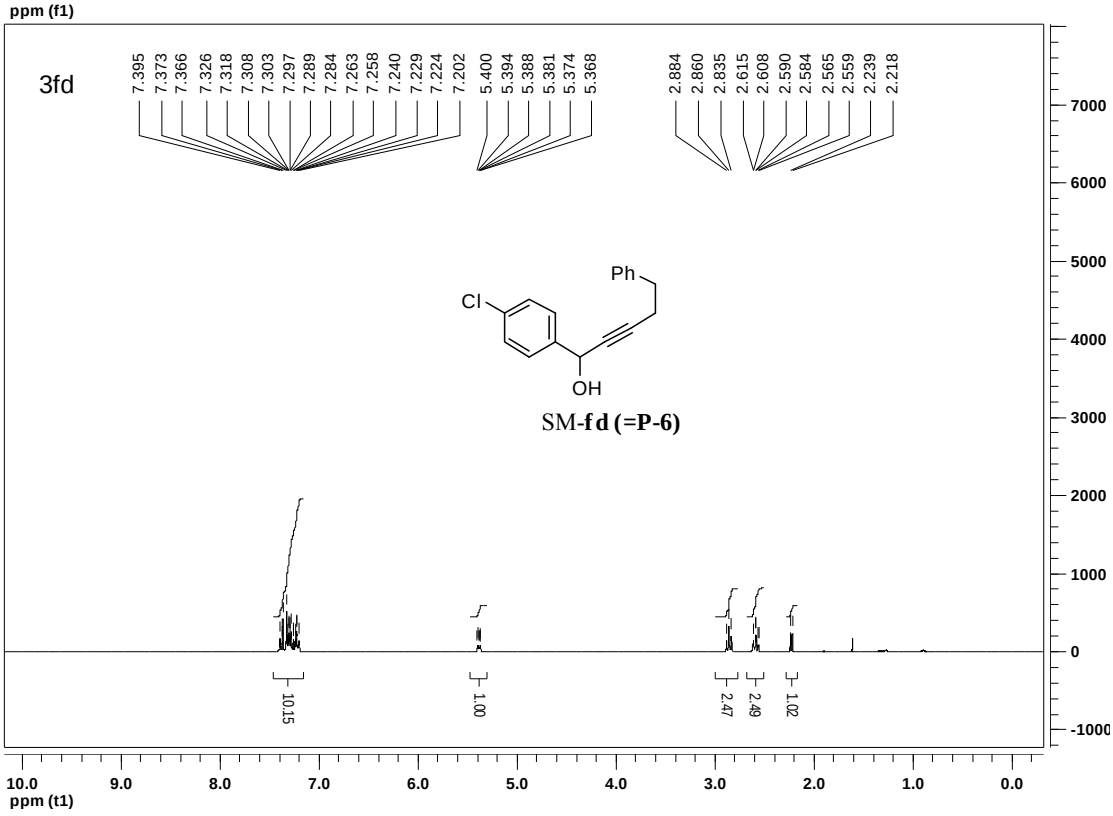

3ed
7.537
7.532
7.437
7.411
7.405
7.351
7.306
5.498
5.492
5.488
5.479
2.962
2.937
2.929
2.913
2.905
2.682
2.676
2.657
2.651
2.642
2.633
2.626
2.436
2.417
Ph
OH
SM-ed
1000
500
0
1.12
0.87
2.94
2.64
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

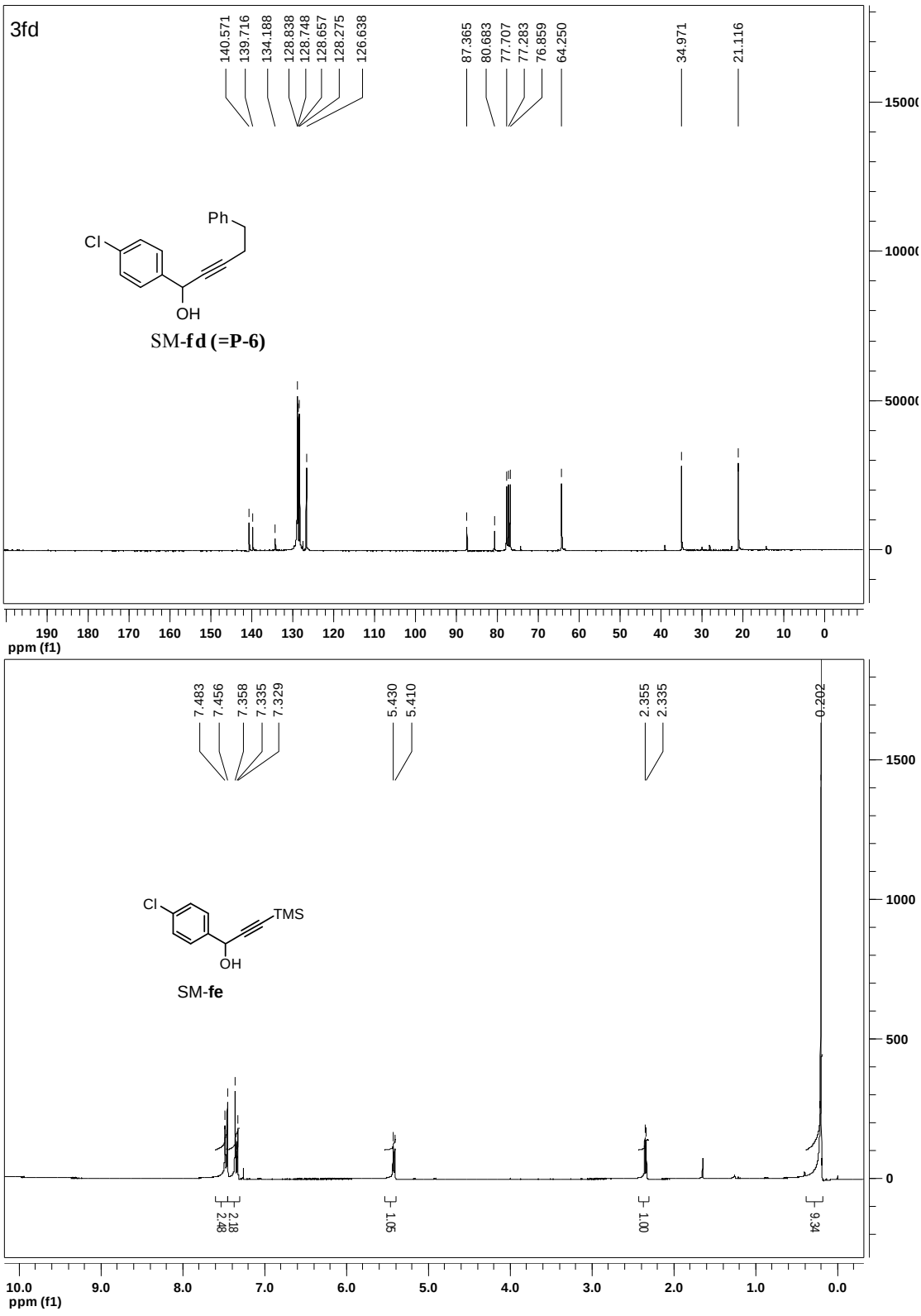

3ed
141.383
140.790
128.824
128.722
128.494
126.959
126.657
87.030
81.162
65.021
35.172
21.289
Ph
OH
SM-ed
50000
40000
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (f1)

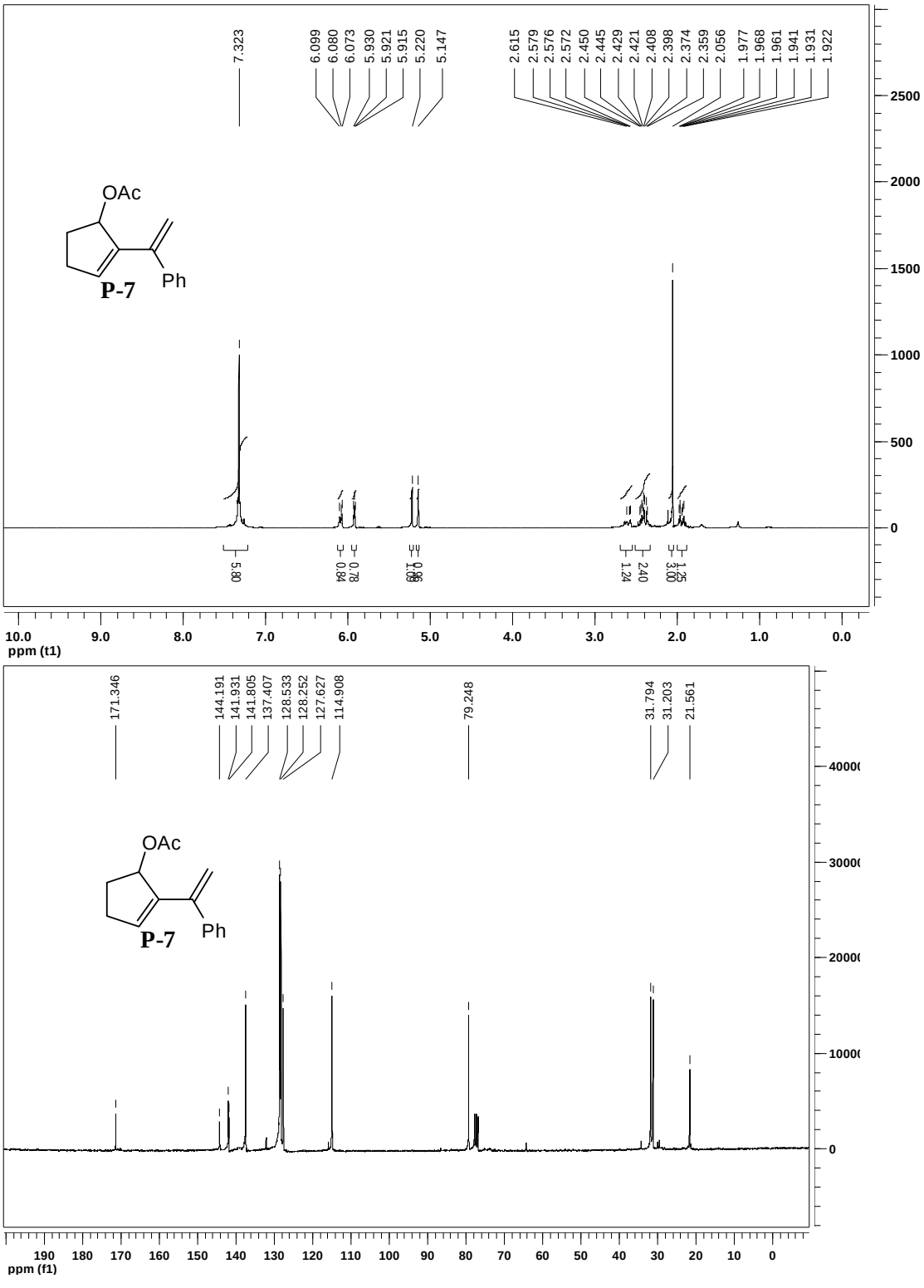

3ee
7.604
7.582
7.579
7.433
7.407
7.398
5.509
5.488
2.304
2.283
0.254
TMS
OH
SM-ee
2.27
3.27
0.90
1.00
11.70
ppm (f1)

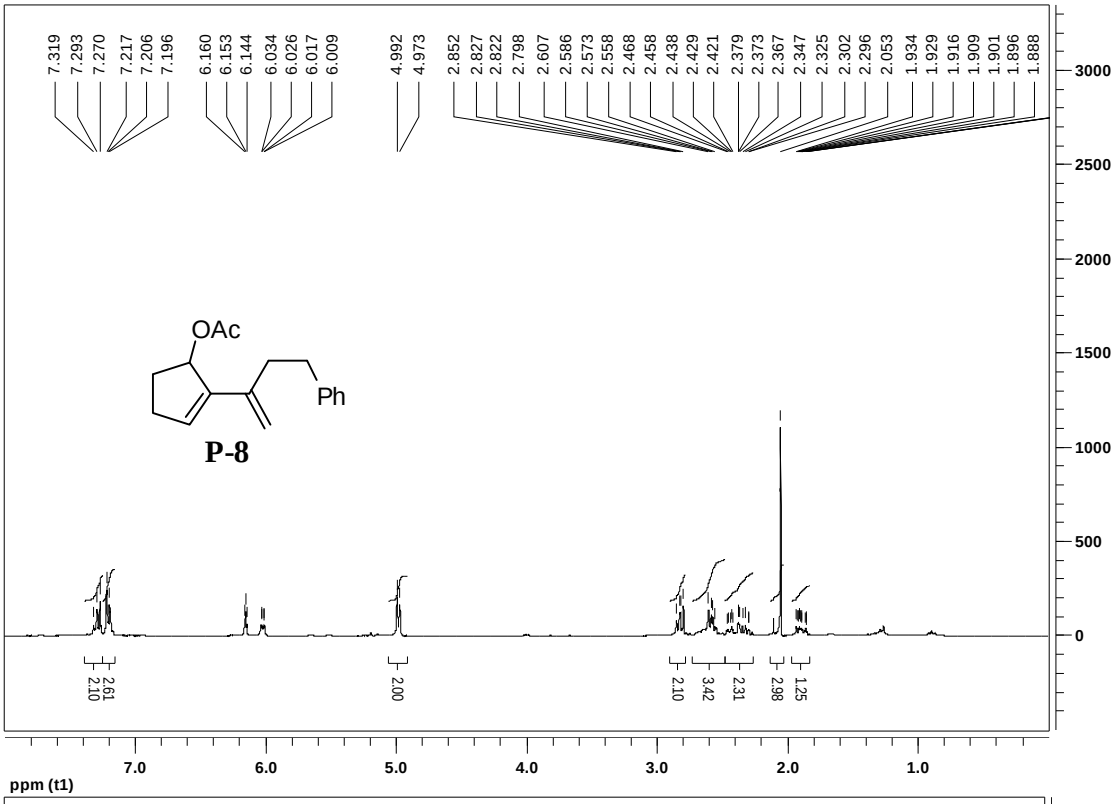

3fa
7.460
7.432
7.380
7.373
7.366
7.351
7.344
7.258
5.550
3.789
2.798
OH
Cl
CO2Me
SM-fa
2.21
1.93
1.00
3.53
1.09
ppm (t1)

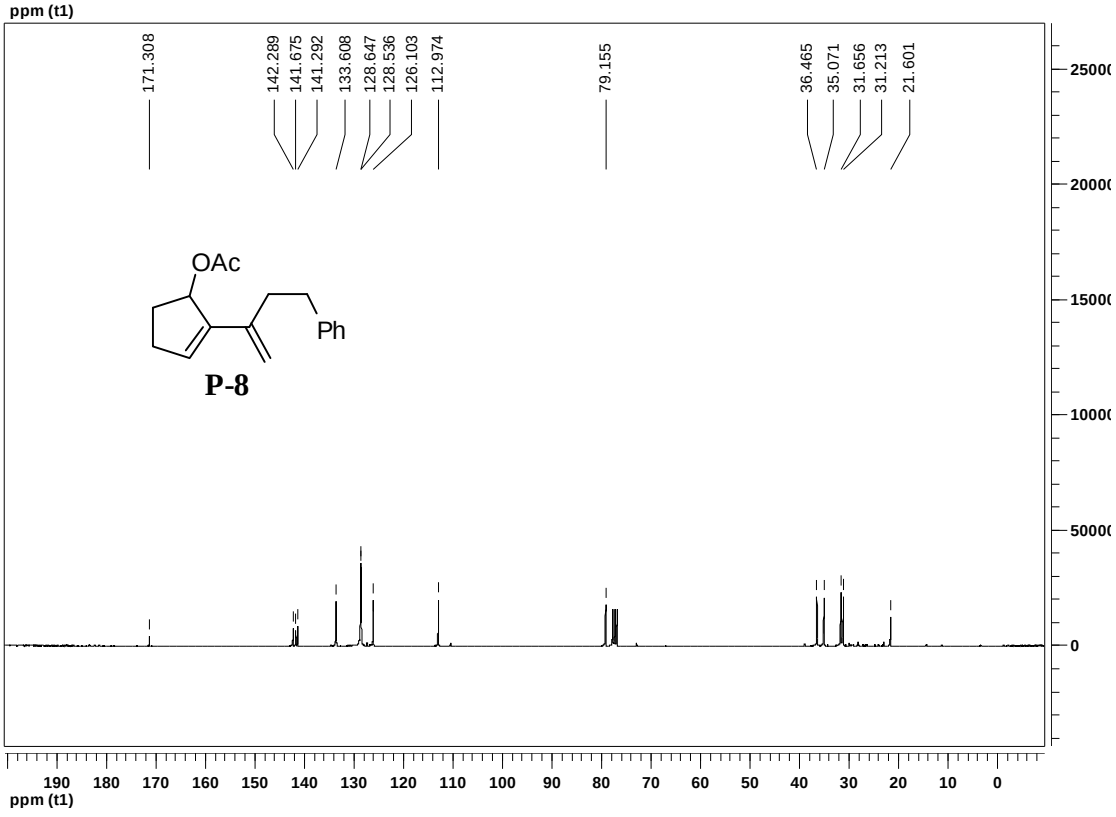

7.549
7.521
7.481
7.464
7.455
7.372
7.344
7.322
5.669
5.650
2.833
2.813
Cl
Ph
OH
SM-fc
1000
500
0
2.17
5.16
1.03
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

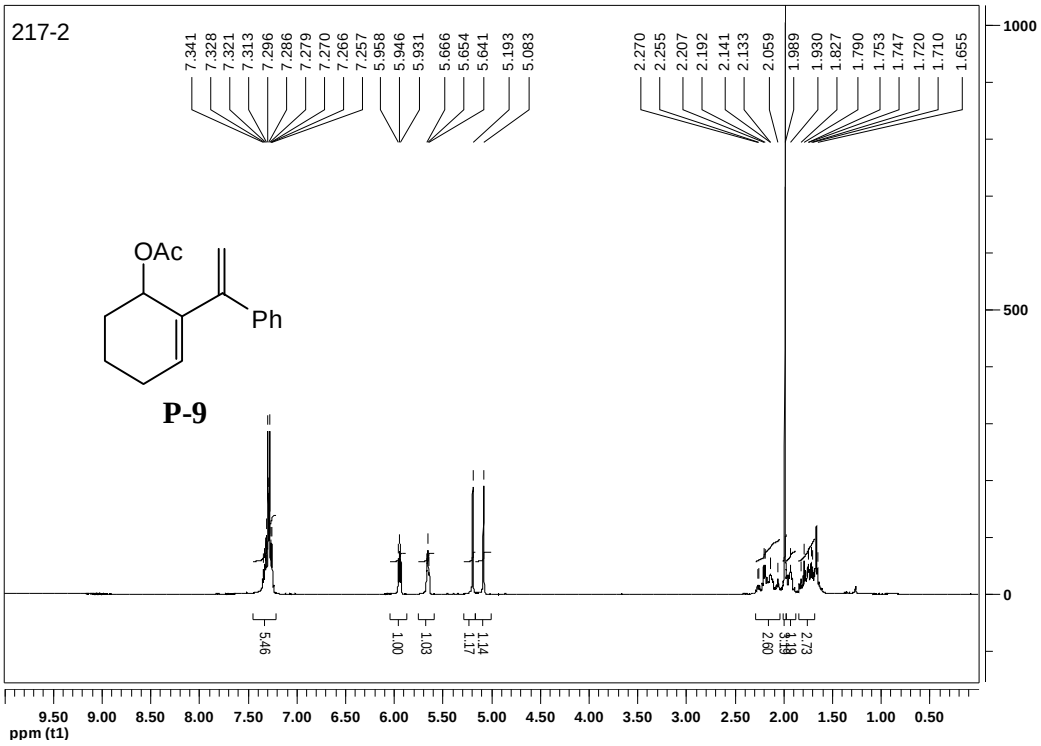

3fd
7.395
7.373
7.366
7.326
7.318
7.308
7.303
7.297
7.289
7.284
7.263
7.258
7.240
7.229
7.224
7.202
5.400
5.394
5.388
5.381
5.374
5.368
2.884
2.860
2.835
2.615
2.608
2.590
2.584
2.565
2.559
2.239
2.218
Ph
Cl
OH
SM-fd (=P-6)
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.15
1.00
2.47
2.49
1.02
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

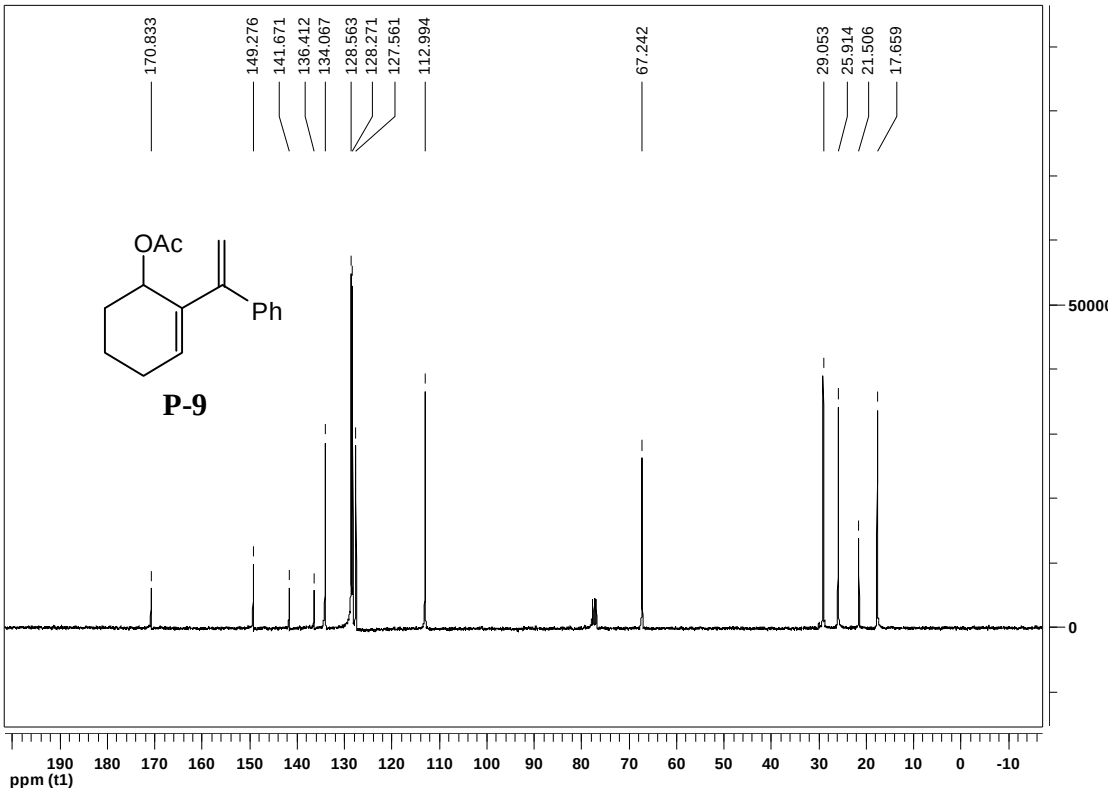

3fd
140.571
139.716
134.188
128.838
128.748
128.657
128.275
126.638
87.365
80.683
77.707
77.283
76.859
64.250
34.971
21.116
Ph
Cl
OH
SM-fd (=P-6)
ppm (f1)
7.483
7.456
7.358
7.335
7.329
5.430
5.410
2.355
2.335
0.202
TMS
Cl
OH
SM-fe
2.48
2.18
1.05
1.00
9.34
ppm (f1)

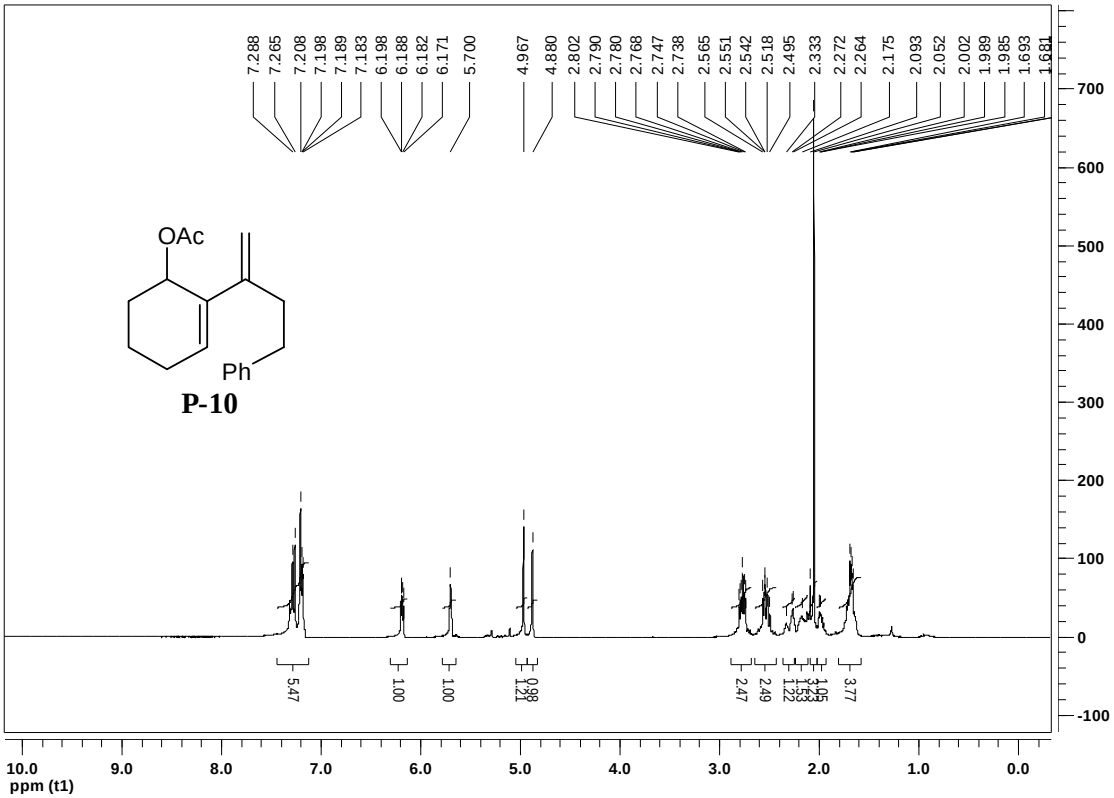

7.323
6.099
6.080
6.073
5.930
5.921
5.915
5.220
5.147
2.615
2.579
2.576
2.572
2.450
2.445
2.429
2.421
2.408
2.398
2.374
2.359
2.056
1.977
1.968
1.961
1.941
1.931
1.922
OAc
Ph
P-7
ppm (t1)
171.346
144.191
141.931
141.805
137.407
128.533
128.252
127.627
114.908
79.248
31.794
31.203
21.561
OAc
Ph
P-7
ppm (f1)


7.319
7.293
7.270
7.217
7.206
7.196
6.160
6.153
6.144
6.034
6.026
6.017
6.009
4.992
4.973
2.852
2.827
2.822
2.798
2.607
2.586
2.573
2.558
2.468
2.458
2.438
2.429
2.421
2.379
2.373
2.367
2.347
2.325
2.302
2.296
2.053
1.934
1.929
1.916
1.909
1.901
1.896
1.888
OAc
Ph
P-8
2.10
2.61
2.00
2.10
3.42
2.31
2.98
1.25
ppm (t1)

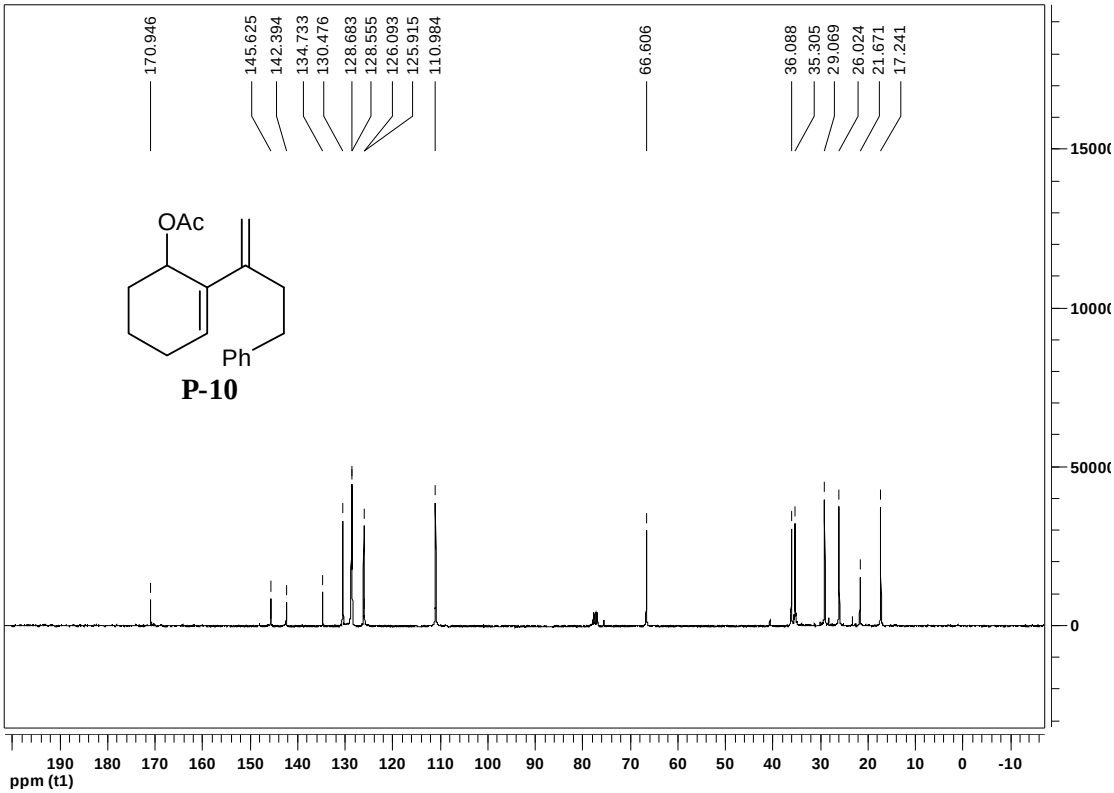

171.308
142.289
141.675
141.292
133.608
128.647
128.536
126.103
112.974
79.155
36.465
35.071
31.656
31.213
21.601
OAc
Ph
P-8
ppm (t1)


217-2
7.341
7.328
7.321
7.313
7.296
7.286
7.279
7.270
7.266
7.257
5.958
5.946
5.931
5.666
5.654
5.641
5.193
5.083
2.270
2.255
2.207
2.192
2.141
2.133
2.059
1.989
1.930
1.827
1.790
1.753
1.747
1.720
1.710
1.655
OAc
Ph
P-9
1000
500
0
5.46
1.00
1.03
1.14
1.17
2.60
2.72
9.50 9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50
ppm (t1)

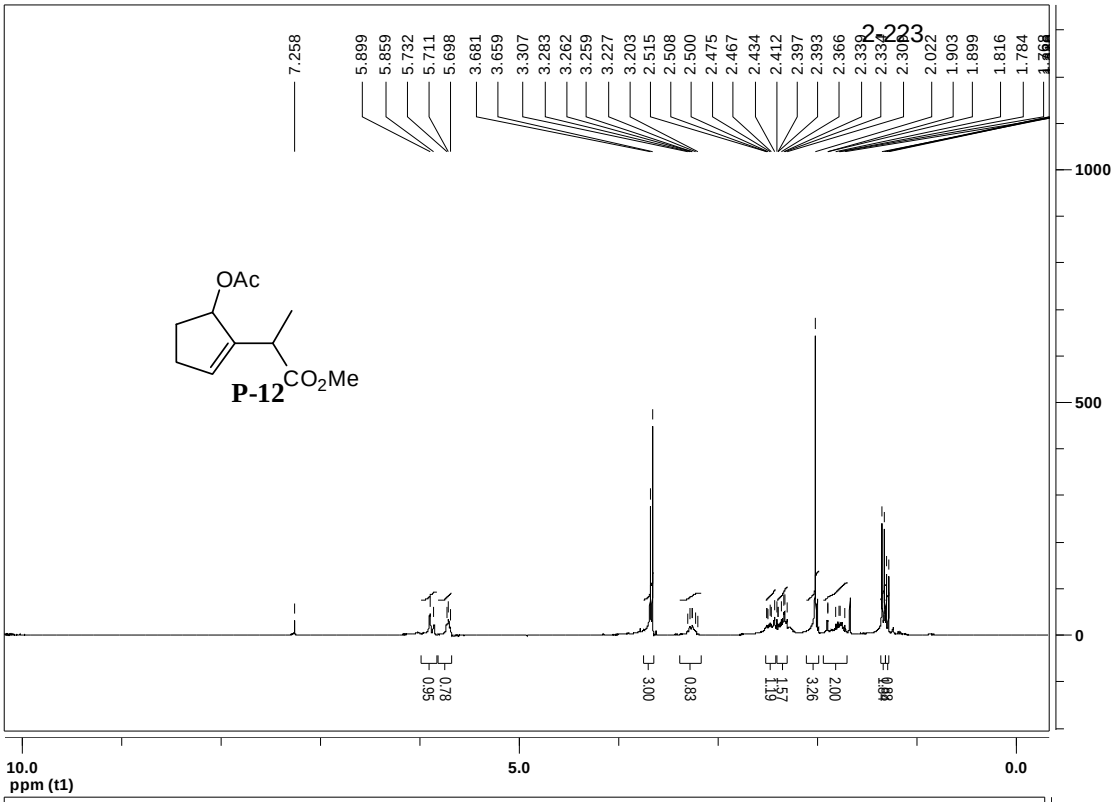

170.833
149.276
141.671
136.412
134.067
128.563
128.271
127.561
112.994
67.242
29.053
25.914
21.506
17.659
OAc
Ph
P-9
50000
0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm (t1)

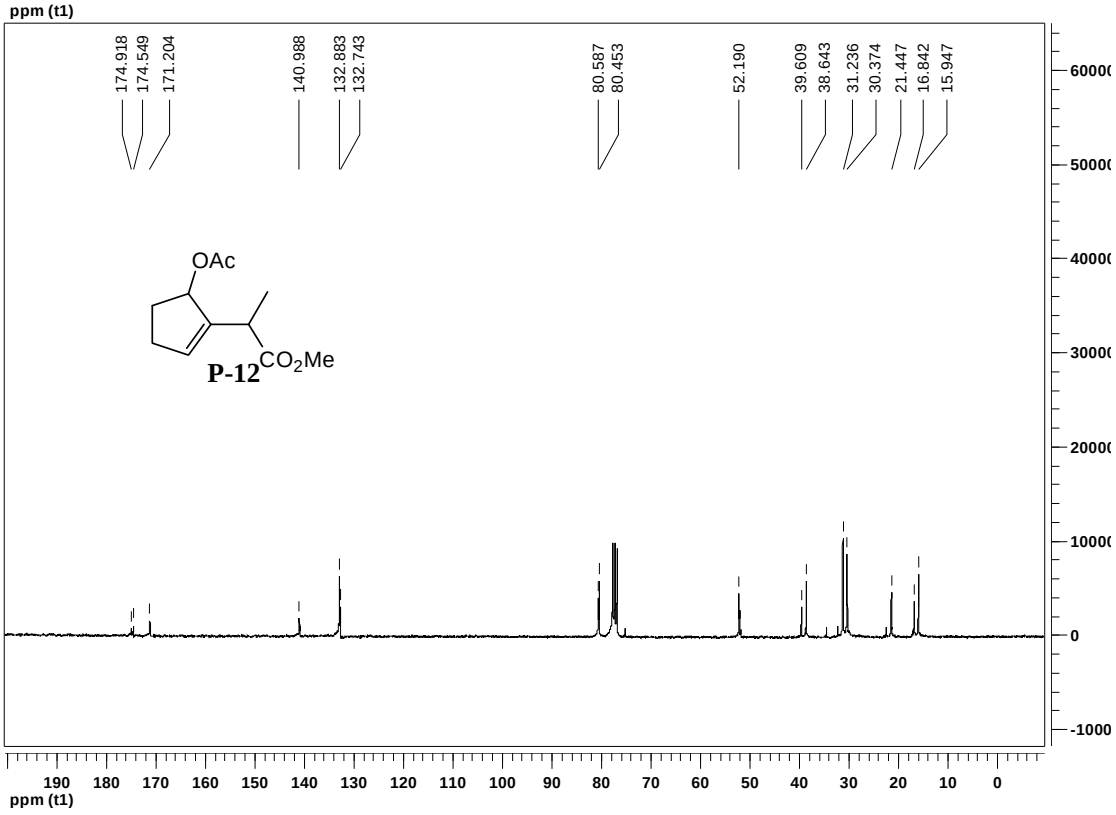

7.288
7.265
7.208
7.198
7.189
7.183
6.198
6.188
6.182
6.171
5.700
4.967
4.880
2.802
2.790
2.780
2.768
2.747
2.738
2.565
2.551
2.542
2.518
2.495
2.333
2.272
2.264
2.175
2.093
2.052
2.002
1.989
1.985
1.693
1.681
OAc
Ph
5.47
1.00
1.00
0.98
1.21
2.47
2.49
3.77
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

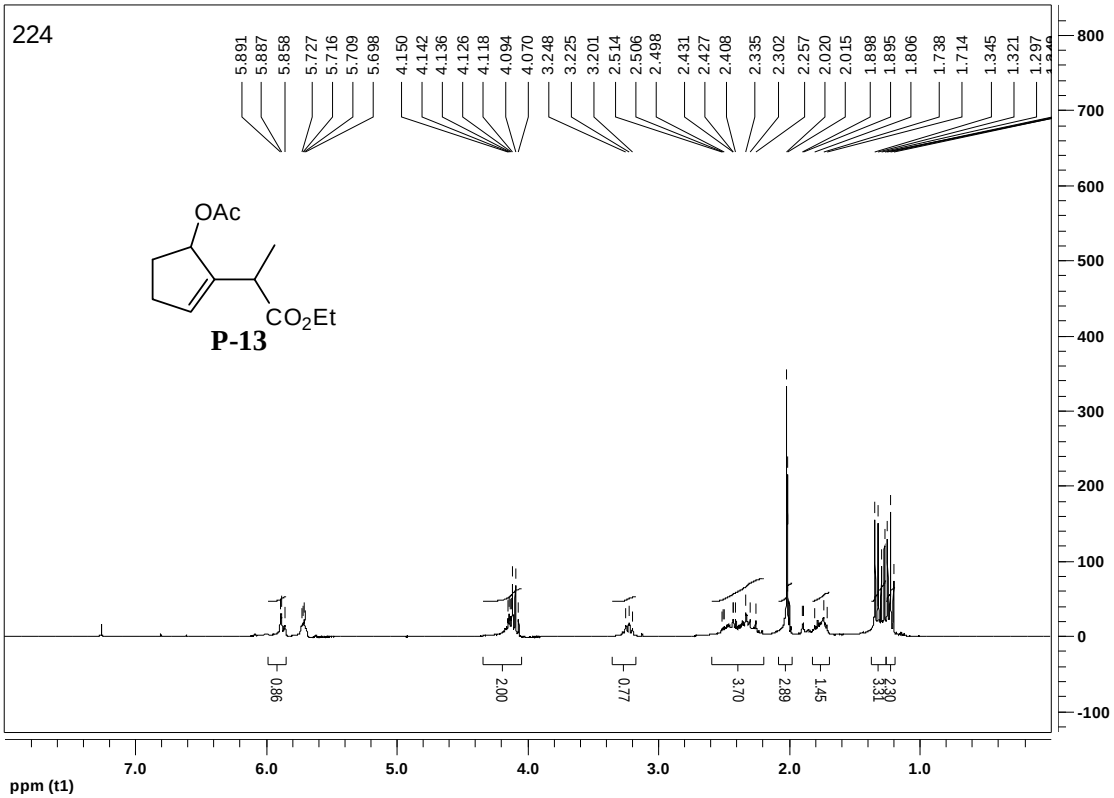
P-10

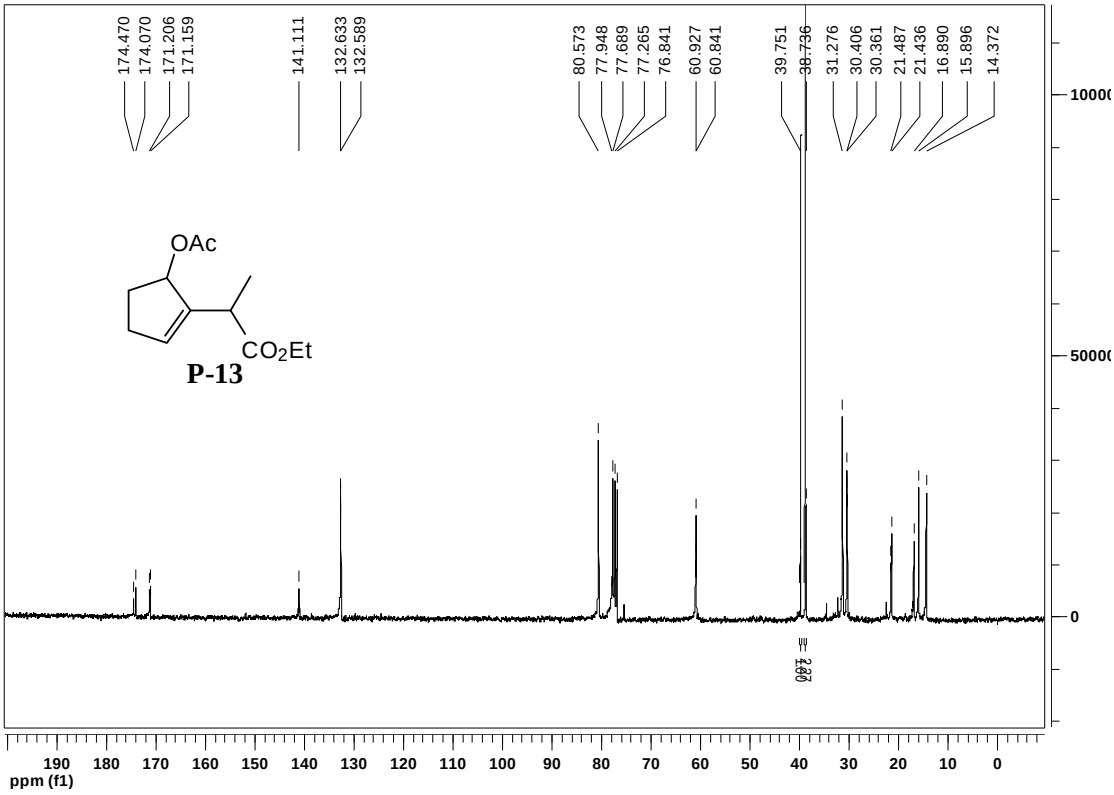

170.946
145.625
142.394
134.733
130.476
128.683
128.555
126.093
125.915
110.984
66.606
36.088
35.305
29.069
26.024
21.671
17.241
OAc
Ph
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm (t1)

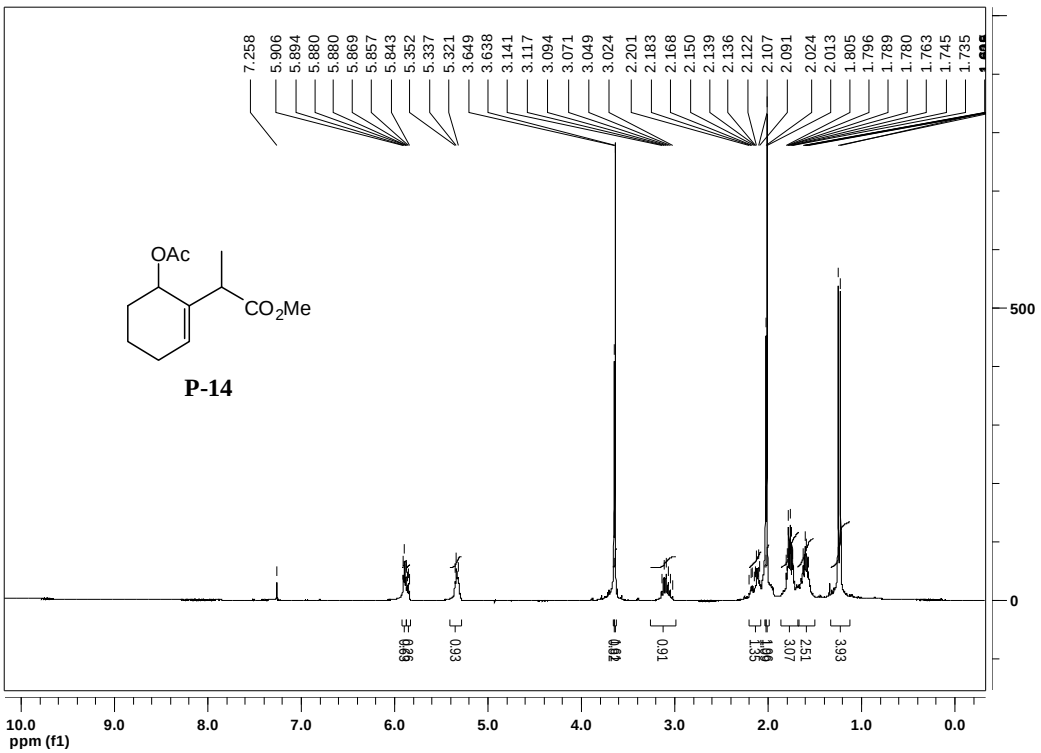
P-10

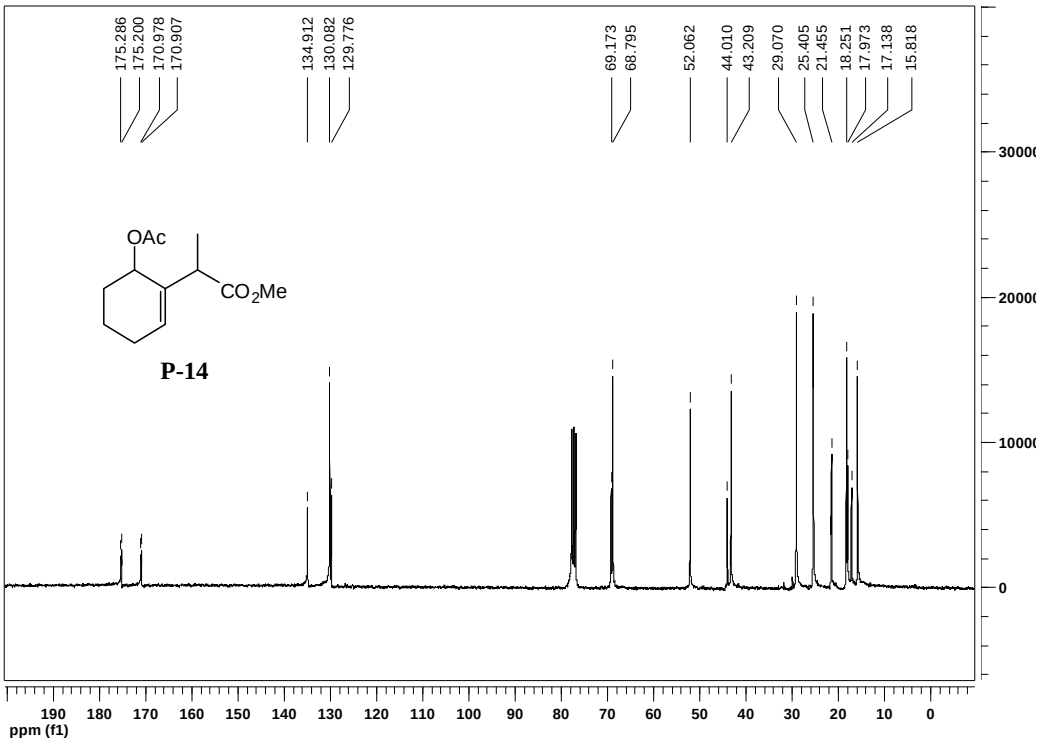

2-223
7.258
5.899
5.859
5.732
5.711
5.698
3.681
3.659
3.307
3.283
3.262
3.259
3.227
3.203
2.515
2.508
2.500
2.475
2.467
2.434
2.412
2.397
2.393
2.366
2.338
2.334
2.308
2.022
1.903
1.899
1.816
1.784
OAc
P-12 CO2Me
1000
500
0
0.95
0.78
3.00
0.83
1.57
1.19
3.26
2.00
10.0
ppm (t1)
5.0
0.0

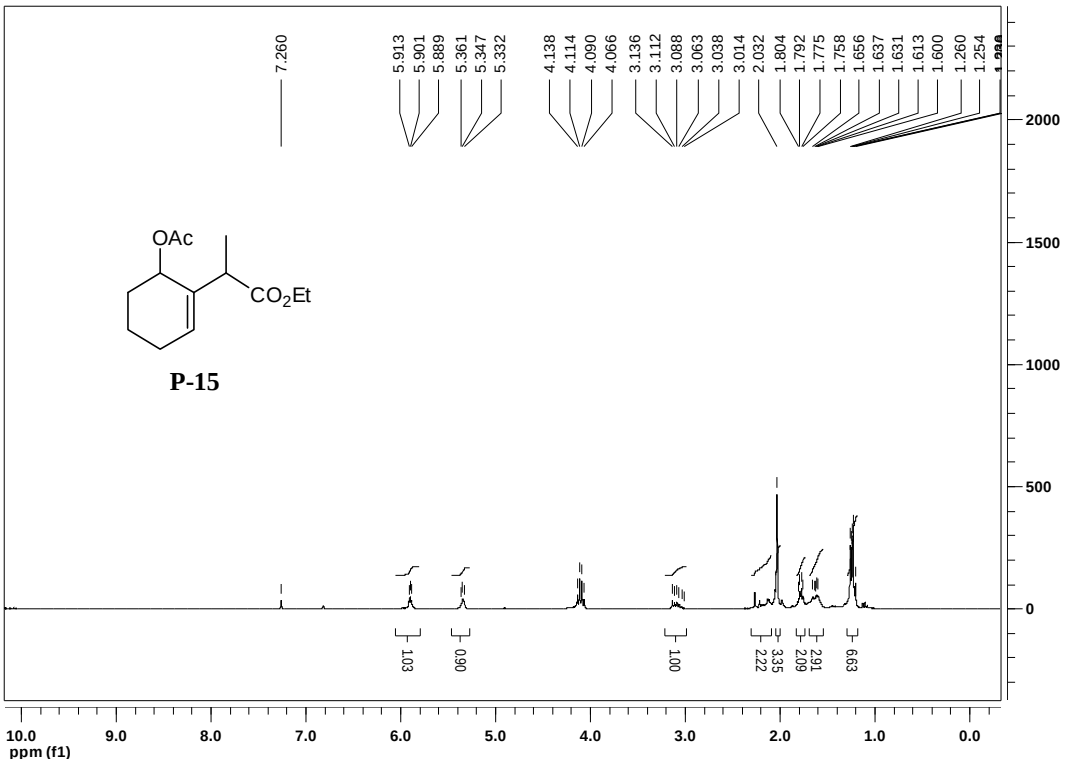

174.918
174.549
171.204
140.988
132.883
132.743
80.587
80.453
52.190
39.609
38.643
31.236
30.374
21.447
16.842
15.947
OAc
P-12 CO2Me
60000
50000
40000
30000
20000
10000
0
-10000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

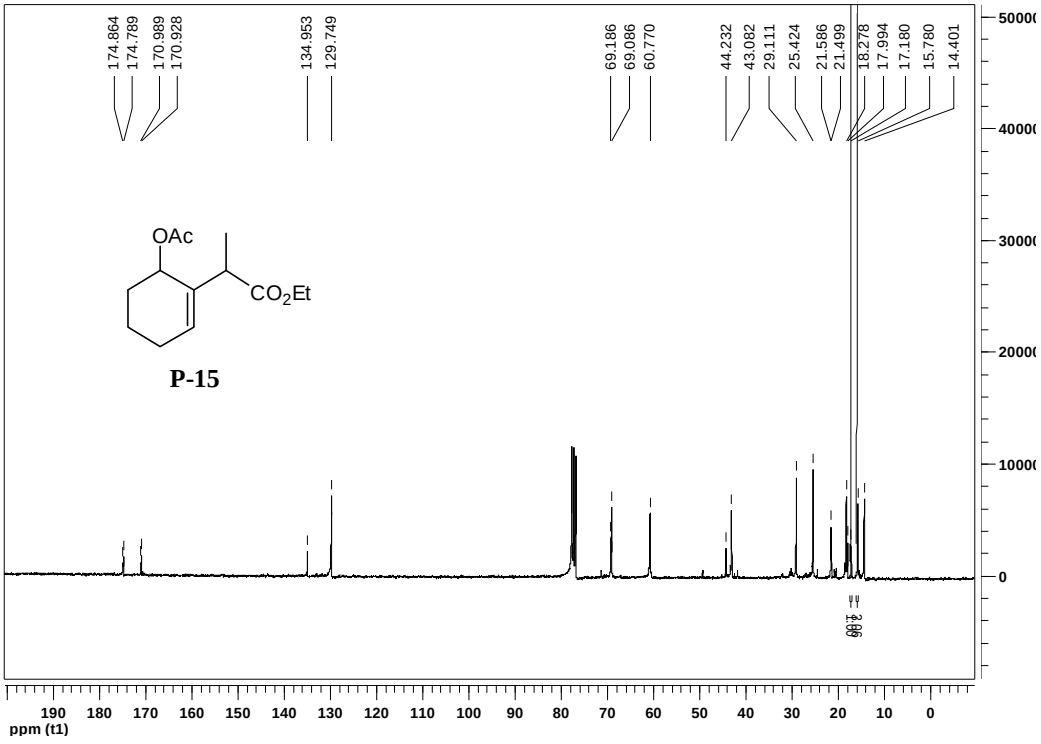

224
5.891
5.887
5.858
5.727
5.716
5.709
5.698
4.150
4.142
4.136
4.126
4.118
4.094
4.070
3.248
3.225
3.201
2.514
2.506
2.498
2.431
2.427
2.408
2.335
2.302
2.257
2.020
2.015
1.898
1.895
1.806
1.738
1.714
1.345
1.321
1.297
OAc
CO2Et
P-13
0.86
2.00
0.77
3.70
2.89
1.45
2.30
3.31
ppm (t1)

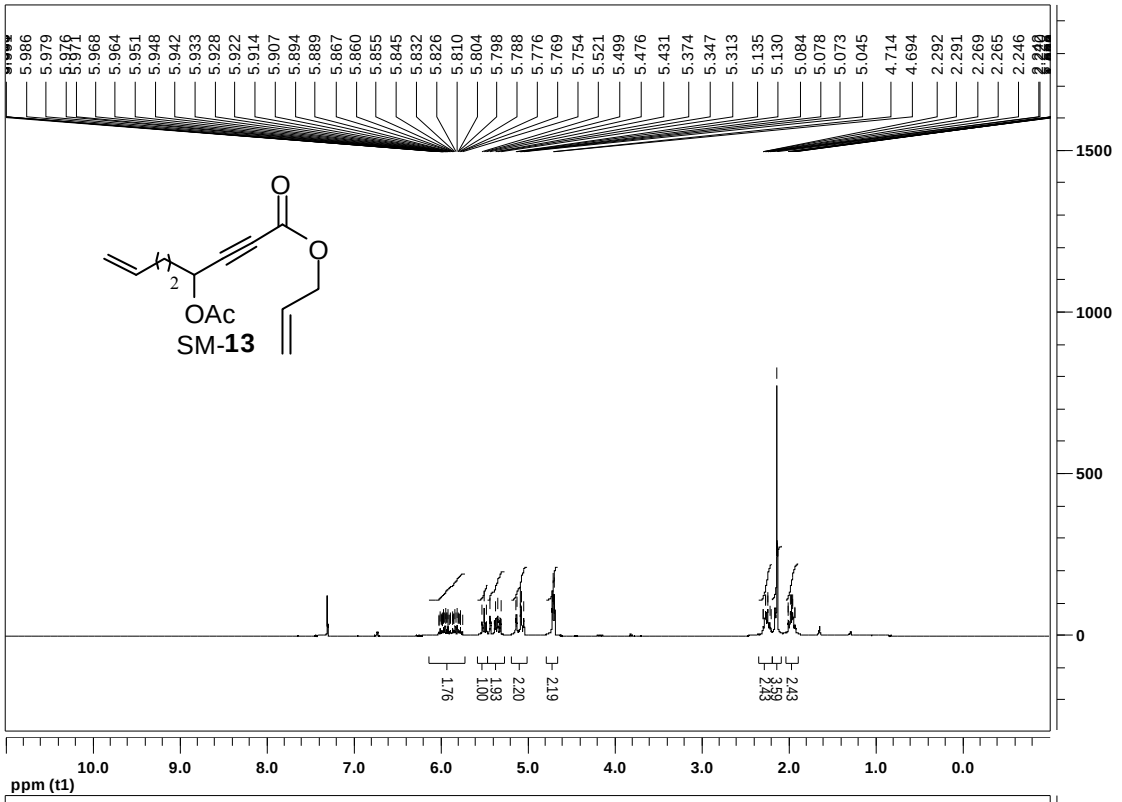

174.470
174.070
171.206
171.159
141.111
132.633
132.589
80.573
77.948
77.689
77.265
76.841
60.927
60.841
39.751
38.736
31.276
30.406
30.361
21.487
21.436
16.890
15.896
14.372
OAc
CO2Et
P-13
ppm (f1)

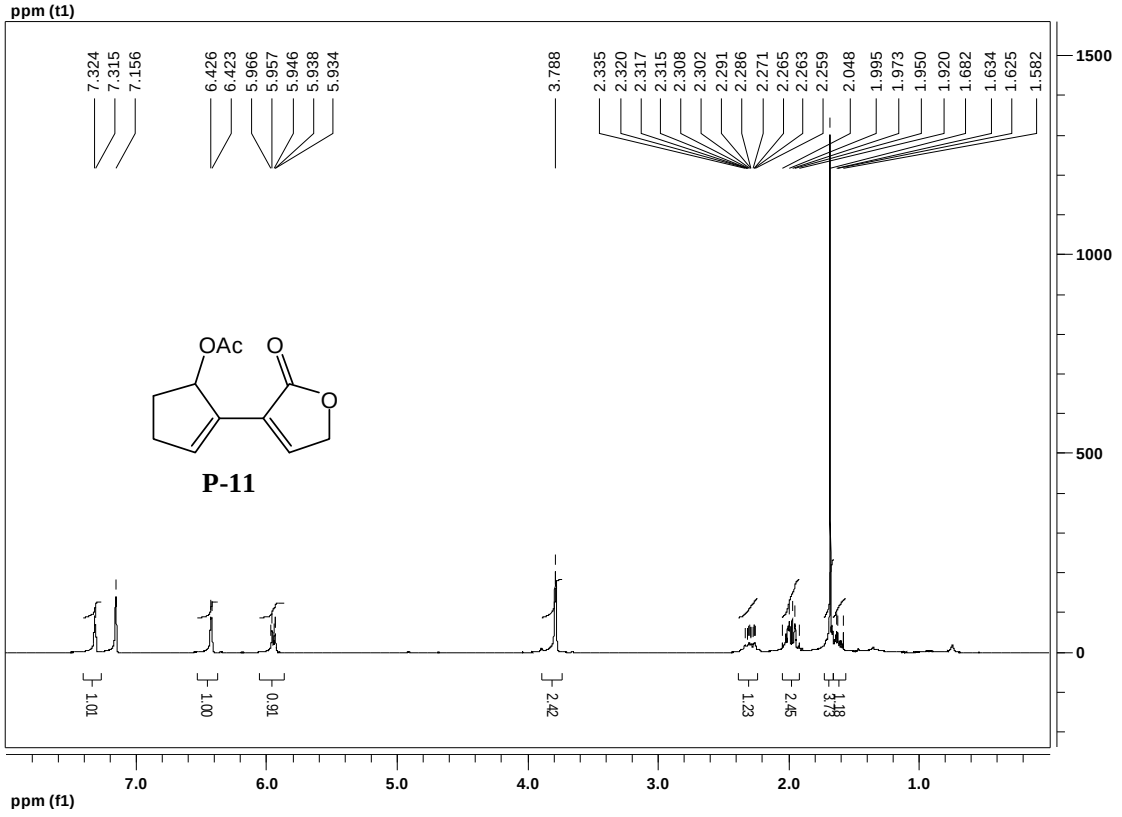

7.258
5.906
5.894
5.880
5.880
5.869
5.857
5.843
5.352
5.337
5.321
3.649
3.638
3.141
3.117
3.094
3.071
3.049
3.024
2.201
2.183
2.168
2.150
2.139
2.136
2.122
2.107
2.091
2.024
2.013
1.805
1.796
1.789
1.780
1.763
1.745
1.735
OAc
CO2Me
P-14
500
0
0.89
0.93
4.00
0.91
1.35
3.07
2.51
3.93
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

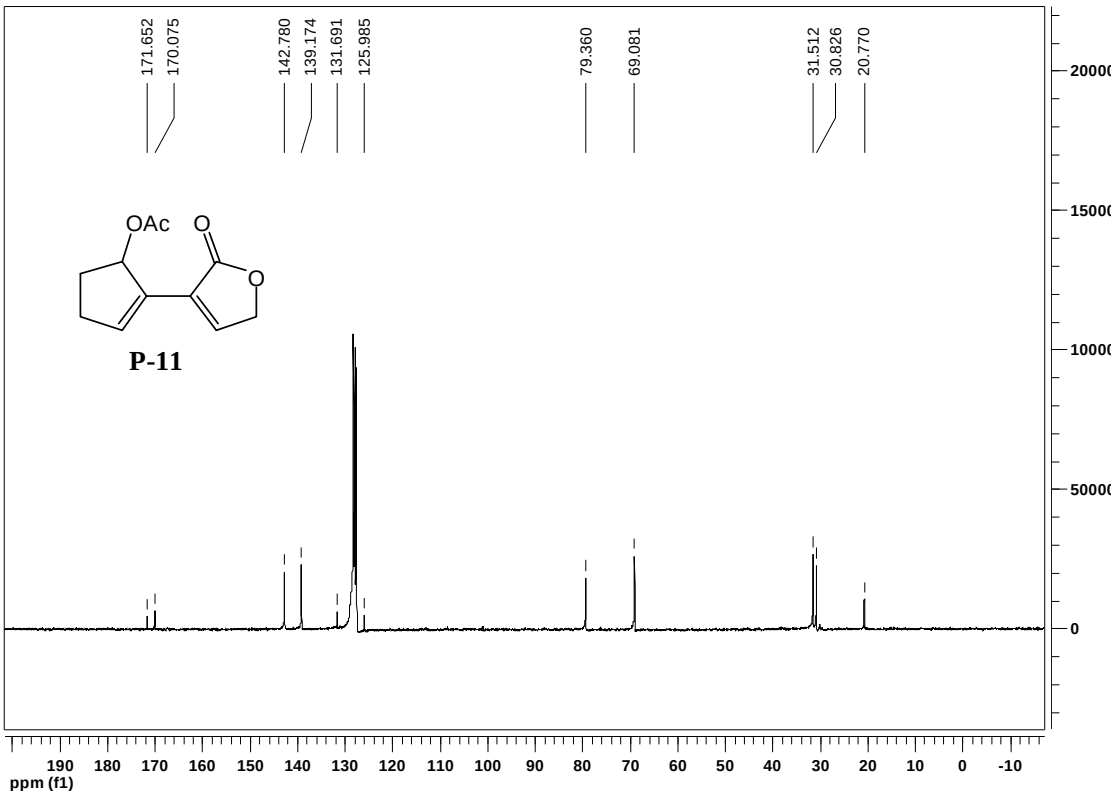

175.286
175.200
170.978
170.907
134.912
130.082
129.776
69.173
68.795
52.062
44.010
43.209
29.070
25.405
21.455
18.251
17.973
17.138
15.818
OAc
CO2Me
P-14
30000
20000
10000
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (f1)

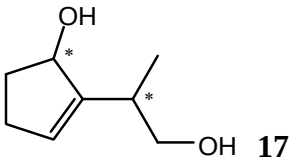

7.260
5.913
5.901
5.889
5.361
5.347
5.332
4.138
4.114
4.090
4.066
3.136
3.112
3.088
3.063
3.038
3.014
2.032
1.804
1.792
1.775
1.758
1.656
1.637
1.631
1.613
1.600
1.260
1.254
OAc
CO2Et
P-15
2000
1500
1000
500
0
1.03
0.90
1.00
2.22
3.35
2.09
2.01
6.63
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


174.864
174.789
170.989
170.928
134.953
129.749
69.186
69.086
60.770
44.232
43.082
29.111
25.424
21.586
21.499
18.278
17.994
17.180
15.780
14.401
OAc
CO2Et
P-15
50000
40000
30000
20000
10000
0
2.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm (t1)

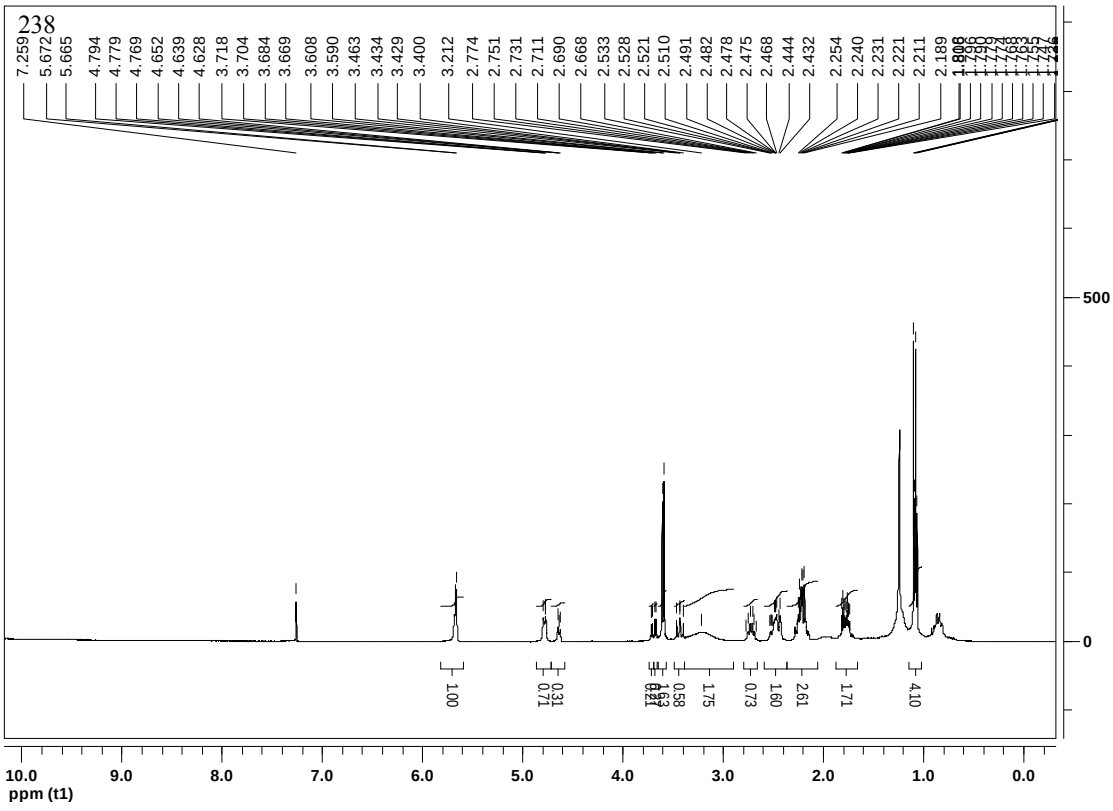

5.986
5.979
5.968
5.964
5.951
5.948
5.942
5.933
5.928
5.922
5.914
5.907
5.894
5.889
5.867
5.860
5.855
5.845
5.832
5.826
5.810
5.804
5.798
5.788
5.776
5.769
5.754
5.521
5.499
5.476
5.431
5.374
5.347
5.313
5.135
5.130
5.084
5.078
5.073
5.045
4.714
4.694
2.292
2.291
2.269
2.265
2.246
1500
1000
500
0
O
O
2
OAc
SM-13
1.76
1.93
1.00
2.20
2.19
2.43
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

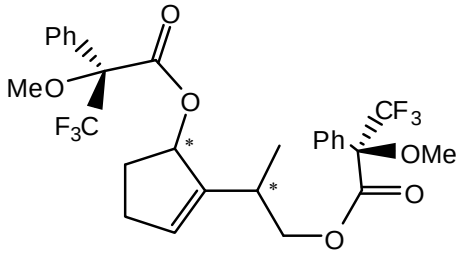

7.324
7.315
7.156
6.426
6.423
5.966
5.957
5.946
5.938
5.934
3.788
2.335
2.320
2.317
2.315
2.308
2.302
2.291
2.286
2.271
2.265
2.263
2.259
2.048
1.995
1.973
1.950
1.920
1.682
1.634
1.625
1.582
1500
1000
500
0
OAc
O
O
P-11
1.01
1.00
0.91
2.42
1.23
2.45
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


171.652
170.075
142.780
139.174
131.691
125.985
79.360
69.081
31.512
30.826
20.770
OAc
O
O
P-11
ppm (f1)

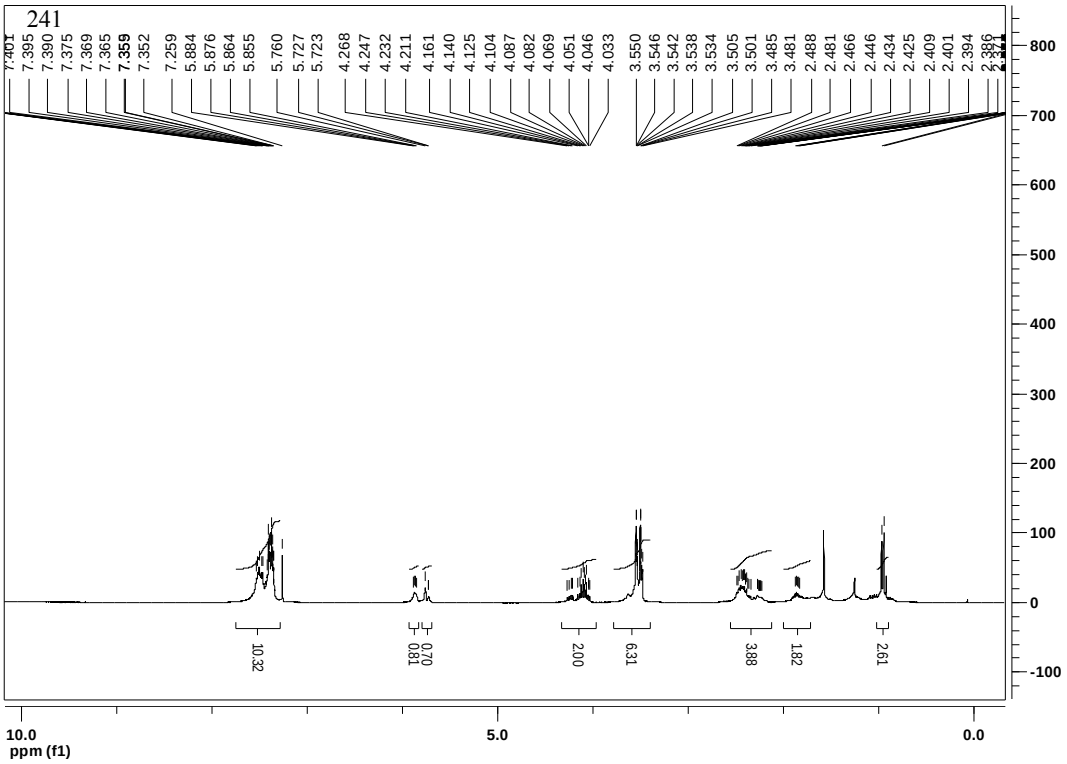

OH
*
*
OH

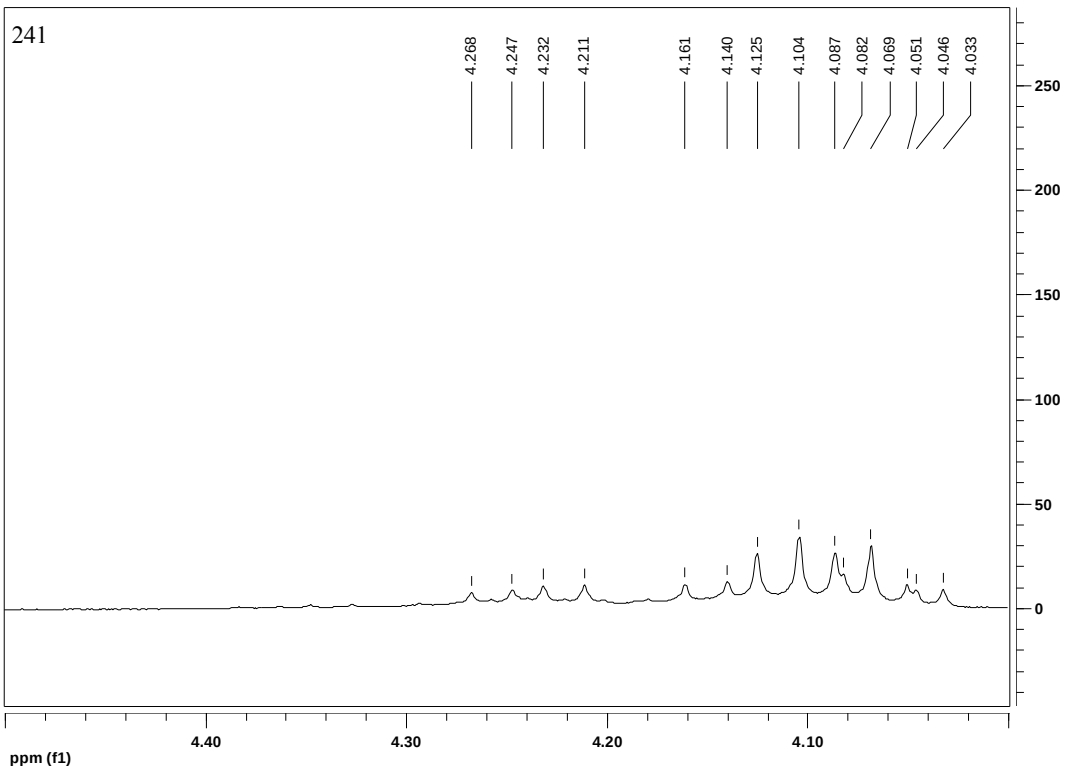
17

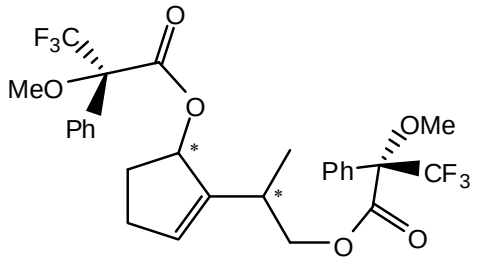

238
7.259
5.672
5.665
4.794
4.779
4.769
4.652
4.639
4.628
3.718
3.704
3.684
3.669
3.608
3.590
3.463
3.434
3.429
3.400
3.212
2.774
2.751
2.731
2.711
2.690
2.668
2.533
2.528
2.521
2.510
2.491
2.482
2.478
2.475
2.468
2.444
2.432
2.254
2.240
2.231
2.221
2.211
2.189
1.00
0.71
0.31
0.58
1.75
0.73
1.80
2.61
1.71
4.10
ppm (t1)


Ph
MeO
F3C
O
O
*
*
CF3
Ph
OMe
O
O

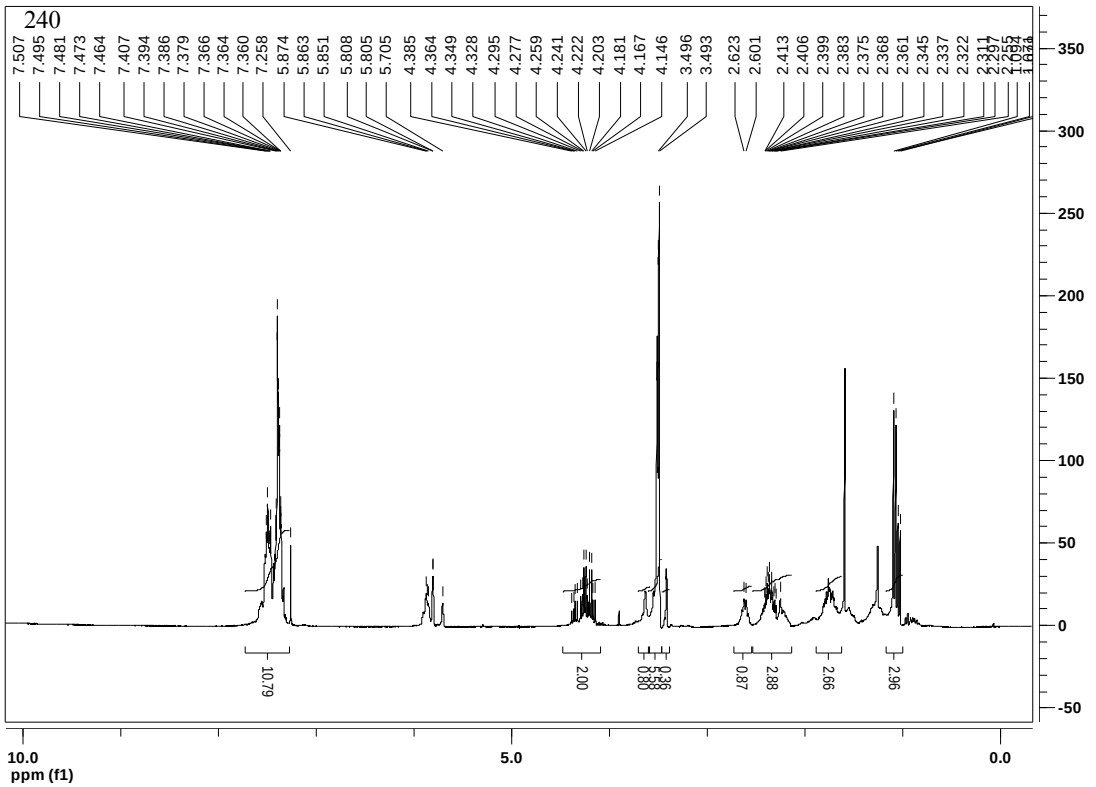
18:

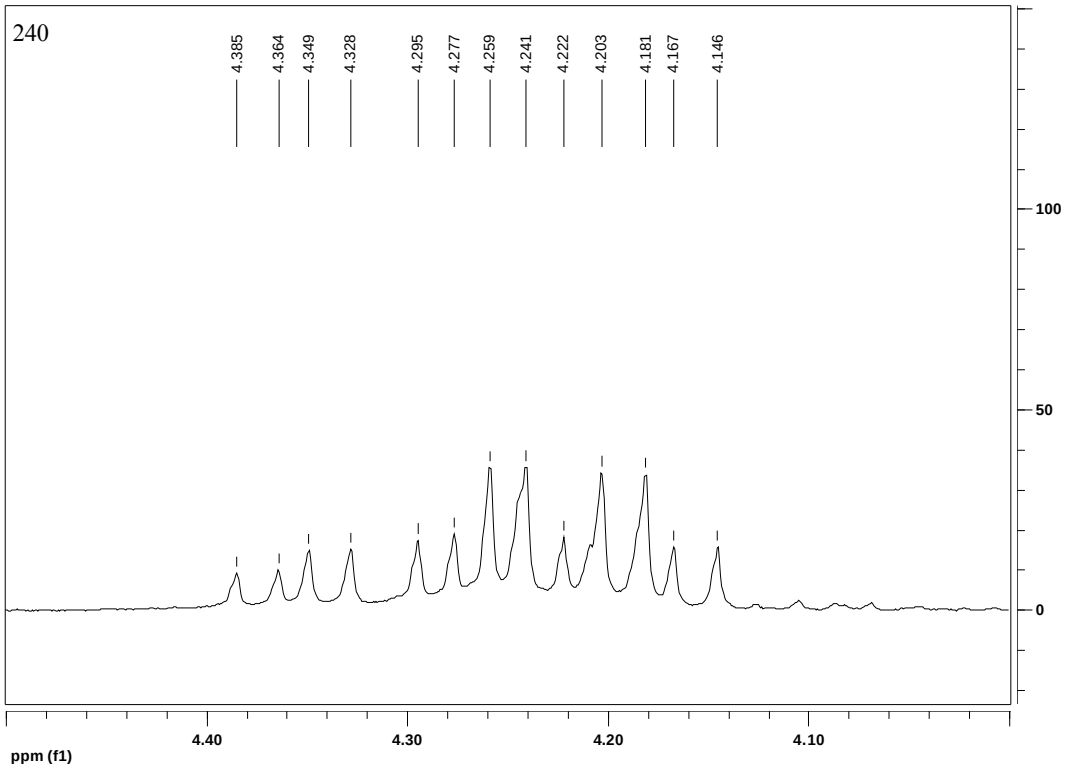

241
7.401
7.395
7.390
7.375
7.369
7.365
7.359
7.352
7.259
5.884
5.876
5.864
5.855
5.760
5.727
5.723
4.268
4.247
4.232
4.211
4.161
4.140
4.125
4.104
4.087
4.082
4.069
4.051
4.046
4.033
3.550
3.546
3.542
3.538
3.534
3.505
3.501
3.485
3.481
2.488
2.481
2.466
2.446
2.434
2.425
2.409
2.401
2.394
10.32
0.81
0.70
2.00
6.31
3.88
1.82
2.61
800
700
600
500
400
300
200
100
0
-100
10.0
5.0
0.0
ppm (f1)


241
4.268
4.247
4.232
4.211
4.161
4.140
4.125
4.104
4.087
4.082
4.069
4.051
4.046
4.033
250
200
150
100
50
0
4.40
4.30
4.20
4.10
ppm (f1)


O
F3C
MeO
Ph
O
*
*
OMe
Ph
CF3
O
O

19


240
7.507
7.495
7.481
7.473
7.464
7.407
7.394
7.386
7.379
7.366
7.364
7.360
7.258
5.874
5.863
5.851
5.808
5.805
5.705
4.385
4.364
4.349
4.328
4.295
4.277
4.259
4.241
4.222
4.203
4.181
4.167
4.146
3.496
3.493
2.623
2.601
2.413
2.406
2.399
2.383
2.375
2.368
2.361
2.345
2.337
2.322
10.79
2.00
0.87
2.88
2.66
2.96
10.0
ppm (f1)
5.0
0.0


240
4.385
4.364
4.349
4.328
4.295
4.277
4.259
4.241
4.222
4.203
4.181
4.167
4.146
100
50
0
4.40
4.30
4.20
4.10
ppm (f1)