# Supporting Information for

## Catalytic Asymmetric Synthesis of Chiral Propargylic Alcohols for the Intramolecular Pauson-Khand Cycloaddition

Mark Turlington,[a] Yang Yue,[a],[b] Xiao-Qi Yu*,[b] and Lin Pu*,[a]

*[a]Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904, [b]Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, China 610064.*

*E-mail: lp6n@virginia.edu, xqyu@tfol.com*

## I. Analytical Instruments:

NMR: Varian 300 MHz, 500 MHz.
HPLC: Waters 600 Pump and Waters 486 Tunable Absorbance Detector, Chiralcel OD, OB-H, or Chiralpak AD-H column.
Polarimeter: Jasco Digital Polarimeter P-2000.
High resolution mass spectra were obtained by ESI analysis and the [$MH^+$] was observed.

## II. General Data:

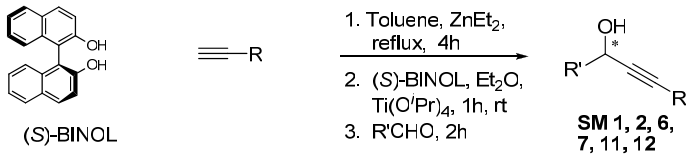
All commercial chemicals were used as received.

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.

All alkynes and aldehydes were passed through a plug of alumina and distilled from 4 Å molecular sieves prior to use and stored under nitrogen atmosphere.

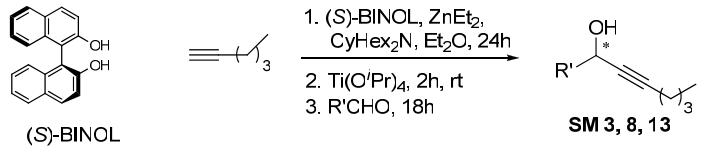
## III. General Procedures:

### 1. Asymmetric Alkyne Addition Method I



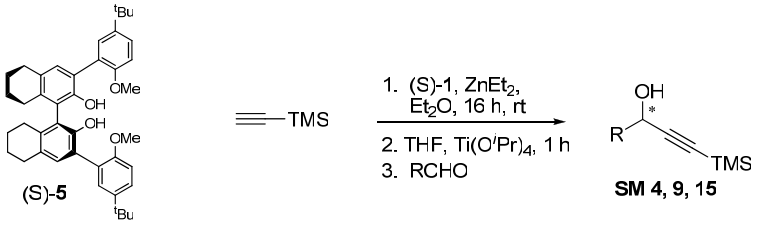

Under nitrogen, toluene (1 mL), alkyne (phenylacetylene or 4-phenyl-1-butyne, 2 mmol, 4 equiv), and $ZnEt_2$ (205 μL, 2 mmol, 4 equiv) were combined in a 25 mL flame dried flask. The flask was mounted with a flame dried reflux condenser fitted with a stopcock vacuum/nitrogen adaptor. The reaction mixture was then heated at reflux (oil bath 120-130 °C) for 4 h during which a gray precipitates formed. After cooled to rt, (*S*)-BINOL (>99% ee, 57.2 mg, 0.2 mmol, 40 mol%), $Et_2O$ (8 mL), and $Ti(O^iPr)_4$ (150 μL, 0.5 mmol, 1 equiv) were added and the resulting dark orange solution was stirred for 1 h. An aldehyde (0.5 mmol) was then added. After consumption of the aldehyde (typically 2 h, monitored by TLC or crude $^1H$ NMR) the reaction was quenched with saturated aqueous ammonium chloride (5 mL). The reaction mixture was extracted three times with $CH_2Cl_2$ and the organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel, eluted with hexanes/ethylacetate (0-15% ethyl acetate) to give the product in 83-95% yield and 85-96% ee.

## 2. Asymmetric Alkyne Addition Method II



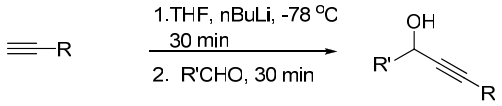

Under nitrogen, (*S*)-BINOL (57.2 mg, 0.2 mmol, 40 mol%), dicyclohexylamine (5 μL, 0.025 mmol, 0.05 equiv), 1-hexyne (230 μL, 2 mmol, 4 equiv), and $ZnEt_2$ (205 μL, 2 mmol, 4 equiv) were combined in $Et_2O$ (6 mL) in a 10 mL flame-dried flask and stirred at room temperature for 24 h. $Ti(O^iPr)_4$ (150 μL, 0.5 mmol, 1 equiv) was then added and the reaction mixture was stirred for 2 h. To the resulting dark orange solution, an aldehyde was added and the reaction was monitored by TLC or crude NMR. Upon consumption of the aldehdye (approximately 18 h), the reaction was quenched with saturated aqueous ammonium chloride (5 mL). The reaction mixture was extracted three times with $CH_2Cl_2$ and the organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography eluted with hexanes/ethylacetate (0-10% ethyl acetate) to give the product as an oil in 73-83% yield and 81-89% ee.

## 2. Asymmetric Alkyne Addition Method III



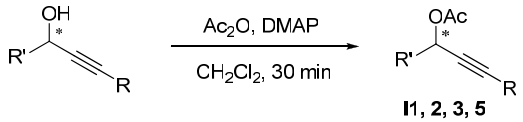

Under nitrogen, (*S*)-**5** (61.9 mg, 0.1 mmol, 20 mol%) was dissolved in $Et_2O$ (1 mL) in a 10 mL flame-dried flask. $ZnEt_2$ (103 μL, 1 mmol, 2 equiv) and trimethylsilylacetylene (141 μL, 1 mmol, 2 equiv) were added sequentially and the mixture was stirred for 16 h at room temperature, yielding a light tan solid. After the reaction flask was vented to release the build-up of the ethane gas, the solid was dissolved in THF (5 mL). $Ti(O^iPr)_4$ (74 μL, 0.25 mmol, 50 mol%) was then added and the reaction mixture was stirred for 1 h. To the resulting dark orange solution, an aldehyde was added and the reaction was monitored by TLC or crude NMR. Upon consumption of the aldehdye (typically 2 h), the reaction was quenched with saturated aqueous ammonium chloride (5 mL). The reaction mixture was extracted three times with $CH_2Cl_2$ and the organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel. First eluting with 2:1 $CH_2Cl_2$:hexanes cleanly separates the ligand from the product. After removal of the ligand, the column was eluted with hexanes/ethylacetate (5-10% ethyl acetate) to give the product as an oil in 79-90% yield and 88-91% ee.

## 3. Preparation of Racemic Propargylic Alcohols




Under nitrogen in a 10 mL flame dried flask, an alkyne (2 mmol, 2 equiv) in THF (5 mL) was cooled to -78 °C. $^{n}$BuLi (2 mmol, 2 equiv) was added and the mixture was stirred for 30 min. An aldehyde was then added. After 30 min, the reaction was quenched with saturated aqueous ammonium chloride (5 mL). The reaction mixture was extracted three times with $CH_2Cl_2$ and the organic layer was dried with sodium sulfate and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel eluted with hexanes/ethylacetate (0-15% ethyl acetate).

## 4. Acetate Protection of Propargylic Alcohols

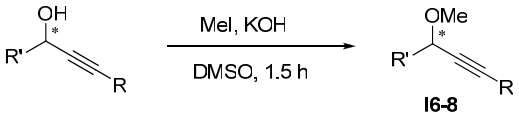



**I1, 2, 3, 5**

Under nitrogen in a 10 mL flame-dried flask, a propargylic alcohol (~0.4 mmol, 1 equiv), DMAP (0.1 equiv), and acetic anhydride (2 equiv) were combined in $CH_2Cl_2$ (5 mL). After consumption of the starting material (30 min), the reaction mixture was directly loaded onto a short silica gel column and purified by flash chromatography eluted with hexanes/ethylacetate (0-5% ethyl acetate) to yield the product in 97-99% yield.

## 5. Methyl Protection of Propargylic Alcohols

### a. Method a:

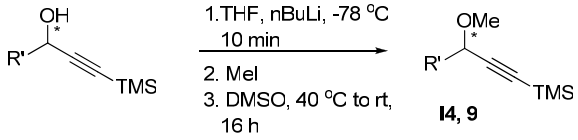



**I6-8**

Under nitrogen in a 10 mL flask, a propargylic alcohol (0.4 mmol) and methyl iodide (75 μL, 1.2 mmol, 3 equiv) were dissolved in DMSO (4 mL). KOH pellets (45 mg, 0.8 mmol, 2 equiv) were ground up and added to the flask. After 1.5 hours the reaction mixture was directly loaded onto a short silica gel column and purified by flash chromatography eluted with hexanes/ethylacetate (0-5% ethyl acetate) to yield the product in 83-87% yield.

### b. Method b:[1]

[1] Furstner, A.; Nevado, C.; Waser, M.; Tremblay, M.; Chevrier, C.; Teply, F.; Aissa, C.; Moulin, E.; Muller, O. *J. Am. Chem. Soc.* **2007**, 129, 9150-9161.

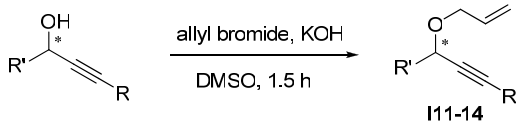


**I4, 9**

Due to the incompatibility of the TMS group with the strongly basic conditions of Method a, Method b was employed for all substrates containing the TMS group. Under nitrogen in a 10 mL flask, a propargylic alcohol (0.4 mmol) was dissolved in THF (2 mL) and cooled to -78 °C. $^{n}$BuLi (0.4 mmol, 1 equiv) was added and the mixture was stirred for 10 min. Methyl iodide (200 μL, 3.2 mmol, 8 equiv) was then added. The reaction flask was warmed to -40 °C and DMSO (57 μL, 0.8 mmol, 2 equiv) was added resulting in white precipitates. The reaction flask was allowed to warm to room temperature over night. Upon consumption of the starting material, the reaction mixture was quenched with saturated aqueous ammonium chloride (5 mL), extracted three times with $CH_2Cl_2$, dried with sodium sulfate, and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel eluted with hexanes/ethylacetate (0-5% ethyl acetate) to give the product in 90-98% yield.

## 6. Allyl Protection of Propargylic Alcohols

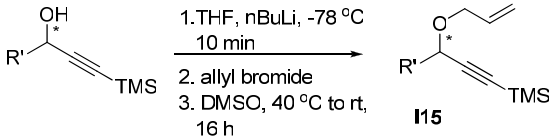
### a. Method a:



**I11-14**

Under nitrogen, in a 10 mL flask, a propargylic alcohol (0.4 mmol) and allyl bromide (104 μL, 1.2 mmol, 3 equiv) were dissolved in DMSO (4 mL). KOH pellets (45 mg, 0.8 mmol, 2 equiv) were ground up and added to the flask. After 1.5 h the reaction mixture was directly loaded onto a short silica gel column and purified by flash chromatography eluted with hexanes/ethylacetate (0-5% ethyl acetate) to yield the product in 57-73% yield.

### b. Method b:[1]

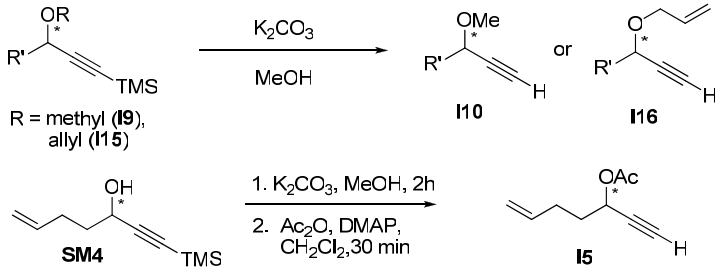


**I15**

Due to the incompatibility of the TMS group with the strongly basic conditions of Method a, Method b was employed for substrates containing the TMS group. Under nitrogen in a 10 mL flask, a propargylic alcohol (0.4 mmol) was dissolved in THF (2 mL) and cooled to -78 °C. $^{n}$BuLi (0.4 mmol, 1 equiv) was added and the mixture was stirred for 10 min. Allyl bromide (277 μL, 3.2 mmol, 8 equiv) was then added. The reaction flask was warmed to -40 °C and DMSO (57 μL, 0.8 mmol, 2 equiv) was added resulting in white precipitates. The reaction flask

was allowed to warm to room temperature over night. Upon consumption of the starting material, the reaction mixture was quenched with saturated aqueous ammonium chloride (5 mL), extracted three times with $CH_2Cl_2$, dried with sodium sulfate, and concentrated by rotary evaporation. The resultant oil was purified by flash column chromatography on silica gel eluted with hexanes/ethylacetate (0-5% ethyl acetate) to give the product in 73% yield.

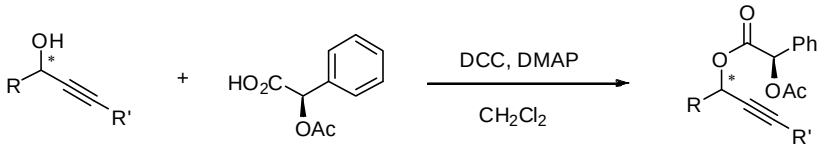
## 7. Removal of Acetylene TMS Group




The TMS group was removed under basic conditions. **I10** and **I16** were prepared from **I9** and **I15** respectively. The protected propargylic alcohol (0.4 mmol) was dissolved in MeOH (8 mL) and $K_2CO_3$ was added. The reaction mixture was stirred for 2 h and then purified by a short silica gel column eluted with hexanes/ethylacetate (0-10% ethyl acetate) to give the product in 80-94% yield. *Note: Due to the volatility of **I10** the rotovap water bath was kept below 25* °C *during concentration of the product.*

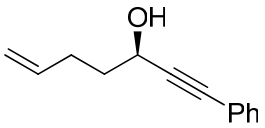
**I5** was prepared from **SM4**. The TMS group was first removed under basic conditions ($K_2CO_3$, MeOH, see above). Following consumption of the starting material, the reaction mixture was filtered through a pad of silica gel, concentrated and redissolved in methylene chloride. Subsequent protection with acetic anhydride (see above) and purification by silica gel column chromatography eluted with hexanes/ethylacetate (0-10% ethyl acetate) produced **I5** in 80% yield over 2 steps.

## 8. Preparation of Mandelic Esters

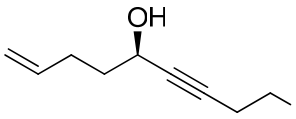



The propargylic alcohol (20 mg), DCC (2 equiv), DMAP (2 equiv), and (*R*)-O-acetylmandelic acid (2 equiv) were dissolved in $CH_2Cl_2$ (5 mL). The reaction was monitored by TLC. After consumption of the starting material (30 min to 1 h), the crude mixture was passed through a short silica gel column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

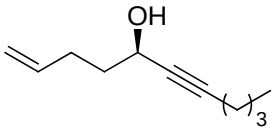
## IV. Characterization Data for the Propargylic Alcohols (SM1-SM15)



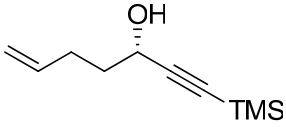

**(R)-1-phenylhept-6-en-1-yn-3-ol (SM1, Table 1, entry 5).** 88% yield. 94% ee determined by HPLC analysis: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 8.5, $t_{minor}$ = 22.7. $[\alpha]_{D}^{25}$ = -3.5 (c = 1.19, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.32 (m, 3H), 5.86 (m, 1H), 5.09 (m, 2H), 4.64 (q, 1H, J = 6.0 Hz), 2.32 (q, 2H, J = 6 Hz), 1.92 (m, 3H). These data are consistent with those reported.[2]



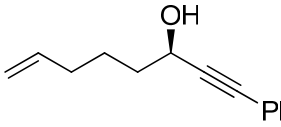

**(R)-9-phenylnon-1-en-6-yn-5-ol (SM2, Table 1, entry 6).** 95% yield. 95% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, λ = 215 nm, retention time: $t_{major}$ = 65.8, $t_{minor}$ = 61.7. $[\alpha]_{D}^{25}$ = -4.8 (c = 0.87, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5H), 5.82 (m, 1H), 5.02 (m, 2H), 4.36 (m, 1H), 2.83 (t, 2H, J = 9.0 Hz), 2.52 (td, 2H, J = 9.0, 3.0 Hz), 2.18 (q, 2H, J = 9.0 Hz), 1.75 (m, 2H), 1.67 (d, 1H, J = 9.0 Hz). These data are consistent with those reported.[1]




**(R)-undec-1-en-6-yn-5-ol (SM3, Scheme 4, text).** 73% yield. 89% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_{D}^{25}$ = -9.0 (c = 0.76, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.03 (m, 2H), 4.38 (m, 1H), 2.22 (m, 4H), 1.75 (m, 3H), 1.45 (m, 4H), 0.91 (t, 3H, J = 6.0 Hz). These data are consistent with those reported.[3]



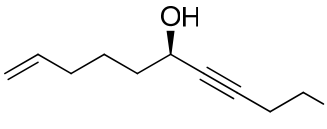

**(S)-1-(trimethylsilyl)hept-6-en-1-yn-3-ol (SM4, Figure 1).** 90% yield. 88% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_{D}^{25}$ = 10.3 (c = 1.21, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.84 (m, 1H), 5.04 (m, 2H), 4.39 (q, 1H, J = 9.0 Hz), 2.24 (q, 2H, J = 6.0 Hz), 1.80 (m, 3H), 0.17 (s, 9H). These data are consistent with those reported.[1]



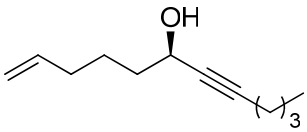

**(R)-1-phenyloct-7-en-1-yn-3-ol (SM6, Table 1, entry 9).** 87% yield. 93% ee determined by HPLC analysis: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate =

[2] Yue, Y.; Turlington, M.; Yu, X.-Q.; Pu, L. *J. Org. Chem.* **2009**, 74, 8681-8689.
[3] Du, Y.H.; Turlington, M.; Zhou, X.; Pu, L. *Tetrahedron Lett.* **2010**, in press.

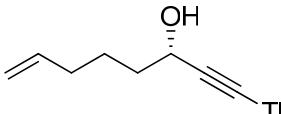
1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 7.6, $t_{minor}$ = 24.4. $[\alpha]_D^{25}$ = -7.0 (c = 0.35, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.43 (m, 2H), 7.31 (m, 3H), 5.84 (m, 1H), 5.00 (m, 2H), 4.61 (q, 1H, J = 6.0 Hz), 2.14 (q, 2H, J = 6.0 Hz), 1.82 (m, 3H), 1.64 (m, 2H). These data are consistent with those reported.[1]



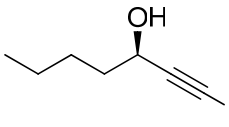

**(R)-1-phenyldec-9-en-3-yn-5-ol (SM7, Table 2, entry 10).** 83% yield. 90% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^i$PrOH, flow rate = 0.3 mL/min, λ = 215 nm, retention time: $t_{major}$ = 62.6, $t_{minor}$ = 58.4. $[\alpha]_D^{25}$ = 2.7 (c =1.17, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.26 (m, 5H), 5.80 (m, 1H), 5.00 (m, 2H), 4.44 (q, 1H, J = 6.0 Hz), 2.82 (t, 2H, J = 9.0 Hz), 2.51 (td, 2H, J = 9.0, 3.0 Hz), 2.08 (q, 2H, J = 6.0 Hz), 1.66 (m, 3H), 1.51 (m, 2H). These data are consistent with those reported.[1]




**(R)-dodec-1-en-7-yn-6-ol (SM8).** 83% yield. 83% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D^{25}$ = 6.4 (c = 0.79, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.00 (m, 2H), 4.36 (q, 1H, J = 6.0 Hz), 2.21 (td, 2H, J = 6.0, 3.0 Hz), 2.10 (q, 2H, J = 6.0 Hz), 1.71-1.64 (m, 3H), 1.57-1.38 (m, 6H), 0.91 (t, 3H, J = 6.0 Hz). These data are consistent with those reported.[4]

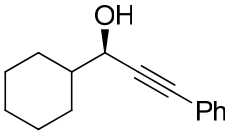



**(S)-1-(trimethylsilyl)oct-7-en-1-yn-3-ol (SM9, Figure 1).** 91% yield. 91% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D^{25}$ = -1.3 (c = 1.19, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 4.99 (m, 2H), 4.37 (q, 1H, J = 6.0 Hz), 2.10 (q, 2H, J = 6.0 Hz), 1.71 (m, 3H), 1.58 (m, 2H), 0.17 (s, 9H). These data are consistent with those reported.[1]

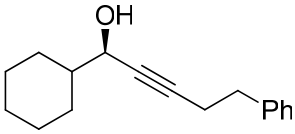



**(R)-1-phenylhept-1-yn-3-ol (SM11, Table 2, propargylic alcohol 1).** 89% yield. 95% ee determined by HPLC analysis: Chiralcel OD column, 90:10 hexanes:$^i$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 7.0, $t_{minor}$ = 17.8. $[\alpha]_D^{25}$ = -1.4 (c = 1.50, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.29 (m, 3H), 4.60 (q, 1H, J = 6.0 Hz), 2.02 (bs, 1H), 1.81 (m, 2H), 1.50 (m, 2H), 1.39 (m, 2H), 0.94 (t, 3H, J = 6.0 Hz). These data are consistent with those reported.[1]

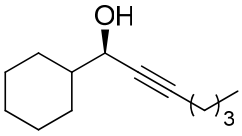
[3]Albert, B. J.; Koide, K. *J. Org. Chem.* **2008**, 73, 1093-1098.



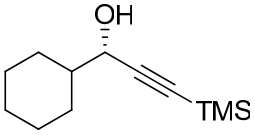
**(R)-1-cyclohexyl-3-phenylprop-2-yn-1-ol (SM12, Table 2, propargylic alcohol 2).** 88% yield. 96% ee determined by HPLC analysis: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, $\lambda$ = 254 nm, retention time: $t_{major}$ = 7.1, $t_{minor}$ = 14.6. $[\alpha]_D^{25}$ = -10.8 (c = 0.64, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.44 (m, 2H), 7.31 (m, 3H), 4.38 (t, 1H, J = 6.0 Hz), 1.88 (m, 2H), 1.80 (m, 3H), 1.70 (m, 2H), 1.23 (m, 5H). These data are consistent with those reported.[1]



**(R)-1-cyclohexyl-5-phenylpent-2-yn-1-ol (SM13, Table 2, propargylic alcohol 3).** 94% yield. 84% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D^{25}$ = -0.7 (c = 1.07, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.25 (m, 5H), 4.10 (m, 1H), 2.83 (t, 2H, J = 9.0 Hz), 2.53 (td, 2H, J = 9.0, 3.0 Hz), 1.71 (m, 4H), 1.60 (d, 1H, J = 3.0 Hz), 1.46 (m, 1H), 1.13 (m, 6H). These data are consistent with those reported.[1]



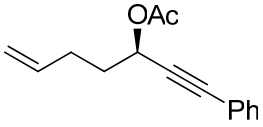
**(R)-1-cyclohexylhept-2-yn-1-ol (SM14, Table 2, propargylic alcohol 4).** 84% yield. 81% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D^{25}$ = -5.8 (c = 0.79, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.13 (m, 1H), 2.22 (t, 2H, J = 6.0 Hz), 1.83 (m, 4H), 1.63 (d, 1H, J = 6.0 Hz), 1.40 (m, 5H), 1.18 (m, 6H), 0.91 (t, 3H, J = 6.0 Hz). These data are consistent with those reported.[5]



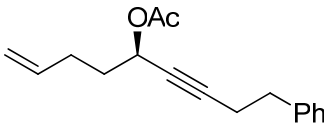
**(S)-1-cyclohexyl-3-(trimethylsilyl)prop-2-yn-1-ol (SM15, Table 2, propargylic alcohol 5).** 88% yield. 88% ee determined by analyzing the $^1$H NMR spectrum of the (R)-mandalate ester derivative. $[\alpha]_D^{25}$ = 6.0 (c = 1.15, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.13 (t, 1H, J = 6.0 Hz), 1.82 (m, 4H), 1.70 (d, 1H, J = 6.0 Hz), 1.53 (m, 1H), 1.15 (m, 6H), 0.17 (s, 9H). These data are consistent with those reported.[1]

## V. Characterization Data for the En-Yne Intermediates (I1-I16)

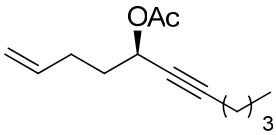
[5]Lettan, R.B. II; Scheidt, K.A. *Org. Lett.*, **2005**, 7, 3227–3230.



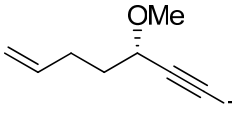
**(R)-1-phenylhept-6-en-1-yn-3-yl acetate (I1, Table 3, enyne 2).** 99% yield. $[\alpha]_D^{25}$ = 115.0 (c = 0.42, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.31 (m, 3H), 5.85 (m, 1H), 5.62 (t, 1H, J = 6.0 Hz), 5.06 (m, 2H), 2.28 (q, 2H, J = 9.0 Hz), 2.12 (s, 3H), 1.96 (m, 2H).



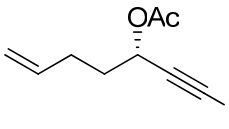
**(R)-9-phenylnon-1-en-6-yn-5-yl acetate (I2, Table 3, enyne 3).** 97% yield. $[\alpha]_D^{25}$ = 74.8 (c = 1.01, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.25 (m, 5H), 5.79 (m, 1H), 5.34 (tt, 1H, J = 6.0, 3.0 Hz), 5.01(m, 2H), 2.82 (t, 2H, J = 9.0 Hz), 2.51 (td, 2H, J = 9.0, 3.0 Hz), 2.12 (q, 2H, J = 6.0 Hz), 2.07 (s, 3H), 1.80 (m, 2H).



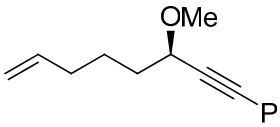
**(R)-undec-1-en-6-yn-5-yl acetate (I3, Table 3, enyne 4).** 98% yield. $[\alpha]_D^{25}$ = 84.8 (c = 0.76, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.36 (tt, 1H, J = 6.0, 3.0 Hz), 5.03 (m, 2H), 2.21 (m, 4H), 2.07 (s, 3H), 1.83 (m, 2H), 1.43 (m, 4H), 0.90 (t, 3H, J = 6.0 Hz).



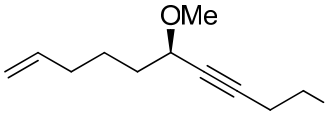
**(S)-(3-methoxyhept-6-en-1-ynyl)trimethylsilane (I4, Table 3, enyne 8).** 96% yield. $[\alpha]_D^{25}$ = -46.0 (c = 1.01, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.82 (m, 1H), 5.02 (m, 2H), 3.94 (t, 1H, J = 6.0 Hz), 3.40 (s, 3H), 2.21 (q, 2H, J = 6.0 Hz), 1.78 (m, 2H), 0.18 (s, 9H).



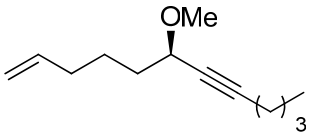
**(S)-hept-6-en-1-yn-3-yl acetate (I5, Table 3, enyne 6).** 85% yield over 2 steps. $[\alpha]_D^{25}$ = -68.9 (c = 1.07, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.36 (td, 1H, J = 6.0, 3.0 Hz), 5.04 (m, 2H), 2.47 (d, 1H, J = 3.0 Hz), 2.22 (q, 2H, J = 9.0 Hz), 2.09 (s, 3H), 1.88 (m, 2H).



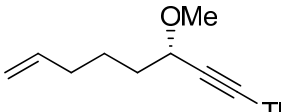
**(R)-(3-methoxyoct-7-en-1-ynyl)benzene (I6, Table 4, enyne 2).** 83% yield. $[\alpha]_D^{25}$ = 61.0 (c = 1.49, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.29 (m, 3H), 5.83 (m, 1H), 5.01 (m, 2H), 4.18 (t, 1H, J = 6.0 Hz), 3.47 (s, 3H), 2.12 (q, 2H, J = 6.0 Hz), 1.82 (m, 2H), 1.64 (m, 2H).



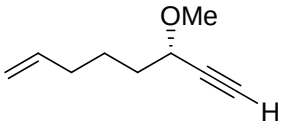
**(R)-(5-methoxydec-9-en-3-ynyl)benzene (I7, Table 4, enyne 3).** 87% yield. $[\alpha]_D^{25}$ = 40.6 (c = 0.95, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 5H), 5.80 (m, 1H), 4.99 (m, 2H), 3.90 (t, 1H, J = 6.0 Hz), 3.33 (s, 3H), 2.84 (t, 2H, J = 9.0 Hz), 2.53 (td, 2H, J = 9.0, 3.0 Hz), 2.06 (q, 2H, J = 6.0 Hz), 1.66 (m, 2H), 1.51 (q, 2H, J = 9.0 Hz).



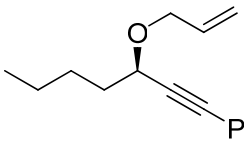
**(R)-6-methoxydodec-1-en-7-yne (I8, Table 4, enyne 4).** 84% yield. $[\alpha]_D^{25}$ = 51.0 (c = 1.27, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 4.99 (m, 2H), 3.92 (tt, 1H, J = 6.0, 3.0 Hz), 3.38 (s, 3H), 2.23 (td, 2H, J = 6.0, 3.0 Hz), 2.08 (q, 2H, J = 6.0 Hz), 1.68 (m, 2H), 1.47 (m, 6H), 0.91 (t, 3H, J = 6.0 Hz).



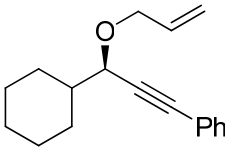
**(S)-(3-methoxyoct-7-en-1-ynyl)trimethylsilane (I9, Table 4, enyne 5).** 98% yield. $[\alpha]_D^{25}$ = -56.4 (c = 1.02, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.81 (m, 1H), 5.00 (m, 2H), 3.93 (t, 1H, J = 6.0 Hz), 3.39 (s, 3H), 2.08 (q, 2H, J = 6.0 Hz), 1.70 (m, 2H), 1.55 (m, 2H), 0.17 (s, 9H).



**(S)-oct-7-en-1-yn-3-yl acetate (I10, Table 4, enyne 8).** 80% yield. *Note: Due to volatility of product water bath is not heated above 25℃ during rotary evaporation.* $[\alpha]_D^{25}$ = -14.9 (c = 1.02, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.80 (m, 1H), 5.00 (m, 2H), 3.94 (td, 1H, J = 6.0, 2.0 Hz), 3.41 (s, 3H), 2.44 (dd, 1H, J = 3.0, 0.6 Hz), 2.09 (q, 2H, J = 6.0 Hz), 1.73 (m, 2H), 1.57 (m, 2H).

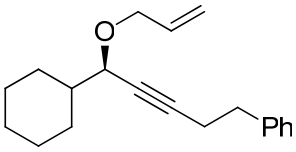


**(R)-(3-(allyloxy)hept-1-ynyl)benzene (I11, Table 2, enyne 1).** 73% yield. $[\alpha]_D^{25}$ = 112.4 (c = 1.18, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.44 (m, 2H), 7.31(m, 3H), 5.97 (m, 1H), 5.28 (m, 2H), 4.32 (m, 2H), 4.04 (m, 1H), 1.83 (m, 2H), 1.51 (m, 2H), 1.38 (m, 2H), 0.94 (t, 3H, J = 6.0 Hz).

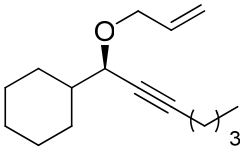


**(R)-(3-(allyloxy)-3-cyclohexylprop-1-ynyl)benzene (I12, Table 2, enyne 2).** 69% yield. $[\alpha]_D^{25}$ = 93.9 (c = 1.10, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.45 (m, 2H), 7.31

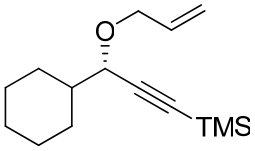
(m, 3H), 6.96 (m, 1H), 5.28 (m, 2H), 4.33 (m, 1H), 4.08 (d, 1H, J = 6.0 Hz), 4.03 (m, 1H), 1.94 (m, 2H), 1.71 (m, 4H), 1.21 (m, 5H).



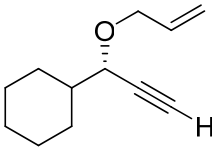

**(R)-(5-(allyloxy)-5-cyclohexylpent-3-ynyl)benzene (I13, Table 2, enyne 3).** 73% yield. $[\alpha]_D^{25}$ = 37.1 (c = 1.00, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.27 (m, 5H), 5.90 (m, 1H), 5.21 (m, 2H), 4.17 (m, 1H), 3.85 (m, 2H), 2.84 (t, 2H, J = 6.0 Hz), 2.54 (t, 2H, J = 6.0 Hz), 1.77 (m, 5H), 1.14 (m, 6H).




**(R)-(1-(allyloxy)hept-2-ynyl)cyclohexane (I14, Table 2, enyne 4).** 57% yield. $[\alpha]_D^{25}$ = 58.8 (c = 0.87, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.92 (m, 1H), 5.24 (m, 2H), 4.24 (m, 1H), 3.93 (m, 1H), 3.83 (dt, 1 H, J = 6.0, 3.0 Hz), 2.23 (td, 2H, J = 6.0, 3.0Hz), 1.84 (m, 2H), 1.68 (m, 3H), 1.48 (m, 5H), 1.19 (m, 5H), 0.91 (t, 3H, J = 6.0 Hz).

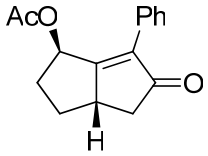



**(S)-(3-(allyloxy)-3-cyclohexylprop-1-ynyl)trimethylsilane (I15, Table 2, enyne 5).** 73% yield. $[\alpha]_D^{25}$ = -65.6 (c = 0.92, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.92 (m, 1H), 5.24 (m, 2H), 4.25 (m, 1H), 3.94 (m, 1H), 3.84 (d, 1H, J= 6.0 Hz), 1.85 (m, 2H), 1.74 (m, 1H,), 1.60 (m, 2H), 1.17 (m, 6H), 0.18 (s, 9H).

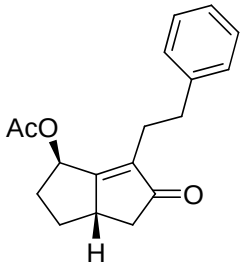



**(S)-(1-(allyloxy)prop-2-ynyl)cyclohexane (I16, Table 5, enyne 8).** 94% yield. $[\alpha]_D^{25}$ = -60.7 (c = 0.67, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.91 (m, 1H), 5.26 (m, 2H), 4.27 (m, 1H), 3.96 (m, 1H), 3.86 (dd, 1H, J = 6.0, 3.0 Hz), 2.42 (d, 1H, J = 3.0 Hz), 1.87 (m, 2H), 1.75 (m, 2H), 1.65 (m, 2H), 1.18 (m, 5H).

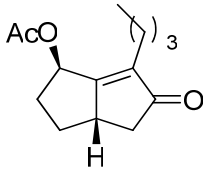
## VI. Characterization Data for the PK Reaction Products (P1-P16)



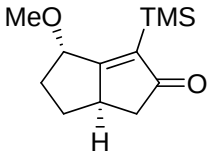

**(1R,3aS)-5-oxo-6-phenyl-1,2,3,3a,4,5-hexahydropentalen-1-yl acetate (P1, Table 3, entry 2).** 94% yield. 95:5 dr determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, $\lambda$ = 254 nm, retention time: $t_{major}$ = 56.3, 60.1 $t_{minor}$ = 77.1. 94% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, $\lambda$ = 254 nm, retention time: $t_{major}$ = 56.3 $t_{minor}$ = 60.1. $[\alpha]_D^{25}$ = -89.1 (c = 0.89, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.50 (m, 2H), 7.37 (m, 3H), 5.65 (m, 1H), 3.22 (m, 1H), 2.90 (dd, 1H, J = 18.0, 6.6 Hz), 2.65 (p, 1H, J = 7.2 Hz), 2.31 (m, 2H), 2.17 (s, 3H), 1.94 (m, 1H), 1.17 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 208.5, 175.7, 170.0, 138.3, 130.5, 128.8, 128.5, 128.0, 70.8, 43.1, 41.9, 35.1, 29.2, 21.2. HRMS ($MH^+$) for $C_{16}H_{17}O_3$ Calcd: 257.1183 Found: 257.1179.



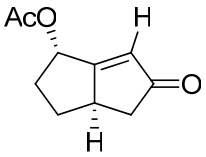

**(1R,3aS)-5-oxo-6-phenethyl-1,2,3,3a,4,5-hexahydropentalen-1-yl acetate (P2, Table 3, entry 3).** 81% yield. 93:7 dr determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, $\lambda$ = 235 nm, retention time: $t_{major}$ = 39.7, 43.0, $t_{minor}$ = 56.2. 94% ee determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, $\lambda$ = 235 nm, retention time: $t_{major}$ = 39.7 $t_{minor}$ = 43.0. $[\alpha]_D^{25}$ = -84.5 (c = 1.00, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.17m, 5H), 5.17 (m, 1H), 2.94 (m, 1H), 2.85-2.75 (m, 1H), 2.66 (m, 4H), 2.11 (m, 3H), 2.01 (s, 3H), 1.82 (m, 1H), 0.95-0.82 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 210.6, 176.1, 170.1, 141.3, 138.1, 128.7, 128.2, 125.9, 68.6, 42.3, 40.8, 33.7, 33.2, 28.9, 25.8, 21.0. HRMS ($MH^+$) for $C_{18}H_{21}O_3$ Calcd: 285.1496 Found: 285.1493.



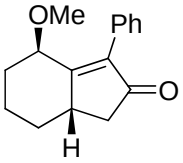

**(1R,3aS)-6-butyl-5-oxo-1,2,3,3a,4,5-hexahydropentalen-1-yl acetate (P3, Table 3, entry 4).** 85% yield. 95:5 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, $\lambda$ = 221 nm, retention time: $t_{major}$ = 7.6 $t_{minor}$ = 9.6. $[\alpha]_D^{25}$ = -91.9 (c = 1.14, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.74 (m, 1H), 3.02 (m, 1H), 2.69 (dd, 1H, J = 18.0, 6.0 Hz), 2.52 (p, 1H, J = 6 Hz), 2.24 (m, 3H), 2.07 (s, 3H), 2.06 (dd, 1H, J = 18.0, 3.0 Hz), 1.94 (m, 1H), 1.33 (m, 4H), 1.06 (p, 1H, J = 9.0 Hz), 0.88 (t, 3H, J = 6 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 210.7, 174.9, 170.2, 139.9, 68.8, 42.1, 41.3, 34.1, 30.3, 29.2, 23.6, 22.5, 21.0, 13.8. HRMS ($MH^+$) for $C_{14}H_{21}O_3$ Calcd: 237.1491 Found: 237.1485.



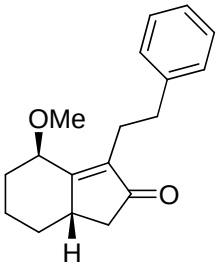

**(4S,6aR)-4-methoxy-3-(trimethylsilyl)-4,5,6,6a-tetrahydropentalen-2(1H)-one (P4, Table 3, entry 8).** 69% yield. >99:1 dr determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, $\lambda$ = 235 nm, retention time: $t_{major}$ = 19.3. $[\alpha]_{D}^{25}$ = 138.4 (c = 1.07, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 4.41 (m, 1H), 3.33 (s, 3H), 3.08 (m, 1H), 2.64 (dd, 1H, J = 18.0, 9.0 Hz), 2.24 (m, 2H), 2.03 (dd, 1H, J = 18.0, 3.0 Hz), 1.94 (m, 1H), 1.08 (m, 1H), 0.23 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 215.0, 192.0, 139.0, 76.4, 56.2, 43.9, 43.7, 32.8, 28.1, -1.1. HRMS ($MH^+$) for $C_{12}H_{21}O_2Si$ Calcd: 225.1311 Found: 225.1308.



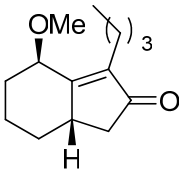

**(1S,3aR)-5-oxo-1,2,3,3a,4,5-hexahydropentalen-1-yl acetate (P5, Table 3, entry 6).** 83% yield. 75:25 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, $\lambda$ = 215 nm, retention time: $t_{major}$ = 24.7, $t_{minor}$ = 29.3. $[\alpha]_{D}^{25}$ = 94.8 (c = 0.67, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 6.13 (m, 1H), 5.67-5.63 (m, 1H), 3.12 (m, 1H), 2.69 (dd, 1H, J = 18.0, 6.0 Hz), 2.50 (p, 1H, J = 7.2 Hz), 2.31-2.22 (m, 1H), 2.11 (dd, 1H, J = 18.0, 3.0 Hz), 2.07 (s, 3H), 2.05-1.95 (m, 1H), 1.21-1.10 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 210.6, 182.8, 170.3, 128.5, 69.5, 43.6, 42.6, 33.1, 28.9, 20.9. HRMS ($MH^+$) for $C_{10}H_{13}O_3$ Calcd: 181.0865. Found: 181.0873.



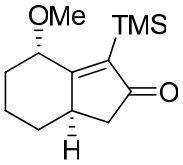

**(4R,7aS)-4-methoxy-3-phenyl-5,6,7,7a-tetrahydro-1H-inden-2(4H)-one (P6, Table 4, entry 2).** 93% yield. 92:8 dr determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, $\lambda$ = 254 nm, retention time: $t_{major}$ = 43.9, 45.8, $t_{minor}$ = 56.8. 93% ee determined by HPLC analysis: Chiralcel OB-H column, 98:2 hexanes:$^{i}$PrOH, flow rate = 2 mL/min, $\lambda$ = 254 nm, retention time: $t_{major}$ = 17.10 $t_{minor}$ = 12.78. $[\alpha]_{D}^{25}$ = -96.6 (c = 0.69, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.38 (m, 3H), 7.24 (m, 2H), 4.43 (t, 1H, J = 3.0 Hz), 3.19 (s, 3H), 3.10-3.04 (m, 1H), 2.74 (dd, 1H, J = 18.0, 6 Hz), 2.23 (m, 2H), 2.12 (dd, 1H, J = 18.0, 3.0 Hz), 1.92 (m, 1H), 1.57 (m, 2H), 1.18 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 206.9, 174.2, 139.6, 130.8, 129.0, 128.3, 127.9, 72.9, 56.1, 41.7, 36.1, 35.6, 31.9, 19.7. HRMS ($MH^+$) for $C_{16}H_{19}O_2$ Calcd: 243.1385. Found: 243.1285.



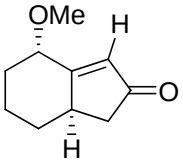

**(4R,7aS)-4-methoxy-3-phenethyl-5,6,7,7a-tetrahydro-1H-inden-2(4H)-one (P7, Table 4, entry 3).** 77% yield. 93:7 dr determined by HPLC analysis: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 221 nm, retention time: $t_{major}$ = 37.5, 38.5, $t_{minor}$ = 44.5. $[\alpha]_D^{25}$ = -58.3 (c = 0.86, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.16 (m, 5H), 3.99 (t, 1H, J = 3.0 Hz), 3.09 (s, 3H), 2.62 (m, 6H), 2.05 (m, 1H), 1.93 (dd, 1H, J = 18.0, 3 Hz), 1.85 (m, 1H), 1.72 (m, 1H), 1.41 (m, 1H), 0.85 (m, 1H), 0.70 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 208.9, 173.2, 141.2, 138.5, 128.7, 128.3, 126.0, 72.6, 55.9, 41.5, 36.2, 35.3, 34.0, 31.6, 25.0, 19.6. HRMS ($MH^+$) for $C_{18}H_{23}O_2$ Calcd: 271.1698. Found: 271.1688.



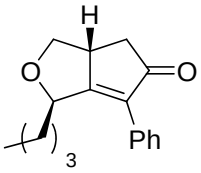

**(4R,7aS)-3-butyl-4-methoxy-5,6,7,7a-tetrahydro-1H-inden-2(4H)-one (P8, Table 4, entry 4).** 79% yield. 95:5 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: $t_{major}$ = 5.7, 6.1, $t_{minor}$ = 6.8. $[\alpha]_D^{25}$ = -118.0 (c =1.335, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 4.36 (t, 1H, J = 3 Hz), 3.24 (s, 3H), 2.86 (m, 1H), 2.56 (dd, 1H, J = 18.0, 6.3 Hz), 2.20 (m, 4H), 1.94 (dd, 1H, J = 18.0, 3 Hz), 1.84 (1H), 1.58 (m, 1H), 1.37 (m, 5H), 1.01 (m, 1H), 0.90 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 209.1, 172.2, 140.3, 72.8, 56.1, 41.5, 36.0, 35.5, 32.3, 31.1, 22.7, 22.5, 19.8, 13.9. HRMS ($MH^+$) for $C_{14}H_{23}O_2$ Calcd: 223.1698. Found: 223.1694.



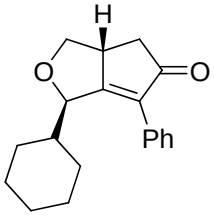

**(4S,7aR)-4-methoxy-3-(trimethylsilyl)-5,6,7,7a-tetrahydro-1H-inden-2(4H)-one (P9, Table 4, entry 5).** 47% yield. 94:6 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, retention time: $t_{major}$ = 5.5, $t_{minor}$ = 7.1. $[\alpha]_D^{25}$ = 100.8 (c =0.70, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 4.48 (t, 1H, J = 3Hz), 3.26 (s, 3H), 2.97 (m, 1H), 2.53 (dd, 1H, J = 18.0, 6.9 Hz), 2.17 (m, 2H), 1.92 (dd, 1H, J = 18.0, 2.4 Hz), 1.85 (m, 1H), 1.49 (m, 2H), 1.09 (m, 1H), 0.24 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 213.2, 188.4, 139.7, 74.5, 56.0, 42.6, 39.1, 36.1, 32.7, 19.5, -0.1. HRMS ($MH^+$) for $C_{13}H_{23}O_2Si$ Calcd: 239.1467. Found: 239.1468.



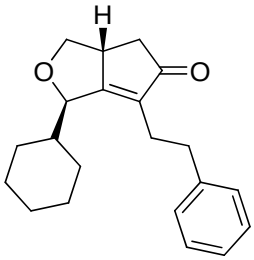

**(4S,7aR)-4-methoxy-5,6,7,7a-tetrahydro-1H-inden-2(4H)-one (P10, Table 4, entry 8).** 61% yield. 84:16 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 235 nm, retention time: $t_{major}$ = 11.2, $t_{minor}$ = 15.6. $[\alpha]_D^{25}$ = 76.9 (c =0.37, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 5.99 (m, 1H), 4.23 (bs, 1H), 3.25 (s, 3H), 2.95 (m, 1H), 2.61 (dd, 1H, J = 18.0, 6.0 Hz), 2.20 (m, 1H), 2.16 (m, 1H), 2.00 (dd, 1H, J = 18.0, 1.8 Hz), 1.83 (m, 1H), 1.55 (m, 2H), 1.10 (m, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 208.9, 181.2, 129.2, 75.0, 56.3, 42.2, 37.7, 35.2, 32.6, 19.6. HRMS ($MH^+$) for $C_{10}H_{15}O_2$ Calcd: 167.1072. Found: 167.1074.



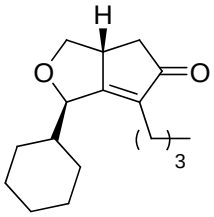

**(1R,3aR)-1-butyl-6-phenyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P11, Table 5, entry 1).** 82% yield. 87:13 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 14.5, 15.3, $t_{minor}$ = 19.7. $[\alpha]_D^{25}$ = 165.1 (c =1.28, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 5H), 4.81 (m, 1H), 4.39 (t, 1H, J = 6.0 Hz), 3.32 (m, 2H), 2.82 (dd, 1H, J = 18.0, 6.0 Hz), 2.30 (dd, 1H, J = 18.0, 3.0 Hz), 1.82 (m, 2H), 1.42 (m, 4H), 0.90 (t, 3H, J = 7.2 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 207.4, 179.9, 135.0, 130.9, 128.5, 128.4, 128.2, 76.3, 71.2, 42.7, 39.7, 34.9, 27.5, 22.5, 13.9. HRMS ($MH^+$) for $C_{17}H_{21}O_2$ Calcd: 257.1542. Found: 257.1535.



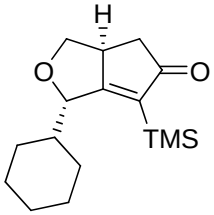

**(1R,3aR)-1-cyclohexyl-6-phenyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P12, Table 5, entry 2).** 83% yield. >99:1 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 17.00. 96% ee determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:$^i$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 17.0, $t_{minor}$ = 14.2. $[\alpha]_D^{25}$ = 247.0 (c =2.18, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 5H), 4.72 (d, 1H, J = 3.0 Hz), 4.38 (t, 1H, J = 6.0 Hz), 3.36-3.25 (m, 2H), 2.80 (dd, 1H, J = 18.0, 6.0 Hz), 2.28 (dd, 1H, J = 18.0, 3.0 Hz), 1.72-1.56 (m, 6H), 1.25-1.17 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 207.3, 179.6, 135.9, 131.2, 128.4, 128.2, 80.7, 71.2, 43.4, 43.1, 39.5, 29.4, 28.0, 26.2, 26.0. HRMS ($MH^+$) for $C_{19}H_{23}O_2$ Calcd: 283.1698. Found: 283.1699.



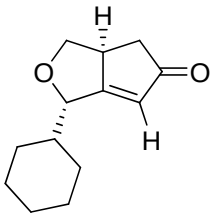
**(1R,3aR)-1-cyclohexyl-6-phenethyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P13, Table 5, entry 3).** 66% yield. >99:1 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 11.3. $[\alpha]_D^{25}$ = 144.3 (c =0.6, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.20 (m, 5H), 4.21 (t, 1H, J = 6.0 Hz), 3.91 (d, 1H, J = 6.0 Hz), 3.01 (m, 2H), 2.80 (m, 2H), 2.56 (m, 3H), 2.05 (dd, 1H, J = 18.0, 3 Hz), 1.68 (m, 5H), 1.46 (m, 1H), 1.23 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 209.2, 179.1, 141.2, 136.5, 128.5, 128.4, 126.2, 80.2, 71.4, 43.0, 42.6, 39.1, 33.4, 29.2, 26.2, 26.1, 25.9. HRMS ($MH^+$) for $C_{21}H_{27}O_2$ Calcd: 311.2011. Found: 311.2005.



**(1R,3aR)-6-butyl-1-cyclohexyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P14, Table 5, entry 4).** 64% yield. >99:1 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:$^i$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 7.2. $[\alpha]_D^{25}$ = 71.18 (c =1.16, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 4.43 (d, 1H, J = 6.0 Hz), 4.29 (t, 1H, J = 6.0 Hz), 3.17 (m, 2H), 2.62 (dd, 1H, J = 18.0, 6.0 Hz), 2.20 (m, 2H), 2.06 (dd, 1H, J = 18.0, 2.7 Hz), 1.69 (m, 6H), 1.26 (m, 9H), 0.90 (t, 3H, J = 6.9 Hz). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 209.2, 177.7, 137.7, 80.3, 71.4, 42.9, 42.7, 38.9, 29.8, 29.1, 28.7, 26.1, 26.0, 25.9, 24.2, 22.7, 13.8. HRMS ($MH^+$) for $C_{17}H_{27}O_2$ Calcd: 263.2011. Found: 263.2007.



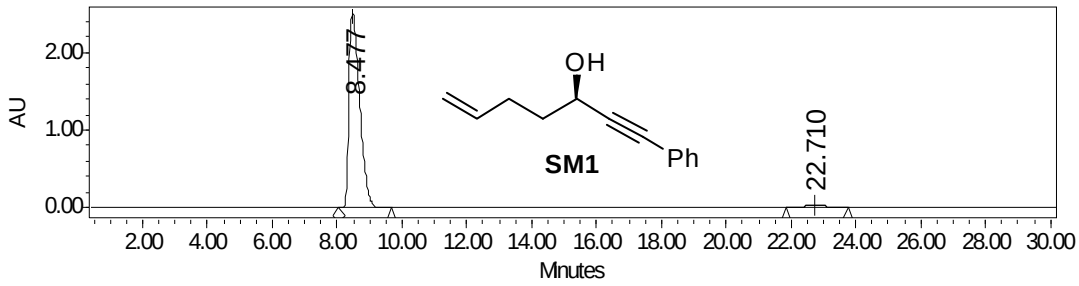
**(1S,3aS)-1-cyclohexyl-6-(trimethylsilyl)-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P15, Table 5, entry 5).** 50% yield. >99:1 dr determined by HPLC analysis: Chiralcel OD column, 98:2 hexanes:$^i$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, retention time: $t_{major}$ = 6.2. $[\alpha]_D^{25}$ = -152.9 (c =0.95, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$) δ 4.48 (d, 1H, J = 3.0 Hz), 4.29 (t, 1H, J = 6.9 Hz), 3.21 (m, 2H), 2.56 (dd, 1H, J = 18.0, 6 Hz), 2.05 (dd, 1H, J = 18.0, 3.6 Hz), 1.77 (m, 2H), 1.65 (m, 4H), 1.23 (m, 5H), 0.21 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 213.3, 192.6, 136.3, 80.8, 71.0, 46.3, 42.8, 40.6, 30.0, 27.4, 26.5, 26.1, 26.0, -1.1. HRMS ($MH^+$) for $C_{16}H_{27}O_2Si$ Calcd: 279.1780. Found: 279.1778.



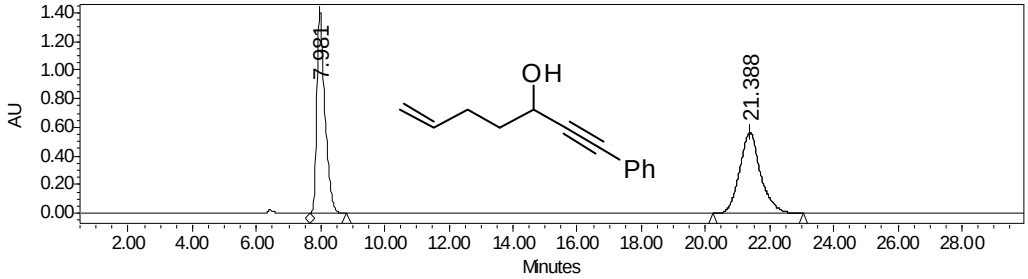
**(1S,3aS)-1-cyclohexyl-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one (P16, Table 5, entry 8).** 55% yield. 65:35 dr determined by HPLC analysis of the minor enantiomers since the peaks of these diastereomers are fully resolved: Chiralcel OD column, 98:2 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, $\lambda$ = 221 nm, retention time: $t_{major}$ =15.4, $t_{minor}$ =14.1. $[\alpha]_{D}^{25}$ = -151.2 (c = 0.62, $CHCl_3$). $^{1}$H NMR (300 MHz, $CDCl_3$) $\delta$ 5.99 (s, 1H), 4.36 (d, 1H, J = 9.0 Hz), 4.31 (t, 1H, J = 6.0 Hz), 3.26 (m, 2H), 2.60 (dd, 1H, J = 18.0, 6 Hz), 2.11 (dd, 1H, J = 18.0, 3.0 Hz), 1.74 (m, 6H), 1.12 (m, 5H). $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ 209.1, 186.6, 125.3, 81.3, 71.3, 45.7, 41.7, 39.5, 29.1, 28.5, 26.2, 25.8. HRMS ($MH^+$) for $C_{13}H_{19}O_2$ Calcd: 207.1385. Found: 207.1377.

**VII.** HPLC Plots for the Determination of the ee's of **SM 1, 2, 6, 7, 11, 12**.

**SM 1**: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, 94% ee.

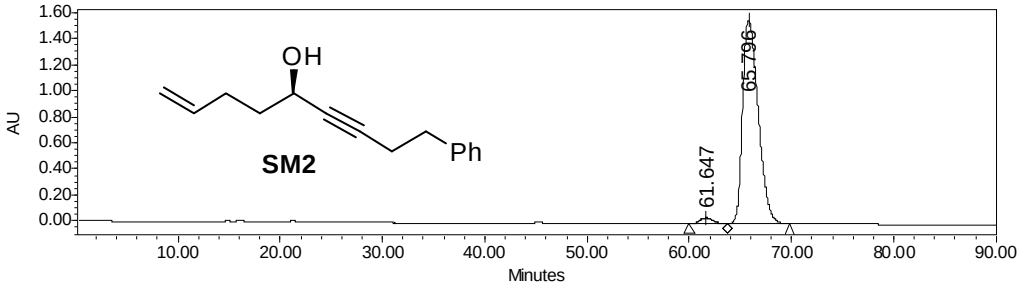



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 8.477 | 57847767 | 96.85 |
| 2 | 22.710 | 1879142 | 3.15 |

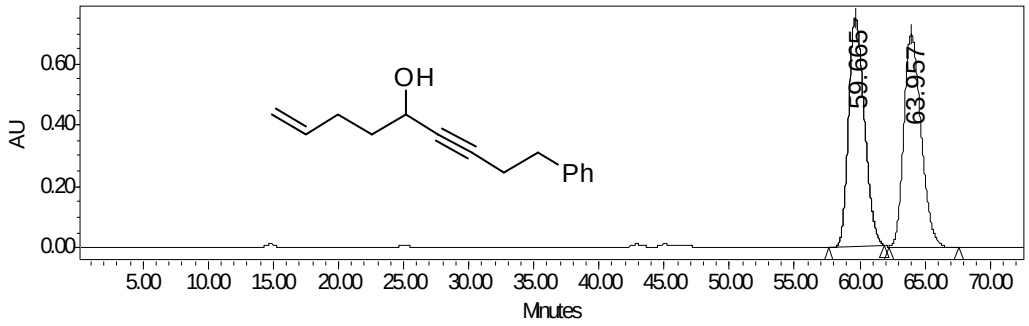



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.981 | 24208236 | 48.37 |
| 2 | 21.388 | 25842525 | 51.63 |

**SM 2**: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, λ = 215 nm, 95% ee.

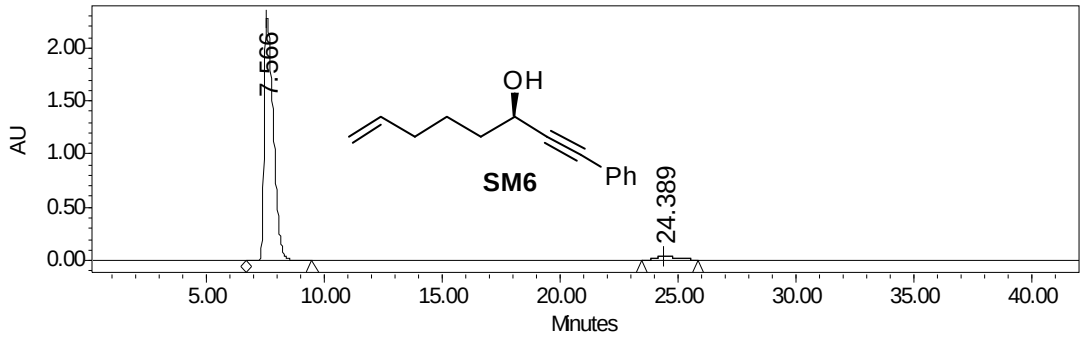



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 61.647 | 4023299 | 2.37 |
| 2 | 65.796 | 165866562 | 97.63 |

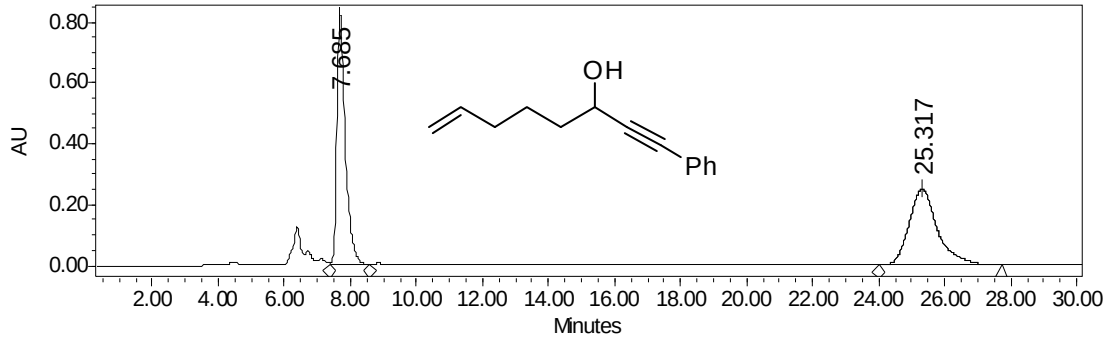



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 59.665 | 63512079 | 49.71 |
| 2 | 63.957 | 64256267 | 50.29 |

**SM 6**: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, 93% ee.

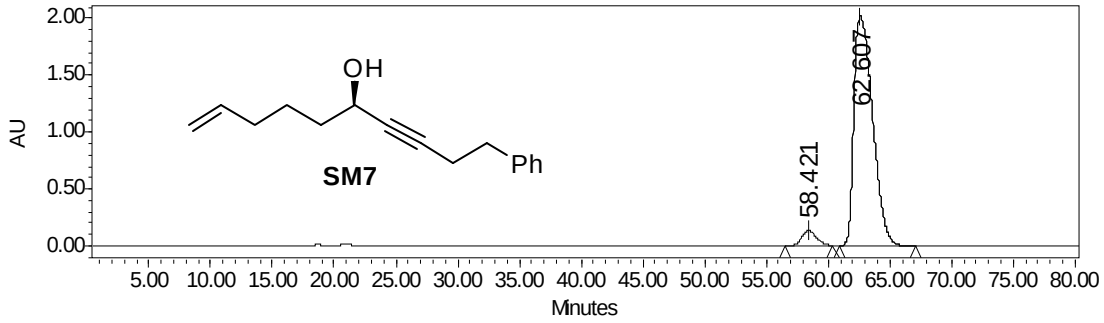



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.566 | 62043867 | 96.39 |
| 2 | 24.389 | 2325974 | 3.61 |

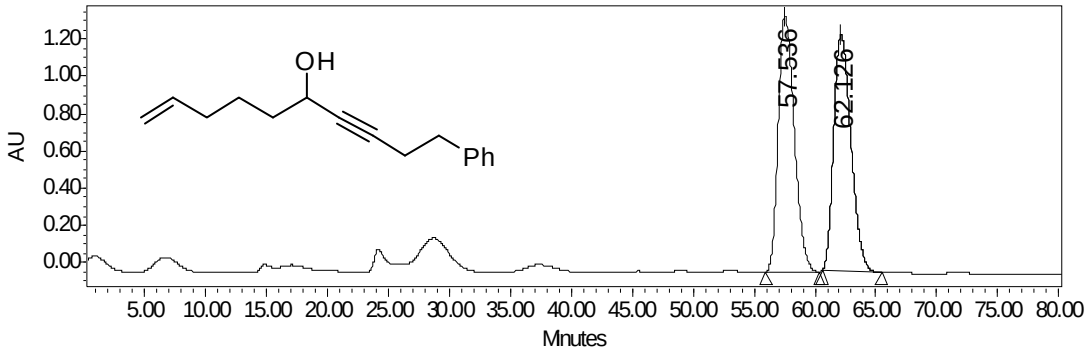



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.685 | 14684888 | 49.49 |
| 2 | 25.317 | 14988343 | 50.51 |

**SM 7**: Chiralpak AD-H column, 99:1 hexanes:$^{i}$PrOH, flow rate = 0.3 mL/min, λ = 215 nm, 90% ee.

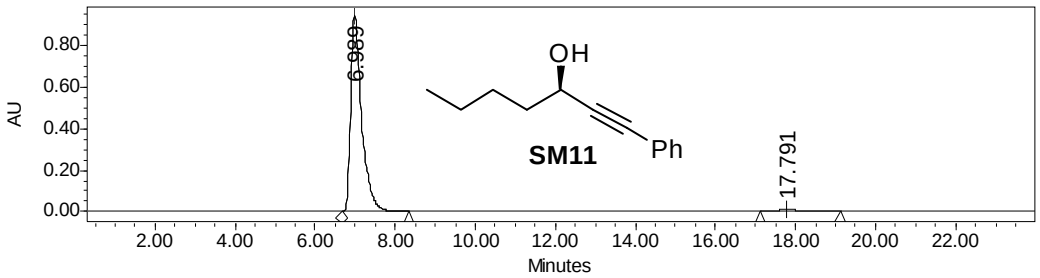



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 58.421 | 11703762 | 5.19 |
| 2 | 62.607 | 213944032 | 94.81 |

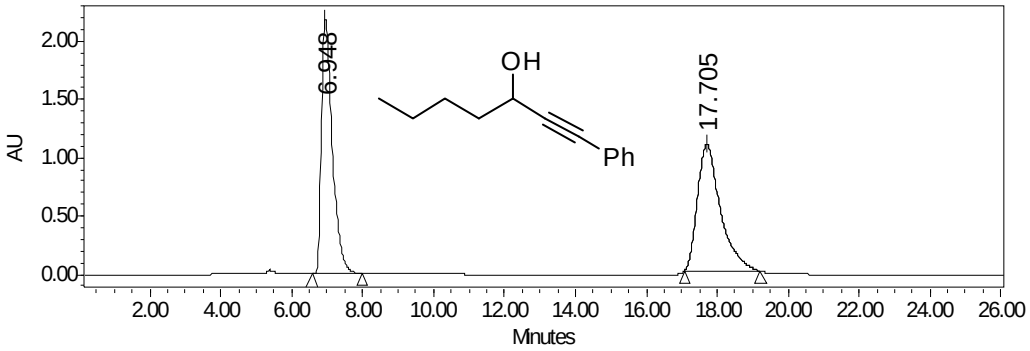



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 57.536 | 127134318 | 50.33 |
| 2 | 62.126 | 125459031 | 49.67 |

**SM 11**: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, 95% ee.

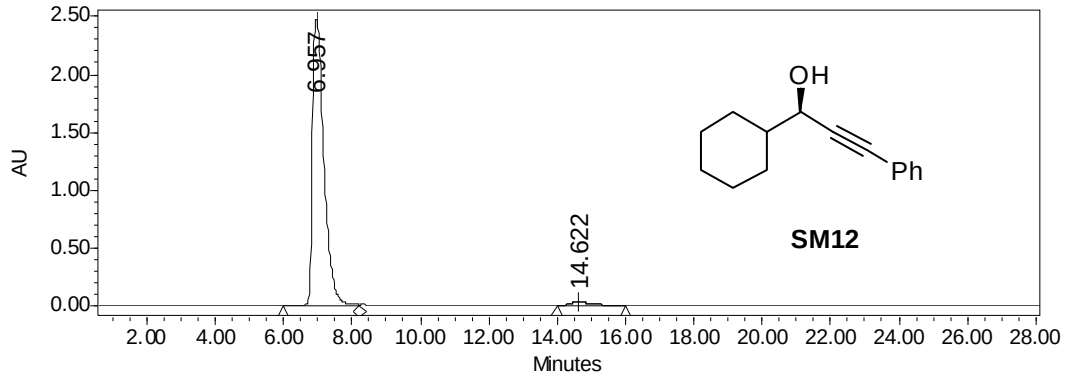



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.989 | 18029459 | 97.72 |
| 2 | 17.791 | 420771 | 2.28 |

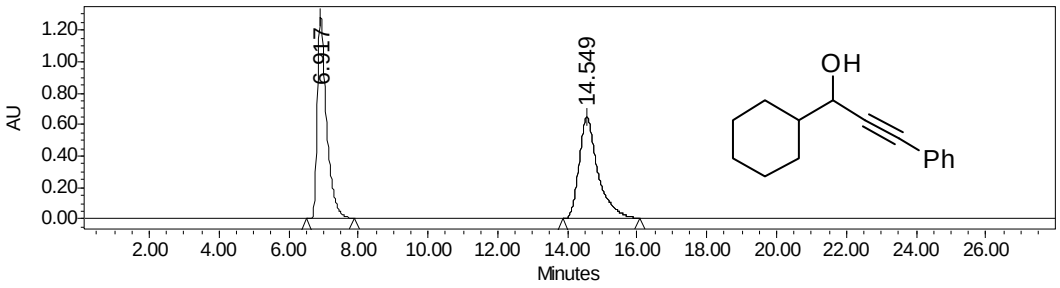



| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.948 | 46653781 | 48.68 |
| 2 | 17.705 | 49183579 | 51.32 |

**SM 12**: Chiralcel OD column, 90:10 hexanes:$^{i}$PrOH, flow rate = 1.0 mL/min, λ = 254 nm, 96% ee.

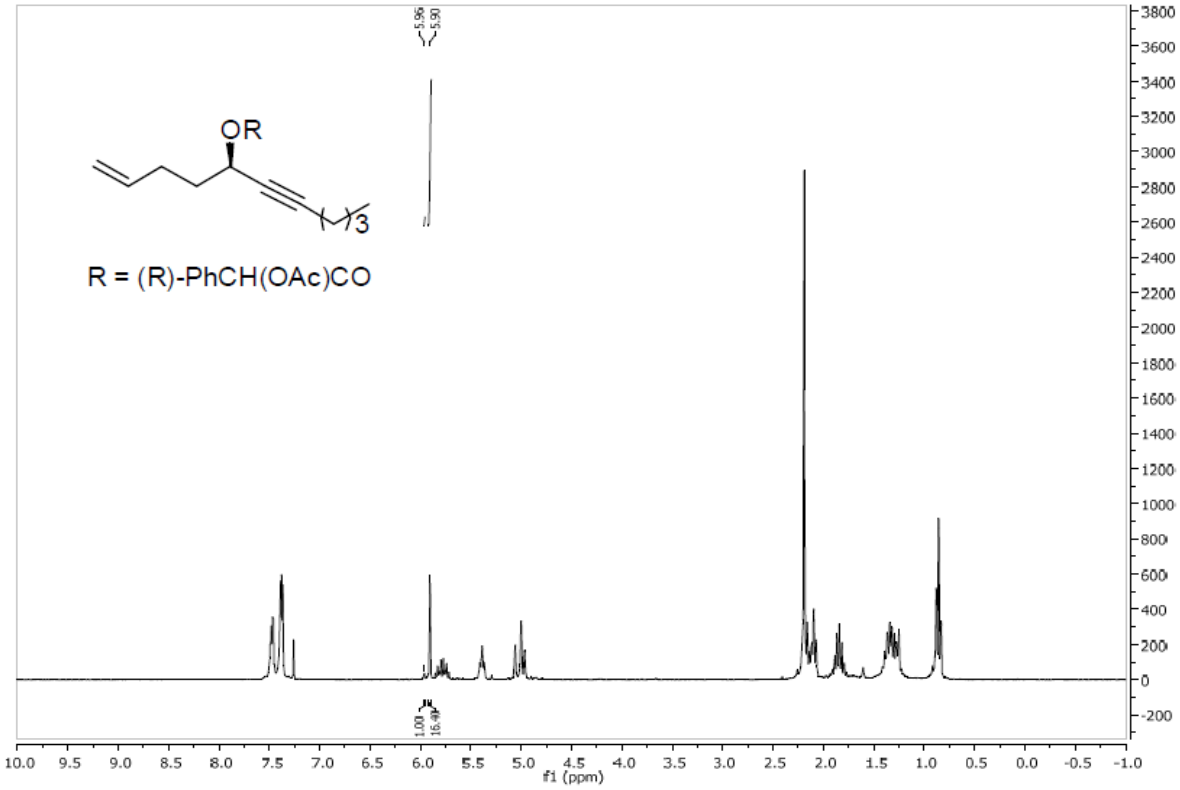


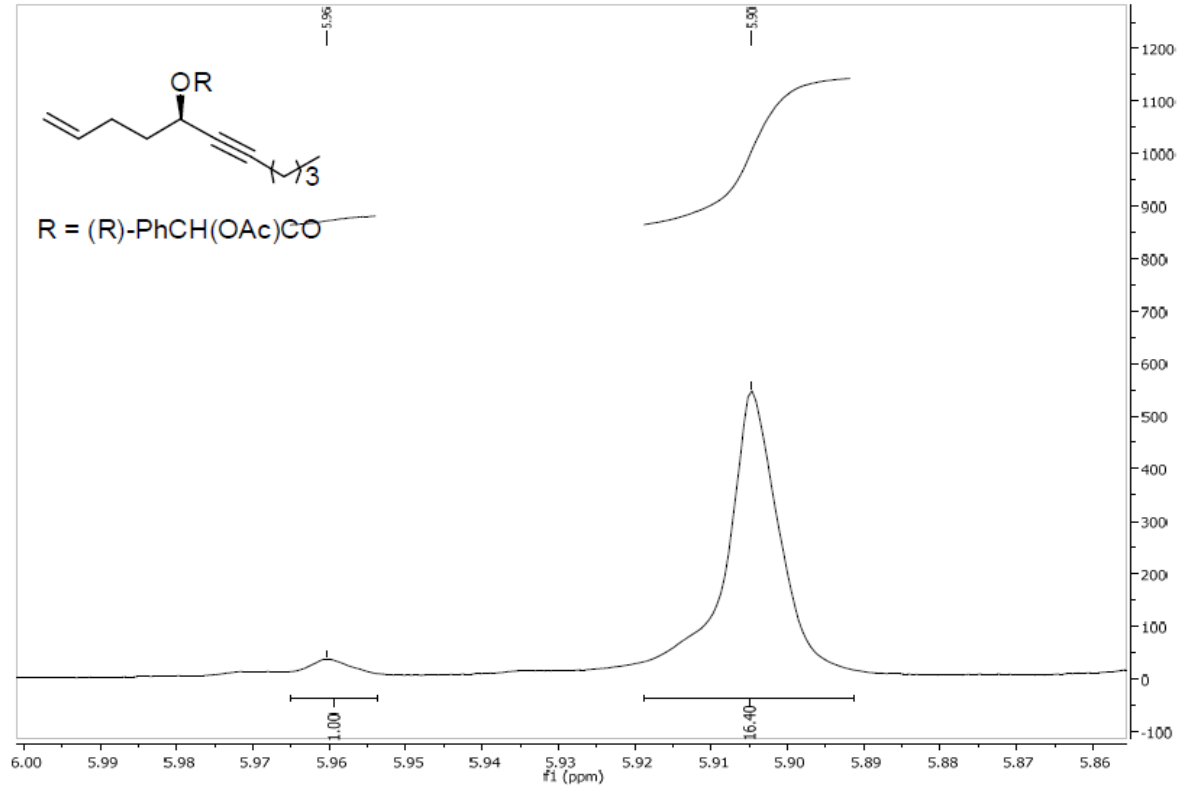

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.957 | 58360400 | 97.82 |
| 2 | 14.622 | 1298125 | 2.18 |

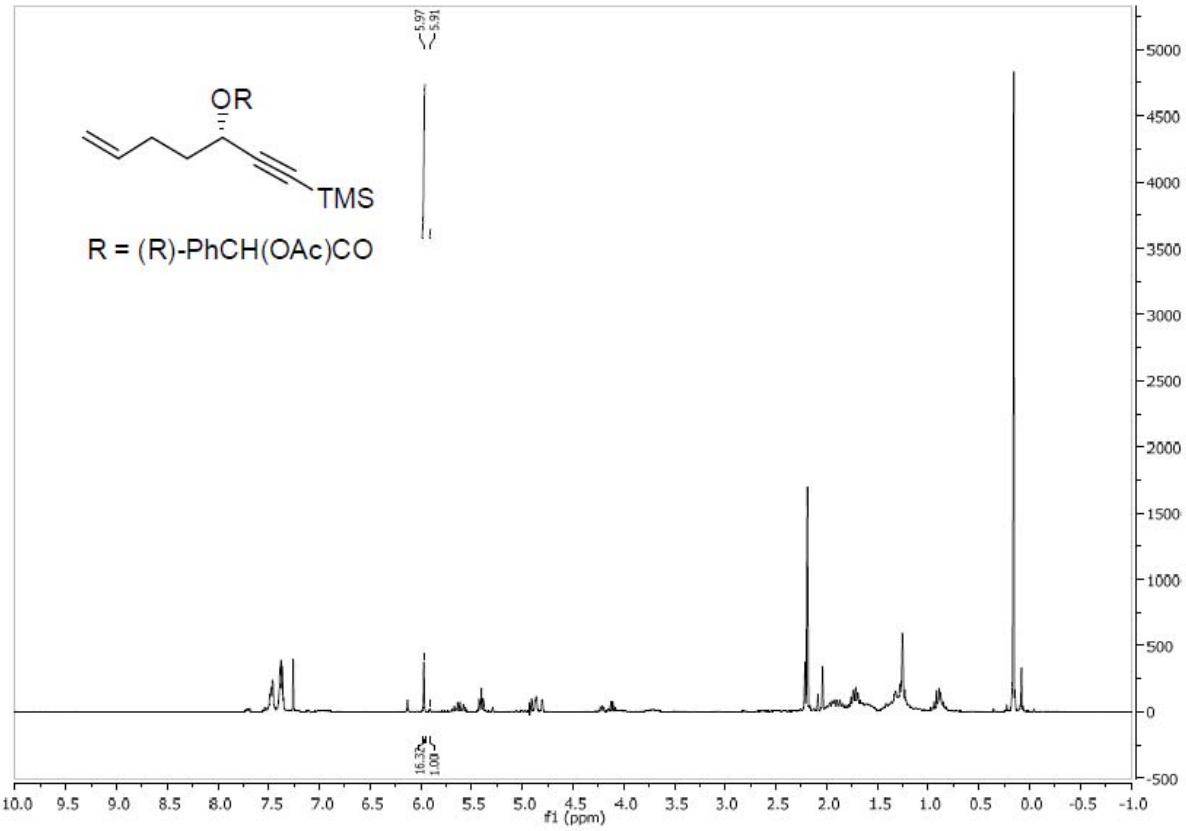


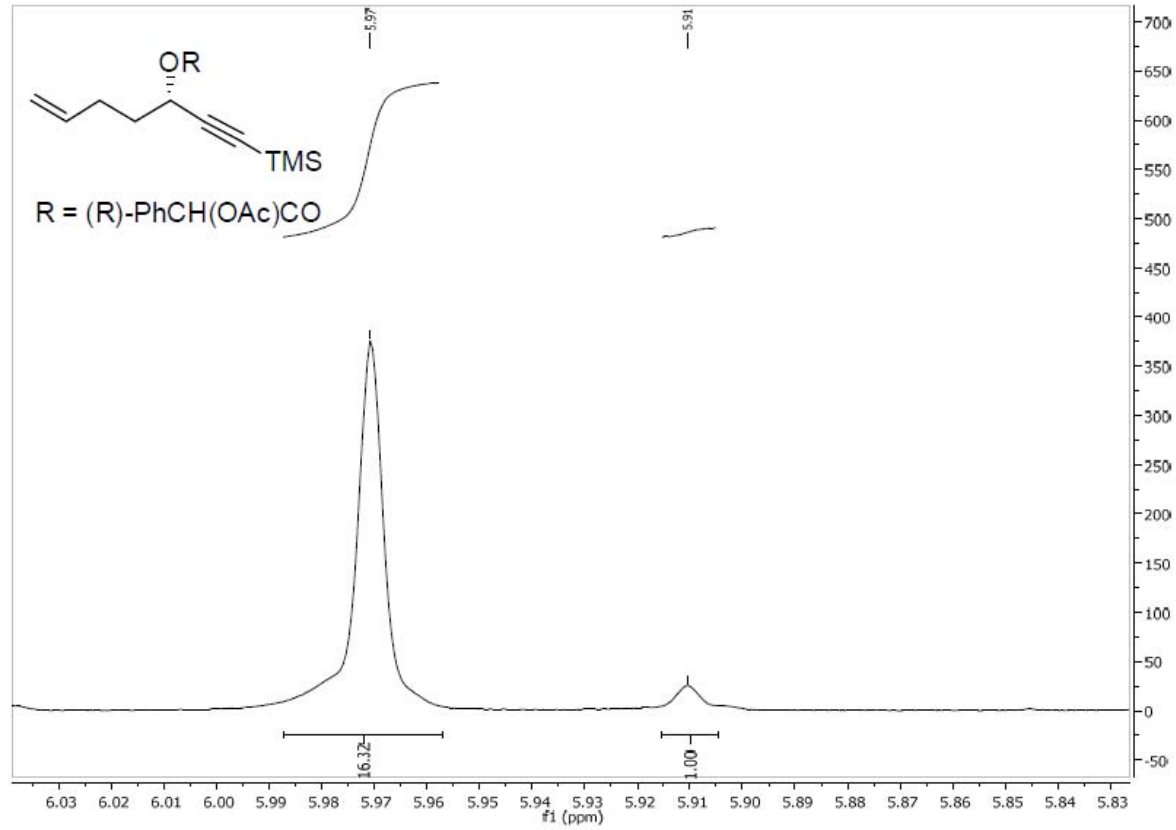

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.917 | 24114411 | 49.85 |
| 2 | 14.549 | 24255732 | 50.15 |

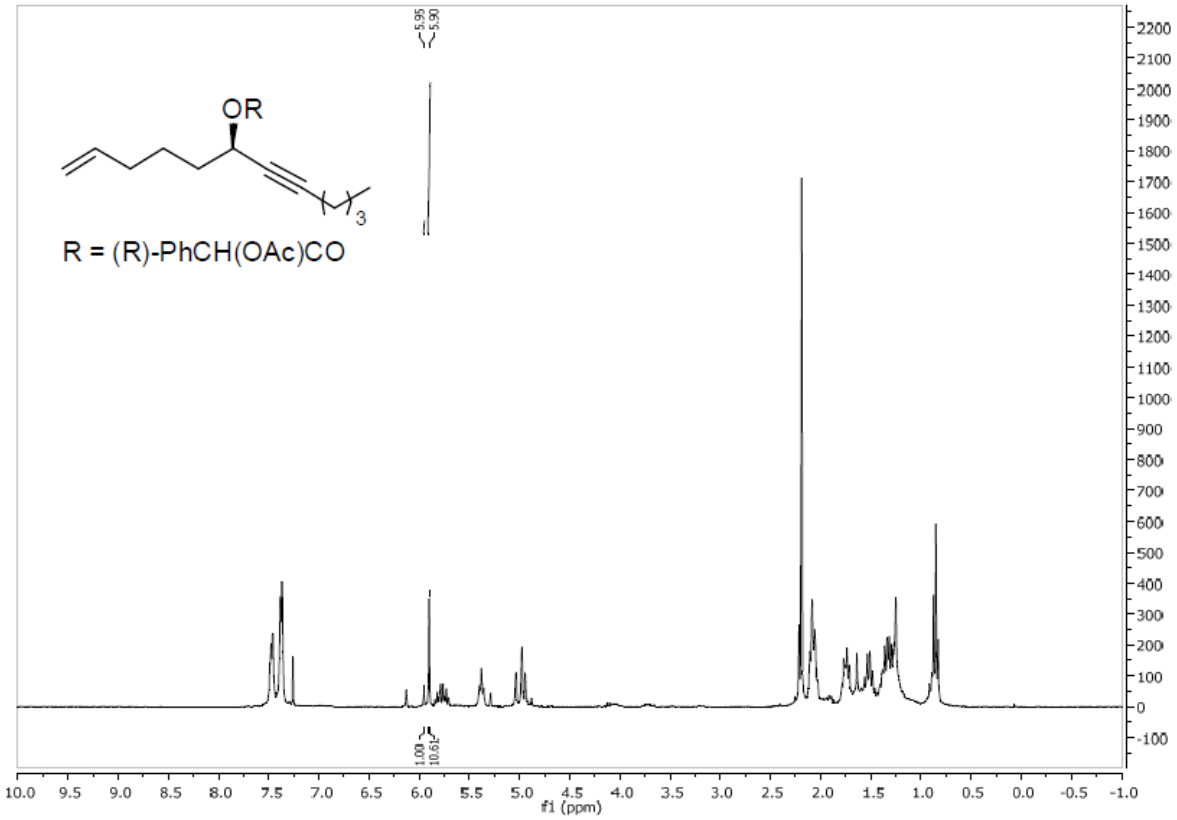
## VIII. $^{1}$H NMR spectra used for ee determination of SM 3, 4, 8, 9, 13, 14, 15.

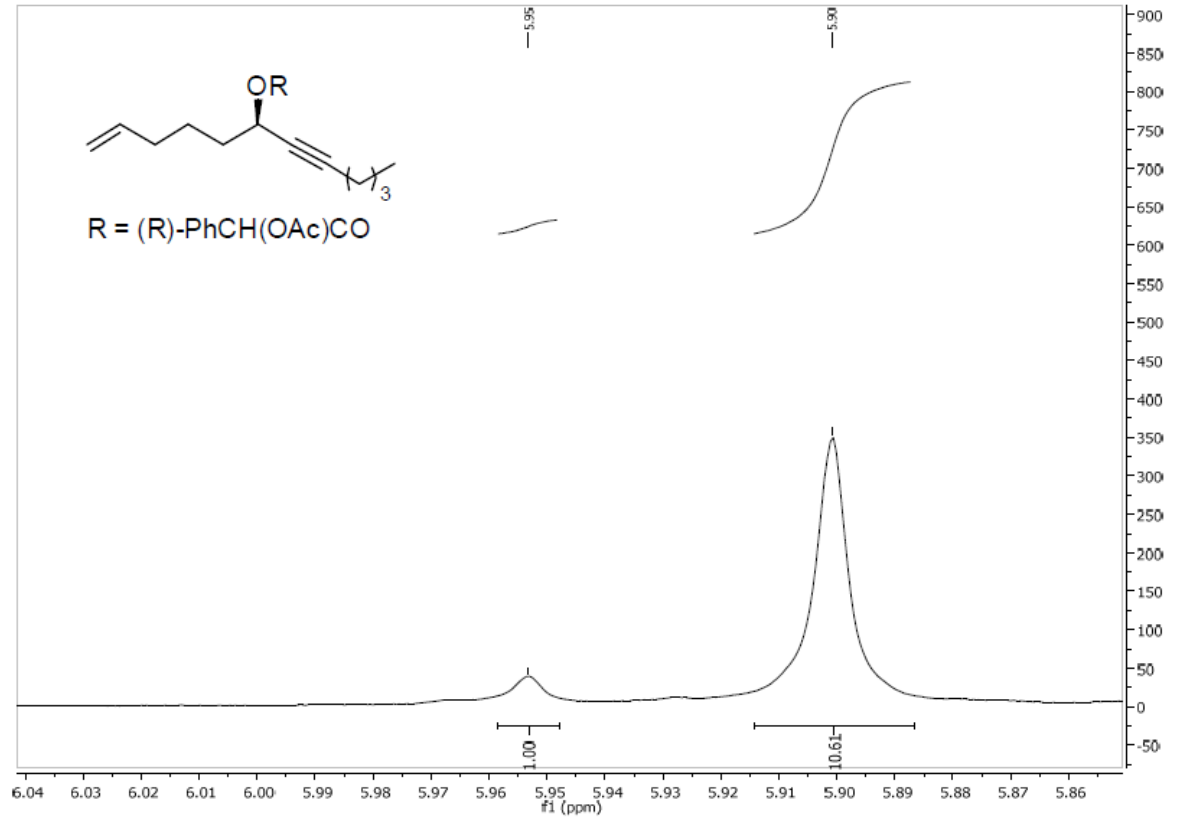


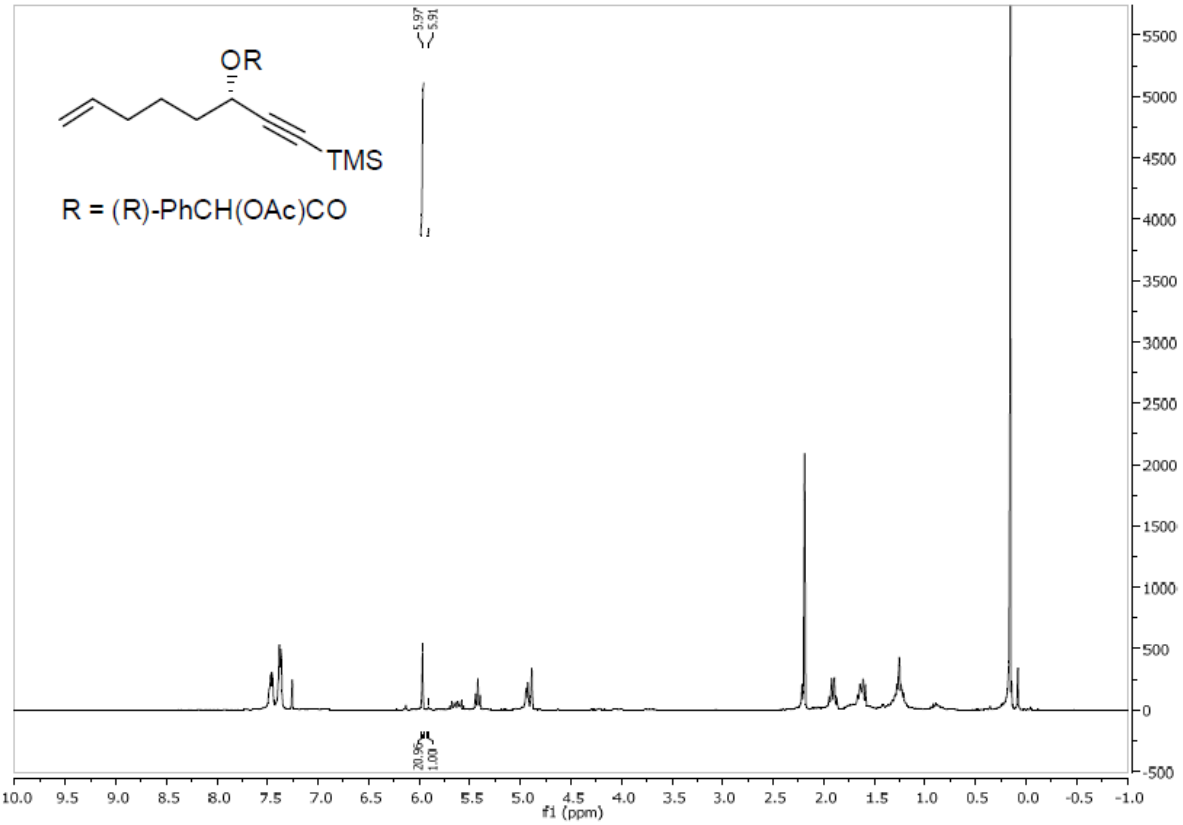



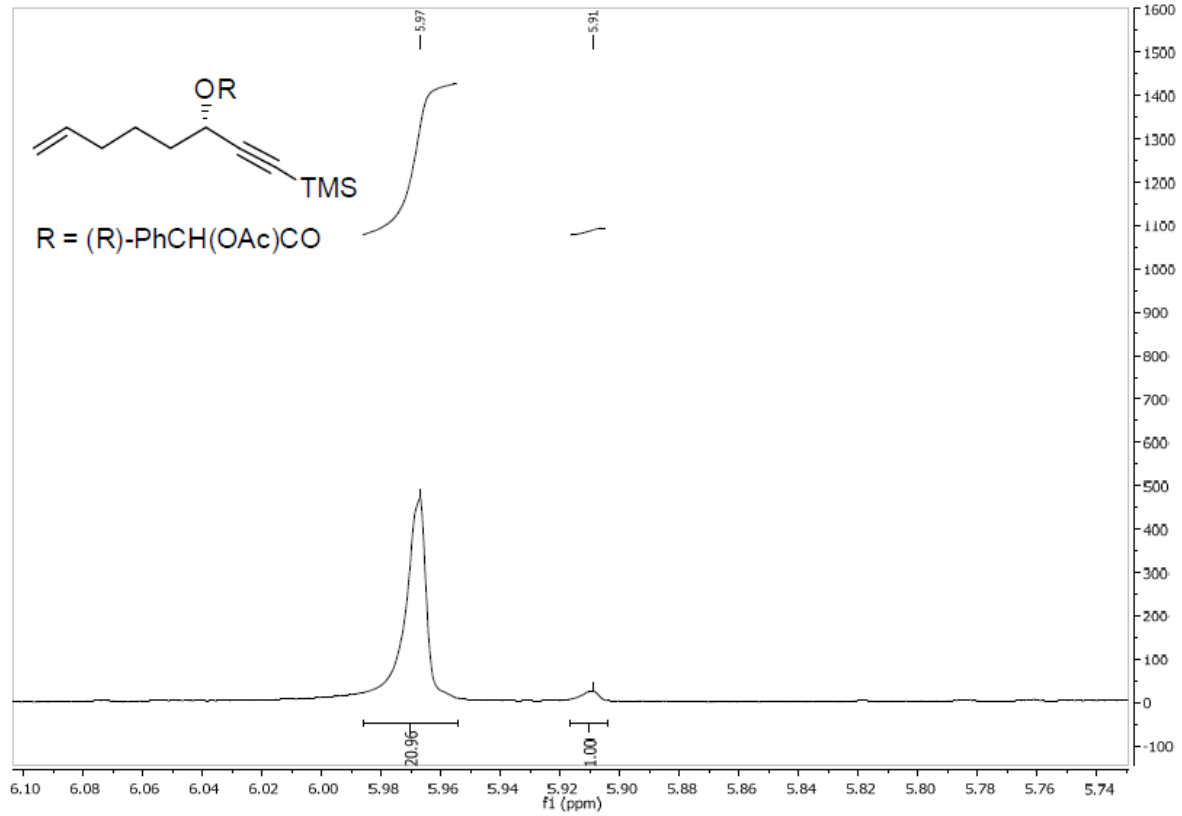

OR
TMS
R = (R)-PhCH(OAc)CO
5.97
5.91
16.32
1.00
f1 (ppm)

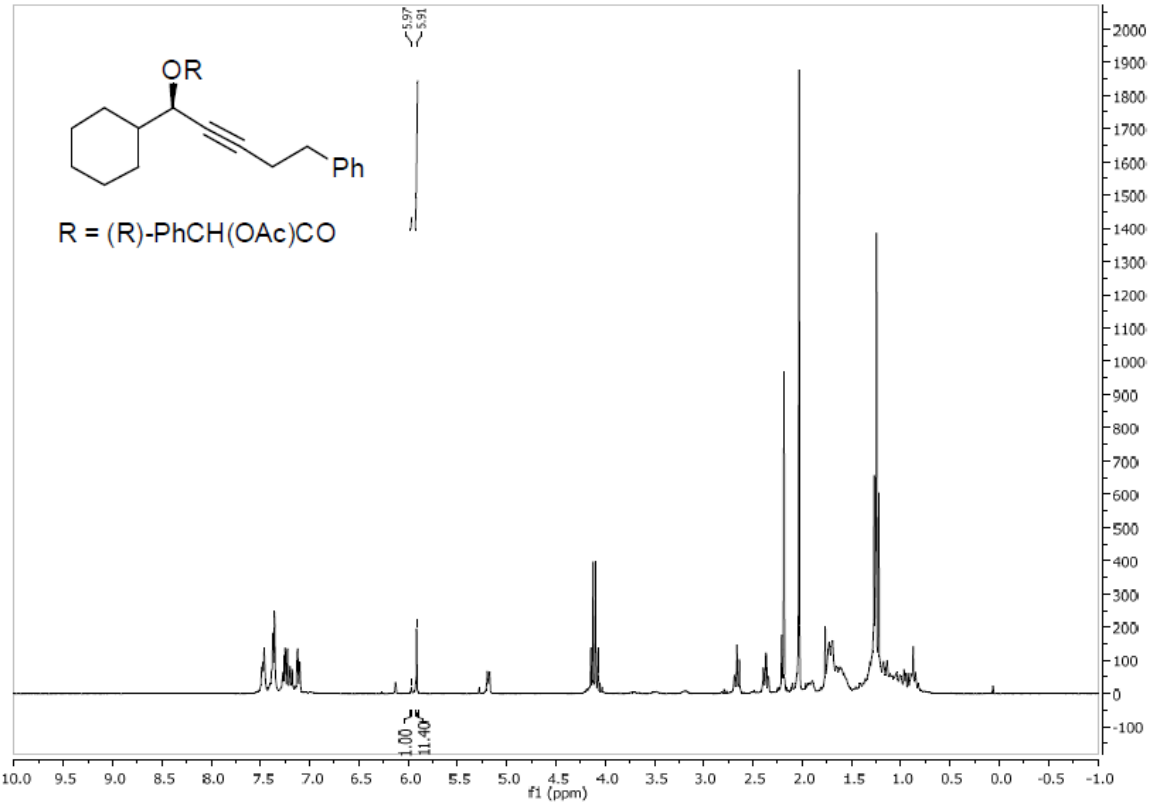

OR
TMS
R = (R)-PhCH(OAc)CO
5.97
5.91
16.32
1.00
f1 (ppm)

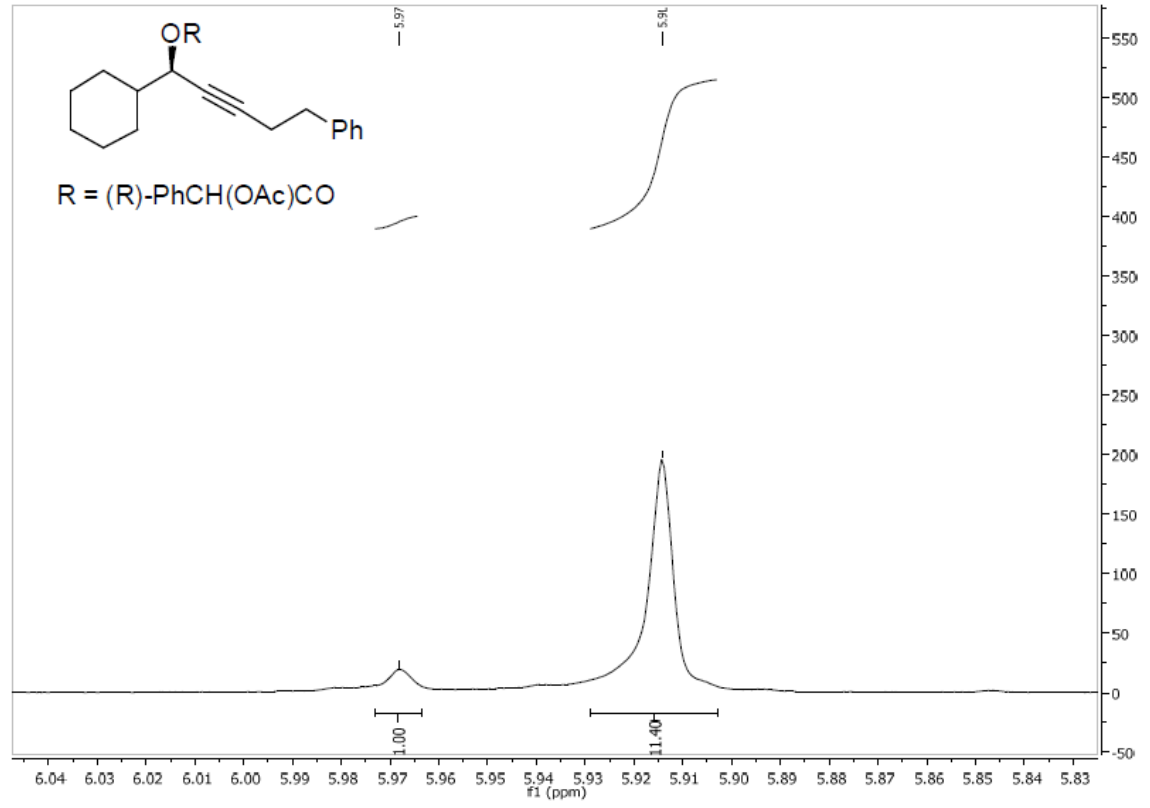

OR
3
R = (R)-PhCH(OAc)CO
5.95
5.90
1.00
10.61
f1 (ppm)

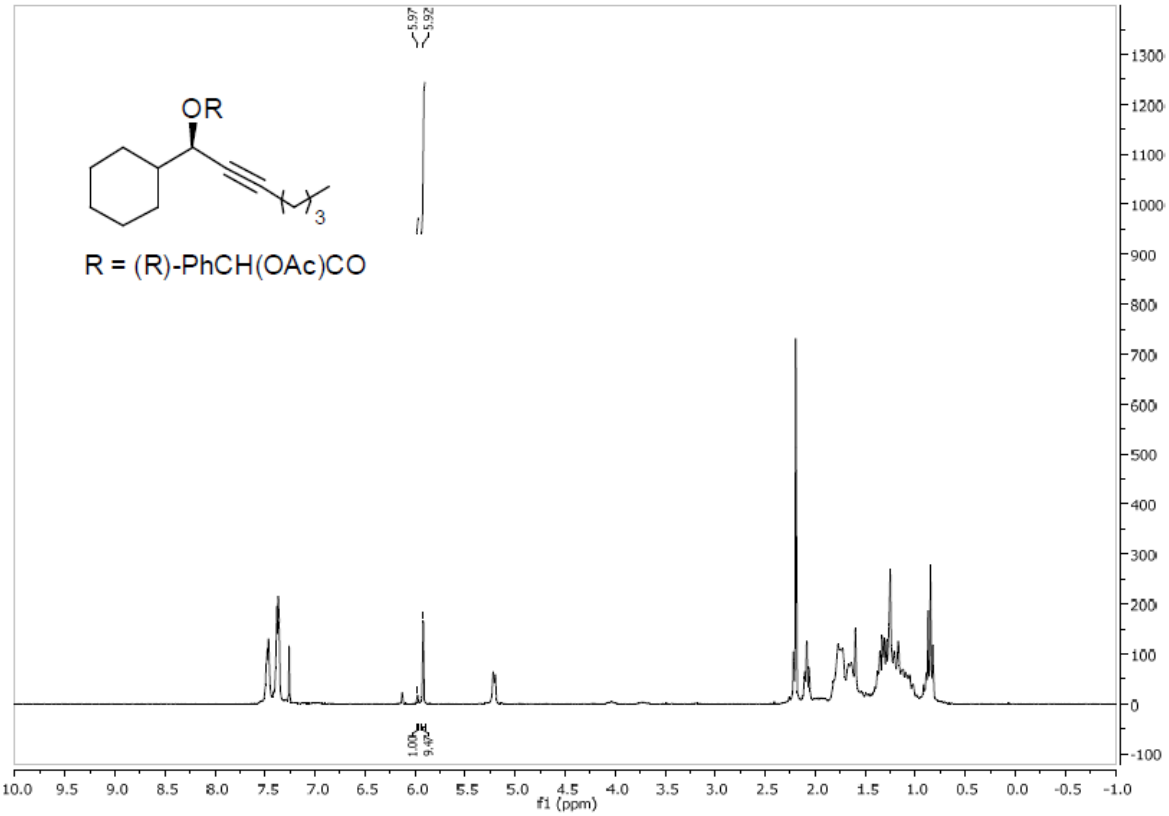

OR
3
R = (R)-PhCH(OAc)CO
5.95
5.90
1.00
10.61
f1 (ppm)

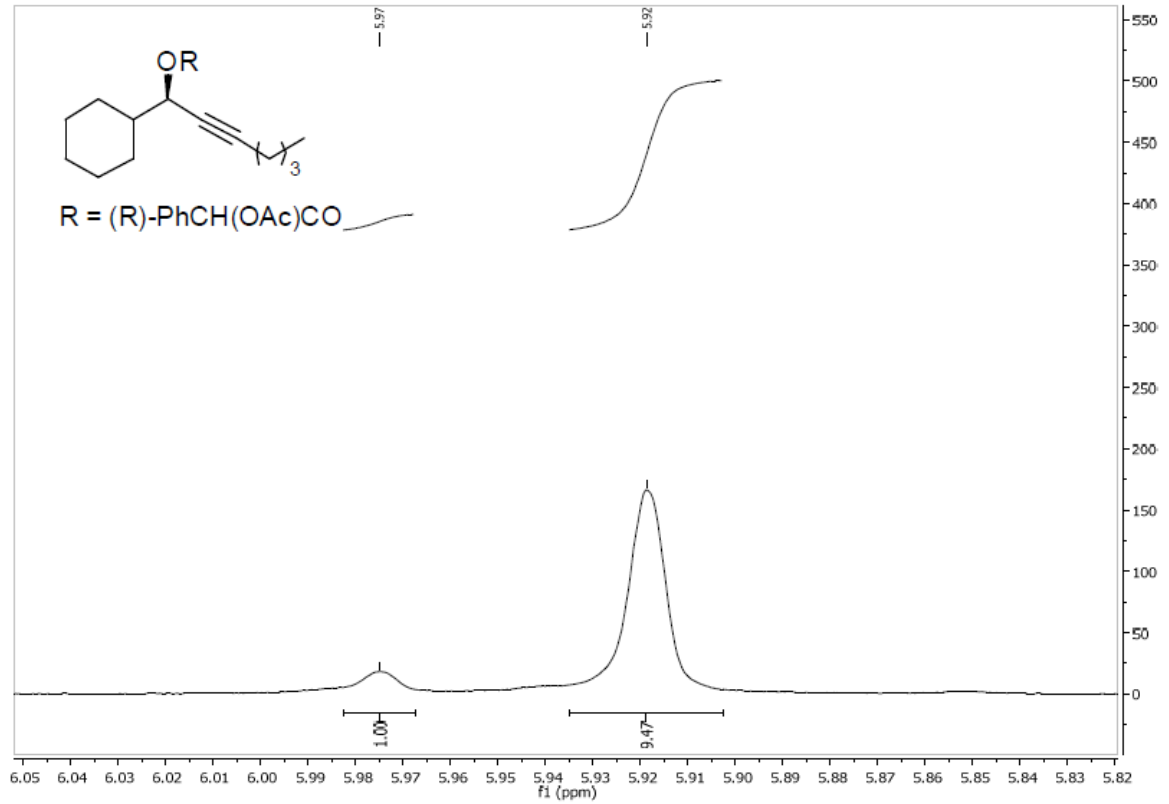

OR
TMS
R = (R)-PhCH(OAc)CO
5.97
5.91
20.96
1.00
f1 (ppm)

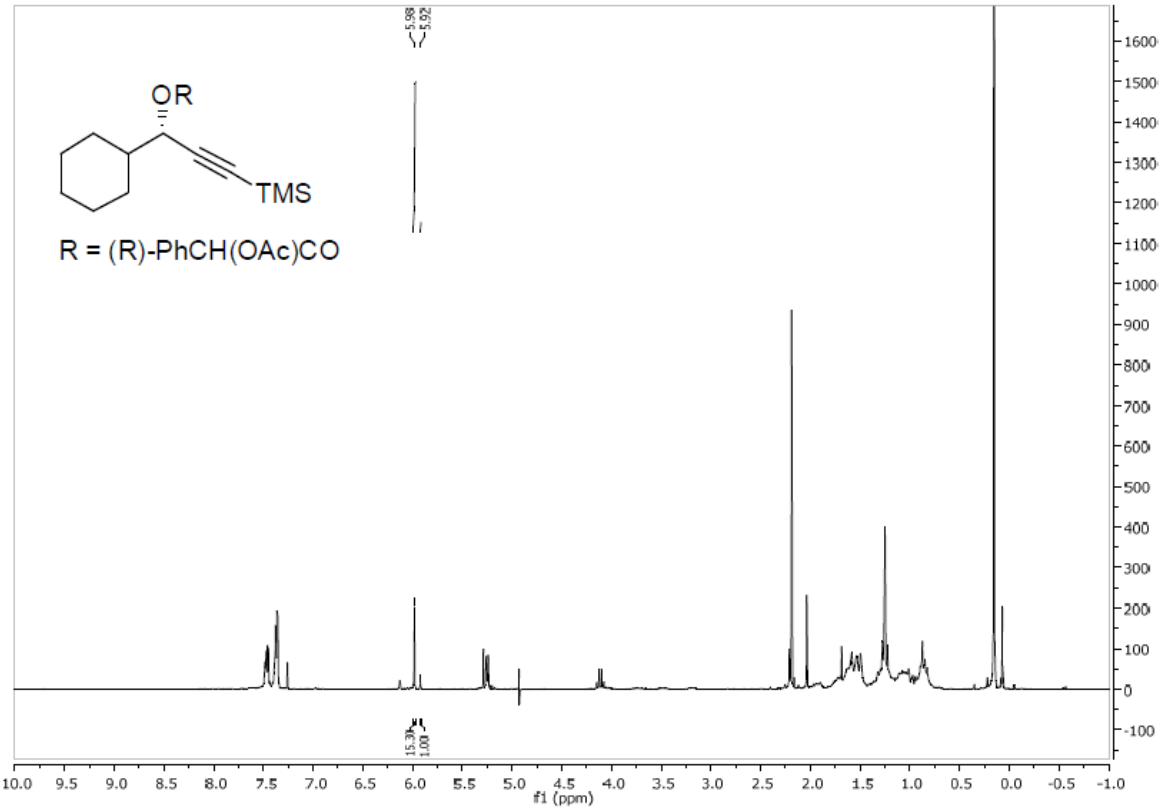

OR
TMS
R = (R)-PhCH(OAc)CO
5.97
5.91
20.96
1.00
f1 (ppm)

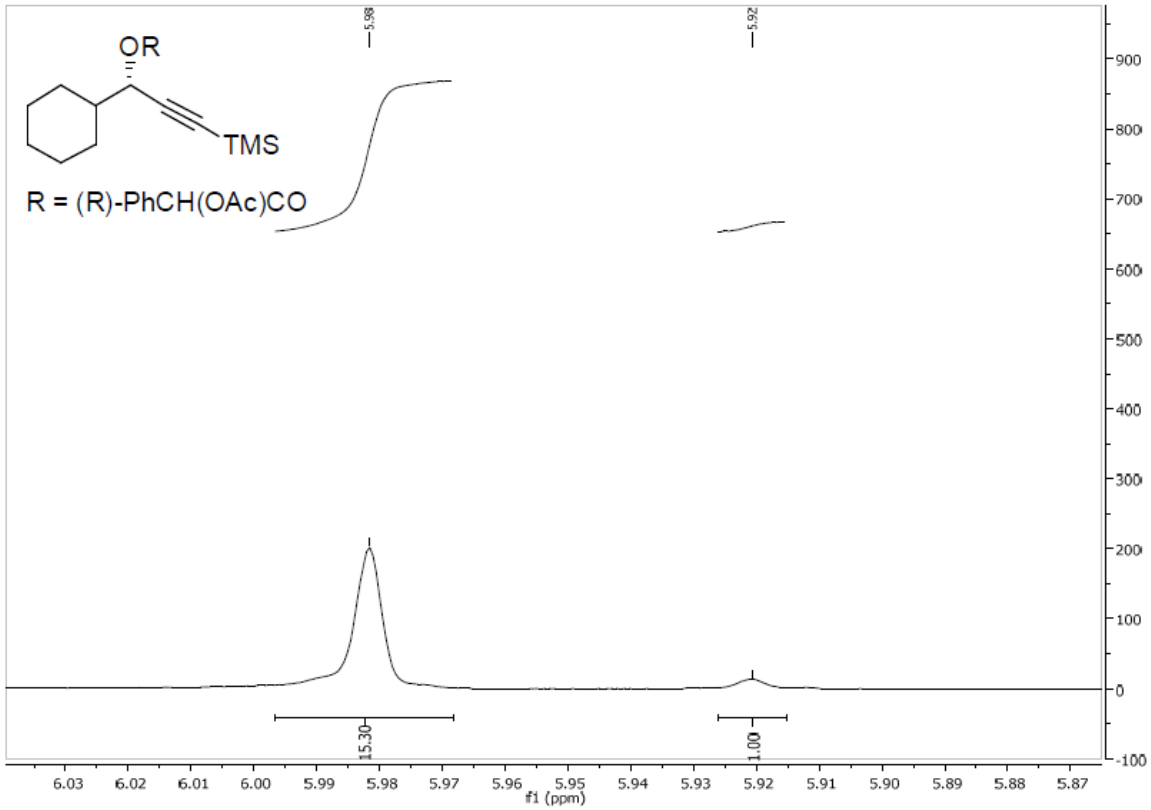

OR
Ph
R = (R)-PhCH(OAc)CO
5.97
5.91
1.00
11.40
f1 (ppm)


OR
Ph
R = (R)-PhCH(OAc)CO
5.97
5.91
1.00
11.40
f1 (ppm)


OR
3
R = (R)-PhCH(OAc)CO
5.97
5.92
1.00
9.47
f1 (ppm)

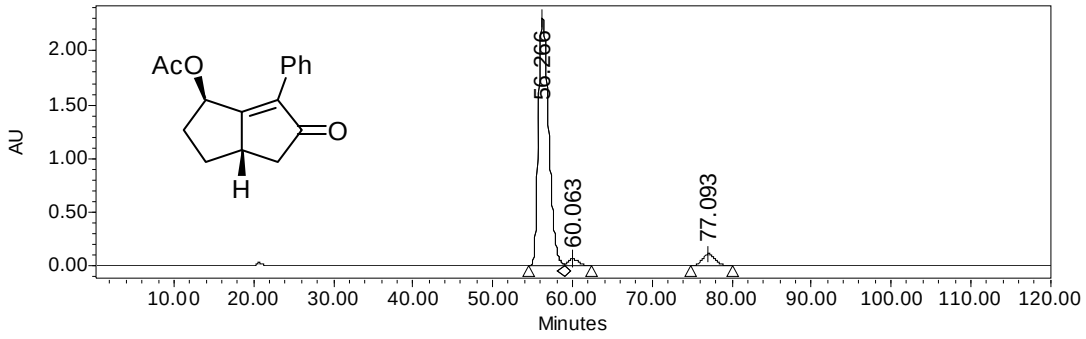

OR
3
R = (R)-PhCH(OAc)CO
5.97
5.92
1.00
9.47
f1 (ppm)


OR
TMS
R = (R)-PhCH(OAc)CO
5.98
5.92
15.30
1.00
f1 (ppm)


OR
TMS
R = (R)-PhCH(OAc)CO
5.98
5.92
15.30
1.00
f1 (ppm)

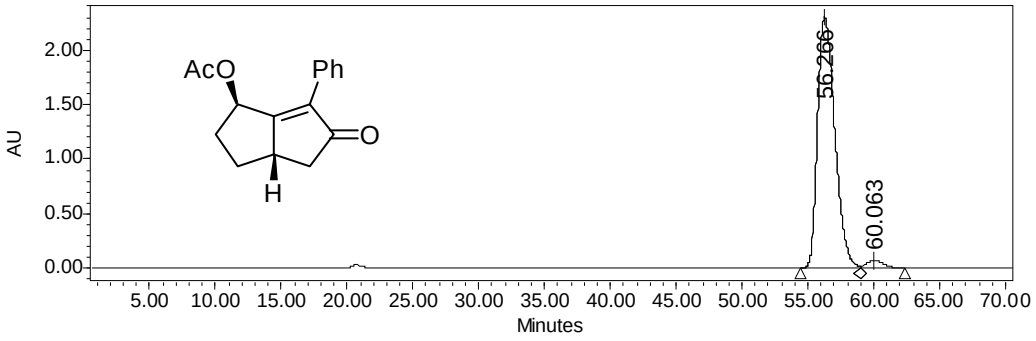
## IX. HPLC Plots for the Determination of the dr for P1-P16.

**P1**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 254 nm, 95:5 dr.



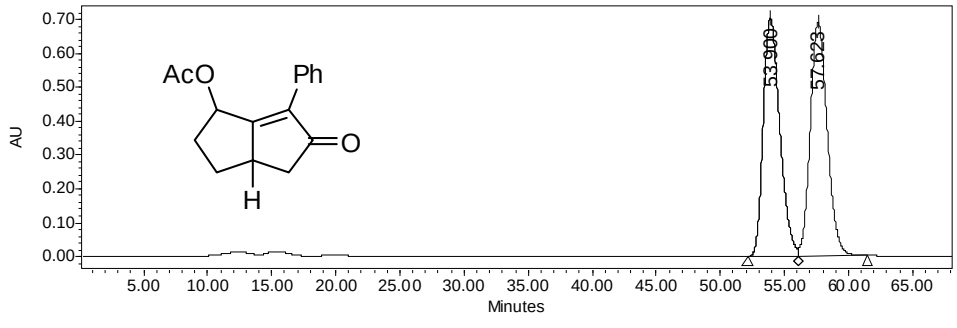

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 56.266 | 209747897 | 91.97 |
| 2 | 60.063 | 6097992 | 2.67 |
| 3 | 77.093 | 12226676 | 5.36 |

**P1**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 254 nm, 94% ee (ee is maintained from **SM1**).



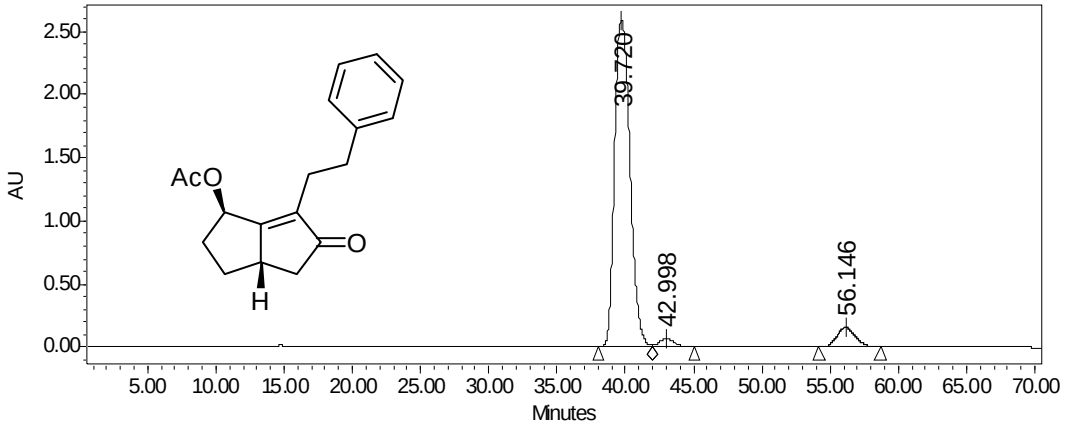

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 56.266 | 209747897 | 97.17 |
| 2 | 60.063 | 6097992 | 2.83 |

Racemic



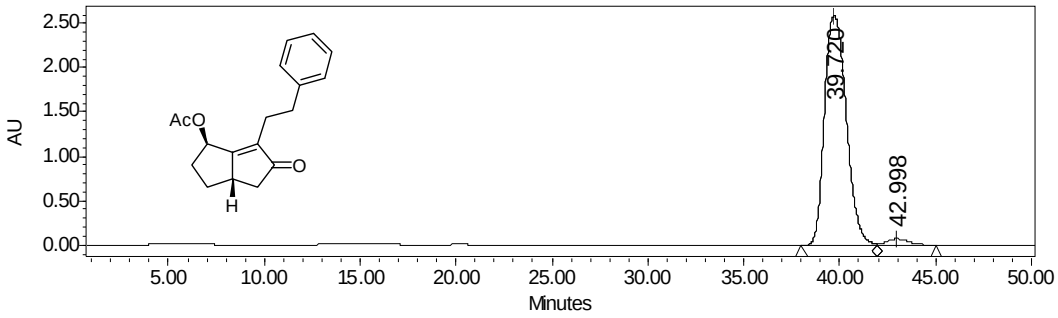

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 53.900 | 63272160 | 49.84 |
| 2 | 57.623 | 63670134 | 50.16 |

**P2**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 235 nm, 93:7 dr.



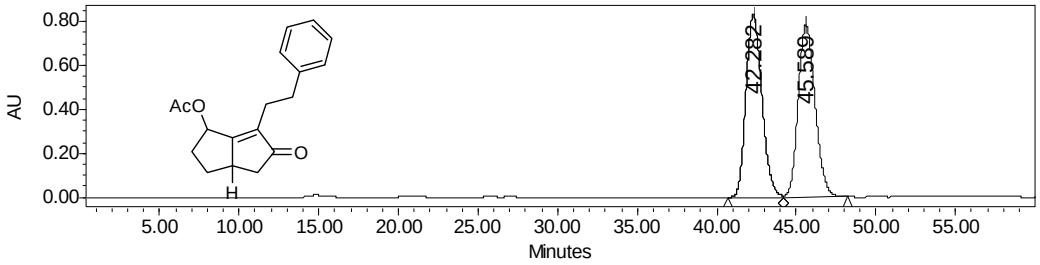

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 39.720 | 204681194 | 90.91 |
| 2 | 42.998 | 5486080 | 2.44 |
| 3 | 56.146 | 14986683 | 6.66 |

**P2**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 235 nm, 95% ee (ee is maintained from **SM2**).



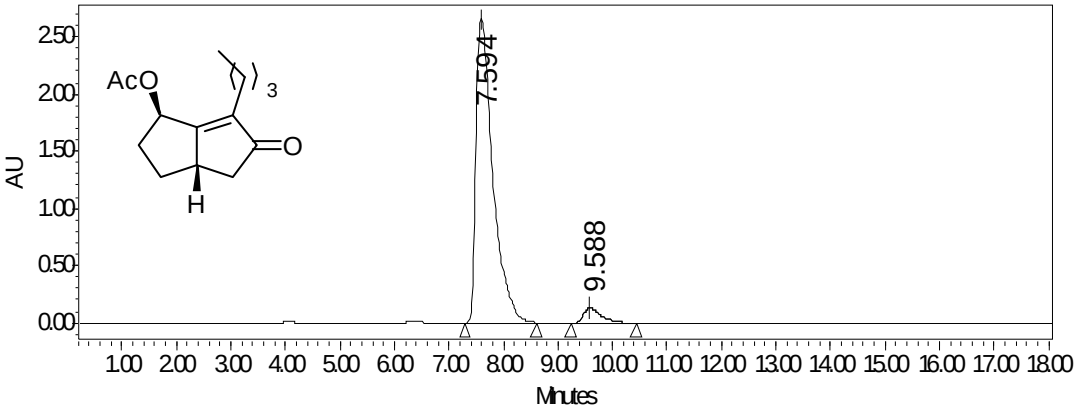

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 39.720 | 204681194 | 97.39 |
| 2 | 42.998 | 5486080 | 2.61 |

Racemic



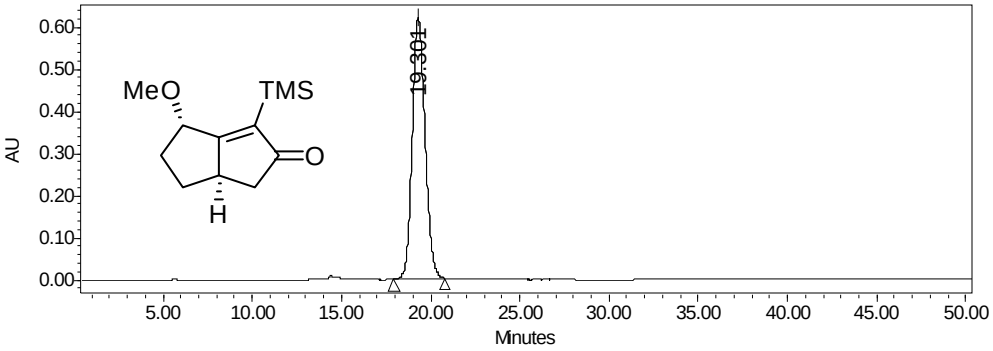

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 42.282 | 58270672 | 50.07 |
| 2 | 45.589 | 58109288 | 49.93 |

**P3**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 95:5 dr.



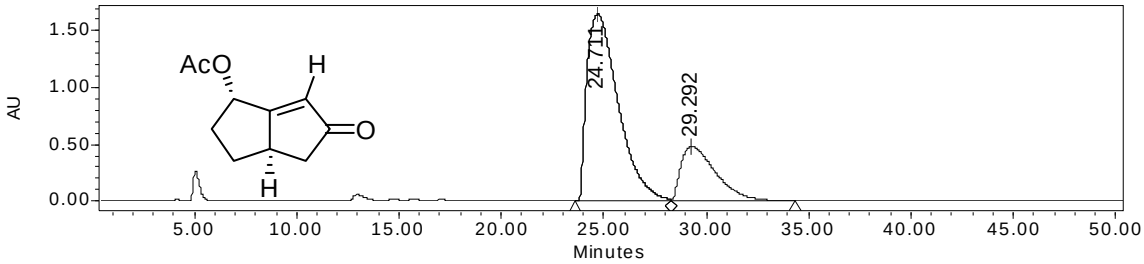

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.594 | 57232879 | 94.76 |
| 2 | 9.588 | 167817 | 5.24 |

**P4**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 235 nm, >99:1 dr.



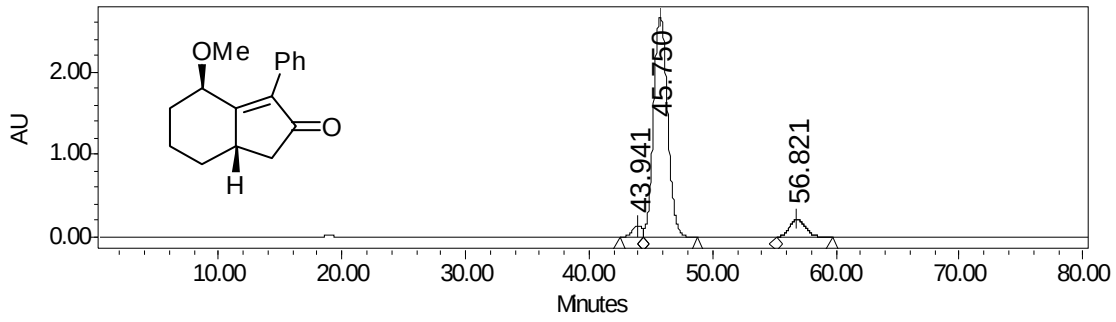

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 19.301 | 30857732 | 100.00 |

**P5**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 215 nm, 75:25 dr.



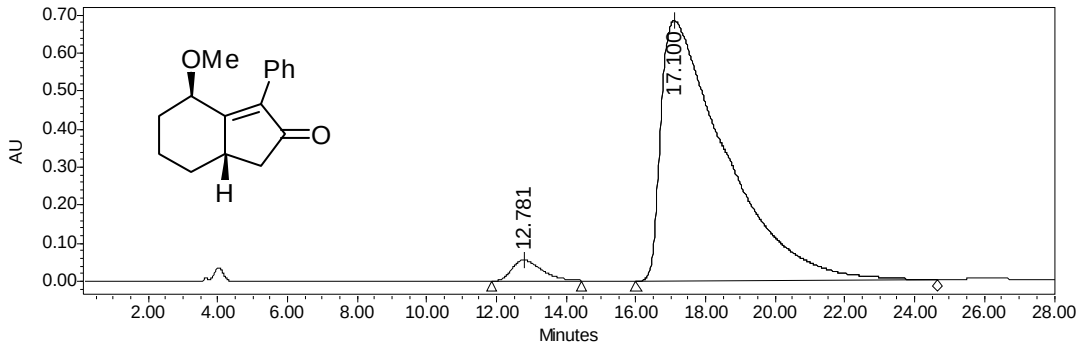

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 24.711 | 176525735 | 75.47 |
| 2 | 29.292 | 57375198 | 24.53 |

**P6**: Chiralpak ADH column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 254 nm, 92:8 dr.



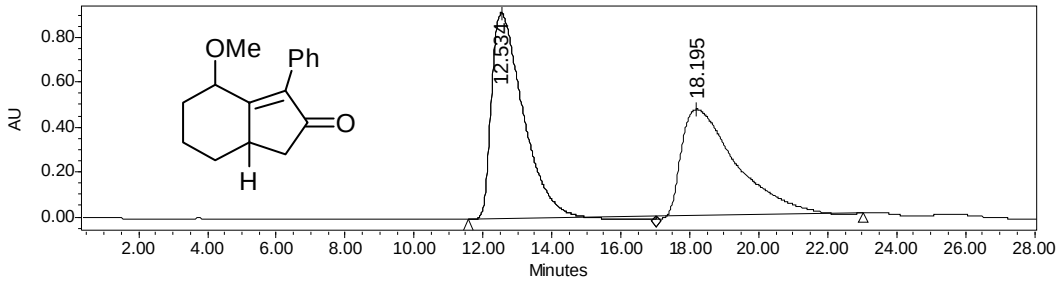

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 43.941 | 7725720 | 3.22 |
| 2 | 45.750 | 212367128 | 88.56 |
| 3 | 56.821 | 19697514 | 8.21 |

**P6**: Chiralcel OB-H column, 98:2 hexanes:*i*PrOH, flow rate = 1 mL/min, λ = 254 nm, 93% ee (ee is maintained from **SM6**).



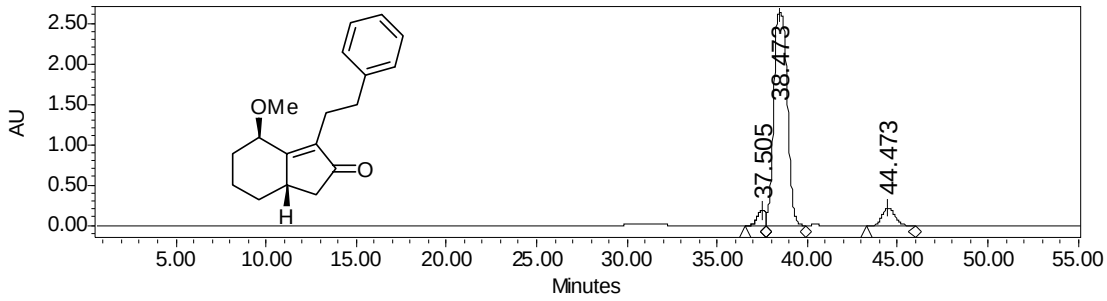

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 12.781 | 3229090 | 3.51 |
| 2 | 17.100 | 88779954 | 96.49 |

Racemic



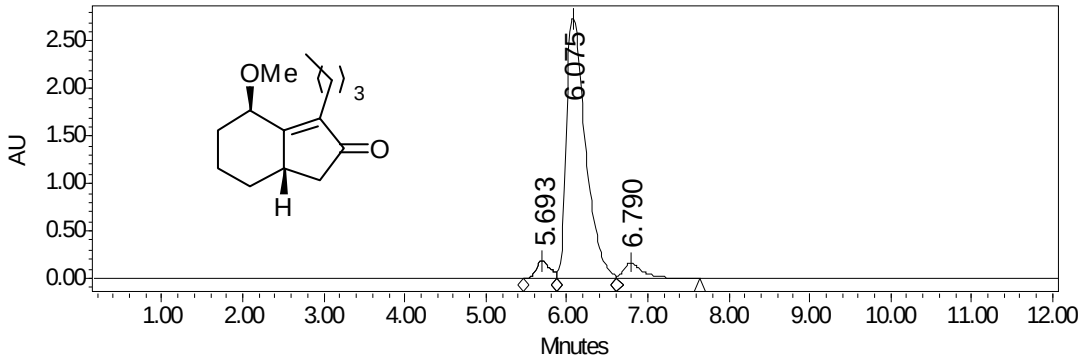

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 12.534 | 59465313 | 53.08 |
| 2 | 18.195 | 52558842 | 46.92 |

**P7**: Chiralpak AD-H column, 99:1 hexanes:*i*PrOH, flow rate = 0.3 mL/min, λ = 221 nm, 93:7 dr.



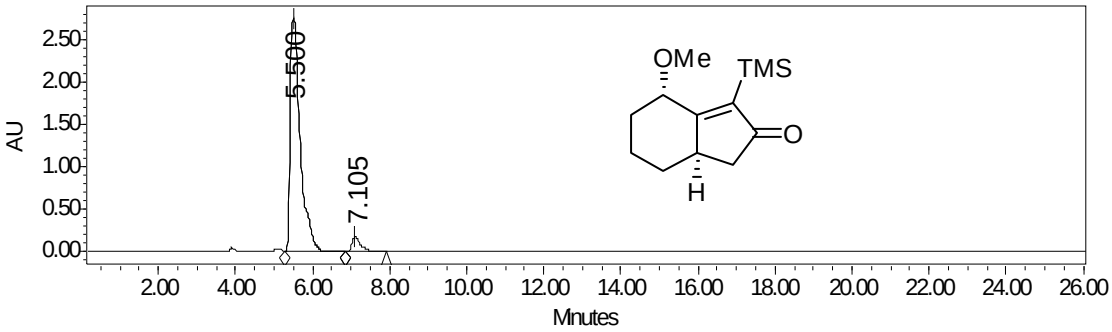

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 37.505 | 6040472 | 3.87 |
| 2 | 38.473 | 138389033 | 88.68 |
| 3 | 44.473 | 11621918 | 7.45 |

**P8**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 95:5 dr.



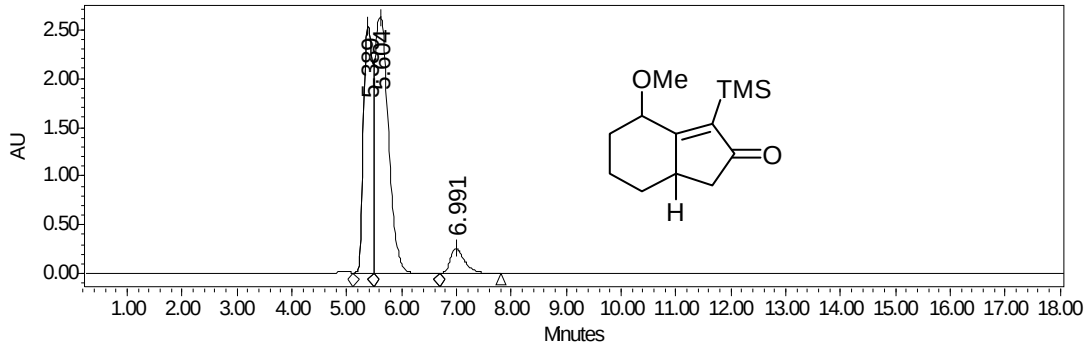

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.693 | 2124436 | 4.24 |
| 2 | 6.075 | 45299325 | 90.44 |
| 3 | 6.790 | 2666056 | 5.32 |

**P9** (From Method B—heating in acetonitrile): Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 94:6 dr.



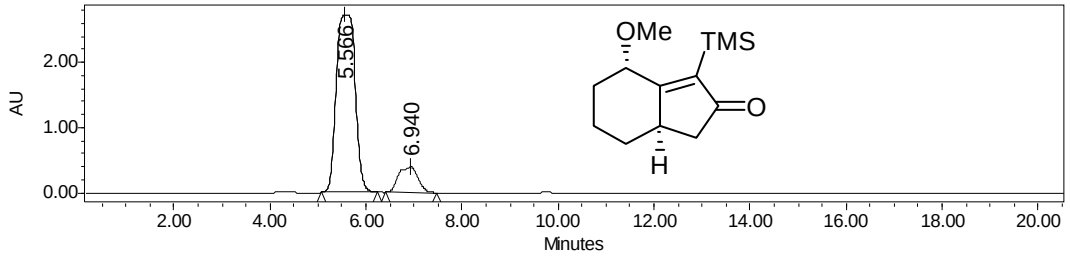

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.500 | 49271045 | 94.48 |
| 2 | 7.105 | 2876627 | 5.52 |

**P9** (from Method C—$^{n}$BuSMe as additive in refluxing 1,4-dioxane): Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 94:6 dr. (racemic compound)



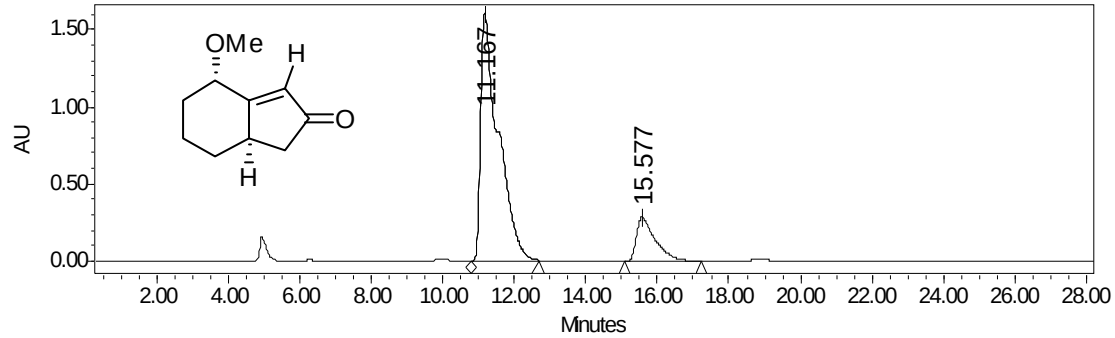

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.389 | 28150346 | 35.69 |
| 2 | 5.604 | 45908350 | 58.20 |
| 3 | 6.991 | 4823214 | 6.11 |

**P9** (from Method D—TMTU as additive in refluxing toluene): Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 87:13 dr.



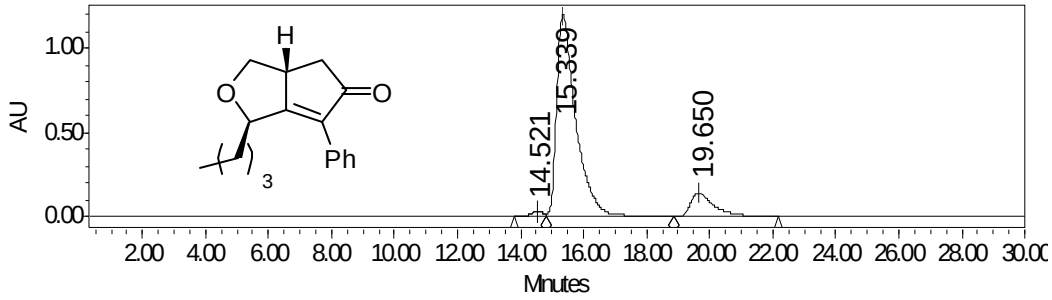

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 5.566 | 74063608 | 86.82 |
| 2 | 6.940 | 11240005 | 13.18 |

**P10**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 235 nm, 84:16 dr.



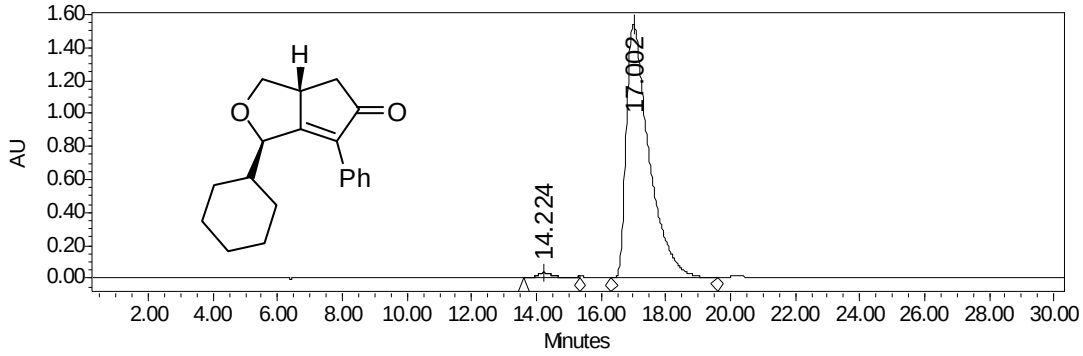
| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 11.167 | 55056962 | 84.37 |
| 2 | 15.577 | 10202198 | 15.63 |

**P11**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, 87:13 dr.



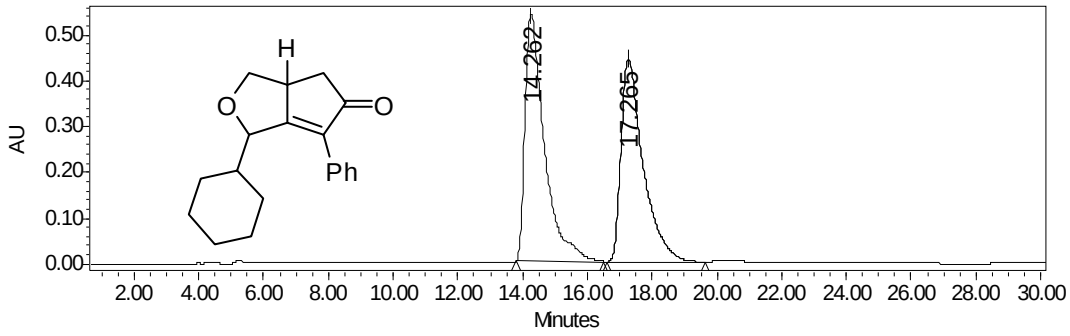

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 14.521 | 964117 | 1.62 |
| 2 | 15.339 | 50924237 | 85.58 |
| 3 | 19.650 | 7617144 | 12.80 |

**P12**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, >99:1 dr, 96% ee (ee is maintained from **SM12**).



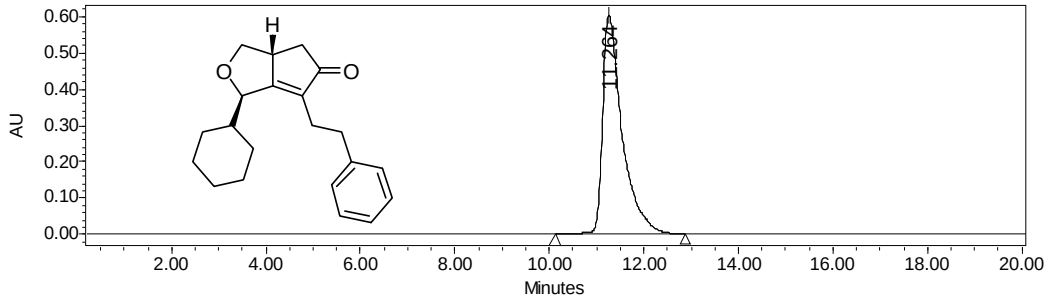

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 14.224 | 1440841 | 1.87 |
| 2 | 17.002 | 75694337 | 98.13 |

Racemic



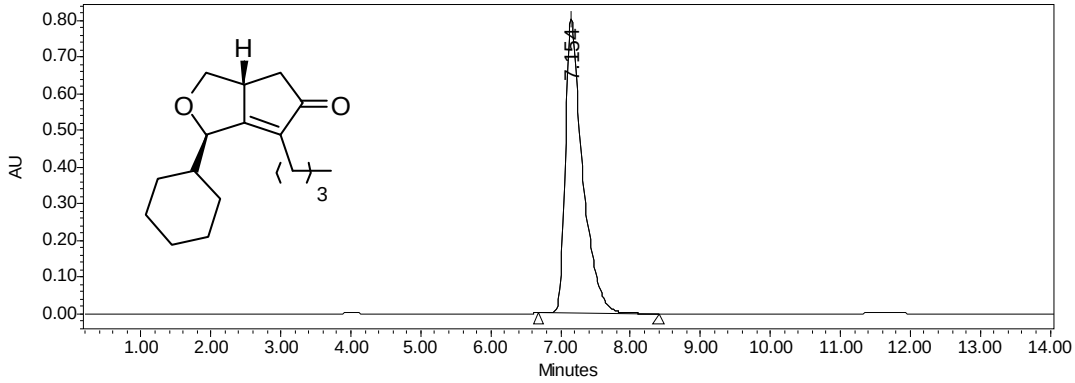

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 14.262 | 22530228 | 51.76 |
| 2 | 17.265 | 20993948 | 48.24 |

**P13**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, >99:1 dr.



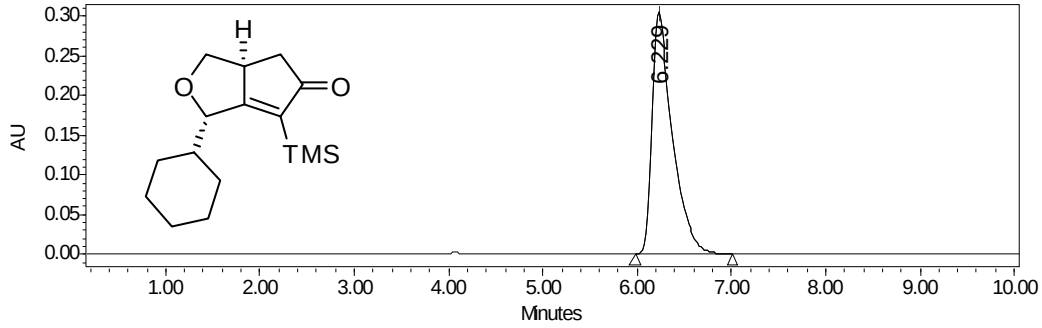

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 11.264 | 17318493 | 100.00 |

**P14**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, >99:1 dr.




| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 7.154 | 13833456 | 100.00 |

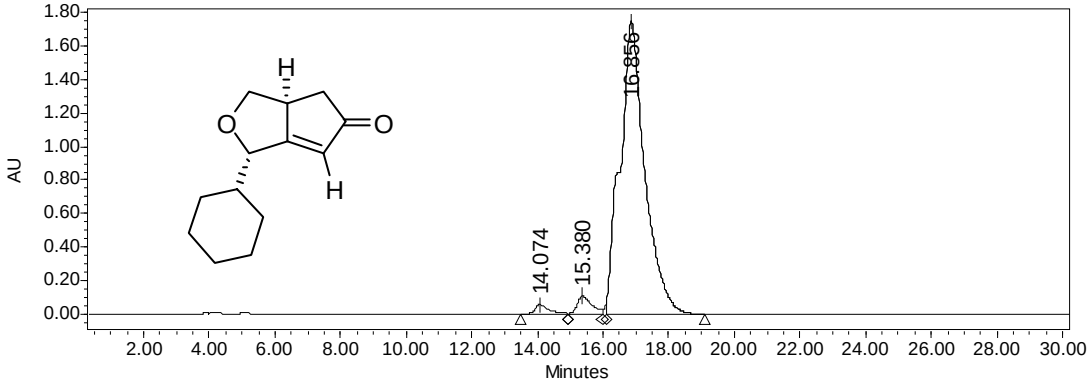
**P15**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 254 nm, >99:1 dr.




| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 6.229 | 4570366 | 100.00 |

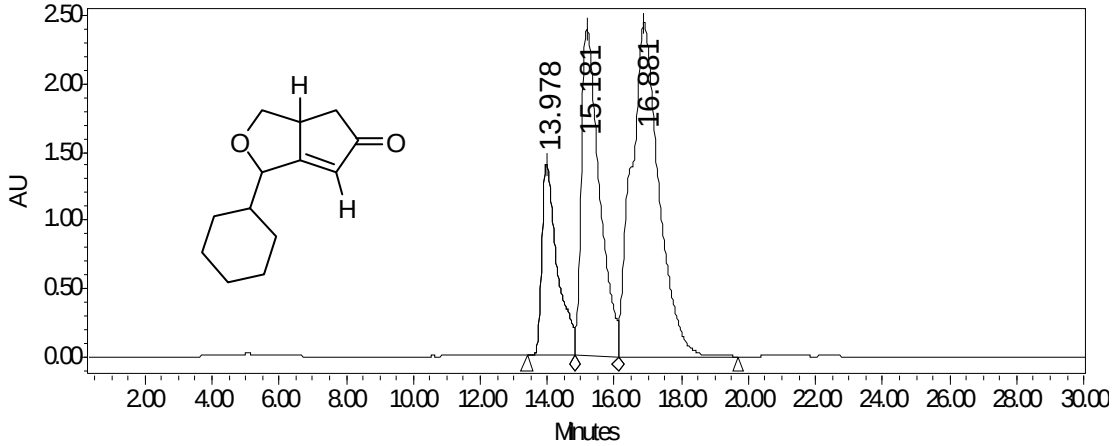
**P16**: Chiralcel OD column, 98:2 hexanes:*i*PrOH, flow rate = 1.0 mL/min, λ = 221 nm, 65:35 dr.

(Determined from area of the diastereomeric pair of the minor enantiomers, $t_{major\text{-}diastereomer}$ = 15.38; $t_{minor\text{-}diastereomer}$ = 14.07, since these peaks are fully resolved. This dr is confirmed by analysis of the $^{1}$H NMR spectra of the combined diastereomers.)




| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 14.074 | 1697586 | 1.75 |
| 2 | 15.380 | 3348589 | 3.46 |
| 3 | 16.856 | 91821526 | 94.79 |

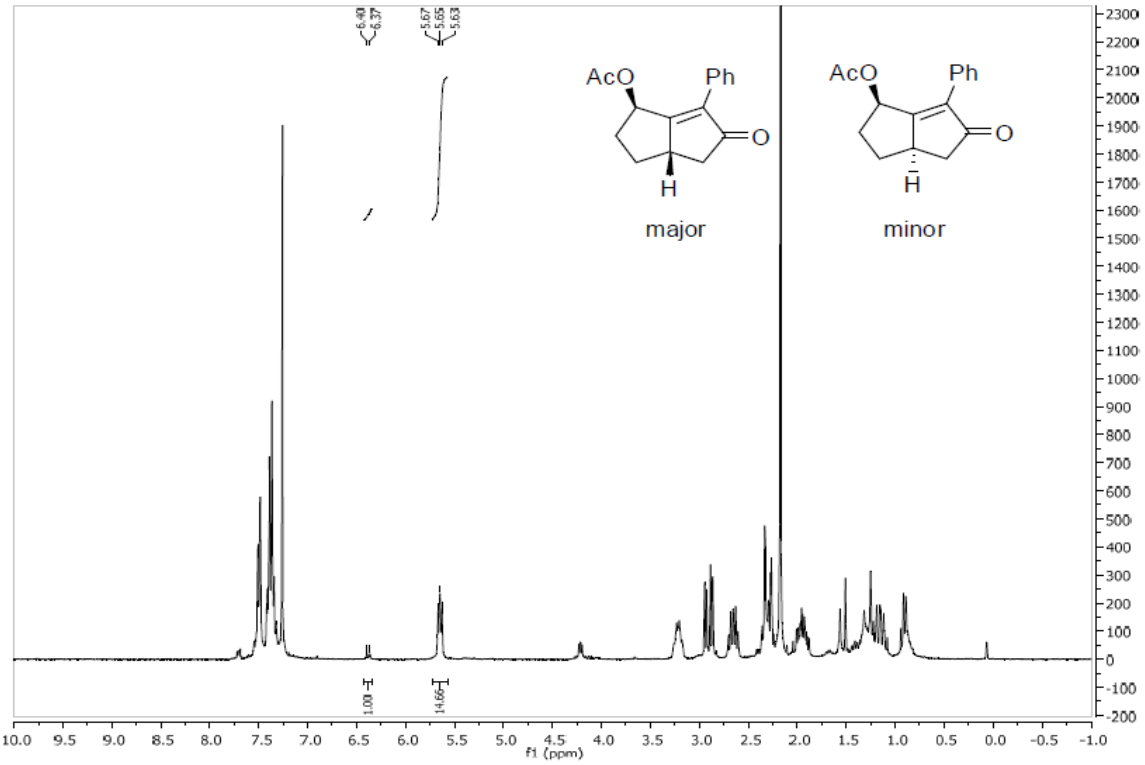
Racemic



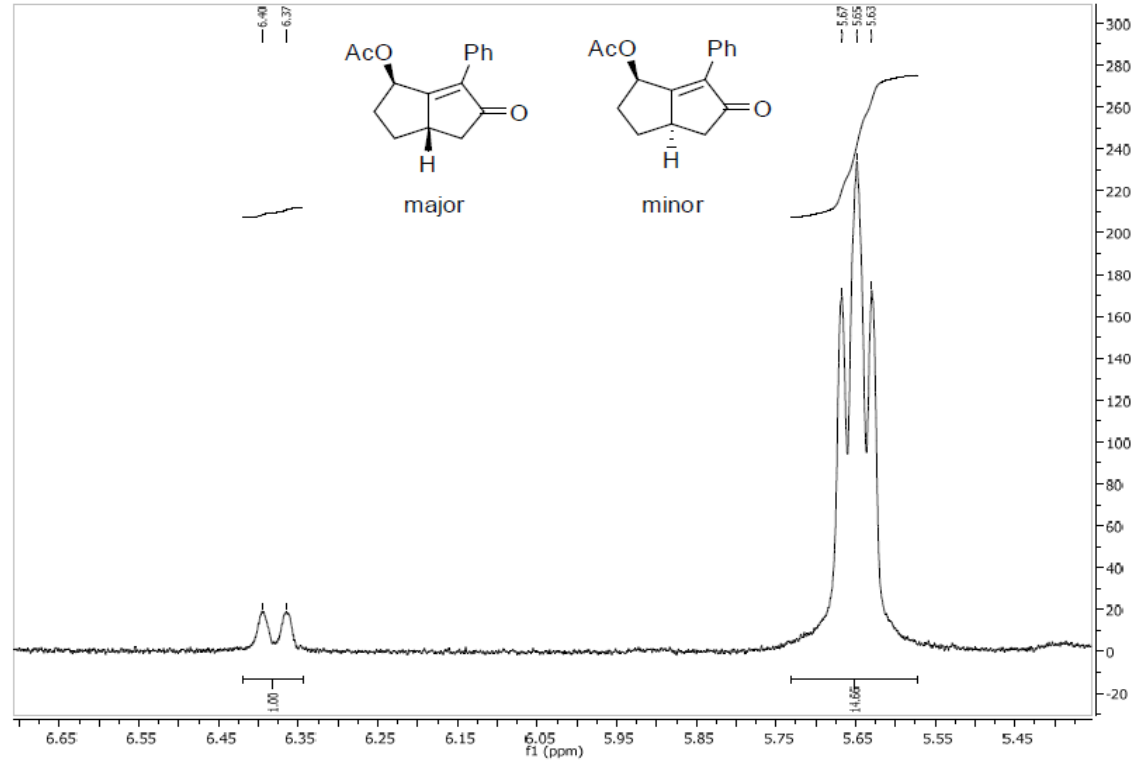

| Name | Retention Time | Area | % Area |
|---|---|---|---|
| 1 | 13.978 | 45568969 | 16.50 |
| 2 | 15.181 | 90435663 | 32.76 |
| 3 | 16.881 | 140087853 | 50.74 |

## X. $^{1}$H NMR spectra used for the dr determination of P1-P16.

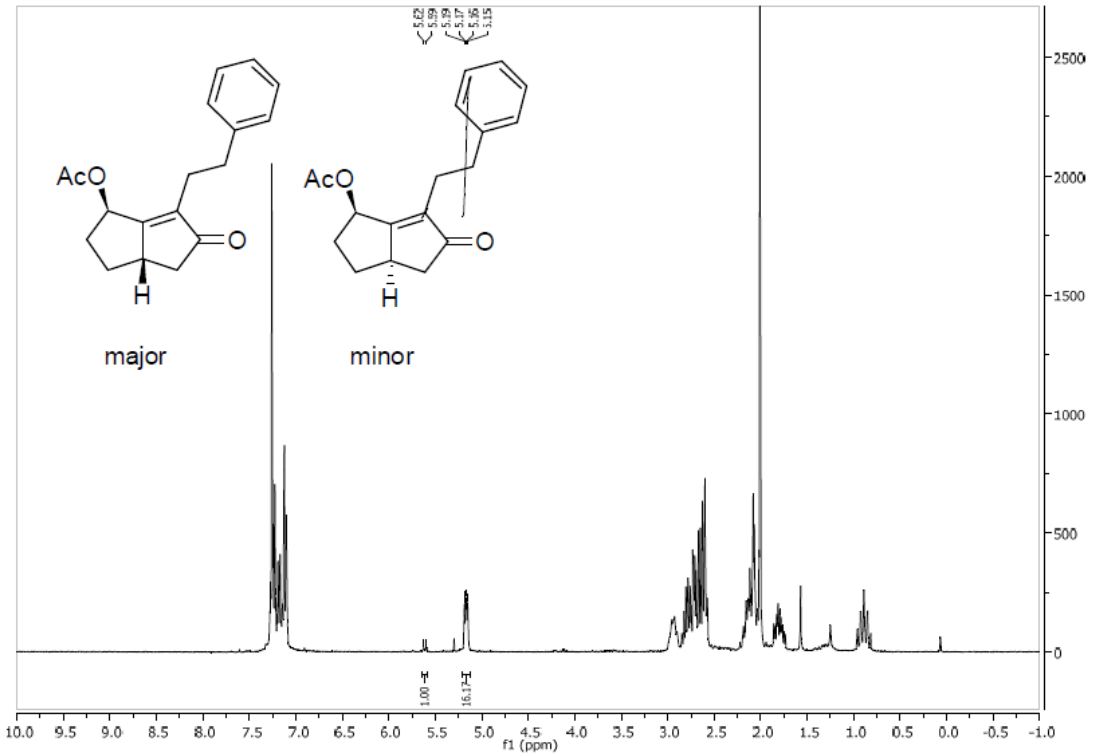
**P1**



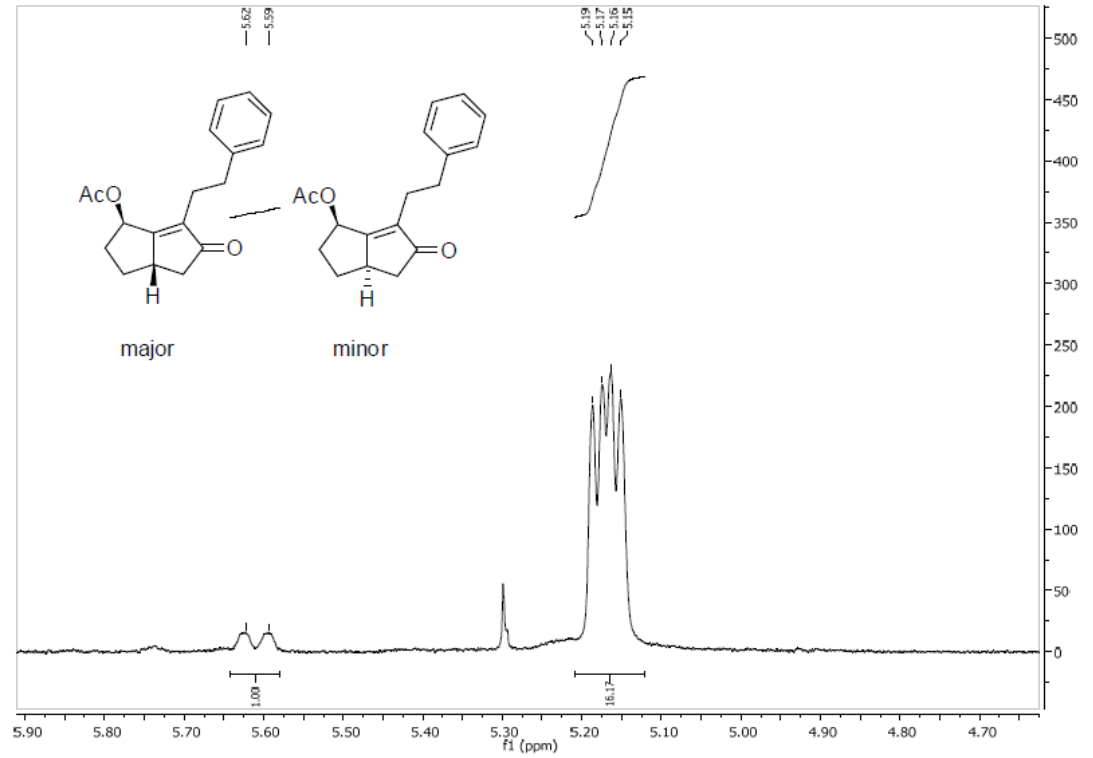

**P1**



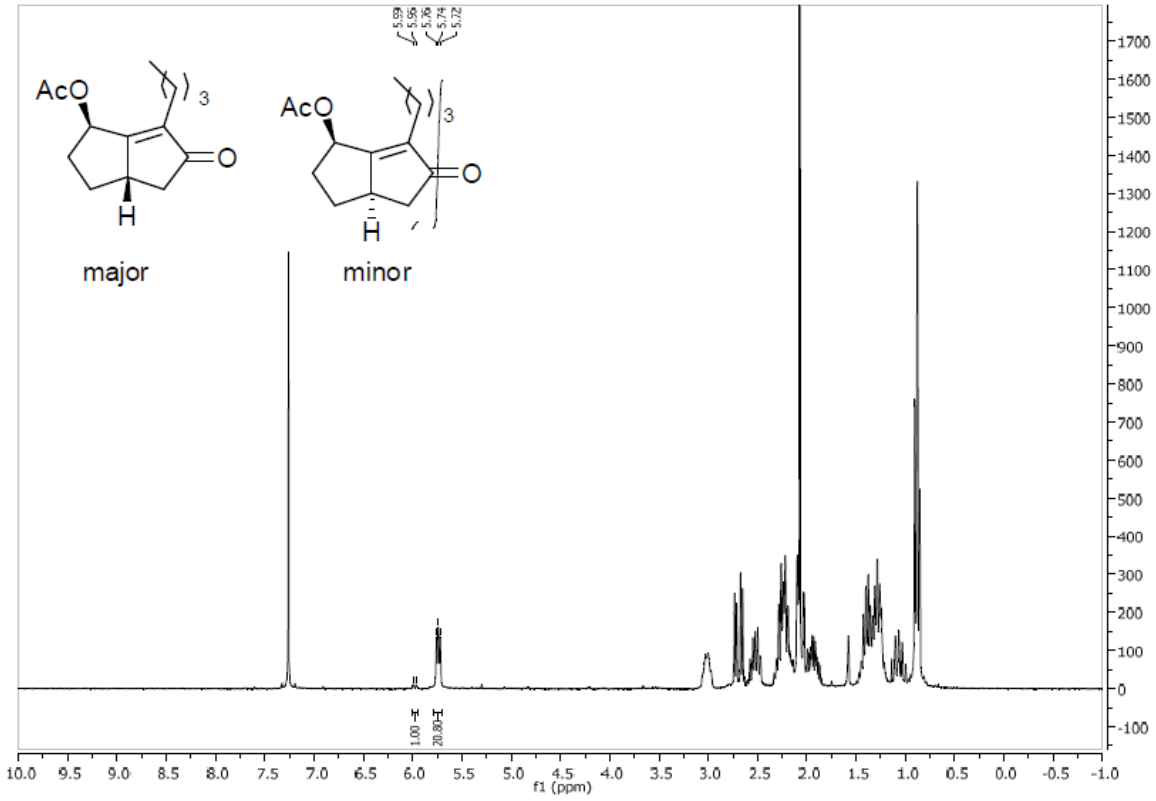
**P2**


AcO
O
H
major
AcO
O
H
minor
5.62
5.59
5.19
5.17
5.16
5.15
1.00
16.17
f1 (ppm)

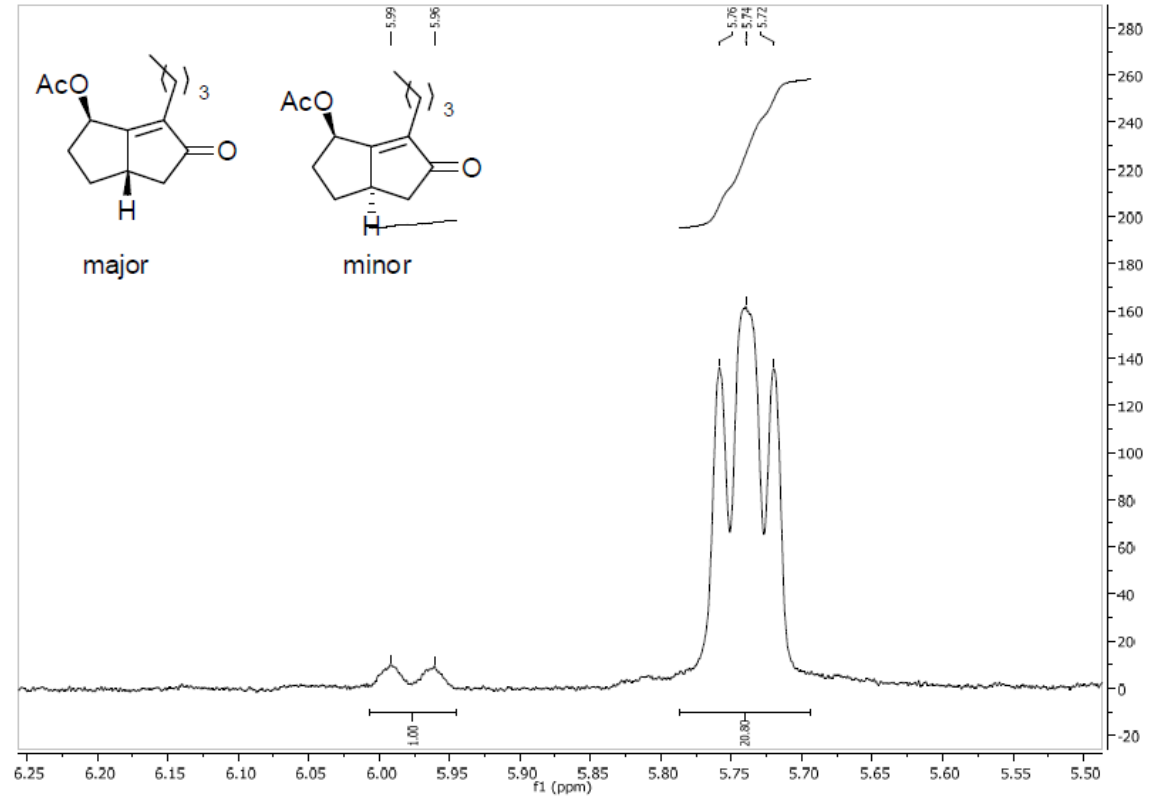
**P2**


AcO
O
H
major
AcO
O
H
minor
5.62
5.59
5.19
5.17
5.16
5.15
1.00
16.17
f1 (ppm)

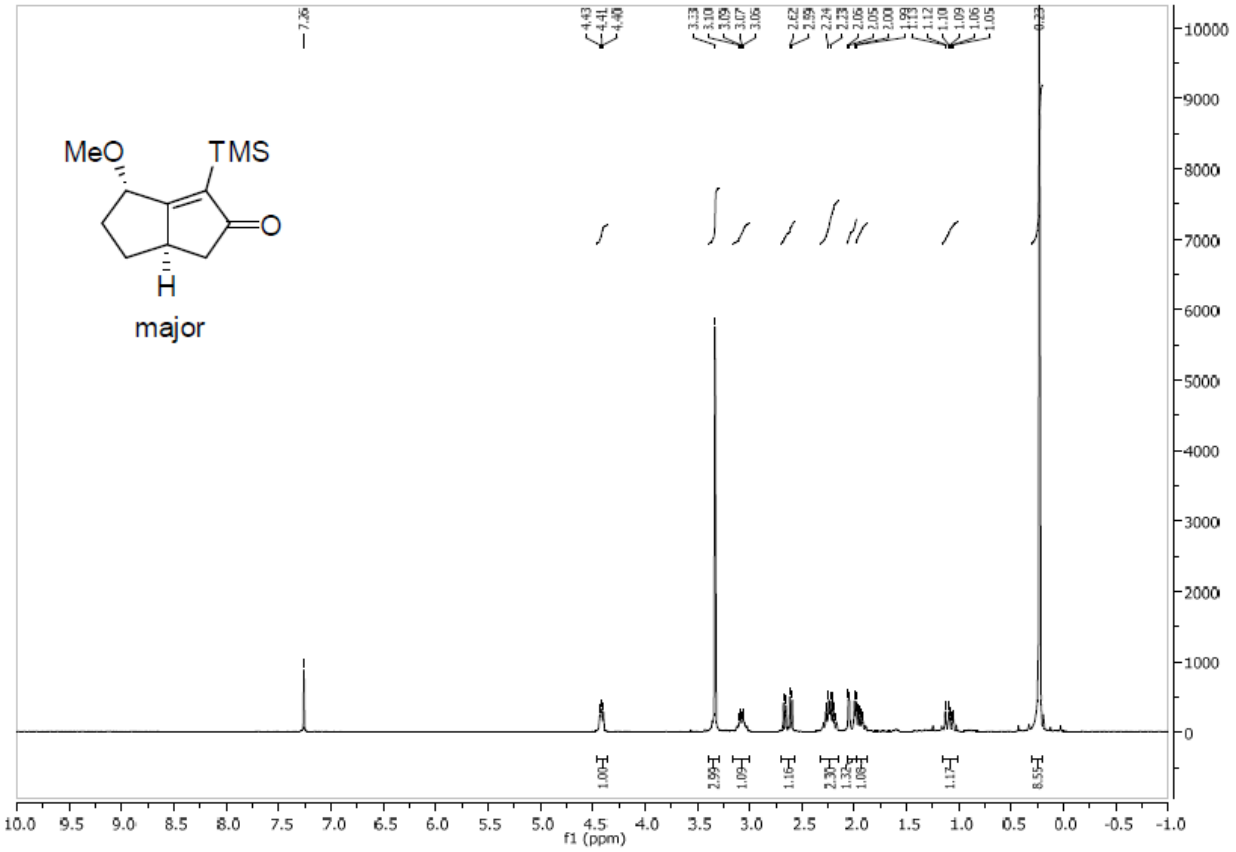
**P3**


AcO
3
O
H
major
AcO
3
O
H
minor
5.99
5.96
5.76
5.74
5.72
1.00
20.80
f1 (ppm)

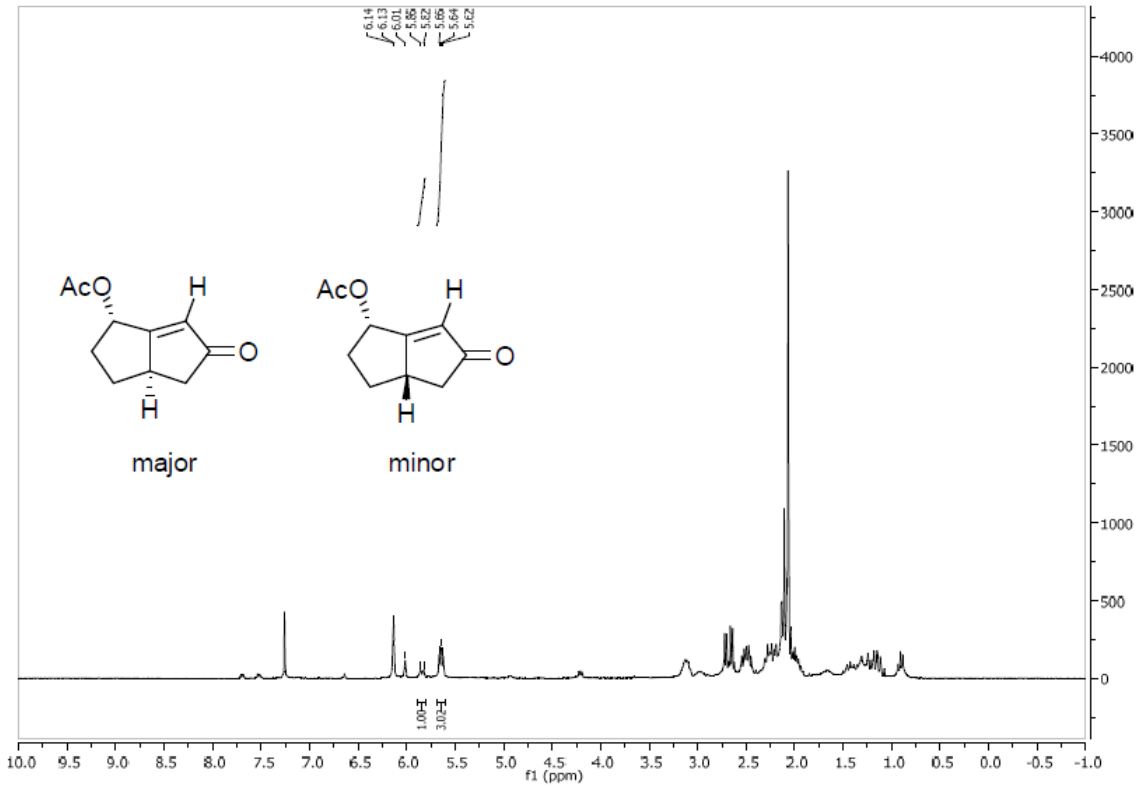
**P3**


AcO
3
O
H
major
AcO
3
O
H
minor
5.99
5.96
5.76
5.74
5.72
1.00
20.80
f1 (ppm)

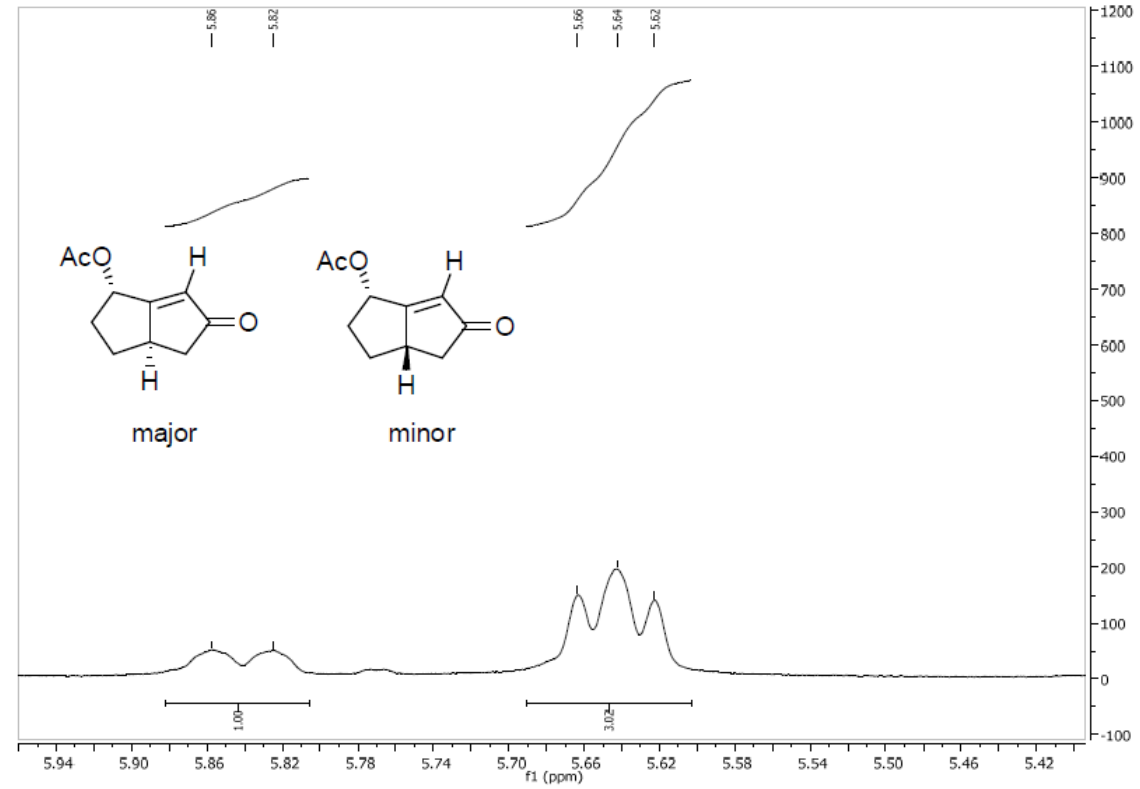
**P4**



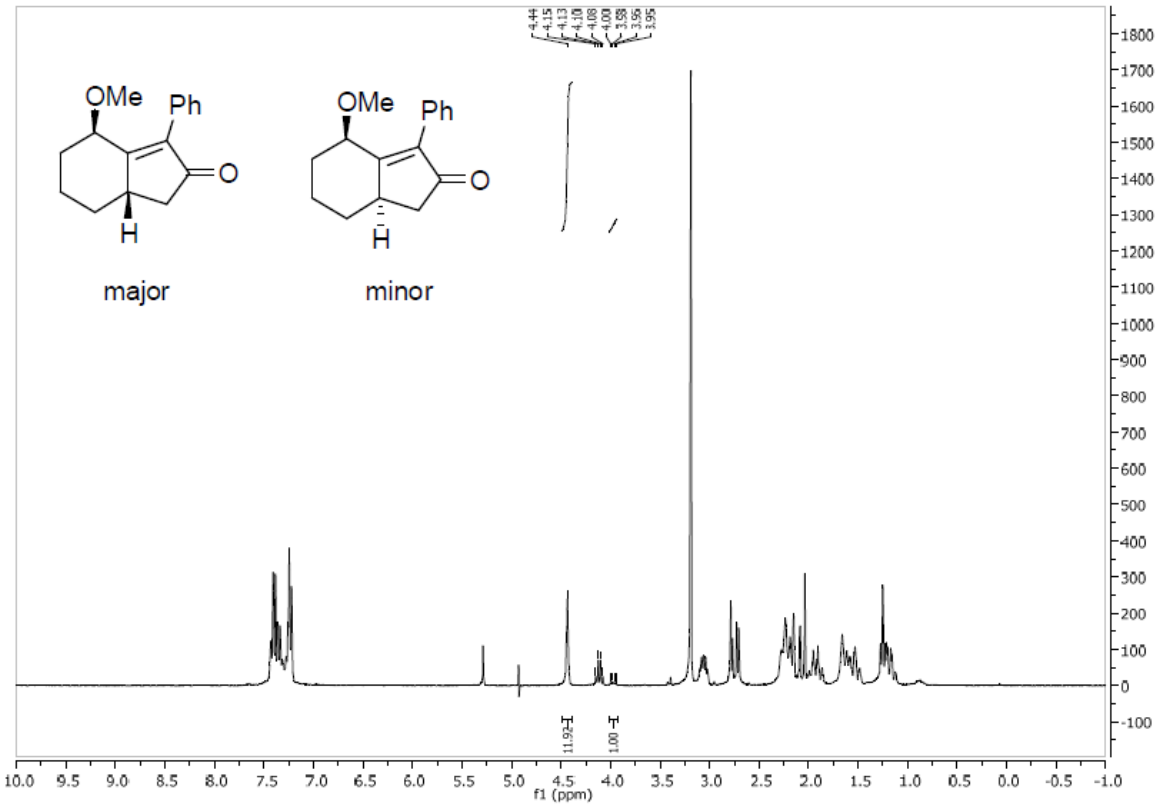
**P5**


6.14
6.13
6.01
5.86
5.82
5.66
5.64
5.62
AcO
H
O
H
major
AcO
H
O
H
minor
1.00
3.02
f1 (ppm)

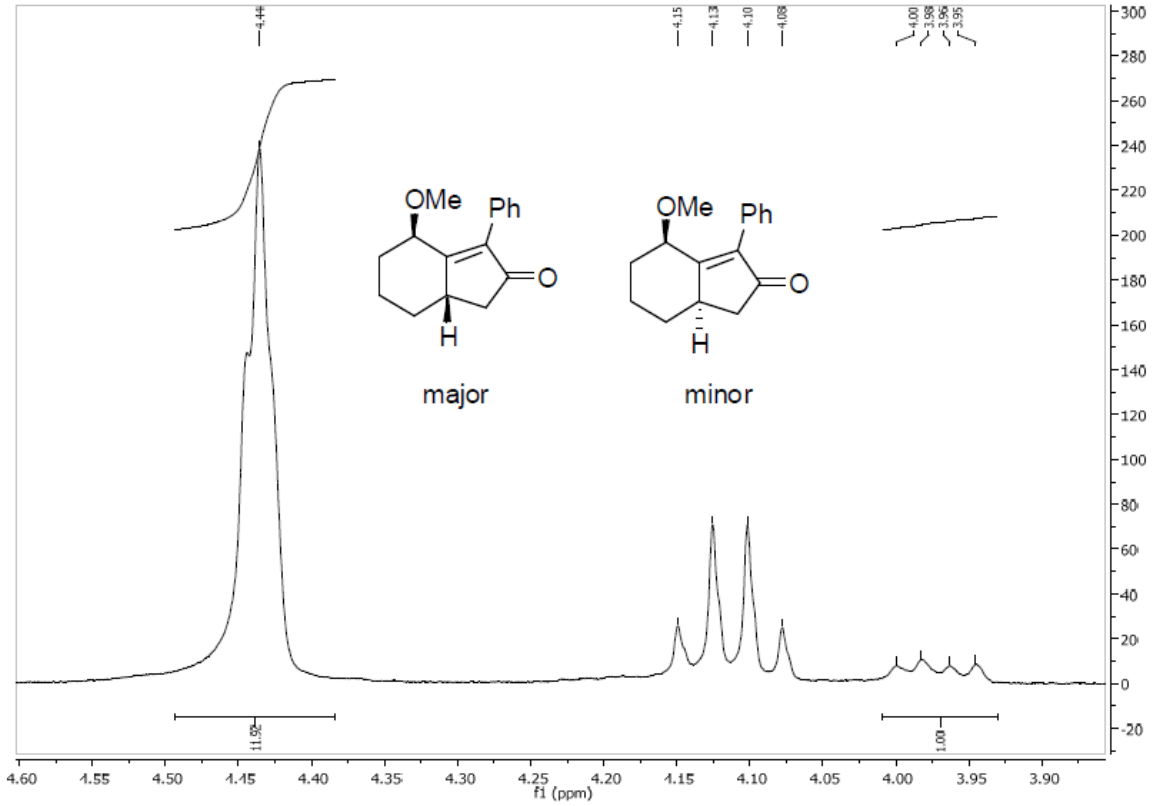
**P5**


5.86
5.82
5.66
5.64
5.62
AcO
H
O
H
major
AcO
H
O
H
minor
1.00
3.02
f1 (ppm)

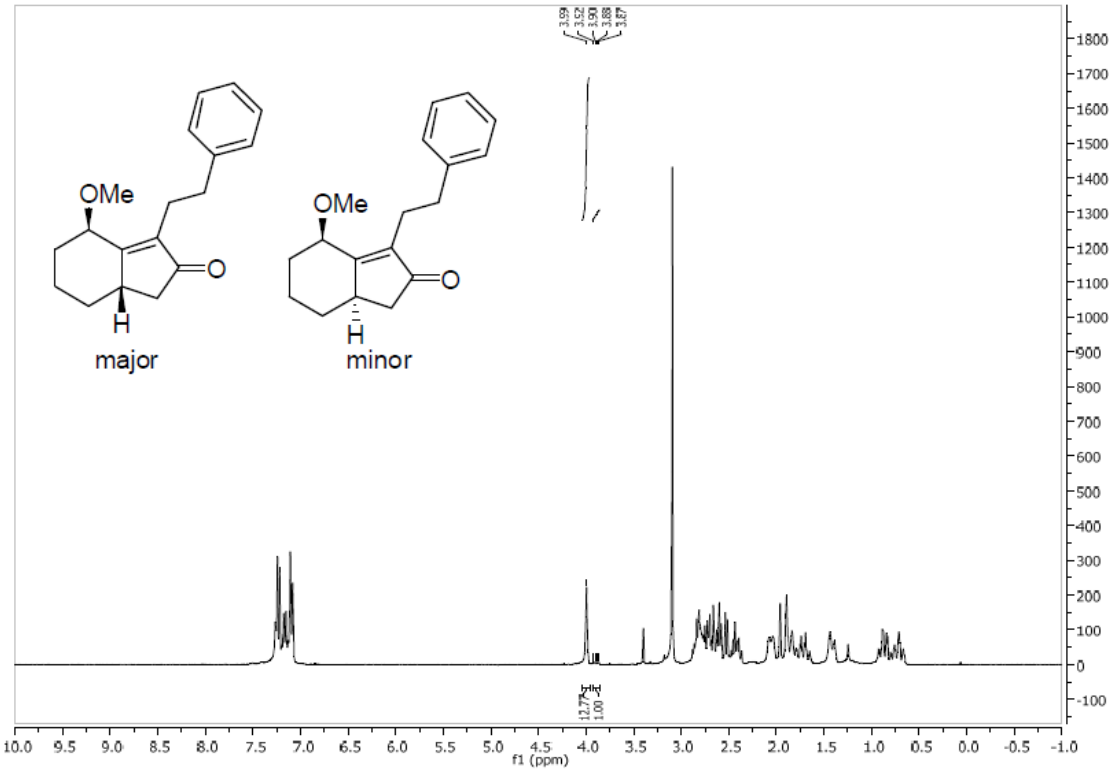
**P6**


OMe
Ph
O
H
major
OMe
Ph
O
H
minor
f1 (ppm)

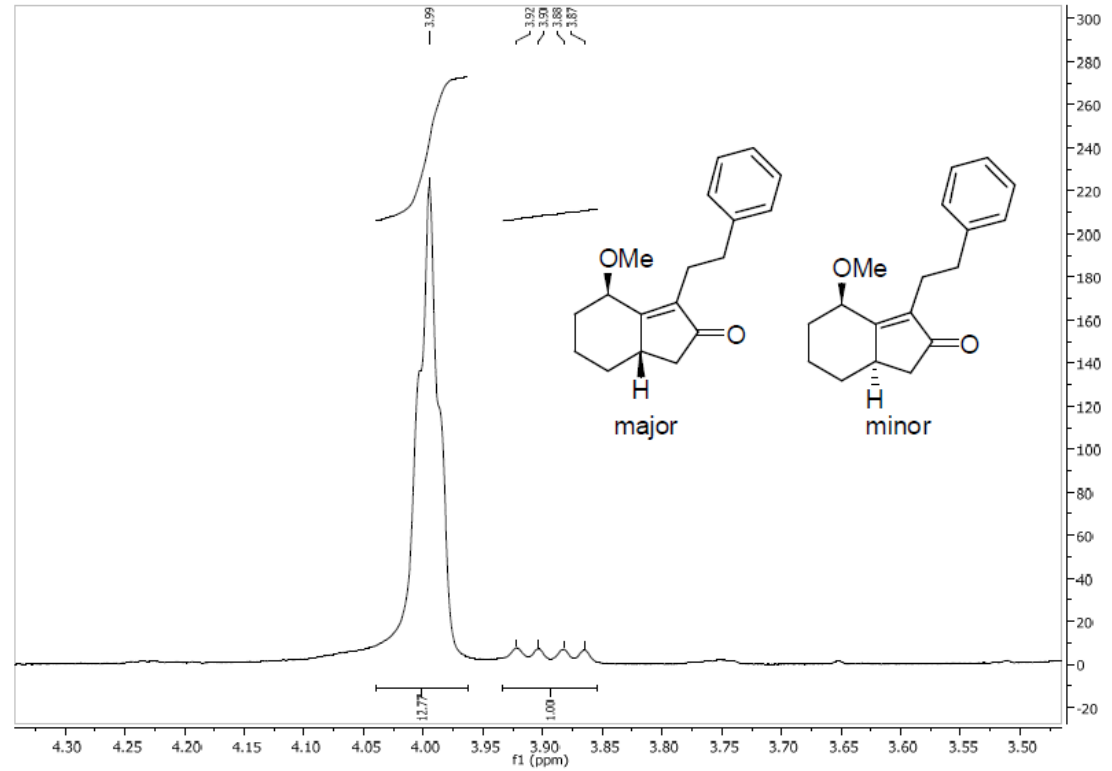
**P6**


OMe
Ph
O
H
major
OMe
Ph
O
H
minor
f1 (ppm)

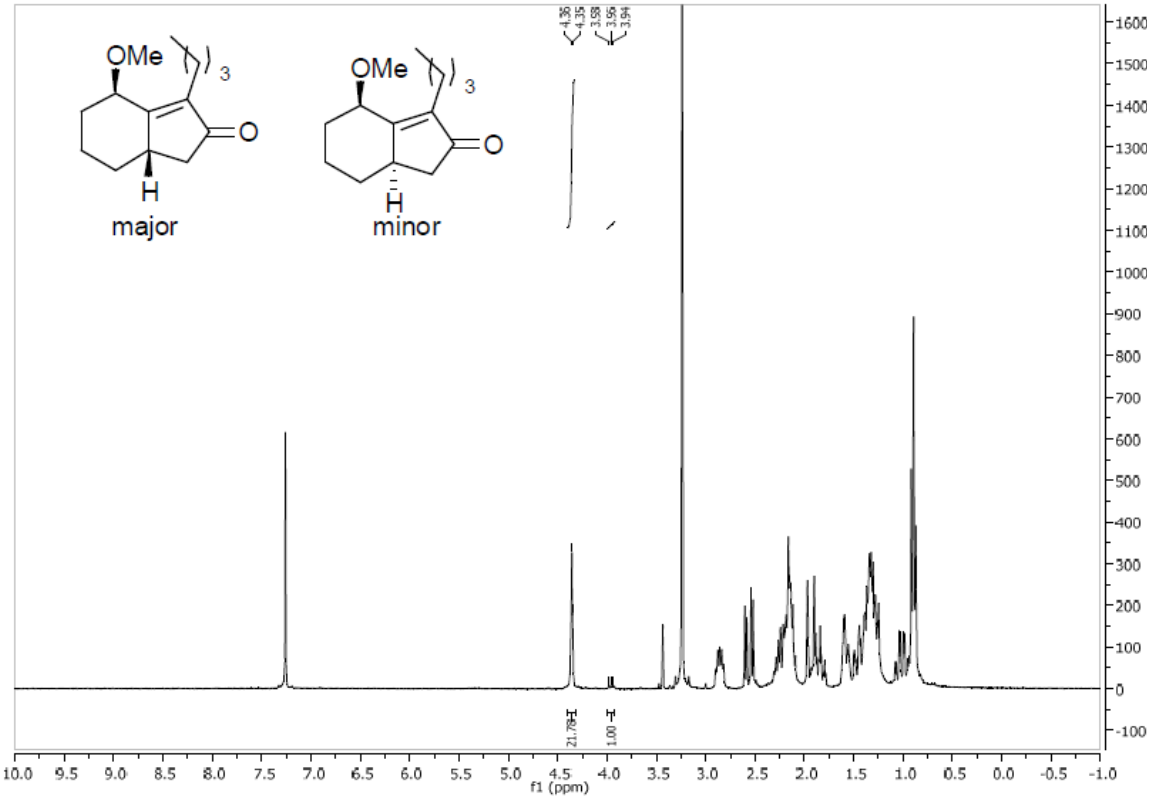
**P7**


OMe
O
H
major
OMe
O
H
minor
f1 (ppm)

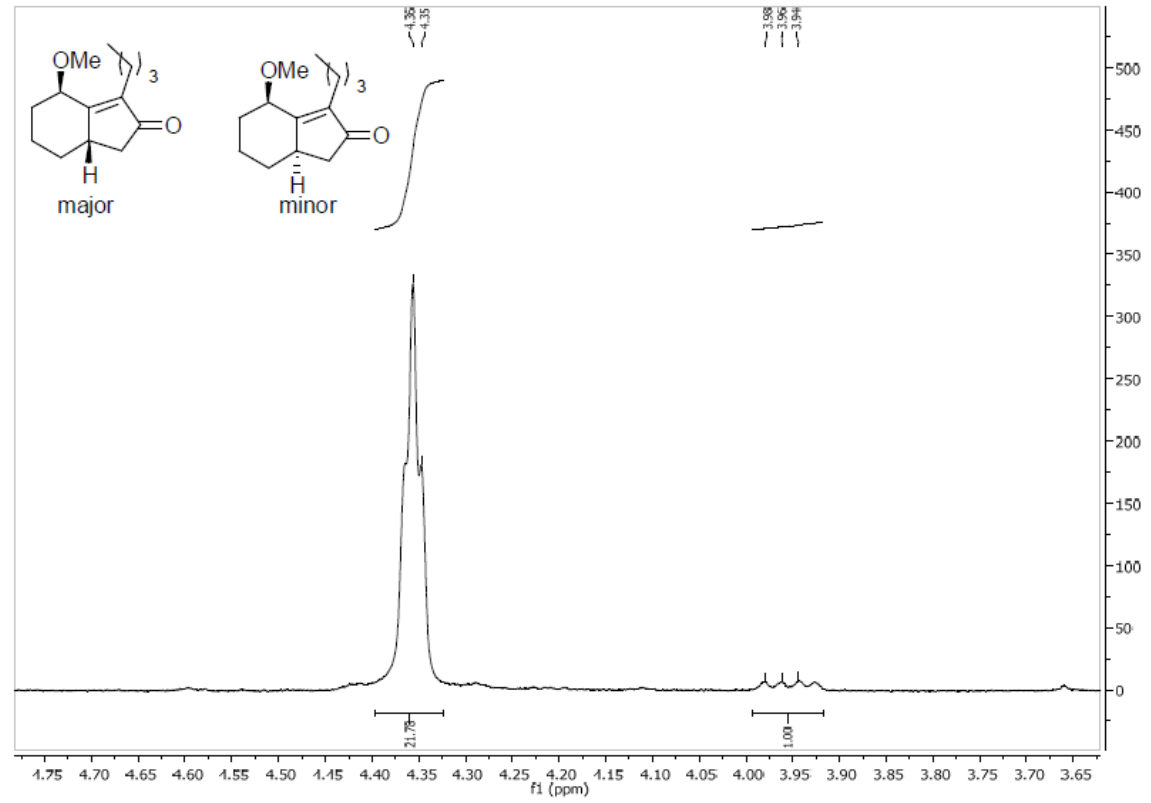
**P7**


3.99
3.92
3.91
3.88
3.87
OMe
O
H
major
OMe
O
H
minor
12.77
1.00
f1 (ppm)

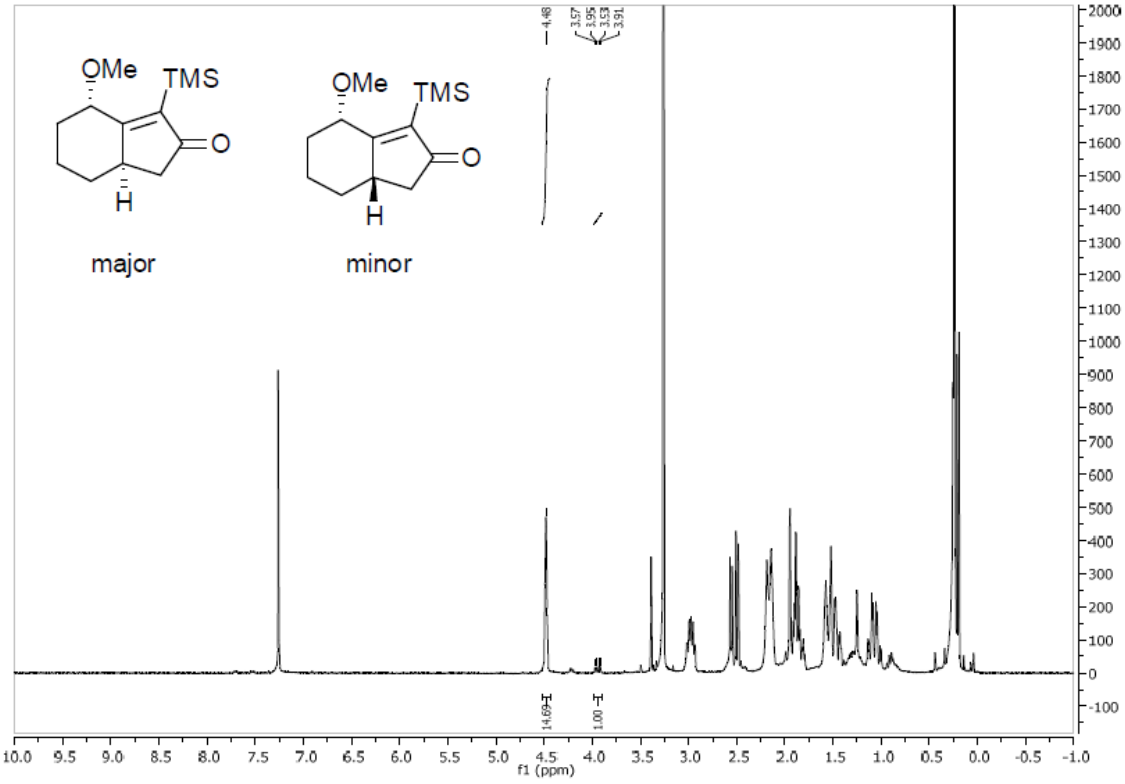
**P8**


OMe
3
O
H
major
OMe
3
O
H
minor
4.36
4.35
3.58
3.55
3.54
21.78
1.00
f1 (ppm)

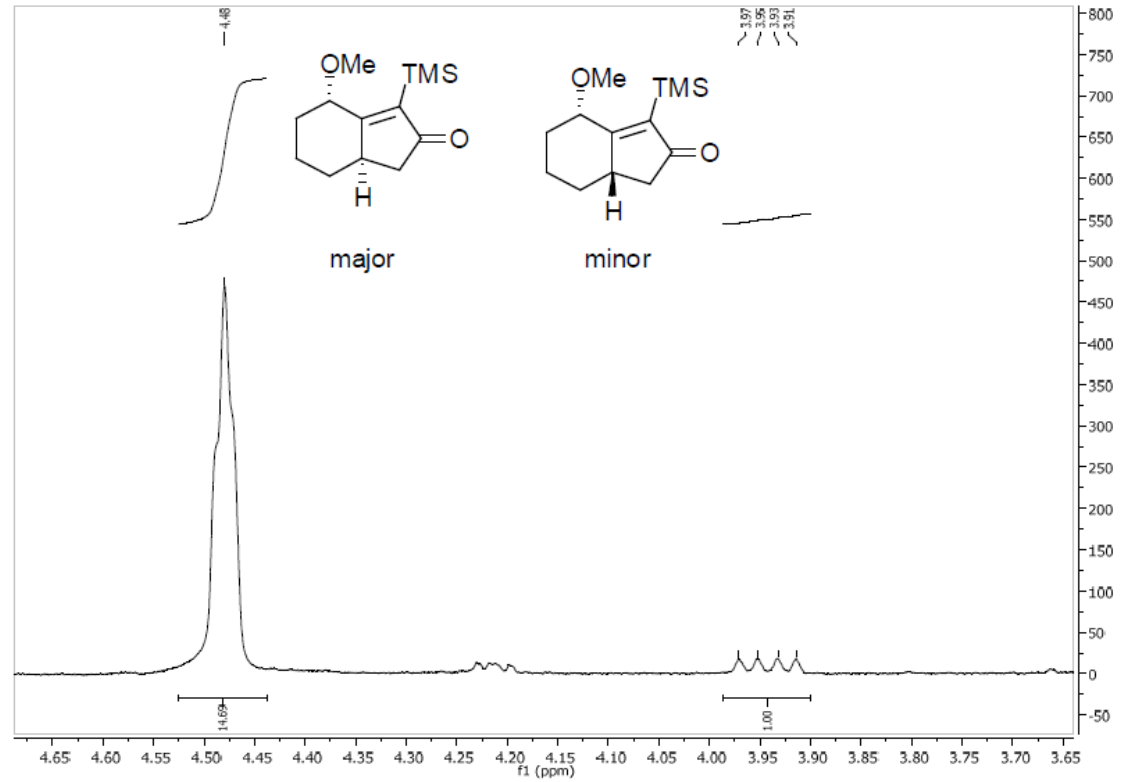
**P8**


OMe
3
O
H
major
OMe
3
O
H
minor
4.36
4.35
3.98
3.96
3.94
21.78
1.00
f1 (ppm)

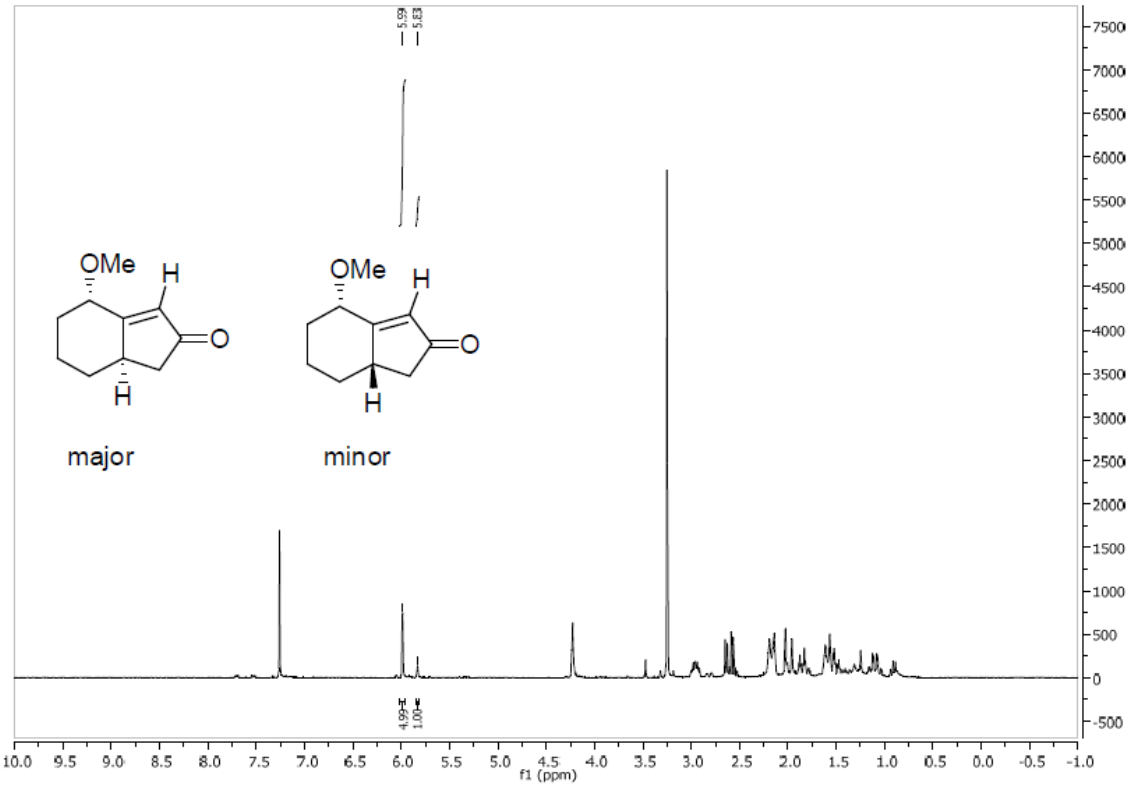
**P9**


OMe
TMS
O
H
major
OMe
TMS
O
H
minor
4.48
3.97
3.96
3.93
3.91
14.69
1.00
f1 (ppm)

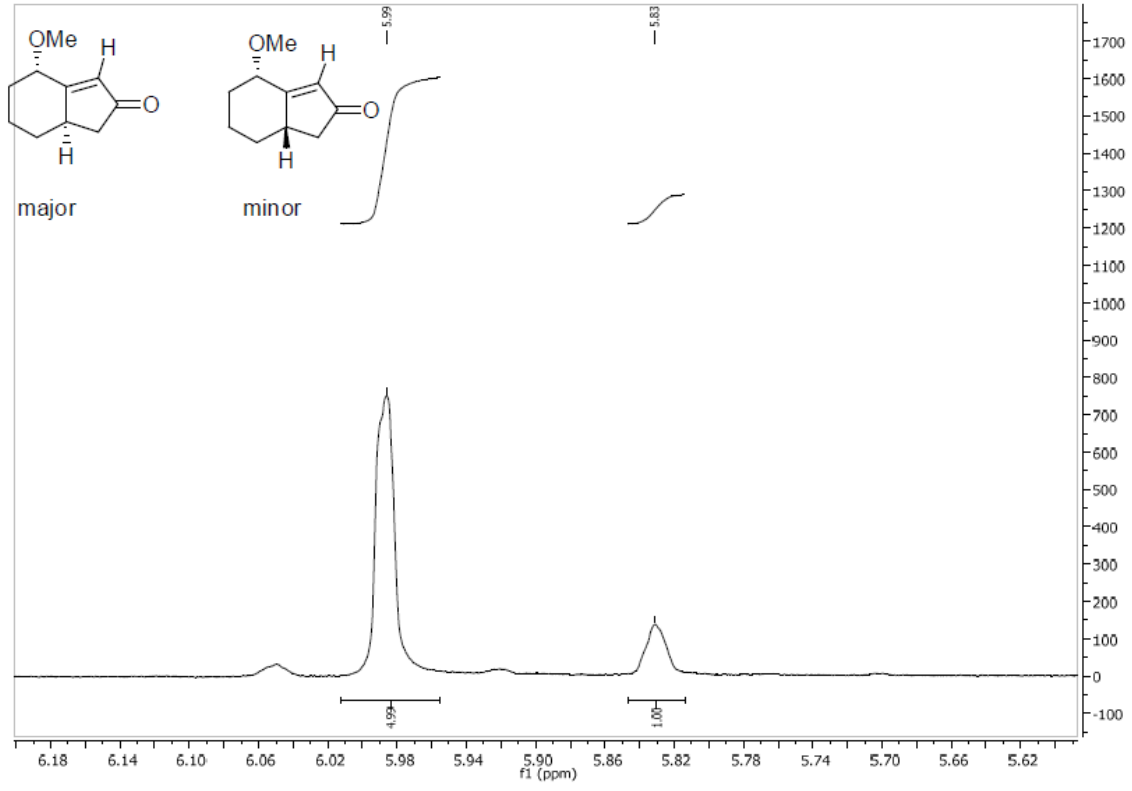
**P9**


4.48
3.97
3.96
3.93
3.91
OMe
TMS
O
H
major
OMe
TMS
O
H
minor
14.69
1.00
f1 (ppm)

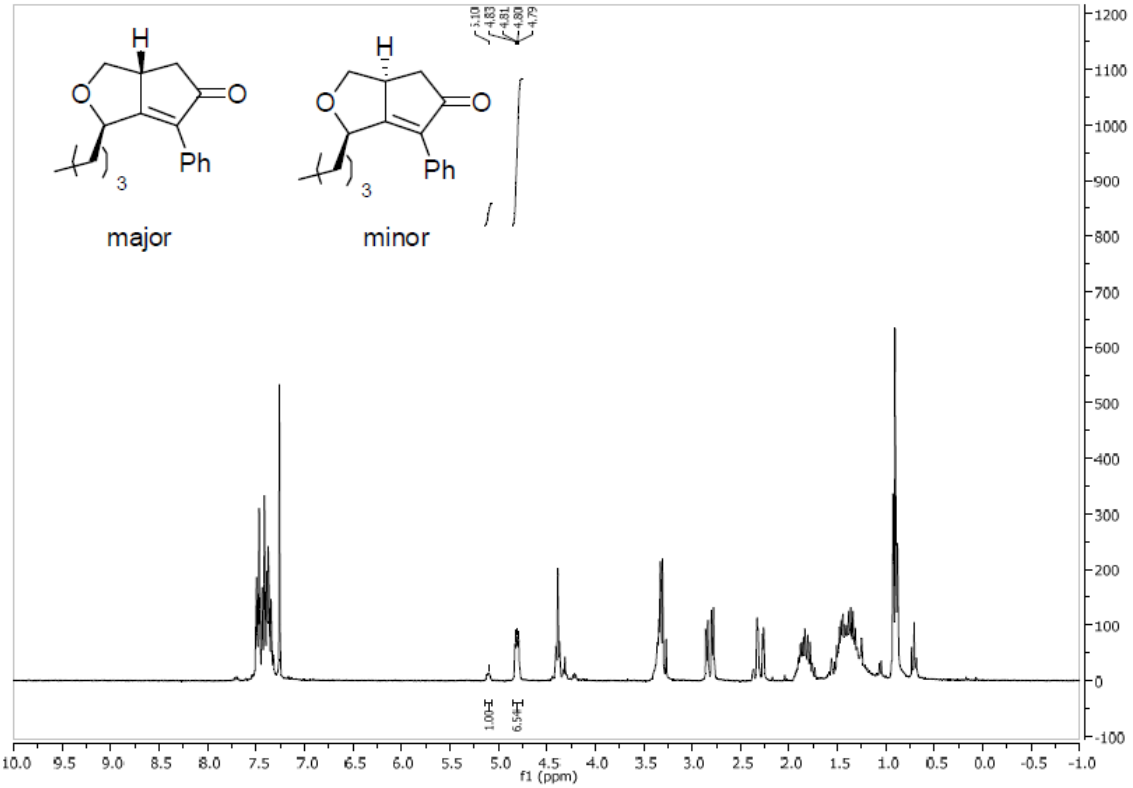
**P10**


OMe
H
O
H
major
OMe
H
O
H
minor
5.99
5.83
4.99
1.00
f1 (ppm)

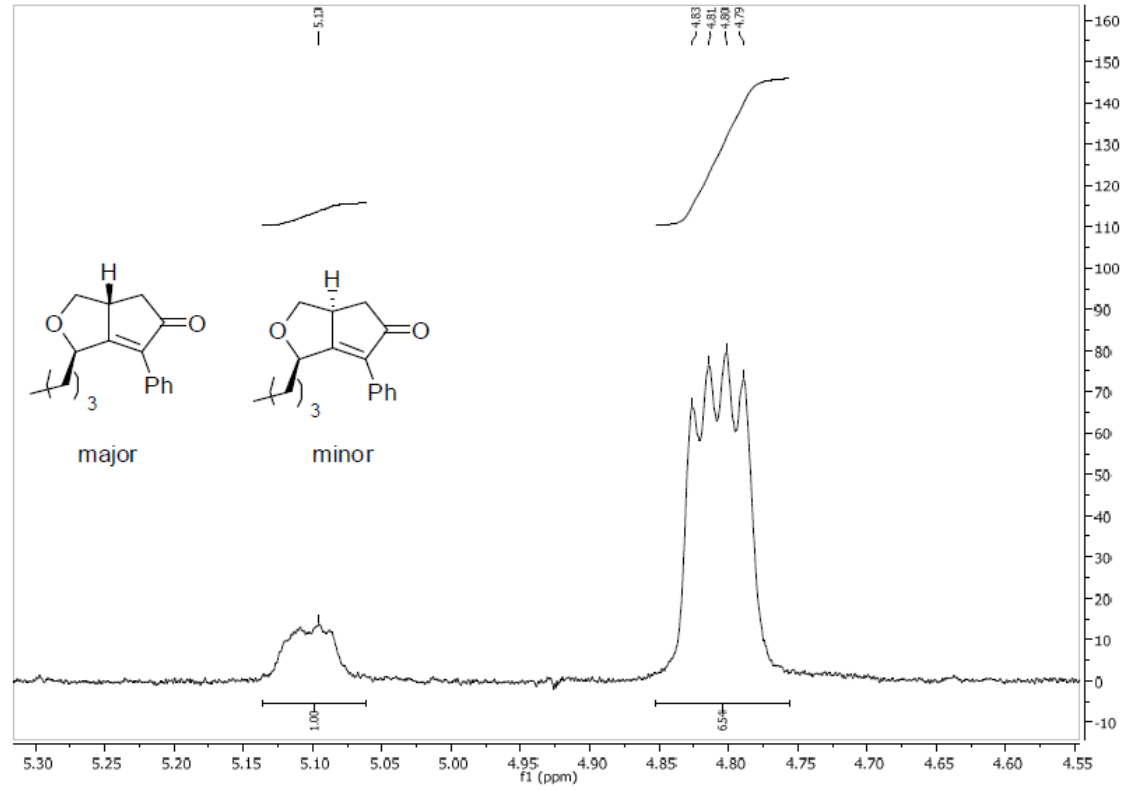
**P10**


OMe
H
O
H
major
OMe
H
O
H
minor
5.99
5.83
4.99
1.00
f1 (ppm)

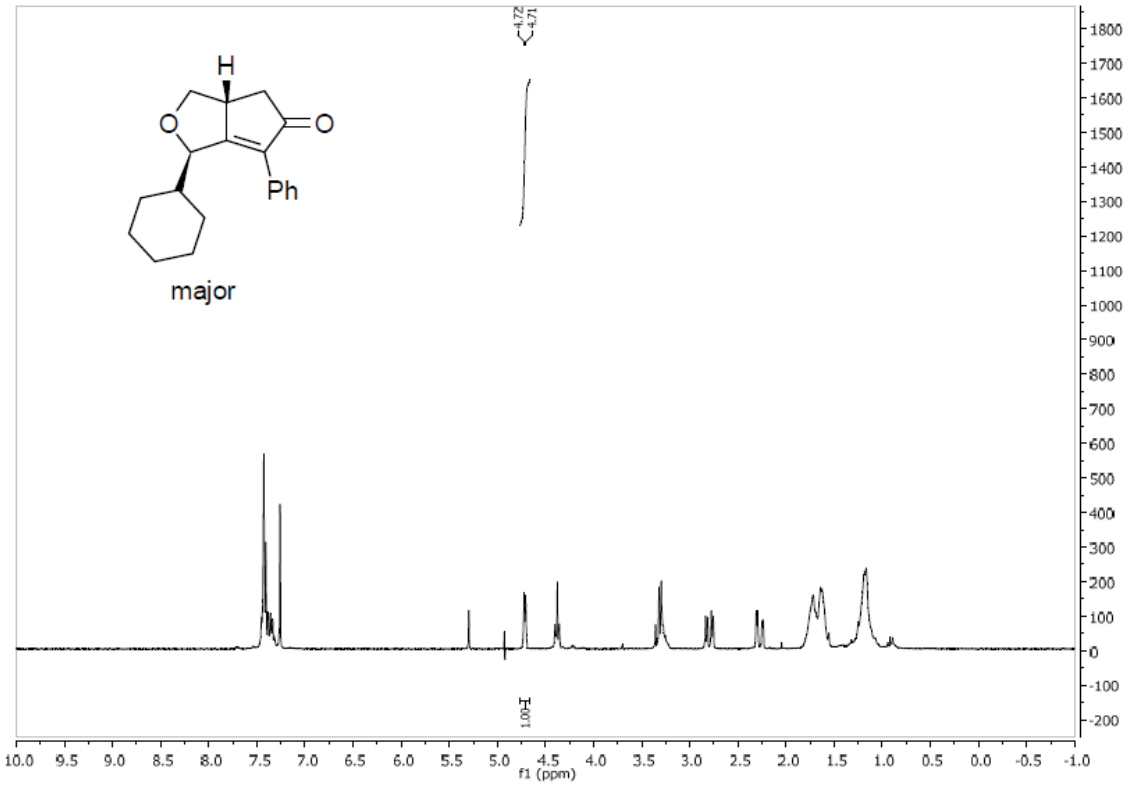
**P11**



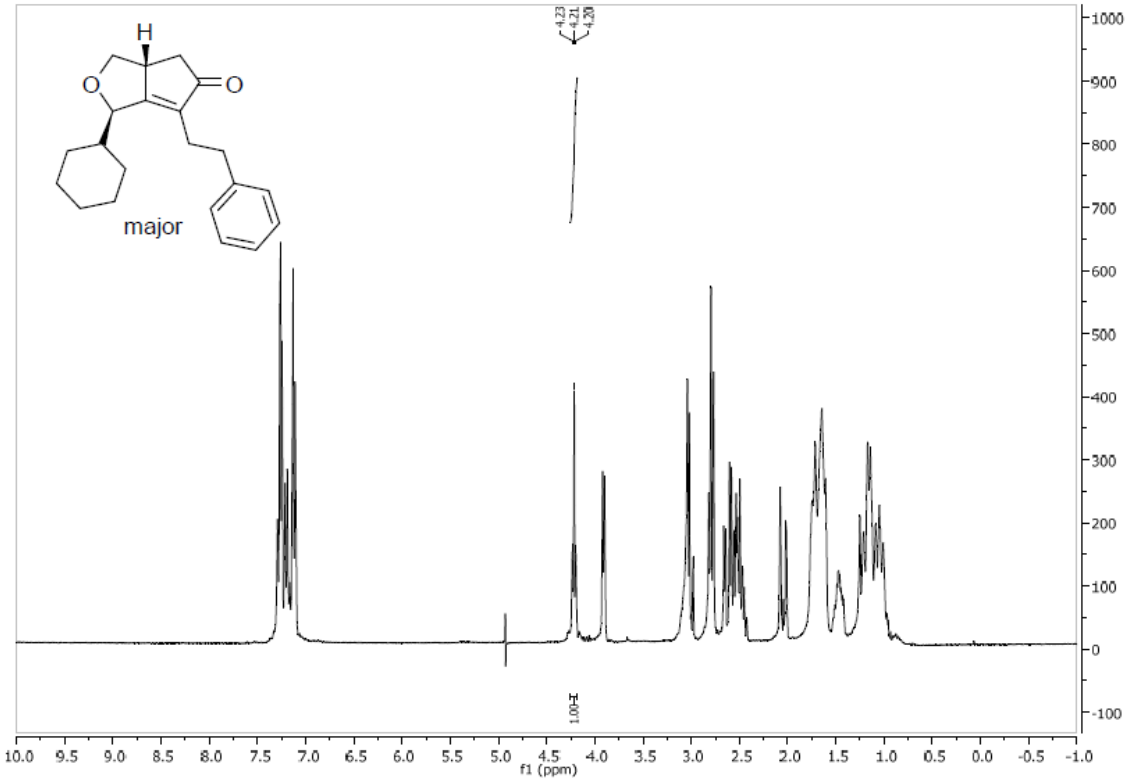

**P11**



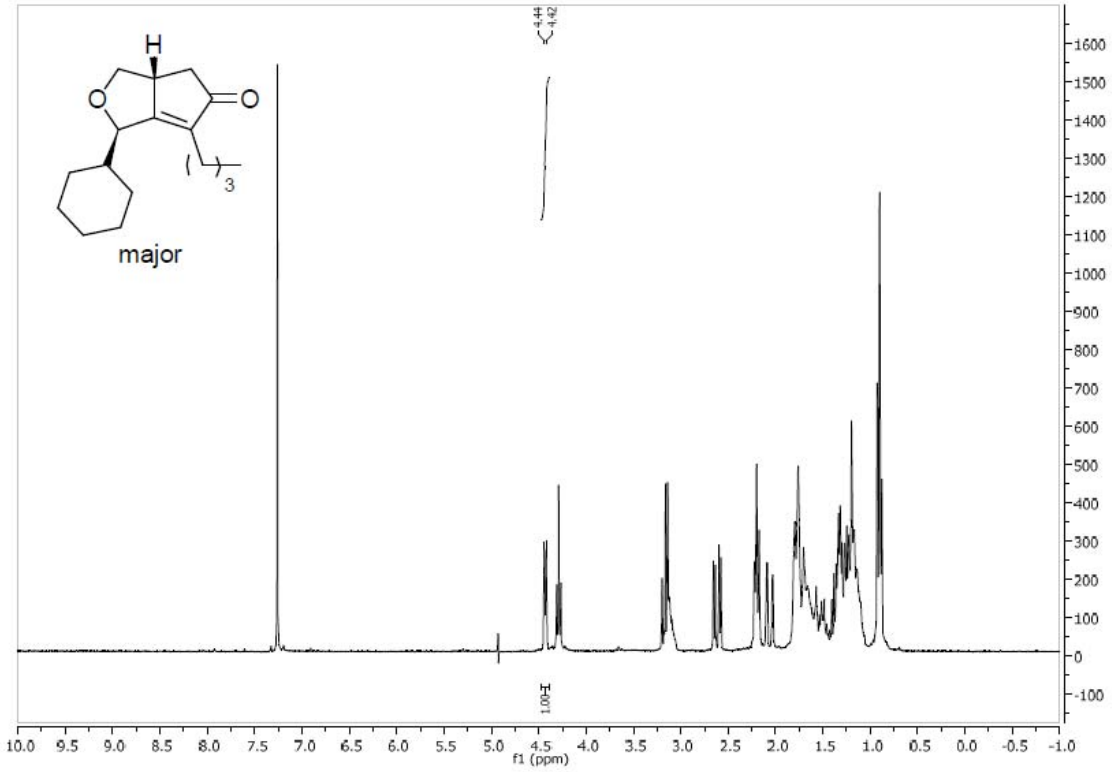
**P12**



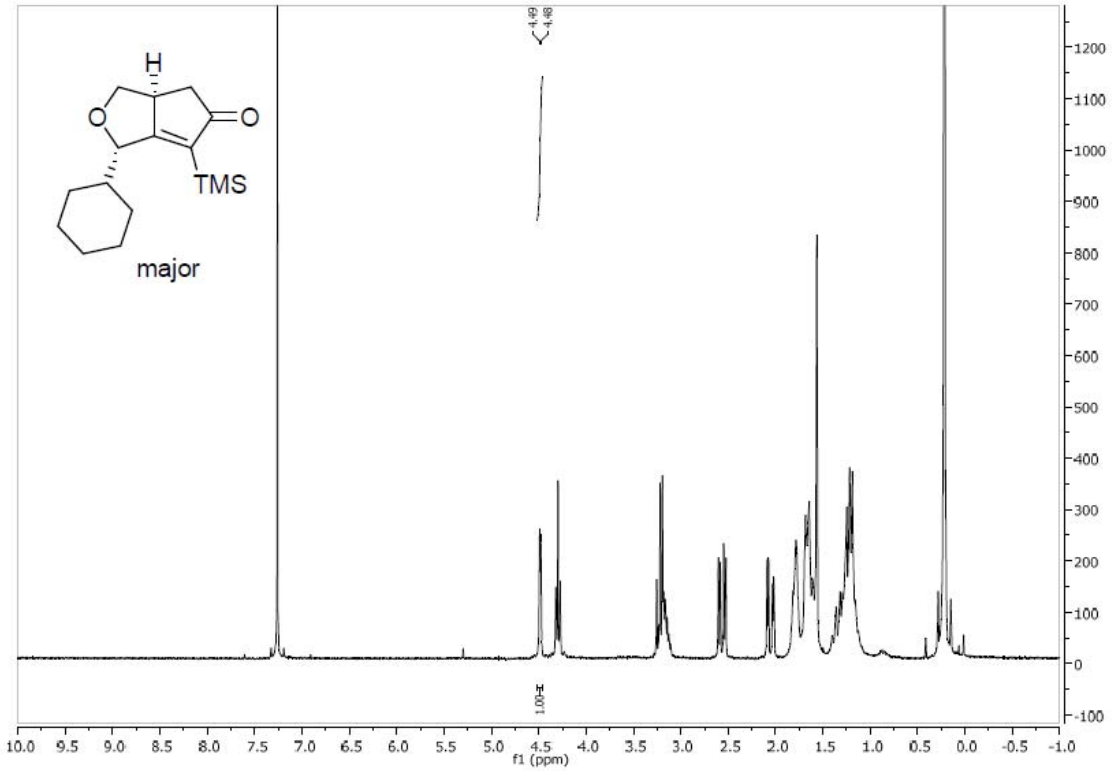

**P13**



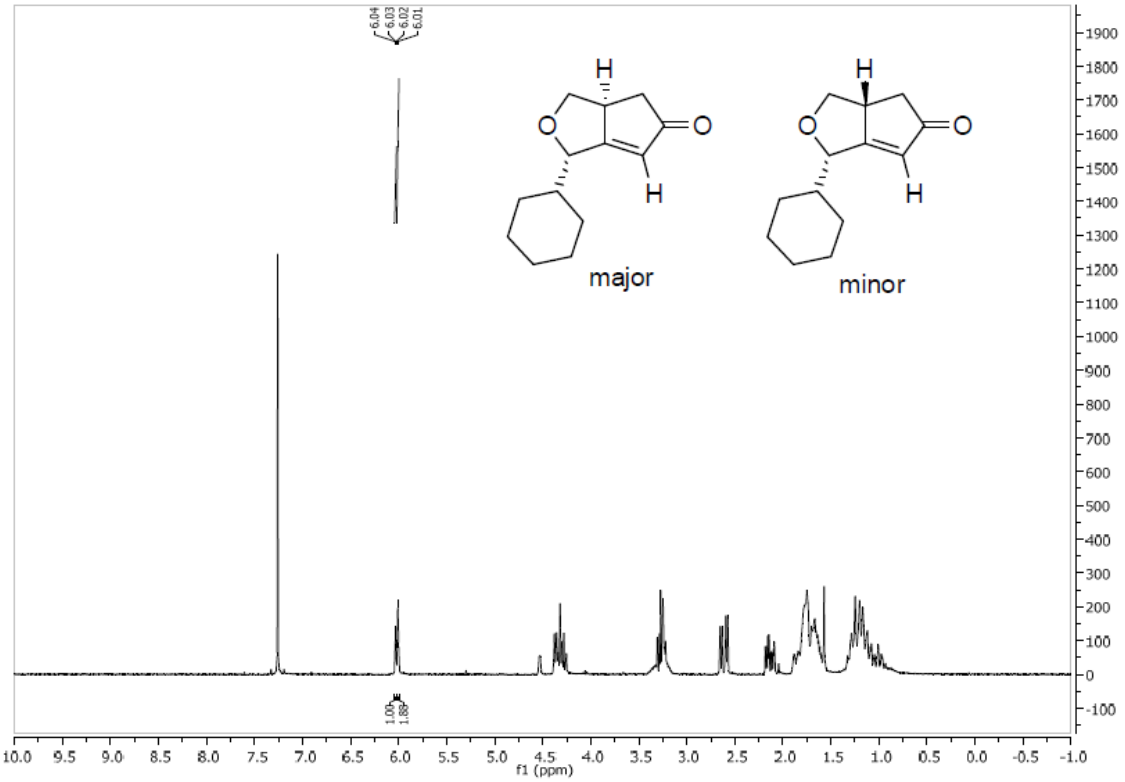
**P14**


H
O
O
3
major
4.44
4.42
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

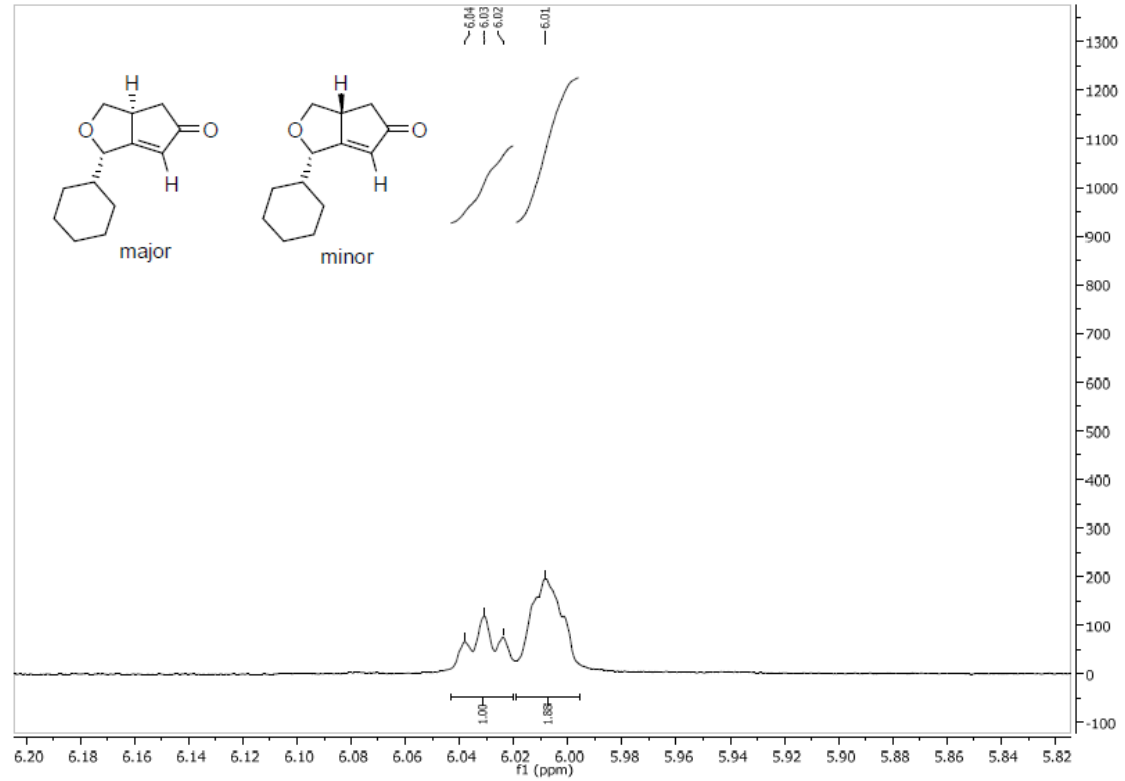
**P15**


H
O
O
TMS
major
4.49
4.48
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100

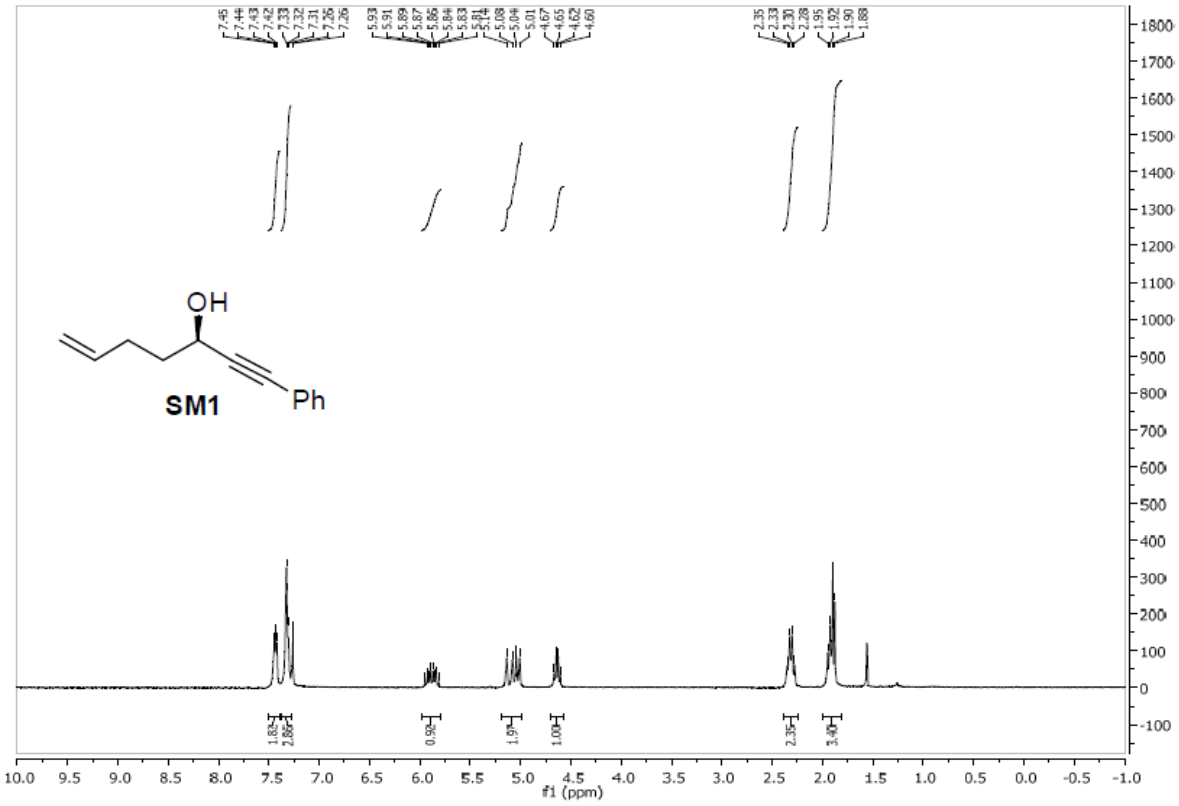
**P16**

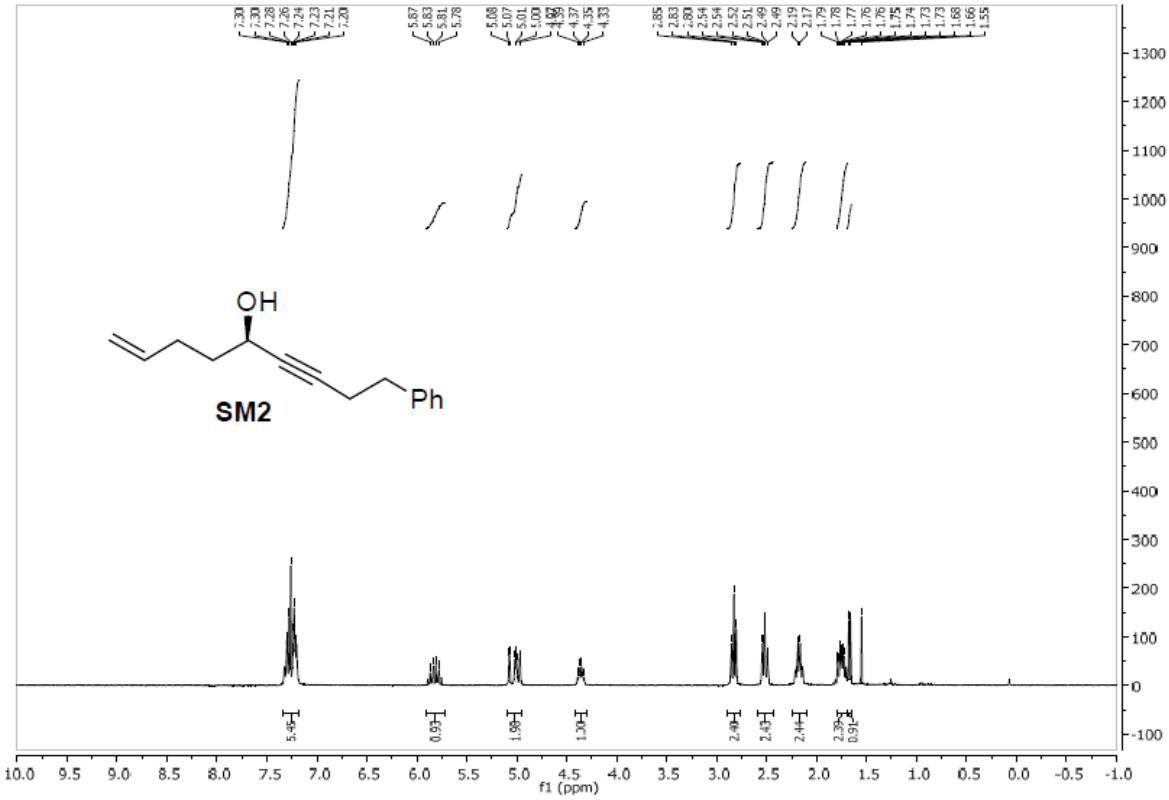

6.04
6.03
6.02
6.01
major
minor
1.00
1.89
f1 (ppm)

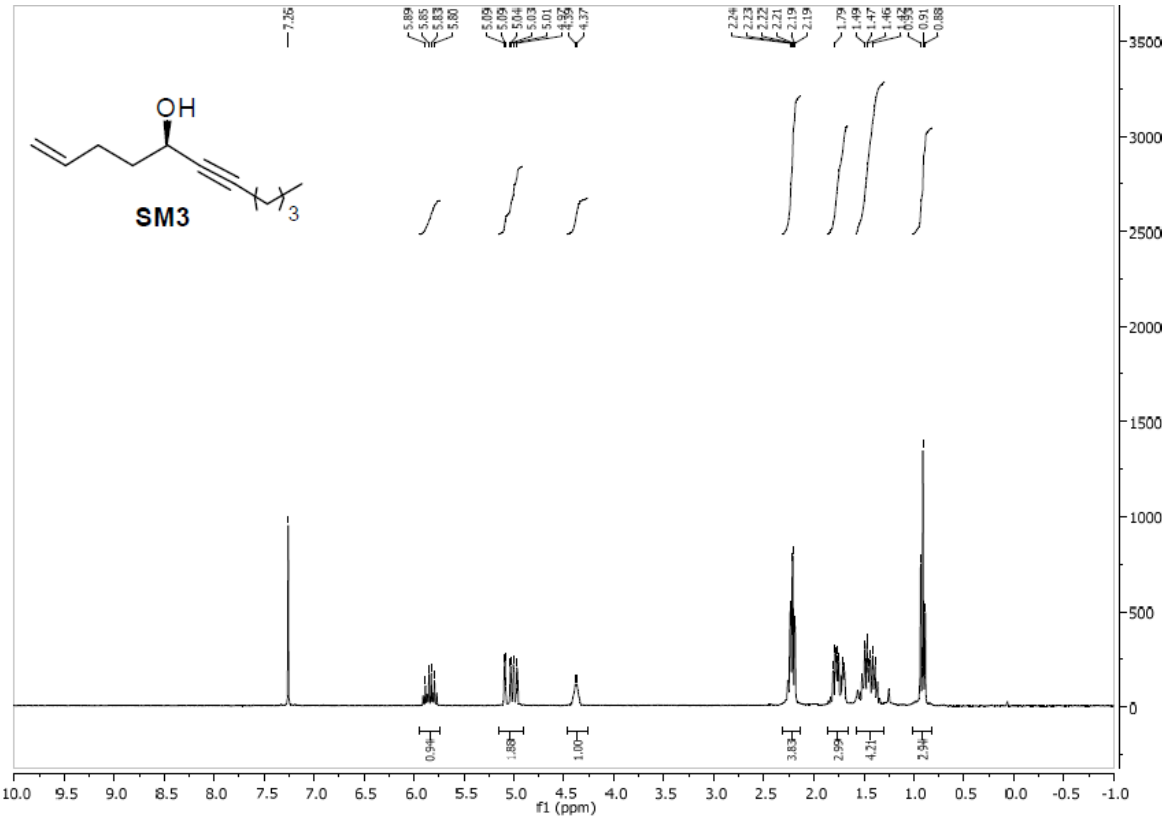
**P16**

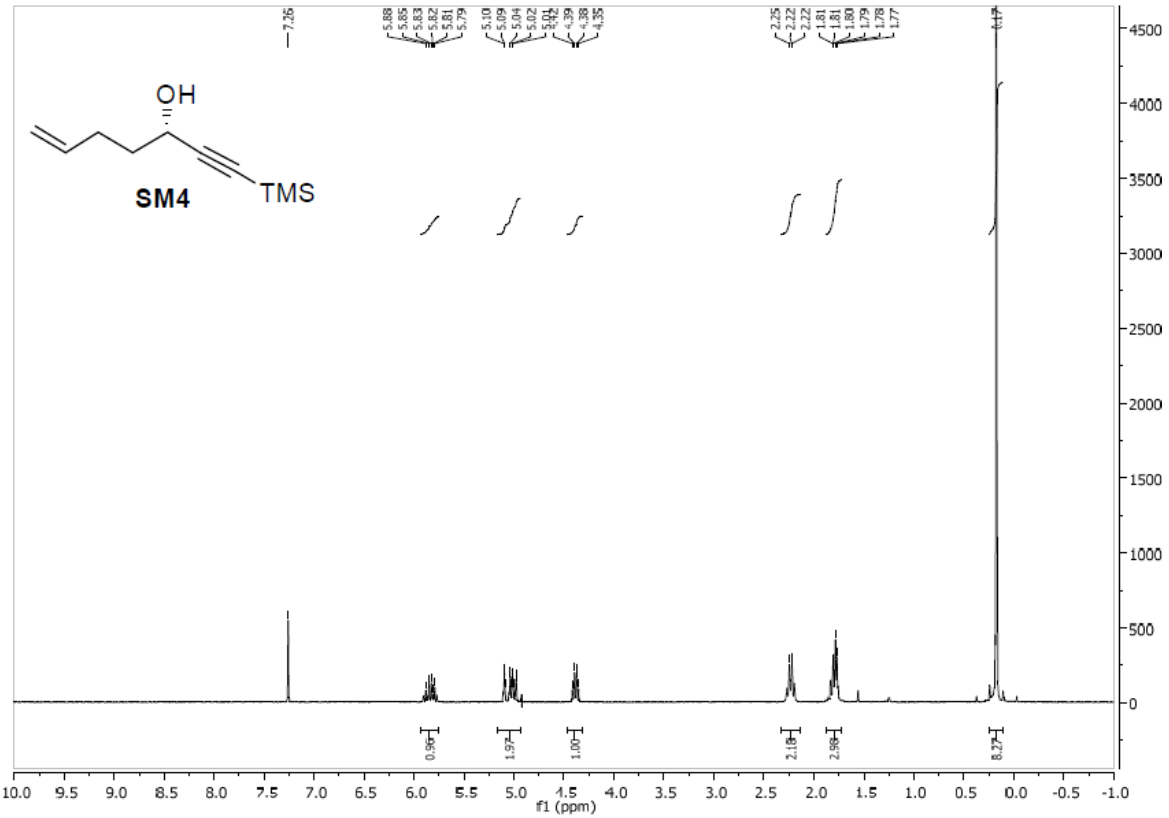

6.04
6.03
6.02
6.01
major
minor
1.00
1.89
f1 (ppm)

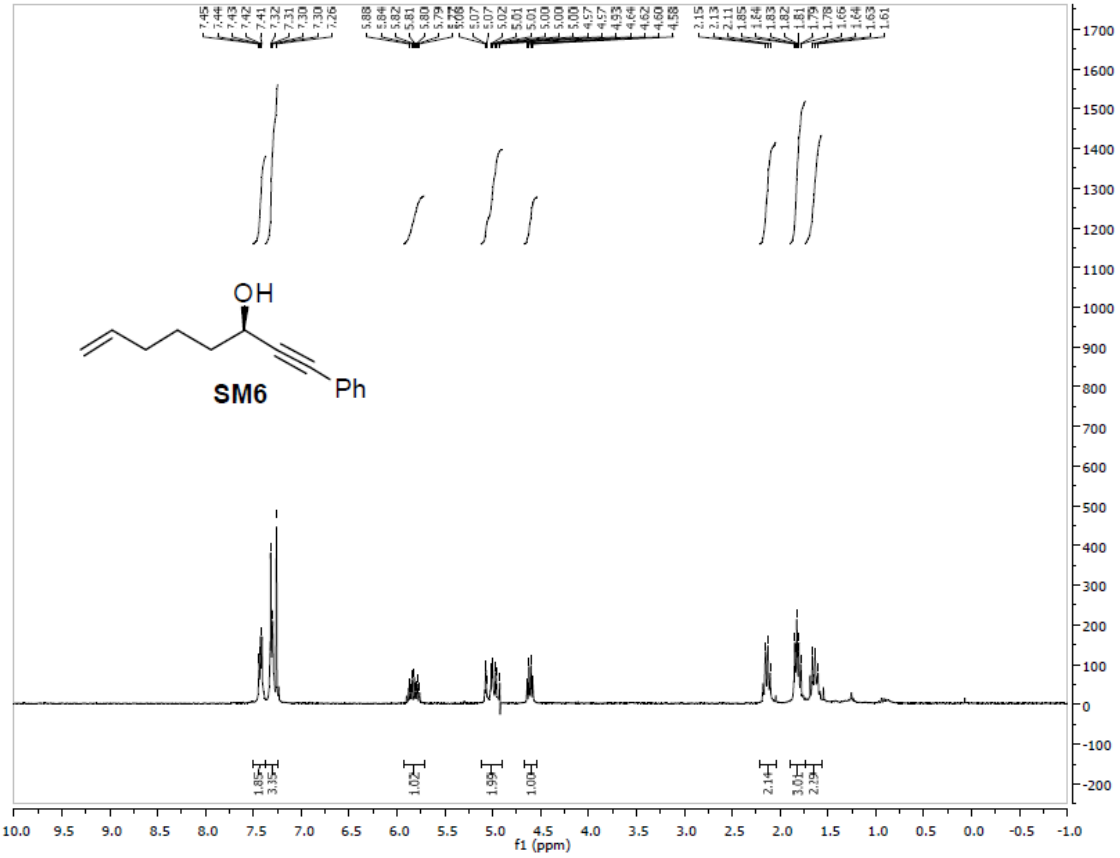
## XI. $^{1}$H NMR of SM 1-15.

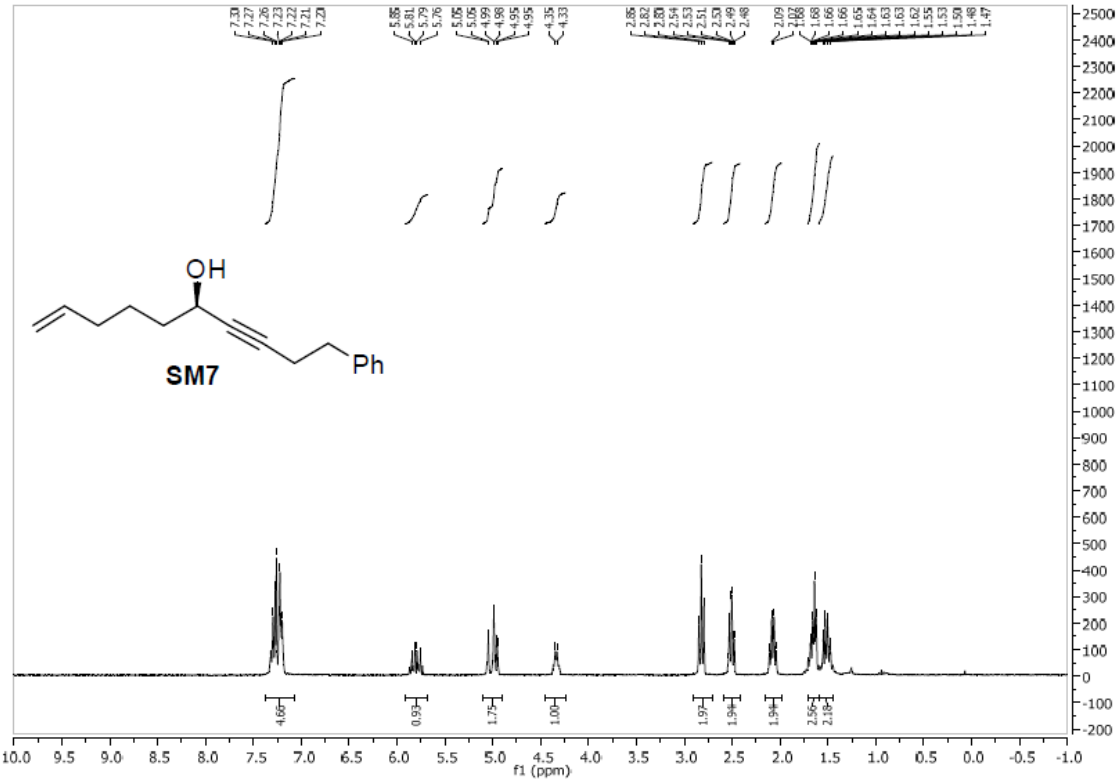


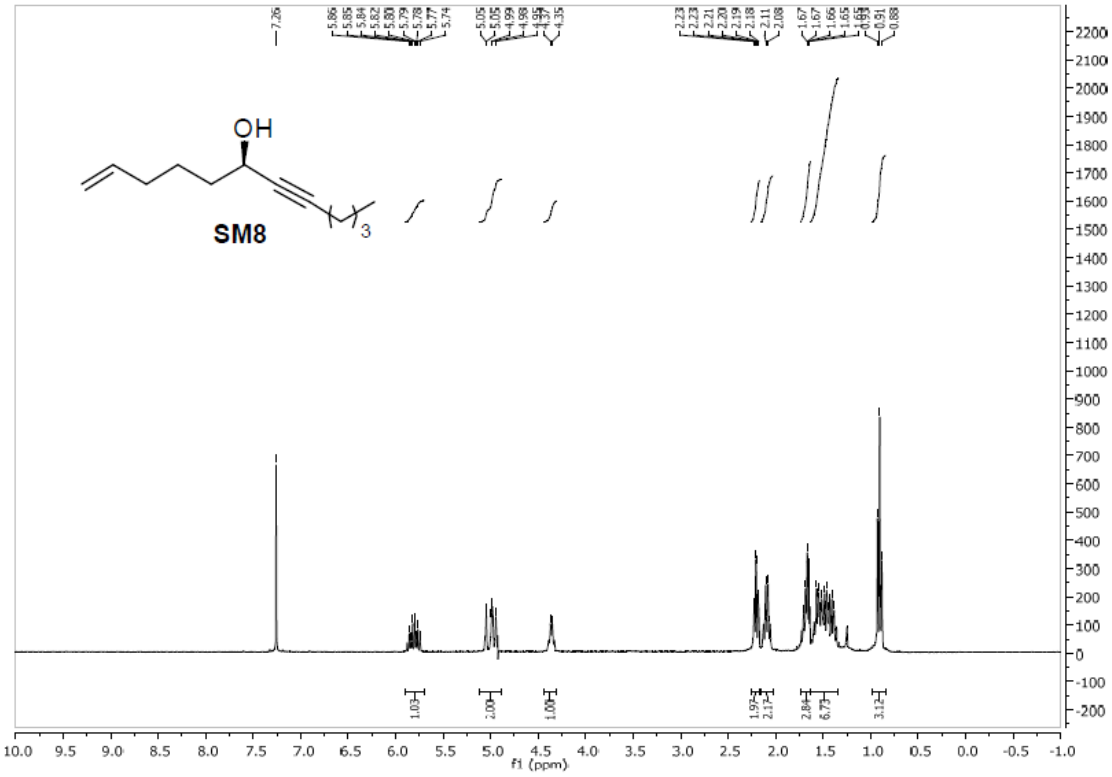



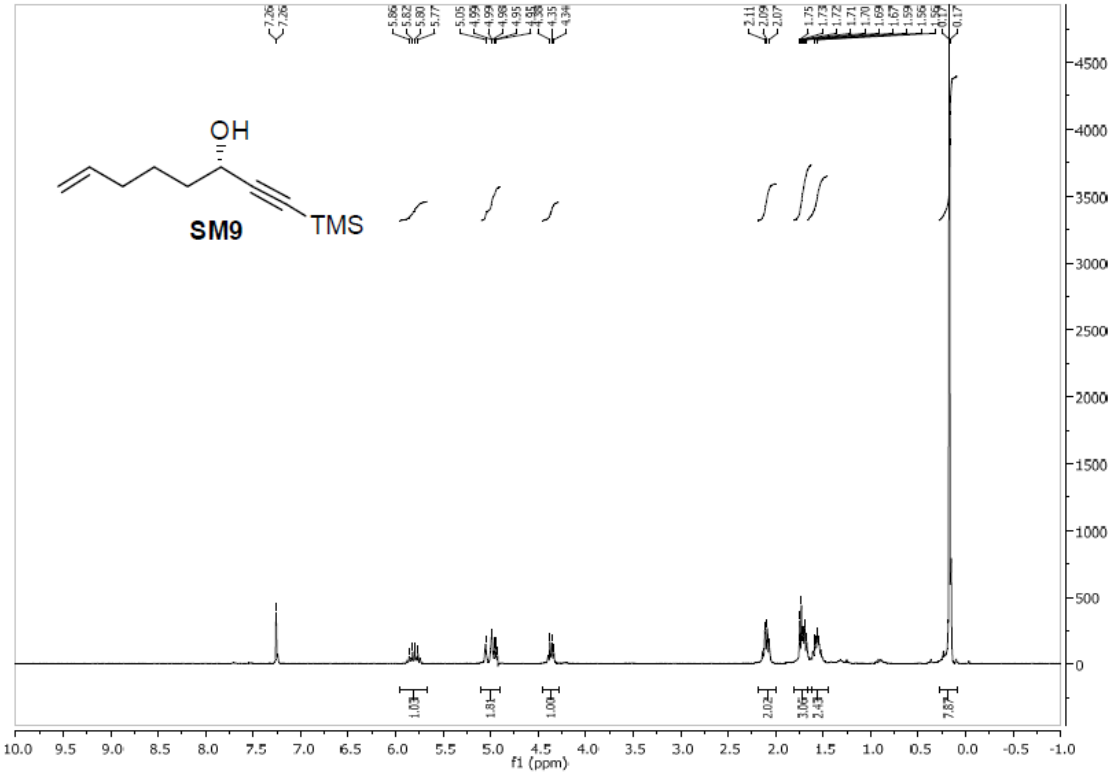

OH
SM3
3
f1 (ppm)

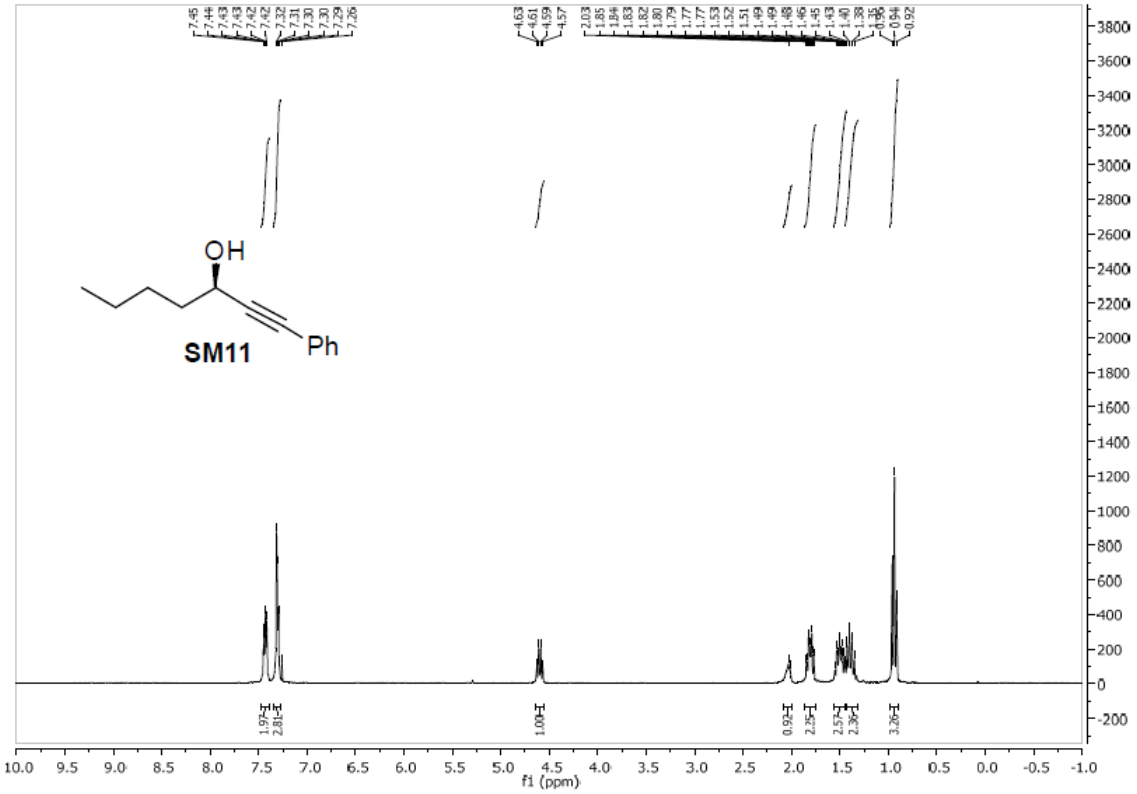

OH
SM4
TMS
f1 (ppm)

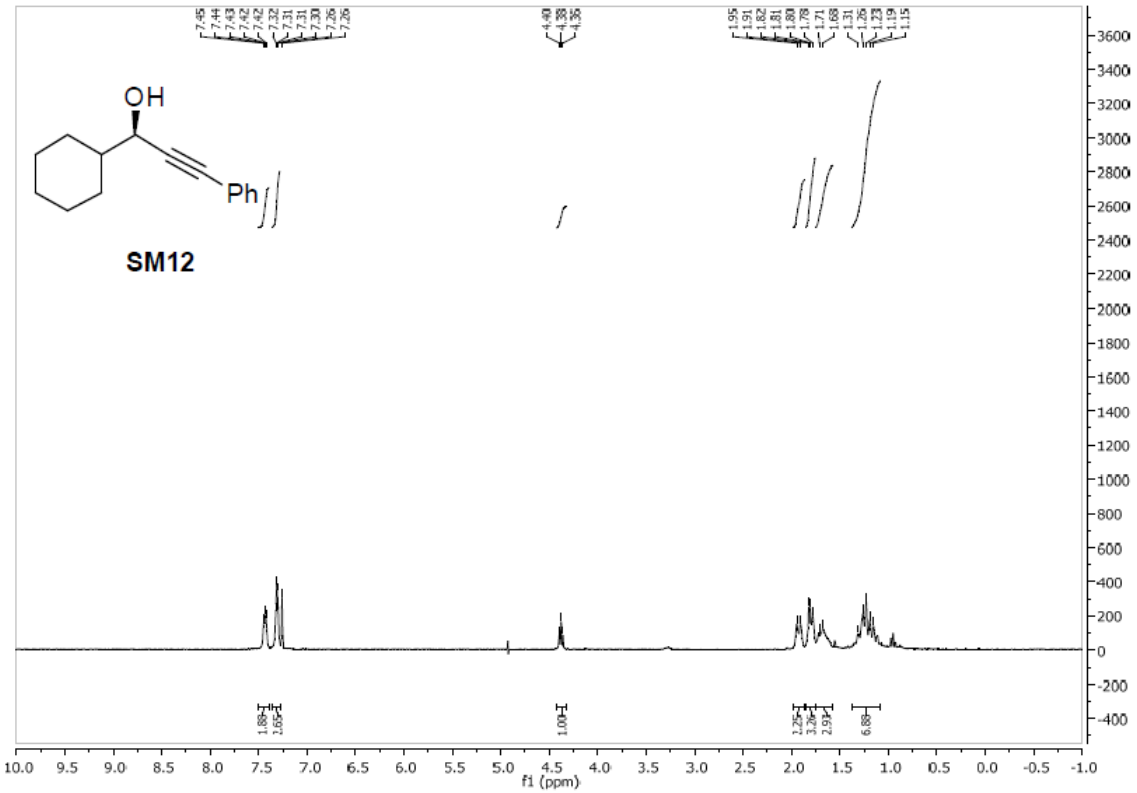

OH
Ph
SM6
f1 (ppm)

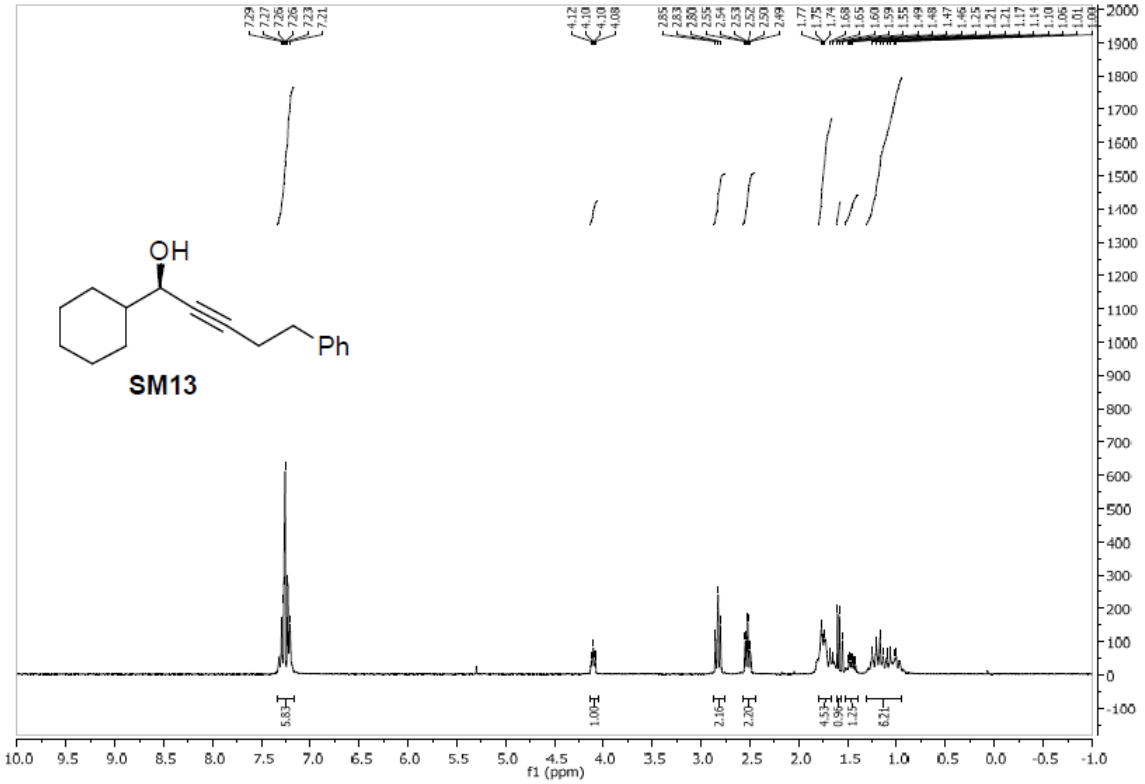

OH
Ph
SM7
f1 (ppm)

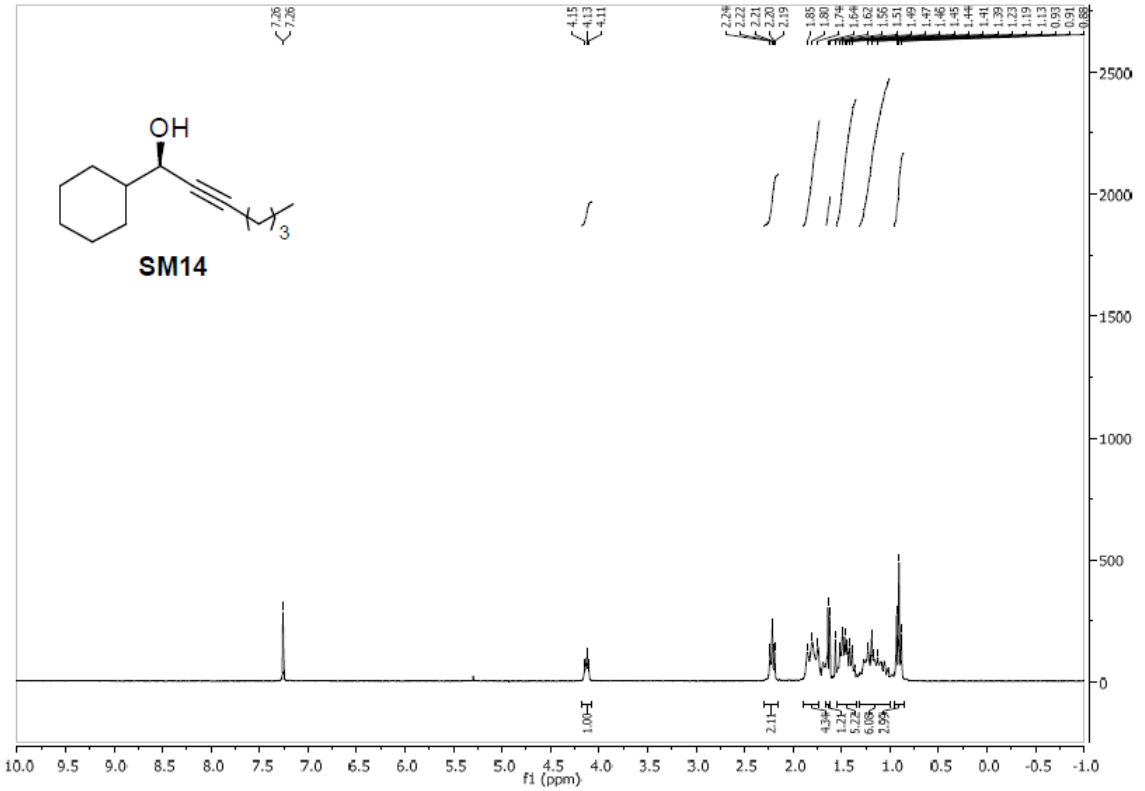

OH
SM8
3
f1 (ppm)

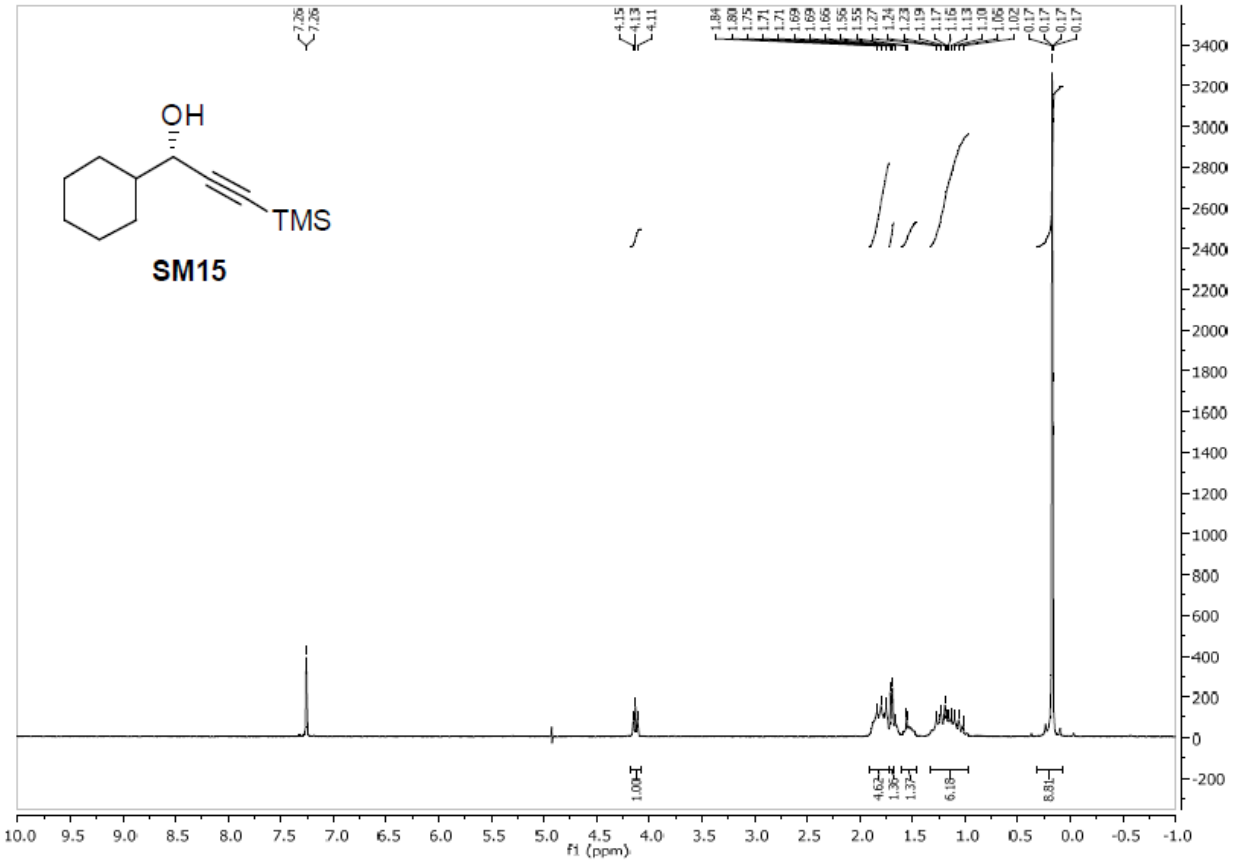

OH
SM9
TMS
f1 (ppm)


OH
Ph
SM11
f1 (ppm)

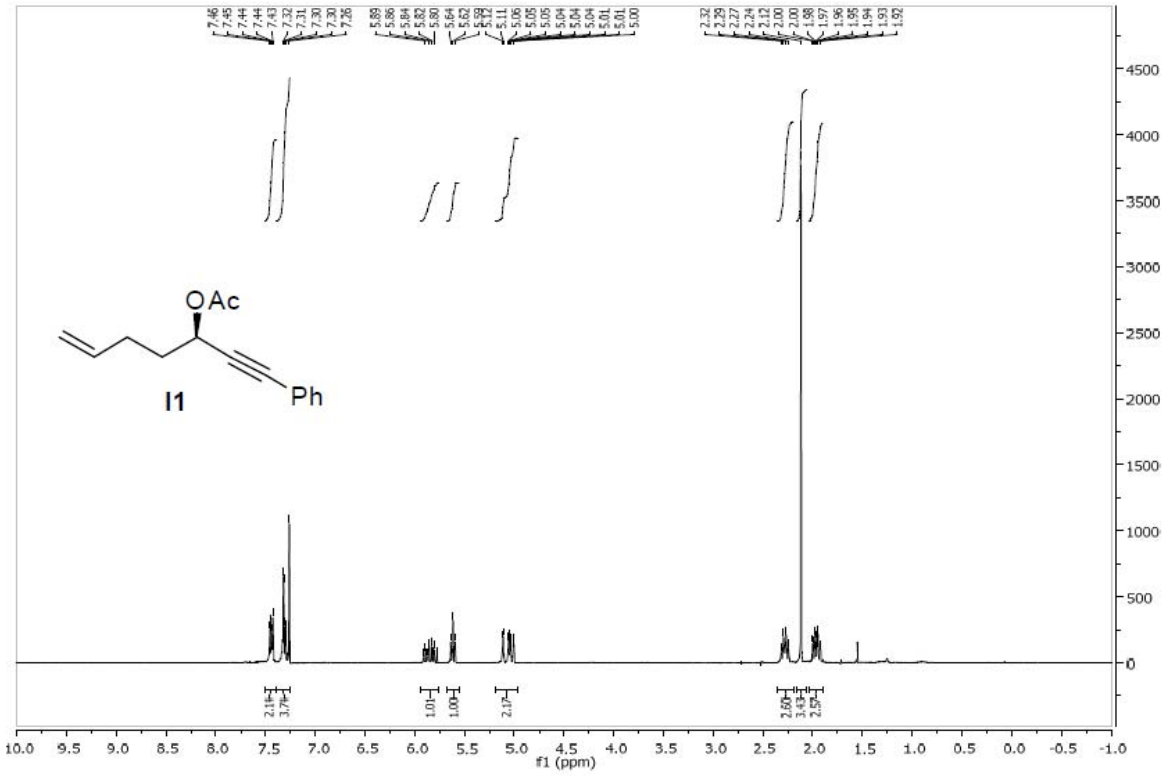

OH
Ph
SM12
f1 (ppm)

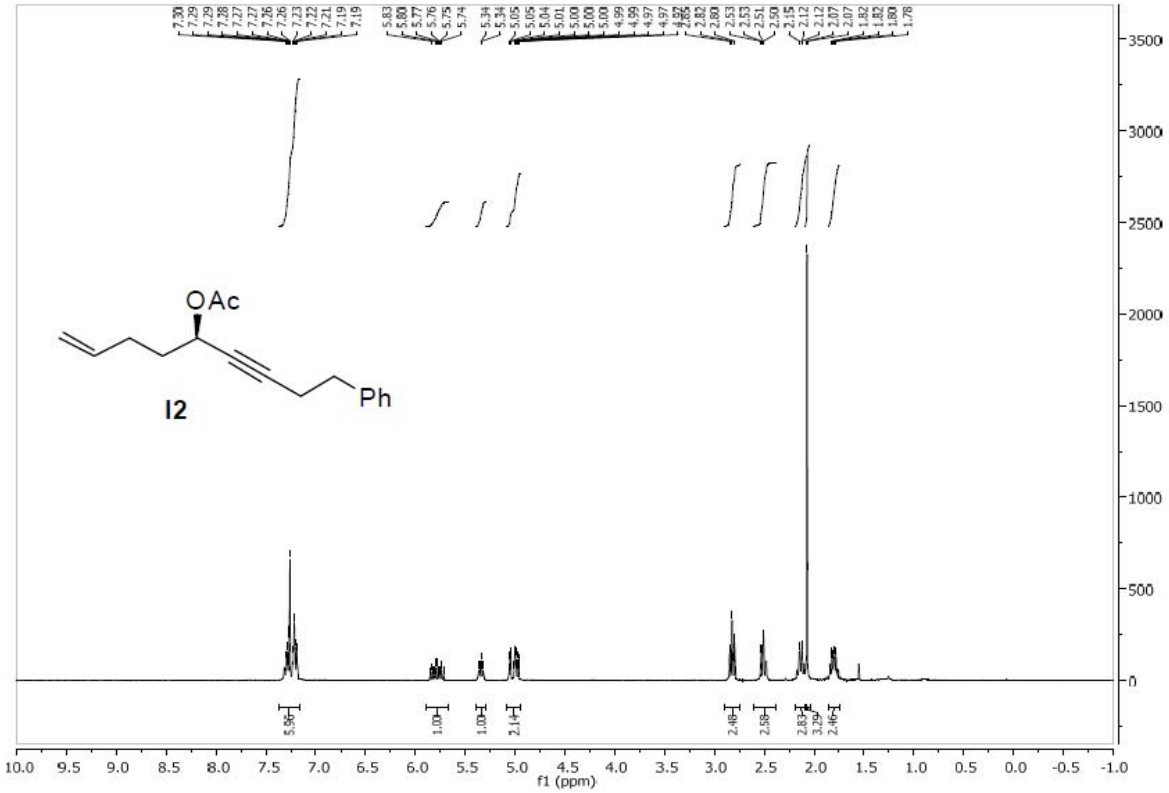

OH
Ph
SM13
f1 (ppm)

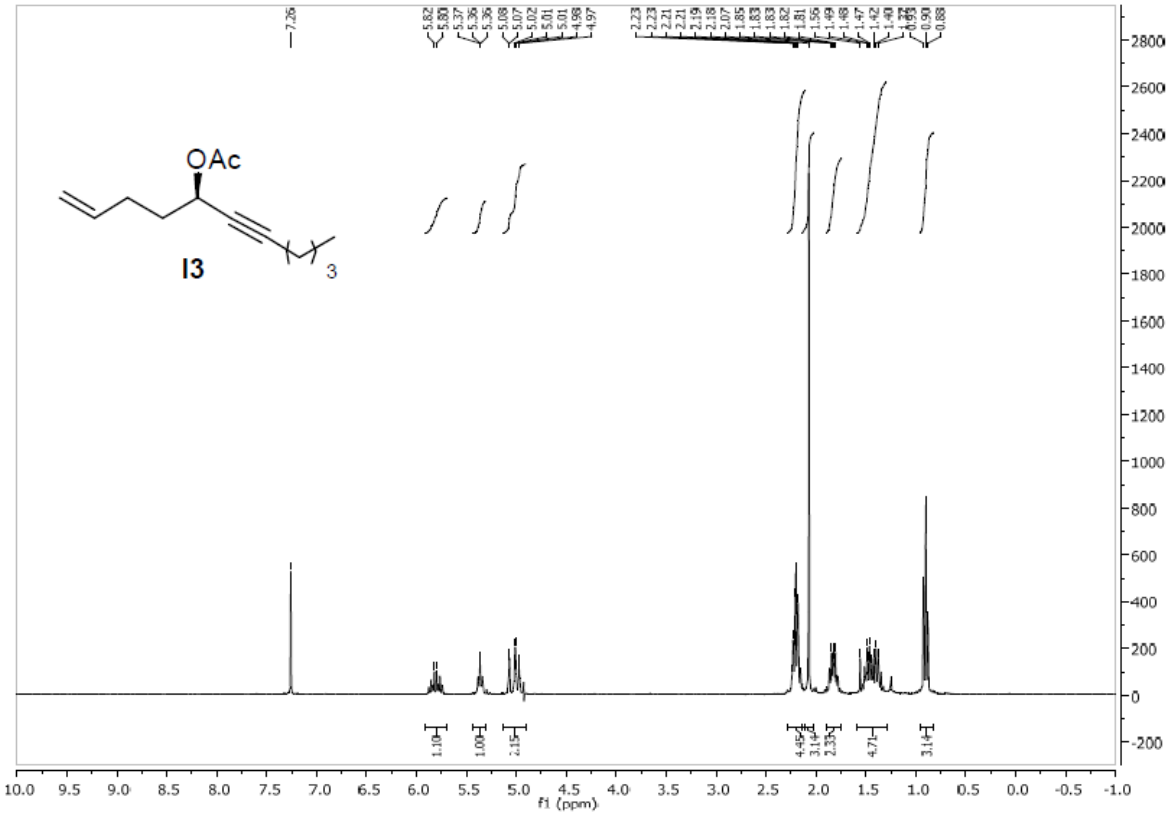

OH
3
SM14
f1 (ppm)

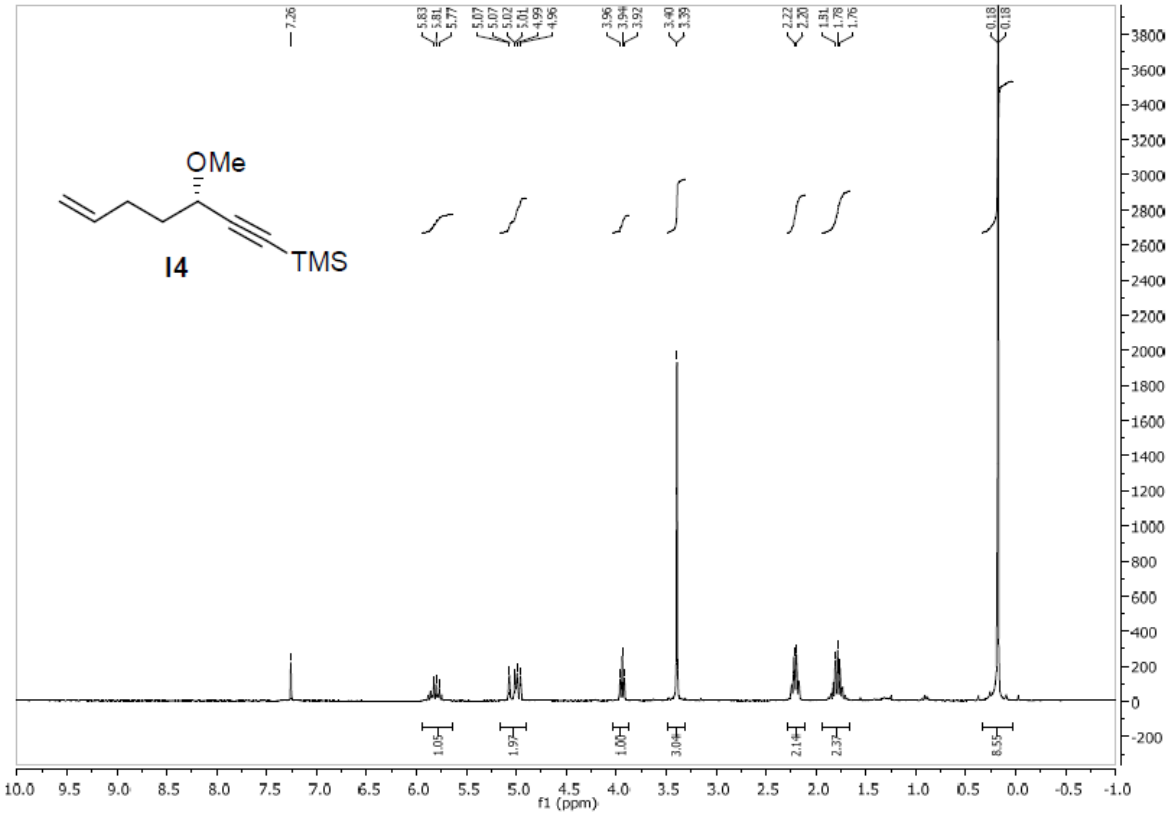

OH
TMS
SM15
f1 (ppm)

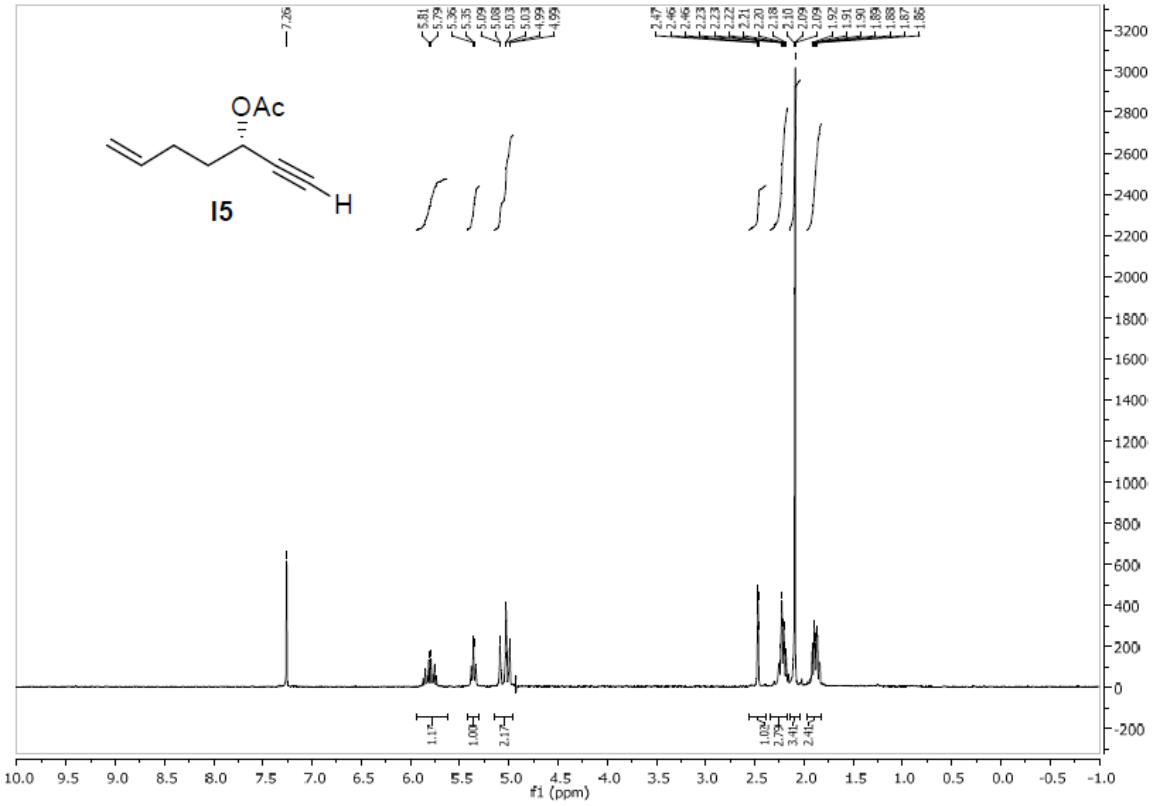
## XII. $^{1}$H NMR of I1-I16.

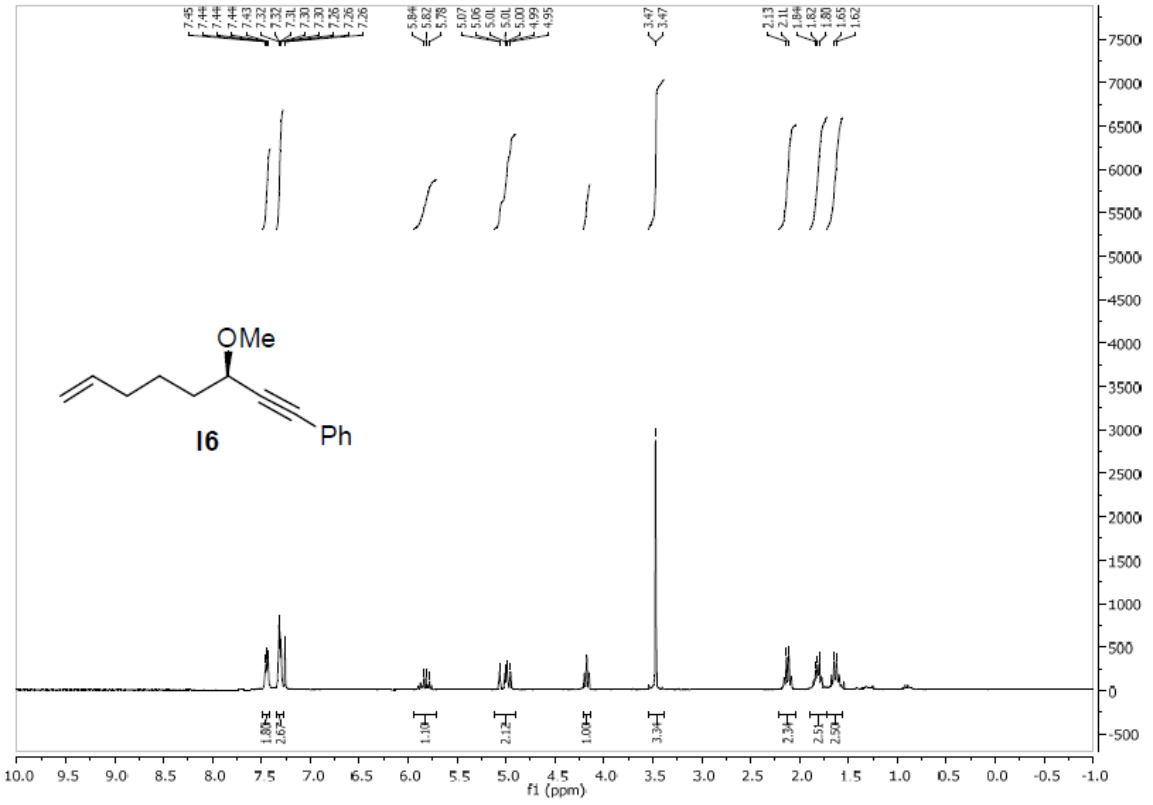


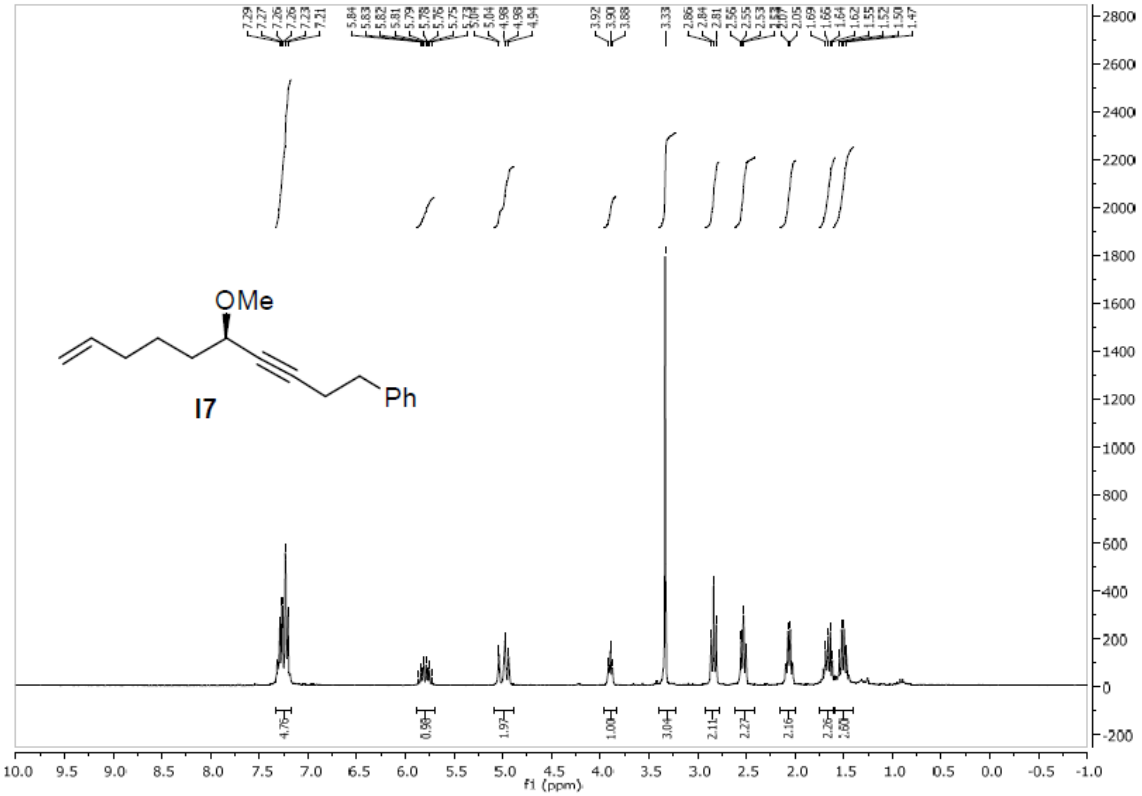



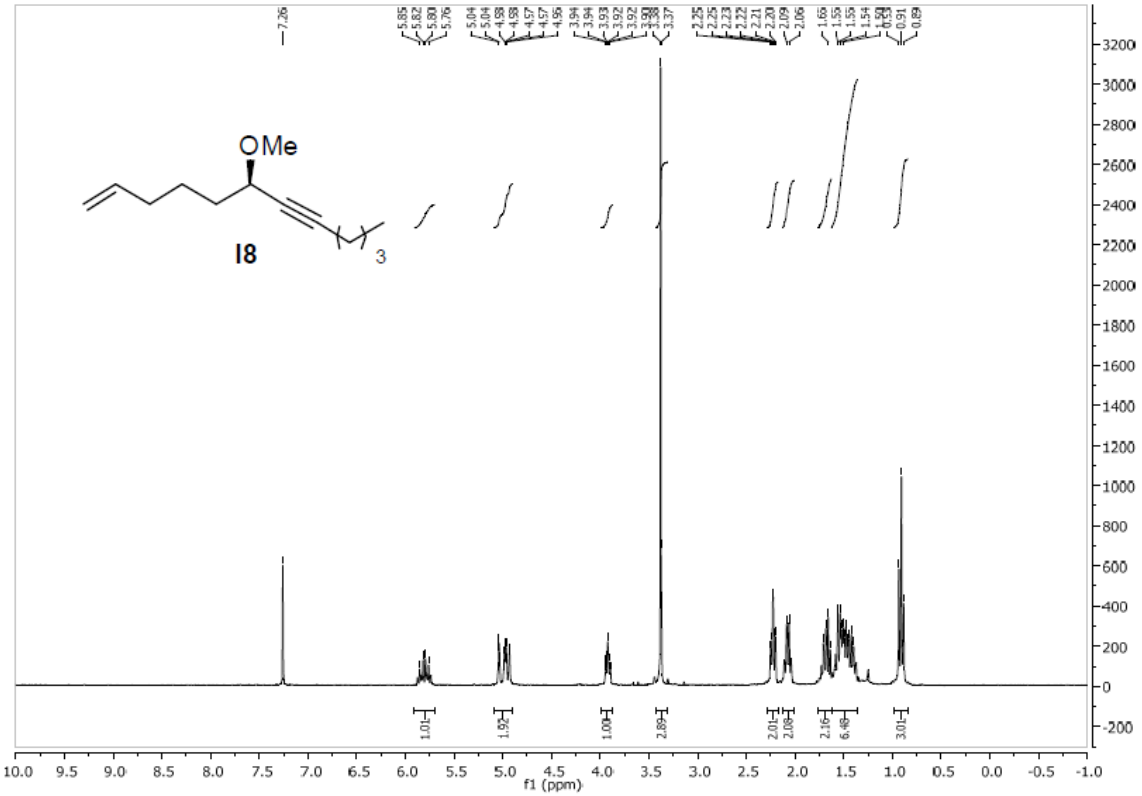

OAc
I3
3
f1 (ppm)

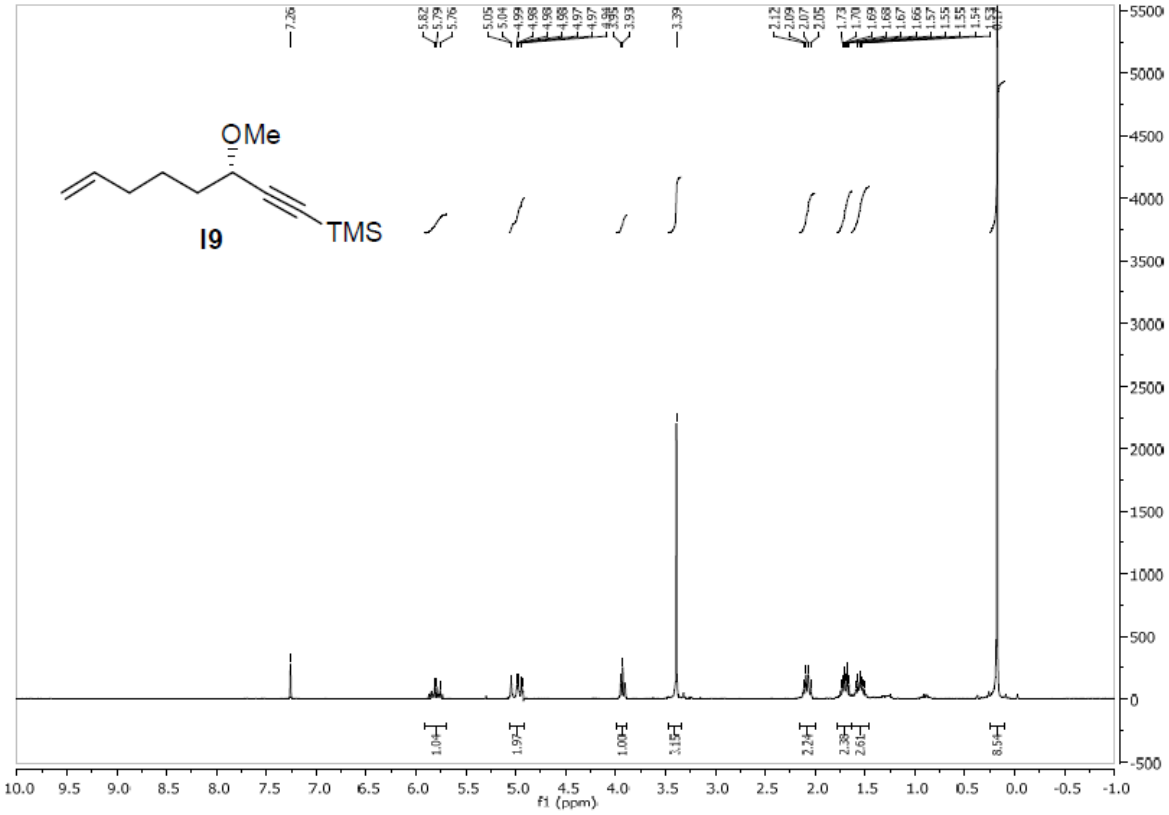

OMe
I4
TMS
f1 (ppm)

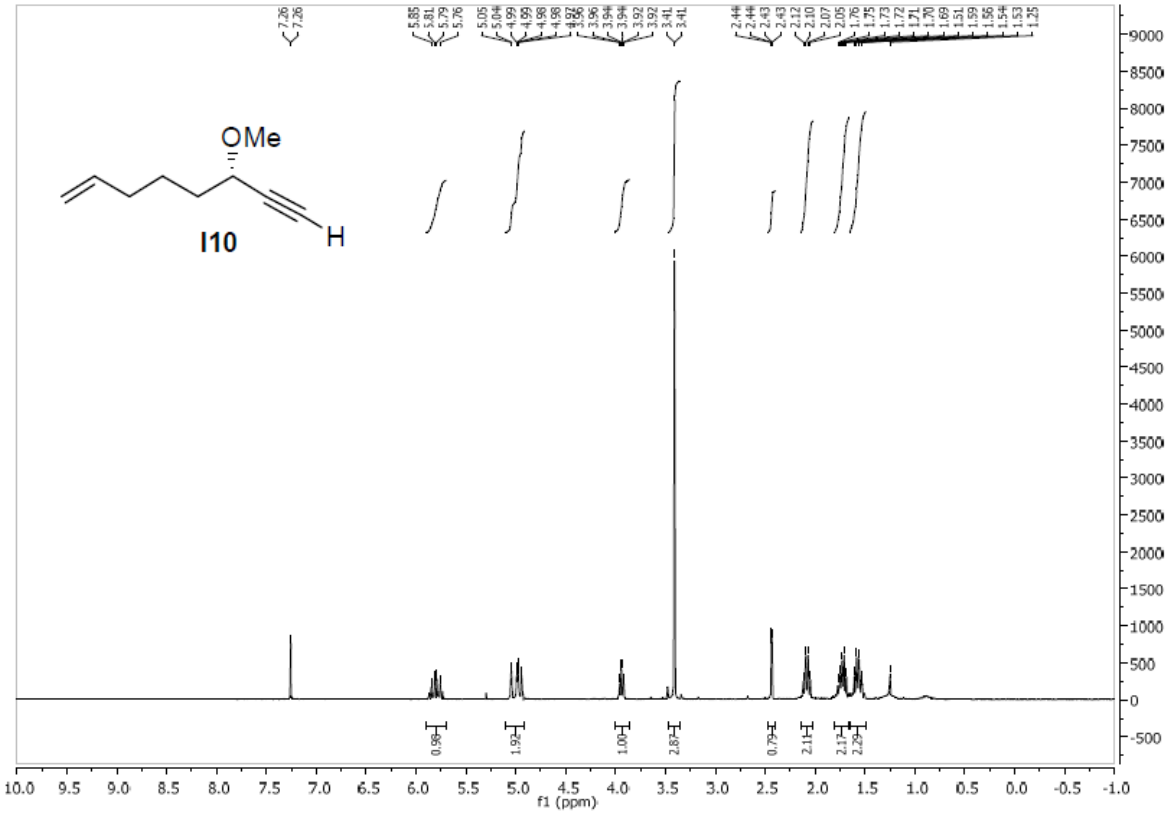

OAc
H
I5
f1 (ppm)

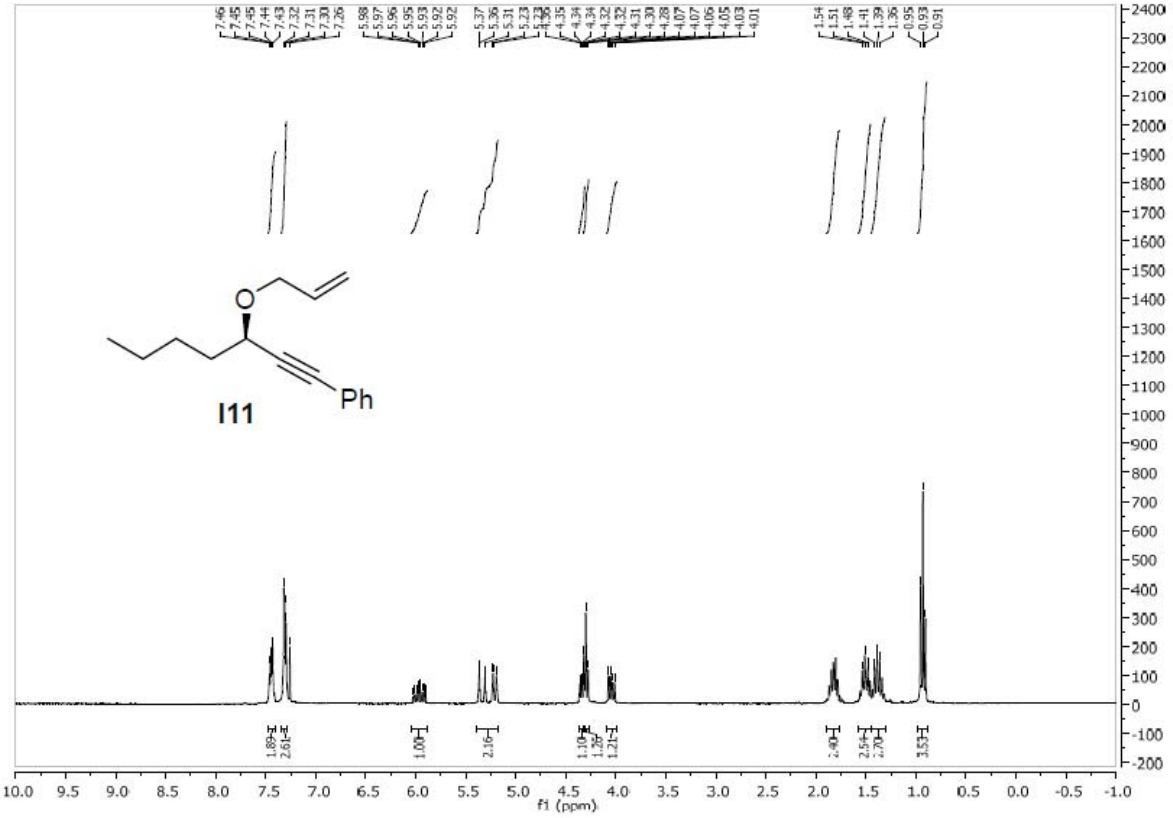

OMe
Ph
I6
f1 (ppm)

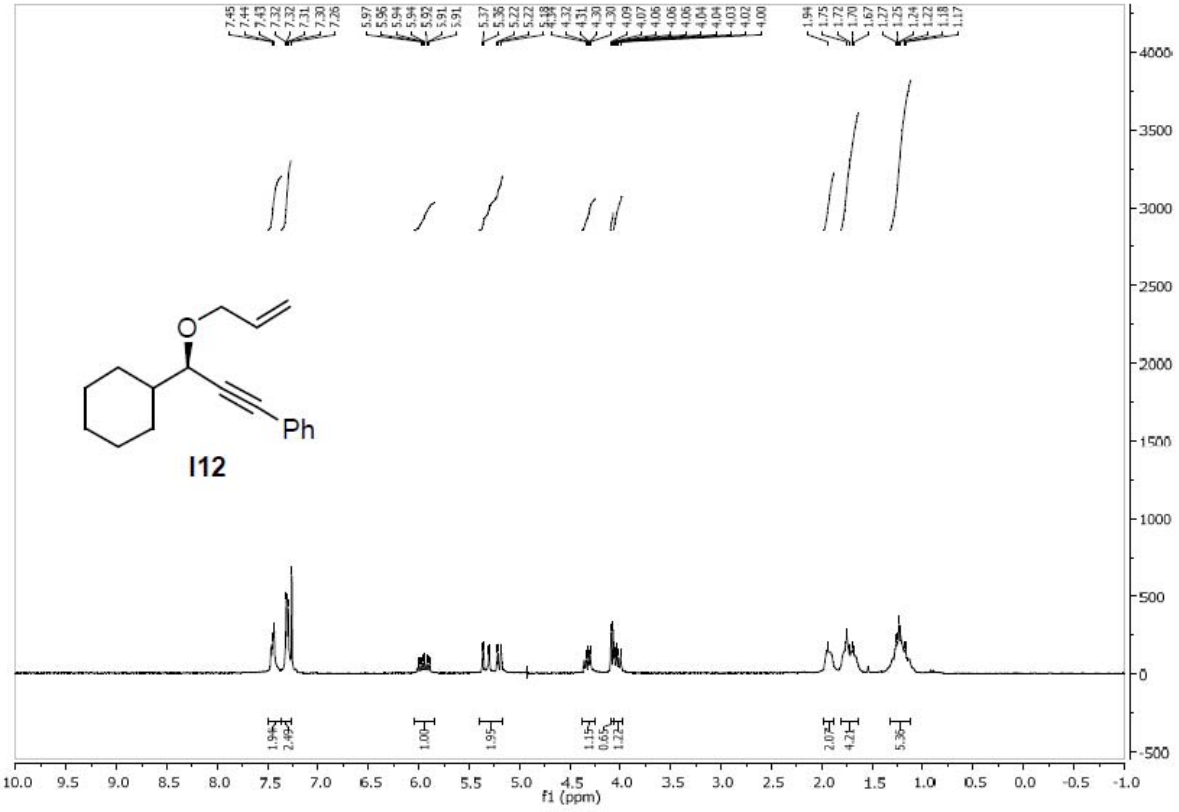

OMe
Ph
I7
f1 (ppm)

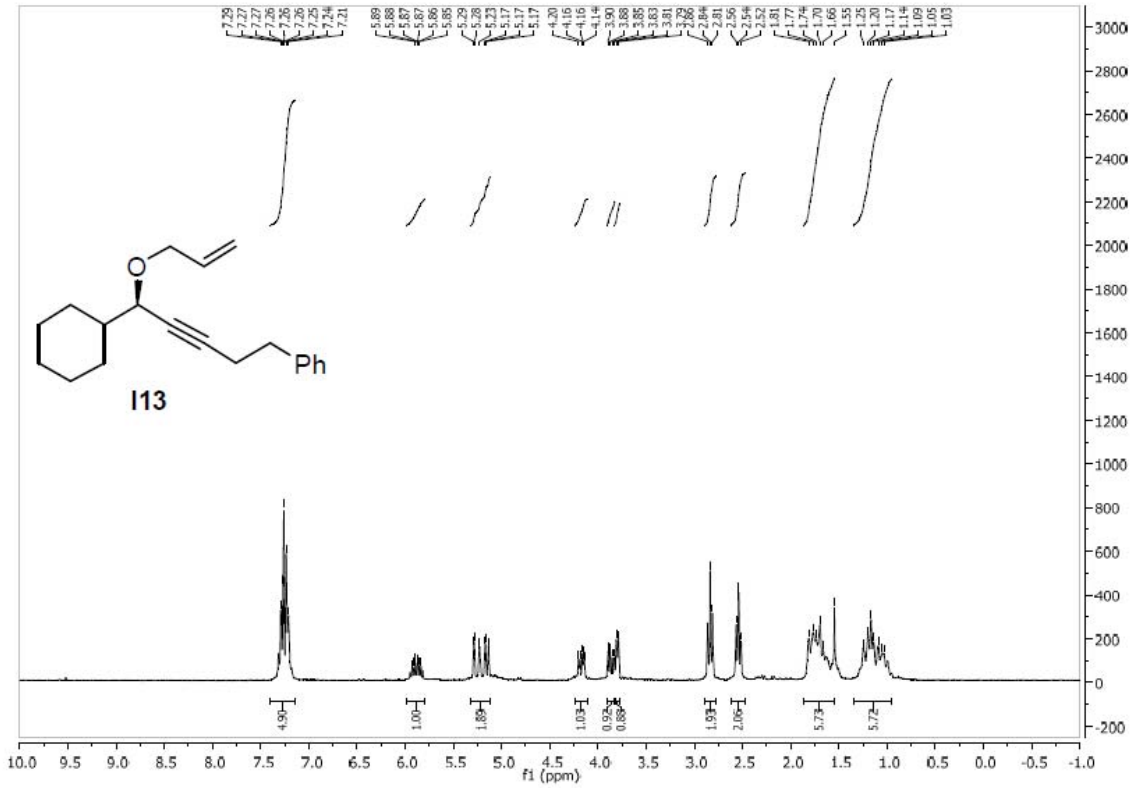

OMe
3
I8
f1 (ppm)

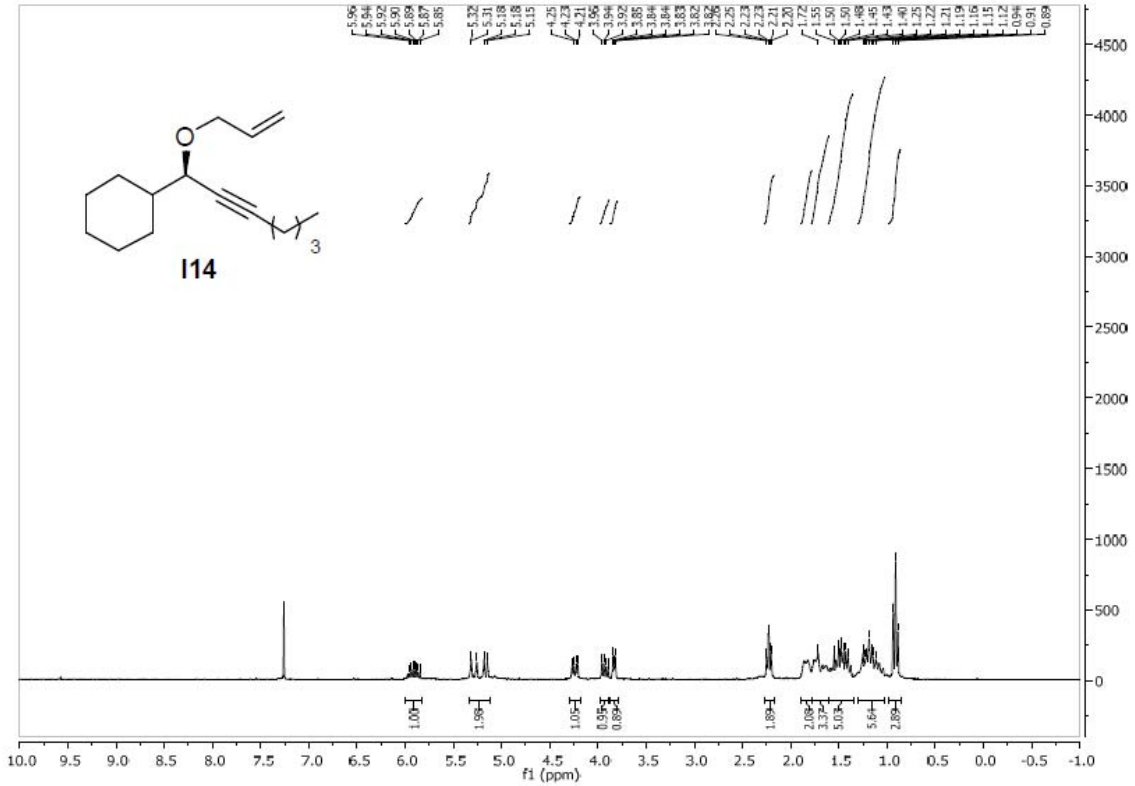

OMe
TMS
I9
f1 (ppm)

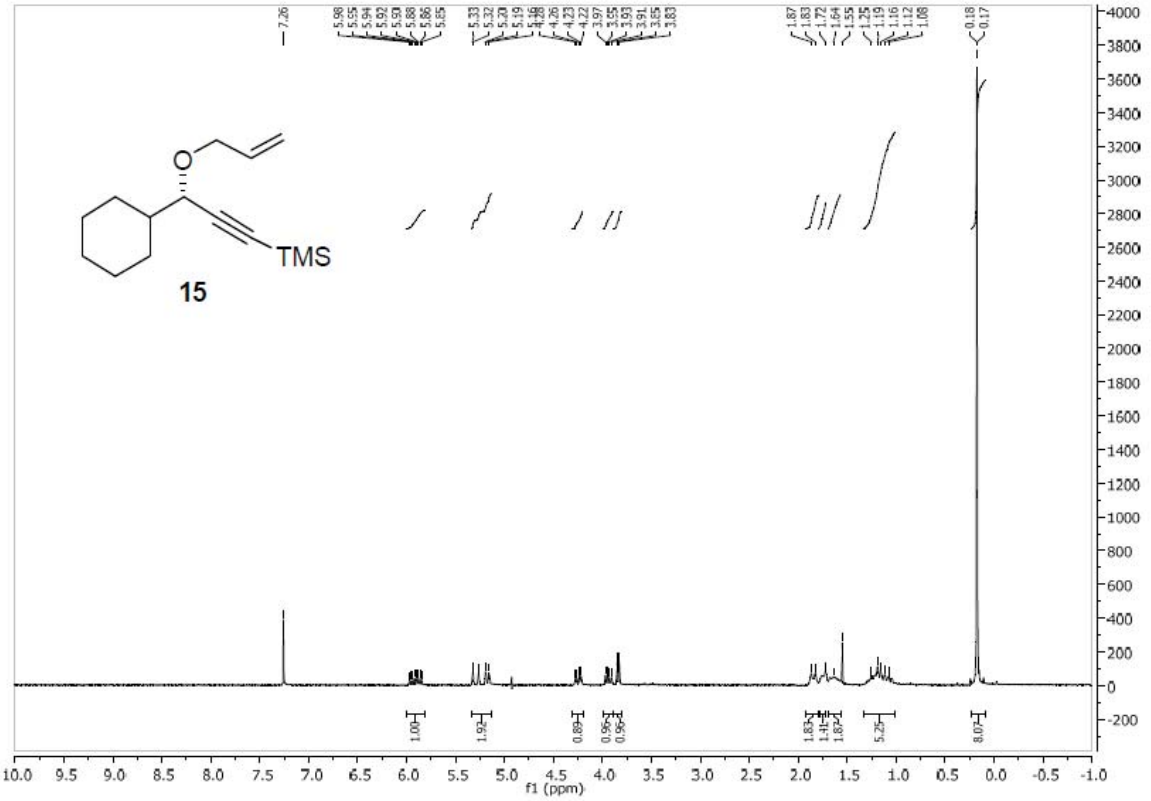

OMe
H
I10
f1 (ppm)

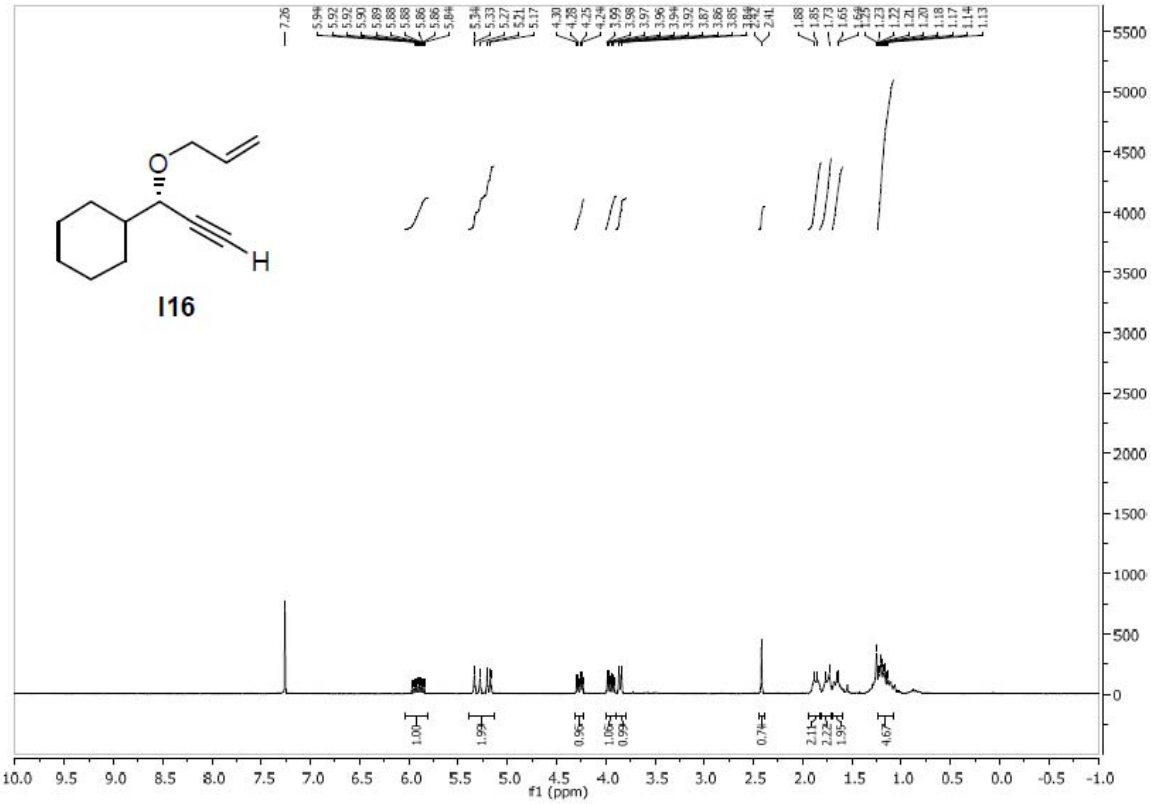

O
Ph
I11
f1 (ppm)


O
Ph
I12
f1 (ppm)

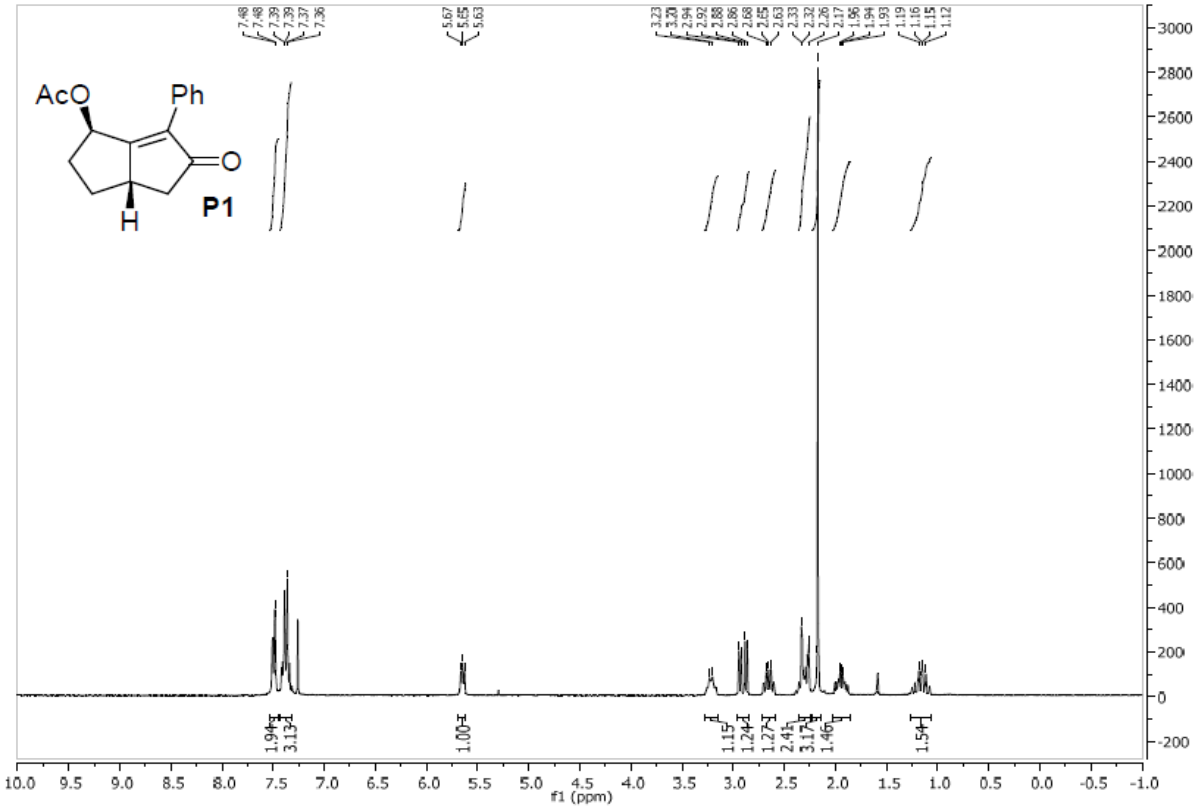

O
Ph
I13
f1 (ppm)

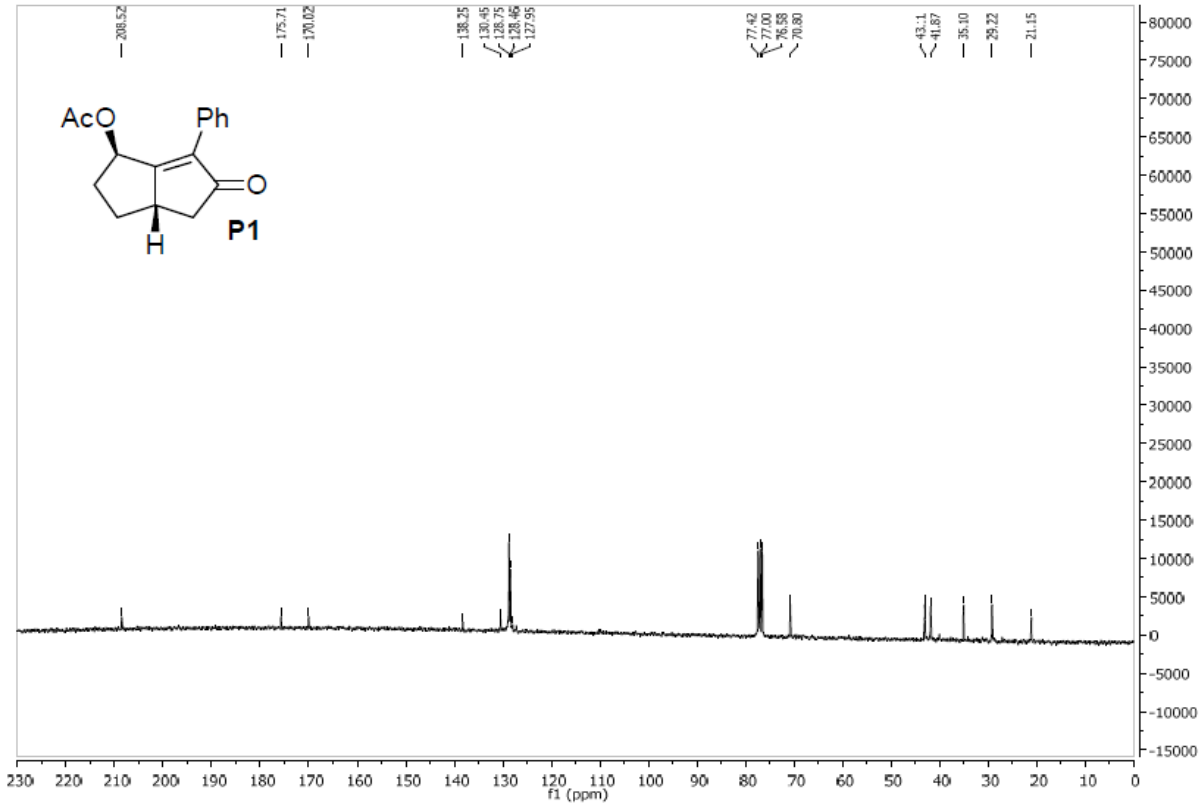

O
3
I14
f1 (ppm)

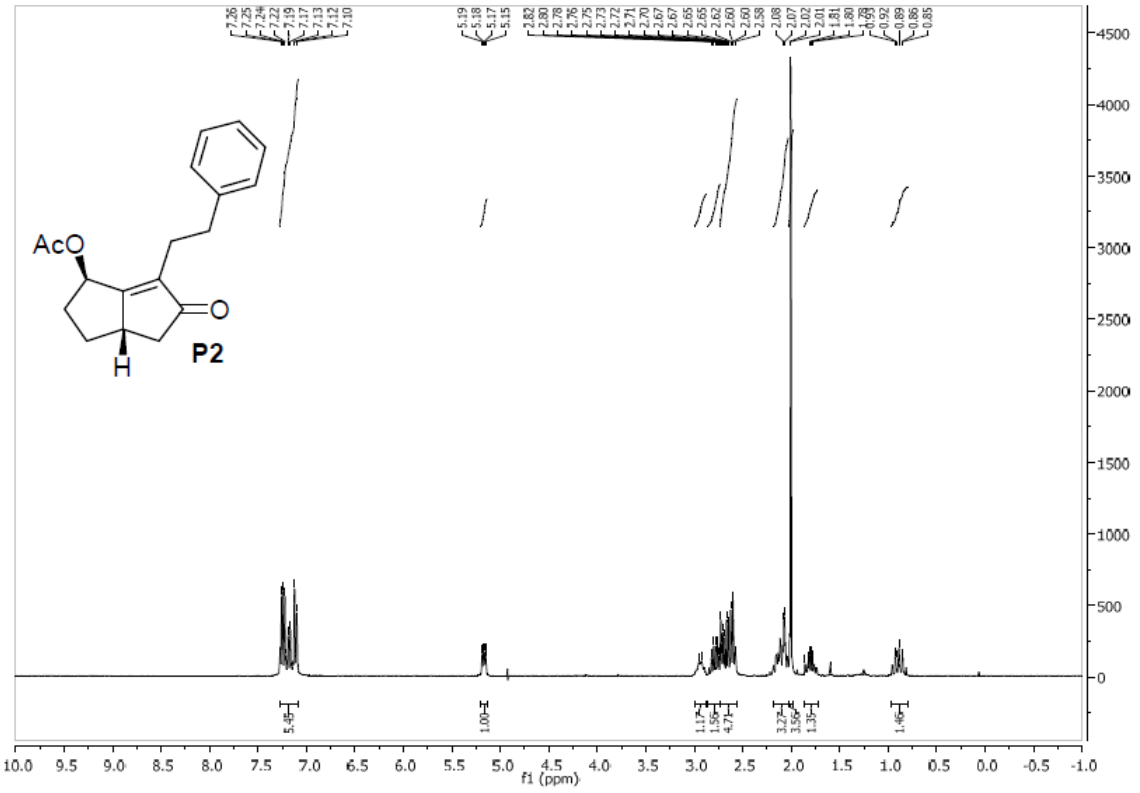

TMS
15
f1 (ppm)

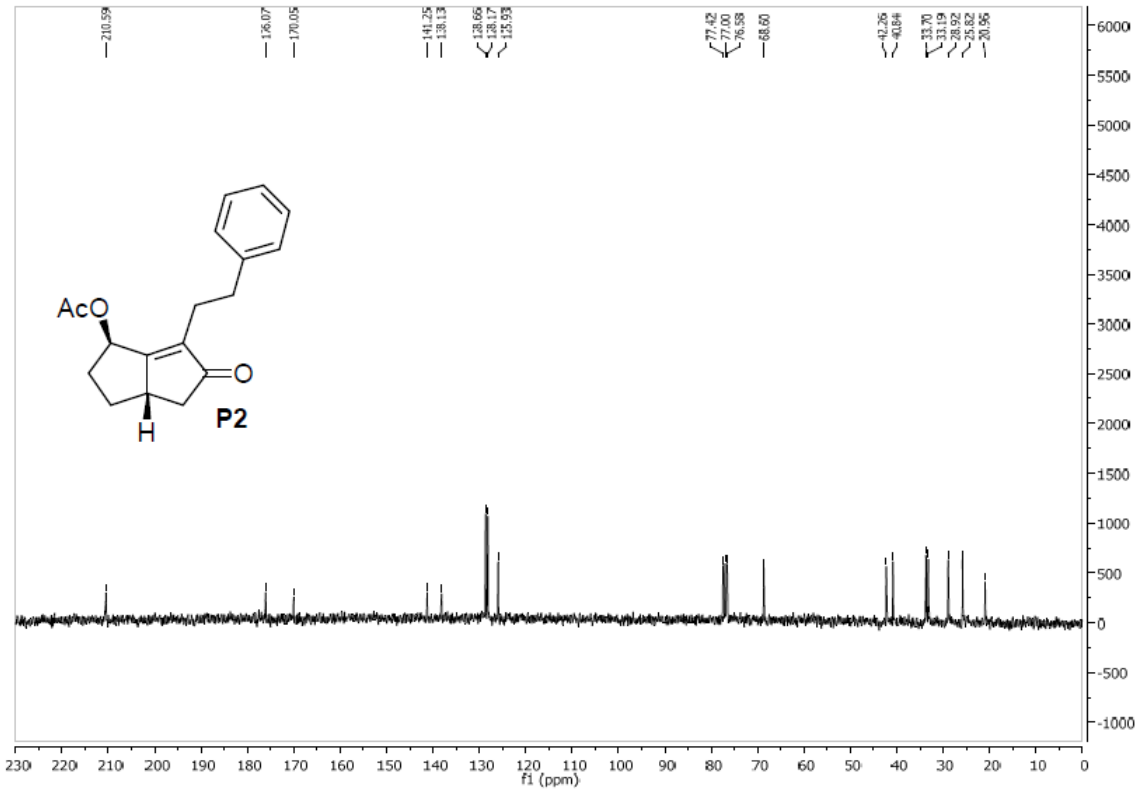

H
I16
f1 (ppm)

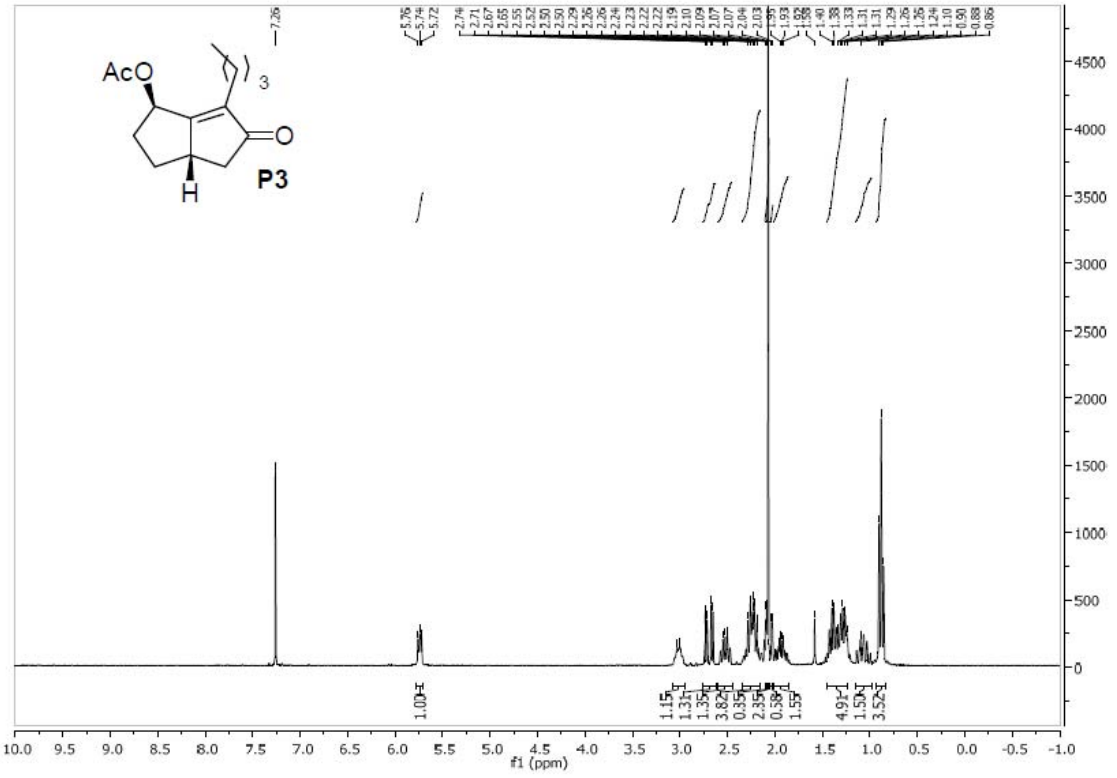
## XIII. $^{1}H$, $^{13}C$ NMR of P 1-16.

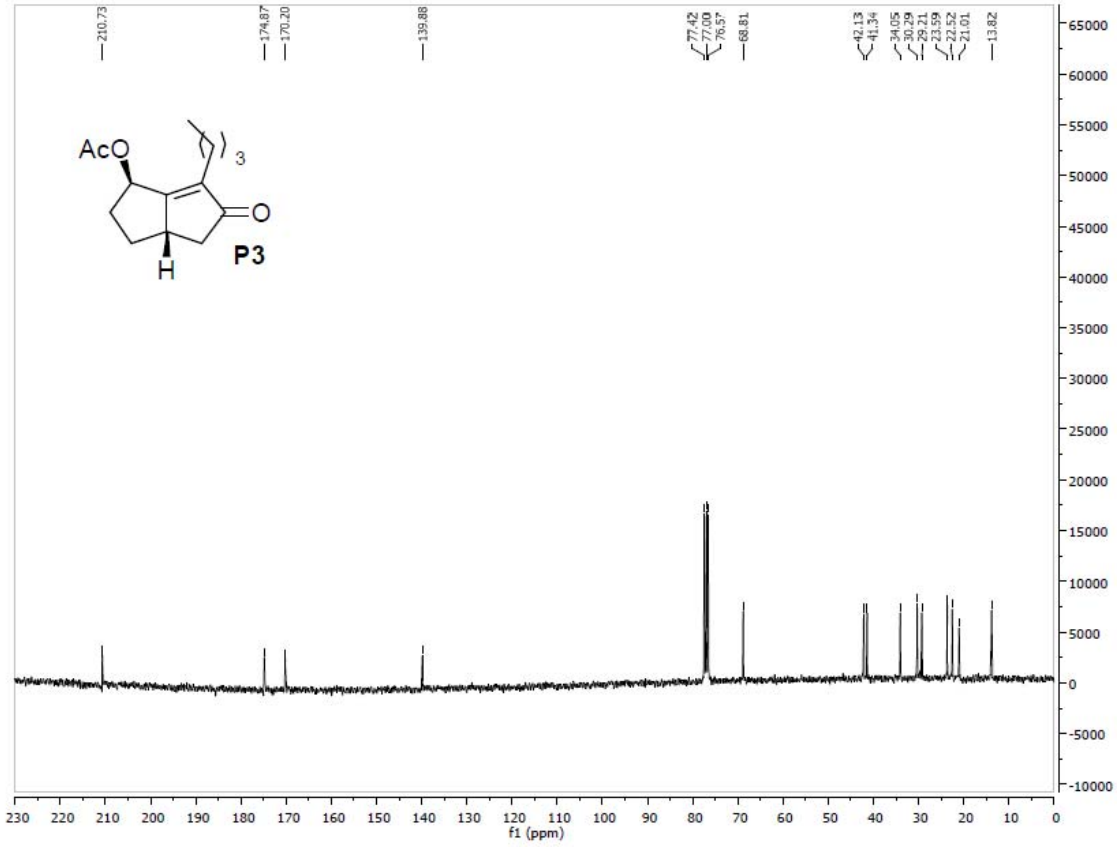


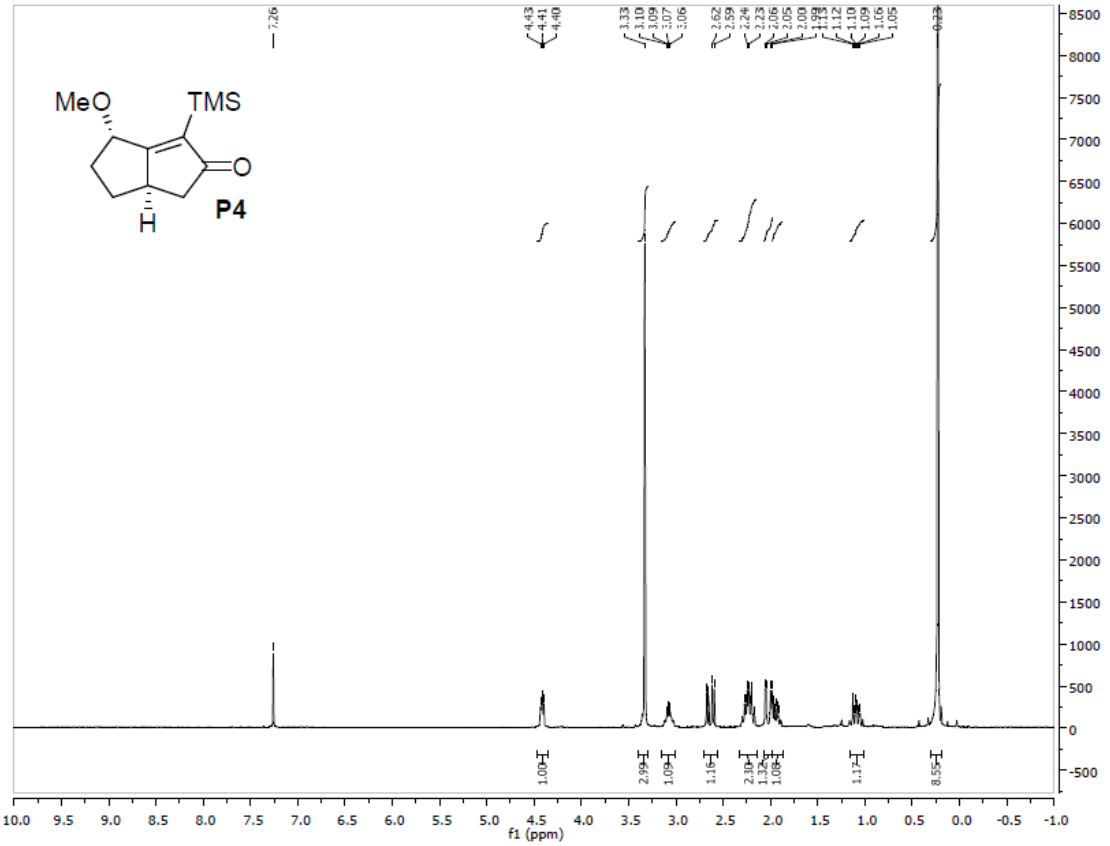



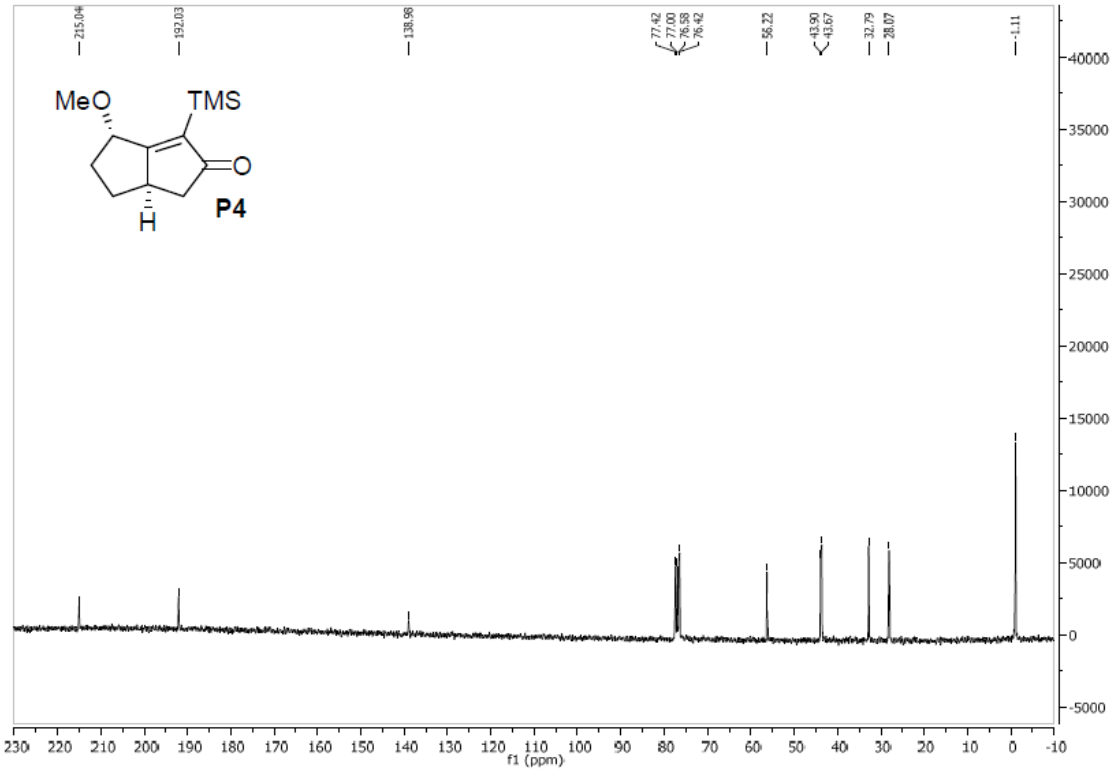

AcO
O
H
P2
f1 (ppm)

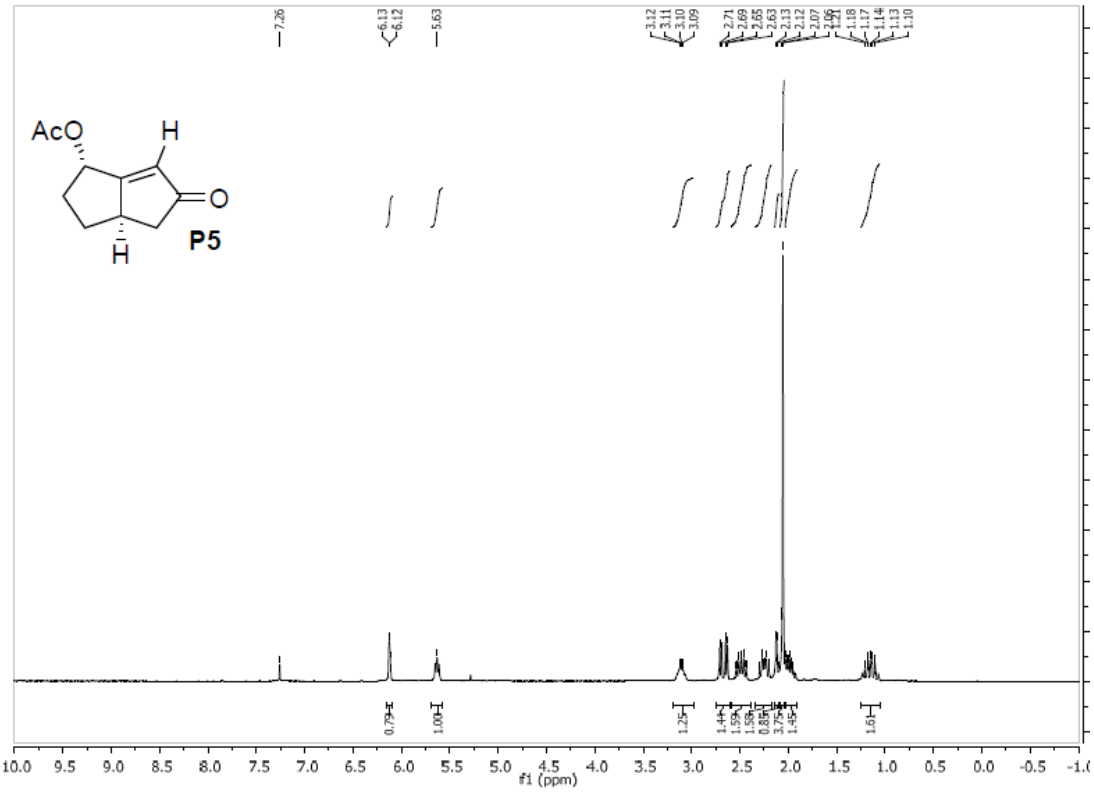

AcO
O
H
P2
f1 (ppm)

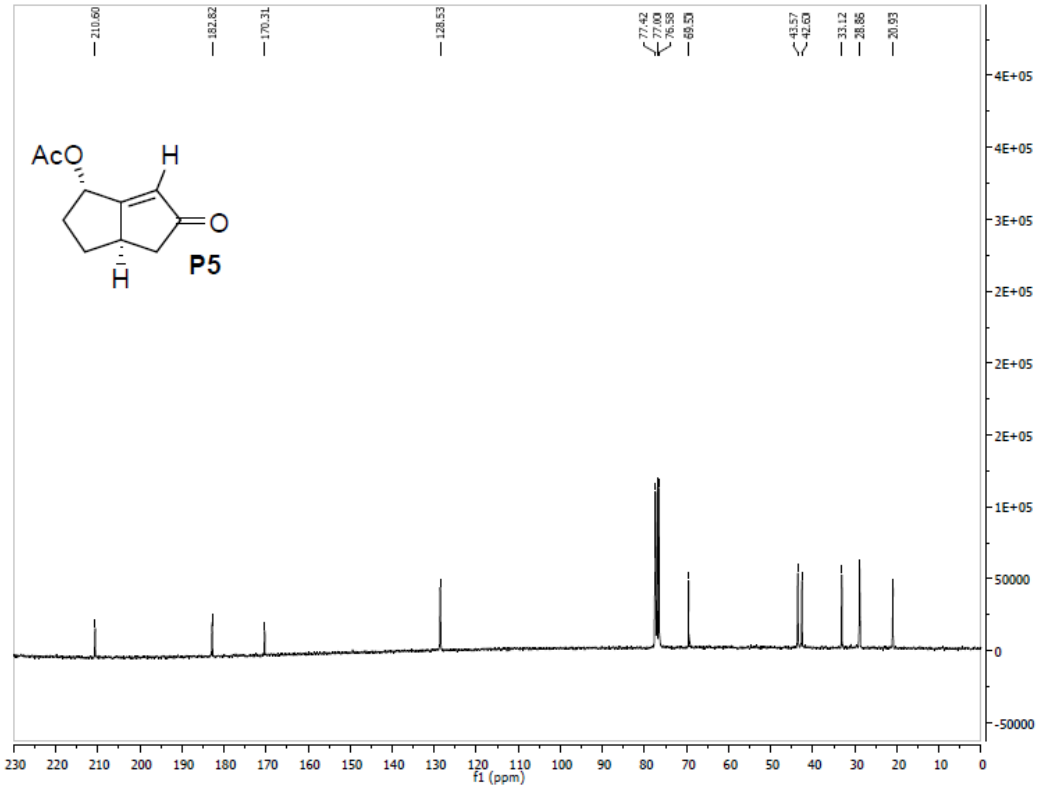

AcO
3
O
H
P3
f1 (ppm)

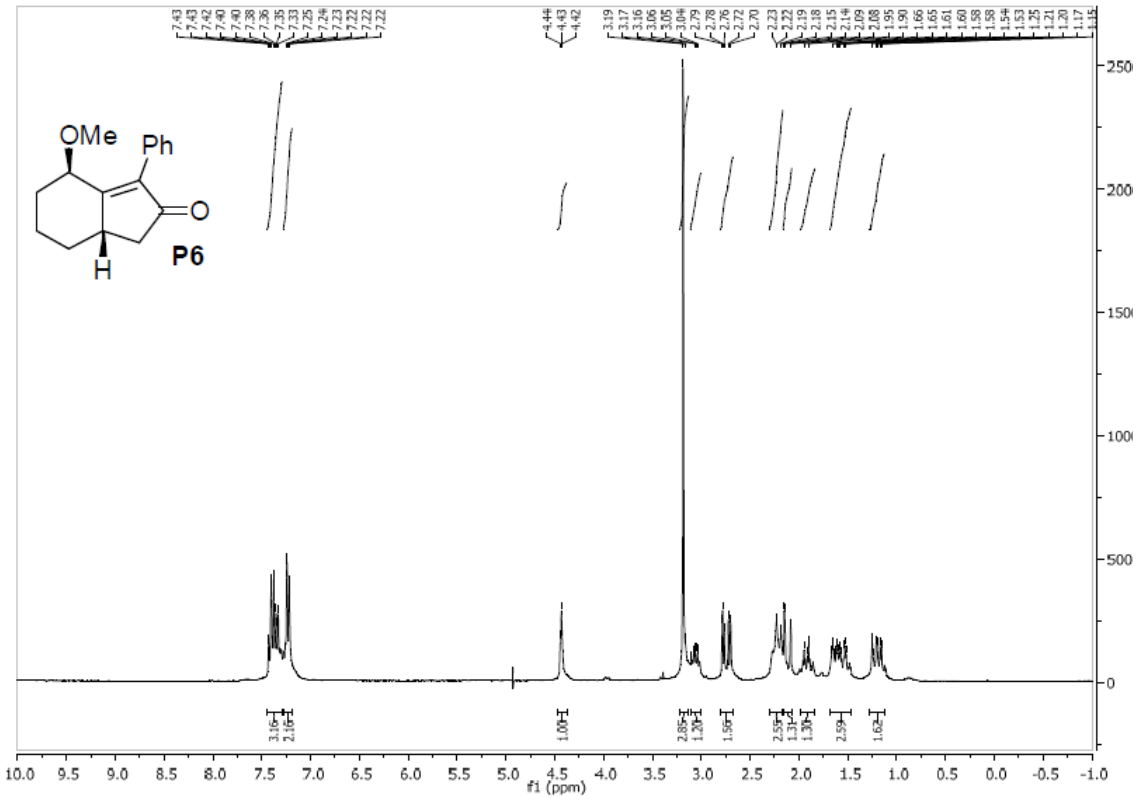

AcO
3
O
H
P3
f1 (ppm)

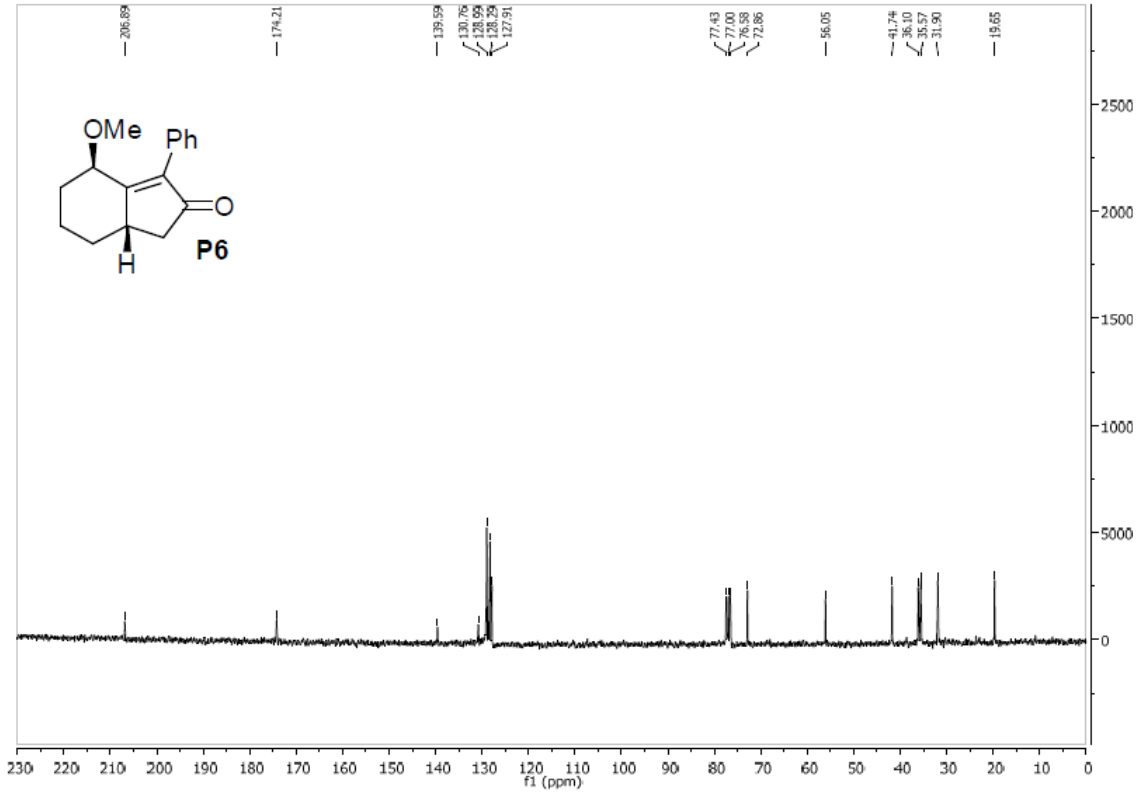

MeO
TMS
O
H
P4
f1 (ppm)

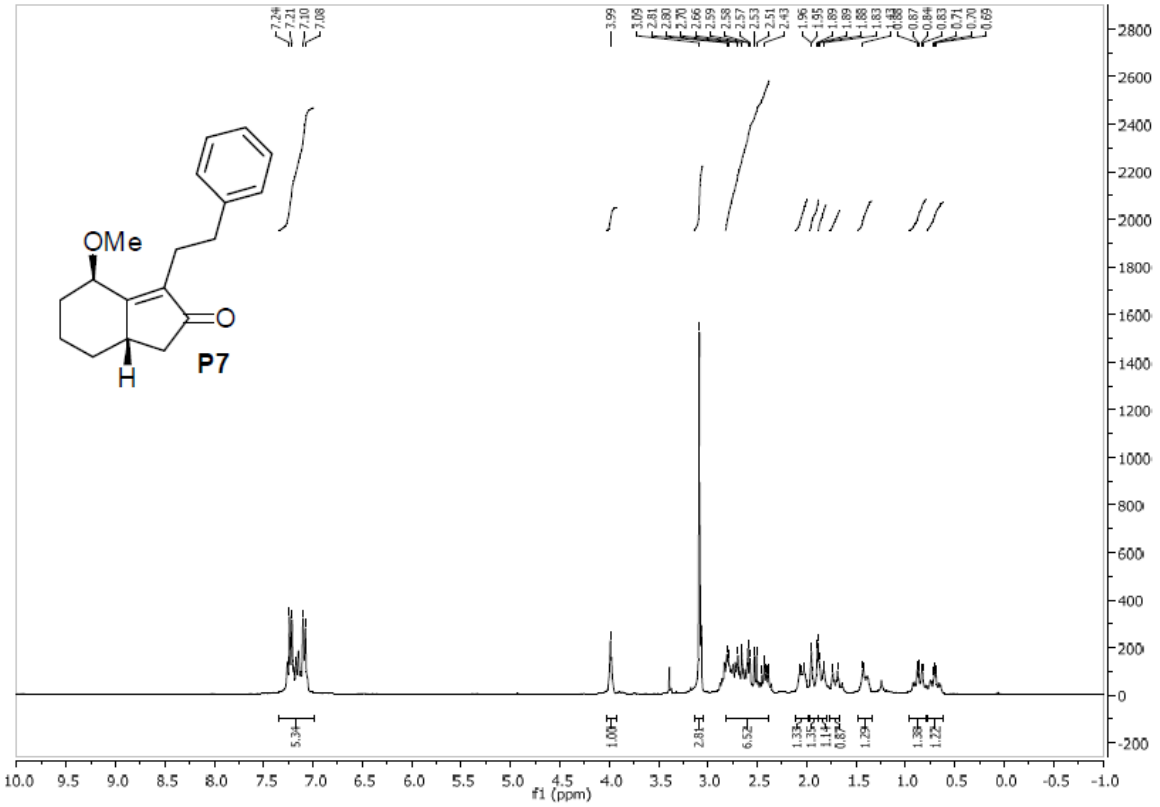

MeO
TMS
O
H
P4
f1 (ppm)

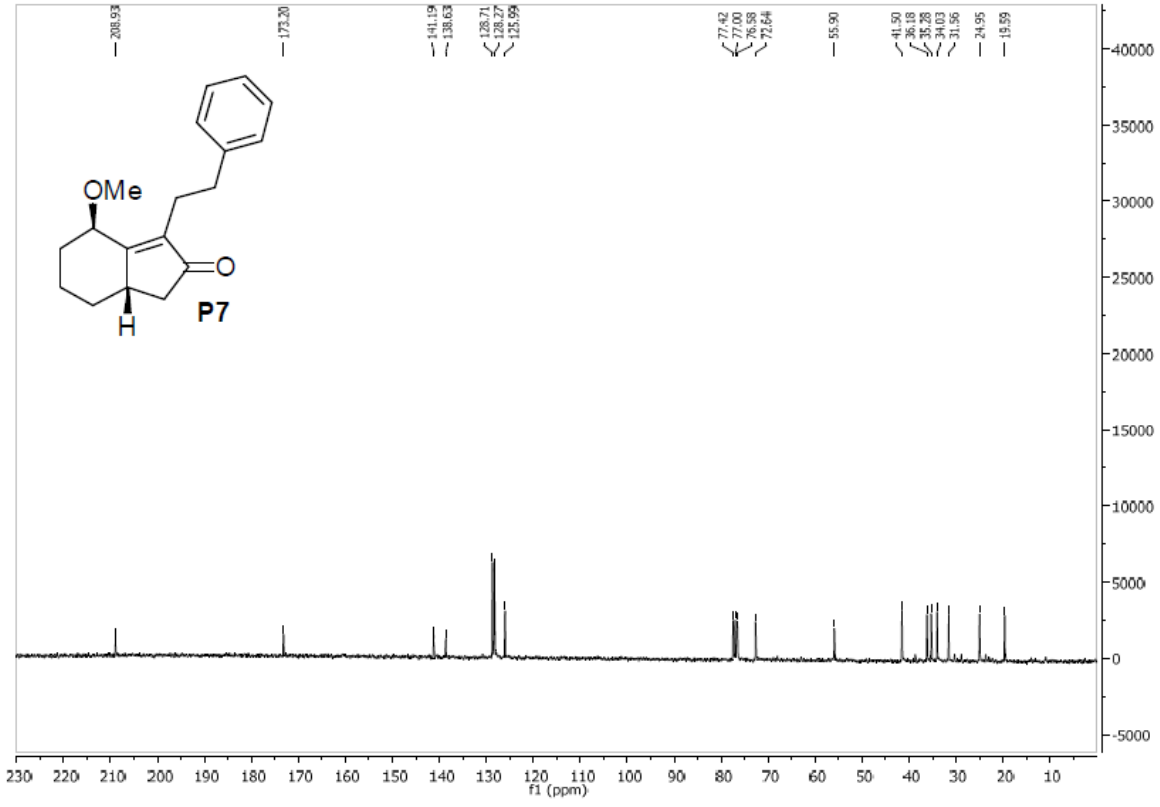

AcO
H
O
H
P5
f1 (ppm)

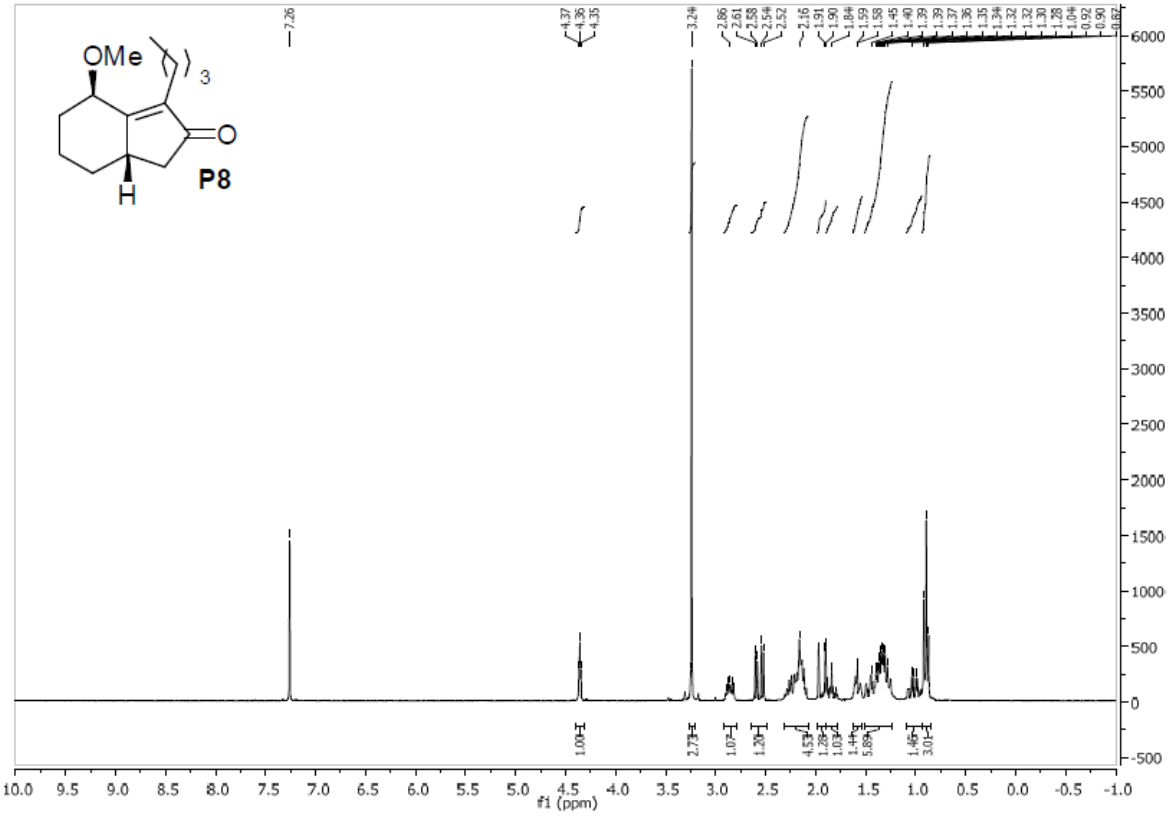

AcO
H
O
H
P5
f1 (ppm)

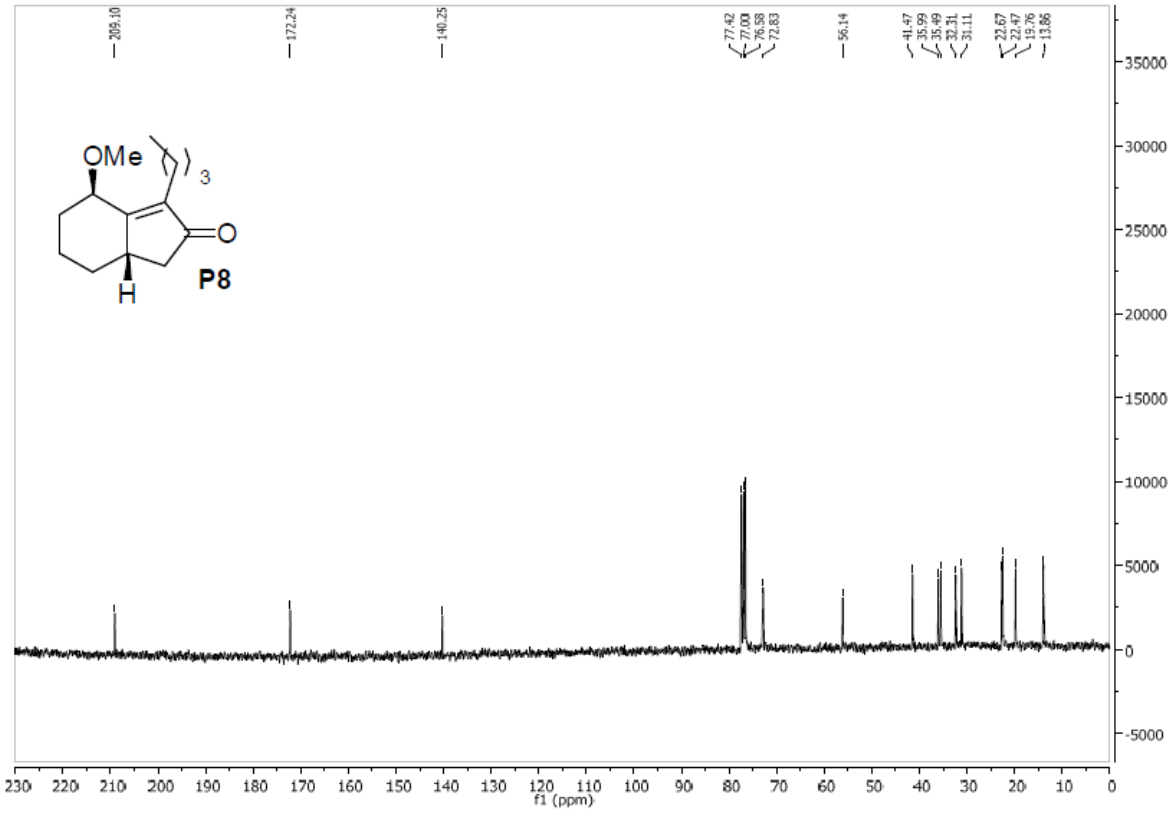

OMe
Ph
O
H
P6
f1 (ppm)

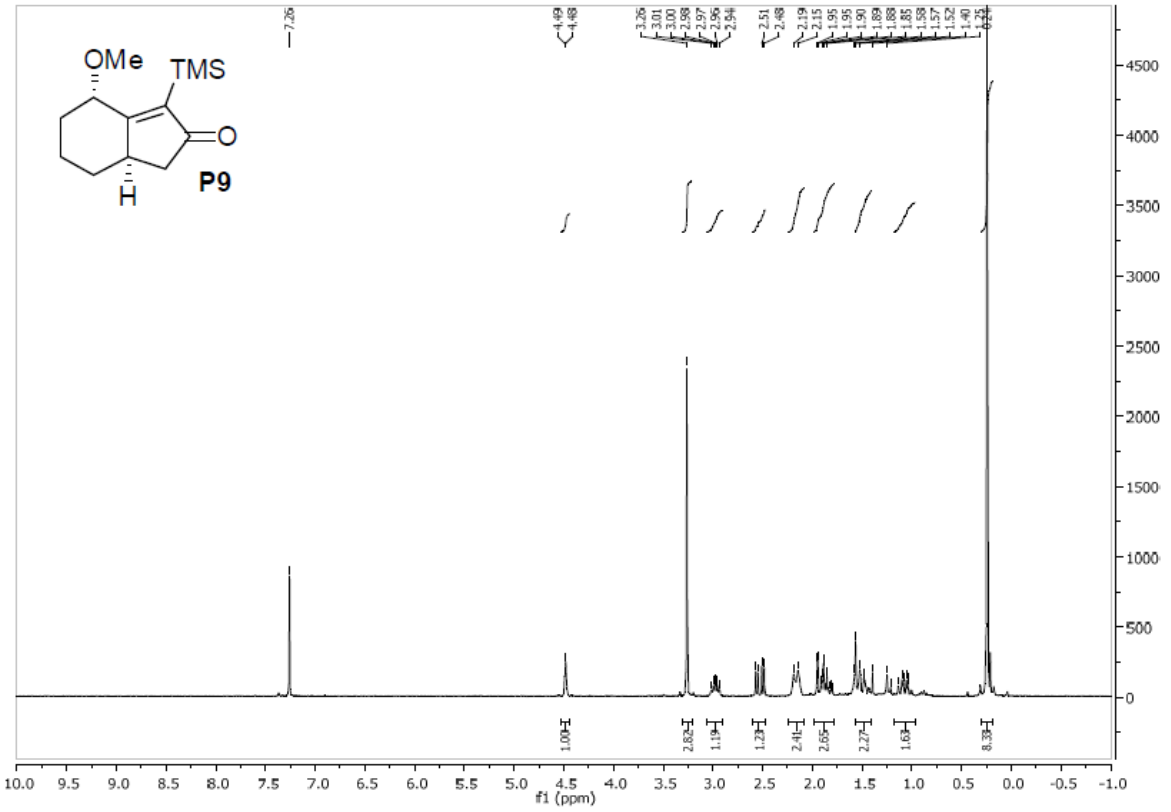

OMe
Ph
O
H
P6
f1 (ppm)

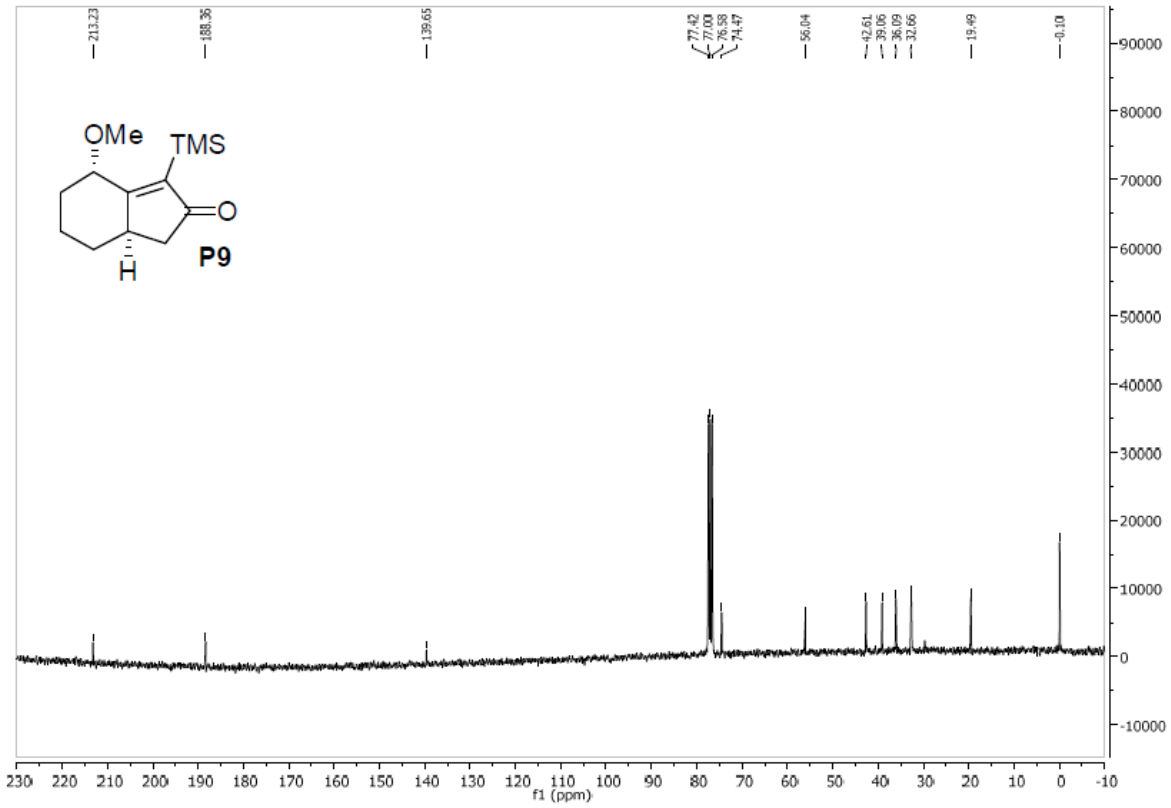

OMe
O
H
P7
f1 (ppm)

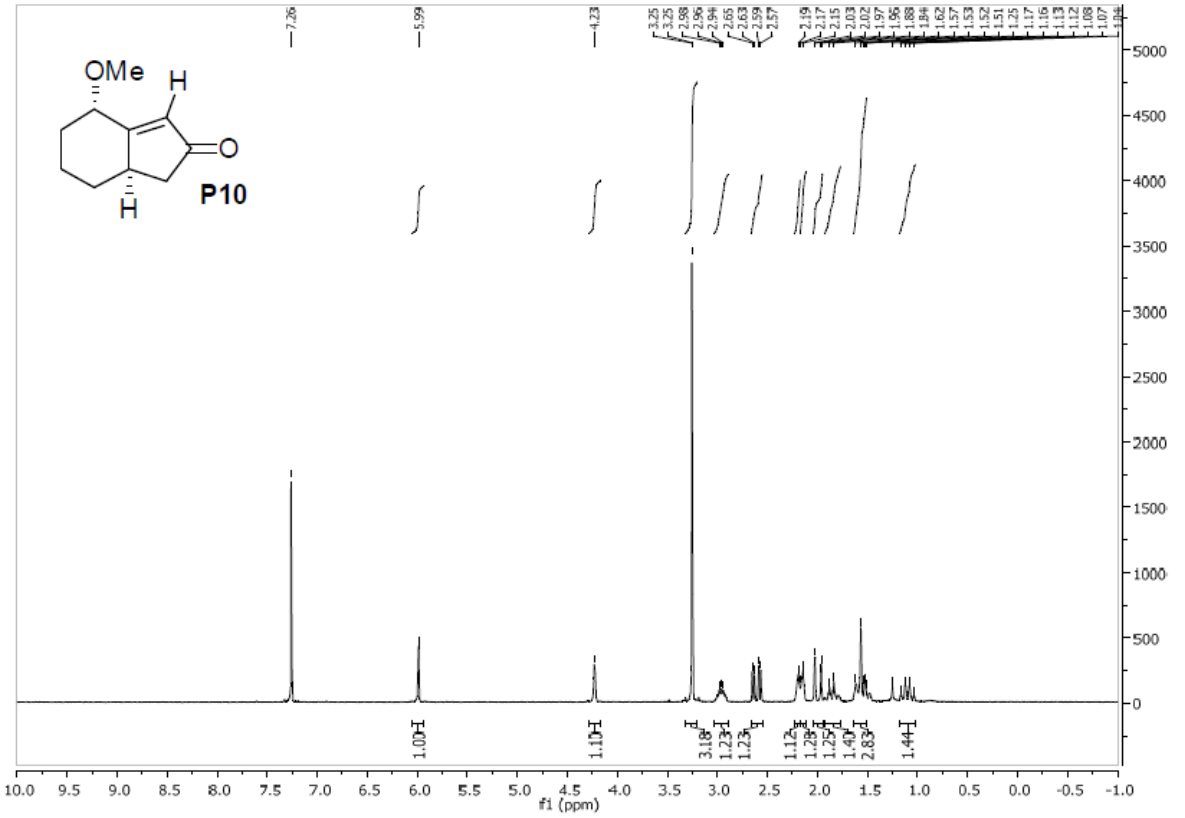

OMe
O
H
P7
f1 (ppm)

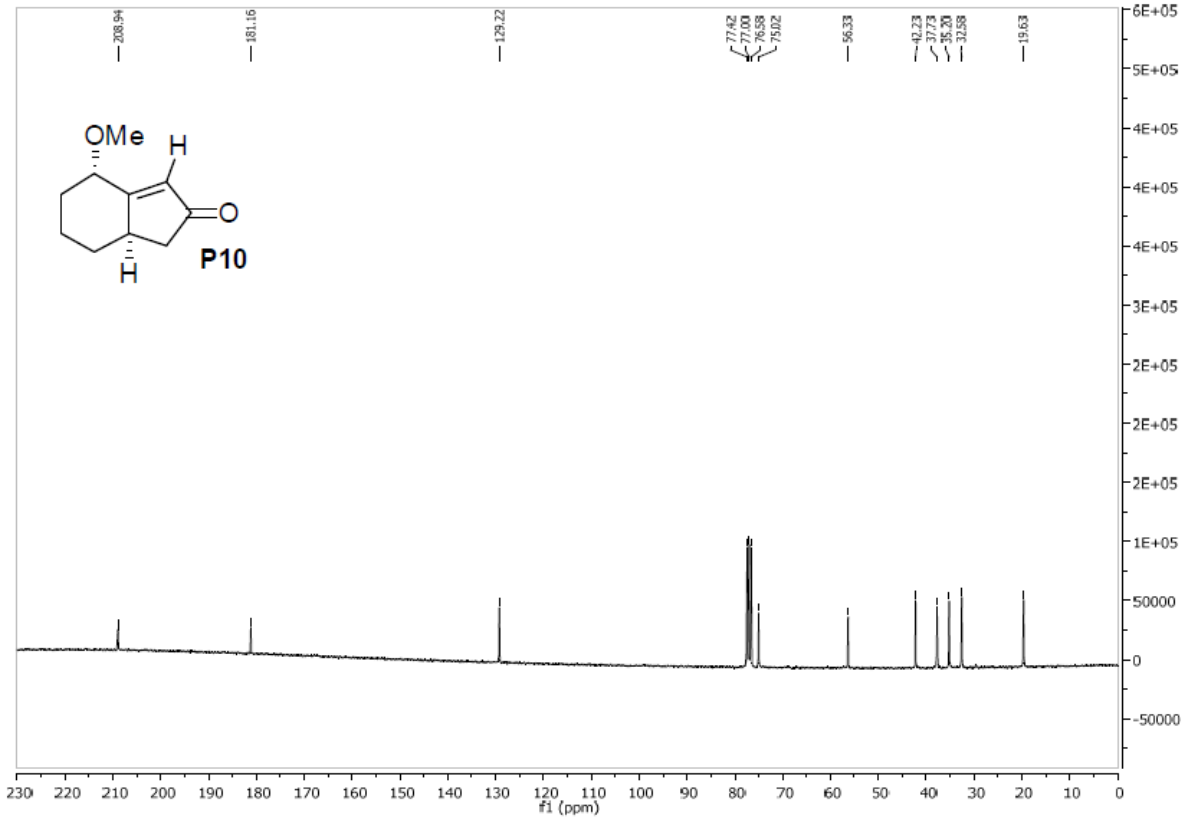

OMe
3
O
H
P8
f1 (ppm)

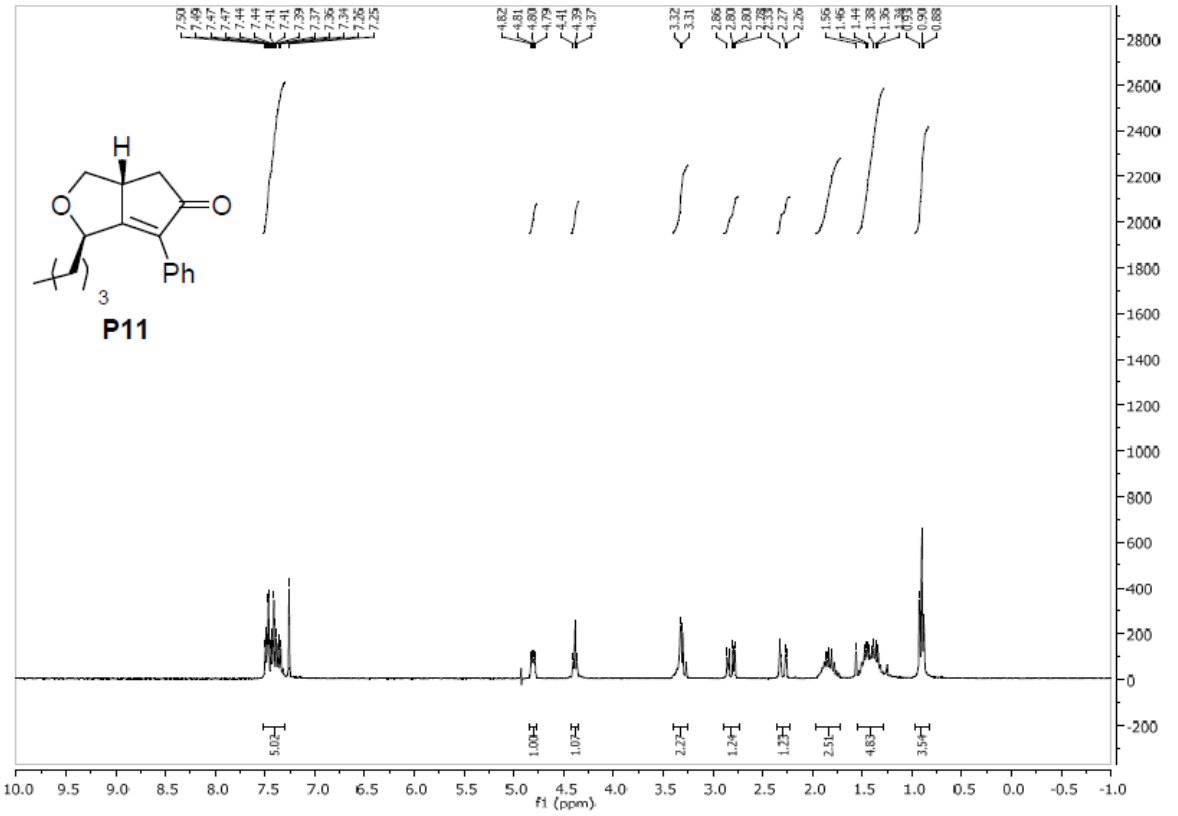

OMe
3
O
H
P8
f1 (ppm)

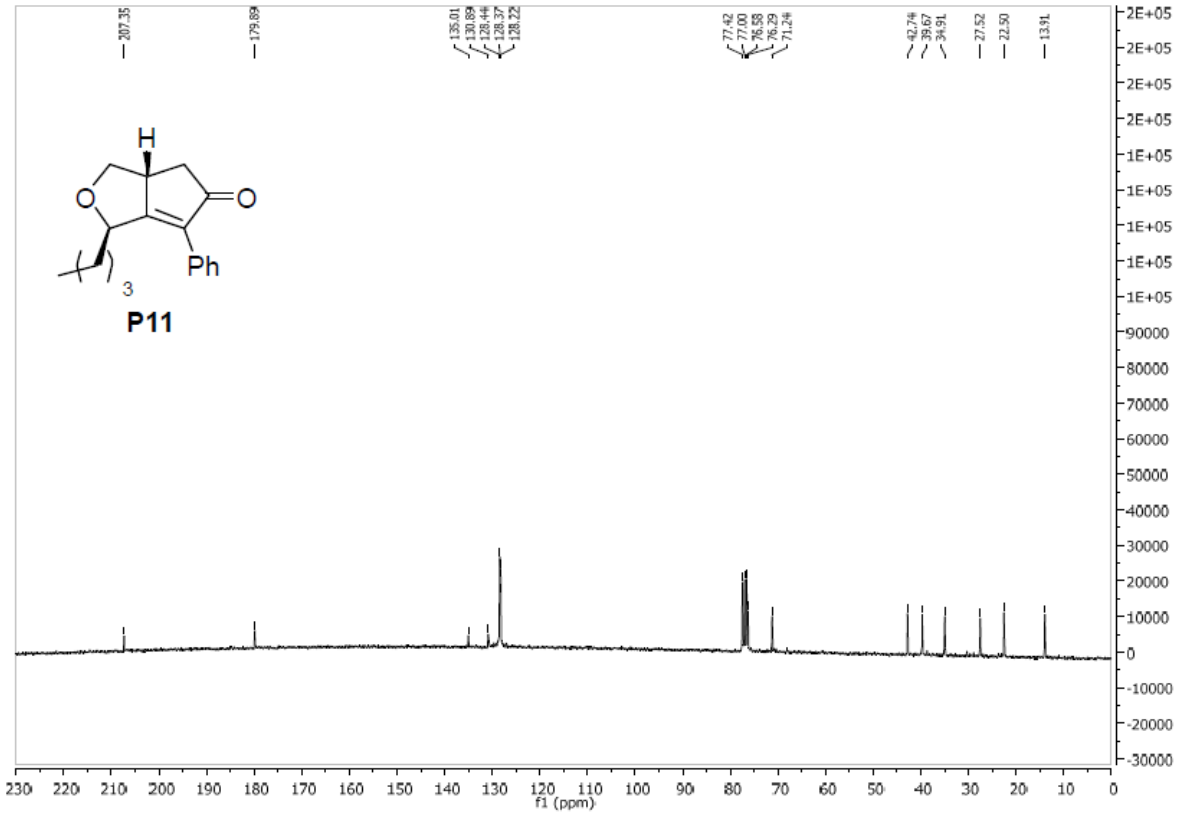

OMe
TMS
O
H
P9
f1 (ppm)

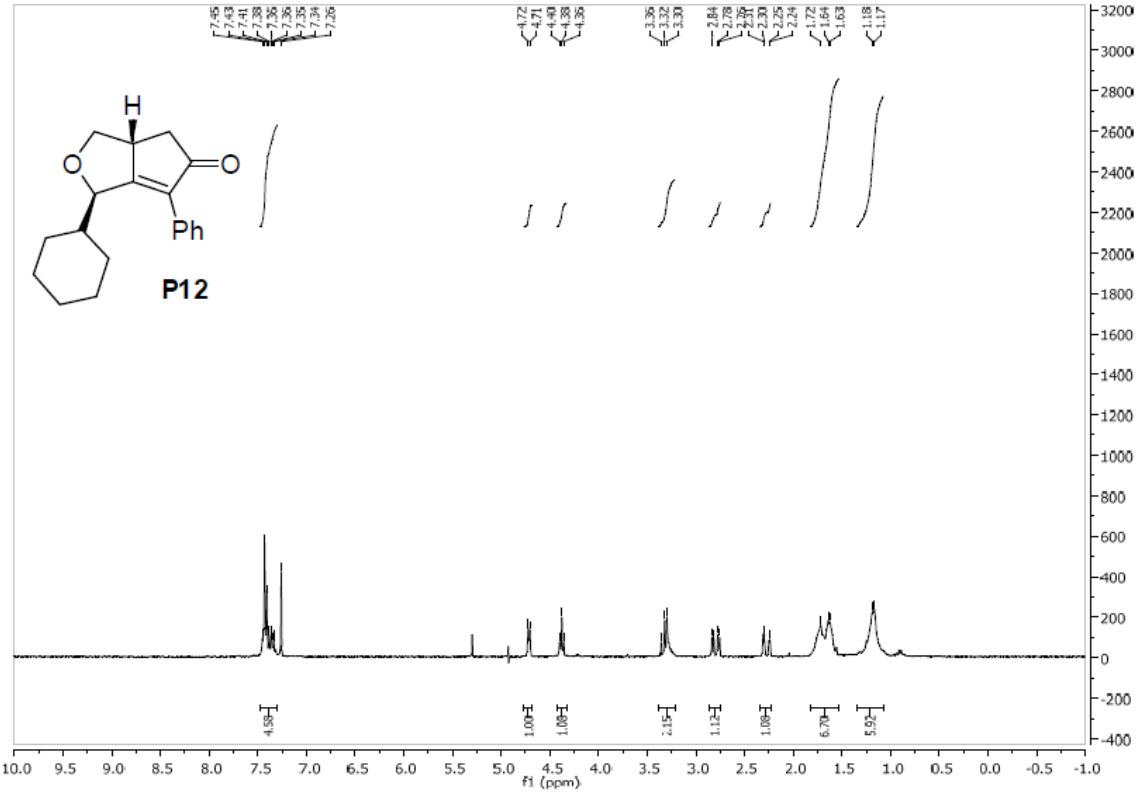

OMe
TMS
O
H
P9
f1 (ppm)

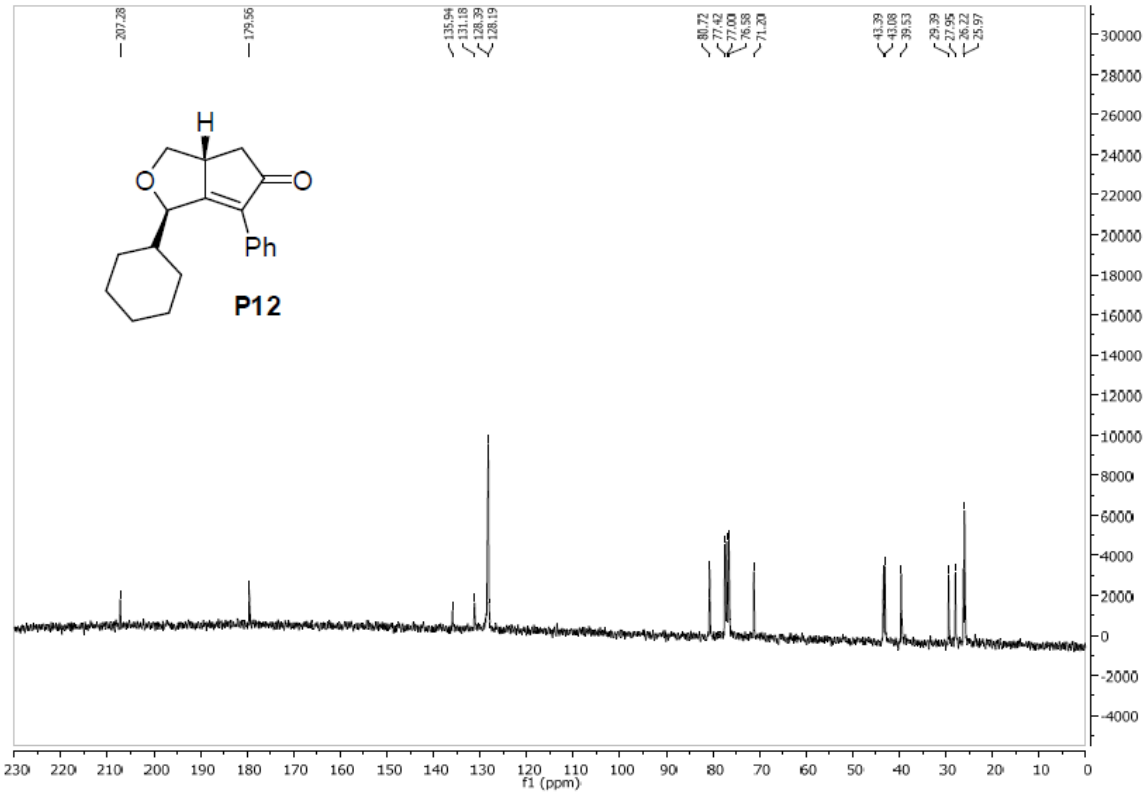

OMe
H
O
H
P10
f1 (ppm)

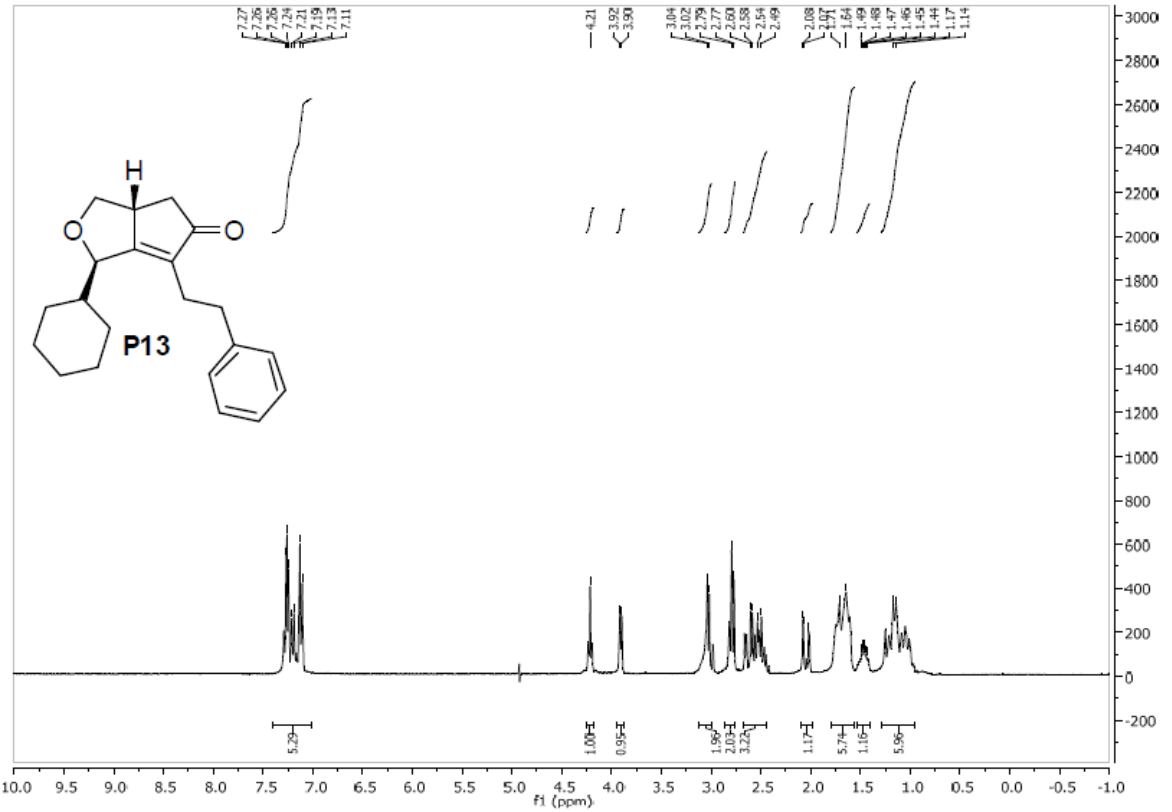

OMe
H
O
H
P10
f1 (ppm)

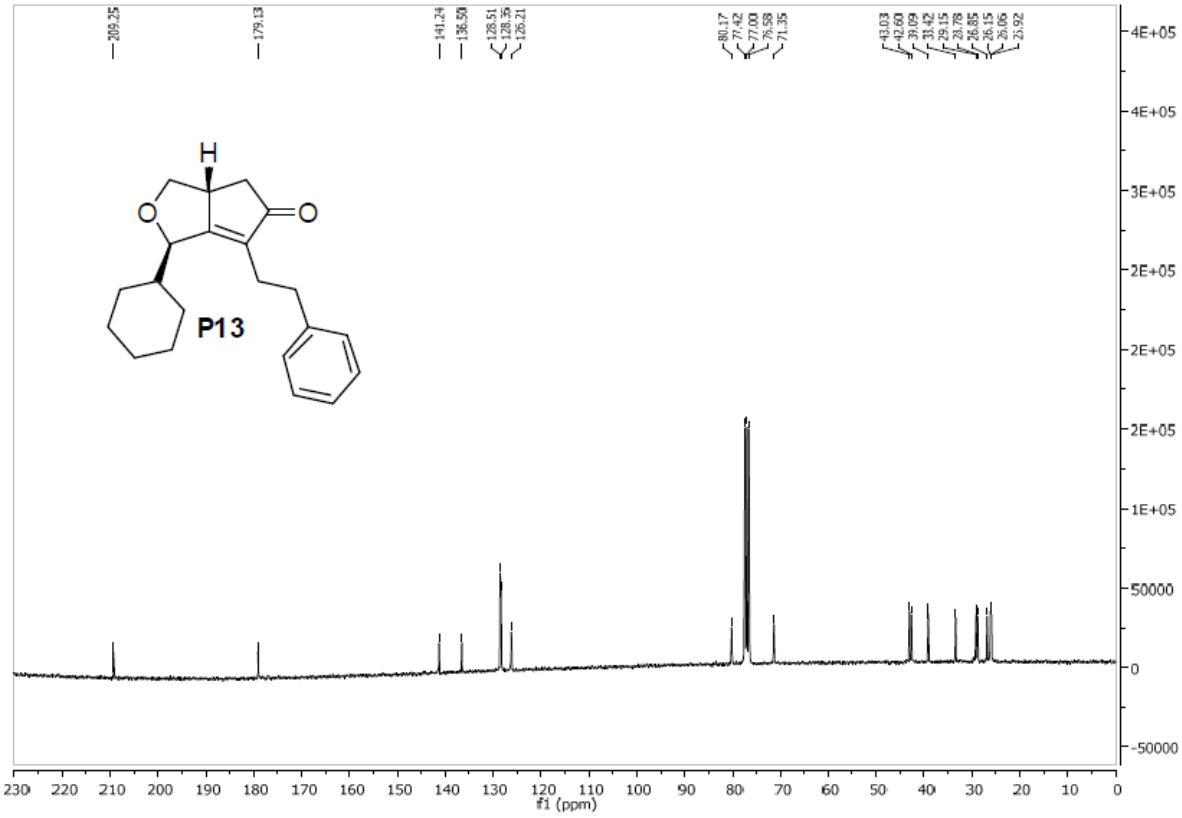

H
O
O
Ph
3
P11
f1 (ppm)

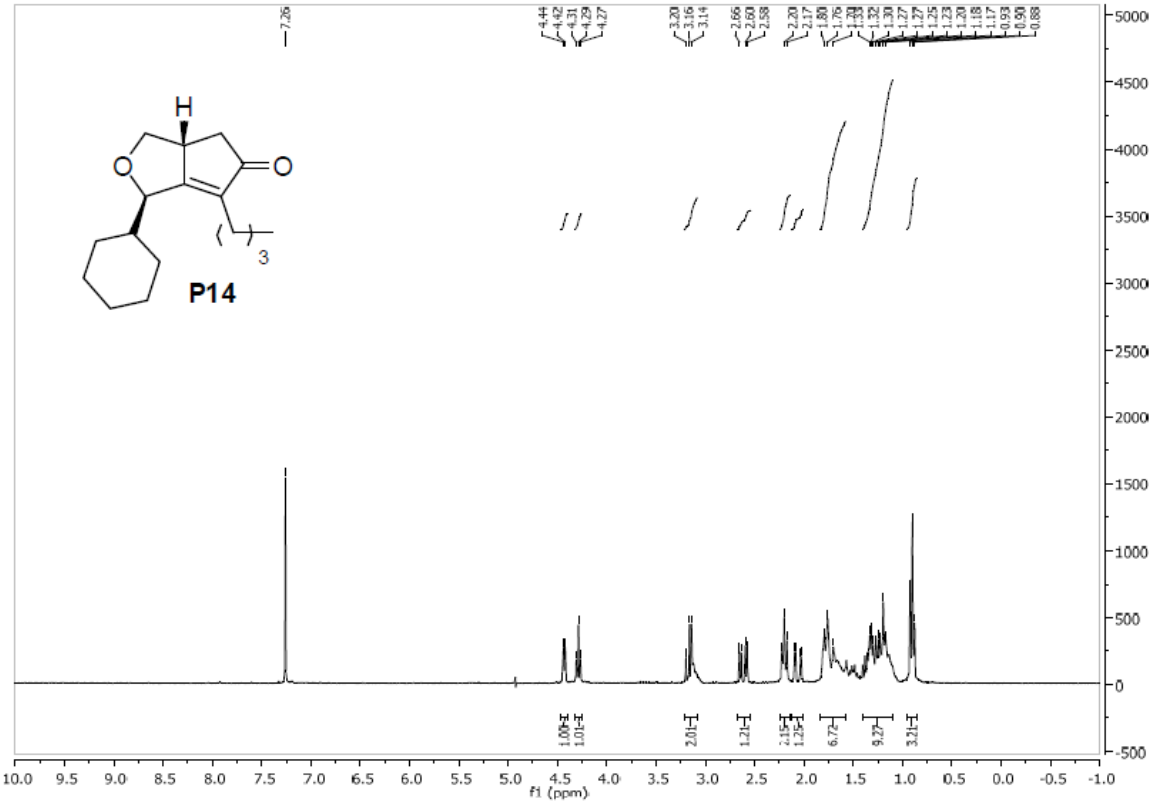

H
O
O
Ph
3
P11
f1 (ppm)

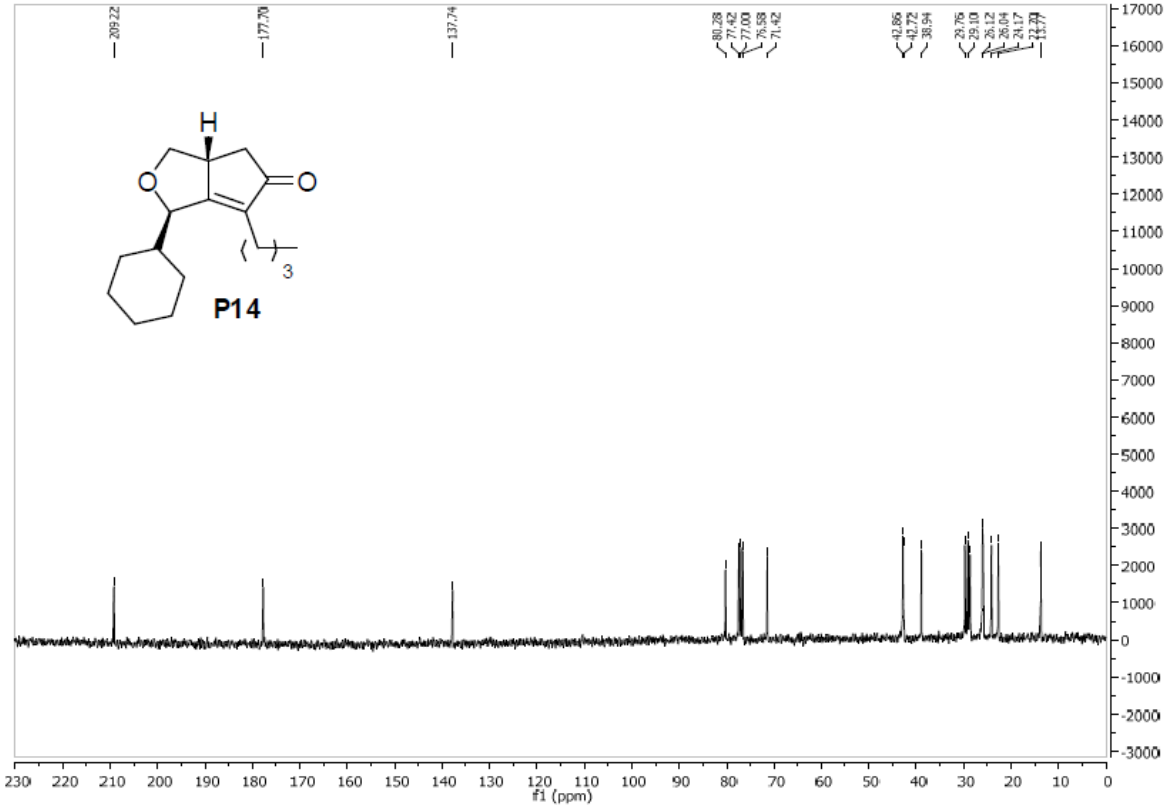

H
O
O
Ph
P12
f1 (ppm)

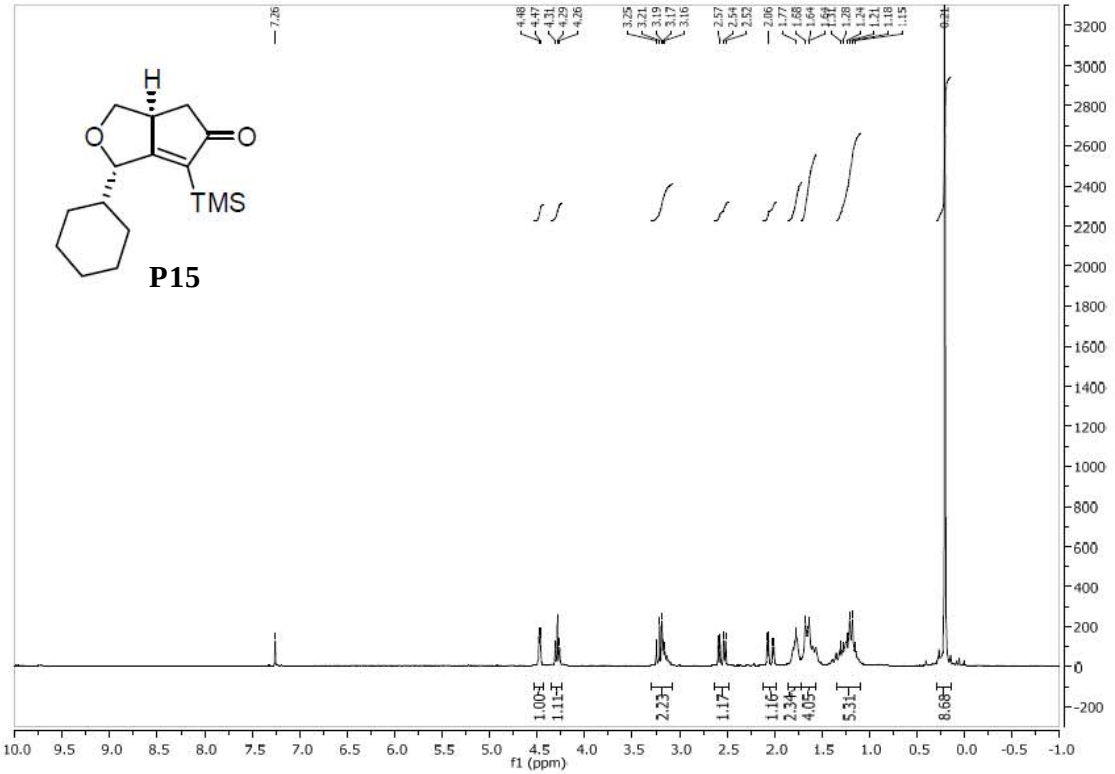

H
O
O
Ph
P12
f1 (ppm)

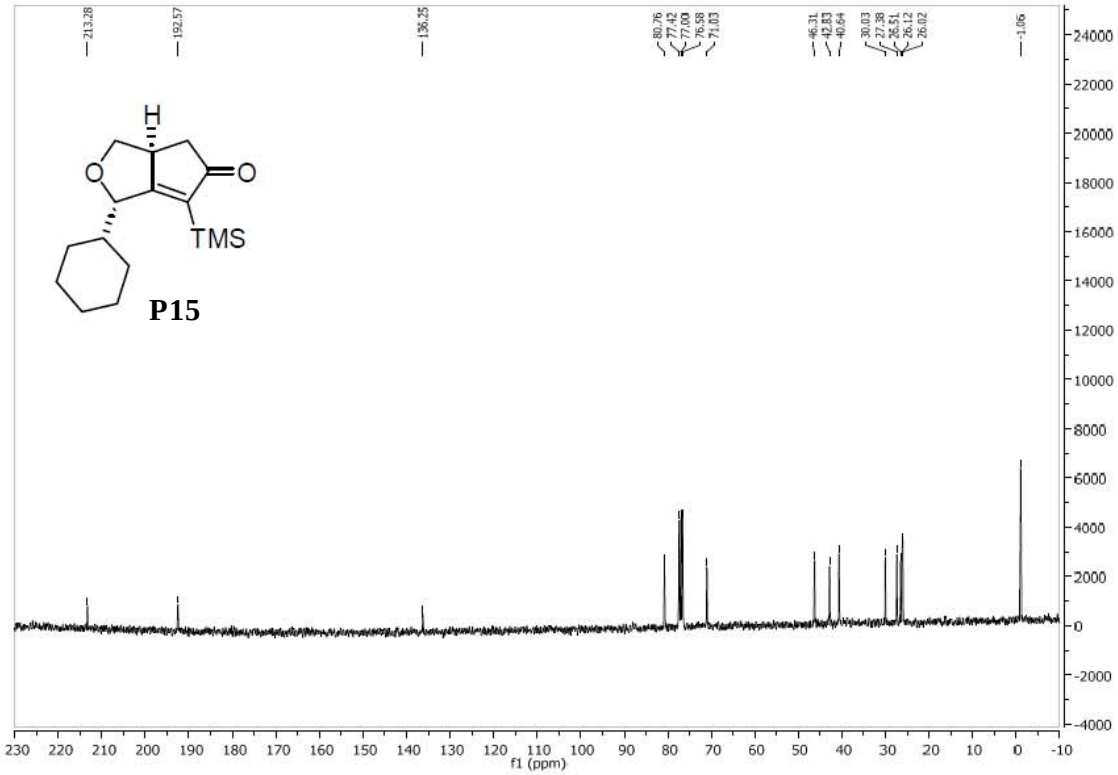

P13
f1 (ppm)

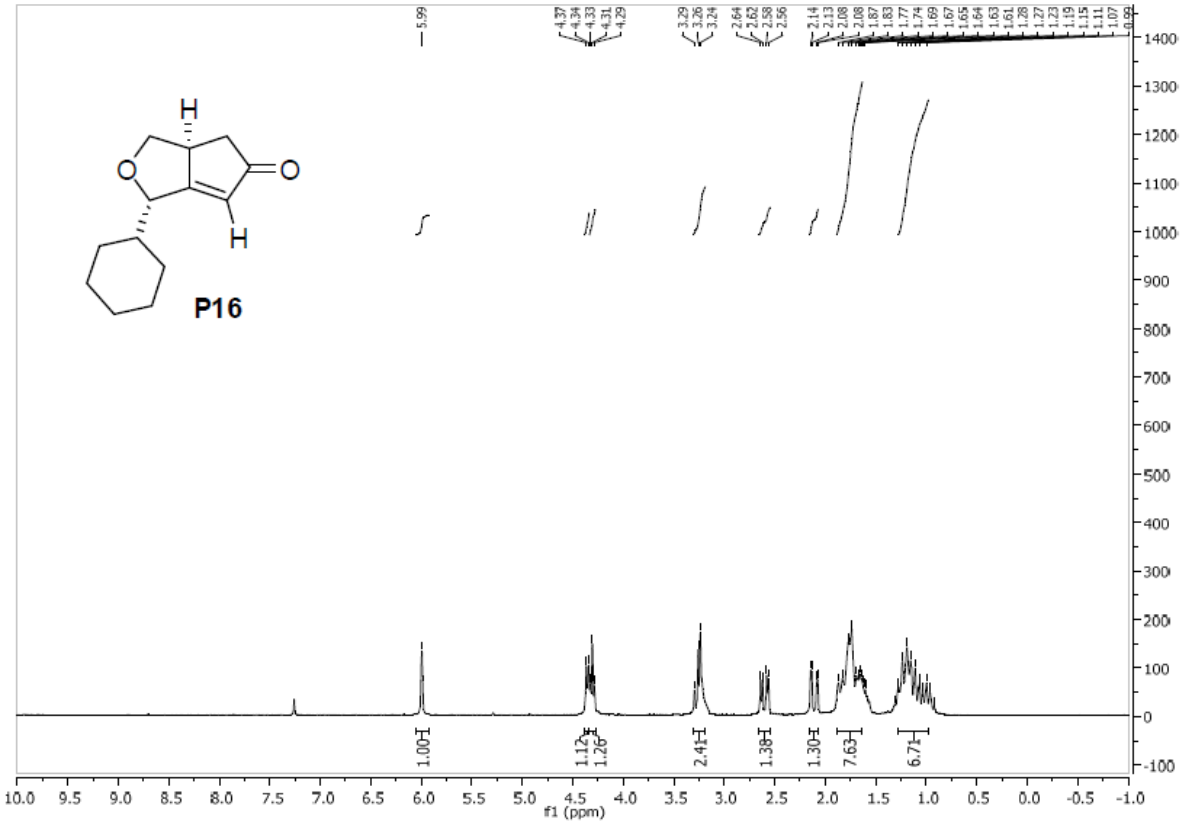

P13
f1 (ppm)

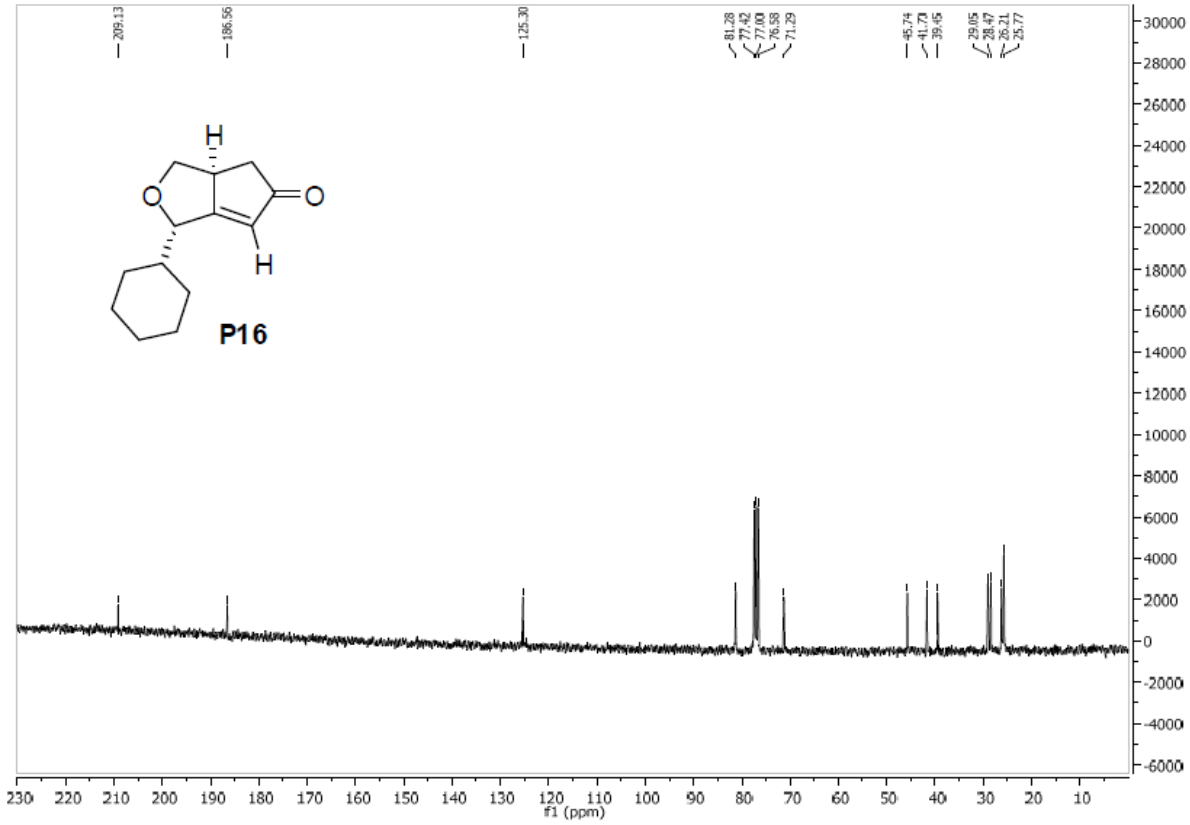

P14
f1 (ppm)


P14
f1 (ppm)


H
O
O
TMS
P15
f1 (ppm)

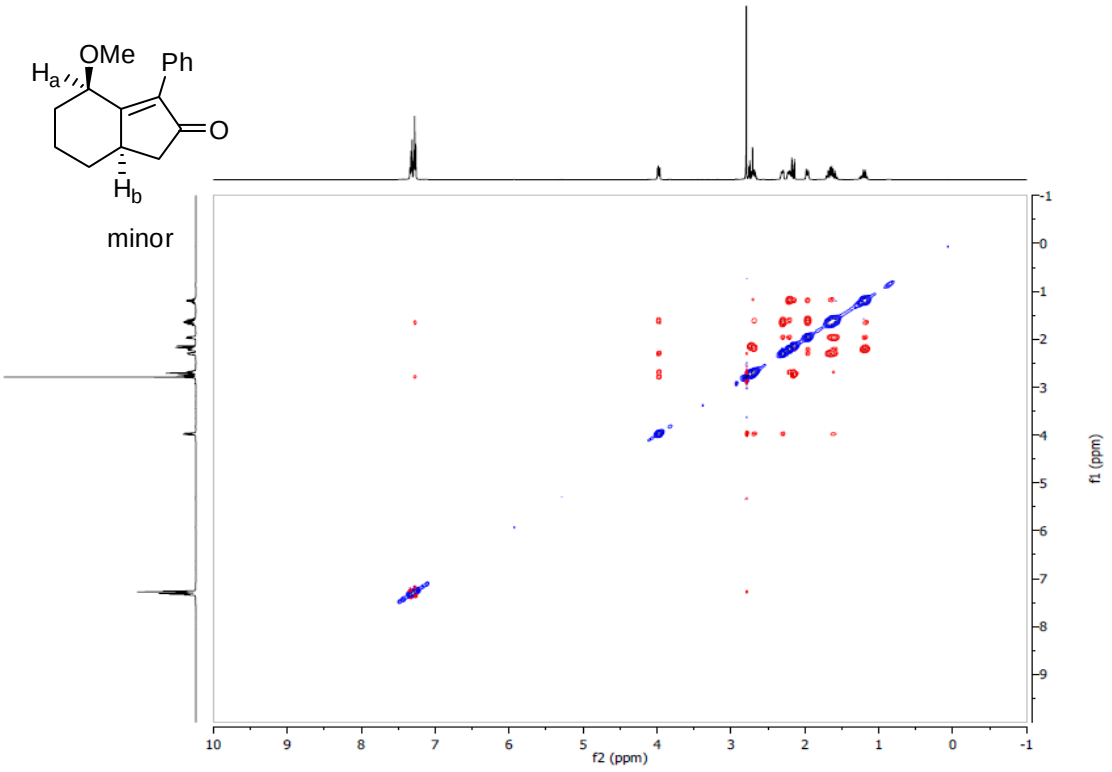

H
O
O
TMS
P15
f1 (ppm)

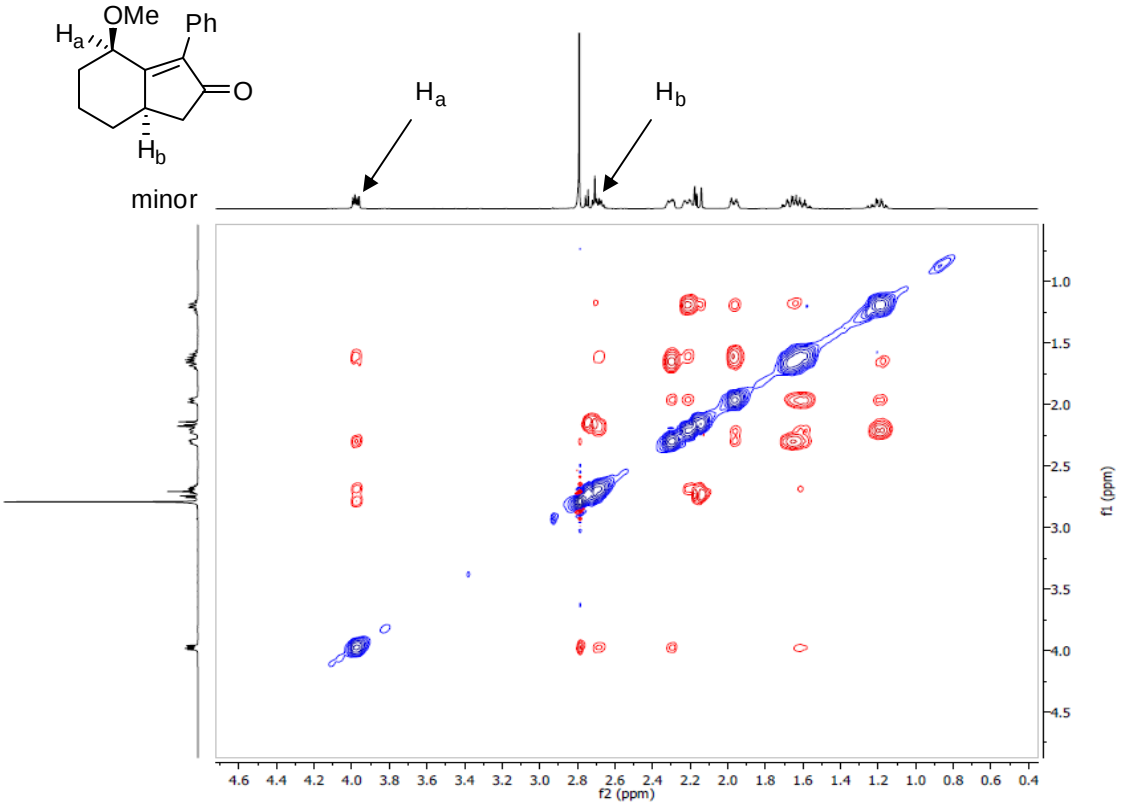

P16
f1 (ppm)


P16
f1 (ppm)

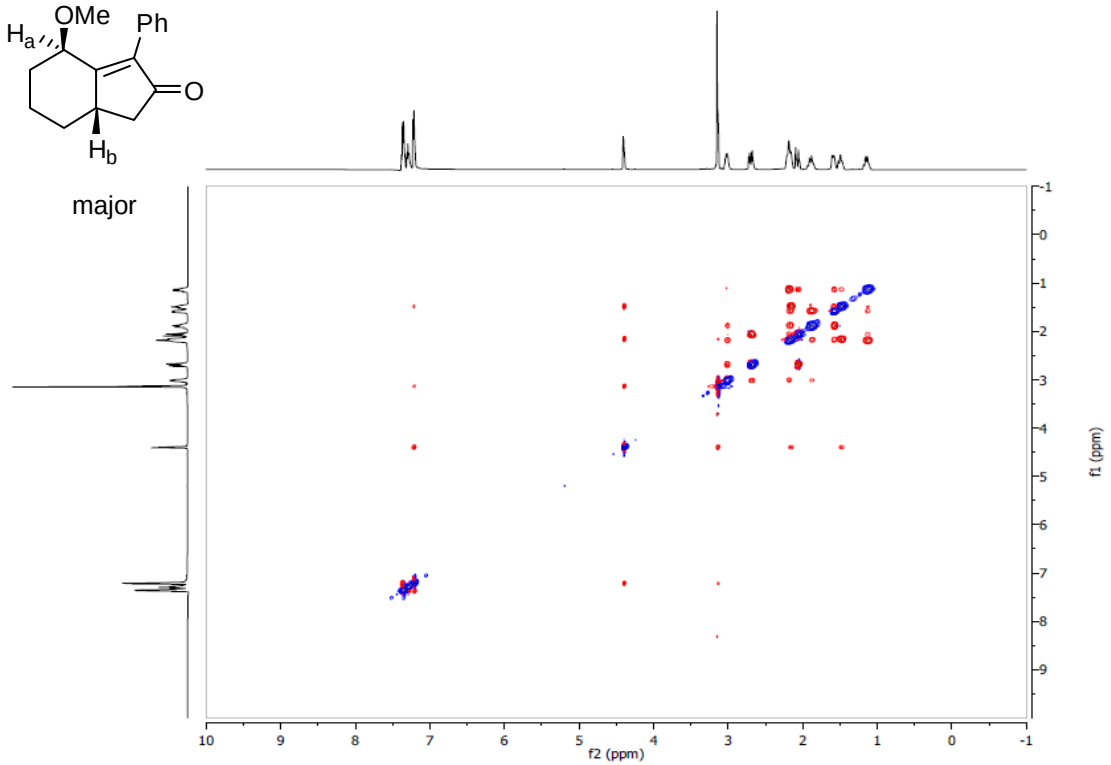
## XIV. NOESY NMR of P6 and P11.

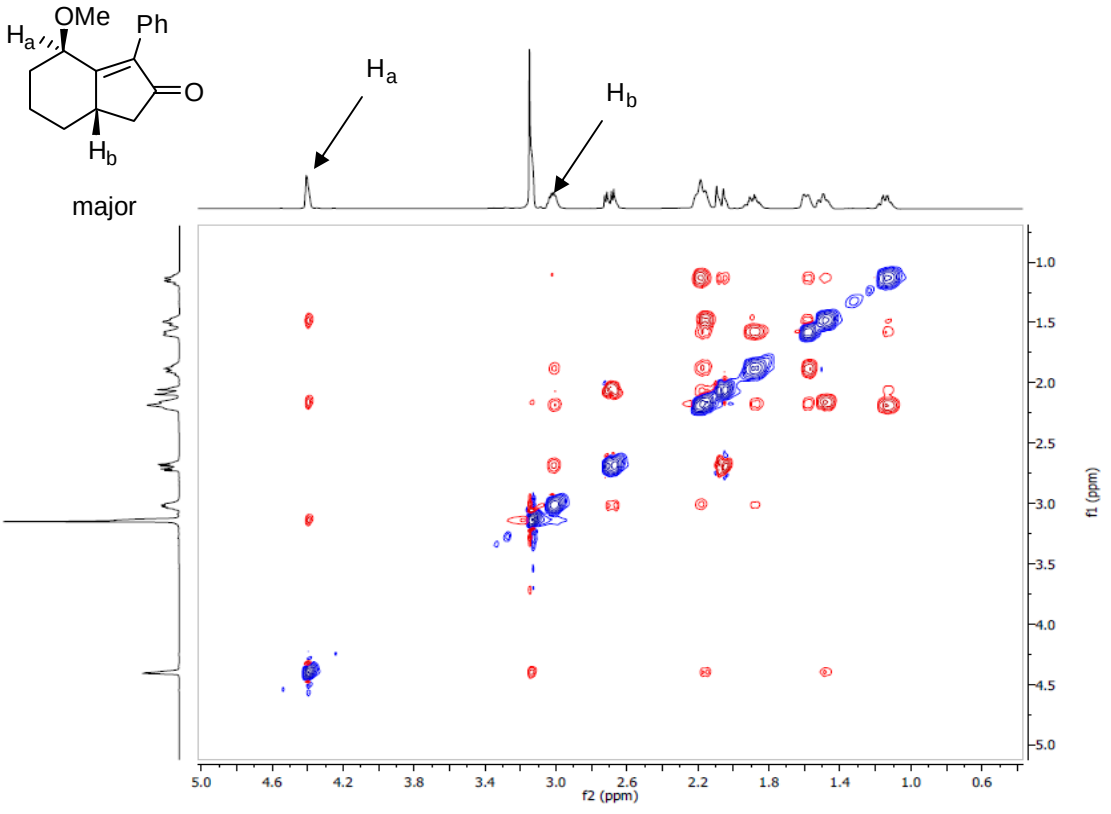
### P6 Minor Diastereomer



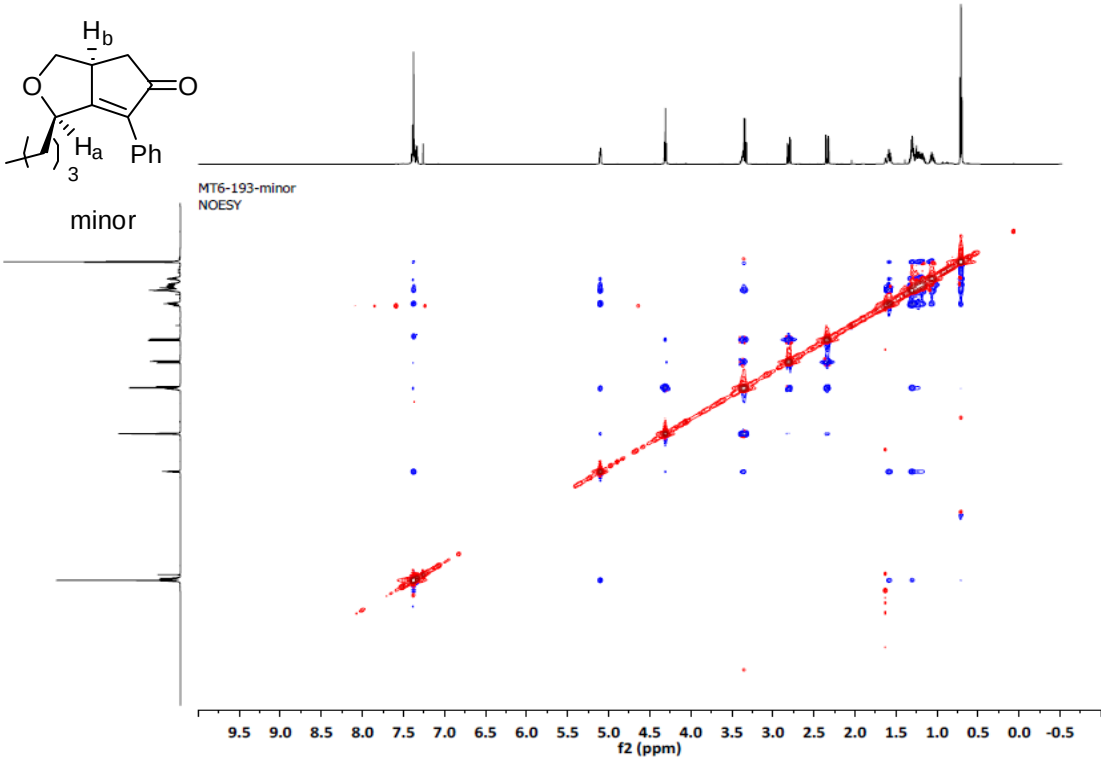



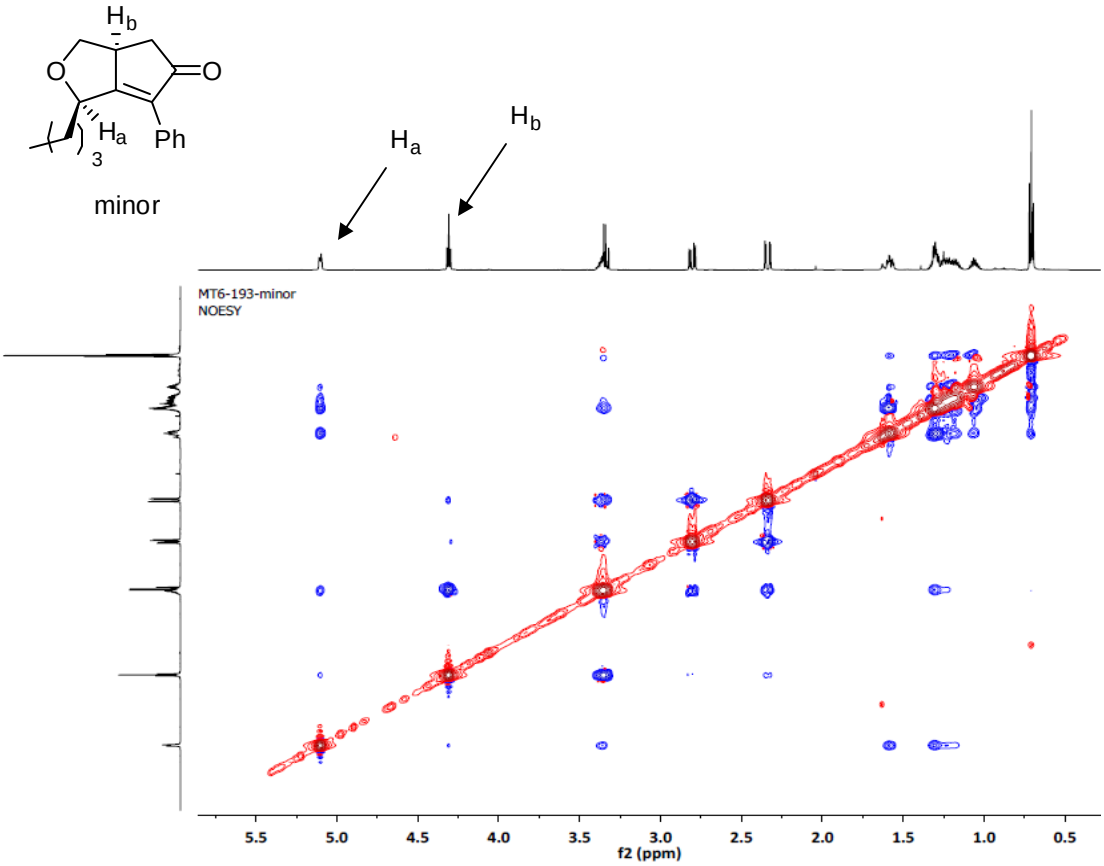
**P6 Major Diastereomer**

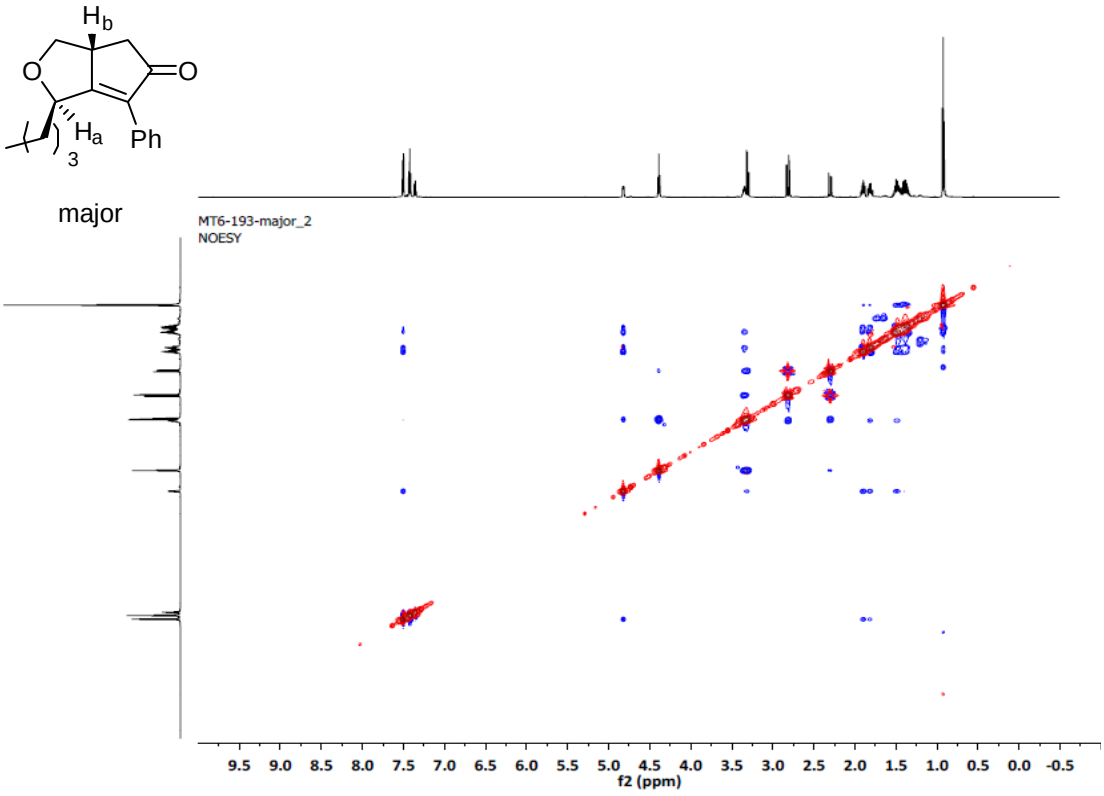


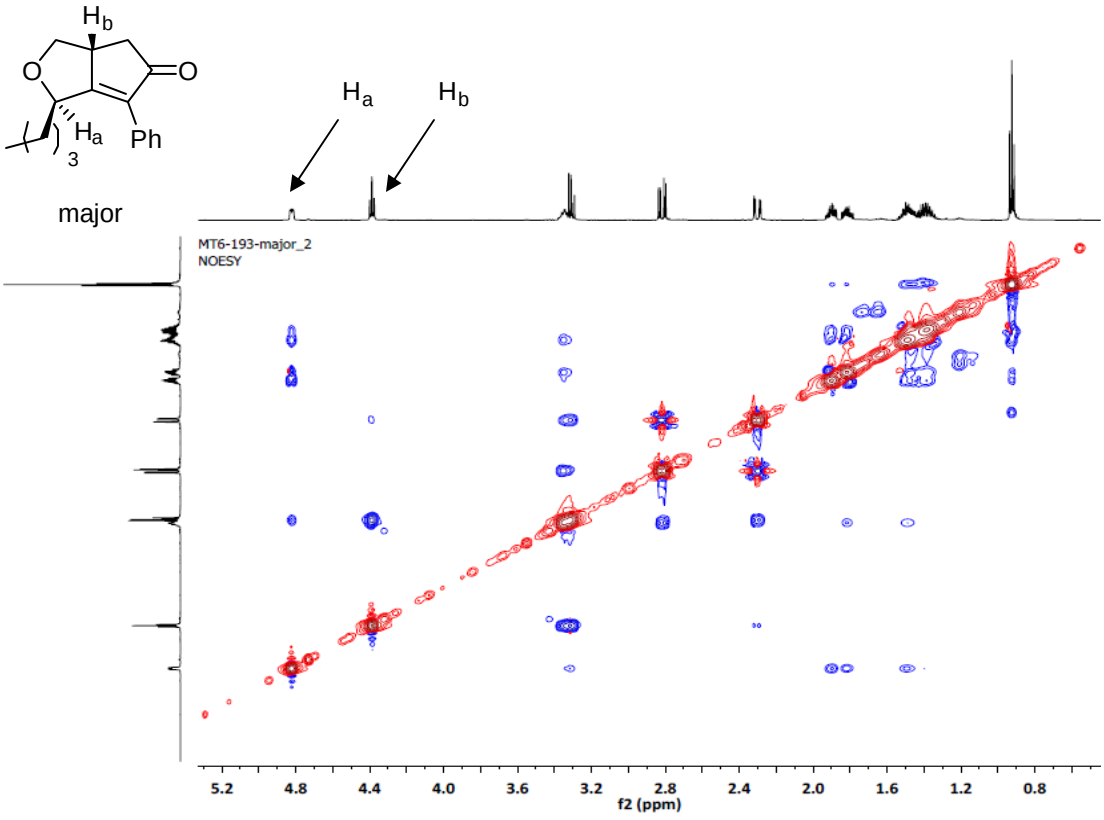



**P11 Minor Diastereomer**




Hb
O
O
Ha
3
Ph
major
MT6-193-major_2
NOESY
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f2 (ppm)


Hb
O
O
Ha
3
Ph
major
Ha
Hb
MT6-193-major_2
NOESY
5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8
f2 (ppm)