

# *Supporting Information*

## **Asymmetric Synthesis of (*E*)-Secobutanolides: Total synthesis and Structural Revision of (+)-Litseakolides F and G**

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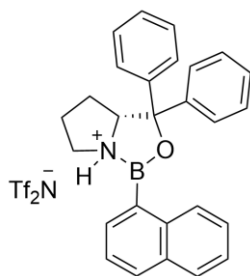
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## 1. General Information

Unless stated otherwise, reactions were carried out under a dry argon atmosphere in vacuum-flame-dried glassware. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254. Flash chromatography was performed using E. Merck silica gel (40-60  $\mu\text{m}$  particle size).  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker instrument at 500 and 125 MHz, respectively. Chemical shift values are reported in ppm from tetramethylsilane as the internal standard (TMS:  $\delta$  7.26 for  $^1\text{H}$  and  $\delta$  77.16 for  $^{13}\text{C}$ ). Data are reported as follows: chemical shifts, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, dd = doublet of doublets, dq = doublet of quartets, app. d = apparent doublet, app. t = apparent triplet, m = multiplet), and coupling constants in Hz. Infrared spectra were recorded on a Bruker Vertex 70. HRMS were recorded on ESI-Q-TOF mass spectrometer (compact, Bruker Daltonic Inc., Bremen, Germany) and LRMS were recorded on a Bruker impact HD quadrupole time-of-flight instrument. Analytical high-performance liquid chromatography (HPLC) was performed on YL 9100 HPLC system using the indicated chiral column (*Daicel Chiralcel*, 4.6 mm  $\times$  25 cm). Optical rotations were determined on a Jasco P-2000 polarimeter PTC-262 at 589 nm.

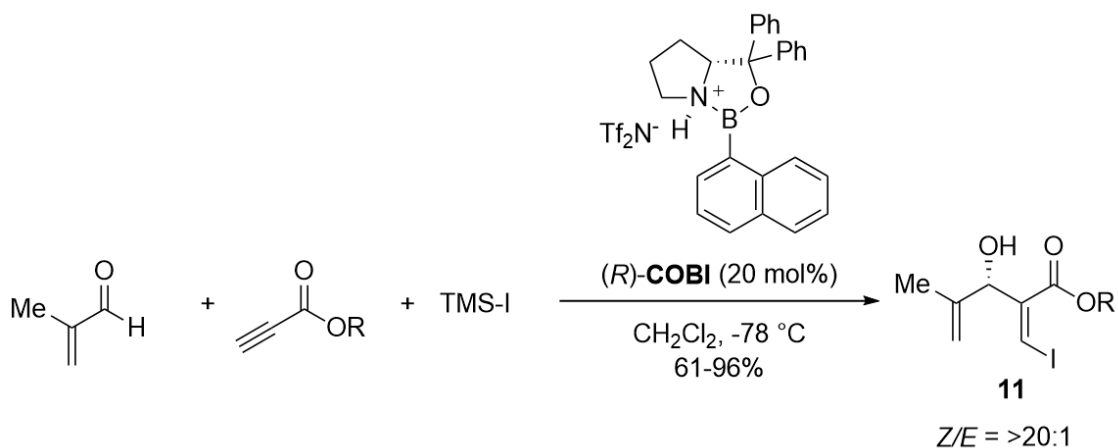
## 2. Preparation of Chiral Oxazaborolidinium Ion Catalyst ((*R*)-COBI)



A 25 mL round-bottomed flask equipped with a stirring bar and a Dean-Stark trap (fully charged with activated 4Å molecular sieves) and fitted on top with a reflux condenser and an argon inlet adaptor, was charged with (*R*)-(+)- $\alpha,\alpha$ -diphenyl-2-pyrrolidinemethanol (0.30 mmol), 1-naphthyl boronic acid (0.30 mmol) and 20 mL of toluene (for (*S*)-COBI catalyst, (*S*)-(-)- $\alpha,\alpha$ -diphenyl-2-pyrrolidinemethanol was used). The resulting mixture was heated to reflux under an argon atmosphere. After 3 hours, the reaction mixture was cooled to 60 °C, and the addition funnel and condenser were quickly replaced with a short-path distillation head. The mixture was concentrated by distillation (air-cooling) to a volume of 5.0 mL. This distillation protocol was repeated three times by re-charging with 3 x 5.0 mL of toluene. The solution was then allowed to cool to room temperature, and the distillation head was quickly replaced with a vacuum adaptor. Concentration *in vacuo* (0.10 mmHg, 0.5 hours) afforded the corresponding oxazaborolidine as clear oil.

To an aliquot of oxazaborolidine precursor (0.30 mmol) in 1.0 mL of dichloromethane at -78 °C, bistriflimide (0.20 M solution in dichloromethane, freshly prepared, 0.25 mmol, 1.25 mL) was added dropwise under argon atmosphere. After 15-20 minutes at -78 °C, a homogeneous catalyst solution was ready for use in the asymmetric synthesis of *Z*-iodo Morita-Baylis-Hilman (MBH) esters.

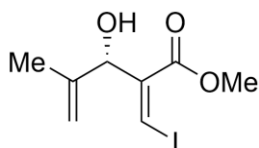
### 3. General Procedure for Enantioselective Synthesis of MBH ester 11



To a *(R)*-COBI catalyst solution (7.25 mL dichloromethane), methacrolein (1.25 mmol, 1.0 equiv) was added, followed by alkyl propiolate (6.25 mmol, 5.0 equiv) and trimethyl iodide (1.50 mmol, 1.2 equiv) at -78 °C. The resulting mixture was stirred at the same temperature until the complete consumption of methacrolein under an argon atmosphere. After the reaction was complete, the reaction mixture was quenched with *aq.* HCl (2 M, 6 mL) and ethyl acetate (6 mL) and vigorously stirred for 35 minutes at 0 °C. After the complete removal of the TMS group, the aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated *in vacuo*. The residue was purified by column chromatography (10% ethyl acetate in hexane) on silica gel to afford the desired products as a colorless oil.

#### 4. Characterization of Chiral MBH esters

##### methyl (*S,Z*)-3-hydroxy-2-(iodomethylene)-4-methylpent-4-enoate (**11a**(*Z*))



The compound was prepared according to the general procedure. Purification by column chromatography (10% ethyl acetate in hexane) afforded the desired product (61%) as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.21 (d, *J* = 1.2 Hz, 1H), 5.07 (d, *J* = 0.7 Hz, 1H), 4.98 (d, *J* = 0.5 Hz, 1H), 4.89 (d, *J* = 5.2 Hz, 1H), 3.81 (s, 3H), 2.58 (d, *J* = 5.8 Hz, 1H), 1.69 (s, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 166.8, 144.6, 143.7, 113.6, 85.9, 77.7, 52.1, 18.3.

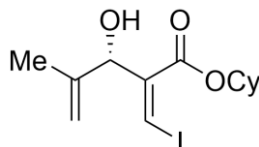
**IR**  $\nu_{\max}$  3007, 2990, 2361, 2342, 1496, 1276, 1261, 764, 750, 545, 477, 456, 432 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for C<sub>8</sub>H<sub>11</sub>IO<sub>3</sub>Na: *m/z* 304.9645 ([M+Na]<sup>+</sup>), found: *m/z* 304.9647 ([M+Na]<sup>+</sup>).

**HPLC**: ee = 91%, Chiralcel OJ-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 254nm, *t*<sub>R</sub> = 11.7 min (minor) and *t*<sub>R</sub> = 13.1 min (major).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = -9.2 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

##### cyclohexyl (*S,Z*)-3-hydroxy-2-(iodomethylene)-4-methylpent-4-enoate (**11c**(*Z*))



The compound was prepared according to the general procedure. Purification by column chromatography (10% ethyl acetate in hexane) afforded the desired product (96%) as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.13 (d, *J* = 1.2 Hz, 1H), 5.07 (d, *J* = 1.1 Hz, 1H), 4.98 – 4.97 (m, 1H), 4.94 (td, *J* = 9.0 Hz, 4.5 Hz, 1H), 4.85 (d, *J* = 6.2 Hz, 1H), 2.63 (d, *J* = 6.3 Hz, 1H), 1.93 – 1.87 (m, 2H), 1.79 – 1.73 (m, 2H), 1.71 (s, 3H), 1.56 – 1.49 (m, 3H) 1.44 – 1.27 (m, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 165.8, 144.6, 143.6, 113.3, 84.7, 77.9, 74.4, 31.4, 31.4, 25.3, 23.6, 18.3.

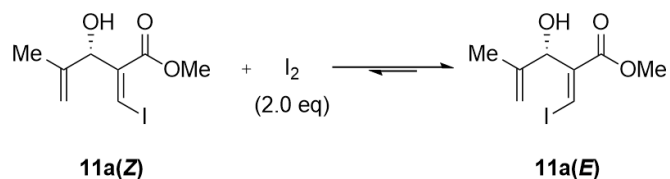
**IR**  $\nu_{\max}$  2941, 2863, 2358, 2336, 2121, 1713, 1455, 1231, 1109, 1013, 911, 807 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for C<sub>13</sub>H<sub>19</sub>IO<sub>3</sub>Na: *m/z* 373.0271 ([M+Na]<sup>+</sup>), found: *m/z* 373.0271 ([M+Na]<sup>+</sup>).

**HPLC**: ee = 93%, Chiralpak<sup>®</sup> IC, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm, *t*<sub>R</sub> = 6.1 min (major) and *t*<sub>R</sub> = 6.5 min (minor).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = for (*R*) -4.8 (*c* = 1.0, CHCl<sub>3</sub>, 93% ee), for (*S*) +4.9 (*c* = 1.0, CHCl<sub>3</sub>, 93% ee).

## 5. Photochemical and Thermal Isomerization Screening Table<sup>a</sup>



entry	condition	additive	time	solvent	yield (%) <sup>b</sup>
1	<i>hν</i>	-	3.5h	CH <sub>2</sub> Cl <sub>2</sub>	69
2 <sup>c</sup>	<i>hν</i>	-	3.5h	CH <sub>2</sub> Cl <sub>2</sub>	45
3	40 °C	-	18h	CH <sub>2</sub> Cl <sub>2</sub>	64
4	50 °C	-	18h	THF	N.R
5	50 °C	-	18h	PhMe	N.R
6	50 °C	-	18h	DCE	80
7	<i>hν</i> , 50 °C	-	18h	CH <sub>2</sub> Cl <sub>2</sub>	46
8	<i>hν</i> , 50 °C	-	18h	DCE	27
9 <sup>d</sup>	50 °C	NaI	18h	DCE	Trace
10 <sup>d</sup>	50 °C	<i>t</i> -Bu <sub>4</sub> I	18h	DCE	Trace
11	50 °C	NaHCO <sub>3</sub>	18h	DCE	50
12	50 °C	SnCl <sub>4</sub>	18h	DCE	20
13 <sup>e</sup>	25 °C	-	18h	DCE	78
14 <sup>f</sup>	<i>hν</i>	TEMPO	3.5h	CH <sub>2</sub> Cl <sub>2</sub>	0
15 <sup>f</sup>	50 °C	TEMPO	18h	DCE	80

<sup>a</sup>Photochemical conditions: the reaction was performed in quartz round bottom flask at -78 °C irradiation by UV lamp with **11a(Z)** (0.059 mmol, 1.0 equiv) and iodine (0.118 mmol, 2.0 equiv), Thermal conditions: the reaction was performed in round bottom flask with **11a(Z)** (0.216 mmol, 1.0 equiv) and iodine (0.432 mmol, 2.0 equiv). <sup>b</sup>Isolated yield. <sup>c</sup>The reaction was performed with 0.216 mmol of **11a(Z)**. <sup>d</sup>The reaction was performed with absence of Iodine. <sup>e</sup>The reaction was performed with cyclohexyl ester. <sup>f</sup>The reaction was performed using 4.0 equiv of TEMPO reagent. (DCE = 1,2-dichloroethane, TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl)

## 6. General Procedure for *Z*→*E* isomerization

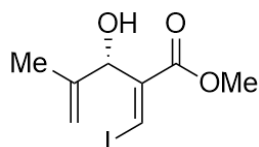
### 6.1 General Procedure for (*S,E*)- $\beta$ -Iodo MBH Ester **11(E)** using Photo Isomerization.

Iodine (0.118 mmol) was added to a CH<sub>2</sub>Cl<sub>2</sub> solution (15 mL) of (*S,Z*)- $\beta$ -Iodo MBH Ester **11(Z)** (0.059 mmol) in a quartz round-bottom flask and then the reaction mixture was cooled to -78 °C. This solution was irradiated with a 300W OSRAM ULTRA-VITALUX lamp for 30 min and took a 15 min break. This process was repeated for seven times and more. To remove Iodine, the resulting solution was quenched by saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (10 mL) and stirred while the solution turned colorless. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 5 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by silica gel (hexane/ethyl acetate = 20:1) to afford the desired product.

### 6.2 General Procedure for (*S,E*)- $\beta$ -Iodo MBH Ester **11(E)** using Heat.

Iodine (0.432 mmol) was added to a 1,2-dichloroethane solution (44 mL) of (*S,Z*)- $\beta$ -Iodo MBH Ester **2(Z)** (0.216 mmol) and then the reaction mixture was heated to 50 °C for 18 hours. To remove Iodine, the resulting solution was quenched by saturated Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> aqueous solution (20 mL) and stirred while the solution turned colorless. The organic layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 20 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by silica gel (hexane/ethyl acetate = 20:1) to afford the desired product.

### methyl (*S,E*)-3-hydroxy-2-(iodomethylene)-4-methylpent-4-enoate (**11a(E)**)



The compound was prepared according to the general procedure. Purification by column chromatography (10% ethyl acetate-hexane) afforded the desired product (80%) as colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (s, 1H), 5.07 (d, *J* = 11.2 Hz, 1H), 5.03 (s, 1H), 4.95 (s, 1H), 3.91 (d, *J* = 11.4 Hz, 1H), 3.78 (s, 3H), 1.78 (s, 3H).

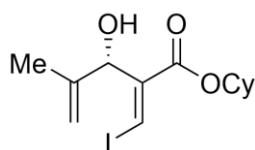
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  163.7, 144.3, 141.7, 111.1, 101.6, 78.0, 52.6, 19.7.

IR  $\nu_{\max}$  3007, 2989, 1624, 1276, 1261, 1077, 764, 750, 537, 477 cm<sup>-1</sup>.

HRMS (ESI-QTOF): Calcd. for C<sub>8</sub>H<sub>11</sub>IO<sub>3</sub>Na: *m/z* 304.9645 ([M+Na]<sup>+</sup>), found: *m/z* 304.9646 ([M+Na]<sup>+</sup>).

$[\alpha]_{\text{D}}^{20} = +83.7$  (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

### cyclohexyl (*S,E*)-3-hydroxy-2-(iodomethylene)-4-methylpent-4-enoate (**11c(E)**)





The compound was prepared according to the general procedure. Purification by column chromatography (10% ethyl acetate-hexane) afforded the desired product (78%) as colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.99 (s, 1H), 5.06 (dd, *J* = 11.1 Hz, 1H), 5.03 (dt, *J* = 2.0 Hz, 1.0 Hz, 1H), 4.94 (h, *J* = 1.5 Hz, 1H), 4.86 (tt, *J* = 9.0 Hz, 3.8 Hz, 1H), 4.00 (d, *J* = 11.3 Hz, 1H), 1.90 – 1.81 (m, 2H), 1.77 (s, 3H), 1.73 – 1.70 (m, 2H), 1.58 – 1.50 (m, 1H), 1.49 – 1.46 (m, 2H), 1.42 – 1.34 (m, 2H), 1.33 – 1.24 (m, 1H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 162.8, 144.5, 142.3, 111.0, 100.8, 78.0, 74.5, 31.56, 31.43, 25.4, 23.71, 23.69, 19.7.

**HRMS** (ESI-QTOF): Calcd. for C<sub>13</sub>H<sub>19</sub>IO<sub>3</sub>Na: *m/z* 373.0271 ([M+Na]<sup>+</sup>), found: *m/z* 373.0271 ([M+Na]<sup>+</sup>).

**HPLC**: ee = 93%, Chiralpak<sup>®</sup> IC, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm, *t*<sub>R</sub> = 5.9 min (minor) and *t*<sub>R</sub> = 6.3 min (major).

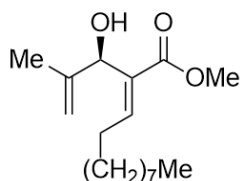
**IR** ν<sub>max</sub> 2941, 2863, 2358, 2336, 2121, 1713, 1456, 1232, 1109, 1013, 911, 807 cm<sup>-1</sup>.

[α]<sub>D</sub><sup>20</sup> = for (*R*) +10.2 (*c* = 1.0, CHCl<sub>3</sub>, 93% ee), for (*S*) -10.1 (*c* = 1.0, CHCl<sub>3</sub>, 93% ee).

## 7. General Procedure for β-alkylidene MBH Methyl Ester

LiCuBr<sub>2</sub> (0.5 M in THF, 0.204 mL, 0.102 mmol) was added to a THF solution (1 mL) of β-Iodo MBH Ester (0.341 mmol), and then alkylmagnesium bromide (0.5 M in THF, 1.076 mL, 0.853mmol) was slowly added dropwise. The resulting solution was quenched by addition of NH<sub>4</sub>Cl saturated solution (3 mL) and stirred while the aqueous layer turned blue. The organic layer was extracted with hexane (3 × 2 mL) and the combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The crude product was purified by silica gel (hexane/ethyl acetate = 10:1) to afford the desired product.

### methyl (*R,E*)-2-(1-hydroxy-2-methylallyl)dodec-2-enoate (**14a**)



Prepared according to the general procedure to afford of the desired product **14a** in 81% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, *J* = 7.6 Hz, 1H), 4.98 (s, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.90 (dd, *J* = 2.9, 1.4 Hz, 1H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.73 (s, 3H), 2.31 (dq, *J* = 15.4, 7.7 Hz, 1H), 2.21 (dq, *J* = 14.9, 7.3 Hz, 1H), 1.72 (s, 3H), 1.50 – 1.43 (m, 2H), 1.34 – 1.24 (m, 12H), 0.88 (t, *J* = 7.0 Hz, 3H).

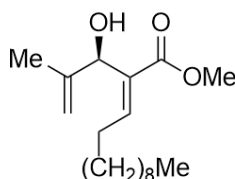
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 168.0, 145.9, 145.7, 131.1, 110.4, 71.4, 51.9, 32.0, 29.6, 29.5, 29.5, 29.4, 28.8, 28.5, 22.8, 19.8, 14.2.

**IR** ν<sub>max</sub> 2923, 2853, 2361, 2342, 1720, 1463, 1436, 1350, 1315, 1220, 1207, 1139, 1029, 901, 803, 776 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>17</sub>H<sub>30</sub>O<sub>3</sub>Na: *m/z* 305.209 ([M + Na]<sup>+</sup>), found: *m/z* 305.202 ([M + Na]<sup>+</sup>).

[α]<sub>D</sub><sup>20</sup> = +72.0 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

**methyl (*R,E*)-2-(1-hydroxy-2-methylallyl)tridec-2-enoate (**14b**)**



Prepared according to the general procedure to afford of the desired product **14b** in 80% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, *J* = 7.6 Hz, 1H), 4.99 – 4.97 (m, 1H), 4.95 (d, *J* = 10.3 Hz, 1H), 4.91 (h, *J* = 1.5 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.74 (s, 3H), 2.31 (dq, *J* = 15.4 Hz, 7.7 Hz, 1H), 2.20 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.74 (s, 3H), 1.50 – 1.43 (m, 2H), 1.27 (m, 14H), 0.88 (t, *J* = 6.9 Hz, 3H).

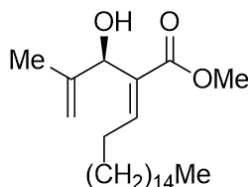
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 168.1, 146.0, 145.8, 131.1, 110.4, 71.4, 51.9, 32.0, 29.7, 29.7, 29.6, 29.5, 29.5, 28.8, 28.5, 22.8, 19.8, 14.3.

**IR**  $\nu_{\max}$  2954, 2924, 2853, 2360, 1701, 1437, 1253, 1051, 898, 671 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>18</sub>H<sub>32</sub>O<sub>3</sub>Na: *m/z* 319.224 ([M + Na]<sup>+</sup>), found: *m/z* 319.220 ([M + Na]<sup>+</sup>).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +71.7 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

**(*R,E*)-methyl 2-(1-hydroxy-2-methylallyl)nonadec-2-enoate (**14c**)**



Prepared according to the general procedure to afford of the desired product **14c** in 72% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, *J* = 7.6 Hz, 1H), 4.98 (s, 1H), 4.95 (d, *J* = 8.6 Hz, 1H), 4.90 (q, *J* = 1.5 Hz, 1H), 3.96 (d, *J* = 9.9 Hz, 1H), 3.74 (s, 3H), 2.31 (dq, *J* = 15.4, 7.7 Hz, 1H), 2.20 (dq, *J* = 14.9, 7.3 Hz, 1H), 1.73 (s, 3H), 1.52 – 1.42 (m, 2H), 1.26 (m, 26H), 0.88 (t, *J* = 6.9 Hz, 3H).

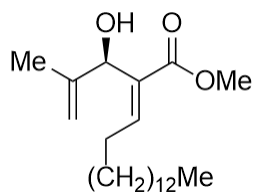
**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>): δ 168.1, 146.0, 145.8, 131.1, 110.4, 71.4, 51.9, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 28.8, 28.5, 22.8, 19.8, 14.3.

**IR**  $\nu_{\max}$  2925, 2855, 2360, 2341, 1699, 1489, 1437, 1255, 1053, 772 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>24</sub>H<sub>44</sub>O<sub>3</sub>Na: *m/z* 403.318 ([M + Na]<sup>+</sup>), found: *m/z* 403.319 ([M + Na]<sup>+</sup>).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = +27.0 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

**(*R,E*)-methyl 2-(1-hydroxy-2-methylallyl)heptadec-2-enoate (**14d**)**



Prepared according to the general procedure to afford of the desired product **14d** in 70% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, J = 7.6 Hz, 1H), 4.98 (s, 1H), 4.95 (d, J = 10.9 Hz, 1H), 4.91 (dd, J = 2.9, 1.4 Hz, 1H), 3.96 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 2.31 (dq, J = 15.4, 7.7 Hz, 1H), 2.20 (dq, J = 14.9, 7.3 Hz, 1H), 1.74 (d, J = 0.5 Hz, 3H), 1.50 – 1.43 (m, 2H), 1.34 – 1.22 (m, 22H), 0.89 (d, J = 6.8 Hz, 3H).

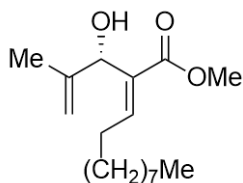
**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.1, 146.0, 145.8, 131.1, 110.4, 71.4, 51.9, 32.1, 29.8, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5 – 29.5 (m), 29.5, 28.8, 28.5, 22.8, 19.8, 14.3.

**IR**  $\nu_{\max}$ : 2998, 2925, 2853, 1703, 1437, 1079, 1028, 982, 643 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>22</sub>H<sub>40</sub>O<sub>3</sub>Na:  $m/z$  375.287 ([M + Na]<sup>+</sup>), found:  $m/z$  375.288 ([M + Na]<sup>+</sup>).

$[\alpha]_{\text{D}}^{20} = +55.0$  (c = 1.0, CHCl<sub>3</sub>, 91% ee).

**(S,E)-methyl 2-(1-hydroxy-2-methylallyl)dodec-2-enoate (14e)**



Prepared according to the general procedure to afford of the desired product **14e** in 83% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, J = 7.6 Hz, 1H), 4.98 (s, 1H), 4.96 (d, J = 11.0 Hz, 1H), 4.90 (dd, J = 2.9, 1.4 Hz, 1H), 3.97 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 2.31 (dq, J = 15.4, 7.7 Hz, 1H), 2.21 (dq, J = 14.9, 7.3 Hz, 1H), 1.74 (s, 3H), 1.50 – 1.43 (m, 2H), 1.34 – 1.24 (m, 12H), 0.88 (t, J = 7.0 Hz, 3H).

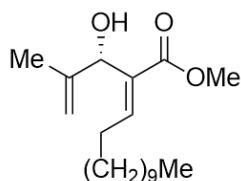
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 168.0, 145.9, 145.8, 131.1, 110.4, 71.4, 51.9, 32.0, 29.6, 29.5, 29.5, 29.4, 28.8, 28.5, 19.8, 14.2.

**IR**  $\nu_{\max}$ : 2955, 2926, 2856, 2359, 2328, 1700, 1437, 1254, 1051, 898 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>17</sub>H<sub>30</sub>O<sub>3</sub>Na:  $m/z$  305.208 ([M + Na]<sup>+</sup>), found:  $m/z$  305.202 ([M + Na]<sup>+</sup>).

$[\alpha]_{\text{D}}^{20} = -72.1$  (c = 1.0, CHCl<sub>3</sub>, 91% ee).

**(S,E)-methyl 2-(1-hydroxy-2-methylallyl)tetradec-2-enoate (14f)**



Prepared according to the general procedure to afford of the desired product **14f** in 80% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.89 (t, *J* = 7.6 Hz, 1H), 4.98 (s, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.90 (dd, *J* = 2.9, 1.4 Hz, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.74 (s, 3H), 2.31 (dq, *J* = 15.4, 7.7 Hz, 1H), 2.20 (dq, *J* = 14.9, 7.3 Hz, 1H), 1.74 (s, 3H), 1.51 – 1.43 (m, 2H), 1.34 – 1.24 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).

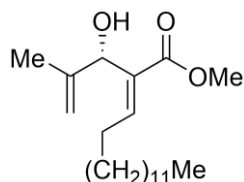
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 168.0, 146.0, 145.8, 131.1, 110.4, 71.4, 51.9, 32.0, 29.7, 29.6, 29.5, 29.5, 29.5, 28.8, 28.5, 22.8, 19.8, 14.2.

**IR**  $\nu_{\max}$ : 2953, 2924, 2853, 2355, 1699, 1436, 1255, 1050, 898 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>19</sub>H<sub>34</sub>O<sub>3</sub>Na: *m/z* 333.240 ([M + Na]<sup>+</sup>), found: *m/z* 333.232 ([M + Na]<sup>+</sup>).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = -70.2 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

**(*S,E*)-methyl 2-(1-hydroxy-2-methylallyl)hexadec-2-enoate (14g)**



Prepared according to the general procedure to afford of the desired product **14g** in 77% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.87 (t, *J* = 7.6 Hz, 1H), 4.96 (s, 1H), 4.94 (s, 1H), 4.89 (d, *J* = 1.5 Hz, 1H), 3.96 (s, 1H), 3.72 (s, 3H), 2.30 (dq, *J* = 15.4 Hz, 7.7 Hz, 1H), 2.19 (dq, *J* = 14.9 Hz, 7.3 Hz, 1H), 1.72 (s, 3H), 1.45 (p, *J* = 7.2 Hz, 2H), 1.24 (m, 20H), 0.86 (t, *J* = 6.9 Hz, 3H).

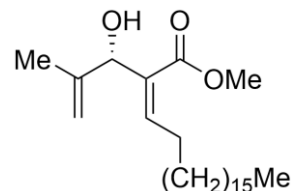
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): 168.0, 145.9, 145.7, 131.1, 110.3, 71.4, 51.8, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.5, 28.8, 28.5, 22.8, 19.7, 14.2.

**IR**  $\nu_{\max}$ : 3509, 3454, 2924, 2854, 1701, 1645, 1436, 1301, 1254, 1051, 897 cm<sup>-1</sup>.

**LRMS** (QTOF): Calcd. for C<sub>21</sub>H<sub>38</sub>O<sub>3</sub>Na: *m/z* 361.271 ([M+Na]<sup>+</sup>), found: *m/z* 361.263 ([M+Na]<sup>+</sup>).

[ $\alpha$ ]<sub>D</sub><sup>20</sup> = -57.3 (*c* = 1.0, CHCl<sub>3</sub>, 91% ee).

**methyl (*S,Z*)-2-(1-hydroxy-2-methylallyl)icos-2-enoate (15)**



Prepared according to the general procedure to afford of the desired product **15** in 80% yield as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.18 (td, *J* = 7.5, 0.6 Hz, 1H), 5.06 (d, *J* = 0.8 Hz, 1H), 4.94 (dd, *J* = 2.7, 1.4 Hz, 1H), 4.73 (d, *J* = 7.1 Hz, 1H), 3.76 (s, 3H), 2.78 (d, *J* = 7.2 Hz, 1H), 2.43 (dd, *J* = 15.0, 7.5 Hz, 2H), 1.72 – 1.65 (m, 3H), 1.44 (dt, *J* = 14.8, 7.3 Hz, 2H), 1.34 – 1.18 (m, 28H), 0.88 (t, *J* = 7.0 Hz, 3H).

**<sup>13</sup>C NMR** (126 MHz, CDCl<sub>3</sub>) δ 168.1, 145.3, 144.3, 132.0, 111.7, 51.6, 32.1, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7,

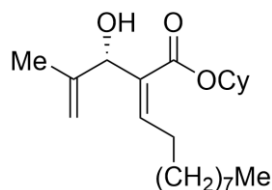
29.6, 29.5, 29.5, 29.3, 22.8, 19.3, 14.3.

**IR**  $\nu_{\max}$ : 2923, 2853, 2363, 1719, 1216, 901, 667  $\text{cm}^{-1}$ .

**LRMS** (QTOF): Calcd. for  $\text{C}_{25}\text{H}_{46}\text{O}_3\text{Na}$ :  $m/z$  417.334 ( $[\text{M}+\text{Na}]^+$ ), found:  $m/z$  417.325 ( $[\text{M}+\text{Na}]^+$ ).

$[\alpha]_{\text{D}}^{20} = -9.4$  ( $c = 1.0$ ,  $\text{CHCl}_3$ , 91% ee).

**cyclohexyl (S,Z)-2-(1-hydroxy-2-methylallyl)dodec-2-enoate (16(Z))**



Prepared according to the general procedure to afford of the desired product **16(Z)** in 99% yield as a colorless oil.

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.11 (t,  $J = 7.6$  Hz, 1H), 5.03 (s, 1H), 4.90 (s, 1H), 4.86 (dq,  $J = 8.7, 4.3$  Hz, 1H), 4.67 (s, 1H), 3.03 (s, 1H), 2.42 (q,  $J = 7.5$  Hz, 2H), 1.90 – 1.80 (m, 2H), 1.73 – 1.68 (m, 2H), 1.67 (s, 3H), 1.56 – 1.36 (m, 6H), 1.32 – 1.22 (m, 14H), 0.86 (t,  $J = 6.9$  Hz, 3H).

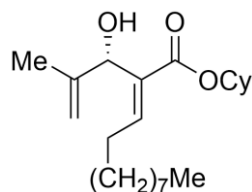
**$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.2, 145.4, 143.1, 132.5, 111.5, 77.14, 73.1, 32.0, 31.68, 31.67, 29.60, 29.54, 29.52, 29.46, 29.37, 29.28, 25.4, 23.75, 23.73, 22.8, 19.3, 14.2.

**IR**  $\nu_{\max}$  2958, 2928, 2365, 2341, 1649, 1454, 1379, 1362, 1216, 1039, 1015, 902, 756  $\text{cm}^{-1}$ .

**HRMS** (ESI-QTOF): Calcd. for  $\text{C}_{22}\text{H}_{38}\text{O}_3\text{Na}$ :  $m/z$  373.2713 ( $[\text{M}+\text{Na}]^+$ ), found:  $m/z$  373.2719 ( $[\text{M}+\text{Na}]^+$ ).

$[\alpha]_{\text{D}}^{20} =$  for (*R*) +15.4 ( $c = 1.0$ ,  $\text{CHCl}_3$ , 93% ee), for (*S*) -15.5 ( $c = 1.0$ ,  $\text{CHCl}_3$ , 93% ee).

**cyclohexyl (S,E)-2-(1-hydroxy-2-methylallyl)dodec-2-enoate (16(E))**



Prepared according to the general procedure to afford of the desired product **16(E)** in 99% yield as a colorless oil.

**$^1\text{H}$  NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.87 (t,  $J = 7.6$  Hz, 1H), 5.00 – 4.96 (m, 1H), 4.95 (d,  $J = 10.7$  Hz, 1H), 4.90 – 4.89 (m, 1H), 4.88 – 4.80 (m, 1H), 4.03 (d,  $J = 10.8$  Hz, 1H), 2.25 (ddt,  $J = 44.3, 15.0, 7.6$  Hz, 2H), 1.86 (dq,  $J = 10.9, 3.4$  Hz, 2H), 1.85 (s, 3H), 1.74-1.69 (m, 2H), 1.57 – 1.43 (m, 4H), 1.42 – 1.16 (m, 16H), 0.88 (t,  $J = 6.9$  Hz, 3H).

**$^{13}\text{C}$  NMR** (125 MHz,  $\text{CDCl}_3$ ): 167.1, 145.9, 145.3, 131.6, 110.2, 73.2, 71.4, 32.0, 31.7, 31.5, 29.6, 29.6, 29.5, 29.4, 28.8, 28.4, 25.5, 23.8, 23.8, 22.8, 19.8, 14.2.

**IR**  $\nu_{\max}$  2956, 2927, 2362, 2340, 1649, 1456, 1382, 1360, 1219, 1031, 1016, 911, 751  $\text{cm}^{-1}$ .

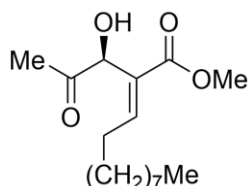
**HRMS** (ESI-QTOF): Calcd. for  $\text{C}_{22}\text{H}_{38}\text{O}_3\text{Na}$ :  $m/z$  373.2713 ( $[\text{M}+\text{Na}]^+$ ), found:  $m/z$  373.2719 ( $[\text{M}+\text{Na}]^+$ ).

$[\alpha]_{\text{D}}^{20}$  = for (*R*) +46.1 ( $c = 1.0$ ,  $\text{CHCl}_3$ , 93% ee), for (*S*) -46.3 ( $c = 1.0$ ,  $\text{CHCl}_3$ , 93% ee).

## 8. General Procedure for Ozonolysis

To a solution of  $\beta$ -alkylidene MBH methyl ester (0.1 mmol) in 1.7 mL of  $\text{CH}_2\text{Cl}_2$  was cooled to  $-78\text{ }^\circ\text{C}$  and ozonolyzed until color of reaction mixture converted to blue (<3 min). The resulting solution was treated with dimethyl sulfide (0.6 mL), stirred for 1 hour at  $-78\text{ }^\circ\text{C}$  and 10 min at rt with  $\text{N}_2$  bubbling, and then quenched with  $\text{H}_2\text{O}$  (2 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 2$  mL). The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The crude product was purified by silica gel (hexane/ethyl acetate = 10:1) to afford the desired product.

### (+)-Secoisolancifolide (**2**)<sup>[1]</sup>



Prepared according to the general procedure to afford of the desired product **2** in 82% yield, 96% ee as a colorless oil.

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.07 (t,  $J = 7.7$  Hz, 1H), 4.89 (d,  $J = 4.6$  Hz, 1H), 4.01 (d,  $J = 4.8$  Hz, 1H), 3.72 (s, 3H), 2.34 (dd,  $J = 15.1, 7.6$  Hz, 2H), 2.14 (s, 3H), 1.50 (dd,  $J = 15.1, 7.5$  Hz, 2H), 1.37 – 1.22 (m, 12H), 0.87 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5, 166.7, 149.3, 129.9, 73.5, 52.1, 32.0, 29.6, 29.5, 29.5, 29.4, 28.8, 28.8, 25.0, 22.8, 14.2.

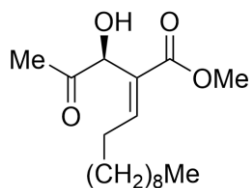
$\text{IR } \nu_{\text{max}}$  : 2955, 2926, 2854, 2362, 2315, 1726, 1238, 1049, 658  $\text{cm}^{-1}$ .

$\text{HRMS}$  (ESI-QTOF): Calcd. for  $\text{C}_{16}\text{H}_{29}\text{O}_4$ :  $m/z$  285.2060 ( $[\text{M}+\text{H}]^+$ ), found:  $m/z$  285.2063 ( $[\text{M}+\text{H}]^+$ ).

$\text{HPLC}$ : ee = 96%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm,  $t_{\text{R}}$  = 8.9 min (major) and  $t_{\text{R}}$  = 9.8 min (minor).

$[\alpha]_{\text{D}}^{25}$  = +95.2 ( $c = 0.29$ ,  $\text{CHCl}_3$ , 96% ee).

### Secoaggregatalactone A (**3**)<sup>[2]</sup>



Prepared according to the general procedure to afford of the desired product **3** in 93% yield, 90% ee as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.06 (t, J = 7.7 Hz, 1H), 4.89 (d, J = 4.9 Hz, 1H), 4.00 (d, J = 4.9 Hz, 1H), 3.71 (s, 3H), 2.34 (dd, J = 15.0, 7.6 Hz, 2H), 2.13 (s, 3H), 1.54 – 1.45 (m, 2H), 1.37 – 1.24 (m, 14H), 0.86 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 206.4, 166.6, 149.2, 129.8, 73.5, 52.1, 32.0, 29.7, 29.6, 29.5, 29.5, 29.4, 28.8, 28.8, 24.9, 22.8, 14.2.

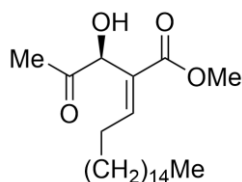
**IR**  $\nu_{\max}$ : 2955, 2926, 2854, 1726, 1437, 1309, 1235, 1071 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for C<sub>17</sub>H<sub>31</sub>O<sub>4</sub>: *m/z* 299.2217 ([M+H]<sup>+</sup>), found: *m/z* 299.2218 ([M+H]<sup>+</sup>).

**HPLC**: ee = 90%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm, *t*<sub>R</sub> = 8.4 min (major) and *t*<sub>R</sub> = 9.5 min (minor).

**[α]<sup>25</sup><sub>D</sub>** = +114.6 (*c* = 0.5, CHCl<sub>3</sub>, 90% ee).

### Macrocarpolides **4** (4)<sup>[3]</sup>



Prepared according to the general procedure to afford of the desired product **4** in 80% yield, 86% ee as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.07 (t, J = 7.7 Hz, 1H), 4.90 (d, J = 4.9 Hz, 1H), 4.01 (d, J = 4.9 Hz, 1H), 3.73 (s, 3H), 2.35 (dd, J = 15.0, 7.6 Hz, 2H), 2.15 (s, 3H), 1.55 – 1.47 (m, 2H), 1.39 – 1.17 (m, 26H), 0.88 (t, J = 7.0 Hz, 3H).

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 206.5, 166.7, 149.3, 129.9, 73.5, 52.2, 32.1, 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 28.9, 28.8, 25.0, 22.8, 14.3.

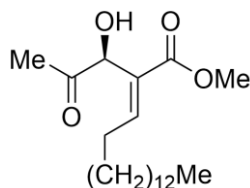
**IR**  $\nu_{\max}$ : 2998, 2906, 2852, 2360, 2344, 1727, 1080, 1028, 972 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for C<sub>23</sub>H<sub>43</sub>O<sub>4</sub>: *m/z* 383.3156 ([M+H]<sup>+</sup>), found: *m/z* 383.3157 ([M+H]<sup>+</sup>).

**HPLC**: ee = 86%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm, *t*<sub>R</sub> = 7.1 min (major) and *t*<sub>R</sub> = 7.8 min (minor).

**[α]<sup>25</sup><sub>D</sub>** = +53.0 (*c* = 0.25, CHCl<sub>3</sub>, 86% ee).

### Macrocarpolides **5** (5)<sup>[3]</sup>



Prepared according to the general procedure to afford of the desired product **5** in 80% yield, 93% ee as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 7.07 (t, J = 7.7 Hz, 1H), 4.90 (d, J = 4.8 Hz, 1H), 4.01 (d, J = 4.9 Hz, 1H), 3.73

(s, 3H), 2.35 (dd,  $J = 15.0, 7.6$  Hz, 2H), 2.15 (s, 3H), 1.55 – 1.48 (m, 2H), 1.39 – 1.17 (m, 22H), 0.88 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5, 166.7, 149.3, 129.9, 73.5, 52.2, 32.1, 29.8, 29.8, 29.8, 29.8, 29.6, 29.6, 29.5, 29.5, 28.9, 28.8, 25.0, 22.8, 14.3.

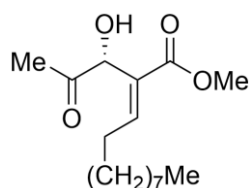
IR  $\nu_{\text{max}}$ : 2924, 2853, 2362, 2332, 1727, 1235, 1076, 666  $\text{cm}^{-1}$ .

HRMS (ESI-QTOF): Calcd. for  $\text{C}_{21}\text{H}_{39}\text{O}_4$ :  $m/z$  355.2843 ( $[\text{M}+\text{H}]^+$ ), found:  $m/z$  355.2848 ( $[\text{M}+\text{H}]^+$ ).

HPLC: ee = 93%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm,  $t_{\text{R}} = 7.5$  min (major) and  $t_{\text{R}} = 8.3$  min (minor).

$[\alpha]_{\text{D}}^{25} = +94.2$  ( $c = 0.4$ ,  $\text{CHCl}_3$ , 93% ee).

#### (-)-Secoisolancifolide (*ent*-2)<sup>[1]</sup>



Prepared according to the general procedure to afford of the desired product *ent*-2 in 83% yield, 93% ee as a colorless oil.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.07 (t,  $J = 7.7$  Hz, 1H), 4.89 (d,  $J = 4.6$  Hz, 1H), 4.01 (d,  $J = 4.8$  Hz, 1H), 3.72 (s, 3H), 2.34 (dd,  $J = 15.1, 7.6$  Hz, 2H), 2.14 (s, 3H), 1.50 (dd,  $J = 15.1, 7.5$  Hz, 2H), 1.37 – 1.22 (m, 12H), 0.87 (t,  $J = 6.9$  Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  206.5, 166.7, 149.3, 129.9, 73.5, 52.1, 32.0, 29.6, 29.5, 29.5, 29.4, 28.8, 28.8, 25.0, 22.8, 14.2.

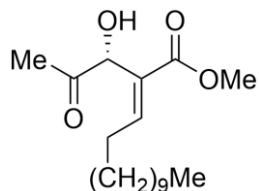
IR  $\nu_{\text{max}}$ : 2955, 2926, 2854, 2362, 2315, 1726, 1238, 1049, 658  $\text{cm}^{-1}$ .

HRMS (ESI-QTOF): Calcd. for  $\text{C}_{16}\text{H}_{29}\text{O}_4$ :  $m/z$  285.2060 ( $[\text{M}+\text{H}]^+$ ), found:  $m/z$  285.2063 ( $[\text{M}+\text{H}]^+$ ).

HPLC: ee = 93%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm,  $t_{\text{R}} = 8.94$  min (major) and  $t_{\text{R}} = 9.7$  min (minor).

$[\alpha]_{\text{D}}^{25} = -60.6$  ( $c = 0.16$ ,  $\text{CHCl}_3$ , 93% ee).

#### Secolincomolide A (**6**)<sup>[4]</sup>



Prepared according to the general procedure to afford of the desired product **6** in 81% yield, 95% ee as a colorless oil.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.07 (t,  $J = 7.7$  Hz, 1H), 4.89 (d,  $J = 3.8$  Hz, 1H), 4.01 (d,  $J = 4.4$  Hz, 1H), 3.73 (s, 3H), 2.35 (dd,  $J = 15.0, 7.6$  Hz, 2H), 2.15 (s, 3H), 1.55 – 1.47 (m, 2H), 1.39 – 1.17 (m, 16H), 0.88 (t,  $J = 6.9$  Hz, 3H).



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 206.5, 166.7, 149.3, 129.9, 73.5, 52.2, 32.0, 29.8, 29.7, 29.6, 29.5, 29.5, 28.9, 28.8, 25.0, 22.8, 14.3.

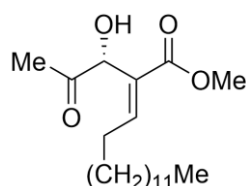
IR  $\nu_{\max}$ : 2955, 2925, 2853, 1727, 1437, 1236, 1106, 662 cm<sup>-1</sup>.

HRMS (ESI-QTOF): Calcd. for C<sub>18</sub>H<sub>33</sub>O<sub>4</sub>:  $m/z$  313.2373 ([M+H]<sup>+</sup>), found:  $m/z$  312.2376 ([M+H]<sup>+</sup>).

HPLC: ee = 95%, Chiralcel OD-H, 2-propanol:*n*-hexane=2:98, flow: 1.0mL/min, 220nm,  $t_R$  = 9.1 min (minor) and  $t_R$  = 9.9 min (major).

$[\alpha]_D^{25}$  = -43.9 ( $c$  = 0.39, CHCl<sub>3</sub>, 95% ee).

### Secokotomolide A (7)<sup>[5]</sup>



Prepared according to the general procedure to afford of the desired product **7** in 73% yield, 93% ee as a colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.07 (t,  $J$  = 7.7 Hz, 1H), 4.89 (s, 1H), 4.00 (s, 1H), 3.72 (s, 3H), 2.34 (q,  $J$  = 7.6 Hz, 2H), 2.14 (s, 3H), 1.51 (p,  $J$  = 7.4 Hz, 2H), 1.39 – 1.25 (m, 21H), 0.87 (t,  $J$  = 6.9 Hz, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 206.5, 166.7, 149.3, 129.8, 73.5, 52.1, 32.1, 29.79, 29.77, 29.74, 29.6, 29.6, 29.53, 29.50, 29.48, 28.84, 28.81, 25.0, 22.8, 14.2.

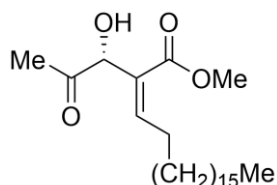
IR  $\nu_{\max}$ : 3464, 2921, 2851, 1727, 1645, 1462, 1437, 1236, 1072 cm<sup>-1</sup>.

HRMS (ESI-QTOF): Calcd. for C<sub>20</sub>H<sub>37</sub>O<sub>4</sub>:  $m/z$  341.2686 ([M+H]<sup>+</sup>), found:  $m/z$  341.2690 ([M+H]<sup>+</sup>).

HPLC: ee = 93%, Chiralcel OZ-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 220nm,  $t_R$  = 10.5 min (major) and  $t_R$  = 14.6 min (minor).

$[\alpha]_D^{25}$  = -75.5 ( $c$  = 0.42, CHCl<sub>3</sub>, 93% ee).

### Secomahubanolide (8)<sup>[6]</sup>



Prepared according to the general procedure to afford of the desired product **8** in 81% yield, 91% ee as a colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 6.33 (t,  $J$  = 7.5 Hz, 1H), 4.54 (d,  $J$  = 3.6 Hz, 1H), 4.04 (d,  $J$  = 4.2 Hz, 1H), 3.73 (s, 3H), 2.52 (dp,  $J$  = 26.0, 7.5 Hz, 2H), 2.18 (s, 3H), 1.46 (qq,  $J$  = 14.1, 6.9 Hz, 2H), 1.33 – 1.25 (m, 28H), 0.87 (t,  $J$  = 6.8 Hz, 3H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 206.5, 166.4, 149.5, 130.3, 80.6, 51.8, 32.1, 29.86 – 29.77 (m), 29.68, 29.52 – 29.46 (m), 29.1, 24.9, 22.8, 14.3.

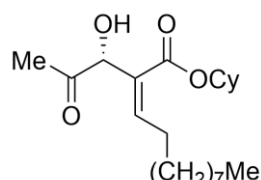
IR  $\nu_{\max}$ : 2926, 2854, 2365, 2328, 1733, 1081, 667 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for  $C_{24}H_{45}O_4$ :  $m/z$  397.3312 ( $[M+H]^+$ ), found:  $m/z$  397.3316 ( $[M+H]^+$ ).

**HPLC**: ee = 91%, Chiralcel OD-H, 2-propanol:*n*-hexane=5:95, flow: 1.0mL/min, 254nm,  $t_R$  = 7.1 min (minor) and  $t_R$  = 7.7 min (major).

$[\alpha]^{25}_D$  = -147.0 ( $c$  = 0.03,  $CHCl_3$ , 91% ee).

**cyclohexyl (*R,Z*)-2-(1-hydroxy-2-oxopropyl)dodec-2-enoate (**17(Z)**)**



Prepared according to the general procedure to afford of the desired product **17(Z)** in 80% yield as a colorless oil.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  6.30 (t,  $J$  = 7.6 Hz, 1H), 4.90 – 4.81 (m, 1H), 4.50 (d,  $J$  = 4.2 Hz, 1H), 4.06 (d,  $J$  = 4.2 Hz, 1H), 2.64 – 2.46 (m, 2H), 2.20 (s, 3H), 1.84 (q,  $J$  = 9.4, 8.7 Hz, 2H), 1.75 – 1.63 (m, 2H), 1.57 – 1.20 (m, 20H), 0.88 (t,  $J$  = 6.9 Hz, 3H).

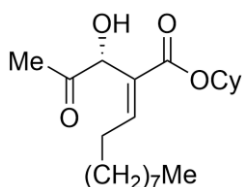
**$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ): 206.6, 165.3, 148.9, 130.8, 80.8, 73.7, 32.0, 31.6, 31.6, 29.8, 29.7, 29.5, 29.5, 29.4, 29.2, 25.4, 24.9, 23.7, 22.8, 14.2.

**IR**  $\nu_{max}$  2923, 2852, 2362, 2341, 2332, 1737, 1462, 1377, 1245, 1117, 1019, 646  $cm^{-1}$ .

**HRMS** (ESI-QTOF): Calcd. for  $C_{21}H_{36}O_4Na$ :  $m/z$  375.2506 ( $[M+Na]^+$ ), found:  $m/z$  375.2511 ( $[M+Na]^+$ ).

$[\alpha]^{20}_D$  = for (*R*) +43.7 ( $c$  = 0.4,  $CHCl_3$ , 93% ee), for (*S*) -44.2 ( $c$  = 0.4,  $CHCl_3$ , 93% ee).

**cyclohexyl (*R,E*)-2-(1-hydroxy-2-oxopropyl)dodec-2-enoate (**17(E)**)**



Prepared according to the general procedure to afford of the desired product **17(E)** in 80% yield as a colorless oil.

**$^1H$  NMR** (500 MHz,  $CDCl_3$ ):  $\delta$  7.07 (t,  $J$  = 7.7 Hz, 1H), 4.88 (d,  $J$  = 4.8 Hz, 1H), 4.82 (ddt,  $J$  = 12.7, 8.7, 3.9 Hz, 1H), 4.01 (d,  $J$  = 5.0 Hz, 1H), 2.35 (q,  $J$  = 7.9 Hz, 2H), 2.15 (s, 3H), 1.85 (s, 2H), 1.75 – 1.64 (m, 2H), 1.60 (s, 1H), 1.52 – 1.46 (m, 19H), 0.88 (t,  $J$  = 6.9 Hz, 3H).

**$^{13}C$  NMR** (125 MHz,  $CDCl_3$ ):  $\delta$  206.5, 165.6, 148.7, 130.4, 73.8, 73.5, 32.0, 31.6, 31.6, 29.6, 29.5, 29.4, 28.9, 28.8, 25.5, 25.0, 23.7, 22.8, 14.2.

**IR**  $\nu_{max}$  2925, 2850, 2342, 2332, 1738, 1469, 1378, 1241, 1112, 1017, 636  $cm^{-1}$ .

**HRMS** (ESI-QTOF): Calcd. for  $C_{21}H_{36}O_4Na$ :  $m/z$  375.2506 ( $[M+Na]^+$ ), found:  $m/z$  375.2511 ( $[M+Na]^+$ ).

$[\alpha]^{20}_D$  = for (*R*) +61.7 ( $c$  = 0.4,  $CHCl_3$ , 93% ee), for (*S*) -61.2 ( $c$  = 0.4,  $CHCl_3$ , 93% ee).

## 9. General Procedure for Hydrolysis and Cyclization

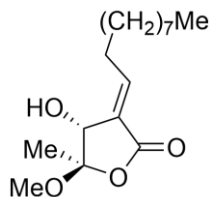
### 9.1. General Procedure for hydrolysis

Aluminum chloride ( $\text{AlCl}_3$ ) was added to a solution of  $\beta$ -alkylidene hydroxy oxopropyl enoate (0.1 mmol) in 2.0 ml of nitromethane and the solution was refluxed in 1h. After complete reaction, the resulting solution was quenched by  $\text{H}_2\text{O}$  and filtered by celite column. The crude product was concentrated for next steps without purification.

### 9.2. General Procedure for cyclization

To a solution of crude mixture above (0.1 mmol), trifluoroacetic acid (TFA), triethyl orthoformate ( $\text{CH}(\text{OMe})_3$ ) was added and the solution was refluxed 5h. After complete reaction, the resulting solution was quenched by  $\text{NaHCO}_3$  (aq) and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, and concentrated. The crude product was purified by silica gel (dichloromethane/methanol = 20:1) to afford the desired product.

#### (3*R*, 4*R*)-Litseakolide F (**9**)<sup>[7]</sup>



Prepared according to the general procedure to afford of the desired product **9** in 59% 2-step overall yield, 80% ee as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.99 (td,  $J = 7.8, 1.6$  Hz, 1H), 4.53 (d,  $J = 4.4$  Hz, 1H), 3.38 (s, 3H), 2.38 (qd,  $J = 7.4, 4.1$  Hz, 2H), 1.81 (d,  $J = 6.7$  Hz, 1H), 1.61 (s, 3H), 1.52 (p,  $J = 7.4$  Hz, 2H), 1.34 – 1.25 (m, 12H), 0.88 (t,  $J = 6.9$  Hz, 3H) ppm.

**<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  168.9, 148.4, 130.0, 109.3, 72.5, 50.3, 31.9, 29.9, 29.5, 29.34, 29.26, 28.4, 22.7, 16.1, 14.1 ppm.

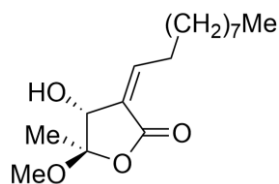
**IR**  $\nu_{\text{max}}$  3504, 3077, 2936, 2859, 1692, 1588, 1450, 1303, 1264, 1218, 1090, 1051, 1037, 1011, 959, 937, 899, 752  $\text{cm}^{-1}$ .

**HRMS** (ESI-QTOF): Calcd. for  $\text{C}_{16}\text{H}_{28}\text{O}_3\text{Na}$ :  $m/z$  307.1880 ( $[\text{M}+\text{Na}]^+$ ), found:  $m/z$  307.1885 ( $[\text{M}+\text{Na}]^+$ ).

**HPLC**: ee = 80%, Chiralpak<sup>®</sup> IC (2-propanol:*n*-hexane = 5:95), 25 °C, flow: 1.0mL/min,  $\lambda = 220\text{nm}$ ,  $t_{\text{R}} = 13.1$  min (major) and  $t_{\text{R}} = 17.6$  min (minor).

$[\alpha]_{\text{D}}^{25}$  = for (3*R*, 4*R*) -19.0 ( $c = 1.0$ ,  $\text{CHCl}_3$ , 80% ee), for (3*S*, 4*S*) +18.7, ( $c = 1.0$ ,  $\text{CHCl}_3$ , 80% ee).

#### (3*R*, 4*R*)-Litseakolide G (**10**)<sup>[7]</sup>



Prepared according to the general procedure to afford of the desired product **10** in 57% 2-step overall yield, 93% ee as a colorless oil.

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>): δ 6.55 (td, *J* = 7.7, 1.4 Hz, 1H), 4.39 (d, *J* = 4.3 Hz, 1H), 3.39 (s, 3H), 2.86 – 2.60 (m, 2H), 2.33 (d, *J* = 5.4 Hz, 1H), 1.54 (s, 3H), 1.46 (p, *J* = 7.2 Hz, 2H), 1.35 – 1.12 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm.

**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>): δ 167.7, 150.5, 129.1, 109.1, 75.9, 50.6, 32.0, 29.6, 29.5, 29.4, 29.4, 28.9, 28.2, 22.8, 16.4, 14.2 ppm.

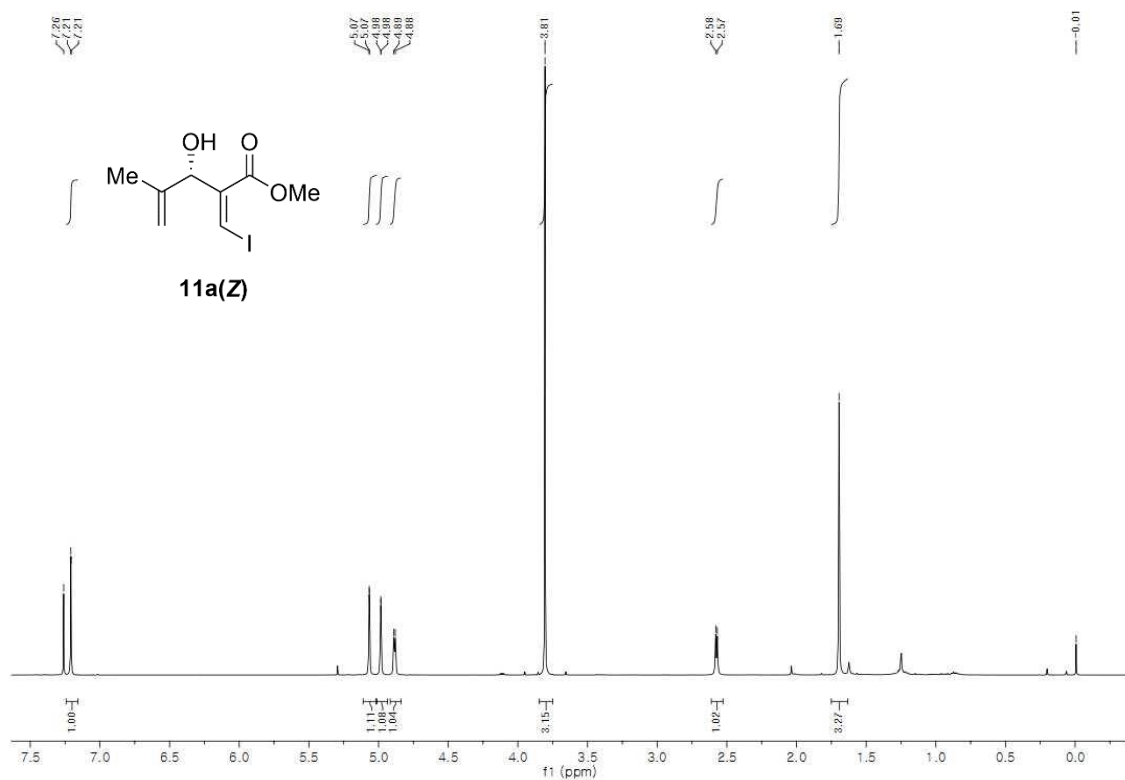
**IR** ν<sub>max</sub> 3493, 2939, 2860, 1709, 1654, 1611, 1451, 1302, 1190, 1122, 1093, 1041, 1011, 908 cm<sup>-1</sup>.

**HRMS** (ESI-QTOF): Calcd. for C<sub>16</sub>H<sub>28</sub>O<sub>3</sub>Na: *m/z* 307.1880 ([M+Na]<sup>+</sup>), found: *m/z* 307.1885 ([M+Na]<sup>+</sup>).

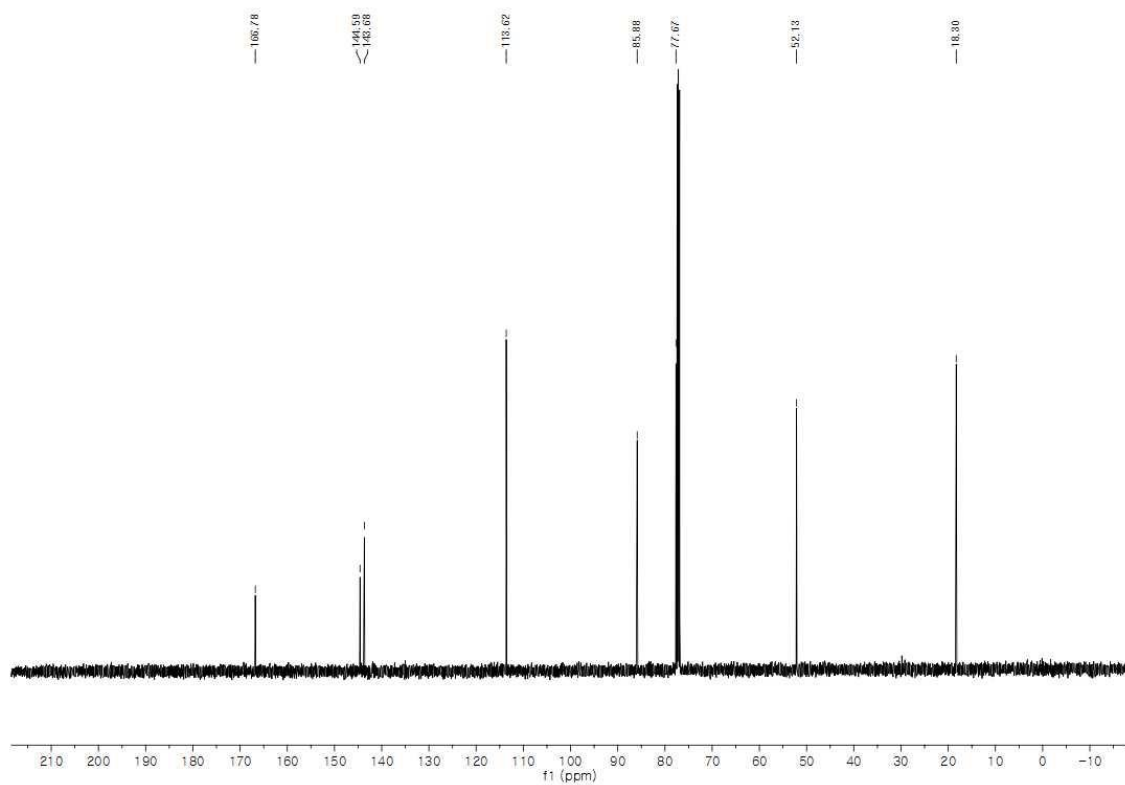
**HPLC**: ee = 93%, Chiralcel OJ-H (2-propanol:*n*-hexane = 5:95), 25 °C, flow: 1.0mL/min, λ = 254nm, *t*<sub>R</sub> = 6.7 min (minor) and *t*<sub>R</sub> = 7.0 min (major).

[α]<sub>D</sub><sup>25</sup> = for (3*R*, 4*R*) -26.0 (*c* = 1.0, CHCl<sub>3</sub>, 93% ee), for (3*S*, 4*S*) +26.7 (*c* = 1.0, CHCl<sub>3</sub>, 95% ee).

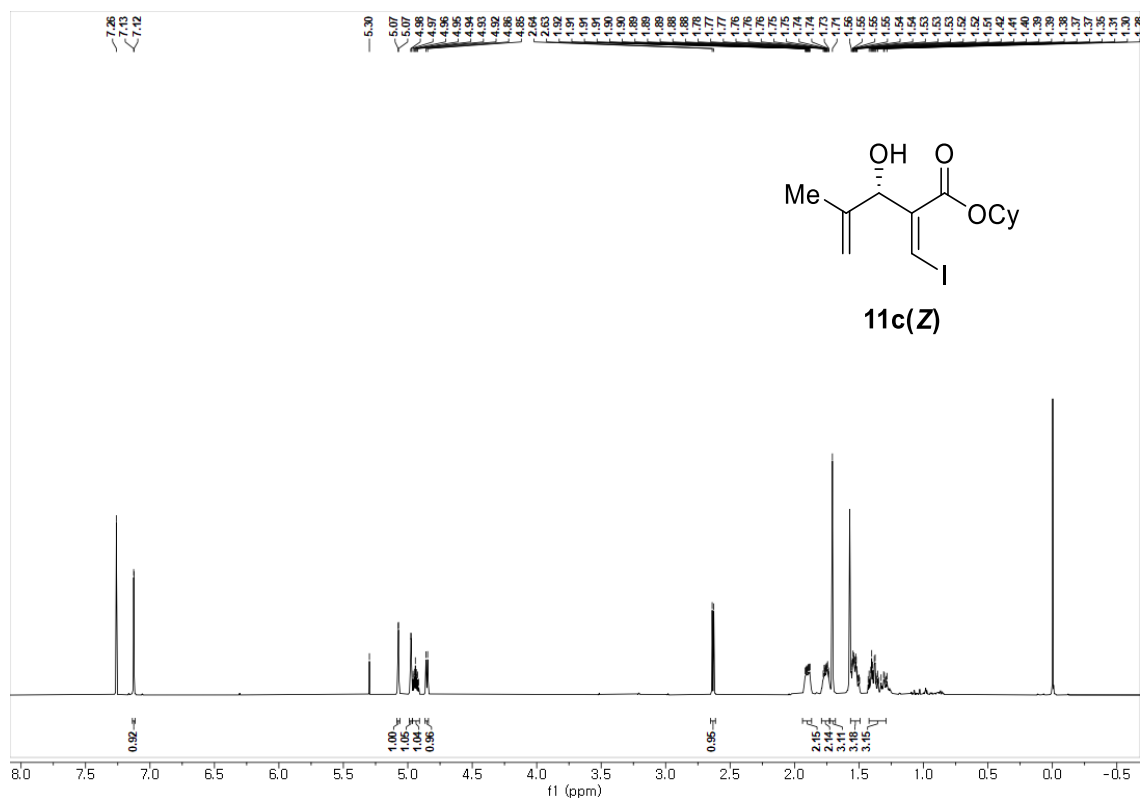
## 10. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra



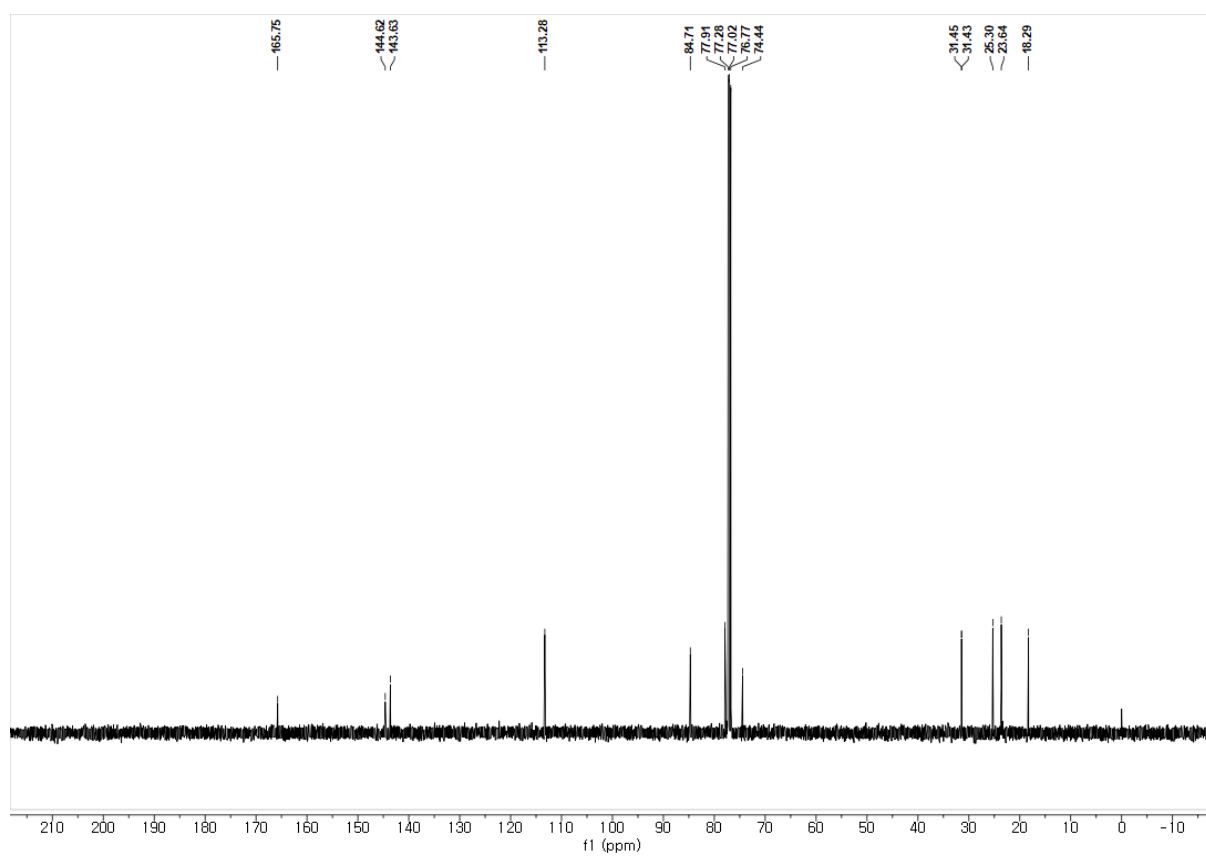
$^1\text{H}$  NMR spectrum of compound **11a(Z)** (500 MHz,  $\text{CDCl}_3$ )



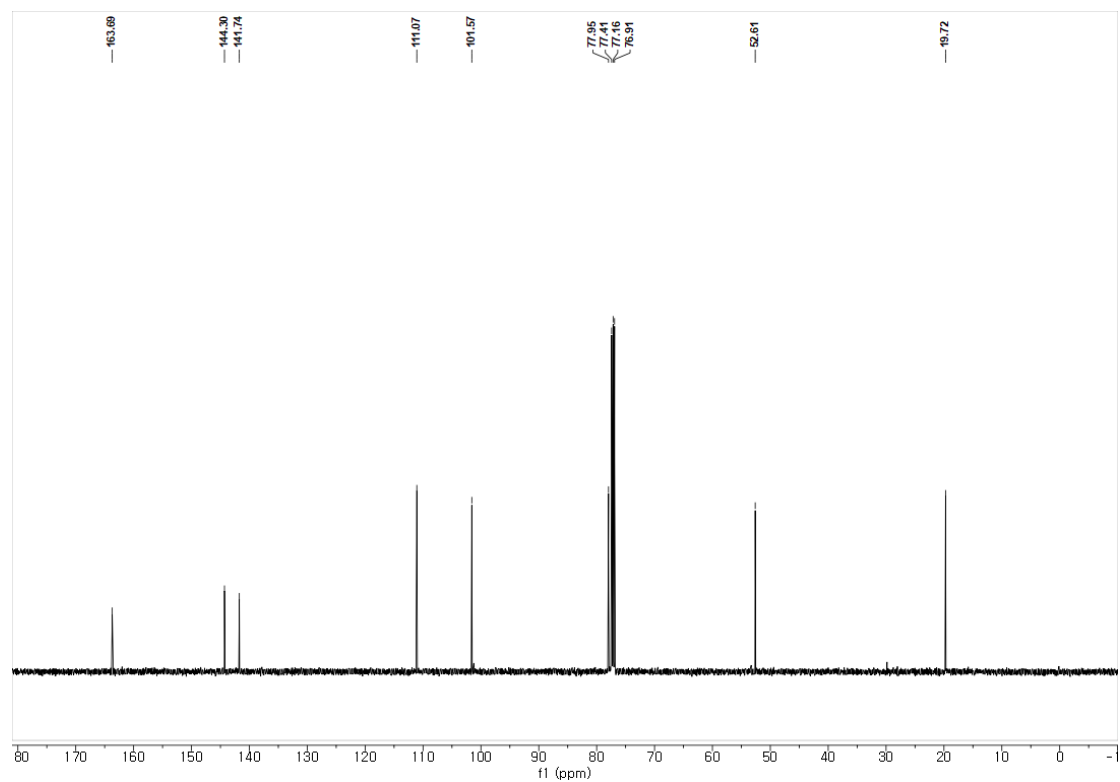
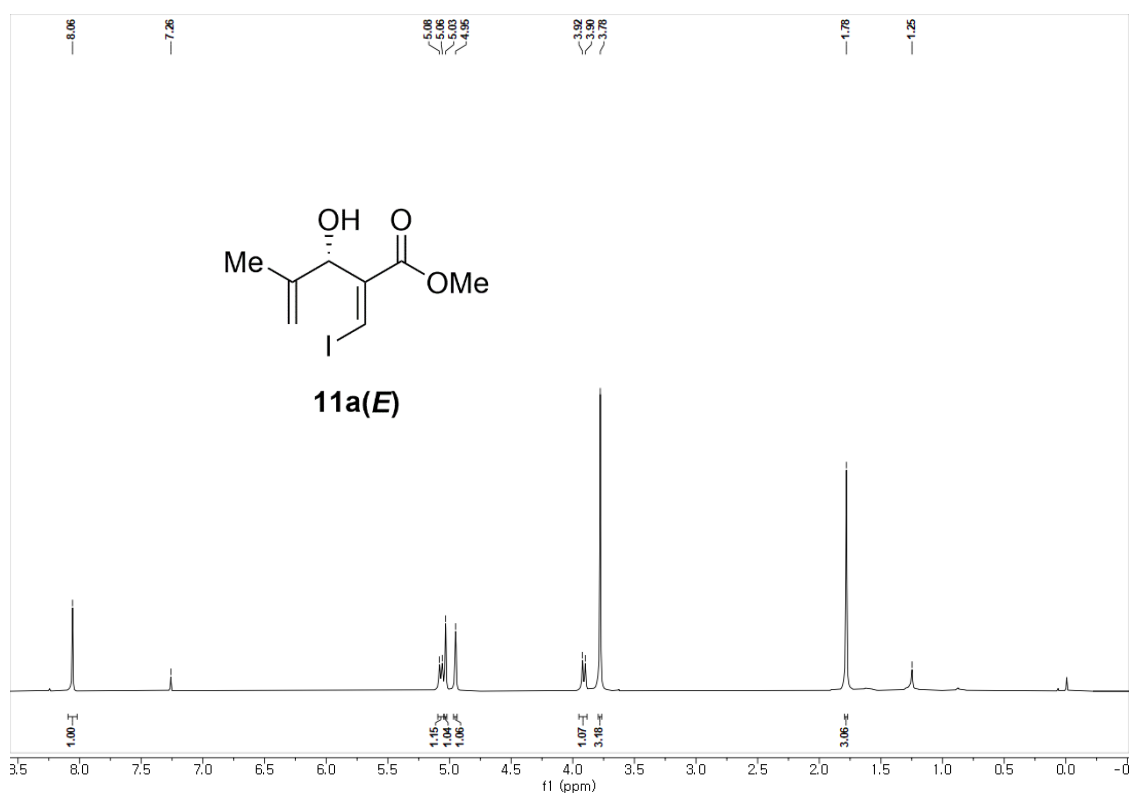
$^{13}\text{C}$  NMR spectrum of compound **11a(Z)** (125 MHz,  $\text{CDCl}_3$ )

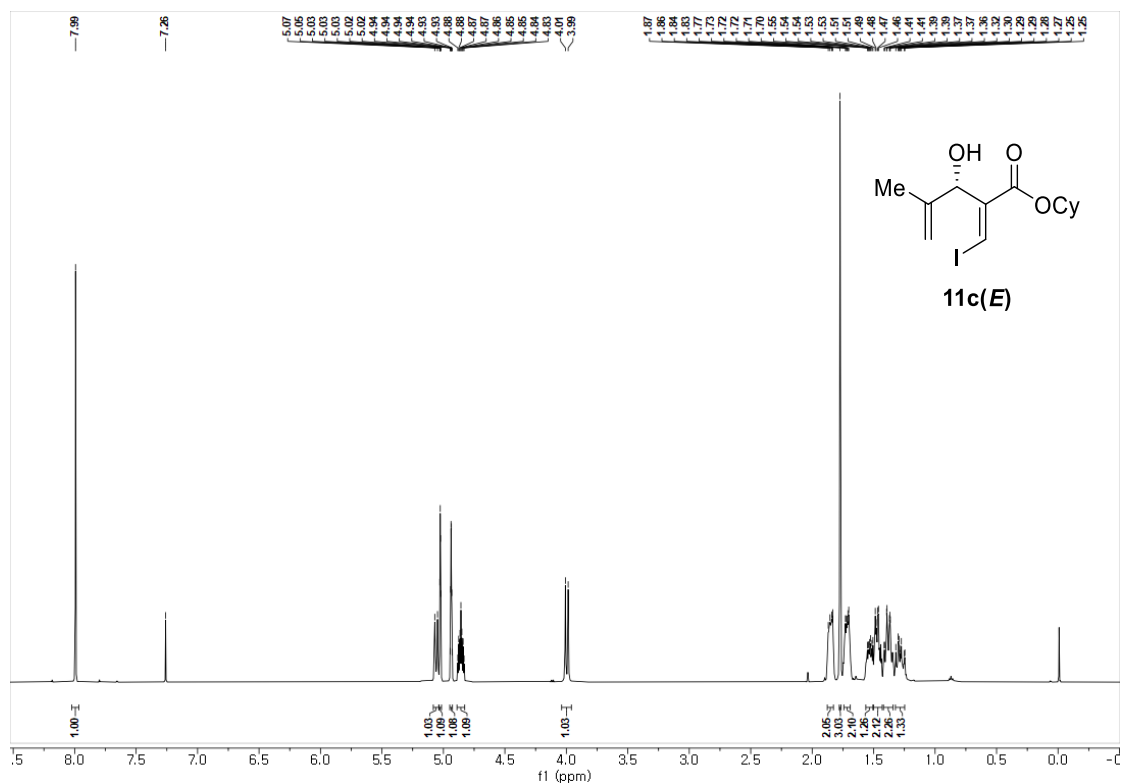


<sup>1</sup>H NMR spectrum of compound **11c(Z)** (500 MHz, CDCl<sub>3</sub>)

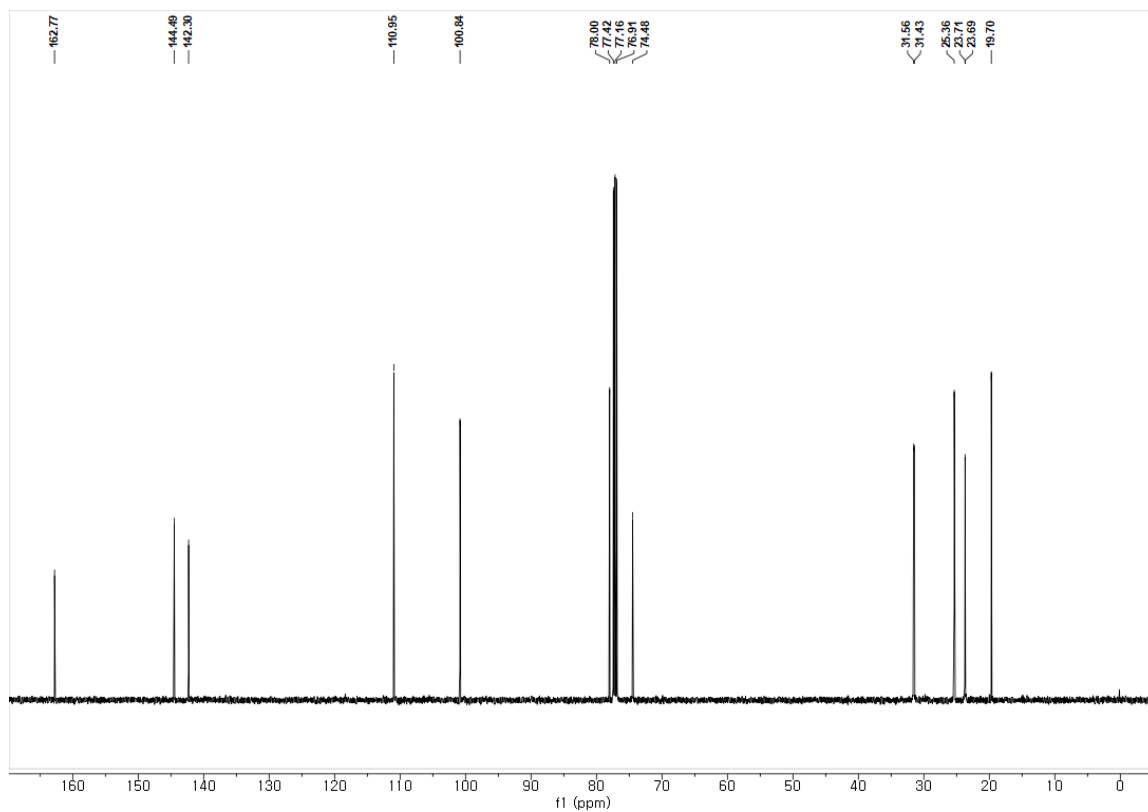


<sup>13</sup>C NMR spectrum of compound **11c(Z)** (125 MHz, CDCl<sub>3</sub>)



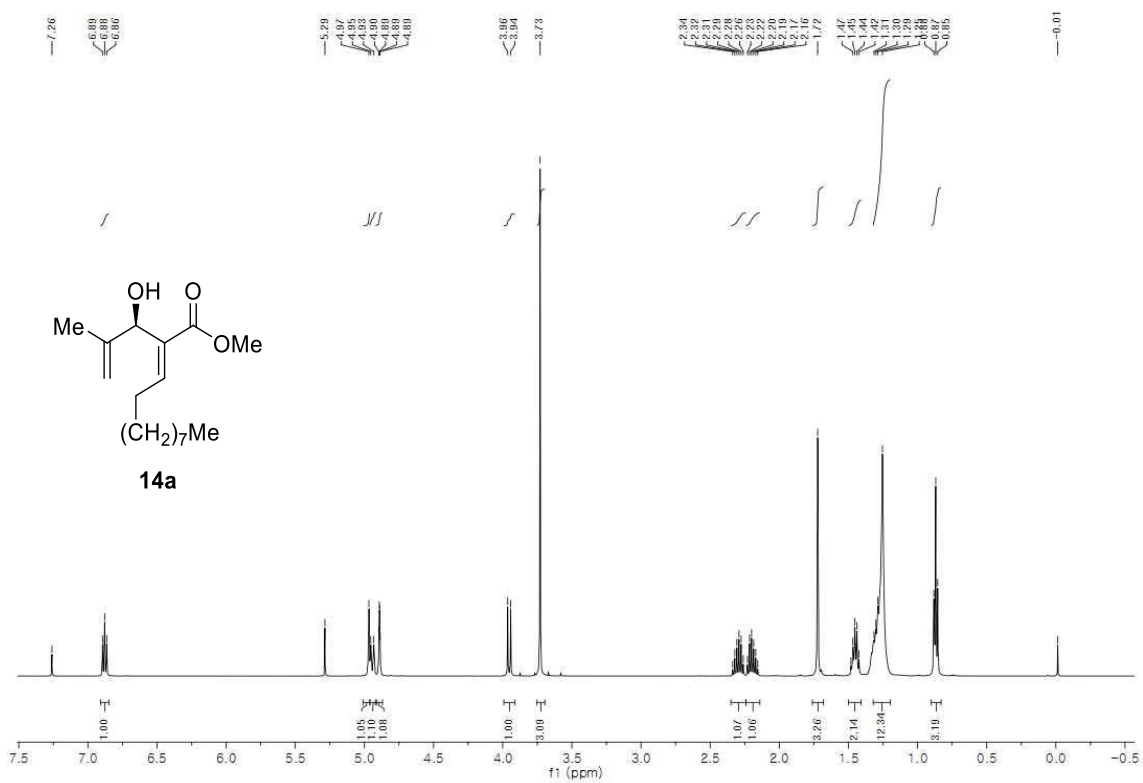


<sup>1</sup>H NMR spectrum of compound **11c(E)** (500 MHz, CDCl<sub>3</sub>)

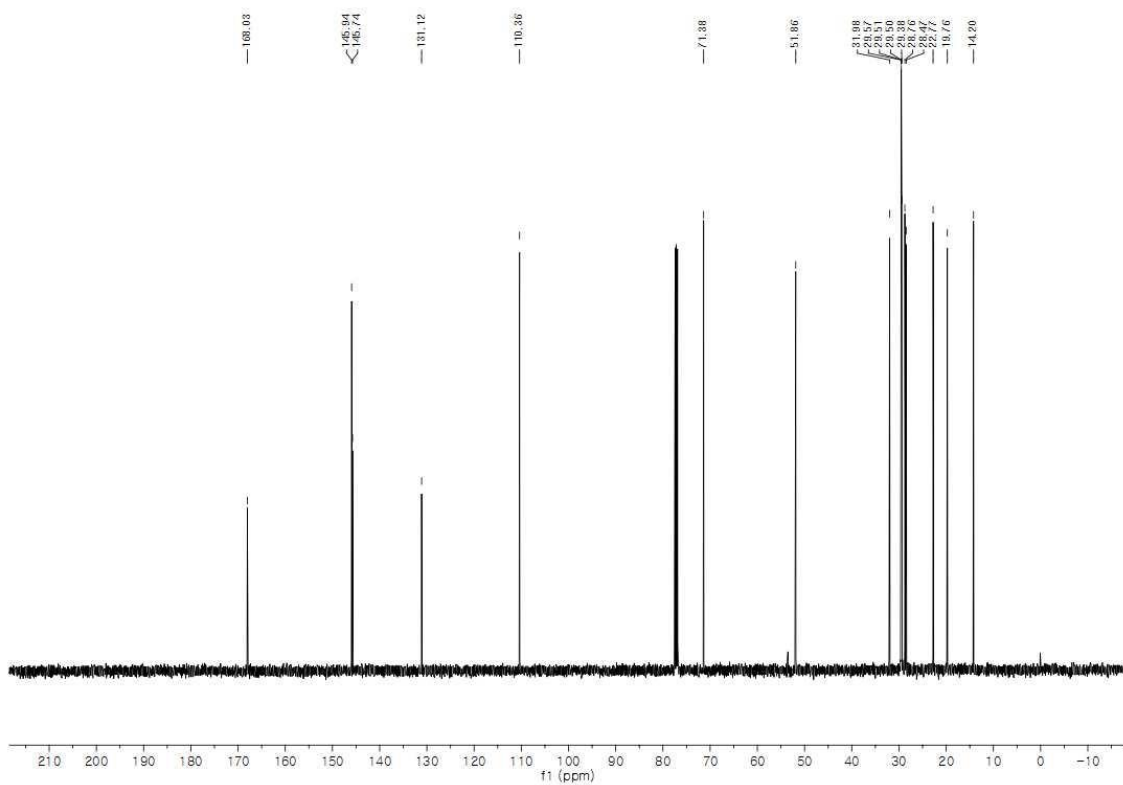


<sup>13</sup>C NMR spectrum of compound **11c(E)** (125 MHz, CDCl<sub>3</sub>)

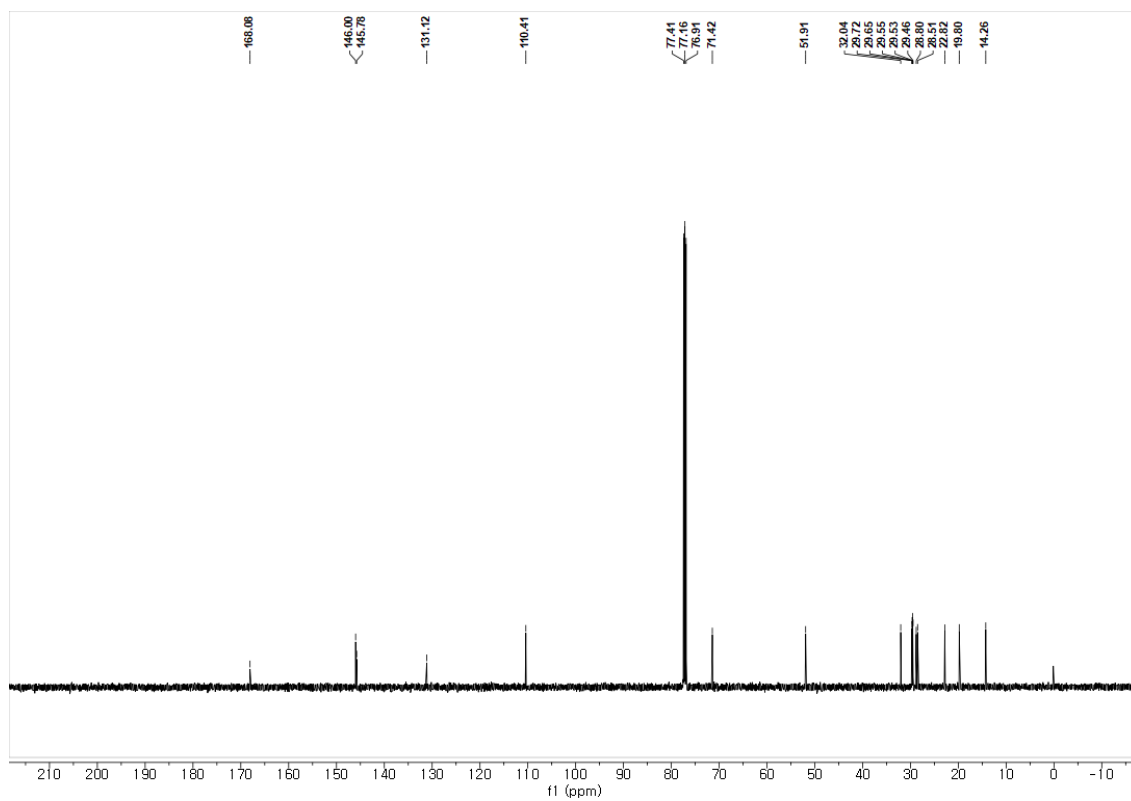
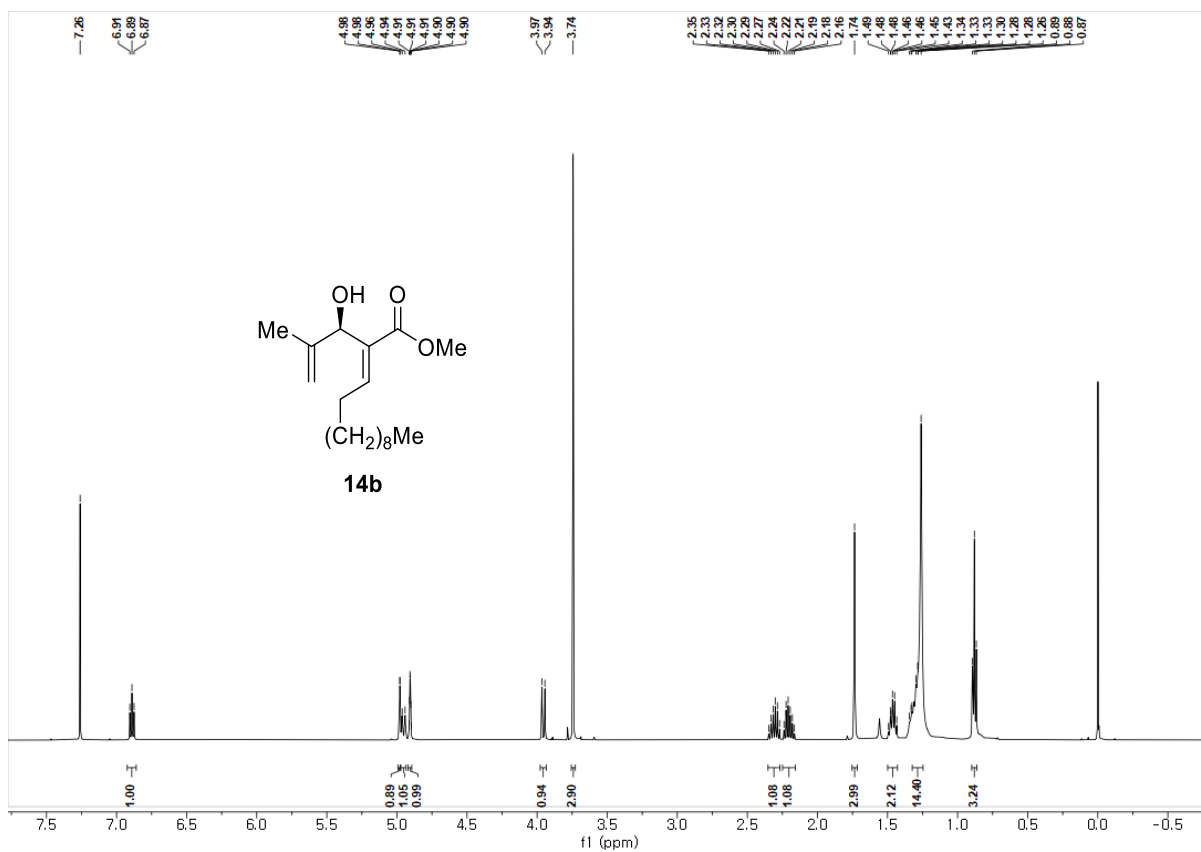


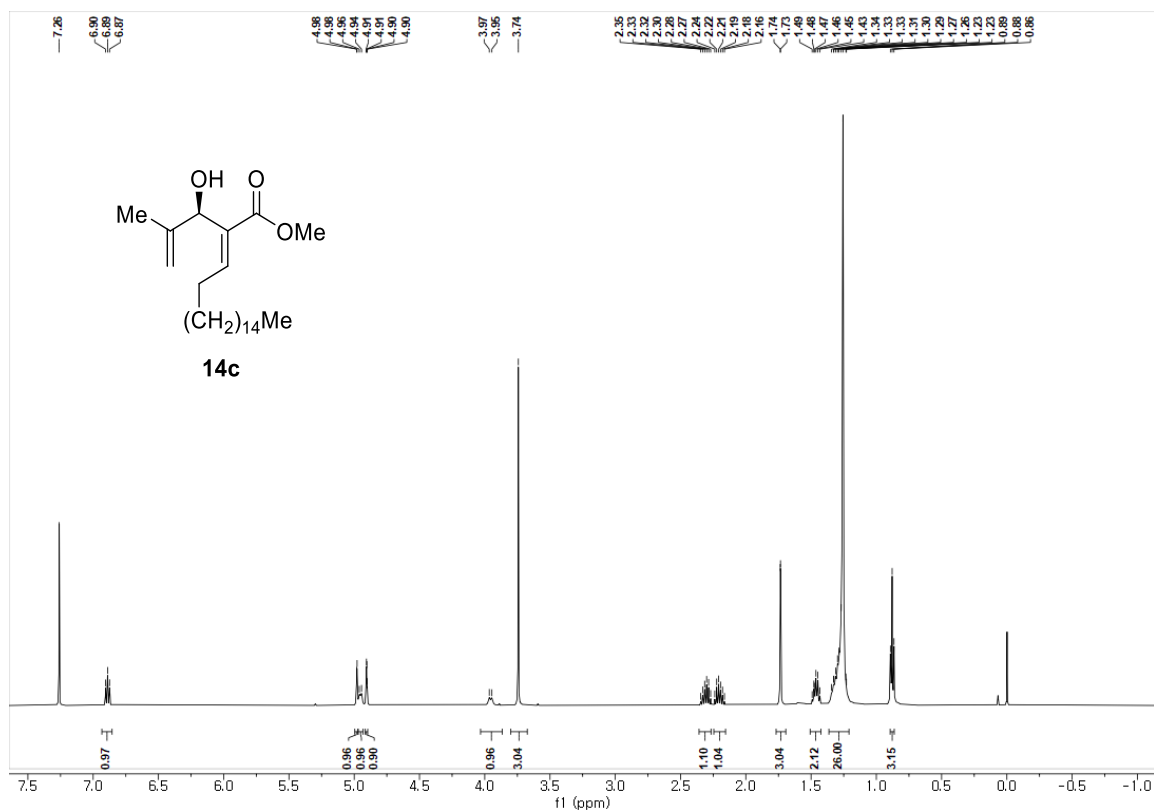


<sup>1</sup>H NMR spectrum of compound **14a** (500 MHz, CDCl<sub>3</sub>)

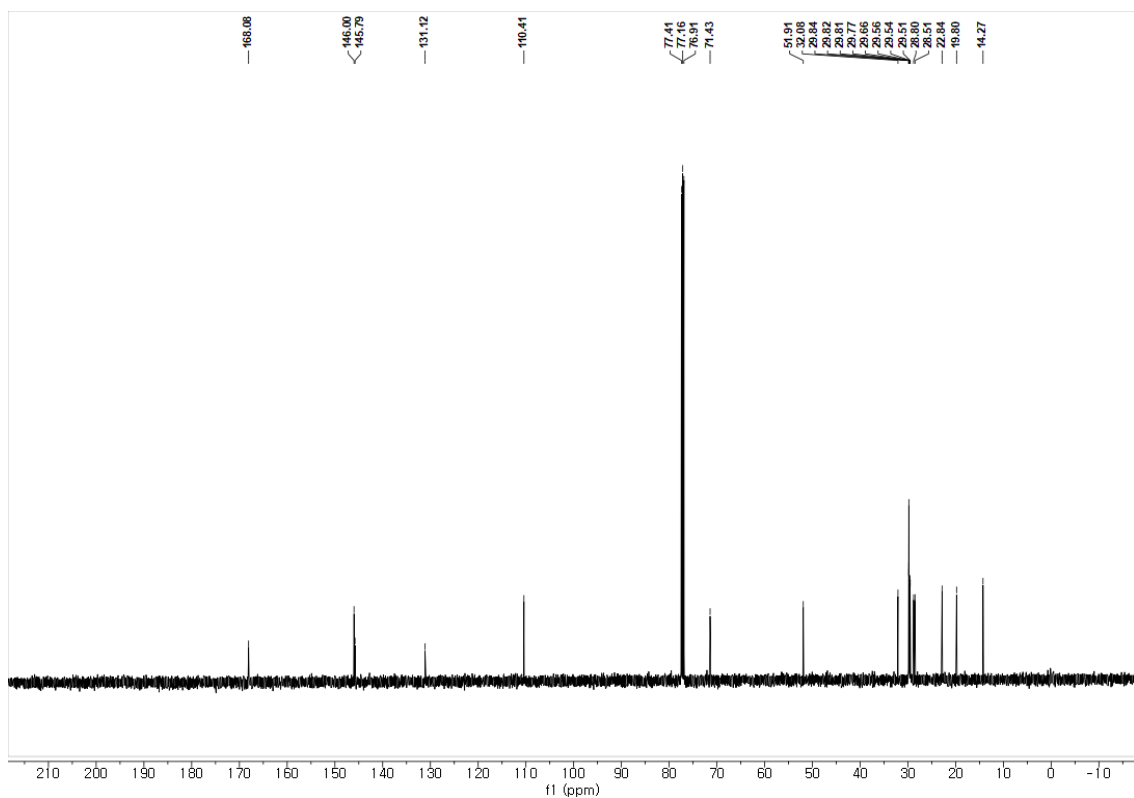


<sup>13</sup>C NMR spectrum of compound **14a** (125 MHz, CDCl<sub>3</sub>)

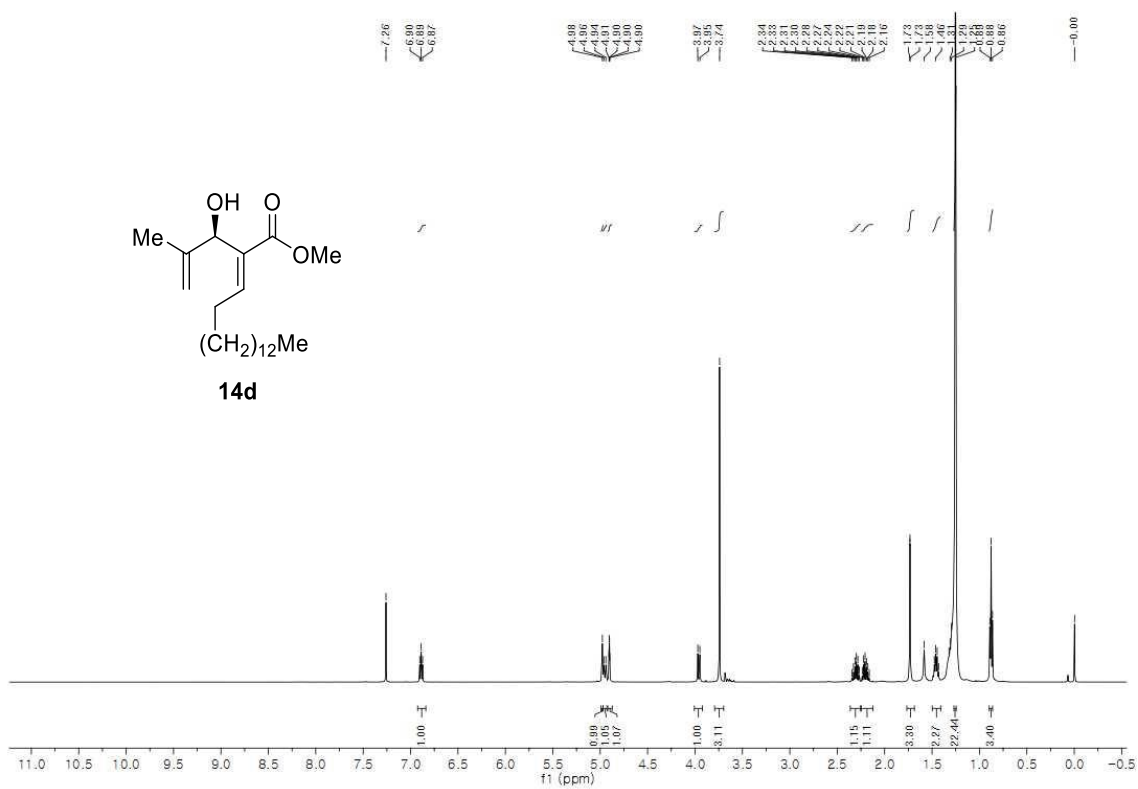




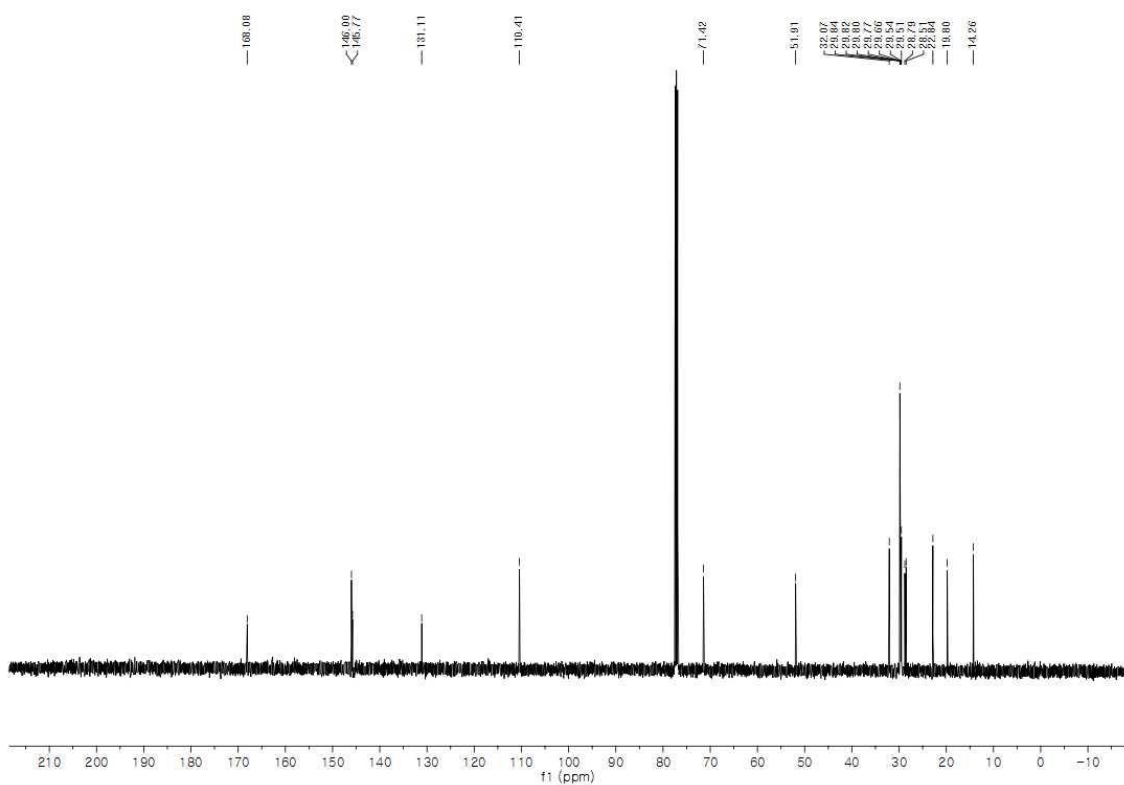
<sup>1</sup>H NMR spectrum of compound **14c** (500 MHz, CDCl<sub>3</sub>)



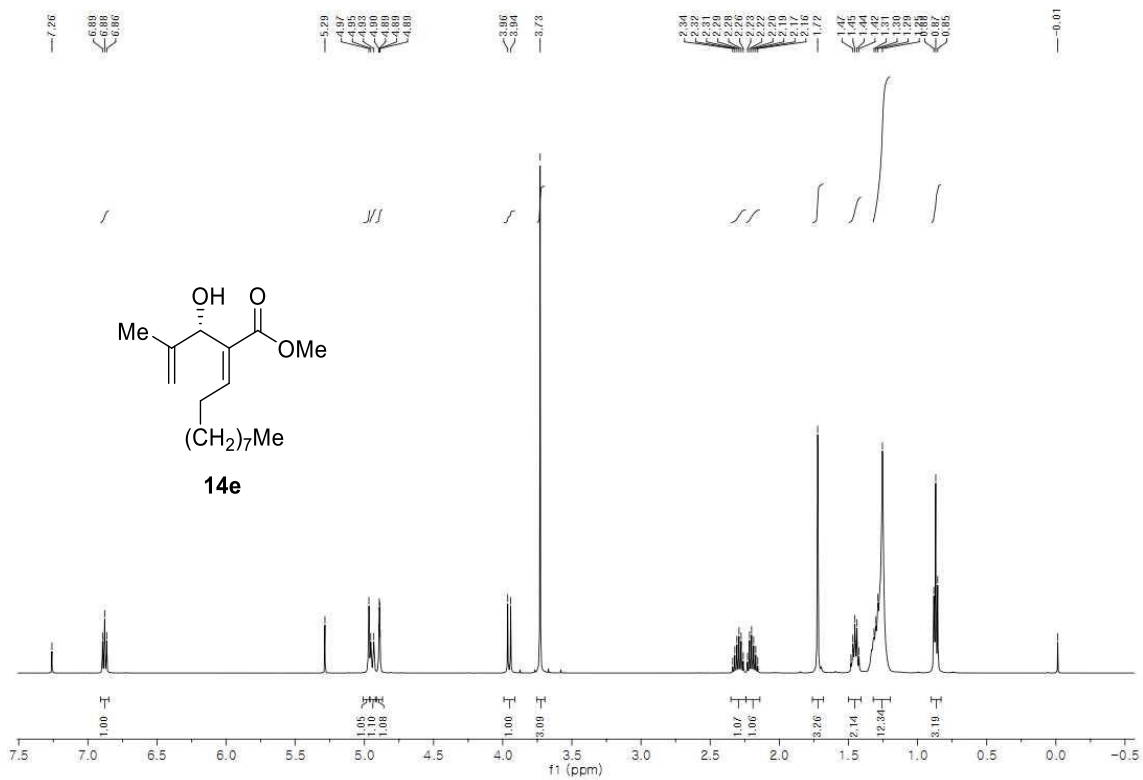
<sup>13</sup>C NMR spectrum of compound **14c** (125 MHz, CDCl<sub>3</sub>)



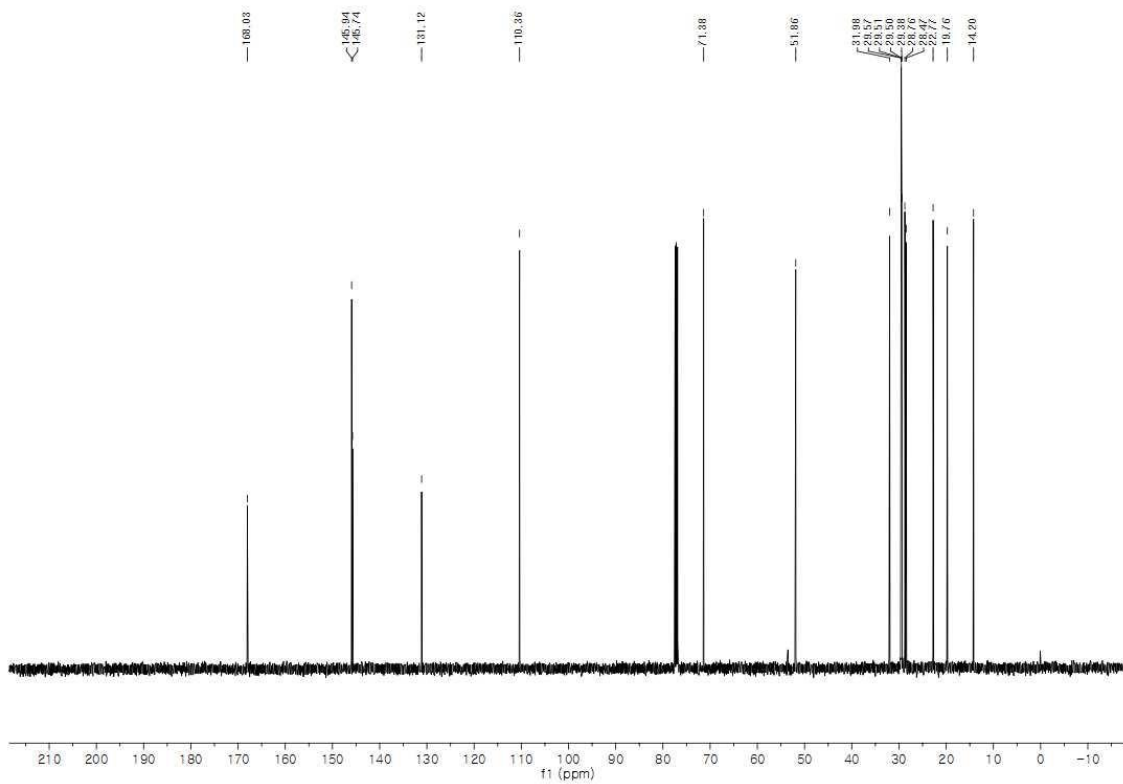
<sup>1</sup>H NMR spectrum of compound **14d** (500 MHz, CDCl<sub>3</sub>)



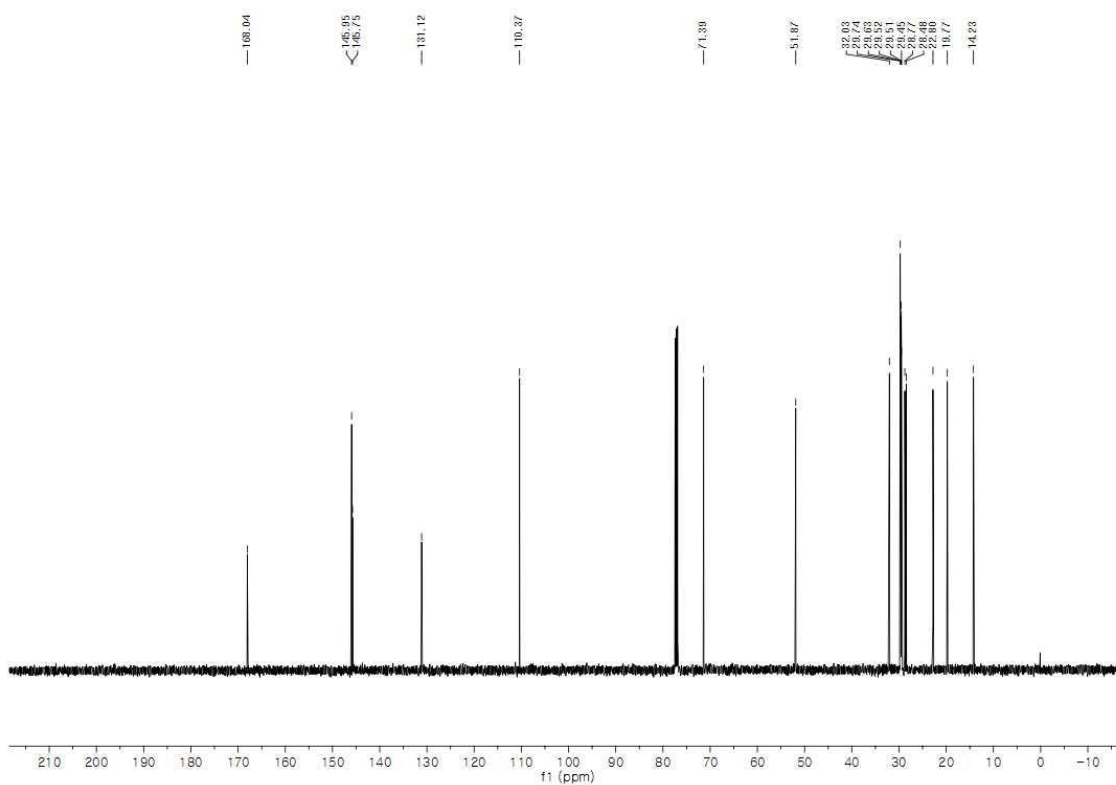
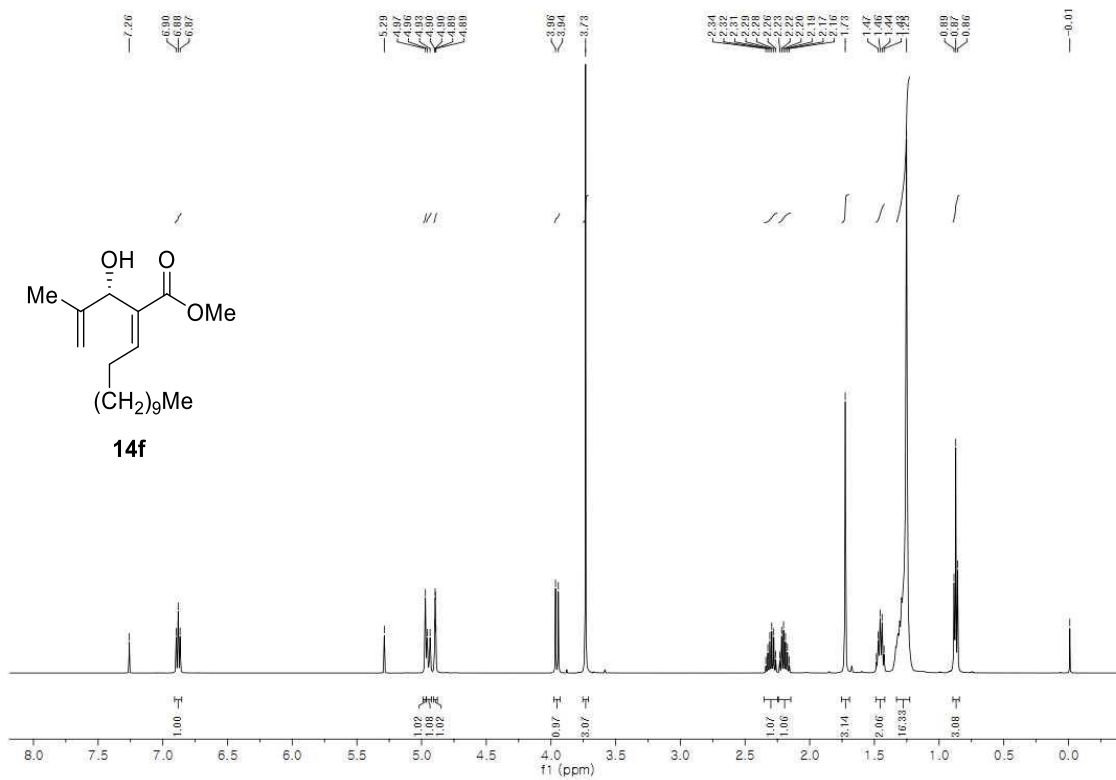
<sup>13</sup>C NMR spectrum of compound **14d** (125 MHz, CDCl<sub>3</sub>)

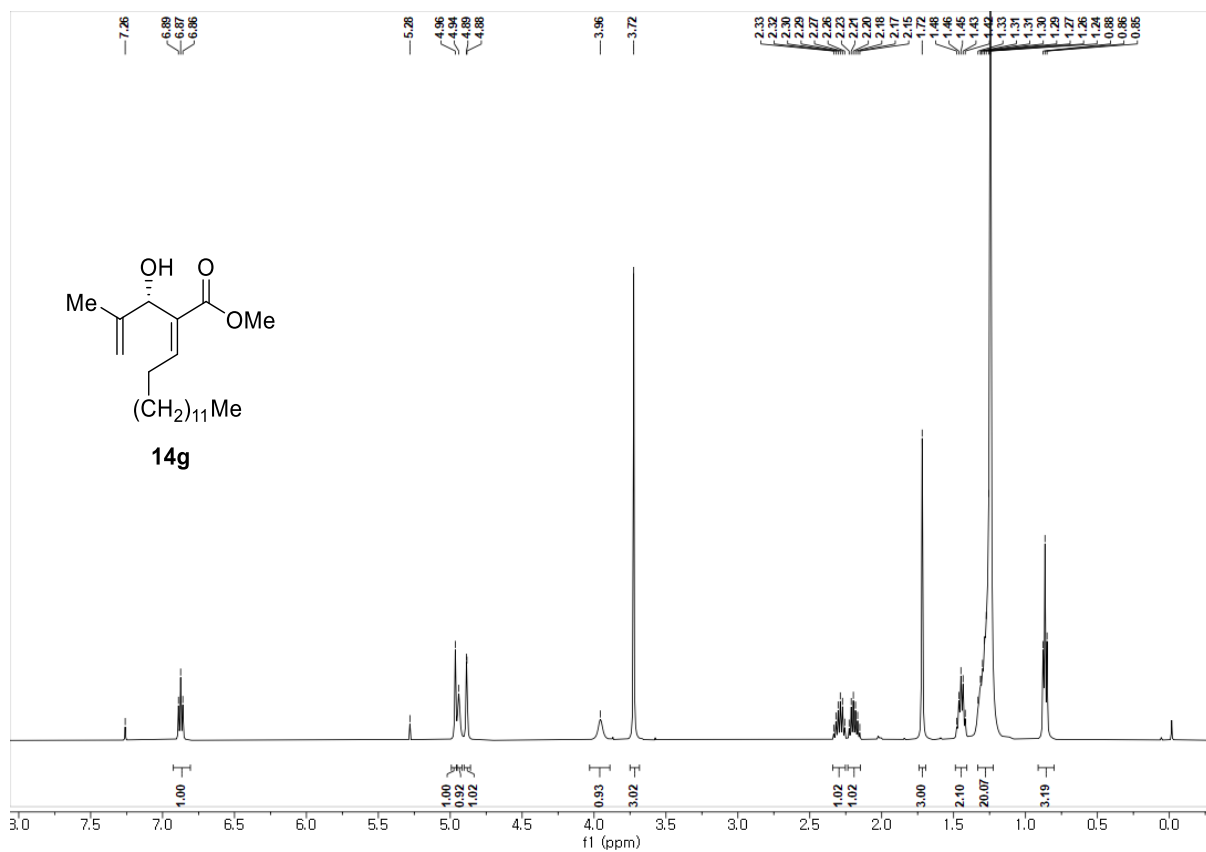


<sup>1</sup>H NMR spectrum of compound **14e** (500 MHz, CDCl<sub>3</sub>)

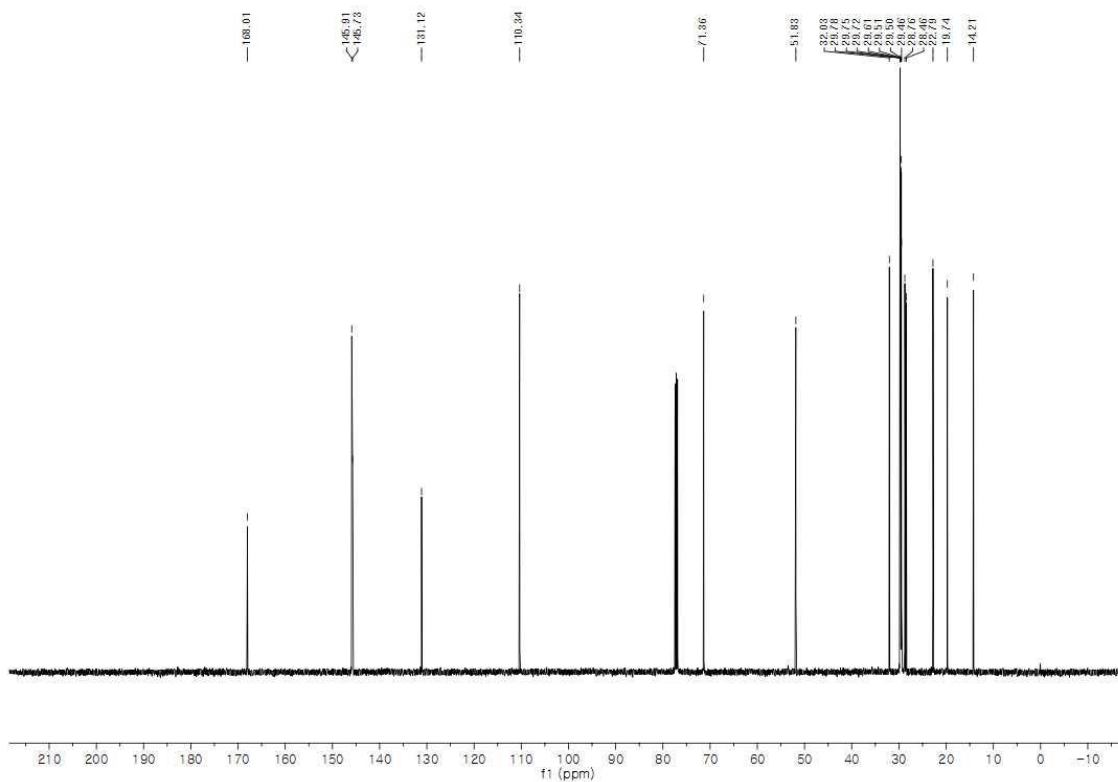


<sup>13</sup>C NMR spectrum of compound **14e** (125 MHz, CDCl<sub>3</sub>)

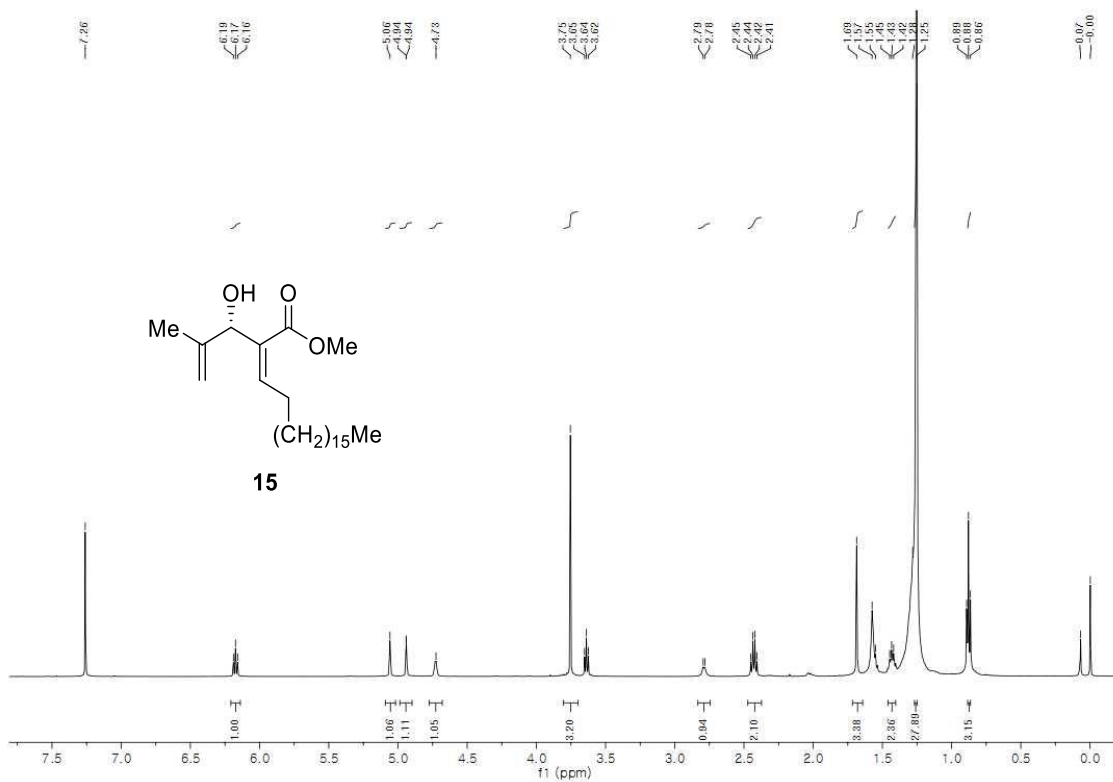




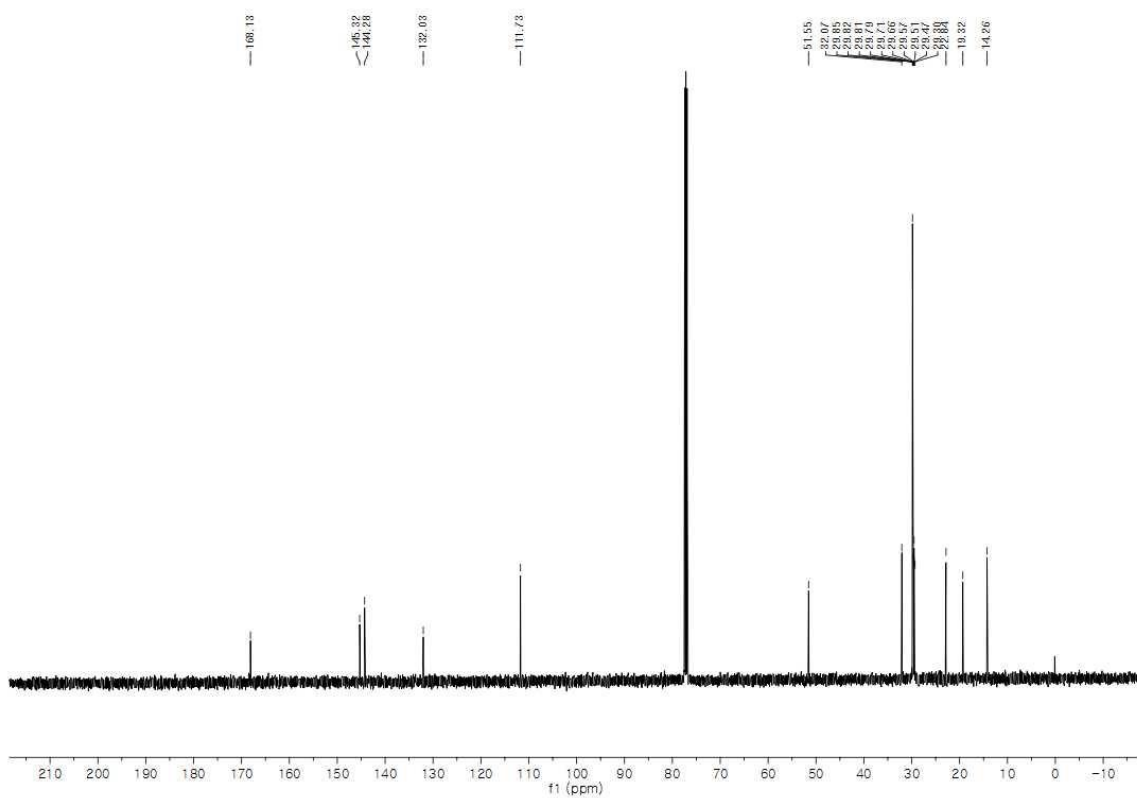
**<sup>1</sup>H NMR spectrum of compound 14g (500 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR spectrum of compound 14g (125 MHz, CDCl<sub>3</sub>)**

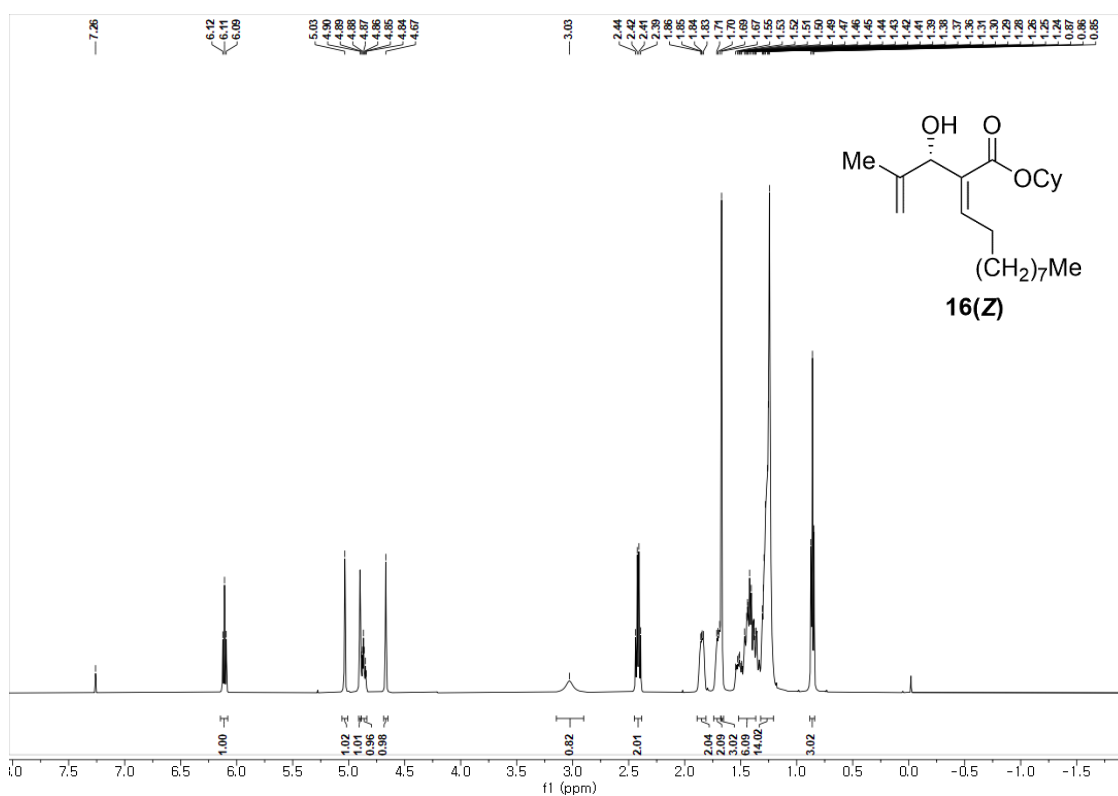


<sup>1</sup>H NMR spectrum of compound **15** (500 MHz, CDCl<sub>3</sub>)

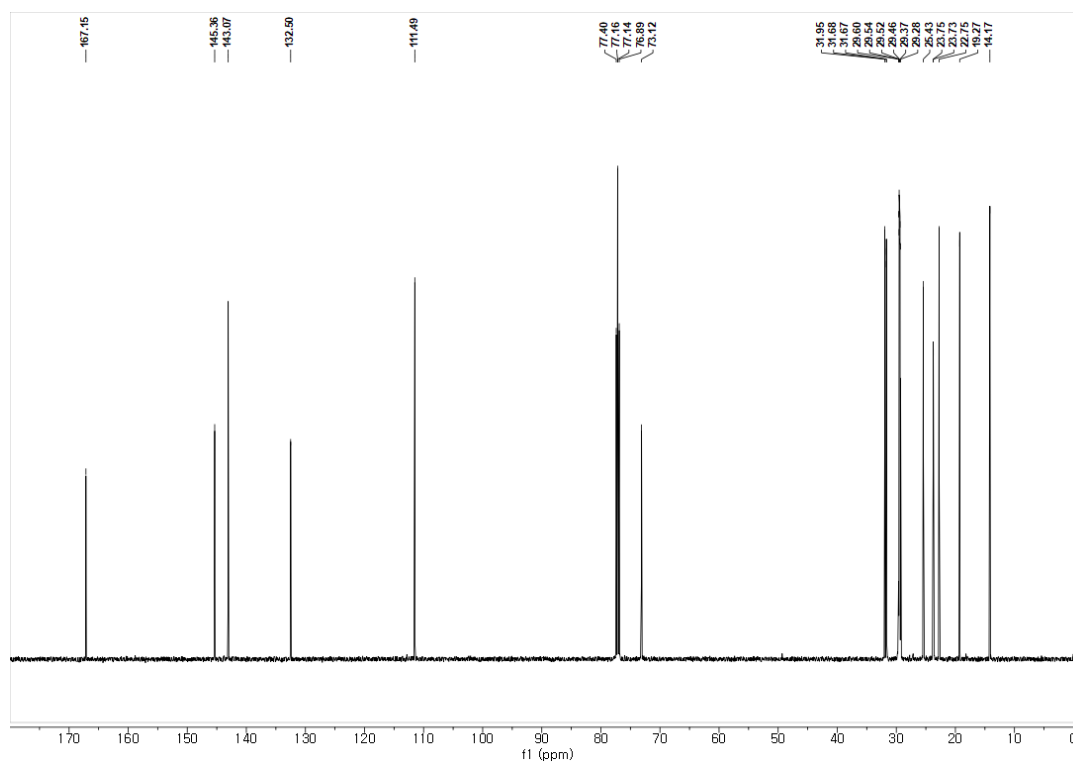


<sup>13</sup>C NMR spectrum of compound **15** (125 MHz, CDCl<sub>3</sub>)

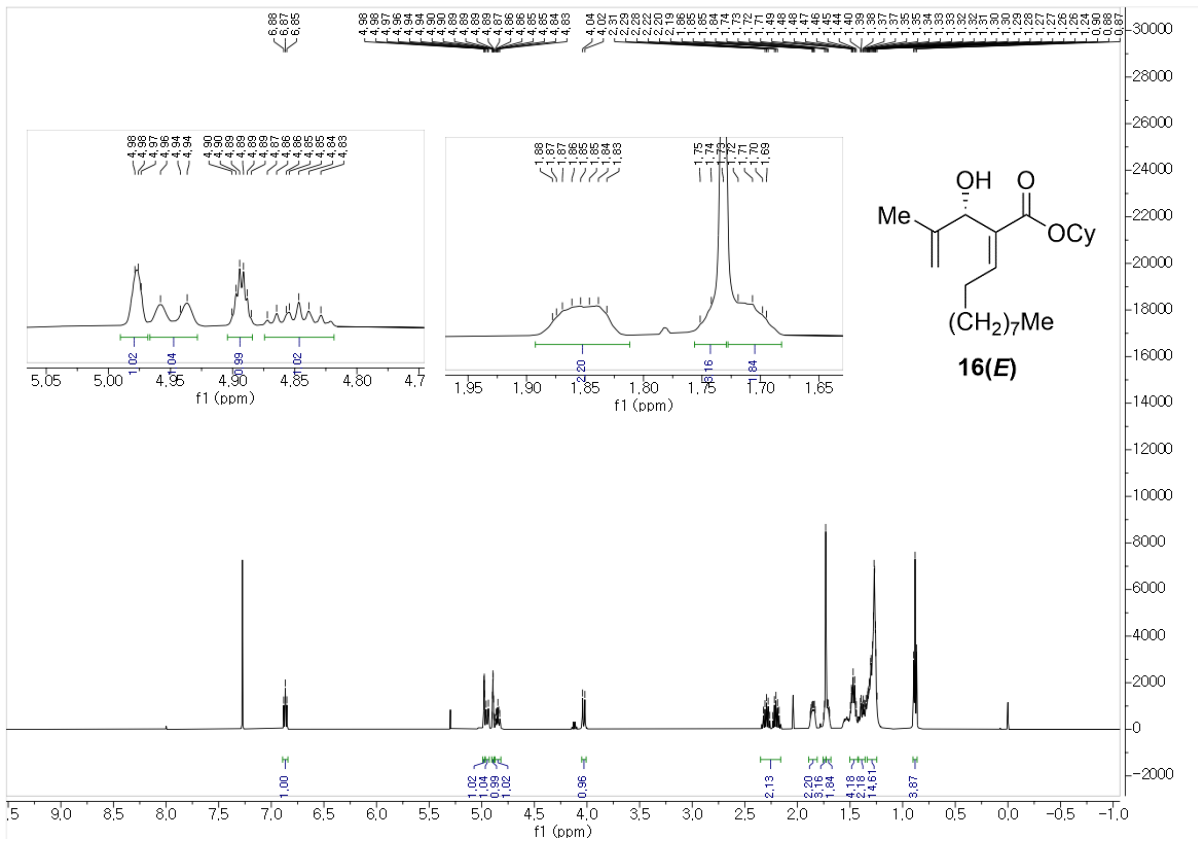




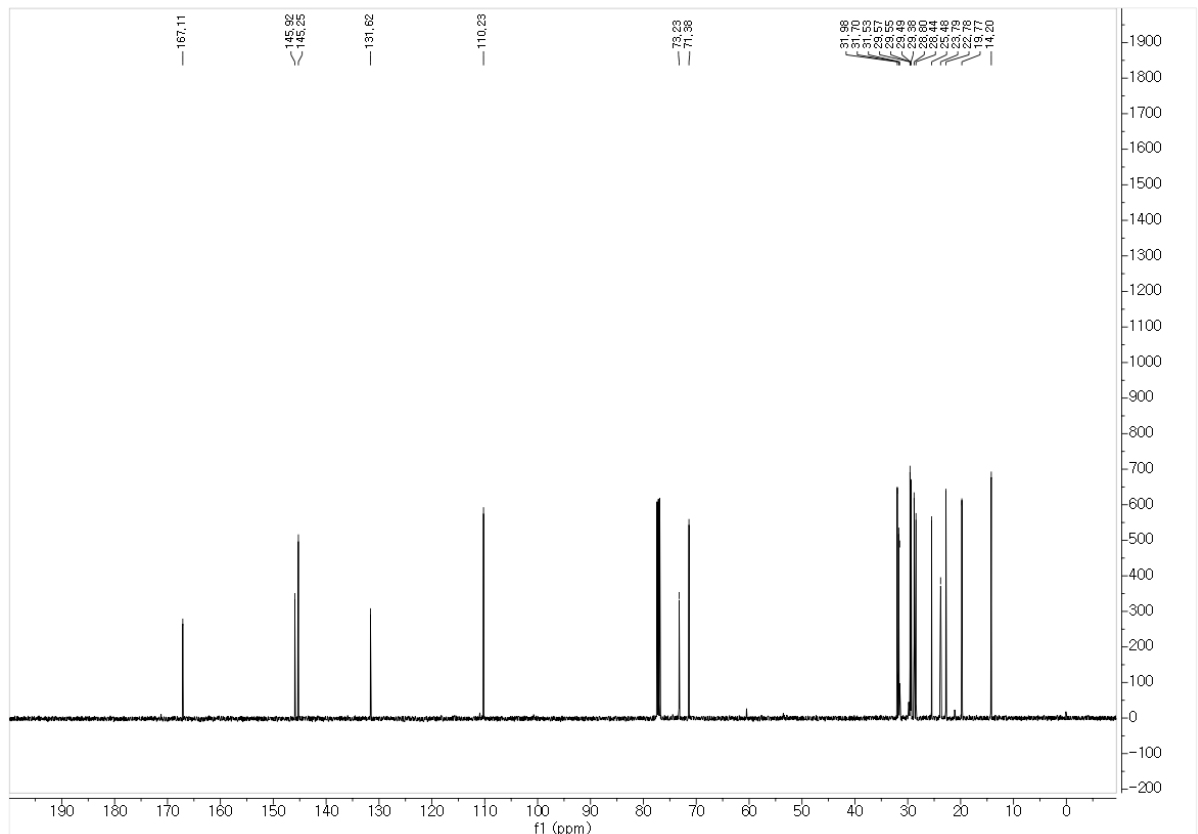
<sup>1</sup>H NMR spectrum of compound **16(Z)** (500 MHz, CDCl<sub>3</sub>)



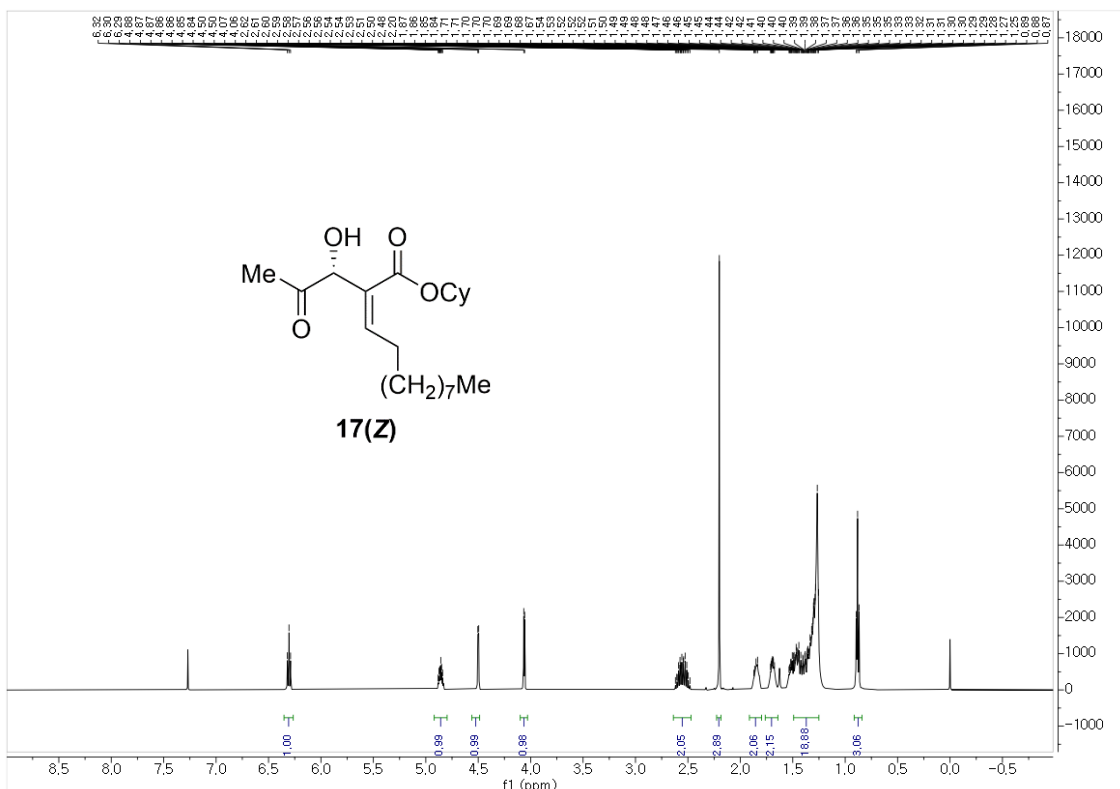
<sup>13</sup>C NMR spectrum of compound **16(Z)** (125 MHz, CDCl<sub>3</sub>)



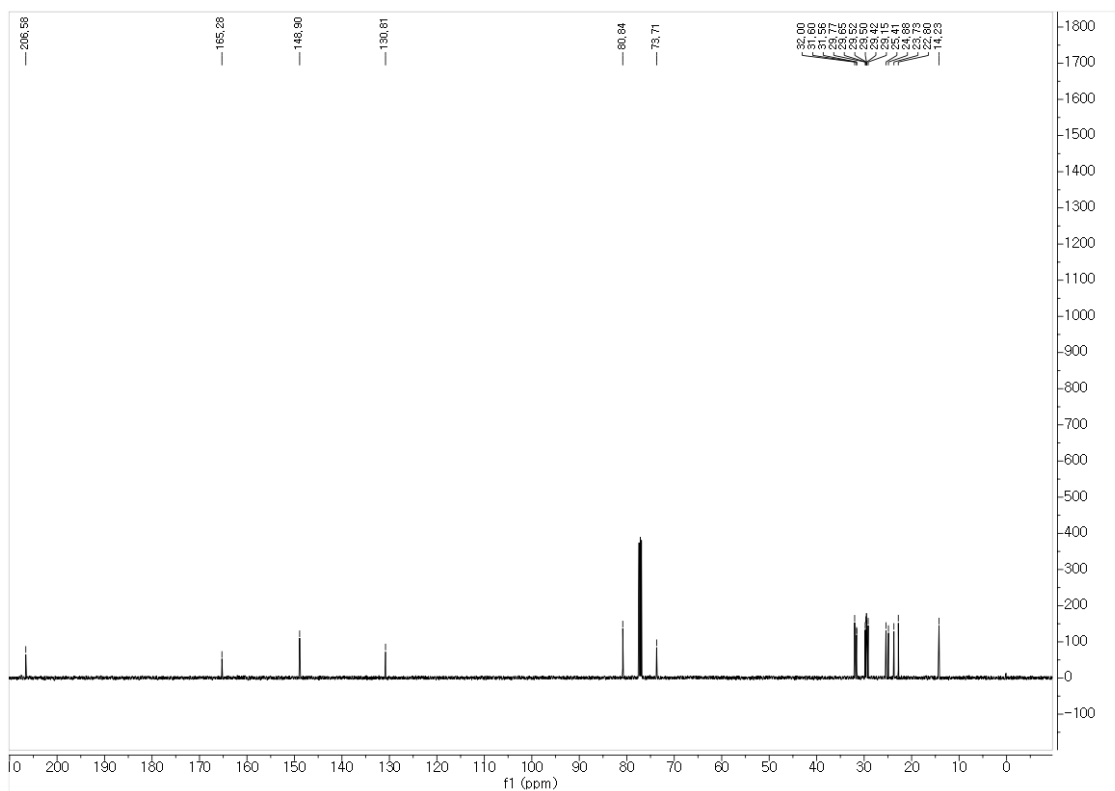
**<sup>1</sup>H NMR spectrum of compound 16(E) (500 MHz, CDCl<sub>3</sub>)**



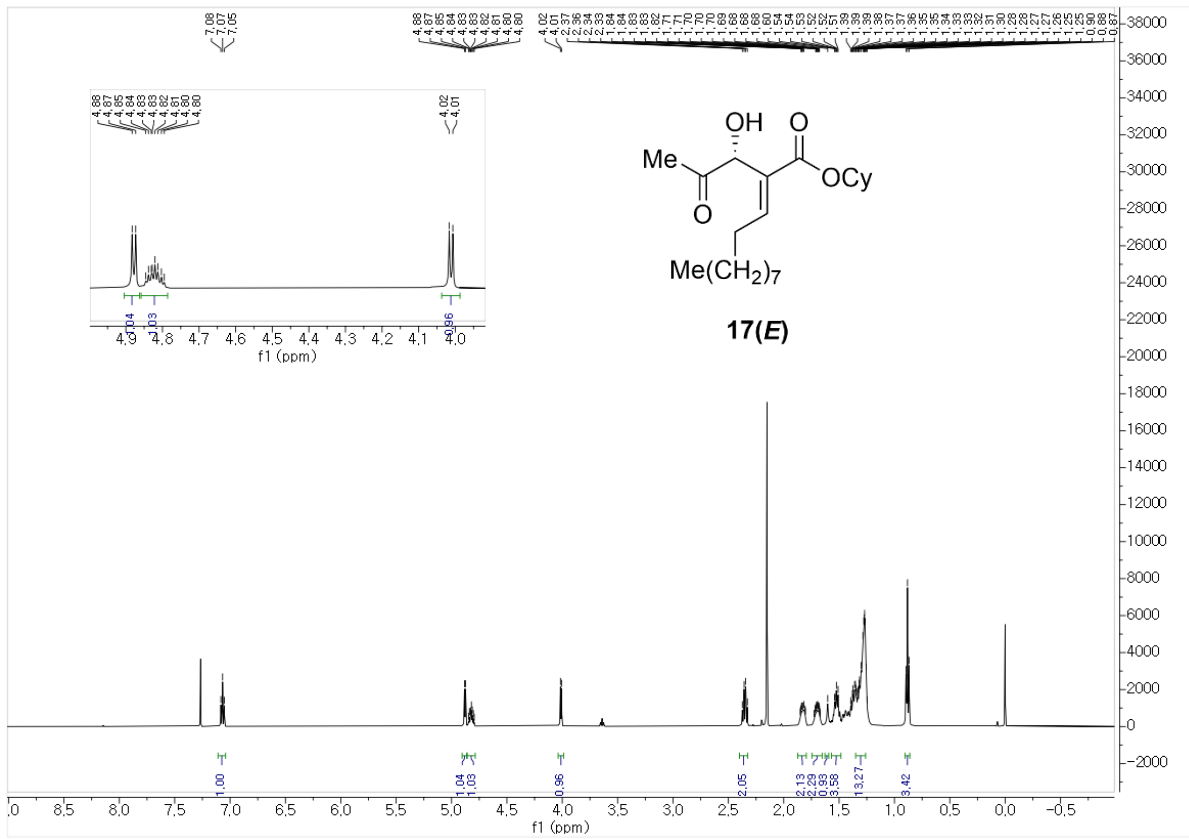
**<sup>13</sup>C NMR spectrum of compound 16(E) (125 MHz, CDCl<sub>3</sub>)**



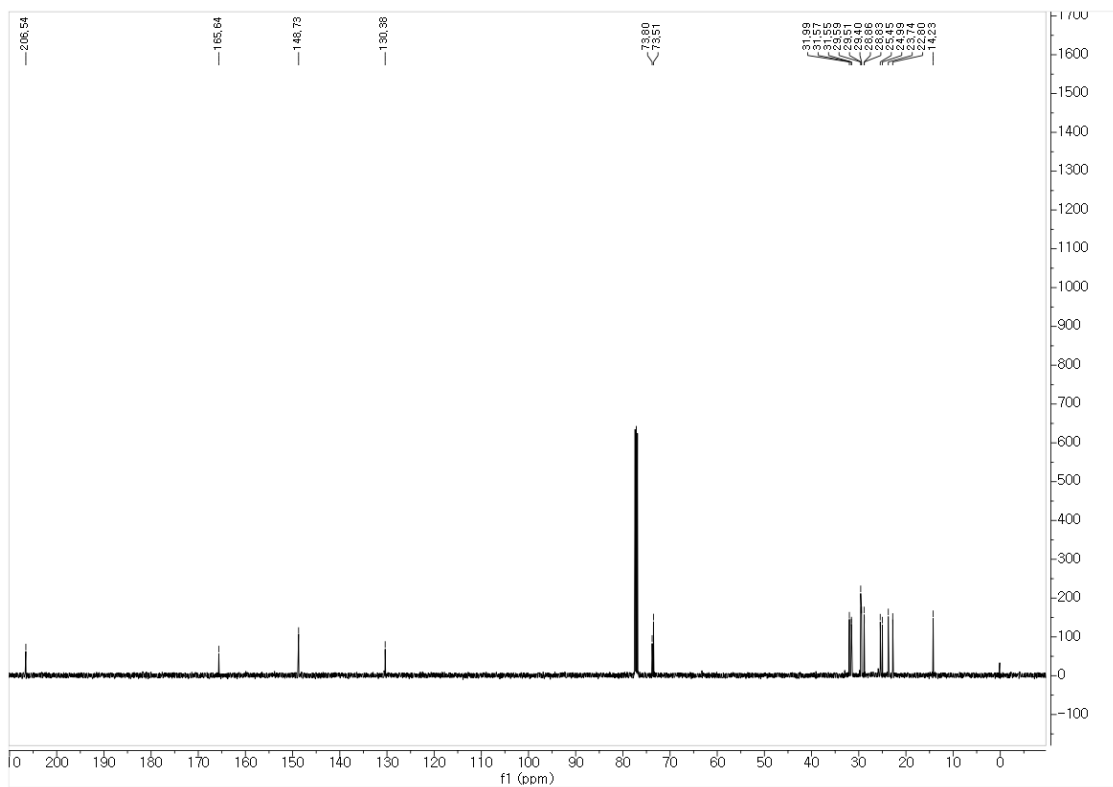
<sup>1</sup>H NMR spectrum of compound **17(Z)** (500 MHz, CDCl<sub>3</sub>)



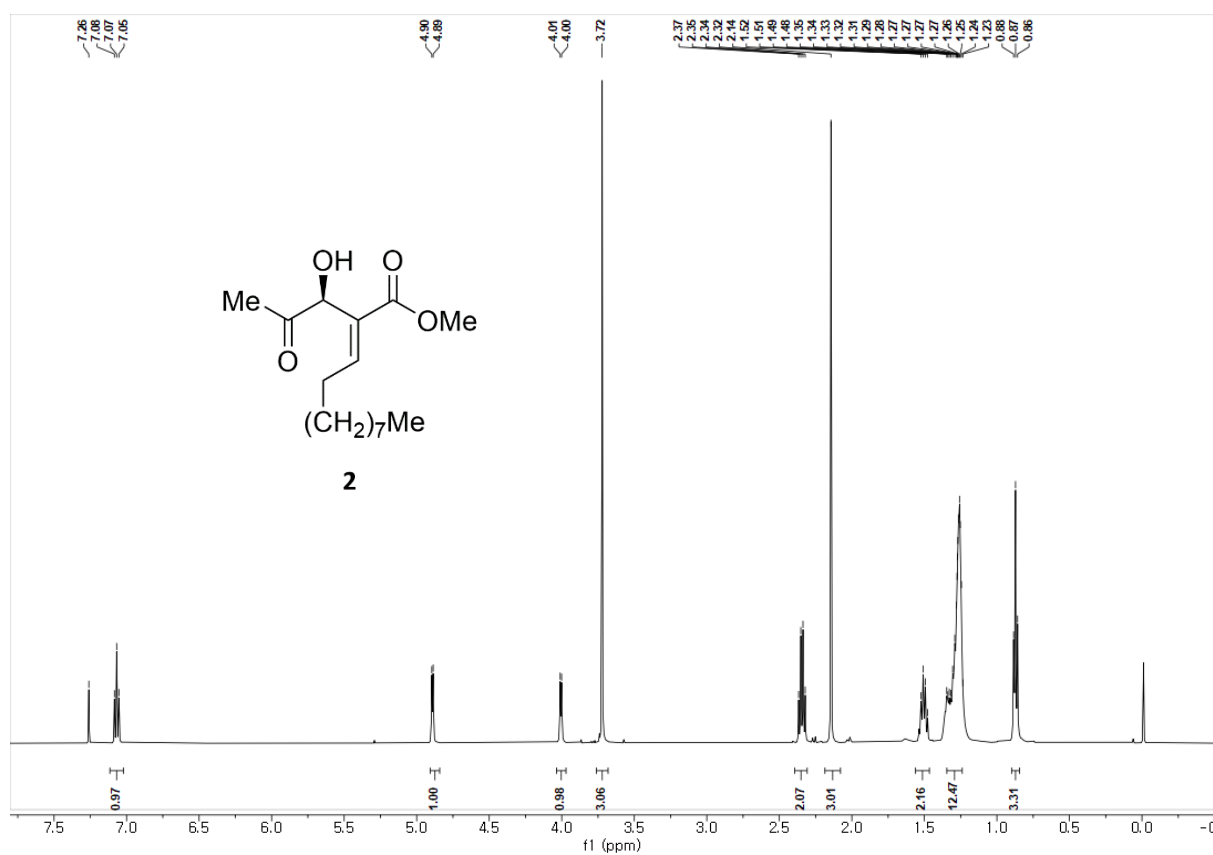
<sup>13</sup>C NMR spectrum of compound **17(Z)** (125 MHz, CDCl<sub>3</sub>)



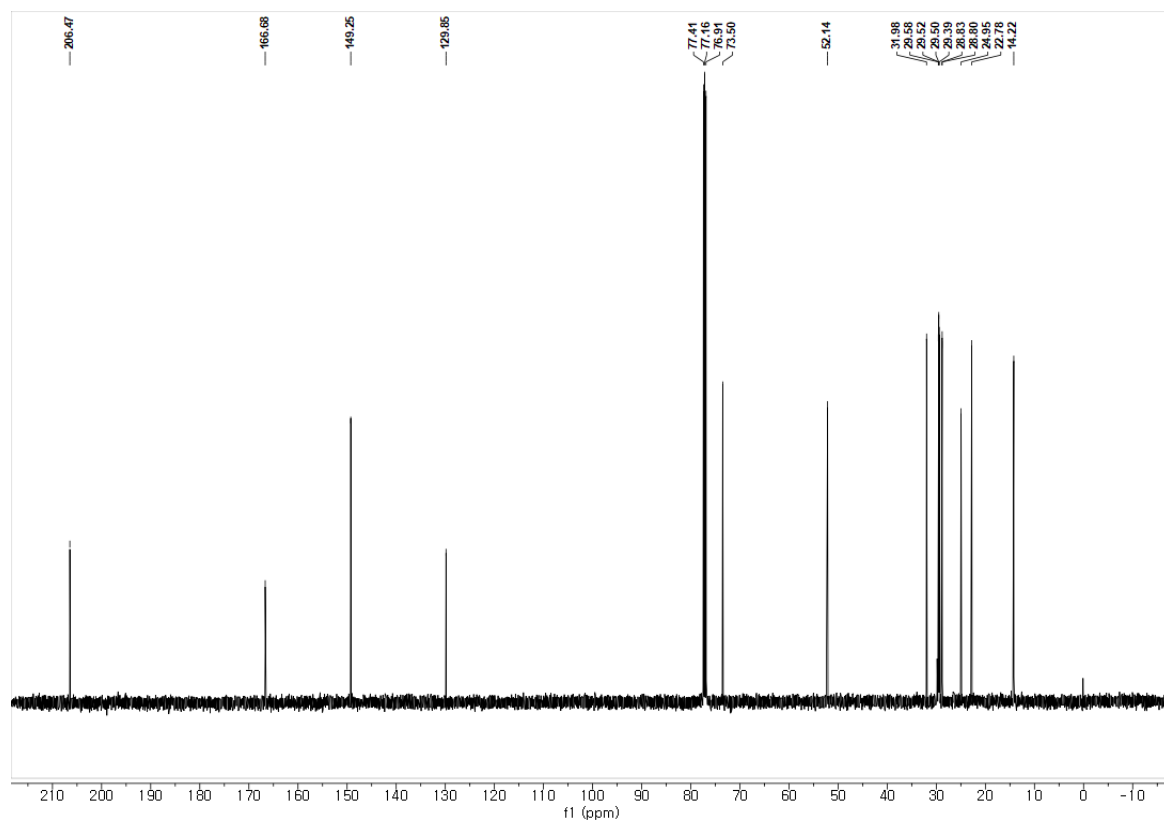
<sup>1</sup>H NMR spectrum of compound **17(E)** (500 MHz, CDCl<sub>3</sub>)



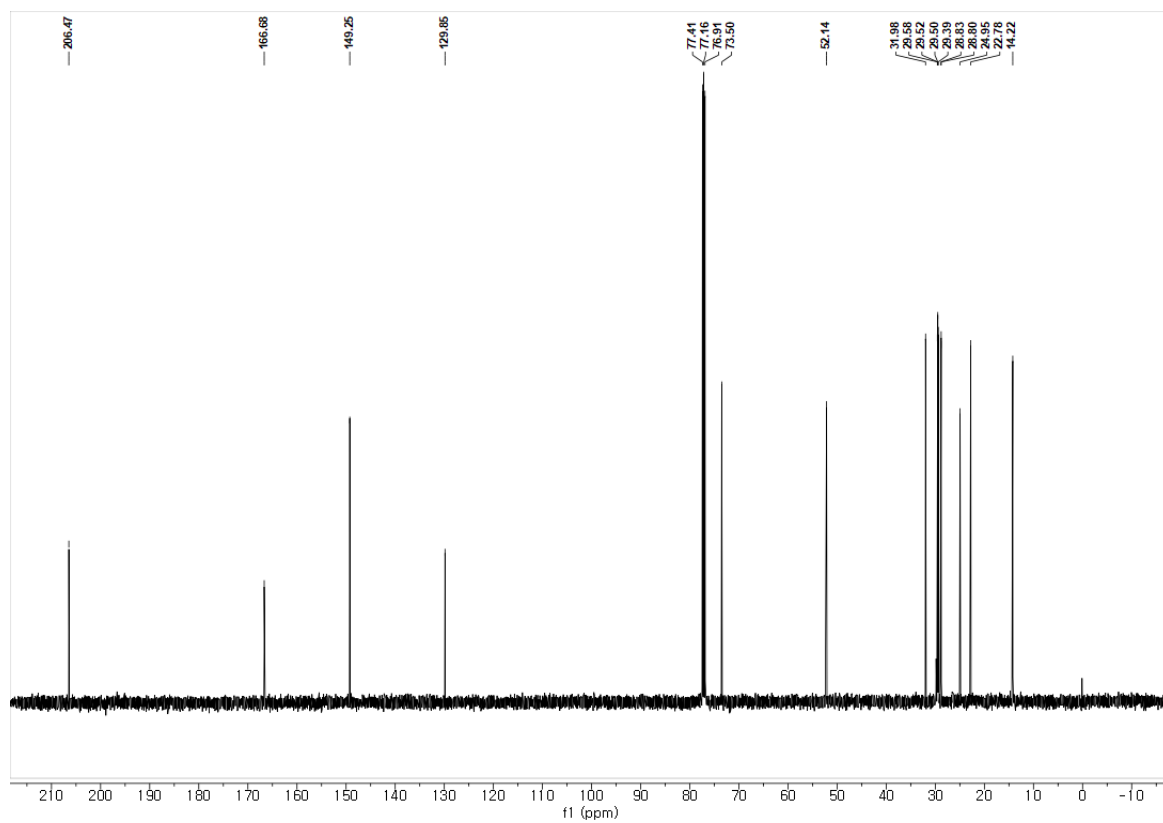
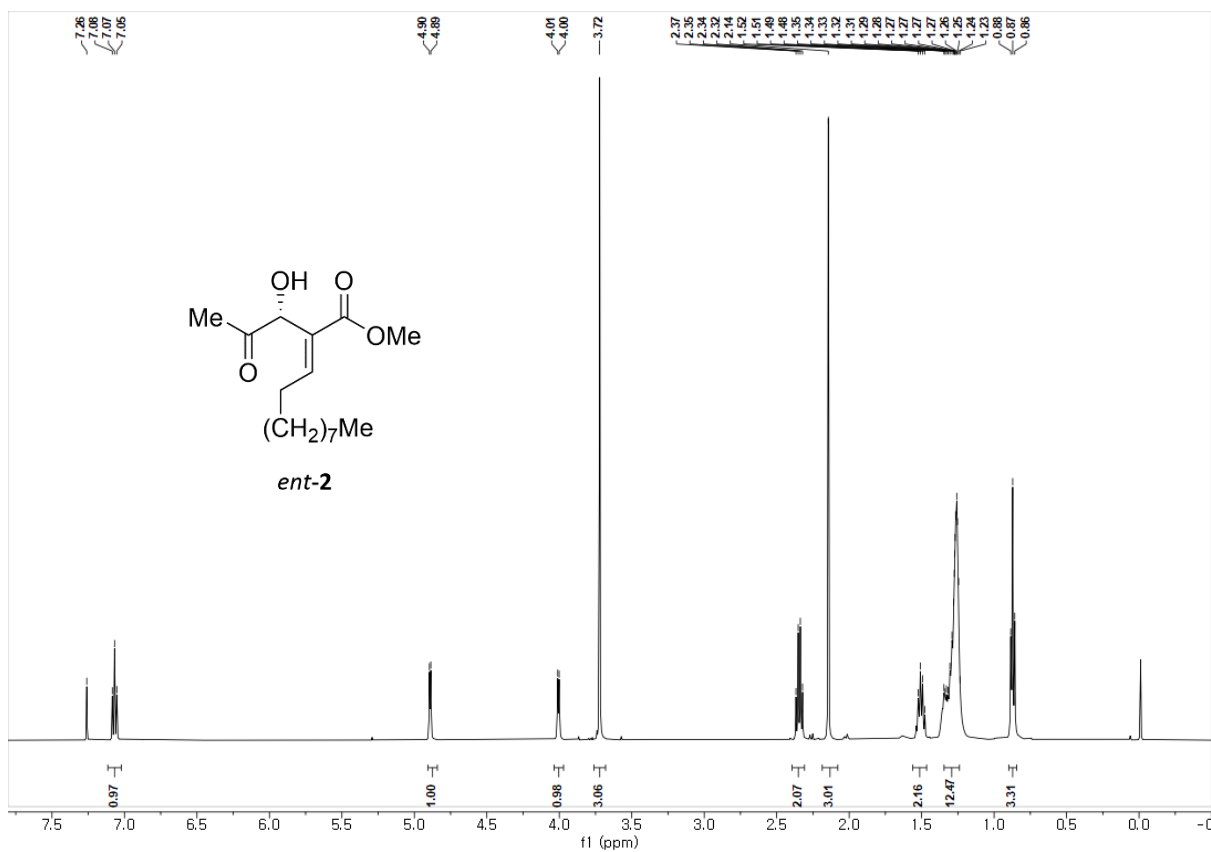
<sup>13</sup>C NMR spectrum of compound **17(E)** (125 MHz, CDCl<sub>3</sub>)



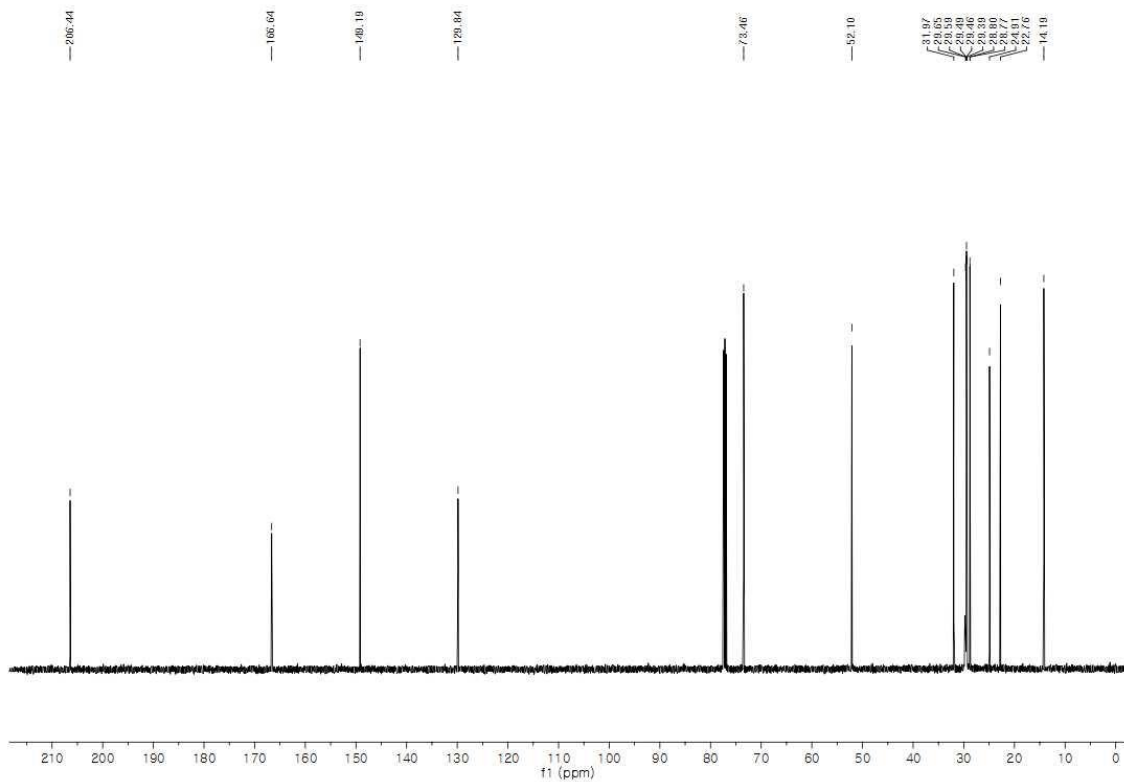
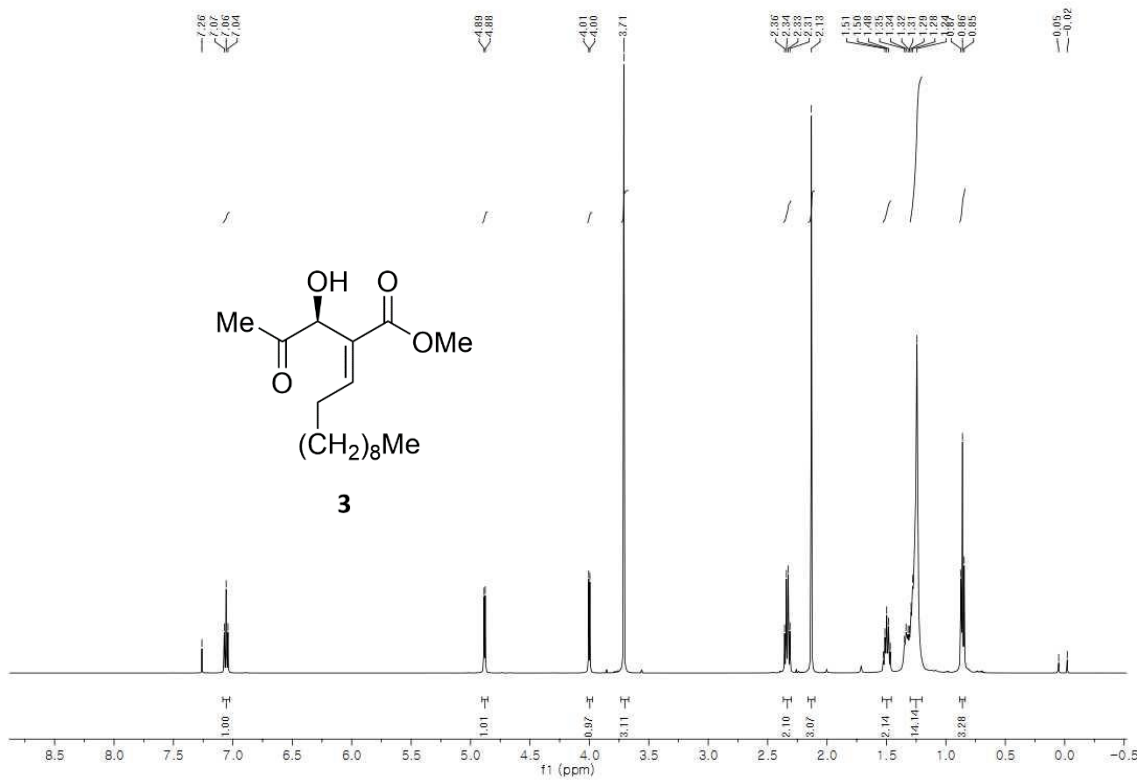
<sup>1</sup>H NMR spectrum of compound **2** (500 MHz, CDCl<sub>3</sub>)

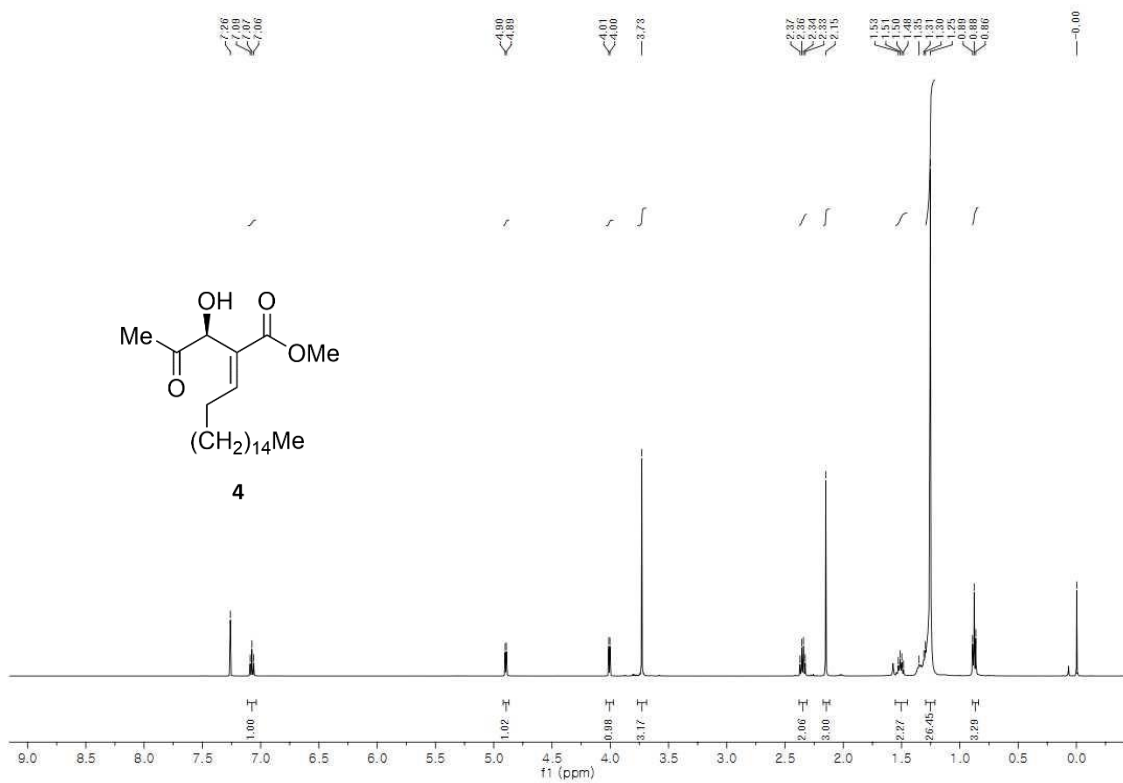


<sup>13</sup>C NMR spectrum of compound **2** (125 MHz, CDCl<sub>3</sub>)

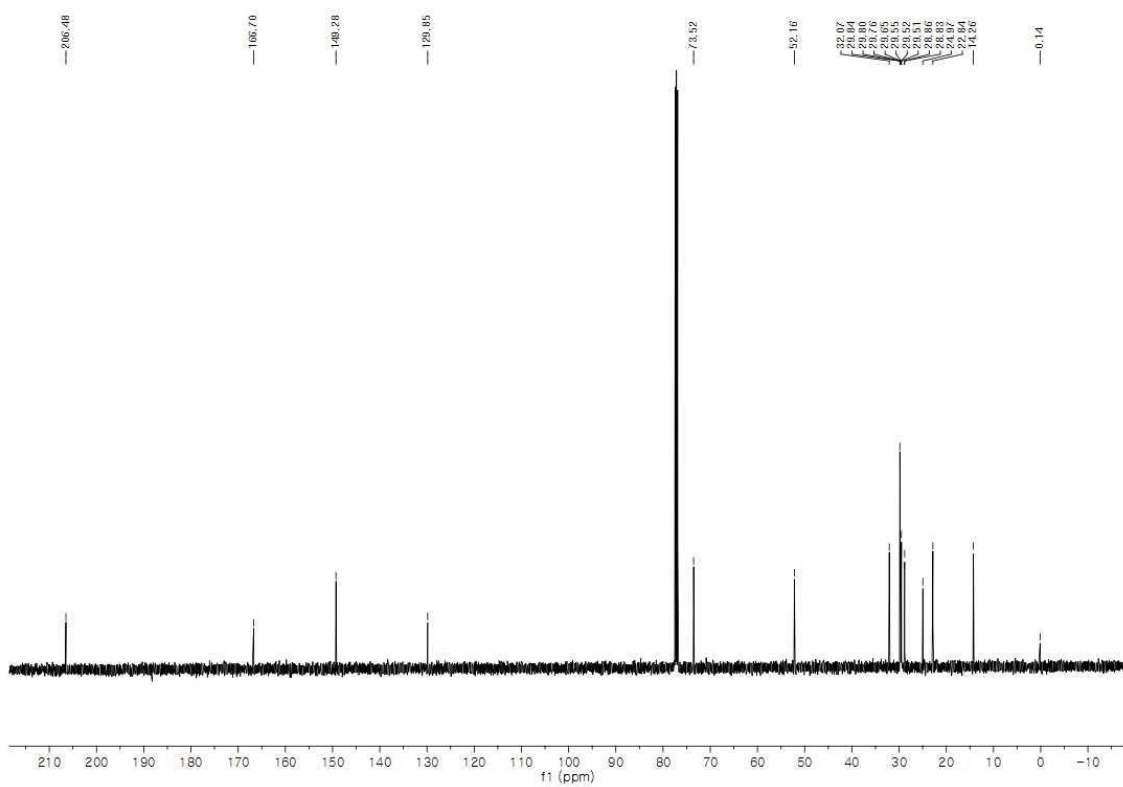


<sup>13</sup>C NMR spectrum of compound *ent-2* (125 MHz, CDCl<sub>3</sub>)



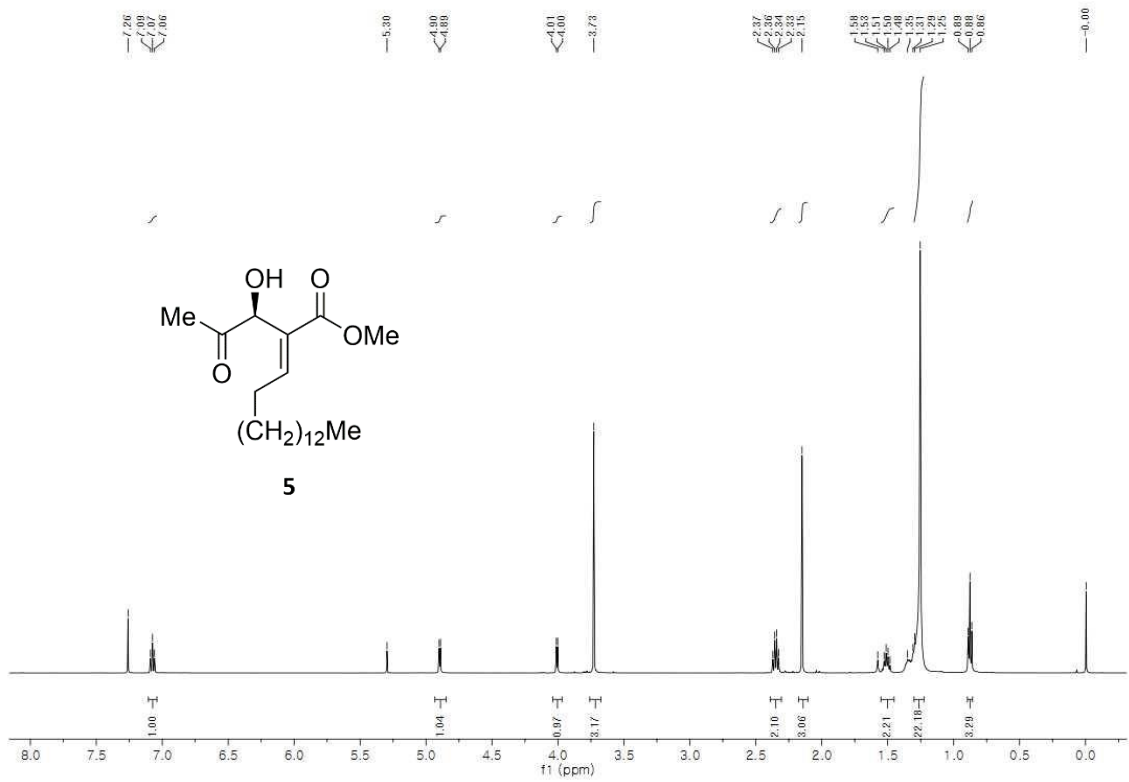


<sup>1</sup>H NMR spectrum of compound **4** (500 MHz, CDCl<sub>3</sub>)

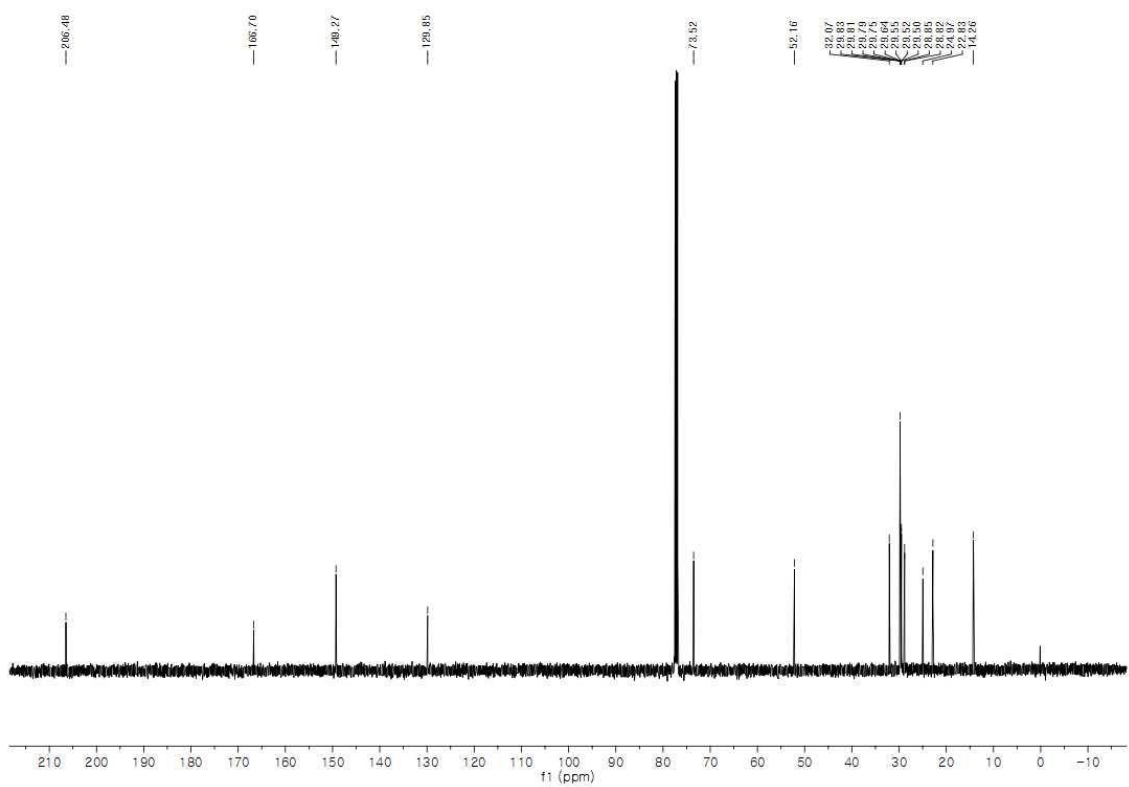


<sup>13</sup>C NMR spectrum of compound **4** (125 MHz, CDCl<sub>3</sub>)

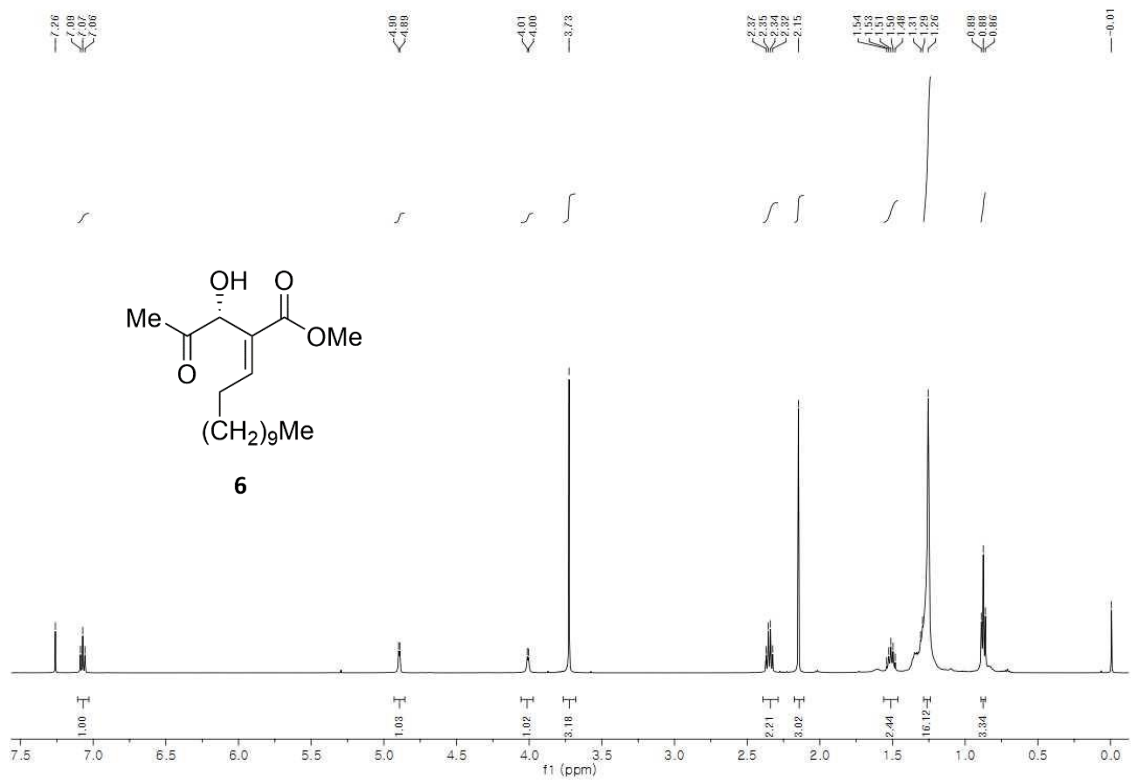




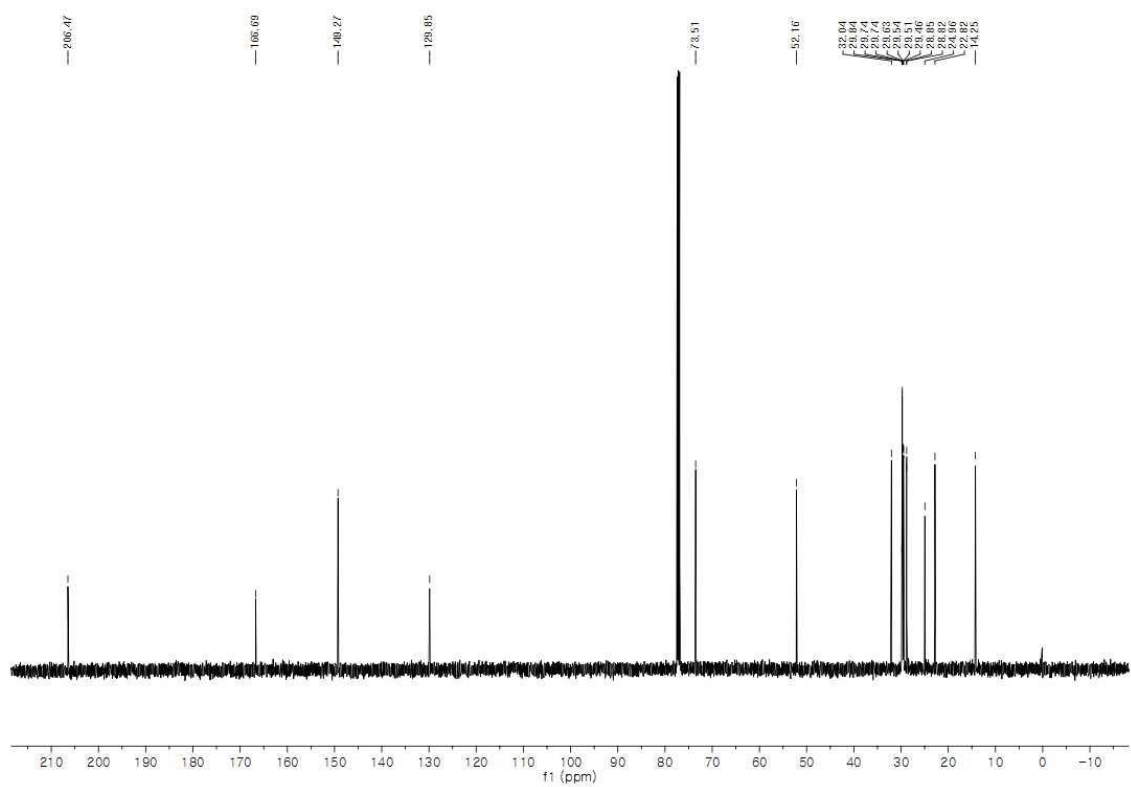
<sup>1</sup>H NMR spectrum of compound **5** (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR spectrum of compound **5** (125 MHz, CDCl<sub>3</sub>)

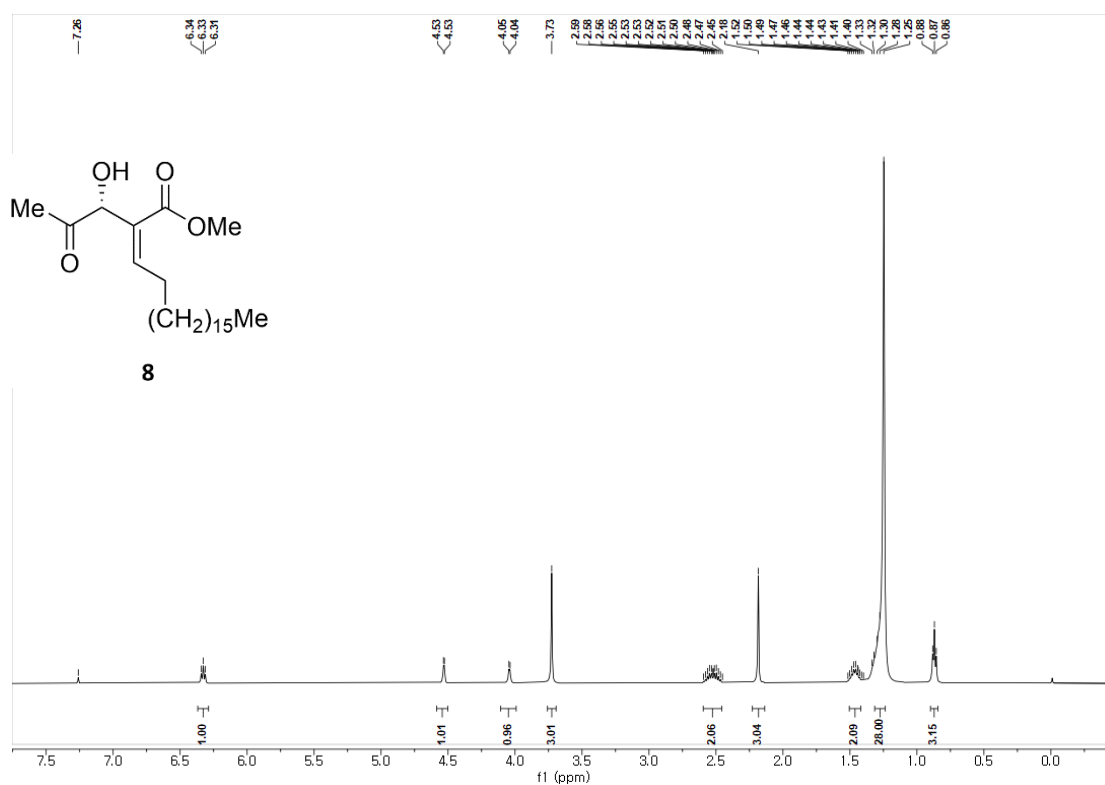


<sup>1</sup>H NMR spectrum of compound **6** (500 MHz, CDCl<sub>3</sub>)

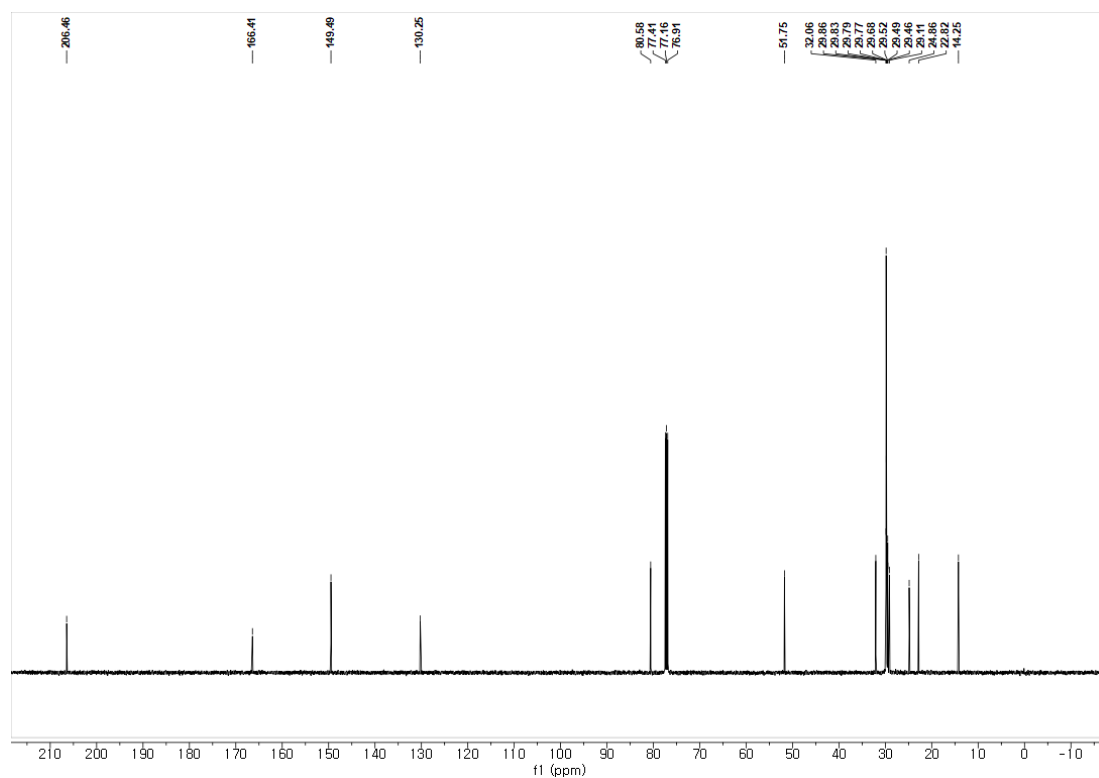


<sup>13</sup>C NMR spectrum of compound **6** (125 MHz, CDCl<sub>3</sub>)

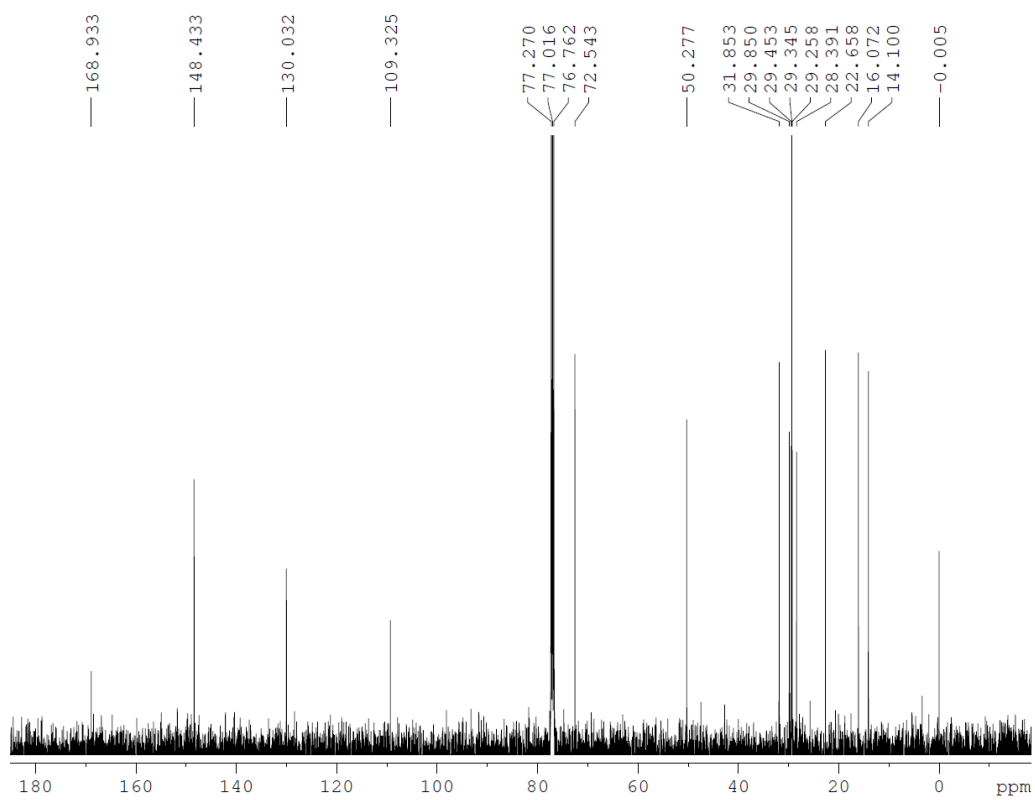
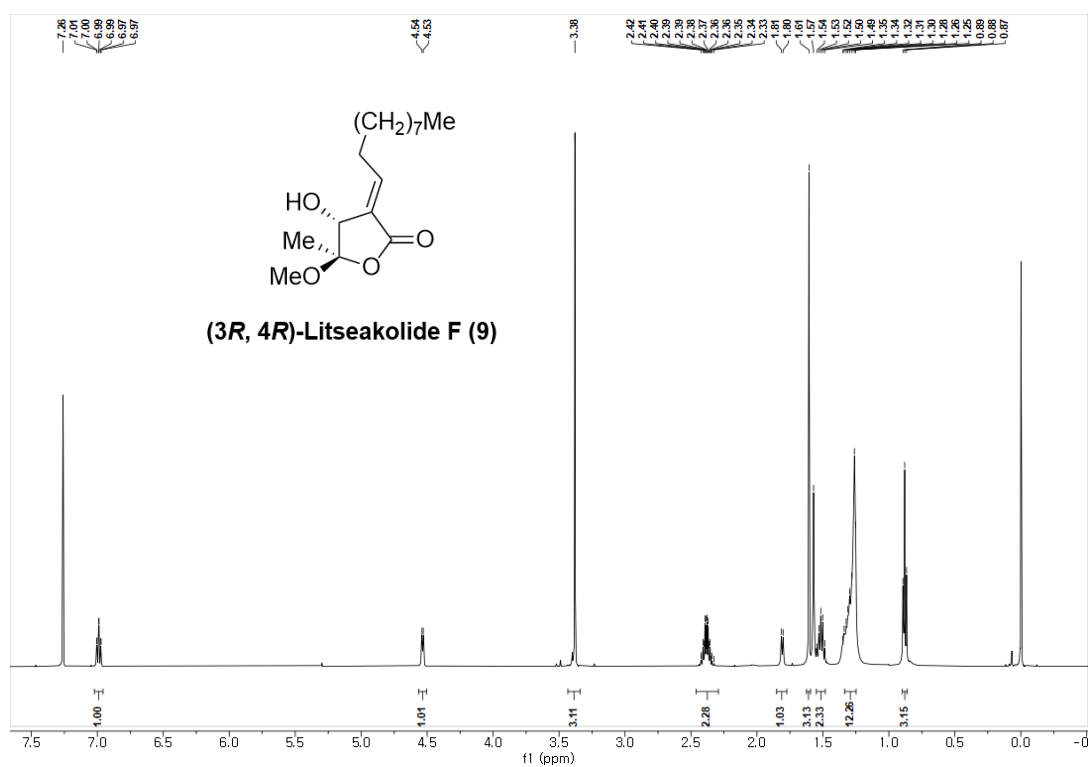


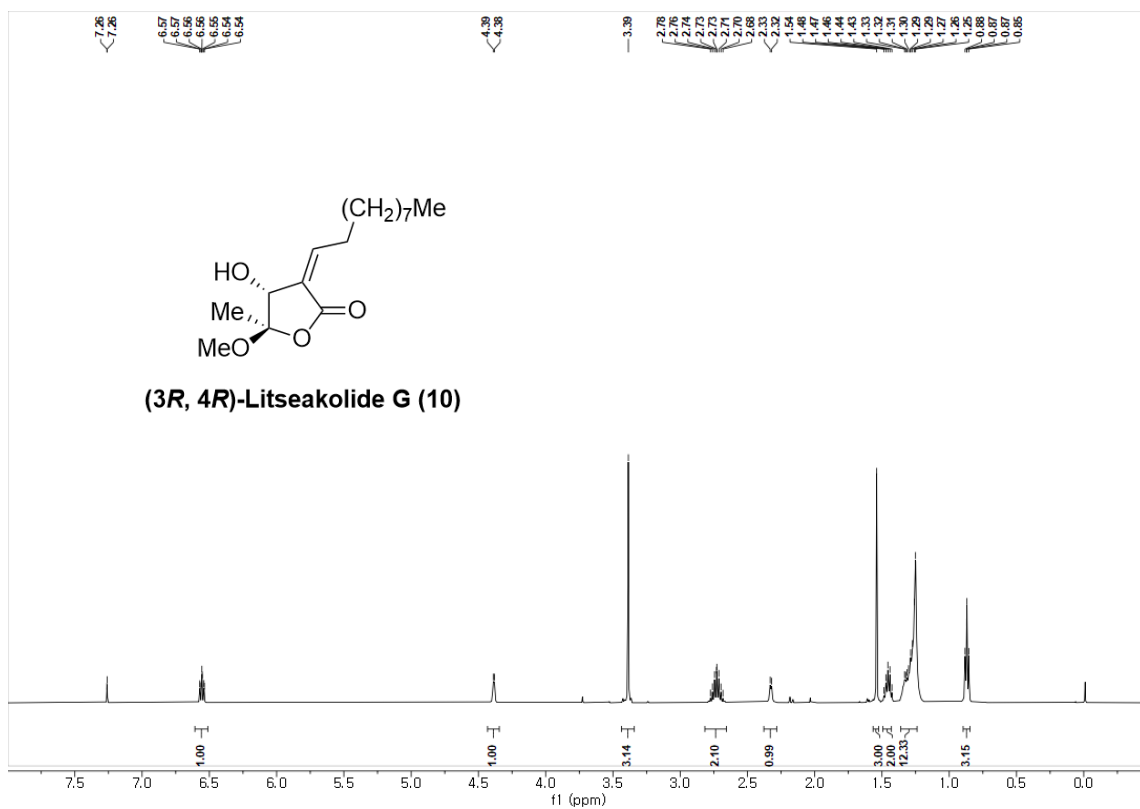


<sup>1</sup>H NMR spectrum of compound **8** (500 MHz, CDCl<sub>3</sub>)

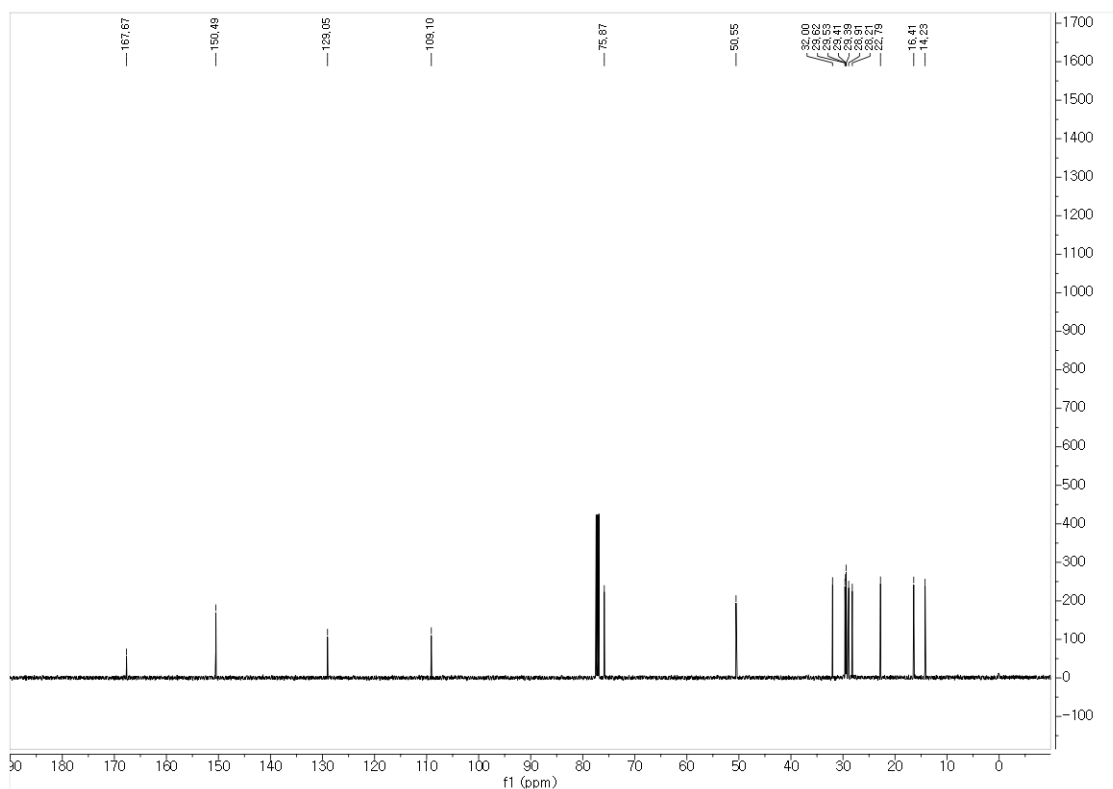


<sup>13</sup>C NMR spectrum of compound **8** (125 MHz, CDCl<sub>3</sub>)



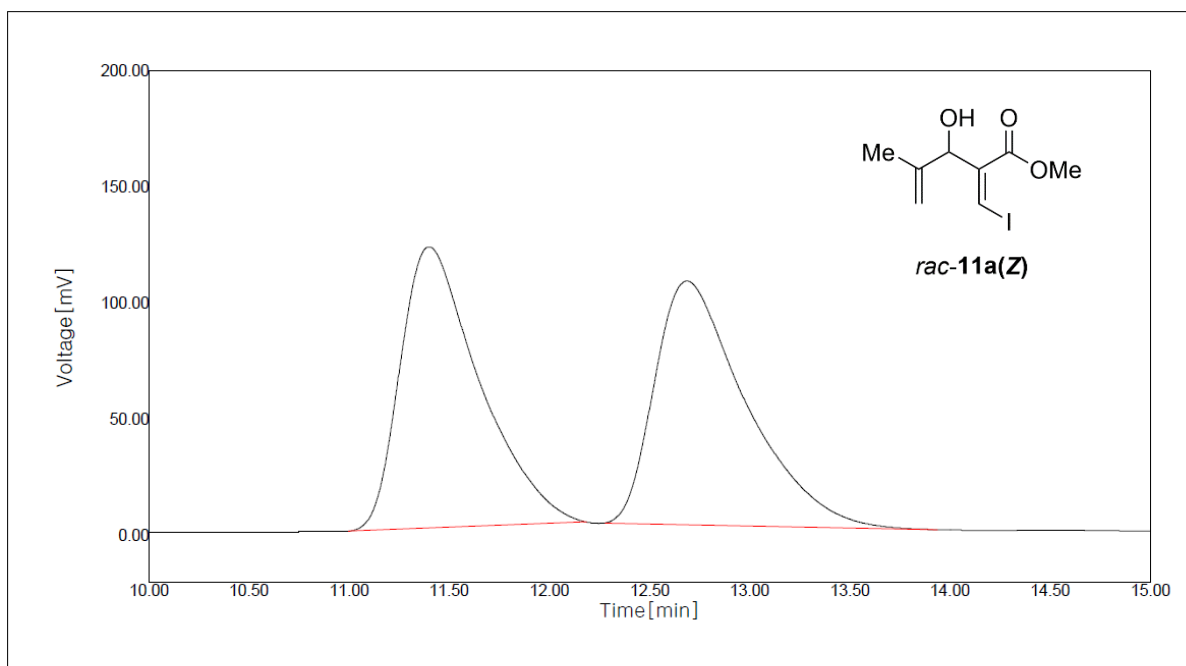


<sup>1</sup>H NMR spectrum of compound **10** (500 MHz, CDCl<sub>3</sub>)

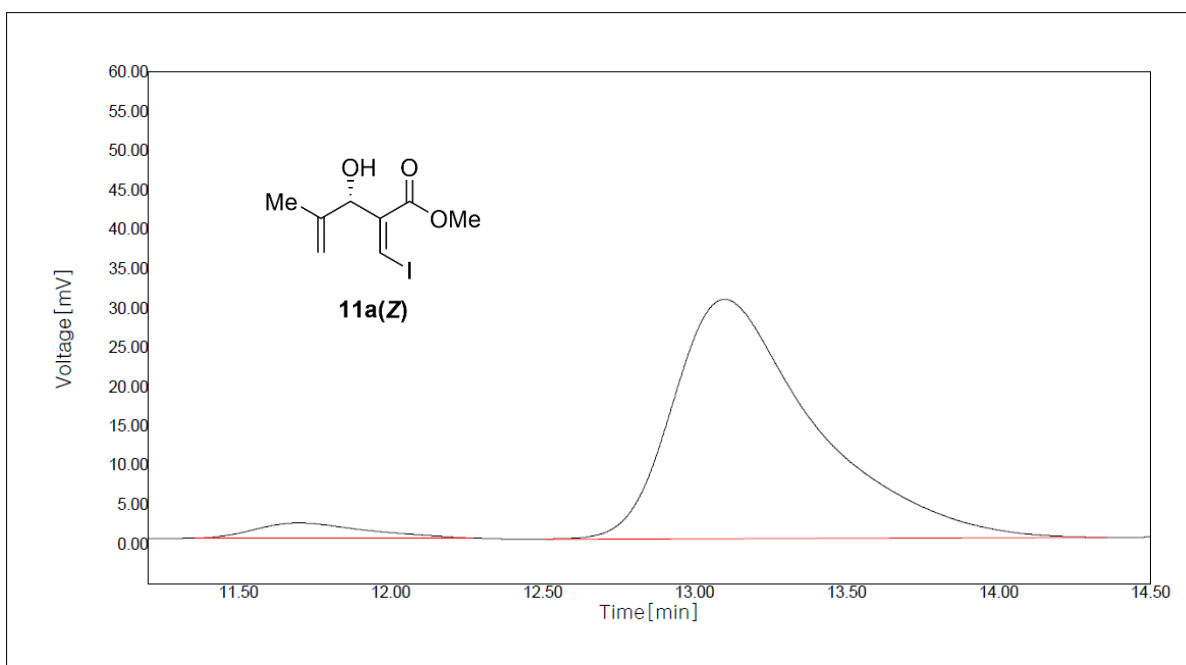


<sup>13</sup>C NMR spectrum of compound **10** (125 MHz, CDCl<sub>3</sub>)

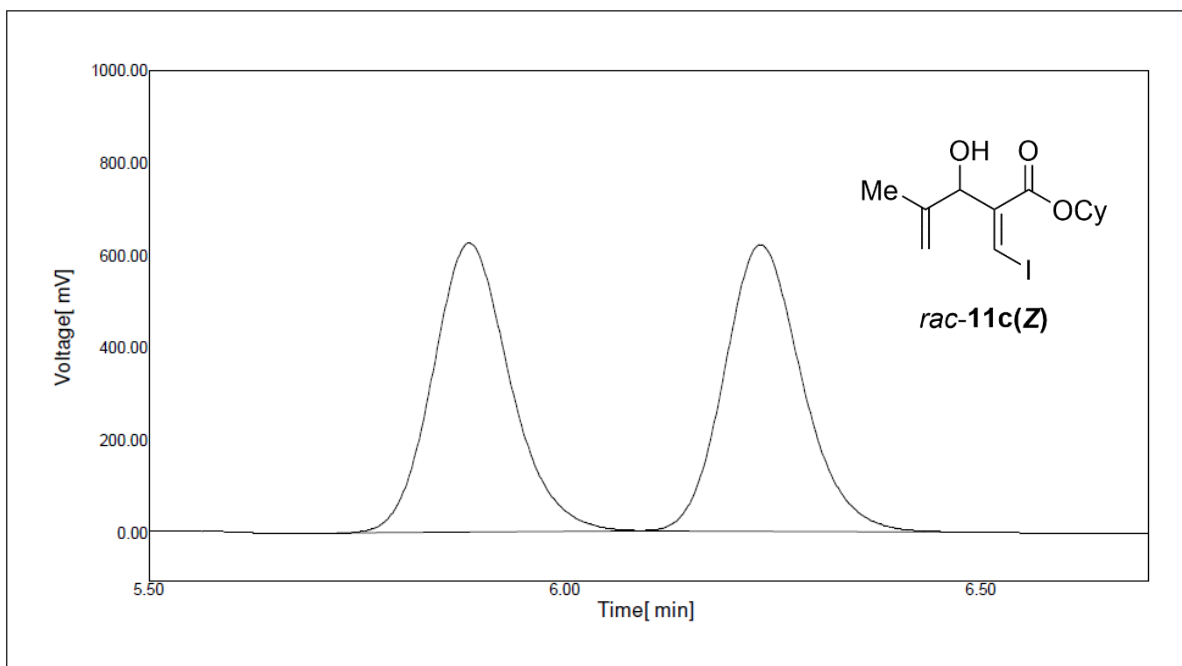
## 11. HPLC Spectra



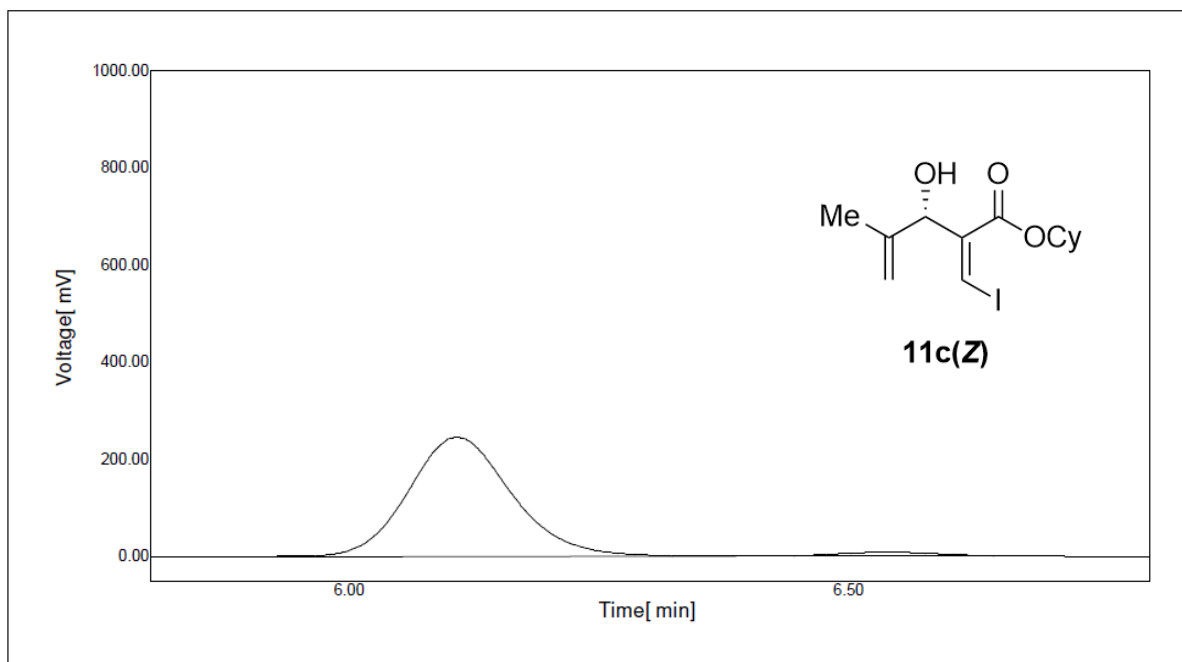
No	Time(min)	Area ratio
1	11.4000	50.11
2	12.6867	49.89



No	Time(min)	Area ratio
1	11.6967	4.66
2	13.0983	95.34

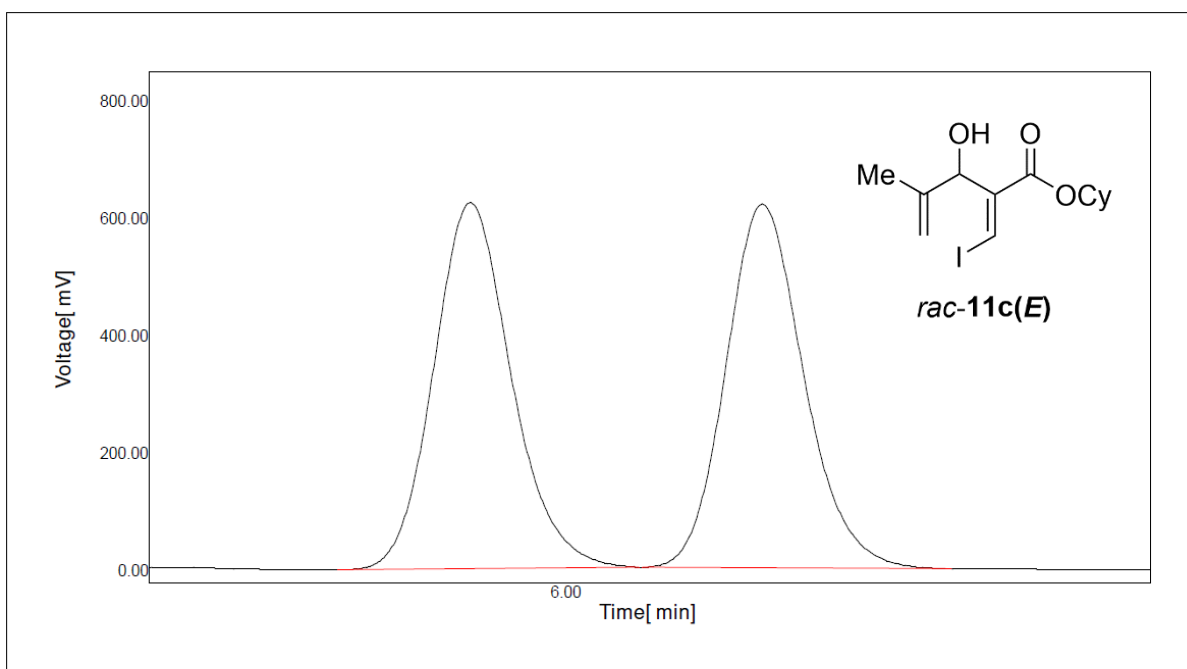


No	Time	Area ratio
1	5.8850	50.04
2	6.2350	49.96

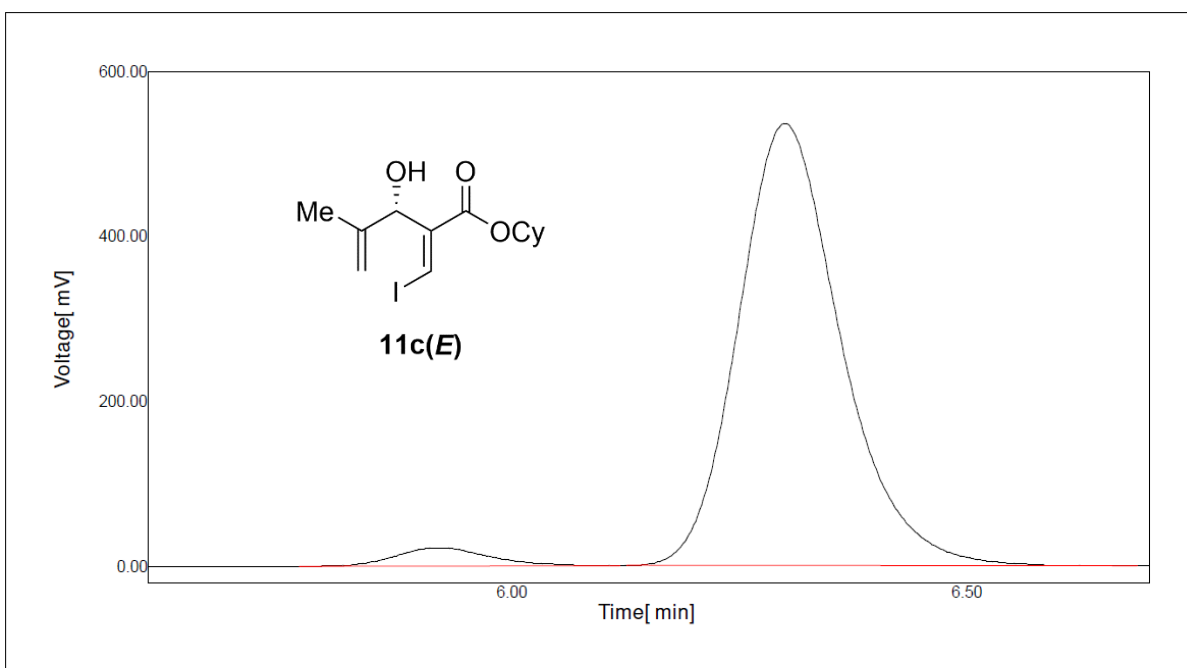


No	Time	Area ratio
1	6.1083	96.72
2	6.5383	3.28

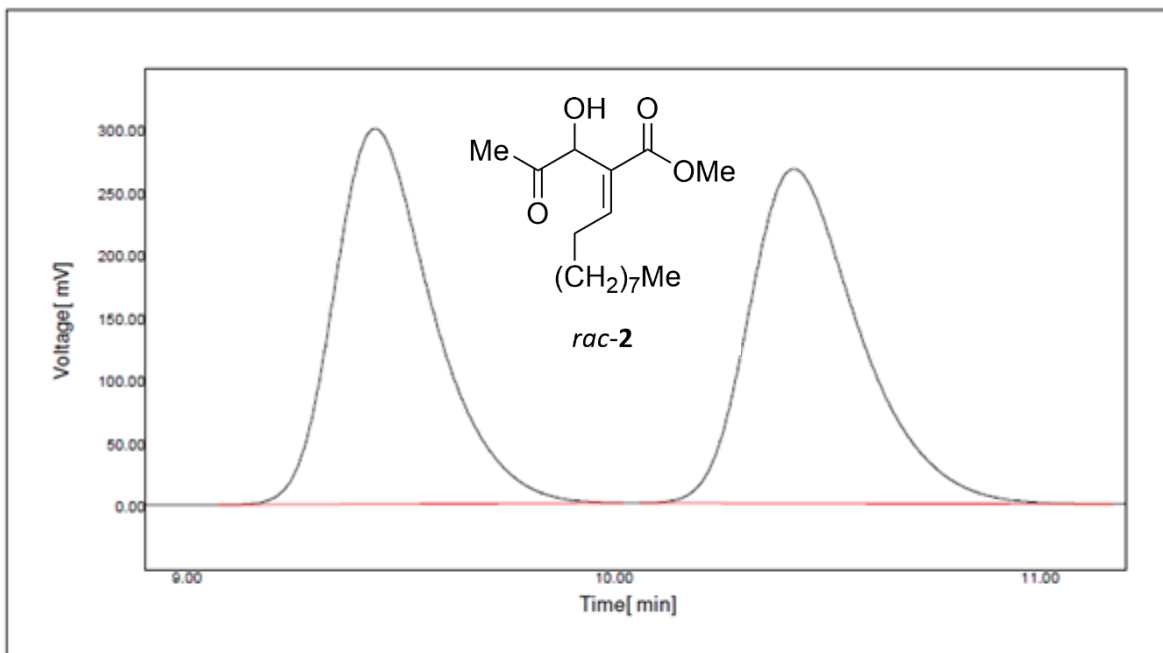




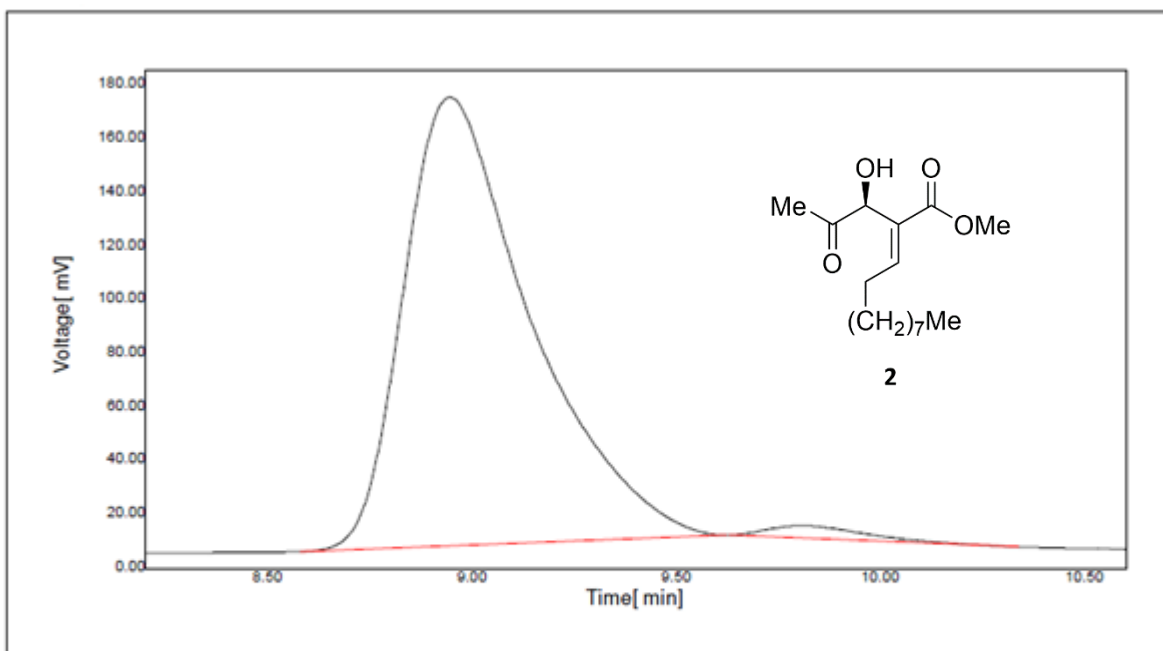
No	Time	Area ratio
1	5.8850	50.04
2	6.2350	49.96



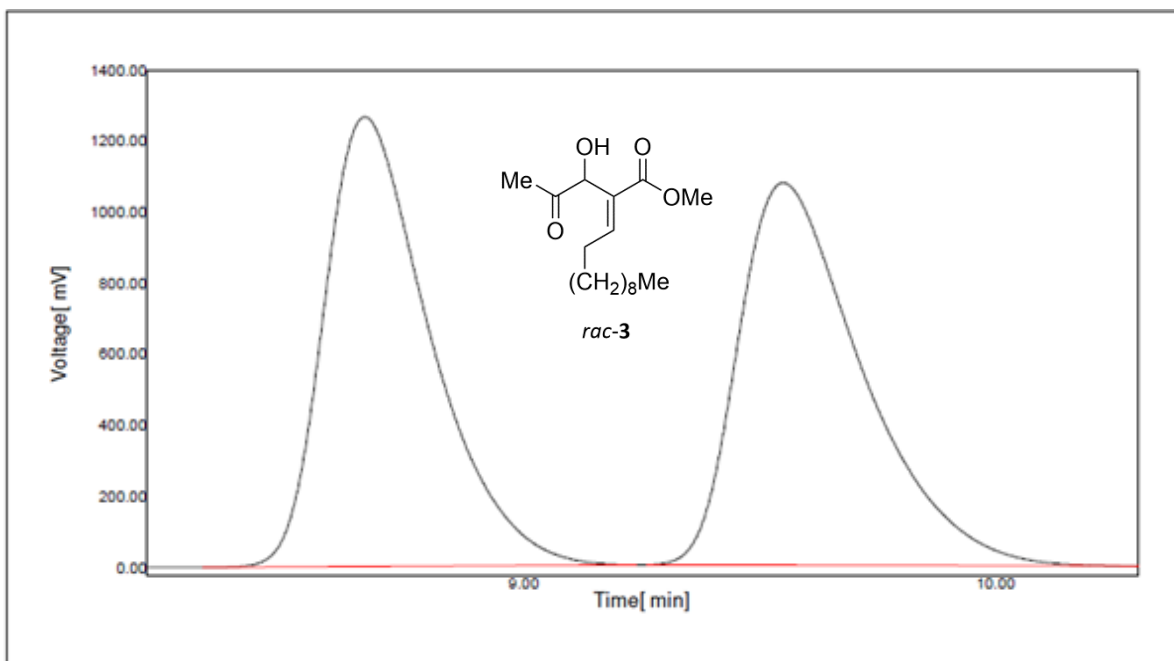
No	Time	Area ratio
1	5.9200	3.61
2	6.3000	96.39



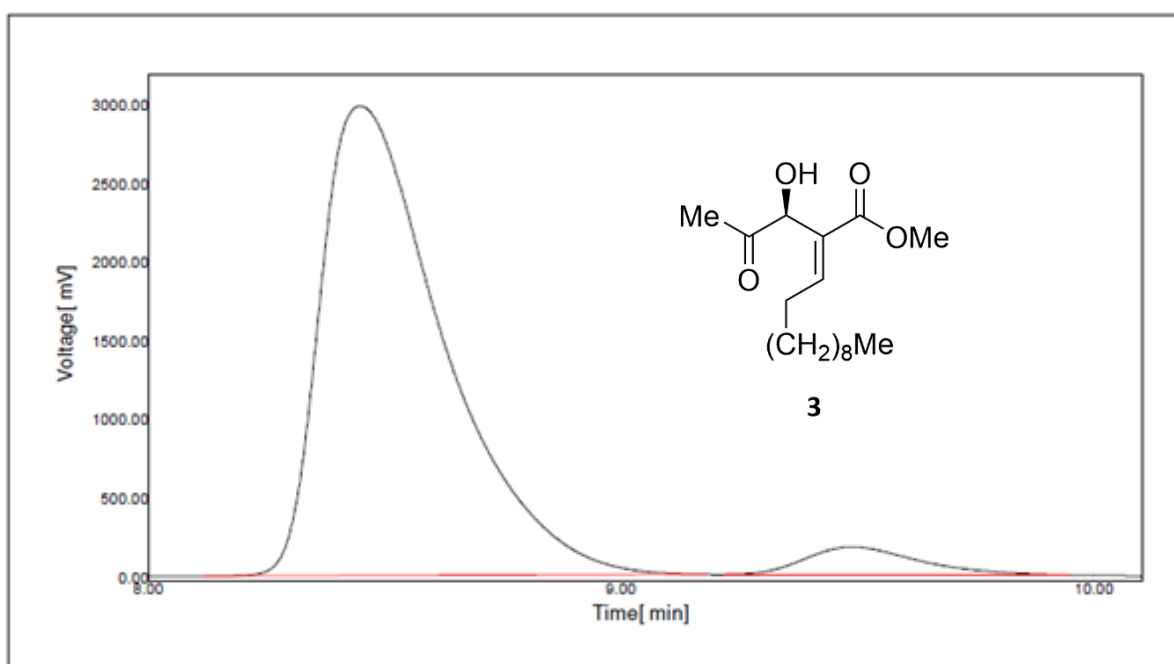
No	Time	Area ratio
1	9.4400	50.04
2	10.4233	49.96



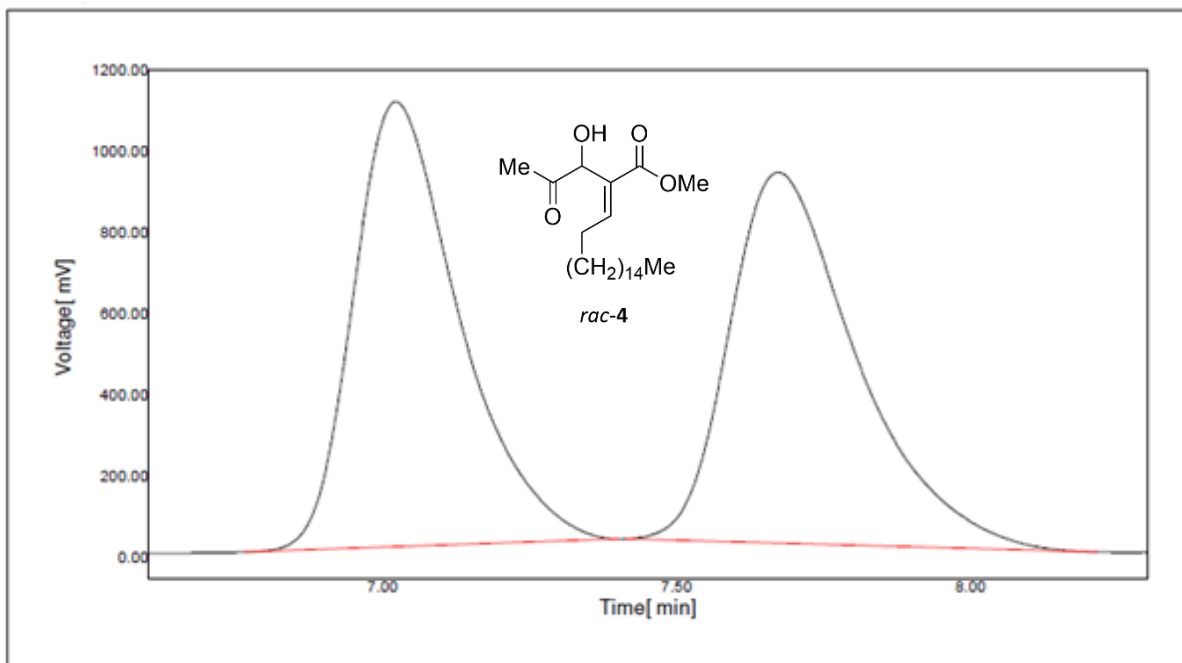
No	Time	Area [mV*s]	Area ratio
1	8.9467	3612.0750	97.88
2	9.8067	78.3741	2.12



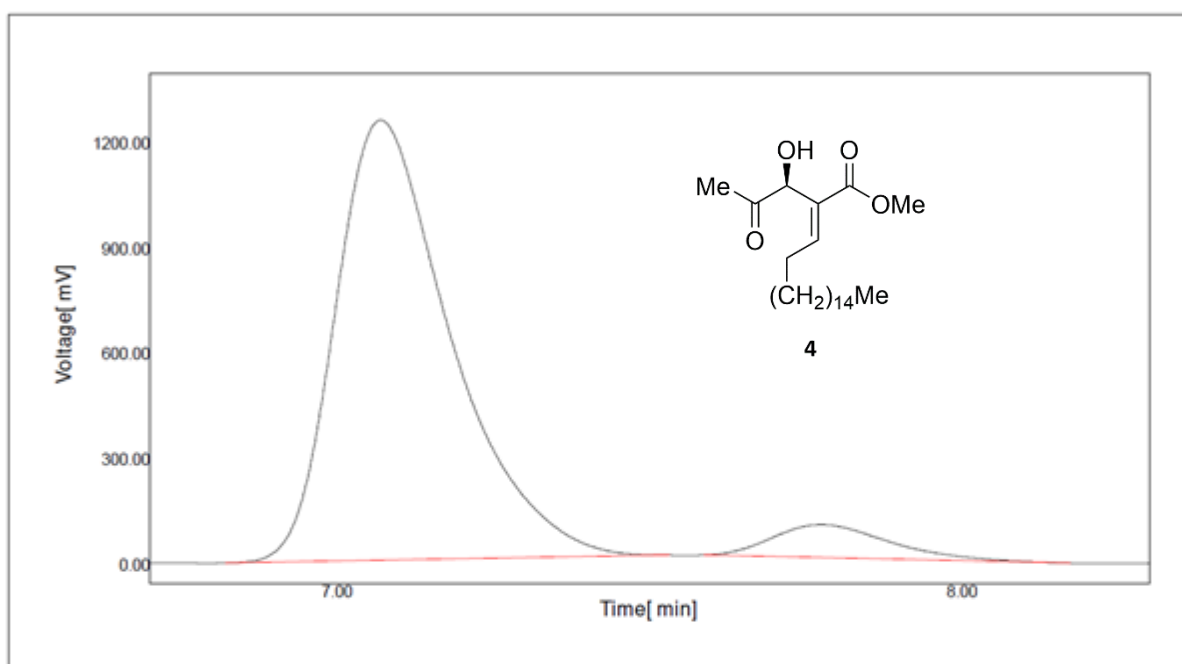
No	Time	Area ratio
1	8.6633	50.17
2	9.5500	49.83



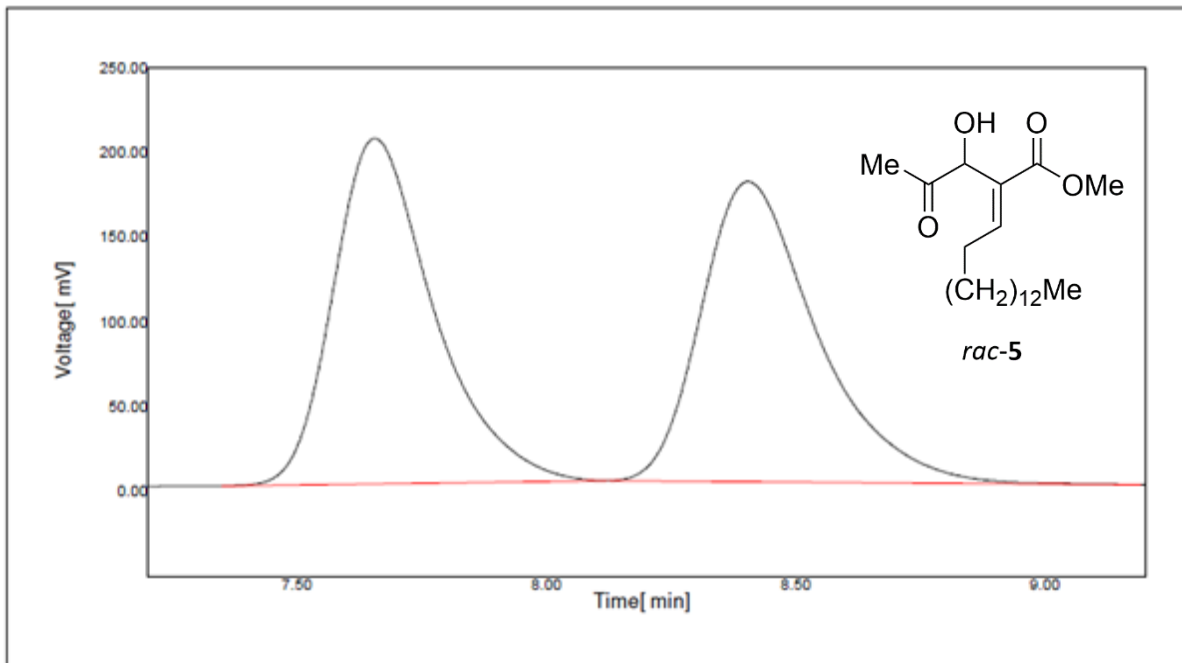
No	Time	Area ratio
1	8.4483	94.83
2	9.4883	5.17



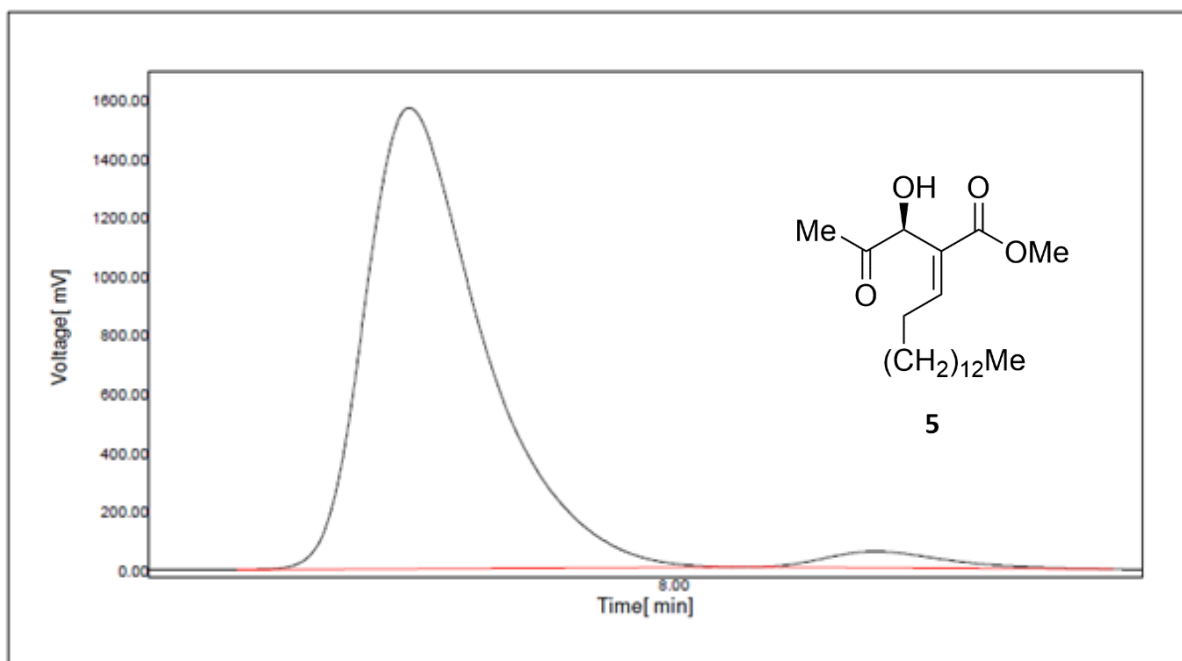
No	Time	Area	Area ratio
1	7.0217	13716.9984	49.90
2	7.6733	13769.9875	50.10



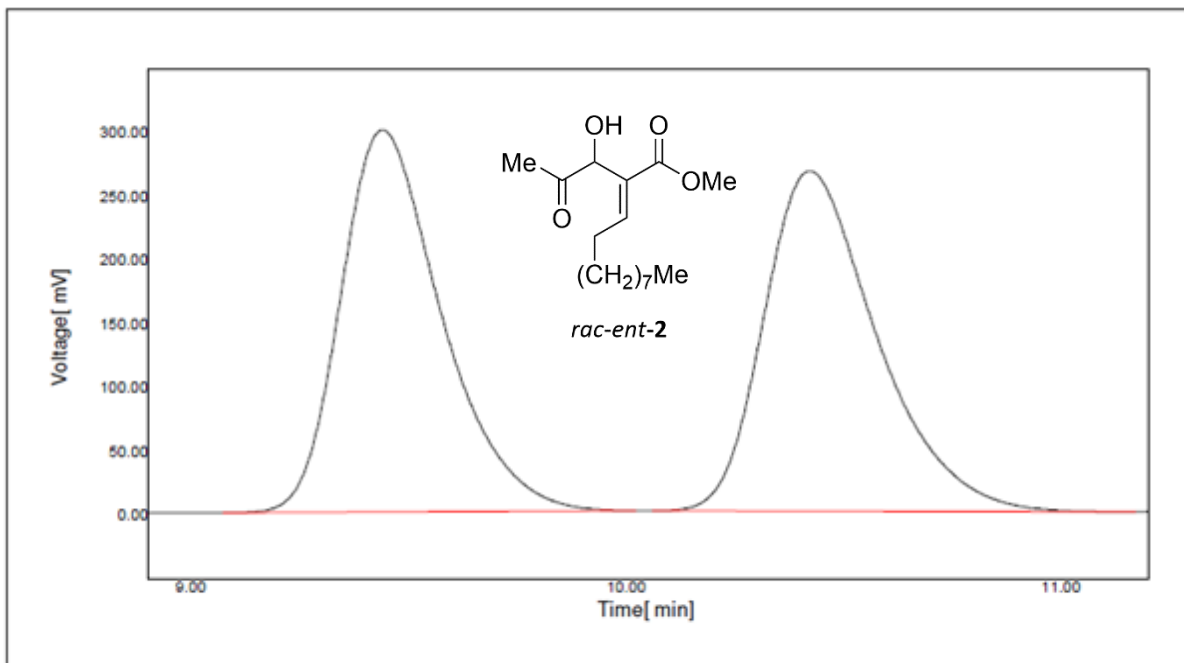
No	Time	Area ratio
1	7.0700	92.89
2	7.7750	7.11



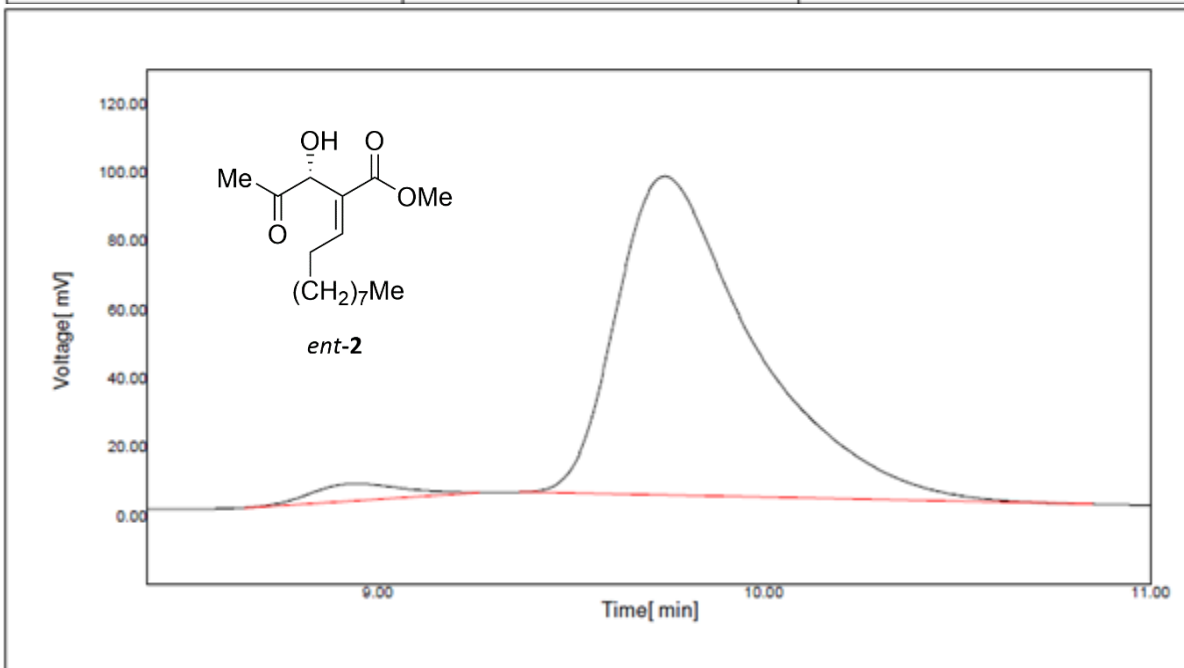
No	Time	Area	Area ratio
1	7.6567	2859.8227	50.04
2	8.4050	2854.8777	49.96



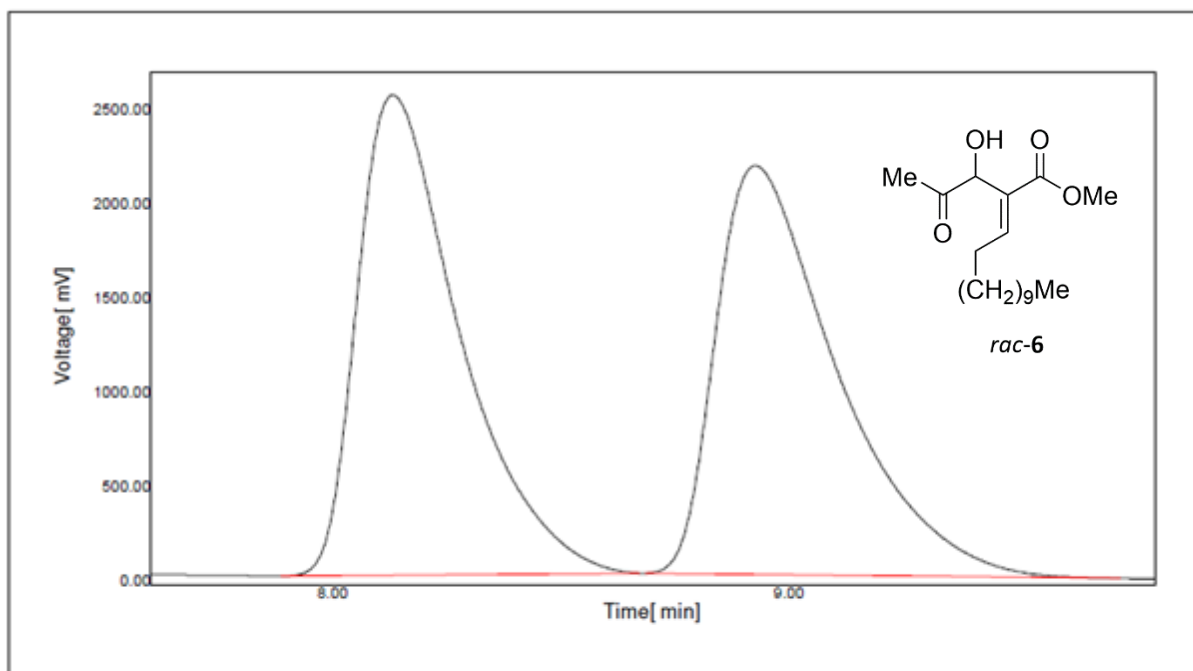
No	Time	Area ratio
1	7.5467	96.53
2	8.3450	3.47



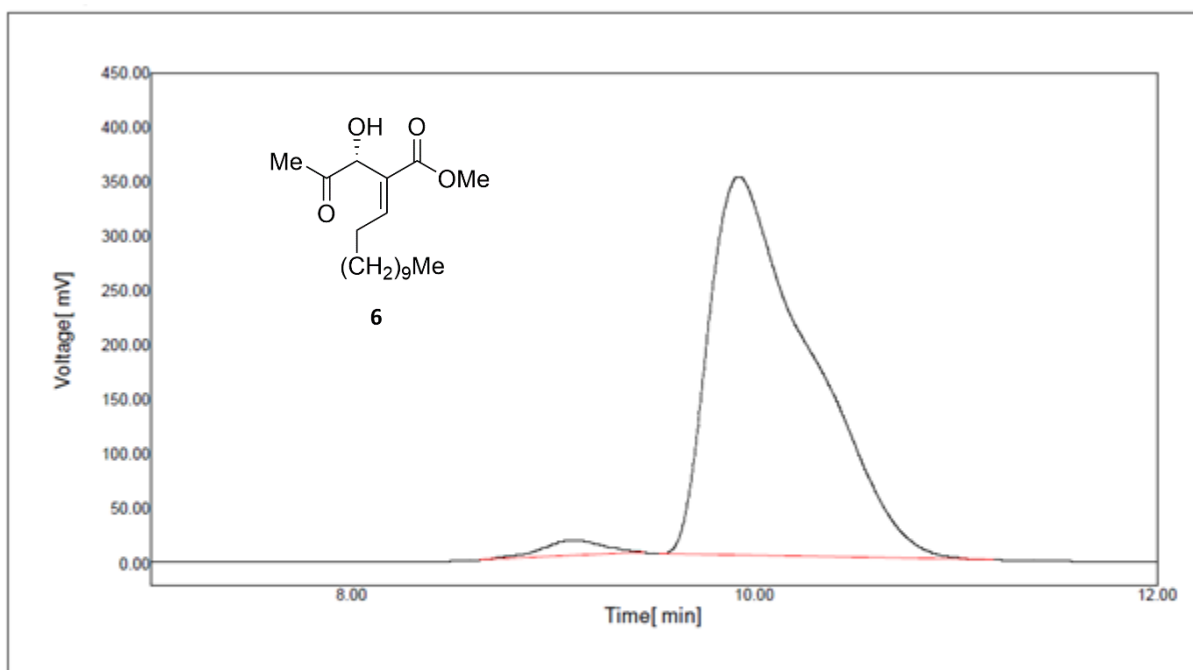
No	Time	Area ratio
1	9.4400	50.04
2	10.4233	49.96



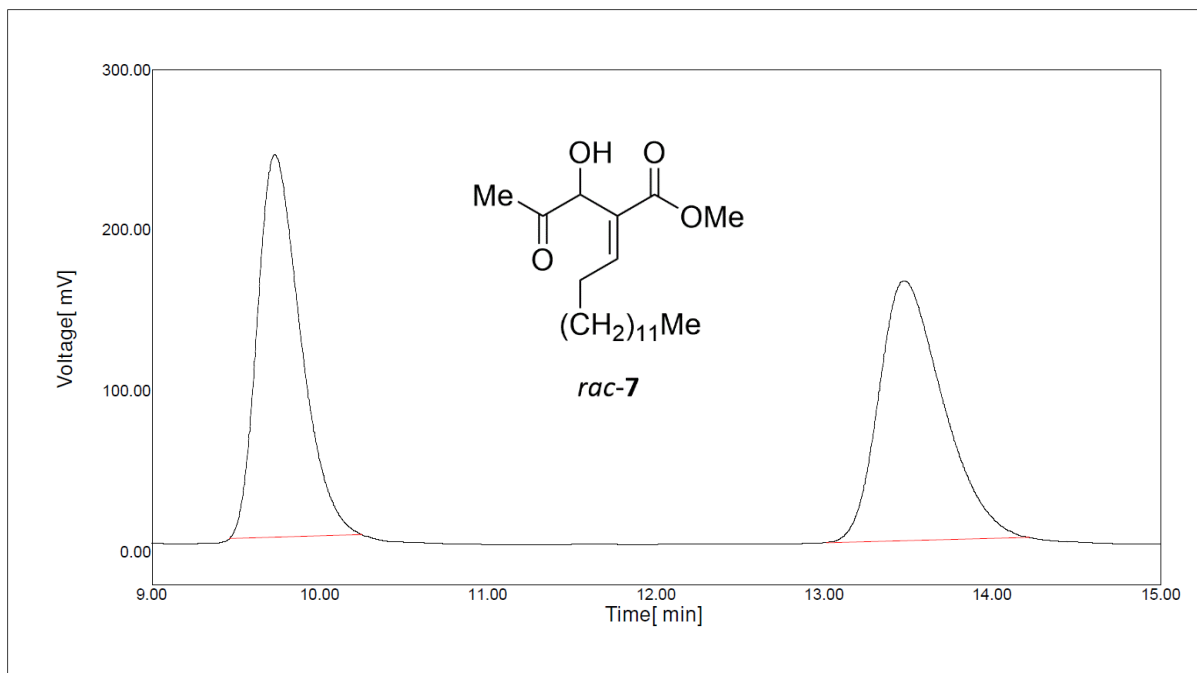
No	Time	Area ratio
1	8.9417	3.39
2	9.7433	96.61



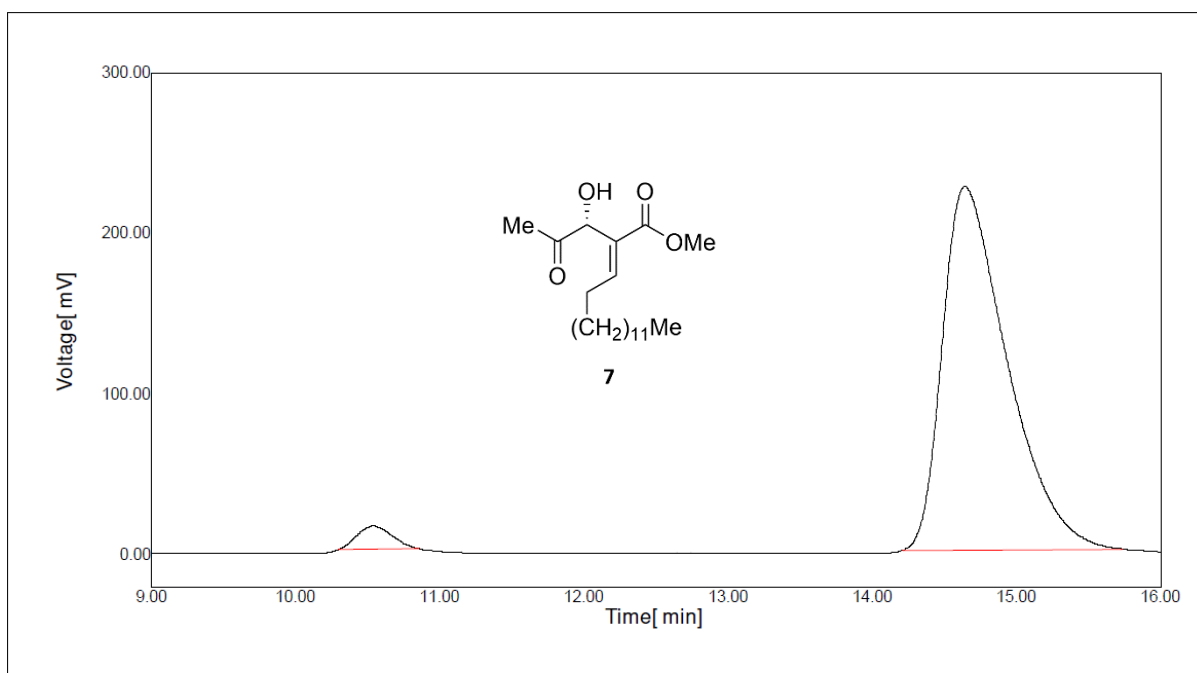
No	Time	Area ratio
1	8.1317	49.81
2	8.9250	50.19



No.	Time	Area
1	9.1000	2.42
2	9.9217	97.58

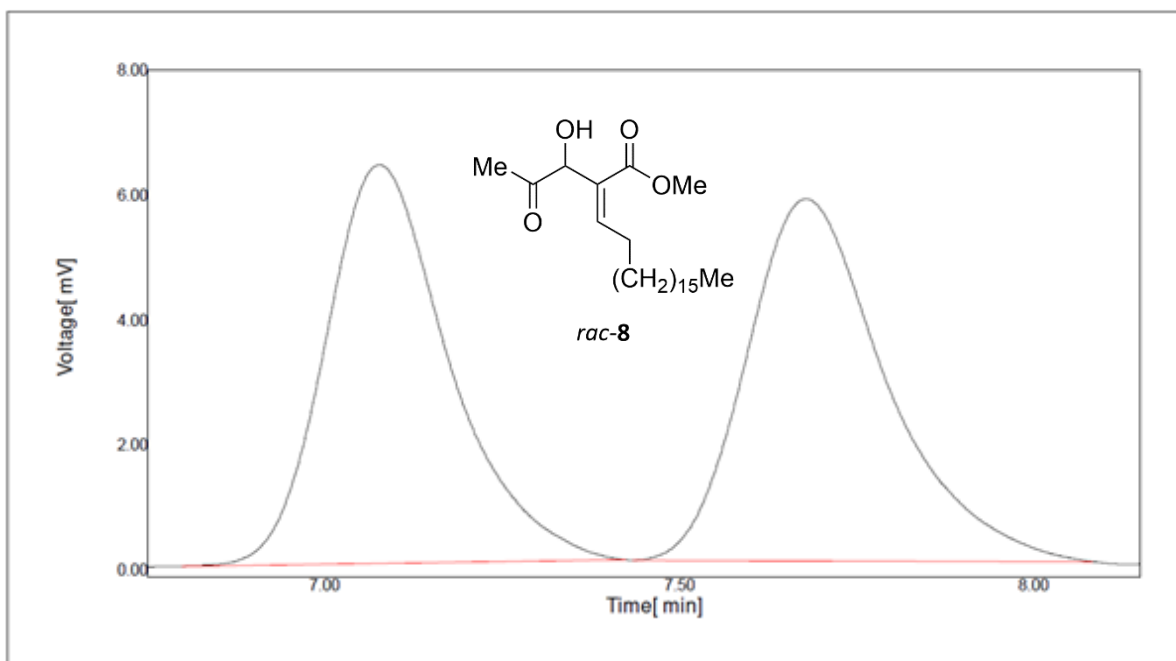


No	Time	Area ratio
1	9.7333	49.8
2	13.4767	50.2

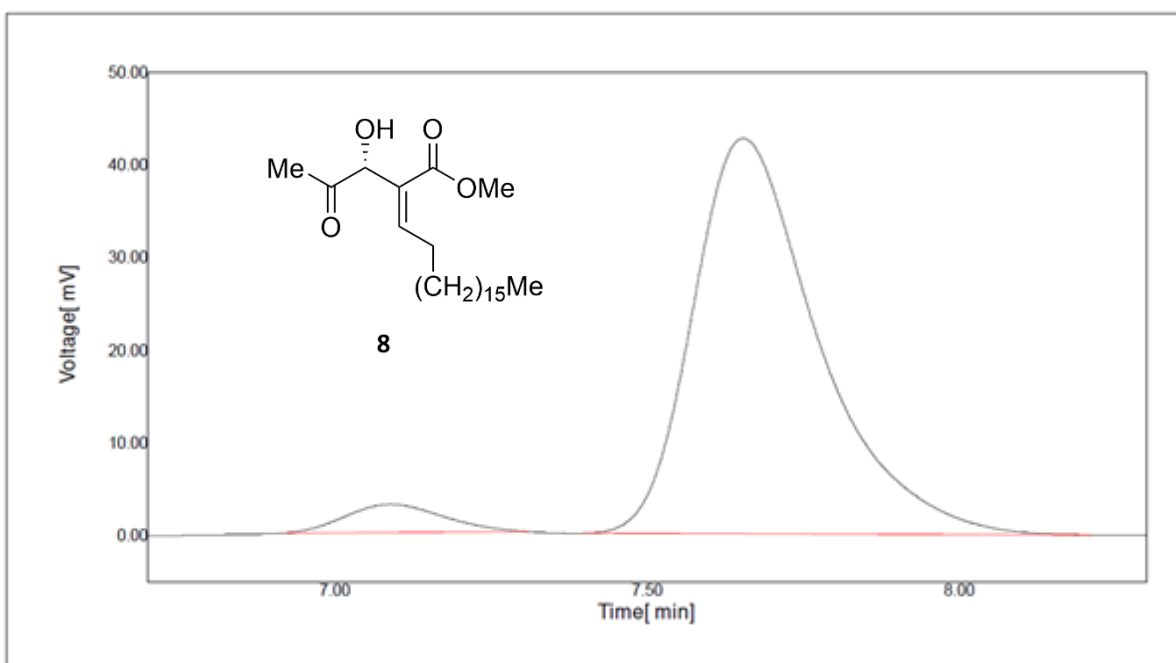


No	Time	Area ratio
1	10.5383	3.4
2	14.6417	96.6

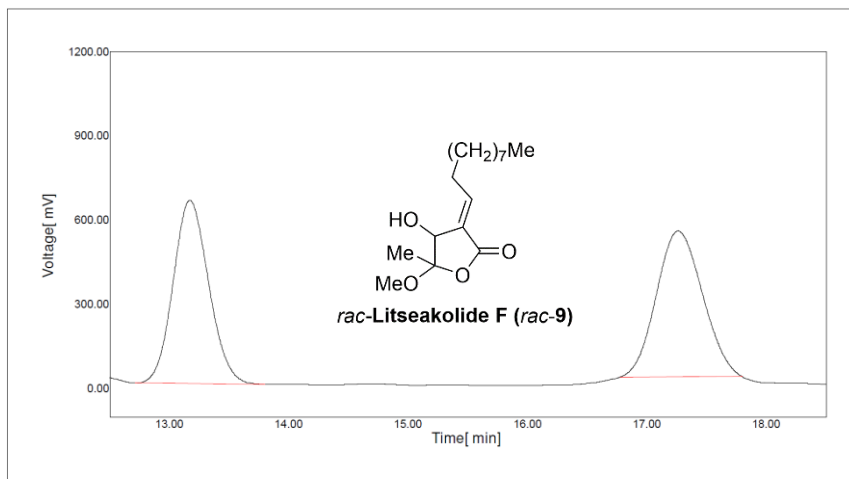




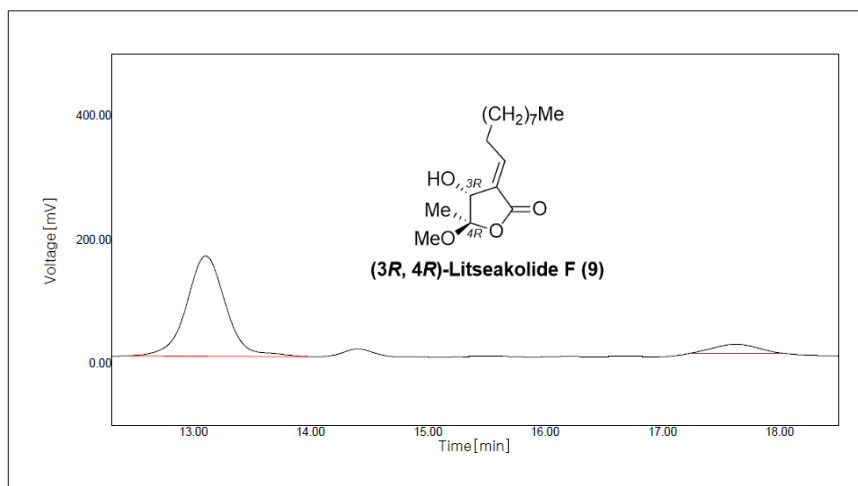
No	Time	Area	Area ratio
1	7.0767	77.1385	49.40
2	7.6783	79.0230	50.60



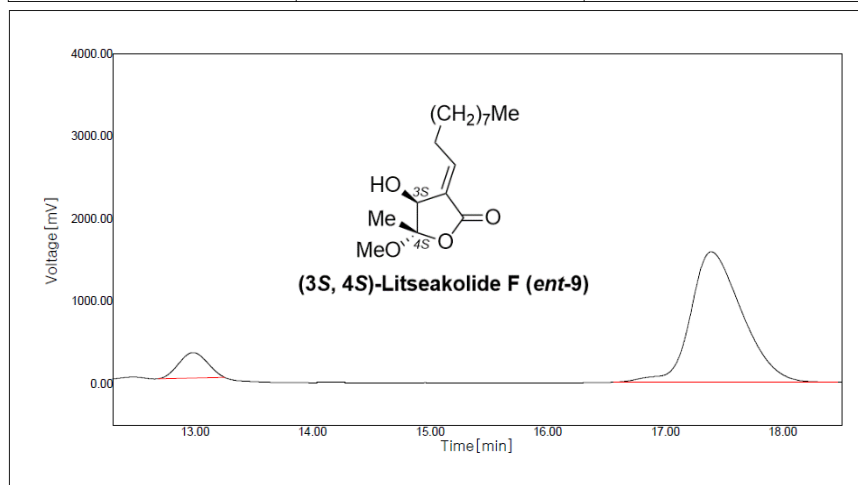
No	Time	Area	Area ratio
1	7.0900	32.9444	5.25
2	7.6550	595.1376	94.75



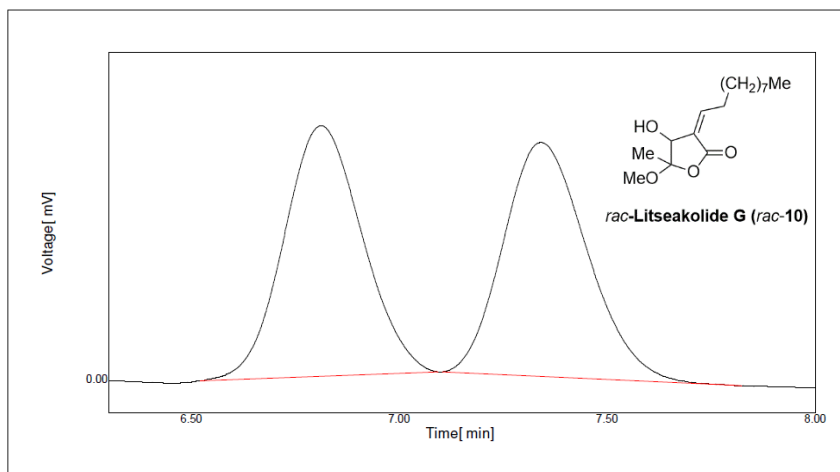
No	Time	Area ratio
1	13.1733	49.2
2	17.2600	50.8



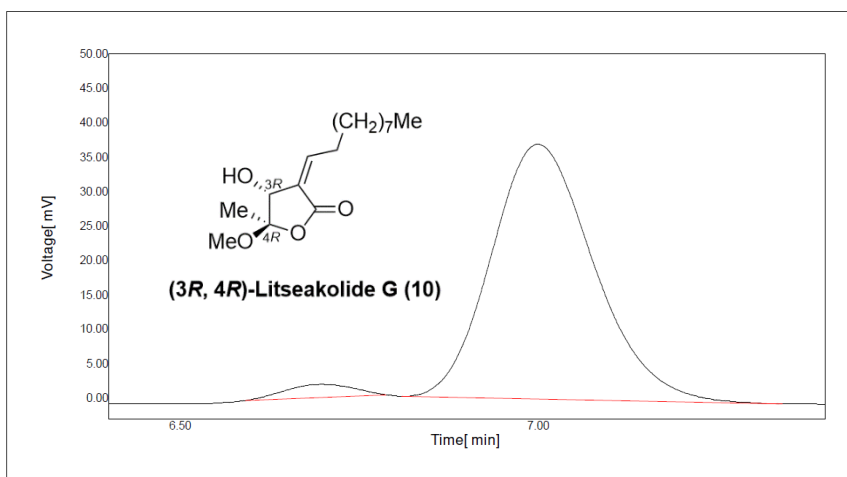
No	Time	Area ratio
1	13.1067	90.5
2	17.6267	9.5



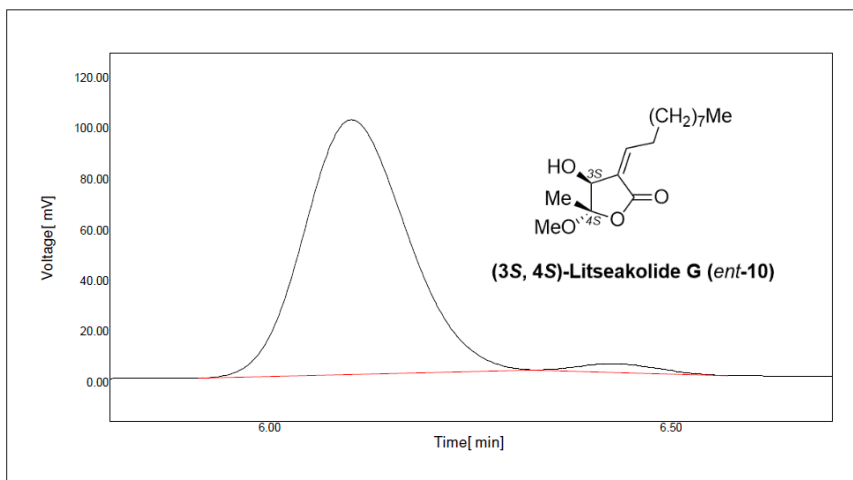
No	Time	Area ratio
1	12.9850	9.7
2	17.3917	90.3



No	Time	Area ratio
1	6.8117	50.05
2	7.3417	49.95



No	Time	Area ratio
1	6.6967	3.32
2	7.0000	96.68



No	Time	Area ratio
1	6.1017	97.52
2	6.4267	2.48

## 12. Reference

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- [7] Cheng, H.-I.; Lin, W.-Y.; Duh, C.-Y.; Lee, K.-H.; Tsai, I.-L.; Chen, I.-S. New Cytotoxic Butanolides from *Litsea acutivena*. *J. Nat. Prod.* **2001**, 64 (12), 1502-1505.